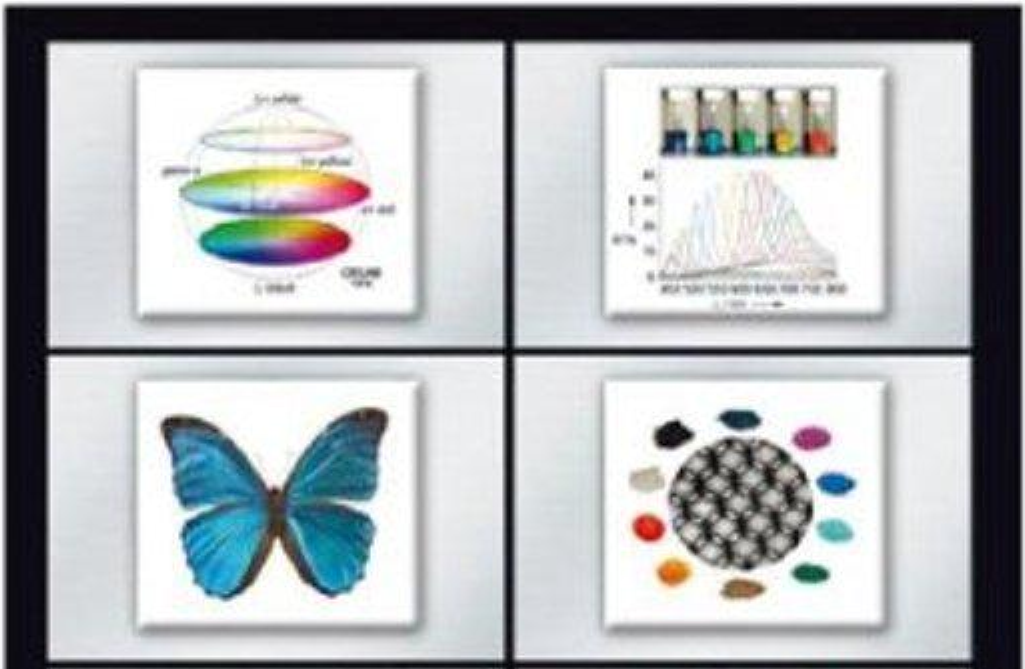
2nd Edition

Peter Bamfield and Michael G Hutchings

Chromic Phenomena

Technological Applications of Colour Chemistry



RSC Publishing

Chromic Phenomena
Technological Applications of Colour Chemistry
Second Edition

Chromic Phenomena

Technological Applications of Colour Chemistry

Second Edition

Peter Bamfield
Consultant, Penarth, UK

Michael G. Hutchings
DyStar UK Ltd, Manchester, UK

RSC Publishing

ISBN: 978 1 84755 868 8

A catalogue record for this book is available from the British Library

Published by The Royal Society of Chemistry,
Thomas Graham House, Science Park, Milton Road,
Cambridge CB4 0WF, UK

Registered Charity Number 207890

For further information see our web site at www.rsc.org

Preface to Second Edition

It is almost a decade since the appearance of the first edition of "Chromic Phenomena" in 2001 when its stated aim was "to provide an overview of the many applications that colour chemistry, in its widest sense, has found in the last couple of decades". The rate of increase in such applications and underpinning chemistry has accelerated to such an extent that a second edition has become fully justified. A recent issue of *Chemical Communications* (issue 24, 2009) is fairly typical. Amongst two feature articles and 38 communications, one of the feature articles and 15 comms – 40% of the total – are concerned in some way with aspects of colour in chemistry, spread across four of the five main themes of this book. To further emphasise this timeliness we recall the award of the 2008 Nobel Prize for Chemistry for studies into colour: the case of Green Fluorescent Protein. This was a fitting tribute not just to the individuals concerned, but to the core role that modern colour chemistry is playing through many aspects of today's technology.

This time the scale of the task of producing a new edition has benefited from re-establishing a collaboration between the two of us that started more than 30 years ago in ICI. Whilst maintaining the same five-chapter structure as in the first edition, a considerable amount of new material has been added to the areas previously covered. On top of that, introduction of new topics has resulted in almost doubling the size of the book. We have occasionally allowed ourselves to stray into the fringes of what is strictly physics, biology or medicine. We also include topics that we regard as "tomorrow's technology" even if their commercialisation is not yet with us. And we also highlight a few others which some might simply regard as quirky: the lobster's thermochromism during its cooking; the coloured materials that non-intuitively cool down when irradiated by a laser; and the male mosquito larvae with green fluorescent organs are three that spring to mind. Cutting edge research into the newer colour-producing materials such as metallic nanoparticles, quantum dots and photonic crystals is spread throughout the book. The impact of now cheap solid state lasers and their applications in multi-photon absorption processes in fields ranging from fluorescence imaging, optical data storage, photomedicine, lasers and nonlinear

Chromic Phenomena: Technological Applications of Colour Chemistry, Second Edition
By Peter Bamfield and Michael G. Hutchings

Published by the Royal Society of Chemistry, www.rsc.org

optics comprise another new theme throughout. Any remaining imbalance in the material included (and the corollary – the unavoidable omission of a mass of wonderful new science and technology) is also our responsibility. This second edition also benefits from the generous use of colour in many of the figures and formulae.

We acknowledge innumerable stimulating discussions and collaborations with many, both in industry and academia, during our many years' involvement with the colour industry in particular and chemistry more generally. We both fondly recall the fine examples of "Blackley Man" (some of them female) we worked with in the colours research group at ICI, who are too numerous to mention. Additionally, MGH acknowledges others in BASF, especially Jim Bullock and Manfred Patsch; his current colleagues in DyStar John Easton, Warren Ebenezer, Nigel Hall, Anthony Lawrence and Werner Russ; and recent collaborations with Harry Anderson (Oxford), Adrian Geisow (HP Research), Tony Gorman (Manchester), Anita Jones (Edinburgh) and Andrew Mills and John Parkinson (Strathclyde), plus an array of Ph.D. and M.Chem. students. All have contributed, sometimes indirectly and unwittingly, to his continuing education. We also thank Larry Dalton (Washington University) for providing a pre-publication article and valuable commentary, and Garry Rumbles (National Renewable Energy Laboratory, Colorado) for comment on his rhodamine dye upconversion experiment.

But it is the intellectual interplay between the two of us over the last 18 months that has led to the new character of this second edition, as well as providing us with fresh personal perspectives on the fun that colour and chemistry continue to bring to us.

Of course working on such a volume has required spending many hours alone in our offices peering at screens full of data and text, in the case of one of us during hours outside his full-time employment. It is through these periods that the support and understanding of our wives and families has been paramount and immeasurably valued. Without it this book would not have appeared, and for that reason we dedicate it to Domini, and to Julie and Chris.

Peter Bamfield
Michael G. Hutchings
peter.bamfield@btinternet.com
mghutchings@btinternet.com

Preface to the First Edition

The aim of this book is to provide an overview of the many applications that colour chemistry, in its widest sense, has found in the last couple of decades. Not only have there been developments in the traditional areas of colorants for textiles, paints and inks but also in an exciting variety of newer technologies. Several of these are at the cutting edge of research, such as photodynamic therapy, electroluminescent displays, artificial photosynthesis, holographic data storage and photonics, and any report on the current position can only be interim. Most of the newer technologies are multidisciplinary, where the active collaboration of chemists with physicists, biologists, biochemists, materials scientists, electronics engineers *etc.* is essential if any progress is to be made. Covering as it does a very wide field, this book will provide an entry point for both new researchers and established ones who wish to broaden their horizons and accept the challenge of finding new applications for colour chemistry.

During my more than four decades involvement in the colorants industry I have had many stimulating discussions and collaborations with innumerable colleagues to whom I am indebted. I would particularly like to mention Peter Austin, Gerald Booth, Peter Gregory, Paul Gordon, Colin Greenhalgh, Nigel Huges, Mike Hutchings, Brain Parton, Duncan Phillips, Ray Price, Peter Quan, Peter Tasker, Hunter Renfrew, Dennis Ridyard, John Schofield and John Taylor from my ICI/Zeneca days.

Finally, but most of all, I wish to thank my wife Mary for her unstinting support during the books gestation period and particularly whilst I was producing the manuscripts.

Peter Bamfield

Chromic Phenomena: Technological Applications of Colour Chemistry, Second Edition
By Peter Bamfield and Michael G. Hutchings

Published by the Royal Society of Chemistry, www.rsc.org

Contents

Chromic Phenomena: Technological Applications of Colour Chemistry, Second Edition
By Peter Bamfield and Michael G. Hutchings

Published by the Royal Society of Chemistry, www.rsc.org

Introduction

Colour plays an extremely important role in our everyday lives. Most of us take this for granted, but just think what life must be like for those people who have hereditary total colour-blindness.[1] Why colour is so important has exercised the minds of some of our greatest philosophers for many centuries.[2,3] What is colour, what role does it play in Nature, and in our social and intellectual environment? Even today the answers to these questions are far from known and arguments over the psychological and social impact of colour continue to rage.[4,5] However, ever since Newton recognised the relationship between light and colour in the late seventeenth century, our understanding of the hard science behind colour and its myriad applications has been increasing gradually, until it has reached today's level of sophistication.[6 8] Rather interestingly, a marriage between our understanding of the physics and chemistry of colour and their utilisation in both art and technology has become a topic of growing interest to many authors.[9 10]

Obviously the main use of colour in technology is to impart a visual stimulus as part of the overall aesthetic of the object being viewed. The discussion in the previous paragraph is predicated on this use of colour. At the risk of labouring the point, colour is the *raison d'être* of the colouring material; the primary value of red paint is in being able to impart a red colour to its substrate. If it fails in this role, for example by changing colour in daylight, it ceases to have value.

Yet colour can have less obvious applications. Colour can be an enabler. We shall meet many applications where the actual colour is unimportant. Its value now is in being present or absent, as a label or signal. Do any of the cells in a tissue sample fluoresce when treated with a particular fluorescent agent? If so, the presence of colour signifies that the cell is malignant and is a health alert. The actual colour of the fluorescent signal is immaterial. If it's there it signifies it's a harbinger of bad news, and no one cares if it's red, green or whatever. Or a series of four objects can be distinguished by one of four colours. It is immaterial what the actual colour labelling object 1 is, as along as that colour reliably

Chromic Phenomena: Technological Applications of Colour Chemistry, Second Edition
By Peter Bamfield and Michael G. Hutchings

Published by the Royal Society of Chemistry, www.rsc.org

and inevitably represents object 1 and none of the other three *etc*. This exact problem is central to the identification of the sequence of the four nucleotides comprising any DNA strand, part of the multi-billion dollar genomics industry.

We can take this a step further. The fact that a material is coloured might be totally irrelevant to its further function, and thus application. The important feature might be that the physical properties of the material cause a desirable technological effect, and yet might simultaneously be responsible for colour as an unavoidable, perhaps even undesirable, by-product. This combination can turn up in some nonlinear optical materials, where the electron-donor/π-conjugation/electron-acceptor molecular design motif of many dyes, thus giving colour, is what is significant for imparting quadratic optical nonlinearity (see Chapter 5, Section 5.6). It was once fashionable to refer to dyes (or colouring matters in general) whose primary purpose was not to act as colorants as "functional dyes". We do not use that descriptor, but we shall meet coloured materials which have non-colouring applications throughout this book.

As stated in the first edition, this book is concerned with the technological applications of colour chemistry and not the theoretical aspects. However, in some of the newer areas it has been considered necessary to provide a little more theoretical understanding to help put the technology into context, for example in describing the chromic phenomena deriving from excitonic coupling within dimers and aggregates of dyes, and plasmonic coupling amongst colloidal metal particles. Other specific aspects of colour theory are covered as needed in the main body of the text. For those requiring a more detailed treatment of the theoretical aspects of colour physics excellent texts are available,[7,8] whilst they are summarised in very readable forms in others of a more general nature.[10,11]

There are many ways in which colour can be caused to arise by both chemical and physical means, all of which are used or have potential in technological applications. These different ways of producing colour can be grouped into five fundamental classes, as shown in Table I.1. These can be further split into what Nassau has called "the fifteen causes of colour".[6] The main Nassau groupings of I and V can be considered as physical phenomena, II and IV are borderline between chemistry and physics, and III covers purely chemical phenomena. The relationship between light and the optical properties of materials, using the fifteen causes of colour as a basis, has been covered in a text that is recommended reading.[12]

The "fifteen causes" can be rather prescriptive when it comes to pulling together those technologically important chromic phenomena that rely largely on chemistry for their effect. An alternative method is to follow a technology/structure based classification.[13–16] However, whilst this in turn has advantages, it fails to relate the chemistry/physics across particular technology boundaries, *e.g.* luminescence phenomena in pigments, sensors and probes. Since the main purpose of this book was to describe the technological applications of colour, *via* a variety of chromic phenomena, a somewhat different system was adopted for the first edition.[17] This involved classification of the various chromic

Table I.1 Nassau's five groupings of the causes of colour.

Group	*Causes*	*Examples*
I	Vibrations and simple excitations (external heat or energy transfer within molecules)	Incandescence, vapour lamps, some lasers
II	Ligand field effects (from unpaired electrons in transition metal ions and complexes)	Phosphorescence, lasers
III	Transition between molecular orbitals	Absorbing dyes and pigments, both organic and inorganic, fluorescence
IV	Transition between energy bands	Metals, pure and doped semi conductors
V	Geometrical and physical optics	Interference phenomena, iridescence, diffraction, liquid crystals

phenomena according to whether they fall into five broad groupings involving the following processes, where "light" obviously implies "colour":

- Stimulated colour change, often reversible;
- Absorption and reflection of light;
- Absorption of energy followed by emission of light;
- Absorption of light and energy transfer (or conversion);
- Manipulation of light.

Whilst arguably this is an over-simplification of the colour-producing phenomena, it has proved to be an effective way of gathering together the vast array of colour-based technological applications into an understandable mosaic and has been retained for this second edition (Figure I.1). In practice we find very few examples of chromic phenomena that do not conveniently fit into one of these categories, and even the few exceptions can be shoe-horned into one of the five at a pinch. Research into these five areas has been very active since publication of the first edition in 2001, not only in the topics covered but also by expansion into new fields, which will no doubt have commercial potential in the coming years. The content of each chapter of the book has been expanded to include this new work. To partially compensate for this expansion in material, we have removed the reaction schemes in the first edition that described syntheses of some of the dyes and pigments of interest. The main technologies dependent on chromic phenomena are shown in Figure I.2.

Chapter 1 covers the chemistry and applications of the stimulated colour change grouping. This group contains all the well-known "isms" of chromic phenomena: photochromism, thermochromism, ionochromism, electrochromism and solvatochromism, as well as the lesser-known but increasingly important gasochromism, vapochromism and mechanochromism. "Chromisms" impinge on our everyday lives, as in photochromic spectacle lenses, thermochromic paints and temperature indicators, thermal papers, smart windows and mirrors, and in visual displays. This chapter has been expanded to

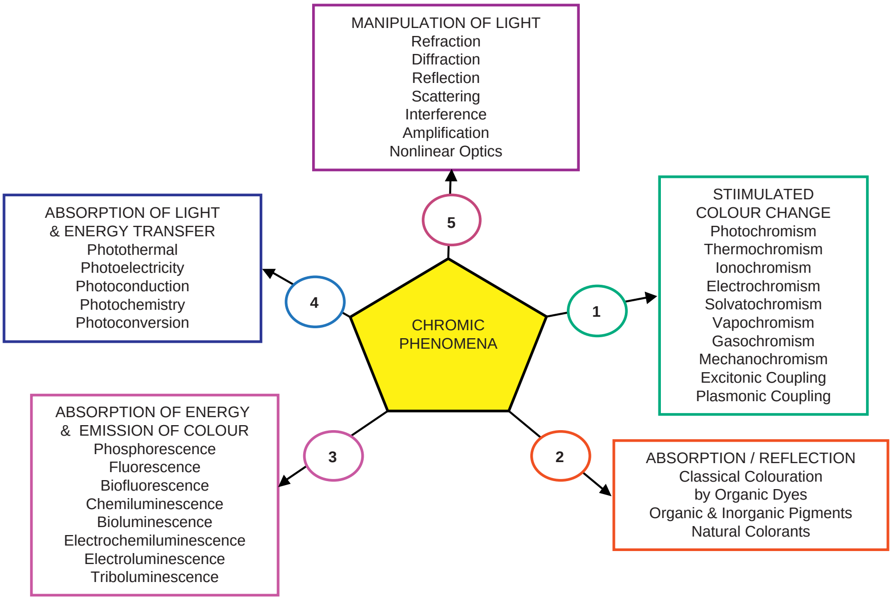


Figure I.1 Classification of chromic phenomena with chapter numbers.

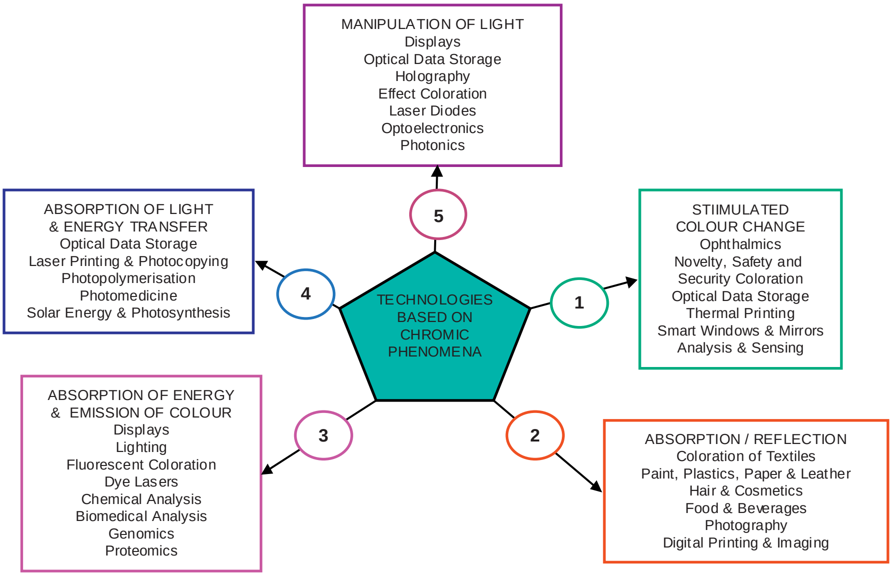


Figure I.2 The main technologies dependent on chromic phenomena.

include areas not covered in the first edition. The effect on colour of stacked chromophores due to their interaction by excitonic coupling has been known for many years. We now include a section covering its significance. In the meantime "aggregachromism" has been coined for this phenomenon. The source of colour displayed by colloidal metal particles is due to plasmon resonance and thus differs fundamentally from conventional dyes. The corresponding colour changes due to plasmonic coupling as the metallic nanoparticles interact with one another comprise another new topic.

At this point it seems appropriate to make a general comment about the nomenclature which is being allowed into the colour chemistry literature. Those working on colour change phenomena are responsible for the invention of some of the ugliest compound names encountered in chemistry. All "chromisms" that we know of are listed later in Table 1.1 of Chapter 1, but citation there should not be taken as our approval or sanction of their general use. In fact we would recommend the avoidance and abandonment of the worst.

By far the largest commercial application of colour in volume terms still comes *via* the classical light absorbing dyes and pigments, which are covered in Chapter 2. However, their use has spread way beyond textile coloration, into paints and inks, or as cosmetics and hair colorants, and in the coloration of food and beverages. Almost every household in the developed world has a digital printer used in conjunction with their PCs, typically an ink-jet printer. Digital photography, *via* cameras and other hand-held devices such as mobile phones, is now the main way that people capture images. There has been a massive growth of photorealistic digital printers leading to a corresponding reduction in the use of silver halide technology, so long the mainstay of colour photography. With the growth of green/environmental consumers, consideration is given in Chapter 2 to questions surrounding natural colorants.

Chapter 3 is the longest of the five, and covers the chromic phenomena where an input of energy leads to the emission of colour (light). Several technically very important applications find their home here. One of the most important results from excitation by light, leading to phosphorescence or fluorescence (or photoluminescence in general). We expand the coverage of molecules and materials which fall within these groups to include quantum cutters and a more extended section on up-converters amongst more conventional phosphors; and add a variety of emitting nanoparticles, including quantum dots, carbon nanotubes, silicon dots, metal nanoparticles, metal ions and multi-photon absorbers to more conventional fluorophores. Besides their brightening effect in conventional coloration and application in dye lasers, we extend the survey of their rapidly expanding range of important analytical applications in biomedicine and elsewhere. Alongside these we highlight the topical GFP and other natural fluorophores, and finish the fluorescence section with their use in logic systems. The other technologically most significant luminescence derives from electric current as an excitation source. This underpins the variants of light-emitting diodes, based on inorganic and organic systems, for which a recent major theme is white-light generation. The various chemical means to cause luminescence are also applied for technologically important analysis, particularly by electrochemiluminescence, as well as chemiluminescence for non-electric lighting. The main role of phosphors is of course also in lighting, as well as in cathode ray tubes. The increasingly important energy up-converters, mainly based on rare earth ions, leads to several interesting effects, including as a component of security measures, and as cooling elements for optical refrigeration.

The availability of cheap solid-state lasers that cover a wide range of the spectrum has meant that the need for molecules that can absorb their energy and convert it for use in a variety of applications has continued to grow. Large-scale uses include optical data storage discs and the photoreceptors for laser printers, as described in Chapter 4. Photosensitisers are another important group of chemicals that are used both in photochemical applications, *e.g.* polymerisation, and also in important medical applications such as the treatment of cancers *via* photodynamic and photothermal therapies. Solar energy conversion, *via* photovoltaic cells or mimicking Nature's skill with photosynthesis for the production of useful chemicals, occupies a great deal of research energy which is starting to pay off. Solar cells and photobiological processes are commercially available that will no doubt play a future role in helping to preserve the world's dwindling stock of non-renewable energy supplies.

The manipulation of light is the topic of the last chapter in the book. A now classical example of light manipulation is the use of liquid crystals in flat panel display screens for PC monitors and TVs. Combinations of reflection, refraction, diffraction, scattering and interference are remarkably common as means of generating colour in Nature, and are increasingly being used in synthetic pigments formed by thin multi-layered composites, to give pearlescent and iridescent coloration effects. They also find a use alongside other chromic materials as security elements on banknotes, passports and similar. When the periodicity of the material composite is changed from two dimensions to three, as in colloidal photonic crystals formed from colloidal-sized particles to give synthetic opals and inverse opals, again chromic materials result. These show a parallel set of "chromisms" to conventional dyes (Chapter 1). Their main use will be as the optical equivalent to electronic band-gaps in semi-conductors, to control light in the all-optical devices for all-optical communications and computing. Interference coupled with reflection of laser light is used to produce the diffraction gratings comprising holograms. Their most popular manifestation is in the graphic arts, but this technology can be used to give media for high-density 3D-holographic data storage, which reportedly is about to be launched commercially (2009). In another aspect of all-optical systems, optical modulators have appeared where the active components comprise silicon channel waveguides clad in third-order nonlinear optical material. Third-order materials also include multi-photon absorbing dyes, spread throughout the book, and optical limiters used to cut off intense laser radiation. The hybrid opto-electronics technology, interfacing electronics and photonics, also depends on nonlinear optically active materials. Future high-bandwidth communications will depend on faster interfaces, which is where electro-optic modulators based on quadratic NLO materials formed from polymeric dyes are anticipated to impact. Commercialisation of these, in competition to conventional lithium niobate EOM, has started.

No classification system can hope to encompass all the possible components without any overlap from one group to another, and this is true with the one used in this book. To overcome these difficulties there is extensive cross-referencing within the body of the text, designed to help the reader see where these overlaps occur. Such a vast array of technologies is covered that it would have to run to a multi-volume work if each had been given full justice. The objective has been to provide enough material in each area for the reader to gain a basic understanding of the theory, with greater detail provided on the chemistry and applications of the technology. In fact even the smallest sub-section is sometimes served by a monograph or at least a hefty review. We have tried to identify these so that for each topic a major source text is suggested and the reader can obtain further detailed information as required.

References

1. O. Sacks, *The Island of the Colour-blind*, Picador, London, 1996.
2. J. Gage, *Colour and Culture. Practice and Meaning from Antiquity to Abstraction*, Thames and Hudson, London, 1993.
3. J. Gage, *Colour and Meaning. Art, Science and Symbolism*, Thames and Hudson, London, 1999.
4. C. A. Riley II, *Color Codes. Modern Theories in Philosophy, Painting and Architecture, Literature, Music and Psychology*, University Press of New England, Hanover, NH, 1995.
5. A. Byrne and D. R. Hilbert (ed.), *Readings on Color, Volume 1, The Philosophy of Color*, MIT Press, Cambridge, USA, 1997.
6. K. Nassau, *The Physics and Chemistry of Color*, Wiley-Interscience, New York, 1983.
7. R. McDonald (ed.), *Colour Physics for Industry*, SDC, Bradford, UK, 1997.
8. (a) A. Valberg, *Light Vision and Color*, Wiley, Chichester, 2005; (b) A. Byrne and D. R. Hilbert (ed.), *Readings on Color, Volume 2, The Science of Color*, MIT Press, Cambridge, USA, 1997.
9. T. Lamb and J. Bourriau (ed.), *Colour. Art & Science*, Cambridge University Press, Cambridge, UK, 1995.
10. K. Nassau (ed.), *Color for Science, Art and Technology*, Elsevier, Amsterdam, North Holland, 1998.
11. H. Zollinger, *Color. A Multidisciplinary Approach*, Wiley-VCH, Weinheim, 1999.
12. R. J. D. Tilley, *Colour and the Optical Properties of Materials*, Wiley, Chichester, 2000.

13. P. Gregory, *High-Technology Applications of Organic Colorants*, Plenum, New York, 1991.
14. H. Zollinger, *Color Chemistry*, VCH, Weinheim, 1991, 2nd edn., pp. 347–353.
15. K. Hunger (ed.), *Industrial Dyes*, Wiley-VCH, Weinheim, 2003.
16. W. Herbst and K. Hunger, *Industrial Organic Pigments*, 3rd edn., Wiley-VCH, Weinheim, 2004.
17. P. Bamfield, in *Proceedings of ChemiChromics USA '99*, January 1999, New Orleans, Spring Innovations Ltd, UK.

CHAPTER 1

Phenomena Involving a Stimulated Colour Change

1.1 Introduction

Colour is perceptually conspicuous, a property we can discern directly using our eyes. Therefore any change in the colour of an object, whether this is achromatic from white to black, or chromatic from colourless to coloured or one colour to another, can be easily detected in a direct way by an observer or in a secondary way by the use of simple spectrophotometric instruments. As such, changes in colour provide very important visual signals that can be used to convey useful information to the observer, the most obvious in everyday experience being traffic control signals. Red means stop, green go and amber take care, easily seen and unambiguously understood. In addition, by selective absorption or transmission of light by a material, it is possible to restrict the light energy impinging upon an observer, as experienced on sunny days by users of spectacles with darkened glass lenses. When a third parameter, namely an external stimulus, whether this is chemical or physical, is the cause of the change in colour or the restriction of light transmission, especially when this change is reversible, the potential applications significantly widen. Consequently, research into chemicals that undergo changes in colour upon the application of an external stimulus, especially when this change can be effected in real time, has been extensive. Chemical and material products of this work have found uses in a wide variety of outlets, in both low- and high-technology areas, and the number of applications shows no sign of diminishing.

Some clarification is required on the terminology used in this area. *Chromic materials* is a term widely used to cover products that exhibit *chromic* phenomena, finding applications in what are known as smart or intelligent materials.[1] *Chromogenic phenomena*, whilst synonymous with *chromic phenomena*, has been adopted as the preferred one in the automotive and architectural

Chromic Phenomena: Technological Applications of Colour Chemistry, Second Edition
By Peter Bamfield and Michael G. Hutchings

Published by the Royal Society of Chemistry, www.rsc.org

Table 1.1 List of chromisms.

Electrochromism	***Ionochromism***	***Mechanochromism***	***Photochromism***	***Solvatochromism***	***Thermochromism***	***Hybrids (dual stimulus)***	***Miscellaneous***
Gasochromism	Acidochromism	***Piezochromism***	Diastereophotochromism	Aquachromism, Hydrochromism, Hygrochromism	Diastereothermochromism	Photoelectrochromism	**Group A** Affinochromism Affinitychromism Biochromism
	Halochromism	***Tribochromism***	Heliochromism	Rigidochromism		Thermosolvatochromism Halosolvatochromism	**Group B** ***Aggregachromism*** Amorphochromism Crystallochromism Concentratochromism
	Metallochromism	Barochromism	Chirochromism	Sorptiochromism		Electromechanochromism Electropiezochromism	**Group C** Cathodochromism Magnetochromism Radiochromism
	Alkalinochromism			Aromachromism ***Vapochromism***		Chronochromism	Goniochromism

Notes

1. There are six main classes of chromic phenomena, plus some hybrids and a miscellany of others.
2. There are sub-chromisms in all of these, especially *Solvatochromism*, many of which have been given alternative names historically.
3. Hybrids are ones where more than one chromic phenomenon is at work, although quite commonly we have used the term “indirect chromism”.
4. The miscellaneous ones can be put into three groups A, where stimulus is biological/-chemical; B, involving some change in shape or form; C, involving an external field or radiant energy.
5. Those in bold italics will have separate sections in Chapter 1. The rest will appear within the text of the main ones as appropriate or in a miscellaneous section. ***Goniochromism*** is covered in Chapter 5.

6. ***Rigidochromism*** is usually reserved for luminescent behaviour as more obviously are ***Fluorochromism*** and ***Phosphochromism*** (Chapter 3).
7. Generic term ***Chemichromism*** (hence ***chemichromics***) and therefore ***Photochemichromism***, ***Electrochemichromism***.
8. ***Multichromism*** *(multichromic)* – commonly used term for multi-coloured forms *e.g.* Chromic Phenomena in polymers.
9. ***Polychromism*** *(polychromics)* – several coloured forms, can be related to *Aggregachromism*, *Crystallochromism*, *etc.*
10. Only one or very few refs in Google to ***Elastochromic*** but not *chromism*, colour change on deforming rubbery films of colloidal crystals; *Lyochromic* not *chromism*; *Sonochromism* and *(sonochromic)*; ***Tautochromism*** but not *chromic*; *Varichromism* and *Waterchromism*.
11. ***Cryptochromism*** – camouflage *(Cryptochromic)*.
12. *Bathochromism (bathochromic)*, *Hyperchromism (hyperchromic)*, *Hypochromism (hypochromic)*, *Hypsochromism (hypsochromic)*, *Ipsochromism (ipsochromic)* – all relate to effects on absorption bands.
13. *Panchromism (panchromic)* – wide spectral response.
14. *Monochromism (monochromic)* having only one colour; *Dichromism (dichromic)* two colours in defective vision or having two distinct colours; *Trichromism* (*trichromic*) similarly three distinct colours; *Tetrachromism* (*tetrachromic e.g.* bird vision) four distinct colours. No *chromisms of following but do have *chromic references *pentachromic*, *hexachromic* and *heptachromic*. Most relate to aspects of vision, but can be confused with salts of chromium in searches.
15. *Pleochromism* – colour change in gemstones.
16. *Phytochromism* – colour reaction of phytochromic pigments.
17. *Achromism* – colourless often used in a race context. *Heterochromism (heterochromic)* – medical term, *e.g.* differently coloured iris in eyes, but also skin. *Homochromism (homochromic)* having one colour (usually a medical term). *Metachromism (metachromic*) in evolutionary theory, *Xanthochromism* applied to birds, fish and other animals whose coloration is unusually yellow through an excess of yellow pigment.
18. *Synchromism (synchromic*) – idea in art that colour and sound are the same phenomenon.
19. The following have only the *chromic and not *chromism ending. *Antichromic* (anticancer), *Arkyochromic* (medical), *Autochromic* (biochemical and in dimming mirrors), *Cytochromic*, *Karyochromic*, *Lipochromic* (lipid pigments), *Normachromic* or *Normochromic* (medical – blood count), *Ommochromic* (natural pigments), Optochromic, *Quadrichromic – four-colour printing technique*, *Somatochromic*, *Spectrochromic*, *Stichochromic*, *Superchromic*, *Transchromic* (transgenic animals), *Xantochromic*.

areas, hence *chromogenic materials*.[2(a),(b)] There is a further complication in inorganic chemistry, especially where metal complexes are involved, as here the topic is called chromotropism, but definitely not chromotropic, which is reserved for the naphthalene sulfonic acid of that name.[2(c)]

These colour change phenomena, whether known as chromic or chromogenic, are classified and named after the stimulus that causes the change. Accordingly, photochromism is a change in colour, usually colourless to coloured, brought about by light, and the material or chemicals undergoing this change are photochromic. Electrochromism is a reversible colour change upon oxidation or reduction brought about by an electrical current or potential, thermochromism is a colour change brought about by heat, solvatochromism by solvents and ionochromism by ions, *etc*. A long list of names, shown in Table 1.1, has been devised to describe such chromic phenomena, many of which are very specific and others which seem to have been invented on the whim of a particular researcher, *e.g*. waterchromism for which alternatives like aquachromism and hydrochromism already existed. We have made an attempt to rationalise the nomenclature applied to these chromic phenomena in Table 1.1. To date the most important commercially of these phenomena are photochromism, thermochromism, electrochromism, ionochromism and solvatochromism, and consequently these will be covered in some detail in the sections below. Among the miscellaneous chromisms some are growing in commercial importance, namely gasochromism, vapochromism, mechanochromism and those due to aggregation or morphological changes, called aggregachromism, and the more recent one due to plasmonic effects in metal nanoparticles.

1.2 Photochromism

Photochromism is a chemical process in which a compound undergoes a reversible change between two states having separate absorption spectra, *i.e*. different colours, whether the compound is in a crystalline, amorphous or solution state. The change, as illustrated in Figure 1.1, from a thermodynamically stable form A to B occurs under the influence of electromagnetic radiation, usually UV light, and in the reverse direction, B to A, by altering or removing the light source or alternatively by thermal means. When the back reaction occurs photochemically this is known as type P photochromism and when thermally as type T photochromism. The change in colour in the forward direction is usually to longer wavelength, or bathochromic, as shown in Figure 1.1. The reversibility of this distinct colour change is key to many of the uses of photochromism.

In many systems, including spiropyrans, spirooxazines and chromenes, the back reaction is predominantly thermally driven, but in others the photochemically induced state is thermally stable and the back reaction must be driven photochemically, as in fulgides and diarylethenes. The assistance of heat in the reversion of colour can be regarded as an example of thermochromism, but in this text the term is reserved for those systems where heat is the main cause of the colour change (see 1.3).

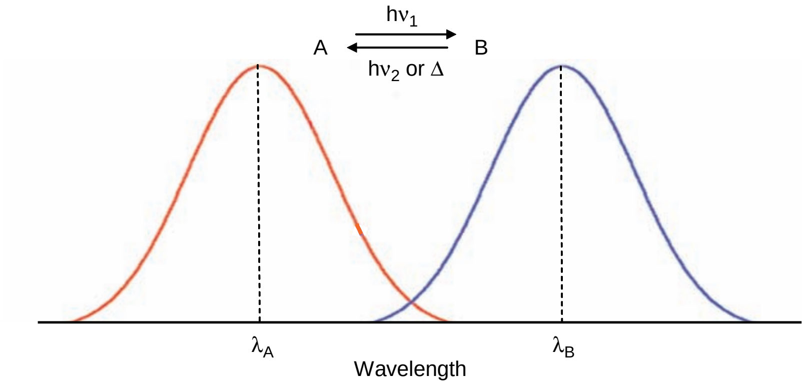


Figure 1.1 Reversible photochromism.

Photochromism is a vast field and in this section of the book we will only be able to describe in any detail the main classes of photochromic compounds. However, whilst the main emphasis will be on the current commercial applications for these materials, this is a constantly changing field and so some applications of a more speculative nature, especially those having potential in the near future, will also be described. For more detailed accounts of the classes of photochromic materials the reader should consult the books on photochromics edited by Crano and Guglielmetti[3,4] or the book and review by Bouas-Laurent and Durr.[5,6]

1.2.1 Main Chemical Classes

For most commercial applications the minimum properties required for practical use from any class of organic photochromic compounds are:

1. *Colour development*. The material must develop a strong colour rapidly upon irradiation with UV light.
2. *Control of return back to colourless state*. The fade rate back to the colourless state must be controllable.
3. *Wide colour range*. The range of colours must be across the visible spectrum.
4. *Long life*. The response must be constant through many coloration cycles.
5. *Colourless rest state*. The rest state must have as little colour as possible, preferably colourless.

There are five main classes of compounds which can approach these ideal requirements: spiropyrans, specifically spiroindolinobenzopyrans, spironaphthoxazines, naphthopyrans, fulgides and diarylethenes.

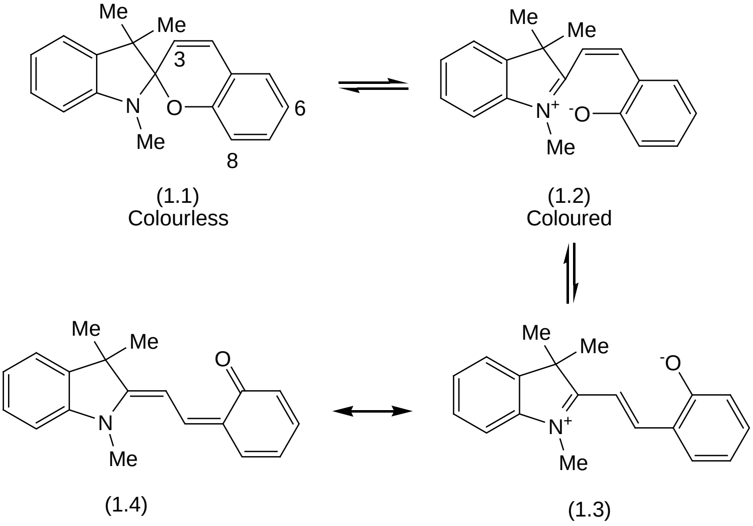


Figure 1.2 Spiroindolinobenzopyran and ring opened merocyanine quinonoid form.

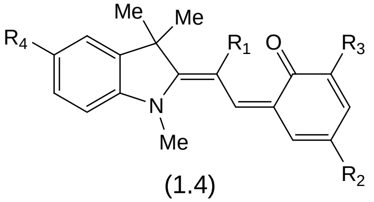
1.2.2 Spirobenzopyrans

Spirobenzopyrans are a very widely studied chemical class of compounds which exhibit photochromism. They consist structurally of a pyran ring, usually a 2H-1-benzopyran, linked *via* a common spiro group to another heterocyclic ring (1.1). Irradiation of the colourless spirobenzopyran (1.1) with UV light causes heterolytic cleavage of the carbon-oxygen bond forming the ring-opened coloured species, often called the "merocyanine" form, which can be present as either *cis*- (1.2) or *trans*- (1.3) isomers (Figure 1.2). They can also be drawn as for the *ortho*-quinoidal form, as represented by (1.4) for the *trans*-isomer (1.3). The structure of the ring-opened form is probably best represented by a delocalised system with partial charges on nitrogen and oxygen atoms. For simplicity's sake we will use the equivalent of the *trans* merocyanine structure (1.4) in this text.

A very large number of possibilities exists for varying the components of the spiropyran ring. The pyran ring is usually substituted benzo- or naphthopyran but the heterocyclic component can be chosen from a long list of ring systems including indole, benzthiazole, benzoxazole, benzselenazole, quinoline, acridine, phenanthridine, benzopyran, naphthopyran, xanthene, pyrrolidine and thiazolidine. The thiopyran analogues have attracted much interest, as on ring opening they absorb at longer wavelengths than the corresponding pyrans. Spiroindolinobenzopyrans are readily synthesised typically by reacting Fischer's base or a derivative with aromatic hydroxyaldehydes (salicylaldehydes).

The open-chain form of the spirobenzopyran shows a strong, intense absorption in the visible region of the spectrum typical of merocyanine dyes (see Chapter 2). Because of the thermal instability of the open-chain form it is

Table 1.2 Absorption maxima (ethanol) of the coloured form of substituted spiroindolinobenzopyrans.



(1.4)

Compound	*R_1*	*R_2*	*R_3*	*R_4*	*λ_{max}, nm*
(1.4a)	Ph	NO_2	OMe	H	625
(1.4b)	H	NO_2	OMe	Ph	568
(1.4c)	H	OMe	NO_2	Ph	625
(1.4d)	H	NO_2	H	H	532
(1.4e)	H	H	NO_2	H	544

necessary to use a rapid scanning spectrophotometer to measure the absorption spectrum. The ring-opened form of spiroindolinobenzopyran (1.4) has absorption at λ_{max} 531 nm in toluene. This class of compounds exhibits a strongly positive solvatochromic effect (see Section 1.7), with the shape of the absorption curve changing and its position moving hypsochromically as the solvent polarity increases.[7] A review of these and other closely related spiroheterocycles provides good insight into the origins of their photochromic, thermochromic and solvatochromic properties.[8] From the data given in Table 1.2, it can be seen that substituents in the 3-, 6- and 8-positions of the original spiropyran ring (see 1.1) have the biggest influence on the spectral properties of the coloured form.[9] The large bathochromic shift in (1.4a) *versus* (1.4b) is credited to steric hindrance caused by the group in position 3, whilst that from the nitro group at position 8 is considered to be due to interaction of the phenolate anion with the oxygen atom of the nitro group. Replacing the isoindoline group in (1.4a) with a benzoxazole ring causes a hypsochromic shift (600 nm) whilst a benzthiazole ring moves the absorption bathochromically (635 nm).

1.2.3 Spironaphthoxazines

Spirooxazines, the nitrogen-containing analogues of the spiropyrans, are very resistant to photodegradation. Known in this field as fatigue resistance, it is an essential property for those photochromic materials designed for applications in solar protection uses, such as sun spectacles. The photochromic ring opening of the benzannelated spironaphthoxazine analogue to its coloured form is shown in Figure 1.3.

Nitrosonaphthols (1.5), the precursors used in the synthetic route to spirooxazines, are much more stable than the nitrosophenols required for the

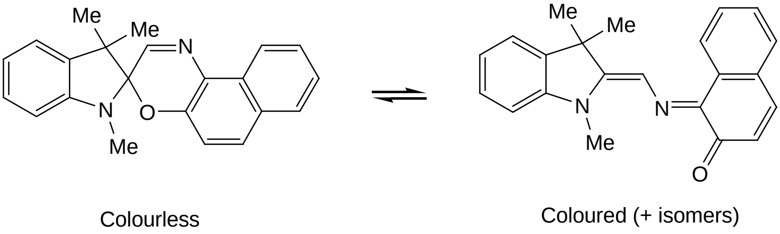
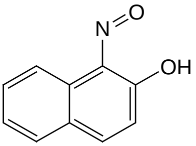
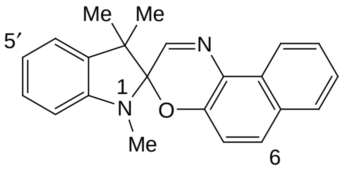


Figure 1.3 Spironaphthoxazine photochromic forms.

parent benzo analogue and hence all the commercially available products are based on the spiroindolinonaphthoxazines ring structure (1.6).



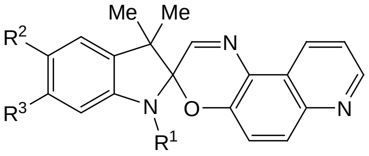
(1.5)



(1.6)

The spiroindolinonaphthoxazine derivatives became commercially important compounds once detailed research work led to products which overcame many of their initial weaknesses, such as relatively poor fatigue resistance and a poor colour range (550–620 nm). The important positions for substitution in the ring of (1.6) are the 5′-position, which has a large effect on the colour; the 6′-position, which has a major effect on both the colour and properties such as optical density (OD) and extinction coefficient; and the alkyl group on position 1, which has a kinetic effect on the rate of loss of colour back to the colourless state.[10]

Another group of commercially important spirooxazines are those where the naphthalene ring is replaced by quinoline to give the spiroindolinopyridobenzoxazines (1.7).



(1.7)

a, R^1 = n Pr, R^2 = OMe, R^3 = H
b, R^1 = n Pr, R^2 = Me, R^3 = Me
c, R^1 = Me, R^2 = Me, R^3 = Me

Table 1.3 Substituent effects on the absorption maxima (acetone) of the coloured state of spiroindolinonaphthoxazines (1.6).

6 substituent	*5′ substituent*	*λ_{max}, nm*
H	H	605
Indolino	H	592
Indolino	OMe	623
Indolino	Piperidino	637
Piperidino	H	578
Piperidino	Cl	568
Piperidino	CF_3	560
Morpholino	H	580
Diethylamino	H	574

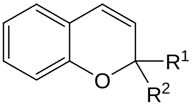
The spectrum of the ring-opened form of the parent spiroindolinonaphthoxazine (1.6) has λ_{max} at 590 nm (acetone). Spiroindolinonaphthoxazines also show a negative solvatochromic shift, the absorption moving hypsochromically (20–60 nm) in less polar solvents (*e.g.* toluene *versus* ethanol), the converse of what happens with spiroindolinobenzopyrans (see Section 1.2.2.1).

Introduction of dialkylamino substituents in the 6′-position of (1.6) causes a hypsochromic shift in the absorption maximum of the coloured state and also an increase in its intensity. This hypsochromic shift can also be increased by introducing electron-withdrawing groups into the 5-position of (1.6), whilst electron-donating groups move the absorption maximum in the opposite direction (Table 1.3).[10,11]

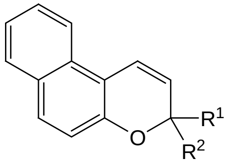
Changing the alkyl substituent on the 1-position of (1.6) has little or no effect on the absorption maxima and no effect on the fatigue resistance. However, there is a very marked and technically important effect on the loss in the initial optical density of the coloured state after activating with UV light. This is frequently reported as the percentage loss in initial optical density ten seconds after removing the UV source, the $IODF_{10}$ value. The more highly branched the alkyl group the lower the $IODF_{10}$; methyl shows an $IODF_{10}$ of 29% whilst for neopentyl this drops to 9%. Additionally, increasing the branching causes a lowering of the temperature dependence of the thermal conversion back to the colourless state.[10]

1.2.4 Benzo- and Naphthopyrans (Chromenes)

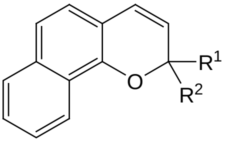
The photochromic compounds of potential interest, based on the 2H-chromene-ring system, are the 2H-benzopyrans (1.8) or the three isomeric naphthopyrans (1.9–1.11). However, 2H-naphtho[2,3-b]pyrans (1.11) show little or no useful photochromic behaviour and can be discounted from any further discussion. Although R^1 and R^2 can be part of a carbocyclic spiro ring, they are more commonly unconnected substituents such as gem dialkyl or aryl groups.



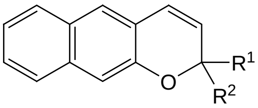
(1.8)



(1.9)



(1.10)



(1.11)

The photochromic mechanism for the chromenes is very similar to that for spiropyrans given in Figure 1.1. Under the influence of UV the C–O bond in the pyran ring is broken as in Figure 1.4, where formation of the *cis*-quinoidal species occurs in picoseconds, followed by isomerisation to the *trans*-form in nanoseconds.

The two naphthopyrans of interest (1.9) and (1.10) show quite different photochromic behaviour. Isomer (1.10; R^1, $R^2 = Ph$) produces a more bathochromic coloured state than (1.9; R^1, $R^2 = Ph$), ($\lambda_{max} = 481$ nm *versus* 432 nm in toluene), a large increase in coloration, but a very slow fade rate back to the colourless state.[12(a)] Because of the slow kinetics, coupled with a greater ease in synthesis, most of the work, until the mid 1990s when these problems were overcome, concentrated on the 3H-naphtho[2,1-b]pyrans (1.9).

Simple 2,2-dialkyl-2H-benzopyrans can be synthesised by several well-established routes.[12] [15] 3H-Naphtho[2,1-b]pyrans (1.9) with an amino or alkoxy residue in the 6-position (1.14), which show particularly high

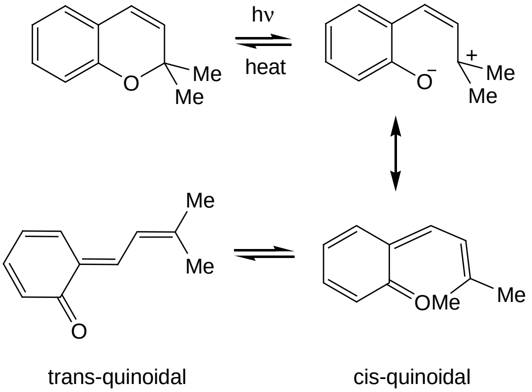
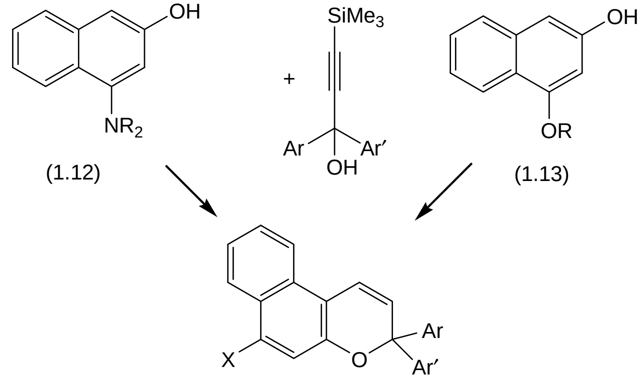


Figure 1.4 Photochromic behaviour of chromenes.



(1.14; X = NR_2 or OR)

Figure 1.5 Synthetic route to 6 amino and 6 alkoxy 3,3′ 3H naphtho[2,1 b]pyrans.

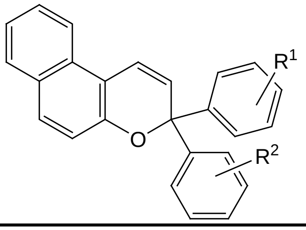
colourability, are synthesised from the corresponding 1-amino- and 1-alkoxy-3-hydroxynaphthalenes (1.12 and 1.13) as illustrated in Figure 1.5.[16]

As mentioned in Sections 1.2.2 and 1.2.3, the photochromic reactions of spirobenzopyran and spironaphthoxazines show a marked solvent dependency and this is also the case with benzo- and naphthopyrans. Consequently, spectral data collected from the literature are only comparable within any one study or where the same solvent has been used. This accounts for any discrepancies between one set of results and any other one listed in this and related sections of the chapter. The data normally quoted when discussing the properties of photochromic materials relate to the absorption maximum (λ_{max}) of the coloured state, the change in optical density on exposure to the xenon light source (ΔOD) and the fade rate ($T_{1/2}$), which is the time in seconds for the ΔOD to return to half of its equilibrium value. Two other measurements, often quoted in the literature, are the IOD (initial optical density) at λ_{max} and the $IODF_{10}$ value already described in Section 1.2.3.

The influences on the absorption spectra and the other photochromic properties of compounds with substituents in the 3H-naphtho[2,1,b]pyran ring and on the 3,3′-aryl groups have been studied in detail.[12,16] Electron-donating groups in one or both of the 3-phenyl groups, especially in the *para*-position, show a marked bathochromic shift in the absorption maxima of the coloured state, whilst electron-withdrawing groups have the opposite effect (Table 1.4). Substitutions in the *ortho*-position have little effect on the absorption maxima but have a very marked effect on the rate of return back to the colourless state, presumably due to stabilisation of the open-chain form (Table 1.4).

Substitution in the naphthopyran ring is most effective in the 6- and 8-positions, especially the former. Electron-donating groups in the 8-position cause a bathochromic shift and an increase in IOD. In position 6, electron-donating groups have the opposite effect on the absorption maximum, but more importantly produce an even larger increase in IOD and a dramatic

Table 1.4 Influence of substituents in the 3-phenyl rings on the properties of 3,3-diaryl-3H-naphtho[2,1-b]pyrans[16] (reproduced with permission of Springer Science and Business Media).

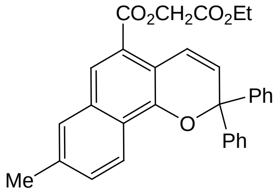


R^1	*R^2*	*λ_{max} nm*	*ΔOD*	*$T_{1/2}$ sec*	*Solvent*
H	H	430		11	A
H	4 MeO	458		8	A
H	4 CF_3	422		28	A
4 MeO	4 MeO	475		3	A
4 MeO	4 CF_3	440		4	A
4 MeO	4 NMe_2	512		1	A
4 NMe_2	4 NMe_2	544		0.5	A
H	H		0.36	45	B
2 F	4 MeO	456	1.0	170	B
2 F	3,4 diMeO	472	1.05	203	B
2 Me	4 MeO	469	2.40	600	B
2,6 diF	4 MeO	450	2.23	1800	B

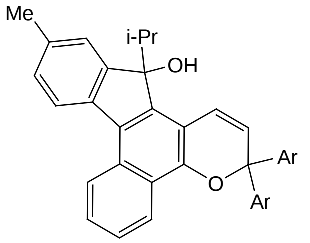
A toluene
B imbibed into diethyleneglycol bis(allyl carbonate) polymer.

reduction in the $IODF_{10}$ figure, an effect that is described as "hyperchromic" (Table 1.5).[12]

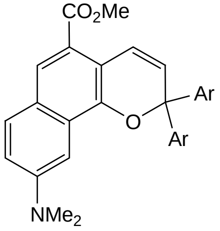
As mentioned above, the main problem with the 2H-naphtho[1,2-b]pyran ring system (1.10) is the very slow rate of fading back to the colourless state: (1.10: R^1, $R^2 = Ph$), $T_{1/2} = 1800$ sec *versus* 45 sec for (1.9; R^1, $R^2 = Ph$). These problems have largely been overcome to produce materials suitable for ophthalmic uses by introducing electron-withdrawing groups in the 5-position, as in (1.15), and, more intriguingly, by having an indeno group fused onto the 5- and 6-positions (1.16) (see also in Section 1.2.8.1).[16,17]



(1.15)

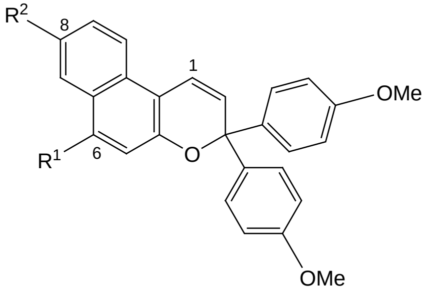


(1.16)
Ar = 4-MeOC$_6$H$_4$



(1.17)
Ar = 4-piperidinylC$_6$H$_4$

Table 1.5 Influence of substituents in 6- and 8-positions on the properties of 3,3-diaryl-3H-naphtho[2,1-b]pyrans[12(a)] (reproduced with permission of University of Leeds, Department of Colour Chemistry).



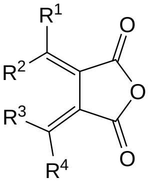
R^1	R^2	λ_{max} nm	IOD	$IODF_{10}\%$	Solvent/host
H	H	475	0.20	50	A
MeO	H	456	1.89	7	A
H	MeO	502	0.55	41	A
H	H	475	0.12	45	B
MeO	H	456	1.42	10	B
Piperidino	H	452	1.95	11	B
Morpholino	H	452	1.95	13	B

A polyurethane
B Spectralite

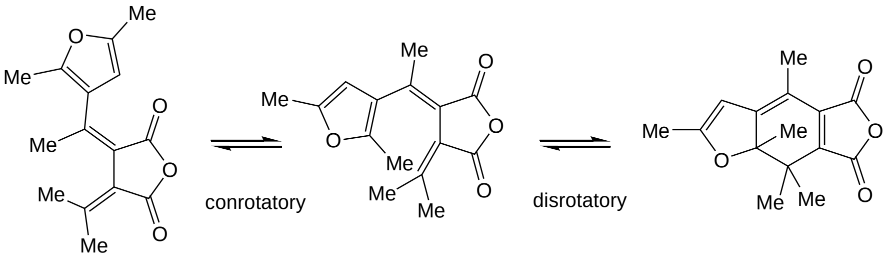
Of particular interest for ophthalmic outlets are neutral grey-coloured photochromics. To meet this objective 2H-naphtho[1,2-b]pyrans with matched twin absorption peaks have been synthesised which produce various shades of grey. For example (1.17) has λ_{max} 490 and 581 nm in toluene.[12(b)]

1.2.5 Fulgides

Stobbe was the first to observe photochromism in fulgides (1.18) when he synthesised them by the condensation of an arylaldehyde or ketone with a substituted methylene succinate.[18] However, it was not until the 1970s, during the course of the extensive work carried out by Heller and his collaborators, that their chemistry and use in photochromism was truly exploited.[19] [21] Heller's work showed, amongst many other things, the importance of R^1 in (1.18) being a 5-membered ring heterocycle, *e.g.* furan.



(1.18)



(1.19)
Z-

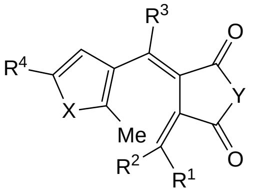
(1.20)
E-

(1.21)
C

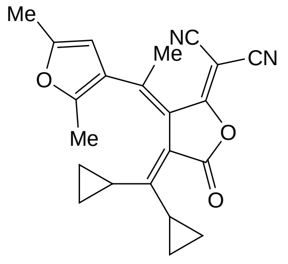
Figure 1.6 Photochromic process for fulgides[22] (reproduced with permission of University of Leeds, Department of Colour Chemistry).

Fulgides can exist as *E*- or *Z*-isomers by virtue of rotation around the double bonds in (1.18). This is illustrated for the furano derivative in Figure 1.6. Isomerisation of the yellow *Z*-fulgide (1.19) to the *E*-fulgide (1.20) and cyclisation of this to the red photochrome (1.21), designated as C here but often called the P state, occurs on irradiation with UV light. The coloured species (1.21) is converted back to the *E*-fulgide (1.20) by white light but not by heat. Thermally assisted reversion of coloured to colourless is not observed, because the interactions between the two syn methyl groups prevent the symmetry-allowed, disrotatory mode of electrocyclic ring opening.[22] Since both the forward and back reactions require light energy it is important that they both show good quantum yields.

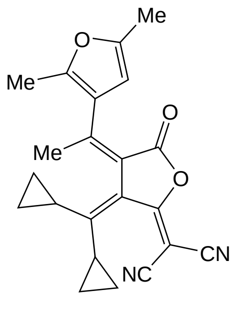
The Stobbe condensation, as described above, is the preferred route to fulgides as exemplified by the synthesis of the 5-membered ring analogues such as the anhydrides (1.22), which can be readily converted to the corresponding fulgimides (1.23), or further functionalised by reaction with for example malononitrile to give (1.24) from the corresponding *E*-fulgide and (1.25) from the *Z*-isomer.[23]



(1.22) Y = O
(1.23) Y = NR



(1.24)



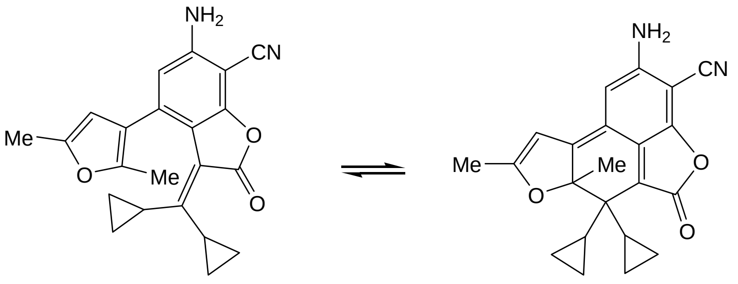
(1.25)

The main areas for molecular manipulation of the heterocyclic fulgides (1.26; Table 1.6) are the hetero atom X in the five-membered ring; the substituent R^4

on this ring; R^3 on the bridging methylene group; changes in the exomethylene group substituents R^1 and R^2; changes from fulgides (1.26, A = O) to give fulgimides (1.26, A = NR); and conversion of the ring carbonyl groups to imides (1.26; B or C = NR) or dicyanomethylene groups as in (1.24).

The change from X = O to X = S and NR causes the absorption of the coloured state to move bathochromically, from red to purple and blue. Major bathochromic shifts are also observed when R^4 is a phenyl group carrying electron-donating groups in the 4-position. The substituent R^3 has a marked influence on the quantum efficiency of the coloration process; isopropyl has in some cases given a 20–60% increase over methyl. Again the main effect of changing substituents R^1 and R^2 is photochemical, where replacing isopropylidene with a adamantylidene group results in a six-fold increase in the decoloration efficiency. Changing from a fulgide to a fulgimide has little effect on the photochromic properties but does make the ring system more resistant to hydrolysis. Replacement of either of the ring carbonyls of the fulgide by NR gives the isofulgimides. When B = NR the change in colour is hypsochromic but for C = NR there is little change in the absorption maximum but a large increase in extinction coefficient. Both of the dicyanomethylene derivatives (1.24) and (1.25) move bathochromically, the effect being most marked in the latter case. The thienyl analogue of (1.25) is even more bathochromically absorbing.[24] The results from some of these key structural modifications are summarised in Table 1.6.

Treatment of (1.24) with base causes one of the cyano groups to cyclise onto the methyl group at R^3, producing phenyl ring compound (1.27a). The photoproduct (1.27b) absorbs into the near infrared (NIR) at 720 nm, whilst the thienyl analogue is even more bathochromic at 760 nm.[22] Absorption in this region of the spectrum is essential in applications where semi-conducting diode lasers are used as the light source.[25]

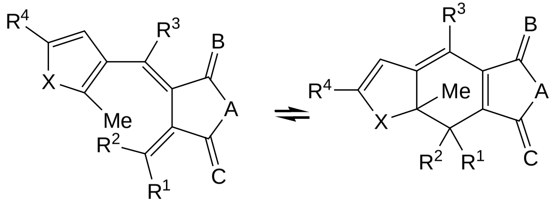


(1.27a) (1.27b)

1.2.6 Diarylethenes

Pioneering work by Irie in the 1980s brought the well-known photoisomerisation of stilbenes into the useful photochromic range by replacing the phenyl rings with thiophenes, and the bridging ethylene group by a maleic anhydride, imide or perfluorocyclopentene group, as shown in Figure 1.7. The

Table 1.6 Effect of substituents of the properties of fulgides and derivatives.



(1.26e) (1.26c)

X	R^1	R^2	R^3	R^4	A	B	C	λ_{max} nm	ε_{max}	ϕ_{EC}	ϕ_{CE}
O	Me	Me	Me	Me	O	O	O	496	8200	0.20	0.055
S	Me	Me	Me	Me	O	O	O	525	8000	0.15	0.01
NPh	Me	Me	Me	Me	O	O	O	630	7300	–	–
O	Me	Me	Me	Ph-4-NR_2	O	O	O	588	26500	–	–
O	Me	Me	i-Pr	Me	O	O	O	500	9000	0.58	0.043
O	Adamantyl		i-Pr	Me	O	O	O	519	6900	0.51	0.26
O	Cyclopropyl	Cyclopropyl	Me	Me	O	$C(CN)_2$	O	594	–	–	–
O	Cydopropyl	Cyclopropyl	Me	Me	O	O	$C(CN)_2$	633	–	–	–
O	Me	Me	Me	Ph	O	O	$C(CN)_2$	669	–	–	–

Colour properties refer to (1.26c).

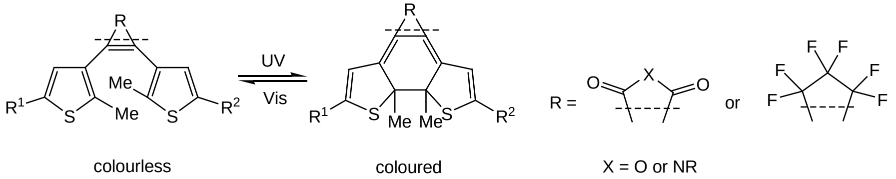


Figure 1.7 Photochromic behaviour of dithiophenylethenes.

thiophene ring can be annulated with a benzene ring or replaced with indoles, furans and thiazole rings.

The reversible electrocyclic interconversion between the colourless ring-opened state and the coloured ring-closed state on irradiation with light occurs at well-separated wavelengths. The thermal conversion is not favoured and the compounds show very high fatigue resistance.[26,27] It is these properties that have made this type of photochrome much studied for use in applications such as optical switches and memories.

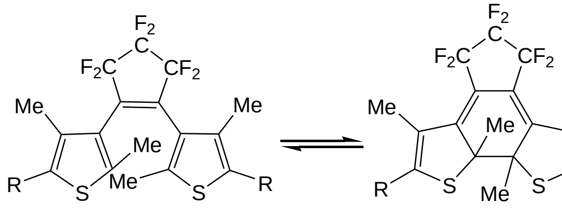
A wide variety of routes is available for the synthesis of both symmetrical and non-symmetrical diarylethenes and their further functionalisation.[26 28] These have been exploited to produce a myriad of complex structures.[29]

The absorption spectra of symmetrical dithiophenylethenes (1.28) are dependent on the substituents on the thiophene ring. Introduction of phenyl groups in the 2-position cause bathochromic shifts, and significantly higher molar extinction coefficients. These are further enhanced by electron-donating groups in the *para*-position of the phenyl ring. There is, however, a large drop in the quantum efficiency of the cyclo-reversion reaction (Table 1.7).[26]

A move to even longer wavelengths can be achieved by using non-symmetrical maleic anhydrides, especially those containing thiophenes and indole rings, having a coloured form of the general formula (1.29). Bathochromic shifts, with a combined effect of 102 nm, can be achieved by replacing the 2-methyl group in the thiophene ring and putting a methoxy group in position 5 of the indole ring (Table 1.8).[26,27] A more extensive list of the spectral properties of thermally irreversible diarylethenes has been produced recently.[30] Good correlation is claimed between the calculated and observed colours of ring-closed diarylethenes using *ab initio* calculations based on a time-dependent density functional theory approach.[31]

The fatigue resistance of materials of this class, measured as the number of photochromic cycles at which the absorbance of the coloured species decreases to 80% of the first cycle, can be raised to quite high levels. For instance, for the simple symmetrical maleic anhydride (1.30), the repeatable cycle number in air is only 70, but for the non-symmetrical benzothiophene analogue (1.31; R = Me) this rises to 3700, and to greater than 10,000 for (1.31; R = OEt).[27] The figures are even higher in vacuum due to either the absence or the lower formation of singlet oxygen. The thermal stability of (1.30) is over 90 days at 80 °C and at least five years at room temperature, whilst products like (1.31) are only quoted to be "stable", having lifetimes longer than 12 hours at 80 °C.

Table 1.7 Properties of symmetrical dithiophenylperfluorocyclopentenes[26] (reproduced with permission of Springer Science & Business Media).

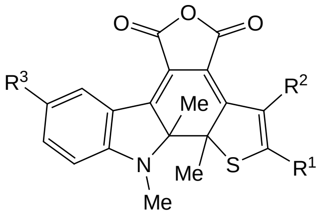


(1.28)

R	$\lambda_{max\ COL}$ nm^a	$\varepsilon_{max\ COL}$	Φ_{cyc}	Φ_{cycrev}
H	534	5,050	0.21	0.13
Ph	562	11,000	0.46	0.015
C_6H_4 4 OMe	570	14,000	0.48	0.008
C_6H_4 4 NEt_2	597	18,000	0.37	0.0025

[a]Hexane

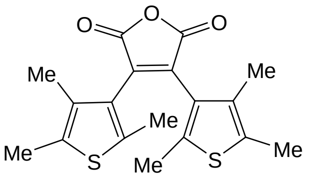
Table 1.8 The absorption maxima of non-symmetrical maleic anhydride-based photochromes[26] (reproduced with permission of Springer Science & Business Media).



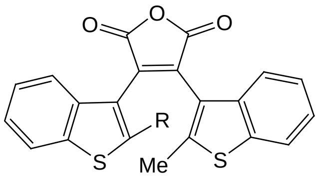
(1.29)

R^1	R^2	R^3	λ_{max} nm^a
Me	Me	H	578
Me	Me	OMe	611
CN	Me	H	628
CN	Me	OMe	680

[a]Hexane



(1.30)



(1.31)

1.2.6.1 Gated Photochromism in Diarylethenes

Gated photochromism is the term used to describe a type of photochromism where the photochromic process is controlled by passing through a gate, the opening and closing of which is governed by a non-photochemical process, which can be chemical (*e.g.* protonation, esterification, oxidation-reduction), or by physical means (*e.g.* solvation or thermal). This type of reactivity is indispensable if photochromism is to be applied in display and optical memory technologies.

Whilst methods have been attempted with fulgides the most successful to date have been using diarylethenes. This is because they show excellent thermal stability in both open and closed ring forms coupled with good fatigue resistance. An example of such a system is that described by Irie involving a chemically gated diarylethene derivative containing a hydroxyphenyl group, as outlined in Figure 1.8.[32]

In the compounds containing the hydroxy group, the excited states of the molecules are efficiently quenched by intramolecular proton transfer and therefore they are not photochromic. However, when the hydroxyl group is masked by esterification the esterified diarylethenes undergo typical photochromic reactions. Therefore the photochromic reaction of diarylethene derivatives can be controlled by the addition of acid, giving ester hydrolysis.

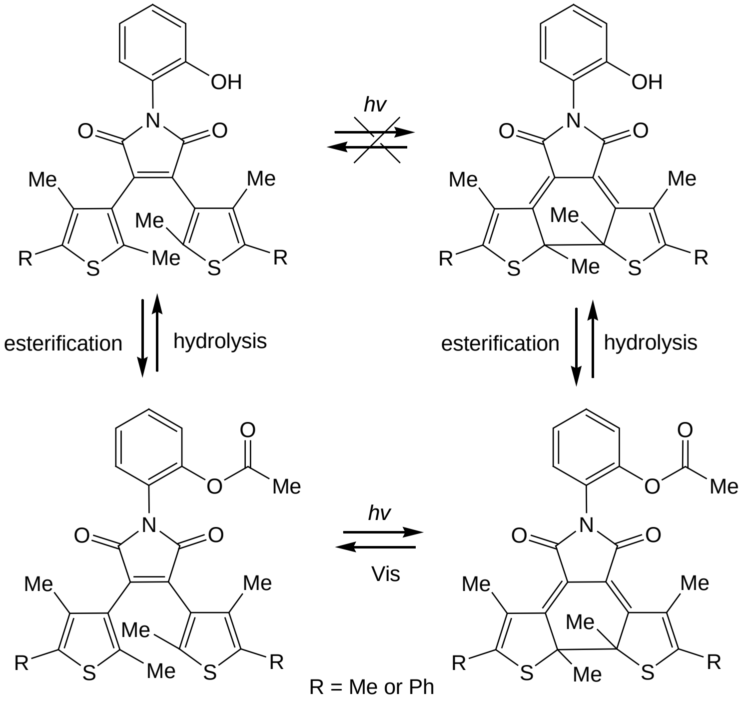


Figure 1.8 Chemically gated diarylethene derivatives.

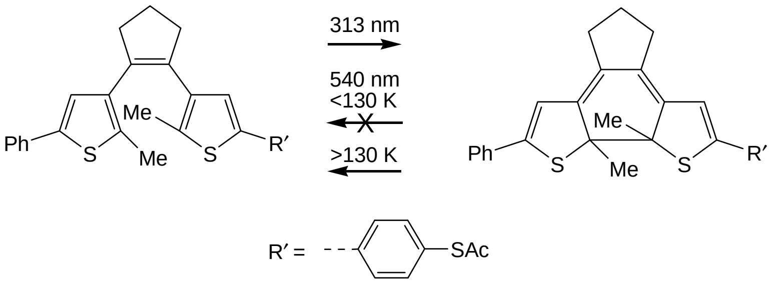


Figure 1.9 Gated photochromism controlled by thermal means.

An example where the gate is controlled by thermal means is shown in Figure 1.9. Here the ring-opening process is suppressed with decreasing temperature, leading to the complete absence of the photoreaction below a cut-off temperature of around 120–130 K. By contrast, the reverse ring-closure process to the coloured form shows no significant temperature dependence. This means there is a temperature-dependent region where photochemical ring opening is observed and a temperature-independent region, below 130 K, where no photochemistry is observed. Reversibility of the photoprocesses can thus be controlled by temperature.[33]

These types of chemically gated systems should make them suitable for application as display materials, memory media and molecular logic gates, and further aspects of this topic will be discussed in Section 1.2.8.3.

1.2.7 Miscellaneous Photochromic Systems

Whilst the foregoing classes of photochromic compounds are the most widely studied and applied technically, there are others which have significant importance in this still developing field.

1.2.7.1 Azobenzenes

Azobenzenes undergo photoinduced isomerisation from the *trans* (*E*) to the *cis* (*Z*) forms, which can be reversed either by photochemical or thermal means (see Figure 1.10).[34]

However, when the azo compound is a dye then there is a significant colour shift on switching from the more highly coloured *E*- to the *Z*-form, a technical disadvantage being easily observed on cloth exposed to daylight (see Chapter 2). The structure of the *cis* isomer has proved difficult to explore experimentally, but its presence in a series of commercial dyes, exemplified by (1.32), has been demonstrated using ^{1}H NMR spectroscopy coupled with *in-situ* laser irradiation.[35(a)] However, since the absorption bands of the *E* and *Z* isomers overlap, photochromism in simple azobenzenes is not accompanied by any

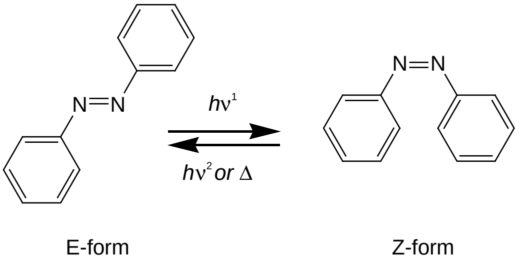
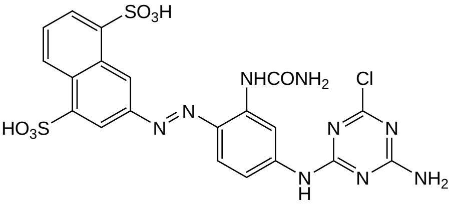
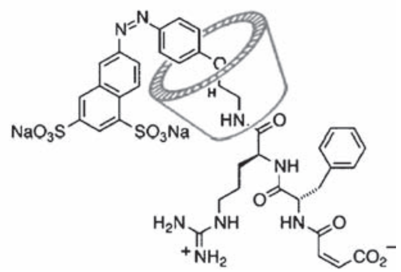


Figure 1.10 Photoisomerisation of azobenzenes.

distinct colour change, but significantly there are other changes in the chemical and physical properties of the isomers which make this molecular system suitable for use in a variety of applications.[35(b)]



(1.32)



(1.33)

This is especially the case when the chromophore is attached to another photochrome or in a polymer for switching applications (see also Section 1.2.8.3). Recent examples include photoswitchable enzymatic cleavage of a peptide-linked rotaxane, shown here in the *Z*-form (1.33),[36(a)] and the reversible photoisomerisation of the azobenzene side chain on a peptide oligomer, where *Z* to *E* isomerisation is realised by thermal means (Figure 1.11).[36(b)]

1.2.7.2 Other Organic Photochromes

Salicylidenanilines (Schiff bases or anils), whilst probably better known for their thermochromic behaviour (see Section 1.3), were one of the earliest recorded photochromic systems.[37] Of particular interest is the fact that anils undergo photochromism in the solid state, a property they share with other photochromes including diarylethenes, making them potentially useful in a variety of outlets.[38,39] Photochromic behaviour of crystalline anils is based upon tautomerism involving intramolecular hydrogen transfer from the

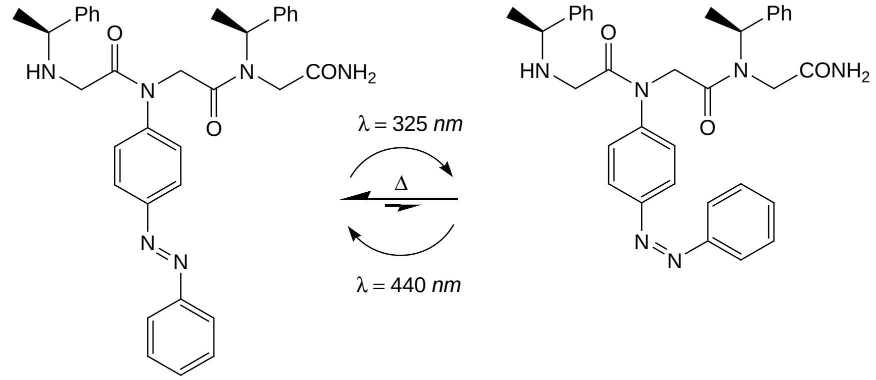
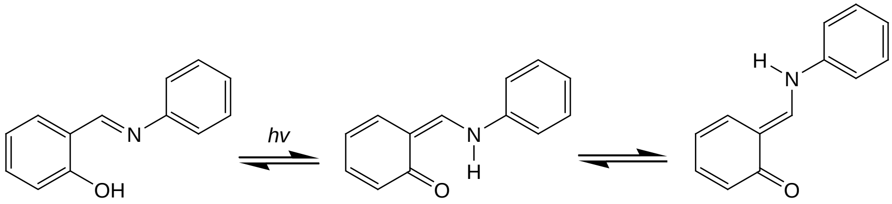


Figure 1.11 Photoresponsive peptoid oligomers bearing azobenzene side chains.

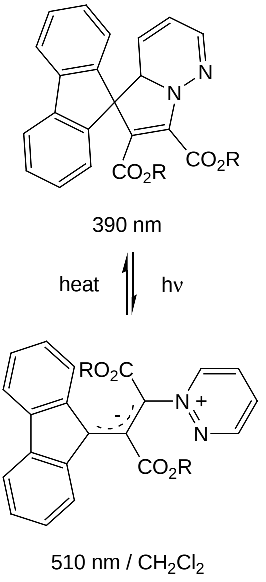


trans enol form (E OH) *cis* keto form (Z NH) *trans* keto form (E NH)

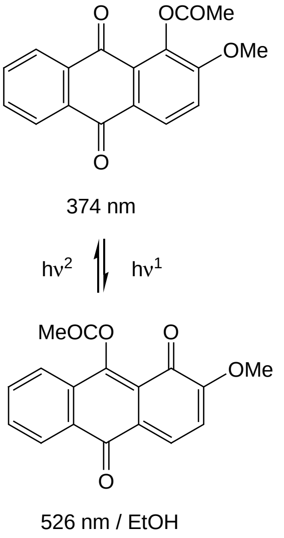
Figure 1.12 Photoinduced isomerisation of salicylidenaniline.

ortho-hydroxy group to the nitrogen atom of the imine excited electronic state, *via* a six-membered ring transition state, producing the *trans*-keto form with the spectrum shifted bathochromically (Figure 1.12).[38]

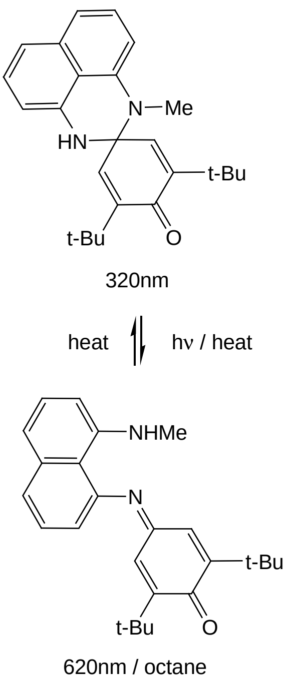
Several other photochromic systems are being studied for a variety of outlets and detailed accounts are available in the literature.[40] [42] Dihydroindolizine-based systems, containing a five-membered ring, undergo photochemical ring-opening to give a coloured zwitterion (1.34). The process can be reversed either photochemically or by thermal means.[40] Photochromic quinones undergo a colour change by photochemical migration of a proton or an R group across the peri positions to produce an extended quinonoid chromophore (1.35), and the process is photoreversible.[41] Photochemical cleavage of a C–N bond in perimidinespirocyclohexadienones, followed by intermolecular rearrangement, produces the deeply coloured quinoneimines (1.36), similar to indophenol dyes in structure; decolourisation is achieved thermally.[42] Bianthrylidenes also show useful photochromism that has been exploited in light-triggered switches (see Section 1.2.8.3), but are more noted for their thermochromic behaviour (see Section 1.3.2.2).



(1.34)



(1.35)



(1.36)

Polymer systems similar to those described for azobenzenes but carrying other photochromes, *e.g.* spiropyrans,[43] pendant to their side chains show photochromic behaviour, as do conjugated polymers, *e.g.* polythiophenes, but they are more noted for their thermochromism (Section 1.3.2.3) and electrochromism (Section 1.5.3.5).

1.2.7.3 Inorganic Photochromes

Silver halide crystals trapped in a glass matrix were used in the earliest successful ophthalmic lenses with photochromic properties. This type of material offered significant practical benefits over other systems, having remarkable fatigue resistance. However, poor darkening and slow fading was a problem, and when there was a switch to plastic lenses it became necessary to move to other more compatible materials (see Section 1.2.8.1). However, the high fatigue resistance of inorganic photochromes makes them ideal candidates for photonic applications.

Several transition-metal oxides exhibit photochromism upon band-gap excitation, including tungsten oxide, molybdenum oxide, titanium dioxide, vanadium pentoxide, niobium pentoxide and zinc oxide.[44] When working with these oxides it is important to use visible light in order to differentiate between thermochromic and photochromic effects, as exemplified by the work on vanadium pentoxide.[45] Continuing interesting developments in this field

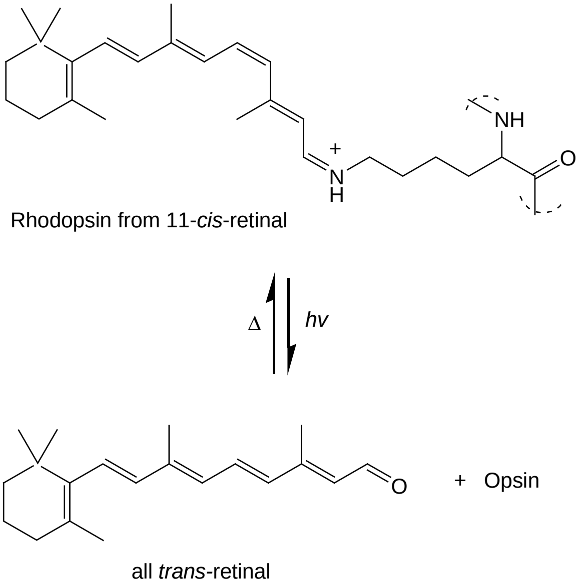


Figure 1.13 Rhodopsin photochromic cycle.

include visible light coloration in molybdenum oxide-titanium dioxide composites,[46,47] and the use of silver nanoparticles deposited on titanium dioxide to give multi-colour photochromism.[48(a),(b)] But there is still a long way to go before practical applications are realised.

1.2.7.4 Biological Photochromes

The visual system is highly dependent on a complex photochromic photocycle, where the chromophore 11-*cis*-retinal is attached to the protein opsin *via* a protonated Schiff base of a lysine residue. This linkage is broken by light and reversed thermally as shown in Figure 1.13.

Bacteriorhodopsin (BR) is a seven-helical transmembrane protein, also with the retinal co-factor, found in the so-called "purple membranes" of bacterium *H. salinarium*. It converts the energy of "green" light (500–650 nm, max 568 nm) into an electrochemical proton gradient, which in turn is used by a second membrane protein, ATP synthase, to generate chemical energy in the form of ATP. The photocycle is initiated by the absorption of a photon by the all-*trans* retinal co-factor. Photon absorption causes rapid rearrangement of the electronic structure of the extended conjugated retinal system which results in *trans*→*cis* isomerisation and deprotonation with consequent colour change from the purple B intermediate to the yellow M intermediate as shown schematically in Figure 1.14.

This reversible colour change gives bacteriorhodopsin the potential for applications in a variety of outlets including optical memories and switches.

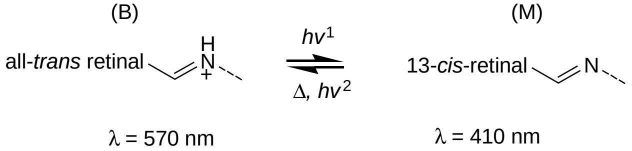
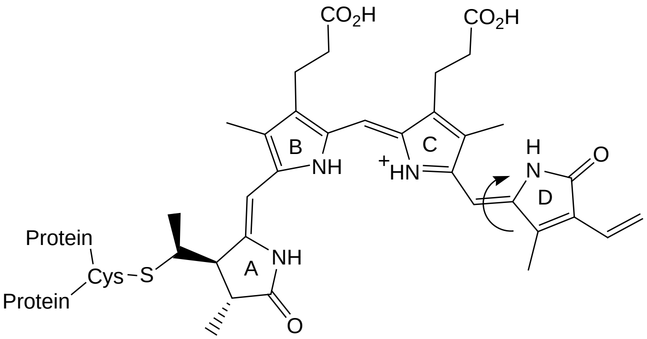


Figure 1.14 Simplified photochemical cycle of bacteriorhodopsin.

However, the protein occurring in Nature does not meet the standards in overall efficiency required for its use in commercial applications and all successful photonic devices use chemical or genetic variants of bacteriorhodopsin.[49]



(1.37; Pr)

Plant phytochromes (1.37) are chromoproteins that control a variety of photomorphogenic processes in plants. There are two forms: phytochrome Pr absorbs red light and the biologically active Pfr far-red light. It is this property that leads to photoperiodism, for instance the photoperiodic induction of flowering (see Figure 1.15). In this way the phytochrome is acting as a light-operated molecular switch. It is also involved in chloroplast development (not including chlorophyll synthesis), leaf senescence and leaf abscission. The phytochrome photocycle is a complicated process but the interconversion of Pr to Pfr involves isomerisation of the bond between rings C and D as shown in (1.37) and proton transfer.

As with bacteriorhodopsin, the native protein will need either chemical or more likely genetic modification to render it of any use in technical applications outside the horticultural field. An example is the conversion of phytochromes to fluorescent probes and reporters.[50]

1.2.7.5 Polymers, Matrices and Amorphous Materials

The incorporation of photochromic groups into polymers whether covalently bonded as part of the backbone, as pendant groups, or in admixture has been

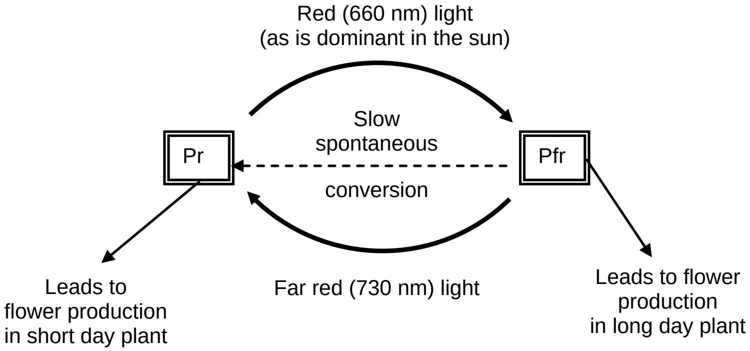
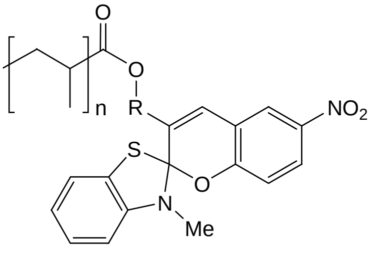


Figure 1.15 Phytochromes in the photomorphogenic process in plants.

much studied because it offers easy fabrication of materials of potential use in many application areas. Of the many photochromic polymeric systems those involving azobenzenes (see Section 1.2.7.1), diarylethenes and fulgides have been the most extensively studied.[51,52]

The presence of photochromic groups in polymer matrices not only influences their colour change properties but also leads to novel photoinduced properties. The matrix has an effect on photochromism but also photochromism has an effect on the matrix. Ichimura suggests that these effects are best understood by considering them in terms of orderedness of molecular structures of matrices, as outlined in Table 1.9.[51]

In this section of the book the zero-dimensional phase materials and their applications will be considered, whilst birefringence and dichroism involving two-dimensional phases will be dealt with in Chapter 5 under liquid crystals. A typical polymer containing a pendant covalently bonded photochromic group is shown in (1.38).



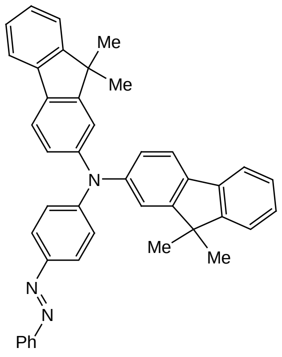
(1.38)

Photochromic amorphous molecular materials have been suggested as alternatives to photochromic polymers and molecularly dispersed polymer systems for applications such as optical data storage and optical switching. These are a class of photochromic materials that form uniform amorphous

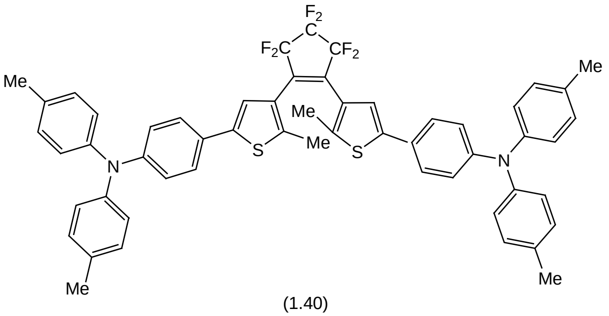
Table 1.9 Dimensional differentiation in molecular structures of matrices.

Orderedness	*Matrix*	*Optical Properties*
Zero dimensional	Solution	Absorption
	Amorphous polymer	Refraction
		Emission
		Reflection
One dimensional	Phase separated state	Light scattering
	Micelle	
	Inclusion complex	
Two dimensional	Stretched film	Birefringence
	Liquid crystal (N,Sm)	Dichroism
	Bi layer membrane	
	Langmuir Blodgett films	
Three dimensional	Cholesteric liquid crystal	Optical rotary power
	Multi layer	Circular dichroism
	Single Crystal	

films by themselves, do not crystallise at high concentrations, and there is no dilution of the photochromic chromophores.[53] The materials are based upon azobenzene and diarylethene photochromes, as shown in examples (1.39) and (1.40). They readily form amorphous glasses with well-defined T_g values when the melt samples are cooled on standing in air, and show reversible photochromic behaviour.



(1.39)



(1.40)

1.2.8 Applications of Photochromic Materials

A reversible change in colour is not the only alteration in physical property experienced during photochemical transformations of photochromic materials. There are also changes in refractive index, dielectric constant, oxidation/reduction potentials, and of course geometrical structure. Besides the well-established use of photochromic materials in ophthalmics, especially in plastic lenses for sunglasses, there is therefore a growing list of other potential application areas, including cosmetics; actinometry and heat measurement; optical memories for data storage, both 3D and near-field; photo-optical switches, filters, displays; self-developing photography, and many others.[27]

1.2.8.1 Applications in Ophthalmics

Spectacle lenses that darken when exposed to strong sunlight and reverse back to colourless in low-light situations, such as indoors, offer the wearer personal comfort and safety. During most of the last century spectacle lenses were made of glass and the photochromic systems of choice were inorganic systems, based on silver halide crystals trapped in a glass matrix. The first of these was developed and launched by Corning Inc. in 1966, and over the years proved to be quite satisfactory in protecting wearers, but their popularity was limited by the fact that they switched very slowly when going from sunlight into a darkened room. However, in the latter decades of the twentieth century, plastic lenses were introduced and rapidly replaced glass as the material of choice in the developed world. The established silver halide photochromic systems could not be adapted to work well in plastic and hence there was a need for alternative materials, and these have turned out to be photochromic dyes. Pioneers of the research into this application area were Pilkington in the UK and PPG industries in the USA with their Transitions photochromic plastic lenses.

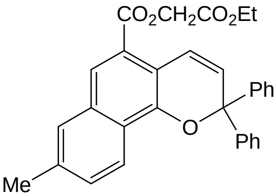
The demands on the photochromic materials are quite severe. A major issue is the ability to obtain the “correct” colour and optical density in the lens. The generally preferred tints in photochromic eyewear are switchable neutral greys or browns, because they allow the sky to look blue and do not interfere with red danger signals. These shades are readily obtainable in glass because the silver halide system absorbs broadly in the visible and can be manipulated to obtain greys or browns. Until fairly recently there was no single photochromic compound that could do this and colour formulators needed to resort to mixtures of products to produce the desired colours in the lens. To be of use in these mixtures photochromic materials have to satisfy other criteria, including a matching of the activation and fade rates, showing a balanced response to UV absorbance, having matching temperature dependency on the change from coloured to colourless, and also matching fatigue rates and life expectancy in use. If this is not the case users will find that they are looking out at the world through variably coloured spectacles in changing light conditions.

The three main classes that have been much studied for ophthalmic applications are spiroindolinonaphthoxazines (Section 1.2.3.), diarylnaphthopyrans

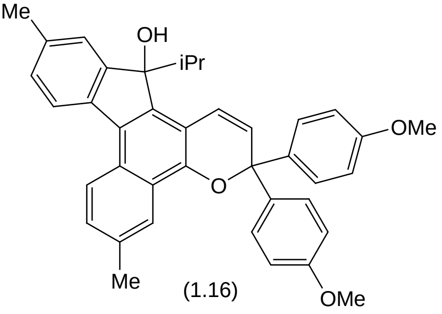
Table 1.10 Photochromic properties of commercially available classes.

Class	*Performance (OD, act/fade rate)*	*Temperature dependency*	*Fatigue*
Spiroindolinonaphthoxazines	Good	High	Good
Naphthopyrans	Good	Medium	Good
Fulgides	Good	Medium	Fair

Table 1.11 Photochromic properties of naphthopyrans in ophthalmic plastic.



(1.15)

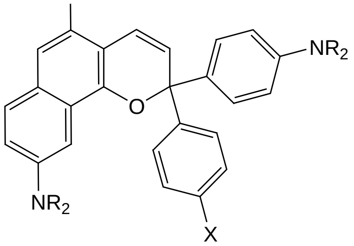


(1.16)

Compound	λ_{max} *nm*	*Optical density*			$T_{1/2}$ *(Fade)*
		30 sec	*120 sec*	*At saturation*	
(1.15)	464	0.16	0.29	0.37	60 sec
(1.16)	582	0.12	0.25	0.36	80 sec

(Section 1.2.4) and fulgides (Section 1.2.5). How these different photochromic classes match up to the desired criteria for use in lenses is shown in Table 1.10. Fulgides exhibit only a fair fatigue resistance and spiroindolinonaphthoxazines suffer from a high temperature dependency. Consequently, for this photochromic outlet, naphthopyrans have become the molecules of choice. Typical compounds used to produce greys and browns are the yellow (1.15) and the blue (1.16), the properties of which are given in Table 1.11. This pair offers a well-matched build-up to saturation optical density but their fade rates, whilst close, are far from perfectly matched.[54] Commercial products have been produced that do achieve the correct balance, but information on their actual composition is commercially sensitive and hence is not disclosed in detail in the open literature.

In 1999 the James Robinson company in the UK largely overcame the balanced mixture problem by developing single-molecule neutral grey colouring naphthopyrans, having the general structure (1.41).[12(b),55] By suitable molecular manipulation it is possible to balance the twin peaks in the absorption spectrum to get the desired colour and kinetics. From this they introduced three commercial products, Reversacol Midnight Grey, Misty Grey and Graphite, which are being used in commercial sunglasses and ski goggles.



(1.41)

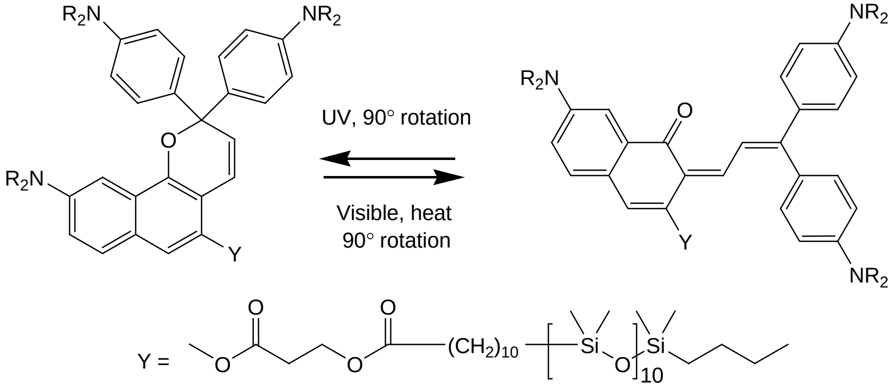


Figure 1.16 Approach to facile photochromic switching.

In spite of these very significant advances there is still a need to improve the speed at which the molecules switch in the rigid polymer matrix. Fade speeds are normally more strongly affected than coloration speeds. Thermal fade speeds are typically many times slower in a rigid polymer matrix suitable for ophthalmic lenses than fade speeds observed for the same dye in solution. The problem of slow switching speed is essentially one of rotational mobility of the molecule in the host matrix. Davis and his co-workers adopted a novel approach to overcome this problem.[56] By creating a photochromic siloxane oligomer conjugate of low T_g, which coiled around the chromophore, they were able to protect the dye from the high T_g surrounding matrix, allowing facile photochromic switching (Figure 1.16).

1.2.8.2 Novelty Items, Fashion, Cosmetics and Security

The use of photochromics in both novelty printing and incorporation into plastics are significant commercial outlets for this colour change effect. For instance, it is possible to produce mass pigmented polypropylene by dissolving different photochromic materials into molten polypropylene. By melt spinning, a thread is produced that is photoactive and is used to embroider designs on textile garments. Indoors, away from UV light, the design is white on the fabric but changes its colour on exposure to UV radiation in daylight.[57] Typical uses for photochromic effects are on children's toys and for logos on T-shirts, but the list of items is extensive and includes lunch boxes, crayons, jelly shoes, hair clips, hair combs, shoe laces, coasters, craft beads, PVC belts, watch bands, drinking straws, spoons, cups, frisbees, combs, greeting cards, stickers and business cards. In the cosmetic area a use has been found in nail polishes, light-enhancing make-up and temporary hair colorants.

A range of colours is available commercially, yellow through red to purple and green.[58] The products are also available from several companies in a variety of forms for these outlets including inks, microencapsulated and plastic resin concentrates.

Photochromics can also be used as anti-counterfeit markers on garments and anti-tampering devices on packaging printed documents. For instance, a significant use is as security markers on documents, banknotes and passports, as exemplified by the US passport.[59]

1.2.8.3 Optical Memories and Switches

The establishment of the recording of information by light in digital optical systems has triggered the search for molecular materials that will allow much higher storage densities and faster switching rates. Consequently, photoactive materials which can interchange between one or more distinct states are of particular interest. The major target for work on molecular switches has been their use in reversible data storage.

The term optical data storage (ODS) refers to those systems that use laser light to record and reproduce information. A more detailed discussion of ODS systems is given in Chapter 4 (Section 4.3). The main targets for developers of ODS systems in recent years have been CD-R (recordable) and CD-RW (rewriteable) compact discs, digital versatile discs (DVD, and DVD +/−R) and most recently high-density H-DVD and Blu-ray. The most highly developed erasable and rewritable media are either magneto-optic or phase change materials (inorganic and dyes), both of which utilise heat-mode effects. The development of phase change systems based on organic dyes has meant that products based on other organic systems, such as photochromics, are more likely to be accepted by the industry.

Photochromic optical memories, in contrast to heat-mode recording systems, use photon-mode recording, operating on changes in physical properties such as transmittance, reflectance or fluorescence. Potential advantages of photon-mode over heat-mode recording include higher resolution and speed of writing, and multiplex recording capability by use of wavelength, polarisation and phase changes.

For a photochromic material to be of any use in optical memories it must meet the minimum requirements in the following physical properties:[60]

- Thermal stability – very low thermal re-conversion;
- Fatigue resistance – long-term stability during read and write cycles;
- Non-destructive readout capability – the readout process must not induce interconversion of the two forms;
- High efficiency of the photoreaction – high quantum yields and molar coefficients;
- High speed of the photoreactions;
- Diode laser susceptibility;
- Solubility in polymer matrix.

Of those properties on the list, the most difficult to attain is a non-destructive readout procedure. Two approaches have been adopted to overcome this problem.[22,30]

1. Single-mode system
   Detect the two forms, A (colourless) and B (coloured), using light of a lower energy than the UV-visible light used for the interconversion (A to B, B to A). The readout can be measured as the difference in the reflecting light intensity of the laser (*e.g.* diode), or by fluorescence or IR absorption signals in the two forms.[27,61]
2. Dual-mode system
   This involves two reversible processes. In the first, irradiation with light in the UV-visible range causes the interconversion of A and B. In the second process a photon, an electron, or a proton is used to prevent the interconversion of A and B by transforming them to stable A′ and B′ products. The two forms in the system can therefore be locked or unlocked.[62]

Photochromic systems that have been examined in both of these approaches include spiropyrans, spirooxazines, diarylethenes, dihydroindolizines and azobenzenes.[27,30 32,60,63] A schematic of a disc structure is shown in Figure 1.17. To produce the recording layer the photochromic material is laid down in an acrylic resin (*e.g.* PMMA) onto a reflective layer of gold or aluminium. In this case a recording/writing laser *e.g.* He-Cd laser at 325 nm, or a frequency-doubled diode laser, addresses the recording medium, and a readout laser such as a AlGaAs 784 nm diode laser, operating through the glass substrate.

Since a halving of the wavelength of the laser reduces the spot radius by 2, and therefore increases the recorded, two-dimensional density by 4, the development of short-wavelength blue lasers has enabled the commercial development of DVDs, such as Blu-ray, to move data storage to a new level and hence achieve a much higher quality in the derived video images (Chapter 5, Section 5.5).

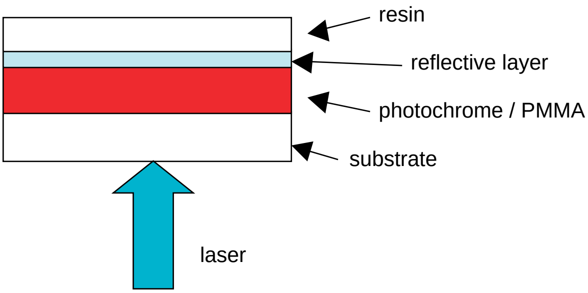
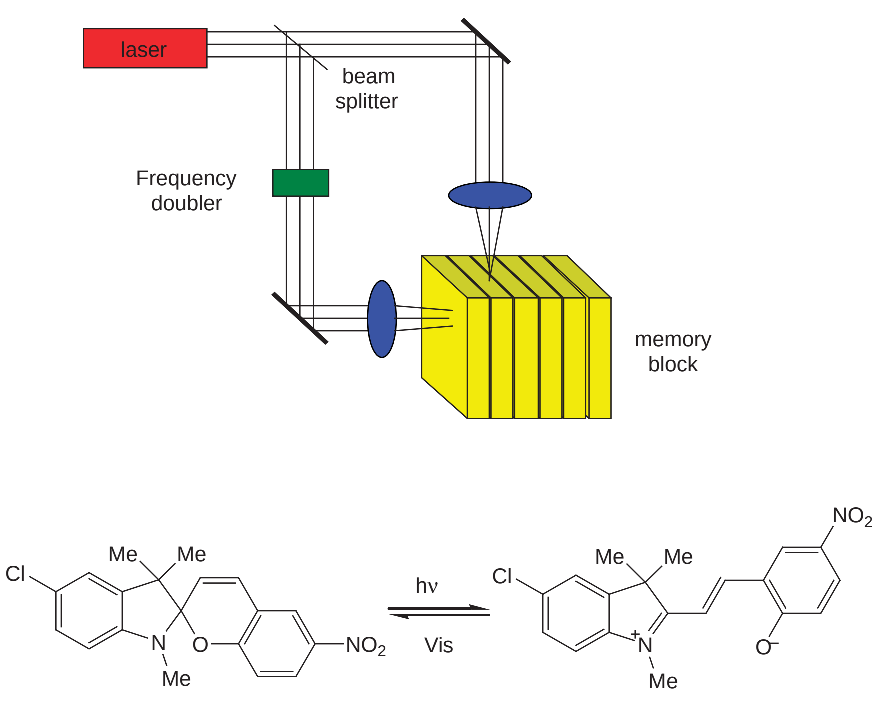


Figure 1.17 Schematic of an optical memory disc.

To move to an even higher level requires an all-optical, molecular level system. To meet these needs the following methods are being examined in the field of optical recording and memories.

1. Near field optics, in which recording density depends only on the size diameter of the probe tip aperture.[27,64]
2. 3D memory by use of additional axial dimensions to the recording system.[65]
3. Optical holography (see Chapter 5, Section 5.4.3).
4. Excitonic waveguides.[66]

Rentzepis in 1989 was the first to propose the use of photochromic compounds in 3D optical memories, the principle of which is illustrated in Figure 1.18. The potential for this 3D-memory principle was demonstrated using a spirobenzopyran.[67] It is a two-photon process in which two laser beams are used to access a point in a 3D memory block. Writing requires excitation in the UV range and for this purpose a two-photon absorption is usual *e.g.* a 1064 nm



A B

Figure 1.18 Principle of 3D optical memory and a model photochrome[67] (reproduced with permission of the American Association for the Advancement of Science).

and a 532 nm photon (equivalent to 355 nm excitation) or two 532 nm photons (equivalent to 266 nm excitation). Absorption of two photons by A causes it to isomerise to B, the coloured form. Reading can also be carried out by a similar two-photon process, for instance two 1064 nm photons to excite fluorescence in only the written molecules in form B, but the process is destructive due to partial reversion of B to A. Consequently, alternative readout procedures must be used. One of the most promising is the detection of refractive index changes observed when photoisomerisation is induced by long-wavelength light.[65]

In order to overcome some of these problems of read/write stability most recent research has been focused on bisthienylethenes, which, as already noted, have excellent fatigue resistance and thermal stability in both isomeric forms, high cyclisation and cycloreversion quantum yields, rapid response time and reactivity in the solid state.[68,69]

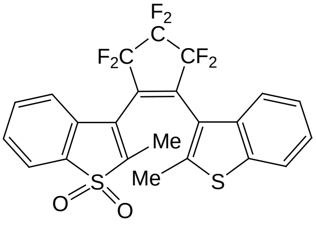
The high thermal stability in both the open-ring and closed-ring isomers allows novel photo-switching effects to be observed. These include changes in fluorescent intensity and absorption spectra, electrochemical properties, optical rotation, magnetic properties, electron-transfer interaction, refractive index, dielectric constant and geometrical structure.

The various types of photochromic materials being actively researched fall into the following categories:[69]

- Photochromic fluorescent switches;
- Photochromic polymeric switches;
- Photochromic chiral switches;
- Photochromic liquid crystals;
- Multi-addressable photochromic switches;
- Photochromic magnetic switches.

An example of photochromic fluorescent switches is provided by the work of Tian and co-workers, who attached a fluorescent naphthalimide to either side of a bisthienylethene as shown in Figure 1.19. The open and closed isomers of the molecule represent "1" and "0" binary digital codes, respectively, and its use in rewritable two-dimensional optical recording was demonstrated.[70]

Improved fatigue resistance and other photochromic properties have been achieved by oxidation of one or more of the sulfur atoms in diarylethenes (1.42).[71] These results may help in constructing photochromic fluorescent molecules showing the necessary improved performance for fully effective switches.



(1.42)

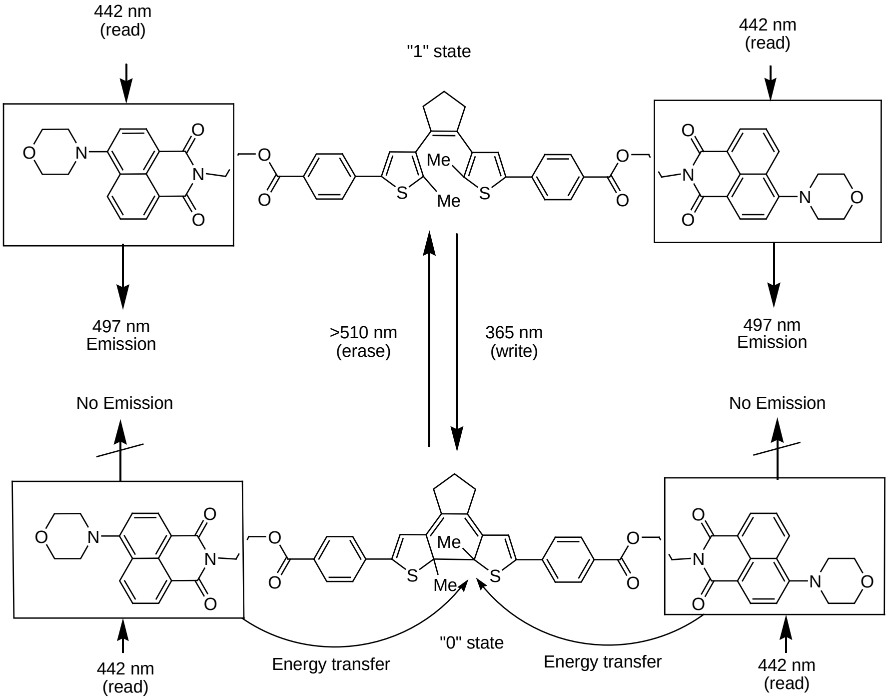


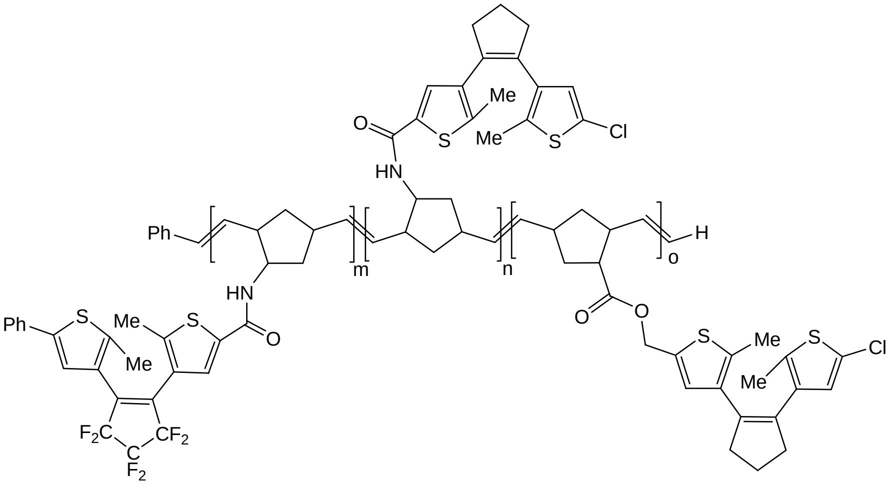
Figure 1.19 Photochromic fluorescent switch[70] (reproduced with permission of the American Chemical Society).

One-component photochromic systems can only interconvert between the two states "colourless" and "coloured". But by means of multi-photochromic systems comprising different kinds of photochromic units, reversible multi-state switching between several states can be realised by combination of the binary states of each component. Thus in a two-component system four states could be produced, and eight states from a three-component system.[61] Multi-photochromic copolymers offer the best approach to solid materials for practical applications because they show excellent rotating spread film property and photochromism in solid films as exemplified by the multi-component polymer (1.43).[72,73] This is an area of very active research with new structures appearing regularly in the literature.[69]

Chiroptical switches based on photochromic compounds are of particular interest because the reversible photochemical change leads to a change in chirality, a property which can be exploited as it is in most natural chemical processes.[74] Chiral switches based on photochromic molecules can be subdivided into the following categories:[75]

- Switching of enantiomers;
- Switching of diastereoisomers;

- Functional chiral switching;
- Switching of macromolecules or supramolecular organisation.



(1.43)

Figure 1.20 provides an example using diastereoisomers where the homochiral pinene-containing bisthienylethene underwent stereoselective cyclisation to produce >98% of a single diastereoisomer. Being thermally stable in both states and exhibiting large changes in circular dichroism and ORD spectral properties, it is the type of system required for the construction of a successful chiroptical photoswitch.[76] Several approaches are being adopted in the search for this type of operational switch, but particularly interesting is the use of low-molecular-weight gelators as supramolecular assemblies, which can be controlled by chirality.[77]

Whilst liquid crystals (LC) and their applications will be covered in detail in Chapter 5, one aspect is mentioned here. If the optical properties of an LC phase could be readily changed by interaction with light it would provide an entry point for molecular devices and their use in optical storage systems. One method of achieving the switching of LC phases is to use a photochrome as a light-addressable centre. Several approaches have been adopted in attempts to produce viable systems. The mesogenic group can be linked to the photochromic molecule either by using a spacer or directly as part of the chromophore, or *via* another, such as an azo linkage, to produce bi-chromophoric systems.[69,78]

Multi-component systems that have a combination of different photochromic units which display different properties offer ways into high-density storage as well as non-destructive readout, one of the first of which was demonstrated by Fernandez-Acebes and Lehn. They used a four-component mixture of diarylethenes to set up a multi-colour system whose absorption properties could be modulated by controlling the wavelength, duration and slit-width of the applied irradiation.[79] Whilst the formation of multi-component mixtures of photochromic materials continues to be a fruitful area for research,[80] an alternative approach of combining the photochromic units into

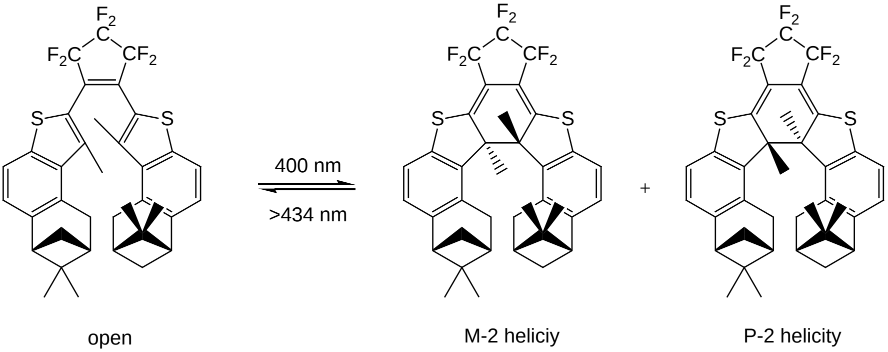
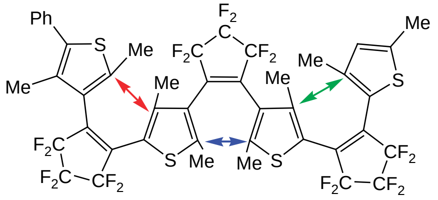
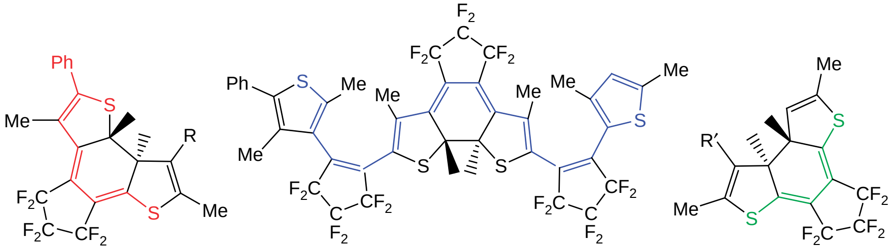


Figure 1.20 Photochromic process of chiral switches.

one molecule is also producing interesting results. An example is provided by the trimeric diarylethene (1.44), which exhibits a three-colour, yellow, red and blue, photochromic performance by choosing the correct wavelengths of light.[81] Three possible photo-initiated electrocyclisations are possible, indicated by the three arrows in (1.44). These result in the production of the three differently coloured chromophores, (sub-)structures of which are shown below, alongside a graphic of their hexane solutions. The starting substrate (1.44) is colourless (left vial).



(1.44)



The two interconvertible states of a photochromic switch differ in structural and electronic properties. Therefore their distinct stereo-electronic character can be exploited to modulate electron and energy transfer processes when the photochrome is operated in conjunction with complementary donors and acceptors. If either the donor or the acceptor is fluorescent, the photoregulated transfer of energy or electrons results in the modulation of the emission intensity. The energy transfer can occur either intramolecularly when the photochrome and donor are in the same molecule, or intermolecularly when they coexist in mixtures such as supramolecular assemblies.[82] Molecular switches, logic gates and combinational logic circuits based on molecules and ensembles with photochromic spiropyran units undergo reversible structural transformation among multi-states in response to external inputs such as light, protons and metal ions.[83]

1.2.8.4 Other Optical Applications

Photochromic compounds have been incorporated into organic or inorganic hybrid materials, or preformed polymers have been synthesised to produce photoresponsive materials.[84,85] The ability to incorporate organic chromophores, for example photochromes, into inorganic oxide matrices to produce functional hybrid organic–inorganic nanocomposites has been helped greatly by the development of sol-gel methods.[86] Another example involves dispersing photochromic molecules, such as spirooxazines, in hybrid mesoporous films.[87] These materials are being designed for use in optical applications such as waveguides, shutters, light modulators *etc.*, systems.

Photochromic crown ether compounds are an interesting new class of artificial receptor in which the recognition of metal cations induces a conformational change in the receptor framework accompanied by a colour signal. In addition, since binding of cations is sensitive to the ligand environment, the binding constant can be controlled effectively by employing photochromic systems. Thus, incorporation of a crown ether moiety able to bind metal ions into the photochromic skeleton can help tune the photochromic properties by using complex formation. A large variety of photochromic systems has been used in the construction of these molecules exemplified by the crowned spironaphthoxazine (1.45) in Figure 1.21 (see also Section 1.2.3). The potential applications for these macrocyclic crown ether systems include not only optical data storage but also photoswitching transport through membranes and optoelectronic and nonlinear optical devices.[88]

1.2.8.5 Biological and Bio-medical Applications

Photochromic materials have the potential to be used as chemotherapeutic agents, biosensors and bio-electronic materials.[89] Attaching photochromic molecules onto naturally occurring receptors and enzymes allows photoregulation of their binding and catalytic activities. Among recent examples are a fluorescent photochromic dyad comprising a diarylethene and fluorescein, used for the labelling of bio-molecules,[90] and an MRI and optical contrast agent in which a spiropyran group is attached to a Gd-DO3A moiety as shown

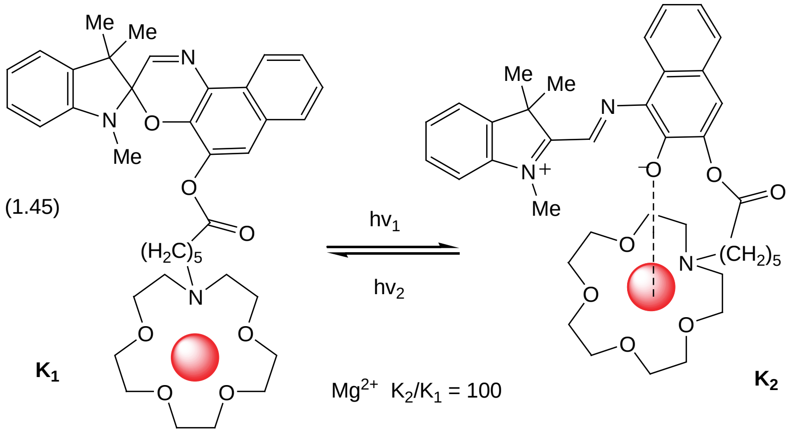


Figure 1.21 Light controlled complexing capacity of a photochromic crown ether.

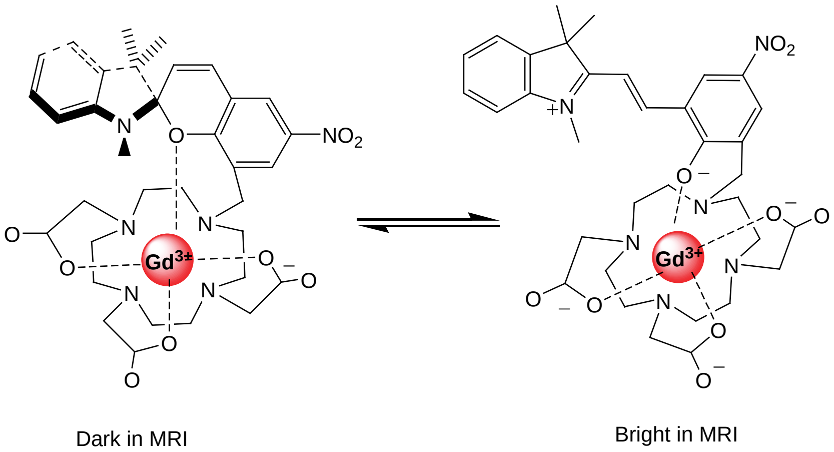


Figure 1.22 Photochromically controlled, reversibly activated MRI.

in Figure 1.22.[91] The main use of fluorescent labels in bio-medical applications will be covered in Chapter 3.

1.3 Thermochromism

Day, in his seminal work, defined thermochromism as "an easily noticeable reversible colour change brought about by the boiling point of each liquid, the boiling point of the solvent in the case of a solution or the melting point for solids."[92]

Whilst this definition is academically accurate for many inorganic and organic materials, the label "thermochromic" has also been applied to important technical areas that involve other external influences as well as heat in the observed colour change, *e.g.* thermochromic pigments.

A technically more appropriate approach is to separate reversible organic thermochromism into "intrinsic" systems, where heat is the sole cause of the colour change, and "indirect" systems, in which the colour variation involves changes in the environment around the chromophore brought about by heat.[93] Technical applications where the indirect colour change is desired to be irreversible, as for thermal fax colour formers, will be covered under ionochromism (see Section 1.4), as these systems are probably best considered as being essentially initiated by changes in pH, similar to indicator dyes.

1.3.1 Inorganic and Organometallic Materials

Many inorganic materials, usually involving transition metals and their complexes, and organometallics exhibit a thermochromic response over a wide range of temperatures and by a variety of mechanisms.[93–97] Examples include the following:

- The transition between different phases of different colour *e.g.* Cu_2HgI_4 is red at 20 °C and black at 70 °C.[92]
- A decrease in the band-gap of semi-conductors with rise in temperature *e.g.* white ZnO becomes yellow at high temperatures; In_2O_3 is yellow at lower temperature and changes to yellow-brown on heating.[95]
- Variations in the crystal field *e.g.* 1:9 Cr_2O_3-Al_2O_3 is red at 20 °C and grey at 400 °C.[96]
- A change in ligand geometry *e.g.* $(Et_2NH_2)_2CuCl_4$ is bright green at 20 °C (square planar) and yellow at 43 °C (tetrahedral).[97]
- A change in coordination number *e.g.* isopropanolic $CoCl_2$ at 25 °C exists in its pink octahedral geometry around the Co^{2+} ion and changes to the blue of the tetrahedral geometry at 75 °C.[94]

A range of transition metal complexes exhibit thermochromic behaviour in both the solid state and in solution, where temperature-dependent solvatochromic effects are also observed, directly related to the polarity of the solvent.[98–100] Since most inorganic thermochromic compounds are crystalline solids and the colour change irreversible, their application is restricted. One approach to overcoming this disadvantage is to use inorganic–organic hybrids. For instance, incorporating inorganic dopants into silica-based materials by low-temperature sol-gel processes is claimed to produce thermochromic materials that are suitable for use in a variety of optical applications.[101] Of particular interest in this area are reversible thermochromic systems that involve thermally induced changes in the way ligands associate with transition metal ions, as shown in the list above. This has led to the development of novel materials for thermochromic windows and will be described in greater detail below (see Section 1.3.4.2).

1.3.2 Reversible Intrinsically Thermochromic Organic Systems

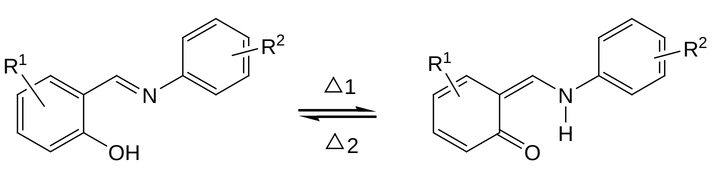
In these systems, heating alone, without the need for any other agent, causes the change in colour of a chromophore, and on removal of the source of heat the colour reverses to its thermally more stable state. Systems and molecules showing intrinsic reversible thermochromism can be classified as follows:

- Molecular rearrangement of molecules by the breaking of covalent bonds, *e.g.* spirooxazines;
- Stereoisomerism in molecules; interchange between stereoisomers that have different colours, *e.g.* bianthrones;
- Macromolecular systems, *e.g.* polythiophenes, polysilanes, polydiacetylene, polyanilines;
- Supramolecular systems, *e.g.* cholesteric liquid crystals (see Chapter 5, Section 5.2.2).

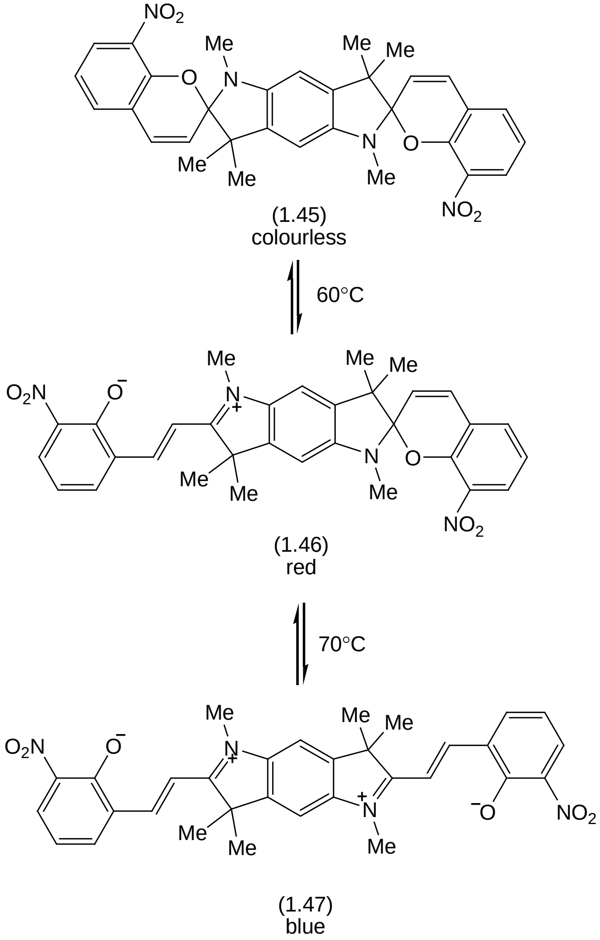
1.3.2.1 Molecular Rearrangements

Spiropyrans and spirooxazines, better known for their photochromic behaviour (see Sections 1.22 and 1.23), also exhibit thermochromism. The ring opening to produce the highly coloured merocyanine form is induced by heating either the solid or a solution. They also show a strong solvatochromic effect, polar solvents favouring the formation of the more polar merocyanine form.[102] It is possible to produce sequential colour changes using bis-spiropyrans.[103] The colourless bis-spiropyran, (1.45) in Figure 1.23, when heated in *n*-propanol to 60 °C changes to a red colour, due to the formation of the mono-merocyanine (1.46), and at 70 °C it becomes blue as the bis-merocyanine (1.47) appears.

Schiff bases exhibit either solid-state photochromic or thermochromic behaviour, caused by hydrogen transfer between the enol-keto tautomeric forms (see Section 1.2.7.2 and Figure 1.12). Whether the molecule exhibits photo- or thermochromism is strongly dependent on its crystal structure. Thermochromism in Schiff bases is highly favoured in planar molecules, whilst for photochromism the opposite is the case.[38] The tautomeric equilibrium in thermochromism is toward the *cis*-keto form, which absorbs at a longer wavelength (1.48), the colour change being normally from yellow to orange or red.[103] The aryl rings can be substituted with a range of both electron-withdrawing and -donating groups R^1 and R^2. If the phenyl ring on the aniline is changed to a pyridyl ring then the products exhibit only thermochromic behaviour.



(1.48)



(1.45)
colourless

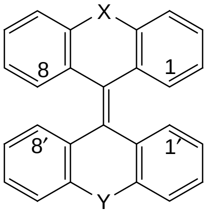
(1.46)
red

(1.47)
blue

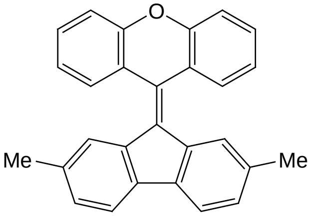
Figure 1.23 Sequential thermal colouration of a bis spiropyran.

1.3.2.2 Stereoisomerism

Bianthrylidene systems, with the generic structure (1.49), have been known to show thermochromic as well as photochromic and piezochromic behaviour for over a century.[92] Bianthrylidenes such as bianthrones (1.49; X and Y = CO) undergo reversible thermochromic colour change, due to two distinct and interconvertible A and B forms. The A species existing at room temperature is yellow ($\lambda_{\max}$ 380 nm) and this is partially converted to the green B form ($\lambda_{\max}$ 680 nm) on heating in solution.[103]



(1.49)



(1.50)

Many theories have been put forward to explain this thermochromic behaviour but the most favoured has been that the A form adopts a folded and the B form a twisted conformation (Figure 1.24). Whilst the crystal structure of the folded forms of several bianthrylidenes have been confirmed, it was not until recently that both forms were unambiguously characterised by a single-crystal X-ray structure analysis of (1.50).[104] Bulky R substituents in the 1,1′ or 8,8′ positions raise the energy barrier between A and B to such a level that they do not exhibit thermochromism. Other sterically overcrowded ethenes that exhibit thermochromic behaviour include dixanthrylidenes, bithioanthrylidene and mixed bianthrylidenes, such as xanthylideneanthrone.[103,104]

1.3.2.3 Macromolecular Systems

Conjugated polymers, such as polyacetylenes,[105] polydiacetylenes,[106] polyanilines[107] and polythiophenes,[108] in many cases show thermochromic behaviour.[109] Good examples are provided by poly(3-alkylthiophene)s and poly (3-alkoxythiophene)s, which, as well as exhibiting electrochromism and photochromism, show a strong colour change upon heating in both the solid state and in solution.[108] The colour change, which is reversible, is blue-shifted, a phenomenon that is known as "negative thermochromism". For instance poly[3-oligo(oxyethylene)-4-methylthiophene] at room temperature has an

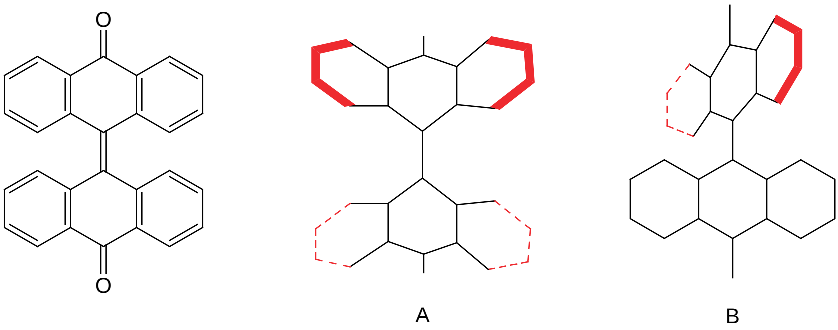


Figure 1.24 Thermochromic bianthrones; folded A form and twisted B form.

absorption band at 550 nm, which on heating decreases and a new band appears at 426 nm, becoming the sole absorption at over 100 °C. The change in colour is ascribed to the fact that at low temperatures the polymers form planar, highly conjugated assemblies (red-violet coloured) that upon heating become disordered and either twisted or non-planar and hence less conjugated (yellow coloured), as shown in Figure 1.25. By putting solubilising groups on the side chain of the polymer the colour change can be effected in a variety of solvents, including water when the side chain contains an ethanesulfonate group. Changing the length and flexibility of the side chains alters the temperature range of the solid-state thermochromic effect.

An attractive way of making thermochromic pigments is to incorporate a thermochromic polymer into a different polymer matrix. For instance poly(3-alkylthiophene)s of differing molecular structures can be dispersed in low concentrations (up to 1%) in many common commercial polymers to produce polymer pigments, which are designed to change colour reversibly over a range of temperatures from −35 °C to + 125 °C.[110] Although the products only have a limited colour range, this method avoids encapsulation of the thermochrome which widens their application in the important area of temperature indicators (see Section 1.3.4.1).[111]

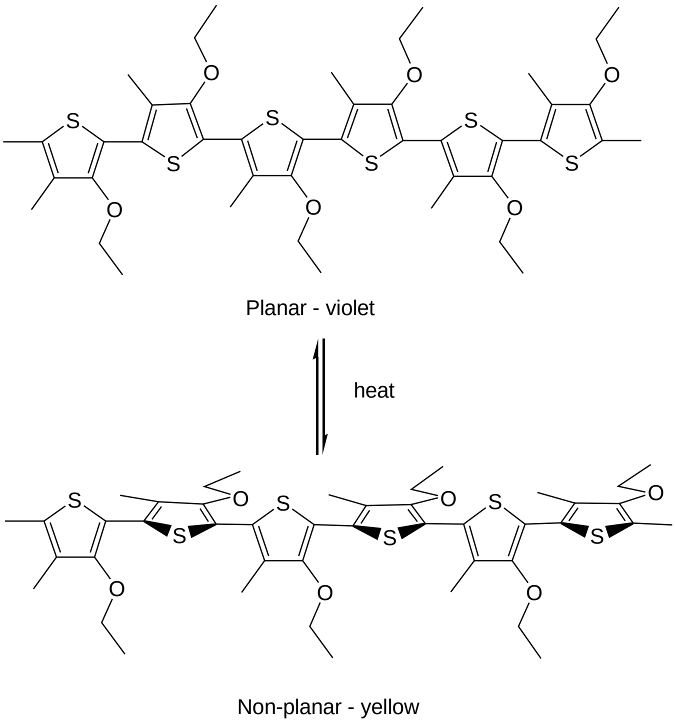
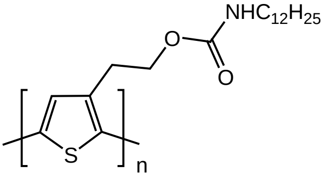


Figure 1.25 Conformational changes leading to thermochromism in regioregular poly(thiophene)s.

A new approach to the production of polymeric thermochromes is in the area of nanotechnology. The colour of nanoparticles of both semi-conductors, typically CdSe, and metals, commonly gold, is known to be very dependent on their particle size and these important topics will be covered in detail elsewhere in Section 1.12. Colour/size and property relationships relative to this section of the book have also been studied in organic polymeric materials. For instance nanoparticles of a poly(substituted thiophene) (1.51) have been prepared, ranging from 40 to 400 nm, and their spectroscopic properties and thermochromic behaviour investigated. It was found that their absorption, fluorescence and thermochromic transition temperature are clearly size-dependent.[112]



(1.51)

1.3.3 Reversible Indirect Thermochromic Systems

Although in theory intrinsically thermochromic compounds should be the materials of choice for many applications, in practice, with the major exceptions of the polymers described above and thermotropic liquid crystals (Chapter 5, Section 5.2.2), they often require quite high temperatures to effect the change, and this has limited their use. Additionally, there is also a problem with synthesising compounds to cover the desired colour gamut across the visible spectrum. Consequently, indirect systems, in which the chromophoric material reacts to changes in its environment brought about by heat, have been the subject of much development work. The colorants themselves in these systems are not thermochromic, but they display chromic behaviour due to differences in their physical environment brought about when the temperature is raised or lowered.

Typically the chromophores used are pH sensitive, *i.e.* acidochromic or ionochromic (see Section 1.4), and the medium is one whose pH varies with temperature. A variety of pH sensitive chromophores are known that are readily synthesised and can be modified to provide a wide range of shades. Application of these pH sensitive dyes in pressure and thermally sensitive papers for digital printing, such as fax papers, where the whole objective is for the process to be irreversible, will be covered under ionochromism. The main area of application for reversible indirect thermochromic materials is as thermochromic organic pigments, as will be described below (Section 1.3.4.1).

1.3.3.1 Composite Thermochromic Pigments

Composite thermochromic pigments consist of three components: a pH-sensitive dye, a proton donor which acts as the colour developer and a hydrophobic, non-volatile co-solvent. To achieve the desired effect the components are mixed in specific ratios and usually encapsulated to protect the system in subsequent applications. A review of the patent literature up to the mid 1990s on these compositions has been published.[113]

The pH sensitive dyes, often called leuco dyes or colour formers, most commonly used belong to the spirolactone class, including diaryl phthalides (see Section 1.4.1.1) or fluorans (see Section 1.4.1.3). Ring opening of the colourless lactones on protonation by the weak acid developer gives the coloured form. Many compounds have been claimed for use as the colour developer, but especially phenols, the most important commercially of which is Bisphenol A because it develops bright colours and changes of high contrast.[93] The most frequently used co-solvents are low-melting fatty acids, amides and alcohols, such as stearyl alcohol. In the production of the pigments, the colour former, developer and co-solvent are melted together and cooled to give the coloured pigment. Encapsulation of the mixture is essential for commercial use and this is achieved by the standard techniques of coacervation or interfacial polymerisation.[113] The resultant pigment formulations offer the following advantageous features:

- Switching of colour over a few degrees change in temperature;
- Variable switching temperature by choice of co-solvent;
- Wide choice of colours from yellow to red, blue, green and black.

The pigment is coloured in the solid form of the material because in this state there is an interaction between the colour former and the developer. Melting of the composite interferes with this interaction, leading to a negative thermochromic effect and a loss of colour. This is shown schematically in Figure 1.26.

In the past several possible mechanisms for the colour change were examined and from this work it was concluded that it could not be explained by a simple acid-catalysed ring opening of the lactone.[113,114] From more recent studies it is now clear that in the coloured state the dye forms complexes with the developer, for instance crystal violet lactone (CVL) forms a 1:4 complex with Bisphenol A.[115] In another study the lactone was found to form a 1:3 complex with the lauryl gallate developer in the coloured state, but in the higher temperature colourless state the developer becomes associated with the solvent.[116] On the basis of these results the following rules for optimising the reversible properties of thermochromic pigments were proposed. "*High color contrast, low equilibrium colour density, and rapid decolorisation rates can be optimised by selecting developer-solvent combinations that show strongly attractive interactions, preferably displaying binary compound formation in the solid state*."[117]

The normal colour change is from coloured to colourless but, by careful selection of the pH-sensitive dye, it can also be from one colour to another. It is also possible to use mixtures of thermochromic pigments of different melting points. As one component of the mixture shade becomes colourless on melting, the colour changes to that of the remaining, higher melting pigment. Alternatively a secondary chromophore can be present in the spirolactone molecule as with the azo group in (1.52).

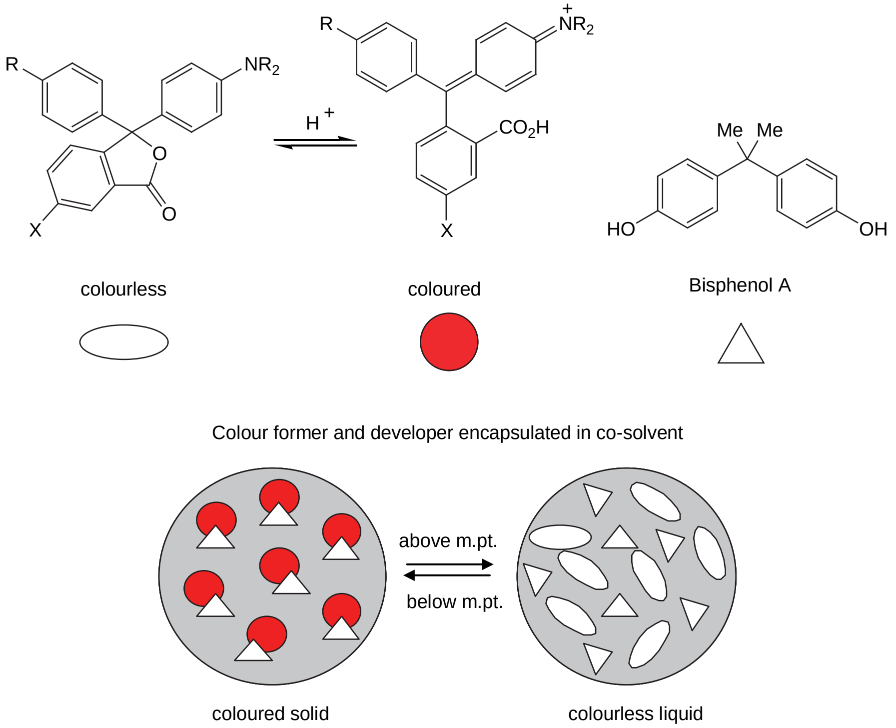
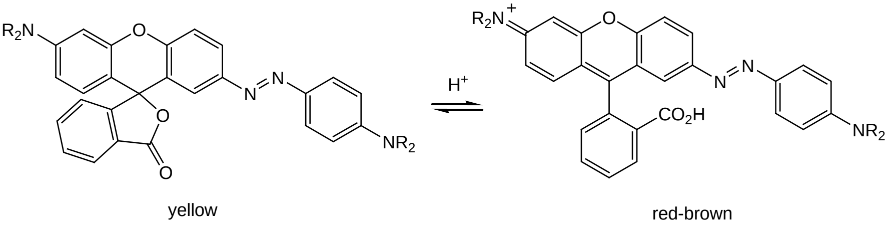


Figure 1.26 Schematic of a composite organic thermochromic pigment.



(1.52)

Composites can also be made by incorporating leuco dyes, such as crystal violet lactone, developer and solvent into matrices of thermoplastics, such as polyethylene and polypropylene, to show thermochromic behaviour.[118] These can be extruded to form flat foils or injection moulded into plastics in which the thermochromic dye is evenly distributed in the total polymer volume.[119]

1.3.3.2 Chromogenic Gels

It is possible to create thermochromic gels by mixing pH-sensitive dyes into either polyvinyl alcohol/borax/surfactant or polyalkoxy polymer/LiCl/buffer hydrogel

Table 1.12 Thermochromic gels

Hydrogel matrix	*Indicator dye*	*Colour change (5 80 °C)*
PVA borax	Phenol Red	Yellow purple
PVA borax	Thymol Blue	Yellow green
PVA borax	Phenolphthalein	Colourless red
PVA borax	Bromothymol Blue	Green blue
Polyalkoxide LiCl	Bromothymol Blue	Green yellow
Polyalkoxide LiCl	Chlorophenol Red	Red yellow
Polyalkoxide LiCl	Nitrazine Yellow	Blue green

matrices.[120] For instance, in the latter matrix Bromothymol Blue (see Section 1.4.2.1) gives a gel that is coloured green and transparent at $-5\,^{\circ}$C, when the phenolate ion absorption (λ_{max} 617 nm) dominates over the phenol (λ_{max} 408 nm) absorption band. On raising the temperature the ratio of the two species changes, and over the range 33–37 °C the gel becomes yellow and opaque, due to phase separation. There is a pH change in the gel from pH 7.8 at 0.5 °C to pH 6.8 at 32.5 °C. Cooling can reverse the process. Table 1.12 contains some representative examples.[121] Although these gels have the potential for use as temperature sensors, similar to the way in which liquid crystals and thermochromic pigments are used, their wider application is severely limited by poor light stability.

Gels that reversibly change from a transparent state to a milky white, reflective state at a specific temperature or a range of temperatures are called thermotropic not thermochromic gels as they involve light scattering and not a colour change. These gels are made up of colourless inorganic salts dissolved in a mixture of water and a water miscible polymer, such as polyvinyl alcohol (PVA). The change in the transparency of these gels is due to the formation of liquid crystalline phases and also phase separation. They are of interest because of their potential use as both light and heat filters in the milky state, and a special target is in switchable glazing units for sun protection in buildings.[122]

1.3.4 Applications of Thermochromic Materials

Inorganic systems have found only relatively few applications, mainly in paints and crayons for indicating hot spots on equipment *etc.* in temperatures from 120–200 °C.[123,124] But recently the reversible colour change in transition metal complexes has found an outlet in thermochromic windows (see Section 1.3.4.2). Of the intrinsically thermochromic organic materials it is only liquid crystals (see Chapter 5) and conjugated polymers that have any serious practical application, for instance the latter are used in optical temperature indicators.[118] The majority of current commercial applications use composite materials based on indirect thermochromism of leuco dye formulations.

1.3.4.1 Paints, Plastics and Textiles

Thermochromic composite pigments formulated for use in a range of outlets, especially in inks, paints and apparel, are commercially available from several companies although primary manufacturers of the pigments are few, including Matsui, Japan, and Color Change Corporation, USA.[125] Masterbatch plastic concentrates of the pigments can be made from ABS, polystyrene, polypropylene, PVC, nylon and polyester. Paints are available for use on a variety of substrates, including metals, ABS, polypropylene, polyethylene, PVC and polystyrene. Inks have been developed for many types of printing processes, such as screen, gravure and flexographic, and offset lithography.[126] Change from one colour to another, rather than from coloured to clear, is achieved in thermochromic inks by combining a leuco dye with a permanently coloured ink formulation. For example, the ink manufacturer may formulate green ink by adding a blue leuco dye to yellow ink. In its cool state, the printed ink layer is green, and, once warmed, reverts to yellow as the leuco dye becomes clear or translucent.[127]

Examples of the use of these materials include temperature indicators for children's food containers (colour change plastic mugs and spoons); as indicator stripes on beer and colas to indicate correct chilling; on milk cartons to indicate that they have been refrigerated; and even on toilet seats to show time between uses. In the security area heat from the finger on cold days or by cooling on warm days provides a simple verification of a document's authenticity; for message security where a message will appear when a copy is made with photocopiers, alerting for a check on authenticity. In the novelty area, logos on mugs, umbrellas, golf balls and in jewellery and cosmetics are common uses.

For apparel applications, thermochromic materials have been incorporated into embroidery and weaving threads and coated onto transfer papers for thermal printing of a variety of textile fabrics and garments, such as T-shirts. This topic is often dealt with under the generic title of "*smart textiles*".[128,129] A most interesting recent review looks at the interface between science and design in the utilisation of thermochromism to produce products that are not only colourful and artistic but also display added functionality.[130]

A process has been developed recently to produce cellulosic fibres containing a thermochrome by using the same technology as used to make Lyocell fibres. This involves spinning fibres from a concentrated solution of cellulose in a solvent, usually *N*-methylmorpholine-*N*-oxide, and by a dry-wet method into aqueous solidification bath. Chromicolor AQ-INK, Magenta type #27, a composite thermochromic pigment from Matsui, was added to the solvent bath prior to spinning, producing fibres containing 1–10% of the thermochrome. These thermochromic fibres are said to meet the technical requirements for the production of textile materials.[131] There are limitations to the use of this technology, not the least of which is the generally poor fastness of thermochromic pigments to UV in sunlight, generally restricting its use on garments and printed articles that are not likely to be left in the daylight for any length of time, and consequently the addition of light stabilisers has been examined. UV absorbers bearing groups capable of acting as an amphoteric counter-ion are claimed to play a very important role in improving the light fastness of the leuco dye colour formers. In this context zinc and nickel

5-(2-benzotriazolyl)-2,4-dihydroxybenzoates have been proposed as effective stabilisers for use on cellulose fibres.[132] Of course they are intrinsically temperature dependent and articles containing these materials must be protected from any unwanted heat source.

1.3.4.2 Architectural Uses

Thermochromic materials are finding an increasing usage in architectural structures. Tiles with thermochromic properties have been designed for both internal and external application. Internally their use is either for totally aesthetic reasons, changing colour to suit the environmental mood of the room and its occupants; or for practical and safety reasons, such as indicating thermal hot spots on walls and floors due to splashes of hot liquids and oils. Multi-layer laminates for the control of the temperature of structures have been designed to include a UV-absorbing layer in order to increase their lifetime in external uses.[133,134]

One of the most important applications of chromic materials in architecture is in the environmental control of the temperature of a building using smart glazing in windows. The main commercial products to date have been constructed using electrochromic materials (Section 1.5.4.2) and in a more limited way thermotropic gel materials (Section 1.3.3.2) and polymer dispersed liquid crystals (Chapter 5). However, an alternative system involving reversible thermochromic materials has been developed by Pleotint in the USA.[135,136] This is based upon a temperature-dependent, reversible ligand exchange reaction between a transition metal complex of low absorption coefficient with a different complex having a high absorption coefficient. This is shown schematically in Figure 1.27 where a 6-coordinate complex undergoes ligand exchange to give a more highly coloured 4-coordinate complex. In order for the absorption of the system to increase with increasing temperature the equilibrium position must shift to the right as the temperature rises. Pleotint's ligand exchange systems are extruded into plastic to give films of variable tints. These films are then laminated between glass, using a similar process to that used to manufacture standard laminated glass. Double or triple pane insulated glass units combining the thermochromic glass laminate with a low-emissive coated

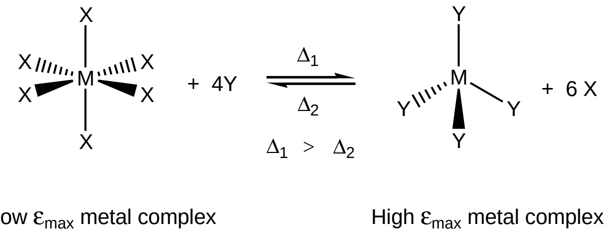


Figure 1.27 Mechanism of ligand exchange thermochromic systems.

sheet of glass at the back make up the complete assembly. The basic idea behind the windows is that the lightly tinted thermochromic film warms up in the presence of direct sunlight and darkens to absorb a significant portion of the sunlight shining directly on the window. The tinted film in combination with the low emittance layer allows the window to prevent undesirable heat load in a building. In the absence of direct sunlight the window clears to allow much of the indirect sunlight into a building.[137]

1.4 Ionochromism

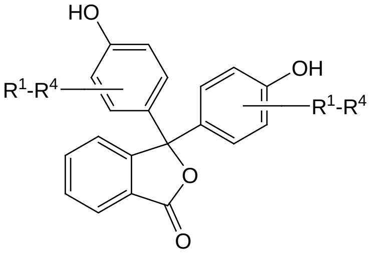
Ionochromism is the name applied to the phenomenon of a colour change associated with the interaction of a compound or material with an ionic species. The organic structures that undergo the colour change on interaction with the ions are called ionochromes or ionophores. The colour change can be from colourless to coloured or coloured to coloured and is usually reversible. A closely related topic is that of fluoroionophores, covered in Chapter 3 (Section 3.5.7) of this book, where ions cause a change in the fluorescent emission of the molecule. Ionochromism can be subdivided into chromisms based on the types of ions that instigate the colour change. Halochromism refers to the colour change caused by a change in pH, due to either acids or bases; acidochromism is reserved for the change instigated specifically by acids. Metallochromism applies where metal ions cause the change.

1.4.1 Ionochromic Compounds

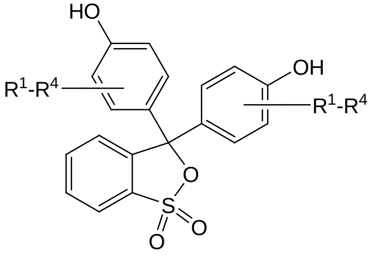
Many types of organic molecules exhibit ionochromic behaviour but in this book only the main chemical classes will be described. The main commercially important pH sensitive dyes are phthalides, triarylmethanes and fluorans. In fact, several major chromophores undergo useful colour changes on protonation, including simple neutral azo dyes, styryl dyes, merocyanines and indophenols. A very extensive useful compilation of acid-base indicators should be consulted for details of individual pH-sensitive dyes.[138] With metal ions a whole range of chelating ligands, some attached to chromophores, can be employed as colour indicators and sensors, but of special importance are crown ethers and cryptands for a range of non-traditional uses, such as the sensing of biologically important anionic species.

1.4.1.1 Phthalides

pH indicator dyes having the phthalide structure fall into two types: the phthaleins, shown in the lactone form of general structure (1.53), and the sulfophthaleins (1.54). They are readily synthesised by the reaction of phenol with either phthalic anhydride or sulfobenzoic anhydride in the presence of a Lewis acid catalyst.



(1.53)



(1.54)

The response of phthaleins to changes in pH is best exemplified by the parent dihydroxy derivative, the well-known indicator phenolphthalein (1.55). The colourless lactone (1.55) on adding alkali undergoes a successive conversion to the mono- and then the diphenolate ion (1.56), which ring opens to give the red dianion (1.57) (Figure 1.28). The process is reversible and therefore provides an easily visible method for measuring pH change in the range of 8.5–9.0. The ionisation reactions of sulfophthaleins follow a similar pathway. Substitution in the phenolic rings of the phthaleins and sulfophthaleins provides a variety of coloured dianions, which change colour over different ranges of pH (see Section 1.4.2.1).

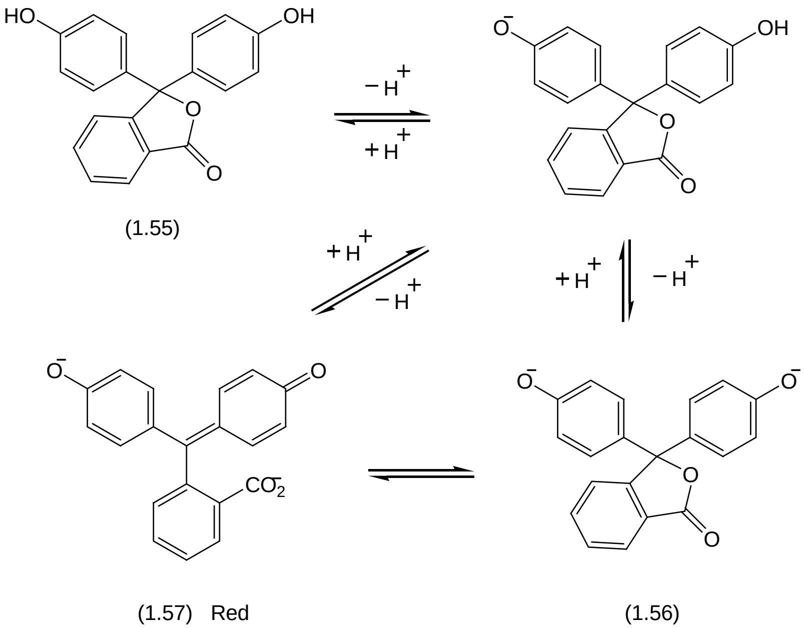
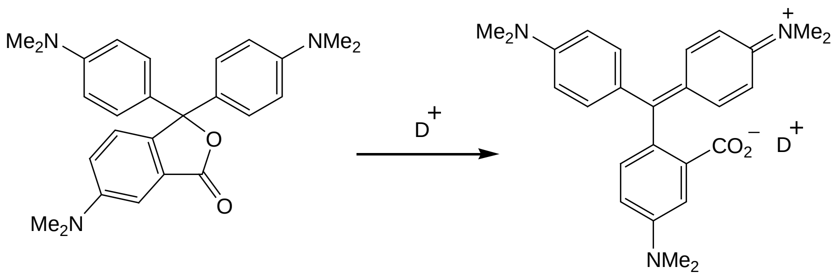


Figure 1.28 Ionisation pathway of phenolphthalein.



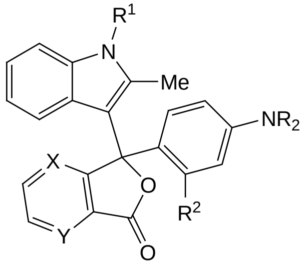
Colourless
(1.58)

Violet
(1.59)

Figure 1.29 Colour formation in Crystal Violet Lactone/developer system.

The most technologically important of the phthalides are those based on the Crystal Violet Lactone (CVL) structure (1.58) and its heterocyclic analogues,[139] used as colour formers in carbonless copying papers and other digital printing outlets (see Section 1.4.2.4). These processes depend on the fact that the lactone ring of the colourless form (1.58) opens in the presence of a Lewis acid D^+ to give a coloured cationic dye (1.59), as exemplified by CVL in Figure 1.29.

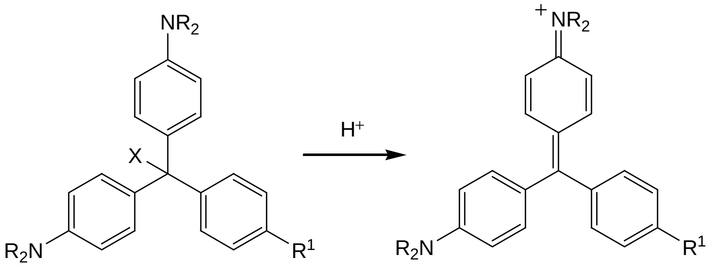
Whilst CVL has had great commercial success as a colour former, it has very poor light fastness and requires shading components to produce the desired colour. Consequently, many other related phthalides have been examined in seeking to improve on CVL's properties. The most important of these are the heterocyclic ring analogues, especially those with indole and pyridine rings (1.60). Of the colour formers carrying pyridyl rings, the isomeric compounds (1.60; $X = N$, $Y = CH$, R, $R^1 = Et$, $R^2 = OEt$) and (1.60; $X = CH$, $Y = N$, R, $R^1 = Et$, $R^2 = OEt$) and their mixtures have enjoyed commercial success because they yield intense blue images with excellent fastness when used in conjunction with organic developers.[139]



(1.60)

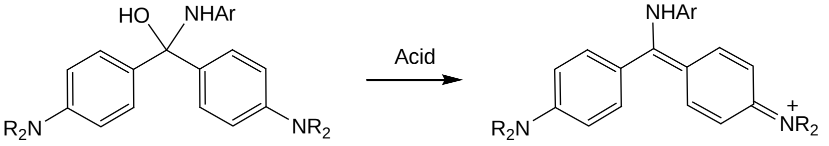
1.4.1.2 Leuco Di- and Tri-arylmethanes

One of the earliest known group of organic dyes was the leuco di- and triarylmethanes, also known as arylcarbenium dyes. These are converted to their coloured form by hydride abstraction, chemical or photooxidation, or in some cases by acids, as exemplified by (1.61).



(1.61) X = OH, OR^2, NR^2_2, CN, N-Heterocycle

A class of pH-sensitive leucodiarylmethanes that have found use as dark blue colour formers in pressure-sensitive papers are (1.62), a topic covered later in this Chapter (see Section 1.4.2.2). The synthesis of most common ionochromic di- and tri-arylmethanes use 4,4′-bis(dimethylamino)benzhydrol, commonly known as Michler's Hydrol, as the starting material for condensation with phenols or amines.[140]



(1.62)

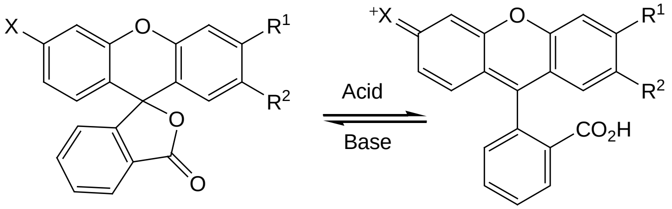
1.4.1.3 Fluorans

Fluoran is the trivial name that is commonly used for the spiro(isobenzofuran-1,9′-xanthen)-3-one class of compounds (1.63). The colour-forming reaction involves ring opening of the lactone ring by acid to give the coloured delocalised form (1.64) again; colour reversion can be achieved by adding a base. As colour formers, the big advantage offered by fluorans is that they can provide a wide variety of colours, including a single component black, as opposed to the blue and orange mixtures required to give blacks from phthalides and triarylmethanes.[141] Colours ranging from yellow to black can be obtained from fluorans (Table 1.13). Typical of the fluorans used commercially as black colour formers are (1.63, $X = NEt_2$ or NEt(iso-pentyl), $R^1 = Me$, $R^2 = NHPh$).[141]

1.4.1.4 Azo and Styryl Dyes

Azo dyes with amino groups in the 4-position undergo mono-protonation to give the ammonium (B) and/or the azonium (C) tautomers followed by further

Table 1.13 Colour range available from fluorans



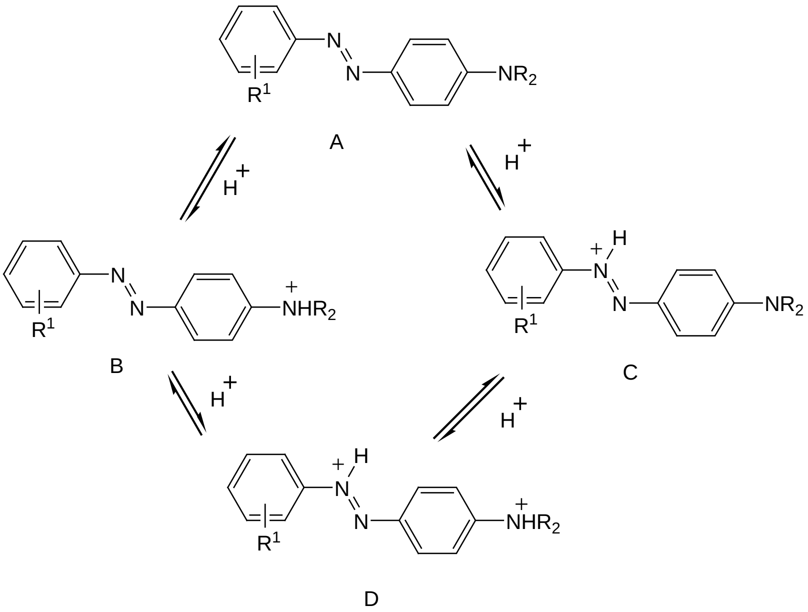
(1.63) (1.64)

Colour	*X*	*R¹*	*R²*
Yellow	OR	OR	Me
Orange	NHalkyl	Cl	H
Red	NEt_2	Me	H
Blue	NAr_2	NAr_2	H
Green	NEt_2	H	NEt_2
Black	$Nalkyl_2$	H,Me	NHAr

protonation to give (D) (Figure 1.30). The azonium tautomer is stabilised where R^1 is an electron-withdrawing group *meta* or *para* to the azo linkage, whilst conversely the ammonium tautomer is stabilised when R^1 is electron-donating. The colour change for the ammonium isomer is hypsochromic and weaker (even colourless), while the azonium isomer is strongly bathochromic and more intense. The di-protonated product (D) is nearly the same colour as the base dye (see Table in Figure 1.30).[142,143] The discoloration produced by the ammonium form is exploited with styryl dyes in certain applications (see Section 1.4.2.4).

1.4.1.5 Metallochromism in Chelates and Crown Ethers

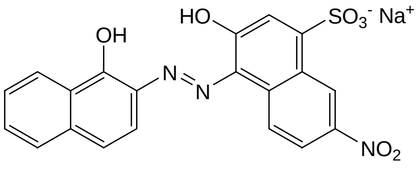
Metal ions, especially transition metal ions, can form coloured complexes with chelating ligands that are the basis of the analytical methods and indicators for these ions that have been used for many decades.[144,145] The term metallochromism has been applied to this phenomenon, especially in applications outside the area of analysis, where they are also known as metallochromic indicators. Because the change of colour is based on complex formation reactions the metallochromic behaviour is usually reversible, unless kinetic factors, mainly connected with the nature of the metal ions, are significant. Typical bidentate ligands are dimethylglyoxime, 1,2-dihydroxybenzenes, 1-hydroxyanthraquinones, 8-hydroxyquinoline, 2,2′-bipyridine, hydroxyazo and pyridylazo dyes and *o*-phenanthroline; tridentates include *o*,*o*′-dihydroxyazo dyes and multi-dentates such as formazans. They can also be classified as O,O-, O,N- and N,N-reagents according to the nature of their coordinating atoms. A typical dihydroxyazo dye is Eriochrome Black T (1.65), which has long been used as a complexometric indicator on its own or in conjunction with the



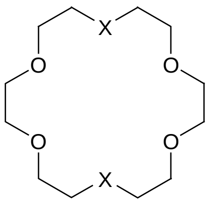
Structure	*R*	*R^1*	*λ_{max} nm*	*ε_{max}*
A	Me	H	402	44,000
B	Me	H	320	34,000
C	Me	H	520	79,000
D	Me	H	410	45,000
A	Et	4-NO_2	480	30,400
B	Et	4-NO_2	326	16,000
C	Et	4-NO_2	515	43,500

Figure 1.30 Tautomeric and spectral changes on protonation of aminoazo dyes.

complexing agent EDTA for the estimation of a variety of metal ions, but especially calcium and magnesium.[144]



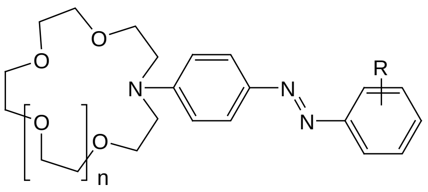
(1.65)



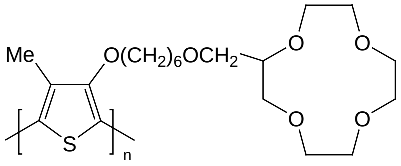
(1.66; X = O or NH)

Following the Nobel Prize winning discovery by Pedersen in 1967 of crown ethers and their ability to form complexes with alkali metal ions, there has been a tremendous amount of work done on the complex-forming behaviour of these materials.[146] Their ring sizes can vary from 12 upward, and the size of the crown cavity and its conformational behaviour control what size of metal ion can be incorporated. Typical examples are 18-crown-6 (1.66; X = O) and its diaza analogue (1.66; X = NH).

To make these crowns more strongly coloured, and hence more widely applicable as indicators or sensors, chromophores such as azos, indoanilines and styryl dyes have been attached to the ring, producing a wide range of chromoionophores, simple examples being the azo dye derived compounds (1.67).[147,148] An interesting variant on this approach involves the use of crown ethers attached to the side chain of polythiophenes. Depending on the nature of the complexation of the side chain crown with alkali metal ions, there is either ordering or disordering of the backbone polymer. Complexation of (1.68) with sodium ions in acetone solution causes rigidification and a shift in absorption maximum from 440 to 545 nm.[108(a)]



(1.67)



(1.68)

1.4.1.6 Chromogenic Anion Sensors and Metallochromism

Anions play an important role in environmental, biological and medicinal areas, and consequently in recent years there has been a considerable body of work looking for effective ways of sensing their presence by changes in colour or luminescence (Chapter 3). Chromogenic sensors and probes offer advantages in biological systems, as the guest-host reaction is visible and would not suffer interference from factors such as auto-fluorescence and light scattering (Section 3.5.9.1).

Optical anion sensors, especially those designed for biological anions, consist essentially of two parts. One part is an anion-binding site employing various combinations of anion receptor units and the other a chromophore unit that, on binding, converts the recognition phenomena to optical signals. These two parts can be either covalently attached or intermolecularly linked to each other (see also Section 1.4.2.2). The interaction between anions and receptors can be classified basically into the formation of hydrogen bonds, electrostatic interactions and interactions with metal centres. Neutral anion receptors employ hydrogen bonding donors, whilst positively charged anion receptors use ammonium derivatives or guanidinium centres for binding anions. For metal-ion-involved chromogenic hosts, the change in colour comes from interaction with metal complexes, especially those of transition metal ions. In these cases their electronic properties are perturbed upon coordination to anions, and can be regarded as specific examples of metallochromism (see Section 1.4.1.5). The other way to generate a chromogenic sensor is to displace the coordinated chromophore by specific anions. Colour changes can also occur when chromogenic hosts react with anions to form a new molecule, producing an observable colour change.[149] Therefore many of the approaches to developing anion recognition can be collated under three generic groupings, as listed below and shown schematically in Figure 1.31.[150]

In the binding site-signalling approach the chromophoric molecule contains a receptor site that is specific for an anion, and on binding that anion it changes its colour, hence providing the signal. Sensors that work with hydrogen bonding

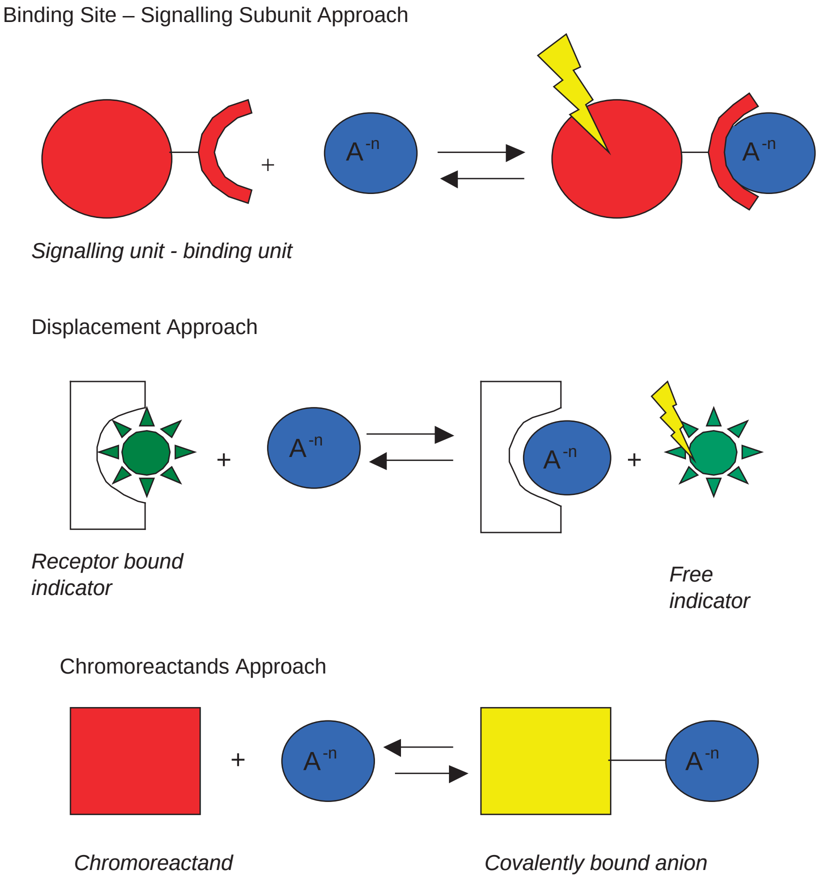
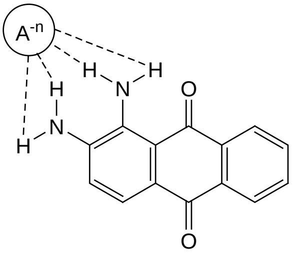
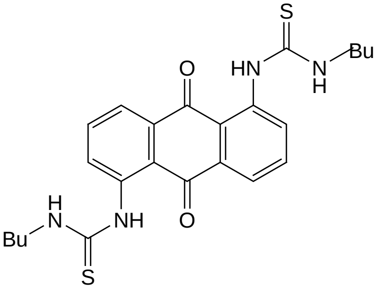


Figure 1.31 Chromogenic approaches to anion signalling[150] (reproduced with permission of the American Chemical Society).

hosts include simple anion sensor systems containing urea, thiourea, amine, amide, alcohol and pyrrole groups linked to chromophores. Chromophores used in this type of chromogenic anion sensor are mainly organic dyes such as azobenzene, nitrobenzene, indoanilines and anthraquinone or extensively conjugated aromatic compounds such as quinoxaline, oxadiazole and porphyrin. The colour change occurs upon binding of anion guests that affect the electronic properties of the chromophores. Good examples are provided by 1,2-diaminoanthraquinone, which shows distinctive colour changes in CH_2Cl_2 in the presence of a range of anions, including, F , Cl , Br , H_2PO_4 , AcO , BzO and CN (1.69),[151] and a thiourea derivative of 1,5-diaminoanthraquinone (1.70) which is selective for F .[152]



(1.69)

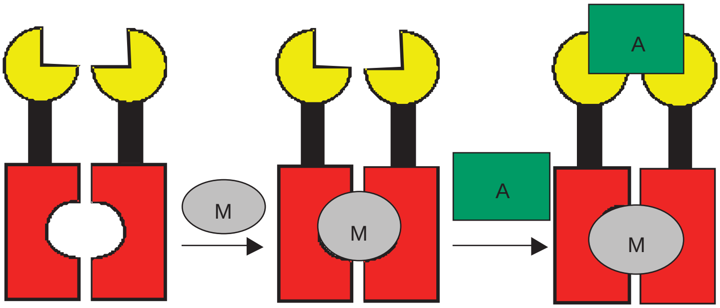


(1.70)

Metal complexes can be used as optical signals in two ways. The first involves using a metal ion-templated chromogenic host, where the coordinating ligand has groups that can bind to metal ions and anions, so that on addition of a metal ion a ligand reorganisation takes place which creates a binding site for anions (Figure 1.32).[149] An example is the terpyridine derivative (1.71), which after coordination with Fe(II) or Ru(II) binds various dicarboxylate anions *e.g.* glutarate and adipate.[153] The second way is to use transition metal complexes which have vacant binding sites for specific anions or have pendant arms containing anion receptor units.[149]

An indicator present in the binding site of a host molecule can be displaced by an incoming anion and freed to provide a signal. In the example shown in Figure 1.33 the ensemble complex (1.72), formed by the binding of the pyrocatechol dianion with the colourless zinc complex, is violet. Addition of phosphate anions to an aqueous solution of (1.72) causes the displacement of the dye in its protonated form to give (1.73) and the solution turns yellow.[154]

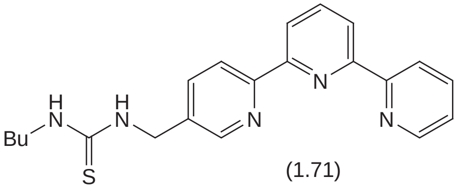
The third approach to anion signalling is the use of chromoreactands and chemodosimeters. These involve selective chemical reactivity between a particular anion and chromogenic hosts, which then displays a dramatic colour change. With chromoreactands the reaction is reversible and it can be used for the continuous monitoring of an analyte, for example bisulfite anion with the aldehyde group of the azo dye in Figure 1.34.[155] With a chemodosimeter the



Coordinating Compound

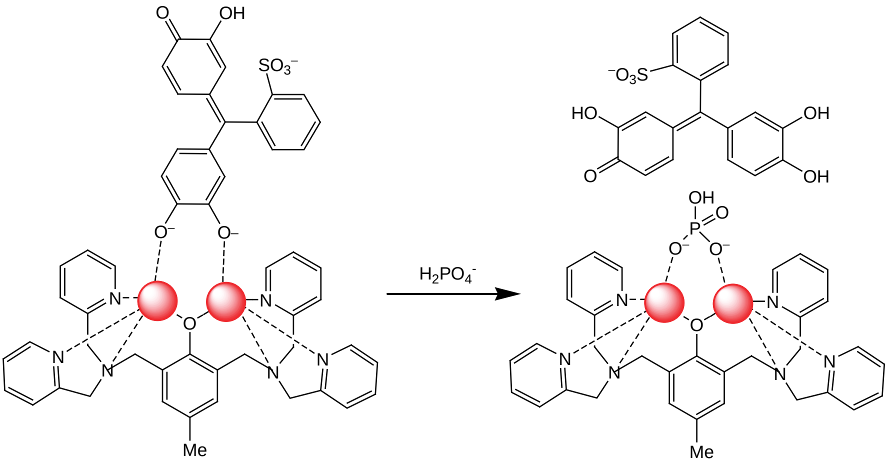
Metal Ion Complex

Metal Ion - Anion Signal



(1.71)

Figure 1.32 Binding site arrangement for metal ion template effects.[149]



(1.72)

(1.73)

Figure 1.33 Anion signalling *via* displacement of indicator.

colour change is irreversible and the reaction is used as a probe for the analyte. An example of the latter is shown in Figure 1.35, where the cyanide anion reacts with the benzoxazine fragment causing ring opening and the formation of a 4-nitrophenylazophenolate chromophore with consequent colour change.[156]

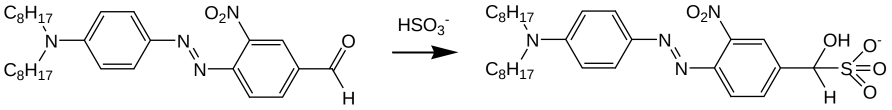


Figure 1.34 Chromoreactand for bisulfite anion.

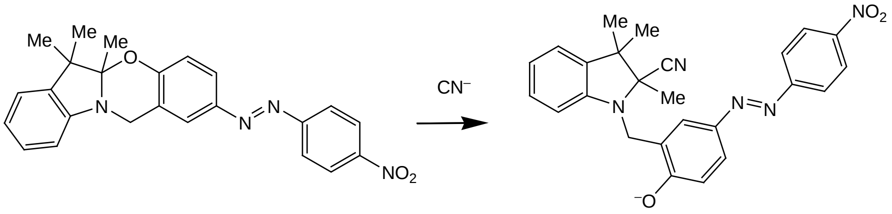


Figure 1.35 Cyanide detection with a chemodosimeter.

1.4.2 Applications of Ionochromism

Ionochromism and its sub-chromisms have several very important technological applications. The original use of pH sensitive dyes was as reversible indicators in analytical chemistry, in which area complexometric methods have been further developed in order to detect and estimate metal ion concentrations. Variations in the colour of certain dyes with changes in pH can also be used to visualise changes in many physical environments, for instance their use as humidity indicators in the presence of pH modifiers such as carboxylic acids, which are also called hydrochromic inks. Of particular interest are the cases where the acidic, ionic or donor species are generated on exposure to light or heat. Examples include the use of ionochromes as colour formers in pressure and thermal sensitive copying papers, in facsimile papers, and in digital and other forms of imaging, where irreversibility is one of the desired properties. The commercial use of pH-sensitive dyes as one of the components in reversible, composite thermochromic pigments has already been described (Section 1.3.3.1).

1.4.2.1 Analytical Chemistry

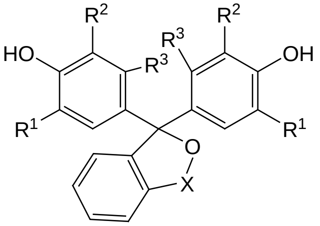
With the advent of instrumental techniques and the development of miniaturised, hand-held machines, suitable for field work, the use of pH-sensitive dyes in spot papers and volumetric analysis has very much diminished. In spite of this diminution in their traditional uses, these compounds are finding new uses where the ionic response of dyes is exploited (see also Section 1.3.3.2). Consequently, a brief description of their properties is justified.

The ionic pathways for the phthaleins have already been shown earlier in Figure 1.28. By modifying the chemical structure of the phthaleins, and especially the closely related sulfophthaleins, a whole range of reagents can be made with different colour changes. It should be noted that the change of colour is not sharp but occurs over a narrow pH range. The structures of some of the more common reagents and their properties are given in Table 1.14.[138]

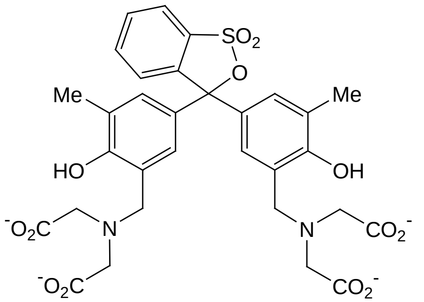
Protonation of azo dyes is also used as a method for producing analytical indicators. The two best known ones are Methyl Orange and Methyl Red, whose colour change is generated by formation of the azonium tautomer (Figure 1.36) as shown earlier in Section 1.4.1.4. It should be noted that some azo-dye-based indicators (*e.g.* Methyl Yellow and Congo Red) are no longer used, as they are potential carcinogens (see Chapter 2, Section 2.3.1.1).

The use of complexometric titrations for metal ions was a later but widely applicable development, which is dealt with in great detail in specialised texts.[144] Examples include Eriochrome Black (1.65), which as already stated is used for calcium, magnesium and aluminium; Xylenol Orange (1.74) for gallium, indium and scandium; and Calcein (1.75) with EDTA for calcium.

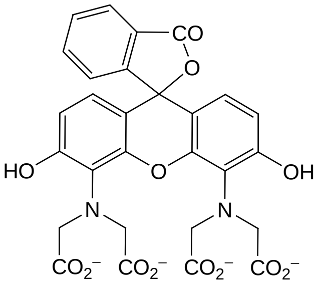
Table 1.14 Phthalein and sulfophthalein indicators.



Name	*R¹*	*R²*	*R³*	*X*	*pH range*	*Colour change*
Phenolphthalein	H	H	H	CO	8.5 9.0	Colourless Red
Cresolphthalein	Me	H	H	CO	8.2 9.8	Colourless Red
Thymolphthalein	i Pr	H	Me	CO	9.3 10.5	Colourless Blue
Phenol Red	H	H	H	SO_2	6.8 8.4	Yellow Red
Cresol Red	Me	H	H	SO_2	7.2 8.8	Yellow Red
Chlorophenol Red	Cl	H	H	SO_2	4.8 6.4	Yellow Red
Bromophenol Red	Br	H	H	SO_2	5.2 6.8	Yellow Red
Bromophenol Blue	Br	Br	H	SO_2	3.0 4.6	Yellow Blue
Bromothymol Blue	i Pr	Br	Me	SO_2	6.0 7.6	Yellow Blue
Bromocresol Green	Br	Br	Me	SO_2	3.8 5.4	Yellow Blue
Bromocresol Purple	Me	Br	H	SO_2	5.2 6.8	Yellow Purple
Thymol Blue	i Pr	H	Me	SO_2	1.2 2.8	Red Yellow
					8.0 9.6	Yellow Blue
Xylenol Blue	Me	H	Me	SO_2	1.2 2.8	Red Yellow
					8.0 9.6	Yellow Blue



(1.74)



(1.75)

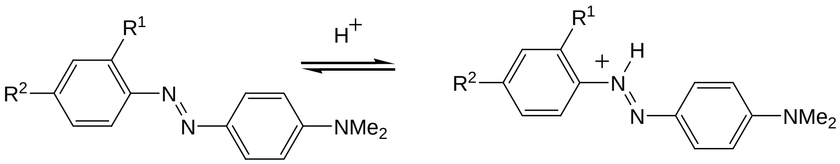
Anion sensors have been developed for use in the biological medicine field because a large number of biological processes involve molecular recognition of anionic species. One approach that has been adopted involving the construction of effective optical anion sensors is described in Section1.4.1.6.

1.4.2.2 Absorbance-based Ion-selective Optical Sensors

"*Chemical sensors are miniaturised devices that can deliver real time and on-line information on the presence of specific compounds or ions in even complex samples.*"

As the name implies optical sensors rely on an optical method for the detection of a specific chemical species. Such sensors have found many applications in industry (*e.g.* process control), medical diagnostics and clinical assays, and in environmental monitoring areas.[157] Optical sensors essentially consist of a chemical recognition phase which is coupled with an optical transduction element leading to the output of an analytical signal, as shown schematically in Figure 1.37.

Optical sensors, or optodes, can be used in several formats, *e.g.* planar coatings in bio-reactors, disposable single-shot devices (more correctly termed



Indicator	*R¹*	*R²*	*pH range*	*Base λ_{max} nm*	*Azonium λ_{max} nm*
Methyl Orange	H	SO_3H	3.1 (red)		506
			4.4 (yellow)	442	
Methyl Red	CO_2H	H	4.4 (red)		520
			6.2 (yellow)	435	

Figure 1.36 Azo dye based indicators.

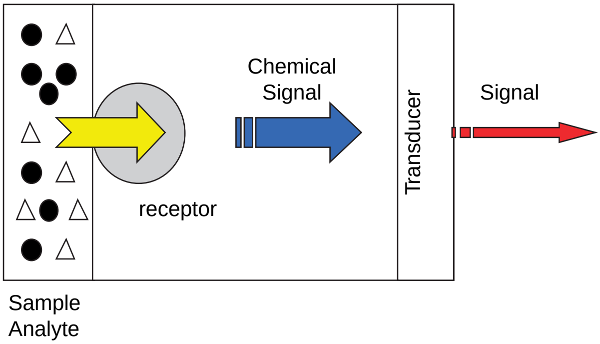


Figure 1.37 Composition and function of a chemical sensor.

probes), planar membranes, and especially fibre-optic coupled devices. The advent of fibre-optic devices has allowed light to be carried into areas that are otherwise difficult to reach, greatly extending the applications for optical sensing. Research into fibre-optic coupled devices has been a major area in the last ten years and a review of this field should be consulted for those requiring much greater detail.[158]

When the analyte has no intrinsic optical property, such as IR and UV absorption, that can be used for its detection, it is necessary to use the indirect method of reagent-mediated sensors. Here indicators that modify their optical properties when they interact with the analyte are used, and it is their response and concentration that is being measured in the sensors. The most extensively used optical chemical and biochemical sensors rely on luminescence, for their signalling, and these are covered in detail in Chapter 3 (Sections 3.5–3.7). In this section we will deal with those cases where the optical sensing of ions is by changes in absorption, due to interaction with the indicators.[159,160]

To be useful in sensors, rather than in single-shot probes, any indicator should exhibit the following properties:

- Be very sensitive to the analyte;
- Show complete reversibility on removal of the analyte;
- Respond quickly;
- Show a high degree of selectivity for the analyte;
- Exhibit photostability;
- Show no reagent leaching;
- Be compatible with semi-conductor light sources *e.g.* LEDs.

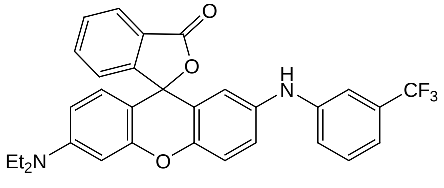
Indicators that are used in indirect pH optical sensors include those that have already been described in detail in Section 1.4.1 and listed in Table 1.14 and Figure 1.36. These operate in a relatively narrow pH range but, by combining several of these ionochromic indicators, it is possible to produce sensors with a linear pH response over a wide range. Indirect detection of cations and anions requires the employment of a variety of chromoionophores, which change from one colour to another on reaction with the ions.[158,161,162] Metallochromic ionophores that are used in sensors for the detection of metal ions and cations, such as NH_4^+, and for anions have already been described in detail earlier (see Sections 1.4.1.5 and 1.4.1.6).

As stated above in the list of attributes for an effective indicator in sensors, it is important that it does not leach out whilst still remaining accessible to the analyte. In most reagent-based optical sensors, the reagent is immobilised in a solid matrix usually in the form of a monolith or a thin film. The most commonly used matrices for this purpose are sol-gels or polymers.[158]

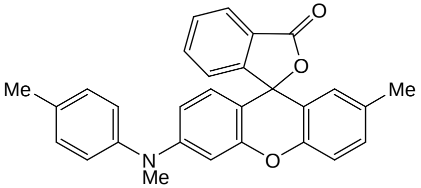
The measurement of CO_2 is important in several areas including environmental monitoring, in bio-medical diagnostics, *e.g. in vivo* gastric diagnosis, and in the food packaging industry. The colorimetric sensing of this gas can be achieved by dissolution in water to give carbonic acid, so that normal pH indicators can be used for absorption-based sensing in a variety of matrices. Examples include Thymol Blue immobilised in a sol-gel matrix for gaseous CO_2 sensing,[163] while Bromothymol Blue in an ionic liquid matrix has been used for both gas-phase and dissolved CO_2 sensing.[164] Forming an ion pair with bulky quaternary ammonium ions makes it possible to dissolve an ionochrome into a polymer film, thus producing a dry CO_2 indicator.[165] The sol-gel method has also been employed in making sensors for use in the very corrosive environments of strong acids and bases, such as hydrochloric acid and sodium hydroxide.[166]

1.4.2.3 Carbonless Copying Paper

This, as its name implies, is a process by which multiple copies of a document can be produced without using carbon paper. The first system was launched by the National Cash Register Company of the USA in 1954. Since that time many improvements have been made to the process but the underlying technology is the same as it was when first developed. At its most basic level the process consists of two sheets of specially coated paper on which the elements of the image are implanted using pressure; hence the term pressure-sensitive papers is often used for these materials. The top sheet is coated on the reverse side with microcapsules containing a non-volatile solvent and a pH-sensitive leuco dye, known as the colour former *e.g.* (1.76) for black, Crystal Violet Lactone (1.58) for blue and (1.77) for red.



(1.76)



(1.77)

The microcapsules are produced either by a coacervation process using gelatine or more commonly nowadays by coating with resins such as urea/formaldehyde, polyester or polyurethane.[167] The surface of the lower sheet is coated with an acidic material, which can be selected from acidic clays, zinc salicylate and zinc-modified phenolic resins. On application of pressure to the top sheet, the dye is released from the microcapsules and reacts with the acidic clay on the lower sheet to produce the coloured image. The process is illustrated schematically in Figure 1.38(a). Commercial use of the system is very large, mainly in the continuous production of multiple copy business bills and receipts from computer-generated customer lists, where more than two layers of paper is the norm.[168] The multi-part set of papers comprises the following and is illustrated in Figure 1.38(b).

- CB (coated back) – the paper is coated on its back with a micro-encapsulated solution of colour formers in oil.

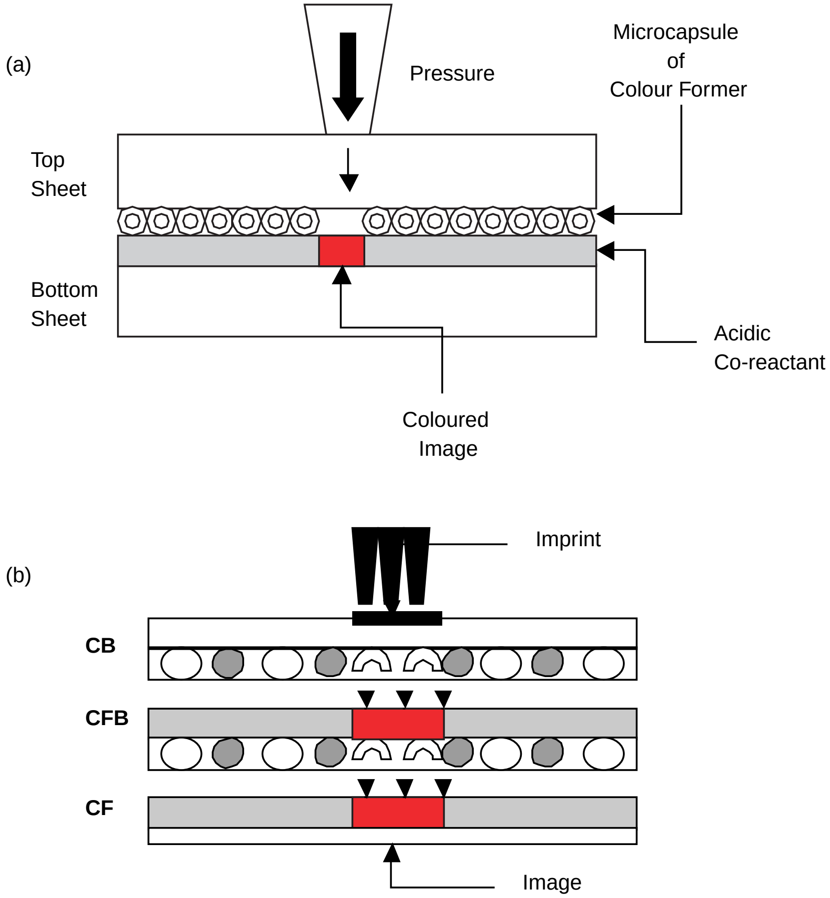


Figure 1.38 Schematic representation of single and multi layer carbonless copying paper process.

- CFB (Coated Front and Back) – the paper is coated on its front with a colour developer and on its back with a microencapsulated solution of colour formers in oil.
- CF (Coated Front) – the paper is coated on its front with a colour developer.

1.4.2.4 Direct Thermal Printing

The production of a digitised image on a coated paper by a thermal head is known as direct thermal printing.[169] The essential difference between this process and carbonless copying paper is that the thermosensitive layer contains both the colour former and the acidic co-reactant, and hence can be a single-layer process. Simply heating the surface of the paper with a thermal head causes the components to react and produce the coloured image. The preferred colour formers for the desired black images are the fluorans (*cf.* 1.63), although blue *e.g.* Pyridyl Blues (1.60) and yellow shading components are available. All the co-reactants used commercially are phenols, most commonly Bisphenol A, often incorporating a sensitiser such as benzyl-2-naphthyl ether to reduce the energy input and speed up the printing process. Poor image stability to light and heat is an inherent problem with the system and to help counteract these disadvantages hindered phenols are included as stabilisers. To prevent wear on the thermal heads which come in direct contact with the paper, a lubricant such as zinc stearate is added and to retain the smoothness of the surface of the paper anti-pressure agents such as paraffin waxes are included. Typical binders used to hold the materials to the surface of the paper are polyvinyl alcohol or hydroxyethyl cellulose. The process is shown schematically in Figure 1.39.

By far the largest use of direct thermal printing was in facsimile machines for digital data and image transfer but this has diminished markedly in recent years. Although the machines are very cheap and highly reliable in use, there

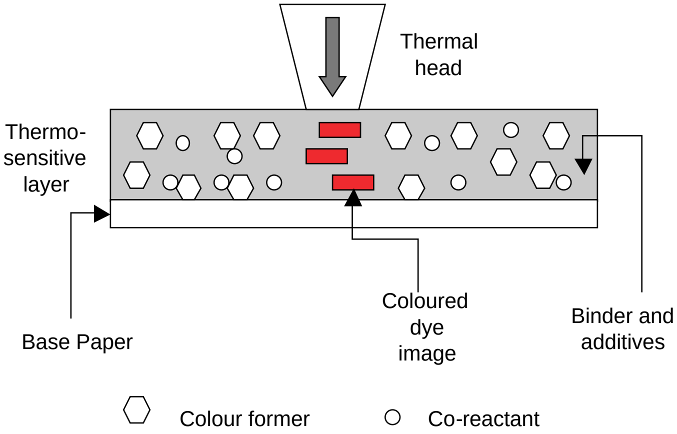


Figure 1.39 Direct thermal printing process.

are disadvantages. The system relies on specially coated papers, the cost of which is somewhat offset by the fact that no special inks or other materials are required; and the light stability of the images on the paper are poor, which means they are of little use for archiving. The arrival of plain paper fax machines using ink-jet printers to produce the image, and especially e-mail and the Internet, have also severely curtailed the growth of direct thermal printing for data and image transfer (see Chapter 2, Section 2.9). However, there are still very significant uses of direct thermal printing in point of sales receipts, admission, transportation and lottery tickets, medical records, baggage tags, postage stamps, fax paper and delivery and food retailing labels.

Nowadays it is an essential requirement that the printing of digital images be in full colour. Whilst many attempts have been made to develop full-colour direct thermal printing, the Thermo Autochrome process from Fuji is the only one that has shown success. In this process there are three colour-producing coatings: yellow, magenta and cyan with only the latter involving an ionochromic compound. Because of the complexity of the process it is very unlikely ever to compete effectively with ink-jet printers in the bulk desktop printer market. However, the printing equipment is relatively simple and compact, the derived prints are of photo quality, and therefore the process has found a niche outlet in printing images from digital cameras. This will be covered in greater detail in Chapter 2 (Section 2.9).

1.5 Electrochromism

When an electroactive species undergoes a change in colour upon electron transfer (oxidation/reduction) the process is known as electrochromism. This process normally involves the passage of an electric current and is reversible. In the late 1960s, it was suggested that because of their reversible change in colour, electrochromic materials could be used to make coloured displays. However, in spite of the early enthusiasm, it took until the last decade of the twentieth century for genuine commercial applications to appear, and then not in displays but in switchable rear-view mirrors and so-called smart windows.[170] Recent developments in devising red, green and blue colouring polymeric electrochromes has once again raised the prospect of a commercially acceptable display device based on electrochromism, and even their use in optical data storage.[171,172] In this section of the book the mechanism of electrochromism in cells will be discussed only briefly, followed by a more detailed description of the various classes of electrochromic materials, and finally an account will be presented of the burgeoning applications for these systems. Those wanting a more complete picture should consult a recent comprehensive monograph on the topic.[173]

1.5.1 Electrochromic Cells

During the process of coloration in electrochromic cells by passing a charge in one direction, a colour can form in one or both of the electrodes or in the electrolyte adjacent to the electrodes. When the colour is formed by reduction at a negative electrode it is called cathodic coloration and, conversely, at the anode it is anodic coloration. Two different types of cells are shown schematically in Figure 1.40.[170] The most common is the coloured-electrode type, in which the transparent electrodes are coated with an organic or inorganic polymer which becomes coloured on passing a charge through the cell (see Section 1.5.2.3). If both electrodes change colour they must display complementary electrochromism; the colour change that occurs by oxidation at the first electrode must be the same as that occurring by reduction at the second electrode. The degree of coloration can be controlled by the amount of charge passing through the cell. The cell is bistable: it remains coloured, even in the absence of applied voltage, until an equal charge is passed in the opposite direction through the cell. In other words the coloration of the electrochromic cell is controllable and switchable on demand.

In the case of the coloured electrolyte type, the two complementary electrochromes are dissolved in the electrolyte between the transparent electrodes. One becomes coloured by oxidation and the other by reduction and consequently the electrolyte becomes coloured (see 1.5.2.1). The electrolyte remains coloured only whilst a current is being passed, becoming colourless once the charge is removed.

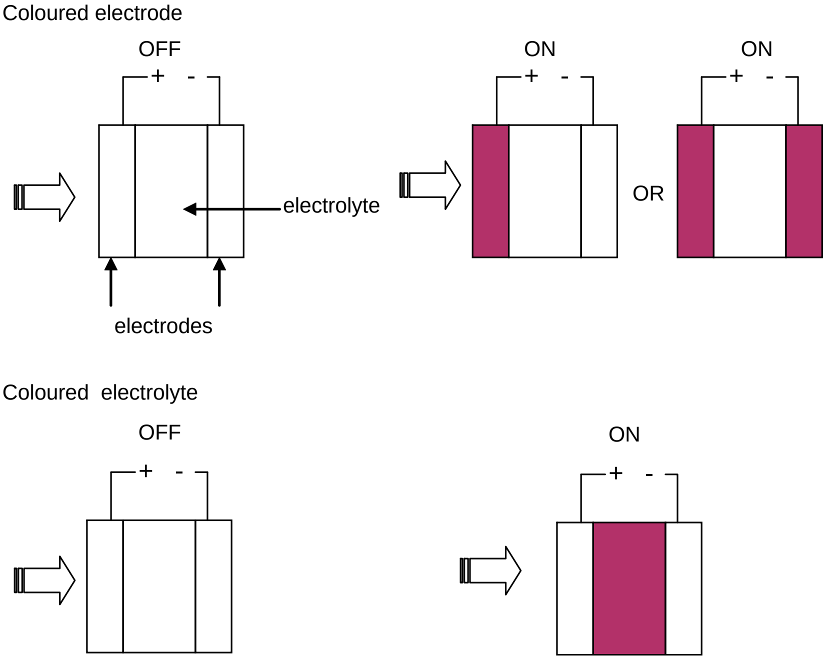


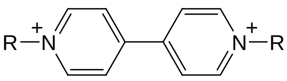
Figure 1.40 Schematic of electrochromic cells.

1.5.2 Electrochrome Types

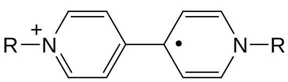
The materials that change colour on passing a charge are called electrochromes, and these can be classified into three groups. In the first type (Type-I) the colouring species remain in solution at all times during electrochromic usage; in Type-II the reactants are in solution but the coloured product forms a solid on the surface of the electrode following electron transfer; the third type (Type-III) encompasses those where all the materials are solids at all times, *e.g.* in films. The first type is used in car, anti-dazzle, rear-view mirrors; the second type in larger mirrors for commercial vehicles, and the third type in smart windows (Section 1.5.4.2).

1.5.2.1 Solution Electrochromes (Type-I)

In these systems the soluble electrochrome undergoes an electron transfer interaction on the surface of the appropriate electrode, involving either anodic oxidation or cathodic reduction, where it changes colour and then returns back to the solution phase, producing a coloured electrolyte (Figure 1.40). The most widely studied solution electrochrome is the dimethyl-4,4′-bipyridylium dication, also known as methyl viologen (1.78; R = Me), which undergoes a one-electron reduction to the bright-blue-coloured radical cation (1.79; R = Me).[174]



(1.78)



(1.79)

1.5.2.2 Solution-Solid Electrochromes (Type-II)

This type of electrochrome, in its pale or colourless state, is soluble in the electrolyte. However, on electron transfer, the coloured species becomes insoluble and is deposited onto the surface of an electrode. Viologens with hydrophobic chains, such as heptyl (1.78; $R = C_7H_{15}$), form deeply coloured radical cation salts (1.79; $R = C_7H_{15}$) in water that appear as a thin film deposited on the electrode. Other examples are *N*,*N*′-bis(4-cyanophenyl)-4,4′-bipyridylium salts (1.78; R = 4-cyanophenyl) in water, and methoxyfluorenone in acetonitrile solution.

1.5.2.3 Solid Electrochromes (Type-III)

All inorganic electrochromes exist in the solid state in both the colourless and coloured states *e.g.* Prussian Blue and tungsten trioxide. Conducting polymers such as polyanilines, polypyrroles and polythiophenes also fall into this class (see Section 1.5.3.5).

1.5.3 Electrochromic Chemicals

A wide range of both inorganic and organic chemicals exhibit electrochromism and it is only possible to cover those of the greatest importance in this text. Readers requiring greater details should refer to specialised texts.[173 175]

1.5.3.1 Inorganic Oxides

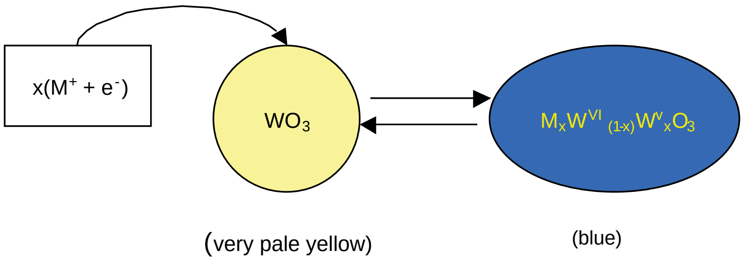
Oxides from a wide range of transition metals exhibit electrochromism: cerium, chromium, cobalt, copper, iridium, iron, manganese, molybdenum, nickel, niobium, palladium, praseodymium, rhodium, ruthenium, tantalum, titanium, tungsten and vanadium.[175] The most important of the primary electrochromes, those that are used for their strong colour formation in two-electrode cells, are based on molybdenum trioxide, iridium oxide, copper oxide and especially tungsten trioxide. Some of the other metal oxides form a group of secondary electrochromes used as the feebly colouring components in two-electrode cells. The colours formed by selected metal oxide electrochromes are shown in Table 1.15.

Mechanistically the colour is formed by an optical charge-transfer between metal centres in the solid-state lattice. In tungsten trioxide this involves partial reduction of the pale yellow W^{VI} to the blue W^{V} state. This reduction requires partial insertion of a balancing cation, as shown schematically in Figure 1.41, where M is usually lithium or hydrogen. Therefore tungsten trioxide is a cathodically colouring electrochemical material.

The pure tungsten trioxide, WO_3, is very pale yellow and practically colourless in thin films, whilst the reflected colour of the reduction product, $M_xW^{VI}{}_{(1\ x)}W^{V}{}_{x}O_3$, is proportional to the charge injected. The colour changes from blue ($x = 0.2$), through purple ($x = 0.6$) and red ($x = 0.7$) to bronze ($x = 0.8$–1.0). Thin films of WO_3 can be laid down by thermal evaporation under vacuum, by chemical vapour deposition using $W(CO)_6$, by thermal sputtering in an oxygen rich atmosphere or by electrodeposition onto an electrode surface with peroxytungstate anion. The most widely adopted procedure, and one well suited to the production of large areas as in windows, is the sol-gel method using colloidal hydrogen tungstate, followed by thermal curing.[176]

Table 1.15 Colours of selected metal oxide electrochromes.

Metal	*Oxidised form*	*Reduced form*
Cobalt	Pale yellow	Dark brown
Copper	Black	Red brown
Iridium	Colourless	Blue grey
Manganese	Dark brown	Pale yellow
Molybdenum	Colourless	Intense blue
Nickel	Brown black	Colourless
Tantalum	Colourless	Very pale blue
Tungsten	Very pale yellow	Intense blue
Vanadium	Brown yellow	Very pale blue



$$WO_3 + x(M^+ + e^-) \rightarrow M_xW^{VI}_{(1-x)}W^{V}_xO_3$$

Figure 1.41 Mechanism of colour formation in tungsten oxide.

1.5.3.2 Prussian Blue and Metal Hexacyanometallates

Prussian Blue is a long established blue pigment for paints and inks, whose use in photographic prints is the origin of the term "blueprint". The chemical also exhibits electrochromic behaviour and its application in this field has been widely studied.[177] Chemically Prussian Blue is Fe(III) hexacyanoferrate(II), with a distribution of Fe(III) and Fe(II) oxidation states. Prussian Blue belongs to a general class of potentially electrochromic metal hexacyanometallates, $M^1_x[M^2CN_6]_z$, where M are transition metal ions in different oxidation states, *e.g.* iron(III) hexacyanoruthenate(II) also known as *ruthenium purple*, nickel, vanadium, copper, palladium and indium hexacyanoferrates.[178] Thin films of Prussian Blue can be electrochemically deposited onto electrode surfaces by electroreduction of solutions containing Fe(III) and hexacyanoferrates(III).[179] Prussian Blue produces the colourless Prussian White on reduction and is therefore an anodically colouring electrochrome:

$$\underset{\text{(blue)}}{[Fe^{III}Fe^{II}(CN)_6]^1} + e \rightarrow \underset{\text{(colourless)}}{[Fe^{II}Fe^{II}(CN)_6]^2}$$

Since tungsten trioxide is cathodically colouring it can be used in conjunction with the anodically colouring Prussian Blue electrochrome in a single device.

1.5.3.3 Metal Phthalocyanines

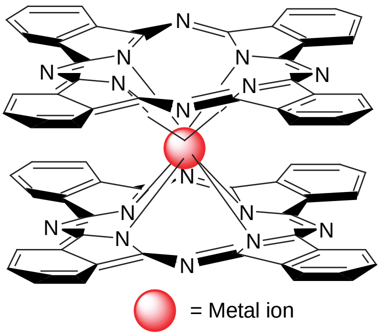
Metal phthalocyanines are extremely important materials in a variety of fields outside their traditional use as dyes and pigments (Chapter 2, Sections 2.3.1.6 and 2.4.1.5), including electrochromism. The properties of metallophthalocyanines make them attractive as potential electrochromic materials: high light stability, high extinction coefficients, stable and sublimable at high temperatures, and the possibility of multi-colours within one structure. The metallophthalocyanines which have found application as electrochromes are mainly the rare earth derivatives, especially lutetium, and second-row transition metals

Table 1.16 Colours of sandwich metallophthalocyanines under redox conditions.

Metal oxidation state	*Red (yellow/red)*	*Green*	*Blue*	*Purple*
III	$[\mathrm{M(PC^{\bullet-})_2}]^{+}$	$[\mathrm{M(PC^{\bullet-})(PC)}]$	$[\mathrm{M(PC)_2}]^{-}$	$[\mathrm{M(PC)_2}]^{2-}$
IV	$[\mathrm{M(PC^{\bullet-})_2}]^{2+}$	$[\mathrm{M(PC^{\bullet-})(PC)}]^{+}$	$[\mathrm{M(PC)_2}]$	$[\mathrm{M(PC)_2}]^{-}$

$\mathrm{PC}^{\bullet}$ phthalocyanine radical anion

such as zirconium and molybdenum.[180] Synthesis of these molecules follows the traditional routes, *e.g*. condensation of 1,2-dicyanobenzene with metal acetate in a high boiling solvent (see Chapter 2). These compounds have structures in which the metal is sandwiched between two phthalocyanine rings *e.g*. zirconium bisphthalocyanine (1.80; M = Zr) and lutetium bisphthalocyanine (180; M = Lu), the latter protonated on one of the meso N atoms to balance the charge.



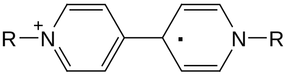
(1.80)

The phthalocyanines can be laid down as vividly coloured thin films by sublimation at high temperatures, *e.g*. at 400–600 °C under vacuum. The thin blue films of the bisphthalocyanines are polyelectrochromic, undergoing electrochemical oxidation to give first green and then yellow-red or red colours (anodic products) and blue-purple colours on reduction (cathodic products). The various constitutions of these coloured products are shown in Table 1.16.

1.5.3.4 Viologens (4,4′-bipyridylium salts)

Salts of quaternised 4,4′-bipyridine are herbicides, manufactured on a large scale, and called generically "paraquats". The ready availability of 4,4-bipyridine and the ease of varying the nature of the quaternising agent has meant that the behaviour of these derivatives is the most extensively studied of all the organic electrochromes.[174] In electrochromism this class of compounds is known as "viologens", the stable, colourless dications (1.78) undergoing one-electron reduction to the brilliantly coloured radical cation (1.79). They can be rendered soluble in water or organic solvents or insoluble, depending on the

Table 1.17 Optical properties of viologen radical cations.



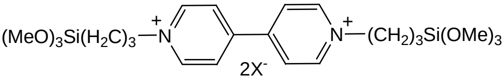
(1.79)

R	λ_{max} nm (solution)	Solvent	ε_{max}	Colour (film)
Methyl	605	H_2O	13,700	blue
Ethyl	603	DMF	12,200	blue
Heptyl	545*	H_2O	26,000	mauve
Octyl	543*	H_2O	28,900	crimson
Benzyl	604	H_2O	17,200	mauve
4 CN Ph	674	PC	83,300	green/black

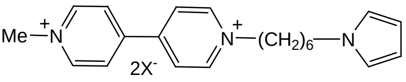
*radical cation dimer

nature of the quaternising group. The former are used as solution electrochromes and the latter as solution-solid electrochromes (see Section 1.5.2 above). The colour produced on reduction to the radical cation is strongly dependent on the length and nature of the alkylating agent used to form the diquat salt. The short-chain alkyl groups produce bright blue coloured radical cations, while the mid-length chains give purple and the longer chains mauve/red. Alkylation with aryl groups, *e.g.* 4-cyanophenyl, produces green or black coloured radical cations. The optical properties of selected viologen radical cations are shown in Table 1.17.[174]

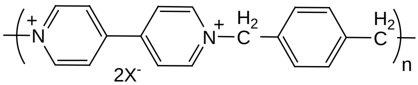
The quaternary groups in viologens can be further derivatised to produce compounds capable of chemically bonding to a surface, especially electrode surfaces. These include symmetrical silanes such as (1.81), which can bond to the oxide lattice on the electrode surface, and a viologen with a pyrrole side chain (1.82) that undergoes anodic polymerisation to form a film of the viologen-bearing polypyrrole on the electrode. Polymeric bipyridylium salts such as (1.83) have also been prepared for use in polymeric electrolytes.[174]



(1.81)



(1.82)



(1.83)

1.5.3.5 Polymeric Electrochromes

Many aromatic ring systems, including aniline, pyrroles, furans, carbazole and thiophenes, form extensively conjugated, electroactive polymers. These have found applications in a range of areas, some of which will be covered elsewhere in this book, *e.g.* sensors and organic light-emitting diodes (Chapter 3), photovoltaics (Chapter 4) and lasers (Chapter 5). The fact that conjugated polymers can be oxidised or reduced between an electrically neutral colourless state and a coloured charged state, in the presence of a charge-balancing counterion, often called "p doping", means they can be used as solid electrochromes in thin films.[181,182]

Electroactive conducting polymers offer the following advantages over inorganic compounds:

- Outstanding coloration efficiency;
- Fast switching ability;
- Multiple colours from same material;
- Fine tuning of band-gap by chemical modification.

Polyaniline films are formed by galvanostatic polymerisation of aniline in aqueous 2 M HCl at a current density of 0.1 mA cm ^{2}. Polyaniline can exist in four different redox states, with the historical names of leucoemeraldine, emeraldine salt, emeraldine base and pernigraniline (Figure 1.42). Electrode

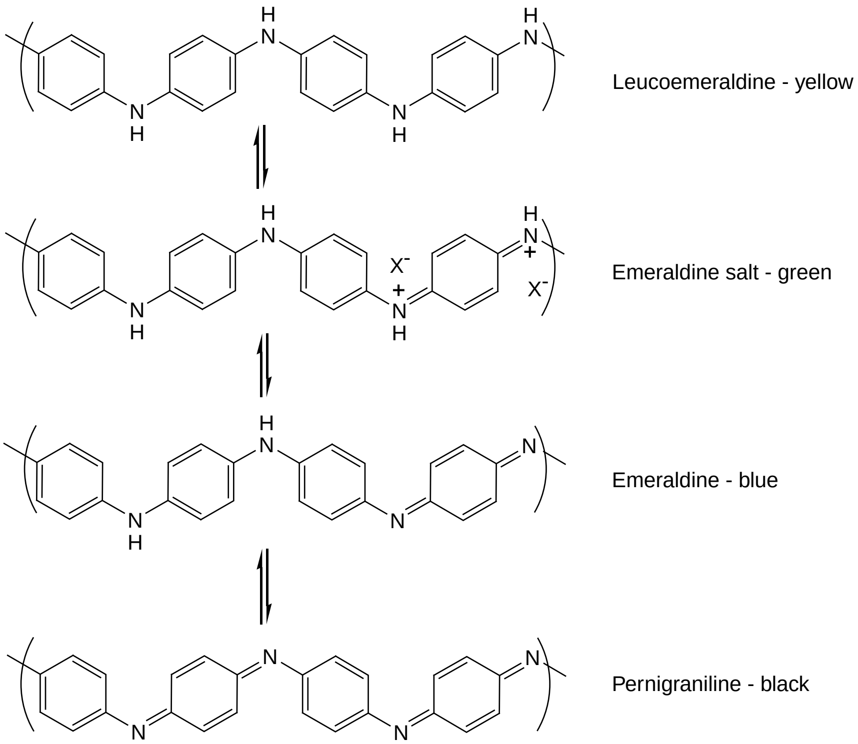
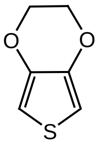


Figure 1.42 Oxidation states of polyaniline.

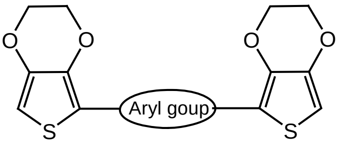
films of polyanilines are therefore polyelectrochromic showing colour changes of yellow (305 nm) to green (740 nm) and from dark blue to black, depending on the potential (range from –0.2 V to + 1.0 V). Substituted anilines such as 2-anisidines produce electrochromic polymers with different wavelength maxima.

Other very important electrochromic polymers are the polypyrroles and polythiophenes, obtained by polymerisation of the parent pyrrole and thiophene or, more importantly, their 3,4-disubstituted derivatives. The most widely studied of these two classes of polymers in electrochromic outlets are the polythiophenes, readily synthesised by the reaction of the substituted monomer, either chemically or electrochemically. The colour change properties of a variety of polythiophenes in the presence of a counter ion are shown in Table 1.18.[182]

The synthesis and development of a variety of electroconductive polymers has been assisted by the commercial availability of the monomer 3,4-(ethylenedioxy)thiophene (EDOT) (1.84) as Baytron M from Bayer AG, and the derived polymer PEDOT as a water-soluble complex (PEDOT:PSS) with the polyelectrolyte poly(styrenesulfonate), called Baytron P (Bayer AG) or Orgatron (Agfa Gevaert).[183] PEDOT is blue in the neutral state and transmissive sky blue in the oxidised state. By polymerising bisarylene-bridged EDOT monomers (1.85) it is possible to make polymers showing a spectrum of colours from yellow through red to blue in the neutral state.[184]



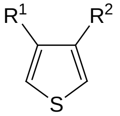
(1.84)



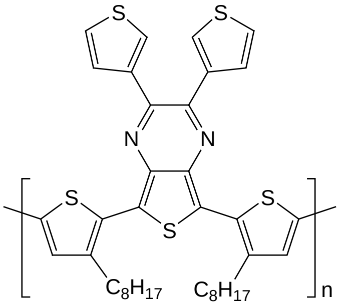
(1.85)

For use in electrochromic displays it is essential that there are matched switching states in the three additive colours of red, green and blue. Whilst

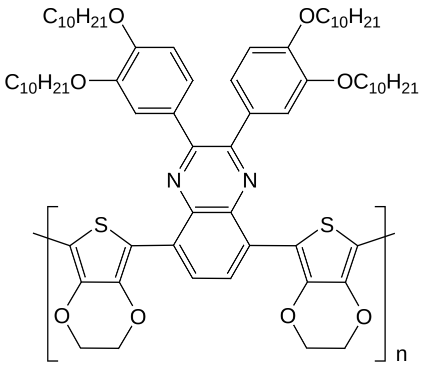
Table 1.18 Electrochromic colour change properties of polythiophenes[182] (reproduced with permission of Wiley-VCH).

			λ_{max} *nm (shade)*	
R¹	*R²*	*Anion*	*Oxidised*	*Reduced*
H	H	BF_4^-	730 (blue)	470 (red)
H	Me	BF_4^-	750 (deep blue)	480 (red)
Me	Me	ClO_4^-	750 (deep blue)	620 (pale brown)
H	Ph	BF_4^-	(green/blue)	(yellow)
Ph	Ph	BF_4^-	(blue/grey)	(yellow)

good red and blue polymeric electrochromes have been known for some time it was not until recently that a green became available that met some of the requirements for displays.[185] This was achieved by constructing a polymer which had two isolated conjugated systems built into the backbone; one which absorbed blue and the other red light and therefore reflected green light in the neutral state (1.86). Ideally on depletion the oxidised polymer should be clear and transparent, but unfortunately (1.86) leaves an unattractive transmissive brown colour. Subsequently a neutral state green polymer (1.87) has been devised, which is claimed to be highly transmissive in the oxidised state.[186] The potential use of these polymers in displays will be discussed in Section 1.5.4.3.



(1.86)

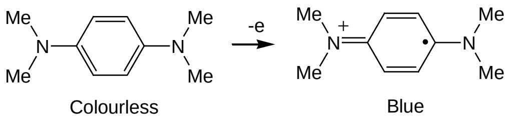


(1.87)

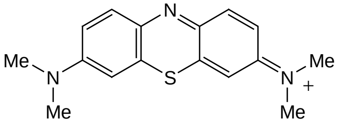
One of the big drawbacks associated with the use of many conducting polymers as electrochromic materials is their low cycle-life stability. In order to overcome this and other electrochromic properties many composite materials have been studied. These composites include mixtures with other optically complementary, conducting polymers and inorganic electrochromes, such as tungsten trioxide and Prussian Blue, and colour-enhancing agents or redox indicators, exemplified by the inherently electrochromic Indigo Carmine.[187(a)]

1.5.3.6 Other Organic Electrochromes

Several other organic systems have been studied as potential electrochromes because of their redox behaviour. These include carbazoles, methoxybiphenyls, fluorenones, benzoquinones, napthoquinones and anthraquinones, tetracyanoquinodimethane, tetrathiafulvalene and pyrazolines.[187(b)] Of particular interest are the 1,4-phenylenediamines, known as Wurster's salts, *e.g.* Wurster's Blue (1.88), and the related thiazines, including Methylene Blue (1.89), which on oxidation form highly coloured species. Being anodically colouring these types of materials have found an important outlet in composite electrochromic systems for car rear-view mirrors (see Section 1.5.4.1).



(1.88)



(1.89)

1.5.4 Applications of Electrochromism

Whilst many areas have been proposed for the application of electrochromic systems, to date by far the most successful ones are in electrically switchable rear-view car mirrors for anti-dazzle, and in glazing units for temperature and light control in buildings. However, there has recently been significant progress in the area of visual displays and data storage. The big advantage offered by electrochromic systems in heat and light control applications is the fact that the cells can be made very large – one cell can comprise a whole glazing unit. In these types of applications the generic term "chromogenic materials" is often used.

1.5.4.1 Rear-view Mirrors

Electrically switchable automatic-dimming rear-view mirrors for cars and trucks have been in commercial production in the US since the early 1990s. The leading company is the Gentex Corporation with its Night Vision System (NVS), whose mirrors are said to feature as standard or optional equipment on more than 200 vehicle models.[188]

The Gentex mirror consists of an ITO-glass surface at the front, with the conductive side inwards, and a metal rear electrode with a highly reflective surface, spaced less than a millimetre apart. In the gap between these two electrodes is the solution or gel electrolyte containing dual electrochromes (a Type-I system).[189] One of these electrochromes is coloured at the anode by formation of the stable radical cation, using either a Wurster's Blue (1.88) or more likely a thiazine (1.89) analogue, whilst for the other a viologen is reduced at the cathode. The colours are complementary and produce a deep blue-green coloration. It is essential that a current be applied to the cell whilst it is coloured, in order to avoid the electrode reaction being reversed in solution. This is because the two types of coloured electrochromes can diffuse away from their respective electrodes and react with each other, restoring the bleached states (Figure 1.43). This process of self-erasing helps to make the automatic dimming rear-view mirror fail-safe since it spontaneously reverts to the clear condition in the case of power failure.

In operation the mirrors are coupled with sensors as follows:

- forward-facing sensor recognises low ambient light levels and signals the mirror to begin looking for glare.

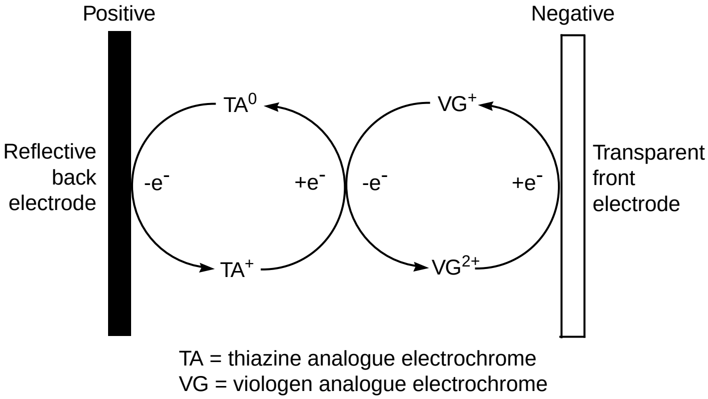


Figure 1.43 Schematic of redox cycles in Gentex anti glare mirror[187] (reproduced with permission of Cambridge University Press).

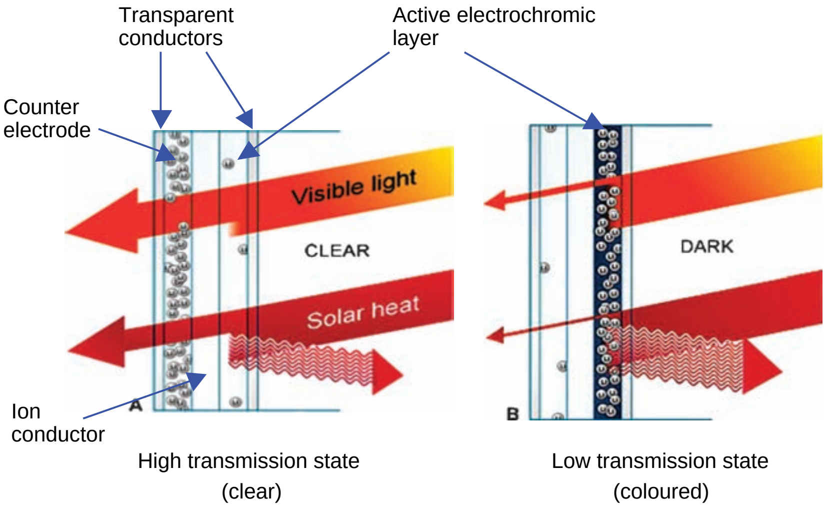
- A rear-facing sensor then detects glare from the vehicles travelling behind, sending voltage to the mirror's EC gel in proportion to the amount of glare detected.
- The mirror dims in proportion to the glare and then clears when the glare is no longer detected.
- The interior mirror's sensors and electronics control the dimming of both interior and exterior mirrors.

The Donnelly Corporation (now Magna Donnelly) has also devised rear-view mirrors. In one example, a hybrid system comprising a solid metal oxide (WO_3) electrochromic layer is used in conjunction with a non-electrochromic reversible redox complex, a mixture of ferrocene, phenothiazine and lithium perchlorate, in the contacting solution.[190]

1.5.4.2 Smart Windows Chromogenic Glazing

The control of the solar gain within buildings occurring through the glazing units, although always a highly desirable objective, has become even more so with the rapid rise in cost of the energy needed to support air-conditioning systems *etc.* Because it would be most attractive for the glazing to operate dynamically and change in response to environmental conditions, this has led to the devices being called "smart windows". When using smart windows instead of conventional static solar control windows, it has been estimated that the energy for space cooling, on an annual basis, could be reduced by as much as 40 to 50% in a range of European countries.[191]

Whilst glass manufacturers, such as Pilkington, Saint Gobin and PPG, have carried out most of the application research in the past, widespread fundamental research in recent years has provided new insights into potential commercial products displaying higher energy efficiency.[192] Although several



High transmission state (clear)

Low transmission state (coloured)

Figure 1.44 Schematic of a WO_3 electrochromic glazing unit.[193]

designs have been proposed, typical of the systems that have been commercialised to date is the one by Sage Electrochromics Inc. illustrated in Figure 1.44.[193]

Of the electrochromes available the most widely used in such glazing units are those based on the cathodically colouring WO_3 (see Section 1.5.3.1). The glass used in such glazing units is coated with a transparent conducting surface, *e.g*. indium tin oxide (ITO), In_2O_3:Sn, or SnO_2:F. The electrochromic cell comprises an active electrode layer of WO_3 coated onto the conducting surface of one of the glass sheets, and a counter electrode of the non-stoichiometric lithium vanadium oxide ($Li_xV_2O_5$) or lithium nickel oxide (Li_xNiO_2) laid down on the conducting surface of the other glass sheet. In between these two there is a thicker layer of a lithium ion polymer electrolyte. On applying a potential of around 1.5 V to the cell, lithium ions are discharged and dissolved at the WO_3 surface, the lithium being supplied from the counter electrode $Li_xV_2O_5$. The colourless WO_3 becomes blue coloured (Li_xWO_3) on lithium ion insertion, the precise depth of colour depending on the degree of insertion; *e.g*. insertion of 12 millicoulombs cm ^{2} produces a sky-blue colour, which reduces the visible light transmission by a factor of 4. The colour of the window cell is erased on reversing the applied charge.[170]

Smart windows darken automatically when the ambient sunlight reaches a pre-determined level. One suggestion for attaining this goal was to combine solar cells and electrochromic cells, giving a photoelectrochromic cell. The design principle behind these smart windows was the use of an electrochromic film that undergoes changes in colour in response to changes in the applied voltage, the power source being supplied by a photovoltaic cell working independently but in tandem with the electrochromic film.[194] Subsequently this was

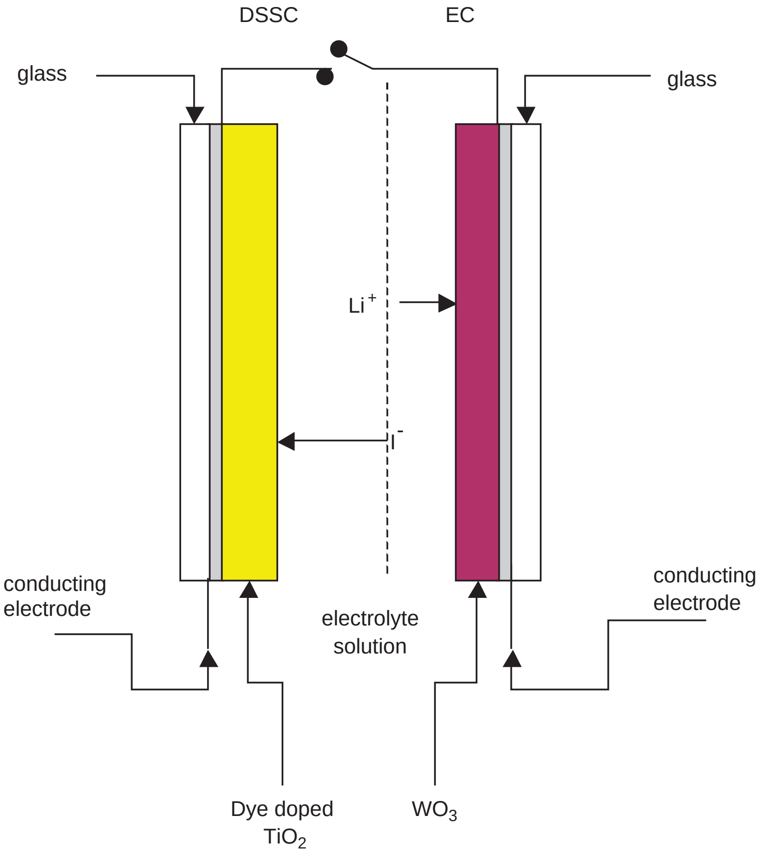


Figure 1.45 Smart window from combined DSSC and EC cells.

adapted to use the principle of dye-sensitised solar cells devised by Grätzel *et al.* in the early 1990s, the developments of which will be described in greater detail in Chapter 4, Section 4.8.1.4. In the photoelectrochromic cell (Figure 1.45) the dye-sensitised semi-conductor electrode is a transparent conducting sheet of glass coated (5 μm) with nanocrystalline TiO_2 (diameter 20 nm) doped with a ruthenium bipyridyl complex chromophore. The dye absorbs light, becomes excited and injects electrons into the TiO_2 electrode. The electrons travel into the transparent WO_3 film and then, in order to balance the charge, lithium ions from the electrolyte solution insert into the WO_3 and in so doing create the coloured species as described above. If the light source is removed then the cell is bleached back to its original colour. However, if the cell is disconnected from the circuit before the light is removed it remains coloured, because the electrons cannot escape from the reduced WO_3 film. A variety of dye chromophores and electrochromes and structures have been described for this type of cell.[195,196]

By devising a way of anchoring the electrochrome it has been possible to derivatise nanocrystalline TiO_2 film with a variety of agents, for instance using

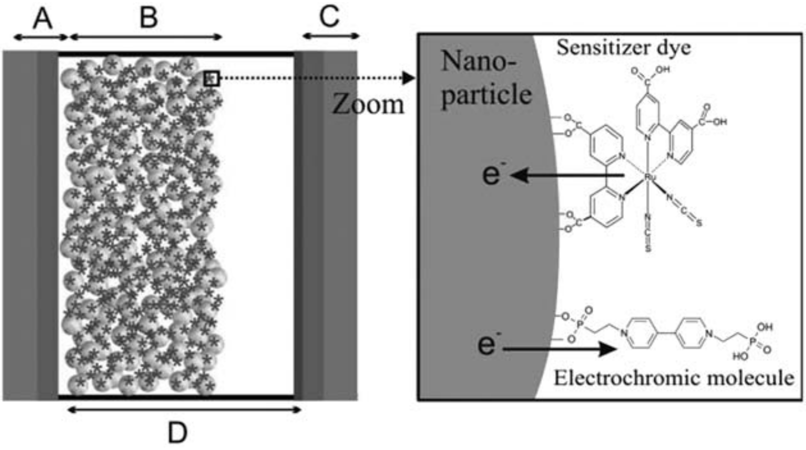


Figure 1.46 Description of the dual function cell. (A) F doped SnO_2 coated glass, (B) TiO_2 layer containing ruthenium and viologen dye, (C) F doped SnO_2 coated glass containing Pt and (D) electrolyte[197] (reproduced with per mission of the European Society for Photobiology and the European Photochemistry Association).

phosphonated viologens (see Section 1.5.4.3 below). The obvious step is to incorporate both the electrochrome and the light-harvesting chromophore onto the same nanocrystalline film (Figure 1.46). In this device an electrochromic dye (viologen) co-absorbs with the sensitiser dye and the device can be used as a solar cell as well as an electrochromic device such that two opposite electron transfer processes occur in the same electrode.[197] However, whilst this offers the prospect of a compact device its properties will need further optimisation to be viable commercially.

Thin films of inorganic electrochromic materials have been studied extensively as ways of producing novel flexible polyester-foil-based devices.[198] In this work the operational EC device was constructed from two polyester-based foils. The cathodic tungsten oxide foil was coloured by sputtering in the presence of H_2, and the anodic nickel oxide foil coloured by post-deposition ozone exposure. These foils were laminated together by a PMMA-based electrolyte using roll-pressing at 80 °C, the edges sealed and electrical contacts attached to give the working device (Figure 1.47). The properties of this film were sufficient to be developed for use in smart windows, eye wear such as motorcycle helmet visors and ski goggles and in semi-static displays (see Section 1.5.4.3).[199]

The use of nanocrystalline materials has been extended into inorganic electrochromes such as tungsten trioxide and Prussian Blue, in a field which has come to be called "nanochromics".[200] Examples include porous films of WO_3 nanoparticles made by a deposition suitable for large area applications,[201] and nanocomposite films of Prussian Blue nanoparticles and linear poly (ethyleneimine) fabricated using layer-by-layer (LBL) assembly.[202]

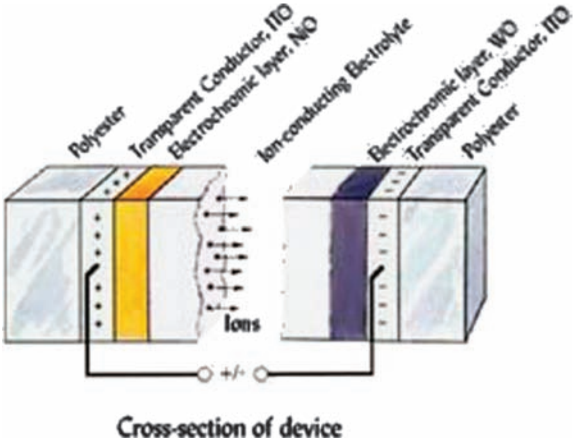


Figure 1.47 Polyester film EC device[199] (reproduced with permission of Chromo genics Sweden AB).

Electrochromic polymer films are of particular interest because of their potential ease of fabrication and flexibility for applications in both glazing and displays. They have therefore generated much interest and some recent examples of this work are solid plastic electrochromic (EC) films, prepared by introducing viologens and plasticisers into preformed solid thermoplastic polymers,[203] flexible poly(ethylene terephthalate)- (PET-)based film by the deposition of TiO_2 nanoparticles on a PET conductive substrate and bonding a modified Methylene Blue onto the TiO_2 film by means of phosphate groups.[204]

Whilst this section has emphasised the applications of electrochromism in architectural glazing there are other important areas where protection from solar heat is important, for example motor vehicles, aircraft, buses and railway carriages. A collaboration between Gentex, PPG Aerospace and Boeing has put Gentex's electrochromic windows into Boeing's B787 long-range aircraft in 2008.[205] A feasibility study of electrochromic windows in vehicles, for example self-dimming sunroofs, has been carried out but to date there is no report of a commercial use.[206]

1.5.4.3 Displays

The big difference between devising electrochromic systems for displays and for glazing is the need to construct arrays of smaller cells rather than one large one and hence the need for multiplexing. The use of electrochromic devices as display units has been a long time in coming to fruition but this is now happening. In the 1980s IBM had a prototype small area, monochrome EC display that used viologens as the electrochromes.[207] At the time this did seem to offer scope for further development but most projects in the area were dogged by long-term stability problems. Several other companies have used variations on metal plating–deplating technology to lay down films on both electrodes, for instance ones made of bismuth, using electrolytes containing bismuth bromide and lithium bromide.[208] However, the difficulty in getting full colour and uniform large area coloration, coupled with the cost of manufacture, meant that liquid crystals remained the dominant technology competing with those based on inorganic phosphors, especially in small-area displays, until the early years of the twenty-first century. The main challenge to LCD dominance is now coming from organic light-emitting diodes (see Chapter 3, Section 3.9.5) but recently electrochromic devices have started to make commercial headway in niche areas.

An example of this new approach is the extension of Grätzel's work on dye-modified nanocrystalline TiO_2, discussed above in Section 1.5.4.2 and more fully in Chapter 4, which has been extended into the displays area.[209] One system uses one metal oxide film as cathode and a second as anode to create a flexible display. The negative F-doped SnO_2 conducting glass electrode is coated with a layer of colourless TiO_2 semi-conductor (5 μm) and then with a monolayer of a viologen, for instance bis(phosphonoethyl)-4,4′-bipyridylium dichloride, by chemisorption. The positive F-doped SnO_2 conducting counter electrode is coated with a film of heavily doped SnO_2:Sb particles (3 μm) and then with a layer of a phosphonated phenothiazine. An electrolyte comprising $LiClO_4$ and ferrocene in γ-butyrolactone is placed between these two plates and the edges sealed.[210] The electrodes are micro-patterned for display purposes in a manner similar to LCD displays. Such a device has been commercialised by NTera Ltd as NanoChromics™ and can be made to look paper-like by placing a layer of ion permeable nanostructured solid TiO_2 film between the electrodes.[211]

An electrochromic paper-type display has been made entirely from electroactive organic polymers and an organic electrolyte on ordinary double-coated fine paper. A low-voltage robust display technology is claimed where each individual smart pixel device combines an electrochemical transistor with an electrochromic display cell (Figure 1.48). Poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS) served as the active material in the electrochemical smart pixels, as well as the conducting lines, of the monolithically integrated active-matrix display. The manufacturing process for this device involves only five discrete patterning steps, designed to achieve a robust display technology that is easily manufactured using a standard label-printing press.[212,213]

1.6 Gasochromism

Gasochromism is closely related to electrochromism. The process involves an electrochrome, usually a metal oxide, especially WO_3 interacting with oxidising or reducing gases, most commonly hydrogen and oxygen, to produce reversible colour changes. The gasochromic properties of WO_3 films are much improved when coated with a thin catalytic layer of platinum or palladium. The catalyst dissociates hydrogen molecules into protons and electrons, which then diffuse

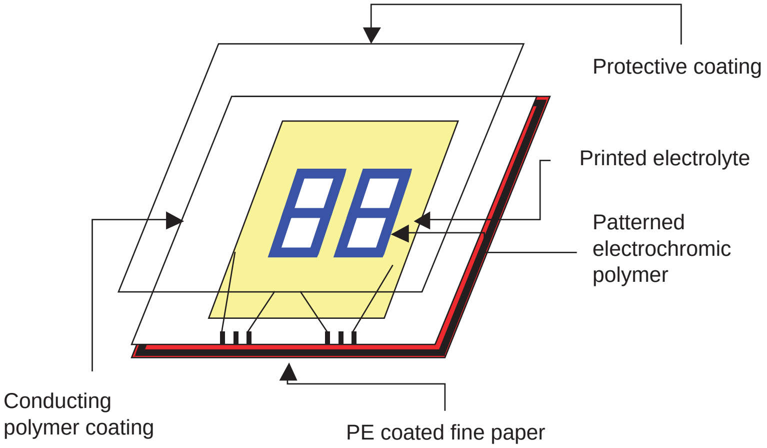


Figure 1.48 Flexible organic electrochromic display element.

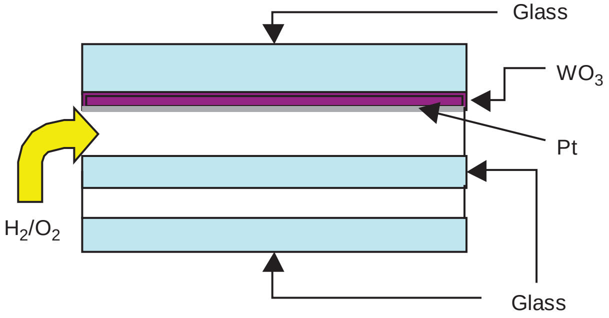


Figure 1.49 Gasochromic integrated glazing unit.

into the WO_3 layer. This causes a change in the optical transmittance through small-polaron transitions just like the electrochromic process.[214] The main applications of gasochromism are in gas sensors and smart windows for glazing.[215]

One of the potential advantages of gasochromic over electrochromic windows is their ease of construction into larger glazing units, since there is only one relatively thin layer of WO_3 on the inside of one of the outer panes of glass in the sandwich of an integrated unit (Figure 1.49). The interspace between two of the glasses is filled with low concentrations of either hydrogen or oxygen in an inert carrier such as nitrogen or argon. If the hydrogen concentration in the interspace is increased the WO_3 film turns blue. The backwards process of achromatisation is obtained by regulating oxygen concentration. A small electrolyser and a pump installed at the window's balustrade control the gas concentration between the glasses.[216]

Although not a gasochromic process by accepted terminology, a closely related topic is that of metal-hydride switchable mirrors. First devised by Griesen in the 1990s, these involve the reaction of a film of rare earth metal alloys with hydrogen gas causing a change from a transparent state to one with high reflectivity.[217] Building on this technology a gasochromic/electrochromic mirror has been designed using transition metal-magnesium alloy films, which are more stable than the original rare earths, and which switch between a highly reflective state and a colour neutral transparent state by reaction with hydrogen. The insulating gas space in a standard integrated glazing unit (IGU) is used to store hydrogen (2% in argon) for switching the active electrode, eliminating the need for a solid ion storage layer, thereby reducing complexity and manufacturing cost of the thin film device, its overall thickness and its optical absorbance.[218]

One of the obvious uses for gasochromism is in the very important area of hydrogen gas sensing. Since the change in the optical transmittance can be measured remotely using optical fibres, the electrical currents that are needed for electrical-conductivity-based sensor technologies are avoided in a potentially dangerous environment.[219] In this application films of electrochromic oxides such WO_3 and V_2O_5 covered with palladium have been employed. Gasochromic sensing has also been applied to a variety of gases such as O_2, H_2S, NO and CO.[220]

Since it encourages the growth of aerobic microorganisms, responsible for the spoilage of food, oxygen is another important gas for sensing, especially in the area of food packaging.[221] One approach to the development of oxygen sensors for this outlet has been the use of colorimetric redox-based indicators. Although not strictly within the current usage of the term *gasochromic*, they do involve a gas in a redox reaction and are therefore included in this section as a broadening of the area of gasochromism.

Colorimetric redox dye-based oxygen indicators involve oxidation of the colourless leuco form of a dye to its highly coloured form. The dye is maintained in its reduced state by the presence of a reductant, usually a reducing sugar in alkali, metal ion (often Fe^{2+}) or ascorbic acid. On ingress of oxygen the leuco form is oxidised to the readily observed parent, coloured chromophore, as shown schematically in Figure 1.50.[221]

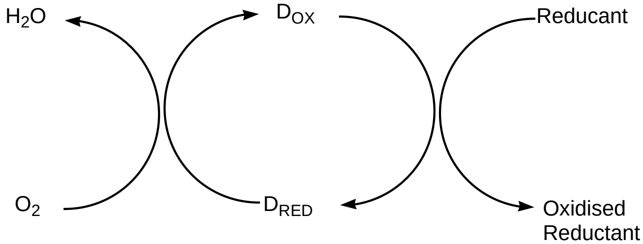


Figure 1.50 Basic process of colorimetric redox dye based indicator.

Mitsubishi Gas Company produces the most commonly employed colorimetric redox dye-based leak indicator used in food, called Ageless Eye™, as part of their Ageless™ range of oxygen scavengers for use in food containers. Ageless Eye™ comprises a redox dye, probably Methylene Blue, and a strong reducing agent, such as glucose in an alkaline medium, but the product is said to contain metal, probably iron, salts. The device also contains a red dye (CI Acid Red 52) so that the background remains pink and visible whilst the dye is in the reduced state.[222,223] Ageless Eye™, which is available in either tablet or laminated sheet form, can be used to test for oxygen depletion during sealing (pink state), or oxygen ingress to a damaged package on storage (blue state). Their cost and need to be stored under anaerobic conditions has limited their general use in the food-packaging industry.

One way of overcoming these difficulties is to use a colorimetric redox dye-based oxygen indicator that only operates after being activated by light, and which can therefore be stored in an aerobic environment, provided it is dark, prior to use. Indicators of this type use a sacrificial electron donor to react with a dye in its photoexcited state, producing its leuco form, which only reverts to the coloured form on exposure to oxygen. A good example is one which uses riboflavin (sensitiser dye) and EDTA (sacrificial electron donor), encapsulated in gelatin and coated on paper to give an orange-coloured indicator. Upon UV/Vis irradiation the film is bleached, provided no oxygen is present, and recovers its initial colour only upon exposure to oxygen.[224]

However, such oxygen indicators respond to visible light and are not suitable for use in the real environment of a supermarket shelf or food cabinet. A practical device would be one that was only activated by UV light like the ink recently described by Mills and co-workers.[221,225] This ink comprises a UV-absorbing semi-conductor photosensitiser (TiO_2), an appropriate redox indicator (Methylene Blue, suitably ion-paired for solvent solubility), a mild reducing agent (triethanolamine or glycerol) as the sacrificial electron donor (SED) and a polymer-encapsulating material (*e.g.* hydroxyethylcellulose). The ink can be printed onto a range of substrates such as glass, paper, plastic and metal foil.[226] The mechanism proposed for this oxygen indicator is as follows. Upon UV-excitation of the nanocrystalline TiO_2 semi-conductor (SC) powder particles encapsulated in the polymer film, electron–hole pairs are generated. The photogenerated holes are able to oxidise readily and irreversibly the SED present, leaving the photogenerated electrons to accumulate on the semi-conductor particles [SC(e)]. These electrons reduce the highly coloured redox indicator (D_{ox}) to its usually bleached form (D_{red}). This latter species is only oxidised back to D_{ox} when it encounters oxygen as illustrated in Figure 1.51.[221]

The big advantage of this type of indicator is that it is inactive until initiated by a burst of UV light and hence does not need to be stored under anaerobic conditions. Additionally, once it has responded to the presence of oxygen and returned to its readily detected coloured form, this persists regardless of any subsequent changes in the oxygen level. It can only be made to function again as an oxygen indicator if it is reactivated upon exposure to another burst of UVA light.

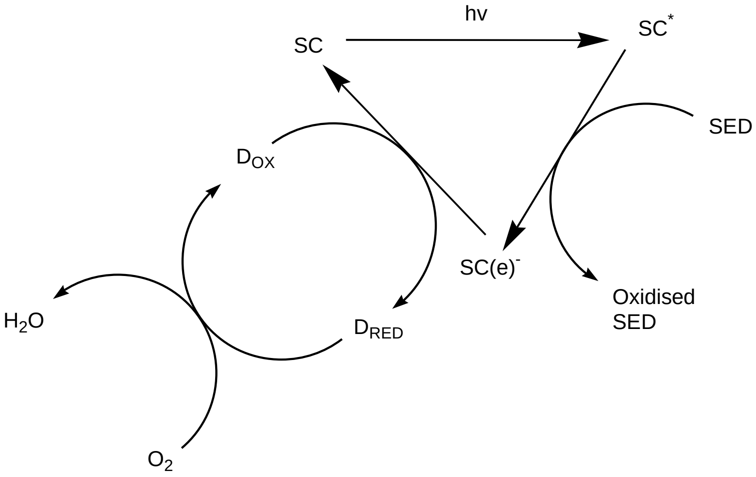


Figure 1.51 Schematic illustration of the basic processes associated with a UV activated oxygen indicator.[221]

1.7 Solvatochromism

Solvatochromism can be defined as the phenomenon whereby a compound changes colour, by a change in either its absorption or emission spectra, when dissolved in different solvents. It is one of the oldest of the chromisms, having been described as long ago as 1878, but nowadays it is usual to extend the concept of the "solvent" to include gels, micelles, polymers and films, as well as various surfaces. The theoretical aspects of solvatochromism have been covered in detail in books and reviews, and consequently in this section will be dealt with only briefly before moving onto practical applications.[227] Interaction with a solvent resulting in a change in emission spectrum is also known as "solvatofluorochromism" (Section 1.7.2.3 and Chapter 3). When the spectrum of a compound changes on increasing the rigidity of the medium, usually when fluid solutions are frozen to form rigid glasses, the effect is known as "rigidochromism". This is usually encountered as a luminescence phenomenon, particularly associated with transition metal carbonyl complexes, and it will be covered in Chapter 3 (Section 3.5.11.3).

1.7.1 Solvent Polarity and Solvatochromic Shifts

In solvatochromism, the observed shifts in the maxima of the absorption or emission spectra of molecules in solution are due to differences in the solvation energies of the ground (E^0_s) and excited (E^1_s) states as the nature of the solvent is varied, as shown in Figure 1.52. The "solvent property" of Figure 1.52 is usually a measure of solvent "polarity". Unfortunately "polarity" is an ill-defined property, and can reflect one or more of a number of physical

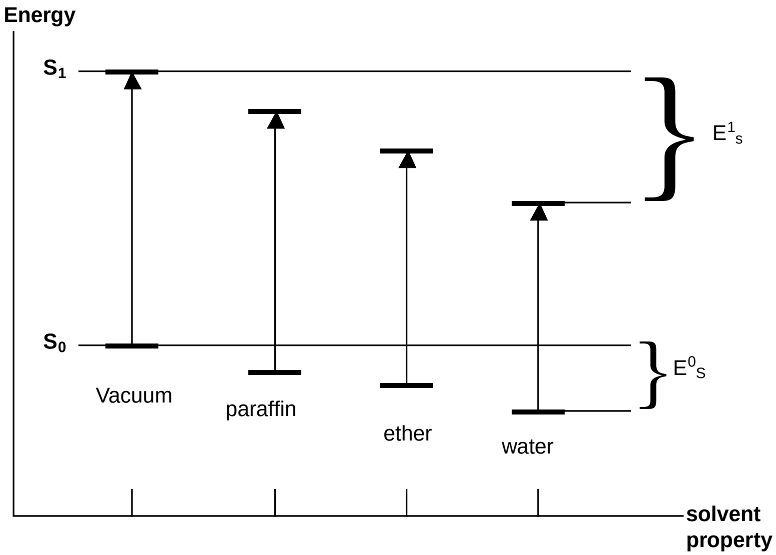
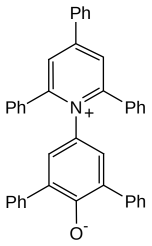


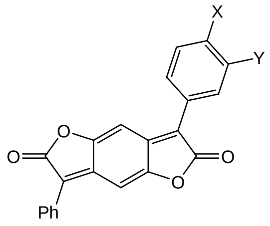
Figure 1.52 Simplified energy diagram of solvatochromic shift.

phenomena such as solvent dipolarity, polarisability, H-bonding properties, Lewis acidity/basicity *etc*. Each of these effects can influence the energetics of both ground and excited states but to different degrees depending on the chromophoric solute under study. In Figure 1.52 an increase in solvent "polarity" will be recognised from left to right across the four media indicated. Two general solvatochromic trends with "polarity" are frequently observed:

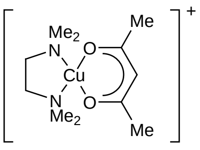
- When the excited state is more polar than the ground state, more polar solvents favour its stabilisation. There is a decrease in transition energy and a bathochromic shift in the spectrum (positive solvatochromism, as shown in Figure 1.52);
- Conversely, a more polar ground state leads to the opposite effect and a hypsochromic shift in the spectrum (negative solvatochromism).



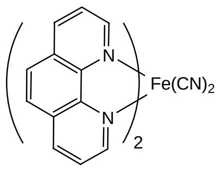
(1.90)



(1.91a) X = NH_2 Y = Me
(1.91b) X = OMe Y = H



(1.92)



(1.93)

The variations in the absorption energies of various dyes have been used to characterise various media and create empirical solvatochromic scales of "polarity". For example, a widely used dye is the highly negatively solvatochromic betaine (1.90), often known as Reichardt's dye, whose transition energy $E_T(30)$ in kcal mol ^{1}, measured in a particular solvent, characterises the polarity of that solvent as illustrated for two extreme cases in Figure 1.53.

The $E_T(30)$ scale in fact reflects a particular and by no means general blend of solvent dipolarity and H-bond donor ability. Other solvatochromic probes and their derived polarity scales reflect different combinations of intermolecular interactions between solvent and solute. To reflect this complexity multiparameter treatments have been devised.[227] These can be used to analyse complicated solvatochromic behaviour as for example in the highly solvatochromic benzdifuranone dye (1.91a), which is influenced by solvent dipolarity (increase leads to red-shift), solvent H-bond acceptor ability (red-shift) and solvent H-bond donor ability (blue-shift).[228]

However, descriptions of solvatochromism become even more complex once it is recognised that solvatochromism can be caused by simple dispersion effects alone, resulting from solvent polarisability, where "polarity" in any conventional sense ceases to be the cause of solute colour change. Examples of such behaviour include essentially non-polar polyenes (*e.g.* Ph-$(CH = CH)_n$-Ph)[229(a)] and less obviously the benzdifuranone (1.91b).[229(b)] When polarisability becomes the sole or dominant physical cause of solute solvatochromism, the expressions "positive" and "negative" solvatochromism lose their meanings. For example the dye (1.91b) shows a red-shift from acetonitrile to cyclohexane

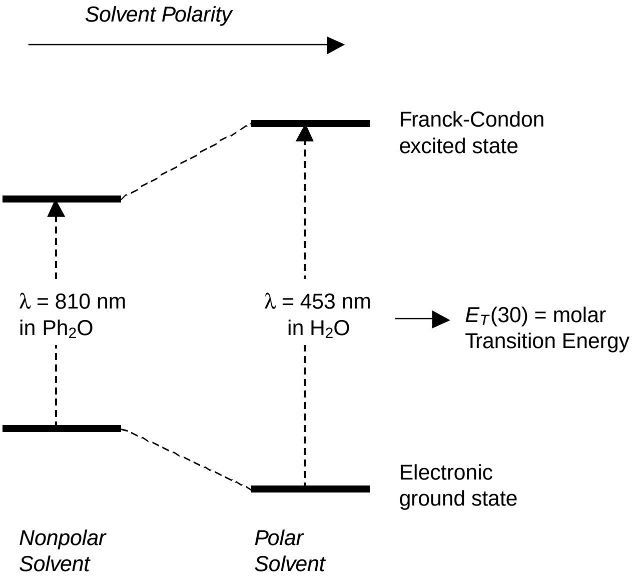


Figure 1.53 Schematic of derivation of $E_T(30)$ values of betaine dye.

(conventionally negative solvatochromism), and another red-shift on moving from cyclohexane to DMSO (conventionally positive solvatochromism). All polarity scales place cyclohexane as the least polar solvent of these three, followed by acetonitrile (medium polarity), then DMSO (highly polar). So is dye (1.91b) "positively" or "negatively" solvatochromic?

While this discussion may appear somewhat academic and abstruse, it is important to recognise the complexity of the causes of solvatochromism and understand the resultant effects on different indicator dyes, since the latter are used as analytical probes in the investigation of various substrate properties as discussed in the next sections. If the solvatochromic behaviour of the indicators is not fully understood, interpretation of solvatochromic data in unknown situations must be equally ill-defined.

Whilst very many organic chromophores exhibit solvatochromism it also occurs widely in coloured transition-metal complexes.[230] These can be used as solvatochromic Lewis acid and Lewis base indicators, exemplified by the four-coordinate copper-based Lewis base indicator (1.92) and the six-coordinate iron-based Lewis acid indicator (1.93). The interaction of metal complexes with solvents is proving a useful mechanism for devising vapochromic sensors as discussed in Section 1.8.

1.7.2 Applications of Solvatochromism

For decades solvatochromism has been a phenomenon without any great technical importance in commercial applications, being used largely to characterise solvents or to understand the excitation behaviour of chromogenic solutes including commercial azo dye models.[231] However, since the 1990s there has been a rapid growth in the use of optical probes and sensors, an area where solvatochromic effects now play an important role, and this has led to a renewed interest and expansion in research on solvatochromism.

1.7.2.1 Analysis of Liquids

An obvious application of solvatochromism is the measurement of concentrations of small amounts of polar molecules in non-polar environments *e.g.* methanol in naphtha. Fuel oil is a key market, as the various fractions are often "marked" with solvent dyes to ease their identification for tax purposes *e.g.* red diesel in the UK (see Chapter 2, Section 2.5), but not for adulteration.

With the rapid increase in the use of alcohols as fuels, both on their own and in admixture with gasoline, it has been necessary to have a rapid means of measuring their quality. A derivative of the betaine dye (1.90) is very soluble in gasoline–ethanol mixtures with strong preferential solvation by ethanol in all mixtures. Solutions in gasoline are blue–green, violet in ethanol and green–blue in gasoline with 25% of ethanol. These colour changes allow the naked-eye detection of the presence of ethanol in gasoline and the development of an analytical method for the determination of the quality of the fuels.[232]

In the food and drink industries solvatochromic analysis is employed in evaluating oil-based spreads such as margarine, in cooking oils and in wines and other alcoholic and non-alcoholic drinks.

1.7.2.2 Polymers and Polymer-bound Probes

Solvatochromic probes have found applications in polymer characterisation, where they can be used to look for localised polar features at the molecular level. Two distinct approaches can be adopted, where the chromophore can be part of the polymer of the chain, or the chromophore can be dissolved in a solvent and then this solution used to penetrate the polymer matrix. In the first case, the environment is fixed and so the probe is unable to choose a preferred site for its colour change, but can give information on chain orientation *etc.* In the second, the probe is mobile and will seek out the most favourable site over a period of time, enabling areas of differing polarity within the polymer to be identified.

Incorporation of solvatochromic dyes in polymers is also used to construct commercially useful polymer bound sensors. When coupled with fibre optics, these offer a safe way of examining flammable solvents for their composition and levels of liquid impurities. For example, dissolving the probe dye in PMM and spin coating the solution to give a film on a sensor tip provides a suitable product.

Solvatochromic dyes have also been used for the determination of the surface polarity of zeolite cages of solid poly(α-amino acids), as well as of native polysaccharides (cellulose, glycogen, amylopectin, amylose, starch, *etc.*) and various cellulose ester derivatives. When solvatochromism is used to characterise empirically the surface properties of moderately strong solid acids, including silicas, aluminas, and aluminosilicates, the chromic phenomenon has been called "sorptiochromism".[233]

1.7.2.3 Biological Probes and Solvatofluorochromism

The use of fluorescent dyes in biological probes and sensors is covered in some detail in Chapter 3 (Section 3.5.9). Because there are marked solvatochromic effects on the luminescence spectra of many fluorophores, this phenomenon is utilised to tune their performance and application in biological and other systems. Examples of its use include protein and nucleic acid detection, enzyme-labelled fluorescence, in the intrinsic fluorescence of normal and cancer cells, as external fluorescence probes of binding sites, as solvatochromic indicators, probes for serum albumin and in looking at the environment of the visual pigments.[234]

1.8 Vapochromism

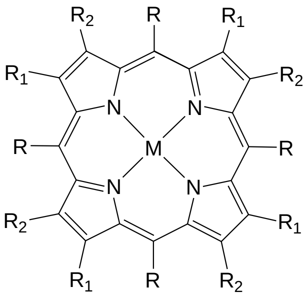
Vapochromic systems are those where dyes change colour, often reversibly, in response to a vapour or an aroma of an organic compound or gas, and there is clearly a strong overlap with solvatochromism. Systems based on this principle can be considered as belonging to the optical branch of the family of "electronic nose" devices.[235]

1.8.1 Vapochromic Materials

The vapochromic behaviour of double salts of arylisocyanide complexes of palladium and platinum, for example $[Pt(CNAr)_4]$ $[Pd(CN)_4]$, in the solid state has been known for some time.[236] But it is only in the last ten years that practical vapour sensing applications have been developed based on this phenomenon. This has led to the discovery of a range of complex salts, mixed and otherwise, reacting colorimetrically with a variety of solvent vapours. The colour change can be reversed in most cases by removal of the vapour atmosphere or more completely by heating, sometimes under vacuum. The mixed complexes finding most favour are those based on platinum, palladium, gold or silver and a selection from the more recent literature is given in Table 1.19.

The specific mechanism for the vapochromic behaviour of these complexes is different for each case, but since they are all solid-state reactions then changes in the crystal lattice on interaction with the solvent molecules are probably involved.[237] For instance, X-ray powder diffraction identified the $Pt(CN\text{-}p\text{-}(Et)C_6H_4)_2(CN)_2$, $Pt(CN\text{-}p\text{-}(Et)C_6H_4)_2(CN)_2 \cdot 0.25$(toluene) and $Pt(CN\text{-}p\text{-}(Et)C_6H_4)_2(CN)_2 \cdot 0.5$(toluene) phases and showed that the sorption of toluene is accompanied by small changes in the unit cell dimensions that include lengthening the Pt ... Pt distances in the structure.[239] The linear-chain polymer $\{Tl[Au(C_6Cl_5)_2]\}_n$ on exposure to vapours such as tetrahydrofuran, acetone, tetrahydrothiophene, 2-fluoropyridine, acetonitrile, acetylacetone and pyridine (VOCs) produces a selective and reversible change in its colour that is perceptible to the human eye. In this case the products formed appear to be intermediate between complex with no VOCs attached and ones in which two organic ligands are coordinated to each thallium.[244]

Vast arrays of metalloporphyrins (1.94; Figure 1.54) exist with many metals acting as the central core and innumerable substituents on the periphery (R_1 and R_2) and meso positions (R). Mechanisms of interaction that can be exploited for vapour sensing are the same as in solvatochromism, and include hydrogen bonding, polarisation and polarity, as well as colour changes due to Lewis acid–base interactions with the central metal atom.[245] Metalloporphyrins are considered to be good models for mammalian olfactory receptors, which have been shown to involve metalloproteins.[246]



(1.94)

Table 1.19 Vapochromic metal complexes.

Complex	*Solvents*	*Reference*
[Pt(CN i Pr)$_4$] [Pd(CN)$_4$]	H_2O, $CHCl_3$, MeOH, CF_3CH_2OH	237
[Pt(CN cyclododecyl)$_4$] [Pt(CN)$_4$]	H_2O	238
Pt(CN p (Et)$C_6H_4)_2(CN)_2$	Aromatic hydrocarbons	239
[Pt(Me$_2$bzimpy)Cl]X	X = Cl; $CHCl_3$, MeOH, MeCN X = PF_6; MeCN (specific)	240, 241
[Pt(tpppb)Cl]Cl	CH_2Cl_2, EtOH, $MeCO_2Et$, MeCN	242
[$Au_2Ag(Ph)_4L_2$]	Me_2CO, MeOH, EtOH	243

Notes.
Me$_2$bzimpy 2,6 bis(*N* methylbenzimidazol 2 yl)pyridine
tpppb 1 terpyridyl 2,3,4,5,6 pentaphenyl benzene.

In one example different metallo-meso-tetraphenylporphyrins (1.94; R = phenyl; M = Sn, Co, Cr, Mn, Fe, Cu, Zn) reacted colorimetrically with a wide variety of solvent vapours. Using these metalloporphyrins it was possible to construct a four-colour array for the visual identification of a wide range of vapours, both ligating (alcohols, amines, ethers, phosphines, phosphites, thioethers and thiols) and even weakly ligating (arenes, halocarbons and ketones).[247,248]

Vapochromism is also observed in some ionic dyes when changes in the dye aggregation states are induced by interaction with vapours (see also Section 1.10). Extensive and vapour-specific colour changes due to this effect were observed in solid thin films of sugar gels containing cationic dyes, such as flavylium and thionine salts, upon exposure to VOCs such as methanol, ethanol, acetone, benzene, ether and pyridine.[249]

1.8.2 Vapochromic Sensors for VOCs and Their Applications

The main applications of vapochromic materials are in sensors for detecting volatile organic compounds in a variety of environments, including industrial, domestic and medical areas.[250] Examples include optical fibre sensors based on vapochromic gold complexes,[251] and on cobalt complexes,[252] and colorimetric sensor arrays for molecular recognition and as opto-electronic noses.[253 255]

An excellent example of the use of colorimetric dyes and indicators is provided by the multi-component array devised by Suslick and his co-workers.[256] The dyes used to construct a 6×6 array were drawn from the following: (1) Lewis acid/base dyes (*i.e.* metal ion-containing dyes), (2) Brønsted acidic or basic dyes (*i.e.* pH indicators) and (3) dyes with large permanent dipoles (*i.e.* zwitterionic solvatochromic dyes). The array, illustrated in Figure 1.54, is in the form of a disposable cartridge that can be readily imaged with a flat-bed scanner and the image compared with a library of 100 VOCs.

An interesting recent use of such arrays is in the analysis of the pattern of VOCs in the exhaled breath of patients with lung cancer, which may be unique to the disease. The sensor array did indeed detect a unique pattern of VOCs in

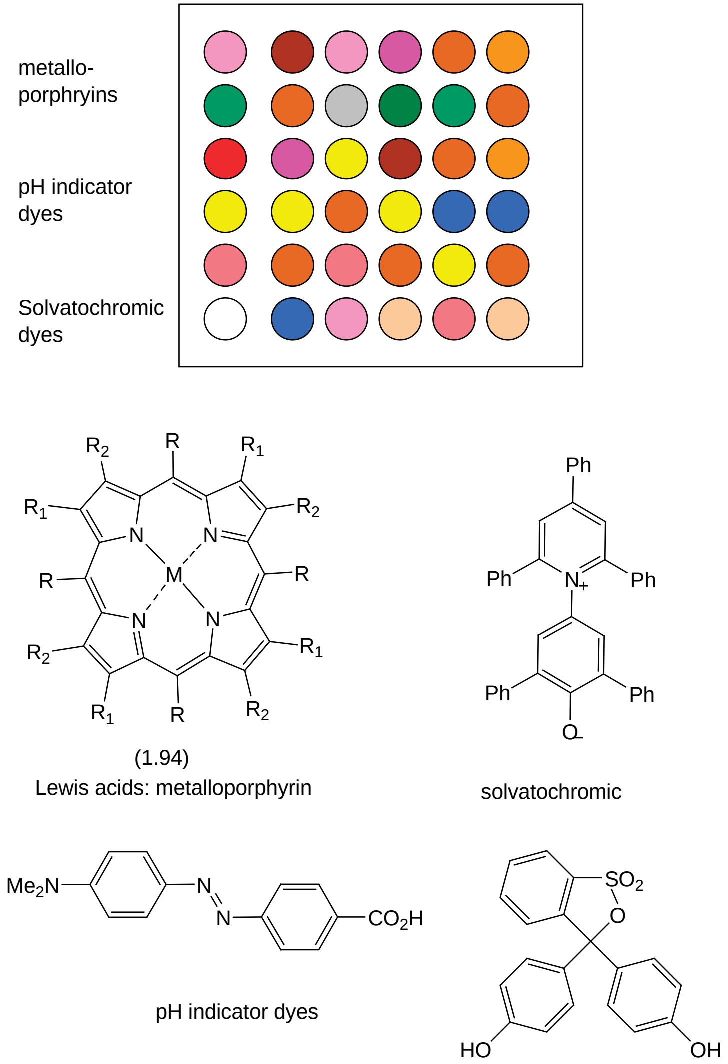


Figure 1.54 Colorimetric sensor array for VOCs.

the breath of patients with moderate accuracy. Further work was required to clarify the nature of the distinct breath constituents but the researchers considered this line of investigation could lead to an inexpensive, non-invasive screening or diagnostic test for lung cancer.[257] Explosives are another important area where vapours of nitrotoluenes, H_2O_2 and acetone need to be sensed quickly and on the spot. Most of the methods devised for colorimetric sensing of these vapours involve fluorescence and hence this aspect will be covered in Chapter 3.

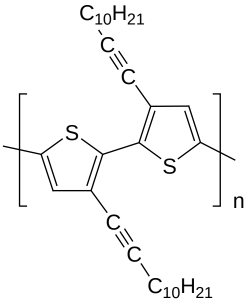
1.9 Mechanochromism

Chemicals can be put under stress in the solid state by mechanical grinding, crushing and milling; by friction and rubbing; or in the solid or solution state by high pressure or sonification. The change of colour under such mechanical actions is called mechanochromism. Pressure-induced colour change is known as piezochromism, and when grinding or attrition is the stimulus the phenomenon is tribochromism.[258] Light emission under these conditions is called triboluminescence (Chapter 3, Section 3.10). The literature is often confusing as the generic term mechanochromic is applied when the effect could be clearly called piezochromic or tribochromic. Additionally, materials used in pressure copying papers have been described, incorrectly as defined in this book, as piezochromic (Section 1.4.2.3). Barochromism is normally reserved for pressure-induced spectroscopic shifts, especially in the study of naturally occurring minerals.[259] On a few occasions the term sonochromism has been used when the colour change occurs under high-energy sonification.[260]

1.9.1 Piezochromism

Piezochromic changes in the colour of a solid can occur by three general mechanisms:[261]

- Perturbation of the ground and excited states by pressure and compression;
- First-order phase transition from one crystal structure to another;
- Change in the molecular geometry of the species that comprise the solid.



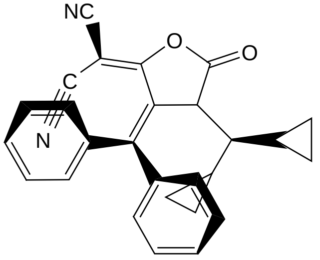
(1.95)

Polymeric materials exhibiting piezochromic behaviour include conjugated systems, such as polydiacetylenes,[262] polythiophenes[263] and polysilanes. For instance, a thin film of poly(3-dodecylthiophene), which is non-planar at high temperatures with absorption maximum at 420 nm, undergoes a bathochromic shift as the pressure is increased, reaching a maximum absorption of 520 nm at 8 kbar. The shift in wavelength is thought to be due to an increase in the length of conjugation in the chain as the packing is improved, reversing conformational changes which occur on heating.[262 264] An even longer wavelength shift is observed with (poly(3-(1-dodecynyl)thiophene)) (1.95) when the change is from 562 nm to 672 nm under 10 kbar pressure.[265]

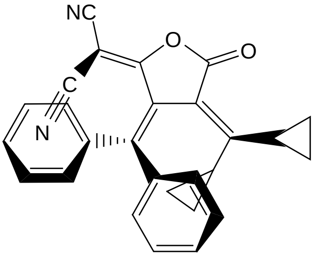
Piezochromism in square planar palladium metal complexes has been reviewed, where very high pressures, 60–100 kbar, are required to cause a red-shift.[266]

1.9.2 Tribochromism

Tribochromism is exhibited when crystalline compounds give a more highly coloured state when they are ground (see also triboluminescence in Chapter 3, Section 3.9). If the compounds crystallise in a metastable state then the colour change is irreversible, as exemplified by the case of the fulgide (1.96). The folded metastable form (1.96a) is bright yellow in its crystalline state, but turns to a dark-red colour on grinding due to the formation of the stable twisted form (1.96b).[267]



(1.96a)
yellow: folded metastable



(1.96b)
red: twisted stable

Tribochromism is also experienced in certain spiropyrans, spirooxazines, and thioindigos.[268]

1.9.3 Applications of Mechanochromism

The literature contains many references to the potential practical uses of mechanochromic effects, especially piezochromism, but to date there appear to be very few commercial applications. Patents have been filed on the use of both piezochromic and tribochromic materials in inks and papers for security outlets, in cosmetic applications, as stress and crack indicators in engineering and as pressure-sensitive paints for aerodynamic flow modelling.[269] More recently mechanochromic properties have been observed in polydiacetylene nanotubes, encapsulated colloidal crystals and ordered colloids.[270,271] These photonic materials have potential uses as sensors and indicators, an area covered in Chapter 5 (Section 5.3.5.1).

1.10 Chromic Phenomena *via* Aggregation

As more-or-less planar molecules, many dyes are frequently prone to attractive face-to-face interactions with one another, leading to the formation of dimers and higher aggregates. The degree of aggregation is influenced not only by the molecular structure of the dye, but also by physical and chemical effects such as concentration, temperature, solvent, neutral or ionic additives, and so on. Resultant electronic interactions between the aggregated chromophores can lead to colour change phenomena, which can be intrinsic properties of the dye, or reflect the external influences or stimuli. This section provides background to the main effects encountered, followed by some applications. It also serves as an introduction to later chapters where chromophore aggregation and interaction is an important factor in observed applications. Furthermore, aggregation effects will be shown to be contributing factors to some of what can be called indirect chromisms already described elsewhere in this chapter.

1.10.1 Excitonic Coupling

The way in which two chromophores interact on photoexcitation has been explained by exciton theory. A simple and idealised explanation of the main effect relies on dipole interactions. When the two chromophores are aligned with their transition dipoles parallel, the transition dipoles interact with resultant energy splitting depending on their relative orientation, as depicted in Figure 1.55. When they are fully face-to-face and parallel (Figure 1.55 left), the in-phase transition dipole combination is destabilising (nearest neighbour +ve aligned with +ve and −ve aligned with −ve), and is of higher energy than the out of phase combination (two stabilising nearest neighbour +ve/−ve adjacencies). In contrast, when one chromophore is "slipped" with respect to the other, to give a head-to-tail arrangement as on the right of Figure 1.55, the in-phase combination becomes lower in energy than the out-of-phase (one stabilising nearest

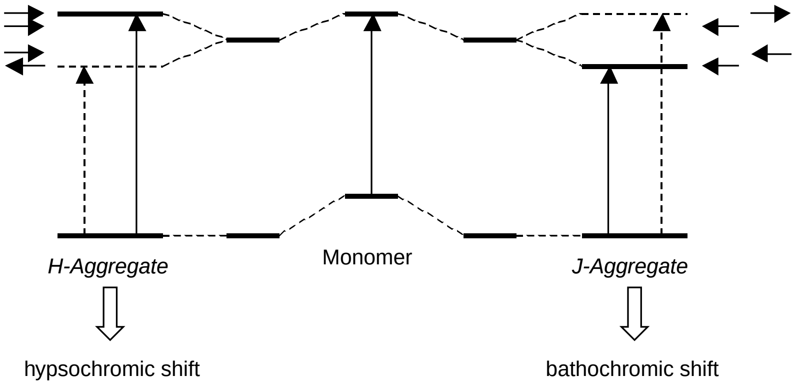


Figure 1.55 Relationship between orientation of chromophores and spectral shifts based upon exciton theory.

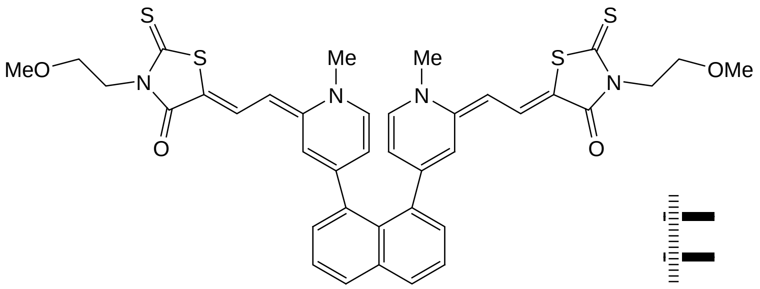
neighbour +/− interaction as opposed to one repulsive like/like interaction). There are thus two theoretical transitions for each of the two dimer arrangements. In practice, quantum mechanical selection rules state that only transition to the in-phase energy level is allowed, while the other is forbidden. Thus a fully face-to-face arrangement, left, will display a hypsochromic shift relative to the monomer, while the head-to-tail arrangement, right, will have a bathochromic shift. The parallel face-to-face arrangement is known as an H-dimer, or more generally H-aggregate for more extensive combinations ("pile of coins"). The head-to-tail arrangement is known as a J-dimer or J-aggregate.

As less idealised chromophore–chromophore arrangements are encountered, both transitions resulting from excitonic coupling may become allowed, so that double absorbances are observed. Their energy separation is known as the Davydov splitting. Chromophore–chromophore interaction can also lead to hyper- or hypochromic effects (higher or lower absorbance, respectively), and emission properties can either be quenched or enhanced.[272]

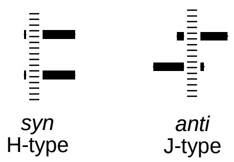
1.10.2 Examples of Excitonic Coupling Effects Aggregachromism

Aggregachromism – one of the less attractive chromism terms – is applied to colour effects which arise from dimerisation and aggregation of chromophores.

The bimerocyanine dual chromophore based on a peri-disubstituted naphthalene (1.97) is a good example of a dye which can exist in both H- and J-dimer forms.[273] It is able to adopt *syn* and *anti* conformations, shown diagrammatically in a plan view. In the former the two merocyanine chromophores are more or less eclipsing one another as in an H-dimer arrangement, and the absorption maximum is at 516 nm (acetonitrile). In the *anti* conformation they are arranged head-to-tail as in a J-dimer, with a bathochromically shifted absorption at 568 nm (chloroform). The proportion of *syn* and *anti* conformers in solution is solvent dependent, so that with different solvents different absorbances and thus different colours are observed. This solvatochromism is not solely due to the conventional influence of solvent on the chromophores (Section 1.7), but is an example of an indirect solvatochromic effect.



(1.97)



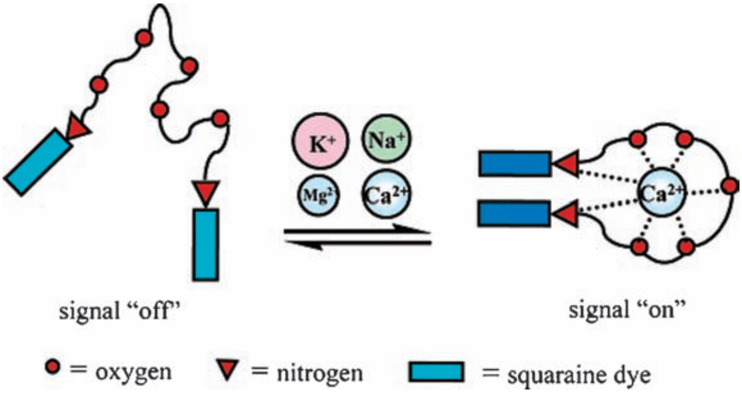
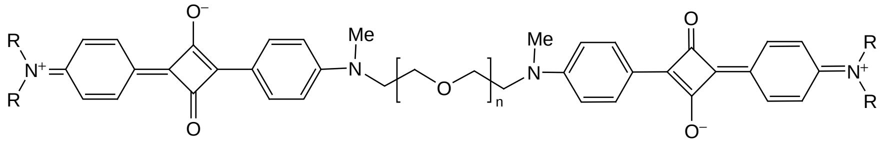


Figure 1.56 Schematic representation of squaraine based chemosensor which oper ates *via* a cation driven exciton interaction in a dye linked podand (reproduced with permission of the American Chemical Society).

The colour change effects resulting from chromophore dimerisation can be used in probes. The bichromophoric squaraine foldamers (1.98) are able to coordinate metal ions *via* their linking ether chains. Metal coordination results in folding of the molecule, bringing the two squaraine chromophores into H-dimer-type overlap (Figure 1.56). In this conformation the bright greenish-blue colour of the non-interacting chromophores is attenuated to a deep-reddish blue. The molecule (1.98e) with n = 5 and R = Me is specific for Ca^{2+} amongst a variety of other group 1 and 2 ions.[274] The fluorescence of foldamers of this general type is affected more sensitively than absorbance, and foldamers are thus more useful sensors in emission mode (Chapter 3).

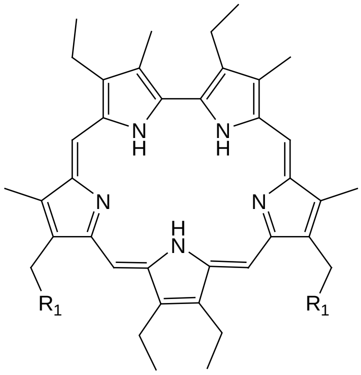


(1.98)

a; n = 1, R = Bu
b; n = 2, R = Bu
c; n = 3, R = Bu

d; n = 4, R = Me
e; n = 5, R = Me
f; n = 6, R = Me

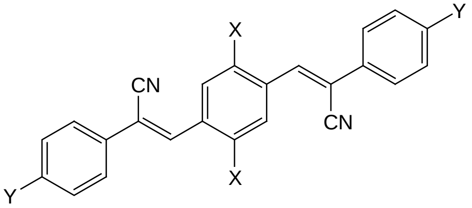
Anion sensing is also possible (see also Section 1.4.1.6). In the case of the sapphyrin (1.99) the mechanism of operation is reversed. In the non-detecting state, the sapphyrin exists as an H-aggregate with absorption at 410 nm in water at pH 7. In the presence of biologically interesting nucleotide anions the aggregate is broken as phosphate anion centres interact with the sapphyrin, and the absorption reverts to that of the monomolecular form at 422 nm. Again for anions, fluorescence is a more sensitive detection mechanism.[150]



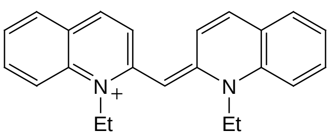
R1 = $CH_2CON(CH_2CH_2OH)_2$

(1.99)

Various applications of colour changes associated with aggregation-disaggregation of polymer-hosted oligo(*p*-phenylene vinylene)s (1.100 and 1.101) have been described. After annealing in the polymer the dyes are J-aggregated and appear orange. Exposure of a film of the dye in polymer to mechanical stress by stretching perturbs the aggregate, and results in colour change to the pale yellow of monomeric dye. This can be regarded as an example of *indirect mechanochromism* (see Section 1.9). Films based on different host polymers have been proposed as temperature and humidity sensors, with detection by colour change or fluorescence.[275] This series of papers was the first to introduce the term "aggregachromism".



(1.100) X = Me Y = $C_{18}H_{37}O$
(1.101) X = C_8H_{17} Y = 4 $EtOC_6H_4$ CH=CH



(1.102)

Historically, the discovery of J-aggregates originated from a study of cyanine dyes in their important commercial application as sensors of silver halides in the conventional photographic process (Chapter 2). Cyanine aggregation on the silver halide surface results in a very marked bathochromic shift and remarkable and characteristic absorption peak sharpening. Aggregation can also be induced in solution or in other phases.[276,277] Despite its long history, the spectroscopy of cyanine aggregation remains a vibrant field with applications beyond photography, including solar energy conversion and photoconductivity (both Chapter 4). Amongst the thousands of known cyanines and related dyes, pseudoisocyanine (PIC) (1.102) has been, and remains, central to studies of the absorption properties of J-aggregates,[278] and even now its properties remain a topic of controversy. For example, a recent paper continues to dispute the nature and properties of the PIC monomer.[279] Because of its non-planarity and packing pattern in the aggregate (“brickstone” model), films of PIC and related cyanines in herringbone aggregates can appear different colours under orthogonally polarised light (*dichroism*).[280]

PIC and other cyanine and merocyanine dyes in aqueous solution are aggregated under the influence of ionic additives such as salt, and it has traditionally been assumed that salt inevitably brings about dye aggregation of ionic chromophores with attendant optical effects. However, a careful study and analysis of solutions of sulfonated copper phthalocyanine (CuPc), another chromophore very prone to aggregate in water, has surprisingly revealed that salt has the opposite effect on the degree of its aggregation (see Chapter 2).[281] H-type aggregation is responsible for the typical hypsochromic shoulders on the main major visible absorption band of CuPc above 600 nm.

Perylene bisimide (PBI) (1.103) is an interesting chromophore with various applications dependent on both its absorption and emission properties. Solubilised PBI usually exists as hypsochromically shifted H-aggregates. However,

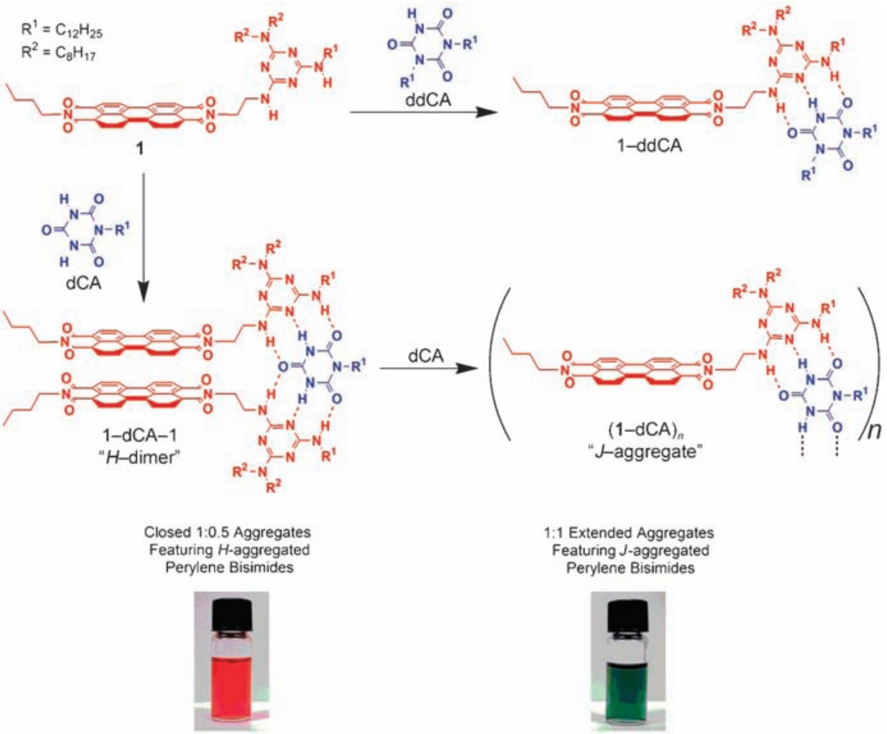
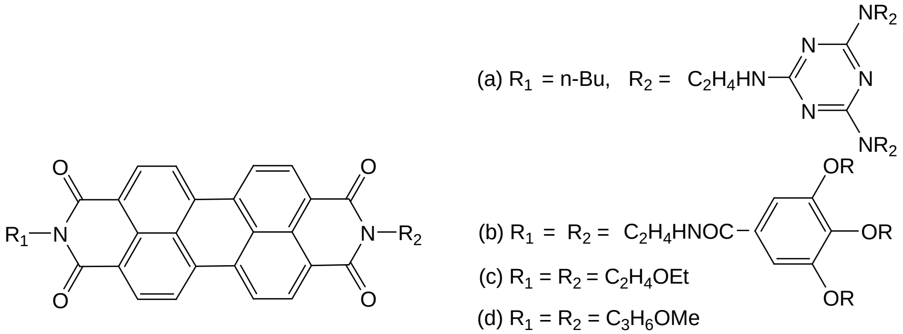


Figure 1.57 H dimers and J aggregates in functionalised perylene bisimides[282] (reproduced with permission of Wiley VCH).

a novel series of effects on the functionalised PBI (1.103a), brought about by differing proportions of a hydrogen-bonding additive, become visually apparent because of the formation of H-dimers or J-aggregates, which are remarkably differentiated by their red and green colours, respectively (see Figure 1.57). Heating and cooling leads to J/H interconversion with resultant colour changes, all reversible (indirect thermochromism).

Scratching of films of the J-aggregates converts the green form to red (indirect piezochromism), which can be reversed by thermal annealing.[282] A similar effect has been observed in gels where a suitably functionalised PBI (1.103b) in a wide range of solvents results in the formation of black gels. The PBI forms J-aggregates with absorption across the visible spectrum.[283]



(1.103)

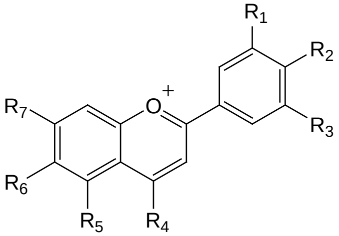
1.10.3 Crystallochromism

Crystal formation can be viewed as the limiting case of aggregation, where solvent has been eliminated and effectively all solute molecules become co-aggregated. Crystal packing is subtly influenced by small changes in molecular structure and is notoriously difficult to predict. The minor changes in molecular constitution of dyes can cause different stacking patterns in their crystals, which can result in significantly different chromophore interaction and thus excitonic coupling and observed colour. *Crystallochromism* is the term applied to drastic colour variations in the crystal (pigment) caused by minor structural modifications of the monomeric dye. As already discussed in the last section, PBI molecules are uniformly red in solution in the absence of special effects. But very minor changes in PBI molecular structure give very differently coloured pigments as exemplified by the three PBI derivatives (1.103c, d and e). The ethoxyethyl-substituted PBI (1.103c) is red, with PBI units H-aggregated face-to-face. Its methoxypropyl isomer (1.103d) resulting from a shift of the ether oxygen atom by just one position along the substituent chain gives a black J-aggregated pigment, where the stacked PBI molecules have been side-slipped by a small amount. If the PBI of (1.103d) is then homologated by one carbon to give ethoxypropyl PBI (1.103e), the pigment colour reverts to red.[284] A straightforward molecular orbital explanation of this crystallochromic phenomenon has appeared.[285] Crystallochromism is also demonstrated by other commercially important pigments such as diketo-pyrrolopyrroles and copper phthalocyanine and are described more fully in Chapter 2.

1.10.4 Excitonic Effects in Nature

Chromophore aggregation and interaction are central to solar energy collection in natural photosynthesis by plants, and underpins much of the current work on the design and synthesis of artificial solar energy devices. This topic is covered in Chapter 4.

The well-known anthocyanin pigments (1.104) responsible for the red, purple and blue coloration of many flowers aggregate with flavonoid chromophores in the flower in complex cyclic arrays.[286] This aggregation, in combination with the nature of the metal counter-ion and degree of ionisation resulting from pH (indirect ionochromism), determines the actual colour observed. The origins of this ionochromic response for aggregation changes has been elucidated in the Japanese morning glory, *Ipomoea nil*, whose reddish purple buds unfurl to give blue open flowers. This colour change is due to a rise in pH in the vacuole, the cellular compartment of the bud containing the anthocyanin pigments. The increases in the vacuolar pH are achieved *via* InNhxi, the protein product of the *Purple* gene. InNhxi controls the flow of Na^+ and H^+, increasing the vacuolar pH in the flower epidermis from 6.6 to 7.7, at which pH the main anthocyanin pigment turns blue.[287] Because the anthocyanin is substituted by a homochiral carbohydrate unit, the aggregate itself is homochiral, and reflected light is circularly polarised (chirochromism). It has been proposed that the resultant chiroptical effect may be detected by insects and contribute to their response to the flower.[288]



(1.104)

The same chromophore and derivatives contribute to the red and purple colours of various berries, including red grapes. In this case it is believed that co-aggregation ("co-pigmentation") with flavonoids affects the colour of derived red wine and, particularly, the intensity of absorption of the pigment. In analysing the anthocyanin content of the wine, of commercial importance to the vintner, knowledge of the absorption properties of the co-aggregate are important.[289]

We conclude this section with an icon of colour change phenomena – the effect of cooking on the colour of lobster. The live lobster *Homarus gammarus* commonly used in gastronomy is a dull slate-grey colour, which converts to the familiar orange-pink on cooking by heating in boiling water, and thus provides a culinary example of thermochromism. Various explanations have been proposed for this colour change, and it now appears that it is due to a combination of factors, one of which relies on chromophore dimerisation and possibly higher aggregation with resultant excitonic coupling. The chromophore from which lobster derives its colour is the carotene astaxanthin (Figure 1.58), which has the typical carotenoid orange-red colour with λ_{max} 472 nm in the free state in hexane solution (492 nm in pyridine). Free astaxanthin is what gives lobster its typical colour after cooking. The colorant responsible for the colour of the live lobster is the protein-astaxanthin complex α-crustacyanin, in which 16 apoprotein units are combined with 16 molecules of astaxanthin, absorbing at 632 nm in aqueous phosphate buffer. However, it is the derived complex β-crustacyanin (absorption maximum 586 nm) that has been characterised in most detail. X-ray structure analysis of β-crustacyanin reveals two astaxanthin molecules each bound to, and bridging, two apoprotein units by H-bonding.[290] The H-bonding itself is responsible for a degree of electronic polarisation of the astaxanthin molecules, and the protein coordination is also responsible for their planarisation and alteration of their conformations into a maximally extended state (Figure 1.58 (a)). These polarisation and conformational effects are believed to be responsible for about one-third of the total bathochromic shift compared with monomeric astaxanthin. The two astaxanthin molecules in β-crustacyanin are held roughly face-to-face about 7Å apart, oriented so that they can interact electronically, resulting in J-type dimer excitonic coupling and a further bathochromic shift.[291] However, it has been pointed out that the two astaxanthins of β-crustacyanin are in fact separated by an unidentified molecule

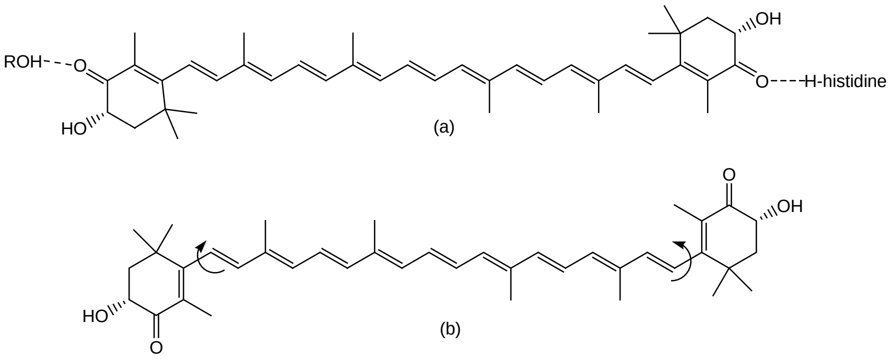


Figure 1.58 Simplified diagrams of (a) astaxanthin in beta crustacyanin and (b) astaxanthin in the free state.

which will inevitably attenuate the excitonic coupling and diminish the resultant bathochromic shift.[292] Finally, further aggregation between the dimeric β-crustacyanin protein units gives α-crustacyanin, which is the complete protein-astaxanthin complex in the live lobster. In this, further excitonic coupling is proposed to result in a yet more extensive bathochromic shift to give the grey-blue colour, which is observed in the uncooked lobster. Cooking denatures the apoprotein units, liberating free (disaggregated) astaxanthin. Astaxanthin is also the chromophore of a coral pigment, alloporin, but is present as a monomer in the protein complex, and without the possibility for excitonic coupling its absorbance remains at 545 nm. A review of the colour of other carotene protein complexes, and blue carotenes in general, is available.[293]

1.11 Miscellaneous Chromisms

Over the years many chromisms have appeared in the literature as shown in Table 1.1. Some of these names seem to have been devised on the whim of the authors and have not found favour in the mainstream literature. However, although still minor, some novel chromic materials are starting to find more general use and commercial applications. It is those chromisms that will be dealt with in this section.

1.11.1 Amorphochromism

Conventional digital thermal imaging involves encapsulated ionochromic dyes melting in the presence of an acid co-reactant, as described in Section 1.4.2.4. Workers at the Polaroid Corporation found that some indicator dyes can exist as either a colourless or a coloured tautomer, depending upon the environment.[294] For instance, certain derivatives of fluoran dyes (fluorescein, rhodol and rhodamine) (see Section 1.4.1.3), which exist in micro-crystalline forms of the colourless tautomers, can also form other crystalline habits or glassy states exhibiting substantial absorption in the visible. These workers referred to amorphochromic behaviour and hence coined the term amorphochromism. The melting of colourless particles of these amorphochromic dyes provides a mechanism for direct thermal imaging, which is claimed to be characterised by high sensitivity for a given level of stability, and is currently being commercialised by ZINK Imaging in the USA.[295] The imaging process will be further discussed under digital printing in Chapter 2 (Section 2.9.3.3).

1.11.2 Chronochromism

Chronochromism has been adopted to describe those processes where there is a change of colour with respect to a defined period of time. In all cases they are examples of indirect chromisms, since the colour change occurs by one of the other chromic phenomena: ionochromism, photochromism, thermochromism, gasochromism or vapochromism.

Systems have been devised using pH indicators, leuco dyes and photochromic materials, placed in environments designed to allow the colour change to take place over a period of time pre-determined by the application and hence giving rise to the term chronochromic. One example is the use in toothpaste of a mixture of Methylene Blue and sodium ascorbate. On brushing the teeth the two chemicals interact and the dye is reduced to a colourless leuco product. Complete disappearance of the original blue colour indicates the correct time for the user to brush their teeth.[296] Another potential outlet is the use of indicator dyes in semi-permanent inks for the temporary marking of documents *e.g.* routes on maps. One such ink uses the ammonium salt of phenolphthalein. Ammonia evaporates with time leaving the colourless phenolphthalein behind.[297] Another important area where time evaluation is important is exposure to sunlight and several systems exist which are designed to change colour after a certain level of exposure to UVB.[298] These involve stickers or wrist bands covered with a formulation containing an acid release agent, *e.g.* iodonium and sulfonum salts or chloral hydrate which are activated by UV, and pH indicator dyes such as thymol blue and malachite green, which change colour as the pH rises over time. Recently it was discovered that adding a base to the formulation allowed greater control over the rate of change in these formulations.[299]

General Electric and Flexplay Technologies have both devised a DVD optical videodisc format which is designed to have a time-limited (usually 48-hour) playback time before it becomes unplayable. It is designed to be cheap and disposed of after use *e.g.* bought at travel stores, or as non-returnable DVDs supplied by rental companies and used for a finite time. Although they are often described as "self-destructing", the principle involves a change from an optically transmissive state to a substantially optically non-transmissive state, not physical destruction.[300,301] The reactive layer on the DVD comprises a polymer resin that acts as a carrier for a suitable leuco dye, which, upon contact with atmospheric oxygen, oxidises to form an opaque or semi-opaque material. Prevention of oxidation being triggered during manufacture of the discs, and also avoiding the need for operating in inert atmosphere, is achieved by protecting the leuco dyes as their triisopropylysilyloxy derivative, which is stable in the presence of oxygen. However, in the presence of nucleophilic reagents, *e.g.* water, the protected leuco dye undergoes hydrolysis, releasing the parent leuco dye. This reaction is slow (several days to a week), and the hydrolytic compound is supplied either as atmospheric moisture, or in the formulation of the resin. The rate of oxidation of the deprotected leuco dye is dependent on the pH of the resin polymer matrix. By adding basic compounds (*e.g.* 1,4-diazabicyclo[2.2.2]octane (DABCO) or other amines), the pH is increased, and the reaction rate increases correspondingly. In contrast, by adding strong protic acids (*e.g.* camphorsulfonic acid) the hydrolysis reaction rate can be decreased and the lifetime of the disc prolonged. After teething problems with an earlier release the product now seems to be taking off in the USA and Japan (Flexplay™).[302]

In 2008 Xerox announced a new photocopying system that uses special coated paper where the image is designed to erase at ambient temperature indoors in a finite time (16–24 h), allowing the paper to be reused multiple times in the copier, thus saving on paper usage. Although Xerox have not described the chemicals that will be used in any commercial product their patents claim the use of a whole range of photochromic materials (see Section 1.2.1), designed so the back reaction can be induced either thermally or by UV light over a specified time.[303]

1.11.3 Radiochromism

Radiochromism is used to describe a process in which a material changes colour directly by absorbing ionising radiation, without the need for any kind of thermal, optical or chemical development or amplification. Such radiochromic materials, in the form of films, have been used for years as radiographic dosimeters and for imaging in the medical field.[304] In the past many chemicals have been used in this application, including leuco dyes, triphenylmethane cyanides, spiropyrans, anils, organic acids, stilbenes and formazan dyes, but now the favoured product uses colour changes in polydiacetylene. Radiochromic film based on polydiacetylene for medical applications is known as GafChromic MD-55 (I and II).[305] The film consists of a thin microcrystalline dispersion of a monomer coated on a flexible polyester film base. The film is clear (translucent) before it is irradiated when it turns progressively blue upon exposure to radiation. The radiochromic chemical mechanism is a relatively slow first-order solid-state topochemical polymerisation reaction initiated by irradiation, resulting in homogeneous, planar polyconjugation along the carbon-chain backbone.

An interesting type of radiochromic effect was observed when a concentrated sol of semi-conducting TiO_2 particles was exposed to γ radiation, the colour changing from colourless to deep blue with absorption maximum at 540 nm. The absorption has been assigned to trapped electrons or Ti^{3+} states in the solid matrix, based on its spectroscopic similarity to the samples irradiated with UV light. Unlike the conduction-band electrons generated from direct excitation by UV radiation, the origin of the trapped electrons during γ-ray irradiation may be traced to a series of reducing species produced by the high-energy electrons, which in turn are the direct result of γ-irradiation.[306]

1.11.4 Magnetochromism

Magnetochromism is the term applied when a chemical compound changes colour under the influence of a magnetic field. In particular the magneto-optical effects exhibited by complex mixed metal compounds are called magnetochromic when they occur in the visible region of the spectrum. Examples include $K_2V_3O_8$, lithium purple bronze $Li_{0.9}Mo_6O_{17}$, and related mixed oxides.[307]

Nanoscale particles of ferromagnetic Fe_3O_4 (magnetite) have to be no greater than 10 nm in size otherwise they behave as permanent magnets and coalesce. Nanoscale magnetite coated with a charged polymer, polyacrylic acid, and suspended in water, assembles to form colloidal photonic crystals, which are

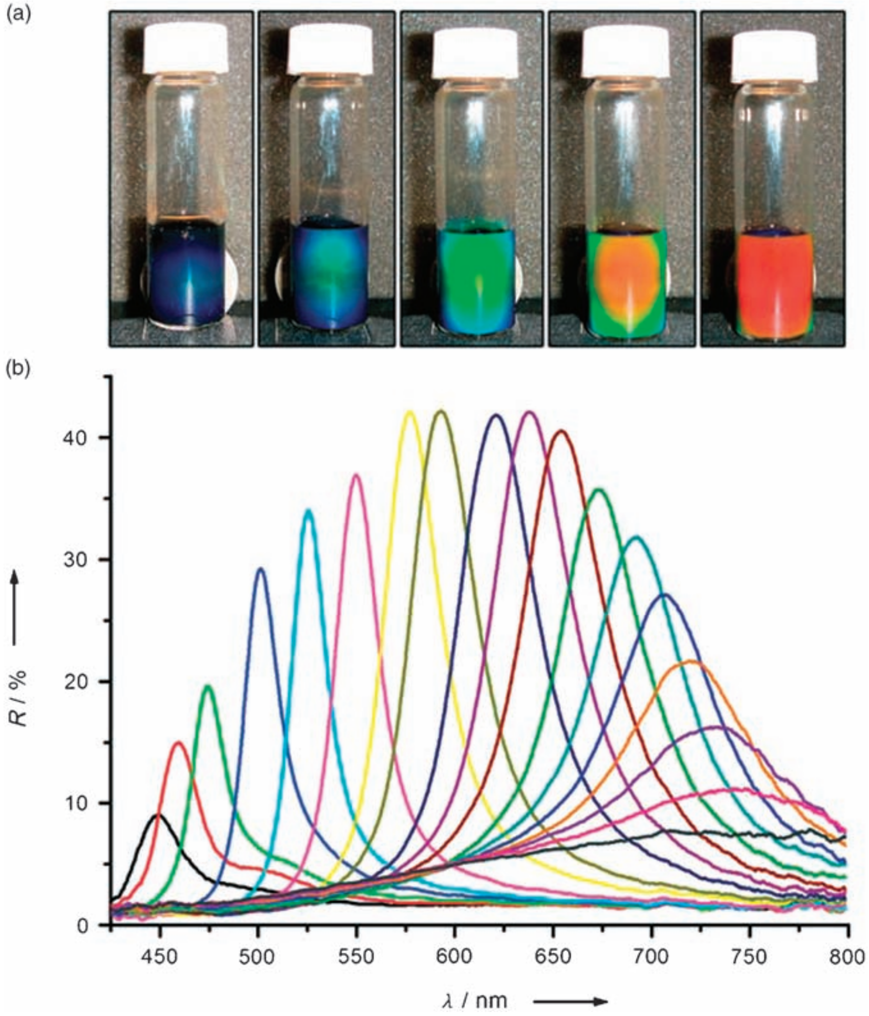


Figure 1.59 Colloidal suspensions of nanoscale particles of ferromagnetic Fe_3O_4 (magnetite)[308] (reproduced with permission of Wiley VCH).

stable for several months (see Section 5.3 in Chapter 5).[308] These brightly coloured colloidal suspensions change colour when approached by a magnet, the actual colour depending on the strength of the magnetic field, the effect being reversible (see Figure 1.59). The effect is not fast enough for use in real-time video imaging but could be used in static signs or electronic paper.

1.11.5 Biochromism

Biochromism, as defined here, is the generic term applied when specifically designed molecules undergo a chromic transition on interfacing with a biological entity. By far the largest number of reports in this field cover the use of modified conjugated polymers *e.g.* polydiacetylene and polythiophenes, as biosensors in the form of membranes, lipids and vesicles.[309] Rather confusingly when the interaction is with polydiacetylenes the colour change phenomenon is often called affinochromism, but when it is with polythiophenes its is called affinitychromism.

Supramolecular assemblies of vesicles composed of natural lipids embedded in a matrix of polydiacetylene undergo blue-to-red colour changes related to specific interactions between the lipids or recognition elements and bio-molecules. The chromic transitions observed in the vesicles are due to structural modifications within the conjugated PDA polymer backbone. Suggested uses include membrane-mimics for detection of interfacial processes, such as peptide-membrane interactions, antibody-antigen binding, enzymatic catalysis and detection of physiological ions.[310,311] Side-chain substituted poly(3-alkyl thiophenes) can be modified to act as biochromes, for instance water-soluble biotinylated polymers showed pronounced chromic effects on contacting with avedin, and there are many more examples in the literature.[312,313]

1.12 Colour Changes Due to Plasmonic Coupling

Possibly the fastest growing area of modern chemical technology is that based on "nanochemistry", where the size of the chemical entity of interest is above that of atomic or many molecular species, but below that of what can be regarded as bulk material. The dimension of relevance is between roughly one and a thousand nanometres, and it is here that bulk and molecular properties disappear and the entity assumes the new properties that make nanoparticles (NPs) of such interest and use. If we divide material into the three classes insulators, semi-conductors and conductors, then most organic molecules fall into the first. Nanoscaled organic molecules can have unique and interesting properties as already mentioned above and will be seen elsewhere in this book. Semi-conductor NPs are mainly of interest because of their luminescence properties, so are introduced in Chapter 3 alongside other luminescent species. In contrast, the significance of nano-dimensioned metallic conductors derives from their light-absorbing and scattering properties, and they undergo colour changes for various reasons. They are thus introduced in this chapter.

The explosion of interest in metallic NPs (MNPs) is demonstrated by Figure 1.60, which displays the result of a SciFinder search based on the search term "metal nanoparticles". The plot depicts the annual number of publications abstracted by CAS over the past 19 years or so, further broken down into journal articles and published patent applications. The rate of increase hardly needs emphasising. Whilst many of these are biased toward life science and medical-related analysis, MNP research has many different aspects and colour-based phenomena have underpinned an appreciable proportion of these publications, and it is these that comprise this section. Because of the daunting amount of material in the literature, and furthermore the rate of increase means that even more topical material will inevitably become available during this

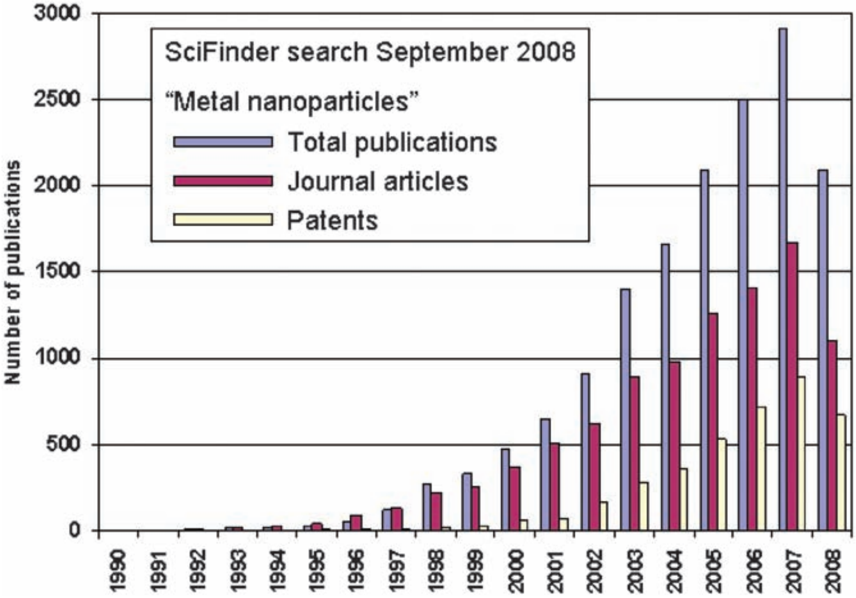


Figure 1.60 Number of annual publications abstracted by CAS found by the search term "metal nanoparticles" (publications for 2008 are incomplete).

book's publication phase, the scope of this section is by necessity abbreviated. However, many recent reviews are cited below and the interested reader requiring more detail should refer to these many excellent resources. In the following, the basic properties of MNPs are introduced, followed by some of the applications and the derived technology.

1.12.1 Metallic Nanoparticles

Everyone is familiar with the colour of bulk metals – most have no visible effect on light other than reflecting it with a more or less neutral "silver" colour, while a few have a distinct colour, such as the yellow of gold and the reddish shade of copper. The physical origin of colour in metals has been described elsewhere, and does not concern us further here.[314] Nanoparticulate metals differ. For example, colloidal gold, known since ancient times to be bright red, comprises nanoparticles of gold (AuNP). The physics responsible for the colour of these materials differs from the molecular electronic excitation underpinning the colour of organic dyes. The oscillating electric field associated with a beam of light of appropriate frequency excites collective oscillations of NP conduction band electrons (Figure 1.61a). The oscillation is known as a localised surface plasmon resonance (LSPR) and has been described as "a wave of electrons sloshing over the surface of the NP".[315] When the LSPR frequency is in the visible region of the spectrum the MNP is coloured (Figure 1.61b).

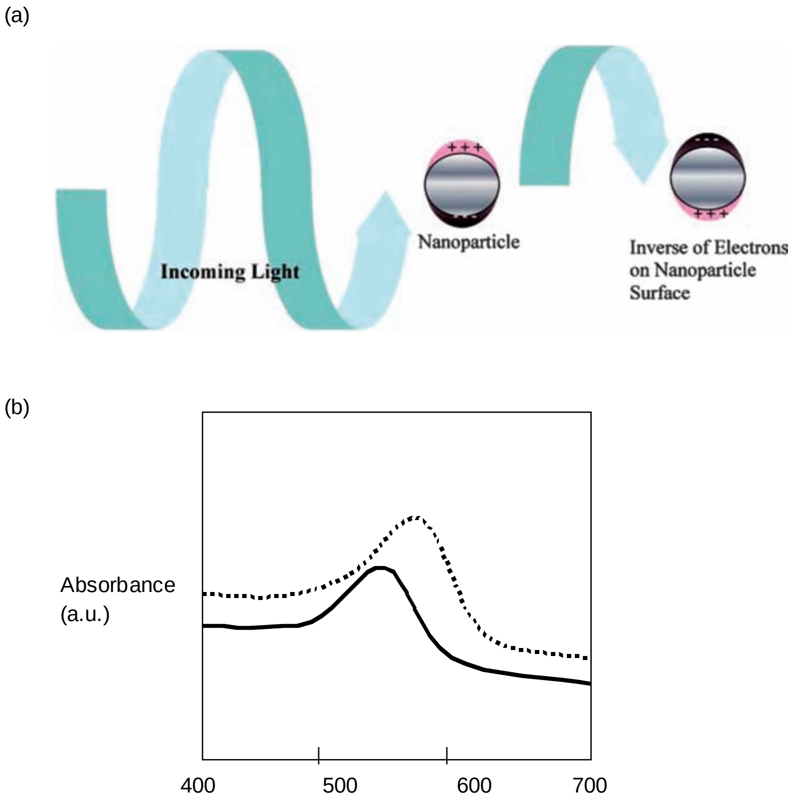


Figure 1.61 (a) Surface plasmon resonance due to coherent interaction of the electrons in the conducting band with light; (b) AuNP LSPR spectra, showing typical maximum at *ca.* 520 nm, red shifted for higher refractive index solvent.[323]

1.12.1.1 Properties of Metallic Nanoparticles

The characteristic optical properties of coloured MNPs differ significantly from those of typical organic dyes, as LSPRs depend on several distinct factors foreign to dyes.

- *Material* – while MNPs can be produced from any metal, in practice chemical stability restricts routine use in optical applications to only those metals that are the most stable under ambient conditions, most importantly the noble metals silver and especially gold. The LSPRs of different MNPs differ in energy, and thus different MNPs will have different colours depending on the various factors below. For example NPs from Cd, In, Hg, Sn, Pb are colourless,[316] but 20 nm spheres of AuNP have their LSPR maxima at 520 nm (red) (Figure 1.61b), and AgNPs of the same size at 420 nm (yellow).[315]

- *Size* – while MNPs can be produced down to molecular size, the LSPR only results in coloration for a spheroidal AuNP of diameter at least 2 nm.[317] For AuNPs with diameters between 9 and 99 nm, the LSPR maxima in water range from 517 to 575 nm, resulting in bright-red shades successively red-shifted toward violet.
- *Shape* – one of the most useful and characteristic properties of MNPs is the variation of their LSPR maxima with shape. Many different MNP shapes can now be synthesised including spheres, triangles, cubes, prisms, rods, ellipsoids, as well as shells and cages, leading to a great variation in LSPR properties. Spheroidal MNPs have a single LSPR maximum, whereas rod-like MNPs have two, associated with their longitudinal and lateral dimensions. The former LSPR is appreciably red-shifted, even reaching into the NIR region. LSPRs of AgNPs can be tuned from 380 nm in the UV to well into the IR at 6000 nm by varying size and shape,[318] with the maxima of triangles, blunted triangles and hemispheres of comparable sizes at 623, 532 and 432 nm, respectively.[319] Au nanoshells comprising silica spheres coated with a nm-thick layer of Au are red-shifted with respect to solid Au spheres, and the LSPR maxima are very sensitive to the thickness of the Au layer.[320]
- *Surrounding environment* – the LSPR maxima of MNPs depend on the nature of the ligands appended to their surfaces, and on the nature of the bulk medium in which they sit. A change of solvent $n_D{}^{20}$ from 1.33 to 1.55 gives an 8-nm red-shift for 5.2 nm AuNP.[317]

Thus all these variables cause chromic effects in their own right. Other significant properties of MNPs and their LSPR include the following:

- *Scattering and absorption* – the LSPR maxima ("extinction spectra") include components due to absorbance and elastic light scattering. The former is usually dominant, although the contribution of each to the spectra again depends on size and shape.[320] Scattering of blue light of wavelength 445 nm by an 80-nm AuNP is 10^6 times more efficient than the luminescence produced by a single fluorescein molecule. Ag is an even better scatterer than Au.[321] Both these properties are exploited in MNP sensor design, discussed below.
- *Photostability* – noble metal NPs are stable to light, which distinguishes them further from organic dyes.
- *Toxicity* – this is an area on which there is conflicting information and clearly more research is needed.
- *Strength* – one of the most useful characteristics of MNPs is the efficiency of light scattering and absorption. The molar absorbances of common dyes typically range from 10^4 to 10^5 M ^{1} cm ^{1}. The corresponding molar absorbances for AuNPs have been reported up to 10^{11} M ^{1} cm ^{1}.[315,316]
- *Synthesis* – AuNPs are traditionally prepared in solution by reduction of $HAuCl_4$ under controlled conditions. A description of the synthesis and fabrication of the many sizes, shapes and material variants of MNPs goes

Table 1.20 A selection of recent reviews including discussion of the fabrication of metal nanoparticles and nanostructures.

Reference	*Year*	*Topic*
322	2003	Chromophore functionalised gold nanoparticles
323	2003	Nanoparticle scaffolds and building blocks
324	2004	Integrated nanoparticle bio molecule hybrid systems
317	2004	Gold nanoparticles: assembly, supramolecular chemistry, properties, applications
320	2006	Gold nanostructures
325	2006	Noble metal SPR and nanocrystals of different shapes
326	2007	Polymer protected gold nanoparticles
316	2007	Interparticle coupling effect on SPR of gold nanoparticles
318	2007	Plasmonic nanostructures: artificial molecules
321	2007	Silver nanostructures with controlled shapes & properties
315	2008	Metallic nanorods
327	2008	Gold nanoparticle superlattices
328	2008	Nanocrystal micelles
329	2008	Polymer and biopolymer mediated self assembly of gold nanoparticles

beyond the scope of this book, but Table 1.20 lists just some of these and points to reviews which will lead the interested reader to the original literature. To prevent unwanted aggregation of the AuNP, a coating layer of ligands is appended to their surfaces. A 5.2-nm diameter spheroidal AuNP contains 2951 atoms, many of which are on the NP surface.[317] There is thus wide scope for appending a variety of ligands for stabilisation and to introduce further chemical functionality. This in combination with the intrinsic MNP colour properties outlined above leads to their optical applications and derived technology described in the next section.

1.12.2 Colour Change Applications of Metallic Nanoparticles

When two AuNPs come close to one another, within about 2.5 times the NP radius or less, the LSPR undergoes an appreciable red-shift, and the colour changes from red to purple-blue. This plasmonic coupling underpins the major use of MNPs, as optical sensors. The shift is easy to measure accurately with modern spectrometers, and frequently a simple visible spot-out test is sufficient to determine NP aggregation, and even its degree, by the colour change generated. Alternatively, the light scattered by the individual MNPs and MNP dimers or clusters can be observed, most easily with an optical microscope operating in a dark-field mode (incoming light normal to the observation direction). The intensity of scattered light is such that single NPs can easily be observed in this way. The basic principle underpinning the sensing application is shown in Figure 1.62.[315] The surface of the NP is modified with a ligand that is intentionally chosen or designed to recognise binding sites in the analyte, which must be able to coordinate with two or more of the NP-ligands. As the

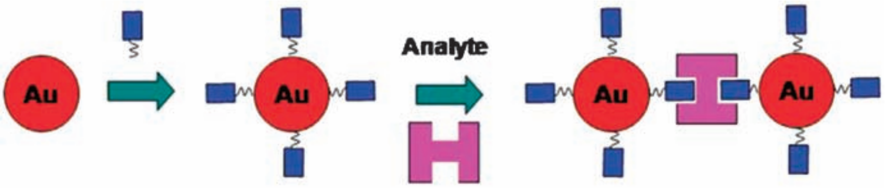
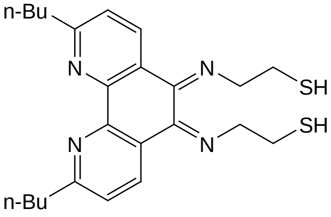


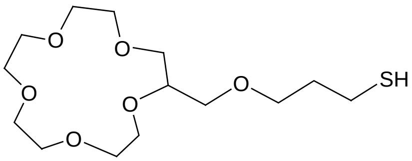
Figure 1.62 Generalised scheme for chemical sensing based on gold (or silver) nanoparticles aggregation.[315]

analyte binds to the NPs, they are brought into close correspondence, with resultant plasmonic coupling and colour change.

This principle has been used in metal ion analysis, where Li^+ is detected by coordination to two 1,10-phenanthroline ligands (1.105) each bound to an AuNP.[315] K^+ is detected and quantified down to micromolar concentration by the colour change induced when it is coordinated by two crown ether ligands (1.106), each again linked to AuNPs.[330] The high affinity of Au for sulfur is exploited by using the latter as the coordinating atom of many different ligands of interest in MNP sensors.



(1.105)



(1.106)

The chromic phenomenon is thus straightforward – a colour change as the MNPs are brought closer together. The subtlety and power of this principle depends on molecular recognition and binding of the analyte by the ligands appended to the NP. The topic of molecular recognition, or supramolecular chemistry, is of course huge and well covered elsewhere.[331]

A further important application is in optical biosensors for nucleic acids and proteins. Start by considering the object of the analysis, which is a single DNA chain, comprising diagrammatically two linked regions, A-B. One of the sensor elements is an AuNP with another single strand of nucleic acid oligomer as ligand, A′, which is the base-pairing binding counterpart of A in the target DNA. A second sensor element comprises another AuNP, this time with ligand B′, the binding complement of B in the target DNA. Thus when a mixture of the two AuNPs encounters and binds with an A-B DNA strand *via* duplex formation, the two AuNP centres are brought close enough for plasmonic coupling, with resultant characteristic colour change from red to violet or blue (Figure 1.63).

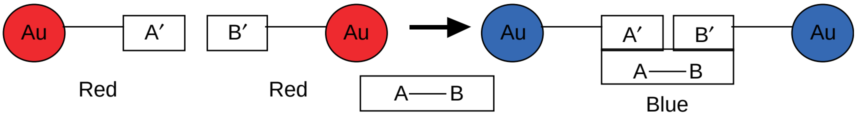


Figure 1.63 Colour change when two functionalised AuNPs encounter and bind with an A B DNA.

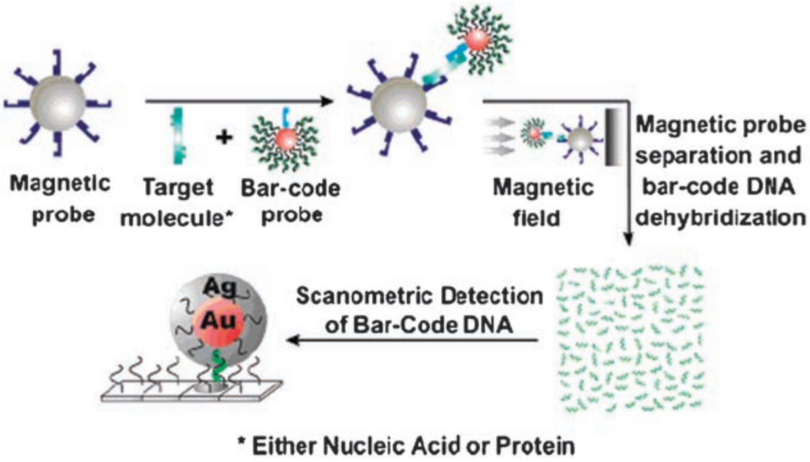


Figure 1.64 Nanostructure based bio barcode. Magnetic particles capture either the target DNA or protein. Au nanoparticles loaded with barcode oligonu cleotides and target capture molecules are added to the assay to form a sandwich system. The sandwich complexes are magnetically separated from the assay mixture and then washed with water to remove the bar code DNA for the target DNA or protein of interest. The barcodes are detected using the scanometric approach[332] (reproduced with permission of the American Chemical Society).

The technique is sufficiently sensitive that it is possible to differentiate between an exact MNP sensor-DNA match and a single base-pair mismatch, and is quick and easy to implement.[332] The initial sensitivity using 4-nm AuNPs was about 1 nM, improved to 50 pM using 50-nm AuNPs. This basic sensing technique was further developed by amplifying the LSPR by coating the AuNP with Ag, and basing the device on a glass chip bearing capture DNA strands. This so-called "scanometric" technique was now sensitive down to 50 fM, subsequently improved to 100 aM. Then a bio-barcode amplification technique as shown in Figure 1.64 took the limit to 500 zM (10 strands in solution). These developments have been reviewed,[332] and details of a modification have been provided in a useful experimental protocol.[333]

The same principles can be applied to protein detection and quantification. Alternatively, rather than monitoring the plasmon coupling shift, the change in LSPR of AgNP triangles merely due to the change in refractive index induced by coordination of analyte to the MNP is sufficient to give limits of detection below 10 fM in analysing for the biomarker ADDL (amyloid-derived diffusible ligand), an oligomer of a 42-amino acid peptide associated with Alzheimer's disease.[334] A further application of LSPR spectroscopy is the determination of distances on the nm scale in macromolecules. AuNPs are coordinated to a target molecule, and the colour shift can be related to the distance between adjacent AuNPs. Conformational changes can be identified.[335] Current (2008) goals in further MNP sensor development include increasing the sensitivity of detection down to the single molecule limit; combining LSPR with other analytical techniques such as mass spectrometry and surface enhanced Raman spectroscopy (SERS; outside the scope of this book); and the practical development of LSPR-based sensors for routine use in high-throughput screening.[336]

1.12.3 Commercial Optical Biosensors Based on Metallic Nanoparticles

Much of the current development of biosensors based on the MNP principles is now being done behind commercial confidentiality, and products are available commercially.[337] The Nanosphere website provides videos of the chemistry behind their nucleic acid and protein detection technology, which expands on the brief outlines presented above.[338] They manufacture optical sensors based on 13–20 nm AuNPs conjugated with DNA or RNA nucleotides or antibodies, for the bio-analysis of nucleic acid or protein targets. They are applied in many different life science and medical areas, including genetics, pharmacogenetics, infectious diseases, oncology, biosecurity and prion detection; other applications are under development. The technique's sensitivity is 2 to 3 orders of magnitude higher than fluorescence-based dye tests (ELISA). Advnt Biotechnologies and Tetracore sell AuNP-based sensors designed to detect biothreat agents (*e.g.* anthrax, ricin toxin, botulinum toxin, *Y. pestis* (plague), SEB).[339,340] Various other companies provide AuNPs and AgNPs for biosensor applications, as well as in some cases bespoke development of the sensors themselves. Their websites provide more details.[341 345]

Other technologies depend on the chromic phenomena displayed by MNPs, just as on conventional dyes. Such topics are covered later in this book: Chapter 2 (2.4.4.5) outlines the use of AuNPs in the coloration of glass; Chapter 3 for the involvement of MNPs in fluorescence-based applications; and Chapter 4 (4.6.4) for the photothermal effects of MNPs, especially in cancer therapy. Gold nanorods also comprise the active component in a new material for multi-dimensional optical data storage (Chapter 5, Section 5.6.5.2).

Another interesting development has been the application of Au and AgNPs to wool as alternatives to conventional dyes or pigments. Because wool is composed of keratin with a high proportion of the amino acid cysteine, which has thiol side chains, the Au and AgNPs have a binding site on wool. Using different MNPs the researchers were able to obtain a range of shades from yellow to purple. In spite of the optical strength of the coloured nanoparticles, their cost means that such materials are likely to be heading for the niche market of celebrity accessories, not everyday apparel.[346]

References

1. P. Talvenmaa, in *Intelligent Textiles and Clothing*, ed. H. Mattila, Woodhead Publishing, Cambridge, 2006.
2. (a) C. M. Lampert, *Mater. Today*, 2004, 28–35; (b) S. A. Jenekhe and D. J. Kiserow, *Chromogenic Phenomena in Polymers*, American Chemical Society, Washington, 2004; (c) C. Y. Fukuda, *Inorganic Chromotropism: Basic Concepts and Applications of Colored Materials*, Springer, Berlin, 2007.
3. J. C. Crano and R. J. Guglielmetti (ed.), *Organic Photochromic and Thermochromic Compounds, Volume 1, Main Photochromic Families*, Plenum Press, New York, 1999.
4. J. C. Crano and R. J. Guglielmetti (ed.), *Organic Photochromic and Thermochromic Compounds, Volume 2, Physicochemical Studies, Biological Applications, and Thermochromism*, Plenum Press, New York, 1999.
5. H. Durr and H. Bouas-Laurent (ed.), *Photochromism: Molecules and Systems*, Elsevier, Amsterdam, 2003.
6. H. Durr and H. Bouas-Laurent, *Pure Appl. Chem.*, 2001, **73**, 639–665.
7. P. Suppan and N. Ghonheim, *Solvatochromism*, The Royal Society of Chemistry, Cambridge, UK, 1997, p. 79.
8. V. I. Minkin, *Chem. Rev.*, 2004, **104**, 2751–2776.
9. H. Nakazumi, in *Chemistry and Applications of Leuco Dyes*, ed. R. Muthyala, Plenum Press, New York, 1997, pp. 1–45.
10. D. A. Clarke, in *Conference Papers from ChemiChromics '95*, Manchester, December 1995, Spring Innovations, UK.
11. S. Maeda, in *Organic Photochromic and Thermochromic Compounds, Volume 1, Main Photochromic Families*, ed. J. C. Crano and R. J. Guglielmetti, Plenum Press, New York, 1999, pp. 85–109.
12. (a) J. D. Hepworth, C. D. Garbutt and B. M. Heron, in *Colour Science '98. Vol. 1: Dye and Pigment Chemistry*, ed. J. Griffiths, University of Leeds, UK, 1999, pp. 161–173; (b) J. D. Hepworth and B. M. Heron, in *Functional Dyes*, ed. Sung-Hoon Kim, Elsevier, Amsterdam, 2006, pp. 85–136.
13. G. Sartori, G. Casiraghi, L. Bolzoni and G. Casnati, *J. Org. Chem.*, 1979, **44**, 803–805.
14. J. L. Pozzo, V. A. Loshkin and R. Guglielmetti, *J. Chem. Soc., Perkin Trans 1.*, 1994, **1**, 2591–2595.
15. A. M. F. Oliveira-Campos, M. M. Oliveira, L. Melode Carvalho, C. Moustrou, A. Sumat, R. Guglielmetti and J. Seita, in *Colour Science '98. Vol 1: Dye and Pigment Chemistry*, ed. J. Griffiths, University of Leeds, UK, 1999, pp. 26–43.

16. B. Van Gemert, in *Organic Photochromic and Thermochromic Compounds, Volume 1, Main Photochromic Families*, ed. J. C. Crano and R. J. Guglielmetti, Plenum Press, New York, 1999, pp. 111–140.
17. B. Van Gemert, in *Conference Papers from ChemiChromics USA '99*, New Orleans, January 1999, Spring Innovations, UK.
18. H. Stobbe, *Chem. Ber.*, 1907, **40**, 3372–3382.
19. H. G. Heller, C. C. Elliott, K. Koh, S. Al-Shihry and J. Whittall, *Spec. Publ. – R. Soc. Chem.*, 1993, **125**, 156–158.
20. M.-G. Fan, L. Yu and W. Zhao, in *Organic Photochromic and Thermochromic Compounds, Volume 1, Main Photochromic Families*, ed. J. C. Crano and R. J. Guglielmetti, Plenum Press, New York, 1999, pp. 141–206.
21. H. G. Heller, *Advances in Colour Science and Technology*, 2001, **4**, 6.
22. H. G. Heller, in *Colour Science '98. Vol. 1: Dye and Pigment Chemistry*, ed. J. Griffiths, University of Leeds, UK, 1999, pp. 147–156.
23. H. G. Heller and J. Langan, *J. Chem. Soc., Perkin. Trans 2.*, 1981, **2**, 341.
24. H. G. Heller, in *Conference Papers from ChemiChromics '95*, Manchester, December 1995, Spring Innovations, UK.
25. H. G. Heller, D. S. Hughes, M. B. Hursthouse and N. G. Rowles, *Chem. Commun.*, 2000, 1397.
26. M. Irie, in *Organic Photochromic and Thermochromic Compounds, Volume 1, Main Photochromic Families*, ed. J. C. Crano and R. J. Guglielmetti, Plenum Press, New York, 1999, pp. 207–222.
27. M. Irie, *Chem. Rev.*, 2000, **100**, 1685–1716.
28. Y. Ushigo, T. Hase, Y. Linuma, A. Takata and J. Yoshida, *Chem. Commun.*, 2007, 2947–2949.
29. Q. Luo, Q. Fan and W. Huang, *Chinese J. Org. Chem.*, 2007, **27**, 175–187.
30. V. A. Barachevsky, Yu. P. Strokach, Yu. A. Puankov and M. M. Krayushkin, *J. Phys. Org. Chem.*, 2007, **20**, 1007–1020.
31. D. Jacquemin and E. A. Perpete, *Chem. Phys. Lett.*, 2006, **429**, 147–152.
32. M. Ohsumi, T. Fukaminato and M. Irie, *Chem. Commun.*, 2005, 3921–3923.
33. D. Dulić, T. Kudernac, A. Pužys, B. L. Feringa and B. J. van Wees, *Adv. Mater.*, 2007, **19**, 2898–2902.
34. H. Rau, in ed. H. Durr and H. Bouas-Laurent, *Photochromism: Molecules and Systems*, Elsevier, Amsterdam, 2003, pp. 166–188.
35. (a) K. M. Tait, J. A. Parkinson, D. I. Gibson, P. R. Richardson, W. J. Ebenezer, M. G. Hutchings and A. C. Jones, *Photochem. Photobiol. Sci.*, 2007, **6**, 1010–1018; (b) J. A. Delaire and K. Nakatani, *Chem. Rev.*, 2000, **100**, 1817–1845.
36. (a) A. G. Cheetham, M. G. Hutchings, T. D. W. Claridge and H. L. Anderson, *Angew. Chem., Int. Ed. Engl.*, 2006, **45**, 1596–1599; (b) N. H. Shah and K. Kirshenbaum, *Org. Biomol. Chem.*, 2008, **6**, 2516–2521.
37. E. Hadjoudis, and references in *Photochromism: Molecules and Systems*, ed. H. Durr and H. Bouas-Laurent, Elsevier, Amsterdam, 2003, pp. 685–710.
38. E. Hadjoudis and I. M. Mavridis, *Chem. Soc. Rev.*, 2004, **33**, 579–588.

39. M. Morimoto and M. Irie, *Chem. Commun.*, 2005, 3895–3905.
40. H. Durr, in *Organic Photochromic and Thermochromic Compounds, Volume 1, Main Photochromic Families*, ed. J. C. Crano and R. J. Guglielmetti, Plenum Press, New York, 1999, pp. 223–266.
41. V. A. Barachevsky, in *Organic Photochromic and Thermochromic Compounds, Volume 1, Main Photochromic Families*, ed. J. C. Crano and R. J. Guglielmetti, Plenum Press, New York, 1999, pp. 267–314.
42. V. I. Minkin, V. M. Komissarov and V. A. Kharlanov, in *Organic Photochromic and Thermochromic Compounds, Volume 1, Main Photochromic Families*, ed. J. C. Crano and R. J. Guglielmetti, Plenum Press, New York, 1999, pp. 315–340.
43. W. Schnabel, *Polymers and Light*, Wiley-VCH, Weinheim, 2007, pp. 113–41.
44. (a) T. He and J. Yao, *Research on Chemical Intermediates*, 2004, **30**, 459–488; (b) T. He and J. Yao, *J. Mater. Chem.*, 2007, **17**, 4547–4557.
45. N. Shigeru and K. Masato, *Chem. Today*, 2003, **389**, 23–27.
46. S. H. Elder, F. M. Cot, Y. Su, S. M. Heald, A. M. Tyryshkin, M. K. Bowman, Y. Gao, A. G. Joly, M. L. Balmer, A. C. Kolwaite, K. A. Magrini and D. M. Blake, *J. Am. Chem. Soc.*, 2000, **122**, 5138.
47. J. Wang, G. J. Zhang, W. S. Yang and J. N. Yao, *Acta. Chim. Sin.*, 2005, **63**, 1951.
48. Y. Ohko, T. Tatsuma, T. Fujii, K. Naoi, C. Niwa, Y. Kubota and A. Fujishima, *Nature Mater.*, 2003, **2**, 29–31.
49. N. Hampp, *Chem. Rev.*, 2000, **100**, 1755–1776.
50. http://www.mcb.ucdavis.edu/faculty-labs/lagarias.
51. K. Ichimura, in *Organic Photochromic and Thermochromic Compounds, Volume 2*, ed. J. C. Crano and R. J. Guglielmetti, Plenum Press, New York, 1999, pp. 9–63.
52. W. Schnabel, *Polymers and Light*, Wiley-VCH, Weinheim, 2007.
53. Y. Shirota, *J. Mater. Chem.*, 2005, **15**, 75–93.
54. B. Van Gemert, in *Conference Papers from ChemiChromics USA 99*, New Orleans, January 1999, Spring Innovations, UK.
55. S. Higgins, *Chem. Br.*, June 2003, 26–29.
56. R. A. Evans, T. L. Hanley, M. A. Skidmore, T. Davis, G. K. Such, L. H. Yee and G. E. Ball, *Nature Mater.*, 2005, **4**, 249–253.
57. Solar Active International, http://www.solaractiveintl.com.
58. James Robinson Ltd, http://james-robinson.ltd.uk.
59. G. Payne, *Chem. Br.*, January 2002, 37.
60. B. L. Faringa, R. A. van Delden, N. Koumara and E. M. Gertsama, *Chem. Rev.*, 2000, **100**, 1789–1816.
61. A. Fernando-Acebes and J.-M. Lehn, *Adv. Mater.*, 1998, **10**, 1519–1522.
62. C. Weber, F. Rustmeyer and H. Durr, *Adv. Mater.*, 2000, **12**, 1348–1351.
63. Y. Yokoyama, *Chem. Rev.*, 2000, **100**, 1717–1740.
64. R. Hildebrand, T. Taubner and F. Keilmann, *Nature*, 2002, **418**, 159.
65. S. Kawata and Y. Kawata, *Chem. Rev.*, 2000, **100**, 1777–1788.
66. K. Lieberman, S. Harush, A. Lewis, R. Kopelman, *Science*, 1990, **247** 59.

67. D. A. Parthenopoulos and P. M. Rentzepis, *Science*, 1989, **245**, 843.
68. H. Tian and S. Yang, *Chem. Soc. Rev.*, 2002, **33**, 85–97.
69. H. Tian and S. Weng, *Chem. Commun.*, 2007, 781–92.
70. G. Y. Jiang, S. Wang, W. F. Yuan, L. Jiang, Y. L. Song, H. Tian and D. B. Zhu, *Chem. Mater.*, 2006, **18**, 235–237.
71. (a) Y. C. Yeong, S. I. Yang, K. H. Ahn and E. Kim, *Chem. Commun.*, 2005, 2502–2505; (b) Y. C. Jeong, D. G. Park, E. Kim, K. H. Ahn and S. I. Yang, *Chem. Commun.*, 2006, 1881; (c) M. Ohsumi, M. Hazama, T. Fukaminato and M. Irie, *Chem. Commun.*, 2008, 3281.
72. T. Wigglesworth, A. J. Myles and N. R. Banda, *Eur. J. Org. Chem.*, 2005, 1233–1238.
73. T. Wigglesworth and N. R. Banda, *Chem. Mater.*, 2005, **17**, 5473–5480.
74. V. Balzani, A. Credi and M. Venturi, *Molecular Devices and Machines*, Wiley-VCH, Weinheim, 2008, p. 219.
75. B. L. Feringa, R. A. van Delden and M. K. J. Wiel, *Molecular Switches*, ed. B. L. Feringa, Wiley-VCH, Weinheim, 2001, p. 123.
76. T. J. Wigglesworth, D. Sud, T. B. Norsten, V. S. Lekhi and N. R. Banda, *J. Am. Chem. Soc.*, 2005, **127**, 7272–7273.
77. (a) J. J. D. de Jong, P. R. Hania, A. Pugžlys, L. N. Lucas, M. de Loos, R. M. Kellogg and B. L. Feringa, *Angew. Chem., Int. Ed. Engl.*, 2005, **44**, 2373–2376; (b) J. J. D. de Jong, T. D. Tiemersma-Wegman, J. H. van Eschand B. L. Feringa, *J. Am. Chem. Soc.*, 2005, **127**, 13804–13805; (c) S. Wang, W. Shen, Y. L. Feng and H. Tian, *Chem. Commun.*, 2006, 1497–1499.
78. M. Frigoli, C. Welch and G. H. Mehl, *J. Am. Chem. Soc.*, 2004, **126**, 15382–15383.
79. A. Fernando-Acebes and J.-M. Lehn, *Adv. Mater.*, 1999, **11**, 910.
80. K. Uchida, M. Saito, A. Murukami, A. Kobayashi, S. Nakamura and M. Irie, *Chem. Euro. J.*, 2005, **11**, 534–542.
81. K. Higashiguchi, K. Matsuda, N. Tanifuji and M. Irie, *J. Am. Chem. Soc.*, 2005, **127**, 8922–8923.
82. F. M. Raymo and M. Tomasulo, *Chem. Soc. Rev.*, 2005, **34**, 327–36.
83. G. Jiang, Y. Sang, X. Guo, D. Zhang and D. Zhu, *Adv. Mater.*, 2008, **20**, 2888–2898.
84. J. A. Delaire and K. Nakatani, *Chem. Rev.*, 2000, **100**, 1817–1845.
85. G. Wernsberger, B. J. Scott, B. F. Chmelka and G. D. Stucky, *Adv. Mater.*, 2000, **10**, 1450–1453.
86. (a) C. Sanchez, B. Lebeau, F. Chaput and J.-P. Boilot, *Adv. Mater.*, 2003, **15**, 1969; (b) C. Sanchez, B. Julian, P. Belleville and M. Popali, *J. Mater. Chem.*, 2005, **15**, 3559–3592.
87. L. Raboin, M. Matheron, J. Biteau, T. Gacoin and J.-P. Boilot, *J. Mater. Chem.*, 2008, **18**, 3242.
88. O. A. Fedorova, E. N. Ushakov, Y. V. Fedorova, Y. P. Strokach and S. P. Gromov, in *Macrocyclic Chemistry: Current Trends and Future Perspectives*, ed. K. Gloe, Springer, Amsterdam, 2005, pp. 235–252.
89. M. Inouye, in *Organic Photochromic and Thermochromic Compounds, Volume 2, Physicochemical Studies, Biological Applications, and*

Thermochromism, ed. J. C. Crano and R. J. Guglielmetti, Plenum Press, New York, 1999. pp. 393–412.

90. N. Soh, K. Yoshida, H. Nakajima, K. Nakano, T. Imato, T. Fukaminato and M. Irie, *Chem. Commun.*, 2007, 5206.
91. C. Tu and A. Y. Louie, *Chem. Commun.*, 2007, 1331.
92. J. H. Day, *Chem. Rev.*, 1963, **63**, 65–80.
93. S. M. Burkinshaw, J. Griffiths and A. D. Towns, in *Colour Science '98, Vol. 1: Dye and Pigment Chemistry*, ed. J. Griffiths, University of Leeds, UK, 1999, pp. 174–183.
94. K. Sone and Y. Fukuda, *Inorganic Thermochromism*, Springer Verlag, Berlin, 1987.
95. R. J. D. Tilley, *Colour and the Optical Properties of Materials*, John Wiley & Sons, Chichester, 2000, p. 236.
96. K. Nassau, *The Physics and Chemistry of Colour*, John Wiley & Sons, New York, 1983, p. 91.
97. R. D. Willett, J. A. Haugen, J. Lesback and J. Morrey, *Inorg. Chem.*, 1974, **13**, 2510.
98. W. Linert, Y. Fukuda and A. Camard, *Coord. Chem. Rev.*, 2001, **218**, 113–152.
99. U. El-Ayaan, F. Murata and Y. Fukuda, *Monatsh. Chem.*, 2001, **132**, 1279–1294.
100. Y. Fukuda (ed.), *Inorganic Chromotropism, Basic Concepts and Applications of Colored Materials*, Springer-Verlag, Berlin, 2007.
101. (a) M. Gardener and C. C. Perry, *Monatsh. Chem.*, 2003, **134**, 381–385; (b) Y. Matsuura, H. Inoue and K. Matsukawa, *Macromol. Rapid Comm.*, 2004, **25**, 623.
102. B. Hellrung and H. Balli, *Helv. Chim. Acta*, 1989, **72**, 1583–1589.
103. A. Samat and V. Lokshin, in *Organic Photochromic and Thermochromic Compounds, Volume 2, Physicochemical Studies, Biological Applications, and Thermochromism*, ed. J. C. Crano and R. J. Guglielmetti, Plenum Press, New York, 1999, pp. 415–466.
104. P. U. Biedermann, J. J. Stezowski and I. Agranat, *Chem. Eur. J.*, 2006, **12**, 3345–3354.
105. D. N. Batchelder, *Contemp. Phys.*, 1988, **29**, 3.
106. R. W. Carpick, D. Y. Sasaki, M. S. Marcus, M. A. Eriksson and A. R. Burns, *J. Phys.: Condens. Matter*, 2004, **16**, 679–R697.
107. J. G. Masters, J. M. Ginder, A. G. MacDiarmid and A. J. Epstein, *J. Chem. Phys.*, 1992, **96**, 4768.
108. (a) M. Leclerc, *Adv. Mater.*, 1999, **11**, 1491–1498; (b) M. Leclerc and K. Faïd, in *Conference Papers from ChemiChromics USA '99*, New Orleans, January 1999, Spring Innovations, UK.
109. A. Seeboth and D. Lötzsch, *Thermochromic Phenomena in Polymers*, Smithers Rapra, Shawbury, UK, 2008, pp. 8–11.
110. B. L. Lucht, W. B. Euler and O. J. Gregory, *Polymer Preprint*, 2002, **43**, 59.
111. B. L. Lucht, W. B. Euler and O. J. Gregory, *US Pat.* 6,706,218, 2004.

112. N. Kurokawa, H. Yoshikawa, N. Hirota, K. Hyodo and H. Masuhara, *Chem. Phys. Chem.*, 2004, **5**, 1609–1615.
113. D. Aitken, S. M. Burkinshaw, J. Griffiths and A. D. Towns, *Rev. Prog. Coloration*, 1996, **26**, 1–8.
114. S. M. Burkinshaw, J. Griffiths and A. D. Towns, *J. Mater. Chem.*, 1998, **8**, 2677.
115. J. Luthern and A. Peredes, *J. Mater. Sci. Lett.*, 2000, **19**, 185.
116. (a) D. C. MacLaren and M. A. White, *J. Mater. Chem.*, 2003, **13**, 1695; (b) D. C. MacLaren and M. A. White, *J. Mater. Chem.*, 2003, **13**, 1701–1704.
117. D. C. MacLaren and M. A. White, *J. Mater. Sci.*, 2005, **40**, 669–676.
118. (a) A. Seeboth, C. Yin, J. Kriwanek, D. Lötzsch and R. Schäper, *J. Appl. Polym. Sci.*, 2005, **96**, 1789–1792; (b) A. Seeboth and D. Lötzsch, *Thermochromic Phenomena in Polymers*, Smithers Rapra, Shawbury, UK, 2008, pp. 21–29.
119. http://www.thermochromic-polymers.com.
120. (a) A. Seeboth and J. Kriwanek, *J. Mater. Chem.*, 1999, **9**, 2277; (b) A. Seeboth, J. Kriwanek and R. Vetter, *Adv. Mater.*, 2000, **12**, 1424–1426.
121. A. Seeboth and D. Lötzsch, *Thermochromic Phenomena in Polymers*, Smithers Rapra, Shawbury, UK, 2008, pp. 51–56.
122. A. Seeboth, J. Schneider and A. Patzak, *Sol. Energy. Mater. Sol. Cells*, 2000, **60**, 263.
123. J. H. Day, in *Kirk-Othmer Encyclopaedia of Chemical Technology*, ed. H. F. Mark, D. F. Othmer, G. C. Overberger and G. T. Seaborg, John Wiley, New York, 1979, Vol. **6**, pp. 129–142.
124. www.colour.therm.co.uk.
125. (a) www.matsui-color.com; (b) www.colorchange.com.
126. (a) www.thermochromicinks.com; (b) www.chroamzone.co.uk; (c) www.sunchemical.com; (d) www.chemsong.com.
127. J. Homola, *Color-Changing Inks*, www.Screenweb.com, 29.1.2003.
128. X. Tao (ed.), *Smart Textiles, Fabrics and Clothing*, Woodhead Publishing, Cambridge, UK, 2001.
129. *Smart and Interactive Textiles: a Market Survey*, International Newsletter Ltd, Droitwich, UK, 2005.
130. R. M. Christie, S. Robertson and S. Taylor, *Colour; Design and Creativity*, 2007, **1**(1), 5, 1–11.
131. M. Rubacha, *Poly. Adv. Technol.*, 2007, **18**, 323–328.
132. H. Oda, *Dyes Pigm.*, 2008, **76**, 270–276, 400–405.
133. F. Bremner, *tiletoday.com.au*, 2006, **50**, pp. 8–9.
134. W. Khaldi, *US Pat.*, 6,500,555, 2002.
135. Final Report, *Sunlight Responsive Thermochromic Window System*, Pleotint LLC, 2006, www.osti.gov/energycitations/servlets/purl/894091-FRpWuI/894091.PDF.
136. *Ligand Exchange Thermochromic Systems*, Pleotint LLC, *US Pat. Appl.*, 2008/0106781 A1, Filed 4.9.2007.

137. www.pleotint.com.
138. R. W. Sabnis, *Handbook of Acid-Base Indicators*, CRC Press, Boca Raton, 2007.
139. J. Fletcher and R. Zink, in *The Chemistry and Applications of Leuco Dyes*, ed. R. Muthyala, Plenum, New York, 1997, pp. 97–124.
140. R. Muthyala and X. Lan, in *The Chemistry and Applications of Leuco Dyes*, ed. R. Muthyala, Plenum, New York, 1997, pp. 125–157.
141. Y. Hatano, in *The Chemistry and Applications of Leuco Dyes*, ed. R. Muthyala, Plenum, New York, 1997, pp. 159–205.
142. P. F. Gordon and P. Gregory, *Organic Chemistry in Colour*, Springer Verlag, Berlin, 1987, p. 115.
143. H. Zollinger, *Color Chemistry: Synthesis, Properties and Applications of Organic Dyes and Pigments*, Wiley-VCH, Weinheim, 2003, pp. 189–190.
144. G. Schwarzenbach and H. Flaschka, *Complexometric Titrations*, 2nd edn., Methuen, London, 1969.
145. E. Bishop (ed.), *Indicators*, Pergamon, Oxford, 1972.
146. (a) J.-M. Lehn, *Supramolecular Chemistry – Concepts and Perspectives*, VCH, Weinheim, 1995; (b) G. W. Gokel, *Crown Ethers and Cryptands*, Royal Society of Chemistry, Cambridge, UK, 1994; (c) A. E. Martell and R. D. Hancock, *Metal Complexes in Aqueous Solution*, Springer, Berlin, 1996.
147. (a) M. Takagi and K. Ueno, *Topics Curr. Chem.*, 1984, **121**, 39; (b) H.-G. Löhr and F. Vögtle, *Acc. Chem. Res.*, 1985, **18**, 65.
148. E. N. Ushakov, M. V. Alfimov and S. P. Gromov, *Nanotechnologies in Russia*, 2008, **3**(1–2), 35–57.
149. (a) C. Suksai and T. Tuntulani, *Chem. Soc. Rev.*, 2003, **32**, 192–202; (b) C. Suksai and T. Tuntulani, in *Anion Sensing, Topics in Current Chemistry 255*, ed. I. Stibor and E. V. Anslyn, Springer, 2005, pp. 163–198.
150. R. Martinez-Máñez and F. Sancenón, *Chem. Rev.*, 2003, **103**, 4419–4476.
151. H. Miyaji and J. L. Sessler, *Angew. Chem., Int. Ed. Engl.*, 2001, **40**, 154.
152. D. Jimenez, R. Martinez-Máñez, F. Sancenón and J. Sato, *Tetrahedron Lett.*, 2002, **43**, 2823.
153. M. S. Goodman, V. Jubian and A. D. Hamilton, *Tetrahedron Lett.*, 1995, **36**, 2551.
154. M. S. Han and D. H. Kim, *Angew. Chem. Int. Ed. Engl.*, 2002, **41**, 3809.
155. (a) G. J. Mohr, *Chem. Commun.*, 2002, 2646–2647; (b) G. J. Mohr, *Anal. Bioanal. Chem.*, 2006, **386**, 1201–1214.
156. (a) R. Martinez-Máòez and F. Sancenón, *Coord. Chem. Rev.*, 2006, 3081–3093; (b) M. Tomasulo, S. Sortino, A. J. P. White and F. M. Raymo, *J. Org. Chem.*, 2006, **71**, 744–753.
157. R. Narayanaswamy and O. S. Wolfbeis (ed.), *Optical Sensors: Industrial, Environmental and Diagnostic Applications*, Springer, Berlin, 2004.
158. C. McDonagh, C. S. Burke and B. D. MacCraith, *Chem. Rev.*, 2008, **108**, 400–422.

159. A. Lobnik, in *Optical Chemical Sensors*, F. Baldini and A. N. Chester, Springer, Netherlands, 2006, pp. 77–98.
160. G. Orellana and D. García-Fresnadillo, in *Optical Sensors: Industrial, Environmental and Diagnostic Applications*, ed. R. Narayanaswamy and O. S. Wolfbeis, Springer, Berlin, 2004.
161. M. Puyol, F. Villuendas, C. Domínguez, V. Cadarso, A. Llobera, I. Salinas, I. Garcés and J. Alonso, *Absorbance-Based Integrated Optical Sensors in Chemical Sensors and Biosensors*, Springer, Berlin, 2005, **3**, pp. 1–44.
162. R. D. Johnson and L. G. Bachas, *Anal. Bioanal. Chem.*, 2003, **376**, 328–341.
163. H. Segawa, E. Ohnishi, Y. Arai and K. Yoshida, *Sens. Actuators, B: Chem.*, 2003, **94**, 276.
164. O. Oter, K. Ertekin, D. Topkaya and S. Alp, *Sens. Actuator. B: Chem.*, 2006, **117**, 295–301.
165. (a) A. Mills, in *Sensors for Environment, Health and Safety*, ed. M.-I. Baraton, Springer, Berlin, 2009, pp. 347–370; (b) A. Mills and Q. Chang, *Carbon dioxide detector*, *US Pat.* 5,480,611, 1996.
166. N. A. Carrington and Z.-L. Xue, *Acc. Chem. Res.*, 2007, **40**, 343–350.
167. Y. Hatano, in *The Chemistry and Applications of Leuco Dyes*, ed. R. Muthyala, Plenum, New York, 1997, pp. 159–205.
168. (a) www.ymdchem.co.jp; (b) www.ciba.com; (c) www.appletonideas.com.
169. (a) P. Gregory, *High Technology Applications of Organic Colorants*, Plenum, New York, 1991, p. 124; (b) R. Bradbury, in *Chemistry and Technology of Printing and Imaging Systems*, ed. P. Gregory, Blackie, London, 1996, pp. 139–167.
170. M. Green, *Chem. & Ind.*, 1996, Sept. 2, 611–644.
171. G. Sonmez and F. Wudl, *J. Mater. Chem.*, 2005, **15**, 20–22.
172. G. Sonmez and H. B. Somnez, *J. Mater. Chem.*, 2006, **16**, 2473–2477.
173. P. M. S. Monk, R. J. Mortimer and D. R. Rosseinsky, *Electrochromism and Electrochromic Devices*, Cambridge University Press, Cambridge, UK, 2007.
174. P. M. S. Monk, *The Viologens: Synthesis, Physicochemical Properties and Applications of the Salts of 4,4′-Bipyridine*, Wiley, Chichester, 1998.
175. G. C. Grandqvist, *Handbook of Inorganic Electrochromic Materials*, Elsevier, Amsterdam, 1995.
176. P. M. S. Monk, R. J. Mortimer and D. R. Rosseinsky, *Electrochromism and Electrochromic Devices*, Cambridge University Press, Cambridge, UK, 2007, pp. 140–141.
177. K. Itaya, I. Uchida and V. D. Neff, *Acc. Chem. Res.*, 1986, **19**, 162.
178. P. M. S. Monk, R. J. Mortimer and D. R. Rosseinsky, *Electrochromism and Electrochromic Devices*, Cambridge University Press, Cambridge, UK, 2007, pp. 282–311.
179. V. D. Neff, *J. Electrochem. Soc.*, 1978, **125**, 886.
180. G. S. Collins and D. J. Schiffrin, *J. Electroanal. Chem.*, 1982, **139**, 335–369.

181. M. Mastragostino, in *Applications of Electroactive Polymers*, ed. B. Scrosati, Chapman & Hall, New York, 1986.
182. P. M. S. Monk, R. J. Mortimer and D. R. Rosseinsky, *Electrochromism: Fundamentals and Applications*, VCH, Weinheim, 1995.
183. J. Roncali, P. Blanchard and P. Frère, *J. Mater. Chem.*, 2005, **15**, 1598–1610.
184. (a) G. A. Sotzing, J. L. Reddinger, A. R. Katritzky, J. Soloducho, R. Musgrave and J. R. Reynolds, *Chem. Mater.*, 1997, **9**, 1578–1587; (b) B. C. Thompson, P. Schottland, K. Zong and J. R. Reynolds, *Chem. Mater.*, 2000, **12**, 1563–1571.
185. G. Somnez, *Chem. Commun.*, 2005, 5251–5259.
186. G. E. Gunbas, A. Durmus and L. Toppare, *Adv. Func. Mater.*, 2008, **18**, 2026–2030.
187. P. M. S. Monk, R. J. Mortimer and D. R. Rosseinsky, *Electrochromism and Electrochromic Devices*, Cambridge University Press, Cambridge, UK, 2007; (a) pp. 332–334; (b) pp. 374–394.
188. www.gentex.com.
189. J. Byker, Gentex Corp., *US Pat.*, 4,902,108, 1990 and *US Pat.*, 5,128,799, 1992.
190. Donnelly Corp., *US Pat.*, 5 668,663, 1994.
191. D. Covalet, X. Fanton, M.-L. Persson, W. Platzer, T. R. Nielsen, H. R. Wilson, M. Zinzi, M. Köhl, M. Heck and B. Chevalier, in *Proc. Int. Conf. on Durability of Building Materials and Components*, Lyon, France, 17–20 April, 2005, published on CD.
192. M. Lampert, *Mater. Today*, March 2004, 28–35.
193. www.sage-ec.com.
194. C. Bechinger, S. Ferrere, A. Zaban, J. Sprague and B. A. Gregg, *Nature*, 1996, **383**, 608–610.
195. P. Bonhote, L. Walder and M. Grätzel, *Electrochromic or Photoelectrochromic Device*, *US Pat.*, 6734305, 2004.
196. F. Campus, P. Bonhote, M. Grätzel, S. Heinen and L. Walder, *Sol. Energy Mater.*, 1999, **56**, 281.
197. H. Santa-Nokki, J. Kallioinen and J. Korppi-Tommola, *Photochem. Photobiol. Sci.*, 2007, **6**, 63–66.
198. G. A. Niklasson and C. G. Granqvist, *J. Mater. Chem.*, 2007, **17**, 127–156.
199. www.chromogenics.se.
200. M. Vidotti and S. I. Córdoba de Torresi, *J. Braz. Chem. Soc.*, 2008, **19**, 1248–1257.
201. S.-H. Lee, R. Deshpande, P. A. Parilla, K. M. Jones, B. To, A. H. Mahan and A. C. Dillon, *Adv. Mater.*, 2006, 763–766.
202. D. M. DeLongchamp and P. T. Hammond, *Adv. Mater.*, 2004, **14**, 224–232.
203. G. Chidichimo, M. De Benedittis, J. Lanzo, B. C. De Simone, D. Imbardelli, B. Gabriele, L. Veltri and G. Salerno, *Chem. Mater.*, 2007, **19**, 353–358.
204. G. De Filpo, F. P. Nicoletta and G. Chidichimo, *Chem. Mater.*, 2006, **18**, 4662–4666.

205. Gentex Ships First Dimmable Aircraft Window Shades to PPG Aerospace for New Boeing 787 Dreamliner, *Market Wire*, October 2007.
206. I. Jaksic and C. Salahifar, *Sol. Energy Mater. Sol. Cell.*, 2003, **79**(4), 409–423.
207. D. J. Barclay and D. H. Martin, in *Technology of Chemicals and Materials for Electronics*, ed. E. R. Howells, Ellis Horwood, Chichester, 1984, pp. 266–276.
208. (a) B. Warszwaski, *US Pat.*, 5,078,480, 1992; (b) B. Edid and J. Themont, *US Pat.*, 5,210,636, 1993.
209. P. Bonhôte, E. Gogniat, F. Campus, L. Walder and M. Grätzel, *Displays*, 1999, **20**, 137–144.
210. D. Cummins, G. Boschloo, M. Ryan, D. Corr, S. N. Rao and D. Fitzmaurice, *J. Phys. Chem. B*, 2000, **104**, 11449.
211. www.ntera.com.
212. Electrochromic Displays page on www.acreo.se.
213. P. Andersson, R. Forchheimer, P. Tehrani and M. Berggren, *Adv. Func. Mater.*, 2007, **17**, 3074–3082.
214. S.-H. Lee, H. M. Cheong, P. Liu, D. Smith, C. E. Tracy, A. Mascarenhas, J. R. Pitts and S. K. Deb, *J. Appl. Phys.*, 2000, **88**, 3076.
215. A. Georg, W. Graf, D. Schweiger, V. Wittwer, P. Nitz and H. R. Wilson, *Sol. Energy*, 1998, **62**, 215.
216. R. Wilson, *The Optical Properties of Gasochromic Glazing*, http://eu-swift.de/pdf/swift_iccg4.pdf.
217. R. Griessen, *Europhys. News*, 2001, **32**, No. 2, http://europhsicsnews.com.
218. L. Slack, J. C. Locke, S.-W. Song, J. Ona and T. J. Richardson, *Sol. Energy Mater. Sol. Cell.*, 2006, **90**, 485.
219. S. W. Kim and K. Park, *J. Korean Phys. Soc.*, 2004, **44**, 785.
220. M. S. Monk, R. J. Mortimer and D. R. Rosseinsky, *Electrochromism and Electrochromic Devices*, Cambridge University Press, Cambridge, UK, 2007, p. 407.
221. A. Mills, *Chem. Soc. Rev.*, 2005, **34**, 1003–1011.
222. (a) Y. Yoshikawa, T. Nawata, M. Otto and Y. Fujii, *US Pat.*, 4169811, 1979; (b) M. Goto, *JP Pat.*, 62 259059, 1987.
223. Mitsubishi Gas Chemical Company Inc., http://www.mgc.co.jp/eng/products/abc/ageless/eye.html.
224. T. A. Blinka, C. Bull, C. R. Barmor and D. V. Speer, *US Pat.*, 5,583,047, 1996.
225. S.-K. Lee, A. Mills and A. Lepre, *Chem. Commun.*, 2004, 1912–1913.
226. A. Mills and D. Hazafy, *Analyst*, 2008, **133**, 213–218.
227. (a) C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, VCH, Weinheim, 2nd edn., 1988; (b) C. Reichardt, *Pure Appl. Chem.*, 2004, **76**, 1902–1919.
228. A. A. Gorman, M. G. Hutchings and D. P. Wood, *J. Am. Chem. Soc.*, 1996, **118**, 8497.
229. (a) B. J. Catalan, *Chem. Phys. Lett.*, 2008, **457**, 87–90; (b) M. G. Hutchings, unpublished results.

230. W. Linert, Y. Fukuda and A. Camard, *Coord. Chem. Rev.*, 2001, **218**, 113–152.
231. M. G. Hutchings, P. Gregory, J. S. Campbell, A. Strong, J.-P. Zamy, A. Lepre and A. Mills, *Chem. Eur. J.*, 1997, **3**, 1719.
232. R. Budag, L. A. Giusti, V. G. Machado and C. Machado, *Fuel*, 2006, **85**, 1494–1497.
233. S. Spange, S. Prause, E. Vilsmeier and W. R. Thiel, *J. Phys. Chem. B Condens. Matter Mater. Surf. Interfaces Biophys*, 2005, **109**, 7280–7289.
234. www.invitrogen.com.
235. (a) F. Röck, N. Barsan and U. Weimar, *Chem. Rev.*, 2008, **108**, 705–725; (b) T. C Pearce, S. S. Schiffman, H. T. Nagle and J. W. Gardner (ed.), *Handbook of Machine Olfaction: Electronic Nose Technology*, Wiley-VCH, Weinheim, 2006.
236. C. Nagel, Vapochromic double complex salts, *US Pat.*, 4,826,774, 1989.
237. E. Buss, C. E. Anderson, M. K. Pomije, C. M. Lutz, D. Britton and K. R. Mann, *J. Am. Chem. Soc.*, 1998, **120**, 7783–7790.
238. W. Grate, L. K. Moore, D. E. Janzen, D. J. Veltkamp, S. Kaganove, S. M. Drew and K. R. Mann, *Chem. Mater.*, 2002, **14**, 1058–1066.
239. E. Buss and K. R. Mann, *J. Am. Chem. Soc.*, 2002, **124**, 1031–1039.
240. J. Grove, J. M. Rennekamp, H. Jude and W. B. Con, *J. Am. Chem. Soc.*, 2004, **126**, 1594–1595.
241. J. Grove, A. G. Oliver, J. A. Krause and W. B. Connick, *Inorg. Chem.*, 2008, **47**, 1408–1410.
242. P. Du, J. Schneider, W. W. Brennessel and R. Eisenberg, *Inorg. Chem.*, 2008, **47**, 69–77.
243. A. Luquin, C. Bariain, E. Vergara, E. Cerrada, J. Garrido, I. R. Matias and M. Laguna, *Appl. Organomet. Chem.*, 2005, **19**, 1232–1238.
244. E. J. Fernández, J. M. López-de-Luzuriaga, M. Monge, M. Montiel, M. E. Olmos, J. Pérez, F. Mendizabal, A. A. Mohamed and J. P. Fackler Jr., *Inorg. Chem.*, 2004, **43**, 3573–3581.
245. C. Di Natale, R. Paolesse and A. D'Amico, *Sens. Actuator. B Chem.*, 2007, **121**238–46.
246. J. Wang, Z. Luthey-Schulten and K. S. Suslick, *Proc. Natl. Acad. Sci. USA*, 2003, **100**, 3035.
247. S. Suslick and N. A. Rakow, *Nature*, 2000, **406**, 710.
248. (a) *US Pat.*, 6,368,558, 2002; (b) S. Suslick, N. A. Rakow and N. A. Sen, *US Pat.*, 6,495,102, 2002.
249. R. Matsushima, N. Nishimura, K. Goto and Y. Kohno, *Bull. Chem. Soc. Jpn.*, 2003, **76**, 1279–1283.
250. C. Elosua, I. R. Matias, C. Bariain and F. J. Arregui, *Sensors*, 2006, **6**, 1440–1465.
251. C. Bariain, I. R. Matias, C. Fdez-Valdivielso, C. Elosua, A. Luquin, J. Garrido and M. Laguna, *Sens. Actuator. B Chem.*, 2005, **108**, 535–541.
252. C. Elosua, C. Bariain, I. R. Matias, A. Rodfriguez, E. Colacio, A. Salinos-Castillo, A. Segura-Carretro and A. Fernandez-Gutierrez, *Sensors*, 2008, **8**, 847–859.

253. S. M. Drew, D. E. Janzen and K. R. Mann, *Anal. Chem.*, 2002, **74**, 2547–2555.
254. K. S. Suslick, N. A. Rakow and A. Sen, *Tetrahedron*, 2004, **60**, 11133–11138.
255. K. S. Suslick, D. P. Bailey, C. K. Ingison, M. Janzen, M. E. Kosai, W. B. McNamara, N. A. Rakow, A. Sen, J. J. Weaver, J. B. Wilson, C. Zheng and S. Nakagakii, *Quim. Nova*, 2007, **30**, 677–681.
256. M. C. Janzen, J. B. Ponder, D. P. Bailey, C. K. Ingison and K. S. Suslick, *Anal. Chem.*, 2006, **78**, 3591–3600.
257. (a) P. J. Mazzone, J. Hammel, R. Dweik, J. Na, C. Czich, D. Laskowski and T. Mekhail, *Thorax*, 2007, **62**, 565–568; (b) www.chemsensing.com.
258. Z. V. Todres, *Organic Mechanochemistry and Its Practical Applications*, CRC Press, Boca Raton, FL, 2006.
259. M. Taran, K. Langer and M. Koch Müller, *Phys. Chem. Minerals*, 2008, **35**, 175–177.
260. P. V. Kamat and K. Vinodgopal, *Langmuir*, 1996, **12**, 5739–5741.
261. A. Samat and R. Guglielmetti, *Chromogenic Materials, Piezochromic, Kirk-Othmer Encyclopaedia of Chemical Technology*, Wiley-VCH, vol. **6**, 2004.
262. R. W. Carpick, D. Sasaki, M. S. Marcus, M. A. Eriksson and A. R. Burns, *J. Phys.: Condens. Matter*, 2004, **16**, R679–R697.
263. M. LeClerc, in *Handbook of Conducting Polymers*, ed. T. A. Skotheim, J. R. Reynolds and R. L. Elsenbaumer, Marcel-Dekker, New York, 2nd edn., 1997, pp. 695–706.
264. K. Yoshino, S. Nakajima, M. Onada and R. Sugimoto, *Synth. Met.*, 1989, **28**, C349.
265. T. Sato, T. Yagi, H. Tajima, T. Fukuda and T. Yamamoto, *React. Funct. Polym.*, 2008, **68**, 369–363.
266. D. Takagi, K. Noda and S. Itoh, *Platinum Metals Rev.*, 2004, **48**, 117–124.
267. M. A. Asiri, H. G. Heller, M. B. Hursthouse and A. Karalulov, *Chem. Commun.*, 2000, 799–800.
268. (a) P. L. Gentili, M. Nochetti, C. Miliani and G. Favaro, *New J. Chem.*, 2004, **28**, 379–386; (b) T. Muzuguchi, N. Tanifuji and K. Kobayashi, *J. Phys. Chem., B*, 2003, **107**, 12635–12638.
269. (a) *US Pat. Appl.*, 2007/0259286, 2007; (b) *US Pat. Appl.*, 2006/0286049, 2006; (c) *US Pat.*, 7,261,680, 2007.
270. (a) *US Pat. Appl.*, 2006/0235086, 2006; (b) *US Pat. Appl.*, 2006/037375, 2006.
271. S. H. Foulger, P. Jiang, A. Lattam, D. W. Smith, J. Ballato, D. E. Dausch, S. Grego and B. R. Stoner, *Adv. Mater.*, 2003, **15**, 685–689.
272. H. Langhals, *Helv. Chim. Acta.*, 2005, **88**, 1309.
273. T. Katoh, Y. Inagaki and R. Okazaki, *J. Am. Chem. Soc.*, 1998, **120**, 3623.
274. E. Arunkumar, A. Ajayaghosh and J. Daub, *J. Am. Chem. Soc.*, 2005, **127**, 3156.
275. (a) J. Kunzelmann, B. R. Crenshaw, M. Kinami and C. Weder, *Macromol. Rapid Comm.*, 2006, **27**, 1981; (b) J. Kunzelmann, B. R. Crenshaw and C. Weder, *J. Mater. Chem.*, 2007, **17**, 2989; (c) B. R. Crenshaw, J.

Kunzelmann, C. E. Sing, C. Ander and C. Weder, *Macromol. Chem. Phys.*, 2007, **208**, 572; (d) J. Kunzelmann, T. Chung, P. T. Mather and C. Weder, *J. Mater. Chem.*, 2008, **18**, 1082.

276. T. Kobayashi (ed.), *J-Aggregates*, World Scientific, 1996.
277. D. Moebius, *Adv. Mater.*, 1995, **7**, 437.
278. Google search on 1.8.08 had *ca.* 3990 hits for PIC alone, the majority on its spectroscopy.
279. D. Guelen and S. Ozcelik, *J. Luminescence*, 2008, **128**, 834.
280. L. Daehne and E. Biller, *Phys. Chem. Chem. Phys.*, 1999, **1**, 1727.
281. P. J. Camp, A. C. Jones, R. K. Neely and N. M. Speirs, *J. Phys. Chem. A*, 2002, **106**, 10725–10732.
282. S. Yagai, T. Seki, T. Karatsu, A. Kitamura and F. Wuerthner, *Angew. Chem., Int. Ed. Engl.*, 2008, **47**, 3367.
283. F. Wuerthner, C. Bauer, V. Stepanenko and S. Yagai, *Adv. Mater.*, 2008, **20**, 1695.
284. G. Klebe, F. Graser, E. Haedicke and J. Berndt, *Acta Crystallogr.*, 1989, **B45**, 69.
285. P. M. Kazmaier and R. Hoffmann, *J. Am. Chem. Soc.*, 1994, **116**, 9684.
286. (a) T. Goto and T. Kondo, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 17–33; (b) T. Kondo, K. Yoshida, A. Nakagawa, T. Kawai, H. Tamura and T. Goto, *Nature*, 1992, **358**, 515.
287. S. Fukada-Tanaka, Y. Inagaki, T. Yamaguchi, N. Saito and S. Iida, *Nature*, 2000, **407**, 581.
288. G. A. Ellestad, *Chirality*, 2006, **18**, 134.
289. (a) S. Gonzalez-Manzano, C. Santos-Buelga, M. Duenas, J. C. Rivas-Gonzalo and T. Escribano-Bailon, *Eur. Food Res. Technol.*, 2008, **226**, 483; (b) M. J. Birse, The colour of red wine, http://digital.library.adelaide.edu.au/dspace/bitstream/2440/42834/1/02whole.pdf; (c) M. Rein, Copigmentation reactions and color stability of berry anthocyanins, http://ethesis.helsinki.fi/julkaisut/maa/skemi/vk/rein/copigmen.pdf.
290. M. Cianci, P. J. Rizkallah, A. Olczak, J. Raftery, N. E. Chayen, P. F. Zagalsky and J. R. Helliwell, *Proc. Natl. Acad. Sci.*, 2002, **99**, 9795.
291. B. Durbeej and L. A. Eriksson, *Phys. Chem. Chem. Phys.*, 2006, **8**, 4053.
292. G. Bartalucci, J. Coppin, S. Fisher, G. Hall, J. R. Helliwell, M. Helliwell and S. Liaaen-Jensen, *Acta Crystallogr.*, 2007, **B63**, 328.
293. S. Liaaen-Jensen and G. Kildahl-Andersen, *Arkivoc*, 2008, **6**, 5.
294. Polaroid Corporation, *US Pat.*, 6,951, 952, 2005; (b) Polaroid Corporation, *US Pat.*, 7,008,759, 2006.
295. www.zink.com.
296. *Eur. Pat.* 298839, 1987.
297. Mahbih Kako, *Jap. Pat.*, 05059312, 1991.
298. (a) www.solarsafe.com; (b) www.sunhealthsolutions.com (March 2009).
299. A. Mills, K. McDiarmid, M. McFarlane and P. Grosshans, *Chem. Commun.*, 2009, 1345–1346.
300. General Electric, *US Pat.*, 6,511,728, 2005.

301. Flexplay Technologies, *US Pat.*, 6,537, 635, 2003 and *US Pat.*, 6,839,316, 2006.
302. www.flexplay.com.
303. Xerox Corporation, *US Pat.*, 7,300,727, 2007.
304. Radiochromic film dosimetry, *Med. Phys.*, 1998, **25**, 2093–2115.
305. www.gafchromic.com.
306. J. Hueng, M. Wang, J. Zho, N. Gao and Y. Li, *Appl. Radiat. Isot.*, 2001, **54**, 475–81.
307. J. Choi, J. D. Woodward, J. L. Musfeldt, X. Wei, M. H. Whangbo, J. He, R. Jin and D. Mandrus, *Phys. Rev.*, 2004, **B70**, 085107.
308. J. Ge, Y. Hu and Y. Yin, *Angew. Chem., Int. Ed. Engl.*, 2007, **46**, 7428–7431.
309. D. Charych, in *Biosensors and Their Applications*, ed. V. C.-M. Yang, V. C. Yang and T. Ngo, Springer, Berlin, 2000.
310. R. Jelinek and S. Kolusheva, *Biotechnol. Adv.*, 2001, **19**, 109–118.
311. B. Ma, Y. Fan, L. Zhang, X. Kong, Y. Li and J. Li, *Colloids Surf. B, Biointerfaces*, 2003, **27**, 209–213.
312. K. Faid and M. LeClerc, *Chem. Commun.*, 1996, 2761–2762.
313. Colorimetric Glycothiophene Biosensors, *US Pat.*, 6.660,484, 2003 and references therein.
314. K. Nassau, *The Physics and Chemistry of Colour*, John Wiley and Sons, Chichester, 2nd end., 2001, p. 157.
315. C. J. Murphy, A. M. Gole, S. E. Hunyadi, J. W. Stone, P. N. Sisco, A. Alkilany, B. E. Kinard and P. Hankins, *Chem. Commun.*, 2008, 544–557.
316. S. K. Ghosh and T. Pal, *Chem. Rev.*, 2007, **107**, 4797–4862.
317. M.-C. Daniel and D. Astruc, *Chem. Rev.*, 2004, **104**, 293–346.
318. H. Wang, D. W. Brandl, P. Nordlander and N. J. Halas, *Acc. Chem. Res.*, 2007, **42**, 53–62.
319. A. J. Haes, D. A. Stuart, S. Nie and R. P. Van Duyne, *J. Fluorescence*, 2004, **14**, 355–367.
320. M. Hu, J. Chen, Z.-Y. Li, L. Au, G. V. Hartland, X. Li, M. Marquez and Y. Xia, *Chem. Soc. Rev.*, 2006, **35**, 1084–1094.
321. B. Wiley, Y. Sun and Y. Xia, *Acc. Chem. Res.*, 2007, **40**, 1067–1076.
322. K. G. Thomas and P. V. Kamat, *Acc. Chem. Res.*, 2003, **36**, 888–898.
323. R. Shenhar and V. M. Rotello, *Acc. Chem. Res.*, 2003, **36**, 549–561.
324. E. Willner and E. Katz, *Angew. Chem., Int. Ed. Engl.*, 2004, **43**, 6042–6108.
325. S. Eustis and M. A. El-Sayed, *Chem., Soc. Rev.*, 2006, **35**, 209–217.
326. J. Shan and H. Tenhu, *Chem. Commun.*, 2007, 4580–4598.
327. B. L. V. Prasad, C. M. Sorensen and K. J. Klabunde, *Chem. Soc. Rev.*, 2008, **37**, 1871–1883.
328. H. Fan, *Chem. Commun.*, 2008, 1383–1394.
329. Y. Ofir, B. Smanata and V. M. Rotello, *Chem. Soc. Rev.*, 2008, **37**, 1825.
330. S.-H. Wu, Y.-S. Wu and C.-H. Chen, *Anal. Chem.*, 2008, **80**, 6560–6566.

331. J.-M. Lehn, J. L. Atwood, J. E. D. Davies, D. D. MacNicol and F. Vögtle (ed.), *Comprehensive Supramolecular Chemistry*, Elsevier, Amsterdam, 1996.
332. N. L. Rosi and C. H. Mirkin, *Chem. Rev.*, 2005, **105**, 1547–1562.
333. J.-M. Nam, K.-J. Jang and J. T. Groves, *Nature Protocols*, 2007, **2**, 1438–1444.
334. A. J. Haes, L. Chang, W. L. Klein and R. P. Van Duyne, *J. Am. Chem. Soc.*, 2005, **127**, 2264–2271.
335. C. Sonnichsen, B. M. Reinhard, J. Liphardt and A. P. Alivisatos, *Nature Biotechnol.*, 2005, **23**, 741–745.
336. J. N. Anker, W. P. Hall, O. Lyandres, N. C. Shah, J. Zhao and R. P. Van Duyne, *Nature Mater.*, 2008, **7**, 442–453.
337. R. Wilson, *Chem. Soc. Rev.*, 2008, **37**, 2028–2045.
338. www.nanosphere.us.
339. www.advnt.org.
340. www.tetracore.com.
341. www.bioassayworks.com.
342. www.bbigold.com.
343. www.bio-rad.com.
344. www.scien-tec.com.
345. www.nanopartz.com.
346. M. J. Richardson and J. H. Johnston, *J. Colloid Interface Sci.*, 2007, **310**, 425–430.

CHAPTER 2

Phenomena Involving the Absorption and Reflectance of Light

2.1 Introduction

Not surprisingly, when the general public are asked to talk about colour outside of Nature, they immediately refer to the coloured items they experience in their daily activities. This can be the colour of the decorations in their home or work environments, the clothing they wear, in the cosmetics they use, their hair colour, the cars that they drive, in the coloured images filling the magazines they read or in any other form of hard copy that comes into their hands, such as photographs and greetings cards, or in the visual images on advertising billboards strung along our urban roadsides, on TV, at the cinema or on computer screens, mobile phones or MP3 players. With the notable exceptions of some luminescent materials, lighting and video images (see Chapter 3), dyes and pigments are the materials used to produce the colours that make an impact on our everyday existence. Consequently, the production of dyes and pigments is by far the largest commercial activity in colour chemistry. In the year 2007 the world production of organic dyes and pigments was approximately 1.5 million metric tons, valued at US$ 13.3 bn, with dyes contributing US$ 7.7 bn and organic pigments US$ 5.6 bn. The value of inorganic pigments was US$ 14.7 bn, heavily dominated by the very large volume iron oxide pigments.

The application areas for dyes and pigments are very varied covering the coloration of textile fibres, paper, leather and plastics, in paint and coatings, in printing inks, in cosmetics, toiletries and hair coloration, in conventional photography, in digital imaging colorants and toners, in the coloration of food and beverages, and in glass and ceramics.

Over the years many detailed texts covering this very important technological area have been produced, but most are now out of print and only available in specialised libraries.[1] For those readers requiring more in-depth

Chromic Phenomena: Technological Applications of Colour Chemistry, Second Edition
By Peter Bamfield and Michael G. Hutchings

Published by the Royal Society of Chemistry, www.rsc.org

information on any particular area, some of the relevant and more recent publications which are likely to be available in libraries or are still in print are listed as source references.[2] [12] The student seeking a broad overview of the area would be advised to consult the textbooks from Christie *et al.*[13]

However, for anybody wishing to work in any area of colour, an understanding of the chemistry and technological applications of dyes and pigments is essential, as these colorants have an impact on most of the other chromic phenomena described in this book, even where their absorption of light does not play a primary role.

2.2 Some Elements of Colour Physics Relating to Colorants

The particular colour which we see from objects coloured with dyes and pigments arises from the absorption and selective reflection and transmission of light from the materials containing the colorants into our eyes, there to be received by the photoreceptors and interpreted by the brain, a subject in its own right.[14]

2.2.1 Additive Colour Mixing

White light is composed of the additive primary colours of red, green and blue. These primary colours cannot be made by mixing any of the other two together. Mixing light of two of these primary colours in equal proportions produces other colours; red plus blue gives magenta, red plus green gives yellow, whilst blue plus green gives cyan.

The process by which the colour of a surface is observed is shown schematically in Figure 2.1. White light strikes a surface and is selectively absorbed by the colorant (the green component in this case); the non-absorbed components of the light (red and blue) are reflected and enter the eye to produce the observer's interpretation of the surface's colour (purple/magenta). In the same way, yellow is the colour observed when blue is absorbed and red and green light reflected, cyan when red is absorbed and blue and green reflected. In practice, some of the non-absorbed light enters below the immediate surface, becomes refracted and then scattered on interaction with particles in the body of the surface, before being reflected back, thus modifying the appearance of the coloured surface.

When visible spectral light is split in a prism or other dispersion medium such as water droplets, the perceived range of colours covers the total visible spectrum, as shown in Table 2.1. The overlap of the various regions on absorption and reflectance on a surface is the reason why the whole spectrum of colours can be seen by the eye (see also Table 2.2).

Additive colour mixing applies to the combination of light beams and is therefore the system employed in colour televisions and other visual display systems (see Chapter 3).

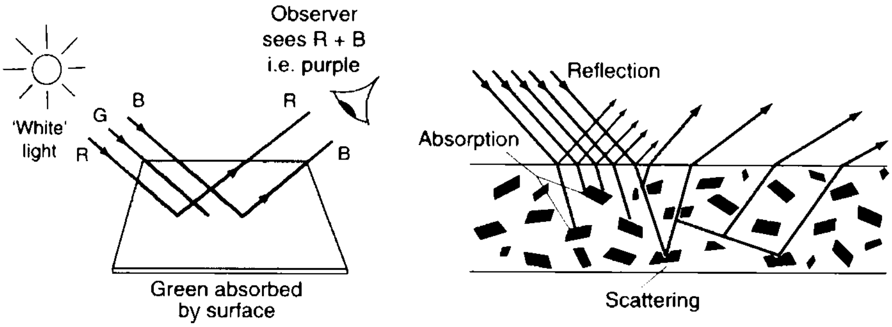


Figure 2.1 Absorption and reflectance of light on a surface[16] (reproduced with permission of the Society of Dyers and Colourists).

Table 2.1 The colours perceived on dispersion of visible light.

Perceived colour	*Wavelength, nm*
Violet	380 400
Indigo	400 435
Blue	435 480
Greenish blue	480 490
Bluish green	490 500
Green	500 560
Yellow green	560 580
Yellow	580 595
Orange	595 605
Red	605 740

Table 2.2 Relationship between light absorbed and observed hue.

Region of light absorption		*Principal hue observed*
Wavelength, nm	*Colour*	
400 430	Violet blue	Yellow
430 470	Blue	Orange
470 500	Blue green	Orange red
500 540	Green	Red purple
540 570	Yellow green	Purple
570 590	Yellow	Violet
590 610	Orange	Blue
610 700	Orange red	Greenish blue

2.2.2 Subtractive Colour Mixing

Subtractive colour mixing, with the primaries of yellow, magenta and cyan (or, less precisely, yellow, red and blue), is used to produce the vast range of colours available in the area of dyes and pigments.

Colour technologists actually use three visual characteristics to describe the general characteristics of dyed or pigmented materials:

1. Hue;
2. Strength or depth;
3. Brightness or dullness.

The accepted definitions of these characteristics, which will be used in this text, are those established by the Society of Dyers and Colourists.[15]

- Hue: that attribute of colour whereby it is recognised as being predominantly red, green, blue, yellow, violet, brown, *etc.*
- Strength (of a dye): the colour yield of a given quantity of dye in relation to an arbitrarily chosen standard (of a dyeing or print) synonymous with depth.
- Depth: that colour quality an increase in which is associated with an increase in the quantity of colorant present, all other conditions (such as viewing conditions) remaining the same.
- Dullness (of a colour): that colour quality an increase in which is comparable to the effect of the addition of a small quantity of a neutral grey, whereby a match cannot be made by adjusting the strength.
- Brightness; the converse of dullness.

The exact hue of a single compound dye, and therefore ultimately any mixture with another compound, depends on its absorption characteristics, *i.e.* both the wavelength (λ_{max}) and the absorption coefficient (ε_{max}) or height at the absorption maximum, but also of importance is the shape and size (the bandwidth) of the area under the curve. The observed hues given in Table 2.2 are due to the wavelengths of light not absorbed.

Idealised positions of absorption for yellow, orange, red, violet and blue colorants are shown in Figure 2.2. A single compound green colorant absorbs in the yellow and blue regions. Greys and blacks are obtained by mixing the whole spectrum of colours in the correct proportions.

2.2.3 The CIE System

The problem of using words to describe the colour of a dye or pigment is that it is very subjective. People may be able to agree that a product is red, but what shade of red? It can be described as rose red or pillar-box red, representing cultural and social differences, and the arguments can be endless. Additionally the appearance of a colour can change in different circumstances, such as the surrounding colours and lighting conditions.

These difficulties are of great practical importance when trying to describe a colour that needs to be reproduced in a recipe by colour technologists in a dyehouse or a paint shop. To overcome this a standard system has been developed and refined over the years by the Commission International de

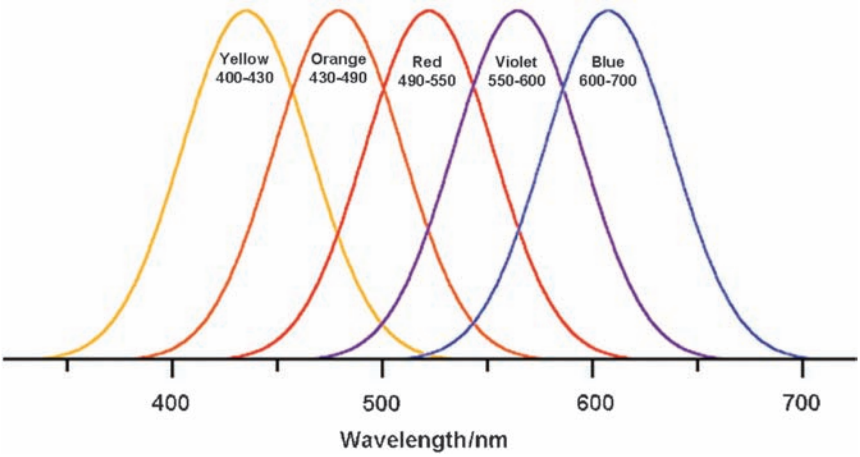


Figure 2.2 Idealised absorption spectra of single compound colorants.

L'Eclairage (CIE), the aim of which is to say how a particular colour might be reproduced by mixing the three red, green and blue primary light sources rather than trying to describe it in words. The CIE chromaticity diagram, or colour map as it is often called, is shown in Figure 2.3.

The system used by colorists in the dyes and pigments industry is the so-called CIELAB system. CIELUV is the system used in the display industries (Chapter 3). In this system the three-dimensional nature of colour space is taken into account: namely hue (the colour attributes), saturation (the absence of white, grey or black) and lightness (also called brightness). In CIELAB colour space the coordinate L* is a measure of lightness-darkness, where a perfect black is 0 (*i.e.* zero whiteness) and a perfect white is 100; a* correlates with red (+a*) and green (–a*); and b* with yellow (+b*) and blue (–b*) (Figure 2.4). Using these parameters a particular colour can be given a unique descriptor. For a detailed account of this and many other aspects of colour physics the reader is recommended to read the text edited by McDonald.[16]

2.3 Classical Organic Dyes

Until the middle of the nineteenth century, when William Perkin (1856) serendipitously discovered mauveine, the first synthetic dyestuff, all dyestuffs had been obtained from natural sources.[17] Perkin's discovery sparked a major revolution in the dyeing industry and, over the ensuing few decades, a whole raft of new chromophores were discovered, laying the foundation for the first major industry based on the manufacture of complicated organic chemicals, the European dyestuffs and pigments industry.[18]

The invention of new man-made fibres and plastics in the middle of the twentieth century sparked a further surge in activity, as different products were required to dye or colour these new materials. Alongside the new ranges of

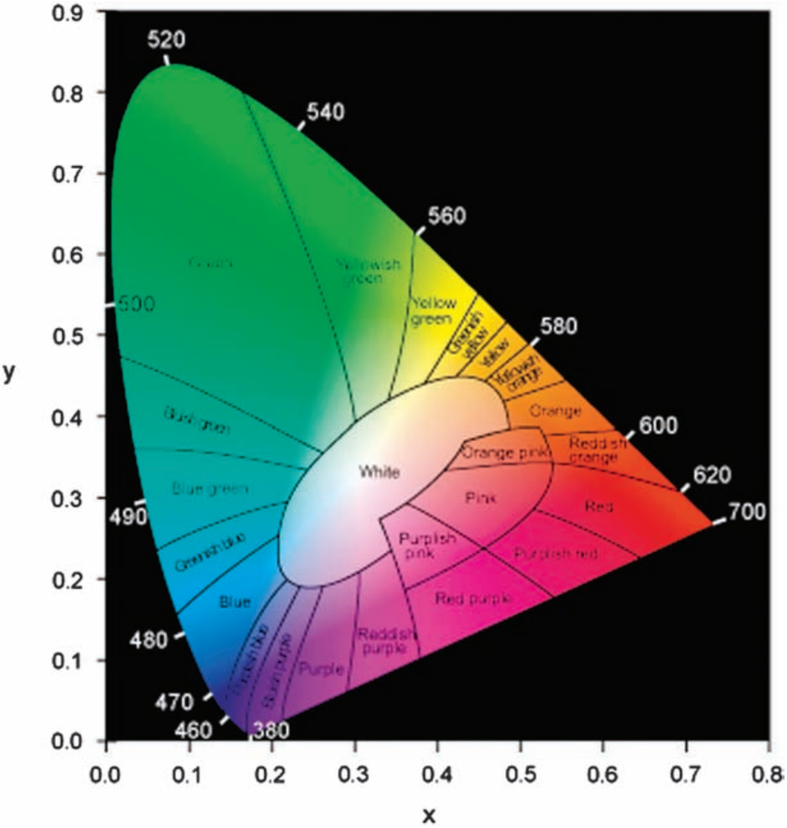


Figure 2.3 The CIE x, y chromaticity diagram.

colorants, new application methods were also being discovered, such as the reactive dyeing of cotton (see Section 2.3.2.1), again leading to increased research activity. The production of dyes and pigments had also changed beyond recognition, the old manually operated wooden vats and filter presses being replaced by enclosed vessels operated with computer controls. At the beginning of the twenty-first century, after 50–60 years of very intensive industrial research, the design, synthesis and application of synthetic dyes had reached such a level of sophistication that making new major advances was going to be very difficult, and so it has proved. Research and development, especially in the traditional dyestuffs industry, is aimed mainly at improving the performance of existing ranges to meet new consumer demands, reducing costs whilst satisfying increasingly stringent environmental targets and legislation, or in applying colorants to new or expanding outlets, such as digital imaging, displays and areas covered in the other chapters of this book. Natural dyestuffs have not gone away, in fact there has been an upturn in their fortunes. Consumer demand has risen for the use of natural materials in cosmetics and in the dyeing of some fashion garments made from natural fibres such as wool and

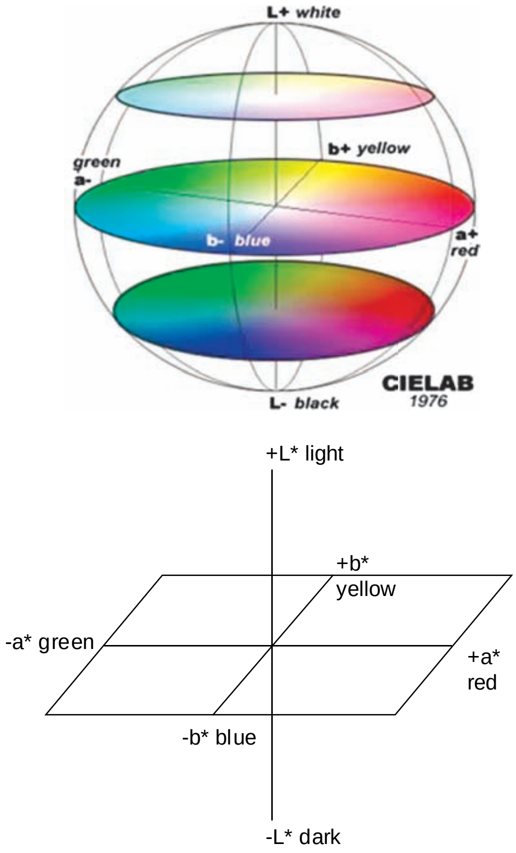


Figure 2.4 The CIE L* a* b* colour space (CIELAB).

cotton, and leather goods, being perceived as "greener" and "safer" by a section of the environmental lobby. Legislation has been tightened up on the products that can be used in the coloration of food and drinks, leading to an increase in the use of natural colorants. However, they still represent currently only a very small percentage of world dyestuff and colorant usage.

The main differentiating performance characteristic between dyestuffs and pigments is solubility. During their application, dyestuffs are solubilised, either in the medium or in the fibre and hence lose any particular aspect of their crystal structure or physical form. Pigments, on the other hand, remain practically insoluble during their application processes, thus retaining aspects of their morphology, which are of importance to both their colour and performance.

2.3.1 Structural Classes

Many dyes and pigments share the same basic chromogenic structure, dyes being differentiated by either physical size of the molecule or by the presence of solubilising groups, such as sulfonic acid and quaternary ammonium groups. The main chromogens used in dyestuffs are azos, anthraquinones (including polycyclic quinones), indigoids, polymethines (cyanines), phthalocyanines, and aryl carboniums (*e.g.* triarylmethanes). To be strictly accurate the term chromogen should be used for the coloured molecular structure, reserving chromophore for the colourless, unsaturated building blocks of colour: –N=N–, CO_2R, NO_2 groups *etc.*[19] However, it is very common in the dyestuff literature for the term chromophore to be used more loosely, applying it to cover the whole of the coloured molecular systems comprising the building blocks plus the conjugated systems linking them together.

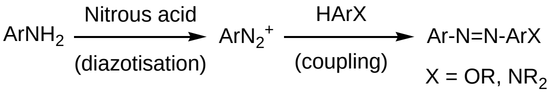
The theoretical interpretation of the origin of colour in organic chromophores is covered in detail in the specialised texts on colorants and interested readers should refer to these.[2,19]

2.3.1.1 Azo Dyestuffs

Azo dyestuffs, those chromogens containing one or more chromophoric –N=N– groups, are by far the most commercially important group of dyestuffs, manufactured on a very large scale and used in most application areas. They are synthesised by treating an aromatic amine (called the diazo component) with nitrous acid (called diazotisation) and then reacting (called coupling) the so-formed diazonium salt derivative with an aromatic or heteroaromatic phenol, amine or an active methylene group (called the coupling component) to produce a monoazo dye (Figure 2.5).

If the monoazo dye contains an amino group, this can be further diazotised and coupled to give a disazo dyestuff. Alternatively, if the monoazo contains an amino or a hydroxy group, then a second diazonium salt can be coupled on to produce the disazo dyestuff. A symmetrical disazo dyestuff can be produced from a diamine, by diazotising both amino groups (tetrazotisation) and then carrying out the coupling onto two molecules of a phenol or amine. These processes can be repeated to give tri- and tetrazo dyestuffs, by a variety of these and other combinations. Some of these routes are shown schematically in Figure 2.6, following a long-standing convention of naming used in the dyes industry.[20]

Five commercial dyestuffs, a monoazo CI Disperse Blue 82 (2.1), an unsymmetrical disazo CI Acid Blue 116 (2.2), a symmetrical disazo CI Reactive Black 5 (2.3), a trisazo CI Direct Blue 78 (2.4) and a disazo formed from two monazos linked *via* a bridging group CI Direct Yellow 132 (2.5) demonstrate products in each class. (Note: sulfonic acids $-SO_3H$ in dyes almost invariably exist in the form of a salt, usually the alkali metal salt.)



$$ArNH_2 \xrightarrow[\text{(diazotisation)}]{\text{Nitrous acid}} ArN_2^+ \xrightarrow[\text{(coupling)}]{\text{HArX}} \text{Ar-N=N-ArX} \quad X = OR, NR_2$$

Figure 2.5 Diazotisation and coupling to give azo dyes.

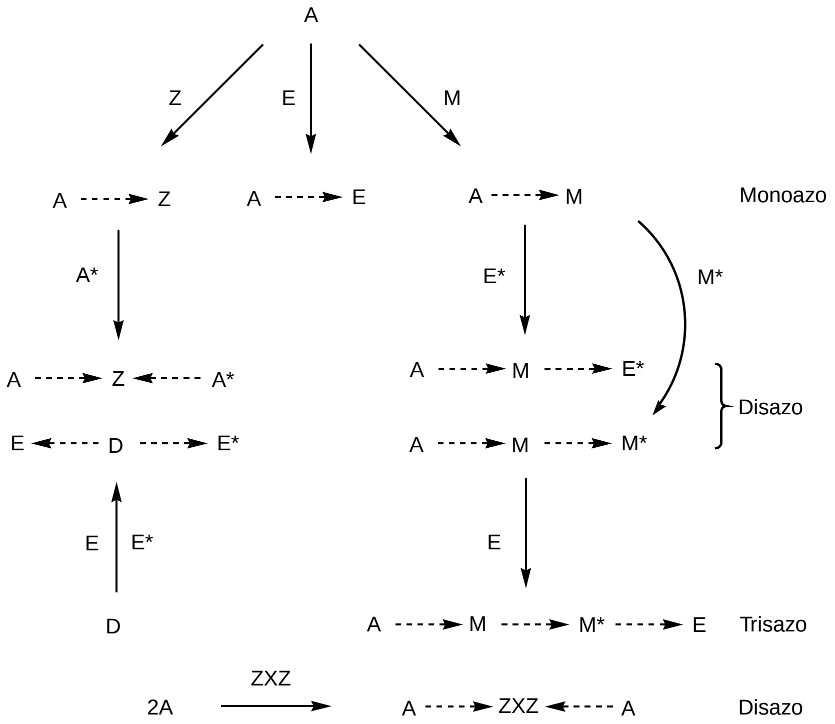
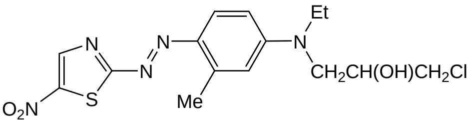
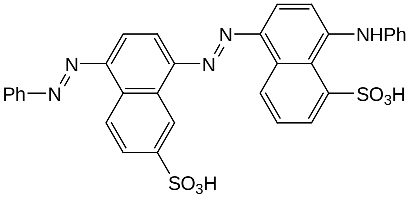


Figure 2.6 Schematic representation of routes to mono , bis and tris azo dyestuffs. Symbols: A is amine to be diazotised (also A*); E is end coupling component (*i.e.* terminal group) (also E*); D is a diamine that can be diazotised twice (tetrazotised); M is an amine that can be first coupled with A and then diazotised (also M*); Z is a coupling component that can couple twice with the same or different diazo components; ZXZ as for Z but with X as a bridging group. Dotted arrow is N=N (azo) group.



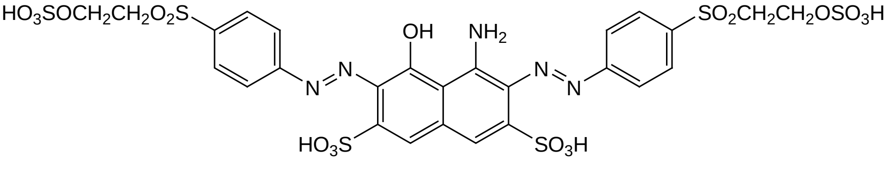
(2.1)

$A \dashrightarrow E$



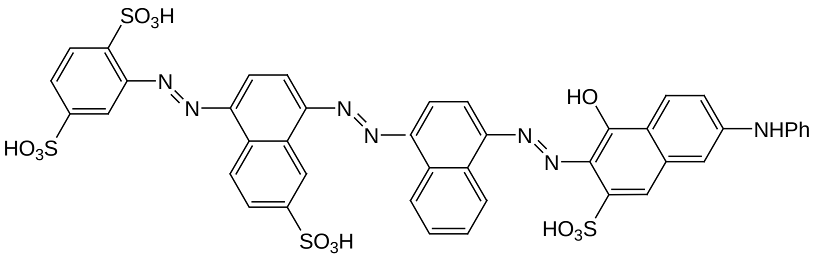
(2.2)

$A \dashrightarrow M \dashrightarrow E$



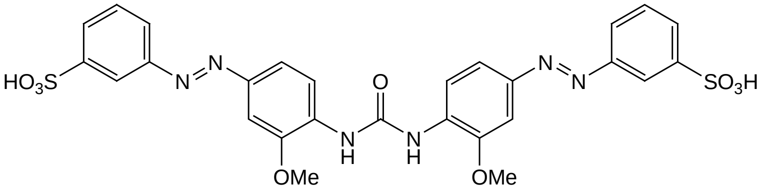
(2.3)

$A \dashrightarrow Z \dashleftarrow A$



(2.4)

$A \dashrightarrow M \dashrightarrow M^* \dashrightarrow E$



(2.5)

$A \dashrightarrow ZXZ \dashleftarrow A$

The nomenclature given for these compounds is a universally recognised system for the naming of dyestuffs devised by the Society of Dyers and Colourists as part of their Colour Index (CI).[20] The CI Generic Name is made up of the application class, the hue and a number. Acid dyes are used on wool and polyamide, direct dyes on cellulosic fibres, paper and leather, disperse dyes on polyester fibres, reactive dyes on cellulosic fibres and basic dyes on polyacrylonitrile and paper.

Colour and Structure. The azo chromogen is one of the many that can be described as falling within the donor–acceptor class. The donor–acceptor system is exemplified in Figure 2.7 by a simple monoazo dye, CI Disperse Red 1, to illustrate the point. The donor part of the molecule, as its name implies, contains donor groups such as amino and alkylamino, hydroxy and alkoxy. Conversely, the acceptor part contains electron acceptor groups such as nitro, cyano, *etc*. These donor and acceptor groups may be attached to either aromatic or heteroaromatic rings, as in CI Disperse Blue 82 (2.1).

Basically the more electron withdrawing the acceptor part and the more electron donating the donor half, the more bathochromic is the resultant dyestuff. Electron acceptors have a greater effect when *ortho* or *para* to the azo linkage, whilst in the other ring donors in the *para* position are most influential, but extra donors *ortho* and *meta* to the azo linkage also have a strong influence. Examples are given in Table 2.3 for a *para*-diethylamino donor dye. The effect

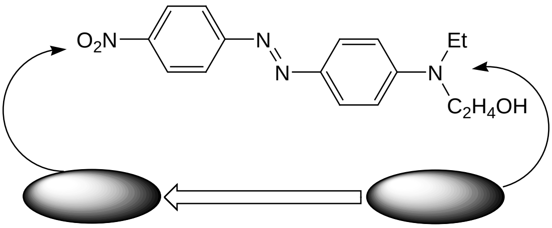
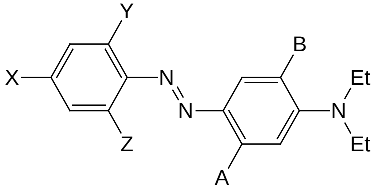


Figure 2.7 Donor acceptor azo chromphore.

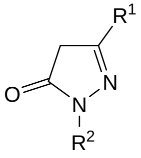
Table 2.3 Influence of substituents on colour of monoazo dyes.



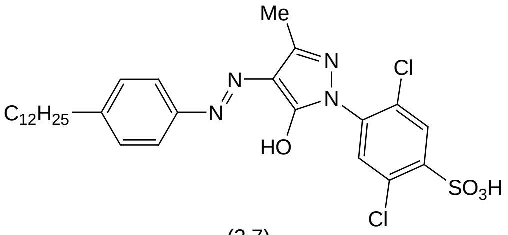
X	*Y*	*Z*	*A*	*B*	λ_{max}, *nm(EtOH)*	ε_{max}
Cl	H	H	H	H	422	26700
CN	H	H	H	H	466	32700
NO_2	H	H	H	H	486	34000
NO_2	H	H	OMe	H	501	32000
NO_2	H	H	H	OMe	488	22600
NO_2	H	H	NHAc	H	511	47000
NO_2	H	H	NHAc	OMe	530	32600
NO_2	NO_2	H	NHAc	H	543	
NO_2	NO_2	Br	NHAc	OMe	608	
NO_2	NO_2	CN	NHAc	H	613	
NO_2	CN	CN	NHAc	H	619	

of substituents on the colour of azo dyes is often constant and additive, leading to the production of tables of substituent increments for azobenzene dyes.[21] It should be remembered that arylazo dyes show strong solvatochromic effects (Chapter 1, Section 1.7.2) and comparisons of their absorption spectra should only be from measurements made in solvents of the same or very similar properties.[22]

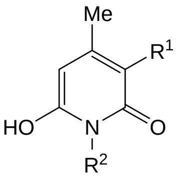
The main aromatic amines used as diazo components are substituted anilines or naphthylamines and the coupling components substituted *N*-alkylanilines, phenols, naphthylamines and naphthols. Heteroaromatic diazo and coupling components are widely used in commercial azo dyestuffs. The main heterocyclic coupling components are pyrazolones (2.6) and especially pyridones (2.8), used to produce bright yellow and orange monoazo dyes, such as CI Acid Yellow 72 (2.7) and CI Disperse Orange 139 (2.9).[23]



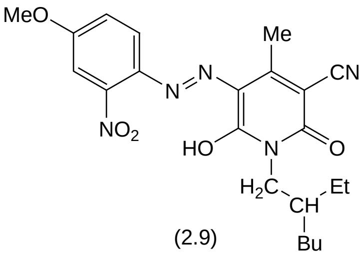
(2.6)
R^1 = alkyl, aryl, CO_2H
R^2 = aryl



(2.7)



(2.8)
R^1 = H, $CONH_2$, CN
R^2 = alkyl



(2.9)

Heterocyclic diazo components used in industry are based on five-ring heterocycles containing one sulfur and bearing a diazotisable amino group. These fall into the following four main groups:[24]

- (Benzo)thiazoles;
- (Benzo)isothiazoles;
- Thiadiazoles;
- Thiophenes.

The range of colours obtainable in monoazo dyes made by coupling representative derivatives of these amino heterocycles with *para*-coupling tertiary amines is shown in Figure 2.8. The diazo components from the thiazole and thiophene rings are especially important in the production of bright-blue azo dyes.[25]

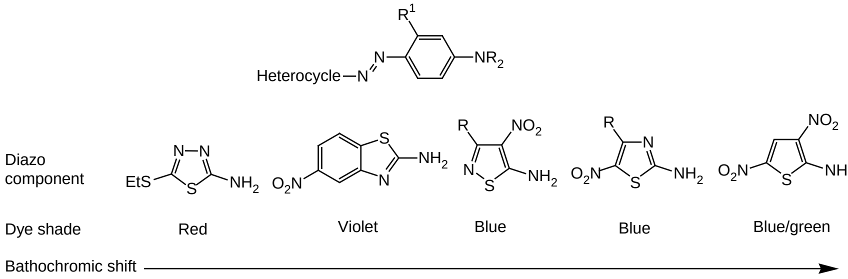
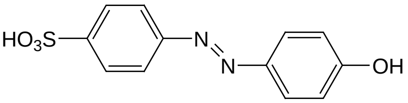


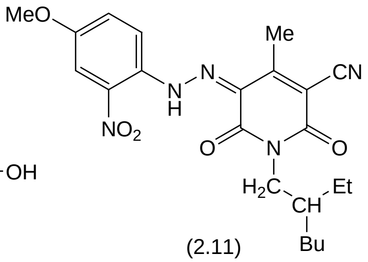
Figure 2.8 Shades obtainable in monoazo dyes from heterocyclic diazo components.

Tautomerism plays an important role in hydroxyazo dyes, having a marked influence on their tinctorial strengths and other properties crucial in a commercial dye, such as fastness to light. The hydroxy azo dyes can be grouped according to whether they exist predominantly in the azo form, predominantly in the hydrazone tautomeric form or as a mixture of both forms.

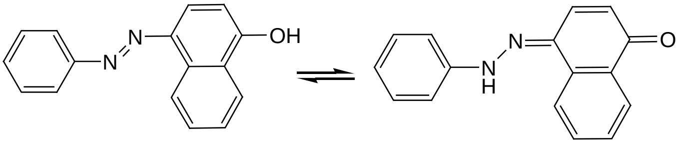
- All azo dyes made from phenols exist in the azo form (2.10).
- All azo dyes from all pyrazolones, pyridones and acetoacetanilides exist solely in the hydrazone form. Consequently (2.7) and (2.9) should be drawn in the hydrazone form *e.g.* (2.11).
- Both forms are present in 4-phenylazo-1-napthols; the hydrazone form is bathochromic relative to the azo form (2.12), and the proportion of each is dependent on substituents and solvent. Increasing solvent H-bond basicity moves the tautomeric equilibrium towards the azo form, whereas H-bond acidity stabilises the hydrazone. The hydrazone proportion, as measured using UV/Vis spectra, is pyridine ($15\,\text{cmol mol}^{1}$), acetone (30), ethanol (31), methanol (40), benzene (56), trichloromethane (79), acetic acid (89).[26]
- In both 2-phenylazo-1-naphthols and 1-phenylazo-2-naphthols the hydrazone forms predominate; hence in the literature they are often drawn in this form as shown for CI Reactive Black 5 (2.2) rewritten in the hydrazone form (2.13).



(2.10)



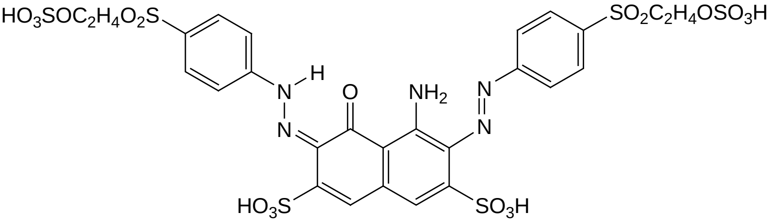
(2.11)



λ_{max} 410nm
ε_{max} 20,000

λ_{max} 480nm
ε_{max} 40,000

(2.12)



(2.13)

- All aminoazo dyes exist exclusively in the azo form as shown in (2.13). The various forms resulting from protonation of aminoazo dyes have already been discussed in Chapter 1 (Section 1.4.1.4).

Toxicology of Certain Azo Dyes. It has been known for over 100 years that certain amines used to manufacture synthetic dyes caused bladder cancer, especially 2-naphthylamine, benzidine and 4-aminobiphenyl. All the major dyestuff manufacturers abandoned the use of these amines in the production of dyes in the early 1970s.

However, since that time it has been recognised that the list of potentially carcinogenic amines is much longer and that these amines could actually be regenerated by metabolic (or chemical) reductive cleavage of those dyes incorporating these particular amines (Figure 2.9 for CI Acid Red 21).

Enzymatic reductive cleavage can occur *via* bacteria in the human gut or indigenously in some organs. Therefore there is a serious medical risk for those people who come into contact with such dyestuffs, for instance dye factory and textile dyeing workers, especially if improper handling and poor environmental standards are present. The German government banned firstly the handling of such dyes and subsequently extended it to cover their use in textile and other articles which come into prolonged contact with the skin. The German ordinance then formed the basis of law now operating throughout the EU, the relevant section being:[27]

> "The following may not be used in the commercial production or treatment of consumer goods that come into contact with human skin or mouth in normal everyday use. Azo dyestuffs, which, by cleavage of one or more azo groups, release the listed amines." (See Table 2.4.)

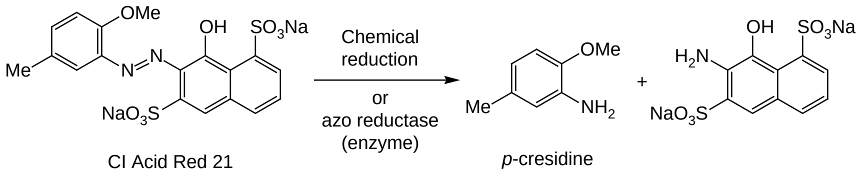


Figure 2.9 Reductive cleavage of azo dyes.

Table 2.4 Amines listed as not to be used in azo dyestuffs.

Listed amines
2 naphthylamine, 4 aminodiphenyl, 4 chloro 2 toluidine, benzidine
2,4,5 trimethylaniline, 2,4 diaminoanisol, 2,4 toluylenediamine
2 amino 4 nitrobenzene, 3,3′ dichlorobenzidine, 3,3′ dimethoxybenzidine
3,3′ dimethylbenzidine, 3,3′ 4,4′ diaminodiphenylmethane
4,4′ diaminodiphenylmethane, 4,4′ methylene bis (2 chloroaniline)
4,4′ oxydianiline, 4,4′ thiodianiline, 2 aminoazotoluene
2 toluidine, 4 chloroaniline, 4 cresidine
2,4 xylidine, 2,6 xylidine

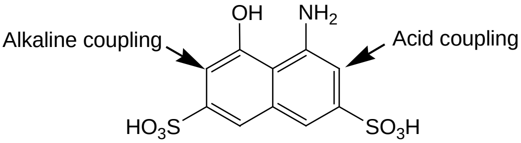
It should be noted that none of the major dyestuff manufacturers now make any of the dyestuffs which have these amines as diazo components. The new laws have also had a marked influence on dye makers in the major producing countries China and India, because they could not use these dyestuffs in consumer goods to be imported into the EU, a great benefit to workers in such countries. An up-to-date listing of tolerance levels for chemicals in the workplace is available.[28]

Synthesis of Azo Dyes. Processes to all the major benzene and naphthalene intermediates that are used in the commercial manufacture of azo dyes have been extensively reviewed.[8,29] Descriptions of the synthetic routes to heteroaromatic diazo components, such as those shown in Figure 2.8, are well covered in literature reviews,[24,30] as are all the major heterocyclic coupling components.[23]

The method used for the diazotisation of amines depends on the basicity of the amine group and the solubility or physical form of the compound.

The method that is employed for aniline and derivatives containing alkyl, alkoxy, halogen and no more than one nitro or cyano group, as well as similarly substituted naphthylamines, involves the use of sodium nitrite in aqueous hydrochloric acid. For weakly basic amines (anilines with polynitro groups *e.g.* 2,4-dinitro-6-bromoaniline), and also most heterocyclic amines, an alternative method must be adopted using nitrosylsulfuric acid.[31]

Coupling with amine coupling components is accomplished under acid conditions and with phenols or naphthols the reaction is carried out under alkaline conditions. If there are both amino groups and hydroxy groups in the molecule, *e.g.* the highly important intermediate H-Acid (2.14), coupling is first done in acid on the amino-substituted ring and then alkaline to react on the hydroxy ring.



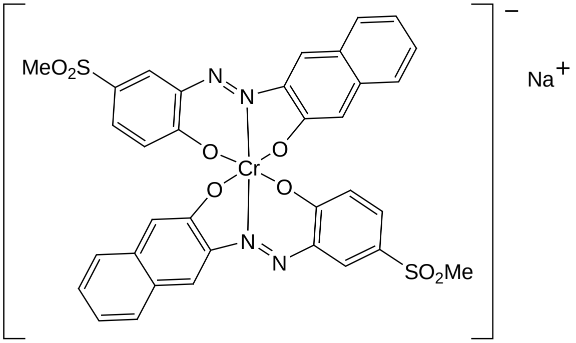
(2.14)

The azo dye is either formed as an insoluble precipitate and is filtered from the mixture or, if it contains solubilising groups such as sulfonate groups, is further precipitated by adding an electrolyte such as salt. Isolation *via* membrane technologies, especially reverse osmosis, is practised on commercial dyestuff plants.[8]

Further chemical reactions of azo dyes fall into three categories:

1. *Metal Complexation.* Azo dyes containing hydroxy or carboxylic acid substituents adjacent to the azo group react with transition metal ions, commonly chromium, cobalt and copper, to produce complexes such as CI Acid Violet 78 (2.15).[32,33] These metal complex dyes are more stable to light than their unmetallised precursors and have been widely used as

dyes for polyamide and wool fibres. However, there is now a move away from chromium complexes due to toxicity concerns (see Section 2.3.2.).



(2.15)

2. *Nucleophilic Substitution*. The copper catalysed replacement of halogen adjacent to the azo link by other nucleophiles is a commercial manufacturing process. Important blue disperse dyes *e.g.* CI Disperse Blue 165 and related dyes, are made by displacement of the bromo derivatives by cyanide, as shown in Figure 2.10.
3. *Further Functionalisation*. Molecular features required for the application of the dyes in a particular application are often added after the formation of the dye. The best examples are the groups required for the reactive dyeing of cellulosics and other fibres and the quaternisation of dyes used on polyacrylonitrile (see Section 2.3.2.1).

2.3.1.2 Cyclic and Polycyclic Quinones

The second most important group of chromogens in dyestuff chemistry are those bearing carbonyl groups, especially when part of the anthraquinone ring system. These ring systems are used mainly to produce bright-blue acid and reactive dyes; bright red and blue disperse dyes; and red, blue and green polycyclic quinone vat dyes. Anthraquinone, the pre-eminent ring system, was at one time entirely dominant in the bright red and blue disperse dye area, but this dominance has been challenged successfully by more cost-effective

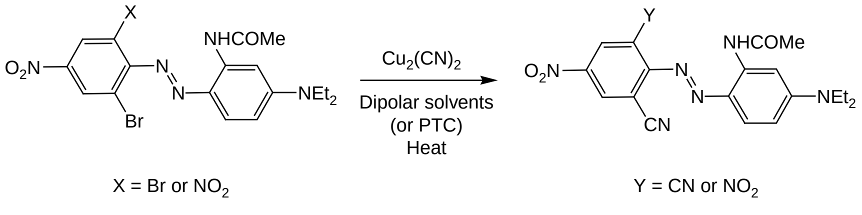
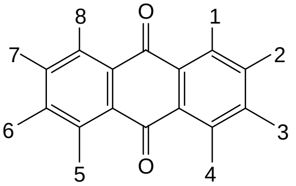


Figure 2.10 Nucleophilic displacement to give bright blue azo disperse dyes.

Table 2.5 Substituent effects in amino- and hydroxy-anthraquinones



1	*4*	*5*	*8*	*Colour*	λ_{max}, *nm (MeOH)*	ε_{max}
OH	OH	H	H	Orange	470	17,000
OH	H	OH	H	Yellow	425	10,000
OH	H	H	OH	Yellow	430	10,960
NH_2	NH_2	H	H	Blue	550	15,850
					590	15,850
NH_2	H	NH_2	H	Red	487	12,600
NH_2	H	H	NH_2	Red violet	507	10,000
NH_2	OH	H	H	Bluish red		
NH_2	OH	OH	NH_2	Violet	590	
NH_2	NH_2	NH_2	NH_2	Blue	610	

technological advances in azo dyes. There has also been a marked swing away from the vat dyeing of cellulosics to reactive dyeing (see Section 2.3.2.1).

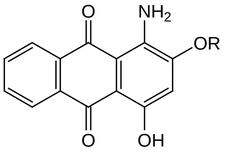
Anthraquinones. The important substitution patterns in anthraquinones are those adjacent to the 9,10 carbonyl groups (1,4-, 1,5-, 1,8- and 1,4,5,8-) as shown in Table 2.5, with further secondary substitution in the 2-, 3-, 7- and 8-positions. The order of the bathochromic shift caused by substituents in the 1-position is $OH < NH_2 < NHMe = NMe_2$, and the order in substitution patterns is $1,5 < 1,8 < 1,4 < 1,4,5,8$. Common substituents in the 2-position (and also 3, 6 or 8) are alkoxy, aryloxy, halogen and sulfonic acid.[34]

The main plus point commercially for anthraquinone dyes is that very bright red and blue dyes with good fastness properties, especially fastness to light, are available. An inherent disadvantage is their low tinctorial strength when compared with azo dyes; their extinction coefficients are less than half those observed with azo dyes of comparable shades (see Tables 2.3 and 2.5). This low tinctorial strength, together with the long synthetic routes involved in their manufacture, means that they are not cost effective in many outlets. They are now mostly used when bright shades and good light fastness are essential requirements.

Red Anthraquinone Dyes. All the most important red disperse dyes are based upon a 1-amino-4-hydroxy substitution pattern. The bluish red shade of the parent dye, CI Disperse Red 15, can be shifted hypsochromically by putting an electron-donating group in position 2. 2-OMe gives CI Disperse Red 4, the important 2-OPh derivative is CI Disperse Red 60, and CI Disperse Red 91 and Red 92. These products (2.16) are synthesised by nucleophilic displacement of the bromine in 1-amino-2-bromo-4-hydroxyanthraquinone with the corresponding alkoxide or phenoxide.

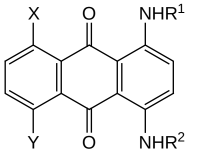
Blue Anthraquinone Dyes. All the important blue anthraquinone disperse dyes contain at least two amino groups in either the 1,4- or 1,5-positions, often with two additional hydroxy groups in the 5,8- or 4,8-positions respectively. The 1,4-di-substituted compounds (2.17) are obtained by condensing the reduction product of quinizarin, 1,4-dihydroxyanthraquinone, often called the leuco form, with the desired amines. Most anthraquinone disperse dyes are mixtures of products and not single compounds as drawn, a fact beneficial to their dyeing performance on polyester.

Other bright-blue dyes are made by further reactions of 1,5-diamino-4,8-dihydroxyanthraquinone, *e.g.* with bromine to give CI Disperse Blue 56, whilst the difficult area of bright turquoises is covered by the derivatives of 1,4-diamino-2,3-dicarboxylic acids such as CI Disperse Blue 60 and Blue 87 (2.18).



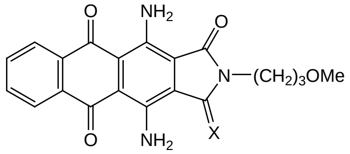
(2.16)

CI Disperse Red 4; R = Me
CI Disperse Red 60; R = Ph
CI Disperse Red 91; R = $(CH_2)_6OH$



(2.17)

CI Disperse Blue 3
R^1 = Me, R^2 = C_2H_4OH
CI Disperse Blue 23
R^1, R^2 = C_2H_4OH



(2.18)

CI Disperse Blue 60; X = O
CI Disperse Blue 87; X = NH

Bromamine acid, 1-amino-4-bromoanthraquinone-2-sulfonic acid, is a very widely used intermediate for producing blue dyes. Condensation of this intermediate with aromatic amines in the presence of a copper catalyst offers a straightforward route to many commercially important acid and reactive dyes, for instance CI Acid Blue 40 and CI Reactive Blue 19 (Figure 2.11).

Polycyclic Quinones. Known as vat dyes when used in the dyeing of cellulosic fabrics (see Section 2.3.2.1), polycyclic quinone chromogens exhibit very high light fastness properties making them suitable for use in furnishing textiles, such as drapes and curtains, where a long lifetime is required.[35] However, in the main, these are complex structures, *e.g.* CI Vat Green 1, and the multi-stage routes for their manufacture are very lengthy, leading to relatively expensive final products (2.19).[36] Therefore, they have become less effective in competing with reactive dyes, especially as the properties of the latter have improved markedly in recent years. Vat dyes are also used as

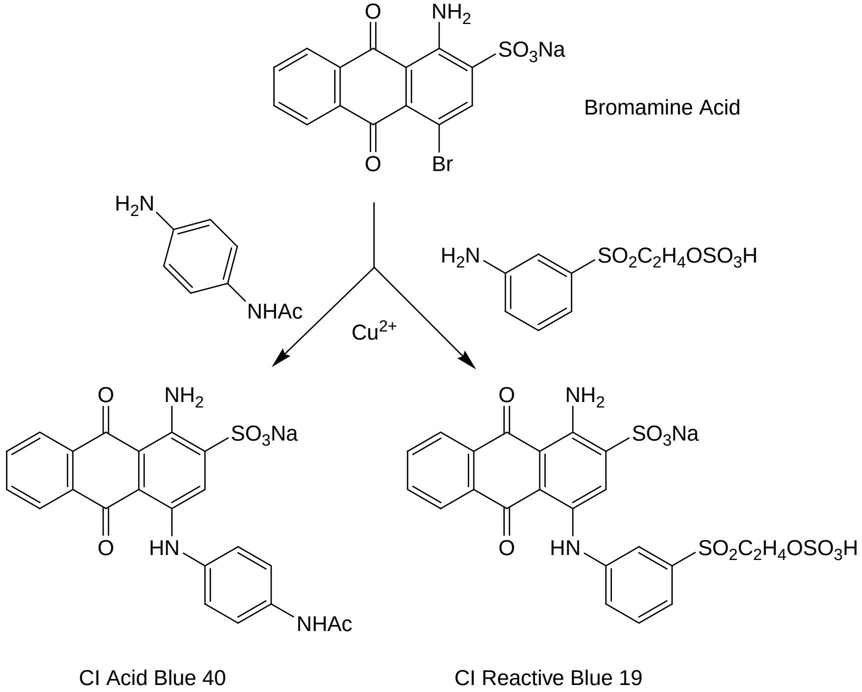
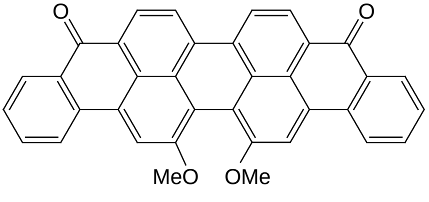


Figure 2.11 Blue dyes from bromamine acid.

organic pigments and their structures will be covered in more detail in Section 2.4.1.8.



(2.19) CI Vat Green 1

Benzanthrones and analogues are discussed in Chapter 3 (Section 3.5.1.4) because of their behaviour as fluorescent dyes.

Indigoid Dyes. The most well-known dye universally is probably indigo. This is because of its widespread use in the dyeing of denim blue, for both fashion and work wear. It is also a vat dye and, although many derivatives have been made and used over the years, it is the only important dye of the

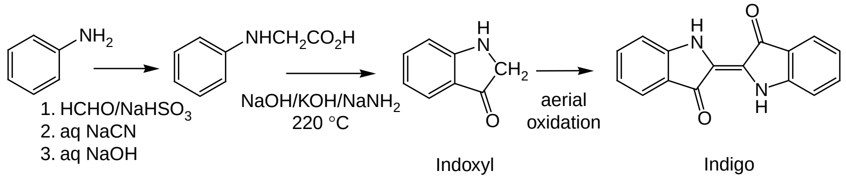
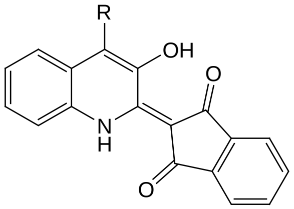


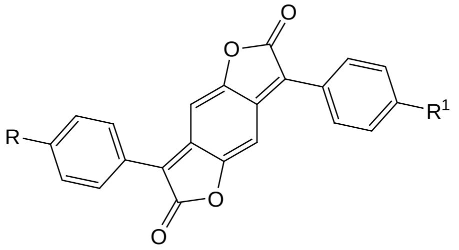
Figure 2.12 Manufacturing route to indigo.

indigoid class. The process used today for its manufacture is essentially the one devised by Pfleger in 1901. *N*-Phenylglycine, made by the reaction of aniline with sodium cyanide in buffered $NaHSO_3$ followed by hydrolysis, is heated in a mixture of molten NaOH/KOH and sodamide at up to 220 °C, followed by drowning out into water and then aerial oxidation of the intermediate indoxyl to give indigo. This all sounds horrendous but it is in fact quite environmentally friendly, in terms of effluent if not energy usage, as practically all the by-products are recycled into the process, including all the alkali. The process scheme is illustrated in Figure 2.12.[36]

Other Quinone Types. Although past researchers have examined many coloured quinonoid molecules, very few have achieved commercial importance. Quinophthalones, made by the condensation of phthalic anhydride with quinaldine derivatives, are one such group, exemplified by CI Disperse Yellow 54 (2.20a) and Yellow 64 (2.20b) used for polyester, especially for transfer printing and also as solvent dyes.



(2.20a) R = H
(2.20b) R = Br



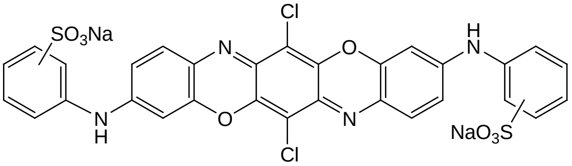
(2.21) R,R^1 = H and/or alkoxy

Benzodifuranones (2.21), made by reacting mandelic acids with 1,4-benzoquinones or hydroquinones, give very bright, strong (ε_{max} *ca.* 50,000) dyes for polyester across the shade spectrum, but especially in the red area. The story behind the pioneering work on this structure by Greenhalgh and his co-workers at ICI in the late 1970s makes fascinating reading.[37]

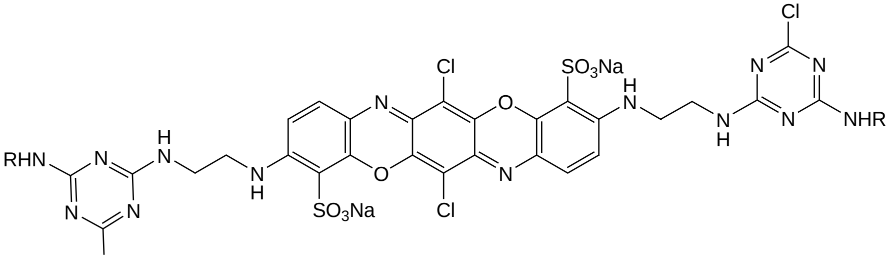
Other chromophores in this class are discussed under fluorescence in Chapter 3, *e.g.* coumarins (Section 3.5.1.1), or under their use as pigments in Section 2.4.1 of this chapter (*e.g.* perylene imides and derivatives in Section 2.4.1.7).

2.3.1.3 Azines, Oxazines and Thiazines

These chromophores have declined significantly in importance as textile dyes but have remained of interest because of their fluorescent behaviour, as discussed in Chapter 3, Section 3.5.1.5. One exception is the triphendioxazine ring system, which is used to produce valuable blue dyes in the Direct (2.22) and Reactive (2.23) dye classes as well as pigments (see Section 2.4.1.8). The dyes from this chromogen have a very high extinction coefficient (*ca.* 80,000) *versus* typical anthraquinone dyes (*ca.* 15,000) and have therefore replaced some of the dyes from this latter chromogen in the reactive dyeing of cotton.[38]



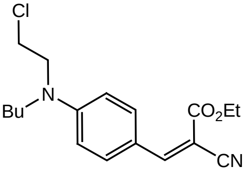
(2.22) CI Direct Blue 105



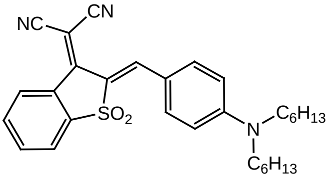
(2.23)

2.3.1.4 Polymethines

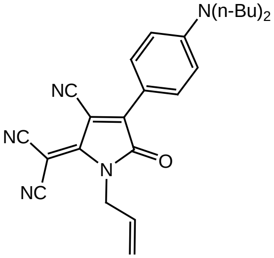
Simple methines were once important as yellow disperse dyes, when they were more usually called styryl dyes *e.g.* CI Disperse Yellow 31 (2.24), but are now only used to produce bright-blue and turquoise dyes. Examples are the monomethine (2.25), the dimethine (2.26) and the azamethine (2.27). Indophenols (2.28), another class of azamethines, have been used as bright-blue dyes for transfer printing onto polyester, and in digital imaging by dye diffusion thermal transfer. Indophenols and the corresponding indamines are the ring systems extensively used in hair dyes (see Section 2.3.2.5).



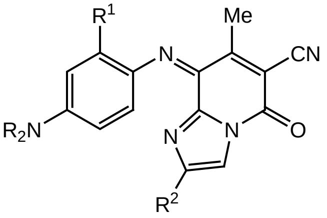
(2.24)



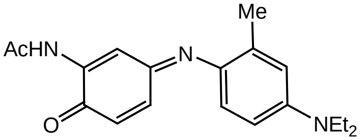
(2.25)



(2.26)



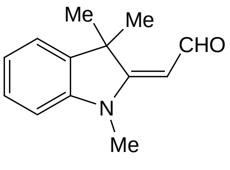
(2.27)



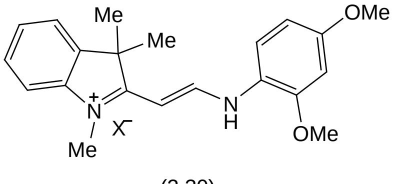
(2.28)

Because they exhibit excellent fluorescence on excitation, the polymethine cyanine dyes are dealt with in greater detail in Chapter 3 (Section 3.5.1.7). They are also used as spectral sensitisers in colour photography (see Section 2.8) and because they can be molecularly engineered to absorb in the near IR are being extensively studied in solar cells and data storage (see Chapter 4, Section 4.8).

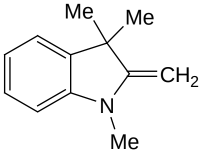
Several high-production products for the dyeing of polyacrylonitrile textile fibres come from the azacarbocyanine class. Examples are the azacarbocyanine Basic Yellow 11 (2.30), synthesised from 2,4-dimethoxyaniline and Fischer's aldehyde (2.29); and the diazacarbocyanine CI Basic Yellow 28 (2.32), synthesised from the diazonium salt of f-anisidine and Fischer's Base (2.31). These dyes, although very bright, tend to suffer from low fastness to light.



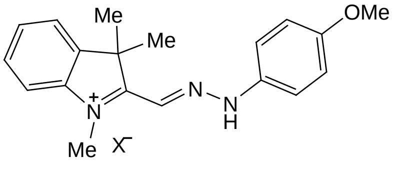
(2.29)



(2.30)



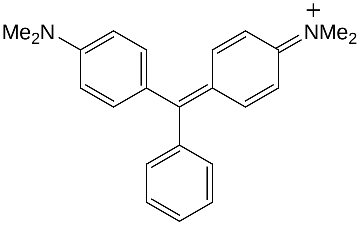
(2.31)



(2.32)

2.3.1.5 Triarylcarbenium Dyes

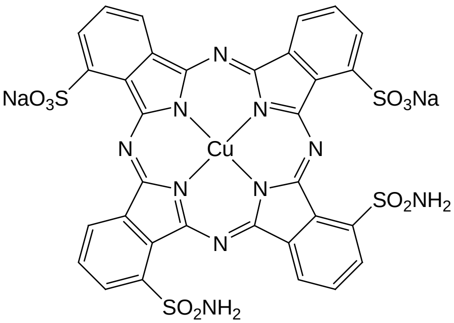
The main triarylcarbenium dyes are those based on the triphenylmethane structure, as exemplified by Malachite Green, CI Basic Green 4 (2.33). They are very bright, but generally of low light fastness, and are consequently used mainly for the coloration of paper and writing inks, where long lifetime is not an issue. (See also Chapter 1, Section 1.4.1.2.)



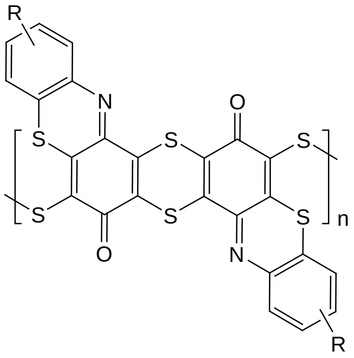
(2.33)

2.3.1.6 Phthalocyanines

Phthalocyanine and its metal derivatives, especially copper, are an extremely important class of organic pigments and their synthesis will be covered in Section 2.4.1.4. References to the use of variously substituted phthalocyanines in a variety of applications will be found throughout this book. Poly-sulfonated copper phthalocyanines form the basis of turquoise/cyan-coloured compounds used as direct and reactive dyes for cotton and as paper dyes. They are very bright in shade and have excellent light fastness properties. A simple derivative is CI Direct Blue 199 (2.34), a sulfonamide that is synthesised *via* sulfonyl chloride. Although invariably shown as single compounds, the phthalocyanine dyes are in fact very complex mixtures due to the combinatorial mix of isomers from the sixteen potential positions for substituents. Because of their high light stability copper phthalocyanine dyes have also found uses in inks for digital printers (see Section 2.9). Nickel phthalocyanine is also used commercially to give dyes of a slightly greener shade than the copper derivatives.



(2.34)



(2.35)

2.3.1.7 Sulfur Dyes

Sulfur dyes are high-volume, cheap dyes used for the coloration of cotton or blends with synthetic fibres such as acrylic fibres, polyamides (nylons) and polyesters. CI Sulfur Black 1, one of the largest commercially produced dyes, is made by a process involving heating 2,4-dinitrophenol with sodium polysulfide. Even today its exact structure is not known. One commonly shown is the S-S cross-linked oligomer (2.35), but an extended linear phenothiazine structure has also been proposed.[39] A range of colours is available by the reaction of various intermediates with sulfur or sulfides but none are as important as the black dye.[34]

2.3.2 Application Processes

An alternative way of classifying dyestuffs is by their application areas, but as there is large overlap between product structural classes and their uses, it is less satisfactory for the purpose of this book. However, from a commercial standpoint it is its use in a particular application method that determines the potential of any dyestuff and the reason for its industrial manufacture and sales. Therefore in this section the different application methods for dyestuff classes will be described mainly in relation to the end use; the dyeing or printing of cotton and other fibres, the coloration of paper or leather, the use in food and cosmetics, *etc*.

2.3.2.1 Dyeing and Printing of Textile Fibres

The split into the various textile dyestuff application areas has, over recent years, seen a shift towards the two main outlets of disperse dyes for polyester and reactive dyes for cellulosics (mainly cotton), at the expense of direct and vat dyes for cotton, cationic dyes for acrylics and acid dyes for polyamide. The latter fibre made a slight comeback when its application in the form of microfibres for sports and leisurewear became established. The position in 1998, with disperse dyes dominating in value terms, was as shown in Table 2.6.

There are three basic ways of applying dyes to a textile substrate:

- The dye liquor is moved and the material is held stationary;
- The textile material is moved and the liquor is held stationary;
- Both the textile material and the dye liquor move.

Table 2.6 Textile dyes by application areas on a global basis (1998).

	Fibres dyed	*Market size \$bn*	*% share*
Disperse	Polyester, acetate	1.440	26.3
Reactive	Cotton, viscose	1.294	23.6
Acid	Nylon, wool	1.019	18.6
Direct	Cotton, viscose	0.421	7.7
Cationic (basic)	Acrylic	0.386	7.0
Others[a]	Various	0.922	16.8
Total		5.484	100

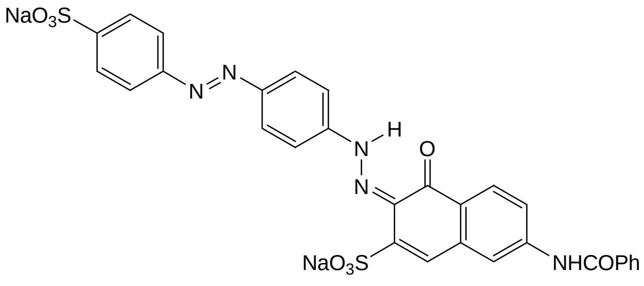
[a] Indigo, vat, sulfur *etc*. Source: Yorkshire Group.

The three main techniques for dyeing are exhaust dyeing, padding and continuous.[40]

The main method of printing on textile substrates is screen printing, both rotary and flat bed, but digital printing[41,42] (ink-jet printing, see Section 2.9.1) is now on a growth path and is predicted to have about 10% market share in about ten years from 2007.[43]

Cotton and Other Cellulosic Fibres. The dominant natural cellulosic fibre is cotton, the other natural cellulosic fibres, or bast fibres, include flax, linen, jute and ramie. The so-called regenerated fibres, which include viscose, modal fibres and lyocell (Tencel), are made by various chemical treatments of cellulosic substrates. The dyeing and printing of cellulosic fibres and materials is carried out, in decreasing order of scale and importance, using reactive, direct, sulfur and vat dyes (Table 2.7).[44 47]

Direct dyeing is the simplest method for achieving the coloration of cellulosic fibres. Direct dyes are large, linear or planar molecules that contain several sulfonic acid groups, dominated by those dyes derived from the azo chromophore (*e.g.* CI Direct Blue 78 (2.4), CI Direct Yellow 132 (2.5) and CI Direct Red 81 (2.36)). Fastness properties are often improved by the use of metal complexes (*e.g.* copper complexes of dihydroxy azo dyes). A large number of the original direct dyes are now banned from use because they were derived from carcinogenic amines, especially benzidine and its congeners (see Section 2.3.1.1).



(2.36)

Table 2.7 Estimated annual worldwide consumption of cellulosic dyes.

	Usage per annum (tonnes)	
Type	*1992*	*2004*
Reactive	109,000	178,000
Direct	74,000	68,000
Sulfur	70,000	70,000
Vat	21,000	22,000
Indigo	12,000	12,000
Azoic	18,000	13,000
Total	290,000	354,000

Direct dyes are applied to cotton from a hot aqueous dyebath containing sodium chloride and auxiliaries, such as wetting and sequestering agents. The long linear dyes have a high substantivity for the fibre, but in water the cellulosic fibre is negatively charged and tends to repel the incoming anionic dye. Salt, added all at the start or portion wise during the dyeing cycle, reduces the electrical potential on the fibre, allowing the dye to interact with the fibre and hence there is a build-up of the colour to the maximum achievable. Much of the dye remains loosely bound to the fibre and, if it is not properly removed in the dyehouse, can cause a nuisance in subsequent laundering. To overcome this problem, cationic agents have been devised for addition to the dyebath after dyeing. These form immobile salts with the dye thus "fixing" it to the fibre. Direct dyes are the cheap and cheerful end of the dyeing market, but they suffer from low fastness properties including light fastness. Although metal complex dyes, as mentioned above, improve fastness properties, they have fallen out of favour because they release metal ions into the effluent.

Vat dyes offer distinct advantages over direct dyes in terms of light and wash fastness properties, which are generally very good. As discussed in Section 2.3.1.2, vat dyes belong to the polycyclic quinonoid and indigoid classes, the former providing the higher performing dyes in terms of fastness. The chromophoric group in these two classes is the carbonyl group and this is capable of being reduced to hydroxy, the "leuco" form, by the process of "vatting". This involves chemical reduction to convert the dye to the soluble leuco form. A solution is then mixed with the fibre in the dyebath in the presence of salt, causing it to be adsorbed onto the fibre. The impregnated fibre is then oxidised, usually by aerial oxidation, giving back the insoluble vat dye within the fibre. Any unfixed vat dye material is then washed off before drying. The process is illustrated in Figure 2.13.

The overall process for dyeing with vat dyes produces a large load on the effluent because of the chemical reducing agent. More environmentally friendly alternatives to $Na_2S_2O_4$ have been proposed, such as the biodegradable hydroxyacetone and reducing sugars, but cost is a big factor. Electrochemical

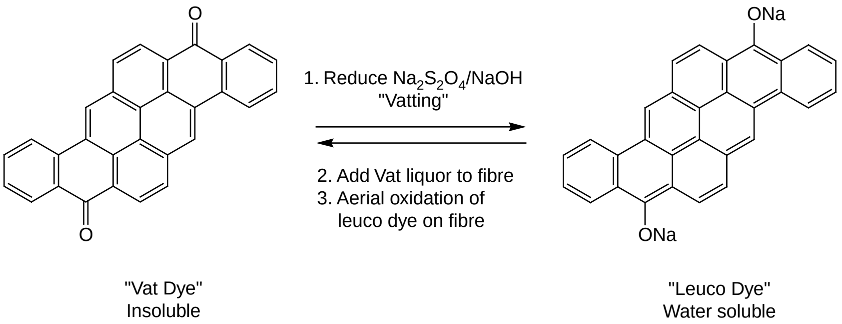


Figure 2.13 Vat dyeing of cellulosic fibres.

methods have been developed for Vat, Indigo and Sulfur and show great promise as a recent review discussed.[47]

Sulfur Dyes continue to occupy an important place in the dyeing of cellulosic fibres and blends, especially as blacks on denims. For water insoluble versions the dyes are dissolved by boiling in a reducing medium, such as sodium sulfide or glucose, similar to vat dyes, and this solution is used to dye yarn in the package, whilst woven fabrics are dyed batchwise or continuously followed by oxidation by peroxide or perborates.[48]

Reactive Dyeing is the most important method of dyeing cotton, producing dyed fibres that combine bright shade with excellent fastness properties, especially fastness to washing. As the name implies, reactive dyeing involves the formation of a covalent bond between the dyestuff and the fibre, specifically by the reaction of functional groups within the dyestuff molecule and the hydroxy groups on the cellulose fibre.

The reactive functional groups fall into two classes:

- Those involving nucleophilic displacement of a leaving group, usually halide;
- Those involving addition across an activated double bond.

Both reactions are carried out under aqueous alkaline conditions, at a sufficiently high pH to ensure ionisation of the hydroxy groups in the cellulose. Salt or another electrolyte is added and the dyeing carried out at a temperature dependent on the nature of the reactive group, but usually in the range 40–80 °C. The competing reaction is with the hydroxyl anion in the dyebath, which causes hydrolysis of the dye. The hydrolysed dye is incapable of further reaction and is lost to effluent (Figure 2.14). The objective in the molecular design of the dye and the application process is to minimise the formation of this hydrolysed by-product, hence achieving a higher percentage reaction, called fixation in dyeing terminology, with the cellulose.

The major reactive heterocyclic halogen systems are chloro and fluoro analogues of 1,3,5-triazine and pyrimidine. Dichlorotriazines are the most reactive, exhaust dyeing of cotton being carried out at 40 °C, whilst monofluorotriazines require dyeing temperatures of 40–60 °C and monochlorotriazines a temperature of 80 °C. The least reactive of the common commercial systems are the trichloropyrimidinyl dyes, which require a dyeing temperature near the boil (98 °C). The structures and reactivities of the various commercial reactive systems are shown in Table 2.8. The halogens can be replaced by other leaving groups, particularly the quaternary ammonium groups formed by reaction of the halogen with nicotinic acid.

Practically all the commercially important reactive dyes based on activated double bonds employ the vinyl sulfone reactive group (2.38), usually as sulfatoethylsulfone derivative (2.37), which converts to (2.38) in the dyebath under the influence of alkali. They are usually applied onto the fibre by exhaustion from the dyebath at around 40–60 °C or by cold padding at 30 °C. The vinylsulfone group is most commonly attached to the dye chromophore *via* an

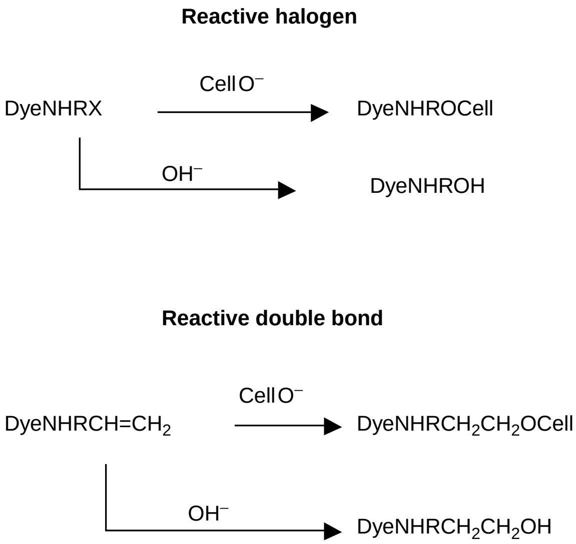
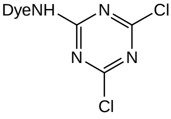
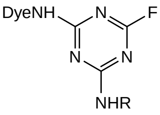
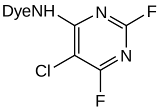
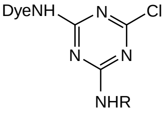
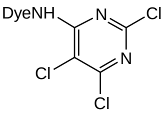
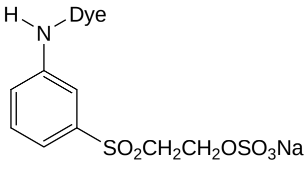


Figure 2.14 Dye fibre bond formation and hydrolysis in reactive dyeing of cellulose.

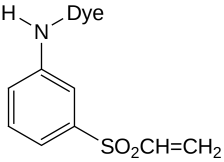
Table 2.8 Heterocyclic reactive systems and typical dyeing temperature.

				
40°C	40-60°C	40-60°C	80°C	98°C

aromatic ring, *cf.* CI Reactive Black 5 (2.2), but in other cases a bridging aliphatic group is employed.[49]

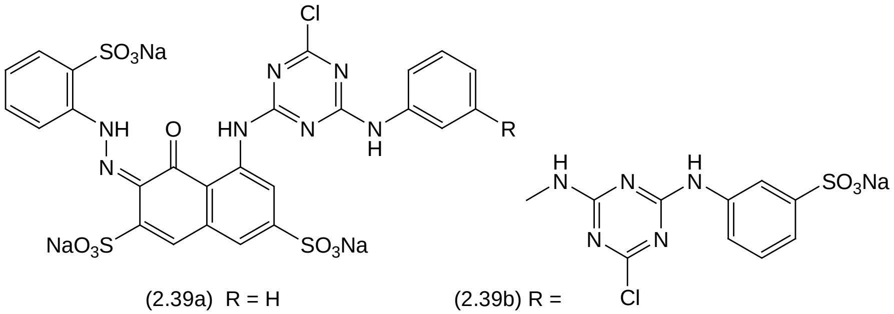


(2.37)

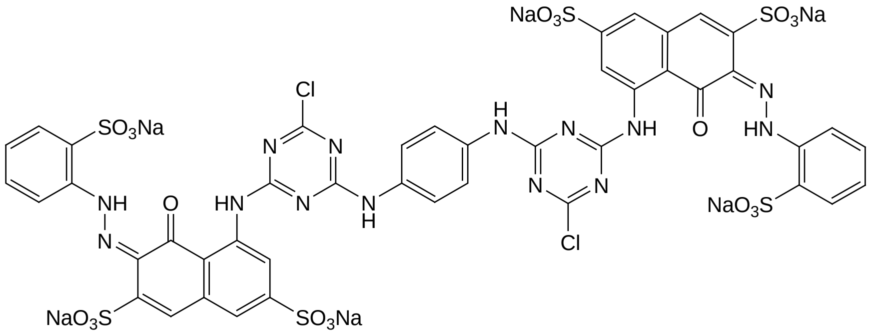


(2.38)

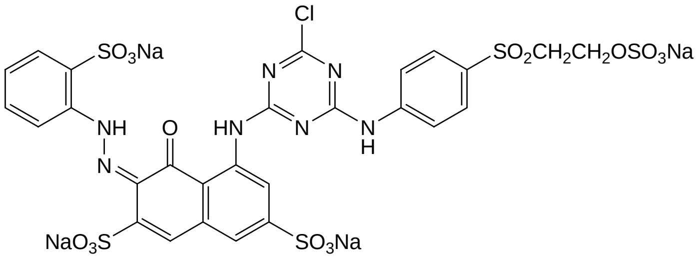
The earliest reactive dyes were of the mono-functional type, *e.g.* CI Reactive Red 3 (2.39a), but very soon in the development phase homo-bifunctional dyes, *e.g.* CI Reactive Red 125 (2.39b) were introduced and later dimeric dyes, again with two reactive groups, *e.g*. CI Reactive Red 120 (2.40). Dyes of the latter structure, having roughly twice the molecular size, showed much improved substantivity for the fibre, and an increased probability of the groups reacting with the cellulose, hence an increased fixation of the dye onto the fibre. Hetero-bifunctional dyes, those with two different reactive groups, as in CI Reactive Red 194 (2.41), were rather late on the commercial scene, not appearing until some 30 years after the initial invention of reactive dyes, but when they did they offered better fixation levels than had previously been obtained.



(2.39a) R = H (2.39b) R =



(2.40)



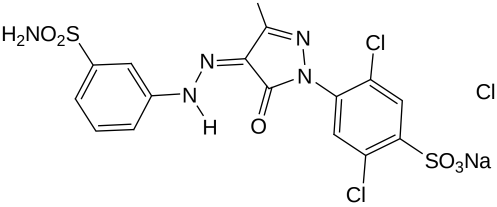
(2.41)

Nylon, Wool and Silk. Because of their common structural features, nylon (generically polyamide), wool and silk are normally considered together, especially as they are coloured using the same or functionally similar dyes. The common structural features of the fibres are amide groups, -NHCO-, linking segments of the polymer chains, and amino and carboxylic acid groups at the end of chains, or on side chains (wool).

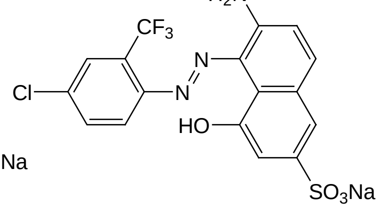
The fibres are also ionic in Nature because of the presence of the weakly basic amino groups and the weakly acidic carboxylic acid groups. On increasing the acidity of a dyebath containing these fibres, the overall charge on the fibre becomes increasingly positive. Consequently, the preferred technique for dyeing of nylon and wool is from an acidic dyebath, at or near the boil, using anionic dyes (acid dyes). The subcategories of acid dyes depending on the application pH are:

- Level Dyeing Acid Dyes at pH 2.5–3.5;
- Fast Acid Dyes at pH 3.5–5.0;
- Acid Milling Dyes at pH 5.0–7.5;
- Super Milling Dyes at pH 7.0.

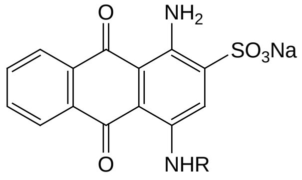
Acid Dyes are basically chromogens containing acid groups, especially sulfonic acid groups, usually 1 or 2 in number but can be up to 4, falling within a relatively low molecular weight range (300–1100). Many of the dyes are metal complexes: 1:1 and 1:2 premetallised azo dyes for nylon dyeing and the so-called "afterchrome" or mordant dyes for wool. The latter complexes are formed as the name implies, after dyeing the cloth with a hydroxyazo dye by treatment with a chroming agent, *e.g.* dichromate. Whilst showing excellent properties chromium-containing metal complex dyes have declined in popularity due to environmental concerns. Consequently the main dyestuff manufacturers offer alternatives such as metal-free reactive dyes for this outlet.[50,51] A very wide colour gamut is available from acid dyes so that almost any desired shade can be obtained. Some typical acid dyes are CI Acid Yellow 172 (2.42), CI Acid Red 266 (2.43), CI Acid Blue 62 (2.44), the 1:2 premetallised dye CI Acid Black 60 (2.45) and the afterchrome dye CI Mordant Black 11 (2.46).



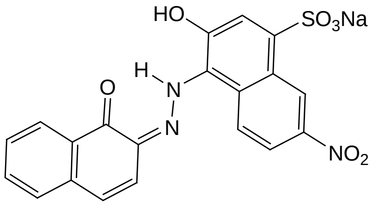
(2.42)



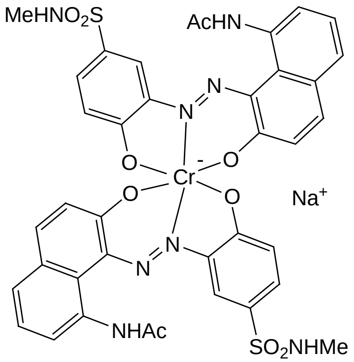
(2.43)



(2.44) R = c-hexyl



(2.46)



(2.45)

Polyester. Polyesters are the most important of the man-made fibres, especially polyethylene terephthalate, to a much lesser extent cellulose acetate and the recently introduced polylactic acid (PLA). Polyethylene terephthalate, which is produced by the reaction of terephthalic acid or its dimethyl ester with ethylene glycol, is a highly hydrophobic polymer, not taking up any water below 80 °C. Consequently it cannot be dyed with ionic dyes and is dyed with a unique group of non-ionic dyes called disperse dyes. These take their name from the fact that they are used as aqueous dispersions in the dyeing process, and are generally small in molecular size. They contain no ionic groups, but do have polar groups present in their molecular structure. Such polar groups help to provide a very limited degree of water solubility and also enhance the interaction with the polyester by H-bonding and dipolar forces. Disperse dyes derived from azo, anthraquinone and related quinones, and also methine chromophores, are the most important. The structures of several typical disperse dyes have already been described earlier in this chapter (see (2.1), (2.9), (2.17), (2.18), (2.20), (2.24–2.28) and Figure 2.10).

Dispersions of the dyes in water are prepared by milling the untreated dye to a fine particle size in the presence of dispersing agents, commonly lignosulfonates. The dispersions are either dried, invariably in a spray dryer, to give re-dispersible granules or they are maintained as a stable "liquid" version. The dispersing agents not only maintain the dyes in suspension during processing but also act as dyeing assistants, helping to produce even or level dyeings. Disperse dyes can exist in a variety of different crystalline forms, and the stability of the dispersions and the performance of the dyes in the subsequent dyeing process are highly dependent on a particular polymorphic form. Much time in development work is spent in designing a process that produces the dye in the best physical form for a particular outlet.

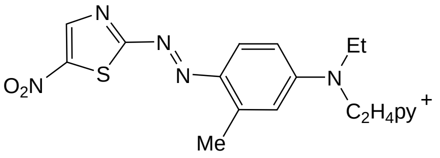
The batchwise application of the dyes to the fibre is carried out under pressure at a high temperature above the glass transition temperature, usually around 130–135 °C, during which time the fine particulate dye dissolves in the polymer by a molecular process. The dye molecules are then held within the polymer by hydrogen bonding, dipole-dipole interaction and dispersion forces. It is also possible to dye at lower temperatures and under normal pressure by using agents, called carriers, *e.g.* *ortho*-phenylphenol, which swell or modify the polymer easing the dissolution of the dye. Disperse dyes can also be dyed or printed onto cloth under normal pressure without agents, but at much higher temperatures because of the volatility of the non-ionic dyes. The Thermosol dyeing process involves padding the dye dispersions onto the cloth and then passing the cloth through a heater at 200–215 °C for 30 seconds, during which time the dye sublimes onto and then dissolves in the fibre. This process is used particularly for the continuous dyeing of polyester-cotton blends. Sublimation printing, also called transfer printing, involves transferring an image printed on paper onto the cloth by passing the cloth and the paper over a heated drum. For a more detailed discussion of the principles of dyeing polyester fibres the reader should consult the various specialised texts on the topic.[6,45,52,53,54]

Polyacrylonitrile. Polyacrylonitrile (PAN) fibres are often called by the shortened name of acrylic fibres. PAN is made by the polymerisation of acrylonitrile incorporating small amounts of co-reactants which provide anionic centres, such as sulfonic acid or carboxylic acid groups. These ionic centres make it possible to dye PAN fibres with basic or cationic dyes, from an aqueous dyebath at pH 3.5–6.0, at temperatures above 80 °C.

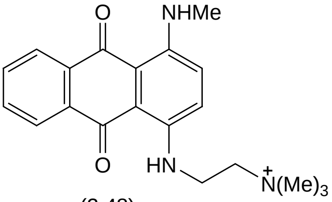
Cationic dyes can be classified into two types:[55]

- Dyes with pendant cationic groups, *i.e.* localised on an atom attached to the chromogen;
- Dyes where the charge is delocalised over the whole chromogen.

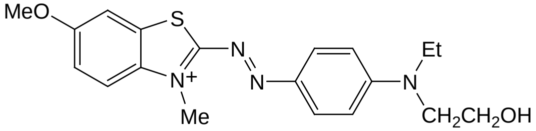
Delocalised dyes are inherently stronger and brighter than those bearing pendant cationic groups, which are usually derived from azo or anthraquinone dyes. Azo dyes are normally made by coupling the diazo component onto a preformed cationic coupling component, exemplified by CI Basic Blue 119 (2.47). Contrastingly, in anthraquinones the quaternisation is usually carried out as a post colour-forming step *e.g.* CI Basic Blue 13 (2.48).



(2.47)



(2.48)



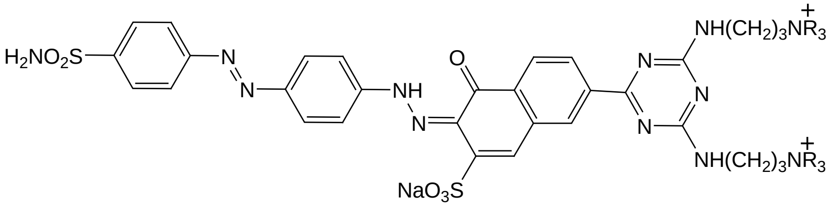
(2.49)

Delocalised charged dyes are dominated by cyanine-type dyes, exemplified by the azacarbocyanine CI Basic Yellow 11 (2.31), the diazacarbocyanine CI Basic Yellow 28 (2.32) and the diazahemicyanine CI Basic Blue 41 (2.49). Where necessary, quaternisation is again carried out as a post colour-forming reaction. Other structural types include oxazines, thiazines and triphenylmethane dyes.

2.3.2.2 Paper

Paper is made from cellulose fibre containing varying amounts of lignin, which depend on the quality of the paper. Low-quality and short-life paper, as used in tissues, wipes and toilet papers, does not require very fast dyes. Indeed it is a positive advantage if they are easily destroyed, as most of these papers end up mixed in with liquid effluent going to the sewage works. In contrast, dyes used on high quality papers are expected to have good all-round fastness properties for archiving, and light stability in particular when used in hard-copy displays, for instance on information notice boards or on the covers of books. These high-quality papers contain fillers, such as titanium dioxide and chalk, to produce a bright white appearance and the dyes must distribute evenly between the paper and the filler.

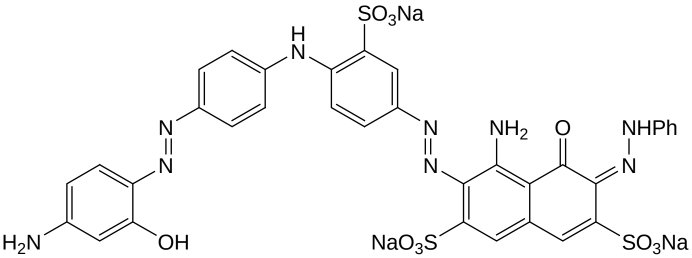
Dyeing of paper has been traditionally carried out with acid, direct and basic dyes, whilst newer systems are based on cationic direct dyes. Some of these are related structurally to reactive dyes with the labile chlorine atoms replaced by pendant cationic groups, as in (2.50).



(2.50)

2.3.2.3 Leather

Leather is a very important material in the world economy, used in footwear, clothing, luggage and upholstery. It is a complex substrate prepared from animal hides and skins by a long series of treatments. After the removal of all organic material and hairs the material is tanned, usually with chromium salts, which causes the protein chains to cross-link. After treating with oils or fats, in order to improve its handle, the leather is dyed with acid, direct or mordant dyes. Many of the direct dyes were based on benzidine and its congeners but, as discussed under the toxicity of certain azo dyes in Section 2.3.1.1, they are no longer an option. In order to improve the light fastness of the dyed leathers, 1:2 premetallised azo dyes have also been used, but once again the use of metal complex dyes is becoming less favoured.[56] Over 50% of leather is dyed black and 24% brown, the rest being largely coloured at the dictates of fashion. An example of a dye used in the dominant black shade area is CI Direct Black 168 (2.51).



(2.51)

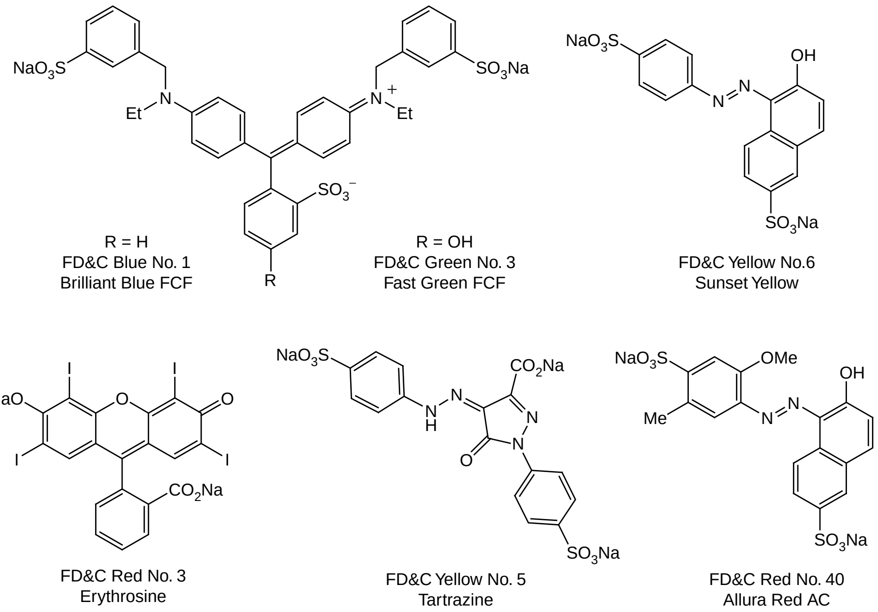
2.3.2.4 Food and Beverages

Unsurprisingly there are commonly held concerns about the safety of the additives in what we eat and drink, but hardly anybody would relish the thought of eating processed food that did not look attractive and appetising. The coloration of food therefore serves several purposes, most of which are aesthetic:

- To offset loss of colour due to environmental conditions during storage;
- To correct colour variations in foods and crops *e.g.* orange crops;
- To enhance weak coloration in natural foods;
- To add colour identity to a flavour, *e.g.* strawberry ice cream;
- To make colourful fun foods, *e.g.* sweets such as rock;
- To protect vitamins from harmful sunlight;
- To meet consumer demand for appealing and wholesome food.

The addition of additives to food, including colour additives, is strictly regulated in the developed world, for example by the USA Food and Drug Administration and the European Food Safety Authority.

The FDA classifies colour additives as being either "certifiable" or "exempt from certification". Certifiable colour additives are synthetic colorants, where both the manufacturer and the regulatory authority test every batch. They are available as water-soluble dyes, or insoluble lakes. The water-soluble dyes are made as powders, grains or liquids for use in beverages, confectionary



R = H
FD&C Blue No. 1
Brilliant Blue FCF

R = OH
FD&C Green No. 3
Fast Green FCF

FD&C Yellow No.6
Sunset Yellow

FD&C Red No. 3
Erythrosine

FD&C Yellow No. 5
Tartrazine

FD&C Red No. 40
Allura Red AC

Figure 2.15 FD&C certified food colorants.

products, dairy products and other foods. The insoluble lakes are of higher stability and are used to colour oils and fats, in coated tablets and hard-boiled sweets and chewing gums. As of 2007 there were seven synthetic dyes certified for use in foods generally in the USA, labelled with FD&C (Food Drug & Cosmetic) numbering. The structures of six of these seven dyes are shown in Figure 2.15, the other being FD&C Blue No. 2, indigo (see Figure 2.12).

Colours that can be used to a maximum level in specified foodstuffs in the European Union, all of which have assigned E numbers, include Tartrazine (E102), Quinoline Yellow (E104), Sunset Yellow (E110), Carmoisine (E122), Ponceau 4R (E124), Allura Red AC (E129), Patent Blue V (E131), Indigo Carmine (E132), Brilliant Blue FCF (E133) and Brilliant Black PN (E151). Erythrosine (E127) is restricted to certain foodstuffs.[57(a)]

Studies published in the UK in 2007 on the effect of synthetic food dyes on the hyperactivity of young children became a major public concern.[57(b)] Results indicated that mixtures of Tartrazine, Ponceau 4R, Sunset Yellow, Carmoisine, Quinoline Yellow and Allura Red AC increased activity in groups of three-year-olds and eight- to nine-year olds. Even though a panel from the European Food Safety Authority's (EFSA) AFC Panel thought the evidence limited, companies voted with their feet; all synthetic colours were dropped from the Smarties range of sweets, and Sainsbury announced a ban on artificial colours and flavours in 120 of its own-label soft drinks following similar moves by Marks & Spencer and the Co-op.

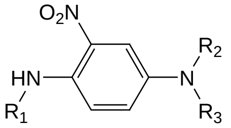
Colour additives that are exempt from certification include those pigments made from natural sources, such as minerals, vegetables and animals, and also man-made counterparts of natural products. For example, heating carbohydrates at temperatures in excess of 150 °C produces caramel browns used for both their colour and flavour. Natural products synthesised by man include carotenoids, *e.g.* β-carotene, which is used for colouring food yellow-orange, and chlorophyll for providing a green coloration. There has been a marked increase in the demand for natural colorants to be used to colour food alongside the move to organically farmed foodstuffs amongst a sizeable body of consumers.[58] Natural colorants and their applications will be covered in Section 2.7.

2.3.2.5 Hair Coloration

Once the domain of women but with a fast growing use by men, hair coloration is a major business for cosmetic manufacturers. Three ranges of coloration systems are available:

- Temporary – surface dyeing, usually for fashion reasons, which washes off readily. Supplied as a mousse, spray-on or styling gel.
- Semi-permanent – gradually fades with cumulative shampoos (normally 5–10), may surface dye or may penetrate slightly depending on size and charge. Supplied as liquids or creams.
- Permanent – by far the most popular coloration method. It cannot be truly permanent, as hair grows and needs to be re-coloured, and the fastness of the dyes is not perfect as it is affected by both the washing process and by exposure to bright sunlight. However, the permanency of the dyeing is greatly assisted by dye formation within the hair fibre rather than on the surface.

For temporary dyeing a variety of colorants can be used but generally bright-coloured pigments and occasionally acid or basic dyes are preferred. For semi-permanent coloration the most common class are nitro dyes, specifically 2-nitro-1,4-phenylenediamines, which have a strong affinity for keratin and give a wide range of colours from orange-red to blue-violet as illustrated in (2.52).[59] Disperse dyes and F&C dyes are also used. Shade formulation is achieved by simply mixing the relevant colours.



(2.52)

$R_1 = R_2 = R_3 = H$; orange-red
$R_1 = R_2 = H$, $R_3 = C_2H_4OH$; red
$R_1 = H$, $R_2 = R_3 = C_2H_4OH$; red-violet
$R_1 = C_3H_6OH$, $R_2 = R_3 = C_2H_4OH$; violet-blue

Permanent coloration involves swelling the hair fibres with an alkaline liquid, opening the scales of the cuticle and allowing the dye precursors to enter. After the oxidative colouring process has taken place the resultant colorants stay inside the hair fibre. In the colouring process a "primary intermediate", *e.g.* a 1,4-pheneylenediamine or 1,4-aminophenol, is oxidised by peroxides to give the

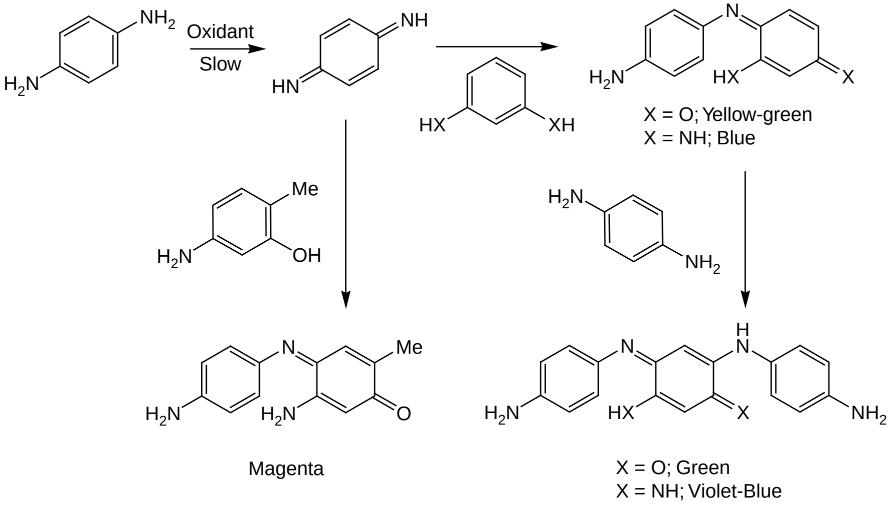


Figure 2.16 Schematic representation of the oxidative colouring process between 1,4 phenylenediamines and 1,3 couplers.

colour intermediate benzoquinonediimines or monoimines, which react with a 1,3-phenylenediamine or 1,3-aminophenol "coupler" to give indoamines or indophenols. Depending on the nature and ratio of the reactants these two component dyes can react with another molecule of a 1,4-phenylenediamine, as shown schematically in Figure 2.16.[60] Further reactions to give complex pigments and deeper shades can also be involved. Heterocyclic intermediates are also used as primaries (diaminopyrimidines and pyrazolones), and as couplers (*e.g.* 2-amino-3-hydroxypyridines). When different couplers are simultaneously present in the dye formulation a mixture of indo dyes are formed of differing colours, the final colour depending on factors such as primary and coupler ratios.

Certain amines are no longer used because of their toxicity and even with existing materials concerns are regularly raised and studies carried out. However, *para*- and *meta*-phenylenediamines are still allowed in the EU with certain restrictions, and warnings are required on the packaging of formulations containing such amines.

More recently a "biomimetic method" has been introduced, which as its name implies mimics Nature's way of colouring hair.[61,62] Melanins are common colorants in the human body, and in hair are biosynthesised within the follicle. Human hair has two types of melanin: black brown eumelanin and red pheomelanin which is much less common. Although the exact structures of either of these melanins are unknown, the biosynthetic pathway to eumelanin is outlined in Figure 2.17. From this it can be seen that the precursor to eumelanin is 5,6-dihydroxyindole and a process has been developed for colouring hair using this as an intermediate. To make this work in practice, 5,6-dihydroxyindole or 5,6-dihydroxyindoline has to be delivered in a stable formulation so

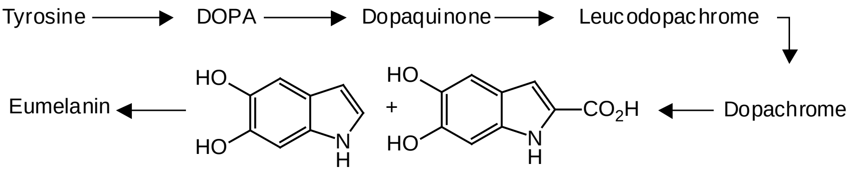


Figure 2.17 Outline of biosynthetic pathway to eumelanin.

that aerial oxidation only takes place after application to the user's hair. Although this method produces a drab coloration it is very similar to natural hair colours.[61] The use of natural dyes for hair coloration will be covered in Section 2.7.1.

2.3.2.6 Biological Stains

Because in the main they show little contrast with their surroundings, biological materials are very difficult to visualise under a light microscope. Consequently, for many years in histology, visualisation of biological tissues has been assisted by coloration with dyes. These dyes, known as stains, can perform several functions:

- They can attach themselves to specific components in the cells;
- They can change colour on undergoing reactions in the cells;
- They can fluoresce in certain environments;
- They can be used to produce an image.

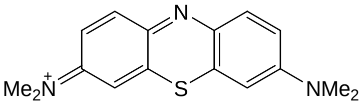
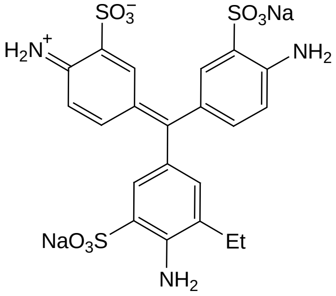
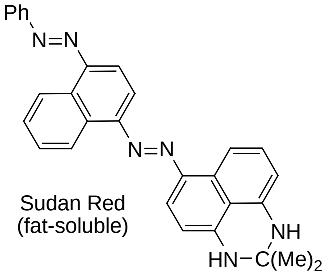
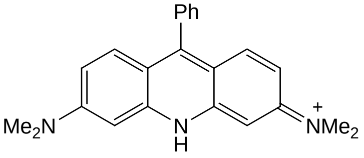
These various staining procedures are used to show the overall structures of microorganisms, to identify internal structures and to help in separating similar organisms. The staining methods are either positive, in which the foreground material is stained, or negative, in which the background is stained, or they can be a combination of both.

Almost every class of dye has been used for histological staining and there is extensive literature on the topic.[63] A simple classification of the dyes is as follows:

- Cationic dyes. These combine with negatively charged cellular constituents such as nucleic acids and acidic polysaccharides;
- Anionic dyes. These combine with positively charged cellular constituents such as proteins;
- Fat-soluble. These combine with fatty materials in the cell and are often used to locate fat droplets or deposits;
- Fluorescent. These emit light or change their fluorescent characteristics on reacting with cell constituents. (The important area of fluorescent probes is covered in detail in Chapter 3, Section 3.5.7.)

Representative stains in each of these chemical classes and some of their applications are shown in Table 2.9.[64]

Table 2.9 Selected biological stains and their applications.

 Methylene Blue (cationic)	Acid-fast bacteria, acid-fast bacilli and as rickettsia stain Cain's Method for mitochondria. Negri bodies in nerve cells
 Acid Fuchsin (anionic)	Connective tissue and erthrocytes Proteinaceous material in liver Cain's method for mitochondria
 Sudan Red (fat-soluble)	Fat in animal tissue Chromosomes, golgi, and leucocyte granules
 Acridine Orange (fluorescent)	Pickett's method for fungi fluorescent against a dark background Differentiation of nucleic acids and cytology

2.4 Pigments

As stated in Section 2.3.1 above, many pigments and dyestuffs belong to the same chemical classes, differing only in their physical properties and hence their applications. The Color Pigments Manufacturing Association (CPMA) of the

USA has devised a more specific definition for pigments, and it is given here to help clarify the position opposite dyes and pigments.[65]

> "Pigments are coloured, black, white or fluorescent particulate organic and inorganic solids which are usually insoluble in, and essentially physically unaffected by the vehicle or substrate in which they are incorporated. They alter appearance by selective absorption and/or by scattering of light. Pigments are usually dispersed in vehicles or substances for application, as for instance inks, paints, plastics or other polymeric materials. Pigments retain a crystal or particulate structure throughout the coloration process. Dyes and pigments differ in their application; dyes penetrate the substrate in a soluble form after which they may or may not become insoluble; pigments when used to colour a substrate remain insoluble as a finely divided solid throughout the coloration process."

The worldwide market for inorganic, organic and special pigments was around 7.4 million tons in 2006, and with expected growth rates of 2.9% *p.a.* is set to rise to 9.8 million tons by 2016, although how the global recession will affect the use figures remains to be seen. Although organic pigments account for only 5% by volume of all pigments they account for 28% based on their value.

2.4.1 Organic Pigments

Organic pigments can be classified according to their chemical class or by the colours they produce, but the former method will be adopted here, as it is in the major text in this area.[9] The make-up of the organic pigment portion of the world pigment market is given in Table 2.10. The high-performance pigments include products from a range of chemical classes including carbazoles, perinones, perylenes, vat pigments, benzimidazolones, isoindolinones, diketo-pyrrolopyrroles and thiazine indigos.[11]

2.4.1.1 Azo Pigments

The main groups of pigments based on the azo chromophore are monoazo, disazo, β-naphthol pigments, Naphthol AS, benzimidazolones and azo pigment lakes. The synthesis of azo pigments closely parallels the methods used to make azo dyestuffs as described in Section 2.3.1.1. However, as pigments are inherently insoluble, care must be taken to remove insoluble impurities from the starting materials and dispersing agents are often used at the coupling stage. In

Table 2.10 World markets make-up of organic pigments.

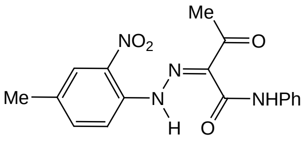
Type	*Azo & other*	*High performance*	*Phthalocyanine Blue*	*Phthalocyanine Green*
Share %	61	8	23	8

this respect the synthetic methods are most like those used to make azo disperse dyes. Azo pigments derived from those amines on the restricted list (see Table 2.4, Section 2.3.1.1) do not fall under the ban on their use as in the case of dyestuffs, provided they cannot be cleaved to produce the amines under the statutory conditions, *e.g.* cleavage under very high temperature applications.

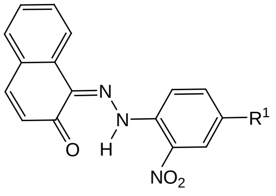
Monoazo pigments cover the shade range from greenish-yellow to deep reddish-yellow or orange shades and are the workhorse products. They suffer from poor properties, especially solvent (bleed) and migration fastness, so that their commercial importance diminished as alternative structures with higher fastness properties became available. The best of the commercial pigments are based on acetoacetanilide coupling components, exemplified by the oldest, CI Pigment Yellow 1, shown in the hydrazone tautomeric form (2.53).

The β-naphthol pigments are monoazo species derived from 2-hydroxynaphthalene as coupling component, and also exist predominantly in the hydrazone form (2.54). Their shades fall within the yellowish-orange to bluish-red range but exhibit rather poor fastness properties to organic solvents and are consequently used mainly in air-drying paints. CI Pigment Orange 5 (2.54a) and CI Pigment Red 3 (2.54b) still sell in very large volumes.

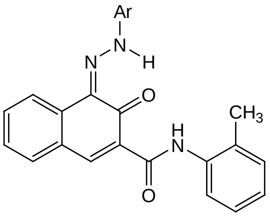
Naphthol AS (Naphthol Reds) pigments are monoazo pigments based on the aromatic amides from 2-hydroxy-3-naphthoic acid (BON Acid) as coupling component, which afford shades from yellowish to very bluish red *e.g.* CI Pigment Red 112 (2.55). Most of these pigments derive their importance from their use in printing inks.



(2.53)

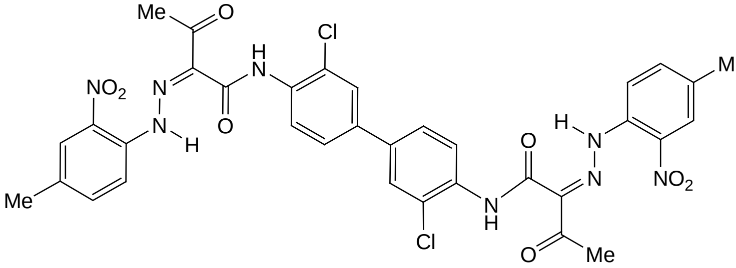


(2.54)
(a) $R^1 = NO_2$
(b) $R^1 = Me$

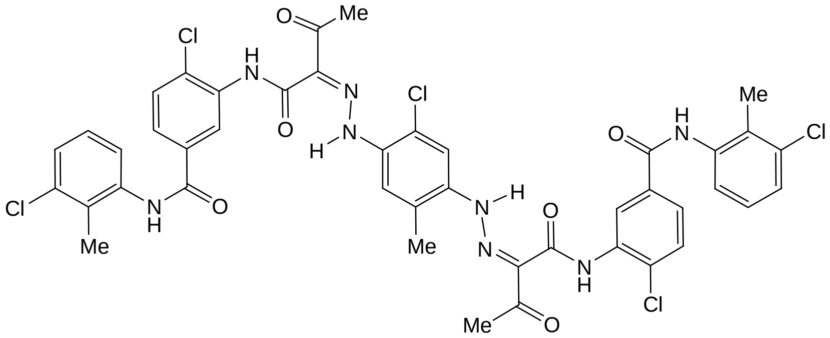


(2.55)
Ar = 2,4,5-$Cl_3C_6H_2$

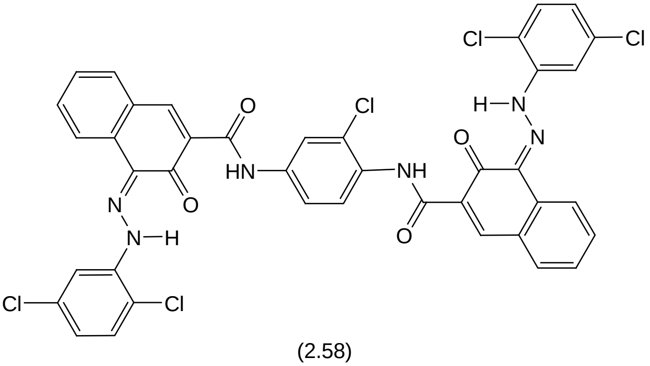
Symmetrical disazo pigments of commercial importance are derived from substituted benzidine diazo components and either an azo pyrazolone or acetoacetanilide coupling component (Diarylides). A good example is CI Pigment Yellow 12 (2.56), which is widely used in printing ink applications. The other type of disazo dyes used as high performance pigments are the so-called diazo condensation pigments. These are basically two monoazo dyes with a bridging group linking the azo chromophores, thus increasing the size of the molecule, leading to an improvement in properties, such as solvent and migration resistance. The most important pigments are those from acetoacetarylides (*e.g.* CI Pigment Yellow 93 (2.57)), and BON Acid arylamides (*e.g*. CI Pigment Red 144 (2.58)). The products are high-quality pigments used in plastics and quality printing inks.



(2.56)



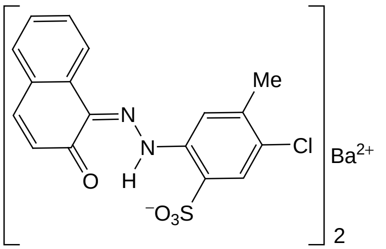
(2.57)



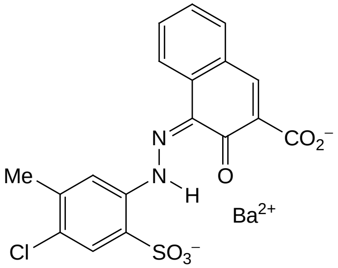
(2.58)

Azo pigment lakes are made from azo colorants bearing sulfonic or carboxylic acid groups by reaction with alkali earth and magnesium salts. Although both yellow and red azo lakes can be made, it is only the latter which have any commercial significance. The red azo lakes are based on four structures: β-naphthol (CI Pigment Red 53:1 (2.59)), BON Acid (CI Pigment Red 48:2

(2.60)) and, of lesser importance, Naphthol AS and naphthalene sulfonic acid-based dyes.[9] β-Naphthol and BON Acid lake pigments are widely used in the printing ink industry and in plastics.



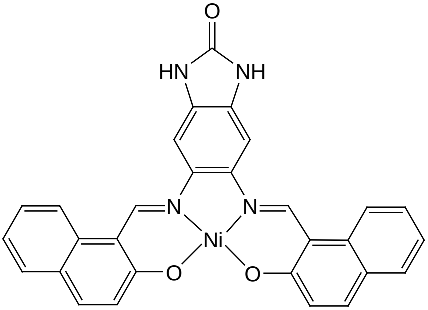
(2.59)



(2.60)

2.4.1.2 Metal Complexes

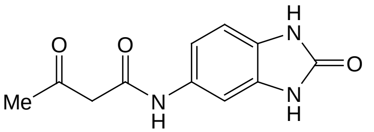
Metal complexes, usually Cu^{2+}, Ni^{2+} or less commonly Co^{2+}, of 2,2′-dihydroxyazo dyes and azo methines have been used to produce yellow to red pigments that have commercially attractive properties. They find application in industrial and automotive finishes and also in plastics. CI Pigment Orange 68 (2.61) is an interesting pigment, which also contains the benzimidazolone moiety, and is actually one of the most heat stable of all the organic pigments.



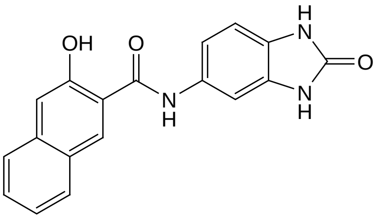
(2.61)

2.4.1.3 Benzimidazolones

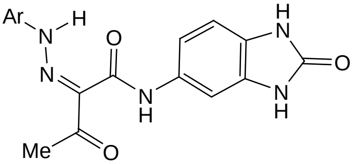
Benzimidazolone pigments are actually monoazo pigments but the convention within the industry is not to use the azo descriptor; they are classified as high-performance pigments. All the pigments in this class are derived from coupling components carrying the 5-aminocarbonyl-benzimidazolone group, typified by the yellow/orange pigments based on 5-acetoacetylamino-benzimidazolone (2.62) and the red and brown pigments from the arylamide (2.63). The presence of the benzimidazolone group helps to reduce the solubility of the derived azo pigments, improving both solvent and migration fastness and also light and weather fastness. They therefore exhibit the best fastness properties of any of the azo-derived pigments and are used in most areas of pigment applications in paints, coatings and plastics. The yellow/orange pigments, *e.g.* CI Pigment Yellow 120, CI Pigment Yellow 151, Pigment Orange 36, have the generic structure (2.64) and the red/browns (2.65), *e.g.* CI Pigment Red 171, CI Pigment Red 175, CI Pigment Red 176.



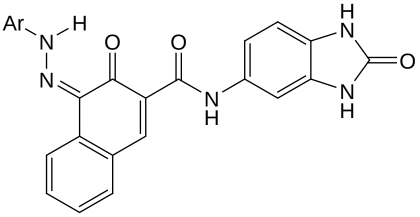
(2.62)



(2.63)



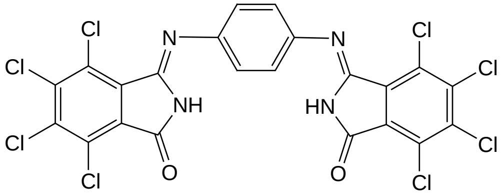
(2.64)



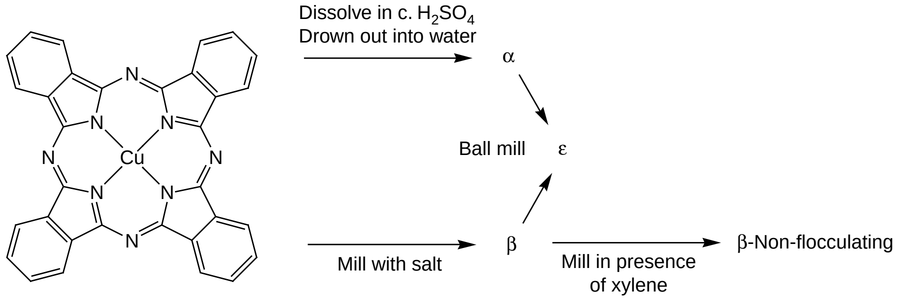
(2.65)

2.4.1.4 Isoindolinone Pigments

All the important isoindolinone pigments are derived from the tetrachloro isoindolinone ring by condensation with aromatic 1,4-diamines. The shades range from yellow through orange to red, but are especially important in the greenish yellow to reddish yellow areas, exemplified by CI Pigment Yellow 110 (2.66). They are high-grade pigments that find application in industrial paints and automotive finishes, plastics and quality printing.



(2.66)



(2.67)

Figure 2.18 Crystal modifications of copper phthalocyanine.

2.4.1.5 Phthalocyanines

The copper complex (2.67 in Figure 2.18) of the parent phthalocyanine macrocycle is the single most important organic pigment, and is a highly stable blue pigment with excellent properties.[51] [53] It is manufactured on a very large scale, and comprises around 21% of the world market for pigments (Table 2.10). Known as CI Pigment Blue 15, it is the first choice blue in inks, paints and plastic outlets. Its use as the basis of bright blue and turquoise textile dyes has been described earlier (Section 2.3.1.6). Phthalocyanine molecules and structural analogues continue to find wide applications in a variety of technologically advanced areas, which are covered elsewhere (see Chapters 4 and 5), but none on anything like the scale of their use as pigments.[66] [67]

The commercial manufacturing routes to copper phthalocyanine are based on either the tetramerisation of phthalonitrile in the presence of copper salts, or of phthalic anhydride or phthalimide in the presence of urea and a copper salt. The manufacture can be carried in a solvent by a batch process or by a continuous dry bake procedure. Alternative metal salts can be used to give other metal phthalocyanines, but these are of no importance as pigments. The metal-free phthalocyanine, which can be synthesised from diiminoisoindoline, made by reacting phthalonitrile with ammonia, by heating in a high-boiling-point alcohol, is of little significance as a pigment.

Copper phthalocyanine (CuPc) like many other phthalocyanines is polymorphous (see also Chapter 4, Section 4.2.1.8), where the order of thermodynamic stability of the main polymorphs is $\beta > \varepsilon > \alpha$. The reddish blue α-form is metastable and is readily converted to the stable, greener shade β-form. The particular crystal modification obtained is defined by the way the crude material is treated, crude in this context meaning untreated rather than impure. Some of the methods for the interconversion of the various forms are shown in Figure 2.18. Of particular interest are the phase-stabilised and non-flocculating versions of the α- and β-forms. The non-flocculating α-form is made by incorporating 3–4% of 4-chlorophthalic anhydride into the manufacturing

Table 2.11 Commercially available copper phthalocyanine pigments[9] (reproduced with permission of Wiley-VCH)

CI name	*Crystal form*	*Stability*	*Shade*	*Halogen atoms*
Pigment Blue 15	α	no	Reddish blue	0
Pigment Blue 15:1	α	yes	Greener than Blue 15	0.5 1 Cl
Pigment Blue 15:2	α	yes non flocculating	Reddish blue	0.5 1 Cl
Pigment Blue 15:3	β		Greenish blue	0
Pigment Blue 15:4	β	non flocculating	Greenish blue	0
Pigment Blue 15:6	ε	yes	Very reddish blue	0
Pigment Green 7			Bluish green	14 15 Cl
Pigment Green 36			Yellowish green	4 9 Br 8 2 Cl

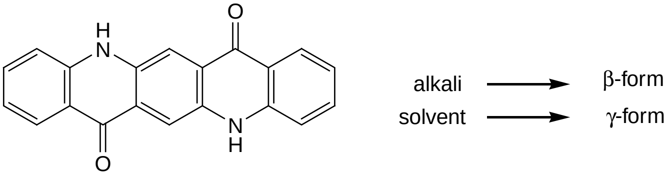
process for the crude phthalocyanine. Another method for producing non-flocculating products involves milling in the presence of substituted copper phthalocyanine derivatives *e.g.* $CuPc(CH_2NR_2)_n$, which absorb onto the surfaces of the pigment, thus helping to maintain its dispersion in a medium by steric stabilisation.[68]

Halogenation of copper phthalocyanine produces green pigments, which are again the pigment of choice in this shade area for coatings, inks and plastics. Halogenation with chlorine and bromine is carried out in a molten eutectic of aluminium chloride and salt. The green contains 14–15 chlorine atoms. Replacing some of these with bromine, up to 12 atoms, makes the shade a much yellower green. Although formally written as single compounds the products are actually statistical mixtures of halogenated products. Consequently, the green phthalocyanines, unlike the unsubstituted products, do not undergo changes in their crystal habit.

A summary of the properties of the commercially available phthalocyanines is given in Table 2.11.[9]

2.4.1.6 Quinacridones

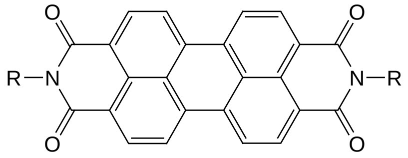
Quinacridone is the trivial name given to the five-ring heterocyclic system, exemplified by the linear *trans*-quinacridone (2.68). The yellow-red to reddish-violet shade pigments based on this ring system show outstanding durability and are used in plastics, in industrial and automotive finishes, and in exterior finishes. Like copper phthalocyanines the unsubstituted linear quinacridone exhibits polymorphism and two crystal forms, the reddish violet β-form and the red γ-form, are commercially available as CI Pigment Violet 19. Substitution in the outer rings by Me and Cl gives the valuable pigments CI Pigment Red 122 and CI Pigment Red 202 respectively.



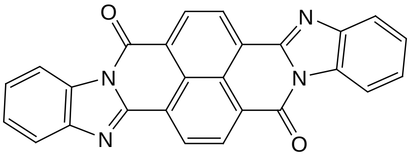
(2.68)

2.4.1.7 Perylenes and Perinones

Perylenes and perinones fall into a class of pigments known as "Vat Pigments", which also contains a range of other polycyclic quinones. They are classified in this way because a large proportion of them were used as vat dyes for textile fibres, many years before their use as pigments (Section 2.3.1.2). Perylene pigments are made by reaction of the perylene tetracarboxylic dianhydride with primary aliphatic or aromatic amines in high-boiling solvents to give the bisimides (2.69). Perylenes provide a range of shades from red through bordeaux to violet, depending on the nature of amide substituent *e.g.* CI Pigment Red 179 (2.69, R = Me). They exhibit high tinctorial strength and good fastness properties to light, weather and solvent and are used in high-grade paints for industrial and automotive outlets.



(2.69)



(2.70)

Perinones are structurally similar to perylenes, being made by condensing naphthalene tetracarboxylic dianhydride with amines, but in this case 1,2-diamines, to give CI Pigment Orange 43 (2.70) or its *cis* isomer. The isomers can be separated from each other by fractionally separating their salts. They offer orange to bordeaux shades with similar properties to perylenes, but are less commercially important.

Both perylenes and perinones show significant fluorescent behaviour and have found new outlets based on this characteristic (see Chapter 3).

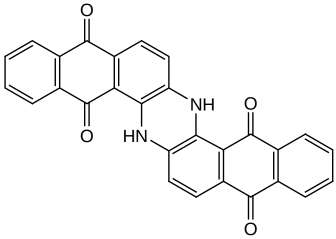
2.4.1.8 Polycyclic Quinones

Anthraquinone and certain polycyclic quinones, some of which have already been discussed under their use as textile dyes (Section 2.3.1.2), also find outlets as pigments. Anthraquinone azo pigments and lakes of hydroxyanthraquinone are not of major importance. However, polycyclic quinones are widely used as pigments because of their high fastness properties, especially weather fastness.

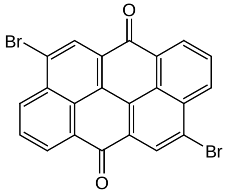
For instance indanthrone (2.71), CI Pigment Blue 60, shows properties that are even better than copper phthalocyanine in light tints. It is consequently used in automotive finishes and general industrial paints.

Another important quinone is anthanthrone, especially its dibromo derivative (2.72), CI Pigment Red 168. This is scarlet in colour, shows excellent resistance to solvents and is one of the most light-fast and weather-fast pigments known. It is used in high-grade paints.

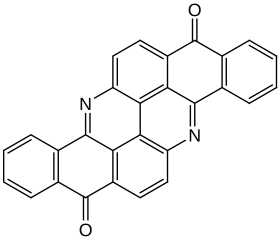
Other ring systems providing valuable pigments include flavanthrone, CI Pigment Yellow 24 (2.73), pyranthrone (2.74), whose halogenated derivatives give high light-fast orange and red pigments used in paint outlets, and especially dioxazine, whose carbazole derivative is CI Pigment Violet 23. This was originally thought to have a linear structure but now has been shown to be angular (2.75). It is a very versatile and important pigment used in all outlets.



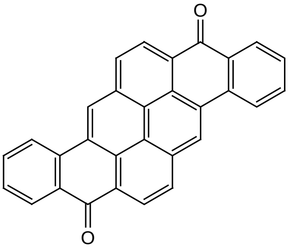
(2.71)



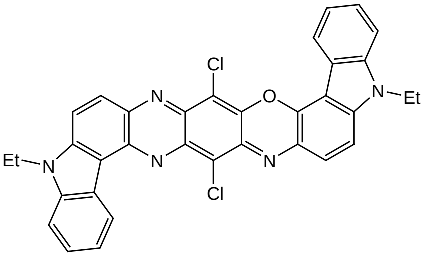
(2.72)



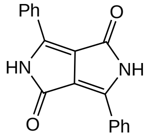
(2.73)



(2.74)



(2.75)



(2.76)

2.4.1.9 *Diketo-pyrrolopyrroles*

Arguably the most important new chromophore introduced in the latter part of the twentieth century was the diketo-pyrrolopyrrole from Ciba in the 1980s. The story behind this "discovery" by Iqbal and his colleagues makes as fascinating a reading as Greenhalgh's work on benzodifuranone dyes (Section 2.3.1.2).[69] The first product to be commercialised, CI Pigment Red 254 (2.76), rapidly established itself as a high-performance bright red of choice for automotive finishes.

2.4.1.10 Triarylcarbeniums

The structures of triarylcarbenium dyes have already been described (see Section 2.3.1.5). In the pigment field, the insoluble complexes of triarylcarbenium dyes with heteropolyacid counter ions (phosphotungstomolybdates) are used to give products that are exceptionally bright and exhibit high clarity. However, they show only moderate to poor fastness to light, and consequently their use is restricted to printing inks designed for areas requiring only low durability, such as in the printing of disposable packaging.

2.4.2 Inorganic Pigments

Two of the most important inorganic pigments are the white opaque titanium dioxide and carbon black.[10] However, in this text we will only consider those pigments which are used for their colour, *i.e.* a specific absorption in the visible spectrum. The origin of the colour in inorganic pigments is due to one of the three following effects:[70]

- Ligand field effects (*e.g.* iron oxide reds and yellows);
- Charge transfer (*e.g.* chromates, ultramarines);
- Pure semi-conductors (*e.g.* cadmium yellows and oranges).

It should be noted that the use of certain inorganic pigments, especially those derived from cadmium derivatives and lead chromates, pose considerable toxicological risks and their use is now subject to legislation in most countries.

2.4.2.1 Iron Oxides

By far the largest class of coloured inorganic pigments are those based on iron oxide. These pigments are non-toxic and are consequently of increasing importance in producing low-price products in a wide range of shades: yellow, orange, red, brown and black. The natural iron oxides, although still widely produced, are of decreasing commercial importance compared to the synthetic oxides, which comprise a million tonnes or about 33% of the total world demand for coloured inorganic pigments (2007). This is because the synthetics generally display superior hues and can be made in a more consistent quality. Their main uses are in concrete coloration and in paint, areas of increasing demand in both developed and developing countries, leading to good growth rates for these materials.

The manufacture of synthetic iron oxides is carried out by three different methods, using raw materials such as scrap iron or by-product liquors from TiO_2 production and steel pickling.

- *Solid-state* – this process involves the calcining of iron oxides, sulfates and chlorides in an oxidising atmosphere to give reds, browns and blacks.
- *Precipitation and hydrolysis* – solutions of iron salts are mixed with alkali and then aerated at temperatures above 90 °C, causing precipitation of the

desired pigment. This method is used to produce yellows, oranges, reds and blacks.

- *Laux Process* – this is a modification of the Béchamp process for the iron reduction of nitrobenzene to aniline, which leaves iron oxide as the residue. Incorporation of iron or aluminium chlorides into the reduction process produces high-quality yellow and red iron oxide pigments.

Typical products include:

- CI Pigment Red 101 (synthetic) and CI Pigment Red 102 (natural; haematite) $Fe_2O_3 \cdot xH_2O$;
- CI Pigment Yellow 42 (synthetic) and Pigment Yellow 43 (natural; sienna) $FeO \cdot xH_2O$;
- CI Pigment Brown 6 (synthetic), also known as brown magnetic iron oxide, $Fe_2O_3 \cdot xFeO \cdot yH_2O$;
- CI Pigment Brown 11 known as magnesium ferrite $MgO \cdot Fe_2O_3$;
- and CI Pigment Black 11, magnetite Fe_3O_4.

2.4.2.2 Chromium Oxide

Chromium (III) oxide is a true, single-component green, CI Pigment Green 17, produced by reducing sodium dichromate with sulfur. Leaching and washing with water readily removes the sodium sulfate by-product. This pigment absorbs in the NIR and has found uses in camouflage paints.

The hydrated product, $Cr_2O_3 \cdot H_2O$, known as Viridian Green, is a blue shade green, CI Pigment Green 18, having excellent fastness properties and is suitable for use in both inks and paints.

2.4.2.3 Mixed Oxides

Mixed metal oxides are solid solutions formed by incorporating coloured cations into a stable oxide lattice.[10] The two stable lattices that are used in commercial products are rutile (TiO_2) and spinel, $MgAl_2O_4$. The pigments are made by solid-state reaction of the components at 800–1400 °C followed by grinding *etc*. The rutile-based products include CI Pigment Yellow 53 $(Ti_{0.85}Sb_{0.10}Ni_{0.05})O_2$ and CI Pigment Brown 24 $(Ti_{0.90}Sb_{0.05}Cr_{0.05})O_2$. Spinel-type phases of commercial importance include cobalt as the colouring cation, *e.g*. Cobalt Blue, CI Pigment Blue 28 ($CoAl_2O_4$); Pigment Blue 36 $[Co(Al,Cr)_2O_4]$; and Cobalt Green, CI Pigment Green 50 $(Co,Ni,Zn)_2TiO_4$.

2.4.2.4 Alternatives for Cadmium Pigments

Because of their brilliant pure red and yellow shades, cadmium pigments (*e.g*. CI Pigment Red 108, $CdS \cdot xCdSe$) have found widespread use in the coloration of plastics, but toxicological problems have led to restrictions on their use and to the introduction of safer replacement products. An example of a newer material without toxicological problems is the brilliant yellow, bismuth vanadate, CI Pigment Yellow 184, made by the reaction of bismuth nitrate with sodium vanadate, followed by calcining at 300–700 °C.

2.4.2.5 Chromate Pigments

Another group of traditional inorganic pigments under a toxicological cloud are the chrome yellows (lead chromate), *e.g.* CI Pigment Yellow 34 and lead molybdate oranges and reds, *e.g.* CI Pigment Red 104. In recent years their use has been severely restricted by legislation to such areas as engineering plastics, where there is no organic pigment with the required stability at temperatures up to 600 °C.

2.4.2.6 Ultramarine Pigments

Ultramarine was the name given by the artists of the Middle Ages to the bright reddish-blue pigment derived from the semi-precious stone, lapis lazuli, brought "over the sea" from Afghanistan. Its high cost meant that its use was reserved for the important symbolic components of religious pictures, such as the Virgin Mary's habit. It was not until 1828, when a synthetic route to ultramarine was discovered in Germany, that it became an economically viable blue pigment for more general use. The process for its manufacture involves heating an intimate mixture of activated clay with feldspar, sodium carbonate, sulfur and a reducing agent at around 700 °C, followed by controlled aerial oxidation at below 500 °C. Following removal of impurities by froth flotation and washing, the product is dried and ground to the pigment grade. Ultramarines are zeolites and can be considered as a three-dimensional aluminosilicate lattice with entrapped sodium and ionic sulfur groups (the chromophores). Ultramarine Blue, CI Pigment Blue 29, formally $Na_6Al_6Si_6O_{24}S_4$, is used as pigment in paints, inks and plastics, but also has a sizeable use as a whitening agent in detergents. Oxidation of Ultramarine Blue produces Ultramarine Violet, CI Pigment Violet 15, widely used in cosmetics and artist colours.

2.4.2.7 Iron Blue Pigments

Iron Blue, CI Pigment Blue 27, which has been known by various names over the years, perhaps the best known being Prussian Blue, is ferric ammonium ferricyanide, $Fe(II)NH_4Fe(III)(CN)_6 \cdot xH_2O$. The first step in its preparation involves the precipitation of complex iron(II) cyanides, *e.g.* potassium hexacyanoferrates(II) with iron(II) salts, in an aqueous solution in the presence of ammonium salts. The white solid that is produced is then "aged" and finally oxidised with hydrogen peroxide or sodium chlorate to give the blue pigment. It has relatively poor properties and production has diminished considerably in recent years. Mainly used in the printing industry as a toner for black inks, it is also used in the colouring of fungicide formulations. Its ability to undergo colour change due to redox reactions has meant that it has found use as an electrochrome in electrochromic devices (see Section 1.5.3.2 in Chapter 1).

2.4.3 Special Effect Pigments

There are six main classes of speciality pigments:

- Anti-corrosive pigments;
- Magnetic pigments;
- Metallic pigments;
- Luminescent pigments;
- Lustre pigments;
- Transparent pigments.

The first three of these are used for specific properties not related to their colour: anti-corrosive pigments for the protection they offer to metal surfaces against environmental corrosive attack; magnetic pigments are ferromagnetic iron oxide pigments used in storage media for electronic data, *e.g.* audio and video cassettes, floppy discs, *etc*; and metallic pigments largely to produce metallic finishes in automotive paints. Luminescent pigments are described in Chapter 3 of this book (Section 3.2) and under fluorescent dyes and pigments (Section 3.5.5). Lustre pigments are discussed under iridescence in Chapter 5 (Section 5.3.1).

Transparent pigments are those that become transparent in binders when the difference between the refractive indices of the pigment and the binders is very low. The particle size of the pigment must be in the range of 2–15 nm, and so they are nanoscale pigments. This is accomplished during synthesis by the use of additives to prevent re-agglomeration of the pigment particles (see also Section 2.4.5). Examples of transparent pigments are:

- CI Pigment Yellow 43 transparent iron oxide α-FeO(OH);
- CI Pigment Red 101 transparent red iron oxide;
- CI Pigment 27 transparent Iron Blue;
- CI Pigment Blue 28 transparent Cobalt Blue;
- and CI Pigment Green 19 transparent cobalt green spinel.

Transparent iron oxides are used to colour clear plastic bottles and films for packaging and in cosmetics, whilst the cobalt blue and green are used in filters for cathode ray tubes.

2.4.4 Applications of Coloured Pigments

The three main application areas for coloured pigments are in printing inks, paints and coatings, and in plastics, comprising some 93% of the total (see

Table 2.12 Organic pigment application areas.

Area	*Printing inks*	*Paints & coatings*	*Plastics*	*Others*
%	60	20	10	10

Table 2.12). The only other areas of any significant importance are textile printing, pigmented fibres and paper.

2.4.4.1 Dispersion of Pigments

Apart from displaying the desired physical properties, such as light, heat and weather fastness, solvent resistance, *etc.*, there is a prime requirement that the pigment be readily and evenly dispersible in the application medium.[9] Stabilisation of the pigment particles in use is achieved by addition of appropriate dispersants depending on the nature of the solvent medium. Most pigments are sold as solids and the ease of dispersion in the medium to be used in the application is very dependent on the size of the particles in these solids.

For instance in azo pigment manufacture, the crude product is given some form of surface treatment, such as with rosin, in order to control crystal growth, control aggregation and to aid in dispersion. The original large agglomerates in the manufactured pigment need to be broken down by either grinding or milling. The methods used include dry milling in rollers or in impact mills, often in the presence of grinding aids such as salt; wet grinding in the presence of glass beads; and thermal crushing. Another method, used particularly with phthalocyanine blues and greens, involves dissolving the pigment in strong sulfuric acid (acid-pasting) and then controlling the particle size during precipitation into water (see Section 2.4.1.5).

An alternative to the drying and grinding method of introducing dispersibility into a pigment dispersion is the use of "flush" pastes. These flush pastes are made by directly transferring the pigments at the end of the manufacturing process from the aqueous to a non-aqueous medium containing the binders and other additives. The flush pastes can then be mixed directly into the application media without drying or any further attrition.

In recent years there has been a move to the production of nanoscale pigment particles for improved performance and use in transparent films, ink-jet inks and other outlets requiring extremely fine particles. These developments will be described in Section 2.4.5.

2.4.4.2 Printing Inks

This is by far the largest single market for organic pigments, representing around 60% of the total world consumption. It is not surprising that it continues to grow at a very respectable rate of around 5–6% per annum when one considers the vast amount of junk mail and packaging that we all have to deal with in our daily activities. The main technologies used for printing, detailed descriptions of which are available in standard texts,[71] and their approximate market share (2004) are:

- Offset lithography (35%);
- Flexography (35%);
- Gravure (18%);
- Digital (4%);
- Others (8%).

Digital printing, although relatively small in 2004, is on a very rapid growth path with the introduction of wide-format machines and developments in ink technology making it competitive for short runs with offset and other technologies. The special requirements for dyes and pigments will be covered in Section 2.9.

All the main classes of pigments are used in the printing ink industry, but the high-performance pigments (quinacridones) can be up to 30 times dearer than azo pigments, and are reserved for use in the highest-quality printing. Organic pigments used in a typical four-colour lithographic printing process of cyan/magenta/yellow/black (CMYK) are CI Pigment Blue 15 (phthalocyanine), Pigment Red 49:1 (β-naphthol lake) and 57:1 (BON Acid lake), CI Pigment Yellow 12 or 13 (diarylide yellows) and CI Pigment Black 7 (carbon black).

In flexographic printing there has been a move away from solvent inks to the more environmentally friendly water-based inks. This has led to a renewed interest in the use of this technology.[72]

2.4.4.3 Paints and Coatings

The second largest user of pigments is the paint and coatings industry, which is not surprising with a world demand for paint in 2007 of 28.5 M tonnes. The make up of the end users for this volume of paint is given in Table 2.13.

Pigment selection for a particular coating is highly dependent on the nature of the coating resin (polyesters, alkyds, acrylics and latex) and whether it is solvent-based, water-based or a powder coating. Improved environmental impact has been achieved by an increase in the use of very high solids in solvent systems, and a move from solvent to water-based coatings and a rise in two-component polyurethane and powder coatings.

Table 2.13 End user sectors of coatings/paint.

Sector	*%*
Architectural Coatings	48 (DIY 18)
Production line finishes (OEM)	39
Speciality	13

2.4.4.4 Plastics

A very wide range of plastics is coloured with pigments including PVC, polystyrene, polyurethane, polyamide, polycarbonate, polyester, elastomers, thermosets and thermoplastics. The choice of pigment is obviously dependent on which plastic is to be coloured, but especially on the processing conditions employed in the coloration and subsequent fabrication processes. High-performance pigments are often used where excellent solvent fastness and stability to severe processing conditions are required.

Many plastic materials are coloured using pre-dispersed concentrates of the colour in the same polymer or a compatible resin; these are known as masterbatches. Masterbatches overcome the problems of dispersing the conventional solid pigments into the polymer matrix.

2.4.4.5 Construction Materials, Ceramics and Glass

The major use (60%) for coloured inorganic pigments, such as iron oxides, is in the construction materials industry. Here they are used to colour roof and flooring tiles, fibrous cement and mortar. Many inorganic pigments are used in coloured baking enamels for metal appliances. Chromium oxide is used in the refractory industry, not for its colour but because of its ability to improve the properties of bricks used in furnace linings.

The coloration of glazed ceramic articles and glass are age-old technologies in which the practitioners used readily available inorganic minerals and metals to produce their coloured artefacts. Ceramic glaze production involves the use of mainly inorganic oxides in an oxidising or reducing environment either in the high temperature of the kiln or in a post-kiln process (raku).[73] For instance in an oxidising kiln, iron(II) oxide gives greys to green, while copper(II) oxide a range of reds or beautiful blues in the presence of alkali. In the potter's hand, glazing is often carried out to a personal recipe and often includes a serendipitous outcome. This is not of course possible in commercial applications where strict control of recipes and firing conditions are required.

Metal oxides form true solutions in glass to produce colours, using anything from grams to kilograms per 100 kg of glass, from the corresponding metal oxides as follows: Ni(II) – violet, Mn(II) – blue-violet, Co(II) – blue, Fe(II) – blue-green (wine bottles), Fe(III) – brown (beer bottles), Cr(III) – green, Cu(II) – green, Cu(I) – red.

Metals form colloidal dispersions of nanoparticles in glass when heated under controlled conditions at 450–500 °C. For gold nanospheres of about 50 nm diameter, the surface plasmon resonance peak is positioned at 520 nm, and is responsible for the "gold–ruby" red colour displayed by gold colloids. Colours obtained using other metals include selenium mixed with CdS to give "selenium–ruby"; manganese to produce purple; copper a dark red; nickel a blue-violet; silver a yellow; and chromium green or black (see Chapter 1, Section 1.12.1).

2.4.5 Nanoscale Pigments

Although the term nanopigments is relatively new in the field, in fact the development of very small particle size pigments, average size less than 100 nm but commonly less than 25 nm for high transparency has been an objective of R&D for many years, and most colorant companies have ranges of such products, both inorganic and organic. What has changed is the availability of more effective size reduction equipment able to achieve nanosize distributions in ways not possible or practical a few years ago. Additionally, synthetic routes have also been developed to control the size, morphology and distribution of inorganic particles, including spray pyrolysis, flux precipitation, the polyol method and template synthesis.[74 78] The difficulty with these materials is controlling in use some of the application properties which are associated with smaller particle size: rheology, stability and durability. Overcoming these problems is essential in outlets where maintenance of stable dispersions over a long time is essential *e.g.* inks for ink-jet printers (see Section 2.9.1.3). Another important outlet is in cosmetics where high opacity and compatibility with nanoparticle TiO_2 is desirable.

2.4.5.1 Monodisperse Nanoscale Pigments

Using the so-called polyol process it is possible to make colloidal suspensions of stable, nanoscale particles of inorganic pigments in a high-boiling-point alcohol (*e.g.* diethylene glycol (DEG)), with solids contents up to 20%. This process involves heating the components (*e.g.* $Zn(OAc)_2$ and $Co(OAc)_2$ for $ZnCo_2O_4$) in DEG at 180 °C for 2 hours with vigorous agitation, the pigment formed being isolated by centrifuging, and excess DEG flushed out with ethanol prior to drying. Some of the pigments made by this process are shown in Table 2.14. The process is made possible because DEG efficiently complexes and stabilises the surface of oxide particles so that they exist almost non-agglomerated in the suspension. Spraying the DEG suspension directly onto a heated glass plate, at a temperature that causes immediate evaporation of the DEG, results in a

Table 2.14 Preparation parameters and body colour of nanoscale pigment powders[79] (reproduced with permission of Wiley-VCH).

Pigment material	*Temperature heating °C*	*Powder colour*
$CoAl_2O_4$	180	Purple
$CoAl_2O_4$	600*	Blue
Cr_2O_3	180	Dark green
$ZnCr_2O_4$	180	Green
$(Ti_{0.85}Ni_{0.05}Nb_{0.10})O_2$	180	Yellow
γ Fe_2O_3	180	Brown
α Fe_2O_3	240	Red
$Cu(Cr,Fe)O_4$	180	Black

Note: All are heated in diethylene glycol except * which is heating of the dry powder.

homogeneous pigment particle layer on the substrate of 200–300 nm thickness, which remains transparent to visible light.[79]

Another method, based on a general phase transfer and separation mechanism occurring at the interfaces of the liquid, solid and solution phases present during the process, can be used to synthesise a large variety of nanoscale crystals, including noble metal, magnetic/dielectric, semi-conducting, rare-earth fluorescent, bio-medical, organic opto-electronic semi-conducting and conducting polymer nanoparticles.[80] This liquid–solid–solution (LSS) phase transfer and separation process produces nearly monodisperse inorganic pigment nanoparticles in cyclohexane, which remain non-agglomerated even after several months, but can be isolated as solids by a similar work-up procedure to the one in the previous paragraph. Nanoscale inorganic pigments made by this process include barium sulfate ($BaSO_4$), lithopone (a mixture of $BaSO_4$ and ZnS), cadmium sulfide (CdS), cadmium yellow (a mixture of CdS and ZnS), red iron oxide (α-Fe_2O_3), black iron oxide (Fe_3O_4), cobalt ferrite ($CoFe_2O_4$), cobalt green ($ZnCo_2O_4$), chrome oxide green (Cr_2O_3), barium chromate ($BaCrO_4$) and lead chromate ($PbCrO_4$).[81]

Based on powder X-ray diffraction line broadenings and transmission electron microscopy images, it has been shown that the Prussian Blue pigment (Section 2.4.2.7) obtained as an insoluble precipitate in quantitative yield from an aqueous mixture of Fe^{3+} and $[Fe^{II}(CN)_6]^{4}$ (Fe^{2+} and $[Fe^{III}(CN)_6]^{3}$) is inherently an agglomerate of 10–20 nm nanoparticles. By crystal surface modification with aliphatic amines, the agglomerate nanoparticles can be dispersed into organic solvents giving a transparent blue solution. Ni-PBA and Co-PBA (nickel and cobalt hexacyanoferrates) are prepared in a similar manner. Consequently PB (blue), Ni-PBA (yellow) and Co-PBA (red) nanoparticles can be used to make three primary colour inks.[82]

As discussed above and in Section 2.4.4.1 nanoscale organic pigments are normally made by physical comminution in a special apparatus, often in the presence of a grinding aid such as salt or glass beads. For outlets such as colour filters for LCD displays (Chapter 5), very pure products are required, so avoidance of the presence of the remnants of any abrasive agents is beneficial. This can be achieved by using the so-called reprecipitation method, which involves the gradual addition of a solution of the pigment in a good solvent into vigorously stirred solvent with poor solubility for the pigment.[83] Using this process quinacridone and diketo-pyrrolopyrrole pigments with particle sizes of 25 nm of high purity were obtained, films of which gave very little light scattering, desirable for improving the performance of colour filters.[84]

2.4.5.2 Core Shell Structures

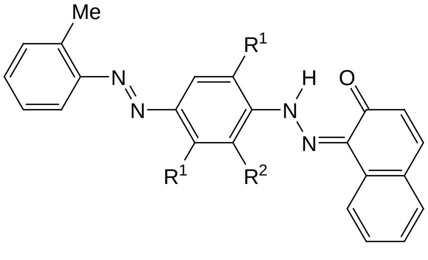
Core shell composite particles consist of a core material surrounded by a shell of a different material. They are of great interest because by manipulating their structure, size, and composition it is possible to control a variety of properties: optical, electro-optical, thermal, electrical and magnetic. The core/shell morphology can be used as precursors for the production of hollow spheres or inexpensive cores to support expensive shell materials, thus lowering their cost in use.

An eminently suitable core material for pigments is silica, whose spherical morphology can be easily controlled down to the nanometre size. Coating these spheres with pigment material gives core shell material whose size is controlled by the size of the silica cores. Additionally, since silica is cheaper than most pigments, the core/shell-structured pigment products are cheaper than the pure pigments per unit mass. A simple sol-gel process gives monodisperse, spherical and core/shell-structured $SiO_2@Cr_2O_3$ (green), $SiO_2@\alpha\text{-}Fe_2O_3$ (red), $SiO_2@MgFe_2O_4$ (brown), $SiO_2@ZnCo_2O_4$ (dark green), $SiO_2@CoAl_2O_4$ (blue) and $SiO_2@CuFeCrO_4$ (black) pigment particles, said to have better dispersing properties than commercial products.[85]

A process developed to produce core/shell hybrid organic pigments involves the mechanical dry milling of organic pigments in the presence of monodispersed silica nanoparticles, prior treated with methylhydrogenpolysiloxane to improve the affinity of the hydrophobic pigments, phthalocyanine blue, green and red diketo-pyrrolopyrrole. The derived pigments had average particle sizes below 50 nm. Spin-casting pigment-dispersed solutions gave highly transparent films with much improved transmittance in visible regions when compared with those of the original pigments, suitable for LCD colour filters.[86]

2.5 Solvent Dyes

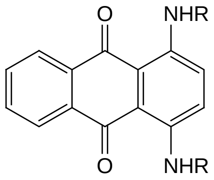
Solvent dyes are intermediate between dyes and pigments as they are insoluble in water, not having any sulfonic or carboxylic acid groups, but soluble in solvents: *e.g.* alcohols, esters and especially hydrocarbons.[87] Structurally, many solvent dyes bear a close similarity and relationship with disperse dyes. The structures of the dyes range from monoazo and disazo dyes (*e.g.* CI Solvent Red 24 and 26 (2.77)) to anthraquinones (*e.g.* CI Solvent Blue 35 and 36 (2.78)), and other quinones such as quinophthalones and perinones. Solvent solubility is also induced into anionic dyes by the use of fatty quaternary ammonium salts as cations, *e.g.* salts of 1:2 chromium complexes of monoazo dyes.



(2.77)

CI Solvent Red 24: R^1 = H, R^2 = Me

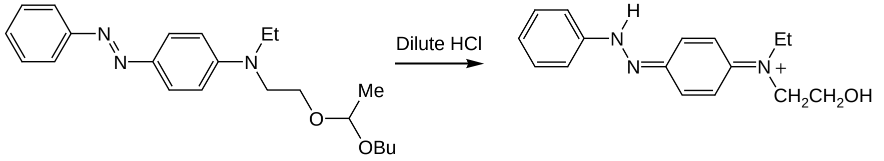
CI Solvent Red 26: R^1 = Me, R^2 = H



(2.78)

CI Solvent Blue 35: R = n-Bu

CI Solvent Blue 36: R = i-Pr



(2.79)
CI Solvent Yellow 124
Fuel soluble; yellow

Hydrolysed, protonated and water soluble; red

Figure 2.19 Mechanism of Euromarker coloration.

Because of their high solubility in hydrocarbons solvent dyes have found widespread use as markers for the identification of the various fractions of hydrocarbons that are produced in oil refineries, for instance in colouring red and blue diesels using CI Solvent Red 24 and CI Solvent Blue 35 (see also Section 1.7.2.1). Although used only in very low quantities the vast amount of fuels consumed in the world means that solvent dyes are manufactured on a very large scale, several thousand tonnes per year. From 2002 the Euromarker was introduced, requiring EU member countries to add $6\,\mathrm{mg\,l}^{-1}$ of Solvent Yellow 124 (2.79) to all low-tax fuels. When fuel containing Solvent Yellow 124 is shaken with dilute aqueous hydrochloric acid it is both hydrolysed and protonated to give a red water-soluble dye, easily detected and estimated in the aqueous phase (see Figure 2.19). This means for instance that 2–3% of red diesel can be detected in otherwise colourless fuels, thus preventing misuse by adulteration.[88]

Several solvent dyes show very high performance in plastics and are used widely in the coloration of thermoplastics and engineering resins, *e.g.* polycarbonate (PC) and acrylonitrile butadiene styrene (ABS). They are also used in the coloration of any solvent or wax-based product, including polishes, cosmetics, crayons, candles, inks, stains and adhesives. Another outlet is in the coloured smokes that are used in outdoor displays, for instance coloured trails from aircraft, and in safety and security applications.

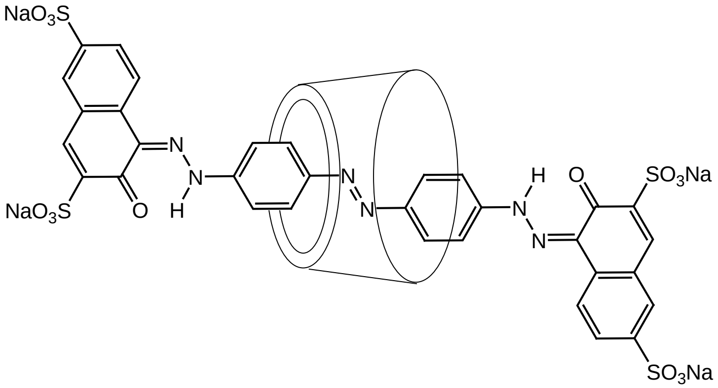
2.6 Dye Stabilisation *via* Molecular Encapsulation

In some of the newer outlets for dyes, described elsewhere in this book, avoidance of molecular aggregation is beneficial whilst almost all outlets would benefit from improved photochemical stability. Amongst the most promising methods for achieving both these objectives in organic dyes is that of molecular encapsulation *via* inclusion in cyclodextrin cavities, inorganic zeolites, dendrimers and supramolecular gels, and as threads within rotaxane molecules.[89]

2.6.1 Cyclodextrins and Related Rotaxanes

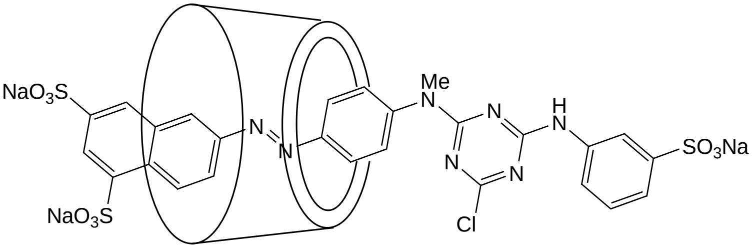
Cyclodextrins (CDs) are cyclic arrays of glucose units, with cylindrical cavities of diameters 4.7–5.3, 6.0–6.5 and 7.5–8.3 Å for α-CD (6 units), β-CD (7 units) and γ-CD (8 units), respectively. The CDs have long been used to encapsulate organic dyes,[90] but research has been more intense over the last decade.[91] It has been observed for instance that dimerisation and aggregation in cyanine dyes could be prevented, and photobleaching of a dye improved by its inclusion in a CD. Structurally related compounds have also been used to form inclusion compounds with dyes, *e.g.* the helical-shaped polysaccharide, amylase, and the cyclic heptamer cucurbit(7)uril.

The supramolecule comprising a dye complexed inside a CD is known as a pseudo-rotaxane. However, a major disadvantage of pseudo-rotaxanes is that the dye can come out just as easily as it went into the CD cavity, or can be physically replaced by another molecule. One way of overcoming this is to build capping groups onto the dye to form a stable rotaxane, thus holding the dye within the cavity because of its geometry and steric interactions with the encircling CD molecule. This is best achieved by synthesising the dye in the presence of the CD. A good example in the context of this chapter is the water-soluble rotaxane (2.80) made by spontaneously threading the tetrazonium salt of 4,4′-diaminoazobenzene into α-CD (thermodynamically favoured), and then twice azo-coupling with 2-hydroxynaphthalene-3,6-disulfonate. The disazo dye is locked in place inside the CD by the bulky sulfonated naphthalene groups.[92]



(2.80)

This type of rotaxane was further developed to study its interaction with solid surfaces, in particular cellulose, using an entrapped monochlorotriazine reactive dye (2.81). However, in this case, in order to avoid reaction of the dye with the hydroxy groups of CD, the CD was pre-methylated to give hexakis(2,3,6-tri-O-methyl)-α-cyclodextrin. When mercerised cotton was dyed with (2.81), and separately with a sample of the free dye under identical conditions, the rotaxane gave a weaker dyeing, which was easily compensated for by using a stronger rotaxane dyebath. Comparing the same strength dyeings on cotton gave very interesting results; the rotaxane dye was much more resistant to reductive bleaching with sodium dithionite and ten times more resistant to photobleaching when measured using a commercial fadeometer.[93]

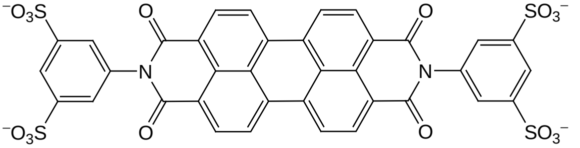


(2.81)

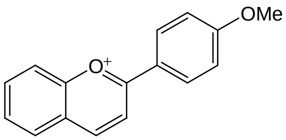
2.6.2 Inorganic Matrices

Protecting dyes within inorganic matrices offers a way of increasing their stability and hence a way of making pigmentary materials for a variety of outlets.[94] Nature after all has been there before us, for instance in the incorporation of fragile colorants such as carotenoids and melanins in seashells. Additionally, the ancients were able to make highly stable pigments by this process, exemplified by Maya Blue which was invented by the Indian cultures of Central America, where indigo is embedded within clays at 125–200 °C, the colour in the pigments remaining stable to light for over twelve centuries.[95]

Developments in sol-gel technology have enabled the ready formation of inorganic-organic hybrids including those involving dyes. Chromophores that have been incorporated into silica or aluminosilicates include the fluorescent rhodamines, pyronines and coumarins, as well as several photochromes (see also Chapter 1, Section 1.2.8.4).[96] These composites can be used to produce transparent films and monoliths with good mechanical integrity and excellent optical quality. Dyes incorporated into the pores of zeolites and macroporous silicates and their potential applications as luminescent pigments, in light-emitting diodes (Chapter 3) and in solar cells (Chapter 4) has been reviewed.[97,98] Incorporation of azo dyes into molecular sieves is reported to increase their stability to photobleaching by triplet state O_2 and their chemical stability.[99] Their incorporation into Ca-aluminosilicate mesoporous substrates increases their fastness to light after thermal annealing of the dye-loaded $Ca(OH)_2$ mesoporous precursors,[100] and the behaviour of azo dyes in zeolitic faujasites and hybrid organic-inorganic mesostructures has been studied.[101] As an example, the anionic perylene dye (2.82), when incorporated into layered double hydroxides (anionic clays) by direct co-precipitation, stacks up in J-type aggregates (see Chapter 1, Section 1.10) in the galleries between the hydroxide layers giving very bright red pigmentary products, but in this case with only a marginal increase in chemical and photochemical stability.[102]



(2.82)



(2.83)

Anthocyanins are the most important pigments in plants.[103] Over 500 different anthocyanins have been isolated, some of which are used as food additives (E163), discussed further in Section 2.7.1. However, they are susceptible towards colour change with pH and have poor stability to temperature, oxygen and UV light. Incorporating the yellow flavylium dye (2.83), used as a model of the chromophore in natural anthocyanins, into a narrow pore zeolite, H-mordenite, produced a composite which showed much increased stability over the free dye when an aqueous dispersion was heated (353 K) at pH 9. Thus zeolite incorporation becomes a candidate method for stabilising natural colorants for commercial uses.[104]

2.7 Natural Organic Colorants

In recent years there has been a significant rise in interest, especially by self-styled ethical consumers, for all things classified as natural as opposed to synthetic. This is particularly the case with colorants in food, beverages and cosmetics but also in textiles and to a lesser degree household paints. Natural colorants are considered by this group to be more environmentally friendly and safer in use, often at the best on very shaky evidence.

So what are natural colorants, often misleadingly called natural pigments? One definition is "pigments that are synthesised and accumulated in, and excreted from living cells or formed during the decay of dying cells." However, this would not cover important products such as indigo, which occurs as the colourless glycoside precursor, only forming the blue dye after isolation and oxidation. Consequently, a better definition is "a pigment formed in living or dead cells of plants, animals, fungi and microorganisms including organic compounds isolated and structurally modified to alter stability, solubility or colour intensity."[105] This definition is broad enough to cover the contentious area of dyes and pigments derived from genetically modified organisms.

2.7.1 Food and Cosmetics

The use of dyes, especially synthetics, in the coloration of food and beverages is covered in Section 2.3.2.4. The global market for food colorants in 2008 was estimated to be $1.2 bn, with natural colorants having 31%, but with growth rate of 5% *versus* only 1% for synthetics. Food standards agencies throughout the world are helping to drive this change, for instance the UK's FSA has asked the food industry to adopt a voluntary code from 2009 eliminating synthetic colours from all food and beverages. An additional factor is the many claims of medicinal benefits (nutriceuticals) of natural colorants, often with minimal or contentious evidence, especially those containing antioxidants such as anthocyanins in wines and lycopene in tomato skins.[106]

Natural colorants used in food and beverages in the USA on the FDA's "Exempt from Certification" list and those approved by the EC's FSA are from

Table 2.15 Sources of natural colorants and E numbers.

Natural occurrence	*Colour*	*Chemical class*	*EC Number*
Black grapes	Red/Blue	Anthocyanins	E163
Blackcurrants			
Cherries			
Elderberries			
Red cabbage			
Strawberries			
Beetroot	Pink	Betalains	E162
Cochineal insect	Red	Carminic Acid	E120
Alfalfa grass	Green	Chlorophyll	E140
		Chlorophyllins	E141
Nettles			
Parsley			
Spinach			
Turmeric	Yellow	Curcumin	E100
Caramel	Brown	Melanoidins	E150a d

a variety of sources including plants, animals and minerals, or they are synthetic duplicates of naturally existing colorants, *e.g.* β-carotene. Switching from synthetic colorants to natural ones is no easy matter as they are often much duller and less attractive in use. Additionally some foods require liquid additives, whereas others call for solids, some need to be water-soluble and others oil, and be able to stand heat processing and exposure to light. Using extra additives, *e.g.* metal salts, and buffers to maintain a pH, can stretch the definition of what is natural. Some sources of natural colorants, their chemical class and E numbers are shown in Table 2.15.[107]

The exempt natural colorants used in food coloration can also be used in cosmetics, such as crèmes, deodorants and soaps. The major natural hair dye is henna, obtained from the plant *Lawsonia inermis* as a red-orange pigment, the active component of which is 2-hydroxy-1,4-naphthoquinone. It imparts a translucent orange–red colour to hair, darkening and mixing with the natural hair to give an attractive brunette to black colour.[108] Some questions still need to be answered over the possible toxicological problems associated with lawsonia, and the conclusion of a study on a submission to the EC Scientific Committee on Consumer Products was that the information submitted was insufficient to assess the safe use of the substance as a hair dye and more work was required.[109] Just as it is from synthetic materials, indigo from natural sources can be used as a hair dye and produces a lustrous black colour.

Another traditional use of henna is in body art to produce yellow, orange and dark-brown temporary tattoos called mehndi. Whilst the FDA classifies 100% pure henna as exempt from regulation for use as a hair dye it is not approved for use in body art and import for this use is illegal. This is because of reported cases of skin irritation and dermatological problems associated with henna. Black Henna is not henna at all but a concoction containing 1,4-phenylenediamine and is dangerous to use, especially on broken skin.

2.7.2 Textiles and Leather

For thousands of years until the middle of the nineteenth century the coloration of textiles and animal skins could only be done using naturally occurring dyes and pigments. During this period a high degree of sophistication had been developed in both extracting these dyes from their natural sources and applying them to various substrates.[110] Classic examples were red dyes from the roots of the madder plant and from cochineal insects, purple from the murex shellfish and blue indigo from *Indigofera tinctoria* and *Isatis tinctoria* (woad).[111,112] However, after the discovery of synthetic dyes natural dyeing's importance as a method of coloration rapidly diminished until it became a niche industry, only carried out on any significant scale in some countries of the Middle East, and in India and China, on traditional wools (*e.g.* Harris Tweed), or on a small scale by artisans and home dyers.[113] Over the last two decades concerns raised by some environmentalists over the impact of synthetic dyes and their production on the environment, and the non-sustainable production of synthetic dyes from fossil fuel sources, have led to a reconsideration of whether natural dyes and dyeing can ever be developed as a significant player in the industrial dyes business. The pros and cons of natural *versus* synthetic dyes have been reviewed from the perspectives of advocates from each side of the debate; little has moved on from these positions in the intervening years.[114,115]

So what are the issues arising from the possible production and use of natural dyes on a large scale?

1. One objection is that the primary production of plants requires the use of a very large area of arable land, which might be better used to produce much-needed food, similar to the problems arising from the production of bio-diesel. This might be less of a problem with those few dyes that are obtained as a by-product from edible crops. The amount of dyes obtainable from animals and plants varies widely, for instance from dyewoods such as fustic, roots such as madder and shrubs such as the indigo plant, the yields vary between 0.5 and 5% on plant weight. It has been estimated that 100 million tonnes year ^{1} of dye-producing plants would be needed to produce the dyes required for the world's annual consumption of textiles.[110] For comparison the global production of edible grains in 2008 was 2000 M tonnes.
2. Whether grown "organically" or not, the large-scale dye crops will need some sort of fertiliser and consume a lot of water, which is becoming a scarce commodity in many regions of the world.
3. Processes for the extraction of dyes from the vegetable matter are energy intensive and/or require other chemicals and enzymes. A very large volume of organic waste, both aqueous and solid, is produced, which will need environmentally friendly disposal.
4. Many natural dyes require a mordant to be added during the dyeing process in order to produce fixation to the fibre and to improve their stability. These are inorganic chemicals, most commonly alum but

traditionally also potassium dichromate and copper salts, some of which will end up in the effluent, needing to be removed before discharge to drain.

5. Most natural dyes have not been safety tested to the same extent as modern synthetic dyes, so we cannot assume that there are no toxicological problems associated with them and their processing. Moving to large world-scale production would require better definition of potential health hazards and the development of safe working practices.
6. The colours produced on textiles by natural dyes are generally duller and less attractive than synthetic dyes and they stand up less well to washing, daylight, *etc*. Consequently garments are likely to be thrown away sooner, putting a greater strain on land use for both fibre (cotton) and dye-crop production, and also animal grazing (wool).

How are some of these issues being addressed technically?

1. Use of biotechnology – in discussing the possibility of producing plant-based dyes in the UK, Hill pointed out that "dye plants discussed here (woad, weld and madder) have been essentially unimproved since historical times. Consequently there is great potential for improvement by classical breeding, selecting the best strains and progeny of crosses. Biotechnology can assist this improvement in various ways. The use of molecular markers may allow traits of interest, such as colour, yield and composition to be followed and selected, without the need for expensive and time consuming biochemical screening. Genetic engineering can also be used to improve the agronomic performance of the plants. In particular, the transfer of genes for herbicide resistance would greatly facilitate weed control using conventional herbicides such as basta."[116]
2. Bacterial synthesis – modifications to the synthetic pathways in bacteria to several important plant pigments have been reported.[117] Indigo, being the most important synthetic textile dye also available from natural sources, has been the subject of much work. A semi-technical fermentation process for indigo has been developed, but the product cost was higher than the commercially available synthetic indigo.[118]
3. Novel processes being adapted for dye extraction from plants include the use of super-heated steam at 120 °C, solvent extraction and recycle, ultrasonification and enzymatic methods for cell-wall break down, all having the potential for reducing the effluent load.
4. Mordants remain a problem; it is weak to claim that the use of aluminium- and iron-containing products is eco-friendly. The proposed environmental quality standard for aluminium is $0.1\,\mu g\,l^{-1}$ for water at $pH < 6.5$, and $0.25\,\mu g\,l^{-1}$ above that value.[119] Estimated levels in effluent from typical natural processes are much higher.[114] Much work is required to overcome this outstanding problem with natural dyeing. It is worth recalling that one of the drivers of the development of the modern synthetic dyestuff industry was the avoidance of mordants.

In conclusion, the best hope for making natural dyes a commercial competitor to synthetics lies in the genetic modification of plants to improve their agronomic performance and produce higher yields of dyes within the plants, or alternatively the development of economic microbial processes from renewables. Whether this would be acceptable to the environmental/organic lobby is a moot point. The dyeing processes currently used are little different from those operated in the middle ages and significant work will be required in developing new, environmentally friendly methods of textile coloration.

Growing the naturally coloured species is a third way of producing coloured cotton. Coloured cotton has been grown since the third millennium BC, in places such as the Indian sub-continent, Egypt, Peru and China, the traditional varieties being mainly yellow and brown in colour, but also pale red and pale green colours can be produced. Until recently little research had been done into these species but now both gene manipulation and natural breeding techniques have been applied to improve its growth and performance.[120,121] However, in spite of this work it is still a very small player, representing only 0.2% of the world's cotton production, with 60% produced in China. Even extravagant growth rates would not lift this out of the niche market it currently occupies.

One of the big successes of genetically modified crops is cotton. In spite of objections mainly from EU countries, the rest of the world is voting with its feet. At the time of publication of the first edition of this book (2001) production of Bt cotton worldwide was only 6.8 M hectares, but this had more than doubled by 2007 to 15 M hectares, representing 43% of cotton production worldwide and further growth is expected.[122] Clearly there is scope for the acceptance of genetically modified cotton-based materials and hence the production of a wider range of brighter colours. For instance, in the late 1980s the biotech company Agrecetus announced that it was working on blue cotton by insertion of the gene responsible for blue flower production in a non-related species. This company was subsequently acquired by Monsanto who, in spite of reports to the contrary, now say that the product was never developed to commercial status.[123] Whether at the moment work such as this can be justified on commercial grounds is questionable, as current production seems to be mainly aimed to meet the demands of "ethical" consumers.

2.8 Photographic Colour Chemicals

The superiority of photographic images produced by silver halide photography and its commercial dominance was, for many decades, never seriously challenged, but in the last ten years the arrival of high-quality digital cameras, and cameras on mobile phones, coupled with the development of photorealistic digital printers and quality inks has shattered this pre-eminence. The traditional photo film market has been falling by more than 20–30% per year during the past several years, more than double the industry's initial estimates of about 10% per year.[124] The major photographic companies faced with a declining conventional photo industry needed to embrace digital-imaging technologies, with these companies switching R&D into ink-jet and related technologies but here the names of the dominant players changed to Hewlett-Packard, Canon, Epson and Lexmark (see Section 2.9). Without a doubt the biggest sufferer in this revolution had been instant photography as exemplified by the Polaroid system, consequently the description of this system given in the first edition has now been omitted. (However, see Section 2.9.3.3 for digital instant photography.) The demise of the colour photographic chemicals industry is clearly on the horizon but the chemistry, perhaps the most complex of any consumer product, is still worth describing even if in a much abbreviated form from that given in the first edition.

2.8.1 Colour Photographic Processes

The underlying process, in both black and white and colour photography, is the interaction of light with a sensitive emulsion of very fine silver halide grains (0.03 μm to 2.5 μm). Silver halide is only blue sensitive and in order to obtain full spectral (panchromatic) sensitivity it is necessary to incorporate red and green spectral sensitising dyes (see Chapter 4, Section 4.5.3). Development of the latent silver image is then achieved by reaction with reducing agents. A more detailed account of the processes involved is given in standard texts.[125]

In colour photography the film is multi-layer, each layer containing the chemicals required to produce one of the three additive or subtractive primaries. In practice, it is those processes which use the subtractive YMC primaries that dominate the market. However, even in these cases the additive process is used to record the blue, green and red components of light in three layers; the yellow, magenta, cyan subtractive primaries being produced in subsequent processing.[126]

2.8.2 Colour Films and Papers

The two basic types of colour film are the colour reversal film for transparencies and the colour negative film used to produce prints on colour papers.

2.8.2.1 Colour Reversal and Negative Films

The films used in the reversal process consist of three light-sensitive layers, red, green and blue, further split into high- and low-speed sensitive layers, containing the developer, coupler and silver halide (incorporated coupler system), with the red and green containing their respective sensitiser dyes. A red filter layer is placed between the red and green layers to improve colour separation and a yellow filter between the blue and green, preventing any blue light entering the red and green layers. The systems used to produce colour transparencies from exposed film are based on the Kodak E-6 process, or further developments, using compatible films.[127]

The basic structure of a colour negative film is the same as in a colour reversal film, with the relevant colour coupler incorporated into each layer. The difference between the two films is that after development the dye image is complementary to the final colour required in the resultant hard-copy print. Processing is usually carried out by the Kodak C-41 process which is simpler than the E-6 colour reversal process.

2.8.2.2 Colour Papers and Prints

The majority of colour papers are used to produce prints from colour negative films, but there are also papers designed to produce hard-copy images of transparencies.[125,126] For making prints from colour negative films the papers are constructed with three separate emulsion layers: blue sensitive, green sensitive and red sensitive, coated onto the substrate in that order. The sensitive layers contain silver halide and the appropriate coupler. The coated paper is covered with a UV absorber layer, usually 2-hydroxyphenylbenzotriazole, essential in order to help protect the dyes from light fading in the final image. The outline structure of the colour paper is shown in Figure 2.20.

2.8.3 Colour-forming Chemicals in Photography

The common term used for the colour forming process in colour photography is chromogenic development. The colours are formed by a chemical reaction between a colour developer and a colour coupler following reduction of the exposed silver halide.

Colour developers are substituted phenylenediamines, which are converted by a two-electron oxidation to a quinone diimine. This diimine then

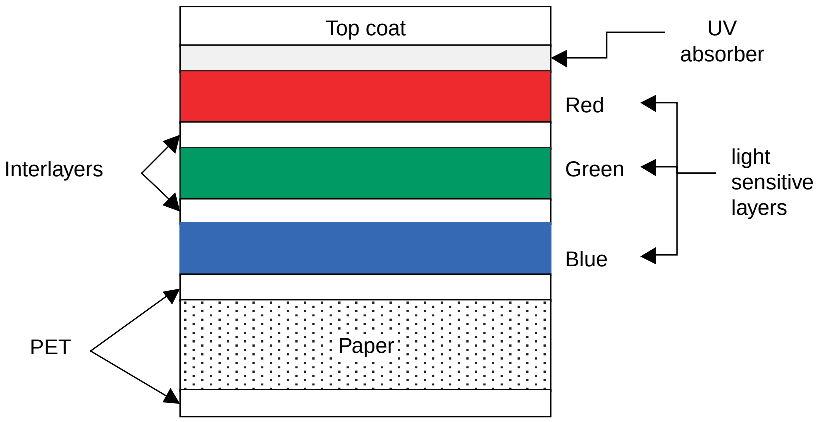


Figure 2.20 Cross section of a colour negative paper.

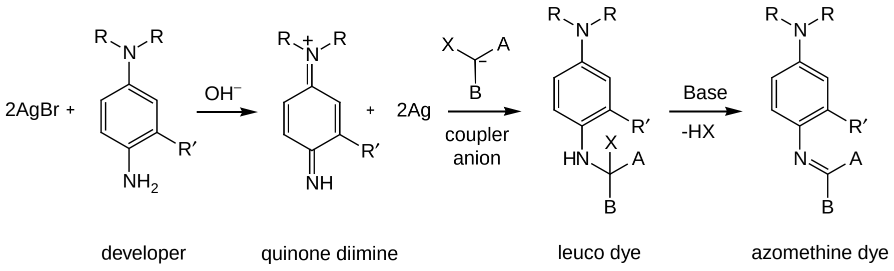
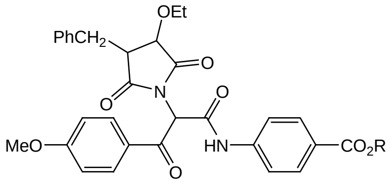


Figure 2.21 Chromogenic development by two equivalent coupling.

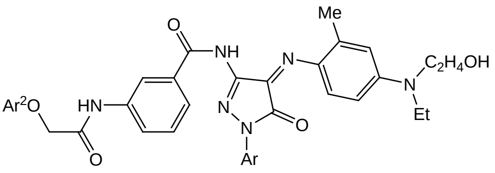
reacts with the anion of the coupler to give the leuco intermediate, which then reacts with base to eliminate a leaving group, forming the azomethine dye. When the leaving group is hydrogen, oxidation is required and consumes a second molecule of quinone diimine, hence four equivalents of silver bromide are required. The two-equivalent process is illustrated in Figure 2.21.

All the couplers used in colour photography contain an active centre, *e.g.* a methylene group that can react with the quinone diimine to produce the azomethine dye as shown in Figure 2.21. The couplers need to remain anchored in their respective layers. The preferred method for meeting this requirement is to have medium-sized hydrophobic groups attached to the molecules. These hydrophobic couplers are introduced into the appropriate layer as oil-in-water dispersions.[126]

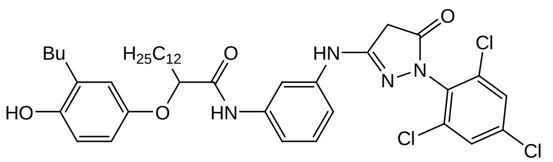
Yellow couplers and dyes. All the useful yellow couplers are based on acetanilides, especially the pivaloyl and benzoyl derivatives (2.84), which react to give the azomethine dyes absorbing at wavelengths in the region 450–480 nm. Pyrazolones are the main ring systems of choice for magenta couplers, *e.g.* (2.85) in colour paper and (2.86) in colour film, the derived dyes absorbing in the region of 530–580 nm. Cyan couplers need to produce very bright dyes absorbing in the region of 630–700 nm and to date only phenols and, to a much lesser degree, naphthols have been found to be commercially acceptable. Typical is the phenol (2.87) used in both colour reversal and colour negative films, depending on the nature of the R group, to produce indophenols.



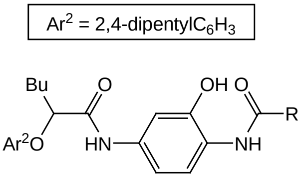
(2.84) R = $CH(Me)CO_2C_{14}H_{29}$



(2.85) R = C_5H_{11}; Ar = 2,4,6-$Cl_3C_6H_2$



(2.86)



(2.87) R = C_3F_7 or 4-CN-C_6H_4NH

2.9 Digital Printing

Digital printing, also known as non-impact printing, is the term used for a group of technologies used to produce an image on a substrate without the intervention of a conventional printing plate or screen. The growth of these technologies has been alongside the upsurge in the use of computers to generate both text and graphical images, which required a method for the simple and rapid production of hard-copy output in single and multiple copies. Initially, the machines were large and expensive (*e.g.* modified photocopiers and printers) and their use was restricted to larger establishments and copy shops, output being predominately black and white. In the late 1980s with the arrival of inexpensive personal computers for use in the small office and the home, a new population of consumers appeared on the scene. These users not only wished to print black and white output from word-processing packages but also coloured images for work, school and leisure uses. This latent demand for colour reproduction, using low-cost printers, was recognised by the machinery manufacturers, who set about developing the necessary hardware and collaborating with colorant companies to produce the required coloured inks. A parallel development has been large-format machines for use in a whole range of commercial printing applications on both paper-based and textile substrates in the relevant industrial sectors (see also Section 2.3.2.1). The rapid switch to digital cameras and imaging *via* camera function mobile phones over the last ten years also required a means of producing high-quality images, met by the development in 2000 and ongoing improvements since of the so-called photorealistic ink-jet printers, which give images when printed on special papers indistinguishable from those produced using 35-mm film (see also Section 2.8). Digital printers and copiers have a different set of material requirements from conventional printers and justifiably are treated here as a separate topic.

From a whole raft of competing reprographic technologies that have been developed (Figure 2.22), two have emerged as the dominant players: namely ink-jet and electrophotography, whilst thermal transfer printing enjoys some success, and even newer developments are taking place.[128] The major technologies and their material requirements and applications will now be considered in greater detail.

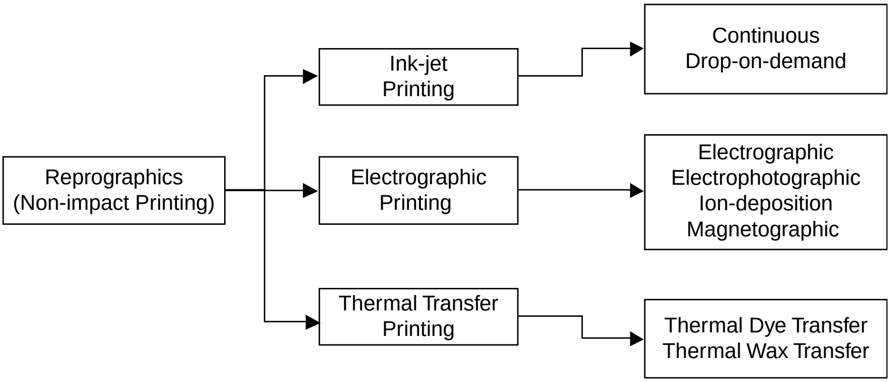


Figure 2.22 Reprographic (non impact) printing technologies.

2.9.1 Ink-jet Printing

Ink-jet printing as its name implies is a printing method in which a jet of ink is fired, in the form of extremely small droplets, onto a receiving medium.[129,130] It is a primary printing technology as the image is printed directly onto the substrate without any intermediate steps. The ink can be supplied in either a continuous manner or intermittently, known as drop-on-demand. Ejection of the ink from the print head is accomplished by either thermal- or mechanical-based processes, the former by bubble-jet or thermal printers, and the latter usually by piezoelectric crystals (piezo printers).

2.9.1.1 Continuous Ink-jet

In continuous ink-jet, a system that is reserved for industrial outlets, the ink is fired through a very fine nozzle, activated by a piezoelectric crystal, as a continuous stream of ink droplets. This stream of droplets passes through a charging electrode, where the droplets are selectively charged as required by the digitised image. After selective charging, the stream goes past a high-voltage deflection plate where the charged droplets are sent in one direction and the uncharged droplets in another. The charged droplets are directed to the substrate to form the image (raster method), with the uncharged droplets going to a gutter drain and back to the ink reservoir, or in exactly the reverse manner, the charged going to drain and the uncharged droplets to the substrate (binary method). The continuous ink-jet method is shown diagrammatically and not to scale in Figure 2.23. In industrial outlets the inks are often based on solvents such as alcohols and ketones containing the binder resins required for the adherence of the colour to a particular substrate, whether this be paper, card, plastic or metal.

2.9.1.2 Drop-on-Demand Ink-jet

Drop-on-demand (DOD) ink-jet is the method that has been universally adopted in the printers designed for use in small office and home environments (SOHO)

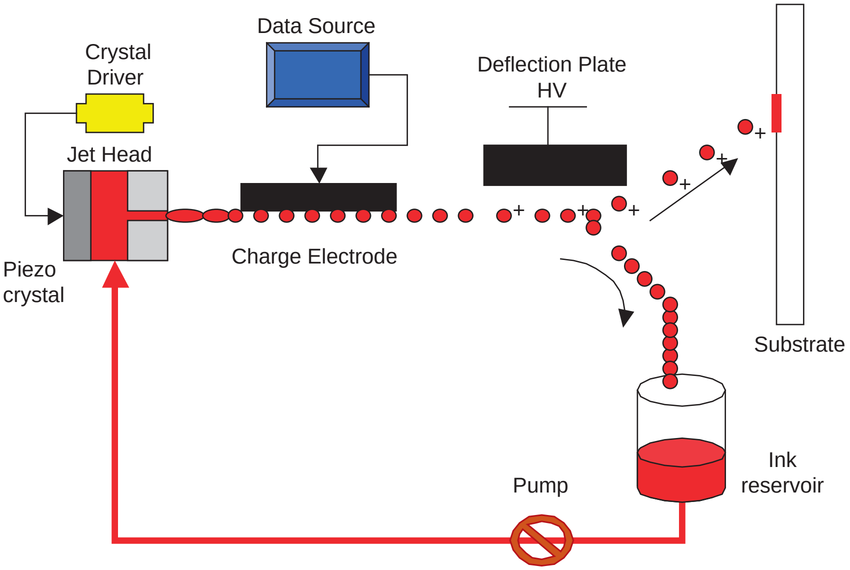


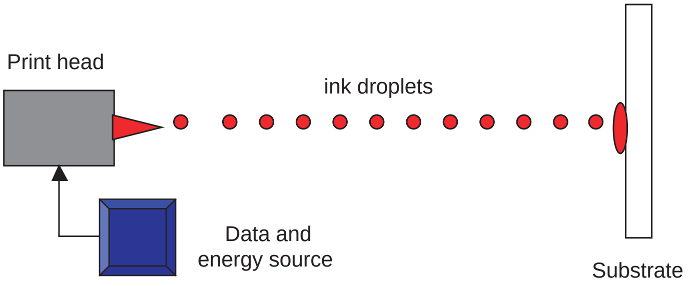
Figure 2.23 Continuous ink jet (raster).

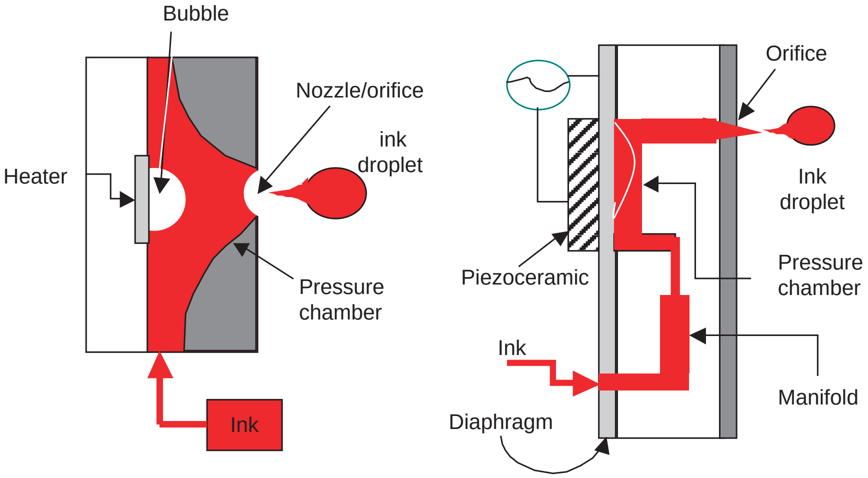
and many, if not all, commercial, wide-format printers. It takes its generic name from the fact that ink is delivered from the ink head directly to the substrate only as demanded by the printing information supplied by the software.

The ink is ejected from the print heads by one of two means:

- Thermal or Bubble-Jet – in this method the print head is heated at the nozzle tip by a pulsed electric current to a temperature greater than 300 °C many thousand times per second. This pulsed heating causes bubbles to form in the ink, which then exert pressure on the nozzle causing fine drops of ink to be ejected onto the substrate. Collapse of the bubble allows ink to refill the nozzle ready for the next pulse of heat (Figure 2.24a). The print head nozzles are very small, in the range of 20–100 microns in diameter, and are constructed in arrays of the cells. The cell in Figure 2.24a is a so-called roof-shooter type as used by Hewlett-Packard, whilst Canon use a side shooter arrangement where the ink flows parallel to the heater to the orifice.[131,132]
- Piezo – this is the same basic print head technology as in continuous ink-jet. The ink-jet droplets are forced out through the nozzle after an electrical signal to the piezoelectric crystal causes a pressure wave to be set up in the ink (Figure 2.24b). The wave can be produced in the bend mode, as in Figure 2.24, or in a push or shear mode.[132] An important variation on piezo technology is the Xaar Microjet system, which uses vibrating walls in the ink-jet channel to emit jets.

In SOHO environments the preferred inks sold for use in printers are essentially aqueous based, for obvious environmental reasons.





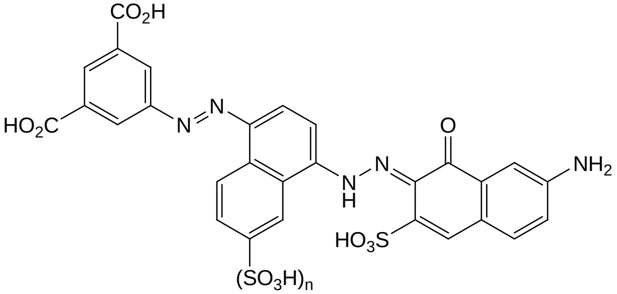
a. Thermal/Bubble Jet Head b. Piezo Head

Figure 2.24 Cross sections of thermal/bubble jet and piezo DOD print heads.

2.9.1.3 Colorants for Ink-jet Printers

The simplest four-colour system of cyan, magenta, yellow and black (CMYK) is used in many SOHO printers, but these are supplemented in higher-quality machines by a light cyan and light magenta giving a six-colour (C LC M LM Y K) system, which reduces image graining and gives smoother colour transitions. In wide-format commercial printers grey, red, green and blue inks are also used to extend the colour gamut, improve colour accuracy and consistency, and reduce metamerism. Improvements have been made in the performance of both dye- and pigment-based inks and several companies have machines and receiving substrates specifically designed for each ink system. The debate about when it is best to use dyes or pigments as the colorants in ink-jet printers is now much clearer.

Dyes – the earliest drop-on-demand printers were all designed to produce output from word-processing packages on computers and consequently only had black ink. The severe conditions in the thermal heads, where temperatures reach up to a mean of 350 °C, would have indicated that pigments such as carbon black were the most suitable colorants. However, because there were problems associated with settling out of the pigment particles in the ink containers and blocking of the orifices with an insoluble pigment making them difficult to clean, water-soluble dyes were chosen initially. The early water-based inks were far from satisfactory, based on dyes such as CI Food Black 2 that showed poor substantivity for the paper, and the prints had a marked tendency to leach out and bleed when splashed accidentally with water or coffee. The first breakthrough came via a collaborative effort between ICI dyestuff chemists (after many changes now part of Fuji Film) and the machinery manufacturer Hewlett-Packard (inventors along with Canon of thermal jet printing).[133,134] The black dyes they devised contained carboxylic acid groups (2.88) instead of the normal sulfonic acid groups. When applied as their ammonium salts a very much improved water fastness on paper was obtained, the mechanism involving loss of ammonia rendering the dye insoluble as the free acid on the slightly acidic paper.



(2.88; n = 0 or 1)

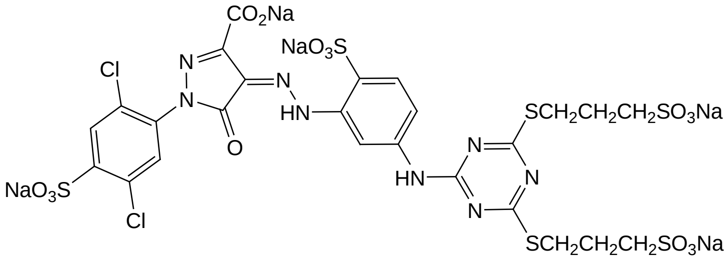
This work confirmed that it was very unlikely that dyes chosen from existing ranges would give adequate performance in ink-jet inks and new molecule research would be needed.

The ink-jet printing of coloured images is a subtractive process and requires a CMY trichromat as in colour photography. Some of the properties required in the dyes are listed below.

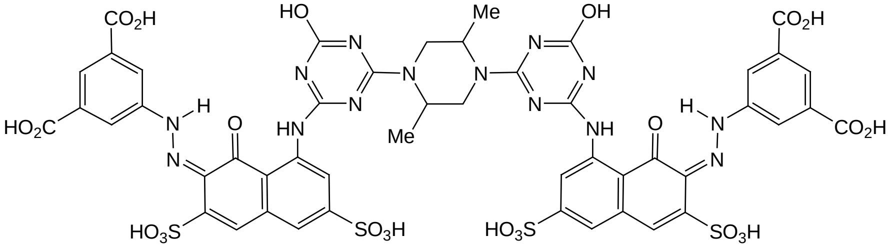
- Brightness of colour (chroma);
- High resolution;
- High number of grey levels;
- Low, if any, colour–colour bleed;
- Light fastness in all kinds of media;
- Water fastness (can be improved by paper coating);
- Thermally and chemically stable;
- Non-toxic and no negative effect on the environment;
- Practically free from inorganic salts (less than 100 ppm);
- High water solubility;
- Produce storage stable inks.

A wide range of textile dyes has been evaluated for use in ink-jet inks for application to paper or film-based substrates but only a few from existing dye ranges came anywhere near meeting the above criteria. Even the best dyes suffer from poor wet-fastness and light-fastness properties, especially in the magenta shade area, or they are not the right shade for the desired trichromat. Some that have found commercial use are listed in Table 2.16.[135]

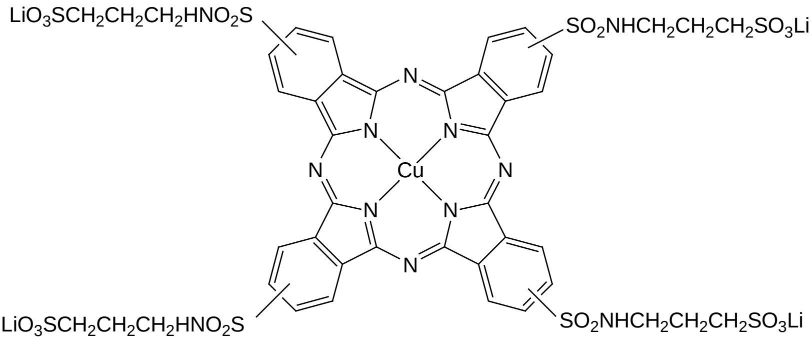
Consequently since the early days of ink-jet printing there has been an explosion of research into new molecules, the results of which have been extensively reviewed.[136,137] Some examples of the dyes commercialised in the various shade areas are the yellow (2.89) from Ilford, the magenta (2.90) from Avecia and the cyan (2.91) from Fuji.



(2.89)



(2.90)



(2.91)

Pigments – Colorants used in the inks need to be not only stable in daylight use, but also sufficiently light fast that they remain relatively unchanged during storage for archival purposes, where stability beyond 25 years is desired.[138] Traditionally to meet this requirement the higher light stable pigments rather

Table 2.16 Dyes for water-based IJ inks.

Shade	*CI name*	*Chemical class*	*Light fastness*
Magenta	Reactive Red 23	Monoazo, Cu complex	6
	Reactive Red 180	Monoazo	4
	Acid Red 52	Xanthene	2
Yellow	Reactive Yellow 37	Monoazo	4
	Acid Yellow 23	Monoazo (Tartrazine)	4
	Direct Yellow 86	Disazo	5
	Direct Yellow 132	Disazo	5
Cyan	Acid Blue 9	Triphenylmethane	2 3
	Direct Blue 199	Phthalocyanine	7

than dyes have been used in printing inks (see Section 2.4.4.2). Carbon black has an excellent track record in this respect and stabilised ink-jet inks are available for ink-jet printers using this pigment. Of course pigments are present as dispersions as opposed to being in solution with dyes, and the development of inks for black and CMY colours that remained stable for up to 18 months has required considerable development work. One difficulty with pigments is obtaining the desired particle size, not only for stability reasons but also in being able to achieve a good colour gamut from the trichromat. However, methods have now been developed to get the particle size down to less than 25 nm, as discussed under nanopigments (see Section 2.4.5), and to hold these in stable dispersions for a workable length of time by such techniques as pigment surface modification.[139] Nanopigments give much improved coverage of the colour space and brightness approaching dye-based inks. Pigments also need binding to the surface of the substrate and this can be achieved by using papers with a receiving surface and/or by micro-encapsulation of the pigment with a binder or by including a post-UV cured resin binder in the ink.[140] Pigments that are used for a typical trichromat (CMY) include:

- phthalocyanines for the cyan, *e.g.* CI Pigment Blue 15.3 and CI Pigment Blue 15.4 (Table 2.11);
- quinacridones for the magenta *e.g.* CI Pigment Red 122 and CI Pigment Red 202 (Section 2.4.1.6);
- and diarylides for the yellow, *e.g.* CI Pigment Yellow 74 and CI Pigment Yellow 155, or the isoindolinone CI Pigment Yellow 110 (2.66, Section 2.4.1.4), or the benzimidazolone CI Pigment Yellow 120.

Solvent Dyes – in the industrial field, such as the printing of cartons and packages with barcodes and other such information, the inks are usually solvent based and consequently solvent dyes are used (Section 2.5). Examples used in CMYK inks are CI Solvent Blue 44 (a phthalocyanine), Solvent Red 91, Solvent Yellow 83:1 and Solvent Black 45 (all 1:2 chromium monoazo complexes).

Textile Dyes and Pigments – printing of textiles with dyes and pigments is more complex as the colorant needs to be fixed to the fabric to survive subsequent laundering.[41,42] With dye-based ink the colorant used is specific for the fibre; reactive dyes for cellulose, acid dyes for wool and nylon and disperse dyes for polyester, and a post printing treatment is required. Pigments do not interact with the fibre and need to be fixed to the textile with special resins, which are usually incorporated into the ink and cured after printing. The dyes and pigments used are commonly selected from the existing ranges of textile colorants manufactured by leading companies *e.g.* DyStar, Clariant, Huntsman, DuPont, Bayer and BASF.

Dyes versus Pigments – the current position in the dye-pigment debate over when it is best to use dyes or pigments on paper- or plastic-based materials is largely resolved. In the SOHO environment, where the hard copies produced are often ephemeral and consequently archival stability is not an issue, dyes take precedence because of brighter shade, better colour gamut and inherently higher stability in the ink cartridges. The borderline case is when the images are reproduced from those captured using digital cameras and similar, where storage and display stability is best obtained with pigment inks, but using a dye-based ink and matched receiving sheet gives acceptable stability of bright, wide-colour gamut images, especially when post-laminated with a UV absorbing film. Commercial printing companies prefer to use pigments, having been handling them in traditional printing inks for generations and understanding their performance characteristics. There are now many excellent pigment inks that give the colour coverage and stability required by commercial printers. In the special case of fine art printing (giclée), it is essential that the colours remain stable for many decades and pigmented inks are available which give over 200 years' archival performance whilst dye-based inks have been commercialised that have over 100 years of estimated lifetime.[141]

2.9.1.4 Commercial Applications of Ink-jet Technology

Ink-jet printing is now a widespread technology used in all areas, from the small machines used in the home and office environments to the wide-format machines used on an increasing scale in the commercial and industrial arenas (Figure 2.25). The application media include paper, card, metal, wood, plastics and textile fabrics, greatly assisted by the development of UV-curable inks. The rate of printing has been greatly speeded up by the introduction of array printheads covering the width of the printable area. In the commercial printing field the advent of digital printing allows a much more rapid and flexible response by the printer to the consumer's needs and has led to new commercial opportunities. The ability of designers to produce their designs using software that can be integrated into the printer means that relatively short runs of products (*e.g.* decorating papers, printed textile fabrics for fashion and home furnishings) can be produced at much lower cost than using the traditional printing plate or silk-screen methods. However, for longer runs the efficiency of the higher speeds of offset lithography in paper, and rotary or flat-bed silk screens in textiles overcome the higher start up costs for the print run.

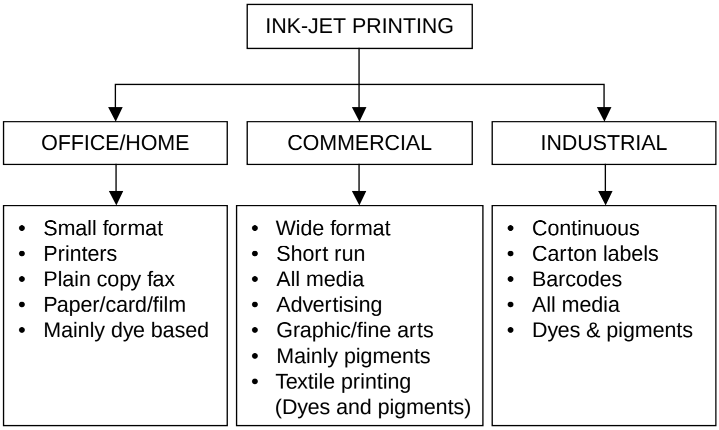


Figure 2.25 Application areas for ink jet printing.

Applications of ink-jet technology outside the more traditional areas are burgeoning. Examples include the printing of electronic paper, flexible circuits, solar panels, in displays (*e.g*. OLEDs in Chapter 3), bio-medical printing such as protein analysis, DNA sampling and blood testing, in producing quantum dots (Chapter 3) and delivering other final particles as used in nanolithography.

2.9.2 Electrophotography

Electrophotography is the correct technical name for the non-impact electrostatic printing processes, which include photocopying, also commonly called xerography because of the company that developed the original systems (Xerox), and laser printing.[142]

The electrophotographic process involves the production of an electrostatic latent image on a photoconductor (also called a photoreceptor), the conversion of this to a visible image with a charged toner, which is then transferred to the substrate (usually paper), where it is fixed. The six individual steps in the process are:

- Charging. The photoconductor, in the form of a drum or a continuous belt, is given a uniform electrostatic charge by corona discharge or by using a primary charge roller. The original photoconductors were inorganic (selenium based) and charged positively, but today the vast majority are organic and charge negatively (see Chapter 4, Section 4.4).
- Expose/write. The image is then transferred to the charged photoconductor by either a flash exposure of the total image with white light (photocopying) to give a positive image or, as in all modern copiers, by sweeping a linear array of photodiodes across the paper. The fastest colour scanners have three rows of photodiodes with each row covered with a red, green or blue filter. Digitised information can also be written with a laser

(laser printing) or an array of LEDs (LED printers) in a raster scan to give a negative image (reverse development). Either method produces a latent image.

- Develop. The latent image is rendered visible by the attachment of oppositely charged toner particles to the drum or belt; positive in the photocopying process and negative in laser printing.
- Transfer. The toner image is then transferred to the substrate.
- Fix. The toner image is thermally fixed to the substrate.
- Clean. The photoconductor is then cleaned ready for another cycle.

The processes are shown schematically in Figure 2.26 for the production of a monochrome image.[143]

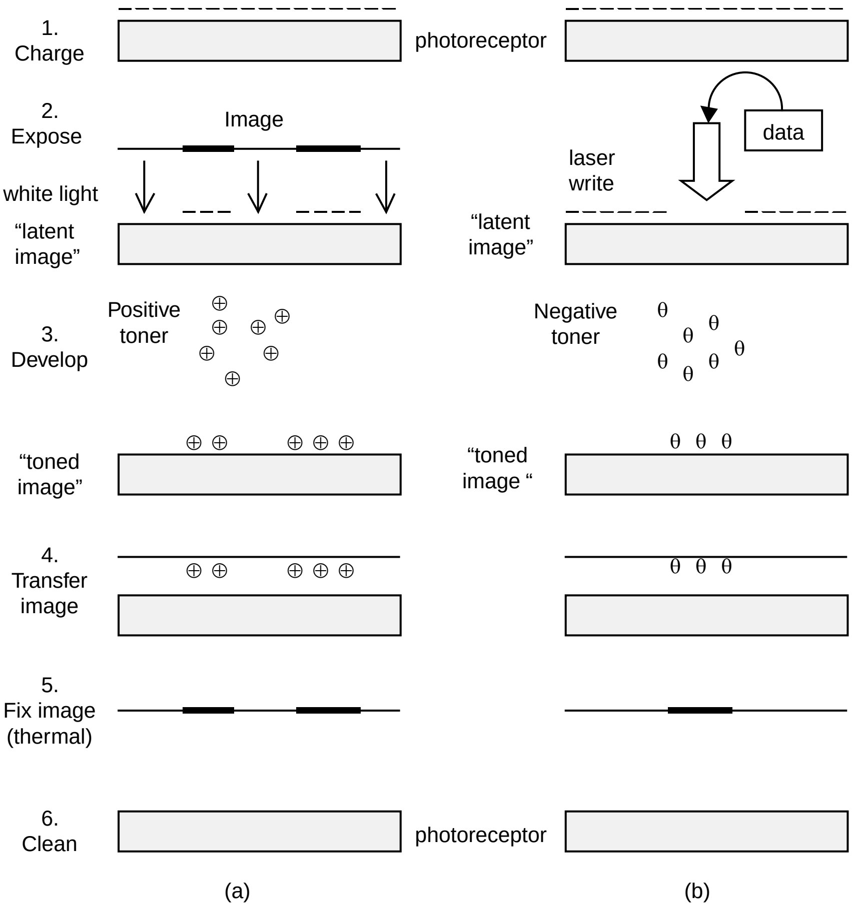


Figure 2.26 The electrophotographic process using organic photoconductors: (a) photocopying and (b) laser printing.

In the production of coloured images a subtractive CMYK methodology is used, full coloration being achieved by a four-pass process, together with a photoconductor that is sensitive to light in the blue, green and red regions, *i.e.* panchromatic. The colour copying process originally involved the use of a conventional set of red, green and blue colour filters to reflect light off the image in a sequential manner onto a fully charged photoconductor plate, but the process was cumbersome and with the advent of laser copiers the system changed.

In laser copiers the light reflected from the image is analysed by an array of charge-coupled devices (CCDs), which separate it into its blue, green and red components. These data on each colour component of the image are then fed to a semi-conductor laser which writes, in three passes, onto the fully charged plate to produce areas that correspond to the yellow, magenta and cyan areas in the original image. In each pass contact is made with the relevant yellow, magenta or cyan toner and the resultant intermediate images transferred to the paper substrate. After the final pass the colour picture is complete and is fixed onto the paper by thermal fusion of the toner resin.

As can be seen these processes are much more complicated than ink-jet printing methods. Consequently, colour laser printers/copiers have not been able to compete economically with the low-cost machines available from the ink-jet manufacturers for use in the small office/home, but prices are converging for the mid-market users. However, recent developments in large, efficient, full-colour roll-fed machines for use by professional printers and copy shops means they are very effective for multiple copy production of business cards, datasheets, brochures, mailings, poster and banners through to wallpaper.

2.9.2.1 Materials for Electrophotography

Coloured materials find application in both toners and organic photoconductors used in electrophotography. Photoconductors will be covered in detail in Chapter 4 (Section 4.4) and only toner resins will be considered in this section.

The three components in toner resins are:[144]

- Binder resins;
- Charge control agents;
- Colorants.

They may be either of the following forms, with dry toners predominating:

- Dry toners (free-flowing powders);
  - Dual component (with large carrier beads);
  - Single component (magnetic or non-magnetic);
- Liquid toners (colloidal dispersions in non-conductive liquids).

The particle sizes in dry toners normally range from 6–10 μm diameters, but in liquid toners they can be down to sub-micron in size (0.2 μm), leading to much thinner layers and a better resolution in the final image. More recently Kao, a major world producer of toner resins, announced that they had developed a coloured dry toner having particle size not more than 5 μm by a novel, so-called mechano-chemical process. This involves sticking silica onto the toner surface and then pulverising to give finely dispersed toner particles which will not agglomerate.[145]

The toner binder resin is the main component of a toner and can comprise anything between 45 and 95% in single-component dry toners. The resin not only carries the colorant onto the photoreceptor, it also performs the important function of binding to the substrate by thermal fusion. Consequently, the resin chosen must melt at a reasonable temperature as well as having good mechanical and electrical properties. The most common resins used are styrene-acrylics and styrene-butadienes with a smaller usage of polyesters.

The triboelectric charge on the toner particles, which is generated by frictional forces between the resin, carriers and additives during the toner preparation, can be positive or negative depending on the resin. It is very important that the toner attains an adequate charge level and rate of charging, and it has been found that certain additives can improve the performance in both respects. These additives are known as charge control agents (CCAs), the presence of which produce sharper and higher density images as well as maintaining these over the lifetime of the toner.[146] They can be positive or negative charge controlling and they can be non-coloured or coloured depending on the outlet for the toner in a particular machine. Clearly non-coloured agents are preferred in toners for coloured copies and prints, but are unimportant in black toners. Many of these CCAs are derived from dyestuffs, but their colour is of little import in this outlet. The structures of representative materials in each class are shown in Figure 2.27.

Carbon black is the colorant used in black and white printers and copiers, and the CMY colorants used in toners are also pigments selected by shade and performance from commercial ranges. It should be noted that these pigments fall into various triboelectric ranges and hence selection of the pigment for the toner will depend on its use in a particular type of machine (Figure 2.28).[147]

2.9.2.2 Commercial Applications of Electrophotography

The world demand for toners in 2003 was 180,000 tonnes rising to 240,000 tonnes by 2007, largely due to the growth in the laser-printing market, which represents some 75% of the toner demand. The laser printer market is being driven by the introduction of lower-cost, full-colour machines that are affordable for most small to medium-sized offices. World sales of monochrome toner have remained fairly constant at US$ 16–17 bn whilst colour toner sales have risen from US$ 1 bn to around US$ 4.5 bn or 21% of the market in 2007. Other outlets, which include plain paper fax machines and multi-functional printers, remain a small but significant market. The battleground between

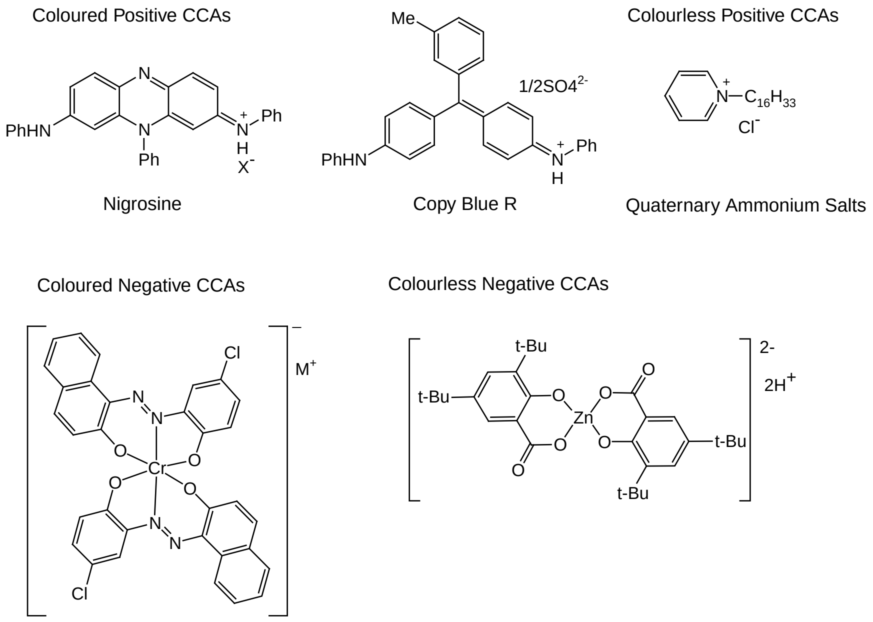


Figure 2.27 Some examples of charge control agents (CCAs).

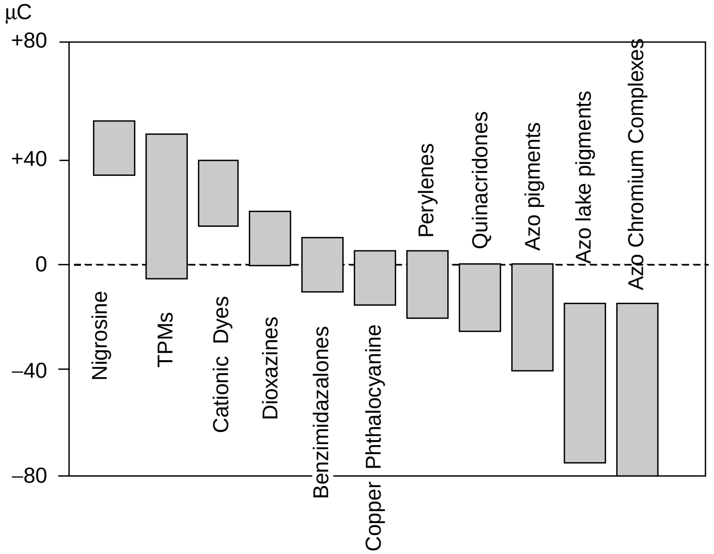
electrophotography and ink-jet is in the area of wide-format commercial digital colour printers.

2.9.3 Thermal Transfer Printing

The third most important technology for digital printing is that involving transfer of a dye or pigment by thermal means onto a receiver sheet. This technology can be further subdivided into thermal wax transfer and dye diffusion thermal transfer.[148] There is also a new thermal printing method which uses direct thermal papers, called zero ink technology.

2.9.3.1 Thermal Wax Transfer

As the name implies this printing process involves the transfer of a coloured wax onto a receiving surface by heating. In the printing process a thin ribbon or sheet (donor sheet), on which the colorant containing wax ink has previously been coated, is passed together with a receiving sheet *via* a platen roller under a heating element which is the width of the sheet. Here the wax layer melts, as defined by the digital input to the heating element, dropping from the donor sheet onto the receiver sheet forming coloured pixels, which then quickly solidify producing the desired image. Monochrome images only require one set of inputs but for CMY this must happen three times as the ink sheet passes in sequence under the heating element.



Cyan	CI Pigment Blue 15:3	Phthalocyanine
Magenta	CI Pigment Red 57:1	Bon Acid Azo lake
	CI Pigment Red 48:2	Bon Acid Azo lake
	CI Pigment Red 146	Naphthol AS
	CI Pigment Red 184	Naphthol AS
	CI Pigment Red 122	Quinacridone
	CI Pigment Violet 19	Quinacridone
	CI Pigment Violet 1	Rhodamine
Yellow	CI Pigment Yellow 12, 13, 14 ,17, 83 and 174	Diarylides
	CI Pigment Yellow 97	Monoazo
	CI Pigment Yellow 180	Benzimidazolone
	CI Pigment Yellow 185	Isoindoline

Figure 2.28 Triboelectric series and selected pigments used in commercial toners.

The ink can be made up in wax or wax-resin. Examples are paraffin wax, montan wax, beeswax, ceresine wax and isocyanate modified waxes, with pure resin being used for printing onto plastics and materials requiring higher abrasion resistance or resistance to environmental impact, *e.g*. solvents. Ideally the wax should be hard enough not to smear, but of low melt viscosity when heated to temperatures around 70 °C, but re-solidification must take place rapidly. The donor sheet can be made using polyester, polypropylene or polyimide film. Carbon Black is almost universally used for monochrome printing, and whilst dyes or pigments can be used for colour printing it is the latter which are most commonly used. A typical trichromat is phthalocyanine CI Pigment Blue 15.3, the quinacridone CI Pigment Red 122 and the diarylide CI Pigment Yellow 12. One of the advantages of thermal wax transfer printing is that any receiving layer can be printed without any need for a special coating; it may be paper, card, plastic, metal or textiles.

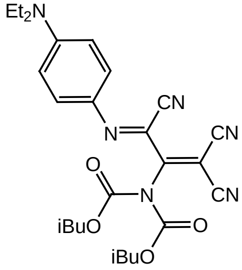
By far the biggest usage of thermal wax printing is in the production of barcode labels for a whole range of outlets. Barcode label printers are conventionally 4, 6 and 8 inches wide with print heads normally delivering 200–300 dpi, but can be 600 dpi for very fine small barcodes. Wax ribbons are used for printing onto plain paper where lifetime needs are relatively short; wax-resin labels are for smooth or coated paper; whilst resin-based ribbons are formulated to print on the plastic labels used on automotive and aircraft parts and in hazardous chemical labelling. Colour thermal wax printers are not in any way as important as ink-jet as they deliver poorer quality images and hence are mainly confined to low-end uses, such as producing the images on paper for subsequent heat transfer onto garments such as T-shirts and sporting apparel.

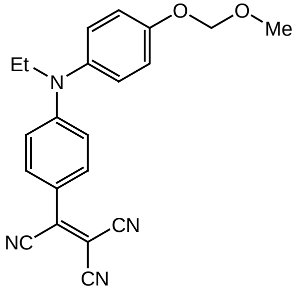
2.9.3.2 Dye Diffusion Thermal Transfer

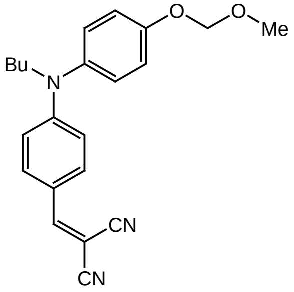
Dye diffusion thermal transfer (D2T2) printing is the high end of the thermal printing area, used to produce coloured images equivalent to conventional photography coupled with high stability. Although at first glance the printing process appears to be the same as wax transfer there are important differences. The ink-containing donor ribbons have sequential bands of CMYK colorants that pass together with a receiver sheet under a thermal source. However, in this case on being heated dyes sublime and diffuse into a layer on top of the receiver sheet, the depth and size of the diffusion depending on the power input from the thermal head. Hence D2T2 printers print by continuous tone, whereas ink-jets print by half tone, which means that pixels are stacked on top of each other to determine colour density and different colours. In D2T2 the print is not made up of individual pixels since the inks combine into a smoothly mixed colour dot, allowing the printer to more accurately reproduce the colour of the original image. This means that a 300 dpi image on a D2T2 printer is equal to 4800 dpi on an ink-jet printer.

The donor sheet consists of a polyester film (4.5–6 μm) back coated with a heat-protecting layer, necessary as the temperature of the thermal heads can reach 400 °C. On top of the polyester film is a sub-layer which helps the dye coat to adhere to the film and also prevents back diffusion of the dyes. Finally the dye layer, which contains the relevant dye plus binders, such as ethylhydroxyethylcellulose and polyvinylbutyral, is coated *via* a gravure type process.

The receiver sheet in D2T2 printing consists of an opaque base film of polymer or paper (150 μm) coated with a layer (<10 μm) receptive to the incoming dye, usually polyester or a mixture with other polymers, and a final thin layer which helps release after printing. Since the D2T2 process involves diffusion of the dye into polyester, the initial research involved trying to apply textile disperse dyes (see Section 2.3.2.1). It was quickly realised that these were not fit for use in this process and a great deal of new molecule research was undertaken to find the dyes achieving the necessary properties.[148,149] The normal CMY trichromat is required, while black is achieved by overprinting each of the primaries. The dyes should have high tinctorial strength in order to obtain the high optical densities required for the top-quality prints. They need to be stable once transferred into the receiving layer, showing no migration or smearing when handled, and exhibit good light stability. Whilst details of the dyes used in available printers remains commercially sensitive, the CMY trichromat of carbostyryl dyes (2.92), (2.93) and (2.94), available from AGFA, are examples of the dyes that are used in the process.


(2.92)


(2.93)


(2.94)

D2T2 print heads are capable of producing 256 levels of each colour (CMY) and are able to create a total of 16.77 million true colours by combining these three primary colours. Using a special over-coating layer, the dye layers are sealed into the paper and the image is protected against UV light, fingerprints, and even water. Because they produce such high photographic quality images they have captured a niche market of producing such images in in-store photo booths and consumer copy shops. Printing images on security cards, driving licences and other photo image cards is another important outlet. Most major companies, such as Sony, Canon, Kodak, Mitsubishi, Citizen, Fuji and Samsung, make D2T2 printers. At a cost of as little as US$ 100 for machines which print 6″×4″, they are attractive to keen amateur photographers. Even though they need special papers the cost for an individual print can be lower than a comparable ink-jet print on photopaper. They are also produced much faster than ink-jet, *e.g.* a 6″×4″ print takes only 7 seconds to print. For the professional photographer or printing company, very fast machines are available that can print up to 8″×10″ with supplies of ribbons/paper for 800 prints.[151]

2.9.3.3 No Ink Direct Thermal Printing

Although direct thermal papers were one of the earliest digital printing technologies they have shown little success in colour printing (Chapter 1, Section 1.4.2.4). A more recent innovation is that employing the colour change of dye crystals embedded in a coating by thermal means in a process that has been called amorphochromic (see Chapter 1, Section 1.11.1) and which has been commercialised by Zink Imaging.[152,153] The papers for this process are complex multi-layered structures comprising sequential layers of CMY colour-forming leuco dyes and developers on a base coat (see Chapter 1, Sections 1.3.3.1 and 1.4).[154] The properties of leuco dyes are tuned so that the colour gamut necessary for full colour prints can be achieved. Activation of each layer is independent and responds to heat pulses of precisely determined duration and temperature to achieve the desired colour. Because the total printing materials are contained on one sheet it is a new type of instant photography for the digital age. The compact nature of the system makes it suitable for small-scale portable printers to be used in conjunction with digital cameras and camera-functional mobile phones. One commercial example is the Polaroid pogo printer that produces 2″×3″ prints from cameras or phones in less than 1 minute.

2.10 Electronic Paper and Flexible Displays

In the area of display technologies one of the most exciting developments taking place currently is that of flexible displays. Electronic paper (e-paper) is the term applied to those displays that are highly flexible and produce images of high contrast similar to paper-based products. They use low power and can provide updateable information to the reader. There are several competing technologies some of which are covered elsewhere in this book:

- Electrochromic technology (Chapter 1; Section 1.5.4.3);
- Cholesteric LCD technology (Chapter 5; Section 5.2.2.1);
- Photonic crystal technology (Chapter 5; Section 5.3.5.1).
- and those covered in this section using electrophoretic technology.

Electrophoretic technology was originally developed at the MIT Media lab,[155] but its commercial success owes a great deal to the effort of the spin-off company, E-Ink Corp.[156] In E-Ink's electrophoretic-based display, an ink containing microcapsules is printed onto a sheet of plastic film that is laminated to a layer of circuitry. The circuitry forms a pattern of pixels that can then be controlled by a display driver. For example in a black-and-white display two different microcapsules are employed, one that contains positively charged particles (*e.g.* white) and another containing negatively charged (*e.g.* black) particles suspended in a clear fluid. When a negative electric field is applied, the white particles move to the top of the microcapsule where they become visible to the user. This makes the surface appear white at that spot. At the same time, an opposite electric field pulls the black particles to the bottom of the microcapsules where they are hidden. By reversing this process, the black particles appear at the top of the capsule, which now makes the surface appear dark at that spot. This is illustrated in Figure 2.29.[156] The inks can be printed using

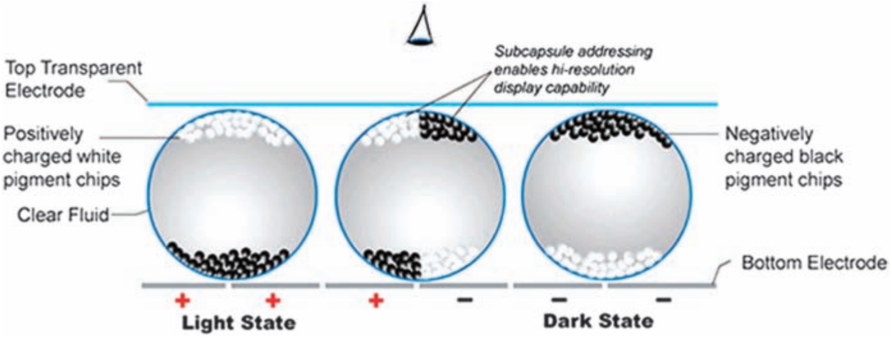


Figure 2.29 Electronic paper using electrophoretic technology.[156]

existing screen-printing processes onto virtually any surface, including glass, plastic, fabric and even paper. Full colour displays require a layer of RGB colour filters whilst maintaining the white background for good contrast.

This is an emerging area and the companies exhibiting new products or prototypes include major players like HP, Fujitsu, Bridgestone and Hitachi.

References

1. K. Venkataraman (ed.), *The Chemistry of Synthetic Dyes*, *Volumes I–VII*, Academic Press, New York, 1952–1974.
2. H. Zollinger, *Color Chemistry*, Wiley-VCH, Weinheim, 2003.
3. P. F. Gordon and P. Gregory, *Organic Chemistry in Colour*, Springer-Verlag, Berlin, 1983.
4. D. R. Waring and G. Hallas (ed.), *The Chemistry and Application of Dyes*, Plenum, New York, 1990.
5. A. T. Peters and H. S. Freeman (ed.), *Modern Colorants: Synthesis and Structure*, Blackie, London, 1995.
6. J. Shore (ed.), *Colorants and Auxiliaries, Vol. 1 Colorants*, Society of Dyers and Colourists, Bradford, UK, 1990.
7. P. Gregory, *High Technology Applications of Organic Colorants*, Plenum, New York, 1991.
8. K. Hunger (ed.), *Industrial Dyes*, Wiley-VCH, Weinheim, 2003.
9. W. Herbst and K. Hunger, *Industrial Organic Pigments*, Wiley-VCH, Weinheim, 2004.
10. G. Buxbaum and G. Pfaff (ed.), *Industrial Inorganic Pigments*, Wiley-VCH, Weinheim, 2003.
11. H. MacDonald Smith, *High Performance Pigments*, Wiley-VCH, Weinheim, 2002.
12. H. S. Freeman and G. N. Mock, in *Riegel's Handbook of Industrial Chemistry*, Springer, Berlin, 2003, pp. 880–962.

13. (a) R. M. Christie, R. R. Mather and R. H. Wardman, *The Chemistry of Colour Application*, Blackwell Science, Oxford, 2000; (b) R. M. Christie, *Colour Chemistry*, Royal Society of Chemistry, Cambridge, 2001.
14. A. Valberg, *Light, Vision and Color*, John Wiley, Chichester, 2005.
15. *Colour Terms and Definitions*, Society of Dyers and Colourists, Bradford, 1988.
16. R. McDonald (ed.), *Colour Physics for Industry, 2nd edn.*, Society of Dyers and Colourists, Bradford, 1997.
17. S. Garfield, *Mauve: How One Man Changed the World*, Faber & Faber, London, 2000.
18. S. Travis, in *Milestones in 150 years of the Chemical Industry*, ed. P. J. T. Morris, W. A. Campbell and H. L. Roberts, Royal Society of Chemistry, Cambridge, 1991, pp. 144–156.
19. J. Griffiths, *Colour and Constitution of Organic Molecules*, Academic Press, London, 1976.
20. *Colour Index*, Society of Dyers and Colourists and the American Association of Textile Chemists and Colorists, *Part 1: Pigments and Solvent Dyes, Part 2: Dyes and Related Products* are available on line at www.colour-index.org.
21. H. Mustroph and J. Epperlein, *J. Prakt. Chem.*, 1982, **323**, 755.
22. M. G. Hutchings, P. Gregory, J. S. Campbell, A. Strong, J.-P. Lepre and A. Mills, *Chem. Eur. J.*, 1997, **3**, 1719.
23. H. R. Schwander, *Dyes Pigm.*, 1982, **3**133–60.
24. A. D. Towns, *Dyes Pigm.*, 1999, **42**, 3–28.
25. R. Egli, in *Colour Chemistry: The Design and Synthesis of Organic Dyes and Pigments*, ed. A. T. Peters and H. S. Freeman, Elsevier, London, 1991, pp. 1–28.
26. C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, Wiley-VCH, Weinheim, 2003, pp. 117–118.
27. SDC Resource File 1999, pp. 144–151.
28. DFG (Deutsche Forschungsgemeinschaft) (ed.), *List of MAK and BAT values. Maximum Concentrations and Biological Tolerance Values at the Workplace*. Report no. 41, Wiley-VCH, Weinheim, Germany, 2005.
29. G. Booth, *in Ullman's Encyclopedia of Industrial Chemistry*, VCH, Weinheim, 1991, **vol. A17**, pp. 9–57 and 411–455.
30. M. A. Weaver and L. Shuttleworth, *Dyes Pigm.*, 1982, **3**, 81–121.
31. P. Rys, in *Physico-Chemical Principles of Color Chemistry*, ed. A. T. Peters and H. S. Freeman, Blackie Academic, London, 1996, pp. 1–42.
32. F. Jones, in *Colorants and Auxiliaries, Vol. 1 Colorants*, ed. J. Shore, Society of Dyers and Colourists, Bradford, UK, 1990, pp. 196–229.
33. R. Price, in *The Chemistry of Synthetic Dyes, Volume III*, ed. K. Venkataraman, Academic Press, New York, 1970, 303–384.
34. G. Hallas, in *Colorants and Auxiliaries, Vol. 1 Colorants*, ed. J. Shore, Society of Dyers and Colourists, Bradford, UK, 1990, pp. 230–306.
35. D. Duff, *Chem. Br.*, 2001, **37**(1), 35.

36. G. Booth, *The Manufacture of Organic Colorants and Intermediates*, Society of Dyers and Colourists, Bradford, 1988.
37. C. W. Greenhalgh, J. L. Carey, N. Hall and D. F. Newton, *J. Soc. Dyers Col.*, 1994, **110**, 178–184.
38. B. Parton, in *Proceedings of International Conference on the Chemistry and Application of Reactive Dyes*, University of Leeds, Department of Colour Chemistry, September 1989.
39. G. Shankarling, R. Paul and M. Jayesh, *Colourage*, 1996, **8**, 47.
40. D. A. S. Phillips, *Adv. Colour Sci. Tech.*, 1998, **1**, 1–11.
41. D. J. Tyler (ed.), *Textile Digital Printing Technologies: Textile Progress*, Woodhead Publishing, Cambridge, UK, vol. **37**, issue no. 4, 2005.
42. H. Ujiie (ed.), *Digital Printing of Textiles, Woodhead Textiles Series No. 53*, Woodhead Publishing, Cambridge UK, 2006.
43. www.just-style.com, 20 April 2007.
44. J. Shore (ed.), *Cellulosics Dyeing*, Society of Dyers and Colourists, Bradford, 1995.
45. J. R. Aspland, *Textile Dyeing and Coloration*, American Association of Textile Chemists and Colorists, Research Triangle Park, NC, 1997.
46. L. W. C. Miles (ed.), *Textile Printing*, Society of Dyers and Colourists, Bradford, 1994.
47. M. A. Kulandainathan, K. Patil, A. Muthukumaran and R. B. Chavan, *Coloration Technology*, 2007, **123**, 143–151.
48. C. Senior, in *Cellulosics Dyeing*, ed. J. Shore, Society of Dyers and Colourists, Bradford, 1995.
49. A. H. M. Renfrew, *Reactive Dyes for Textile Fibres*, Society of Dyers and Colourists, Bradford, 1999.
50. K. Hannemann, *International Dyer*, March 2001, 16–19.
51. K. Parton, in *Colour Science '98. Volume 2: Textile Dyeing and Printing*, University of Leeds, UK, 1999, pp. 120–127.
52. S. M. Burkinshaw, *Chemical Principles of Synthetic Fibre Dyeing*, Blackie, London, 1995.
53. D. M. Nunn (ed.), *The Dyeing of Synthetic-polymer and Acetate Fibres*, Society of Dyers and Colourists, Bradford, 1979.
54. C. M. Brennan and J. F. Bullock, in *Physico-Chemical Principles of Color Chemistry*, ed. A. T. Peters and H. S. Freeman, Blackie Academic, London, 1996.
55. P. Gregory, in *The Chemistry and Application of Dyes*, ed. D. R. Waring and G. Hallas, Plenum, New York, 1990, pp. 165–201.
56. A. Hudson and P. A. Britten, *Rev. Prog. Col.*, 2000, **30**, 67.
57. (a) Food Standards Agency, UK, as of 27.7.07, www.food.gov.uk; (b) D. McCann, A. Barrett, A. Cooper, D. Crumpler, L. Dalen, K. Grimshaw, E. Kitchin, K. Lok, L. Porteus, E. Prince, E. Sonuga-Barke and J. Stevenson, *The Lancet*, 2007, **370**, 1560–1567.
58. V. Emerton (ed.), *Food Colours*, John Wiley & Sons, Chichester, 2008.

59. C. Zviak and J. Millequant, in *The Science of Hair Care*, ed. C. Bouillon and J. Wilkinson, CRC Press, Boca Raton, 2005, pp. 251–276.
60. C. Zviak and J. Millequant, in *The Science of Hair Care*, ed. C. Bouillon and J. Wilkinson, CRC Press, Boca Raton, 2005, pp. 277–301.
61. www.hair-science.com.
62. B. Hefford and K. Brown, *Chem. Br.*, October 2003, pp. 32–34.
63. R. Horobin and J. Kiernan (ed.), *Conn's Biological Stains: A Handbook of Dyes, Stains and Fluorochromes for Use in Biology and Medicine*, BIOS Scientific Publishers, Oxford, 10th edn, 2002.
64. Electron Microscopy Sciences, http://www.emsdiasum.com.
65. P. A. Lewis, in *Color for Science, Art and Technology*, ed. K. Nassau, Elsevier, Amsterdam, 1998, p. 285.
66. C. C. Leznoff and A. B. P. Lever (ed.), *Phthalocyanines: Properties and Applications, Volume 4*, Wiley-VCH, New York, 1996.
67. N. B. McKeown, *Phthalocyanine Materials: Synthesis Structure and Function*, Cambridge University Press, Cambridge, UK, 1998.
68. R. R. Mather, *J. Porphyrins Phthalocyanines*, 1999, **3**, 643–646.
69. A. Iqbal, M. Jost, R. Kirchmayr, J. Pfenninger, A. C. Rochat and O. Wallquist, *Bull. Soc. Chim. Belg.*, 1988, **97**, 615.
70. K. Nassau, in *Color for Science, Art and Technology*, ed. K. Nassau, Elsevier, Amsterdam, 1998, pp. 123–168.
71. R. H. Leach and R. J. Pierce (ed.), *The Printing Ink Manual*, Kluwer Academic, 1993.
72. P. Laden (ed.), *Chemistry and Technology of Water Based Inks*, Blackie Academic, London, 1997.
73. A. A. Denio, *J. Chem. Educ.*, 2001, **78**, 1298–1304.
74. Y. H. Zhou, J. Lin, X. M. Han, S. B. Wang and H. J. Zhang, *Mater. Res. Bull.*, 2003, **38**, 1289.
75. S. H. Cho, J. S. Yoo and J. D. Lee, *J. Electrochem. Soc.*, 1998, **145**, 1017.
76. A. Celikkaya and M. Akinc, *J. Am. Ceram. Soc.*, 1990, **73**, 2360.
77. H. Jungk and C. Feldmann, *J. Mater. Chem.*, 2000, **10**, 1311.
78. K. J. Sreeram, R. Indumathy, A. Rajaram, B. U. Nair and T. Ramasami, *Mater. Res. Bull.*, 2006, **41**, 1875.
79. C. Feldmann, *Adv. Mater.*, 2001, **13**, 1301–1302.
80. X. Wang, J. Zhuang, Q. Peng and Y. Li, *Nature*, 2005, **437**, 121–124.
81. D. Wang, X. Liang and Y. Li, *Chem. Asian J.*, 2006, **1–2**, 91–94.
82. A. Gotoh, H. Uchida, M. Ishizaki, T. Satoh, S. Kaga, S. Okamoto, M. Ohta, M. Sakamoto, T. Kawamoto, H. Tanaka, M. Tokumoto, S. Hara, H. Shiozaki, M. Yamada, M. Miyake and M. Kurihara, *Nanotechnology*, 2007, **18**, 345609.
83. H. Kasai, H. S. Nalwa, S. Okada, H. Oikawa and H. Nakanishi, in *Handbook of Nanostructured Materials and Nanotechnology*, ed. H. S. Nalwa, Academic Press, San Diego, USA, 2000, vol. **5**, ch. 8, 433.
84. Y. Miyashita, K. Baba, H. Kasai, H. Nakanishi and T. Miyashita, *Mol. Cryst. Liq. Cryst.*, 2008, **492**, 268–274.

85. C. Lin, Y. Li, M. Yu, P. Yang and J. Lin, *Adv. Funct. Mater.*, 2007, **17**, 1459–1465.
86. K. Hayashi, H. Morii, K. Iwasaki, S. Horie, N. Horiishi and K. Ichimura, *J. Mater. Chem.*, 2007, **17**, 527–530.
87. *Colour Index International, Part 1 – Pigments and Solvent Dyes*, Society of Dyers and Colourists, Bradford, UK, 4th edn online, 2008.
88. D. McCallein, *Chem. Brit.*, 2002, Aug., 31–33 and *The Colourist*, Issue 4, Winter 2003, 6.
89. E. Arankumar, C. C. Forbes and B. D. Smith, *Eur. J. Org. Chem.*, 2005, 4051–4059.
90. F. Cramer, W. Saenger and H.-C. Spatz, *J. Am. Chem. Soc.*, 1967, **89**, 14.
91. A. Mishra, R. K. Behera, P. K. Behera, B. K. Mishra and G. B. Behera, *Chem. Rev.*, 2000, **100**, 1973.
92. S. Anderson, T. D. W. Claridge and H. L. Anderson, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1310.
93. M. R. Craig, M. G. Hutchings, T. D. W. Claridge and H. L. Anderson, *Angew. Chem., Int. Ed. Engl.*, 2001, **40**, 1071–1074.
94. C. Sanchez, B. Julián, P. Belleville and M. Popall, *J. Mater. Chem.*, 2005, **15**, 3559–3592.
95. H. Burke, *Chem. Soc. Rev.*, 2007, **36**, 15–30.
96. C. Sanchez, B. Lebeau, F. Chaput and J.-P. Boilot, *Adv. Mater.*, 2003, **15**, 1969.
97. G. Calzaferri, M. Pauchard, H. Maas, S. Huber, A. Khatyr and T. Schaafsma, *J. Mater. Chem.*, 2002, **12**, 1–13.
98. G. Brûhwiler and G. Calzaferri, *Micropor. Mesopor. Mater.*, 2004, **72**, 1–23.
99. G. Schulz-Ekloff, D. Wöhrle, B. van Duffel and R. A. Schoonheydt, *Microporous Mesoporous Mater.*, 2002, **51**91–38.
100. Z. Gabelica, S. Valange, M. Shibatra, H. Hotta and T. Suzuki, *Microporous Mesoporous Mater.*, 2001, **44–45**, 645.
101. F. Leese, F. Schüth, U. Simm and M. Wark (ed.), *Host-Guest Systems Based on Nanoporous Crystals*, Wiley-VCH, Weinheim, 2003.
102. J. Bauer, P. Behrens, M. Speckbacher and H. Langhals, *Adv. Func. Mater.*, 2003, **13**, 241–248.
103. D. Lee, *Nature's Palette; The Science of Plant Color*, Chicago University Press, Chicago, 2007.
104. Y. Kohno, Y. Shibata, N. Oyaizu, K. Yoda, M. Shibata and R. Matsushima, *Microporous Mesoporous Mater.*, 2008, **114**, 373–379.
105. G. A. F. Hendry, in *Natural Food Colorants*, ed. G. A. F. Hendry and J.D. Houghton, Blackie Academic, Glasgow, 1996, pp. 1–39.
106. F. Delgado-Vargas and O. Predes-López, *Natural Colorants for Food and Nutriceuticals*, CRC Press, Boca Raton, 2003.
107. Natural Food Colors Association, www.natcol.org.
108. www.hennapage.com.
109. *Opinion on Lawsonia inermis* (*Henna, C169*), SCCP/0943/05, December 2005.

110. A. G. Pütener and U. Schlesinger, in *Colorants for Non-Textile Applications*, ed. H. S. Freeman and A. T. Peters, Elsevier, Amsterdam, 2000, pp. 382–455.
111. A. B Greenfield, *A Perfect Red*, Doubleday, London, 2005.
112. J. Balfour-Paul, *Indigo*, Archetype Publications, London, 2006.
113. G. Fereday, *Natural Dyes*, British Museum Press, London, 2003.
114. B. Glover and J. H. Pierce, *JSDC*, 1993, **109**, 5–7.
115. D. J. Hill, *Rev. Prog. Coloration*, 1997, **27**, 18–25.
116. D. J. Hill, http://www.lapinskas.com/publications/2934.html, EU grant (AIR2-CT940981).
117. K. M. Davies, in *Plant Pigments and their Manipulation (Annual Plant Research, Vol 14)*, ed. K. M. Davis, Wiley-Blackwell, Oxford, 2004, pp. 214–277.
118. R. A. Sheldon, I. Arends and U. Hanefield, *Green Chemistry and Catalysis*, Wiley-VCH, Weinheim, 2007, pp. 353–354.
119. S. D. W. Comber, M. J. Gardner and J. Churchley, *Chemical Speciation and Bioavailability*, 2005, **17**, 117–128.
120. M. L. Musso, *Colour, Design & Creativity*, 2008, **3**, 1–10.
121. X. Du, J. Sun, Z. Pang, Y. Jia and Z. Zhou, *Genetic Improvement of Colored Cotton in China*, National Key Science and Technology R&D Program (Grant No. 2004BA525B05).
122. GMO Compass, www.gmo-compass.org, December 2008.
123. European Chemical News, June 1996, 27.
124. SRI Consulting, *Imaging Chemicals and Materials*, 2007.
125. J. Sturge, V. Walworth and A. Shepp (ed.), *Neblettes's Handbook of Photography and Reprography*, Van Nostrand, New York, 8th edn., 1989.
126. P. Bergthaller, in *Printing and Imaging Systems*, ed. P. Gregory, Blackie Academic, London, 1996.
127. A. Kazlauciunas, *Colour Photography – Past and Present*, Oil & Colour Chemist's Association, Wembley (UK), 1996.
128. N. Ohta and M. Rosen (ed.), *Color Desktop Printer Technology*, CRC, Boca Raton, FL, 2006.
129. P. Gregory, *Chem. Br.*, 2000, **36**(8), 39–41.
130. R. W. Kenyon, in *Printing and Imaging Systems*, ed. P. Gregory, Blackie Academic, London, 1996, pp. 113–138.
131. R. R. Allen, G. Dispoto, E. Hanson, J. D. Meyer and N. Mooney, *Color Desktop Printer Technology*, ed. N. Ohta and M. Rosen, CRC, Boca Raton, FL, 2006, pp. 111–155.
132. H. P. Le, *J. Imag. Sci. Tech.*, 1998, **42**, 49–62.
133. S. L. Hindagolla, D. Greenwood and N. Hughes, in *Proceedings of Sixth International Congress on Advances in Non-Impact Printing and Technologies*, Orlando, 1990, IS&T, Springfield, Virginia, USA.
134. D. Greenwood, N. Hughes, R. W. Kenyon and S. L. Hindagolla, ICI plc, *US Pat.*, 5,053,495, 1991.
135. T. Moretti, *Am. Ink Maker*, February 2000, 32–38.

136. K. Carr, in *Colorants for Non-Textile Applications*, ed. H. S. Freeman and A. T. Peters, Elsevier, Amsterdam, 2000, pp. 1–34.
137. M. Fryberg, *Rev. Prog. Coloration*, 2005, **35**, 1–30.
138. www.wilhelm-research.com.
139. www.cabot-corp.com, *US Pat.*, 5,554,739, 1996 and *US Pat.*, 5,922,118, 1999.
140. S. Magdass (ed.), *The Chemistry of Inkjet Inks*, World Scientific Publishing Ltd, 2008.
141. W. Wilhelm, *NIP 22 Proceedings*, IS&T, Springfield, VA, 2006, pp. 308–315.
142. E. M. Williams, *The Physics and Technology of Xerographic Processes*, Wiley-Interscience, New York, 1984.
143. R. S. Gairns, in *Printing and Imaging Systems*, P. Gregory (ed.), Blackie Academic, London, 1996, pp. 76–112.
144. A. S. Diamond (ed.), *Handbook of Imaging Materials*, CRC Press, Boca Raton, FL, 2001.
145. A. Eida, S. Omatsu and J. Shimizu, *J. Imag. Sci. Tech.*, 2007, **51**(5 September/October), 407–412.
146. R. L. Nash, M. L. Grande and R. N. Muller, *NIP 17 Proceedings*, IS&T, Springfield, VA, 2001, pp. 358–364.
147. R. Baur, H. T. Macholdt, E. Michel and C. Zeh, *NIP 13 Proceedings*, IS&T, Springfield, VA, 1997, pp. 163–167.
148. R. Bradbury, in *Colorants for Non-Textile Applications*, ed. H. S. Freeman and A. T. Peters, Elsevier, Amsterdam, 2000, pp. 35–60.
149. R. Bradbury, in *Modem Colorants Synthesis and Structure*, ed. H. S. Freeman and A. T. Peters, Blackie Academic, London, 1995, pp. 154–175.
150. www.agfa.com.
151. www.ici-imagedata.com.
152. (a) Polaroid Corporation, *US Pat.*, 6,951,952, 2005; (b) Polaroid Corporation, *US Pat.*, 7,008,759, 2006.
153. www.zink.com.
154. Zink Imaging LLC, *US Pat.*, 7,166,558, 2007.
155. B. Comiskey, J. D. Albert and J. Jacobson, *Nature*, 1998, **394**, 253–255.
156. www.eink.com (May 2009).

CHAPTER 3

Phenomena Involving Absorption of Energy Followed by Emission of Light

3.1 Introduction

Those phenomena which involve absorption of energy and subsequent emission of light are classified generically under the term luminescence. This is the unifying theme of this chapter, and the classification of the energy input forms the basis for the breakdown of chromic phenomena dependent on luminescence. Different physical and chemical sources of energy result in an initial transition from the ground to a higher energy state. Most of the energy sources that are responsible for the various ground-state chromic phenomena listed in Table 1.1 and described throughout Chapter 1 are also behind luminescence. They provide the basis for our classification of the corresponding luminescence terminology, given in Table 3.1.

Excitation by absorbance of a photon leads to a major class of technically important luminescent species which fluoresce or phosphoresce. In general fluorescence is "fast" (ns time scale) while phosphorescence is "slow" (longer time scale, up to hours or even days). For convenience, the topic of photoluminescence will be broadly divided into that based on relatively large-scale inorganic materials, mainly exhibiting phosphorescence, and that of smaller dye molecules and small-particle inorganics ("nanomaterials"), which can either fluoresce or phosphoresce. Their applications differ. For many of the derived technical applications, it is irrelevant whether the luminescence is fluorescence or phosphorescence. Either way the current range of applications is extensive, and in one case has been recognised by the award of a Nobel Prize, in 2008.

Electrical excitation leads to electroluminescence. There have been massive developments in both inorganic and organic electroluminescent materials,

---

Chromic Phenomena: Technological Applications of Colour Chemistry, Second Edition
By Peter Bamfield and Michael G. Hutchings

Published by the Royal Society of Chemistry, www.rsc.org

Table 3.1 Sources of energy leading to the various "luminescences".

Electrical	*Photons (light)*	*Chemical*	*Thermal*	*Electron beam*	*Mechanical*
Electroluminescence	Photoluminescence	Chemiluminescence	Thermoluminescence	Cathodoluminescence	Triboluminescence
Galvanoluminescence	Fluorescence	Bioluminescence	Pyroluminescence	Anodoluminescence	Fractoluminescence
Sonoluminescence	Phosphorescence	(Biochemiluminescence)	Candololuminescence	Radioluminescence[b]	Mechanoluminescence
	Biofluorescence	Electrochemiluminescence			Crystalloluminescence
	Rigidochromism[a]				Lyoluminescence
					Elasticoluminescence

[a] More correctly "Luminescence rigidochromism"; see text.
[b] β-emitters only.

underpinning new and still-emerging technologies which are due to revolutionise the technology of illumination.

Some chemical reactions can lead to generation of a product molecule in an electronically excited state, from where it emits light as it reverts to its ground state. Both purely chemical as well as bioluminescent systems are well known – and for the latter are commonplace in the oceans.

Related to photoluminescence is the effect of a beam of electrons on some materials. Cathodoluminescence can result in colour emission and this is the underlying technology of cathode ray tube-based TV. The same effect can result in an electron microscope, or as the result of weak β-emission from radioactive isotopes such as tritium.

Triboluminescent materials emit light as the result of mechanical action – rubbing, fracture, *etc.*

Thermoluminescence results from recombination of charge centres previously separated within a solid by means of photo-irradiation and retained in a metastable state under ambient conditions, brought about by heating. This phenomenon features no more in this chapter. Another thermal effect is pyroluminescence, where ions are excited by the intense heat of combustion, and give out coloured light on relaxation, as in fireworks.

Our treatment will attempt to provide sufficient background science to understand the story from molecule or material through to applied technology. But the reader wanting more detailed background is recommended to look elsewhere.[1,2]

This chapter of the book is primarily concerned with those phenomena where the emission of colour is the important outcome of luminescence, and where this has a technologically significant application. Some of the topics we shall encounter are already responsible for multi-billion-dollar businesses. At the other end of the spectrum we touch on cutting-edge science which is only just starting out on the path toward possible commercial success.

3.2 Photoluminescence 1 –Luminescent Pigments

The following sections concern systems which emit light under the influence of high-energy inputs, either by the effect of electrons generated at a cathode (cathodoluminescence), or from ionised gases or plasma. In either case, the chemical agent which is responsible for the light emission is inorganic in nature, and comprises an ionic pigment. In their current use, these materials are known as luminescent phosphors, phosphorescent pigments or luminescent pigments. They are crystalline compounds comprising a host lattice, which is designed to accommodate dopant ions called activators. Excitation energy impinges on the phosphor and light is emitted at various colours depending on the nature of the phosphor composition.

Despite many years of study the exact mechanism(s) for luminescence in these materials is not known precisely, and various explanations have been proposed. Figure 3.1 depicts one such mechanism which is sufficient to explain

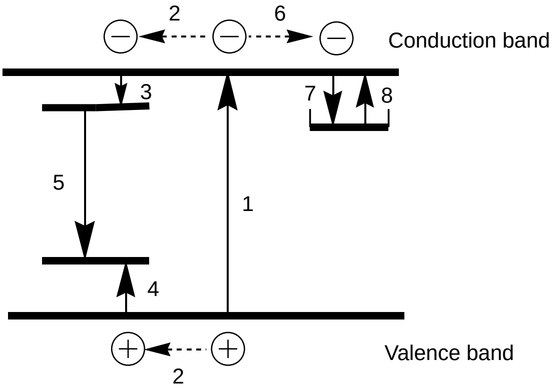


Figure 3.1 Energy transitions within a phosphorescent pigment. For numbers see text.

the chromic features of relevance in one of the common general phosphor types.[3] As an example, we consider the material zinc sulfide, ZnS, doped with cations of the two metals aluminium and copper, Al^{3+} and Cu^{+}. Since the materials are based on inorganic salts, their electronic structures are best explained in terms of simple band-gap theory, where valence electrons are held in a relatively low energy band. An empty conduction band at a higher energy can accommodate added or excited electrons. In the case of cathodoluminescence, impinging excited electrons are sufficient to excite an electron from the VB to the CB, shown as 1 in Figure 3.1. This excited electron is now able to migrate throughout the material *via* the CB (2). Simultaneously, the positive charge, or hole, remaining in the VB can equally well migrate through the material. When the electron reaches a reducible cationic dopant at a lower energy, such as Al^{3+} (in this case 0.1 eV lower in energy than the CB), it migrates to the Al centre generating Al^{2+} (3). The hole correspondingly migrates onto an oxidisable dopant centre such as Cu^{+} at + 1.1 eV above the VB, converting it to Cu^{2+} (4). If these two Al and Cu centres are in suitable juxtaposition, an electron is transferred from Al^{2+} to Cu^{2+}, regenerating Al^{3+} and Cu^{+} dopant ions plus emission of energy (5). In this case the emitted energy is at a wavelength corresponding to green light. Thus, overall a high-energy electron-induced photoexcitation leads to lower energy luminescence, the balance of the energy being converted to thermal energy (phonons, or crystal vibrations).

A second major class of phosphors contains a rare earth (RE) ion as dopant. In this case, the electron and hole recombine at the RE centre, where the absorption energy is transferred to the RE ion. Photoexcited RE ions show characteristic excitation spectra, and examples are available that luminesce across the visible spectrum (as well as UV and NIR).

The main scientific question therefore reduces to what combination of host pigment and dopants can best be used to generate light of different colours.

In particular, for emissive applications it is desirable to combine red, green and blue light as the components for additive colour mixing.

Of course, there are other chemical and physical criteria which must also be satisfied before a new material can achieve technical acceptance. The luminescent material must be easily excited by the appropriate excitation, have high quantum efficiency, be stable under the excitation conditions, undergo electron-hole recombination at the appropriate rate, be readily manufactured and be stable to all the fabrication steps it must endure during final device manufacture.

A further aspect of inorganic phosphors is that there are some uses where a relatively rapid electron-hole recombination is undesirable. Rather the materials should be easy to excite, but continue to luminesce over a much longer time period, such as hours. The resultant applications are discussed below. Materials which give rise to this behaviour are known as "afterglow phosphors". Again there are various explanations for afterglow, one of which is described in Figure 3.1. An excited electron in the CB can drift as before (6) but end up being transferred to a dopant ionic centre, known as a trap, from which it cannot recombine with a hole (7). Rather it remains in the trap until thermal energy re-excites it into the CB (8) from where it drifts slowly through the inorganic lattice until it and a positive hole find a new discharge site, producing the afterglow emission.

3.2.1 Inorganic Phosphor Materials

Over the years literally hundreds of inorganic phosphors have been developed, a very large number of which have been commercialised. Only some of the more important ones, from a colour-producing perspective, are discussed below. Detailed accounts of the major classes can be found in specialised publications.[1,4]

3.2.1.1 Sulfides and Oxysulfides

The oldest pigments are II-VI materials based on high-purity zinc and cadmium sulfides activated by dopants, primarily using copper and silver but also manganese, gold and rare earths. The energy level of the emitted light can be tuned by altering the dopants or the band-gap material. Zinc sulfide pigments activated by copper are widely available, mass-produced, low-cost materials. Their emission can be tuned over a wide range, from short UV to visible, and they work in most commonly encountered lighting conditions. However, copper-activated zinc-cadmium sulfide (Zn,Cd)S:Cu is the most often used green emitter in industrial display applications, while different versions of ZnS:Ag phosphors are exclusively used to obtain a blue emission. Another very important industrial phosphor is the yellow to orange ZnS:Mn, which finds application in monochromatic displays. ZnS:Tb is another very efficient green phosphor.

The main emission lines of $Y_2O_2S{:}Eu^{3+}$ are at 565 and 627 nm but by increasing the Eu content to 4%, a shift in the intensity of the longer-wavelength emission occurs and a deep-red emission is produced, eminently suitable for colour CRT. Strontium thiogallate $SrGa_2S_4{:}Ce^{3+}$, doped with 4 mol% of cerium, gives a very good blue phosphor (λ_{max} 455 nm), useful in thin-film electroluminescent devices (see Section 3.9.1.2).

Alkaline earth sulfides activated with rare earths are of importance for use in CRTs because of the linear dependence of their brightness on applied current over a wide range. For example, MgS activated with 0.004% Eu has a very bright maximum emission at 600 nm. Alkaline earth sulfides are mostly used because of their long afterglow properties. $(Ca,Sr)S{:}Bi^{3+}$ is blue, $CaS{:}Bi^{3+}$ is violet and $CaS{:}Eu^{2+}.Tm^{2+}$ is red. $SrS{:}Ce^{3+}$ has a maximum at 483 nm and is a very useful blue phosphor.

3.2.1.2 Oxygen-dominant Phosphors

These are very wide ranging and include borates, aluminates, gallates, silicates and oxyanions of many other elements.[4,5] Aluminates are particularly useful in trichromatic fluorescent and high-loading photocopying lamps. For instance cerium magnesium aluminate containing terbium, $Ce_{0.65}Tb_{0.35}MgAl_{11}O_{19}$, is a highly efficient green phosphor (λ_{max} 541 nm), and barium magnesium aluminate, $BaMg_2Al_{10}O_{17}{:}Eu^{2+}$ (λ_{max} 447 nm), is a blue component for these lamps. Terbium-doped yttrium aluminium gallium garnet, $Y_2Al_3Ga_2O_{12}{:}Tb^{3+}$, is a green phosphor with high brightness that is used in projection television tubes.

In the mid 1990s a breakthrough was achieved in the development of long-lived afterglow phosphors. It was discovered that co-doping alkaline earth aluminates, especially strontium, with lanthanide ions such as Eu^{2+} and Dy^{3+} gave phosphors with around ten times the afterglow of Cu-activated ZnS and also with ten times the brightness.[6] Excited Eu^{2+} emits green light during its deexcitation. The observed delay in emission, the afterglow, is due to the time the trapped electrons spend in meta-stable states before returning to the luminescence centres.[7] A recent review provides a more detailed discussion of the mechanism of luminescence in lanthanide ions.[8] Since the late 1990s over 100 long-lived afterglow phosphors have been found, important examples being $CaAl_2O_4{:}Eu^{2+}.Nd^{3+}$ (>10 h blue), $SrAl_2O_4{:}Eu^{2+}.Dy^{3+}$ (>10 h green) and $CaS{:}Eu^{2+}.Tm^{3+}$ (>1 h red). Those containing Eu^{3+} can be pumped by sunlight.

Yttrium and europium oxides form mixed crystals without any vacancies due to the very similar sizes of their ionic radii. $Y_2O_3{:}Eu^{3+}$ is used with around 3 mol% europium to give a very intense red phosphor (λ_{max} 612 nm) that is commonly used in colour CRTs.

3.2.1.3 Silicates

Zinc orthosilicate $Zn_2SiO_4{:}Mn^{2+}$, a green phosphor (λ_{max} 525 nm) used in fluorescent lamps, CRTs and plasma display panels, demonstrates low resistance to burn out, excitation by low-energy electrons, and shows a linear increase in brightness with electron beam intensity. Y_2SiO_5:Ce^{3+} is a highly resistant blue CRT phosphor used in projection TV tubes (λ_{max} 400–460 nm depending on the Ce^{3+} content).

Synthesis of efficient phosphors requires the ability to carry out high-temperature chemistry, and to prepare and handle precursors and high-purity starting materials, details of which are given in specialised texts.[4] The performance of phosphorescent pigments is greatly affected by the crystallinity and the physical form, especially in terms of particle size. Importantly, the crystalline structures of luminescent materials must be rigid for both efficiency and chemical stability, and the energy must be able to flow easily from absorption sites to emission sites, which should be plentiful. Generally speaking the larger the crystals the better are the absorption and emission processes, as they have more potential sites than a small pigment particle. The need to keep a largish particle size means that, when grinding phosphors for formulation into inks, care must be taken not to over-reduce the particle size, to avoid reduction of their efficiency. This has been a problem over the years as the lower limit of the particle size for good emission was often too large for incorporation into workable inks, especially for flexo and lithographic outlets. In general the typical particle size of inorganic phosphors is around 5–10 μm (see data in Tables 3.2 and 3.3 below). However, phosphor nanoparticles around a few nm in diameter are also of interest for specific applications (see Section 3.5.2.3).

3.2.2 Applications of Inorganic Phosphors

The main commercial use of inorganic phosphors is in illumination devices and displays, and these will be discussed in separate sections (illumination and plasma panels in 3.4.2; cathode ray tubes in 3.3.1; electroluminescent displays in 3.9.1; light-emitting diodes in 3.9.2 and laser diodes in Chapter 5). The remainder of this section is devoted to other applications of inorganic phosphors.

Inorganic phosphors are used in security applications, such as the coding of cheques, cards, passports, tickets and on bank notes, often in conjunction with machine-readable information. It is distinctly advantageous for security outlets that the pigment is colourless or only of a pale shade, to only be visible under UV (365 nm) and also to exhibit no afterglow. This makes it more difficult for the counterfeiter or thief to see where the coding is placed on the item, and hence more difficult to forge or steal. Consequently information on particular formulations remains confidential to the supplier and user. A long-established non-security application for such materials has been in postal envelope sorting. The orange "flash" afterglow pigment ZnS:Mn is incorporated into stamps enabling the envelopes to be placed in the correct position for machine reading of post/zip codes. A typical set of such commercial materials for this class of uses is shown in Table 3.2.[9]

Phosphorescent pigments which glow-in-the-dark green, initially based on ZnS activated especially by copper, and later on activated alkali earth sufides

Table 3.2 Invisible, no-afterglow phosphorescent pigments.

Composition	*BaMgAl: Eu*	*ZnCdS: Mn*	*BaMgAl: Eu, Mn*	*GdOS:Eu*	Y_2O_3*:Eu*	YVO_4*:Nd*
Body colour	White	Pale yellow	White	White	White	White
Particle size	10 µm	15 µm	13 µm	2.5 µm	10 µm	7 µm
Emission colour	Blue	Yellow	Green	Red	Red[a]	Infrared

[a] Uses short wavelength UV to activate.

Table 3.3 Properties of commercial sulfide-based, UV/daylight excited phosphorescent pigments.

Composition	*ZnS:Cu*	*ZnS:Cu*	*ZnS:Ag*	*CaS:Eu,Cu*	*CaSrS:Bi*
Body colour	Pale yellow	Pale yellow	White	Pink	White
Emission colour	Green	Green	Green	Red	Blue
Particle size	20 µm	5 µm	20 µm	8 µm	8 µm
Afterglow	Long	Short	Long	Long	Long

such as CaS and SrS, have been commercialised for many years. They are used in outlets such as clock, watch and instrument dials, which are required to be visible in temporary, poor lighting conditions, and are still popular today, having found new uses in novelty items such as plastic toys and in sporting goods, for example as fish floats. Some typical commercial materials are shown in Table 3.3.[9]

The more recent commercial availability of RE-doped alkaline earth aluminates (AEAs) extended the scope and uses of phosphorescent pigments because they provide materials with a remarkably persistent afterglow coupled with high stability. The most effective energy saturation is obtained when the pigment is exposed under direct UV from the sun, black lamps, halogen lamps, discharge lamps and other UV-rich sources, because afterglow brightness is proportional to the UV content of the excitation light. A comparison of the properties of AEAs with a common ZnS phosphor is given in Table 3.4.[10]

One particularly important application for long-afterglow phosphors is in what is called Photo Luminescent Low Location Lighting, where they offer cost effective solutions to the demands of health and safety directives. For example I.M.O. A752 requires one hour low-level lighting on ships carrying more than 36 passengers or 1500 tonne for a non-passenger vessel. ZnS phosphors are limited by their low light storage but AEAs meet the requirements of the directive with some ease.

Phosphorescent pigments are now being used safely in a wide variety of applications, which include consumer products, such as clothing, shoes, caps, toys, stationery goods, watches, novelties, fishing tools and sporting goods; in security labels, cheque stubs and other machine readable items; in buildings for decoration and low-level lighting of safety escape routes; on traffic and military

Table 3.4 Comparison of the properties of alkaline earth aluminate and zinc sulfide phosphorescent pigments.

Pigment	*Alkaline earth aluminate*	*ZnS:Cu*
Body colour	Light yellow green	Yellow green
Average particle size/µm	45 65	40 50
Excitation energy/nm	200 450	200 450
Emission wavelength/nm	520	530
Afterglow brightness mcd/m^2	340	16
Afterglow extinction/min	2000	200
Excitation time/min	10	10
Light fastness	> 1000 hrs	100 hrs (65%loss)
Chemical stability	Excellent (except in water)	Poor good

installations and in fire emergency systems; and for cosmetic dentistry. They are available for formulation into paints and coatings, UV-cured and silk-screen inks, and can also be incorporated into a wide range of plastics, including acrylics, polyester, epoxy, PVC, polypropylene and polyethylene (HDPE and LDPE), by casting, dipping, coating, extruding and molding.[11]

3.2.3 Up-conversion

Up-conversion in its most general sense is the phenomenon whereby one or more photons of lower energy are absorbed by a material, and re-emitted as a higher energy photon. Materials able to cause this effect are known as up-converters. A main attraction is that they can be tuned to respond to near IR energy near 980 nm from commonly available and cheap diode lasers, and emit a range of photon energies at visible wavelengths. A major type of up-converter is based on rare earth- (RE)-doped salts of various metals, usually fluorides, in solid crystal or glass matrices. Up-conversion in such materials can occur by several different mechanisms whose full description goes beyond the scope of this book.[12] They rely on the multitude of accessible excited states within the different RE cations. Besides the RE materials there are others which bring about an up-conversion effect on photo-irradiation, and which will be the subject of more detailed description later. They are introduced now for convenience. They in turn follow different mechanisms for up-conversion.

Figure 3.2 summarises diagrammatically some of the absorption-emission processes which lead to up-conversion. The vertical arrows represent absorption or emission of a photon, while the curved arrows represent energy transfer between species (usually ions).

- Mechanism (a) is the most common in RE systems. Here two photoexcited RE ions (same species or different) each transfers its energy to a third ion which emits from the higher-energy state. Ytterbium as Yb^{3+} is commonly used as a primary absorber of input photoradiation, and this transfers energy to emitter ions, commonly Er^{3+} and Tm^{3+}. The efficiency of this energy transfer up-conversion (ETU) is surprisingly high and, of the five

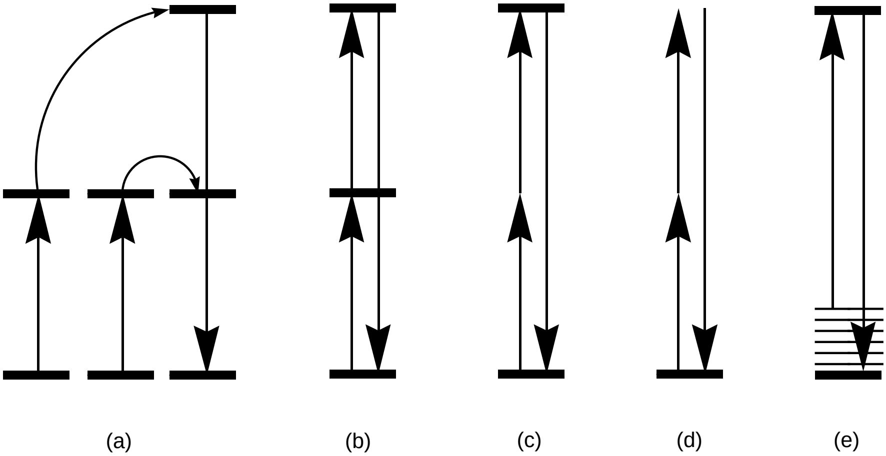


Figure 3.2 Simplified representations of some up conversion processes[12] (reproduced with permission from American Chemical Society).

mechanisms shown in Figure 3.2, this is the most efficient. Three-photon ETU is also well known.

- In (b), initial absorption leads to an intermediate excited state, which lives long enough to allow ready absorption of a second photon to give a higher excited state, hence its name of 2-step absorption. Emission from this clearly gives a higher energy, up-converted, photon. This process is about two orders of magnitude less efficient than (a). Mechanisms related to (a) and (b) can involve subsequent absorption steps to reach yet higher excited states, prior to luminescence. Furthermore, there are not only several other distinct processes for RE up-conversion, but there are also combination processes, some including conventional down-conversion steps, so it must be accepted that the overview presented here for RE up-converters is very limited.
- Mechanism (c) is two-photon absorption, this time without a real intermediate excited state. This implies simultaneous absorption of two photons, which inevitably has a lower probability and the mechanism is thus much less efficient. However, by means of intense laser irradiation, two (or even multi) photon absorption (2PA, 3PA, *etc.*) has become well characterised for some organic dyes and specially modified derivatives, and is discussed in detail below in Section 3.5.3. CaF_2 doped with Eu^{2+} is a 2PA example from RE chemistry. However, up-conversion from this material is about 10^{10} times less efficient than for an ETU material such as YF_3 doped with Er^{3+} and Yb^{3+}.
- Second harmonic generation (d) is discussed in Chapter 5 under nonlinear optics (although mechanisms (a) to (c) are also nonlinear in character). Here the interaction of two photons in the SHG material does not proceed by way of any excited energy state. The efficiency of up-conversion for the traditional SHG material KDP (potassium dihydrogen phosphate) is about eight orders of magnitude less efficient than that for ETU (a).

- Finally, the mechanism of up-conversion represented by (e) is sometimes called hot-band absorption. An electron in a vibrationally excited level of the ground state of a species is preferentially excited. Emission then proceeds back to a lower vibrational level within the ground state, and up-conversion by only a few units of thermal energy is observed.

3.2.3.1 Up-converting Rare Earth or Anti-Stokes Materials

The term up-converter is sometimes restricted specifically to RE-based materials which convert two (or more) IR photons to a visible energy photon. They are also known as anti-Stokes materials, as the usual Stokes red-shift between absorption and emission energies for conventional fluorescent dyes is the opposite in up-converters (blue shift). A plethora of RE-doped inorganic materials has been investigated as up-converters, and the phenomenon in such materials is now regarded almost as routine. The main luminescent RE ions used for UC are the tripositive ions of Er, Tb, Tm, Ho and Pr, with Yb commonly used as a sensitiser. Up-conversion by d-block transition metal and actinide ions has also been reported.[12] Some properties of a well-established up-converting RGB trichromat, discussed further below, are shown in Table 3.5.[13] In all three cases the process is ETU, two of them involving 3-photon excitation, and the other 2-photon.

Both the emissions from the Er^{3+} ion in the two materials shown involve a transition from a quadruplet state ($^4S_{3/2}$ and $^4F_{9/2}$) to the quadruplet $^4I_{15/2}$ ground state. Spin multiplicity is maintained, and so by the formal definition both these emissions correspond to fluorescence of the Er^{3+} ion. In contrast the Tm^{3+} ion emits from a $^1G_4$ excited state to the $^3H_6$ ground state, and as multiplicity is not retained this emission is formally phosphorescence. To avoid the complication of varying spin multiplicities amongst the RE ions, and even for different transitions within the same RE ion, energy emission from photoexcited RE ions is best referred to as luminescence, rather than fluorescence or phosphorescence. Despite the confusion, all these materials are still usually referred to generically as up-converting *phosphors*, whatever their spin-multiplicities.

RE up-converters are usually prepared and used as conventional pigment-size particles (*ca.* 10 microns diameter). However, nanometre scale RE up-converters are becoming of major interest in the bio-medical fields and are discussed further in Section 3.5.2.3 alongside other fluorescent materials. The luminescence of closely related molecular derivatives of RE elements is also discussed there.

Table 3.5 A rare earth up-converter RGB trichromat, used in a new type of display. Data generated as a result of 975 nm laser excitation wavelength at room temperature.[13]

Host	*% Emitter, Sensitiser*	*Emitted colours major (minor)*	*λ_{em}/nm major*	*Up conversion process*
YF_3	Er, Yb (1, 18)	Red (green)	650	3 photon ETU
$NaYF_4$	Er, Yb (1, 18)	Green (red)	545	2 photon ETU
KY_3F_{10}	Tm, Yb (0.4, 20)	Blue (red)	480	3 photon ETU

3.2.3.2 Applications of Up-converting Phosphors Securities

The first two applications of RE up-converters now described are already commercialised. Those then following are works in progress. A major application of RE up-converters is in the area of *anti-counterfeiting* of goods, and *security* labelling of banknotes, legal and financial documents, and similar. It is estimated that counterfeit goods cost the global economy £171 billion *p.a.* Furthermore, use of inferior or downright wrong ingredients in fake pharmaceutical products is illegal at best, and deadly at worst. Up-converters can expose counterfeiting, enable product and manufacturing process authentication and verification, and track and trace goods comprising almost any material. Once immobilised in or on the target product, they are essentially invisible to the naked eye, but can be readily detected by means of simple hand-held NIR diode lasers or similar devices. Mixtures of emitted colours, perhaps in combination with other fluorescers, UV absorbers or conventional dyes, enable individual and unique identification signatures to be designed and applied. Various suppliers advertise RE up-converters for this purpose, but not surprisingly information on their chemical composition and properties is hard to come by.

3.2.3.3 Up-converting Lasers

Efficient RE up-converting phosphors are much studied as the active materials for *up-converting lasers* (visible lasers that are pumped by IR diode lasers).[14] Most currently used up-conversion lasers are based on glass fibres, but usually silica glass is unsuitable and is replaced by heavy-metal fluoride glasses (*e.g.* ZBLAN: a glass comprising fluorides of Zr, Ba, La, Al and Na), which tend to be fragile and expensive. As examples of fibre lasers, blue emission at about 480 nm is achieved from Tm^{3+}-doped materials by pumping at 1120–1140 nm; red from Er^{3+} pumped around 980 nm and lasing around 546 nm; and Pr^{3+}/Yb^{3+}-doped materials pumped around 850 nm and emitting at one of various visible wavelengths in the red (635 nm), orange (605 nm), green (520 nm) or blue (491 nm).

3.2.3.4 Emissive Displays Based on Up-converting Phosphors

The three up-conversion phosphors in Table 3.5 comprise an RGB trichromat, which has been developed for new *emissive display technology*.[13] In a simplistic description of the design, the phosphors are dispersed in a polymeric binder, which is then coated onto a screen. NIR radiation (975 nm) is used to excite the phosphors and initiate visible emission, in either reflective or transmission mode. The main properties of the prototype display are:

- Very high emission brightness (easily visible outdoors in Florida noon sunlight), with no photo damage to emitters and a long operating lifetime;
- Wide shade gamut and very saturated colours, comparable with OLED displays (Section 3.9.9);
- Grey levels achievable, with wide viewing angle;

- White light emission from appropriate mixtures could be a solution for back-light illumination in liquid crystal displays (Section 5.2);
- Efficiencies comparable to existing technologies;
- Simplicity of fabrication and potential for reduction in display weight and depth;
- Scalable and safe; believed to be competitive with all existing technologies;
- A cooling source will be needed for the blue phosphor, as the excited energy levels of the Yb^{3+}/Tm^{3+} pair are not exactly energy-matched, and some non-radiative emission (heat) results.

This display technology is still under development.

Up-converters have also been claimed in a patent application as phosphors for plasma display systems (*cf.* Section 3.4.2).[15]

3.2.3.5 Optical Refrigeration

The final application of RE up-converting phosphors is perhaps the most counter-intuitive and surprising chromic phenomenon in this book, and concerns the use of lasers for cooling and thus *optical refrigeration*. We are used to seeing laser irradiation heating and thus cutting, burning, breaking or generally destroying various materials. But by means of the up-conversion process (e) in Figure 3.2, the exact opposite can result when some up-converting phosphors are irradiated at specific wavelengths. The process implied involves photo-excitation from a vibrationally excited level of the ground state, followed by a slightly higher-energy emission to a lower-energy ground state. The difference in energy between the absorbed photon and the emitted up-converted photon is made up by thermal energy within the phosphor. On prolonged irradiation, the uptake of thermal energy as part of the up-conversion process is reflected by a temperature drop within the material. The directly cooled phosphor can then absorb heat from its surroundings, comprising the mechanism for refrigeration. The emitted photo-radiation is of no consequence, other than it must be removed from the system by absorption by a heat sink to prevent subsequent unwanted phosphor heating. The up-conversion phosphor must itself have a very high luminescence quantum yield, to ensure that essentially all absorbed light is re-emitted as light, and none converted to heat by non-radiative decay, which would otherwise provide another unwanted internal source for thermal repopulation of the vibrationally excited ground state. It is also essential that materials do not contain any impurities, such as Cu or Fe ions, which could act as quenchers and thus also result in internal heat generation.

The effect was first demonstrated at Los Alamos National Laboratories in 1995 by laser pumping of Yb^{3+}-doped ZBLANP fluorozirconate glass, and since then by other Yb-doped glasses.[16 18] Subsequently, laser cooling has been demonstrated in other systems, for example by Tm^{3+} in ZBLANP at 1.9 μm,[19] and Er^{3+}-doped KPb_2Cl_5 crystals at about 870 nm.[20]

A temperature drop from room temperature to 208 K in a Yb:ZPLANP up-converter is the best so far achieved. For real-world application the efficiency needs to be improved, and the optical refrigerators must operate at lower temperatures to compete with alternative technologies. Studies have shown that it will be feasible to achieve temperatures below 100 K. Optical fridges are still under development and not yet at the stage of commercialisation. However Ball Aerospace Corp announced development of the first such refrigerator in 2003.[21]

Optical fridges have appreciable attraction as a potential cooling technology: compactness; no moving parts or fluids, thus vibration-free; silent; high reliability; no need for cryogens; low electromagnetic interference; low power consumption, particularly with the new generation of diode lasers; and thus potentially low cost. It is envisaged they will find use in space satellites, as coolants in small-scale devices subject to unwanted heating such as personal computers or IR cameras; and as thermal compensators to balance the Stokes heating from stimulated emission in solid-state lasers. The latter would enable solid-state laser power to be increased to 100 kW cw or more.

In principle, there is no reason why conventional fluorescent dyes with appropriate properties could not show the same optical cooling effect. In fact at about the same time as the Los Alamos report on up-converting phosphors, just such an experiment on the strongly fluorescent dye rhodamine 101 was reported (Figure 3.3).[22,23] This dye has a fluorescence quantum yield of unity and displays a very small Stokes shift, so that it still absorbs at low-energy wavelengths well to the red of the average fluorescence emission wavelength. These are prerequisites for hot-band up-conversion as in Figure 3.2(e). A temperature drop of 3 K was found when the dye was irradiated by a HeNe laser at 632.8 nm for 4 h.

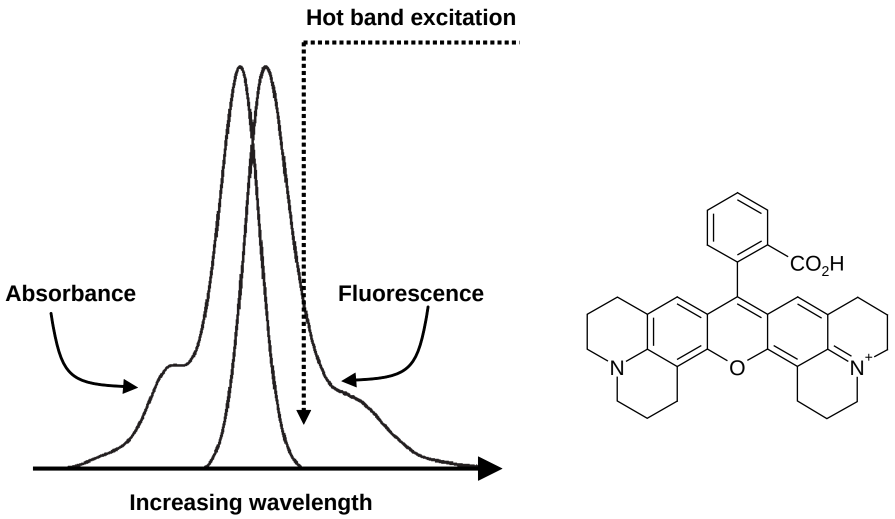


Figure 3.3 Structure of rhodamine 101, and normalised absorbance and fluorescence spectra (EtOH/H^+), with position of hot band excitation indicated. Absorbance maximum *ca.* 585 nm; emission maximum *ca.* 607 nm; average emission 610 nm; hot band excitation wavelength 632.8 nm

However, this appears to be a unique experiment, and to date there has been no further report of fluorophores displaying optical cooling, perhaps because of the difficulty of the experiment and the stringent requirements necessary to avoid parasitic heating by so-called killer impurities, which nullifies the effect.[24]

3.3 Cathodoluminescence

Cathodoluminescence is the phenomenon of production of light (colour) from a phosphor following its irradiation and excitation by electrons.

3.3.1 Cathode Ray Tubes

A major use of inorganic phosphors is in cathode ray tubes (CRT), the technology underpinning conventional television. A wide-ranging market survey covering January to March 2008 revealed the following key figures for the global TV market: 46.1 million TV units were sold; of which 22.1 million were CRT; 21.1 million were based on liquid crystal display technology (LCD; Chapter 5); 2.8 million were plasma display panels (PDP; Section 3.4.2); and 134,00 were rear-projection. Compared to the first quarter of 2007, CRT sales were down 21%, LCD up 45%, plasma up 20% and RPTV was down 79%.[25] So, although more recent flat screen display technologies are making major inroads into the TV market, CRT remains a very important technology. Its main drawbacks are the bulkiness of the unit, and the inability to scale it up for large format display.

The operating principle in CRTs, shown schematically in Figure 3.4, involves an electron beam generated from the cathode located at one end of a glass

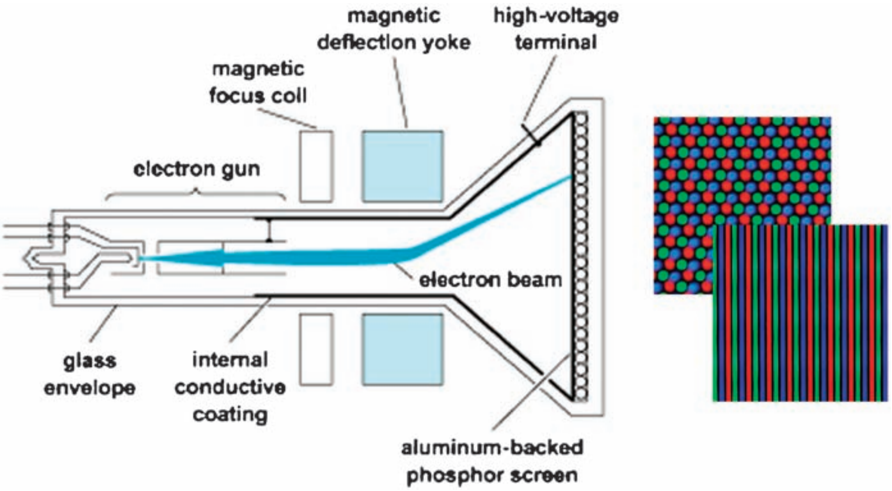


Figure 3.4 Schematic representation of a cathode ray tube. Pixelation schemes on the right.

vessel, which is held under vacuum. The electron beam is accelerated and then moved horizontally or vertically by electrostatic or electromagnetic means. The inner, front surface of the glass vessel is coated with inorganic phosphors and when the beam of highly accelerated electrons hits this surface the phosphors emit visible light.[26]

To avoid any flicker in the image, the electron beam is scanned across and down the screen, many times per second, following a pre-determined set of parallel lines (raster scanning). The phosphor dots are the picture elements or pixels and light up as the beam scans across each one. In colour TVs and monitors additive mixing of the three colours of red, green and blue produces the final colour. The pixels contain three sub-pixels of red, green and blue dots, each of which is excited by its own modulated electron beam. In order to ensure that each of the three electron beams only excites its own R, G or B phosphor a metal shadow mask is necessary, made up of an array of holes, each hole serving a group of three adjacent RGB phosphors. The shadow mask is placed between the guns and the phosphors, just in front of the faceplate of the CRT.

In an alternative system, introduced by Sony as the Trinitron system, the mask is a series of vertical slits and the phosphors are deposited in vertical stripes on the screen.

Construction of the phosphor screen involves laying down the three red, green and blue phosphors on the inner surface of the tube, in a consecutive manner, as dispersions in a photosensitive resin. A photo-mask is put over the resin and the whole exposed to light which reacts with the resin, rendering the exposed area water insoluble. The unexposed areas of the phosphors remain soluble and this excess material is washed off with water. To increase the brightness of the display, any radiation heading back into the tube is required to be reflected forward. This is achieved by vacuum depositing a thin film of aluminium on top of the phosphors. This also prevents any build-up of charge on the phosphor layer of the CRT, eliminating a source of inefficiency. The phosphor particles on normal colour CRTs are around 8–10 μm but higher resolution colour monitors require smaller particles of 4–6 μm.[27]

The CIE chromaticity diagram for the desired red, green and blue phosphors in colour TV is shown in Figure 3.5. There is some tolerance level around the marked positions, but the red, green and blue phosphors have been subject to much refinement since the advent of colour TVs and now are close to ideal for the required systems.

The blue phosphor of long standing is ZnS:Ag, which has a radiant efficiency close to the theoretical limit. It is a donor–acceptor type phosphor, with silver ions acting as the acceptor in the ZnS with either aluminium or chlorine as the donors on zinc or sulfate sites.

For the green phosphor ZnS:Cu is used, with both aluminium and gold acting as the donors. For practical reasons the wavelength can be shifted from 530 nm to slightly longer wavelengths by replacing around 7% of the zinc by cadmium.

The original red phosphors were (Zn,Cd)S:Ag and $Zn_3(PO_4)_2$:Mn. However after it was recognised that a narrow emission around 610 nm would be

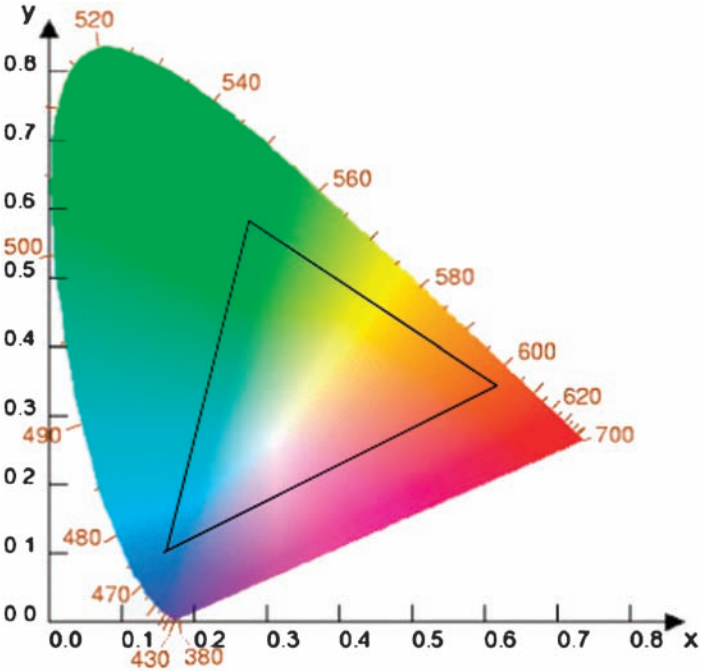


Figure 3.5 CIE chromaticity diagram. The vertices of the triangle define the ideal red, green, blue co ordinates.

beneficial, research into RE-based phosphors led to the development of Eu^{3+} doped into yttrium oxides, for instance YVO_4:Eu, Y_2O_3:Eu and Y_2O_2S:Eu.[28]

For CRT displays requiring areas in excess of 75 cm^2 it is necessary to use projection television. This involves three small, monochrome CRTs projecting red, green and blue images, respectively. The images are optically projected *via* lenses onto a screen, and require much higher illumination levels in order to get an image of any quality. Accordingly much higher current densities have to be used than in conventional direct viewing TVs, and it is difficult to obtain phosphors to meet the needs of this technology. The red phosphor, usually Y_2O_3:Eu, is good for this purpose, but the green $ZnSiO_4$:Mn and especially the blue (Ca, Mg)SiO_3:Ti are less ideal. Sales of RPTV are falling.

Phosphors are also widely used in many other CRT devices, for example in monochrome terminal displays, in oscilloscopes, radar tubes and in X-ray and scintillator technologies.[1,26,29]

3.3.2 Field Emission Displays and Related

The main drawback to CRT technology is the bulkiness of the unit, needed to accommodate the projection of the photoexciting electrons emitted by the electron guns (Figure 3.4). This prevents a flat-screen configuration. More

Table 3.6 Phosphors for low-voltage FED.

Chemical composition	*Particle size/μm*	*Emission peak/nm*
Y_2O_3:Eu	2.5	611
Y_2O_2S:Eu	3.5	627
ZnO:Zn	3.5	505
$Y_3(Al,Ga)_5O_{12}$:Eu	4.0	543
Gd_2O_2S:Tb	3.5	544
$SrGa_2S_4$:Eu	4.0	535
ZnS:Ag	3.5	450
$SrGa_2S_4$:Ce	4.0	415
Y_2SiO_5:Ce	3.5	400

recent technology overcomes this deficiency while retaining other CRT benefits, thus re-positioning CRT back in the competition alongside LCD and PDP. The cathodic electron guns can be replaced by alternative means of generating and projecting electrons onto a phosphor-coated display screen. A recent example is provided by the use of carbon nanotubes (CNTs; see Section 3.5.2.1) as "field emission" electron-emitters. The novelty is that a cluster of many CNTs is used to drive each pixel, and because each pixel is activated individually, there is no longer a requirement for distance between the screen and the electron-emitter, so a flat-screen format, reportedly only a few mm thick, is possible. The technology is known as Field Emission Display or FED.[30] In principle the same phosphors as used in conventional CRT may be used for FED, but there is some debate over whether the device should work at high or low voltages. Table 3.6 lists phosphors which are being sold for low voltage FED.[31]

Although FED has not yet been commercialised, it has been reported that the company Field Emission Technologies (FET) (37.8% owned by Sony) "plans to launch an industry-grade 26 in FED TV at the end of 2009. A 60 in commercial model could follow sometime later".[32]

Another new technology, SED (Surface-conduction Electron-emitter Display), is also based on a novel method for electron emission at a CRT-like display screen, but its development and commercialisation has been inhibited by intellectual property disputes. SED is said to provide the picture quality of CRT, in a flat-panel format, at about 50% of the power consumption of CRT displays and 33% of the power of plasma displays of a comparable size.[30(b),33]

3.3.3 Radioluminescence

The production of light by phosphors due to the impact of particles generated by radioactive decay of an appropriate material is known as radioluminescence. In practice, the radioactivity is restricted to β-emitters which produce electrons that excite phosphors. The phenomenon is therefore a special case of cathodoluminescence. Nowadays radioluminescence is restricted to tritium gas-based devices. The hydrogen isotope tritium is radioactive with a half life of

12.4 years. Its β-emission is very low energy and thus essentially non-hazardous, but of a sufficient energy to excite conventional phosphors coating the inside of its borosilicate glass capillary enclosure. Such devices are known as "trasers", and they are used in small-scale applications where long-lived continuous luminescence is required for night-time use, such as markings of luminous watches, night sights for weapons and in consumer gadgets such as "Power Glow key rings". The colour produced is of course dependent on the phosphor used. In the past radium was used as the β-emitter, particularly for luminescent watch markings, but on safety grounds its use has been abandoned.

3.4 High-energy Photoluminescence

In this section the term photoluminescence is specifically applied to the cases where luminescence occurs after the interaction of luminescent materials with narrow-band, higher-energy ultraviolet radiation, and specifically in lighting and plasma display panel applications.

3.4.1 Lighting

Luminescent lighting, commonly called fluorescent lighting, has been in regular use since it was first introduced in the 1930s. Its dominance in the illumination of offices, department stores and public spaces arises from the fact that it has a much higher efficiency than incandescent lighting. For instance, a 60-W incandescent light tube generates only 15 lm W ^{1} whilst a 40-W luminescent light bulb yields 80 lm W ^{1}.[34]

Luminescent light is generated using UV radiation from a low-pressure mercury discharge from mercury vapour present in a noble gas matrix, which fills the luminescence tube under low pressure. The emitted radiation consists of 85% at 254 nm and 12% at 185 nm, the remainder being mainly in the visible region. The lamp phosphors which coat the inside of the tube convert the 254 nm and 185 nm UV radiation into visible light (Figure 3.6). The light emitted must be "white light" in order to match the ambient natural lighting from the sun. Since the sun is a black-body radiator, a terminology has been developed for the lighting which follows the temperature of the black body, hence "white" is 3500 K, "cool-white" is 3000 K and "warm-white" is 4500 K light. The white light can be generated from component colours in a variety of ways by colour matching from positions on the CIE chromaticity diagram (see Figure 3.5). The simplest method is to mix blue and orange light but mixing the three additive primaries of red, green and blue is also an option.

For over 50 years the phosphors of choice for luminescent lighting have been based on activated calcium halophosphates $Ca_5(PO_4)_3X$ (X=F, Cl), with Sb^{3+} and Mn^{2+} as the usual activators. When Sb^{3+} is used as the dopant the phosphor is a very efficient blue emitter under 254 nm excitation, whilst Mn^{2+} shows an orange emission under these conditions. By careful adjustment of the

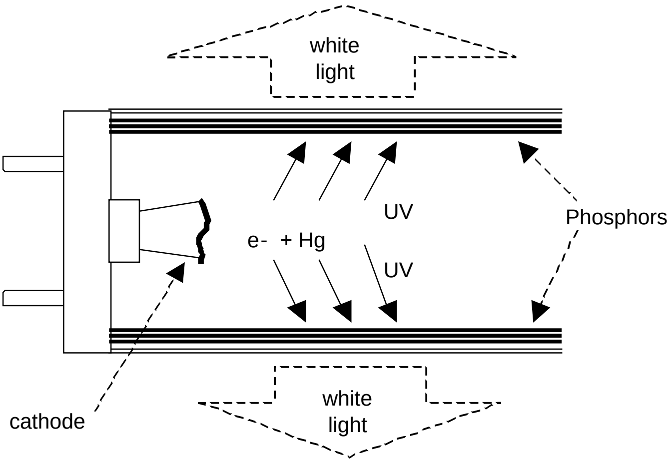


Figure 3.6 Cross section of a low pressure luminescent tube.

ratio of Sb^{3+} and Mn^{2+} it is possible to make white emitting phosphors for general-purpose outlets, which have colour temperatures in the range of 2700–6500 K.

Calcium halophosphate lamps have drawbacks, one of which is that high brightness cannot be coupled with high colour rendering; if the brightness is high the colour rendering drops and *vice versa*. This problem has been overcome by the development of tricolour lamps. These involve the use of three RGB phosphors with very narrow emission wavelength intervals centred on 450, 550 and 610 nm. The red phosphor that fulfils all the requirements is Y_2O_3:Eu emitting at 610 nm. The choice of blue phosphors is between the Eu^{2+}-doped $BaMgAl_{10}O_{17}$:Eu, $Sr_5(PO_4)_3Cl$:Eu and $Sr_2Al_6O_{11}$:Eu, which emit over the range 440 to 460 nm. The green phosphors used in tricolour lamps all contain Tb^{3+} as the emitting ion. However, they also require Ce^{3+} to act as a sensitiser, absorbing the 254 nm wavelength from the mercury radiation and transferring it to the Tb^{3+} ion, in one case also assisted by Gd^{3+}. Examples of these green phosphors are $CeMgAl_{11}O_{19}$:Tb, (La,Ce)PO_4:Tb and (Ce,Gd)MgB_5O_{10}:Tb.

3.4.2 Plasma Displays

Although plasma display panels (PDPs) are not a new technology, they are now one of the methods for producing full-colour, flat and large area TV displays. In early 2008, roughly 6% of the TV market comprised PDPs, a 20% increase since the first quarter of 2007.[25] Modern, full-colour PDPs use ionised gases to energise phosphors, which then emit visible light with the correct colour coordinates.

Structurally a plasma display panel is made up of a series of wells bonded between two glass plates with electrodes on both the top and bottom. The three sub pixels (R, G, B) that are necessary for each full colour pixel are formed by

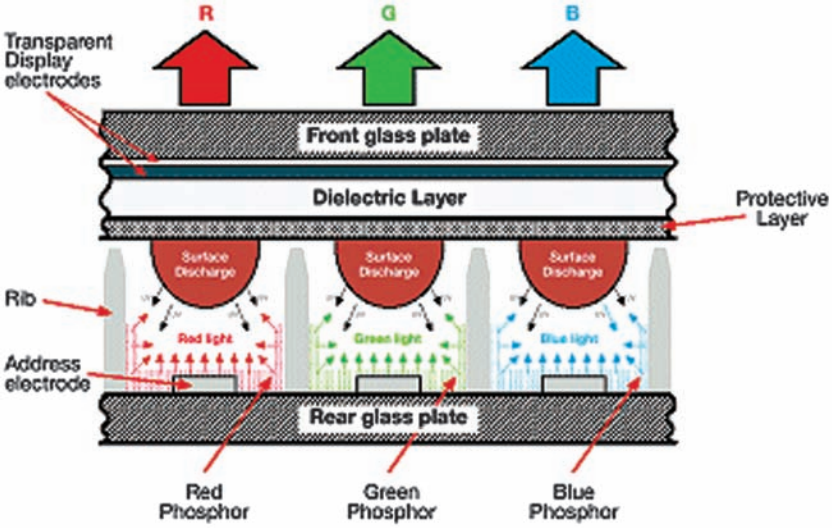


Figure 3.7 Schematic of Fujitsu plasma display panel cells.

constructing an array of barrier ribs at right angles to each other, the wells forming the gaps in the arrays. The cell-like chambers of each sub-pixel are shown diagrammatically in Figure 3.7. Two transparent sustain electrodes are placed on the front glass plate and are used to maintain the plasma burning, whilst ignition and erasing are both achieved by using an address electrode situated on the backplate. Each cell is filled with a mixture of neon and xenon gases, which on igniting form a plasma that emits vacuum ultraviolet light (VUV) in the wavelength range of 140–190 nm. This light interacts with the phosphors, present as a coating on the inside walls of the cell, which emit visible light back through the glass front plate.[35,36]

The conditions required for the construction of these cells place considerable strain on the phosphors, because setting up the transparent electrodes requires annealing in the range 500–600 °C. Additionally the phosphors must be able to stand the constant ion bombardment from the plasma and VUV radiation. Most importantly, the phosphors must convert the VUV to visible light with maximum efficiency to obtain a high brightness display panel. Finally, they must show good colour saturation in order to generate a large colour gamut.

The phosphors used by most manufacturers of plasma display panels have been chosen from existing materials: commonly $BaMgAl_{10}O_{17}$:Eu (blue; high quantum efficiency, colour purity, availability), Zn_2SiO_4:Mn (green; high quantum efficiency, availability) and $(Y,Gd)BO_3$:Eu (red; high quantum efficiency, persistence characteristics, reduced saturation). However, their screen efficiencies of about $1.5\,\mathrm{lm\,W}^{\ 1}$, although suitable for use in consumer devices, are still well below the $3\,\mathrm{lm\,W}^{\ 1}$ found in conventional CRTs, and so further development work on conventional inorganic phosphors is continuing.[37]

Beyond this, fundamentally different science offers an alternative approach to improvements in both PDP and illumination phosphors, as described in the next section.

3.4.3 Quantum Cutters

The luminescent phosphors introduced and discussed above all involve exciting a material with a high-energy photon, and getting in return emission of a lower-energy visible photon. The quantum efficiencies of phosphors are variable, although values as high as 90% are achieved by some RE phosphors. The energy balance is made up by an increase in internal lattice vibrations, detectable by increase in temperature. An approach to improve this efficiency depends on being able to convert one input excitation photon into two output photons, when the quantum efficiency could then theoretically approach 200%. In fact, phosphors that enable just such a conversion, called "quantum cutters", are known and are under development.

Various physical mechanisms describe the overall process, as represented diagrammatically in Figure 3.8.[38] The first possibility (a) shows how absorption of a high-energy photon leads to excitation to a higher excited state. Emission of a first photon leads to an intermediate excited state, which is followed by a second emission back to the ground state. This was demonstrated in YF_3:Pr, where direct excitation of the Pr^{3+} ion to a 5d level by means of UV irradiation below 200 nm is followed by two unequal emissions, first at 408 nm then at 620 nm. The quantum efficiency of visible light emission is about 140%. The second mechanism (b) could apply for a doped phosphor. Here initial excitation is followed by cross-relaxation, which excites the dopant to an excited level from which it luminesces. Meanwhile, the remaining energy on the primary absorber is emitted, so that overall two photons are emitted from two separate

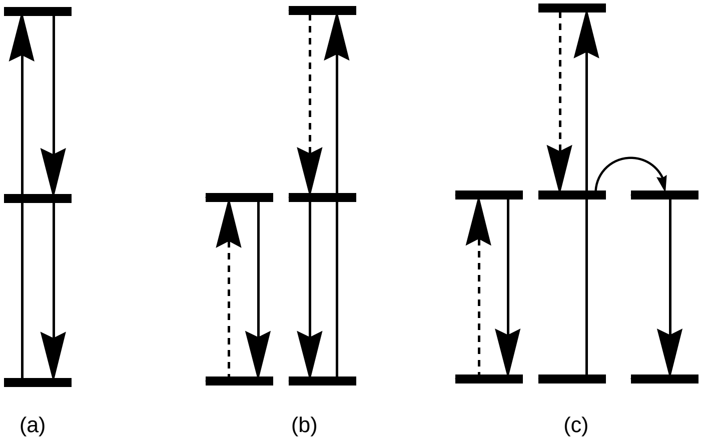


Figure 3.8 Quantum cutter mechanisms.

species. The third possibility (c) is somewhat related, except that the energy remaining on the primary absorber is transferred directly to a nearby dopant ion, followed by luminescence. Here, the two emitted photons can be of very similar energy. An example is the quantum cutter phosphor K_2GdF_5:Eu containing Pr^{3+} as a sensitiser ion.[39] The role of the Pr^{3+} ion is to act to increase the absorption of UV and VUV energy since Gd is only a weak absorber. Excitation at 210 nm leads to emissions from Eu^{3+} ions by mechanism (c), with a calculated quantum efficiency of 138%, found by semi-empirical inference to be 180%.

Thus far, no quantum cutter phosphor has been found that is suited for real application in lighting or plasma display applications. The big attraction in lighting is a desire to avoid mercury vapour as the active material in low-pressure discharge luminescence, for toxicology reasons. Furthermore, the mercury in the lamp must first be vaporised prior to activation, which leads to non-instantaneous start-up. In fact the energy of mercury's main discharge is at 254 nm (4.9 eV), which is insufficient energy to initiate quantum cutting into the visible. In contrast, the vacuum UV emanating from xenon and xenon excimer discharges (147 and 172 nm, respectively) are at sufficiently high energy to activate quantum cutting into two visible photons. Since Xe is the basis of the plasma in PDP, quantum cutters, when developed sufficiently, could have ready application in such display devices. The attraction of quantum cutters as the active materials for both PDP and luminescence lighting awaits further phosphor material innovation.

3.5 Photoluminescence 2 – Fluorescence

We now turn attention to another aspect of light energy absorption leading to light (colour) emission: the phenomenon of fluorescence, which is displayed by a wide range of dye and other molecules, as well as various materials. Although fluorescence is thus another manifestation of photoluminescence, the underlying chemistry and physics are different.[40,41] This is best explained by reference to Figure 3.9, which shows qualitatively the main energy absorption and emission pathways of importance in fluorescent materials. For convenience we shall refer to processes in dyes.

The ground state of a dye, S_0, first absorbs a photon of light energy (1), which can excite it to the first electronic excited state S_1, or in the case of a higher-energy photon (2), to a higher excited state S_2 (or higher). In this latter case, the lifetime is exceedingly short, and the excited dye rapidly decays to the first excited state S_{13}, from where all luminescence activity emanates. The lifetime in S_1 is sufficient for the dye molecule and its environment to relax (4) from its Franck–Condon excited state (vibrationally excited, with solvent non-optimally ordered) to a fully relaxed state within S_1. From here, various further relaxation possibilities next occur. The excited dye can relax to ground state by radiationless decay (5), the excess energy being liberated as heat. Alternatively, the excitation energy can be re-emitted as a photon (6), possibly in the visible

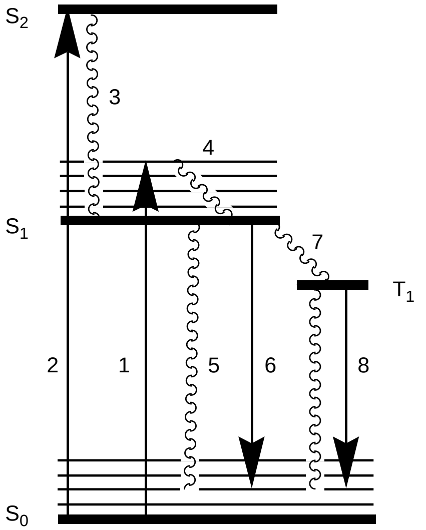


Figure 3.9 An energy diagram describing major events during excitation and emis sion from a dye molecule.

spectrum, and it is this phenomenon that is known as fluorescence. An additional mechanism (7; intersystem crossing) leads to an excited triplet state T_1, which can decay to ground state S_0 by slower emission of a photon, in this case phosphorescence (8), or by non-radiative intersystem crossing. In practice most photoexcited dyes decay by a combination of mechanisms, mainly (5) and (6).

An alternative representation of these processes is given in Chapter 4, Section 4.1, where the emphasis is on emitted heat rather than light.

In general the absorbed energy (1) is higher than that of fluorescence (6), so the absorption wavelength is shorter than the fluorescence wavelength. The difference between absorption and fluorescence spectral maxima is known as the Stokes shift, and this can vary from a few nm to several hundred, depending on the fluorescing material. The efficiency of fluorescence is given as the proportion of fluorescent photons to those absorbed, and this ratio is known as the quantum yield ϕ, or efficiency. If every absorbed photon is then re-emitted as a fluorescence photon, ϕ is unity (or 100%). A non-fluorescing material has $\phi = 0$.

Fluorescence is a very important phenomenon that is exploited in a broad range of technologies. These include enhancing the brightness of dyeings of textile fibres; as daylight fluorescent pigments in a wide variety of media including inks, paints and plastics; in detection of flaws in materials; in dye lasers; as solar collectors; in many very important analytical methodologies, especially in biological and medical applications, for both detection and diagnosis of diseases; in assays; in display applications such as electroluminescence; and in molecular electronics.

However, before discussing applications, we shall survey the wide range of fluorescent chromophores, or fluorophores, and related luminescent materials.

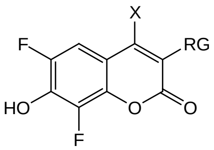
3.5.1 Fluorescent Chromophores Fluorophores

All organic chromophoric ring systems exhibit fluorescence, but to varying degrees. For example, the ubiquitous azo chromophore is for almost all practical purposes non-fluorescent. In some other cases the observed fluorescence is too weak to be of any technological value. In this section the structures of only the main classes of technologically useful fluorophores are discussed. Valuable resources for fluorophore data are Haugland's "Handbook" and its current online version published by the commercial dye supplier Invitrogen,[42] which is particularly useful for biological applications, and the compilation of structures and spectra of Lamdachrome laser dyes.[43]

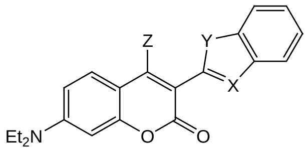
Some generalities apply. Many fluorophores are donor–acceptor-substituted π-aromatic systems. These have limited photostability, particularly in comparison with non-fluorescent species such as arylazo. However, structural modification, such as fluorination, can help to improve basic weaknesses. Molecular flexibility offers mechanisms for non-radiative decay pathways, so building in rigidity helps to improve fluorescence quantum yields. For biological applications aqueous solubility is desirable, and this is conferred by conventional methods such as introduction of anionic sulfonate or carboxylate groups, or of cationic centres, or other hydrophilic units. When fixation to a substrate as a fluorescent label is needed, normal reactive group chemistry has been adopted. Depending on the attachment centre, various activated esters or alkylation sites are common for nitrogen and sulfur reaction sites. Dichlorotriazines, borrowed from the oldest of conventional cellulosic reactive dyes (Section 2.3.2), can be used if labelling of a carbohydrate is required.

3.5.1.1 Coumarins

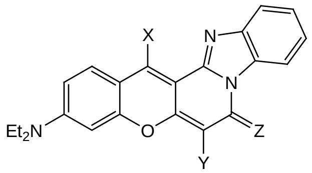
Coumarins constitute one of the oldest known fluorophores. UV absorbers through to bright yellow, orange and red fluorescent dyes offer fluorescence from the violet across the visible spectrum. The donor group in the 7-position is basic for determining the absorbance (and thus fluorescence): O for hypsochromically shifted UVA such as the fluorinated activated esters (3.1; R = H, Me), and nitrogen for coloured species. Many important derivatives are substituted in the 3-position by heteroaryl groups (3.2; X = N; Y = NR, O, S; Z = H), and quaternised for aqueous solubility to give bright cationic dyes suitable for use in dyeing acrylic fibres, exemplified by CI Basic Yellow 40 (3.2; X = MeN^+, Y = NMe, Z = H). Whilst yellow (λ_{max} 434–452 nm; λ_{em} 493–505 nm) is the dominant shade area for coumarins of the generic structure (3.2; Z = H), it is possible to move bathochromically to bright orange dyes, λ_{max} around 520 nm, by introducing an electron-withdrawing substituent, such as the cyano group, into the 4-position, as in the commercial disperse dye (3.2; X = N, Y = S, Z = CN). Even more bathochromic products are formed by having the heteroaryl substituent co-planar with the rest of the molecule, achieved by linking through to the 2-position of the coumarin ring and thus extending the conjugation. For instance, CI Disperse Red 277, CI Solvent Red 196 (3.3, X = H, Y = CN, Z = O) and CI Disperse Red 374, CI Solvent Red 197 (3.3, X = H, Y = CN, Z = NH) are brilliant red dyes for polyester textiles and for the colouration of plastics. Moving the cyano group onto the coumarin, as in the isomeric compound (3.3, X = CN, Y = H, Z = NH), causes a further bathochromic shift, giving a greenish-blue (λ_{max} 639 nm) dye with a red fluorescence (λ_{em} 668 nm), but unfortunately of low fluorescence efficiency.



(3.1)



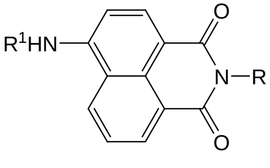
(3.2)



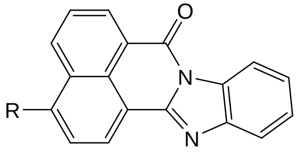
(3.3)

3.5.1.2 *Naphthalimides*

Electron donor groups in the 4-position of naphthalimides increase electron transfer to the electron-withdrawing carbonyl groups in the 1,8-positions, giving products that are strongly fluorescent. Commercially the most important products are based on *N*-substituted 4-aminonaphthalimides, as illustrated by CI Disperse Yellow 11 (3.4; R = 2,4-dimethylphenyl, R^1 = H) and CI Solvent Yellow 43 (3.4; R = R^1 = *n*-Bu). Substitution at the imide nitrogen of (3.4) has little influence on the wavelength of absorption but does have a significant effect on the emission maximum of the derived products. The introduction of a sulfonate group produces fluorescent acid dyes; quaternisation gives cationic dyes suitable for acrylic fibres (3.4; R = C_2H_4-*N*-pyridinium, R^1 = H) and a *m*-sulfatoethylsulfone group in (3.4; R = *p*-MeOphenyl, R^1 = H) produces reactive dyes for cellulosic substrates. The Lucifer Yellows CH and VS used as fluorescent molecular probes in bio-medical applications are in this group of compounds. A related fluorescent ring system, 1,8-naphthoylene-1,2′-benzimidazole, has been studied widely, and has led to the commercialisation of fluorescent yellow disperse dyes for polyester *e.g.* CI Solvent Yellow 187 (3.5; R = COPh).



(3.4)

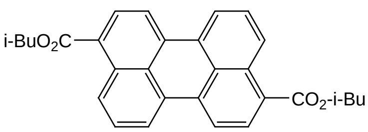


(3.5)

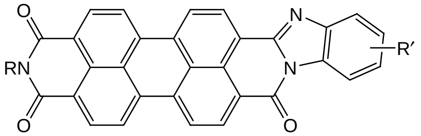
3.5.1.3 *Perylenes*

The pentacyclic aromatic compound perylene exhibits a strong fluorescence and has found application in laser dyes and organic light-emitting diodes

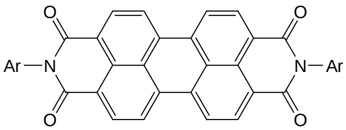
(Section 3.9.5). The di-, tri- and tetra-carboxylic acid esters of perylene are lightfast, yellow to red fluorescent chromophores, exemplified by the di-iso-butyl ester of the 3,9-dicarboxylic acid, CI Solvent Green (3.6). The diimides of perylene-3,4,9,10-tetracarboxylic acids (3.7) form a group of very important high-performance pigments (see Chapter 1, Section 1.10.3, and Chapter 2, Section 2.4.1.7) and these give intense orange and red fluorescent colours. They have very good environmental stability, are bright and have high fluorescence efficiency, some with quantum yields approaching unity (*e.g.* 3.7; Ar = 2,5-di-tert-butylphenyl). Water-soluble versions of these dyes can be made by putting substituents bearing sulfonate on the imide nitrogen. By analogy with naphthalimides, the mono- (3.8) and bis-benzimidazoles (3.9) are fluorescent, giving lightfast yellow and reddish-violet colours respectively.[44]



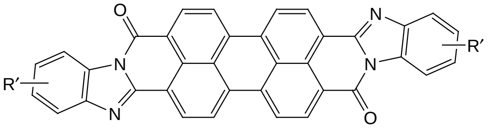
(3.6)



(3.8)



(3.7)

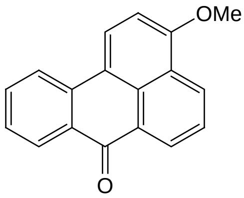


(3.9)

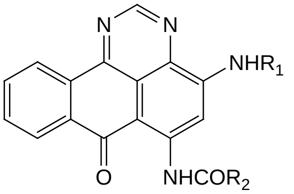
3.5.1.4 Benzanthrones, Anthraquinones, Benzoxanthones and Benzothioxanthones

These ring systems are extensively used in dyes and pigments and are easily fine-tuned by adding substituents following well-known synthetic pathways. Inevitably, as they are planar molecules with donor–acceptor capabilities, fluorescent materials have been developed for a variety of applications.

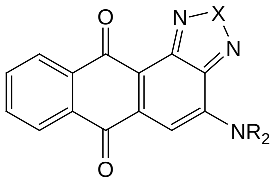
3-Methoxybenzanthrone (3.10) is a yellow-green fluorescent dye (CI Disperse Yellow 13), in both the solid state and in solution, but it has a low quantum efficiency of around 0.1. The heterocyclic analogue, pyrimidanthrone (3.11) gives yellow and red-orange pigments for use in plastics. Many common anthraquinone dyes, especially those with amino and alkoxy groups adjacent to the carbonyl group are very bright, due to a weak but useful fluorescence. To get a more intense fluorescence it is necessary to extend the conjugation beyond the parent ring system as in the anthraquinone diazole ring (3.12). These are red to violet with long wavelength luminescence, and are useful as daylight fluorescent pigments. Dyes derived from extended benzoxanthene and thioxanthene ring systems give extremely bright, lightfast fluorescent disperse dyes for polyester, such as both isomers of the yellowish-red CI Disperse Red 303 (3.13), and also as solvent dyes for plastics, *e.g.* CI Solvent Orange 63 (3.14).



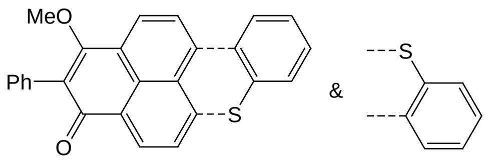
(3.10)



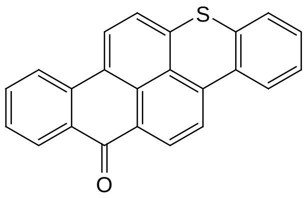
(3.11)



(3.12)



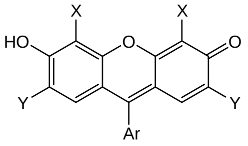
(3.13)



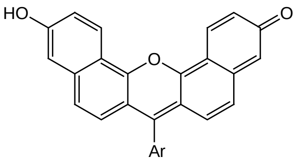
(3.14)

3.5.1.5 Xanthenes, Acridines and Oxazines

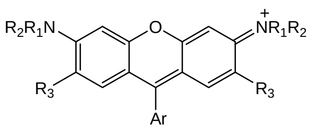
These classes of chemicals contain not only some of the oldest dyes, but also some of the most technologically important fluorophores. The earliest of these discoveries was the xanthene, fluorescein (3.15; X = Y = H, Ar = 2-carboxyphenyl), which was later brominated to give the polybromo derivative eosin (3.15; X = Y = Br, Ar = 2-carboxyphenyl). They are of little importance in textile coloration, but are used in some fluorescent pigments and extensively in analysis and in tracing the course of water in drains and other water outlets. More recently derivatives have become widely used biological and medical analysis tools. Fluorination (3.15; X = H, Y = F) improves the poor photostability of fluorescein, and ring fusion gives the strongly red-shifted naphthofluorescein (3.16; Ar = dicarboxyphenyl), which has a deep-red pH-dependent fluorescence (λ_{max} 598 nm; λ_{em} 668 nm at pH >9) and is used as a biological pH indicator.



(3.15)



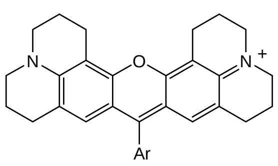
(3.16)



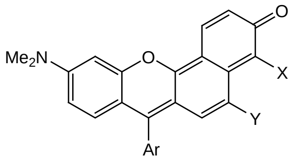
(3.17)

Equally important xanthenes are the delocalised cationic diamino derivatives known as rhodamines, exemplified by rhodamine B (CI Basic Violet 10; λ_{max}

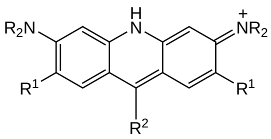
543 nm and λ_{em} 552 nm) (3.17; $R_1 = R_2 = Et$, $R_3 = H$), and rhodamine 6G (CI Basic Red 1; λ_{max} 530 nm and λ_{em} 557 nm) (3.17; $R_1 = Et$, $R_2 = H$, $R_3 = Me$). These are intensely fluorescent dyes with quantum yields close to unity. Rhodamine 6G especially has found wide application in daylight fluorescent pigments (see Section 3.5.5.2) and this ring structure has been much modified for use in many other outlets, especially as laser dyes (see Section 3.5.6.3) and in biological and medical applications (see Section 3.5.9). For example, the rigid ring-condensed rhodamines (*e.g.* 3.18) have higher fluorescence yields and are red-shifted. A cross between rhodamines and fluoresceins is the benzannulated system of (3.19; X,Y = H,F), another pH sensor with double emission.



(3.18)



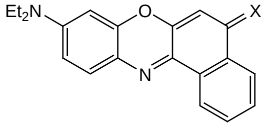
(3.19)



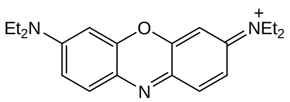
(3.20)

The nitrogen analogues of the rhodamines based on acridine (3.20) are strongly fluorescent but their low stability means they are only suitable for use as indicators in acid-base titrations and as fluorescent probes in some biological applications.

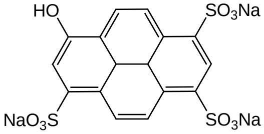
Derivatives of long-established fluorescent dyes based on the phenoxazine ring system, such as the cationic Nile Blue (3.21; $X = NH_2^+$, λ_{max} 627 nm), and the neutral Nile Red (3.21; $X = O$), and also the cationic dye CI Basic Blue 3 (3.22), have found new uses in bio-medical applications because of their NIR fluorescence (Chapter 4), as laser dyes (Section 3.5.6.3) and as dopants in organic light-emitting diodes (Section 3.9.6.4).



(3.21)



(3.22)



(3.23)

3.5.1.6 Hydrocarbons

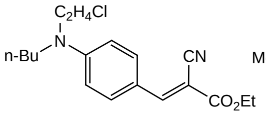
Although many hydrocarbons exhibit fluorescence, they are often colourless and the fluorescence is only just into the violet *e.g.* linear terphenyl and quaterphenyl. Polycyclic ring systems such as anthracene, terrylene and rubicene are used in analytical methods and OLEDs but a large number are ruled out of commercial use because of their potential to act as carcinogens. However, as mentioned in Section 3.5.1.3, perylene is a useful fluorophore in a variety of outlets and pyrene is another polycyclic compound of wider application. One derivative is a yellow-green fluorescent dye (3.23) used in textile applications (CI Solvent Green 7) and in analysis and sensors (see Sections 3.5.8 and 3.5.9).

3.5.1.7 Methines, Hemicyanines, Cyanines and Oxonols

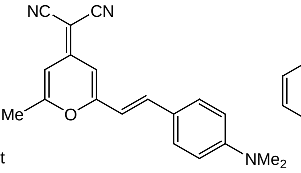
In recent years methine, hemicyanine and cyanine dyes have been the subject of much research as their high absorptions and quantum yields are coupled with a relative ease of molecular manipulation. Simple neutral methine yellow dyes of the dicyanovinyl or cyanoester type (styryl dyes) are exemplified by the bright greenish yellow, CI Disperse Yellow 31 (3.24) used in dyeing polyester. While amongst the brightest yellow dyes, they are readily hydrolysed under alkaline conditions and have been largely replaced by the azo pyridone yellow dyes for polyester dyeing (see Chapter 2, Section 2.3.1.1).

Methine as a class also contains the highly important biofluorophores present in Green Fluorescent Protein and its many analogues and spin-offs. The story of GFP and its applications in bio-analysis is so significant that we devote a separate section (Section 3.5.10) to its further consideration.

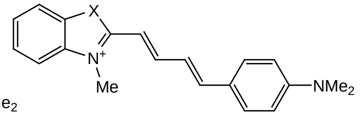
Extending methine conjugation to give polymethines or merocyanines causes a bathochromic shift to orange and orange-red shades. This can be achieved using a simple chain of alternating double bonds or as part of a ring, thus ensuring greater planarity and overlap of the π bonds, for example *via* a pyran ring in (3.25), which is orange-red in colour, emitting in the red and used as a laser dye.



(3.24)



(3.25)

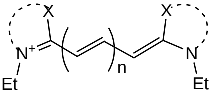


(3.26)

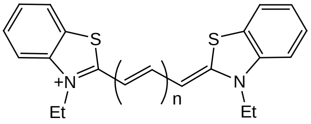
Hemicyanines are polymethines with a cationic centre at one end of the chain. Typically these can be pyridinium, indolenium (3.26; $X = CMe_2$) and benzothiazolium (3.26; $X = S$) derivatives. Their fluorescence ranges from the long-wavelength red region to the NIR, which is a very useful property for certain laser dye outlets and in fluorescence imaging in medicine and biology (Section 3.5.9).

Cyanine dyes are the class of methines where each of the nitrogen atoms is in a ring at opposite ends of the chain (3.27). They are used extensively as sensitisers in the photographic process (see Chapter 4, Section 4.5.3), but are also widely used in other outlets because of their fluorescent properties. All cyanines are subject to poor light and chemical stability, with the indocyanines (3.27; $X = CMe_2$) being the best. The chain length can be varied but is usually kept between $n = 0$ and $n = 5$. Every extra double bond shifts both the absorption and emission maxima around 100 nm towards the red, the extinction coefficients rising from 70,000 for $n = 0$, to 250,000 M^{-1} cm^{-1} for $n = 5$. For example, (3.28; n = 1) has λ_{max} 557 nm whilst (3.28; n = 3) has λ_{max} 760 nm, with Stokes shifts around 35–50 nm. The indocyanines and analogues, especially Indocyanine Green (ICG) absorbing and emitting in the NIR, have important applications in bio-medical imaging (Section 3.5.9).[45]

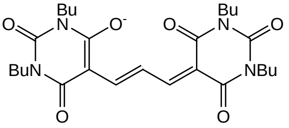
Oxonols may be regarded as anionic analogues of cyanines. They are typified by the barbiturate derivative (3.29), which absorbs at 493 nm and emits at 516 nm in methanol. Oxonols are used in cell membrane polarisation studies.



(3.27)



(3.28)



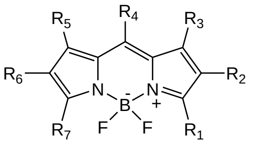
(3.29)

3.5.1.8 Dipyrromethines; Boraindacenes

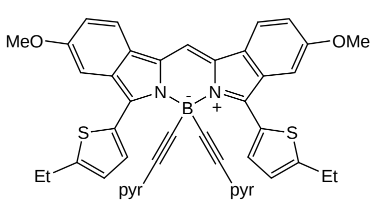
A notable new class of fluorophores are the boron derivatives of dipyrromethines, or boraindacenes (traded commercially under the name of Bodipy dyes).[46] The general structure of these fluorophores is shown in (3.30) and every position, including the two fluorine sites at boron, may be substituted independently by a range of groups. Furthermore, the chromophore can be extended by ring fusion, leading to a huge variation in structural possibilities. Absorption maxima range between 493 nm and 720 nm (3.31; pyr = pyrene), with the emission maxima between 10 and 30 nm red-shifted. The compounds are strong with extinction coefficients frequently greater than 50,000, reaching about 100,000 M ^{1}cm ^{1}, and can have high quantum efficiencies (>90%). Added to this, these fluorophores are relatively insensitive to changes in polarity or pH, they have a narrow emission profile and have improved photostability compared with fluorescein and its cognates.

Even these are improved by one of the newest modifications which comprise rigid aza-analogues typified by (3.32).[47] These are NIR fluorescers (ϕ typically up to 0.46) with remarkably high photostability. Where a standard indocyanine green dye loses about 75% of its fluorescence intensity over 60 min of white-light irradiation, aza-boraindacene dyes only lose about 2%.

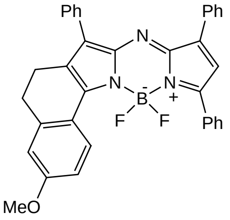
For these reasons, these dyes are being applied in an increasing number of technologies, and the rate of new literature describing their syntheses, properties and applications remains at a high level.[48]



(3.30)



(3.31)



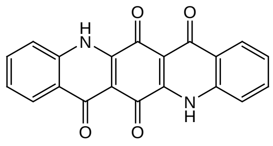
(3.32)

3.5.1.9 Miscellaneous Chromophores

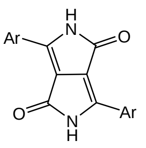
There are other chromophoric systems, some of which are very old compounds, but others that have only been invented in the last couple of decades, which exhibit useful fluorescence.[49] Notably these include the red thioindigo, CI Solvent Red 242; the bluish-red quinacridones (3.33); the bright-orange to red diketopyrrolopyrrole pigments (3.34); the very bright-orange to red benzodifuranone dyes (3.35); and the bright-red disperse dye (3.36). The chemistry of these and other dyes and pigments is discussed in greater detail in Chapter 2.

A promising class of dyes that absorb very strongly and fluoresce across the visible spectrum and into the NIR are the squaraines (*e.g.* 3.37, which can absorb up to 901 nm ($n=1$) with $\varepsilon_{max} > 250{,}000$),[50] as described in Chapter 4 (Section 4.2.1.2). However, they are prone to instability through attack by nucleophiles, and their ready aggregation (*cf.* Section 1.10.2) leads to fluorescence quenching. Encapsulation as a rotaxane improves chemical stability and hinders aggregation, increasing fluorescence.[51,52]

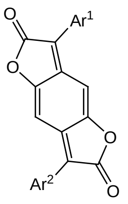
The benzobis(imidazolium) salts (3.38) are new chemically and thermally stable UV absorbers, offering modular synthesis and therefore structural flexibility, which fluoresce from the UV and into the visible up to about 550 nm, with quantum yields as high as 90%.[53]



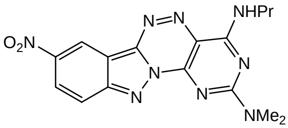
(3.33)



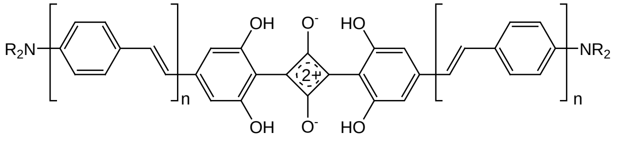
(3.34)



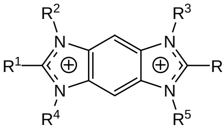
(3.35)



(3.36)



(3.37)



(3.38)

3.5.2 Luminescent Nanoparticles and Related Materials

In recent years, the impact of nanoscale materials on science and technology has been remarkable, and their luminescence properties contribute in no small measure to these developments. Their fields of application parallel those of conventional organic fluorophores, and for that reason we discuss them here. In general, the term "nanoparticle" is applied to particles with diameters ranging from 1 to 100 nm. For convenience we also include fluorescent organic polymers, dendrimers and other nanoscale organic constructs in this section.

3.5.2.1 Semi-conductors Quantum Dots, Silicon and Carbon

Photoexcitation of a bulk semi-conductor (SC) results in promotion of an electron from the valence band to the conduction band, leaving a hole in the valence band. The energetics are dependent on the nature of the SC material, but not its size, until this is reduced so that its diameter is at the mean separation of the electron-hole pair (the Exciton Bohr radius). At this dimension and smaller, the absorption-emission energetics change and a new set of properties is introduced. The dimension at which this occurs is in the tens of nanometres or less, thus leading to "nanoparticles" (NPs) and their derived applications within the field of "nanotechnology". Because the new properties of SC NPs are defined by quantum mechanical concepts,[54] not pursued here, the iconic name of "quantum dot" (QD) has been introduced for the nm-scale, zero-dimensional SC particle.[55] (Quantum wires and quantum wells, the higher dimensioned analogues, are not considered here.)

The main feature of interest to us is the absorption, and particularly emission characteristics of QDs. As they decrease in size below the Bohr radius characteristic of the SC material, the excitation energy increases above the band-gap energy, and the emission energy correspondingly undergoes a blue shift. For SC NPs, the absorption properties are of less interest, whereas the emission characteristics are of paramount importance. Thus for CdSe, an archetypal visibly luminescent QD, a full spectrum of luminescent colours is generated as the size of the QD decreases from about 8 nm for red, through the visible spectrum to 2 nm blue, corresponding to between 50 and 10 atoms across the QD diameter. QDs of other materials can be used for other spectral ranges (*e.g.* PbS for NIR luminescence[56]). By coating a core QD with a thin shell of another SC material with a wider band-gap, optical properties are further refined. For example, in comparison with a simple CdSe QD, a CdSe-ZnS core-shell QD shows a slight red-shift in emission peak, and importantly an increase in luminescence quantum yield up to about 50%. The shell can reduce or remove toxicity if there is a concern that toxic Cd is leaching from the unprotected QD. Because of potential toxicity, and in response to legislative pressures, development of heavy-metal-free QDs is a current commercial goal. Although ranges of QDs are readily available commercially in sub-gram quantities (at appreciable cost), a further goal on the near horizon is economical manufacture at the kg scale.[57]

In comparison with typical fluorescent dyes QDs have the following properties:

- The emission peak shape of QDs is narrower so they appear brighter, and therefore smaller amounts are required.
- Because their absorption band is much broader there is more flexibility in excitation wavelength, so the effective gap between excitation and

emission wavelengths is much higher (*cf.* limited Stokes shifts of fluorescent dyes).
- The photostability of QDs is far better than that of most organic fluorophores.
- The properties of QDs can be tailored by means of surface chemistry: it is possible to attach ligands by means of co-ordination to QD surface metal atoms; potential ligands include phosphine oxide, phosphine, phosphonic acid, carboxylic acid, thiol, amine, nitrile and others.
- Indeed, such ligands control the stability, especially toward aggregation, and solubility of the QD, so that QD soluble in both lipophilic and aqueous environments are available.
- This surface co-ordination ability opens the door to attachment of designer ligands, including many bio-active species, which lead to the many applications and uses of QDs.
- The nature of the surface ligands also influences emission, particularly quantum yield.

QDs are finding application in many spheres where conventional fluorophores have traditionally been used. A restriction is that their size (about that of a protein molecule) can inhibit the application where a smaller dye molecule might be unrestricted.

QD applications mirror those of other luminescent species, including displays and lighting; various aspects of life science analysis, diagnosis and monitoring; securities and forensics; lasers; and others. These will be explored further below.

Silicon is the archetypical bulk SC material of major use in electronics applications. However, both amorphous and nanocrystalline Si can fluoresce, sometimes with very high quantum yields. For example, in a silicon nitride matrix, fluorescence from the NIR to about 400 nm is shown by crystalline Si QD (6 nm down to 2.5 nm), while isolated Si QD gave a 30% quantum yield at 420 nm from 1–2 nm crystals.[58] Fabrication of 2-nm Si QDs into spheroidal polyacrylic acid matrices of diameters from about 60 to about 210 nm gives composite Si NPs, which have excellent water-dispersability, strong photoluminescence and robust photostability.[59] Figure 3.10 shows cell-staining properties of these NPs in comparison with the conventional fluorescein stain, and compares the differences in stability under 488 nm argon laser irradiation. Even more notable is their increased photostability toward 450 W xenon lamp irradiation compared with CdTe and core-double shell CdTe/CdS/ZnS SC QDs. The comparative plots in d) of Figure 3.10 show that the II–VI SC QDs are not photostable, although as expected they are more stable than fluorescein. An alternative approach to stable water-dispersible Si QDs is to oxidise the outer surface of 3-nm H-terminated Si QD particles, to generate a shell coating of SiO_xH_y.[60] Depending on the degree of surface oxidation, the resultant core Si QD diameter can be attenuated, resulting in particles which emit over a full range of visible colours, with luminescence band FWHM about 60 nm. These have so far been applied as photodegradation catalysts (see Chapter 4, Section 4.7).

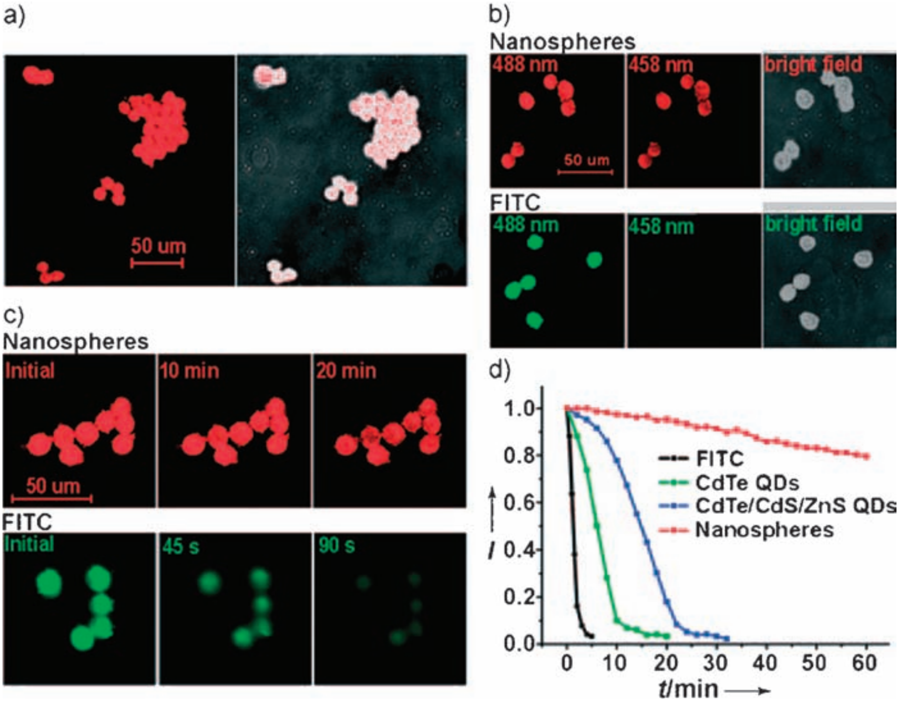


Figure 3.10 (a) Fluorescence microscopy images of HEK293T cells labelled with Si nanospheres excited at 488 nm (left) and superposition of fluorescence and transillumination images (right). (b) Comparison of fluorescent signals of HEK293T cells imaging with Si nanospheres (top) and fluorescein (bottom) excited at different wavelengths. (c) Temporal evolution of fluorescence of the HEK293T cells labelled with the Si nanospheres (top) and FITC (bottom), both excited at 488 nm. (d) Photostability comparison of fluorescent II/VI QDs (CdTe QDs and CdTe/CdS/ZnS core shell shell QDs) and the as prepared nanospheres. All of the samples were continuously irradiated by a 450 W xenon lamp[59] (reproduced with permission of Wiley VCH).

The ability of carbon to form tubes comprising rolled up sheets of fused hexagonal "benzenoid" rings (graphene) can generate three basic patterns of single-walled carbon nanotubes (SWCNTs) (Figure 3.11). One of these has metallic properties, while the other two are SCs.[61] Only the latter fluoresce, in the NIR near 1000 nm, a wavelength that, as already mentioned above, and will be explained further below (Section 3.5.9.1), is ideal for use in whole-body bio-applications. Furthermore, SWCNTs have exceptionally high photostability. Longer nanotubes display significantly enhanced absorption and NIR fluorescence.[62] Surface functionalisation widens the scope of their possible uses.[63] For example attaching a DNA single strand gives a material whose NIR fluorescence wavelength undergoes a characteristic blue-shift after hybridisation with an exactly complementary single strand of DNA, of obvious bio-analytical significance.

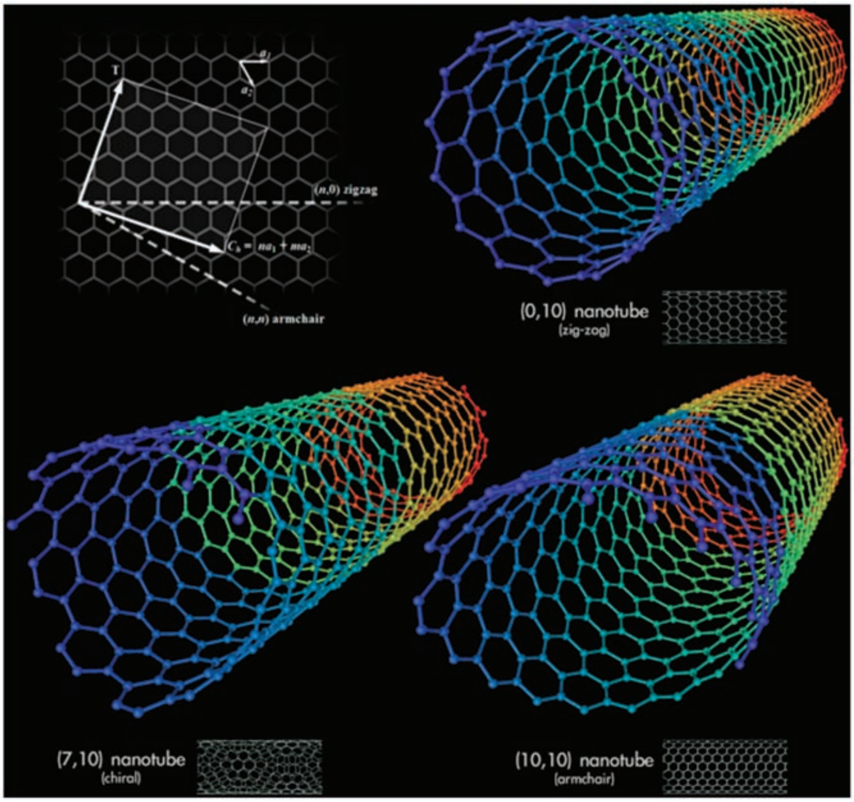


Figure 3.11 The three variants of single walled carbon nanotubes (graphics by Michael Strück; downloaded from Wikipedia May 2009, under the terms of the GNU Free Documentation License).

Less well known are ''carbon dots'' comprising nm-scale particles of amorphous carbon. When their surfaces are passivated by various treatments, those with a diameter of a few nm become bright and colourful emitters in the visible to NIR. Quantum confinement is probably influencing the emission properties, as larger particles (30–50 nm diameter) are far less bright.[64,65] They are being studied for bio-imaging, and for detection and treatment of breast cancers.

The toxicity of SC nanoparticles is discussed in a recent review, which provides plenty of lead references.[66]

3.5.2.2 Organic Systems Conjugated Polymers, Dendrimers and Silica Encapsulated Dyes

Although not conventionally regarded as nanomaterials, where the particle size influences the optical properties in a fundamental way, some organic materials are nevertheless nm scale, and for convenience we consider them here.

Fully conjugated polymers (CPs) are also semi-conductors, and their photo-absorbance and emission properties can be described by band-gap theory. A huge variety of CPs has been synthesised and described; many are coloured and exhibit fluorescence. They are also capable of reduction and oxidation by various means, including electrically, and luminescence can result (technically important electroluminescent polymers are described in Section 3.9.7). The basic conjugated polymer construct comprises a combination of simple unsaturated linkages (alkene, alkyne) and/or aromatic ring systems, and sometimes conjugating heteroatoms. The aromatic units include phenylene, and various aromatic heterocycles such as pyridyl and especially thiophene and its derivatives.[67,68] Substitution of the main-chain CP is built in to give solubility, to inhibit aggregation, to modulate the basic electronic properties of the CP and to provide host binding sites for guest analytes. In fact, development of CPs as sensors by means of colour changes and especially fluorescence modification is a major application. The same sort of application could in principle be equally well based on smaller monomeric units of the same structure. However, a major advantage of CPs is their ability to amplify a sensor response. This derives from the fact that a photo-excited electron–hole pair in the CP (an exciton) is delocalised across the CP, and can migrate from an innocuous site to another at which an analyte is exerting an influence. Amplification of about 100 relative to a monomeric model is typical.[69] Example CPs are shown in Figure 3.12, alongside their main analytes. All are detected by the degree to which they quench the CP fluorescence. Others that are electroluminescent appear in Figures 5.50 and 5.51.

Two or more chromophores in proximity but electrically insulated from one another are sometimes able to transfer energy from one that is photo-excited to another in its ground state, whereupon the newly excited chromophore fluoresces. Through-space energy transfer and dipole–dipole interaction are the two

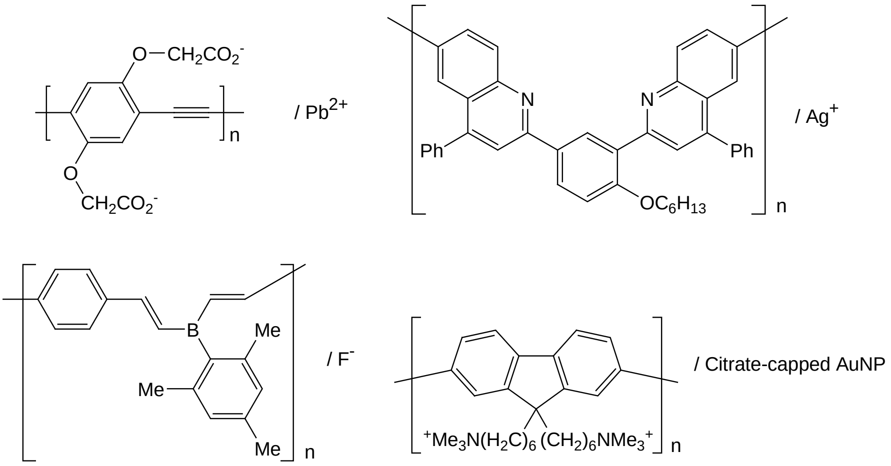


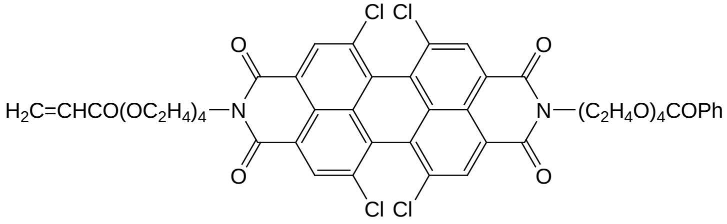
Figure 3.12 Example conducting polymers, and their target analytes.

mechanisms that are followed.[41,70] Förster (sometimes "fluorescence") resonance energy transfer (FRET) is the name for transfer of energy from an excited higher-energy fluorophore (the donor) to a lower-energy fluorophore (the acceptor) by dipole–dipole coupling over distances up to about 10 nm. The Dexter mechanism involves energy transfer between two chromophores by an overlap mechanism, and as such is operative over shorter distances (*ca.* 2 nm). The dendrimer design principle has been adapted to building in composites of chromophores absorbing higher-energy light, and transferring it to a lower-energy emitter, which can be an organic fluorophore or a metal ion.[71] The emitter can be covalently bound into the dendrimer, or be non-covalently hosted within the interstices of the dendrimer. Either way, very efficient luminescence is observed, and the design principle provides a good approach to light harvesting (Chapter 4, Section 4.8.2.1). Other dendrimers which are through- and cross-conjugated organics are the dendrimeric cousins of the fully fledged conjugated polymers just discussed. These are fluorescent, especially in response to an electric potential, and are being applied in light-emitting devices discussed later in this chapter under electroluminescence (Section 3.9.8).[72,73]

Hybrid organic–inorganic nanoparticles have been constructed based on a core of reactively bound conventional fluorescent dye molecules, encapsulated in a silica shell.[74] These particles, of nm-scale radius, have been named "C dots" (not to be confused with the "carbon dots" of Section 3.6.2.1).[75] The shell matrix provides mechanical and chemical stabilisation of the fluorophore, while providing a readily functionalised outer surface. Moreover, the emission properties of the core dye are sometimes markedly enhanced. For example, a particle based on a core of tetramethyl rhodamine isothiocyanate (*cf.* structure (3.17)) is an order of magnitude more stable to photobleaching than the free dye. Its brightness in water is one to two orders of magnitude higher than the dye core itself in the absence of silica encapsulation, and only a factor of 2–3 less bright than SC QDs. The dye chromophores in the core emit independently of one another, so these dots do not suffer the intermittent fluorescence ("stochastic blinking") of QDs. The principle has been applied to a range of different fluorophores, and it has been found that the quantum yield of non-optimised fluorophores can be doubled in the composite dots.

The design principle can be extended in various directions, including building in, or on, further layers of different shells, such as metals. Alternatively, inclusion of a second fluorophore gives dual emitter particles. The first core dye (*e.g.* rhodamine, red) emits at a constant level irrespective of external analyte and acts as an internal reference. The luminescence of the second dye (*e.g.* fluorescein, green) nearer the silica surface, responds to and therefore acts as a sensor for external analytes. The ratio of the two emissions from the same material provides a sensitive and reliable response. Cell pH can be measured in this way because of fluorescein's pH sensitivity.

An alternative approach to improving the properties of conventional fluorophores is to copolymerise them under emulsion polymerisation conditions into functional NPs. The non-aggregating twisted perylene acrylate fluorophore (3.39) has been incorporated into NPs <50 nm in diameter, with resultant high fluorescence quantum yield (*ca.* 0.9) and high photostability.[76]



(3.39)

3.5.2.3 Metals and Metal Ions

Bulk metals are non-luminescent (ϕ *ca.* 10 ^{10} for Au and Cu films). Metal nanoparticles (Chapter 1, Section 1.12.1) share this property, down to at least 15 nm diameter. However, AuNPs below about 2 nm start to show interesting levels of fluorescence; 5-atom Au clusters encapsulated in dendrimers give an impressive 70% luminescence yield in the UV, while larger AuNPs – Au_{12} is about 0.8 nm – emit through the visible up to NIR (10% yield for 31-atom AuNPs).[58] This behaviour is a typical of MNPs, and is probably best regarded as emission from excited states of large metal molecules. The fluorescence is affected by surface coatings, which are in any case necessary to stabilise the otherwise reactive and aggregating NP.

The larger non-fluorescing metallic NPs quench conventional fluorophore emission when the fluorophore is in close proximity (<5 nm).[77] But of much more interest and use, at higher separations between 5 and 200 nm, fluorophore emission is actually enhanced because of coupling between the fluorophore and the intense field effect from the metallic NP's localised surface plasmon resonance (LSPR). The result is enhancement of both absorption cross-section and radiative decay rate. The latter impacts on photostability and enhanced wavelength-tuneable emission. Fluorophore–plasmon interaction is one of the newest photonic phenomena and is still at the stage of discovery and development. Exploitation is in its infancy, but it is already said "the combination of fluorescence and plasmonics will result in a paradigm shift for both technologies".[77] The following possibilities have been suggested: (1) ultrabright probes; (2) ability to measure bio-molecular distances in the inaccessible 10 to 200 nm range; (3) metallic structures that selectively enhance excitation or emission without causing background emission; (4) new diagnosis devices; (5) new sub-wavelength microscopy with 30-nm resolution.

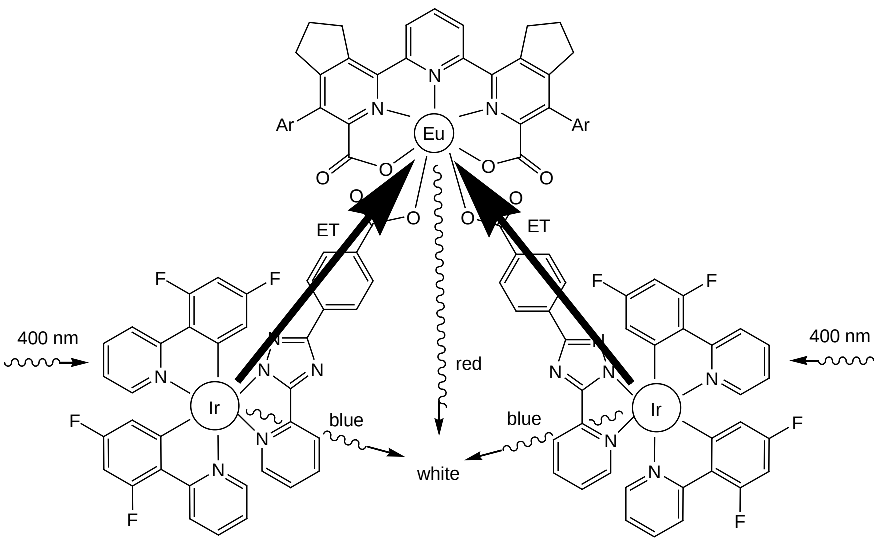
While not an emission phenomenon, it is worth recalling the strong tendency of MNPs above a certain size to scatter impinging light. Up to about 40 nm diameter, spherical AuNPs scatter less than 5% exciting energy, while absorbing the majority. By 80 nm, about 40% is scattered, with larger NPs scattering proportionately more. Thus, in a dark field microscope, it is easily possible to observe coloured light scattered by a single NP. We repeat an observation already noted in Section 1.12.1.1: scattering of blue light of wavelength 445 nm by an 80 nm AuNP is 10^6 times more efficient than the luminescence produced by a single fluorescein molecule. This sensitivity should be borne in mind when comparing sensor and probe technologies.

Luminescence by metal ions, as opposed to metal particles, has already been encountered in the guise of inorganic phosphors (Section 3.2.1). Metal ion dopants in concert with inorganic matrices are responsible for variously coloured light emission following electronic excitation from a variety of sources. The rare earth ions in particular are of increasing interest in various phosphor types. At the time we referred to phosphor luminescence, rather than fluorescence. In fact in formal terms RE ions can both fluoresce and phosphoresce, in some cases both from the same ion, depending on the multiplicities of the excited electronic level from which the emission proceeds and the resultant electronic level after decay. It was also noted that NP versions of the phosphors are becoming of interest, particularly those emitting in the NIR suited for medical and telecommunication applications. A recent straightforward and cheap synthesis of $Y_2O_3{:}Er^{3+}$ NPs (uniformly 200 nm or less) is therefore relevant.[78] This has absorption and emission properties essentially the same as the bulk material (Section 3.2.1.3), luminescing at about 1.5 μm with a lifetime of the order of milliseconds (*cf.* organic fluorophores, with lifetimes around nanoseconds), is photostable and non-toxic, and can be chemically functionalised in various ways. However, RE-doped phosphor NPs do not always retain the properties of the bulk. For example, micron-size particles of the afterglow material $SrAl_2O_4{:}Eu^{2+},Dy^{3+}$ luminesce at 520 nm with an afterglow of 10–15 h. The emission from the same material at nanoparticle scale (20 nm) is blue-shifted to 511 nm, and the afterglow is reduced to about 100 min.[79]

At a further level of sophistication, more functionality can be engineered. NPs of the up-converting phosphor $NaYF_4{:}Yb,Er(Tm)$ have been combined with a magnetic NP in a silica shell to give a 60-nm composite. This has desirable optical properties for bio-imaging, and can be manoeuvred by magnetic fields.[80] A weakness of RE UCs is that the available range of their emission wavelengths is restricted. This limitation has been overcome by coating the surface of the UC NPs with SC QDs, whose own emission properties can of course be flexibly tailored by control of their size. Thus, the UC material $NaYF_4{:}Yb,Er$, emitting normally at 552 nm after excitation at 952 nm, can be engineered to emit at 577, 593, 611 and 631 nm by means of yellow-, orange-, dark orange- and red-emitting CdSe/CdS/ZnS core-shell QDs, respectively. Just a few monolayers of QD on the UC surface are sufficient to ensure high yield of radiative energy transfer, and high emission efficiency.[81]

Not surprisingly, metal ion luminescence is also being exploited in discrete molecular entities. (We continue not to distinguish fluorescence and phosphorescence in this context.) RE ions in the +3 oxidation state are of special interest, with examples luminescing from the UV, through the visible, and into the NIR.[8] Their absorbance is due to electronic reorganisation within the 4f electron shell. Selection rules formally prohibit these transitions, and so the molar extinction coefficients of the core ions are very low, about 1–10 M ^{1} cm ^{1}, compared with 10^4–10^5 for typical fluorescent dyes. Efficient energy absorption, as a precursor to luminescence, thus has to be effected indirectly, and chemistry to achieve indirect excitation is a key development. For example, chromophoric ligands coordinated to the RE ion may absorb energy themselves. This can then be transferred to the RE ion, as a precursor to emission as the RE ion decays to its ground state. The ligand-to-metal energy transfer frequently follows one of the Dexter and Förster mechanisms already mentioned above. Charge-transfer energy transfer from ligand to metal is also possible if the LMCT state is at a high enough energy. This process is analogous to what happens in RE-doped inorganic phosphors. Besides this it is necessary to minimise non-radiative decay pathways, while giving the overall RE-ligand complex thermodynamic and kinetic stability. The molecular design challenge is therefore non-trivial, but has been overcome in a very wide range of usually multi-dentate ligands and their derived RE complexes.[8]

As an alternative to organic ligands as a vehicle for energy transfer into the RE ion, other better-absorbing metallic ions from the d-block elements have been built into RE-based molecular structures. Their higher absorbance followed by energy transfer to the RE ion can again lead to efficient RE luminescence. Ruthenium (II) can excite Gd^{3+} and Yb^{3+} *via* Ru to ligand, and then ligand to RE energy transfer, followed by NIR luminescence by the RE ion. A further example is shown in (3.40). Here the two iridium centres transfer energy in concert to the Eu^{3+} ion after excitation at 400 nm. The Eu ion emits red light at 615 nm, while residual energy on the Ir centres is emitted as broad blue light, so that the overall emission is white.



(3.40)

A major developing use of luminescent RE compounds is as analytical optical probes, especially in the bio-medical field. For this, the luminescence has to be modulated in some way by the target analyte.

- The analyte could displace a ligand from the coordination sphere of the RE, with a resultant change in luminescence (positive or negative).
- It could coordinate to a ligand already attached to the RE, modulating the energy transfer from that ligand to RE and thus the latter's luminescence.
- Or it could coordinate to a ligand and if it itself were a chromophore, it could act as the primary photon absorber and then transfer energy directly into the RE.

Metal ions and pH are prime sensor targets. In the bio-medical field RE-based probes may be used for immunoassays and detection of hybridisation, and in imaging.

The millisecond lifetimes of excited RE ions opens up the possibility of time-resolved spectroscopy. A fast high-energy laser pulse excites the sensor RE ion, as well as any background chromophores in the sample (Figure 3.13). The latter's fluorescence decays rapidly in fractions of a ms; meanwhile the RE ion remains in its photoexcited state. After the background fluorescence has fully died away, the slower emission from the RE can be monitored free of any photocontamination, with an improved signal-to-noise ratio compared with, say, conventional fluorescent dye probes.[8]

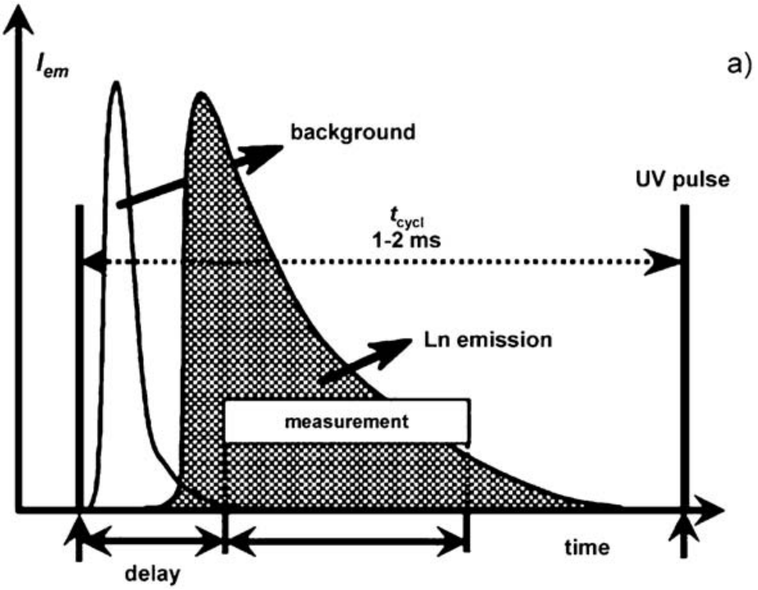


Figure 3.13 Time scales of background fluorescence and luminescence from a rare earth.[8]

Luminescence by the d-block transition metals is a massive topic. The authors of a broad overview of fluorescent species said[82] "we cannot hope to do justice where entire books on inorganic photochemistry struggle to cope with the diversity of phenomena thrown up by the various metal complexes". Nor can we. Of course, the use of Cu and Mn as dopants in inorganic phosphors has already been encountered in Section 3.2.1. We shall meet species based on other metals in Chapter 4 when we discuss dye-sensitised photovoltaic cells. Later in this chapter sensor (Section 3.5.8.1), electrochemiluminescent (Section 3.8.1) and electroluminescent (throughout Section 3.9) properties and applications are described for various transition metals.

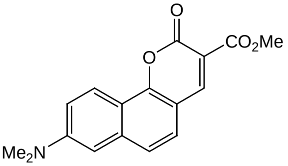
3.5.3 Multi-photon Absorbers

In the earlier section on inorganic phosphors, we saw that there are up-conversion mechanisms whereby more than one photon of energy can be absorbed by the phosphor, leading to emission of just one higher-energy photon. All the discussion so far in this section on fluorescence (more generally, luminescence) has concerned the emission of one photon of light energy per one photon absorbed. However, many organic dyes can also absorb more than one photon before fluorescence. Dye-like molecules have been designed and synthesised that are particularly efficient, and these are known as multi-photon absorbers (MPAs).[83,84,85]

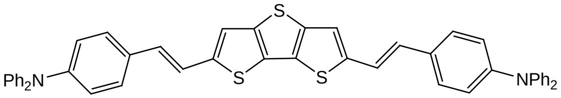
Two-photon absorption (2PA) is most common. The mechanism for 2PA is depicted by process (c) in the energy diagram of Figure 3.2 where two photons are absorbed essentially simultaneously, passing through no intermediate energy state, to reach the first excited state of the 2PA molecule. To ensure any reasonable probability of this occurring, the input energy flux must be very high, and this is achievable only by laser radiation. Resultant fluorescence is similar to that demonstrated following a one-photon excitation, so in one sense 2PAs (and MPAs in general) can be regarded as just another way of injecting energy into a molecule. However, there are significant differences which impact on the ultimate applications of 2PAs. For example, the exciting wavelength is far removed from the fluorescence wavelength, unlike the one-photon case in dyes where the separation is close to the Stokes shift. This separation of excitation and emission wavelength can have useful consequences. Also, the energising source, at about half the energy of a one-photon source (less for higher order processes), can be a commonly available and cheap NIR-emitting diode laser, rather than a visible laser. Furthermore, the emission from the 2PA is not linear with respect to the excitation power, but rather follows a quadratic relationship (at least, under ideal conditions[83]), again with consequences for applications. (Thus 2PAs are nonlinear optical materials, and are encountered again in Chapter 5, Section 5.6.) The efficiency of 2PAs (and MPAs) does not parallel the efficiency of one-photon absorption (*i.e.* the molar extinction coefficient, $\varepsilon_{\max}$); instead it is measured by the 2PA cross-section (σ_2 measured in units of GM where $1\,\mathrm{GM} = 10\ ^{50}\,\mathrm{cm}^4\,\mathrm{s}$). Higher MPA processes have their own absorbance cross-sections.

Many conventional dyes demonstrate 2PA. However, molecules beyond dyes have been developed to optimise their 2PA cross-sections, for which the following design principles have been elucidated. There is a strong correlation between intramolecular charge transfer (CT) and σ_2, and a series of planar one-dimensional materials patterned as D-π-D, A-π-A and D-π-A have shown useful 2PA activity (D is an electron donor unit, A is an electron acceptor and π is a π-conjugating pathway). Increasing the number of conjugation pathways to give 2- and 3-dimensional configurations, and increasing the amount of branching, improves σ_2 further. Beyond the organic chromophores based on these guidelines, other molecular types including coordination and organometallic structures including porphyrins and related structures and fullerenes can also have appreciable 2PA cross-sections. He *et al.*'s comprehensive review[83] lists over 300 species alongside their measured σ_2 and other spectroscopic properties. Figure 3.14 reproduces just a few of those with high reported σ_2 to give a flavour of their general structure types, and to show that 2PA molecules are not dissimilar either to conventional dyes or fluorophores, or to the units comprising some luminescent conjugated organic polymers.

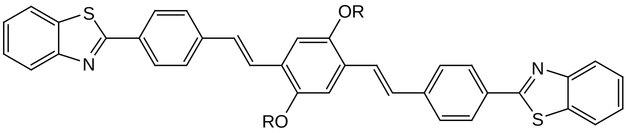
2PA chromophores can be built into dendrimers with resultant brightness comparable to SC QDs, and have been termed "organic nanodots".[86] They are



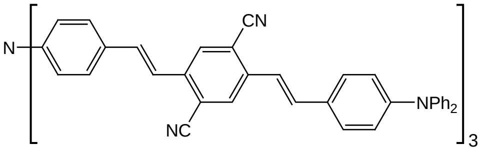
(3.41) D-π-A



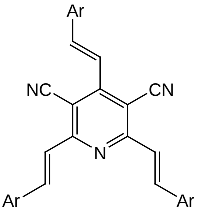
(3.42) D-π-A-π-D



(3.43) A-π-D-π-A; R = alkyl



(3.44) (D-π-A-π)$_3$D octupole



(3.45) (D–π)$_3$A octupole

Figure 3.14 Example 2PA molecules, showing different donor acceptor arrangements.

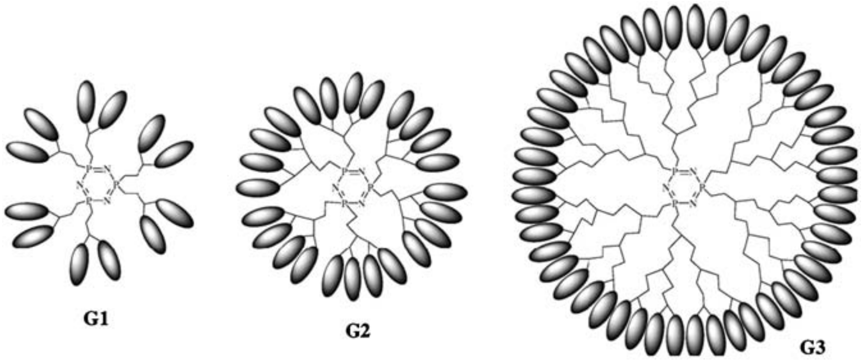


Figure 3.15 Example dendrimer structures used with 2PA chromophores to make "organic nanodots".[86]

free of heavy metal toxicity problems, and unlike SC QDs do not blink under continuous irradiation. Figure 3.15 gives a diagrammatic representation of three generations of spheroidal 2PA-decorated dendrimers based on hexachlorotriphosphazene. Analogous "dumbbell" dendrimers were also studied.

Applications of 2PA include microfabrication, photodynamic therapy (covered in Chapter 4), optical data storage, optical power limiting and frequency up-conversion lasing (Chapter 5), and bio-imaging. It is because of this latter use that we introduce 2PA materials at this stage: they will be discussed alongside the other classes of dyes and materials currently being exploited in bio-medical applications in Section 3.5.9.7 of this chapter.

3.5.4 Summary of Fluorescent and Comparable Luminescent Materials

This completes the survey of the molecular and comparable "small" material types that emit light in response to a photo-exciting source. To an extent they have similar properties, especially their unifying ability to emit light after absorbing light of another wavelength. In other ways they are significantly different. It is these similarities and differences that give them such a wide range of application possibilities, as will be described in the following sections. But first an overview summary of their key properties is given in Table 3.7. The classification in this Table differs somewhat from that used so far in the discussions through Sections 3.5.1 to 3.5.3.

Other systems yet to be introduced in this chapter, giving rise to chemi-, bio- and electrochemiluminescence, have been omitted. Nevertheless, species from these classes may be applied as alternatives to the systems listed in Table 3.7 in a wide range of applications. The scattering properties of metal nanoparticles (as opposed to their luminescence) (Chapter 1) also means they have imaging uses in parallel with lumophores.

The way in which the science and technology of fluorescent and related species has developed in recent years can be estimated by considering how the topic was discussed in the first edition of this book (2001). At that time, "fluorescence" was restricted to organic dyes (fluorophores), with some reference to metal-ion based species. We now see how semi-conductor and other nanoparticulate species are coming to the fore. The most recent (2009) advances are exploiting the myriad possibilities conferred by combinations of molecules and materials in composites and hybrid species. Although some remarkable properties have already been reported and mentioned in the preceding sections, we can look forward to yet more progress in material design and development from this direction.

The following general points refer to the data in Table 3.7.

- Values of some of the properties are subjective, and could only be estimated from studies conducted under very different conditions. Most questionable estimates are given in parentheses ( ).
- Quantitative properties can span very wide ranges, so these are only represented qualitatively: + + + represents "high" values and + "low"; + + is somewhere between.
- "Stokes shift" should be taken as the potential difference between excitation and emission energies. For example, to achieve luminescence of semi-conductor nanoparticles, excitation can be anywhere in the valence band, at much higher energy than the formal band edge.
- Probably the least certain data shown concerns photostability. This depends significantly on local environment within the material and on substrate, amongst other factors, and very few studies have been undertaken under uniformly comparable conditions. One exceptional but limited example was highlighted above (Figure 3.10),[59] but it is clear that there is a need for such a study. Until then, claims and counter-claims for improved photostability of one system with respect to another are made with little benefit to the observer.
- It was tempting to include toxicity data, but since this is even more non-standard it was decided its value would be minimal. The toxicity of heavy-metal-based SC NPs is clearly an issue, and various studies are claiming significance because they overcome this potential problem.
- Commercial availability is what we are aware of early in 2009; new materials are appearing all the time.
- The application labels are C = coloration; S = sensor or probe; L = laser; E = electroluminescence; 4 = one or more of the application areas discussed in Chapter 4; and 5 = an application topic to be covered in Chapter 5.

We now turn our attention to a more detailed consideration of the diverse technologies of these species.

Table 3.7 Properties of luminescent systems (see text for explanation of terms and abbreviations).

	Luminescent system	*Structural variety*	*Excitation range*	*Molar absorbance*	*Emission range*	*Stokes shift*	*Particle size*	*Excitation lifetime*	*Photo stability*	*Commercial availability*	*Applications*
	Organic chromophores										
1	Dyes (fluorophores)	+ + +	UV/vis-NIR	+ +	UV/vis-NIR	+	1–10 nm	ns	+	✓	C,S,L,4,5
2	Dendrimers	+ + +	UV/vis-NIR	+ +	UV/vis-NIR	+	> 10 nm	ns	+		S,E,4
3	Conjugated polymers	+ +	UV/vis-NIR	+ +	UV/vis-NIR	+	> 10 nm	ns	+	(✓)	S,E
4	MPA	+ + +	vis-NIR	(+ +)	vis	+ + +	> 1 nm	ns	+	(✓)	S,4,5
	Semi-conductors										
5	QD	+ +	UV/vis-NIR	+ + +	UV/vis-NIR	+ + +	1–10 nm	10 ns-μs	+ +	✓	S,L,E
6	Si QD	+	UV/vis		vis	+ + +	1–6 nm		+ + +		S
7	Carbon SWNT	+	UV/vis-NIR		NIR	+ + +	nm × ≤ mm		+ + +	✓	S
8	Carbon dots	+	UV/vis		vis-NIR	+ + +	nm		+ + +		S

	Metals & ions										
9	Metal NP (luminescing)	+	UV/vis	+ + +			1–2 nm		+ + +	✓	S,4
10	RE phosphor NP	+ +	UV/vis-NIR	+ +	UV/vis-NIR		20–200 nm	ms	(+ + +)	✓	S,D,E
11	RE UC NP	+ +	NIR	+ +	vis	+ + +	60 nm	ms	(+ + +)	✓	S,D,E
12	RE molecular complex	+ + +	UV/vis-NIR	+	UV/vis-NIR	+ +	1–10 nm	ms	+	✓	S
13	TM molecular complex	+ + +	UV/vis-NIR	+ +	UV/vis-NIR	+ +	1–10 nm	ns-μs	+	✓	S,4
	Composites & hybrids										
14	C dot (dye in silica)	+ + +	UV/vis	+ +	vis-NIR		15 nm–15 μm		+ +		S
15	MNP + dye	+ + +	UV/vis-NIR	+ + +	vis-NIR		> 10 nm		(+)		S
16	Si NP (Si QD in PAA)	+	UV/vis		vis	+ + +	> 60 nm		+ + +		S
17	RE phosphor + SC QD	+ +	UV/vis-NIR		vis-NIR	+ + +			+ +		S

3.5.5 Applications as Fluorescent Dyes, Pigments and Brighteners

Fluorescent colours, especially daylight fluorescent pigments, have become increasingly important as there has been a move towards a society devoted to spending an increasing amount of time on outdoor leisure activities coupled with a greater awareness of the need for safety and security.

3.5.5.1 Fluorescent Dyes in Textile Applications

Fluorescent dyes are used to impart unusual brightness of shade to a textile substrate. The base colour is defined by the *absorption* of the dye, with emitted light originating from ambient excitation, perhaps by the UV component of daylight, adding to its brightness. The main use of fluorescent dyes is in the coloration of synthetic fibres for fashion, leisure and especially sportswear uses. Fluorescent textiles offer not only high design options but also a large degree of safety in use, for instance increasing the visibility of cyclists and runners in busy urban areas.

Very bright fluorescent cationic dyes are used on acrylic fibres, but the largest use is on polyester and many dyestuff companies have disperse dye ranges for this purpose, some of which are also applied to polyamide fibres. Important colours are yellow, through orange, red, pink to violet, with coumarin, methine and perylene dominating the structural classes. "Fluorescent" blue colours comprise very bright absorbers usually in the turquoise shade area, from anthraquinone, methine or indoaniline fluorophores.

3.5.5.2 Daylight Fluorescent Pigments

One of the largest markets for fluorescent colorants is as daylight fluorescent pigments. These have the property of fluorescing when activated by visible light at the blue end of the spectrum, and comprise two components, a fluorophore and a range of special polymers. The dyes are chosen from the classes already described in Section 3.5.1. A typical set would include coumarin and xanthenes (for yellows) and rhodamines (for red and violet). To obtain blues and greens it is common to use copper phthalocyanine and its polyhalogeno derivatives as toners.

The choice of polymer depends on the end application, as it plays a very important role in the fluorescence properties of the pigments. It is responsible for the colour development and also for most of the physical properties such as softening point and solvent resistance of the derived pigments. The polymers must be good dye solvents, be grindable, have the desired softening point and have a high decomposition point. The pigments are made by bulk polymerisation in the presence of the dye, followed by grinding to the desired particle size. Fluorescent ink-concentrates are made by preparing the pigments *in situ* in an alkyd resin, using emulsion polymerisation to give spherical, sub-micron sized particles.[87] The polymers can be categorised as formaldehyde-containing and formaldehyde-free, and as thermoset or thermoplastic resins.

As noted earlier, fluorophores suffer from poor photostability including when in pigment formulations. The excited state molecules have sufficiently long lifetimes to undergo photochemistry leading to chromophore degradation and loss of colour. For example, various oxidation and reduction processes are opened up *via* the hole (partially occupied HOMO) and excited electron (partially occupied LUMO), respectively, as well as energy transfer to O_2 from the triplet state with generation of highly reactive singlet oxygen. In order to improve the light fastness it is usual to add a UV absorber (*e.g.* based on benzotriazole, benzophenone or triazine) either to the pigment formulation or as a clear topcoat on fluorescent films.

The application areas for daylight fluorescent pigments are wide and varied. They are used in printing inks for all the main application areas. Coating applications include the coloration of paper, rubber, textiles and vinyl fabrics, and in solvent- and water-based paints. In plastics they can be extruded or moulded or used in film. Further details can be obtained from the trade literature or websites of such companies as Day-Glo and Sun Chemical Corp (USA) and Sterling Industrial Colours (UK).[88]

Safety uses are very wide and new examples appear regularly. For instance American Tire has IPR relating to the production of urethane ‘‘flat free’’ tyres, including bicycle tyres that are also available in a fluorescent yellow that can be seen at night by headlights from a distance of about 60 m.

3.5.5.3 Fluorescent Brightening Agents

FBAs, also known as optical brighteners and fluorescent whitening agents, are strongly fluorescent substances that absorb in the ultraviolet region between 340 and 380 nm, and emit in the blue-violet area of the spectrum between 425 and 450 nm. On a white substrate, for instance paper or a textile fabric, the FBA increases the apparent white light reflection and the article appears to be whiter than the untreated material.[89] In daylight and from certain orientations, a purple sheen can be observed on FBA-treated paper. The detergent industry is a major purveyor of FBAs in domestic washing powders. Most of the UV-absorbing fluorophores[42,43] find application in FBAs, especially the ubiquitous 4,4′-diaminostilbene-2,2′-disulfonate.

3.5.5.4 Other Coloration Applications

Solvent-soluble fluorescent dyes and pigments are used in a multitude of applications where lipophilic solubility is required as part of the application process. These include their use in the coloration of plastics, in solvent-based inks for the printing of packaging, for marking petroleum fractions, in waxes and polishes, in the detection of flaws in metals, glass, ceramics and plastics and in the characterisation of polymers.

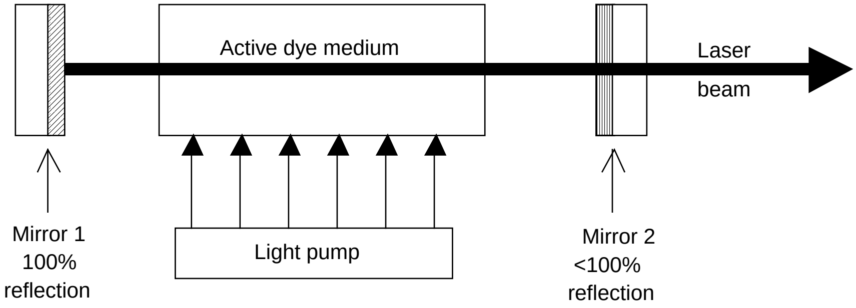


Figure 3.16 Schematic of dye laser[92] (reproduced with permission of Verlag Helvetica Chimica Acta).

3.5.6 Dye Lasers

The significant advances in solid-state and semi-conducting lasers has meant they have gradually displaced dye lasers from their previous pre-eminence. Nevertheless, the latter retain use in various niche areas, where their tunability to otherwise inaccessible wavelengths remains of use. This section addresses the types of dye lasers, the mechanism of lasing as applied to dyes, structural types of laser dyes and a few of their applications.[90,91,92]

3.5.6.1 Types of Dye Lasers

Both continuous wave (CW) and pulsed dye lasers are available. In CW dye lasers, an input beam from another CW source, an ion laser such as Ar, provides excitation or optical pumping. The beam is focused onto a stream of dye in a solvent, causing an extremely high level of fluorescence. This fluorescence is then focused between two highly reflective mirrors that reflect back the emitted light, thus initiating the lasing process.[90] A simple schematic of the process is shown in Figure 3.16.[92] Changing the angle of a diffraction grating placed at the end of the cavity enables wavelength selection and tuning.

The two most common types of pulsed lasers used in dye lasers are the neodymium:yttrium-aluminium-garnet laser (Nd:YAG) and excimer lasers. The performance of pulsed dye lasers is wavelength dependent. The Nd:YAG provides useful pump wavelengths at 266, 355 and 532 nm (fourth, third and second harmonics respectively), which can be matched to the absorption bands of a variety of dyes. Excimer lasers (inert gas halide lasers) cover a wide range of laser wavelengths, from 193 nm (ArF) to 351 nm (XeCl).

3.5.6.2 Mechanism of Dye Lasers

Dyes have the important role in dye lasers of allowing a fixed wavelength laser input to be tuned to a wide range from which a selection can be made appropriate to the end use. The first step involves raising the molecule from its ground state S_0 to an excited state S_1. To act as a laser dye, the population of the molecule in S_1 must reach a higher level than in S_0 *i.e.* it must undergo population inversion, and then be capable of releasing energy by a radiative process back to the ground state. In other words the dye must be an efficient fluorescer. Since the population of the excited S_1 state is increased by optical pumping with the powerful input laser, the dye must be able to absorb energy at the output wavelength of this laser. After pumping, a non-equilibrium population is obtained and further irradiation with a flash equal in energy to the difference between S_0 and S_1 gives rise to the stimulated emission.

3.5.6.3 Laser Dyes

The general requirements for dyes to be suitable for use in dye lasers are:

- strong absorption at the excitation wavelength;
- minimal absorption at the lasing wavelength *i.e.* minimal overlap between absorption and emission spectra;
- high quantum yield (0.3–1.0);
- short fluorescence lifetime (5–10 ns);
- low absorption in the first excited state at the pumping and lasing wavelengths;
- low probability of intersystem crossing to the triplet state;
- good photochemical stability.

Organic dyes in lasers offer certain advantages over inorganic materials. A wide range of dyes are available that provide stimulated emission (lasing) over a broad range of the spectrum. Furthermore, organic dyes can be tuned to emit over a range of wavelengths. Detrimental effects due to any tendency toward intersystem crossing from S_1 to the long-lived and therefore unwanted triplet state T_1 can be minimised by inclusion of a triplet quencher such as cycloheptatriene or cyclooctatetraene. Dye lasers can operate from around 250 to 1285 nm and the individual dye components fine tuned to operate within a range of 30–50 nm. The spectra and other properties of many laser dye classes may be found in the Lambdachrome catalogue.[43] However, the relative instability of most organic fluorophores toward intense light remains a major weakness.

The stability and tunability between about 650 and 1100 nm of the solid-state titanium-sapphire laser, for example, removes the previous benefits of the dye laser in bio-medical applications. Furthermore, the inconvenience (and hazards for the untrained user) in handling solutions of dyes and the complexity of the attendant optical set-up are distinct negatives when compared with the convenience of modern semi-conductor solid-state lasers. Solid-state *dye* lasers would address this particular drawback, and the first experimental CW solid-state dye laser system has recently been described.[93]

3.5.7 Analytical Applications of Fluorescence Sensors and Probes

Optically based sensors, sensing and probes comprise a massive and vibrant area of analytical chemistry and materials science (as well as associated physics, electronics, biology, medicine and information processing). Google Scholar is currently revealing about 4000 citations annually for the search term "optical sensor". Many of these are devoted to non-chemical aspects, but still a great many of the remainder concern our main interest here – the application and study of fluorescent and luminescent molecules and materials in analysis. On top of the volume of published information, the topic is further convoluted by two other factors. First, there is sometimes a lack of care in how the term "sensor" is applied to the various chemical analysis systems under study. And secondly, there is a rather unfortunate trend amongst chemical publications: "Chemical sensors have achieved a rather dubious distinction. They often serve as the default mode for a material or procedure that 'did not quite work out' for its original purpose or to justify results for which there is no obvious 'other use'. The phrase ' . . . and it can also be used for chemical sensing' is typical and unfortunately much too common in the chemical literature." Thus wrote the guest editor in his Introduction to a 2008 edition of *Chemical Reviews*, devoted to Modern Topics in Chemical Sensing.[94]

Regular specialist reviews and books record and evaluate and generally make sense of progress in this area, although few of even these lay claim to being comprehensive in their coverage. For our part we shall attempt in the following sections to give only a flavour of how fluorescence is being used in some of the forefront analytical science and technology of the early 21st century. Of course, Chapter 1 has already addressed aspects of chemical analysis based on colour change, including that based on localised surface plasmon resonance. Analytical technology reliant on other important chemical approaches, such as electrochemistry, does not belong in this book.

Various definitions of chemical sensors and probes have been proposed. In this book we apply "sensor" to a self-contained device based on a platform which acquires, manipulates and reports information continuously and – usually – reversibly. This is to distinguish it from the far more general "sensing system", "analytical assay" or "indicator" which acquires information in discrete steps, may well not be reversible, can adopt any physical format and may report its result simply in terms of "on" or "off", akin to an optical switch. The active fluorescent material in the latter is termed an "optical probe" or "indicator".

3.5.7.1 Fluorophore and Analyte Interaction

The interaction between analyte and fluorescent (luminescent) sensor or probe, leading to observable change in energy emission, can be caused by various mechanisms. The cartoons in Figure 3.17 show important examples.[82,95]

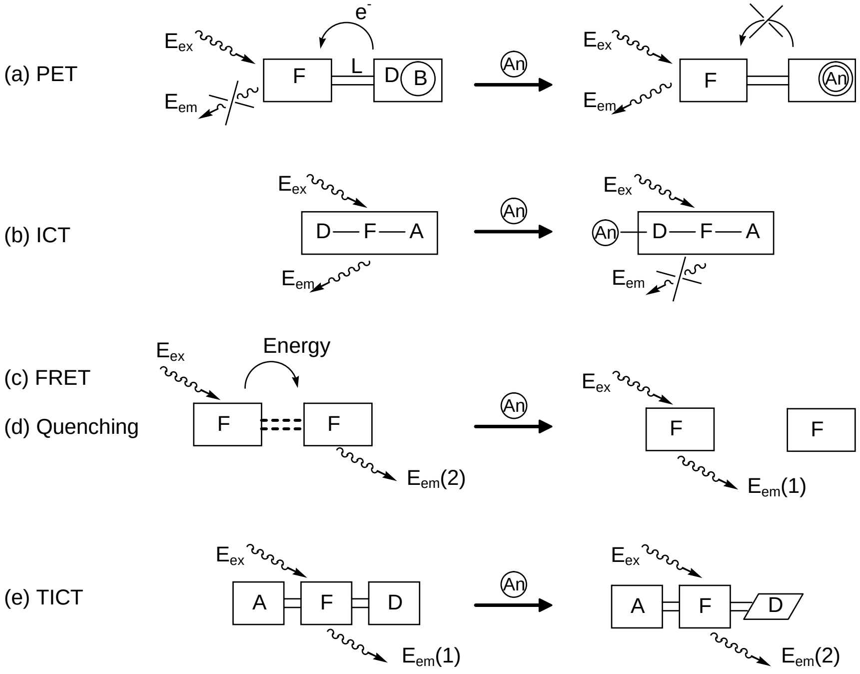


Figure 3.17 Cartoons showing mechanisms of fluorescence modulation by analyte. F fluorophore, D donor, L linker, B binding site, An analyte, E_{ex} excitation energy, E_{em} emission energy. See text for discussion.

(a) *Photoinduced electron transfer (PET)* – a nearby but non-conjugated electron donor transfers an electron to an excited fluorophore, quenching fluorescence. If the electron donation is prevented by coordination of an analyte species, fluorescence is switched on.

(b) *Internal charge transfer (ICT)* – the active fluorophore comprises a π-conjugated donor–acceptor system. If an analyte coordinates directly with the donor, the electronics of the system are changed to the extent that fluorescence is no longer possible. A simple example would be a proton coordinating to a dialkylamino donor group.

(c) *Förster (or fluorescence) resonance energy transfer (FRET)* – if two fluorophores of differing energies are arranged close enough (they need not be bound together), excitation of the higher-energy fluorophore can lead to it transferring energy to the lower-energy fluorophore, and emission therefrom ($E_{em}(2)$). Then if an analyte causes separation of the two fluorophores, energy transfer is no longer possible, and emission results from the initially excited higher-energy fluorophore ($E_{em}(1)$).

(d) *Fluorescence quenching* – this can be viewed as a special case of FRET, where the second, lower–energy, "fluorophore" has an emission quantum yield of zero, resulting in quenching of the fluorescence ($E_{em}(2) = 0$).

When the analyte separates fluorophore from quencher, fluorescence is switched on.

(e) *Twisted intramolecular charge transfer states (TICT)* – some donor–acceptor fluorophores can adopt an excited state geometry, with the originally coplanar donor group twisted out of plane. Emission from the twisted state differs from the fully planar excited state. If an analyte changes the population of the TICT state, modulation of fluorescence may be visible.

(f) *Excimer and exciplex systems* (not shown in Figure 3.15) – photoexcited dimers or bimolecular complexes of fluorophores emit with different energies and intensities compared with monomers. If an analyte changes the concentration of dimer/complex, the fluorescence energy or intensity is correspondingly altered.

Examples of some of these mechanisms in action will be encountered amongst the sensors and probes now introduced.

3.5.8 Fluorescence in Optical Sensors

The basic chemical characteristic of a fluorescent fibre-optic sensor is a fluorescent molecule or material which changes its properties measurably, continuously and reversibly, related to the concentration of the analyte of interest. The sensor element is immobilised in a more or less sophisticated optical device, which enables the measurement, manipulates and interprets the data and gives a read out of the property being measured. A theoretical treatment has suggested there are 10^{21} dimensions to the conceivable variables which could comprise a sensor, a high proportion of which derives from the flexibility of the chemistry underpinning the sensor elements.[96] Thus many basic designs are possible,[97] the simplest of which based on a fibre-optic construction is summarised in Figure 3.18. Key attractions of fibre-optic sensors are their

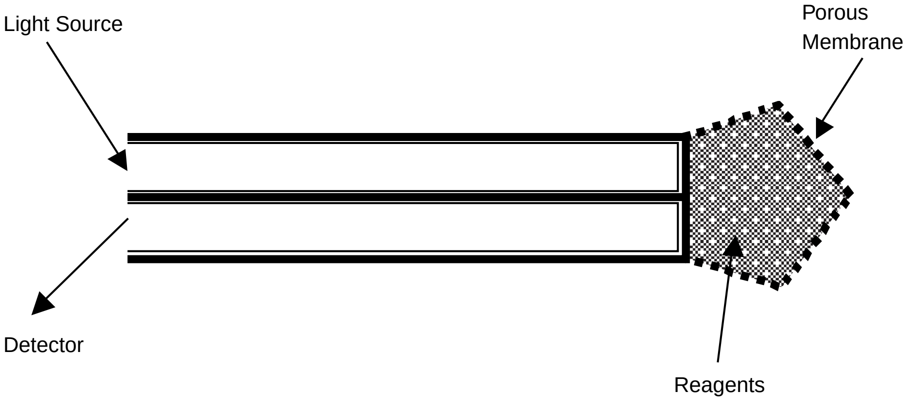


Figure 3.18 Fibre optic based, reagent mediated sensor.

flexibility, ability to operate over a long distance, in hostile environments, without any need for electric power, with multiplexing capability and requiring no hands-on maintenance. Commercialised technology is available from various suppliers,[98] and the uses (and abuses) of such systems have been reviewed.[99]

Attenuation of fluorescence leading to analyte quantification can depend on different measurable responses. The most obvious is a change in fluorescence intensity caused by the analyte. However, this method is compromised by any tendency of the fluorescent dye to undergo photodecomposition, or for it to be leached during use or storage, or for any drift in the device opto-electronics. A more reliable approach is to measure the ratio of the intensities at two fixed emission wavelengths in response to the effect of an analyte. Here the absolute concentration of the sensor fluorophore is unimportant. An alternative which is also independent of sensor concentration and device instability is measurement of fluorescence lifetime as it is modulated by an analyte. All of these are being used in practice.

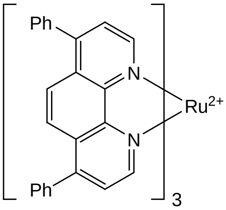
In addition to the fluorescent molecule itself, also of critical importance is the support material in which it resides. This aspect has been overlooked in the past, but is now being recognised as crucial to sensor design and construction.[100]

Biosensors, discussed in a later section, have a biological component in their sensor construction. On the other hand, optical chemical sensors, sometimes referred to as "optodes" or "optrodes" by analogy with "electrode", are characterised by purely chemical sensor elements and these are discussed in the next sections. They may be used to analyse for various species in any environment, biological or otherwise.

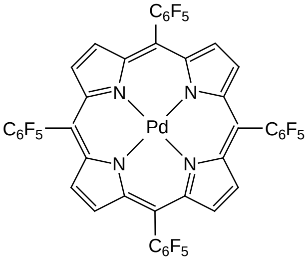
3.5.8.1 Optical Chemical Sensors for Medical Application

A major application of optical chemical sensors is in support of critical care procedures by analysing a patient rapidly and reliably for important bio-analytes, especially in blood. These include the partial pressures of the main biological gases O_2 and CO_2, pH, key metal ions and anions, and some other important metabolites. They are currently used almost exclusively for *in vitro* analyses.

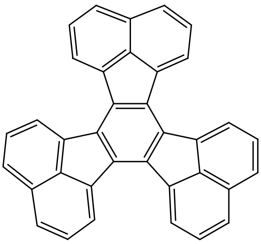
Oxygen – the commonest sensing mechanism for the partial pressure of oxygen, pO_2, is the quenching of fluorescence of transition metal complexes. The fluorescence lifetimes of phenanthroline complexes of Ru (II) (3.46; lifetime 1–5 μs), Pd and Pt porphyrins, fluorinated to improve their photostability (*e.g.* 3.47; 0.1–50 ms), and the hydrocarbon decacyclene (3.48) are all considered practical sensor materials, modified by lipophilic substitution to give them solubility in the preferred silicone substrates.[100] (The related – but different – technique of oximetry directly measures the ratio of oxygenated to deoxygenated blood by ratiometric transmission (through a finger or earlobe) or reflectance (at the forehead) *absorption* measurements at the two wavelengths 650 nm for haemoglobin, and 805 or 905 nm for oxyhaemoglobin.[101])



(3.46)



(3.47)



(3.48)

Carbon dioxide and pH – blood pH is commonly measured by optical sensors based on either of the standard fluorophores 1-hydroxypyrene-3,6,8-trisulfonate (3.23) or fluorescein and its derivatives (3.15), such as the octadecyl ester of chlorofluorescein. Both have ionisable phenolic OH groups with pK_a values in the physiological range, suited for H^+ concentration, and can be used ratiometrically. A novel luminescent pH sensor uses rhodamine B isothiocyanate bound into hydrophilic silica nanoparticles, with a pH range from 5.0 to 10.0.[102]

Dissolved CO_2 is also measured by its effect on pH, for example by means of the equilibrium

$$CO_2 + H_2O + HCO_3 \leftrightarrows 2HCO_3 \; + H^+$$

where the same pH sensor fluorophores may be used to detect the protons liberated in a bicarbonate buffer solution suspended in a hydrophobic polymer with a gas-permeable PTFE layer to exclude external protons. The hydroxypyrene is particularly suited with a pK_a of 7.3, close to that of carbonic acid/carbonate (7.0). It absorbs at 455 nm with fluorescence maximum 512 nm in its deprotonated state. Most CO_2 sensors are sensitive to temperature, and also in some cases to changes in osmotic pressure, so the ideal optical CO_2 sensor is yet to be invented. This is particularly important, given the wide range of environments besides clinical application where knowledge of CO_2 concentration is necessary (for example, environmental monitoring; brewing and biotechnology; food especially concerning modified atmosphere packaging – see Section 3.5.11.1).

Metal ions – various techniques are available for the clinically important cations Na^+, K^+ and Ca^{2+}.[100] The commercial OPTI CCA critical care analyser[103] measures these cations by three variants of the same naphthalimide fluorophore, differing in the ionophores used to bind the target cations (Figure 3.19).[104,105,106] In the absence of a bound cation, fluorescence is quenched by intramolecular photoinduced electron transfer (PET) from the tertiary aniline nitrogen atom to the fluorophore.[107] However, this effect is modulated by coordination of one of the cations, specific to each ionophore, so

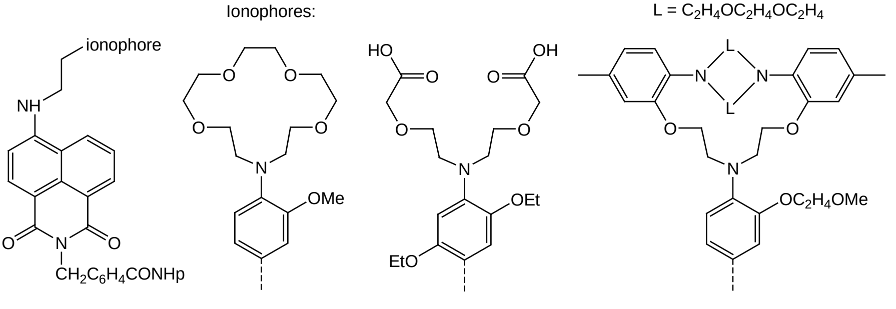
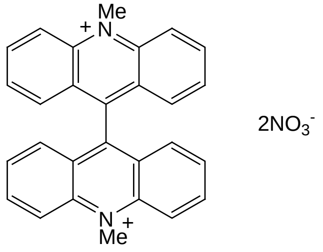


Figure 3.19 Fluoroionophores for blood electrolytes. Left: fluorophore, p polymer support. Ionophores left to right targeted for: Na^+, K^+, Ca^{2+}.

that the degree of switched-on fluorescence quantifies the concentration of that particular cation. In each case, the fluorophore is bound covalently into a polymeric support, attached in turn to the optical fibre of the sensor.

Anions – chloride is the major extracellular anion of clinical importance. It can be quantified through its effect on the fluorescence lifetime of the bisacridinium dye lucigenin (3.49).[108] The previously mentioned commercial OPTI CCA sensor measures Cl in blood by the attenuation of fluorescence of "a proprietary acridinium dye".[103]



(3.49)

Commercialisation of continuous in vivo optical chemical sensors – the many developments of optical sensor science and derived technology has led to successfully marketed products. Sales of the chemistry cassettes that underpin the OPTI sensors are estimated to have reached US$ 50 million by early 2008.[95] Despite this example, commercialisation has not been as successful as once anticipated and predicted. For example, in the late twentieth century, *in vivo* critical care continuous optical sensors for blood gases were considered to have commercial potential of more than $100 m *p.a.* Following R&D investment estimated to be in excess of $250 m, three continuous intra-arterial blood gas monitor systems were commercialised for clinical use. The first was launched in 1993 and discontinued in 1994; a second was commercially available from 1994 to 2002; and a third also appeared in 1994 but was withdrawn the following year. In 2009 there is believed to be just one commercial continuous pO_2 *in vivo* monitoring system on the market, not approved for clinical use, but applied mainly for laboratory animal research.[109] The story of the combination of events which led to this disappointment is complex and an education for those who believe good science inevitably leads to commercial success.[110]

3.5.8.2 Optical Biosensors

Biosensors differ from chemical sensors by their inclusion of a bio-recognition element in the sensor unit. This could be an enzyme, antibody, oligonucleotide or even whole cell or tissue. We recommend the review by Borisov and Wolfbeis for discussions of many aspects of biosensors which go way beyond what we now briefly describe.[111]

Enzymatic optical biosensors – the enzyme is responsible for recognition of the analyte, reacting with it in some way to generate an optical signal directly (*e.g*. bioluminescent system; Section 3.7), or to liberate a simple molecule or ion which acts as the transducer. These in turn are recognised by sensor elements which respond quantitatively by modulation of absorption (colour change; see Chapter 1), chemiluminescence (Section 3.6) or luminescence. Table 3.8 lists the

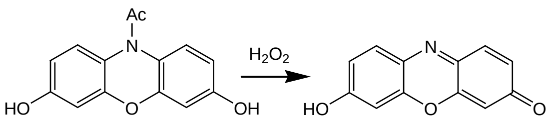
Table 3.8 Example enzymic optical biosensors based on fluorescent indicators (see footnote for abbreviations)[111] (reproduced with permission of the American Chemical Society).

Analyte	*Enzyme*	*Transducer*	*Range*	*LOD*	*Indicators*
acetylcholine	acetylcholine esterase	pH	0 20 μM		SNARF
ethanol	alcohol oxidase (AOx)	O_2	50 500 mM	10 mM	Ru bipy
methanol	AOx + HPOx	O_2	80 μM 60 mM	80 μM	Ru dpp
cholesterol	cholesterol esterase	O_2	0.2 3 mM	0.2 mM	decacyclene
glucose	glucose oxidase (GOx)	O_2			decacyclene, Ru complexes, PtOEP
glucose	glucose oxidase	pH			HPTS, rhodamine
glucose	GOx + HPOx	H_2O_2			Amplex Red, EuTc
glutamate	glutamate oxidase	NH_3	1 12 μM	0.1 μM	carboxyfluorescein
lactate	lactate oxidase	O_2	0.02 0.5 mM		decacyclene
ORP	OPH	pH			carboxy SNARF
penicillin	penicillinase	pH			fluoresceins
phenol	tyrosinase	O_2	0.08 40 mM	0.08 mM	Ru dpp
sulfite	sulfite oxidase	O_2	0 100 ppm		perylene
urea	urease	pH			FITC, SNARF
urea	urease	NH_3			HPTS, Nile Blue, octadecyl DCF
uric acid	uricase + HPOx	H_2O_2	3 30 mM	0.9 mM	thiamine

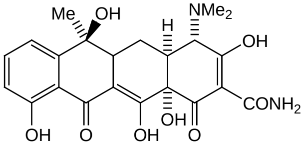
Abbreviations: LOD: limit of detection; ORP: organophosphorus pesticides; HPOx: horseradish peroxidase; OPH: organophosphate hydrolase; SNARF: seminaphthorhodafluor, see Structure (3.19); PtOEP: platinum octaethylporphyrin; HPTS: 3 hydroxypyrenetrisulfonate; see Structure (3.23); EuTc: europium tetracycline complex, see text; FITC: fluorescein isothiocyanate; DCF: dichlorofluorescein.

properties of some fluorophore-based enzymatic biosensors. It includes analytes that are metabolites of clinical importance, as well as some common chemicals found in the environment and various industrial situations. Sensors based on those enzymes that lead to pH change or O_2 as transducers rely on the same sensor fluorophores as purely chemical-based systems described in the previous section. The extended seminaphthorhodafluor (SNARF; 3.19 above) is additionally cited for optical pH measurement, where its double emission maxima at about 480 and 650 nm offer the opportunity for intramolecular ratiometric luminescence intensity spectroscopy. Additionally ammonia resulting from glutamate and urea influences the pH of its aqueous solvent, and can be quantified by optical measurement of pH. One further transducer encountered here is hydrogen peroxide.

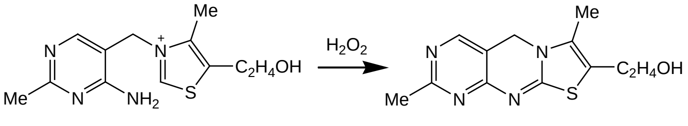
Glucose and hydrogen peroxide in biosensors – many optical sensors have been devised for the key metabolite, glucose. In some of these O_2 or pH are the transducers, but alternatively peroxide can be generated by peroxidase in the presence of glucose oxidase, opening up other luminescence sensor schemes. Colorless Amplex Red (3.50) reacts quantitatively with H_2O_2 to generate the fluorescent resorufin (3.51), quantified by luminescence intensity. Less conventionally, the strong increase in the luminescence of the tetracycline (3.52) 1:1 complex of the rare earth Eu^{3+} ion induced by H_2O_2 forms the basis of a novel luminescence lifetime biosensor for glucose.[112] H_2O_2 is also the transducer for the uricase/peroxidase catalysed biosensing of uric acid. In this case, thiochrome (3.53; λ_{ex} 375 nm, λ_{em} 440 nm) is the novel fluorescent product from peroxide reaction with non-fluorescent thiamine.[113]



(3.50) Amplex Red (3.51) Resorufin



(3.52) tetracycline



Thiamine (vitamin B_1) (3.53) thiochrome

Immunosensors – immunosensors are based on the high affinity of antibodies for their corresponding antigens. A full discussion is well beyond the scope of this book, but the key luminescence phenomena can be introduced by considering one of several recognition formats devised for optical immunosensors (more correctly immunoassays).[112] Figure 3.20 represents the main features of a sandwich type immunosensor. Antibodies specific to a target analyte are immobilised on a solid optical device. A non-immobilised batch of the same

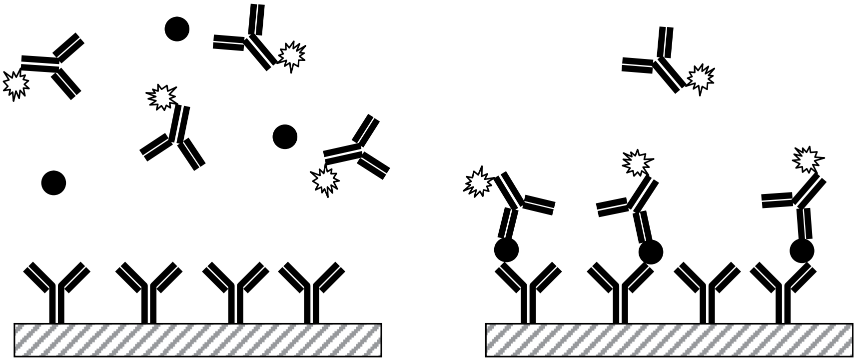


Figure 3.20 Diagram of a sandwich type immunosensor.

antibody is labelled with a fluorophore. In the presence of the analytical sample, any of the target antigen binds to the immobilised antibody, and as long as the antigen has more than one binding site (epitope), further fluorescent antibody also binds to sandwich it. After washing to remove any unbound fluorophore, the device is used to detect and quantify the bound fluorophore, which by virtue of the immobilisation mechanism corresponds exactly to the quantity of analyte antigen present.

This type of sensor has been developed for analysis of many types of protein, bacteria, virus and target foreign molecules such as drugs, explosives, agrochemicals, aqueous pollutants, and so on. The source of fluorescence is our main interest here. Amongst 47 different examples listed in Table 3 of reference 111, the great majority use standard fluorescein, rhodamine and cyanine (mainly Cy5 and Cy5,5) fluorophores for optical quantification of the antigen. Just one example is based on a semi-conductor QD sensor, where luminescence from a core-shell CdSe/ZnS QD labelling an immobilised protein A probe is modulated by fluorescence resonance energy quenching from the target immunoglobulin G (IgG) protein.[114]

Biosensors based on immunosensing and set up for simultaneous multi-analyte detection of (bio)chemical warfare agents and many other analytes have been commercialised (*e.g.* the RAPTOR and BioHawk systems from Research International).[115]

Nucleic acid biosensors – here, the key element is an immobilised single strand nucleic acid (or DNA) on a solid support of an optical device.[111] It relies on the recognition of one ssDNA for a complementary ssDNA, and is attractive because of the inherent stability of nucleic acids. Various detection formats have been devised for this purpose[111,116] but we restrict discussion of this biosensor variant to that dependent on the molecular beacon principle (Figure 3.21). The sensor is composed of a single strand of DNA, functionalised near one end by a fluorophore and the other by a quencher and attached by one end to the solid optical sensor (optical fibre or waveguide). This ssDNA is designed to adopt a stem-and-loop conformation, in which

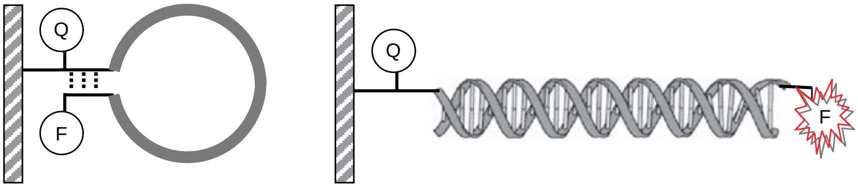
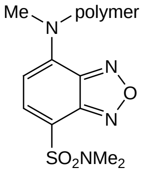


Figure 3.21 A nucleic acid biosensor based on the molecular beacon principle. Left: a single strand of sensor DNA in the loop and stem format, attached by one end to a solid optical support, its ends tagged by a fluorophore, F, and a quencher, Q. Right: the sensor DNA hybridised with the analyte DNA, resulting in an extended duplex, and the fluorophore separated from the quencher and thus able to fluoresce on excitation.

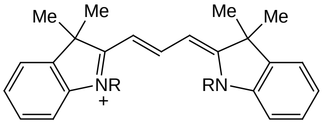
the fluorophore and quencher are held sufficiently close by short complementary strands fused to the sensor ssDNA for fluorescence to be quenched by FRET (fluorescence resonance energy transfer). When a complementary analyte ssDNA is hybridised by the sensor ssDNA, the more stable extended double helix conformation of the duplex results in separation of the fluorophore and the quencher, so that on excitation fluorescence is now observed. The degree of fluorescence is proportional to the concentration of double strand hybrid and thus analyte. The biosensor can be sensitive down to the sub-nM range.

3.5.8.3 Optical Sensors for Temperature Measurements

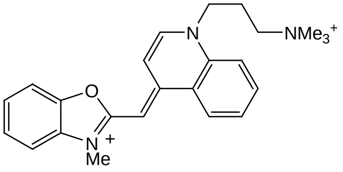
A hydrophilic fluorescent nanogel has been designed to determine intracellular temperature.[117] Nanoparticles of a hydrophilic polyacrylamide gel are doped with the polymer-linked fluorophore (3.54). Below about 30 °C fluorescence is minimal due to quenching by entrained water in the swollen gel. On warming, the gel contracts and expels water, and the fluorophore can emit on excitation. The degree of fluorescence increases to a plateau value over a 10 °C range with a temperature resolution of about 0.5 °C, suitable for monitoring usual temperature variations within human cells. This fluorescence thermometer is superior to previous designs since it is biocompatible (size, sensitivity, solubility) and has negligible interaction with cellular components.



(3.54)



(3.55)



(3.56)

3.5.8.4 *Optical Noses*

Sensor devices which are able to detect and discriminate amongst mixtures of volatile organic compounds are known as electronic noses. Various detection technologies have been used, and the few that are based on optical methods comprise "optical noses". A recent tabulation[118] of 59 commercially available electronic noses mentions just one based on colorimetric effects,[119] (*cf.* Section 1.8.2; vapochromic sensor arrays), and two others that rely on fluorescence. Only one of these is believed to be in current commercial production, CogniScent's ScenTrak™ detection device.[120] One model is designed for detection of mixtures of hazardous volatile industrial chemicals; another for detection, identification, and quantification of precursor chemicals and by-products from the manufacture of methamphetamine; and two others are in development for detection of volatile nitroaromatic and peroxide explosives, and for domestic mould analysis.

The underlying chemistry is believed to depend on solid-state, dye-labelled DNA.[121] It has been found, perhaps surprisingly, that the fluorescence intensity of some dyes covalently immobilised on different ssDNA changes when exposed to different volatile analytes. The optical nose uses an array of such sensors which respond to brief pulses of volatiles, and is based on the three dyes Cy3 (3.55), YO-PRO (3.56) and Oligreen (a proprietary dye from Molecular Probes of unknown structure). The dyes are photoexcited by filtered LEDs and their emitted fluorescence filtered, monitored by photodiodes, digitised and processed by standard chemometric techniques, all on the sensor platform.[122] The commercial sensor takes 2 seconds for sampling, and up to a further second to give its response.

3.5.9 Fluorescent Probes and Labels in Biology and Medicine

Probes and labels differ from sensors in that they are generally "one-shot" analytical species, not usually part of an all-encompassing device, which detect the presence or absence of various analytes, sometimes *in situ*, and which may or may not measure quantitative information. Labels are covalently attached to a species of interest, whereas probes are non-covalently bound. It is this area of analysis, particularly when applied in biology and medicine, that has experienced the astonishing explosion of interest in the last 20 years or so, and which has both led to, and depended on, the new luminescent species that have been introduced in earlier parts of Section 3.5. Considering just one area, a search of "nanoparticles in biotechnology" has revealed that the 11 articles published in 1991 have mushroomed to nearly 10,000 in 2007.[123]

3.5.9.1 *The NIR Transparency Window*

One of the key underlying aspects of the use of fluorescent probes in biomedical analysis has been the basic optical properties of tissue. Firstly, because

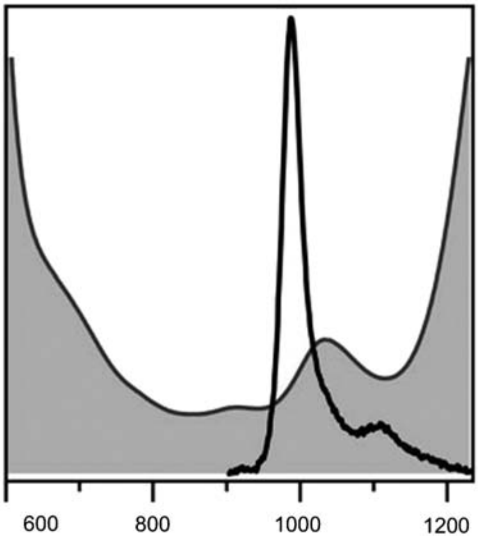


Figure 3.22 The NIR window of tissue. SWCNT emission (black line) over part of pig skin absorption spectrum (shaded area).

of its intrinsic bio-chromophores, tissue has a background fluorescence ("autofluorescence") which is simultaneously induced when a fluorescent probe is excited by UV or visible wavelengths. Thus background visible emission diminishes or even swamps the sought-after fluorescence from the probe, even when appropriate optical filters are employed. Secondly, tissue inhomogeneity leads to visible light scattering. This again interferes with probe emission intensity, and in particular restricts the depth at which any visible probe species can be detected, and thus its analytical or diagnostic value. However, tissue fortunately has relative transparency in the NIR region of the spectrum between about 700 and 1150 nm, and thus there is an NIR window for optical imaging studies. The longer wavelength limit is sometimes put at about 950 nm if water absorbance at about 1050 nm is critical (Figure 3.22). Tissue also has transparency windows at longer wavelengths, which are less exploited. Figure 3.22 shows part of the absorbance spectrum of pig skin, with the NIR emission spectrum of a single-walled carbon nanotube superimposed (SWCNT λ_{em} about 1000 nm; *cf.* Section 3.5.2.1). Thus probe species which emit in the NIR are particularly important for bio-imaging,[124] and this is one reason why they have been emphasised above (see Table 3.7). Furthermore, excitation in the NIR is important for the same reasons, lending significance to visible emitting up-converters, including 2PA materials.

In the following sections we survey just a few of the applications of fluorescent (better: luminescent) probes and labels, starting with the bio-medical area, and then look at some more general technological topics.

3.5.9.2 Fluorophores in Bio-medical Imaging

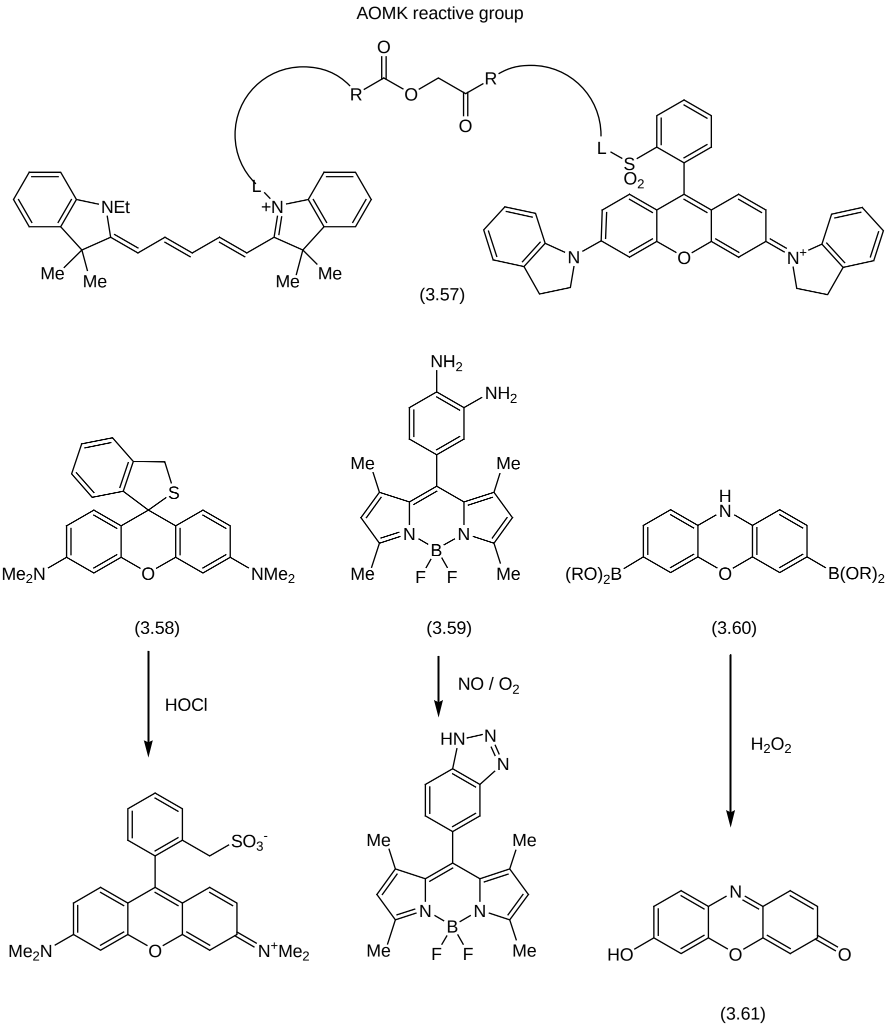
Fluorescence imaging is the modern-day equivalent of histological staining for the visualisation of biological samples (see Chapter 2, Section 2.3.2.6). It opens up the possibility of looking inside living organs and at its most precise inside individual cells, without any of the damaging effects of X-radiation, and with greater precision than magnetic imaging. High-resolution imaging, a component of the new field of Nano-Biophotonics,[125] relies on the advances made in the field of fluorescence microscopy in recent years.[126] It has reached the point where single molecule fluorescence can be detected,[127] and image resolution beyond the diffraction limit and down to 1 nm – the size of a small dye molecule like a coumarin – is now possible.[128] But imaging depends, first and last, on appropriate luminescent probes, tags and labels: "The probe is everything."[129]

We have now come dangerously close to straying into the dense scientific jungle of biology and medicine, which, if unrestrained, could easily dominate this chapter. So we shall skirt around its perimeter and extricate from the fringe just a few examples which have caught our attention.

3.5.9.3 Imaging and Tracking via Fluorescence Switch-on

Figure 3.23 shows examples where *in vivo* generation of a fluorophore from a non-fluorescent probe enables imaging of various biochemical events. In all cases the fluorophores are standard. The underpinning chemistry is specific to the analyte of interest, and makes each probe unique.

- The dual chromophore probe GB137 (3.57; L = linking group; R = part of warhead specific to enzyme binding site) is essentially non-fluorescent prior to target binding, due to FRET quenching. *N*-Aryl rhodamines are particularly effective quenchers. GB137 is designed to bind to and specifically label active cathepsins in a number of cancer cell lines. On enzymic hydrolysis the quencher is liberated and the cyanine's NIR fluorescence is recovered.[130]
- The non-fluorescent spirocyclic probe (3.58) is opened to a highly fluorescent rhodamine product on intracellular oxidation specifically by HOCl, and by no other reactive oxygen species including OCl .[131]
- Nitric oxide and H_2O_2 are essential for cellular signal transduction, and it is important to be able to track them with spatial and temporal resolution. Probes such as (3.59) utilise the NO-specific *in vivo* oxidation of *o*-phenylenediamine (non-fluorescent due to PET) to the equivalent benzotriazole (fluorescent due to an absence of PET). This chemistry has been built into fluorescein, rhodamine and cyanine fluorophores, to cover the visible spectrum.[132]
- H_2O_2 can be tracked through its specific *in vivo* oxidation of non-fluorescent boronate ester probes (*e.g.* 3.60) to fluorophore (3.61). Again, boronate derivatives of other fluorophores are used to achieve a range of emission colours.[132]



(3.57)

(3.58)

(3.59)

(3.60)

(3.61)

Figure 3.23 Various fluorescent probe principles, for *in vivo* imaging.

3.5.9.4 Composite Fluorophore Inorganic Nanoparticles

The NIR fluorophore indocyanine green (ICG) has many favourable properties which have led to FDA approval for human *in vivo* application. Unfortunately, like many other organic fluorophores, it suffers from low quantum yield, photobleaching, solvatochromism and non-specific quenching. Embedding it in bioresorbable calcium phosphate NP (average 16 nm diameter) with a PEG or carboxylate surface coating results in its fluorescence quantum yield being doubled and photostability increased by 5 times compared with the free dye. It is not eliminated 24 h after injection into a mouse model, and allows *in vivo* imaging of breast cancers where it localises. *Ex-situ* imaging of porcine muscle tissue was successful up to 3 cm deep.[133]

3.5.9.5 Protein Walking

Fluorescence imaging with one nanometre accuracy (FIONA) is a technique which has recently been developed to measure nm-scale distances, including the translocation of molecular motors.[128] As an example, the walking motion of the inverted Y-shaped protein myosin V along the protein actin has been defined by two-colour FIONA. This is one of the fundamental processes for ATP-fuelled transportation of a biological cargo within a cell. For the FIONA imaging experiment, the legs of the protein are labelled with two differently coloured fluorophores and, by monitoring their mutual positions simultaneously over time, it is possible to confirm a hand-over-hand motion for the myosin V. Pairs of cyanine fluorophores have been used for the imaging, as well as cyanine plus rhodamine. Two differently coloured QDs are also effective, with the added advantage of simultaneous photoexcitation by one source. Other dynamic processes in single molecules have been described in these fascinating reviews (Figure 3.24).[128]

In the FIONA experiment, brightness and photostability are significant problems for conventional fluorophores under the continuous excitation required. QDs and metal nanoparticles (*via* scattering) overcome these problems, but other questions are raised as we next review.

3.5.9.6 Quantum Dot Applications

The superior optical properties of QDs in bio-medical imaging and sensing applications compared with organic fluorophores is indisputable – brightness, strength, narrow line width, large Stokes shift, variable excitation wavelengths well away from emission, photostability and long fluorescence lifetime are all advantages. On the other hand non-trivial drawbacks have been encountered, if not generally, then enough to detract from a universal vote of confidence: low labelling efficiency, blinking, large and non-uniform effective size, non-uniform shape, non-uniform excitation and emission characteristics, cytotoxicity and alteration of cell function and inferior tissue penetration. Doubts remain over both *in vivo* toxicity, as well as incomplete knowledge of the QD fate with regard to distribution and breakdown products. Yet the extent of application studies of QDs testifies to the impact they are making in bio-medical analysis: *in vivo* animal imaging, cell tracking, labelling of cellular proteins, gene technology, pathogen and toxin detection, components in FRET analysis in sensing and probes and tumour biology analysis have all been reported.[134,135] Figure 3.25 shows a DNA analysis by a QD-Cy5 FRET pair.[136]

The Alliance for Nanotechnology of the US National Cancer Institute provides up-to-date news of the evolving applications of all classes of nanomaterials and nanotechnologies in cancer.[137]

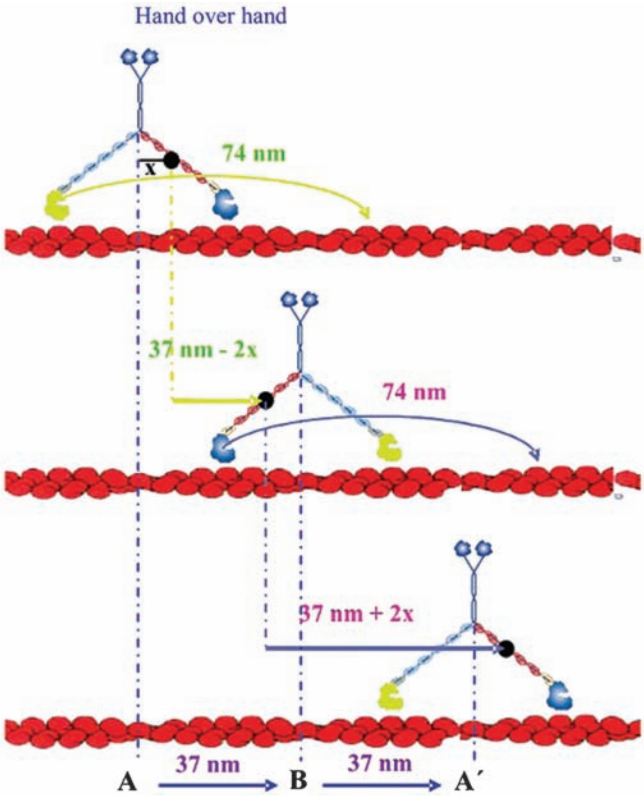


Figure 3.24 Hand over hand motion of myosin V (inverted Y shaped protein) on actin (red). In moving from position to A to B, and then from B to A′, the rear head passes by the front head, translating a total of 74 nm, while the front head stays stationary. Therefore, a fluorescent dye attached to the head (blue) moves alternating 0 and 74 nm steps. A second, different, fluorescent dye on the light chain (black), moves $37+2x$, followed by $37+2x$ nm, where x is the distance between the dye and the centre. The positions of these dyes can be imaged independently to near nm resolution[128(b)] (reproduced with permission of the American Chemical Society).

3.5.9.7 Two-photon Microscopy in Bio-medical Imaging

Many conventional fluorophores can also be excited by multi-photon absorbance (usually 2PA), while other molecules have been specially designed for improved 2PA (Section 3.5.3). They can be used in the same way as one-photon-excited species for bio-medical imaging purposes, but MPA introduces various potential advantages.[83,138]

- For emission wavelengths in the visible, excitation for 2PA is in the NIR window. Thus substrate absorbance and resultant autofluorescence are minimised. Scattering is also reduced at NIR wavelengths.

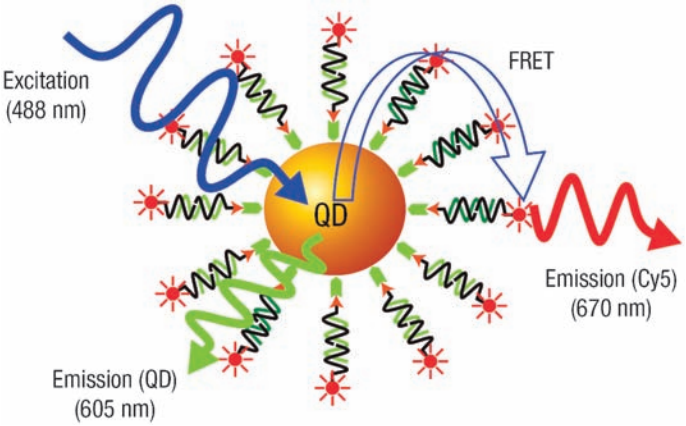


Figure 3.25 A QD cyanine FRET pair. The QD is excited at 488 nm, and the energy is either emitted directly at 605 nm, or is transferred by FRET to a cyanine label on a DNA analyte, and re emitted at 670 nm[136] (repro duced with permission of Macmillan Publishers Ltd).

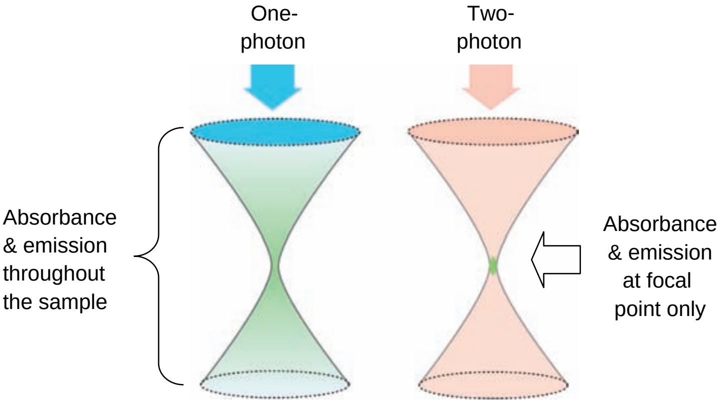
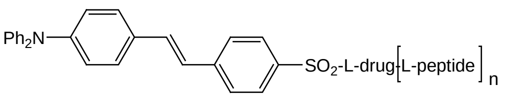


Figure 3.26 The I^2 dependence of 2PA results in excitation and emission solely near the focal point.

- 2PA has a quadratic dependence on excitation intensity, I, resulting in a much tighter definition of excitation locality than achieved for linear one-photon excitation. Excitation is solely at the focal point where I^2 is highest (Figure 3.26).
- Because of negligible absorption and scattering, two-photon excitation can penetrate further into a tissue sample, enabling deeper imaging.
- Elimination of short-wavelength excitation improves cell viability, because of lower photodamage.
- To minimise potential undesirable thermal effects during continuous wave irradiation at the necessarily high intensity for 2PA, the excitation energy

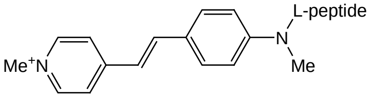
is applied as ultra-short laser pulses (*e.g.* typically from a Ti:sapphire laser producing 100 fs pulses at around 800 nm at a repetition rate of 80 MHz, with a very large peak power value (*ca.* 50 kW)).

Applications of two-photon fluorescence microscopy are becoming increasingly important for imaging of thick tissue and live animals. Example applications can be found in the two reviews cited,[83,138] and include Ca^{2+} dynamics in the brain; *in vivo* studies of angiogenesis in cancer research; investigation of lymphocyte trafficking by immunologists; for monitoring embryos; for monitoring cell structure and function and imaging of cellular network dynamics. By studying a dye-doxorubicin-peptide targeting unit conjugate (3.62; n = 1), alongside doxorubicin and peptide each conjugated separately with red- (3.63) or green- (3.62; n = 0) emitting 2PA dyes, it has been possible to identify the function of each of the two units. The doxorubicin enters the cell nucleus and is responsible for cell death, whereas the function of the peptide is a carrier hormone which helps penetrate the cell wall and carry the drug into the cell. The 2PA dyes are each variants of common styryl fluorophores.[139]



(3.62) n = 0,1

L = inert linker units



(3.63)

3.5.9.8 Up-conversion Nanophosphors for in vivo Animal Imaging

The first example of the *in vivo* use of an RE up-converting nanophosphor applied Y_2O_3:Yb,Er particles to image the digestive system of a nematode worm.[140] Excitation led to green luminescence which lost no intensity after 24 h, and because of excitation well into the NIR, there was no background autofluorescence. Interestingly, luminescence was also visible due to electron impact in an electron microscope – an unusual example of cathodoluminescence.

In another study, PEI-coated $NaYF_4$:Yb,Er excited at 980 nm was used to image human cancer cells in a rat at a depth of up to 10 mm.[141] The up-converted luminescence was estimated to be 10^7 times more intense than from a green QD, and was easily visible to the naked eye *in vivo* when the QD luminescence was all but invisible. Furthermore, the UC NP was non-toxic to bone marrow stem cells, and was photostable. It is early days, but these few initial results suggest UC NPs will receive wider examination and exploitation for *in vivo* imaging applications.

Other applications of fluorophores especially those derived from natural sources are described after an introduction to biofluorescence in Section 3.5.10.

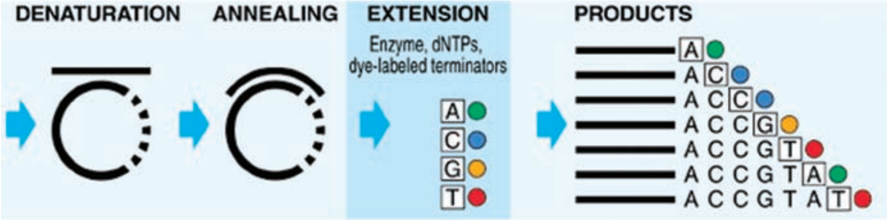


Figure 3.27 Simplified dye terminator chemistry for cycle sequencing of DNA, showing the application of the four dye labelled terminators in the process[143] (copyright owned by Applied Biosystems, and reproduced with permission).

3.5.9.9 Fluorescent Labels for Proteomics and Genomics

Fluorophore labelling of components in proteomic and genomic studies to enable detection is commonplace, and is an important component of what has become a multi-billion-dollar industry.[142] This has been powered by many new young companies offering a range of services, equipment and consumables for a diverse range of applications. We will outline just one of these here – the underpinning technology of DNA sequencing.

The most popular method relies on dye terminator chemistry, and is outlined in Figure 3.27.[143] At its simplest the basic process involves the following steps:

- The ssDNA to be identified (Z) is fused to another DNA strand of known sequence (X).
- A second ssDNA (Y) complementary to (X) is added and anneals with (X).
- DNA synthesis is initiated by adding a reaction mixture containing the necessary enzyme, the four mononucleotides (A, C, G, T) and four terminators. The terminators are dideoxy mononucleotides, which when built into a growing DNA strand cause the polymerisation to cease. Each is uniquely labelled with a fluorescent dye. In practice the proportion of terminators is appreciably lower than the amount of main ACGT mononucleotides.
- DNA polymerisation then proceeds, resulting in a mixture of sizes of new DNA, each comprising the complementary sequence of the target DNA strand, but eventually each terminated by one of the four terminators.
- After synthesis, the new ssDNA fragments are denatured.
- The DNA fragments are separated by electrophoresis according to ssDNA chain length generated.
- After separation each is analysed, obviously in order of length. The emitted colour for each single strand reveals its end nucleotide and thus the overall sequence can be built up.
- In the case of Figure 3.27, the size order reveals the sequence ACCGTAT by virtue of the colours detected.

The whole process is now well automated and can be very rapid. This and its modifications are being used in a multitude of genomic analysis applications, and are already a huge business.

Applied Biosystems has offered various selections of fluorescent terminators, including one based on pairs of dyes (trademarked "BigDyes").[144] Each pair comprises a donor fluorescein component, with one of a range of lower energy acceptor dyes, for example one of four rhodamine dyes, and is tagged to one of the four dideoxy mononucleotide terminators. The photoexcited fluorescein unit excites its paired rhodamine by FRET leading to emission of one of four distinguishable colours. The dyes are selected to optimise the evenness of the fluorescence across all four terminators, and minimise dye-related mobility effects.

A more recent innovation is the use of four different fluorophores, again covering the visible spectrum, in combination with sequenced pulses of laser irradiation at four wavelengths corresponding to the excitation wavelengths of the dyes.[145] The advantages of this method are higher and normalised signals from all dyes, elimination of spectral cross-talk between the dyes and higher signal collection efficiency. The four dyes used are all based on standard fluorophores.

3.5.10 Biofluorescence

Biological materials that fluoresce are everywhere. We have already noted the problem of tissue autofluorescence which hinders *in vivo* imaging. Of course many naturally occurring pigments and other molecular components of Nature are capable of fluorescing to a lesser or greater extent.[146]

Fluorescent pigments play crucial roles in natural light harvesting processes (Chapter 4, Section 4.8.2.1), and phycoerythrin, for example, has also been applied as a label in genomics and proteomics (Section 3.5.9.9) and in flow cytometry (Section 3.5.10.4). But there is one dominating area of biofluorescence so significant that it has been recognised by the award of the 2008 Nobel Prize in Chemistry to Shimomura, Chalfie and Tsien – the case of Green Fluorescent Protein and its offspring science and technology.[147]

3.5.10.1 Green Fluorescent Protein

GFP is a protein originally isolated from the jellyfish *Aequorea victoria*. The history leading to its current significance can be broken down into various phases.[148]

- GFP was isolated and its fluorophore identified (Shimomura).
- The GFP gene was cloned, followed by its recombinant expression in *E. coli* and *C. elegans* (Chalfie). It was shown that the fluorophore forms spontaneously, in the absence of any enzymic catalysis. GFP could thus be expressed as a fluorescence marker in any organism.

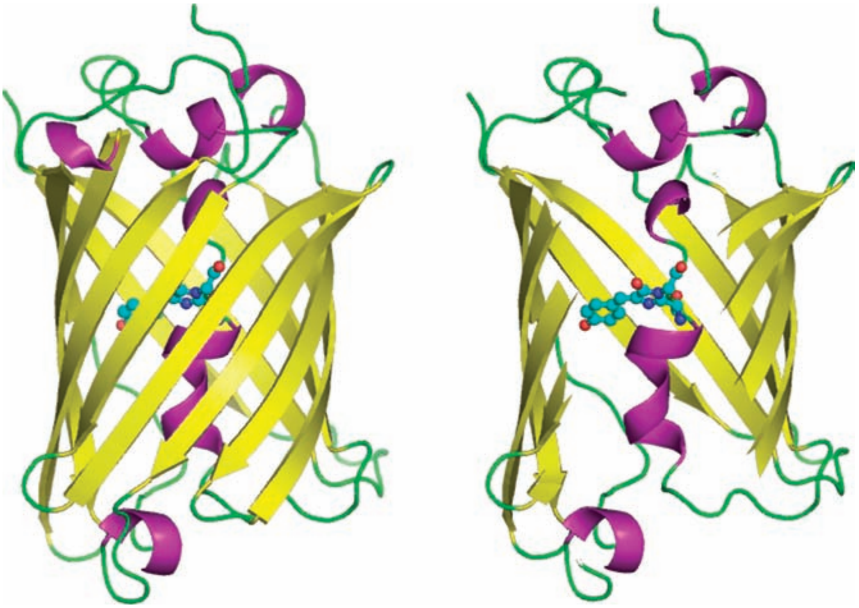


Figure 3.28 Green fluorescent protein. The image on the right shows the β can partly cut away to reveal the fluorophore (graphics by Raymond Keller, from PDB 1GFL, Wikipedia May 2009; original structure determination: F. Yang, L. G. Moss and G. N. Phillips, *Nature Biotech.*, 1996, **14**, 1246 1251).

- The 3D structure of GFP was solved. Its essential can-shaped construct enclosing a methine fluorophore has achieved iconic status (Figure 3.28).
- Protein engineering led to GFP mutants that had improved properties and whose fluorescence ranged across blue, cyan and yellow, besides the natural and enhanced green. This enabled multi-colour combinations in cell imaging, FRET studies of protein–protein interactions and the development of biosensors (Tsien).
- Proteins of the GFP family isolated from coral sources led to orange and red FPs. These not only widen the colour range of the FPs, but are more useful for cell imaging, further away from autofluorescence and cellular scattering.

The basic structures of the GFP fluorophore and some analogues are shown in Figure 3.29.[149] All are methine dyes based on an imidazolone core. Each is biosynthesised through reaction between the components of a tripeptide sequence within the barrel protein, in an autocatalytic process known as maturation. Native GFP fluorophore, for example, results from a serine-tyrosine-glycine tripeptide. Different FPs are derived from maturation of genetically modified proteins, where the first and second amino acids of the tripeptide are altered. The basic emission maxima of a particular fluorophore can be red

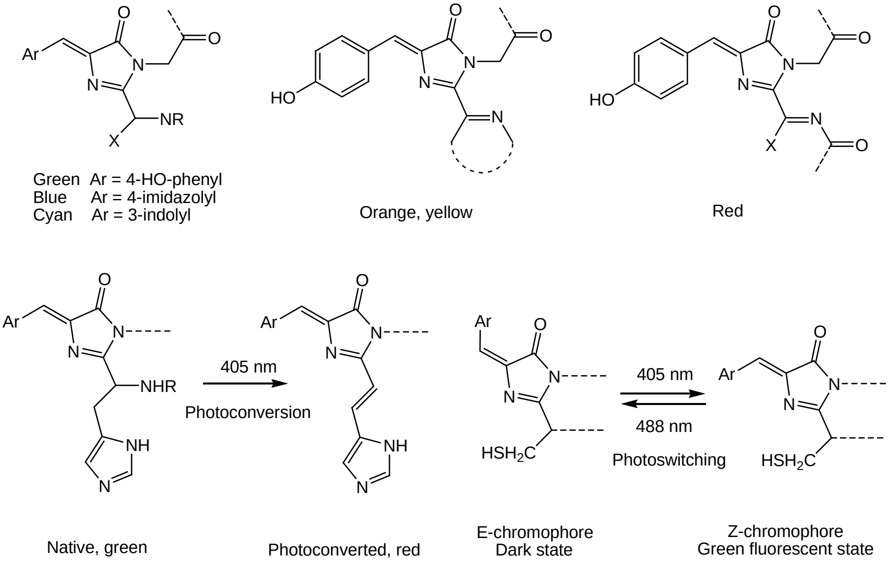


Figure 3.29 GFP fluorophores. Top: variants of the basic methine fluorophore. Bottom left: photo induced elimination, converting a GFP to red. Bottom right: reversible photochromism of an FP fluorophore.

or blue shifted by as much as 40 nm by changing the amino acid residues surrounding it, such as alteration of charged residues, H-bonding networks, π-stacking arrangements and hydrophobic interactions within the protein matrix. For example, engineering a nearby 4-hydroxyphenyl group of a tyrosine residue to sit anti-parallel over the hydroxyphenyl group of the GFP fluorophore itself gives a yellow FP variant (not shown). Extending fluorophore conjugation leads to orange- and red-emitting FPs. Other FPs known as "optical highlighters" can be switched on by photo-irradiation, or their emission colour can be changed between two states. Ionisation of the phenolic OH group switches on much higher fluorescence. *In vivo* photoelimination converts a native green emitter to red. Other FPs are photochromic due to isomerisation about the exocyclic C=C bond of the imidazolone ring, and can be interconverted by irradiation at appropriate wavelengths. There is thus a huge armoury of FPs, some commercially available, tailored to give a selection of photo and other physical properties.

3.5.10.2 Applications of GFP

Because the FP gene can be introduced into cellular DNA the cell can synthesise FP. Furthermore, the FP gene can be fused to the gene of any other protein of interest and can be modified such that when it is synthesised *in vivo* it is fused with (covalently attached to) an FP label. A full range of colours is possible. The behaviour of the protein is frequently not modified by its appended FP label, so it carries on its biological role as before, but can now be tracked by its fluorescent label. By photo-exciting the label, the behaviour of the fused protein in a cell can be imaged to high precision with the aid of modern fluorescence microscopy techniques. Both spatial and temporal information about specifically labelled proteins is achievable. This is an extremely powerful strategy for investigating the molecular biology of a cell and has been described as a revolution in cellular biology. There are now many examples in the literature, some attractively presented on various websites.[150]

More generally, specific organelles can be labelled with FPs. Examples of transgenic fluorescent whole animals have been well publicised in the general press and news. The visually most spectacular example is the "Brainbow" approach, in which individual brain cells within transgenic mice have been fluorescently coloured with about 90 different colours derived from mixtures of different basic FPs.[151] The approach opens up brain studies at a level never previously possible. Figure 3.30 shows some of the images recorded with the aid of fluorescence microscopy.

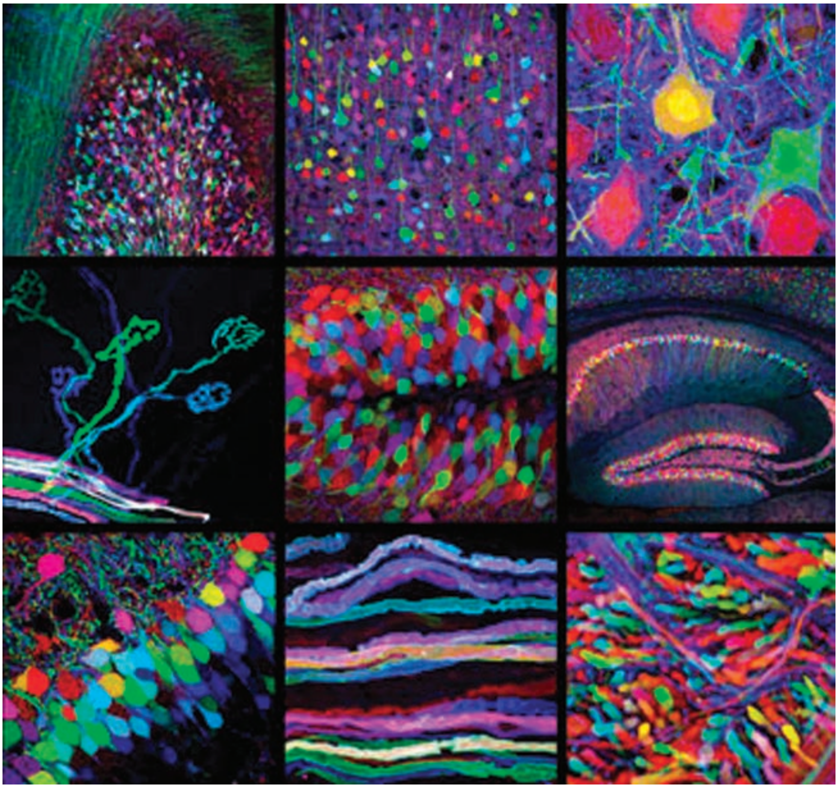


Figure 3.30 "Brainbow" images of mouse brain[151] (reproduced with permission of Macmillan Publishers Ltd).

The FRET technique for probing the interaction between two fluorophores has been described earlier (Section 3.5.2.2). Excitation of a higher emission energy fluorophore can lead to energy transfer to a lower energy emitter, if they are separated by no more than about 10 nm. FRET is being used to investigate intermolecular interactions between differently labelled proteins *in vivo*, where the labels are differently coloured FP pairs. CyanFP and yellowFP has been the favoured combination but the newer red FPs are opening up new options when paired with green. The FRET experiment using FP labels is by no means routine and the various pitfalls and possible solutions have been addressed.[152] Oligomerisation of protein receptors is an example application.

Alternatively two FRET-paired FPs can be genetically engineered into the same peptide or protein, within interaction distance of one another. The connecting protein is designed to respond to an outside influence, such as a metal ion changing its conformation and thus the separation of the two FPs, or an enzyme which causes protein scission and thus total separation of the two FPs. The result is to attenuate or altogether remove the FRET interaction, and the observed fluorescence colour changes. This effect thus introduces the basis for an intracellular biosensing mechanism. Calcium ions[153] and protease activity have been monitored using such FP-based FRET probes.

The science and technology of FPs has developed at breakneck speed over just the last 20 years, but is nevertheless already served by several books, both popular and overtly scientifically specialist.[154] They will provide the interested reader with the detail that this chapter can only skate over. To complete our own version of FP we outline a clever GFP application that *via* sex and violence could lead to a massive health benefit for the world.

Mosquitos are well known to be the vector for transport of the malaria parasite, estimated to be still responsible for 515 million cases per annum worldwide, and between one and three million deaths of mainly young children in sub-Saharan Africa. Mosquito elimination thus remains a major goal in the fight to control malaria. Figure 3.31 shows larvae of transgenic Asian mosquito *Anopheles stephensi* bred in captivity, which have been genetically engineered to contain enhanced GFP in their sexual organs.[155] The two bright green dots visible along the sides of the larvae are due to GFP in the gonads of the male. Green fluorescence is absent from females. These signals are sufficient to enable a laser-based sorting device to discriminate between male and female larvae, and separate them automatically, at the rate of 18,000 an hour. The male larvae can then be sterilised without otherwise harming them, prior to their release into a wild mosquito population. Female mosquitoes mate only once, so if their encounter is with a sterilised male there are no offspring. If the wild population is diluted by a sufficient proportion of infertile males, its offspring will be reduced with attenuation of the malaria risk. Prior separation of males and females is essential, as release of females alongside the sterilised males would both dilute the influence of the sterilised males, as well as introduce yet more potentially disease-carrying vectors into the wild. Hence a mechanism for their ready separation is essential and is conveniently provided in this case by GFP. The female larvae never make it into the wild.

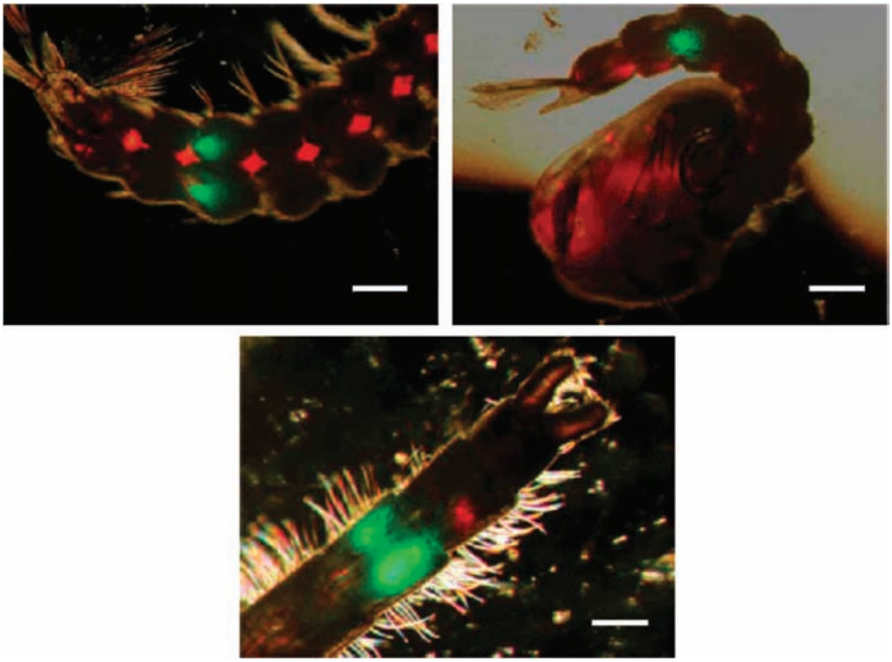


Figure 3.31 Views of male mosquito larvae (*Anopheles stephensi*) genetically modified to display enhanced green fluorescent protein (EGFP) in their sexual organs[155] (reproduced with permission of Macmillan Publishers Ltd).

3.5.10.3 Phycobiliproteins

Another important family of fluorescent proteins is the phycobiliproteins, found in cyanobacteria, red algae and elsewhere, where their role is part of the light-harvesting process in photosynthesis (Chapter 4, Section 4.8.2.1). The main fluorophores in these proteins are tetrapyrrole derivatives at various oxidation levels as shown in Figure 3.32. Natural evolution has led to a collection of attractive properties: intense excitation and emission; large Stokes shifts; high quantum efficiency; protection of the fluorophores by the protein backbone and therefore not subject to quenching by external influences; high aqueous solubility; homogeneous; and multiple reaction sites for conjugation to substrates of interest.[156] The importance of the proteins is as fluorescent probes in various applications, as outlined in the following section.

3.5.10.4 Fluorescent Probes in Flow Cytometry

The technique of flow cytometry involves investigation of small particles such as single cells suspended in a liquid flowing through an optical apparatus. The surface of the particles is modified by means of fluorescent dyes, coordinating by non-covalent interactions. It is possible to define characteristics of the

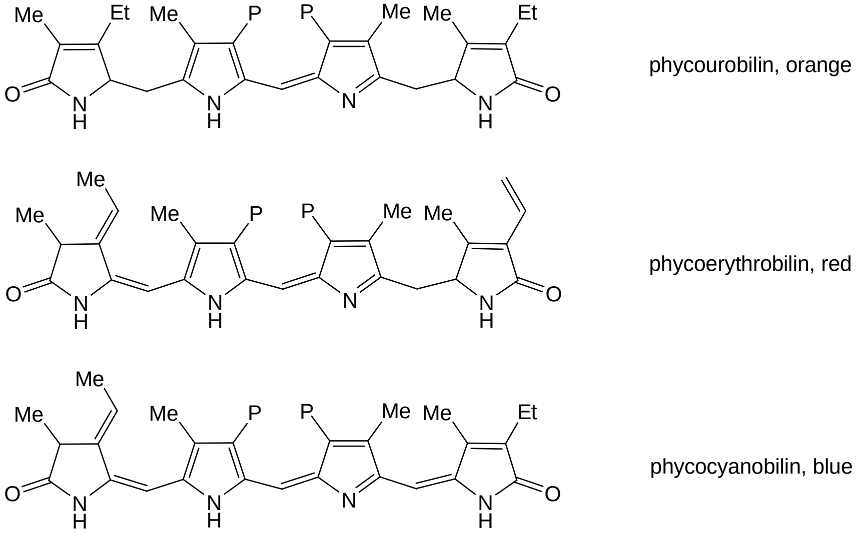


Figure 3.32 The main fluorophores of phycobiliproteins (P $C_2H_4CO_2^-$).

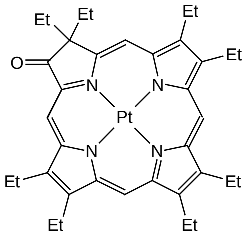
particles by investigating the nature of the labelling, and measuring a great number of physical, chemical and biological parameters. A variety of fluorescent labels may be used, and the choice depends on the excitation source used. The introduction of phycoerythrin (PE) made a major impact in 1962. Its excitation energy is conveniently located at the wavelength of the common argon laser at 488 nm. Common flow cytometers probe the particles by irradiation at this wavelength, and measure and classify fluorescence in four channels FL1 (responding to green fluorescence), FL2 (orange), FL3 (red) and FL4 (NIR). Green fluorophores include fluorescein and related dyes. PE is used for FL2. By multiple labelling with PE and a lower emission energy fluorophore, the same excitation wavelength can be used to generate longer wavelength emission by means of FRET. PE with Cy5-type dyes generates red (FL3), and PE with Cy7 gives NIR fluorescence (FL4). Further developments have led to 11-colour analyses.[157] Photostability of the fluorophores used in flow techniques, such as cytometry and DNA sequencing, is less critical than in imaging. In the latter, continuous excitation has a far more deleterious impact than the brief period of irradiation for label identification in the former.

3.5.11 Fluorescent Probes and Indicators in Non-bio Analysis

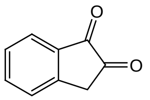
Despite the heavy biological bias of the preceding sections, it is clear that much of the progress on luminescent probes and indicators in biology and medicine is built on the back of more-or-less straightforward organic and inorganic chemistry. This chemistry is of course equally applicable to non-bio analysis. We have already cited the very readable account of the general status of luminescent sensing molecules up to 2004, which is illustrated by the structures of 140 species alongside descriptions of the relevant properties of many others.[82] These have been applied in many other sensing systems besides those already exemplified, for main group and transition metal ions, anions, various organic molecules, reaction types and physical properties. Rather than systematically repeat all of these, we now give some examples which have achieved, or soon will, technological significance.

3.5.11.1 Fluorescent Oxygen Indicators in Food Packaging

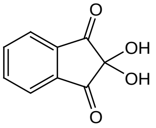
Colorimetric indicators for oxygen in modified atmosphere food packaging (MAP) have already been described in Section 1.6. Fluorescent detection systems are also known, and the OxySense™ system for oxygen in MAP has been commercialised.[158] The indicator elements, named O_2xyDots™, are based on the same materials as used in clinical blood oxygen sensors (Section 3.5.8.1), $Ru(dpp)_3^{2+}$ (e.g. 3.46) and the Pt complex of octaethylporphyrin ketone (3.64), immobilised in silicone rubber. Again fluorescence lifetime rather than intensity is the parameter measured to indicate oxygen, avoiding dye photoinstability problems. The equipment and O_2xyDots™ are currently too expensive for routine use in MAP, and are restricted to packaging research. The simple semiconductor-based photo-redox colorimetric system of Mills is a better bet for future routine smart packaging of food.



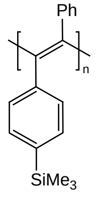
(3.64)



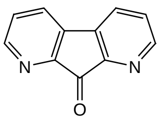
(3.65; indanedione)



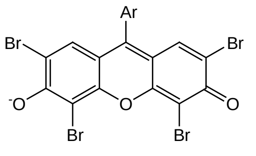
(3.67; ninhydrin)



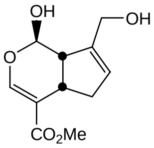
(3.72)



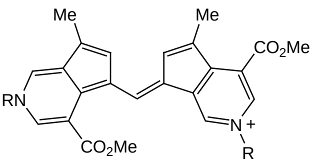
(3.66; DFO)



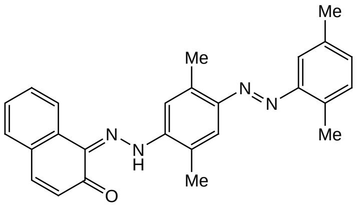
(3.71; eosin, Ar = 2-carboxyphenyl)



(3.68 genipin)



(3.69)



(3.70; Oil Red O)

3.5.11.2 Fluorescent Materials in Forensics Fingerprint Detection

"The comparison and identification of fingerprints remains one of the best means of linking an individual with a scene or item related to a criminal investigation."[159] The search for better materials for fingerprint detection is encompassing traditional developers, and extending to some of the newer luminescent materials. Topical approaches include the following:

- Indanedione (3.65) formulations containing a small amount of $ZnCl_2$ are being explored as an improvement over conventional developers 1,8-diazafluoren-9-one (DFO; 3.66) and ninhydrin (3.67).
- The natural product genepin (3.68) from *Gardenia spp* leads to blue fluorescent cyanine-like colorants (*e.g.* 3.69) when in contact with even trace amounts of primary amino groups (*e.g.* from amino acids or proteins deposited by skin).[160]
- Oil Red O (Solvent Red 27; Sudan Red 5B; 3.70) can detect sebaceous residues after water-soluble amino acids have been removed by water (rain, *etc.*).
- Alumina nanoparticles coated with luminescent eosin (3.71) have improved effectiveness.
- Metal NP (Au stabilised by *n*-alkanethiols, developed by Ag) and CdSe/ZnS core-shell semi-conductor QDs stabilised by alkylamines show advantages over conventional coloration developers.[161]
- NIR dyes enable imaging outside the visible region.
- RE up-converters (NIR to visible) improve detection on highly fluorescent substrates (*e.g.* some banknotes).
- S_2N_2 vapour turns black due to formation of polymeric $(SN)_x$ by interaction with fingerprints, importantly on many substrates.[162]
- Films comprising the highly conjugated polymer (3.72) absorb fatty residues present in fingerprints. This causes polymer expansion with resultant increase in its fluorescence at a sensitivity sufficient to enable detection and resolution of the fingerprint pattern.[163]

3.5.11.3 Luminescent Signalling via Rigidochromism

Luminescence applications can also depend on the chromic phenomenon of rigidochromism. This term was originally coined to describe a change in colour of chromophores as the normally fluid solvent or substrate freezes or otherwise becomes rigid.[164] At the time "luminescence rigidochromism" was introduced for the corresponding change in emission maximum, but in the meantime the abbreviated "rigidochromism" has frequently been adopted for luminesence shifts. Its physical basis is described by Figure 3.33.

Photoexcitation of a fluorophore in a fluid medium initially leads to the vibrationally excited Franck–Condon state within the excited S_1 state, followed by relaxation of solvent to accommodate optimally the new S_1 geometry and electronic distribution, and finally by fluorescence emission from the relaxed S_1

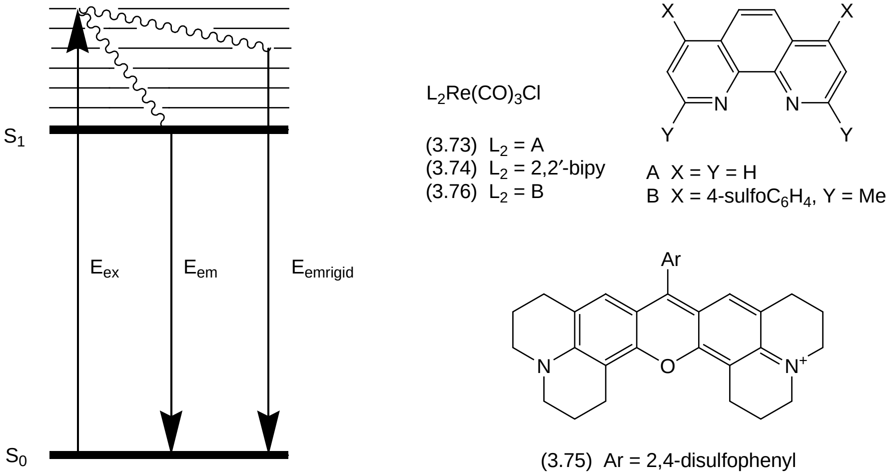


Figure 3.33 Left: photoexcitation, followed by (partial) relaxation and emission from fully relaxed (fluid medium) and partially relaxed (rigid medium) excited states; right: rigidochromic fluorophores.

state back to the ground state S_0. The difference in energy between E_{ex} and E_{em} is of course the Stokes shift. Rigidification of the medium prevents full relaxation by, for example, dipole reorientation or H-bond reorganisation within S_1. Thus luminescence in a rigid medium occurs from a vibrationally excited S_1 state, and the emission energy $E_{emrigid}$ is higher than E_{em}, commonly observed as a blue-shifted emission wavelength.

Rigidochromism has been used as a mechanism to monitor various thermal and photopolymerisations.

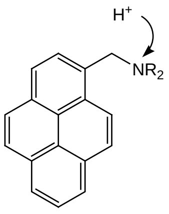
- The Re(I) complex (3.73) shows an emission shift from 592 nm in uncured epoxy resin, to 543 nm after thermal curing.[165]
- The related complex (3.74) as well as the conventional laser dye Sulforhodamine 640 (3.75) have both been used as probes in separate studies to follow the progress and mechanism of gelation of $(EtO)_4Si$ and related systems.[166]
- The rigidochromic shift of the fluorescence of water-soluble Re(I) derivative (3.76) signifies setting of gypsum plaster.[167]

Rigidochromism thus has some of the characteristics of solvatochromism. A related application is the use of conventional fluorophores in polyurethane-acrylate films as potential humidity sensors.[168] As the coloured polymer film absorbs moisture it softens, and in this case the fluorescence intensity is attenuated, rather than shifted, to a degree which reflects the moisture content of the film. Softening implies a rigidochromic effect, but here the mechanism could be solvatochromic shifting of the emitting S_1 state, comparable to ground state solvatochromism as discussed in Section 1.7.

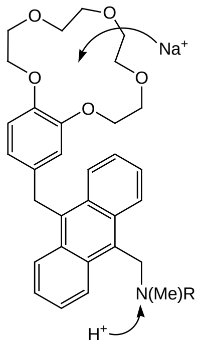
3.5.12 Molecular Information Processors

The theme of molecular "signals" has pervaded much of this section on analysis by luminescence. Is the blood Ca^{2+} concentration outside a clinically acceptable level? Do bright spots in a microscope image indicate cancerous tissue? Can we detect a fingerprint on this sheet of paper? Is the plaster cast set yet? The response of fluorescent molecules signals the answer. But an alternative way to look at all these questions is in terms of formal logic. The fluorescence response is also expressing TRUE or NOT TRUE. The realisation that molecular behaviour can be used to determine the logical outcome to a set of propositions, expressed as chemical inputs, has opened up the area of molecular logic. From here it is conceptually a small step to molecular computing. The development of molecular logic devices has borrowed from many areas of chemistry,[169] but in our context the most significant is the use of molecular luminescence, or its absence, to signal output.

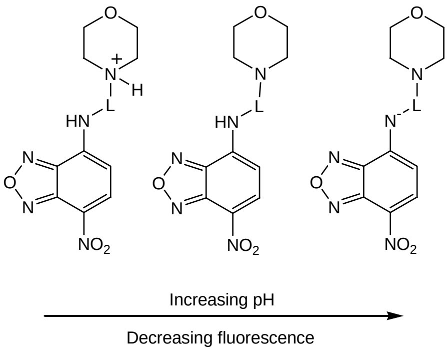
A few examples illustrate how clever yet simple molecular design has led to some of the various Boolean logic gates that are possible. The pyrene (3.77) does not fluoresce in the absence of acid because of quenching by intramolecular photoinduced electron transfer from the pendant amine group to the excited fluorophore. Acid results in amine protonation and switches off PET, resulting in a YES gate. A NOT gate molecule is the reverse, where fluorescent emission is switched off when H^+, for example, is added. An extension to include two receptor sites as in (3.78) results in a molecule with two possible PET routes. Addition of acid protonates the amine and excludes one PET route. Na^+ coordinates with the crown ether, and prevents PET from that source. But it is only when both H^+ and Na^+ are present that (3.78) signals this combination by fluorescing, corresponding to AND logic. In fact molecules have been designed which result in all binary logical outcomes for one- and two-input combinations: YES, NOT, PASS 1, PASS 0, AND, OR, INH, XOR, XNOR and NOR.



(3.77)



(3.78)



(3.79; L = C_3H_6)

Combinations of the simple binary molecular logic elements give rise to the fundamental components of molecular calculators or "moleculators":

half-adders and -subtractors, and most recently full-adders and -subtractors.[170] While achievement of such demonstrator molecular devices at the laboratory scale is impressive, there remain non-trivial hurdles to their further development into truly useful molecular computers. Downscaling to the nanoworld as represented by a few molecules, immobilisation on a solid support, gate-to-gate communication and selective addressing of logic gates are all awaiting solutions.[170]

Electronic devices of course depend on binary logic. But chemical logic gates can be more flexible: the molecule (3.79) is able to exist in three pH-dependent states, each with a unique fluorescence signature, and thus can lead into ternary logic.[171] This is just one example of where the richness of chemistry opens the opportunity for applications of molecular logic beyond the mere mimicry of binary-based systems, such as conventional silicon-based electronics. It has been recognised that the promise of future technology needs to be leavened with real-world applications today. Perhaps the main achievement of the remarkable results on molecular logic so far in the first decade of the twenty-first century is the recognition of unimagined opportunities beyond the aspiration for molecule-based computing. One such application making use of these principles is the development of a series of distinguishable tags, used to encode a large population of small objects, in this case 100-μm polystyrene beads as used for the synthesis of combinatorial libraries.[172] By combining different and easily distinguished excitation colours, different emission colours, a range of orthogonal chemical inputs, different logic gate formats as represented by variously functionalised fluorophores in controlled but different ratios and monitoring under various pH conditions, a high number of possible tags rapidly becomes available. A demonstration using just a few of these combinations is easily able to distinguish the tags on different beads under a fluorescence microscope (Figure 3.34).

With this taste of one of tomorrow's technologies, we now leave the obviously huge topic of fluorescence, and photoluminescence in general, and move on to luminescence induced by other stimuli.

3.6 Chemiluminescence

Chemiluminescence is the production of light from chemical substances without the aid of other energy sources; in effect it is the conversion of energy stored in chemical bonds into light. The basic process is the formation of a high-energy chemical species, which on decomposition leaves one or more of its reaction products in an electronically excited state. This then emits light as it falls to its ground state. To emit light in the visible region of the spectrum (400–700 nm) the reaction enthalpy must be in excess of $40\,\mathrm{kcal\,mol^{-1}}$. Light emitted directly is known as direct chemiluminescence, as opposed to indirect chemiluminescence in which the electronically excited state transfers energy to a suitable acceptor which itself emits light.

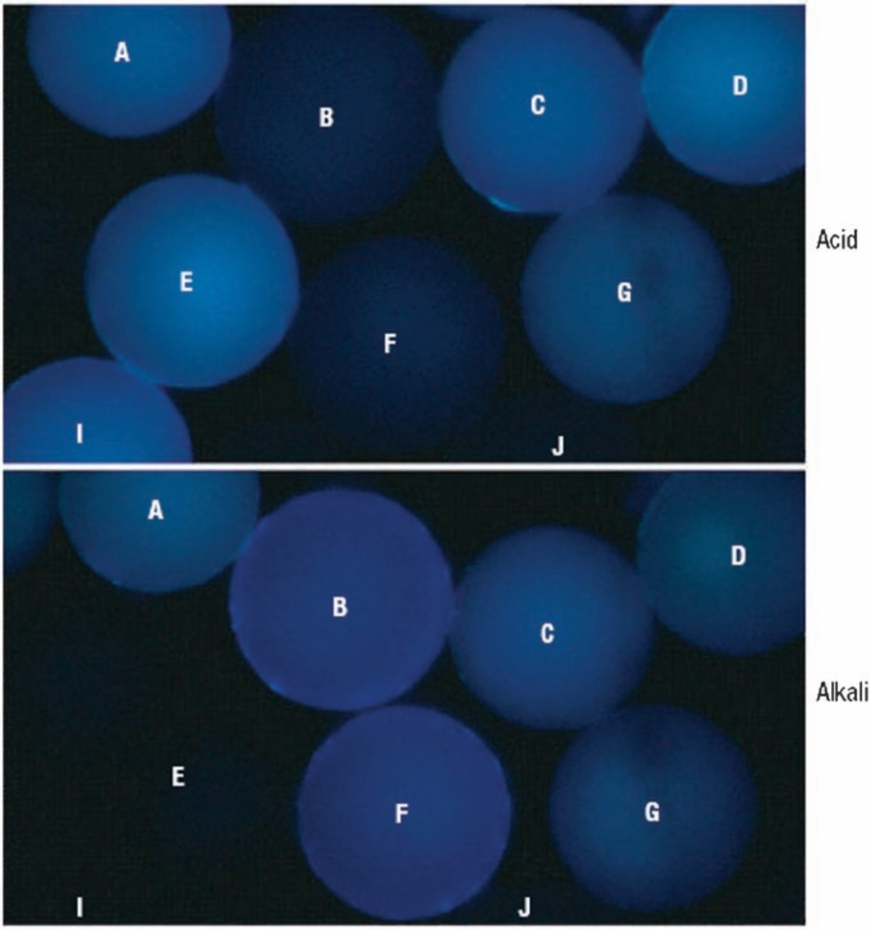


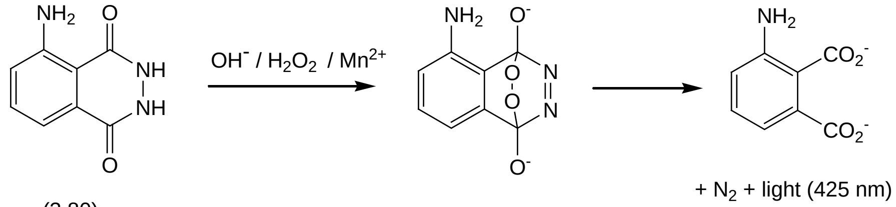
Figure 3.34 Demonstration of single bead logic operations. Fluorescence microscope images on mixed beads with different logic tags in methanol/water in the presence of acid and alkali. The logic type of each bead is A: PASS, B: NOT, C: PASS 1, D: PASS 1 + YES, E: YES, F: NOT, G: PASS 1, I: YES, J: PASS 0[172] (reproduced with permission of Macmillan Publishers Ltd).

3.6.1 Chemiluminescent Reactions

The most useful chemiluminescent reactions fall into a restricted number of categories.

3.6.1.1 Luminol Oxidation

The best known and most useful of the chemiluminescent reactions is the oxidation of luminol (3.80) or its derivatives in alkaline medium, with liberation



(3.80)

Figure 3.35 Reaction of luminol oxidation.

of bright-blue luminescence. The oxidant can be hydrogen peroxide, sodium ferricyanide or hypochlorite, usually with a catalyst that can be a transition metal ion, such as Cu^{2+}, Co^{2+}, Fe^{3+} or Mn^{3+}, or haem and haemproteins such as peroxidases. The reaction mode is shown in Figure 3.35.[173]

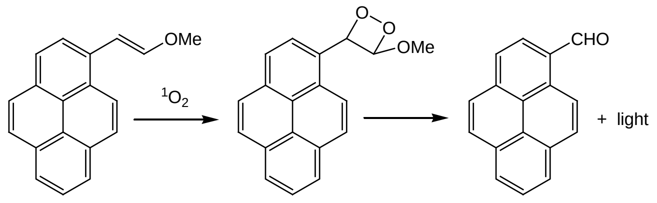
Quantum yields from luminol are only around 1%, limiting its sensitivity and applicability. Replacing the amino group with a nitro or chloro group leads to a decrease in the luminescence intensity, whilst alkylation of the amino group renders it non-luminescent.

3.6.1.2 Acridinium Compounds

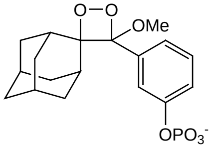
The best-known chemiluminescent acridinium derivative is lucigenin (10,10′-dimethyl-9,9′-biacridinium dinitrate; 3.49). The reaction with alkaline peroxide produces *N*-methylacridone, with emission of blue light at 442 nm.

3.6.1.3 Dioxetanes

A large number of chemiluminescent reactions involve cyclic peroxides, especially the very strained 1,2-dioxetanes. The pyrene vinyl ether (3.81) reacts readily with singlet oxygen to generate an unstable dioxetane (3.82), which decomposes to excited pyrene carbaldehyde (3.83). The emitted light can be measured and is a sensitive assay for singlet oxygen down to concentrations as low as nM, in both bio and non-bio environments.[174] Other sources of active oxygen do not interfere.

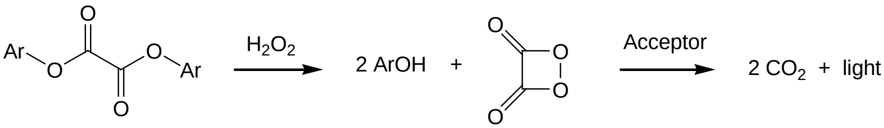


(3.81) (3.82) (3.83)



(3.84)

The commercially available dioxetane AMPPD (3.84) is a stable chemiluminescent probe.[175] Its stability is provided by the adamantyl group whilst the



(3.85) (3.86)

Acceptor fluorophores:

Blue	9,10-diphenylanthracene
Blue-green	1- and 2-chloro-9,10-diphenylanthracene
Green	9,10-bis(phenylethynyl)anthracene
Yellow-green	1-chloro-9,10-bis(phenylethynyl)anthracene
Green	2-chloro-9,10-bis(phenylethynyl)anthracene
Yellow	1,8-dichloro-9,10-bis(phenylethynyl)anthracene
Yellow	Rubrene
Red	Rhodamine B (unstable in the mixture)
Orange	5,12-bis(phenylethynyl)naphthacene

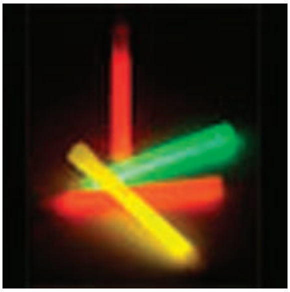


Figure 3.36 The Cyalume process, showing the colours generated by different acceptor fluorophores, and Cyalume sticks.

strained dioxetane ring is the energy source. Hydrolysis of the phosphate ester with alkaline phosphatase produces the adamantyldioxetane phenolate anion, which is less stable and decomposes readily at room temperature with bright-light emission. This chemiluminescent reaction has a quantum yield of between 20 and 30%, and is applied in several types of assay based on phosphate ester hydrolysis.

One of the most important commercial sources of chemiluminescence derives from the reaction of diaryl oxalate diesters (3.85) with H_2O_2. Peroxide hydrolysis leads to the high-energy intermediate dioxetanedione (3.86), which on decomposition in the presence of appropriate acceptor molecules gives a full range of colours (Figure 3.36). This chemistry is the basis of commercial ranges of chemiluminescent lighting systems.[176]

3.6.2 Chemiluminescence Applications

3.6.2.1 Chemiluminescent Analysis

The degree of luminescence of luminol is quantitatively related to the concentration of H_2O_2. Since H_2O_2 is itself produced quantitatively by several enzymatic processes, it can be used as the transducer in luminol-based chemiluminescent assays for various analytes.[111] Analysis of glucose in biological systems can be achieved using a three-enzyme system of mutarotase, glucose oxidase and horseradish peroxidase by correlation with the amount of H_2O_2 released. Similarly, cholesterol is measured using cholesterol oxidase. Other analytes reported include glutamate, lactate, ethanol, choline, lysine, sulfite, xanthine and hypoxanthine, in each case using an appropriate combination of

Table 3.9 Chemiluminescent assays using luminol and its derivatives.

Analyte	*Label*	*Chemiluminescent reactants*
Human IgG	Luminol	H_2O_2 Haemin
Testostorone	Luminol derivative	H_2O_2 Cu^{2+}
Thyroxine	Luminol derivative	Microperoxidase
Biotin	Isoluminol	H_2O_2 lactoperoxidases
Hepatitis B	Isoluminol derivative	Microperoxidases peroxide
Rabbit IgG	Isoluminol	Microperoxidases peroxide
Cortisol	Isoluminol	Microperoxidases peroxide

enzymes. A fibre-optic biosensor for H_2O_2 has been made by immobilising peroxidases on a polyacrylamide gel containing luminol on the end of the fibre. With no light source required the sensor could be connected directly to a photodiode detector. The limit of detection is reported to be 1 µM H_2O_2 with a response time of 2 minutes.[177] Some examples of the use of luminol, isoluminol (6-amino isomer of luminol) and their derivatives in immunoassays are shown in Table 3.9.[178]

Antioxidants in wine can suppress luminol chemiluminescence.[179] The effect has been proposed as a method to quantify total antioxidant capacity of wine, and therefore its quality and potential to modulate the negative effects of ambient free radicals on ageing and health.

The fact that the rate of luminol oxidation depends on the concentration of the catalyst can be used as a method for determination of Co^{2+}, Fe^{3+}, Cr^{3+} and Mn^{3+} and other catalytic metal ions.[180,181,182] The sensitivity of luminol oxidation to metal catalysts is also the basis for its forensic application in detecting trace amounts of blood (haem catalyst of chemiluminescence), and is sold under the trade name Hemaglow. A blue glow lasting about 30 seconds is evidence for blood (or, unfortunately, one of several competing materials that may also induce chemiluminescence).[183]

3.6.2.2 Chemiluminescent Lighting

The diaryl oxalates depicted in Figure 3.36 form the basis of chemiluminescent lighting. A solution of the chemilumophore in a sealed glass ampoule is immersed in a solution of H_2O_2 and other reagents inside a sealed flexible plastic tube. Bending the tube snaps the glass ampoule, enabling mixing of all components and generation of coloured light (Figure 3.36). Devices based on this principle find application in many fields. The Cyalume website lists many military and civilian uses: signalling, search and rescue; evacuations; illumination of stairways and walkways; marking routes and obstructions, accidents, exits, checkpoints, landing zones, hazardous materials; medical triage; personnel ID; safety kits; work lights, confined space lighting, explosive atmospheres; surveillance, perimeter control; underground surveying; underwater diving torch and marker and fishing lights; firefighting.[176(a)] Many of these concern emergency and other scenarios where risk of explosion due to sparking must be avoided. Besides these serious applications, the same chemistry is used in party lights and related luminescent toys.

Omniglow sell what they refer to as a "bovine beacon".[176(b)] This is a chemiluminescent light device which is stuck to the back of a cow to reveal when she has mated. The weight of the bull is sufficient to break the glass ampoule inside the flexible plastic device, initiating a readily visible signal which alerts the farmer.

3.7 Bioluminescence

Bioluminescence is the production of light by living systems. The best-known example of this phenomenon is the characteristic glow of the firefly, but other luminous species include bacteria, fungi and especially marine organisms such as jellyfish, scaleworms, deep-sea squid, prawn and fish. Bioluminescence is relatively uncommon amongst terrestrial life, but very common in the oceans.[184] In animals bioluminescence is used as a diversionary tactic when disturbed or threatened, to attract prey or a mate, as camouflage, as a means of communication and – rarely – as a means of illumination.

Bioluminescence is essentially a chemiluminescent reaction catalysed by a specific enzyme, and is therefore perhaps better termed biochemiluminescence, which is in fact sometimes encountered in the literature. However, to produce bioluminescence in an organic system the substrate must meet the requirements of the particular protein, which are highly specific to its structure. Quantum yields in bioluminescent systems are high, usually in the range of 0.1–0.9, the firefly's chemistry exhibiting a quantum yield of 0.88. The protein catalysts in bioluminescence are all oxidases, with the light emission originating in most cases by the oxidation of a substrate by oxygen or hydrogen peroxide.

3.7.1 Bioluminescent Systems

A bioluminescent system requires a luciferin, which is the molecule that eventually gives rise to luminescence, and a luciferase, which is the enzyme that catalyses the luminescence process. The structures of the luciferins and luciferases depend on their source in Nature. Four examples are introduced here, three of which are being used as the basis for derived technology.

3.7.1.1 Firefly Luciferins

The firefly luciferin, the structure of which is based on two thiazole units (3.87), undergoes a luciferase catalysed oxidation with the emission of light (562–570 nm), in the presence of the co-factor MgATP (adenosine triphosphate). The chemical processes leading to light emission are shown in Figure 3.37.[185] Luciferin reacts with MgATP, eliminating pyrophosphate to form luciferyl adenylate (3.88), which reacts with oxygen in a two-stage process to produce a dioxetanone intermediate (3.89) with elimination of AMP. The reactive

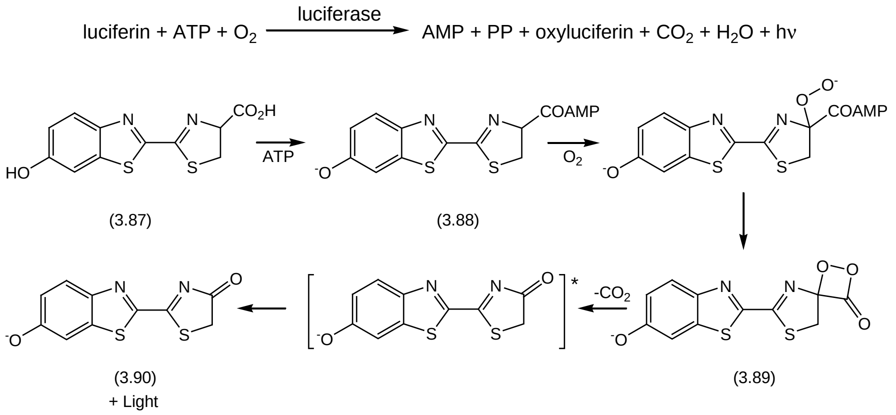
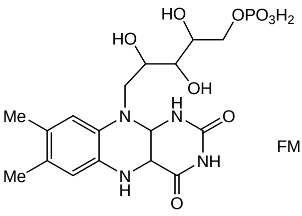


Figure 3.37 Mechanism of luminescence in firefly luciferin.

dioxetanone then decarboxylates to give the excited state of oxyluciferin, which returns to its ground state (3.90) with the emission of light.

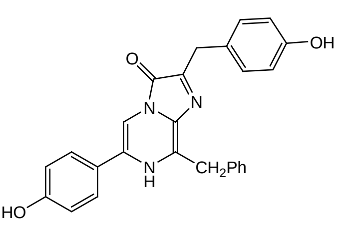
3.7.1.2 *Bacterial Luciferases*

Luminous bacteria are found under a variety of guises. They are present on higher animals, which stimulate them to glow *via* special light organs or in their intestinal gut, and in a variety of organisms living in the oceans. The angler fish's luminescent lure comprises captive bioluminescent bacteria. The bacterial luciferases react with aldehydes and oxygen, in the presence of reduced flavins, such as $FMNH_2$ (3.91), to produce carboxylic acids and an oxidised flavin FMN with the emission of blue light (478–505 nm).



(3.91)

$$FMNH_2 + O_2 + RCHO \xrightarrow{\text{luciferase}} FMN + RCO_2H + H_2O + h\nu\ (490\ \text{nm})$$



(3.92)

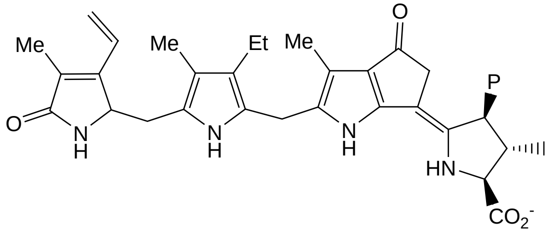
3.7.1.3 *Imidazopyrazine Luciferins and Photoproteins*

The imidazopyrazine substructure typified by the coelenterazine luciferin (3.92) occurs in luciferins from a wide range of organisms living in the sea and in ostracod crustaceans, *e.g. Cypridina*. The chemistry of the luminescent effect in these systems involves reaction with oxygen to form a cyclic dioxetanone, analogous to the firefly luciferin. Decarboxylation of this intermediate on reaction with a trigger produces the activated oxyluciferin intermediate, which emits light on returning to the ground state.

Coelenterazine (3.92) is the prosthetic group of photoproteins found in aquatic organisms *e.g*. aequorin from the jellyfish *Aequorea Victoria*. This emits blue light on the addition of Ca^{2+} at a wavelength of 469 nm. In the case of the luciferin of *A. Victoria*, or the sea pansy, *Renilla*, the green luminescence at 509 nm that is observed *in vivo* is due to the transfer of energy from the excited oxyluciferin to the green fluorescent protein (GFP; Section 3.5.10.1), with which it forms a complex. Thus in these organisms light is generated by a bioluminescent protein system and emitted by a separate biofluorescent protein.

3.7.1.4 Dinoflagellates and Marine "Phosphorescence"

Dinoflagellates are marine microorganisms, some of which are capable of photosynthesis, and which contain various chlorophylls. Coloristically they are perhaps best known as the source of "red tide" and also the misnamed "phosphorescence" sometimes observable as a blue glow within the sea at night. In fact, the source of the blue light has nothing to do with "phosphorescence" (or fluorescence) but is another manifestation of bioluminescence, brought about within the organism when it is disturbed, such as in crashing waves, or in the water churned up by a ship's propeller, or even the splashing of a swimmer's arms. Tribobiochemiluminescence might therefore be a more accurate term. The luciferin is the linear tetrapyrrole derived from chlorophyll (3.93).



(3.93) The dinoflagellate luciferin

3.7.2 Applications of Bioluminescence

3.7.2.1 Bioluminescence in Analysis

The firefly luciferin system is very sensitive and can be coupled to any enzymatic reaction that produces or uses ATP. The limit of detection can be as low as picomolar. For example, creatine phosphokinase can be determined by this method and hence be used in the diagnosis of myocardial infarction and muscle disorders. The creatine phosphokinase converts AMP to ATP which then undergoes the reaction with luciferin as shown in Figure 3.37. ATP production is essential for every known life form and the firefly luciferin system can be used to check for microbial life. Hence systems have been developed that use a portable luminescence workstation to monitor sanitation in food manufacturing and to check for sterile environments in technological workplaces. The system can also be applied in checking cell viability, for instance in cell cultures and to measure the toxic effects of chemicals on cells.

Bacterial luciferase has been used as the basis of bioluminescent biosensors for sorbitol, ethanol, lactate dehydrogenase and oxaloacetate.[111] The sensitivity of the imidazopyrazine biolumophore system to Ca^{2+} led to its early development as an *in vivo* assay for Ca^{2+}.

The firefly luciferase gene was isolated and cloned in the 1980s and this has allowed it to be used in an increasing number of applications in the biological and medicinal areas.[186,187,188] The genes that encode luciferase have been transferred into cells from other organisms by standard molecular biology techniques. On introduction into the cell all other daughter cells are tagged with the bioluminescent properties and are replicated as the cell divides. These can be modified in ways that mean that they will only be expressed in cells under certain conditions and hence can be used to indicate whether a gene is active in a cell. They have been called "optical reporter genes".[188]

Biosensors based on whole cells genetically engineered to express bioluminescent species have also been developed to respond to various analytes such as Hg^{2+} (LOD fM), Cu^{2+} and aromatic hydrocarbons.[111]

3.7.2.2 *Bioluminescence Imaging*

DNA encoding for a luminescent protein from one of the three firefly, bacterial or sea anemone bioluminescent systems described above is introduced into a laboratory animal, either by a virus or by creating a transgenic animal. In one example, luciferin is added as an initiator of bioluminescence to the blood supply. When the blood reaches a cell engineered to carry the firefly gene, light is emitted. The effect of drugs designed to choke off blood supply to cancerous cells can therefore be monitored by imaging with a sensitive camera.[189] Other applications include *in vivo* studies of infection, and cancer progression.

3.8 Electrochemiluminescence

Electrochemiluminescence, or electrogenerated chemiluminescence (ECL), is the phenomenon whereby light results from a chemical reaction based on excited species derived by anodic oxidation and/or cathodic reduction. Many species luminesce when electrolysed, and ECL has given rise to an important analytical technology. The topic is dominated by the chemistry of Ru(II) species, especially analogues of the parent 2,2′-bipyridyl complex $Ru(bipy)_3{}^{2+}$.

3.8.1 The Chemistry of Electrochemiluminescence

Various mechanisms underlie ECL. The earliest and simplest involves ion annihilation. Ru(II) ions are simultaneously oxidised and reduced, and the resultant Ru(III) and Ru(I) species interact to regenerate Ru(II) ions, one in its ground state, the other in an electronically excited state. The latter emits light as it reverts to its GS.

Anodic oxidation	$Ru^{2+} - e \rightarrow Ru^{3+}$
Cathodic reduction	$Ru^{2+} + e \rightarrow Ru^{+}$
Ion annihilation	$Ru^{+} + Ru^{3+} \rightarrow Ru^{2+} + [Ru^{2+}]^{*}$
Luminescence	$[Ru^{2+}]^{*} \rightarrow Ru^{2+} + h\nu$

In practical application, this chemistry has been superseded by a co-reactant process. In this the active species (the emitter) is electrolysed alongside a further species which plays a central part in the chemistry leading to an excited state of the emitter. The mechanism can become very complicated, and recent reviews should be consulted for more detail.[190,191] The following simplified description is sufficient to underpin further description. Various co-reactants have been developed, but again a favoured system has come to the fore, involving tertiary aliphatic amines. A simplified reaction scheme for the commonly used tri-*n*-propylamine (TPrA) involves the following steps.

Co-reactant oxidation	$TPrA - e \rightarrow TPrA^{\bullet +}$
Deprotonation	$TPrA^{\bullet +} - H^{+} \rightarrow TPrA^{\bullet}$
Emitter reduction	$TPrA^{\bullet} + Ru^{2+} \rightarrow X + Ru^{+}$
Generation of excited emitter	$TPrA^{\bullet +} + Ru^{+} \rightarrow TPrA + [Ru^{2+}]^{*}$
Luminescence	$[Ru^{2+}]^{*} \rightarrow Ru^{2+} + h\nu$

In this scheme the emitter is continuously recycled, but the co-reactant is gradually destroyed (X, above). In other ECL variants, the Ru(II) species is itself also involved in anodic oxidation, as well as the co-reactant, and the reaction sequences become increasingly more complicated. ECL emission wavelength from excited Ru(II) depends on its ligands, the nature of the co-reactant, solvent and other physical conditions, but is usually in the red at about 600–620 nm. Ru(II) has retained its initial popularity in ECL systems because of its strong luminescence and solubility in a range of both organic and aqueous solvents at room temperature, and its ability to undergo a range of one-electron transfer reactions at easily attainable potentials. Ligand modification opens up the possibility of covalently attaching the emitter to other molecules for assay development (below).

A range of tertiary amines can be used as co-reactant as long as they possess at least one α-H atom (the source of oxidised amine deprotonation in the second step shown). Common alternative co-reactants are oxalate and persulfate ($S_2O_8^{2}$) anions. Other metal ions behave as emitters in ECL chemistry; the main alternative to Ru is Ir, usually luminescing somewhat to the blue of Ru. Besides metal ions, a wide range of organic luminophores undergo ECL, but have attained minimal technological significance. Most recently, semi-conductor QDs have been shown to luminesce in both annihilation and co-reactant ECL processes. The wavelength of ECL emission from capped QDs does not match their usual photofluorescence energies, but rather corresponds to the wavelength anticipated for the material comprising the outer surface layer.

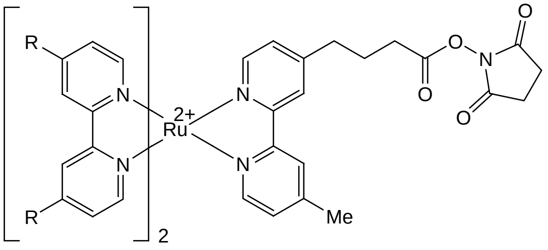
3.8.2 Analytical Technology Based on Electrochemiluminescence

ECL electrode configuration has been miniaturised, and in combination with the intrinsic intensity of ECL emission and the sensitivity of light measurement devices (photodiodes, photomultipliers or charged coupled device cameras), a variety of integrated analytical ECL instruments and methodologies has been developed and sold commercially as an important analytical technology. ECL offers various advantages over photoluminescence methods for analysis in the bio area in particular.[192,193] There is no requirement for an external light excitation source, usually a laser. And because of this, there is no concern about background autofluorescence of bio samples. The luminescence signal being measured derives purely from the emitter and is therefore much clearer. On the other hand, *in vivo* analysis or imaging is not possible because of the need for an electrode.

ECL is used as a detector methodology for a variety of standard separation and analysis techniques, including capillary electrophoresis, HPLC and flow-injection analysis. In co-reactant mode the analyte of interest must be a secondary or tertiary amine. Carboxylic acids are also suitable once functionalised as amides containing pendant tertiary amine groups. Amino acids are best functionalised with aldehydes, to give 20–70-fold increase in sensitivity. The Ru(II) emitter may be applied to the analyte stream, or is immobilised on an ECL detector. Limits of detection for many pharmaceutically related amines can be down to nM concentration, while for functionalised carboxylic acids LOD has been reported down to fM. Advantages of ECL detection are high resolving ability, selectivity, high sensitivity, easy sample preparation, fast data measurement and no interference.

Many solid phase ECL assays have been developed for various bio species, including peptides, proteins and DNA. These analytes do not necessarily contain the required co-reactant functionality, so co-reactant must be added to the analyte matrix. The analyte recognition chemistry underpinning the solid phase configurations is extensive, and very reminiscent of methods already encountered in fluorescence-based assays (Section 3.5.8.2). It is invariably necessary to covalently label either the analyte or the analytical host, and Ru(II) complexes have had to be designed and synthesised for this purpose.

Example commercial tags based on activated esters are shown as structures (3.94) and (3.95).



MSD (sulfo-)TAG $^{(TM)}$ NHS-esters
(3.94) R = $CH_2SO_3^-$
(3.95) R = H

A DNA hybridisation assay is shown in Figure 3.38(a). In this a host ssDNA unit designed to recognise a particular target ssDNA analyte is immobilised on an electrode (frequently carbon). The analyte matrix is tagged with an ECL luminophore during a pre-treatment step. Recognition leads to hybridisation bringing the tag into the proximity of the electrode surface. In the presence of the added co-reactant ECL is generated and the ssDNA analyte may be quantified. The method has high sensitivity for full base-pair matching and the LOD of ssDNA analysis can be as low as fM. A single base-pair mismatch can still give a weaker ECL signal, whereas more than one mismatch results in zero ECL.

In another example, a target protease enzyme can be measured by tagging a suitable peptide substrate and immobilising on an electrode. Protease concentration is determined by measuring the decrease in ECL as it cleaves the peptide and liberates the tag from the electrode and into the matrix where it is no longer sufficiently close to the electrode to demonstrate ECL (Figure 3.38(b)).

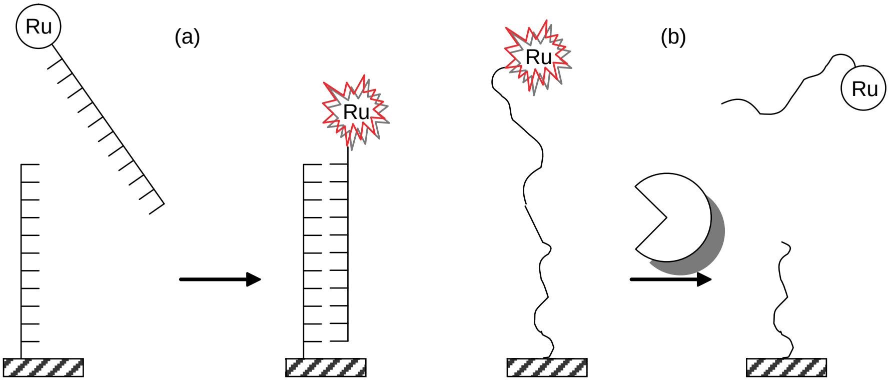


Figure 3.38 (a) Host ssDNA immobilised on an electrode hybridises with target ssDNA and switches on its ECL tag. (b) A tagged ECL active peptide immobilised on an electrode is specifically hydrolysed by a target protease and the ECL is switched off. Co reagent is present throughout but not shown.

ECL technology for antibody-antigen assays is well developed; Meso Scale Discovery[191] offers about 150 immunoassays. Figure 3.20 in Section 3.5.8.2 describing a sandwich-type fluorescence immunoassay can be applied equally to the ECL case. The solid platform shown now represents an electrode, and the fluorophore becomes an ECL emitter.

The sensitivity of ECL can be further increased by loading multiple labels onto micro-sized polystyrene spheres, silicon nanoparticles, carbon nanotubes or immobilised AuNP.

Overall, the range of applicability of ECL analysis in bio-medicine and elsewhere is extensive, with examples from amongst amino acids; drugs; clinical, food, water and bio-agent analytes; toxins; biomarkers for diseases; pathological conditions in pregnancy; various antibodies; and bacteria.[190,191] A realistic future aim is claimed to be single bio-molecule detection.[191]

3.9 Electroluminescence

Electroluminescence (EL) involves the conversion of electrical energy into non-thermal light. The materials used to achieve this conversion can be either inorganic or organic. Inorganic high-field powder phosphor electroluminescence materials are insulating II–VI compounds. Low-field light-emitting diodes (LEDs) are constructed from monocrystalline semi-conducting materials, mostly III–V compounds.[194] Organic LEDs (OLEDs) are made from either thin films of vapour-deposited low-molecular-weight materials or conjugated polymers put down by spin coating or other means. Laser diodes which are closely related to LEDs are covered in Chapter 5 (Section 5.5).

The utilisation of EL in lighting applications and display devices has been a major commercial success story over the last 20 years. Currently, the majority of lightweight flat-panel displays are active matrix liquid crystal displays (see Chapter 5, Section 5.2), but they have certain shortcomings, including the need to provide constant illumination to the screen by a back light, which in itself has proved to be an important outlet for white-light powder EL and LEDs. Displays based on thin film EL have the advantage of giving bright colours as needed with the power on and are black in the off state. Initially the materials used in these display outlets were inorganic but in recent years organic LEDs (OLEDs) and polymer light-emitting diodes (PLEDs) have been developed and led to commercial products.

3.9.1 Inorganic EL Materials and Displays

High-field inorganic electroluminescent display devices (EL) are made from insulating materials, where the active material is a II–VI compound, *e.g.* ZnS, and rely on an electrical breakdown for the excitation process. The mechanism of EL display involves electrons entering the phosphor at the junction with the insulating coating. They are then accelerated under the influence of high-electric-field materials, colliding with luminescent centres in the phosphor and transferring energy. The activated luminescent centres then fall back to the ground state releasing energy as visible light.[195] There are two broad classes of EL displays, with different areas of application: powder displays are the oldest and have found uses in devices for signalling and lighting applications, and the more successful thin film devices, which are used in high-information-content displays. They are further classified in respect of current, either AC (ACEL) or DC (DCEL).

3.9.1.1 Powder EL (PEL)

Although discovered in 1936 by Destriau, high-field EL was not really investigated in a practical way until the 1950s and 1960s when NASA used small alphanumeric devices in the modules of their space programme. However, there are serious problems with the maintenance and lifetimes of PEL devices and, with the advent of thin-film EL (TFEL), they are nowadays mainly used in low-information-content applications although back-lighting applications have been claimed. A typical DC PEL device is shown in Figure 3.39. The active material is ZnS powder doped with copper and possibly other elements such as chlorine and manganese, held together with an organic binding material. Standard colours are green, blue-green, white and yellow depending on the dopant (see also Section 3.2).[196]

3.9.1.2 Thin-film EL

Early work in the 1960s on thin-film EL (TFEL) involved the excitation of Al/ZnS (activated by Mn or Cu) deposited on glass, but the key step forward was taken when the double-insulator structure was developed as shown in Figure 3.40. The ZnS film is sandwiched between two insulating layers, limiting the amount of charge transferred to the device and also totally encapsulating the phosphor film. In spite of this the EL device still suffered from lifetime problems and it was not

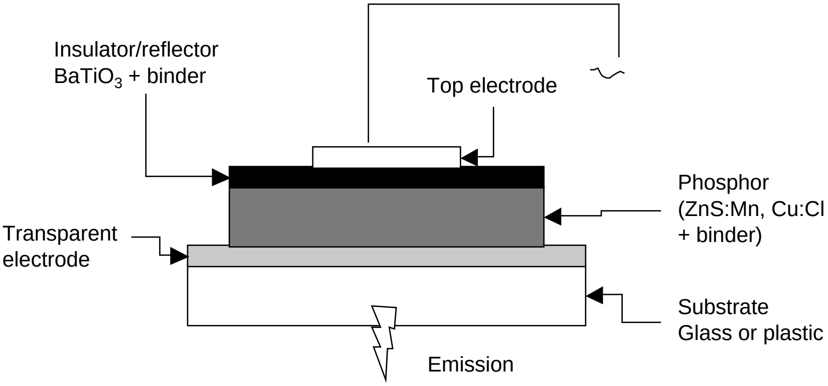


Figure 3.39 DC powder phosphor EL device.

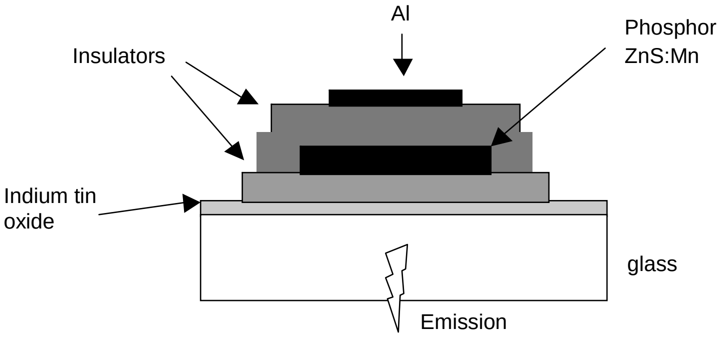


Figure 3.40 AC thin film EL device.

until 1978, when Sharp demonstrated a 240×320 display, that this problem was overcome.

The operating principle of a TFEL display is as follows. The dissolved Mn atoms in the ZnS lattice are subjected to direct impact excitation by electrons that have been accelerated in an electric field of 1.5–2 MV cm ^{1}. Electrons then escape by tunnelling from interface states located at the ZnS/insulator interface into the conduction band of the ZnS. The key processes in the TFEL device are the injection and acceleration of electrons of sufficiently high energies and the subsequent impact excitation of a Mn atom. The excited Mn can return to the ground state radiatively or, undesirably, non-radiatively, as is the case at high Mn concentrations. Finally the emitted photon must escape from the thin-film structure. Some 20% of such photons can escape if the surface of polycrystalline ZnS layer is roughened, thus encouraging scattering of the trapped photons.

It is possible to obtain red, green and blue phosphors for TFEL, thus giving the potential for full-colour displays to be constructed. The classical ZnS:Mn is an efficient thin-film phosphor used in most, if not all, of the commercial monochromatic products. It has a broad yellow-orange emission centred around 580 nm, and is generally used with a filter to produce red. By replacing some of the Zn by Mg the wavelength can be shifted to the green but the most efficient green phosphor is made from ZnS:Tb. The requirement of a stable blue phosphor of high-colour purity was met in the early 1990s by using alkaline earth thiogallates (MGa_2S_4; M = Sr, Ca, Ba) as host for a cerium activator, *e.g.* $(CaSr)Ga_2S_4$:Ce.

There are basically two methods of constructing full-colour TFEL displays. The first involves putting the RGB colour phosphor pixels next to each other in the "patterned" or "structured phosphor" approach. Excitation of the phosphors to give R, G or B luminescence is obtained by varying the voltage distribution between the aluminium and indium tin oxide electrodes. The second method involves using a white-light-emitting phosphor, and a series of colour filters in the so-called "colour by white" system. Several variants on the system have been developed but most use ZnS:Mn/SrS:Ce as the phosphor.[197] The two methods are shown schematically in Figure 3.41.

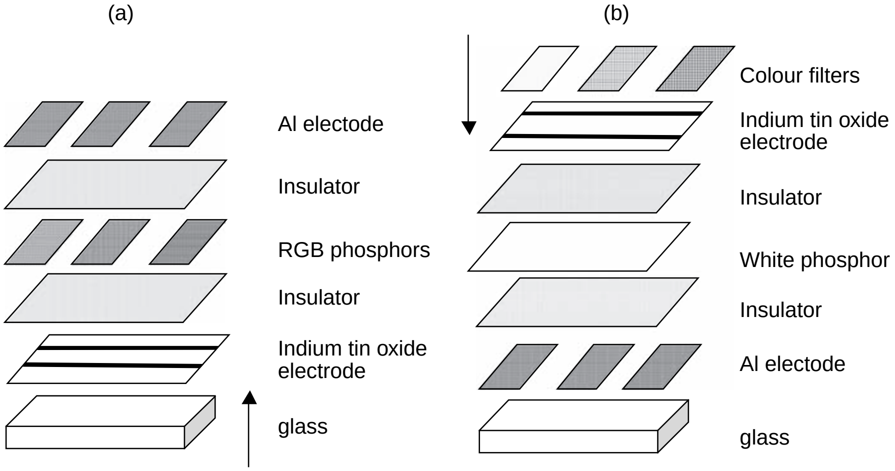


Figure 3.41 Schematic ACTFEL display: (a) patterned approach (b) colour by white (reproduced with permission of John Wiley and Sons).

Table 3.10 Luminance levels for "patterned phosphor" and "colour by white approach" (60 Hz)[198] (reproduced with permission of Springer Science and Business Media).

Material	*Emission colour*	*CIE coordinates*		*Luminance* (*cd* m^{-2})
		x	*y*	
ZnS:Mn/filtered	Red	0.65	0.35	75
ZnS:Tb	Green	0.32	0.60	125
$CaGa_2S_4$:Ce	Blue	0.15	0.19	10
ZnSMn/SrS:Ce	"white"	0.39	0.48	340
filtered	Red	0.65	0.34	39
filtered	Green	0.20	0.61	90
filtered	Blue	0.10	0.26	18

In terms of performance the patterned phosphor approach offers advantages in luminance and efficiency, since the colour by white has losses in the colour filters (see Table 3.10).[198] In theory the colour by white system should be easier to manufacture because of a simpler monochrome methodology *versus* the additional photolithographic steps. More recently a "colour by blue" method has been suggested as an alternative to the patterned phosphor approach.[199]

3.9.2 Semi-conductor Light-emitting Diodes (LEDs)

Conventional semi-conductor LEDs are made by growing a region of n-type semi-conductor material doped with donors, and p-type semi-conductor material doped with acceptors, as a single crystal. This is shown

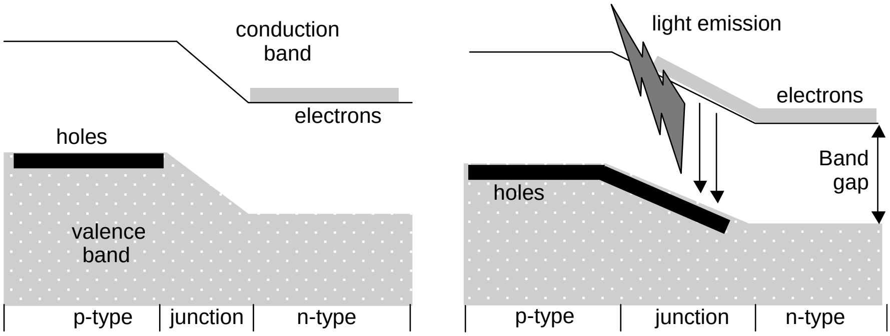


Figure 3.42 Schematic for semi conductor LED. Left: equilibrium situation; right: influence of applied potential.

diagrammatically in Figure 3.42.[200] At equilibrium, the charge in the junction region prevents movement of electrons and holes. By applying a forward bias, or positive charge, to the p-type side of the junction electrons are injected into the p-type region (anode) and holes into the n-type region (cathode), combining in the junction region with the majority carriers, leading to emission of light with an energy approximately equal to the band-gap. (Note: a material is classified as a semi-conductor when the band-gap energy lies in the range of 0.1–6 eV).

3.9.3 LED Materials

In 1961 it was discovered that gallium arsenide (GaAs) p-n diodes emitted infrared light when a current was applied, leading to the award of the first LED patent and commercialisation by Texas Instruments. Commercially usable coloured LEDs were developed shortly afterwards by General Electric following the work of Nick Holonyak, who used gallium arsenide phosphide (GaAsP) to obtain a red light source at 655 nm.[201] Orange, yellow and green LEDS followed quickly using different semi-conductor materials and dopants. Although these early LEDs were a breakthrough technology, they suffered from relative unreliability in use. AlGaAs (aluminium gallium arsenide) developed in the 1980s offered superior performance and brightness over 10 times greater than standard LEDs. AlGaInP, developed in the late 1980s, is a luminescent material which allows flexibility in the design of LED output colour simply by adjusting the size of the energy band-gap. Consequently, green, yellow, orange and red LEDs can be produced using the same basic technology.

Today the most commonly used materials for red-yellow and NIR LEDs are GaP, GaAsP, AlGaAs, AlGaAsP and AlGaInP (Table 3.11).[202]

Development of blue-green and UV emitters proved to be the most difficult area and was only successfully addressed after the pioneering work by Isamu Akasaki at Nagoya and Shuji Nakamura at Nichia Chemical Company in

Table 3.11 LED materials and colours.

Colour of Light Emitted	*Wavelength λnm*	*Semi conductor materials*
Infrared	>760	GaAs, AlGaAs
Red	610 760	AlGaAs, GaAsP, AlGaInP, GaP
Orange	590 610	GaAsP, AlGaInP, GaP
Yellow	570 590	GaAsP, AlGaInP, GaP
Green	500 570	InGaN/GaN, GaP, AlGaInP, AlGaP
Blue	450 500	ZnSe, InGaN,
Violet	400 450	InGaN
Ultraviolet	<400	AlN, AlGaN, AlGaInN
White	Broad spectrum	Blue/UV diode with phosphor

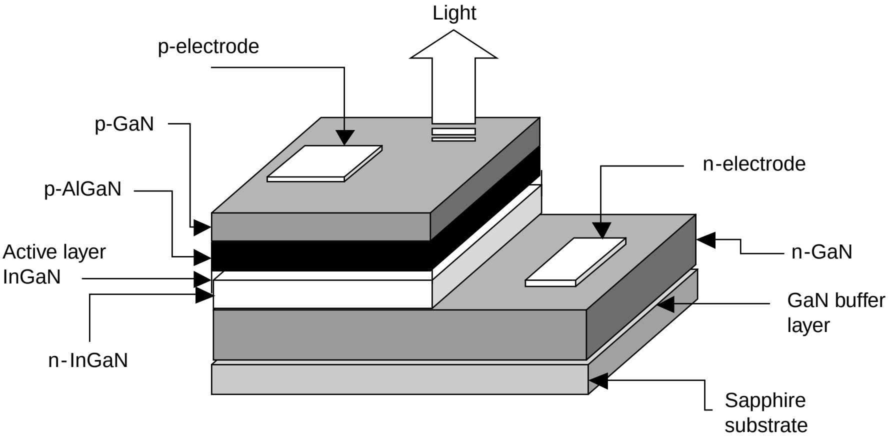


Figure 3.43 Schematic of top emitting blue LED (reproduced by permission of the Society of Chemical Industry).

Japan in 1995. This led to highly efficient blue gallium nitride (GaN) based diodes commercialised in 1997, with lasers following in early 1999 (see also Chapter 5, Section 5.5).[203] The process involves use of metal organic vapour phase epitaxy (MOVPE) to produce the high-quality GaN crystalline films, with p-doping by irradiating the GaN with low-energy electrons or by thermal annealing in a nitrogen atmosphere. The preferred materials are GaN, InGaN and AlGaN and a typical structure of a blue top-emitting LED is shown in Figure 3.43. But much more efficient structures have been demonstrated by combining flip chip mounting, substrate removal, reflective metal contacts and surface texturing. Constructing LEDs with active quantum well layers of GaN instead of alloyed InGaN or AlGaN gives devices which emit near UV-light wavelengths (350–370 nm).

Quantum dots (QDs) are semi-conductor nanosize particles that combine size-controlled emission colours and high emission efficiencies with excellent photostability and chemical flexibility (see Section 3.5.2.1). Using QDs to

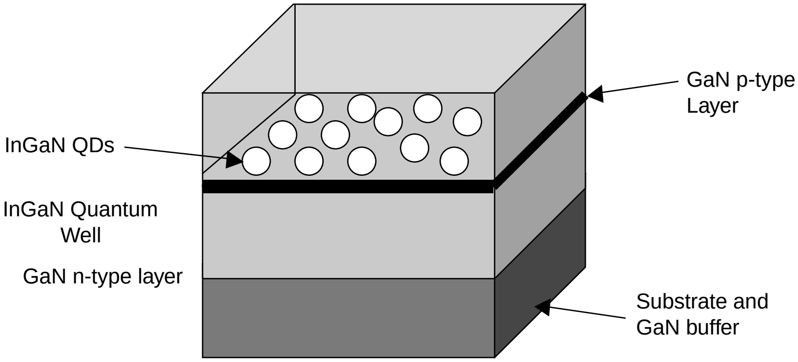


Figure 3.44 Schematic of Quantum Dot Heterostructure LED.

construct LEDs (QDLEDs) is a very active area with a variety of ways being examined. For instance at Los Alamos Laboratory they incorporate QDs into a p-n junction formed from GaN injection layers by energetic neutral atom beam lithography/epitaxy, a novel deposition technique allowing encapsulation of the QD within the matrix without adversely affecting its integrity or emission efficiency. Charge injection into the QDs from both p-type and n-type GaN layers is achieved by biasing the junction above the threshold voltage.[204] A schematic of a QDLED constructed using InGaN QDs is shown in Figure 3.44. Another method is to prepare colloidal dispersions of QDs and incorporate these in a host matrix such as polystyrene, polyimides and epoxy resins.[205]

3.9.4 Applications of LEDs

LEDs as single-colour status indicators on a variety of instruments, as displays, especially alphanumeric ones on instruments, on outdoor billboards and other displays where they are used in arrays, are universal. However, the development of efficient blue-green LEDs making it possible to cover the whole spectrum of the eye's response has widened the application potential of these devices.

3.9.4.1 Coloured Lighting

The use of red LEDs as bright warning lights, such as those on the rear of cars, trucks, motorbikes and bicycles, has been common for many years. Use as road traffic lights and related pedestrian signals had to await the development of efficient bright green LEDs. Once achieved the LED lights had reduced power consumption and longer lifetimes compared to conventional colour-filtered incandescent bulbs, offering enormous savings in energy (around 40%) and labour costs. As a result in most developed countries, new and replacement traffic lights are LEDs. An additional advantage for LED lights is that they fade gradually with time rather than suddenly failing and so offer an early warning of the need for replacement.

3.9.4.2 White Lighting

Artificial light is so highly desirable that we consume huge amounts of energy in its production, estimated as 8.9% of total global primary energy in 2003. Consequently any reduction in energy consumed in artificial lighting is extremely valuable in both cost to the consumer and impact on the environment, and this is where LEDs have an important role to play.[206] White light LEDs are constructed in three main ways:

- Use of high-intensity blue InGaN LEDs and phosphors, *e.g.* $Y_3Al_5O_{12}$:Ce, which give a yellow fluorescence to mix with the blue. Known as "blue-YAG white" they offer a more compact route to white light LEDs and are the most successful commercially.[207]
- Combination of two or more phosphors, covering the blue and red spectrum, applied to UV or violet LEDs (365–420 nm).[208]
- Mixing three primary colours from separate red, green and blue LEDs without involvement of phophors.[209]

These types of devices, especially blue-YAG white, have found many applications as replacements for conventional light bulbs and lamps, *e.g.* in domestic and business buildings, in automobile lighting systems and in novelty outlets such as low-energy Christmas tree lights. Street lighting is an enormous area for the application of new forms of artificial light. Unlike sodium lamps LEDs can focus all of their power in a chosen direction, so less energy is wasted in illuminating the sky and upper levels of buildings.

As mentioned above QDs give very bright emission on activation. This property has been exploited in the construction of white hybrid LEDs by coating the surface of an InGaN blue LED with a dispersion of yellow-light-producing CdSe QDs in a polyurethane resin.[210] Photonic crystal LEDs (PXLED) are another development showing promise for improvements in light production. Periodic structures, such as a lattice of holes, are etched on the surface of top-emitting LEDs. These photonic crystals (see Chapter 5) manipulate the light emitted from the LED with greater directionality leading to increased brightness (Figure 3.45).[211,212]

3.9.4.3 Lighting for Displays

Back lights or edge lights for full-colour LCD displays in mobile phones and MP3 players, PCs and laptops, and flat-panel TVs are an important outlet for LEDs. Displays on mobile phones and other hand-held devices were initially yellow-green, but now blue and white LED back lights are more common. The LED LUX back lighting system for flat-panel displays from Phillips uses an array comprising a total of 1152 RGB LEDs, split into 128 segments. Each of the 8 rows contains 16 segments, with 9 LEDs in each segment. These LEDs can be individually dimmed to precisely control the output of each pixel. Edge lighting, which allows construction of much thinner display units, employs

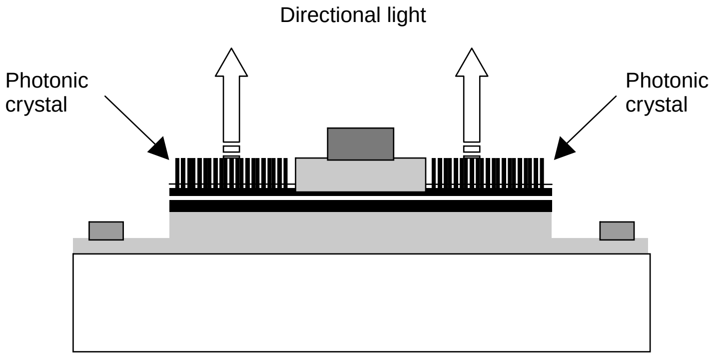


Figure 3.45 Schematic of a photonic crystal LED.

white light-emitting phosphor-based LEDS situated along the edges of the panel.

3.9.4.4 LED Displays

Large-scale LED displays are very common in outdoor public areas such as pedestrian plazas, and at sporting venues and music festivals. For instance, one installed in Times Square in 2005 was a 51.2×52.5 foot display integrating 1280×1248 LEDs to output the HD image using pixel-sharing technology developed by Toshiba that uses adjacent pixels to create virtual pixels. Technology more suited for application in conventional HDTV uses digital light processing (DLP) to manipulate the light coming from three separate arrays of R, G and B LEDs onto the display panel.[213]

3.9.5 Organic Light-emitting Diodes Introduction

In the last decade one of the most significant developments in luminescent phenomena, both scientifically and commercially, has been the use of organic materials in light-emitting diodes (OLEDs). Although electroluminescence in organic compounds has been known since the 1950s it was not until 1987 that an efficient device based on a multi-layer of small organic molecules was devised by workers at Kodak,[214] followed shortly afterwards by its production using conjugated polymers by a team at Cambridge.[215] In the intervening period an enormous amount of work has been done, both in academia and industry, resulting in the development of materials and structures that emit RGB light that can compete with plasmas and LCs in the flat-panel display area, and probably more excitingly be used in a new form of white EL lighting.[216,217,218]

The field of OLEDs can be split into five distinct areas:

- Small Molecule OLEDs (SMOLED)
- Polymer LEDs (PLED)

- Dendrimer LEDs (DLED)
- White Light OLEDs (WOLED)
- Hybrid Inorganic Organic LEDs – (down conversion for white light).

One problem, as will be seen, in presenting an overview of the literature in this field is that it is littered with acronyms, both for the systems and the chemicals used to construct the various devices.

3.9.6 Small Molecule OLEDs

The basic structure of a small molecule OLED consists of an emission layer (EML) sandwiched between an electron transporting layer (ETL) and a hole-transporting layer (HTL). However, in practice the structure is often more complicated than this, having extra layers added in order to improve the efficiency of the device. These include blocking layers for holes and electrons (HBL and EBL), and injection layers (HIL and EIL) for both holes and electrons as shown in Figure 3.46. Applying an electric field to the device causes electrons to be injected from the cathode into the LUMO of the material in the ETL and holes from the anode into the HOMO of HTL material. The radical ions that are formed move *via* a charge-hopping mechanism through the electron transport material (ETM) and hole transport material (HTM) to the EML. In this layer the opposite charges combine to give excitons, which radiatively decay resulting in singlet-state fluorescence or triplet-state phosphorescence, depending on the emission materials in the EML.

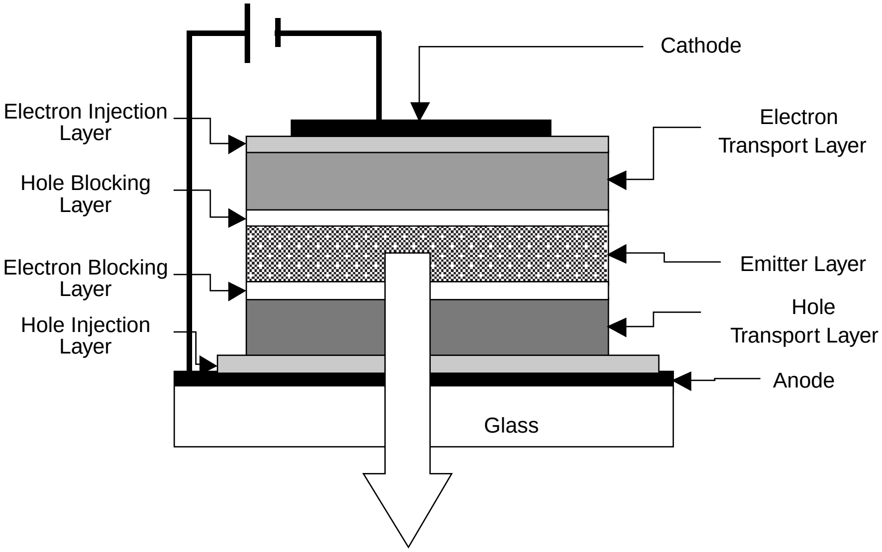


Figure 3.46 Schematic of a multi layer SMOLED.

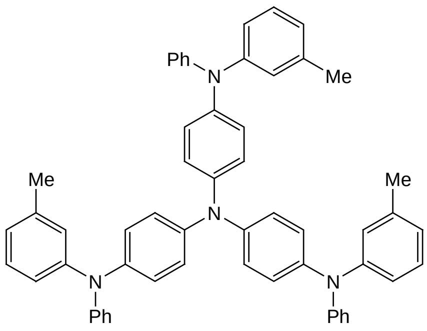
The cathode is generally a pure metal or alloy *e.g.* Ca/Al, and the anode transparent ITO coated onto a glass or plastic substrate. The most common hole injection materials are copper phthalocyanines or conducting polymers such as PEDOT-PSS, polyanilines and polypyrroles. Materials such as LiF and CsF are coated at the interface with the cathode, designed to increase electron injection by lowering the high chemical reactivity of the cathode metals. In the context of this book the three main materials for us to consider in OLEDs are those used in the hole transport, electron transport and emission layers, which form the core layers of the devices.

Another important way of constructing OLEDs is to create a *p-I-n* type semiconductor. This is done by adding dopants, which either donate an electron to the electron-conducting (LUMO) states (n-type doping) in the ETM, or remove an electron from the hole-conducting (HOMO) states (p-type doping) in HTM to generate a free hole. The three layers on the anode are p-doped HTL, EML and n-doped ETL, topped with a cathode. The *p-I-n* type structure is designed to reduce the operating voltage of both fluorescent- and phosphorescent-based devices.

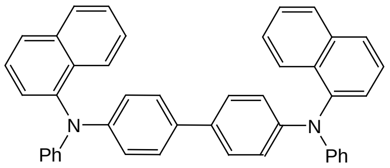
3.9.6.1 Hole Transport Materials

These materials serve as the hole-conducting pathway from the anode to the EML. Consequently, they need to be easily oxidised to the radical cation form but relatively stable after this oxidation. Materials displaying this behaviour were originally developed to act as the charge transport materials in organic photoconductors which are used in photocopiers (Chapter 4; Section 4.4.2 and Figure 4.15), and were adopted for use in the early developments of SMOLEDs. Typical molecules are triphenylmethanes *e.g.* *m*-MTDATA (3.96), α-NPD (3.97), spiro-TAD (3.98) and also poly(*N*-vinylcarbazole).

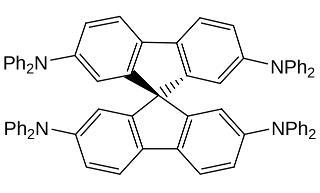
Hole-transport materials can also function as the electron blocking materials in the EBL thus preventing the flow of electrons from the EML to the anode.



(3.96)
m-MDTA



(3.97)
α-NPD



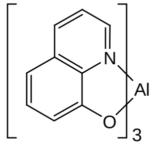
(3.98)
Spiro-TAD

3.9.6.2 Electron Transport Materials

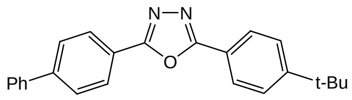
These materials help transport electrons from the cathode to the EML and involve the transient production of anion radicals. A good EML should display the following properties:[219]

- High electron affinity – reducing the energy barrier difference between cathode and emitter.
- Reasonably good electron transport mobility – aiding transport to and confining excitons in the EML.
- Stable electrochemistry and field stability (reversible one-electron reduction).
- Match the optical band-gap of the emitters – avoiding light absorption and scattering.
- Phase compatibility and processing without defects.

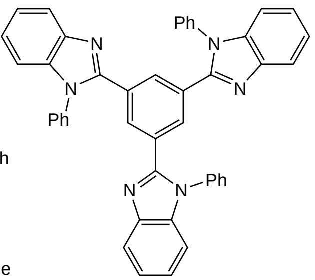
Materials that meet these criteria include some metal chelates, oxadiazoles and polycyclic nitrogen heteroaromatic compounds. The most commonly used chelates are those derived from 8-hydroxyquinoline ligands with Al, Ga and In ions (3.99), which as we will see can also be used as EM materials. Oxadiazoles have also been widely studied and used as ETMs exemplified by PBD (3.100) and its spiro analogues. Examples of polycyclic nitrogen heterocycles include BCP (3.101) and TPBI (3.102). These compounds can also function as the materials for the HBL, thus preventing leakage of positive charge carriers to the cathode.

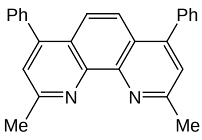


(3.99)
Alq_3



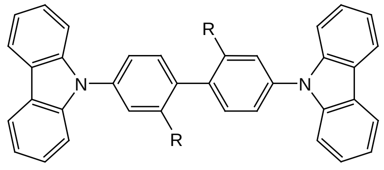
(3.100)





(3.101)
BCP

(3.102)
TPBI



(3.103)
CBP: R = H

3.9.6.3 Light-emitting Materials

The function of the EML is to produce light of the colour desired by the application. To operate effectively the EML layer must be able to transport both holes and electrons so that they are able to combine and create the excited state of the EM, which collapses emitting a photon of light of the desired wavelength. This process must also involve an absolute minimal loss of the input energy as heat. For practical devices the materials must be capable of good film-forming properties. In practice in order to achieve these properties the EML comprises a host material with a guest emitter, but such dopants must not migrate in the film layer over time.

Host materials – the basic properties required in host materials are as follows:[220]

- Good electron and hole conduction coupled with thermal, chemical and electrochemical stability.
- Matching HOMO and LUMO energy levels with guest emitters.
- For phosphorescent guests the triplet energy level of the host must be higher than the guest.
- Fast energy transfer processes.
- Phase compatibility with guest materials.

Electron transport hosts normally used with guest emitters (dopants) are natural hole transporters as exemplified by Alq_3 (3.99) and TPBI (3.102). Hole transport hosts on the other hand, such as CBP (3.103) and its analogues, are used with electron-dominated emitters.

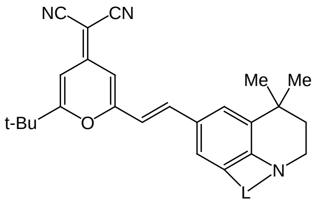
3.9.6.4 Fluorescent Emitters as Hosts and Dopants

Whilst matching their host in the list of properties 1–5 above, guest/dopants must also meet the standards of the CIELUV system for red, green and blue chromaticity coordinates as used in the display industries (see also Chapter 2; Section 2.2.3).

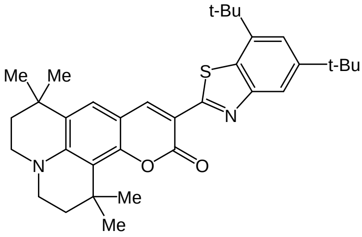
Compounds that have been examined as possible red emitters fall into four chemical classes:[221]

- Pyran-containing donor–acceptor chromophores;
- Other donor–acceptor chromophores;
- Polyacenes;
- Metal chelates.

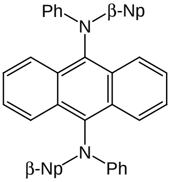
Pyran-containing methine chromophores, which have been known and used as fluorescent and laser dyes for many decades (see Section 3.5.6.3), were used as the red-emitting dopant in the first SMOLEDs constructed at Kodak, and have been developed further since that time *e.g.* DJCTB (3.104a). Many related structures have been examined since this early work, for instance recently (3.104b) has been claimed to show improved colour purity and luminous efficiency.[222] Red emitters from this class of fluorescent compounds continue to be used in SMOLEDS. One disadvantage of the planar methine chromophores is their tendency to form aggregates in the solid state, thus confining their use to that of dopants. Other donor–acceptor red chromophores have been devised which are non-planar, showing much less tendency to aggregate and consequently can be used both as dopants and undoped emitters. For instance (3.105) from Sony, which emits at 630 nm, has been used in a device showing high colour stability and luminous efficiency. Rare earth metal chelates, such as Eu complexes, emit strongly in the red region but have shown little practical value as lumophores. On the other hand other metal complexes are extremely valuable as phosphorescent emitters and are described below.



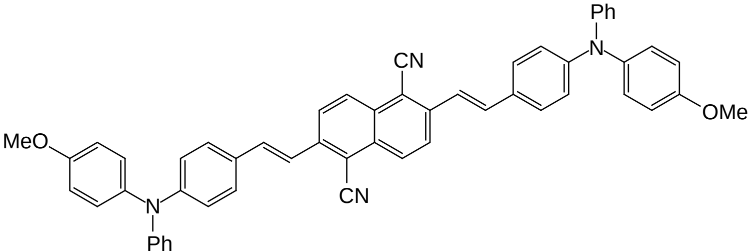
(3.104a) DCJTB L = $Me_2CC_2H_4$
(3.104b) L = CH_2CHMe



(3.106)



(3.107)



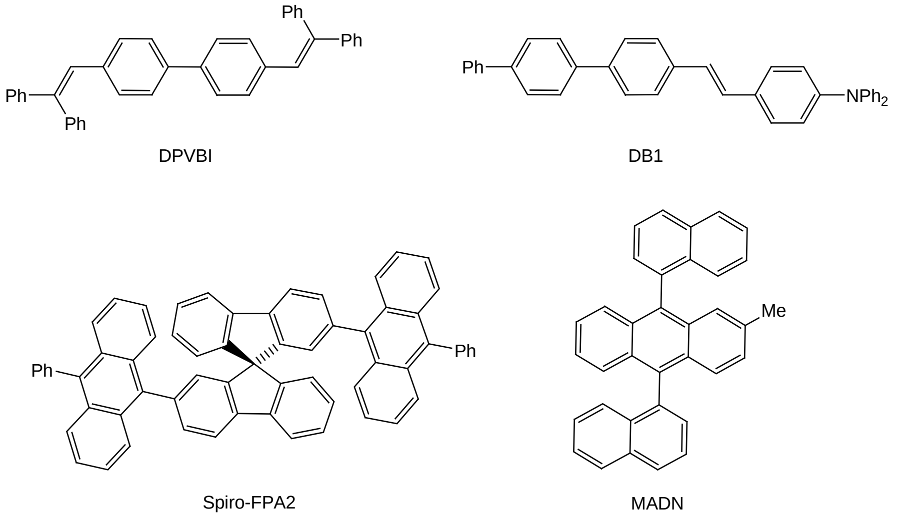
(3.105)

Coumarin dyes (3.106) have been widely examined as green fluorescent dopants,[223] as have quinacridones, both using Alq_3 as a host material, whilst the anthracene derivative β-NPA (3.107; β-Np = 2-naphthyl) can be used in a neat film.

Many chemical structures have been examined in attempts to meet the requirements of the relatively large band-gap needed for blue emitters. This large band-gap means that dopants with even higher band-gaps are required to optimise energy transfer requirements, whilst still coupling this property with device stability. Distyrylarylenes are amongst the most efficient blue fluorescent emitters yet reported.[224] Other polycyclic aromatics and spiro analogues can also function as efficient blue emitters and hosts, a selection of which is shown in Figure 3.47. The production of improved blue emitters still remains a target and results claiming superior materials appear regularly in the literature.

3.9.6.5 Phosphorescent Dopants in SMOLEDs

Excitons formed by a recombination of holes and electrons generated electronically can either be in a singlet state and fluoresce more or less



DPVBI DB1

Spiro-FPA2 MADN

Figure 3.47 Some polycyclic blue emitters and hosts.

spontaneously, or in the triplet state and decay more slowly with a low quantum yield for light generation. Spin statistics show that the theoretical efficiency of a device comprising fluorescent emitters, which only uses the singlet state, cannot be more than 25% photoluminescence efficient, as the singlet to triplet state ratio is 1:3. However, in phosphorescent materials recombination of the electron and the hole in the exciton is trapped, where spin-orbit coupling occurs leading to singlet-triplet state mixing. The use of both singlet and triplet states by phosphorescent emitters means that they can in theory show 100% internal quantum efficiencies. (Internal quantum efficiency is the total number of photons generated inside the device per electron–hole pair injected into the device. External quantum efficiency is the total number of photons emitted from the device per electron–hole pair injected into the device). This is the area where the most exciting developments in SMOLEDs and PLEDS (see below) are taking place, as this methodology has given rise to a step change in performance.

Since the first report in 1998 on the use of cyclometalated transition metal complexes as phosphorescent materials in OLEDs, giving much improved external quantum efficiencies,[225] a huge number of different phosphorescent metal complexes, containing metals such as iridium, platinum, osmium and ruthenium, have been devised for this purpose.[226,227] Problems experienced with phosphorescent metal complexes include triplet-triplet annihilation, and concentration quenching occurring in pure layers of the materials. The latter is much diminished when the emitters are used as guests/dopants in host materials, many of which are the same as those used with fluorescent dopants, especially carbazoles *e.g.* PBD. Some typical red, green and blue dopants of the particularly important class of iridium(III) complexes are shown in Figure 3.48.

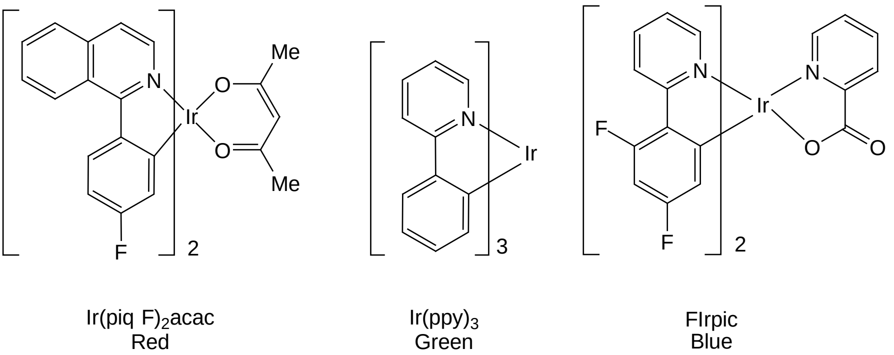


Figure 3.48 Phosphorescent donors based on Ir(III) complexes.

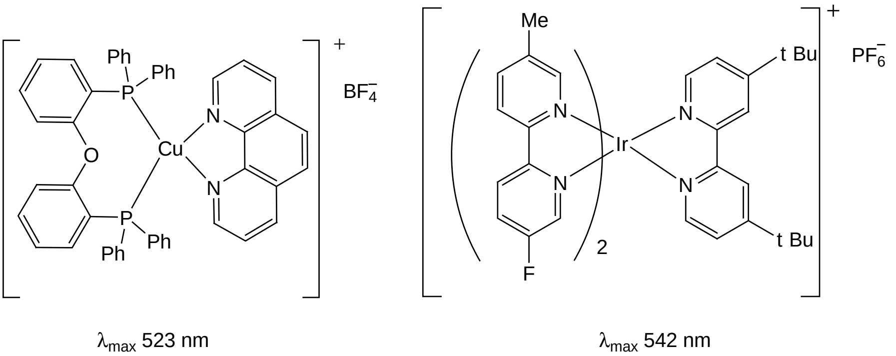


Figure 3.49 Examples of ionic transition metal complexes used in OLEDs.

Variations on the organic ligands are great in number and even polymerisable groups have been appended. Although materials with high efficiencies in all colours have been attained, at this time the blue materials still lag some way behind the red and green emitters in overall performance.

Another and potentially simpler way of using phosphorescent dopants is the use of ionic transition metal complexes in single-layer devices.[228] In these the complexes themselves support all three processes of charge injection, charge transport and emissive recombination, and their excellent stability in multiple redox states means that electronic charges can be readily injected and transported. Additionally, their ionic nature allows efficient injection of electrons from air-stable metals. The ionic complexes involved are formed by the reaction of substituted bi- and ter-pyridyl ligands with Ru(II), Ir(III) and Cu(I), with counterions PF_6 and BF_4 (Figure 3.49). These materials need to be laid by spin casting from solution, but sublimable materials have been developed for alternative processing.[229]

3.9.7 Polymer LEDS

In conjugated polymers the lower-energy, bonding π orbital forms the valence band, whilst the higher-energy, non-bonding π* orbital is the conduction band. The π-π* energy difference between the bonding and antibonding orbitals provides the band-gap and hence the potential for semi-conducting or polymer EL behaviour. The wavelength of the emitted light is also directly related to the π-π* energy gap, and, by molecular engineering of the conjugated polymer structure, the HOMO-LUMO gap can be manipulated so that emission across the whole of the visible spectrum is possible.

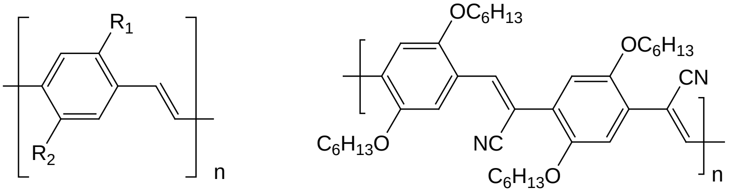
Polymeric materials also have many attractive properties when it comes to processing and constructing devices. One prime advantage is the ease with which it is possible to lay down thin films on large areas of a substrate, either by spin coating, molten or from a solution, or by using a doctor blade technique, or dip coating. Furthermore, polymer films are more robust than amorphous films as they do not suffer to the same extent from the problems of crystallisation associated with the latter. Constructing complex devices such as large-area flat-panel displays should therefore be easier with polymer LEDs (PLEDs) than with SMOLEDs. At their simplest, PLEDs are just a layer of light-emitting polymer coated or printed onto an ITO anode, itself coated with PEDOT:PSS for hole injection, mounted onto clear plastic or a glass base plate and topped off with a cathode laid down by vacuum deposition.

3.9.7.1 Light-emitting Polymers (LEPs)

There are three main classes of LEPs: poly(*p*-phenylene vinylenes) (PPV), polyfluorenes and polythiophenes. Many reviews are available on this topic but a particularly comprehensive one is included in the book edited by Li and Meng.[230]

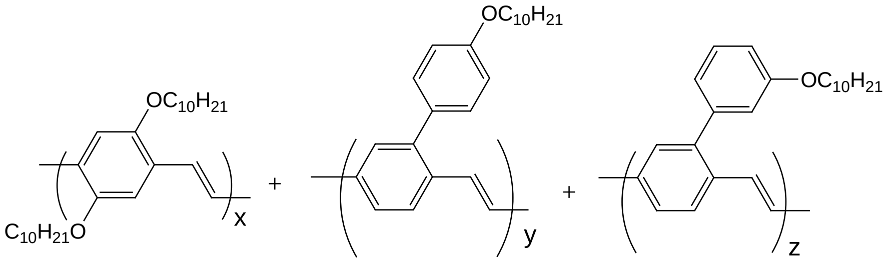
PPV was the polymer used in the classic paper outlining the discovery of EL in these materials and has consequently been at the centre of much of the research effort in this field. PPV-type polymers can be either homopolymers or copolymers and have a variety of side chains on the aryl rings or on the vinyl linkages, as exemplified by CN-PPV and others shown in Figure 3.50. Colour tuning has been achieved over the range from blue to the near IR, as listed in Table 3.12, and the lifetime of PPV-based LEDs in use has exceeded 20,000 hrs.

Polyfluorenes are a class of conjugated polymers which demonstrate both optical and electronic properties and are the only class of LEPs that show relatively high quantum efficiency across the whole visible range of derived colours. An astounding number have been synthesised; both homo- and copolymers, ring- and side-chain substituted, and end-capped. A very promising RGB trichromat drawn from the literature is shown in Figure 3.51 (see also Table 3.12). Polyfluorenes currently offer the best prospects for achieving a fully acceptable polymeric blue emitter.



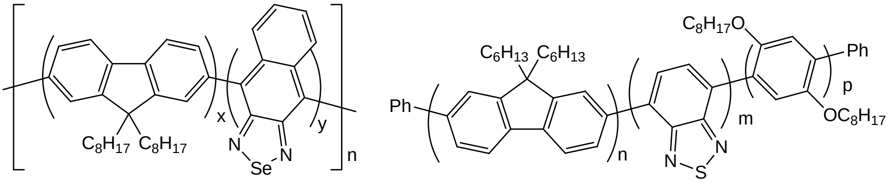
PPVs

CN-PPV



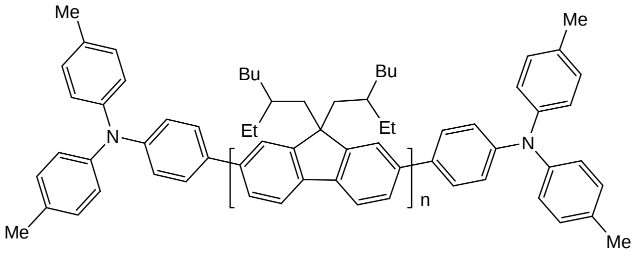
Copolymer

Figure 3.50 Examples of PPV light emitting polymers.



Red
x:y = 99:1

Green
n = 75, m = 12.5, p = 12.5



Blue

Figure 3.51 Three colour polyfluorene light emitting polymers.

Table 3.12 Colour from selected light-emitting polymers.

Polymer	*Chemical name*	*Colour*	λ_{max} *nm*
MEH PPV	Poly[2 (2′ethylhexyloxy) 5 methoxy 1,4 phenylene vinylene	Red orange	610
OC1C10 PPV	Poly[2 (3,7 dimethoxyoctyloxy) 5 methoxy 1,4 phenylene vinylene]	Red orange	610
CN PPV	Poly[2,5 bis(hexyloxy) 1,4 phenylene (1 cyanovinylene)]	Red	710
MEH CN PPV	Poly[2 (2′ethylhexyloxy) 5 methoxy 1,4 phenylene vinylene]	Red orange	600
	Polythiophene		
	Polythiophene	Red	662
PPV	Poly(para phenylene vinylene)	Green	550
DMOS PPV	Poly[2 (dimethyloctylsilyl) 1,4 phenylene vinylene]	Green	500
BUEH PPV	Poly[2 (2′ ethylhexyl) 5 butyl 1,4 pheylene vinylene]	Green	554
BDOH PF	Poly[9,9 bis(methoxyethoxyethyl)fluorene]	Blue green	450
PPP	Poly(para phenylene)	Blue	459
DO PPP	Poly(2 decyloxy 1,4 phenylene)	Blue	440
m LPPP	Ladder type poly(para phenylene)	Blue green	491
P3V/P5V	Copolymer	Blue	460

3.9.7.2 LEPs as Hosts for Phosphorescent Dopants

The method of utilising the triplet-state energy by adding phosphorescent dopants to low-molecular-weight materials, as discussed in Section 3.9.6.5, can also be applied to polymers. Polymeric hosts for phosphorescent dopants may be either conjugated or non-conjugated but it is the non-conjugated hosts, basically poly(9-vinylcarbazole) (PVK), that have to date produced the most significant improvements.[231] Whilst PVK has reasonable T_g and film-forming capability, it is difficult to inject holes from the PEDOT:PSS injection layer into the bulk material. Because of this it is usually mixed with other conducting materials, such as PDP and TPD as well as the low-molecular-weight phosphorescent dyes, such as those shown in Figure 3.48. An interesting development is that of PLEDs fabricated from polymers that have phosphorescent Ir(III) complexes as pendant groups, offering potentially simpler fabrication and diminution of the losses in phosphorescence due to aggregation.[232]

3.9.8 Dendrimer LEDs

Light-emitting dendrimers (DLEDs) are the latest addition to the armoury of chemists designing and producing OLEDs.[233] Dendrimers are highly branched macromolecules consisting of a core surrounded by a structure of many dendrons. This highly branched structure makes them different from the more linear polymers, producing distinctive properties rendering them of use not only in LEDs but also in several other areas, including as 2PA organic

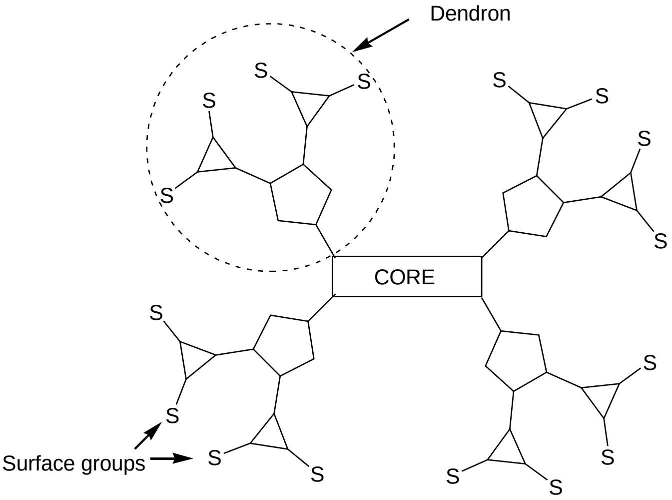


Figure 3.52 Schematic of design features of dendrons used in DLEDs.

nanodots (Section 3.5.3), solar cells and light harvesting (Chapter 4; Section 4.8.2.1). They have also been used as transport materials in OLEDS but to be of more general application they need to contain a light-emitting chromophoric unit. The generic structure of dendrimers designed for use in DLEDs is shown in Figure 3.52. The design of these dendrimers is characterised by the following points:

- Core has one or more dendrons attached;
- Dendrons can have two components;
  - Branching units
  - Linking moieties
- Levels of branching indicate the "generation" of dendrimer;
- Emissive chromophore is best located at the core;
- Surface groups assist solubility/processing in device.

Samuels and co-workers synthesised dendrimers using distyrylbenzene as fluorescent cores to obtain blue emission; a distyrylanthracene for green; and Pt meso-phenylporphyrin for red, and showed that they could be used to construct DLEDs, if a little low when used in single-layer devices. However, it was the move into using phosphorescent cores that brought the most impressive advances. The methodology involved incorporating the well-established phosphorescent Ir(III) complexes at the core of the dendrimers, made from biphenyl groups topped with 2-ethylhexyloxy groups, to give red, green and blue products as shown in Figure 3.53. The green DLED was particularly effective when blended with the oxadiazole CBP to increase the space in the dendrimer, giving an external quantum efficiency of 8.1%. Using this in a device with a layer of an electron transporting material (TPBI) raised this even

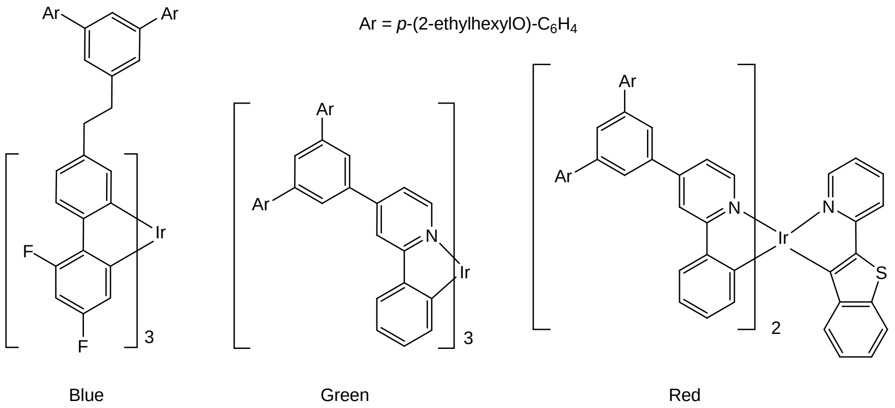


Figure 3.53 Examples of phosphorescent dendrimers having phenylene based den drons attached.

further to 16%, representing an internal quantum efficiency of around 80%. Whilst external efficiency with the red dendrimer was good at 6% the blue one was only modest and its shade was too pale. As with other areas in OLEDs getting a satisfactory shade of blue coupled with good external quantum efficiency remains the problem area.

Others in this field are following different lines. For instance dendrimers with Ir(III) complex cores and carbazole-containing dendrons have been prepared, the green dendrimer of which in a bi-layer device with TPBI gave an external quantum efficiency of 8.8%.[234] Starburst dendrimers bearing a 4,4′,4″-tris(-carbazol-9-yl)-triphenylamine core and six uniform oligofluorene arms are said to have excellent photoluminescence and electroluminescence properties as hole-transporting materials and deep-blue-light emitters.[235]

This is clearly an area of great promise and is being pursued in the commercial world, where a red-emissive dendrimer-containing OLED was reported by Cambridge Display Technology in 2007 to have a lifetime of an amazing 250,000 hrs. Once again getting a satisfactory shade of blue coupled with good external quantum efficiency remains an area ripe for resolution.

3.9.9 Applications of OLEDs in Displays

In displays there are two types of addressing schemes, passive matrix and active matrix drivers. Passive matrix drivers (PMOLEDs) read one line at a time on the display, switching on and off as each pixel is required. Power analyses have shown that PMOLED displays are most practical in sizes smaller than 2″ to 3″ in diagonal, or having less than approximately 100 row lines, so they are used in smaller hand-held devices, such as mobile phones, cameras, MP3 players and watches. Active matrix addressing (AMOLED), which is used in most current LCDs (see Chapter 5) and is also being used in the larger-area OLED panels, has

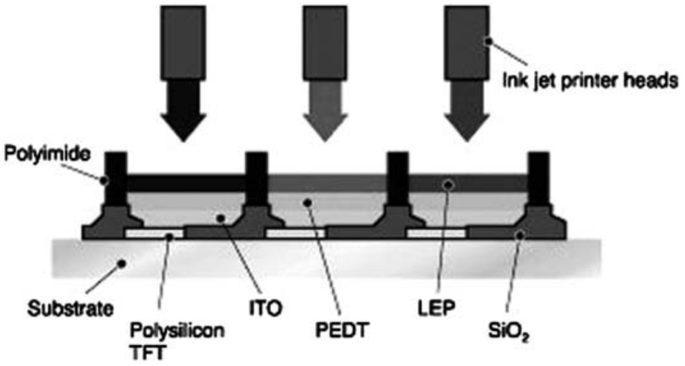


Figure 3.54 CDT ink jet method for PLED RGB matrix.

an active device circuit containing one or more TFTs connected to each pixel in the array, so that power to each pixel can be left on until it receives another signal.

The construction of devices to be used in the important area of displays requires that the RGB materials be laid down accurately and without defects on such addressing systems. For SMOLEDs, by the very nature of these materials, vapour deposition has to date been the preferred method, whereas with PLEDs and DLEDs print-based methods can be used *e.g.* ink-jet printing as developed by Cambridge Display Technology (Figure 3.54), and in fact this is seen as one of the advantages for these types of materials. It is possible that the newer printing methods such as laser thermal imaging can be applied for laying down sublimable SMOLEDs. In spite of these differences most of the manufacturing difficulties in producing displays from both SMOLEDs and PLEDs have been or are in the process of being overcome.

A significant benefit of OLED displays over LCDs is that they do not require a back light to function, hence using much less power, and can be much thinner. The response time for OLEDs is also faster than LCD screens, 0.01 milliseconds compared to an LCD average of 8 to 12 milliseconds, thus avoiding the "blur" which tends to occur when viewing rapid motion sports programs on LCDs. Companies have now claimed to have overcome the short lifetime problem in the blue colour area when using phosphorescent OLEDs, attaining 20,000-hour lifetimes. However, this is still well below the 60,000 hours claimed for modern LCD TVs.

Commercialisation, which has been under way since the early years of this century, is very rapid even for the electronics field, with new announcements coming out regularly from the major companies. Initially the technology was used in small displays of less than 2.5 inches, before Kodak led the way towards the flat-panel display area, with their 7.5-inch wireless digital picture frame. Sony in 2008 produced a commercial TV/computer monitor, 11 inches in size but only 1/10 inch in thickness, demonstrating the potential for this technology to produce truly wall-mountable flat panels. In the same year Samsung, who had previously demonstrated a 40-inch TV at trade shows, followed this up with a 14-inch AMOLED display panel and a 30-inch OLED HDTV offering 1080p resolution and 1,000,000:1 contrast ratio, being extra thin at less than 4/10 inch including glass plates, due for commercialisation in 2009/10. Companies such as LG, Toshiba and Matsushita (Panasonic) are also investing heavily and hope to market 30-inch size OLED HDTVs by 2010. However, a word of caution was expressed by Samsung in March 2009 when they said that it could be four or five years before OLED is mainstream. The exact technology being used by these companies is obviously commercially sensitive, but a key step in determining whether SMOLEDs or PLEDs are used is the deposition technology being adopted to produce the panels.

According to iSuppli Corp, the worldwide AM-OLED market was set to grow to US$ 4.6 billion by 2014, representing a CAGR of 83.3%, up from US$ 67 million in 2007. In terms of shipments, growth from 2.6 million units in 2007 to 185.2 million units by 2014 is anticipated.

3.9.10 White Light OLEDS

OLEDs are a flat light source emitting diffuse light over an area, whereas inorganic LEDs (see Section 3.9.1) are point light sources needing light distribution elements to produce a lighting panel. Consequently WOLEDS potentially offer a whole new way of both lighting spaces and back lighting display panels. Research has been intense, with progress rapid since 2000 and commercialisation imminent at the end of the decade.

To be useful as white light devices WOLEDS must meet certain criteria. Clearly their luminous efficiency and lifetimes must compete with lighting that is currently being used in existing outlets. Incandescent bulb efficiency is $15\,\mathrm{lm\,W^{-1}}$ and in fluorescent tubes $90\,\mathrm{lm\,W^{-1}}$, with respective lifetimes of 750 hrs and 10,000 hrs. For comparison inorganic white LEDs have reached $44\,\mathrm{lm\,W^{-1}}$ and lifetimes greater than 9000 hrs. Another very important aspect is colour quality as defined by the colour rendering index (CRI) and the CIE chromaticity coordinates. CRI, a numerical measurement of how true colours look when illuminated with the light source, is measured on a 0–100 scale, where 100 represents true colour reproduction, and must be greater than 75 in white lighting. The CIE ideal x,y white point is 0.33, 0.33 but all current white light sources vary from these figures, the nearest of the common ones being "fluorescent cool white" at 0.375, 0.367 with a CRI of 89.

The approaches adopted in attempts to achieve these criteria in WOLEDs fall into two main types:[236,237,238]

- Color mixing;
  - Multi-layer structures
  - Host-Guest Structures
    - Förster/Dexter energy transfer
    - Exciplex/excimer charge transfer
  - Microcavity structure
  - Horizontally/vertically mixed pixels

  - ○ Blending
- Wavelength conversion – down conversion with phosphors.

3.9.10.1 Colour Mixing

Multi-layer Structures – in a multi-layer device two or more emitters are placed on top of each other, which when activated combine to produce white light (see Figure 3.55(a)). In order to achieve a good colour balance the thickness and composition of each layer has to be precisely controlled.

Host-Guest Structures – in one such structure different phosphorescent triplet emitters (*e.g.* RGB iridium complexes in Figure 3.40) are used as guests in host layers (*e.g.* CBP; 3.101), the thickness of each layer being adjusted to serve as the recombination zone for the appropriate fraction of excitons formed initially in the HTL/EM interface.

One way of reducing the number of dopants required in the emissive layer is to use a broadly emitting exciplex *i.e.* one whose wavefunction overlaps with an adjacent but dissimilar molecule, or an excimer, one whose wavefunction overlaps with two adjacent, structurally similar molecules. Unlike the multiple-dopant system, in excimers there are no complicated intermolecular interactions to make colour balancing difficult. For instance, only a single species is responsible for both blue light (monomer) and orange-red light (excimer) emission.[239] An example of an exciplex charge transfer complex used for white light emission is a blend of tris(5-mesitylsulfone-8-hydroxyquinolato)aluminium [$Al(MSq)_3$] and TPD.[240]

Microcavity Structure – in a microcavity system a pair of highly reflecting mirrors about one micron apart are used to ensure that light only comes out at one end of the device, making it more efficient. A disadvantage is that the mirrors make the colour emission angular dependent, and hence it changes depending on the position of the viewer.

Horizontally/vertically mixed pixels – this method of arranging emitters is very similar to the arrangement of the pixels in LCD devices (see Chapter 5), being arranged either horizontally or vertically as shown in Figure 3.55 (b) and (c).[241] The horizontal arrangement can be in the form of pixels or stripes, each individually addressed and optimised to operate at a minimum operating voltage and highest efficiency. In the vertical arrangement RGB OLEDs are stacked so that they can be addressed independently to produce red, green, blue or a combination to give white light.

3.9.10.2 Wavelength Conversion

In this technology a blue-emitting OLED is coupled with one or more down-conversion phosphor layers, usually orange and red organic chromophores, in which one of the phosphor layers contains the inorganic light scattering phosphor, Y(Gd)AG:Ce. A schematic of one such structure, sometimes called hybrid OLEDs, is shown in Figure 3.56. Although a portion of the blue light is

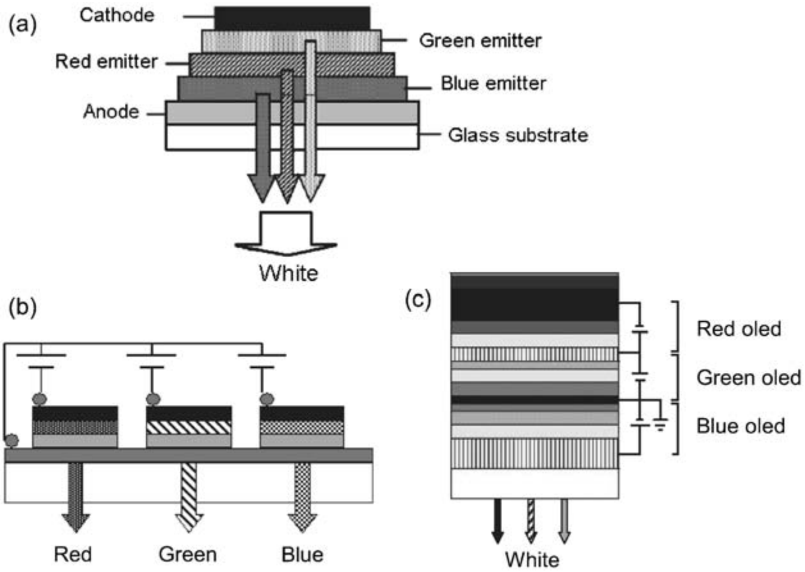


Figure 3.55 WOLED architectures: (a) multi layer, (b) stacked horizontal, (c) stacked vertically (reproduced with permission of Institute of Physics Publishing Ltd).

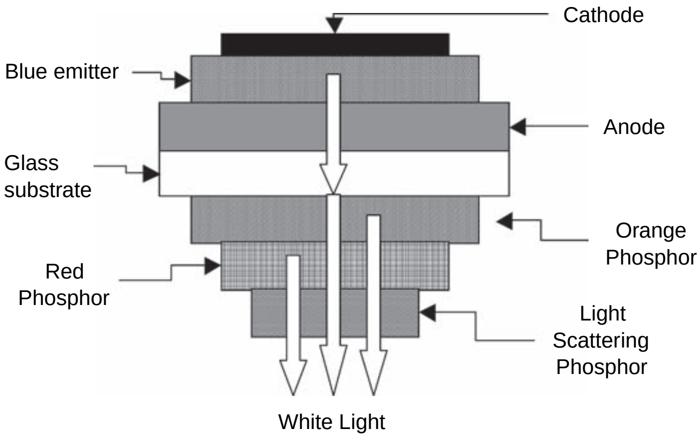


Figure 3.56 Schematic of a structure used for down conversion to white light (reproduced with permission of Institute of Physics Publishing Ltd).

scattered most of it excites the phosphors, each of which emits a different colour. Mixing of these colours with some of the blue light leaking through helps to produce a broad wavelength white light.

Once again the improvements observed by using phosphorescent dopants have been displayed in down conversion. Osram employs polyvinyl-carbazole as the host and iridium (III) complex Flrpic (see Figure 3.40) as the phosphorescent dopant, and an electron-transport material, excited by an Osram down-conversion product based on a nitridosilicate phosphor to give a white light with a luminous efficiency of 25 lm W^{-1}.[242]

3.9.10.3 Commercialisation of WOLEDs

Most major lighting manufacturing companies which include Osram, Phillips, Lumiotec, GE and Konica Minolta have products in the development pipeline based on WOLEDS. In late 2008 Osram announced that collaboration with BASF had produced a white OLED with an efficiency of over 60 lm W^{-1} and light output falling within the international Energy Star SSL Standard. There are many start-up companies hoping to benefit from the technology that they have developed *e.g.* Cambridge Display Technology, Novaled and Universal Display Technology. As examples of the latter, the OLLA project consortium developed the basic technology for a WOLED light source, with an efficacy of 50.7 lm W^{-1} at an initial brightness of 1.000 cd m^{-2} based on the Novaled PIN OLED technology. Universal Display demonstrated a white OLED light source in 2008 with record luminous efficiency of 102 lm W^{-1}.

Whilst there is no doubt that new and improved materials are required, and are being developed, just as much work is going into construction methods for novel lighting arrangements such as panels that are clear during the day but can be converted to lights as night approaches. Exciting days lie ahead both scientifically and aesthetically.

3.10 Triboluminescence

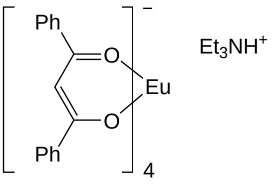
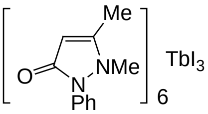
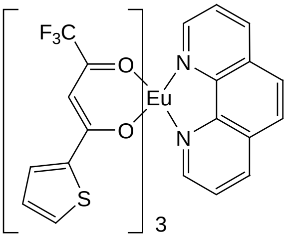
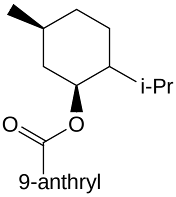
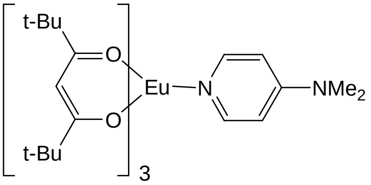
Triboluminescence – sometimes alternatively called fractoluminescence and mechanoluminescence – is the phenomenon that is observed when coloured light is emitted on rubbing, grinding, crushing or fracturing certain crystalline compounds, *e.g.* the bluish-white light emitted from sugar. This phenomenon has been known for over 400 years but has remained a curiosity without an obvious application until recently, when Sage postulated that this effect could be used to detect flaws in composite materials.[243,244]

The proposal was based on the reported high triboluminescence efficiency exhibited by certain crystalline compounds, especially complexes with lanthanides (Table 3.13), some of which have already been described under electroluminescence (Section 3.9). The light emission from a few of these materials is sufficient for the phenomenon to be observed in a well-lit room.

The mechanism of the origin of the triboluminescence effect is not fully understood but there appear to be three types:

- Many of the brightest triboluminescent compounds are also piezoelectric and photoluminescent. Thus triboluminescence in these compounds can be explained by a fracturing of the crystal causing electrical charges to be

Table 3.13 Triboluminescent compounds.

Compound	*Emission wavelength/nm*	*Emission lifetime*
	612	470 μs
	542	4.8 ms
	612	666 μs
	437	3.4 ns
	550	538 μs

formed along the new surfaces, from which an electrical discharge occurs in the crack line. Nitrogen from the air present in this discharge emits UV light, which is absorbed into the crystal and then re-emitted as blue visible light.

- For centrosymmetric crystals this cannot happen as the surfaces will be the same on both sides of the crack line. In these cases it is postulated that traces of impurities could play an important role in the effect.
- In a third class, compounds exhibiting poor photoluminescent properties still show the emission at wavelengths characteristic of the metal ion in the complex. The cause of the emission in these cases is put down to excitation by direct electron impact rather than UV light.

This triboluminescent phenomenon has been applied in devising sensors for the detection of cracks, caused by physical impact, in panels made from composite materials used in aircraft bodies, high-performance cars, *etc*. In one method the panel is coated with an epoxy resin containing the triboluminescent materials. When there is an impact on the panel of sufficient force to cause stress cracks, the resin layer fractures emitting a flash of light, which is detected by an array of detectors along the panel. An alternative method uses the triboluminescent material and fibre-optic cable fixed within the composite. In this case fracture is detected by light emitting from the end of the fibre waveguide.

A further interesting observation of triboluminescence, again with potential rather than real application, is the burst of colour seen as common adhesive tape is unpeeled or stripped from a surface in a vacuum in a blackened room. This has recently been re-discovered[245] after a couple of earlier reports.[246,247] Besides the luminescence, short pulses of 100 mW X-rays can also be detected, which could have some conceivable application.

3.11 Pyroluminescence

The final luminescence which we briefly touch on in this chapter is responsible for a very well known commercial technology – that of fireworks. An atom or ion can become electronically excited when exposed to a high degree of heat, for example in a combustion process. From this excited state, energy is emitted as luminescence as the ion relaxes to its ground state, sometimes in very specific colours depending on the nature of the element being excited. This thermal excitation followed by luminescence is responsible for the range of colours seen as fireworks explode, and is known as pyroluminescence, leading to "pyrotechnics". Besides their use as the mainstays of entertainment during celebrations, fireworks also have military applications.

The main sources of colours derived from particular elements are shown in Table 3.14. A more detailed description of firework science can be found in various books.[248,249]

Table 3.14 Sources of various colours in fireworks.

Colour	*Metal*
Red	Strontium, lithium
Orange	Calcium
Yellow	Sodium
Green	Barium
Blue	Copper
Purple	Potassium or strontium + copper
Gold	Charcoal, iron
White	Ti, Al, Mg powders

References

1. G. Blasse and B. C. Grabmaier, *Luminescent Materials*, Springer-Verlag, Berlin, 1994.
2. D. R. Vij (ed.), *Luminescence of Solids*, Plenum, New York, 1998, p. 256.
3. L. Ozawa and M. Itoh, *Chem. Rev.*, 2003, **103**, 3835–3856.
4. W. M. Yen, S. Shinoya and H. Yamamoto, *Practical Applications of Phosphors*, CRC Press, Boca Raton, FL, 2007.
5. G. Buxbaum and G. Pfaff (ed.), *Industrial Inorganic Pigments*, Wiley-VCH, Weinheim, 2003.
6. T. Matsuzawa, Y. Aoki, N. Takeuchi and Y. Murayama, *J. Electrochem. Soc.*, 1996, **143**, 2670.
7. X. Wang and D. Jia, in *Practical Applications of Phosphors*, ed. W. M. Yen, S. Shinoya and H. Yamamoto, CRC Press, Boca Raton, FL, 2007, pp. 453–478.
8. J.-C. G. Bünzli and C. Piguet, *Chem. Soc. Rev.*, 2005, **34**, 1048–1077.
9. www.Capricorn.co.uk/glowbug.
10. P. Befumo and A. N. Becidyan, *American Ink Maker*, January 1999, 31–36.
11. www51.Honeywell.com/sm/lumilux.
12. F. Auzel, *Chem. Rev.*, 2004, **104**, 139–173.
13. A. Rapaport, J. Milliez, M. Bass, A. Cassanho and H. Jenssen, *J. Display Tech.*, 2006, **2**, 68–78.
14. http://www.rp-photonics.com/upconversion_lasers.html.
15. NEC Corporation, *US Pat.*, 6265825, 2001.
16. M. Sheik-Bahae and R. I. Epstein, *Nature Photonics*, 2007, **1**, 693–699.
17. C. E. Mungan, M. I. Buchwald and G. L. Mills, in *Cryocoolers 14*, ed. S. D. Miller and R. G. Ross Jr., ICC Press, Boulder, CO, 2007, pp. 539–548.
18. X. L. Ruan and M. Kaviany, *J. Heat Transfer*, 2007, **129**, 3–10.
19. C. Hoyt, M. Hasselbeck, M. Sheik-Bahae, R. Epstein, S. Greenfield, J. Thiede, J. Distel and J. Valencia, *J. Opt. Sci. Am. B*, 2003, **20**, 1066–1074.
20. A. J. Garcia-Adeva, R. Balda and J. Fernandez, *Opt. Mater.*, 2008, **31**, 1075–1081.
21. http://www.ballaerospace.com/page.jsp?page = 30&id = 163.
22. J. L. Clark and G. Rumbles, *Phys. Rev. Lett.*, 1996, **76**, 2037–2040.
23. C. E. Mungan and T. R. Gosnell, *Phys. Rev. Lett.*, 1996, **77**, 2840; G. Rumbles and J. L. Clark, *Phys. Rev. Lett.*, 1996, **77**, 2841.
24. G. Rumbles, personal communication.
25. http://www.digitalhome.ca/content/view/2538/206/.
26. L. Ozawa, *Cathode Luminescence*, VCH, Weinheim, 1990.
27. G. Buxbaum, *Industrial Inorganic Pigments*, Wiley-VCH, Weinheim, 1998, p. 254.
28. G. Blasse and B. C. Grabmaier, *Luminescent Materials*, Springer-Verlag, Berlin, 1994, p. 138.

29. G. Buxbaum, *Industrial Inorganic Pigments*, Wiley-VCH, Weinheim, 1998, pp. 237–264.
30. (a) www.computerpoweruser.com/articles/archive/c0505/26c05/26c05.pdf; (b) R. Fink and Z. Yaniv, EE Times-Asia, August 2007, p. 1, see http://www.eetasia.com/ARTICLES/2007AUG/PDF/EEOL_2007AUG16_OPT_TA.pdf?SOURCES = DOWNLOAD.
31. http://www.phosphor-technology.com/products/crt.htm.
32. http://www.reghardware.co.uk/2008/07/07/sony_fet_fed_plans/.
33. http://www.oled-display.info/.
34. G. Blasse and B. C. Grabmaier, *Luminescent Materials*, Springer-Verlag, Berlin, 1994, pp. 109–133.
35. R. J. D. Tilley, *Color and the Optical Properties of Materials*, Wiley, Chichester, 2000, pp. 286–287.
36. T. Jüstel, *Adv. Mater.*, 2000, **12**, 527–30.
37. R. P. Rao, *Proc. of ASID '06*, October 2006, p. 7.
38. C. Ronda, *J. Luminesc.*, 2002, **100**, 301–305.
39. T.-J. Lee, L.-Y. Luo, B.-M. Cheng, W.-G. Diau and T.-M. Chen, *Appl. Phys. Lett.*, 2008, **92**, 081106.
40. B. Valeur, *Molecular Fluorescence: Principles and Applications*, Wiley-VCH, 2002.
41. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer, 2006.
42. R. P. Haugland, *The Handbook – A Guide to Fluorescent Probes and Labeling Technologies*, Molecular Probes, 2005; http://probes.invitrogen.com/handbook/index.html.
43. U. Brackmann, *Lambdachrome® Laser Dyes*, see http://bcp.phys.strath.ac.uk/ultrafast/Blue_book/Lamdachrome-laser-dyes.pdf.
44. H. Langhals, *Helv. Chim. Acta*, 2005, **88**, 1309–1343.
45. R. Raghavachari (ed.), *Near-Infrared Applications in Biotechnology*, Marcel Dekker, New York, 2000.
46. G. Ulrich, R. Ziessel and A. Harriman, *Angew. Chem., Int. Ed. Engl.*, 2008, **47**, 1184–1201.
47. W. Zhao and E. M. Carreira, *Chem. Eur. J.*, 2006, **12**, 7254–7263.
48. A Google Scholar search November 2008 gave the number of annual article hits for "Bodipy" as 1190 (2004), 1220 (2005), 1200 (2006) and 1120 (2007).
49. A. P. Chorlton, in *Modern Colorants: Synthesis and Structure*, ed. A. T. Peters and H. S. Freeman, Blackie, London, 1995.
50. S. Sreejith, P. Carol, P. L. Chithraa and A. Ajayaghosh, *J. Mater. Chem.*, 2008, **18**, 264–274.
51. E. Arunkumar, C. C. Forbes, B. C. Noll and B. D. Smith, *J. Am. Chem. Soc.*, 2005, **127**, 3288.
52. E. Arunkumar, N. Fu and B. D. Smith, *Chem. Eur. J.*, 2006, **12**, 4684.
53. A. J. Boydston, P. D. Vu, O. L. Dykhno, V. Chang, A. R. Wyatt, A. S. Stockett, E. T. Ritschdorff, J. B. Shear and C. W. Bielawski, *J. Am. Chem. Soc.*, 2008, **130**, 3143–3156.
54. P. N. Prasad, *Nanophotonics*, Wiley-Interscience, Hoboken, 2004.

55. The Evident Technologies website provides simple graphical explanations of QD phenomena: http://www.evidenttech.com/quantum-dots-explained.html.
56. E. H. Sargent, *Adv. Mater.*, 2005, **17**, 515–522.
57. http://www.nanocotechnologies.com/.
58. G. Hodes, *Adv. Mater.*, 2007, **19**, 639–655.
59. Y. He, Z.-H. Kang, Q.-S. Li, C. H. A. Tsang, C.-H. Fan and S.-T. Lee, *Angew. Chem., Int. Ed. Engl.*, 2009, **48**, 128–132.
60. Z. Kang, Y. Liu, C. H. A. Tsang, D. D. D. Ma, X. Fan, N.-B. Wong and S.-T. Lee, *Adv. Mater.*, 2008, **20**, 1–4.
61. P. J. F. Harris, *Carbon Nanotubes and Related Structures; New Materials for the Twenty-first Century*, Cambridge University Press, Cambridge, 2000.
62. J. A. Fagan, J. R. Simpson, B. J. Bauer, S. H. De Paoli Lacerda, M. L. Becker, J. Chun, K. B. Migler, A. R. Hight Walker and E. K. Hobbie, *J. Am. Chem. Soc.*, 2007, **129**, 10607–10612.
63. C. Y. Hong and C.-Y. Pan, *J. Mater. Chem.*, 2008, **18**, 1831–1836.
64. Y.-P. Sun, B. Zhou, Y. Lin, W. Wang, K. A. Shiral Fernando, P. Pathak, M. J. Meziani, B. A. Harruff, X. Wang, H. Wang, P. G. Luo, H. Yang, M. E. Kose, B. Chen, L. M. Veca and S.-Y. Xie, *J. Am. Chem. Soc.*, 2006, **128**, 7756–7757.
65. L. Cao, X. Wang, M. J. Meziani, F. Lu, H. Wang, P. G. Luo, Y. Lin, B. A. Harruff, L. M. Veca, D. Murray, S.-Y. Xie and Y.-P. Sun, *J. Am. Chem. Soc.*, 2007, **129**, 11318–11319.
66. P. Juzenas, W. Chen, Y.-P. Sun, M. A. Neto Cuelho, R. Generalov, N. Generalova and I. L. Christensen, *Adv. Drug Deliv. Rev.*, 2008, **60**, 1600–1614.
67. D. T. McQuade, A. E. Pullen and T. M. Swager, *Chem. Rev.*, 2000, **100**, 2537–2574.
68. G. Barbarella, M. Melucci and G. Sotgiu, *Adv. Mater.*, 2005, **17**, 1581–1593.
69. S. W. Thomas, G. D. Joly and T. M. Swager, *Chem. Rev.*, 2007, **107**, 1339–1386.
70. http://www.olympusfluoview.com/applications/fretintro.html.
71. V. Balzani, P. Ceroni, M. Maestri, C. Saudan and V. Vicinelli, *Top. Curr. Chem.*, 2003, **228**, 159–191.
72. S.-H. Hwang, C. N. Moorefield and G. R. Newkome, *Chem. Soc. Rev.*, 2008, **37**, 2543–2557.
73. V. Balzani, P. Ceroni, M. Maestri, C. Saudan and V. Vicinelli, *Top. Curr. Chem.*, 2003, **228**, 159–191.
74. A. Burns, H. Ow and U. Wiesner, *Chem. Soc. Rev.*, 2006, **35**, 1028–1042.
75. H. Ow, D. Larson, M. Srivastava, B. Baird, W. Webb and U. Wiesner, *Nano Lett.*, 2005, **5**, 113–117.
76. Z. Tian, A. D. Shaller and A. D. Q. Li, *Chem. Commun.*, 2009, 180–182.
77. J. R. Lakowicz, *Plasmonics*, 2006, **1**, 5–33.

78. J. B. Gruber, D. K. Sardar, K. L. Nash, R. M. Yow, W. Gorski and M. Zhang, *J. Appl. Phys.*, 2007, **101**, 113116; see also http://www.laserfocusworld.com/display_article/305705/12/none/none/News/BIO-PHOTONICS:-Synthesized-nanoparticle-taggant-is-nontoxic-54k-2007-09-01.
79. P. Sharma, D. Haranath, H. Chander and S. Singh, *Appl. Surf. Sci.*, 2008, **254**, 4052–4055.
80. Z. Liu, G. Yi, H. Zhang, J. Ding, Y. Zhang and J. Xue, *Chem. Commun.*, 2008, 694–696.
81. T.-L. Nguyen, P. Spizzirri, G. Wilson and P. Mulvaney, *Chem. Commun.*, 2009, **1**, 174–176.
82. J. F. Callan, A. P. de Silva and D. C. Magri, *Tetrahedron*, 2005, **61**, 8551–8588.
83. G. S. He, L.-S. Tan, Q. Zheng and P. N. Prasad, *Chem. Rev.*, 2008, **108**, 1245–1330.
84. F. Terenziani, C. Katan, E. Badaeva, S. Tretiak and M. Blanchard-Desce, *Adv. Mater.*, 2008, **20**, 4641–4678.
85. H. M. Kim and B. R. Cho, *Chem. Commun.*, 2009, 153–164.
86. O. Mongin, A. Pla-Quintana, F. Terenziani, D. Drouin, C. Le Droumaguet, A.-M. Caminade, J.-P. Majoral and M. Blanchard-Desce, *New J. Chem.*, 2007, **31**, 1354–1367.
87. M. D. Choubal, Sun Chemical Corporation, Conference Papers, ChemiChromics USA '99, New Orleans, January 1999, Spring Innovations, UK.
88. http://www.dayglo.com/; http://www.sunchemical.com/products.aspx.
89. A. V. Mercer, in *Colorants and Auxiliaries*, ed. J. Shore, Society of Dyers and Colourists, Bradford, UK, 1990, vol. **2**, pp. 470–511.
90. U. Brackmann, *Lambdachrome Dyes*, Lambda Physik GmbH, 2000.
91. P. F. Gordon, in *The Chemistry and Application of Dyes*, ed. D. R. Waring and G. Hallas, Plenum, New York, 1990.
92. H. Zollinger, *Color Chemistry*, VHCA and Wiley-VCH, 3rd edn., 2003, pp. 492–498.
93. R. Bornemann, U. Lemmer and E. Thiel, *Opt. Lett.*, 2006, **31**, 1669–1671.
94. J. Janata, *Chem. Rev.*, 2008, **108**, 327–328.
95. A. P. de Silva, T. P. Vance, M. E. S. West and G. D. Wright, *Org. Biomolec. Chem.*, 2008, **6**, 2468–2481.
96. W. Göpel, *Sens. Actuators, B*, 1998, **52**, 125–142.
97. C. McDonagh, C. S. Burke and B. D. MacCraith, *Chem. Rev.*, 2008, **108**, 400–422.
98. C. L. Baird and D. G. Myszka, *J. Mol. Recog.*, 2001, **14**, 261–268.
99. R. L. Rich and D. G. Myszka, *J. Mol. Recog.*, 2007, **20**, 300–366.
100. O. S. Wolfbeis, *J. Mater. Chem.*, 2005, **15**, 2657–2669.
101. http://www.oximetry.org/pulseox/principles.htm.
102. F. Gao, L. Wang, L. Tang and C. Zhu, *Microchim. Acta*, 2005, **152**, 131–135.

103. optimedical.com; J. K. Tusa and H. He, *J. Mater. Chem.*, 2005, **15**, 2640–2647.
104. Na^+: H. He, M. A. Mortarello, M. J. P. Leiner, S. T. Young, R. J. Fraatz and J. K. Tusa, *Anal. Chem.*, 2003, **75**, 549–555.
105. K^+: H. He, M. A. Mortarello, M. J. P. Leiner, R. J. Fraatz and J. K. Tusa, *J. Am. Chem. Soc.*, 2003, **125**, 1468–1469.
106. Ca^{2+}: H. He, K. Jenkins and C. Lin, *Anal. Chim. Acta*, 2008, **611**, 197–204.
107. A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515.
108. C. Huber, I. Klimant, C. Krause and O. Wolfbeis, *Anal. Chem.*, 2001, **73**, 2097–2103.
109. www.oxford-optronix.com.
110. B. A. McKinley, *Chem. Rev.*, 2008, **108**, 826–844.
111. S. M. Borisov and O. S. Wolfbeis, *Chem. Rev.*, 2008, **108**, 423–461.
112. M. Schäferling, M. Wu and O. S. Wolfbeis, *J. Fluoresc.*, 2004, **14**, 561–568.
113. Z. Gong and Z. Zhang, *Anal. Lett.*, 1996, **29**, 695–709.
114. S. Aoyagi and M. Kudo, *Biosens. Bioelectron*, 2005, **20**, 1680–1684.
115. http://www.resrchintl.com/raptor-detection-system.html#Assays.
116. A. A. Martí, S. Jockusch, N. Stevens, J. Ju and N. J. Turro, *Acc. Chem. Res.*, 2007, **40**, 402–409.
117. C. Gota, K. Okabe, T. Funatsu, Y. Harada and S. Uchiyama, *J. Am. Chem. Soc.*, 2009, **131**, 2766–2767.
118. F. Röck, N. Barsan and U. Weimar, *Chem. Rev.*, 2008, **108**, 705–725.
119. Chemsensing; http://www.chemsensing.com.
120. http://www.cogniscentinc.com/Technology.html.
121. J. White, K. Truesdell, L. B. Williams, M. S. Atkisson and J. S. Kauer, *PLoS Biology*, 2008, **6**, 30–36.
122. C. N. LaFratta and D. R. Walt, *Chem. Rev.*, 2008, **108**, 614–637.
123. M. De, P. S. Ghosh and V. M. Rotello, *Adv. Mater.*, 2008, **20**, 1–17.
124. C. L. Amiot, S. Xu, S. Liang, L. Pan and J. X. Zhao, *Sensors*, 2008, **8**, 3082–3105.
125. T. Huser, *Curr. Opin. Chem. Biol.*, 2008, **12**, 497–504.
126. R. Yuste, *Nature Methods*, 2005, **2**, 902–904S. Doose, *B.I.F. Futura*, 2008, **23**, 5–14.
127. P. Tinnefeld and M. Sauer, *Ang. Chem., Int. Ed. Engl.*, 2005, **44**, 2642–2671.
128. (a) E. Toprak and P. R. Selvin, *Ann. Rev. Biophys. Biomol. Struct.*, 2007, **36**, 349–369; (b) A. Yildiz and P. R. Selvin, *Acc. Chem. Res.*, 2005, **38**, 574–582.
129. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Plenum Press, New York, 1999.
130. G. Blum, G. von Degenfeld, M. J. Merchant, H. M. Blau and M. Bogyo, *Nature Chem. Biol.*, 2007, **3**, 668–677.
131. T. Terai and T. Nagano, *Curr. Opin. Chem. Biol.*, 2008, **12**, 515–521.

132. E. W. Miller and C. J. Chang, *Curr. Opin. Chem. Biol.*, 2007, **11**, 620–625.
133. E. I. Altinoğlu, T. J. Russin, J. M. Kaiser, B. M. Barth, P. C. Eklund, M. Kester and J. H. Adair, *ACS Nano*, 2008, **2**, 2075–2084.
134. T. Jamieson, R. Bakhshi, D. Petrova, R. Pocock, M. Imani and A. M. Seifalian, *Biomaterials*, 2007, **28**, 4717–4732.
135. J. M. Klostranec and W. C. W. Chan, *Adv. Mater.*, 2006, **18**, 1953–1964.
136. C. Y. Zhang, H. C. Yeh, M. T. Kuroki and T. H. Wang, *Nature Mater.*, 2005, **4**, 826–831.
137. www.nano.cancer.gov.
138. F. Helmchen and W. Denk, *Nature Methods*, 2005, **2**, 932–940.
139. X. Wang, H. E. Pudavar, R. Kapoor, L. J. Krebs, E. J. Bergey, C. Liebow, P. N. Prasad, A. Nagy and A. V. Schally, *J. Biomed. Opt.*, 2003, **6**, 319–325.
140. S. F. Lim, R. Riehn, W. S. Ryu, N. Khanarian, C.-K. Tung, D. Tank and R. H. Austin, *NanoLetts.*, 2006, **6**, 169–174.
141. D. K. Chatterjee, A. J. Rufaihah and Y. Zhang, *Biomaterials*, 2008, **29**, 937–943.
142. A. Waggoner, *Curr. Opin. Chem. Biol.*, 2006, **10**, 62–66.
143. Applied Biosystems, http://www3.appliedbiosystems.com/AB_Home/applicationstechnologies/DNASequencingbyCapillaryElectrophoresis/SequencingChemistries/index.htm.
144. B. B. Rosenblum, L. G. Lee, S. L. Spurgeon, S. H. Khan, S. M. Menchen, C. R. Heiner and S. M. Chen, *Nuc. Acid Res.*, 1997, **25**, 4500–4504.
145. E. K. Lewis, W. C. Haaland, F. Nguyen, D. A. Heller, M. J. Allen, R. C. MacGregor, C. S. Berger, B. Willingham, L. A. Burns, G. B. I. Scott, C. Kittrell, B. R. Johnson, R. F. Curl and M. L. Metzker, *PNAS*, 2005, **102**, 5346–5351.
146. For example, see http://oceanexplorer.noaa.gov/explorations/05deep-scope/background/fluorescence/fluorescence.html for marine examples.
147. http://nobelprize.org/nobel_prizes/chemistry/laureates/2008/; O. Shimomura, *J. Microscopy*, 2005, **2**, 3–15; M. Chalfie, *Photochem. Photobiol.*, 1995, **62**, 651–6; R. Y. Tsien, *Ann. Rev. Biochem.*, 1998, **67**, 509–544.
148. G. U. Nienhaus, *Angew. Chem., Int. Ed. Engl.*, 2008, **47**, 8992–8994.
149. N. C. Shaner, G. H. Patterson and M. W. Davidson, *J. Cell Sci.*, 2007, **120**, 4247–4260.
150. http://learn.hamamatsu.com/galleries/digitalvideo/index.html.
151. J. Livet, T. A. Weissman, H. Kang, R. W. Draft, J. Lu, R. A. Bennis, J. R. Sanes and J. W. Lichtman, *Nature*, 2007, **450**, 56–63.
152. D. W. Piston and G.-J. Kremers, *Trends Biochem. Sci.*, 2007, **32**, 407–414; R. Dixit, R. Cyr and S. Gilroy, *The Plant J.*, 2006, **45**, 599–615.
153. M. Mank and O. Griesbeck, *Chem. Rev.*, 2008, **108**, 1550–1564.
154. (a) M. Zimmer, *Glowing Genes: A Revolution in Biotechnology*, Prometheus Books, 2005; (b) J.R. Lakowicz and C.D. Geddes, (ed.), *Green Fluorescent Protein: 12 (Topics in Fluorescence Spectroscopy)*, Springer, 2009.

155. F. Catteruccia, J. P. Benton and A. Crisanti, *Nature Biotech.*, 2005, **23**, 1414–1417.
156. R. P. Haugland, *The Handbook – A Guide to Fluorescent Probes and Labeling Technologies*, Molecular Probes, 2005, Section 6.4.
157. S. C. De Rosa, J. M. Brenchley and M. Roederer, *Nature Med.*, 2003, **9**, 112–117.
158. A. Mills, in *Sensors for Environment, Health and Security*, ed. M.-I. Baraton, Springer Science + Business Media B.V., 2009, pp. 371–388.
159. C. Lennard, *Austr. J. Forensic Sci.*, 2007, **39**, 73–80.
160. S. Fujikawa, Y. Fukui, K. Koga, T. Iwashita, H. Komura and K. Nomoto, *Tetrahedron Lett.*, 1987, **28**, 4699–4700.
161. M. Sametband, I. Shweky, U. Banin, D. Mandler and J. Almog, *Chem. Commun.*, 2007, 1142–1144.
162. P. F. Kelly, R. S. P. King and R. J. Mortimer, *Chem. Commun.*, 2008, 6111.
163. G. Kwak, W.-E. Lee, W.-H. Kim and H. Lee, *Chem. Commun.*, 2009, 2112–2114.
164. M. Wrighton and D. L. Morse, *J. Am. Chem. Soc.*, 1974, **96**, 998–1003.
165. A. J. Lees, *Coord. Chem. Rev.*, 1998, **177**, 3–35.
166. (a) J. McKiernan, J.-C. Pouxviel, B. Dunn and J. I. Zink, *J. Phys. Chem.*, 1989, **93**, 2129–2133; (b) H. Abbas, K. P. Tiwary, L. S. S. Singh, M. Zulfequar, Z. H. Zaidi and M. Husain, *J. Luminesc.*, 2005, **114**, 162–166.
167. H. Kunkely and A. Vogler, *Mater. Chem. Phys.*, 2008, **109**, 506.
168. P. Bosch, A. Fernandez, E. F. Salvador, T. Corrales, F. Catalina and C. Peinado, *Polymer*, 2005, **46**, 12200–12209.
169. A. P. de Silva and S. Uchiyama, *Nature Nanotech.*, 2007, **2**, 399–410.
170. U. Pischel, *Angew. Chem., Int. Ed. Engl.*, 2007, **46**, 4026–4040.
171. J. F. Callan, A. P. de Silva, J. Ferguson, A. J. M. Huxley and A. M. O'Brien, *Tetrahedron*, 2004, **60**, 11125–11131.
172. A. P. de Silva, M. R. James, B. O. F. McKinney, D. A. Pears and S. M. Weir, *Nature Mater.*, 2006, **5**, 787–790.
173. F. McCapra, in *Biosensors: Fundamentals and Applications*, ed. A. P. F. Turner, I. Karube and G. S. Wilson, Oxford University Press, Oxford, 1987, pp. 617–638.
174. G. H. Posner, J. R. Lever, K. Miura, C. Lisek, H. H. Seliger and A. Thompson, *Biochem. Biophys. Res. Comms.*, 1984, 869–873.
175. I. Bronstein, B. Edwards and J. C. Voyta, *J. Biolum. Chemilum.*, 1989 **4**, 99.
176. http://www.cyalume.com/home.php; http://www.omniglow.com/og/.
177. B. D. MacCrath, in *Principles of Chemical and Biological Sensors*, ed. D. Diamond, Wiley, New York, 1998, pp. 195–233.
178. E. A. Hall, *Biosensors*, Open University Press, Milton Keynes, UK, 1990.
179. S. Girotti, F. Fini, L. Bolelli, L. Savini, E. Sartini and G. Arfelli, *Luminescence*, 2006, **21**, 233–238.
180. N. N. Ugarova, L. Yu. Brovko and E. I. Dementieva, in *Luminescence of Solids*, ed. D. R. Vij, Plenum, New York, 1998, pp. 391–411.

181. J. F. Case, S. H. D. Haddock and R. D. Harper, in *Bioluminescence and Chemiluminescence; Fundamentals and Applied Aspects*, John Wiley, Chichester, 1994, 115.
182. A. K. Campbell, *Chemiluminescence. Principles and Applications in Biology and Medicine*, VCH, Weinheim, 1988.
183. http://www.redwop.com/technotes.asp?ID = 118.
184. E. A. Widder, *Bioscience Explained*, 2001, **1**, 1–9; http://www.bioscience-explained.org/EN1.1/features.html.
185. H. Fraga, *Photochem. Photobiol. Sci.*, 2008, **7**, 146–158.
186. N. N. Ugarova, L. Yu. Brovko and E. I. Dementieva, in *Luminescence of Solids*, ed. D. R. Vij, Plenum, New York, 1998, pp. 391–411.
187. J. F. Case, S. H. D. Haddock and R. D. Harper, in *Bioluminescence and Chemiluminescence; Fundamentals and Applied Aspects*, John Wiley, Chichester, 1994, 115.
188. C. H. Contag and P. R. Contag, *Chem & Ind.*, 6 September 1999, 664–666.
189. http://www.newswise.com/articles/view/541186/; D. Zhao, E. Richer, P. P. Antich and R. P. Mason, *FASEB J.*, 2008, **22**, 2445–2451.
190. M. M. Richter, *Chem. Rev.*, 2004, **104**, 3003–3036.
191. W. Miao, *Chem. Rev.*, 2008, **108**, 2506–2553.
192. Meso Scale Discovery, www.mesoscale.com.
193. Roche Diagnostics Corp., www.roche.com.
194. E. F. Shubert, *Light Emitting Diodes*, Cambridge University Press, Cambridge UK, 2003.
195. R. J. D. Tilley, *Color and the Optical Properties of Materials*, John Wiley & Sons, Chichester, 2000, p. 278.
196. S. Tanaka, H. Kobayashi, H. Sasakura and N. Miura, in *Practical Applications of Phosphors*, ed. W. M. Yen, S. Shionaya and H. Yamamoto, CTC Press, Boca Raton, 2007.
197. P. De Visschere, Conference Papers, *ChemiChromics '97*, June 1997, Spring Innovations, UK.
198. H.-E. Gumlich, A. Zeinert and R. Mauch, in *Luminescence of Solids*, ed. D. R. Vij, Plenum, New York, 1998, p. 256.
199. X. Wu, A. Nakua and D. Cheong, *Journal of the SID*, 2004, 12/3.
200. R. J. D. Tilley, *Color and the Optical Properties of Materials*, Wiley, Chichester, 2000, p. 276.
201. N. Holonyak and S. F. Bevacqua, *Appl. Phys. Lett.*, 1962, **1**, 82–83.
202. Wikipedia, 2008.
203. S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku and Y. Sugimoto, *Japan J. Appl. Phys.*, 1996, **2, 35**(1B), L74–1.
204. www.lanl.gov.
205. Lumileds Lighting LLC and MIT, *US Pat.*, 6,914,265, 2005 and references therein.
206. A. Zukauskas, M. S. Shur and R. Gaska, *Introduction to Solid-State Lighting*, John Wiley & Sons, Chichester & New York, 2002.

207. K. Bando, K. Sakano, Y. Noguchi and Y. Shimizu, *J. Light Vis. Environ.*, 1998, **22**, 2–5.
208. H. Tamaki and Y. Murazaki, in *Practical Applications of Phosphors*, ed. W. M. Yen, S. Shionoya and H. Yamamoto, CRC Press, Boca Raton, 2007, pp. 193–203.
209. Y. Narukawa, J. Narita, T. Sakamoto, T. Yamada, H. Narimatsu, M. Sano and T. Mukai, *Phys. Stat. Sol. (A)*, 2007, **204**, 2087–2093.
210. M. J. Bowers, J. R. McBride and S. J. Rosenthal, *J. Am. Chem. Soc.*, 2005, **127**, 15378–15379.
211. J. J. Wierer, M. R. Krames, J. E. Epler, N. F. Gardner, M. G. Craford, J. R. Wendt, J. A. Simmons and M. M. Sigalas, *Appl. Phys. Lett.*, 2004, **84**, 3885–3887.
212. Phillips Lumileds Lighting and Avago Technologies General, *US Pat.*, 7,279,718, 2007.
213. D. J. Segler, *Light Emitting Diode (LED) Technology and Its Impact on DLP Television Applications*, www.designline.com, November 2008.
214. C. W. Tang and S. A. van Slyke, *Appl. Phys. Lett.*, 1987, **51**, 913.
215. J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn and A. B. Holmes, *Nature*, 1990, **347**, 539.
216. K. Müllen and U. Scherf, (ed.), *Organic Light Emitting Devices, Synthesis, Properties and Applications*, Wiley-VCH, Weinheim, 2006.
217. Z. Li and H. Meng, (ed.), *Organic Light Emitting Materials and Devices*, CRC Press, Boca Raton, FL, 2007.
218. H. Yetsin (ed.), *Highly Efficient OLEDs with Phosphorescent Materials*, Wiley-VCH, Weinheim, 2007.
219. H. Meng and N. Herron, in *Organic Light Emitting Materials and Devices*, ed. Z. Li and H. Meng, CRC Press, Boca Raton, FL, 2007, p. 322.
220. H. Meng and N. Herron, in *Organic Light Emitting Materials and Devices*, ed. Z. Li and H. Meng, CRC Press, Boca Raton FL, 2007, p. 333.
221. C. Chen, *Chem. Mater.*, 2004, **16**, 4389–4400.
222. Y.-S. Yao, Q.-X. Zhou, X.-S. Wang, Y. Wang and B.-W. Zhang, *Adv. Funct. Mater.*, 2007, **17**, 93–100.
223. C. H. Chen and C. W. Tang, *Appl. Phys. Lett.*, 2001, **77**, 3711–3713.
224. Idemitsu Kosan Co. Ltd, *US Pat.*, 5,389,444, 1995.
225. M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson and S. R. Forrest, *Nature*, 1998, **395**, 151–154.
226. E. Holder, B. M. W. Langevals and U. Schubert, *Adv. Mater.*, 2005, **17**, 1109–1121.
227. S. Kappaun, C. Slugovc and E. J. W. List, *Int. J. Mol. Sci.*, 2008, **9**, 1527–1547.
228. J. D. Slinker, J. Rivnay, J. S. Moskowitz, J. B. Parker, S. Bernhard, H. D. Abruòac and G. G. Malliaras, *J. Mater. Chem.*, 2007, **17**, 2976–2988.
229. W.-Y. Wong, G.-J. Zhou, X.-M. Yu, H.-S. Kwok and Z. Lin, *Adv. Funct. Mater.*, 2007, **17**, 315–323.

230. D. F. Peripichka, I. F. Peripichka, H. Meng and F. Wudl, in *Organic Light Emitting Materials and Devices*, ed. Z. Li and H. Meng, CRC Press, Boca Raton, FL, 2007, pp. 45–293.
231. D. F. Peripichka, H. Meng and M.-M. Ling, in *Organic Light Emitting Materials and Devices*, ed. Z. Li and H. Meng, CRC Press, Boca Raton, FL, 2007, pp. 413–449.
232. A. J. Sandee, C. K. Williams, N. R. Evans, J. E. Davies, C. E. Boothby, A. Köhler, R. H. Friend and A. B. Holmes, *J. Am. Chem. Soc.*, 2004, **126**, 7041.
233. P. L. Burn, S.-C. Lo and I. D. W. Samuel, *Adv. Mater.*, 2007, **19**, 1675–1688.
234. S. Li, G. Zhong, W. Zhu, F. Li, J. Pan, W. Huang and H. Tian, *J. Mater. Chem.*, 2005, **15**, 3221.
235. Q.-D. Liu, J. Lu, J. Ding, M. Day, Y. Tao, P. Barrios, J. Stupak, K. Chan, J. Li and Y. Chi, *Adv. Funct. Mater.*, 2007, **17**, 1028–1036.
236. B. W. D'Andrade and S. R. Forrest, *Adv. Mater.*, 2004, **16**, 1585–1595.
237. A. Misra, P. Kumar, M. N. Kamalasanan and S. Chandra, *Semicond. Sci. Technol.*, 2006, **21**, R35–R47.
238. D. Gupta, M. Katiyar and Deepak, *Optical Materials*, 2006, **28**, 295–301.
239. B. W. D'Andrade, J. Brooks, V. Adamovich, M. E. Thompson and S. R. Forrest, *Adv. Mater.*, 2002, **14**, 1032.
240. J. A. Cheng and C. H. Chen, *J. Mater. Chem.*, 2005, **15**, 1179.
241. A. Misra, P. Kumar, M. N. Kamalasanan and S. Chandra, *Semicond. Sci. Technol.*, 2006, **21**, R35–R47.
242. B. C. Krummacher, V.-E. Choong, M. K. Mathai, S. A. Choulis, F. So, F. Jermann, T. Fiedler and M. Zachau, *Appl. Phys. Lett.*, 2006, **88**, 113506–1.
243. I. Sage, *Chem. Brit.*, 2000, **37**(2), 24–27.
244. I. Sage and G. Bourhill, *J. Mater. Chem.*, 2001, **11**, 231–245.
245. C. G. Camara, J. V. Escobar, J. R. Hird and S. J. Putterman, *Nature*, 2008, **455**, 1089–1093.
246. N. E. Harvey, *Science*, 1939, **89**, 460–461.
247. V. V. Karasev, N. A. Krotova and B. W. Deryagin, *Dokl. Akad. Nauk. SSSR*, 1953, **88**, 777–780.
248. M. S. Russell, *The Chemistry of Fireworks*, RSC, Cambridge, 2000.
249. J. Donner, *A Professional's Guide to Pyrotechnics: Understanding and Making Exploding Fireworks*, Paladin Press, Boulder, CO, 1997.

CHAPTER 4

Phenomena Involving Absorption of Light and Energy Transfer

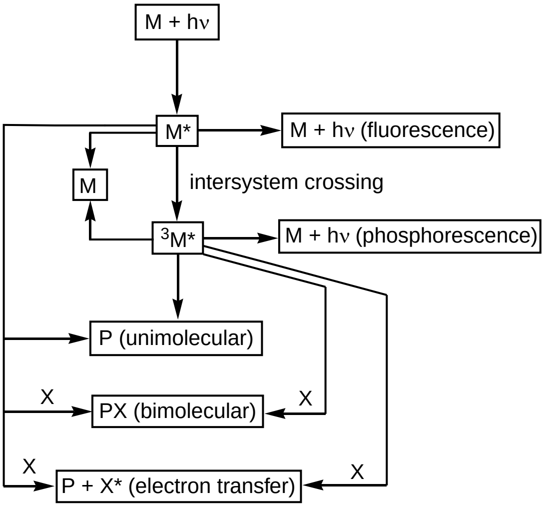
4.1 Introduction

The excited state produced by the interaction of a dye molecule with light can lose or transfer its energy in a variety of ways.[1] We have already discussed aspects of these processes in Chapter 3, when we introduced photoluminescence in Section 3.5. Return to the ground state from the first excited state can be accompanied by the emission of light (fluorescence) or by non-radiative deactivation and output of heat energy as successively lower vibrational levels are occupied. The excited molecule can alternatively undergo intersystem crossing to the triplet state before returning to the ground state with emission of light (phosphorescence) or by non-radiative deactivation and output of heat energy, both at a much slower rate than decay from the singlet state. The excited state (either singlet or triplet) can also undergo unimolecular or bimolecular photochemical reactions to give different products or it can transfer its excitation to another ground state molecule (electronic excitation transfer). Because the triplet excited state is longer lived than the singlet excited state it is often more important in photochemical reactions. These reaction pathways are shown schematically in Figure 4.1.

The photoluminescent processes, fluorescence and phosphorescence, together with the products exhibiting this phenomenon and its applications, are covered throughout Chapter 3 of this book. A unimolecular photochemical process involving internal rearrangement, photochromism, is covered under colour change phenomena in Chapter 1 (Section 1.2). The present chapter will deal with those phenomena involving photochemical reactions of coloured molecules that can transfer electromagnetic energy, often from a laser but also from the sun, into another useful form of energy, *e.g.* thermal (optical data storage) or generation of electrical energy (photovoltaics), or cause sensitisation of oxygen (photodynamic therapy). In the majority of cases the applications for these coloured molecules are not based on their intrinsic colour but on

Chromic Phenomena: Technological Applications of Colour Chemistry, Second Edition
By Peter Bamfield and Michael G. Hutchings

Published by the Royal Society of Chemistry, www.rsc.org



M = ground state molecule
M* = excited state molecule
P = photochemical product
X = second molecule

$M \rightarrow M^* \rightarrow M$ 10^{-11} - 10^{-7} sec
$M \rightarrow M^* \rightarrow {}^3M^* \rightarrow M$ 0.01 - 1 sec

Figure 4.1 Photophysical and photochemical pathways for excited molecules.

the fact that they can be used to absorb light of a particular wavelength as required by the application, hence the use of the term functional dyes.

4.2 Laser Addressable Compounds (Infrared Absorbers)

Since the advent of low-cost semi-conducting diode lasers there has been much interest in compounds that absorb in the near infrared (NIR) region of the spectrum. This is because they can be used to absorb the energy of the laser at a specific wavelength of the spectrum, as for the GaAs-based lasers at 770–840 nm. The resultant energy of the excited state of the molecule can then be used in a variety of applications (see Section 4.2.3). Whilst these functional compounds are usually described in the literature under the generic title of *infrared absorbers* or *dyes*, recent developments in lasers make this too prescriptive. The development of visible light lasers, *e.g.* blue, green lasers, together with the frequency doubling of NIR energy from an Nd:YAG laser from 1064 to 532 nm, has generated interest in absorbers with a specific intense absorption in those regions of the visible spectrum. In addition dyes are used as

Table 4.1 Laser and LED addressable wavelengths.

Laser	*Wavelength, nm*
Third harmonic Nd:YVO_4	355 (violet)
Argon ion	488
KDP/Nd:YAG doubled	532
Ruby (rarely used)	670 725
Helium neon	633
Titanium sapphire	800 1200
Nd:YAG	1064
Dye lasers	310 1285 (tuneable)
Diode (InGaN based)	350 400 (violet)
Red laser diodes	630 650, 670
Diode (GaAlAs based)	770 810, 830
LED	
InGaN	450
GaP	550 or 700
GaAsP	580 or 660
GaAs	880
Si	1100

sensitisers in applications using argon ion lasers (488 nm), helium neon gas lasers (633–635 nm) and red laser diodes and LEDs (630–670 nm) (see Sections 4.5 and 4.6). Hence a more appropriate term for these materials is *laser addressable compounds*. Typical lasers and the required wavelength for addressing are shown in Table 4.1.

In spite of the advent of visible light lasers the interest in NIR absorbers continues because they offer certain advantages, especially if they show little or no absorption in the visible region, for instance their use in invisible security markings and most importantly in human tissue and organ applications.[2,3] The NIR absorbers may be classified according to their chemical structures or the region of the spectrum in which they absorb useful laser energy.[4 6] In this text they will be classified according to their chemical structure. Products are available commercially covering a wide range of absorption maxima that are both oil and water miscible and dispersible in a variety of polymers.[7 11]

This section will be concerned with one-photon NIR absorbers, whilst the important area of two-photon absorbers (2PA), the mechanism of which is described in Chapter 3 (Section 3.5.3), will be alluded to under the relevant areas. The related topic of NIR emission is covered in detail in Chapter 3, with Table 3.7 providing a list of the many luminescent systems which exhibit this property.

4.2.1 Organic and Organometallic NIR Absorbers

A wide range of chemical classes contain compounds which exhibit absorption into the NIR region, but often by tailing from their main absorption bands in the visible region. However, only those which are used to provide IR absorbers of practical importance by absorbing strongly in the range from 700 nm up to around 1500 nm will be covered.

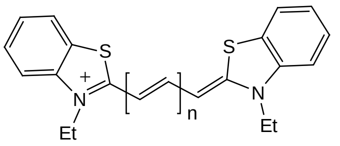
4.2.1.1 Cyanines

Perhaps the most widely studied and applied chemical class of NIR absorbers are the cyanines.[12] The chemistry of cyanines and other applications are discussed in detail elsewhere in this book (Chapter 1, Section 1.10.2, Chapter 2, Section 2.3.1.4 and Chapter 3, Section 3.5.1.7). Applications of cyanines appear throughout this chapter, including their use as photosensitisers in colour photography and photodynamic therapy, in optical data storage and solar cells.

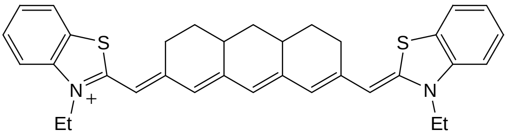
The main factors influencing the position of their absorption maxima and extinction coefficients are:[2,13]

- The length of the conjugating bridge between the terminating heterocyclic donor moieties;
- The electron donating strength of the terminal heterocyclic residues;
- The electronic characteristics of the individual atoms in the conjugating bridge.

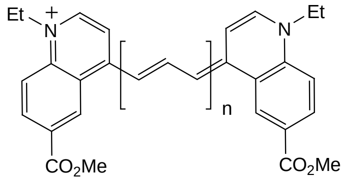
The effect of increasing the length of the conjugating bridge is illustrated in (4.1) where each extra double bond moves the absorption maximum approximately 100 nm further toward or into the NIR region. Unfortunately, the usefulness of this simple method of shifting the maxima by extending the chain starts to break down when n >4. This is because after this point the absorption broadens and the extinction coefficient drops dramatically, as does the dye's stability to light, heat and oxidation. There are ways of overcoming this problem; for instance introducing rigidity into the molecule by having the polyene chain as part of a linear carbocyclic ring system (4.2), or extending the chain through the terminal moiety (4.3). The influence of putting more effective electron donor moieties at the terminal points of the conjugated chain is illustrated in the series (4.4) and (4.5).



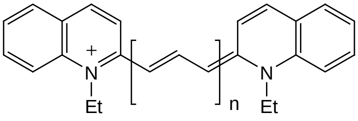
(4.1)
n = 2 λ_{max} 662, ε_{max} 200,000 (EtOH)
n = 3 λ_{max} 772, ε_{max} 165,000 (EtOH)
n = 4 λ_{max} 845, ε_{max} 130,000 (EtOH)



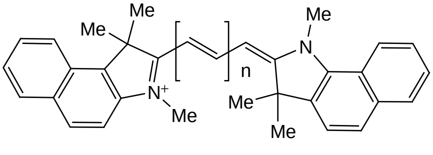
(4.2)
λ_{max} 855 nm, ε_{max} 155,000 (DMSO)



(4.3; n = 3)
λ_{max} 957 nm, ε_{max} 166,000



(4.4; n = 3)
λ_{max} 820 nm, ε_{max} 115,000

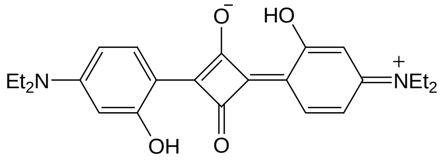


(4.5; n = 3)
λ_{max} 782 nm, ε_{max} 188,000 (EtOH)

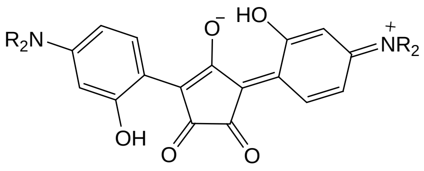
The wavelength of absorption in cyanine dyes in the NIR is also affected by J-aggregate formation as is discussed under their colour-change phenomena in Chapter 1 (Section 1.10).[14]

4.2.1.2 Squarylium and Croconium Dyes

The squarylium (4.6) and croconium (4.7) dyes are closely related structurally to cyanines but are in fact donor–acceptor molecules and consequently the design principles of NIR absorbers based on these chromophores are different.[2,6,15,16] Their synthesis is achieved easily by reacting either squaric acid, or preferably an alkylated derivative such as di-n-butyl squarate, or croconic acid with electron donor molecules, typically *N*,*N*′-dialkylanilines. The croconium dyes absorb at significantly longer wavelengths than the squaryliums.

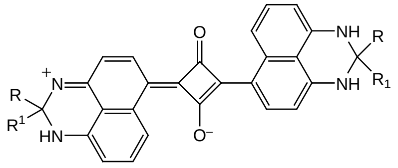


(4.6)
λ_{max} 639 nm, ε_{max} 224,000

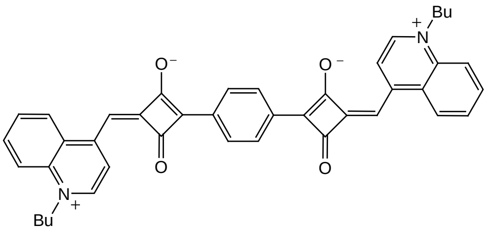


(4.7)
λ_{max} 817 nm, ε_{max} 210,000

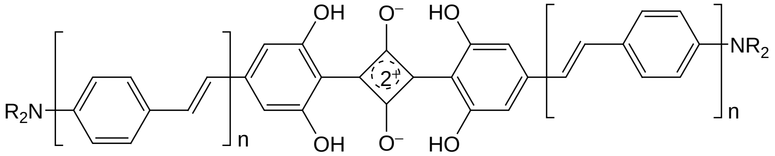
Wide variation of the donor groups on the squarylium dyes of parent structure type (4.6) only gives a maximum wavelength of absorption of not more than 700 nm, and for some of the projected uses of such absorbers this needs to be pushed further into the NIR.[17] To achieve this aim several tactics have been employed. For instance, using strong electron donors such as the dihydroperimidine ring system moves the absorption well into the NIR, as exemplified by (4.8), at 800–810 nm.[18] Combining with the stilbene chromophore is also effective in obtaining this goal as shown by (4.9) where an absorption maximum of 901 nm ($CHCl_3$) when n = 1 is obtained (see also Chapter 3, Section 3.5.1.9).[19] A third way is to use an aryl group as a bridge between two squaric acid derivatives as in (4.10) giving an absorption maximum at 768 nm ($CHCl_3$).[20]



(4.8)
λ_{max} 800-810 nm, ε_{max} 150,000

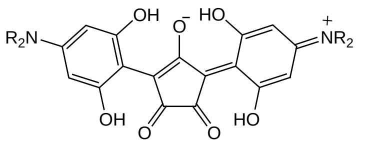


(4.10)
λ_{max} 768 nm, ε_{max} 150,000 ($CHCl_3$)

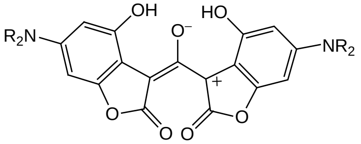


(4.9)
n = 1, λ_{max} 900 nm, ε_{max} 200,000 ($CHCl_3$)

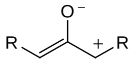
Croconium absorbers with two extra hydroxy groups in the 6′ positions of the phenyl groups in (4.7) are much more thermally stable,[21] and whilst trying to synthesise analogues which could form J-aggregates and hence produce a bathochromic shift, Tian and co-workers discovered a new class of long-wavelength absorbers.[22] Ring opening of the croconic acid moiety in (4.11) followed by cyclisation onto the adjacent hydroxy groups gave a product having the di(benzofuranonyl)methanolate structure (4.12). The solution spectra of (4.12) show a broad absorption centred at 1100 nm ($CHCl_3$) with J-aggregate formation in spin-coated films moving the absorption band to 1228 nm. These are exceptional figures for such a simple molecule and Langhals has suggested that this is due to the presence of what he calls a "super acceptor group" comprising a central mesoionic unit (4.13), aided by the two carbonyl groups of the lactone rings.[23]



(4.11)



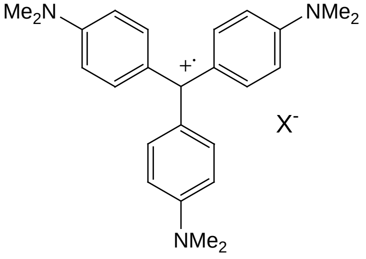
(4.12)
λ_{max} 1100 nm, ε_{max} 80,000 ($CHCl_3$)



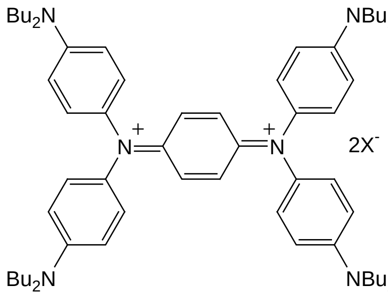
(4.13)

4.2.1.3 Iminium Salts

The salts of the iminium radical cations (4.14) and diiminium dications (4.15), especially the latter, are highly coloured compounds, which absorb well into the NIR with maxima at 920 nm (4.14) and 1064 nm (4.15), ε_{max} 81,300 (EtOH).[7]



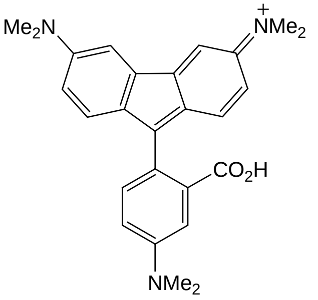
(4.14)
λ_{max} 850 nm (MeOH)



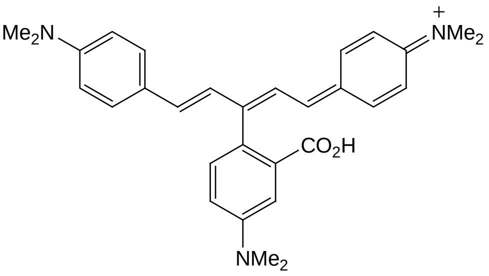
(4.15)
λ_{max} 1064 nm, ε_{max} 81,300 (MeOH)

4.2.1.4 Triphenylmethanes

The blue and green dyes based on the triphenylmethane chromophore (Chapter 2, Section 2.3.1.5) can be modified to move their absorption maxima into the NIR. This can be achieved either by joining two of the aromatic rings *via* a direct link or by extending the conjugation from the trisubstituted central carbon atom. This is exemplified by the two products which are essentially derived from Crystal Violet Lactone, with a bridging bond (4.16) or more effectively by adding ethylenic links on two sides of the central carbon atom (4.17).[24]



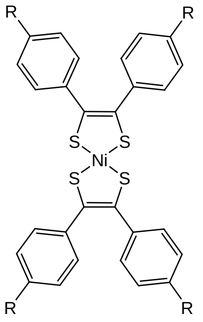
(4.16)
λ_{max} 625 and 850 nm (thermal paper)



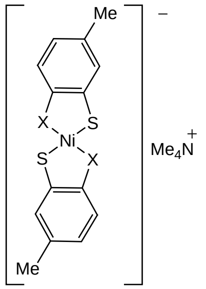
(4.17)
λ_{max} 850 nm

4.2.1.5 Nickel Dithiolenes

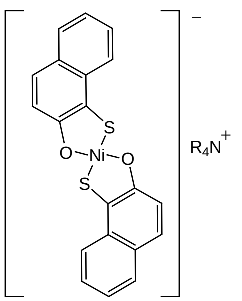
Several transition metal ions form stable complexes with aliphatic 1,2-dithiols which absorb in the NIR. Known as dithiolenes, the nickel complexes in particular have been found to have valuable properties.[25] Their strong NIR absorption maximum is considered to be a function of both extensive electron delocalisation about the dithiolene ring system and interaction of this delocalised system with available d-orbitals on the central metal. The physical properties of dithiolenes can be readily tailored by variations on the substituents attached to the dithiols, see (4.18). Although they have low absorption coefficients when compared to cyanines *etc.*, they do have one big advantage in that they show very little absorption in the visible region, making them useful for areas such as invisible security markings.[26] Structurally analogous dyes can be made from aromatic dithiols and oxothiols (4.19), and the much more bathochromic naphthalene derivatives (4.20), but they are much weaker absorbers. Dithiolenes have been examined for use in outlets such as thermal imaging, photolithography and electrophotography, reverse saturable absorbers and optical limiters, and as guest–host dyes for LC electro-optic devices in NIR applications.[25]



(4.18)
R = H λ_{max} 866 nm ε_{max} 31,000
R = OMe λ_{max} 925 nm ε_{max} 35,000
(CH_2Cl_2)



(4.19)
X = S λ_{max} 890 nm ε_{max} 14,000
X = O λ_{max} 984 nm ε_{max} 14,600
(acetone)

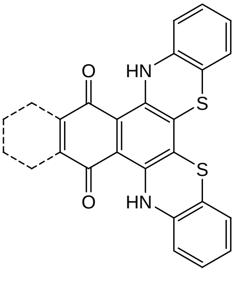


(4.20)
λ_{max} 1110 nm ε_{max} 12,000
(acetone)

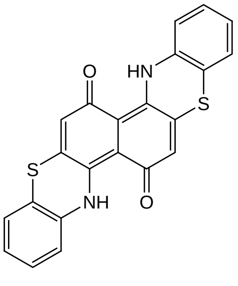
4.2.1.6 Quinones and Indoanilines

Both 1,4-naphthoquinones bearing annulated benzthiazine rings as illustrated by compound (4.21) or its anthraquinone analogue, and 1,5-naphthaquinones (4.22), absorb in the NIR.[27] Unfortunately, the naphthoquinones tend to have low stability and products from both ring systems are strongly coloured, limiting their areas of application.

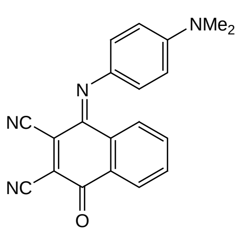
The absorption maxima of indoaniline dyes derived from naphthols can also be extended well into the NIR by having strongly electron withdrawing groups attached to the quinone ring, as shown in (4.23).[28] Heterocyclic indoanilines also form stable metal complexes (4.24) absorbing in the NIR region 745–776 nm (EtOH).[29]



(4.21)
λ_{max} 725 nm ε_{max} 15,200

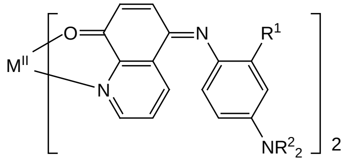


(4.22)
λ_{max} 750 nm ε_{max} 32,000

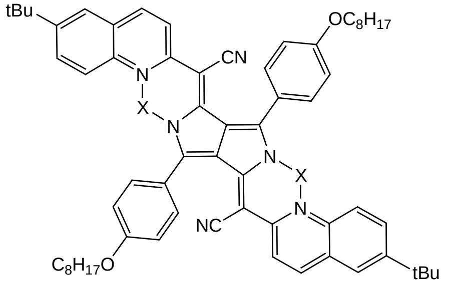


(4.23)
λ_{max} 795 nm ($CHCl_3$)

Reaction of the keto groups in the diketo-pyrrolopyrrole chromophore (Chapter 2, Section 2.4.1.9) with 2-cyanomethyl heteroaromatic compounds gives products absorbing in the NIR, *e.g.* (4.25, X = H) at 731 nm ($CHCl_3$). Substituting the NH bridge protons with either BF_2 or BPh_2 rigidifies the structure, causing a further bathochromic shift to 754 nm and 819 nm respectively.[30]



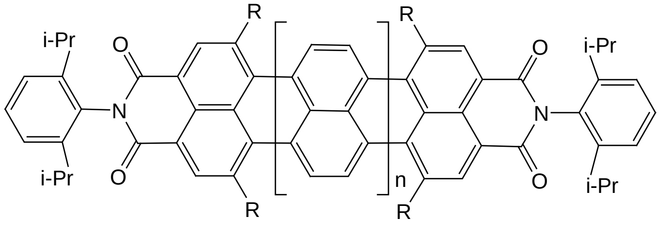
(4.24)
λ_{max} 745-776 nm (EtOH)



(4.25)
X = H, λ_{max} 731nm (CHCl$_3$)
X = BF$_2$, λ_{max} 754 nm (CHCl$_3$)
X = BPh$_2$, λ_{max} 819 nm (CHCl$_3$)

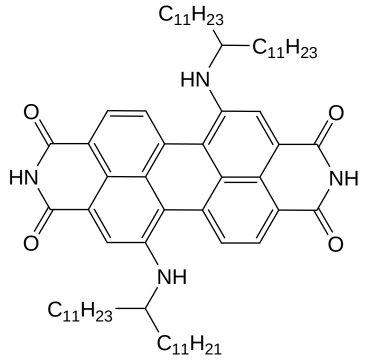
4.2.1.7 Perylenes and Related Structures

Perylene bisimides (PBIs) are well-known stable chromophores used as pigments (see Chapter 2, Section 2.4.1.7) which have been adapted for other technological applications.[31(a)] The parent chromophore exemplified by (4.26a; n = 0) absorbs in the visible region at 520 nm, whilst its homologous terrylene bisimides (4.26b; n = 1) absorb at 660 nm.[31(b)] Further core extension to the higher homologues produces a bathochromic shift of the absorption to the NIR region: quaterrylene bisimide (4.26c; n = 3) absorbing at 760 nm; the pentarylene (4.26d; n = 4) at 830–880 nm; and the hexarylene (4.26e; n = 5) at 950 nm.[32(a)] Replacing the terrylene ring in (4.26b; n = 1) with a dibenzoterrylene ring gives a product with intense absorption at 1020–1024 nm, overlapping with the region required for addressing with the Nd-YAG laser (1064 nm).[32(b)]



(4.26a-e, n = 0-4)
R = 4-t-octylphenoxy

Perylene bisimides are also well known to form J-aggregates with a bathochromic shift in absorption (see Chapter 1, Section 1.10.2). This property has been used to move the so-called "green" PBIs, *i.e.* 1,7-diamino-substituted PBIs,[33] which absorb at 450 and 700 nm, much further into the IR region. The 1,7-dialkylamino PBI (4.27) absorbs at 702 nm with emission at 760 nm in polar solvents, but in aliphatic solvents the fluorescence is completely quenched and the absorption moves to 822 nm.[34] These types of dye aggregate bear distinct similarities to natural light-harvesting bacteriochlorophyll, having a J-type absorption band beyond 800 nm and a second higher energy band at around 450 nm, and consequently are promising materials for NIR light absorption in organic solar cells and photosensitisation.



(4.27)

4.2.1.8 Phthalocyanines, Porphyrins and Analogues

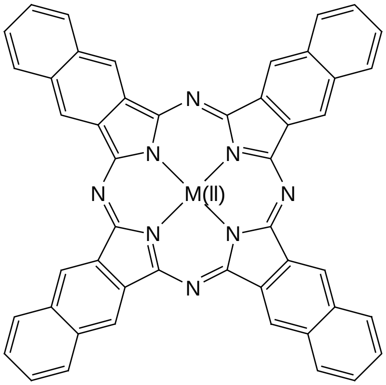
Phthalocyanine, its metal salts, and ring-substituted and benzannulated derivatives form a very important class of NIR absorbers, being extremely strong (ε_{max} *ca.* 200,000), generally very environmentally stable and with wide applications.[35(a)] The synthetic pathways to these molecules are all variations on the methods already described in Chapter 2 (Section 2.4.1.5), the preferred routes starting from a substituted phthalonitrile with tetramerisation in the presence of the appropriate metal salt.[35(b)] An alternative route to copper phthalocyanines bearing arylthio substituents, which are valuable NIR absorbers, involves displacement of the halogen atoms in the polychlorinated derivative.[36,37] As already stated most phthalocyanines exhibit polymorphism, and many of these morphological forms absorb in the NIR, especially in the solid state. For instance, in the case of the metal-free, unsubstituted parent phthalocyanine, usually designated as H_2Pc for convenience, the longest wavelength absorption Q-band in the α-form is at 693 nm, but in the β-form this is at 740 nm and in the X-form at 830 nm, ideal for diode lasers. Incorporation of a transition metal atom has little influence on the Q-band in solution, but it does allow for new morphological forms absorbing in the NIR. Titanyl phthalocyanines are of particular value, offering a variety of forms absorbing in the range 780–830 nm. Substitution in the benzene rings of the phthalocyanine with electron-donating substituents, such as alkoxy, aryloxy and thioxy, shift the Q-band absorption bathochromically by 70–100 nm, depending on the central metal atom.[14] A selection of various NIR absorbing phthalocyanines is shown in Table 4.2.

Benzannulation of the phthalocyanine ring is a way of extending the π-orbitals of the central ring system, and moving the long-wavelength absorption

Table 4.2 Absorption maxima of near IR absorbing phthalocyanines.

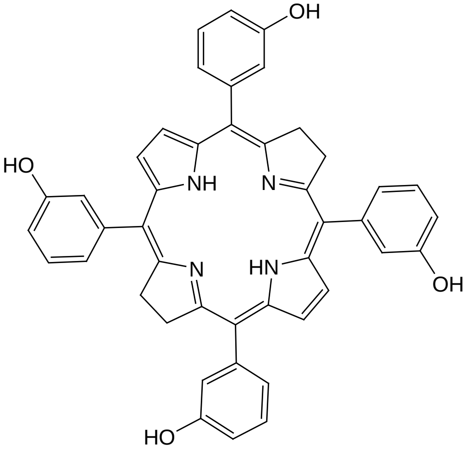
Phthalocyanine	*Form (film)*	λ_{max} *nm*
Metal free phthalocyanine	Solution	699
Metal free phthalocyanine	β form (crystal)	740
Metal free phthalocyanine	X form	830
Copper phthalocyanine	X form	782
Lead phthalocyanine	Triclinic	870
Titanyl phthalocyanine	Phase 1	780
Titanyl phthalocyanine	Phase 2	830
Titanyl phthalocyanine	Y form	830
Vanadyl phthalocyanine	Phase II	834
Chloroindium phthalocyanine		740
Zinc naphthalocyanine		760
Cobalt naphthalocyanine tetra t butyl	Solution	752
Cobalt anthracocyanine tetra t butyl	Solution	832

into the NIR. Of particular value are the naphthalocyanines (4.28) made from 2,3-naphthalonitrile, which are 80 nm more bathochromic than phthalocyanines. Addition of a further benzene ring, by use of anthracene-2,3-dinitrile, produces anthracocyanines that are even more bathochromic (150 nm).

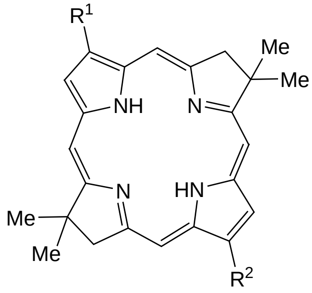


(4.28)

Porphyrins and expanded analogues are proving to be a rich source of NIR-absorbing molecules. Of the naturally occurring porphyrin-based ring systems the bacteriochlorins absorb at the longest wavelength. They have therefore been used as an entry point into NIR absorbers for practical applications. Substitution on the meso positions of the porphyrin ring is one method as in the bacteriochlorin (4.29), an early candidate for use in photodynamic therapy (see Section 4.6.2.3 for others).[38] A range of wavelength-tuneable absorbers can be obtained by putting substituents on the periphery at the 3- and 13- positions of bacteriochlorins causing bathochromic shifts from the unsubstituted ring system (4.30a) of 713 nm to 729–768 nm as exemplified by (4.30b–d).[39]

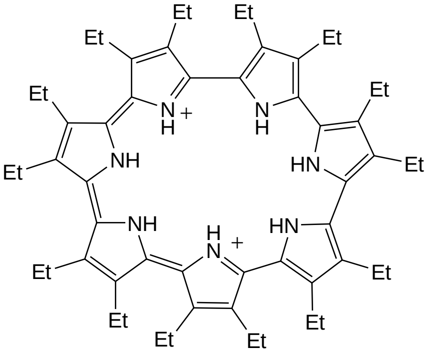


(4.29)
λ_{max} 735 nm (MeOH)



(4.30)
(a) $R^1 = R^2 = H$ λ_{max} 713 nm
(b) $R^1 = R^2 = Br$ λ_{max} 729 nm
(c) $R^1 = R^2 = Ph$ λ_{max} 736 nm
(d) $R^1 = R^2 = COMe$ λ_{max} 768 nm

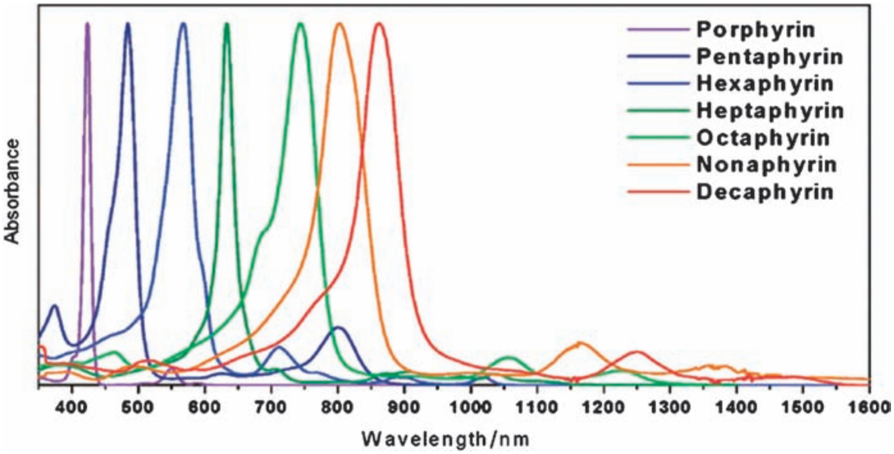
Expanded porphyrins containing more than four pyrrole units in the ring are a recently introduced class of molecules that absorb in the NIR.[40,41] These macrocycles have a more extended π-conjugation pathway and hence give rise to large red-shifted absorption bands from those relative to normal tetrapyrrolic porphyrins, as shown in Figure 4.2, with the [26]hexaphyrin (4.31) as a structural example.[41,42] Strong IR absorption is also shown by related ring systems especially those that obey the (4n + 2) rule *e.g.* the cyclo7pyrrole (4.32).[41] Many dimeric and extended porphyrin molecules have been developed because of their efficient two-photon absorption (2PA).[43]

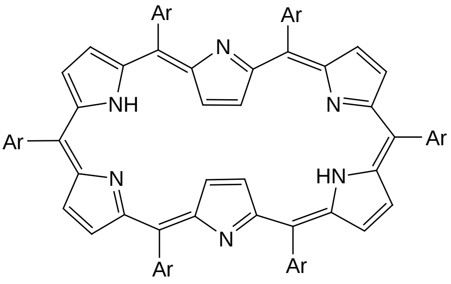


(4.32)
λ_{max} 940 nm

4.2.1.9 Donor Acceptor Extended Conjugated Molecules

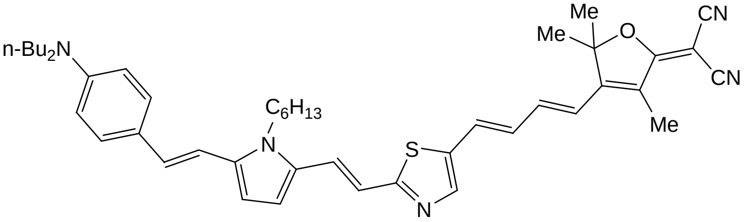
Through-conjugated donor–acceptor chromophores such as (4.33) show absorption in the NIR.[44] NIR absorption can also be achieved by using donors linked *via* extended π-conjugation as in (4.34).[45] An important property of such molecules is their ability to show 2PA at telecommunication wavelengths (1.3–1.5 μm).



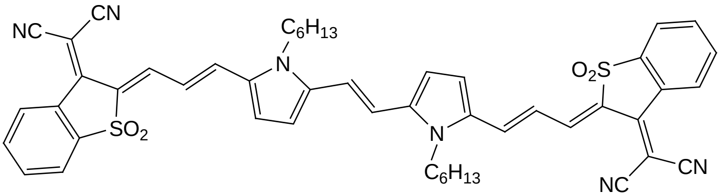


(4.31)

Figure 4.2 The steady state absorption spectra of expanded porphyrins.[41]



(4.33) λ_{max} 720 nm



(4.34) λ_{max} 889 nm

4.2.2 Inorganic NIR Absorbers

Many inorganic compounds, for example iron oxide, absorb broadly into the NIR and consequently are used in applications such as laser welding of plastics, and as transparent pigments when low colour is of importance (see Section 4.2.3). Because of their broad absorption in the NIR they also find use as IR reflectors in materials for controlling solar heating in architectural and other structures.[46] However, the most exciting recent developments of inorganic NIR absorbers are quantum dots and metallic nanoparticles, whose applications are set to grow rapidly.

Quantum dots (QDs) exhibiting NIR luminescence are discussed in Chapter 3 (Section 3.5.2.1) but absorption is another property that can be exploited. For instance they find use as sensitisers in photomedical procedures such as photodynamic therapy, and in photovoltaic applications (see Section 4.8.1)[47] Examples include colloidal nanocrystals of PbS, PbSe and InS whose absorption can be tuned by their size, *e.g.* 6.5 nm PbS QDs absorb at 1300 nm.[48]

Metallic nanoparticles (MNPs) are covered in detail in Chapter 1 (Section 1.12). The most commonly used metals are Ag and especially Au.[49] AuNPs are strong absorbers of visible and NIR light (molar absorption more than 10^5 times that of conventional dyes), and are essentially non-fluorescent above about 2 nm diameter, as all absorbed photo energy is converted to thermal energy making them especially suitable for photothermal medicine (Section 4.6.4).

4.2.3 Applications of Laser Addressable Compounds and NIR Absorbers

The application areas for these materials can be classified as follows:

- *Those involving energy conversion*
  - Optical data storage (see Section 4.3) – thermal
  - Solar heating and shielding – thermal
  - Laser welding of plastics – thermal
  - Fusion of toner resins – thermal
  - Computer to plate lithography – thermal
  - Imaging – thermal
  - Photothermal therapy (see Section 4.6.4) – thermal
  - Organic photoconductors in laser copying/printing (see Section 4.4) – electrical
  - Photovoltaics (see Section 4.8.1) – electrical
- *Those using photosensitisation*
  - Photopolymerisation (see Section 4.5.2)
  - Photodecontamination (see Section 4.7)
  - Photomedicine, PDT *etc.* (see Sections 4.6.1 and 4.6.2)
- *Those involving selective absorption of light*
  - Photographic sensitisers (Section 4.5.3)

- ○ Security and machine-readable data
- ○ Eye protection (*e.g.* laser shields – optical limiting (see Section 5.6.5.3))
- ○ Camouflage

4.2.3.1 Thermal Energy Conversion

Solar shielding and heating. Sunlight contains a significant portion of NIR radiation, which can be either useful or a nuisance, depending on the environment on which it impinges. It is useful in solar-cell applications for the production of electrical energy, but of nuisance value when it strikes through glass in architectural glazing units, greenhouses and in cars and other vehicles, causing excessive heating and hence the need for extra air-conditioning (see also Chapter 1, Section 1.5.4.2). Reflective coatings are the most common answer to this problem and organic pigment NIR reflectors can be used in this context.[50] But it is also possible to absorb the energy in a layer of IR absorbers, *e.g.* in a polymer interlayer in multiplex glass or polymer film coating, and then lose the heat generated to an external atmosphere by convection. In this context organic NIR absorbers are competing with inorganic materials, *e.g.* lanthanum hexaboride nanoparticles, for long-term architectural uses, and must meet demanding standards for light stability, but they are no doubt useful in plastic films for applications where short-term protection from IR radiation is required.[51] Alternatively, the impinging sunlight can also be absorbed in a solvent layer, commonly water, containing an IR absorber, which can then be circulated through heat exchangers and so used to heat water for central heating or other domestic uses, in a modification of the traditional solar water heaters, which use blackened metallic tubes or coated glass as the absorbing component. For these outlets materials that absorb across a wide range of the NIR spectrum are preferred, but often mixtures are used to fill in any gaps in the spectrum.

Laser Welding and Marking. Transmission laser welding is a process developed for joining together plastic materials and produces products where the joints are invisible. It is used in a wide variety of applications: in the medical field for tube joints, implants, dialysis systems; in motor transport vehicle headlights, car keys, instrument panels; in electronics for clocks, mobile phones and other hand-held devices; and in many plastic consumer products. The lasers used are NIR diode lasers in the 808 nm to 980 nm range or Nd:YAG lasers with emission wavelength at 1064 nm, heat transfer being promoted by the presence of IR absorbers. Originally the absorber used was carbon black but this is of no use for clear plastics and the breakthrough came by the use of NIR absorbers, which have very little or no colour in the visible region.[52,53] The absorbers can be derived from most of the chemical classes already described in Section 4.2.1, but especially cyanines, squaryliums, iminiums and extended perylenes, often in conjunction with other absorbers selected from oxides and hexaborides of lanthanum and alkaline earth metals.[54] A variant of laser welding is the process by which coloured marks or inscriptions on plastics are achieved by welding a polymer-containing inscription medium to another plastic with a laser, provided that plastic does not contain any substance which absorbs laser light.[55]

Computer to plate technology in lithographic printing. For many years the production of the plates used in lithographic printing involved the use of a photographic image of the print through which UV light is passed onto a photosensitive resin (see Chapter 1, Section 1.4.2.5 for details).[56] However, in the last decade the technology known as "computer to plate" (CtP), which involves writing the data directly onto the printing plate, has become a major player.[57] The two main CtP technologies use visible light and thermal energy, the lasers used being respectively violet light (395–420 nm) and NIR (830 nm) diode lasers or Nd:YAG (1064 nm). To achieve efficient uptake of the laser energy in thermal plates an NIR absorber is present in the resin on the surface of the plate. The requirements for the NIR absorbers in this outlet are:

- High extinction coefficient;
- Stable $\lambda_{\max}$ in the resin film;
- Broad $\lambda_{\max}$ centred at 830 nm (800–900) or 1064 nm (1030–1140), or 532 nm for frequency-doubled Nd:YAG, 670, 650 and 633 nm for other lasers and LEDs, depending on the imagesetter, which can be a rotating drum both external (Figure 4.3) or internal or a flat-bed type;
- Good organic solvent solubility (*e.g*. THF or MEK) and solution stability.

In common thermal plates the image is formed where there is an induced solubility difference in an alkaline developer between exposed and non-exposed areas of the coating. The rate of dissolution of the resin in the developer is either reduced (negative working) or increased (positive working) by the image-wise exposure. During processing, the solubility differential leads to the removal of the non-image (non-printing) areas of the coating, thereby revealing the hydrophilic support, while the image (printing) areas of the coating remain on the support (Figure 4.3). Variants on the thermal plates are the so-called "chemistry-free", "process-free" and "direct imaging" plates. In these processes the image is written directly onto the plate and there is no need for subsequent development processes except perhaps a wash with gum to seal and protect the image onto the plate before going to the press. Chemistry-free plates can be made using various processes such as ablation or phase change. A competitive process is the use of ink-jet printers to lay down the resin image directly onto the plate. Further details of these developments in printing-plate technology can be obtained at the websites of the leading companies, and many companies have launched products, including Kodak Polychrome Graphics, Agfa, Eastman Kodak, Fuji, Heidelberg and Mitsubishi.

Laser thermal media for imaging. Laser thermal printing involves the use of laser energy to transfer dyes across an air gap, largely by sublimation, and diffusion onto a receiving layer, giving continuous tone prints (see also Chapter 2, Section 2.9.3.2).[58] Outlets for this technology include the original use in colour proofing of images prior to full-scale production of lithographic plates,

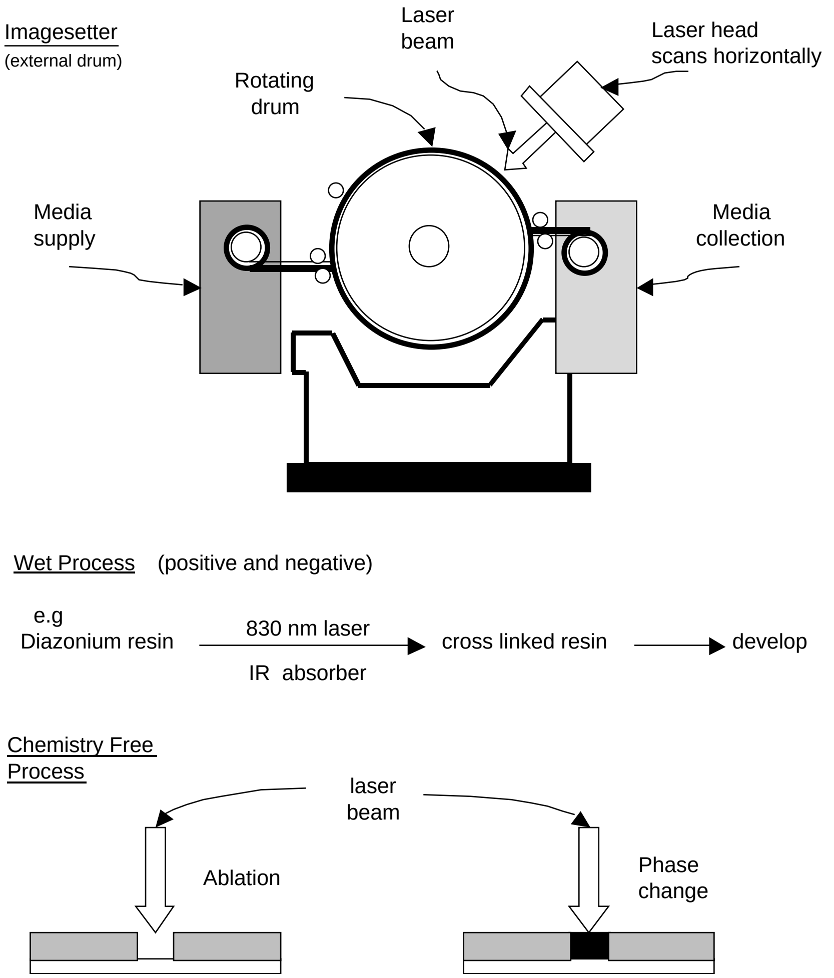


Figure 4.3 Computer to plate thermal technologies.

and also in medical imaging and security cards. The process involves writing the image data, using a focused diode laser beam, onto a dye layer containing the NIR absorber and binder. The IR absorber converts the radiant energy into heat, which in turn causes the dye to transfer to a polymer receiver layer. The colours cyan, magenta, yellow and black (CMYK) are registered sequentially in order to build up the final coloured image. This is illustrated in Figure 4.4.

The choice of the absorber dye is obviously defined principally by the wavelength of the laser used in the process. However, since some of the NIR absorber is likely to be transferred in the process, it should not interfere with the colours in the final print and preferably be colourless. The original developers at Imation Corporation overcame this potential problem by using an IR

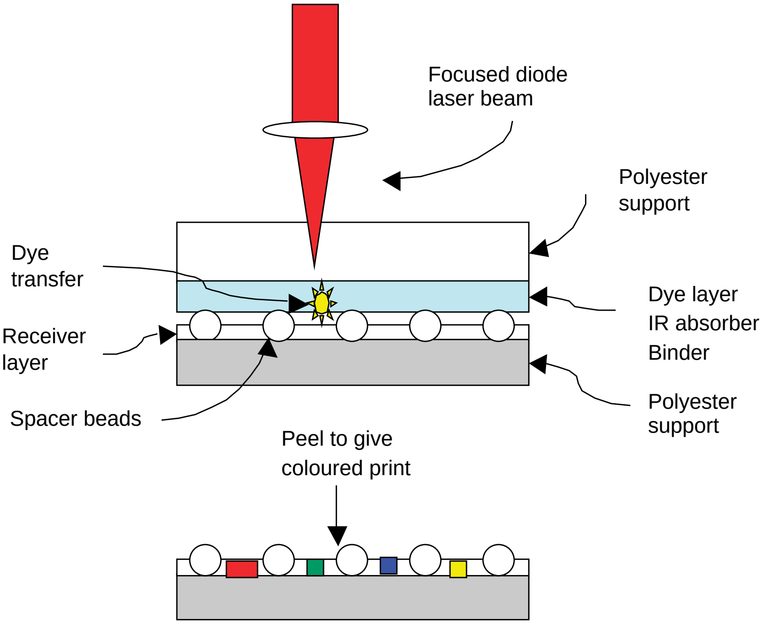
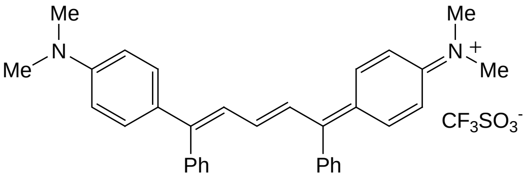


Figure 4.4 Colour proofing with laser thermal media.

absorber (4.35) exhibiting broad absorption at 790–900 nm and addressable at 830 nm, which bleached out during the pocess.[59]



(4.35)

A variant on the direct thermal printing methods (Chapter 1, Section 1.4.2.4) is to use a laser to write rather than thermal heads. Again the process involves the inclusion of an IR absorber to enable the colour former to react with the developer in the resin coating.[60]

Other thermal applications. In electrophotography (Chapter 2, Section 2.9.2) flash fusing is a method in which the toner absorbs light and converts it to heat and so melts the resin more quickly prior to fusion onto the paper, thus speeding up the whole process. To achieve this the toner must efficiently absorb light emitted from the xenon lamp (flash lamp), especially in the NIR region where the emission intensity is strongest. This is not a problem with black-coloured toners as they absorb panchromatically. However, with coloured toners there must be no interference in their colour and therefore NIR absorbers for the 800–1000 nm region showing very little or preferably no visible absorption, such as the metal dithiolenes (Section 4.2.1.5), must be used.

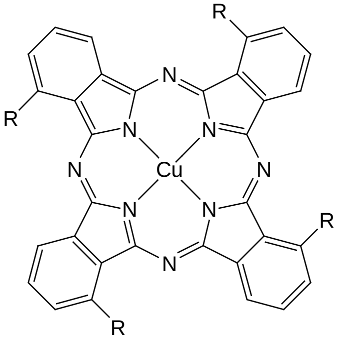
An excellent example of the exploitation of absorbers in the conversion of laser light into thermal energy at specific wavelengths in the NIR is optical data storage. This topic will be covered in detail later (see Section 4.3). Applications involving the conversion of IR radiation into electrical energy are dealt with in the sections on organic photoconductors for laser copying and printing (see Section 4.4) and also under photovoltaics (see Section 4.8.1).

4.2.3.2 Protection from IR Radiation

Light produced during welding is extremely harmful to the eyes, and to offer full protection to the worker radiation from the NIR needs to be eliminated, whilst still allowing the wearer to see clearly. Polymer compatible diiminium and nickel dithiolene NIR absorbers (see Section 4.2.1) have been developed for this outlet, and also for the protection of the eyes of users of higher-powered lasers.[61] Wide attenuation of light from 800–1100 nm is also claimed for a product that can be dispersed in plastics with a high level of photopic luminous transmission for normal light.[61]

Lasers have also become commonplace in military weaponry and their use presents severe hazards to personnel on the receiving end, because of either laser dazzle or laser damage. Laser dazzle, the source of which is usually a continuous-wave laser or a low-power, high-repetition-rate pulsed laser, can cause temporary flash blindness. Laser damage, defined as minimum opthalmically visible lesion or other irreparable damage to human vision, is caused by high-power and high-repetition-rate pulsed lasers. To deal with these problems, visors or other protective devices are required that react to the incoming laser pulse. These must be made from materials that will provide good transmission under normal conditions, but will remove the effect of the laser, either by selective absorption or by becoming temporarily opaque on receiving a flash from a laser. Both electrochromic and photochromic materials have been considered for this outlet but an alternative is the process by which dyes, when excited by short laser pulses, undergo a rapid saturated colour change called reverse saturable absorption.[62] Reverse saturable absorption, or optical limiting, is a nonlinear effect that occurs when the excited state absorption exceeds the ground state absorption and will be discussed in Chapter 5 (Section 5.6.5.3). Several classes of organic colorants have shown very interesting reverse saturable properties, including cyanines and especially porphyrins and metal phthalocyanines, *e.g.* lead phthalocyanine.[63,64] For obvious reasons most of the work in this area is sponsored by the defence agencies and the exact structures of the materials' interesting practical use have not been disclosed.

Another important area for the military is camouflage. This has traditionally been achieved by using patterns of green, olive, brown, khaki and black on clothing and on military vehicles and buildings.[65] Whilst concealment from daylight surveillance by personnel using visual or photographic means is still the main requirement, avoiding detection from technology that uses IR sensors is extremely important. The major work in this area has been in providing coatings to avoid detection from thermal imaging sensors working in the far IR, but there is also a need for materials operating in the NIR region of 700–1300 nm.[66] There are several reasons for this but the main ones are the use of image intensifiers in goggles and weapon sights, which amplify reflected natural visible and IR radiation up to 1200 nm; the use of aerial photography with film sensitive up to 1300 nm; and the use of electron scanning arrays operating at 700–1350 nm. Natural materials, such as grass, leaves, bark, sand and soil all reflect IR at different levels (10–50%) in the region 700–1300 nm. In order to make it difficult for the device to discriminate between the potential target object and its background and avoid contrasts and to break outlines, the NIR reflectance characteristics of the different colours required for camouflage, above, must match the different levels of the environmental background, that is, they must absorb NIR to a certain degree.[66] Again most of the structures of the actual infrared absorbers, dyes and pigments used in the military arena remain secret. However, there are reviews and commercial websites on camouflage materials used in coatings and paints and on textile dyes for apparel,[67] such as vat and reactives for cellulosic fabrics, disperse dyes for polyester, acid dyes for polyamides and pigments for printing of all fabrics.[68] Additives such as (4.36), which absorb in the NIR, can be used in conjunction with other colorants.[69]



(4.36)
R = OMe or SO_2NHi-Pr

The application of NIR absorbers in security outlets is another area where there is a need for secrecy over the exact structures of the chemicals that are employed. A range of thiolated metal phthalocyanines are claimed to be of value in this area, mainly in the security printing of machine-readable items by lasers, and identifiers.[37] Examples of uses in security printing are widespread and include barcodes on labels and packaging, numbers on cheques and logos and other images on bank notes and lottery tickets. On clear paper or other substrates an absorber with minimal visible colour is required, but if hidden behind strongly coloured opaque ink then lightly coloured NIR absorbing dyes can be used.[7] [11]

4.3 Optical Data Storage

The storage and retrieval of data by optical means, which involves the interaction of a medium with a compact laser, focused to sub-micron size, is dominated by direct bit storage onto disc media. There are currently several types of optical data storage media available, from read-only pre-recorded CD and DVD discs to recordable CD-R and DVD-R, rewritable discs (CD-RW and DVD-RW) and Blu-ray, which recently beat its challenger HD-DVD for the high-density-format disc market. These formats and the favoured recording materials are shown in Figure 4.5 with the exception of magneto-optical materials used in some rewritable discs.

The optical disc recording system consists of a recording laser beam, with a power output of several MW, focused to a spot size of less than one micron on a transparent recording medium laid down on a reflecting substrate. The beam is reflected back through optics to the detector. The energy of the laser beam is sufficient to cause changes in the recording medium, either by a phase change or hole formation. A lower intensity beam then reads these changes in the recording medium, as it is guided along grooves in the substrate. Guiding the laser beam along recorded tracks is achieved by a separate servo-optical system. A preformed groove in the substrate diffracts laser light onto a split detector, providing a difference signal used to steer the beam by means of an electronically controlled mirror. This system is shown schematically in Figure 4.6.

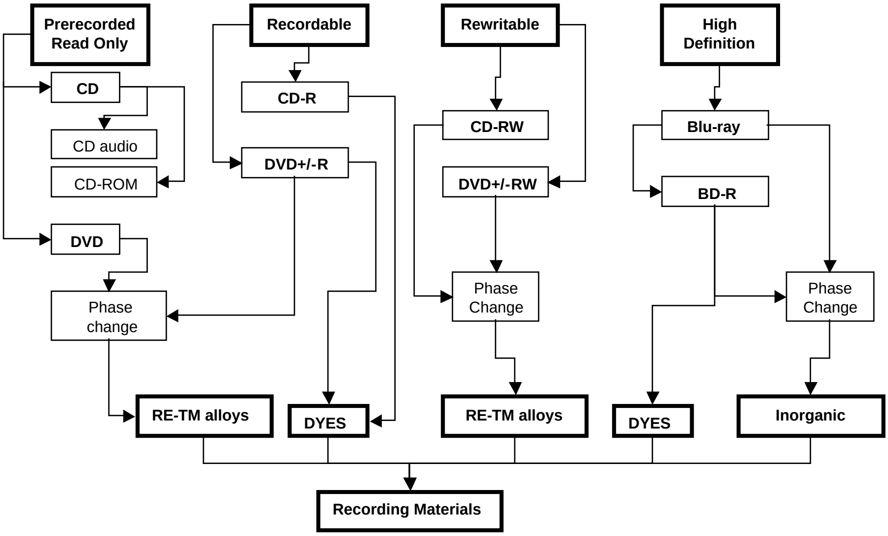


Figure 4.5 The various media, formats and materials used in optical data storage.

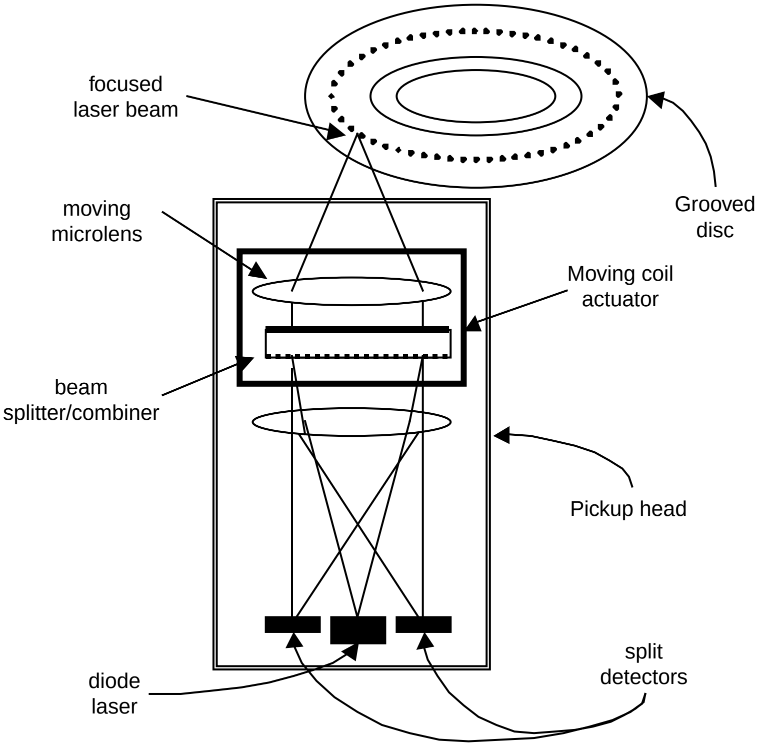


Figure 4.6 Schematic of an optical data recording system.

4.3.1 Magneto-optic and Phase Change Media

Magneto-optic is the oldest of the media for data recording, dating back to the 1950s. In CD-MO the discs are constructed of amorphous films of rare earth–transition metal alloys, *e.g.* GdTbFe, TbFeCo and GbTbFeCo, sputtered onto the surface. When writing to the disc, a laser beam is focused on an extremely small spot, and the alloy is heated to a specific temperature (the Curie point), anything from 200–400 °C. This is sufficient to cause the ferromagnetic properties of the aligned elementary particles to be lost. An electromagnet is positioned on the other side of the disc, changing the polarity of the particles, whose differences will be encoded as binary data for storage on cooling to room temperature. Hence changes in the direction of magnetisation on the coded areas, indicators of the data recorded, are measured by the reading laser as the change in polarisation of light reflected from the surface, so that the reading laser beam is reflected differently on altered areas from on unaltered areas.

Phase change recording media use RE-TM glasses sandwiched between two dielectric layers that draw excess heat from the recording layer, *e.g.* GeSbTe alloys in CD-RW and DVD-RAM and Ag-InSbTe alloys in

DVD + /-R. Annealing the original amorphous glass at a particular temperature causes the alloy to crystallise when it is cooled. Recording is affected by specific local heating with the write power laser (600 °C) causing the crystalline phase to convert to the metastable phase of the glass, which on rapid cooling gives the amorphous phase, which shrinks forming a pit. Crystalline areas (the lands) will reflect the read power laser, while the other amorphous areas (the pits) will absorb some of it, the differences in reflectivity registering as binary data that can be decoded during playback. For erasing the recorded data, the erase power laser heats the alloy above the crystalline transition temperature (200–400 °C) but below the melting point, for sufficient time for it to convert back to the crystalline state.

4.3.2 Optical Data Storage Using Dyes

The main interest in this book is the use of laser addressable dyes in the recording layer of optical data recording media, first devised for CD-R by Taiyo Yuden company in 1988,[70,71] but now commercially available in a range of media, specifically CD-R, DVD +/-R, CD-RW and BD-R.[72]

4.3.2.1 Recordable Media

The mechanism of optical recording with organic dyes involves converting the excitation energy, generated by the focused laser beam, into thermal energy by non-radiative decay. Depending on the laser power and the medium, temperatures in the range of 250–400 °C can be obtained. These temperatures are above the glass transition temperatures of the polycarbonate substrate and where most dyes decompose. Consequently, in the now defunct WORM media, where the laser beam impinged on the surface of the disc, the dye decomposed, causing the formation of a pit, the difference in reflectivity in the pit being measured by the read laser. In CD-R the polycarbonate flows into the gap caused by dye decomposition, leaving a mechanical deformation in the film and reduction in the optical path length. Hence the intensity of light reflected back on the detector when the deformation is hit by the traversing read out laser beam is a measure of the data encoded. The principle using dyes in CD-R is shown in Figure 4.7.

In fact the dyes are laid down over spiral grooves in the surface of the polycarbonate substrate, which are designed to guide the laser during the write and read out operations, creating dye on the surface (the land) and dye in the groove, with most of the dye being in the groove. The equivalent DVD formats are DVD-R and DVD+R, which have many more grooves on the discs. Cross-sections of the CD-R and DVD-R types are shown schematically in Figure 4.8. The DVD+R dual layer introduced by Phillips in 2004 has a more complicated structure (see Figure 4.8) but offers about twice the capacity of the single layer DVD+R.[73]

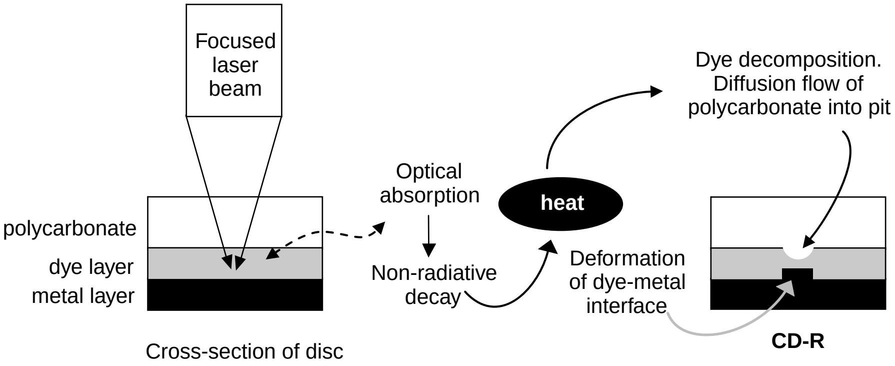


Figure 4.7 Schematic of recording in dye based CD R discs.

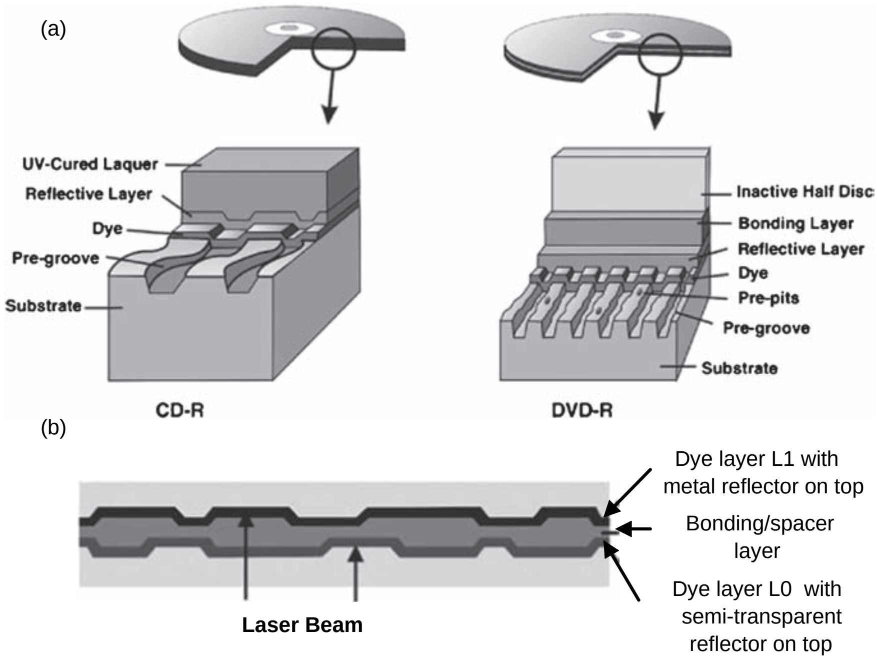


Figure 4.8 Schematic of the design of (a) CD R and DVD R and (b) dual layer DVD+R[72] (reproduced with permission of Wiley VCH).

4.3.2.2 Dye Requirements

Many of the requirements for dyes in CD-R and DVD-R media are very similar but there are important differences:

- Finite light absorption at the laser wavelengths;
  - CD-R at 780 nm

  - ○ DVD-R at 650 nm
- High light reflectivity of the film at the recording/read out wavelengths.

Reflectivity, a crucial property, is related directly to the refractive index of a dye film, which itself is fundamentally related to the extinction coefficient of the dye. The necessary reflectivity of over 25% occurs most often when the film has a refractive index of greater than 2.5. For CD-R, dyes with $\varepsilon_{\max} > 200{,}000$ and for DVD-R $\varepsilon_{\max} > 100{,}000$ are required.

As well as meeting the above technical requirements, dyes for use in optical data recording must also meet a set of operational technical criteria:

- Decomposition must be above the glass transition point of polycarbonate (200 °C);
- Good solubility in the solvent used for spin coating the discs and the ability to form solid films;
- Stable to environmental and processing conditions, including oxidation, hydrolysis and light;
- High thermal stability to metal sputtering (dual layer).

4.3.2.3 Dye Classes

The main classes of dyes that have been evaluated for these outlets include cyanines, squaryliums, azo dye metal complexes, indoanilines, quinones and phthalocyanines and naphthalocyanines. For the longer-wavelength CD-R outlets at 780 nm both cyanines and phthalocyanines are used commercially (see Figure 4.9).[72] The pentamethine cyanine dyes used in CD-R suffer from low light-fastness properties and a light stabiliser, specifically singlet oxygen quenchers, must be included in the film formulation. Commercial companies have devised a range of different stabilisers.[74]

For DVD-R the shorter-wavelength requirements rule out phthalocyanines, as their main absorption band cannot be tailored to absorb in the region required by the 650 nm wavelength laser, but for cyanines this can be achieved by using trimethines. Although azo dyes have too low an extinction coefficient for use in DVD-R, by remarkable manipulation of nickel–azo metal complexes Mitsubishi were able to devise products suitable for use in DVD-R.[75] Structures of dyes used in DVD-R are shown in Figure 4.9.

4.3.2.4 Dyes for High-density Recording Media

The arrival of the blue laser diode in 1999 (see Chapter 5) operating at 405 nm opened up the opportunity of devising much higher density optical recorders and players that would be compatible with HD-TV. This also meant that a new generation of optical disc was needed for these new machines; these could hold anything up to 25 Gb of data on a single side. During the early years of the century there were two competing formats, HD-DVD and Blu-ray, but by 2008

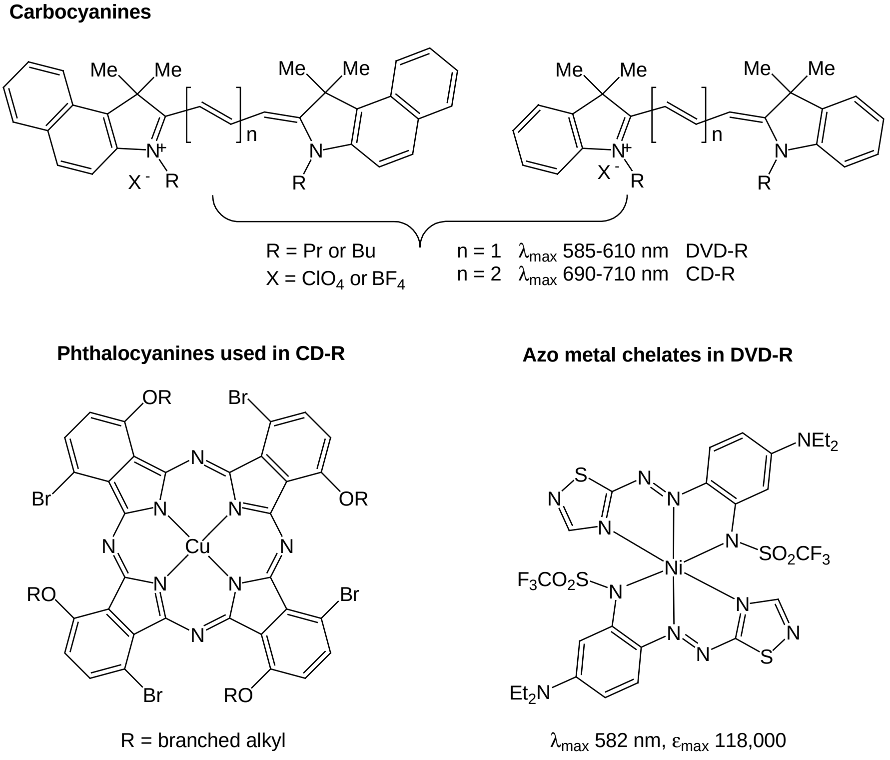


Figure 4.9 Dyes used in CD R and DVD R discs.

HD-DVD, in spite of being the first to market, was abandoned by the Toshiba lead consortium and Blu-ray became the format of choice.[76]

During the course of these developments research was intense into dyes for absorbing in the 405-nm region for use in the new optical recording media. These were initially for HD-DVD as the method of making the disc was essentially the same as for DVD-R and hence spin coating of dyes could be used. Very many patents have appeared covering a myriad of chemical classes including azo dyes, azomethine, methine dyes and their metal complexes, cyanines, styryls, subphthalocyanines, porphyrins and analogues, polyenes, azos, coumarins and pyrimidones, and consequently just a few recent examples are given here as indicative materials (Figure 4.10).[77]

Blu-ray has BD-R (write once) and BD-RE (erasable) based on inorganic recording layers (*e.g.* metal nitrides). In 2008 several companies, including Taiyo Yuden, Mitsubishi, Pioneer, Maxell and Verbatim, announced that they were starting to deliver recordable discs called BD-R LTH (Low to High polarity) based on dyes, but it is not clear which dyes are actually used. Although this format initially had some compatibility problems with Blu-ray, it has now received the necessary software and firmware support, which should enhance commercialisation.

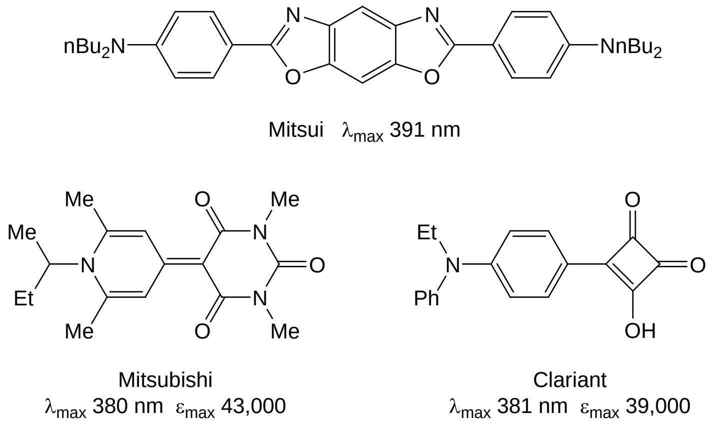


Figure 4.10 Dyes designed for blue laser recording.

Table 4.3 Growth in storage capacity with write laser wavelength and technology.

Technology	*Introduction*[a]	*Write wavelength, nm*	*Approx. storage capacity*[e]
CD R	1992	780	0.75 Gb[f]
DVD R	1999	650	4.7 Gb[f]
Blu ray	2006	405	25 Gb[f]
Kr ion	??	351	47 Gb[f]
Near field Ar ion	??	257	88 Gb[f]
InPhase Holography	(2009)	405	300 Gb (1.6 Tb)
Optware HVD	(2008)[b]	532	500 Gb (9 Tb)
2PA 3D green (blue)	(2009)[c]	532 (405)	1 Tb (5 Tb)
2PA 3D red	(2010)[d]	650	1 Tb (5 Tb)

[a] Actual year of launch (latest manufacturer prediction).

[b] Latest Optware prediction, obviously superseded.

[c] Call/recall projection. Industry commentators suggest 2010 2011 is more likely (http://www.theregister.co.uk/2008/05/28/call_recall_optical_drive/).

[d] Mempile TeraDisc™.

[e] Actual commercial product, or currently reported demonstration model (predicted developmental product).

[f] Single layer.

4.3.3 Developments in Optical Data Storage

Even though optical data storage has reached quite dizzy heights in the last ten years, there are still many areas under development where even greater storage capacity will be required. Whilst the newer solid-state diode lasers have been the technical driving force behind these changes (see Table 4.3) there will be a limit even if complicated multi-layer structures are employed.

The next stages in the development beyond Gb to terabyte (Tb) will be to move to an all-photon mode of recording. Several different technologies are under development. 3D optical data storage can potentially hold up to 100 or more layers of information on a single disc, *e.g.* using photochromic compounds as discussed in Chapter 1 (Section 1.2.8.3). Holographic methods based on photopolymers (Section 5.4.3.1) or photorefractive materials are capable of recording and reading millions of bits in parallel, so enabling data transfer rates greater than those attained by existing optical storage methods. Two-photon absorption 3D recording at 200 layers of data per 1.2 mm disc is outlined in Chapter 5 (Section 5.6.5.2). A photothermal effect on gold nanorods is the writing mechanism during a new 5-dimensional high-volume optical data storage method (Chapter 5, Section 5.6.5.2). The data recorded in Table 4.3, current and projected, show the direction in which the various ODS technologies are taking us.

4.4 Organic Photoconductors

The six-stage process used to produce images in electrophotography, in both copiers and printers, is described in Chapter 2 (Section 2.9.2). Crucial to this process are the photoconductors (also called photoreceptors) used to produce the latent image prior to toning and transfer to the substrate. Originally the photoconductors were inorganic (*e.g.* selenium, but now amorphous silicon in high volume machines), but in the last 25 years there has been a swing to organic materials, to such an extent that greater than 95% of machines currently use organic photoconductors (OPCs).[78,79]

In the electrophotographic process the photoconducting element is present as a coating on the surface of a rotating drum or a continuous belt. This is fully charged for use by means of a corona discharge. The image to be copied or printed is then written onto the photoconductor, either as a whole sheet in one go by discharging with white light (photocopying) or by scanning the digital data of the image with a laser (laser copying and printing). The set-up inside a typical laser copier is shown in Figure 4.11.

Photoconductors can be constructed as a single or a dual layer, more commonly the latter. The two-layer photoconductors consist of a very thin 0.2–2 μm charge generation layer (CGL), and a much thicker 15–30 μm charge transport layer (CTL), as illustrated in Figure 4.12. Often an undercoat layer is placed between the CGL and the aluminium to prevent injection from this substrate. The corona discharge causes a build-up of negative charges on the top surface of the CTL (a). When light impinges on the photoconductor, an ion pair is formed on the CGL, after which the negative charge at the light contact point on the surface is discharged by a hole hopping mechanism through the CTL, as shown in (b). The latent image produced on the surface (c) is a negative of the image in white light copiers and a positive in the case of laser copiers/ printers. This is then toned with the appropriately charged toner and is ready for transfer to the paper substrate to produce the final image.

During the photoelectric process the photoconductor undergoes a series of voltage changes:

- exposure to the corona causes a rapid build-up of voltage, V (charging);

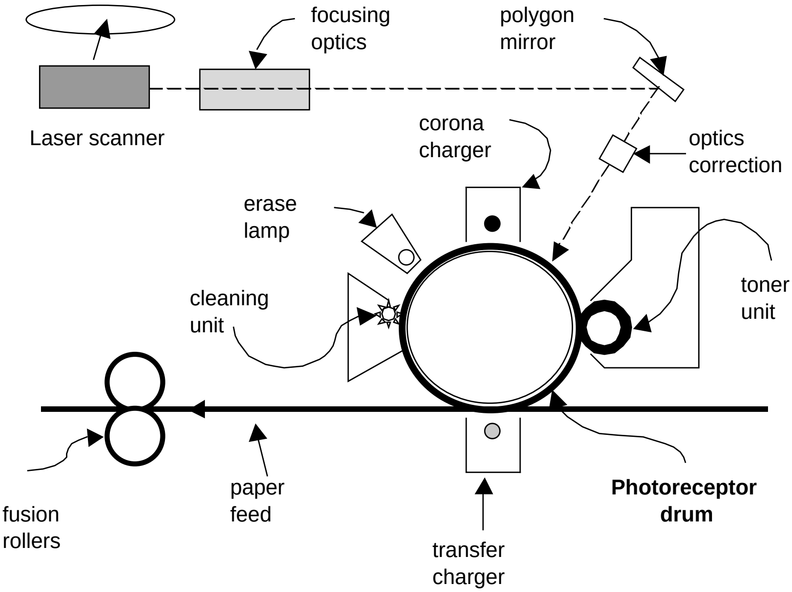
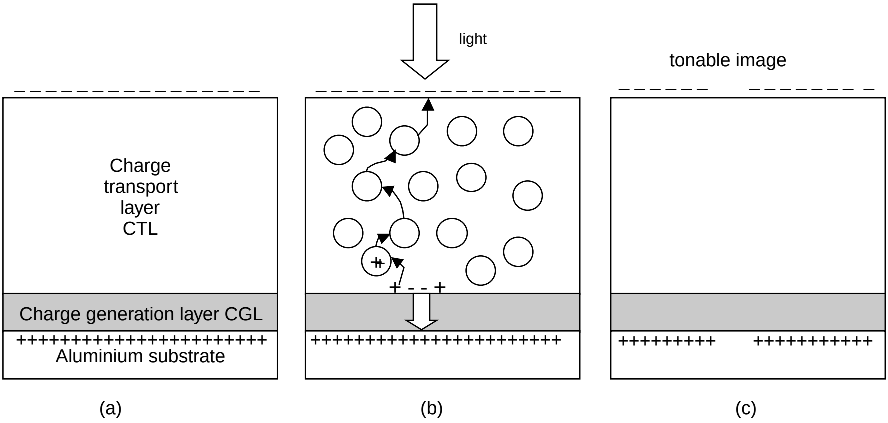


Figure 4.11 Photoreceptor drum in a laser copier.



(a) (b) (c)

Figure 4.12 Mechanism of photoconduction in an organic photoconductor.

- during storage time in the dark there is a small loss of voltage, ΔV (dark decay or discharge);
- exposure to light causes discharge of the initial potential, V_I (photodischarge);
- small residual voltages are left after exposure, V_R (residual potential).

This charge-photodischarge cycle is shown schematically in Figure 4.13. Photosensitivity is expressed as the energy ($E_{0.5}$, ergs cm ^{2}) required to

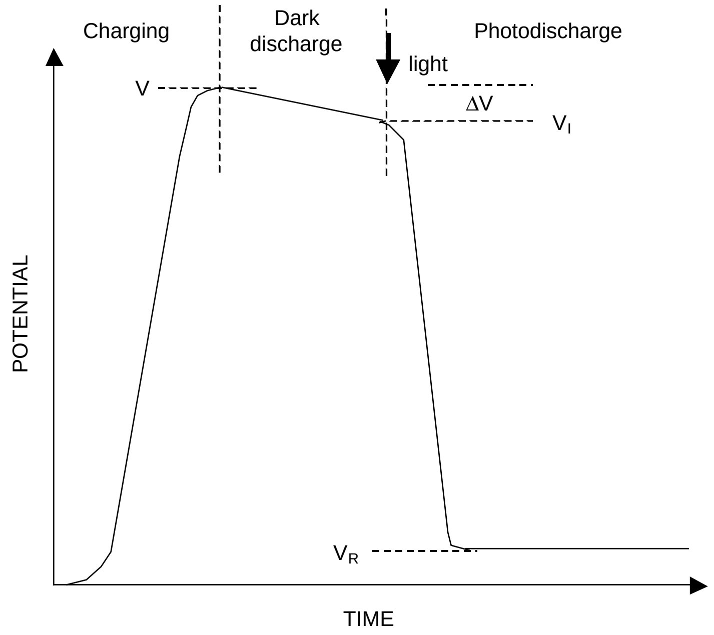


Figure 4.13 The charge photodischarge cycle in photoconductors.

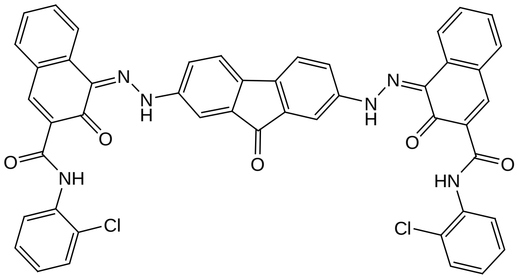
photodischarge to half of the initial potential V_I. The objective in designing an efficient photoconductor is to maximise V, minimise ΔV and hence maximise V_I, and also to minimise V_R. In terms of time, both the charge-up and photodischarge times should be as short as possible, whilst dark decay (V s ^{1}) should be as slow as possible.

4.4.1 Charge Generation Materials

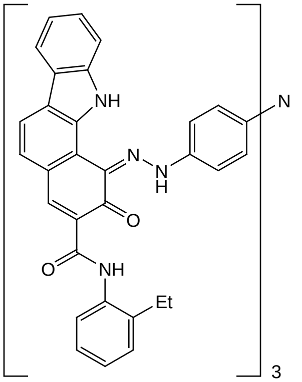
The charge generation materials need to be photoresponsive to either white light or a specific diode laser or LED wavelength. For white light the response should ideally be panchromatic but it has been found adequate to have a broad absorbing material centred around 550 nm. The majority of laser addressable photoconductors operate at 780 nm, with LEDs at 630–660 nm, but the use of lasers emitting in the visible region, as discussed under optical data storage, is increasing as these offer much higher definition images. Charge generation materials (CGMs) are invariably pigments of very high purity, usually in a specific morphological form. Improved performance has also been obtained by using nano-sized pigments (Chapter 2, Section 2.4.5).

4.4.1.1 Azo Pigments

A vast range of azo pigments has been patented for use as CGMs in organic photoconductors, but the most widely studied and used commercially are disazos, especially those based on BON acid arylamides as coupling components (see Chapter 2, Section 2.4.1.1).[78(a)] They have found particular use in white light copiers because their absorption can be molecularly designed to be in the desirable 450–650 nm range. By extending the conjugation on the arylamide-coupling component and by going to a trisazo structure, the absorption can be extended into the NIR region. Two typical azo pigments that have been used in commercial OPCs (Ricoh) are (4.37) in visible light sensitive copiers and (4.38) in NIR printer/copiers.



(4.37)
Range 450-650 nm
$E_{0.5}$ = 3 at 600 nm
Dark decay = -1 V s^{-1}



(4.38)
Range 450-800 nm
$E_{0.5}$ = 3.6 at 790 nm
Dark decay = -25 V s^{-1}

4.4.1.2 *Phthalocyanines*

Phthalocyanines have found great use as CGMs for photoconductors in machines using laser diodes, especially in the popular 780-nm region. The existence of large numbers of polymorphic forms of phthalocyanine (see Section 4.2.1.8) and its metal derivatives has allowed sophisticated tailoring to give a range of electrophotographic properties. Table 4.4 lists some of the phthalocyanines that have been employed in NIR-sensitive organic photoconductors, together with their electrophotographic data.[78(b)]

Most phthalocyanines show inferior dark decay compared with azo pigments, an exception being the titanyl phthalocyanines, where in the best cases, the α- and γ-forms, they show comparable dark decay coupled with superior photosensitivity. Titanyl phthalocyanines are used as the CGMs in commercial organic photoconductors *e.g.* in the engines from Canon, Xerox, Konica and other OEMs.

4.4.1.3 *Other CGMs*

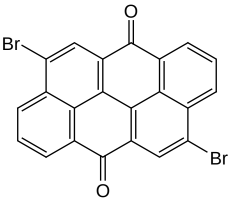
Other molecular classes that have been used at some time as CGMs in commercial organic photoconductors include quinones (dibromanthanthrone

Table 4.4 Electrophotographic data of solution-coated near IR absorbing phthalocyanines (Pc).

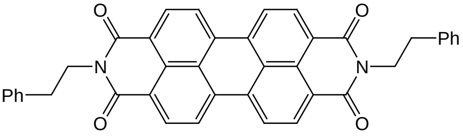
MPc	*Polymorph*	*Electrophotographic data (Spectral range 550 800 nm)*	
		Dark decay (V/s)	*Sensitivity $E_{0.5}$ (Wavelength, nm)*
H_2Pc	τ_1	5.1	4.5 (780)
H_2Pc	τ_2	13	2.5 (780)
H_2Pc	X	20	4.5 (780)
MgPc	Agg.	80	30.0 (810)
VOPc	Phase II	30	4.1 (810)
AlClPc	Agg.	55	10.0 (810)
InClPc	Agg.	60	8.0 (810)
TiOPc	α	65	2.6 (790)
	β	45	3.6 (790)
	γ	54	1.8 (790)
	m	60	2.4 (790)
	Amorph.	58	1.9 (790)
	Y	13	0.75 (800)
	A	32	2.6 (800)
	B	85	1.6 (800)

(4.39) by Xerox and Konica); perylenes (*e.g.* (4.40) by Kodak and Océ, and (4.41) by Xerox); and squaryliums ((4.42) by Lexmark).

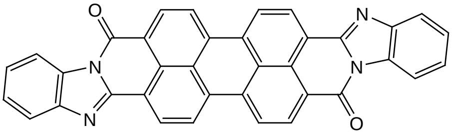
For a comparison of the properties of these classes of CGMs the sensitivity of a selected range is shown graphically in Figure 4.14.



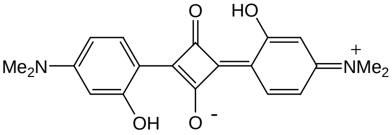
(4.39)



(4.40)



(4.41)



(4.42)

4.4.2 Charge Transport Materials

Most of the materials used as charge transport materials (CTMs) in commercial photoconductors work by a positive hole-transport mechanism, as indicated in

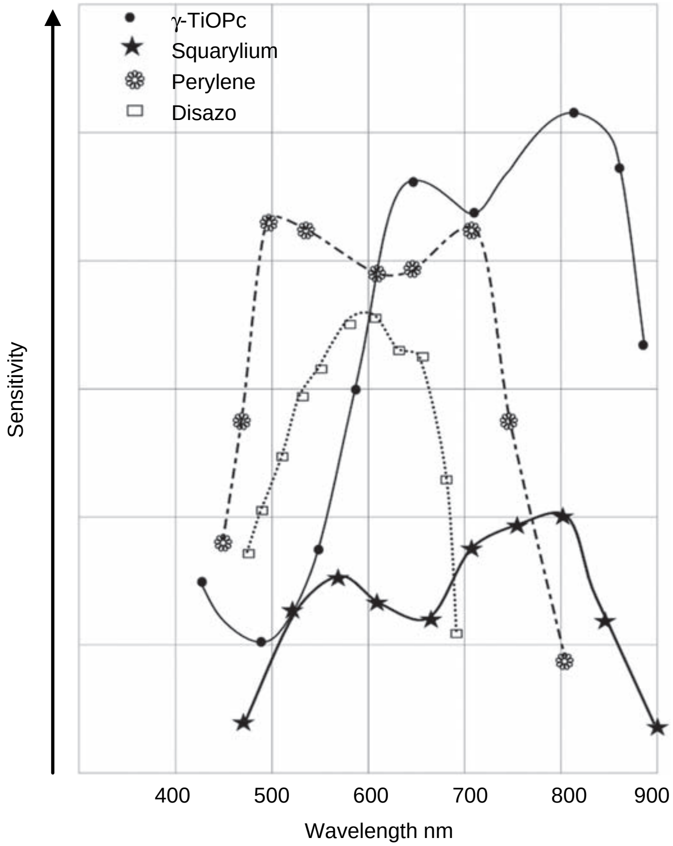


Figure 4.14 Comparative photosensitivity of CGMs.

Figure 4.11. Hole transport p-type semi-conductors are materials that are electron rich and give up their electrons readily. Because of this property they are easily oxidised by air and light, and a balance must be obtained between environmental degradation and performance in the photoconductor. The main chemical classes which give efficient CTMs are triarylmethanes, triarylamines, hydrazones, pyrazoles and oxadiazoles. Selected examples from these five classes of materials are given in Figure 4.15.

4.5 Photosensitisers

Many photochemical reactions and processes do not occur without the intervention of a sensitiser. The sensitiser absorbs the light, raising its energy to the excited singlet state, which can then undergo intersystem crossing to produce the excited triplet state. Here, the sensitiser can undergo chemical reactions, for example dissociation into radicals, ionisation or internal electron transfer, and is then unavailable for return to the original ground state. Alternatively it can

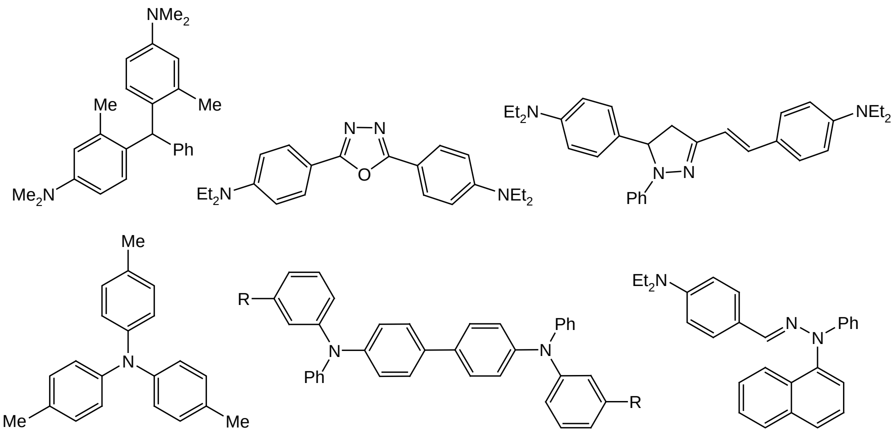


Figure 4.15 Charge transport materials for dual layer photoconductors.

react with other molecules (*e.g.* by electron or excitation transfer, or H-atom abstraction), before returning to its singlet ground state. The role of the sensitiser, in most cases of industrial significance, is to initiate the main reaction by the formation of radicals by dissociation, electron transfer or hydrogen abstraction. Hence sensitisers in these instances are usually called photoinitiators, especially when used in polymerisation reactions.

The sensitiser can also be used to work in a different way in order to initiate polymerisation at selected visible wavelengths of light. For instance the primary sensitiser dye absorbs light at a specific wavelength (*e.g.* from an Argon gas laser), becomes activated and then passes on its energy to a co-initiator which produces the radicals required for polymerisation.

4.5.1 Sensitisers in Photochemical Synthesis

A particularly important use of a sensitiser in photochemical synthesis is to produce the highly reactive singlet oxygen by an energy transfer reaction with ground-state triplet oxygen (see Figure 4.16). Since artificial light is a relatively expensive source of energy, the quantum efficiency of the sensitiser is very important in industrial processes. Several dyes show high quantum efficiencies as sensitisers for the production of singlet oxygen, and a selection is shown together with their singlet oxygen quantum yields (ϕ_Δ) in Figure 4.16.

The photochemical oxidation processes of most value using dye-sensitised production of singlet oxygen are those involving addition across electron-rich enes or dienes to give unstable cyclic peroxides. The reactions are carried out at very low temperatures, typically −78 °C, as the peroxides readily undergo rearrangement and C–C bond scission to give carbonyl compounds by thermolysis. They can also be ring-opened to give carbonyl compounds without C–C bond scission by reaction with oxygen nucleophiles, or can be converted to alcohols in the presence of an appropriate reducing agent.[80]

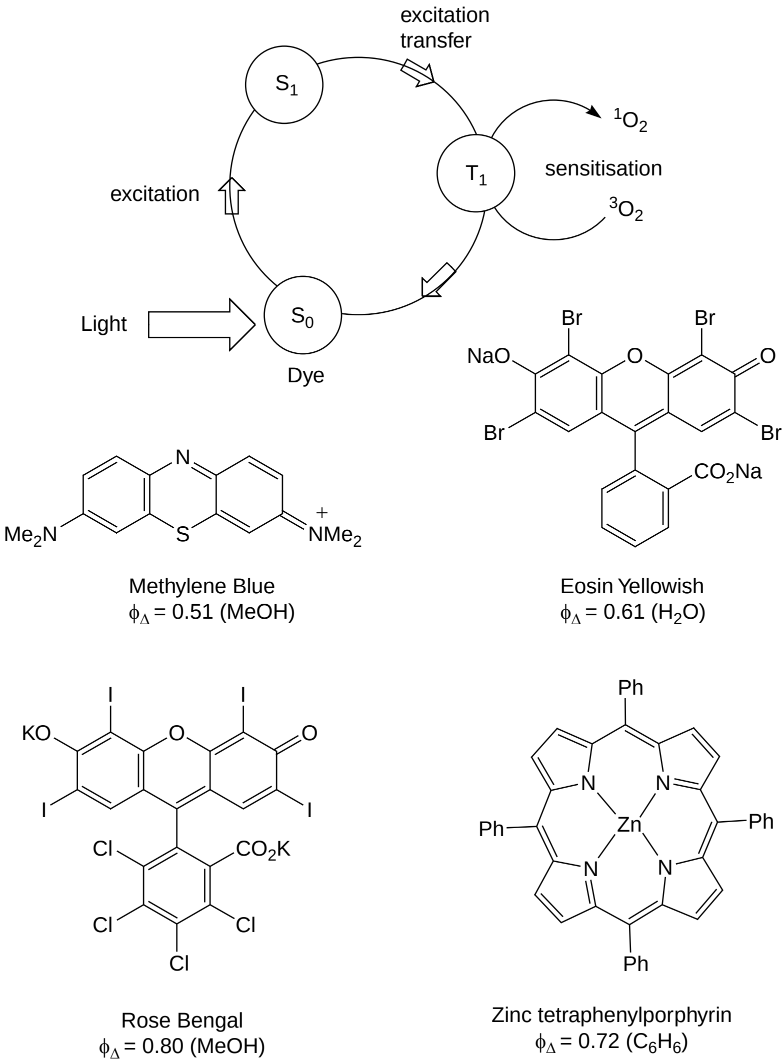


Figure 4.16 Sensitisers used for singlet oxygen production in photochemical synthesis.

Polymer-bound dye sensitisers have been known for some considerable time,[81] the dye-polymer made by reacting Rose Bengal with a Merrifield resin having been commercialised under the trade name of Sensitox. Although such polymer-bound photoinitiators are less efficient than their unbound counterparts the ease of separation from the reaction medium can be advantageous. These, together with their unbound dyes, are of renewed interest with possible applications as green oxidation catalysts in chemical synthesis using concentrated sunlight in specialised reactors, an example being the oxidation of 1,5-dihydroxynaphthalene to give juglone as shown in Figure 4.17.[82]

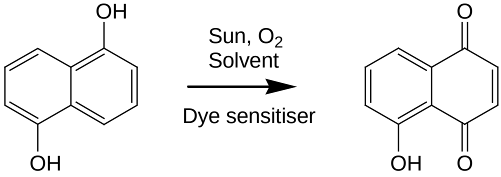


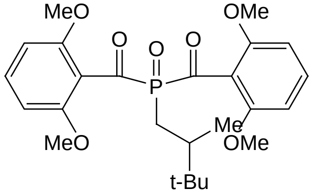
Figure 4.17 Dye sensitised solar chemical synthesis of juglone.

4.5.2 Photoinitiation of Polymerisation

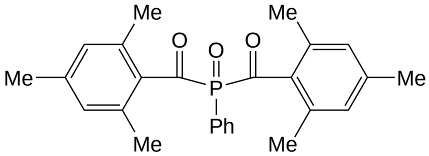
The use of dyes to sensitise the polymerisation of vinyl monomers in the presence of mild reducing agents and oxygen is a long and well-established procedure that can be used to produce high-molecular-weight polymers.[83,84] Typical dyes used in these processes are Rose Bengal, Eosin, acridine orange, Rhodamine B and Methylene Blue (Figure 4.16).

UV polymerisation. The curing (cross-linking) of resins by a photo technique has been well established in commercial polymerisation for decades and is known as radiation curing or "radcure" for short.[85] In radiation curing a reactive resin, usually solvent free, is applied to a substrate and then exposed to high energy radiation (*e.g*. UV or electron beam), which causes the resin to cross-link and polymerise and so form a hard coating. UV is the dominant method (around 90%) of radiation curing, and requires a photoinitiator to be present. Of the common polymerisation methods that are used, the most important involve radical polymerisation of acrylic oligomers (*e.g*. epoxyacrylates, polyester acrylates, polyether acrylates and urethane acrylates). Once of less importance in coatings, cationic polymerisation of epoxy resins is now used to an increasing extent.

Curing is achieved using high-pressure mercury lamps with power outputs in the range 80–120 W cm ^{1}. The two main types of photoinitiators used in the radiation curing of acrylates are mono-acylphosphine oxides operating in the near UV region, and bis-acylphosphine oxides (BAPO-1, 4.43) and (BAPO-2, 4.44) absorb visible light in the region 370–430 nm, polymerisation being initiated after the formation of radicals. This visible absorption allows thicker layers to be cured, including those that are white pigmented, commonly with rutile TiO_2.



(4.43)



(4.44)

Sensitised photopolymerisation is also used in the production of the printing plates used in both the lithographic and flexographic printing processes.[86] As discussed elsewhere (Section 4.2.2.1 and Chapter 1, Section 1.4.2.5), negative lithographic plates are usually constructed by the photoinsolubilisation of the diazonium resins, but there is an alternative lesser-used process in which the photopolymerisation of multi-functional acrylates, such as pentaerythritol tetraacrylate, is achieved using Michler's Ketone as the sensitiser and chlorophenyl-bis-trichloromethyltriazine as the radical photoinitiator. In the flexographic plate process the monomers are mono- and multi-functional acrylates, *e.g.* butanedioldiacrylate, and the photoinitiators are radical producers, *e.g.* benzildimethyacetal, using UV-A (350–370 nm) light.

Moving from UV to visible spectrum sensitisers allows the curing of polymers to be carried out using lasers. An example is the use of the 488 nm argon ion laser in one of the processes that has been commercialised in laser imaging systems.[87] Here the process involves the use of a styryl dye as a sensitiser for the radical-generating agent bis-imidazole, which initiates radical polymerisation of acrylate monomers, as illustrated in Figure 4.18. The mechanism proposed for this photopolymerisation is chain-decomposition of the initiators. In the first step the dye in its excited singlet state causes scission of the bis-imidazole so generating an active radical, a dye radical and an imidazole radical. These radicals then induce polymerisation of the acrylate monomer by the usual chain process. An analogous process can be used in the production of holograms (see Chapter 5, Section 5.4).

Visible light polymerisation. Visible light is advantageous in photopolymerisation as it is generally transmitted at more wavelengths through complex materials. This greater versatility means that it can be used to carry out reactions that otherwise might be limited by competitive absorptions of light at shorter wavelengths. One problem with visible light initiators is that the reactive intermediates they produce for the initiation of polymerisation by chain reactions involve an oxidation–reduction mechanism, which can lead to

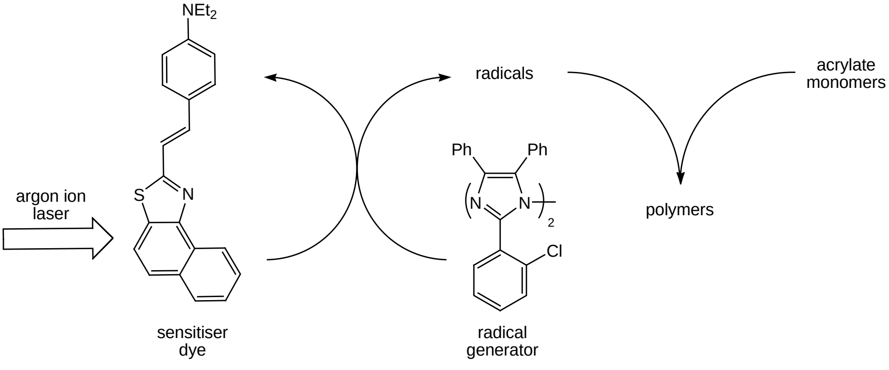
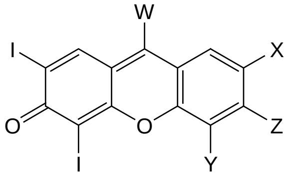


Figure 4.18 Photoinitiation system for acrylate polymerisation using an argon ion laser (488 nm).

bleaching of the sensitiser dye as it absorbs the light. To overcome this problem co-initiators are used, and tetraalkylammonium salts of triarylalkylborates (Ar_3BR) and trialkylarylborates (R_3BAr) have been found to be of particular value, as they decompose on oxidation to organoboranes and a free radical in picoseconds.[88] A commercialised example of this system uses the UV/visible fluorone initiator (4.45a), absorption maximum 470 nm and range 350–530 nm, together with borates or amines as co-initiators in the curing of acrylates.[89] The photoinitiator (4.45a) also sensitises iodonium salts to cure epoxy resins with visible light. Experimental fluorone initiators are available that absorb at 535 nm (4.45b), designed for the frequency-doubled Nd:YAG laser, and at 635 nm (4.45c) for the helium-neon (633 nm) or diode (635 nm) lasers.[89]



(4.45)
(a) W,X,Y = H, Z = n-Bu, 470 nm
(b) W = H, X,Y= I, Z = OH, 535 nm
(c) W = CN, X,Y = I, Z = OH, 635 nm

3D Stereolithography. One application for the radiation curing of resins is in stereolithography.[90] This is a process by which a three-dimensional model is constructed from 3D computer-aided-design data on prototypes (*e.g.* cars and other machines), or from 3D medical data from CAT scan and MRI data, as a multitude of thin slices, typically 0.05–0.2 μm, using specially developed photocuring resins. The process involves using a focused UV laser beam (diameter less than 0.5 mm and in the case of micro-stereolithography down to 5 μm), deflected by a high-speed scanner, to draw cross-sections of the model onto the surface of the liquid photopolymer, triggering reaction with a photoinitiator which causes radical polymerisation of acrylic resins or cationic polymerisation in the case of vinyl ether or epoxy resins. After curing, the support platform is raised and the process repeated for the next layer, and repeated as many times as is required to construct the model. Once the structure is complete, the object is removed, cleaned and finally post-cured in a UV cabinet. A schematic representation of a stereolithographic machine is shown in Figure 4.19. Because the machine in Figure 4.19 is very similar operationally to a laser printer it is sometimes called a 3D printer.

Two-photon microlithography. Whilst the stereolithographic process described above is excellent for producing prototypes and other scale models it is limited to the photopolymerisation of thin layers, making it rather cumbersome, especially when it comes to producing microstructures for chip and memory devices. An alternative approach is to use the nonlinear optical

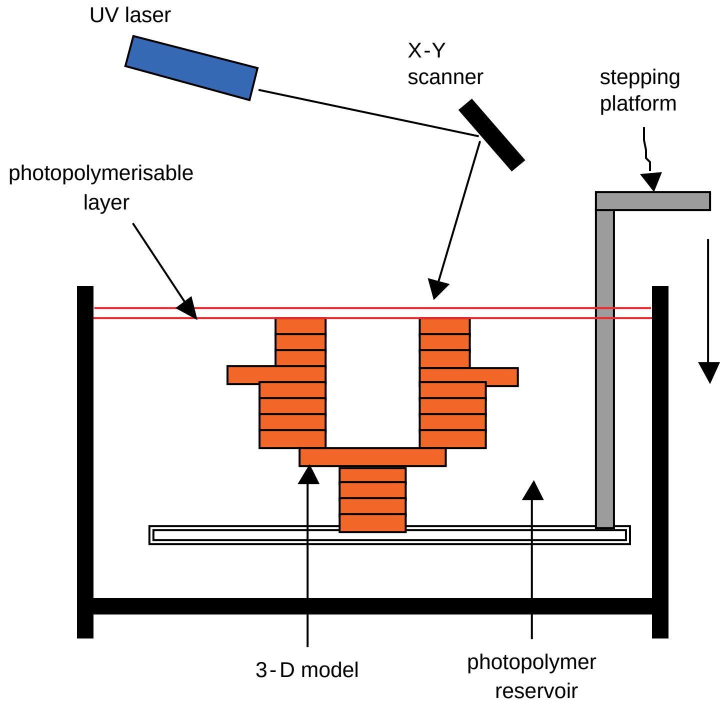
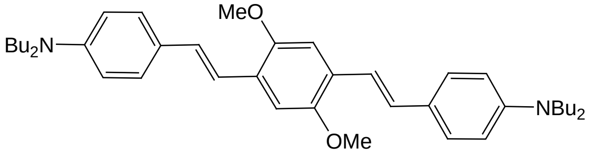


Figure 4.19 The stereolithographic process.

property of two-photon absorption.[91,92] In this process a dye chromophore on irradiation with high intensity light absorbs two photons of light simultaneously; the excited dye molecule then emits a single photon of higher energy. For instance the energy of an NIR laser can be converted into high-energy fluorescence in the visible region. The basis of the design of these efficient two-photon absorbing dyes (2PA) is described in detail in Chapter 3 (Section 3.5.3), where examples are given. The use of internally generated UV/visible radiation from a two-photon initiated fluorescence allows much deeper penetration of the resin than with conventional single photon initiation. In this two-photon photocure system the 2PA and a co-initiator are mixed within a block of resin, *e.g.* triacrylate resin. Since 2PA efficiency follows the square of the excitation intensity, tightly focusing a femtosecond laser beam into the resin, polymerisation occurs only in the close vicinity of the focal point (see Figure 3.26). There are two types, negative-tone (where the materials become less soluble upon exposure) or positive-tone (where the materials become more soluble upon exposure). In either case the soluble material can be washed away allowing the fabrication of a 3D structure by directly writing 3D patterns. Fabrication size of microstructures has been shown to be dependent on the wavelength of excitation of the 2PA. Line widths of 80±7 nm were obtained with 520 nm excitation using 1,4-bis(di-n-butylamino)biphenyl, whereas the longer wavelength 2PA (4.46) gave a minimum line width of 200±20 nm with 730 nm excitation.[93] Many developments are taking place in this area, especially opposite the construction of 3D periodic structures such as photonic crystals (see Chapter 5).



(4.46)

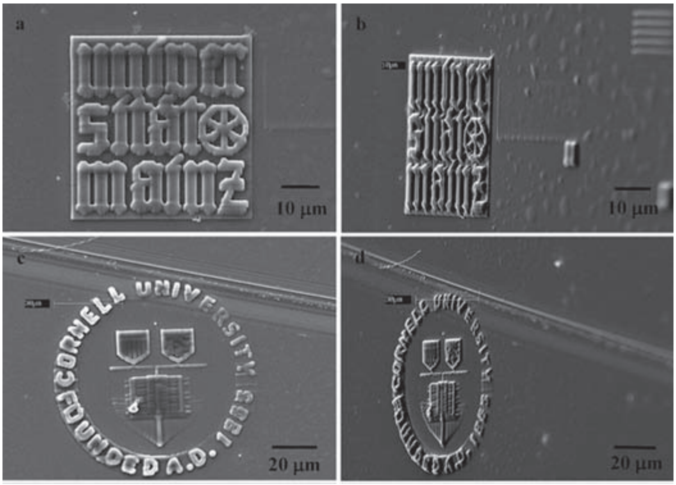
Most of the 2PA materials described so far have been used for polymerising acrylates and other unsaturated imaging materials *via* a free-radical mechanism. Photoacid generators (PAGs) are used in photolithography as they catalyse various reactions by either cationic or radical pathways in a wide range of resins. To test their applications in 2PA 3D microfabrication of both radical and a cationic polymerisable resins, a PAG was specially constructed consisting of a 2PA covalently attached to a photolabile acid group (4.47).[94] Using a confocal laser scanning microscope with titanium:sapphire laser operating mode-locked at a wavelength of 780 nm, and a computer-controlled 3D translation stage, it was possible to produce the 3D microstructures shown in Figure 4.20.

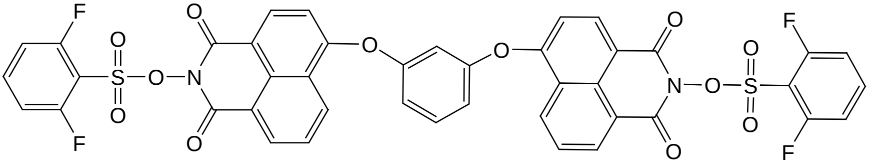
A recent development is the use of colloidal CdS semi-conductor quantum dots (see Chapter 3) and amine co-initiators to promote radical generation in 2PA-induced polymerisation in methyl methacrylate as illustrated in Figure 4.21.[95] Although they showed modest quantum efficiencies for initiation, the large 2PA cross-sections of molecularly passivated QDs suggest potential as efficient 2PA photosensitisers for polymerisation.

4.5.3 Sensitisers in Colour Photography

The production of high-quality images using silver halide photography requires the use of dyes that absorb light energy and then transfer this to adjacent silver halide molecules causing reduction to metallic silver (see Chapter 2, Section 2.8.1). The process involves transfer of an electron from the electronically excited state of the dye to the silver halide crystal. The dye regains its lost electron by receiving an electron from a halide ion situated close by, creating a positive hole. A simplified scheme is shown in Figure 4.22.

The dyes that perform this function are called spectral sensitisers because they are used to sensitise the photographic emulsion to light across the whole visible spectrum and beyond. Since silver halides are naturally blue sensitive, the green and red spectral sensitiser dyes must also be able to reduce the natural





(4.47)

Figure 4.20 Bound photoacid generator in 2PA lithography.[94]

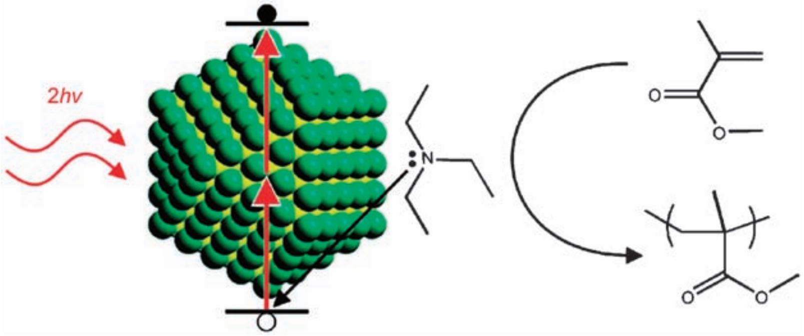


Figure 4.21 Two photon polymerisation with CdS quantum dots of methylmethacrylate[95] (reproduced with permission of the American Chemical Society).

sensitivity of the silver halide emulsion to blue light. The most important class of compounds used in this outlet, as well as in the important area of IR-sensitive films, are the cyanines, especially merocyanines and carbocyanines. Some typical blue, green, red and NIR materials are shown in Figure 4.23.

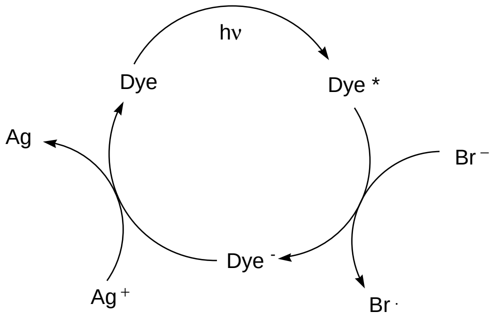


Figure 4.22 Schema for spectral sensitisation of silver bromide.

4.6 Sensitisers in Medicine and Chemical Biology

The generic term for the branch of biological science that is involved in the study of the interaction of light with living organisms is *photobiology*. There are several important interactions of light in Nature, some of which are absolutely essential for our well-being and others that can, under certain conditions, be detrimental to our health.

- At the heart of much of this book is the fact that human beings are able to see colour by the interaction of light with the receptors in the retina of the eye.[96] Any fault in this mechanism, such as red-green colour blindness, is a distinct hindrance in a world constructed around normal colour vision.
- In biology there are other important photosensory mechanisms, such as chronobiology (biological clocks), photomorphogenesis (light signals regulating changes in structure and form in plants), photomovement (*e.g.* sunflowers moving to face the sun), photoreception (perception of light by receptors other than true eyes).
- Photosynthesis, crucial for plant growth, involves the interaction of light with chlorophyll.[97] Man's attempts to reproduce this process in a controllable manner will be discussed under artificial photosynthesis (Section 4.8.2).
- The luminescent production of light by living animals and bacteria, by chemical reactions occurring in special organs, is covered under bioluminescence (see Chapter 3, Section 3.7).
- At certain times of the day, sunlight can be of such intensity that it has effects on the bodies of humans and other animals. Exposure to UV in sunlight can have both beneficial and detrimental side effects for humans.
  - UV-C is light of wavelength below 290 nm, UV-B light between 290 and 320 nm and UV-A 320–400 nm.
  - Although UV-C is mostly filtered out by ozone in the earth's upper atmosphere, even a small amount of light from below 290 nm is very detrimental as it can interact with both nucleic acids and proteins,

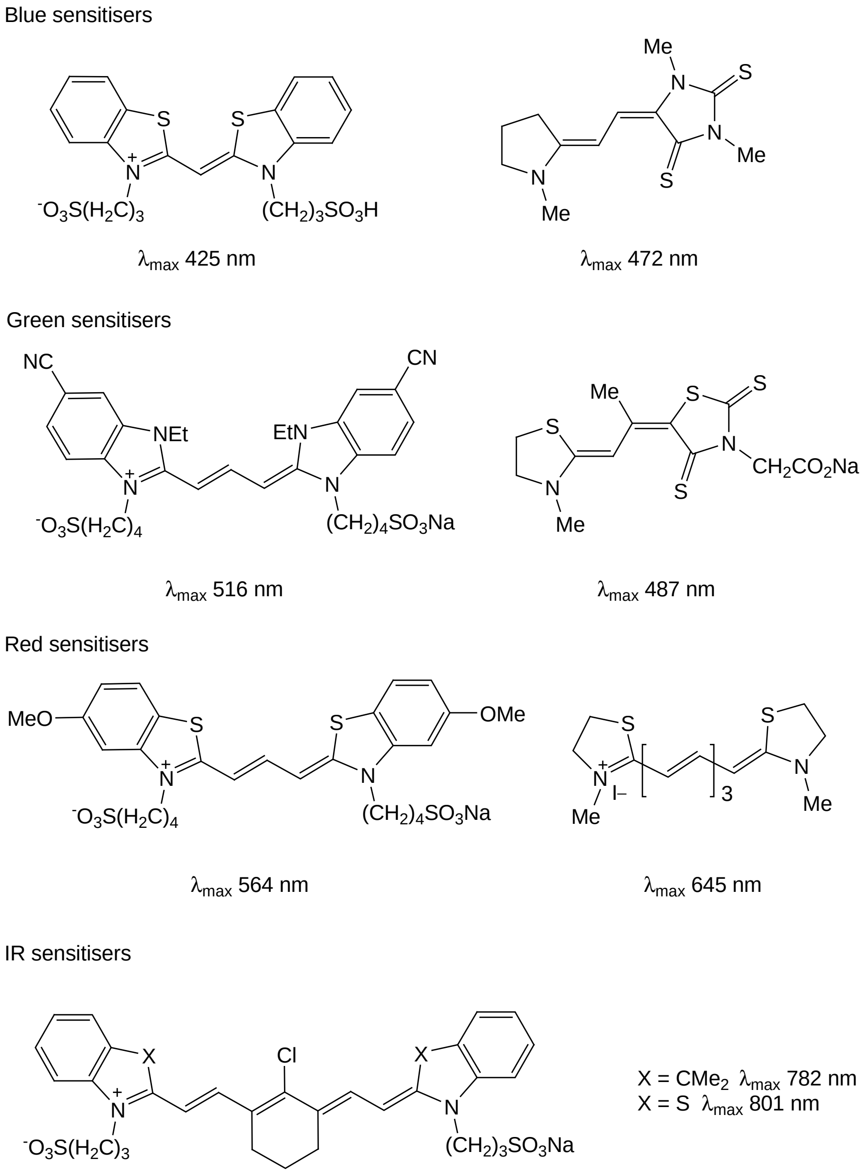


Figure 4.23 Spectral sensitising dyes for photography.

causing in the worst cases illnesses such as skin cancer. Hence the concern for any holes in the ozone layer.

- UV-B in moderation is largely beneficial to humans, for example, *via* the photochemical production of Vitamin D, essential in avoiding illnesses such as rickets. However, UV-B in excess is detrimental, especially to

  light-skinned people, causing sun burning, skin hardening and even skin cancer in exposed parts of the body. The body uses UV-B and, to a lesser extent, UV-A light to produce melanin pigmentation in the skin, which helps protect the skin from excessive sunburn. Unfortunately, browning of the skin is a slow process and during the time that it takes to build up melanin, burning of the skin is a serious problem. To overcome these problems sunscreens have been developed designed to cut out most of the UV-B, whilst allowing UV-A to continue the slower production of melanin and skin tanning. This can be done with physical barrier creams (*e.g.* zinc oxide), or chemically by strong UV-B/A absorbers, commonly anthranilates and benzophenones. The commercialisation of synthetic tanners is a direct result of people wanting the effect without the side effects.
  - Despite the problems associated with exposure to excessively bright sunlight, its absence can have detrimental effects on human behaviour. SAD or seasonal affective disorder, an illness experienced by people living through low daylight winters in northern areas of the northern hemisphere, is caused by a lack of sunlight in their lives. The use of artificial sunlight (heliotherapy) to extend the day has been found to benefit patients with this disorder.
- Light has long been thought to be beneficial in the treatment of physical illnesses but in the last 50 years it has developed into the discipline now known as photomedicine, which includes both phototherapy and photodiagnosis. There is also the developing area of nanobiophotonics, which involves the merging of photonics, nanotechnology and bio-medical science, a subset of which is called nanomedicine.[98]
- Closely related to photomedicine are the photochemical methods used to control organisms detrimental to humans and their needs, by employing photobactericides and photoinsecticides to destroy bacteria and insects, respectively.

4.6.1 Photomedicine

There are two interrelated aspects of photomedicine: phototherapy and photodiagnosis.

- Phototherapy is the use of UV, visible white light or NIR radiation, to treat a variety of diseases;
- Photodiagnosis is the use of optical methods, based on fluorescence, for early diagnosis (optical biopsy), some examples of which are covered in Chapter 3.

Phototherapy is the generic term covering therapies that use light either with or without a sensitiser. It is most commonly applied to patients who do not require a sensitiser but use the natural chromophores within the tissue to perform this function (*e.g.* treatment of Vitamin D deficiency in rickets, and neonatal jaundice), narrow-band UV-B (psoriasis and atopic eczema) *e.g.* using a XeCl excimer laser at 308 nm, and laser therapy operating at 380–780 nm.[99] Those treatments that do use an added sensitiser include photochemotherapy (largely for psoriasis, vitiligo and skin disorders) using UV-A light and psoralen, and photodynamic therapy (currently mainly cancer but also macular degeneration). Photodynamic therapy is differentiated from photochemotherapy by its additional requirement for the presence of oxygen at molecular or ambient levels.[100] Closely related to photodynamic therapy is photothermal therapy in which a sensitiser interacts with laser light converting it into highly localised intense heat, which destroys the targeted cells (see Section 4.6.4).

4.6.2 Photodynamic Therapy

Photodynamic therapy (PDT) has enjoyed a research boom in the last 15–20 years with over 8000 original articles and 600 reviews published.[101] During this period it has become an established methodology for the effective early treatment of some cancers, macular degeneration and in the treatment of certain skin disorders and viral infections. The process used in the treatment of patients by PDT involves the application of the photosensitiser, either topically or by systemic injection, which then selectively accumulates in the tumour (or lesion). In the next step low-energy light is led into the tumour *via* an optical fibre, where it interacts with the sensitiser and oxygen, causing cell destruction. This is shown schematically in Figure 4.24.

The key to PDT is in the photosensitiser and since the introduction of the first product in 1993 (photofrin) five new ones have been approved for clinical use and several others are under clinical evaluation. The comparative properties and uses of the approved drugs are shown in Table 4.5.

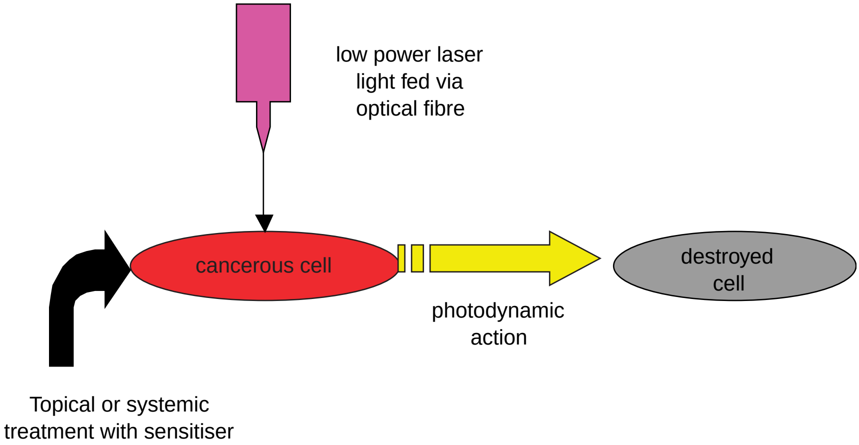


Figure 4.24 Outline of PDT treatment of tumours.

Table 4.5 Approved photosensitising drugs for photodynamic therapy.

Sensitiser and "trade name"	λ_{max} *nm* (ε_{max})	*Singlet oxygen* $\phi_{\Delta}(^1O_2)$	*Drug use* ($mg\,kg^{-1}$)	*Light dose* ($J\,cm^{-1}$)	*Treatment time (s)*	*Indicators*	*Comments*
Hematoporphyrin derivative (HpD), "Photofrin"	628 (3000)	0.89	1.2–5	75–250	750–2500	Superficial bladder, gastric, cervical, oesophageal, lung and endobronchial cancers	Approved in more than 120 countries since1993 Axcan Pharma
BPD "Visudyne"	689 (34000)	0.84	4	150	1500	Age-related macular degeneration	More than 70 countries since 2001 QLT Inc. and Novartis Opthalmics
m-THPc "Foscan"	652 (35000)	0.87	0.15	5–20	50–200	Head and neck cancer	EU, Norway and Iceland 2001 Biolitec AG
5-Aminolevulinic acid (ALA) "Levulan"	635 (5000)	0.56	60	50–150	500–1500	Actinic keratoses of face or scalp	USA 1999 DUSA Pharmaceuticals Inc.
Methyl Aminolevulinate (MAL) "Metvix"	570–670 (activation light range)			60–180	750–2500	Actinic keratoses, basal cell carcinoma	EU and Australia from 2001 Photocure USA
Hexyl Aminolevulinate (HAL) "Hexvix"	410 nm (activation)					Fluorescence diagnosis of bladder cancer	Sweden 2004, EU 2005 Photocure USA

4.6.2.1 The Mechanism of PDT

There are two main ways in which light can react with sensitiser and ground-state triplet oxygen and so cause damage in living tissue.

Type I involves the excited triplet state of the photosensitiser reacting with a substrate, by electron transfer or hydrogen abstraction, giving a radical. This radical reacts with triplet oxygen producing hydroperoxides, which initiate free radical autoxidation.

Type II involves energy transfer from the excited triplet state of the sensitiser to triplet oxygen producing the highly oxidative singlet oxygen ($^1\Delta_g$). This mechanism has already been discussed earlier (see Figure 4.16).

It is now well established that the useful sensitisers in PDT require oxygen and that the dominating mechanism operating in PDT is Type II production of singlet oxygen, which acts as the main cytotoxic agent, presumably by reaction with double bonds in proteins and unsaturated lipids *via* the ene reaction. The process is catalytic and each molecule of photosensitiser can produce many thousands of singlet oxygen molecules, provided it is not subject to too high a rate of destruction by photobleaching (destruction or modification of the chromophore). In fact a controlled rate of photobleaching can be advantageous in avoiding healthy tissue damage during tumour necrosis.[100] [102]

4.6.2.2 Light Sources for PDT

There are two main light sources used in PDT, lamps for topical treatments and lasers when transmission *via* optical fibres is required.

- Lamps – these are used in the treatment of skin diseases, for instance using halogen lamps with filters to give light in the region of 400–500 nm. Developments include a 5-W metal halide lamp delivering 40 nm band in the red and 0.5 W at the end of a light guide.
- Lasers and LEDs, including:
  - Dye lasers pumped by Ar ion, Cu vapour lasers and frequency-doubled Nd:YAG solid state lasers.
  - LEDs operating at 635–652 nm, diode lasers at 635 nm (AlGaInP), 652 nm (InGaAlP) and 730 nm (AlGaAs).
  - Second, third and fourth harmonics of solid-state pulsed lasers (*e.g.* Nd:YAG, Nd:YLF).

4.6.2.3 Photosensitisers for PDT

The development of photosensitisers is ongoing and the products of these developments can be classified as first, second and third generation as their properties have been changed and improved.

First generation. Although there are many dyes which can photosensitise the production of singlet oxygen (see Section 4.5.1), in PDT the first products of

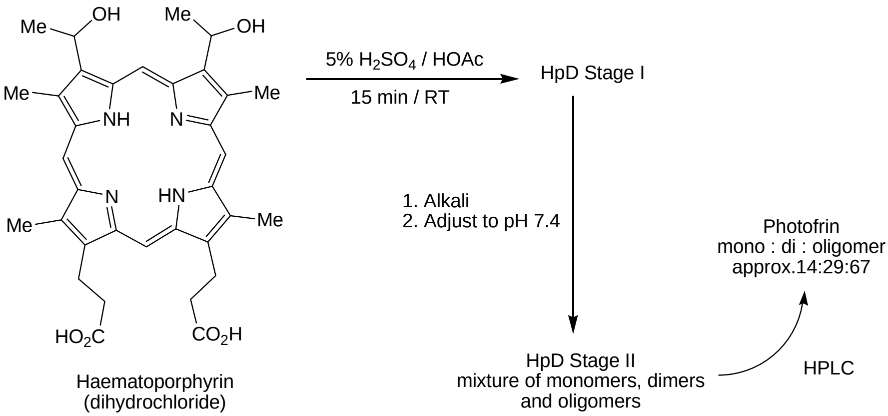


Figure 4.25 Process for the production of haematoporphyrin derivative photo sensitisers[100] (reproduced with permission of Gordon and Breach).

real interest came from haematoporphyrin.[103] This is derived from the blood haematin. Subsequent studies led to the haematoporphyrin derivatives, HpD Stage I and Stage II, which were found to be more active as PDT sensitisers as they localised preferentially in tumours. The first commercially available sensitiser, Photofrin, is based on processed material from HpD Stage II, and is a complex mixture of monomeric, dimeric and oligomeric (*e.g.* hexamer) porphyrins, in an approximate ratio of 14:29:67. The process is outlined in Figure 4.25. The polymers are formed by oligomerisation reactions of the benzylic groups with each other and the propionic acid groups giving esters, ethers and C–C bond formation.[100]

Although Photofrin is still the most widely used clinical sensitiser the first-generation haematoporphyrin derivatives suffer from some inherent deficiencies as sensitisers, including the following:

- Complex mixtures, which are difficult to reproduce;
- Activity is only modest;
- Sensitisation of skin tissue remains for an unacceptable time (4–6 weeks);
    - A patient undergoing actual treatment with Photofrin is required to visit the clinic for an intravenous injection of the sensitiser and then to go home and return in 24–48 hours time. Back in the clinic the tumour in the patient is illuminated for around 10–30 minutes using red light (630 nm) *via* fibre optics. The actual experience is simple and is one of the attractions behind the drive to introduce PDT into clinics. However, with this and other similar reagents there is a side effect. This side reaction is sensitisation to bright sunlight, and the patient may be advised to stay indoors for a time, or at least cover up exposed skin when in sunlight. Sensitisation is due to interaction of solar radiation with the strong absorptions in the 400 nm regions and below, common in porphyrins, as discussed in Section 4.5 above.

- Have low absorption, $\varepsilon_{\max}$ 5,000 in the desirable red-light region ($\lambda_{\max}$ 630 nm);
- Depth of light penetration at 630 nm is low, less than 4 mm (a move to 700 nm would double this figure). See the discussion on the NIR transparency window of tissue in Chapter 3 (Section 3.5.9.1).

Second generation. Second-generation photosensitisers have been sought which not only overcome the deficiencies of the first generation but also display the following characteristics:

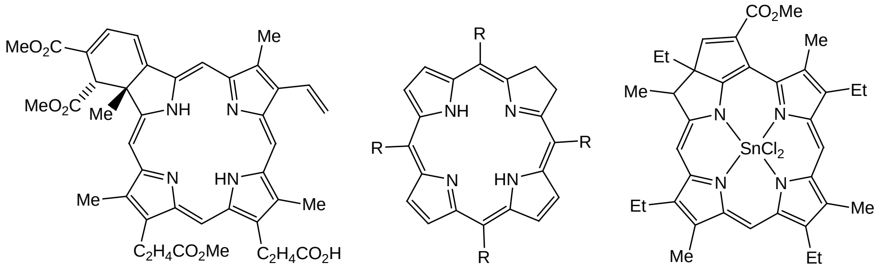
- Constant composition that is easy to synthesise, preferably a single compound;
- Activation at wavelengths greater than 630 nm and preferably in the 650–800 nm range;
- Show low dark toxicity, and do not become cytotoxic until light is applied, and therefore the treatment can be controlled by a light dose for a given drug dose;
- Localise in tumours but clear from the body after it has completed its work;
- Soluble in body tissue fluids, or be capable of formulation for injection, and then be carried around the body.

The search for second-generation sensitisers has covered a wide range of chromophores including phthalocyanines, naphthalocyanins, benzoporphyrins, chlorins, purpurins, texaphyrins, porphycenes, pheophorbides and bacteriochlorins. Two of these, Visudyne and Foscan, have received approval from authorities (see Table 4.5) for clinical uses and a range of others were at various stages of clinical trials in 2007.

The list of those sensitisers undergoing trials includes:

- BOPP (boronated porphyrin; Pacific Pharmaceuticals Inc.);
- Npe6 (mono-*N*-aspartyl chlorin e6, talaporfin; Meiji Seika Kaisha, Ltd);
- hypericin (Pharmaceuticals Inc.);
- AlPcSn (sulfonated aluminium phthalocyanine, Photosense; State Research Center);
- chlorin e6 derivative (Photodithazine; State Research Center);
- ATMPn (porphycene; Glaxo-Wellcome Inc.);
- HPPH (2-[1-hexyloxyethyl]-2-devinyl pyropheophorbide-a, Photochlor; Roswell Park Cancer Institute);
- motexafin lutetium (MLu, lutetium(III) texaphyrin, Lu-Tex, Antrin; Pharmacyclics Inc.);
- SnET2 (tin ethyl etiopurpurin, Sn etiopurpurin, rostaporfin, Photrex; Miravant Medical Technologies).[101]

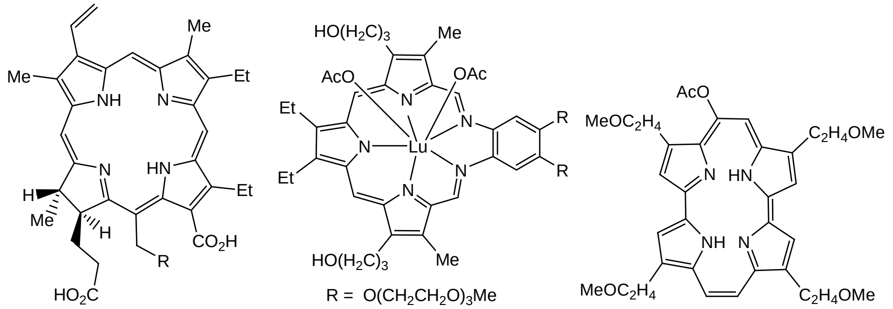
The structures of a selection of the second-generation sensitisers are shown in Figure 4.26.[102,104] From the activation wavelengths given in Figure 4.26 it can



Benzoporphyrin derivative (BPD)
Verteporfin "Visudyne" , 689 nm

m-Tetrahydroxyphenylchlorin
"Foscan", 652 nm

Tin Etiopurpurin ($SnET_2$)
rostaporfin "Photrex", 663 nm



NPe6
R = aspartic acid; talaporfin, 654 nm

Texaphyrin, 732 nm

ATMPn
Porphycene, 650 nm

Also: Sulfonated Al phthalocyanine
"Photosense", 670 nm
2-[1-hexyloxyethyl]-2-devinyl pyropheophorbide-a,
"Photochlor"

Figure 4.26 Second generation photosensitisers under clinical trials.

be seen that they are all red-shifted (650–750 nm) in comparison with Photofrin. Treatment times and the light and drug doses required are all improved and a wider variety of cancers can be treated.

An alternative approach to the photosensitisation in PDT involves the use of 5-aminolaevulinic acid (ALA). This compound itself is not a sensitiser but in human cells it is the key metabolic precursor in the biosynthesis of protoporphyrin IX, which can act as a photosensitiser. Normally the biosynthetic process would continue beyond protoporphyrin IX to the iron-containing haem. However, by adding extra ALA and iron chelators, the ferrochelatase action is inhibited and the normal feedback mechanism bypassed resulting in a build-up of protoporphyrin IX in the cell. The mechanism is illustrated in Figure 4.27.

The properties of protoporphyrin IX working at red light wavelengths are not that impressive, having a weak absorption at 635 nm (5000) similar to Photofrin. But it does show strong absorption in the blue region and hence is ideal for use with light at 410–420 nm. At these wavelengths light penetration is low, but this product is used for the treatment at the epidermis in skin cancer

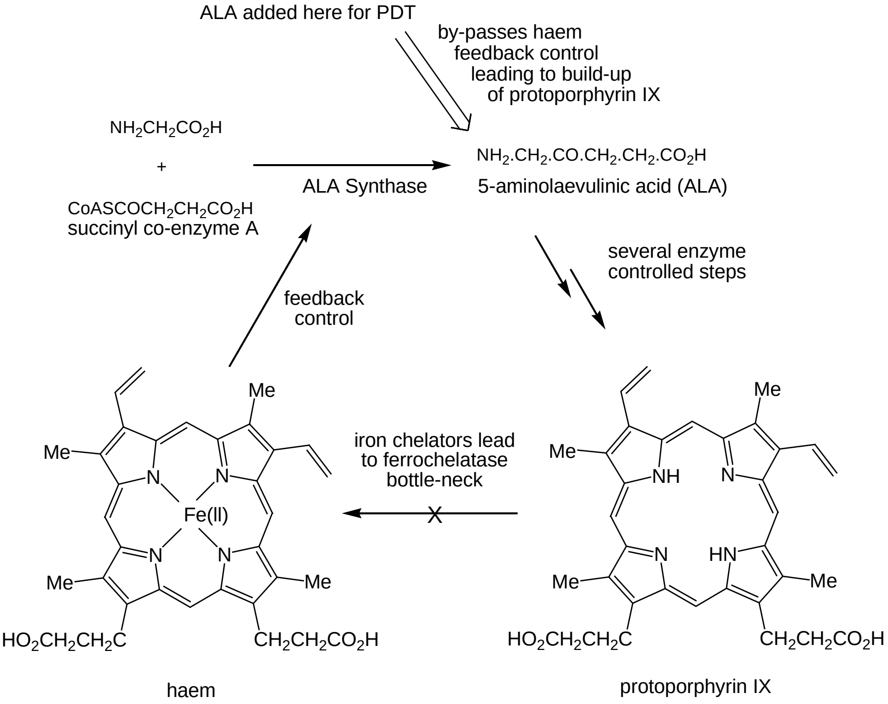


Figure 4.27 Mechanism of build up of protoporphyrin IX in tumour cell.

where protoporphyrin builds up naturally and penetration is not an issue. DUSA have designed a cheap light box powered by fluorescent blue light that is 20 times more efficient in producing singlet oxygen than the red light, and this will be used in treating dermatological conditions, such as acne, in conjunction with ALA (Levulan).[105] It has subsequently been discovered that the esters of ALA are more efficient in inducing porphyrin accumulation in cells. ALA methyl ester (Metvix, PhotoCure ASA) has been approved and widely used for the treatment of skin premalignancies and malignancies. The hexyl ester (Hexvix, PhotoCure ASA), whilst not used in PDT, is being applied in the blue light diagnosis of bladder cancer.

Third generation. Whilst all these advances in photosensitiser design are working their way through the testing and regulatory procedures, research continues into third-generation products. These researches centre on the following approaches:

- Increase the depth of tissue penetration. This could be achieved by moving to longer wavelengths, but not too far into the NIR (830 nm); as the production of singlet oxygen from the triplet photosensitiser becomes low, the photosensitiser itself is also more susceptible to oxidation, and water in tissue cuts down the transmission at wavelengths above about 950 nm.

- Enhancing specificity for tumour cells. For instance attaching the photosensitiser covalently to a monoclonal antibody, which would carry it to the tumour.
- Trigger programmed cell suicide (apoptosis) as opposed to random cell death (necrosis). This allows sub-lethal doses of photosensitiser, preventing damage and inflammatory response in healthy tissue.[106]

Several lines of research are being followed in order to achieve some of these objectives including those acting as carriers for delivery of the photosensitiser to the required site or as energy transducers to the photosensitisers.

Enhancing the accumulation of the photosensitiser in the tumour by changing its degree of hydrophilicity and amphiphilicity is a good target since it directly affects its route of administration and the biodistribution/pharmacokinetic profile.[107] For instance hydrophobic photosensitisers have normal to tumour tissue ratios of 8:1 *versus* 2:1 for hydrophilic equivalents.[108] Another way is to use bio-molecules as carriers of the sensitisers, such as monoclonal antibodies that are specific for tumour-associated antigens,[109] or single-chain antibody fragments.[110] The combination of PDT with different immunological approaches, which offers the possibility of considerable improvement for the treatment of cancer over PDT or immunostimulation alone, has been reviewed.[111]

The rapidly evolving area of nanoparticles has played a big role in these developments.[98,112,113] Recently nanoscale novel drug delivery systems based on supramolecular nanocarriers of dendrimer encapsulated photosensitisers have been applied as photosensitisers in PDT.[114] Formation of a dendrimer porphyrin (DP)-incorporated polyion complex (PIC) micelle through electrostatic interactions between anionic DPs and poly(ethylene glycol)-blockpoly(L-lysine) (PEG-b-PLL) copolymers is shown in Figure 4.28.[114(a),115] Ceramic-based organically modified

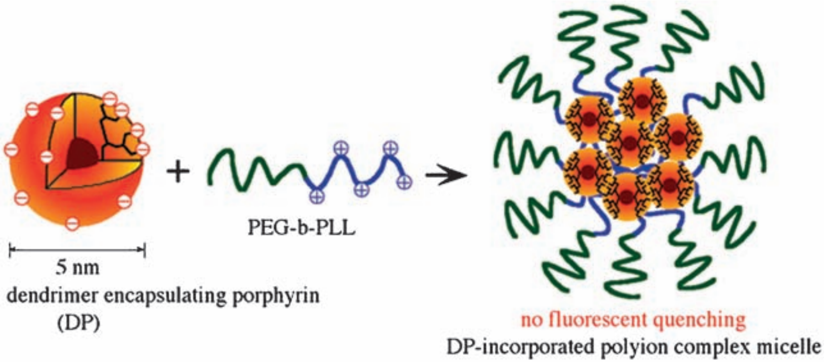


Figure 4.28 Formation of dendrimer porphyrin (DP) incorporated polyion complex micelle.[114(a)]

nanoparticles (diameter *ca.* 30 nm) have been made by entrapping a water-insoluble photosensitiser (*e.g.* 2-devinyl-2-(1-hexyloxyethyl) pyropheophorbide) in the non-polar core of micelles by hydrolysis of triethoxyvinylsilane. The resulting nanoparticles are spherical, highly monodispersed and stable in aqueous system, and were effective at carrying the sensitiser into tumour cells *in vitro*, which could then be irradiated at 650 nm.[116] Greater detail is available in a review on the use of nanoparticles including inorganic oxide-, metallic- and polymer-based nanocomposites as carriers for photosensitisers in PDT.[117]

Quantum dots (QDs; see Chapter 3, Section 3.5.2.1) are tuneable, depending on size and shape, for emission in the NIR region, allowing low-energy light to be used for deep penetration into tissue. QDs are strong absorbers and can be coated to make them water soluble, biocompatible or target specific. The use of QDs as energy donors to photosensitisers *via* fluorescence resonance energy transfer (FRET) is proving to be valuable.[118] In one example thiol-stabilised CdTe QDs synthesised in the aqueous phase were used as energy donors to aluminium tetrasulfonated phthalocyanine (AlPcSn; Photosense) giving improved performance.[119]

Two-photon absorption (2PA, see Chapter 3, Section 3.5.3) is another way of using low-energy NIR light to penetrate deeper into the tissue. Additionally the therapeutic volume of two-photon PDT is very small and localised only within a small spot of a focused laser beam, where high light intensities are obtained. Consequently, it could be of use in treating diseases of sensitive tissue such as in macular degeneration.[120]

Although some of the first- and second-generation photosensitisers exhibit 2PA, *e.g.* Visudyne, it is usually insufficient to serve as an alternative to one-photon PDT.[121] Alternative molecules with much better 2PA cross-section have been examined as alternatives, such as extended porphyrins and porphyrin dimers, and porphycenes, which show promise as 2PA PDT sensitisers.[122] An alternative approach is to use phosphor up-converting nanoparticles (see Chapter 3, Section 3.5.2.3) to interact with NIR lasers. For instance when $NaYF_4$:Yb^{3+},Er^{3+} is excited at 975 nm it produces visible absorption bands at 537 and 635 nm, which can be used to excite the sensitiser and so produce singlet oxygen. Such phosphor up-converting nanoparticles (PUNPs) need to be biocompatible whilst still being efficient producers of singlet oxygen and this is the subject of current research. In one method PUNPs are first coated with a porous, thin layer of silica. During the coating process, photosensitising molecules with high absorbance in the spectral window matching the emission of the PUNPs are included, so that the resulting silica layer contains a certain amount of these photosensitising molecules. Finally, an antibody, specific to antigens expressed on the target cell surface, is covalently attached to the silica-coated nanoparticles as shown schematically in Figure 4.29(a).[123] Another way is to use a 2PA fluorescent dye to absorb the NIR light and then transfer this energy *via* FRET to the photosensitiser, all encased in organically modified silica nanoparticles as illustrated in Figure 4.29(b).[124]

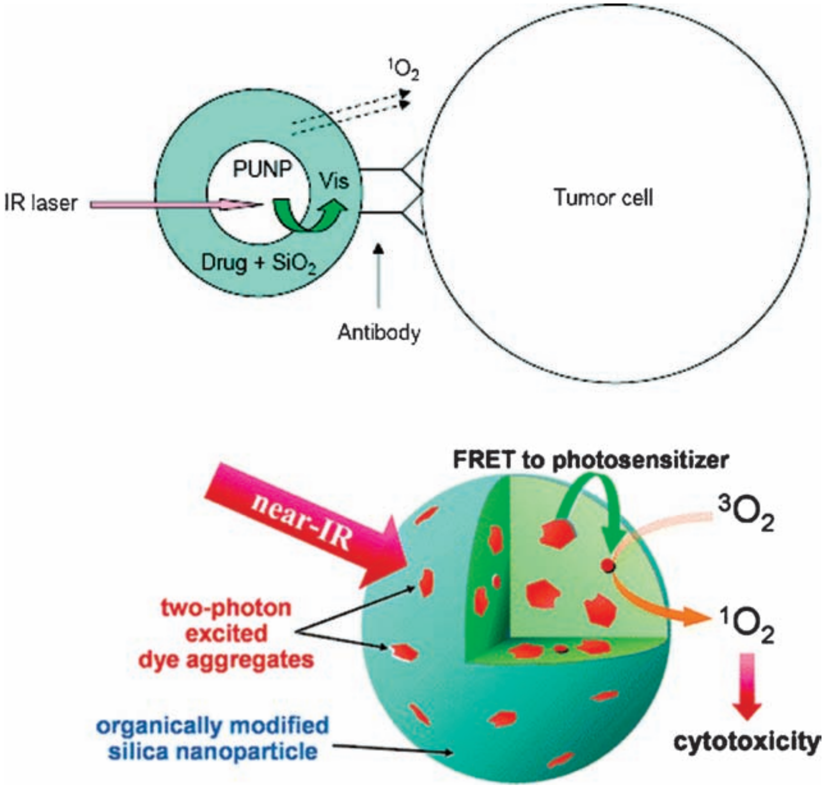


Figure 4.29 (a) Schematic of a phosphor up converting nanoparticle photosensitiser composite for 2PA.[123] (b) Use of 2PA fluorescent dye aggregates[124] (reproduced with permission of the American Chemical Society).

4.6.3 PDT by Production of Nitric Oxide

Nitric oxide (NO), long regarded as a pollutant, has been shown to be involved in many biological events as a pleiotropic bioregulator of important physiological and pathophysiological processes. Consequently much research has been carried out in developing NO-delivering compounds for potential therapeutic applications.[125,126] Two of the most important criteria for effective NO therapy, namely (a) extreme rapidity of delivery and (b) precise control over the amount released, are ideal targets for photochemical methods. Furthermore, the discovery of the destruction of tumour cells by NO suggested that the localised release of NO could be used in PDT.

Integration of suitable NO generators for practical use has been suggested by using hydrogels, mono-, multi-layer and polymer films, amphiphilic, and metal and semi-conductor nanoparticles (NPs and QDs).[127] The methodologies adopted follow those used in singlet oxygen PDT where both single-photon and two-photon excitation of the photosensitisers have been pursued. Examples are given in Figure 4.30: (a) a thiol-modified platinum NP is used as a cage within which a photochemical reaction with an aromatic nitro group on a ligand produces NO,[127] (b) 2PA at 800 nm is used to release NO from a dye-derivatised Fe nitrosyl complex[128] and (c) a water-soluble core-shell CdSe QD is used as an antenna to sensitise the photorelease of NO from a Cr complex.[129] These types of approaches have shown promise with *in vitro* tests on cancer cells but to date there is no report available concerning their use in clinical trials.

4.6.4 Photothermal Therapy

The basic colour properties of noble metal nanoparticles have been introduced in Chapter 1, Section 1.12. In particular gold nanoparticles (AuNPs) are strong absorbers of visible and NIR light (molar absorption more than 10^5 times that of conventional dyes), and are essentially non-fluorescent. All absorbed photo energy is converted to thermal energy. The result is that, for example, a 68-nm gold nanocage laser-pumped at 740 nm near its LSPR maximum can reach a lattice temperature of 1200 K.[130] This photothermal effect is being explored as a novel non-invasive method to destroy cancer cells.

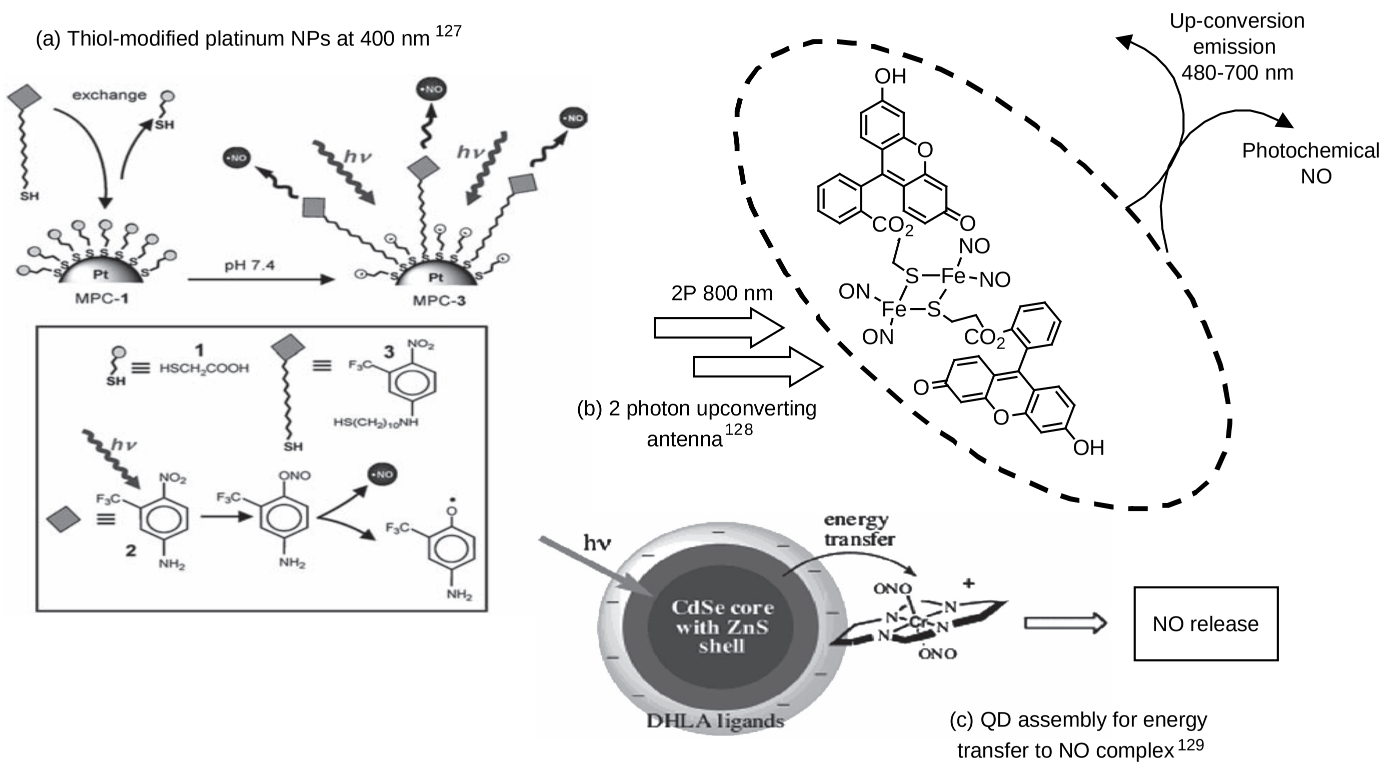
The surface of the AuNP is functionalised with antibodies, *e.g.* HER2-antibody to target the EGFR2 receptor, which over-expresses on the surface of the unhealthy SK-BR-3 breast cancer cells.[131] The AuNP can thus be bound preferentially to the surface of the cancer cell, where on irradiation near its LSPR maximum it heats the cell above the limit of its viability (only about 42 °C in humans) and destroys it. The much lower affinity of the AuNP ligand for healthy cells means they are not heated and remain undamaged on photoirradiation. In practice, visible light can only be used to heat AuNP at the surface of body tissue. However, as tissue is only sufficiently transparent at NIR wavelengths, AuNPS absorbing in the NIR are required for treatment of cells within the tissue. The LSPR of AuNP is readily tailored by modifying the NP shape, so that gold nanorods, nanoshells and nanocages, which all absorb in the NIR, can be applied.

A further aspect of photothermal treatment results from the higher density of AuNPs bound to the target cancer cell compared with healthy cells, and they thus tend to show an aggregation-induced red plasmonic shift. Because of this, even visible light-absorbing gold nanospheres have an absorbance toward the NIR on the surface of the target cell, and thus can be heated with NIR irradiation, while healthy cells are further distinguished and unaffected. Yet another strategy uses 2PA of 800 nm light by gold nanospheres.[132]

Photothermal destruction of viruses and bacteria, as well as controlled denaturation of proteins and nucleic acids for diagnostics or therapy, is also being studied.

4.6.5 Photodynamic Inactivation of Microbes and Viruses

Photodynamically produced singlet oxygen should be effective in killing microorganisms such as bacteria and viruses and this has proved to be the case in what has been called photodynamic inactivation (PDI).[133,134]



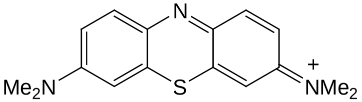
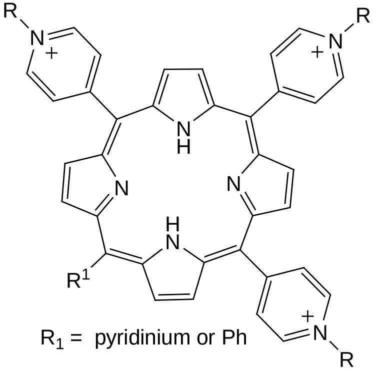
(a) Thiol-modified platinum NPs at 400 nm[127]

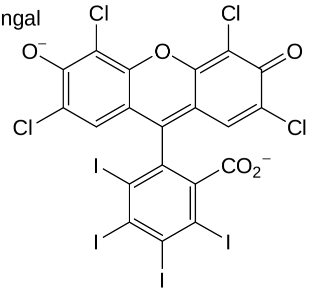
(b) 2 photon upconverting antenna[128]

(c) QD assembly for energy transfer to NO complex[129]

Figure 4.30 Schemas of methods for photochemical NO production[127–129] (reproduced with permission of the American Chemical Society).

Table 4.6 Photodynamic inactivation against bacteria.

Photosensitiser	*Species (gram status)*
Methylene Blue  (and Toluidine Blue)	*S. aureus* (+), *Staphylococcus epidermidis* (+), *Streptococcus pyogenes* (+), *Corynebacterium minutissimum* (–), *Propionibacterium acnes* (–), *Streptococcus pneumoniae* (+), *Enterococcus faecalis* (+), *Haemophilus influenzae* (–), *E. coli* (–), *P. aeruginosa*
"Photosense" Sulfonated Al phthalocyanine	*S.aureus* (+), *S. epidermidis* (+), *P. aeruginosa* (–), *E. coli* (–), *Proteus mirabilis* (–)
 	*E. coli* (–), *S. aureus* (+)

ALA	*E. coli* (–), *Haemophilus parainfluenzae* (–), *Enterococcus hirae* (+)
Hematoporphyrin derivative	*Bacillus subtilis* (+), *Streptocococcus faecalis* (+), *Helicobacter pylori* (–)
Rose Bengal 	*Deinococcus radiodurans* (+), *Brochothrix thermosphacta, D. radiodurans, Streptococcus, Micrococcus, Bacillus, Staphylococcus, Arthrobacter kurthia, Pseudomonas* spp., *Enterobacteriaceae*

4.6.5.1 Photobactericides

Although so far the PDT sensitisers discussed have been based on porphyrin or phthalocyanine rings, others are effective photobactericides including halogenated xanthenes, such as Rose Bengal, perylenequinones, such as hypericin, and especially phenothiazinium salts, such as Methylene Blue and Toluidine Blue O (see Table 4.6). Gram-positive bacteria can be destroyed on irradiation with light in the presence of neutral or anionic sensitisers, but for Gram-negative species the photosensitisers should possess an overall cationic charge and preferably multiple cationic charges. There is an increasing body of evidence that phenothiazinium salts are phototoxic against a broad range of microorganisms. Methylene Blue and Toluidine Blue O are now used clinically for antimicrobial treatments under red light to disinfect blood products and sterilise dental cavities, and are also proposed for the treatment of periodontitis.[135]

A big challenge in antibacterial research is destruction of the Methicillin-resistant *Staphylococcus aureus* (MRSA) and vancomycin-resistant *enterococci*, which are both resistant species that are causing much concern at present. In one example phenothiazinium dyes based on 1,9-methylated Methylene Blue, when used as photosensitisers, were shown to kill MRSA *in vitro* more effectively than vancomycin,[136(a)] and a new porphyrin-based sensitiser was shown to kill colonised MRSA on *ex vivo* porcine skin using 380–480 nm light.[136(b)] A whole range of photosensitisers has been used against a variety of both Gram-positive and Gram-negative bacteria *in vitro* and it is hoped that these will lead to effective PDI methods for the control of bacterial infection. A selection of these photosensitisers is shown in Table 4.6 together with the species inactivated.[133] An interesting development is the use of covalently attached Toluidine Blue-tiopronin onto gold nanoparticles to very effectively kill *S. aureus* with white or 632.6-nm light.[136(c)]

4.6.5.2 Photoantivirals

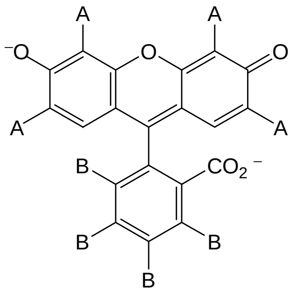
As was the case with the most successful entry point for PDT in cancer (skin), the therapeutic method adopted for the photodynamic inactivation of viruses is most likely to be a topical application of the sensitiser as this offers the simplest way of getting light onto the patient. Consequently the two main viral targets are herpes viruses (HSVs) and papilloma viruses (HPVs). Another important target area is the treatment of blood prior to transfusion to avoid transmission of the immunodeficiency viruses (HIVs, HTLVs) and hepatitis viruses (HBVs, HCVs).[137] Although several approaches have been adopted and tested *in vitro* only the use of ALA and heamatoporphyrins has shown promise, and to date PDT is only used in the treatment of laryngeal papillomata.[133,137]

PDI in blood product disinfection is proving to be a more fruitful area, especially in the treatment of transfused blood going into blood banks, the objective being to inactivate viruses, such as HIV, without affecting erythrocytes. Use of silicon phthalocyanine or naphthalocyanine derivatives allows irradiation at wavelengths where the erythrocytes do not absorb, and the process is reported to be very effective.[138] The use of Photofrin in inactivating HIV-1 in blood has also been described, whilst BPD (see Figure 4.26) has been used to inactivate feline leukaemia retrovirus in both spiked human blood and infected cat's blood.[139] Methylene Blue has been used widely in the photodecontamination of blood plasma by several European transfusion services and has been shown to be particularly effective in the inactivation of enveloped viruses. There are two commercial products which use Methylene Blue as the photosensitiser: Pathinact-MB (Baxter) and Blueflex (MacoPharma) systems.[137]

4.6.6 Photoinsecticides

Research into the use of light-activated dyes as pesticides has a long but sporadic history dating back to the early years of the twentieth century. The first recorded use was in Brazil in 1928, when an aqueous solution of Rose Bengal and erythrosine was found to kill *Culex* and *Anopheles* mosquito larvae in bright sunlight. Some 22 years later the work was repeated in Germany on *Anopheles* and *Aedes* larvae both in the field and in the laboratory. This work suggested that Rose Bengal was the most effective photosensitiser. After another 20 years some very detailed work in Virginia, USA, showed that the halogenated fluoresceins could be used in a bait to kill adult houseflies, *Musca domestica*. Heitz and his collaborators in the USA carried out the most consistent research in this field during the years from 1975–1998, and this led to the first potential commercial application.[140,141]

The process requires a photosensitiser and oxygen to produce singlet oxygen inside the cells of the insects where destruction of important enzymes and cell membranes causes death. From a series of xanthenes (4.47) it was shown that increasing halogenation gave higher phototoxicity, consistent with a lower fluorescence and higher conversion to the excited triplet state. The maximum phototoxicity was shown by phloxine B.



A	B	Name
H	H	Fluorescein
Br	H	Eosin
I	H	Erythrosine B
Br	Cl	Phloxine B
I	Cl	Rose Bengal

(4.47)

The process works by the inclusion of the dye within a bait and successfully kills a wide range of insects including mosquito larvae, houseflies, face flies and fruit flies. It was tested in pilot-scale field trials as an alternative to the use of Malathion in the spraying of fruit crops to kill the Mediterranean fruit fly (*Ceratitis capitata*) in Mexico and Guatemala, and was successful in suppressing fruit-fly populations. Although it was reported to have been adopted to maintain the MedFly Barrier Zone between Mexico and Guatemala, used to protect the USA from any influx of the Mediterranean fruit fly, there were problems for its wider acceptance. Damage can occur in susceptible plants as the dye can cause burn holes to appear in the leaves; the less waxy the leaf surface, the more severe the damage. More obviously it can also stain any surface that it contacts, potentially causing problems when applied in an urban setting. Nevertheless the idea of photoactive insecticides remains an attractive one and other photosensitisers are being examined, including haematoporphyrins and related structures.[142]

4.7 Photodecontamination

Removal of contaminating species, both chemical and biological, is required in many areas of human contact, including the water we drink, the food we eat, the air we breathe and the garments we wear, both in the workplace and our social environment. The majority of the commercial applications of photodecontamination are based on the UV activation of photocatalysts consisting of semi-conductor particles, especially nanocrystalline TiO_2.[143] An interesting recent example is in self-cleaning cotton.[144] For wider applications it is essential that these photocatalysts work in sunlight, hence absorb energy in the 400–650 nm region. No one technology is dominating in this area and consequently examples from the recent literature covering different approaches being adopted will be described below.

Sensitisation by chromophores which absorb in this region is one way of achieving this goal (see also DSCs in Section 4.8.1.4). A core shell nanostructure of titania supported on polystyrene microspheres and sensitised with fluorescein isothiocyanate, absorbing strongly at 400–500 nm, was an efficient photocatalyst when using the decoloration of crystal violet as a model.[145] The use of visible light sensitisers in some of the biological areas has already been discussed in Section 4.6.5, but an interesting extension is the production of bactericidal nanofibres by incorporation of tetraphenyl porphyrin as a singlet oxygen generator.[146] Degradation of chlorinated phenols and other chlorinated aromatic compounds is another important target for visible light photodecomposition. Some recent examples include the use of TiO_2 sensitised with ruthenium complexes for chlorinated hydrocarbons at >420 nm,[147] immobilisation of palladium phthalocyaninesulfonate onto an anionic clay for the oxidation of 2,4,6-trichlorophenol under visible light irradiation[148] and non-aggregating chloro-substituted water-soluble porphyrin derivatives claimed to be excellent candidates for sensitising the photodegradation of phenols with visible light.[149] Because their emission can be tuned to the visible wavelength, quantum dots are proving to have uses as photocatalysts.[150]

An increasingly important area is the decomposition of chemical warfare agents. Self-decontaminating textiles were recently prepared using layer-by-layer deposition of highly active WO_3/titanate nanotubes for the photocatalytic removal of sulfide and organophosphonate simulants and authentic chemical warfare agents by using solar light.[151]

4.8 Solar Energy Utilisation

Three of the main challenges facing mankind during this century are air pollution, dwindling resources and energy security. The use of non-renewable resources, specifically fossil fuels, has a major impact on all three areas and hence the search for alternatives has become both a major political and a technological priority. It has been stated that the best options for producing electricity in a renewable manner are by wind, tidal/wave, hydroelectric, geothermal and solar power generation.[152] Although solar energy is currently only used to produce electrical energy, it has wider applications as it can also be used to make useful chemicals, such as hydrogen *via* water splitting, and to convert carbon dioxide into organic materials *via* an artificial version of photosynthesis. Whilst the use of wind and water are largely engineering-based technologies, the efficient use of solar energy is a subject requiring many chemical answers, and the last decade has seen a massive upsurge in research carried out by chemists in this area.

The inputs to any system are sunlight and the readily available chemicals carbon dioxide, water and nitrogen. The desirable outputs from any system are electricity, hydrogen for use in fuel cells, methane and other hydrocarbons for use as fuels, the distribution network for which already exists, chemical building blocks to support industry and reduced nitrogen products for agricultural uses. The systems that can be used to produce these outputs are photovoltaic and photoelectrochemical, based on semi-conductor technologies; photochemical based on molecular science; and photobiological based on blue-green algae and photosynthetic bacteria. These photosystems can potentially be used in a variety of combinations. The overall schema are shown in Figure 4.31.

4.8.1 Solar Cells and Electrical Energy

Even conservative estimates for the global consumption of energy are that it will rise from a current 14 TW to 27 TW per annum by 2050. The sun provides 120,000 TW of solar energy each year and represents a massive resource to help meet our future energy requirements. One hour of sunlight would be enough to meet the needs of a year of global energy consumption. Even so at 10% efficiency solar cells would need to cover an area equivalent to that of France and Germany combined, and obviously improvements in their efficiency and their cost of production are required.

The utilisation of solar energy to create heating systems has a long history going back to the ancient Greeks.[153] Solar collectors, employing mirrors, glass

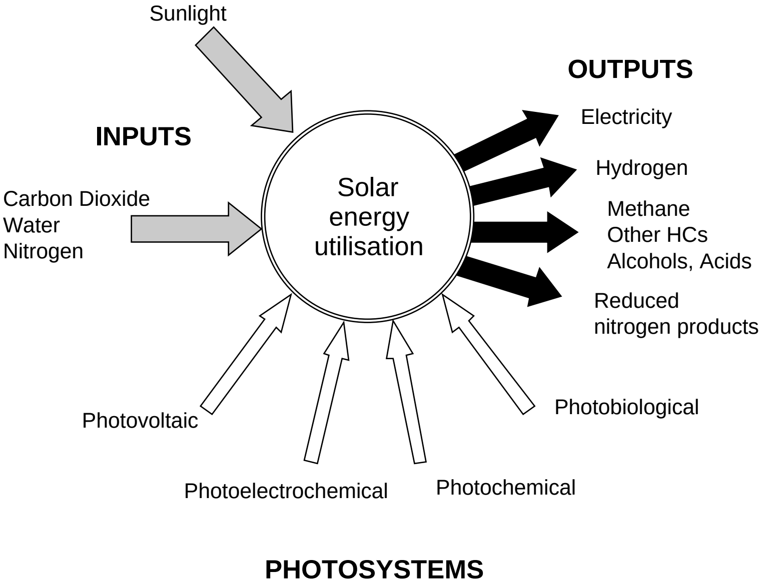


Figure 4.31 Solar energy utilisation, inputs, outputs and systems.

panels and lenses, were employed in the nineteenth century to run static steam engines and especially solar pumps for the distillation of water in arid desert regions. Concentrated solar power has in more recent times been developed into an efficient way of collecting solar energy for power generation. For instance, parabolic mirrors in the form of troughs or dishes direct the sun's energy to heat exchangers containing a fluid *e.g.* molten alkali metal nitrates, in one version at the top of a tower. The heated fluid is then used to produce steam for the power generators. The first large-scale commercial plants were constructed in Spain in 2008.[154] Modern materials chemistry research, driven from the 1970s by successive oil crises, has concentrated on the production of electricity by photovoltaic and photoelectrochemical processes, with the former, based on inorganic semi-conductor technology, having by far the highest commercial success. Even so photovoltaic cells are not yet truly competitive with other forms for producing energy on any scale, and only succeed in this respect where governments provide subsidies for their installation, as in Germany.

4.8.1.1 Inorganic Photovoltaic Cells

Single-crystal silicon-based inorganic photovoltaic cells consist of a sandwich of n-type doped silicon and p-type doped silicon layers. Interaction of the cell with a photon produces a free electron and a hole. The electron moves to the n side and the hole to the p side of the junction of the layers. Provision of external contacts between the layers causes electron flow and hence a current, which

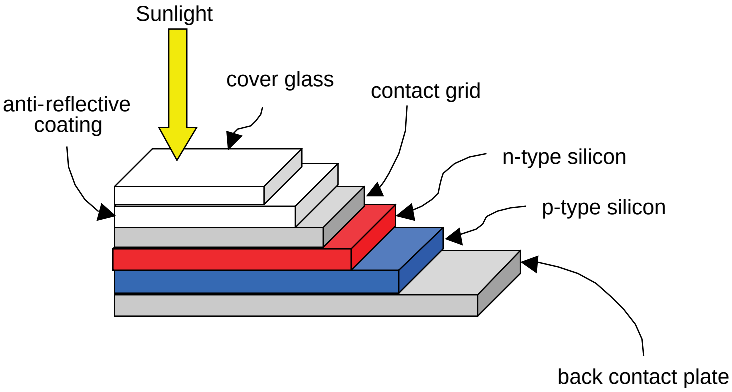


Figure 4.32 Generic structure of single crystal silicon photovoltaic cell.

combined with the voltage of the cell's electric field gives the power. The structure of a cell based on single-crystal silicon is shown in Figure 4.32. The cells can also be constructed using cheaper polycrystalline silicon or amorphous silicon in order to reduce the costs of manufacture, but with some loss in efficiency. Silicon-based photovoltaic cells dominate the market, having approximately 90% share (2007), split into single-crystal 31%, polycrystalline 53%, amorphous 4% and ribbon silicon 3%.[155] Cells with power conversion efficiencies in excess of 20% are available but expensive. More commonly they are at 15%, and at the cheaper end, such as those used in hand-held powered devices, are only 5–6% efficient.

Semi-conducting materials including GaAs, InP and GaSb are ideal materials for high-efficiency solar cells but are expensive. The use of multi-layers with these different band-gap materials has resulted in the highest power conversion efficiency at around 40% from those cells based on GaInP and GaAs on a Ge support as shown schematically in Figure 4.33. These new types of multi-junction cells are set on a growth path to become the next generation of high efficiency solar cells.[156] Thin-film solar cells based on compound CdTe semi-conductors can be constructed because of its intrinsic properties, having a direct optical energy band-gap of 1.5 eV and high optical absorption coefficient for photons with energies greater than 1.5 eV, meaning that only a few microns of CdTe are needed to absorb most of the incident light.[157(a)] Cells made from Cu, In, Ga and Se (CIGS) semi-conductor are reported to have power conversion efficiencies of 19%. In 2007 Nanosolar, a US company, started production of thin-film cells made from this material laid down as nanoparticles from an ink onto an Al foil base, which supported a Mo electrode, followed by melting to give a continuous layer, which was black and an excellent light absorber. The four-layer cell was completed with p/n junction and ZnO electrode layers. At the time these were claimed to be the cheapest solar cells available commercially working out at $1 per watt of power.[157(b)]

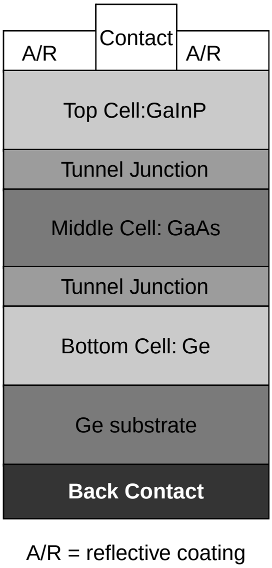


Figure 4.33 Multi junction GaInP/GaAs cell with 39.3% efficiency.

It is theoretically possible to improve on the efficiency of these multi-junction cells to greater than 70% by stacking dozens of different layers together but the technical problems building these devices are immense. An alternative approach is to move to one involving sensitisation of nanocrystalline TiO_2, a technology being applied in dye-sensitised solar cells (see Section 4.8.1.4), and now being pursued in the totally inorganic field with the advent of quantum dots. QDs have tuneable band-gaps dependent upon their size; the larger the size, the longer the wavelength of light absorbed and emitted. By combining QDs of different sizes it is possible to optimise the band-gap to correspond to the highest possible solar-electric energy conversion and harvest the maximum proportion of the incident light. Indeed, the tuning of the photoelectrochemical response and photoconversion efficiency *via* size control of CdSe quantum dots is achievable and further improvement in the photoconversion efficiency is facilitated by charge transport through TiO_2 nanotube architecture.[158] This is shown schematically in Figure 4.34.

4.8.1.2 Organic Solar Cells

In spite of the high level of commercial success of inorganic semi-conductor-based photovoltaic cells, unless there is a state subsidy they are unlikely to challenge seriously electricity generation from fossil fuels, as they are costly to manufacture and it is also difficult to make large area cells. These difficulties have spurred on research into organic alternatives, especially those that can be incorporated into, or are part of, a polymer, thus making cell construction easier and more flexible in application.

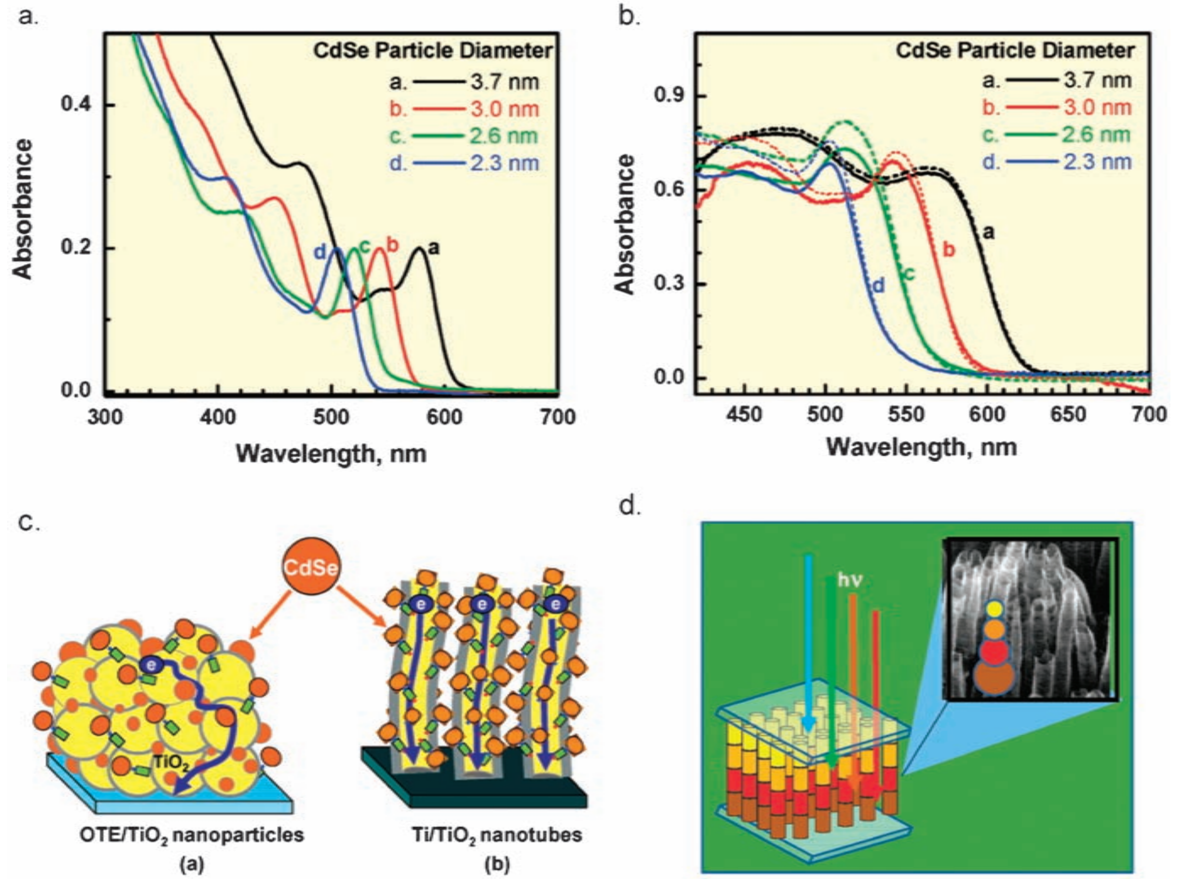


Figure 4.34 (a) CdSe QDs in toluene; (b) CdSe QDs anchored on TiO_2 films; (c) CdSe QDs on TiO_2 random particle and nanotube; (d)Artist's impression of "rainbow solar cell" on nanotube array[158] (reproduced with permission of the American Chemical Society).

In inorganic solar cells the absorption of light leads to the direct formation of free electron-hole pairs in the bulk of the material and the direct production of charge carriers, whilst in organic solar cells the semi-conductors interact with sunlight to produce an exciton, which is a tightly bound electron–hole pair. Hence organic solar cells are sometimes called excitonic solar cells. The exciton can be separated when it reaches the interface between suited donor (D) and acceptor (A) materials. After breaking the binding between the electron in the acceptor and the hole in the donor, the electrons and holes are transported through the acceptor and donor phases, respectively, to the electrodes of the device.

Excitonic solar cells can be further subdivided into organic solar cells (OSCs), hybrid solar cells (HSCs) and dye-sensitised solar cells (DSCs). Organic solar cells are distinguished by the fact that they involve purely organic semi-conductors, whereas the other two also involve an inorganic semi-conductor. The possible ways of constructing OSCs are as follows:

(a) Single layer of semi-conductor – called a Schottky diode;
(b) Two layers of different semi-conductors (hetero-junction);
(c) Blends of semi-conductors (bulk hetero-junction);
(d) Multi-layered laminates of cells of type (b) and (c).

These are illustrated schematically in Figure 4.35. The different forms can also be stacked together in various combinations to form tandem and multi-layered cells.[159]

Cells made of single-layer organic semi-conductors have no practical importance. The first practical approach to OSCs was the dual-layer p/n hetero-junction cell, which is made from small-molecule acceptors and donors. For example α-Cu-phthalocyanine (CuPc) can be used as a donor and 3,4,9,10-perylenetetracarboxylic bis-benzimidazole (PTCBI; see Section 4.4.1.3) as an acceptor, vapour deposited under vacuum sequentially onto an indium tin oxide (ITO) substrate, itself covered by a thin layer of poly (ethylenedioxythiophene):polystyrenesulfonic acid (PEDOT:PSS), which serves as the anode of the device.[160] Efficiencies of these types of cell are only in the range of 0.2–1.9% energy conversion rates but this can be improved by incorporating into multiple cells. A tandem cell constructed from this basic structure with a thin layer of silver separating the two cells is shown in Figure 4.36.[159] Other small molecules that have been used as donors and acceptors in this type of vapour-deposited OSC include metal free phthalocyanine and its other metal derivatives such as zinc and vanadium, fullerene C_{60}, *N*,*N*′-dimethyl-3,4,9,10-perylenetetracarboxydiimide; and 4,4′,4″-tris(3-methylphenylphenylamino)triphenylamine.

However, even with complicated multi-layer structures there remains an inherent problem in this type of p/n junction device: the effective interaction between the electron–donor and the electron–acceptor components is limited to the flat geometrical interface, so that rather low short-circuit photocurrent density values are obtained. Alternatives to having discrete layers forming p-n-junctions

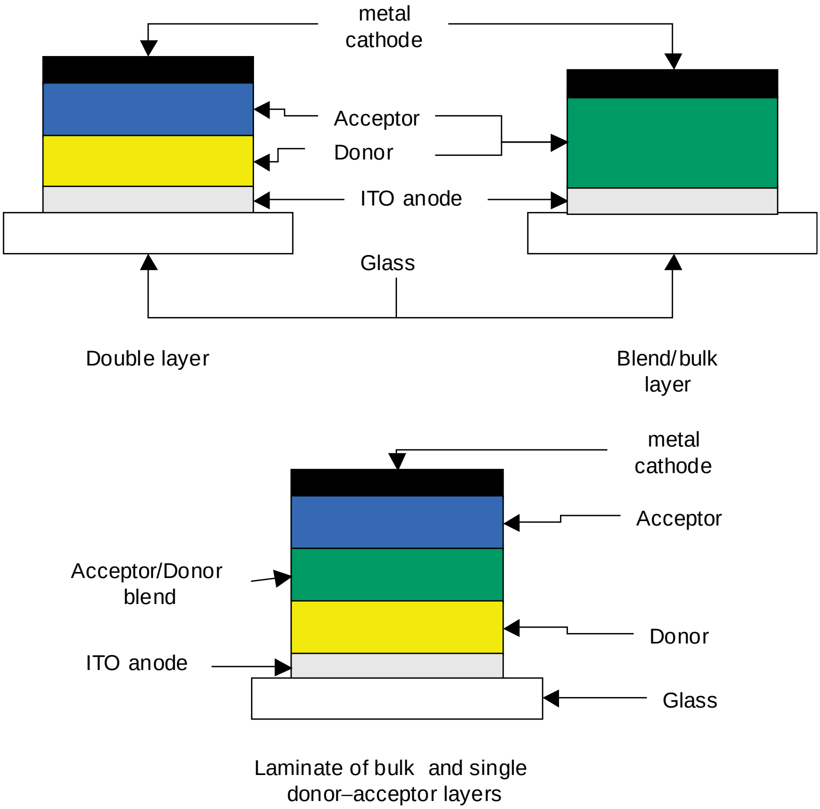


Figure 4.35 Schematic representation of possible structures of organic solar cells.

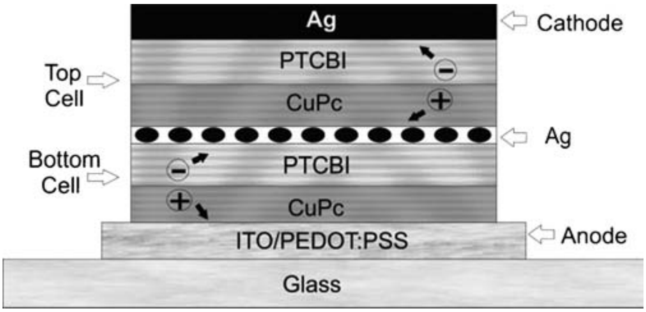


Figure 4.36 Tandem solar cell based on small molecule hetero junction cells[159] (reproduced with permission of Wiley VCH).

include having the hetero-junctions distributed throughout a support material, such as a polymer or polymer blend, called bulk hetero-junction cells.

Several combinations have been considered for these distributed hetero-junctions including dye–dye blends and conducting polymers with other

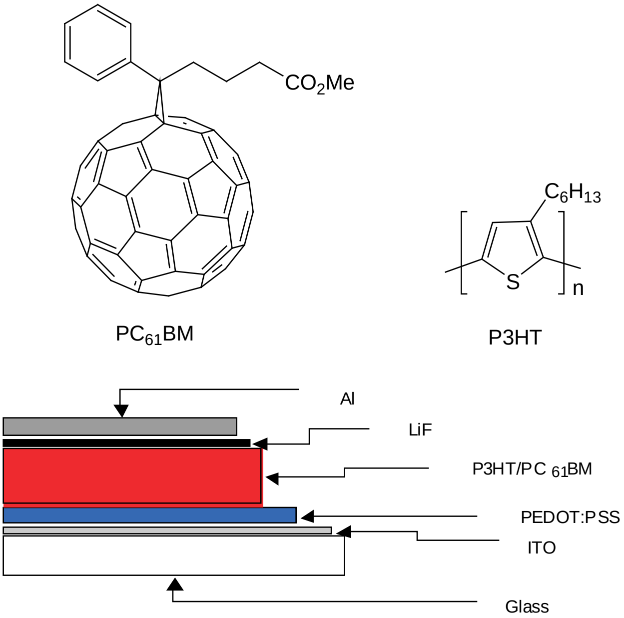
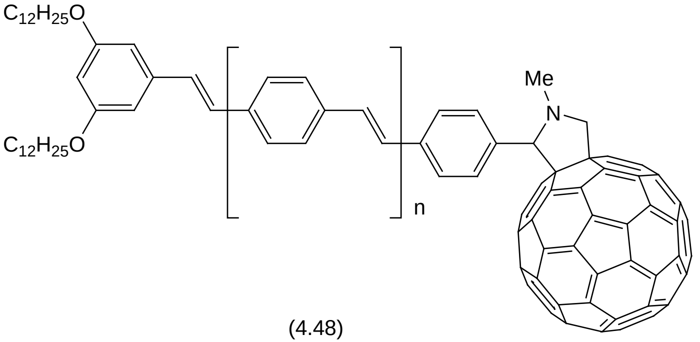


Figure 4.37 Schematic of bulk hetero junction cell using conducting polymer and fullerene derivative.

polymers, dyes and fullerene and its derivatives.[161] One of the advantages in using polymer blends to form bulk hetero-junctions is that they can be laid down by solvent processing at low temperatures, *e.g.* by spin coating, using a doctor blade and by screen or ink-jet printing, and hence potentially be used to produce plastic solar cells of a significant size. The major area of research has involved using C_{60} fullerene and its derivatives as the acceptors with a wide variety of conducting polymers acting as donors, exemplified by polyphenylenevinylenes and poly(3-alkylthiophenes).[162] In one example of a polymer-dye-distributed hetero-junction, a power conversion efficiency of 4–5% was obtained using regio-regular poly(3-hexylthiophene) (P3HT), which has very high hole mobility, as the electron–donor material, and [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) as the acceptor, shown schematically in Figure 4.37.[163] Because P3HT only harvests photons with wavelengths below 650 nm, much work is going on in this area to extend the wavelength cover. Recently improvements in efficiency to 5–6% have been claimed using a condensation polymer of an ester-substituted 2,5-dibromothieno[3,4-b]thiophene and dialkoxyl benzodithiophene distannane monomers as the donor and $PC_{61}BM$ as acceptor.[164]

One of the problems in constructing these types of cells is getting an intimate mixing of the fullerenes with the polymer. Improvements to this blending approach could be achieved by covalently linking the electron acceptor to an oligomeric electron donor or to the backbone of a polymer, called double-cable polymers.[165] For instance, C_{60} fullerene derivative attached to an oligophenylenevinylene unit is shown in (4.48).[166] However, to date, in spite of a great deal of research, solar-cell efficiencies are lower than the two-component mixture bulk hetero-junctions.[167] As well as fullerenes, other carbon-based donors have recently been examined, including single- and multi-walled carbon nanotubes[168] and graphenes.[169]



(4.48)
n = 0 or 1

4.8.1.3 Hybrid Solar Cells

Hybrid solar cells (HSCs) are so called because they are a mixture of inorganic and organic materials. They are constructed from nanocrystalline inorganic semi-conductors and semi-conducting organic polymers or blends as a bulk hetero-junction.[170] This composition makes them well suited for the construction of thin, flexible solar cells.

The advantages from using inorganic semi-conducting nanoparticles are as follows:[162]

- High absorption coefficients and higher photoconductivity than many organic semi-conductor materials;
- n- or p-type character of the nanocrystals can be altered by using different synthetic routes;
- Band-gap of inorganic nanoparticles is a function of nanoparticle size.

Typical conducting polymers are those used in bulk organic hetero-junctions such as polythiophenes and polyvinylenes. Inorganic semi-conducting materials that have been used include CdTe, CdS, Cd/ZnSe, TiO_2, SnO_2, PbS, $CuInS_2$ and $CuInSe_2$. To avoid recombination of the nanoparticles during processing they are often capped with ligands containing thiol or siloxane groups.[170]

There are two main ways of laying down the bulk materials for solar cells:

- Metal oxide nanoparticles and polymer are co-deposited from solution to form a blend film;
- A rigid porous metal compound (*e.g.* oxide) structure is filled with polymer.

Both methodologies have their problems. In blends their morphology and transport between nanoparticles are limitations, whilst in oxide structures performance is limited by the infiltration of polymer into the pores of the metal oxide and control of the nanostructure dimensions.[171] One method proposed for overcoming the latter difficulty is to use nanorods, as exemplified for a TiO_2/P3HT cell shown in Figure 4.38, which has a power conversion efficiency of 1.14%.[172] There is clearly a long way to go before the predicted efficiency of 10% for bulk hetero-junction cells is obtained.[173]

4.8.1.4 *Dye-sensitised Solar Cells*

The main competition to inorganic semi-conductor photovoltaics for producing solar electricity commercially is coming from photoelectrochemical devices based on dye sensitisation, called dye-sensitised solar cells (DSCs) where up to 12% efficiency has been obtained. These devices use relatively inexpensive semi-conducting materials such as titanium dioxide, zinc oxide and tin oxide. They could be classed along with hybrid cells but the difference is the need for an electrolyte in the cell. The pioneering work in this area was carried out by Tributsch and by Fujishima, who observed that a titanium dioxide electrode could be used to split water into hydrogen and oxygen.[174] Subsequently a patent was filed which described the fundamentals of dye-sensitised solar cells.[175] However, the seminal paper published in 1991 by Grätzel and co-worker was the key to turning these observations into a practical reality, and hence they are often called Grätzel cells.[176] There have been many reviews of this important area and only a selection of relevant ones from the most recent literature are given here, which should be consulted for the original papers.[177 183]

The photoactive component in these cells is a dye adsorbed chemically onto the surface of the semi-conductor *e.g.* TiO_2. When light hits this surface, the dye (S) absorbs a photon and becomes excited (S*); in this state it transfers an electron into the conduction band of TiO_2 semi-conductor (injection). Electron transport to the anode occurs *via* diffusion of electrons through the disordered network of TiO_2 nanoparticles to the glass electrode. The positively charged dye (S^+) then interacts with iodide ions in the redox mediator iodide/triiodide couple in the bulk electrolyte and is regenerated. The oxidised redox mediator I_3 is attracted to the counter-cathode electrode where it is reduced back to iodide by electron transfer, and the circuit completed *via* electron migration through the external load.

The typical dye-sensitised solar cell (DSC) is constructed as a sandwich of two conducting glass electrodes filled with a redox electrolyte. One of the electrodes, made of glass or a flexible polymer covered with a transparent conducting layer of fluorine-doped tin dioxide (FTO) or tin-doped indium oxide (ITO), is coated by screen printing a colloidal preparation of mono-dispersed TiO_2 particles to a depth of a few microns. The layer is heat treated to reduce resistivity and then soaked in a solution of the dye until a

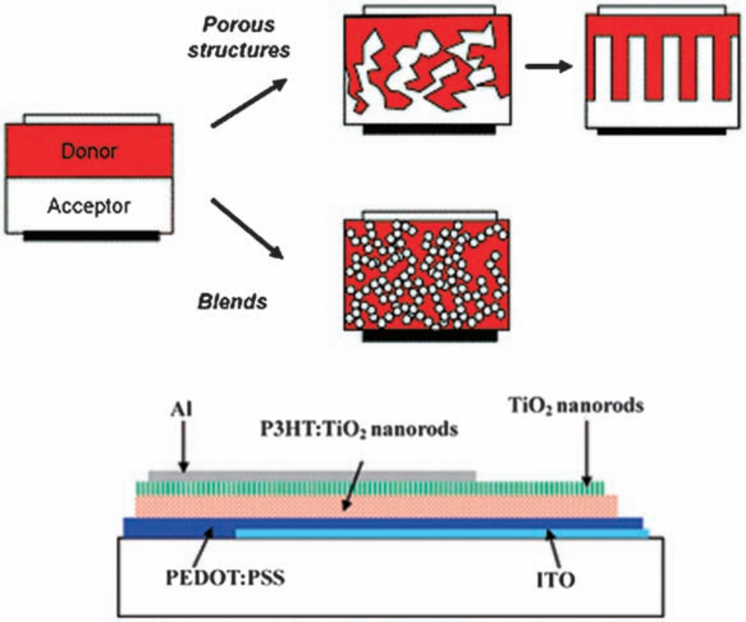


Figure 4.38 Alternatives for constructing hybrid solar cells and an example using TiO_2 nanorods.[171,172]

monomolecular dispersion of the dye on the TiO_2 is obtained. The dye-coated electrode (photoanode) is then placed next to a counter-electrode covered with a conducting oxide layer that has been "platinised", in order to catalyse the reduction of the mediator. The gap between the two electrodes is filled with an electrolyte containing the mediator, *e.g.* an iodide/triiodide couple in acetonitrile. The structure is shown schematically in Figure 4.39.

The three essential components of a DSC, which will be discussed separately, are:

- Dyes used as sensitisers;
- Semi-conducting materials;
- Electrolytes and redox couples.

Dyes – the role of the dye is to sensitise the semi-conductors *via* the incoming sunlight. Therefore ideally it should absorb over a wide range of the visible spectrum and into the NIR. Excited and ground states of the dye must be such that electron transfer from the dye to the TiO_2 occurs before decay back to the ground state of the dye. Since the cell is going to be exposed to sunlight for a long time the dye must show high stability under these conditions. Additionally the dye must bind adequately to the surface of the semi-conductor particles. To date the dyes which have proved to be the best, giving greater than 10% efficiency, are all based upon the original bipyridyl ruthenium complex known as

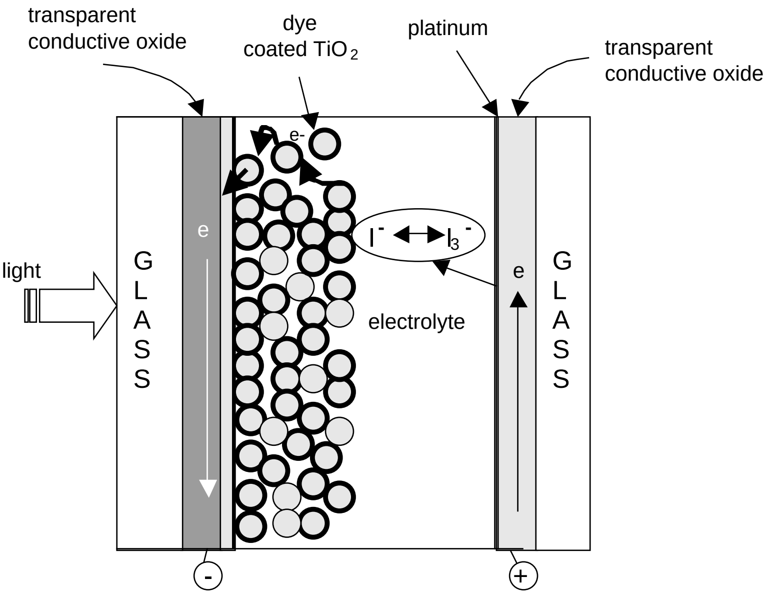


Figure 4.39 Schematic of a dye sensitised solar cell.

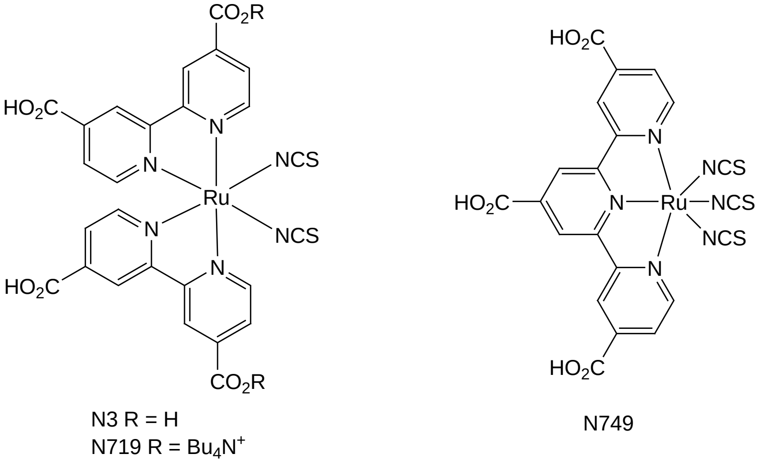
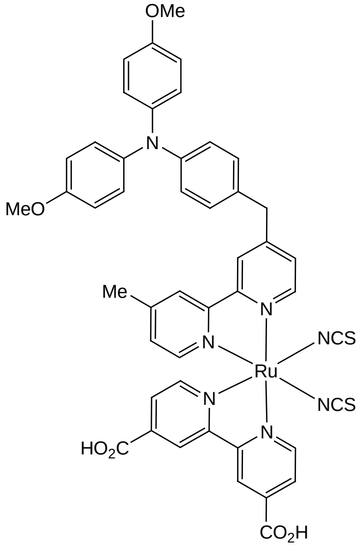


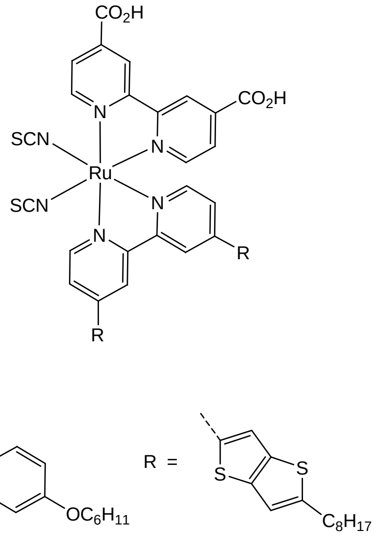
Figure 4.40 Ruthenium complexes used as dye sensitisers in DSCs.

N3, for example N719 or terpyridyls such as in the case of the so-called "black-dye" N749 (see Figure 4.40).[177]

Improving the performance of the currently favoured dyes entails several approaches.[178] One method is to enhance the charge separation in the dyes so that charge recombination is minimised, for instance by attaching triphenylamine electron donors onto the bipyridyl rings as in N845 (4.49). Another method is to look at different ways of attaching the dye to the semi-conductor using acid groups other than carboxylate, such as phosphonates, or by increasing the hydrophobicity of the dye by adding long alkyl groups to the bipyridyl moieties, the latter being coupled with extended conjugation to improve the light-gathering ability of the dyes *e.g.* K19 (4.50) and C104 (4.51). The thiocyanate groups in N719-type dyes are a source of instability and replacing these by a cyclometalated group, namely 2-phenylpyridine, is said to give dyes with much enhanced stability.[184(a)]

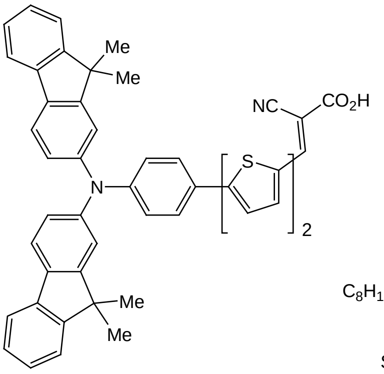


(4.49; N845)

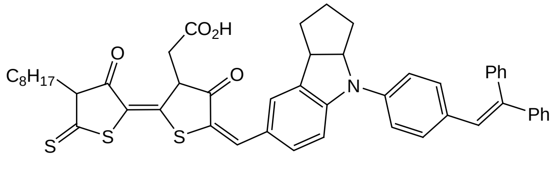


(4.50; K19) (4.51; C104)

Because ruthenium and related metals are expensive, alternatives dyes are being sought. For example zinc phthalocyanines and porphyrins have shown some promise, and more recently Cu(I) complexes with substituted bipyridyl ligands.[184(b)] However, it would be even better if metal-free alternatives could be found. Hence a whole raft of chromophores has been examined including cyanines, merocyanines, hemicyanines, anthocyanines, phthalocyanines, indolines, coumarins, xanthenes, perylenes, anthraquinones, polyenes, pentacenes and triphenylamines, which offer tuneable absorption through to the NIR and much higher extinction coefficients in the visible region. Although most show quite modest efficiencies, encouragingly 8–9% efficiency has been obtained with the triphenylamine (4.52) and indoline (4.53) based dyes.[182,185]



(4.52)



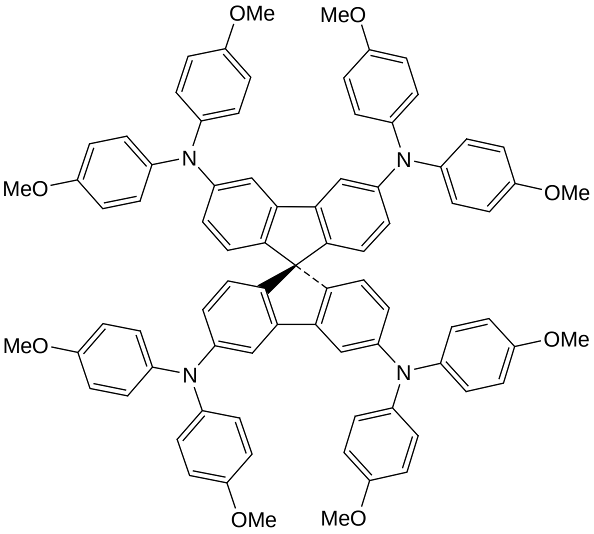
(4.53)

As mentioned in Section 4.8.1.1 quantum dots (QDs) can be used to produce excitons from photons, so they could be potential replacements for dyes in DSCs, and in fact PbS QDs have been used to inject holes into triarylamine hole conductors producing good photoelectrical properties.

Semi-conductors – although semi-conductors ZnO, SnO_2 and Nb_2O_5 have been studied, nanocrystalline mesoporous TiO_2 is still the preferred semi-conductor. It is chemically inert, non-toxic, cheap to produce and has a large internal surface area for dye loading. Crucially it absorbs light only below 388 nm and hence is transparent in important areas of the solar spectrum. Consequently it does not affect the rate at which the photoinjected electrons recombine with the dye. Research in recent years has centred on producing semi-conductors such as TiO_2 and ZnO in the newer morphological forms of nanotubes, nanowires and nanorods, which show particular promise in solvent-free electrolytes.[186 188]

Electrolytes and redox couple – the most effective redox couple used in DSC is the iodide/triiodide couple and this needs to be held in a transporting medium to form an effective electrolyte. In the original and currently favoured Grätzel type DSCs, the solvent used is drawn from alkyl nitriles, such as acetonitrile and valeronitrile or mixtures of these products. Problems associated with the use of volatile solvents as components of the electrolytes include the need for highly efficient sealing to prevent leakage of the solvent and difficulties in the construction of the different entities on a single substrate. Therefore replacements for the traditional solvents have been sought and the three areas that have emerged are room-temperature ionic liquids, and quasi-solid-state and solid-state materials.

Ionic liquids (ILs) have negligible vapour pressure under photovoltaic operating conditions, and high conductivity and thermal stability. The development of electrolytes based on ILs has made impressive progress, the best results being obtained with mixtures of 1,3-dialkylimidazolium iodides and borocyanides which have reached 8.2% efficiency with ruthenium-based dyes, and even 7.2% with the organic dye (4.53).[189] Ideally the electrolyte should be a solid or a polymer of low mobility acting as the p-type semi-conductor layer. Use of N719 with poly(*N*-alkyl-4-vinylpyridine)iodide gave a cell with 5.6% efficiency,[190] but the best obtained using purely organic materials is 4.1% efficiency, using spiro-MeOTAD (4.54) and an indoline dye.[191]



(4.54)

4.8.1.5 Commercialisation of Organic Solar and DSCs

Several companies and organisations have expressed their intention to commercialise products based on flexible plastic solar cells but so far commercialisation has been limited. In Germany a consortium headed by Merck KGaA with industrial partners SCHOTT Solar AG (Mainz), Konarka Technologies (Nuremberg), VARTA Microbattery GmbH (Ellwangen) and institutes at the Universities of Ilmenau, Karlsruhe and Oldenburg, as well as the Center for Solar Energy and Hydrogen Research (Stuttgart) was set up in 2008 to develop flexible organic solar panels. In the US Konarka opened a factory in 2008 with the capacity to produce a gigawatt's worth of solar cells each year.[192] Although such cells are no more than 5% efficient and have relatively short lifetimes, ease of production makes their costs low enough for use in niche markets, *e.g.* for laptop recharging, energy collection in tents, umbrellas and awnings, and in transparent window tinting.

Dye-sensitised cells have shown much greater promise and commercialisation is well under way. Companies who are exploiting this technology include Greatcell and Dyesol (Switzerland), Aisin Seiki (Japan), G24 Innovations (UK), RWE (Germany), Konarka (USA) and Sustainable Technologies (Australia), now part of Dyesol. One product of particular interest is the Dyesol Living

Building Panel (DLBP), an active building product providing light, life and power to the building's skin. Dyesol are also working with Corus in Wales to produce DSCs integrated onto strip steel in a coil coating line.[193] In May 2006, Aisin Seiki announced they were developing DSC modules together with Toyota Motor Company for use in vehicles, on a time scale said to be 4–5 years. These companies have already produced large-scale panels ($2.25 \times 2.4\,\mathrm{m}$) for a $22.5\,\mathrm{m}^2$ façade of a "dream house". Interestingly they observed that these panels gave a faster rise in electricity generation than a conventional Si cell in the morning, and a slower fall in the afternoon, mainly due to a different dependence of electricity generation on the solar insolation angle. Toyota also produced leaf-shaped plants in three different colours that generated electricity, suggesting other aesthetic uses for DSCs.[194] G24i based in Cardiff, South Wales, began producing dye-sensitised thin film in 2007 and has commercialised products designed to be used to directly charge mobile phones or batteries, in multiple adapters allowing phone charging in areas where there is no electricity, and on the back of garments, for instance those used in the field by the military.[195]

4.8.1.6 Solar Concentrators

The solar mirrors used for concentrating sunlight described in Section 4.8.1 are expensive to construct and maintain. They are of no value as solar concentrators for photovoltaic cells because of the excessive heat, and it is necessary to use individual lenses above the surface of the cells, again adding to the cost, and there are again problems with heat. An alternative is to use luminescent solar concentrators, systems which have been known since the 1970s.[196] These consist of a dye dispersed in a transparent waveguide. The dye absorbs incident light and then remits it into the waveguide mode. The energy difference between absorption and emission prevents reabsorption of light by the dye, isolating the concentrated photon population in the waveguide. This means that high optical concentrations can be obtained without the need for the device to track the sun, but there are limitations caused by self-absorption losses that restrict the maximum possible concentration that can be obtained.

Recently a variant on these luminescent solar concentrators was devised, called by the inventors organic solar concentrators, for which high efficiency was claimed.[197] The system uses collectors made of dyes coated onto sheets of glass. Two of these collectors are used in tandem, one with a dye absorbing at short wavelengths and the other at longer wavelengths. Incident solar radiation first encounters an organic solar collector employing a short-wavelength dye. Longer-wavelength light is transmitted through the first OSC and absorbed by a longer-wavelength dye in a second organic solar collector (Figure 4.41). In the demonstration organic solar collector the emitter was a dicyanomethine dye dissolved in the host material, tris(8-hydroxyquinoline)aluminium (Alq_3), and the terminal absorber a platinum mesophenylbenzporphyrin and/or rubrene (Figure 4.41). A tandem cell using these components was able to raise the efficiency of a CdTe photovoltaic cell from 9.6 to 11.9%.

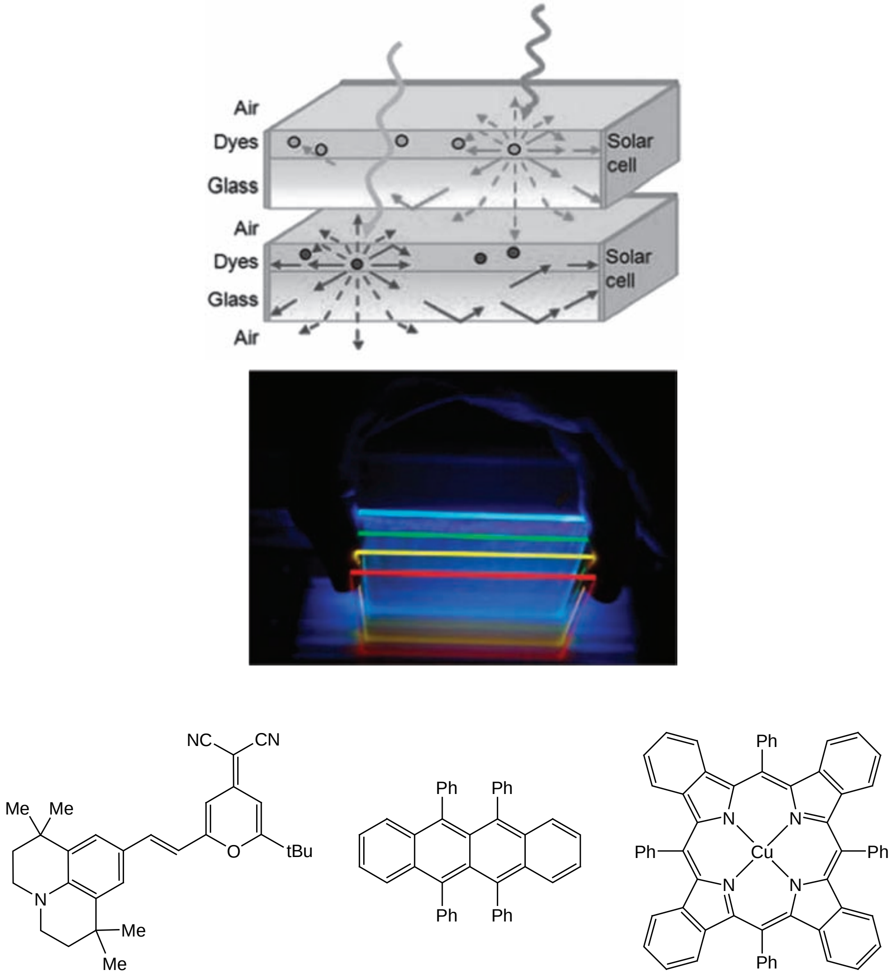


Figure 4.41 Organic solar cell concentrator and dyes used[197] (reproduced with per mission of The American Association for the Advancement of Science).

4.8.2 Artificial Photosynthesis

Photosynthesis, the process by which plants and other organisms use solar energy to convert water and carbon dioxide into complex energy-rich chemicals, the carbohydrates and oxygen, is essential to life on this planet. We now have a greater understanding of how this process works and hence we should be able to construct processes that mimic Nature to our advantage.

In Nature the process of photosynthesis takes place within sub-cellular structures called *chloroplasts*. These are plate-like structures of around 4–10 µm in diameter and 1 µm in thickness, containing the green discs of the *thylakoids*. In all oxygen-producing organisms, the thylakoids have a double membrane, which hold the photosynthetic pigments that drive a series of electron transfer reactions. There are two reactions in the photosynthetic process: the "light" reaction which captures and stores energy from light, and the non-photochemical dark reactions which use this energy to convert carbon dioxide from the air into carbohydrates, a process which is carried out in the colourless *stroma* region of the chloroplast.[198]

The light reaction consists of two photosystems, PS I and PS II. The water-splitting and oxygen-evolution processes occur in the PS II complex. Activation of the light-reactive centre in chlorophyll causes an electron to be pulled from a nearby tyrosine amino acid in the surrounding protein. This then obtains an electron from water, splitting it into H^+ and OH , the latter then being oxidised to oxygen. From this system the electrons flow *via* plastoquinones to another membrane-protein complex, the cytochrome b_6f complex to the PS I. The PS I also catalyses light-induced charge separation, similar to PS II, harvesting light *via* a chlorophyll reaction centre. The electrons are transferred to NADP (nicotinamide adenosine dinucleotide phosphate) reducing it to NADPH, which is the electron source for the dark reactions of carbon fixing. Overall electron transfer through PS I and PS II results in water oxidation, producing oxygen, and NADP reduction, with the energy provided by light (2 quanta per electron). The electron flow from water to NADP is coupled to the pumping of protons across the membrane, which is used for the synthesis of adenosine triphosphate (ATP). ATP and NADH are used for CO_2 fixation in the dark, forming glucose *via* a recyclable process to NADP and ATP, the energy motor. The active light centre in PS I is chlorophyll a, and in PS II both chlorophyll a and chlorophyll b are present. These two chlorophylls allow the photosystems to collect light over a wider range of wavelengths.[199] The process is summarised in Figure 4.42.

Research into artificial photosynthesis is being driven by the desire to understand, and then mimic, the following features of natural photosynthesis.[200]

- Absorption of sunlight by light-harvesting antennae;
- Reaction centre for charge separation where light energy is converted into electrochemical potential energy;
- Transmembrane pumping and transport.

4.8.2.1 Artificial Light-harvesting Antennae

There is a variety of photosynthetic pigments, based on chlorophyll, carotenoids and phycobilins, that are bound to proteins in plants and algae. Large numbers (100–5000) of these pigment molecules act together in the form of an "antennae" to harvest light, allowing light to be collected outside the normal range of the chlorophyll antenna. They are remarkably efficient in transferring light energy, through non-radiative excitation transfer, to chlorophyll, facilitating the maintenance of a high rate of energy transfer to the reaction centre, even under light of lower intensity. Therefore any artificial system needs to be able to mimic this light-harvesting activity.

The best understood of the light-harvesting antennae in Nature are those in photosynthetic purple bacteria and hence they have become the model for

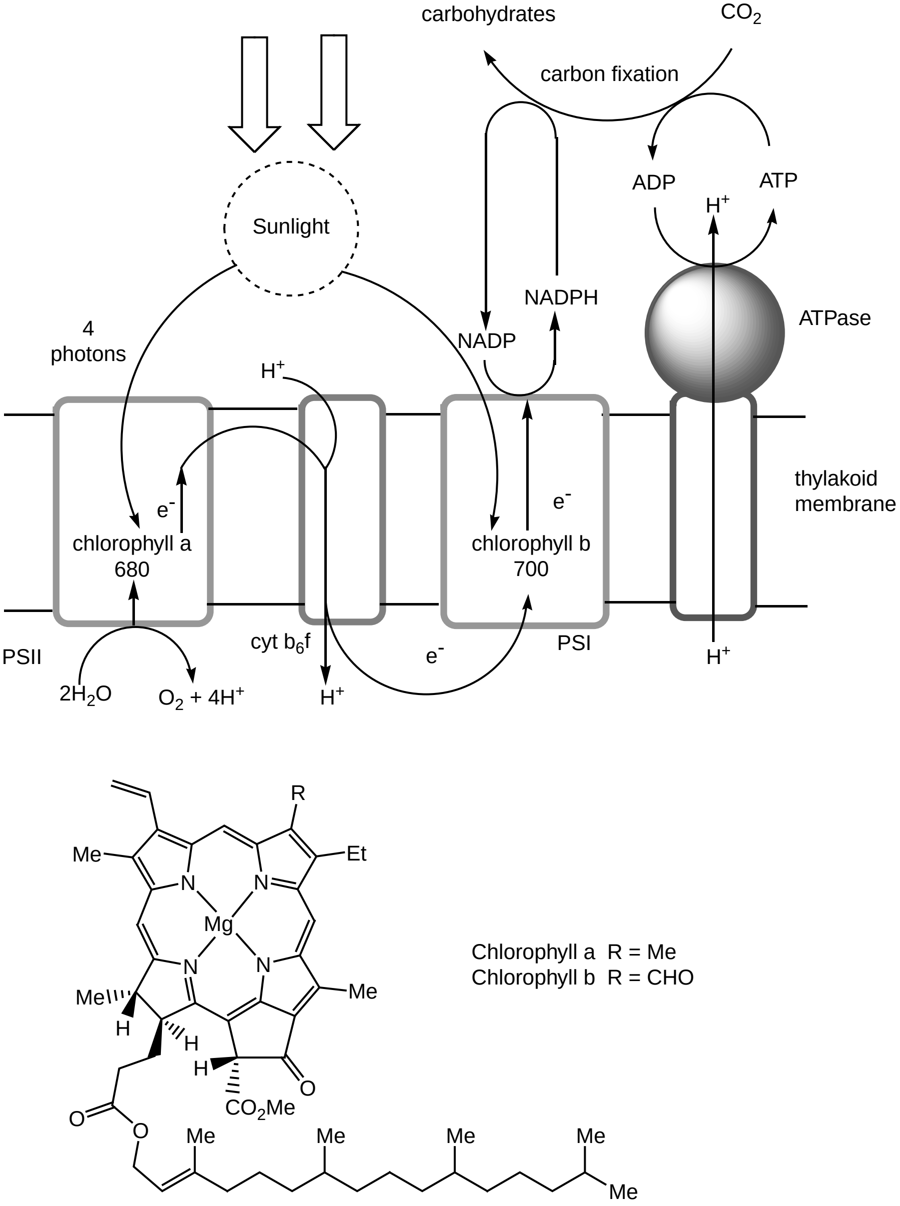


Figure 4.42 Schematic for mechanism of photosynthesis.

attempts to mimic Nature.[201] In these bacteria arrays of bacteriochlorophylls and carotenoid chromophores absorb light in the visible and NIR regions. The complex is composed of two rings of bacteriochlorophyll in a highly symmetric wheel-like supermolecular architecture. For instance in *Rhodopseudomonas*

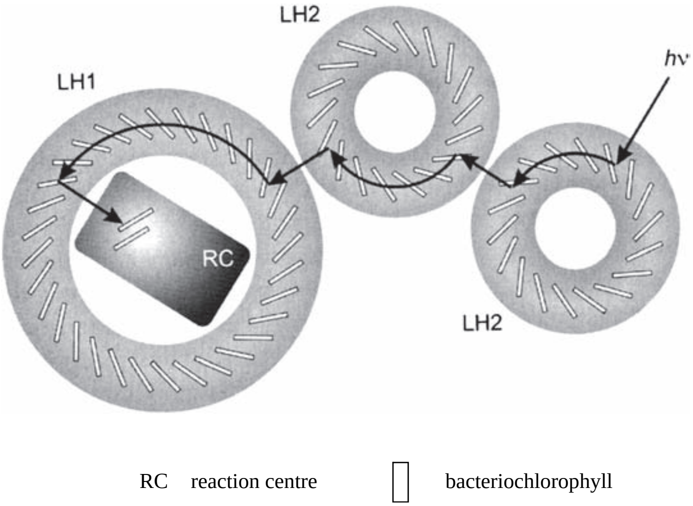


Figure 4.43 Schematic of the light harvesting antenna in purple bacteria[202] (reproduced with permission of Wiley VCH).

acidophila the core antenna (LH1) is a structure made up of 18 bacteriochlorophyll molecules (called B850) and an outer antenna (LH2) of 9 such molecules (B800). This is shown schematically in Figure 4.43.[202]

Carotenoids are also associated with these structures, contributing to light harvesting and acting as singlet O_2 quenchers arising from photosensitisation.

The obvious starting point for mimicking the natural light-harvesting antenna is to construct arrays of porphyrins and a great deal of work has been done in this area using both covalent and self-assembling methodologies.[203 205] These arrays have been arranged in four basic formats: ring-shaped, star-shaped, windmill-shaped and dendritic scaffolds. The latter seem to offer the best direction for developing artificial antennae based on porphyrins, an example of which is shown in Figure 4.44.[203]

Other examples of the dendrimer approach include arrays of ruthenium and osmium complexes of polypyridines, arrays containing entities which can be used for frequency up-conversion and two-photon absorption, and a variety of self-assembled host-guest systems.[206] An example of the latter is the ionic fluorescent dye associated with a dendritic *p*-phenylenevinylene network, shown in Figure 4.45.[207] Other self-assembling systems include the encapsulation of chromophores in zeolite crystals[208] or cyclodextrins,[209] hydrogen-bonded supramolecular assemblies[210] and organogels.[211]

4.8.2.2 Artificial Reaction Centres

In Nature the reaction centre's function in photosynthesis is to convert light energy into chemical energy so that it can be transported, stored and then used

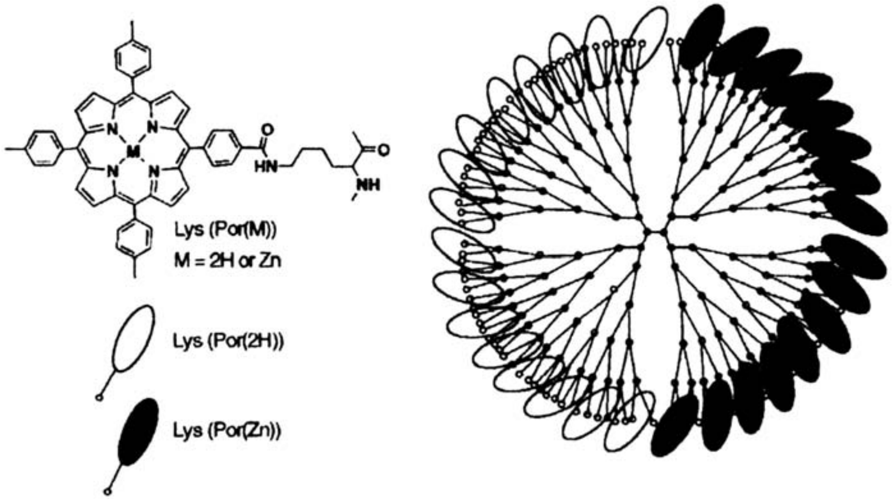


Figure 4.44 Light harvesting antenna based on a porphyrin dendrimer[203] (repro duced with permission of Wiley VCH).

in the chemical processes that support the life of the organism. The chlorophyll chromophores in plants are able to handle high-energy electrons and donate them to acceptors, other chlorophylls or plastoquinones (lipid-soluble benzoquinones). A protein matrix, which governs the electronic coupling between the donor and acceptor, is also the medium within which electron transfer takes place. Therefore any artificial reaction centre needs, as a minimum, to have the following features:

- Chromophore that can absorb light and can act as a donor;
- An electron acceptor;
- Organisation principle that controls electronic interaction between donor and acceptor and hence the rate and yield of electron transfer;
- Long-lived charge separation between acceptor and donor.

The simplest artificial reaction centre is one where an electron-donating chromophore is electronically coupled to an electron acceptor, where the chromophore absorbs strongly in the visible region. One way of creating systems with a long-lived charge separation, as experienced in the protein matrix, is to create a physical environment where the donor and acceptor are spatially separated by a long molecular distance. The most common way has been to have a porphyrin donor covalently bonded to an electron acceptor such as a quinone or a fullerene as a dyad, or extended into triads and tetrads, for instance, by using a dendrimer with the donor at its centre and acceptors way out on the periphery. Another way is to make a photoexcitable chromophore that is flanked on either side by an electron donor and an acceptor. For

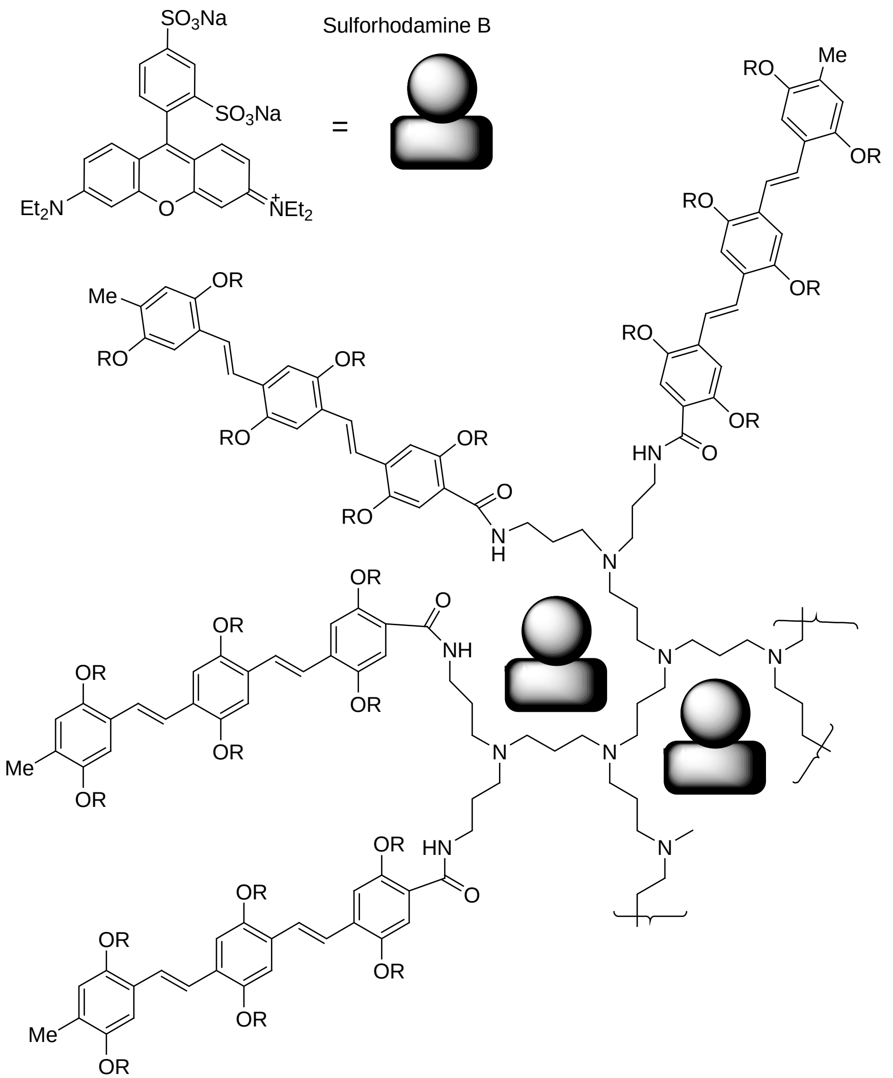


Figure 4.45 Partial structure of light harvesting host guest dendrimer.

example, the carotene-porphyrin-quinone triad which has a porphyrin acting as both a light acceptor and a charge separator, causes a two-step electron transfer from the carotenoid moiety on one side to a quinone on the other side.[201]

4.8.2.3 Artificial Reaction Centre-Antenna Couples

Combining the two activities of light harvesting from an antenna and charge separation of the acceptor–donor in the reaction centre is essential for progress

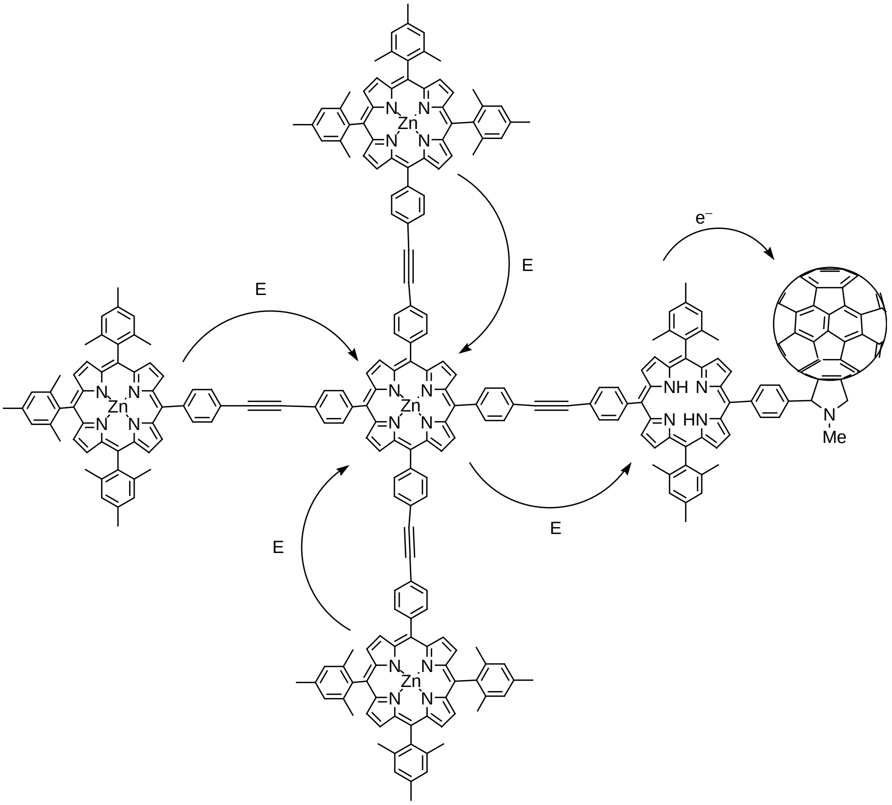


Figure 4.46 Artificial antenna reaction centre complex; four Zn porphyrins in antenna and metal free porphyrin linked to fullerene as the reaction centre.

in artificial photosynthesis. Many structures have been devised in attempts to perform these functions. An example is the hexad in Figure 4.46. Excitation of the peripheral Zn porphyrins leads to singlet–singlet energy transfer to the central Zn porphyrin. Energy then migrates to the metal-free porphyrin, followed by very rapid electron transfer from the excited state to the fullerene unit. In this case the lifetime of the charge-separated state is 1.3 ns.[201]

4.8.2.4 Transmembrane Pumping

The electrochemical potential energy generated by the reaction centre is used by photosynthetic bacteria to power the translocation of hydrogen ions across the membrane, a goal which must be met by artificial photosynthetic production of biologically useful energy. Moore and Gust have used the CPQ triad mentioned above, together with a second lipid-soluble quinone, placed inside an artificial phospholipid membrane vesicle, to light-drive a proton pump and hence drive the synthesis of ATP.[212] The process is shown diagrammatically in Figure 4.47.

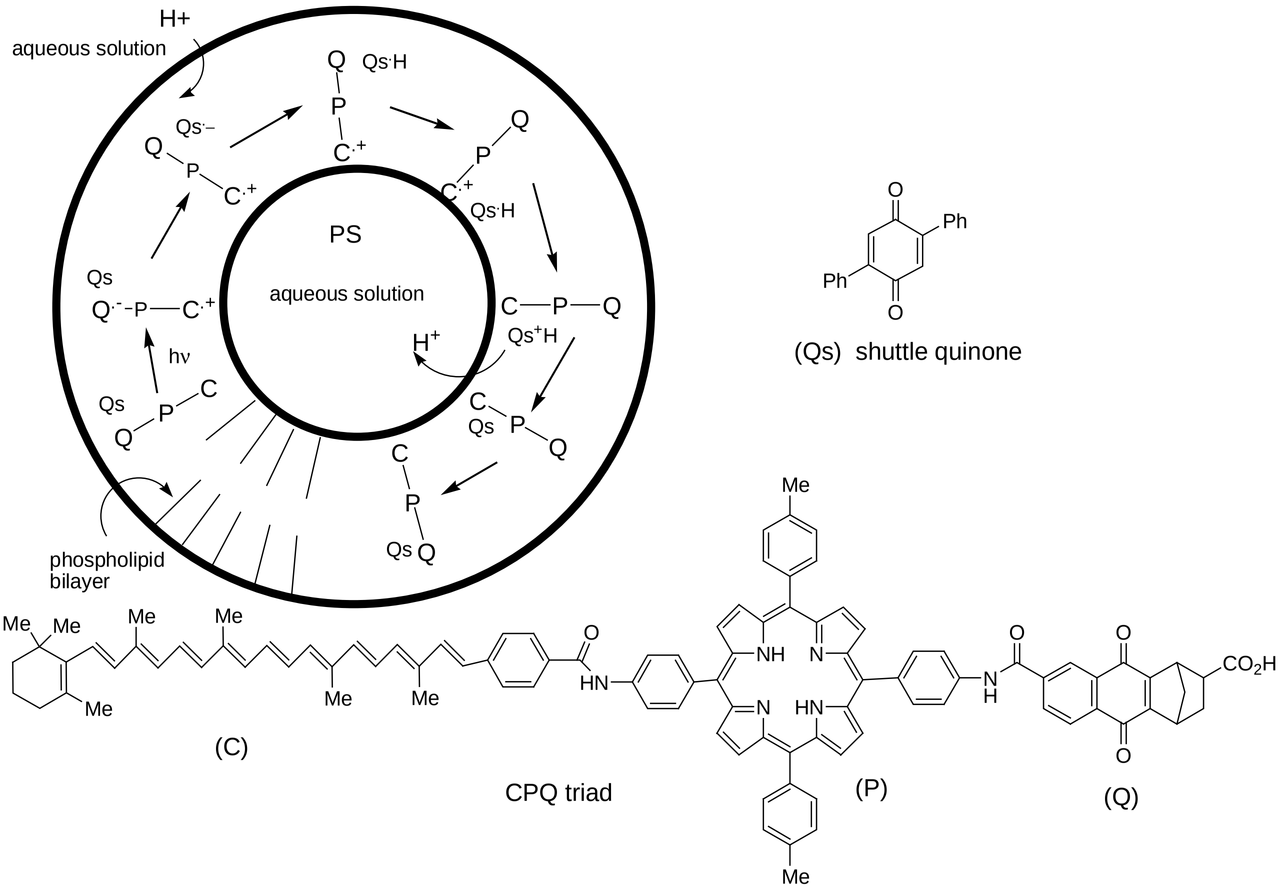


Figure 4.47 Light-driven proton pump using a donor–chromophore–acceptor triad and quinone proton transporter across a phospholipid bilayer membrane.

Whilst these approaches are extremely interesting scientifically, and demonstrate that mimics of photosynthesis can be constructed, to be of any real commercial value in solar energy utilisation the stability of the systems must advance by orders of magnitude and will involve much new research.

4.8.3 The Production of Useful Chemicals and Fuels

Solar energy is only available during the daytime and hence a storage method is required for the converted energy produced during this period. The most obvious method is to store it in the form of fuels for later use. One option for carrying this out is to mimic aspects of the important photosynthetic processes, for instance, by producing useful organic chemicals by the controlled reduction of carbon dioxide. The carbohydrates and other organic compounds formed by this process are then available for bioconversion into alcohols or other substituted hydrocarbons. However, in terms of producing fuels directly the splitting of water into hydrogen and oxygen using solar energy is probably the most attractive. This is the basic step in the so-called "hydrogen economy". The hydrogen produced can be used as an energy source for fuel cells. Coupling the water splitting reaction with the reduction of carbon dioxide to produce methane as a fuel is an extremely attractive option, since the burning of methane using oxygen produces no more than the amount of carbon dioxide used initially, therefore not adding to the environmental load.

4.8.3.1 Water Reduction/Splitting

Economically any system for producing hydrogen from water by either reduction or splitting must in the short term compete with the current process of producing hydrogen chemically from coal or natural gas. The economics are extremely tight and once again the initial driving force for the implementation of water splitting will be environmental rather than commercial, because using hydrogen as a fuel only produces water and no CO_2. There are four main ways of producing solar hydrogen:

- Direct, indirect and hybrid solar thermal processes;
- Electrolysis of water using a solar cell; hydroelectric power generation, *etc.*;
- Photocatalytic or photoelectrochemical water splitting (artificial photosynthesis);
- Reforming of biomass.

Many of the systems studied under these headings are largely outside the scope of this book, *e.g.* solar thermal and those using nanostructured metal oxides.[213,214] One approach is to use conventional photovoltaic cells in tandem with an electrolyser,[215] for instance a conventional electrolyser, or one comprising a metal oxide photoanode such as WO_3 and a platinum electrode in the electrolyte system.[216] However, the cost of the photovoltaic cells makes this approach, even at the 12% levels of efficiency, uncompetitive currently with the fossil-fuel route.

In this book we are mainly interested in those processes that use chromophores or light energy absorbers in the sensitised or direct production of solar hydrogen under visible light and NIR illumination. In this context the use of dye-sensitised solar cells may offer a way around the cost issue. Grätzel has used these, again in conjunction with a tungsten oxide photoelectrode, to split water. The process involves absorption of blue light by the nanocrystalline tungsten oxide photoelectrode, causing band-gap excitation and the oxidation of water to oxygen. The band-gap electron is then transferred to the titanium dioxide electrode sensitised with a ruthenium dye (see Section 4.8.1.4), where the absorption of a second photon, from green and red light, generates a photovoltage that flows back to the other cell causing reduction of hydrogen ions to hydrogen.[217] To date, the overall efficiency reported is around 4%. The target efficiency of such cells of 10% has not yet been achieved. The use of platinum electrodes is also costly and water splitting without the necessity for an electrolyser would be the ideal option.

Production of hydrogen by the reduction of aqueous protons can be achieved using a variety of means, for example CdS quantum dots in glasses[218] and CdS nanocomposites of $Ni/NiO/KNbO_3$,[219] using light irradiation at 400–420 nm in the presence of electron donors or electron shuttles *e.g.* methyl viologen. Several Ru and Pt complexes of bi- and terpyridines have been used to produce hydrogen, but again a sacrificial electron donor, such as an alkanolamine or EDTA is required. Another recent example is a homogeneous photocatalyst containing rhenium light absorbers (LAs) and a rhodium electron collector (EC) for H_2 production when excited with visible light (470 nm) in the presence of dimethylaniline as electron donor.[220] Working on a narrow wavelength region and the need for sacrificial donors raises questions over the commercial applications of such methods in the production of solar hydrogen.

One very interesting proposal is to mimic Nature's use of proton motive force in key biological half-reactions, but in the absence of biological transducers such as flagella and ATP synthase. An example is water splitting using a cell designed for this purpose, as shown in Figure 4.48.[221] "Blue" photons from sunlight are absorbed by a photoanode, such as WO_3 or a dye-sensitised semi-conductor, driving charge separation which is coupled to water oxidation catalysts producing O_2 and H^+. "Red" photons pass through the initial blue absorber, and are absorbed by photosynthetic proton-pumps embedded in an ion-impermeable membrane separating the two solutions. Provided that the proton "current" is greater than the electrical current, this device generates ΔpH, thereby reducing the voltage required for the overall water-splitting reaction. Electrons would migrate toward the back-contact of this photoanode, and then through an external circuit to a cathode, driving the electroreduction of H^+ and the production of H_2 in the other half of the cell. The type of products that could be used in this process can be classified as biohybrids.

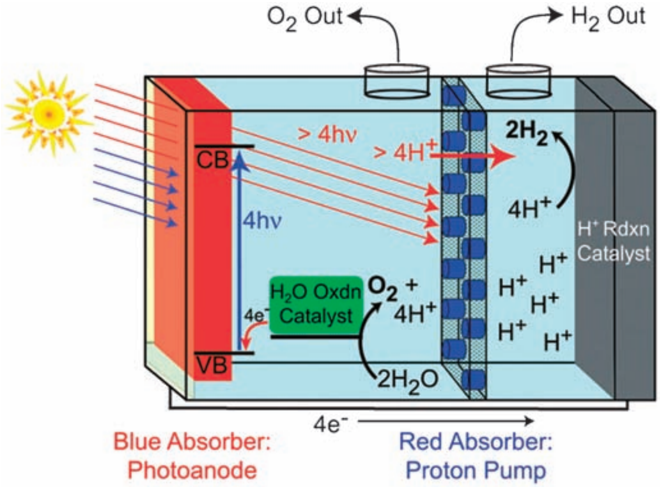


Figure 4.48 A schematic drawing of the proposed dual photosystem device.[221]

4.8.3.2 Carbon Dioxide Photoreduction

The production of useful chemicals by the photoreduction of CO_2 has long been recognised as an outstanding goal, but research remains at the feasibility or demonstration stage.

Much of the work on the photoreduction of carbon dioxide has centred on the use of transition metal catalysts to produce formic acid and carbon monoxide. A large number of these catalysts are metalloporphyrins and phthalocyanines. These include cobalt porphyrins and iron porphyrins, in which the metal in the porphyrin is first of all photochemically reduced from M(II) to M(0), the latter reacting rapidly with CO_2 to produce formic acid and CO.[222] Because the M(0) oxidises in the process to M(II) the process is catalytic with high percentage conversion rates. However, there is a problem with light-energy conversion and the major issue of porphyrin stability.

A more attractive process is to convert CO_2 into CH_3OH, which is a very useful fuel, a process that can be carried out photocatalytically using noble-metal-coated TiO_2 nanoparticles. Alternatively the reaction of CO_2 with alkanes to give alcohols and CO is a target. The development of practical solar-light-driven processes for CO_2 reduction will require much further work.

4.8.3.3 Photobiological Processes

One obvious approach to producing useful chemicals using solar energy is to let Nature carry out the essential steps. The main photosynthetic organisms are the prokaryotic bacteria, and eukaryotic algae and plants. The photosynthetic bacteria can be split into those that do not produce oxygen as by-product (non-oxygenic), *e.g.* purple bacteria, and those that do (oxygenic), *e.g.*

cyanobacteria. These bacteria and algae can be used to produce hydrogen from water or to convert CO_2 into carbohydrates, the latter as biomass for use as a fuel or as a chemical feedstock.

Algae are a very large group ($>$30,000) of eukaryotic organisms, most of which contain pigments that are used in photosynthesis, and in aquatic habitats are the dominant photosynthetic life forms. Green algae (chlorophytes) are the most widely studied, and like plants use chlorophyll a and chlorophyll b as the photopigments.[198(b)] Work on their use as producers of fuel chemicals, both hydrogen and CO_2 reduction products, on a commercial scale is now well advanced. It has been estimated that algae can produce between 6 and 10 times more energy per hectare than conventional crop-based biofuels. They can be sited anywhere there is a plentiful water supply, even saline, and a rich carbon dioxide source and a nutrient supply. Although they can operate at 100% photon utilisation efficiency this is not the case in direct sunlight where the utilisation is rather poor. This is because the rate of photon absorption by the photopigments *via* the antennae is greater than the rate at which they can be used, so that up to 80% of the photons are lost as heat. Consequently in high-density mass culture the surface algae absorb too much energy whilst the lower layers do not get enough, necessitating their use in shallow pond-like structures. One way round this problem is to bioengineer the chlorophyll antennae in the photosystems so that each algal cell has a lower probability of absorbing sunlight, thus allowing deeper penetration into the mass culture.[223]

Some of the companies involved in green algae technology as of 2009 include Sapphire Energy and Greenfield Technologies in the US, and Seambiotic in Israel.[224] They are using carbon dioxide from a variety of sources including industrial emissions from coal-fired generators, cement works, fermentors or geothermal sources.

In terms of producing hydrogen, green algae and cyanobacteria (hydrogenase based), which are photochemically active over the range 400–700 nm, are the most efficient organisms with an estimated maximum light efficiency of 10–13%, whilst purple bacteria, which absorb 400–600 nm and 800–1010 nm are estimated at 6%, but in practice neither of these efficiencies are achieved as discussed in the previous paragraph.[225] Fermentation of biomass is another way of producing hydrogen but this also has a problem, the relatively low theoretical molar yield of $4H_2$/glucose.

Because of these problems methods for using photosynthetic algae and bacteria in conjunction with biomass fermentation have been proposed, for instance the three-component system illustrated in Figure 4.49. The cyanobacteria operating at 400–700 nm utilise 45% of the solar energy whilst the photosynthetic bacteria add another 25% from light at 400–600 and 800–1000 nm, thus increasing the overall efficiency. The role of the photobioreactors is to produce H_2, using both oxygenic and non-oxygenic photosynthesis, and to accumulate cell biomass.[225]

There is now little doubt that the photobiological production of useful chemicals using sunlight as the energy source is an area where many commercial developments will take place in the coming years.

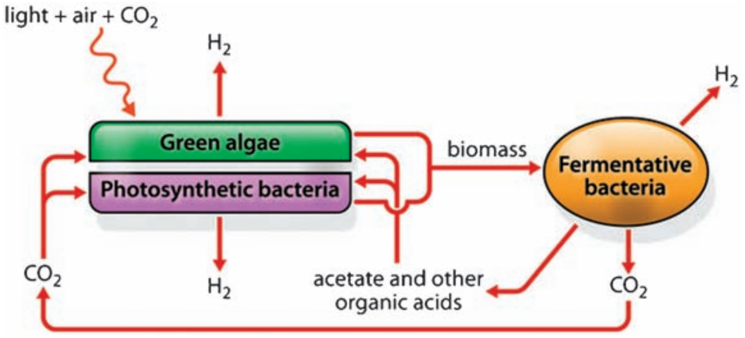


Figure 4.49 Three component integrated biological system for H_2 production.[225]

4.9 Conversion of Light into Kinetic Energy

Although in the plants light is predominantly used to produce chemicals which fuel the growth of the plant, there are other processes in which it is used to initiate directional movement, the best known of which are phototropism, which involves directional growth *via* light stimulation, especially by blue light, and heliotropism, the diurnal movement of plants in response to the direction of the sun. In these cases light interacts with photoreceptors in the plant initiating a cascade of reactions which lead to changes in osmotic pressure in the cells on one side of the plant, causing their swelling or elongation and hence directional movement.

Mimicking Nature's ability to cause movement in bulk materials using light energy has been the source of increasing interest to scientists in recent years. A large proportion of this research involves the interaction of light with photoswitchable groups, especially the isomerisation of the azo group in polymers.[226] This type of photomechanical effect can be utilised in valuable ways: in photochromic switches and optical memories (see Chapter 1) and in polymeric liquid crystals and holographic gratings (see Chapter 5).

In this section discussion will concentrate on the utilisation of light to create kinetic energy and hence movement, often in conjunction with another stimulus such as heat, in what can be considered to be molecular or nanoscale tools, machines and motors. There is so much exploratory work going on in this area that the selection given below is only intended to be indicative of the directions the research is taking.[227 230]

Machine-device type activities resulting from a defined light energy input, either UV and/or visible light, can be categorised as follows:

- Devices involving assembly and disassembly;
  - Tweezers and harpoons
  - Pedals
  - Locks
- Directional movement;

  - Rotators
- Linear movements;
  - Threads and shuttles
  - Pumps and pistons

Assembly and Disassembly. Photoinduced interactions in molecules specially constructed so that they can act as molecular-scale tools, such as tweezers or harpoons for capturing or enclosing other molecules *e.g*. metal ions, is an active area of research. The classic early example is the *cis-trans* isomerisation of the azo bridge in the crown ether shown in Figure 4.50, originally described as "butterfly wings" (see also Chapter 1, Section 1.2.7.1).[231] Later examples include the use of the photochromic behaviour of diarylethenes to effect the tweezers activity (see also Chapter 1, Section 1.2.6). Such tweezers have been utilised to carry out ion transport through membranes, and in drug delivery where the payload is released by light.

Isomerisation of the azo group has also been used to devise complex molecular assemblies that can perform the function of hinges and light-powered molecular pedals.[232,233] Forming molecular structures that can act as a device or tool by self-assembly has yielded interesting results. For instance a platinum complex can act as a molecular lock in a ring as illustrated in Figure 4.51. Irradiating the complex causes the otherwise stable Pt(II)-pyridyl bond to ring open, which then undergoes quantitative catenation with another molecule in aqueous solution. Unlocking is achieved by irradiation of the rings in a MeCN/MeOH mixture.[234]

Directional movement. To build molecular rotary motors the following criteria need to be satisfied;

- Rotation must be repetitive and 360°;
- Energy must be consumed;
- There must be control over directionality.

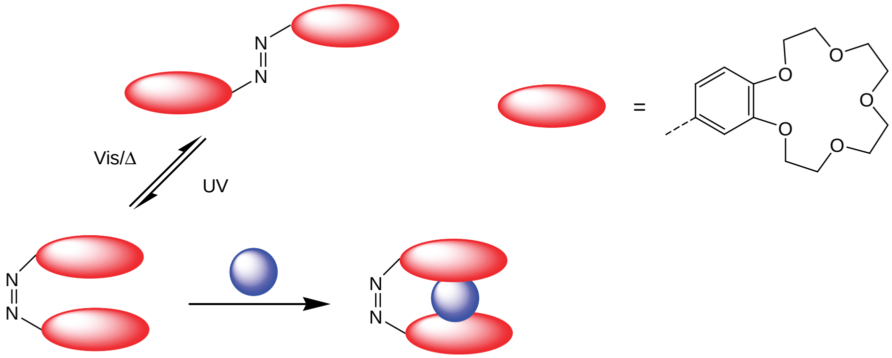


Figure 4.50 Light activated molecular tweezers.

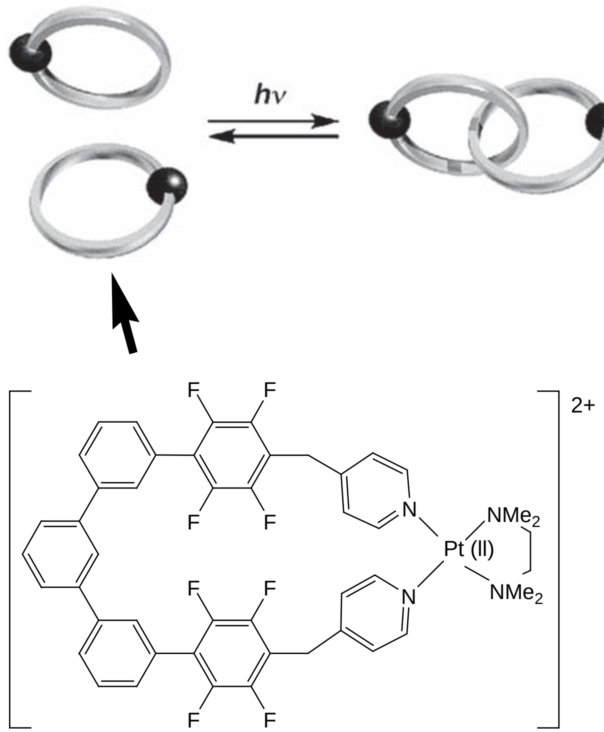


Figure 4.51 Photoswitchable molecular lock.

Feringa and co-workers have shown that using light to cause *cis-trans* isomerisation in overcrowded alkenes is an effective way to achieve motor-like rotation. Development of prototypes, based on a rotary cycle of sequential photochemical and thermal steps in such molecular structures has led to rapid increases in the rate of their rotation, such that the latest structures can operate at 44 rotations per second (Figure 4.52). The landmark objective to attain the speed of Nature's rotary motor, F1-ATPase, which is capable of 130 rotations per second, is now within sight.[235]

Linear Movement. This area of research is dominated by rotaxanes, which are supramolecular species composed of a macrocycle encircling a dumbbell-shaped rod or shaft (see also Chapter 2, Section 2.6.1).[236] In these molecular systems the ring component either rotates or shuttles reversibly between stations on the shaft, being controlled by a variety of stimuli including light, but physically constrained by the stoppers at the end of the shaft.[237] Of particular interest to the scope of this book is where the geometrical photoisomerisation of azobenzenes and stilbenes is used to control the shuttling of the macrocyclic component, for instance cyclodextrin (CD) or the macrocyclic amine cucurbit[6 or7]uril, along the shafts. One such example is shown in Figure 4.53. Here the macrocycle is α–CD and the shaft an azobenzene linked to a stilbene moiety,

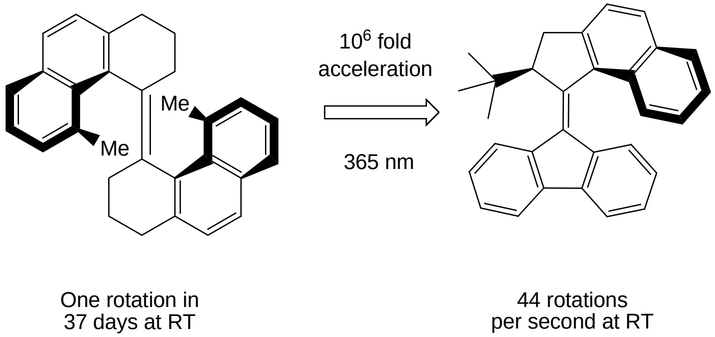


Figure 4.52 Rate of light activated rotation in a molecular motor.

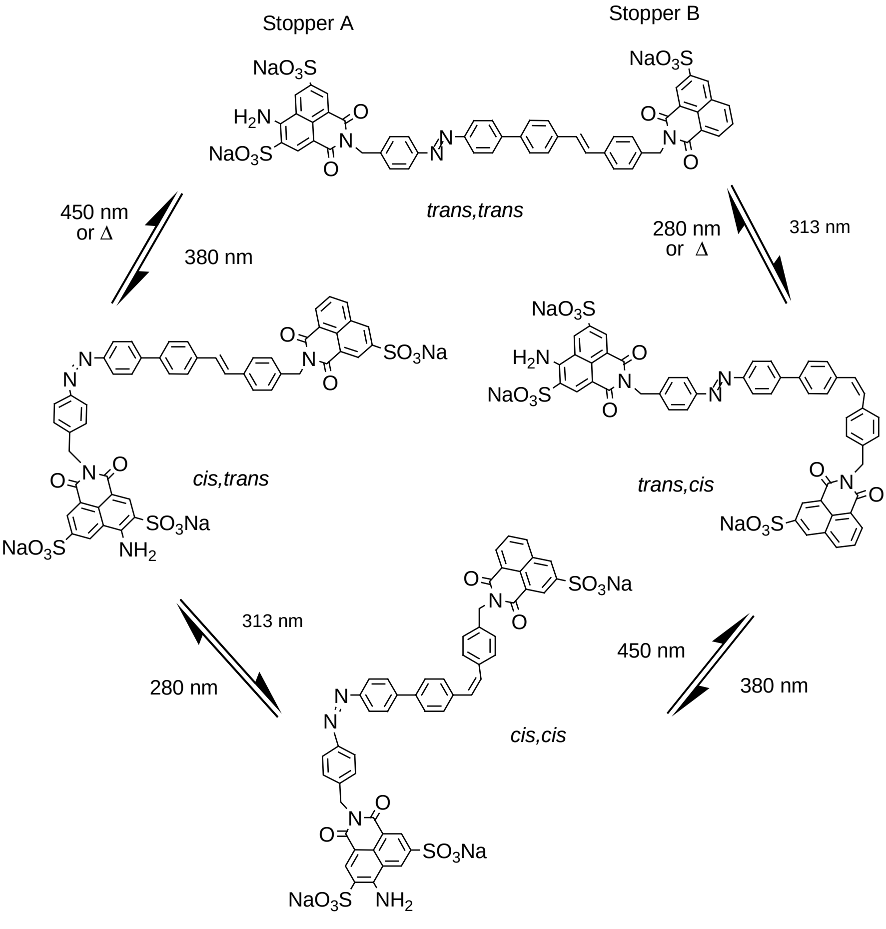


Figure 4.53 Rotaxane linear motor of cyclodextrin on an azobenzene stilbene shaft.

the stoppers being two different naphthalimide fluorescent molecular units. Isomerisation of the azobenzene and stilbene units is accomplished by treating with different wavelengths of UV/visible light, giving four possible stations for the α–CD unit to come to rest. Each movement is fully reversible by a change of irradiating wavelength of light. As the α–CD approaches either of the fluorescent stopper groups the emission spectrum changes and hence can be used as a marker.[238] Functionalising cyclodextrin so that it can act as an anchor for the movement of attached molecular units has also been employed, for instance to make what is in effect the cylinder and piston, respectively, of a molecular pump.[239]

This whole field represents next-generation technology and as such it is unlikely that any large-scale technological applications will arise in the very near future. A few of these structures are finding potential applications as switches, sensors and in manipulating microscopic particles, and some structures have also been suggested as components of machines to be used in lab-on-a-chip devices. As with all leading-edge research the options are only limited by the researcher's ability to see how blue is the sky.

References

1. P. Suppan, *Chemistry and Light*, Royal Society of Chemistry, Cambridge, UK, 1994.
2. J. Griffiths, in *Modern Colorants: Synthesis and Structure*, ed. A. T. Peters and H. S. Freeman, Blackie Academic, London, 1995, pp. 40–62.
3. S. Doehne, U. Resch-Genger and O. S. Wolfbeis (ed.), *Near Infrared Dyes for High Technology Applications*, Springer, Berlin, 1998.
4. M. Matsuoka, *Infrared Absorbing Dyes*, Plenum, New York, 1990.
5. M. Matsuoka, *Absorption Spectra of Dyes for Diode Laser*, Bunshin, Tokyo, 1990.
6. J. Fabian, H. Kakazumi and M. Matsuoka, *Chem. Rev*, 1992, **92**, 1197.
7. www.hwsands.com.
8. www.adsdyes.com.
9. www.epolin.com.
10. www.exciton.com.
11. www.fujifilmic.com.
12. L. Strekowski (ed.), *Heterocyclic Polymethine Dyes, Topics in Heterocyclic Chemistry*, **14**, Springer, Berlin, 2008.
13. S. Doehne and M. L. Dekhtyar, in *Near Infrared Dyes for High Technology Applications*, ed. S. Doehne, U. Resch-Genger and O. S. Wolfbeis, Springer, Berlin, 1998, pp. 327–362.
14. A. L. Tolmachev, Y. L. Slominskii and A. A. Ishchenko, in *Near Infrared Dyes for High Technology Applications*, ed. S. Doehne, U. Resch-Genger and O. S. Wolfbeis, Springer, Berlin, 1998, pp. 385–428.

15. S. Yagi and H. Nakazumi, in *Functional Dyes*, ed. S.-H. Kim, Elsevier, Amsterdam, 2006, pp. 215–256.
16. S. Sreejith, P. Carol, P. Chithra and A. Ajayaghash, *J. Mater. Chem*, 2008, **18**, 265–274.
17. S. Yagi and H. Nakazumi, in *Heterocyclic Polymethine Dyes Topics in Heterocyclic Chemistry*, **14**, ed. L. Strekowski, Springer, Berlin, 2008, pp. 133–181.
18. K. A. Bello, N. S. Korn and J. Griffiths, *J. Chem. Soc., Chem. Commun.*, 1993, 452.
19. H. Meier, R. Petermann and J. Gerold, *Chem. Commun.*, 1999, 977–978.
20. S. Yagi, S. Murayama, Y. Hodo and H. Nakazumi, *J. Chem. Soc., Perkin Trans 1*, 2002, **1**, 1417.
21. H. Tian, M. Furuki, I. Isawa, Y. Sato, L. S. Pu and S. Tatsu, *J. Phys. Chem. B*, 2002, **106**, 4370.
22. H. Tian, S. Tatsuura, M. Furuki, I. Isawa, Y. Sato and L. S. Pu, *J. Am. Chem. Soc.*, 2002, **125**, 348–349.
23. H. Langhals, *Angew. Chem., Int. Ed. Engl.*, 2003, **42**, 4286–4288.
24. P. Gregory, *High-Technology Applications of Organic Colorants*, Plenum, New York, 1991, pp. 225–227.
25. K. L. Marshall, G. Painter, K. Lotito, A. G. Noto and P. Cheng, *Mol. Cryst. Liq. Cryst.*, 2006, **452**, 47–79.
26. T. Kitao, *Dyes Pigm.*, 1987, **8**, 381.
27. NEC, *Jap. Pat.*, 60 150,243A, 1983.
28. J. Griffiths, *J. Chem. Res.*, 1978, 2319.
29. Y. Kubo, K. Sasaki and K. Yoshida, *Chem. Lett.*, 1987, 1563–1566.
30. G. M. Fischer, A. P. Ehlers, A. Zambusch and E. Datrazzo, *Angew. Chem., Int. Ed. Engl.*, 2007, **46**, 3750–3753.
31. (a) A. Herrmann and K. Müllen, *Chem. Lett.*, 2006, **35**, 978–985; (b) M. Adachi and M. Yukinori, *Chem. Mater.*, 2001, **13**, 662–669.
32. (a) N. G. Pschirer, C. Kohl, F. Nolde, J. Qu and K. Müllen, *Angew. Chem., Int. Ed. Engl.*, 2006, **45**, 1401–1404; (b) Y. Avlasevich and K. Müllen, *Chem. Commun.*, 2006, 4440–4442.
33. J. M. Giaimo, A. V. Gusev and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2002, **124**, 8530.
34. H. Wang, T. E. Kaiser, S. Uemura and F. Würthner, *Chem. Commun.*, 2008, 1181–1183.
35. (a) K. Kadish, K. M. Smith and R. Guilard, *The Porphyrin Handbook*, Academic Press, Amsterdam, 2002, **vol. 19**; (b) N. B. McKeown, *Phthalocyanines. Synthesis, Structure and function*, Cambridge University Press, Cambridge, UK, 1998.
36. ICI, *Eur. Pat.*, 155,780, 1984.
37. P. Gregory, *J. Porphyrins Phthalocyanines*, 1999, **3**, 468–476.
38. R. Bonnett, *Chemical Aspects of Photodynamic Therapy*, Gordon Breach, Amsterdam, 2000, pp. 190–198.

39. M. Taniguchi, D. L. Cramer, A. D. Bhise, H. L. Kee, D. F. Bocian, D. Holten and J. S. Lindsey, *New J. Chem.*, 2008, **32**, 947–958.
40. J. L. Sessler and S. J. Weghorn, *Expanded, Contracted and Isomeric Porphyrins*, ed. J. E. Baldwin, Pergamon, New York, 1997.
41. J. M. Lim, Z. S. Yoon, J.-Y. Shin, K. S. Kim, M.-C. Yoon and D. Kim, *Chem. Commun.*, 2009, 261–273.
42. Z. S. Yoon, J. H. Kwon, M.-C. Yoon, M. K. Koh, S. B. Noh, J. L. Sessler, J. T. Lee, D. Seidel, A. Aguilar, S. Shimizu, M. Suzuki, A. Osuka and D. Kim, *J. Am. Chem. Soc.*, 2006, **128**, 14128.
43. H. M. Kim and B. R. Cho, *Chem. Commun.*, 2009, 153–164.
44. L. Beverina, J. Fu, A. LeClercq, E. Zojer, P. Pacher, S. Barlow, E. W. Van Stryland, D. J. Hagan, J. L. Bredas and S. R. Marder, *J. Am. Chem. Soc.*, 2005, **127**, 7282–7283.
45. S. J. Zheng, A. LeClercq, J. Fu, L. Beverina, L. A. Padilha, E. Zojer, K. Schmidt, S. Barlow, J. D. Luo, S. H. Jiang, A. K. Y. Jen, Y. P. Yi, Z. G. Shuai, E. W. Van Stryland, D. J. Hagan, J. L. Bredas and S. R. Marder, *Chem. Mater.*, 2007, **19**, 432–442.
46. A. K. Bendiganavale and V. C. Malshe, *Recent Patents on Chemical Engineering*, 2008, **1**, 67–79.
47. E. H. Sargent, *Adv. Mater.*, 2005, **17**, 515–522.
48. M. A. Hines and G. D. Scholes, *Adv. Mater.*, 2003, **15**, 1844.
49. M. E. Stewart, C. R. Anderton, L. B. Thompson, J. Maria, S. K. Gray, J. A. Rogers and R. G. Nuzzo, *Chem. Rev.*, 2008, **108**, 494–521.
50. Ciba Specialty Chemicals, PCT WO2007/082811 A2, 2007.
51. G. Savineau, in *Passive and Low Energy Cooling for the Built Environment Proceedings*, May 2005, www.inive.org.
52. I. A Jones and R. J. Wise, The Welding Institute, *Eur. Pat.*, 11173502.
53. "Clearweld" from www.twi.co.uk and www.clearweld.com.
54. BASF, *US Pat. Appl. No.* 2007/0221321 A2.
55. N. Stockum and S. Klein, *US Pat. Appl. No.* 2007/0080146 A1.
56. T. S. Jewitt, in *Chemistry and Technology of Printing and Imaging Systems*, ed. P. Gregory, Blackie Academic, London, 1996, pp. 4–34.
57. (a) R. M. Adams and F. J. Romano, *Computer-To-Plate Primer*, GATF Press, 1999; (b) T. King, CtP – *Reviewing the Trends and the Technology*, AGFA, www.agfa.com, 2004.
58. C. DeBoer, *J. Imaging Sci. Technol.*, 1998, **42**(1), 63–69.
59. Imation Corp., *US Pat.*, 5,935,758, 1999.
60. Hewlett-Packard, *US Pat.*, 7,141,360, 2006.
61. http://gentexcorp.com and http://Epolin.com.
62. W. Kaiser, *Ultrashort Laser Pulses and Applications*, Springer-Verlag, 1988.
63. H. S. Nalwa and J. S. Shirk, in *Phthalocyanines: Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, VCH, Weinheim, 1995.
64. J. S. Shirk, R. G. S. Pong, F. J. Bartoli and A. W. Snow, *Pure. Appl. Opt.*, 1996, **5**, 701–707.

65. (a) *Disruptive Pattern Manual*, DPM Ltd, London, 2004; (b) *List of Camouflage Patterns*, http://en.wikipedia.org/wiki/List_of_camouflage_patterns.
66. US Secretary for the Navy, *US Pat.*, 6,805,957, 2004 and references therein.
67. (a) S. M. Burkinshaw, G. Hallas and A. D. Towns, *Rev. Prog. Col.*, 1996, **26**, 47; (b) R. A. Scott, in *Handbook of Technical Textiles*, ed. A. R. Horrocks and S. C. Anand, Woodhead Publishing Limited, Cambridge, England, 2000.
68. (a) www.myjiax.com; (b) H. Zhang and J. Ch. Zhang, *J. Textil. Inst.*, 2008, **99**(1), 83–88; (c) V. Rubežiene, I. Padleckiene, J. Baltušnikaite and S. Varnaite, *Mater. Sci.*, 2008, **14**, 361–365.
69. Huntsman Advanced Materials, *WO Pat. Appl.*, 2007/017430 A1.
70. Taiyo Yuden Co. Ltd, *US Pat.*, 4940618, 1989.
71. E. Hamada, Y. Shin and T. Ishiguro, *SPIE*, 1989, **1078**, 80–87.
72. H. Mustroph, M. Stollenwerk and V. Bressau, *Angew. Chem., Int. Ed. Engl.*, 2006, **45**, 2016–2035.
73. Philips Intellectual Property & Standards, *Mediaware*, 2004, **2**, 11–12.
74. H. Tiang and F. Meng, in *Functional Dyes*, ed. S.-H. Kim, Elsevier, Amsterdam, 2006, pp. 61–84.
75. (a) Mitsubishi Chemical Co., *US Pat.*, 6214519, 1998; (b) Mitsubishi Chemical Co. *US Pat.*, 6225023, 1998; (c) Mitsubishi Chemical Co. *US Pat.*, 6284877, 2000.
76. *Origins and Successors to the Compact Disc: Phillips Research*, Springer, Netherlands, 2009, vol. 11.
77. (a) Mitsui Chemicals, *US Pat.*, 7,094,516, 2006; (b) Mitsubishi Chemical Co., *US Pat. Appl.*, 2007/0184386; (c) Clariant International Ltd, *US Pat. Appl.*, 2007/0196767.
78. (a) P. M. Borsenberger and D. S. Weiss, *Organic Photoreceptors for Imaging Systems*, Marcel Dekker, New York, 1993; (b) K.-Y. Law, *Chem. Rev.*, 1993, **93**, 449–486; (c) R. S. Gairns, in *Chemistry and Technology of Printing and Imaging Systems*, ed. P. Gregory, Blackie Academic, London, 1996, pp. 76–112.
79. S. Kasap and P. Capper (ed.), *Handbook of Electronic and Photonic Materials*, Springer, Berlin, 2006, pp. 953–978.
80. C. S. Foote, J. S. Valentine, A. Greenberg and J. F. Liebman (ed.), *Active Oxygen in Chemistry*, Blackie Academic, London, 1995.
81. (a) B. Paczkowska, J. Paczkowski and D. C. Neckers, *Macromolecules*, 1986, **19**, 863; (b) A. P. Schapp, A. L. Thayer, E. C. Blossey and D. C. Neckers, *J. Am. Chem. Soc.*, 1975, **97**, 3741; (c) E. C. Blossey, D. C. Neckers, A. L. Thayer and A. P. Schapp, *J. Am. Chem. Soc.*, 1973, **95**, 5820.
82. (a) M. Oelgemöller, N. Healy, L. de Oliveira, C. Jung and J. Mattay, *Green Chem.*, 2006, **8**, 831–834; (b) M. Oelgemöller, C. Jung and J. Mattay, *Pure Appl. Chem.*, 2007, **79**, 1939–1947.
83. A. Ravve, *Light Assisted Reactions of Synthetic Polymers*, Springer, Berlin, 2006.

84. W. Schnabel, *Polymers and Light*, Wiley-VCH, Weinheim, 2007.
85. (a) P. T. K. Oldring (ed.), *Chemistry & Technology of UV and EB Formulations for Coatings, Inks and Paints*, SITA Technology, London, 1994, **vol. I–IV**; (b) C. G. Roffey, *Photogeneration of Reactive Species for UV Curing*, Wiley, New York, 1997; (c) J. P. Fouassier and J. F. Rabek (ed.), *Radiation Curing in Polymer Science and Technology*, Elsevier, London, 1993, **vol. I–V**; (d) J. P. Fouassier, *Photoinitiation, Photopolymerization and Photocuring: Fundamentals and Applications*, Hanser, Munich, 1995.
86. J. A. G. Drake (ed.), *Chemical Technology in Printing and Imaging Systems*, Royal Society of Chemistry, Cambridge, 1993.
87. F. Matsuo, T. Urano, H. Ito, K. Takahama and T. Yamakoa, in *Colour Science '98. Vol. 1: Dye and Pigment Chemistry*, ed. J. Griffiths, University of Leeds, 1999, pp. 217–222.
88. A. P. Polykarpov, S. Hassoon and D. C. Neckers, *Macromolecules*, 1996, **29**, 8274–8276.
89. Spectra Group Limited, Inc., http://www.sglinc.com.
90. (a) C. W. Hull, *US Pat.*, 4,575,330, 1986; (b) P. Dario, M. C. Carrozza, N. Croce, M. C. Montesi and M. Cocco, *J. Micromech. Microeng.*, 1995, **5**, 64; (c) A. Bertsch, H. Lorenz and P. Renaud, *Sens. Actuat. A. Phys.*, 1999, **73**, 14.
91. S. R. Marder, *Chem. Commun.*, 2006, 131–134.
92. (a) B. H. Cumpston, S. Ananthavel, S. Barlow, D. L. Dyer, J. E. Ehrlich, L. L. Erskine, A. A. Heikal, S. M. Kuebler, I.-Y. Sandy Lee, D. McCord-Maughon, J. Qin, H. Röckel, M. Rumi, X.-L. Wu, S. R. Marder and J. W. Perry, *Nature*, 1999, **398**, 51–54; (b) K. D. Belfield, X. Ren, E. W. Van Stryland, D. J. Hagan, V. Dubikovsky and E. J. Miesak, *J. Am. Chem. Soc.*, 2000, **122**, 1217.
93. J. W. Perry, V. W. Chen, W. Haske, J. M. Hales, W. Dong, J. Zhou, Y. Zhang, K. J. Perry, S. Barlow and S. R. Marder, in *Proceedings of CLEO 2007, Conference on Lasers in Electro Optics*, 2007, pp. 1–2.
94. L. Steidl, S. J. Jhaveri, R. Ayothi, J. Sha, J. D. McMullen, S. Y. C. Ng, W. R. Zipfel, R. Zentel and C. K. Ober, *J. Mater. Chem.*, 2009, **19**, 505–513.
95. N. C. Strandwitz, A. Khan, S. W. Boettcher, A. A. Mikhailovsky, C. J. Hawker, T.-Q. Nguyen and G. D. Stucky, *J. Am. Chem. Soc.*, 2008, **130**, 8280–8288.
96. A. Valberg, *Light Vision Color*, Wiley, Chichester, UK, 2005.
97. L. R. Milgrom, *The Colours of Life*, Oxford University Press, Oxford, 1997.
98. (a) P. N. Prasad, in *Photon-based Nanoscience and Nanobiotechnology*, ed. J. J. Dubowski and S. Tanev, Springer, Berlin, 2006, pp. 55–65; (b) P. N. Prasad, *Nanophotonics*, John Wiley & Sons, New York, 2004; (c) P. N. Prasad, *Introduction to Biophotonics*, John Wiley & Sons, New York, 2003.
99. (a) T. I. Karu, in *Biomedical Photonics Handbook*, ed. T. VoDinh, CRC Press, Boca Raton, FL, 2003, pp. 1–25; (b) J. Krutmann, H.

Honigsmann, C. A. Elmuts and P. R. Bergerstresser (ed.), *Dermatological Phototherapy and Photodiagnostic Methods*, Springer, Berlin, 2001.

100. R. Bonnett, *Chemical Aspects of Photodynamic Therapy*, Gordon Breach, Amsterdam, 2000.
101. A. Juzeniene, Q. Peng and J. Moan, *Photochem. Photobiol. Sci.*, 2007, **6**, 1234–1245.
102. R. K. Pandey, *J. Porphyrins Phthalocyanines*, 2000, **4**, 368–373.
103. T. J. Dougherty, J. E. Kaufman, A. Goldfarb, K. R. Weishaupt and A. Mittelman, *Cancer Res.*, 1978, **38**, 2628–2635.
104. (a) B. Röder, in *Encyclopaedia of Analytical Chemistry, Volume 1*, ed. R. A. Meyers, 2000, pp. 316–322; (b) R. Bonnett, *Chem. Soc. Rev*, 1995, **24**, 19–33.
105. www.dusapharma.com/levulan-photodynamic-therapy.
106. N. L. Oleinick, R. L. Morris and I. Belichenko, *Photochem. Photobiol. Sci.*, 2002, **1**, 1–21.
107. I. J. MacDonald and T. J. Dougherty, *J. Porphyrins Phthalocyanines*, 2001, **5**, 105–129.
108. L. B. Josefen and R. W. Boyle, *Br. J. Pharamacol.*, 2008, **154**, 1–3.
109. Y. N. Konan, R. Gurny and E. Allemann, *J. Photochem. Photobiol. B Biol.*, 2002, **66**, 89–106.
110. C. Staneloudi, K. A. Smith, R. Hudson, N. Malatesti, H. Savoie, R. W. Boyle and J. Greenman, *Immunology*, 2007, **120**, 512–517.
111. M. Kwitniewski, A. Juzeniene, R. Glosnicka and J. Moan, *Photochem. Photobiol. Sci.*, 2008, **7**, 1011–1017.
112. B. C. Wilson, in *Photon-based Nanoscience and Nanobiotechnology*, ed. J. J. Dubowski and S. Tanev, Springer, Berlin, 2006, pp. 121–157.
113. M. De, P. S. Ghosh and V. M. Rotello, *Adv. Mater.*, 2008, **20**, 4225–4241.
114. (a) N. Nishiyama, W.-D. Jang and K. Kataoka, *New. J. Chem.*, 2007, **31**, 1074–1082; (b) Y. Li, W.-D. Jang, N. Nishiyama, A. Kishimura, S. Kawauchi, Y. Morimoto, S. Miake, T. Yamashita, M. Kikuchi, T. Aida and K. Kata, *Chem. Mater.*, 2007, **19**, 5557–5562.
115. N. Nishiyama, S. Okazaki, H. Cabral, M. Miyamoto, Y. Kato, Y. Sugiyama, K. Nishio, Y. Matsumura and K. Kataoka, *Cancer Res.*, 2003, **63**, 8977–8983.
116. I. Roy, T. Y. Ohulchanskyy, H. E. Pudavar, E. J. Bergey, A. R. Oseroff, J. Morgan, T. J. Dougherty and P. N. Prasad, *J. Am. Chem. Soc.*, 2003, **125**, 7860–7865.
117. S. Wang, R. Gao, F. Zhou and M. Selke, *J. Mater. Chem.*, 2004, **14**, 487–493.
118. (a) A. C. S. Samia, S. Dayal and C. Burda, *Photochem. Photobiol.*, 2006, **82**, 617–625; (b) A. C. S. Samia, X. Chen and C. Burda, *J. Am. Chem. Soc.*, 2003, **125**, 15736–15737.
119. M. Idowu, J.-Y. Chen and T. Nyokong, *New. J. Chem.*, 2008, **32**, 290–296.
120. K. S. Samkoe and D. T. Crumb, *J. Biomed. Optics*, 2003, **8**, 1–8.

121. M. Khurana, H. A. Collins, A. Karotki, H. L. Anderson, D. T. Crumb and B. C. Wilson, *Photochem. Photobiol.*, 2007, **83**, 1441–1448.
122. (a) J. Arnbjerg, A. Jiménez-Banzo, M. J. Paterson, S. Nonell, J. I. Borrell, O. Christiansen and P. R. Ogilby, *J. Am. Chem. Soc.*, 2007, **129**, 5188–5199; (b) E. Dahlstedt, H. A. Collins, M. Balaz, M. K. Kuimova, M. Khurana, B. C. Wilson, D. Phillips and H. L. Anderson, *Org. Biomol. Chem.*, 2009, **7**, 897.
123. P. Zhang, W. Stelant, M. Kumarand and M. Scholfield, *J. Am. Chem. Soc.*, 2007, **129**, 4526–4527.
124. S. Kim, T. Y. Ohulchanskyy, H. E. Pudavar, R. K. Pandey and P. N. Prasad, *J. Am. Chem. Soc.*, 2007, **129**, 2669–2675.
125. L. J. Ignarro (ed.), *Nitric Oxide Biology and Pathobiology*, Academic Press, San Diego, CA, 2000.
126. P. G. Wang, M. Xian, X. Tang, X. Wu, Z. Wen, T. Cai and A. J. Janczuk, *Chem. Rev.*, 2002, **102**, 1091.
127. M. Barone, M. T. Sciortino, D. Zaccaria, A. Mazzagliac and S. Sortino, *J. Mater. Chem.*, 2008, **18**, 5531–5536.
128. S. R. Wecksler, A. Mikhailovsky, D. Korystov and P. C. Ford, *J. Am. Chem. Soc.*, 2006, **128**, 3831–3837.
129. D. Neuman, A. D. Ostrowski, R. O. Absalonson, G. F. Strouse and P. C. Ford, *J. Am. Chem. Soc.*, 2007, **129**, 4146–4147.
130. M. Hu, J. Chen, Z.-Y. Li, L. Au, G. V. Hartland, X. Li, M. Marquez and Y. Xia, *Chem. Soc. Rev.*, 2006, **35**, 1084–1094.
131. S. E. Skrabalak, J. Chen, L. Au, X. Lu, X. Li and Y. Xia, *Adv. Mater.*, 2007, **19**, 3177–3184.
132. P. K. Jain, X. Huang, I. H. El-Sayed and M. A. El-Sayed, *Acc. Chem. Res.*, 2008, **41**, 1578–1586.
133. M. R. Hamblin and T. Hasan, *Photochem. Photobiol. Sci.*, 2004, **3**, 436–450.
134. G. Jori, C. Fabris, M. Ferro, O. Coppellotti, D. Dei, L. Fannett, G. Chitin and G. Rococo, *Las. Surge. Med.*, 2006, **38**468–448.
135. M. Wainwright, *Biotech. Histochem.*, 2003, **78**, 147–155.
136. (a) M. Wainwright, D. A. Phoenix, M. Haskell and B. Marshall, *J. Antimicrob. Chemother.*, 1999, **44**, 823–825; (b) T. Maisch, C. Bosl, R.-M. Szeimies, B. Love and C. Abels, *Photochem. Photobiol. Sci.*, 2007, **6**, 545; (c) J. Gil-Tomas, S. Tubby, I. P. Parkin, N. Narband, L. Dekker, S. P. Nair, M. Wilson and C. Street, *J. Mater. Chem.*, 2007, **17**, 3739.
137. M. Wainwright, *Photochem. Photobiol. Sci.*, 2004, **3**, 406–411.
138. X. J. Shako, S. Ulsterman, Y. S. Li, M. E. Kenney and E. Ben-Hurl, *Photochem. Photobiol.*, 1997, **66**, 282–287.
139. R. K. Pander, *J. Porphyrins Phthalocyanines*, 2000, **4**, 368–373.
140. J. R. Heitz, in *Light Activated Pesticides*, ed. J. R. Heitz and K. R. Dowrum, American Chemical Society Symposium Series, Washington, D.C, 1987, pp. 1–21.

141. J. L. Nicanor, R. T. Cunningham, J. R. Heitz and J. P. Spencer, *US Pat.*, 5,728,394, 1998 and J. R. Heitz, R. L. Mangan and D. S. Moreno *US Pat.*, 5,798,112, 1998.
142. (a) T. Ben Amor, L. Bortolotto and G. Jori, *Photochem. Photobiol.*, 2000, **71**, 124–128; (b) B. Dondji, S. Duchon, A. Diabate, J. P. Herve, V. Corbel, J.-M. Hougard, R. Santus and J. Schrevel, *J. Med. Entomol.*, 2005, **42**, 652–656; (c) H. H. Awad, T. A. El-Tayeb and N. M. Abd El-Aziz, *J. Agri. Soc. Sci.*, 2008, **4**, 85–88.
143. K. Mori, *KONA*, 2005, **23**, 205–214.
144. K. Qi, W. A. Daoud, J. H. Xin, C. L. Mak, W. Tang and W. P. Cheung, *J. Mater. Chem.*, 2006, **16**, 4567–4574.
145. Y. Li, H. Zhang, X. Hu, X. Zhao and M. Han, *J. Phys. Chem. C*, 2008, **112**, 14973–14975.
146. J. Mosinger, O. Jirsák, P. Kubát, K. Lang and B. Mosinger Jr., *J. Mater. Chem.*, 2007, **17**, 164.
147. E. Bae and W. Choi, *Environ. Sci. Technol.*, 2003, **17**, 147–152.
148. Z. Xiong and Y. Xu, *Chem. Mater.*, 2007, **19**, 1452–1468.
149. C. J. Montneiro and G. B. Strambini, *Photochem. Photobiol. Sci.*, 2005, **4**, 617–624.
150. (a) Z. Kang, C. H. A. Tsang, N.-B. Wong, Z. Zhang and S.-T. Lee, *J. Am. Chem. Soc.*, 2007, **129**, 12090–12091; (b) Z. Kang, Y. Liu, C. M. A. Tsang, D. D. D. Ma, X. Fan, N.-B. Wong and S.-T. Lee, *Adv. Mater.*, 2009, **21**, 661–664.
151. M. Grandcolas, A. Louvet, N. Keller and V. Keller, *Angew. Chem., Int. Ed. Engl.*, 2009, **48**, 161–164.
152. M. Z. Jacobson, *Energy Environ. Sci.*, 2009, **2**, 148–173.
153. C. McVeigh, in *Milestones in 150 Years of the Chemical Industry*, ed. P. J. Morris, W. A. Campbell and H. L. Roberts, Royal Society of Chemistry, Cambridge, 1991.
154. www.trec-uk.org.uk (February 2009).
155. M. Tao, *Interface*, 2008, **Winter**, 30–35.
156. H. Cotal, C. Fetzer, J. Boisvert, G. Kinsey, R. King, P. Hebert, H. Yoon and N. Karam, *Energy Environ. Sci.*, 2009, **2**, 174–192.
157. (a) R. W. Miles, G. Zoppi and I. Forbes, *Mater. Today*, 2007, **10**(11), 20–27; (b) J. M. Crow, *Chem. World*, February 2008, **15**.
158. A. Kongkanand, K. Tvrdy, K. Takechi, M. Kuno and P. V. Kamat, *J. Am. Chem. Soc.*, 2008, **130**, 4007–4025 and references therein.
159. A. Hadipour, B. de Boer and P. W. M. Blom, *Adv. Func. Mater.*, 2008, **18**, 169–181.
160. P. Peumans, V. Bulovic and S. R. Forrest, *Appl. Phys. Lett.*, 2000, **76**, 2650.
161. (a) M. Granström, K. Petritsch, A. C. Arias, A. Lux, M. R. Andersson and R. H Friend, *Nature*, 1998, **395**, 257; (b) N. S. Sariciftci and A. J. Heeger, in *Handbook of Organic Conductive Molecules and Polymers*, ed. H. S. Nalwa, Wiley, New York, 1997, **vol. I**, p. 414; (c) J. J. Dittmer, R. Lazzaroni, P. Leclère, P. Moretti, M. Granström, K. Petritsch, E. A. Marseglia, R. H. Friend, J. L. Brédas, H. Rost and A. B. Holmes, *Sol.*

Energy Mater. Sol. Cells., 2000, **61**, 53; (d) K. Petritsch, J. J. Dittmer, E. A. Marseglia and R. H. Friend, *Sol. Energy Mater. Sol. Cells.*, 2000, **61**, 63.

162. S. Gûnes, H. Neugebauer and N. S. Sariciftci, *Chem. Rev.*, 2007, **107**, 1324–1338.
163. (a) F. Padinger, R. Rittberger and N. S. Sariciftci, *Adv. Funct. Mater.*, 2003, **13**, 85; (b) G. Li, V. Shrotriya, J. S. Huang, Y. Yao, T. Moriarty, K. Emery and Y. Yang, *Nature Mater.*, 2005, **4**, 864; (c) W. L. Ma, C. Y. Yang, X. Gong, K. H. Lee and A. J. Heeger, *Adv. Funct. Mater.*, 2005, **15**, 1617.
164. Y. Liang, Y. Wu, D. Feng, S.-T. Tsai, H.-J. Son, G. Li and L. Yu, *J. Am. Chem. Soc.*, 2009, **131**, 56–57.
165. A. Carvino and N. S. Sariciftci, *J. Mater. Chem.*, 2002, **12**, 1931–1933.
166. J.-F. Niergarten, J.-F. Eckert, J.-F. Nicoud, N. L. Quali, V. Kranikov and G. Hadziioannou, *Chem. Commun.*, 1999, 617.
167. J. Roncali, *Chem. Soc. Rev.*, 2005, **34**, 483–495.
168. S. Berson, R. de Bettignes, S. Bailly, S. Guillerez and B. Jouesselme, *Adv. Func. Mater.*, 2007, **17**, 3363–3370.
169. (a) X. Feng, M. Liu, W. Pisula, M. Takase, J. Li and K. Müllen, *Adv. Mater.*, 2008, **20**, 2684–2689; (b) Z. Liu, Q. Liu, Y. Hang, Y. Ma, S. Yin, X. Zhang, W. Sun and Y. Chen, *Adv. Mater.*, 2008, **20**, 3924–3930.
170. E. Arici, N. S. Sariciftci and D. Meissner, in *Encyclopedia of Nanoscience and Nanotechnology*, ed. H. S. Nalwa, 2004, vol. 3, pp. 929–944.
171. J. Bouclé, P. Ravirajan and J. Nelson, *J. Mater. Chem.*, 2007, **17**, 3141–3153.
172. C.-H. Chang, T.-K. Huang, Y.-T. Lin, Y.-Y. Lin, C.-W. Chen, T.-H. Chu and W.-F. Su, *J. Mater. Chem.*, 2008, **18**, 2201–2207.
173. M. Scharber, D. Müuhlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger and C. Brabec, *Adv. Mater.*, 2006, **18**, 789.
174. (a) H. Tributsch, *Photochem. Photobiol.*, 1972, **16**, 261–269; (b) A. Fujishima and K. Honda, *Nature*, 1972, **238**, 37–38.
175. T. Skotheim, *US Pat.*, 4,190,950, 1980.
176. B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737–740.
177. M. Grätzel, *Inorg. Chem.*, 2005, **44**, 6841–6851.
178. N. Robertson, *Angew. Chem., Int. Ed. Engl.*, 2006, **45**, 2338–2345.
179. J. R. Durrant, S. A. Haquea and E. Palomares, *Chem. Commun.*, 2006, 3279–3289.
180. L. M. Peter, *Phys. Chem. Chem. Phys.*, 2007, **9**, 2630–2642.
181. H. J. Snaith and L. Schmidt-Mende, *Adv. Mater.*, 2007, **19**, 3187–3200.
182. L. M. Goncalves, V. de Zea Bermudez, H. A. Ribeiroa and A. Mendes, *Energy Environ. Sci.*, 2008, **1**, 655–667.
183. S. Ardo and G. J. Meyer, *Chem. Soc. Rev.*, 2009, **38**, 115–164.
184. (a) T. Bessho, E. Yoneda, J.-H Yum, M. Guglielmi, I. Tavernelli, H. Imai, U. Rothlisberger, M. K. Nazeeruddin and M. Grätzel, *J. Am. Chem. Soc.*, 2009, **131**, 5930–5934; (b) T. Bessho, E. C. Constable,

M. Graetzel, A. Hernandez Redondo, C. E. Housecroft, W. Kylberg, M. K. Nazeeruddin, M. Neuburger and S. Schaffner, *Chem. Commun.*, 2008, 3717.

185. S. Kim, J. Lee, S. Kang, J. Ko, J. Yum, S. Fantacci, F. DeAngelis, D. DiCenso, M. Nazeeruddin and M. Grätzel, *J. Am. Chem. Soc.*, 2006, **128**, 16701–16707.
186. I. Gonzalez-Valls and M. Lira-Cantu, *Energy Environ. Sci.*, 2009, **2**, 19–34.
187. S. Ito, S. Zakeruddin, R. Humphry-Baker, P. Liska, R. Charvet, P. Comte, M. Nazeeruddin, P. Péchy, M. Takata, H. Miura, S. Uchida and M. Grätzel, *Adv. Mater.*, 2006, **18**, 1202–1205.
188. T. W. Hamann, R. A. Jensen, A. B. F. Martinson, H. Van Ryswykac and J. T. Hupp, *Energy Environ. Sci.*, 2008, **1**, 66–78.
189. D. Kuang, S. Uchida, D. Kuang, S. Uchida, R. Humphry-Baker, S. M. Zakeeruddin and M. Grätzel, *Angew. Chem., Int. Ed. Engl.*, 2008, **47**, 1923–1927.
190. J. Wu, S. Hao, Z. Lam, J. Lin, M. Huang, Y. Huang, P. Li, S. Yin and T. Sato, *J. Am. Chem. Soc.*, 2008, **130**, 11568–11569.
191. L. Schmidt-Mende, U. Bach, R. Humphry-Baker, T. Horiuchi, H. Miura, S. Ito, S. Uchida and M. Grätzel, *Adv. Mater.*, 2005, **17**, 813–815.
192. www.konarka.com (February 2009).
193. (a) www.greatcell.com; (b) www.dyesol.com; (c) www.sta.com.au (February 2009).
194. K. Higuchi and N. Kato, R&D Review of Toyota CRDL, 2006, Volume 41, Issue 1.
195. www.g24i.com (February 2009).
196. W. H. Weber and J. Lambe, *Appl. Opt.*, 1976, **15**, 2299.
197. M. J. Currie, J. K. Mapel, T. D. Heidel, S. Goffri and M. A. Baldo, *Science*, 2008, **321**, 226–228.
198. (a) D. O. Hall and K. F. Rao, *Photosynthesis*, Cambridge University Press, Cambridge, 1999, 6th edn; (b) R. E. Blankenship, *Molecular Mechanism of Photosynthesis*, Blackwell Science, Oxford, 2002; (c) M. D. Archer and J. Barber, *Molecular to Global Photosynthesis*, Imperial College Press, London, 2004.
199. J. Barber, *Chem. Soc. Rev.*, 2009, **38**, 185–196.
200. A. F. Collings and C. Critchley (ed.), *Artificial Photosynthesis: From Basic Biology to Industrial Application*, Wiley-VCH, Weinheim, 2005.
201. D. Gust, T. A. Moore and A. L. Moore, in *Artificial Photosynthesis: From Basic Biology to Industrial Application*, ed. A. F. Collings and C. Critchley, Wiley-VCH, Weinheim, 2005, pp. 187–210.
202. V. Balzani, A. Credi and M. Venturi, *Molecular Devices and Machines*, Wiley-VCH, Weinheim, 2008, 2nd edn, pp. 171–208.
203. M.-S. Choi, T. Yamazaki, I. Yamazaki and T. Aida, *Angew. Chem., Int. Ed. Engl.*, 2004, **43**, 150–158.
204. Y. Kobuke, *Struct. Bond.*, 2006, **121**, 49–104.
205. N. Nagata, Y. Kuramochi and Y. Kabuke, *J. Am. Chem. Soc.*, 2009, **131**, 10–11.

206. V. Balzani, P. Ceroni, M. Maestri and V. Vicinelli, *Curr. Opin. Chem. Biol.*, 2003, **7**, 657–665.
207. A. P. H. Schenning, E. Peeters and E. W. Meijer, *J. Am. Chem. Soc.*, 2000, **122**, 4489.
208. C. Minkowski, R. Pansu, M. Takano and G. Calzaferri, *Adv. Funct. Mater.*, 2006, **16**, 273.
209. K. Sasaki, H. Nakagawa, X. Zhang, S. Sakurai, K. Kano and Y. Kuroda, *Chem. Commun.*, 2004, 408.
210. E. H. A. Beckers, P. A. van Hal, A. P. H. Schenning, A. Elghayoury, E. Peeters, M. T. Rispens, J. C. Hummelen, E. W. Meijer and R. A. J. Janssen, *J. Mater. Chem.*, 2002, **12**, 2054.
211. A. Ajayaghosh, V. K. Praveen and C. Vijayakumar, *Chem. Soc. Rev.*, 2008, **37**, 109–122.
212. G. Syteinberg-Yfrach, J.-L. Rigaud, A. L. Moore, D. Gust and T. A. Moore, *Nature*, 1998, **392**, 479.
213. S. Licht, *Chem. Commun.*, 2005, 4635–4646.
214. A. Kudo and Y. Miseki, *Chem. Soc. Rev.*, 2009, **38**253–78.
215. J. R. Durrant, *Chem. Ind.*, 1998, **Oct. 19**, 838–841.
216. B. D. Alexander, P. J. Kulesza, I. Rutkowska, R. Solarska and J. Augustynski, *J. Mater. Chem.*, 2008, **18**, 2298.
217. M. Grätzel and A. J. McEvoy, *Basic Research for the Hydrogen Economy*, American Physical Society, Montreal, 2004.
218. B. B. Kale, J.-O. Baeg, S. K. Apte, R. S. Sonawane, S. D. Naik and K. R. Patil, *J. Mater. Chem.*, 2007, **17**, 4297–4303.
219. J. Choi, S. Y. Ryu, W. Balcerski, T. K. Lee and M. R. Hoffmann, *J. Mater. Chem.*, 2008, **18**, 2371.
220. M. Elvington, J. Brown, S. M. Arachchige and K. J. Brewer, *J. Am. Chem. Soc.*, 2007, **129**, 10664.
221. M. Hambourger, G. F. Moore, D. M. Kramer, D. Gust, A. L. Moore and T. A. Moore, *Chem. Soc. Rev.*, 2009, **38**, 25–35.
222. D. Behar, T. Dhanasekaran, P. Neta, C. M. Hosten, D. Ejeh, P. Hambright and E. Fujita, *J. Phys. Chem. A.*, 1998, **102**, 2870.
223. A. Melis, in *Artificial Photosynthesis: From Basic Biology to Industrial Application*, ed. A. F. Collings and C. Critchley, Wiley-VCH, Weinheim, 2005, pp. 229–240.
224. (a) www.sapphireenergy.com; (b) www.greenfuelonline.com; (c) www.seambiotic.com.
225. M. L. Ghirardi, A. Dubini, J. Yu and P.-C. Maness, *Chem. Soc. Rev.*, 2009, **38**, 52–61.
226. A. Natansohn and P. Rochon, *Chem. Rev.*, 2002, **102**, 4139–4175.
227. M. Schliwa (ed.), *Molecular Motors*, Wiley-VCH, Weinheim, 2003.
228. K. Kinbara and T. Aida, *Chem. Rev.*, 2005, **105**, 1377–1400.
229. W. R. Browne and B. L. Feringa, *Nature Nanotechnology*, 2006, **1**, 25–34.
230. V. Balzani, A. Credi and M. Venturi, *Molecular Devices and Machines*, Wiley-VCH, Weinheim, 2nd edn, 2008, pp. 315–329.

231. S. Shinkai, T. Nakaji, T. Ogawa, K. Shigematsu and O. Manabe, *J. Am. Chem. Soc.*, 1981, **103**, 111.
232. Y. Norikane and N. Tamaoki, *Org. Lett.*, 2004, **6**, 2595.
233. T. Muroaka, K. Kinbara and T. Aida, *Nature*, 2006, **440**, 512.
234. K. Yamashita, M. Kawano and M. Fujita, *J. Am. Chem. Soc.*, 2007, **129**, 1850–1851.
235. M. M. Pollard, M. Klok, D. Pijper and Ben L. Feringa, *Adv. Funct. Mater.*, 2007, **17**, 718–729.
236. J. F. Stoddart, *Acc. Chem. Res.*, 2001, **34**, 410–411.
237. E. M. Perez, D. T. F. Dryden, D. A. Leigh, G. Teobaldi and F. A. Zerbetto, *J. Am. Chem. Soc.*, 2004, **126**, 12210–12211.
238. D.-H. Qu, Q.-C. Wang and H. Tian, *Angew. Chem., Int. Ed. Engl.*, 2005, **44**, 5296.
239. R. J. Coulston, H. Onagi, S. F. Lincoln and C. J. Easton, *J. Am. Chem. Soc.*, 2006, **128**, 14750–14751.

CHAPTER 5

Chromic Phenomena Involving the Manipulation of Light

5.1 Introduction

This last chapter covers those phenomena that use materials to control light in a variety of ways in order to produce useful colour effects. In some of these phenomena light is manipulated by particular orientations of molecular materials to produce a visual effect, as in liquid crystal displays. In others, light produces colour effects by physical interactions with materials, as in lustre and optically variable pigments, and with colloidal photonic crystals, and in holography. Molecular materials are also used to increase the intensity of light, as in lasers, or to modify the transmission of light through materials by electrical means, as in opto-electronics, or by all-optical systems, as in optical limiters, and other nonlinear optical systems underpinning photonics. The volume markets remain in liquid crystals, lasers and lustre pigments, but the ultimate commercial application goal for many of these phenomena is high-density optical data storage and electro-optic transmission devices, and eventually in all-optical computers.

5.2 Liquid Crystals

Although the existence of liquid crystals has been known since the nineteenth century, their use in displays is a relatively new technological application. For instance we had the technology to put men on the moon in the 1960s but they would have never seen a watch with a digital display made from liquid crystals. Since the advent in the 1970s of the first really useful liquid crystal materials from George Gray's work in the UK and by workers at Hoffmann-La Roche in Switzerland, the all-pervasive presence of the technology indicates how strong was the commercial pull.[1,2] Over the intervening years a vast amount of research has gone into providing both advanced materials and methods of construction of liquid crystal cells.[3] Examination of the more recent

---

Chromic Phenomena: Technological Applications of Colour Chemistry, Second Edition
By Peter Bamfield and Michael G. Hutchings

Published by the Royal Society of Chemistry, www.rsc.org

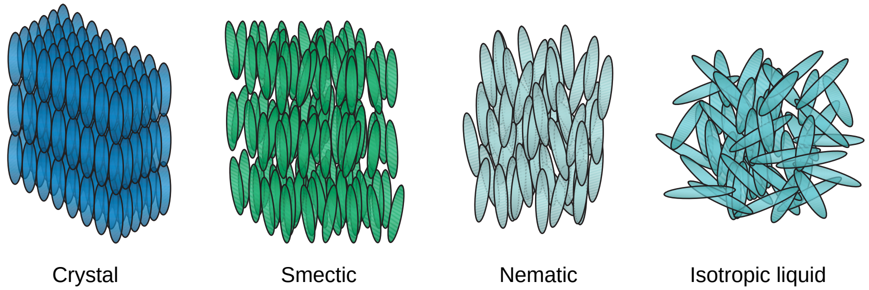


Figure 5.1 Idealised representations of crystal, liquid crystal and isotropic liquid phases formed by rod like (calamitic) molecules.

publications, in both scientific journals and trade magazines, shows that developments in this field are far from over as new applications are found for these complex materials.

Liquid crystals are materials that exist in a state that is intermediate between a liquid state and a solid. They are most commonly formed by anisotropic molecules, known as calamitic molecules, which are long and narrow, *i.e.* have a large length-to-breadth ratio. These rod-shaped molecules orientate themselves in different ways as they change from the rigorously 3D-ordered crystalline phase, shown schematically in Figure 5.1, to the disordered isotropic liquid state at increasing temperatures, passing through one or more specific liquid crystalline phases: smectic (ordered within planes that can pass over one another; one of several alternatives is shown) and nematic (ordered along one main axis). The latter is the most important for most technological applications.[4]

Discotic or disc-shaped materials and supramolecular structures also form other types of liquid crystal phases and are also finding applications. Another very important class of liquid crystalline materials comprises polymers, both in-chain (*e.g.* Kevlar) and side chain.

More recently developed and potentially valuable liquid crystals are those forming the meta-stable blue phases, which occur between the chiral nematic phase and an isotropic liquid phase. In these the molecules assemble into cylindrically shaped arrays in which the direction of alignment twists in a helix, while the helices themselves criss-cross in three dimensions. The structure repeats regularly with a period of several hundred nanometres, near the wavelengths of visible light. This means that blue phases reflect visible light of a particular colour. Although blue phases are normally very temperature sensitive over only a few degrees, ways have been found recently to increase this temperature range considerably (0–60 °C), opening up ways for producing three-colour (red-green-blue) pixels for full-colour displays.[5,6]

Although liquid crystals have found many applications across different fields of chemistry, only those where they interact with light, especially coloured light, are of interest in this text. A list of such interactions is given in Table 5.1.

Table 5.1 Interaction of light with liquid crystal phases and their applications.

Interaction/behaviour	*Application*
Twisted polarised light	Twisted nematic displays
Switchable birefringence film	Supertwisted nematic (STN), ferroelectric (FLC), electrically controlled birefringence (ECB) displays
Refraction of light	Polymer dispersed liquid crystals (PDLC) smart windows, gel and polymer network displays
Electrically switchable host for dichroic dyes	Guest host and dyed phase change displays
Selective reflection of light	Thermochromic cholesteric devices, gel displays
	Blue phase 3 colour displays
Dye doped LC lasing	LC lasers; LC displays

5.2.1 Nematic Liquid Crystals and Their Applications

By far the most important commercial application of nematic liquid crystals is in the multi-billion-dollar display industry.[7,8] This application has grown so fast since the turn of the century that in 2007 LCDs overtook CRTs as the major technology used in displays, driven of course by the desire for flat-panel screens. Flat-screen LCD TV monitor sales were roughly on a par with CRTs in early 2008, but proportionately increasing (Chapter 3, Section 3.3.1). Cholesteric or chiral nematic liquid crystals have also been used in a wide variety of thermochromic applications, and in coloured guest-host display panels, where the most exciting new application is that of electronic paper (e-paper).

5.2.1.1 Twisted Nematic Displays

Most liquid crystal cells are constructed in a similar manner, in which the liquid crystal (LC) material is held between two glass sheets, typically 0.7 mm thick, held apart with spacers of around 5 μm, and glued together around the edges. Transparent ITO electrodes, coated on the inside of these glass walls and in contact with the LC, are used to apply voltages across the cell, controlling orientation of the LC material. Polarising filter sheets, which are put on either side of the LC cell, are required to give the light and dark areas in the display. The light source is either ambient light with a reflecting mirror (reflective mode), or a back light placed behind the liquid crystal cell (transmissive mode).

The leading LCD technologies in display panels are based on twisted nematic liquid crystals, and rely on the ability of these molecules to twist the plane of polarised light through 90°. The cells in this case are constructed by use of alignment layers consisting of grooved polymers, so that the molecules in contact with one cell wall are at right angles to those on the other, producing a twisted helix across the cell when no voltage is passing. The polarisers are cross polarised, *i.e.* at right angles to each other, so that light passing through one polariser needs to be rotated through 90° by the twisted helix before coming out of the cell through the other polariser. On applying a voltage to a cell

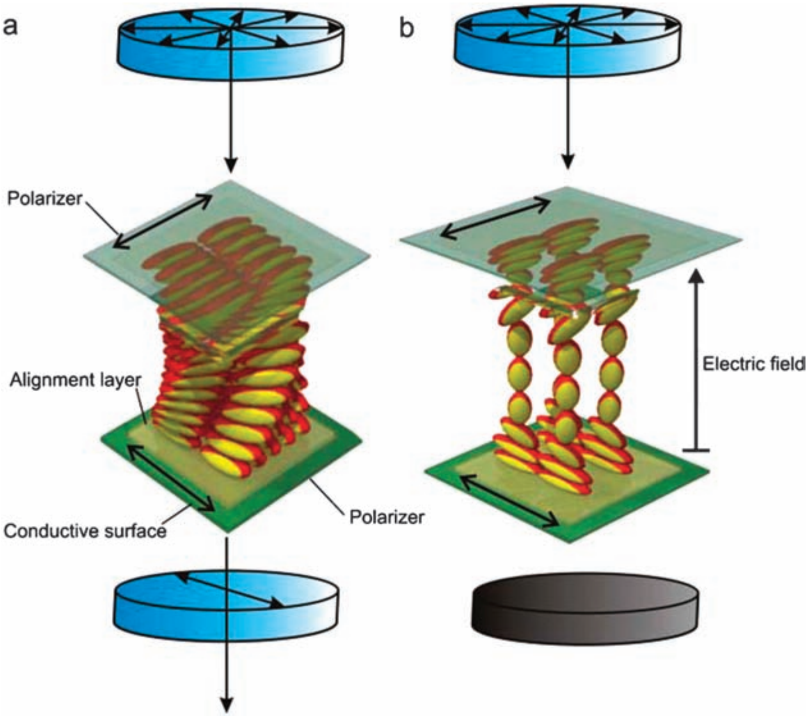


Figure 5.2 Schematic of a twisted nematic LC display (a) off state, (b) on state.[9]

containing LC materials exhibiting positive dielectric anisotropy, the molecules line up parallel to the electrical field, destroying the helical arrangement, so that polarised light can no longer pass and the cell appears dark. This methodology is illustrated schematically in Figure 5.2.[9]

The simplest LC panels, such as those used in calculators and watches, use direct driving of segmented displays. However, to produce larger area display panels, especially coloured ones, it is necessary to address an array of pixels simultaneously. This can be achieved by multiplexing or using a matrix arrangement of transistors, known as passive and active matrix devices. These methods are illustrated in Figure 5.3.[10]

Passive matrix or direct drive multiplex systems have an array of electrodes on one of the substrates that addresses the rows, and another set on the other substrate that addresses the columns (Figure 5.3c). The set-up allows a pixel to be addressed at each intersection of a row and a column. This works fine for nematic LCs in modest sized displays, up to 120,000 pixels, but beyond this size there is an increase in switching times and cross-talk between adjacent pixel elements leads to a loss in contrast. This problem was overcome by using super-twisted nematic liquid crystals (STN LCs), which are materials where the helical twist is increased to between 180° and 270°. These super-twist LCs give a much sharper image than the 90° materials. The system is ideal for

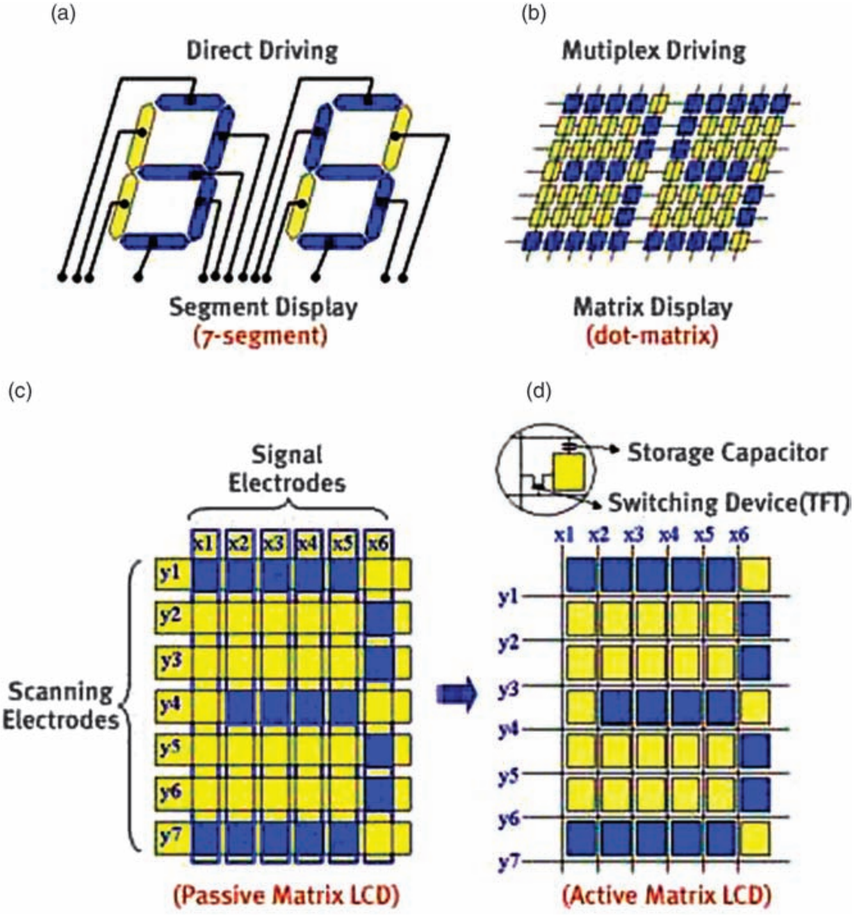


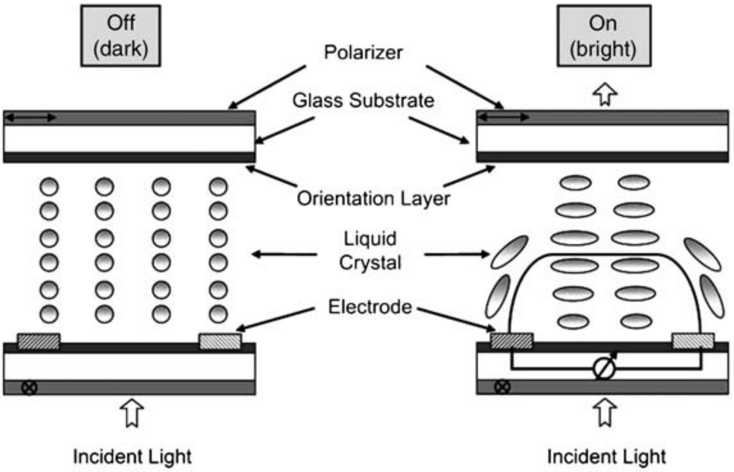
Figure 5.3 Alternative methods for addressing LC cells.[10]

monochrome displays but even with these materials the response times start to become very slow with the several million pixels that are required for high-contrast, full-colour displays.

The alternative active matrix system is known as active matrix thin film transistors (AMTFTs). In AMTFTs an array of amorphous silicon transistors is vapour-deposited onto one side of the substrate, each transistor being positioned below each pixel (Figure 5.3b). These are much better for colour displays since they give improved viewing angles, response times and resolution than STNs. Systems based on AMTFTs have become the dominant technology used in full-colour display panels.

However, the viewing angle dependency of the optical effect, especially contrast and colour shift, had to be improved, and the two main alternatives are the in-plane switching (IPS) mode and the vertically aligned switching (VAS) mode (Figure 5.4).[8]

(a) IP Switching mode



(b) VA Switching mode

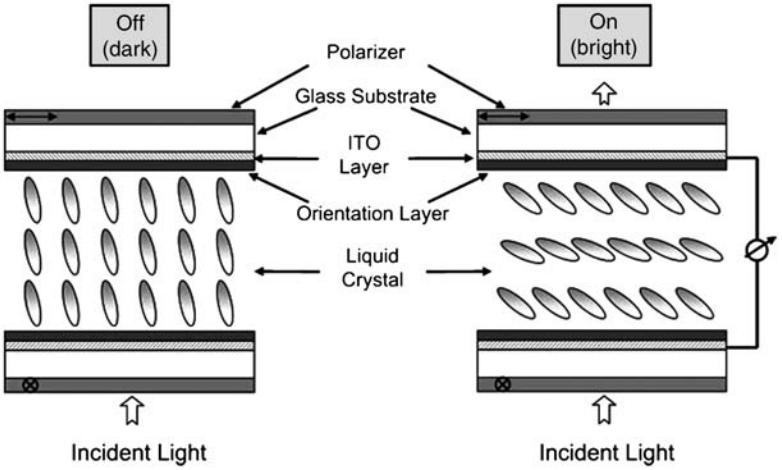


Figure 5.4 Alternative switching modes in LC displays.[8]

In IPS mode, introduced in 1996, the reorientation of the LC upon switching takes place in a plane parallel to the substrates making an angle with each of the polarisers and hence the cell is birefringent (Figure 5.4a). The viewing angle dependency of the change of birefringence thus becomes homogeneous. A good viewing angle is obviously a highly desirable feature for TV viewing, and fabrication methods have been devised to achieve significant improvements in multi-domain LCDs.

The VAS mode, introduced in 1998 for monitor displays, requires LC materials which exhibit negative dielectric anisotropy. Cells using these materials can be constructed so that the LCs align vertically and twist on applying a field, exactly the converse to the twisted nematic effect from positive anisotropic LCs (Figure 5.4b). Cells of this type form a superior black state independent of the wavelength of light and temperature.

Dye-doped liquid crystals are finding application in new tuneable lasers, and are being applied in laser displays. These are covered in Section 5.5.2.4.

5.2.1.2 Nematic Liquid Crystal Materials

The important breakthrough in the design of chemically, photochemically and electrochemically stable liquid crystals came *via* the work of George Gray at Hull University in the UK in the early 1970s. These LC materials, based on substituted cyanobiphenyls and subsequently cyanoterphenyls, were commercialised by BDH (UK) and Merck (Germany).[1] The original LC materials were successfully deployed in the manufacture of relatively simple, directly addressed, monochrome digital displays for watches, clocks and calculators. Later improvements came *via* the cyanophenylpyrimidines and the pentylcyclohexanes and bicyclohexanes. The structures of some typical materials used in direct-drive displays are illustrated in Figure 5.5. In practice commercial liquid crystal materials are complex mixtures. The wide operating temperature range in combination with other properties requires mixtures of typically 10 to 20 compounds, tailored to meet the variety of technical demands of a particular application or outlet.

The polar cyano-group-containing LC materials, used in direct-drive displays, were not directly suitable for use in the more complex multiplex addressing displays. Fortunately, mixtures of these materials with relatively simple benzoate esters gave materials with acceptable properties. Subsequent developments have led to the use of apolar materials such as the three-ring compound molecules containing fluorine atoms and *trans-trans* bicyclohexanes, in admixture with polar materials. Some typical materials are shown in Figure 5.6.

The next important breakthrough in designing compounds specifically for use as STN materials in multiplex addressing systems came with the discovery that converting the terminal alkyl group to a non-conjugated alkenyl substituent gave polar molecules that showed the desired behaviour. Further detailed work has shown that the preferred product is the *trans*-isomer *e.g.* (5.1). Apolar components such as (5.2) are also included in LC mixtures for

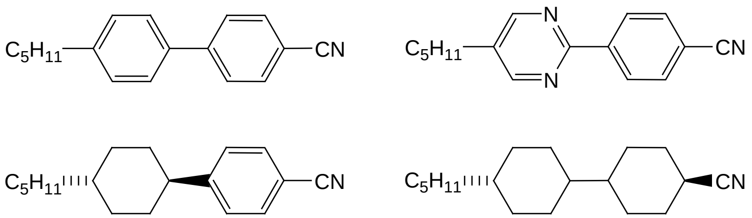


Figure 5.5 Twisted nematic materials for direct drive displays.

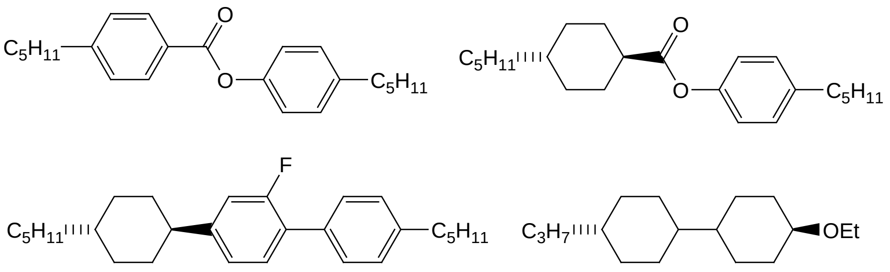


Figure 5.6 Twisted nematic materials for multiplex addressing.

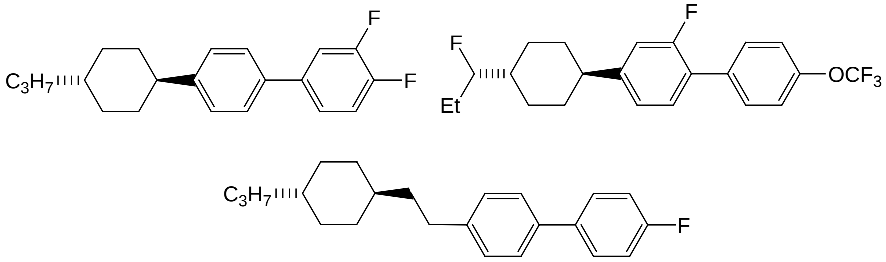
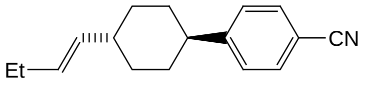
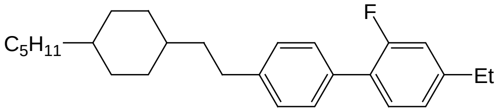


Figure 5.7 Twisted nematic materials for active matrix addressing.

STN, in order to lower the viscosity and melting points, thus improving their multiplexing properties.



(5.1)



(5.2)

New materials were also required for AMTFT displays, since the materials existing at the time were too low in resistivity, too high in viscosity and insufficiently stable. Very high resistivity is required because the TFT maintains the charge on the pixel, until it is readdressed on the next scan or frame of the device. Therefore any loss of charge is in effect reducing the voltage which is applied across the pixel. Most of the specifically designed materials contain fluorine atoms, and some typical materials are shown in Figure 5.7.

5.2.1.3 Colour Displays from Twisted Nematic Liquid Crystals

The biggest growth area in displays has been in full-colour flat-panel LC displays for use in conjunction with computers and stand-alone TVs. The two major technologies used in this area, as stated above, are STN-LCDs and

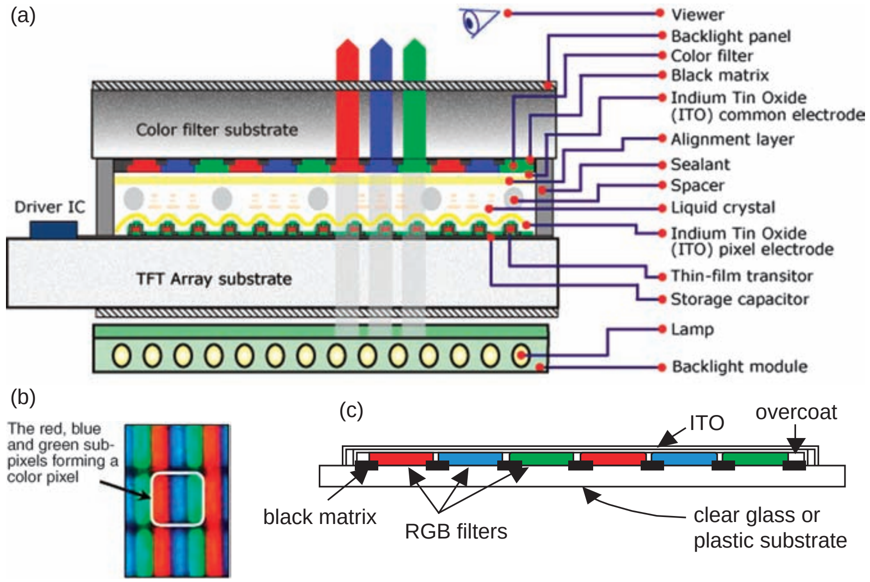


Figure 5.8 The structure of AMTFT colour panel and the RGB pixels.

AMTFT-LCDs, with the latter taking the major share of the market as their production costs have significantly diminished. This is because they exhibit a more uniform, wide viewing angle and superior display brightness.[7]

Whichever system is used, in order to produce the full colour gamut, it is necessary to display one-third of the pixels as red, one-third as green and one-third as blue. This is achieved by having a colour filter layer as one of the substrates within the display panel. A schematic of this arrangement and a pixel element are shown in Figure 5.8a and b. The role of the LC material in this system is to act as a light switch.

The colour filter layer consists of the RGB colour elements set inside the so-called black matrix, which prevents leakage of light from the different pixels and also stops any photoelectrical conversion in the TFT. The structure of the colour filter layer, illustrated in Figure 5.8c, is constructed on a clear substrate, and comprises the RGB filter units, the black matrix interlayer, an overcoat layer and an ITO film. Amongst the preferred methods for construction of pigment-based colour filter layers are photolithography, printing and electrodeposition.[8]

The idealised spectral characteristics of the colorants required for this outlet are shown in Figure 5.9. Although dyes are used to make colour filters, giving very bright colours, their heat resistance and light fastness are generally inferior to pigments, which are consequently preferred. It is also important to get high transparency and colour ratio, and this requires the preparation of a fine dispersion of the pigment in the process solvent or in a photopolymerisable resin carrier. Pigments that have been used for this outlet are taken from the high-performance class: generally anthraquinone vat pigments and perylenes for red, and phthalocyanines for blue and green (see Chapter 2).

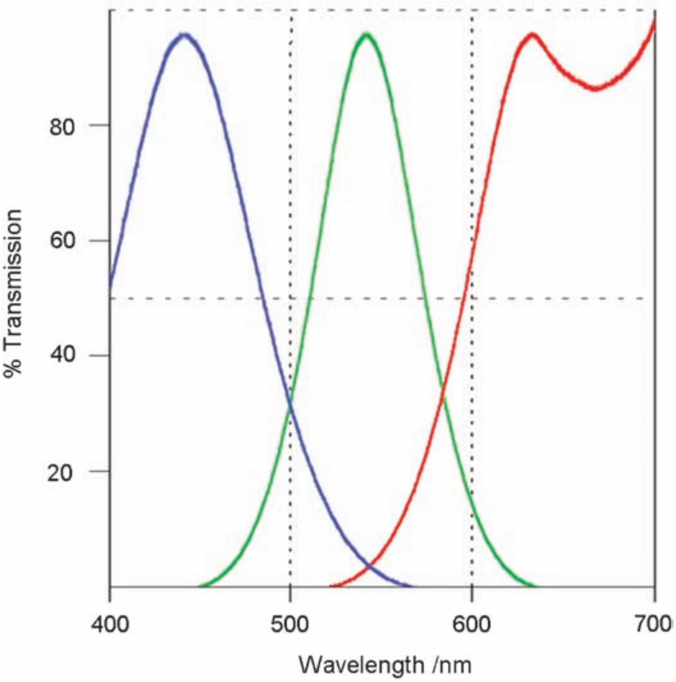
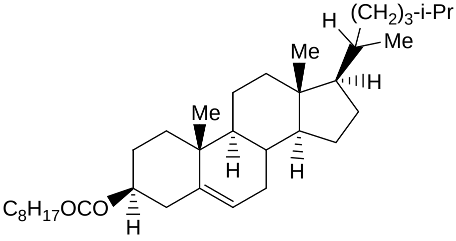


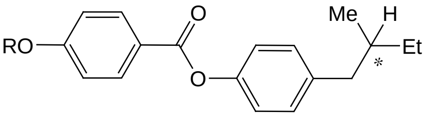
Figure 5.9 Transmission spectral characteristics of colour filter.

5.2.2 Cholesteric/Chiral Nematic Liquid Crystals and Their Applications

The cholesteric phase in liquid crystals is analogous to the nematic phase but is formed by materials that are homochiral. Historically these were derivatives of cholesterol (5.3), hence they were given the name cholesteric LCs. Since other synthetic chiral molecules can also be used on their own or as dopants for nematic LCs *e.g.* (5.4), chiral nematic would be a more appropriate term for those materials not based on cholesterol.



(5.3)



(5.4)

Chiral nematic type LC materials are able to reflect visible light and also respond to temperature changes causing variations in the shade of the reflected

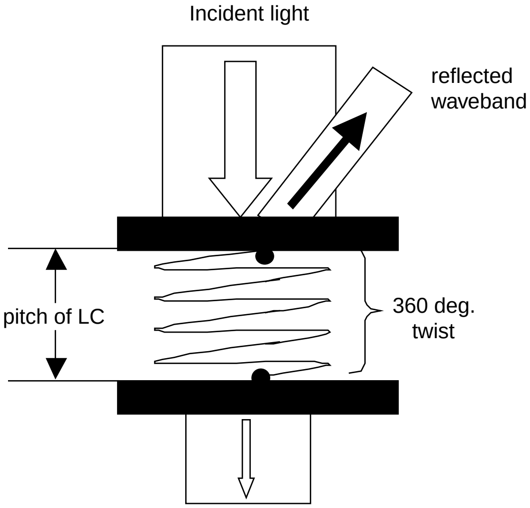


Figure 5.10 Schematic of chiral nematic interaction with light.

colour. The wavelength of light that is selectively reflected from chiral nematic films is circularly polarised in the same sense as the chiral helix, the other 50% of the light is transmitted with opposite handedness. In order to see the reflected light it is necessary to use a black backplate (Figure 5.10).

In nematic LCs the term "director" refers to the average direction of the molecular axes. In each layer of chiral nematic LC molecules there is a gradual twist against the director in adjacent layers. As the layers build up the twist is additive until the total turn is 360° *versus* the original director. The length from the top to the bottom of the layers making up the 360° turns is called the "pitch length", and is normally in the range of 300–800 nm. The wavelength (λ_o) of the centre of the reflected band is related to the pitch length (p) and the average refractive index (n) of the LC phase as:

$$\lambda = \mathrm{np}$$

The bandwidth of the reflected light is given by:

$$\Delta\lambda = \mathrm{p}(\mathrm{n_e} - \mathrm{n_o}) = \mathrm{p}\Delta\mathrm{n}$$

where $\mathrm{n_e}$ is the refractive index parallel to the director and $\mathrm{n_o}$ at right angles to it in the same plane.

The thermochromic behaviour of cholesteric LCs results from the fact that the pitch length, and hence the wavelength of the reflected light, is dependent on the temperature.

Cholesteric LCs can act as hosts for dyes to produce coloured displays, memory-saving panels and electronic paper (see Section 5.2.2.1 below).[7,8] Their temperature-dependent colour change has found a whole range of applications in industrial, medical and general purpose areas, when encapsulated and used in thermochromic inks,[11] as pigments and in copy-safe colours.[12,13] Their selective reflecting capabilities have been applied in colours and filters for reflective displays and projection systems and in reflective polarisers, and their electrical-field-induced switching in displays and electronic paper.

5.2.2.1 Cholesteric Liquid Crystal Displays, Memory Panels and Electronic Paper

The classical cholesteric phase materials show only a weak anisotropic interaction with electric fields and hence are of limited use in electro-optical response applications. Cholesteric phases for these outlets are consequently produced by adding chiral dopants to nematic liquid crystals. There are three main commercial outlets for these materials in displays: in guest-host systems; as three-colour reflectors in projectors; and in electronic notepads and papers.

Guest-Host Systems – interest in the use of these materials as hosts for dyes arises from the potential for making true black LCDs, with a good angle of vision and the avoidance of the costly polarising layers used in TN LCDs.

The dyes used as guests in these guest-host (GH) LCDs are dichroic *i.e.* coloured molecules whose optical absorption is dependent on the angle of incidence which plane polarised light makes with the long axis of the molecule. Dichroic dyes are therefore long rod-like molecules that dissolve in the LC host in a random manner but which, on application of an electric field, reorientate in such a way that their long molecular axis lies parallel with the field in the same way as the LC host. Consequently there is a change in appearance of the LC display from coloured to colourless. This is shown schematically in Figure 5.11.

To be of any value in this outlet the dyes must show certain characteristics:

- Soluble in the LC host;
- Non-ionic;
- Very pure;
- Chemically, photochemically and electrochemically stable;
- Available in a range of colours; able to mix to give a black;
- High absorption coefficient in order to minimise both dye use and the effect on LC viscosity;
- High-order parameter – the transition moment of the dye must align well with the nematic director.

A high-order parameter (S) is essential in order to maximise the contrast between the ON and OFF states. The theoretically maximum order parameter is 1.0, but this is never attained. Acceptable values depend on the system and its use; it has been found that a value higher than 0.73 gives good contrast between the ON and OFF states in simple cholesteric LCDs. For positive contrast GH LCDs, *i.e.* those that use dyes with a positive dichroic ratio, black figures against a white background exhibit a higher contrast than coloured against white. Mixing yellow, red and blue dyes in the correct proportions makes the

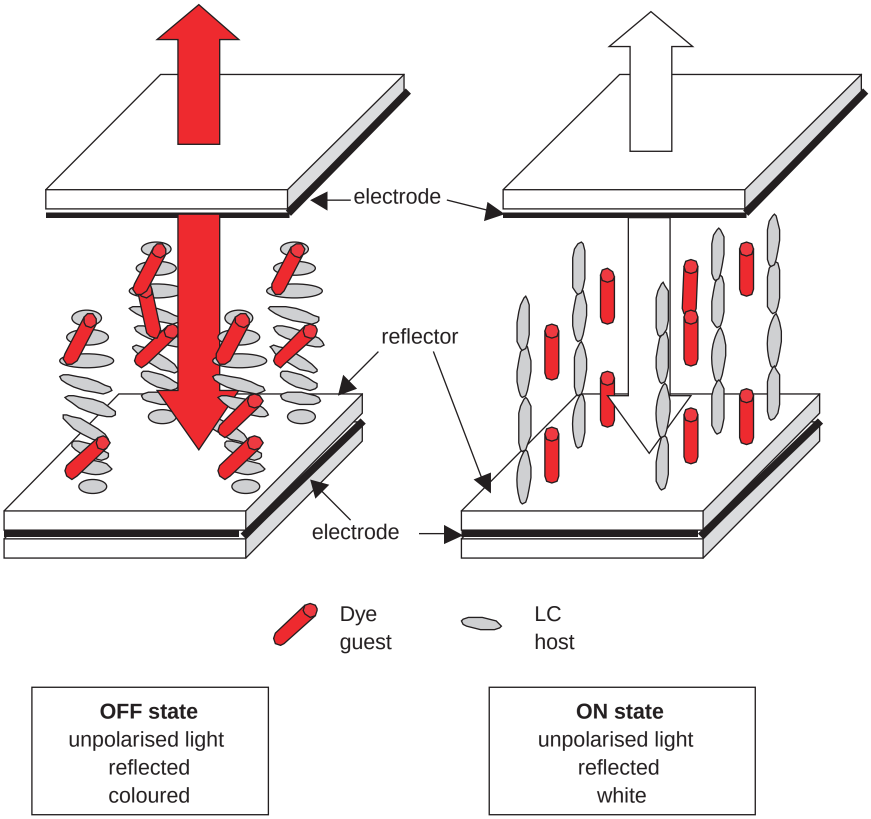
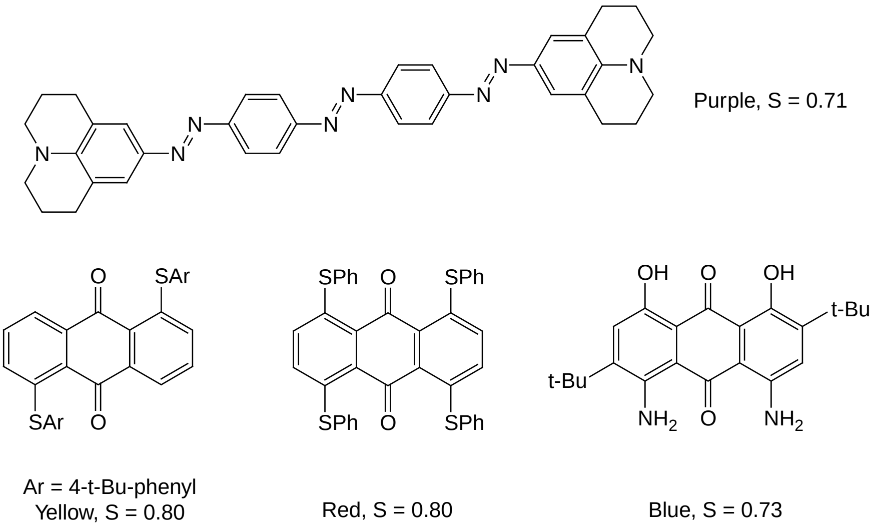


Figure 5.11 Schematic of a reflective mode GH LCD using dichroic dyes and a chiral nematic host.

necessary black dyes.[7] Suitable dyes are rod-shaped, like the LC hosts. Although many chromophore types have been investigated, suitably high-order parameters are almost exclusively displayed by anthraquinones, and less commonly by polyazo types. Typical dyes, together with their order parameters, used in GH LCDs are shown in Figure 5.12.

Whilst great effort was put into GH LCDs in the 1970s and 1980s the main application has been in single-colour information boards, as the drive voltage has proved to be high and even small amounts of dye decomposition can cause unacceptable power drain. However, in recent years there has been a renewed interest in chiral nematic guest-host LCDs as they offer a simple way for constructing thin, larger area displays required for new outlets in erasable electronic papers and related reading materials.

Liquid Crystal on Silicon Displays (LCoS) – this mode is used in modern projectors and projection TVs. It has had a chequered history but projectors have been on the market for some time and large scale HDTVs are starting to appear. In these devices the chiral nematic LC is mounted onto a silicon



Purple, S = 0.71

Ar = 4-t-Bu-phenyl
Yellow, S = 0.80

Red, S = 0.80

Blue, S = 0.73

Figure 5.12 Dichroic dyes for guest host LCDs. S is the order parameter.

wafer above a reflection layer and between alignment layers as illustrated in Figure 5.13a. The wavelength of the light reflected by the chip is controlled by the electronics and the alignment layers on the LC. LCoS-based projectors typically use three such chips, one each to modulate light in the red, green and blue channels. There are several alternative arrangements for such devices and a schematic of one used in projectors is shown in Figure 5.13b.

Electronic paper and flexible displays – this is an area of high activity with several competing technologies of relevance in the context of this book.[14]

1. Electrophoretic Technology (Chapter 2; Section 2.10);
2. Cholesteric LCD Technology (this section below);
3. Electrochromic Technology (Chapter 1; Section 1.5.4.3);
4. Photonic Crystal Technology (Section 5.3.5.1; "P-ink").

Examples of flexible and micro displays using cholesteric LCs are those manufactured by Kent Displays Inc. in the US and widely licensed to other companies.[15,16] Bistable cholesteric liquid crystal displays are purely reflective, do not use polarisers, compensation films or back lights, and are driven with simple row and column addressing (passive drive). Typically the cholesteric liquid crystal is encapsulated by any of the well-known methods, and the encapsulated LCs then laid down between polymer substrates, separated by spacers. The polymer substrates also have transparent conducting electrodes, such as PEDOT:PES, on the inner surface as shown in Figure 5.14.[17] A three-stack layer that produces RGB is needed for full colour. As an alternative to encapsulation it is possible to use polymer dispersed liquid crystals (see also Section 5.2.3). A whole raft of possible applications for these flexible and low-energy displays is envisaged.

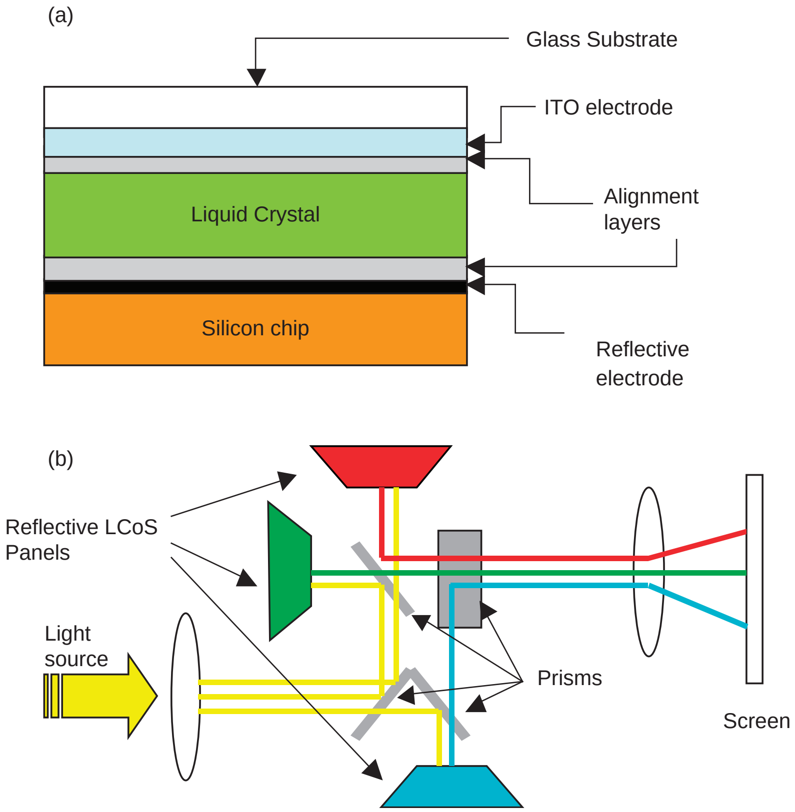


Figure 5.13 Schematic structures of a typical (a) LC on Silicon device and (b) an arrangement in a projector.

5.2.2.2 Temperature Sensing and Novelty Applications

The pitch length of cholesteric LCs varies with temperature and hence so does the wavelength of the reflected light. Cooling a cholesteric LC causes the pitch length to increase and hence move the reflected light to longer wavelengths, resulting in a shift in colour from blue to red. This colour change is reversed on heating. To take technical advantage of this colour-change phenomenon the liquid crystals need to be encapsulated in a polymer matrix, and are therefore closely related to the thermochromic pigments described in Chapter 1 (Section 1.3.3.1).

Microcapsules of cholesteric liquid crystals can be incorporated into a liquid vehicle to give inks or coatings for a variety of applications utilising the temperature-change properties. Obviously they can be used as temperature indicators. For example by coating onto a black substrate a simple, safe thermometer can be constructed for use with babies and young children, and in many medical applications. These inks and coatings have also been used as

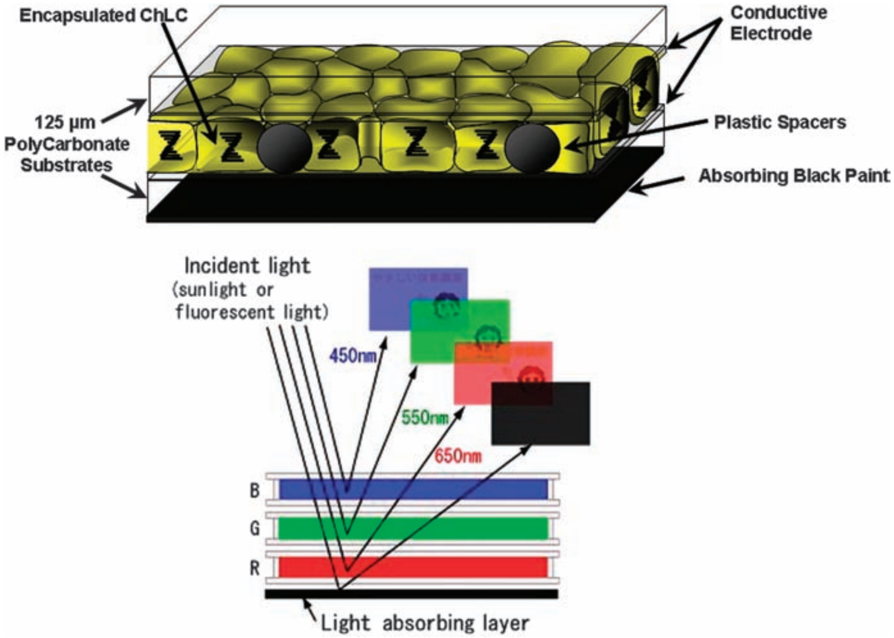


Figure 5.14 Schematic of encapsulated flexible cholesteric LC display and arrangement for full colour.[17]

indicators for thermal hot spots on machines, vehicles and aeroplanes. More decorative applications include logos or images which change colour on clothing when exposed to environmental changes during leisure use, in hot night clubs or when skiing.[11]

5.2.2.3 Polymeric Cholesteric Liquid Crystals and Colour

It is possible to make the colour of a cholesteric LC independent of temperature by locking it covalently into a polymer matrix. This can be achieved by cross-linking parts of the sample at different temperatures or by quenching locally at temperatures below the glass transition temperature.

An attractive process for locking in the colour was developed by BASF, which involves cross-linking of LC oligomers with a chiral monomer in a specific ratio. The cross-linking is carried out using UV and a photoinitiator to give a three-dimensional network in which the colour is systematically adjusted by increasing the content of the chiral component of the copolymer (Figure 5.15). The chiral component causes more twisting in the helix so that, as more is included, the reflected light moves to shorter wavelengths. Because these LCs are transparent they appear pearlescent on a white background and rainbow coloured on a black background. By varying the colour of the background they flip-flop across the colour spectrum by additive mixing (see also

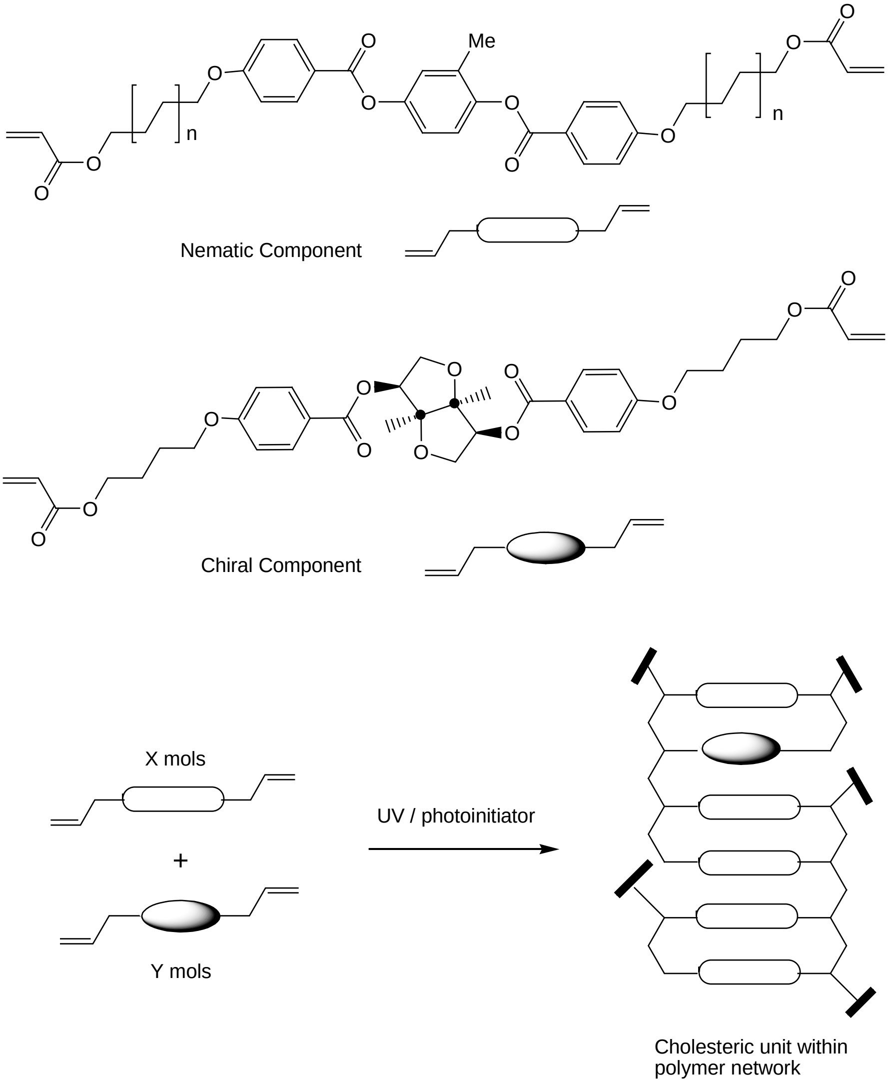


Figure 5.15 Variable colour pigments formed by polymerisation of chiral nematic liquid crystals.

Section 5.2.3). The individual components have been marketed by BASF as Paliocolor LCs, when polymerisation by the customer allows their use in a variety of thin-film outlets, such as the coatings layer in flat-panel screens to improve viewing angle, contrast and brightness.[18]

Pigment particles can be made by breaking into small flakes a film cast from polymeric cholesteric liquid crystals locked into a cholesteric phase.[13] The periodic structure of these pigments results in a strong colour travel effect by reflection, but the fact that this light is circularly polarised allows them to be used in novel applications. An example is in security applications, where left-handed pigments are invisible when viewed through a right-handed polariser.[19] The topic of colour generation by purely physical effects on light is treated more fully in Section 5.3, following.

5.2.3 Polymer-dispersed Liquid Crystals

Polymer-dispersed liquid crystals (PDLCs) are made up of nematic LCs dispersed in a solid continuous polymer matrix. These can be prepared by two main methods.[20]

1. Encapsulation – in this method the LC is vigorously mixed with a polymer dissolved in a solvent. On evaporation the LC is coated with a layer of polymers, giving microcapsules which are distributed through the bulk polymer.
2. Phase separation – in the polymerisation-induced phase separation method the LC is mixed with a prepolymer in a solvent until a homogeneous solution is obtained, at which point polymerisation is initiated. Small droplets of the LCs are formed and become entrapped as the polymer matrix grows. Variants on this include thermally-induced and solvent-induced methods.

Using these methods it is possible to capture the LCs as dispersed droplets, with diameters (*ca.* 1 μm) greater than the wavelength of visible light. These PDLC materials can be switched from opaque to clear using an electrical current provided the refractive indices of the polymer and the LC are well matched. In the off state the directors in the LC droplets are randomly aligned, and when the refractive index does not match that of the polymer, incoming light is scattered and the device appears opaque. In the on state the directors in the LC are aligned, and when the refractive index matches that of the polymer, incoming light is no longer scattered and the device is clear. The process was invented at Kent State University, and these are the materials most widely used commercially to produce large-area, switchable glazing units for energy conservation, and for decorative and safety purposes in buildings.[21] The process is shown schematically in Figure 5.16.

PDLCs are compatible with flexible displays since they are not based on polarisation and provide a wide viewing angle while avoiding problems with polymer-substrate birefringence.[22]

An alternative approach is to add gelling agents to LCs. Small amounts of these organise into a continuous network and divide the nematic phase into many small domains, and thereby a highly scattering state is obtained.[23]

Holographic optical elements can also be made by the preparation of polymer-dispersed liquid crystals using twin lasers in transmission holographic photopolymerisation (see Section 5.4.3.4). They have also been made using photorefractive composites of polymer-dispersed liquid crystals (see Section 5.6.6.3).

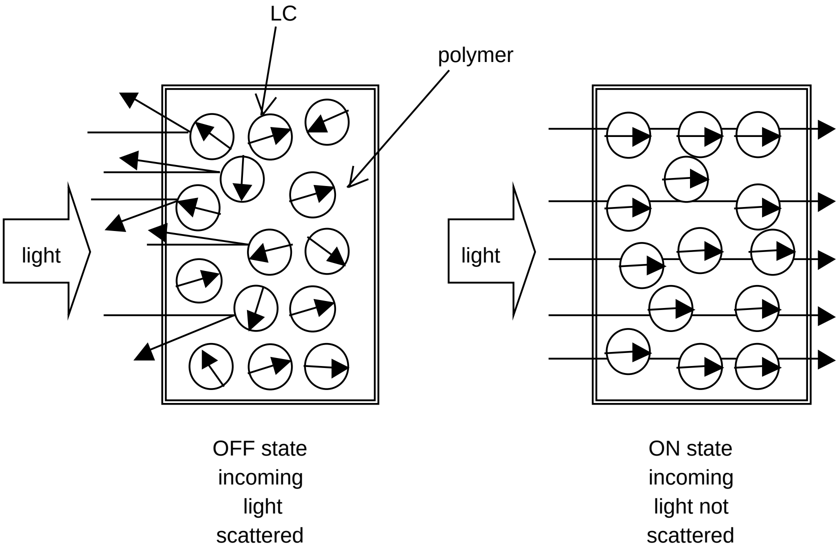


Figure 5.16 Polymer dispersed LC switchable devices.

5.2.4 Side-chain Polymeric Liquid Crystals

Liquid crystal polymers exist in both main-chain and side-chain forms. The side-chain structures offer greater flexibility in the construction of polymers for a variety of effects and potential outlets.[24] They are constructed around a main backbone with the mesogenic groups located in the side chains, separated from the backbone by flexible spacers. One role for the spacer group is to ensure that the polymer does not behave like a rigid rod, and hence they play a big part in lowering the melting point of the polymer. The mesogens on the polymer side chain tend to self assemble, whilst the backbone polymers tend to randomly coil, and the function of the spacers groups is to decouple these two tendencies within the overall macromolecular system. This molecular feature allows the polymer to exhibit both glassy behaviour and electro-optic properties. The mesogens can be rods, discs, amphiphiles or mixtures of all three (Figure 5.17).

The photochromic behaviour of azobenzene side chains can be utilised in a full-colour recording process, where such polymers are used as dopants in cholesteric LCs.[25] There have been many publications on polymers with side-chain azobenzenes, where the induced birefringence of their films under polarised light has been utilised for optical data recording systems.[26,27] The conversion of the *trans* form rod-like nematic phase to the optically transparent, isotropic phase of the *cis* form in side-chain azobenzenes is achieved by irradiation with laser light. The transparent isotropic areas written by the laser can be locked in below the glass transition temperature, thus providing a means of optical data storage.[28,29]

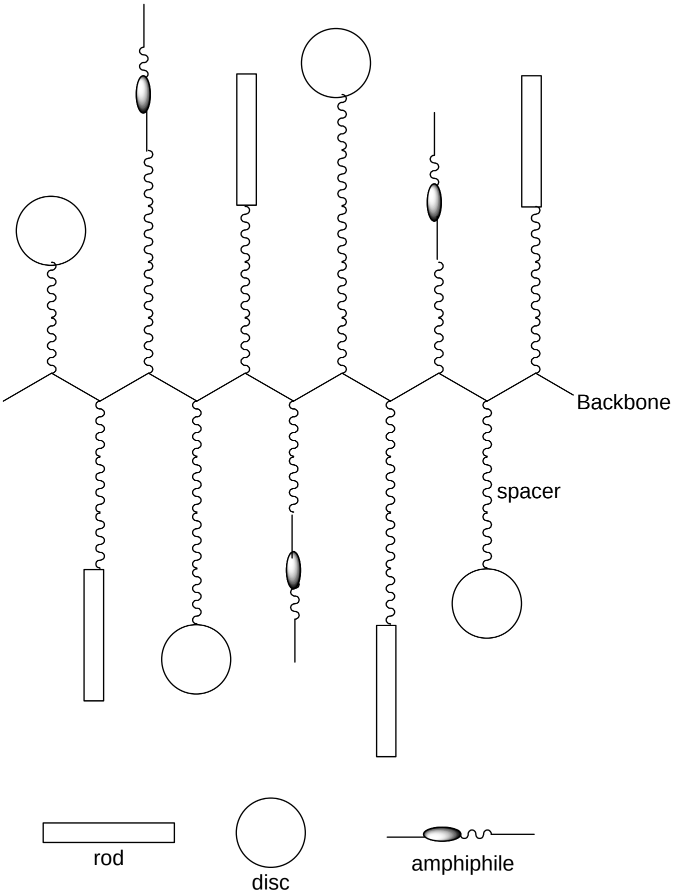


Figure 5.17 Schematic of side chain polymeric LCs, showing possible mesogens.

5.3 Colour from Physical Effects

In our descriptions of chromic phenomena in previous chapters we have drawn analogies with coloration found in the natural world, for dyes and pigments, for biofluorescence and bioluminescence. All these are based on the chemistry of various chromophores. But Nature also uses other mechanisms to generate colour,[30] mechanisms which have only relatively recently begun to be incorporated by scientists and engineers in their design of coloured and colour-changing materials. Unlike most of the earlier discussions, these mechanisms rely on purely physical effects, including scattering, reflectance, refraction, diffraction and interference.[31,32] The colours of the sky and rainbows, as well as the non-pigmentary coloration of many creatures fall into this broad general category. Some spectacular examples from the latter are shown in Figure 5.18.

In combination with one another – and sometimes also with chromophores – these effects can give rise to phenomena such as iridescence, where hue changes

Figure 5.18 Examples of colour by physics in the natural world; left to right: Morpho butterfly (*Morpho menelaus*); jewel beetle; true bug (*Heteroptera*) (uploaded to Wikipedia by Gregory Phillips, Sindhu Ramchandran, John Hill, respectively. Reproduced under the terms of the GNU Free Documentation License Version 1.2).

depending on angle of observation, something absent from conventional dyes and pigments, but shown perfectly by the Morpho butterfly and insects of Figure 5.18. The terms "structural colour" and "colour by physics" are sometimes used to describe this field. Until relatively recently, their exploitation has not gone much beyond the use of natural products such as peacock feathers, pearl essence from fish scales and opal gemstones for decorative purposes.[33,34] In this section we review how they are now being exploited technologically starting with straightforward coloration, through displays and securities, to the beginnings of advanced photonics technologies in the case of colloidal crystals. Section 5.4 on holography is related, and of course we have already encountered physical effects in the way liquid crystals generate colour in the preceding section, especially LC-derived pigments in Section 5.2.2.3.

5.3.1 Lustre- and Colour-variable Pigments

Several names are applied to pigments that show an angle-dependent colour produced by light interference in thin films.[35] For example nacreous, interference, pearlescent, lustre and colour variable are a selection of the more common ones to be found in the literature. Whilst many of the terms are used interchangeably, no attempt is made in this brief overview to rationalise the nomenclature.

5.3.1.1 Optical Basis of Pigments Based on Interference and Diffraction

Lustre pigments comprise platelets of layers of inorganic materials, which reflect light from the surfaces and phase boundaries in the multi-layers. Light reflected from these platelets performs three functions. Direct reflection causes

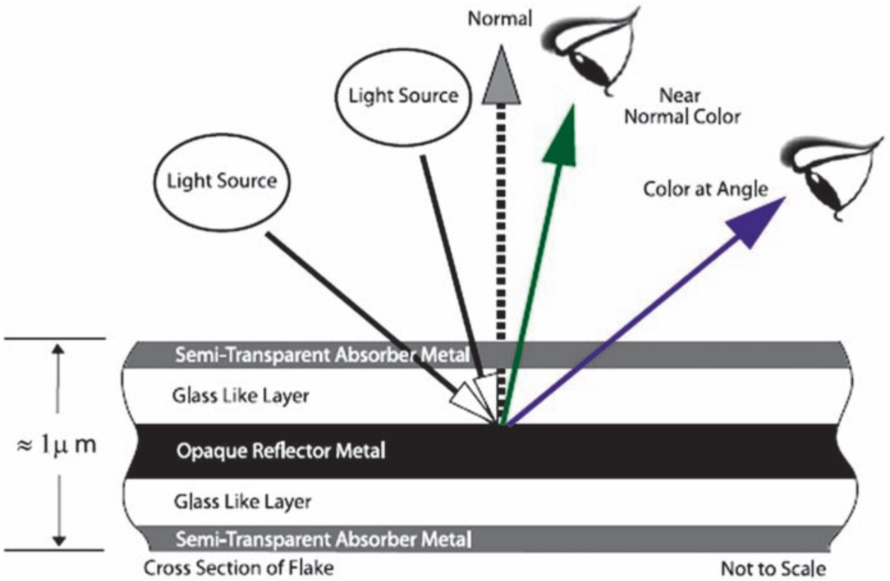


Figure 5.19 Variable colour generation by light interference in a multi layer flake[36] (copyright JDSU with permission).

lustre and lightness; multiple reflections are responsible for the depth of the colour; whilst interference colours result when film thickness is in the range of the wavelength of visible light. This is shown schematically in Figure 5.19. Interference between light waves of the same wavelength can be constructive or destructive, so they can add or subtract with each other. This interaction is angle dependent. Therefore the colour observed is also dependent on the angle of illumination and on the angle from which the pigment film is observed. The generation of colour by a combination of absorption, reflection and diffraction is covered by the general term "goniochromism".

Absorption also plays a part in lustre pigments, since having transparent inorganic pigment layers, such as iron oxide, in the platelets causes them to act as selectively absorbing materials. Incoming light is therefore absorbed or transmitted by the platelets and the observed colour, which again is angle dependent, is a result of the additive mixing of the interference colour with that from the absorbed or transmitted light. In a similar way, because of the transparent nature of the film, a coloured background can also be used to produce new additive colours. Classical absorption pigments can also be incorporated into the resin film, but they must be transparent or extremely finely divided.

A pearlescent effect can be seen in other pigments. In these the surface of a pigment flake is corrugated or otherwise engineered to result in different colours being generated by diffraction. The viewer will see a combination of subtle rainbow-like colours on a plane background (Figure 5.20).

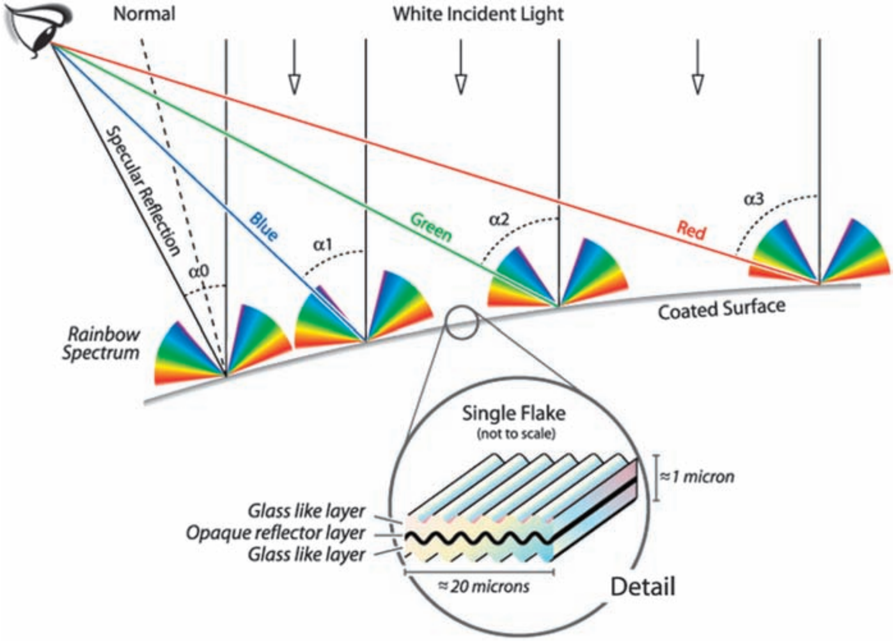


Figure 5.20 Variable colour generation by light diffraction[36] (copyright JDSU with permission).

5.3.1.2 Materials, Construction and Processes

Lustre pigments are based on metal oxide coatings of platelets of mica, silica or alumina flakes, or reflective metal platelets, such as aluminium. The interference colours shown in reflection are based on the thickness of the oxide layers.

For mica-based products the shift is from yellow through red and blue to green with increasing thickness. They are 1–200 μm in size and range from 200–500 nm in thickness. Combination colours are formed by having an additional layer of a transparent pigment on top of a TiO_2 layer: Fe_2O_3 for gold, carmine for red, iron-blue for blue, Cr_2O_3 for green and Fe_3O_4 for black. As shown in Figure 5.19, from the face angle the effect is dominated by thin-film reflection, while from a more acute position (the grazing angle) by the colour of the transparent absorption colour. In combination colours a lustre colour flop is observed from all angles if two layers are matched, but if they are not a two-tone colour pigment flop is seen as well as the lustre. Organic colorants can also be used to form the absorption layer. By using layers of Fe_2O_3 brilliant, intense colours can be obtained from layers only 50–250 nm in thickness. The Fe_2O_3-mica pigments form absorption and interference colours simultaneously, the observed colours again being dependent on the layer thickness.

Silica and alumina are absolutely flat and therefore allow the production of very intense interference colours that can be coupled with a variety of goniochromic properties. The flakes have precisely controlled thickness and high chemical purity and with the highly refractive metal oxides, Fe_2O_3 or TiO_2, produce highly transparent pigments. Varying the thickness of the TiO_2 layer produces silver, pearl and the interference colours of gold, red, blue and green, whilst Fe_2O_3 gives bronze-, copper- and red-effect pigments as already described for mica-based materials. The pigments also demonstrate very good colour travel in coatings. For instance, a colour travel from green to blue to lilac is possible using a two-coat formulation of the Fe_2O_3/SiO_2 pigment in conjunction with a mixture of Phthalocyanine Blue (CI Pigment Blue 15.1) and Phthalocyanine Green (CI Pigment Green 36) and Carbon Black.

Metal reflector-based systems consist of a metal disc, usually aluminium, coated with a dielectric layer, such as SiO_2 or MgF_2, followed by an ultra thin transparent layer or an absorbing layer. The hue of the pigment can be adjusted, within certain limits, by varying the size of the dielectric or low-refractive-index layer. For instance, layers of SiO_2 of thickness 330–350 nm give green-gold shades at the face angle which change to reddish grey when viewed at the grazing angle, whilst layers of 380–400 nm in thickness show red at the face angle that change to gold at the grazing angle.

A more recent modification adds increased sparkle to the visual effect. The thin-layer technology is the same, with hexagonal particles manufactured within very fine tolerance.[36] The available colour combinations are blue through purple to red; red to orange to yellow to green; gold to blue silver; and green through blue and red to orange (Figure 5.21).

5.3.1.3 Applications of Lustre-/Colour-variable Pigments

The market volume of pearlescent and colour variable pigments amongst the broader class of effect pigments is substantial (Table 5.2).[37] There are now three

Figure 5.21 Chromaflair® ColorShift Glitter[36] (copyright JDSU with permission).

Table 5.2 Effect pigments market 2005 (SRI Consulting 2005).[37]

	$ M		*'000 tonnes*
Total	1400	Total	65.0
Paints	888	Metal effect	44.2
Cosmetics	197	Pearlescent	17.6
Plastics	141	Colour variable	3.2
Inks	83		
Other	91		

main manufacturers, BASF (now including the business of the previous Engelhard Corporation), JDSU Flex Products and Merck.

Paints and plastics – a major outlet in the paint sector is as automotive finishes, but there are many other applications. The JDSU website gives a good idea of the wide variety of consumer goods being finished with colour-variable pigments.[38]

Cosmetics – the colour cosmetics sector is huge. Over 5000 new cosmetic products launched between May 2007 and May 2008 were colour-based, roughly a quarter of all new cosmetic launches in that period.[37] The 2006 value of worldwide colour cosmetic sales was an astonishing $36.2 billion. A fair proportion involved pearlescent and colour-variable products, as a quick survey of Google Images will reveal. (Note the high added value for cosmetics implied by the difference between specialist pigment sales (Table 5.2) and finished cosmetic product sales.)

Securities – colour-variable pigments have also found a valuable niche market in security applications, sold as Optically Variable Inks (OVI) by SICPA, and as SecureShift® by JDSU Flex Products.[39] Their variable colour effects cannot be copied, and along with holograms and other invisible colour-based features, such as fluorescent inks, cholesteric liquid crystal polymers and up-converting phosphors (Section 3.2.3.1), they add to the level of security now having to be built into banknotes, passports and other key documentation to protect against fraud (Figure 5.22).[40]

5.3.2 Interferometric Modulator (IMOD) Technology

IMOD technology, commercialised by Qualcomm, involves the same basic interference principle as the colour-variable pigments just discussed.[41] But here the effect is not driven by engineering of materials (chemistry-based), but rather is based on a micro-electro-mechanical system (MEMS), and is solely physical. Because of that it probably doesn't belong in this book, but we mention it for comparison with the other chemistry-based display technologies covered here, and because it is unique. The IMOD display is divided into three sets of pixels to produce reflected RGB colours (Figure 5.23). The interference colour reflected is controlled by the size of the air-filled gap between the surface reflector and the back mirror. The gaps are controlled mechanically and, when

De La Rue MLIS Passport Secure Sample

Passport / Passeport

Type / Type P

Country code / Code de pays GBR

Passport no. / Passeport N° 0000786

Surname / Nom GREY

Given names / Prénoms AMANDA CAROLINE

Nationality / Nationalité BRITISH CITIZEN

Date of birth / Date de naissance 11 NOV/NOV 1971

Personal no. / N° personnel 00000587

Sex / Sexe F

Place of birth / Lieu de naissance BASINGSTOKE

Date of issue / Date de délivrance 05 NOV/NOV 2002

Issuing office / Bureau d'émission LONDON

Date of expiry / Date d'expiration 05 NOV/NOV 2012

Holder's signature / Signature du titulaire

P<GBRGREY<<AMANDA<CAROLINE<<<<<<<<<<<<<<<<<<<<

0000786<<1GBR7111114F1211056000000587<<<<<<24

Figure 5.22 Left: a dummy passport showing hidden colour effects visible only under UV irradiation. Right: two views of a portion of the passport showing the use of colour variable inks as a security feature[40] (copyright De La Rue International Ltd with permission).

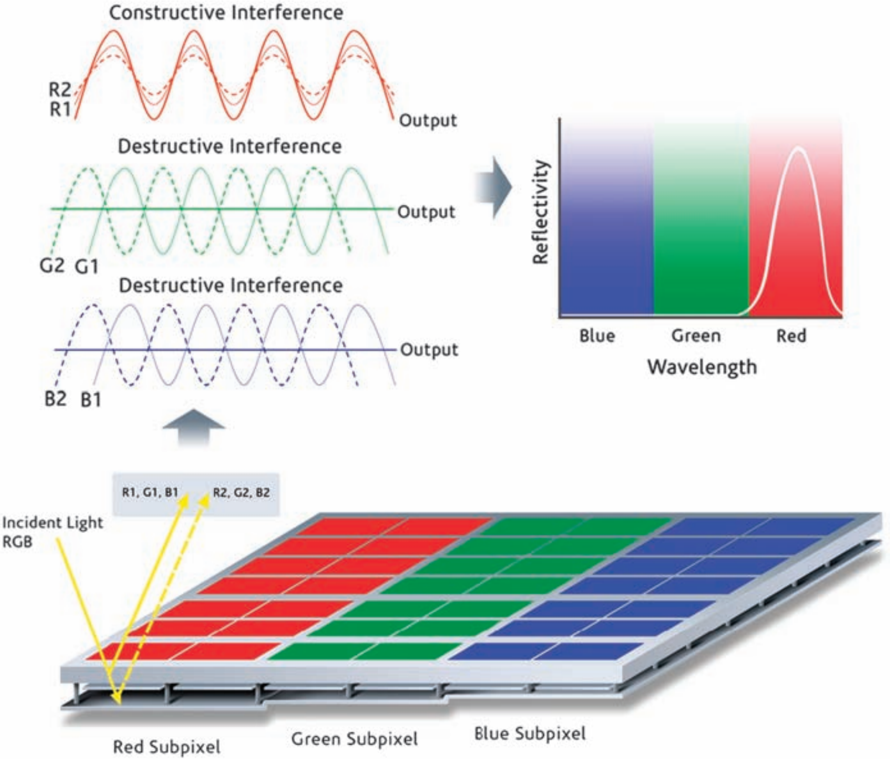


Figure 5.23 IMOD structure showing light reflecting off the thin film stack and mirror interfering constructively to produce red colour, and destructively to give no green and blue reflection[41] (copyright Qualcomm MEMS Technologies Inc. with permission).

compressed, full interference occurs, and a black colour results. IMOD technology is thus an example of electromechanochromism. The speed of the mechanical closing and opening of the pixel gaps is fast enough for real-time display. Furthermore, since the colour appearance is solely due to reflection, the perceived brightness and contrast improves in brighter ambient light *e.g.* sunlight, in contrast to emissive displays such as an LCD.

5.3.3 Iridescent Fibres

Iridescence in many of the textile fabrics that are available commercially is basically a two-colour effect due to the absorption of light from dyes in two differently coloured yarn bundles, constructed in such a way that the reflected light comes from one particular bundle in one direction and from another in a different direction. Whilst this is not truly iridescence it is a useful effect, but the process is very limiting on the construction of the fabric.

A better alternative is for fibres that show multiple colours based on the direction of view. One model for this is a fibre that consists of a concentric core and a sheath, each made from different types of polymers. For instance, constructing a fibre where one component is acid-dyeable nylon and the other basic dyeable nylon makes it possible to dye the sheath and the core in different colours. The colour change (*i.e.* hue shift) then varies with the angle of incidence of light on the fibre. In one example given in the literature, a 19.3-µm diameter nylon/nylon fibre, with 30% core volume, dyed with a blue dye in the sheath and a red dye in the core was predicted to have a shift in hue angle of 40° to the red as the angle of incidence decreased from 70° to 15°. The iridescence effect was most pronounced in the 10–40% range of core volumes. These predicted values were confirmed in practice and a range of attractive colour shifts is seen when incident light hits the fibre at a lower angle than at other locations on the fabric, for instance in folds.[42]

The "Angelina" range of fibres marketed by Meadowbrook Inventions Inc. produce their iridescence in fibres by a true light-interference effect. This is achieved by constructing the fibre from polymers having different refractive indices, similar to that which results from interference in the thin multi-layers of inorganic materials in pigments.[43]

5.3.4 The Blackest Black High Absorption and Low Reflection

Conventional highly absorptive black pigments, such as Carbon Black, still reflect a certain degree of impinging light, and so do not appear absolutely black especially in very bright light. A new material based on a low-density array of carbon nanotubes is reported to give the darkest ever black material measured.[44] Because of its low density and thus refractive index, not much above unity, it has very low reflectivity. Thus irradiation is absorbed, and essentially none reflected (0.045%; three times lower than the previous best).

Such a material could have technological applications ranging from solar energy conversion to pyroelectric detectors.

5.3.5 Colloidal Photonic Crystals

The reflectance, diffraction and interference effects just discussed result from interactions of light in layers of different materials, in effect in two dimensions. There is a whole branch of comparable optical science based on similar effects operating in three dimensions. Here the periodic 3D nature of the materials involved is analogous to the chemically familiar crystal packing of atoms, ions or molecules. Depending on the dimensions and features of the components, new chromic effects become apparent. Such materials comprise photonic crystals.

The angstrom and nanometre scale of regular 3D chemical crystals enables X-ray diffraction. To cause corresponding diffraction of light waves, the dimensions of the particles causing the effect should be of the same order as the wavelength of light, say between 100 and 1000 nm, if we are to include UV and NIR. This is the typical repeat distance within photonic crystals. Construction of photonic crystals had not been easy until it was recognised that colloidal particles also have the same dimension. Colloidal crystals can form when such particles self-assemble into 3D close-packed structures (Figure 5.24, top left

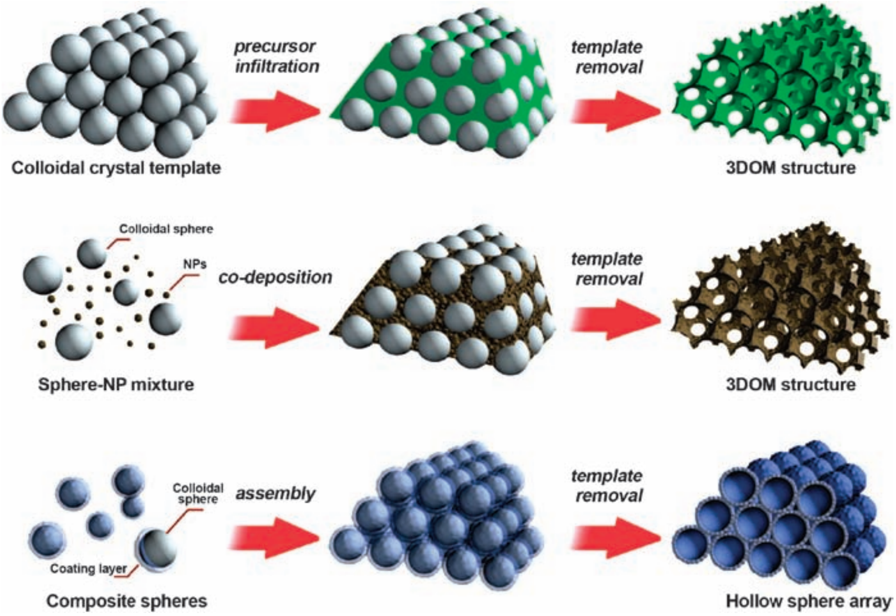


Figure 5.24 Some methods for preparing inverse opal structures or 3D ordered macroporous solids[45] (reproduced with permission of the American Chemical Society).

structure).[45] Because of the resultant optical properties, colloidal crystals are a sub-set of photonic crystals.

The nature of the optical interaction between colloidal crystals and light depends on the materials comprising the colloidal particles and the interstices between them, more especially the difference between their refractive indices, as well as their dimensions. In the limit, a full optical band-gap is possible, where all impinging light is reflected. In other cases, a partial band-gap is found, where some but not all light is reflected, dependent on particular wavelengths, with the result that the photonic crystal is coloured. Again Nature provides precedent. The colour of the Morpho butterfly in Figure 5.18 is due to regular layers of scales and air which is another realisation of a photonic crystal. The blue colour of some birds is due to the optical effects of air-chitin regular periodic structures.[46] The mineral opal owes its various colours to its composition, deriving from natural deposition of regular-sized silica particles.

In fact, opal provides a model for colloidal crystal formation, where silica or other regular sized mineral or polymer spheroidal particles are deposited in a close-packed arrangement to give colloidal crystals, or synthetic opals.[47,48] However, the particles commonly available for such material synthesis have relatively low refractive index, and with air as the interstitial material, the refractive index difference is insufficient to bring about the desired full band-gap. Various modifications have been developed to achieve this goal.

In the most flexible, a conventional colloidal crystal is treated as a template, where its interstitial voids have been filled with another material, sometimes of high refractive index. Examples include organic polymers; carbon (graphitic, diamond, glassy); SiO_2, TiO_2, ZrO_2 and ternary and mixed oxides; chalogenides such as CdS and CdSe; and AuNP. In some cases the filling material is synthesised *in situ* and is derived from suitable precursors *e.g.* UV-curable prepolymers, metal alkoxides (sol-gel), and dispersed nanoparticles.[49] The template materials are then removed, normally by calcining or etching, and clearly a restriction on the interstitial material is that it must withstand this after-treatment. Depending on the material used to fill the voids, a polymeric, ceramic or carbon structure is produced. This is now an "inverse opal", where spheres of air are surrounded by higher refractive index solids. Methods for fabricating inverse opals, including that comprising the shell remaining from coated colloidal particles, are shown in Figure 5.24.[45]

For some photonic applications it is desirable to build point, line or plane defects into the colloidal crystal. "Bottom-up" structure building methods to achieve these have also been developed.[50]

"Top-down" photolithographic techniques coupled with etching and deposition allow construction of photonic band-gap materials, but are not as convenient as the self-assembly methods. Stacked structures of silicon rods (Figure 5.25) have been constructed which show a large photonic band-gap in the infrared region.[51,52] A similar log pile structure, based on GaAs or InP, gave a material which was a breakthrough in photonic band-gap crystals. These

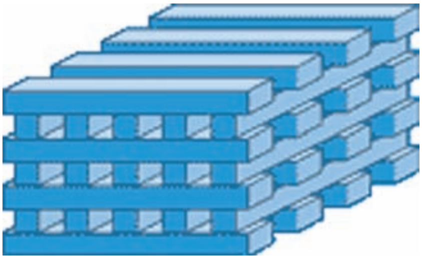


Figure 5.25 Log pile photonic crystal arrangement of silicon or other semi conductor rods.

structures, laid down with nanometre precision, attenuate 99.99% of incident light at optical communication wavelengths.[53]

5.3.5.1 Chromic Phenomena of Photonic Crystals and Their Applications

Many applications have been proposed for inverse opal structures.[54] These include electrochemical sensors, batteries, supercapacitors, medicinal structural materials, catalysts and interfacial materials. In the following sections, we shall only be concerned with the properties of these and other colloidal photonic crystals when they impact on chromic phenomena.

Colour – many inverse opals are coloured, and are potential non-toxic pigments that are colourfast, and available in any colour depending on the composition of the material, the pore size and the relative refractive index of any material filling the pores. Figure 5.26 shows a selection of coloured inverse opals, surrounding a TEM image of 3D-ordered macroporous silica.

Just like conventional dyes, opals and especially inverse opals can change colour under various physical and chemical influences (see Chapter 1), and because of that they have some of the same potential applications.

Solvatochromism – the stopband (defining the colour) of an inverse opal based on a phenolic resin shifts reversibly on sorption of various oils.[55] A variation in refractive index of 0.02 results in a shift of 26 nm, easily observed by the corresponding change in colour. The inverse opals are therefore potentially sensitive and selective sensors for different petroleum oils. The effect of methanol on the colour of the ZrO_2 materials shown in Figure 5.26 clearly demonstrates the novel solvatochromic effect in an analogous system.

Thermo- and photochromism – inverse opal structures based on "soft materials" such as porous hydrogels, formed from various polymers, are especially sensitive to outside physical influences. The partially cross-linked polyacrylamide (5.5) containing an arylazo side group is sensitive to both temperature and light. Its colour is dependent on the size of its pores, and these are sensitive to the amount of water absorbed. As the temperature is increased water is expelled, the pore size decreases and the reflected colour changes markedly (Figure 5.27).[56]

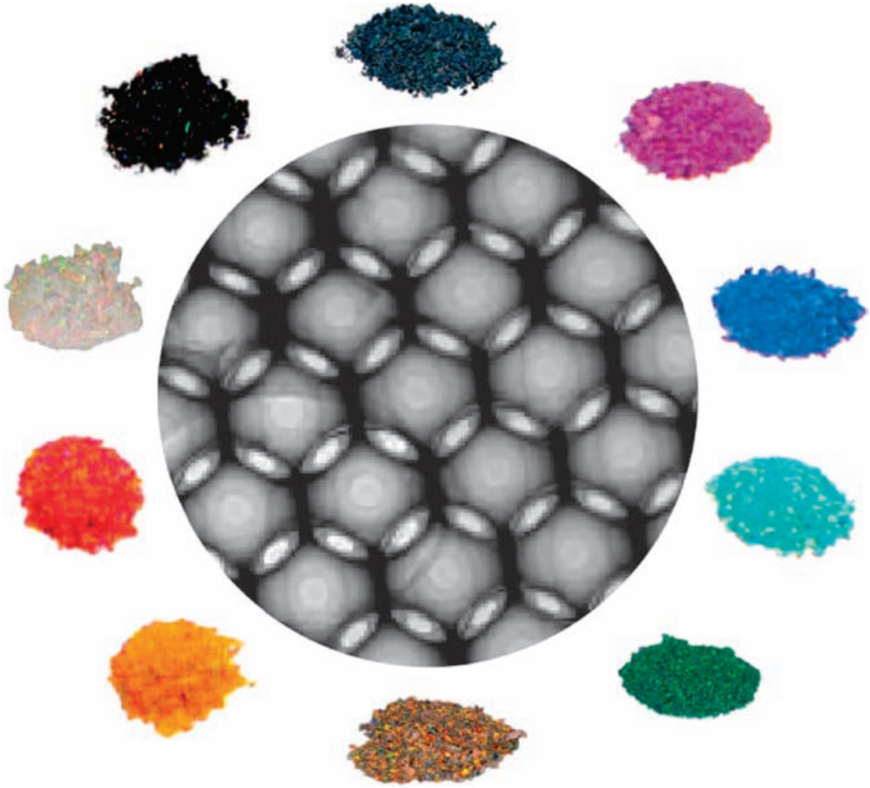
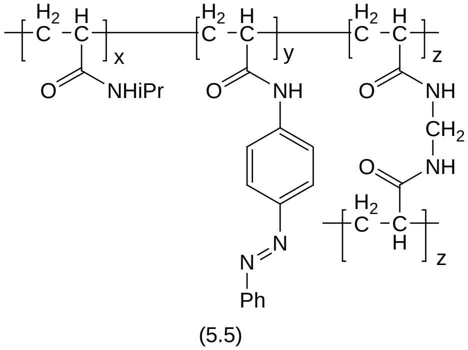


Figure 5.26 TEM image of 3D ordered macroporous silica, surrounded by inorganic samples demonstrating their colour and opalescent properties; clockwise from top: TiO_2, three ZrO_2 samples differing in their pore sizes, NiO, ZrO_2, two ZrO_2 containing methanol in the pores, SiO_2, carbon[45] (reproduced with permission of the American Chemical Society).



(5.5)

Photochromic isomerisation of the arylazo side groups in (5.5) also leads to pore size variation, and marked colour change in the hydrogel. This colour change is reversible on warming, as usual.

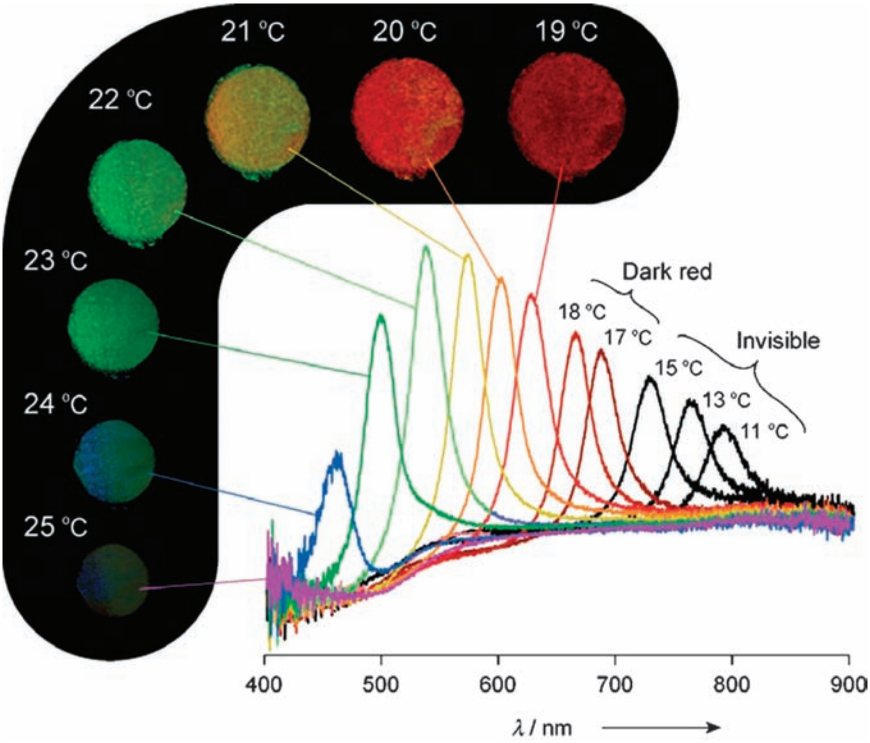


Figure 5.27 Spectroscopic characterisation of a thermochromic porous gel[56] (repro duced with permission of Wiley VCH).

Electropiezochromism; "P-ink" – the colour of an opal structure whose voids are filled with a redox-active polyferrocenylsilane gel is sensitive to an applied voltage. Variation of the latter causes the gel to swell and shrink reversibly and in synch, and simultaneously the repeat dimensions of the opal are altered. As a consequence the stopband wavelength, and thus the transmitted and reflected colours, change. In fact it is possible to cover the colours of the whole visible spectrum with this "photonic ink", or "P-ink", as it has been named by its owner Opalux Incorporated.[57] If P-ink is coated into pixels, the colour of each pixel can be varied at will, depending on its applied voltage. Colour is generated by reflection, and this is an advantage in bright outdoors light, and advertising boards are therefore a potential application. The material can also be integrated into flexible substrates, and could thus form the active component of electronic paper. Other potential applications identified by Opalux include colour-changing walls, portable electronics and fashion accessories and a colour-based on-board sensor to reveal the charge remaining in batteries.

Piezochromism; "Elast-ink" – the colour of inverse opal composed of a flexible, elastic material is sensitive to pressure. As it is compressed, the periodic dimensions of the lattice are diminished, and the resulting stopband, and derived colour, is also changed. A potential application is as another difficult-to-copy security feature, for banknotes and similar. No special equipment would be necessary to detect the Elast-ink – simply applying finger pressure is enough to generate a characteristic change in colour.[57] The phenomenon can be considered as another example of mechanochromism (see Chapter 1, Section 1.9).[58]

Light emission – incorporation of photonic crystals in white-light-emitting diodes has already been mentioned in Chapter 3 (Section 3.9.4.2 and Figure 3.45), where their role is to improve directionality and increase brightness. Photonic crystal lasers are described in the next section of this chapter.

Photonics – we have alluded to the need for a complete band-gap in photonic crystals. The importance derives from the wish to develop all optical information-processing systems, where the photon takes the place of the electron in the analogous electronic systems. Just as the electron is controlled in semiconductors by the electronic band-gap, the requirement is for a photonic band-gap, and this is where the properties of photonic crystals become of interest and importance. The field is vibrant and expanding, but belongs to physics rather than chemistry, so we go no further with this topic, other than to point out these materials are likely to become central to the all-optical computer, when and if it arrives.

5.4 Holography

Another important optical phenomenon that relies on light interference and diffraction is holography, the process by which holograms (interference patterns) are produced.[59] Whilst holograms are best known for the reproduction of near-perfect 3D images of an object in the graphic arts, they also find applications in areas such as laser eye protection, LCDs, diffractive optical elements, optical processing and data storage.

5.4.1 Principles of Holography

A two-beam transmission hologram is produced using a recording laser beam of monochromatic light to reflect wavefronts from a 3D object. A reference beam from the same laser interacts with the object beam causing an interference pattern. The key step is to record the interference pattern on a substrate. A simple schematic representation of the process is shown in Figure 5.28. After development the hologram is visualised by illumination with the same laser beam, which recreates the wavefronts of the object, and produces a 3D image of the object to the viewer.

As indicated in Figure 5.28 transmission holograms need to be lit from behind. When the reconstructing light passes through the plate storing the hologram, the interference pattern diffracts light to give an image at the same position as the original but behind the plate. The back-light effect is

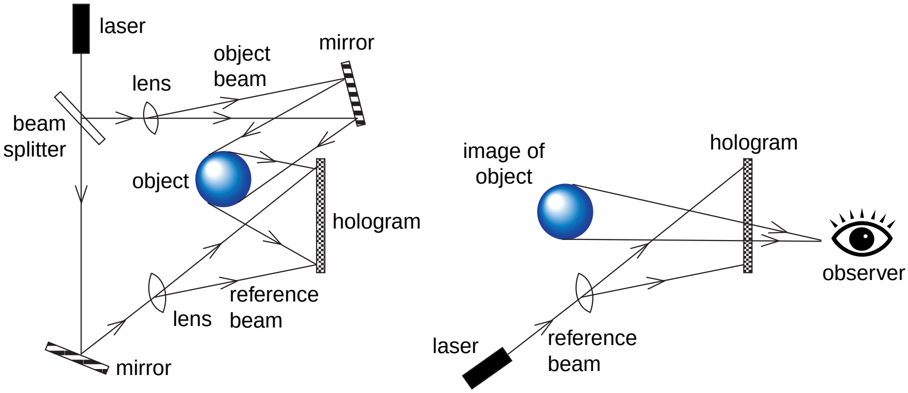


Figure 5.28 Left: the mechanism for recording a hologram; right: visualisation of the image.

conventionally generated by coating the image with a mirrored backing, allowing white light to be used for reconstruction.

Transmission holography is the technique used to mass-produce holographic images as security features on credit cards, tickets and magazine covers. These are usually produced from a master hologram that can be used for the production of embossed images using pressure-sensitive mouldings of metallised plastics or films.

Another way of overcoming some of the problems of back lighting is to use the technique of reflection holography. In this process the recording reference beam is brought in from the opposite side of the hologram recording material, allowing visualisation of the reflected wavefront with white light. The image produced by this method has the appearance of looking through a window, and for this image to be viewed correctly it is necessary for the reconstructing light source to come in from the same direction/angle as when recording. Reflection holograms can be copied by optical processes using commercial films of photopolymers.

It is also possible to record digitally or compute the data required for a diffracting structure and then use this data to produce relief holograms, usually *via* a photolithographic process.

5.4.1.1 Full-colour Holography

To achieve full-colour reproduction in a holographic image, it is first necessary to record the hologram with at least three complementary colour lasers (RGB), and then to be able to record the three (or more) coloured wavefronts simultaneously, but independently, in the same hologram material. In practice, this has been solved by using a krypton ion laser (647 nm; red), a CW Nd:YAG laser (532 nm; green) and an argon laser (476 nm; blue) for writing.[60] The image is recorded in a photographic emulsion, sensitised to respond to RGB. A main problem to be overcome is that conventional-sized silver halide particles in the emulsion have tended to scatter light during hologram reading, particularly in the blue where scattering is most sensitive to particle size. It has been necessary to reduce particle size to 8–15 nm, by restricting crystal growth. The same techniques as used for other nanoparticle pigments are applicable (Chapter 2, Section 2.4.5). Hologram illumination by tuneable white light from LED or OLED sources has given the best quality image reproduction.

5.4.2 Materials Used in Holography

Apart from the laser, the active materials in holography are those that are used to record the image onto a substrate. Several types of material can be used for recording the image. Most may only be used once (they are not erasable and re-usable).

- *Photographic emulsions* have already been introduced above, and are very commonly used. The ultra-fine grain size silver halide emulsions are coated on glass or transparent polymer film. The emulsions are available for response to a range of laser wavelengths. This is the main method for graphics art outlets.
- *Dichromated gelatine* is based on the photoreduction of dichromate to lower oxidation state Cr which binds the gelatin protein more strongly, and influences the local refractive index. It is particularly sensitive to light in the blue and UV regions, but not the red. It is used to produce volume holograms that approach the theoretical limit in diffraction efficiencies.
- *Photoresists* are used in holography because they can be employed to map holographic exposures into surface relief. This property is utilised in the production of embossing masters, reflection and transmission gratings, and in computer generated holograms.
- *Photorefractive materials* are based on nonlinear optically active chromophores in a photoconducting polymer matrix, and are described in Section 5.6.6. Photorefractives are useful where erasing and re-use are required.
- *Photochromics* were described in Chapter 1 (Section 1.2). Photo-initiated isomerisation of a chromophore (*e.g. trans* → *cis* in arylazo compounds) in a polymer matrix can result in refractive index changes. They have also been proposed for rewritable holograms for data storage (see below).
- *Photopolymers* are the most active area of research into newer materials and have wide applications. They are now considered in greater detail.

5.4.2.1 Photopolymers in Holography

Several companies have been involved in the development of photopolymers specifically designed for producing the gratings required for holographic recording. In some systems the holograms were based on differences in the refractive index of the voids created after polymerisation of photoreactive monomers in the bulk polymer. Example commercial systems involved poly(vinylcarbazole),[61] and poly(ethyleneimine/methacrylate).[62] Both of these require solvent post-treatment to enhance the holographic image.

Alternative products utilise the difference in refractive index between a bulk polymer binding material and the polymers produced by polymerisation of photoactive monomers. Because there is no subsequent processing the holographic patterns can be laid down in real time.[63]

The photopolymeric system of DuPont (OmniDex®) consists of polymeric binder resins, reactive acrylic monomers, a dye sensitiser and a radical or charge transfer photoinitiator, *e.g.* DEAW and HABI respectively (see Chapter 4, Section 4.5.2), plus plasticisers. An early OmniDex process for producing the refractive index structures involves patterned exposure by twin laser beams; non-patterned UV exposure at 100 mJ cm ^{2}; and finally heat treatment (2–120 min at 100–160 °C). The pattern produced consists of bright and dark regions due to constructive and destructive interference. Photoinitiation of polymerisation occurs in the bright regions, the unreacted monomers in unilluminated regions migrate to this area as polymerisation proceeds and irradiation with UV fixes the image. The heat-curing step completes the polymerisation and allows further diffusion to give a sharp difference in refractive indices between the light and dark regions. Careful selection of both conditions and reactants gives excellent photo speeds from the UV to the near infrared (350–700 nm).[63]

InPhase Technologies use this two-chemistry approach as the basis of their holographic data storage system (below).[64] The holographic data storage system of STX Aprilis differs. It involves cationic ring-opening polymerisation (CROP) of epoxide monomers during the laser irradiation.[65]

Desirable properties of a photopolymer for data storage include:

- high dynamic range;
- high photosensitivity;
- dimensional stability;
- high optical quality;
- environmental robustness;
- readout durability;
- ready manufacture.

The dimensional stability issue is important, as a problem with photopolymers for holographic application is their shrinkage as polymerisation progresses. Relatively well-separated non-bonded monomers become relatively tightly packed on covalent bond formation. This is reflected in the actual dimensions of the refractive index grating generated by the wavefront interference. In display holograms this results in a shift in the base colour of the observed hologram, and may not be significant. However, for data storage, where precise reading of the hologram is essential to enable accurate recovery of stored data, shrinkage is a serious problem. Both the two-chemistry and

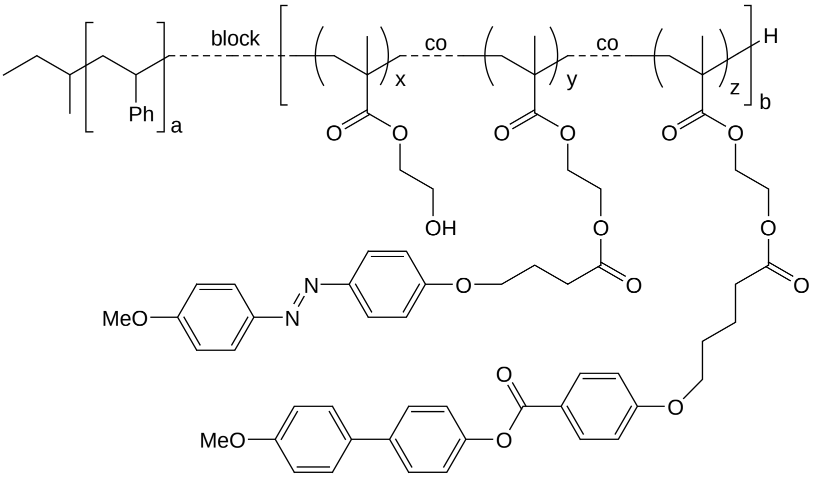
CROP approaches reportedly minimise this problem. Shrinkage can also be compensated by development of the electronics and optics of the overall data storage system.

Photopolymers can only be used for WORM systems. For data erasure and re-writing, other holographic materials are required (see Section 5.4.2.2 following).

Switchable diffractive elements can be produced by one-photon, holographic photopolymerisation of active monomers in the presence of an inert liquid crystal producing polymer dispersed LCs (see also Section 5.2.4).[66] Using spatially periodic polymerisation gives planes (150 nm to several micron spacing) of small (50–200 nm) LC domains separated by dense polymer. Alternatively dye-sensitised two-photon-induced polymerisation (Chapter 4, Section 4.5.2) of acrylate monomers in the presence of a nematic liquid crystal, using an ultra-fast laser in a transmission hologram set-up, gave good delineation of polymer-rich and LC-rich regions with a grating spacing of 3.0 μm.[67]

5.4.2.2 Rewritable Holographic Media

Rewritable holograms are of particular interest for multi-writable storage systems. One of the main ways to achieve this is *via* liquid crystals. In particular, photo-absorbing units are incorporated that respond physically to impinging light, and cause a change in the local refractive index. The effect can be locked in for as long as required, but then removed by further treatment, for example by heating or further broad-band irradiation.[68] The polymer (5.6) is the active component of a recent well-characterised system.[69] The arylazo dye unit is a convenient source of photoactivity, and on laser irradiation can undergo *trans* to *cis* isomerisation with the usual substantial change in shape. Concerted reorientation of the adjacent but non-absorbing mesogens in the local environment is sufficient to cause a refractive index change between illuminated and non-illuminated bands of the interference pattern. However, for mass volume data storage it is required to be able to write many holograms in the storage material necessitating absorbance at different depths. If the concentration of azo dye is too high, the writing beam will be absorbed in the first few layers and never penetrate to deeper material. This has been overcome by diluting the chromophore concentration in a block copolymer configuration, with inert polystyrene as the co-block. The whole is further diluted in a PS matrix. Further benefits of the copolymer arrangement are, first, that the dye-mesogen blocks are concentrated in spherical micro-phases with diameters about 10–20 nm and, second, there is no surface distortion of the material. This material was injection moulded into films 1.1 mm thick, and holograms written with an Ar ion laser at 514 nm. Stability was good. The same source but at higher power was used for erasure (*cis* to *trans* reversion). The gratings generated were read with a laser diode at 685 nm, well away from the absorption envelope of the azo dye to avoid further isomerisation (forward or back). For this material it has been possible to write 80 angular multiplexed holographic gratings with uniform diffraction efficiencies.



(5.6)

5.4.3 Applications of Holography

5.4.3.1 Holographic Data Storage

The continuing massive increase in data being generated by various IT-dependent organisations and industries is putting pressure on current methods of data storage. To date these are based on surface (2D) properties of magnetic tape, CDs, DVDs or Blu-ray media. Although ways to pack more and more data onto a given surface area are continually being developed, there is nevertheless a need and opportunity for new data storage technology. Moving from 2D to 3D media is an obvious extension, and the multiplexing possibilities of optical processes has led to holography as one realistic option for data storage, at orders of magnitude higher capacity levels at higher write-read speeds.

The basic process involves digitisation of whatever data are to be stored, and their representation essentially as squares on a massive irregular chequers board, with black squares representing one binary value (say "1"), and white the other ("0"). These data are then written page-wise onto the object beam of a holographic writing device by a spatial light modulator. Interaction of the modulated object beam with a reference beam (Figure 5.29)[64] allows writing of a phase grating in the holographic storage medium (a photopolymer as introduced in Section 5.4.2.1). The data may then be read with a reference beam and passed into a detector such as a CCD to convert the optical signal to electronic, and thus recover the original data. In this way data can be written and read a page at a time, rather than bit-by-bit. Furthermore by multiplexing data into a single holographic storage unit the storage capacity is well above that of conventional media.[64]

The potential impact of holographic and other high-density 3D data storage (Section 5.6.5.2) on society has been recognised by their classification as an "emerging technology" in the IT field.[70]

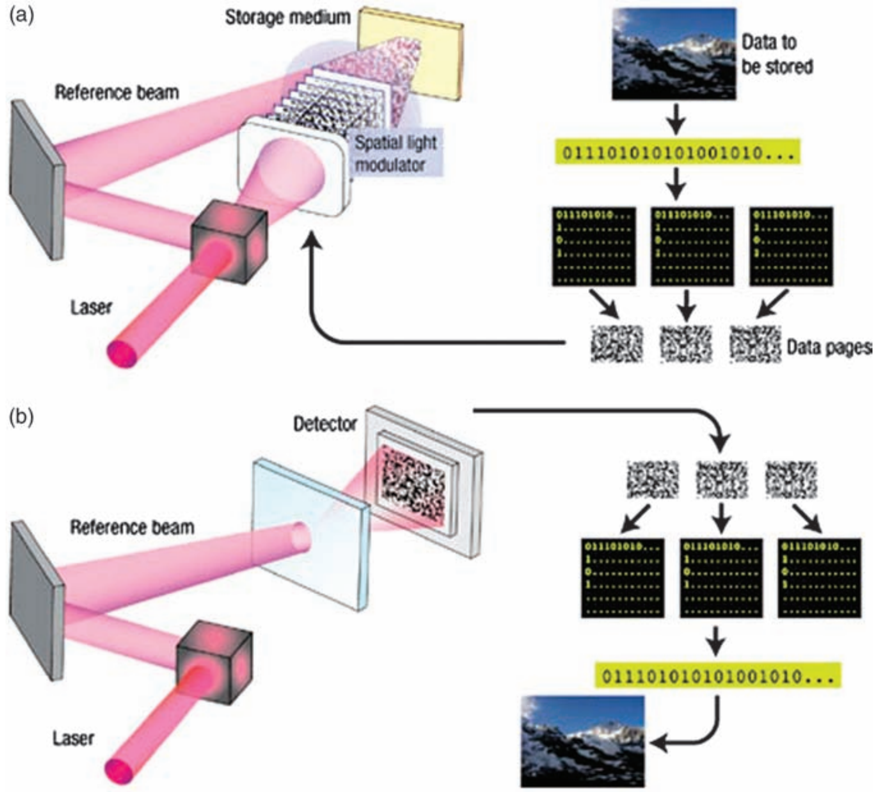


Figure 5.29 Data storage by (a) holographic recording, and (b) reading processes[64] (reproduced with permission of Nature Publishing Group).

InPhase Technologies, an off-shoot of Bell Labs, has developed the Tapestry 300r system.[64] This is designed for specialist storage of high-volume data, such as that being generated by government agencies including the military, and by broadcasters, medical firms, IT companies and the music and entertainment industries. For the latter, high-definition movies must be stored digitally for periods as long as 100 years. Tapestry is not aimed at the general mass consumer market. Using a GaN laser, page sizes of 1000×1000 pixels (up to 10 μm size) can be written at kHz frame rates. 300 Gb can be stored in the first-generation 13-cm discs, while later versions at 1.6 Tb disc ^{1} are already planned. Data transfer proceeds at 160 Mbits s ^{1} (960 Mbits s ^{1} planned). Prototype versions of Tapestry 300r have been implemented apparently very successfully by users such as Turner Network Television, but commercial birth-pangs have evidently been far from painless. Despite several announcements of Tapestry's impending general commercial launch, it has yet to appear. The most recent news is that it is due late 2009.[71]

Meanwhile, Polaroid spin-off STX Aprilis has its own holographic data storage material.[72] Here, the expected outlets will be more consumer-oriented, with developments being made alongside third-party optical storage developers. The media has been used to demonstrate a 1 gigabit holographic storage application with real-time recording and reading from a continuously spinning disc. STX Aprilis claims the highest dynamic range and recording densities per unit thickness in its CROP holographic photopolymer materials for both data page and micro-hologram implementations.

Optware (Japan) has a totally different holographic storage technology known as the Holographic Versatile Disc (HVD).[73,74] This is targeted to store 9 terabytes of data, although the current maximum is 500 Gb. Again, despite an original announced launch date of end 2006, by March 2009 there has been no reported launch.[75]

Not surprisingly, commercial re-writable holographic storage media are yet to appear.

5.4.3.2 Graphic Arts and Design

This is the area where holography comes into contact with the general public *via* its use in publicity and advertising materials, packaging, giftware and, increasingly, as security tags on currency, credit cards and consumer goods, since holograms are difficult to imitate and cannot be photocopied. The technology has come a long way from the early days, some 40–50 years ago, when grainy monochrome images were produced by enthusiasts, to the position today when high-definition, full-colour holograms are manufactured commercially using newer media, such as photopolymers.

The holograms used in credit cards and other security applications are produced mostly by embossing a relief pattern on the surface of a film. Metallisation at the rear of the hologram acts as a mirror for reflected light enabling good visibility of the image. Mass production of photopolymer holograms involves the use of photo-lithographic techniques using a master hologram to produce a printing plate or photomask. Adhesives are applied to the rear of the hologram so that it can be fixed to whatever other medium is to be used in the application.

5.4.3.3 Large-scale Displays

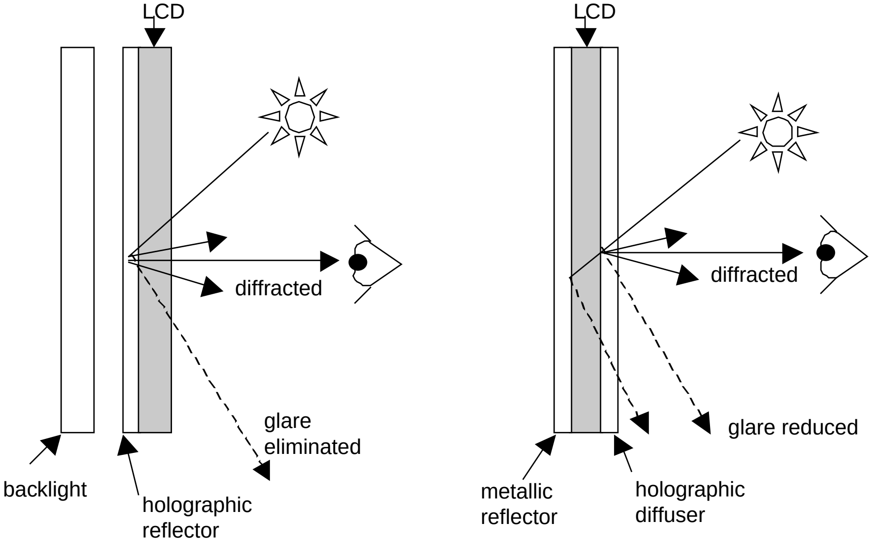
Larger-scale 3D holographic displays viewable from 360° have military and civilian applications such as geospatial awareness, training, simulation, situational awareness, architectural and urban planning, medical visualisation, chemical modelling, CAD, gaming and 3D data visualisation. It is of course difficult to reproduce the 3D aspects of holograms in a 2D illustration in a book like this, but short videos can give a good impression. As two examples, the website of Zebra Imaging has several impressive examples from different technologies,[76] and others are to be seen on the View Holographics website.[77]

5.4.3.4 Holographic Optical Elements in Liquid Crystal Display Systems

As discussed in Section 5.2, one of the big problems faced by manufacturers of LCDs is the need for a strong back light to make the panel visible in poor ambient light. This requires a relatively heavy battery and/or regular recharging with consequent disadvantages in weight for portability, as in laptops and mobile phones requiring real-time connection to the Internet in full colour. For this reason in a lot of applications a reflective "mirror" is placed at the back of the LCD to replace the power-driven back light. In either case there is the additional problem of glare, which affects the viewing angle of the display, requiring constant adjustment in its position by the user. More effective use of incident light would be beneficial to LCDs.

In a backlit application the holographic element (HE) is placed between the back light and the LCD front panel. Ambient light is diffused and reflected by the HE at an angle perpendicular to the display, increasing the brightness by 4–5 times, and glare is eliminated. The application area for this HE is in monochrome, hand-held displays, like mobile phones. In reflective-mode LCDs the HE is placed at the front of the LC panel and acts as a light diffuser, giving much reduced glare and increased brightness in colour displays. The two systems are illustrated in Figure 5.30.

Coloured LCD displays require a colour filter plate consisting of RGB pixels, the construction of which using classical absorbing dyes and pigments is



(a) Holographic reflector (b) Holographic front diffuser

Figure 5.30 Holographic elements in LCD incident light management.

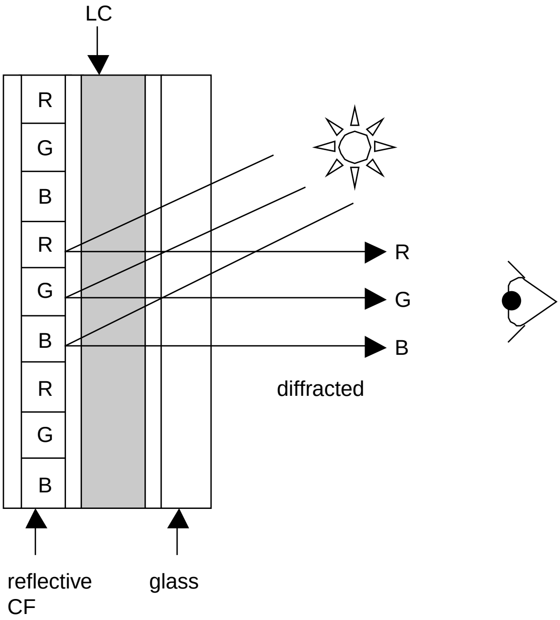


Figure 5.31 Reflective RGB colour filter in LC display.

described in Section 5.2.1.3. An alternative system using reflective colour filters became available from DuPont. In this reflective system, the proper colour is reflected at each holographic pixel, resulting in increased brightness as none of the incoming light is absorbed. The operating mechanism of a reflective colour filter is illustrated in Figure 5.31.

A holographic colour filter and splitter has been devised for use in rear-projection LCD displays in HDTV (DuPont/JVC). In this system the holographic colour splitter separates the incoming light into its RGB components and focuses them down onto the RGB pixels in a single-panel reflective colour LCD. The reflected colours then pass back through the holographic element to the projection optics (Figure 5.32).

5.4.3.5 Holographic Optical Elements in Other Engineering Designs

Holographic optical elements can be used more widely, and take the place of many conventional optical elements. They are used in architecture as lenses, shades, light guides to augment natural lighting and diffusers.[78,79] Other common examples are as beam formers on traffic signals, and as diffusers of arrays of LEDs, to homogenise an array of essentially independent LEDs into a single panel of more uniform coloured lighting (Figure 5.33).[79]

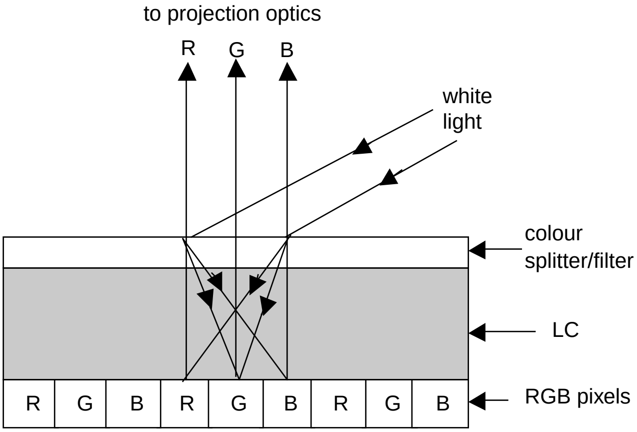


Figure 5.32 Holographic colour splitter/filter for rear projection LC HDTV.

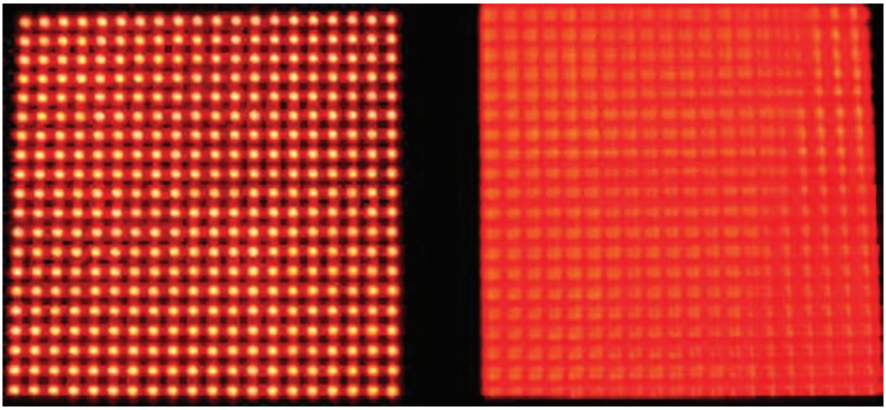


Figure 5.33 Use of a diffuser on a 20×20 array of LEDs to give a panel of uniform light.

5.5 Laser Diodes

So many of the phenomena covered by this book rely on the interaction of materials with coherent light from a laser for their effect that descriptions of various types of lasers and their mode of action, in some form or other, appear throughout the text. For instance, dye lasers and the basics of lasing action are covered in Chapter 3 when discussing dyes for lasers (Section 3.5.6). Light-emitting diodes (Section 3.9.5) are very closely related to laser diodes, the subject of this section, whilst an overview of the operating wavelengths of a variety of lasers is given in Chapter 4 when laser addressable compounds are being discussed (Section 4.2). Laser diodes are numerically the most common type of laser, with 2004 sales of approximately 733 million units,[80] as compared to 131,000 of other types of lasers.[81]

5.5.1 Inorganic Semi-conductor Laser Diodes

Basic laser diodes and light-emitting diodes (LEDs) consist of a *p-n junction*, where free electrons in n-type materials diffuse under forward bias into the p-type region material and there encounter a majority of holes and recombine. When the materials on either side of the junction are derived from the same semi-conductor it is called a *homojunction*, and a *heterojunction* when the semi-conductors are different. There is usually an undoped layer between the p- and n-type regions. All p-n junctions emit light on the passage of forward-biased current, but laser diodes are so constructed that light emerges from the ends rather than through the wide gap as in LEDs. Light manipulation and amplification in laser diodes occurs in the undoped active layer and is achieved by the following means:

- A narrow active layer contains holes or grooves across the whole length;
- The ends are cleaved, polished, made flat and parallel (*mirror facets*);
- The sides are roughened to trap light inside the crystal;

The light, which is generated from the p-n junction, is reflected back and forth between the polished ends, causing stimulated emission and the lasing action, providing the applied current is sufficiently high. The laser beam of coherent light comes out through a narrow exit at the end of the laser diode. This simplified scheme is illustrated in Figure 5.34.

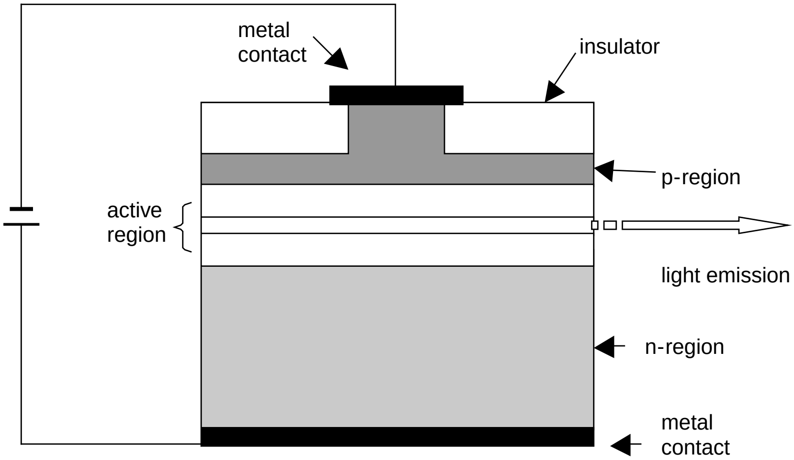


Figure 5.34 Schematic representation of a laser diode.

The development of laser diodes has always followed that of LEDs. Those operating in the infrared and red region, based on GaAs, have been available for decades. However, UV and blue LEDs have only been commercialised relatively recently (1995; see Chapter 3, Section 3.8.1) and lasers even more recently (by Nichia Corporation, 1999).[82] The driving force behind the research for a blue laser is that data storage density increases proportionally with the square of the light source frequency. Consequently, switching from a red to a blue laser for writing a DVD would show a roughly four-fold increase in capacity, *i.e.* rise from 4–5 Gb to 16–20 Gb. Additionally, the use of blue lasers in laser printers would improve the resolution of the image by a similar amount. Operating at or near the UV end of the visible spectrum increases the potential for the laser addressing of organic materials, such as dyes, in medical imaging and diagnosis, and in photochemical applications, such as photolithography.

The target had been a true-blue laser, characteristic wavelength of 425 nm, operating at room temperature. The early work in this area concentrated on the use of II–VI materials, *e.g.* ZnSe, since they possess larger band-gap energies making them potentially better suited to operation at the higher energy end of the visible spectrum than III–V materials, which are better for the infrared end of the spectrum.[83] However, as discussed under LEDs (Chapter 3, Section 3.9.2) Nichia's first commercial lasers, having lifetimes in excess of 10,000 hours, are actually based on the III–V material gallium nitride (GaN).[84,85] Their laser diodes are based upon AlGaN semi-conducting materials and are very complicated multi-layer devices, as can be seen from the schematic of the earliest blue laser diode shown in Figure 5.35.[82] The Nichia laser diode emits 5 mW of 400 nm (violet) wavelength at a current of 40 mA and a voltage of 5 V.

5.5.2 Organic Lasers

Organic lasers offer many attractions, not least of which is the ease of fabrication of laser diodes, especially if the materials are polymeric. Organic materials could be printed, laminated or bent, and made into micro or macro structures. Additionally they could cover a wider spectral range and be more easily tailored for lasing at a specific wavelength than inorganic materials. Consequently there are distinct economic advantages from having lasers made from organic materials and this is stimulating research in many centres.[86,87]

5.5.2.1 Luminescent Conjugated Polymers

The use of conjugated light-emitting polymers in the construction and commercialisation of organic LEDs is described in the section on electroluminescence phenomena in Chapter 3 (Section 3.9). The rapid expansion of the development work on LEDs has inevitably led to the examination of luminescent conjugated polymers as materials for constructing laser diodes.

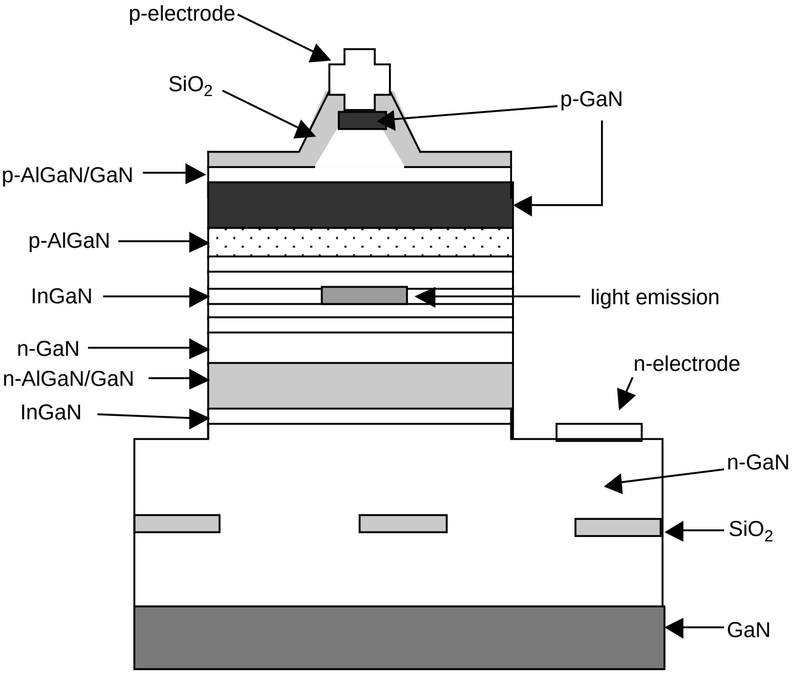


Figure 5.35 Schematic of GaN based blue laser diode.

The lowest excited states in luminescent conjugated polymers are very similar to those of the dyes used in dye lasers (Chapter 3, Section 3.5.6). Therefore the conjugated polymers can be used to achieve population inversion by optical pumping as with the laser dyes.

Examples of the optical pumping of solutions of luminescent conjugated polymers include laser action at 596 nm of poly(2-methoxy-5-(2′-ethyl-hexyloxy)-*p*-phenylenevinylene) (MEH-PPV) using excitation with 6 ns Nd:YAG third harmonic pulses (354.7 nm).[88] Tuning of hexane solutions of the copolymer poly(2,2′,5,5′-tetraoctyl-*p*-terphenyl-4,4′-xylene-vinylene-*p*-pneylenevinylene) (TOP-PPV) was possible between 414 and 456 nm, similar to the classical coumarin laser dyes.[89]

An important difference between luminescent conjugated polymers and laser dyes is that the former still exhibit strong optical gain in the solid state. This property means that they can be used to produce stimulated emission in thin films of these materials.

The first report of lasing action (at 600 nm) in the solid state involved the use of MEH-PPV as a blend with dispersed nanoparticulate TiO_2, which acted as scatterers to achieve lasing.[90] This was quickly followed by the first non-blended, microcavity laser, using PPV, that could support high current densities.[91] A range of semi-conducting polymers has now been shown to exhibit lasing action under optical pumping, using a variety of physical structures and geometries.

5.5.2.2 Single-crystal Organic Materials

Although stimulated emission from single crystals of conjugated aromatic molecules, such as anthracene, has been observed for some considerable time, its practical realisation in lasing has only come about following pioneering work by Lucent Technologies' Bell Laboratories, using electrical injection rather than optical pumping.[92] One of the problems with the use of organic materials is the positioning of the electrodes, which is deleterious to high-power light emission. This problem was overcome by using field effect transistors (FETs) instead of electrodes on either side of the organic crystal. The light emitter used is highly purified tetracene, grown as single crystals by vapour phase deposition until the face dimensions are some square millimetres and the thickness 1–10 mm. The small size of these crystals means that the circuitry has to be built up by evaporation through shadow masks. The structure of the tetracene laser is shown in Figure 5.36.

Upon applying a potential difference between the top and bottom FETs as a pulse, one side of the crystal is enriched with electrons and the other side injected with holes. The next pulse causes electron-hole recombination and the emission of light. The crystal acts as both a waveguide and a resonator between the reflective crystal–air interfaces, leading to the eventual production of a yellow-green coherent beam. The lasing action in these materials occurs at high current densities ($>500\,\mathrm{A\,cm}^{2}$) at 5 K and an emission wavelength of 575.7 nm.

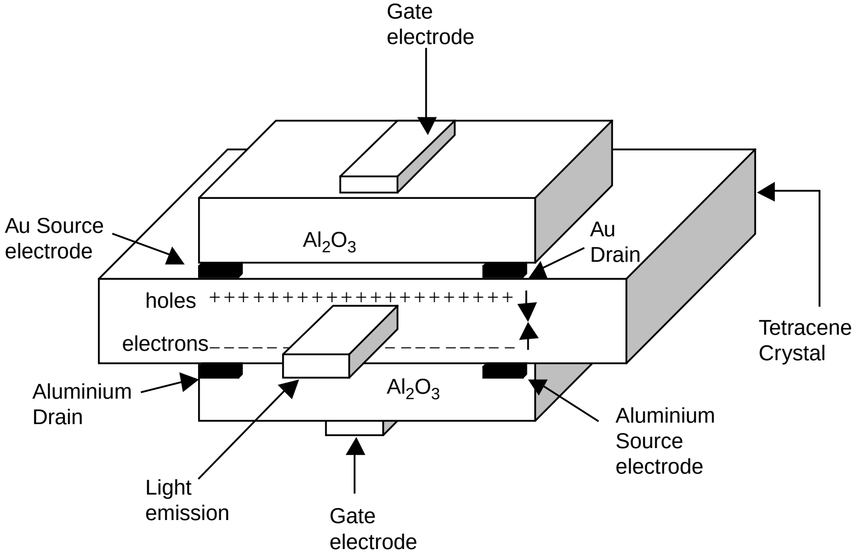
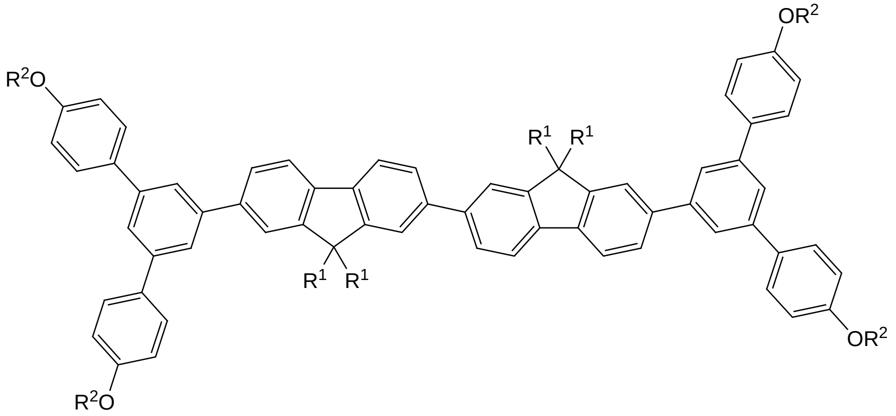


Figure 5.36 Tetracene laser using FETS for charge injection.

5.5.2.3 Two-photon Lasing in Dendrimers

Two-photon pumping of laser gain media is becoming of interest because of the suitability of readily available red or NIR laser diodes to generate up-converted emission toward the blue end of the visible spectrum. Application where the gain medium is a rare earth ion has already been mentioned in Chapter 3 (Section 3.2.3.3). Organic semi-conductors such as the conjugated polymers already discussed in Section 5.5.2.1 are also attractive candidates, because of their high gain coefficients, low concentration quenching and optical losses, and ultimately their ease of processing. Besides these, conjugated dendrimers have additional attractions because of their modular construction, leading to flexible molecular engineering, and they are also 2PA in ideal cases. Examples are the series of difluorene-cored first-generation dendrimers, typified by (5.7), which are showing potential as two-photon laser gain materials, where the emission can be tuned between about 412 and 422 nm.[93]



(5.7) R^1 = *n*-hexyl; R^2 = 2-ethyl-hexyl

5.5.2.4 Liquid Crystal Lasers and Laser Displays

Displays based on lasers are now appearing. In these, pixels of light emission are generated from separate RGB laser sources. They offer desirable advantages over conventional displays: wider shade gamut, higher resolution and contrast ratio, and high colour saturation, amongst others. A disadvantage is that with semi-conductor lasers, for example, three differently fabricated units are required to achieve the RGB trichromat. Full integration is desirable, and a single-material alternative is an important goal. Towards this, potential solutions based on liquid crystal lasers are now appearing. In one, a trichromat (or more) can be generated from a single liquid crystal cell, having structural variation due to its macroscopic composition.[94]

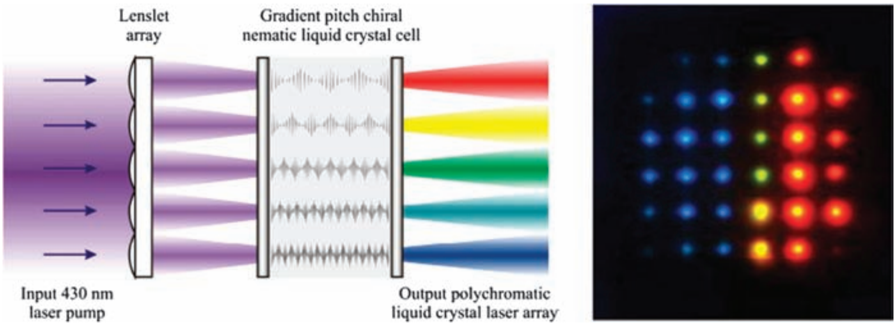
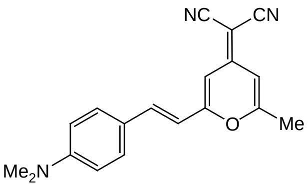
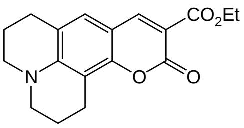


Figure 5.37 (a) Left: a polychromatic liquid crystal laser array. Pump light is focused using an array of lenslets onto a gradient pitch chiral nematic LC cell doped with laser dyes. Multiple wavelength laser emissions are emitted simultaneously from different regions of the same cell. (b) Right: an image produced by an actual LC cell[94] (reproduced with permission of Optical Society of America).

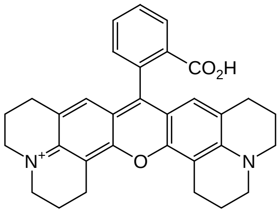
In this, the LC cell is based on a chiral nematic phase, containing two fluorescent dyes and a chiral dopant. The laser dyes (5.8) and (5.9) are chosen to absorb at a similar pump wavelength (in this case 430 nm), but with substantially different Stokes shifts, to emit individually red and blue, respectively. The pitch of the helical structure of the doped chiral LC has a periodic refractive index whose pitch can be controlled by the amount of chiral dopant added. A combination of the two different LC/dye/dopant mixtures built into the same cell gives a lasing system which emits differently depending on the area of the cell being pumped. This latter is controlled by an array of "lenslets", pumped by a single source, but each giving rise to its own laser emission (Figure 5.37a). In this way, an array of different emission colours can be generated from the same LC cell (Figure 5.37b), a feature not readily available from conventional laser technologies. In the image reproduced, the extreme right and left emissions reflect the red and blue emitting systems respectively, while the central green and yellow emissions result from phase mixing of the two LC-dye components.



(5.8)



(5.9)



(5.10)

The trichromat generated covers a wider colour space than conventional display systems, such as a CRT (see Figure 3.5 in Chapter 3). But besides

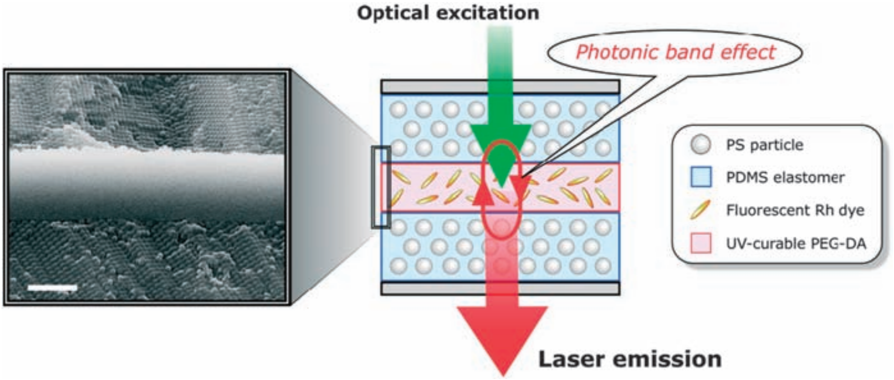


Figure 5.38 Colloidal crystal laser device[95] (copyright Wiley VCH Verlag GmbH & Co. KGaA. Reproduced with permission).

display applications, this type of multi-colour generation from a single source could have wider application in medical diagnostics, telecommunications and holographic projection.

5.5.2.5 *Colloidal Photonic Crystal Lasers*

A novel and potentially technically valuable use of colloidal photonic crystals is in flexible polymer laser devices.[95] The basic structure is shown diagrammatically in Figure 5.38. This is an example of a defect photonic crystal,[96] where a planar defect has intentionally been built into the structure, clearly visible in the SEM image shown on the left of Figure 5.38. The laser dye rhodamine 640 (5.10) is used as the gain medium in a UV-curable system, sandwiched between two parts of the colloidal crystal which in turn is embedded in an elastomer. The overall device is flexible and can be deposited on non-planar substrates, where it still retains its lasing power. Flexible lasers of this type are future technology.

5.6 Nonlinear Optics

Electronics is based on the controlled transmission of electrons, and has been the dominant technology for over 50 years in both the computing and communications industries. But it is not without problems that are increasing as ever higher demands are being placed on the technology. Many of these problems are inherent since electrons can interact with each other, tending to degrade signals sent over long distances, and causing noise which limits the speed by which signals can be transmitted.

Photonics is the roughly parallel technology that relies on the properties of photons (light) in place of electrons. It does not suffer from the same problem as electronics since photons interact much less with each other. They are therefore better at transmitting data without degradation, a fact which is used to advantage in fibre waveguides for the transfer of optical communication signals. But fully fledged all-optical systems are still to be developed. Later in this section and the next we glimpse some of the exploratory work which is leading down this path.

The half-way house technology of electro-optics has been developed to interface some of the desirable properties of optical systems into an electronic framework. This has become a major area of research since the 1980s, depending not least on the nonlinear optical properties of molecules and materials. It is in these that a major interface between electrons and light takes place, and they comprise the first part of the subject matter of this section.[97]

5.6.1 Basis of Nonlinear Optics

Nonlinear optics (NLO) involves the interaction of light with materials, this interaction causing changes in some of the properties of the materials, and at the same time altering some of the properties of the light. The fundamental property of interest is the polarisation of the material. At the molecular level, the polarisation is given by the following equation:

$$\mu = \mu_o + \alpha E + \beta E.E + \gamma E.E.E$$

where μ_o is the basic molecular polarisation in the absence of any external field; E is a component of an electric field; α is the linear polarisability, and β and γ are the first and second hyperpolarisability terms, respectively, reflecting the sensitivity of the molecule's polarisation to higher order electric field terms; and μ is the overall molecular polarisation accounting for the various effects of electric fields. Yet higher order terms are possible, but are not shown. In classical optics, only the linear polarisability term has been significant, and a molecule's polarisation has been linear with respect to external electric field because β and γ are increasingly small, and negligible relative to α. Their impact only becomes evident when the electric field E is very high, as in an intense optical beam from a laser, where now the polarisation response becomes dependent on higher-order terms in E, and is thus nonlinear. A key aspect of the above equation is that the second-order NLO term β is only non-zero for non-centrosymmetric molecules.

The corresponding equation for NLO activity in bulk material is

$$\mathrm{P} = \mathrm{P}_0 + \chi^{(1)}E + \chi^{(2)}E.E + \chi^{(3)}E.E.E$$

where P is now the bulk polarisation and the linear and nonlinear polarisation increments are related to optical susceptibilities $\chi^{(1)}$ (linear), $\chi^{(2)}$ (second-order NLO) and $\chi^{(3)}$ (third-order NLO). The β term is related to $\chi^{(2)}$, and γ to $\chi^{(3)}$, but in non-trivial ways. Again, the second-order term $\chi^{(2)}$ is only non-zero for a non-centrosymmetric bulk material. This imposes a unique design criterion on molecules and materials for second-order or quadratic NLO.

The following sections describe some of the materials being used for NLO applications. We shall make no effort to derive relationships between the NLO properties of interest and their mathematical underpinnings, but will try to describe the nonlinear aspect of the relationship phenomenologically.

5.6.2 Nonlinear Optical Materials Second-order or Quadratic Nonlinearity

The requirement for a non-centrosymmetric structure in quadratic NLO materials was first approached by application of crystals of suitable symmetry.

The earliest quadratic NLO materials were inorganic crystals, typified by lithium niobate, $LiNbO_3$, which became the NLO workhorse and is taken as the benchmark. Despite perceived deficiencies, such as cost, the need for specialised optical quality crystal growth techniques, and sub-optimal NLO performance, this became established as an adequate NLO material. Over the years it has stubbornly refused to be displaced by newer materials. But research into organics for NLO started in the 1980s because of the deficiencies of inorganics, as well as the prospect that organic materials offered more scope for molecular variation and thus higher resultant optical nonlinearity, alternative options for generating and retaining non-centrosymmetry in derived materials, flexible fabrication, easier manufacture and lower cost. In the following sections we explore some of the aspects of the development of organic quadratic NLO materials, engineering of their non-centrosymmetric structures and their major applications. These include wavelength converters such as second harmonic generators (SHGs) and electro-optic modulators (EOMs).

5.6.2.1 Quadratic NLO Chromophores

The quadratic NLO requirement for an easily polarisable yet non-centrosymmetric molecule was first addressed by species where an electron donor unit is conjugated to an electron acceptor, *via* a π-conjugating molecular linker unit (D-π-A). The π-system was recognised to be an easily polarisable core for the molecule, and the D/A substitution should lead to greatest asymmetry in the molecule's electronic structure, particularly on excitation. In fact D-π-A is familiar as the design paradigm of many simple dyes we have encountered earlier in this book, typified by donor–acceptor-substituted azobenzenes such as Colour Index Disperse Red 1 (5.11; DR1). DR1 was one of the first chromophores to be widely studied and exploited for NLO, not least since it also offers a convenient reaction site for linking into polymers (see below). Extensive research over the years has exploited the wide variety of donor groups based on R_2N, RO and RS motifs; an even wider array of acceptor groups; and π-linking units covering phenylene, heteroaromatics, simple alkene ($C{=}C$) and its derived oligomers [$(C{=}C)_n$], azo ($N{=}N$), imine ($C{=}N$), and many of the possible combinations of these units. The D-π-A molecule has usually been constrained into a planar geometry, to optimise through-conjugation and

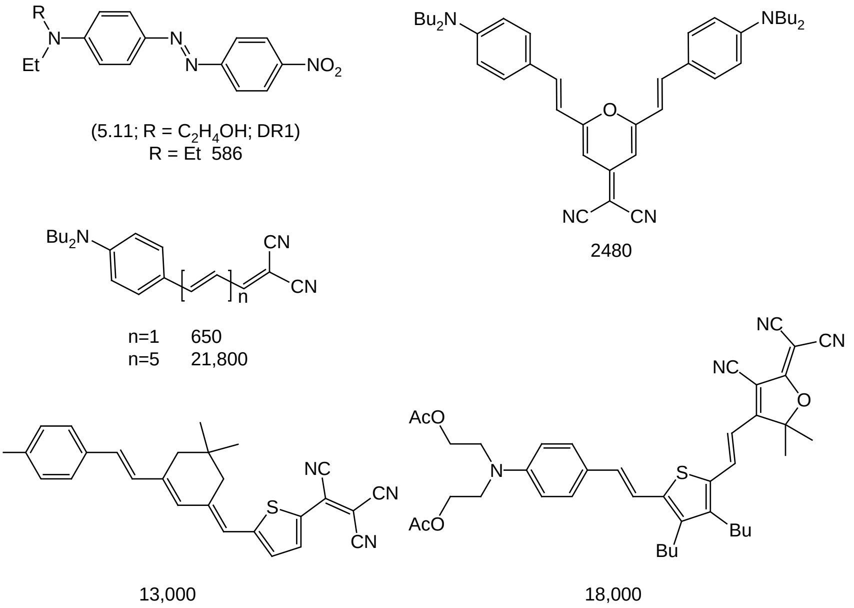


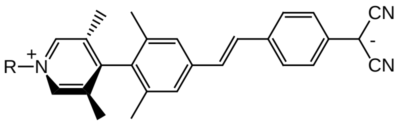
Figure 5.39 Selected quadratic NLO chromophores with their μβ values ($\times10^{-48}$ esu) measured at 1.9 μm.

electron-delocalisation on excitation. In this way, and following early study of the NLO properties of conventional dyes, many new dyes have been made explicitly for NLO.

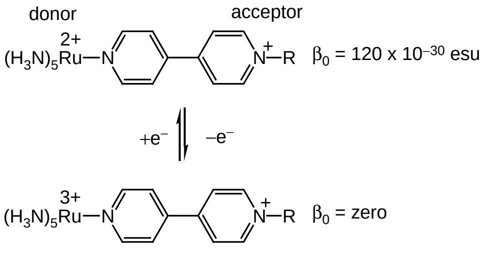
A primary aim has been to optimise the optical nonlinearity of the molecule, as reflected by its β hyperpolarisability coefficient. In practice, because of the evaluation technique, this value is frequently reported as the μβ product, where μ is the molecule's static dipole moment. Example values of μβ are shown in Figure 5.39 alongside the structures of some D-π-A NLO dyes, showing how the optical nonlinearity has been developed from the days of DR1 to chromophores typical of those currently being studied and exploited. The D-π-A model remains the preferred system for quadratic NLO molecules. However, other chromophore types have been developed alongside these.

5.6.2.2 Other Designs for Quadratic NLO Chromophores

Twisted π-electron Systems – a non-intuitive D-π-A variant which nevertheless provides molecules with exceptionally high μβ values comprises zwitterions based on donor-substituted 4-arylated pyridinium ions, intentionally deplanarised so that the two π-planes are near orthogonal, by virtue of substituents ortho to the pyridinium-aryl bond, as in (5.12). Molecules of this type have astonishing μβ values reaching as high as $488{,}000\times10\ ^{48}$ esu at 1.907 μm.[98] Removing the steric congestion to allow relaxation of the molecular geometry back toward planarity reduces the optical nonlinearity.[99] As yet, their exploitation awaits further molecular modification to permit fabrication into NLO-stable materials.



(5.12; R = 2-Pr-n-C_7H_{15})



(5.13)

Metal Complexes – metal-centred units can be used to act as electron donors when coordinated to π-acceptor ligands. A whole new range of NLO active molecules can be accessed, exemplified by (5.13). The NLO activity can be switched because of the redox properties of the transition metals incorporated.[100,101]

Dendrimers and Aggregates – azobenzene D-π-A units have been built into cone-shaped dipolar dendron units, for incorporation into dipolar dendrimers. This modification has the effect of enhancing the β value per chromophore by up to 85%.[102] Other supramolecular aggregate designs also introduce cooperative phenomena leading to enhanced NLO activity.[103]

Octupoles – other non-centrosymmetric geometries are possible, beyond the simple rod-like D-π-A model. Zyss and colleagues have introduced interesting octupolar species based on 3-fold symmetry variants, with example donor–acceptor substitution patterns shown in Figure 5.40. All exhibit quadratic NLO activity.[104,105,106]

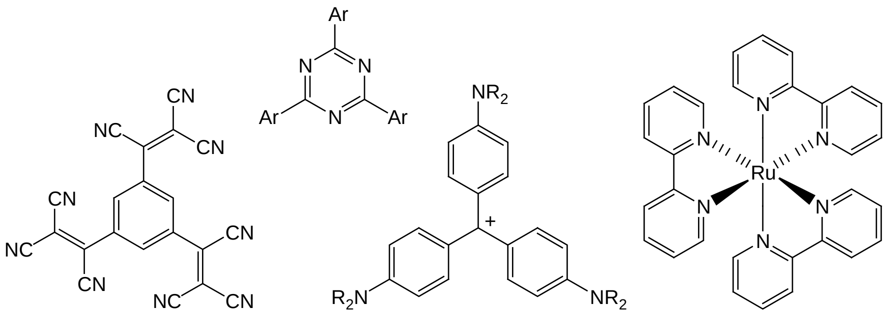


Figure 5.40 Example quadratic NLO active non centrosymmetric octupolar molecules of D_3, D_{3h}, C_{3h} symmetry.

5.6.2.3 Quadratic NLO Materials Poled Polymers

To be of any practical use, quadratic NLO molecules must be fabricated into a non-centrosymmetric material. Ideally for D-π-A molecules, this means they should be aligned more-or-less parallel with their dipole vectors pointing in the same direction. Various methods have been investigated to achieve this.

Non-centrosymmetric crystals – the most obvious approach derives from the acentricity conferred by some crystal space groups, as found for $LiNbO_3$ and other inorganic NLO materials. Unfortunately the common space groups for small organic molecules are centrosymmetric, and worse, the tendency is for strongly dipolar molecules to crystallise with their dipoles opposing each other, emphasising the undesirable tendency toward centrosymmetry. Crystal engineering has made some progress toward favouring NLO active crystals for some species, especially in the hands of Zyss and colleagues.[107] But in general crystallisation of NLO molecules into non-centrosymmetric space groups is too uncommon to offer a widespread solution.

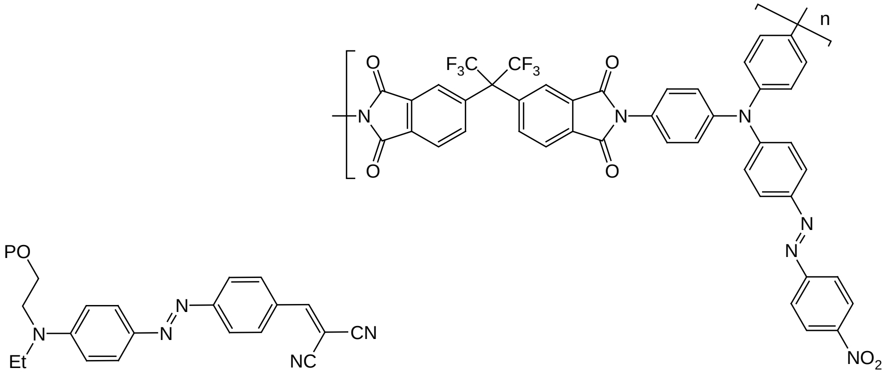
Some non-centrosymmetric *Langmuir-Blodgett film* configurations built from one or more NLO active amphiphiles demonstrate high NLO activity.[108] Their instability and the inconvenience of the LB technique have prevented this becoming a general approach so far.

Layer-by-layer deposition techniques (self-assembled multi-layers) can lead to NLO active non-centrosymmetric structures.[109] However, the effort involved in building up a film of sufficient thickness to be useful is non-trivial, and the number of steps inevitably leads to optical loss as defects are propagated.

By far the most successful fabrication method for NLO materials relies on *poled polymers*.[110,111,112,113] In this, the dipolar NLO chromophores in a polymer matrix are oriented by a strong external DC electric field. The aligned chromophores are then "trapped" by some means into this non-centrosymmetric geometry.

In the first and simplest oriented polymer variant, guest NLO active dye in a host polymer matrix above its glass transition temperature is oriented by means of the strong electric field. While the NLO chromophores are held in this favourable non-centrosymmetric arrangement, the matrix is cooled below its glass transition temperature (T_g) locking the dyes in position. Unfortunately, physical polymer solutions such as this are unstable and the dyes gradually relax by reorientation to give thermodynamically more stable centrosymmetric head-to-tail dimers, which are NLO inactive. While NLO materials based on this method have now been surpassed, guest-host polymers using NLO guests have been extensively studied in the area of photorefractive polymers (see Section 5.6.3).

A second variant involves amorphous polymers in which the chromophore is covalently linked either as a side chain of a polymer, or as part of the polymer backbone, with or without additional cross-linking. The next generation NLO polymers were side-chain polymers, usually made by copolymerisation of a monomer bearing the chromophore bridged by a flexible spacer group with a comonomer, commonly methacrylate. This is a flexible process allowing a wide range of copolymers to be made. A typical example of this type of polymer is the methyl methacrylate azo dye copolymer (5.14).



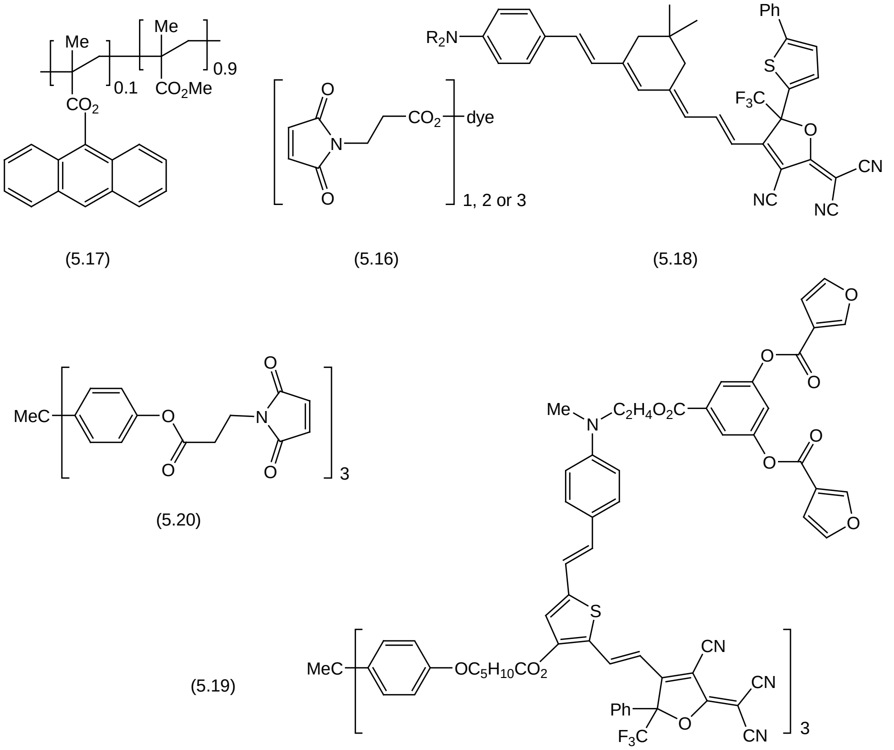
(5.14; P = methacrylate co-polymer) (5.15)

Whilst polymeric materials of this type showed very promising NLO properties after poling, they also tend to become disordered with time, leading to a slow decay in their optical nonlinearity. This is considered to be due to the T_g of the polymers being too close to the operating temperature of the devices, which can range from the lowest range of 85–100 °C to as high as 250–350 °C in some integrated optic applications. One way to cope with this problem is to use polymers that are inherently thermally stable, such as polyimides. A polymer with exceptional thermal stability is the copolymer (5.15), which is made from thermally stable polyimide and chromophore monomers, the chromophore making up part of the backbone in a transverse manner. This was stable up to 350 °C and could be poled at 310 °C. It maintained over 90% of its NLO activity at 225 °C for 100 hours, but the activity was still too low for commercial application.[114]

The most successful approach involves cross-linking of the side chain NLO polymer, after poling, at multiple sites by a different polymerisation reaction. Subsequent curing and hardening produces a lattice that permanently locks in the oriented dipole.

There has been a steady and continuing improvement in measured optical nonlinearity of poled polymers, resulting from various factors:

- gradual development of the β value of NLO chromophores, including the effect of adventitious group substitution;[115]
- changes to the basic shape of chromophores (rod-like giving way to more spherical);
- the nature of the copolymer and poling procedure;
- the use of mixtures of different chromophores;
- doping cross-linked matrices with additional unfixed chromophore.



(5.17) (5.16) (5.18)

(5.20)

(5.19)

Figure 5.41 The NLO and cross linking components of two Diels Alder variants used to prepare poled quadratic NLO polymers.

Recent example systems which have given high optical nonlinearities include copolymers based on Diels–Alder addition as the cross-linking step (Figure 5.41). In the first, the chromophore shown in Figure 5.42 is functionalised with 1, 2 or 3 maleimide units (5.16), and reacts with a cross-linkable polymer host containing anthryl units (5.17) in the Diels–Alder step. The composite is completed by addition of another D-π-A chromophore guest (5.18) held within the polymer matrix. After poling and cross-linking, the optical nonlinearity is about an order of magnitude higher than that of $LiNbO_3$.[116] In another Diels–Alder variant, a low-order dendrimeric trichromophore (5.19) plus a monomeric chromophore are immobilised by cross-linking with a tris maleimide unit (5.20), again with resultant high nonlinearity.[117]

Other immobilisation mechanisms are possible. An example is shown in Figure 5.42. Attractive face-to-face π–π interactions between pendant phenyl and pentafluorophenyl groups hold adjacent chromophores in non-centrosymmetric alignment after poling. Despite the lack of covalent cross-linking, the material retains about 85% of its initial NLO activity after 3 months at room temperature.[118]

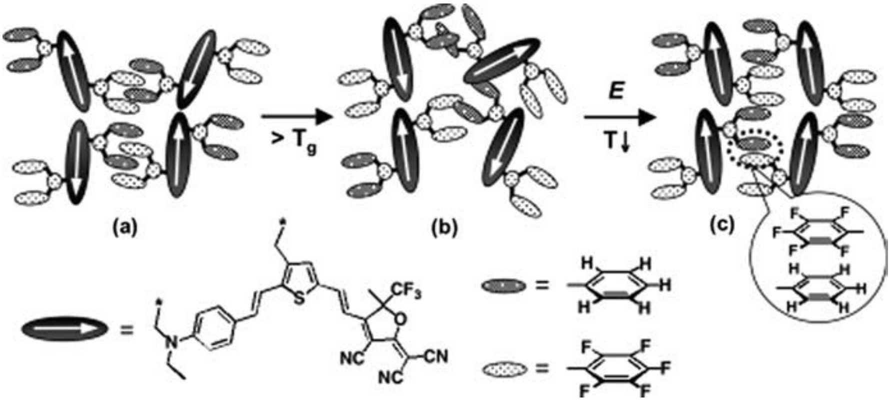


Figure 5.42 Graphical illustration of the alignment formation of self assembled chromophore by Ar ArF interactions: (a) locked random dipoles (shown as arrows) before poling; (b) unlocked random dipoles before poling; (c) locked acentric dipoles after poling followed by cooling[118] (reproduced with permission of American Chemical Society).

As in many other applications, building the physical effect into a polymeric material brings several advantages:

- High optical quality. This is achieved by ensuring an amorphous structure and avoiding microcrystallites and phase boundaries which could lead to scattering losses;
- Mechanically strong;
- Flexible fabrication opportunities, permitting many shapes and forms including layered composite structures;
- Essential macroscopic properties can be engineered into the molecules;
- Other critical physical properties can be tailored *e.g.* T_g, clearing temperatures, absorption/transmission windows, stability to thermal treatments and use under extreme conditions.

Since many of these NLO polymers have been synthesised for electro-optic applications (see Section 5.6.3, following), they are frequently termed electro-optic (EO) polymers.

5.6.3 Electro-optic Modulators

The interface between electronics and photonics – electro-optics – depends on devices which enable electrons and photons to communicate, which brings us to the major application of electro-optic modulators (EOM). These are devices which depend on the Pockels effect, the phenomenon whereby the refractive index of a quadratic NLO material is altered by an external electrical field, resulting in a change of the speed of an optical wave travelling through the

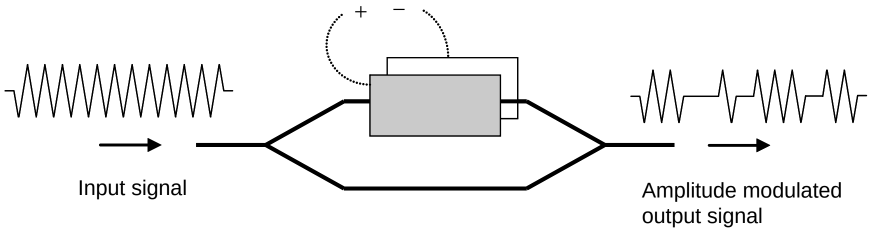


Figure 5.43 A Mach Zehnder electro optic modulator. The input light signal is a simple sine wave (left). A varying electric field applied across the top arm of the EOM is written onto the light signal, resulting in amplitude modulation of the output signal (right).

NLO material. A common EOM design is based on a Mach-Zehnder modulator, shown in Figure 5.43. An incoming optical signal is split in a waveguide composed of a quadratic NLO material. One arm of the waveguide is subject to a varying electric field (*ca.* several volts for $LiNbO_3$; modern polymer variants less than 1 V), which thus causes the optical signal passing through that arm to be phase-modulated in synch with the electric field. The optical signal in the other arm is unaffected. As the two signals in the two arms re-merge, they are either in-phase and thus unchanged, or out of phase in which case the amplitude of the resultant optical signal is modulated due to interference. The degree of modulation reflects the variation of the electrical field – the information carried by the electric signal has been written onto the optical signal.

The usual figure of merit which reflects the optical nonlinearity in EO polymers is r_{33}, given in pm V ^{1}. Figure 5.44 shows how the activity of EO polymers has been improved in recent years.[119] The benchmark $LiNbO_3$ has an r_{33} value of about 30 pm V ^{1}, so it is only relatively recently that this has been surpassed. The most recent EO polymers are an order of magnitude higher, with newer even stronger materials in the pipeline.

The values in Figure 5.44 refer to poled films of the chromophores, in the absence of full device fabrication. In fact, cladding layers of devices attenuate poling efficiencies, and thus final device EO efficiencies do not reflect the full NLO potential of the chromophore.[113]

It had been believed that increased telecommunication bandwidth (currently being expanded to 40 Gb s ^{1}, moving to 100 Gb s ^{1} in the next jump in technology) would necessitate a move from inorganics such as $LiNbO_3$ to poled polymer systems, based on the sort of high-β chromophores described above. However, $LiNbO_3$ technology has proved resilient and 40 Gb s ^{1} $LiNbO_3$ EOMs are readily available commercially. Early-generation poled-polymer EOMs were launched commercially but apparently without impact, for example, ROITech's polyimide-based NLO material, Optimer (5.21).[120] Lumera Corporation, now merged with GigOptix, currently (2009) advertises two 40 Gb s ^{1} polymer EOM demonstrator models. Polymer NLO devices also continue to be developed and applied within larger telecommunication and defence corporations, but without publicity.

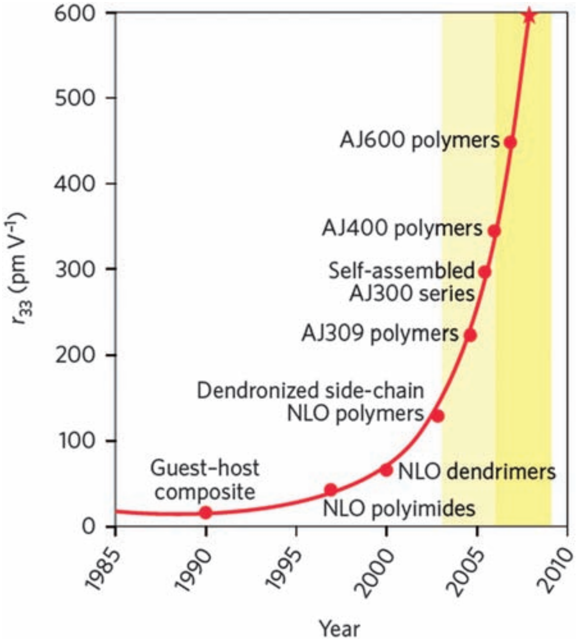
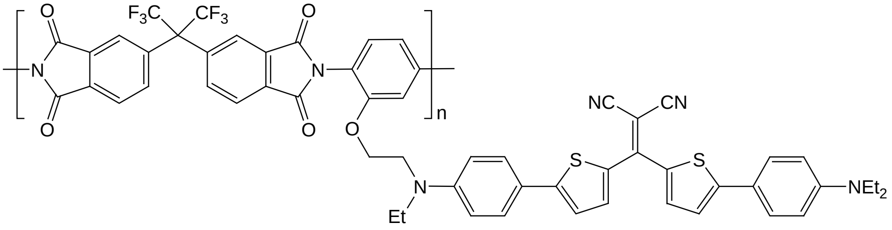


Figure 5.44 The development of EO polymers. Figure by L. Dalton[119] (reproduced with permission of Nature Publishing Group).



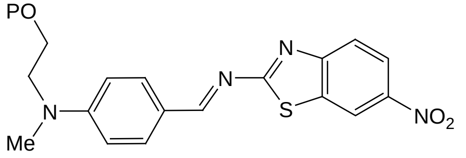
(5.21)

5.6.4 Wavelength Converters Harmonic Generation

A second application of quadratic NLO materials derives from their ability to generate harmonics of input laser wavelengths. Second harmonic generation (SHG) is reminiscent of 2-photon absorption followed by fluorescence of the up-converted photon (Sections 3.2.3 and Figure 3.2(d); and Section 5.6.5.1 below), and in fact itself comprises another up-conversion mechanism. 2PA differs in that two photons are absorbed by the dye, leaving it – however briefly – in a different, excited, electronic state. From here it can fluoresce as discussed in Section 3.5.3, and/or it can lose thermal energy by non-radiative mechanisms. In contrast, the conversion of two lower-energy photons to one higher-energy photon by SHG in an NLO material involves no absorbance, and thus no energy loss, and takes place by a fundamentally different, scattering, mechanism.

SHG and higher harmonic generation are used in laser technology to generate shorter wavelengths from one laser source. For example, the NIR 1064 nm emission wavelength of a Nd:YAG laser is used as the basis for green 532 nm lasers by frequency doubling by lithium triborate (LiB_3O_5; LBO), and higher frequency emission by generation of third, fourth, *etc.* harmonics. The Nd:YAG 946 nm emission and output from a pulsed Ti:sapp laser can both be frequency doubled by bismuth borate (BiBO) to give very efficient blue lasers.[121]

Poled polymer NLO materials could be used in principle for SHG. An imposition when using dyes in polymers for SHG is the requirement for transparency not just at the fundamental wavelength, but now also at the second harmonic wavelength. In practice, this means SHG materials must absorb at wavelengths hypsochromic to the second harmonic. This in turn limits the freedom for molecular design (degree and nature of delocalisation and the strength of donors and acceptors), thus weakening the polarisation and the resultant NLO effect. An example of a polymeric SHG material is the Schiff base (5.22).[122]



(P = methacrylate co-polymer)

(5.22)

5.6.4.1 Second Harmonic Imaging Microscopy

Just as 2PA imaging microscopy has been developed to take advantage of the NIR window of tissue (Section 3.5.9.7), the same benefit applies to SHG.[123,124] Furthermore, because the SHG mechanism does not involve photo-excitation of chromophores, imaging by SHG should cause no phototoxicity or photobleaching. The requirement for successful second harmonic imaging microscopy (SHIM) is for an NLO active probe within the biological target sample. Naturally occurring examples include the biopolymer collagen,[125] microtubules and muscle myosin, which are all non-centrosymmetric and can give SHG signals on illumination, typically by a Ti:sapphire laser.[126] A benefit is that centrosymmetric structures present in the target give no SHG response, so background optical noise due to autofluorescence should be minimal. Other studies have incorporated SHG-active labels into species of interest, and these too can be imaged by SHIM.[127]

5.6.5 Nonlinear Optical Materials Third-order or Cubic Nonlinearity

Because the γ coefficient of the third-order NLO term in the field-dependent expansion of polarisation is even smaller than β, cubic NLO phenomena are less well developed than quadratic. Nevertheless, some important chromic phenomena can be traced back to this term.

5.6.5.1 Multi-photon Absorption

Multi-photon absorbing dyes including many that have now been designed with large 2PA cross-sections were introduced in Section 3.5.3. Previous sections have also covered some of their applications: probes for 2PA imaging microscopy (Section 3.5.9.7), microfabrication and lithography, 3D photopolymerisation and photodynamic therapy, all in Chapter 4. All these applications derive their use from the resolution offered because of the dependence of 2PA response on the square of the intensity of the exciting light as shown earlier in Figure 3.26. Clearly 2PA is a nonlinear optical property, but in fact it is a third-order NLO effect (cubic), and not second order (quadratric).[128] The final 2PA application addressed here is yet another aspect of optical data storage.

5.6.5.2 2PA for High-density Optical Data Storage

In the earlier section on holography for high-density optical data storage in Section 5.4.3.1, we highlighted the attraction – perhaps necessity – of moving from 2D surface-based storage to 3D volume storage. Holography is one technology that enables this goal. Another relies on the heightened focusing precision of 2PA materials. The basic material is an optically transparent PMMA matrix, about 1 mm thick, into which are dissolved two components (Figure 5.45). The first is a 2PA material which generates acid on relatively high

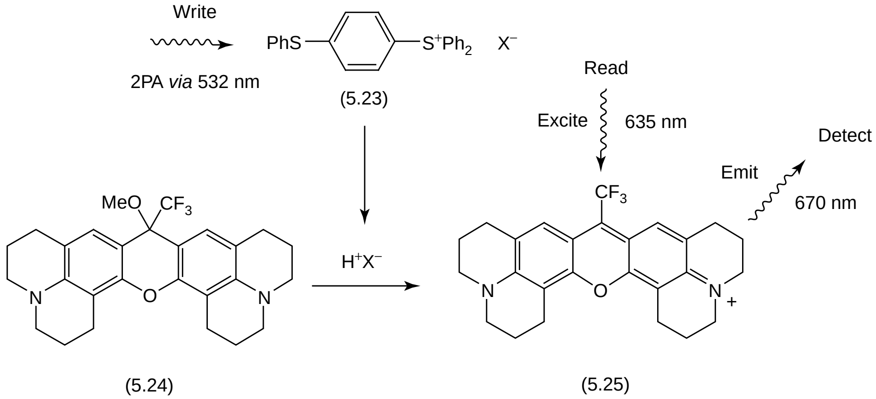


Figure 5.45 The basic photochemical processes in the Call/Recall 3D ODS system.

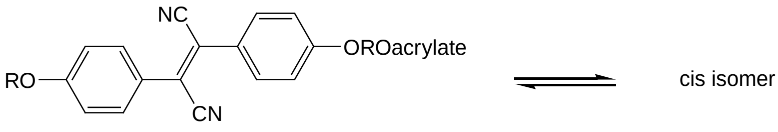
intensity shorter wavelength irradiation. Triarylsulfonium salts are favoured, with (5.23) having λ_{max} at about 300 nm.[129] It is thus excitable by 2PA of 532 nm light from a commercial green laser. The second active component is a colourless leuco fluorophore (5.24), which becomes coloured by the action of the photo-generated acid. Rhodamine 700 (5.25) has the necessary high quantum yield and is sufficiently stable to storage conditions within the PMMA matrix. The stored fluorescence provides a convenient read-out mechanism: a low-intensity read beam at a wavelength well removed from the write wavelength, typically from a red 635-nm diode, photoexcites the fluorophore, and its 670-nm emission is readily detected by a suitable optical sensor.

The key aspect leading to 3D ODS is the facility to focus the write beam into very tightly defined regions of the data storage material due to the quadratic dependence of 2PA excitation on light intensity (see Section 3.5.9.7 and Figure 3.26). The exact depth of 2PA within the matrix is controlled by a high-aperture lens whose focal length is adjusted by means of fluid contained within it. Thus, 2PA acid-precursor (5.23) can be excited at the surface or at any depth into the material, and thus generate the fluorophore at that spot only. Any attempt to excite by one photon absorbance is doomed to failure, as the inability to focus with the same degree of precision would result in consequent photoexcitation of a wide region of the material rather than a tightly controlled spot.

This technology is being developed to commercialisation by Call/Recall.[130] A 12-cm disc with 1.2 mm thick storage layer accommodates the equivalent of 200 DVD discs, giving a storage density of 1 Tb per disc. It may be written at the rate of 25 Mbit s^{-1} (anticipated to increase to 100 Mbit s^{-1}), with data recorded in 200 layers through the disc. The most recent developments have moved to a 405-nm blue laser to write by 2PA to the UV-absorbing acid generator, thus increasing data density even further, and with read-out excitation at 540 nm. The capacity of the disc then becomes 5 Tb.

The above system is of course WORM, but Call/Recall say they are working on an erasable-rewritable version.

Another new high-density ODS WORM system based on 2PA is the TeraDisc™ being developed by Mempile.[131] This technology involves photoisomerisation of a photochromic dicyanostilbene (5.26) locked covalently into a PMMA matrix, with 2PA writing by red laser. Again because of the sharp focusing potential of 2-photon processes, accurate writing onto a tightly restricted volume of the disc is possible, at multiple depths. Reading is by 2-photon excitation of the chromophores, and differential detection of the dicyanostilbene isomers *via* their different fluorescences. A data density of near one Tb per disc is planned for initial launch, predicted to be 2010, with the prospect of moving to 5 Tb.



(5.26)

The most radical new announcement is for a 5D optical data storage system, which relies on polarisation (two options) and three "colours" (700, 840, 980 nm in the experimental version) to write by photothermal modification of three differently sized gold nanorods within a matrix. The written material is read by a low-power excitation source, in a 2-photon excitation mode. A conventional DVD-size disc is predicted to be able to store 7.2 Tb.[132]

5.6.5.3 Reverse Saturable Absorption Optical Limiters

Another property which derives from cubic optical nonlinearity is reverse saturable absorption (RSA). This was introduced in the preceding chapter (Section 4.2.3.2), but we continue the topic here to emphasise its NLO derivation. RSA is the phenomenon exhibited by some dyes whereby their excited-state absorption cross-section is higher than the ground-state absorption cross-section. Thus as the dye absorbs light and its excited state becomes populated, it absorbs yet more light because of the absorbance of the excited state. In practice, since the lifetime of the excited state has to be long enough to survive until the second photon is absorbed, the excited state of relevance is usually a triplet (lifetime μs) rather than the initially formed singlet (lifetime ns). Figure 5.46 shows the $S_0 \rightarrow S_1$ and $T_1 \rightarrow T_n$ spectra of a condensed porphyrin example.[133]

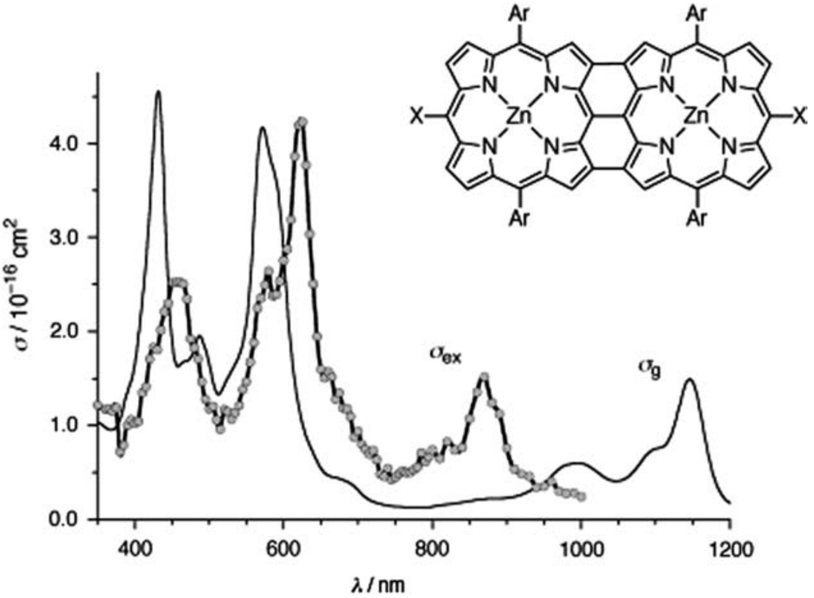
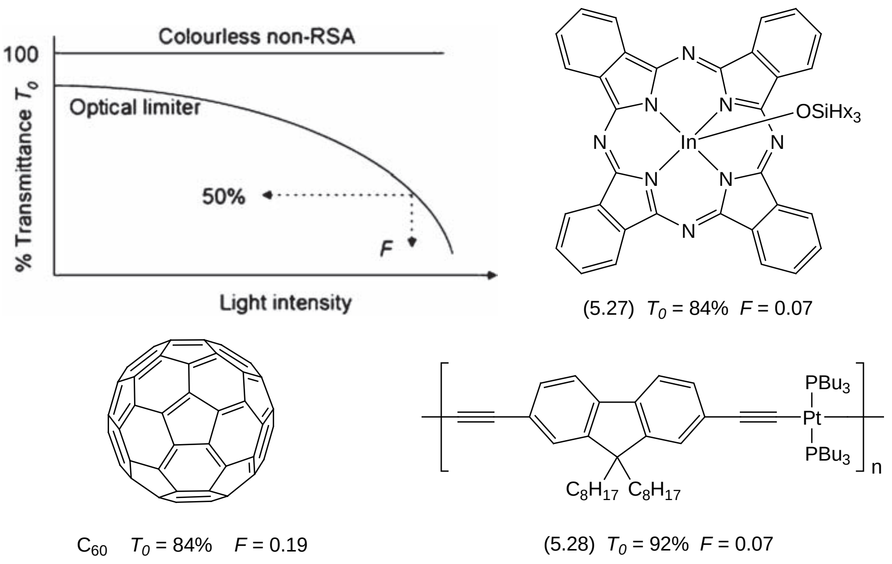


Figure 5.46 $S_0 \rightarrow S_1$ (σ_g) and $T_1 \rightarrow T_n$ (σ_{ex}) spectra of the porphyrin dye shown (X = Br, Ar = 3,5 di(t butyl)phenyl)[133] (reproduced with permission of Wiley VCH Verlag GmbH & Co KGaA).



(5.27) $T_0 = 84\%$ $F = 0.07$

C_{60} $T_0 = 84\%$ $F = 0.19$

(5.28) $T_0 = 92\%$ $F = 0.07$

Figure 5.47 Top left: transmittance of non RSA species and optical limiter; example optical limiters and their figures of merit.

A consequence is that the more light is absorbed, the less transparent the RSA material becomes. This leads to a major application of RSA, as optical limiters. These are a special type of optical filter, that in the presence of very intense light only allow a reduced light intensity transmission as RSA becomes dominant (Figure 5.47). Optical limiters are used to protect equipment from intense laser beams, and in goggle and spectacle lenses and visors to protect eyes against exposure to intense laser light, in industrial, laboratory and military environments.

Molecules with high RSA cross-sections include buckminsterfullerene (C_{60}) and derivatives,[134] many porphyrins[135,136] and phthalocyanines,[137,138] cyanines,[139,140] and more recently acetylide complexes of platinum and other transition metals.[141,142] As with other optical materials encountered in this book, composites have certain benefits. The combination of an RSA cyanine dye with nonlinear scattering carbon nanotubes offer superior performance compared with the individual components.[143] Figure 5.47 shows two examples of the better optical limiting materials and their key figure-of-merit properties compared with C_{60}.[141] The latter is frequently taken as a benchmark optical limiter material.

5.6.5.4 All-optical Signalling

We know that the speed of data handling in communications and computing is increasing. For this increase to continue new technologies will be required, and it

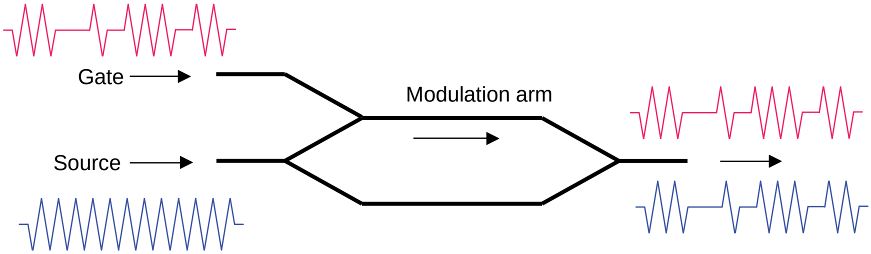


Figure 5.48 An all optical Mach Zehnder modulator. The waveguides shown are silicon, clad in a third order NLO polymer.

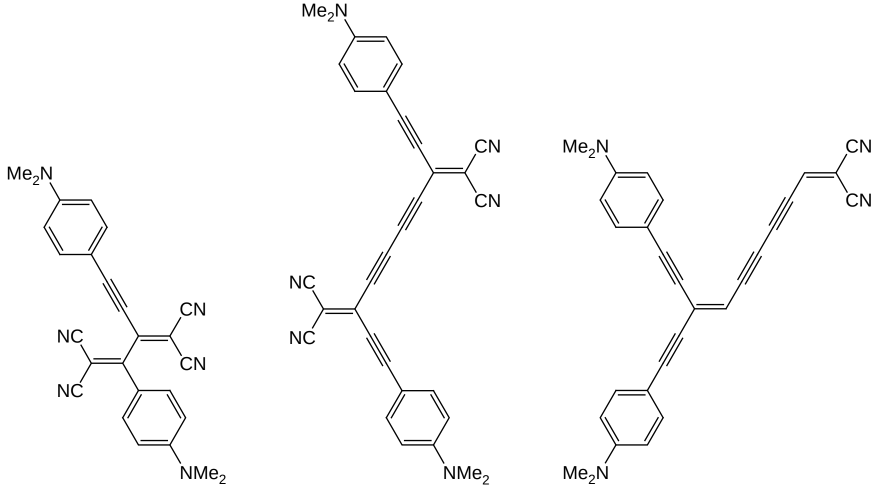
is expected that all-optical devices will replace electro-optics. One way for this to progress will be for purely light-based networks to be built onto a single chip. An important breakthrough in this direction has been the discovery that the optical properties of silicon-on-insulator slot waveguides are critically influenced when they are clad in NLO active polymer. The silicon technology has of course been well developed by the electronics industry. Introducing the optical polymer component into such a device is a relatively straightforward back-end treatment, which should be technologically easy to implement. The initial applications[144] of these new polymer-silicon hybrids are already leading to astonishing levels of performance, including electro-optic devices based on quadratic NLO polymers.[145]

In parallel with opto-electronics, an important component of all-optical systems will be the all-optical modulator, where one light signal is controlled by another. Here again, NLO materials will play a big part. Figure 5.48 is a diagram of an all-optical Mach–Zehnder modulator.[146] The waveguide is silicon, clad in a third-order NLO polymer. Light travelling through the waveguide is influenced evanescently by the NLO material. The main source signal splits, and that in the upper modulation arm is phase modulated by a gate light signal in a 4-wave mixing process, based on the optical Kerr effect (a third-order NLO process). As the two arms of the source signal re-merge, the out-of-phase components interact by interference, and the output source signal is intensity modulated reflecting the input gate signal. The major attraction of this type of all-optical device is that it can operate at terahertz frequency, two orders of magnitude faster than electro-optic devices.[147]

Even more recently, all-optical demultiplexing has been described in an all-optical hybrid polymer-silicon device.[119,148] Again, the cladding is a third-order NLO material, in this case the donor–acceptor molecule (5.29 in Figure 5.49), deposited onto the device as an amorphous film, optically transparent and non-scattering toward the 1.55-μm telecommunication wavelength.

5.6.5.5 Cubic NLO Chromophores

Third-order molecules and materials have been described based on many chromophores and other unsaturated molecules and polymers.[149] The most



(5.29)
λ_{max} 526 γ 12

(5.30)
λ_{max} 600 γ 53

(5.31)
λ_{max} 530 γ 33

Figure 5.49 Example molecules with high third order optical nonlinearity. Values shown are absorption maxima λ_{max} (nm) and second hyperpolarisability γ ($\times 10^{-48}$ cm^5 V^{-2}).

active species per unit molecular weight are relatively small organic molecules based on donor–acceptor substitution across various conjugating units (Figure 5.49).[150,151,152] Their nonlinearities are within a factor of 50 of the theoretical limit. Although dyes do not have to be unsymmetrically substituted to demonstrate third-order NLO activity, many are. Nor do they have to be fabricated into non-centrosymmetric materials. The unusual application of acetylenic conjugating units in the series shown is more or less absent from conventional dyes, and from chromophores used for second-order NLO (β).

5.6.6 Photorefractive Polymers

In the 1960s it was observed that undesirable optical damage was occurring in inorganic crystals such as $LiNbO_3$, which were being examined in electro-optical applications. This damage was found to be due to light-induced changes in the refractive index, and became known as the photorefractive effect.[153] Whilst this property was detrimental to the use of these crystals as modulators and frequency doublers, it could be used to advantage in holographic recording materials. Developments in this area have led to the use of these inorganic materials in real-time holography, required in applications where memories need to be refreshed rapidly, such as optical correlators, phase conjugators and optical limiters. The discovery in 1991 that the photorefractive effect could be reproduced in certain organic polymers sparked a new wave of interest that has led to the newer materials[154] and applications[155] including holography (Section 5.4).

5.6.6.1 *The Photorefractive Effect*

In the photorefractive effect, periodic changes are induced in the refractive index of a material by a redistribution of photogenerated charges. In polymers there are four different processes involved in the production of this effect.

1. Two coherent light beams intersect in the material and create a diffraction grating due to a sinusoidal light-intensity pattern.
2. Application of an external electric field causes the charges generated by photoexcitation of a photogenerator material in the bright regions of the pattern to migrate (in polymers, mobile charge carriers are holes).
3. The charges are trapped in the dark regions of the pattern forming a space-charge grating.
4. Changes in the refractive index by the Pockels effect acting on quadratic NLO chromophores lead to phase encoding of the incident light distribution.

This effect allows optical information to be recorded, erased and rewritten in real time.

The mechanism of the photorefractive effect has implications for the design of photorefractive polymers, which must demonstrate the following characteristics:

- Support photogeneration of electron–hole pairs;
- Be capable of transporting holes or electrons;
- Be able to trap charge carriers;
- Show the Pockels effect (field-dependent change in refractive index).

5.6.6.2 *Amorphous Polymers and Composites*

A photorefractive polymer or composite usually contains four elements: a photosensitiser to generate mobile charge carriers on irradiation with light; a conductor for the charge carriers; a quadratic NLO chromophore to reflect refractive index changes in the space-charge field generated; and a plasticiser to lower the T_g to enhance the EO effect. Many different schemes for producing photorefractive materials have been pursued.

Polymer composites have given some of the best results, but there are many problems to be overcome, such as the high loading requirements of the NLO chromophores and charge carriers, which together with low T_g, make many of the higher performing composites metastable (potential phase separation and crystallisation). Example components are shown in Figure 5.50. Common photoinitiators are C_{60} or the TNF derivative (5.32) for red light initiation, and

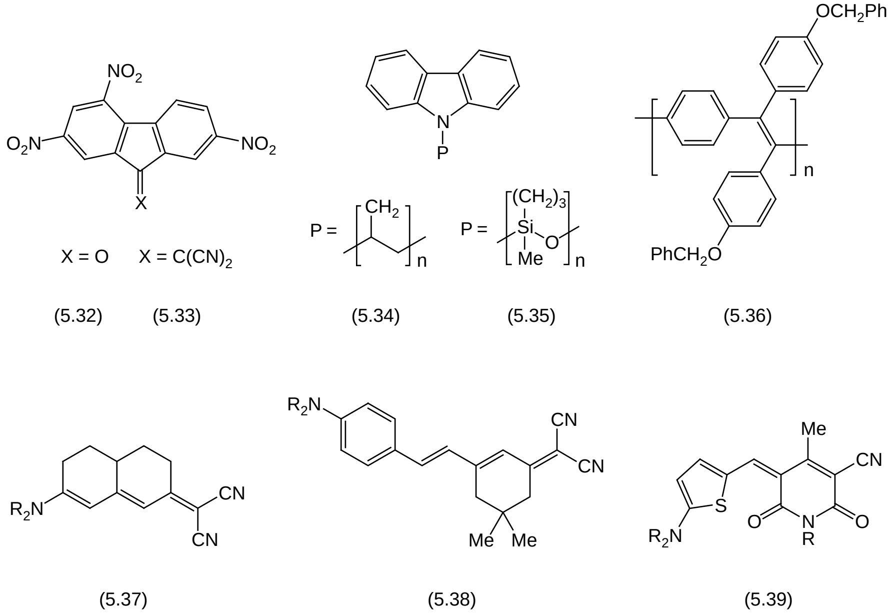


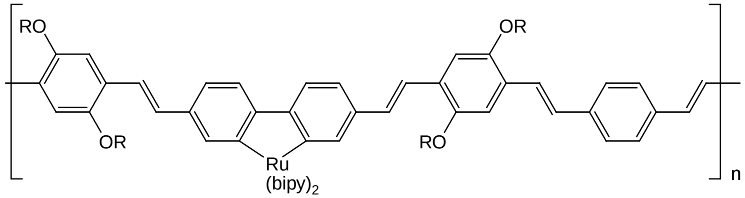
Figure 5.50 Examples of components of photorefractive polymers. Photogenerators (5.32), (5.33); photoconducting polymers (5.34 5.36); and quadratic NLO chromophores (5.37 5.39).

(5.33) for NIR initiation. Carbazole polymers such as (5.34) and (5.35), and polyphenylvinylenes (5.36) are effective charge transport materials. The molecules (5.37), (5.38) and (5.39) are example NLO chromophores, but azobenzenes, stilbenes and many other D-π-A systems have been applied. Plasticisers are phthalate diesters or *N*-ethylcarbazole. Other optional additives have also been investigated. For example, AuNPs improve the trapping properties of the material, and increase the photorefractive efficiency.

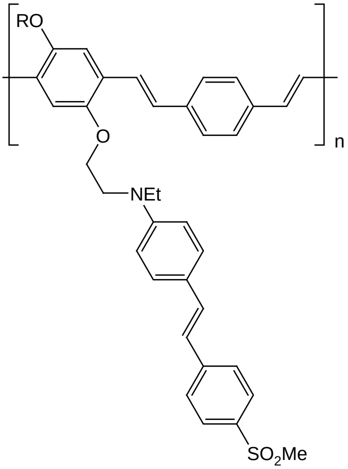
The ease of processing of such composites has been demonstrated by injection moulding a mixture containing the chromophore (5.37) as NLO and photoconductor component, to give optical-quality films with good photorefractive performance.[156]

Organic glasses are alternative materials. Here, there is no amorphous polymer, and one primary component acts as both photoconductor and NLO chromophore, so there is less dilution of activity. However, by removing one component, the flexibility in photorefractivity tuning has been decreased.

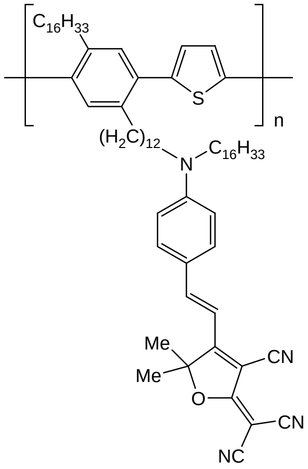
Ultimately, all components have been combined into a single polymer. This decreases the flexibility of formulation even further, but removes problems of phase separation and crystallisation. Good activities have been observed, for example in the polymers shown in Figure 5.51. The first is a copolymer based on 95% of (5.40) with 5% of (5.41). Each has a photoconducting PPV backbone, while the former contains a major proportion of side-chain NLO



(5.41)



(5.40)



(5.42)

Figure 5.51 Examples of fully functional photorefractive polymers.

chromophore, and the latter an Ru(II) sensitiser. In the second example, all functionality is contained in a single monomer unit of homopolymer (5.42).

5.6.6.3 Photorefractive Polymer Dispersed Liquid Crystals

Photorefractive PDLCs are designed to combine the high efficiency at low fields of LC materials with the high resolution of photorefractive polymers.[153,157] The polymer matrix provides photogeneration, charge transport and trapping properties to create a space-charge field. There is no need for an NLO chromophore in this system as the reorientation of LC material is responsible for the spatially averaged refractive index change. In a typical photorefractive PDLC, the matrix is the highly transparent poly(methyl methacrylate), containing photosensitiser and charge carrier. In this case a nematic LC eutectic of high resistivity (T202, Merck) is added to the mixture and the whole homogenised. Cells of this material (53 μm) with transparent ITO electrodes can be written with gratings that offer potential for real-time processing, if a little slow. However, replacing the PMMA with PVK instead gives photorefractive PDLCs with sub-picosecond response times.

5.6.6.4 Applications of Photorefractive Materials

Holography – the main application of photorefractive materials is as a 3D storage medium in holography (Section 5.4).

Medical imaging – an important imaging application is in medicine where biological tissues, transparent in the NIR, could be subject to holographic recording. By time gating, directly transmitted light can be filtered from that which is scattered and more slowly transmitted. The image of the tissue is then recorded holographically in an NIR-sensitive photorefractive polymer composite. More generally the technique can be used to reconstruct an image that has been distorted on passing through any turbid medium.

Image processing – other imaging applications include optical phase conjugation, optical correlation and image amplification and edge enhancement.

Non-destructive testing and non-contact testing of mechanical components using holographic interferometry is common in industry. The materials used currently in this method are the wet/chemical processing chemicals described in the section on holography (Section 5.4). Low-cost polymeric photorefractive materials offer distinct advantages as they do not require any further processing and could operate in real-time.

The use of the NIR and other laser-addressable photorefractive materials in security applications has been described, such as the authentication of cheques, passports, *etc.* by optical encoding and correlation of the information with a master copy.

References

1. G. W. Gray, in *Advances in Liquid Crystals*, Academic Press, New York, 1976, vol. **2**, p. 1.
2. C. E Hilsum, in *Technology of Chemicals and Materials for Electronics*, ed. E. R. Howells, Ellis Horwood, Chichester, 1984, pp. 43–58.
3. (a) D. Demus, J. W. Goodby, G. W. Gray, H.-W. Speiss and V. Vill (ed.), *Handbook of Liquid Crystals*, Wiley-VCH, Weinheim, 1998; (b) D. Demus, J. W. Goodby, G. W. Gray, H.-W. Speiss and V. Vill (ed.), *Physical Properties of Liquid Crystals*, Wiley-VCH, Weinheim, 1999.
4. P. J. Colling, *Liquid Crystals; Nature's Delicate Phase of Matter*, Princeton University Press, Princeton NJ, 2002.
5. H. Kikuchi, M. Yokota, Y. Hiakado, H. Yang and T. Kajiyuma, *Nature Mater.*, 2003, **1**, 64–68.
6. H. J. Coles and M. N. Pivnenko, *Nature*, 2005, **436**, 997–1000.
7. S. M. Kelly, *Flat Panel Displays. Advanced Organic Materials*, Royal Society of Chemistry, Cambridge, 2000.
8. D. Pauluth and K. Tarumi, *J. Mater. Chem.*, 2004, **14**, 1219–1227.
9. J. Hoogboom, T. Raising, A. E. Rowan and J. M. Nolte, *J. Mater. Chem.*, 2006, **16**, 1305–1314.
10. www.ercservice.com/learning/what-is-tft-lcd.html (May 2009).

11. LCR Hallcrest, www.liquid-crystal.com (May 2009).
12. Eur. Com. News, 22–28 May, 2000, 36.
13. www.chelix.com (May 2009).
14. www.epapercentral.com (May 2009).
15. D.-K. Yang, J. L. Watt, L.-C. Chien and J. W. Doane, *J. Appl. Phys.*, 1994, **76**, 20.
16. www.kentdisplays.com (May 2009).
17. A. Khan, T. Schneider, E. Montbach, D. J. Davis, N. Miller, D. Marhefka, T. Ernst and J. W. Doane, *SID Symposium Digest Tech. Papers*, 2007, **38**, 54–56.
18. www.inorganics.basf.com (Archive 6.5.2008).
19. Y. Jiang, B. Wilson, A. Hochbaum and J. Carter, *Proc. SPIE*, 2002, **4677**, 247–254.
20. L. Bouteiller and P. Le Barny, *Liq. Cryst.*, 1996, **21**, 157–174.
21. S. Park and J. W. Hong, *Thin Solid Films*, 2009, **517**, 3183–3186.
22. C. D. Sheraw, L. Zhou, J. R. Huang, D. J. Gundlach, T. N. Jackson, M. G. Kane, I. G. Hill, M. S. Hammond, J. Campi, B. K. Greening, J. Francl and J. West, *Appl. Phys. Lett.*, 2002, **80**, 1088.
23. N. Mizoshita, Y. Suzuki, K. Kishimoto, K. Hanabusa and T. Kato, *J. Mater. Chem.*, 2002, **12**, 219.
24. (a) A. Blumstein (ed.), *Polymeric Liquid Crystals*, Plenum Press, New York and London, 1985; (b) C. B. McArdle (ed.), *Side Chain Liquid Crystal Polymers*, Blackie and Son Ltd, Glasgow, 1989; (c) N. A. Plate (ed.), *Liquid Crystal Polymers*, Plenum, New York, 1993.
25. N. Tamaoki, S. Song, M. Moriysama and H. Matsuda, *Adv. Mater.*, 2000, **12**, 94–97.
26. C. B. McArdle (ed.), *Applied Photochromic Polymer Systems*, Blackie, London, 1992.
27. V. P. Shibaev (ed.), *Polymers as Electrooptical and Photooptical Active Media*, Springer, Berlin, 1996.
28. T. Ikeda and O. Tsutsumi, *Science*, 1995, **268**, 1873.
29. Y.-K. Han and B.-S. Ko, *Opt. Mater.*, 2003, **21**, 621–625.
30. S. Kinoshita and S. Yoshioka, *ChemPhysChem*, 2005, **6**, 1442–1459.
31. S. Kinoshita, S. Yoshioka and J. Miyazaki, *Rep. Prog. Phys.*, 2008, **71**, 1–30.
32. S. Berthier, *Iridescences: The Physical Colors of Insects*, Springer, 2007.
33. K. Nassau, in *Color for Science, Art and Technology*, ed. K. Nassau, Elsevier, Amsterdam, 1998, pp. 158–163.
34. H. Zollinger, *Color: A Multidisciplinary Approach*, Wiley-VCH, Weinheim, 1999, pp. 28–35.
35. G. Buxbaum (ed.), *Industrial Inorganic Pigments*, Wiley-VCH, Weinheim, 2nd edn., 1998, pp. 211–230.
36. http://www.jdsu.com/products/custom-color-solutions/product-line/details/chromaflair-and-spectraflair-pigment-a-comparision.html (May 2009).
37. R. Adams, *Focus on Pigments*, August 2008, 1–3.
38. http://www.jdsu.com/products/custom-color-solutions (May 2009).

39. Y. Jiang, B. Wilson, A. Hochbaum and J. Carter, *Proc. SPIE*, 2002, **4677**, 247–254.
40. http://www.eurim.org.uk/whats_new/events/showcase080610/DeLaRue_MLIS.pdf (May 2009).
41. http://www.qualcomm.com/common/documents/white_papers/QMT_Technology_Overview_12-07.pdf, Qualcomm (May 2008).
42. B. Rubin, *Adv. Mater.*, 1998, **10**, 1225–1227.
43. Angelina Fibers, http://www.meadowbrookinventions.com.
44. Z.-P. Yang, L. Ci, J. A. Bur, S.-Y. Lin and P. M. Ajayan, *Nano Letts.*, 2008, **8**, 446–451.
45. A. Stein, F. Li and N. R. Denny, *Chem. Mater.*, 2008, **20**, 649–666.
46. E. R. Dufresne, H. Noh, V. Saranathan, S. G. J. Mochrie, H. Cao and R. O. Prum, *Soft Matter*, 2009, **5**, 1792–1795.
47. B. Lange, F. Fleischhaker and R. Zentel, *Macromol. Rapid Commun.*, 2007, **28**, 1291–1311.
48. G. Ozin, *Chem. Commun.*, 2003, 2639–2643.
49. M. Fierke, F. Li and A. Stein, *Mater. Matters*, 2008, **3**, 10–12.
50. Q. Yan, L. Wang and X. S. Zhao, *Adv. Funct. Mater.*, 2007, **17**, 3695–3706.
51. S. Y. Lin, J. G. Fleming, D. L. Hetherington, B. K. Smith, R. Biswas, K. M. Ho, M. M. Sigalas, W. Zubrzycki, S. R. Kurtz and J. Bur, *Nature*, 1998, **394**, 251–253.
52. S.-Y. Lin and J. G. Fleming, *J. Lightwave Technol.*, 1999, **17**, 1944–1947.
53. S. Noda, K. Tomoda, N. Yamamoto and A. Chutinan, *Science*, 2000, **289**, 604–606.
54. J. C. Lytle and A. Stein, in *Ann. Rev. Nano Res.*, ed. G. Cao and C. J. Brinker, World Scientific Publishing Co., NJ, 2006, **1**, 1–79.
55. H. Li, J. Wang, L. Yang and Y. Song, *Adv. Funct. Mater.*, 2008, **18**, 3258–3264.
56. K. Matsubara, M. Watanabe and Y. Takeoka, *Angew. Chem. Int. Ed. Engl.*, 2007, **46**, 1688–1692.
57. G. A. Ozin and A. C. Arsenault, *Mater. Today*, 2008, **11**, 44–51.
58. P. Jiang, D. W. Smith, Jr., J. M. Ballato and S. H. Foulger, *Adv. Mater.*, 2005, **17**, 179–184.
59. S. A. Benton and V. M. Bove, *Holographic Imaging*, Wiley-Interscience, Hoboken, NJ, 2008.
60. H. I. Bjelkhagen and E. Mirlis, *Appl. Opt.*, 2008, **47**, A123–A133.
61. T. Kuwayama, N. Taniguchi, Y. Kuwae and N. Kushibiki, *Appl. Opt.*, 1989, **28**, 2455.
62. R. T. Ingwall and H. L. Fielding, *Opt. Eng.*, 1985, **24**, 808.
63. T. J. Trout, J. J. Schmieg, W. J. Gambogi and A. M. Weber, *Adv. Mater.*, 1998, **10**, 1219–1224.
64. L. Dhar, K. Curtis and T. Fäcke, *Nature Photonics*, 2008, **2**, 403–405.
65. L. Hesselink, S. S. Orlov and M. C. Bashaw, *Proc. IEEE*, 2004, **92**, 1231–1280.

66. R. T. Pogue, R. L. Sutherland, M. G. Schmitt, L. V. Natarajan, S. A. Siwecki, V. P. Tondiglia and T. J. Bunning, *Appl. Spectrosc.*, 2000, **54**, 12A–28A.
67. T. J. Bunning, S. M. Kirkpatrick, L. V. Natarajan, V. P. Tondiglia and D. W. Tomlin, *Chem. Mater.*, 2000, **12**, 2842–2844.
68. A. S. Matharu, S. Jeeva and P. S. Ramanujam, *Chem. Soc. Rev.*, 2007, **36**, 1868–1880.
69. M. Häckel, L. Kador, D. Kropp and H.-W. Schmidt, *Adv. Mater.*, 2007, **19**, 227–231.
70. http://en.wikipedia.org/wiki/List_of_emerging_technologies (December 2008).
71. http://www.enterprisestorageforum.com/technology/features/article.php/3795361 (January 9th 2009).
72. http://stxaprilis.com/company.htm (2008).
73. D. Graham-Rowe, *Nature Photonics*, 2007, **1**, 197–200.
74. J. Layton, http://electronics.howstuffworks.com/hvd2.htm (2009).
75. http://en.wikipedia.org/wiki/Holographic_Versatile_Disc (March 2009).
76. http://www.zebraimaging.com/html/gallery.html.
77. http://www.viewholographics.co.uk/gallery/ (June 2009).
78. S. C. M. Hui and H. F. O. Müller, *Architect. Sci. Rev.*, 2001, **44**, 221–226.
79. C. G. Stojanoff, *Proc. SPIE*, 2006, **6136**, 1–15.
80. R. V. Steele, *Laser Focus World*, 2005, **41**(2).
81. K. Kincade and S. Anderson, *Laser Focus World*, 2005, **41**(1).
82. R. Martin, *Chem. Ind.*, 1999, **March 1**, 173–177.
83. D. A. Gaul and W. S. Rees, Jr., *Adv. Mater.*, 2000, **12**, 935–946.
84. S. Nakamura, M. Senoh, S. Ngahama, N. Iwasa, T. Matsushita and T. Mukai, *Appl. Phys. Lett.*, 2000, **76**, 22.
85. S. Nakamura, S. J. Pearton and G. Fasol, *The Blue Laser Diode: The Complete Story*, Springer, 2nd edn., 2000.
86. D. A. Gaul and W. S. Rees, Jr., *Adv. Mater.*, 2000, **12**, 935–946.
87. N. Tessler, *Adv. Mater.*, 1999, **11**, 363–370.
88. D. Moses, *Appl. Phys. Lett.*, 1992, **60**, 3215.
89. W. Holzer, A. Penzkofer, S.-H. Gong, A. Bleyer and D. D. C. Bradley, *Adv. Mater.*, 1996, **8**, 974; and references therein.
90. F. Hide, B. J. Schwartz, M. A. Diazgarcia and A. J. Heeger, *Chem. Phys. Lett.*, 1996, **256**, 424.
91. N. Tessler, N. T. Harrison and R. H. Friend, *Nature*, 1996, **382**, 695.
92. J. H. Schon, C. Kloc, A. Dobaldapur and B. Batlogg, *Science*, 2000, **289**, 599.
93. G. Tsiminis, J.-C. Ribierre, A. Ruseckas, H. S. Barcena, G. J. Richards, G. A. Turnbull, P. L. Burn and I. D. W. Samuel, *Adv. Mater.*, 2008, **20**, 1940–1944.
94. A. M. Morris, P. J. W. Hands, S. Findeisen-Tandel, R. H. Cole, T. D. Wilkinson and H. J. Coles, *Opt. Express*, 2008, **16**, 18827–18837.
95. S. Furum, H. Fudouzi, H. T. Miyazaki and Y. Sakka, *Adv. Mater.*, 2007, **19**, 2067–2072.

96. Q. Yan, L. Wang and X. S. Zhao, *Adv. Funct. Mater.*, 2007, **17**, 3695–3706.
97. S. R. Marder, *Chem. Commun.*, 2006, 131–134.
98. H. Kang, A. Facchetti, H. Jiang, E. Cariati, S. Righetto, R. Ugo, C. Zuccaccia, A. Macchioni, C. L. Stern, Z. Liu, S.-T. Ho, E. C. Brown, M. A. Ratner and T. J. Marks, *J. Am. Chem. Soc.*, 2007, **129**, 3267–3286.
99. Y. Wang, D. L. Frattarelli, A. Facchetti, E. Cariati, E. Tordin, R. Ugo, C. Zuccaccia, A. Macchioni, S. L. Wegener, C. L. Stern, M. A. Ratner and T. J. Marks, *J. Phys. Chem. C*, 2008, **112**, 8005–8015.
100. B. J. Coe and N. R. M. Curati, *Comments Inorg. Chem.*, 2004, **25**, 147–184.
101. B. J. Coe, *Acc. Chem. Res.*, 2006, **39**, 383–393.
102. A. Yokoyama, A. Otomo, T. Nakahama, Y. Okuno and S. Mashiko, *Top. Curr. Chem.*, 2003, **228**, 205–226.
103. A. Datta and S. K. Pati, *Chem. Soc. Rev.*, 2006, **35**, 1305–1323.
104. J. Zyss, *Nonlinear Optics*, 1991, **1**, 3–18.
105. J. Zyss and I. Ledoux, *Chem. Rev.*, 1994, **94**, 77–105.
106. S. Brasselet and J. Zyss, *J. Opt. Soc. Am. B*, 1998, **15**, 257–288.
107. J. Zyss, I. Ledoux and J. F. Nicoud, in *Molecular Nonlinear Optics: Materials Physics and Devices*, ed. J. Zyss, Academic Press, 1994, pp. 130–200.
108. G. J. Ashwell, *J. Mater. Chem.*, 1999, **9**, 1991–2003.
109. K. E. Van Cott, M. Guzy, P. Neyman, C. Brands, J. R. Heflin, H. W. Gibson and R. M. Davis, *Angew. Chem., Int. Ed. Engl.*, 2002, **41**, 3236.
110. L. Dalton, *Adv. Polym. Sci.*, 2002, **158**, 1–75.
111. F. Kajzar, K.-S. Lee and A. K.-Y. Jen, *Adv. Polym. Sci.*, 2003, **161**, 1–85.
112. S.-H. Jang and A. K.-Y. Jen, in *Introduction to Organic Electronic and Optoelectronic Materials and Devices*, ed. S.-S. Sun and L. Dalton CRC Press, Boca Raton, 2008.
113. S. J. Benight, D. H. Bale, B. C. Olbricht and L. R. Dalton, *J. Mater. Chem.*, in press.
114. D. M. Burland and R. D. Miller, *Science*, 1995, **268**, 1604.
115. Y.-J. Cheng, J. Luo, S. Huang, X. Zhou, Z. Shi, T.-D. Kim, D. H. Bale, S. Takahashi, A. Yick, B. M. Polishak, S. H. Jang, L. R. Dalton, P. J. Reid, W. H. Steier and A. K.-Y. Jen, *Chem. Mater.*, 2008, **20**, 5047–5054.
116. T.-D. Kim, J. Luo, J.-W. Ka, S. Hau, Y. Tian, Z. Shi, N. M. Tucker, S.-H. Jang, J.-W. Kang and A. K.-Y. Jen, *Adv. Mater.*, 2006, **18**, 3038–3042.
117. P. A. Sullivan, B. C. Olbricht, A. J. P. Akelaitis, A. A. Mistry, Y. Liao and L. R. Dalton, *J. Mater. Chem.*, 2007, **17**, 2899–2903.
118. T.-D. Kim, J.-W. Kang, J. Luo, S.-H. Jang, J.-W. Ka, N. Tucker, J. B. Benedict, L. R. Dalton, T. Gray, R. M. Overney, D. H. Park, W. N. Herman and A. K.-Y. Jen, *J. Am. Chem. Soc.*, 2007, **129**, 488–489.
119. T. Baehr-Jones and M. Hochberg, *Nature Photonics*, 2009, **3**, 193–194.
120. T.-A. Chen, A. K.-Y. Jen and Y. Cai, *J. Am. Chem. Soc.*, 1995, **117**, 7295.

121. M. Ghotbi, M. Ebrahim-Zadeh, A. Majchrowski, E. Michalski and I. V. Kityk, *Opt. Lett.*, 2004, **29**, 2530–2532.
122. S. K. Park, J. Y. Do, J.-J. Ju, S. Park, M.-S. Kim and M.-H. Lee, *Macromol. Rapid Commun.*, 2003, **24**, 772–777.
123. F. Helmchen and W. Denk, *Nature Methods*, 2005, **2**, 932–940.
124. P. J. Campagnola and L. M. Loew, *Nature Biotech.*, 2003, **21**, 1356–1360.
125. R. M. Williams, W. R. Zipfel and W. W. Webb, *Biophys. J.*, 2005, **88**, 1377–1386.
126. N. Sandeau, L. Le Xuan, D. Chauvat, C. Zhou, J.-F. Roch and S. Brasselet, *Opt. Express*, 2007, **15**, 16051–16060.
127. L. Moreaux, T. Pons, V. Dambrin, M. Blanchard-Desce and J. Mertz, *Opt. Lett.*, 2003, **28**, 625–627.
128. G. S. He, L.-S. Tan, Q. Zheng and P. N. Prasad, *Chem. Rev.*, 2008, **108**, 1245–1330.
129. E. Walker, A. Dvornikov, K. Coblenz and P. Rentzepis, *Proc. SPIE*, 2008, **7053**, 705308-1–705308-9.
130. E. Walker and P. M. Rentzepis, *Nature Photonics*, 2008, **2**, 406–408.
131. http://www.mempile.com/ (May 2009).
132. P. Zijlstra, J. W. M. Chon and M. Gu, *Nature*, 2009, **459**, 410–413.
133. K. J. McEwan, P. A. Fleitz, J. E. Rogers, J. E. Slagle, D. G. McLean, H. Akdas, M. Katterle, I. M. Blake and H. L. Anderson, *Adv. Mater.*, 2004, **16**, 1933–1935.
134. F. Wudl, *J. Mater. Chem.*, 2002, **12**, 1959–1963.
135. K. McEwan, K. Lewis, G.-Y. Yang, L.-L. Chng, Y.-W. Lee, W.-P. Lau and K.-S. Lai, *Adv. Funct. Mater.*, 2003, **13**, 863–867.
136. M. O. Senge, M. Fazekas, E. G. A. Notaras, W. J. Blau, M. Zawadzka, O. B. Locos and E. M. Ni Mhuircheartaigh, *Adv. Mater.*, 2007, **19**, 2737–2774.
137. G. de la Torre, P. Vázquez, F. Agulló-López and T. Torres, *Chem. Rev.*, 2004, **104**, 3723–3750.
138. Y. Chen, M. Hanack, Y. Araki and O. Ito, *Chem. Soc. Rev.*, 2005, **34**, 517–529.
139. G. Y. Yang, M. Hanack, Y. W. Lee, D. Dini and J. F. Pan, *Adv. Mater.*, 2005, **17**, 875–879.
140. P.-A. Bouit, G. Wetzel, G. Bergine, B. Loiseaux, L. Toupet, P. Feneyrou, Y. Bretonnière, K. Kamada, O. Maury and C. Andraud, *Chem. Mater.*, 2007, **19**, 5325–5335.
141. G.-J. Zhou, W.-Y. Wong, C. Ye and Z. Lin, *Adv. Funct. Mater.*, 2007, **17**, 963–975.
142. R. Westlund, E. Malmström, C. Lopes, J. Öhgren, T. Rodgers, Y. Saito, S. Kawata, E. Glimsdal and M. Lindgren, *Adv. Funct. Mater.*, 2008, **18**, 1939–1948.
143. S. Webster, M. Reyes-Reyes, X. Pedron, R. López-Sandoval, M. Terrones and D. L. Carroll, *Adv. Mater.*, 2005, **17**, 1239–1243.
144. T. W. Baehr-Jones and M. J. Hochberg, *J. Phys. Chem. C*, 2008, **112**, 8085–8090.

145. T. Baehr-Jones, M. Hochberg, G. Wang, R. Lawson, Y. Liao, P. A. Sullivan, L. Dalton, A. K.-Y. Jen and A. Scherer, *Opt. Express*, 2005, **13**, 5216–5226.
146. M. Hochberg, T. Baehr-Jones, G. Wang, M. Shearn, K. Harvard, J. Luo, B. Chen, Z. Shi, R. Lawson, P. Sullivan, A. K.-Y. Jen, L. Dalton and A. Scherer, *Nature Mater.*, 2006, **5**, 703–709.
147. M. Lipson, *Nature Photonics*, 2007, **1**, 18–19.
148. C. Koos, P. Vorreau, T. Vallaitis, P. Dumon, W. Bogaerts, R. Baets, B. Esembeson, I. Biaggio, T. Michinobu, F. Diederich, W. Freude and J. Leutold, *Nature Photonics*, 2009, **3**, 216–219.
149. U. Gubler and C. Bosshard, *Adv. Polym. Sci.*, 2002, **158**, 125–191.
150. T. Michinobu, J. C. May, J. H. Lim, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, I. Biaggio and F. Diederich, *Chem. Commun.*, 2005, 737–739.
151. J. C. May, J. H. Lim, I. Biaggio, N. N. P. Moonen, T. Michinobu and F. Diederich, *Opt. Lett.*, 2005, **30**, 3057–3059.
152. J. C. May, I. Biaggio, F. Bures and F. Diederich, *Appl. Phys. Lett.*, 2007, **90**, 251106.
153. O. Ostroverkhova and W. E. Moerner, *Chem. Rev.*, 2004, **104**, 3267–3314.
154. P. Günter and J.-P. Huignard (ed.),*Photorefractive Materials and Their Applications 2*, Springer, New York, NY, 2006.
155. P. Günter and J.-P. Huignard (ed.), *Photorefractive Materials and Their Applications 3*, Springer, New York, NY, 2007.
156. J. A. Herlocker, C. Fuentes-Hernandez, J. F. Wang, N. Peyghambarian, B. Kippelen, Q. Zhang and S. R. Marder, *Appl. Phys. Lett.*, 2002, **80**, 1156–1158.
157. I. C. Khoo, *Phys. Rep.*, 2009, **471**, 221–267.

Subject Index

References to images are given in *italic type*. References to tables are given in **bold type**.