Chromic Phenomena

The Technological Applications of Colour Chemistry

Peter Bamfield
Consultant

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Preface

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 Hughes, Mike Hutchings, Brian 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 manuscript.

Peter Bamfield

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Glossary

The following terms are some of the common ones used in relation to colour chemistry and its applications.

Achromatic colours resemble only black and white (grey).
Acidochromism is a colour change, shift in absorption band and intensity, brought about by a change in pH (acidochromic).
Additive Colour Mixing used with light, the primary colours being red, green and blue.
After-glow occurs where a luminescent material continues to emit light long after excitation.
After-image in a complementary hue is seen after prolonged viewing of an intensely coloured object.
Anodoluminescence is radioluminescence caused by α-particles.
Bathochromic – when an absorption band moves towards longer wavelengths (also called a red-shift).
Bioluminescence is the production of light by living systems.
Candololuminescence is the luminescence in incandescent solids.
Cathodoluminescence is the luminescence observed upon excitation by high-energy electrons.
Chemiluminescence is the production of light by chemical substances without the help from other energy sources; in effect it is the conversion of energy stored in chemical bonds into light.
Cholesteric – the liquid crystal phase formed by molecules with a chiral centre (also called the chiral nematic phase).
Chroma is the attribute of a colour that expresses the degree by which it differs from an achromatic colour of the same lightness.
Chromatic – colours possessing a hue (do not resemble grey).
Chromaticity coordinates are two numbers (denoted x and y) which together represent in the CIE system the colour quality.
Chromaticity diagram is a diagram which shows the colour stimulus in terms of two of its three attributes; hue and chroma.
Chromogen is the coloured molecular structure (often used synonymously with the term chromophore).
Chromogenic development is the dye-coupling process in colour photography.
Chromophore – the unsaturated building blocks of colour, *i.e.* –N=N–, carbonyl and nitro groups *etc.* (see also chromogen).

Colour Index is the descriptive catalogue of synthetic colorants in terms of generic name and constitution (where disclosed) published by the SDC.

Crystalloluminescence is the light production as solutions crystallise.

Dichroic – exhibiting two different colours when viewed in different directions.

Electrochromism is a reversible change in colour upon oxidation or reduction brought about by an electrical current or potential (electrochromic).

Electroluminescence is excitation by an electric field to produce non-thermal light.

Fluorescence involves activation by photons (UV visible and near-IR) where the emission of light is almost instantaneous (1–30 ns).

Fluorophore – a fluorescent compound.

Fluorionophore – a chromophore whose fluorescence changes is the presence of an ion.

Gasochromism is a colour change brought about by a gas (see also vapochromism).

Halochromism is a colour change brought about by a change in pH (see also acidochromism) (halochromic).

Hue is the attribute of colour whereby it is recognised as being predominantly red, blue, yellow, green, *etc*.

Hyperchromic is an increase in the intensity of an absorption band.

Hypochromic is a decrease in the intensity of an absorption band.

Hypsochromic is when an absorption band moves towards shorter wavelengths (also called a blue-shift).

Incandescence is the emission of radiation over the UV, visible and near-IR regions from a heated body.

Ionochromism is a colour change brought about by ions (ionochromic).

Ionophore – a chromophore that changes colour in the presence of ions.

Iridescence is the colour produced by the phenomena of light interference and diffraction; involves these two optical phenomena in combination with reflection.

Luminescence is the emission of light from atoms or molecules in an electronically excited state.

Luminance is the luminous flux emitted per unit solid angle or per unit projected area of a surface; in a light source it is a measure of brightness.

Lumophore – a compound capable of luminescence.

Lyoluminescence is where the emission of light occurs when a material goes into solution.

Mechanoluminescence arises from mechanical action on solids (also called piezoluminescence or triboluminescence).

Metallochromism is the colour change observed as metal ions coordinate to a ligand (metallochromic).

Metamerism is a change of colour under different illuminants.

Pearlescence is the iridescence produced by refracted and reflected light from a surface (pearl-like colour).

Phosphor – a material that converts radiation into visible light.

Phosphorescence involves activation by photons, where there is a delay in the emission causing an after glow.

Photochromism is a change in colour brought about normally by UV light (photochromic).

Photoelectrochromic systems are systems which change colour electrochemically on illumination.

Photoluminescence involves excitation by electromagnetic, often ultraviolet, radiation. Also used generically for all those processes that absorb incident light and later re-emit part of that energy as visible light.

Piezochromism is a change in colour brought about by pressure (piezochromic).

Piezoluminescence is luminescence brought about by pressure (see also triboluminescence).

Polarisability is a tensor which relates the electric field vector to the induced dipole moment vector.

Pyroluminescence is the luminescence resulting from atoms produced at high temperatures, *e.g.* in a flame.

Radioluminescence occurs where the energy source is radioactive decay.

Saturation is the relative optical purity of a colour (also called intensity).

Solvatochromism is a colour change brought about by a change in solvent polarity (solvatochromic).

Sonoluminescence arises from the impact of high energy sound *e.g.* ultrasound.

Subtractive colour mixing is used for dyes and pigments where the primary colours are red, yellow and blue.

Thermochromism is a change in colour brought about by heat (thermochromic).

Thermoluminescence is observed during the heating of a solid that has previously absorbed energy from radiation as ions recombine.

Thermotropism is a change in transparency brought about by heat (thermotropic).

Tribochromism is a colour change brought about by mechanical grinding or fracture (tribochromic).

Up-converters are materials that absorb infrared radiation and convert this into visible wavelengths.

Vapochromism is a colour change brought about by a vapour (see also gaseochromism).

X-ray luminescence occurs where X-rays supply the energy.

Abbreviations

AEA	Alkaline Earth Aluminates
AMLCD	Active Matrix Liquid Crystal Display
AMTFT	Active Matrix Thin Film Transistor
BAPO	Bisacylphosphine Oxides
CCA	Charge Control Agents
CCD	Charge-coupled Device
CGL	Charge Generation Layer
CGM	Charge Generation Materials
CI	Colour Index
CIE	Commission Internationale de l'Éclarage
CPMA	Color Pigments Manufacturing Association
CRT	Cathode Ray Tubes
CTL	Charge Transport Layer
CTM	Charge Transport Materials
CVL	Crystal Violet Lactone
CW	Continuous Wave
CMYK	Cyan, Magenta, Yellow and Black
DAST	4,4′-Diaminostilbene-2,2′-disulfonic acid
DOD	Drop-on-demand
DSSC	Dye Sensitised Solar Cell
DVD	Digital Versatile Disks
EET	Electronic Energy Transfer
EL	Electroluminescence
EML	Light Emitting Layer
ETL	Electron Transport Layer
FBA	Fluorescent Brightening Agent
FD&C	Food, Drugs & Cosmetic
FET	Field Effect Transistors
GFP	Green Fluorescent Protein
GH	Guest–Host
HE	Holographic Element
HTL	Hole Transport Layer
HTS	High Throughput Screening
ICT	Internal Charge Transfer
IJ	Ink Jet
IOD	Initial Optical Density

$IODF_{10}$	Initial Optical Density 10 s after removing UV source
ITO	Indium Tin Oxide
LC	Liquid Crystal
LED	Light Emitting Diode
LEP	Light Emitting Polymers
MAPO	Monoacylphosphine Oxides
MLCT	Metal-to-ligand Charge Transfer
MOVPE	Metal Organic Vapour Phase Epitaxy
NLO	Non-linear Optical
OD	Optical Density
ODS	Optical Data Storage
OEL	Organic Electroluminescent
OLED	Organic Light Emitting Diode
PAN	Polyacrylonitrile
PDLC	Polymer-dispersed Liquid Crystal
PDT	Photodynamic Therapy
PEL	Powder Electroluminescence
PET	Photoinduced Electron Transfer
PLED	Polymer Light Emitting Diode
PMMA	Poly(methyl methacrylate)
PPP	Poly(*p*-phenylene)
PPV	Poly(phenylene vinylene)
PS	Photosynthesis
PVA	Polyvinyl Alcohol
PVK	Polyvinylcarbazole
RGB	Red, Green, Blue
SOHO	Small Office Home Office
STN	Super Twisted Nematic
TFEL	Thin Film Electroluminescence
TFT	Thin Film Transistor
T_g	Glass Transition Temperature
TICT	Twisted Internal Charge Transfer States
VUV	Vacuum Ultraviolet Light
WORM	Write Once Read Many Times
ε	Molar Absorption Coefficient
λ	Wavelength
Φ	Quantum Yield

Introduction

Colour plays an extremely important role in our everyday lives. Why this should be so has exercised the minds of some of our greatest philosophers for many centuries.[1,2] 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.[3,4] However, ever since Newton recognised the relationship between light and colour in the late 17th century, our understanding of the hard science behind colour and its myriad of applications has been increasing gradually, until it has reached today's level of sophistication.[5,6] 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.[7–9]

This book is concerned with the technological applications of colour chemistry and there is no intention in this introduction to cover the theoretical aspects of the topic. Specific aspects of colour theory are covered as needed within the main body of the text. For those requiring a more detailed treatment of the theoretical aspects of colour physics excellent texts are available,[5,6] whilst they are summarised in very readable forms in others of a more general nature.[8,9]

There are many ways in which colour can be caused to arise both by chemical and physical forces, all of which are used or have the potential to be used in technological applications. These different ways of producing colour can be grouped into five fundamental mechanisms, as shown in Table I.1. The five groupings can be further split into what Nassau has called "the fifteen causes of colour".[5] The main Nassau groupings of I, IV and V can be considered as physical phenomena, II is borderline between chemistry and physics and III covers purely chemical phenomena.

This methodology has recently been used to produce a text which explores the relationship between light and the optical properties of materials, which is recommended reading.[10] Whilst the fifteen causes of colour is no doubt a scientifically accurate method for the classification of the origin of the causes of colour, it can be rather prescriptive when it comes to pulling together those technologically important chromic phenomena, which rely largely on chemistry for their effect. An alternative method is to follow a technology based classification.[11,12] However, whilst this does have advantages, it fails to relate the chemistry/physics across particular technology boundaries, *e.g.* luminescence phenomena in pigments, sensors and probes. Consequently, for the purpose of this book, which is to describe the technological applications of colour, *via* a variety of various chromic phenomena, a somewhat different system is used.[13] This involves the classifications of the various chromic

Table I.1 *The 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.

- Reversible colour change
- Absorption and reflection of light
- Absorption of energy and emission of light
- Absorption of light and energy transfer (or conversion)
- Manipulation of light

Whilst arguably this is an oversimplification 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 (Figure I.1).

The chemistry and applications of the colour change grouping, containing all the well-known ‘isms’ of chromic phenomena, namely photochromism, thermochromism, ionochromism, electrochromism and solvatochromism, as well as the lesser-known ones such as tribochromism and vapochromism, are covered in Chapter 1. These chromic phenomena impinge on our everyday life, *e.g.* in photochromic spectacle lens, thermochromic temperature indicators, fax paper, smart windows and mirrors and in visual displays.

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, in paints and inks, as cosmetics or as food colorants. We are all now well aware of their use in one of the newer areas, digital printing, following the widespread availability of cheap ink jet printers, which are used in conjunction with PCs in both home and the office. Digital printing is now a serious competitor to the silver halide technology, so long the mainstay of colour photography.

The use of luminescent materials, the subject of Chapter 3, which was at one time confined largely to the production of fluorescent lamps and cathode ray tubes has spread further into everyday life. It is a common sight to see phosphorescent safety signage in low-light environments, to wear fluorescent garments, to look at electroluminescent displays and to use light emitting diodes in traffic control and vehicle

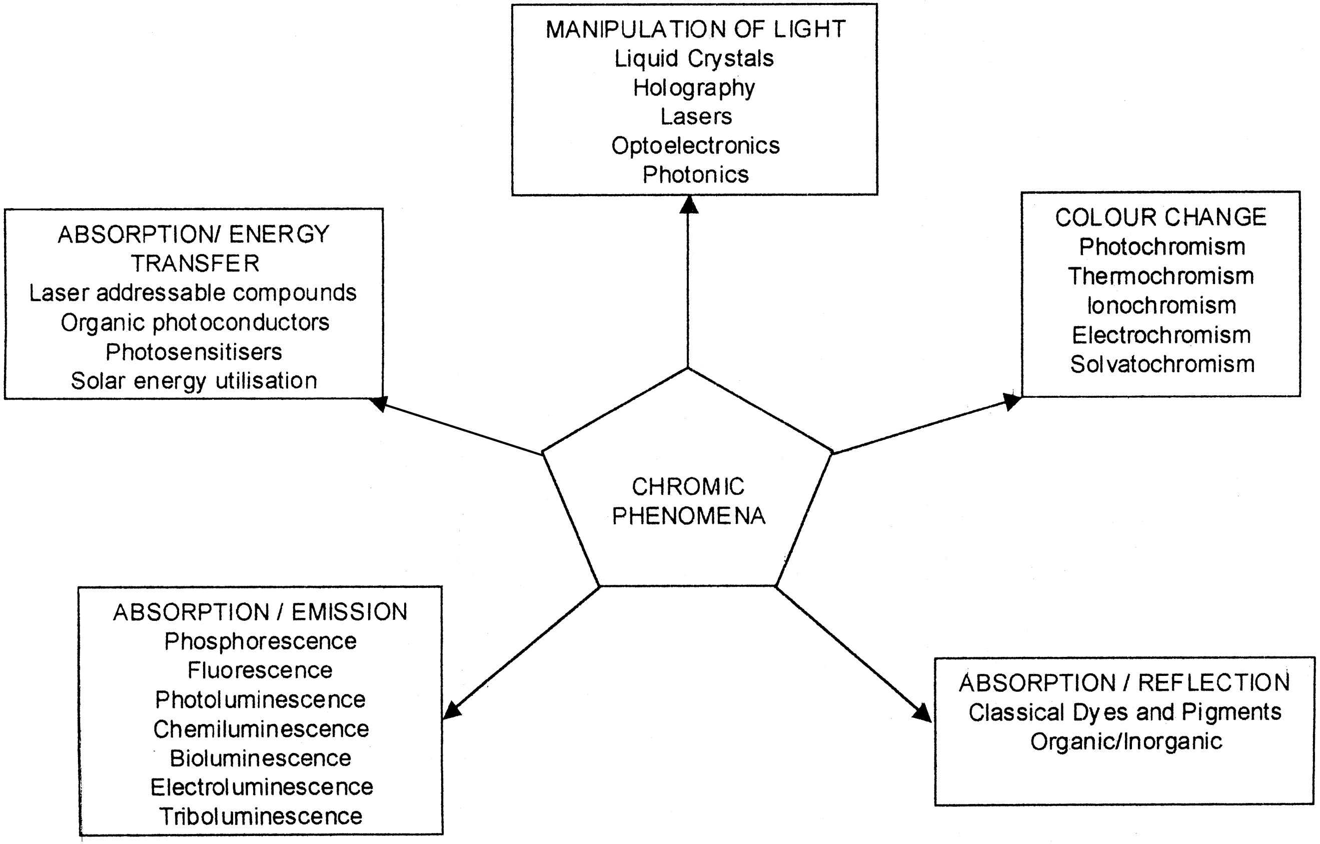

Figure I.1 *Classification of chromic phenomena* indicator lights. In the laboratory the use of fluorescent analytical reagents, sensors and probes is now invaluable in the medical and molecular biology arenas, as exemplified by the human genome project.

With the advent of cheap lasers, the need for molecules that can absorb their energy and convert it for use in a variety of applications has grown. A large scale use is in optical data storage discs and in the photoreceptors in laser printers, as described in Chapter 4. Photosensitisers are another important group of chemicals that are used both in photochemical applications, *e.g.* polymerisation, but also in important medical applications such as the treatment of cancers *via* photodynamic therapy. Solar energy conversion, mimicking natures skill with photosynthesis, occupies a great deal of research energy which is starting to pay off. Prototype cells are now 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 displays such as watches and clocks and in flat panel displays on portable PCs. Interference coupled with reflection coherent laser light is used to produce the diffraction gratings used in the well-known holograms in graphic arts, but extending this technology has led to its use in the leading edge 3D-holographic data storage technology. Synthetic or pearlescent pigments have been around for some 50 years but in recent years great strides have been made in more effective control of the nature of the iridescence. Colour variable pigments, *i.e.* those whose colour changes depending on the angle of vision, are the latest addition to this group of pigments. They are fast becoming important niche colorants in automotive finishes. Opto-electronics is the hybrid technology, between electronics and photonics, where materials respond to electrical impulses by changing their refractive index in a non-linear manner. Progress in this area has reached the point where devices, such as wave-guides, are now available commercially. The ultimate manipulation of light is in photonics where the desire is to replace the electron with the photon as a means of transferring data. Photonic crystals are macroporous materials which can trap photons of a particular wavelength, which would have been the stuff of science fiction a decade ago. They therefore constitute what are known as the photonic band gap materials or the photonic equivalent of the semi-conductor for electrons. Photonic band gap materials will underpin the future development of all optical communications and computing.

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 are covered within this book that it would have 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 more detail provided on the chemistry and applications of the technology. For each topic a major source text is suggested so that the reader can obtain further detailed information as required.

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CHAPTER 1

Phenomena Involving a Reversible Colour Change

1.1 Introduction

Any changes in the colour of an object, whether this is from white to black, colourless to coloured or from one colour to another, can be easily detected by the human eye or by using simple spectrophotometric instruments. Such changes in colour therefore provide very important visual signals that can be used to convey useful information to an observer, the most obvious being traffic control signals. 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 with the darkened glass in sun spectacles. When a third parameter is introduced, namely an external stimulus, whether this is chemical or physical, that causes the change of colour or the restriction of light transmission, especially when this change is reversible, the potential applications significantly widen. Consequently, research into chemicals that undergo reversible changes in colour upon the application of an external stimulus has been extensive, and the products of this work have found uses in a wide variety of outlets, in both low and high technology areas.

These colour change phenomena are classified and named after the stimulus that causes the change. Accordingly, photochromism is a change in colour, usually colourless to coloured, brought about normally by UV light, 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 list of these and other phenomena are given in Table 1.1, together with a selection of the many areas where they have found application. The most important commercially of these phenomena, namely photochromism, thermochromism, electrochromism and ionochromism, will be covered in some detail in the sections below.

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. The change in one direction occurs under the influence of electromagnetic radiation,

Table 1.1 *Colour change phenomena and their applications*

Phenomena	*Stimulus*	*Applications*
Photochromism	Light	Ophthalmic lenses, novelty printing, security printing, cosmetics, optical data storage, memories and switches, sensors
Thermochromism	Heat (intrinsic and indirect)	Thermochromic pigments, temperature indicators and thermometers, security and novelty printing
Electrochromism	Electrical current	Windows, mirrors, displays
Solvatochromism	Solvent polarity	Analysis, sensors, monitoring of polymers and polymerisation
Ionochromism	Ions	Colour formers, thermal fax papers, indicators, metal ion detection
(Halochromism)	(pH change)	(ditto)
Tribochromism	Mechanical friction	
Piezochromism	Mechanical pressure	

usually UV light, and in the other direction by altering or removing the light source or alternatively by thermal means.

Usually the change in colour in the forward direction is to longer wavelength, *i.e.* bathochromic, and reversibility of this change is key to the many uses of photochromism. In many systems, *e.g.* 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 (*e.g.* 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 section 1.3).

Photochromism is a vast field and in this section of the book we will cover only the main classes of photochromic compounds and their synthesis and then go on to describe the current commercial applications for these materials and also some of a more speculative nature. For more detailed accounts the reader should consult the books on photochromics edited by Crano and Guglielmetti [1,2] and Durr and Bouas-Laurent.[3]

1.2.1 Main Chemical Classes

The ideal properties required from any class of organic photochromic compounds are

1. *Colour development.* The material must develop rapidly a strong colour 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 colouration cycles
5. *Colourless rest state.* The colourless 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.

1.2.2 Spirobenzopyrans

Spirobenzoyrans are a very widely studied chemical class of compounds which exhibit photochromism. They consist structurally of a pyran ring, usually a 2*H*-1-benzopyran, linked *via* a common spiro group to another heterocyclic ring, *e.g.* (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 either *cis*-(1.2) or *trans*-(1.3), or the *ortho*-quinoidal form represented by (1.4) in Figure 1.1. In fact 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*-merocyanines structure (1.3) in this text.

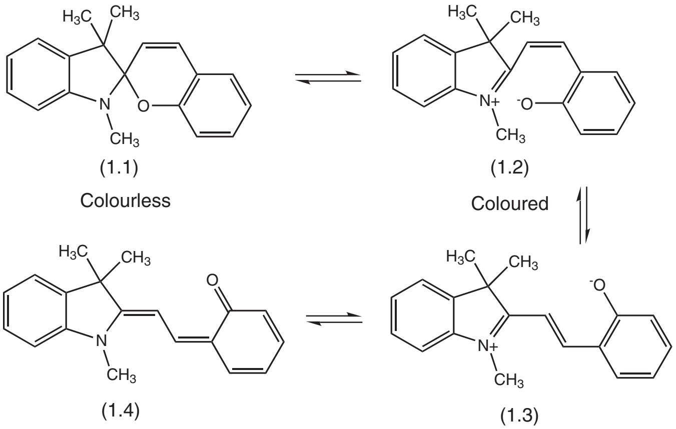


Figure 1.1 *Spiroindolinobenzopyran and ring opened merocyanine quinonoid form.*

A very large number of possibilities exist for varying the components of the spiropyran ring. The pyran ring is usually a 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.

1.2.2.1 Synthesis of Spiroindolinobenzopyrans

The synthetic pathway to spiroindolinobenzopyrans (1.8) illustrated in Figure 1.2 is representative of the methodology used to make this class of compounds. The parent spiroindolino compound (1.1) is made by the condensation of the readily available

Fischer's base (1.6; R = H) with salicylaldehyde (1.7). The same route can be used with an indolinium compound bearing different N-alkyl groups (1.6; R = alkyl) and ring substituents; synthesised as shown in Figure 1.2 by alkylation of a 2-methylindole to produce (1.8; R = alkyl). Substituted salicylaldehydes and also 2-hydroxynaphthaldehydes can also be used to give other analogues.

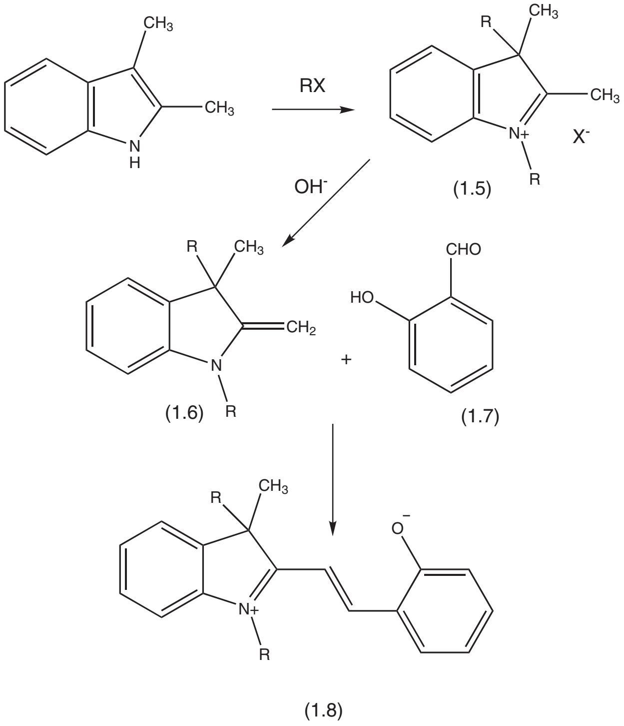
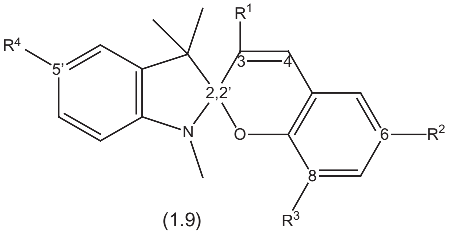


Figure 1.2 *Synthetic pathway to BIPS and derivatives.*

1.2.2.2 Spectral Properties of Spiroindolinobenzopyrans and Analogues

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 necessary to use a rapid scanning spectrophotometer to measure the absorption spectrum. The spiroindolinobenzopyran (1.9 in Table 1.2; R^1–R^4 = H) has an absorption at λ_{max} 531 nm (in toluene). This class of compounds exhibit a strongly positive solvatochromic effect (see section 1.6), with the shape of the absorption curve changing and its position moving hypsochromically as the solvent polarity increases.[4] From the data given in Table 1.2, it can be seen that substituents in the 3,6,8-positions (see 1.9) of the spiropyran ring have the biggest influence on the spectral properties of the coloured form.[5] The large bathochromic shift in (1.9a) *versus* (1.9b) is put down 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 (1.9a) with a benzoxazole ring causes a hypsochromic shift (600 nm) whilst a benzthiazole ring moves the absorption bathochromically (635 nm).

Table 1.2 *Absorption maxima of the coloured form of substituted BIPS*



(1.9)

Compound	*R^1*	*R^2*	*R^3*	*R^4*	*λ_{max}/nm*
(1.9a)	Ph	NO_2	OCH_3	H	625
(1.9b)	H	NO_2	OCH_3	Ph	568
(1.9c)	H	OCH_3	NO_2	Ph	625
(1.9d)	H	NO_2	H	H	532
(1.9e)	H	H	NO_2	H	544

In ethanol.

1.2.3 Spironaphthoxazines

Spirooxazines, the nitrogen containing analogues of the spiropyrans, are very resistant to photodegradation This resistance to photodegradation, known in this field as fatigue resistance, is an essential property for those photochromic materials designed for applications in solar protection uses, *e.g.* in sun spectacles. The photochromic ring opening of a spironaphthoxazine derivative to its coloured form is shown in Figure 1.3.

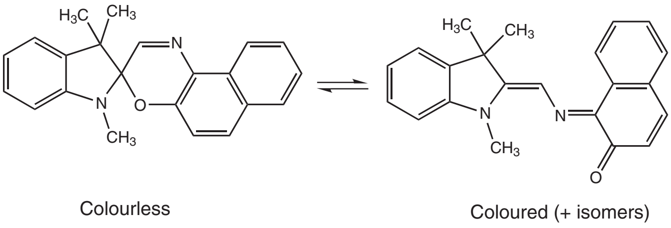


Figure 1.3 *Spironaphthoxazine photochromic forms.*

1.2.3.1 Synthesis of Spiroindolinonaphthoxazines and Analogues

The commercially available spirooxazines are based on the spiroindolinonaphthoxazines (1.11) ring structure. The synthetic route to this ring system involves the reaction of a 1-hydroxy-2-nitoso bearing aromatic ring with a 2-alkylidene heterocycle, such as Fischer's base (1.6; R = H). The naphthoxazines are the derivatives of choice since the nitrosonaphthols starting materials are much more stable than the nitrosophenols required for the parent benzo analogue. Unsubstituted nitrosonaphthols (1.10), higher benzo- and hetero-ring analogues can be synthesised by acidification of an aqueous solution of the corresponding phenolate and sodium nitrite. Condensation of the nitrosonaphthols with the indolines is readily achieved by heating the mixture, in methanol or other polar solvents, under reflux. This synthetic route, shown in Figure 1.4, can be used as a general synthetic method for alkyl substituted naphthoxazines, and benzo- and heterobenzo-annulated derivatives.[5,6]

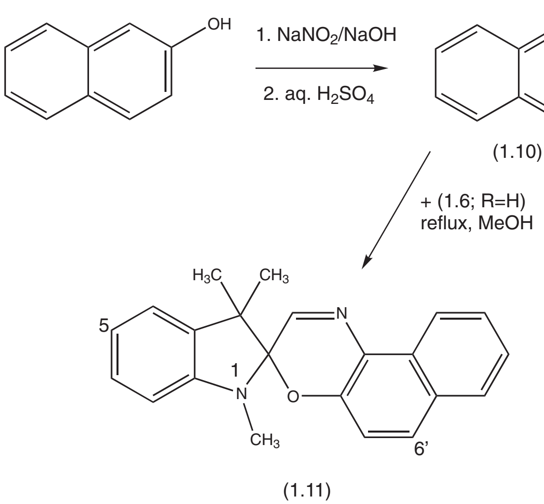
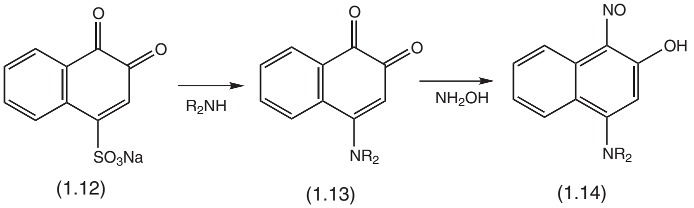


Figure 1.4 *Synthetic route to spiroindolinoaphthoxazine.*

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 (1.11) 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 molar absorption 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.[7]

The important products bearing amino substituents in the 6’-position are synthesised from 4-substituted-1-nitroso-2-naphthols (1.14), which are prepared from (1.12) *via* (1.13).[7]



The synthesis of simple *N*-alkylated-2-methyleneindolines (1.6) has already been described in Figure 1.2. However, highly branched N-alkyl derivatives, which are required for wider variations on the 1-substituent in the spiroindolinonaphthoxazines, are best prepared by the Katritzky method shown in Figure 1.5.

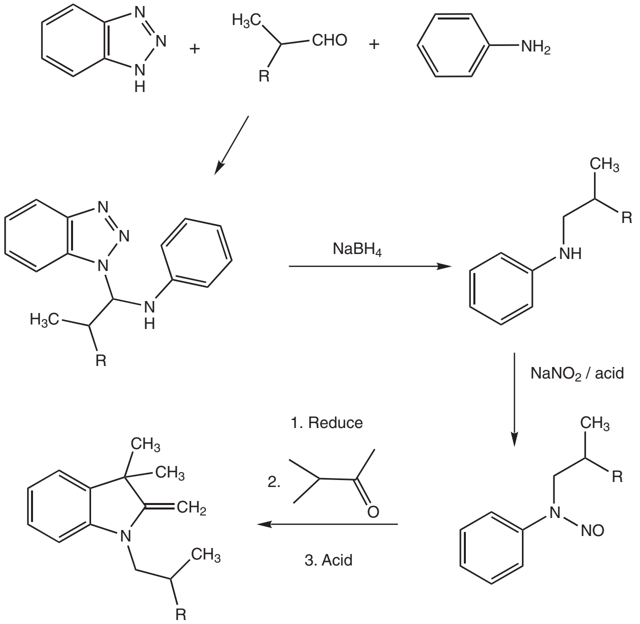


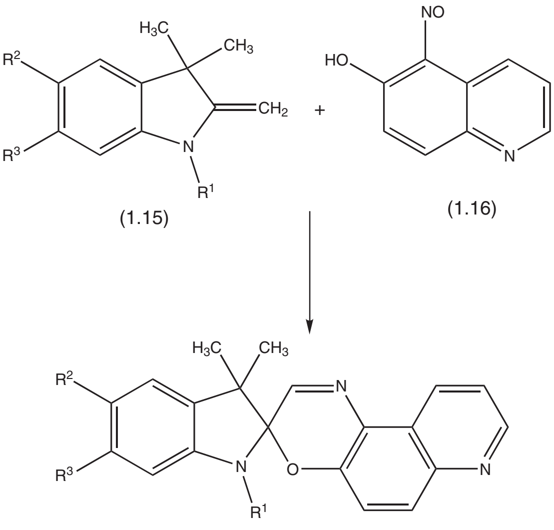
Figure 1.5 *Synthetic route to N-alkylated-2-methyleneindolines.*

Another group of commercially important spirooxazines are those where the naphthalene ring is replaced by quiinoline to give the spiroindolinopyridobenzoxazines (1.17). These are synthesised by reaction of 5-nitroso-6-hydroxyquinoline (1.16) with alkyl substituted 2-methyleneindolines (1.15).[8]

1.2.3.2 Spectral and Physical Properties of Spiroindolinonaphthoxazines

The spectrum of the ring-opened form of the parent spiroindolinonaphthoxazine (1.11) has λ_{max} at 590 nm. 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 1.2.2.2).

Introduction of dialkylamino substituents in the 6′-position of the spiroindolinonaphthoxazine (1.11) 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 (1.11), whilst electron-donating groups move the absorption maximum in the opposite direction.[6,7] The data for these effects are given in Table 1.3.



(1.15) (1.16)

(1.17)
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

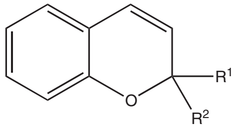
Table 1.3 *Substituent effects on the absorption maximum of the coloured state of spiroindolinonaphthoxazines (1.11)*

6′-substituent	*5-substituent*	λ_{max}/nm
H	H	605
Indolino	H	592
Indolino	OCH_3	623
Indolino	Piperidino	637
Piperidino	H	578
Piperidino	Cl	568
Piperidino	CF_3	560
Morphilino	H	580
Diethylamino	H	574

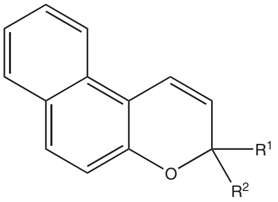
Changing the alkyl substituent on the 1-position of (1.11) has little or no effect on the absorption maxima and no effect on the fatigue resistance. However, there is a very marked effect on the percentage loss in the initial optical density of the coloured state after activating with UV light. This can be measured as the percentage loss in initial optical density 10 s 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 into the colourless state.[7]

1.2.4 Benzo and Naphthopyrans (Chromenes)

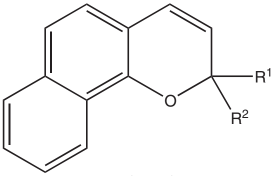
The photochromic compounds of potential interest, based on the 2*H*-chromene ring system, are the 2*H*-benzopyrans (1.18) or the three isomeric naphthopyrans (1.19–1.21). However, 2*H*-naphtho[2,3-*b*]pyrans (1.21) show little or no useful photochromic behaviour and can be discounted from any further 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.



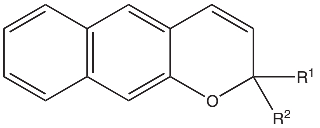
(1.18)



(1.19)



(1.20)



(1.21)

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 to give either the zwitterionic form or, more likely, the *cis*- and *trans*-quinoidal forms (Figure 1.6). Studies suggest that formation of the *cis*-quinoidal species occurs in picoseconds, followed by generation of the *trans*-form in nanoseconds.

The two naphthopyrans of interest (1.19) and (1.20) show quite different photochromic behaviour. Isomer (1.20; R^1, R^2 = Ph) produces a more bathochromic coloured state than (1.19; R^1, R^2 = Ph), (λ_{max} = 481 nm *versus* 432 nm), a large

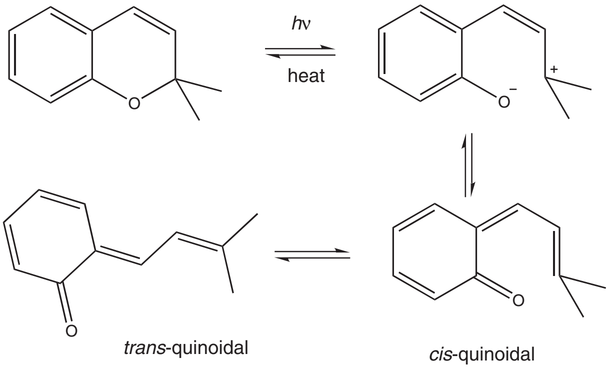


Figure 1.6 *Photochromic behavior of chromenes.*

increase in coloration, but a very slow fade rate back to the colourless state.[9] 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 3*H*-naphtho[2,1-*b*]pyrans (1.19).

1.2.4.1 Synthesis of Benzopyrans and Naphthopyrans

Simple 2,2-dialkyl-2*H*-benzopyrans, or chromenes as they are very often called in the photochromic literature, can be synthesised by several well established routes, a selection of which are shown in Figure 1.7.[5,9]

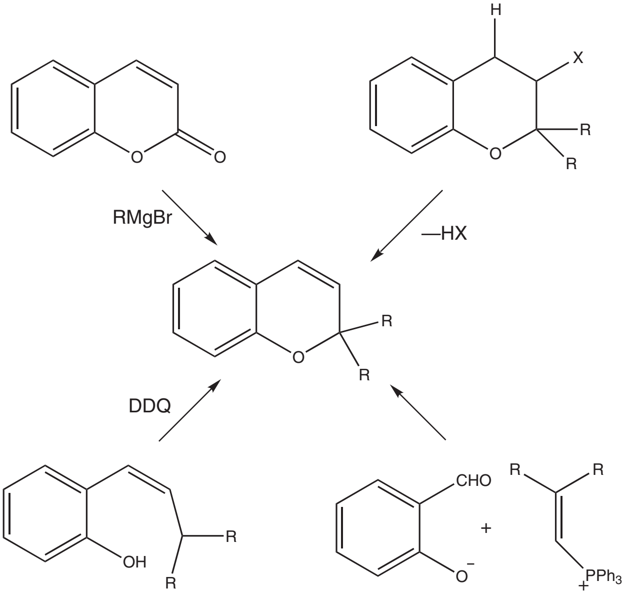


Figure 1.7 *Synthetic routes to 2,2-dialkyl-2H-benzopyrans.*

However, when it comes to the more important 2,2-diaryl derivatives (1.25), the routes illustrated in Figure 1.7 are not very useful. For these derivatives the almost universally adopted synthetic method involves the reaction of a 1,1-diarylprop-2-yn-1-ol (1.24) with a substituted phenol or naphthol in the presence of an acid catalyst. The acid catalyst can be alumina, an acidic clay or Nafion for heterogeneous reactions, or trifluoroacetic acid, *p*-toluenesulfonic acid and dodecylbenzenesulfonic acid for reactions carried out in solution. The alkynols are prepared by reaction of a benzophenone (1.22) with a Na or Li derivative of an alkynide, such as the trimethylsilyl acetylide (1.23), (Figure 1.8).[9]

An alternative procedure, which was devised for the synthesis of heteroannulated chromenes, involves the reaction of the titanium salt of the phenol with an α,β-unsaturated carbonyl compound.[10,11] This is illustrated for the reaction of *N*-methyl-3-hydroxycarbazole (1.26) with β-phenylcinnamaldehyde, which produces the carbazolopyran (1.27) in 35% yield.[12]

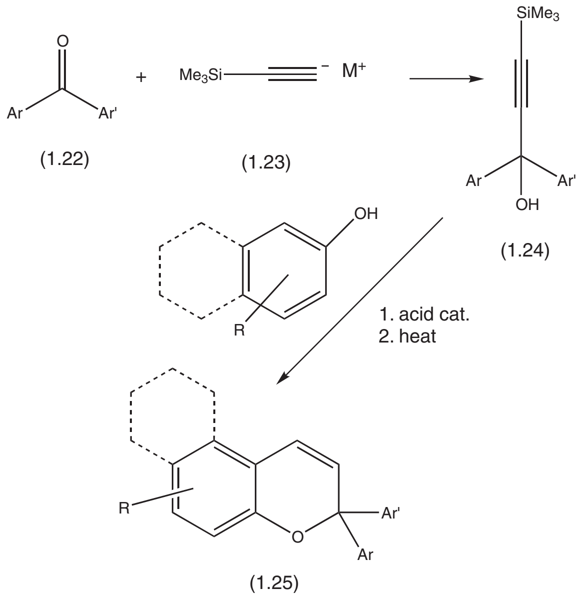
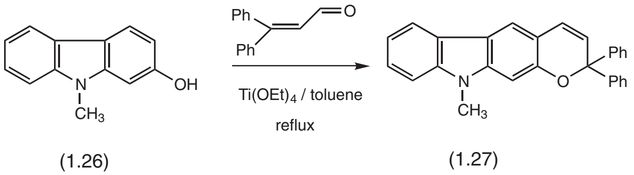


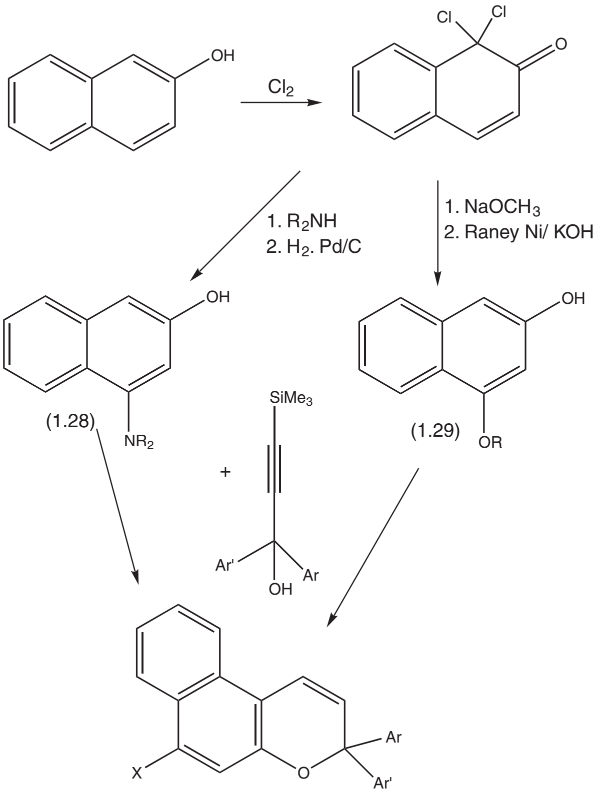
Figure 1.8 *Synthesis of diaryl benzo- and naphthopyrans.*



3*H*-Naphtho[2,1-*b*]pyrans (1.19) with an amino or alkoxy residues in the 6-position (1.30) show particularly high colourability. The 1-amino- and 1-alkoxy-3-hydroxynaphthalenes (1.28 and 129) required for the synthesis of these compounds are prepared from 2-naphthol as illustrated in Figure 1.9.[13]

1.2.4.2 Spectral and Physical Properties of Diarylnaphthopyrans

As mentioned in sections 1.2.2.2 and 1.2.3.2, 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 is 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 this 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 (absorbance) 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.



(1.30; X = NR_2 or OR)

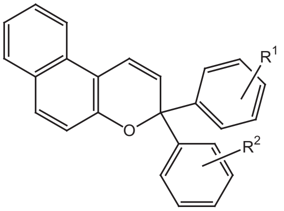
Figure 1.9 *Synthetic route to 6-amino and 6-alkoxy-3,3-diaryl-3H-naphtho[2,1-b]pyrans.* (Reproduced with permission of Kluwer Academic/Plenum Publishers.)

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 1.2.3.2.

The influences on the absorption spectra and the other photochromic properties of compounds with substituents in the 3*H*-naphtho[2,1-*b*]pyran ring and on the 3,3′-aryl groups have been studied in detail.[9,13] Electron-donating groups in one or both of the 3-phenyl groups, especially in the *p*-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 σ-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 reduction in the $IODF_{10}$ figure, an effect that has been described as ‘hyperchromic’ (Table 1.5).[9]

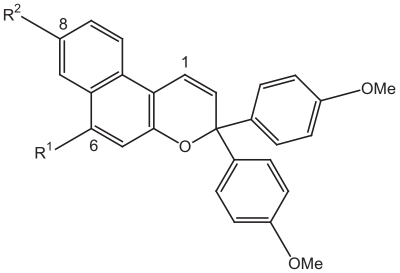
Table 1.4 *Influence of substituents in the 3-phenyl rings on the properties of 3,3-diaryl-3H-naphtho[2,1-b]pyrans*
(Reproduced with permission of Kluwer Academic/Plenum Publishers)



R^1	*R^2*	*λ_{max}/nm*	*ΔOD*	*$T_{1/2}$/s*	*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_2	4-MeO	450	2.23	1800	B

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

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



R^1	*R^2*	*λ_{max}/nm*	*IOD*	*$IODF_{10}$%*	*Solvent*
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

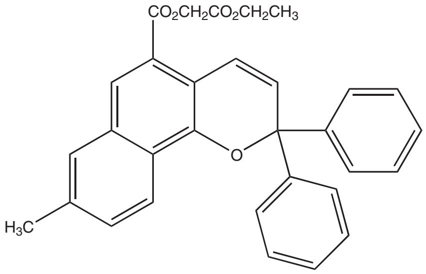
A = polyurethane. B = Spectralite.

As mentioned above, the main problem with the 2*H*-naphtho[1,2-*b*]pyran ring system (1.20) is the very slow rate of fading back to the colourless state: (1.20: R^1, R^2 = Ph), $t_{1/2}$ = 1800 s *versus* 45 s for (1.19; R^1, R^2 = Ph). These problems have largely been overcome to produce materials suitable for ophthalmic uses by introducing electron-withdrawing groups at the 5-positon, as in (1.31), and, more intriguingly, by having an indeno group fused onto the 5- and 6-positions (1.32) (see also in section 1.2.8.1).[13,14]

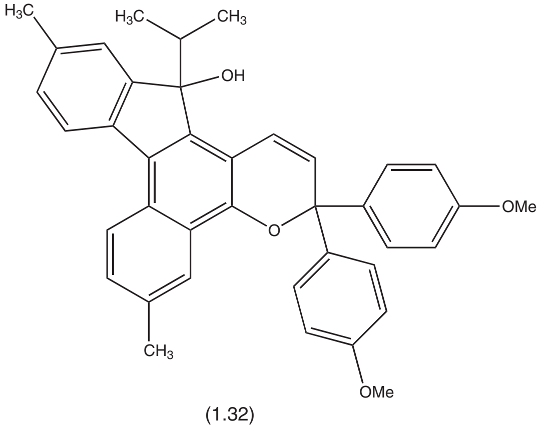
1.2.5 Fulgides

Stobbe was the first to observe photochromism in fulgides (1.33) when he synthesised them by the condensation of an arylaldehyde or ketone with a substituted methylene succinate.[15] 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.[16,17] Heller's work showed, amongst many other things, the importance of R^1 in (1.33) being a 5-membered ring heterocycle, *e.g.* furan.

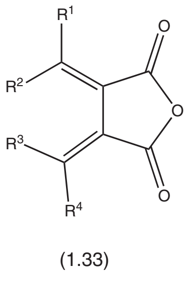
Fulgides can exist as *E* or *Z* isomers by rotation around the double bonds in (1.33). This is illustrated for the furano derivative in Figure 1.10. Isomerisation of the yellow *Z*-fulgide (1.34) to the *E*-fulgide (1.35) and cyclisation of this to the red coloured photochrome (1.36), designated as C here but often called the P state, occurs on irra-



(1.31)



(1.32)



(1.33)

diation with UV light. The coloured species (1.36) is converted back into the *E*-fulgide (1.35) 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 opening of the electrocyclic ring from occurring.[18] Since both the forward and back reactions require light energy it is important that they both show good quantum yields.

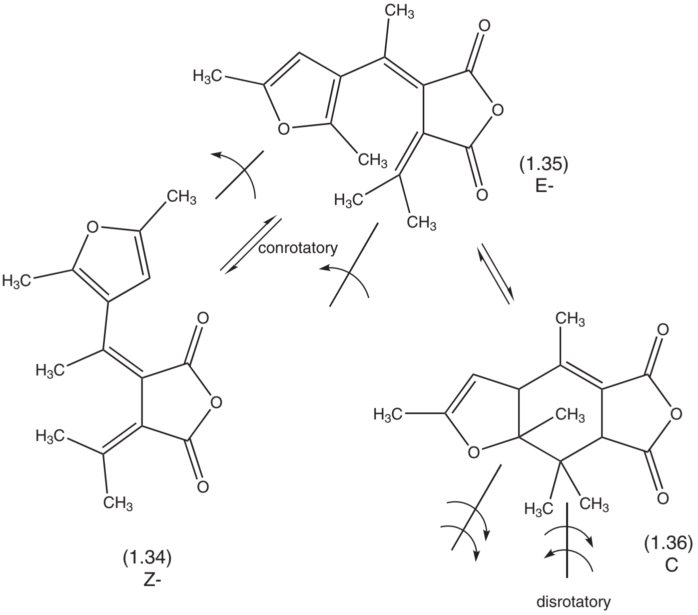
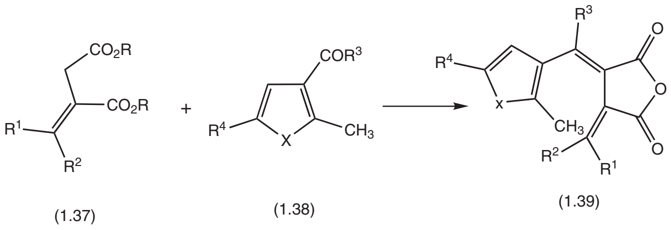


Figure 1.10 *Photochromic process for fulgides.*
(Reproduced with permission of University of Leeds, Department of Colour Chemistry.)

1.2.5.1 Synthesis of Fulgides and Derivatives

The Stobbe condensation is the preferred route to fulgides. This is exemplified by the synthesis of the 5-membered ring analogues (1.39) which involves reacting a dimethyl alkylidenesuccinate (1.37) with a heterocycle bearing a ketone group in the 3-position (1.38) in the presence of a strong base; *e.g.* sodium ethoxide, potassium *t*-butoxide, sodium hydride or lithium diisopropylamide. A typical solvent is toluene and the time and temperature of the reaction depends on the reactivity of the ketone



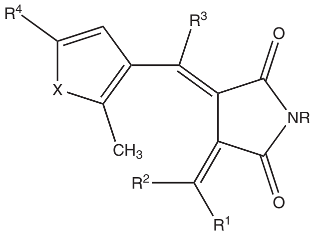
and the base that is used. The di-acid intermediate is converted into the anhydride (1.39) by reaction with either acetyl chloride or acetic anhydride.[19]

The corresponding imides (1.40), called fulgimides, are most readily synthesised by conversion of the fulgide into the succinamic acids by reaction with amines, followed by dehydration. Functionalisation of the anhydride can also be achieved by reaction of the fulgides with malononitrile in the presence of diethylamine and subsequent recyclisation with acetyl chloride to give (1.41) from the corresponding *E*-fulgide and (1.42) from the *Z*-isomer.

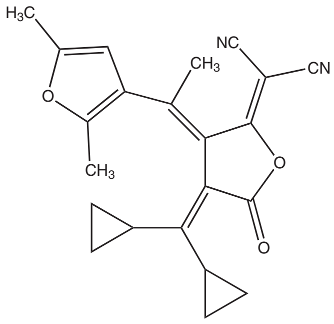
1.2.5.2 Spectral and Physical Properties of Fulgides and Derivatives

The main areas for molecular manipulation of the heterocyclic fulgides (1.43) are the hetero atom X in the 5-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 (1.43, A = O) to give fulgimides (1.43, A = NR) and conversion of the ring carbonyl groups into imides (143; B or C = NR) or methylene groups as in (1.41).

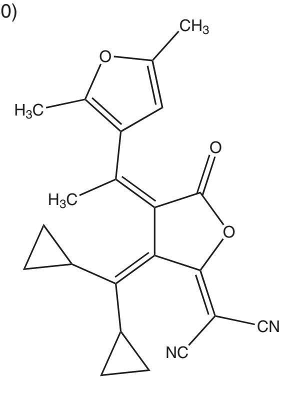
The change from X = O to X = S and NR causes the absorption of the coloured state to move bathochromically, from red to purple and blue. Major bathochromic shifts are also observed when R^4 is a phenyl group carrying electron-donating groups in the 4-position. The substituent R^3 has a marked influence on the quantum efficiency of the colouration process, *e.g.* 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,



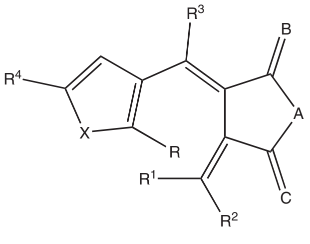
(1.40)



(1.41)



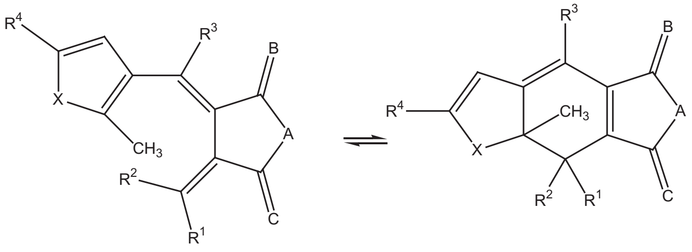
(1.42)



(1.43)

e.g. replacing isopropylidene with a spiro adamantyl group results in a six-fold increase in the decolouration 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 molar absorption coefficient. Both of the dicyanomethylene derivatives (1.41) and (1.42) move bathochromically, the effect being most marked in the latter case. The thienyl analogue of (1.42) is even more bathochromically absorbing.[20] The results from some of these key structural modifications are summarised in Table 1.6.

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



(1.43E) (1.43C)

X	*R¹*	*R²*	*R³*	*R⁴*	*A*	*B*	*C*	$\lambda_{max\ Col/nm}$	$\varepsilon_{max\ Col/}$	ϕ_{EC}	ϕ_{CE}
O	CH_3	CH_3	CH_3	CH_3	O	O	O	496	8200	0.20	0.055
S	CH_3	CH_3	CH_3	CH_3	O	O	O	525	8000	0.15	0.01
NPh	CH_3	CH_3	CH_3	CH_3	O	O	O	630	7300	–	–
O	CH_3	CH_3	CH_3	Ph-4-NR_2	O	O	O	588	26500	–	–
O	CH_3	CH_3	*i*-Propyl	CH_3	O	O	0	500	9000	0.58	0.043
O	Adamantyl		*i*-Propyl	CH_3	O	O	O	519	6900	0.51	0.26
O	*c*-Propyl	*c*-Propyl	CH_3	CH_3	O	$C(CN)_2$	O	594	–	–	–
O	*c*-Propyl	*c*-Propyl	CH_3	CH_3	O	O	$C(CN)_2$	633	–	–	–
O	CH_3	CH_3	CH_3	Ph	O	O	$C(CN)_2$	669	–	–	–

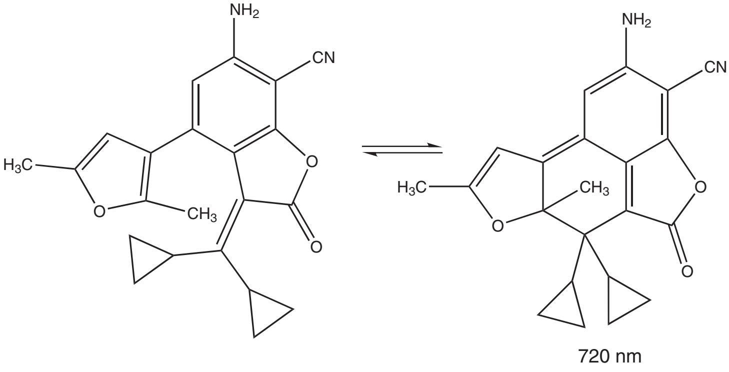
c-Propyl = cyclopropyl

Treatment of (1.41) with base causes one of the cyano groups to cyclise onto the methyl group at R^3, producing a phenyl ring compound (1.44). This product absorbs into the near-infrared at 720 nm, whilst the thienyl analogue is even more bathochromic at 760 nm.[18] Absorption in this region of the spectrum is essential in applications where semi-conducting diode lasers are used as the light source.

1.2.6 Diarylethenes

The well-known photoisomerisation of stilbenes has been brought into the useful photochromic range by replacing the phenyl rings with thiophenes, and the bridging ethylene group by a maleic anhydride or perfluorocyclopentene group, as shown in Figure 1.11. The 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-open 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.[21,22]



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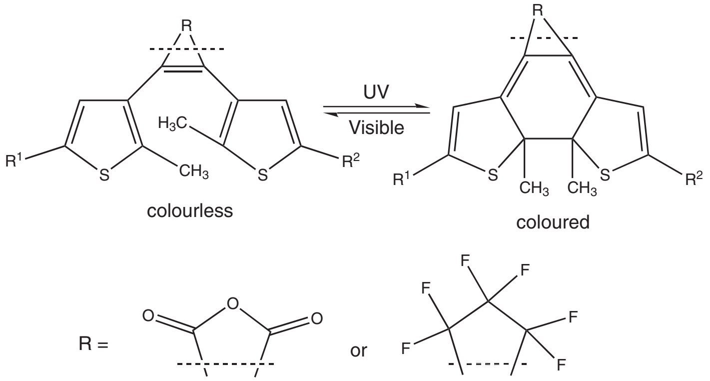
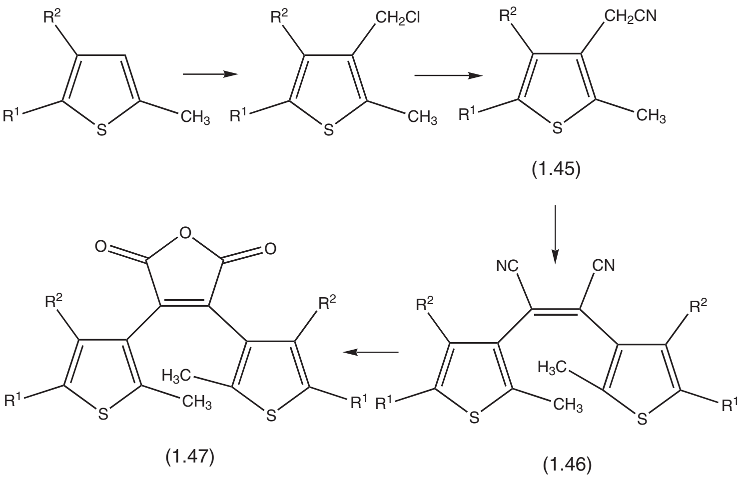


Figure 1.11 *Photochromic behaviour of dithiophenylethenes.*

1.2.6.1 Synthesis of Diheteroarylethenes

The synthesis of 1,2-bis(thiophen-3-yl)maleic anhydride involves the dimerisation of a 3-cyanomethyl derivative of thiophene (1.45) by reaction with aqueous NaOH in the presence of CCl_4. Alkaline hydrolysis of the dinitrile (1.46) and dehydration produces the anhydride (1.47) as shown in Figure 1.12.[21]

The synthesis of both symmetrical and non-symmetrical dithiophenylperfluorocyclopentenes is facilitated by selective elimination of fluorine from perfluorcyclopentene, using a thiophenylithium (1.48), prepared from the corresponding bromo derivative by reaction with *n*-BuLi in THF. The symmetrical product (1.51) is normally made without isolating the mono-substituted product (1.49), but the non-symmetrical compound (1.52) requires controlled production of (1.49) for reaction



(1.45)

(1.47)

(1.46)

Figure 1.12 *Synthesis of 1,2-bis(thiophen-3-yl)maleic anhydrides.*

with a different thiophenylithium (1.50) (Figure 1.13).[21–23] More recently, a versatile synthesis utilising a McMurray cyclisation of bis acylated thiophenes has been described.[22]

1.2.6.2 Spectral and Physical Properties of Dithiophenylethenes

The absorption spectra of symmetrical dithiophenylethenes are dependent on the substituents on the thiophene ring. Introduction of phenyl groups in the 2-position cause bathochromic shifts, and significantly higher molar absorption coefficients. These are further enhanced by electron-donating groups in the *p*-position of the phenyl ring. There is, however, a large drop in the quantum efficiency of the cycloreversion reaction (Table 1.7).[21]

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 (1.53). 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).[22]

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 (1.54), the repeatable cycle number in air is only 70, but for the non-symmetrical benzothiophene analogue (1.55; R = CH_3) this rises to 3700, and to greater than 10 000 for (155; R = OEt).[22] The figures are even higher in vacuum due to either the absence or lower formation of singlet oxygen. The thermal stability of (1.54) is over 90 days at 80 °C and at least five years at room temperature, whilst products like (1.55) are only quoted to be ‘stable’, *i.e.* having lifetimes longer than 12 h at 80 °C.

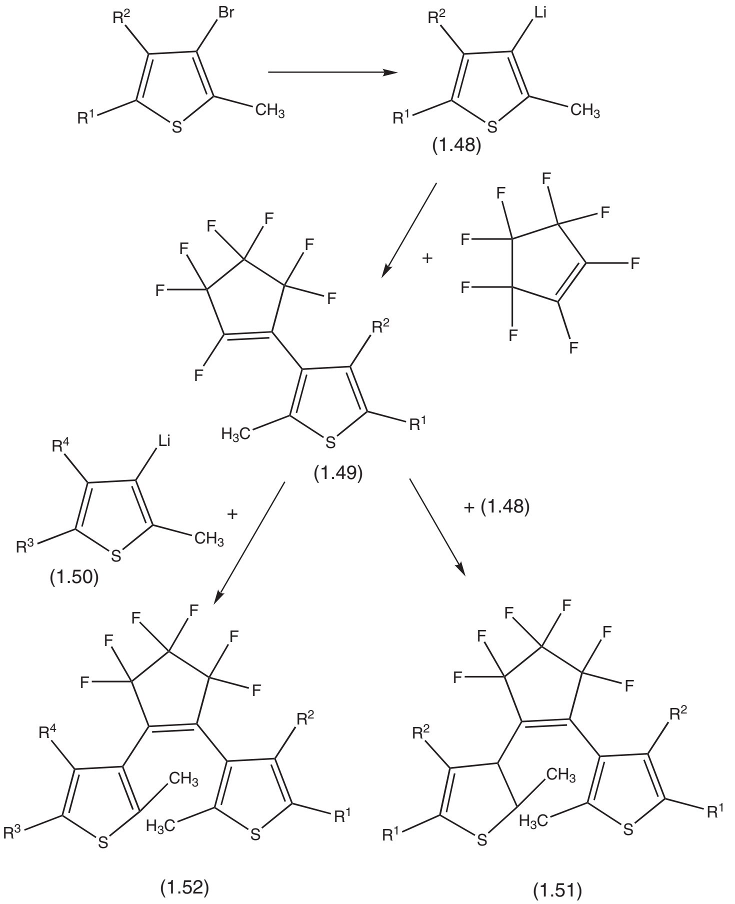
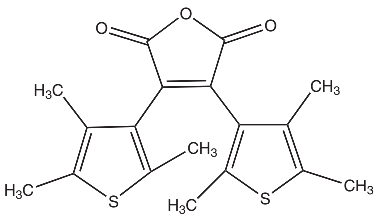


Figure 1.13 *Synthetic route to symmetrical and non-symmetrical dithiophenylperfluorocyclopentenes.*



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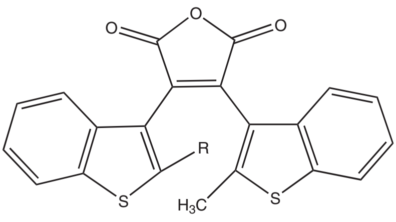

(1.55)

1.2.7 Miscellaneous Photochromic Systems

Several other photochromic systems are being studied for a variety of outlets and detailed accounts are available in the literature.[24–26] Dihydroindolizine based systems, containing a 5-membered ring, undergo photochemical ring opening to give a

Table 1.7 *Properties of symmetrical dithiophenylperfluorocyclopentenes*
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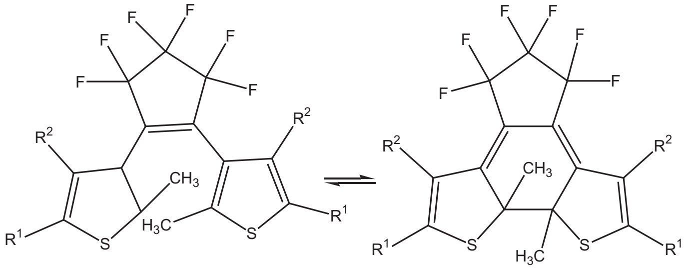
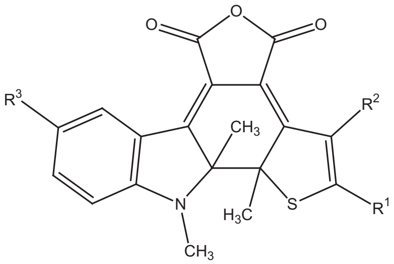


(1.51)

R^1	R^2	$\lambda_{max\ COL}$/nm	$\varepsilon_{max\ COL}$/	Φ_{cyc}	Φ_{cycrev}
H	CH_3	534	5 050	0.21	0.13
C_6H_5	CH_3	562	11 000	0.46	0.015
C_6H_4-4-OCH_3	CH_3	570	14 000	0.48	0.008
C_6H_4-4-NEt_2	CH_3	597	18 000	0.37	0.0025

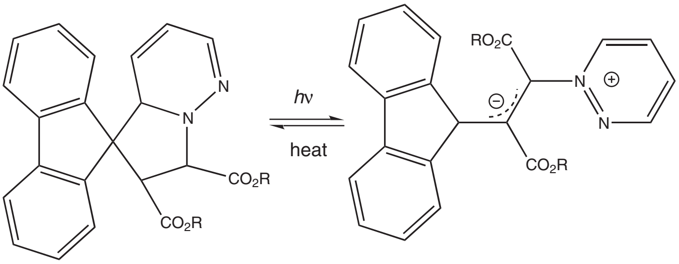
Table 1.8 *The absorption maxima of non-symmetrical maleic anhydride based photochromes*
(Reproduced with permission of Kluwer Academic/Plenum Publishers)



(1.53)

R^1	R^2	R^3	λ_{max}/nm
CH_3	CH_3	H	578
CH_3	CH_3	OCH_3	611
CN	CH_3	H	628
CN	CH_3	OCH_3	680

coloured zwitterion (1.56). The process can be reversed either photochemically or by thermal means.[24] 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 (1.57), the process is photoreversible.[25] Photochemical cleavage of a C–N bond in perimidinespirocyclohexadienones, followed by intermolecular rearrangement, produces the deeply coloured quinoneimines (1.58), similar to indophenol dyes in structure; decolourisation being achieved by thermal means.[26] Another useful type of photochromism that has been exploited, especially in polymeric structures, is that exhibited by the *cis–trans* isomerisation of azobenzenes.[27]



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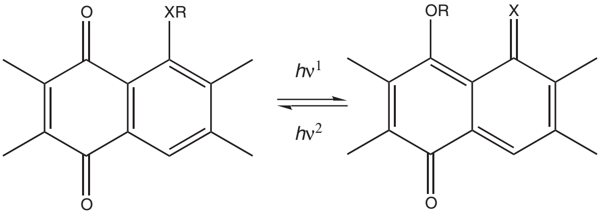

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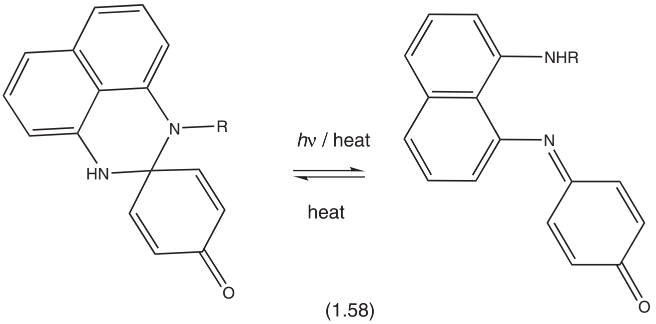


(1.58)

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, relative permittivity (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 sun glasses, there is therefore a growing list of other potential application areas, including 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.[22] The incorporation of photochromes into polymers, both in chain and side chain, is also an active area of research.[28]

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. 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. However, in the last decade of the 20th 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 in this application area were PPG industries 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. There is no single photochromic compound that can do this and colour formulators need to resort to mixtures of products to produce the desired colours in the lens. Apart from being able to deliver the desired colour, 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.

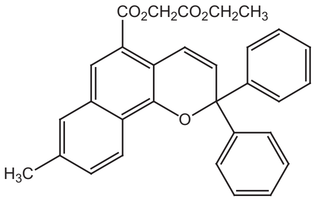
The three main classes that have been much studied for ophthalmic applications are spiroindolinonaphthoxazines (see section 1.2.3), diarylnaphthopyrans (see section 1.2.4) and fulgides (see section 1.2.5). How these different photochromic classes match up to the desired criteria for use in lenses is shown in Table 1.9. From this it can be seen that 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

Table 1.9 *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

compounds used to produce greys and browns are the yellow (1.31) and the blue (1.32), the properties of which are given in Table 1.10. This pair offer a well matched build up to saturation optical density but their fade rates, whilst close, are far from perfectly matched.[14] 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.

Table 1.10 *Photochromic properties of naphthopyrans in ophthalmic plastic*



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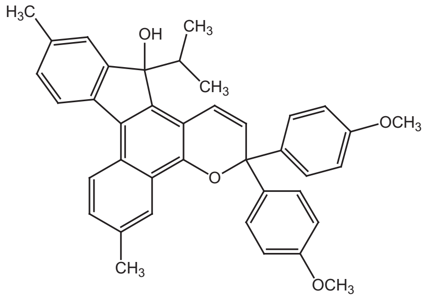


(1.32)

Compound	*λ_{max}/nm*	*Optical density*			*$T_{1/2}$ (Fade)/s*
		30 s	*120 s*	*At saturation*	
131	464	0.16	0.29	0.37	60
132	582	0.12	0.25	0.36	80

1.2.8.2 Novelty Printing and Textile Applications

The use of photochromics in novelty printing is a significant commercial outlet. Because of their ability to show resistance to thermal fade rates fulgides have been the class most commonly used for this application. Typical uses are on children's toys and for logos on T-shirts.

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 apparel garments *etc.* Indoors, away from UV light, the design is white on the fabric but changes its colour on exposure to UV radiation in daylight. A range of colours is available from yellow through red to purple and green.[29]

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 (rewritable) compact disks and digital versatile disks (DVDs). The most highly developed erasable and rewritable media are either magneto-optic or phase change materials, 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:[30]

- Thermal stability – very low thermal re-conversion
- Fatigue resistance – long-term stability during read and write cycles
- Non-destructive readout capability – the read out process must not induce interconversion of the two forms
- High efficiency of the photoreaction – large 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.[22,27]

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 into B, B into A). The readout can be measured as the difference in the reflecting light intensity of the laser (*e.g.* diode), or by fluorescence or infrared absorption signals in the two forms.[22,23]
2. Dual-mode system
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 into stable A' and B' products. The two forms in the system can therefore be locked or unlocked.[31]

Photochromic systems that have been examined in both of these approaches include spiropyrans, spirooxazines, diarylethenes, dihydroindolizines and azobenzenes.[22,27,30–33] A schematic of a disk structure is shown in Figure 1.14. To produce the

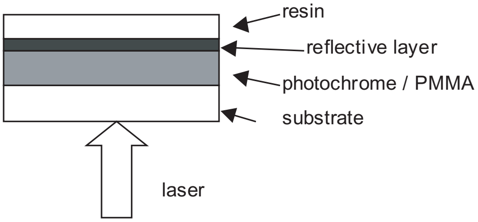


Figure 1.14 *Schematic of an optical memory disk.*

recording layer the photochromic material is laid down in an acrylic resin (*e.g.* PMMA) onto a reflective layer of gold or aluminium. The recording medium is addressed by a recording/writing laser, *e.g.* He-Cd laser at 325 nm, or a frequency doubled diode laser, and a readout laser such as a AlGaAs 784 nm diode laser, operating through the glass substrate.

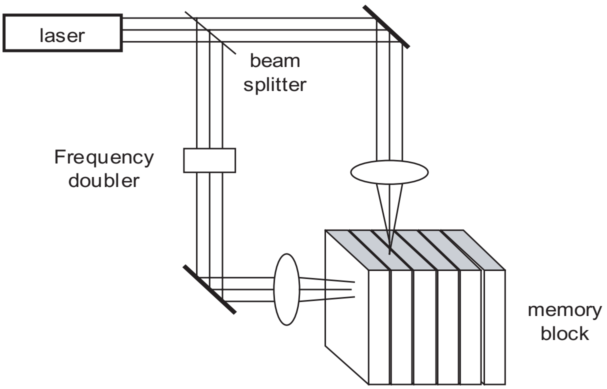
Several approaches can be adopted when trying to achieve very high-density optical storage. These include the development of short wavelength blue lasers; a halving of the wavelength of the laser reduces the spot radius by 2 and therefore the recorded, two-dimensional density by 4 (See Chapter 5, section 5.5). In the field of optical recording and memories the following methods are being examined.

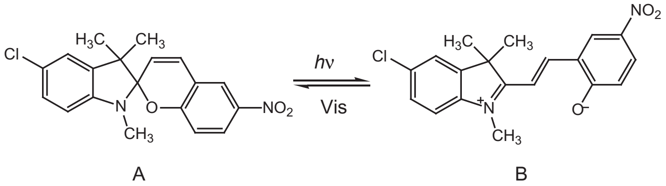
1. Near-field optics, in which recording density depends only on the size diameter of the probe tip aperture[22]
2. 3D-Memory by use of additional axial dimensions to the recording system[33]
3. Optical holography (see Chapter 5, section 5.4)

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 1.15. The potential for this 3D memory principle was demonstrated using the spirobenzopyran (1.59).[34] 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, *e.g.* a 1064 nm and a 532 nm photon (equivalent to 355 nm excitation) or two 532 nm photons (equivalent to 266 nm excitation), is used. 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 read out procedures must be used, the most promising of which is the detection of refractive index changes observed when photoisomerisation is induced by long-wavelength light.[33]

1.2.8.4 Other Optical Applications

A considerable amount of work has been done on incorporating photochromic compounds into organic or inorganic hybrid materials or synthesising preformed polymers to produce photoresponsive materials.[28,35] These materials are being designed for use in optical applications such as wave-guides, shutters, light modulators *etc.*, systems which are considered further in Chapter 5.





(1.59)

Figure 1.15 *Principle of 3D optical memory and a model photochrome.* (Reproduced with permission of the American Chemical Society.)

1.2.8.5 Biological Applications

It is possible to attach photochromic molecules onto naturally occurring receptors and enzymes and by so doing be able to photoregulate their binding and catalytic activities. These materials have the potential to be used as chemotherapeutic agents and biosensors, and as bioelectronic materials.[36,37] In most of this work to date spiropyrans have been used as the photochromic element in the system.

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”.[38]

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, from ‘indirect’ systems, in which the colour variation involves changes in the environment around the chromophore brought about by heat.[39] Technical applications where the indirect colour change is desired to be irreversible, *e.g.* 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

Inorganic materials, usually involving transition metals, and organometallics exhibit a thermochromic response over a wide range of temperatures and by a variety of mechanisms.[39,40] Examples include:

- The transition between different phases of different colour, *e.g.* Cu_2HgI_4 is red at 20 °C and black at 70 °C[38]
- 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[40]
- 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,[41]
- 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)[42]
- A change in co-ordination 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[39]

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
- Supramolecular systems, *e.g.* cholesteric liquid crystals (see Chapter 5, section 5.2)

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 show a strong solvatochromic effect, polar solvents favouring the formation of the more polar merocyanine form.[43]

It is possible to produce sequential colour changes using bis-spiropyrans.[44] The colourless bis-spiropyran (1.60), in Figure 1.16, when heated in *n*-propanol to 60 °C changes to a red colour, due to the formation of the mono-merocyanine (1.61), and at 70 °C it becomes blue as the bis-merocyanine (1.62) appears.

Schiff bases, from the condensation of salicylaldehydes with anilines, exhibit either solid-state photochromic or thermochromic behaviour, caused by hydrogen transfer between the enol–keto tautomeric forms. Whether the molecule exhibits photo or thermochromism is strongly dependent on their crystal structures. The thermochromic effect in Schiff bases is restricted to planar molecules, where the tautomeric equilibrium is toward the keto form, which absorbs at a longer wavelength (1.63), the colour change being normally from yellow to orange or red.[44] The aryl rings can be substituted with a range of both electron-withdrawing and electron-donating groups. If the phenyl ring on the aniline is changed to a pyridyl ring then the products exhibit only thermochromic behaviour.

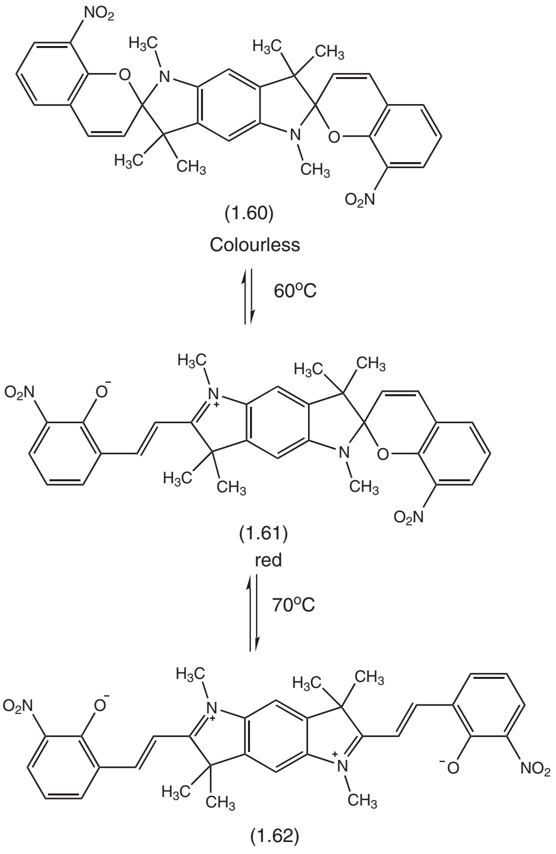
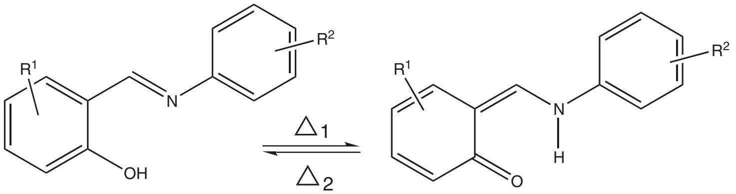


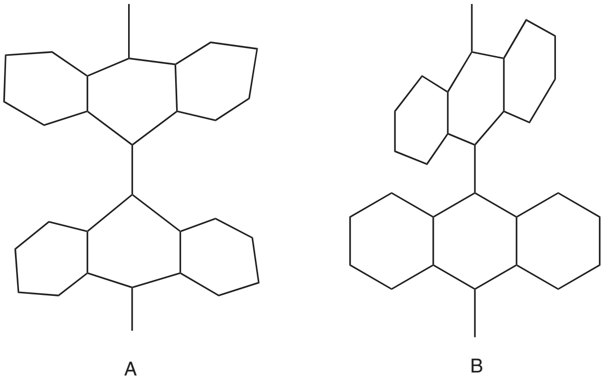
Figure 1.16 *Sequential thermal colouration of a bis-spiropyran.*

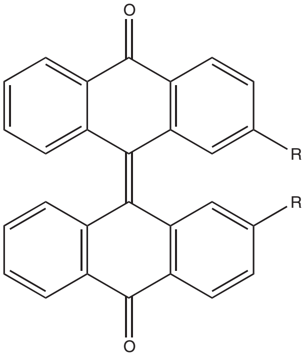


(1.63)

1.3.2.2 Stereoisomerism

Bianthrylidene systems, such as bianthrones (1.64), undergo reversible thermochromic colour change, due to two distinct and interconvertible A and B forms. In the parent bianthrones (1.64; R = H), the A species existing at room temperature is yellow (λ_{max} 380 nm) and this is partially converted into the green B form (λ_{max} 680 nm) on heating in solution.[44] The A form adopts a folded and the B form a twisted conformation (Figure 1.17). Bulky R substituents raise the energy barrier in going from A to B to such a level that they do not exhibit thermochromism. Other sterically overcrowded ethenes, which exhibit thermochromic behaviour include dixanthylidenes, bithioanthylidene, and mixed bianthrylidenes, *e.g.* xanthylideneanthrone.[44]





(1.64)

Figure 1.17 *Thermochromic bianthrones; folded A-form and twisted B-form.*

1.3.2.3 Macromolecular Systems

Conjugated polymers, *e.g.* poly(3-alklythiophene)s and poly(3-alkoxythiophene)s, as well as exhibiting electrochromism and photochromism, also show a strong colour change upon heating, in both the solid state and in solution.[45,46] The colour change, which is reversible, is blue-shifted or hypsochromic, a phenomenon that is known as 'negative thermochromism'. For instance poly[3-oligo(oxyethylene)-4-methylthiophene] at room temperature has an 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 (violet coloured) that upon heating become disordered and either twisted or non-planar and hence less conjugated (yellow coloured), as shown in Figure 1.18. 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. The temperature range of the solid-state thermochromic effect can also be altered by changing the length and flexibility of the side chains.

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 exception of thermotropic liquid crystals (see 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

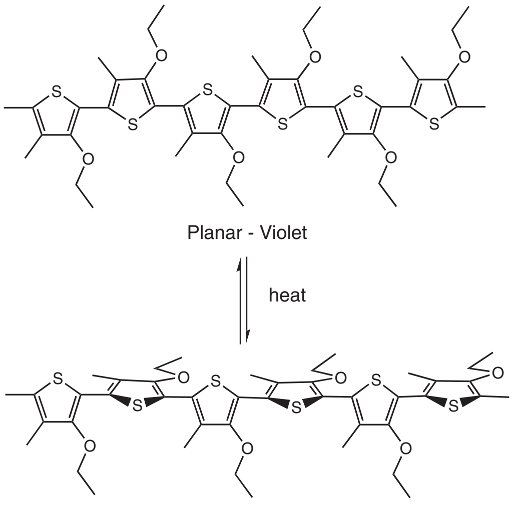


Figure 1.18 *Conformational changes leading to photochromism in regioregular poly(thiophene)s.*

been the subject of much development work. The colorants themselves in these systems are not thermochromic, but they do 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, *e.g.* fax papers, where the whole object 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).

1.3.4 Applications of Thermochromic Materials

Inorganic systems have found only relatively limited applications being mainly used in paints and crayons for indicating hot spots on equipment *etc.*[38,47] Of the intrinsically thermochromic organic materials it is only liquid crystals and conjugated polymers that have found any serious practical application, for instance the latter are used in optical temperature indicators and thermal recording.[48] The majority of current commercial applications use composite materials based on indirect thermochromism.

1.3.4.1 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 on these compositions has been published.[49]

The pH sensitive dyes, often called colour formers, that are most commonly used belong to the spirolactone class, *e.g.* diaryl phthalides (see section 1.4.1.1) or fluorans (see section 1.4.1.3). Ring opening of the colourless lactone on protonation by the weak acid developer occurs to give the coloured form. Many compounds have been claimed for use as the colour developer, but the most important commercially is Bisphenol A, which develops bright colours and changes of high contrast.[39] The most frequently used co-solvents are low-melting fatty acids, amides and alcohols. In the production of the pigments, the colour former, developer and co-solvent are melted together and cooled to give the coloured pigment; encapsulation for commercial use being achieved by the standard techniques of coacervation or interfacial polymerisation.[49] 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 the colour former interacts with the developer, possibly *via* an ion-pair complex. 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 1.19. Possible mechanisms for the colour change have been examined.[39]

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 (1.65).

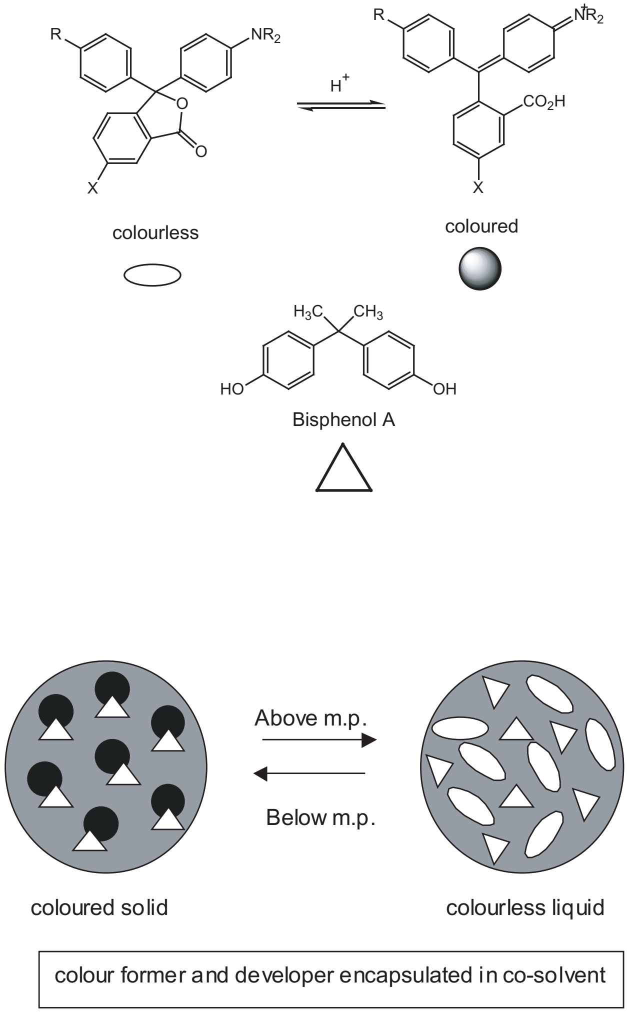
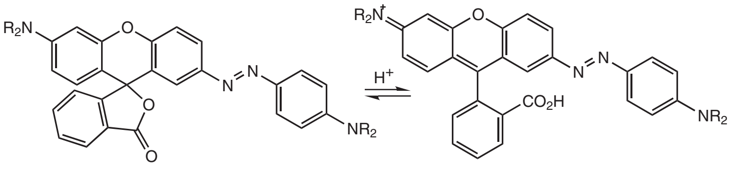


Figure 1.19 *Schematic of a composite organic thermochromic pigment.*



(1.65)

Thermochromic pigments are finding an ever increasing number of outlets, especially in inks, paints, and in apparel.[50,51] 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 more recently the arrival of pigment formulations that are compatible with offset vehicles has extended the range of application to offset lithography. Masterbatch plastic concentrates can be made from ABS, polystyrene, polypropylene, PVC, nylon and polyester. For apparel applications, thermochromic materials have been incorporated into embroidery and weaving threads and onto transfer papers for thermal printing of a variety of fabrics.

Examples of the use of these materials include temperature indicators for children's food by colour change plastic mugs, indicator stripes on beer and colas to indicate correct chilling, and on milk cartons to indicate that they have been refrigerated. In the security area they can be used for simple verification of a document's authenticity, *e.g.* by heat from the finger on cold days or by cooling on warm days; for message hiding, *e.g.* a message will appear when a copy is made with photocopiers, alerting for a check on authenticity. In the novelty area, logos on mugs and printed textiles, such as T-shirts, and in jewellery are common uses.

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. Of course they are intrinsically temperature dependent and articles containing these materials must be protected from any unwanted heat source.

1.3.4.2 Chromogenic Thermotropic Gels

Thermotropic gels or liquids are materials that reversibly change from a transparent state to a milky white, reflective state at a certain temperature or over a specific range of temperature. The materials are gels made up of colourless inorganic salts dissolved in a mixture of water and a water miscible polymer, such as poly(vinyl alcohol). The change in the transparency of these gels is due to the formation of liquid crystalline phases and also phase separation. They can be used as both light and heat filters in the milky state, and a special target is their use in switchable glazing units for sun protection in buildings.[52]

It is possible to create gels that are also thermochromic by incorporating pH sensitive dyes into the gels.[53,54] The gel is made by up mixing a 4800 MW polyalkoxy polymer, PO:EO ratio of 87:13, with lithium chloride and an aqueous buffer and a pH sensitive dye. Using Bromothymol Blue (see section 1.4.2.1) the gel is coloured green and transparent at –5 °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 also 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. The process can be reversed by cooling. Using Nitrazine Yellow the colour change is from blue at 25 °C to green above 33 °C, whilst with Chlorophenol Red the change is from red at 5 °C to yellow at 32 °C.[54] These gels have the potential for use as temperature sensors, in the same way as liquid crystals and thermochromic pigments are used. However, to be used in coloured glazing much more light stable dyes will be required.

1.4 Ionochromism

Ionochromism is the name applied to the phenomenon of a colour change associated with the interaction of compounds or materials with an ionic species. For the purpose of this book, the main ionic species is the solvated hydrogen ion, in which case the terms halochromic, acidochromic or pH sensitive are often used. However, other common ions include metal ions, and onium cations such as tertiary ammonium and phosphonium. 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 section 3.5.6, where ions cause a change in the fluorescent emission of the molecule.

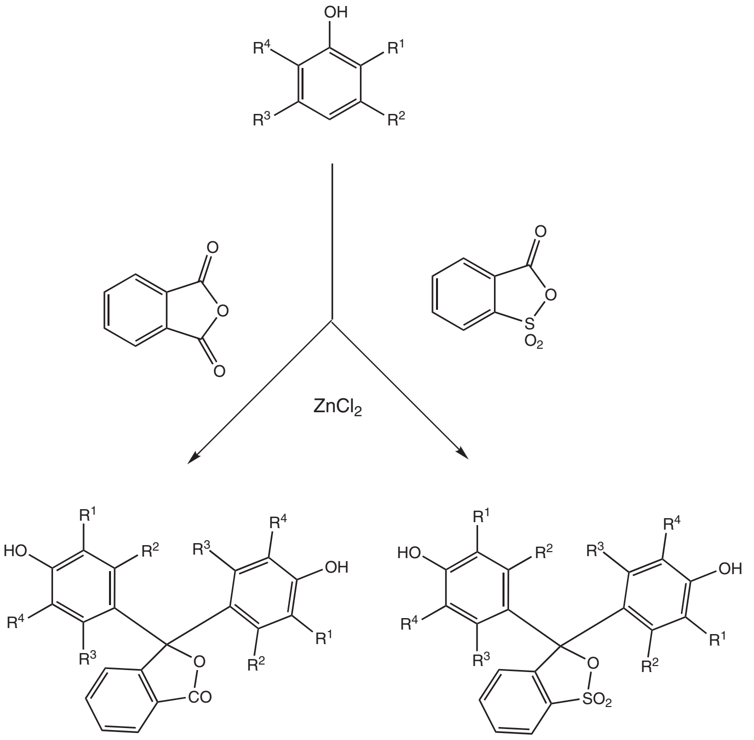
1.4.1 Ionochromic Compounds

The main classes of commercially important pH sensitive dyes are phthalides, triarylmethanes and fluorans. In fact, several chromophores undergo useful colour changes on protonation, including simple, neutral azo dyes, styryl dyes and indophenols. With metal ions a whole range of chelating ligands can be employed as colour indicators and sensors, but of special importance are crown ethers and cryptands for a range of non-traditional uses.

1.4.1.1 Phthalides

Indicator dyes for pH having the phthalide structure fall into two types, the phthaleins, shown in the lactone form of general structure (1.66) and the sulfophthaleins (1.67). The synthetic pathways to these products are very similar. The phthaleins (1.66) are made by reacting phenol with phthalic anhydride in the presence of Lewis acid catalyst, *e.g.* $ZnCl_2$, whilst (1.67) are obtained by using 2-sulfobenzoic anhydride (Figure 1.20).

The response of phthaleins to changes in pH is best exemplified by the parent dihydroxy derivative, the well-known indicator, with the trivial name of phenolphthalein (1.68). The colourless lactone (1.68) on adding alkali undergoes a successive conversion into the mono and then the diphenolate ion (1.69), which then rearranges *via* ring opening of the lactone to give the planar dianion (1.70), which is red (Figure



(1.66) (1.67)

Figure 1.20 *Synthesis of phthaleins and sulfophthaleins.*

1.21). 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).

The most important technologically of the phthalides are those based on the Crystal Violet Lactone structure (1.71) and its heterocyclic analogues.[55] This is because they are used as colour formers in carbonless copying papers and other digital printing outlets (see section 1.4.2.2). These processes use the fact that the lactone ring of the colourless form (1.71) opens in the presence of an electron-accepting donor to give a coloured cationic dye (1.72), as exemplified for Crystal Violet Lactone in Figure 1.22.

There are two main synthetic routes to Crystal Violet Lactone (CVL) and its analogues (Figure 1.23). The first involves the condensation of 4,4'-bismethyhydrol (1.73), also called Michler's Hydrol, with 3-dimethylaminobenzoic acid in dilute acid to give the leuco CVL, which is then oxidised to CVL. A wide variety of oxidants can be used but the preferred method uses hydrogen peroxide in basic solution. The oldest, and most versatile route starts by reacting 4-dimethylaminobenzaldehyde

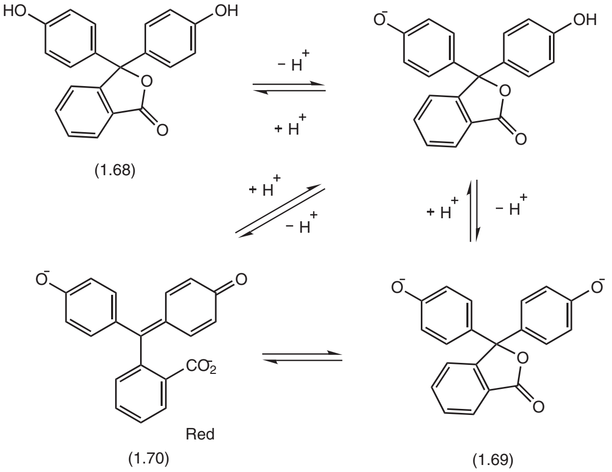


Figure 1.21 *Ionisation pathway of phenolphthalein.*

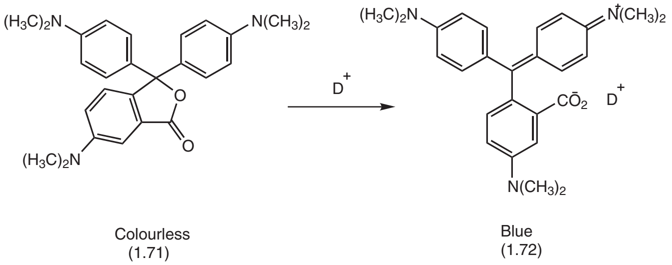


Figure 1.22 *Colour formation in Crystal Violet Lactone/developer system.*

with 3-dimethylaminobenzoic acid to give the 3-(4-dimethylaminophenyl)-6-dimethylaminophthalide, which is then oxidised to the intermediate bisdimethylaminobenzophenone carboxylic acid (1.74). This intermediate is reacted with *N*,*N*-dimethylaniline in acetic anhydride to give CVL.

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 shade. 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 having the generic formula (1.76). The general synthetic route to these derivatives involves condensation of phthalic anhydride, or a pyridine analogue, with a *N*-alkyl-2-methylindole to give the indolylbenzoic acid (1.75), followed by reaction with a substituted *N*,*N*-dimethylaniline in acetic anhydride to produce the substituted phthalide (1.76), as shown in Figure 1.24. The blue producing indolyl phthalides (1.76; X and Y = CH) have much improved light fastness over CVL. Of the colour formers carrying pyridyl rings, the isomeric compounds (176; X = N, Y = CH, R, R^1 = Et, R^2 = OEt) and (176; X = CH, Y = N, R, R^1 = Et, R^2 = OEt) and their mixtures have enjoyed commercial

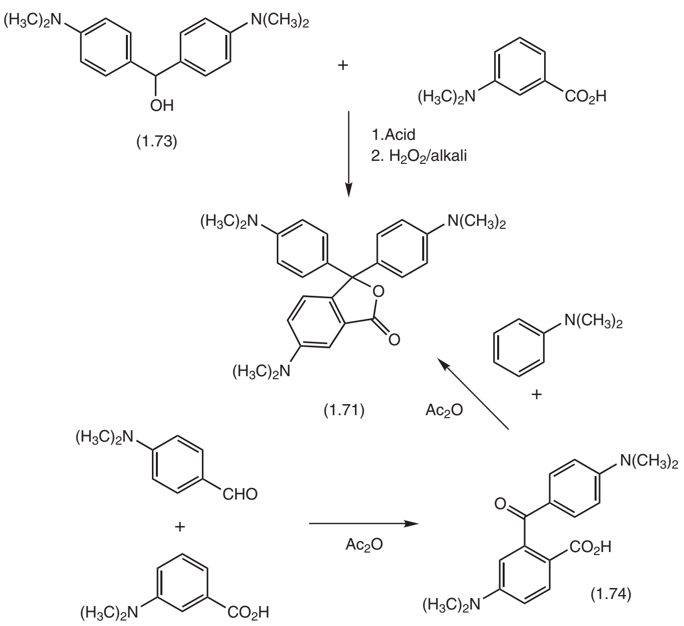


Figure 1.23 *Synthetic routes to CVL and analogues.*

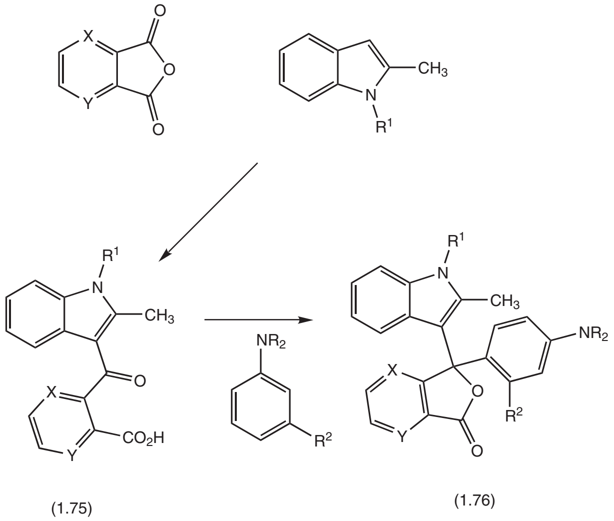
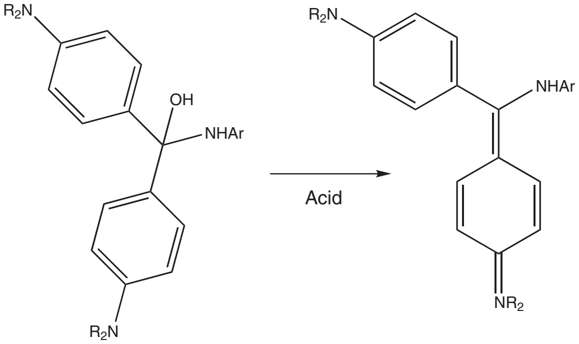


Figure 1.24 *Synthetic route to heteroaryl phthalides and aza analogues.*

success because they yield intense blue images with excellent fastness when used in conjunction with organic developers. They are commonly called Pyridyl Blues in this application.[55]

1.4.1.2 Leucotriarylmethanes

Closely related to the phthalides, leucotriarylmethanes are converted into the coloured form by hydride abstraction, chemical and photooxidation and in some cases by acids. A class of pH sensitive leucotriarylmethanes that have found use in dark blue colour formers are (1.77). They are readily synthesised from Michler's Hydrol (1.73) by reaction with aromatic or heteroaromatic amines in the presence of an acid catalyst.

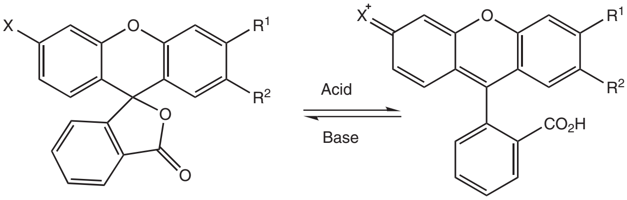


(1.77)

1.4.1.3 Fluorans

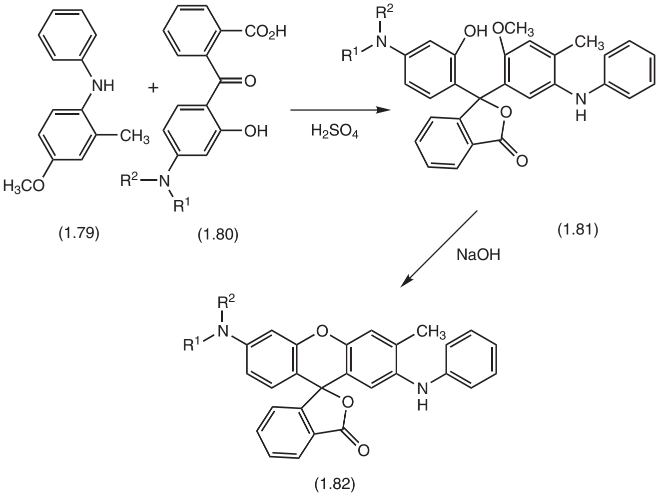
Fluoran is the trivial name that is commonly used for the spiro[isobenzofuran-1,9'-xanthen]-3-one class of compounds (1.78). The colour-forming reaction involves ring opening of the lactone ring by acid to give the coloured quinone form; colour reversion can be achieved by adding a base. As colour formers, 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.[56]

Yellow colours are derived from dialkoxy fluorans, *e.g.* (1.78; X and R^1 = OR, R^2 = CH_3); orange from mono-alkylamine derivatives, *e.g.* (1.78; X = NHcyclohexyl, R^1 = Cl, R^2 = H); red from mono-dialkylamines, *e.g.* (1.78; X = NEt_2, R^1 = CH_3, R^2 = H); blue from bis-diarylamines, *e.g.* (1.78; X and R^1 = NAr_2 , R^2 = H), green by moving one of the amino substituents into the 2'-position, *e.g.* (1.78; X = NEt_2, R^1 = H, R^2 = NEt_2); and finally black by changing the 2'-substituent to an arylamino group, *e.g.*



(1.78)

(1.78; X = NEt$_2$, R^1 = H, R^2 = NHAr). The blacks that are used as commercial colour formers, (1.82a and 1.82b), are synthesised by reacting 4-alkoxydiphenylamines (1.79) with the keto acids (1.80) in sulfuric acid to give the intermediate phthalides (1.81), which are converted into the fluorans by reaction with sodium hydroxide (Figure 1.25).[56]



(a) R^1= C$_2$H$_5$, R^2 = (CH$_2$)$_2$C(CH$_3$)$_2$
(b) R^1= R^2 = (CH$_2$)$_3$CH$_3$

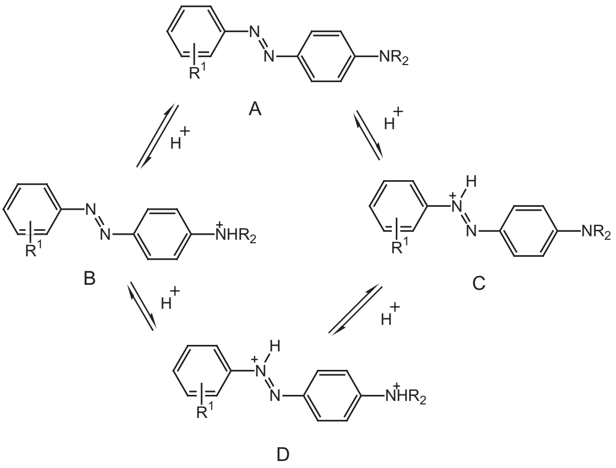
Figure 1.25 *Synthetic route to black fluoran colour formers.*

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) or the azonium (C) tautomer, followed by further protonation to give (D) (Figure 1.26). 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 by electron-donor groups. The colour change for the ammonium is hypsochromic and weaker (colourless), for the azonium it is strongly bathochromic and more intense, whilst the di-protonated product is nearly the same colour as the base dye (see table in Figure 1.26).[57,58] 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 Chelates and Crown Ethers

Metal ions, especially transition metal ions, 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.[59a,b] The term metallochromism has been applied to this phenomenon, and hence metallochromic indicators. Typical bidentate ligands are dimethylglyoxime, 1,2-dihydoxybenzenes and 1-hydroxyanthraquinones, 8-

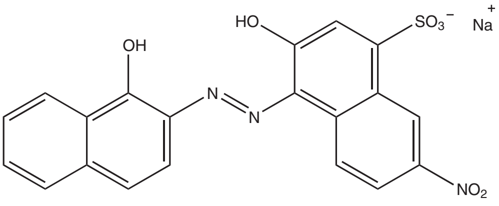


Tautomer	*R*	*R¹*	λ_{max}*/nm*	ε_{max}
A	CH_3	H	402	44 000
B	CH_3	H	320	34 000
C	CH_3	H	520	79 000
D	CH_3	H	410	45 000
A	C_2H_5	4-NO_2	480	30 400
B	C_2H_5	4-NO_2	326	16 000
C	C_2H_5	4-NO_2	515	43 500

Figure 1.26 *Tautomeric and spectral changes on protonation of aminoazo dyes.*

hydroxyquinoline, 2,2′-bipyridine and σ-phenathroline, and tridentates include σ-σ′-dihydroyaxo dyes, and multi-dentates such as formazans. The combination of complex forming coloured dyes, *e.g.* Eriochrome Black T (1.83), with the complexing agent EDTA is used for the estimation of a variety of metal ions.[60]

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 on the complex forming behaviour of these materials.[61] To make these crowns more strongly coloured, and hence more widely applicable as indicators or sensors, chromophores such as azos and indoanilines have been attached to the ring (1.84), the crown ring size determining which metals can co-ordinate.[62,63] An interesting variation on this approach involves the use of crown ethers attached to the side chain of polythiophenes. Depending on the nature of the



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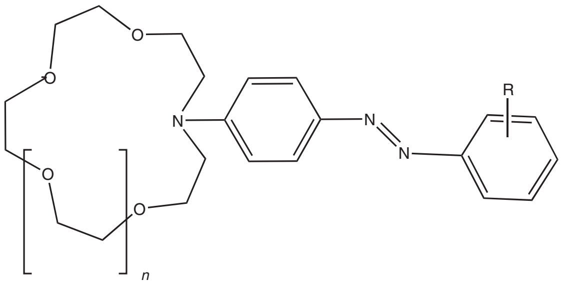

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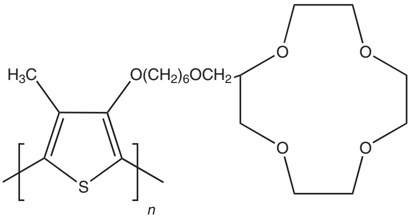


(1.85)

complexation of the side chain crown with alkali metal ions, there is either ordering or disordering of the backbone polymer; for instance, complexation of (1.85) with sodium ions in acetone solution causes rigidification and a shift in absorption maximum from 440 to 545 nm.[45]

1.4.2 Applications of Ionochromism

Ionochromism has 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 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. This is particularly the case where the acidic, ionic or donor species is 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, *e.g.* lithographic plate processing. The use of pH sensitive dyes as one of the components in reversible, composite thermochromic pigments has already been described (section 1.3.4.1).

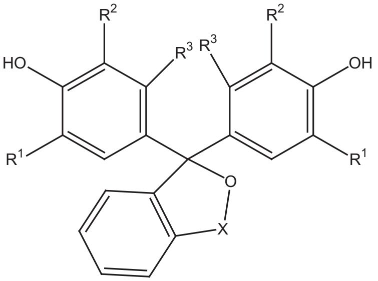
1.4.2.1 Analytical Chemistry

Historically, pH sensitive dyes have been extensively used as indicators in acid–base titrations and in simple spot test papers, even leading to a common phrase in our everyday language, when people or topics are described as "having passed the litmus test". The use of complexometric titrations for metal ions was a later but widely applicable development, which is best dealt with in specialised texts.[63] However, 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 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 1.3.4.2). Consequently, a brief description of their properties, as given below, is justified.

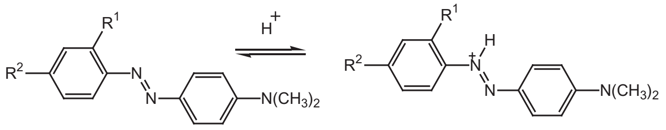
The ionic pathways for the phthaleins have been shown earlier in Figure 1.21. By modifying the chemical structure of the phthaleins, and especially the closely related sulfophthaleins, a whole range of reagents can be made with different colours changes. It should be noted that the change of colour is 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 1.11.

Protonation of azo dyes is also used as a method for producing analytical indicators, the two best known ones being Methyl Orange and Methyl Red, the colour change being generated by formation of the azonium tautomer (Figure 1.27). 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).

Table 1.11 *Phthalein and sulfophthalein indicators*



Name	*R^1*	*R^2*	*R^3*	*X*	*pH range*	*Colour change*
Phenolphthalein	H	H	H	CO	8.5–9.0	Colourless–red
Cresolphthalein	CH_3	H	H	CO	8.2–9.8	Colourless–red
Thymolphthalein	$CH(CH_3)_2$	H	CH_3	CO	9.3–10.5	Colourless–blue
Phenol Red	H	H	H	SO_2	6.8–8.4	Yellow–red
Cresol Red	CH_3	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	$CH(CH_3)_2$	Br	CH_3	SO_2	6.0–7.6	Yellow–blue
Bromocresol Green	Br	Br	CH_3	SO_2	3.8–5.4	Yellow–blue
Bromocresol Purple	CH_3	Br	H	SO_2	5.2–6.8	Yellow–purple
Thymol Blue	$CH(CH_3)_2$	H	CH_3	SO_2	1.2–2.8 8.0–9.6	Red–yellow Yellow–blue
Xylenol Blue	CH_3	H	CH_3	SO_2	1.2–2.8 8.0–9.6	Red–yellow Yellow–blue



Indicator	R^1	R^2	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 1.27 *Azo dye based indicators.*

1.4.2.2 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 basic 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 element 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 pH sensitive leuco dye, known as the colour former, *e.g.* Crystal Violet Lactone (1.71), in a non-volatile solvent. 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.[56] 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 1.28. 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.

1.4.2.3 Direct Thermal Printing

The production of a digitised image on a coated paper by a thermal head is known as direct thermal printing.[64,65] 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 is 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 (1.82a and b). All the co-reactants used commercially are phenols, the most widely used being 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

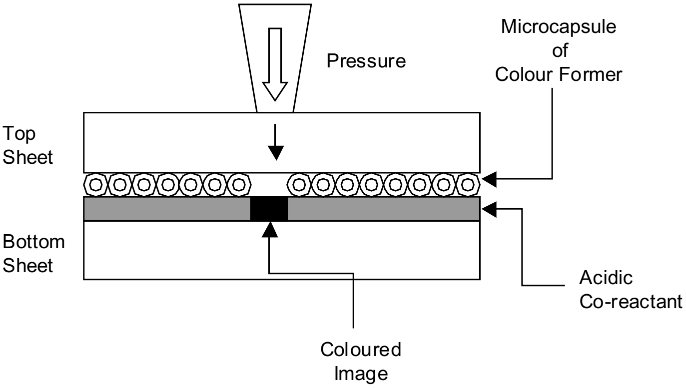


Figure 1.28 *Schematic representation of carbonless copying paper process.*

counteract these problems hindered phenols are included as stabilisers. To prevent wear on the thermal heads, which come in direct contact with the paper, a lubricant such a 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 poly(vinyl alcohol) or hydroxyethyl cellulose. The process is shown schematically in Figure 1.29.

By far the largest use of direct thermal printing is in facsimile machines where digital images transferred *via* telephone lines are reproduced. There are two weaknesses in the use of this method of direct printing; firstly the need for specially coated papers and secondly the poor light stability of the images on the paper. The special paper problem is somewhat offset by the fact that no special inks or other materials are required. The machines are very cheap and highly reliable in use; it is therefore a cost benefit calculation as to which system is used when disposable information is involved. However, when the document is required for archival purposes then image stability is a serious problem. Plain paper fax machines using ink jet printers to produce the image overcome both of these problems and their arrival on

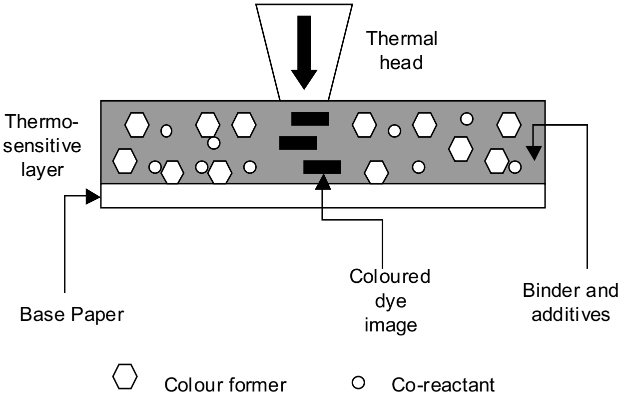


Figure 1.29 *Direct thermal printing process.*

the market has severely curtailed the growth of direct thermal printing (see Chapter 2, section 2.7). Another very significant competitor is the rapid growth of file transfer of data and images *via* e-mail.

Increasingly there is a requirement for the printing of digital images in full colour. Whilst some progress has been claimed for direct thermal printing, *e.g.* the Thermo Autochrome from Fuji, the complexity of the multilayer papers means that they are very unlikely to ever compete effectively with ink jet printers.[65]

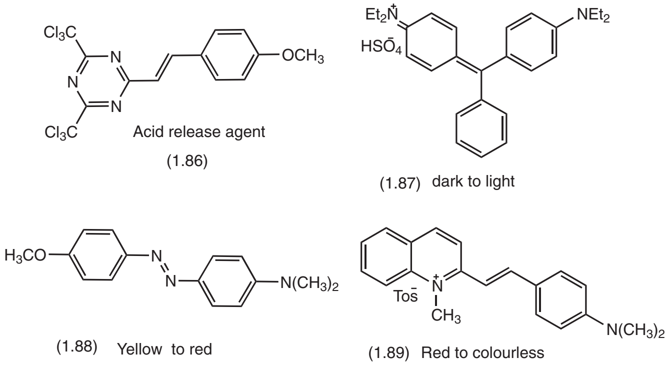
1.4.2.4 Visualisation of Printing Plates

Lithography, the main commercial method of long run printing on paper, requires the preparation of printing plates. These plates consist of a light sensitive organic coating on a hydrophilic aluminium base plate. Exposing the light sensitive coating to light through a photographic negative or positive mask, for each of which different types of resins are required, produces the image on the plate. With positive systems, based on diazonaphthaquinone resin chemistry, the radiation causes solubilisation of the coating in the exposed areas, whilst with negative working systems, based on diazonium resins, exposure causes insolubilisation of the photosensitive coating. After removing the soluble material produced by either process with aqueous alkali, an oleophilic image is created on the plate. The hydrophilic areas on the plate are covered with water and then an ink film is applied to the oleophilic image. The water is removed from the plate and then the inked image is transferred to a rubber off-set 'blanket' and from this to the paper substrate, giving the desired printed image. At the high end of the industry the plates can be used in excess of two million times, providing reproducible high-quality images.[66]

There are times during the production of the plate when its progress needs to be visually examined. This examination is carried out under yellow safelight and consequently the coating needs to be visible under these conditions. To achieve this end the resin is usually coloured blue, green, red or violet by adding a shading pigment. The coatings also need to exhibit colour changes after exposure and baking, so that the plate can be examined for imperfections prior to passing onto the printing step. This is where pH sensitive dyes and agents that generate an acidic species on exposure to UV light are used. A typical acid release agent is the triazine (1.86), which produces chlorine containing free radicals on irradiation that react further to form HCl in the coating. The dyes used can either change colour or bleach out to colourless. Triphenylmethane dyes, which fade in colour on protonation, are widely used, *e.g.* Brilliant Green (1.87); azo dyes, which go deeper in shade on protonation, are also very commonly used, *e.g.* (1.88); whilst onium dyes, which bleach out to colourless, are also used, *e.g.* Quinaldine Red (1.89). The structures of these materials are shown in Figure 1.30.[67]

1.4.2.5 In Flower Coloration

The colour of the flowers of many plants show a strong dependence on the nature of the soil, whether this be its pH or the presence of other ions such as trace metals. The mechanism for this change in colour has been elucidated for the Japanese morning



Acid release agent (1.86)

(1.87) dark to light

(1.88) Yellow to red

(1.89) Red to colourless

Figure 1.30 *Visualisation chemicals used in lithographic plate processes.*

glory, *Ipomoea nil*, whose reddish purple buds unfurl to give blue open flowers.[68] 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. The authors of this work postulate that the *Purple* gene could be manipulated to produce new flower colours, for instance the elusive blue rose.

1.5 Electrochromism

When an electroactive species undergoes a change in colour upon electron transfer or oxidation/reduction the process is known as electrochromism. This process normally involves the passage of an electric current or potential and is reversible. In the late 1960s, because of their reversible change in colour, it was suggested that electrochromic materials could be used to make coloured displays. However, in spite of the early enthusiasm, it took until the last decade of the century for genuine commercial applications to appear, and then not in displays but in switchable rear-view mirrors and the so-called smart windows.[69] In this section 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.[70]

1.5.1 Electrochromic Cells

During the process of colouration 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 1.31.[69]

The most common is the *coloured electrode type*, in which the transparent

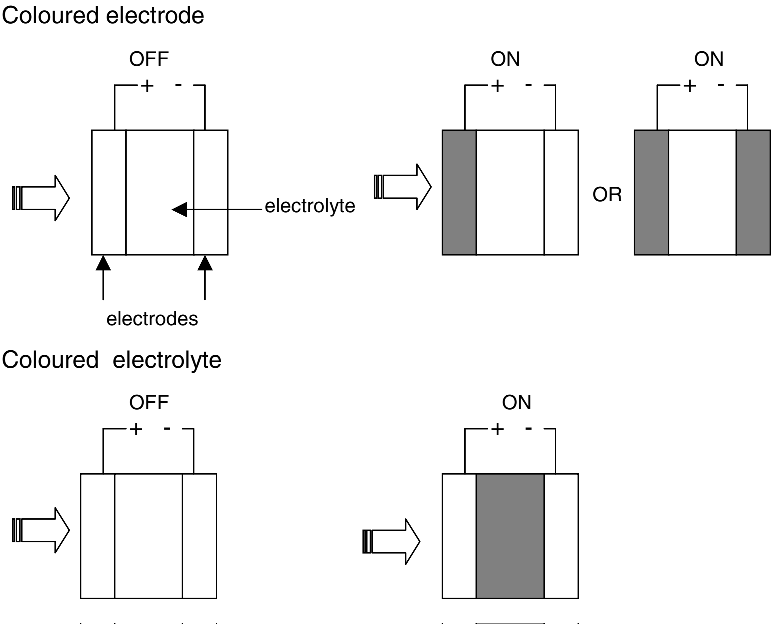


Figure 1.31 *Electrochromic cells.*

electrodes are coated with an organic or inorganic polymer which becomes coloured on passing a charge through the cell (see 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 colouration can be controlled by the amount of charge passing through the cell. The cell is bistable; *i.e.* 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.

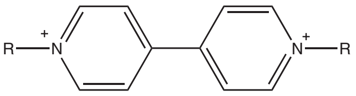
In the case of the *coloured electrolyte type*, the two complementary electrochromes are dissolved in the electrolyte between the transparent electrodes. One becomes coloured by oxidation and the other by reduction and consequently the electrolyte becomes coloured (see 1.5.2.1). The electrolyte remains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

1.5.2 Electrochrome Types

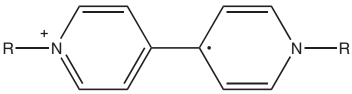
The materials that change colour on passing a charge are called electrochromes, and these can be classified into three groups. In the first type the colouring species remain in solution; in the second type the reactants are in solution but the coloured product is a solid; the third type are those where all the materials are solids, *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 (see section 1.5.4.2).

1.5.2.1 Solution Electrochromes

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, *i.e.* a coloured electrolyte is produced (see Figure 1.31). The most widely studied solution electrochrome is the dimethyl-4,4′-bipyridylium dication, also known as methyl viologen, (1.90; R = CH_3), which undergoes a one-electron reduction to the bright blue coloured radical cation (1.91; R = CH_3).[71] Another aqueous phase electrochrome is Fe(III) thiocyanate, whilst hexacyanoferrates and quinones such as TCNQ can be used in acetonitrile solution.[70]



(1.90)



(1.91)

1.5.2.2 Solution–Solid Electrochromes

This type of electrochrome, in its pale or colourless state, is soluble in the electrolyte. However, on electron transfer, the coloured form of the electrochrome that is produced is insoluble and is deposited onto the surface of an electrode. Viologens with hydrophobic chains, such as heptyl (1.90; R = C_7H_{15}), form deeply coloured radical cation salts (1.91; 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 (1.90; R = 4-cyanophenyl) in water and methoxyfluorenone in acetonitrile solution.

1.5.2.3 Solid Electrochromes

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 of electrochromes (see 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.[70,71]

1.5.3.1 Inorganic Oxides

Inorganic oxides exhibiting electrochromism include cobalt oxide, nickel oxide, molybdenum trioxide, vanadium oxide, tungsten trioxide and their mixtures. The most important of these are those based on tungsten trioxide.

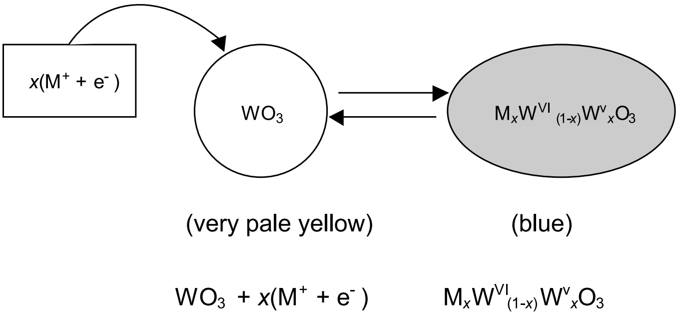


Figure 1.32 *Mechanism of colour formation in tungsten trioxide.*

Mechanistically the colour is formed by an optical charge-transfer between metal centres in the solid-state lattice, *e.g.* 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 1.32, where M is usually lithium or hydrogen.

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 are either amorphous, formed by thermal evaporation under vacuum, or microcrystalline, produced by thermal sputtering in an oxygen rich atmosphere. An alternative procedure, well suited to the production of large areas as in windows, is the sol–gel method using colloidal hydrogen tungstate, followed by thermal curing.[72]

1.5.3.2 Prussian Blue

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.[72,73] 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 hexacyanometallates, $M^1_x[M^2CN_6]_z$, where M are transition metal ions in different oxidation states, *e.g.* ruthenium purple, iron(III) hexacyanoruthenate(II). Thin films of Prussian Blue can be electrochemically deposited onto electrode surfaces by electroreduction of solutions containing Fe(III) and hexacyanoferrates(II).[74] Prussian Blue produces the colourless Prussian White on reduction and is therefore an anodically colouring electrochrome.

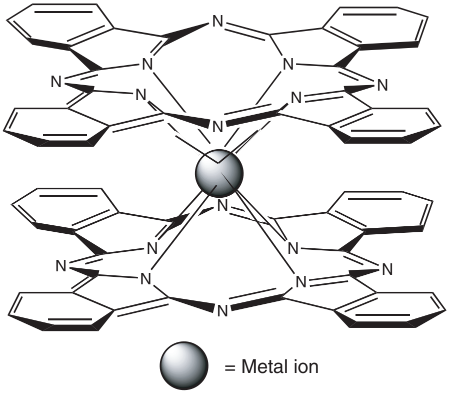
$$\underset{\text{(blue)}}{[Fe^{III}Fe^{II}(CN)_6]^{1-}} + e^- \rightarrow \underset{\text{(colourless)}}{[Fe^{II}Fe^{II}(CN)_6]^{2-}}$$

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 2.4.1.4), including electrochromism. The properties of metallophthalocyanines make them attractive as potential electrochromic materials, *e.g.* high light stability, high molar absorption 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 such as zirconium and molybdenum.[72,75] Synthesis of these molecules follows the traditional routes, *e.g.* condensation of 1,2-dicyanobenzene with a metal acetate in a high boiling solvent (see Chapter 2). These compounds have structures in which the rare earth element is sandwiched between two phthalocyanine rings, *e.g.* zirconium bisphthalocyanine (1.92; M = Zr) and lutetium bisphthalocyanine (192; M = Lu), the latter protonated on one of the meso N atoms to balance the charge.

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 bis-phthalocyanines 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 structures of these coloured products are shown in Table 1.12.



(1.92)

Table 1.12 *Colours of sandwich metallophthalocyanines under redox conditions*

Metal oxidation state	*Red (yellow/red)*	*green*	*blue*	*purple*
III	$[M(PC^{\bullet-})_2]^+$	$[M(PC^{\bullet-})(PC)]$	$[M(PC)_2]^-$	$[M(PC)_2]^{2-}$
IV	$[M(PC^{\bullet-})_2]^{2+}$	$[M(PC^{\bullet-})(PC)]^+$	$[M(PC)_2]$	$[M(PC)_2]^-$

$PC^{\bullet-}$ = phthalocyanine radical anion.

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.[71] In electrochromism this class of compounds are known as ‘viologens’, the stable, colourless dications (1.90) undergoing one-electron reduction to the brilliantly coloured radical cation (1.91). They can be rendered soluble in water or organic solvents or insoluble, depending on the nature of the quaternising group; the former being used as solution electrochromes and the latter as solution–solid electrochromes (see section 1.5.2 above).

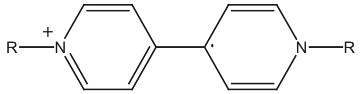
The colour produced on reduction to the radical cation is strongly dependent on the length and nature of the alkylating agent used to form the diquat salt. Short chain alkyl groups produce bright blue coloured radical cations, while mid-length chains give purple and longer chains mauves/reds. Alkylation 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 1.13.[71,76]

The quaternary groups in viologens can be derivatised to produce compounds capable of chemically bonding to a surface, especially electrode surfaces. These include symmetrical silanes, *e.g.* (1.93), which can bond to the oxide lattice on the electrode surface, and a viologen with pyrrole side chain (1.94) that undergoes anodic polymerisation to form a film of the viologen bearing polypyrrole on the electrode. Polymeric bipyridilium salts such as (1.95) have also been prepared for use in polymeric electrolytes.[71]

1.5.3.5 Polymeric Electrochromes

Many aromatic ring systems including aniline, pyrroles and thiophenes form extensively conjugated, electroactive polymers, which can be oxidised or reduced between

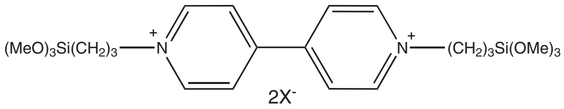
Table 1.13 *Optical properties of viologen radical cations*



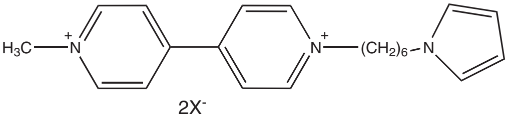
(1.91)

R	*λ_{max}/nm (solution)*	*ε_{max}*	*Colour (film)*
Methyl	605	13 700	Blue
Ethyl	603	12 200	Blue
Pentyl	–	–	Purple
Heptyl	545[a]	26 000	Mauve
Octyl	543[a]	28 900	Crimson
Benzyl	604	17 200	Mauve
4-CN-Ph	674	83 300	Green/black

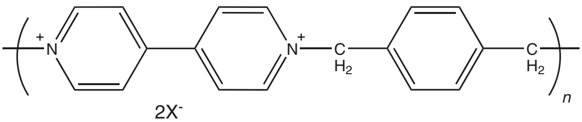
[a] Radical cation dimer.



(1.93)



(1.94)



(1.95)

an electrically neutral colourless state and a coloured charged state, in the presence of a balancing counter-ion, often called doping. They can therefore be used as solid electrochromes in thin films.[70,77]

Polyaniline films are formed by galvanostatic polymerisation of aniline in aqueous 2M 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 (see Figure 1.33). Electrode 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, *e.g.* 2-anisidines produce electrochromic polymers with different wavelength maxima.

The other important electrochromic polymers are the polypyrroles and polythiophenes, obtained by polymerisation of the parent pyrrole and thiophene or, more importantly, their 3,4-substituted derivatives. The most widely studied of these two classes of polymers in electrochromic outlets are the polythiophenes, which are readily synthesised by the reaction of the substituted monomer with $FeCl_3$ in chloroform solution. The colour change properties of a variety of polythiophenes in the presence of a counter-ion are shown in Table 1.14.[76]

One of the big drawbacks associated with the use of many conducting polymers as electrochromic materials is their low cycle life stability. 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 (1.96).[78,78–80]

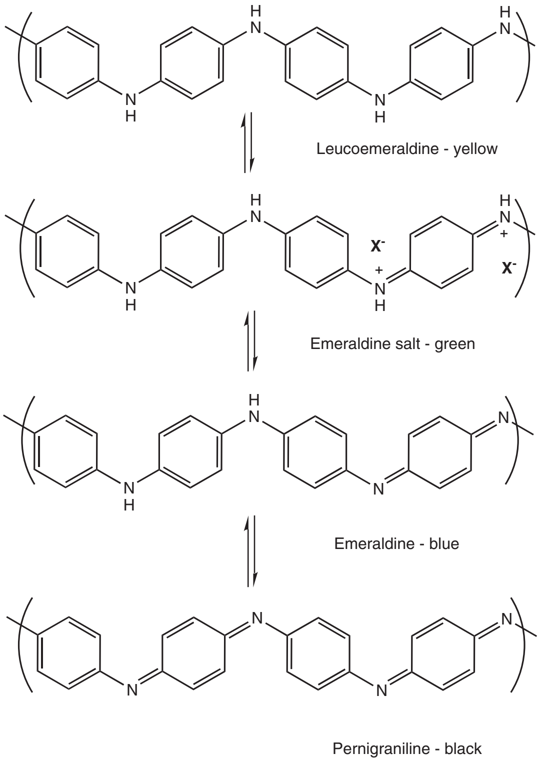
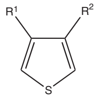
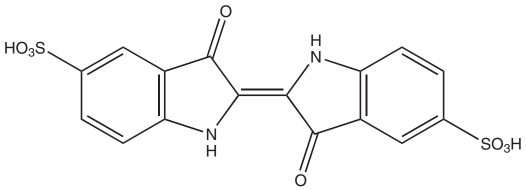


Figure 1.33 *Oxidation states of polyaniline.*

Table 1.14 *Electrochromic colour change properties of polythiophenes* (Reproduced with permission of Wiley-UCH)

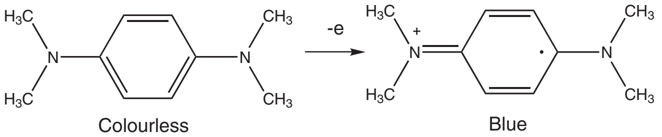
		*Anion*	*λ_{max}/nm (shade)*	
R^1	*R^2*		*Oxidised*	*Reduced*
H	H	BF_4^-	730 (blue)	470 (red)
H	CH_3	BF_4^-	750 (deep blue)	480 (red)
CH_3	CH_3	ClO_4^-	750 (deep blue)	620 (pale brown)
H	Ph	BF_4^-	– (green/blue)	– (yellow)
Ph	Ph	BF_4^-	– (blue/grey)	– (yellow)



(1.96)

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, naphthaquinones and anthraquinones, tetracyanoquinodimethane, tetrathiafulvalene and pyrazolines.[70] Of particular interest are the 1,4-phenylenediamines, which form highly coloured species on oxidation. These, known as Wurster's salts, exemplified by Wurster's Blue (1.97), are anodically colouring and this type of material has found use in composite electrochromic systems for car rear-view mirrors (see 1.5.4.1).



(1.97)

1.5.4 Applications of Electrochromism

The main application areas for electrochromic systems are in electrically switchable rear-view car mirrors for anti-dazzle, in glazing units for temperature and light control and in visual displays. The main advantage offered by electrochromic systems in the first two of these applications is the fact that the cells can be made very large, *i.e.* one cell can comprise a whole glazing unit.

1.5.4.1 Rear-view Mirrors

The desirable properties of an electrochromic system for use in both rear-view mirrors or glazing units are:[81]

- Colours – blue, green, red and grey
- Size – up to 2 m × 2 m (flat)
- Glass – curved for car mirrors
- Long Life – 25 years in buildings, 5 years in cars
- Transmission range – 15 to 75%
- Total cycles – 5000+ per year
- Temperature range – –20 to +80 °C operating
  –40 to +120 °C survival

Electrically switchable rear-view mirrors for cars and trucks have been in commercial production since the early 1990s, the leading company being the Gentex Corporation.[82] The Gentex mirror consists of an ITO–glass surface, with the conductive side inwards, and a reflective metallic surface, spaced less than a millimetre apart. In the gap between these two electrodes is the solution electrolyte that is coloured at the anode by formation of the stable radical cation, similar to Wurster's

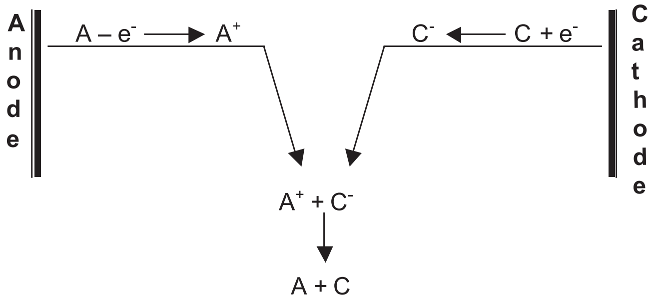


Figure 1.34 *Mechanism of an electrochromic cell for a car mirror.*

Blue (1.97), whilst a viologen is reduced at the cathode (Figure 1.34), the colours being complementary, producing a deep green colouration. It is essential that a current be applied to the cell whilst it is coloured, to avoid the electrode reaction being reversed in solution. This is because the two types of coloured molecules can diffuse through the system and react with each other, restoring the bleached states. The coloration may be cleared more rapidly by briefly reversing the polarity.

The Donnelly Corporation have also devised a rear-view mirror using an hybrid system. A metal oxide electrochromic layer is used in conjunction with a non-electrochromic reversible redox complex in the contacting solution.[83]

The electrochromic, self-dimming mirror market is expanding rapidly, comprising around 6 M of the estimated 150 M total for mirrors in cars and trucks in 2000. The market is set to grow to around 15 M by 2010, with additional growth in self-dimmable sunroofs and sun visors.

1.5.4.2 Smart Windows

The control of the solar gain within buildings occurring through the glazing units (Figure 1.35) is a highly desirable objective and has been the subject of much research, especially by glass manufacturers such as Pilkington, Saint Gobain and PPG. It would be most attractive to be able to do this dynamically, *i.e.* change in response to environmental conditions, and this has led to the idea of 'smart windows'.

The most widely studied systems for glazing units are those based on tungsten trioxide. A schematic of a cross section through a typical cell is shown in Figure 1.36.

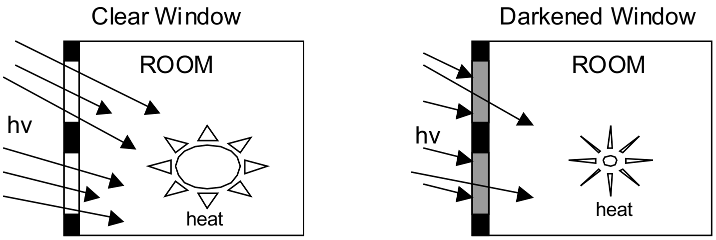


Figure 1.35 *Heat reduction by darkened glazing.*

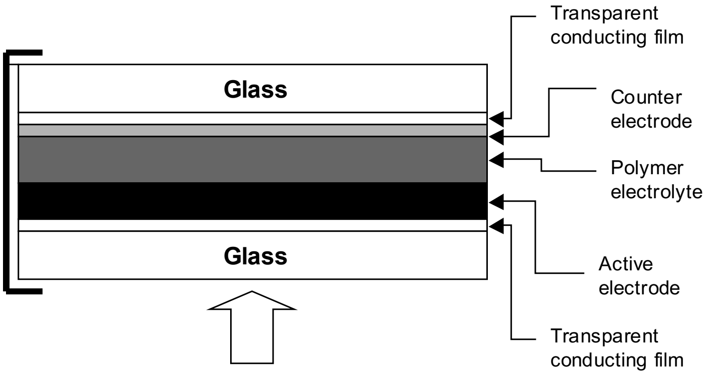


Figure 1.36 *Cross section through an electrochromic window.*

The glass used in the glazing units is coated with a transparent conducting surface, *e.g.* indium tin oxide (ITO) or stannic fluorine oxide (SFO). The electrochromic cell is composed of an active electrode layer of tungsten trioxide (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 of $Li_xV_2O_5$. 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 mC 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.[69]

Smart windows are ones which automatically darken when the ambient sunlight reaches a predetermined level. One of the most promising approaches to achieving this goal involves a combination of dye sensitised solar cells and electrochromic cells.[84,85] This work is based on the use of the dye-sensitised solar cells devised by Grätzel *et al.* in the early 1990s, which will be described in greater detail in Chapter 4, section 4.7.1.2. The design principle behind these smart windows is the use of electrochromic films that undergo 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. This is known as a photoelectrochromic cell and is illustrated schematically in Figure 1.37.

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. 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, 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

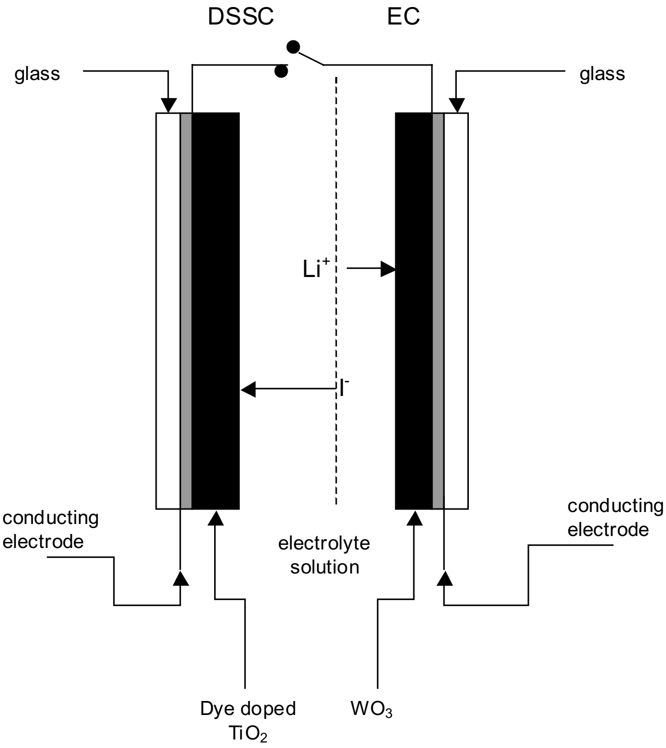


Figure 1.37 *Smart window from combined DSSC and EC cells.*

cell is disconnected form the circuit before the light is removed it remains coloured, because the electrons cannot escape from the reduced WO_3 film.

1.5.4.3 Displays

The big difference between devising electrochromic systems for displays and glazing is the need to construct arrays of smaller cells rather than one large one. and hence the need for multiplexing. Since coloration in EC cells is caused by a chemical change rather than by a light-emitting effect or interference, the colour remains even when the current is turned off. This has led to the suggestion that the memory effect could be used in low power large area information billboards.

In the 1980s IBM had a prototype small area, monochrome EC display that used viologens as the electrochromes.[86] At the time this did seem to offer scope for further development but most projects in the area have been 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.[87,88]

However, the difficulty in getting full colour and uniform large area coloration, coupled with the cost of manufacture, has meant that liquid crystals have remained the dominant technology into the early years of the 21st century.

More recently, Grätzel's work on nanocrystalline TiO_2 has been extended into the displays area.[89,90] In this system an electrochromic molecule is linked to the surface of the colourless TiO_2 semiconductor on conducting glass. On applying a negative potential, electrons are injected into the conduction band of the semi-conductor and the absorbed molecule is reduced and changes colour. Applying a positive potential reverses the process. The nanocrystalline TiO_2 layer (5 μm) is highly porous and able to absorb several hundred monolayers of the electrochromic molecules, enabling the system to produce deep colours. Using phosphonated viologens, colour absorbance changes of more than 2 have been achieved in 0.1 to 0.5 s. To construct closed cells for use as display units, a counter electrode of zinc was coated with a white reflector of microcrystalline TiO_2 or ZrO_2. In operation, short-circuiting of the two electrodes causes electrons to flow from the zinc electrode, it being oxidised to Zn^{2+}, to the viologens on the nanocrystalline electrode. The process is reversed by applying a voltage of 1–2 V. The oxidation–reduction process is said to be very fast, but the system needs rapid ion migration in the electrolyte so that the charge can be compensated, and polar solvents of low viscosity polar solvents, *e.g.* acetonitrile (switching time of 100 ms). Stability looks good at 150 000 oxidation–reduction cycles without degradation. The system is shown schematically in Figure 1.38.

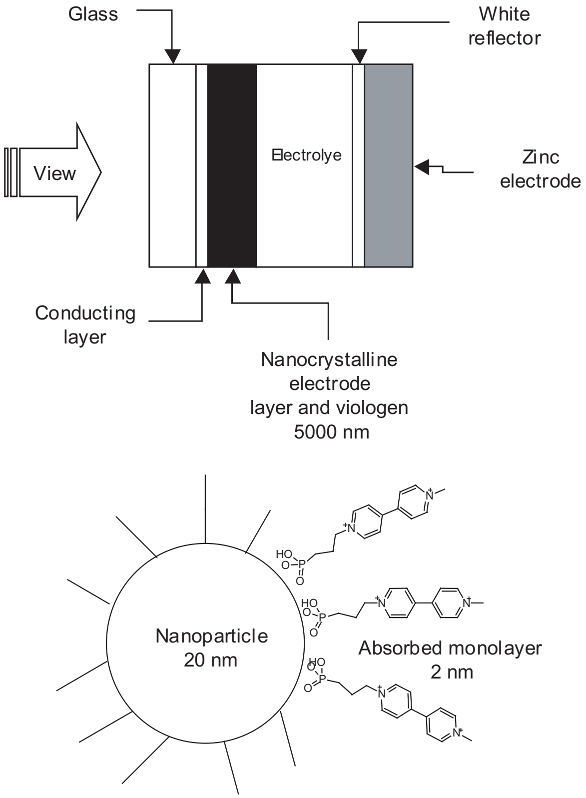


Figure 1.38 *Nanocrystalline electrochromic display cell.*

1.6 Solvatochromism

Solvatochromism can be defined as the phenomenon whereby a compound changes colour, either by a change in the absorption or emission spectra of the molecule, 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 solids, micelles and films. A textbook published recently covers in detail the theoretical aspects of solvatochromism.[91] Consequently in this section, the theoretical aspects will be dealt with only briefly before moving onto the practical applications of the topic, which have increased noticeably in the last decade.[92]

1.6.1 Solvent Polarity and Solvatochromic Shifts

In solvatochromism, the observed shifts in the maxima of the absorption or emission spectra of molecules are due to differences in the solvation energies of the ground (E_S^0) and excited states (E_S^1) as the nature of the solvent is varied, as shown in Figure 1.39.

This leads to two observable phenomena:

- When the excited state is more polar than the ground state, its stabilisation is favoured by more polar solvents. There is a decrease in transition energy and a bathochromic shift in the spectrum. (Positive solvatochromism, as shown in Figure 1.39.)
- Conversely, a more polar ground state leads to the opposite effect and a hypsochromic shift in the spectrum (negative solvatochromism).

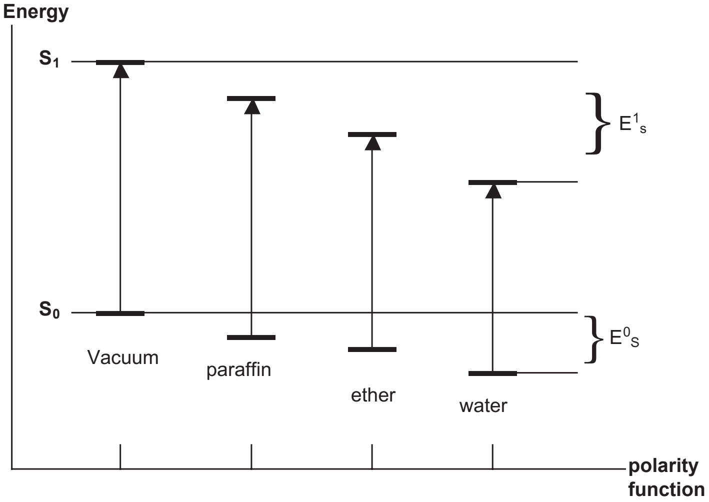


Figure 1.39 *Simplified energy diagram of solvatochromic shift.*

The variations in the absorption energies of various dyes have been used to characterise the polarity of various media and create empirical scales. For this purpose, the most widely used dye is the highly, negatively solvatochromic betaine (1.98), known as Reichardt's dye, whose transition energy $E_T(30)$ in kcal mol^{-}*, measured in a particular solvent, characterises the polarity of that solvent.

This method of deriving the $E_T(30)$ has the advantage of providing polarities for a wide range of solvents due to the solubility of (1.98) in both polar and non-polar solvents (see Table 1.15).[93] However, this scale is an over-simplification as there are other interactions occurring between solvents and solutes, *e.g.* hydrogen bonding effects, and this needs to be borne in mind.

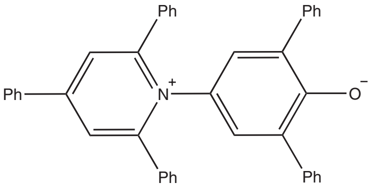
Solvatochromic shifts have important implications for the applications of coloured compounds in a variety of outlets, especially where changes in the polarity of the medium are part of the process.

1.6.2 Applications of Solvatochromism

For decades solvatochromism was 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, *e.g.* commercial azo dyes.[94] However, in the last two decades of the 20th century there was a rapid growth in the use of optical probes and sensors in a range of outlets, and this led to a renewed interest in solvatochromism.

1.6.2.1 Analysis of Oils

An obvious outlet for solvatochromism is the measurement of the concentrations of small amounts of polar molecules in non-polar environments, *e.g.* methanol in naphtha. Fuel oil is obviously a key market, as the various fractions are often 'marked'



(1.98)

Table 1.15 *Empirical solvent parameter for solvent polarity $E_T(30)$*

Solvent	*Heptane*	*Pyridine*	*DMF*	*Acetic acid*	*Methanol*	*Water*
$E_T(30)$/ kcal mol^{-}	31.1	40.5	43.2	51.7	55.4	63.1

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* 1 cal = 4.184 J.

with solvent dyes, which ease their identification for tax purposes, *e.g.* blue diesel. Prior identification to avoid fraud can be carried out by using a solvatochromic dye that differentiates between the fractions and (1.99) has been claimed to be of value in this process.

1.6.2.2 Polymer Probes and Sensors

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:

- The chromophore can be part of the polymer of the chain
- 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 of 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.

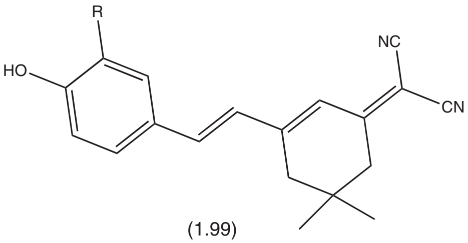
These two methods can be adapted for use in the commercially attractive area of polymer bound sensors. These offer, especially when coupled with fibre optics, a safe way of examining flammable solvents for their composition and levels of liquid impurities.

For example, dissolving the betaine (1.98) or another negative solvatochromic dye in PMM and spin coating the solution to give a film on a sensor tip provides a product suitable for the analysis, in visible absorption or transmission mode, of alcohols and ethers in gasoline.

1.6.2.3 Biological Probes

The use of fluorescent dyes in biological probes and sensors is covered in some detail in Chapter 3 (section 3.5.6). Because there are marked solvatochromic effects on the luminescent 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



(1.99)

fluorescence probes of binding sites, as solvatochromic indicators, probes for serum albumin and in looking at the environment of the visual pigments.[91]

1.7 Miscellaneous Chromisms

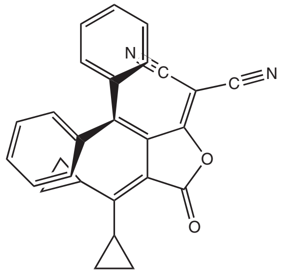
Many of the other chromisms that have been described are irreversible and much less important in terms of commercial applications. However, they do display interesting behaviours, which could well prove to be of value in the future.

1.7.1 Piezo and Tribochromisms

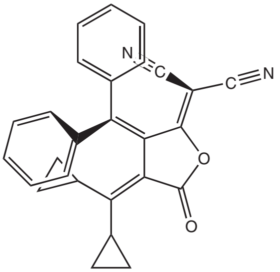
Piezochromism and tribochromism are both colour change phenomena that occur by mechanical means, the former under applied pressure and the latter by friction or grinding. They have been observed in a few systems, but have not been exploited in any commercial way.

Poly(3-alkylthiophenes) exhibit piezochromism, *i.e.* they change colour as pressure is applied. For instance, a thin film of poly(3-dodecylthiophene), which is nonplanar at high temperatures with an absorption maximum at 520 nm, undergoes a bathochromic shift as the pressure is increased, reaching an 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, compensating for conformational changes which also occur on heating.[45,95,96]

Tribochromism is exhibited when compounds crystallise in a metastable state and give a more highly coloured state when they are ground (see also triboluminescence in Chapter 3, section 3.9). In these cases the colour change is irreversible, as exemplified by the case of the fulgide (1.100). The folded metastable form (1.100a) 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 (1.100b).[20]



(1.100a)
yellow
folded metastable



(1.100b)
red
twisted stable

1.7.2 Gasochromism

The term gasochromism has been applied to systems which change colour by redox reactions involving gases; it is closely related to electrochromic behaviour.

The following system has been applied to switchable windows. Hydrogen, at a concentration below its flammability level, in admixture with nitrogen, is dissociated by a catalyst and intercalated into a tungsten layer on the glass. The layer turns deep blue in colour and bleaching is achieved with oxygen. The energy consumption is said to be lower than in comparable electrochromic systems, with solar transmission of 75% reduced to 5% in a few seconds.[97]

1.7.3 Vapochromism

In vapochromic systems dyes change colour in response to a vapour or an aroma, and therefore an alternative name is aromachromic. Systems based on this principle can be considered as belonging to the family of 'synthetic nose' devices.

In a recent example metalloporphyrins are used as the sensing dyes for a wide variety of odorants, including alcohols, amines, arenes, ethers, halocarbons, ketones, phosphines, thioethers and thiols.[98] An array of four different metalloporphyrins are placed on a substrate and exposed to the vapours for 30 s. The various vapour molecules coordinate onto the central metal atoms of the porphyrins, causing them to change colour and producing a unique four-colour array. The resulting colour array is compared with a library of known chemicals or mixtures and identification is achieved.

1.7.4 Chronochromism

Chronochromic systems are usually made from pH indicator type dyes, which are placed in environments designed to allow the colour change to take place over predetermined period of time.[99] One example is their use in toothpaste containing methylene blue and sodium ascorbate. On brushing the teeth the two chemicals interact and the dye is reduced to a colourless product. Complete disappearance of the original blue colour indicates the correct time for the user to brush their teeth.[100] Another outlet is in semi-permanent inks for the temporary marking of documents, *e.g.* routes on maps. This uses the ammonium salt of phenolphthalein; the volatile ammonium cation evaporates with time leaving the colourless phenolphthalein behind.[101]

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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, 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. With the notable exceptions of luminescent materials, lighting and electronic 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 2000 the world production of textile dyes was approximately 800 000 tonnes (valued \$5 bn), around 250 000 tonnes (\$4.3 bn) of organic pigments, whilst the value of inorganic pigments was \$2.7 bn, being heavily dominated by the very large volume white TiO_2 and iron oxide pigments.

The application areas for dyes and pigments are very varied covering the coloration of textile fibres, leather and plastics, in paint and printing inks, in cosmetics and hair colouration, in photography and digital imaging, 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 information on any particular area, some of the relevant, more recent publications are listed as source references.[2–9] The student seeking a broad overview of the area would be advised to consult the recent textbooks from Christie *et al.*[10]

An understanding of the importance 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.

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.

2.2.1 Additive Colour Mixing

White light is composed of the *additive* primary colours of red, green and blue. These primary colours are the ones which cannot be made by mixing any of the other two together. Mixing light of two of these primary colours in equal proportions produces the following colours:

Red + Blue = Magenta
Red + Green = Yellow
Blue + Green = 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 blue component in this case); the non-absorbed components of the light (red and green) are reflected and enter the eye to produce the observer's interpretation of the surface's colour (yellow). In the same way, magenta is the colour observed when green is absorbed and red and blue 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

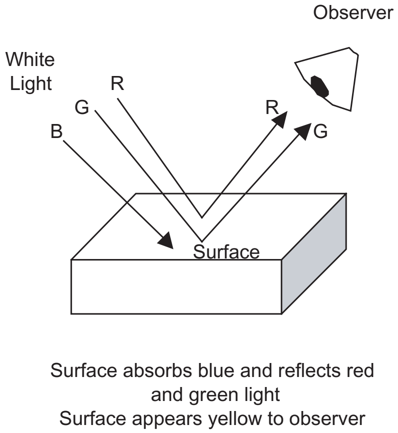


Figure 2.1 *Absorption and reflectance of light on a surface.* (Reproduced with permission of Society of Dyers and Colourists.)

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 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 television and other display systems (see Chapter 3).

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

2.2.2 Subtractive Colour Mixing

The type of colour mixing most familiar to people is *subtractive* colour mixing with the primaries of yellow, magenta and cyan (or less precisely, yellow, red and blue). Subtractive colour mixing is the one used to produce the vast range of colours available in the area of dyes and pigments. We all know that mixing a yellow and a blue dye or pigment produces a green colour, but how does this arise? The situation is as follows:

- A yellow dye absorbs light in the blue region
- A cyan dye absorbs light in the red region
- The mixture therefore absorbs both red and blue and reflects only green light

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:[11]

- Hue: those attributes 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 molar absorption coefficient (ε_{max}) or height at the absorption maximum, but also of importance is the shape and size (the band width) 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? It can be described as rose red or pillar-box red, 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 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, with the gamut available from YMC subtractive mixing indicated, is given in Figure 2.3.

Table 2.2 *Relationship between light absorbed and observed hue*

Region of light absorption		
Wavelength/nm	*Colour*	*Principal hue observed*
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

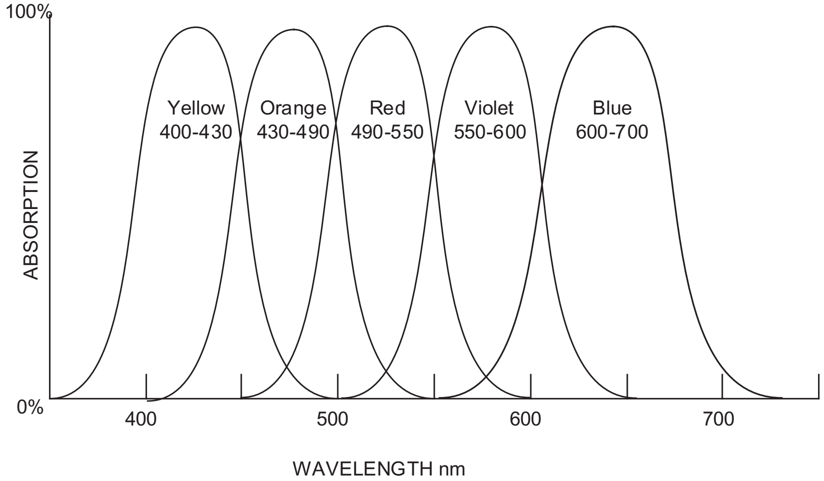


Figure 2.2 *Idealised absorption spectra of single compound colorants.*

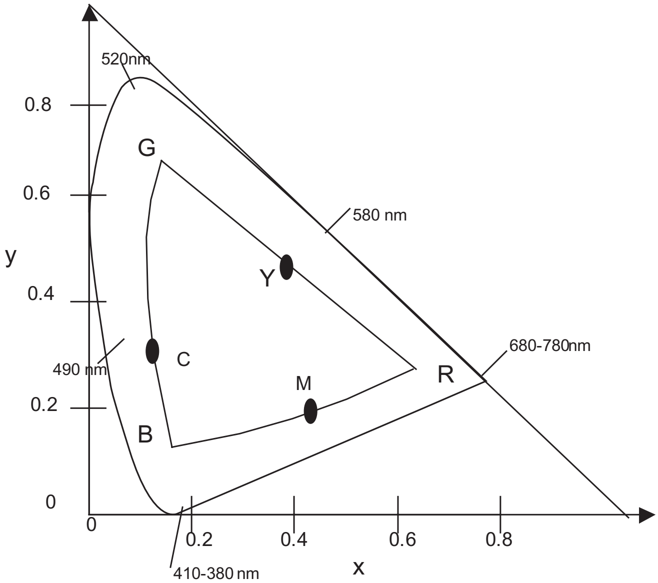


Figure 2.3 *The CIE x, y chromaticity diagram.*

The system used by colourists in the dyes and pigments industry is the so-called CIELAB system. [Note: CIELUV is the one 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 of 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.[12]

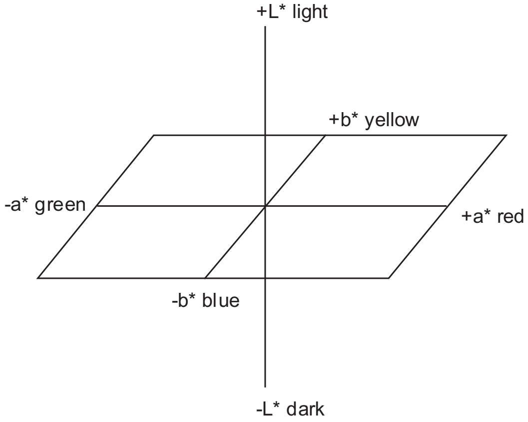


Figure 2.4 *The CIEL *a*b* colour space (CIELAB).*

2.3 Classical Organic Dyes

Until the middle of the 19th century, when William Perkin (1856) discovered serendipitously mauveine, the first synthetic dyestuff, all dyestuffs had been obtained from natural sources.[13] 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 dyestuff industry.[14]

The invention of new man-made fibres in the middle of the 20th century sparked a further surge in activity, as different products were required to dye these new materials. Alongside the new dyestuffs, 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 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 21st century the design, synthesis and application of synthetic dyes has reached such a level of sophistication that making any new major advances is going to be very difficult. Research and development in the dyestuffs industry is aimed mainly at improving the performance of dye ranges to meet new consumer demands, to meet increasingly stringent environmental targets or in applying dyestuffs to new outlets, such as digital imaging or displays.

Natural dyestuffs have not gone away, in fact there has been an upturn in their fortunes as consumer demand has risen for natural materials to be used in the coloration of their food and drinks, in cosmetics and in the dyeing of fashion garments made from natural fibres such as wool and cotton, and leather goods. However, they represent currently only a very small percentage of world dyestuff usage.

The main differentiating performance characteristic between dyestuffs and pigments is solubility. During their application, dyestuffs are solubilised, either in the medium or 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.

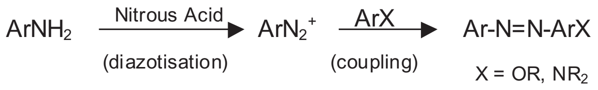
2.3.1 Structural Classes

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). (Note: 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 *i.e.* –N=N–, carbonyl and nitro groups *etc.*[15] However, it is very common in the literature for the term *chromophore* to be used more loosely, applying it to cover the whole of the coloured molecular systems, *i.e.* the building blocks plus the conjugated systems linking them together.)

2.3.1.1 Azo Dyestuffs

Azo dyestuffs, *i.e.* 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 diazo 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 an hydroxy group, then a second diazonium compound 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 dyestuff, by a variety of these and other combinations. Some of these



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

Figure 2.5 *Diazotisation and coupling to give azo dyes.*

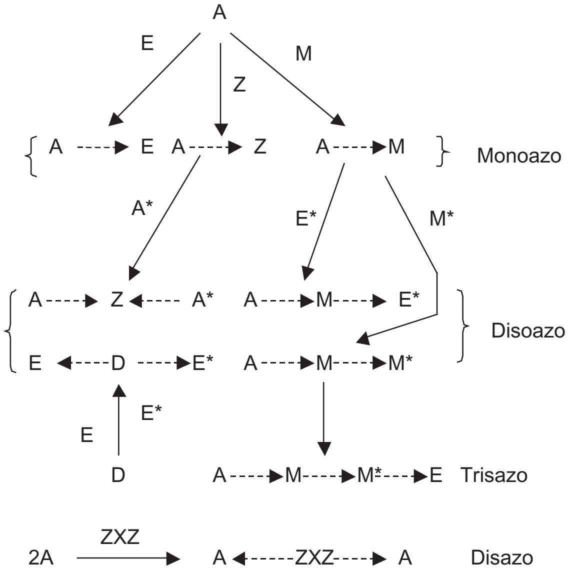
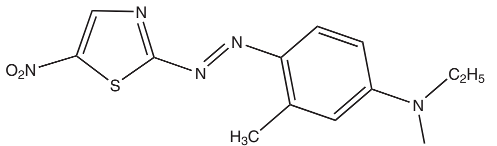


Figure 2.6 *Schematic representation of routes to mono-, dis- and tris-azo dyestuffs. Symbols: A is amine to be diazotised (also A*); E is end coupling component (*i.e.* terminal group) – (also E*); D is a diamine than can be diazotised twice (tetrazotised); M is an amine that can be first coupled with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

routes are shown schematically in Figure 2.6, following a long-standing convention of naming used in the dyes industry.[16]

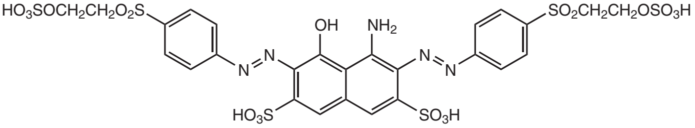
Five commercial dyestuffs, a monoazo CI Disperse Blue 82 (2.1), a symmetrical disazo CI Reactive Black 5 (2.2), an unsymmetrical disazo CI Acid Blue 116 (2.3), a trisazo CI Direct Blue 78 (2.4) and a disazo formed from two monazos linked *via* a bridging group, CI Direct Yellow 132 (2.5), demonstrate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

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).[16] 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.



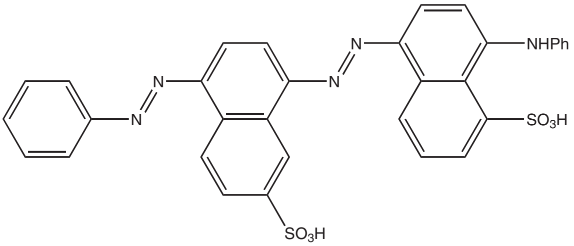
(2.1)

A ---▶ E



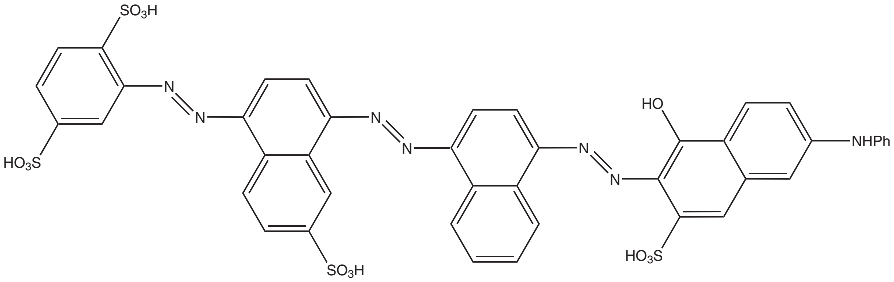
(2.2)

$A \dashrightarrow Z \dashleftarrow A$

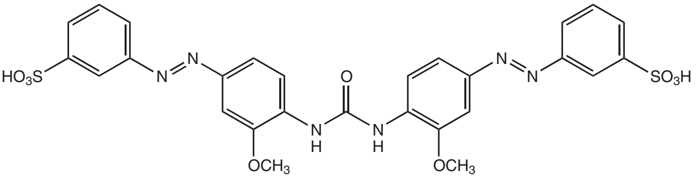


(2.3)

$A \dashrightarrow M \dashrightarrow E$



(2.4)



(2.5)

$A \dashrightarrow ZXZ \dashleftarrow A$

Colour and Structure. The azo chromogen is one of the many that can be described as falling within the donor–acceptor group. The donor–acceptor system is shown in Figure 2.7 with a simple mono azo 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

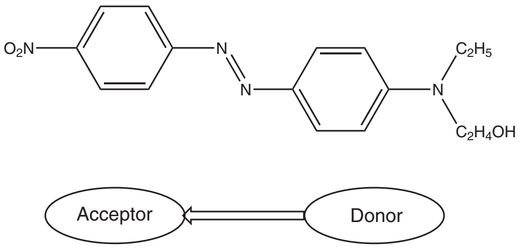
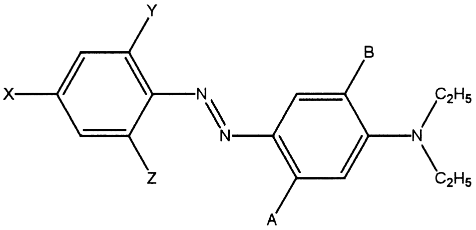


Figure 2.7 *Donor–acceptor azo chromophore.*

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. The order of effect for the influence of electron acceptors is *ortho* or *para* to the azo linkage, and 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 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.[17] It should be remembered that arylazo dyes show strong solvatochromic effects (Chapter 1, section 1.6.2) and comparisons of their absorption spectra should only be from measurements made in solvents of the same or very similar polarities.[18]

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	26 700
CN	H	H	H	H	466	32 700
NO_2	H	H	H	H	486	34 000
NO_2	H	H	OCH_3	H	501	32 000
NO_2	H	H	H	OCH_3	488	22 600
NO_2	H	H	$NHCOCH_3$	H	511	47 000
NO_2	H	H	$NHCOCH_3$	OCH_3	530	32 600
NO_2	NO_2	H	$NHCOCH_3$	H	543	–
NO_2	NO_2	Br	$NHCOCH_3$	OCH_3	608	–
NO_2	NO_2	CN	$NHCOCH_3$	H	613	–
NO_2	CN	CN	$NHCOCH_3$	H	619	–

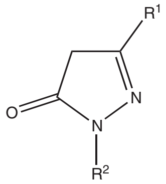
The main aromatic amines used as diazo components are substituted anilines or naphthylamines and the coupling components substituted *N*-alkylanilines, phenols, naphthylamines and naphthols. Heteroaromatic diazo and coupling components are widely used in commercial azo dyestuffs. The main heterocyclic coupling components are pyrazalones (2.6) and, especially, pyridones (2.8). These are used to produce bright yellow and orange monoazo dyes, such as CI Acid Yellow 72 (2.7) and CI Disperse Orange 139 (2.9).[19]

All the main heterocyclic diazo components are based on five-membered ring heterocycles containing one sulfur and bearing a diazotisable amino group. These fall into the following four main groups:[20]

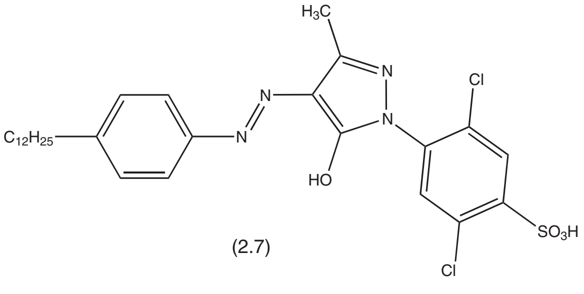
- (Benzo)thiazoles
- (Benzo)isothiazoles
- Thiadiazoles
- Thiophenes

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.[21]

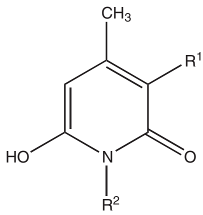
Tautomerism plays an important role in hydroxyazo dyes, having a marked influence on their tinctorial strengths and other properties crucial in a commercial dye, such as fastness to light. The hydroxy azo dyes can be grouped according to whether



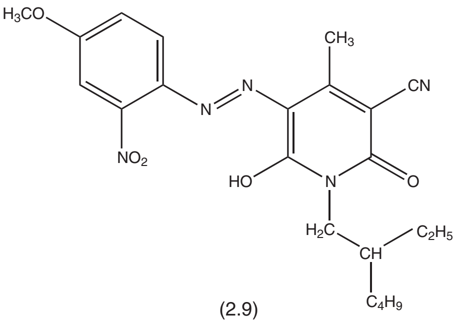
(2.6)
R^1 = alkyl,aryl, CO_2H
R^2 = aryl



(2.7)



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



(2.9)

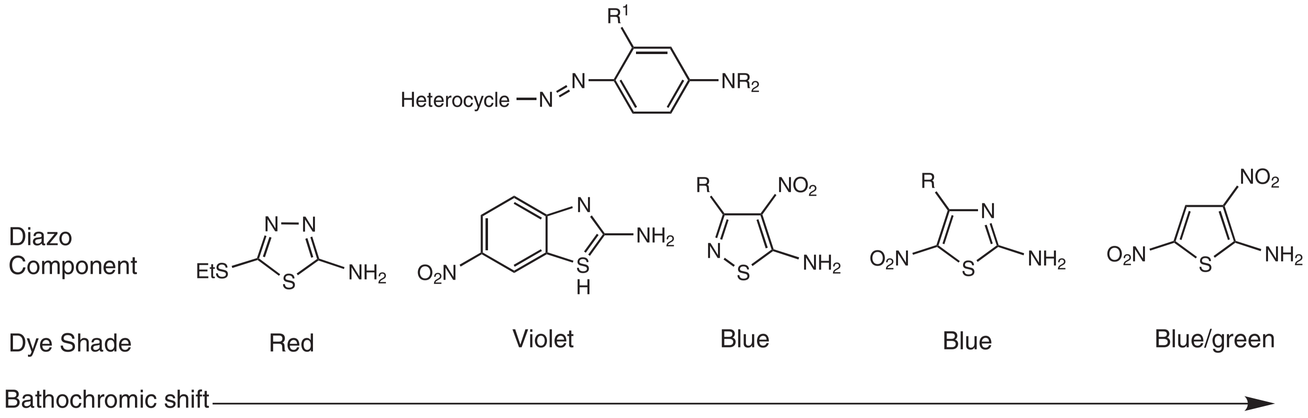
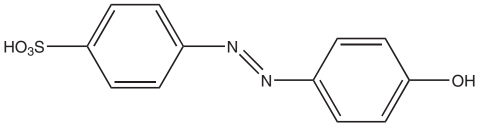


Figure 2.8 *Shades obtainable in monoazo dyes from heterocyclic diazo components.*

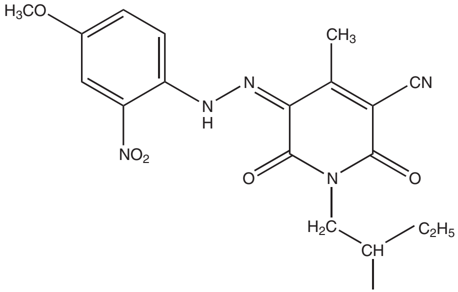
they exist predominantly in the azo form, predominantly in the hydrazone tautomeric form or as a mixture of both forms.

- All azo dyes made from phenols exist in the azo form (2.10).
- All azo dyes from all pyrazalones, 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-naphthols; the hydrazone form being bathochromic relative to the azo form (2.12), and the proportion of each dependent on substituents and solvent.
- 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).

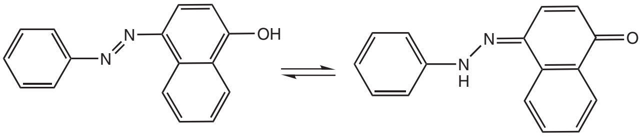
All aminoazo dyes exist exclusively in the azo form as shown in (2.13). The various forms formed on protonation of aminoazo dyes have already been discussed in Chapter 1 (section 1.4.1.4).



(2.10)



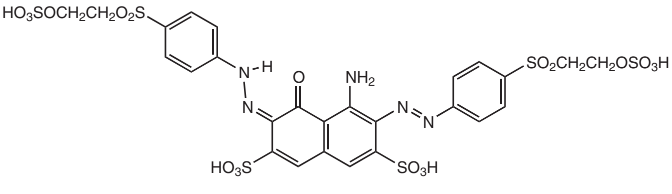
(2.11)



λ_{max} 410nm
ε_{max} 20,000

λ_{max} 480nm
ε_{max} 40,000

(2.12)



(2.13)

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-aminodiphenyl. 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 that are made using these particular amines as their diazo components. (Figure 2.9 for CI Acid Red 21.)

This cleavage can occur *via* bacteria in the human gut or, in some organs, by enzymatic reduction. 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 proper handling and poor environmental standards are present. The German government banned firstly the use and 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 has formed the basis of law now operating throughout the EU, the relevant section being:[22]

> 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).

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 such countries as India and China, because they cannot now use these dyestuffs in consumer goods to be imported into the EU.

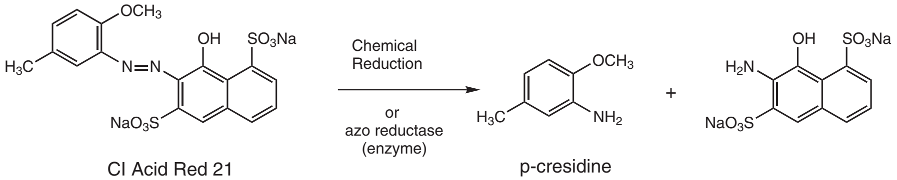


Figure 2.9 *Reductive cleavage of azo dyes.*

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

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.[23] Description of the synthetic routes to heteroaromatic diazo components, such as those shown in Figure 2.8, are well covered in literature reviews,[20,24] as are all the major heterocyclic coupling components.[19]

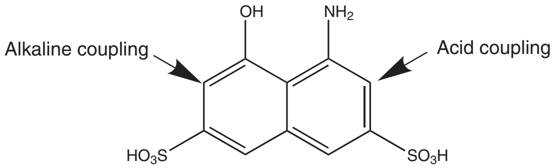
The method used for the diazotisation of amines depends on the basicity of the amine group and the solubility or physical form of the compound.

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. The amine is dissolved in a sufficient quantity of aqueous hydrochloric acid to ensure that the reaction medium remains acid throughout the process (at least 2.25 equivalents). After cooling to 0–5 °C, one molar equivalent of sodium nitrite is added drop-wise as an aqueous solution or portion wise as a solid, until a slight excess is indicated. Any excess nitrous acid is removed before coupling by adding sulfamic acid. For amines that are insoluble in acid medium, *e.g.* aminobenzene and naphthylamine sulfonic acids, an alternative 'inverse' method of diazotisation is employed. In this method sodium nitrite is added to a solution of the amine in aqueous alkali, and then this solution is then run slowly into an excess of acid and ice.

For weakly basic amines, *i.e.* anilines with poly nitro groups, *e.g.* 2, 4,-dintro-6-bromoaniline, and also most heterocyclic amines, an alternative method must be adopted using nitrosylsulfuric acid.[25] This diazotising medium can be made by dissolving sodium nitrite in concentrated sulfuric acid, but is also available preformed from chemical suppliers. The weakly basic amine is added gradually to the nitrosylsulfuric acid with cooling, and after reaction is complete the mixture is poured into ice and water to give a solution of the diazonium salt.

Coupling with amine coupling components is accomplished under acid conditions, by direct addition of the diazonium salt to an acid solution of the amine. In phenols and naphthols the reaction is carried out under alkaline conditions. The solution of the diazonium salt is added to a solution of the sodium salt of the phenol under pH control 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 ring and then in alkaline to react on the hydroxy ring.

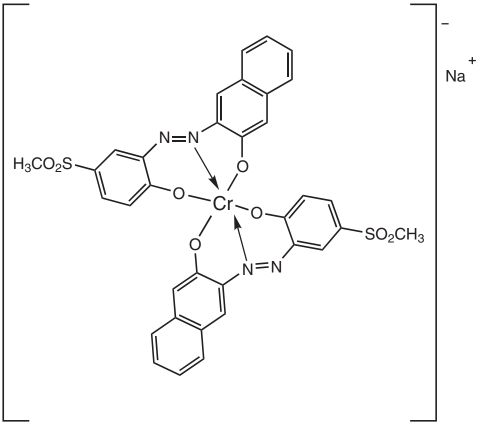
The azo dye is either formed as an insoluble precipitate and is filtered off from the mixture or, if it contains solubilising groups such as sulfonic acid groups, further precipitated by adding an electrolyte such as salt. Isolation *via* membrane technologies, *e.g.* reverse osmosis, is practised on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



(2.14)

Further chemical reactions of azo dyes fall into three categories:

1. *Metal Complexation*. Azo dyes containing hydroxy or carboxylic acid group substituents adjacent to the azo group react with transition metal ions, *e.g.* chromium, cobalt and copper to produce complexes, *e.g.* CI Acid Violet 78 (2.15).[26] 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. *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).



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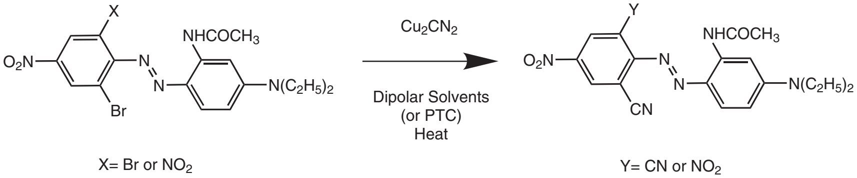


Figure 2.10 *Nucleophilic displacement to give bright blue azo disperse dyes.*

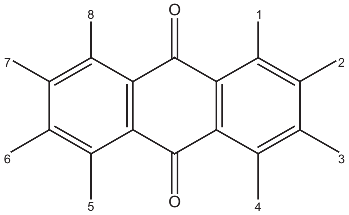
2.3.1.2 Cyclic and Polycyclic Quinones

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 major one of these ring systems, 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 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 namely 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- and 7- and 8-positions. The order of the bathochromic shift caused by substituents in the 1-position is $OH < NH_2 < NHCH_3 = N(CH_3)_2$, 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.[27]

As mentioned above, 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 molar absorption 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,

Table 2.5 *Substituent effects in amino- and hydroxyanthraquinones*



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	550 590	15 850 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	–

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, *e.g.* the 2-OCH_3 (CI Disperse Red 4), the important 2-OPh derivative, CI Disperse Red 60 and CI Disperse Red 91 and Red 92. The synthetic pathway to these red anthraquinone disperse dyes is shown in Figure 2.11.

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-respectively. The 1,4-substituted compounds are obtained by condensing the reduction product of quinizarin, 1,4-dihydroxyanthraquinone, often called the leuco form, with the desired amines as shown in Figure 2.12. It should be noted that 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 blues are made by further reactions of 1,5-diamino-4,8-dihyroxyanthraquinone, *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, *e.g.* CI Disperse Blue 60 and Blue 87 (2.16).

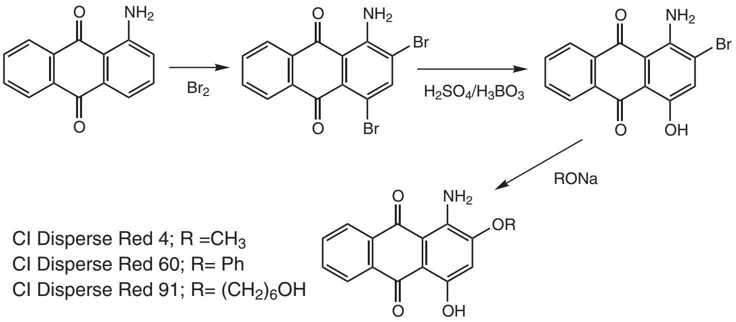
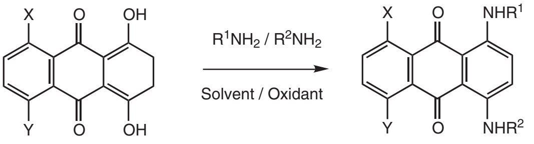
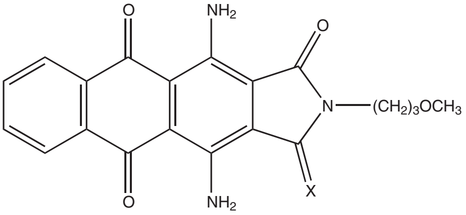


Figure 2.11 *Synthetic pathway to red anthraquinone disperse dyes.*



	X	Y	R^1	R^2
CI Disperse Blue 3	H	H	CH_3	C_2H_4OH
CI Disperse Blue 23	H	H	C_2H_4OH	C_2H_4OH

Figure 2.12 *Blue dyes from leuco 1,4-dihyroxyanthraquinones.*



(2.16)

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

Bromamine acid, 1-amino-4-bromoanthraquinone-2-sulfonic acid, is a very useful 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 2.13).

Polycyclic Quinones. Known as vat dyes when used in the dyeing of cellulosic fabrics (see section 2.3.2), 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 life time is required.[28] 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, making the final products relatively expensive (Figure 2.14).[29] 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 organic pigments and their structures will be covered in more detail in section 2.4.1.7.

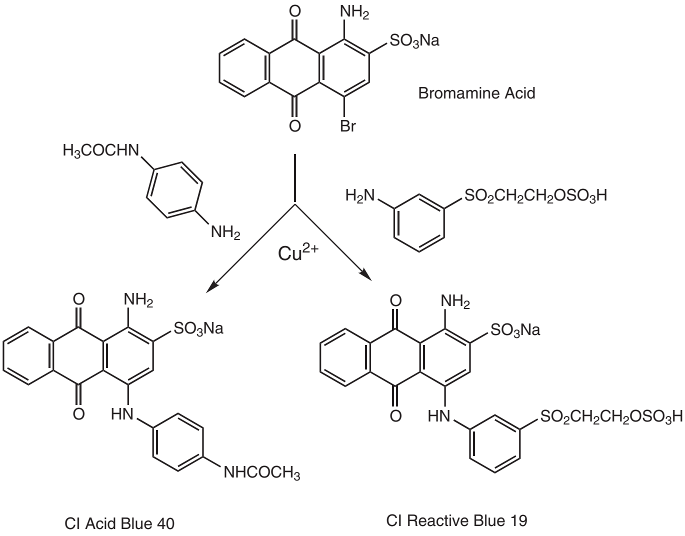


Figure 2.13 *Blue dyes from bromamine acid.*

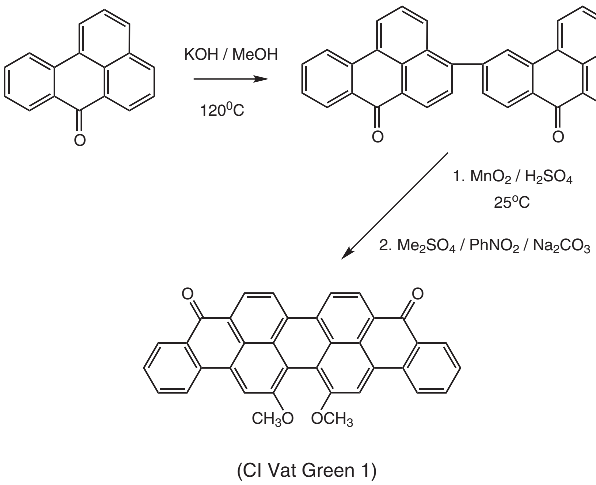


Figure 2.14 *Synthesis of CI Vat Green 1.*

Benzanthrones and analogues are discussed in Chapter 3, section 3.5.1.4, because of their behaviour as fluorescent dyes.

Indigoid Dyes. The most universally known dye 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 indigoid class. The process for its manufacture, which involves heating of *N*-phenylglycine in a mixture of molten NaOH/KOH and sodamide at over 220 °C, followed by drowning out into water and then aerial oxidation, sounds horrendous but it is in fact quite environmentally friendly, as practically all the by-products are recycled into the process, including all the alkali. The process is illustrated in Figure 2.15.[29]

Other Quinone Types. Although past researchers have examined many coloured quinonoid molecules very few have achieved commercial importance.

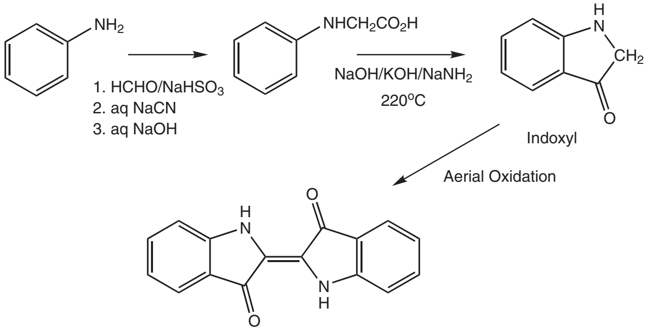


Figure 2.15 *Manufacturing route to indigo.*

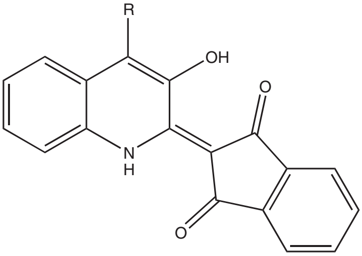
Quinophthalones, made by the condensation of phthalic anhydride with quinaldine derivatives, are one such group, exemplified by CI Disperse Yellow 54 (2.17a) and Yellow 64 (2.17b) used for polyester, especially for transfer printing and also as solvent dyes.

Benzodifuranones (2.18), made by reacting mandelic acids with 1,4-benzo 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.[30]

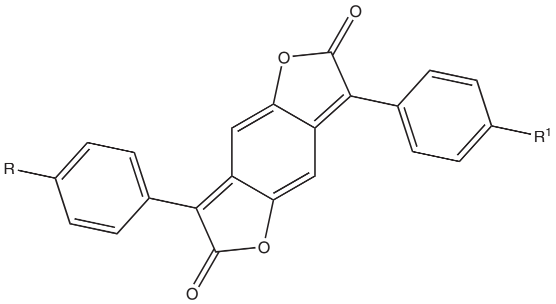
Other chromophores in this class are discussed under fluorescence in Chapter 3, *e.g.* coumarins (section 3.5.1.1), or under their use as pigments in section 2.4.1 of this chapter, *e.g.* perylene imides and derivatives (section 2.4.1.6).

2.3.1.3 Azines, Oxazines and Thiazines

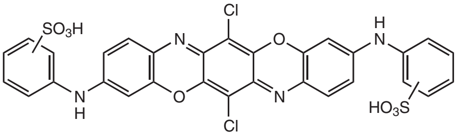
These chromophores have declined significantly in importance as textile dyes but have remained of interest because of their fluorescent behaviour, as discussed in Chapter 3, section 3.5.1.5. One exception is the triphenodioxazine ring system, which is used to produce valuable blue dyes in the Direct (2.19) and Reactive dye classes (2.20) as well as pigments (see section 2.4.1.7). The dyes from this chromogen have a very high molar absorption 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.[31]



(2.17a) R = H
(2.17b) R = Br

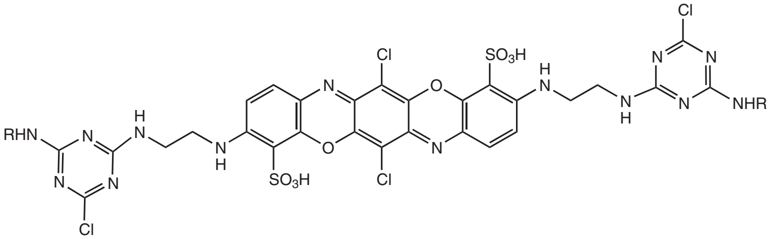


(2.18) R,R^1 = H and/or alkoxy



CI Direct Blue 105

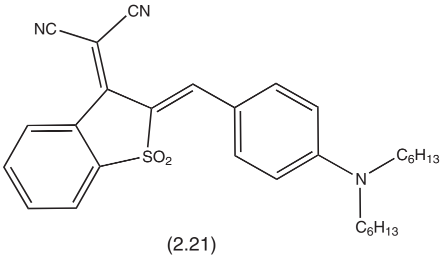
(2.19)



(2.20)

2.3.1.4 Methines

Simple methines, often called styryl dyes, were once important as yellow disperse dyes but are now only used to produce bright blue and turquoise dyes. Examples are the mono-methine (2.21), the dimethine (2.22) and the azamethine (2.23). Indophenols (2.24), another class of azamethines, have been used as bright blues for transfer printing onto polyester and in digital imaging by dye diffusion thermal trans-



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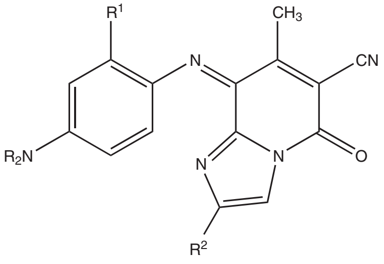

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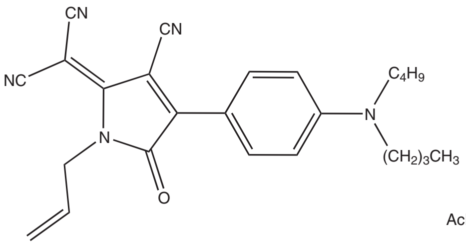
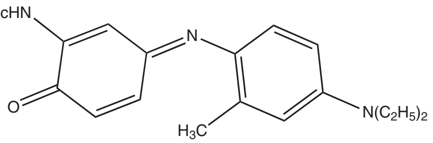


(2.22)



(2.24)

fer. Indophenols and the corresponding indamines are the ring systems extensively used in hair dyes (see section 2.3.2.5).

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 photography (see section 4.5.3).

Several high production products for the dyeing of polyacrylonitrile textile fibres come from the azacarbocyanines class. Example in this class are the azacarbocyanine Basic Yellow 11 (2.27), synthesised from 2,4-dimethoxyaniline (2.26) and Fischer's aldehyde (2.25); the diazacarbocyanine CI Basic Yellow 28 (2.30), synthesised from the diazonium derivative of (2.29) and Fischer's base (2.28) as shown in Figure 2.16. These dyes, although they are very bright, do tend to suffer from low fastness to light.

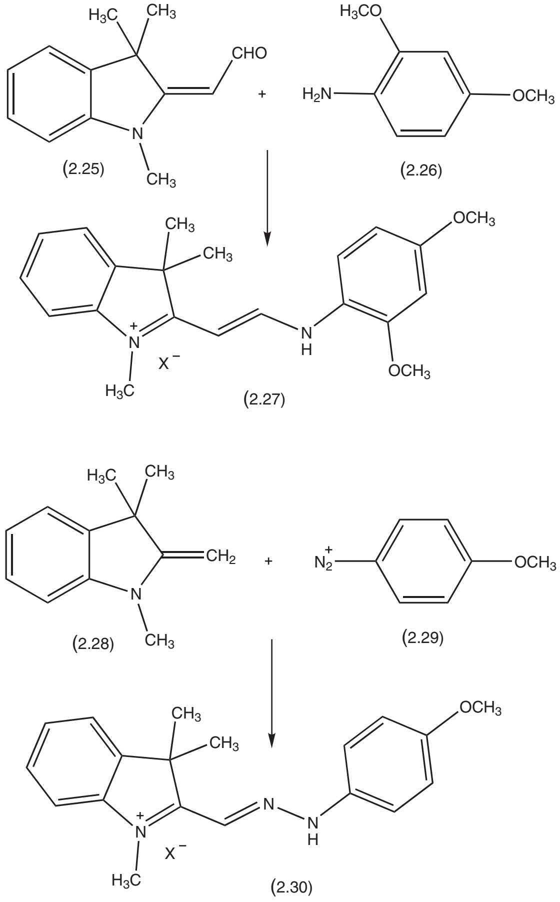


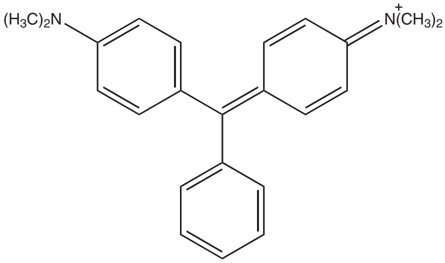
Figure 2.16 *Synthesis of azacarbocyanine basic dyes.*

2.3.1.5 Triaryl Carbonium Dyes

The main triaryl carbonium dyes are those based on the triphenylmethane structure, as exemplified by Basic Green 4 (2.31). They are very bright, but generally of low light fastness, and are consequently used for the coloration of paper and writing inks, where long lifetime is not an issue. (See also Chapter 1, section 1.4.1.2.)

2.3.1.6 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. Polysulfonated copper phthalocyanines form the basis of turquoise/cyan coloured compounds used as direct dyes 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 (2.32), a sulfonamide that is synthesised *via* the sulfonchloride. Although invariably shown as a 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. Nickel phthalocyanine is also used commercially to give dyes of a slightly greener shade than the copper derivatives.



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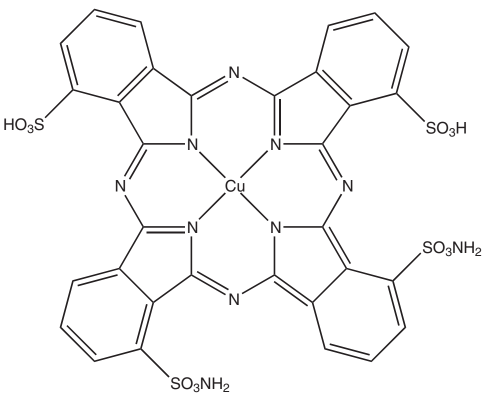


(2.32)

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. However, from a commercial standpoint it is the application method that determines the potential of a dyestuff and the reason for its industrial manufacture and sales. In this section the different application methods will be described mainly in relation to the end use, *e.g.* 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 The 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 directs and vat dyes for cotton, cationic dyes for acrylics and acid dyes for polyamide. The latter fibre has shown a comeback in recent years with the popularity of microfibres in sports and leisure wear. 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

The three main techniques for dyeing are exhaust dyeing, padding and continuous.[32]

The main method of printing on textile substrates is screen printing, both rotary and flat bed, but digital printing, *e.g.* ink jet printing (see section 2.7.1) is now starting to make its presence felt, especially for on-demand short runs.[33,34]

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 using, in decreasing order of scale and importance, reactive, direct and vat dyes.[33,35–37]

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

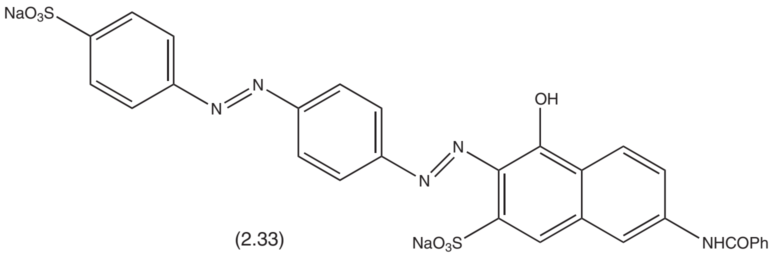
[a] Indigo, vat, sulfur *etc.* Source: Yorkshire Group.

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 (2.33). 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).

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 do suffer from low fastness properties including light fastness. Although metal complex dyes, as mentioned above, do improve fastness properties they are falling 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’. The vatting process involves chemical reduction to convert the dye into the soluble leuco form. A solution of the soluble leuco form 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 2.17.

The overall process for the dyeing with vat dyes produces a large load on the effluent because of the chemical reducing agent. More environmentally friendly alternatives to hydros have been proposed, *e.g.* the biodegradable hydroxyacetone, but cost



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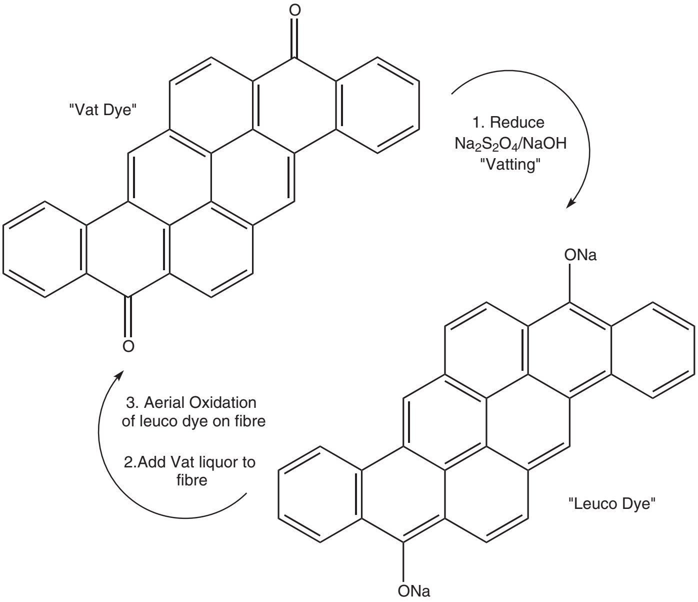


Figure 2.17 *Vat dyeing of cellulosic fibres.*

is a big factor. Electrochemical methods have been developed by BASF that show great promise.[38]

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 reactive halogen
- 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 on 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 hydroxy anion in the dyebath, which causes hydrolysis of the dye. The hydrolysed dye is incapable of further reaction and is lost to effluent. (See Figure 2.18.) 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.

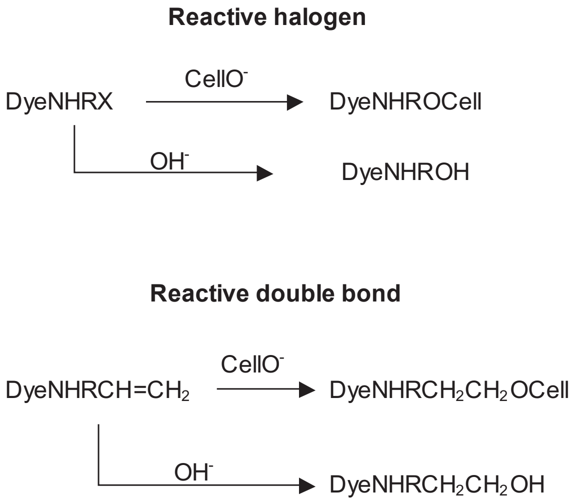


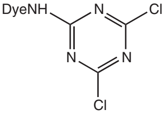
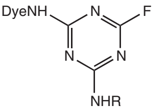
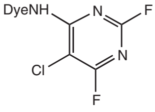
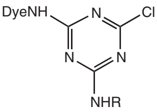
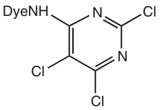
Figure 2.18 *Dye fibre bond formation and hydrolysis in reactive dyeing of cellulose.*

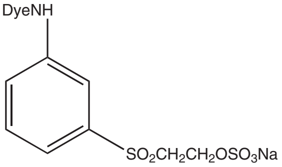
The major reactive heterocyclic halogen systems are chloro and fluoro analogues of 1,3,5-triazine and pyrimidine. Dichlorotriazines are the most reactive, the dyeing of cotton being carried out at 40 °C, whilst monofluorotriazines require dyeing temperatures of 40–60 °C and monochlorotriazines a temperature of 80 °C. The least reactive of the 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 2.7. 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 (2.35), usually as the sulfatoethylsulfone derivative (2.34), which converts into (2.35) in the dyebath under the influence of alkali at pH 11 to 12.5. 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 aromatic ring, *e.g.* CI Reactive Black 5 (2.2), but in a few cases a bridging aliphatic group is employed.[37]

The earliest reactive dyes were of the mono-functional type, *e.g.* CI Reactive Red 3 (2.36), but very soon in the development phase homo-bifunctional dyes, *e.g.* CI

Table 2.7 *Heterocyclic reactive systems and dyeing temperature*

				
40 °C	40-60 °C	40-60 °C	80 °C	98 °C



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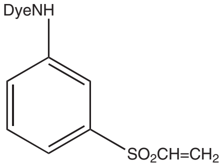
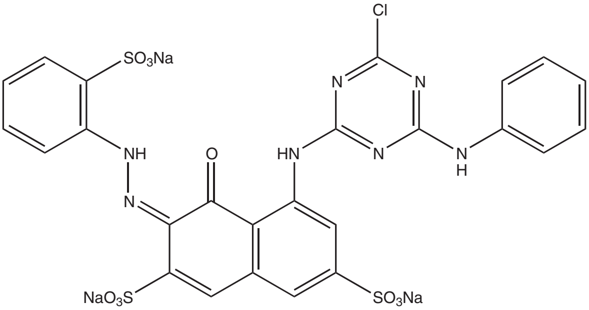


(2.35)

Reactive Red 125 (2.37), were introduced. This was done to improve the substantivity of the dyes for the fibre and to increase the probability of the groups reacting with the cellulose, hence increasing the fixation of the dye onto the fibre. Hetero-bifunctional dyes, those with two different reactive groups, *e.g.* CI Reactive Red 194 (2.38), were rather late on the commercial scene, not appearing until some thirty years after the initial invention of reactive dyes, but when they did they offered better fixation levels than had previously been obtained.

Nylon, Wool and Silk. Because of their common structural features, nylon (generically polyamide), wool and silk are normally considered together, especially as they



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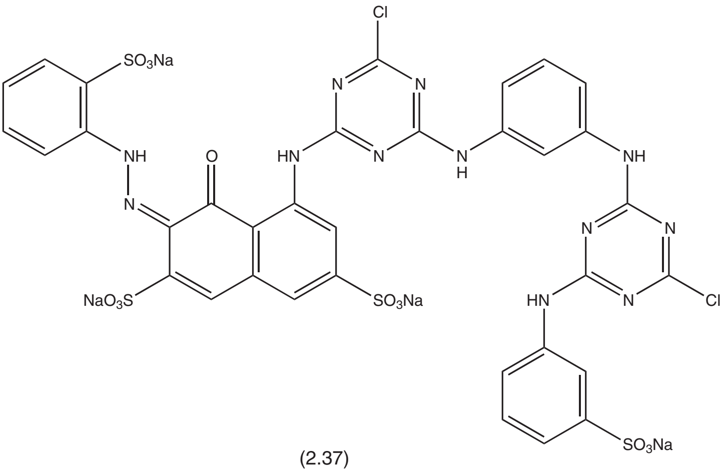

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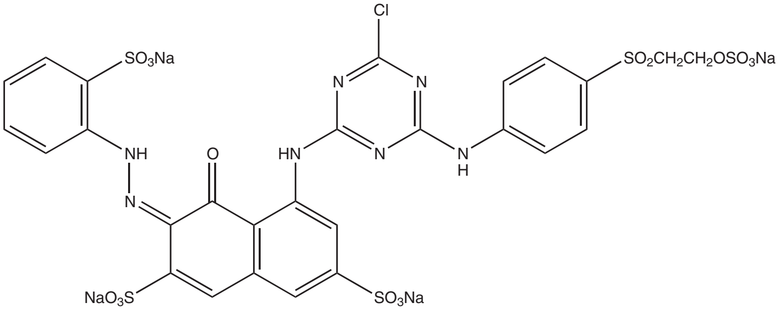


(2.38)

are coloured using the same or functionally similar dyes. The common structural features of the fibres are:

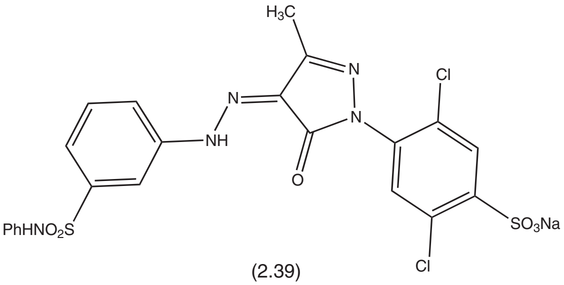
- Amide groups, –NHCONH–, linking segments of the polymer chains
- Amino and carboxylic acid groups at the end of chains, or on side chains (wool)

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 and hence cationic. Consequently, the preferred technique for dyeing of nylon and wool is from an acidic dyebath, at or near the boil, using anionic dyes, *e.g.* acid dyes. The sub-categories of acid dyes depending on the application pH are:

- Level Dyeing Acid Dyes – pH 2.5–3.5
- Fast Acid Dyes – pH 3.5–5.0
- Acid Milling Dyes – pH 5.0–7.5
- Super Milling Dyes – 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 an hydroxyazo dye by treatment with a chroming agent, *e.g.* dichromate. Metal complex dyes are declining in popularity due to environmental concerns and dyestuff manufacturers are introducing metal-free reactive dyes for this outlet, *e.g.* the ranges from Ciba and Clariant.[39,40] 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 (2.39), CI Acid Red 266 (2.40), CI Acid Blue 62 (2.41), the 1:2 premetallised dye CI Acid Black 60 (2.42) and the afterchrome dye CI Mordant Black 11 (2.43).

Polyester. The most important of the man-made fibres are polyesters, especially polyethylene terephthalate and to a much lesser extent cellulose acetate.



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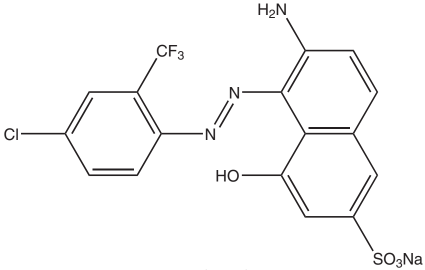

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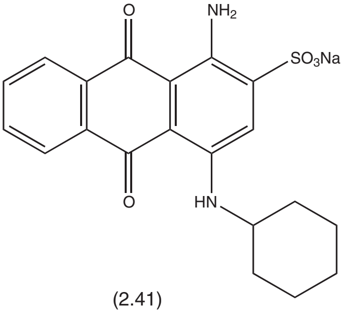

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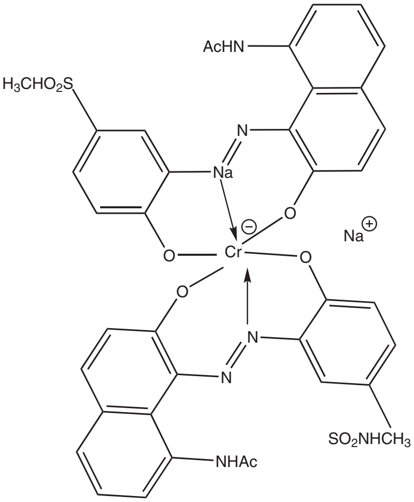

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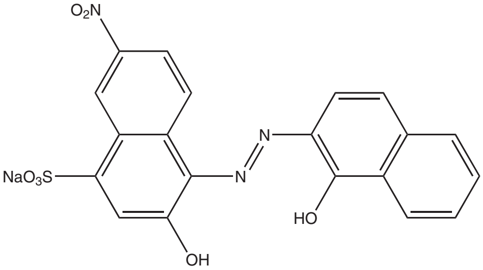


(2.43)

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. Disperse dyes, which take their name from the fact that they are used as aqueous dispersions in the dyeing process, are generally small in molecular size, without any ionic groups, but do have polar groups present in their molecular structure. The polar groups help to provide a very limited degree of water solubility and also enhance the interaction with the polyester by dipolar forces. The most important disperse dyes are derived from azo, anthraquinone and related quinones and also methine chromophores. The structures and synthesis of several typical disperse dyes have already been described earlier in this chapter; see (2.1), (2.9), (2.16), (2.17), (2.21–2.24) and Figures 2.10. 2.11 and 2.12.

Dispersions of the dyes in water are prepared by milling the untreated dye to a fine particle size in the presence of dispersing agents, *e.g.* lignosulfonates. The dispersions are either dried, invariably in a spray drier, 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 under pressure at high temperatures, *i.e.* 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 molecules then being 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.* σ-phenylphenol, which swell or modify the polymer easing the dissolution of the dye. Dyeings 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 disperse 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 s, 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.[6,36,41–43]

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.

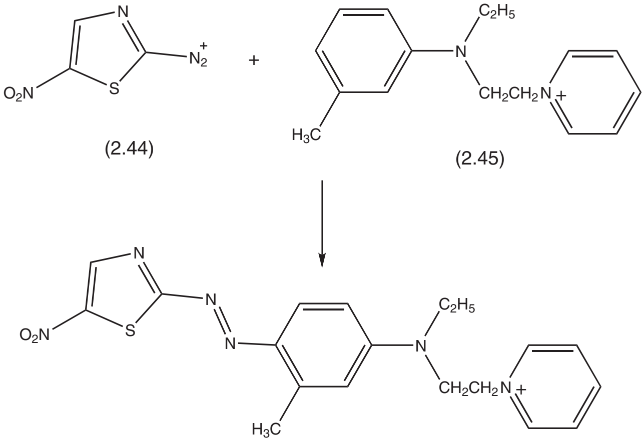
The cationic dyes can be classified into two types:[40]

- 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

The delocalised dyes are inherently stronger and brighter than the pendant types.

The dyes bearing pendant cationic groups are usually derived from azo or anthraquinone dyes. The azo dyes are normally made by coupling the diazo component onto a preformed cationic coupling component, exemplified by CI Basic Blue 119 (2.46) from (2.44) and (2.45). Contrastingly, in anthraquinones the quaternisation is usually carried as a post colour forming step, *e.g.* CI Basic Blue 13 (2.48) from (2.47).

The delocalised charged dyes are dominated by cyanine dyes, exemplified by the azacarbocyanine CI Basic Yellow 11 (2.27), the diazacarbocyanine CI Basic Yellow 28 (2.30) and the diazahemicyanine CI Basic Blue 41 (2.49). Where necessary quaternisation is carried out as a post colour forming reaction. Other structural types include oxazines, thiazines and triphenylmethane dyes.



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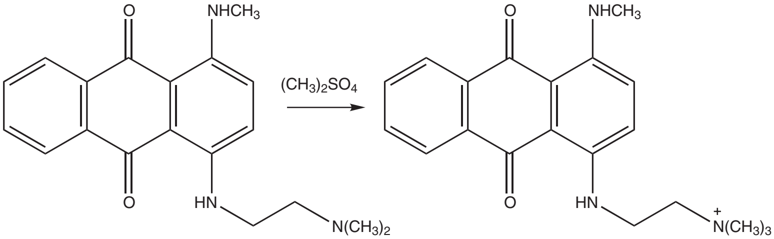

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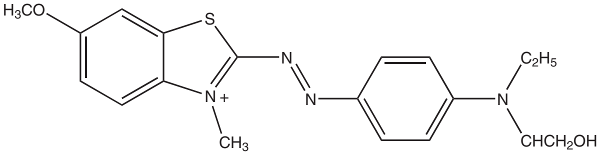


(2.49)

2.3.2.2 Paper

Paper is made from cellulose fibre containing, depending on the quality of the paper, varying amounts of lignin. Low quality and short life paper, *e.g.* as used in tissues and wipes, 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 a good fastness properties as the coloured papers are required to have good archival properties and light stability 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. These cationic direct dyes are related structurally to reactive dyes with the labile chlorines replaced by pendant cationic groups, *e.g.* (2.50).

2.3.2.3 Leather

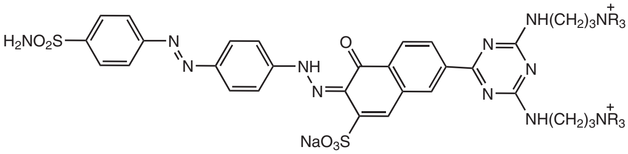
Leather is an important material in the world economy, being used in footwear, clothing, luggage and upholstery. It is a complex substrate prepared from animal hides and skins by a long series of treatments. After the removal all organic material and hairs the material is tanned, usually with chromium salts, which causes the protein chains to cross-link. After treating with oils or fats, to improve its handle, the leather is dyed.

Leather can be dyed with acid, direct and mordant dyes. Many of the direct dyes were based on benzidine and its congeners but the German Ordinance, covered under the toxicity of certain azo dyes in section 2.3.1.1, has meant that this is no longer an option. 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.[45]

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).

2.3.2.4 Food

The coloration of our food and drink is something about which everybody has an opinion. These days there are commonly held concerns about the safety of the additives in what we eat, but hardly anybody would relish the thought of eating processed



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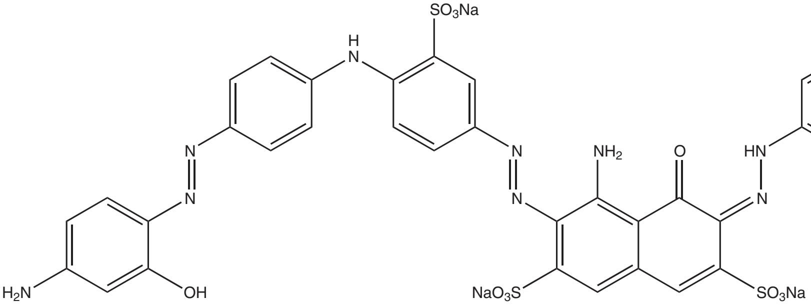


(2.51)

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 Food and Drug Administration in the USA.[46] Colour additives are classified by the FDA as 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 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. There are nine dyes certified for use in the USA, labelled with FD&C (Food Drug & Cosmetic) numbering. The structures of six of these nine dyes are shown in Figure 2.19, another being FD&C Blue No. 2, indigo carmine.

Colour additives that are exempt from certification include those pigments made from natural sources, such as minerals, vegetable 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 these natural colorants as the move to organically farmed foodstuffs has caught on with the consumers. This has resulted in major manufacturers investing in biotechnology to produce these products in improved yields and consistent quality.

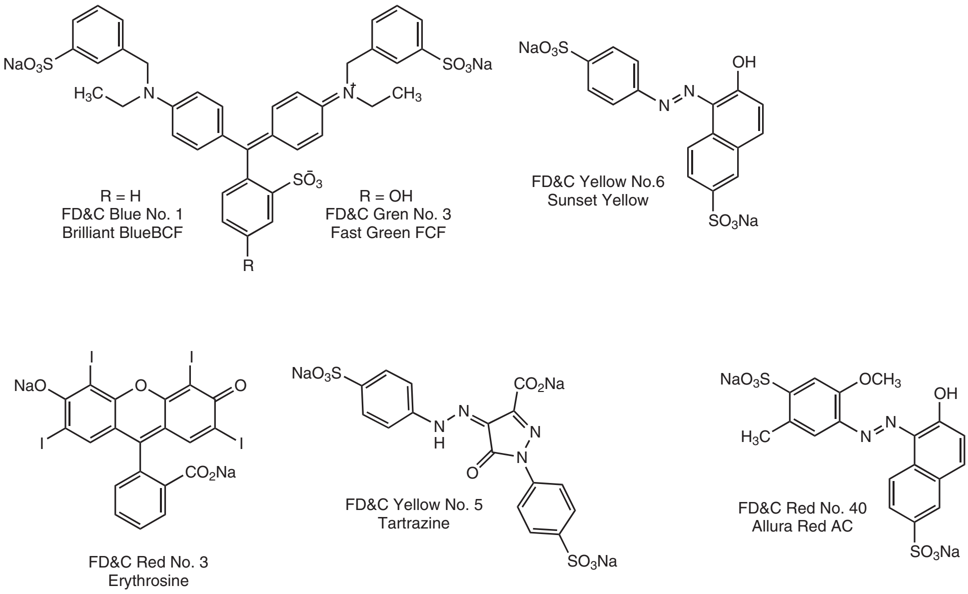


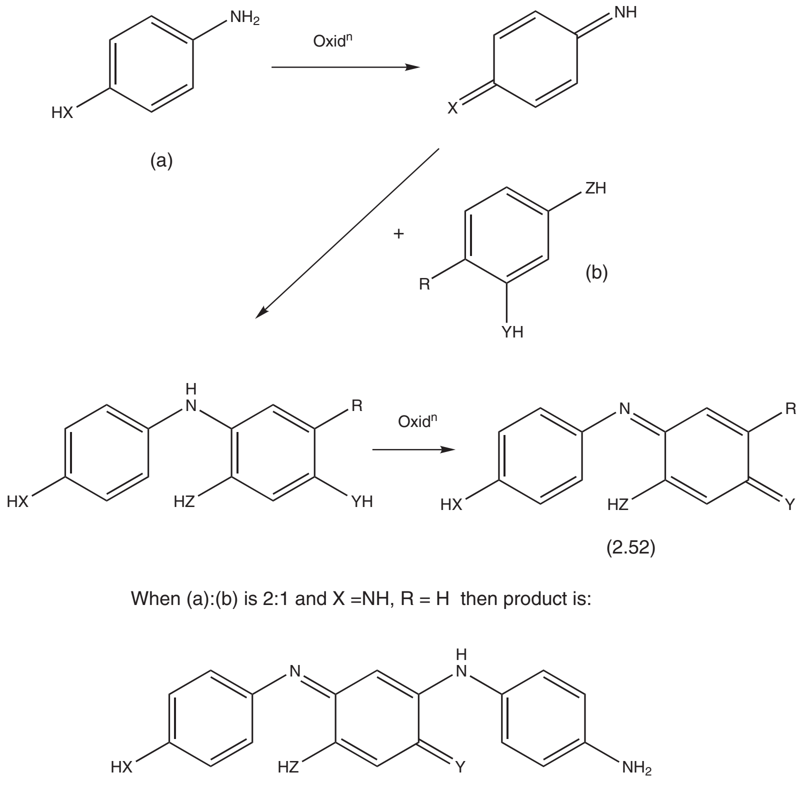
Figure 2.19 *FD&C certified food colorants.*

2.3.2.5 Hair Coloration

Hair coloration is increasingly popular throughout the world with the industry expanding at above average world economy growth rates. Once the domain of women it is growing fastest amongst the male population, albeit from a much smaller baseline. The coloration systems can range from temporary (surface dyeings, usually for fashion reasons) through semi-permanent (5–10 shampooings) to permanent. Nothing in this field can be truly permanent, as obviously hair grows and needs to be re-coloured, and the fastness of the dyes is not perfect, being 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.

The main dye producing system used in hair coloration involves the oxidation of a 'primary intermediate' in the presence of a 'colour coupler' to produce the coloured molecule. The primary intermediates are 1,4-phenylenediamines or 1,4-aminophenols and the colour couplers are 1,3-phenylenediamines or 1,3-aminophenols. The primary intermediates are oxidised by peroxides to give the coloured benzoquinonediimines or monoimines, which react with the couplers to give indoamines or indophenols, *e.g.* (2.52) and (2.53), depending on the nature and ratio of the reactants, as shown schematically in Figure 2.20.[47]

Certain amines are no longer used because of toxicity concerns, but there is still a wide range of colours available from the system. A few of the colours obtainable are illustrated in Table 2.8. They range from brown to blue depending on the primary intermediate and the colour coupler.



(2.53)

Figure 2.20 *Routes to indoamine and indophenol hair dyes.* (Reproduced with permission of Elsevier.)

Table 2.8 *Hair colours*

Primary intermediate	*Coupler*	*Shade*
1,4-phenylenediamine	Pyrogallol	Brown
	Resorcinol	Green/brown
	3-Aminophenol	Magenta
	1,3-Phenylenediamine	Blue
	2,4-Diaminophenetole	Blue
4-aminophenol	5-Amino-2-methylphenol	Orange–red

2.8.2.6 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 chemicals 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 ones, in which the foreground material is stained or negative ones, 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.[48,49] 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. (For more details on fluorescent probes *etc.*, see Chapter 3, section 3.5.6)

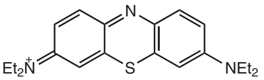
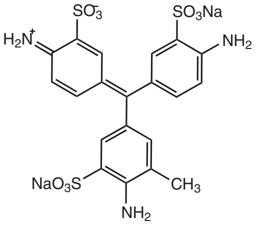
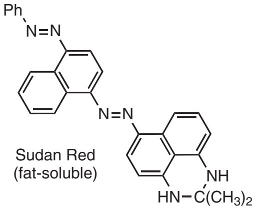
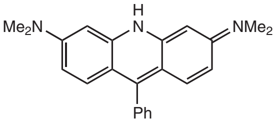
Representative stains in each of these chemical classes and some of their applications are shown in Table 2.9.[50]

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 regarding dyes and pigments.[51]

> 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 be become insoluble; pigments when used to colour a substrate remain insoluble as a finely divided solid throughout the coloration process.

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 For staining Negri bodies in nerve cells
 Acid Fuchsin (anionic)	Stain for connective tissue and erthrocytes For proteinaceous material in liver Cain's method for mitochondria
 Sudan Red (fat-soluble)	Stain for fat in animal tissue For chromosomes, golgi, and leucocyte granules
 Acridine Orange (fluorescent)	Pickett's method for fungi fluorescent against a dark background For differentiation of nucleic acids and cytology

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.[7] The make up of the organic pigments portion of the world pigments 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-pyrrolo pyrroles and thiazine indigos.

Table 2.10 *World markets make up of organic pigments (1998)*

Type	*Azo & other*	*High performance*	*Phthalocyanine Blue*	*Phthalocyanine Green*
% Share	47	25	21	7

2.4.1.1 *Azo Pigments*

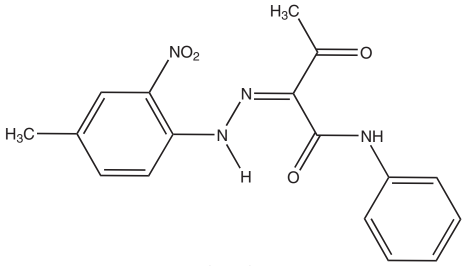
The main groups of pigments based on the azo chromophore are monoazo, disazo, β-naphthol pigments, Naphthol AS, benzimidazolones and azo pigment lakes. The synthesis of azo pigments closely parallels the methods used to make azo dyestuffs as described in section 2.3.1.1. However, as pigments are inherently insoluble, care must be taken to remove insoluble impurities from the starting materials and dispersing agents are often used at the coupling stage. In this respect the synthetic methods are most like those used to make azo disperse dyes. It should be noted that 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.

Monoazo pigments cover the shade range from greenish-yellow to deep reddish-yellow or orange shades. They suffer from poor fastness properties, especially solvent (bleed) and migration fastness, so that their commercial importance has diminished as alternative structures with higher fastness properties have become available. The best of the commercial pigments are based on acetoacetanilides as coupling components, exemplified by the oldest, CI Pigment Yellow 1, shown in the hydrazone tautomeric form in (2.54).

The β-naphthol pigments are monoazos derived from 2-hydroxynaphthalene (β-naphthol) as coupling component, which exist predominantly in the hydrazone form (2.55). Their shades fall within the yellowish orange to bluish red range. They exhibit rather poor fastness properties to organic solvents and are used mainly in air-drying paints, but CI Pigment Orange 5 (2.55a) and CI Pigment Red 3 (2.55b) 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 reds. Most of these pigments derive their importance from their use in printing inks. The synthetic pathway to these pigments is shown in Figure 2.21, using the brilliant mid-red CI Pigment Red 112 (2.56) as the example.

Benzimidazolone pigments are actually monoazo pigments but the convention within the industry is to not use the azo descriptor; they are classified as high-performance pigments. All the pigments in this class are derived from coupling



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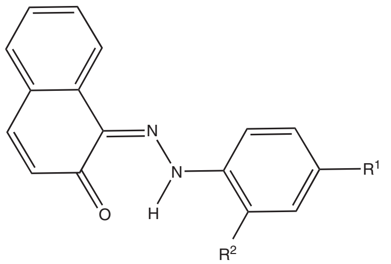
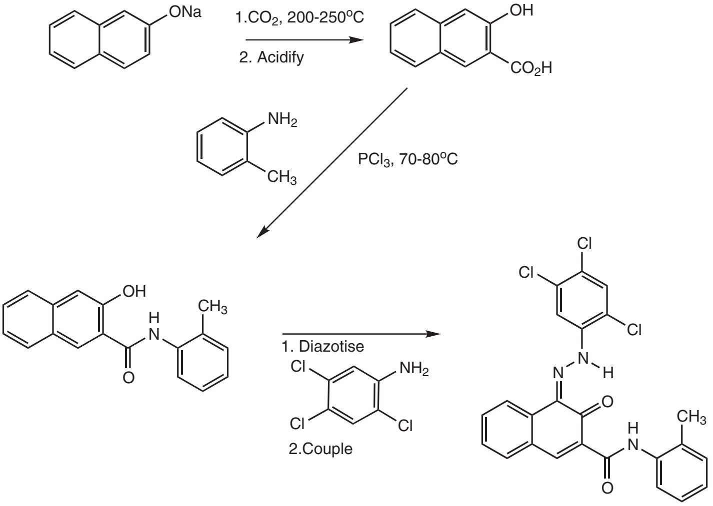


(2.55)

(a) $R^1,R^2 = NO_2$

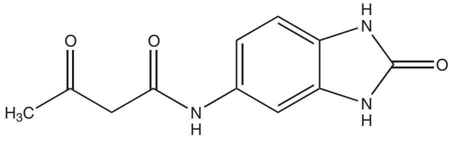
(b) $R^1 = CH_3$, $R^2 = NO_2$



(2.56)

Figure 2.21 *Synthetic route to Naphthol AS (Reds) pigments.*

components carrying the 5-aminocarbonylbenzimidazolone group, typified by the yellows/oranges based on 5-acetoacetylaminobenzimidazalone (2.57) and the red and brown pigments from the arylamide (2.58). 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, *e.g.* CI Pigment Yellows 120, 151, Pigment Orange 36, have the generic structure (2.59) and the red/browns, *e.g.* CI Pigment Red171, 175, 176, (2.60).



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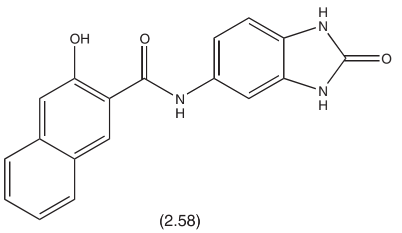

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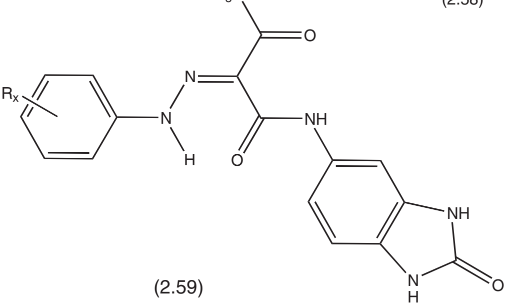

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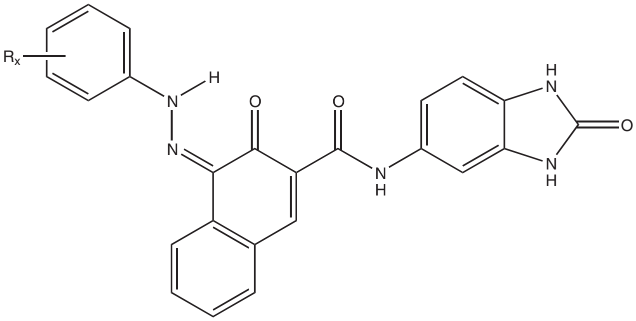
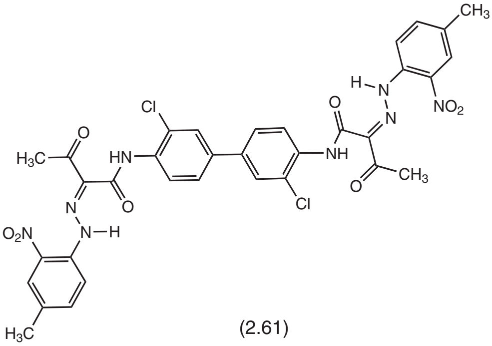


(2.60)

Symmetrical disazo pigments of commercial importance are derived from substituted benzidine diazo components and either an azo pyrazalone or acetoacetanilide coupling component (diarylides). A good example is CI Pigment Yellow 12 (2.61), 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 (2.62), and BON Acid arylamides, *e.g.* CI Pigment Red 144 (2.63). The products are high quality pigments used in plastics and quality printing inks.



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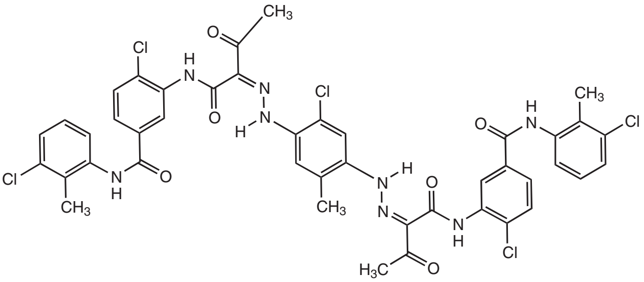

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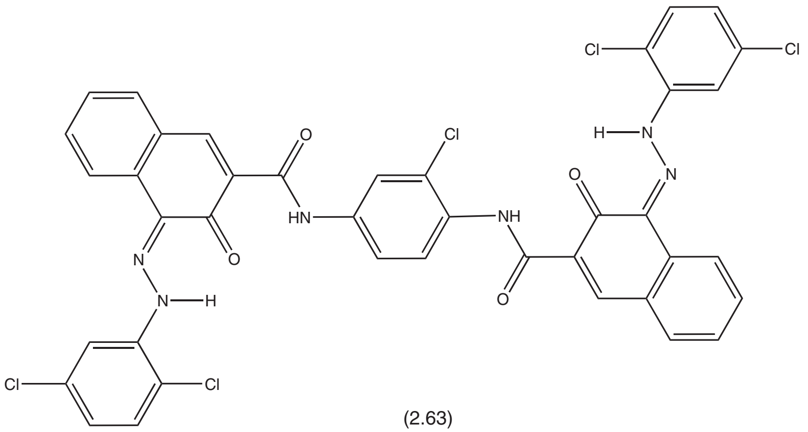
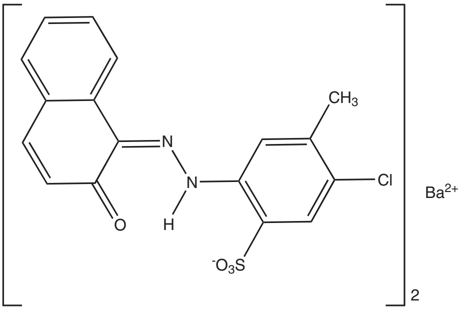


(2.63)

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, *e.g.* CI Pigment Red 53:1 (2.64), BON Acid, *e.g.* CI Pigment Red 48:2 (2.65) and, of lesser importance, Naphthol AS and naphthalene sulfonic acid based dyes.[7] The β-naphthol and BON Acid lake pigments are widely used in the printing ink industry and in plastics.



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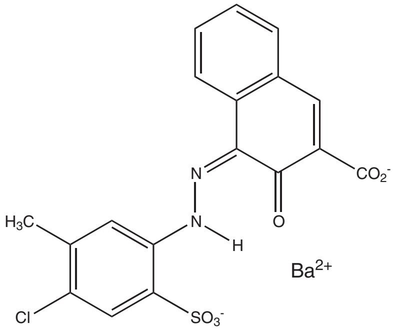
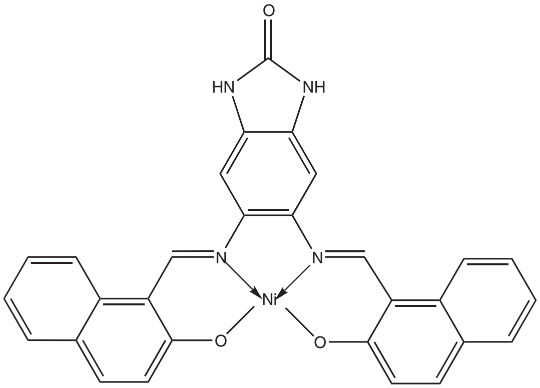


(2.65)

2.4.1.2 Metal Complexes

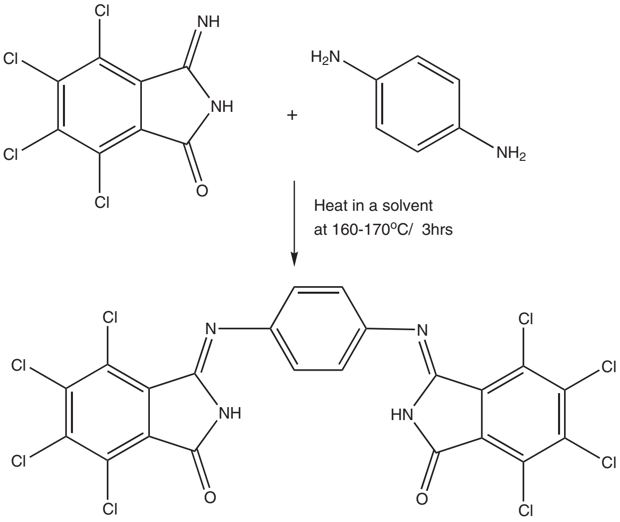
Metal complexes, usually Cu^{2+}, Ni^{2+} or less commonly Co^{2+}, of 2,2′-dihydroxyazo dyes and azo methines have been used to produce yellow to red pigments that have commercially interesting properties. They find application in industrial and automotive finishes and also in plastics. CI Pigment Orange 68 (2.66) is an interesting pigment, which also contains the benzimidazolone moiety, and is actually one of the most heat stable of all the organic pigments.



(2.66)

2.4.1.3 Isoindolinone Pigments

All the important isoindolinone pigments are derived from the tetrachloroisoindolinone ring by condensation with aromatic diamines, as shown in Figure 2.22. The shades range from yellow through orange to red, but are especially important in the greenish yellow to reddish yellow shade areas, exemplified by CI Pigment Yellow 110 (2.67). They are high-grade pigments that find application in industrial paints and automotive finishes, plastics and quality printing.



(2.67)

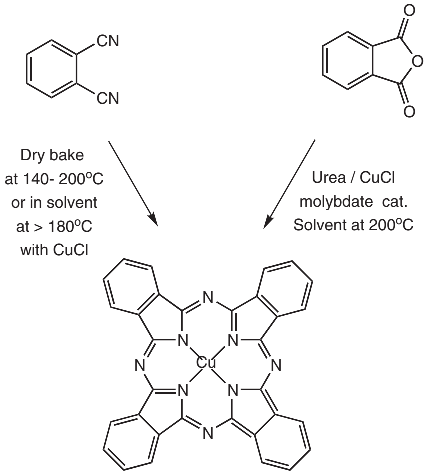
Figure 2.22 *Synthesis of isoindolinone pigments.*

2.4.1.4 Phthalocyanines

The copper complex (2.68) of the parent phthalocyanine macrocycle is the single most important organic pigment, being a highly stable blue pigment with excellent properties.[52–54] 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). Phthalocyanines have found wide application in many technologically advanced areas (see Chapter 4), but none on anything like the scale of their use as pigments.[55–57]

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. These routes are shown in Figure 2.23. 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 like many other phthalocyanines is polymorphous, (see Chapter 4, section 4.2.1.7), the order of thermodynamic stability of the main ones being β > ε > α. The reddish blue α-form is metastable and is readily converted into 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 2.24. 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



(2.68)

Figure 2.23 *The manufacturing routes to copper phthalocyanine.*

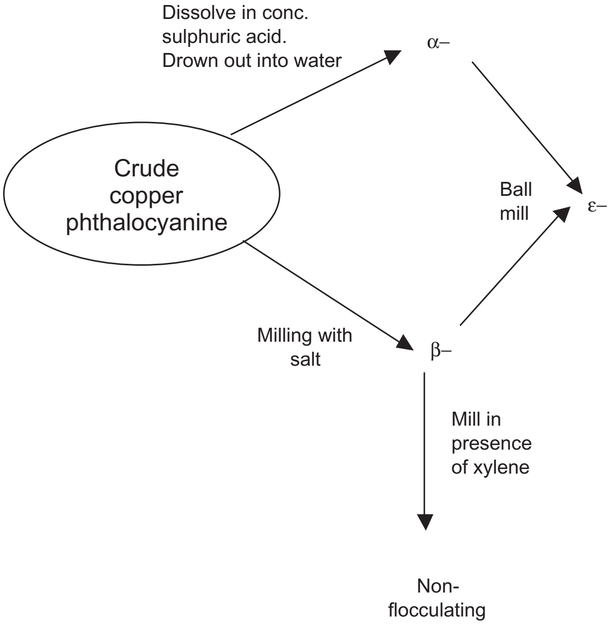


Figure 2.24 *Crystal modifications of copper phthalocyanine.*

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.[58]

Halogenation of copper phthalocyanine produces greens, which are again the pigment of choice in this shade area for coatings, inks and plastics. Halogenation with chlorine and bromine is carried in a molten eutectic of aluminium chloride and salt. The blue shade of 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 phthalocyanine is given in Table 2.11.[7]

2.4.1.5 Quinacridones

Quinacridone is the trivial name given to the five-ring heterocyclic system exemplified by the linear *trans*-quinacridone (2.69). 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

Table 2.11 *Commercially available copper phthalocyanine pigments* (Reproduced with permission of Wiley – VCH)

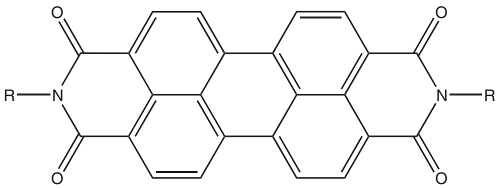
CI name atoms	*Crystal modification*		*Stability Shade*	*Halogen atoms*
Pigment Blue 15	α	No	Reddish-blue	0
Pigment Blue 15:1	α	Yes	Greener than Blue 15	0.5–1 Cl
Pigment Blue 15:2	α	Yes Non-flocculating	Reddish-blue	0.5–1 Cl
Pigment Blue 15:3	β		Greenish-blue	0
Pigment Blue 15:4	β	Non-flocculating	Greenish-blue	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

available as CI Pigment Violet 19. Substitution in the outer rings by CH_3 and Cl gives other valuable pigments. A manufacturing route to linear quinacridone is shown in Figure 2.25.

2.4.1.6 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 (see section 2.3.1.2). Perylene pigments (2.70) are made by reaction of the perylene tetracarboxylic dianhydride with primary aliphatic or aromatic amines in high boiling solvents. Perylenes provide a range of shades from red through bordeaux to violet depending on the nature of the amide substituent, *e.g.* CI Pigment Red 179 (2.70, R = CH_3). 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.

Perinones are structurally similar to perylenes being made by condensing naphthalene tetracarboxylic dianhydride with amines, but in this case 1,2-diamines, *e.g.* CI Pigment Orange 43 (2.71), or its *cis* isomer. The isomers can be separated by fractionation of their salts. They offer orange to bordeaux shades with similar properties to perylenes, but are less commercially important.



(2.70)

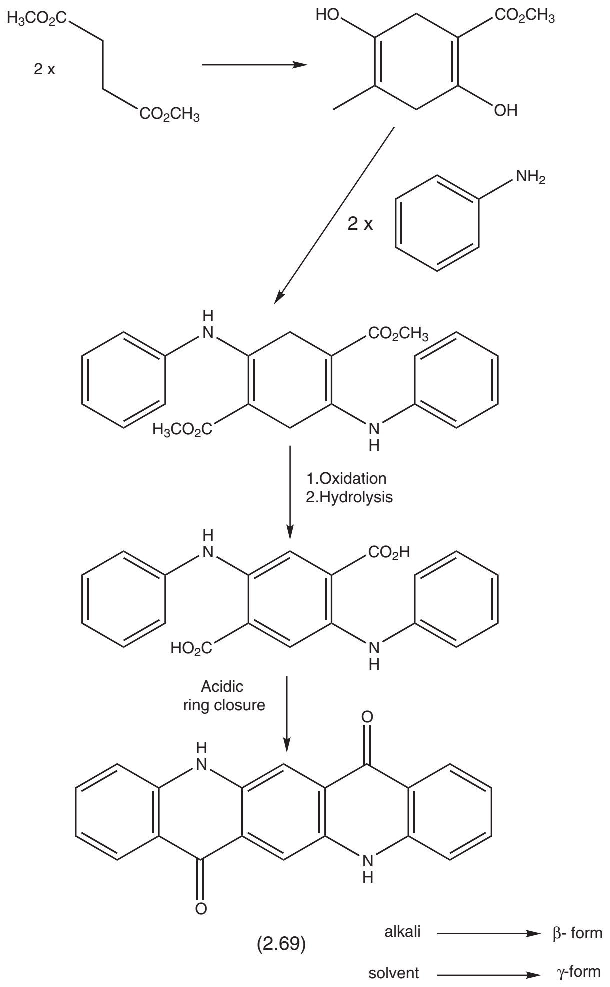
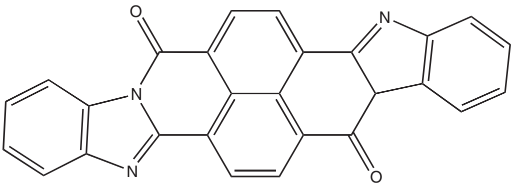


Figure 2.25 *Manufacturing route to linear quinacridone.*



(2.71)

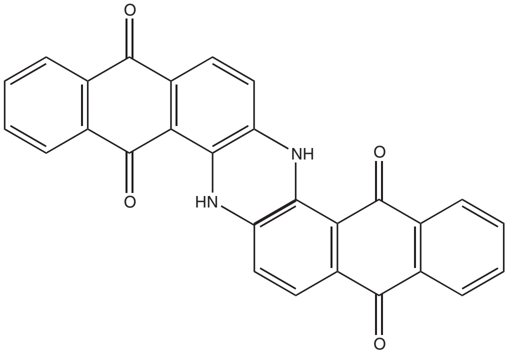
Both perylenes and perinones show significant fluorescent behaviour and have found outlets based on this characteristic (See Chapter 3, section 3.5.1.3).

2.4.1 7 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 hydroxy anthraquinone 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 (2.72), CI Pigment Blue 60, shows properties that are even better than copper phthalocyanines in light tints. It is consequently used in automotive finishes and general industrial paints.

Another important quinone is anthanthrone, especially its dibromo derivative (2.73), CI Pigment Red 168. This latter pigment is scarlet in colour and 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 (2.74), and pyranthrone (2.75), whose halogenated derivatives give high light fast oranges and reds used in paint outlets, and especially dioxazine, whose carbazole derivative is CI Pigment Violet 23. CI Pigment Violet 23 was originally thought to have a linear structure but now has been shown to be angular (2.76). It is a very versatile and important pigment used in all outlets.



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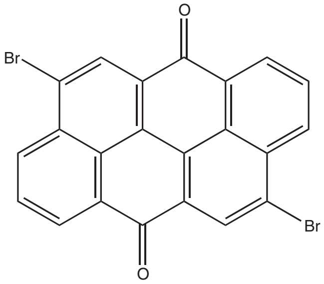

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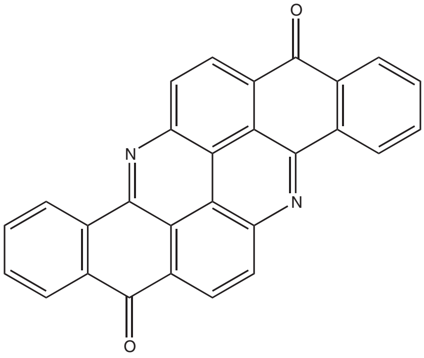

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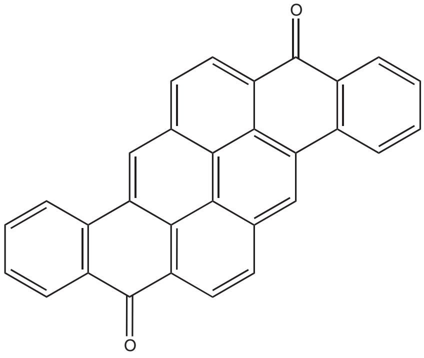

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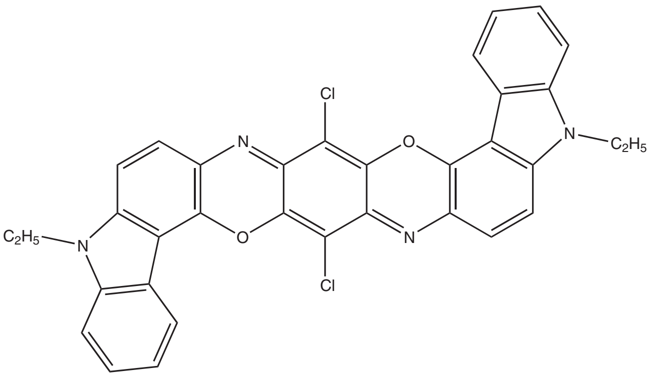


(2.76)

2.4.1.8 *Diketo-pyrrolopyrroles*

Arguably the most important new chromophore introduced in the latter part of the 20th 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 benzodifuranones (see section 2.3.1.2).[59] The first product to be commercialised, CI Pigment Red 254 (2.77), rapidly established itself as a high-performance bright red of choice for automotive finishes. The synthetic pathway to this product is illustrated in Figure 2.26.

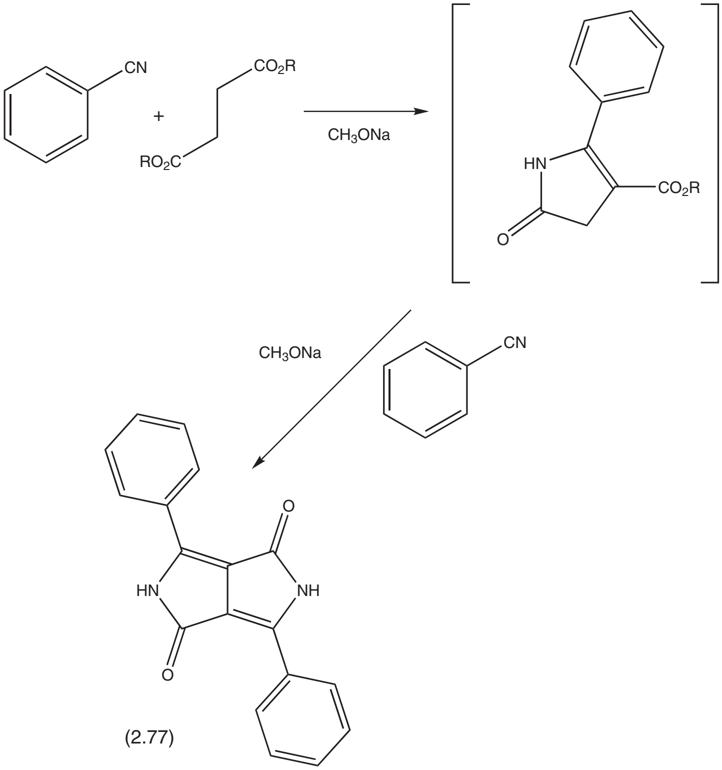
2.4.1.9 *Triaryl carboniums*

The structures of triaryl carbonium dyes have already been described (see section 2.3.1.5). In the pigment field, the insoluble complexes of triaryl carbonium dyes with heteropolyacids, *e.g.* phosphotungsto molybdates, 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.[8] 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:[60]

- 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)



(2.77)

Figure 2.26 *Synthetic route to the diketo-pyrrolopyrrole red pigment CI Pigment Red 254.*

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 (*ca.* 250 000 tonnes in 1999) are of decreasing commercial importance compared to the synthetic oxides (550 000 tonnes in 1999), which generally display superior hues and can be made in a more consistent quality. Their main uses are in concrete coloration and in paint, which are areas of increasing demand in both developed and developing countries, leading to good growth rates for these materials. The forecast for world consumption is for it to rise to 1M tonnes year^{-1} by 2009, with Western Europe at 330 000 tonnes, North America at 292 000 tonnes and Asia Pacific at 273 000 tonnes.[61]

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 and reds
- 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

Some typical products are CI Pigment Red 101 (synthetic) and CI Pigment Red 102 (natural; haematite) $Fe_2{\cdot}xH_2O$, 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, $Fe_2O3{\cdot}xFeO{\cdot}yH_2O$, CI Pigment Brown 11 known as magnesium ferrite $MgO{\cdot}Fe_2O_3$ and CI Pigment Black 11.

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. CI Pigment Green 17 absorbs in the near-infrared and has found uses in camouflage paints.

$$Na_2Cr_2O_7 + S \rightarrow Cr_2O_3 + Na_2SO_4$$

The hydrated product, $Cr_2O_3{\cdot}H_2O$, known as Viridian Green, is a blue shade of 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.[8] The two stable lattices that are used in commercial products are rutile (TiO_2) and spinel, Mg Al_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 to 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 new 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.

Research work in this area continues and a recent claim in the literature describes the use of the perovskites $CaTaO_2N$ and $LaTaO_2N$ to give bright yellow to reds.[62]

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 an activated clay with felspar, 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 artists 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, $FeNH_4Fe(CN)_6(xH_2O$. The first step in its preparation involves the precipitation of complex iron(II) cyanides, *e.g.* potassium hexacyanoferrates(II) with iron(I) salts, *e.g.* the sulfate or chloride, 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. It is mainly used in the printing industry as a toner for black inks. In addition, it is also used in the colouring of fungicide formulations.

2.4.3 Special Effect Pigments

There are five main classes of speciality pigments:

- Anti-corrosive pigments
- Magnetic pigments
- Luminescent pigments
- Lustre pigments
- Transparent pigments

The first two 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 disks *etc*. Luminescent pigments are described in Chapter 3 (section 3.2) and under fluorescent dyes and pigments (section 3.5.2). Lustre pigments, often described as 'colour by physics' are discussed under iridescence in Chapter 5 (section 5.3).

Transparent pigments are those that become transparent in binders when the difference between the refractive index 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 this is accomplished during synthesis by the use of additives, which prevent re-agglomeration of the pigment particles. Examples include CI Pigment Yellow 43, transparent iron oxide α-FeO(OH), CI Pigment Red 101, transparent red iron oxide, CI Pigment Red 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, 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 88% of the total. The only other areas of any significant importance are textile printing, pigmented fibres and paper (see Table 2.12).

Table 2.12 *Organic pigment application areas*

Area	*Printing inks*	*Paints & coatings*	*Plastics*	*Textile printing*	*Pigmented fibres*	*Paper*	*Others*
%	53	23	12	4	3	2	3

2.4.4.1 Dispersion of Pigments

Apart from displaying the desired physical properties, such as light and weather fastness, heat fastness, solvent resistance *etc.*, there is a prime requirement that the pigment be readily and evenly dispersible in the application medium.[7] 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, 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 and thermal crushing.

Another method, used particularly with phthalocyanine blues and greens, involves dissolving the pigment in a strong sulfuric acid (acid-pasting) and then controlling the particle size during precipitation into water.

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 *etc*. The flush pastes can then be mixed directly into the application media without drying or any further attrition.

2.4.4.2 Printing Inks

This is by far the largest single market for organic pigments, representing over 50% 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,[63,64] and their approximate market share (1999) are;

- Offset Lithography (48%)
- Flexography (21%)
- Gravure (15%)
- Others (13%)
- Digital (3%)

Digital printing, although it was very small in 1999, is on a very rapid growth path as end users increasingly wish to print digitally produced text and images. This technology also has special requirements for dyes and pigments and will be covered separately (section 2.7).

All the main classes of pigments are used in the printing ink industry, but the high-performance pigments, *e.g.* quinacridones, which can be thirty times dearer than azo pigments, 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.[65]

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 2000 of 25 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 be solvent-based, water-based or a powder coating.[66] The desire to be more environmentally friendly has seen an increase in use of very high solids in solvent systems, a move from solvent to water-based coatings and a rise in two-component polyurethane and powder coatings.

2.4.4.4 Plastics

A very wide range of plastics are coloured with pigments including PVC, polystyrene, polyurethane, polyamide, polycarbonate, polyester, elastomers, thermosets and thermoplastics. The choice of pigment is obviously dependent on which plastic

Table 2.13 *End user sectors of coatings/paint*

Sector	*%*
Architectural coatings	48.
• Exterior house paints	(DIY 18)
• Interior house paints	
• Stains	
• Undercoats	
Production line finishes (OEM)	39
• Appliances	
• Automotive	
• Electrical insulation	
• Film	
• Furniture (wood and metal)	
• Metal containers	
• Marine	
Speciality	13
• Automotive refinish	
• Arts and crafts	
• Aerosols	
• Traffic paint	
• Heavy duty coatings	

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.

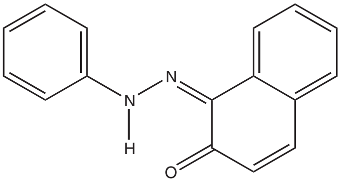
Many plastic materials are coloured using pre-dispersed concentrates of the colour in the same polymer or a compatible resin; these are known as masterbatches. Masterbatches overcome the problems of dispersing the conventional solid pigments into the polymer matrix.

2.4.4.5 Construction Materials and Ceramics

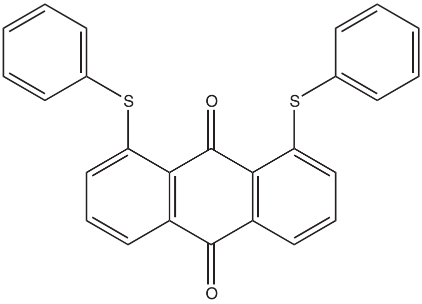
The major use (60%) for coloured inorganic pigments, such as iron oxides, is in the construction materials industry. Here they are used to colour roof and flooring tiles, fibrous cement and mortar. Many inorganic pigments are used in coloured baking enamels for metal appliances. Chromium oxide is used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

2.5 Solvent Dyes

Solvent dyes are really intermediate between dyes and pigments being insoluble in water but soluble in solvents, especially hydrocarbons. Structurally many solvent dyes bear a close similarity and relationship with disperse dyes. The Colour Index has an issue on Solvent Dyes, where several hundred dyes are described, unfortunately many of the structures remain confidential.[67] The structures of the disclosed dyes range from very simple monoazo dyes, *e.g.* CI Solvent Yellow 14 (2.78) to the higher performing anthraquinones, *e.g.* CI Solvent Yellow 163 (2.79) and Blue 36 (2.80), quinophthalones



(2.78)



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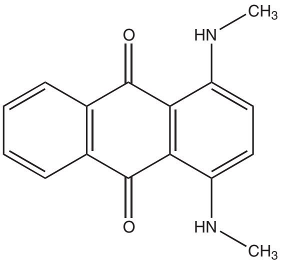


(2.80)

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.

Because of their high solubility in hydrocarbons they have found a widespread use as markers for the identification of the various fractions of hydrocarbons that are produced in oil refineries. For instance, red and blue diesels (see also 1.6.2.1). Although used only in very low quantities the vast amount of fuels used in the world means that solvent dyes are manufactured on a very large scale.

Several solvent dyes show very high performance in plastics and are used widely in the coloration of thermoplastics and engineering resins, *e.g.* PC and ABS.

Solvent dyes are also used in the coloration of any solvent or wax based product, including polishes, cosmetics, crayons, candles, inks, stains and adhesives. They are also in the coloured smokes that are used in outdoor displays, for instance coloured trails from aircraft, and in safety and security applications.

Because several solvent dyes are fluorescent they are used in the production of fluorescent dyes and pigments for a variety of outlets, as described in Chapter 3 (sections 3.5.1 and 3.5.2).

2.6 Photographic Colour Chemicals

The dominant use of silver halide photography is to produce coloured images (80%), with the vast majority (90%) of these being produced *via* colour negatives (86%) and the remainder by colour reversal (transparencies). The superiority of photographic images produced by silver halide photography was, for many decades, never seriously questioned, but in recent years its commercial dominance has come up against a serious challenge from the newer digital imaging and printing technologies. Today, for many people and outlets, the quality from digital imaging is more than adequate (see section 2.7), and, in fact, with the arrival of photorealistic ink jet printers and vastly improved media, it is so good that it is even being used by professional photographers.

2.6.1 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 to 2.5 μm). Silver halide is only blue sensitive and 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.[68]

In colour photography the film is multilayer, 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.[69]

2.6.2 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.

2.6.2.1 Colour Reversal Film

The films used in this 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. This is shown schematically in Figure 2.27.

The systems used to produce colour transparencies from exposed film are based on the Kodak E-6 process, or further developments, using compatible films.[70] A simplification of the process is as follows:

- The black and white negative in each layer is developed using conventional developers of the metol/hydroquinone or phenidone/hydroquinone type
- Unexposed emulsion is ‘fogged’ using potassium borohydride rendering it developable
- Colour development
  - The fogged emulsion is developed to give a black silver positive image, at the same time oxidising the phenylenediamine colour developers
  - The oxidised colour developers then react with the colour couplers to form the dyes (see later) in their respective layers
- At this stage the film is very dark and consists of
  - Black silver separation-negatives in all three layers
  - Black silver positive separation-images in all three layers
  - Dye positive images in the yellow, cyan and magenta layers
- Bleach/fix stage involves removal of
  - The silver formed during the monochrome and colour development stages
  - The anti-halation layer
  - The dye filter layers

The results of this process are shown schematically in Figure 2.27.

2.6.2.2 Colour Negative Film

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 (see Figure 2.28).

Processing is usually carried out by the Kodak C-41 process. This is simpler than the E-6 colour reversal process, involving only colour development, using a different

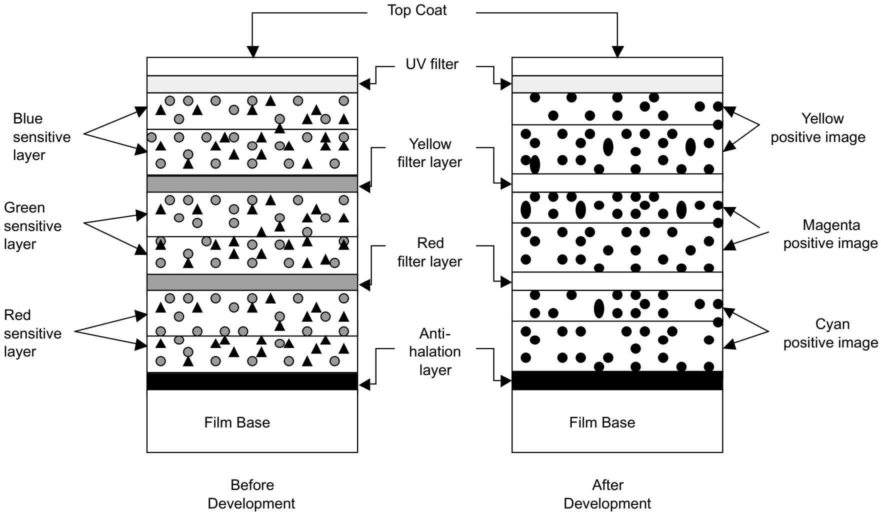


Figure 2.27 *Schematic of colour reversal film and E-6 processing.* (Reproduced with permission of Oil and Colour Chemists Association.)

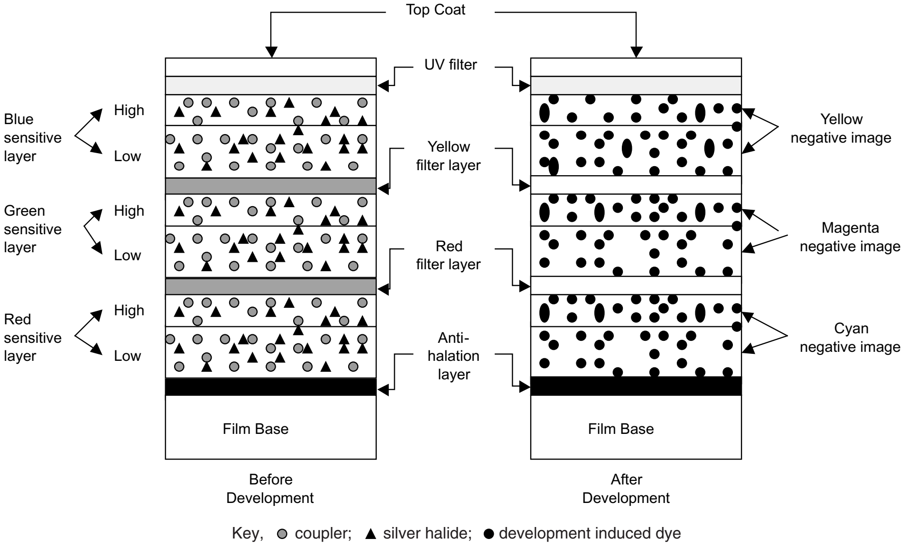


Figure 2.28 *Schematic of colour negative film and C-41 processing.* (Reproduced with permission of Oil and Colour Chemists Association.)

phenylenediamine colour developer, bleaching and fixation. The film produced is a colour negative with the following features:

- White areas of original image are black
- Black areas of original image are white
- Blue areas of original image are yellow

- Green areas of the original image are magenta
- Red areas of original image are cyan

2.6.2.3 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.[68,69] 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 to help protect the dyes from light fading in the final image. The outline structure of the colour paper is shown in Figure 2.29.

2.6.2.4 Instant Colour Photographic Films and Paper

Without a doubt the best known of the instant colour photographic processes is that invented and developed by the Polaroid Corporation.[71–73] The original Polacolor system led to the famous Polaroid SX-70 system in 1972. This is a dye diffusion system involving a dye developer in a tripack negative arrangement, placed on top of a receiver sheet, as shown in Figure 2.30.

The system consists of a preformed dye joined to a photographic developer moiety (hydroquinone) by an inert chemical link, *e.g.* –CH_2CH_2–, so that they move together within the film (see section 2.6.3.3). After exposure the silver halide is converted into metallic silver and the dye-developer molecule is oxidised and rendered immobile. The un-oxidised dye developer remains in solution and then diffuses through the alkaline pod reagent to the image-receiving layer where it is bound with mordants.

2.6.3 The 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

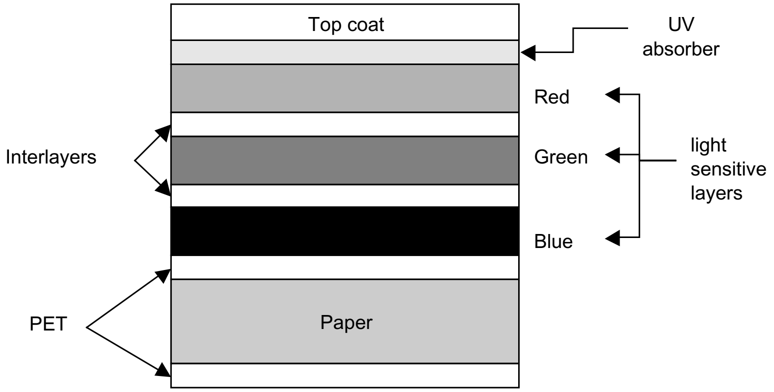


Figure 2.29 *Cross section of a colour negative paper.*

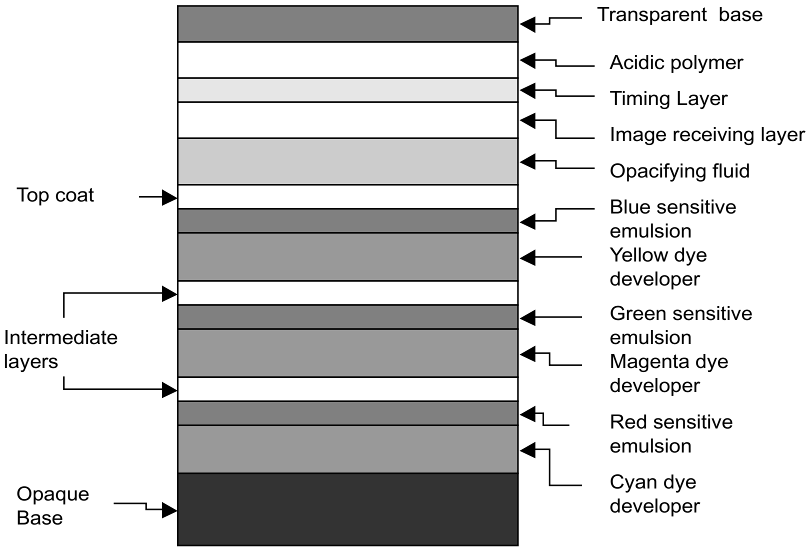


Figure 2.30 *The Polaroid SX-70 film.*

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 into a quinone diimine. This diimine then 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 2.31.

2.6.3.1 Colour Developers

The two main colour developers are both substituted 1,4-phenylenediamines. The more active of the two (2.81) is used in the colour negative C-41 process, whilst the less toxic and more brilliant dye-producing compound, the sulfonamide (2.82) is used in the colour reversal E-6 process.

2.6.3.2 Colour Couplers and Derived Dyes

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 2.31. 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.[69]

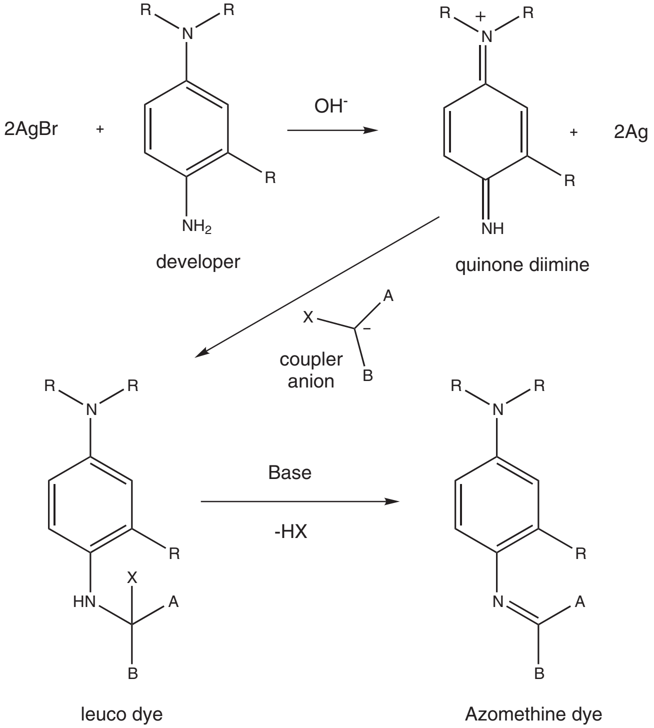
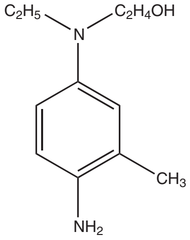
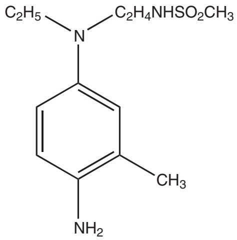


Figure 2.31 *Chromogenic development by two-equivalent coupling.*



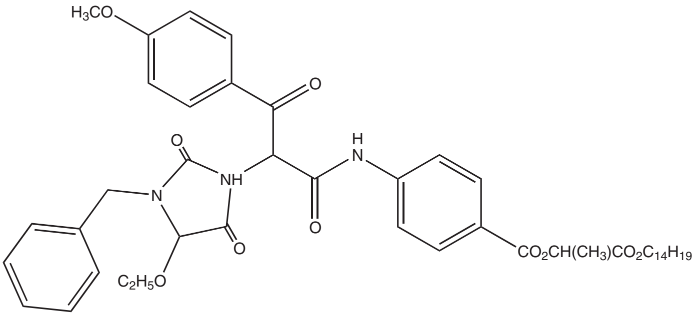
(2.81)



(2.82)

Yellow Couplers and Dyes. All the useful yellow couplers are based on acetanilides, especially the pivaloyl and benzoyl derivatives (2.83), which react to give the azomethine dyes (2.84) absorbing at wavelengths in the region 450–480 nm.

Magenta Couplers and Dyes. 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 absorb in the region of 530–580 nm, but they do suffer from a secondary absorption in the blue region, e.g. (2.87) absorbs at both 553 nm and 437 nm. This disadvantage can be overcome by the use of pyrazolotriazoles, e.g. (2.88) as the coupler, which also give very bright shades.



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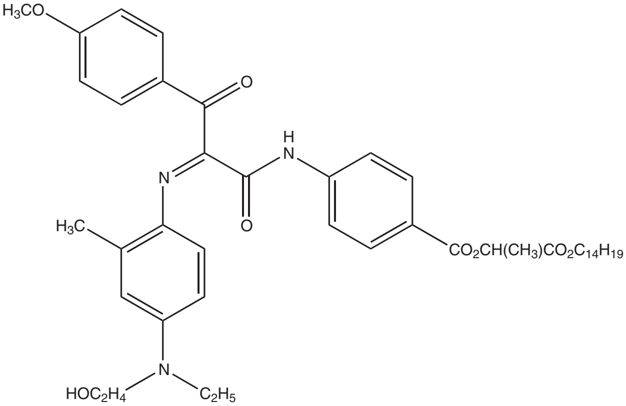

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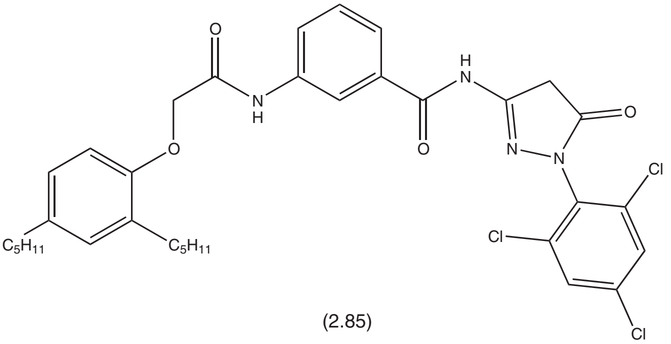
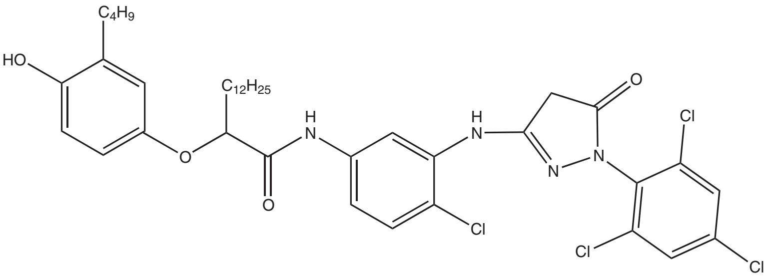


(2.85)

Cyan Couplers and Dyes. 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 (2.89) used in both colour reversal and colour negative films, depending on the nature of the R group, to produce indophenols, *e.g.* (2.90).



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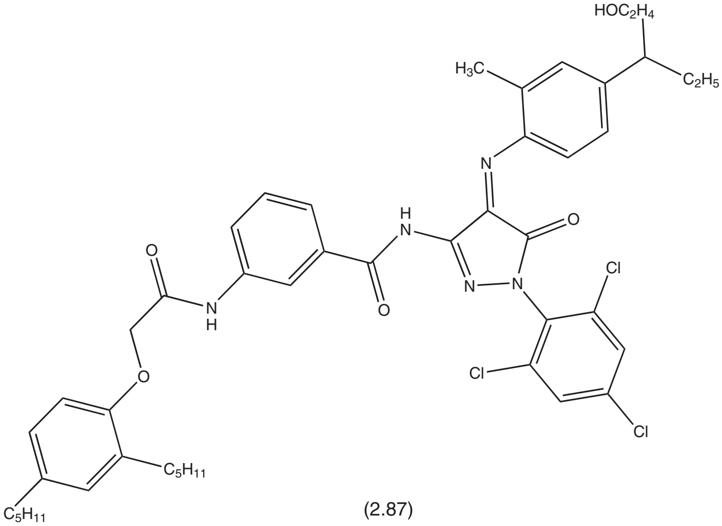

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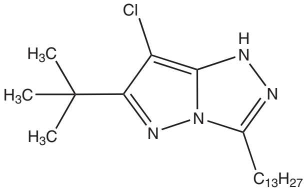

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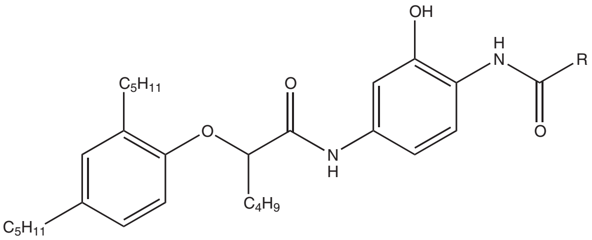
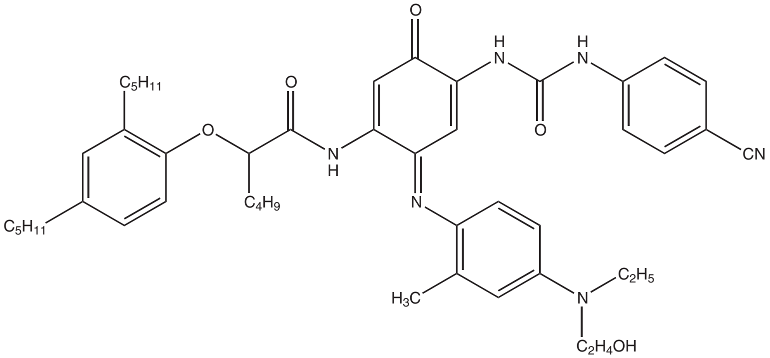


(2.89)



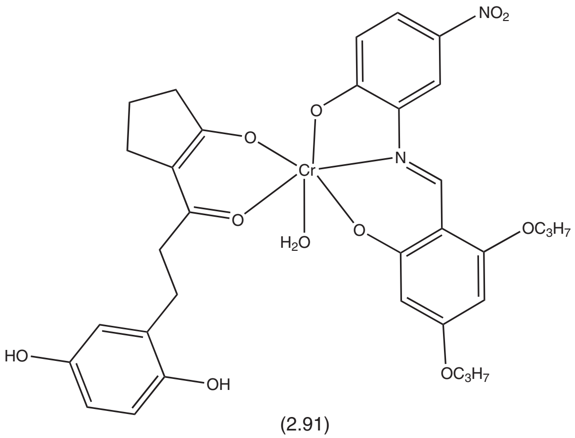
(2.90)

2.6.3.3 *Diffusion Couplers*

In the Polaroid process the dye is covalently attached to one or more diffusion-controlling hydroquinone moieties. Severe requirements are placed on the dye used in the process; the dye must be chemically stable in the highly alkaline medium, its spectra must be stable to variations in pH, it should be photographically inert and stable to light in the final image. All of these constraints can be met largely by using the more stable of the available dye chromophores, such as azo dye metal complexes, anthraquinones and phthalocyanines. A selection of those that have been used in the Polaroid SX-70 system are the yellow (2.91), the magenta (2.92) and the cyan (2.93).[73]

2.7 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 paral-



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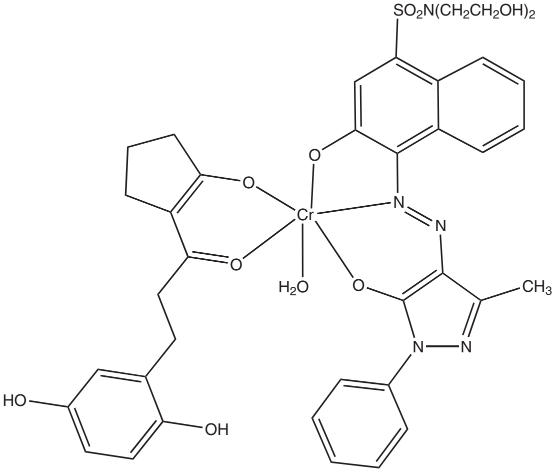
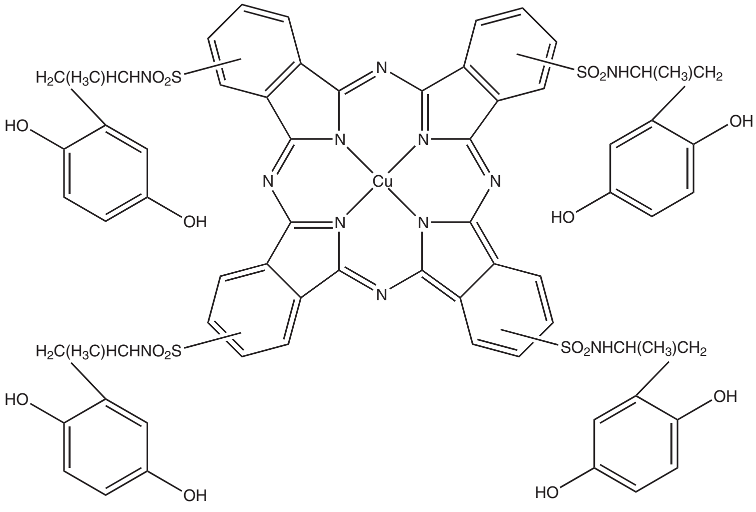


(2.92)



(2.93)

leled 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, and also the output was predominately black and white. With the arrival of inexpensive personal computers, for use in the home and the small office, a new population of consumers arrived 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. The most recent development has been the rapid commercialisation of large format machines for use in a whole range of commercial printing applications, and in the last five years digital printing has grown in importance in the industrial sector (see sections 2.3.2.1 and 2.4.4.2).

Digital printers and copiers have a different set of material requirements to conventional printers and justifiably are treated here as a separate topic.

From a whole raft of competing reprographic technologies (Figure 2.32) at the beginning of the 1990s two have emerged as the dominant players: namely ink-jet and electrophotography, whilst thermal transfer printing enjoys some success (see also Chapter 4, section 4.2.2.1).[9] The two major technologies and their material requirements and applications will now be considered in greater detail.

2.7.1 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.[74,75] 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 inter-

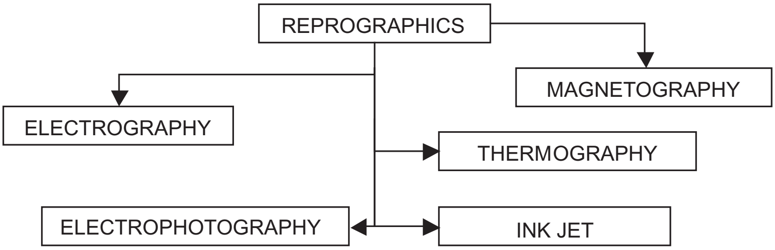


Figure 2.32 *Reprographic technologies (non-impact printing).*

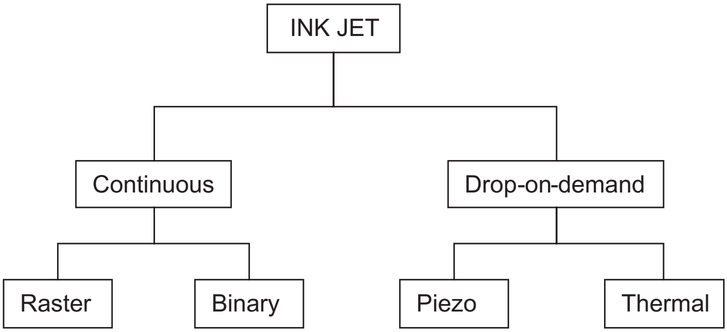


Figure 2.33 *Types of ink jet printers.*

mittently, known as drop-on-demand (Figure 2.33). Ejection of the ink from the print head is accomplished by either thermal (bubble jet or thermal printers) or mechanical, usually by piezoelectric crystals (piezo printers), based processes.

2.7.1.1 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 sent either 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 2.34.

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.

2.7.1.2 Drop-on-demand Ink Jet

Drop-on-demand (DOD) ink jet is the method that is universally adopted in the printers used in the home and the office environments. 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.

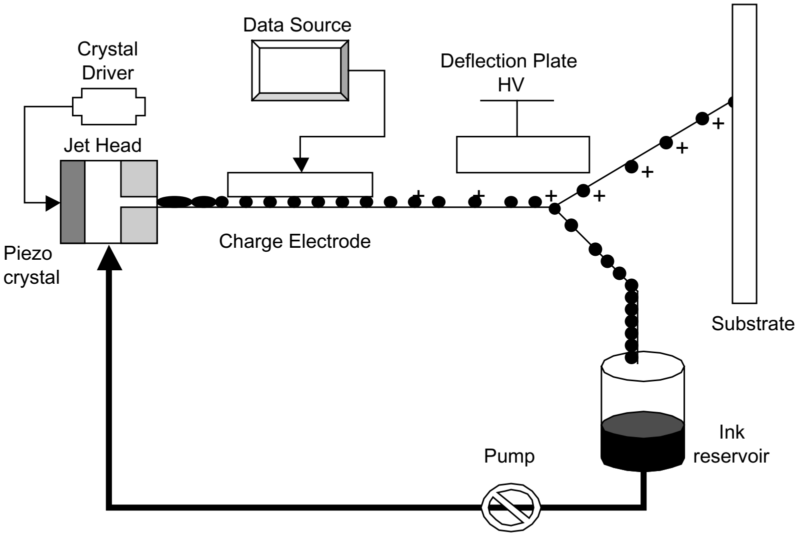
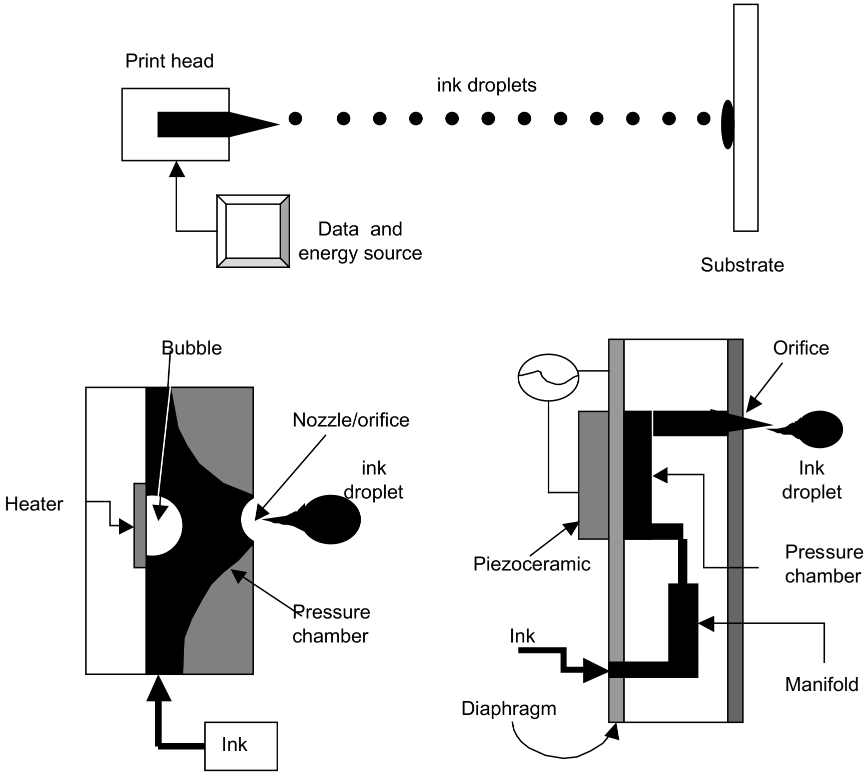


Figure 2.34 *Continuous ink jet (raster).*

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 of around 300–400 °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 2.35a). The print head nozzles are very small, being in the range of 20–100 μm in diameter, and are constructed in arrays of the cells illustrated in Figure 2.35. The cell in Figure 2.35a 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.[76]
- 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 2.35b). The wave can be produced in the bend mode, as in Figure 2.35b or in a push or shear mode.[76] An important variation on piezo technology is the Xaar



a. Thermal/Bubble Jet Head b. Piezo Head

Figure 2.35 *Cross sections of thermal/bubble Jet and piezo DOD print heads.*

Microjet system, which uses vibrating walls in the inkjet channel to emit jets, and whose ease of construction makes it a strong contender in wide-format machines.

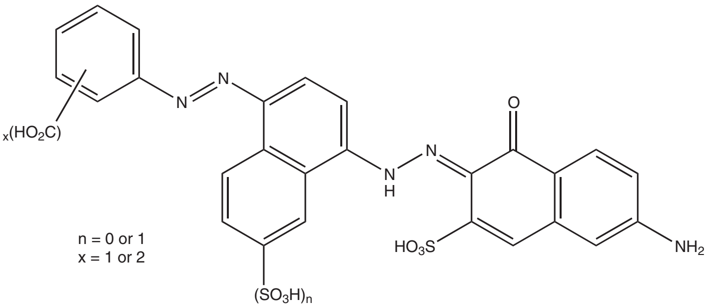
For use in small office/home office (SOHO) printers the preferred inks, for obvious environmental reasons, are essentially aqueous.

2.7.1.3 Colorants for Ink Jet Printers

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 were the most suitable colorants. However, because the orifices are so small, less than 100 μm, with the inherent danger of clogging in use by particulate matter, water-soluble dyes were chosen initially. The early water-based inks were far from satisfactory being based on dyes 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 (now part of Avecia) and the machinery manufacturer Hewlett-Packard, (inventors along with Canon of thermal jet printing).[77] The black dyes they devised contained carboxylic acid groups (2.94) which, when applied as their ammonium salts, gave much improved water fastness on paper. The mechanism involves the loss of ammonia rendering the dye insoluble as the free acid on the slightly acidic paper.

The ink jet printing of coloured images is a subtractive process and requires a YMC 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
- No colour–colour bleed
- Light fastness



(2.94)

- Water fastness (can be improved by paper coating)
- Thermally stable
- Non-toxic
- Practically free from inorganic salts (less than 100 ppm)
- Produce storage stable inks

A wide range of dyes have been evaluated but only a few of existing dye ranges have found commercial use, the best are listed in Table 2.14.

Many of these 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.

Much research work has been done and continues to be done on the development of new dyes for this outlet. For instance, Avecia have a range of yellow magenta and cyan dyes, based on the ammonium salt principle above, which do show improved wet fastness properties. An alternative approach adopted by workers at Ilford, based on their experience in colour photography, involves the molecular tailoring and formulation of dyes which aggregate and hence have light fastness properties nearer to pigments (Archiva Inks).

The colorants in the inks need to be light fast so that they are not only stable in daylight use but also for archival purposes, where stability beyond 25 years is desired. Traditionally to meet this requirement the higher light stable pigments have been used in the inks (see section 2.4.4.2). Carbon black has an excellent track record and ink jet inks are available for DOD ink jet printers using this pigment (*e.g.* Hewlett-Packard DeskJet 1200C). The pigments need to bound to the paper with a resin and the development of stable inks for black, and other colours, has required some ingenuous development work using polymeric dispersants.[79] The big problem with pigmented inks is particulate size, but methods have been developed to get this down to less than 0.02 μm in stable dispersions, giving much improved coverage of the colour space and brightness approaching dye based inks. A typical pigment trichromat is CI Pigment Red 122, 2,9-dimethylquinacridone, CI Pigment Yellow 77 a non-benzidine azo yellow, and a modified phthalocyanine blue.[80]

The current position in the dye–pigment debate is that, where light fastness is not a problem, dyes take precedence because of brighter shade, better colour gamut and inherently more stable inks. Commercial printers prefer to use pigments as they have

Table 2.14 *Dyes for water based IJ inks*[78]

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

been used to handling them in printing inks for generations and they understand their performance characteristics better than they do the newer dyes.

In the industrial field, such as the printing of cartons and packages with bar codes and other such information, the inks are 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).

2.7.1.4 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 in the commercial and industrial arenas (Figure 2.36). The application media include paper, card, metal, wood, plastics and textile fabrics. 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, can be produced at much lower cost than using the traditional printing plate or silk screen methods. However, for longer runs the higher speed of offset lithography overcomes the higher start up costs for the print run.

2.7.2 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.[81]

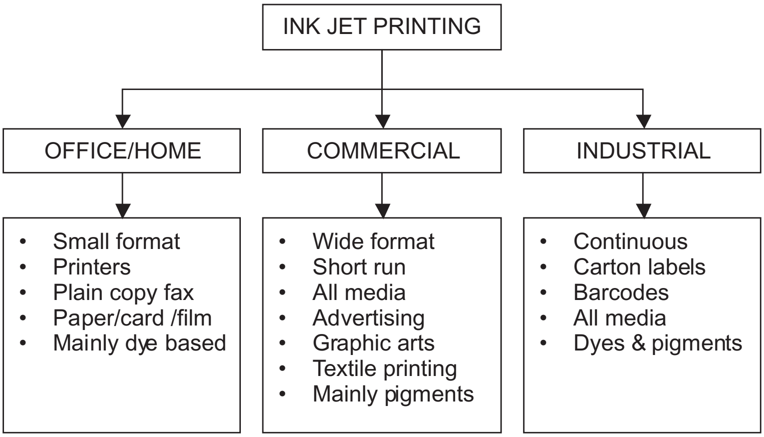


Figure 2.36 *Application areas for ink jet printing.*

The electrophotographic process involves the production of an electrostatic latent image on a photoconductor (also called a photoreceptor) and the conversion of this into 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. 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 by writing with a laser the digitised information in a raster scan (laser printing and also LED printers) 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 2.37 for the production of a monochrome image.[82]

In the production of coloured images a subtractive CYM 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.[9]

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. This data on each colour component of the image is 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 on to the paper by thermal fusion of the toner resin.

As can be seen from these processes they 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. However, in the large copy shop area they are very effective for multiple copy production of, for instance, business fliers.

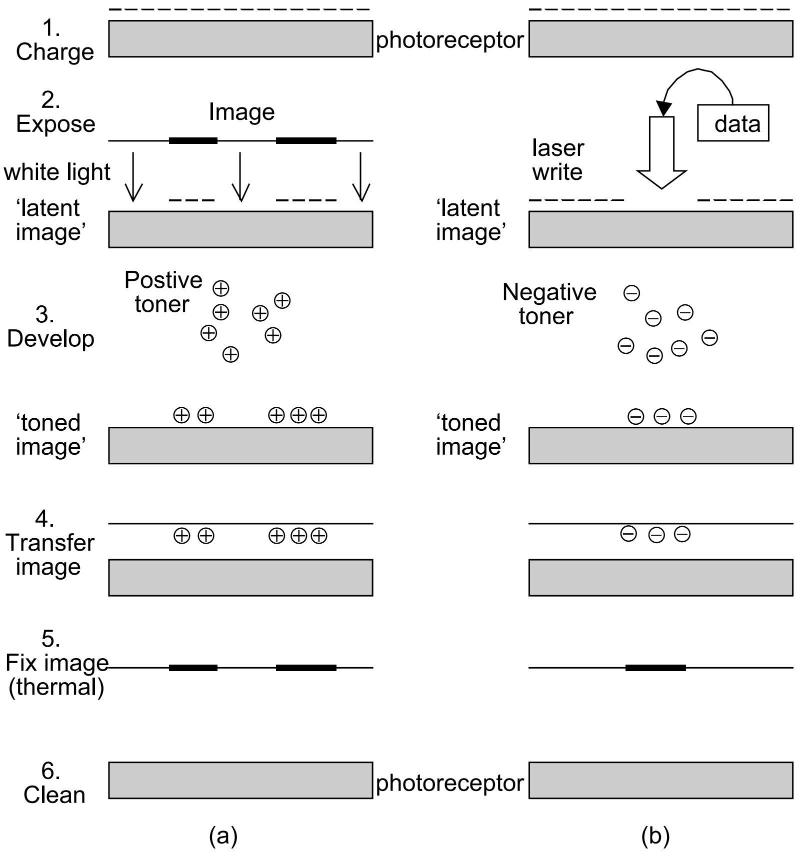


Figure 2.37 *The electrophotographic process using organic photoconductors:* (a) *photocopying and* (b) *laser printing.*

2.7.2.1 Materials for Electrophotography

Coloured materials find application in both toners and organic photoconductors fused 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:[83]

- 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 nonmagnetic)
- Liquid toners (colloidal dispersions in non-conductive liquids)

The particle sizes in dry toners range from 6 to 10 μm diameter, but in liquid toners they can be down to sub-micron in size (0.2 μm), leading to much thinner layer thickness and a better resolution in the final image. The toner binder resin is the main component of a toner and can make up anything between 45 and 95% in single component dry toners. The resin not only carries the colorant onto the photoreceptor it 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 reasonable mechanical and electrical properties. The most common resins used are styrene–acrylics and styrene–butadienes, with polyesters used to a lesser degree.

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. They can be positive or negative charge controlling and they can be non-coloured or coloured

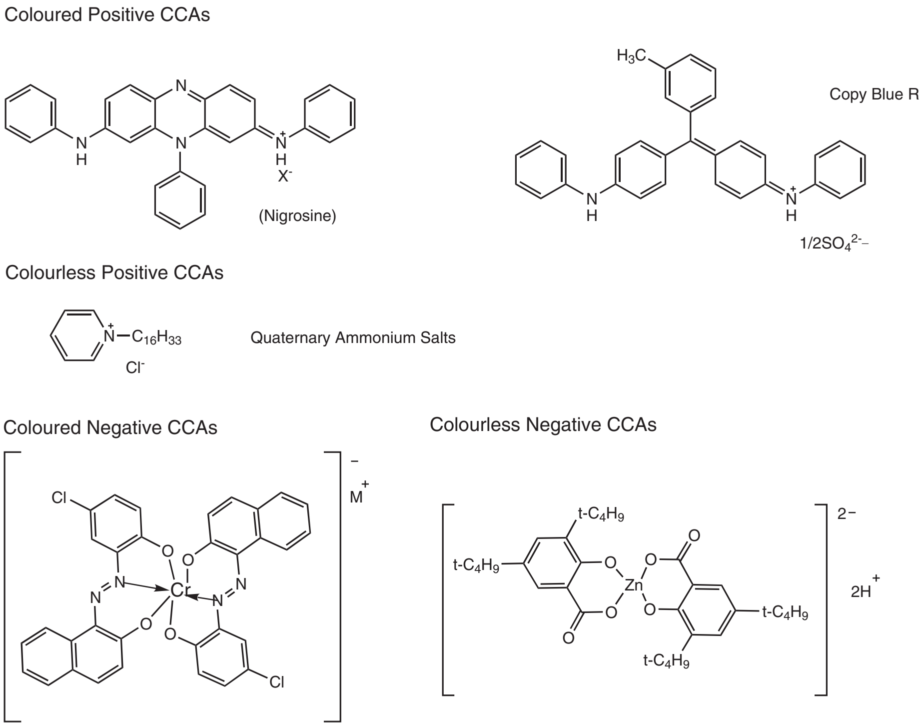


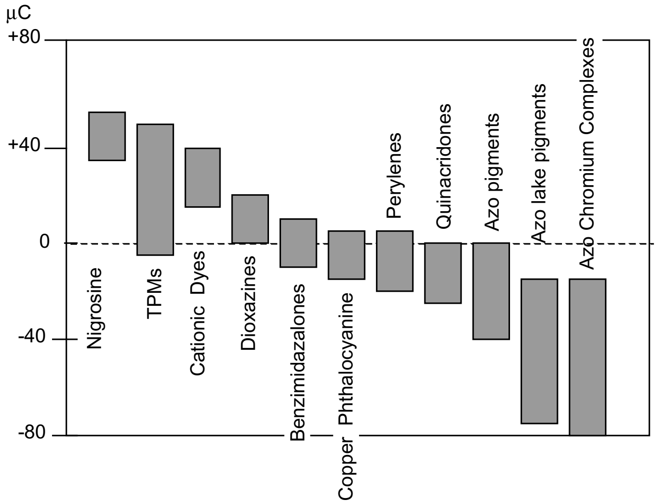
Figure 2.38 *Some examples of charge control agents (CCAs).*

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 2.38.

Carbon black is the colorant used in black and white printers and copiers and the other CYM colorants used in toners are also pigments. It should be noted that these also fall into various triboelectric ranges and selection of the pigment also depends in which type of machine the toner is to be used (Figure 2.39).[84]

2.7.2.2 Commercial Applications of Electrophotography

The world demand in 2001 was for 145 000 tonnes of black and for 10 000 tonnes of coloured toners, with growth rates of around 5% for black and some 25% for colour. The main outlet for toners was originally in copiers but the growth is now coming



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 2.39 *Triboelectric series and selected pigments used in commercial toners.*

largely from printers, especially in the colour area. Other outlets include plain paper fax machines and the multifunctional printers (fax/copy/print), which has shown exceptional growth since its introduction in the mid-1990s. The battleground between electrophotography and inkjet is in the area of commercial digital colour printers, *i.e.* wide-format. Whilst developments in toner technology and the introduction of new machines are happening each year, the hot money is on ink jet becoming the major technology in this field.

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CHAPTER 3

Phenomena Involving Absorption of Energy and Emission of Light

3.1 Introduction

Those phenomena that involve absorption of energy and subsequent emission of light are classified generically under the term luminescence. This phenomenon is observed when a substance emits visible radiation when energy is transferred from a higher to a lower electronic or molecular energy state. Different methods can be used to accomplish the transition from the lower to the higher energy state: the excitation of the radiating entity, leading to a subset of luminescent phenomena. The following method of classification covers the known phenomena:[1]

- *Associated with prior irradiation*
    - Photoluminescence
    - Cathodoluminescence
    - Anodoluminescence
    - Radioluminescence
- *Associated with electrical phenomena*
    - Electroluminescence
    - Galvanoluminescence
    - Sonoluminescence
- *Associated with chemical reactions*
    - Chemiluminescence
    - Bioluminescence
- *Associated with structural rearrangements in solids*
    - Triboluminescence (piezoluminescence)
    - Crystalloluminescence
    - Lyoluminescence
- *Associated with heating (excluding incandescence)*
    - Thermoluminescence
    - Candololuminescence
    - Pyroluminescence

Cathodoluminescence involves excitation by high-energy electrons, photoluminescence excitation by electromagnetic, often ultraviolet radiation. Photoluminescence is also regularly used as a catch all phrase for all those processes that absorb incident light and later re-emit part of that energy as visible light, including phosphorescence and fluorescence. Phosphorescence is activation by photons, where there is a delay in the emission causing an afterglow and fluorescence where the emission of light is instantaneous. Radioluminescence is where the energy source is radioactive decay and X-ray luminescence where X-rays supply the energy.

Electroluminescence involves excitation by an electric field to produce non-thermal light, sonoluminescence from the impact of high energy sound, *e.g.* ultrasound. Chemiluminescence is the production of light by chemical substances without the help from other energy sources; in effect it is the conversion of energy stored in chemical bonds into light. Bioluminescence is the production of light by living systems. However, many bioluminescence phenomena, once understood, turn out to be based on chemical principles and these phenomena can then be reproduced in the laboratory with non-living materials.

Mechanoluminescence or triboluminescence arises from the mechanical action on solids; lyoluminescence is where the emission of light occurs when a material goes into solution. Thermoluminescence is observed during the heating of a solid that has previously absorbed energy from radiation, as ions trapped in the solid recombine. (See also Glossary for an explanation of the terms.)

For a more detailed discussion of many of these luminescent phenomena, especially the theory of how they arise, the reader should consult the treatise by Blasse and Grabmaier[2] and by Vij.[3]

This book is primarily concerned with those phenomena where the emission of colour is the technologically important outcome of luminescence. The main types of luminescence falling within this category and some of their applications are summarised in Table 3.1.

Table 3.1 *Types of luminescence and applications*

Luminescence	*Energy source*	*Typical uses*
Cathodoluminescence	High energy electrons	Cathode ray tubes (CRTs)
Photoluminescence	High energy UV	Fluorescent lighting, plasma display panels
Phosphorescence	Photons (UV or visible)	Pigments, safety signs, low energy lighting, analysis
Fluorescence	Photons (UV, visible or near-IR)	Pigments, inks, optical brighteners, safety signs and clothing, analysis, biology, molecular electronics
Chemiluminescence	Chemical reactions	Analysis, sensors,
Bioluminescence	Various luminous organisms	Analysis, diagnostics, sensors
Electroluminescence	Electric field	LEDs, displays, backlighting, opto-electronics
Triboluminescence	Mechanical shaking, rubbing or crushing	Crack detection in composite materials

3.2 Luminescent Pigments

As stated above, there is no intention to provide any detailed discussions of the theory of luminescent phenomena; however, a basic understanding is essential. A simplified outline, the vibrational levels at each state being omitted, of the energy diagram for fluorescence and phosphorescence is shown in Figure 3.1. On absorption of light the molecule is excited from its ground level state S_0 to the first excited singlet state S_1. Energy can be dissipated from this state by collision deactivation causing a reduction in the intensity of the resultant emitted light. If the molecule returns to the ground state rapidly then fluorescence occurs at a longer wavelength than absorption due to a loss of vibrational energy in the excited state; this difference in absorption is called the Stokes shift. Another process involves intersystem crossing from S_1 to the triplet state. Energy emission from this triplet state T_1 back to the ground state S_0 causes phosphorescence. Phosphorescence always occurs at a longer wavelength than fluorescence because the energy difference between T_1 and S_0 is always lower than that between S_1 and S_0.

The vast majority of commercially important luminescent phosphors or pigments are inorganic. The use of organic phosphors is usually restricted to those applications where particle size requirements limit the use of inorganic materials. The luminescent materials are often called phosphorescent pigments when used commercially, especially in non-lighting uses. These inorganic phosphors are crystalline compounds, which comprise a host lattice designed to hold on tightly to the dopant ions, which are called activators. Additional sensitiser ions are also often present in the materials. The luminescence behaviour of these phosphor materials involves three basic processes.

(a) Absorption and excitation. The energy of the exciting radiation, from photons, electrons or X-rays, is absorbed by the activator, which is raised to an excited state. The exact mechanism of excitation depends on which type of energy is involved.

(b) Emission. Loss of energy from the excited triplet state of the excited luminescent centre produces radiant light which, whilst dependent on the excitation energy,

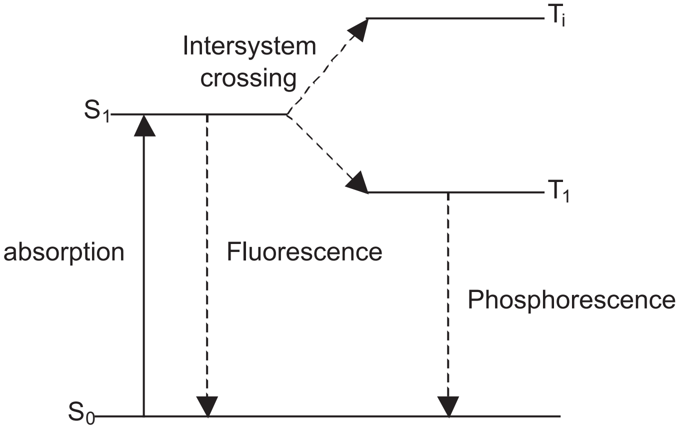

Figure 3.1 *Schematic energy diagram for phosphorescence and fluorescence.*

is usually of a lower energy as some is also lost to the matrix in the form of heat, i.e. non-radiative energy.

(c) Energy transfer. Energy transfer involves getting the absorbed energy from the excited luminescent centre to another before emission occurs. Sensitizers present in the crystal lattice are used to transfer energy to the activator. (Note: if emission from the second centre occurs non-radiatively the process is known as quenching.)

Afterglow, where a material continues to emit light long after excitation, is a very important phenomenon exploited in many industrial applications. Afterglow arises when an excited electron undergoes spin inversion and may not be able to decay quickly. The excited electrons and positive holes they leave behind drift slowly through an inorganic lattice until they find a new discharge site, producing the afterglow emission

3.2.1 Inorganic Phosphors

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 relatively recent publications.[2,4]

3.2.1.1 Sulfides and oxysulfides

The main sulfide phosphors are the group II–V ones based on high purity zinc and cadmium sulfides activated by dopants, primarily using copper and silver but also manganese, gold and rare earths. The nature and concentration of the activator, the composition of the flux and the firing conditions, normally in furnaces at 800–1500 °C, influence the luminescent properties.

Zinc sulfides 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 so the phosphors work in most commonly encountered lighting conditions. However, the green emitting ZnS:Cu phosphors, together with copper activated zinc–cadmium sulfide (Zn,Cd)S:Cu, are the ones most often used in industrial applications. The different versions of ZnS:Ag phosphors are exclusively used industrially 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 a very efficient green phosphor.

The alkaline earth sulfides activated with rare earths are also of importance. They are suitable 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.

The 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 Ca S:Eu^{2+}, Tm^{2+} is red. SrS:Ce^{3+} has a maximum at 483 nm and is a very useful blue 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 is produced, eminently suitable for colour CRT.

3.2.1.2 Oxygen-dominant phosphors

Oxygen-dominant phosphors are very wide ranging and include borates, aluminates, gallates and thiogallates, silicates, germinates, halophosphates, originally the largest manufacture of phosphors used in lighting (see section 3.4.1), phosphates, oxides, arsenates, niobates and tantalates, sulfates, tungstates and molybdates.[4] From a colour standpoint the aluminates, thiogallates, oxides and silicates are of most interest.

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) used in trichromatic fluorescent lamps. A blue component for these lamps is barium magnesium aluminate, $BaMg_2Al_{10}O11_{17}:Eu^{2+}$ (λ_{max} 447 nm). 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 1990s a breakthrough was achieved in the development of long-lived afterglow phosphors. It was discovered that by co-doping rare earth aluminates, especially strontium, with europium and dysprosium gave phosphors with around ten times the afterglow of copper activated zinc sulfide and also with ten times the brightness.[5,6]

Strontium thiogallate $SrGa_2S_4:Ce^{3+}$, doped with 4 mol% of cerium, gives a very good blue phosphor (λ_{max} 455 nm), which has found to be useful in thin-film electroluminescent devices (see section 3.8.3.2).

Yttrium and europium oxides form mixed crystals without any vacancies due to the very similar size 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 used in colour CRTs.

Zn orthosilicate $Zn_2SiO_4:Mn^{2+}$ is a green phosphor (λ_{max} 525 nm) used in fluorescent lamps, CRTs and plasma display panels. It demonstrates a low resistance to burn out, is excited 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).

3.2.2 Synthesis and Formulation of Inorganic Phosphors

The manufacturing process for the important zinc and cadmium sulfide phosphors involves precipitation of the sulfide from purified salt solutions, *e.g.* the sulfate, with hydrogen sulfide. For ZnS:Cu, the copper activator is added, as a readily decomposed derivative, to the sulfides and after grinding the components are fired in furnaces at temperatures in the range 800–1200 °C. ZnS:Ag, the blue phosphor used in CRTs, is prepared by firing zinc sulfide with silver nitrate at 1000 °C, usually in the presence of sodium chloride to give the co-activating chloride ions.

Oxygen-dominant phosphors are made by a solid-state reaction between the intimately mixed components of the phosphor, generally the oxides or oxide forming derivatives, at 500–1500 °C. For instance, $Y_2Al_3Ga_2O_{12}:Tb^{3+}$ is made by mixing stoichiometric quantities of the oxides, containing 5–7 mol% of terbium, with 20% BaF_2 in ethanol. The mixture is dried and then fired for 2 h at 1500 °C. The resultant flux is washed with 20% nitric acid.

Strontium thiogallates, such as $SrGa_2S_4$:Ce^{3+}, are produced by firing a mixture of high purity sulfides, containing 4 mol% Ce^{3+} in a stream of hydrogen sulfide gas at 900–950 °C for 2 h.

Orthosilicates for use in CRT and projection TV tubes are made by solid-state reactions, *e.g.* Zn_2 SiO_4:Mn^{2+} by firing a mixture of ZnO, SiO_2 and $MnCO_3$ at 1200 °C for 2 h.

These are selected syntheses from a whole range and the limited details are only intended to provide an insight into the types of synthetic methods that are employed. Any reader wishing to have further information should consult the book edited by Gunter Buxbaum as this contains more details and a list of primary reference sources for the methods of manufacture.[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, as this will reduce 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.

3.2.3 Up-converters

Up-converters are inorganic luminescent colours, which absorb infrared radiation and convert this into visible wavelengths. This is illustrated schematically in Figure 3.2.[2] Simplistically, an ion in the ground state A is excited to energy level B, normally with a short lifetime this decays with radiative emission; however, if the lifetime of level B is not short the ion can be further excited from B to C. As a final step emission form C to A will occur. In effect two or more photons are absorbed for every single visible photon emitted. This results in the anti-Stokes shift from lower energy to higher energy, from the infrared to the green visible wavelength. To get from the infrared into the blue region of the visible spectrum, a highly desirable and much sought after target, requires three photon jumps, *i.e.* A to B to C to D and back to A (Figure 3.2).

The design of up-converters requires an optically active ion with relatively stable energy levels at precisely regular intervals, so that two or more photons of the same wavelength can be absorbed before emission occurs. This has been achieved with single ions and by co-doping with two ions working together by energy transfer. One ion absorbs the energy in two jumps, then transfers its total accumulated energy to a second ion which discharges its energy in one go. The receiving ion has no intermediate energy level of its own.

The materials used as up-converters consist of a rigid host lattice with rare earth dopants. Fluorides and oxides have been used as host lattices, the latter being slightly

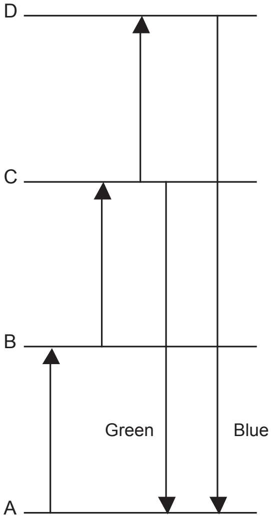

Figure 3.2 *Up-conversion involving two and three equal energy photon absorptions and a single, higher energy photon emission.*

less suitable because of lower stability at the intermediate energy levels. Sodium yttrium fluoride, strontium, fluoride and lanthanum fluorides are all practical lattices for up-converting ions. Dopants are typically trivalent rare earths, Yb^{3+}, Er^{3+} and Tm^{3+}.[7]

3.2.4 Applications of Inorganic Phosphors

Inorganic phosphors are very widely used in illumination devices and displays. The largest tonnage usage is in fluorescent lighting (see section 3.4.1) and the second is in cathode ray tubes (see section 3.3). Other large uses are in X-ray phosphors and scintillators. Increasingly important outlets are in plasma panel (see section 3.4.2) and electroluminescent displays (see section 3.8.2), in light emitting diodes and laser diodes (see Chapter 5), in safety paints and inks, in security outlets and in analysis.[2,5] Several of these application areas are covered elsewhere in this book, as indicated above, and this section will only deal with the commercial area of phosphorescent pigments.

3.2.4.1 Phosphorescent Pigments

Traditionally the most popular of the phosphorescent pigments are based on activated zinc sulfide, especially by copper, which glow green. These find their outlets in clock, watch and instrument dials, which are required to be visible in temporary, poor lighting conditions. They are also widely used in novelty items such as plastic toys and in sporting goods, for example as fish floats. Some typical commercial materials are shown in Table 3.2.[6]

Phosphorescent pigments are used in security applications, such as the coding of

Table 3.2 *Properties of commercial sulfide based, UV/daylight excited phosphorescent pigments*

Composition	*ZnS:Cu*	*ZnS:Ag*	*ZnS:Cu*	*ZnS:Cu*	*SrS:Eu*	*SrCaS:Bi*
Body colour	Pale yellow	White	Pale yellow	Off-white	Orange	White
Emission colour	Green	Green	Green	Green	Red	Blue
Particle size/µm	20	20	7 10	25	25	
Afterglow	Very long	Short	Moderate	Long	Moderate	Moderate

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, and to be only visible under long wavelength (365 nm) UV 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. A long established, non-security application for such materials has been in postal envelope sorting. The orange 'flash' afterglow pigment, manganese activated zinc sulfides, is incorporated into stamps enabling the envelopes to be placed in the correct position for the machine reading of post/zip codes. A typical set of such commercial materials for this class of uses is shown in Table 3.3.[6]

The availability in the mid-1990s of commercial quantities of doped alkaline earth aluminates (AEAs) was the first serious challenge to the traditional sulfide phosphors. There availablity extended the scope and uses of phosphorescent pigments. AEAs are commonly based on strontium aluminate, which provide a remarkably long afterglow of over 12 h, 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. Afterglow brightness is proportional to the UV content of the excitation light. A comparison of the properties of the alkaline earth aluminates with zinc sulfide phosphors is given in Table 3.4.

The alkaline earth aluminates are available for formulation into paints and coatings, UV cured and silk screen inks. They 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.[8,9]

Table 3.3 *Invisible, no afterglow phosphorescent pigments*

Composition	*BaMgAl: Eu*	*ZnCdS: Mn*	*BaMgAl: Eu, Mn*	*GdOS:Eu*	*YtO:Eu*	$YtVO_4{:}Nd$
Body colour	White	Pale yellow	White	White	White	White
Particle size/µm	10	10	13	2.5	10	7
Emission colour	Blue	Yellow	Green	Red	Red[a]	Infrared

[a] uses short UV to activate.

Table 3.4 *Comparison of the properties of alkaline earth aluminate and zinc sulfide phosphorescent pigments*

Pigment	*Alkaline earth aluminate*	*ZnS: Cu activated*
Body colour	Light yellow–green	Yellow–green
Av. 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 h	100 h (65% loss)
Chemical stability	Excellent (except in water)	Poor–good

For a number of years one particular application for phosphors has been in the so-called Photo Luminescent Low Location Lighting. Here afterglow phosphors are seen as cost effective solutions to the demands of a maritime directive, requiring 1 h low level lighting on ships carrying more than 36 passengers. Zinc sulfide phosphors have been used but they are limited by their low light storage and emission capacity. The arrival of the new generation of strontium aluminate phosphors has meant that the requirements of the directive (I.M.O. A752) can now be met with some ease.[10]

With these and other developments, phosphorescent pigments are 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 buildings for decoration and safety escape routes, on traffic and military installations and in fire emergency systems.

3.3 Cathodoluminescence

Cathode ray tubes (CRTs) are almost universally used in colour televisions and still dominate in the display monitors of desktop computers. They are obviously not suitable for laptop PCs, because of bulk and weight, where currently liquid crystal displays are the systems of choice. Neither are they the most suitable technology for very large area displays, where other display techniques such as plasma panels and electroluminescent devices offer advantages.

The operating principle in CRTs, shown schematically in Figure 3.3, involves an electron beam generated from the cathode located at one end of a glass 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 hit this surface the phosphors emit visible light. This process is known as cathodoluminesence.[11]

To avoid any flicker in the image, the electron beam is scanned across and down the screen, many times per second, following a predetermined set of parallel lines, the method being known as raster scanning. The phosphor dots are the picture elements or pixels and light up as the beam scans across each one. In colour televisions and monitors additive mixing of the three colours of red, green and blue produces the

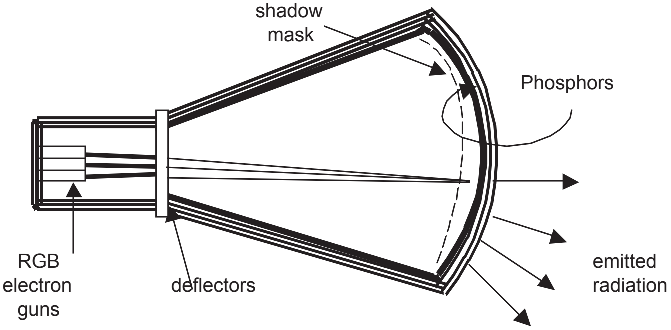

Figure 3.3 *Schematic representation of a colour cathode ray tube.*

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. The array of RGB dots is as shown in Figure 3.4. To ensure that each of the three electron beams only excites its own R, G or B phosphor it is necessary to have a metal shadow mask 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 face-plate of the CRT.

There is an alternative system, introduced by Sony as the Trinitron system, where 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 photomask 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 aluminium film also prevents any build-up of charge on the phosphor layer of the CRT, also a source of inefficiency. The phosphor particles on colour CRTs are around 8–10 μm but the higher resolution colour monitors require smaller particles of 4–6 μm.[12]

The CIE chromaticity diagram for the desired red, green and blue phosphors in colour television is given in Figure 3.5. There is some tolerance level around the

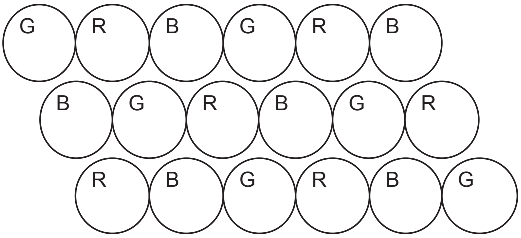

Figure 3.4 *The three colour RGB arrangement of the phophor dots on a CRT.*

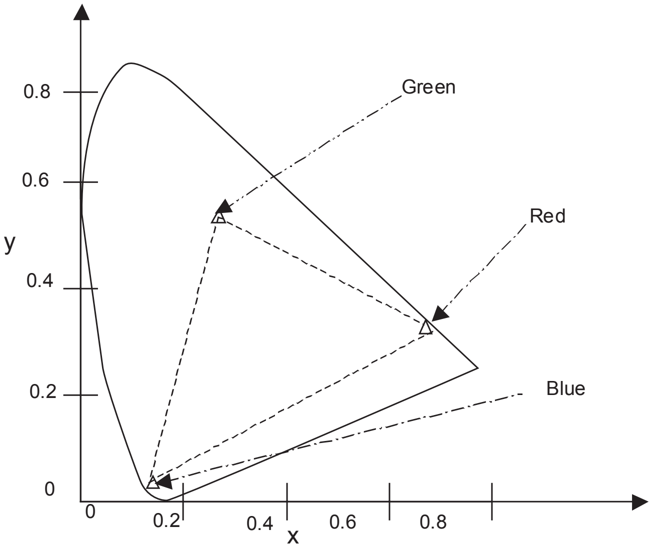

Figure 3.5 *CIE chromaticity diagram for the desired phosphors in colour television.*

marked positions, but the red, green and blue phosphors have been subjected 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 again used, but 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 phosphor was (Zn, Cd)S:Ag and $Zn(PO_4)_2$:Mn^{2+}; however, it was predicted that a narrow emission around 610 nm would be beneficial. Much work resulted in the development of Eu^{3+} doped into yttrium oxides, for instance YVO_4:Eu^{3+}, Y_2O_3:Eu^{3+} and Y_2O_2S:Eu^{3+}.[13]

The CIE colour coordinates of these red, green and blue phosphors are shown in Table 3.5.

For displays requiring areas in excess of 75 cm^2 it is necessary to use projection television. This involves using three small monochrome CRTs projecting red, green and blue images respectively. The images are optically projected *via* lenses onto a screen. This requires much higher illumination levels 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^{3+} is good for this purpose but the green $ZnSiO_4$:Mn^{2+} and especially the blue (Ca, Mg)SiO_3:Ti^{4+} are far from ideal.

Phosphors are also widely used in many other cathode ray tubes, for example, in

Table 3.5 *CIE colour coordinates for colour TV phosphors*

Phosphor	*Emission colour*	*CIE colour coordinates*	
		x	*y*
ZnS:Cu, Au^+, Al	Green	0.310	0.598
ZnS:Cu	Green	0.290	0.611
$ZnS:Ag^+$	Blue	0.136	0.070
$Y_2O_3:Eu^{3+}$	Red	0.640	0.335
$Y_2O_2S:Eu^{3+}$	Red	0.630	0.340

monochrome terminal displays, in oscilloscopes, radar tubes and in X-ray and scintillators technologies. However, these topics are outside the scope of this book and specialist texts should be consulted.[2,4,11]

3.4 High Energy Photoluminescence

Photoluminescence is a term widely applied to the range of phenomena where light emission occurs from a material after energising by photons. In this section of the book the term is specifically applied to the cases where luminescence occurs after the interaction of luminescent materials with narrow band, higher energy ultraviolet radiation, namely in lighting and plasma display panel applications.

3.4.1 Lighting

Luminescent lighting, commonly called fluorescent lighting, has been in regular use for decades 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}.[14]

Luminescent light is generated using ultraviolet radiation from a low-pressure mercury discharge, the mercury vapour being present in the noble gas, which fills the 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 light 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 is to mix blue and orange light but mixing the three 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, $Ca_3(PO_4)_3X$ (where X = F, Cl), the usual activators being Sb^{3+} and Mn^{2+}. 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

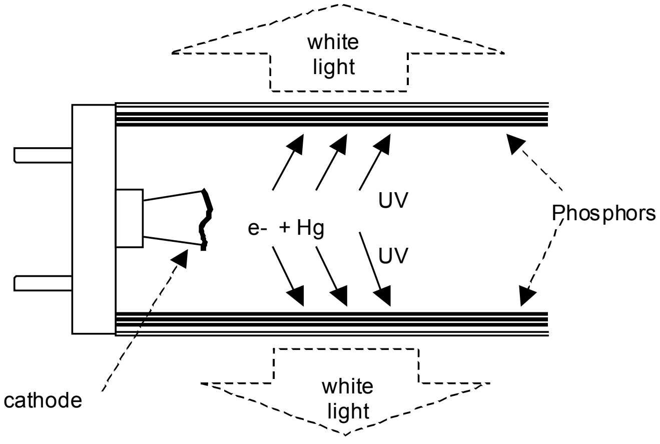

Figure 3.6 *Cross section of a low-pressure luminescent tube.*

emission under these conditions. By careful adjustment of the 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 (see in Figure 3.7(A)).

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 the 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^{3+} emitting at 610 nm. The choice of blue phosphors is between $BaMgAl_{10}O_{17}$:Eu^{2+}, $Sr_5(PO_4)_3Cl$:Eu^{2+} and $Sr_2Al_6O_{11}$:Eu^{2+}, 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^{3+}, (La,Ce)PO_4:Tb^{3+} and (Ce,Gd)MgB_5O_{10}:Tb^{3+}. A schematic representation of the emission spectra of a tricolour lamp is shown in Figure 3.7(B).

3.4.2 Plasma Displays

A monochromatic version of plasma display panels, employing an ionised gas similar to neon lights, was used in early portable computers but this technology has been replaced by the currently favoured liquid crystal displays. However, although plasma display panels are not a new technology, they are regarded as one of the most promising methods for producing full colour, flat and large area TV displays. As opposed to the early monochromatic versions, modern full colour plasma display panels use the 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

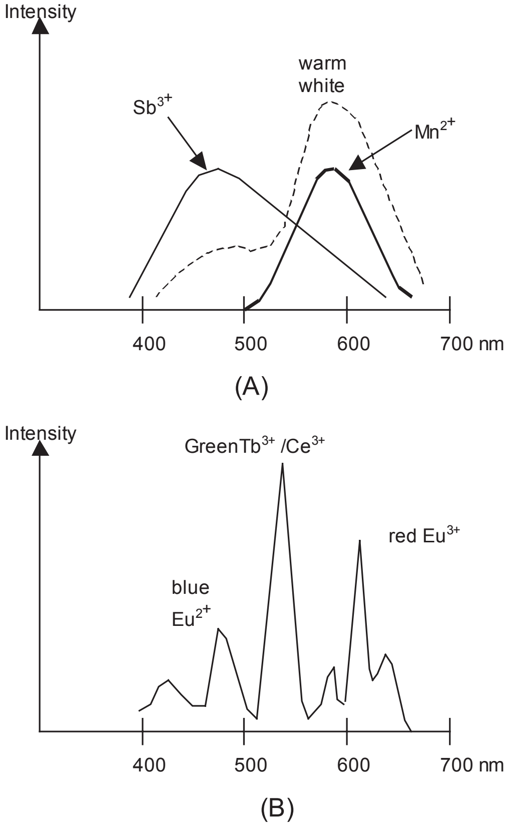

Figure 3.7 *Schematic of emission spectra,* (A) *calcium halophosphate lamp and* (B) *tricolour lamp.*
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two glass plates with electrodes on both the top and bottom. The three sub-pixels (R, G, B) that are necessary for each full colour pixel are formed by 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 3.8. 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 back plate. 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.[15,16]

The conditions required for the construction of these cells place considerable strain on the phosphors. This is 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 into visible light with maximum

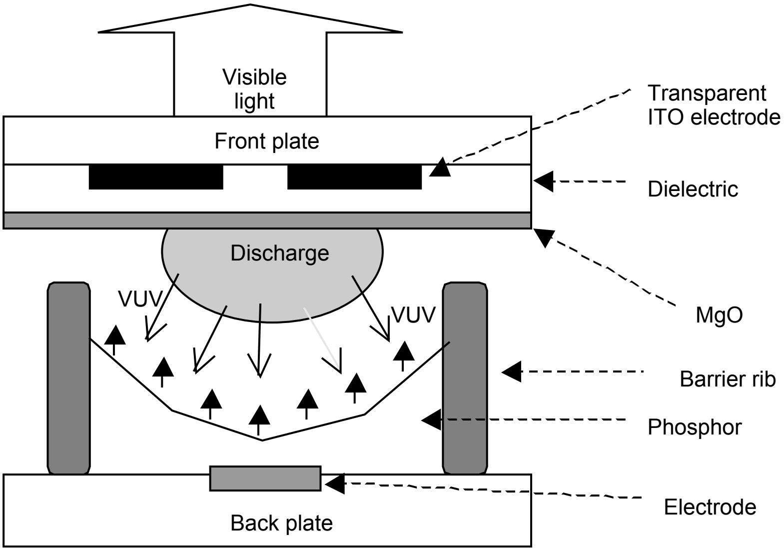


Figure 3.8 *Schematic of a plasma display panel cell.*

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 are chosen from existing materials. The blue emitting phosphor is $BaMgAl_{10}O_{17}$:Eu, the green emitter is Zn_2SiO_4:Mn and the one emitting red is $(Y,Gd)BO_3$:Eu. However, their screen efficiencies of about 1.5 lm W^{-1}, although suitable for use in consumer devices, are still well below the 3 lm W^{-1} found in conventional CRTs, and a breakthrough in research on new phosphors is required. Development work is centred on improving the properties by engineering changes in crystal morphology and surface design, alongside the use of coatings to prevent degradation.[16]

3.5 Fluorescence

Fluorescence from organic materials is a very important phenomenon that is exploited in a broad range of application areas. These include their use in the dyeing of synthetic 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 and in biological and medical applications in both detection and diagnosis of diseases, in assays and in display applications such as electroluminescence (see section 3.8) and in molecular electronics.[17]

Some of the theoretical aspects of fluorescence have already been discussed alongside phosphorescence in section 3.2 and shown schematically in Figure 3.1. In organic fluorophores, especially dyes, excitation from the ground level S_0 to the first excited state S_1 is generally a π–π^* electronic transition. During the extremely short time ($1–10 \times 10^{-9}$ s) that the excited molecule spends in the various higher vibrational levels of the excited S_1 state it loses energy by various actions in its molecular environment. If the molecule returns to the ground state emitting the radiation as visible light it exhibits fluorescence, which, due to the loss of vibrational energy, is at a longer wavelength than the initially absorbed light. As already stated this difference in wavelength between absorption and emission is known as the Stokes shift. In general the Stokes shift is in the region of 30–70 nm but can be as high as 150–250 nm, a necessary condition in some applications where it is essential to separate the absorption maximum from the emission maximum in the spectra, *e.g.* in dye lasers and certain biological applications. The quantum yield of a fluorescent molecule is defined as the ratio between the emitted and the absorbed quanta.

3.5.1 Fluorescent Chromophores

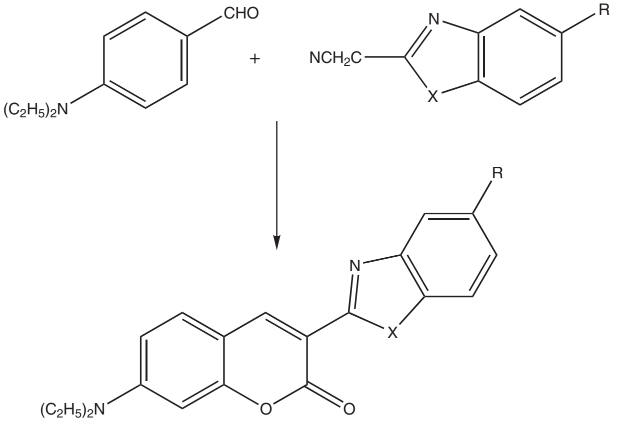
A vast range of organic chromophoric ring systems exhibit fluorescence, with the notable exception of the ubiquitous azo chromophore. However, in many cases the observed fluorescence is too weak to be of any commercial or technological value. In this section the structures and synthesis of only the main classes of fluorescent chromophores are discussed. More detailed accounts are available in recent reviews of the field.[17,18]

3.5.1.1 Coumarins

Coumarins are one of several classes of fluorescent structures containing the carbonyl group as an essential molecular substructure and showing the features typical of donor–acceptor molecules. Others include naphthalimides, perylene esters, perylenediimides, benzanthrones, anthraquinones, benzoxanthones and benzothioxanthones (see below).

Bright yellow and orange red fluorescent dyes based on the coumarin ring, with the generic structure shown in (3.1), have for many years been used commercially. The most important derivatives are those substituted in the 3-position by heteroaryl groups. For example, benzimidazolyl (3.1a), a commercial product being CI Solvent Yellow 185, benzoxazolyl (3.1b) or benzothiazolyl (3.1c), with the diethylamino donor substituent in the 7-position. The heteroaryl moiety may also carry substituents on the benzene ring, as in CI Disperse Yellow 232 (3.1b; R = Cl). There are several synthetic routes to fluorescent coumarin dyes and a common one is shown in Figure 3.9. Water solubility can be achieved by quaternisation of the benzimidazole ring as in (3.1a), producing cationic dyes suitable for use in dyeing acrylic fibres, exemplified by CI Basic Yellow 40 (3.2).

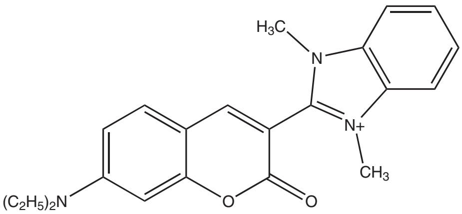
Whilst yellow (λ_{max} 434–452 nm: λ_{em} 493–505 nm) is the dominant shade areas from coumarins of the generic structure (3.1a–c), it is possible to move bathochromically to bright oranges, λ_{max} around 520 nm, by introducing an electron-withdrawing substituent, such as the cyano group, into the 4-position, as in the commercial disperse dye (3.3). An alternative is to put in a cyano group and extend conjugation at the 3-position as in (3.4). 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 conjuga-



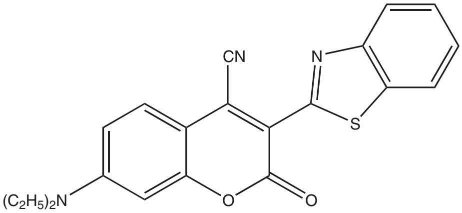
3.1a; X = NH, R = H
3.1b; X = O, R = H
3.1c; X = S, R = H
3.1d: X = O, R = Cl

Figure 3.9 *Fluorescent coumarins.*

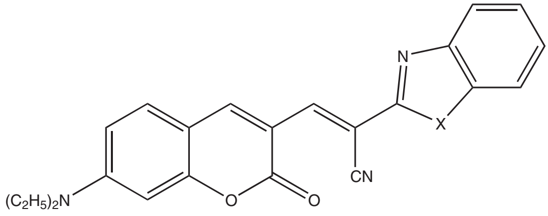
tion. For instance, CI Disperse Red 277, CI Solvent Red 196 (3.5, X = H, Y = CN and Z = O) and CI Disperse Red 374, CI Solvent Red 197 (3.5, X = H, Y = CN and Z = NH) are brilliant red dyes for polyester and for the colouration of plastics. Moving the cyano group onto the coumarin, as in the isomeric compound (3.5, X = CN, Y = H, Z = NH), causes further a 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.



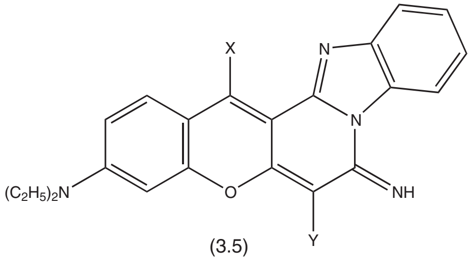
(3.2)



(3.3)



(3.4)

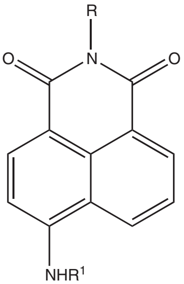


(3.5)

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 (3.6), as illustrated by CI Disperse Yellow 11 (3.6a) and CI Solvent Yellow 43 (3.6b).

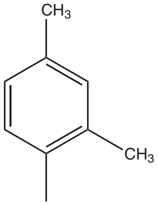
In naphthalimides the simplest structural modification that can be made involves changing the substituent on the imide nitrogen. Almost all the possibilities have been explored, including having alkyl, aryl, aralkyl, heteroaryl, alkoxy and amine on the imide nitrogen. Making these changes has little influence on the wavelength of absorption but does have a significant effect on the emission maximum of the derived products. The introduction of water solubilising substituents, such as the sulfonic acid group produces acid dyes, *e.g.* CI Acid Yellow 7 (3.7) and CI Mordant Yellow 33 (3.8), quaternisation gives cationic dyes suitable for acrylic fibres (3.9) and a



(3.6)

(3.6a) : R =

R^1=H

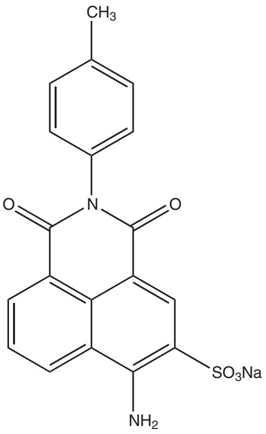


(3.6b) R,R^1 = $(CH_2)_3CH_3$

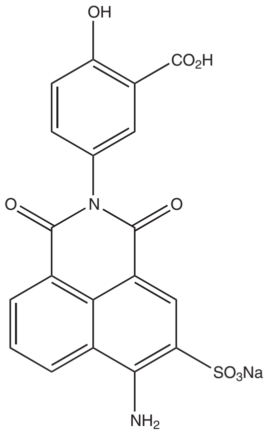
sulfatoethylsulfone group produces reactive dyes for cellulosic substrates (3.10). The Lucifer Yellows CH and VS used as fluorescent molecular probes in biomedical applications are in this group of compounds. A related fluorescent ring system, 1,8-naphthoylene-1,2′-benzimidazole (3.11), readily synthesised by the condensation of the naphthalic anhydride with 1,3-phenylenediamines, has been studied widely and this work has led to the commercialisation of yellow disperse dyes for polyester, *e.g.* CI Solvent Yellow 187 (3.11, R = COPh).

3.5.1.3 Perylenes

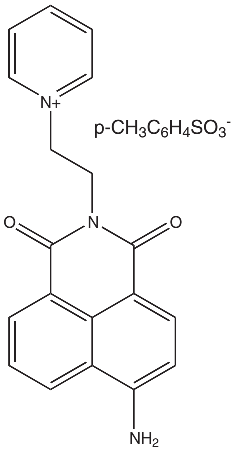
Perylene, a parent pentacyclic aromatic compound, which exhibits a strong fluorescence has found application in laser dyes and organic light emitting diodes (see section 3.8.5.1). The esters of di-, tri- and tetra-carboxylic acids of perylene are lightfast, yellow to red fluorescent chromophores, exemplified by the diisobutyl ester of the



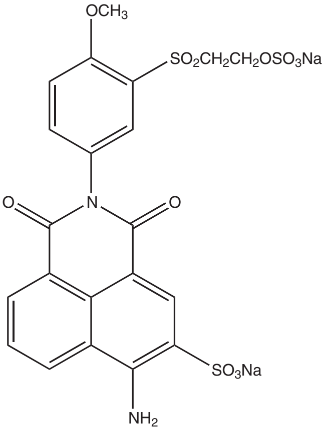
(3.7)



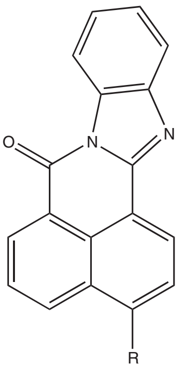
(3.8)



(3.9)



(3.10)

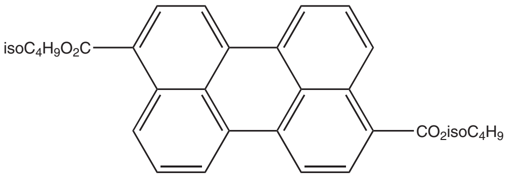


(3.11)

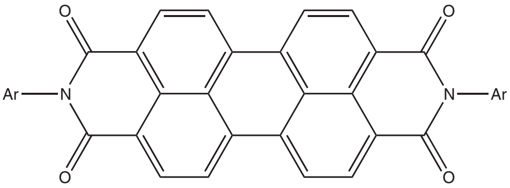
3,9-dicarboxylic acid, CI Solvent Green 5 (3.12). The diimides of perylene-3,4,9,10-tetracarboxylic acids (3.13) form a group of very important high-performance pigments (see Chapter 2) and much research work has been put into this system to produce intense red and orange fluorescent colours. These fluorescent dyes have very good environmental stability, are bright and have high fluorescent efficiency, with some with quantum yields approaching unity (3.13a). Water-soluble versions of these dyes can be made by putting substituents bearing sulfonic acids on the imide nitrogen. By analogy with naphthalimides, the mono- (3.14a) and the bis-benzimidazoles (3.14b) are fluorescent, giving light fast yellow and reddish-violet colours respectively.

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,

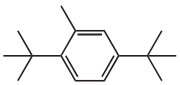


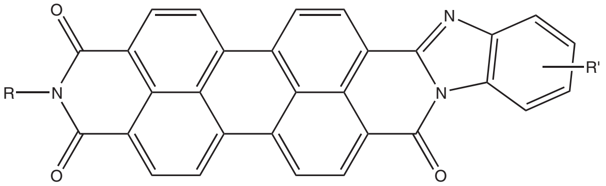
(3.12)



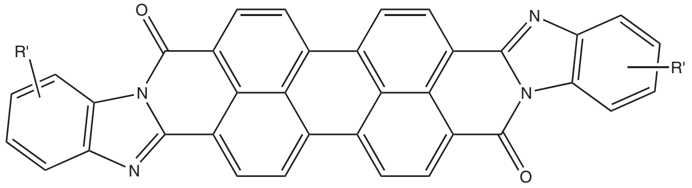
(3.13)

(3.13a) Ar =





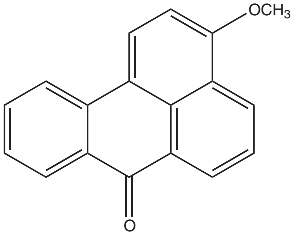
(3.14a)



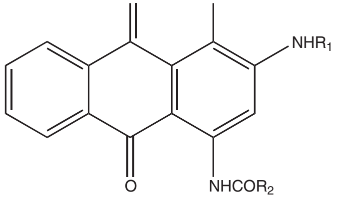
(3.14b)

as they are flat planar molecules with donor–acceptor capabilities, fluorescent materials have been developed for a variety of applications.

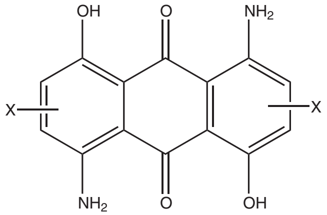
3-Methoxybenzanthrone (3.15) is a yellow–green fluorescent dye (CI Disperse Yellow 13), in both the solid state and in solution, but it has a low quantum efficiency of around 0.1. The nitrogen analogue, pyrimidanthrone (3.16) gives yellow and red–orange pigments for use in plastics. Many common anthraquinone dyes, *e.g.* 1,4-di-*N*-ethylaminoanthraquinone, CI Solvent Blue 59, especially those with amino and hydroxy groups adjacent to the carbonyl group (3.17) 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 (3.18). These are reported to be red to violet with long wavelength luminescence making then useful as daylight fluorescent pigments. Dyes derived from extended benzoxanthene and thioxanthene ring systems give extremely bright, light fast fluorescent disperse dyes for polyester, such as the yellowish red CI Disperse Red 303, which is a mixture of the two isomers (3.19a) and (3.19b) and also as solvent dyes for plastics, *e.g.* CI Solvent Orange 63 (3.20).



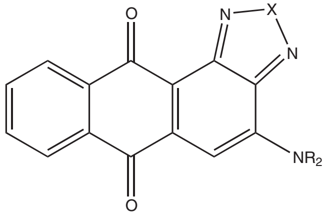
(3.15)



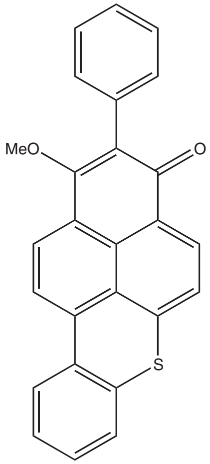
(3.16)



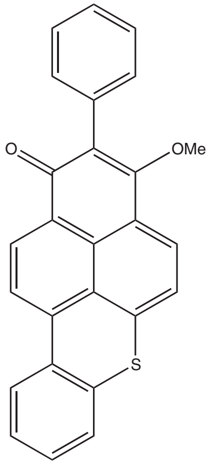
(3.17)



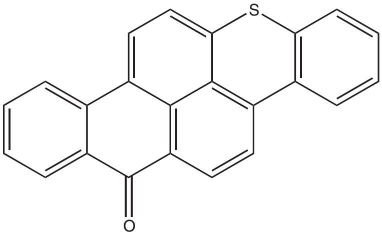
(3.18)



(3.19a)



(3.19b)



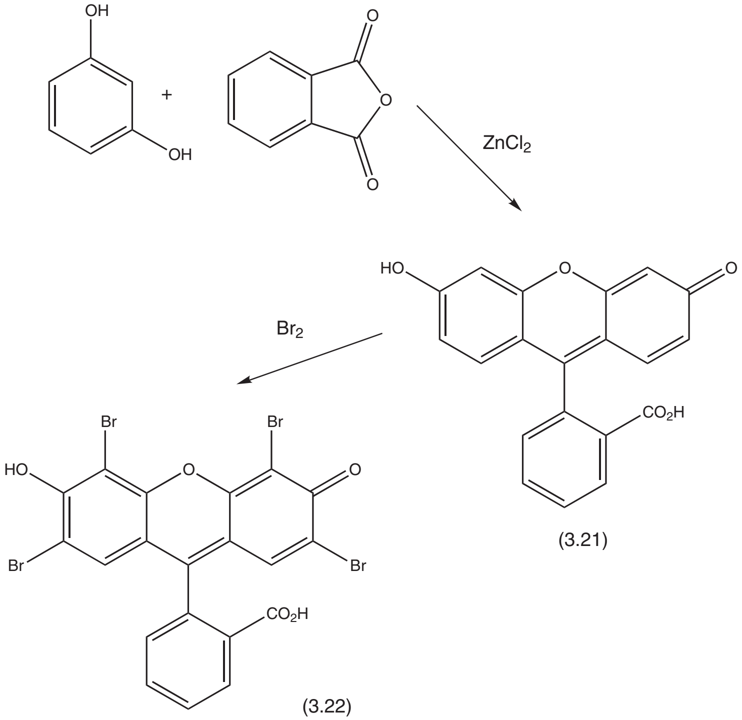
(3.20)

3.5.1.5 *Xanthenes, Acridines and Oxazines*

These classes of chemicals contain not only some of the oldest dyes, dating back to the 19th century, but also some of the most important fluorescent chromophores. The earliest of these discoveries was fluorescein (3.21), which was later brominated to give the polybromo derivative eosin (3.22) (Figure 3.10). They are of little importance in textile coloration processes but are used in some fluorescent pigments and extensively in analysis and biological methods and also in tracing the course of water in drains and other water outlets.

The most important xanthenes are the imino derivatives known as rhodamines, exemplified by rhodamine B (CI Basic Violet 10) (3.23a), λ_{max} 543 nm and λ_{em} 552 nm and rhodamine 6G (CI Basic Red 1) (3.23b), λ_{max} 530 and λ_{em} 557 nm (Figure 3.11). These are intensively fluorescent dyes with quantum yields close to unity. Rhodamine 6G especially has found wide application in daylight fluorescent pigments (see section 3.5.2) and this ring structure has been much modified for use in many other outlets, especially as laser dyes (see section 3.5.3) and in biomedical applications (see section 3.5.6).

The nitrogen analogues of the rhodamines based on acridine (3.24) are strongly

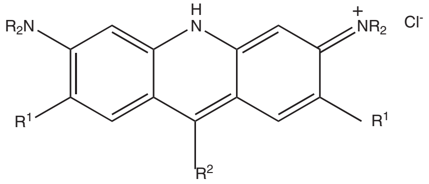


(3.21)

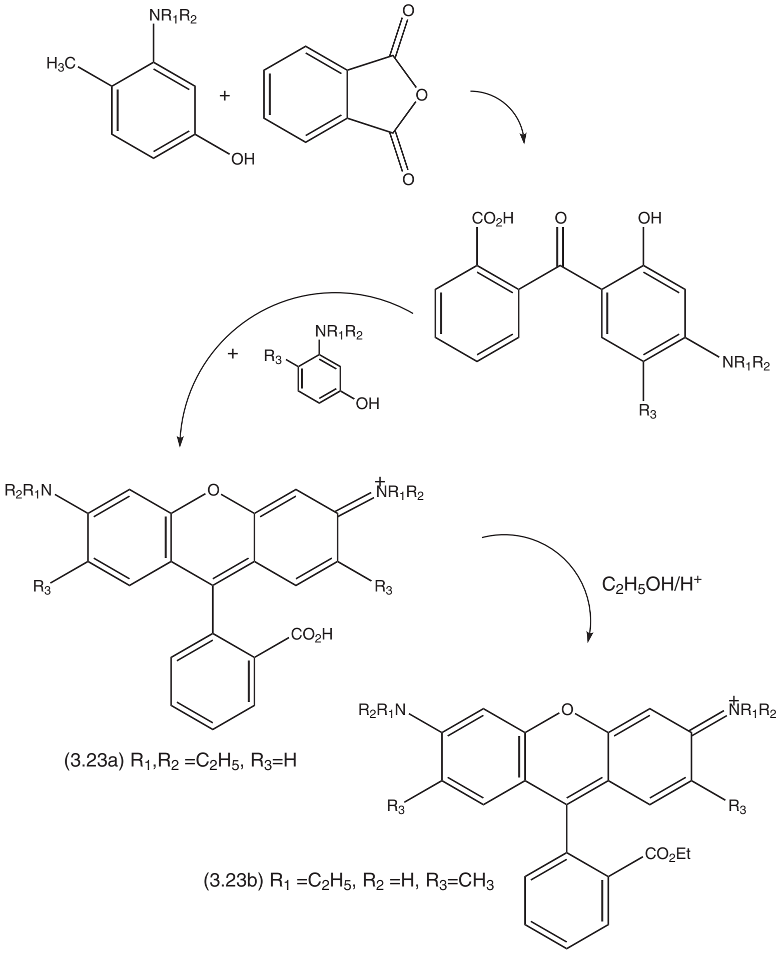
(3.22)

Figure 3.10 *Synthesis of fluorescein and eosin.*

fluorescent but their low stability makes them only suitable for use as indicators in acid–base titrations and as fluorescent probes in biological applications, the latter being an important application of these dyes. Acridine Yellow is (3.24a), Acridine Orange (3.24b), Acridine Orange R (3.24c) λ_{max} 494 nm and λ_{em} 530 nm, and Proflavine (3.24d).



	R	R^1	R^2
(3.24a)	H	CH_3	H
(3.24b)	CH_3	H	H
(3.24c)	CH_3	H	Ph
(3.24d)	H	H	H

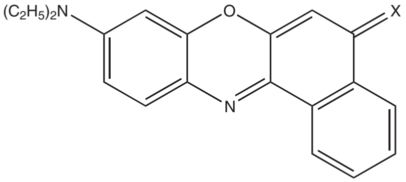


(3.23a) $R_1,R_2 = C_2H_5$, $R_3 = H$

(3.23b) $R_1 = C_2H_5$, $R_2 = H$, $R_3 = CH_3$

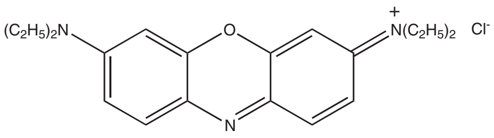
Figure 3.11 *Synthesis of rhodamine B and rhodamine 6G.*

Derivatives of long established fluorescent dyes based on the phenoxazine ring system, such as the cationic Nile Blue (3.25a) λ_{max} 627 nm, and the neutral Nile Red (3.25b) and also the cationic dye CI Basic Blue 3 (3.26), have found new uses in biomedical applications (see section 3.5.6), as laser dyes (section 3.5.3) and as dopants in organic light emitting diodes (section 3.8.5).



(3.25a); $X = {}^+NH_2\ Cl^-$

(3.25b); $X = O$



(3.26)

3.5.1.6 Hydrocarbons

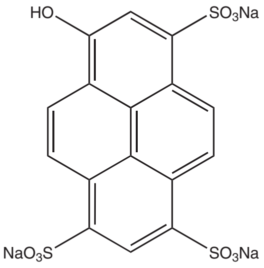
Although many hydrocarbons exhibit fluorescence, often they are colourless and the fluorescence is only just into the blue, *e.g.* the linear terphenyl and quaterphenyl. Polycyclic ring systems such as terrylene and rubicene are used in analytical methods and OLEDs but a large number are ruled out of 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 interest. One derivative of pyrene (3.27) is a yellow–green fluorescent dye used in textile applications (CI Solvent Green 7) and in analysis and sensors (see section 3.5.6.4).

3.5.1.7 Methines, Hemicyanines and Cyanines

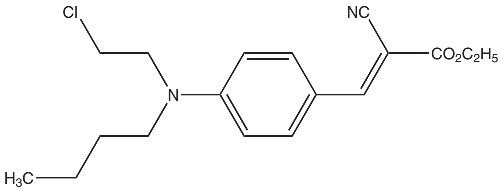
In recent years methines, hemicyanines and cyanines have been the subject of much research as they couple high molar absorption and emission coefficients with a relative ease of molecular manipulation to change the wavelength of absorption, making them an obvious target for chemical designers.

Simple neutral methine yellows are of the dicyanovinyl or cyanoesters type exemplified by the bright greenish yellow, CI Disperse Yellow 31 (3.28) used in dyeing polyester. This class of dyes, more commonly called styryl dyes, are amongst the brightest yellow dyes, but they are readily hydrolysed under alkaline conditions and have been largely replaced by the so-called pyridone yellows for polyester dyeing (see Chapter 2, section 2.3.1.1). Extending the conjugation to give polymethines, or merocyanines, causes a bathochromic shift to oranges and orange reds. 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 (3.29), which is orange–red in colour, emitting in the red and used as a laser dye.

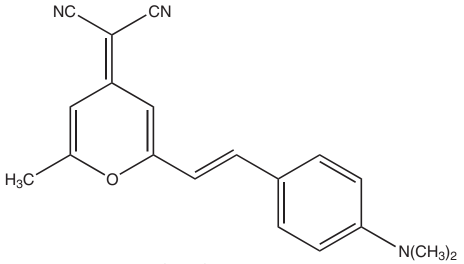
Hemicyanines are polymethines with an ammonium salt at one end of the chain. Typically these can be pyridinium (3.30), indolenium (3.31a, X = $C(CH_3)_2$) and benzothiazolium (3.31b, X = S) derivatives. The pyridinium derivatives fluoresce in the long wavelength red region, whilst the others are in the near-infrared, which is a very useful property for certain laser dye outlets and in fluorescent imaging in medical diagnosis and biological probes.



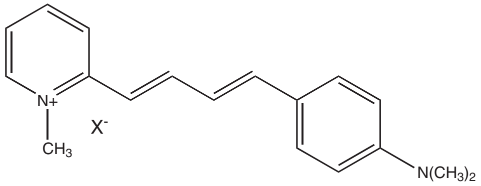
(3.27)



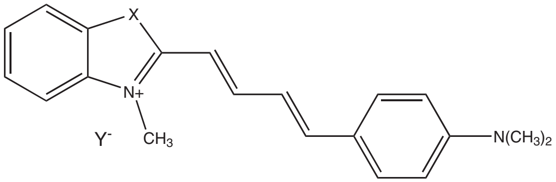
(3.28)



(3.29)



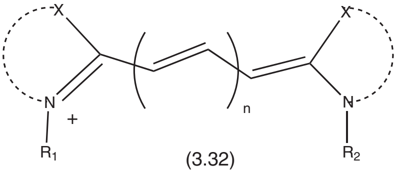
(3.30)



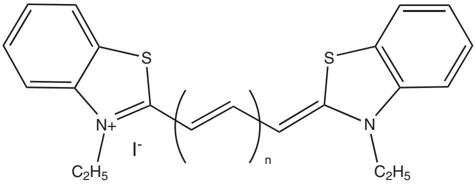
(3.31a); X = $-CH(CH_3)_2$
(3.31b); X = S

Cyanine dyes is the name given to the class of methines where each of the nitrogen atoms are in rings at opposite ends of the chain, as in the general formula (3.32). When X and Y = $C(CH_3)_2$ they are called indocyanines, when X and Y = S they are the thiacyanines and where X and Y = O they are known as oxacyanines. Cyanines are used extensively as sensitisers in the photographic process (see Chapters 2 and 4), but are also widely used in other outlets because of their fluorescent properties. All three cyanines are subject to poor light and chemical stability with the indocyanines being the best. The chain length can be varied but is usually kept in the range *n* = 0–5. (Note: in molecular probe applications these are given the acronyms Cy1 when *n* = 0, Cy3 where *n* = 1 , Cy5 where *n* = 2, Cy7 where *n* = 3 *etc.*, see section 3.5.6.) Every extra double bond shifts both the absorption and emission maxima around 100 nm towards the red, the molar absorption coefficients rising from 70 000 for *n* = 0 to 250 000 dm^3 mol^{-1} cm^{-1} for *n* = 5. For example, (3.33, *n* = 1) has λ_{max} 557 nm whilst (3.33; *n* = 3) has λ_{max} 760 nm, with Stokes shifts in the emission spectra of around 35–50 nm.

The indocyanines and analogues, especially Indocyanine Green, absorbing and



(3.32)



(3.33)

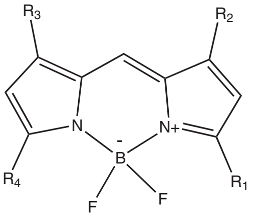
emitting in the near-infrared have important applications in biotechnology (see section 3.5.6).[19]

3.5.1.8 Dipyrromethines

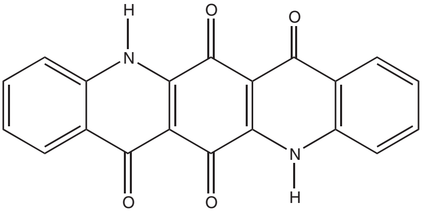
A series of compounds, which has been extensively developed by Molecular Probes Inc. for use in biomedical applications, and given the acronym BODIPY, are the boron difluoride complexes of dipyrromethines. The general structure of these fluorophores is shown in (3.34). The compounds are strong absorbers, molar absorption coefficients of 75–100 000 dm^3 mol^{-1} cm^{-1}, with high quantum efficiencies and relatively small Stokes shift. The basic structure (3.34; R^1–R^4 = CH$_3$) has λ_{max} = 506 nm and λ_{em} 515 nm with bathochromic shifts induced by increasing the donor strength of the ring nitrogen atoms, as in (3.34; R^1, R^4 = 2-thiophenoyl, R^2, R^3 = H) λ_{max} 624 nm, λ_{em} 637 nm.

3.5.1.9 Miscellaneous Chromophores

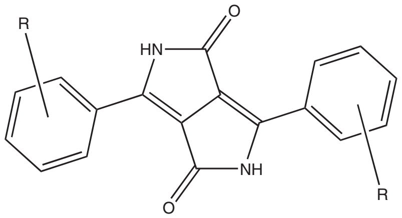
There are several other chromophoric systems, some of which are very old compounds, but others that have only been invented in the last couple of decades, which exhibit useful fluorescence.[20] Notably these include the red thioindigo, CI Solvent Red 242, the bluish-red quinacridones (3.35), the bright orange to red diketopyrrolopyrrole pigments (3.36), the very bright orange to red benzodifuranone dyes (3.37) and the bright red disperse dye (3.38). The chemistry of these and other dyes and pigments are discussed in greater detail in Chapter 2.



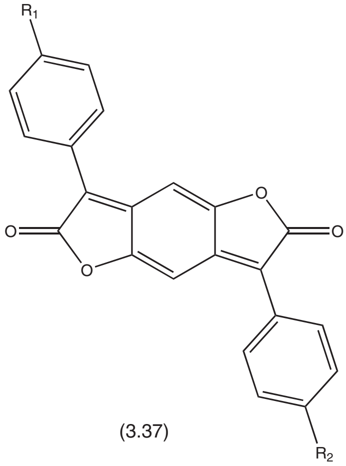
(3.34)



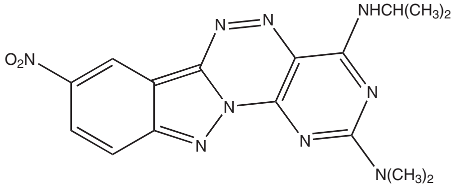
(3.35)



(3.36)



(3.37)



(3.38)

3.5.2 Applications as Fluorescent Dyes and Pigments

Fluorescent colours, especially daylight fluorescent pigments, have become increasingly important as there has been a sociological move in the developed world 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, especially visibility, and security in all aspects of our everyday lives.

The world market for fluorescent pigments in 2000 was for 11 600 tonnes with the split into geographical and European application areas as shown in Table 3.6.

Table 3.6 *Fluorescent pigments consumption in 2000*

Geographical region	*Tonnes*
North America	5500
Europe	2000
Japan	600
Other Asia	3000
Latin America	400
Africa	50
Oceania	50
Europe by end use	
Paper	650
Paint	450
Plastics	400
Printing ink	450
Textiles	50

3.5.2.1 Fluorescent Dyes in Textile Applications

The main use of fluorescent dyes is in the coloration of synthetic fibres, especially polyester, polyamide and acrylics in conjunction with elastane fibres, for fashion, leisure and especially sportswear uses. The 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.

The largest usage is in polyester and many dyestuff companies have disperse dye ranges for this purpose, some of which are also applied to polyamide fibres. The main colours are in the yellow, orange, red, pink and violet areas with coumarins, methines and perylene dominating the structural classes.

Fluorescent blue colours are less common and are usually in the bright turquoise shade area, with anthraquinones such as CI Disperse Blue 60 or the newer methines such as CI Disperse Blue 354 or indoanilines being the products of choice. Typical products from the ranges of DyStar and BASF (textile colours business is now part of DyStar) are given in Table 3.7.

Many cationic dyes for acrylic fibres, especially methines, such as CI Basic Red 13, CI Basic Violet 7 and CI Basic Red 74 are very bright and fluorescent and hence this fibre has a place in fluorescent textiles.

3.5.2.2 Daylight Fluorescent Pigments

One of the largest markets for fluorescent colorants is as daylight fluorescent pigments. Daylight fluorescent pigments are those that have the property of fluorescing when activated by visible light at the blue end of the spectrum. They are composed of two components, fluorescent dyes and a range of special polymers.

The dyes are chosen from the classes already described in section 3.5.1. A typical set is CI Basic Yellow 40 (3.2), fluorescein (3.21), eosin (3.22), Coumarin 7 (3.1a), CI Basic Red 1 (3.23a), CI Basic Violet 10 (3.23a; $R_1 = C_2H_5$, R_2, R_3 = H) and Basic Violet 11 (3.23b; $R_1 = C_2H_5$, R_2, R_3 = H). To obtain blues and greens it is common to use copper phthalocyanine and its polyhalogeno derivatives as toners.

The polymer, the choice of which depends on the end application, plays a very important role in the fluorescent properties of the pigments, being 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 fulfil certain

Table 3.7 *Fluorescent disperse dyes from DyStar/BASF*

Trade name	*Chemical class*
Dianix Brilliant Yellow 10G	Coumarin
Dianix Brilliant Orange G	Perylene
Dianix Brilliant Red B	Coumarin
Dianix Brilliant Red 5B	Indigoid
Palanil Luminous Yellow GN	Coumarin
Palanil Luminous Red G	Coumarin derivative
Palanil Luminous Red GN	Coumarin derivative
Palanil Cyanine B	Heterocyclic indoaniline

criteria to be of use in these pigments; they must act as good dye solvents, exhibit grindability, have the desired softening point and have a high decomposition point. The pigments are made by bulk polymerisation of the polymer 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.[21]

The polymers can be categorised as formaldehyde containing and formaldehyde free and as thermoset or thermoplastic resins. Typical formaldehyde containing resins are melamine formaldehyde sulfonamide resins, where the sulfonamide is *ortho* and *para* toluenesulfonamide. The sulfonamide, which is a solvent for the dye, undergoes a condensation polymerisation with formaldehyde and melamine, the latter acting as a cross-linking agent. Non-formaldehyde, thermoplastic resins are usually polyamides and polyesters.

Fluorescent pigments suffer from poor fade resistance compared with conventional pigments. This is caused by the excited state molecules, which have relatively long lifetimes, transferring their energy to oxygen, creating singlet oxygen which then reacts with other fluorescent dye molecules causing degradation. To improve the light fastness it is usual to add a UV absorber, *e.g.* benzotriazoles, benzophenones, triazines *etc.*, 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 areas, including letterpress, silkscreen, gravure, offset litho, flexo, textile and also the newer digital printing methods such as inkjet. Coating applications include the coloration of paper, rubber, textiles and vinyl fabrics, in solvent and water based paints. In plastics they can be extruded or molded or used in film. Further details can be obtained from the trade literature or websites of such companies as Day-Glo and Sun Chemical Corps (USA) and Sterling Industrial Colours (UK).

Safety uses are very wide and many new examples appear regularly. For instance, American Tire has patents and patents pending 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 200 feet.

3.5.2.3 Other Applications

Fluorescent dyes/pigments of the solvent dye class, the structures of many of these having already been given in section 3.5.1, are used in a multitude of applications where solvent 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 *etc.*, including digital printing methods, *e.g.* ink jet, in the marking of petroleum fractions, in waxes and polishes, in the detection of flaws in metals, glass, ceramics and plastics and in the characterisation of polymers.

3.5.3 Dye Lasers

Whilst many significant advances in solid state and semi-conducting lasers (see Chapter 5) have meant that they have made inroads into applications previously the domain of dye lasers, the latter still have a strong position in many areas where they offer several advantages:[22]

- Easy tunability over a wide range of wavelengths
- Hyperfine tuning
- High average power in both pulsed and continuous modes
- High feed power
- Ideal light source for the generation of short pulses

In this section the types of dye lasers, the mechanism of lasing as applied to dyes, structural types of laser dyes and a few of the applications of dye lasers will be discussed.[22–24]

3.5.3.1 Types of Dye Lasers

There are two main types of dye lasers: continuous wave (CW) and pulsed lasers. 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 focussed onto the dye stream causing an extremely high level of fluorescence. This fluorescence is then focussed between two highly reflective mirrors that turn back the fluorescent light, thus initiating the lasing process.[22] A simple schematic of the process is shown in Figure 3.12.[24] A diffraction grating placed at the end of the cavity enables wavelength selection and tuning by changing the angle of the grating.

The two most common types of pulsed lasers used in dye lasers are the neodymium: yttrium-aluminium-garnet, Nd:YAG, and excimer lasers. The performance of pulsed dye lasers is wavelength dependent. The Nd:YAG laser provides useful pump wavelengths at 266, 355 and 532 nm (second harmonic), which can be matched to the absorption bands in a variety of dyes. Excimer lasers, formerly called rare gas halide lasers, cover a wide range of laser wavelengths. These range from 193 nm (ArF) to 351 nm (XeCl). One of the strongest bands occurs at 308 nm in the XeCl laser and, since most commercial dyes have some absorption in this region, the XeCl laser finds wide application.

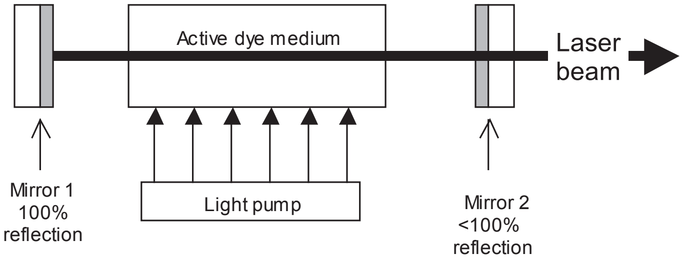


Figure 3.12 *Schematic of a dye laser.*
(Reproduced with permission of Wiley-UCH.)

3.5.3.2 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 of the dye laser.

As previously discussed, under fluorescence (section 3.5), the first step in the mechanism involves raising the molecule from the ground state to an excited state S_1. To act as a laser dye, the population of molecules in the excited state must reach a higher level than in ground S_0 state, *i.e.* must undergo population inversion, and then be capable of releasing the stored energy by a radiative process back to the ground state, in other words 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. This stimulated emission is strictly coherent, has the same phase and polarisation, in contrast to spontaneous emission, and has a high intensity.

3.5.3.3 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:

1. A wide range of dyes are available that provide stimulated emission (lasing) over a broad range of the spectrum
2. Organic dyes can be tuned to emit over a range of wavelengths

Dye lasers can operate from around 250–1285 nm and the individual dye components can be fine tuned to operate in the range of 30–50 nm. As detailed in section 3.5.1, there are several classes of fluorescent dyes that can be used in dye lasers; the approximate spectral coverage of these are shown in Table 3.8.

3.5.3.4 Applications of Dye Lasers

In recent years dye lasers operating in the spectral region of 600–750 nm have been of particular interest as they have found applications in photodynamic therapy of

Table 3.8 *Working ranges of laser dyes*

Dye class	*Working range/nm*
Stilbenes	340–430
Oxazoles	360–480
Anthracenes	410–440
Acridines	440–520
Coumarins	460–540
Xanthenes	510–700
Dipyrromethines	540–600
Cyanines	540–1200
Oxazines	630–720

cancer (see section 4.6.2), medical diagnostics, surgery, dermatology, urology, fluorescent immunoassays, laser isotope separation and environmental monitoring.

3.5.4 Fluorescent Brighteners

Although strictly falling outside the scope of this book on colour chemistry, fluorescent brightening agents (FBAs) are of such importance and interest that an exception will be made in their case. The global consumption of brighteners was 170 000 tonnes in 1997 and is predicted to reach 230 000 tonnes by 2003.

FBAs, also known as optical brighteners and fluorescent whitening agents, are strongly fluorescent substances that absorb in the ultraviolet region and emit in the blue–violet area of the spectrum. A typical FBA absorbs light between 340 and 380 nm and re-emits between 425 and 450 nm. When on a substrate, for instance paper or a textile fabric, the FBA increases the apparent reflection in the blue–violet region of the spectrum and the article appears to be whiter than the untreated material.[25] The mechanism behind this fluorescent behaviour has already been explained at the beginning of section 3.5.

FBAs can be classified according to their application, *e.g.* in detergents, by far the major use, on paper, the second largest, or on a variety of textiles and plastics.[25] Alternatively, they can be grouped according to their chemical class.[26] In this book the latter will be used, together with an indication of the main application areas of the various major products.

3.5.4.1 Stilbene Based Brighteners

By far the most important class of FBAs are those based on stilbenes especially the acylation products of 4,4′-diaminostilbene-2,2′-disulfonic acid (3.39), which is usually given the acronym DAST. The DAST based brighteners are extensively used on cotton, paper and in detergent formulations. These are of commercial importance because DAST can be readily synthesised from cheap, readily available common starting materials and then simply converted into a variety of acylated products. The synthetic pathway to the FBAs is illustrated in Figure 3.13. The most commonly used acylating agent is cyanuric chloride (3.40), giving the chloro derivative (3.41), which

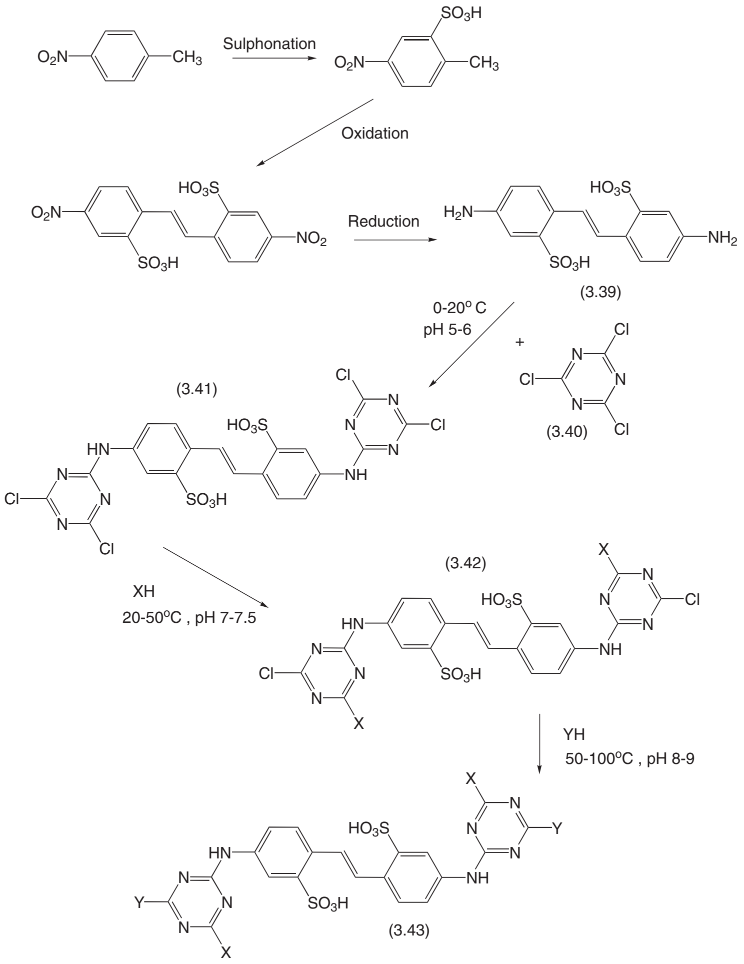


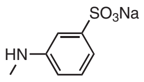
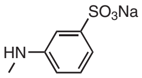
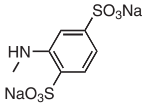
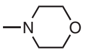
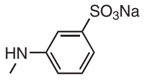
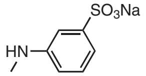
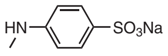
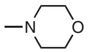
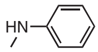
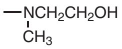
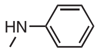
Figure 3.13 *Synthesis of DAST derived FBAs.*

can be sequentially substituted with nucleophiles to produce the largest group of FBAs having the generic structure (3.43).[25]

On cotton the FBAs are applied by similar methods to those used for direct dyes; the less water-soluble product by exhaust dyeing methods and the more soluble, less substantive products by pad batch or continuous methods. A very large number of DAST based FBAs have been commercialised over the years and a typical set is shown in Table 3.9. In the main these products give slightly violet shades of white and have a light fastness in the range 3–4. The substantivity for cotton increases from (3.44) to (3.50), the lower substantive ones being used in continuous application and the higher substantive ones in exhaust application processes.

In the preparation of white paper the FBA is added either at the pulping stage, prior to producing the paper sheet (one-third of the manufacture), or during a subsequent sizing procedure on the preformed sheet (two-thirds of the manufacture). The

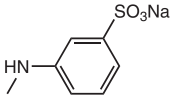
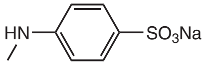
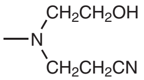
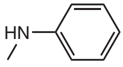
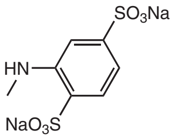
Table 3.9 *FBAs for cotton, based on structure (3.43)*
(Reproduced with permission of Society of Dyers and Colourists)

Compound	*X*	*Y*
(3.44)		
(3.45)		
(3.46)		$-N(CH_2CH_2OH)_2$
(3.47)		$-NHCH_2CH_2OH$
(3.48)		
(3.49)		 $-\underset{CH_3}{N}CH_2CH_2OH$
(3.50)		$-OCH_3$

most commonly used FBAs are DAST based, which for the pulping stage addition must show good affinity, exhaust at low temperatures and be stable at pH 3. In the sizing process the FBA must be compatible with the resins, *e.g.* starch, casein, urea–formaldehyde. Some typical FBAs for paper are shown in Table 3.10.

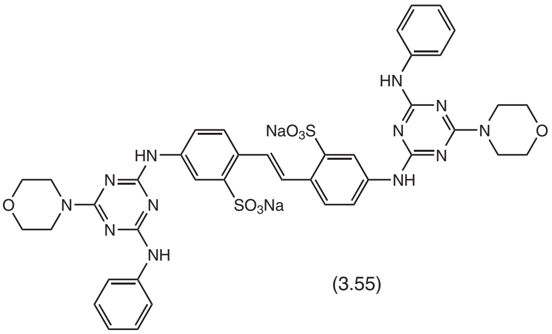
By far the largest use of FBAs is in detergents, where they must meet the needs of a continually evolving technology and a market place dominated by a small number of very large players who dictate the commercial terms to a select number of suppliers. The loading of FBAs in detergents is in the range 0.02–0.05%. There are functional differences between the use of FBAs on substrates such as textiles and paper and in detergents. In the former the FBA is there to brighten dull materials whereas in detergents they are required to maintain the brightness of textile materials during many cycles in the washing machine. The textile material, which is being

Table 3.10 *DAST based FBAs for paper, based on structure (3.43)* (Reproduced with permission of Society of Dyers and Colourists)

Compound	*X*	*Y*	*Application*
(3.46)		$-N(CH_2CH_2OH)_2$	Pulp & size
(3.51)		 $-N(CH_2CH_2OH)(CH_2CH_2CN)$	Pulp & size
(3.52)		$-N(CH_2CH_2OH)_2$	Pulp
(3.53)		$-N(C_2H_5)_2$	Size
(3.54)	$-NH_2$	$-N(CH_2CH_2OH)_2$	Size

brightened, is generally cotton. Whilst low toxicity and environmental impact influence the choice of FBA, they must also be stable to attack from the various oxidants used in commercial detergents.

For many years one of the most important FBAs for detergent has been the DAST based product (3.55). However, DAST brighteners are susceptible to both chlorine



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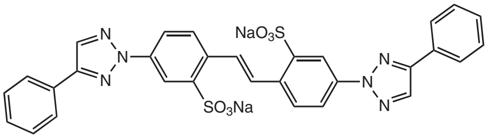

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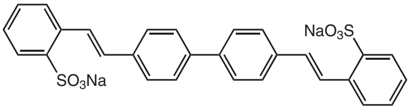


(3.57)

based bleaches and those based on per-acids, such as the very important development of bleaches based upon sodium perborate activated by tetra-acetylethylenediamine. One way round this instability has been to encapsulate either the FBA or the activator.

Other stilbenes of use in detergents are the DAST based (3.49), the triazolo compound (3.56), derived from DAST, and the bis-stilbene (3.57). The latter two are more stable to the newer bleaches but are also more expensive than the simpler DAST based FBAs. They are also used as premium brighteners for cotton and nylon/cotton blends.

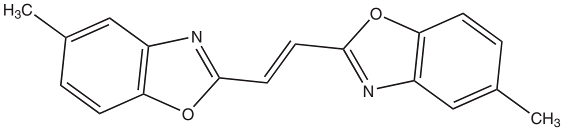
3.5.4.2 Ethylenic and Vinylic Based Brighteners

Closely related structurally to stilbenes are a class of compounds containing one or more ethylenic bridges between aromatic or heteroaromatic rings, exemplified by (3.58).

Most of the compounds in this group are used for the brightening of synthetic fibres, especially polyester. Application to polyester is either by exhaustion at 125–30 °C, with or without carriers, or by continuous pad bake methods at 160–200 °C with FBAs of a larger molecular size. The benzoxazole group is an important feature of this class, other examples being (3.59) and the bis(benzoxazolyl)stilbene (3.60), which is used to produce pre-brightened polyester by adding to the melt prior to extrusion of the fibre.

3.5.4.3 Coumarins

The fluorescent properties of the coumarin ring system have already been described in the section on fluorescent chromophores 3.5.1.1 and not surprisingly colourless



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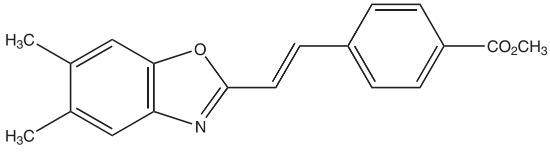

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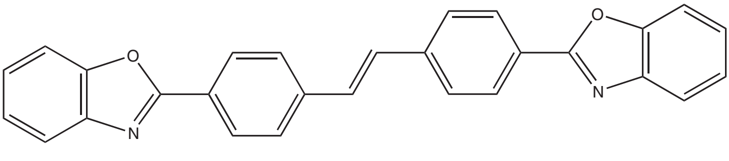


(3.60)

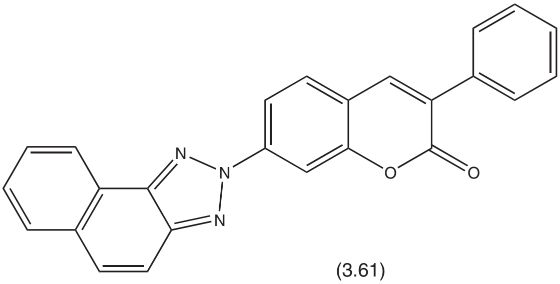
products of this class are used as FBAs, especially for polyester. They are normally derivatives of 7-amino-3-phenylcoumarin, *e.g.* (3.61).

3.5.4.4 1,3-Diphenyl-2-pyrazolines

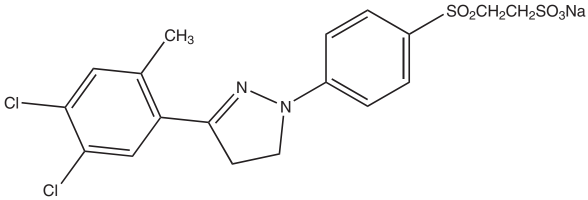
Pyrazolines are a class of FBAs for use on cellulose acetate and more importantly commercially on polyamide fibres. For polyamide, anionic derivatives such as (3.62) are used, applied by pad-thermosol and related methods.

3.5.4.5 Naphthalimides

Another well-known fluorescent chromophore that has found application in FBAs is naphthalimide. Product (3.63) is widely used in synthetic fibres, especially polyester and cellulose acetates and also in plastic applications.



(3.61)



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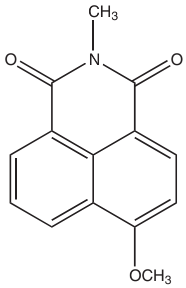


(3.63)

3.5.4.6 Polycyclics

Rather surprisingly the only polycyclic ring system to have found significant commercial application in FBAs is pyrene. The triazinyl derivative (3.64), which is synthesised by a Friedel–Crafts reaction between pyrene and 2-chloro-4,6-dimethoxy-1,3,5-triazine, is an important brightener for polyester and cellulose acetate.

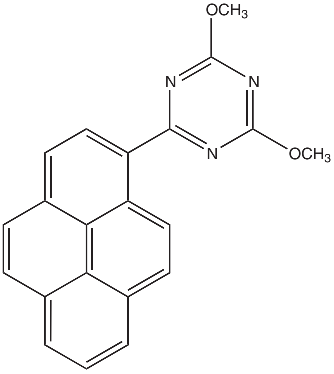
3.5.4.7 Quaternary Ammonium Compounds

Cationic FBAs are used to brighten polyacrylonitrile fibres. The brightening of acrylic fibres is carried by the exhaust method at an acid pH, usually in the presence of sodium chlorite or bisulfite bleach. Pyrazolines produce very high whites but are unstable to bleach and therefore the quaternary benzimidazoles are the preferred class, *e.g.* (3.65) and (3.66).

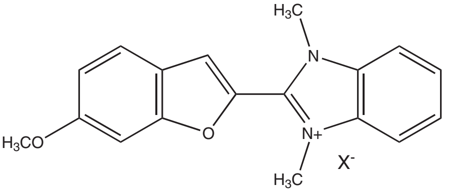
3.5.5 Fluorescence in Elemental Analysis

The use of fluorescence techniques in analysis is very extensive and any detailed discussion is way beyond the scope of this book. There are several textbooks on this topic and, to aid any reader requiring further information, two of the most recent books are given in the references.[27, 28]

Fluorometric methods have been developed for determining the concentrations of more than 50 elements in the periodic table. These methods depend on the measurement of changes in the fluorescence intensity of a fluorescent dye on interaction with the species to be analysed. The concentration of the substance being analysed is proportional to the fluorescence intensity, determined from calibration curves. The interactions can take the form of ionic associates between a dye cation and a metal complex anion, *e.g.* $AgBr_2^-$ with a rhodamine cation, or alternatively with a fluorescent dye anion, *e.g.* fluorescein and a complex cation. In another method, the changes



(3.64)



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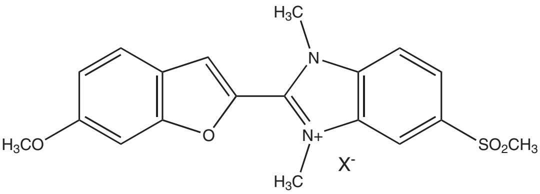


(3.66)

in fluorescence intensity on complexation of a metal ion with a coordinating dye species, *e.g.* 1,8-dihydroxyanthraquinones and 8-hydroxyquinoline, is used.

3.5.6 Fluorescence in Biological, Medical and Drug Development Applications

In this text the objective will be to provide an outline of some of the application areas where fluorescent techniques are applied in biological, medical and drug development, concentrating on the fluorophores used in these applications. In these areas fluorescent labels and probes are used in immunoassay, flow cytometry, fluorescence microscopy, DNA sequencing, detection on arrays, gel based quantification of nucleic acids and proteins, capillary electrophoresis and single molecule detection.[19,29,30] The development of automated, high throughput screening (HTS) of drug candidates produced by combinatorial synthetic methods has been a significant new outlet for fluorescent probes and reagents.

Visible and near-infrared fluorescent emitters are being applied in the medical imaging field.[31] Examples include cancer diagnosis, ophthalmology, cardiac surgery and in the treatment of burns.[32] (See also Chapter 4, section 4.6).

3.5.6.1 Fluorescence Instrumentation for Analysis

In any application the fluorescence detection systems must have four compatible elements:[33]

- An excitation source
- A fluorophore
- Wavelength filters to isolate emission photons from excitation photons
- A detector that registers emission photons and produces a recordable output, usually as an electrical signal or a photographic image

There are four main types of fluorescence instruments, each providing distinctly different information:

- *Spectrofluorometers* and *microplate readers* measure the *average* properties of bulk (μL to mL) samples
- *Fluorescence microscopes* resolve fluorescence as a function of spatial coordinates in two or three dimensions for microscopic objects (less than 0.1 mm diameter).
- *Fluorescence scanners* resolve fluorescence as a function of spatial coordinates in two dimensions for macroscopic objects such as electrophoresis gels, blots and chromatograms
- *Flow cytometers* measure fluorescence per cell in a flowing stream, allowing subpopulations within a large sample to be identified and quantitated.

3.5.6.2 Fluorophores and their Modification

The fluorophores used in these analytical and biological outlets are based on the standard list of chromophores described in section 3.5.1. Of course, they need to be modified to work in the biological environments. For instance, fatty chains are introduced for lipid specificity, sulfonic acid groups for water solubility and both non-covalent and covalent reactive groups, *e.g.* *N*-hydroxysuccinimide esters, for labelling purposes on proteins and DNA. Solvatochromic effects are also very important in these applications as discussed under Solvatochromism in Chapter 1 (section 1.6). In the following sections some of the main outlets for these fluorophores will be outlined.

3.5.6.3 Probes for Calcium and Other Ions

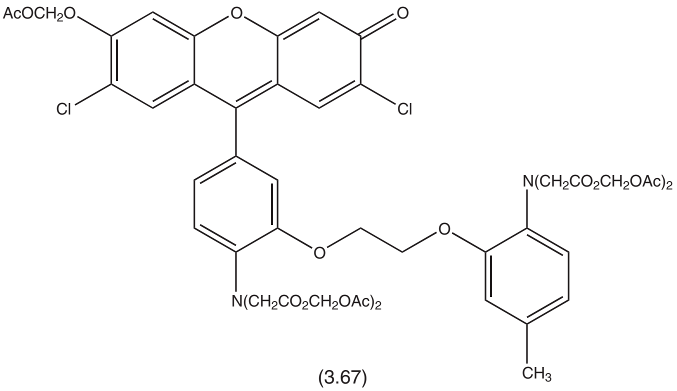
Changes in intracellular free Ca^{2+} concentrations can be measured, using fluorescent probes that show a spectral response upon binding Ca^{2+}, using fluorescence microscopy, flow cytometry and fluorescence spectroscopy. Fluorescent Ca^{2+} indicators are available in the form of the salt or ester, or conjugated with, for example, dextran. They are able to detect changes in intracellular Ca^{2+} over the range of <50 nM to >50 μM. Choice of indicator will dependant on the particular use and stimulating emission source.

A product that is widely used, and one that has also grown in importance since the advent of high throughput screening methods, is the AM (acetoxymethyl) ester of the fluoran derivative, Fluo-3 (3.67). This product, Fluo-3AM, does not itself bind Ca^{2+} but is readily hydrolysed to Fluo-3 by endogenous esterases once the dye is in the cells.

Fluorophores exist for other physiologically important ions, *e.g.* K^+, Na^+, Mg^{2+}, *etc*. (See also section 3.5.9.1.)

3.5.6.4 pH Indicators

The use of indicator dyes, such as phenolphthalein, methyl orange *etc.*, is an age-old practice in industry (Chapter 1, section 1.4), but measurement of pH within a cell requires a different strategy. Greater sensitivity is required for optical pH measurements inside living cells and this can only be provided by specially adapted fluorescent indicator dyes. It is possible to measure pH with microelectrodes but the



(3.67)

fluorescent technique is operationally simpler and more compact. To quantitatively measure pH it is essential to match the indicator's pK_a to the pH of the experimental system. Consequently, it is necessary to have some pH indicators that can operate at near-neutral pH and others that work in acidic environments.

The main fluorescent pH indicator probes are based on fluorescein and therefore it is important to understand the pH-dependent ionic equilibria of it and its derivatives. In aqueous solutions above pH 9 the phenolic and carboxylic acid functional groups in the molecule are almost totally ionised (Figure 3.14). Upon acidification of the di-anion, firstly, protonation of the phenolic group occurs ($pK_a \approx 6.4$) to yield the mono-anion followed by the carboxylic acid ($pK_a < 5$), giving the neutral species of fluorescein. On further acidification the fluorescein cation ($pK_a \approx 2.1$) is generated. In strongly acidic environments fluorescein is non-fluorescent, only the mono-anion and di-anions are fluorescent, with quantum yields of 0.37 and 0.93, respectively. The pH-dependent absorption spectrum of fluorescein exhibits a blue-shift and

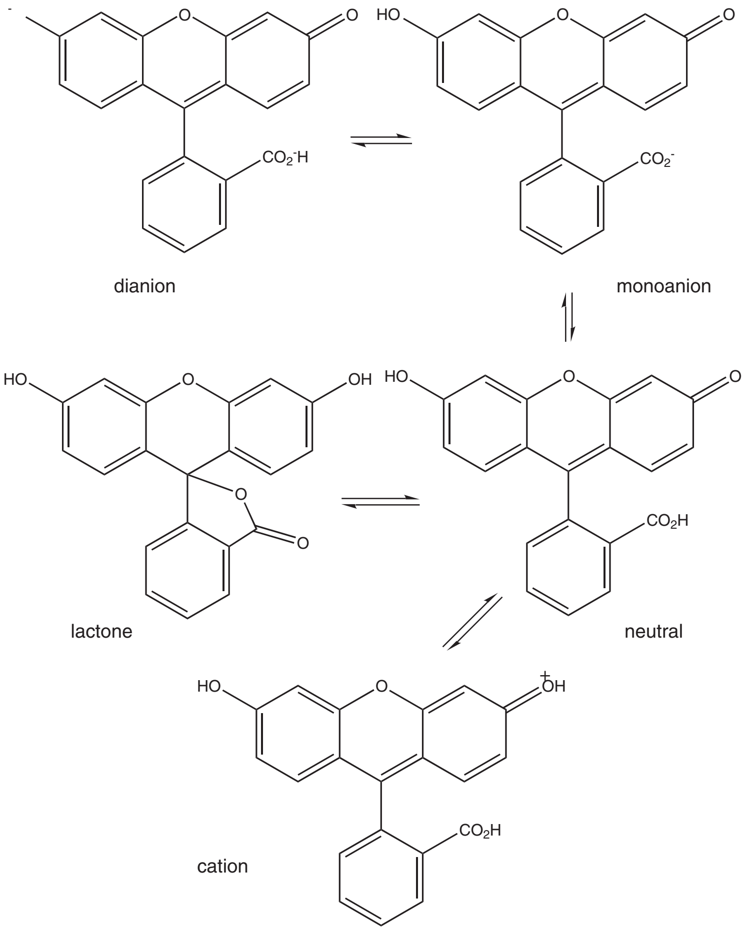


Figure 3.14 *Ionisation equilibria of fluorescein.*

decreased absorption indicating the formation of the protonated species, but the fluorescence emission spectrum of most fluorescein derivatives is dominated by the di-anion. As a result, upon excitation the wavelength and shape of the emission spectra is close to the di-anion absorption peak at 490 nm and relatively independent of pH. However, the fluorescence intensity is dramatically reduced at acidic pH. Although substitutions in the fluorescein molecule may shift the absorption and fluorescence maxima and change the pK_a of the dye, the effects of acidification on the spectral characteristics are generally maintained in fluorescein derivatives.

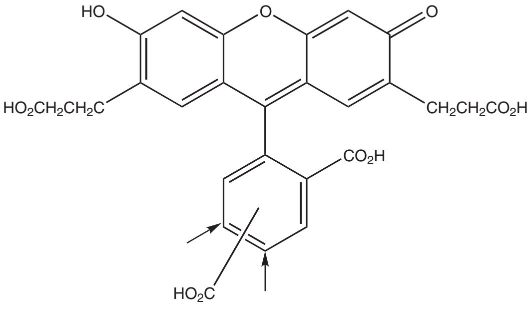
The most widely used pH indicator is the fluorescein derivative BCECF (3.68). Importantly, because its pK_a (6.97) is close to physiological pH, BCECF can detect cytosolic pH change with high sensitivity. At low pH, the dye is weakly fluorescent, becoming increasingly fluorescent as the pH rises. The excitation spectrum of the dye undergoes a slight shift during pH change, while the wavelength of the emission maximum remains unchanged. The pH is determined by the ratio of the relative fluorescent intensities measured at 535 nm when the dye is excited at 439 and 505 nm respectively (ratiometric method).

The fluorescent dye hydroxypyrenetrisulfonic acid (3.27), described in section 3.5.1.6, is used in medical monitoring devices for the pH of blood. Absorption (excitation) bands occur at 405 nm (acid form) and 475 nm (basic form) with emission (fluorescence) at 520 nm.

3.5.6.5 Membrane Potential Probes

Increases and decreases in cell membrane potential play a central role in many physiological processes, including nerve-impulse propagation, muscle contraction, cell signalling and ion-channel gating. When cells and organelles are too small to allow the use of microelectrodes, membrane potential measurements can be carried out using potentiometric optical probes. After many years of research fluorescent dyes have been developed that allow optical recording of important activities, e.g. brain activity, using real-time spectroscopy.[34]

The main classes of dyes used as potentiometric probes are cationic or zwitterionic styryl dyes, cationic carbocyanines and rhodamines, anionic oxonols and hybrid oxonols and merocyanines. The particular class of dye determines factors such as accumulation in cells, response mechanism and toxicity.



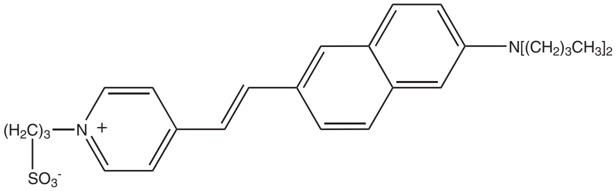
(3.68)

The styryl dye Di-4-ANEPPS (3.69) is a fast-responding membrane potential probe, particularly useful for the studies of neuronal membrane potentials.

Slow-responding dyes have a much higher fluorescent response than fast-response dyes. Carbocyanines are fast responding probes that accumulate in the cytoplasm of cells and then further accumulate in the cell organelles. The most commonly used carbocyanine is DiOC$_6$(3) (3.70). The barbituric acid derived dye, DiBAC$_4$(3) (3.71), is also a slow-responding dye that is widely used in measuring membrane potential. DiBAC$_4$(3) is also the dye of choice for HTS because its fluorescence is highly sensitive to membrane potential change (~1% mV^{-1}), and also because it can be optimally excited by the Ar$^+$ laser used in automated systems.

3.5.6.6 Lipid Membrane Probes

The dyes used for probing lipid membranes consist of a fluorophore with a long lipophilic tail. The lipophilic tail inserts itself into the membrane thus locating the fluorophore label on the membrane. These products are used as lipid labels and in cell tracking as part of biophysical studies. There are two main classes of fluorophore, aminostyryls and indocarbocyanines. The most widely used indocarbocyanine is the 18-carbon derivative of Cy3 known as diI, (3.72).



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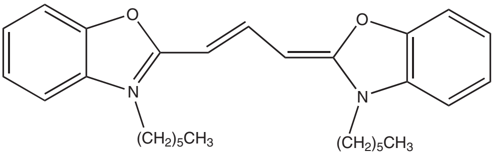

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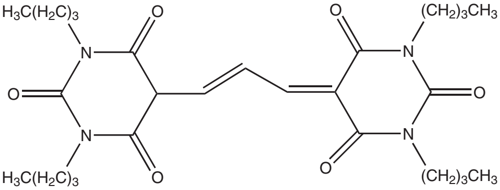

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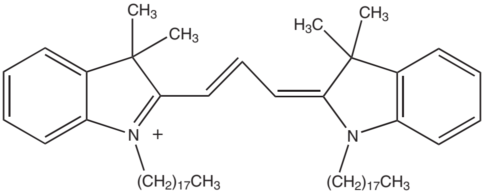


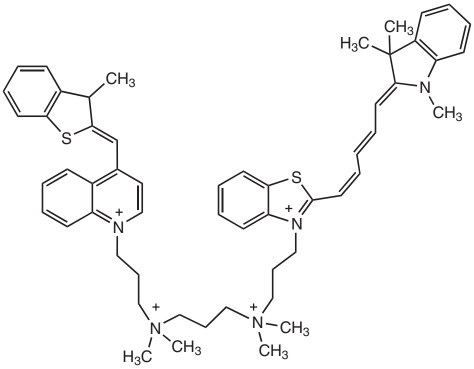
(3.72)

3.5.6.7 Non-covalent Labelling Agents for DNA

Where DNA within cells is being measured quantitatively, cyanine dyes are the products of choice. These dyes are assumed to bind to nucleic acids *via* intercalation with the purine and pyrimidine bases which leads to an increase in fluorescence. Increased affinity of the dyes with the nucleic acids is achieved by having two fluorophores linked *via* a short bridging group. The bridge can be between two molecules of the same cyanine or between two different cyanines, as in (3.73). By judicious molecular engineering of the two cyanines, one acting as an acceptor and the other as a donor, emission maxima over a range of wavelengths can be achieved. The high affinity of these bridged cyanines allows sample staining prior to capillary or gel electrophoretic analysis with similar detection sensitivity to radioisotopes.[29]

3.5.6.8 Covalent Labelling of Proteins and DNA

Visualising proteins by microscopy goes back over 50 years when fluorescent antibodies based on fluorescein and rhodamine isothiocyanates were first developed for this purpose. However, from the mid-1980s onwards research has produced many new reagents that give fluorescent antibodies having a wide range of colours, allowing simultaneous visualisation of multiple antigens. These developments have produced an explosion in application technologies. Examples include: immunoassay, microscopy, flow cytometry, high-throughput DNA sequencing, DNA mutation detection *etc*. High throughput, automated sequencing of nucleic acids was the fun-



(3.73)

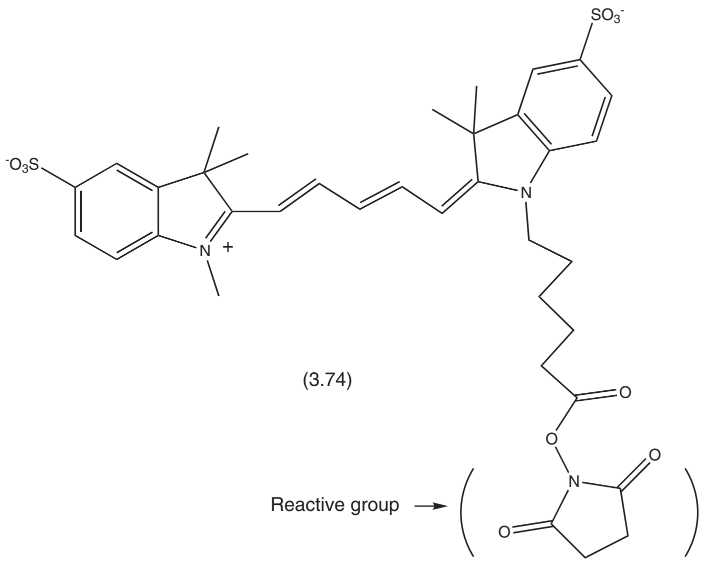
damental technique used in the human genome project and this was based on fluorescent labelling.

The factors required for a dye to act as a good covalent fluorescent label have been defined.[29] Some of the chromophore dependent issues are discussed below.

Brightness. Brightness of a fluorophore is proportional to the product of the molar absorption coefficient at the excitation wavelength times its quantum yield. This is the theoretical value, but in practice it can be much reduced by fluorescent quenching on interaction with other labels on the protein or DNA surfaces. Sulfonic acid groups on the aromatic rings of cyanines reduce this interaction, giving very much improved protein fluorescence.

Labelling Chemistry and Sequencing. The two main groups for labelling proteins are amine reactive and thiol reactive. For reaction with the amino groups in proteins the fluorophore is converted into the succinimidyl ester derivative by reaction with *N*-hydroxysuccinimide, *e.g.* (3.74), and for reaction with thiols group this is achieved by making iodoacetamide or maleimide derivatives, *e.g.* (3.75).

An alternative to this chemical labelling involves the use of labelled nucleotide analogues. These are produced by the coupling of dyes to amino modified nucleotides and are used in DNA sequencing. The sequencing of DNA relies on the fact that labelled nucleotides will pair with complementary stretches of the chain: guanine on one chain links to a cytosine counterpart (G-C) and adenine links to thymine (A-T). In one method, dye-labelled primers are added before elongation, which is followed by termination with a dideoxynucleotide in a two-vessel process, Alternatively the use of dye-labelled terminators, which are labelled dideoxynucleotides, allows elongation and termination of DNA polymerisation in a single ves-



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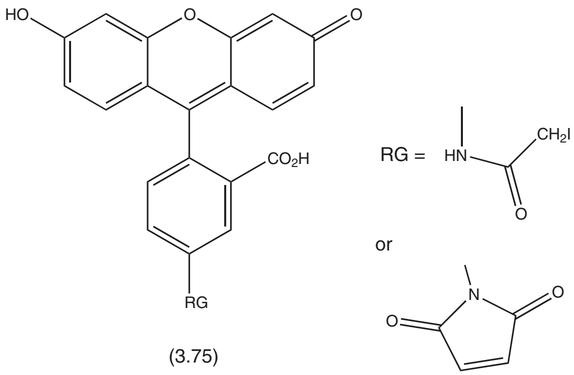


(3.75)

sel. This is shown schematically in Figure 3.15. In both methods subsequent analysis is by electrophoresis using fluorescent detection.

Photochemical Stability and the Wavelength of Excitation. Cyanines of chain length beyond Cy3 suffer from increasing photochemical instability. This can be a problem when they are used in conjunction with solid-state lasers operating around 630–650 nm. To overcome these problems workers at Boehringer Mannheim have developed the so-called 'pentacyclic' fluorescent labels based on either the oxazine or rhodamine ring systems, *e.g.* Light Cycler Red 640 NHS (3.76).[35]

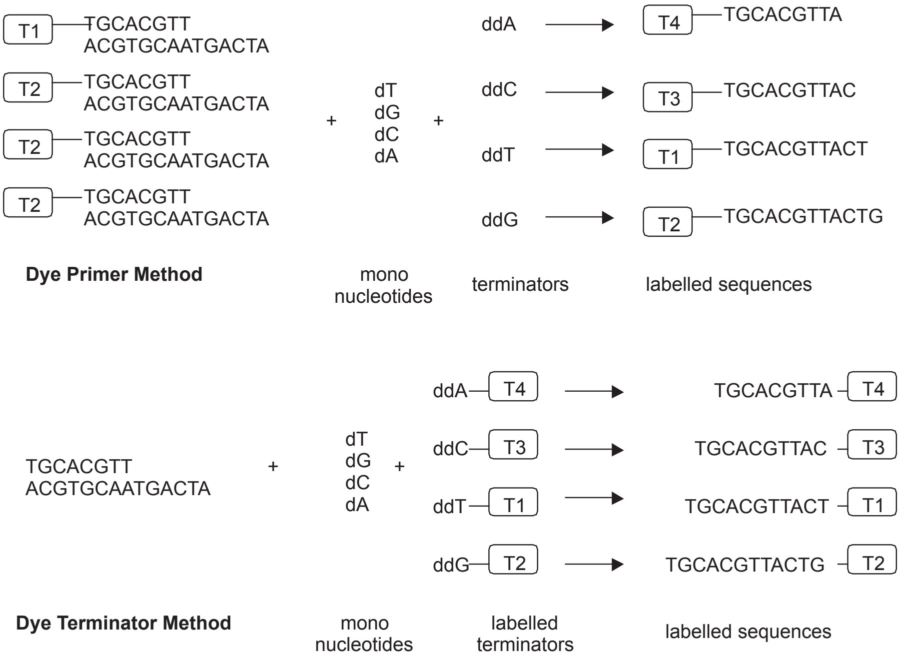
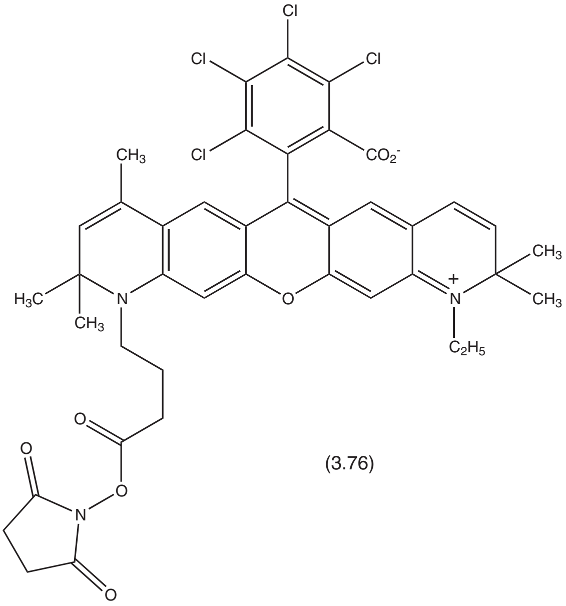


Figure 3.15 *DNA sequencing by dye primer and dye terminator methods.*



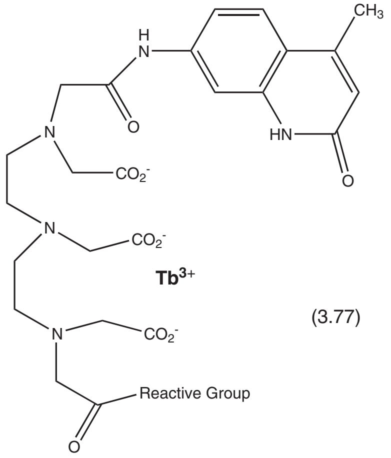
(3.76)

3.5.6.9 Lanthanide Chelates in DNA and Protein Studies

The use of lanthanide chelates in biological assays is largely restricted to those from Eu^{3+} and Tb^{3+} ions. To produce luminescence in the lanthanide^{3+} ions the f–f transitions need to be excited, something that is quite difficult. The problem has been overcome by using photonic antennae. These are intrinsically strong photon absorbers that channel their excited state energy across to the nearby metal centred excited states causing luminescence. The chelates are chosen so that they tightly bind the lanthanide ion, excluding water from the coordination that would otherwise quench the luminescence. A variety of antennae have been attached to many ligand systems for this purpose, including acetylacetonates, macrocyclic polyaminocarboxylates, crown ethers, cryptands and polypyridines.[36]

For protein and DNA studies several methods of locating the lanthanide probe onto the chain have been employed. In one example the antenna fluorophore is covalently attached to one leg of the chelate of europium or terbium, which is further attached to the specific site through thiol reactive, *e.g.* maleimide, or amine reactive, *e.g.* *N*-hydroxysuccinimide, groups. A typical example is shown in (3.77).[37]

An alternative procedure has been devised for the homogeneous assay of single stranded DNA. This involves using a probe strand of DNA carrying the Eu^{3+} chelate. A short spacer is used to attach phenanthradinium intercalator group to a photon antenna as in (3.78). Upon hybridisation of the probe and the target strands of DNA the antenna comes close to the Eu^{3+} centre, causing luminescence.[36] This is illustrated schematically in Figure 3.16.



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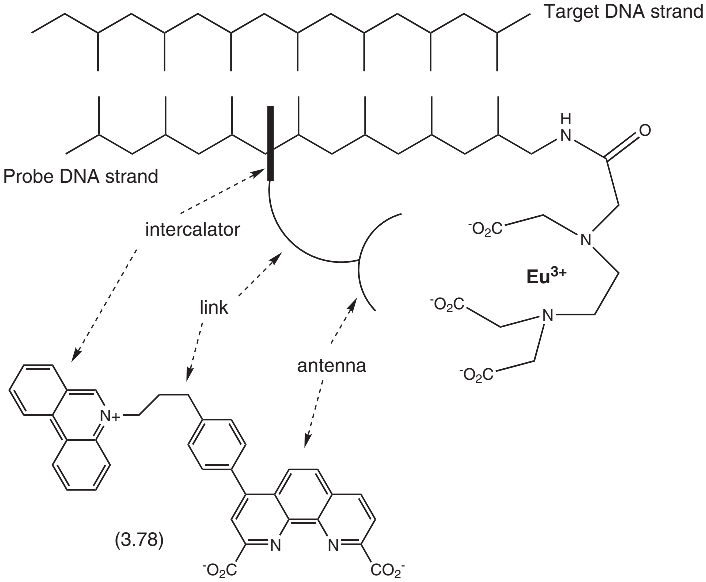


(3.78)

Figure 3.16 *Schematic of Sammes' homogeneous DNA assay.* (Reproduced with permission of the American Chemical Society.)

3.5.7 Luminescent Signalling for Sensors and Switches

Although in this text they are not described as such, many of the applications described in section 3.5.6 fall into the category of luminescent signalling. For instance, the detection of Ca^{2+} in section 3.5.6.3, the measurement of pH in section 3.5.6.4, and the use of lanthanide chelates in DNA studies outlined in section 3.5.6.9 all use the change in fluorescence for both the signalling and quantification of the target.

Luminescent signalling systems can be devised to show both molecule–molecule and molecule–atom interactions. The signalling principles of the most useful systems have been classified into the following main categories:[36]

- Metal centred excited states; emission from lanthanides
- Charge transfer excited states: internal charge transfer (ICT) states, metal-to-ligand charge transfer (MLCT) and twisted internal charge transfer (TICT) states
- Photoinduced electron transfer (PET) systems
- Electronic energy transfer (EET) systems

As stated, examples of the enabling of the emission by the use of lanthanides have already been given in 3.5.6.9.

3.5.7.1 Charge Transfer Excited States (ICT and TICT)

Conjugated, donor–acceptor systems containing π-electron undergo internal charge transfer on photoexcitation. These ICT excited states react with dipolar solvents (solvatochromism – see Chapter 1, section 1.6) and ions causing shifts in fluorescence excitation and emission spectra. It is by measuring these shifts that the properties of the species causing the changes can be evaluated.

There are very many diverse examples of the ICT phenomenon, a classic one being the use in Ca^{2+} binding exemplified by (3.67) in section 3.5.6.3. One neatly contained area, and also an important one, is that covering the use of crown ethers, cryptands and related molecules attached to fluorophores in the analysis and sensing of metal ions. The determination or detection of metal ions in various complex situations is of great interest to those working in the biological, medicinal and environmental fields, and some examples have already been given in section 3.5.6.3. The methodology involves the use of derivatives of chelates whose fluorescence intensity and wavelength undergo changes on formation of complexes with metal ions. Since they coordinate with metal ions these products are known as fluoroionophores. The major products in this area are based upon crown ethers, cryptands and the related calixarenes.

Structurally the fluoroionophores are made up of a fluorophore and a receptor chelate, sometimes linked by a spacer. Three different ways of connecting the fluorophores with the receptors are shown in Figure 3.17.[36]

In this book we will categorise these fluoroionophores according to the chemical class of the fluorophore that is attached to the receptor.[38]

Crowns and Cryptands Containing Coumarins. The complexing receptor group can be attached to the fluorescent coumarin in several ways. It has been fused onto the benzene ring at the 6,7-positions (3.79), linked to the 3-position (3.80) and attached to give a 7-amino derivative as in (3.81). Compound (3.79) is used for extracellular K^+, (3.80) complexes with alkaline earth and transition metals showing a shift to longer wavelengths, whilst (3.81) is used for targeting Li^+.

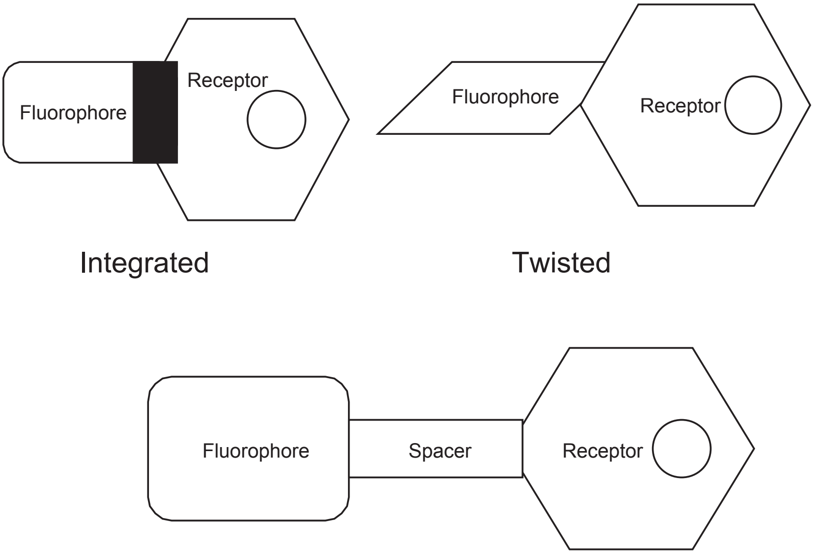
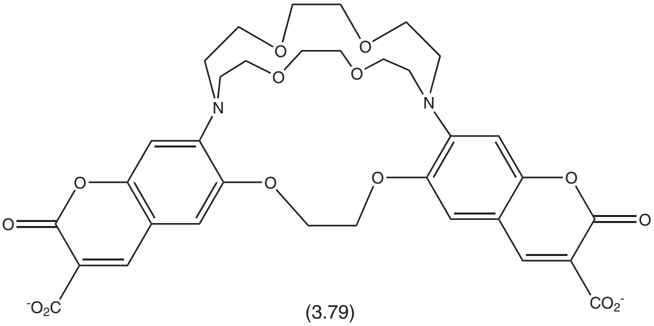
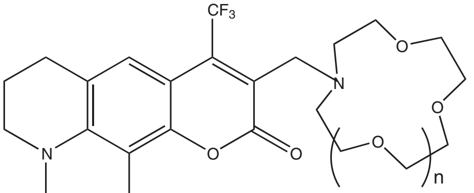


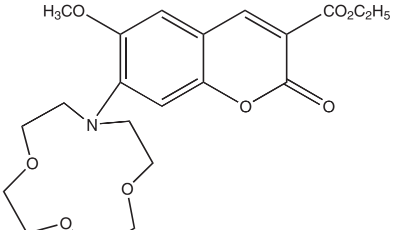
Figure 3.17 *Different ways of connecting fluorophores and receptors.* (Reproduced with permission of the American Chemical Society.)



(3.79)

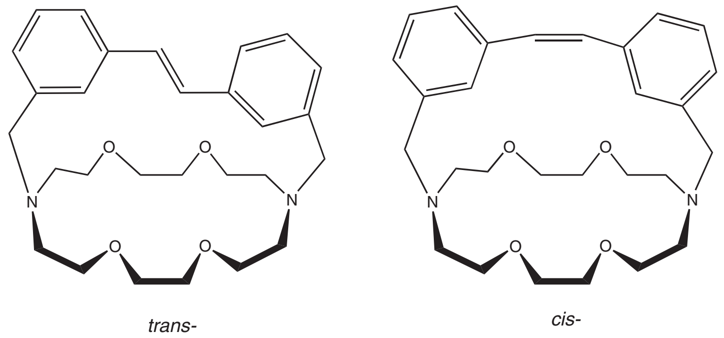


(3.80)



(3.81)

Crowns with Stilbene Fluorophores. Stilbenes undergo *cis–trans* isomerism on irradiation and this feature is exploited in (3.82). In the case of the *trans*-isomer, large ionic radius ions such as K^+, Rb^+ and Cs^+ give fluorescent complexes whilst the smaller Li^+ and Na^+ cause quenching. UV irradiation to the *cis*-isomer causes a considerable change in the conformation of the crown ether substructure and increases its ability to extract alkali metals, including Li^+ and Na^+, from water into benzene.



(3.82)

Crowns with Polymethines Dyes. The ready synthesis, see Figure 3.18, of crown ethers attached to polymethines or hemicyanines has made these compounds a fertile area of research and application in metal ion sensing. All of these polymethine derivatives are cation responsive: e.g. (3.84b) forms complexes with Na^+, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} with an increase in fluorescence intensity.

Metal-to-ligand charge transfer (MLCT) systems are mostly based upon complexes of ruthenium and rhenium. The simplest and best known example of a MLCT lumophore is tris(2,2'-bipyridyl)ruthenium(II) where photon absorption leads to an excited state composed of a Ru^{3+} centre and a radical anion on one of the bipyridyl units.

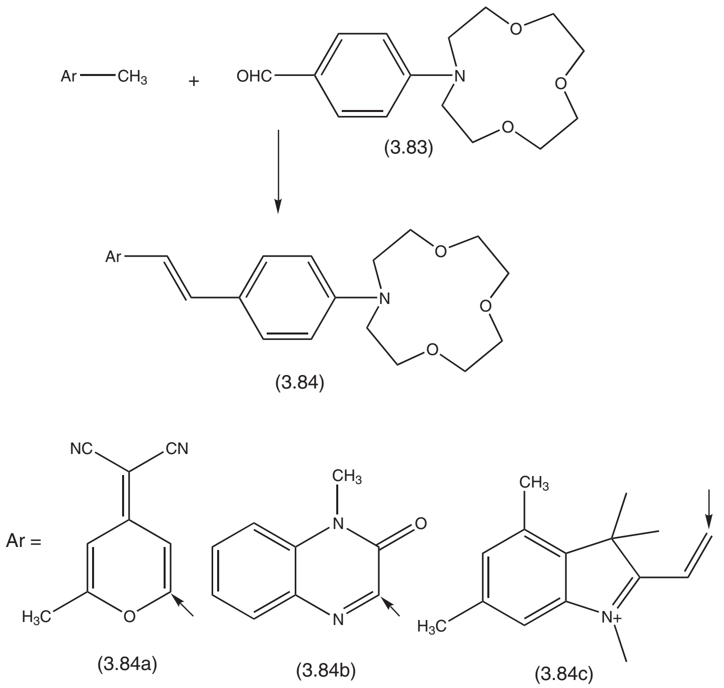


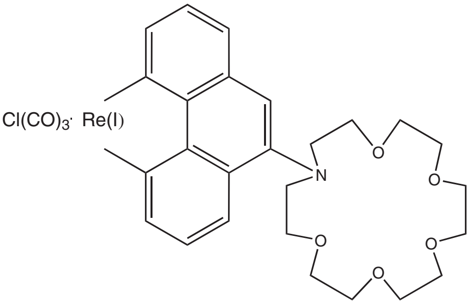
Figure 3.18 *Polymethine bearing crown ethers.*

Such systems can undergo ion recognition when made up of a ruthenium or rhenium polypyridyl lumophore and a crown ether receptor for metal ions, similar to the ICT examples given above. There are many examples in the literature, but one will have to suffice in this context.[36] Compound (3.85) is interesting because it shows significant luminescence enhancement with Pb^{2+}.

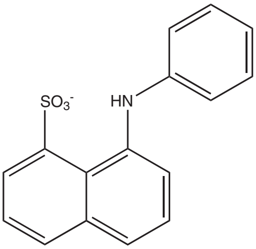
A TICT state is observed when the donor–acceptor components of a π-electron system in an excited state are twisted around a central σ-bond. This causes a larger charge separation, an enhancement of fluorescence and a greater sensitivity to environmental effects. Some of the oldest sensors for assessing local environmental effects in systems are derived from compound (3.86). These show a switching on of fluorescence, with a blue-shift, when moved from an aqueous to a hydrophobic environment and hence are used for measuring environmental polarity. TICT excited states can also be used for recognition of ions such as H^+, Ca^{2+}, and Zn^{2+}, *e.g.* (3.87) for H^+, and for organic molecules in conjunction with β-cyclodextrins, where the fluorophore is displaced from the cyclodextrin cavity by the incoming molecule, *e.g.* 1-adamantol and related structures, causing a large reduction in emission.

3.5.7.2 Photo Induced Electron Transfer States (PET)

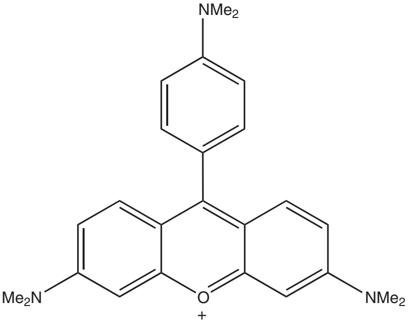
Upon photoexcitation, lumophores, especially those with groups held outside but close to the π-electron system of the lumophore, show an increased susceptibility to redox reactions. Knowledge of the redox potentials of these reactions can be used



(3.85)



(3.86)



(3.87)

to tailor PET processes that can be switched on or off. Guest binding to the molecules also causes large changes in redox potential, a feature that has important consequences in designing PET sensors and switches.

The OFF and ON states for fluorescent PET signalling using stoichiometric host–guest recognition are shown schematically in Figure 3.19. In the OFF state the excited state energy must be bigger than that required to oxidize the receptor and to reduce the fluorophore thus allowing PET from receptor to fluorophore. In the ON state a cation in the receptor cavity raises its oxidation potential, causing the thermodynamic condition for PET to be removed and the fluorophore to undergo emission.[36] In other words when the sensor molecule is subjected to light energy an electron is transferred from the receptor to the fluorophore, taking energy from its excited state and rendering the system non-luminescent, the process being reversible in the absence of light. However, if the receptor traps a guest its lone pair of electrons become bound up, electron transfer does not occur and the excited state energy of the system is released as emission from the fluorophore.

Some examples of OFF/ON sensors are (3.88) for Na^+, (3.89) for pH in acidic interiors of lysosomes within cells, (3.90) signals glucose, all of use in medical outlets, whilst (3.91) can signal for Cu^{2+}, useful in monitoring for the metal in the environment. Systems can also be devised where the converse is true, *i.e.* ON/OFF systems where the fluorescence is switched off by the incoming guest.[39]

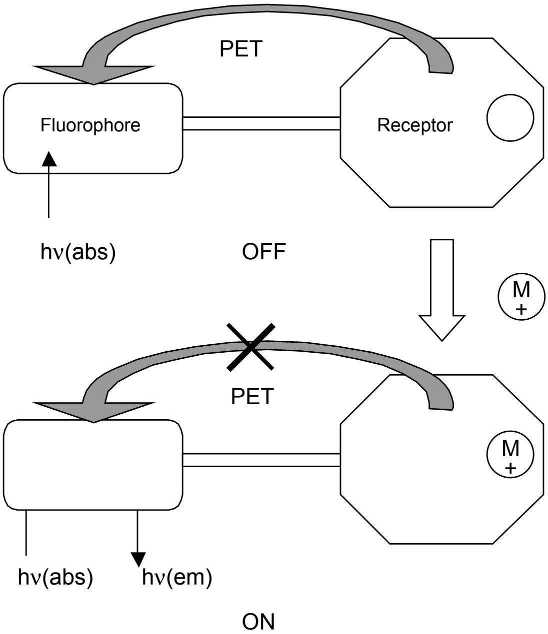
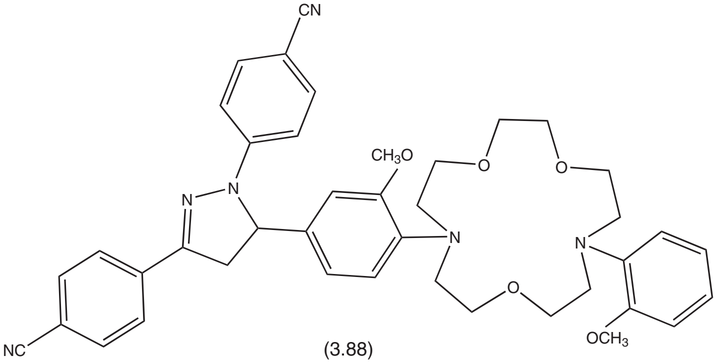
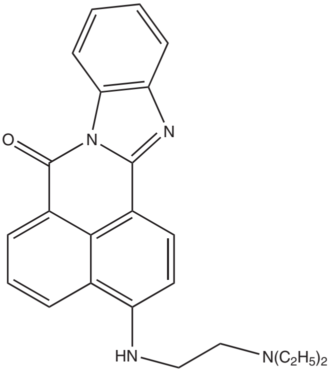


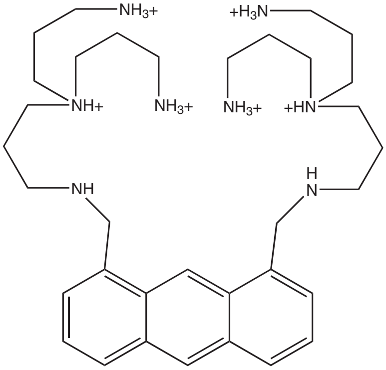
Figure 3.19 *OFF and ON states for PET.*
(Reproduced with permission of the American Chemical Society.)



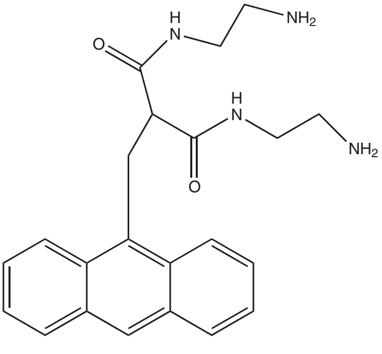
(3.88)



(3.89)



(3.90)

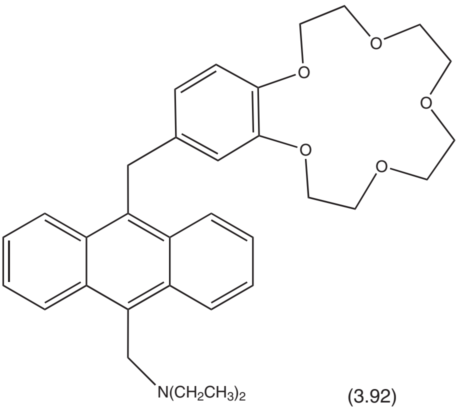


(3.91)

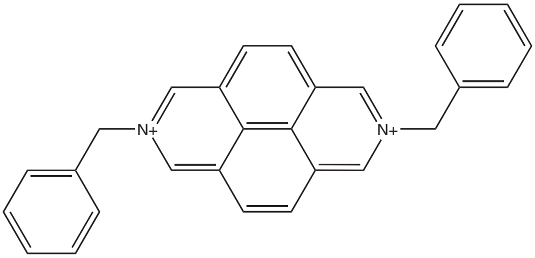
3.5.7.3 Molecular Information Processors

A very interesting extension of the use of PET, being explored by several schools of researchers, is in the construction of molecular scale information processors as YES, NOT, AND or XOR (exclusive-OR) and other logic gates. The use of chemical input and photonic output is a developing field of research. For example, a YES gate molecule is one that fluoresces in the presence of H^+, and a NOT gate molecule is one whose fluorescent emission disappears when H^+ is added. An example of an AND logic gate action would be when two molecular recognition events occur at the same time. Compound (3.92) is a case in point; the inputs are Na^+ in the crown moiety and H^+ on the tertiary amine and when both are bound there is no PET and the system fluoresces.[40]

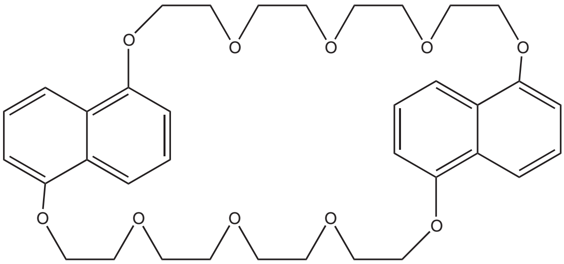
Pseudorotaxanes formed by the interaction of (3.93) and (3.94) provide an example of XOR logic gates. The pseudorotaxane is non-fluorescent due to PET type charge transfer, but is dissociated either by association of (3.93) with tributylamine or by protonation of (3.94) and the system fluoresces. A stoichiometric addition of each causes neutralisation and the non-fluorescent pseudorotaxane reassembles.[41]



(3.92)



(3.93)



(3.94)

This is a burgeoning area of research and it is now obvious that this type of work holds out the potential for molecular computers and neural networks using photon mode input (see also Chapter 5, section 5.7).[42]

3.5.8 Fluorescent Sensing of Biologically Important Gases

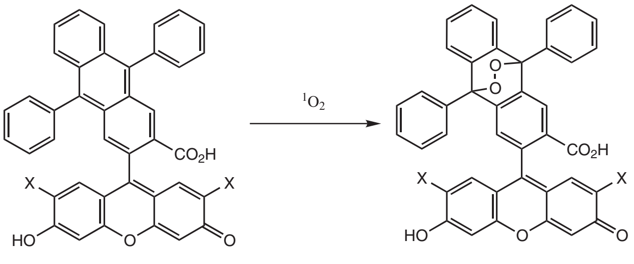
The detection and measurement of gases has important applications in environmental monitoring (see section 3.5.9) and in the biological and medicinal fields, where much work is being carried out on both singlet oxygen and nitric oxide.

The excited state of molecular oxygen, singlet oxygen ($^1O_2$) is an important toxic reagent because it can oxidise a range of biological molecules, including DNA, proteins and lipids. It is involved as the active species in important new therapies for the treatment of cancer and other diseases, *e.g.* by photodynamic therapy (see Chapter 4, section 4.6.2). The first fluorescent probe for singlet oxygen involves trapping it on to a 9,10-diphenylanthracene moiety attached to a fluorescein fluorophore. Compound (3.95) reacts specifically with singlet oxygen, being unaffected by peroxide, superoxide and nitric oxide, to give the endoperoxide (3.96) which is strongly fluorescent.[43]

Nitric oxide is a gaseous free radical that plays a signalling role in the cardiovascular system and is implicated in many areas of the central nervous system. Therefore its real-time detection in living cells is a prime target for sensor researchers. A sensor for NO in bioimaging must react at normal temperature and pressure in water at neutral pH, be specific, high yielding and stable, localised in cells and show a marked change in fluorescence on visible light excitation. Significant progress has been made recently towards fulfilling these requirements.[44] The method involves the use of a diaminofluorescein derivative (3.97), which permeates into the cell where it is hydrolysed by an esterase to the non-permeable (3.98). Reaction with NO produces the highly fluorescent triazole derivative (3.99) as shown in Figure 3.20.

3.5.9 Fluorescent Reagents in Photometric Chemical Sensors

Since this book is concerned with colour chemistry only those sensors that rely on measuring an optical response, whether this is a change in absorption or emission,



X = H. Cl, F

(3.95)

(3.96)

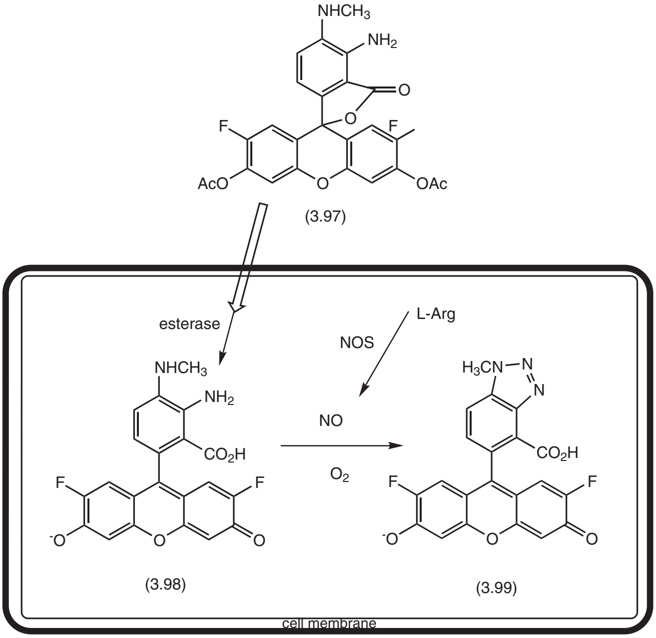


Figure 3.20 *Schematic of NO sensor behaviour in the cell.*
(Reproduced with permission of Wiley-VCH.)

will be considered. A chemical sensor is one that provides information about its chemical environment whilst a biosensor is one that incorporates a biological entity in its sensing process. However, chemical sensors can be used in a biological environment, *e.g.* the use of chemical sensors to measure pH or Na^+ and K^+ in biological fluids, and this can lead to a confusion of the terms.

The main photometric behaviours that are exploited in chemical and biosensors are as follows:[45]

- UV–Visible absorption
- Fluorescence
- Chemiluminescence
- Bioluminescence

Photometric sensors are known as 'optrodes' (as opposed to electrodes) or 'optodes'. Those reagents, which rely on an ionochromic response, leading to a change in the visible absorption spectrum are known as chromoionophores, and are described in Chapter 1 (section 1.4). The use of chemiluminescence and bioluminescence will be covered later in this chapter, sections 3.6 and 3.7 respectively. References to the use of fluorescent reagents in sensing have been scattered throughout the preceding sections of this chapter (sections 3.5.6, 3.5.7 and 3.5.8) and the objective of this part is to draw the various strands together and to provide specific examples of their application in practical photometric sensors.

As a means of communicating optical information many sensors employ fibre optic technology. The fibre can be used purely as a light guide for carrying spectroscopic information from a sensing source, *e.g.* detecting fluorescent contaminants in underground waters, or it can be combined with reagents that respond in the sensing environment and with the resulting information transferred back along the fibre to the detector. Therefore, reagent-mediated chemical or biosensors consist of a light source, an optical detector, optical fibres and immobilised reagents as shown schematically in Figure 3.21.[46] Optical fibres were originally made from a variety of glasses but are now normally made of a polymeric material. The light sources can be dye lasers (see section 3.5.3), LEDs (3.8.1) or laser diodes (see Chapter 5, section 5.5), which with the advent of blue lasers allows the whole visible spectrum to be covered. Immobilisation of the reagent is achieved by several means including entrapment in polymeric matrices, such as plasticised PVC or by using sol–gel methods, cross-linking to give fine films and covalent bonding onto the optical substrate, either the fibre or a wave-guide.

The fibre can also be used as an active component rather than as just a means of transporting light, one example being the so-called evanescent wave systems. An optical fibre consists of an optical core surrounded by a plastic cladding of lower refractive index. The electromagnetic field of light propagating in an optical fibre extends beyond the core into the external cladding, creating the evanescent wave. Replacing the internal cladding with the sample solution or a coating allows this to act as the lower refractive index medium and so interact with the evanescent wave. A typical evanescent wave sensor is one where fluorescent labelled antibodies are bonded onto the outside of the optical core.[47]

3.5.9.1 Ion-selective Optrodes

Mention has already been made in section 3.5.6.4 of a sensor designed for measuring the pH in biological fluids, such as blood, based on the pH dependent changes of trisodium 8-hydroxypyrene-1,3,6-trisulfonate (3.27), which occur in the physiologically important range of pH 7.0–7.5. The fluorescent reagent is immobilised onto aminoethylcellulose fibres *via* its sulfonochloride derivative and then these are embedded in an ion-permeable polyurethane based hydrogel material.

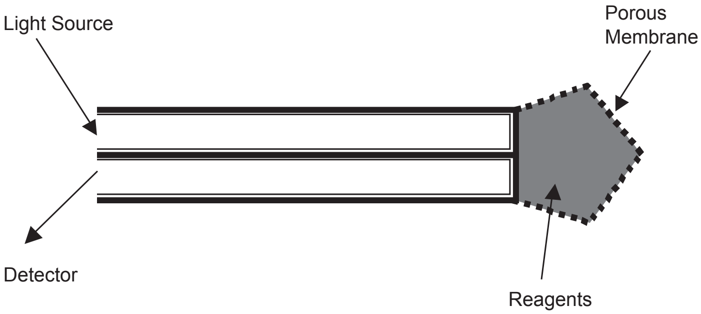


Figure 3.21 *Fibre optic based, reagent-mediated sensor.*

A sensor for halides, Cl^-, Br^- and I^-, using fluorescence quenching of either acridinium or quinidinium-based fluorescent reagents covalently bound to a glass support *via* carbodiimide has been described.[45] Other examples are sensors for Na^+, K^+ and Ca^{2+}. [45,46]

3.5.9.2 Gas Sensors

Oxygen and other gases are very efficient fluorescence quenchers and this property has been used to produce sensors. For oxygen sensing, a butyric acid derivative of perylene is placed on a polyacrylamide support, which when it is excited by light of wavelength 468 nm emits at 514 nm. The intensity of the emission decreases as oxygen levels increase. A similar method has been used for sulfur dioxide using benzo[*b*]fluoranthrene. An alternative method is to use fluorescence lifetime as the means of transduction. This type of sensor uses Ru^{2+} complexes of 1,10-phenathroline or 2,2'-bipyridyl entrapped in thin films made by a sol–gel process which are dip coated onto the fibre. Excitation is by light from a blue LED at 450 nm passing down the fibre and the lifetime of the emission at 610 nm is 205 ns in the absence of oxygen.

3.6 Chemiluminescence

Chemiluminescence is the production of light by chemical substances without the help from other energy sources; in effect it is the conversion of energy stored in chemical bonds into light. Mechanistically, chemiluminescence involves several consecutive processes. The first step is the chemical reaction to form a product, which can undergo further highly exothermic transformations of sufficient energy to emit light in the visible region (400–700 nm) of the spectrum. For this to occur the reaction enthalpy must be in excess of 40 kcal mol^{-1}. In the second step, chemical potential energy is transformed into electron excitation energy by a reaction intermediate entering an electronically excited state. The final step is the loss of energy from this excited state, as fluorescence or phosphorescence depending on whether the orientation of the spin in the excited intermediate is singlet or triplet (see Figure 3.1). This is called direct chemiluminescence as opposed to indirect chemiluminescence in which the electronically excited state transfers energy to a suitable acceptor which itself emits light.

3.6.1 Chemiluminescent Reactions

The most useful chemiluminescent reactions fall into three catogories.[1,48]

- *Reactions involving electron transfer.* Reaction of free ion radicals, oxidation of anion radicals of aromatic and heteroaromatic hydrocarbons. Usually an energy acceptor is required to be present
- *Reactions of singlet oxygen.* Singlet oxygen, *e.g.* generated by the action of chlorine on alkaline hydrogen peroxide, transfers its energy to a fluorophore acceptor, which emits light

- *Peroxide decomposition.* Singlet oxygen can also react with organic molecules to form endo- and cycloperoxides (oxetanes), which undergo thermal decomposition in a highly exothermic process. In the presence of an acceptor molecule this process offers the most effective chemiluminescent reaction with high intensity light emission

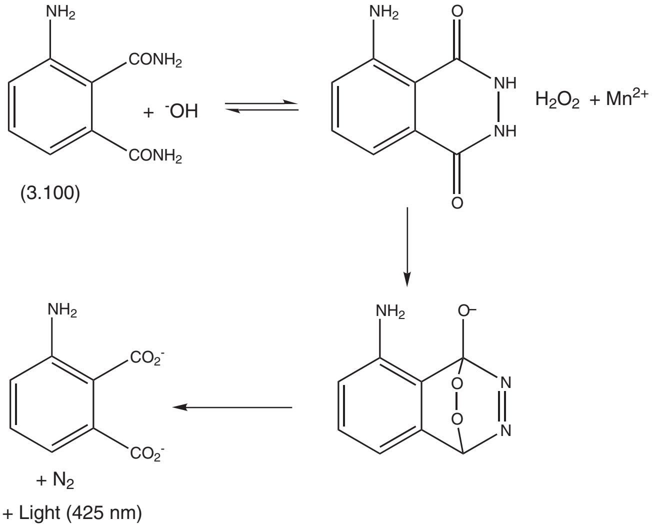
3.6.1.1 Luminol Oxidation

The best known and most useful of the chemiluminescent reactions involving electron transfer is the oxidation of luminol (3.100) or its derivatives in alkaline medium. 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+} and Mn^{3+}, or haem and haemproteins, *e.g.* peroxidases. The reaction mode is shown in Figure 3.22.[49]

Quantum yields from (3.100) 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). The reaction with alkaline peroxide produces *N*-methylacridone, which emits light at 442 nm.



(3.100)

Figure 3.22 *Luminol oxidation.*

3.6.1.3 Dioxetanes

A very large number of chemiluminescent reactions go *via* peroxides, especially the very unstable 1,2-dioxetanes. The origin of the chemiluminescent effect is shown schematically in Figure 3.23, where further enhancement occurs in the presence of an acceptor.

In 1989 a new design procedure for a more stable chemiluminescent sensor was proposed using dioxetanes.[50] This is illustrated in Figure 3.24, together with a commercially available dioxetane AMPPD (3.101), that is based on these principles. In (3.101) stability is provided by the adamantyl group whilst the dioxetane is the energy source. Hydrolysis of the phosphate ester with alkaline phosphotase produces the adamantyldioxetane anion (3.102), which is unstable, decomposing readily at room temperature with bright light emission. This chemiluminescent reaction, which has a quantum yield of 20–30%, is of use in many types of assay that involve phosphate ester hydrolysis using alkaline phosphatase.

3.6.2 Chemiluminescent Applications

The oxidation reactions of luminol and lucigenin can be used to assay for H_2O_2. For example, 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 can be measured using cholesterol oxidase. 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 catalysts.[1,48] Some examples of the use of luminol, isoluminol and their derivatives in immunoassays are shown in Table 3.11.[47]

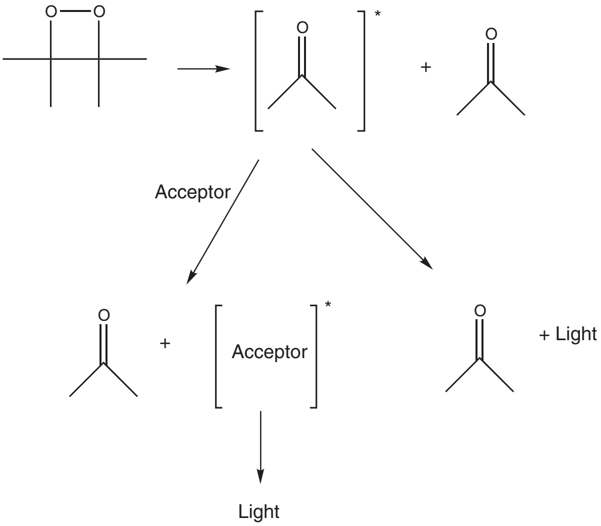


Figure 3.23 *Chemiluminescent decomposition of dioxetane.*

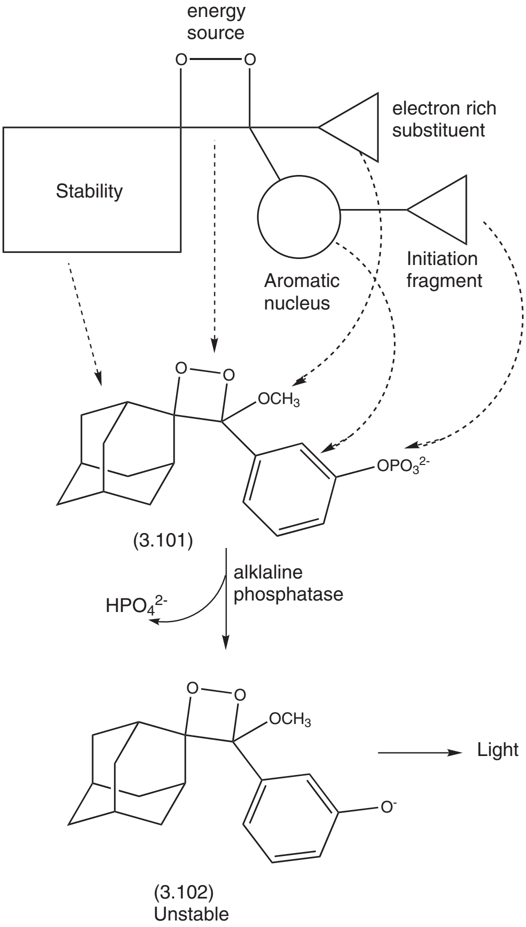


Figure 3.24 *Design principles and reactions of AMPPD (3.101).*

Table 3.11 *Chemiluminescent assays using luminol and its derivatives*

Analyte	*Label*	*Chemiluminescent reactants*
Human IgG	Luminol	H_2O_2–Haemin
Testosterone	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

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 detection limit is reported to be 1–10 mM H_2O_2 with a response time of 2 min.[45]

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 other animals such as jellyfish, scale-worms, deep-sea squid, prawn and fish. In animals bioluminescence is used as a diversionary tactic when disturbed, to attract prey and of course as a mating signal during courtship.

Bioluminescence is essentially a chemiluminescent reaction catalysed by a specific enzyme, *e.g.* luciferase in the case of the firefly *Photinus pyralis*. 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 exhibiting a 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 and a luciferase, a substrate, a trigger, and sometimes an ancillary emitter. The structure of the luciferins and luciferases depend on their source in nature and this method of categorisation will be followed in the text below.[48b]

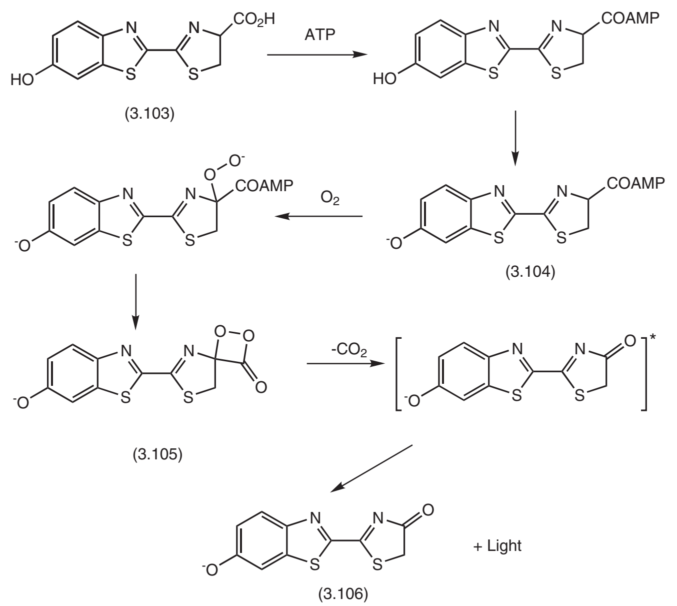
3.7.1.1 Firefly Luciferins

The firefly luciferin, the structure of which is based on two thiazole units (3.103), undergoes a luciferase-catalysed oxidation with the emission of light (562–570 nm), in the presence of the cofactor MgATP (adenosine triphosphate). The chemical processes leading to light emittance are shown in Figure 3.25. Luciferin reacts with MgATP, eliminating pyrophosphate to form luciferyl adenylate (3.104), which reacts with oxygen in a two-stage process to produce the dioxetanone (3.105) with elimination of AMP. The reactive dioxetanone then decarboxylates to give the excited state of oxyluciferin, which returns to its ground state (3.106) 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 planktons living in the oceans. The bacterial luciferases react with aldehydes and oxygen, in the presence of reduced flavins, such as $FMNH_2$ (3.107), to produce carboxylic acids and an oxidised flavin FMN with the emission of blue light (478–505 nm).

$$\text{luciferin} + \text{ATP} + O_2 \xrightarrow{\text{luciferase}} \text{AMP} + \text{PP} + \text{oxyluciferin} + CO_2 + H_2O + h\nu$$



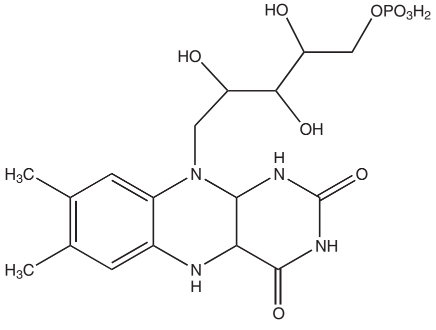
(3.103)

(3.104)

(3.105)

(3.106)

Figure 3.25 *Mechanism of luminescence in firefly luciferin.*



(3.107)

$$FMNH_2 + O_2 + RCHO \xrightarrow[\text{luciferase}]{} FMN + RCO_2H + H_2O + h\nu \text{ (490 nm)}$$

3.7.1.3 Imidazopyrazine Luciferins and Photoproteins

The imidazopyrazine substructure 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 stable cyclic dioxetanone, similar to the firefly luciferin as indicated in (3.108).

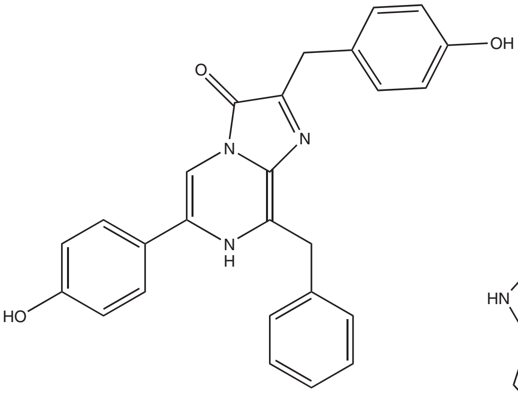
Decarboxylation of this intermediate on reaction with a trigger produces the activated oxyluciferin intermediate, which emits light on returning to the ground state.

The coelenterazine luciferin (3.108) can be covalently bound to a photoprotein, *e.g.* aequorin from the jellyfish *Aequorea victoria*, which after reaction with oxygen forms a complex that emits light on the addition of Ca^{2+} at a wavelength of 460–490 nm. In the case of the luciferin of 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), with which it forms a complex.[48*a*] The structure of the luciferin in *Cypridina* (3.109) is structurally analogous to the coelenterazine luciferin.

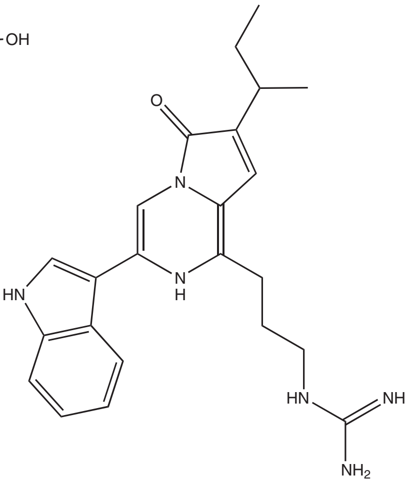
3.7.2 Applications of Bioluminescence

The firefly luciferin system is very sensitive and can be coupled to any enzymatic reaction that produces or uses ATP. 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 into ATP which then undergoes the reaction with luciferin as shown in Figure 3.25. 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.

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.[48*a*,*b*,51] 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 prop-



(3.108)



(3.109)

erties 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'.[51]

The GFP from the jellyfish *Aequorea victoria* is widely used a marker in gene expression. Cloning has been used to produce a structurally similar red analogue (λ_{em} 583 nm), called Ds Red, which is related to the red glowing protein in *Discosoma* corals.[32]

3.8 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. Low field devices are the conventional light emitting diodes (LEDs), which are constructed from monocrystalline semi-conducting materials, mostly group III–V compounds. Inorganic EL displays are generally high field and are made of insulating materials, where the active material or phosphor is a II–VI compound. Organic LEDs are made from either thin films of vapour deposited low molecular weight materials or conjugated polymers put down by spin coating or other means.

3.8.1 Semi-conductor Light Emitting Diodes

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, grown as a single crystal. This is shown diagrammatically in Figure 3.26.[52] When the material is 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 and holes into the n-type region, they then combine 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.)

In 1961 it was discovered that gallium arsenide (GaAs) p–n diodes emitted infrared light and this led to the first commercial LED from Texas instruments in late 1962. Around that time visible light emitting LEDs were developed by General Electric using gallium arsenide phosphide (GaAsP) and this quickly led to the development of yellow–orange LEDs by the use of different semi-conductor materials and dopants. Today the most commonly used materials for red–yellow and near-infrared LEDs are GaP, GaAsP, AlGaAs, and AlGaAsP.

Typical emission wavelengths for LEDs are:

GaP	550 or 700 nm
GaAsP	580 or 660 nm
Ga As	880 nm
Si	1100 nm
Ge	1810 nm

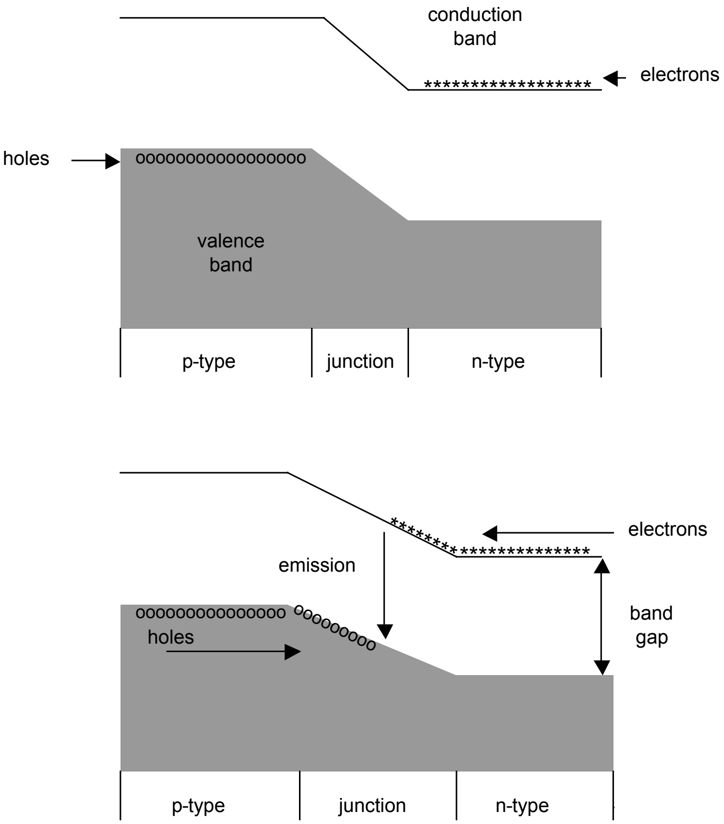


Figure 3.26 *Schematic for semi-conductor LED.*
(Reproduced with permission of John Wiley & Sons.)

The most difficult area over the years has been the development of blue–green and ultraviolet emitters and this was not successfully addressed until the early 1990s when 3M reported pulsed action from a ZnSe-based laser operating at 450 nm. This was followed by reports from Japan in 1995 of highly efficient blue gallium nitride (GaN) based diodes, commercialised in 1997 and with lasers following in early 1999 (see also Chapter 5, section 5.5).[53] Isamu Akasaki at Nagoya and Shuji Nakamura at Nichia Chemical Company in Japan carried out this pioneering work on the GaN based devices. The process involves the use of metal organic vapour phase epitaxy (MOVPE) to produce high quality GaN crystalline films and p-doping by irradiating doped 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 LED is shown in Figure 3.27.

The traditional outlets for LEDs have until recent years been in single colour displays, especially alphanumeric ones on instruments, and outdoor billboards and other displays, where they are used in arrays. Another use has been in bright warning lights such as those on the rear of cars and bicycles. However, with the development

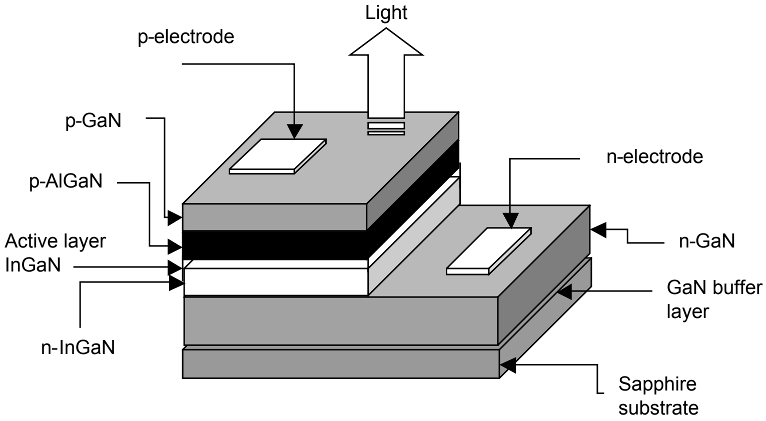


Figure 3.27 *Schematic of a blue LED.*
(Reproduced with permission of the Society of Chemical Industry.)

of efficient blue–green LEDs it is now possible to cover the whole spectrum of eye response (Figure 3.28), thus widening the application potential of these devices.

A good example of a new opportunity is the use of LEDs is in traffic lights and related pedestrian signals. These offer reduced power consumption and long lifetimes compared with conventional colour filtered incandescent bulbs and hence enormous savings in energy (around 40%) and labour costs. Penetration into the US market is predicted to reach 60% by 2005.[54] Very exciting opportunities have also been opened up in making novel white light LEDs. It is possible to make white light LEDs by mixing light from separate red, green and blue LEDs, but now the use of high intensity blue LEDs to excite phosphors offers a more compact route. Nichia have commercialised a device that uses a blue InGaN LED to excite yellow fluorescence from a yttrium aluminium garnet phosphor. The white light results from a mixing of the blue light from the LED and the yellow from the phosphor. These types of

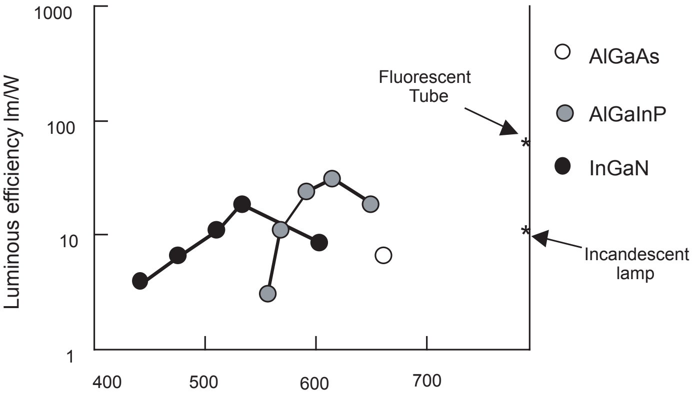


Figure 3.28 *Wavelength coverage of LEDs.*
(Reproduced with permission of the Society of Chemical Industry.)

devices are known as Hybrid LEDs. The way is now open for their use as backlights for full-colour LCD displays and replacing conventional light bulbs and lamps, *e.g.* in automobile lighting systems.

The main drawbacks in all this exciting technology are the cost of crystalline semi-conductor technology coupled with high power consumption, which may limit its application in the large area, high information, full-colour display panels.[55] Consequently, in recent years there has been a big drive to develop organic light emitting diodes (OLEDs) and polymer (PLEDs). These developments are described in the section below on EL display technologies (section 3.8.4). Closely related to LEDs are laser diodes and these will be covered in Chapter 5 (section 5.5).

3.8.2 Electroluminescent Display Technologies

Until the 1990s the majority of display devices were based on CRT technology (see section 3.3) but with the development of laptop computers there was a need for lightweight, flat panel displays and the system of choice to date has been the one based on liquid crystals (see Chapter 5, section 5.2), notably active matrix liquid crystal displays (AMLCD). However, AMLCD displays suffer from several drawbacks, which include the need to provide constant illumination to the screen by a backlight, leading to energy inefficiencies; the limited viewing angle and speed of response, which has restricted their use in video applications and the difficulty in manufacturing large area displays. Research and development of systems based on semi-conductor LED technology, which have the advantage of giving bright colours as needed with the power on and are black in the off state, has been going on for many years.[55] The devices can also be classified in respect of current, either AC (ACEL) or DC (DCEL). ACEL involves a thin film of luminescent material that is sandwiched between two neutral insulating layers separating the film from metallic contacts and excitation is by AC voltage waves or pulses. DCEL is produced by applying injecting electrodes to single crystal or thin films. Originally these materials were inorganic but a very active development area in recent years, leading to commercial products, has been that of organic LEDs (OLEDs).

3.8.3 Inorganic EL 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.[56] There are two broad classes of EL displays, with different areas of application: thick-film powder displays (PEL) are the oldest and have found uses in devices for signalling and lighting applications and the more successful thin-film devices (TFEL) which are used in high information content displays.[57]

3.8.3.1 Powder EL

Although discovered in 1936 by Destriau, high field EL was not really investigated in a practical way until the 1950s and 60s 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 TFEL, they are nowadays only used in low information content applications. A typical AC PEL device is shown in Figure 3.29, 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.[57] Standard colours are green, blue green, white and yellow depending on the dopant (see also section 3.2).

3.8.3.2 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 3.30. As can be seen 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 until 1978, when Sharp demonstrated a 240 × 320 display, that this problem was overcome.

The operating principle of a TFEL display is as follows.[57] The dissolved Mn atoms in the ZnS lattice are subjected to direct impact excitation by electrons that have been

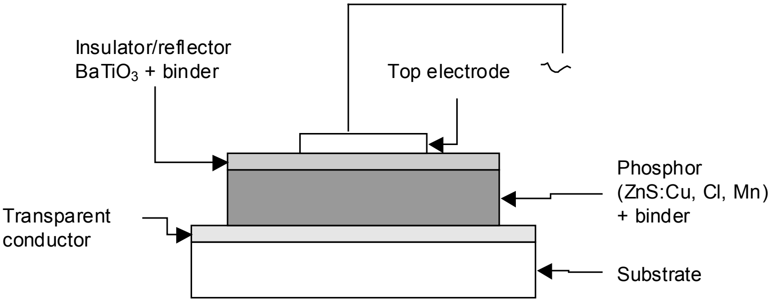


Figure 3.29 *An AC powder EL device.*

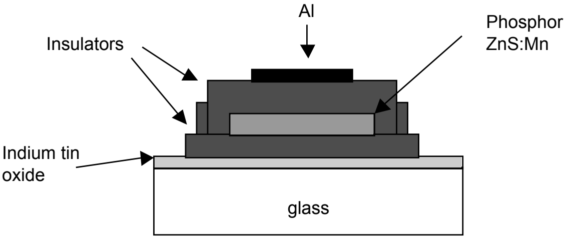


Figure 3.30 *Thin-film EL device.*

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 either 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, 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 (see also section 3.2.1).

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.[57] The two methods are shown schematically in Figure 3.31.

In terms of performance the patterned phosphor approach offers advantages in

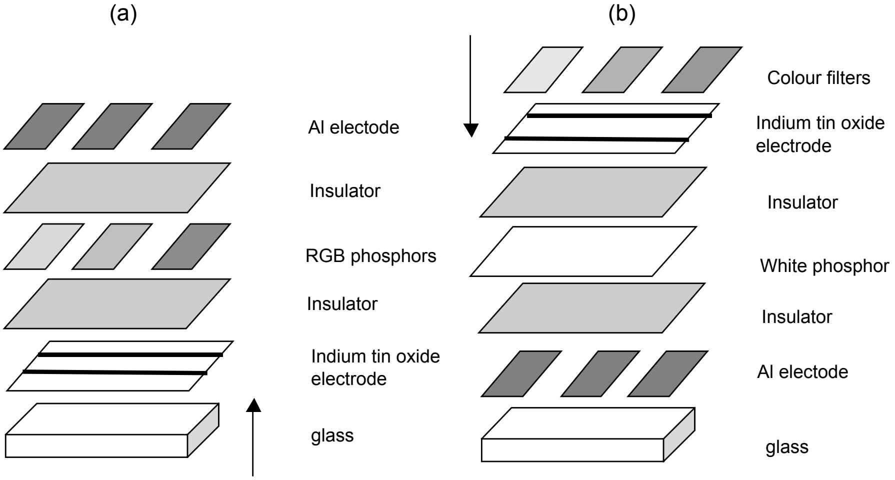


Figure 3.31 *Schematic ACTFEL display:* (a) *patterned approach* (b) *colour by white.* (Reproduced with permission of John Wiley & Sons.)

terms of luminance and efficiency, since the colour by white has losses in the colour filters (see Table 3.12).[3] In theory the colour by white system should be easier to manufacture because of a simpler monochrome methodology *versus* the additional photolithographic steps. Similar problems in constructing full-colour OLED displays are discussed in section 3.8.5.2.

3.8.4 Organic Light Emitting Diodes

The driving forces behind the high level of R&D into organic light emitting diodes (OLED) has been the ease of tailoring of the molecular properties, potential low cost, low voltage operation and relative simplicity of processing and fabrication into devices when compared with the more standard crystalline semi-conductor technology. There have been two basic streams of research: one based on multilayers of vapour deposited, low molecular weight materials and the other on polymeric materials, either by precursor polymerisation or by casting from solution and subsequent processing.[58,59] For a more detailed discussion see the book on flat panel displays by Kelly.[55]

3.8.5 Low Molecular Weight Organic LED

The main starting point for thin-film low molecular weight materials was the work reported by Ching W. Tang and Steven van Slyke of Kodak in 1987, when they described the green electroluminescence obtained from a thin film of vapour deposited aluminium tris(8-hydroxyquinoline) (Alq).[60] Since that time the development of multilayer device structures and several new important classes of organic EL materials has led to substantial improvements and to the commercial development of display technologies based on this system.[61]

A typical vapour deposited EL device consists of a glass substrate coated with a conducting transparent indium tin oxide electrode, on top of which is a 100–500 Å hole transport layer (HTL), followed by a thin (= 100 Å) light emitting layer (EML), then a 100–500 Å electron transport layer (ETL) and finally a cathode of an alloy such as Mg:Ag. This is illustrated in Figure 3.32.

Table 3.12 *Luminance levels for 'patterned phosphor' and 'colour by white approach' (60 Hz)*
(Reproduced with permission of Kluwer Academic/Plenum Publishers)

Material	*Emission colour*	*CIE coordinates* *x*	*y*	*Luminance/ cd m^{-2}*
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

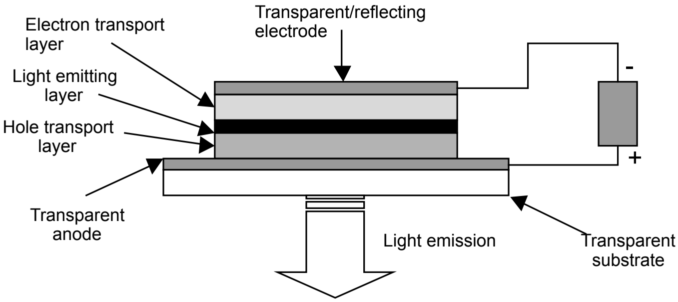


Figure 3.32 *Diagrammatic arrangement of layers in an OLED.*

Applying a voltage to the OLED causes the light emitting compound to accept charges of opposite polarities; electrons and holes from the cathode and anode respectively. The external voltage drives these carriers into the EML where they combine to form an unstable excited neutral state or ‘exciton’, which rapidly relaxes and emits light or heat. In theory the internal quantum efficiency of the OLED is the ratio of the emitted photons to the number of injected electrons, but the observed external quantum efficiency is less than this due to the influence of the refractive index of the layers making up the device.[59]

3.8.5.1 Low MW Materials

A wide variety of low molecular weight materials have been designed for high performance as EL materials. The HTL materials are normally substituted aromatic amines, which are known to have high hole mobility. Such amines have a low ionisation potential coupled with a small electron affinity associated with a large energy gap. The amine based HTL can therefore also function as an electron blocking layer in the multilayer EL device.[61] The most commonly used HTL materials, TPD and NPD, are shown in Figure 3.33.

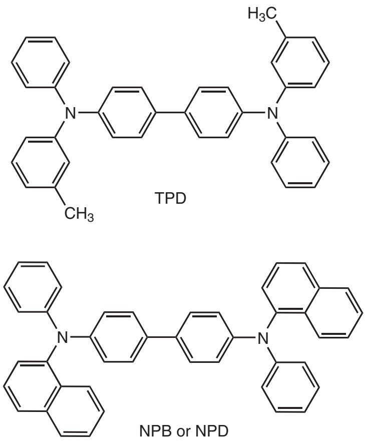


Figure 3.33 *Common hole transport materials.*

More complex bulky amines, especially dendrimers, have been developed to enhance the properties of the HTL materials. These include starburst products such as ST638 and compounds with spiro structures (Spiro-TAD) from Covion.[62] These are shown in Figure 3.34.

ETL materials that are used most often are emissive metal complexes, especially aluminium but also beryllium and lanthanides such as europium and terbium, of ligands such as 8-hydroxyquinoline, benzoquinolines and phenanthroline, whilst other effective compounds include extended conjugated compounds, *e.g.* distyrylarylene derivatives. Some ETL materials are chosen because they are non-emissive to act as combined ET and hole blocking layers.[63] A selection of these ETL materials is illustrated in Figure 3.35.

For highest efficiency it has been discovered by Kodak workers that the EML layer should consist of an ETL host material doped with a small number of fluorescent molecules.[61] These fluorescent dopants include polycyclic aromatics, known fluorescent dyes and pigments, laser dyes and also porphyrins. The structures of some of the most commonly used materials are shown in Figure 3.36. This methodology has the advantage that a range of colours can be obtained from a common host material. For example, efficient green and orange–red ELs can be obtained by doping Alq_3 with Coumarin 6, Quinacridone (QA) and DCJT (a laser dye). To be most effective in covering the desired areas of colour space a blue emitter must be used.

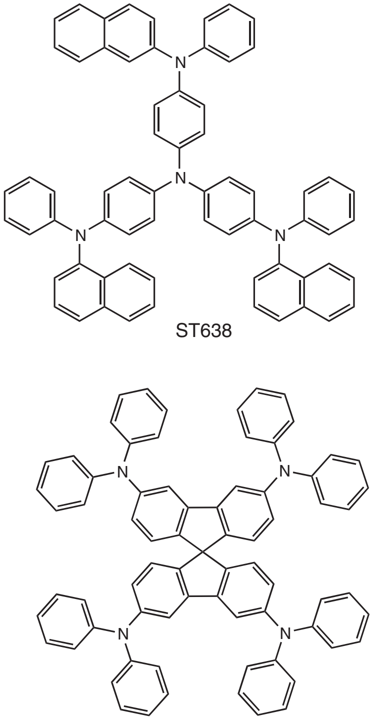


Figure 3.34 *Bulky amine HTLs.*

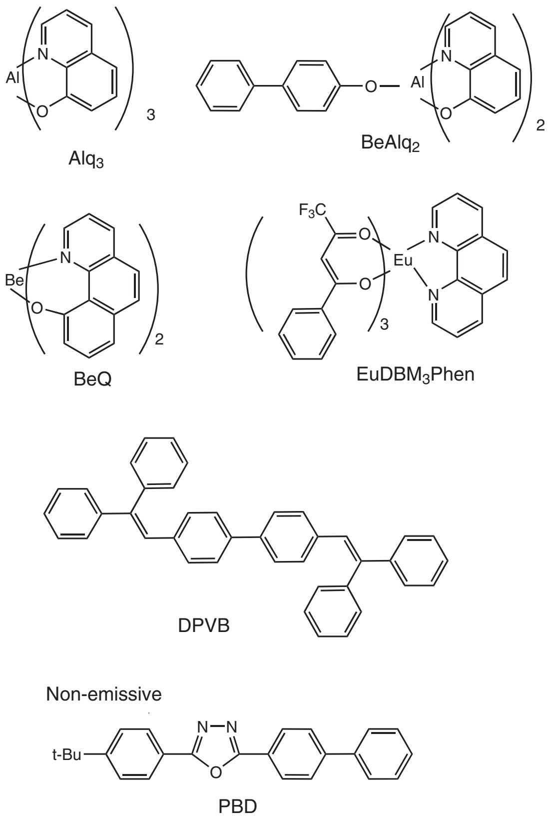


Figure 3.35 *Electron transport/emitting materials.*

3.8.5.2 Full-colour OLED Displays

To achieve full-colour displays it is necessary to have efficient low MW OLEDs that emit in the red, green and blue areas of the spectrum. Intensive research in this field has shown that this requirement can be met by careful selection of the ET host and loading this with the correct amount of a specific dopant, although there is a tendency for lower quantum efficiency. Some examples of the types of the emitters and host/dopants that produce the RGB trichromat are illustrated in Table 3.13.

There are two possible architectures for OLED displays, either passive or an active matrix. Passive displays, which are used for low-resolution applications, consist of a grid made from intersecting rows of anodes and cathodes in between which are columns of emitting materials forming the pixel elements. When the rows are pulsed the pixels at the intersections emit light. For higher resolution it is necessary to use active-matrix arrangements. In these each pixel is connected to a transistor and a capacitor, which allows the pixel to remain on during the scan time, thus avoiding any flicker. For full colour each pixel is split into RGB sub-pixels, which involves putting down each of the sub-pixels by a standard photolithographic technique on an active matrix TFT using photomasks. However, although this is being used to pro-

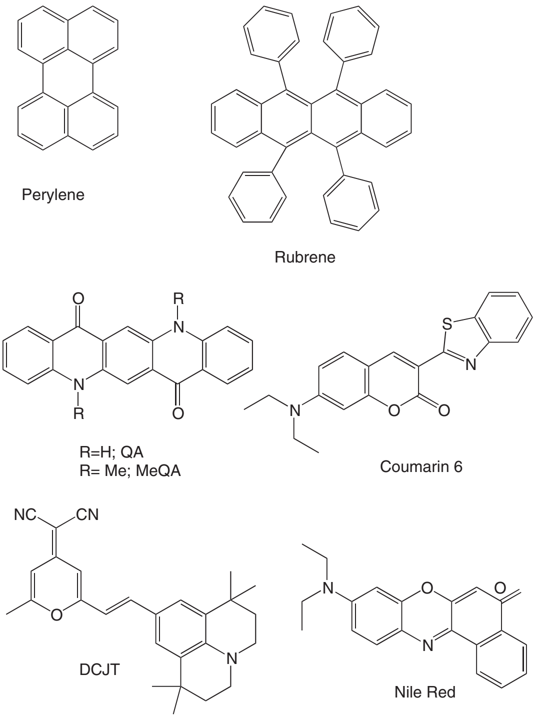


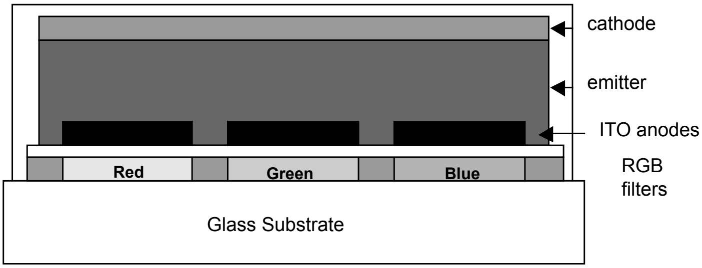
Figure 3.36 *Dopants.*

Table 3.13 *RGB organic luminescent materials*

ET material/host	*Dopant*	*EL colour*
Alq_3	DCJT	Red
$EuDBM_3Phen$	None	Red
Alq_3	MQA	Green
Alq_3	Coumarin 6	Green
BeQ	QA	Green
$BAlq_2$	Perylene	Blue
DPVBi	None	Blue
DCBi	Perylene	Blue

Note: for key to abbreviations see Figures 3.35 and 3.36

duce small area full colour panels, it is expensive, as each individual segment has to be constructed sequentially *in situ*, a very delicate procedure. A possible alternative method, demonstrated by TDK, is to use a white light emitting OLED and then filter the light through RGB passband optical filters as shown in Figure 3.37, but efficiency to date is low.[64] A variation of this process has been developed by Idemitsu-Kosan, who use a blue emitter on top of a blue converting filter, with red and green filters to down-convert the blue, with much better efficiency (Figure 3.37). A third, and more energy efficient way, is to use UV or blue light emitting OLEDs to pump organic fluorescent wavelength down-converters, analogous to the Hybrid LEDs described in



White emitter : RGB passband filters
Blue emitter : RG fluorescent, B absorptive filters

Figure 3.37 *Schematic representation of full-colour display using white or blue light emitters.*

section 3.8.1 above. These down-converters are materials that efficiently absorb blue light and reemit this as either green or red light.[59]

3.8.6 Polymer Light Emitting Diodes

Polymeric materials have many attractive properties when it comes to 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 from a solution or by the use of a doctor blade technique or by 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. Consequently, they were an obvious area for intensive research after Richard Friend and his co-workers at Cambridge, UK in 1990 made the breakthrough with their discovery of green emission from a thin film of poly(phenylene vinylene) (PPV) sandwiched between two electrodes (Figure 3.38).[65]

The mechanism operating within a polymer LED involves injection, *via* a metal electrode, of electrons into the conduction band and holes into the valence band of the polymeric semi-conductor. The electrons and holes diffuse towards each other and then combine to form an exciton, which can move along the polymer chain. These excited states then decay to the ground state with a characteristic fluorescence.

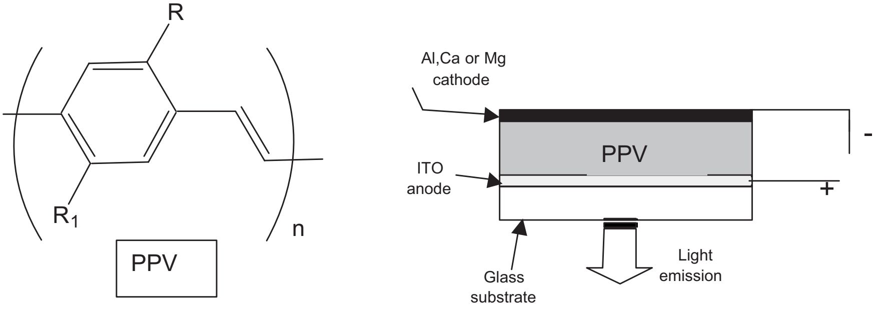


Figure 3.38 *Polymer LED.*

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 orbital provides the band gap and hence the potential for semi-conducting or polymer EL behaviour. The wavelength of the emitted light is directly related to the π–π* energy gap, and thus by manipulation of the HOMO–LUMO gap, by molecular engineering of the conjugated polymer structure, emission across the whole of the visible spectrum is possible.[66]

The principle requirements for the commercial application of light emitting polymers (LEPs) are high efficiency and reliability. To obtain long lifetimes in devices, the target for researchers must be maximum power efficiency and brightness coupled with minimum drive voltage and current density. The ideal LEP should have a solid-state photoluminescence efficiency approaching 100%. However, the excitons produced can either be in a singlet state, and fluoresce 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 the device cannot be more than 25% of the photoluminescence efficiency. Therefore it is essential that all other parameters having a negative effect on efficiency be minimised. Below is a list of preferred LEP characteristics.[67]

- Be processable as transparent and defect-free thin films
- Be amorphous
- Have high photoluminescence efficiency
- Exhibit approximately comparable low barriers to charge injection
- Have reasonable charge mobilities
- Exhibit appropriate colour qualities according to the specifications used in the displays industry
- Have a high glass transition temperature
- Be resistant to photooxidation

3.8.6.1 Synthesis of the Polymers

Andrew Holmes and his co-workers at Cambridge, who have made major contributions to the synthesis of LEPs, have written a valuable review of the many synthetic routes to the materials.[66] In this section only descriptions of the major classes of LEPs currently used to make devices will be given.

The basic poly(phenylene vinylene) (PPV) polymer is commonly prepared by the sufonium prepolymer route developed by Wessling and Zimmerman in 1968 but much modified by subsequent workers.[68] The synthesis starts from 1,4-bis(chloromethyl)benzene, *via* the bis-sulfonium salt formed by reaction with tetrahydrothiophene, and then polymerisation is effected to give the prepolymer by reaction with lithium hydroxide (Figure 3.39). Because of the inherent insolubility of PPV it is this prepolymer that is used to form the film coating on the substrate, for example by using a doctor blade technique. The prepolymer is converted into PPV on the substrate by heating in an oven under vacuum at 200 °C for 8–10 h.

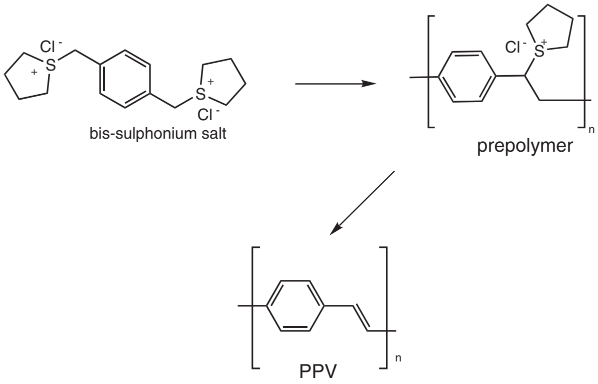


Figure 3.39 *Synthetic route to PPV.*

To overcome the insolubility of polymers it is usually necessary to put solubilising groups into the polymer, most simply at the monomer stage. This can be achieved in PPV derivatives by having alkoxy or other groups in the 2- and 4-positions of the benzene ring. For instance, by starting with hydroquinone a wide variety of 1,4-dialkoxybenzenes can be synthesised, which, after forming the bis(chloromethyl) or the bromomethyl derivative, can be converted into the substituted polymers, by the Gilch dehyrohalogenation condensation polymerisation, on treatment with potassium *t*-butoxide in a solvent such as tetrahydrofuran.[69] This route is shown in Figure 3.40.

The properties of PPVs can also be modified by the introduction of groups on the ethylenic bridge. A particularly valuable material, whose synthesis was devised by Holmes, and currently used by CDT, is the cyano derivative, CN-PPV. The synthetic pathway to CN-PPV is shown in Figure 3.41.[66]

Phenyl substituted PPVs generally suffer from poor solubility and low molecular weights are required to render them soluble. Workers at Aventis and Phillips discovered that by combining an alkoxy substituent in 2-phenyl PPVs they were able to get good solubility and film forming properties combined with high molecular weights, and most importantly with high EL performance. These properties were further improved if co-polymers were made, using a modified Gilch process, as shown in Figure 3.42.[70]

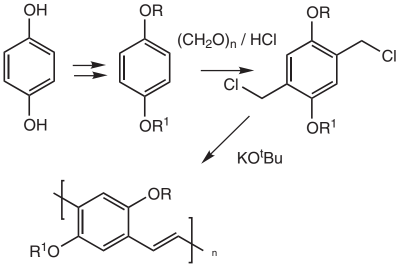
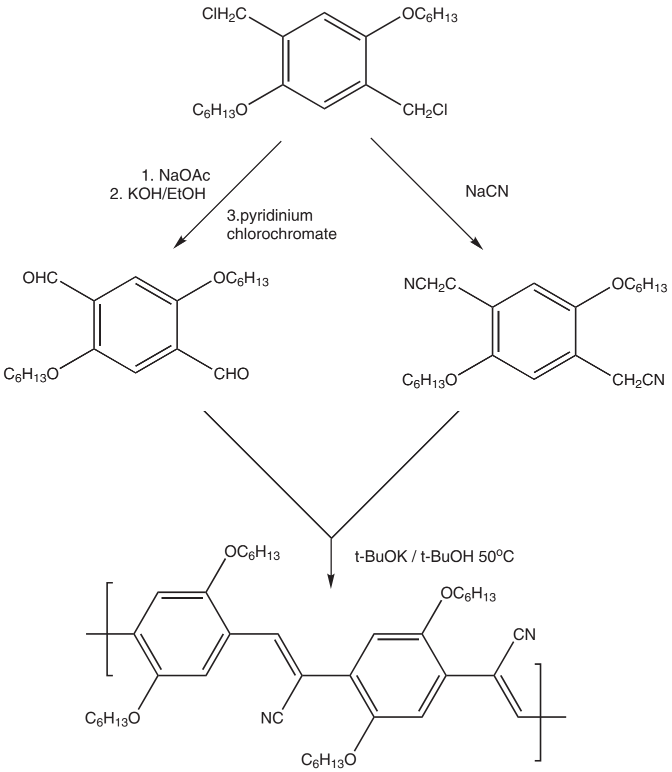


Figure 3.40 *The dehydrohalogenation route to PPV derivatives.*



(CN-PPV)

Figure 3.41 *Synthesis of CN-PPV.*

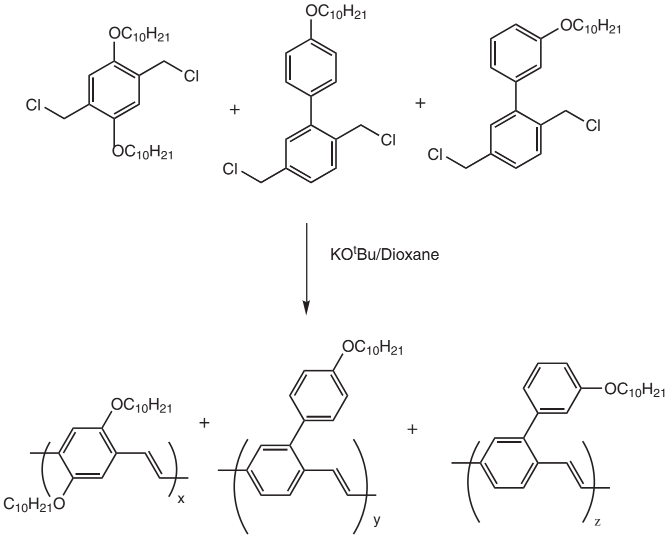
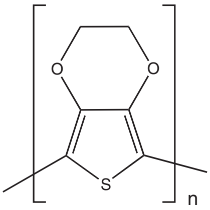
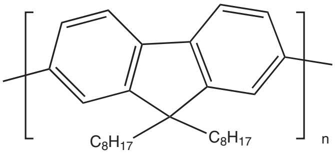


Figure 3.42 *Phenyl substituted PPVs.*



(3.110)



(3.111)

Many other polymeric systems are of interest in polymer LEDs. Polythiophenes have been known for some time but it was not until improved synthetic methods were developed that their potential was realised. The process involves the reaction of the substituted monomer with $FeCl_3$ in chloroform solution. After polymerisation has occurred the product precipitates and is isolated and washed. Further special purification methods are required to obtain satisfactorily pure materials.[62] One product, of commercial interest, developed by Bayer is poly(ethylenedioxy)thiophene, known as PEDOT (3.110). This product when doped with polystyrene sulfonate, sold as Baytron P, has been found to be effective as a conducting, hole-injecting layer on the ITO electrode.[71]

Polyfluorenes are another class of very promising conjugated polymers for EL applications, exemplified by the blue emitter, poly(9,9-dioctylfluorene) (3.111, PF8).[72] These are formed by reductive polycondensation of the appropriate 9,9-dialky derivatives of 2,7-dibromofluorene using a catalyst, *e.g.* $Pd(PPh_3)_4$ (Suzuki coupling) or $Ni(COD)_2$ (Yamamoto coupling).[73,74] Suzuki coupling is also used to produce polyfluorene co-polymers incorporating groups such as triphenylamine, which help to control the colour, MW and solubility of the derived polymers. These are shown in Figure 3.43.[75,76]

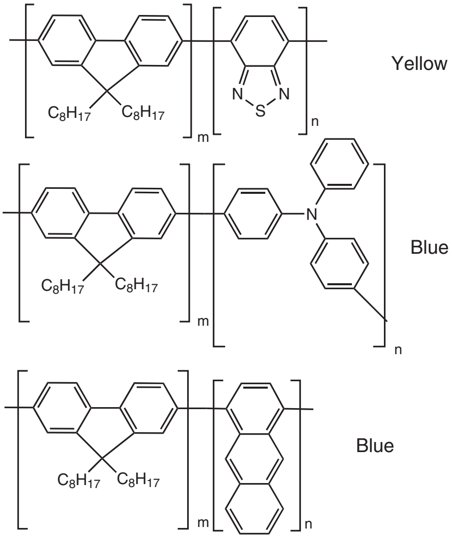


Figure 3.43 *Fluorene co-polymers.*

3.8.6.2 Full Colour LEP Displays

Whilst PPV emits green light it is possible, by varying the side chain groups, to manipulate the band gap to produce yellow and orange red light emission, for example with 2,5-dialkoxy derivatives. Blue emitters can be obtained from polyfluorenes, an area being exploited by Dow Chemical. Polyfluorenes can also be doped with red fluorescers to give red emitters. Blue can be obtained from poly(*p*-phenylenes) (PPPs), but these have solubility problems. An innovative way around this solubility with PPPs came from workers at Hoechst (now Covion) who made short chain orthoganally linked polymers, for example spiro-6-paraphenylene.[77–79] Many developments of new materials for the required RGB emitters are taking place in the various companies working in this area, but their detailed structures are commercially sensitive and remain to be disclosed. Target RGB colours now are close to the position in colour space required by the PAL system and suitable for commercialisation. Some typical polymers and their spectral properties are given in Table 3.14.[80] For a more comprehensive list the reader should consult recent publications.[55]

Construction of a three-coloured patterned screen can be achieved by conventional methods using lithographic techniques, as described previously above for low molecular weight materials, which are expensive and complex. A significant step forward has come from the collaborative work between Seiko Epson and Cambridge Display Technology. They have used high-resolution ink jet printers to put the component RGB layers for the pixels directly onto the substrate, pre-patterned with polyimide, for use with an active matrix driver, as illustrated in Figure 3.44.[66,71]

Table 3.14 *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	Co-polymer	Blue	460

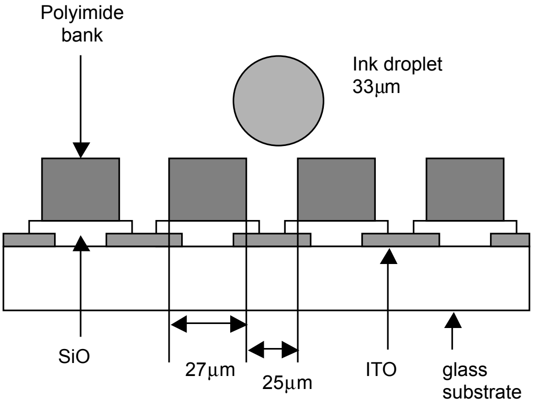


Figure 3.44 *Patterning of LEPs by ink jet technology.*

3.8.7 Commercial Prospects for OLEDs

High growth was the conclusive outcome from a Stanford Resources survey of the market potential for OLED (organic light emitting diode) technology carried out in 1998.[81] It was forecast that the year 2000 would see the first significant use of OLED technology in the market place with sales of \$18 M. This was predicted to rise rapidly to \$200 M in 2002, to \$350 M in 2004 and to over \$700 M in 2005. The drivers for this rapid market growth will be partial replacement of existing display technology and also new uses. Replacement of the monochrome vacuum fluorescent displays as used in VCRs, microwave ovens, and clock and car radio displays *etc.* with a wider colour choice will be one of the first targets. Another important target is the market currently dominated by LCDs in displays where OLEDS offer better viewing characteristics and appearance, for example in laptops where backlighting is required. The use of so-called white light OLEDs in backlighting is a potential outlet.[81]

Kodak is commercialising its low molecular weight OLEDs for use in both passive and active matrix display architectures. It has also licensed its technology to Pioneer Corp who have commercialised passive matrix displays for car radios and cellular phone displays. TDK has displays for cellular phones, personal digital assistants and car instrumentation clusters. Perhaps the most significant collaboration to date has been with Sanyo. Sanyo's capabilities in low-temperature polycrystalline silicon have been married with Kodak's low MW materials to produce a full colour, 5 inch active matrix display, commercialisation of which was expected in 2001.

A larger number of companies are active in the LEP area. DuPont's purchase of Uniax and its technology gave them the necessary intellectual property to marry with their expertise in plastic substrates. Their aim is to produce devices on thin flexible substrates such as nylon and PET *etc.* that, they believe, will bring a manufacturing cost advantage over low MW materials. It is collaborating with Phillips who has a production scale unit in Holland for small alphanumeric displays suitable for watches and mobile phones.

Cambridge Display Technology in the UK, following its collaboration with Seiko Epson, outlined above, have described small full colour displays for use in hand held devices such as mobile phones. They are also working with Bayer who have developed polythiophenes for use in superior charge transport materials. Dow Chemical is basing its drive into LEPs on polyfluorenes which they say have superior light, oxygen and moisture stability advantages over other polymers. They have a green polymer and will launch red and blue in 2000. Covion, a joint venture between Aventis and Avecia, is developing and selling PPV-based polymers to clients such as Phillips. DuPont Displays announced in April 2001 that it was to build a facility to deliver its first polymer OLED displays, initially monochrome, by the fourth quarter of 2001.

It is clear from all this activity, both in industry and academia, that OLED technology is one of the most exciting new display technologies that has come along in the last decade. Progress to date is very good and its influence is set to grow in the first decade of the millennium. Just when the display market seemed set to be mature along comes a technology that has shaken all developers out of their complacency.[82]

3.9 Triboluminescence

Triboluminescence is the phenomenon that is observed when coloured light is emitted on grinding, crushing or fracturing certain crystalline compounds, *e.g.* the bluish white light emitted from sugar. This phenomenon has been known for over 300 years but has remained a curiosity without an obvious application, until very recently when Sage postulated that this effect could be used to detect flaws in composite materials.[83]

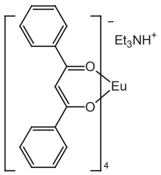
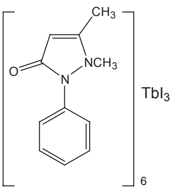
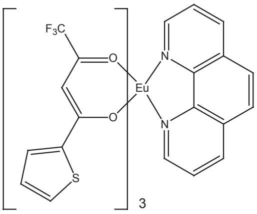
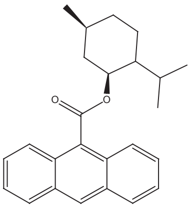
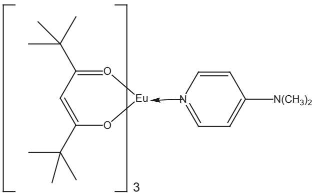
This was based on the reported high triboluminescence efficiency exhibited by certain crystalline compounds, especially complexes with lanthanides (Table 3.15), some of which have already been described under electroluminescence (section 3.8.5.1). The light emission from a few of these materials is sufficient 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 appears to be three types.[83]

- 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 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 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 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.

Sage and his co-workers have used this triboluminescent phenomenon in devising

Table 3.15 *Triboluminescent compounds*
(Reproduced with permission from *Chemistry in Britain*)

Compound	*Emission wavelength/nm*	*Emission lifetime*
	12	470
	542	4.8 μs
	612	666 μs
	437	3.4 ns
	550	538 μs

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 a fibre optic cable fixed within the composite. In this case fracture is detected by light emitting from the end of the fibre wave-guide.

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CHAPTER 4

Phenomena Involving Absorption of Light and Energy Transfer

4.1 Introduction

The excited state produced by the interaction of a molecule with light can lose or transfer its energy in various ways.[1] Return to the ground 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 in Chapter 3 of this book. A unimolecular photochemical process, involving internal rearrangement, namely photochromism, is covered in Chapter 1 under colour change phenomena. The present chapter will deal with those phenomena involving photochemical reactions of coloured molecules, *e.g.* sensitisation of oxygen in photodynamic therapy, and the use of others that can transfer electromagnetic energy, often from a laser, into another useful form of energy, *e.g.* thermal (optical data storage) or electrical (photovoltaics). In the majority of cases the applications for these coloured molecules are not based on their intrinsic colour but on the fact that they can be used to absorb light of a particular wavelength as required by the application.

4.2 Laser Addressable Compounds (Infrared Absorbers)

Since the advent of the semi-conducting diode lasers there has been much interest in compounds that absorb in the near-infrared region of the spectrum. This is because they can be used to absorb the energy of the laser at a specific wavelength of the

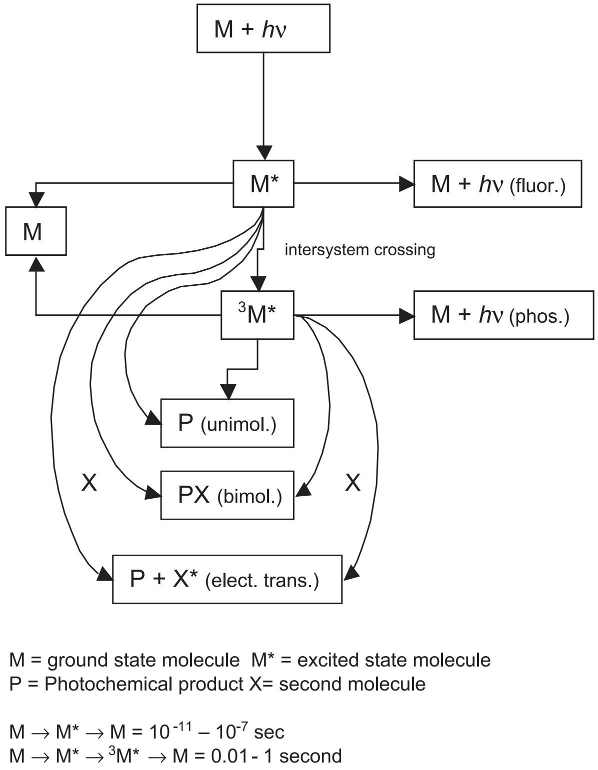


Figure 4.1 *Photophysical and photochemical pathways for excited molecules.*

spectrum, *e.g.* the GAs 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. Whilst these 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 and the frequency doubling of near high energy Nd:YAG lasers of 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 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.

4.2.1 Chemical Classes of Near-IR Absorbers

In spite of the advent of visible light lasers the interest in near-infrared (NIR) absorbers continues because they do offer certain advantages, especially if they show little or no low absorption in the visible region, for instance their use in invisible security markings.[2] The near-IR absorbers may be classified according to their

Table 4.1 *Laser and LED addressable wavelengths*

Laser	*Wavelength/nm*
Third harmonic Nd:YVO_4	355 (violet)
KDP/Nd:YAG Doubled	532
Ruby (rarely used)	670–725
Helium neon	633
Titanium sapphire	800–1200
Nd:YAG	1064
Dye lasers	310–1285 (tunable)
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

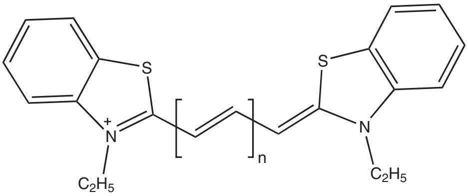
chemical structures or the region of the spectrum in which they absorb useful laser energy.[3–5] In this text we will classify them by their chemical structure. Products are available commercially covering a wide range of absorption maxima, that are both oil and water miscible and dispersable in a variety of polymers.[6–8]

4.2.1.1 Cyanines

Perhaps the most widely studied chemical class of near-IR absorbers are the cyanines. The chemistry and synthetic routes to cyanines are discussed in other parts of this book (Chapter 2, section 2.3.1.4 and Chapter 3, section 3.5.1.7). The factors influencing the position of their absorption maxima and molar absorption (extinction) coefficients are:[2,9]

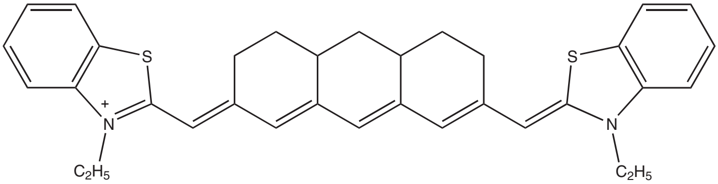
- The length of the conjugating bridge between the terminating heterocyclic donor moieties
- The electron donating strength of the terminal heterocyclic residues
- The electronic characteristics of the individual atoms in the conjugating bridge

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 into the near-IR 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 molar absorption coefficient drops dramatically, as does the dye's stability to light, heat and oxidation. There are two ways of overcoming this problem; introduce rigidity into the molecule by having the polyene chain as part of a linear carbocyclic ring system (4.2) or extend 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 (4.4) and (4.5).



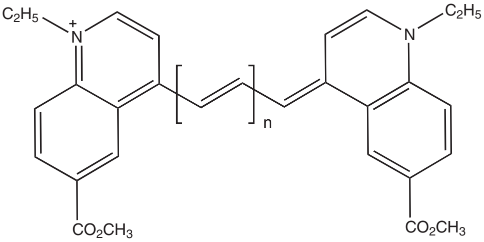
(4.1)

n=2, λ_{max} 662 nm, ε_{max} 200,000
n=3, λ_{max} 772 nm, ε_{max} 165,000
n=4, λ_{max} 845 nm, ε_{max} 130,000



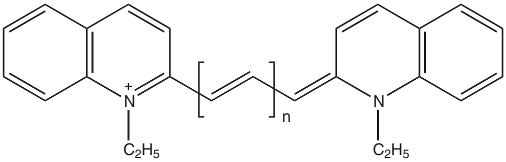
(4.2)

λ_{max} 855 nm ε_{max} 155000



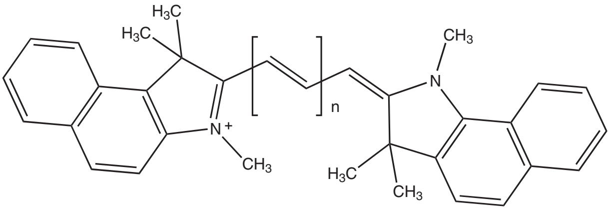
(4.3; n = 3)

λ_{max} 957 nm ε_{max} 166,000



(4.4; n = 3)

λ_{max} 820 nm ε_{max} 115000



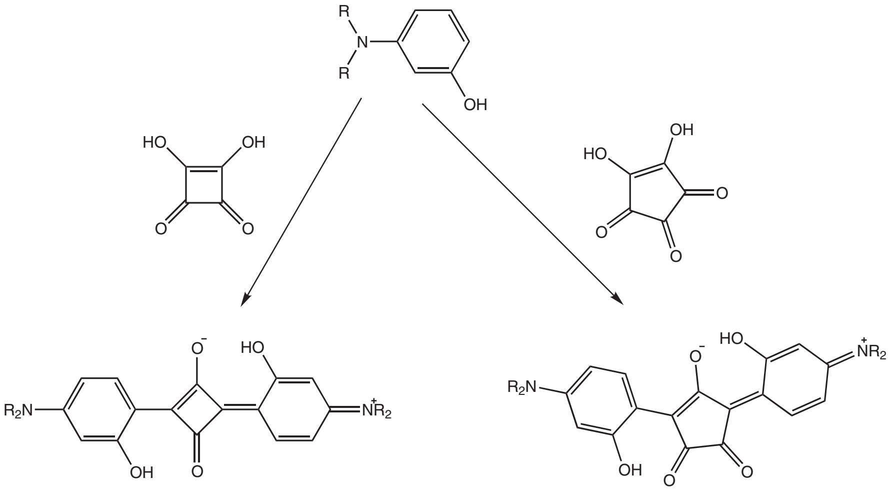
(4.5; n = 3)

λ_{max} 855 nm ε_{max} 155000

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 near-IR absorbers based on these chromophores are different.[2] The synthesis of these chromophores is achieved easily by reacting either squaric acid, or preferably an alkylated derivative, *e.g.* di-*n*-butyl squarate, or croconic acid with electron-donor molecules. The croconium dyes absorb at significantly longer wavelengths than the squaryliums as shown in Figure 4.2.

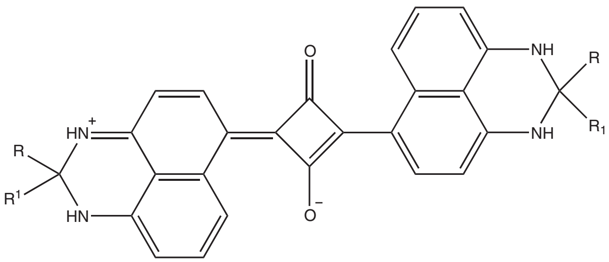
Wide variation of the donor groups on the squarylium dyes of structure type (4.6) only gave a maximum wavelength of absorption of 708 nm, and it was necessary to use the strongly electron-donating dihydroperimidine ring system to achieve absorption fully into the near-IR, as exemplified by (4.8), λ_{max} 800–810 nm, ε_{max} 150 000.[10]



(4.6)
λ_{max} 639 nm ε_{max} 224000

(4.7)
λ_{max} 817 nm ε_{max} 210000

Figure 4.2 *Squarylium (4.6) and croconium (4.7) absorbers.*



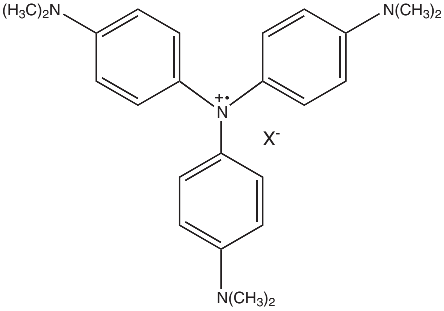
(4.8)

4.2.1.3 Iminium Salts

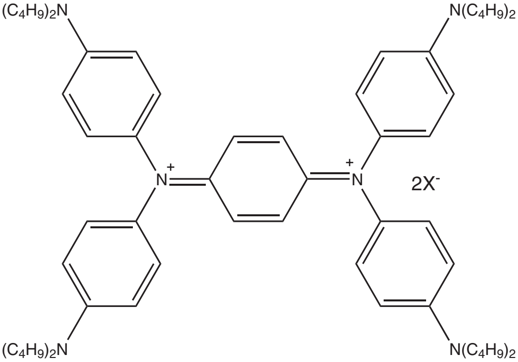
The products of interest here are the salts of the iminium radical cations (4.9) and diiminium dications (4.10), especially the latter. These are highly coloured compounds, which absorb well into the near-IR, (4.9) at λ_{max} 920 nm and (4.10) at 1064 nm, ε_{max} 81 300.[6]

4.2.1.4 Triphenylmethanes

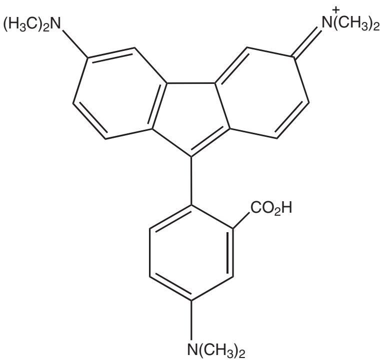
The blue and green dyes based on the triphenylmethane chromophore, (see Chapter 2, section 2.3.1.5) can be modified to move their absorption maxima into the near-IR. This can be achieved either by joining two of the aromatic rings *via* a direct link or by extending the conjugation from the trisubstituted central carbon atom. This is exemplified by the two products which are essentially derived from Crystal Violet Lactone: (4.11) with a bridging bond and (4.12) by adding ethylenic links on two sides of the central carbon atom.[9] These types of products were developed by companies working on laser or LED writeable thermal papers (Chapter 1, section 1.4.2.3).



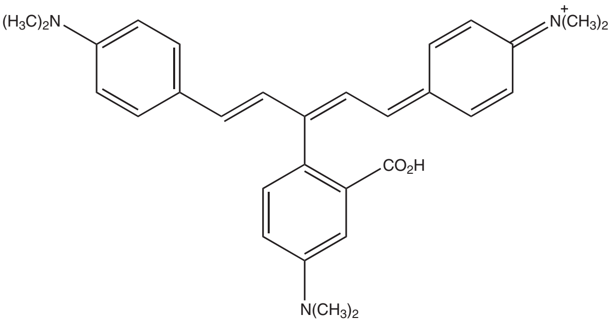
(4.9)



(4.10)



(4.11)



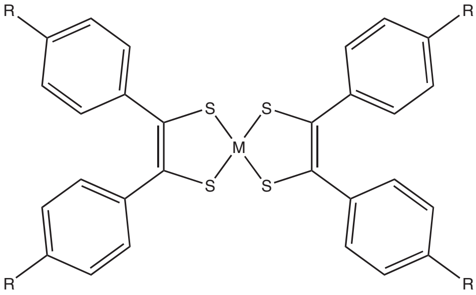
(4.12)

4.2.1.5 Nickel Dithiolenes

Several transition metal ions form stable complexes with aliphatic 1,2-dithiols, which absorb in the near-IR. Known as dithiolenes, their nickel complexes in particular have been found to have valuable properties. The physical properties of dithiolenes can be readily tailored by variations on the substituents attached to the dithiols, see (4.13). Although they have low molar absorption coefficients, when compared to cyanines *etc.*, they do have one big advantage in that they show very little absorption in the visible region.[11] Structurally analogous dyes can be made from aromatic dithiols and oxothiols (4.14), and the much more bathochromic naphthalene derivatives (4.15), but they are much weaker absorbers.

4.2.1.6 Quinones

Both naphthoquinones and anthraquinones bearing annulated benzothiazine rings, as illustrated by compounds (4.16), (4.17) and (4.18), absorb in the near-IR. Unfortunately, the naphthoquinones tend to have low stability and products from both ring systems are strongly coloured, limiting their areas of application.

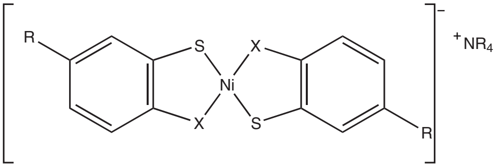


(4.13)

M = Ni, R = H λ_{max} 866 nm ε_{max} 31000

M = Pt, R =H λ_{max} 802 nm ε_{max} 43000

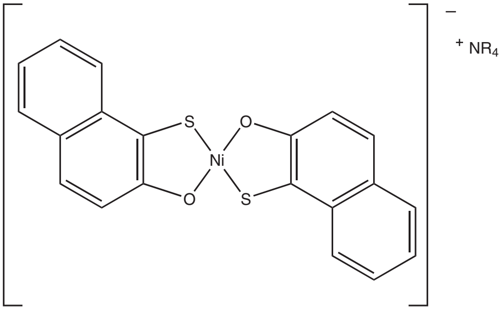
M = Ni, R = OCH3 λ_{max} 925 nm ε_{max} 35000



(4.14)

X = S, R = CH_3, λ_{max} 890 nm ε_{max} 14000

X = O, R = CH_3, λ_{max} 984 nm ε_{max} 14600



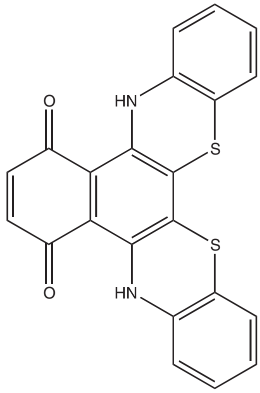
(4.15)

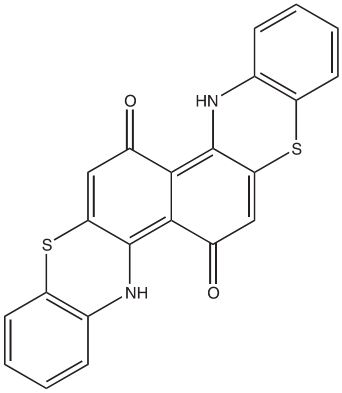
M = Ni, λ_{max} 1110 nm ε_{max} 12000

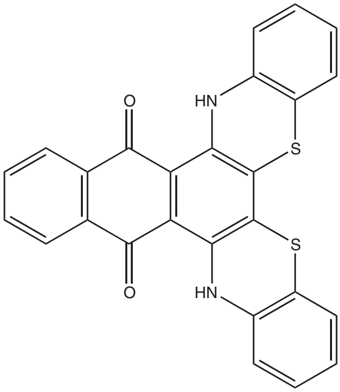
M = Co, λ_{max} 1150 nm ε_{max} 14000

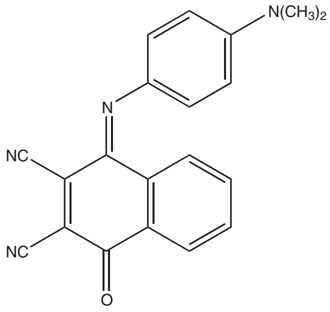
M = Pt, λ_{max} 1200 nm ε_{max} 15000

The absorption maxima of indoanilines dyes derived from naphthols can also be extended well into the near-IR by having strongly electron-withdrawing groups attached to the quinone ring, as shown in (4.19).


(4.16)
λ_{max} 725 nm ε_{max} 15200


(4.17)
λ_{max} 750 nm ε_{max} 32000


(4.18)
λ_{max} 712 nm ε_{max} 15000


(4.19)
λ_{max} 795 nm

4.2.1.7 Phthalocyanines

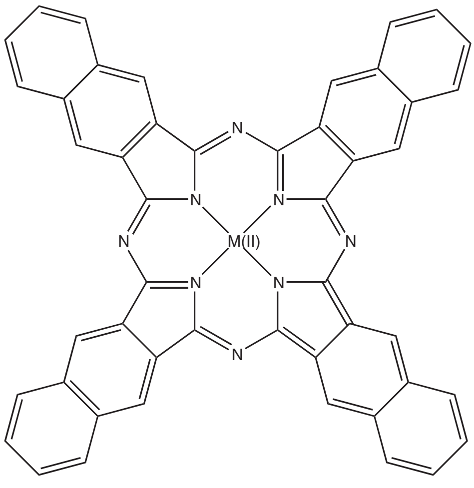
Phthalocyanine, its metal salts, ring substituted and benzoannulated derivatives form a very important class of near-IR absorbers, being extremely strong absorbers (ε_{max} approx 200 000) and generally very stable environmentally. The synthetic pathways to these molecules are all variations on the methods already described in Chapter 2 (section 2.4.1.4), the preferred routes starting from a substituted phthalonitrile with tetramerisation in the presence of the appropriate metal salt.[12] An alternative route to copper phthalocyanines bearing arylthio substituents, which are valuable near-IR absorbers, involving displacement of the halogens atoms in the polychlorinated derivative has been described.[13,14]

As already stated most phthalocyanines exhibit polymorphism, and many of these morphological forms absorb in the near-IR, 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 does allow for new morphological forms absorbing in the near-IR; titanyl phthalocyanines being 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, *e.g.* alkyl and aryloxy and thioxy shift the Q-band absorption bathochromically by 70–100 nm, depending on the central metal atom.[14] A selection of various near-IR absorbing phthalocyanines are shown in Table 4.2.

Benzoannulation of the phthalocyanine ring is a way of extending the π-orbitals of the central ring system, and moving the long wavelength absorption into the near-IR. Of particular value are the naphthalocyanines (4.20) made from 2,3-naphthalonitrile,

Table 4.2 *Absorption maxima of near-IR absorbing phthalocyanines* (Reproduced with permission of Cambridge University Press)

Phthalocyanine	*Form (film)*	λ_{max}/*nm*
Metal-free phthalocyanine	Solution	699
	β-form (crystal)	740
	X-form	830
Copper phthalocyanine	X-form	782
Lead phthalocyanine	Triclinic	870
Titanyl phthalocyanine	Phase 1	780
	Phase 2	830
	Y-form	830
Vanadyl phthalocyanine	Phase II	834
Chloroindium phthalocyanine		740
Zinc naphthalocyanine		760
Cobalt phthalocyaninetetra-*t*-butyl	Solution	660
Cobalt naphthalocyaninetetra-*t*-butyl	Solution	752
Cobalt anthracocyaninetetra-*t*-butyl	Solution	832



(4.20)

which are 90 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 (170 nm).

4.2.2 Applications of Laser Addressable Compounds and Near-IR Absorbers

The application areas for these materials can be classified as follows:[14]

- *Those involving energy conversion*
  - Optical Data Storage (see 4.3) – thermal
  - Solar heating and shielding – thermal
  - Laser welding of plastics – thermal
  - Computer to plate lithography – thermal imaging
  - Organic photoconductors in laser copying/printing (see section 4.4) – electrical
  - Photovoltaics (see section 4.7) – electrical
- *Those using photosensitisation*
  - Photopolymerisation (see section 4.5.2)
  - Photomedicine, PDT *etc*. (see sections 4.6.1 and 4.6.2)
- *Those involving selective absorption of light*
  - Photographic sensitisers (see section 4.5.3)
  - Security and machine readable data
  - Eye protection (*e.g.* laser shields)
  - Camouflage

4.2.2.1 Energy Conversion

Solar Heating and Shielding. The two most important energy conversions of IR radiation are into thermal and electrical energy. The thermal conversion is important because sunlight contains a significant portion of near-IR radiation, which can be either useful or a nuisance, depending on the environment on which it impinges. It is of nuisance value when it strikes through glass in both architectural glazing units and in cars and other vehicles, causing excessive heating and hence the need for extra air-conditioning. Reflective coatings are the most common answer to this problem, but it is also possible to absorb the energy in a layer of infrared absorbers, *e.g.* in a polymer interlayer in multiplex glass, and then lose the heat generated to an external atmosphere by convection. Alternatively, the impinging sunlight can also be absorbed in a solvent layer containing an IR absorber, *e.g.* water, which can then be circulated through heat exchangers and so used to heat water for central heating or other domestic uses. For these outlets materials that absorb across a wide range of the near-IR spectrum are preferred, but often mixtures are used to fill in any gaps in the spectrum.

Lasers can be used to weld practically invisible joints in plastic sheeting, in which heat transfer is greatly assisted by the presence of infrared absorbers.[8]

Computer to Plate Technology in Lithographic Printing. For many years the production of the plates used in lithographic printing has involved the use of a photographic image of the print through which UV light is passed onto a photosensitive resin (see Chapter 1, section 1.4.2.4 for details).[15] This is an expensive process, especially for short run prints, as each plate has to be constructed by this photographic process. Most data for printing is now available in digital form and a process for transferring this data directly to the plate has been developed. Known as 'computer to plate', the technology involves writing the data directly onto a photosensitive plate, using a semi-conducting diode or other laser. To achieve this an absorber for the laser energy needs to be within the photosensitive resin on the plate. The cheapest product that can perform this function is carbon black, but there are problems in using this material and consequently near-IR absorbing dyes, such as cyanines, and more recently visible dyes have been used as alternatives.[16] The requirements for the dyes in this outlet are:

- High molar absorption coefficient
- Stable λ_{max} in the resin film
- Broad λ_{max} centred at 830 nm (800–900) or 1064 nm (1030–1140) or 532 nm for frequency doubled Nd:YAG, 670 nm, 650 nm and 633 nm, for other lasers and LEDs, depending on the imagesetter
- Good organic solvent solubility (*e.g.* THF or MEK) and solution stability

One such process involves the thermal decomposition of a diazo compound to give an acid that cross-links phenol formaldehyde resins upon heating, similar to the conventional UV initiated plates used in the industry (Figure 4.3), but other sensitisation methods are also used (see section 4.5). It is also possible to produce plates in a dry resin process by ablation or phase change methods.

This is a very important development in printing plate technology and many companies have launched products, including Kodak Polychrome Graphics, Agfa, Fuji, Mitsubishi and Lastra.

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.[17] One of the outlets for this technology is in colour proofing of images prior to full scale production of lithographic plates as described above. The process involves writing the image data, using a focused diode laser beam, onto a dye layer containing the near-IR dye and binder. The IR dye 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.[18]

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 near-IR absorbing dye is likely to be transferred in the process, it should not interfere with the colours in the final print and preferably be colourless. Colourless near-IR absorbers are difficult to find and workers at the Imation Company overcame this problem by using an IR absorber (4.21), exhibiting broad absorption at 790– 900 nm and addressable at 830 nm, which bleached out during the process.[18]

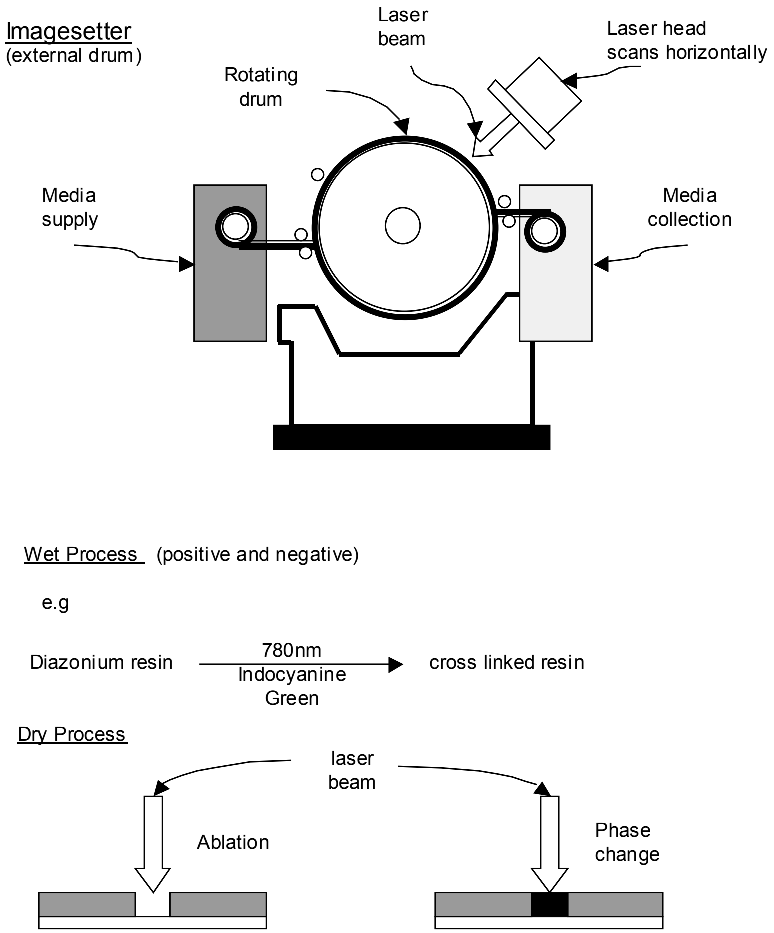


Figure 4.3 *Computer to plate technologies.*

Other Applications. An excellent example of the exploitation of absorbers in the conversion of laser light into thermal energy at specific wavelengths in the near-IR is optical data storage. This topic will be covered in detail later (see section 4.3). Applications involving the conversion of infrared 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 4.7).

4.2.2.2 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 near-IR needs to be eliminated, whilst still allowing the wearer to see clearly. Polymer compatible diiminium and nickel dithiolene near-IR absorbers have been developed for this outlet, and also for the protection of the eyes of users of higher-powered lasers.[8] Wide attenuation of light

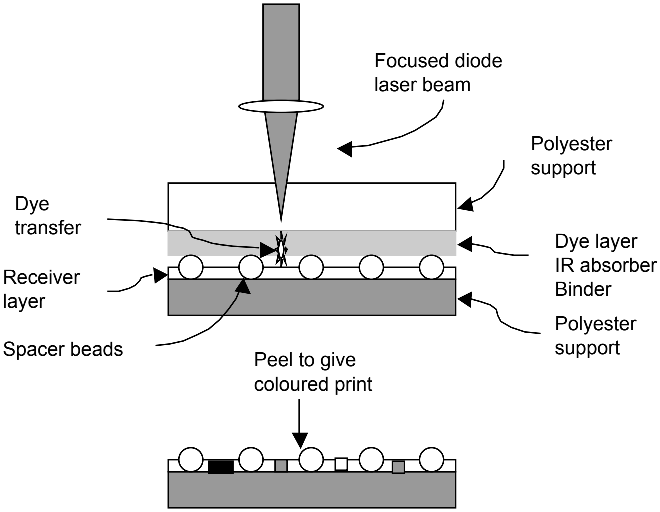
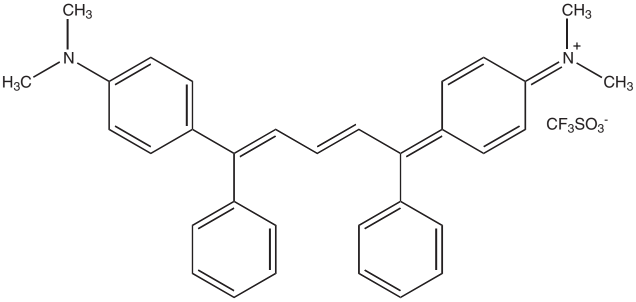


Figure 4.4 *Colour proofing with laser thermal media.*



(4.21)

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.[8]

Lasers have also become commonplace in military weaponry and their use presents severe hazards to personnel on the receiving end, either because of 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 ophthalmically 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.[9] 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.[20] Reverse saturable absorption, or optical limiting, is a non-linear effect that occurs when the excited state absorption exceeds the ground state absorption. Several classes of organic colorants have shown very interesting reverse saturable properties, including cyanines and especially porphyrins and metal phthalocyanines, *e.g.* lead phthalocyanine.[21] For obvious reasons most of the work in this area is sponsored by the defence agencies and the exact structures of the most recent materials of interest have yet to be disclosed.[22]

Another important area for the military is camouflage. This has traditionally been done by using patterns of green, olive, brown, khaki and black on clothing and on military vehicles and buildings. Whilst concealment from daylight surveillance by personnel using visual or photographic means is still the main requirement, there is also the need to avoid detection from technology that uses infrared sensors. The major work in this area has been in providing coatings to avoid detection from thermal imaging sensors working in the far-infrared, but there is also a need for materials operating in the near-IR region of 700–1300 nm.[23] 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. Again most of the structures of the actual infrared absorbers, dyes and pigments used in this area remain secret. However, there are reviews on camouflage materials used in coatings and paints and on textile dyes for apparel.[23,24]

The application of near-IR 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 have been claimed to be of value in this area, mainly in the security printing of machine readable items, by lasers, and identifiers.[14] Example uses in security printing are widespread and include bar-codes 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 very little visible colour is required, but if hidden behind strongly coloured opaque ink then lightly coloured near-IR absorbing dyes can be used.[9]

4.3 Optical Data Storage

The storage and retrieval of data by optical means, which involves the interaction of some medium with a compact laser, focused to sub-micron size, is dominated by direct bit storage onto disc media. The various types of storage media, from read only compact discs (CD-ROM) to rewritable digital versatile discs (DVD-RW), and the favoured recording materials are shown in Figure 4.5.[25]

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 onto 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

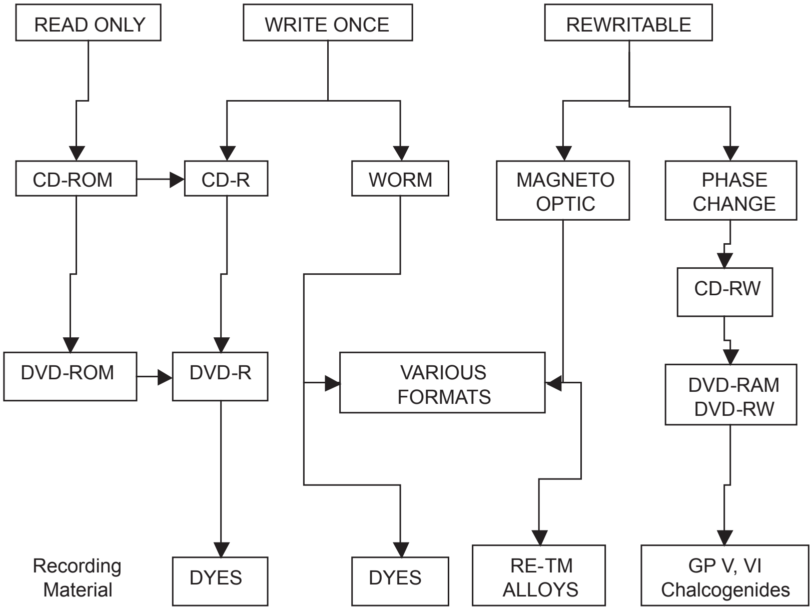


Figure 4.5 *The various media and systems used in optical data storage.*

guided along grooves in the substrate. This system is shown schematically in Figure 4.6.

Magneto optic media, the oldest of the media for data recording, dating back to the 1950s, consists typically of sputtered amorphous films of rare earth–transition metal alloys, e.g. GdTbFe, TBFeCo and GbTbFeCo alloys. After heating locally to 200–300 °C, the direction of the magnetisation of the alloy is changed and then fixed by cooling to room temperature. Changes in the direction of magnetisation, indicators of the data recorded, are measured as the change in polarisation of light reflected from the surface.

Phase change media, as used in CD-RW, DVD-RW and DVD-RAM media, are chalcogenide glasses, *e.g.* GeSbTe alloys. Recording is effected by local heating of a metastable phase of the glass, causing it to melt and become amorphous. Conversion back into the metastable phase is achieved by heating the amorphous phase to slightly below the melting point at a slower rate than used in recording.[26]

The main interest in this book is the use of laser addressable dyes in optical data recording, specifically WORM (write once read many times) used in the industrial and institutional arena for the mass storage of data, and CD-R used in smaller scale computing, educational and entertainment outlets.

4.3.1 Optical Data Storage using Dyes

The mechanism of optical recording with organic dyes involves converting the excitation energy, generated by the focused laser beam, into thermal energy by non-

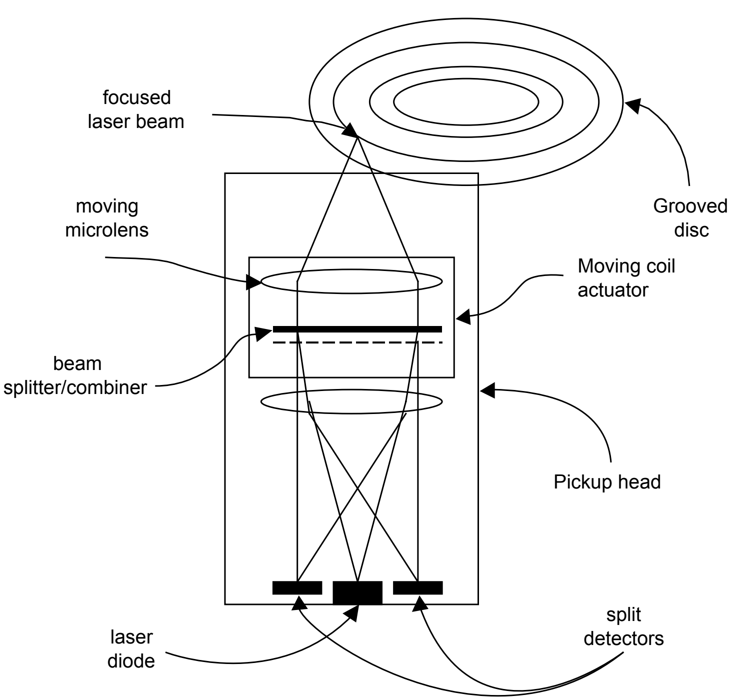


Figure 4.6 *Schematic of optical data recording system.*

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, where the laser beam has impinged on the surface of the disc the dye decomposes, causing the formation of a pit in WORM media, or polycarbonate to flow into the gap, and a mechanical deformation of the film in the case of CD-R. In WORM discs the difference in reflectivity in the pit is measured, and in CD-R the reduction in the optical path length and hence the intensity of light falling on the detector when the deformation is hit by the traversing read out laser beam. The principles behind WORM and CD-R recording using dyes are shown in Figure 4.7.[25]

As well as meeting the normal commercial requirements, *i.e.* cost and availability, dyes for use in optical data recording need to meet a set of technical criteria:

- High reflectivity of the solid film at the recording wavelength
- Good solubility in the solvent used for spin coating the discs and the ability to form solid films
- Stable to environmental and processing conditions, *e.g.* oxidation, hydrolysis and light

Reflectivity, a crucial property, is related directly to the refractive index of a dye film, which itself is fundamentally related to the molar absorption coefficient of the dye. It

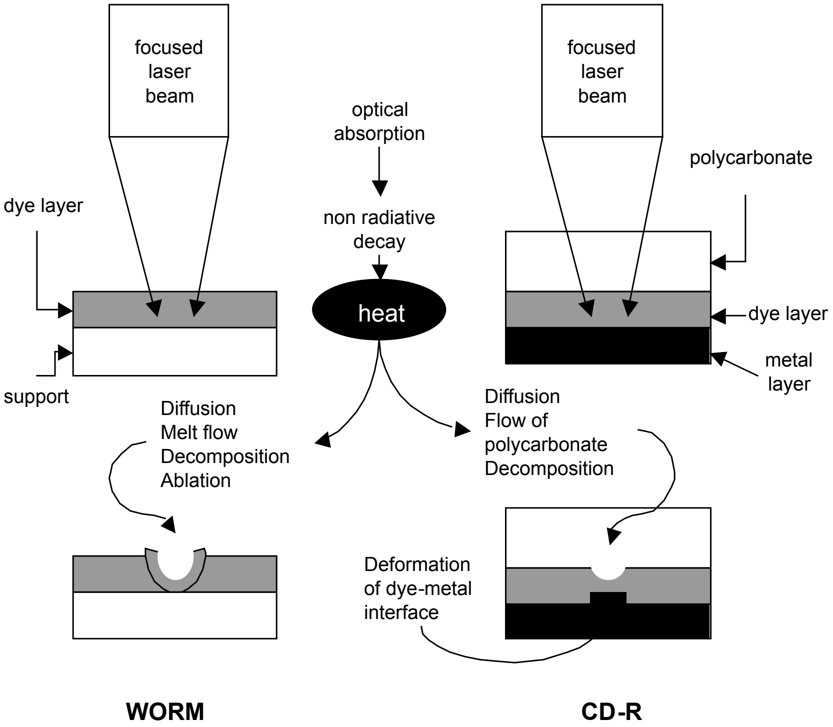


Figure 4.7 *Recording in WORM and CD-R dye based discs.*

has been shown that the necessary reflectivity of over 25% occurs most often when the film has a refractive index of greater than 2.5, obtainable with certain dyes with $\varepsilon_{\max}$ greater than 200 000. The requirements for dyes in WORM media, CD-R and DVD-R media are very similar but there are differences.

- Dyes for WORM discs must produce films with high absorbance and reflectivity in the wavelength range 775–830 nm
- Dyes for CD-R must produce film with high reflectivity and a small but finite absorbance at 775–830 nm
- Dyes for DVD-R as for CD-R but at wavelengths in the region 630–650 nm

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.[27] For the longer wavelength outlets at 775–830 nm both cyanines and phthalocyanines are used commercially.[28] However, for DVD-R the shorter wavelength requirements rule out phthalocyanines, as their main absorption band cannot be tailored to absorb in the required 630–650 nm range. Carbocyanine dyes do suffer from low light fastness properties and a light stabiliser must be included in the film formulation. Examples of carbocyanines and phthalocyanines used in WORM, CD-R and DVD-R are shown in Figure 4.8.

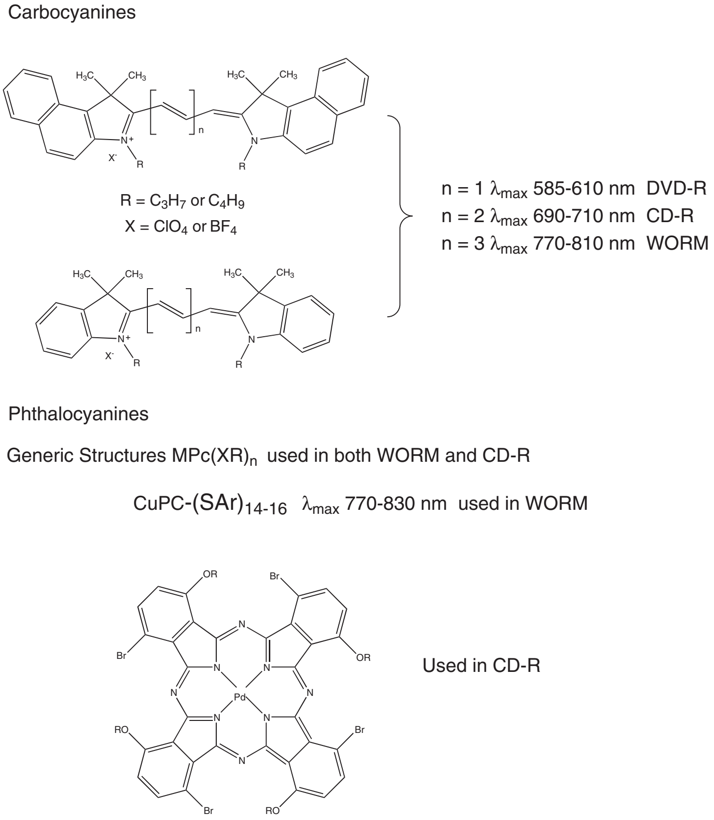


Figure 4.8 *Dyes used in WORM, CD-R and DVD-R discs.*

4.3.2 Developments in Optical Data Storage

With the ever-increasing need for the storage of large volumes of data, developments in optical storage media are occurring at a very fast rate. The introduction of new solid-state diode lasers has been the technical driving force behind these changes. The storage capacity potential from the use of these lasers is shown in Table 4.3. The development of new dyes, which can be addressed effectively by these lasers, is the current challenge to chemists.

Table 4.3 *Growth in storage capacity with lasing wavelength*

Lasing wavelength/nm	*Introduction year*	*Approx. storage capacity/Gb*
780	1992	0.75
630–650	1999	2.3
520	2001	10
430	2003(?)	20

The next stages in the development beyond 20 Gb will be to move away from heat mode recording to photon mode recording. This is discussed elsewhere in this book, under photochromics (Chapter 1, section 1.2.8.3) and under holography, optoelectronics and photonics in Chapter 5.

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 2.7.2). 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 or more recently amorphous silicon in high volume machines, but since the 1980s there has been a swing to organic materials, to such an extent that greater than 95% of machines currently use organic photoconductors.[29–31]

In the electrophotographic process the photoconducting element is present as a coating on the surface of a rotating drum or a continuous belt. The drum or belt is fully charged for use by means of a corona discharge. The image to be copied or printed is then written on to 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 4.9.

Photoconductors can be constructed as a single or a dual layer, but more commonly the latter. The two layer photoconductors consist of a very thin charge generation layer (CGL), 0.2–2 μm, and a much thicker charge transport layer (CTL), 15–30 μm, as illustrated in Figure 4.10. 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

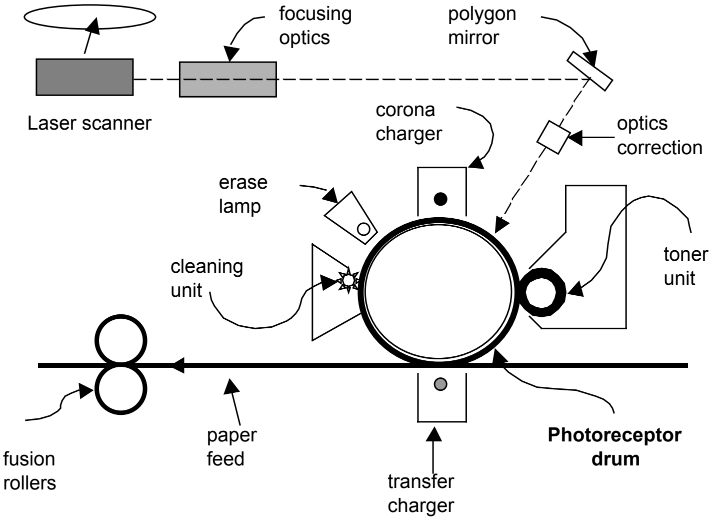


Figure 4.9 *Photoreceptor drum in a laser copier.*

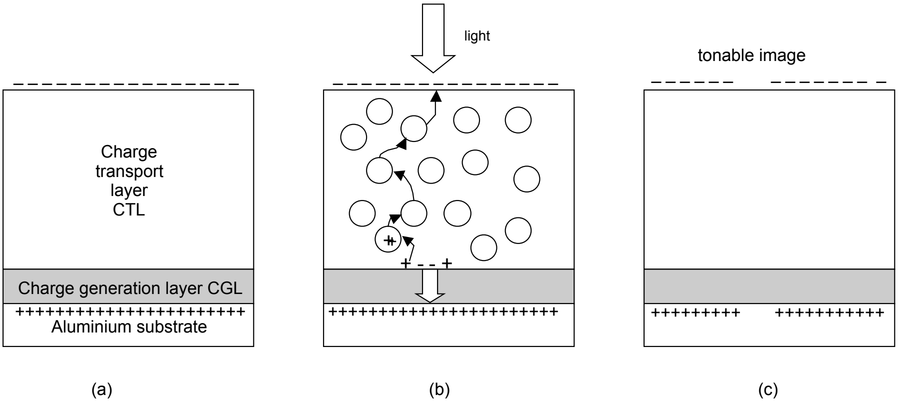


Figure 4.10 *Mechanism of photoconduction in an organic photoconductor.*

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)
- 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 4.11. Photosensitivity is expressed as the energy ($E_{0.5}$, erg cm^{-2}) required to 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 to a specific diode laser or LED. 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 and usually in a specific morphological form.

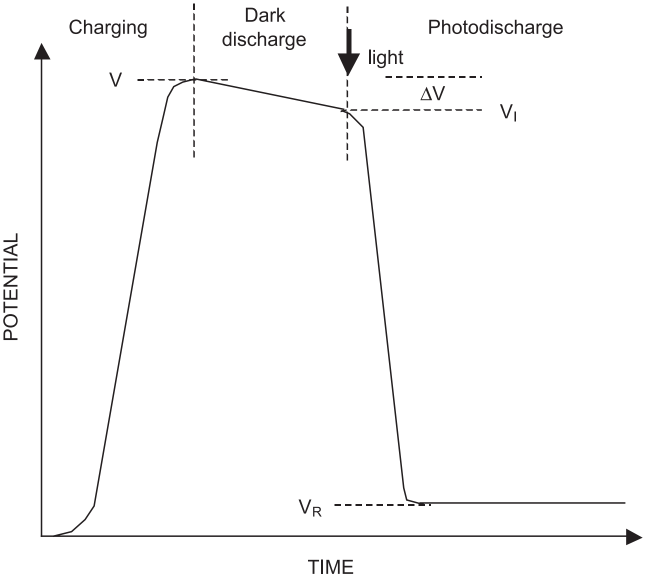
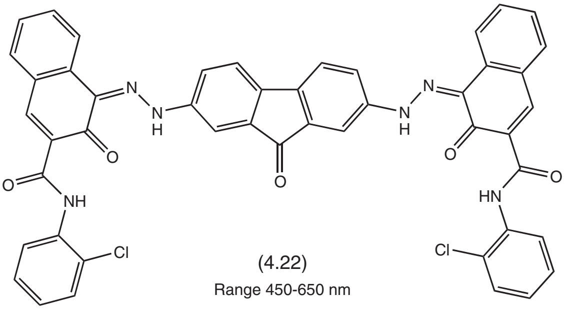


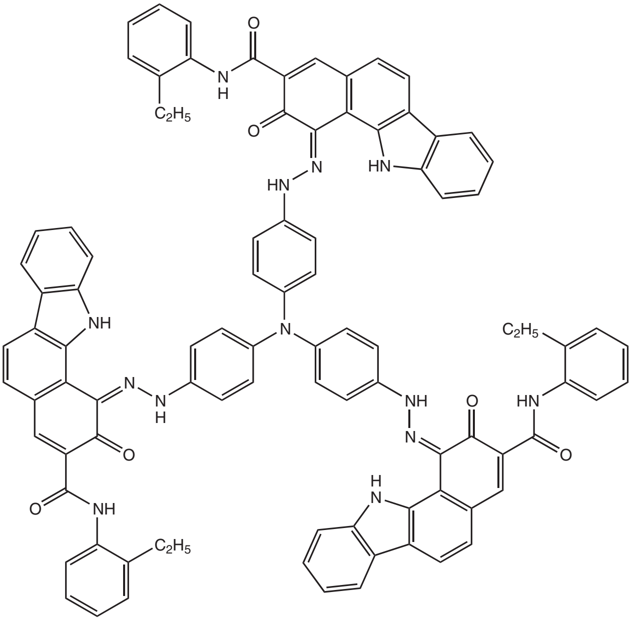
Figure 4.11 *The charge–photodischarge cycle in photoconductors.*

4.4.1.1 Azo Pigments

A vast range of azo pigments have 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).[29] 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 tris-azo structure, the absorption can be extended into the near-IR region. Two typical azo pigments that have found commercial applications (Ricoh) are (4.22) in visible light sensitive copiers and (4.23) in near-IR printer/copiers.



(4.22)
Range 450-650 nm
$E_{0.5}$ = 3 at 600 nm
Dark decay = -1 V s^{-1}



(4.23)
Range 450-800 nm
$E_{0.5}$ = 3.6 at 790 nm
Dark decay = -25 Vs^{-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 4.2.1.7) 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 near-IR sensitive organic photoconductors, together with their electrophotographic data.[30]

Most phthalocyanines show inferior dark decay to azo pigments, an exception being the titanyl phthalocyanines, where in the best cases, *e.g.* the α- and *Y*- forms, they show comparable dark decay coupled with superior photosensitivity. A comparison of the sensitivity of azo pigments and selected polymorphs of phthalocyanines is shown graphically in Figure 4.12.

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 as CGMs in commercial organic photoconductors include quinones, *e.g.* dibromanthanthrone (4.24) by Xerox and Konica,

Table 4.4 *Electrophotographic data of solution coated near-IR absorbing phthalocyanines (Pc)*
(Reproduced with permission of the American Chemical Society)

		Electrophotographic data (spectral range 550 – >800 nm)	
MPc	*Polymorph*	*Dark decay/V s^{-1}*	*Sensitivity $E_{0.5}$ (wavelength/nm)*
H_2Pc	τ_1	–5.1	4.5 (780)
H_2Pc	τ_2	–13.0	2.5 (780)
H_2Pc	*X*	–20	4.5 (780)
MgPc	Agg.	–80	30 (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)

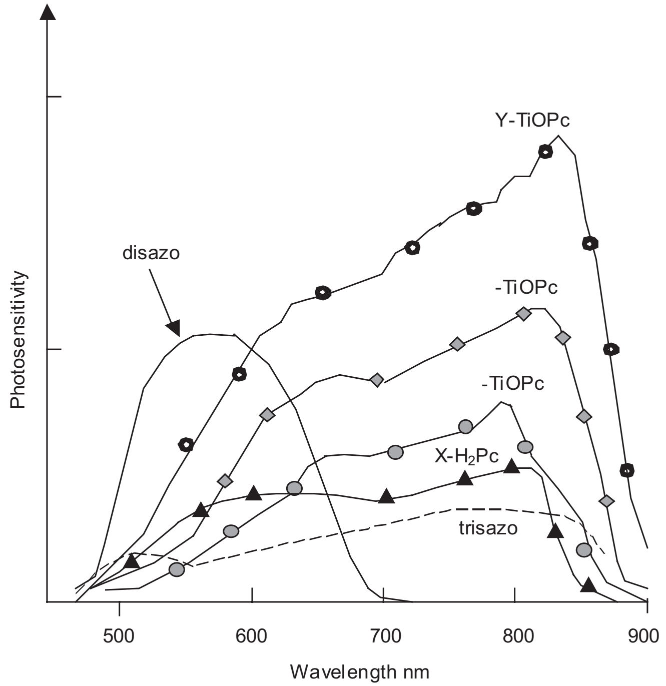
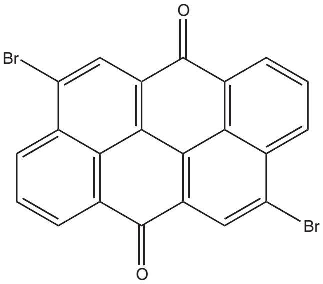


Figure 4.12 *Comparative photosensitivity of azo pigments and phthalocyanines.*

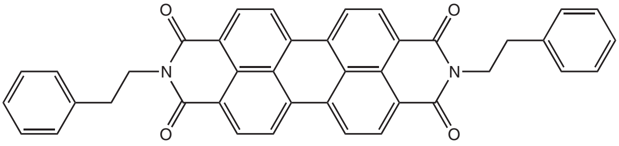
perylenes, *e.g.* (4.25) by Kodak and Océ and (4.26) by Xerox, and squaryliums, *e.g.* (4.27) by Lexmark.

4.4.2 Charge Transport Materials

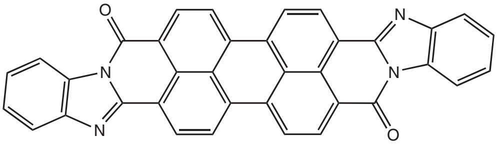
Most of the materials used as charge transport materials (CTMs) in commercial photoconductors work by a positive hole-transport mechanism, as indicated in Figure 4.10. Hole transport p-type semi-conductors are materials that are electron rich and give up their electrons readily. Because of this property they are easily oxidised by air and light, and a balance must be obtained between environmental



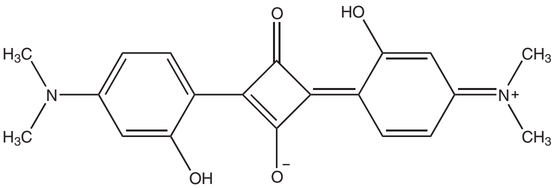
(4.24)



(4.25)



(4.26)



(4.27)

degradation and performance in the photoconductor. The main chemical classes, which give efficient CTLs, are triarylmethanes, triarylamines, hydrazones, pyrazoles and oxadiazoles. A selection from these five classes of materials is given in Figure 4.13.

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. In the triplet excited state the sensitiser can undergo chemical reactions, *e.g.* dissociation into radicals, ionisation, internal electron transfer and is then not available for return to the original ground state, or alternatively it can react with other molecules, *e.g.* electron excitation transfer, H-atom abstraction, before returning to

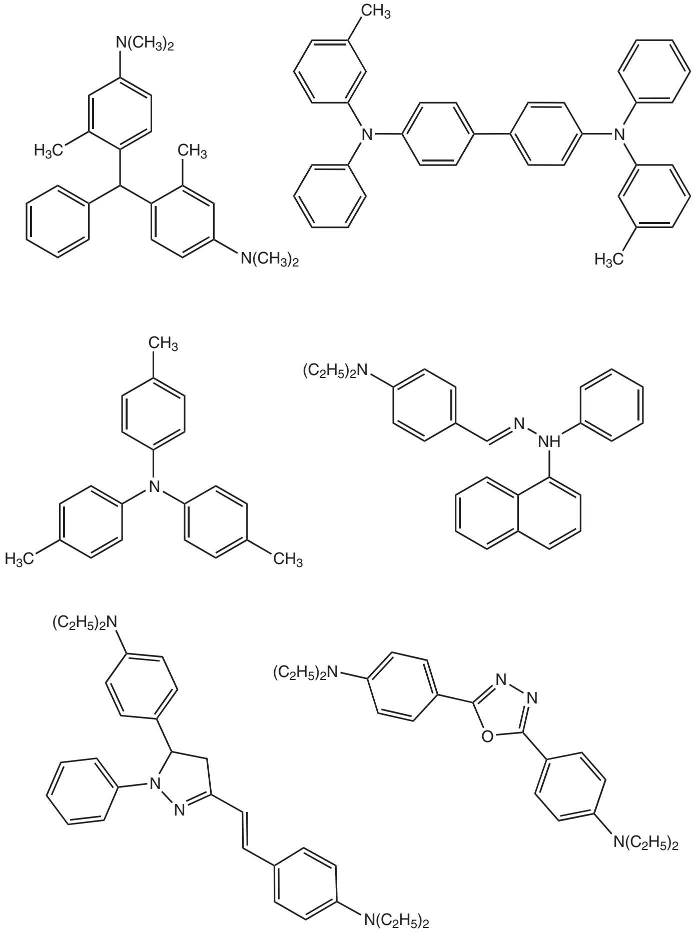


Figure 4.13 *Charge transport materials for dual layer photoconductors.*

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 either 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 in work in a different way in order to initiate polymerisation at selected visible wavelengths of light. For instance the 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 oxidative singlet oxygen by an electron transfer reaction with ground-state triplet oxygen (Figure 4.14). Since 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 are shown, together with their singlet oxygen quantum yields (ϕ_Δ), in Figure 4.14.

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 cyclo peroxides. The reactions are carried out at very low temperatures, *e.g.* –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 into alcohols in the presence of an appropriate reducing agent.[32,33] Some typical reactions are shown in Figure 4.15.

4.5.2 Photosensitisers in 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.[34] Typical dyes used in these processes are Rose Bengal, Eosin, acridine orange, Rhodamine B and Methylene Blue (see also Figure 4.14).

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.[32,33,35–38] In radiation curing a reactive resin, usually solvent free is applied to a substrate and then exposed to high energy radiation, *e.g.* ultraviolet and electron beam, which causes the resin to cross-link and polymerise and so form a hard coating. Ultraviolet, which is the dominant method (around 90%) of radiation curing, requires a photoinitiator to be present. Of the common polymerisation methods that are used, radical polymerisation of acrylic oligomers, *e.g.* epoxy acrylates, polyester acrylates, polyether acrylates and urethane acrylates, is by far the most important. Of less importance in coatings is the cationic polymerisation of epoxy and vinyl ether resins.

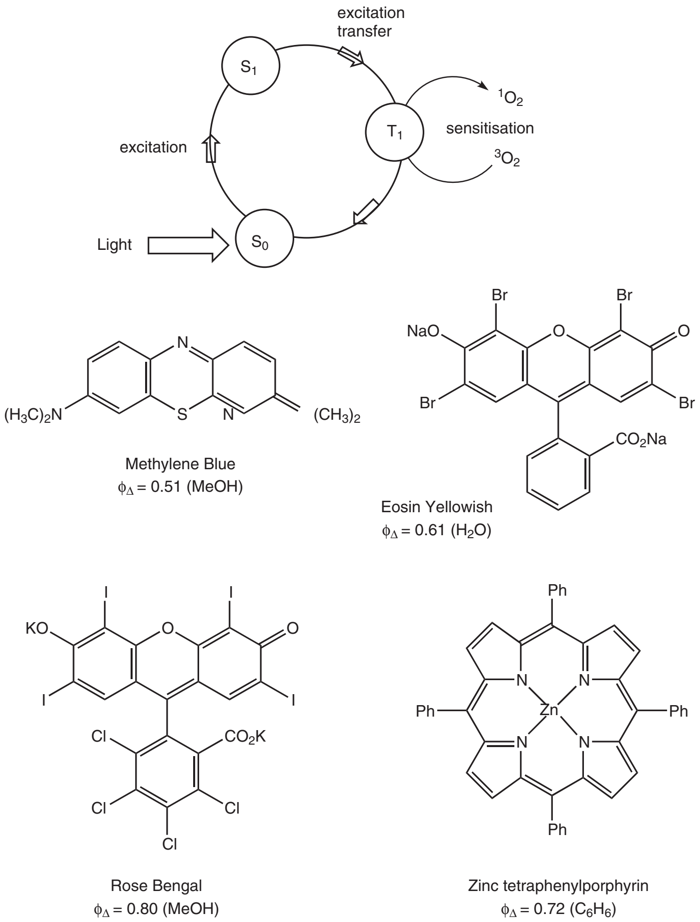


Figure 4.14 *Sensitisers used for singlet oxygen production in photochemical synthesis.*

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 (MAPO, 4.28) and bis-acylphosphine oxides, (BAPO-1, 4.29) and (BAPO-2, 4.30), polymerisation being initiated after the formation of radicals. The MAPO initiators operate in the near-UV region whilst the BAPOs absorb visible light in the region 370–430 nm. This visible absorption allows thicker layers to be cured, including those that are white pigmented (*e.g.* with rutile TiO_2).

Sensitised photopolymerisation is also used in the production of the printing plates used in both the lithographic and flexographic printing processes.[39] As discussed elsewhere (see sections 4.2.2.1 and Chapter 1, section 1.4.2.4), negative lithographic plates are usually constructed by the photoinsolubilisation of the diazonium resins, but there is an alternative, but lesser used process, in which the photopolymerisation of multi-functional acrylates, *e.g.* pentaerythritol tetraacrylate, is achieved using

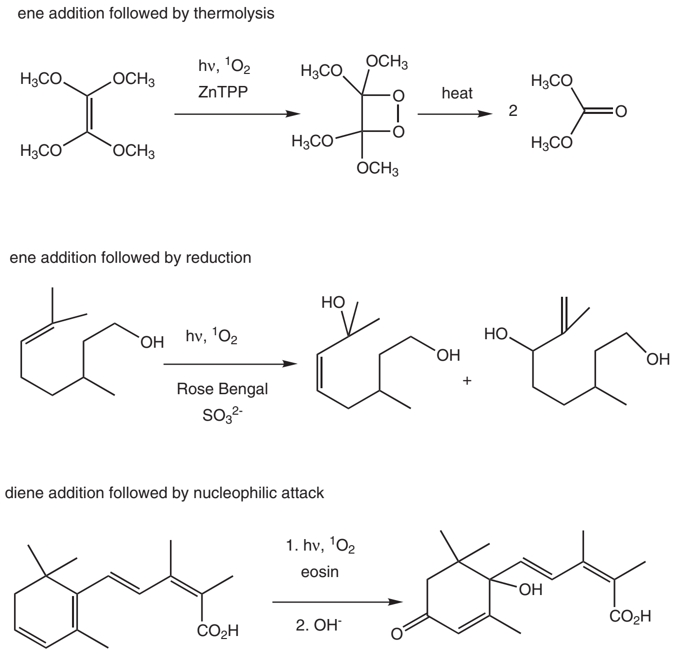
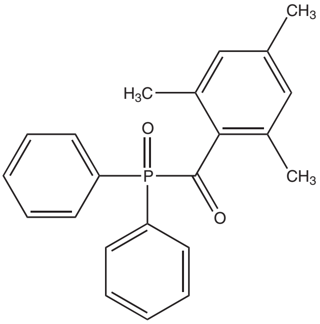
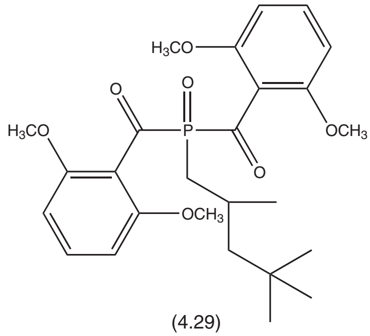


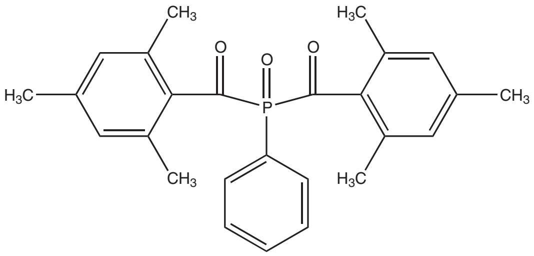
Figure 4.15 *Dye sensitised singlet oxygen photooxidation reactions.*



(4.28)



(4.29)



(4.30)

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 computer to plate technology.[40] 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 4.16. 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 is used in the production of holograms (see Chapter 5, section 5.4.2).

Visible light is advantageous in photopolymerisation as it is generally transmitted at more wavelengths through complex materials. It is therefore more versatile and can be used in carrying 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 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.[41] An example of this system, that is available commercially (Spectra Group), uses the UV–Visible fluorone initiator (4.31), absorption maximum 470 nm and range

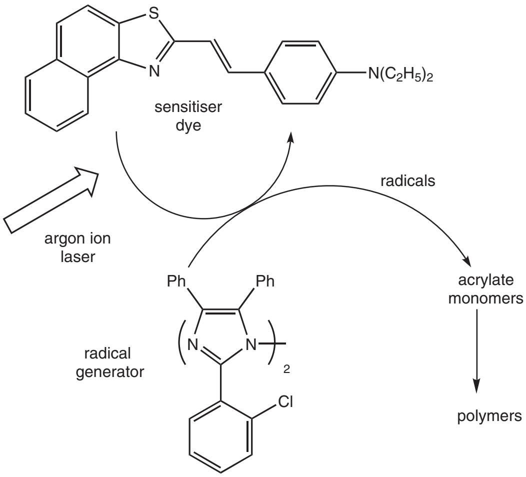
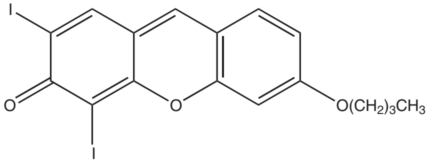


Figure 4.16 *Photoinitiation system for acrylate polymerisation using an argon ion laser (488 nm).*



(4.31)

350–530 nm, together with borates, *e.g.* tetramethylammonium triphenylborate or amines as co-initiators in the curing of acrylates.[42] The photoinitiator (4.31) also sensitises iodonium salts to cure epoxy resins with visible light.

Experimental fluorone initiators are available from the Spectra Group that absorb at 535 nm, designed for the frequency doubled Nd:YAG laser, and at 635 nm for the helium–neon (633 nm) or diode (635 nm) lasers.[42]

One application for the radiation curing of resins is in stereolithography. Stereolithography 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 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 4.17. Because the machine in Figure 4.17 is very similar operationally to a laser printer it is sometimes called a 3D printer.

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 making microstructures. An exciting alternative approach is to use the non-linear optical property of two-photon absorption. 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 photon of higher energy. In this case the energy of a near-IR laser can be converted into high-energy fluorescence in the visible region. Examples of the dyes that show this two-photon fluorescence are the stilbene (4.32) and the fluorene (4.33).[43,44] The basis of the design of these efficient two-photon dyes is to have a highly fluorescent aromatic core, sitting between a thermally stable π electron donor on the one side and a heteroaromatic ring π electron acceptor on the other side, as shown for (4.33).[45a]

The use of internally generated UV–Visible radiation from an infrared two-photon initiated fluorescence allows much deeper penetration of the resin than with conventional single photon initiation.[45b] In this two-photon photocure system the

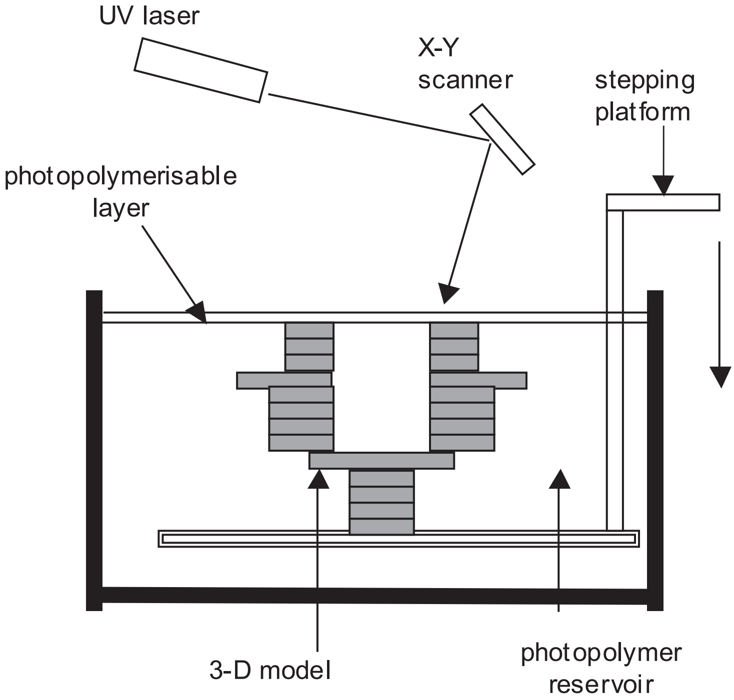
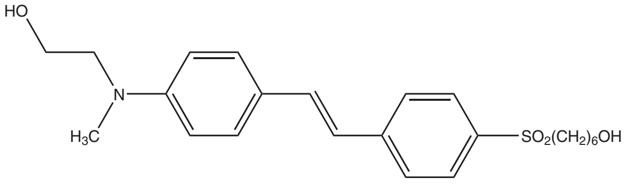


Figure 4.17 *The stereolithographic process.*



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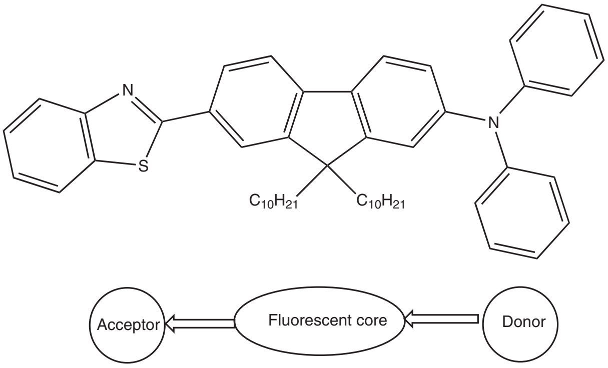


(4.33)

chromophore is mixed in with the resin and a co-initiator and then irradiated with a near-IR laser in very short pulses. As an example, irradiation of methyl acrylate in the presence of photosensitiser (4.31), and an amine co-initiator, at 780 nm using 80 fs pulses at 88 MHz repetition rate, gave coiled forms of the resultant polymer at least 10 μm thick (see Figure 4.18).[46]

The use of two-photon processes is also being extensively studied in the use of photochromics in 3D data storage (Chapter 1, section 1.2.8.3) and in the holographic storage of data, which is covered in Chapter 5 (section 5.4).

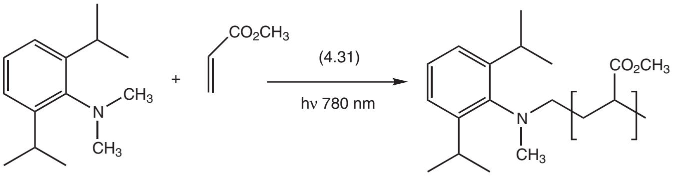


Figure 4.18 *Two-photon initiated polymerisation of methyl acrylate.*

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 2.6.1). 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 closely situated halide ion, creating a positive hole. A simplified schema is shown in Figure 4.19.

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 sensitivity of the silver halide emulsion to blue light. The most important class of compounds used in this

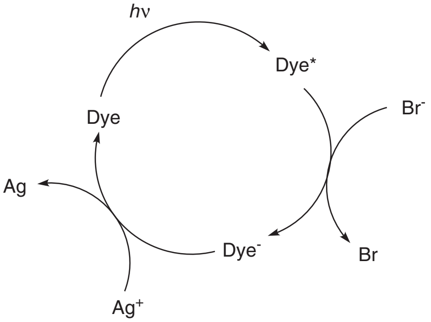


Figure 4.19 *Schema for spectral sensitisation of silver bromide.*

outlet, and in the important area of infrared sensitive films, are the cyanines, especially merocyanines and carbocyanines. Some typical blue, green and red materials and near-IR materials are shown in Figure 4.20.

4.6 Applications of Sensitisers in Medicine and Chemical Biology

The generic term for that branch of biological science which 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:

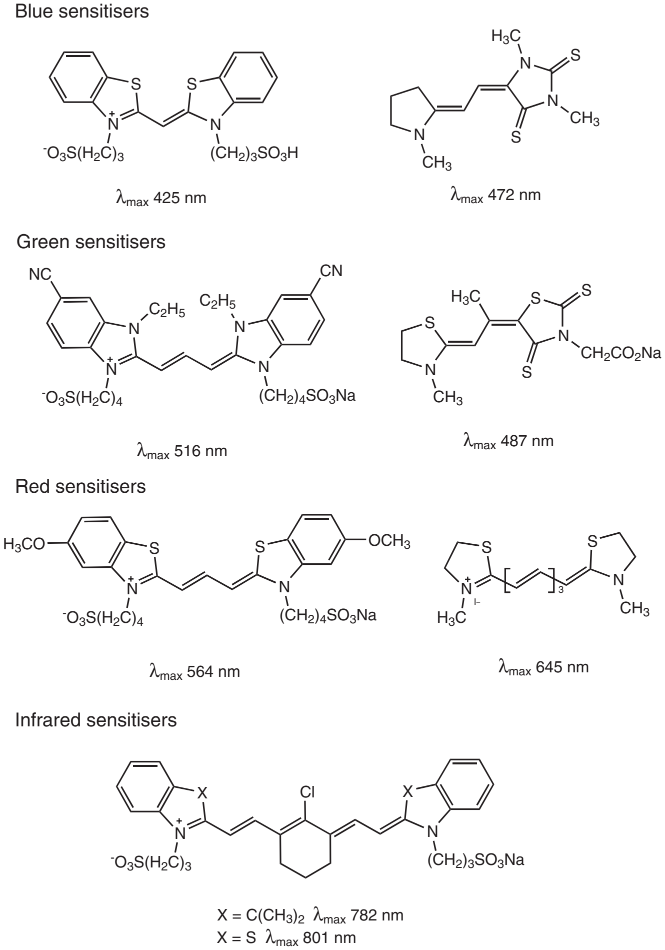


Figure 4.20 *Spectral sensitising dyes for photography.*

- 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.[47,48] Any fault in this mechanism, such as red–green colour blindness, is a distinct hindrance in a world constructed around normal colour vision.
- Photosynthesis, crucial for plant growth, involves the interaction of light with chlorophyll.[49] Man's attempts to reproduce this process in a controllable manner will be discussed under artificial photosynthesis (section 4.7.2).
- 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 below 290 nm, UV-B, light between 290 and 320 nm and UV-A 320–400 nm light.
    - 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, 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, *e.g.* 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 barriers, *e.g.* barrier creams of zinc oxide, or chemically by strong UV-B/A absorbers, *e.g.* 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 fifty years it has developed into the discipline now known as *photomedicine*.
- 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, namely phototherapy and photodiagnosis:

- Phototherapy is the use of ultraviolet, visible white light or near-infrared radiation, to treat a variety of diseases
- Photodiagnosis is the use of optical methods, based on fluorescence, for early diagnosis (optical biopsy)

Phototherapy is the generic term covering therapies which use light either with or without a sensitiser. Those that do not require a sensitiser use the natural chromophores within the tissue to perform this function (*e.g.* treatment of vitamin D deficiency in rickets, and neonatal jaundice). Those that do use an added sensitiser include photochemotherapy (largely psoriasis and skin disorders) and photodynamic therapy (currently mainly cancer). Photodynamic therapy is differentiated from photochemotherapy by its additional requirement for the presence of oxygen at molecular or ambient levels.[33] In this text we will deal only with photodynamic therapy since, at the present time, this is the main driving force in phototherapy.[33,50,51]

4.6.2 Photodynamic Therapy

Work during the last ten years on photodynamic therapy (PDT) has established the methodology as effective in the early treatment of cancers, and in the treatment of certain skin disorders and viral infections. Approval by the regulatory authorities for sensitisers in this process began in 1993 when Canada allowed the use of Photofrin (QLT Therapeutics), an action followed later by most countries around the world. Now many other companies have sensitisers at late stage clinical trials (2001), see below in Table 4.5. An excellent introduction to the chemistry of this topic is provided in the book written by Bonnett.[33]

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* a fibre optic, where it interacts with the sensitiser and oxygen, causing cell destruction. This is shown schematically in Figure 4.21.

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 h time. Back in the clinic the tumour in the patient is illuminated for around 10–30 min 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 to is due to interaction of solar radiation with the strong absorptions in the 400 nm region and below, common in porphyrins, as discussed in section 4.5 above.

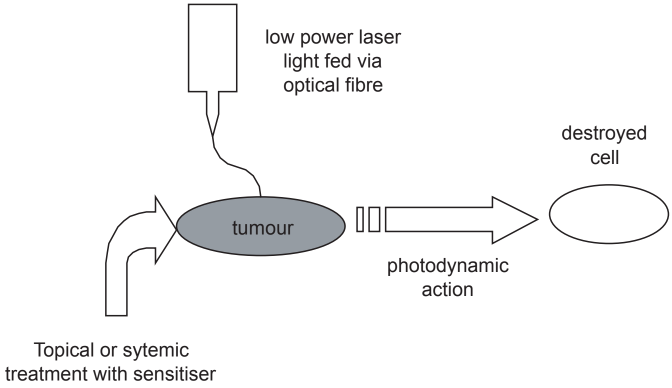


Figure 4.21 *Outline of photodynamic therapy (PDT) treatment of tumours.*

4.6.2.1 The Mechanism of PDT

There are two main ways in which light can react with a 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 electron transfer from the excited triplet state of the sensitiser to triplet oxygen producing the highly oxidative singlet oxygen. This mechanism has already been discussed (see Figure 4.14).

It is now well established that the sensitisers in PDT, with the exception of cyanines, require oxygen. The dominating mechanism operating in PDT is Type II production of singlet oxygen, and this 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.[33,51]

4.6.2.2 Photosensitisers for PDT

Although there are many dyes which can photosensitise the production of singlet oxygen (see section 4.4.1), in PDT the first products of real interest came from haematoporphyrin.[52] Subsequent, studies led to the haematoporphyrin derivatives HpD Stage I and Stage II, which were found to be more active as PTD 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 4.22. 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.[33]

Sensitisers of the haematoporphyrin derivative class are called first generation sensitisers, because they do suffer from some inherent deficiencies, 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)
- Have low absorption, ε_{max} 5000 in the desirable red light region (λ_{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)

New, second generation photosensitisers were needed to overcome these deficiencies and also to display the following characteristics:

- Constant composition that is easy to synthesise, preferably a single compound
- Activate at wavelengths greater than 630 nm and preferably over 650 nm
- Show low dark toxicity, *i.e.* does not become cytotoxic until light is applied and therefore treatment can be controlled by a light dose for a given drug dose
- Must localise in tumours but clear from the body after it has completed its work
- Must be soluble in body tissue fluids, or be capable of formulation for injection, and then be carried around the body

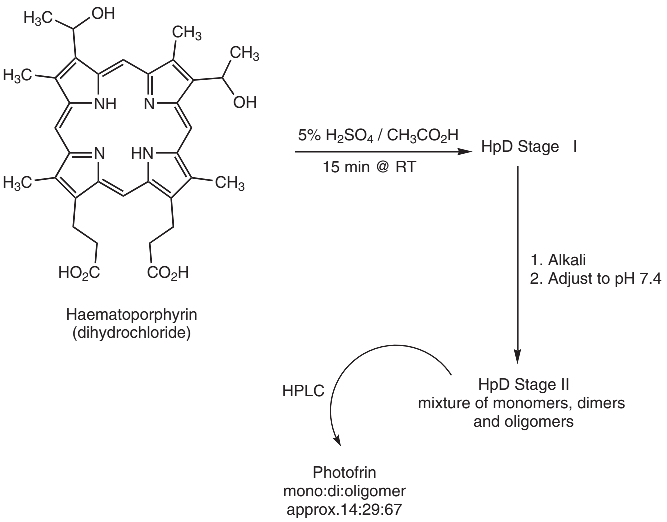
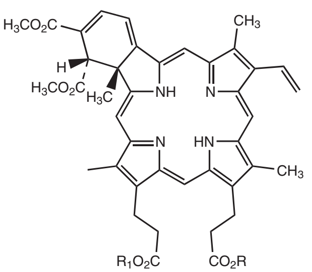


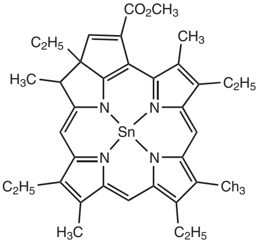
Figure 4.22 *Process for the production of haematoporphyrin derivative photosensitisers.* (Reproduced with permission of Gordon and Breach.)

The search for second generation sensitisers has yielded several leading candidates. The structures of some of those that are undergoing clinical trials are shown in Figure 4.23.[50,51,53]

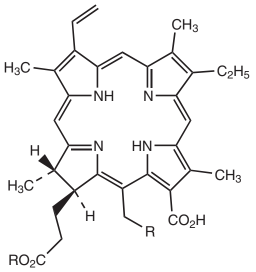
A comparison of the photodynamic properties of these lead candidates with Photofrin is given in Table 4.5. They are all red-shifted in comparison with Photofrin; treatment times are marginally smaller as are light and drug doses. On this evidence, one of the better-looking materials is m-THPc, also known as Foscan. However, as an indication of the pitfalls that can arise in this area, it was found that certain people were extremely sensitive to this product in sunlight, and in the end the FDA turned down Scotia's application for US marketing approval for Foscan, delivering a near fatal blow to the company.[54]



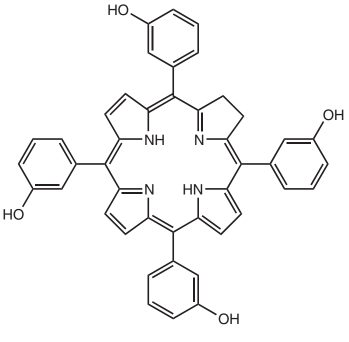
Benzoporphyrin derivative (BPD)
Mixture R,R_1 = H or CH_3



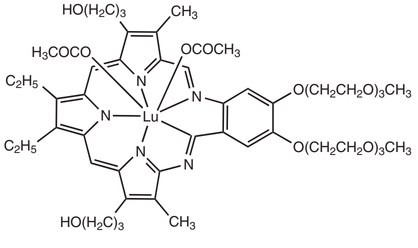
Tin Etiopurpurin ($SnET_2$)



NPe_6
R = aspartic acid



m-Tetrahydroxyphenylchlorin
(m-THPc)



Texaphyrin

Figure 4.23 *Second generation photosensitisers under clinical trials.*

Table 4.5 *Comparison of 2nd generation sensitisers with photofrin*

Sensitiser (Company)	*λmax/ nm (εmax)*	*Singlet oxygen* $\phi_\Delta(^1O_2)$	*Drug use/* $mg\ kg^{-1}$	*Light dose/* $J\ cm^{-1}$	*Treatment time/s*	*Indicators*	*Comments (US Approval)*
Photofrin (QLT)	628 (3000)	0.89	1.2–5	75–250	750–2500	Early treatment of bladder, lung, esophagus, cervix, stomach and mouth Palliative in later stages	Skin phototoxicity (up to 4 weeks) is a problem (Approved, esophegal and lung)
BPD (QLT) 'Visudyne' (Cibavision)	690 (34 000)	0.84	4	150	1500	Skin cancer Age-related macular degeneration	No skin phototoxicity. Difficult synthesis (Approved, age-related macular degeneration)
m-THPc 'Foscan' (Scotia)	652 (35 000)	0.87	0.15	5–20	50–200	Chest pancreas ENT tumours	Skin phototoxicity high in certain patients
SnEt2 'Puryltin' (Miravant)	665 (30 000)	0.71	1.2	150–200	1500–2000	Metastatic breast carcinoma, basal cell carcinoma. Macula degeneration cancers	
NPe6 Nippon Lab	660 (40 000)	0.77	1.0	25–200	1500	Skin cancers Lung	No skin phototoxicity
Lu-Tex 'Lutrin' (Pharmacyclics)	732 (42 000)	0.56	1.0	150	1500	Breast cancer, malignant melanoma, basal cell carcinoma	No skin phototoxicity Pain associated in skin during light treatment
ALA-protoporphyrin IX 'Levulan' (DUSA)	635 (5000)	0.56	60	50–150	500–1500	Skin cancers, dermatological conditions (psoriasis)	No skin phototoxicity Can be used topically with blue light for skin disorders (Approved, actinic keratoses)

Other photosensitisers in clinical or pre-clinical trials include; zinc phthalocyanine, aluminium sulphonated phthalocyanines, benzoporphyrins, benzochlorins and purpurin-18-*N*-alkylamides, all of which absorb strongly in the 675–700 nm region.[51]

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 by-passed resulting in a build up of protoporphyrin IX in the cell. The mechanism is illustrated in Figure 4.24.[55]

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 400 nm. At these wavelengths light penetration is low, but this product is aimed at the treatment of the epidermis where protoporphyrin builds up naturally and penetration is not an issue.[56] 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.

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 around the following approaches:

- Increase the depth of tissue penetration. This could be achieved by moving to

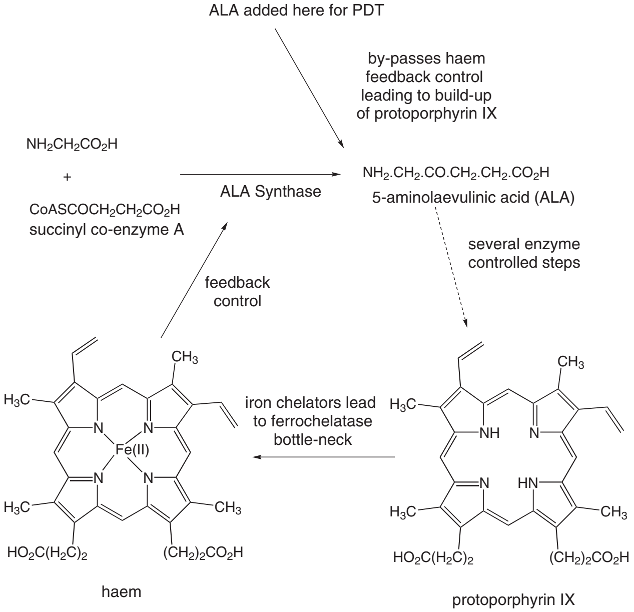


Figure 4.24 *Mechanism of build-up of protoporphyrin IX in tumour cell.*

longer wavelengths, but not too far into the near-IR (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 in this region. One way round this would be to use two-photon excitation; exciting at 830 nm by two photon absorption which converts into a single 430 nm photon, which then acts on absorptions in that region of the photosensitiser's absorption spectrum. Because of low light tissue penetration this will be most beneficial in the treatment of superficial lesions.

- Enhancing specificity for tumour sells. One possible way is to attach the photosensitiser covalently to a monoclonal antibody, which would carry it to the tumour.
- Trigger programmed cell death (apoptosis) as opposed to random cell death (necrosis). This allows sub-lethal doses of photosensitiser, preventing damage and inflammatory response in healthy tissue.

4.6.2.3 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.

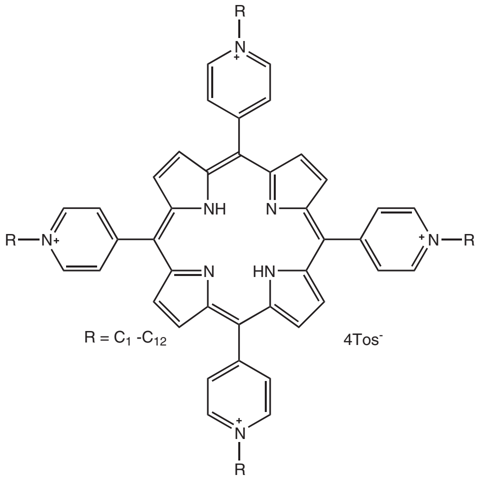
- *Lamps*. These are used in the treatment of skin diseases, for instance using halogen lamps with filters to give light in the region of 400–500 nm. Developments include a 5 W metal halide lamp delivering 40 nm band in the red and 0.5 W at the end of a light guide.
- *Lasers and LEDs*. Dye lasers pumped by Ar ion, Cu ion and frequency doubled Nd:YAG solid state lasers. LEDs operating at 635–652, diode lasers at 635 (AlGaInP), 652 (InGaAlP) and 730 nm (AlGaAs). Solid state pulsed lasers, (*e.g.* Nd:YAG, Nd:YLF) operating at second, third and fourth harmonic generation.

4.6.2.4 Use against Viruses and Bacteria

PTD has been evaluated 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.[57] The use of Photofrin in inactivating HIV-1 in blood has also been described, whilst BPD (see Figure 4.23) has been used to inactivate feline leukaemia retrovirus in both spiked human blood and infected cat's blood.[51]

Photodynamically produced singlet oxygen should be effective in killing bacteria and this has proved to be the case. Gram-positive bacteria can be destroyed on irradiation with light in the presence of neutral or anionic sensitisers, including Photofrin, protoporphyrin IX and sulfonated phthalocyanines. Using cationic sensitisers, *e.g.* the cationic porphyrin (4.34), it was possible to destroy both Gram-positive and Gram-negative bacteria.

An alternative approach is to photoactivate existing antibacterials that are known to act *via* DNA intercalation. For example using a simple light box over the treated



(4.34)

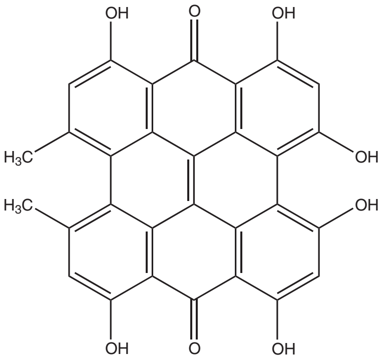
culture gave a ten-fold increased the activity of the amino acridine antibacterial, Aminacrine, against *S. aureus*.[58] A big challenge in antibacterial research is destruction of the Methicillin-resistant *S. aureus* (MRSA) bacteria. Phenothiazinium dyes, based on methylated methylene blue, when used as photosensitisers were shown to kill MRSA *in vitro* more effectively than vancomycin.[59]

4.6.3 Photodiagnosis and Imaging

Since PDT photosensitisers locate preferentially in tumours they should be in theory of value in the diagnosis of the disease. The procedure of diagnosis would involve measuring the fluorescence of the tumour area before and after treatment with the sensitiser (see Chapter 3, section 3.5.6). For this to work effectively the fluorescence quantum yield should be as high as possible. However, the most effective photosensitisers are those with a high triplet-state quantum yield and hence a low fluorescence quantum yield. Therefore it is unlikely that the more active photosensitisers can be used for this purpose.

Progress has been made using the ALA-protoporphyrin IX photosensitiser system in *in vivo* fluorimetry, because the fluorescent protoporphyrin concentration in tumour cells is much higher than in healthy cells. An example of its use is in the successful diagnosis of bladder tumours, giving superior results to visual examination. A new generation of pentyl and hexyl esters show an even more intense fluorescence.

Another interesting development is the use of the naturally occurring herbal extract hypericin (4.35), which has the extended quinone structure (4.35), in both photodiagnosis and therapy. This is given to the patient, either orally or topically, who is then illuminated with blue light. The cancer tumours show up as red spots, the light from which can be recorded on a red sensitive camera, subjected to computational analysis and then converted into an image on the computer.



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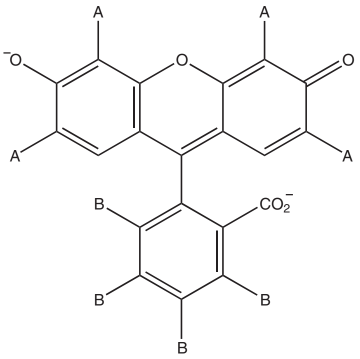
4.6.4 Photoinsecticides

Research into the use of light activated dyes as pesticides has a long, but sporadic history dating back to the early years of the 20th 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 in both 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 have carried out the most consistent research in this field, during the years from 1975–1998, and this has led to the first large scale commercial application.[60,61]

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 (4.36) it was shown that increasing halogenation gave higher phototoxicity, consistent with a lower fluorescence and higher conversion into 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

(4.36)

The process worked with mosquito larvae, houseflies, face flies and fruit flies, and it was the latter that presented the first commercial opportunity. The use of malathion in the spraying of fruit crops was under severe environmental challenge due to toxicity concerns and a safer alternative was required. Phloxine B has low mammalian toxicity and trials in its use as a photoinsecticide in the control of Mediterranean Fruit Fly, which can devastate citrus crops, began as a collaboration between PhotoDye International (Heitz's spin off company) and the U.S. Department of Agriculture.

Since the insects need to digest the photosensitiser, a suitable bait had to be devised that could be sprayed effectively onto the crop. The bait that was devised consisted of phloxine B, Mazoferm, high fructose corn syrup, an adjuvant, soya bean oil, PEG and acetic acid. Pilot field trials in Mexico and Guatemala were successful in suppressing fruit fly populations, and in determining the dosage rates and application intervals. The agent was shown to have no detrimental effect on the important honey bee population. Consequently in 1997 the technology was adopted to maintain the MedFly Barrier Zone between Mexico and Guatemala, used to protect the USA from any influx of the Mediterranean Fruit Fly.

4.7 Solar Energy Utilisation

Man seems to have a demand for energy that is ever-increasing and unstoppable, and which is met currently almost entirely by the use of fossil fuels. As these are non-renewable resources, that also have great use in providing the building blocks of the worldwide chemical industry, there is an urgent requirement for alternatives to take us through the 21st century and beyond. The natural elements of wind and water have long been used, but the greatest energy source of them all, solar energy, has until very recently been largely the reserve of plant life. In the last couple of decades, research and development into systems that can produce clean fuels such as hydrogen and other chemical feed stocks, as well as the more obvious electricity, has accelerated and is now bearing fruit.[62,63]

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 and chemical building blocks, and reduced nitrogen products for agricultural uses. The systems that can be used to produce these outputs are photovoltaics and photo-electrochemical, based on semi-conductor technologies, photochemical based on molecules and photobiological based on blue–green algae and photosynthetic bacteria. These photosystems can potentially be used in a variety of combinations. The overall schema is shown in Figure 4.25.

4.7.1 Solar Cells and Electrical Energy

The utilisation of solar energy to create heating systems has a long history going back to the ancient Greeks.[64] Solar collectors, employing mirrors, glass panels and lenses were employed in the 19th century to run static steam engines and especially solar pumps for the distillation of water in arid desert regions, *e.g.* Egypt. Modern research, driven from the 1970s by successive oil crises, has concentrated on the

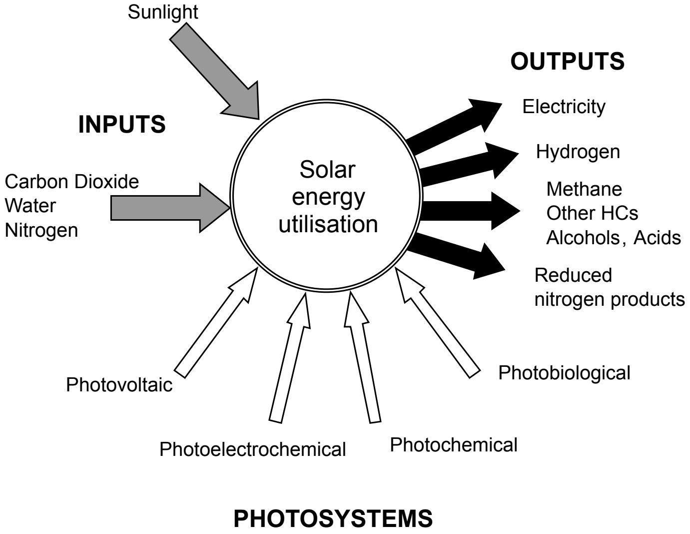


Figure 4.25 *Solar energy utilisation: inputs, outputs and systems.*

production of electricity by photovoltaic and photoelectrochemical processes, with the former, based on inorganic semi-conductor technology, having by far the highest commercial success.

4.7.1.1 Inorganic and Organic Photovoltaics

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 combined with the voltage of cell's electric field gives the power. The structure of a cell based on single crystal silicon is shown in Figure 4.26. 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. Other semi-conducting materials include gallium arsenide, copper indium diselenide and cadmium telluride. The use of multiple layers with these different band gap materials can result in much higher efficiency cells. Cells with energy conversion efficiencies in excess of 20% are available but expensive, more commonly they are at 15%, and at the cheaper end, *e.g.* those used to power calculators are only 5–6% efficient.

In spite of the high level of commercial success of inorganic semi-conductor based photovoltaic cells, they are unlikely to challenge seriously electricity generation from fossil fuels because 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 be part of a polymer, thus making cell construction easier.

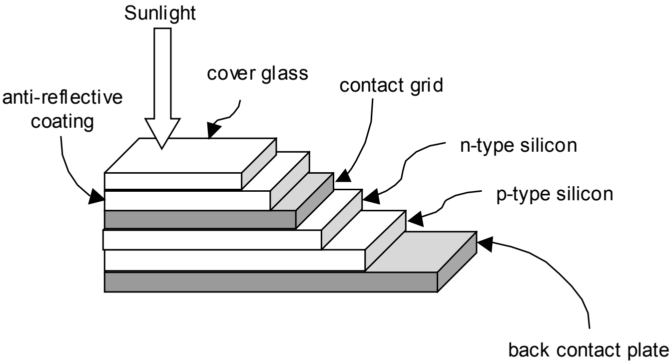


Figure 4.26 *Generic structure of a single crystal silicon photovoltaic cell.*

One big problem to be overcome with dyes and pigments is that of environmental stability to light, as they will be exposed to very bright sunlight for up to twenty years in a solar cell. Phthalocyanines, which usually demonstrate high light stability, are obvious candidates and have been the subject of much research.[12,65] The cells used in this procedure are double layers (multilayers are also possible), constructed by vapour decomposition of the phthalocyanine, *e.g.* α-Cu phthalocyanine or α-vanadyl phthalocyanine as the p-type layer and diimide derivatives of perylene tetracarboxylic anhydride pigments (see Chapter 2, section 2.4.1.6) as the n-type layer, using ITO and Au electrodes, as illustrated in Figure 4.27. Efficiencies are only in the range of 0.2–1.9% energy conversion rates but progress is being made.

Alternatives to having discrete layers forming p–n-junctions include having the heterojunctions distributed throughout a support material, such as a polymer or polymer blend. Several configurations are being considered for these distributed heterojunctions, including polymer–polymer,[66] polymer–fullerene,[67] polymer–dye[68] and dye–dye blends.[69] One example of a polymer–dye distributed heterojunction is the use of poly(3-hexylthiophene), which has a very high hole mobility, with a perylene diimide dye which acts as both an electron-acceptor and an electron-transport material. In this method a solution, containing an 80:20 blend of dye and polymer, was spin-coated onto a transparent ITO electrode and with an upper aluminium

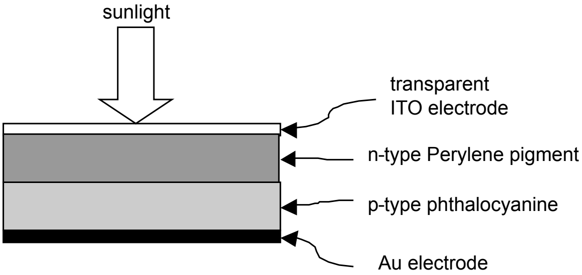


Figure 4.27 *Phthalocyanine–perylene p–n junction photovoltaic cell.*

electrode, as shown in Figure 4.28. Excitation at 500 nm gave an energy conversion efficiency of 0.4%, which, though too low to be of usable value, is very encouraging from such a simple device.[70]

Research has shown that this blending approach can be avoided by covalently linking the electron acceptor to an oligomeric electron donor. For instance, by attaching a C_{60} fullerene derivative to an oligophenylenevinylene unit, as shown in (4.37). The device had a similar configuration to that shown in Figure 4.28. Compound (4.37) not only generated electrons and holes under light irradiation but also provided a pathway for their subsequent collection at the electrodes, thus generating a photocurrent.[71]

It is regarded as early days in this field of molecular photovoltaics and certainly much too early to say if these approaches will in the end provide viable commercial products.

4.7.1.2 Dye-sensitised Solar Cells

The main competition to semi-conductor photovoltaics for producing solar electricity commercially is coming from photoelectrochemical devices based on dye sensitisation. These devices use relatively inexpensive semi-conducting materials such as titanium dioxide, zinc oxide and tin oxide. Grätzel in Switzerland [72] has carried out the seminal work in this area, following on from the initial observation by Fujishima and Honda in Japan that a titanium dioxide electrode could be used to split water into hydrogen and oxygen.

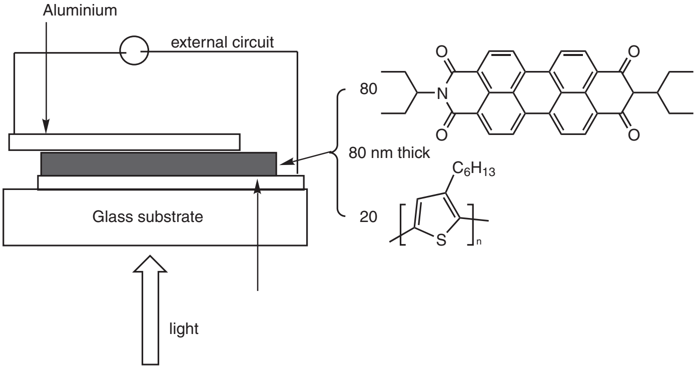
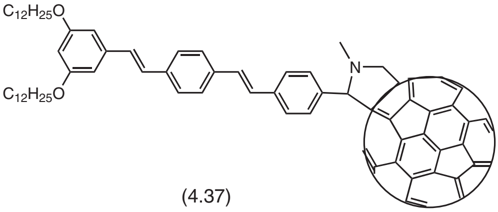


Figure 4.28 *Dye-polymer blend, distributed heterojunction photovoltaic cell.*



(4.37)

The photoactive component in these cells is a dye adsorbed chemically onto the surface of the semi-conductor. When light hits this surface, the dye (S) absorbs a photon and becomes excited (S^*); in this state it transfers an electron into the TiO_2 semi-conductor (injection). The positively charged dye (S^+) then passes its positive charge to a redox mediator in the bulk electrolyte. The oxidised mediator is attracted to the counter electrode where it is reduced back by electron transfer, thus completing the circuit.

The dye-sensitised solar cell (DSSC) is constructed as a sandwich of two conducting glass electrodes filled with a redox electrolyte. One of the electrodes is coated, using a colloidal preparation of monodispersed 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 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, an iodide/triodide couple in acetonitrile. The structure is shown schematically in Figure 4.29.

The 'dyes' used by Grätzel in these cells are ruthenium complexes of bipyridine and terpyridine. A complex with an almost panchromatic response through the visible and into the near-infrared is the terpyridyl complex (4.38). Using this complex a DSSC was constructed that gave an energy conversion factor of around 11%, with a cycle lifetime of around twenty years exposure to sunlight equivalent to that found in Switzerland.[73,74] This technology offers a serious challenge to inorganic photovoltaics, especially in lower end uses, and the DSSC technology has been widely licensed. It has also been used as an energy provider for devices using electrochromic cells in smart windows and displays (See Chapter 1, sections 1.5.4.2 and 1.5.4.3).

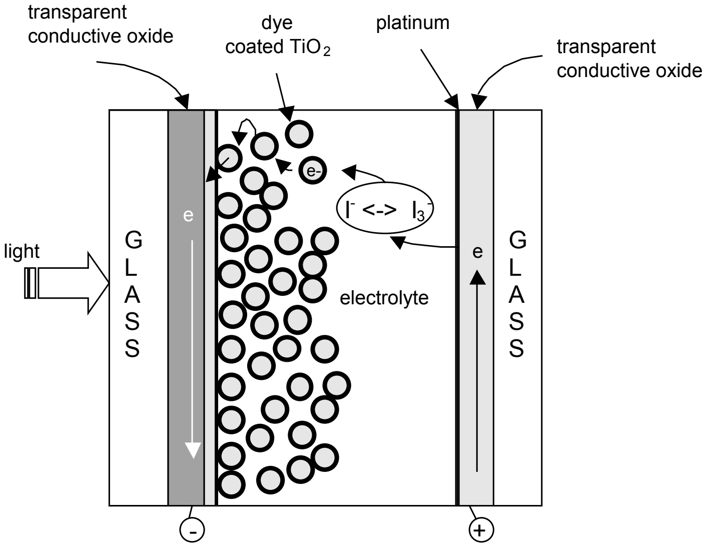
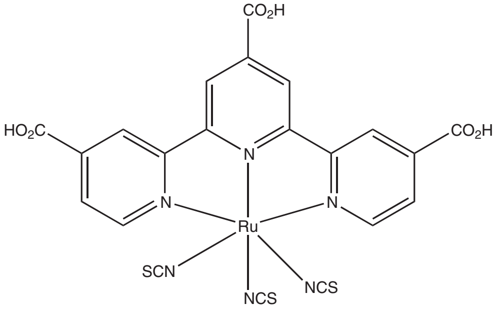
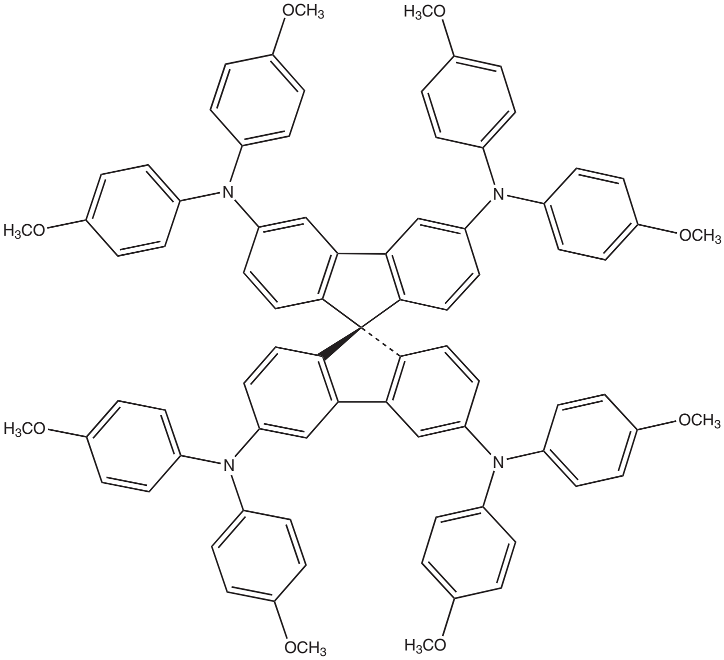


Figure 4.29 *Schematic of a dye sensitised solar cell.*



(4.38)



(4.39)

Other workers have employed different sensitiser systems, *e.g.* duel sensitisation by a zinc porphyrin and copper phthalocyanine on TiO_2,[75] Eosin Y or tetrabromophenol blue on ZnO,[76] and a ZnO/SnO_2 mixture with a ruthenium bipyridyl complex,[77] to produce good energy conversion factors.

Whilst producing energy conversion factors comparable with semi-conducting photovoltaics, the original Grätzel type DSSCs do suffer from some problems around the use of liquid electrolytes. These problems 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.[78] Replacement of the liquid electrolyte has now been shown to be possible using an amorphous organic hole transporting molecule (4.39),[79] and a penetrating p-conducting polymer.[80] Toshiba have been able to develop solid electrolytes that can be combined with DSSC technology, but on polymer rather than glass substrates.[81] These are exciting developments opening the way for cheaper, lighter materials that can be used for applications in home, wall mounted solar batteries, and in hand held personal digital products, such as watches and mobile phones.

4.7.2 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 on in the colourless *stroma* region of the chloroplast.[82]

The light reaction consists of two photosystems, PSI and PSII. The water splitting and oxygen evolution processes occur in the PSII complex. Activation of the light reactive centre in chlorophyll causes an electron to be pulled from a nearby amino acid (tyrosine) in the surrounding protein. This then obtains an electron from water, splitting it into H^+ and OH^-, the latter being then oxidised to oxygen. From this system the electrons flow, *via* plastaquinones, to another membrane–protein complex, the cytochrome b_6f complex to the PSI. The PSI also catalyses light-induced charge separation, similar to PSII, 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 PSI 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 are 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 PSI is chlorophyll a and in PSII both chlorophyll a and chlorophyll b are present. These two chlorophylls allow the photosystems to collect light over a wider range of wavelengths. The process is summarised in Figure 4.30.

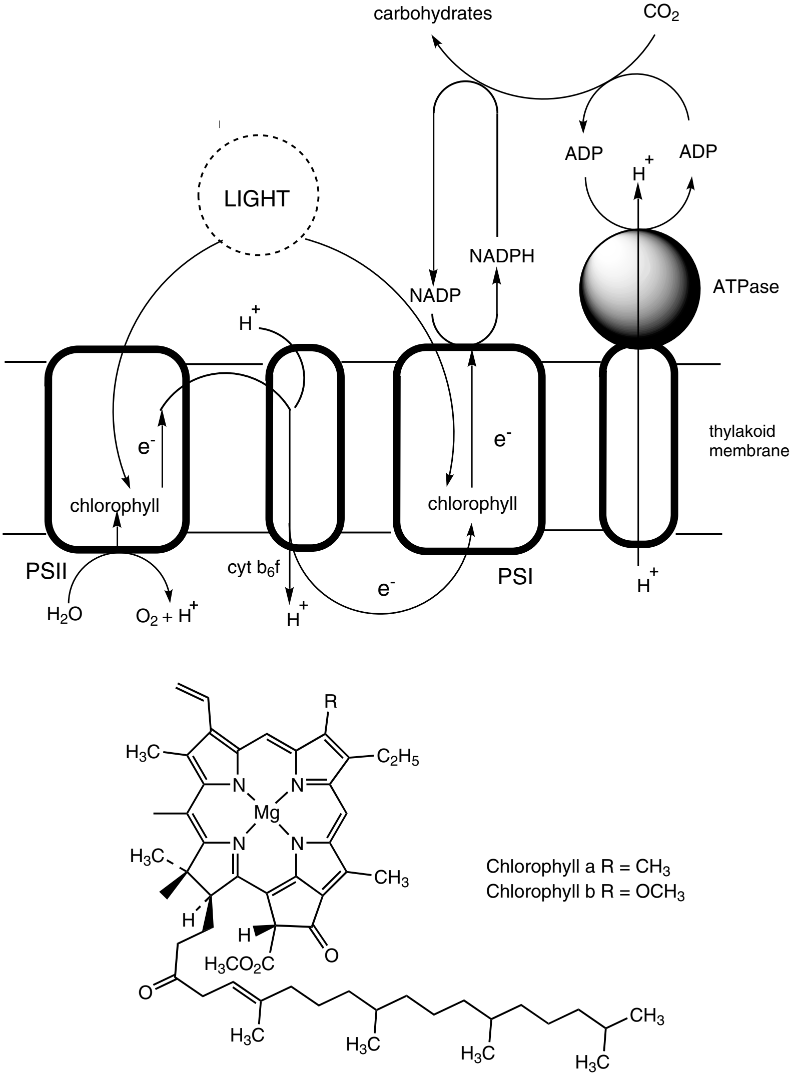


Figure 4.30 *Schematic for mechanism of photosynthesis.*

Research into artificial photosynthesis is being driven by the desire to understand, and then mimic, the following features of natural photosynthesis.[83]

- Antennae for light harvesting
- Reaction centre for charge separation
- Membrane for physical separation

4.7.2.1 Light Harvesting Antennae

There are 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.

One approach to developing synthetic antennae is to build chromophores and/or fluorophores into macromolecules. Some examples include dendrimers built on arrays of ruthenium and osmium complexes of polypyridines,[84] on arrays of a fluorophore around a central porphyrin core,[85] using an array containing a harvesting coumarin and an acceptor coumarin,[86] to an ionic fluorescent dye associated with a dendritic *p*-phenylenevinylene network,[87] see Figure 4.31. In the latter example the dendritic chromophores are activated at 420 nm, transferring their energy to the entrapped sulphorhodamine B molecules, which then emit light at 593 nm.

4.7.2.2 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 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 plastaquinones (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:

- A 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[88]

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. 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 example a triad which has a porphyrin acting as a light acceptor and a charge separator causes a two-step electron transfer from a carotenoid moiety on one side to a quinone on the other side. Moore and Gust have used these types of triad molecules, together with a second lipid-soluble quinone,

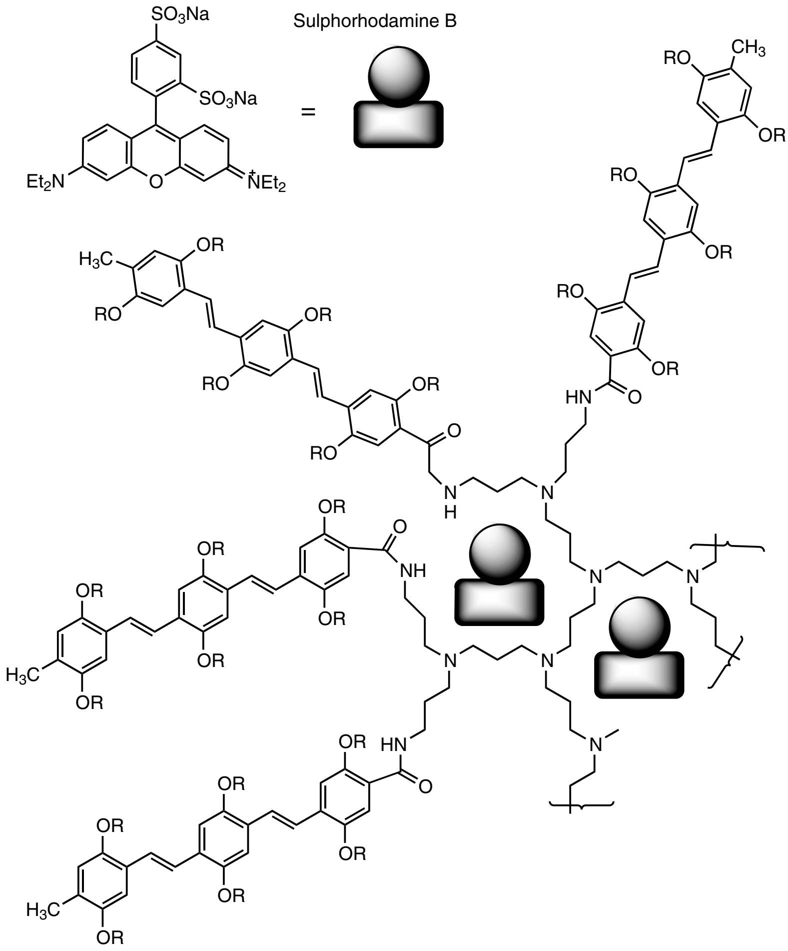


Figure 4.31 *Partial structure of a light harvesting dendrimer.*

placed inside an artificial phospholipid membrane vesicle, to light-drive a proton pump and hence drive the synthesis of ATP.[89] The process is shown diagrammatically in Figure 4.32.

Whilst these approaches are extremely interesting scientifically, to be of any real commercial value in solar energy utilisation the stability of the systems must advance by orders of magnitude.

4.7.3 The Production of Useful Chemicals

The important photosynthetic processes that can be mimicked to produce useful chemicals are the reduction of carbon dioxide by the use of water, producing carbohydrates and oxygen. However, in terms of producing fuels the splitting of water into hydrogen and oxygen, because hydrogen can be used directly as an energy source for

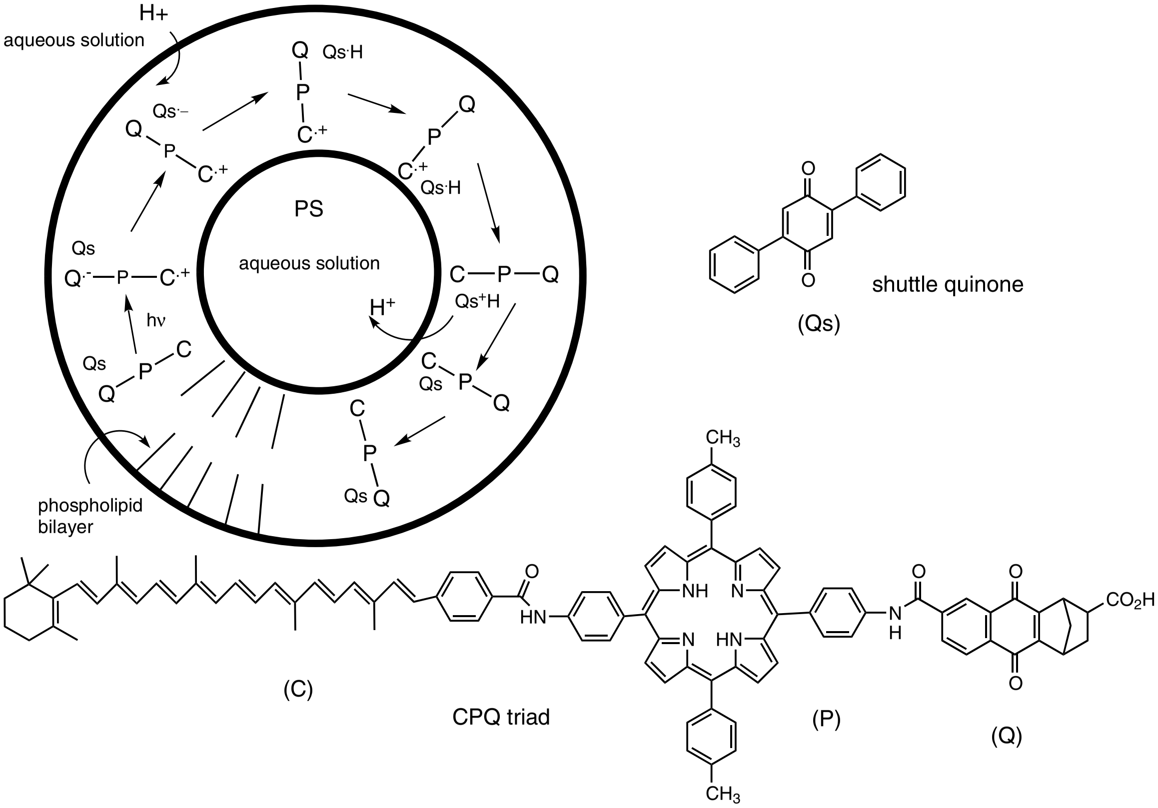


Figure 4.32 *Light driven proton pump using a donor–chromophore–acceptor triad and quinone proton transporter across a phospholipid bilayer membrane.*

fuel cells, is probably a target more amenable to the current state of knowledge. Additionally, the coupling of 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 carbon dioxide, therefore not adding to the environmental load.

4.7.3.1 Water Splitting

In the short term any system for producing hydrogen from water splitting must compete with the current process of producing hydrogen chemically from coal or natural gas, where the economics are extremely tight. Systems based on the use of conventional solid state photovoltaics and commercially available water electrolysers have been devised to produce hydrogen from water using solar energy in overall energy conversions around 10%.[88] However, the cost of the photovoltaic cells makes this approach, even at these levels of efficiency, uncompetitive currently with the fossil fuel route.

The use of the much cheaper dye sensitised solar cells may offer a way around the cost issue. Grätzel has used these 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 dye sensitised titanium dioxide electrode, 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. To date, the overall efficiency reported is around 4% with a target of 10%.[83]

4.7.3.2 Carbon Dioxide Reduction

Much of the work on the photoreduction of carbon dioxide centres 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.[80] Because the M(0) is oxidised 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.

4.7.4 Enhancement of Natural Photo-processes

A remarkably simple technology for improving plant growth and crop yields involves the use of a coloured plastic mulch to reflect light onto the growing crop. For instance, a red plastic mulch laid on the soil surface not only maintains water in the soil and diminishes weed growth, but also stimulates tomato plants to produce more and larger fruits, harvests increasing by 12–20%. The specific red dye in the plastic film is believed to selectively reflect long wavelength red light into the plant's natural growth regulating phytochrome system, causing improved energy transfer and hence increased growth rates. The system was developed by researchers in the

US Department of Agriculture and was licensed to agricultural film manufacturer SONOCO in 1996, and is sold for use on a variety of fruit crops.[91]

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CHAPTER 5

Phenomena Involving the Manipulation of Light

5.1 Introduction

This last chapter covers those phenomena that use materials to manipulate light in a variety of ways in order to produce useful 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 by physical interactions with materials, as in lustre and optically variable pigments 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 optoelectronics or by all optical systems, as in photonics. Whilst the volume markets currently are in liquid crystals, lasers and lustre pigments, the ultimate commercial application goal for many of these phenomena is optical data storage and transmission devices and in all optical computers.

5.2 Liquid Crystals

Liquid crystals displays have become such an integral part of our daily life that it is a sobering thought that the first men to go to the moon in the 1960s would have never seen a watch with a digital display made from liquid crystals. The all-pervasive commercialisation of the technology 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 Hofmann-La Roche in Switzerland, indicated that the commercial pull was very strong.[1,2] It is also indicative of the vast amount of research that has gone on over the intervening years to provide advanced materials and methods of constructions. Full details of this work can be found in two standard reference texts on the topic.[3,4]

Liquid crystals are materials that exist in a state that is intermediate between a liquid state and a solid. They are 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 crystalline to the liquid state at different temperatures, existing in the smectic and nematic phases, as shown in Figure 5.1.

Molecules which form other types of liquid crystal phases are also finding

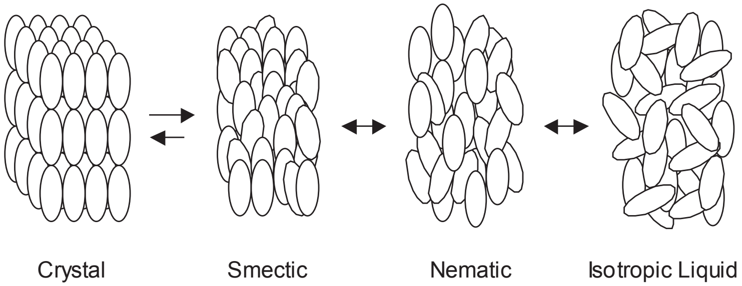


Figure 5.1 *Liquid crystal phases formed by rod-like (calamitic) molecules.*

applications, *e.g.* discotic or disc shaped materials. A very important class of liquid crystalline materials are the polymers, both in chain (*e.g.* Kevlar) and side chain.

Liquid crystals can interact with light in several ways and such interactions have found wide application as shown in Table 5.1.[5]

5.2.1 Nematic Liquid Crystals and their Applications

By far the most important commercial applications of nematic liquid crystals are in the a multi-billion dollar display industry.[6,7] Cholesteric, or chiral nematic liquid crystals have been used in coloured guest–host displays and in thermography/thermochromic applications.

5.2.1.1 Twisted Nematic Displays

All 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

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), 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

with a reflecting mirror (reflective mode) or a backlight placed behind the liquid crystal cell (transmissive mode).

The leading LCD technology in display panels is based on twisted nematic liquid crystals, and relies on the ability of these molecules to twist 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°, *i.e.* by the twisted helix, before coming out of the cell through the other polariser. On applying a voltage to a cell 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.

In the case of those LC materials which exhibit negative dielectric anisotropy, cells can be constructed which align vertically and twist on applying a field, exactly the converse to the twisted nematic effect from positive anisotropic LCs. Cells of this type are of interest because they can form a superior black state.

To produce display panels it is necessary to address a large array of pixels. This can be achieved in two basic ways, either by multiplexing or by using a matrix arrangement of transistors.

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.

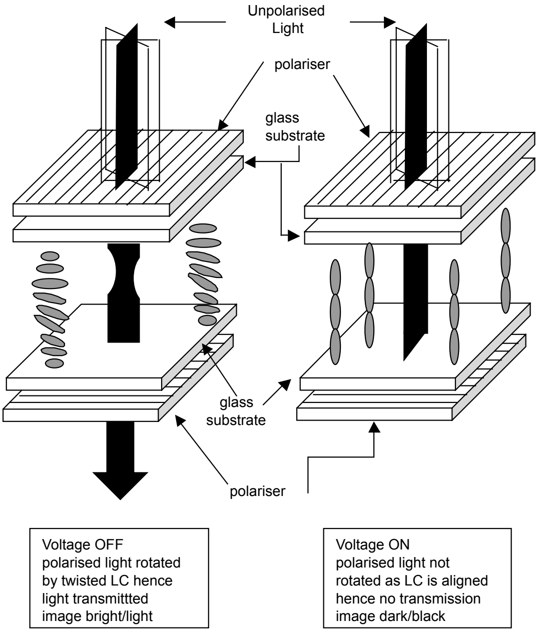


Figure 5.2 *Schematic of a twisted nematic LC display.*

This 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, *i.e.* up to 120 000 pixels, but beyond this size there is an increase in switching times and cross-talk between adjacent pixel elements leading to a loss in contrast. This problem can be overcome by using 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. This system is ideal for monochrome displays but even with these materials the response times start to get very slow with the several million pixels that are required for high contrast, full-colour displays.

Thin film transistors (TFTs) based systems are much better for colour displays since they give better viewing angles, response times and resolution than STNs. Those systems in which an array of amorphous silicon transistors is vapour-deposited onto one side of the substrate, each transistor being positioned below each pixel, are known as active matrix TFT (AMTFT) displays.

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).[1,2] These 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 cyano phenylpyrimidines and the pentylcyclohexanes and bicyclohexanes. The structures of some typical materials used in direct drive displays are illustrated in Figure 5.3. It should be noted that commercial liquid crystal materials are complex mixtures, often composed of 10–20 components, tailored to meet the variety of technical demands of a particular application or outlet.

The highly 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, *e.g.* the three-ring compound molecules containing fluorine atoms and *trans–trans* bicyclohexanes, in admixture with polar materials. Some typical materials are shown in Figure 5.4.

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 alky group into a non-conjugated alkenyl substituent gave polar molecules, which showed the desired behaviour. Further detailed work has shown that the preferred product is the *trans*-isomer, *e.g.* (5.1). Apolar components are also included in LC mixtures for STN, in order to lower the viscosity and melting points, thus improving their multiplexing properties, *e.g.* (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

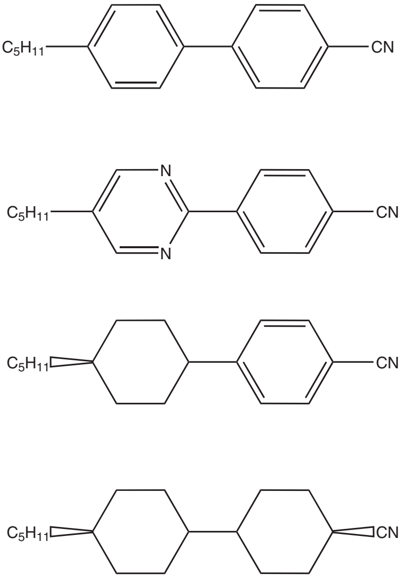


Figure 5.3 *Twisted nematic materials for direct drive displays.*

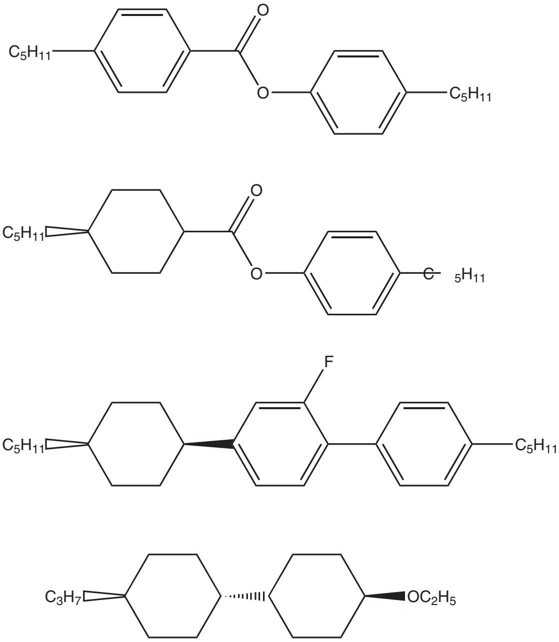
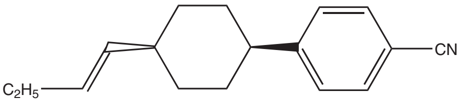


Figure 5.4 *Twisted nematic materials for multiplex addressing.*



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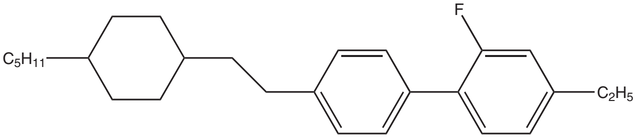


(5.2)

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 5.5.

5.2.1.3 Colour Displays from Twisted Nematic Liquid Crystals

The biggest growth area in LC based displays has been in full-colour flat panel displays for use in conjunction with computers, especially portable machines. The two major technologies used in this area, as stated above, are STN-LCDs and AMTFT-LCDs, with the latter, as their production costs diminished, taking the major share of the market. This is because they exhibit a more uniform, wide viewing angle and superior display brightness.[7]

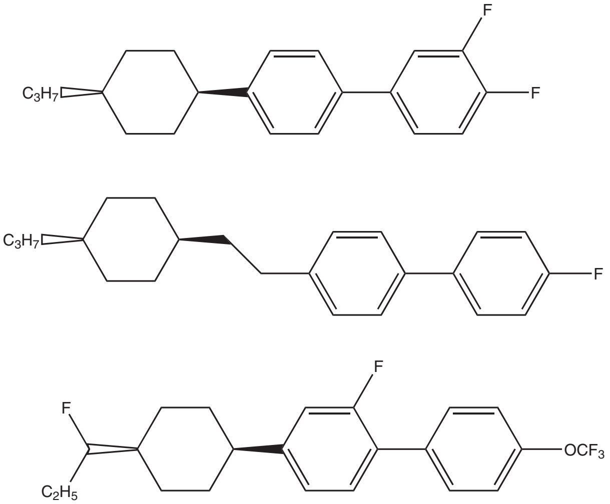


Figure 5.5 *Twisted nematic materials for active matrix addressing.*

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 is shown in Figure 5.6. 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 5.7, is constructed on a clear substrate, and consists of 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 photolithographic printing and electrodeposition processes.[8]

The idealised spectral characteristics of the colorants required for this outlet are shown in Figure 5.8. 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

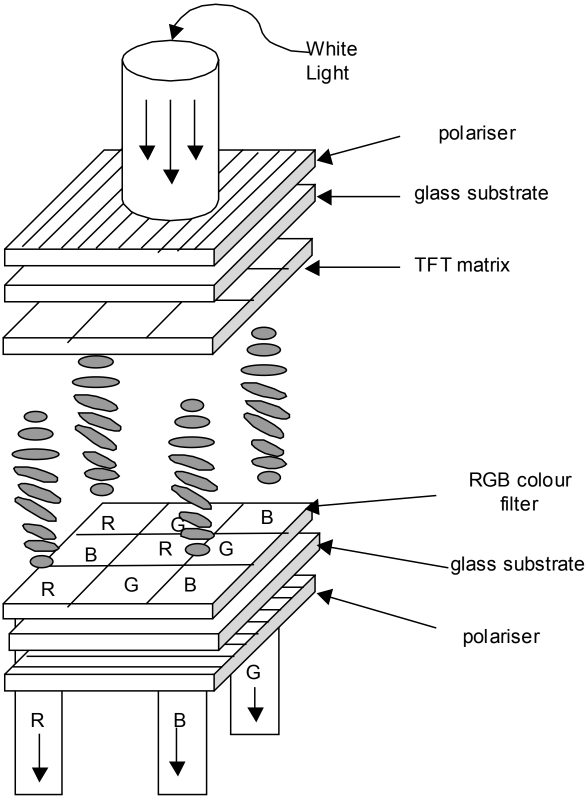


Figure 5.6 *Schematic representation of AMTFT colour display.*

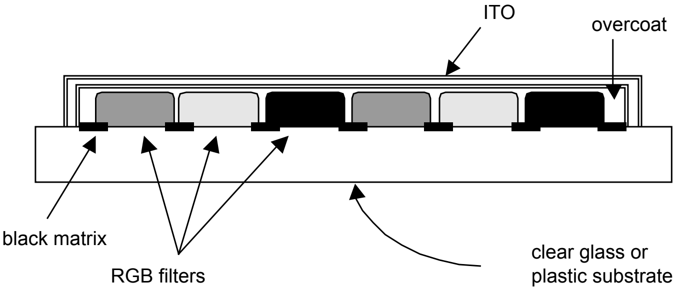


Figure 5.7 *Schematic of colour filter for LCD display.*

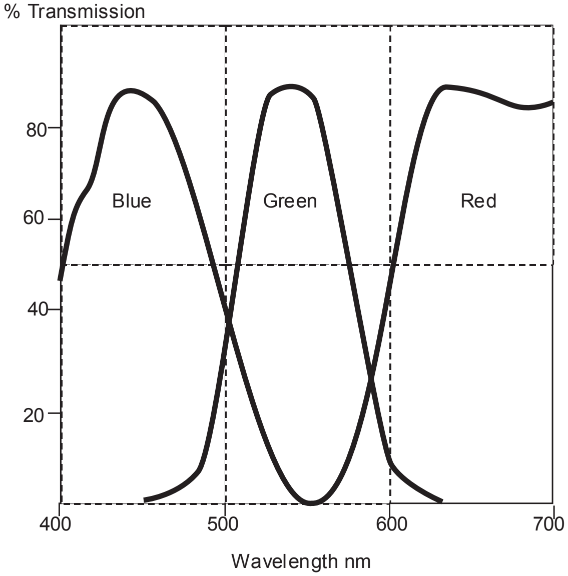


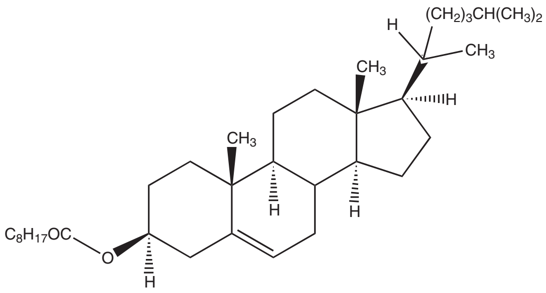
Figure 5.8 *Transmission spectral characteristics of a colour filter.*

been used for this outlet are taken from the high-performance class; generally anthraquinone vat pigments and perylenes for reds, phthalocyanines for blues and greens (see Chapter 2).

5.2.2 Cholesteric Liquid Crystals and their Applications

The cholesteric phase in liquid crystals is analogous to the nematic phase but it is formed by materials that contain a chiral centre, initially derivatives of cholesterol (5.3), hence the name cholesteric LCs. Since synthetic chiral molecules can also be used on their own or as dopants for nematic LCs, *e.g.* (5.4), chiral nematic is probably a more appropriate term for these materials.

Cholesteric LC materials are able to reflect visible light and also respond to temperature changes causing variations in the shade of the reflected colour. The



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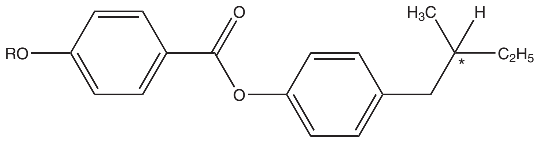


(5.4)

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. To see the reflected light it is necessary to use a black backplate (see Figure 5.9).[5]

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

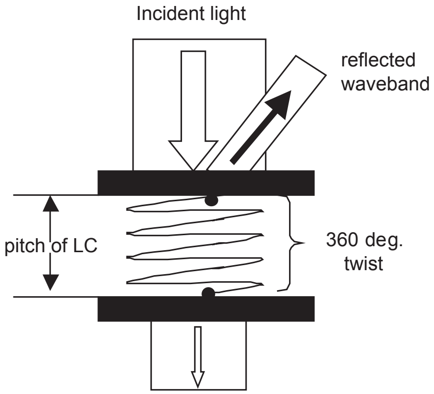


Figure 5.9 *Schematic of chiral nematic interaction with light.*

related to the pitch length (*p*) and the average refractive index (*n*) of LC phase as follows;

$$\lambda = np$$

The bandwidth of the reflected light is given by:

$$\Delta\lambda = p(n_e - n_o) = p\Delta n$$

where n_e is the refractive index parallel to the director and 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 (see section 5.2.2.1 below);[9] their temperature dependent colour change has found applications in thermochromic inks,[10,11] and as pigments and copy safe colours;[12] their selective reflecting capabilities have been applied in colours and filters for reflective displays[13] and projection systems,[14] reflective polarisers;[15] and their electrical field induced switching in displays and smart reflectors,[16,17] in colour patterning for full-colour recording.[18,19]

5.2.2.1 Guest–Host LCDs

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.

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 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 5.10.

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

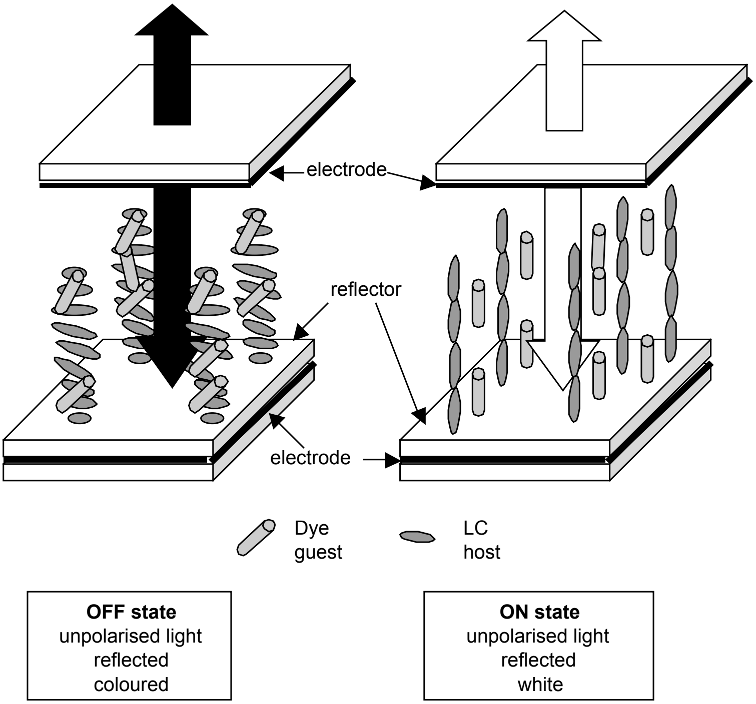


Figure 5.10 *Schematic of a guest–host (GH) LCD using dichroic dyes and a chiral nematic host.*

- High molar absorption coefficient to minimise dye use and the effect on LC viscosity
- The transition moment of the dye should align well with the nematic director – the order parameter

A high order parameter (*S*) is essential to maximise the contrast between the ON and OFF states. The maximum order parameter is 1.0, but it has been found that a value higher than 0.73 gives good contrast between the ON and OFF states. 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 necessary black dyes.[9,20] Typical dyes, together with their order parameters, used in GH LCDs are shown in Figure 5.11.

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, there has been a renewed interest in cholesteric LCDs as they offer a simple way of constructing thin larger area displays required for new outlets in erasable electronic newspapers and related reading materials

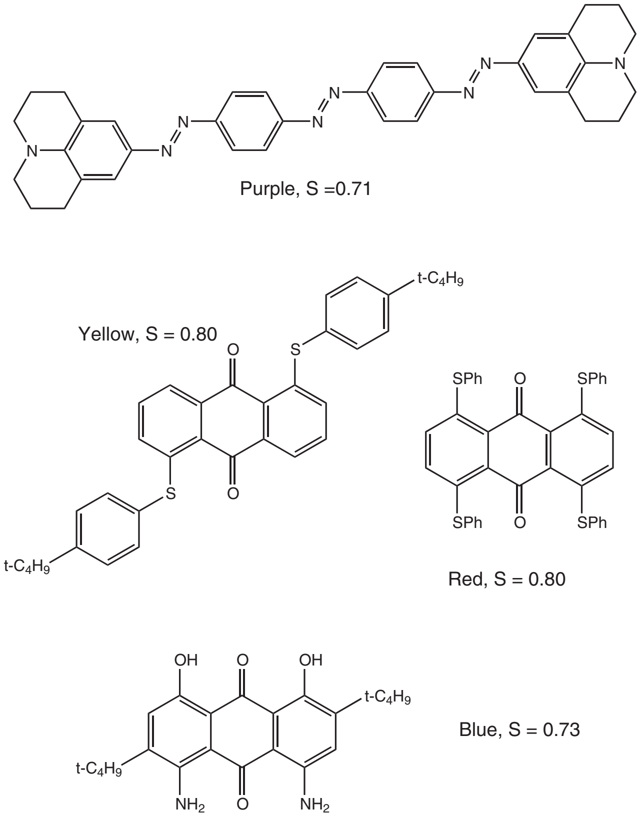


Figure 5.11 *Dichroic dyes for GH LCDs.*

5.2.2.2 Temperature Sensing and Novelty Applications

As mentioned above, 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 a move to longer wavelengths in the reflected light, 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 1.3.4).

These 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. These inks and coatings have also been used as 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, *e.g.* in hot night clubs or when skiing.

5.2.2.3 Polymeric Cholesteric Liquid Crystals

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 has been developed by researchers at BASF, which involves the cross-linking of LC oligomers with a chiral monomer in a specific ratio. In this process 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 co-polymer (see Figure 5.12). The chiral component causes more twisting in the helix so that, as more is included, the reflected light moves to shorter wavelengths. Using this process high gloss and durable coatings can be obtained on a range of substrates, including paper, wood or metal, giving a range of colours without any additional colorant. They are available commercially from BASF in a range of colours under the Paliocolor 400 and 630 trade names. Because they 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 section 5.3). Another interesting technical point about these colours is that they cannot be copied using simple photocopiers, and therefore have outlets in security printing.

5.2.2.4 Full-colour Recording using Cholesteric Phases

Whilst the use of chiral nematic polymers to produce colour variable coatings is an exciting technological development, to meet the highly desirable target of *rewritable* full-colour recording it is necessary to be able to selectively write different areas in the matrix, especially using light.

One approach adopted to meet this challenging target is to use a non-polymeric low molecular weight cholesteric LC in admixture with an azobenzene derivative that displays photochromic behaviour *via cis–trans* isomerisation.[21] This method involves heating a mixture of the cholesteric LC and the azobenzene derivative at 120 °C and then cooling to 87 °C to form a thin film on a glass plate. Exposing this film to UV light (366 nm) of different energies produces reflected light of different colours, from red to green to blue, which can then be fixed by super-cooling. Using a mask and different amounts of energies, coloured images can be produced. These can be optically read or removed by heating to 120 °C, giving this type of system the potential for development into a rewritable full-colour recording system (Figure 5.13).

One alternative approach is to use photoisomerisable chiral compounds where the *E* and *Z* isomers have different helical twisting powers, *e.g.* menthone derivatives.[19] By incorporating co-polymers, prepared from menthone containing monomers and cyano esters (5.5), as dopants into nematic LC mixtures materials, *e.g.* a mixture of cyanobiphenyls and cyanoterphenyls (E7 available from Merck), colour change can be effected by irradiating with UV light (365 nm). The colour obtained is dependent

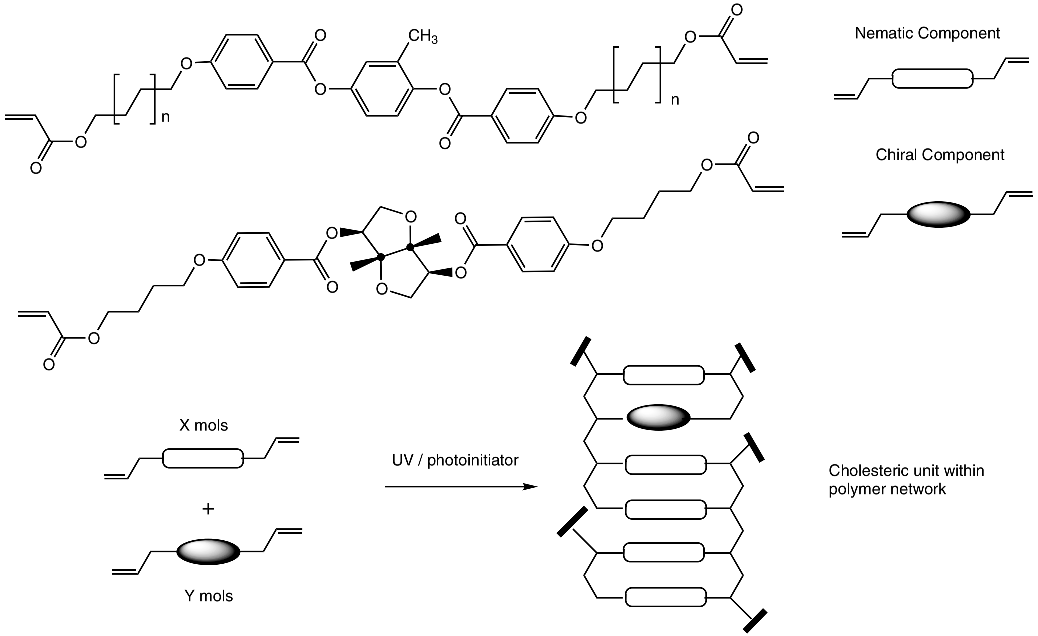
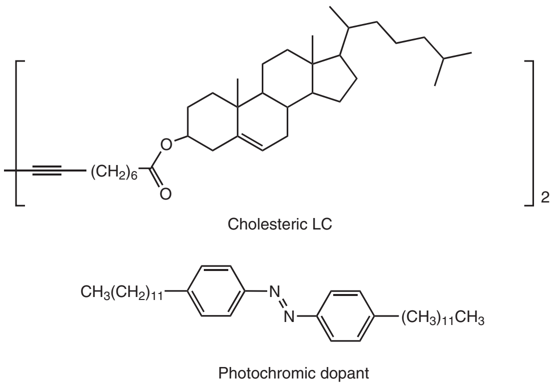


Figure 5.12 *Variable colour pigments formed by polymerisation of chiral nematic liquid crystals.*



98:2 Cholesteric:Azo
366 nm UV light at 87°C

Energy (mJ/cm^2)	Colour
0	Red
33	Green
246	Blue

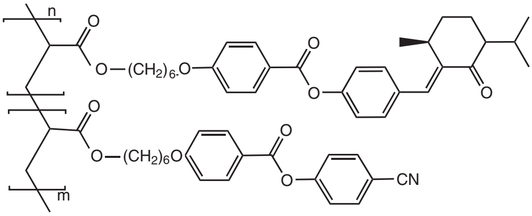
Figure 5.13 *Prototype full-colour re-writable recording with low MW cholesteric LC.*

on the dosage of UV light; the wavelength of the reflected light showing a more or less linear response with irradiation time. Return to the colourless state is possible by heating at 120 °C, if rather slowly in this case, again offering the potential for being rewritable.

5.2.3 Luminescent Liquid Crystals

5.2.3.1 Fluorescent Liquid Crystals

Production of fluorescent LCs by dissolving fluorescent dyes in host materials has been an active area of study for many years.[22,23] This is because it is the simplest method for producing fluorescent LCs and also because the absorption and emission profiles of the dyes can be altered by application of an electric field. Examples of potential applications include polarised organic lasers, but the main problem with the use of fluorescent dyes in guest–host systems is the limited solubility of the



(5.5)

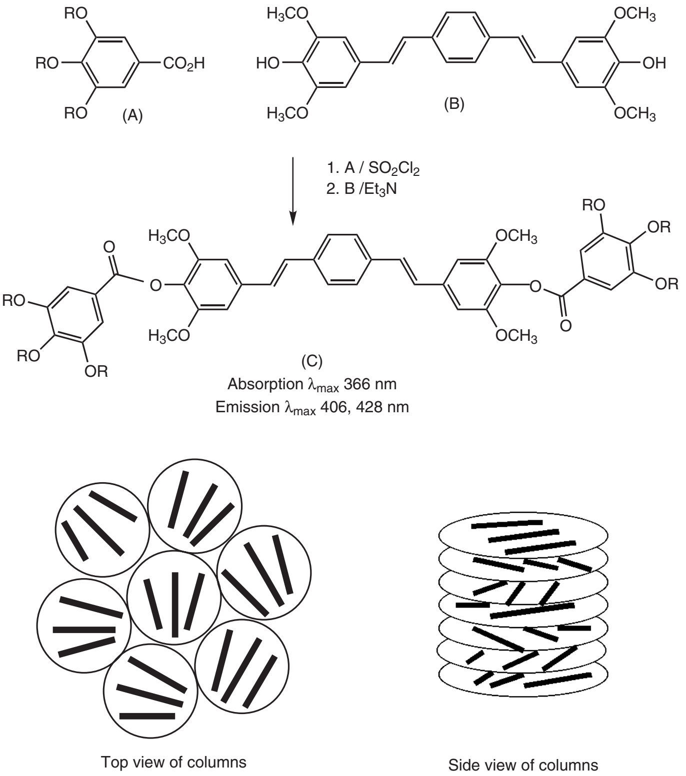
dyes in the host. It would therefore be distinctly advantageous to have inherently luminescent LCs.

Approaches used to the development of LC materials with valuable luminescent properties include the synthesis of rod-like mesogens from fluorescent moieties, *e.g.* benzopyrans,[24] and discotic LCs with a fluorescent polyaromatic core.[25]

A newer family of thermotropic mesogens are the phasmidic or polycatenar LCs. These are materials which consist of a rod-like core of three aromatic linkages and two half-disk shaped end groups containing two or three flexible tails. They are named after the number of tails on the molecule, *e.g.* tetracatenar, pentacatenar *etc.* By incorporating a di-styryl moiety as the central aromatic core and varying the chain length on the tails, phasmidic LCs have been produced that exhibit intrinsic luminescence (Figure 5.14).[26]

5.2.3.2 Polarised Electroluminescent Liquid Crystals

One application for organic electroluminescent materials is in the construction of lightweight backlights for LC displays (see Chapter 3, section 3.8). If organic electroluminescent (OEL) materials emitted polarised light they could make the polariser



Absorption λ_{max} 366 nm
Emission λ_{max} 406, 428 nm

Top view of columns

Side view of columns

Figure 5.14 *Hexacatenar fluorescent LC materials.*
(Reproduced with permission of Wiley-VCH.)

in conventional LCDs redundant. Consequently, since the late 1990s, the development of efficient polarised luminescent materials has been a target for researchers in the OEL field.[27]

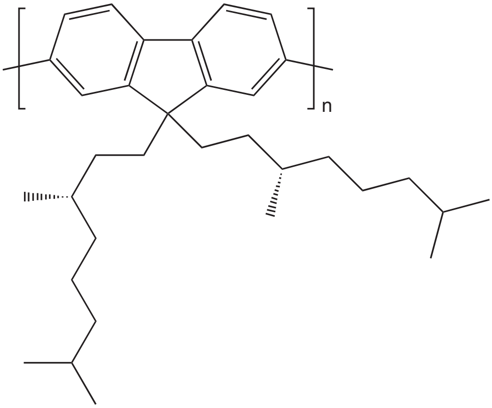
The methods that have been examined for producing polarised EL include the use of liquid crystalline chiral oligomers and polymers.[28,29] Promising results have been obtained using conjugated polymers where fluorene makes up the backbone, *e.g.* (5.6), which was synthesised from the dibromo monomer *via* Yamamoto coupling. These types of material exhibit LC behaviour at transition temperatures of 100–200 °C, and produce blue polarised EL (425 nm) from thin films.[30]

5.2.4 Polymer-dispersed Liquid Crystals

Polymer-dispersed liquid crystals (PDLCs) are made up of nematic liquid crystals dispersed in a solid continuous polymer matrix. These are prepared by mixing a reactive monomer into a non-polymerisable LC medium and then polymerising the reactive monomer to create a polymer matrix, at the same time capturing the LCs as dispersed droplets, greater than 1 μm in diameter, *i.e.* the wavelength of visible light.[31–33]

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. These materials are available commercially and are used to produce large area, switchable glazing units for energy conservation, decorative and safety purposes in buildings. The process is shown schematically Figure 5.15.

Holographic optical elements can also be made by the preparation of polymer-dispersed liquid crystals using twin lasers in transmission holographic photopolymerisation (see section 5.4.2). They have also been made using photorefractive composites of polymer dispersed liquid crystals (see section 5.6.3).



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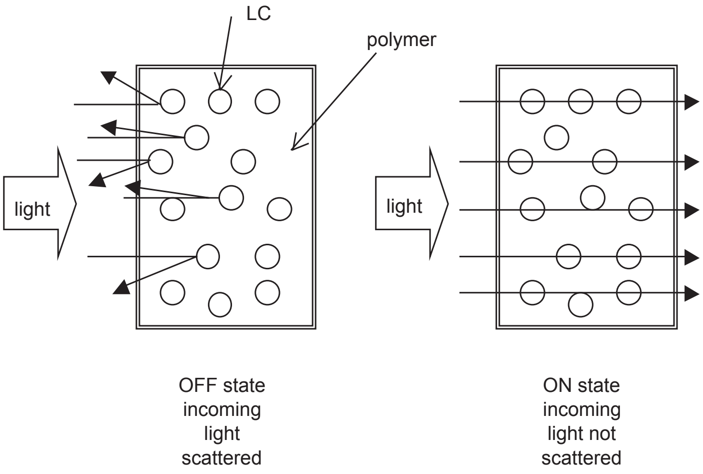


Figure 5.15 *Polymer dispersed LC devices.*

An alternative approach is to add gelling agents to LCs. The gelling materials that have been used range from low MW materials to dendrimers. Potential applications include large area displays and electro-optical switches.[34]

5.2.5 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.[35–36] These side chain polymers 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. This is shown schematically in Figure 5.16.

The utilisation of the photochromic behaviour of azobenzene side chains in full-colour recording has already been described in section 5.2.2.4 above, where such polymers were used as dopants in cholesteric LCs. There have been many publications on polymers with side-chain azobenzenes, where the induced birefringence of the films of such polymers under polarised light has been utilised for optical data recording sytems.[37,38] The conversion of the *trans* form rod-like nematic phase into 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.[39]

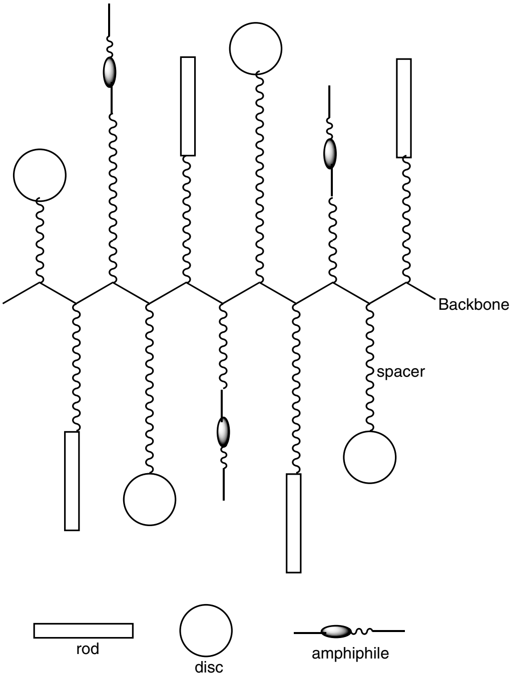


Figure 5.16 *Schematic of side chain polymeric LCs, showing possible mesogens.*

There has also been more recent work on the application of these types of materials in dynamic holographic recording, and this will be covered in section 5.4.3.3.

5.3 Colours from Reflection, Interference and Diffraction

In the natural world, colour produced by the phenomena of light interference and diffraction, *e.g.* iridescence, which involves these two optical phenomena in combination with reflection, is such a common feature that it is very surprising that it has taken man until the last few decades to utilise these phenomena in a large commercial way, other than by using natural products such as peacocks feathers, pearl essence from fish scales and opal gemstones for decorative purposes.[40,41] However, times and technologies have changed and now many new methods for the production of 'colour by physics' have been commercialised,[42] especially in the rapidly growing area of colour variable pigments. Other areas relying on interference and reflection include holography (section 5.4), dielectric mirrors, interference filters and low emissivity windows.[43]

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.[44] 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, and no attempt is made in this brief overview to rationalise the nomenclature, the statistics on sales of special effect pigments usually split the group into two, namely pearlescents and colour variable, the former being a much larger market.

5.3.1.1 Optical Basis of Lustre Pigments

The pearlescent effect in natural pearls arises because of the interaction of incident light with alternating layers of high refractive index ($CaCO_3$) and low refractive index (protein), reflected and diffracted light from which leads to the observed iridescent colours.

Lustre pigments imitate this effect by having platelets that are comprised of layers of inorganic materials, which reflect light from the surfaces and phase boundaries in the multilayers. Light reflected from these platelets performs three functions. Direct reflection causes lustre and lightness; multiple reflections are responsible for the depth of the colour, whilst interference colours occur when film thickness is in the range of the wavelength of visible light. This is shown schematically in Figure 5.17.

Interference between light waves of the same wavelength can be constructive or destructive, *i.e.* they can add to or subtract from each other, and 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.

Absorption also plays a part in lustre pigments, since having transparent inorganic pigment layers, *e.g.* iron oxide, on 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 product 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 back-

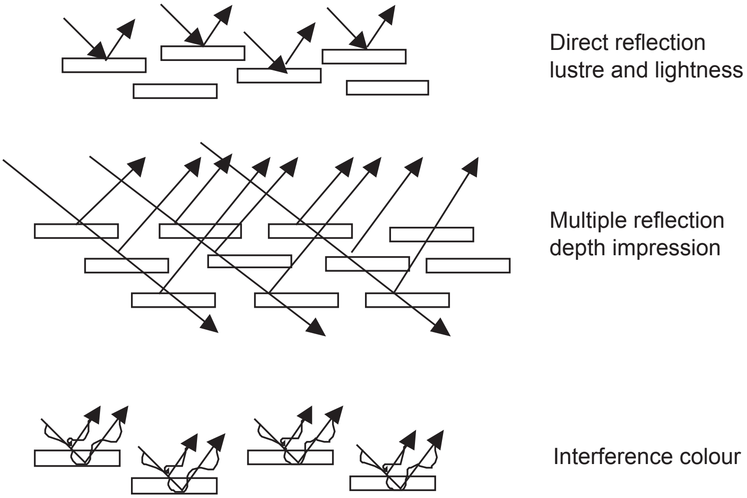


Figure 5.17 *Optical effects in plate-like layered pigments.*

ground 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. The combination of absorption, reflection and diffraction is called 'goniochromism'.

5.3.1.2 Materials, Construction and Processes

The dominant class of lustre pigments is based upon oxide coatings of mica platelets, but newer materials have appeared *e.g.* silica and alumina flakes from Merck, with better performance characteristics than traditional mica.[45,46] There has also been developments in the technology for the coating of reflective metal platelets, *e.g.* aluminium, with oxides using chemical vapour deposition that has led to exciting new products.[47]

Mica based pigments. These multilayer pigments were first marketed in the 1960s using titanium dioxide as the oxide layer. Traditionally they are produced by coating mica-platelets, usually transparent muscovite, with thin layers of TiO_2 by precipitation from an aqueous slurry, or by a sol–gel technique, followed by calcining. The interference colours shown in reflection are dependent on the thickness of the oxide layers; 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 the TiO_2 layer, *e.g.* Fe_2O_3 for gold, carmine for red, iron-blue for blue, Cr_2O_3 for green (Figure 5.18) and Fe_3O_4 for black. Viewed from point A (the face angle) the effect is dominated by thin film reflection and from position B (the grazing angle) by 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.

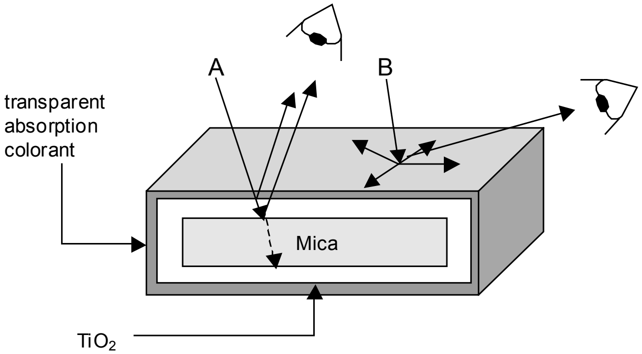


Figure 5.18 *Combination TiO_2–mica pigment.*
(Reproduced with permission of Wiley-UCH.)

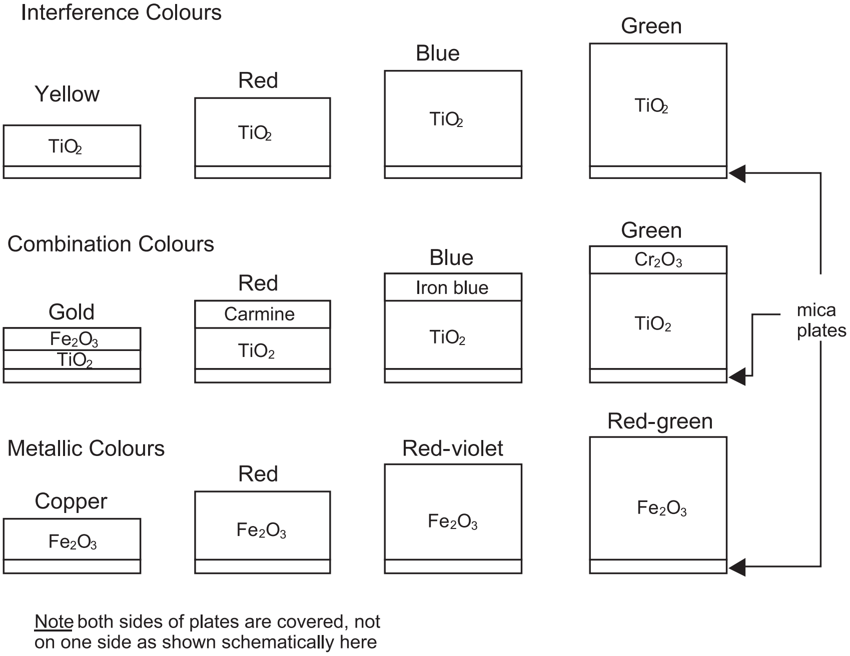


Figure 5.19 *Metal oxide – mica based pigments.* (Reproduced with permission of Wiley-VCH.)

The position on mica based lustre pigments is summarised in Figure 5.19.

Silica and alumina based pigments. These new substrate materials, SiO_2 and Al_2O_3, which were developed by Merck, are absolutely flat and therefore allow the production of very intense interference colours that can be coupled with a variety of goniochromic properties.[46]

The SiO_2 flakes are manufactured by a web coating process. An aqueous solution of a silica compound is wetted onto a moving web, the film is dried to a specified film thickness, between 50 and 100 nm, and then removed and processed to form flakes that are fractionated and then coated with high refractive metal oxides. The alumina flakes are made by a crystal growth technique. Hydrated alumina doped with titanate and phosphate is mixed with Na_2SO_4 in an aqueous suspension and then dried to a uniform powder followed by treatment at 1200 °C, during which there is crystal growth of the Al_2O_3. After cooling, the flux is dissolved in hot water, the flakes separated and coated with Fe_2O_3 or TiO_2.[48]

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 (Figure 5.19). 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 plate based pigments. Metal reflector based systems, developed by DuPont, Flex Products and BASF,[49–51] 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, *e.g.* Fe_2O_3. Some of the possible combinations are shown in Figure 5.20.

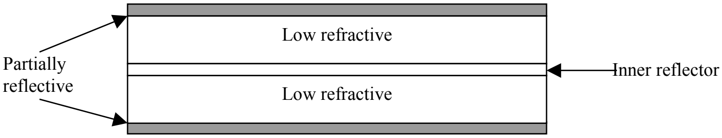
The methods used for coating the metal platelets are a mixture of wet processes and chemical vapour deposition.[52] The first step involves coating the flakes with the low refractive layer. This is carried out by treating a dispersion of the flakes with tetraethoxysilane in an aqueous solution of ammonia, during which time a smooth film of SiO_2 is formed on the flakes. Alternatively coating can be carried out continuously in a fluidised-bed reactor using vapours of $Si(OR)_2(O_2CR)_2$ compounds at greater than 200 °C. The second step is the addition of the reflecting layer, which is carried out by chemical vapour deposition in a fluid bed reactor at 200 °C using inert gases charged with metal carbonyl compounds, *e.g.* $Fe(CO)_5$ which is oxidised to give the desired Fe_2O_3. The process is illustrated in Figure 5.21.

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.

5.3.1.3 Applications of Lustre/Colour Variable Pigments

There are four main manufacturers of pearlescent or colour variable pigments with properties of the types discussed in this section, namely Merck, Engelhard, BASF and Flex Products. Some of the current ranges from these manufacturers are given in Table 5.2.

The Engelhard product based on calcium borosilicate glass flakes is said to give a star-like glitter to coatings.



Partially reflective	Al	Cr	MoS_2	Fe_2O_3	Fe_2O_3	MoS_2	Fe_2O_3
Low refractive	SiO_2	MgF_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2
Inner reflector	Al	Al	Al	Al	Fe_2O_3	Mica/oxide	Mica/oxide

Figure 5.20 *Structure of colour variable pigments and possible combinations of layer materials.*

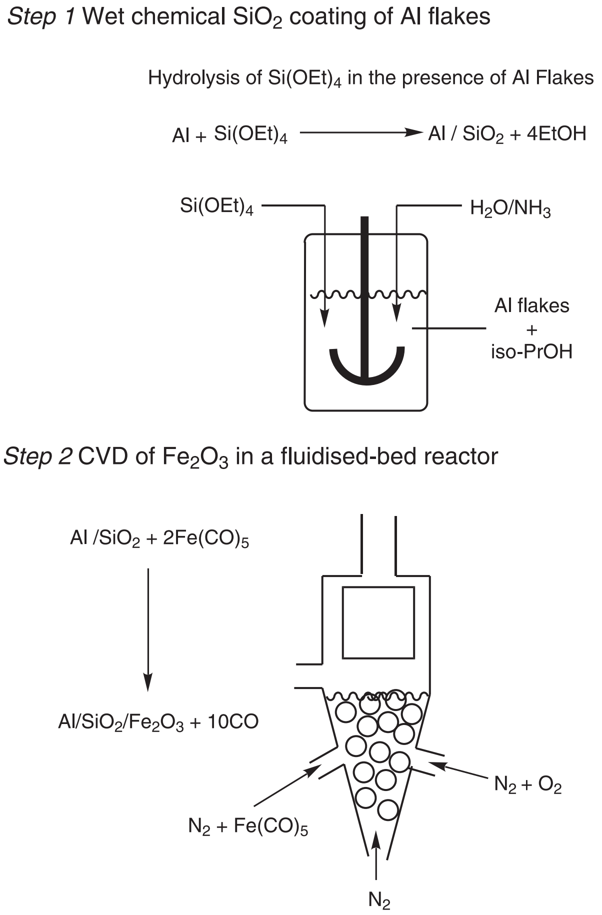


Figure 5.21 *Process for producing colour variable pigments by CVD.*

Table 5.2 *Manufacturers of pearlescent/lustre/optically variable pigments*

Company	*Trade name*	*Type of flake*
Merck	Iroidin	Mica
	Colorstream	SiO_2
	Xirallic	Al_2O_3
Engelhard	Mearlin	Mica
	Santa Fe	Mica
	Firemist	Ca borosilicate
BASF	Variocrom	Aluminium
Flex Products	Chromoflair	Aluminium

Lustre/pearlescent pigments have found wide application in automotive coatings, coloured plastics, synthetic leather, printing inks, ceramic products and cosmetics, *e.g.* nail polish, lipstick and mascara.

The majority of pearlescent coatings in the automotive industry are based on a two-stage process, in which pearlescent pigments with good opacity are included in the basecoat, which is followed by a clear coat. However, three-stage finishes are growing in use, which require the pearlescent pigments to be relatively transparent. The first coat or ground coat gives the system its opacity and is a specific colour, often white. This is followed by basecoat containing transparent or semi-transparent pearlescent pigments. The system is then completed by the application of a clear coat.

A novel application for the metal flake based materials is in security outlets because they are non-photocopyable. Pigments from Flex Products have been used by SIPCA to produce optically variable green-to-black inks for printing secure images on US dollar bills.[53]

5.3.2 Iridescent Fibres

Iridescence in many of the 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 would be to have fibres that in their own right could 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 fibre is acid dyeable nylon and the other basic dyeable nylon make 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 is decreased from 70° to 15°. The analysis also showed that the iridescent effect was most pronounced in the 10–40% range of core volumes. These predicted values, shown in Figure 5.22, have been confirmed in practice and a range of attractive colour shifts are seen when incident light hits the fibre at a lower angle than at other locations on the fabric, for instance in folds.[54]

A 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 thin multi-layers of polymer films.[55]

5.4 Holography

Another important optical phenomena that relies on light interference and diffraction is holography, the process by which holograms (interference patterns) are produced.[56] 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 newer areas such as laser eye protection, LCDs, diffractive optical elements, optical processing

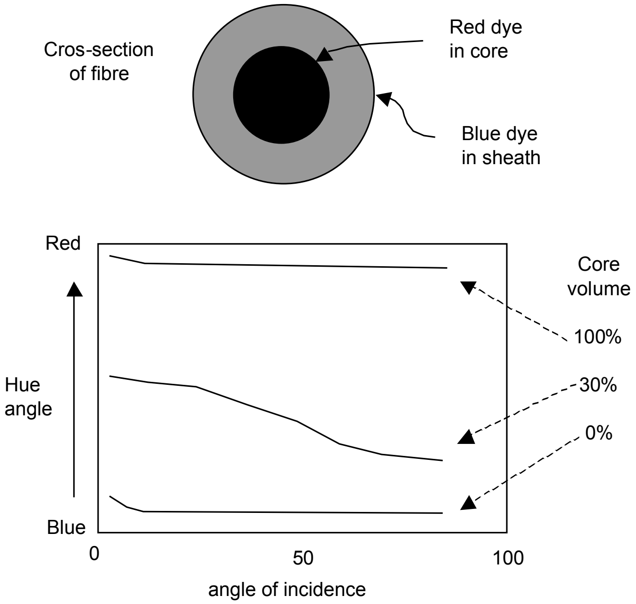


Figure 5.22 *Predicted dependence of hue angle on the angle of incidence of light to the fibre axis.*
(Reproduced with permission of Wiley-VCH.)

and data storage. Many of the newer applications rely on the use of optical photopolymers.[57]

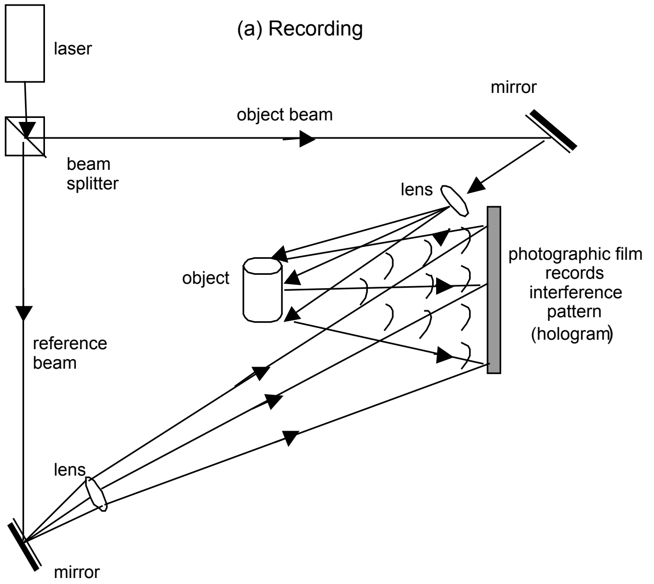
5.4.1 Principles of Holography

A two-beam transmission hologram is produced using a recording laser beam of monochromatic light to reflect wavefronts from a 3D object, using a reference beam from the same laser to record the interference pattern onto an appropriate medium, *e.g.* a photographic emulsion. After development the hologram is visualised by illumination with the same laser beam, which recreates the wave fronts of the object, producing a 3D image of the object to the viewer. A schematic representation of the process is given in Figure 5.23.[43]

As indicated in Figure 5.23 transmission holograms need to be lit from behind. When the reconstructing light passes through the plate the interference pattern diffracts light to give an image at the same position as the original but behind the hologram. The back light problem is usually overcome 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 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.[56]

Another way of overcoming some of the problems of backlighting is to use the technique of reflection holography. In this process the recording reference beam is


(a) Recording

(b) Visualisation

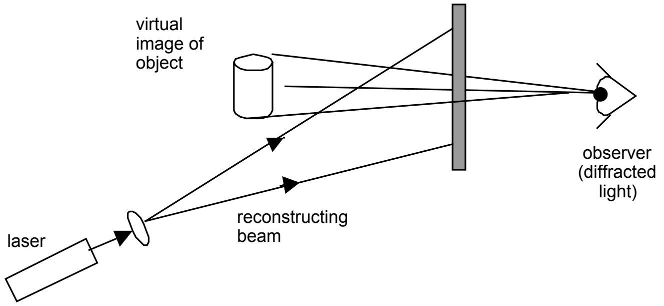


Figure 5.23 *Schematic of two-beam recording of a hologram and laser beam visualisation of image.*
(Reproduced with permission of John Wiley & Sons.)

brought in from the opposite side of the glass photographic plate, allowing visualisation of the reflected wavefront with white light. Because of the arrangement it is also possible to clamp the object to minimise the effects of vibrations on the final hologram. The schematic for reflection-type holograms is shown in Figure 5.24.[43] 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, such as DuPont's Omnidex film (see below).

It is also possible to digitally record or compute the data required for a diffracting structure and then uses this data to produce relief holograms, usually *via* a photolithographic process.

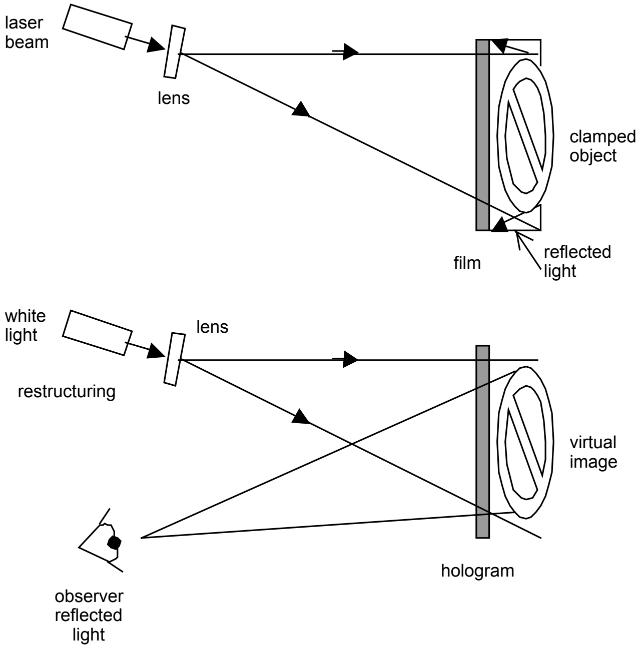


Figure 5.24 *Schematic of reflection mode hologram.*
(Reproduced with permission of John Wiley & Sons.)

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. There are four main types of materials used for recording the image:

- Photographic emulsions. These are very commonly used, the silver halide emulsions are coated on glass or transparent polymer film. The emulsions, which involve the use of ultrafine grain size silver halide, are available for response to a range of laser wavelengths. This is the mainstay method in graphics art outlets.
- Dichromated gelatin. This material is particularly sensitive to light in the blue and UV regions, but not the red. They are used to produce volume holograms that approach the theoretical limit in diffraction efficiencies.
- Photoresists. These 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.
- Photopolymers. This is a most active area of research with newer materials and wide applications, and will therefore be considered in greater detail.

Several companies have been involved in the development of photopolymers specifically designed for producing the gratings required for holographic recording. Canon have a system based on poly(vinylcarbazole),[58] and Polaroid have one that utilises poly(ethyleneimine/methacrylate),[59] but both of which require subsequent solvent treatment to enhance the holographic image. The holograms are based on differences in the refractive index of the created voids and the bulk polymer. In contrast, the products developed by DuPont (OmniDex) utilise the difference in refractive index of the bulk polymer binding material and the polymers produced by photopolymerisation of the photoactive monomer. Because there is no subsequent processing the holographic patterns can be laid down in real time.[57]

The DuPont photopolymeric system consists of polymeric binder resins, *e.g.* PVA, PMMA, cellulose acetates and styrene-acrylates, reactive acrylic monomers, *e.g.* aryloxy or alkoxy acrylates, a dye sensitiser and a radical or charge transfer photoinitiator, *e.g.* DEAW and HABI respectively (see Chapter 4, section 4.5.2), and plasticisers. The process for producing the refractive index structures is as follows:

1. Patterned exposure, (twin laser beams for holograms and photomasks for wave-guides)
2. Non-patterned UV exposure, 100 mJ cm^{-2}
3. 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 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 reflective 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).[57] A whole range of holographic films have been produced for commercial use by DuPont and some of their applications are given in the next section.[60]

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).[61,62] Using spatially periodic polymerisation gives planes (150 nm to several micron spacing) of small (50–200 nm) LC domains separated by dense polymer. More recently 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.[63]

5.4.3 Applications of Holography

5.4.3.1 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 credit cards and consumer goods, since they are difficult to imitate and are non-photocopyable. 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 photolithographic 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.

5.4.3.2 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 backlight 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, *e.g.* 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.

Systems have now been commercialised, based on holographic elements produced using photopolymers, which utilise wavelength selectivity and controlled spectral bandwidth to use and control the incident light.[60]

In a backlit application the holographic element (HE) is placed in 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, *e.g.* 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 5.25.

Coloured LCD displays require a colour filter plate consisting of RGB pixels, the construction of which using classical absorbing dyes and pigments is described in section 5.2.1.3. An alternative system using reflective colour filters is now available.[60] 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 5.26.

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 5.27).

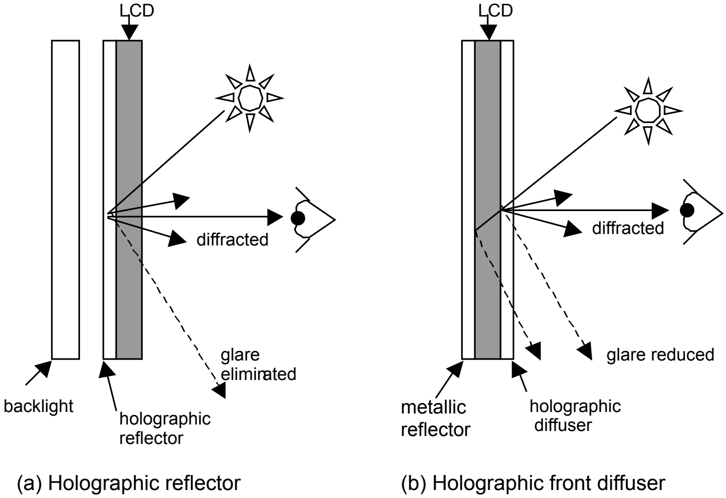


Figure 5.25 *Holographic elements in LCD incident light management.*

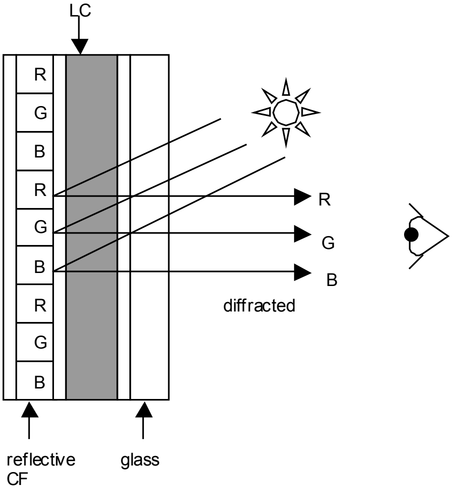


Figure 5.26 *Reflective RGB colour filter in LCD display.*

5.4.3.3 Holographic Data Storage

Holographic patterns caused by the interference of an object beam, which carries the information, with a reference laser beam can be recorded and stored in holographic media as phase gratings. The holographic data can subsequently be scanned with a reference laser and the resultant beam passed though CCDs, converting the optical into an electrical signal and the data interpreted. Photopolymers can be used to perform this task but only to produce WORM memories, as the current holographic recording process with this media is irreversible (see also Chapter 4, section 4.3).

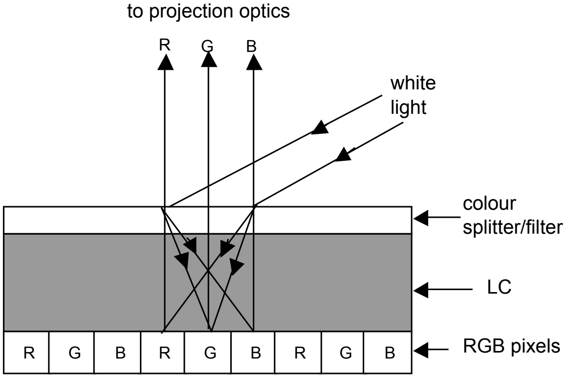
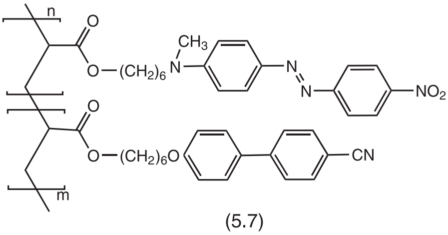


Figure 5.27 *Holographic colour splitter/filter for rear projection LC HDTV.*

Even with these limitations, holographic data storage using an all optical procedure is an attractive option since it offers the potential for storing terabytes of information with high transfer rates and short access times.[64]

To move to re-writable discs the process needs to be preferably dynamic, *i.e.* recording, reading and erasing need to be performed in real time. Consequently, holographic materials for this dynamic process need to be able to change their refractive index with light in a reversible manner, with a response time of a few tens of milliseconds. Many different approaches have been used to meet this challenging target, but amongst the most promising are polymers containing side chain mesogenic photochromic groups, especially azobenzenes utilising *cis–trans* isomerisation (see also section 5.2.5). On irradiation, the geometrical changes in the azobenzene moieties modulate the structure of the polymer causing local changes in its refractive index and the creation of a hologram.

This is a developing field and to date no materials have been devised that could fully justify commercialisation, but a good example of this type of material is the copolymer LC (5.7).[65] An optically clear film (200 nm in thickness) of (5.7) can be written onto with two linearly polarised Ar$^+$ laser beams operating at 488 nm, and the resulting grating read at 633 nm with a weak intensity He–Ne laser beam, the latter being used to avoid grating destruction. The response time was 150 ms for writing the grating (fringe spacing 1.4 μm) and 190 ms for erasure, not quite fast enough but encouraging. Optical switching of the grating was achieved by turning the writing beams on and off. Long-term storage stability of the written hologram is one of the issues still to be resolved.



(5.7)

Photorefractive polymers are also being developed for use in both permanent and real-time holography (see section 5.6.3).

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 lasing action are covered in Chapter 3, when discussing laser dyes (section 3.5.3), as are light emitting diodes (sections 3.8.1 and 3.8.4), which 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).

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 where they meet 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 schema is illustrated in Figure 5.28.

Laser diodes, whose development has always followed those in LEDs, operating in the infrared and red region, based on GaAs, have been available for decades. However, UV and blue LEDs have only been commercialised in the last five years (1995, see Chapter 3, section 3.8.1) and lasers even more recently (Nichia, 1999).[66] The driving force behind the research for a blue laser is that data storage density increases proportionally with the square of the light source wavelength. Consequently, a DVD, on switching from a red to a blue laser, would show a 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 spectrum increases the potential for

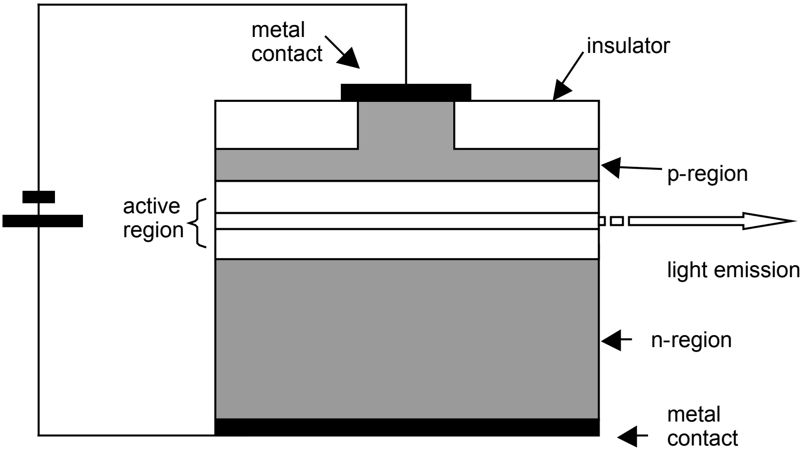


Figure 5.28 *Schematic representation of a laser diode.*

the laser addressing of organic materials, such as dyes, in medical imaging and diagnosis and in photochemical applications, such as photolithography.

The target for research is a true blue laser, characteristic wavelength of 425 nm, operating at room temperature. The early work in this area concentrated on the use of group II–VI materials, *e.g.* ZnSe, since they possess larger band-gap energies making them potentially better suited to operation at the UV end of the spectrum than III–V materials, which are better for the infrared end of the spectrum.[67] However, as discussed under LEDs (Chapter 3, section 3.8.1) the first commercial lasers (Nichia), having lifetimes in excess of 10 000 h, are actually based on a III–V material, namely gallium nitride (GaN).[68] The Nichia laser diodes are based upon AlGaN semi-conducting materials and are very complicated multilayer devices, as can be seen from the schematic of the earliest blue laser diode shown in Figure 5.29.[66] The Nichia laser diode emits 5 mW of 400 nm (violet) wavelength at a current of 40 mA and a voltage of 5 V. This is cutting edge research and modified or new materials and structures will definitely appear from many companies throughout the world in the coming years.

5.5.2 Organic Lasers

All 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.[65,69]

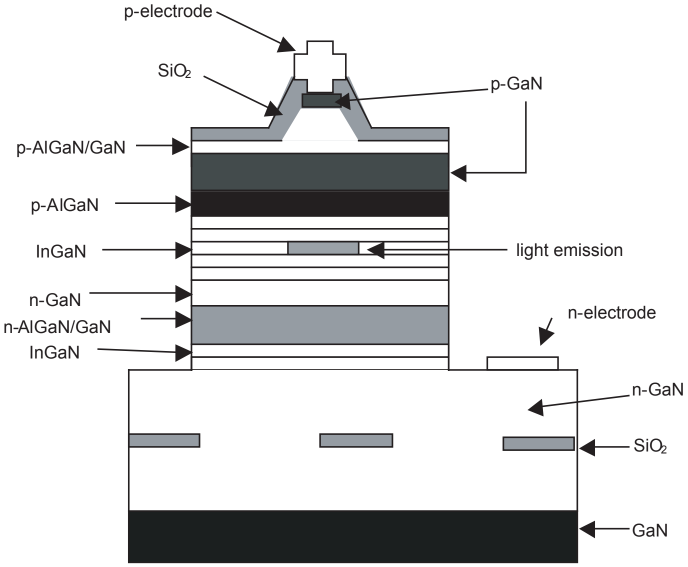


Figure 5.29 *Schematic of GaN based blue laser diode.*

5.5.2.1 Use of Luminescent Conjugated Polymers

The use of conjugated light emitting polymers in the construction and commercialisation of organic LEDs is described in the section 3.8.6 on electroluminescence phenomena of Chapter 3. 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.

The lowest excited states in luminescent conjugated polymers are very similar to the dyes used in dye lasers (Chapter 3, section 3.5.3). 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-ethylhexyloxy)-*p*-phenylenevinylene] (MEH-PPV) using excitation with 6 ns Nd:YAG third harmonic pulses (354.7 nm).[70] Tuning of hexane solutions of the co-polymer poly(2,2′,5,5′-tetraoctyl-*p*-terphenyl-4,4′-xylene-vinylene-*p*-phenylenevinylene) (TOP-PPV) was possible between 414 and 456 nm, similar to the classical coumarin laser dyes.[71]

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 luminescent conjugated polymers can be used to produce stimulated emission in thin films of these materials.

The first report of lasing action (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.[72] This was quickly followed by the first non-blended, microcavity laser, using PPV, that could support high current densities.[73] To date a whole range of semi-conducting polymers have been shown to exhibit lasing action under optical pumping, using a variety of physical structures and geometries, and progress is being made towards the ultimate goal of a commercial laser.[69]

5.5.2.2 Single Crystal Organic Materials

Although stimulated emission from single crystals of conjugated aromatic molecules, *e.g.* anthracene, has been observed for some considerable time, its practical realisation as lasing action has taken pioneering work by Lucent Technologies' Bell Laboratories researchers to bring this about, using electrical injection rather than optical pumping.[74]

One of the problems with the use of organic materials is the positioning of the electrodes, which is deleterious to high-power light emission. The Bell Labs workers have overcome this problem 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 5.30.

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 wave-guide 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 A cm^{-2}) at 5 K and an emission wavelength of 575.7 nm. There is no doubt that this is just a beginning and the search is on for new chromophores to produce lasing at a variety of wavelengths and also work is ongoing to optimise the device design.

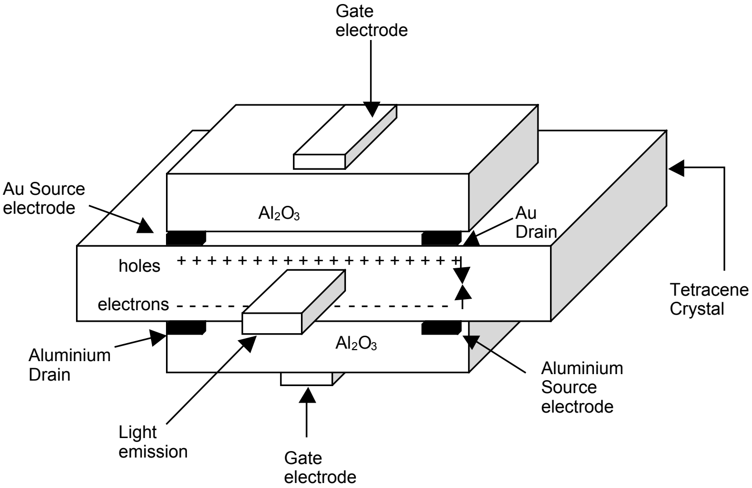


Figure 5.30 *Tetracene laser using FETS for charge injection.*

5.6 Opto-electronics

Whilst electronics, which is based on the controlled transmission of electrons, has been the dominant technology for over 50 years in both the computing and communications industries, it is not without its problems, which are increasing as ever higher demands are being placed on the technology. Many of these problems are inherent since electrons interact with each other, tending to degrade signals sent over long distances, causing noise which limits the speed by which signals can be transmitted.

Photonics, which relies on using the properties of light, 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 wave-guides for the transfer of communication signals. However, the use of photonics in all-optical information processing and optical computing is still some way away, even though significant progress has occurred very recently, as described in section 5.7.

Because of the limitations of both electronics and photonics a hybrid technology, opto-electronics, has been a major area of research since the 1980s, especially into the non-linear properties of molecules and their potential applications in communications, data storage and information processing.[75–78]

5.6.1 Basis of Non-linear Optics

Non-linear optics (NLO) involves the interaction of light with materials, this interaction causing changes in the properties of the materials, *e.g.* refractive index and transparency, which at the same time alter the properties of the light, *e.g.* frequency and amplitude. Electro-optical activity, applying a field to change the refractive index of a material, means that the incoming light can be manipulated from one path to another. The potential applications of NLO in electro-optic devices and systems are indicated in Table 5.3

For an organic material to show electro-optical activity it must exhibit high second order non-linear behaviour. This is one of the terms in the equation that defines the polarisation (μ) of an organic molecule as shown below, where E is the perturbing electric field.

$$\mu = \mu_o + \alpha E + \beta E^2 + \lambda E^3 + \ldots\ldots$$

Table 5.3 *Non-linear applications*

Devices	*Systems*
High speed modulators	Telecommunications
Optical switches	Optical computing
Wave-guide couplers	Signal processing
Tunable lenses	Telecommunications
Crossbar switches	Laser communications

In this equation α is the usual linear polarisability, whilst the others are the hyperpolarisability terms, β, γ *etc*. Macroscopically this equation turns into

$$P = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3$$

Where P is the polarisation and the others the linear (1) and non-linear, second (2) and third order (3) terms. Examples of important second order effects are frequency doubling and linear electro-optic effects (Pockles effect), third order effects are third-harmonic generation, four-wave mixing and the quadratic electro-optic effect (Kerr effect).

Each term can converted into a bulk response as follows

$$\chi^{(2)} = Nf{<}\beta{>}$$

Where $\chi^{(2)}$ is the bulk second order NLO property, N is the number of molecules and f the local field factors. From this equation it can be readily seen that the target must be for molecules with a high β in order to achieve high bulk activity, although in practice the relationship is not quite so simple.

5.6.2 Non-Linear Optical Materials

Crystalline lithium niobate was for many years the only material that could be used in devices, an example of its use being in electro-optic modulators for interfacing with fibre optic technologies. Unfortunately, this material is not very satisfactory because it is difficult to grow, and hence expensive, and only shows modest electro-optic properties.

As a consequence attention over the last decade has been focused on finding alternatives and the materials of choice have been organic chromophores particularly in conjunction with polymers.

5.6.2.1 Non-linear Optical Chromophores

One requirement for second-order non-linearity in optical molecules is that they exhibit non-centrosymmetric symmetry, *i.e.* they must be dipolar in nature and all point in the same direction. Hence, materials suitable for electro-optical uses should have high figures for the multiplier $\mu\beta$, where μ is the dipole moment and β the molecular second order optical non-linearity parameter.[79]

The majority of molecules with the required properties are donor–acceptor chromophores which fall into the following structural pattern: electron-donor–(-electron-bridge–electron-acceptor, typical of many classical absorbing dyes (Chapter 2).

The molecular hyperpolarisability term β is described by the two-state quantum mechanical mode:

$$\beta = (\mu_{ee} - \mu_{gg})\,(\mu_{ge})^2/(E_{ge})^2$$

where $\mu_{ee} - \mu_{gg}$ is the difference between excited and ground state dipole moments,

μ_{ge} is the transition dipole moment and E_{ge} is the optical (HOMO–LUMO) gap.

This can be interpreted for molecular design purposes as:[80]

- β varies in a sinusoidal manner with double/single bond length alternation
- β values can be altered systematically by considering the effect that a given structural variation will have on bond length alternation

Using these and other design principles, very large increases in the β values of chromophores have been obtained since the original work on the simple red monoazo dyes of the disperse dye class. These new NLO chromophores are known as 'high $\mu\beta$ chromophores', a selection of which are shown in Figure 5.31, the $\mu\beta$ values quoted being measured by electric field induced second harmonic at (EFISH) 1.9 μm.[79–82] It should be noted that the convention in NLO chromophores is to draw the donor on the left of the molecule, the converse of that used in absorbing dyes and pigments.

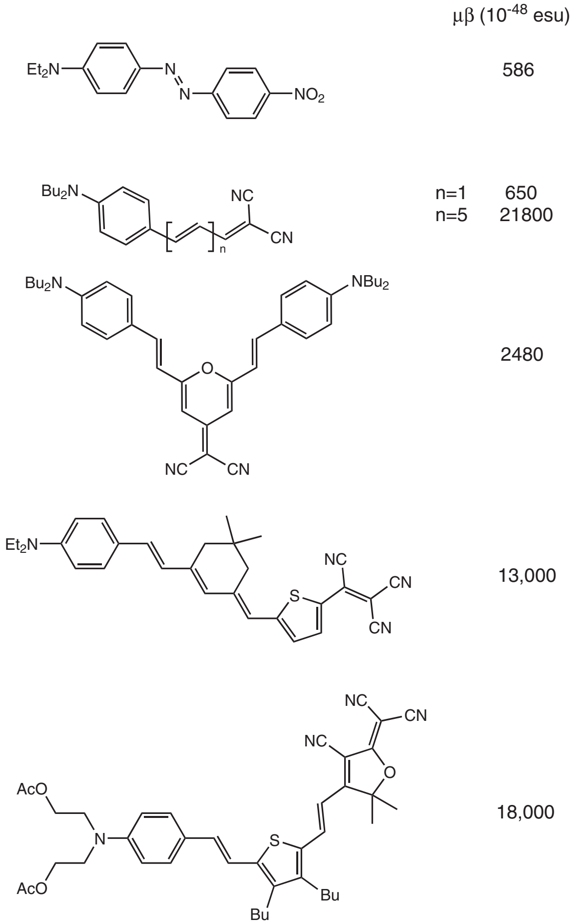


Figure 5.31 *Selected electro-optic chromophores with the products of their dipole moments and second order hyperpolarisabilities at 1.9 μm.*

Thermal stability of these new high $\mu\beta$ chromophores is still a problem, especially those containing a tricyanovinyl group (FTC), and compromises need to be made against high $\mu\beta$ and high thermal stability, as exhibited by (5.8).

5.6.2.2 Non-Linear Optical Polymers

As stated above, for a molecule to demonstrate bulk second order properties it is necessary for the dipole of all the molecules to lie in the same direction. This situation is very difficult to attain in small molecules where the tendency is for the molecules to crystallise with their dipoles opposing each other. This fact has led to a switch of interest to polymers that incorporate the small NLO molecule.

Using polymers allows the dipoles to be aligned by two methods:

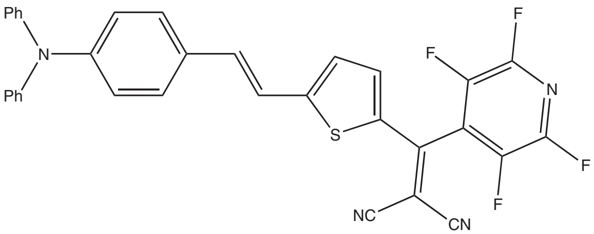
- Heating these polymers above their glass transition temperature (T_g) and then poling with an electric field, the dipoles of the small molecule moieties can be aligned. Subsequent cooling below T_g locks the dipoles of the small molecules in the desired direction.[83]
- Restricting the movement of the chromophore moiety after poling by cross-linking the polymer matrix.

As in many other applications, having the effect contained in polymeric materials carries several advantages:

- High optical quality and transmission can be achieved over many wavelengths
- Mechanically strong in use
- Capable of fabrication into many shapes and forms including layered composite structures
- Essential macroscopic properties can be engineered into the molecules
- Critical other physical properties can be tailored, *e.g.* T_g, clearing temperatures, absorption/transmission windows

Several polymeric configurations have been examined for the production of NLO polymers, but the two basic approaches are:

- Guest–host in which the guest chromophore is 'dissolved' in the host polymer matrix



(5.8)

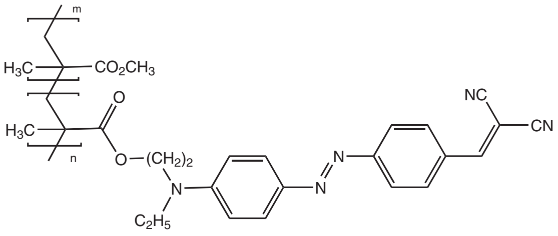
- Amorphous polymers in which the chromophore is covalently linked either as a side chain or as part of the polymer backbone, with or without additional cross-linking

The dominant methodology is that based on covalent bonding of the chromophore to the polymer, as this shows much improved long term stability over simple guest–host systems. Guest–host polymers using NLO guests have been extensively studied in the area of photorefractive polymers (see section 5.6.3).

The first generation NLO polymers were side chain polymers, usually made by co-polymerisation of a monomer bearing the chromophore bridged by a flexible spacer group with a co-monomer, commonly methacrylates. This is a flexible process allowing a wide range of co-polymers to be made. A typical example of this type of polymer is the methyl methacrylate azo dye co-polymer (5.9).

Whilst polymeric materials of this type showed very promising NLO properties after poling, they do tend to become disordered with time, leading to a slow decay in their optical non-linearity. 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. Therefore, to be used in these applications, poling of the NLO polymer must be carried out above these temperatures.[84]

One way to cope with this problem is to use polymers that are inherently stable thermally, such as polyimides. A polymer with exceptional thermal stability is the co-polymer (5.10), which is made from thermally stable polyimide and chromophore



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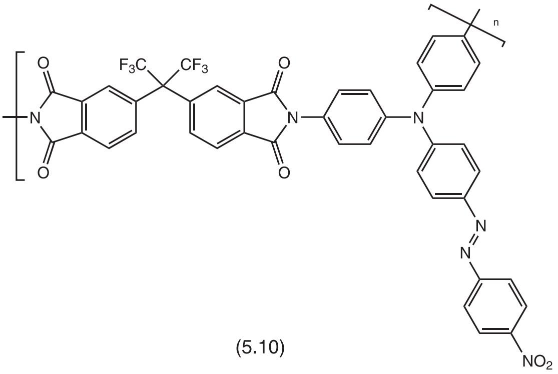

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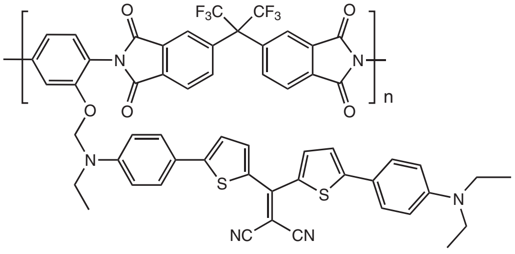


(5.11)

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 non-linearity properties at 225 °C for 100 h, but unfortunately these were an order of magnitude too low for commercial application.[85] Subsequent work elsewhere overcame these problems and led to the commercialisation of a polyimide based NLO material by ROITech called Optimer. This material (5.11), which has the chromophore more in a hybrid side-chain-transverse arrangement, offers good thermal stability and non-linear properties.[86]

Another successful approach involves the cross-linking of the side chain NLO polymer, after poling, at multiple sites by a different type of polymerisation mechanism. Subsequent curing and hardening produces a lattice that locks in the poled dipole.[79,81,87]. One such process is outlined in Figure 5.32.

The function of the bulky butyl groups on the thiophene ring of the chromophore is the prevention of unwanted chromophore–chromophore interactions.[79] This and other design principles have led to the development of new materials, such as (5.12) and related chromophores, which when embedded in a polymer matrix give materials with dramatically improved performance.[88]

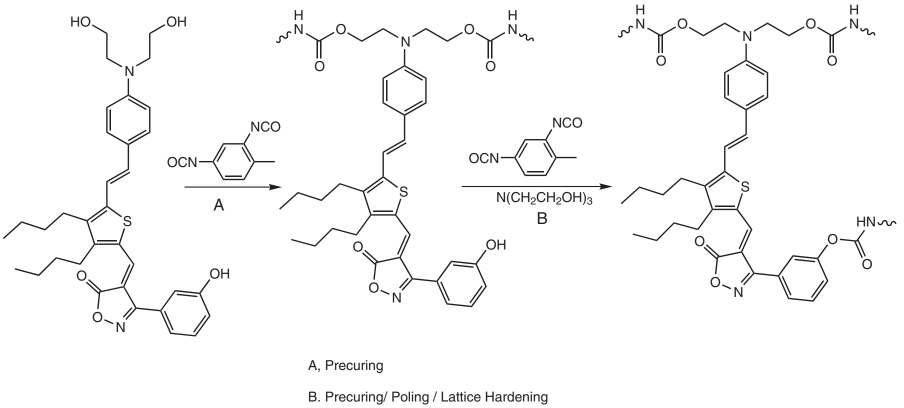
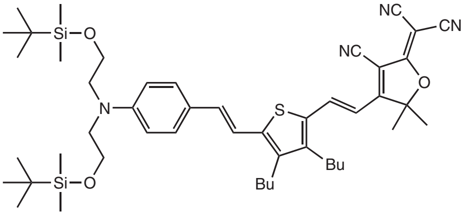


Figure 5.32 *Cross-linking and poling of NLO chromophore into a hardened lattice.* (Reproduced with permission of the Society of Chemical Industry.)



(5.12)

Electro-optic modulation (Pockels effect) using a poled polymer is shown schematically in Figure 5.33, where an optical signal confined in a wave-guide is modulated by the application of an external voltage, known as a Mach-Zender Interferometer.

Using the newer polymeric materials, derived from NLO chromophores such as (5.12), it has been possible to construct complex wave-guides, using techniques such as reactive ion and photochemical etching.[81,88] These polymeric modulators are designed for use as components in a range of devices, including analogue to digital converters, optical switching elements, voltage sensors and in cable TV applications, where they have been found to be competitive with lithium niobate based modulators.[79,81,84,88]

5.6.3 Photorefractive Polymers

In the 1960s it was observed that undesirable optical damage was occurring in inorganic crystals, *e.g.* lithium niobate, being examined in electro-optical applications. This damage, which was due to light induced changes in the refractive index, became known as the photorefractive effect.[89] 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, *e.g.* in optical correlators, phase conjugators

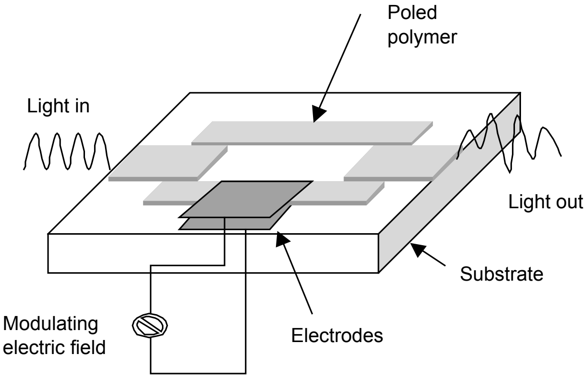


Figure 5.33 *Electro-optic modulation in a wave-guide using a poled polymer.*

and optical limiters. The discovery in 1991 that the photorefractive effect could be reproduced in certain polymers sparked a new wave of interest that has led to the newer materials and applications that are available today.[90]

5.6.3.1 The Photorefractive Effect

The photorefractive effect is the term used for the changes induced in the refractive index of a material by a redistribution of photogenerated charges.

There are four different processes involved in the production of this effect.

1. Two coherent light beams intersect in the material creating a sinusoidal light intensity pattern
2. Application of an external electric field causes the charges generated 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 electro-optic effect lead to phase encoding of the incident light distribution

This effect allows optical information to be recorded, erased and rewritten in real time.

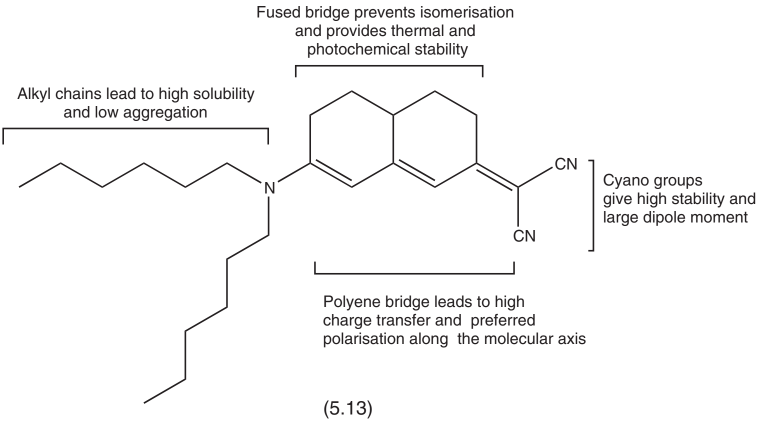
The mechanism for the photoelectric effect has implications for the design of photorefractive polymers, which must demonstrate the following characteristics.

- Support photogeneration of electron–hole pairs
- Capable of transporting holes or electrons
- Able to trap charge carriers
- Show the Pockels effect (electro-optic modulation)

5.6.3.2 Amorphous Polymers and Composites

Any photorefractive polymer or composite has to contain three elements, a NLO chromophore for refractive index changes on application of the electric field, a photosensitiser to generate mobile charge carriers on irradiation with light and a conductor for the charge carriers. Many different schema for producing photorefractive polymers have been pursued but it has proved very difficult to combine all three functionalities in one polymer.[91] Consequently, polymer composites, using photoconducting poly(*N*-vinylcarbazoles) and polysiloxanes carrying carbazoles side groups, have given some of the best results to date.[92] However, even with composites there are many problems to be overcome, such as the high loading requirements of the standard NLO chromophores, sensitisers and charge carriers, which together with low T_g, make many of the higher-performing composites metastable.

The polyene chromophore (5.13), designed by Marder and utilised by Peyghambarian and co-workers, has specific features built into the structure that make it both an effective NLO chromophore for refractive index change and for it to



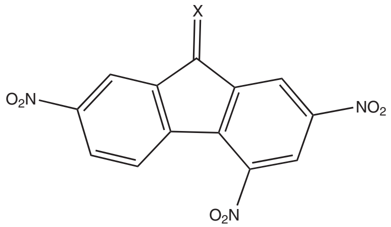
(5.13)

be able to act as a charge transport material, which goes some way towards reducing the number and quantity of small molecules which need to be present in the composite.[93]

In an example, a composite made up of (5.13) in a poly(*N*-vinylcarbazole) (PVK) matrix, *N*-ethylcarbazole as the plasticiser and hole transporter, with 2,4,7-trinitro-9-fluorenone (5.14a) as the sensitiser to provide sensitivity in the visible region (633 nm), is cast into a 100 μm thick film. When placed between transparent ITO electrodes, this film shows a dynamic range, which is a measure of the refractive index changes, higher than any other material available (1998). Changing the sensitiser to the dicyanovinyl analogue (5.14b) gives a composite that is sensitive into the near-infrared (830 nm). Using (5.13) as the dopant, functioning as both a charge transporter and refractive index changer, in the PTCB co-polymer, poly(methyl methacrylate-*co*-tricyclodecyl methacrylate-*co*-*N*-cyclohexyl maleimide-*co*-benzyl methacrylates) gives thermally stable materials with high performance, the total diffraction occurring at 633 nm.

5.6.3.3 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.[94] The polymer



(5.14)
a, X = O
b, X = $C(CN)_2$

matrix provides photogeneration, charge transport and trapping properties to create a space charge field. There is no need for a 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), PMMA. Into this matrix are added purified *N*-ethylcarbazole as the hole transport agent and (5.14b) as the sensitiser, forming a charge transfer complex with photosensitivity at 633 nm. All three materials are subjected to prior purification before use to increase the dielectric strength and avoid screening of the applied field. 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.

5.6.3.4 Applications of Photorefractive Materials

To date most of the polymeric materials have demonstrated potential rather than actual commercial applications. The two-beam coupling behaviour has obvious applications in real-time optical processing and holographic data storage.

Non-destructive testing, 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 would offer distinct advantages as they do not require any further processing and could operate in real time.

The near-IR sensitive polymer composites offer opportunities in areas where addressability with cheap diode lasers or commercially available titanium sapphire lasers is required. For instance, in holographic time gating, which is used to reconstruct an image that has been distorted on passing through a turbid medium. A very important imaging application is in medicine where biological tissues, which are transparent in the near-IR region, could be subject to holographic recording. The use of the near-IR and other laser addressable materials in security applications, such as the authentification of cheques, passports *etc.* by optical encoding and correlation of the information with a master copy, has been described.[95]

5.7 Photonics

Photonic crystals, structures made from material having different relative permittivities (dielectric constants), which can scatter coherent light from both the visible and near-infrared regions, require lattice dimensions in the same range as the light's wavelength, *i.e.* hundreds of nanometers. They are therefore very different from normal molecular crystals where diffraction arises from interaction between crystal spacings and X-ray wavelengths on the ångström size scale. The selective light diffraction properties of photonic crystals are the basis for constructing photonic devices.

However, to make these photonic devices some method of controlling light is required so that it can be manipulated for a particular application. In other words there is a need to be able to trap a photon of a particular wavelength, and then release it only as required. This is the photonic equivalent of the semi-conductor which controls the flow of electrical current in electronic devices such as transistors. These light manipulating materials would have a photonic band gap that performs an equivalent role for photons as do electronic band gap semi-conductors for electrons. This new class of materials, known as *photonic band gap crystals*, was first proposed in 1987,[96] and the construction of these artificial crystals has been an area for intensive research since the mid-1990s.[97]

5.7.1 Photonic Band Gap Crystals

Photonic band gap crystals can be defined as long-range ordered structures whose relative permittivity varies as a spatially periodic function. These three-dimensional periodic structures have a feature size comparable to or shorter than the wavelength of visible light.

It is a very difficult task to construct such materials and so far three major methods have been utilised in attempts to produce useful photonic band-gap materials.

- Self-assembled colloidal crystals
- Inverse opal structures
- Lithographic fabrication of photonic materials

5.7.1.1 Photonic Crystals via Self-assembly of Colloidal Spheres

Self-assembly of highly charged colloidal spheres can, under the correct conditions, lead to 3D crystalline structures. The highly charged spheres used are either polystyrene beads or silica spheres, which are laid down to give the ordered structures by evaporation from a solvent, by sedimentation or by electrostatic repulsion (Figure 5.34).[98] The structures created with these materials do not show full photonic band gap, due to their comparitively low relative permittivity, although the voids can be in-filled with other materials to modify the relative permittivity.

Whilst not showing full band gap capability self-assembled photonic crystals do show interesting incomplete bands, known as stop gaps. For instance, 3D crystalline arrays from differently sized PS beads show different colours in transmission; 270 nm beads give a red colour (absorbance at $\lambda = 650$ nm), 220 nm beads a green colour (absorbance at $\lambda = 550$ nm) and 206 nm beads a blue colour (absorbance at $\lambda = 460$ nm).

5.7.1.2 Inverse Opals

A better way of achieving a complete 3D photonic band gap is considered to be by constructing a lattice of air balls surrounded by an interconnecting matrix of material with a higher refractive index. The successful construction of such crystals by growth techniques is unlikely and likewise the build up by deposition techniques is no simple procedure.

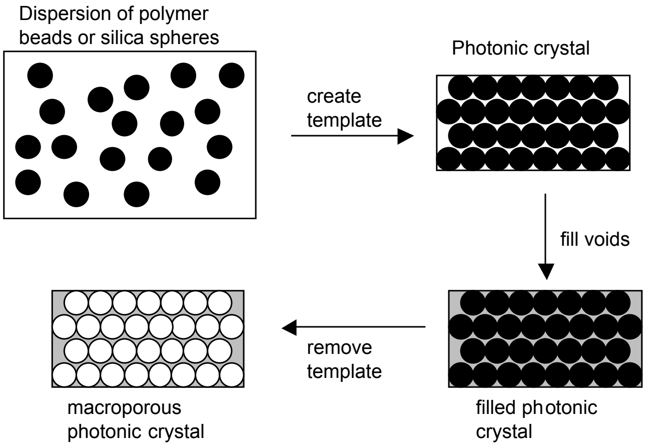


Figure 5.34 *Outline of self-assembly route to photonic, filled photonic and macroporous photonic band gap crystals.*

The most popular way for producing these 3D macroporous crystals is to use the self-assembled colloidal structures as templates. In this process the voids in between the assembled colloidal spheres are filled with a material that subsequently solidifies, before finally removing the spheres by an appropriate method.[98] By creating arrays that are similar to natural opals in structure (opaline), voids with tightly controlled sizes are produced, and these crystals form templates for the highly ordered 3D porous structures required for photonic band-gap materials. The colour of these porous materials is independent of electronic absorption and instead is dependent on the refractive index of the solid and the periodicity of the containing walls that is comparable to the wavelength of light. They are typically iridescent and are known as *inverse opals*.

The general process for producing photonic band gap materials *via* the use of template photonic crystals is shown schematically in Figure 5.34. A whole range of materials have been used to fill the gap, including organic co-polymers, carbon, SiO_2, TiO_2, ZrO_2, CdSe derived from suitable precursors, *e.g.* UV-curable prepolymers, metal alkoxides (sol–gel) and dispersed nanoparticles.[98] The template materials are normally removed by calcining or etching. Depending on the material used to fill the voids either a ceramic or a carbon structure is produced.

In one example, the colloidal structure, is made by sedimentation of polystyrene beads, giving voids in the range 120–1000 nm, and the voids are filled with TiO_2 generated from titanium tetrapropoxide. The polystyrene bead lattice is then removed by calcining to give an iridescent material, but not with a full photonic band gap.[99] In this case one of the controlling factors is the refractive index of the matrix, which needs to be greater than 2.8.

However, recently, material constructed using silica sphere photonic crystals as the template has given a complete 3D-photonic band gap centred on 1.46 μm, which is a favoured wavelength for fibre-optic communications. Sintering of the silica array causes each sphere to be joined by short necks. Silicon is then grown in the voids using disilane gas. After removing the silica spheres by chemical etching, the structure is one of interconnecting air spheres surrounded by silicon shells. Because they are made from silicon interfacing with silicon based microelectronics is a possibility.[100]

5.7.1.3 Lithographic Fabrication of Photonic Band Gap Materials

The use of photolithographic techniques, coupled with etching and deposition would seem to be the most obvious way to construct photonic band gap materials, but it does require extreme precision and to be carried out on extremely flat surfaces. In one approach a stacked structure of silicon rods was made which showed a large photonic band gap in the infrared region.[101,102] Using a similar stacked log structure, but based on gallium arsenide or indium phosphide, gave a material which was a breakthrough in photonic band gap crystals (see Figure 5.35). These structures, laid down with nanometer precision, attenuate 99.99% of incident light at optical communication wavelengths.[103]

5.7.2 Applications of Photonic Crystals

Photonic crystals that are able to confine, control and manipulate light in three dimensions would have many potential uses, especially where the following properties can be utilised.[104]

- Blocking of the propagation of protons irrespective of polarisation or direction
- Localisation of photons to a specific area and of restricted frequencies
- Inhibition of the spontaneous emission from excited chromophores
- Modulation and control of stimulated emission
- Lossless wave-guide for the propagation of photons in a specific direction

Exploitation of these is possible in LEDs that display coherence properties, in thresholdless laser diodes, and in many other optical, opto-electronic and quantum electronic devices.

Whilst true 3D photonic band gap materials operating in the microwave and millimetre range have been produced, those operating in the visible region of the spectrum are still awaited. When this eventually happens the optical computer will no longer be a pipe dream.

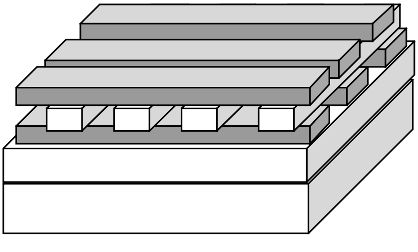


Figure 5.35 *Stacked log structure for 3D photonic crystals.*

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