Chapter 4
Photochemical Materials: Absorbers, Emitters, Displays, Sensitisers, Acceptors, Traps and Photochromics

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Abstract In this chapter we discuss some of the typical materials used in photochemistry. We describe, in general terms, how their suitability for application as absorber, emitter, sensitiser, energy acceptor or quencher, depends on the energy states within the material and the routes of interconversion between these states, and also how suitability as a redox or chemical sensitiser/acceptor/trap is determined by specific chemical reactivities. We describe the application of photochemical principles to the design of light sources and displays, and describe the photochemical principles and applications of photochromics and molecular switches. A table giving the structures, characteristics, and uses, of a number of compounds widely used in photochemistry is provided at the end of the chapter.

4.1 Introduction

Whether a material will act as a *passive absorber*, an *emitter*, or *sensitiser*, depends, for the most part, on how excitation energy is deactivated in that material. If deactivation is *via* a fast non-radiative process, the material will act as a passive

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R. C. Evans et al. (eds.), *Applied Photochemistry*,
DOI: 10.1007/978-90-481-3830-2_4,

absorber. If deactivation goes *via* an emissive excited-state, then the material may be a useful emitter. If deactivation proceeds *via* a relatively long lived excited-state, then the excited state may be useful as an energy transfer sensitiser, since the long lifetime may allow transfer of the excited-state energy to another species. If deactivation goes *via* a chemical reaction which leads to products of interest e.g. singlet oxygen, radicals, or redox active species (*i.e.* strong oxidants or reductants), then the material may be a useful photochemical sensitiser for these species.

Whether a material is useful as an *excited-state acceptor*, depends on the energy level of excited states within the material and the way those states deactivate once populated. A useful *redox* or *chemical acceptor/trap* will show efficient and specific reactions: redox traps will undergo a specific reduction or oxidation; singlet oxygen acceptors have specific reactions with singlet oxygen; and radical quenchers or traps have specific reactions with radicals.

In the following discussion, a number in bold indicates an entry for that compound in the table of commonly used compounds, their uses and properties, Table 4.1, found at the end of the chapter.

4.2 Passive Absorbers

The major uses of passive absorbers are as colorants and sunscreens, although in passive solar heaters the heat generated during excited-state deactivation is the important photo-product. Dyes and pigments are used as passive absorbers in established technologies such as: paints, plastics, textiles, paper, printing, imaging, and foodstuffs. In sunscreen formulations, UV absorption rather than visible absorption is required. High technology applications of passive absorption include: biochemical "stains" where not only colour intensity, but also selective binding to particular biochemical substrates, is required; recording dyes for optical storage in CDs and DVDs; and imaging and digital printing where a combination of the need for accurate colour reproduction, chemical and photochemical stability, and compatibility with printing processes, requires highly specialised dye design [1–3]. In the space available here we can give only a very brief account of what is commonly termed *colour chemistry*, but the interested reader is directed to references [1–3] which between them provide an excellent introduction and overview of this very important aspect of applied photochemistry.

Important characteristics for colorants are: intensity, brightness and stability. Relative costs mean that only colorants with high intensity absorptions are commonly used. This restricts the types of transition involved to: molecular charge transfer bands, π–π^* bands, n–π^* bands with a high degree of π–π^* coupling, or direct bandgap semiconductor transitions. The brightness of a colorant depends primarily on absorption band width; narrow bands give bright colours. The absorption band width is influenced by the width of ground and excited state potential energy curves, how similar the molecular geometries in ground and excited state are, and also the presence of close or overlapping transitions.

Photostability/lightfastness is very important for all colorants; poor lightfastness causes loss of colour in imaging and printing, and leads to conservation problems for artwork and artefacts. Stability towards thermal degradation is important in colouring plastics which may be moulded at high temperatures, in colorants for outside structures, metalwork and cars, as well as for sublimable dyes. Stability towards hydrolysis is important in imaging, printing and artist's materials. Washfastness is a particularly important feature for textile dyes.

Colorants are used as *dyes* or *pigments. Dyes* are colouring materials which are *soluble* either in the medium in which they are incorporated, or, as the term is commonly used in textiles technology, in a dyeing solution applied to the medium in which they are incorporated. (Disperse 'dyes' are applied as a fine dispersion to synthetic textiles, but dissolve in the textile to give a 'solid solution'). *Pigments* are colouring materials which are *insoluble* in the medium in which they are incorporated. The principle applications of pigments are in paints, printing inks and plastics, although they are also used to colour cement, ceramics, concrete, cosmetics, glass, paper and rubber. Usually the application of pigments involves their incorporation into a liquid medium, a wet paint, or a molten thermoplastic material, by a dispersion process in which the pigment aggregates are broken down into very small primary particles or aggregates. When the medium solidifies, the individual pigment particles become fixed in the solid polymeric matrix. Apart from imparting colour, pigments also provide *opacity* by scattering light. The size and size distribution of the pigment particles is important in terms of both colour and opacity; particle sizes of $\sim$0.2–0.3 μm are often used since these provide maximum opacity.

4.2.1 Inorganic Colorants

Most inorganic colouring materials are pigments. Surface treatments are often applied to inorganic pigments, e.g. coating with surfactants may improve ease of dispersion, while coating with inert inorganic oxides, such as silica, can give improved lightfastness and chemical stability. Among the most important inorganic pigments are titanium dioxide (white); carbon black; metal oxides e.g. iron and manganese (yellow, brown, red, black) and chromium (green); cadmium/zinc sulfides/selenides (yellow/orange/red); cobalt aluminate (cobalt blue); ultramarine blue; and Prussian blue. The origin of colour in these materials is varied.

TiO_2 (**9.1**) and Cd-Zn/S-Se (**9.3–9.5**) are semiconductors. TiO_2 has a band gap of 3.0–3.2 eV, *i.e.* it absorbs in the UV region. It is used as a white pigment because it has a very high refractive index, and therefore a high scattering efficiency and excellent opacity for all visible wavelengths. A surface coating is generally required to prevent photoreactions on the TiO_2 surface from damaging the dispersion medium, a phenomenon known in the paint industry as *chalking*. With a band gap of 1.6 eV CdSe absorbs all visible photons and therefore appears black; at 2.6 eV CdS absorbs blue photons and therefore appears yellow. Changing the S/Se ratio shifts the band gap from 2.6 to 1.6 eV, taking the colour through the yellow-orange-red–black range. Replacement of Cd by Zn gives greenish-yellow tones.

In many oxide pigments the colour is due to ligand–metal charge transfer (LMCT) transitions (see Chap. 3). Natural iron oxide based pigments include: *yellow ochre*, *red haematite*, and the browns, *sienna* and *burnt sienna*; *umber* and *burnt umber* are iron oxide with manganese dioxide. Synthetic red iron oxides are anhydrous Fe_2O_3, while synthetic yellow pigments are iron(III) oxide/hydroxides, FeO(OH), and black pigments are non-stoichiometric Fe(II)/Fe(III) oxides. They have excellent durability, high opacity, low cost, and low toxicity. Cr(III) oxide, which gives a dull green pigment with outstanding durability, is another important oxide pigment. Lead chromate pigments, which have now been almost completely replaced because of their toxicity, are important historically. Pure $PbCrO_4$ gives a rich yellow pigment, the colour of which originates from a charge transfer transition on the chromate CrO_4^{2-} ion; the role of lead is to make a highly insoluble pigment. Lemon shades are obtained by the addition of lead sulfate, while addition of molybdate gives orange red tones.

Cobalt blue is a cobalt aluminate, $CoAl_2O_4$, with a spinel crystal structure in which Co atoms sit in a tetrahedral environment (the same coordination geometry which gives self-indicating silica gel a blue colour when dry—the pink colour when wet is due to cobalt in octahedral coordination). Here the colour originates from metal-centred *d–d* transitions on Co(II). A blue/green analogue, $CoCr_2O_4$, has Co in tetrahedral sites and Cr in octahedral sites in the crystal structure.

Ultramarines are complex sodium aluminosilicate structures, containing trapped sulfur anions, S^{2-} and S^{3-}, which absorb in the red spectral region, e.g. the S^{3-} anion has an absorption maximum, λ_{max}, at $\sim$600 nm [4]. Originally from the mineral *lapis lazuli* (blue stone), brought to Europe from Afghanistan, where it is still mined today, and described as *ultramarine* (beyond the sea). It was very expensive, partly because of the source, but also due to difficulty in preparation, and in Western religious art it was often reserved for the mantle of the Virgin Mary [5]. Today, it is made synthetically as French ultramarine, after a synthetic route was discovered by Jean Baptiste Guimet in 1826.

Prussian blue is a mixed Fe(II)/Fe(III) complex polymeric species in which Fe(II) is octahedrally coordinated by C, and Fe(III) is octahedrally coordinated by N, to give a structure containing Fe(II)-C–N-Fe(III)-N–C-Fe(II)-linkages, in which the colour originates from electron transfer between the two metal oxidation states. It was discovered in 1704, and used in 'blueprints' and also in the cyanotype photographic process developed by Herschel (see Chap. 11). The cyanotype process is made possible by the photochemical reduction of Fe(III) citrate (or oxalate) to Fe(II), which reacts with ferricyanide present in the coating formulation to give Prussian blue. A similar photoreduction of Fe(III) oxalate to Fe(II) is used in the ferrioxalate actinometer (see Chap. 14).

4.2.2 Organic Colouring Materials

Here, pigments and dyes are both important. There is an enormous range of organic dyes available, and a number of classification methods have been used, but that based on the electronic nature of the transition is most relevant here [1].

Donor–acceptor colorants. These are by far the most important group of organic colorants, they include azo-, anthraquinone- and carbonyl-based dyes. Colour originates from transitions in which there is a significant shift in electron density from the donor to the acceptor parts of the molecule. Azo dyes account for over 50 % of all commercial dyes. There is a vast range available. They can contain multiple azo, (–N=N–), groups, but monoazo dyes are the most important (e.g. methyl orange **11.13**). These contain an electron donating group (often hydroxy or amine) and an electron accepting (often aryl) group on either side of the azo bond. The electronic transition occurs across the azo bridge from the electron donor to the electron acceptor group. These dyes cover the whole spectral range but yellows, oranges and reds are most important. Synthesis is relatively straightforward from cheap starting materials, so they are very cost effective. Azo dyes can also exhibit *cis–trans* photoisomerisation across the azo bond, which results in *photochromism* (see later), although this is not common in modern dyes. Addition of a hydroxy group adjacent to the azo bond generally improves light stability, since proton transfer between O and N atoms in the excited state can act as a rapid mechanism for loss of excitation energy. Metal complex azo dyes are also very common, with copper, cobalt and chromium being common metal ions used. The metal ion leads to improved lightfastness. There are probably a number of factors at play in this, e.g. reduction of electron density at the chromophore and therefore a reduction in ease of photooxidation, excited-state deactivation by low lying *d–d* levels, and steric protection of the chromophore. Metal dyes also show improved washfastness because of the larger size of the metal complex, and stronger fibre interactions. However metal complexes are generally duller colours than the parent azo due to their broader absorption bands, which result from additional overlapping *d–d* transitions and charge-transfer bands, and sometimes the presence of isomers with slightly different absorption spectra.

Anthraquinone dyes are the second most important group of organic colorants. The basic structure is 9,10-anthraquinone (**11.3**) but with electron donor groups in 1, 4, 5, and 8 positions. The absorption maximum can be shifted by choice of type and number of substituent. The historically important natural dye *alizarin* is 1,2-dihydroxyanthaquinone (**11.4**), originally obtained by extraction from the root of the madder plant. Hydrogen bonding from the carbonyl oxygen to an adjacent OH, or NH group is an important factor in light stability, since reversible proton transfer in the excited state can act as a rapid mechanism for loss of excitation energy (similar to putting a hydroxy group ortho to the azo group in azo dyes). It is possible to get the whole spectral range, but violets, blues and green are particularly important since these complement the yellow, oranges, and reds best obtained in azo dyes. Anthraquinone dyes have good brightness and fastness;

however they cost more than azo dyes because the molar absorption coefficient is lower and they are more expensive to make. They are not used much as pigments because pigment blues and green are best provided by phthalocyanines.

Indigo and 6,6-dibromoindigo (*tyrian purple*) (**11.11**) are two of the oldest known dyes [6]. Natural indigo is extracted from plants, indigo (*Indigofera tinctoria*) in the Far-East or woad (*Isatis tinctoria*) in Europe; tyrian purple is extracted from shellfish. In both cases the dyestuff itself is not present in the natural source but is generated by fermentation and/or air oxidation. Nowadays, only indigo is important commercially, and it is almost exclusively synthetic. It is used mainly for denim (*de-Nîmes*, where the thick cotton cloth was originally made), where fading without change of shade only, at points of textile stress and wear is a key fashion feature.

Polyenes. These are systems of extended conjugation in which the molecular orbitals extend over a large part of the molecule and the π–π^* transition does not result in a major shift in electron density from one part of the molecule to another. As the degree of conjugation increases, the spacing of electronic energy levels decreases, and λ_{max} shifts to longer wavelengths. Phthalocyanines (**5.5, 5.6**) are the most important synthetic commercial polyene colorants. Metallophthalocyanines (**5.6**) give brilliant intense blue/green colours of high stability. The intensity of colour is due to very high molar absorption coefficients, while the brilliance is due to very narrow absorption bands due to the rigidity of the molecular structure. They are most commonly used as pigments. They are too large to penetrate into many fibres, but can be used for polyester and as reactive dyes for cotton, where they are covalently bound onto the cotton surface. Naphthalocyanines have absorption maxima in the NIR which makes them interesting dyes for optical data storage and 'invisible' security printing. Carotenoids are important natural polyene colorants, and are used commercially in foodstuffs, the most important being β-carotene (**11.5**).

Cyanines, squaraines, rhodamines, xanthenes. Cyanines (**4.6, 4.7**) are similar to polyenes, but with remarkably low energy transitions for such small molecules. This is because they have an odd number of atoms carrying *p* orbitals in the conjugated chain (polyenes have an even number), and the terminal N, rather than C, atoms results in two extra electrons per chain compared to polyene dyes. The resulting MO structure has a relatively high energy HOMO with significant non-bonding character, as opposed to the bonding HOMO of polyenes, and there is, therefore, a relatively low energy HOMO → LUMO transition (see Chap. 1). These molecules give intense bright colours due to their high molar absorption coefficients and quite narrow absorption bands. The λ_{max} is dependent upon chain length, and dyes absorbing from the blue to IR spectral regions are available. 'Hidden cyanines', in which the cyanine structure is not so obvious, e.g. phenolphthalein, rhodamines (**4.1, 4.2**), squaraines (**11.19, 11.20**) and other dyes such as methylene blue, (**11.12**) nile blue (**11.15**) and triarymethane dyes (**11.7**), and xanthenes (fluoresceins) (**4.3–4.5**), which can be considered oxygen analogues of cyanines, also give intense bright colours. Rigid structures such as rhodamines and fluoresceins are often highly fluorescent, whereas 'looser' structures like phenolphthalein are not. Dyes spanning the full spectral range can be made. Although historically important dyestuffs, particularly the triarymethane dyes, cyanines and hidden cyanines are not so chemically and photochemically stable as other dyes and so are not used as absorptive colorants, except in specialist applications such as biological 'stains' for microscopy, and as colorimetric pH indicators. The highly fluorescent variants e.g. rhodamines, are widely used as laser dyes, and also as biological stains and fluorescent markers. They are also used as fluorescent colorants, e.g. in artist's inks, where the resultant brilliant colours are a product of both absorption and emission, but in this application their poor light stability is a significant disadvantage.

4.2.3 Sunscreens

Sunscreens are UV absorbing materials suspended in a cream or spray. The two main types of UV absorbers used are: (1) colloidal semiconductor particulates, notably ZnO (**9.2**) and silica- or alumina-coated TiO_2 (**9.1**), and (2) organic absorbers. Key photochemical requirements are high UV absorption with no visible absorption, (although scattering of visible light in opaque white sunscreens is acceptable), and high photostability with a complete lack of any photoreactions which may lead to phototoxicity. Chemical requirements are low toxicity, and compatibility with cream formulations. Ideally, excitation energy is rapidly lost as heat, and typical mechanisms for this in organic sunscreens are proton transfer in hydroxyl benzophenone (**11.6**) based sunscreens and molecular twisting in cinnamates (**11.17**).

4.3 Emitters

There are many type of emitters: gas phase atoms and ions; molecules in the gas, solution, or solid phase; metal ions as an integral part of a solid state lattice; energy traps or 'activator' sites, which may be a specific ion or site defect, in a semiconductor or other solid; conjugated polymers; semiconductors as either a solid, or as a colloidal dispersion in some other medium or solution; and hot metals. In all but the latter three cases emission is from a localised emitter, with both states involved in the transition localised in a small region of space, on an atom, ion, or molecule. However, for semiconductors, some emissive polymers, and hot metals, the states involved in the transition extend across a relatively large region of space and a large number of atoms.

The characteristics of the light emitted are determined by the following.

(1) **The energy levels of the emitter in the medium used.** These determine the emission wavelength(s), and shape of the emission band(s). For semiconductors, and some emissive polymers (**3.1–3.9**), emission is a property of the whole material, and control of the size of the semiconductor particle or chain length of the polymer may be important, e.g. in semiconductor *quantum dots* (**9.3–9.7**).

For semiconductor materials on the macroscale the valence and conduction bands have band widths associated with the continuum of orbitals. However, on going from the macroscale to nanometre (nm) dimensions two effects occur due to the removal of atoms (and hence orbitals); firstly, the bands cease to be a continuum and individual orbitals, and hence quantised energy levels are observed (hence the term *quantum dot*); secondly, orbitals are removed from the edges of the valence and/or conduction bands, which increases the band gap. The size of the quantum dot dictates the absorption and emission characteristics; the smaller the quantum dot, the larger the band gap, and hence the more blue-shifted (shorter wavelength) the emission (Fig. 4.1) [7].

In metallic solids, the presence of a continuum of states means that there are many transitions possible, and so when heated, as in an electric tungsten filament bulb, these materials emit a continuous spectrum which is very different to the line or band emission of atomic or molecular species. Other hot solids, and hot high pressure gases, often emit a mix of line or bands on top of a continuum (see for example the spectrum of high pressure Hg or Xe lamps in Chap. 14).

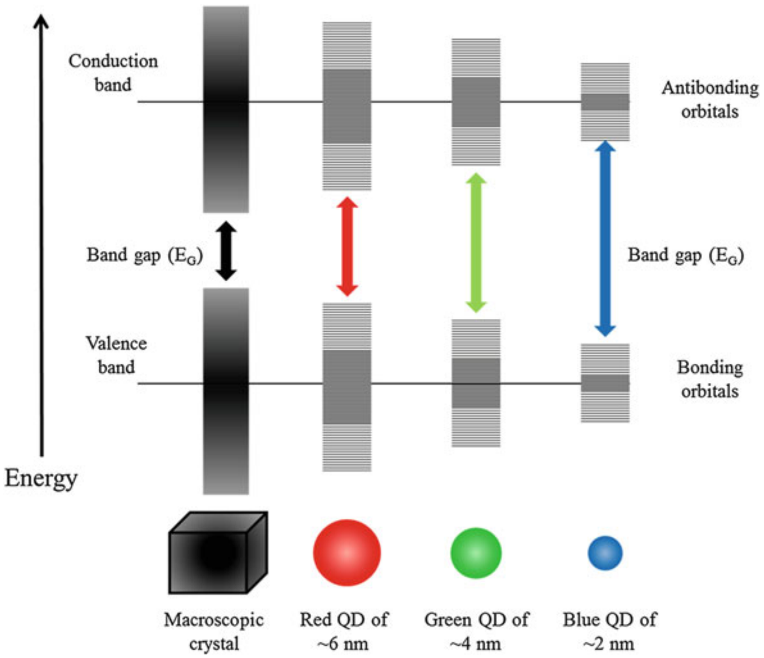


Fig. 4.1 Schematic representation of the effect of size on semiconductor properties, *i.e.* changes on going from the macro-scale (continuum of energy levels) to the nano-scale (quantised energy levels). The average energy position of the bands do not change (represented by the *lines* dissecting the relevant bands and orbitals) however, the band gap increases with decreasing size as extreme energy levels are removed. Figure adapted from Ref. [8]

(2) **The nature of the emissive transition.** Typically, allowed transitions, such as fluorescence or direct bandgap semiconductor emission, have radiative lifetimes between a few and a hundred ns. Forbidden transitions, such as molecular phosphorescence, have radiative lifetimes longer than μs, usually much longer.
(3) **Competition with other deactivation routes for the excitation energy**. The competition between emission and other deactivation routes determines the emission quantum yield. Competing deactivation processes are important for almost all emitters, even those for which emission is a highly probable process; there are few emitters with an emission quantum yield approaching 1. Competing deactivating processes are particularly important for forbidden transitions, where radiative rates are relatively slow. Most reasonably efficient room temperature phosphorescent compounds are heavy metal complexes where the degree of forbiddeness is reduced by heavy-atom spin–orbit coupling, and the radiative lifetime is in the μs–ms range. Most organic molecules, which do not have such coupling, show phosphorescence only in a low temperature glass, with radiative lifetimes in the ms to tens of seconds range.
(4) **The method of population of the emissive state.** If population is achieved directly from the initial excitation source, then as soon as that source is removed the emission intensity will decrease with a rate determined by the deactivation processes of the emissive state. However if the excited-state is populated by processes which occur after the initial excitation process, e.g. energy transfer, energy migration, exciton migration, or delayed fluorescence, then the emission intensity will decrease at a rate determined by both deactivation and population processes. In some cases, where the rate of population of the emissive state can be made very slow, e.g. by energy or exciton migration within a solid, very long lived *phosphors* (**9.3**) are possible.
(5) **Population inversion**. If the emissive state can be formed such that a population inversion is obtained it may be possible to obtain laser emission (e.g. Nd^{III} ions (**10.5**) in the Nd/YAG laser, see Chap. 14).

Emitters can be classified in terms of those which emit in the gas phase, the solution phase, or the solid state, and also by mode of excitation, *i.e.* electroluminescence, thermoluminescence, chemiluminescence, radioluminescence and photoluminescence. We are most concerned with photoluminescent materials, but thermoluminescence and electroluminescence, in both gas and solid phases, are important technologies.

4.3.1 Solid State Thermoluminescence

The first commercial electric lamps of Edison and Swann involved *incandescence* produced by passing an electric current through a carbon filament. Modern incandescent lights use the same principle, but with the fragile carbon thread

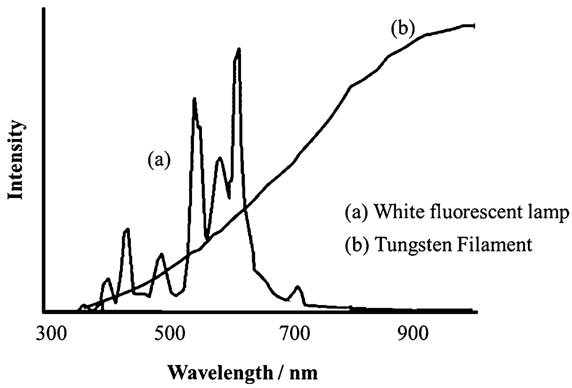


Fig. 4.2 Emission spectra of: **a** 5000 K fluorescent lamp, **b** 2800 K tungsten filament lamp. Figure adapted from Ref. [10]

replaced by tungsten. The incandescent lamp has the advantage of good spectral output. Like the Sun, the broadband emission (Fig. 4.2) is, to a good approximation, that of a black body radiator [9]. However, although the cost of the incandescent lamp is low, the efficiency of energy conversion is limited (5–10 %) since most of the electrical energy used is lost as heat, and the lifetime of the lamps is limited. Although modest increases in efficiency are possible, there is a global tendency to phase out incandescent lamps for domestic use in favour of more energy efficient forms of lighting.

Other common incandescent emitters are the 'glowbar' used in IR spectroscopy which is also a good approximation to a black body emitter, and burning magnesium and the incandescent lanthanide oxides used in the mantles of gas lamps; for these emission is a combination of a broad band continuum with specific emission lines superimposed.

The measurement of *thermally-activated luminescence* from radiation-induced defects in minerals, particularly those in ceramics, is usually termed *thermoluminescence* when used in archeological dating, although the role of thermal excitation here is not the generation of emissive states but rather to allow defect relaxation, and concomitant emission, to occur. The general principle is as follows. When ceramics are fired, the high temperatures allow complete defect relaxation in the ceramic minerals, such that immediately after firing the thermoluminescence signal would be zero. Over time, natural radiation damage causes defect formation within the ceramic, and thus the intensity of thermoluminescence at any time after firing is related to the rate of defect formation and, the key archeological factor, the time since the firing.

4.3.2 Gas Phase Plasma Emission

All atoms and ions have some excited states which relax by emission in the UV/Vis spectral region. This forms the basis of atomic emission/fluorescence spectroscopy. Excitation may be: thermal in a flame; electrical in an arc; or by radio- or microwave-frequency radiation. This produces a *plasma*, which leads to production of excited states of the atoms and molecules of the gas. These then emit light. Apart from its use in analysis *via* atomic emission spectrometry and flame photometry, and the generation of colours in fireworks and flares, thermal excitation is not widely used to generate gas phase excited-states. (The yellow/white emission of candle/spirit lamp and low air flow Bunsen flames is due to incandescent carbon particles rather than specific atom or molecular emission—these generate the blue component of the light of the flame.) However, electrically excited plasmas in *gas discharge* lamps give us many of our light sources. These have been known since the nineteenth century. Important gas discharge lamps used in experimental photochemistry are: (i) low, medium and high pressure mercury lamps which are excellent sources of UV radiation; (ii) the Xe arc lamp, which is widely used as an intense continuous or μs pulsed UV/vis source; (iii) Xe and Kr flash lamps which give UV/Vis emission with *ca.* μs pulse duration, (also used as photographic flashlamps); (iv) gas phase lasers; (v) the nitrogen and oxygen pulse spark lamps used in single photon counting; and (vi) the deuterium lamp which is used as a UV source in UV/Vis spectrophotometers and other instruments (see Chap. 14 for further information on light sources).

Gas discharge lamps exhibit higher energy conversion efficiency than incandescent lamps and are widely used for general industrial and domestic illumination. They can be divided in terms of systems in which there is local thermal equilibrium (*LTE plasmas*) and those in which there is not (*non-LTE plasmas*) [11]. LTE plasmas, sometimes termed high intensity discharge (HID) lamps, operate at high gas pressures. A good example is the high-pressure sodium lamp, produced by adding sodium metal to the mercury lamp and used as an intense yellow light source for many outside applications, such as street lighting and freight yards. For these applications, the colour of the illumination is less important than the cost. An intense white HID lamp can be obtained by adding metal halide salts, and is frequently used in outdoor floodlighting. The most important non-LTE plasmas are low pressure mercury or sodium lamps. Gas discharge lamps have the disadvantage that the light is emitted in discrete lines rather than a broad band obtained through incandescence, as can be seen in the spectra of mercury lamps discussed in Chap. 14 (see Fig. 14.3). In addition, in many cases, much of the light is in the UV (such as the 254 nm line in the mercury discharge lamp) and is not of itself useful for lighting, although it can be converted to visible light by a phosphor, e.g. the white phosphor coating on the inside of a fluorescent lamp.

4.3.2.1 Fluorescent Lamps and Phosphors

During the early part of the twentieth century, considerable effort was made to convert the UV component of gas discharge lamps into broadband visible light through the use of solid state luminescent materials, commonly termed *phosphors*. Phosphors have been studied since the middle of the nineteenth century, and are, typically, inorganic semiconductors, such as zinc sulfide (**9.3**), zinc silicate, or calcium tungstate [12, 13], frequently doped with other species. The first practical “fluorescent” lamps, invented in Germany in the 1920s and commercialised in the US in the following decade, involved low pressure mercury discharge lamps with the walls of the tube coated with appropriate phosphors. The same phosphors could be excited by high energy radiation, such as electron beams (cathode rays), and the search for new luminescent materials for fluorescent lamps has paralleled that for cathode ray tubes (CRTs) for television or other display applications. Much of the early research on phosphors was empirical [12]. However, by the middle of the twentieth century there was sufficient knowledge on electronic structure, luminescence spectra and photophysics of inorganic materials to apply a more rational approach to the design of phosphors. Luminescence of inorganic materials can be divided into that of localised centres, such as metal ions, and emission involving delocalised semiconductor bands [13]. In general, emission involving semiconductor bands will give a rather broad spectrum, while that from localised centres will involve sharp, well defined spectral lines. For display applications, it is often advantageous to have rather sharp spectra, such as is found with the *f–f* transitions of lanthanide ions (**10.1–10.6**). A major breakthrough in luminescent materials for CRTs came with the development of a good red phosphor involving europium(III) in yttrium vanadate (**10.1**) [14]. Full colour displays are obtained by combining emission from different coloured phosphors, typically red, green and blue (RGB) using the Commission Internationale de l’Éclairage (CIE) chromaticity diagram (Fig. 14.3) [15]. An entertaining account of the development of this diagram is given elsewhere [16].

Since the seminal work on europium(III) based phosphors, lanthanides have become some of the most important materials for both lighting and displays [17]. With the normal fluorescent lamps containing mercury vapour, electronic energy transfer is crucial for efficient conversion of UV into visible light. This can involve both Förster [18] and Dexter [19] mechanisms. As discussed in Chap. 1, the Förster mechanism involves dipole–dipole interactions which require good overlap between the emission spectrum of the energy donor and the absorption spectrum of the acceptor, while the Dexter mechanism involves electron exchange, and needs close proximity between the donor and acceptor. Frequently, cerium(III) is used as an intermediate in fluorescent lamps for good photochemical reasons. The electronic transitions in most lanthanide ions involve two *f* orbitals, and are very weak, since they are forbidden by the Laporte selection rule (Chap. 1). However, the electronic transitions in Ce(III) involve transition of an electron between 4*f* and 5*d* orbitals, which is allowed by both spin and Laporte selection rules. This gives the Ce(III) ion a good molar absorption coefficient, which favours energy transfer from excited mercury atoms. In addition, the lifetime of the Ce(III) fluorescence is short, which avoids problems of saturation of excited states at high light intensities. The consequence is that excited Ce(III) in the solid phosphor layer can transfer energy efficiently to neighbouring terbium(III) or other lanthanide ions. Although this discussion is an oversimplification, and there are many parts of the sensitisation mechanism that are still poorly understood, it does indicate some of the photochemical ideas used in optimising the efficiency of fluorescent lamps. A schematic description of energy transfer from excited mercury atoms (Hg^*) to Tb(III) (**10.2**) *via* Ce(III) is given below.

$$Hg^* + Ce(III) \rightarrow Hg + Ce(III)^* \quad (4.1)$$

$$Ce(III)^* + Tb(III) \rightarrow Ce(III) + Tb(III)^* \quad (4.2)$$

$$Tb(III)^* \rightarrow Tb(III) + h\nu \quad (4.3)$$

In comparing the properties of different light sources, three parameters are commonly used. The first is the *luminous efficacy*, which is the response of the average eye to light over the visible spectral region (380–780 nm), and is measured in lumens (visible light) produced per watt of electrical power (lm/W). The second property, the *correlated colour temperature*, is a measure of the appearance of the light source and is given as the temperature of the black body which most closely represents the light source. The spectrum of sunlight depends upon altitude and time of day, but at noon typically has a correlated colour temperature of 5000–7500 K. Finally, the *colour-rendering index* is an indication of how accurately the light source can reproduce colours of objects compared with natural light (daylight), and is measured by comparison of the apparent colours of reference pigments using the light source and a black body standard [9].

A 35 W fluorescent lamp has a luminous efficacy of about 104 lm/W, compared with 16 lm/W for a 100 W incandescent lamp [20]. However, fluorescent lamps have a number of disadvantages. In particular, they need an electric ballast to produce the initial discharge in the mercury vapour, which requires a longer start-up than an incandescent lamp. This limits applications in areas, such as traffic lights, which need fairly rapid switching. In addition, white light is important for illumination, particularly for indoor applications, and although the phosphor in a fluorescent lamp can be developed to give a good spectral distribution, often by using a mixture of materials, there are always some lines present in the emission spectrum from the mercury lamp. This can influence the perceived appearance of colours. Most people will be familiar with the experience of buying clothes in a shop lit with fluorescent lighting and then finding the colour appears different in sunlight. This is because of differences in the emission of the light sources; spectra of typical incandescent and fluorescent lamps are compared in Fig. 4.2; the colour-rendering index is 100 for the incandescent lamp and 85 for the fluorescent one.

Fluorescent lamps have much higher luminous efficacy than incandescent ones. Although they are more expensive, their usable lifetimes are an order of magnitude longer. There are, thus, very real economic advantages of these systems, particularly the recently developed energy-saving compact fluorescent lamps (CFL), over tungsten filament lamps. However the majority of fluorescent lamps still use the toxic heavy metal mercury, although other gases are being tried. This has a long term environmental impact and has stimulated the development of other sources of lighting, in particular light-emitting diodes (LEDs).

4.3.3 Electroluminescence and Optoelectronic Displays

4.3.3.1 Cathode Ray Tubes (CRTs)

For much of the twentieth century, the dominant optoelectronic display device was the cathode ray tube, where an electron beam is scanned across a phosphor screen in a vacuum tube. Nowadays, conventional CRTs are being superseded in the display area by flat-panel displays for applications in television, laptop computers, mobile phones, etc. The main competitors in this area at the moment are liquid crystal displays (LCDs) [9, 21], plasma display panels (PDP) [22] and LEDs [23]. Plasma display panels generate a plasma discharge in a mixture of Xe and Ne to produce vacuum UV radiation. This is then used to excite a phosphor screen. This has the advantage that it is possible to prepare large area screens with high brightness [22]. The limitation is that it requires relatively high power consumption. Related technologies being developed for flat screen displays use field emission with a cold cathode and microcavity plasmas [22].

4.3.3.2 Liquid Crystal Displays (LCDs)

These are not, intrinsically, photochemical systems, however, they are optoelectronic systems, and backlighting is fundamental to both their functioning and overall energy efficiency. The most common LCDs involve an oriented twisted nematic phase of an organic material sandwiched between two optically transparent electrodes (typically indium tin oxide, ITO) [21]. This is illuminated by polarised light and the anisotropic liquid crystal changes the plane of polarisation. When observed through a second polariser, light is transmitted when this is parallel to the plane of polarisation or blocked when it is perpendicular. The orientation of the liquid crystal can be changed by application of an electrical potential. In displays this is used to switch between the light (transmitting) and dark (non-transmitting) states, with each pixel corresponding to a liquid crystal cell. A schematic of an LCD based on a typical twisted nematic liquid crystal is shown in Fig. 4.3. The initial monochrome liquid crystal displays were used in watches and calculators [21]. Full colour high definition LCDs are now common, and represent a multibillion pound sector of the display industry. Colour is achieved by dividing the pixels into three, with red, green and blue filters in separate layers. One of the early limitations was that the angle of vision of the displays was limited. This has been partially overcome by using thin film transistors (TFT) to address the cells in active matrix LCDs [21, 24], and has led to the high definition LCD screens currently in use for television, mobile phone and laptop applications. These displays have the advantage that they need very little power for switching. However, one limitation is that the need for backlighting increases the energy consumption, since light is lost on going through the polarisers and colour filters. The battery lifetime of laptop computers is frequently limited by energy usage by LCD backlights. More energy efficient

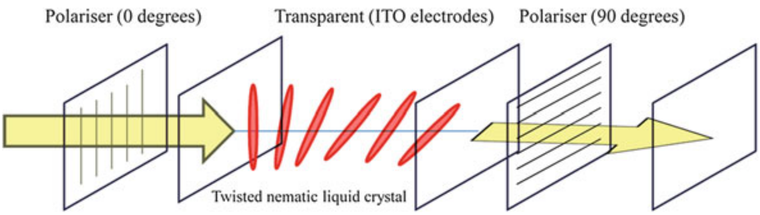


Fig. 4.3 Schematic diagram of one pixel of a twisted nematic liquid crystal display. Polarised light is twisted on passing through the twisted nematic liquid crystal. The orientation of this is changed by applying an electric field. Figure adapted from Ref. [166]

lighting systems, particularly involving light emitting diodes, are under development and are helping overcome this problem [25].

4.3.3.3 Electroluminescence: LEDs, OLEDs and PLEDs

LEDs. Electroluminescence is the emission of light from materials upon application of an electric field [24]. Although electroluminescence from carborundum (a form of amorphous silicon carbide) was first reported over a century ago [26], the development for practical applications in lighting and displays started in the early 1960s with the first report of a red light-emitting diode involving a GaAsP semiconductor [27]. The luminous efficacy of this early inorganic semiconductor LED was only 0.15 lm/W. The initial use focused on red indicator lights and low definition displays on calculators and watches. Since then the area has shown enormous developments in terms of luminous efficacy, available spectral output, intensity, cost and stability [25, 26], and high power LEDs, typically involving elements from Groups III (3) and V (15) of the Periodic Table, now occupy a major role as high-brightness visible light sources. The structure of a typical inorganic semiconductor LED is shown in Fig. 4.4a. Apart from their efficacy, which approaches that of fluorescent lamps, inorganic semiconductor LEDs have very fast switching times (ns), which makes them excellent candidates for technological applications in areas such as traffic signals and red car stop lights [25], and also pulsed sources for photochemical studies (see Chap. 14). A major advance for practical applications was the development of stable, intense blue LEDs based on wide band-gap nitride semiconductors, such as InGaN/AlGaN [28]. As well as expanding the spectral range of LEDs, which now extend into the UV, it has led to the development of high intensity white LEDs, with applications ranging from car headlights to solid state lighting for both domestic and industrial use [25, 26, 29, 30]. Various methods can be used to produce white semiconductor LEDs [25]. One involves combining red, green and blue LEDs. Although this gives high efficiency, and is used in backlighting for liquid crystal displays, the problem is matching the colours, particularly as they will age at different rates. Alternatives are to use a UV emitter to excite red, green and blue phosphors in a similar fashion to their excitation in fluorescent lamps, or to use a blue LED to excite a yellow phosphor, such as YAG:Ce, mixing the blue with the yellow to give white light [25]. There is intense competition to develop good white LEDs using these ideas for solid state lighting [29, 30], and they are likely to shortly become one of the main sources of lighting. One problem which limits their unit cost is that it is only possible to prepare efficient inorganic semiconductor LEDs with a relatively small surface area. Lamps will typically require a number of these LEDs. As described in the next section, this problem can be overcome by replacing the inorganic semiconductors with organic ones.

OLEDs and PLEDs. Electroluminescence in aromatic molecules (**1.1–1.7**), such as single crystals of anthracene (**1.1**), has been known since the 1960s [21, 31]. However, very high voltages were needed to generate light emission. In 1987, Tang and Van Slyke at Eastman Kodak showed that it was possible to obtain efficient green light electroluminescence from an *organic light-emitting diode* (OLED) containing a thin, vacuum deposited film of tris(8-hydroxyquinoline)aluminium(III), Alq_3 (**6.1**) [51, 32]. The device had the metal complex sandwiched between an optically transparent ITO anode and a Mg:Ag cathode (Fig. 4.4b). The basic mechanism of electroluminescence in organic compounds [31] involves electron injection into the lowest unoccupied molecular orbital (LUMO) at the cathode and positive charge (*hole*) injection at the anode (Fig. 4.4c) to produce the

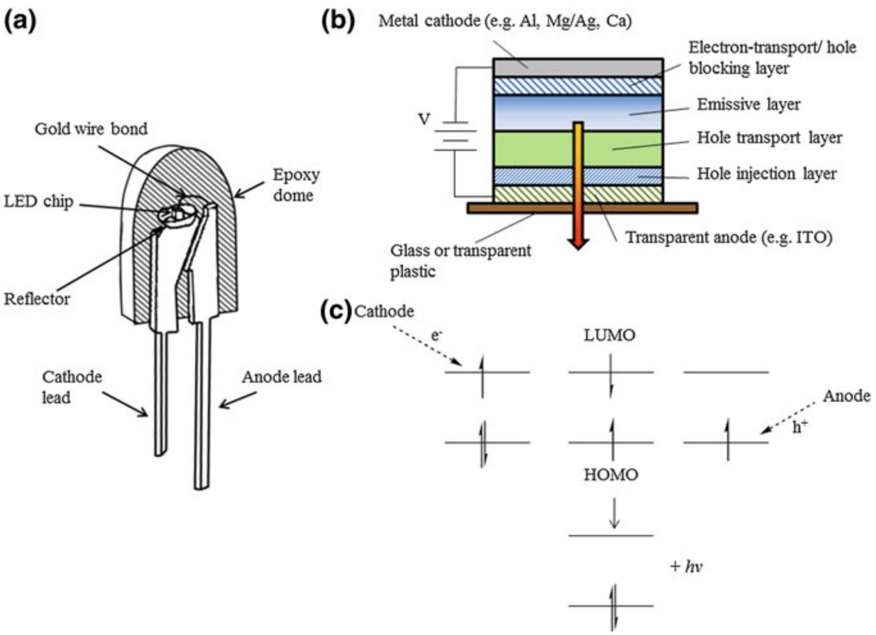


Fig. 4.4 **a** Structure of an inorganic semiconductor LED; **b** structure of an OLED; **c** charge injection and excited state formation in an OLED. Figure adapted from Ref. [167]

excited singlet state of Alq_3, which then fluoresces. As expected from this mechanism the electroluminescence spectrum is very similar to the photoluminescence. Luminous efficacy of the initial device was 1.5 lm/W, but subsequent developments, in particular, using charge injection or blocking layers at the electrodes [23], led to rapid increases in efficiency of OLEDs, which are now major materials in the display area. One advantage for certain applications is that they can be prepared on flexible supports [31]. About 3 years after the first report of an OLED, Friend and coworkers at Cambridge showed that it is possible to use conjugated polymers (CPs) such as poly(*p*-phenylenevinylene) (**3.2**) as the light-emitting layer to give a *polymer light emitting diode* (PLED) [14, 33, 34]. This has the advantage in device preparation that these can be deposited from solution by using standard printing techniques, such as ink-jet printing, which makes them particularly suitable for preparation of large area displays. It is also feasible to perform large scale commercial production of displays through reel-to-reel printing methodologies. Structures of some commonly used conjugated polymers are shown in **3.1–3.9**. A more detailed description of conjugated polymers for electroluminescent applications is given elsewhere [35].

One limitation of electroluminescence in organic materials is that charge injection produces both singlet and triplet excited states. Statistically these will be produced in the ratio 1:3. Since only the singlet state is normally luminescent, this reduces the maximum efficiency possible from these devices to 25 %, although there are suggestions that for PLEDs it may be possible to have higher singlet:triplet ratios. Forrest and co-workers showed that it is possible to overcome this problem, and obtain increased luminescence efficiency, using room-temperature metal organic phosphorescent materials [45, 36]. The initial room temperature phosphor was a platinum porphyrin (**5.4**). Since then a wide range of other complexes [37, 38], in particular phenylpyridine complexes of iridium(III), have been developed (**6.6–6.8**). Both OLEDs and PLEDs are now on the market in high definition displays. The next step will be the use of both small molecule organics and conjugated polymers in white organic light emitting diodes (WOLEDS) for artificial lighting [37, 39]. These have the advantages of broad spectral output, giving good colour rendering indices, and good CIE coordinates (See Chap. 14). Key practical problems at the moment include light out-coupling efficiency, practical operating voltages and long-term operational stability. However, devices are now available with lifetimes greater than that of typical incandescent sources ($\approx$1000 h), and the attractive design possibilities available with WOLEDS suggests that they will shortly make an important contribution to the technologies available for artificial lighting.

4.3.4 Radioluminescence

Radioluminescence is produced by the bombardment of a material with ionising radiation such as beta particles. One application is in tritium light sources, in which gaseous tritium is encased in a glass tube lined with a phosphor, e.g. zinc sulfide (**9.3**). Since no electrical excitation source is required, tritium light sources are self-powered, and find application in emergency exit lighting and wristwatch illumination. The colour of the emitted luminescence depends on the phosphor. Radioluminescence is also used in scintillation counters to measure radiation levels. The scintillator consists of either an organic crystal, e.g. anthracene (**1.1**), or a mixture of lumophores (e.g. *p*-terphenyl, 2,5-diphenyloxazole) dispersed in an organic solvent or plastic film, that luminesces when struck by ionising radiation. A photomultiplier tube is used to quantify the emitted photons. Depending on the lumophore used, the emission may either be fluorescence, phosphorescence or delayed fluorescence. Scintillators are used in homeland security radiation detectors, medical diagnostics and high energy particle physics experiments.

4.3.5 Chemiluminescence

Chemiluminescence is the emission of light as the result of a chemical reaction. The classic example is luminol oxidation. When a basic solution of luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) is mixed with hydrogen peroxide in the presence of a suitable catalyst (e.g. Cu^{2+} or ferricyanide), it becomes oxidised, forming an unstable peroxide radical in its excited state. The excited state radical relaxes radiatively emitting a blue glow. *Luminol* is used by forensic crime scene examiners to detect the presence of blood traces with a sensitivity at the parts per million (ppm) level, since the iron present in haemoglobin also catalyses this reaction. However, perhaps the most familiar application of chemiluminescence is in glow sticks. In this case, a chemical reaction is used to sensitise the emission from a lumophore. The glow stick contains a solution of a suitable fluorescent dye and diphenyl oxalate and a glass ampule containing hydrogen peroxide. When the glow stick is 'snapped', the glass ampule is broken, releasing the hydrogen peroxide which reacts with diphenyl oxalate forming a peroxyacid ester intermediate. This unstable intermediate decomposes spontaneously to carbon dioxide, releasing its excess energy and exciting the dye, which then relaxes by emitting a photon. The colour of the glow stick depends on the dye used.

A number of biological species, including fire flies, glow worms and marine organisms, emit light. This is termed *bioluminescence* and involves chemiluminescent reactions within the organism. Bioluminescence is a useful tool in genetic engineering and bioluminescence imaging can be used to study biological process *in vivo*.

4.3.6 Photoluminescent Materials: Fluorescent and Phosphorescent Emitters

4.3.6.1 Fluorescent Dyes and Pigments

Optical brighteners. These are used as additives in papers, plastics, fabrics, and fabric detergents, to convert the small fraction of sunlight which lies in the near UV into visible (usually blue) light. The photochemical requirements are: (i) efficient near UV absorption with no absorption tailing out into the visible, otherwise a yellow coloration will be produced; (ii) a high emission quantum yield in the blue spectral region; and (iii) high photochemical stability. Chemically, the compounds must adhere to the required substrate, and so optical brighteners with different chemical substituents may be required for cotton and nylon/silk fabrics. They must also be chemically and thermally stable. Triazole-stilbene derivatives are some of the most common optical brighteners (**2.1–2.3**). However, these tend to fade on long-term exposure to UV light, and when long-term stability is important non-stilbene compounds are favoured. Many optical brighteners are available from fine chemical suppliers, but relatively few are in the standard research chemical catalogues.

Fluorescent probes. Fluorescence probes are materials which indicate, by fluorescence, the presence of some specific chemical species or environment. There are two types: passive and active. Passive probes indicate the presence of the material of interest simply by physically or chemically binding to it. They thus indicate the presence of an analyte substrate by their own fluorescence (although this may also be altered by the presence of the analyte), the intensity of which can be used to determine the presence of the analyte either qualitatively or in some cases quantitatively. A typical use of such probes is in fluorescence microscopy, and there are a wide range of commercially available probes for this purpose (e.g. **4.3**). Active probes undergo a photochemical change in the presence of the chemical or environmental feature to which they are sensitive. This results in a change in some emission property such as wavelength, intensity, polarisation, or lifetime (e.g. **1.4**, **4.8**). Optical probes are discussed in detail in Chap. 12.

Laser dyes. The role of a laser dye is to absorb the pump radiation efficiently, and convert this absorbed energy into an excited-state which can itself act as the upper state in a laser transition (see Chap. 14). Photo- and chemical stability are important, but the key photochemical features are: (i) absorption at the excitation wavelength; (ii) a lifetime sufficiently long to allow a population inversion to build, (although the lifetime required may be quite short, depending upon the duration of the pump pulse); and (iii) a low absorption at the lasing wavelength. In assessing and controlling the latter it is the absorption profile of the solution during the population inversion which is relevant, so it is the transient absorption as much as the ground state absorption which is important. Absorption due to long lived triplet states is a particular problem and so a very low triplet quantum yield is desirable. Triplet quenchers are sometimes used to reduce the lifetime and hence *quasi*-steady-state concentration of triplets during the population inversion. There are now many laser dyes available which cover the full spectral range from the IR to the UV, and the best sources of up to date information are manufacturer's catalogues. However there are a few dye classes which are particularly useful as laser dyes, where the basic chemical skeleton is retained but changes in substituent are used to shift absorption and emission wavelengths, e.g. basic structures of **2.1**, **4.1, 4.2, 4.6**.

Emissive polymers. One of the major current areas of research is on emissive conjugated polymers (CPs) (**3.1–3.9**) due to their exceptional optical, electronic and mechanical properties [40]. Ionic conjugated polyelectrolytes (CPEs) tend to be highly sensitive to changes in their physical and chemical environment and, hence, one of their major potential uses is in biological and chemical sensors [41]. They have the advantage of high sensitivity with short luminescent lifetimes and the possibility of *amplified* fluorescence energy transfer or quenching processes (see Chap. 12) [42]. Recent research on the application of CPEs in biological and chemical sensors has led to a greater structural diversity and new synthetic protocols for their preparation [43]. Neutral CPs are also important technological materials, with applications in optoelectronic devices, such as PLEDs [34] and solar cells [44]. Part of the interest stems from the possibility of implementing solution-based deposition methods as part of the device fabrication process. Incorporation of ionic side groups increases solubility in polar organic solvents and water, which may allow more environmentally friendly manufacturing processes. Current interest in solar cells based on CPs stems from the promise of low cost fabrication. Research into cationic conjugated polymers (CCPs) has recently been mainly focussed on sequence specific DNA assays, designed by utilising the electrostatic interactions between cationic conjugated polymers and negatively charged DNA. These assays commonly exploit the ability of CCPs for efficient excitation energy transfer using, for example, protein nucleic acids (PNA) and Förster resonance energy transfer (FRET) to luminescent acceptors, such as fluorescein.

4.3.6.2 Phosphorescent Dyes and Materials

Phosphorescent molecular species in solution or matrices. Many organic molecules and dyes are phosphorescent in rigid low temperature glasses, where processes which might deactivate long lived triplet states are inhibited. Phosphorescent yields and lifetimes of many organic molecules, (and some inorganic complexes), are given in [45], quantum yields can be very high and triplet lifetimes can easily be up to a few tens of seconds at 77 K (the determination of these parameters is described in Chap. 15). However few organic molecules are phosphorescent at room temperature. Those commonly available organic compounds that, such as bromonaphthalene, usually carry heavy atom substituents, but even so they are usually only very weakly phosphorescent at room temperature. One particular group of organics which are strongly phosphorescent at room temperature are the thiocarbonyls (**11.21)**. Although thiocarbonyls show an interesting, rich, and unusual, photochemistry they are relatively photochemically and chemically unstable, which limits their uses.

A number of inorganic complexes show room temperature (and low temperature) phosphorescence, with two groups widely used as phosphorescent materials namely: Pt and Pd porphyrins (**5.4**), and Au (either in the monovalent or trivalent oxidation states), Ru(II), Rh(III) and Ir(III) complexes in which the metal is usually complexed by nitrogen, sulphur or heterocyclic rings (**6.2–6.8**). Further examples may be found in Ref. [38]. In these complexes the presence of the heavy transition metal gives those orbitals with some metal character spin–orbit coupling, which enhances both radiative and non-radiative singlet–triplet interconversion rates. The most important effect is a relative increase in the rate of the T_1 to S_0 radiative process; thus, while triplet quantum yields are much higher than those in organic molecules, emission lifetimes are much shorter, typically $\sim$1 μs–1 ms.

Delayed fluorescence. It is possible to generate relatively long lived fluorescence emission if there is a mechanism for repopulation of the singlet from the triplet. This is termed *delayed fluorescence*, and there are two common mechanisms.

(1) Thermal repopulation, where the triplet level is close enough to the singlet level that the singlet state can be thermally populated from the triplet. Sometimes called *E-type* delayed fluorescence, after the compound *eosin* (**4.4**) which exhibits this behaviour. The lifetime of E-type delayed fluorescence is equal to the triplet lifetime. Other materials which exhibit E-type delayed fluorescence are palladium porphyrins (**5.4**) and thiocarbonyls (**11.21**).
(2) *Triplet–triplet annihilation* in which two triplet states combine to give an excited singlet which generates fluorescence and a ground state singlet, called *P-type* delayed fluorescence after the molecule *pyrene* (**1.4**) which exhibits this behaviour. The lifetime of P-type delayed fluorescence is equal to one half that of the corresponding triplet.

Although named after the archetypical molecular examples, both types of delayed fluorescence are reasonably common. Delayed fluorescence is discussed in more detail in Chap. 1.

4.4 Sensitisers, Donors, Acceptors, Quenchers and Traps

Sensitisers are absorbing materials which can be used in photochemical processes in very specific ways; to make specific reactions occur, or force a specific reaction route by the generation of specific singlets, triplets, radicals or redox active chemicals *via* energy transfer, electron transfer, or radical reactions. When used as *donors* (D) in energy transfer reactions they can be used to generate singlets or triplets of *acceptor* (A) molecules which might not available by direct excitation, or to generate acceptor triplet states without the need for direct excitation of the acceptor. Sensitisers can also be used to probe molecular arrangements and distributions since, if a sensitiser is expected to generate a specific product by reaction with an acceptor, the presence or absence of sensitisation, as well as the efficiency of the process, can be used as a measure of either the proximity of the sensitiser and acceptor molecules, or the viscosity of the medium (see Chap. 12).

The term *acceptor* is used to describe: (1) a compound, or atom, which accepts energy from a higher energy donor in excited-state energy transfer, and which becomes, as a consequence, excited; or (2) a compound which reacts with an excited-state (or less frequently some other chemical species, notably singlet oxygen), to give a recognisable specific product. In both of these processes the acceptor undergoes a recognisable change, indicating its role in the reaction.

The term *quencher* is broader, and includes any material which acts to reduce emission, or the yield of a photochemical reaction, by interaction with an excited-state. This interaction may be physical, or chemical, and either reversible or irreversible, and nothing about the nature of the quenching process or any change in the state of the quencher is necessarily inferred.

The term *trap* has two uses. (1) In solid state chemistry a trap is a site, a part of the structure, into which energy, or an electron (or hole) can migrate, be trapped, and lost to the system. (2) The term trap is also used for chemical species which give specific, and usually measurable, reactions with species of interest, notably free radicals, *i.e.* free radical traps (**8.1–8.3**). Here, trap sense (2) is very similar to acceptor sense (2), but there is a subtle difference because of the different type of mobility free radicals and chemical species exhibit. Once formed, chemical species migrate by molecular diffusion. Free radicals also migrate by molecular diffusion but they also undergo transport and population growth through a series of propagation and branching reactions, and so the free radical itself is mobile, even though the molecular carrier itself is exchanged, in a similar way to the mobility of 'energy' in energy transfer migration in solids.

4.4.1 Excited State Sensitisers and Acceptors

For organic molecules, and most inorganic complexes, molecular singlet and triplet states are most important, and therefore singlet and triplet sensitisation are most commonly encountered. For some other groups of materials, notably those involving atomic transitions, such as gas phase atoms or lanthanide ions in solids or solution, sensitisation involving states of other spin multiplicities is important. In *singlet sensitisation* the required reaction is the transfer of singlet energy from the sensitiser, which is the donor, to another molecule, the acceptor. Any excited singlet state higher in energy than the acceptor singlet can thermodynamically act as a sensitiser, but as discussed in Chap. 1, other conditions must be right for the energy transfer process. Energy transfer requires energy matching between donor and acceptor states. In practise, for molecules of moderate size the high density of states (DOS) means that almost any sensitiser of higher energy than the acceptor will act as a sensitiser by collisional or Dexter energy transfer, provided the donor and acceptor are, or can become, close enough within the donor lifetime. For Dexter transfer involving states localised on atoms or ions, which do not have a high DOS, energy matching becomes a more stringent condition. For atomic states in a solid state lattice, energy matching can sometimes be promoted by coupling with the lattice vibrations (*phonons*). FRET involves coupling of molecular dipoles, and can occur over a much longer range because orbital overlap is not required. However, overlap of donor emission with an acceptor absorption band for an allowed transition is necessary for efficient energy transfer.

In general, the most effective singlet sensitisers will be those with long lifetimes, and as a consequence, high fluorescence quantum yields. The short lifetime of molecular singlet states means that for efficient Dexter singlet–singlet energy transfer the acceptor must be adjacent to the donor, or, if contact is diffusion controlled, the acceptor must be present at high concentration in a low viscosity medium.

Molecular triplet energy transfer is usually *via* Dexter energy transfer. However, because of the long lifetime of some triplets, FRET is also possible from a triplet donor to a singlet acceptor, where the long donor lifetime compensates for what must be, because the radiative transitions involves are spin forbidden, a slow energy transfer rate constant.

Generally, if the energy difference between D and A triplet states is greater than a few kJ mol^{-1}, energy transfer in solution will occur at every encounter between D and A and therefore the rate constant is close to the diffusion controlled value. However, if the molecular structure of one or both D and A is significantly different in the triplet state as compared to the ground state then the reaction requires major molecular structural reorganisation, and this can slow the energy transfer rate considerably. Balzani *et al.* have analysed the effect of structural rearrangement in a similar way to that used in the Marcus theory of electron transfer reactions [46].

For the determination of the triplet energy of an acceptor, a series of sensitisers with differing triplet energies and known transient difference spectrum are required; the experimental approach is described in Chap. 15 which also gives triplet state properties for selected compounds (Table 15.2). The porphyrins (**5.1, 5.2**), phthalocyanines (**5.3, 5.5**) and naphthalocyanines (**5**.7) make a useful series of relatively low energy triplet sensitisers because of their structural similarity (**5**). Unfortunately only a few of these compounds are phosphorescent and therefore flash photolysis is required for direct kinetic studies of most triplet sensitisation.

Triplet sensitisers can generally be placed in one of three categories:

1. High to moderate energy polyaromatic and polyaromatic derivatives (such as **1.1–1.7**), or other organics, which are not phosphorescent at room temperature, but are often phosphorescent at 77 K. Most have triplet lifetimes of ~ms duration and well-characterised triplet transient difference spectra. Many are commercially available.
2. The relatively low energy porphyrins (**5.1, 5.2**), phthalocyanines (**5.3, 5.5**), naphthalocyanines, and their metallated derivatives, some of which are phosphorescent at room temperature, but many of which are not phosphorescent at either room temperature or 77 K. Lifetimes are typically 100 μs to a few ms,

and most have well-characterised triplet transient difference spectra. Many are commercially available.

3. Moderate to low energy Au, Pt, Pd, Ir and Ru complexes which are phosphorescent at room temperatures with lifetimes typically 1–20 μs, some of which are commercially available (**6.2, 6.6–6.8**).

The use of triplet state acceptors has generally two roles. (1) Where the triplet state is to be removed and the transferred energy degraded as heat. Any passive absorber with lower triplet state energy than the donor will act in this way. Such a triplet state acceptor is also a photochemical *stabiliser*. (2) Where the triplet energy is to be trapped in a triplet state to be used for measurement or some specific function, e.g. energy transfer to an acceptor of known transient triplet absorption spectrum or emission. Here the acceptor triplet state photophysics and photochemistry must be known. Identification of energy transfer to such another known triplet state is often used as confirmatory evidence that a triplet state species is involved in the reaction under study.

Sensitisation is often used to generate electronic excited states in lanthanide (Ln) complexes and Ln-containing solid-state phosphors (e.g. **10.1–10.6**). Ln-materials emit over the entire visible spectrum: red (Eu^{3+}, Pr^{3+}, Sm^{3+}), green (Tb^{3+}, Er^{3+}) and blue (Tm^{3+}, Ce^{3+}). They are therefore interesting for a wide variety of applications including solid-state lighting, lasers, and optical communications and storage. The optical transitions of Ln^{3+} ions take place predominantly within the 4*f* manifold, where the electrons are largely shielded from external crystal field effects by the filled 5*s* and 5*p* levels. Consequently, Ln^{3+} ions give rise to much narrower, atomic-like line absorption and emission spectra compared to organic small molecules or polymers. The Ln^{3+} electronic configuration gives rise to ground and excited states with a variety of multiplicities other than singlets and triplets (e.g. quartet, quintet etc.); consequently some ions are fluorescent ($\Delta S = 0$), others are phosphorescent ($\Delta S \neq 0$), and some are both.

However, *f–f* transitions are formally electric dipole forbidden by the Laporte selection rule, (a change in orbital angular momentum of ±1 is required to accommodate the loss of photon spin upon absorption), although they are allowed by electric quadrupole, magnetic dipole and forced electric dipole mechanisms to some extent. Direct excitation of the Ln^{3+} ion is therefore not easily achieved, due to the low molar absorption coefficients associated with these transitions ($\varepsilon \sim 5$–$10\ mol^{-1}\ dm^3\ cm^{-1}$). In Ln-complexes, indirect excitation *via* a sensitising ligand or *antenna* is used to overcome this limitation [46]. The sensitising ligand absorbs light, initially forming its excited singlet state. The excitation energy is transferred to the ligand's triplet state *via* intersystem crossing (the efficiency of this process being improved due to enhanced spin–orbit coupling induced by the heavy atom effect of the Ln^{3+} centre). Population of the Ln^{3+} excited emissive state is subsequently achieved through intramolecular energy transfer from the ligand triplet state. This process therefore requires that the ligand triplet state is higher in energy than the Ln^{3+} excited state being sensitised.

4.4.2 Singlet Oxygen Sensitisers, Quenchers and Acceptors

Most singlet oxygen sensitisers are triplet states. Singlet oxygen sensitisation is very similar to triplet sensitisation, except the spin state of the acceptor, ground-state oxygen, is a triplet, and the products are two singlets, *i.e.* singlet oxygen and the singlet ground state sensitiser [47, 48]. The energetic and spin conservation rules are the same as triplet energy transfer, but the spin statistics are different because the two reacting species are triplets. The spin angular momentum quantum number along any reference axis of each triplet state (*i.e.* the triplet sensitiser and ground state oxygen) can take one of three values; −1, 0, +1; thus when any two triplets combine in the encounter pair there are 3×3 possible combinations. $1/9^{th}$ of the encounters will give an overall singlet encounter pair, $3/9^{th}$ a triplet, and $5/9^{th}$ a quintet encounter pair. Of these three: only the singlet encounter pair can lead to two singlet state products; the triplet pair can, energetics allowing, give two electron transfer radical doublet states; while in the quintet case there are no spin-allowed energy transfer or electron transfer products possible, so that, in the absence of spin relaxation, the quintet encounter pair can only separate back into reactants. Thus singlet oxygen generation can be expected to occur with a maximum rate of around $1/9^{th}$ the encounter rate, and this is usually borne out experimentally.

Most species which generate a triplet state of significant lifetime and energy higher than that of singlet oxygen (94.3 kJ mol^{-1}, 0.98 eV, corresponding to a transition in the NIR at $\sim$1270 nm—see Fig. 15.3) have the potential to be singlet oxygen sensitisers, since oxygen quenching of such triplet states generally goes predominantly *via* energy transfer (although electron transfer to give superoxide radical can be a significant, and interfering, reaction). For many such compounds the singlet oxygen yield in fluid air-equilibrated solution can be expected to be similar to the triplet yield. However the term *singlet oxygen sensitiser* is usually reserved for compounds which have: high triplet quantum yields; high oxygen quenching rate constants in which singlet oxygen predominates as the reaction product; reasonably high molar absorption coefficients and are thus efficient absorbers; low singlet oxygen quenching rates; and a well-characterised and quantified photochemistry. The measurement of the singlet oxygen yield is discussed in Chap. 15.

The role of a singlet oxygen quencher is usually just to remove singlet oxygen, often to inhibit singlet oxygen induced photodegradation. There are two main mechanisms by which this can be achieved.

(1) Energy transfer into a low energy triplet acceptor in which molecule the triplet energy is rapidly degraded to heat; typical examples are Ni complexes (**11.10**).
(2) Electron transfer into a molecule in the encounter complex followed by rapid reverse electron transfer before dissociation of the encounter complex. Typical examples of this type of quencher are hindered amines such as DABCO (**11.8**).

Quenching rate constants for triplet energy transfer quenchers are often faster than for electron transfer quenchers. However the requirement for a triplet state lower than singlet oxygen invariably implies singlet state energies in the visible region, and thus singlet oxygen triplet energy acceptors are coloured to varying degrees. Apart from anything else this means they will also act as competitive absorbers in almost any mechanistic study. Amine electron transfer quenchers are usually colourless, often with longest wavelength absorptions in the mid UV.

The role of a singlet oxygen acceptor is usually to show evidence of singlet oxygen in mechanistic studies. The development of detectors for the direct detection of singlet oxygen emission (Chaps. 14, 15) has alleviated the need for indirect measurements where the singlet oxygen yield is reasonably high, but singlet oxygen acceptors are still useful especially when the singlet oxygen yield is so low as to be undetectable directly. Three common approaches are used.

(1) Kinetic studies where the triplet state acceptor can be identified. A good example of this is shown by use of β-carotene (**11.6**). β-carotene itself has a very low quantum yield of triplet state formation by direct excitation, the triplet energy is lower than that of singlet oxygen and the triplet lifetime and transient absorption spectrum are known. Thus if the system under study allows the photochemical formation of singlet oxygen then this can be studied using ns laser flash photolysis by following the kinetics of energy transfer from singlet oxygen to β-carotene and formation of β-carotene triplet. β-carotene triplet will also be populated by energy transfer from any triplet state used in the initial formation of singlet oxygen but consideration of the kinetics shows that, because of the combination of rapid quenching of triplet state singlet oxygen sensitisers by oxygen in aerated solution and the relatively long lifetime of singlet oxygen, it is possible to separate out these two processes. Quenching of singlet oxygen by carotenoids is discussed in detail in Chap. 8.
(2) Where the rate of loss of acceptor can be followed, either spectroscopically, or by chromatographic analysis such as GC or HPLC (in which case the specific involvement of singlet oxygen can often be confirmed by product analysis). Spectroscopic detection requires an acceptor of known absorption or emission characteristics. If ns laser flash photolysis is available then the kinetics of decay of the acceptor absorption or emission can be followed, and kinetic analysis can be used to confirm a singlet oxygen process. Diphenylisobenzofuran (**11.9**) and rubrene (**1.7**) have been widely used as singlet oxygen acceptors in these types of experiments, with reaction with singlet oxygen followed by either loss of absorption or of fluorescence.
(3) Where the involvement of singlet oxygen can be identified by product analysis. Here the product from reaction between singlet oxygen and the acceptor gives rise to a stable molecular species which can be identified either spectroscopically or by chemical analysis such as GC or HPLC.

It is worth noting that the lifetime of singlet oxygen is highly dependent on solvent [49]. The lifetime is particularly short in solvents with OH bonds, which provide high frequency vibrations into which the electronic energy of singlet oxygen can be transferred, or in solvents, such as amines where electron transfer is possible, and it is particularly long in halogenated solvents which only have low frequency vibrations. Due to the effect of OH oscillations in providing a quenching mechanism, the lifetime is also highly dependent upon solvent deuteration. Thus a comparison of rates or yields in H_2O and D_2O, or normal and deuterated alcohols, is a useful tool in helping unravel or identify a singlet oxygen mechanism.

4.4.3 Redox Sensitisers

An excited-state is simultaneously both a better oxidant and better reductant than the ground-state molecule. The difference in redox potentials between ground and excited-state is given, to a reasonable approximation, by the excited-state energy in eV. Redox sensitisers create charge transfer from an excited state. This can be either unimolecularly across a molecule or semiconductor, or bimolecularly *via* a process in which the excited-state undergoes a charge transfer reaction with the solvent, a redox quencher, or a semiconductor. The generated charge transfer products can then be used in further reactions. Photo-redox reactions lie at the heart of most photochemical process for solar energy conversion and redox sensitisation of solution phase reactions and electron injection into semiconductors have been widely studied with this application in mind. Although there has been a recent burst of interest in compounds which will inject electrons into semiconductor conduction bands because of their potential use in the dye sensitised solar cells (**6.3–6.5, 11.19, 11.20**) described in Chap. 7, the process has been of technological importance since the discovery of spectral sensitisation of silver halides in the late eighteen hundreds and the subsequent use of cyanines (e.g. **4.7**) and other dyes as irreversible electron injection sensitisers in panchromatic photographic films (see Chap. 11). Photo-redox processes are also important in imaging science, semiconductor photocatalysis (see Chap. 6), and photo-redox based actinometers such as the ferrioxalate (see Chap. 14) and uranyl actinometers [45].

4.4.4 Radical Sensitisers, Quenchers and Traps

The products of redox sensitisation are usually radical ions. Neutral radicals can be generated unimolecularly by homolytic cleavage of an excited state molecule, or by bimolecular homolytic cleavage, the most common example of such being hydrogen abstraction from solvent. Energetically, electron transfer reactions become significantly less favourable as the polarity of the solvent is decreased, whereas the energetics of neutral radical reactions are relatively solvent independent. Photochemical radical initiation processes are important in gas, solution and solid-state radical reactions.

For aqueous phase studies, where, because of solvent polarity, radical ions are of most interest, the Ru(II)trisbipyridyl (**6.2**)/persulfate reaction pair [50] can be used. For organic solvents, benzophenone (**11.5)** in the presence of a hydrogen abstractable solvent is a widely studied/used radical photoinitiator. Radical initiators are very important in photopolymerisations, and there are many commercially available photoinitiators (**7.1–7.3**). Where the molar absorption coefficient of the photo-produced radical is known, then flash photolysis allows a determination of the yield of subsequent radicals.

The essential feature of a radical quencher or trap is the availability of a radical state of low energy which is therefore relatively stable to further reaction. There are a wide range of radical quenchers available commercially as stabilisers, particularly polymer stabilisers. Electron spin resonance (ESR) is the obvious method of radical characterisation but some radical traps can be identified spectrophotometrically. Radical sensitisers, quenchers and traps are discussed in further detail in Chap. 8.

4.5 Photochromism and Molecular Switches

4.5.1 Chromism and Photochromism

Chromism is the reversible change in colour of certain materials upon application of external stimuli such as heat (*thermochromism*), light (*photochromism*), electrical current (*electrochromism*) or solvent polarity (*solvatochromis*m) [24]. In this section we will concentrate on photochromism—light-induced colour changes. These have a variety of actual and potential applications, one of the most important of which is in photochromic ophthalmic lenses which darken in bright sunlight and become colourless in normal light. Photochromism involves a molecular system interconverting between two forms which have different absorption spectra. The process is reversible and the back reaction can either be induced by heat (designated *T-type*) or photochemically, using light of a different wavelength from the forward process, (*P-type*). The concept of photochromism is indicated schematically for a unimolecular process in Fig. 4.5, where light absorption by species A (normally absorbing in the UV) produces the longer wavelength absorbing species B through some photoinduced process; it is also possible to have bimolecular photochromic processes.

The first reports of photochromism in the scientific literature date back to the middle of the nineteenth century with the observation of bleaching of orange coloured solutions of tetracene in daylight and the regeneration of the coloured solution in the dark [51]. The reaction involves a photodimerisation [52]. The photochromic behavior of tetracene contrasts with that in Fig. 4.5, since the photoproducts absorb at shorter wavelengths than their precursor. This is termed *negative photochromism*. In addition, the forward reaction is a bimolecular process. A more common scenario is that the initial photochromic species absorbs in the UV and on photolysis produces a coloured photoproduct absorbing in the visible region of the spectrum (*positive photochro*mism), and the process involves interconversion of a single molecule between two chemically distinct forms.

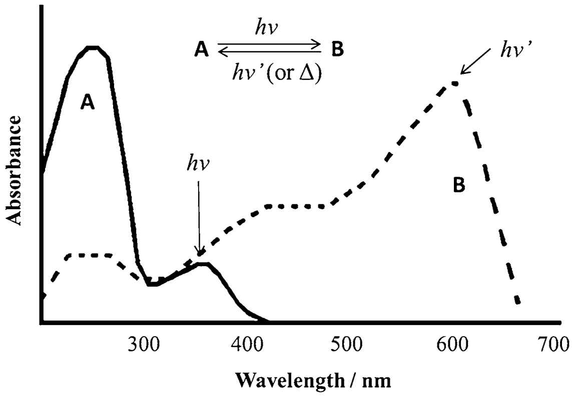


Fig. 4.5 Absorption spectra of a unimolecular two-state photochromic system. Figure adapted from Ref. [51]

The term photochromism is attributed to the distinguished Israeli scientist Yehuda Hirshberg [51, 53], who correctly identified the importance of chemical transformations in these systems. Some of the earlier literature used the term "phototropy" for the observed colour changes, suggesting that purely physical phenomena are involved [51]. However, it is now recognised that all important photochromic processes involve reversible chemical changes, and the term *phototropism* is reserved for the effect of light on the growth of plants, which may be directed either towards or away from the sun or other light sources [51]. Interest in photochromism in the early part of last century was rather limited [54], but was stimulated in the 1950s by the potential strategic importance of materials which could undergo reversible changes with light for various applications [55], including photochromic glasses which would darken rapidly following intense light pulses, such as those produced in nuclear explosions. These have been termed optical power-limiting substances [51]. Various reversible organic and inorganic photoprocesses were considered as possible systems for these applications, including formation of triplet excited states of aromatic molecules, isomerisations, electron and atom transfer. Subsequent developments concentrated on non-military uses, and the first serious practical application came with the development by Corning Glass in the U.S.A, of photochromic silicate glasses sensitised by silver halides, modulated by the presence of small amounts of copper(I) salts [55, 56]. The general reaction scheme can be summarised as:

$$Ag^+ + X^- + h\nu \rightleftarrows Ag^\bullet + Cl^\bullet \tag{4.4}$$

$$Ag^+ + Cu^+ + h\nu \rightleftarrows Ag^\bullet + Cu^{2+} \tag{4.5}$$

The silver halide system is similar to that involved in the silver-based photographic process (see Chap. 11), but irreversible formation of photoproducts is inhibited by the fact that the silver halides are present as nanometre sized particles dispersed in a non-conducting silicate matrix. This prevents the permanent photochemical reactions which take place in the photographic system to form the silver based latent images. Work on the silver halide glasses led to the development of the first viable photochromic lenses, which went on the market in the mid-1960s. The lenses have good optical properties, show excellent reversibility for their photochromic processes and reasonable darkening and bleaching times. However, the system involves silicate glass lenses, and in the following decade the ophthalmic market was moving towards plastic lenses [57]. While the silver halide system is excellent for silicate-based glasses, it is less suited for inclusion in the organic polymer systems used in plastic lenses. For this, organic photochromic systems involving thermal back reactions (T-type) are much more suitable [57, 58].

4.5.2 Organic Photochromic Systems

A variety of photochemical processes in organic molecules lead to photochromic changes, including pericyclic reactions, *cis–trans* (*E/Z*) isomerisations, intramolecular hydrogen transfer, photodissociation processes and electron transfer [51]. The area has been reviewed extensively [54, 59–62], and some typical examples of photochromic materials are given in Table 4.1 (**12.1–12.6**). The most important T-type ones for technical and industrial applications in areas such as ophthalmic lenses involve spiropyrans (**12.1**), spirooxazines (**12.2**) and naphthopyrans (chromenes, **12.3**). In all three cases, light absorption leads to production of a coloured (merocyanine) form, where extended conjugation is achieved through ring opening. The absorption spectra of both the colourless and coloured forms can be modified by appropriate substitution of the aromatic rings. This allows colour tuning to produce the best properties for optical usage. There are a number of factors which need to be controlled, including the transmission (absorption) spectra of the coloured form, the light response, speed of recovery of the colourless form, the number of cycles the system can undergo and the long term stability of the system [51]. While the spiropyrans were some of the first systems to be studied, the spiroxazines show much lower fatigue on extended use [58], and the first commercial plastic photochromic lenses, which were introduced in the 1980s, involved an indolinospironaphthoxazine incorporated in a polycarbonate matrix [57]. More recently, the naphthopyrans have become the commercially most important class of photochromic materials for this type of application [58]. However, they still have some failings in terms of long term applications and there is considerable interest in the development of new photochromic materials involving these cyclisation/ring opening processes.

The way that the photochromic material is incorporated into the lenses is of importance for the commercial application of these materials. This can be achieved by injection-moulding in a thermoplastic or precursor monomer or resin system, surface coating, diffusion into lens surfaces (imbibition) or formation of

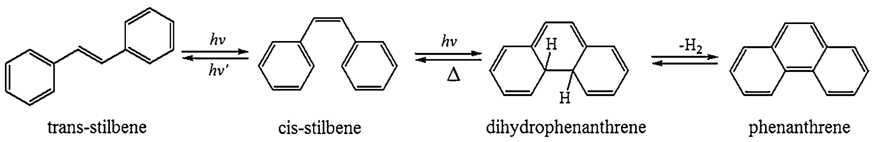


Fig. 4.6 *Cis–trans* isomerisation and cyclisation in stilbene

laminate structures, where a photochromic layer is placed between two halves of the lens structure [58].

Another important type of photochromic reaction involves *cis–trans* photoisomerisation [63]. With azobenzenes (**12.4**), the *trans* (*anti*) form has a strong absorption, attributed to a π,π^* transition in the near UV region and a weaker n,π^* band in the blue region of the spectrum. Upon photoexcitation with light of appropriate wavelengths ($\sim$340 nm for the unsubstituted derivative) the π,π^* band shifts to the blue and the longer wavelength n,π^* band increases in intensity due to formation of the *cis*(*syn*) form. Although photochromism will lead to a photostationary state, up to 90 % of the *cis* form can be produced. The reverse *cis–trans* reaction can take place either thermally or by irradiation with longer wavelength light [54, 63, 64]. This possibility of interconverting between two structures using light of different wavelengths is termed *photoswitching*. The *trans* isomer of azobenzene is planar but, due to steric hinderance, the *cis* form is bent. In addition to the colour change, this leads to changes in dipole moment, polarisability and, in the solid state, packing in crystal structures. This will also lead to modifications in the properties of the surrounding medium, which can enhance the applications of photochromic materials. For example, if azobenzenes (or other photochromic materials) are incorporated into a polymeric matrix their photochromic reaction can affect properties, such as shape, refractive index, phase, solubility and surface wettability [65]. This is termed a *photoresponsive system*. These have a number of important applications which are discussed later.

Reversible *trans–cis* isomerisations with alkenes (Fig. 4.6) are also relevant for photochromism and photoswitching. With the simple systems, normally only photoinduced processes are involved because of the high energy barrier between the two forms. These alkene-based photoswitches can be useful in molecular devices. With polyenes, both thermal and photochemical processes are possible, and these can be used as P-type and T-type photochromics. A rare, naturally occurring photochromic system involving *cis–trans* isomerisation process occurs with *bacteriorhodopsin*, which is found in halobacteria [66]. Its structure and photochemical processes are very similar to the visual pigment rhodopsin present in the retina of the eye. In both cases, the structure involves the polyolefin, retinal, linked to a protein through a Schiff's base (see Fig. 1.1). With bacteriorhodopsin, photochromism involves interconversion between the all-*trans* form absorbing at 570 nm and the 13-*cis* isomer absorbing around 410 nm. The system can be recycled many times without any signs of fatigue and shows excellent long-term stability, which makes it a good candidate for use in optical memories and data processing.

With the *cis* isomer of diarylethenes, a second photochromic process can occur: photocyclisation [61, 67]. In the simplest case, *cis*-stilbene, the initially formed dihydrophenanthrene is rapidly oxidised to phenanthrene in an irreversible process (Fig. 4.6), making it unsuitable for photochromic applications. However, this can be overcome by replacing the phenyl rings by heterocyclic groups, such as thiophene (**12.5**). These diarylethenes are important P-type photochromic systems showing good thermal stability, resistance to fatigue, and are important as photo switches. Relatively large spectral shifts are seen between the shorter wavelength absorbing open structure and the long wavelength closed form. The spectral properties can be tuned by introducing substituents into the heterocyclic rings. The structural changes on ring closure affect properties such as fluorescence, refractive index, polarisability and electrical conductivity. A related P-type photochromic system involves the fulgides and fulgimides (**12.6**). Again, the photochromism involves a colourless open form, sometimes referred to as the *E*-form, and the product of photocyclisation, termed the *C*-form [68]. There is an additional photochemical pathway leading to the colourless *Z*-form. This competing process decreases the efficiency of the photochromic system, but can be minimised by appropriate design of the molecules.

While many other organic photochromic systems exist, the above are the most important types currently used for practical applications.

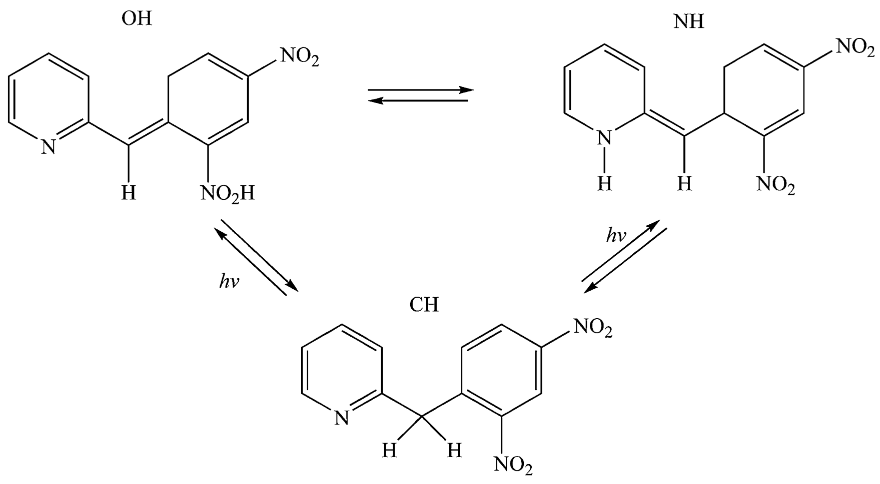


Fig. 4.7 Three photochromic forms produced from 2-(2′,4′-dinitrobenzyl)pyridine (DNBP). Figure adapted from Ref. [69]

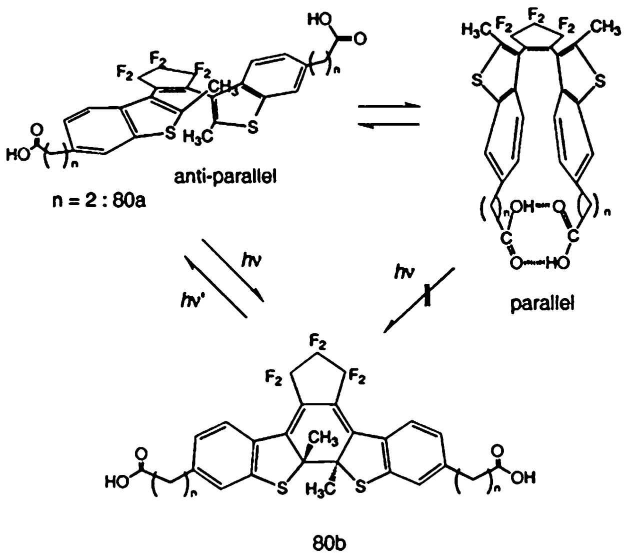


Fig. 4.8 Solvent gated photochromism in a diarylethylene. Reprinted with permission from Irie et al. [71]. Copyright (1992) American Chemical Society

4.5.3 Three State and Gated Photochromics and Two-Photon Systems

The previous section describes photochromic systems in which interconversion between two forms can be induced by absorption of light. However, more complex scenarios also exist and some have particular practical importance. With 2-(2′,4′-dinitrobenzyl)pyridine (DNBP), photochromism involves phototautomerisation with hydrogen transfer [69, 70]. However, this can either be transferred to the pyridine nitrogen giving the blue NH form or to the oxygen of the nitro group to give the yellow OH form (Fig. 4.7). These can revert thermally or photochemically to the most stable colourless CH form.

For certain applications of photochromics, it is useful to be able to convert one or more of the forms reversibly into a stable non-photochromic structure. These systems are termed *gated photochromics* [51] and are of particular importance for optical data storage. Figure 4.8 shows an example of a gated photochromic involving diarylethenes [71]. According to the *Woodward-Hoffmann rules*, the photocyclisation is a conrotatory process and is only possible through the anti-parallel form. In hydrophobic solvents, such as cyclohexane, the parallel open form is stabilised by hydrogen bonding and cannot photocyclise. However, upon addition of a hydroxylic solvent, such as ethanol, or heating, the hydrogen bonds are broken leading to formation of the antiparallel open form which can undergo the photochromic reaction.

Chromism may also be induced by two separate external stimuli. This is termed *dual-mode photochromism* [51]. A particularly versatile example involves the flavylium system, the basic structure of anthocyanin dyes. With these, because of the complex acid–base behavior, interconversion between the various coloured species formed can be controlled by the dual application of light and pH changes [72]. It is possible in this way to have a pH gated photochromic system.

With photochromic systems, as with other areas of photochemistry, we are normally using monophotonic processes in which a molecule absorbs one photon. However, it is possible to have two-photon or multi-photon photochromic systems. These have certain attractive properties. Two possibilities exist [51]. In the first (sequential) case, a molecule absorbs one photon to form its excited state. This (or a subsequent species) may then absorb a second photon to give the product:

$$A + h\nu \rightarrow A^* \tag{4.6}$$

$$A^* + h\nu \rightarrow B \tag{4.7}$$

An example of this sequential two-photon photochromism has been reported with a naphthopyran derivative [73]. This has the advantage, when it is used for optical data storage, of non-destructive readout capacity.

In the second case, a molecule simultaneously absorbs two photons *via* a virtual level to produce the excited state, which is subsequently transformed into the photo-product:

$$A + 2h\nu \rightarrow A^* \rightarrow B \tag{4.8}$$

Since it is only necessary that the sum of the energies of the two photons is sufficient to produce the excited state, the exciting light can be of longer wavelength than the absorption band of A. This means that NIR light can be used, minimising photochemical degradation. In addition, the probability of simultaneous interaction of two photons and one molecule is very low so an intense light source is necessary, typically a pulsed laser, and the effect can be limited optically to a small region of the sample. If the photochromic system is incorporated into a polymeric host this opens the possibility of achieving 3D data storage through focusing the laser at different points in the sample [74].

4.5.4 Some Applications of Photochromic Materials

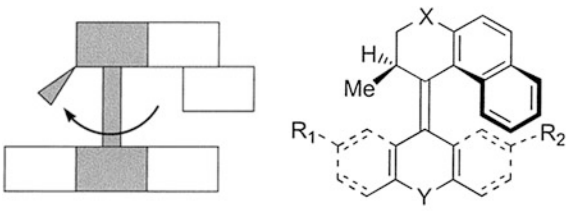
By far the biggest application of photochromic systems is in ophthalmic lenses. These now normally involve T-type spiroxazine or napthopyran photochromics in thermoplastic polymers. The lens colours under the UV component of sunlight, but not significantly under artificial light, which lacks this part of the spectrum. As the optimal systems involve neutral colours grey or brown, frequently mixtures of photochromics are used [75]. Design of commercial formulations is complicated by the need for the various components to fade and undergo fatigue at the same rate, and there is currently considerable interest in the development of dyes which are intrinsically neutral in colour.

T-type photochromic thermoplastic systems are also finding non-opthalmic specialty applications in areas such as colouring drinks bottles, toys (including dolls which develop suntans) and crash helmet visors for motorcyclists. Photochromic systems are also used in formulations for surface coatings, and have been used for security printing, such as in passports. In addition, they show potential for personal care use, such as in cosmetics and hair dyes. A good description of these applications is given in Ref. [58].

Interesting effects can be produced in textiles by using photochromic colorants. Because of stability problems in processing, these are often either incorporated into a polymer matrix inside textile fibres [76] or microcapsules containing the photochromic material are coated onto textile surfaces [77]. While products, such as T-shirts which change colour in sunlight, are available on the market, at present the development of this area is limited due to difficulties in obtaining cost-efficient, durable products [58].

Photochromic transformations in matrices such as polymers can lead to changes in the bulk properties of the matrix. Such photoresponsive systems can have various applications. We will indicate two of these. If a photochromic system, such as an azobenzene, is incorporated into a liquid crystalline polymer system, photoconversion can lead to changes in the ordering and orientation of the liquid crystalline mesophase [65]. This leads to changes in various physical properties, including the optical anisotropy, which can be used in display and other applications. A second case involves photo-responsive biomaterials [65]. Incorporation of photochromic molecules can be used in areas such as photo-regulation of biological properties, controlled drug release and photo-regulated membrane permeability.

The area of information technology (IT) has been based upon the electronic properties of semiconductors. Gordon Moore, one of the founders of Intel, published an article in 1965 which indicated that the capacity of computer processing will double about every 18 months [78]. This empirical law is still valid, but is reaching its limits, in particular because as electronic memories become smaller, they start to have problems of heating and cross-talk, and there is a need for development of new systems. Three characteristics are required for a memory, the ability to write, read and erase information. Optical (photonic) systems using photochromic materials can achieve these requirements while overcoming many of the problems of limitations of purely electronic systems, since the ultimate data density achievable is limited by the area which can be resolved, which depends upon light wavelength, as discussed in Chap. 1. Photonic systems also have the advantage that they can be multiplexed by using more than one property, e.g. wavelength, polarisation and phase, while memories can be further enhanced using 3D data storage through two-photon absorption [74, 79]. A further possibility is to obtain sub-diffraction limited systems through near-field optics [80]. Until recently, erasable memory systems have tended to use inorganic materials using magneto-optic effects or phase change for data recording. While these may have organic pigments to enhance spectral



12: X = S, Y = S, R_1 = OMe, R_2 = H
13: X = S, Y = O, R_1 = H, R_2 = H

Fig. 4.9 Schematic view and structure of a molecular motor. Reprinted with permission from Feringa [86]. Copyright (2001) American Chemical Society

properties [24], the IT industry had been wary of purely photonic organic systems because of doubts on long-term stability. However, a number of good, stable, low-fatigue photochromic systems have now been developed and show considerable promise for purely optical data storage. The desirable properties of photochromic systems for these applications are good thermal stabilities of the two photochromic forms, fast response, resistance to fatigue, high sensitivity and non-destructive read-out. The P-type photochromics, diarylethenes and fulgides [61, 67, 68, 81], fulfill many of these properties. One limitation of photochromic systems is that reading one photochromic form, either through absorption or emission spectra, can convert it back to the other form. However, as noted above, photochromism also leads to changes on other properties, such as the refractive index of the medium, and this can be used to address the system.

A somewhat different application of P-type photochromics is their use as ‘smart’ receptors in sensing cations, anions and biologically relevant systems [82]. This is based on photoinduced switching between two forms, only one of which is tailored to bind to the analyte through host–guest interactions. The possibility of switching between the two forms provides the attractive potential of reusing these sensors. A more detailed discussion of the general area of optical sensors and probes is given in Chap. 12.

4.5.5 Photoswitches: Molecular Logic, Rotors and Machines

The ideas of molecular memories and data storage described in the previous section can be extended to molecular computing. IT systems are based on logic gates with specific input–output behavior. These typically involve binary systems, where the input can be 0 or 1, and the output is, equally, 0 or 1. Photochromic systems fulfill the requirements of such a two-state system, and have been used in molecular logic devices [83]. These can be extended to applications in more complex logic functions by using a second input, such as addition of a metal ion or a change in pH. Although the area is in its infancy, photochromic systems show excellent possibilities for application in molecular scale computing.

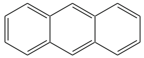
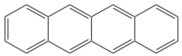
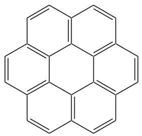
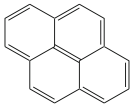
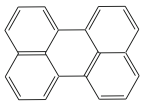
The distinguished physicist Richard Feynman in a famous talk to the American Physical Society entitled “There’s plenty of room at the bottom” [84] issued the challenge that it should be possible to make machines out of molecules. In addition to the intellectual and synthetic challenges of designing and making such systems, they also have potential for applications as pumps and motors in a variety of chemical and biomedical applications. There is now considerable research activity devoted to the use of molecular switches to produce such molecular machines [81, 85–87]. The basic requirement of a molecular machine is that it should involve "*an assembly of a discrete number of molecular components (that is, a supramolecular structure) designed to perform specific mechanical movements as a consequence of appropriate external stimuli*" [81]. Light is a particular valuable external stimulus [88], and, as shown in Fig. 4.6, photoswitching through *cis–trans* isomerisation does provide a possible basis for molecular rotor. However, for a true rotor it is necessary to have a unidirectional 360° rotation. This can be achieved by having a chiral photochromic system [86], as indicated in Fig. 4.9. This forms the basis for the development of true molecular motors and machines.

4.6 Conclusions

This chapter has discussed some of the most important and commonly encountered photochemical materials, whose properties and subsequent applications are primarily dependent on their absorption and emission characteristics. The most important factors are; (i) the available energy states of a given material and the routes of interconversion between these states and (ii) the excited state deactivation pathways. These factors dictate whether a material will act as a passive absorber, an emitter, or sensitiser. Absorbers, both organic and inorganic, find use in areas such as colorants, sunscreens, paints, pigments and dyes; high molar absorption coefficients are required to produce intense colours, while narrow absorption bands give rise to bright colours. For emitters, a high emission quantum yield in the required medium for the intended use is of obvious importance. The emission quantum yield is dependent on competition with other deactivation routes, while the emission wavelength (and therefore colour) and band structure depend on the relative energy levels of the emitter in any given medium. The emission lifetime is dependent on the probability of the radiative transition, i.e. whether it is 'allowed' (typically 10–100 ns) or 'forbidden' (μs or longer). The application of efficient emitters in light sources and display technology has been discussed. Excited state and radical sensitisers are useful for a variety of applications, including photodynamic therapy (e.g. singlet oxygen sensitisation, see Chap. 9) and photopolymerisation and device fabrication (see Chap. 13) and examples of the most commonly exploited sensitisation mechanisms have been provided. Photochromism and photochromic materials, including molecular switches, have also been discussed at length. For photochromic materials it is the absorption characteristics of both isomers that are most important for potential applications (change of colour, colourless to coloured or *vice versa*).

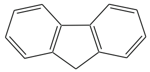
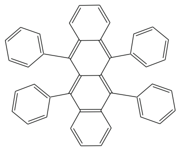
Table 4.1 A collection of data, structures, characteristics, uses and noteworthy properties of some commonly used photochemical materials

1. Polyaromatics. Rigid planar structures with low internal conversion efficiencies and therefore moderate to high fluorescence and moderate to high triplet yields, often with $\phi_F + \phi_T \sim 1$. Their well-characterised fluorescence and phosphorescence spectra, long-lived triplet states with well-known T–T absorption spectra, and the range of triplet energies available, make them useful singlet and triplet sensitisers, and useful standard materials for both steady-state and time resolved fluorescence and flash photolysis. They show a high singlet-triplet energy gap characteristic of π–π* singlets and triplets. The decrease in singlet and triplet energy with increasing conjugation is illustrated by the data below. For some, a high symmetry leads to transitions being symmetry-forbidden, resulting in low fluorescent radiative rate constants and relatively long lived singlet states (e.g. **1.4**). Although insoluble in water, substitution with soluble groups such as sulfonates, amines and carboxylic acids, can give some degree of water solubility.

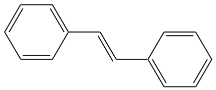
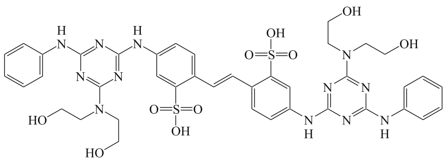
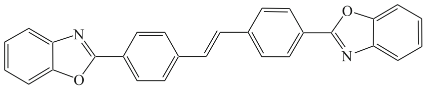
Compound	Structure	Specific uses	Physical, photophysical and noteworthy properties
1.1 Anthracene		An organic semiconductor. It is used as a scintillator for detectors of high energy photons electrons and alpha particles. Anthracene has the highest light output of all organic scintillators and thus the output of other scintillators are sometimes expressed as a percent of anthracene light [89]. Anthracene is also a precursor to anthraquinone dyes.	Photodimerises under UV light; the dimer reverts to anthracene thermally or with UV irradiation below 300 nm. λ_{abs} in near-UV; $\lambda_{em} \sim$ 350–500 nm; $E_S = 318$ kJ mol^{-1}; $\phi_F = 0.3$; $\tau_s = 5.3$ ns; $E_T = 178$ kJ mol^{-1}; $\phi_T = 0.71$; $\tau_T = 670$ µs [45].
1.2 Tetracene		An organic semiconductor used in organic field-effect transistors (OFETs) and as a dopant in OLEDs. A sublimed tetracene film was the first reported example of an OFET [90]. A light-emitting transistor made of a single tetracene crystal has been demonstrated [91].	$E_S = 254$ kJ mol^{-1}; $\phi_F = 0.17$; $\tau_s = 6.4$ ns; $E_T = 123$ kJ mol^{-1}; $\phi_T = 0.62$; $\tau_T = 400$ µs [45].
1.3 Coronene		An n-channel organic semiconductor. Emission intensity and number of bands is dependent on the solvent, as such coronene can be used as a solvent probe. Coronene is a UV phosphor, and is used in charge-coupled devices (CCDs) in digital imaging; notably coronene-coated CCDs are used on the Hubble Space Telescope.	$\lambda_{abs} \sim$ 275–400 nm; $\lambda_{em} \sim$ 400–550 nm. Shows an easily detected long lived green phosphorescence in plastics at r.t.; $\phi_P = 0.04$; $\tau_P = 6.0$ s in poly(methyl methacrylate) at 23 °C [92].
1.4 Pyrene		The fluorescence emission spectrum of pyrene is very sensitive to solvent polarity, and as such pyrene and its derivatives are useful polarity probes (*cf.* **1.3**). Excimers are formed even at moderate concentrations, and this can be used as a probe of viscosity and molecular mobility [93].	$E_S = 322$ kJ mol^{-1}; $\phi_F = 0.65$; $\tau_s = 650$ ns; $E_T = 203$ kJ mol^{-1}; $\phi_T = 0.37$; $\tau_T = 180$ µs. λ_{abs} in near UV. Classic example of excimer formation, with structured near UV monomer emission and broad band blue excimer emission [95].
1.5 Perylene		Perylene, and substituted perylenes, are used as blue-emitting dopants in OLEDs. Perylene can be also used as an organic photoconductor. It is used as a fluorescent lipid probe and is sensitive to fluorescence quenching by metal ions [94].	$E_S = 275$ kJ mol^{-1}; $\phi_F = 0.75$; $\tau_S = 6.4$ ns; $E_T = 148$ kJ mol^{-1}; $\phi_T = 0.014$. High $\varepsilon = 38{,}500$ mol^{-1} dm^{-3} cm^{-1} at 436 nm [45].

(continued)

Table 4.1 (continued)

Compound	Structure	Specific uses	Physical, photophysical and noteworthy properties
1.6 Fluorene		Named after its violet fluorescence, fluorene itself has few applications, but is a precursor to a number of important compounds. 2-Aminofluorene, 3,6-bis-(dimethylaminofluorene), and 2,7-diiodofluorene are precursors to dyes. Polyfluorenes (**3.6**) are used in electroluminescent devices.	$E_S = 397$ kJ mol^{-1}; $\phi_F = 0.68$; $\tau_S = 10$ ns; $E_T = 282$ kJ mol^{-1}; $\phi_T = 0.22$; $\tau_T = 150$ μs [45].
1.7 Rubrene (5,6,11,12-tetraphenylnaphthacene)		An organic electronic material useful as a red dopant in OLEDs and as *p*-type organic semiconductors [95]. Reagent for chemiluminescence research. Singlet oxygen acceptor.	$\lambda_{em} = 550$ nm; $E_S = 221$ kJ mol^{-1}; $\phi_F = 0.98$; $\tau_S = 16.5$ ns; $E_T = 110$ kJ mol^{-1}; $\phi_T = 0.0092$; $\tau_T = 120$ μs [45].

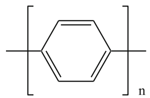
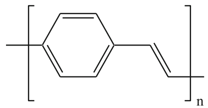
2. Stilbenes. Have the potential for photochemical isomerisation across the double bond, a reaction which has been widely studied. Addition of appropriate groups inhibits isomerisation and some substituted stilbenes have very high fluorescence yields. Stilbenes are commonly used as optical brighteners and laser dyes, and also find use as phosphors and scintillators.

Compound	Structure	Specific uses	Physical, photophysical and noteworthy properties
2.1 Stilbene (1,2-diphenylethylene)		*Cis-trans* isomerisation possible (*trans* isomer shown). Used in manufacture of dyes and optical brighteners, and also as a phosphor and a scintillator.	$E_S = 358$ kJ mol^{-1}; $\phi_F = 0.036$; $\tau_S = 0.075$ ns. (data for *trans*-stilbene in a crystalline medium) [45].
2.2 4,4′-(diamino-2,2′-stilbenedisulfonic acid), (Fluorescent Brightener 28, Tinopal)		Fluorescent brightening agent for cellulose and polyamide fabrics, paper, detergents and soaps.	λ_{abs} range ~340–370 nm; λ_{em} range ~420–470 nm. Water soluble. High ϕ_F.
2.3 4,4′-Bis(2-benzoxazolyl)stilbene		Optical brightener for plastics.	λ_{abs} range ~340–320 nm; λ_{em} range ~420–470 nm; high ϕ_F.

(continued)

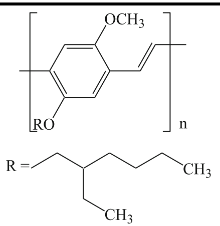
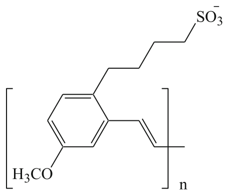
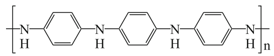
Table 4.1 (continued)

3. Conjugated polymers (CPs). CPs have conjugated double bonds in the polymer chain which results in an extensively conjugated system with strong delocalisation of electrons along the chain. The low energy π occupied orbitals form a valence band, while the higher energy π^* orbitals form an unoccupied conduction band. The relatively low band gap between valence and conduction band gives the polymers semi-conducting behaviour. They have a great deal of potential for applications due to their remarkable properties such as: light weight, low cost, conductivity, mechanical flexibility, and easy processing. CPs form a broad class of materials with potential applications dominated by their emissive and conductive properties and as such find use in electroluminescent devices (OLEDs, LEPs and PLEDs) as well as chemical and biological sensors and efficient, low cost, solar cells. Other common uses are in field-effect transistors (FETs), photochemical resists, non-linear optic devices, batteries and antistatic coatings. Solubility is a common problem with CPs, with a great deal of research focussed on the synthesis of soluble derivatives. Absorption, emission and chemical properties of soluble CPs are dependent on chain length and aggregation properties. CPs are also known for their compatibility with biological molecules, and are able to transfer electric charge from biochemical reactions to electronic circuits. Recent applications of CPs in optoelectronic devices are reported in detail in Refs. [96, 35].

Compound	Structure	Specific uses	Physical, photophysical and noteworthy properties
3.1 PPP (poly(p-phenylene))		PPP was one of the first blue electroluminescent CPs to be reported, and blue LEDs can be made from PPP and its various derivatives [97].	Structurally simplest CP based on phenylene rings. PPP is insoluble and has poor conductivity but soluble PPPs can be synthesised [98, 99]. Substituted PPPs emit deep blue light with a significant portion of the emission in the near UV region; e.g. poly(2-decyloxy-1,4-phenylene) which exhibits both high photo- and electro-luminescence. $\lambda_{em} \sim 410$ nm.
3.2 PPV (poly(p-phenylenevinylene))		PPV was used as the emitter in the first PLED in 1990 [100]. PPV and PPV derivatives have also found wide use in electronic materials e.g. electrochemical sensors and integrated circuits. PPV is also used as an electron-donating material in organic photovoltaic solar cells [101]. Although PPV-based devices suffer from poor absorption and photodegradation, PPV and PPV derivatives (especially MEH-PPV, see below) find frequent application in research cells. Ladder-type PPV derivatives have been studied as blue emitters in OLEDs [102].	$\lambda_{abs} \sim 400$–420 nm (dependent on synthesis); band gap of ~ 2.5 eV. The yellow/green fluorescence of PPV has a structured emission band with λ_{em} 520 and 551 nm [103]. PPV has very low solubility in common organic solvents, and thus there has been a great deal of research on making soluble PPV derivatives (such as MEH-PPV and MPS-PPV, see below), see Ref. [104].

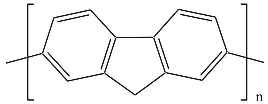
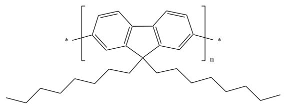
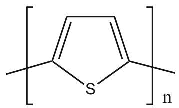
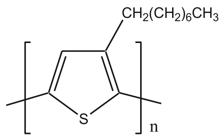
(continued)

Table 4.1 (continued)

Compound	Structure	Specific uses	Physical, photophysical and noteworthy properties
3.3 MEH-PPV (poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene])		MEH-PPV is one of the most studied electroluminescent materials. It finds use as a CP in solar cells and carbon nanotube OLEDs [103, 104, 105]. Useful in producing bright and efficient white polymeric LEPs [106]. Although solid-state lasing has yet to be demonstrated in an organic LEP, MEH-PPV has been proven to be a promising laser dye due to its high fluorescence efficiency in solution [107].	Highly soluble in common organic solvents. Bright orange ($\lambda_{abs} \sim 490$ nm) with red/orange emission ($\lambda_{em} \sim 560$ nm). High ϕ_F in solution [103].
3.4 MPS-PPV (poly[5-methoxy-2-(3-sulfopropoxy)-1,4-phenylenevinylene])		MPS-PPV has found use in optoelectronic devices and LEDs [90, 108]. The highly charged backbone of MPS-PPV, with a charge density comparable to DNA, also makes it a model polymer for understanding the interactions and self-assembly properties of charged biopolymers.	Water-soluble. Blue absorber, green emitter ($\lambda_{abs} \sim 451$ nm $\lambda_{em} \sim 525$ nm in H_2O).
3.5 PANI (polyaniline)		p-type semiconductor, has been commercialised and is one of the most important conductive polymers. Potential uses include: antistatics, charge dissipation or electrostatic dispersive (ESD) coatings, electromagnetic interference (EMI) shielding, anti-corrosive coatings, hole injection layers [101], conducting layers, actuators, chemical vapour and solution based sensors, electrochromic coatings (for colour change windows, mirrors etc.), active electronic components such as for non-volatile memory. Photoluminescent conducting PANI can be useful as an electron mediator in biosensors [109].	Relatively cheap. Has three distinct oxidation states with different colours. High electrical conductivity. Amongst the family of conducting polymers and organic semiconductors, PANI is unique due to its ease of synthesis, environmental stability, and simple doping chemistry.

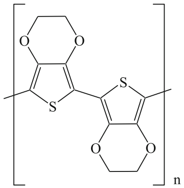
(continued)

Table 4.1 (continued)

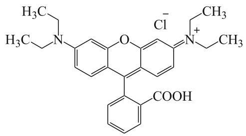
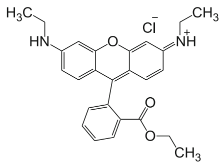
Compound	Structure	Specific uses	Physical, photophysical and noteworthy properties
3.6 PF (polyfluorene)		PF derivatives are much investigated for use in OLEDs and polymer solar cells. PF derivatives are particularly useful because they contain a rigid biphenyl unit with large band gap and efficient blue emission, and substitution at the 9,9-positions in the 5-membered ring provides (e.g. **3.7**) the possibility of improving the solubility and processing of polymers without significantly increasing the steric interactions in the polymer backbone [110].	PFs emit in the blue with high photo- and electroluminescence yields [111, 112]. They possess high charge carrier mobility, good processability, excellent thermal stability and high stability against oxidants. PFs are relatively wide band-gap materials and thus the emission colour can be tuned *via* energy transfer to smaller band-gap chromophores which can be incorporated into the polymer as co-monomers or substituents. With the right groups, PFs can be made which emit across the entire visible range with high efficiency and low operating voltage [113].
3.7 PFO (poly(9,9′-dioctylfluorene))		One of the most widely studied PF derivatives. It is a key blue emitter in OLEDs [103]. A two photon pumped PFO solid state laser has been reported [114]. Charged PFO based polymers have been used in the study of compaction of DNA with potential applications in DNA sensors [113, 114].	Solubility, photochemical and aggregation properties are very much dependent on chain length. λ_{abs} in the near UV and λ_{em} in the blue with $\phi_F \sim 0.5$ [103, 110].
3.8 PT (polythiophene)		Widely studied for a wide range of applications such as; FETs, solar cells, non-linear optics, resists, batteries, diodes, electroluminescent devices, chemical sensors. Most potential applications arise due to the fact that PTs become highly conducting when doped to a metallic level. A fluorene substituted PT has achieved efficiencies of 7 % in polymer-fullerene solar cells [115].	Insoluble in common solvents but many soluble PT derivatives are available that are chemically and thermally stable and offer processing advantages such thin film casting and inkjet printing.
3.9 P3OT (poly(3-octylthiophene-2,5-diyl))		P3OT is a conducting LEP that finds use in: OLED and PLED materials, FETs, and, probably most widely studied, polymer-based solar cells [116, 117]. Other alkyl substituted derivatives (particularly the regioregular 3-hexyl P3HT) are also widely used and are important materials for bulk heterojunction PV systems.	λ_{abs} range $\sim$380–620 nm (max film = 506 nm); $\phi_L = 0.27$ in solution, $CHCl_3$; $\phi_L = 0.04$ as a film [103].

(continued)

Table 4.1 (continued)

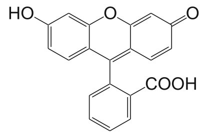
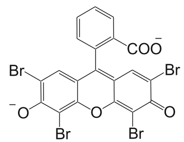
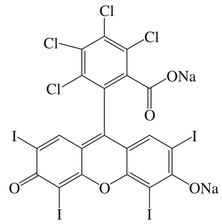
Compound	Structure	Specific uses	Physical, photophysical and noteworthy properties
3.10 PEDOT (poly(3,4-ethylenedioxythiophene))		PEDOT is a widely used *p*-type semiconductor. Typical applications include: hole injection layers in OLEDs and LCD, antistatic coatings, electrically switchable windows, and polymer solar cells. In most of these applications, PEDOT–poly(styrenesulfonic acid) (PEDOT-PSS) co-polymer is used because of improved solubility, film forming properties and stability [118].	Excellent transparency in the visible range, high conductivity, high stability, moderate band gap, low redox potential and good thermal stability [118]. A disadvantage is poor solubility which is partly circumvented by using copolymers e.g. PEDOT–PSS.

4. Rhodamines, cyanines and xanthenes. Three groups of widely used dyes. Most are highly fluorescent and widely used as: fluorophores; laser dyes; fluorescent labels in biotechnology; in fluorescence microscopy and flow cytometry; in fluorescence correlation spectroscopy and ELISA; they are also widely used in photochemical studies as singlet energy donors and/or acceptors. Heavy-atom substitution leads to a decrease in ϕ_F and increase in ϕ_T, and heavy-atom substituted xanthenes such as eosin and rose bengal are also used as triplet and singlet oxygen sensitisers. Some cyanines can also be used as electron transfer sensitisers, and are used as such in silver halide photography.

Compound	Structure	Specific uses	Physical, photophysical and noteworthy properties
4.1 Rhodamine B		A common fluorophore and laser dye, used in fluorescence correlation spectroscopy and ELISA. Often used as a tracer dye to determine the rate and direction of flow and transport. A concentrated solution in glycerol is used as a quantum counter out to ~600 nm.	λ_{abs} ~ 460–600 nm; $\phi_F = 0.65$ in basic ethanol, 0.49 in ethanol. ϕ_F is temperature dependent [119, 20].
4.2 Rhodamine 6G		Widely used fluorophore and laser dye, readily pumped by the 532 nm harmonic from a Nd:YAG laser, or nitrogen laser [121, 122].	λ_{abs} ~ 425–600 nm; very high ϕ_F (0.95) [120]. Remarkably high photostability. Like most rhodamines it has a small Stokes' shift and its lasing range (555–585 nm) is close to its λ_{max} ~ 530 nm. Can be bought as; chloride, perchlorate, or tetrafluoroborate salts.

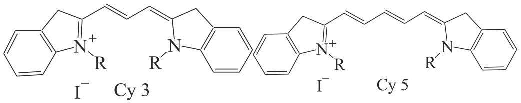
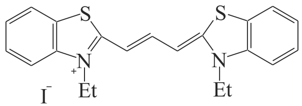
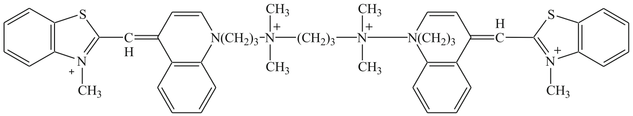
(continued)

Table 4.1 (continued)

Compound	Structure	Specific uses	Physical, photophysical and noteworthy properties
4.3 Fluorescein		Widely used fluorophore. Finds use in microscopy, as a laser dye in forensics and serology to detect latent blood stains, and in dye tracing. When substituted with reactive groups can be used to covalently label proteins. The excitation maximum (494 nm) is conveniently close to the spectral line of the argon-ion laser (488 nm) which makes fluorescein an important fluorophore for confocal scanning laser microscopy [123]. A common donor for FRET applications.	$\lambda_{abs} \sim$ 410–525 nm; $\lambda_{max} = 494$ nm; $\lambda_{em} = 521$ nm (water); very high $\phi_F = 0.97$ in ethanol; $E_T = 197.5$ kJ mol^{-1} [124, 125]. High ε; good water solubility. ϕ_F is pH dependent, decreasing with decreasing pH. Relatively high rate of photo-bleaching which can limit applications.
4.4 Eosin		Eosin and its derivatives show weak room temperature phosphorescence and are particularly useful as phosphorescent probes for measuring the rotational properties of proteins and other biomolecules in solution and in membranes. Also useful for FRET studies and fluorescence recovery after photobleaching (FRAP) measurements of diffusion.	$\lambda_{abs} \sim$ 425–580 nm; $\varepsilon \sim$ 112,000 mol^{-1} dm^3 cm^{-1} at 525 nm [125]. $\phi_T = 0.67$ in ethanol. Br, 'heavy atom' substituents reduce ϕ_F to typically only 10–20 % that of fluorescein and increase the triplet yield. Singlet oxygen sensitiser with $\phi_\Delta \sim 0.57$.
4.5 Rose Bengal sodium salt)		Rose bengal is used as a singlet oxygen sensitiser in photochemical synthesis. A form of rose bengal, PV-10, is currently undergoing clinical trials for melanoma and breast cancer. Also an active ingredient for the treatment of eczema and psoriasis; (drug known as PH-10 also currently in clinical trials). Used as a biological stain, e.g. to stain necrotic tissue and devitalised cells of the cornea and thereby identify damage to the eye.	$\lambda_{abs} \sim$ 455–615 nm; high $\varepsilon = 90{,}400$ mol^{-1} dm^3 cm^{-1} (EtOH); $\phi_F \sim$ 0.05–0.11 (EtOH); $E_T = 175.7$ kJ mol^{-1} [124, 125]. I, 'heavy atom' substituents reduce ϕ_F and increase triplet yield compared to fluorescein or eosin.

(continued)

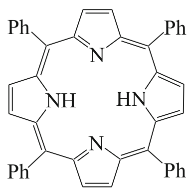
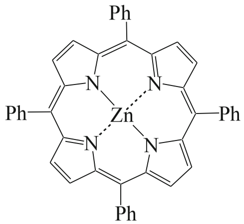
Table 4.1 (continued)

Compound	Structure	Specific uses	Physical, photophysical and noteworthy properties
4.6 Cy3 and Cy5		They are usually synthesised with reactive groups, R, on either one or both of the nitrogen atoms so that they can be chemically linked to nucleic acids or proteins. Used mainly for protein and nucleic acid labelling. Cy3 and Cy5 are commonly combined for 2 colour detection; Cy3 dyes fluoresce yellow-green while Cy5 dyes fluoresce red.	The effect of increasing cyanine dye chain length is illustrated by a comparison of absorption/emission wavelengths: Cy3 $\lambda_{abs} \sim 550$ nm, $\lambda_{em} \sim 570$ nm; Cy5 $\lambda_{abs} \sim 649$ nm, $\lambda_{em} \sim 650/670$ nm [126].
4.7 Thiacarbocyanine		Thiacarbocyanine and its derivatives are used in sensitising silver halide photographic emulsions. New applications of the dyes include use in LEDs. A great deal of research has been carried out on understanding the aggregation properties of cyanine dyes in solution [127].	Weak absorption in range ~250–340 nm; main λ_{abs} range ~440–610 nm; abs $\lambda_{max} = 559$ nm; λ_{em} range ~555–700 nm. Emission $\lambda_{max} = 625$ nm, 571 nm; $\phi_F = 0.05$ (EtOH). Readily aggregates in solution [127].
4.8 TOTO-1		Active fluorescent probe, widely used in fluorescence microscopy and flow cytometry for the study of nucleic acids [126].	Green emitter; cell-impermeable, high-affinity for nucleic acid; essentially non-fluorescent in the absence of nucleic acids; exhibits excitation/emission maxima ~514/533 nm when bound to nucleic acids. Sensitivity is sufficient for detecting single molecules of labelled nucleic acids [126].

(continued)

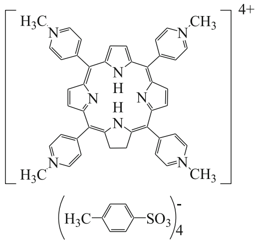
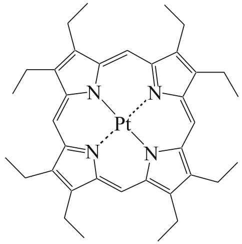
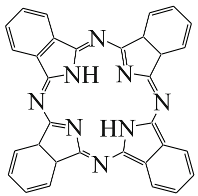
Table 4.1 (continued)

5. Porphyrins and Phthalocyanines. Porphyrins are highly conjugated rigid structures and as such tend to have very intense vibrationally-structured absorption bands in the visible region. Their properties can be readily modified by both ring substitution and metallation. Their well characterised fluorescence, moderate to high triplet yields, long-lived triplet states with well-known T–T absorption spectra, and the range of triplet energies available, make them useful singlet and triplet sensitisers and acceptors, and singlet oxygen sensitisers. They are also useful standard materials for both steady-state and time-resolved fluorescence and flash photolysis. Porphyrins have a characteristic sharp Soret band around 390–430 nm with very high absorption coefficients, and less intense Q bands in the visible. Phosphorescent Pt and Pd porphyrins are widely studied as oxygen sensors. The commercial uses of porphyrins and metalloporphyrins include: (i) photodynamic therapeutics such as Photofrin® to fight viral infections and cancer; (ii) commercial oxidation catalysts to make fine chemicals; (iii) components of printing inks and toners; (iv) protective coatings. There have been several hundreds of patents issued in the past few years for the use of porphyrins in molecular electronics, catalysts, inks, and other new materials. Phthalocyanines are red-absorbing compounds with intense bands around 650–750 nm, a reasonable spectral window in the green/blue, and further absorption about 400 nm. Unsubstituted phthalocyanine, and metal phthalocyanines generally have quite poor solubility, but ring substitution can be used to increase solubility in either aqueous or organic solvents. Approximately 25 % of all artificial organic pigments are phthalocyanine derivatives.

Compound	Structure	Specific uses	Physical, photophysical and noteworthy properties
5.1 H_2TPP (tetraphenylporphyrin)		Photosensitiser for the production of singlet oxygen [128]. TPP and its derivatives are related to the electron relay stations in the electron transport chain which form part of chlorophyll in plants. There are also various reduced forms of the cyclic tetrapyrrole ring structure, such as chlorins and bacteriochlorins, which are becoming increasingly important materials for a wide variety of photochemical applications.	$\lambda_{abs} \sim$ 370–440 nm and bands across 490–615 nm; high $\varepsilon = 1.89 \times 10^4$ mol^{-1} dm^3 cm^{-1} at 515 nm (toluene); $\lambda_{em} \sim$ 615–770 nm; $\phi_F = 0.11$ (toluene) [129]. High triplet yield, long lived (ms) triplet with well characterised T–T absorption spectrum. Dark purple solid that dissolves in nonpolar organic solvents such as chloroform and benzene, not soluble in water.
5.2 ZnTPP		Photophysics of ZnTPP are well understood and it is often used as a ‘model’ metalloporphyrin to study other systems or as a reference compound. Derivatives have been used in dye sensitised solar cells (DSCs).	$\lambda_{abs} \sim$ 385–450 nm and two bands across ~520–600 nm; very high $\varepsilon = 5.74 \times 10^5$ mol^{-1} dm^3 cm^{-1}; $\lambda_{em} \sim$ 570–760 nm; $\phi_F = 0.03$ (toluene), high triplet yield, long lived (ms) triplet with well characterised T–T absorption spectrum [129, 130].

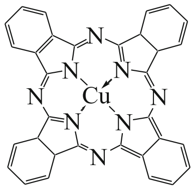
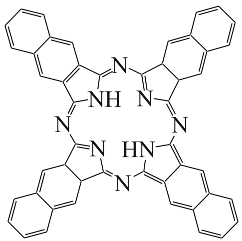
(continued)

Table 4.1 (continued)

Compound	Structure	Specific uses	Physical, photophysical and noteworthy properties
5.3 TMPyP (5,10,15,20-Tetrakis(1-methyl-4-pyridinio)porphyrin tetra(*p*-toluenesulfonate))		TMPyP is a water-soluble porphyrin that finds use as a chelating agent for the quantitative analysis for many metals. TMPyP intercalates to G-quadruplexes (nucleic acid sequences rich in guanine which form a four-stranded structure) and has been used to study such structures.	Water soluble; pK_{a1} = 0.8, pK_{a2} = 2.06. λ_{max} = 422 nm, $\varepsilon = 2.3 \times 10^5$ mol^{-1} dm^3 cm^{-1} (H_2O); in 1 M HCl (protonated), λ_{max} = 445 nm, $\varepsilon = 2.9 \times 10^5$ mol^{-1} dm^3 cm^{-1}.
5.4 PtOEP (platinum octaethylporphyrin)		Red triplet emitter with high quantum yield for OLEDs which has shown exceptionally high efficiency (~7 %) at low injection current [131]. Used as a dopant in host materials like 4,4′-bis(N-carbazolyl)-1,1′-biphenyl (CBP) and Alq_3 (**6.1**). Has also been used as a phosphorescent dye in LEDs [132]. Widely studied as a phosphorescent oxygen sensor. The Pd analogue is also used in oxygen sensors studies; it has weaker emission, but a much longer triplet lifetime.	Red r.t. phosphorescence ~650 nm depending on solvent, host material and processing conditions, ϕ_P = 0.45 (deoxygenated toluene/DMF, r.t.), τ_P = 83 μs [103, 128].
5.5 Pc (phthalocyanine)		Intensely blue/green coloured, widely used as a pigment. Properties can be varied by metallation and/or ring substitution. Phthalocyanines form coordination complexes with most elements of the periodic table. These complexes are also intensely coloured and many are also are used as pigments.	Poor solubility, (chloronaphthalene is a good solvent for phthalocyanines). Structured abs in the λ_{abs} range ~530–740 nm; intensely coloured, $\varepsilon = 1.62 \times 10^5$ mol^{-1} dm^3 cm^{-1} at 699 nm; λ_{em} ~ 650–800 nm; strongly fluorescence, ϕ_F = 0.6 (chloronaphthalene), moderate triplet yield [125, 133].

(continued)

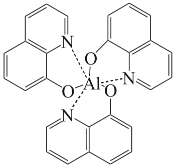
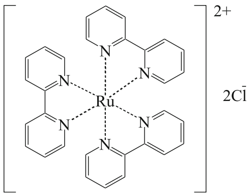
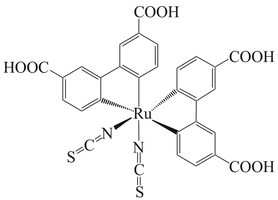
Table 4.1 (continued)

Compound	Structure	Specific uses	Physical, photophysical and noteworthy properties
5.6 CuPc (copper phthalocyanine)		First developed as a pigment, phthalo-blue, in the mid-1930s. Due to its brilliant colour and stability, it is a standard pigment used in paints, printing ink and packaging. The first OPV solar cell was made using CuPc and a perylene derivative giving 1 % efficiency [134]. CuPc and derivatives are still leading materials used in OPV solar cell research. The analogous ZnPc is also a widely used absorber in OPV solar cells. Bulk hetro-junction solar cells using ZnPc as the donor and C60 as the acceptor have shown efficiencies greater than 2.5 % [135]. Fluorine derivatives of ZnPc, such as hexadecafluorophthalocyanine, have shown promise for use in photodynamic therapy (PDT).	CuPc is a bright, greenish-blue pigment, highly valued for its superior pigment properties such as lightfastness, tinting strength, covering power and resistance to the effects of alkalis and acids. CuPc is non-fluorescent due to the presence of a low lying metal-based excited state. The corresponding ZnPc is intensely coloured, $\lambda_{abs} \sim 600–750$ nm; $\varepsilon = 2.82 \times 10^5$ mol^{-1} dm^3 cm^{-1} at 674 nm, and is moderately fluorescent, $\phi_F = 0.3$; it also has a fairly high triplet yield [125, 133].
5.7 Naphthalocyanine		Potential use in OLEDs, OPV and OFETs. Used as a component in the development of IBM's single-molecule logic switch. Metallated derivatives also find use as gas sensors and in PDT.	Absorbs strongly in the NIR with the absorption maxima red-shifted in relation to **5.5** and **5.6**. $\lambda_{abs} \sim 700–800$ nm; $\varepsilon = 23{,}800$ mol^{-1} dm^3 cm^{-1} [136].

(continued)

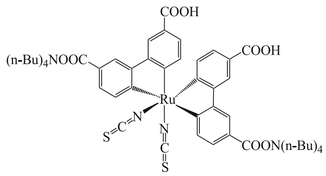
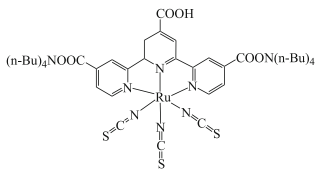
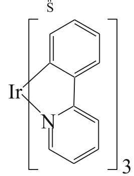
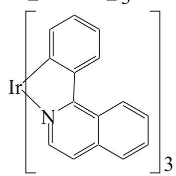
Table 4.1 (continued)

6. Aluminium(III), iridium(III) and ruthenium (II) complexes. Tris(8-hydroxyquinoline)aluminium(III) was the first material to be used in efficient OLEDs, and continues to be important for devices. Ir(III)-based triplet emitters have attracted substantial interest for OLED technology, with several highly efficient green devices reported along with blue, yellow and red. There are many Ru(II) bipyridine and terpyridine complexes. Many are phosphorescent with long-lived (μs) triplets which are efficient photooxidants and photoreductants. The long-lived phosphorescence is quenched by oxygen, which has led to their use as oxygen sensors. Ruthenium complexes which absorb light throughout the visible spectrum are currently the most widely used sensitisers for dye-sensitised solar cell (DSC) research.

Molecule	Structure	Specific uses	Physical, photophysical and noteworthy properties
6.1 Alq3 (tris(8-quinolinolato)aluminum(III))		Green electroluminescent emitter for OLEDs [137].	Relatively high quantum yield of electroluminescence; broad fluorescence band peaking at ~478 nm (in methanol/ethanol at 77 K). Emission bands at 578 and 605 nm are assigned to phosphorescence; 478 nm band is assigned to delayed fluorescence [138].
6.2 Tris(bipyridine) ruthenium(II) dichloride		$[Ru(bipy)_3]^{2+}$ has been examined as a photosensitiser for both the oxidation and reduction of water. A $[Ru(bipy)_3]^{2+}$ persulfate combination can be used as a water-soluble free radical initiator.	λ_{abs} max = 452 nm; $\varepsilon = 1.15 \times 10^4$ mol^{-1} dm^3 cm^{-1}. The triplet excited state has a comparatively long lifetime τ_T: 890 ns in acetonitrile, 650 ns in water, and shows a broad band emission, $\phi_P = 0.05$ at $\lambda_{em} \sim 620$ nm.
6.3 N3 (*cis*-bis(isothiocyanato)bis (2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II))		Sensitiser used by O'Reagan and Gratzel *et al.* in their 1991 breakthrough work in the field of DSCs. Highly stable dye for solar cell applications. Has showed light to electric energy conversion efficiency of 7.9 % [139].	Broad λ_{abs} range ~310–775 nm; λ_{abs} max = 534 nm; moderate $\varepsilon = 1.42 \times 10^4$ mol^{-1} dm^3 cm^{-1} (EtOH). N3 starts to absorb light at around 800 nm when sorbed to TiO_2; however the moderate molar extinction coefficient limits the efficiency of DSC devices.

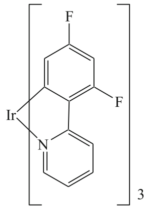
(continued)

Table 4.1 (continued)

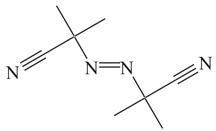
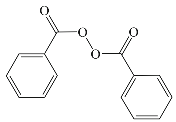
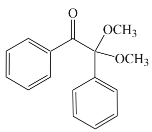
Compound	Structure	Specific uses	Physical, photophysical and noteworthy properties
6.4 N719 (di-tetrabutylammonium *cis*-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II))		Sensitiser for solar cells analogous to N3; however has tetrabutyl ammonium counter ions; this has a significant positive impact on the light to electric energy conversion efficiency. N719 is one of the most widely studied dyes for DSC applications. Has showed light to electric energy conversion efficiency of 11.1 % [140].	Broad λ_{abs} range ~310–775 nm; λ_{abs} max = 535 nm; moderate $\varepsilon = 1.36 \times 10^4$ mol^{-1} dm^3 cm^{-1} (EtOH). N719 has a moderate molar extinction coefficient (when compared to organic dyes) which limits solar cell efficiencies. Very stable dye for DSC research.
6.5 'Black' dye (tris(cyanato)-2,2′,2′′-terpyridyl-4,4′,4′′-tricarboxylate)Ru(II))		Panchromatic sensitiser for DSC. Has showed light to electric energy conversion efficiency of over 10 % [141].	Broad λ_{abs} range ~310–800 nm; λ_{abs} max = 605 nm; moderate $\varepsilon = 7.48 \times 10^3$ mol^{-1} dm^3 cm^{-1} (EtOH). Onset of absorption is 920 nm when sorbed to TiO_2. Very stable dye for DSC research; has been subjected to the equivalent of 10 years' exposure to the sun with no loss of performance [141].
6.6 Ir(ppy)$_3$ tris[2-phenylpyridinato-C^2,*N*]iridium(III)		Green emitter used in PLEDs, in a poly(9-vinylcarbazole) (PVK) matrix gives an efficiency of 7.5 % [103]. This was the first reported PLED device with an efficiency of greater than 5 %. Also used as an optical oxygen sensor.	Green emitter, λ_{em} max = 514 nm (solution) and 516 nm (film); $\phi_L = 0.40$ [103].
6.7 Ir(piq)$_3$ (tris(1-phenylisoquinoline-C^2,N) iridium(III))		Red-emissive complex used in PLEDs. Has achieved an external quantum efficiency of 10.3 % and a power efficiency of 8.0 % lm W^{-1} at 100 cd m^{-2} [103]. Originally, it was hoped that Ir(piq)$_3$ could be directly applied as dopant into the polymer host for red emission. Unfortunately its use in LED technology is limited by its solubility which hinders cheap solution processing for device fabrication.	Red emitter; λ_{em} max = 624 nm; $\phi_L = 0.45$; $\tau = 1.25$ μs [142]. Use in OLED devices is limited by poor solubility and processability. Not soluble in many common solvents.

(continued)

Table 4.1 (continued)

Compound	Structure	Specific uses	Physical, photophysical and noteworthy properties
6.8 $Ir(Fppy)_3$ (tris[2-(2,4-difluorophenyl)pyridine]iridium(III))		This was one of the first blue OLED triplet emitters. However, its long term stability is limited which has led to a search for more stable phosphors for this spectral region.	$\lambda_{em} \sim 480$ nm ($CHCl_3$).

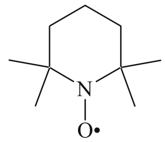
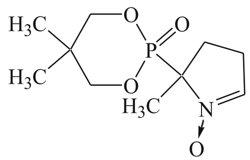
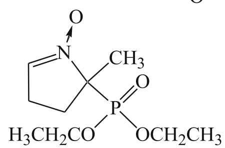
7. Radical Initiators. These are substances that can produce radical species under mild conditions (i.e. have low bond dissociation energies and are thus inherently unstable) and promote radical reactions. Radical initiators are utilised in industrial processes such as polymer synthesis. Typical examples are halogen molecules, azo compounds, and organic peroxides. Here we concentrate on initiators than undergo cleavage upon UV/Vis irradiation, although they will also act as thermal radical initiators.

Molecule	Structure	Specific uses	Physical, photophysical and noteworthy properties
7.1 AIBN (2,2′-azobis(2-methylpropionitrile)		Decomposes upon irradiation with UV, or upon heating, eliminating a molecule of nitrogen gas to form two 2-cyanoprop-2-yl radicals. These radicals can be used to initiate free radical polymerisations and other radical reactions. A classic example of a radical reaction that can be initiated by AIBN is the *anti*-Markovnikov hydrohalogenation of alkenes.	UV absorber; not water soluble; but soluble in methanol and ethanol. AIBN is highly toxic, but is a safer alternative to benzoyl peroxide (**7.2**) because the risk of explosion is far smaller. Decomposition temperature = 64 °C; slow decomposition at r.t.
7.2 Benzoyl peroxide		It is one of the most important organic peroxides in terms of applications and the scale of its production. Widely used initiator, curing agent, and cross-linking agent in polymerisation processes. Other major applications are based on its antiseptic and bleaching properties.	UV absorber; λ_{abs} max = 235 nm. Poor solubility in water; but soluble in ethanol and organic solvents. Decomposition temperature = 103 °C.
7.3 2,2-Dimethoxy-2-phenylacetophenone		Important photocuring agent used mainly for acrylic and unsaturated polyester resins. A great deal of work has been devoted to the unravelling of its photochemistry [143].	Primary reaction is a photochemical cleavage from a very short-lived triplet state ($\tau < 100$ ps) to radicals followed by fragmentation of the dimethoxybenzyl radical to methyl benzoate [143].

(continued)

Table 4.1 (continued)

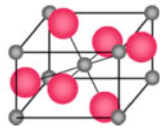
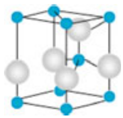
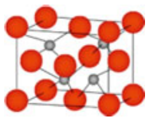
8. Free radical traps (also known as free radical scavengers or spin traps). React with unstable short lived free radicals to form a relatively stable free radical (normally through the addition of the radical to the trap to form a nitroxide radical). Spin traps are normally used in conjunction with EPR spectroscopy for the detection and identification of short-lived free radicals. The identity of the radical can be inferred from the EPR spectrum of the spin adduct.

Molecule	Structure	Specific uses	Physical, photophysical and noteworthy properties
8.1 TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy)		TEMPO is widely used as a radical trap, as a structural probe for biological systems in conjunction with EPR spectroscopy, as a reagent in organic synthesis, and as a mediator in controlled free radical polymerisation. As well as alcohol oxidation, TEMPO also finds use in the oxidation of other functional groups, including amines, phosphines, phenols, anilines, sulfides and organometallic compounds [144].	Remarkably stable nitroxyl radical. The stability of the radical has been proposed to be due to the steric influence of the methyl groups which flank the nitroxyl group.
8.2 CYPMPO		CYPMPO is a free radical spin trap with excellent trapping capabilities toward hydroxyl and superoxide radicals in biological and chemical systems [145].	The high melting point (126 °C), low hygroscopic properties, and long shelf-life in aqueous solutions are significant practical advantages for use of CYPMPO.
8.3 DEPMPO		DEPMPO is frequently used as a spin trap for the measurement of superoxide by EPR spectrometry. Most efficient spin trap for the *in vitro* and *in vivo* detection of O-, N-, S- and C-centred free radicals.	DEPMPO is water-soluble, rapidly penetrates lipid bilayers, has low toxicity, and can be used *in vitro* and *in vivo*. Half-life is still fairly short at r.t. and thus measurements need to be made at low temperatures [146].

(continued)

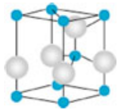
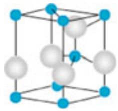
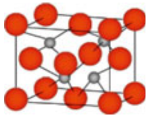
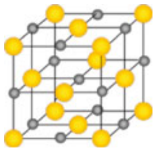
Table 4.1 (continued)

9. Semiconductors and semiconductor quantum dots (QDs). Semiconductors have moderate band gap energies (E_g) and as such they have the potential to conduct electricity. Most common are metal oxides, sulfides, sellenides, or tellurides; they have many applications. Semiconductors on the nanoscale are known as quantum dots, the difference between nano- and macroscale semiconductors is the fact that quantum dots have quantised energy levels (hence the name), whereas energy levels in a macroscale semiconductor form a continuum of energy levels. This tends to change the characteristics of the material significantly, usefully, and most notably, this tends to change the photochemistry of the material. Quantum confinement is size dependent, and the properties of QD nanoparticles are tuneable by size [e.g. **9.5, 9.6**].

Compound	Structure	Specific uses	Physical, photophysical and noteworthy properties
9.1 TiO_2		Common white pigment in paints, toothpaste, sunscreens and foodstuffs. Filters both UV-A and UV-B and used as nanoparticles in sunscreen formulations to increase transparency on the skin. It is the most widely studied semiconductor for DSC applications. Nano-particulate titania has a very high surface area which allows significant dye sorption to absorb visible light and to inject electrons into the conduction band (CB) of TiO_2 forming a PV device.	Relatively wide E_g semiconductor; direct band gap of ~3.0–3.2 eV (depending on crystal form). Stable, non-toxic oxide with a high refractive index (n = 2.4–2.5). The crystal form of TiO_2 is dependent on the method of production. *Anatase* and *rutile* forms are most common; rutile is the thermodynamically most stable form; anatase is the preferred form in DSCs, because it has a larger bandgap (3.2 vs. 3.0 eV) and higher CB edge energy which leads to a higher output voltage [147].
9.2 ZnO		Widely used as an additive in; plastics, ceramics, glass, cement, lubricants, paints, ointments, adhesives, sealants, pigments, foods, batteries, ferrites, fire retardants, and first aid tapes. Also used in emerging applications for transparent electrodes in LCDs, in energy-saving or heat-protecting windows, and in electronics as thin-film transistors and LEDs. Shows promise as a material for fast scintillators. Studied as a possible alternative to TiO_2 as a semiconductor for DSCs.	Relatively wide E_g semiconductor. The bandgap can be tuned across ~3–4 eV by doping. Most ZnO has *n*-type character (due to oxygen vacancies), even in the absence of intentional doping. Controllable *n*-type doping is easily achieved while reliable *p*-type doping remains difficult. Exhibits excitonic luminescence even at r.t. in the blue region with a relatively short lifetime (50 ps at 16 K) [148].
9.3 ZnS		In its dense synthetic form, ZnS can be transparent and is used as a window for visible and infrared optics. With addition of a suitable *activator*, ZnS finds use as a phosphor in several applications, from cathode ray tubes through X-ray screens to glow in the dark products. When silver is used as activator, the resulting colour is bright blue, manganese yields an orange/red colour and copper provides a long glow time and the familiar 'glow-in-the-dark' green colour. Cu-doped ZnS is used in electroluminescent panels.	Intrinsic, wide-bandgap semiconductor. The cubic form, (*zinc blende* structure) has a band gap of 3.54 eV at 300 K whereas the hexagonal form (*wurtzite*) has a band gap of 3.91 eV. Can be doped as both an *n*-type or *p*-type semiconductor. It may exhibit phosphorescence, due to impurities, on illumination with blue or UV light.

(continued)

Table 4.1 (continued)

Molecule	Structure	Specific uses	Physical, photophysical and noteworthy properties
9.4 CdS		CdS is a pigment used in plastics. CdS and CdSe (**9.5**) are used in manufacturing of photoresistors sensitive to visible and near NIR light. In thin-film form, CdS can be combined with a *p*-type semiconductor for PV applications; a CdS/Cu_2S solar cell was one of the first efficient cells to be reported (1954) [149]. Also used as a phosphor and in solid state lasers, and as nanoparticulate QDs.	Direct band gap semiconductor; $E_g = 2.42$ eV. Like ZnS (**9.3**), has two crystal forms; the more stable hexagonal, wurtzite, structure and the cubic, zinc blende, structure. The conductivity increases when irradiated with light (hence its use as a photoresistor). CdS pigments tend to have high thermal stability, good light and weather fastness as well as chemical resistance and high opacity.
9.5 CdSe		CdSe thin-film transistors were used in LCDs in 1973. Developed for use in optoelectronic devices, laser diodes, nano-sensing, biomedical imaging and film solar cells. CdSe QDs have potential use in optical devices, such as laser diodes that can cover a large part of the visible spectrum.	The wurtzite crystal structure is an important *n*-type semiconductor. Difficult to dope *p*-type, however *p*-type doping has been achieved using nitrogen. CdSe QDs have tunable absorption and emission across the visible spectrum.
9.6 CdTe		Used in thin film solar cells; has achieved a maximum efficiency, to date, of 16.5 %. This is lower than Si but at lower production costs. CdTe PV is the first thin-film PV technology to compete with crystalline silicon PV. Alloying with mercury gives a versatile infrared detector material (HgCdTe). Alloying with zinc gives an excellent solid-state X-ray and γ-ray detector.	Absorption range of bulk CdTe is dependent on sample thickness but generally λ_{abs} range ~475–850 nm. $E_g =$ 1.44 eV at 300 K. Transparent in the IR out to wavelengths greater than 2000 nm Bulk CdTe is fluorescent at 790 nm; with QDs the fluorescence peak is tuneable through the visible range to the UV [150].
9.7 PbS		PbS is one of the oldest and most common materials for the detection of IR radiation. Can be used to measure radiation in either of two ways: by measuring the tiny photocurrent the photons cause, or by measuring the change in the material's electrical resistance; resistance change is the more commonly used method. PbS QDs have been studied for DSC applications.	At r.t., PbS is sensitive to radiation at wavelengths between approximately 1000 and 2500 nm. Cooling to 77 K shifts its sensitivity range to between approximately 2000 and 4000 nm. PbS has shown $\eta \sim 1.23$ % in DSCs [151].

(continued)

Table 4.1 (continued)

10. Lanthanides. After lanthanum, the energy of the 4*f* sub-shell falls below that of the 5*d* sub-shell and electrons start to fill the 4*f* sub-shell before the 5*d* sub-shell. Because the lanthanides differ only in the occupancy of this 4*f* sub-shell they are chemically very similar. The colour of the lanthanide ions is mainly dependent on the number of unpaired electrons for example, Eu^{3+} and Tb^{3+} have 6 unpaired electrons and appear pale pink, whereas Er^{3+} and Nd^{3+} have 3 unpaired electrons and appear a reddish colour. Lanthanides are used in lamps, lasers, magnets, phosphors, motion picture projectors, and X-ray intensifying screens. Terbium 'green' phosphors (which luminesce a brilliant lemon-yellow) are combined with divalent europium blue phosphors and trivalent europium red phosphors to provide 'trichromatic' lighting technology. Due to the weak, Laporte forbidden *f–f* absorption bands of lanthanides, they are frequently complexed with *antenna* aromatic ligands when used as luminescent probes or energy acceptors.

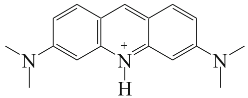
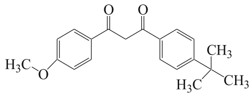
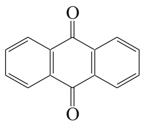
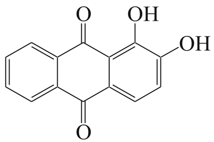
Compound	Specific use	Physical, photophysical and noteworthy properties
10.1 Europium(III) oxide	Widely used as a red phosphor in television sets and fluorescent lamps, and as an activator for yttrium-based phosphors. Europium photoluminescence is used in the anti-counterfeiting phosphors in Euro banknotes.	Red phosphorescent material.
10.2 Terbium (III) oxide	Terbium oxide is used in fluorescent lamps and TV tubes. Terbium green phosphors with Eu(II) blue phosphors and Eu(III) red phosphors provide a high-efficiency white light used for standard illumination in indoor lighting.	Green phosphorescent material.
10.3 Eu(II) based phosphors	Luminescence of Eu(II) depends on the host lattice, but tends to be on the blue side. Investigations of Eu(II) phosphors date back to the 1960s, first reported by Wanmaker *et al.* $ABPO_4{:}Eu^{2+}$ (A = Li, Na, K, B = Ca, Sr, Ba) have been extensively studied [152].	$LiCaPO_4{:}Eu^{2+}$ phosphors have superior luminescence properties for UV-LED application among $ABPO_4{:}Eu^{2+}$ type phosphors because of their high quantum efficiency and thermal stability.
10.4 Lanthanide ions :Eu^{3+} and Tb^{3+}	Lanthanide ions are visible to NIR ultra narrowband emitters with long luminescence lifetimes and thus have potential applications in lasing, up-conversion, and bioimaging. They have found use as potential emitters in OLEDs (see [38]).	Of the luminescent Ln ions, Eu^{3+} and Tb^{3+} are the two most extensively studied in practical applications. Luminescence is vibrationally quenched in common solvents. Lanthanide luminescence quenching can be suppressed by doping the lanthanide ions into the crystalline lattice of rare earth nanocrystals, e.g., LaF_3, $NaYF_4$, $LaPO_4$.
10.5 $Nd{:}Y_3Al_5O_{12}$	Nd(III) is used to dope a host crystal structure of yttrium aluminium garnet (YAG) (the Nd^{3+} and Y^{3+} ions are of similar size) at ~1 % level to produce a solid-state lasing medium. The Nd^{3+} provides the lasing activity in the crystal. Laser operation of Nd:YAG was first demonstrated by J. E. Geusic *et al.* at Bell Laboratories in 1964. More recently research has been carried out on ceramic Nd:YAG lasers [153].	The principle emission wavelength is 1064 nm (from a $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition), but for many applications, the IR is frequency-doubled or -tripled using non-linear optical materials Nd:YAG can be also made to lase at its non-principal wavelength. The line at 946 nm, doubled to 473 nm is typically employed in blue laser pointers, while a frequency doubled $Nd{:}YVO_4$ diode pumped solid state (DPSS) laser can be used as a green laser pointer.

(continued)

Table 4.1 (continued)

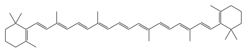
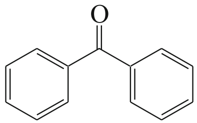
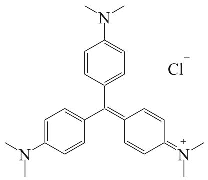
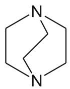
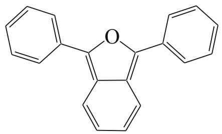
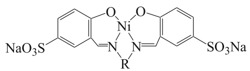
Molecule	Structure	Specific uses	Physical, photophysical and noteworthy properties
10.6 Erbium(III) oxide	Erbium oxide is pink and is sometimes used as a colorant for glass, cubic zirconia and porcelain. It is particularly important as a near infrared emitted in optical data transmission. The Er(III) emission bands in the 1500–1600 nm region correspond to a region of high transmission in optical fibres. This is extensively used in high density communications, e.g. broadband internet or telecommunications.		Erbium oxides can up convert energy. Erbium oxide nanoparticles are visibly photoluminescent when excited at 379 nm (in water).

11. Miscellaneous compounds

Compound	Structure	Specific uses	Physical, photophysical and noteworthy properties
11.1 Acridine orange (AO) N,N,N′, N′-Tetramethylacridine-3,6-diamine		Fluorescent cationic dye, useful for fluorescence microscopy. Used in nucleic acid studies since it can be used to differentiate between DNA and RNA. AO intercalates with DNA (emitted radiation is green) and interacts electrostatically with RNA to form a complex where the emitted light is orange [126].	Similar spectrally to fluorescein when bound to DNA; λ_{ex} ~ 502 nm; λ_{em} max ~525 nm. When it associates with RNA λ_{ex} shifts to ~460 nm and λ_{em} max shifts to ~650 nm [126].
11.2 Avobenzone (Parsol)		Absorbs UV light over a wide range of wavelengths; widely used in 'broad spectrum' sunscreens.	UV absorber; λ_{abs} max = 357 nm. May photodegrade faster when used in combination with mineral UV absorbers like ZnO and TiO_2, though with the right coating, or doping, of the mineral particles this reaction can be reduced [154].
11.3 Anthraquinone		Building block of many dyes (e.g. **11.4**). Very important precursor for the production of several drugs. Precursors of anthraquinone are also used in the production of hydrogen peroxide.	Colourless and very photochemically active with high ϕ_T and hydrogen abstraction from hydrogen donor solvents. Ring substitution, and introduction of routes for excited-state deactivation, notably proton transfer, gives the anthraquinone dyes e.g. **11.4.**
11.4 Alizarin		Main ingredient for the manufacture of the madder lake pigments known to painters as rose madder and alizarin crimson. Used as a staining agent in biological research; stains free calcium and certain calcium compounds. Also used commercially as a red textile dye and, notably, is still the colour for French military cloth. Derivatives are commonly used as indicators of specific free ions and as pH indicators.	Reddish-orange solid and is very colour-fast.

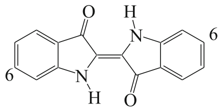
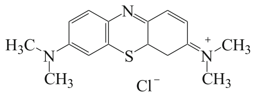
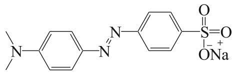
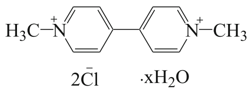
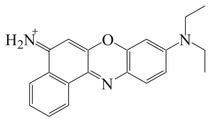
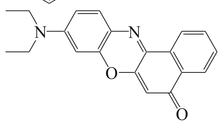
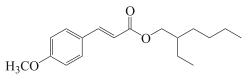
(continued)

Table 4.1 (continued)

Compound	Structure	Specific uses	Physical, photophysical and noteworthy properties
11.5 *β*-Carotene		*β*-carotene is a strongly-coloured red–orange pigment abundant in plants and fruits. Very low triplet energy acceptor. Energy transfer quencher of singlet oxygen.	λ_{abs} range ~350–520 nm; $\varepsilon \sim 139{,}500$ mol^{-1} dm^3 cm^{-1}; highly conjugated; deeply coloured; lipophilic, insoluble in water but soluble in diethyl ether and acetone. Very slightly soluble in methanol [155].
11.6 Benzophenone/hydroxybenzophenone		Benzophenone is a common photosensitiser. Free radical formation by hydrogen abstraction from solvent leads to use in UV-curing applications such as inks, imaging, and clear coatings in the printing industry. By way of contrast, hydroxy benzophenones with the OH group adjacent to the carbonyl are useful photostable UV absorbers because reversible proton transfer is an efficient deactivation route leading to very short lived excited-states.	Near UV absorbing with $\phi_T \sim 1$, and a triplet state which undergoes efficient solvent hydrogen abstraction with many solvents to generate ketyl and solvent radicals. Insoluble in water; soluble in benzene, THF, ethanol, propylene glycol.
11.7 Crystal violet (CV)		Used as a non-toxic stain for cells, DNA and bacteria. Important colouring dye for paper, printing inks and pen ink. CV is antibacterial and antifungal and thus finds medicinal used for treatment of skin conditions.	Intense visible absorption bands with λ_{abs} max = 590 nm; $\varepsilon \sim 87{,}000$ mol^{-1} dm^3 cm^{-1}. Absorption is pH dependent with the colour changing from purple through blue to yellow with decreasing pH. Shows very little fluorescence due to rapid non-radiative decay from the first excited singlet to the ground state in a few ps [156].
11.8 DABCO (1,4-diazabicyclo[2.2.2]octane)		Classic example of a hindered amine physical quencher of singlet oxygen: widely used as antioxidant to improve the lifetime of materials exposed to light, e.g. image dyes, laser dyes, probes and samples for fluorescence microscopy.	Effective physical quencher of singlet oxygen. Colourless and transparent throughout much of the UV, good solubility in many solvents.
11.9.9 DPBF (diphenylisobenzofuran)		Has been used as diagnostic tests for the presence of singlet oxygen in both chemical and biological processes.	λ_{max} in methanol = 410 nm; $\varepsilon \sim 22{,}200$ mol^{-1} dm^3 cm^{-1}. Strong blue fluorescence. DPBF reacts rapidly with singlet oxygen. The only reaction of DPBF with singlet oxygen is chemical. It does not react with ground state molecular oxygen or with the superoxide anion. The disappearance of DPBF in solution can be monitored by absorption and/or emission spectroscopy [124].
11.10 Disodium [NN′-ethylenebis (5-sulphosalicylideneiminato)] nickelate (II)		Typical Ni complex singlet oxygen quencher.	Water soluble, yellow/green complex.

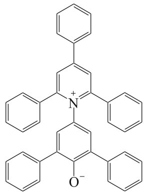
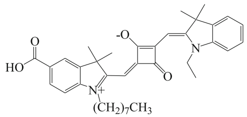
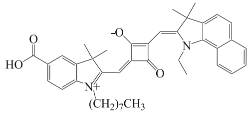
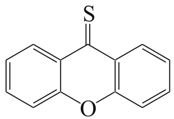
(continued)

Table 4.1 (continued)

Compound	Structure	Specific uses	Physical, photophysical and noteworthy properties
11.11 Indigo and tyrian purple		Indigo is mainly used as a fabric dye for the production of denim cloth for blue jeans. The closely related tyrian purple (mainly 6,6′-dibromoindigo), is a purple-red dye, obtained in minute amounts from sea snails and highly prized in antiquity.	λ_{abs} range ~520–680 nm; λ_{abs} max = 610 nm. Insoluble in water, alcohol, or ether; soluble in DMSO and chloroform. The dyeing process uses the reduced form of indigo, leuco-indigo, which is then oxidised to indigo on exposure to air.
11.12 Methylene blue (MB)		Widely used blue dye: a redox indicator in analytical chemistry (colourless when reduced or oxidised); efficient singlet oxygen sensitiser; standard compound for modelling TiO_2 photosensitised destruction of pollutants. The interaction of MB and DNA has been widely studied [157].	E_T = 133.9 kJ mol^{-1}; λ_{abs} max ~670 nm; red fluorescence; high triplet and singlet oxygen yield [124]. Characteristic absorption spectrum which is dependent on a number of factors, including protonation, adsorption to other materials, the formation of dimers and higher-order aggregates depending on concentration, solvent and other interactions.
11.13 Methyl orange		Widely used azo dye: pH indicator and model compound for photodegradation studies. Also finds use as a biological stain.	Yellow in alkali, red in acid.
11.14 Methyl viologen (MV)		Charge transfer quencher, electron acceptor and transfer catalyst in redox reactions, use as an electron relay in photochemical systems designed for solar energy conversion.	Reduced MV is intensely blue with a characteristic absorption spectrum which makes monitoring its formation and decay relatively easy, and viologens can be used in electrochromic displays.
11.15 Nile blue		Stain used in biology; it may be used with live or fixed cells, and imparts a blue colour to cell nuclei. Derivatives of Nile blue are potential photosensitisers in photodynamic therapy of malignant tumours.	High fluorescence quantum yield in non-polar solvents. The absorption and emission maxima of Nile blue are strongly dependent on pH and solvent.
11.16 Nile red		Stain and polarity indicator. Nile red stains intracellular lipid red. Will not fluoresce in most polar solvents, however when in a lipid-rich environment can be intensely fluorescent, with colours varying from a deep red to strong yellow-gold emission [126].	Generally excitation/emission is 485/525 nm (552/636 nm in methanol), however, the fluorescence of the dye is heavily dependent on the solvent used, and in polar solvents it does not fluoresce at all.
11.17 Octyl methoxycinnamate (OMC)		Common UV-B filter used in various cosmetic formulations.	λ_{abs} max = 310 nm; ε ~ 24,000 mol^{-1} dm^3 cm^{-1}. On exposure to sunlight undergoes *trans* to *cis* isomerisation [158].

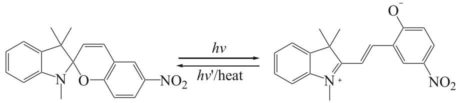
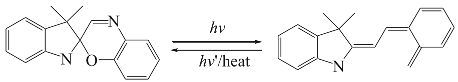
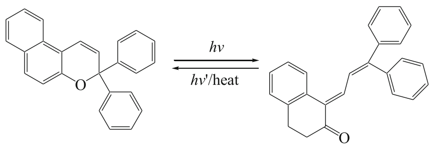
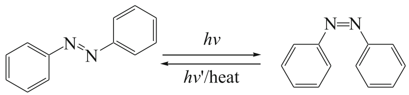
(continued)

Table 4.1 (continued)

Compound	Structure	Specific uses	Physical, photophysical and noteworthy properties
11.18 Reichardt's dye (2,6-Diphenyl-4-(2,4,6-triphenyl-1pyridinio)phenolate)		Solvatochromic dye for use as a solvent polarity indicator [158].	Charge transfer transition with very high solvatochromism. The range of transition energies is extremely large, from 263.8 kJ mol^{-1} (453 nm) for water to 147.1 kJ mol^{-1} (882 nm) for tetrachloromethane [159].
11.19 SQ1		Blue organic sensitiser dye for DSCs. Device efficiencies of ca. 4.5 % have been achieved in a single dye system; has shown promise for use in co-sensitised DSC devices with $\eta \sim 8$ % in combination with the Ru dye N719 [160].	High absorption coefficient ($\varepsilon \sim 160{,}000$ mol^{-1} dm^3 cm^{-1}) with a relatively narrow absorption band at λ_{abs} max $\sim$ 630 nm. Absorption shifts slightly bathochromically and broadens when anchored to TiO_2.
11.20 SQ2		Analogous to SQ1 but supposedly more stable in DSC devices. Commercialised for use in DSCs.	Slightly higher absorption coefficient than SQ1; λ_{abs} max $\sim$ 635 nm.
11.21 Xanthione		Xanthione, and aromatic thioketones in general, are exceptions to Kasha's rule, and as a consequence show unusual photophysics.	Red emitter. Direct fluorescence is from S_2 ($\phi_F = 0.002$–0.04) rather than S_1 due to a large S_2–S_1 energy gap ($\Delta E \sim 7600$ cm^{-1}). Strong spin–orbit coupling results in intense phosphorescence from the first triplet excited state T_1. Shows both E-type and P-type delayed fluorescence with thermally activated delayed fluorescence from S_1, and delayed fluorescence by triplet–triplet annihilation from S_2. The S_2 ϕ_F and τ (450 ps) are very solvent dependent [161].

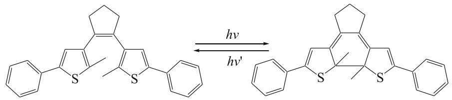
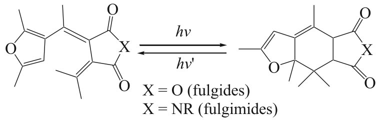
(continued)

Table 4.1 (continued)

Compound	Structure	Specific uses	Physical, photophysical and noteworthy properties
12. Photochromics. There are two main types of photochromic systems; (i) when the isomer obtained after irradiation is unstable, the back reaction occurs thermally and these are *T-type* (thermally reversible) and (ii) *P-type* (photochemically reversible), which contain structural units that can be converted to the original state photochemically, but not thermally. Most known photochromic compounds are T-type with two of the most extensively studied families being azobenzenes (**12.4**) and spiropyrans (**12.1, 12.2,** and **12.3**). Due to their thermal stability P-type switches are considered the most promising candidates for applications. Two common groups of P-type photochromics are diarylethenes (**12.5**) and furylfulgides (**12.6**). Photochromic compounds find applications in photonic devices such as erasable optical memory and photophysical switch components. Upon the discovery of the photochromic reactions of spiropyrans, (made by Fisher and Hirshberg in 1952) Hirshberg suggested using the phenomena for a "photochemical erasable memory", research into which continues today.			
12.1 Spiropyran		Extensively studied for use in many applications including: data storage, temperature measurement, as a trigger for biological reactions and in molecular optical switches [162].	Pronounced change in geometry on going from the spiropyran (SP) to the merocyanine (MC) form (perpendicular to planar), that occurs on the sub-ns time scale and shifts the absorbance from the UV into the visible spectral range. This is due to the planarity of the MC form, which allows the previously uncoupled π-systems of chromene and indoline to become extended across the entire structure [162, 163].
12.2 Spirooxazine		Proposed use in displays, as filters, in eye-protective laser goggles, in self-developing photography, photoswitching of protein activity, and in optical data storage.	Analogous to **12.1**. Different relaxation times (a long-lived and short-lived component) at various temperatures indicate two distinctly different pathways back to the closed form (SP) [164].
12.3 Naphthopyran		Best known for their commercial application in the ophthalmic lens industry. Other applications include electronic devices, optical memories and photo-switches.	UV irradiation of the colourless closed form results in electrocyclic ring opening of the pyran moiety *via* cleavage of the C(sp^3)–O bond. This produces a distribution of MC isomers which are intensely coloured. As is the case for **12.1** and **12.2,** this is due to their extended conjugation and *quasi*-planar conformations [165].
12.4 Azobenzene		The photochromic *trans–cis* isomerisation of azobenzenes has been used extensively in molecular switches. Monolayers can provide light-controlled changes in surface properties and when incorporated into crown ethers gives switchable receptors.	Undergoes a reversible photochemical *trans–cis* isomerisation upon irradiation with UV light (~ 340 nm) [64]. The *cis* form is energetically unfavourable and as such returns back to the *trans* form by a thermal isomerisation pathway or *via* irradiation with longer wavelength visible light.

(continued)

Table 4.1 (continued)

Compound	Structure	Specific uses	Physical, photophysical and noteworthy properties
12.5 Dithienylethene		Can be used in both solid state and solution. Proposed use in optical data storage.	Undergoes open-closed ring isomerisation and not *cis–trans* isomerisation. Thus isomerisation requires very little change of shape which results in isomerisation in a solid matrix proceeding more quickly than with most other photochromic molecules. Closed ring form is thermally stable; ring opening is achieved with visible light.
12.6 Fulgides and fulgimides		Used in recording media, particularly in erasable optical memory devices.	Possess high temperature stability and high fatigue resistance; usually lack fluorescence but fluorescent derivatives are possible. The closed coloured form can be reversed to the open bleached form by visible light (>500 nm).

The aim of this chapter was to provide an overview of the most common and useful photochemical materials and their primary photophysical properties that allow for use, or potential use, in a given application. In this vein, we have presented a comprehensive table detailing the most common structures, physical and photophysical properties, and specific applications of each of the classes of photochemical materials discussed.

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