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Photoinduced Charge Transfer: from Photography to Solar Energy

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ABSTRACT

To celebrate the centenary of *Science Progress* we offer a short survey of the progress made over the past one hundred years in the research and application of photoinduced charge transfer. After a brief historical overview and introduction to photoinduced charge transfer, we discuss developments in the theory and practice of photography, photovoltaics, photocatalysis, fluorescent probes and chemosensing.

Keywords: chemosensing, fluorescent probes, photocatalysis, photography, photoinduced charge transfer, photovoltaics, solar energy.

1. Introduction

1.1. Historical overview

In 1917 the world of atomic chemistry was that of the Old Quantum Theory of Planck, Einstein, Bohr and Sommerfeld. The electron had been known for twenty years, identified as the particle of cathode rays by Thompson in 1897. Planck had introduced quantisation in his theory of the emission spectrum of a ‘black-body’ radiator in 1900; Einstein used ‘light quanta’ to explain the photoelectric effect and the low temperature heat capacity of solids; and Bohr, in 1913 ‘solved’ the problem of atomic structure thrown up by Rutherford’s studies of alpha particle scattering by combining Rutherford’s model with Planck’s quantisation.¹

Within 10 years, the Old Quantum Theory was replaced by the new quantum (or wave) mechanics of Schrödinger and Heisenberg, and the structure of atoms and molecules and the interaction between matter and light had been described in much the same terms we use today.^{2,3}

But the experimental study of the interaction between light and chemical change and light and electricity already had a long history in 1917. Two hundred years earlier, Schulze had observed the light sensitivity of silver salts and used it to make images of stencilled words on chalk containing a little silver nitrate, although he was unable to make the image permanent. The chemical effects of visible and ultraviolet light were studied by numerous scientist in the following hundred years.⁴ The first permanent photographic image, which is not silver halide based but rather a bitumen photoresist, is due to Niépce in 1826, and Daguerre and Fox-Talbot introduced their Daguerreotype and Calotype silver halide photographic processes in 1839 and 1841, respectively. At around the same time, 1839, Becquerel created the world’s first photovoltaic (PV) cell from an illuminated silver chloride electrode in an acidic solution.⁵ By 1917, technologies which we know now involve photoinduced charge separation were in operation across the world with every click of a camera shutter and in every engineer, architect, and pattern-maker’s blue-print. Figure 1 give a time-line of significant developments related to photoinduced charge transfer.⁶

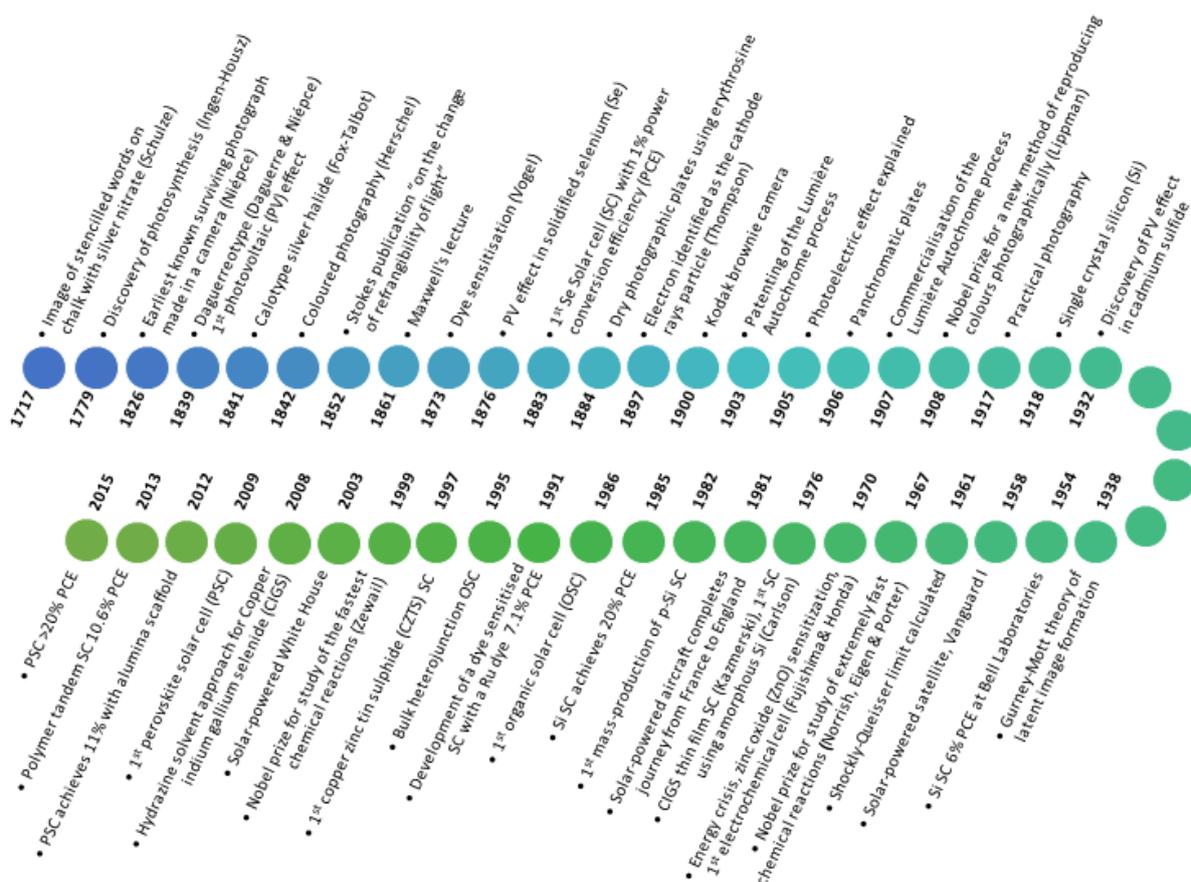


Figure 1. Time-line of developments related to photoinduced charge transfer.

2. Concepts and Applications

We now interpret atomic and molecular structure in terms of the electronic orbitals of the Schrodinger equation. The absorption of a photon (light ‘particle’ of energy $h\nu$ where h is Planck’s constant and ν the frequency) causes the transition of an electron from one orbital to a higher energy orbital to give an excited-state. The excited-state has a different electronic distribution to that of the ground-state. In some cases, this can involve quite significant charge separation, and, since the excited-state also has considerable excess energy over the ground-state, its chemistry is often very different from that of the ground-state. Our discussion here will concentrate on processes involving the photoinduced movement of charge, charge transfer.

Charge transfer (CT) is sometimes used in a broad sense referring to the transfer of: energy, charge, electrons and/or ions,⁷ it can be intra or intermolecular. Excited-states have lower ionisation potentials and greater electron affinities than their corresponding ground-states. Thus the probability that they react by charge transfer processes is greater than that for ground-state molecules. Table 1 shows the general processes involved, while Figure 2Figure 1 gives pictorial representations of the key processes of energy and electron transfer.

Table 1. Photoexcitation and subsequent charge transfer processes between A and B, which may or may not be linked together by L.

Processes		Intermolecular	Intramolecular
Photoexcitation		$A + h\nu \rightarrow A^*$	$A-L-B + h\nu \rightarrow A^*-L-B$
		$B + h\nu \rightarrow B^*$	$A-L-B + h\nu \rightarrow A-L-B^*$
Charge transfer		$A^* + B \leftrightarrow (A\cdots B)^*$ $B^* + A \leftrightarrow (B\cdots A)^*$	$A^*-L-B \leftrightarrow \begin{matrix} L \\ / \quad \backslash \\ (A\cdots B)^* \end{matrix}$
Oxidative	Electron transfer	$A^* + B \rightarrow A^+ + B^-$	$A^*-L-B \rightarrow A^+-L-B^-$ $A^*-L-B \rightarrow A^+-L + B^-$
Reductive		$A^* + B \rightarrow A^- + B^+$	$A^*-L-B \rightarrow A^-L-B^+$ $A^*-L-B \rightarrow A^-L + B^+$
Energy transfer		$A^* + B \rightarrow A + B^*$	$A^*-L-B \rightarrow A-L-B^*$

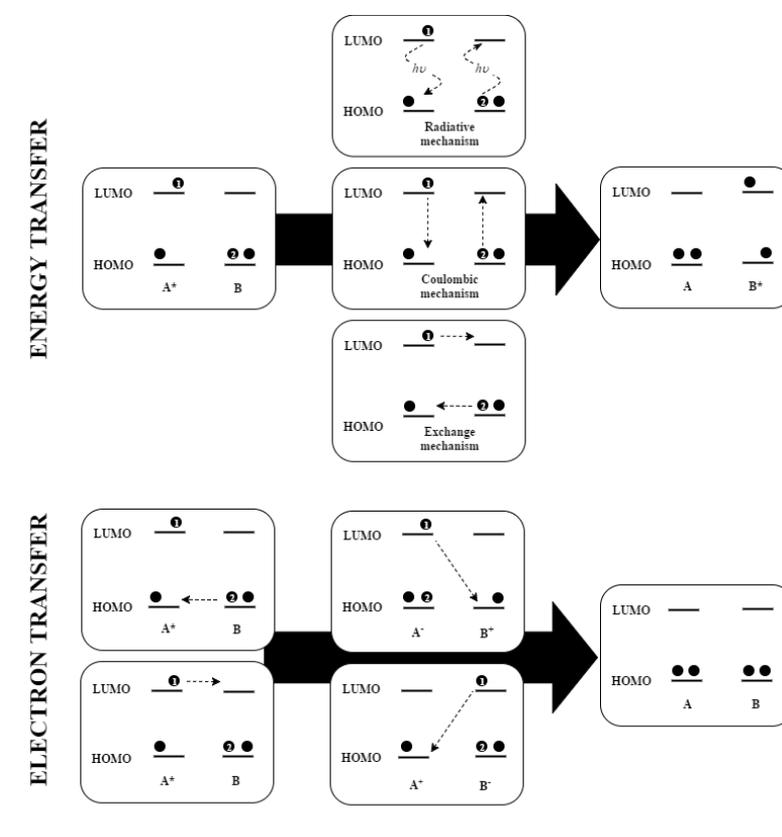


Figure 2. Pictorial representations of radiative, coulombic/Förster and exchange energy transfer, and electron transfer, adapted from refs. ^{8,9}. HOMO and LUMO are the highest occupied and the lowest unoccupied molecular orbitals, respectively. Note that Figure 2 is a simplified schematic; we have not assigned spins to the electrons, although this is a topic we discuss towards the end of this review.

2.1. Photography

Fox-Talbot's 1841 Calotype process,¹⁰ laid the basis of the positive-negative photographic process involving the 'capturing' of a latent image in a silver halide 'emulsion' of microcrystals, followed by chemical 'development' and 'fixing' to give an image. By 1917 many improvements had been made to give more sensitive emulsions more stable prints, and easier to use processes.^{11,12} The most important technological advance for the discussion here was dye sensitisation.

Silver halides absorb in the UV and blue spectral region but not much beyond, so early photographs lack a green and red response, and therefore sometimes give very obvious poor tonal rendition. In fact, Maxwell's famous 1861 lecture at the Royal Institution where he demonstrated his theory of 'three colour reproduction' by superposition of projections through three separate images of a brightly coloured tartan ribbon recorded in the red, green, and blue spectral region made in collaboration with the photographer Sutton¹³ only just about worked because the filter dyes used also give different UV transmissions and fabric dyes absorb differently in the UV as well as the visible.¹⁴ Dye sensitisation,¹⁵ (the primary mechanism of which we now know is electron injection into the silver halide crystal from a photoexcited adsorbed dye), was discovered by Vogel in 1873.¹⁶ 'Dry photographic plates' using erythrosine (Figure 5G) as the green sensitising dye were introduced in 1884 and by 1906 'panchromatic plates' were available which had both red and green sensitising dyes, and which could give a tonal response across the whole visible spectrum comparable to that experienced by the human eye.¹⁷

So practical photography was in an advance stage by 1917:¹¹ black and white photography was widespread as an amateur hobby and recording medium for family events (the Kodak Brownie camera with roll film was introduced in 1900 at a price of \$1.00). It was a well-established art form, and recording medium for news, social commentary, historical record, and exploration.¹⁸ Practical colour photography was available through the Lumière Autochrome process, based on a light filtration 'screen' process using a mosaic of red, green, blue, dyed starch grains, overlain on a silver halide emulsion i.e. essentially black and white made colour through a matrix of colour micro-filters. Colour motion pictures using additive red, green, blue processes were being developed, and Lippman had been awarded the 1908 Nobel Prize in Physics "for his method of reproducing colours photographically based on the phenomenon of interference".¹⁹

However, in photography, like many technologies with immediate commercial application, scientific understanding lagged behind practical development. Insight into the science of silver halide photography had to wait for an understanding of the structure and photoelectronic properties of dyes and semiconductors, and the Gurney-Mott theory of latent image formation in 1938.²⁰

Silver halides are semiconductors, and the electronic structure and photoelectronic properties of semiconductors is described in a different way from that in molecules.²¹ In molecules, electronic orbitals are localised on molecular species; in semiconductors there are two 'bands' of orbitals, which can be considered to be the results of overlap of many molecular orbitals, which extend across the whole structure: the valence band holds the valence electrons, while above this, and separated by the semiconductor band-gap, is the conduction band. Direct absorption causes the transition of an electron from the valence to the conduction band, both the resultant positively charged hole in the valence band, and the negatively charged electron

in the conduction band are mobile and can be trapped at various trap sites in the semiconductor structure.

Figure 3 shows the general photo-electronic properties of a semiconductor, and the process of dye sensitisation. In the unsensitised photographic process, the conduction band electron produced by direct excitation is trapped at a shallow trap site, and subsequently leads to reduction of an Ag^+ to Ag^0 . Repetition of this process by successive photon absorption events leads to a speck of at least 4 silver atoms which can catalyse reduction of the whole silver halide grain by the chemical developer used in the development process. The distribution of silver grains with and without these catalytic $\text{Ag}_{>4}^0$ sites is the invisible latent image. In practise, because of loss processes, it takes at least ~ 10 -15 photons to create one $\text{Ag}_{>4}^0$ site.²²

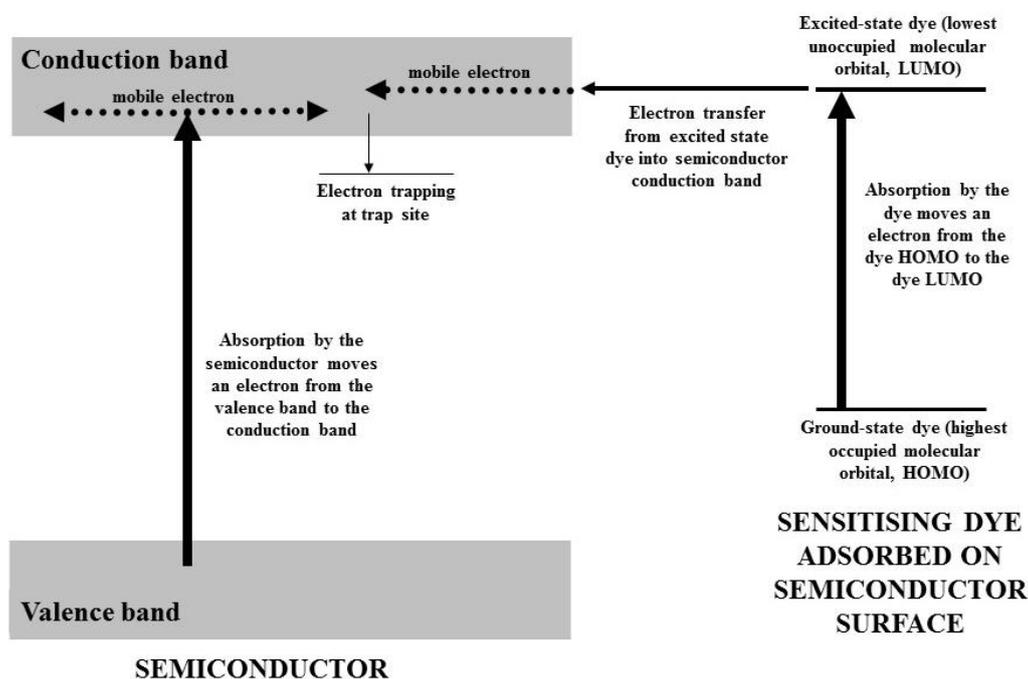


Figure 3. Direct absorption and dye sensitisation in semiconductors.

In dye sensitisation, the dye, which is present at a very low concentration and is adsorbed onto the surface of the silver halide grain, absorbs the photon to generate an excited-state which then injects an electron into the silver halide conduction band. This leaves an oxidised dye molecule, and while the fate of the oxidised dye is not so important in photography, highly efficient regeneration of the dye from oxidised dye is essential in dye sensitised solar energy conversion discussed later.

The ability to make three different emulsions sensitive to blue, green, and red light, also allowed the possibility of colour reproduction if the colour response could be coupled with a coloured output, for example in the form of a dye associated with each blue, green, red sensitive emulsion layer. Great advances in colour photography were made from the 1920's onwards until by the mid to latter part of the 1900's colour photography was a very mature industry supported by a well understood science.^{23,24} Much, but not all, colour photography is now made

using digital technologies, even so, the ideas developed, in part at least in response to silver halide photography, of semiconductor structure, photochemistry, and dye sensitised charge injection, remain key concepts in two of the emerging technologies discussed here, namely, photo-purification of water by semiconductors, and PV solar energy conversion.

2.2. The ferrioxalate chemical actinometer and blueprints

A chemical actinometer measures the number of photons in a light beam by the chemical reaction the beam produces. The most useful is probably the ferrioxalate actinometer.^{25,26} Photolysis of ferrioxalate, $[\text{Fe(III)(ox)}_3^{3-}]$, in solution generates ferrous ions in a high quantum yield²⁷ by a ligand to metal charge transfer (LMCT) transition. The amount of Fe(II) produced can be measured spectrophotometrically using phenanthroline (phen) which gives an intensely coloured red $\text{Fe(II)(phen)}_3^{2+}$ complex.

The formation of a blueprint involves similar reactions, although the first iron complex used by Herschel, who introduced the process as the *Cyanotype* in 1842,^{10,28} was ferric citrate rather than ferric oxalate. In the blueprint/*Cyanotype* process, the paper is sensitised with a mixture of ferric citrate and potassium ferricyanide and upon exposure to light the photoproducted Fe(II) ions complex with ferricyanide to give the insoluble pigment Prussian Blue with its characteristic blueprint colour (Figure 4 **Error! Reference source not found.** shows a modern *Cyanotype*).



Figure 4. A modern Cyanotype print of the Paço das Escolas (Scholars' Square) of Coimbra University. Printed from a negative on photoinkjet paper made from a scanned B&W 35 mm negative.

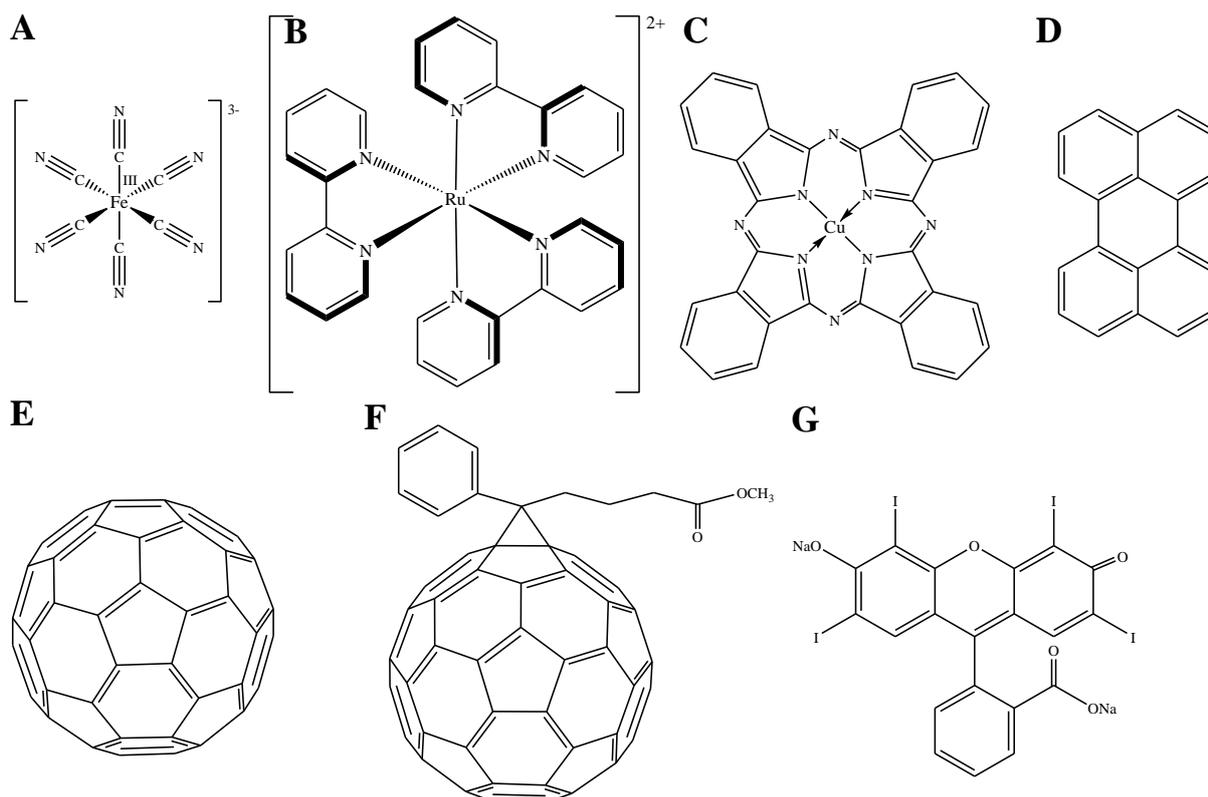


Figure 5. Structure of (A) ferricyanide, (B) $\text{Ru}(\text{bipy})_3^{2+}$, (C) copper phthalocyanine (D) perylene, (E) fullerene C60 (buckminsterfullerene), (F) PCBM (phenyl-C61-butyric acid methyl ester) and (G) erythrosine.

2.3. Molecular photoredox reactions, solar energy conversion by water splitting?

The energy crisis of the early 1970's brought urgency to the development of methods for solar energy conversion and storage. The scientific community response since then has been an enormous body of work on ways of converting light energy into thermal, electrical or chemical energy.

One approach is to catch the photon energy in formation of molecular excited-states and use excited-state photoredox reactions to split water into H_2 and O_2 . The H_2 produced could then be stored as an environmentally friendly chemical fuel for a 'hydrogen economy' to replace the 'oil economy'.^{29,30}

Much early work in the field used porphyrins,³¹ and ruthenium polypyridyl complexes, such as $\text{Ru}(\text{bipy})_3^{2+}$ (Figure 5B).³² $\text{Ru}(\text{bipy})_3^{2+}$ is an orange complex with a relatively long lived charge transfer triplet state made in ~100% yield, and has ground and excited-state redox couples which straddle those for water reduction and oxidation. Figure 6 shows the redox energetics and processes involved in this approach.

While water oxidation and water reduction can be made quite efficient individually using sacrificial electron donors or acceptors, coupling the two together has, to date, been unsuccessful in any practical sense. However, the enormous body of research on photoredox

reactions of metal complexes since the 1970s has provided a firm foundation for much subsequent work on photoredox and photocatalytic chemistry, as well as colloidal metal, and metal oxide, redox-catalysis. In particular, the work on photoredox reactions of Ru(II) compounds led directly to the development of dye sensitised solar cells.

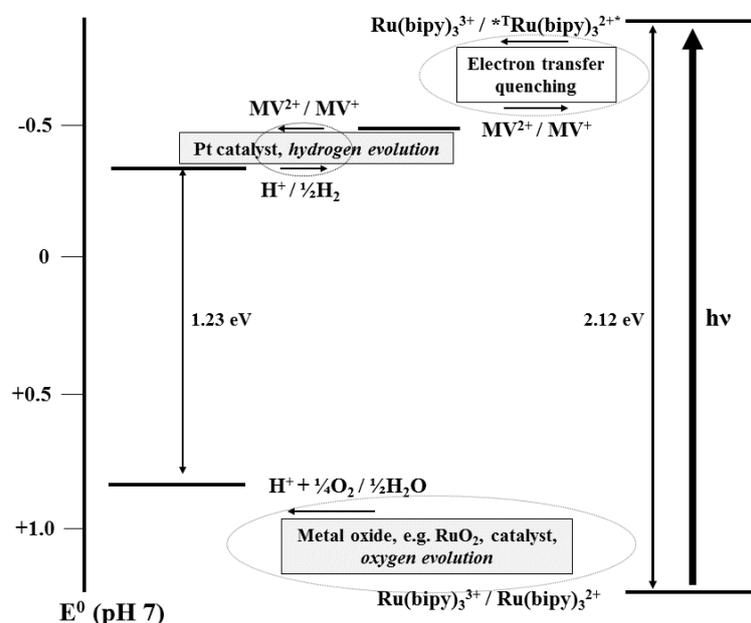


Figure 6. Energetics of redox processes in water splitting via electron transfer quenching of $*^T Ru(bipy)_3^{2+}$, where $*^T$ signifies the triplet excited state.

2.4. Photoredox reactions at electrodes – solar energy conversion by semiconductor water splitting, and photocatalytic water and air purification

Another way of photocatalytic water splitting involves light excitation of a semiconducting material like TiO_2 to generate electrons (e^-) and holes (h^+), followed by a series of charge transfer steps at the semiconductor-water interface to dissociate water into H_2 and O_2 . In 1970, Fujishima and Honda reported the first electrochemical cell which successfully evolved H_2 from water solutions using TiO_2 .³³ The cell consisted of two compartments (Figure 7) which housed a TiO_2 electrode (where water was oxidised to O_2) and a platinum (Pt) counter-electrode (where water was reduced to H_2). Since then much research has been conducted to develop materials and cells with better solar to hydrogen conversion efficiencies. The key challenges lie in the difficulty of designing a photocatalyst which can (i) absorb most of the visible solar spectrum, (ii) dissociate water without the need of much additional applied electrical bias and (iii) be water stable.

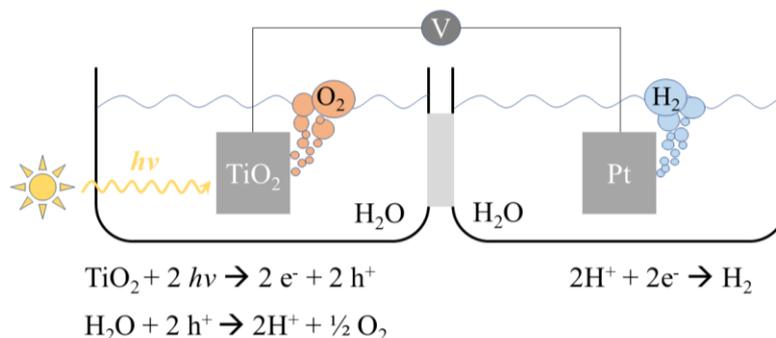


Figure 7. Electrochemical cell for water splitting, in which TiO_2 is the light absorber and active water oxidising catalyst. The charges are then used up at the two electrodes for the half-cell reactions for water splitting.³³

In addition to water splitting, photocatalysis has potential in other applications including waste water and air purification, self-cleaning surfaces and CO_2 reduction. For example, for water treatment, TiO_2 is the most frequent choice as a catalyst, because of its ability to drive single step oxidation of water to hydroxyl radicals.³⁴ Once created, the hydroxyl radicals are extremely reactive and break most bonds in organic molecules. Whilst waste water treatment via photocatalysis is not yet commercially viable due to low rates of destruction of molecules, self-cleaning surfaces employing this process are used in different parts of the world.³⁵

2.5. Photovoltaics

2.5.1. Dye Sensitised Solar Cells

The working mechanism of dye-sensitised solar cells (DSSCs) is analogous to the mechanism described for the sensitisation of silver halide in photography. In DSSCs charge generation and transport are separated and facilitated by a dye sensitizer adsorbed on a semiconductor (Figure 3) of an appropriate band gap (usually TiO_2 , but others such as ZnO have also been used).^{36,37} An electrolyte redox couple is needed, usually I^-/I_3^- or $\text{Co(II)}/\text{Co(III)}$, to reduce the oxidised dye remaining after electron injection into the semiconductor. Electron transfer from the electrolyte to the dye prevents the recombination of the electron injected into the semiconductor with the oxidised dye, and the redox couple receives an electron from the counter electrode, which is supplied from an external load, to complete the circuit (Figure 8). In an optimised DSSC electron injection and transport is faster than the recombination processes thus minimising losses through recombination pathways (Figure 8).

Sensitisation of ZnO was initially carried out in the 1970s but the big breakthrough in the field was made in 1991 when O'Regan and Grätzel published work on sensitised nanospheres of TiO_2 with a Ru dye to produce a DSSC with an efficiency of 7.1%.³⁸ This was a significantly higher efficiency than had previously been reported and is attributed to the increase in surface area, and hence dye loading, from using TiO_2 nanoparticles. Between 1991 and 2017 lab based efficiencies increased steadily to just over 13%.^{39,40} Many Ru dyes with various ligands have been investigated along with several other classes of dyes such as: triaryl amines,^{41,42} squaraines,⁴³ thiophenes,⁴⁴ indolines,⁴⁵ coumarins,⁴⁶ porphyrins⁵⁰ and phthalocyanines⁴⁷ in an

effort to improve the light harvesting efficiency of devices. Generally, organic dyes have higher extinction coefficients than Ru dyes, and can offer better response in the near-infrared region, but have narrower absorption bands and can have problems with aggregation.⁴⁴ The development of co-sensitisation (the use of more than one dye) allows the absorption over complementary regions of the visible spectrum to increase the overall light harvesting efficiency of devices.^{39,40,48,49} Co-sensitisation, together with the use of cobalt electrolytes, has led to some of the highest performing DSSC devices.^{39,40,50} For example the use a zinc porphyrin (YD2-o-C8) co-sensitised with organic dye (Y123) yielded 12.3% efficiency under standard conditions (AM1.5) and 13% at low light level conditions.⁵⁰

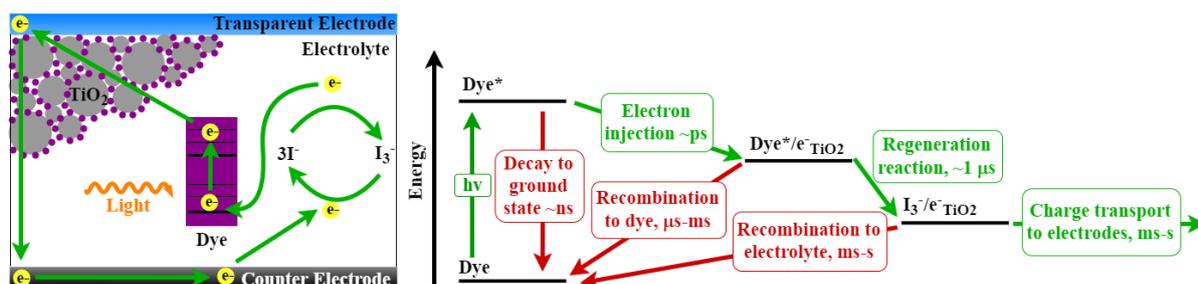


Figure 8. Structure of a typical dye-sensitised solar cell (left) and electron transfer processes within a device (right), desirable pathways are shown in green while recombination pathways are shown in red.

The first publication on organohalide lead perovskite materials for solar cells, where the dye component of a DSSC is replaced with a perovskite material, was in 2009.⁵¹ (The term perovskite refers to particular crystal structure of general formula ABX₃.) The perovskite materials reported were methylammonium lead bromide and methylammonium lead iodide producing efficiencies of 3.1 and 3.8%, respectively,⁵¹ however, these devices were fairly unstable as the electrolyte dissolved the perovskite material. Two years later Park *et al.* replaced the liquid electrolyte with a solid hole transport material producing a cell with 6.5% efficiency and Snaith *et al.* achieved an efficiency of close to 11% using an alumina scaffold. The device efficiencies have continued to rise, with the current certified record efficiency of ~22%.^{52,53}

The work using alumina produced a step change in the field, alumina is an insulator and thus charge injection is not energetically possible at this interface, showing that the perovskite material itself has sufficient charge transport properties to function efficiently (more akin to a thin-film solar cell). This widened the research field increasing the potential device architectures that could successfully be employed.⁵⁴⁻⁵⁶ The current major challenge is the stability of the perovskite material which is susceptible to degradation by moisture, and the combination of light and oxygen.⁵⁷ To overcome this, a range of mixed-cation and mixed-anion perovskites have been developed that have improved stability, changing the halides can also change the band gap (e.g. replacing some of the iodide anions with smaller bromide anions) allowing the colour to be tuned.⁵⁸⁻⁶⁰ There are also environmental concerns over the use of lead that will need to be addressed for successful commercialisation, possibly through the use of encapsulation or lead replacement. The current situation is that, despite the concerns, the high efficiencies, which are on par with market dominating silicon PVs, but at a potential fraction of the monetary and energy cost, have drawn unparalleled research interest.

2.5.2. Organic Solar Cells

Organic solar cells (OSC) are devices, with a very thin film of a polymer or organic molecule between two conductive electrodes. Light absorption initiates a series of very fast charge transfer processes that lead to the formation of electrical charges (Figure 9).

The field of organic PVs started in 1986, when Tang *et al.* described the first operational device consisting of a double-layered structure of copper phthalocyanine and a perylene derivative (Figure 5C and D, respectively).⁶¹ This device demonstrated that solid organic electron donor-acceptor interfaces can undergo charge transfer and then generate electrical current. Although not efficient, this first device sparked widespread interest in organic PVs, which holds to this day. OSC offer the numerous advantages over other PVs, including cheap production via printing, the possibility to make the devices on flexible materials/substrates, and their efficient operation at low light levels, making possible their use for indoor applications.

The most efficient devices are not simple bilayer structures, but are based on bulk-heterojunction films with finely mixed donor and acceptor materials. The materials are usually conjugated polymers, small molecules and fullerenes. Many new donors and acceptors have been developed in the past ten years providing much better control over light harvesting and charge transfer at the donor-acceptor interface. This has resulted in very reasonable device efficiencies of ~12% keeping this technology attractive for researchers and commercialisation.⁶²⁻⁶⁴ However, a further boost in efficiency and long terms stability are required to make organic solar cells competitive with silicon or perovskite PVs.

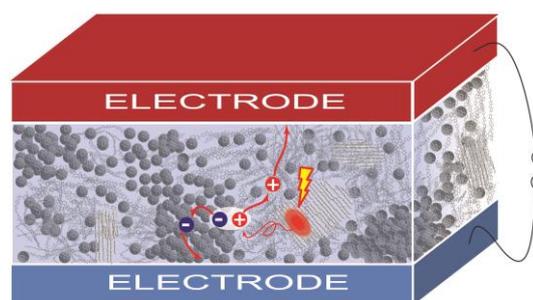


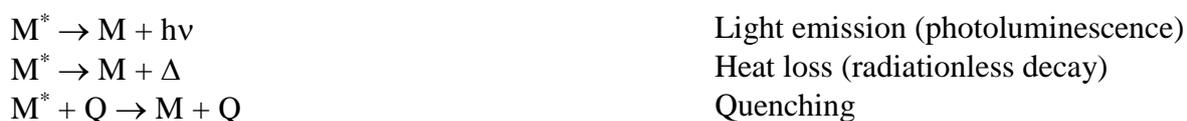
Figure 9. Illustration of the structure of typical polymer-fullerene organic photovoltaic device. It depicts the charge transfer process in the device and the movement of the electrical charges towards the electrodes. Taken with permission from ref.⁶⁵.

2.6. Probes and Chemosensors

The emission of light by molecules as either fluorescence or phosphorescence provides the basis of highly sensitive analytical methods for studying and imaging chemical and biological systems. The sensitivity is such that, under appropriate conditions, it is possible to detect close to the level of single molecules. Stokes was probably the first person to demonstrate the potential of this technique when he showed that light is emitted at longer wavelengths than

where it is absorbed.⁶⁶ This difference, normally referred to as the Stokes shift, has many practical applications, such as in fluorescence brightening agents, which are included in detergents, paper and other commercial products, where they absorb light in the ultraviolet region of the spectrum and emit in the blue to make things seem “whiter than white”. You have probably seen the effect when white clothes appear blue upon irradiating with ultraviolet light. It is also fundamental for providing the high sensitivity used in the analytical applications of luminescence techniques.

Optical sensors and probes may involve either the absorption or emission of light. This has been described in detail elsewhere.⁶⁷ In this section we will concentrate on photoluminescence (PL) sensors, in which changes in the intensity, lifetime or other properties of light emitted by one molecular system are produced by the interaction with a second species, the analyte. One typical case involves “quenching”, where the second molecule reduces the intensity of light emitted by the first. The excited-state of the first molecule (M^*) is produced by absorption of light, and can either decay by light emission, heat loss, or “quenching” by the analyte (Q).



The quenching competes with the other two processes in a way which depends on the concentration of the analyte. This will lead to a decrease in both the intensity and lifetime of the PL, and by measuring either of these we can have a direct measure of the concentration of Q. This is frequently expressed mathematically as the Stern-Volmer equation, which expresses the intensity (I , I_0) or lifetime (τ , τ_0) of fluorescence as a linear function of the concentration of concentration of Q. K_{sv} is the so-called Stern-Volmer constant, and the subscript 0 refers to the property in the absence of quencher.

$$I_0/I = \tau_0/\tau = 1 + K_{sv}[Q]$$

Measurements of either fluorescence intensity or lifetime can, then, directly provide information on quencher concentration. Such luminescence sensors have considerable advantages over other techniques; they are cheap, respond rapidly to changes in concentration, do not require any electrical contacts, and can easily be miniaturised. Since the field of PL sensors is huge, we will limit ourselves to three important examples in which charge or electron transfer are involved.

The applications of the metal complex $Ru(bipy)_3^{2+}$ (Figure 5B) in solar energy conversion through water splitting or DSSCs have been discussed earlier in this article. The same complex has a very nice light emission in the visible region. This and closely related compounds are widely used as PL sensors for oxygen.^{68,69} Emission is from the triplet metal to ligand charge transfer (MLCT) state, which has a sufficiently long lifetime to readily be quenched by a variety of species through energy or electron transfer. One of the most important examples is molecular oxygen, and this is the basis for luminescent oxygen sensors, which are finding applications in areas as diverse as blood gas analysis, oceanographic deep sea oxygen measurements, combustion, food product quality control, and pressure sensitive paints for studying the behaviour of cars and planes in wind tunnels. The metal complexes can be incorporated into a wide variety of supports, including synthetic polymers, siloxanes and zeolites. These are

chosen to optimise efficiency under the working conditions, which may in some cases involve extremes of temperature or pressure. These luminescence-based sensors, sometimes called optrodes, are now one of the most convenient ways of measuring oxygen concentration in solution.

Another area where PL quenching based on charge transfer is of great practical importance is in explosives sensing. Current global political instabilities and the increasing awareness of terrorist attacks are driving the development of more sensitive techniques for the detection of explosive materials. Nitroaromatic compounds are a very important group of these, and are used as both commercial and military explosives.⁷⁰ One particularly well known examples is 2,4,6-trinitrotoluene (TNT, Figure 10A). Nitroaromatic compounds have a very high electron affinity, i.e. a tendency to attract electrons, aromatic molecules in their excited-states are good electron donors. If the aromatic molecule is also luminescent, interaction with the nitroaromatics will lead to quenching, providing a good way of detecting and quantifying TNT or other explosives. The sensitivity can be enhanced still further through fluorescence quenching using conjugated polymer-based PL sensors^{71,72} Conjugated polymers are formed by joining together a series of π -conjugated systems, such as benzene, acetylene, aniline and thiophene to form highly conjugated systems in which the electrons are delocalised over the whole molecule. They behave as organic semiconductors, and examples are given in Figure 10C-F. In some cases, these are luminescent. Such systems are now widely used in large area flat screen light emitting diode televisions, computer monitors and other displays. However, they are also becoming increasingly important as light emitters in various optical sensors and probes. When the polymer is excited by absorption of light, the excitation is delocalised along the polymer chain as what is termed an exciton. Emission can be from anywhere along the chain, and these are termed amplifying fluorescent polymers. This leads to an enhancement of the fluorescence quenching by analytes, such as TNT, which makes these excellent candidates for highly sensitive explosive sensors. An example of the principle of superquenching is shown in Figure 10C where the fluorescence of the conjugated polymer poly(9,9-dioctylfluorene-2,7-diyl)-co-bisthiophene] (PF2T) is quenched by dinitrobenzene. This forms the basis of a handheld device for the detection of explosives.⁷³

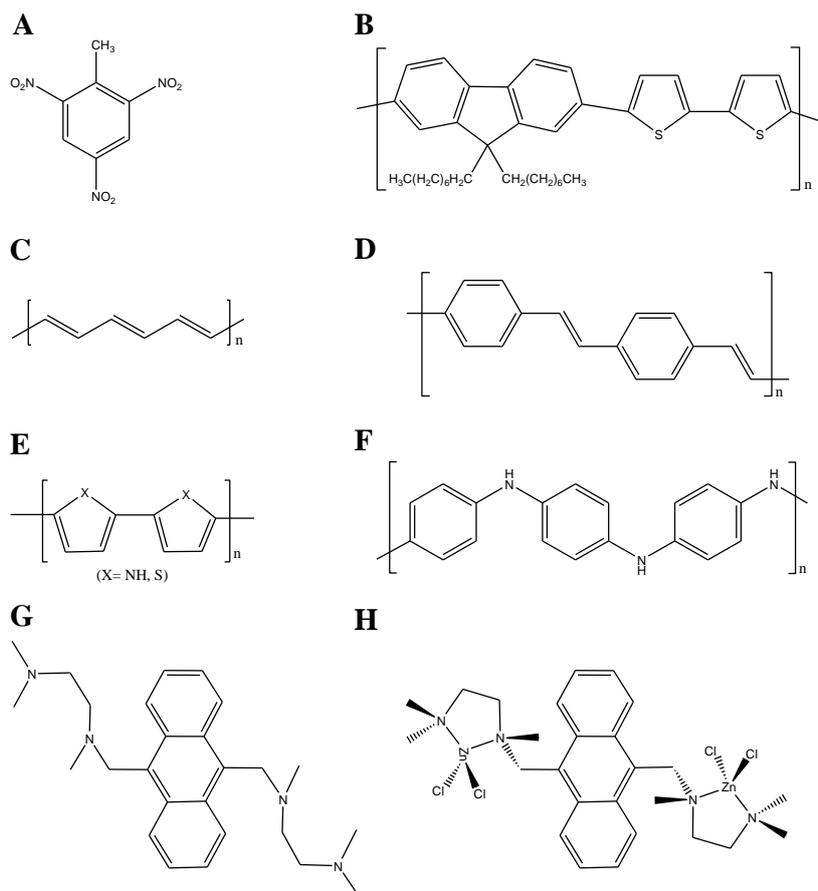


Figure 10. Structures of (A) 2,4,6-trinitrotoluene (TNT) and examples of conjugated polymers: (B) poly(9,9-dioctylfluorene-2,7-diyl]-co-bisthiophene (PF2T), (C) poly(acetylene); (D) poly(*p*-phenylene vinylene); (E) poly(pyrrole) ($X = \text{NH}$) and poly(thiophene) ($X = \text{S}$), (F) poly(aniline), (G) anthracene based chemosensor and (H) its zinc complex.

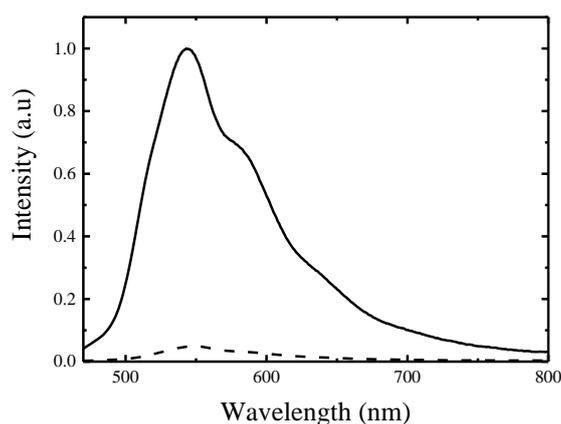


Figure 11. Fluorescence spectrum of PF2T in ethylcellulose films alone (solid line) and exposed to dinitrobenzene (dashed line).⁷³

As a final example, we choose a system where interaction of the analyte with the sensor leads to an increase in fluorescence intensity. The anthracene derivative in Figure 10G has two substituted ethylenediamine groups chemically bonded to the aromatic moiety, and, unlike many anthracene derivatives, is not fluorescent. Amine groups are known to be capable of

transferring electrons to excited aromatic molecules, and electron or charge transfer quenches the normal fluorescence of the anthracene. However, ethylenediamine groups also bind to metal ions, such as zinc(II), very strongly to form chelate complexes. In contrast to compound A, the zinc complex in Figure 10H is strongly fluorescent (see emission spectra in Figure 11).⁷⁴ This complexation “switches on” the fluorescence, and this provides the possibility of probing metal ions such as zinc and calcium, which is particularly valuable for studying them in biological systems. Compounds such as this, containing a fluorescent unit (the fluorophore), a binding site, and a mechanism by which one affects the other are termed “fluorescent” chemosensors. A large number of these have been prepared, and are valuable for sensing metal ions, protons (H^+), anions, and various organic and biological targets.⁷⁵

2.7. Optimisation of device efficiencies; triplet or singlet state photochemistry?

In this article we have concentrated on the general charge transfer features of the technologies described, rather than the detailed photochemistry, but one important aspect of photochemical behaviour is worth discussing because it is a very active area of current research in device design; that is the difference in the properties of triplet and singlet excited states.

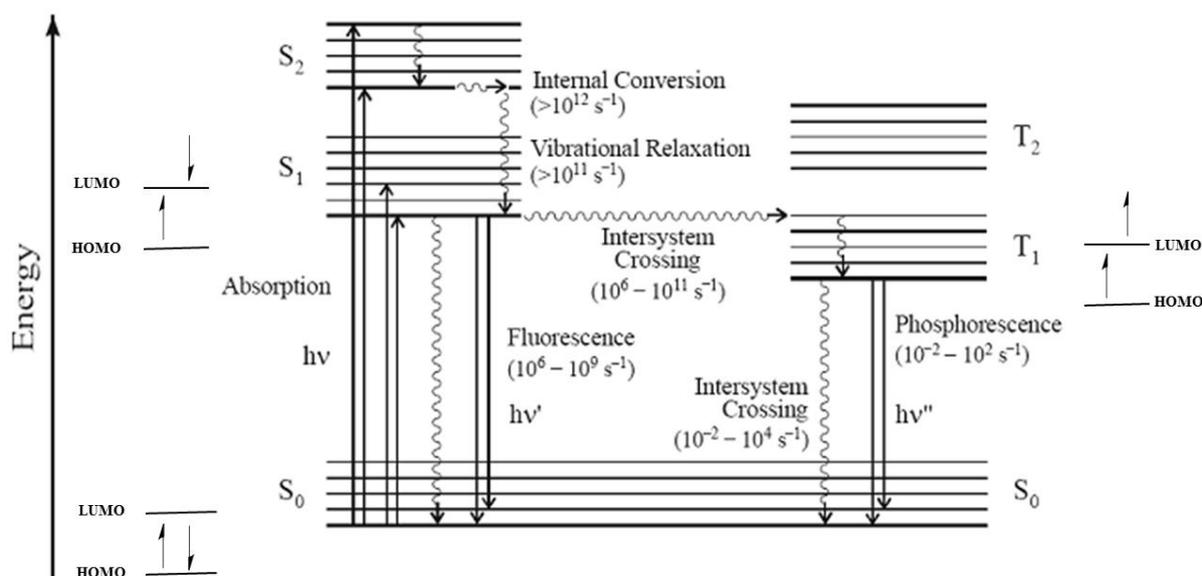


Figure 12. The Jablonski Diagram. Radiative transitions are indicated by straight line arrows whereas non-radiative transitions are represented by wavy line arrows. The range of rate constants generally observed is given in parentheses

Triplet excited-states in molecules and polymers are formed via intersystem crossing (Figure 12), which is a radiationless process from a singlet to a triplet state involving a spin flip of one of the electrons.⁷⁶ Triplets are different from singlets in their spin multiplicity, which makes the transition between them very slow, sometimes taking seconds; hence, most triplet state lifetimes are milliseconds (ms) and even seconds. The formation of triplets opens a photochemical degradation channel in conjugated polymers and molecules, used for electronic

applications, because they make possible energy transfer to molecular oxygen (which has a triplet ground-state), thus promoting oxygen to its highly reactive singlet state.⁷⁷ There are other mechanisms of triplet state formation including electron recombination at donor-acceptor interfaces and singlet fission.^{78,79} The former is a common process in organic-light emitting diodes, used nowadays in displays. In such devices, electrons are injected into an organic film, where they encounter each other and form emissive excited-states via back electron transfer. Due to the lack of spin correlation between electrons, three in every four of these encounters generate non-emissive triplet excitons, which has implications for design and device stability.⁷⁸ Singlet fission requires close interaction between two chromophores with a triplet state energy half of the singlet.⁷⁹ It leads to the formation of two triplet states from one photoexcited singlet. This process has a high potential for application in PVs, where two electrons can be generated from a single absorbed photon, thus doubling electrical current, although reducing photovoltage.⁸⁰ Optimisation of charge transfer from these triplets is part of the implementation of this process for actual devices; it has recently been demonstrated to be highly efficient for pentacene-CdSe interfaces, but further work is required for its utilisation in PVs.⁸¹

3. Summary and Outlook

Photoinduced charge transfer is the key chemical reaction in many technologies. In 1917 science lagged behind application, imaging technologies using these reactions were already well established but the fundamental science was little understood. Over the past one hundred years, developments in chemical applications of quantum mechanics have provided a deep understanding of molecular and semiconductor structure and the interaction of light and matter. Developments in the application of photoinduced charge transfer have led to new technologies e.g. the various types of solar cells, photocatalysts for water purification, and devices for ultra-sensitive chemical sensing discussed here. We do not know what *Science Progress* will give us over the next one hundred years, but there can be little doubt that photoinduced charge transfer will continue to play an important role in the technologies of the future.

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