Molecular approaches to solar energy conversion: the energetic cost of charge separation from molecular-excited states

James R. Durrant

Centre for Plastic Electronics and Department of Chemistry, Imperial College London, London SW7 2AZ, UK

This review starts with a brief overview of the technological potential of molecular-based solar cell technologies. It then goes on to focus on the core scientific challenge associated with using molecular light-absorbing materials for solar energy conversion, namely the separation of short-lived, molecular-excited states into sufficiently long-lived, energetic, separated charges capable of generating an external photocurrent. Comparisons are made between different molecular-based solar cell technologies, with particular focus on the function of dye-sensitized photoelectrochemical solar cells as well as parallels with the function of photosynthetic reaction centres. The core theme of this review is that generating charge carriers with sufficient lifetime and a high quantum yield from molecular-excited states comes at a significant energetic cost—such that the energy stored in these charge-separated states is typically substantially less than the energy of the initially generated excited state. The role of this energetic loss in limiting the efficiency of solar energy conversion by such devices is emphasized, and strategies to minimize this energy loss are compared and contrasted.

1. Introduction

There is increasing academic and commercial interest in photovoltaic solar cells based on molecular light absorbers. Such devices include dye-sensitized photoelectrochemical solar cells (DSSCs), organic solar cells based on polymer and molecular donor/acceptor junctions and an increasingly diverse range of hybrid...
Figure 1. Illustration of the distinction between light absorption in molecular materials, leading to formation of bound, excited states or 'excitons', and light absorption by crystalline silicon, which leads to formation of delocalized conduction band (CB) electrons and valence band (VB) holes. In molecular materials, the binding energy of the exciton is high (hundreds of meV) owing to the relatively localized nature of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) wave functions, and lower material dielectric constant compared with silicon. (Online version in colour.)

In molecular-based solar cells, the excited state generated by light absorption is a molecular, and therefore bound, excited state or 'exciton' (for this reason, such devices are often referred to as 'excitonic' solar cells). This contrasts to crystalline silicon-based devices, where light absorption leads directly to the generation of free conduction band electrons and valence band holes, as illustrated in figure 1. Such molecular-excited states are short-lived (typically hundreds of picoseconds to a few nanoseconds). Solar energy conversion in such excitonic solar cells therefore requires separation of these short-lived excitons into dissociated electrons and holes. These electrons and holes must exhibit sufficiently long lifetimes to allow efficient transport to device contacts where they can generate an external current (typical transport times for molecular devices range from 100 ns to milliseconds depending on the device design).

The requirement of molecular-based solar cells for the separation of short-lived, excited states into longer-lived charge carriers shows clear parallels with the function of photosynthetic reaction centres. The reaction centres of photosynthetic organisms are probably the most sophisticated examples of molecular-based solar energy conversion systems. They have inspired chemists to synthesize artificial photosynthetic systems capable of emulating at least key elements of their function. Perhaps the simplest examples of such photosynthetic model systems are molecular donor/acceptor complexes. In such complexes, optical excitation initiates an electron-transfer reaction from a molecular donor, D, to a molecular acceptor, A, resulting in a charge-separated radical pair state \( D^+A^- \). Extensive studies of such donor/acceptor systems in solution have led to a detailed understanding of their structure/function relationship in terms of non-adiabatic electron transfer theory. This has, in turn, led to impressive advances in the molecular control of charge-separation dynamics in such systems, demonstrating how molecular redox relays can be used to convert short-lived, molecular-excited states into long-lived, charge-separated states with
high quantum efficiencies and reasonable thermodynamic efficiencies [4]. This understanding is increasingly being applied to the design of molecular-based photovoltaic solar energy conversion.

This review starts with a brief overview of the technological potential of molecular-based solar cell technologies. It then goes on to focus on the core scientific challenge associated with using molecular light-absorbing materials for solar energy conversion, namely the separation of short-lived, molecular-excited states into sufficiently long-lived, energetic, separated charges capable of generating an external photocurrent. Comparisons are made between different molecular-based solar cells technologies, with particular focus on the function of DSSCs as well as parallels with the function of photosynthetic reaction centres and the broader challenge of artificial photosynthetic systems capable of using solar energy to drive renewable fuel synthesis. The core theme of this review is that generating charge carriers with sufficient lifetime and a high quantum yield from molecular-excited states comes at a significant energetic cost—such that the energy stored in these charge-separated states is typically substantially less than the energy of the initially generated excited state. The role of this energetic loss in limiting the efficiency of solar energy conversion by such devices is emphasized, and strategies to minimize this energy loss are compared and contrasted.

2. Technological potential of molecular-based solar cells

Figure 2 illustrates two examples of the molecular-based solar cells we will focus on in this review: a DSSC and an organic polymer/fullerene (OSC) device. The design and function of such devices has been extensively reviewed elsewhere [1–3,5,6]. The function of both classes of devices is based on photoinduced charge separation at nanostructured interfaces to separate the initially generated molecular-excited states into long-lived charge carriers—a dye-sensitized metal oxide/electrolyte interface for the DSSC and a polymer/fullerene interface for the OSC. In both cases, a nanostructured interface is used to overcome a key limitation of molecular materials, namely that their excited state (exciton) diffusion length (the distance a molecular-excited state can diffuse within its lifetime, typically approx. 10 nm) is less than the thickness of material required for strong light absorption (typically approx. 100 nm). In the DSSC devices, light absorption is achieved by a dye monolayer adsorbed to the surface of the metal oxide, resulting in photoactive layer thicknesses of approximately 10 µm for efficient light absorption. In the OSC devices, the polymer and fullerene materials function both as light-absorbing and charge-transport materials, leading to much thinner device thicknesses (typically approx. 100 nm). This difference in device thickness, as well as differences in carrier mobilities and transport mechanisms, results in differences in the charge carrier lifetimes required to enable efficient charge collection by device electrodes—for DSSC, typical charge collection times are of the order of milliseconds, whereas for OSC, they are of the order of 100 ns–1 µs.

There have been extensive reviews of the technological potentials of these devices [3,7]. In the UK alone, more than 10 companies are directly engaged in the commercial development of these technologies, including substantial investments by both g24i and TATA in DSSC roll-to-roll fabrication lines, at least four new start-ups targeting OSC cell and module development (eight19, Molecular Solar, Ossila and Solar Press), a start-up targeting hybrid solid-state DSSCs (Oxford Photovoltaics) and several further companies addressing materials development and processing for these technologies. Similar (and indeed often larger) commercial development programmes are present worldwide, including particularly in Germany, the USA, Japan, China, Korea and Australia. This represents a very significant financial investment in what are as yet commercially unproven technologies, and is indicative of the excitement these technologies are generating.

There continue to be substantial advances in the performance of these technologies. In the field of OSC devices, efficiency advances driven primarily by the development of new donor polymers have been particularly striking, with now several reports of efficiencies exceeding 8 per cent [8] and unpublished reports of efficiencies approaching 10 per cent. A notable recent development has been advances in the efficiency of solution processed small molecule blend solar cells, potentially combining the ease of synthesis and purification of small molecules with
the low cost of solution rather than vacuum processing [9]. Further advances are being made in device stabilities, with accelerated trials already indicating lifetimes of more than 10 years. For DSSCs, a key recent advance has been the development of efficient DSSC devices using a range of new redox couples which potentially avoid the corrosion limitations associated with iodide/iodine-based couples, and have led, in combination with new sensitizer dyes, to device efficiencies exceeding 12 per cent [10]. Further studies of excitonic solar cells have shown the advances towards a range of high-efficiency concepts, such as singlet fission and multiple exciton generation [11]. Nevertheless, efficiencies of both OSC and DSSC devices remain substantially below those achievable, in principle, with molecular materials. Theoretical modelling suggests no fundamental barriers to excitonic solar cells achieving efficiencies approaching the Shockley–Queisser limit (so approaching more than 30% for a single junction optimum band gap) [12], whereas semi-empirical estimates based on more realistic materials properties suggest efficiencies exceeding 15 per cent should be achievable [11] comparable to current inorganic devices. Achieving such device efficiencies, coupled with advances in stability and reductions in fabrication cost, is central to the large-scale commercial viability of these technologies.

The remainder of this review is concerned with understanding the factors currently limiting the efficiency of molecular-based devices. Clearly, this a complex issue with many factors, including not least the development of light absorbers with optimal band gaps, and film microstructures and carrier mobilities that enable efficient collection of photogenerated charge carriers. In this review, we focus on one specific issue which has received rather less attention to date in reviews, namely the energy cost of achieving a high quantum efficiency of long-lived,
charge-separated states from molecular-excited states, and the impact of this energy cost on device efficiency. We focus particularly on DSSCs for this issue, although similar considerations underlie the function of all excitonic-based solar cells, and indeed many strategies currently being considered for solar driven fuel synthesis. We start discussion of this issue by considering briefly the impact of this energy cost on the efficiency of biological photosynthesis.

3. Solar energy conversion in photosynthetic reaction centres

In photosynthetic systems, light absorption leads to the generation of chlorophyll singlet-excited states. These excited states are separated in reaction centres by a series of electron transfers which result in the energy being stored as charge-separated states $D^+A^-$. In contrast to photovoltaic devices, the energy in these charge-separated states is used not to generate electrical power but rather used to generate energy-rich chemical products. In plant photosynthesis, for example, the reducing potential stored in the reduced electron acceptor is ultimately used in the reduction of carbon dioxide to sugars, whereas the oxidizing potential of the oxidized donor is used to oxidize water to molecular oxygen. However, both systems exhibit the same requirement for a long lifetime of the charge-separated state—to enable charge collection by the external circuit in photovoltaic devices, and enable coupling to multi-electron oxidation/reduction reactions (e.g. water oxidation) in photosynthesis. For photosynthetic reaction centres, this lifetime requirement is of the order of milliseconds (comparable to DSSCs). Reaction centres achieve this lifetime gain by a sequence of electron-transfer reactions across the reaction centre, spatially separating the electron and ‘hole’, as illustrated in figure 3. These reactions proceed with a near unity quantum efficiency but typically at an energy efficiency of the order of 50 per cent (at least for type II reaction centres such as photosystem II)—in other words, approximately half the energy of the initial chlorophyll exciton is lost in driving the forward electron-transfer reactions required to achieve this charge separation.

The increase in carrier lifetime achieved by the sequence of electron-transfer events within the reaction centre primarily results from the increasing spatial separation of the charge carriers, such that the direct recombination reaction of the two charge carriers requires electron tunnelling through an increasing distance of protein. Given that the rate of such tunnelling decays exponentially with distance (typically by $1/e$ every approx. 0.7 Å), this increase in spatial separation results in a substantial increase in carrier lifetime (from nanoseconds to more than milliseconds) for spatial separations of only a couple of nanometres. The use of a redox relay allows each forward step to proceed over a short distance, enabling rapid charge separation. The high quantum efficiency for these forward charge-separation steps is achieved by ensuring that each forward electron transfer is several orders of magnitude faster than the competing recombination pathway to ground. In this regard, the rates of the forward electron-transfer steps are maximized by ensuring that these reactions are activationless (corresponding to the maxima of so-called ‘Marcus’ plots of reaction rate constant versus $\Delta G$), whereas the recombination reactions exhibit a high activation barrier (corresponding to the ‘Marcus-inverted region’).

The key consideration for this paper is the energy cost required to drive the forward charge-separation reactions in the reaction centre. Some energy loss is required to ensure the reverse, thermally activated recombination back to the singlet exciton is not a significant loss pathway. If we assume that a lifetime gain of $10^6$ is required (from approx. 1 ns to 1 ms), detailed balance indicates this minimal energy loss should be approximately $400 \text{ meV} \left( k_B T \ln(10^6) \right)$. In practice, the energy loss driving these reactions in reaction centres is approximately double this (approx. $800 \text{ meV}$ or half the photon energy). This larger energy loss can be understood, at least in part, by the requirement that forward steps are activationless to enable them to proceed with maximal rate (and therefore high quantum efficiency), such that $\Delta G \sim \lambda$, where $\lambda$ is the reorganization energy, and therefore limited by the magnitude of the reorganization energy associated with each reaction step, which, in turn, reflects the response of the reaction centre structure to the electron-transfer events. This additional energy loss can therefore, at least to some extent, be understood in terms of the specific materials properties of the reaction centre structure.
We add a brief note on overall photosynthetic efficiencies, as literature discussions of this are often rather limited [13]. When considering the overall photosynthetic efficiency, the earlier-mentioned arguments for the reaction centre energetics are complicated by several factors, not least by the ability of the reaction centres also to pump protons across the biological membrane (approx. three protons per electron), resulting in additional energy storage as a pH gradient. If we take higher plant photosynthesis under typical operating conditions (with a pH difference across the membrane of 2 pH units and a membrane potential of 100 mV, corresponding to approx. 21 kJ per mole of protons pumped), then the overall efficiency of conversion of two band gap, 700 nm, photons (one for each photosystem) to chemical energy in the form of reduced nicotinamide adenine dinucleotide phosphate (NADPH), oxygen and proton gradient can be estimated to be approximately 55 per cent (this assumes two photons (700 nm, 170 kJ mol$^{-1}$) and a potential difference between water oxidation and NADPH reduction of 1.27 V, or 125 kJ mol$^{-1}$; energy conversion efficiency $= (125 + (3 \times 21))/(2 \times 170) = 0.55$)—in reasonable agreement with the earlier-mentioned discussion. Extending this to the energy stored in carbohydrate, we obtain a monochromatic efficiency of approximately 35 per cent, lower due to energy losses in adenosine triphosphate synthesis and CO$_2$ reduction (each glucose molecule requires 48 photons assuming no quantum efficiency losses; free energy of formation for glucose is 2870 kJ mol$^{-1}$ and thus overall energy conversion efficiency $= 2870/(48 \times 170) = 0.35$). If we now account for the panchromatic rather than monochromatic nature of sunlight (approx. 55% loss) and account for typical reflection losses from a leaf’s surface (approx. 10%), we obtain a limiting efficiency for the conversion of sunlight to biomass of the order of $0.35 \times 0.45 \times 0.9 \sim 13$ per cent. This approaches the maximal energy conversion rates reported for biological solar conversion determined for an algal culture under ideal growing conditions (approx. 7%) [14]. Of course, in practice, biological photosynthetic energy conversion efficiencies are typically substantially less than this (typically less than 1%) owing to the other requirements and functions of biological organisms. Nevertheless, it is interesting to note that the primary energy conversion efficiency of the reaction centres in converting a short-lived, molecular-excited state into a sufficiently long-lived, charge-separated state is of the order of 50 per cent, comparable to or exceeding the equivalent performance of current state-of-the-art molecular-based photovoltaic devices, as we discuss below.
4. The energetics of charge separation in a dye-sensitized solar cell

Charge separation in DSSCs can be regarded as a two-step redox cascade, resulting in the injection of electrons into the TiO$_2$ electrode and the subsequent oxidation of the redox electrolyte, with the latter also resulting in regeneration of the dye ground state, as illustrated in figure 4. Both the injection and regeneration charge-separation reactions are thermodynamically downhill. As for the reaction centre, these forward electron-transfer steps result in the spatial separation of charge carriers, in this case across a nanostructured, dye-sensitized electrochemical interface.

The overall energetic efficiency of these forward reactions can be considered by comparing the maximum free energy stored by the charge carriers, corresponding to the device open circuit voltage, relative to the energy of the sensitizer dye-excited state. For the state-of-the-art 12.3 per cent DSSCs [10], the open circuit voltage is 935 mV, and the optical band gap approximately 1.72 eV, corresponding to a maximal, monochromatic energetic efficiency of conversion of the short-lived, sensitizer dye-excited state into a long-lived charge-separated state of 54 per cent (neglecting quantum efficiency losses). We note that the monochromatic power conversion efficiency of the device operating at its maximum power point is lower than this due to additional energy and quantum efficiency losses including those associated with collecting charge carriers at the device electrodes, as has been reviewed previously [6]. We turn now to consider what factors are limiting these primary energy losses, focusing primarily on the initial electron injection step.

As for the photosynthetic reaction centre, the charge carrier lifetime required to enable efficient collection by the device electrodes is approximately 1 ms, whereas the lifetime of the dye-excited state in the absence of electron transfer is approximately 1 ns. Thus, the minimal free energy loss required to prevent thermal driven recombination to the excited state and decay to ground from this state is approximately 400 meV, as discussed earlier. However, as for the reaction centre, in practice, the energy losses required to achieve this lifetime gain with a high quantum yield in state-of-the-art DSSCs are substantially larger than this (more than 800 mV).

Figure 5 illustrates the energetics associated with the primary charge-separation step in DSSCs. The first point to note is that, unlike photosynthetic reaction centres, achieving activationless electron transfer is relatively straightforward for this system. The TiO$_2$ electron acceptor presents a band of available acceptor states (its conduction band) such that it is relatively easy to achieve the condition $\Delta G \sim \lambda$. (We note that the overall rate of injection is obtained by integration of the electron-transfer rate over all energetic accessible TiO$_2$ conduction band states.) Therefore, the reorganizational energy associated with each reaction is probably not a significant factor for DSSCs. Therefore, we must look for alternative origins of the energetic loss.

The energetics of the TiO$_2$ acceptor density of states relative to the energy of the dye-excited state determines the number of energetically accessible acceptor states, and is therefore a key factor determining the rate of electron injection $k_{\text{inj}}$. The other key factor is the electronic coupling between the dye lowest unoccupied molecular orbital and these acceptor states. For efficient electron injection, we require $k_{\text{inj}} \gg 1/\tau_0$, where $\tau_0$ is the dye-excited state lifetime in the absence of electron transfer. The relative energetics can be modulated by the dye-excited state energy, and therefore optical band gap. In general, low optical band gap dyes, which absorb more solar photons, will exhibit slower injection rates owing to the lower energy of their excited state. These interfacial energetics can also be modulated by the surface charge of the TiO$_2$ (determined by the concentration of ‘potential determining ions’ in the electrolyte such as lithium ions or electrolyte pH) and by the presence of surface dipoles. The addition of lithium ions to the electrolyte is widely used to lower the conduction band of the TiO$_2$ relative to the dye-excited state, thereby increasing the rate and therefore quantum efficiency of electron injection [15].

It follows from the preceding paragraph that a key factor determining the kinetics, and therefore quantum efficiency, of electron injection is the energy offset between the dye excited state reduction potential and the TiO$_2$ conduction band. However, the free energy stored by electron injection is determined by the difference in energy between the TiO$_2$ Fermi level and the oxidation potential of the sensitizer dye. The difference in energy between the TiO$_2$ conduction band edge (assuming this is well defined, which is probably not the case for nanocrystalline
Figure 4. Energetics of operation of dye-sensitized solar cells. The primary free energy losses are associated with electron injection from the excited sensitizer into the TiO$_2$ conduction band (CB) and regeneration of the dye by the redox couple. The voltage output of the device is approximately given by the splitting between the TiO$_2$ Fermi level (dashed line) and the chemical potential of the redox electrolyte. Adapted from Listorti et al. [15]. (Online version in colour.)

Figure 5. Illustration of the energetics and kinetics of the primary charge-separation step in dye-sensitized solar cells. The figure illustrates the TiO$_2$ acceptor density of states (d.o.s.) observed typically—with this increasing exponentially with distance. Electron injection proceeds with a rate constant $k_{inj}$ into this density of states. Recombination of injected electrons with oxidized dyes is illustrated by the red arrow—this recombination may proceed either directly from thermalized TiO$_2$ electron states, or via thermal excitation back up to TiO$_2$’s mobility edge. (Online version in colour.)
TiO₂) and its Fermi level arises from the increase in entropy of the electrons owing to the large number of acceptor states available to them within the TiO₂ film. Thus, the free energy stored by charge separation is determined not only by the materials energetics (i.e. for TiO₂, its conduction band) but also by Fermi level of the TiO₂ which, in turn, depends on device operating conditions (light intensity, cell voltage, etc.). This again is different from a photosynthetic reaction centre, where the charge carriers only access single final redox species within each reaction centre. Finally, we note that the lifetime of the charge carriers generated by electron injection again depends on device operating conditions. In general, in the absence of the redox couple, the carrier lifetime is limited by bimolecular recombination of injected electrons with oxidized dyes. This carrier’s lifetime is typically found to depend on electron density in the TiO₂ and thereby TiO₂ Fermi level (in practice, this dependence derives primarily from the effects of electron trapping in intraband states within the TiO₂ film). Similar arguments can be used for the full device, where the free energy stored is the difference in free energy between the TiO₂ Fermi energy and electrolyte Nernst potential, and the primary recombination pathway is electron recombination with oxidized redox couple.

It follows from the above arguments that there is a direct tension between competing requirements of a high quantum efficiency of electron injection, a large free energy stored and large gain in carrier lifetime in DSSCs. For example, the addition of lithium ions to increase the quantum efficiency of electron injection by lowering the TiO₂ conduction band causes, for a fixed electron density in the TiO₂ (corresponding to an unchanged carrier lifetime), a loss in the free energy stored (as the film Fermi level will be lower to maintain a fixed position relative to the TiO₂ acceptor density of states).

It can be concluded from the above arguments that there is an energy cost associated with lifetime gain in DSSCs. This is analogous to the function of photosynthetic reaction centres, and is arguably the fundamental factor limiting the efficiency of this technology. The factors determining the magnitude of this energy cost include the electronic properties of the TiO₂ (and particularly the shape of the TiO₂ acceptor density of states), the magnitude of the lifetime gain required (i.e. the difference between the excited state lifetime and the charge carrier collection time), the electronic couplings for each of the reaction steps and the homogeneity of the interface, and particularly the shielding of the TiO₂ from the electrolyte redox species. Many of the strategies aimed at enhancing the efficiency of DSSCs are directly or indirectly aimed at minimizing this energetic cost of lifetime gain. For example, the report of 12.3 per cent efficient devices was critically dependent on the use of sensitizer dyes with long alkyl chains to prevent the redox couple from accessing the TiO₂ surface, thereby increasing the lifetime gain associated with charge separation without compromising the energetic cost or quantum efficiency [10].

5. Towards 15 per cent efficient molecular solar cells

Sections 3 and 4 have looked in some detail at the mechanistic origins of the energetic cost of achieving a high quantum efficiency of sufficiently long-lived charge carriers—using the examples of a photosynthetic reaction centre and a DSSC. In each case, the mechanistic origins of this energy cost, and thus the strategies to minimize it, are different. However, in both cases, this energetic loss is a fundamental limitation on the overall efficiency of solar energy conversion. It appears likely that considerations such as those detailed in this review will be relevant to all solar energy conversion systems where optical excitation generates a short-lived excited state, but device operation requires the generation of relatively long-lived charge carriers. We and others have discussed these issues elsewhere in the context of organic solar cells and photoanodes for water oxidation [5,16].

In terms of the fundamental limits to solar energy conversion, the minimal energy loss is associated with the detailed balance limit preventing thermal re-excitation back to the molecular-excited state and decay from this state. This energy loss is dependent on the magnitude of the lifetime increase required for efficient function. For a lifetime gain requirement of $10^6$ (typical for photosynthetic reaction centres and DSSCs), this minimal energy loss is of the order of
approximately 400 meV. Obvious strategies to reduce this minimal energy loss requirement in molecular solar cells include decreasing the rate of molecular-excited state decay to ground or accelerating the time scale of charge carrier collection to the external circuit. In practice, the energy loss associated with charge separation in current devices is significantly greater than this minimal energy loss. Approaching the detailed balance limit in practical, low cost devices is therefore a key challenge for enhancing the efficiencies of molecular solar cells towards 15 per cent and beyond.

The author gratefully acknowledges helpful discussions with many colleagues working on solar energy conversion, and in particular for this article with Jenny Nelson, Bill Rutherford and Brian O’Regan. Financial support from the EPSRC Supergen, Apex and Scallops programmes is also gratefully acknowledged.

References