

Chapter 8.

ORGANIC SOLAR CELLS

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8.1 Introduction to organic solar cells

Conventional solar cells were invented in the 1950s and first commercialized in the 1960s for use in space programs. Since then there have been rapid advances in the efficiency and reliability of these cells, along with a substantial decrease in their fabrication costs. As a result the photovoltaic industry has been growing rapidly. Nevertheless the price of solar electricity is still greater than the price of electricity from the electrical grid in industrialized countries. For this reason there is an increasing amount of research devoted to potentially less expensive types of solar cells such as those based on organic dyes and polymers. These cells have been studied since the late 1950s albeit at a fairly low level until recently. One of the great promises of organic electronics is that synthetic chemists can produce compounds matching the opto-electronic properties desired.

A fundamental difference between solar cells based on organic materials and conventional inorganic photovoltaic (IPV) cells is that light absorption results in the formation of excitons in molecular materials, rather than in free electrons and holes. An exciton in an organic semiconductor can be considered as a tightly coulombically bound electron hole pair. Due to its electrical neutrality and the strong binding energy between the hole and the electron it can be regarded as a mobile excited state. Due this fundamental difference the processes involved in the conversion of photons into electrical energy are not

the same as those occurring in IPV cells. In this chapter, solar cells in which excitons are generated due to light absorption, hereafter denoted as organic solar cells will be discussed. First some more relevant properties of organic materials based on dye molecules or on polymers (often referred to as molecular materials) are given in 8.2. Paragraph 8.3 deals with the topic of excited states in molecular materials. Section 8.4 describes the processes in organic solar cells relevant for the conversion of incident photons into electric energy. In section 8.5 more details about the most successful approaches towards organic solar cells *i.e.* dye sensitized solar cells, organic bilayer cells and bulk heterojunction cells are discussed. Future prospects regarding lifetimes and efficiencies for organic solar cells are the topic of the last section 8.6 of this chapter.

8.2. Molecular materials

Organic molecules and polymers have the immense advantage of facile, chemical tailoring to alter their properties, such as the optical band gap. For example conjugated polymers (see Figure 1) combine the electronic properties known from the traditional semiconductors with the ease of processing and mechanical flexibility of plastics. The research on these kinds of organic materials was initiated by Heeger, MacDiarmid and Shirakawa, who discovered that the conductivity of polyacetylene (PA) could be increased by seven orders of magnitude. Since then, this new class of materials has attracted considerable attention owing to its potential of providing environmentally safe, flexible, lightweight, and inexpensive electronics.

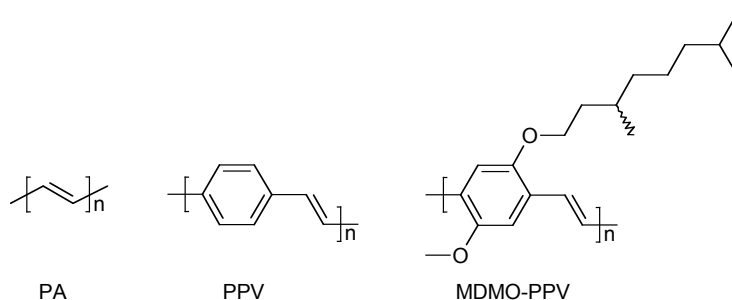


Figure 8.1. Molecular structures of the conjugated polymers trans-polyacetylene (PA), poly(p-phenylene vinylene) (PPV), and a substituted PPV (MDMO-PPV).

The cost reduction mainly results from the ease of processing from solution. However, solution processing requires soluble polymers. Poly[p-phenylene vinylene] (PPV, Figure 1) is hardly soluble. Attachment of side-groups to the conjugated backbone, as in poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO-PPV, Figure 1), enhances the solubility of the polymer enormously.

Recent developments in ink-jet printing, micro-contact printing, and other soft lithography techniques have further improved the potential of conjugated polymers for low-cost fabrication of large-area integrated devices on both rigid and flexible substrates. A good example of the use of this kind of polymers in commercial products are the light emitting diodes. Architectures to overcome possible electronic scale-up problems related to thin film organics are being developed. In contrast to conjugated polymers, conjugated molecules are mainly thermally evaporated under high vacuum. Despite the fact that gradual improvement

of the efficiency has been achieved of solar cells based on this deposition technique, this method is more expensive than solution processing and, therefore, less attractive.

The energy levels in molecular materials can be related to the energy levels of inorganic semiconductors (see Figure 8.2). As already discussed in previous chapters the energy needed to release an electron from the valence band of an inorganic semiconductor to the vacuum level is denoted as the ionisation potential, while the electron affinity denotes the energy gained when an electron is transferred from the vacuum level to the conduction band edge. In molecular materials also electrons can be liberated from the so-called highest occupied molecular orbital (HOMO) to the vacuum. The energy involved can roughly be estimated on basis of the electrochemical oxidation potential (vs. NHE) of the molecules using the relation: $E_{\text{HOMO}} \approx E_{\text{NHE}} - V_{\text{ox}}$, with $E_{\text{NHE}} = -4.5 \text{ V vs. vac.}$ In a similar way the electron affinity can be estimated from the reduction potential of the molecules using: $E_{\text{LUMO}} \approx E_{\text{NHE}} - V_{\text{red}}$. The difference between both energy levels corresponds to the optical bandgap of the molecules. Alternative methods to determine the energy levels in molecular layers include: Ultraviolet photoelectron spectroscopy (UPS) and Kelvin probe measurements. The concentration of mobile charge carriers within intrinsic molecular layers in the dark at room temperature is usually small. The resulting conductivity of these layers is therefore relatively small. Intentional doping to form n- or p-type layers is not straightforward, since this causes often degradation of the organic material.

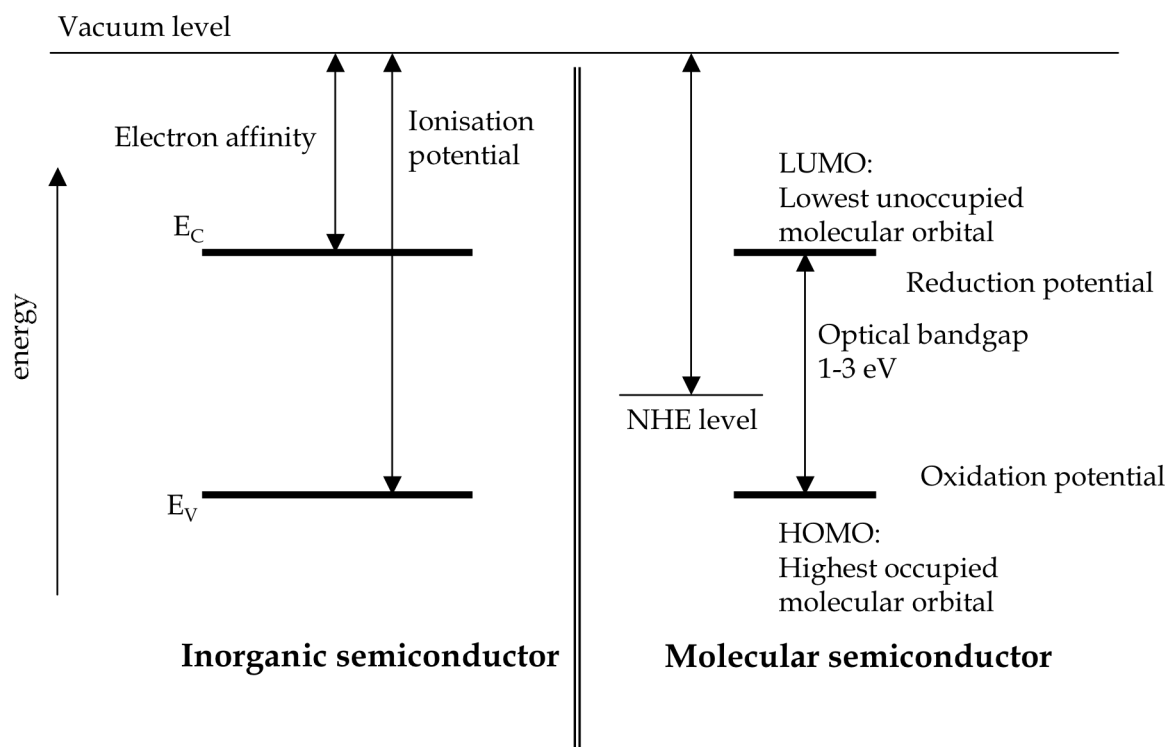


Figure 8.2. Overview of energy levels in inorganic semiconductors (left) and molecular semiconductors (right).

Molecular materials that have a low ionisation potential and thus can easily donate an electron are denoted as electron donors. Materials that have a high electron affinity and thus can easily take up an electron are denoted as electron

acceptors. If a molecule is an electron donor or an electron acceptor is an intrinsic property of the compound.

8.3 Excited states in molecular materials

A key difference between organic solar cells and IPVs is the relative importance of interfacial processes. This difference is related to the charge carrier generation mechanism. Light absorption in IPV cells results directly in the formation of free charge carriers. This means that charges are created throughout the bulk of the semiconductor. In contrast, light absorption in organic materials almost always results in the production of a mobile excited state rather than in free charge carriers. This is due to two reasons: First the dielectric constant of the organic material is usually low as compared to inorganic semiconductors. This creates an attractive Coulomb potential well around charges. Secondly in molecular materials the non-covalent electronic interactions between the molecules are weak as compared to the strong interatomic electronic interactions of covalently bound inorganic semiconductors like in silicon. For these two reasons the wavefunction of the electron is spatially restricted to the potential well induced by its positive counterpart. Therefore the usual product of light absorption in molecular materials is a tightly bound, neutral electron/hole pair or exciton.

To envisage the effect of a potential well in more detail the binding energy, E_B , between two opposite charges in a molecular material is calculated using:

$$E_B = \frac{q^2}{4\pi\epsilon_r\epsilon_0r_c} \quad (8.1)$$

with r_c the critical distance between both charged carriers, ϵ_r is the relative dielectric constant and ϵ_0 is the permittivity of free space. A charge carrier becomes free from the Coulomb attraction of an opposite charge when $E_B \leq k_B T$, which amounts to 25 meV at room temperature. This yields together with 8.1

$$r_c \geq \frac{q^2}{4\pi\epsilon_r\epsilon_0k_B T} \quad (8.2)$$

Figure 8.3 shows the effect of the temperature and the dielectric constant on the critical distance. For molecular excitons r_c is typically in the order of 1 nanometer which corresponds to a binding energy exceeding 0.25 eV. However, to obtain a photovoltaic effect in an organic solar cell the exciton must be dissociated. To overcome this problem, organic solar cells commonly utilize two different materials that differ in electron donating and accepting properties. Dissociation of the exciton is accomplished by electron transfer between the two compounds. The energy gained by this process should then exceed the exciton binding energy. In this way the photogeneration of free charge carriers is much more efficient as compared to the individual, pure materials, in which the formation of bound electron-hole pairs, or excitons is generally favoured.

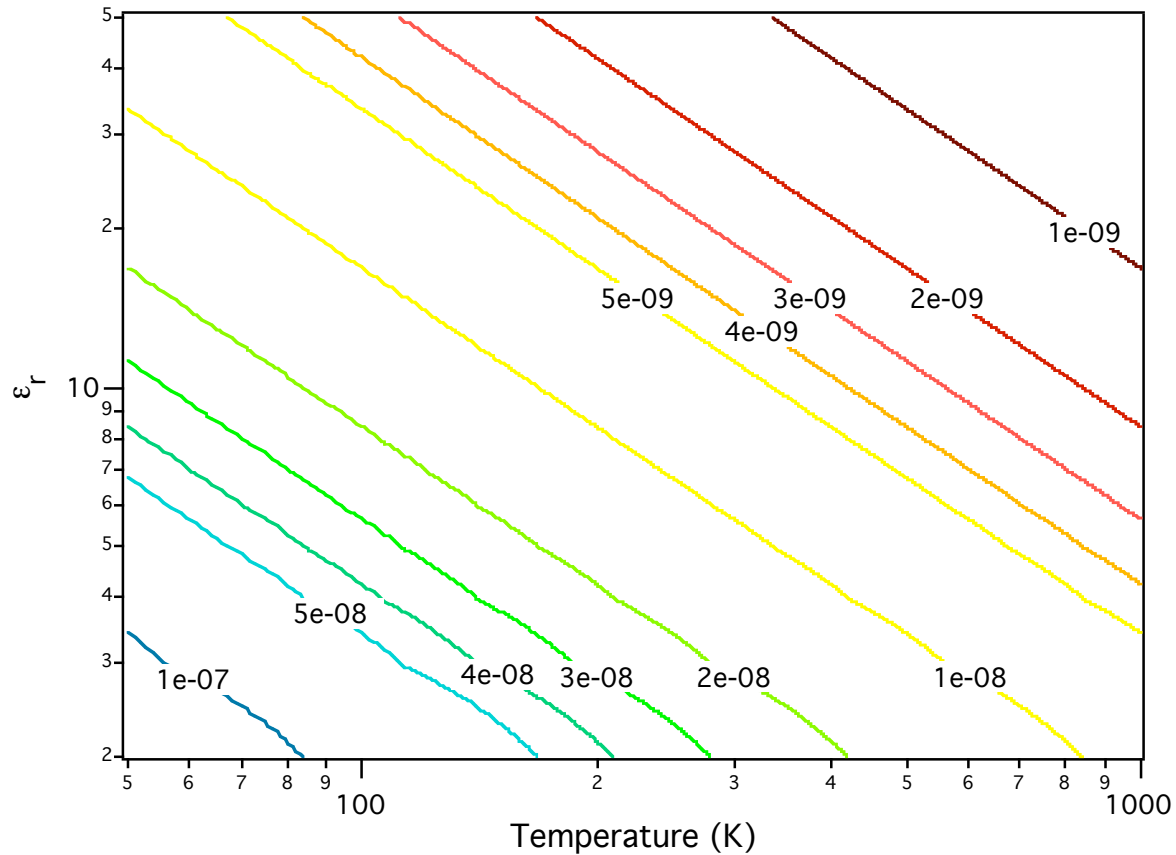


Figure 8.3. Illustration of the critical distance between a positive hole and an electron as function of the temperature and the dielectric constant. At room temperature in molecular materials with an ϵ_r of 3.5 r_c is approximately 20 nm while at the same temperature for Si with an ϵ_r of 11.7 this value is close 6 nm.

8.4 Basic processes in organic solar cells

In general, for a successful organic photovoltaic cell five important processes have to be optimized to obtain a high conversion efficiency of solar energy into electrical energy:

1. Absorption of light and generation of excitons
2. Diffusion of excitons to an active interface
3. Charge separation
4. Charge transport
5. Charge collection

To create a working photovoltaic cell, the two photoactive materials are sandwiched between two (metallic) electrodes (of which one is transparent), to collect the photogenerated charges (see Figure 8.4). After the charge separation process, the charge carriers have to be transported to these electrodes without recombination. Finally, it is important that the charges can enter the external circuit at the electrodes without interface problems.

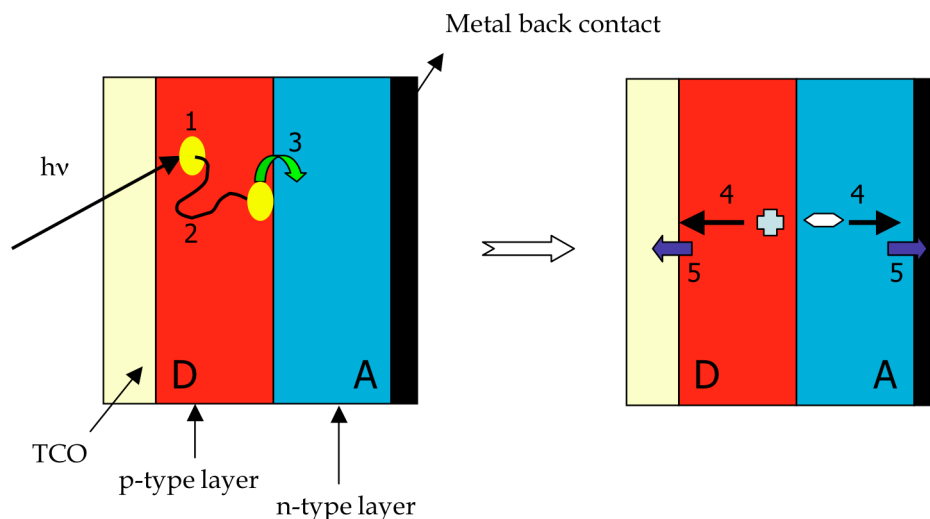


Figure 8.4. Schematic drawing of the working principle of an organic photovoltaic cell. Illumination of a donor material (in red) through a transparent electrode (ITO) results in the formation of an exciton (1). Subsequently, the exciton is transported by diffusion (2) to the interface between the donor material and an acceptor material (in blue). Electron is transferred to the acceptor material (A^-), leaving a hole at the donor material (D^+) (3). The photogenerated charged carriers are then transported (4) to and collected at opposite electrodes (5). A similar charge generation process can occur, when the acceptor is photoexcited instead of the donor.

8.4.1. Light absorption

For an efficient collection of photons (process 1), the absorption spectrum of the photoactive organic layer should match the solar emission spectrum and the layer should be sufficiently thick to absorb most of the incident light. Generally the optical absorption coefficient (α) of organic materials is much higher than that of crystalline or multicrystalline silicon as shown in Figure 8.5. For the conjugated polymers MDMO-PPV and P3HT and for the molecular dye, zinc phthalocyanine (ZnPc) α exceeds $1 \times 10^5 \text{ cm}^{-1}$ in the major part of the visible spectrum. Using Equation 3.38 this implies that a 100 nm thick organic layer is sufficient to reduce the light intensity to $1/e$ times its original value. For comparison, to obtain a similar decrease of the light intensity the crystalline silicon layer should be two orders magnitude thicker.

The absorption coefficient spectra of MDMO-PPV and P3HT shown in Figure 8.5 lack absorption in the red and NIR part of the spectrum. As discussed previously for a photovoltaic cell based on a single light absorbing medium a band-gap of approximately 1.1 eV is optimal. By lowering the band gap of the organic material it is possible to harvest more sunlight and therefore an increase in the photocurrent can be expected. For this reason much research effort is presently devoted to obtain organic polymers with an optical band in the NIR, so called small band-gap polymers. Though increasing the layer thickness is often advantageous for light absorption, charge transport might be hampered. This results in a lower the fill factor.

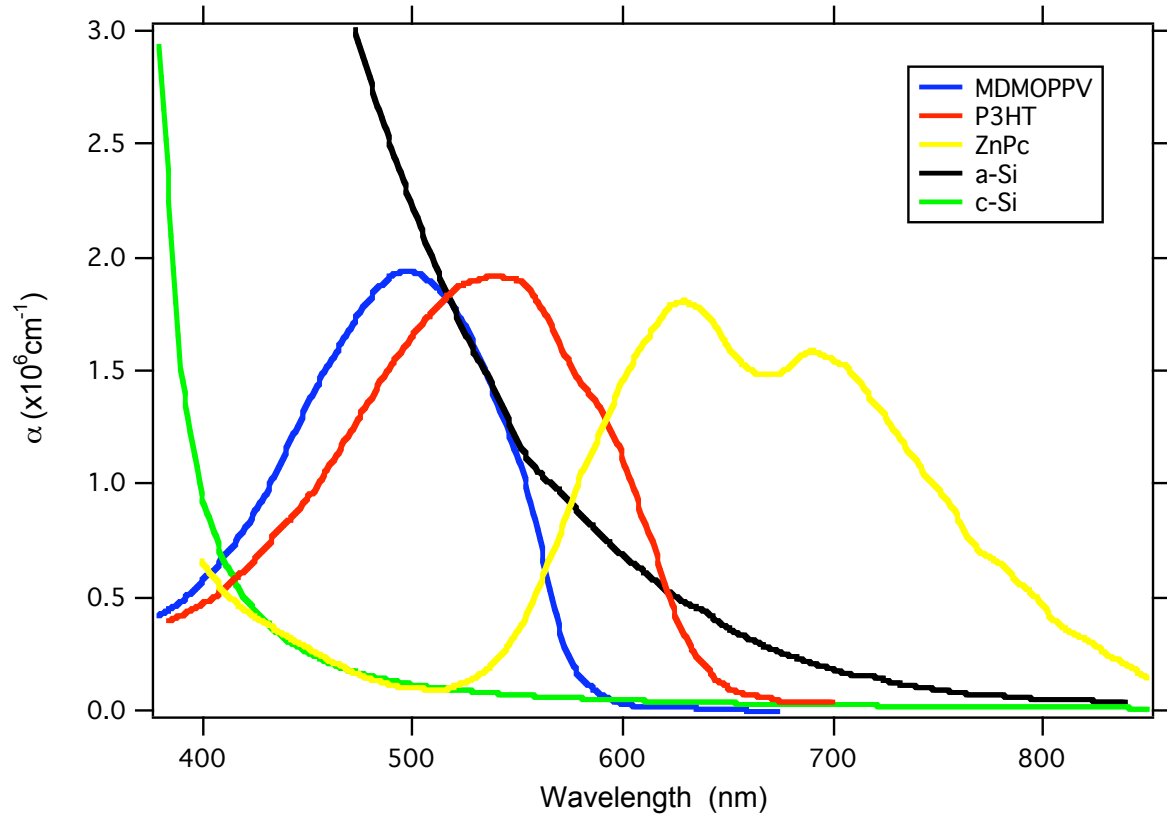


Figure 8.5. Absorption coefficients of various solar energy materials.

8.4.2. Exciton transport

For realisation of an efficient organic solar cell all excitons formed due to light absorption should lead to the formation of free charge carriers. However exciton transport is in competition with other decay processes such as luminescence or radiative recombination to the ground state. The exponential lifetime of an exciton (τ_{EXC}) is determined by the reciprocal value of all radiative and non radiative decay rates together. For an efficient solar cell all excitons have to reach the photo-active interface within τ_{EXC} . Transport of the excitons occurs by diffusion and the distance an exciton is able to cross, L_{EXC} , is given by:

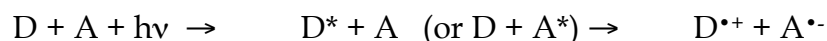
$$L_{\text{EXC}} = \sqrt{D_{\text{EXC}}\tau_{\text{EXC}}} \quad (8.3)$$

in which D_{EXC} is the diffusion coefficient of the excitons. Since for molecular materials τ_{EXC} is often only several nanoseconds at most, L_{EXC} is generally limited to 10 nm. In practice this implies that only those excitons formed within a distance of L_{EXC} from the interface will contribute to charge separation. To avoid this problem, research has been devoted to increase the diffusion coefficient of excitons or to make the interfacial area much larger, so that each generated exciton is always close to an interface. Each of these approaches has led to completely different cell designs as will be shown in section 8.5.

8.4.3. Charge separation

Creation of charges is one of the key steps in the conversion of solar light into electrical energy. In most organic solar cells, charges are created by photoinduced electron transfer. In

this process an electron is transferred from an electron donor (D) material to an electron acceptor (A) material with the aid of the additional input energy of an absorbed photon with energy $h\nu$. An electron donor is characterized by a molecular material with a small electron affinity. Vice versa an electron acceptor is a material with a high electron affinity. The difference between both electron affinity levels is the driving force required for the exciton dissociation. In the photoinduced electron transfer process an exciton at the D/A interface decays by creation of the charge-separated state consisting of the radical cation of the donor ($D^{\bullet+}$) and the radical anion of the acceptor ($A^{\bullet-}$).



For an efficient charge generation, it is essential that the charge-separated state is the thermodynamically and kinetically most favourite pathway for the exciton. Therefore, it is important that the energy of the absorbed photon is used for generation of the charge-separated state and is not lost via competitive processes like fluorescence or non-radiative decay. In addition, the charge-separated state should be stabilized, so that the photogenerated charges can migrate to one of the electrodes. Therefore, the back electron transfer or recombination should be slowed down as much as possible.

In a homojunction between a p-type and an n-type silicon semiconductor under illumination electrons flow from the p-type to the n-type semiconductor. In a heterojunction based on an electron donor layer D and an electron accepting layer A, under illumination electrons flow from the D to the A layer as illustrated in Figure 8.4. Therefore the D layer is also denoted as the p-type layer and the A layer as the n-type layer in analogy with a silicon pn junction. Therefore molecular materials with a low ionisation potential are commonly p-type and materials with a high electron affinity n-type.

8.4.4. Charge transport

The charge transport mechanisms operating in IPV cells and organic solar cells to drive charge carriers towards the electrodes are again very different. Light absorption in IPV cells leads directly to the production of electrons and holes in the same material. Since the two carrier types have the same spatial distribution, the concentration gradient, which is the driving force for the transport by diffusion is identical (See Figure 8.6). Therefore both charge carriers are driven in the same direction. Since this is a small driving force in IPV cells, the electrical potential gradient present at the interface of a p-n junction (the band bending) is able to separate the photo-induced electrons from the holes effectively. In contrast to IPV cells in organic solar cells after the charge transfer the electrons and holes are in close proximity. Therefore there is a large chemical potential gradient that drives the charge carriers away from the exciton dissociating interface.

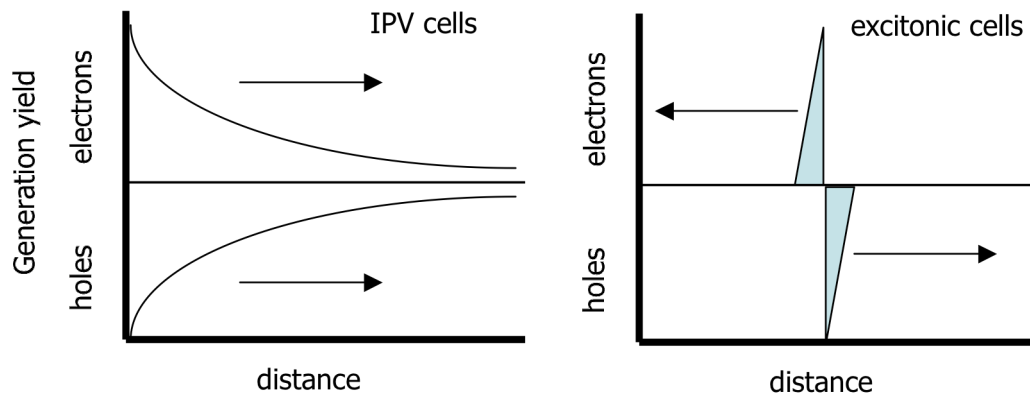


Figure 8.6. Schematic description showing the effect on the charge carrier distributions induced by the different charge carrier generation mechanisms in IPV cells (left) and organic solar cells (right).

Though for IPV cells the electric field is the main driving force for charge transport, it is not yet clear to what extent the internal electrical field contributes to the charge transport in organic solar cells. This is due to the differences in mobilities in molecular materials and inorganic semiconductors. The velocity charge carriers acquire under the influence of an electric field (ξ) is given by the relation:

$$v_{di} = \mu_i \xi \quad (8.4)$$

in which μ_i is the mobility. The mobility in molecular materials is relatively small ($< 0.1 \text{ cm}^2/\text{Vs}$) as compared to inorganic semiconductors ($100 - 10000 \text{ cm}^2/\text{Vs}$). In addition it is not yet clear if and how an electrostatic potential in an organic bilayer is formed. This is due to the fact that molecular materials contain only low densities of mobile charge carriers. In view of the above the rate kinetics for the various charge carrier recombination processes are important parameters in particular for organic solar cells. These processes should be sufficiently slow to allow the charge carriers to reach the electrodes.

8.4.5. Charge collection

The collection of charge carriers at the electrodes is regularly accomplished by a transparent conductive oxide (TCO) such as ITO or $\text{SnO}_2\text{:F}$ on one side and a metal contact on the other side. Care has to be taken that an Ohmic contact between the electrodes and the molecular layers is formed. In practice special contact layers have been developed to obtain better performance of the solar cell. Examples of contact layers are a PEDOT:PSS layer, which is a charged conducting polymer layer at the TCO side and LiF layers at the metal contact. The exact reason how these layers improve the cells is unclear.

For IPV cells the V_{OC} is limited by the electrostatic potential at the junction (see Chapter 4). For organic solar cells reasonable open circuit voltages have been measured for cells build up by using a single photoactive molecular material and identical electrodes. From this observation it is evident that the V_{OC} is determined by other factors than for an IPV cell. For an organic solar cell based on two molecular materials as depicted in Figure 8.4 optical excitation leads to the formation of an exciton in one of the layers. For the charge separation process part of the original energy of the photon is lost, yielding an electron in the n-type material and a positive charge carrier in the p-type material. In case there is no potential loss at the electrodes the maximum observed potential can be obtained by as shown schematically in Figure 8.7:

$V_{\text{OC}} = \text{Ionisation potential of the p-type material} - \text{electron affinity of the n-type layer}$
 In practice a potential loss at the electrodes in the order of 0.2 V is often observed.

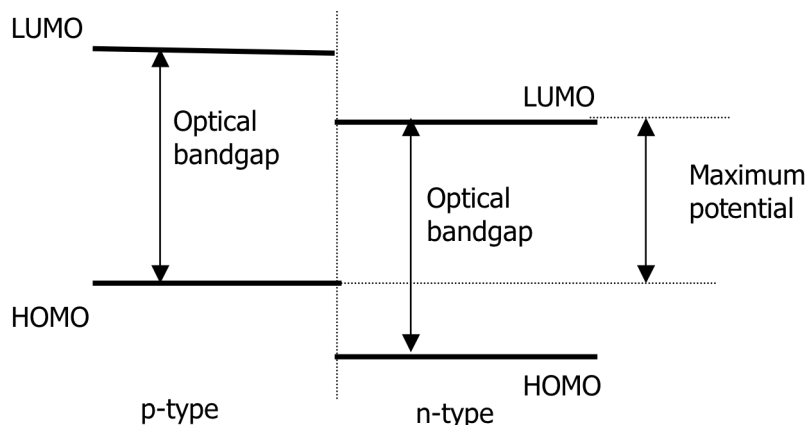


Figure 8.7. Energy levels involved in determining the maximum potential generated by an exciton solar cell. The offset in the energy levels corresponding to LUMO forms the driving force for the dissociation of the exciton.

8.5. Organic solar cells

In this paragraph a short overview is given of the most successful approaches towards organic solar cells to date. First, cells will be described in which organic molecules are only used for absorption of light, followed by cells in which an organic or polymeric material is used for absorption of light and for charge transport.

8.5.1 Dye-sensitized solar cells

In a dye-sensitized solar cell, an organic dye adsorbed at the surface of an inorganic wide-band gap semiconductor is used for absorption of light and injection of the photoexcited electron into the conduction band of the semiconductor. The research on dye-sensitized solar cells gained considerable impulse, when Grätzel and co-workers greatly improved the interfacial area between the organic donor and inorganic acceptor by using nanoporous titanium dioxide (TiO_2). To date, ruthenium dye-sensitized nanocrystalline TiO_2 (nc- TiO_2) solar cells reach an energy conversion efficiency of about 10%. In the Grätzel cell (Figure 8.9), the ruthenium dye takes care of light absorption and electron injection into the TiO_2 conduction band. An I^-/I_3^- redox couple, contained in an organic solvent, is used to regenerate (i.e. reduce) the photooxidized dye molecules. In the cells, the positive charge is transported by the liquid electrolyte to a metal electrode, where I_3^- takes up an electron from the external circuit (counter electrode), while the negative charges injected in nc- TiO_2 are collected at the TCO electrode.

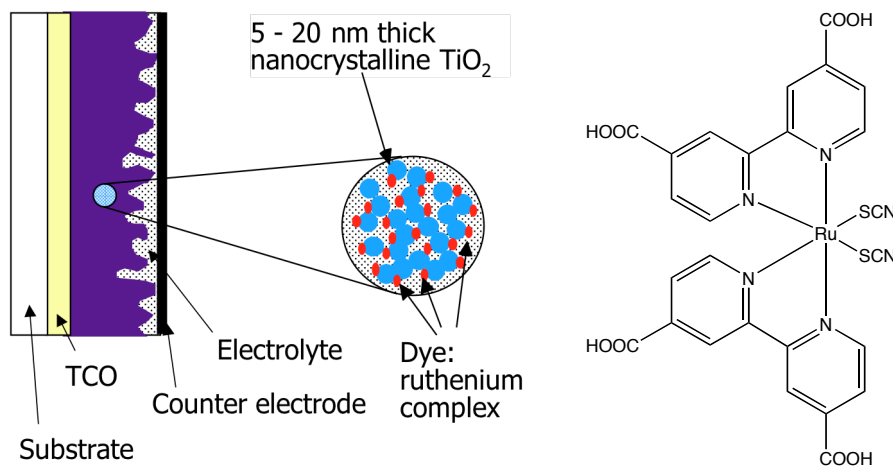


Figure 8.8. The dye-sensitized solar cell. After absorption of light by the ruthenium dye, a photogenerated electron in the dye is transferred to the conduction band of the TiO_2 nanoparticles. The dye is then reduced by a redox electrolyte, I^-/I_3^- , which in turn, is reduced at the metal counter electrode. As a result, a positive charge is transported from the dye to the metal electrode via the electrolyte. The electron in the nanocrystalline TiO_2 is transported to the TCO electrode.

The nanoporous TiO_2 ensures a dramatic enlargement of the contact area between the dye and semiconductor, compared to a flat interface. High quantum efficiencies for charge separation are achieved, because the dye molecules are adsorbed directly on the n-type semiconductor. The positive charges are transported efficiently by the liquid electrolyte and,

as a consequence the thickness of the photovoltaic device can be extended to the μm range, resulting in optically dense cells. From a technology point of view, however, the liquid electrolyte represents a drawback. Hence, much research has focused on replacing the liquid electrolyte by a solid hole transporting material. The most promising replacement is a solid, wide-band gap hole transporting material resulting in power conversion efficiencies of 3%.

Another new concept for a solid-state Grätzel cell consists of a polymer or organic semiconductor that combines the functions of light-absorption and charge (hole) transport in a single material and, therefore, is able to replace both the dye and the hole transporting material. The photoinduced charge separation at the interface of an organic and inorganic semiconductor has been studied in relation to photovoltaic devices. When an organic or polymeric semiconductor is excited across the optical band gap, the excitation energies and valence band offsets of this molecular semiconductor may allow electron transfer to the conduction band of an inorganic semiconductor, similar to the ruthenium dye. The dimensions of the nanopores in TiO_2 are even more important here, because excitations are no longer created at the interface only, but throughout the whole organic material. Because essentially all excitons must be able to reach the interface with the TiO_2 for efficient charge separation and energy conversion, the distance between the site of excitation and the interface must be within the exciton diffusion length. As discussed previously, in most organic materials, the exciton diffusion length is limited to 5-10 nm by the fast intrinsic decay processes of the photoexcited molecules. Creating nanoporous TiO_2 of such dimensions, and filling it completely with an organic semiconductor, is currently one of the challenges in this area.

8.5.2 Double layer cells

The first attempts to create all-organic solar cells were made by sandwiching a single layer of an organic material between two dissimilar electrodes. In these cells, the photovoltaic properties strongly depend on the nature of the electrodes. Heavily doped conjugated materials resulted in low power conversion efficiencies up to 0.3%.

In 1986, a major breakthrough was realized by Tang, who introduced a double-layer structure of a p- and n-type organic semiconductors (see Figure 8.4). A 70 nm thick two-layer device was made using copper phthalocyanine as the electron donor, and a perylene tetracarboxylic derivative as the electron acceptor (Figure 8.9). The photoactive material was placed between two dissimilar electrodes, indium tin oxide (ITO) for collection of the positive charges and silver (Ag) to collect the negative charges. A power conversion efficiency of about 1% was achieved under simulated AM2 illumination (691 W/m^2).

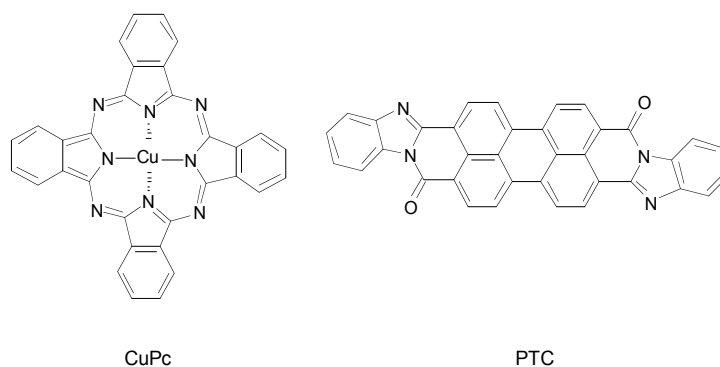


Figure 8.9. Molecular structures of copper phthalocyanine (CuPc) and a perylene diimide derivative.

In the double-layer configuration the photogenerated excitons in the photoactive material have to reach the p-n interface (Figure 8.4, centre) where charge transfer can occur, before the excitation energy of the exciton is lost via intrinsic radiative and non-radiative decay processes to the ground state. Because the exciton diffusion length of the organic material is in general limited to 5-10 nm, only absorption of light within a very thin region around the interface contributes to the photovoltaic effect. This limits the performance of double-layer devices, because such thin layers cannot absorb all the incident light. A strategy to improve the efficiency of the double-layer cell is related to structural organization of the organic material to extend the exciton diffusion length and, therefore, create a thicker photoactive interfacial area.

8.5.3 Bulk heterojunction cells

In combining electron donating and electron accepting materials in the active layer of a solar cell, care must be taken that excitons created in either material can diffuse to the interface and undergo charge separation. Due to their short lifetime and low mobility, the diffusion length of excitons in organic semiconductors is limited to about ~ 10 nm only. This imposes an important condition to efficient charge generation. Anywhere in the active layer,

the distance to the interface should be on the order of the exciton diffusion length. Despite their high absorption coefficients, exceeding 10^5 cm^{-1} , a 20 nm double layer of donor and acceptor materials would not be optical dense, allowing most photons to pass freely. The solution to this dilemma is elegantly simple. By mixing the *p* and *n*-type materials, junctions throughout the bulk of the material are created that ensure each photogenerated exciton leads to charge transfer, irrespective of the thickness of the layer.

Mixtures, or in other words blends, based on substituted fullerenes (with acronym PCBM) and DMOM-PPV (See Figure 8.10) were among the first materials to utilize this bulk-heterojunction principle. Nevertheless, this attractive solution poses a new challenge. Photogenerated charges must be able to migrate to the collecting electrodes through this composite material. Because holes are transported by the *p*-type semiconductor and electrons by the *n*-type material, these materials should be preferably mixed into a bicontinuous, interpenetrating network. In Figure 8.10 a bulk heterojunction solar cell is schematically depicted. The bulk heterojunction is presently the most widely used photoactive layer for realisation of organic solar cells. The name bulk-heterojunction solar cell has been chosen, because the interface between two different components (heterojunction) is all over the bulk, in contrast to the classical (bi-layer) junction. Control of morphology is not only required for a large charge-generating interface and suppression of exciton loss, but also to ensure percolation pathways for both electron and hole transport to the collecting electrodes.

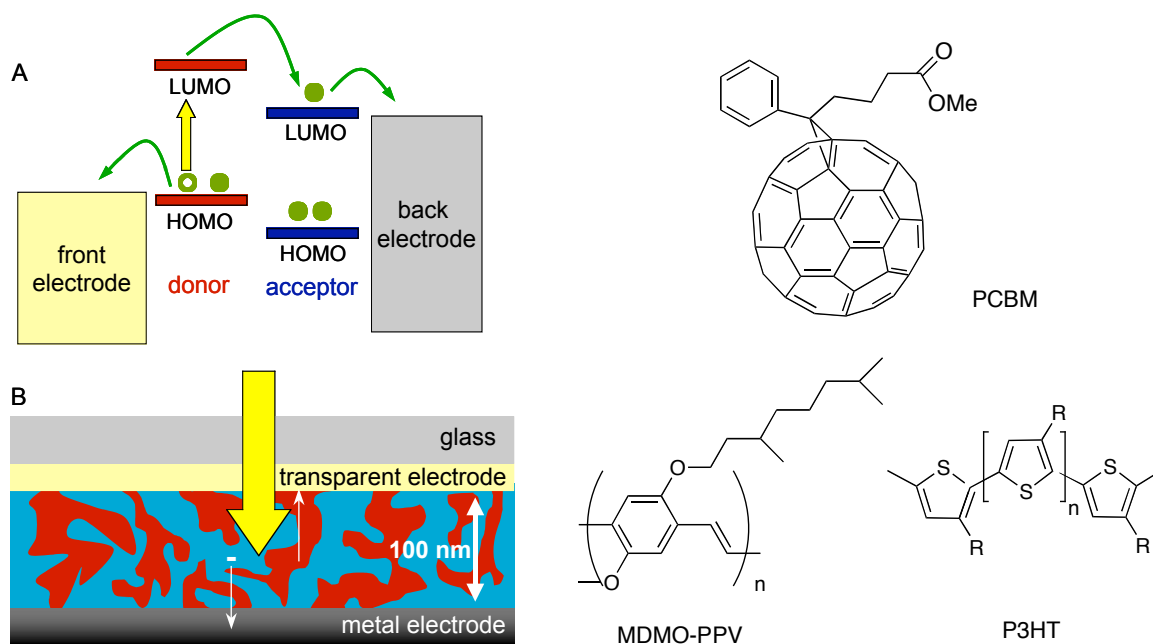


Figure 8.10. (left) The bulk-heterojunction concept. After absorption of light by the polymer, fast charge transfer occurs due to the nanoscopic mixing of the donor and acceptor materials. Subsequently, the photogenerated charges are transported and collected at the electrodes. (right) Donor and acceptor materials used in polymer-fullerene bulk-heterojunction solar cells. Acceptors: PCBM: 3'-phenyl-3'H-cyclopropa[1,9][5,6]fullerene-C₆₀-I_h-3'-butanoic acid methyl ester. Donors: MDMO-PPV = poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-p-phenylene vinylene]; P3HT = poly(3-hexylthiophene);

A breakthrough to truly appealing power conversion efficiencies exceeding 2.5% under simulated AM1.5 illumination was realized for bulk-heterojunction solar cells based on MDMO-PPV as a donor and PCBM as an acceptor. In PCBM, the fullerene cage carries a

substituent that prevents extensive crystallization upon mixing with the conjugated polymer and enhances the miscibility.

The electrical current densities are mainly limited by incomplete utilization of the incident light due to a poor match of the absorption spectrum of the active layer with the solar spectrum, and low charge carrier mobilities of the organic or polymer semiconductors. In this respect, the use of P3HT (Figure 8.10), which is known to have a high charge-carrier mobility and reduced bandgap compared to MDMO-PPV, has been considered for use in solar cells in combination with PCBM. P3HT/PCBM blends indeed exhibit an increased performance compared to MDMO-PPV. These higher efficiencies were obtained through the use of post-production treatment. After spin coating of the active layer and deposition of the aluminium top electrode, treating P3HT/PCBM solar cells by applying a voltage higher than the open circuit voltage and a temperature higher than the glass transition temperature of approximately 120 °C led to an improved overall efficiency. This post-production treatment enhances the crystallinity of the P3HT and improves the charge carrier mobility. Photovoltaic devices of P3HT/PCBM have reached power conversion efficiencies of close to 5%.

8.6. Future developments regarding lifetimes and efficiencies

Of course any practical application of bulk-heterojunction polymer-fullerene solar cells requires that the cells are stable during the operation. Similar to the polymer light-emitting diodes, the present-day organic, polymer-based solar cells must be protected from ambient air to prevent degradation of the active layer and electrode materials by the effects of water and oxygen. Even with proper protection there are several degradation processes that need to be eliminated to ensure stability. Apart from device integrity, the materials must be photochemically stable and the nanoscale uniformity of donor-acceptor blend in the active layer should be preserved.

New combinations of materials that are being developed in various laboratories focus on improving the three parameters that determine the energy conversion efficiency of a solar cell, *i.e.* the open-circuit voltage (V_{oc}), the short-circuit current (J_{sc}), and the fill factor (FF) that represents the curvature of the current density-voltage characteristic. For ohmic contacts the open-circuit voltage of bulk-heterojunction polymer photovoltaic cells is governed by the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of donor and acceptor, respectively. In most polymer/fullerene solar cells, the positioning of these band levels of donor and acceptor is such that up to 0.4 to 0.8 eV is lost in the electron-transfer reaction. By more careful positioning of these levels, it is possible to raise the open-circuit voltage well above 1 V. The trade-off of increasing the donor-HOMO to acceptor-LUMO energy is that eventually a situation will be reached in which the photoinduced electron transfer is held back by a loss of energy gain.

One of the crucial parameters for increasing the photocurrent is the absorption of more photons. This may be achieved by increasing the layer thickness and by shifting the absorption spectrum of the active layer to longer wavelengths. Although the first improvement may seem trivial at first sight, an increase of the layer thickness is presently limited by the charge carrier mobility and lifetime. When the mobility is too low or the layer too thick, the transit time of photogenerated charges in the device becomes longer than the lifetime, resulting in charge recombination. The use of polymers such as P3HT that are known

to have high charge carrier mobilities allows an increase in film thickness from the usual ~100 nm to well above 500 nm, without a loss of current.

The absorption of the active layer in state-of-the-art devices currently spans the wavelength range from the UV up to about ~ 650 nm. In this wavelength range the monochromatic external quantum efficiency can be as high as 70% under short-circuit conditions, implying that the vast majority of absorbed photons contribute to the current. The intensity of the solar spectrum, however, maximizes at ~700 nm and extends into the near infrared. Hence, a gain in efficiency can be expected when using low-band gap polymers. The preparation of low-band gap, high mobility and soluble low-band gap polymers is not trivial and requires judicious design in order to maintain the open-circuit voltage or efficiency of charge separation. Because the open-circuit voltage of bulk-heterojunction solar cells is governed by the HOMO of the donor and the LUMO levels of the acceptor, the most promising strategy seems to lower the band gap by adjusting the other two levels, *i.e.* decrease the LUMO of the donor, or increase the HOMO of the acceptor, or both.

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