

A PERSPECTIVE STUDY OF ORGANIC SOLAR CELLS

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ABSTRACT

Solar cells based on organic semiconductors have attracted much attention. The thickness of the active layer of organic solar cells is typically only 100 nm thin, which is about 1000 times thinner than for crystalline silicon solar cells and still 10 times thinner than for current inorganic thin film cells. The low material consumption per area and the easy processing of organic semiconductors offer a huge potential for low cost large area solar cells. However, to compete with inorganic solar cells the efficiency of organic solar cells has to be improved by a factor of 2-3. Several organic semiconducting materials have been investigated so far, but the optimum material still has to be designed. Similar as for organic light emitting devices (OLED) small molecules are competing with polymers to become the material of choice. After a general introduction into the device structures and operational principles of organic solar cells the three different basic types (all polymer based, all small molecules based and small molecules mixed with polymers) are described in this review.

INTRODUCTION

Organic photovoltaic devices have gained a broad interest in the last few years due to their potential for large-area low-cost solar cells. From the first reports on molecular thin film devices more than 30 years ago, their power conversion efficiencies have increased considerably from 0.001% in 1975 [1] to 1% in 1986 [2] and more recently to 5.5% in 2006 [3]. The progresses in efficiency will possibly make them a competitive alternative to inorganic solar cells in the near future. Different concepts have been published using either small molecules [4], conjugated polymers [5], combinations of small molecules and conjugated polymers [6], or combinations of inorganic and organic materials [7] as the active layer. "Active layer" refers here to the layer in which the majority of the incident light is absorbed and charges are generated. Small molecules and polymers differ in their molecular weights. Commonly, macromolecules with a molecular weight larger than 10 000 amu are called polymers, whereas lighter molecules are referred to as "oligomers" or "small molecules."

Historically, small molecules were mainly deposited by vacuum deposition techniques since they showed limited solubility in common solvents. In contrast to these small molecule thin films, the preparation of thin polymer layers does not require high vacuum sublimation steps. Large

polymer thin film areas can be deposited by several methods, such as spin-coating, screen printing, spray coating, or ink jet printing, allowing for large-area, ultrathin, flexible, and lowcost devices. Currently, there is a head-to-head race going on between solution processed and sublimed organic solar cells, but the ease of processability may finally tip the balance in favour of polymers or small molecules blended with polymers. Although it should be noted that currently there are some efforts to develop soluble oligomers to allow for cost efficient solution processing techniques, the concept of efficient complete small molecules-based devices prepared from solution processing has yet to be proven.

DEVICE STRUCTURE AND OPERATION

Organic semiconductors differ from classical crystalline inorganic semiconductors (e.g., silicon) in many fundamental aspects. First of all, the mobilities of organic semiconductors are several orders of magnitude less than those found in crystalline inorganic semiconductors [8]. Transport processes in organic semiconductors are best described by hopping transport in contrast to the band transport in most crystalline inorganic semiconductors. Even the highest reported hole mobilities (μ_h) for organic semiconductors reach currently only about $15 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for single crystals of small molecules [9] and $0.6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for liquid crystalline polymers [10] (silicon: $\mu_h = 450 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). Highest electron mobilities (μ_e) for organic materials are typically lower, hovering around $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ reaching higher values only in particular TFT structures using highly crystalline small molecules [11] (silicon: $\mu_e = 1400 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). The mobility values for amorphous organic materials as used most commonly in organic solar cells are even several magnitudes lower. These low mobilities limit the feasible thicknesses of the organic layer in solar cells to a few hundred nanometres.

Fortunately, organic semiconductors are very strong absorbers in the UV-VIS regime. Thus only *ca.* 100nm thick organic layers are needed for effective absorption. Second, the exciton binding energy in organic semiconductors is much higher than, for example, in silicon. Upon absorption of a photon of sufficient energy by the organic semiconductor, an electron is promoted into the lowest unoccupied molecular orbital (LUMO), leaving behind a hole in the highest occupied molecular orbital (HOMO). However, due to electrostatic interactions, this electron-hole pair forms a tightly bound state which is called singlet exciton. The exact binding energy of this exciton is still under debate but it is expected to be in a range of 200–500 meV [12]. Hence, the exciton binding energy for organic semiconductors is roughly one order of magnitude larger than for inorganic semiconductors like silicon, where photoexcitations typically lead directly to free carriers at room temperature.

The thermal energy at room temperature ($\sim 25 \text{ meV}$) is not sufficient to efficiently generate free charge carriers in organic materials by exciton dissociation, even at typical internal electric fields

($\sim 10^6$ – 10^7 V/m). For example, in the widely used Poly(2-methoxy-5-(2'-ethyl-hexyloxy)-p-phenylene vinylene) (MEH-PPV) [13] experiments revealed that only 10% of the excitons dissociate into free carriers in a pure layer, while the remaining excitons decay via radiative or nonradiative recombination pathways. Thus, the energy efficiencies of single-layer polymer devices remain typically below 0.1%.

The most important discovery on the route to high efficiency organic solar cells was the finding that solar cells containing a heterojunction between hole and electron accepting organic materials exhibited performances far superior to single component devices [2]. Using the heterojunction approach, photogenerated excitons (bound electron-hole pairs) in the polymer layer can be efficiently dissociated into free carriers at the interface, whereas in single component devices most excitons recombine after a short time. The charge separation occurs at the interface between donor and acceptor molecules, mediated by a large potential drop. After photo-excitation of an electron from the HOMO to the LUMO, the electron can jump from the LUMO of the donor (the material with the higher LUMO) to the LUMO of the acceptor if the potential difference $\Delta\phi$ between the ionization potential of the donor and the electron affinity of the acceptor is larger than the exciton binding energy (see Figure 1). However, this process, which is called photoinduced charge transfer, can lead to free charges only if the hole remains on the donor due to its higher HOMO level.

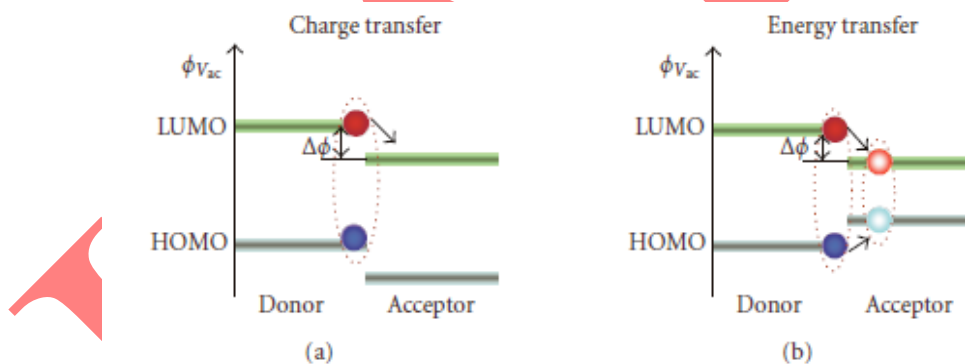


Figure 1: The interface between two different semiconducting polymers (D = donor, A = acceptor) can facilitate either charge transfer by splitting the exciton or energy transfer, where the whole exciton is transferred from the donor to the acceptor.

In contrast, if the HOMO of the acceptor is higher, the exciton transfers itself completely to the material of lower-band gap accompanied by energy loss. For efficient exciton dissociation at the heterojunction, the donor and acceptor materials have to be in close proximity. The optimum length scale is in the range of the exciton diffusion length, typically a few tens of nanometres. On the other hand, the thickness of the active layer should be comparable to the penetration length of the incident light, which for organic semiconductors is typically 80–200 nm.

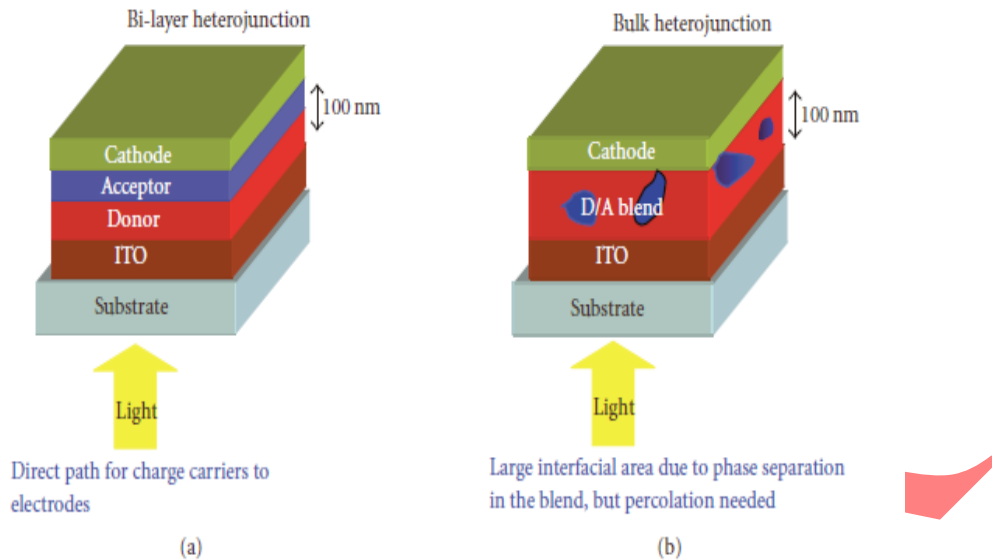


Figure 2: Two approaches to heterojunction solar cells.

A heterojunction can be realised in several ways (see Figure 2). The most straightforward approach is the preparation of a bilayer by subliming or by spin-coating a second layer on top of the first, resulting in a more or less diffused bilayer structure. If polymers are used and both materials are soluble in the same solvents, laminating techniques can be used. This bilayer geometry guarantees directional photoinduced charge transfer across the interface.

Since both types of charge carriers travel to their respective electrodes in pure *n*-type or *p*-type layers, the chances for recombination losses are significantly reduced. However, the interfacial area and thus the exciton dissociation efficiency are limited. Higher interfacial areas and thus improved exciton dissociation efficiencies can be achieved if layers containing both the electron donor and electron acceptor in a mixture are prepared. These so-called bulk heterojunctions can be deposited either by cosublimation of small molecules or by spin-coating mixtures of polymers.

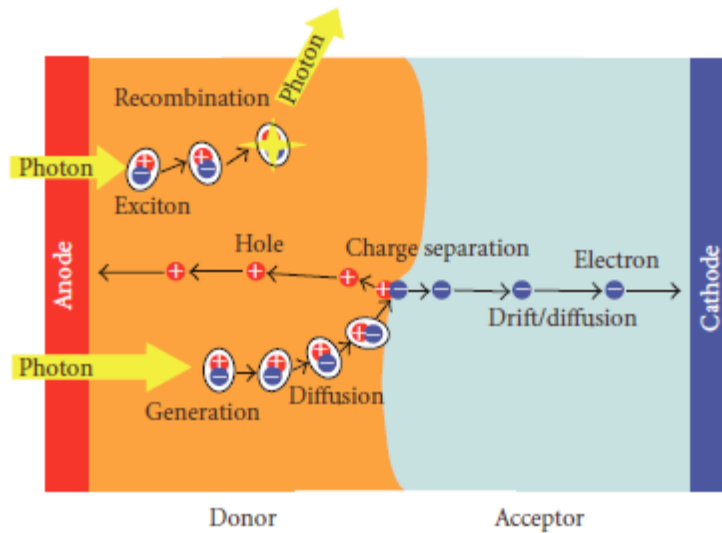


Figure 3: Principle of charge separation in a solar cell.

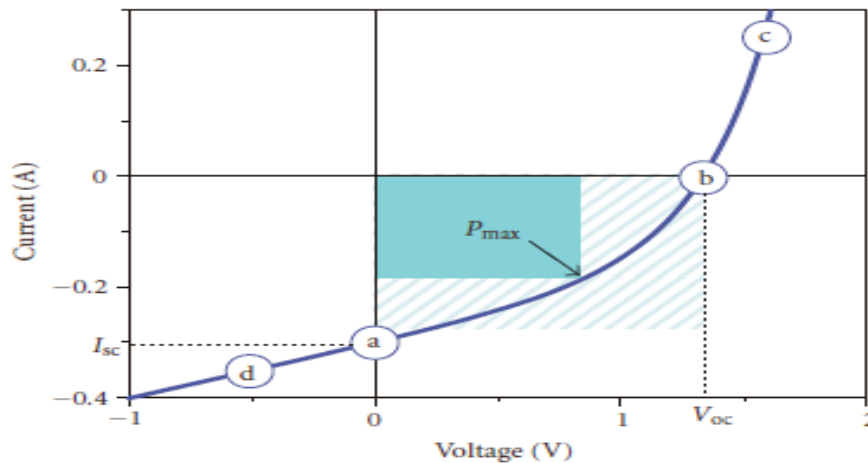
The drawback of the bulk heterojunction structure is that a percolating pathway for the hole and electron transporting phase to the electrodes is needed in order that the separated charge carriers can reach their corresponding electrodes. If the individual layer thicknesses (in case of a bilayer structure) or the phase separated domains (in case of a blend layer) is larger than the exciton diffusion length, then most excitons will recombine (Figure 3). If, however, the excitons are generated in close proximity to an interface, they have a chance to be separated into free charge carriers which may diffuse or drift to the corresponding electrodes. The overall efficiency of this process is described by the incident photon to converted electron efficiency (IPCE). The IPCE is calculated by the number of electrons leaving the device under short circuit condition per time and area divided by the number of photons incident per time and area:

$$\text{IPCE} = \frac{\# \text{ extracted electrons}}{\# \text{ incident photons}} \quad (1)$$

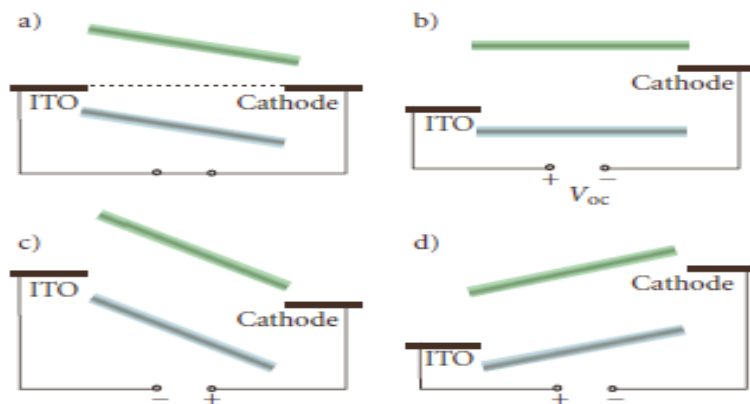
Note that the IPCE is a measure of the external quantum efficiency, meaning that losses due to reflection at the surface or transmission through the device are included in the IPCE value. Subtracting these two loss channels would lead to the internal quantum efficiency, which is, however, rarely used to compare solar cells.

Solar cells are further characterised by measuring the current-voltage $I(V)$ curve under illumination of a light source that mimics the sun spectrum. A typical current-voltage $I(V)$ curve of a polymer solar cell is shown in Figure 4. Since organic semiconductors show very low intrinsic carrier concentration, the metal-insulator-metal (MIM) model seems to be best suited to explain this characteristic.

The characteristic points used to characterise a solar cell are labelled in Figure 4. In addition, for each of these points, the energy diagram for a single-layer cell with an indium tin oxide (ITO) anode and aluminium cathode is displayed.



(a)



(b)

Figure 4: Current (voltage) characteristics of a typical organic diode shown together with the metal-insulator-metal (MIM) picture for the characteristic points. (a) Short circuit condition. (b) Open circuit condition. (c) Forward bias. (d) Reverse bias.

(a) The current delivered by a solar cell under zero bias is called short circuit current (I_{sc}). In this case, exciton dissociation and charge transport is driven by the so-called built-in potential. In the MIM picture, this potential is equal to the difference in work function (W_f) of the hole- and electron-collecting electrodes. For polymer solar cells, the transparent ITO electrode is often chosen ($W_{f,ITO} = 4.7$ eV) in combination with a low work function material ($W_{f,Ca} = 2.87$ eV, $W_{f,Mg} = 3.66$ eV, $W_{f,Al} = 4.24$ eV) as counter-electrode to achieve a high internal field. For example, the difference in work functions between ITO and Ca is approximately 2 eV.

(b) The voltage where the current equals zero is called open circuit voltage (V_{oc}). In the MIM picture this situation is described by the case where the band is flat, since the applied voltage equals the difference in the work function of the electrodes. (Note that diffusion effects are neglected in this simplified picture.)

(c) When $V > V_{oc}$, the diode is biased in the forward direction. Electrons are now injected from the low work function electrode into the LUMO and holes from the high work function electrode into the HOMO of the organic layer, respectively.

(d) When $V < 0$, the diode is driven under a reverse biased condition the solar cells works as a photodiode. The field is higher than in (a) which often leads to enhanced charge generation and/or collection efficiency. The point where the electrical power $P = I \cdot V$ reaches the maximum value represents the condition where the solar cell can deliver its maximum power to an external load. It is called the maximum power point. The ratio of this maximum electrical power P_{max} to the product of the short circuit current and the open circuit voltage is termed the fill factor (FF):

$$FF = \frac{P_{max}}{I_{sc} \times V_{oc}} \quad (2)$$

Ideally, the fill factor should be unity, but losses due to transport and recombination result in values between 0.2–0.7 for organic photovoltaic devices. As an example, a constant slope of the $I(V)$ characteristic corresponds to $FF = 0.25$. The photovoltaic power conversion efficiency (η) is then calculated for an incident light power P_{light} :

$$\eta = \frac{I_{sc} \times V_{oc} \times FF}{P_{light}} \quad (3)$$

The different basic types (all polymer based, all small molecules based and small molecules mixed with polymers) are described as follows.

1. Small Molecule-Based Solar Cells
2. Polymer-Based Solar Cells
3. Blends of Polymer and Small Molecules
4. Tandem Solar Cells

SUMMARY

Recently, organic solar cells have broken the 5% power conversion efficiency barrier. While currently small molecules (e.g., CuPc) and polymers (e.g., P3HT) are similarly well suited as

electron donor materials, these high efficiencies cannot currently be obtained using polymeric electron acceptors due to the low electron mobilities in these materials.

Fullerenes and fullerene derivatives like PCBM are currently needed to reach 5% efficiency. However, it seems that P3HT:PCBM or CuPc:C60 devices have already been pushed fairly close to their theoretical efficiency limits, with quantum efficiencies greater than 80% already quite common. Therefore, it seems sure that new materials are needed to push the efficiencies into the 10% region, which is the generally agreed upon benchmark for economically viable photovoltaic devices. Either the open circuit voltage has to be raised by better matching of the energy levels of donor and acceptor materials or a broader spectrum of the sunlight needs to be absorbed using low-bandgap absorbers. Developing novel crystalline electron acceptors with high electron mobilities and tunable energy levels to replace fullerene derivatives might be one promising direction for the future to achieve higher open circuit voltages, especially since not much research has been done in this direction. The tandem approach might be the key for harvesting a broader fraction of the sunlight in conjunction with novel low-bandgap materials.

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