

Introduction to polymer solar cells

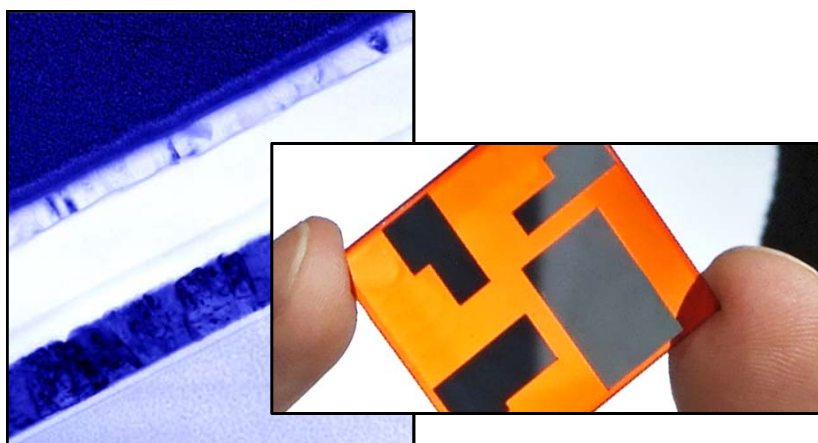
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New photovoltaic (PV) energy technologies can contribute to environmentally friendly, renewable energy production, and the reduction of the carbon dioxide emission associated with fossil fuels and biomass. One new PV technology, plastic solar cell technology, is based on conjugated polymers and molecules. Polymer solar cells have attracted considerable attention in the past few years owing to their potential of providing environmentally safe, flexible, lightweight, inexpensive, efficient solar cells. Especially, bulk-heterojunction solar cells consisting of a mixture of a conjugated donor polymer with a methanofullerene acceptor are considered as a promising approach. Here a brief introduction and overview is given of the field of polymer solar cells.

1. Introduction

It is expected that the global energy demand will double within the next 50 years. Fossil fuels, however, are running out and are held responsible for the increased concentration of carbon dioxide in the earth's atmosphere. Hence, developing environmentally friendly, renewable energy is one of the challenges to society in the 21st century. One of the renewable energy technologies is photovoltaics (PV), the technology that directly converts daylight into electricity. PV is one of the fastest growing of all the renewable energy technologies, in fact, it is one of the fastest growing industries at present.¹ Solar cell manufacturing based on the technology of crystalline, silicon devices is growing by approximately 40% per year and this growth rate is increasing.¹ This has been realized mainly by special market implementation programs and other government grants to encourage a substantial use of the current PV technologies based on silicon. Unfortunately, financial support by governments is under constant pressure.

At present, the active materials used for the fabrication of solar cells are mainly inorganic materials, such as silicon (Si), gallium-arsenide (GaAs), cadmium-telluride (CdTe), and cadmium-indium-selenide (CIS). The power conversion efficiency for these solar cells varies from 8 to 29% (Table 1). With regard to the technology used, these solar cells can be divided into two classes. The crystalline solar cells or silicon solar cells are made of either (mono- or poly-) crystalline silicon or GaAs. About 85% of the PV market is shared by these crystalline solar cells.¹ Amorphous silicon, CdTe, and CI(G)S are more recent thin-film technologies.

Table 1. Status of the power conversion efficiencies in February 2002, as reached for inorganic solar cells and the technology used to prepare these solar cells. Source: Photovoltaic Network for the Development of a Roadmap for PV (PV-NET).

Semiconductor material	Power conversion efficiency [%]	Technology
Mono-crystalline silicon	20-24	Crystalline
Poly-crystalline silicon	13-18	Thick and thin-film
Gallium-arsenide	20-29	Crystalline
Amorphous silicon	8-13	Thin-film
Cadmium telluride	10-17	Thin-film
Cadmium indium selenide	10-19	Thin-film

The current status of PV is that it hardly contributes to the energy market, because it is far too expensive. The large production costs for the silicon solar cells is one of the major obstacles. Even when the production costs could be reduced, large-scale production of the current silicon solar cells would be limited by the scarcity of some elements required, e.g. solar-grade silicon. To ensure a sustainable technology path for PV, efforts to reduce the costs of the current silicon technology need to be balanced with measures to create and sustain variety in PV technology. It is, therefore, clear that 'technodiversity', implying new solar cell technologies, is necessary.² In the field of inorganic thin-films, technologies based on cheaper production processes are currently under investigation.

Another approach is based on solar cells made of entirely new materials, conjugated polymers and molecules. Conjugated materials are organics consisting of alternating single and double bonds. The field of electronics based on conjugated materials started in 1977 when Heeger, MacDiarmid, and Shirakawa discovered that the conductivity of the conjugated polymer polyacetylene (PA, Figure 1) can be increased by seven orders of magnitude upon oxidation with iodine,³ for which they were awarded the Nobel Prize in Chemistry in 2000.^{4,5,6,7} This discovery led, subsequently, to the discovery of electroluminescence in a poly(p-phenylene vinylene) (PPV, Figure 1) by Burroughes et al. in 1990.^{8,9} The first light-emitting products based on electroluminescence in conjugated polymers have already been launched at the consumer market by Philips (The Netherlands) in 2002, whereas light-emitting products based on conjugated molecules have been introduced by the joint venture of Kodak and Sanyo (Japan). Going from discovery to product within a little bit more than one decade truly holds a huge promise for the future of plastic electronics. Other emerging applications are coatings for electrostatic dissipation and electromagnetic-interference shielding.¹⁰

Conjugated polymers and molecules have the immense advantage of facile, chemical tailoring to alter their properties, such as the band gap. Conjugated polymers (Figure 1) combine the electronic properties known from the traditional semiconductors and conductors with the ease of processing and mechanical flexibility of plastics. Therefore, this new class of materials has attracted considerable attention owing to its potential of providing environmentally safe, flexible, lightweight, inexpensive electronics.

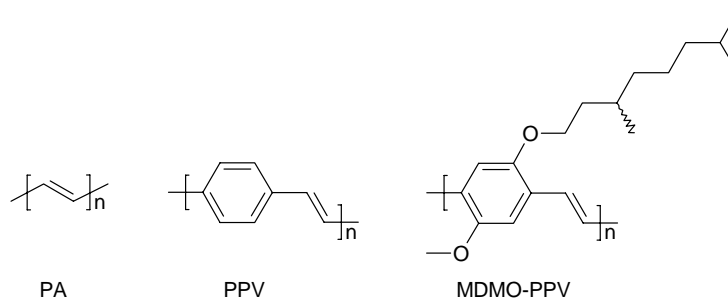


Figure 1. Molecular structures of the conjugated polymers trans-polyacetylene (PA), poly(p-phenylene vinylene) (PPV), and a substituted PPV (MDMO-PPV).

The cost reduction mainly results from the ease of processing from solution. 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. Furthermore, the nanoscale morphology, affecting the opto-electronic properties of these polymer films, can be controlled by proper choice of the position and nature of these side-groups.

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. Architectures to overcome possible electronic scale-up problems related to thin film organics are being developed.¹¹ In contrast to conjugated polymers, conjugated molecules are mainly thermally evaporated under high vacuum. This deposition technique is much more expensive than solution processing and, therefore, less attractive.

The necessity for new PV technologies together with the opportunities in the field of plastic electronics, such as roll-to-roll production, have drawn considerable attention to plastic solar cells in the past few years. Apart from application in PV, it is expected that plastic solar cells will create a completely new market in the field of cheap electronics.

2. The need for two semiconductors

Photovoltaic cell configurations based on organic materials differ from those based on inorganic semiconductors, because the physical properties of inorganic and organic semiconductors are significantly different. Inorganic semiconductors generally have a high

dielectric constant and a low exciton binding energy (for GaAs the exciton binding energy is 4 meV). Hence, the thermal energy at room temperature ($k_B T = 0.025$ eV) is sufficient to dissociate the exciton created by absorption of a photon into a positive and negative charge carrier. The formed electrons and holes are easily transported as a result of the high mobility of the charge carriers and the internal field of the p-n junction. Organic materials have a lower dielectric constant and the exciton binding energy is larger than for inorganic semiconductors, although the exact magnitude remains a matter of debate. For polydiacetylene 0.5 eV is needed to split the exciton and, hence, dissociation into free charge carriers does not occur at room temperature. To overcome this problem, organic solar cells commonly utilize two different materials that differ in electron donating and accepting properties. Charges are then created by photoinduced electron transfer between the two components. This photoinduced electron transfer between donor and acceptor boosts the photogeneration of free charge carriers compared to the individual, pure materials, in which the formation of bound electron-hole pairs, or excitons is generally favored.

3. Basic processes in an organic solar cell

Various architectures for organic solar cells have been investigated in recent years. In general, for a successful organic photovoltaic cell four important processes have to be optimized to obtain a high conversion efficiency of solar energy into electrical energy.

- Absorption of light
- Charge transfer and separation of the opposite charges
- Charge transport
- Charge collection

For an efficient collection of photons, the absorption spectrum of the photoactive organic layer should match the solar emission spectrum and the layer should be sufficiently thick to absorb all incident light. A better overlap with the solar emission spectrum is obtained by lowering the band gap of the organic material, but this will ultimately have some bearing on the open-circuit voltage. Increasing the layer thickness is advantageous for light absorption, but burdens the charge transport.

Creation of charges is one of the key steps in photovoltaic devices in the conversion of solar light into electrical energy. In most organic solar cells, charges are created by photoinduced electron transfer. In this reaction an electron is transferred from an electron

donor (D), a p-type semiconductor, to an electron acceptor (A), an n-type semiconductor, with the aid of the additional input energy of an absorbed photon ($h\nu$). In the photoinduced electron transfer reaction the first step is excitation of the donor (D^*) or the acceptor (A^*), followed 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 important that the charge-separated state is the thermodynamically and kinetically most favorite pathway after photoexcitation. 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, it is of importance that the charge-separated state is stabilized, so that the photogenerated charges can migrate to one of the electrodes. Therefore, the back electron transfer should be slowed down as much as possible.

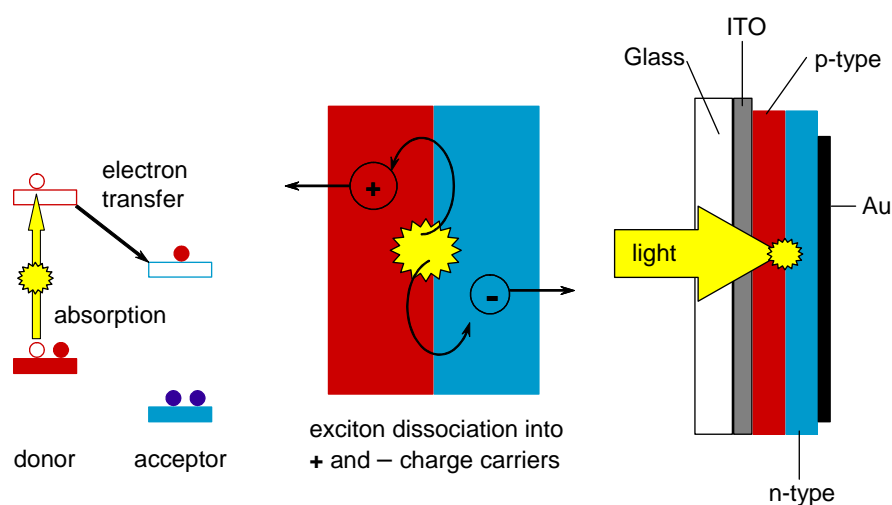


Figure 2. Schematic drawing of the working principle of an organic photovoltaic cell. Illumination of donor (in red) through a transparent electrode (ITO) results in the photoexcited state of the donor, in which an electron is promoted from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the donor. Subsequently, the excited electron is transferred to the LUMO of the acceptor (in blue), resulting in an extra electron on the acceptor ($A^{\bullet-}$) and leaving a hole at the donor ($D^{\bullet+}$). The photogenerated charges are then transported and collected at opposite electrodes. A similar charge generation process can occur, when the acceptor is photoexcited instead of the donor.

To create a working photovoltaic cell, the photoactive material (D+A) is sandwiched between two dissimilar (metallic) electrodes (of which one is transparent), to collect the photogenerated charges. After the charge transfer reaction, the photogenerated charges have to migrate to these electrodes without recombination. Finally, it is important that the photogenerated charges can enter the external circuit at the electrodes without interface problems.

4. Actual 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 light, followed by cells in which an organic or polymeric material is used for absorption of light and charge transport.

4.1 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 (TiO₂).¹² To date, ruthenium dye-sensitized nanocrystalline TiO₂ (nc-TiO₂) solar cells reach an energy conversion efficiency of about 10% in solar light.¹³ In the Grätzel cell (Figure 3), the ruthenium dye takes care of light absorption and electron injection into the TiO₂ conduction band. An I⁻/I₃⁻ 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 I₃⁻ takes up an electron from the external circuit (counter electrode), while the negative charges injected in nc-TiO₂ are collected at the fluorine doped tin oxide (SnO₂:F) electrode.

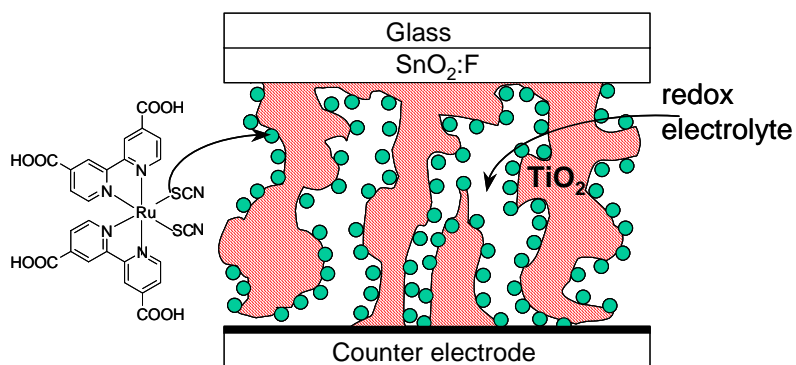


Figure 3. The dye-sensitized solar cell. After absorption of light by the ruthenium dye, an electron is transferred to TiO_2 . The dye is then reduced by a redox electrolyte, I^-/I_3^- , which in turn, is reduced at the metal counter electrode. As a result, a positive charge is transported from the dye to the metal electrode via the electrolyte. The electron in TiO_2 is transported to the $\text{SnO}_2:\text{F}$ 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 directly adsorbed 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%.¹⁴

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 hole transporting material.¹⁵ The photoinduced charge separation at the interface of an organic and inorganic semiconductor has been studied in relation to photovoltaic devices.¹⁶ 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 TiO₂ for efficient charge separation and energy conversion, the distance between the site of excitation and the interface must be within the exciton diffusion length. In most organic materials, the exciton diffusion length is limited to 5-10 nm¹⁷ by the fast intrinsic decay processes of the photoexcited molecules. Creating nanoporous TiO₂ of such dimensions, and filling it completely with an organic semiconductor, is currently one of the challenges in this area.

4.2 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.¹⁸ In these cells, the photovoltaic properties strongly depend on the nature of the electrodes. Heavily doped conjugated materials resulted in reasonable power conversion efficiencies up to 0.3%.¹⁸

In 1986, a major breakthrough was realized by Tang, who introduced a double-layer structure of a p- and n-type organic semiconductor (see Figure 2).¹⁹ 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 4). 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/m²). Important aspect in this concept is that the charge generation efficiency is relatively independent of the bias voltage.

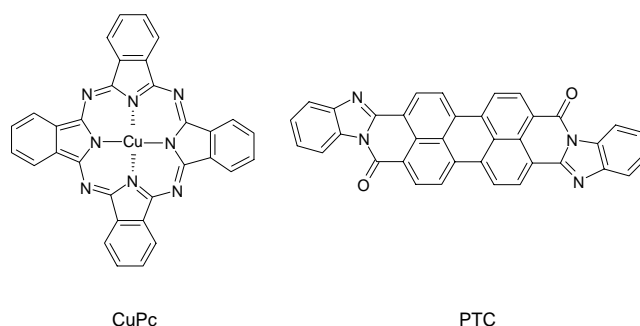


Figure 4. Molecular structures of copper phthalocyanine (CuPc), a perylene tetracarboxylic derivative (PTC).

In the double-layer structure the photoexcitations in the photoactive material have to reach the p-n interface (Figure 2, middle) where charge transfer can occur, before the excitation energy of the molecule 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 5-10nm,¹⁷ only absorption of light within a very thin layer around the interface contributes to the photovoltaic effect. This limits the performance of double-layer devices, because such thin layer can impossibly absorb all the 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.

4.3 Bulk heterojunction cells

In combining electron donating (*p*-type) and electron accepting (*n*-type) materials in the active layer of a solar cell, care must be taken that excitons created in either material can diffuse to the interface, to enable 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.^{20,21} By simple mixing the *p* and *n*-type materials and relying on the intrinsic tendency of polymer materials to phase separate on a nanometer dimension, junctions throughout the bulk of the material are created that ensure quantitative dissociation of photogenerated excitons, irrespective of the thickness. Polymer-fullerene solar cells were among the first to utilize this bulk-heterojunction principle.²⁰ Nevertheless, this attractive solution poses a new challenge. Photogenerated charges must be able to migrate to the collecting electrodes through this intimately mixed blend. 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 which inclusions, cul-de-sacs, or barrier layers are avoided. The close-to-ideal bulk heterojunction solar cell, may look like depicted in Figure 1. When such a bulk-heterojunction is deposited on an ITO substrate and capped with a metal back electrode, working photovoltaic cells can be obtained (Figure 5).

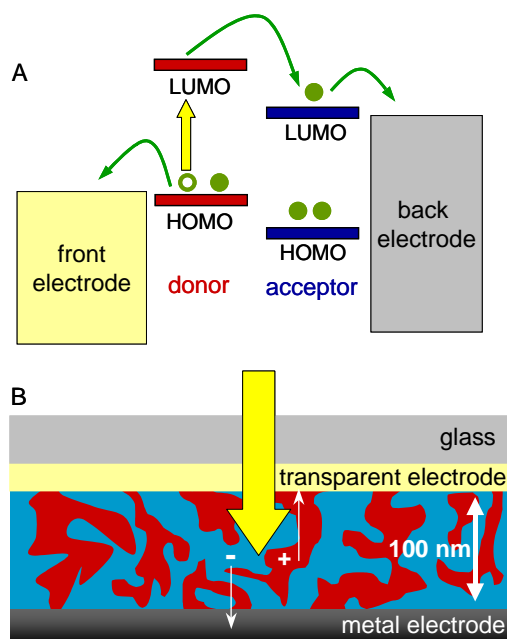


Figure 5. The bulk-heterojunction concept. After absorption of light by the photoactive material, charge transfer can easily occur due to the nanoscopic mixing of the donor and acceptor (solid and dashed area). Subsequently, the photogenerated charges are transported and collected at the electrodes.

The bulk heterojunction is presently the most widely used photoactive layer. The name bulk-heterojunction solar cell has been chosen, because the interface (heterojunction) between both components is all over the bulk (Figure 5), in contrast to the classical (bilayer-) heterojunction. As a result of the intimate mixing, the interface where charge transfer can occur has increased enormously. The exciton, created after the absorption of light, has to diffuse towards this charge-transfer interface for charge generation to occur. The diffusion length of the exciton in organic materials, however, is typically 10 nm or less. This means that for efficient charge generation after absorption of light, each exciton has to find a donor-acceptor interface within a few nm, otherwise it will be lost without charge generation. An intimate bicontinuous network of donor and acceptor materials in the nanometer range should suppress exciton loss prior to charge generation. 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.

5. State-of the-art in bulk-heterojunction solar cells

Various combinations of donor and acceptor materials have been used to build bulk-heterojunction solar cells in which the composite active layer is inserted between two electrodes. One of the most promising combinations of materials is a blend of a semiconducting polymer as a donor and a fullerene, C_{60} derivative as acceptor. It is well established that at the interface of these materials a sub-picosecond photoinduced charge transfer occurs that ensures efficient charge generation.^{22,23} Surprisingly, the lifetime of the resulting charge-separated state in these blends extends into the millisecond time domain.^{24,25} This longevity allows the photogenerated charge carriers to diffuse away from the interface (assisted by the internal electric field in the device) to be collected in an external circuit at the electrodes.

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 (names and structures of these compounds are given in Figure 6).²⁶

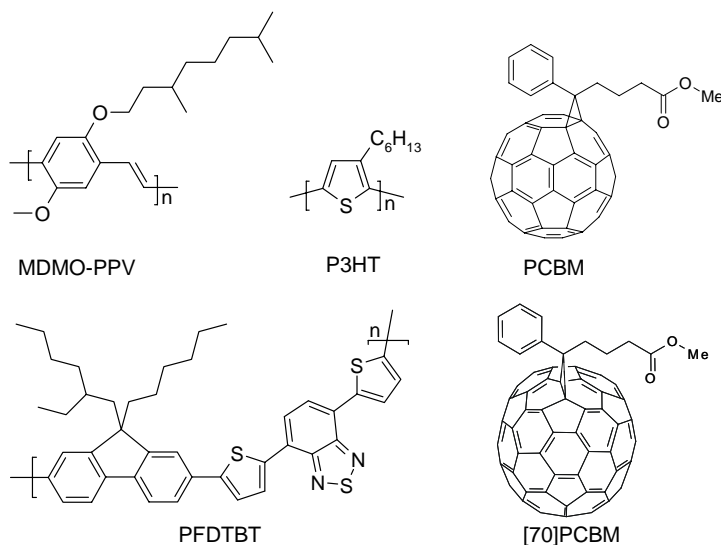


Figure 6. Donor and acceptor materials used in polymer-fullerene bulk-heterojunction solar cells. Donors: MDMO-PPV = poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-p-phenylene vinylene]; P3HT= poly(3-hexylthiophene); PFDTBT: poly[2,7-[9-(2'-ethylhexyl)-9-hexylfluorene]-alt-5,5-(4',7'-di-2-thienyl-2',11',3'-benzothiadiazole)].

Acceptors: PCBM: 3'-phenyl-3'H-cyclopropa[1,9][5,6]fullerene- C_{60} -I_h-3'-butanoic acid methyl ester; [70]PCBM: 3'-phenyl-3'H-cyclopropa[8,25][5,6]fullerene- C_{70} -D_{5h}(6)-3'-butanoic acid methyl ester.

In PCBM, the fullerene cage carries a substituent that prevents extensive crystallization upon mixing with the conjugated polymer and enhances the miscibility. In these 2.5%-efficient cells, the photoactive composite layer is sandwiched between two electrodes with different work functions: a transparent front electrode consisting of indium tin oxide covered with a conducting polymer polyethylenedioxythiophene:polystyrenesulfonate (PEDOT:PSS) for hole collection and a metal back electrode consisting of a very thin (~ 1 nm) layer of LiF covered with Al for electron collection. The layout of this device and a cross-sectional transmission electron microscopy (TEM) image of an actual device slab are shown in Figure 7. Except for LiF, all layers are about 100 nm thick.

Although the combination MDMO-PPV and PCBM had been used several times before, the crucial step that improved the performance came from using a special solvent in the spin coating of the active layer that improves the nanoscale morphology for charge generation and transport.²⁶ Atomic force microscopy (AFM) and TEM studies have resolved the details of the phase separation in these blends.²⁷ In the best devices, which consist of a 1:4 blend (w/w) of MDMO-PPV/PCBM, nanoscale phase separation occurs in rather pure, nearly crystalline PCBM domains and an almost homogenous 1:1 mixture of MDMO-PPV and PCBM (Figure 7).

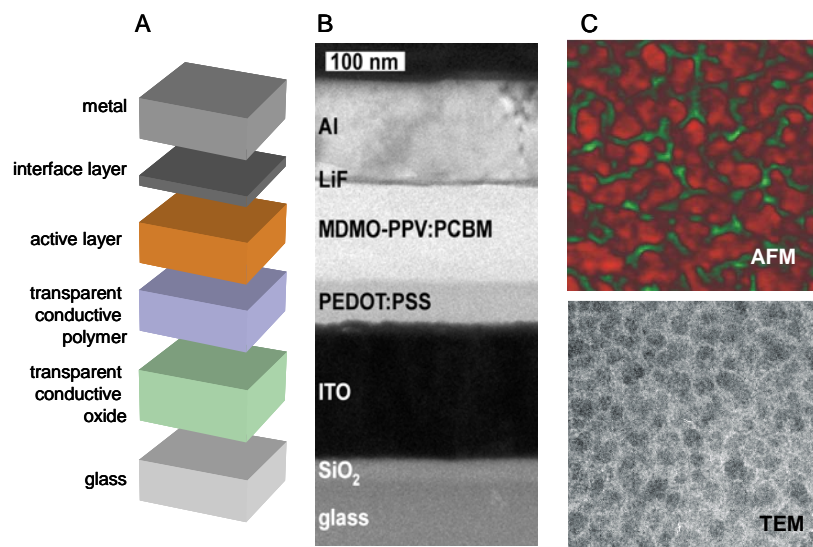


Figure 7. (a) Schematic layout of the device architecture of a polymer-fullerene bulk-heterojunction solar cell. (b) TEM image of a thin slab of an actual device, showing the individual glass, ITO, PEDOT:PSS, MDMO-PPV/PCBM (1:4 by wt.), LiF, and Al layers. (c) AFM phase and TEM images ($1 \times 1 \mu\text{m}^2$) of a MDMO-PPV/PCBM (1:4 by wt.) composite film showing phase separation into a PCBM (red in AFM, dark in TEM) and polymer-rich phase (green in AFM, light in TEM).

In recent years numerous studies have focused on a generating a deeper understanding of these MDMO-PPV/PCBM bulk heterojunctions. Investigations into the morphology, electronic structure, and charge transport have provided detailed understanding of the degree and dimensions of the phase separation in the active layer,^{27,28} on the origin of the open-circuit voltage,^{29,30} the influence of electrode materials,³¹ and the magnitude of charge carrier mobilities for electrons and holes.³² These studies revealed that PCBM has high electron mobility compared to many other organic or polymer materials that can be deposited by spin coating. Photophysical studies have provided insights on charge generation, separation, and recombination in these layers, and more recently in working devices. These detailed insights have resulted in quantitative models describing the current-voltage characteristics under illumination that serve as a guide for further development.

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 emission spectrum, and low charge carrier mobilities of the organic or polymer semiconductors. In this respect, the use of P3HT (Figure 6), 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 provide an increased performance compared to MDMO-PPV.^{33,34} These higher efficiencies were obtained through the use of post-production treatment.³³ After spin coating of the active layer and deposition of the aluminum top electrode, treating P3HT/PCBM solar cells with a potential higher than the open circuit voltage and a temperature higher than the glass transition temperature 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 with external quantum efficiencies above 75% and power conversion efficiencies of up to 3.85% have been reached.³⁵

Modification of the acceptor material has been considered also. In this respect it is important to note that PCBM—which may amount to as much as 75% of the weight of the photoactive layer—has a very low absorption coefficient in the visible region of the spectrum and, hence, provides a relatively small contribution to the photocurrent. The low absorption of C₆₀ derivatives is due to their high degree of symmetry that makes many of the low-energy transitions forbidden and hence of low intensity. When the C₆₀ moiety is replaced by a less symmetrical fullerene, such as C₇₀, these transitions become allowed and a dramatic increase in light absorption can be expected. Consequently, when [70]PCBM (which is

similar to PCBM but incorporates C_{70} instead of C_{60} , see Figure 7) was used in combination with MDMO-PPV instead of PCBM, the external quantum efficiency increased from ~50% to ~65% (Figure 8), while the current density of the solar cell increased by 50% and the power conversion efficiency to 3.0 %.³⁶

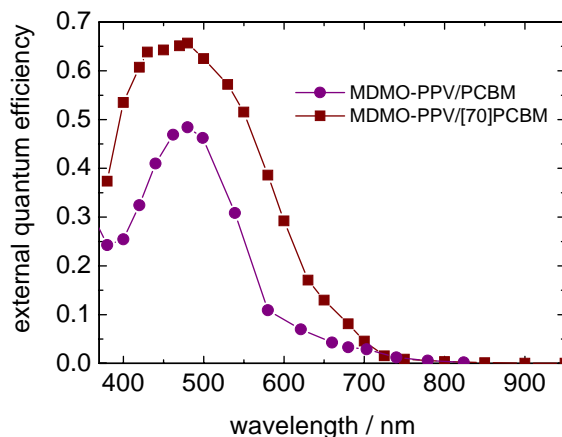


Figure 8. External quantum efficiency (EQE) of bulk-heterojunction solar cells with MDMO-PPV/PCBM (purple circles) and MDMO-PPV/[70]PCBM (brown squares) active layers. The increased EQE of the layer with [70]PCBM compared to PCBM results from an increased absorption in the visible range of the spectrum.

6. What about lifetimes?

Of course any practical application of bulk-heterojunction polymer-fullerene solar cells requires that the cells be stable. 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 bicontinuous donor-acceptor in the active layer should be preserved. A recent study revealed that MDMO-PPV/PCBM solar cells show an appreciable degradation under accelerated lifetime testing conditions (increased temperature).³⁷ Interestingly, the degradation is not so much associated with the chemical stability.³⁷ At elevated temperatures, the PCBM molecules can diffuse through the MDMO-PPV matrix and form large crystals, thereby increasing the dimension and extent of phase

segregation.³⁸ This behavior has been observed for temperatures $\sim 20^\circ\text{C}$ below the glass transition temperature, T_g , of the polymer.

Fortunately, several strategies can be envisaged that may alleviate the limited thermal stability of the morphology. In general, high T_g polymers will increase the stability of as-prepared morphologies. An example has already been established for the combination of poly(3-hexylthiophene) and fullerene derivatives, where thermal annealing was used to improve the performance.³³

Upon cooling to operating temperatures, it may be expected that no further changes occur in the morphology. Another appealing method to preserve an as-prepared morphology in these blends is by chemical or radiation induced cross-linking, analogous to methods recently employed for polymer light-emitting diodes.³⁹ Finally, the use of *p-n* block copolymers seems an interesting option, because here phase separation will be dictated by the covalent bonds between the two blocks.⁴⁰ Nevertheless, creation of nanoscale bulk-heterojunction morphologies that are stable in time and with temperature is one of the challenges that must be met before polymer photovoltaics can be applied successfully.

In this respect it is important that testing of a novel semiconductor blend showed that all relevant device parameters changed less than 20% during 1000 hours of operation at 85°C .³⁷ This demonstrates that outstanding high stabilities are within reach.

7. Future directions for improving efficiencies

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 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 $\sim 0.4\text{--}0.8$ 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. A very encouraging result in this respect is PFDTBT (Figure 2) that gives $V_{oc} = 1.04$ V in combination with PCBM,⁴¹ compared to 0.8–0.9 V for MDMO-PPV and 0.5–0.6 V for P3HT.

The tradeoff 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 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 processable low-band gap polymers is not trivial and requires judicious design in order to maintain the open-circuit voltage or efficiency of charge separation.⁴² 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. Several groups are actively pursuing low-band gap polymers and the first, promising results are emerging.

A high fill factor (strongly curved J - V characteristic) is advantageous and indicates that fairly strong photocurrents can be extracted close to the open-circuit voltage. In this range, the internal field in the device that assists in charge separation and transport is fairly small. Consequently a high fill factor can be obtained when the charge mobility of both charges is high. Presently the fill factor is limited to about 60% in the best devices, but values up to 70% have been achieved recently.⁴³

Apart from developing improved materials, a further gain in device performance can be expected from the combined optimization of the optical field distribution present in the device. Optical effects, such as interference of light in multilayer cavities, have received only limited attention so far but will likely contribute to a better light-management in these devices.

8. Conclusions

The prospect that lightweight and flexible polymer solar cells can be produced by roll-to-roll production, in combination with high energy-conversion efficiency, has spurred interests from research institutes and companies. In the last five years there has been an enormous increase in the understanding and performance of polymer-fullerene bulk-heterojunction solar cells. Comprehensive insights have been obtained in crucial materials parameters in terms of morphology, energy levels, charge transport, and electrode materials. To date, power conversion efficiencies close to 3% are routinely obtained and some laboratories have reported power conversion efficiencies of ~4-5⁴⁴ and now aim at increasing the efficiency to 8-10%. By combining synthesis, processing, and materials science with device physics and fabrication there is little doubt that these appealing levels of performance will be achieved in the near future.

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