

Invited Review

Recent Developments in Conjugated Polymer Based Plastic Solar Cells

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Summary. Recent developments on photovoltaic elements based on solid state composites of conjugated, semiconducting polymers mixed with buckminsterfullerene are reviewed. The photo-induced charge transfer from donor-type semiconducting conjugated polymers onto acceptor-type conjugated polymers or acceptor molecules such as buckminsterfullerene is reversible, ultrafast (within 100 fs) with a quantum efficiency approaching unity, and the charge separated state is metastable (up to ms at 80 K). This phenomenon of photoinduced electron transfer leads to a number of potentially interesting applications which include, among others, sensitization of the photoconductivity, reverse saturable absorption (optical limiting), and photovoltaic phenomena. Recent studies on the realization of photovoltaic elements with 3% power conversion efficiency are reported.

Keywords. Organic photovoltaics; Solar cells; Conjugated polymers; Fullerenes.

Introduction

Recent developments in realizing light emitting diodes based on conjugated semiconducting polymers (Fig. 1) have stirred a large scientific and technological effort [1–5]. If photoinduced free charge carrier generation is allowed at the same time, the electroluminescence device shows light emission under forward bias and a significant photocurrent under a reverse bias field (dual function) [6]. Using the devices for photodetection under reverse bias, the potential difference between the electrodes has to be high enough to overcome the *Coulomb* attraction of the photogenerated excitons. Otherwise, the absorbed photons will mainly create excitons which decay geminately (either radiatively, with photoluminescence, or non-radiatively). Some improvement has been reported for photodiodes utilizing a *Schottky* type junction formed between the conjugated polymer and one of the metal electrodes; however, the problem of inefficient charge generation in conjugated polymers has not been resolved by this approach [7–9]. To overcome

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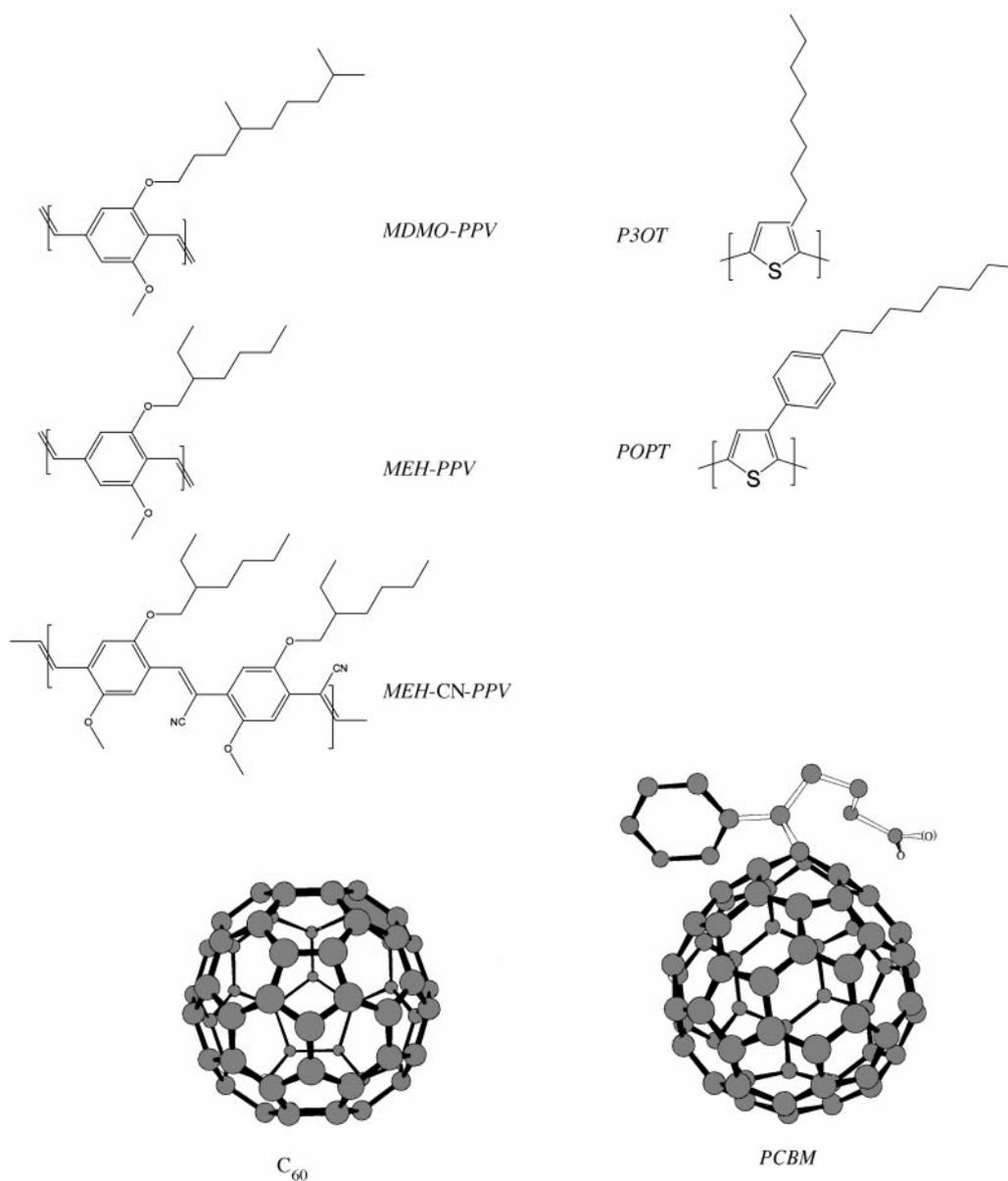


Fig. 1. Structural formulae of some conjugated polymers and fullerene derivatives

this limitation of photoinduced charge carrier generation, a donor/acceptor (dual molecule) approach has been suggested [10–13] consisting of a composite thin film with a conjugated polymer/fullerene mixture. In such single composite photoactive films, a bulk heterojunction is formed between the electron donors and acceptors (Fig. 2) [11, 12], and the efficiency of photogeneration of charges is near 100%.

Many conjugated polymers (see Fig. 1) in their undoped, semiconducting state are electron donors upon photoexcitation (electrons promoted to the antibonding π^* band). The idea of using this property in conjunction with a molecular electron acceptor to achieve long-living charge separation was based on the stability of the

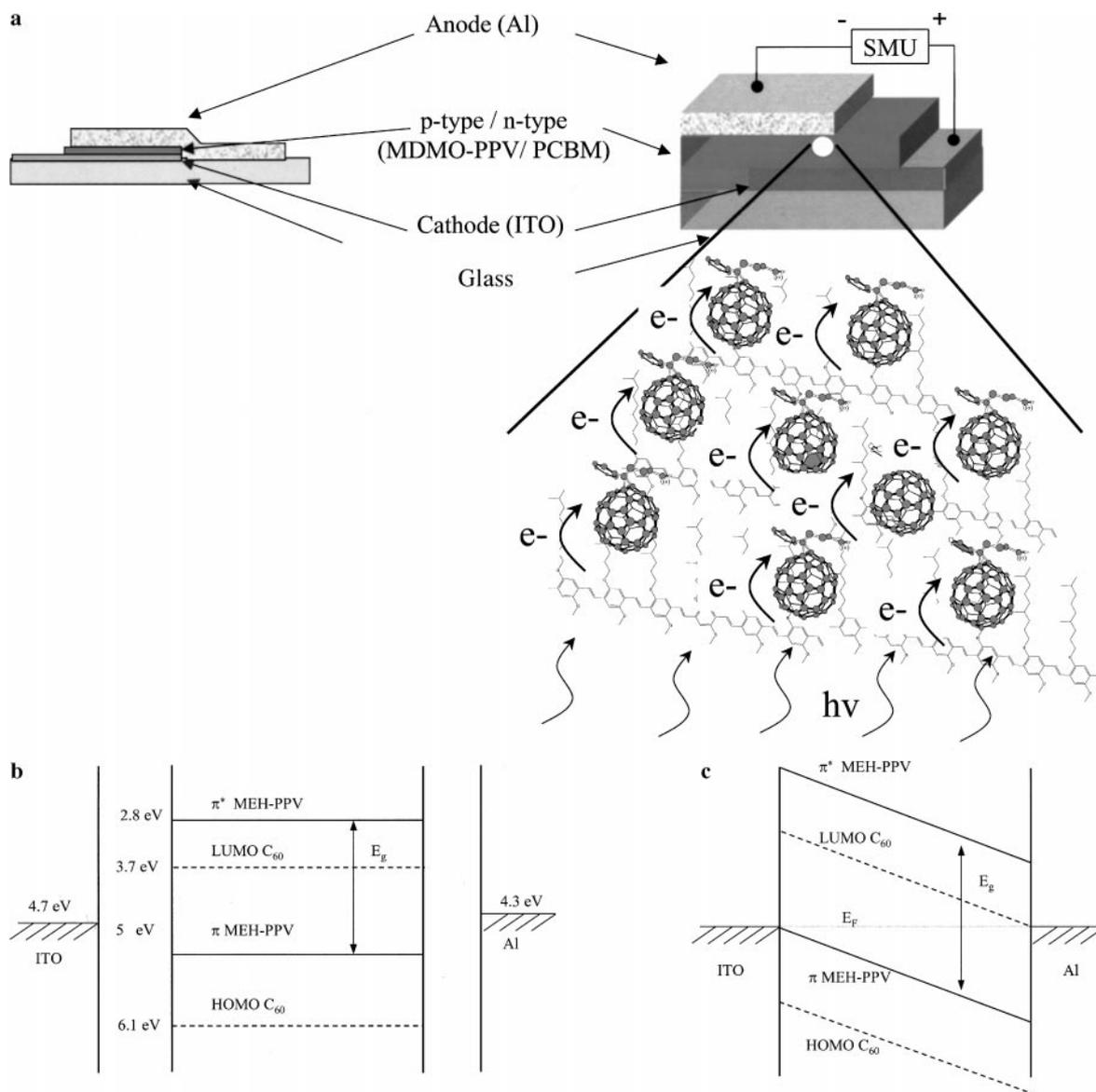


Fig. 2. Formation of a bulk heterojunction and subsequent photoinduced electron transfer inside a composite formed from the interpenetrating donor/acceptor network plotted with the device structure for such a kind of junction (a); the diagrams with the energy levels of a *MDMO-PPV/C₆₀* bulk heterojunction system (as an example) under flat band conditions (b) and under short-circuit conditions (c) do not take into account possible interfacial layers at the metal/semiconductor interface

photoinduced nonlinear excitations (such as polarons) on the conjugated polymer backbone. Once the photoexcited electron is transferred to an acceptor unit, the resulting cation radical (positive polaron) species on the conjugated polymer backbone is known to be highly delocalized, mobile, and stable as shown in electrochemical and/or chemical oxidative doping studies. Analogous to the chemical doping process, we will term the photoinduced electron transfer from the conjugated polymer donor onto an acceptor moiety as photodoping.

Background of Conjugated Polymer Based Solar Cells

Independently, *Sariciftci et al.* and *Yoshino et al.* have reported studies on the photophysics of mixtures of conjugated polymers with fullerenes [10, 14–22, 25]. The observations clearly evidenced an ultrafast, reversible, metastable photoinduced electron transfer from conjugated polymers onto buckminsterfullerene in solid films; for a schematic description of this phenomenon, see Fig. 2. Using this molecular effect at the interface of bilayers consisting of a semiconducting polymer (poly-(2-methoxy-5-(2'-ethyl-hexoxy)-*p*-phenylene) vinylene, hereafter referred to as *MEH-PPV*) and C_{60} films, diodes with rectification ratios in the order of 10^4 and a photovoltaic effect [11, 23] have been manufactured. Significant improvement of the relatively low charge collection efficiency of the D/A bilayer was achieved by using phase separated composite materials, processed through control of the morphology of the phase separation into an interpenetrating network (bulk heterojunction). The power conversion efficiency of solar cells made from *MEH-PPV*/methanofullerene composites was subsequently increased dramatically [12]. Parallel, the group of *Alan Heeger* in Santa Barbara and *Richard Friend* in Cambridge, developed an approach using acceptor-type conjugated polymers in an interpenetrating polymer-polymer composite with *MEH-PPV*, yielding polymeric photovoltaic devices with efficiencies comparable to fullerene mixed devices [13, 24, 25].

Using sub-picosecond photoinduced absorption studies [15, 26, 27], ultrafast (< 1 ps) photoinduced electron transfer has been demonstrated in the composites of conjugated polymers with fullerenes. Very recently, the forward transfer of the photoexcited electrons from conjugated polymer donors onto *PCBM* (cf. Fig. 1) acceptors was resolved by pump-probe experiments with an unprecedented time

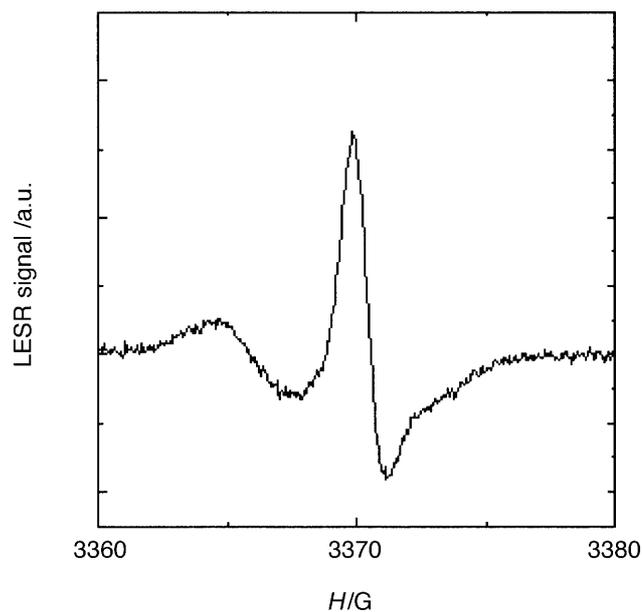


Fig. 3. Integrated light induced electron spin resonance spectra of *MDMO-PPV/PCBM* upon successive illumination with a 2.41 eV argon ion laser (reproduced with permission of the American Physical Society after Ref. [31])

resolution of 10 fs [28]. In these studies, the relaxation of the photoinduced excitations on the polymer chain switched from radiative (intense stimulated emission in pristine polymer, $\Delta T > 0$) to non-radiative (electron transfer in composites, photoinduced absorption, $\Delta T < 0$) upon mixing *PCBM* into the polymer matrix. This experimental setup allowed to time-resolve the forward photoinduced electron transfer time with ~ 40 fs after an initial relaxation (*Kasha* relaxation). As such, this photoinduced electron transfer is indeed ultrafast, resulting in a quantum yield of photoinduced charge generation of 100%.

The time-resolved transient photocurrent (PC) of *MEH-PPV/C₆₀* composites with different *C₆₀* content [29] shows an increase of initial photocurrent by an order of magnitude upon admixture of 1% of *C₆₀* [29]. Figure 3 shows the integrated ESR signal upon illuminating the *MDMO-PPV/PCBM* (cf. Fig. 1) composites with light of $h\nu = E_{\pi-\pi^*}$, where $E_{\pi-\pi^*}$ is the energy gap of the conjugated polymer (donor). Two photoinduced ESR signals can be resolved, one at $g = 2.0026$ and the other at $g = 1.9997$. The higher g -value line is assigned to the conjugated polymer cation (polaron), and the lower g -value line to the *PCBM*⁻ anion [30, 31].

Other Organic Solar Cell Architectures

Organic bilayers for photovoltaic applications have been investigated heavily during the last couple of decades (for a summary, see for example Refs. [11, 32–35]). *Tang* demonstrated [33] in his pioneering work using a vacuum evaporated copper-phthalocyanine (250 Å)/perylene derivative (450 Å) system sandwiched between *In₂O₃* and silver electrodes a white light photovoltaic power conversion efficiency of around 1%. Other examples in the literature exist on the fabrication of solar cells based on small molecular dyes as well as donor-acceptor systems (see for example Refs. [36, 37] and references therein). Using electron transfer from organic dyes onto inorganic nanoparticles, charge separation and photovoltaic conversion with *ca.* 10% efficiency have been demonstrated (see for example Refs. [38, 39] and references therein). *Yamashita* and coworkers have reported a bilayer photodiode based on the organic donor tetrathiafulvalene (*TTF*) and *C₆₀* [40]. *Meissner et al.* [41–44] enhanced the performance of a zinc-phthalocyanine (*ZnPc*)/*N,N'*-dimethylperylene-3,4,9,10-tetracarboxylic diimide (*MPP*) bilayer device by inserting a 30 nm thick *C₆₀-ZnPc* composite layer between *ZnPc* (50 nm) and *MPP* (20 nm) [42]. Last but not least, in photovoltaic cells made of bilayers of conjugated polymer and *C₆₀*, monochromatic energy efficiencies as high as 1% and IPCE efficiencies as high as 15% have been measured [45, 46].

The Bulk Heterojunction Concept

For photovoltaic cells made from pure conjugated polymers, energy conversion efficiencies were typically 10^{-3} – 10^{-1} %, too low to be used in practical applications [47–49]. Consequently, interpenetrating phase separated D/A network composites, *i.e.* bulk heterojunction, would appear to be ideal for photovoltaic materials [12]. Through control of the morphology of the phase separation into an interpenetrating network, one can achieve a high interfacial area within a bulk material. If any point in the composite is within a few nanometers of a D/A interface, such a composite is

a called a bulk D/A heterojunction material. If the D/A networks in a device are bicontinuous, as shown schematically in Fig. 2, the collection efficiency can be equally efficient.

It is important to note that the idealized schematic description in Fig. 2 is by far not realistic in any actual composite sample studied here. As shown below using AFM pictures, it is rather a disordered juxtaposition of islands of its two components. In addition, it is well known that polymer blends frequently tend to cleave into separate phases rather than to form one uniform medium. Decreasing the size of the islands results directly in an increase of the effective contact area between both components.

Important progress has been made towards creating bulk D/A heterojunction materials [12, 13, 24, 50]. *Gang Yu et al.* utilized the bulk heterojunction formed in a solid state composite of conjugated polymers and methanofullerene *PCBM* [12] with a short-circuit current of $I_{SC} = 0.5 \text{ mA/cm}^2$ under 20 mW/cm^2 illumination, approximately two orders of magnitude higher than that of pure *MEH-PPV* tunnel diodes as well as of the *MEH-PPV/C₆₀* heterojunction device described in the previous section. Uniform films with even higher concentrations of *PCBM* were cast from 1,2-dichlorobenzene solutions containing weight ratios of *MEH-PPV:PCBM* up to 1:4.

The groups of *Richard Friend* in Cambridge and *Alan Heeger* in Santa Barbara also simultaneously constructed a photovoltaic bulk heterojunction using two different conjugated polymers [24, 13, 50]. Both approaches employ *MEH-PPV* as donor conjugated polymer in composite with a cyano substituted *MEH-PPV*-type polymer. The cyano substitution was originally introduced into the light emitting device materials because of the lowered LUMO level of this derivative relative to the unsubstituted polymer [51]. This lower LUMO of the high electron affinity material eases the electron injection from a medium workfunction metal such as aluminum. Recent reports on polymer/polymer devices led to considerable improvement of the general efficiencies of these types of photovoltaic cells [50] using different stoichiometry of two laminating layers creating a gradient for hole conducting and electron conducting components in the bulk heterojunction.

At the University of Linz, large area ($6 \text{ cm} \times 6 \text{ cm}$ and, in a later stage, $10 \text{ cm} \times 15 \text{ cm}$) photovoltaic elements on flexible *ITO* (indium tin oxide) coated plastic (*PET*) substrates have been prepared. A picture of such an element is shown

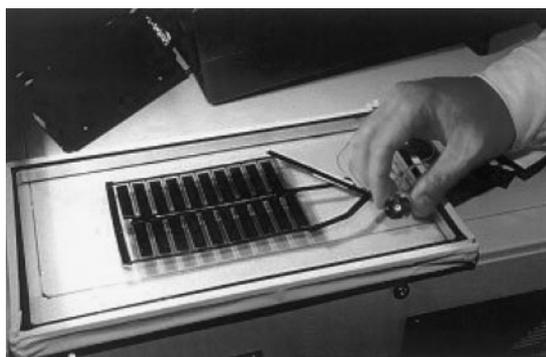


Fig. 4. Picture of a large area plastic solar cell running a small motor

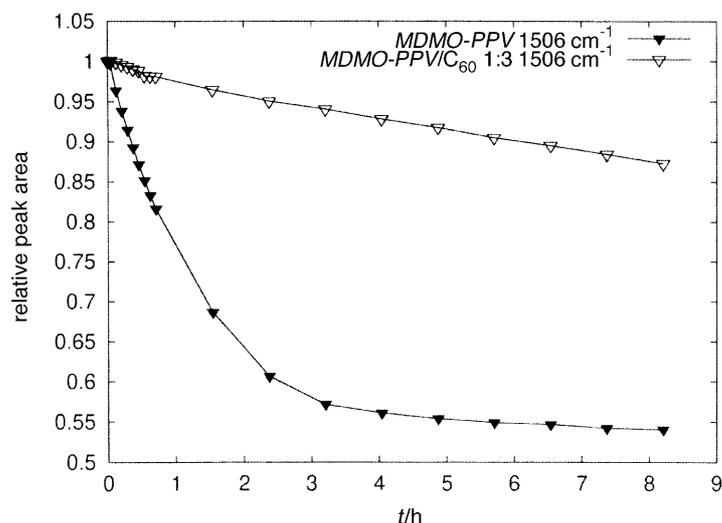


Fig. 5. Time dependence of specific absorption bands: *MDMO-PPV* at 1506 cm^{-1} (downward full triangles) and 1:3 mixture of *MDMO-PPV/C₆₀* at the *MDMO-PPV* band at 1506 cm^{-1} (downward open triangles) during controlled degradation test (reproduced by permission of Wiley-VCH from Ref. [35])

in Fig. 4. Large area devices with AM 1.5 simulated efficiencies around 2% can now be routinely fabricated.

Furthermore, systematic studies showed that upon addition of the fullerene derivatives to the conjugated polymer matrix, the stability of the matrix is increased [52, 53]. Figure 5 clearly shows the enhancement of the stability of the conjugated polymer/*PCBM* composite compared to the conjugated polymer component alone. Since the studies are directly related to specific infrared absorption of the conjugated polymer itself, it is concluded that the stability of the conjugated polymer component is increased upon addition of *C₆₀*. This is proposed to originate from the photostabilizing effect of the fullerenes because of the ultrafast photo-induced electron transfer:

- i*) Since the electrochemical potentials of the excited conjugated polymer (one electron excited to the LUMO level) and of the excited fullerene component (one hole left in the HOMO level) are both very high, it might immediately lead to direct electrochemical interactions with ambient air humidity *etc.* The ultrafast electron transfer from this LUMO level of the conjugated polymer onto the LUMO of *C₆₀* (or hole transfer from the HOMO level of *C₆₀* onto the HOMO of the conjugated polymer) immediately empties the excited state of the polymer (or of the fullerene) and lowers the electrochemical energy by bringing it down to more stable potentials.
- ii*) The intersystem crossing of the polymer (or the fullerene) produces triplet excited states, and these may in turn react by energy transfer creating singlet oxygen. This highly reactive form of oxygen is expected to react with the polymer backbone, creating carbonyl type defects and thus eliminating conjugation. By the ultrafast photoinduced electron transfer, the intersystem crossing to the triplet state is also completely quenched as shown above.

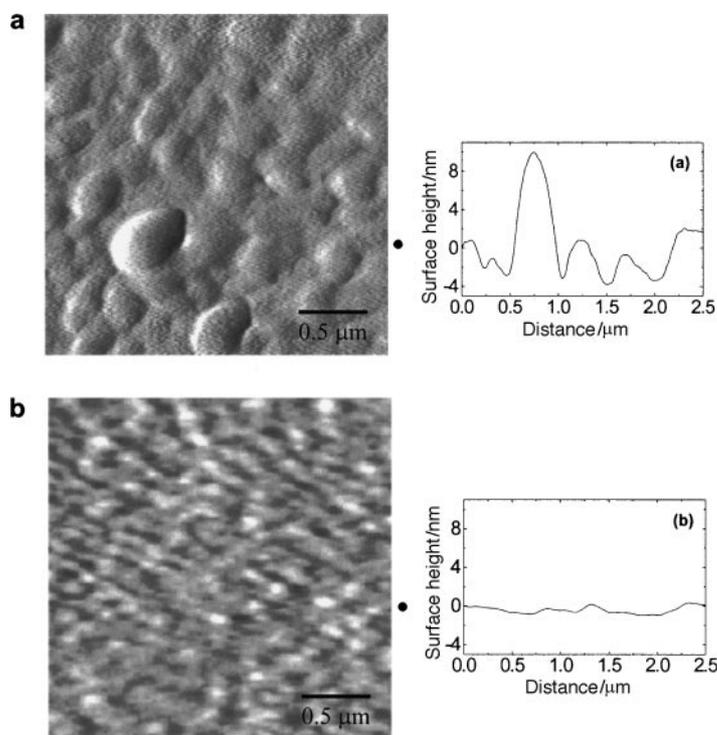


Fig. 6. AFM images showing the surface morphology of *MDMO-PPV:PCBM* (1:4 w/w) blend films with a thickness of approximately 100 nm and the corresponding cross sections; (A) spin-coated from a toluene solution, (B) spin-coated from a chlorobenzene solution; the images show the first derivative of the actual surface heights; the cross-sections of the true surface heights for the films were taken horizontally from the points indicated by the dots

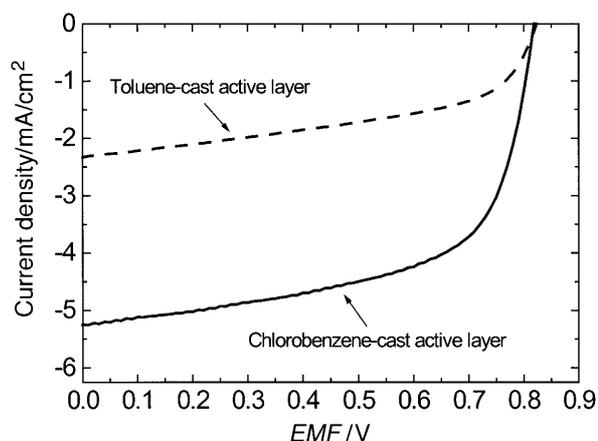


Fig. 7. Characteristics for devices with an active layer that is spin-coated from a toluene solution (dashed; $J_{SC} = 2.33 \text{ mA/cm}^2$, $V_{OC} = 0.82 \text{ V}$, $FF = 0.50$, $\eta_{AM1.5} = 0.9\%$) and from a chlorobenzene solution (full line; $J_{SC} = 5.25 \text{ mA/cm}^2$, $V_{OC} = 0.82 \text{ V}$, $FF = 0.61$, $\eta_{AM1.5} = 2.5\%$); data refer to devices illuminated with an intensity of 80 mW/cm^2 with an AM 1.5 spectral mismatch factor of 0.753; the temperature of the samples during measurement was 50°C

The power conversion efficiency of bulk heterojunction solar cells can be improved dramatically by manipulating the morphology of the components as well as of the blend. The resulting several-fold enhancement in the short-circuit current of photovoltaic devices originates from improved mobility of the charge carriers [54, 55]. Figure 6 shows AFM images of the surfaces of *MDMO-PPV:PCBM* blend films spin-coated using either toluene or chlorobenzene. The images show clearly a much more uniform mixing of the constituents using chlorobenzene. A plot of the current density vs. voltage for the two devices is shown in Fig. 7. The optical absorption spectra of the active layer films are nearly identical, but the external quantum efficiency, or incident photon to converted electron (IPCE) ratio, as a function of wavelength shows a large increase [56, 57]. The hole mobility in pristine *MDMO-PPV* is approximately one order of magnitude greater in films spin-coated from chlorobenzene as compared to toluene cast ones [55].

Future Aspects

One of the limiting parameters in plastic solar cells is their mismatch to the solar spectrum. The use of low bandgap polymers ($E_g < 1.8$ eV) to expand the spectral region of bulk heterojunction solar cells can enhance the spectral photon harvesting. Further optimization of device performance can be achieved by optimization of the device physics:

- i) Optimize the choice of metallic electrodes to achieve good ohmic contacts on both sides for collection of the oppositely charged photocarriers
- ii) Optimize the choice of the D/A pair (the energetics determine the open circuit potential)
- iii) Optimize the network morphology of the phase separated composite material for enhanced transport and carrier generation

In organic photovoltaic elements, generally two different tasks are to be clearly distinguished: The photoinduced charge generation (electron transfer efficiency) and the transport of created charges to the electrodes (charge carrier mobility). These two different tasks are expected to be fulfilled by one and the same material simultaneously. A possible strategy is to separate the two tasks by using separate components in a device for the charge transport and for the charge generation.

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