Plastic Solar Cells**

By *Christoph J. Brabec*, *N. Serdar Sariciftci*,* and *Jan C. Hummelen*

Recent developments in conjugated-polymer-based photovoltaic elements are reviewed. The photophysics of such photoactive devices is based on the photo-induced charge transfer from donor-type semiconducting conjugated polymers to acceptor-type conjugated polymers or acceptor molecules such as Buckminsterfullerene, C_{60}. This photo-induced charge transfer is reversible, ultrafast (within 100 fs) with a quantum efficiency approaching unity, and the charge-separated state is metastable (up to milliseconds at 80 K). Being similar to the first steps in natural photosynthesis, this photo-induced electron transfer leads to a number of potentially interesting applications, which include sensitization of the photoconductivity and photovoltaic phenomena. Examples of photovoltaic architectures are presented and their potential in terrestrial solar energy conversion discussed. Recent progress in the realization of improved photovoltaic elements with 3 % power conversion efficiency is reported.

1. Prologue

It is intriguing to think of photovoltaic (PV) elements based on thin plastic films. The flexibility offered through the chemical tailoring of desired properties, as well as the cheap technology already well developed for all kinds of plastic thin film applications would make such an approach a sure hit. The mechanical flexibility of plastic materials is welcome for all PV applications onto curved surfaces for architectural integration. By casting semi-transparent plastic PV thin films between insulating window glass, large unused areas (the windows) can be employed for power generation in addition to the limited roof areas of crowded cities. Even the color of such PV elements can be varied by sacrificing some parts of the visible solar spectrum.

An encouraging breakthrough in realizing higher efficiencies has been achieved by mixing electron–donor-type polymers with suitable electron acceptors. The photophysics of conjugated polymer/fullerene solid composites has been particularly well investigated over the last eight years. An understanding of the photophysics in detail has allowed the realization of prototype PV devices with solar power conversion efficiencies of around 3 %, and this has in turn triggered enhanced emphasis

from several groups worldwide, pursuing this research with increasing support from industry as well as public funding agencies.

On the other hand there is a common problem for all the applications of conjugated polymers: stability. Even though the expectation on the lifetimes of electronic devices is shrinking due to very short life/fashion cycles of such applications and even though industry may be interested in the cost of an item rather than in a very long durability of it, a shelf lifetime of several years as well as an operational lifetime of tens of thousands of hours are requested for all durable applications. Conjugated polymers have to be protected from air and humidity to achieve such lifetimes. These protection methods are being developed for light emitting diodes (LEDs) as well as PV elements. Their effectiveness is going to be crucial for the success of any applications using these materials. Recent reports from LED research indicate that the stability problem has been sufficiently overcome in order to enter into large scale applications, which in turn is a good sign for plastic solar cells.

It is the purpose of this review to give a state of the art report on plastic solar cells based on conjugated polymers as well as to give a basic introduction to the underlying photophysics.

2. Device Architectures

2.1. Single Layer Diodes

The simplest and most widely used organic semiconductor device is a metal–insulator–metal (MIM) tunnel diode with metal electrodes of asymmetrical workfunction (Fig. 1). Under forward bias, holes from the high workfunction metal and electrons from the low workfunction metal are injected into a thin film of a single-component organic semiconductor. Because of the asymmetry of the workfunction of the cathode and the anode, forward bias currents for a single carrier type material are orders of magnitude larger than reverse bias currents at low voltages. The rectifying diode characteristics can be accompanied by radiative

[*] Prof. N. S. Sariciftci, Dr. C. J. Brabec
Linzer Institut für organische Solarzellen (LIOS)
Physikalische Chemie, Johannes Kepler Universität Linz
Altenbergerstr. 69, A-4040 Linz (Austria)
E-mail: serdar.sariciftci@jk.uni-linz.ac.at
Prof. J. C. Hummelen
Organic and Molecular Inorganic Chemistry, University of Groningen
Nijenborgh 4, NL-9747 AG Groningen (The Netherlands)
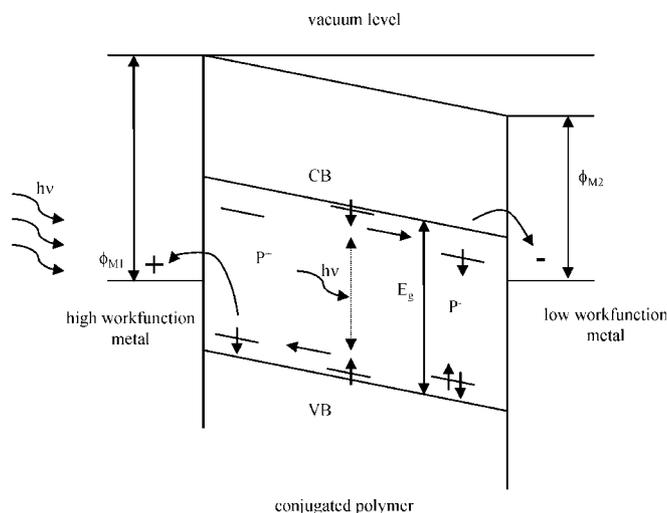
Fig. 1. Charge generation process in a single layer conjugated polymer device under short circuit conditions in the MIM model. VB valence band, CB conduction band, E_g bandgap, P^+, P^- positive and negative polarons.

recombination channels of the injected electrons and holes within the molecular solid; the result is an LED.[1–5] If photo-induced free charge carrier generation is allowed at the same time, the device emits light under forward bias and exhibits a significant photocurrent under a reverse bias field (dual function).[6]

In order to use the devices for photodetection under reverse bias, the potential difference between the electrodes has to be high enough to overcome the Coulomb attraction for the photogenerated excitons. Otherwise the absorbed photons will mainly create excitons which decay geminately (either radiatively, with photoluminescence, or non-radiatively). Thus the photocurrent efficiency of such devices will be limited. In the PV mode, where no external voltage is applied and short circuit conditions exist, the potential difference available in the MIM device is caused by the difference between the workfunctions of the metal electrodes. In most of the cases (e.g., indium tin oxide, ITO, and Al) the potential difference due to this workfunction difference is not high enough to give efficient photo-induced charge generation, limiting the operation of the

Niyazi Serdar Sariciftci received his masters degree in Experimental Physics and a doctorate degree in Semiconductor Physics under the mentorship of Prof. H. Kuzmany at the University of Vienna, Austria, in 1986 and 1989, respectively. After a post doctoral period at Stuttgart University, Germany, with Prof. M. Mehring he joined the Institute for Polymers and Organic Solids at the University of California, Santa Barbara, with Prof. Alan Heeger. He was appointed Chair and Professor in Physical Chemistry at the Johannes Kepler University of Linz, Austria, in 1996. He is the Founding Director of the Christian Doppler Laboratory for Plastic Solar Cells and of the newly established Linz Institute for Organic Solar Cells (LIOS). His main research activities are on organic semiconductor physics and chemistry.

Christoph Brabec received his masters degree in Theoretical Physics in 1992 followed by a Ph.D. in Physical Chemistry under the mentorship of Prof. Hermann Janeschitz-Kriegl at the Johannes Kepler University of Linz, Austria, in 1995. After a post-doctoral stay at the Institute for Polymers & Organic Solids at the University of California, Santa Barbara, with Prof. Alan Heeger he joined the Christian Doppler Laboratory for Plastic Solar Cells at the Johannes Kepler University of Linz in 1998. His main research activities are in the photophysics and photochemistry of conjugated polymeric semiconductors and the development of plastic solar cells.

Jan C. (Kees) Hummelen received his masters degree in Chemistry and a doctorate degree in Science under the mentorship of Prof. H. Wynberg at the University of Groningen, The Netherlands, in 1979 and 1985, respectively. He continued working on the subject of his Ph.D. research until 1989. After four years of playing jazz (piano) and doing art video production in The Netherlands, he spent two years as a post-doctoral fellow with Prof. Fred Wudl at the Institute for Polymers and Organic Solids at University of California, Santa Barbara. After spending six months with Prof E. W. Meijer at the Eindhoven Technical University, he returned to the University of Groningen where he was appointed Universitair Hoofdocent in 1998, and full Professor in Chemistry in 2000. Over the last seven years, his main research activities have been in fullerene chemistry and the development of plastic photovoltaic technology.

PV cells. Some improvement was reported for photodiodes utilizing a Schottky-type junction formed between the conjugated polymer and one of the metal electrodes (Fig. 2); however, the problem of inefficient charge generation in conjugated polymers was not overcome by this approach.[7–9]
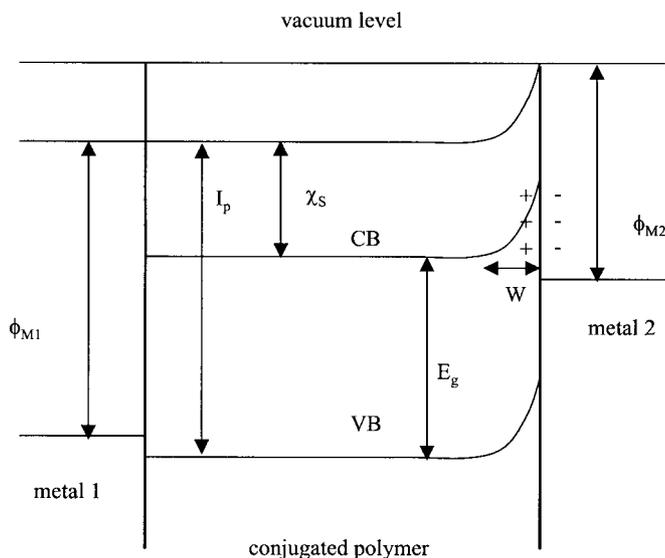
Fig. 2. Energy diagram of a metal1/semiconductor/metal2 Schottky barrier under open circuit conditions, when the metals have different work functions (ϕ workfunction, χ_s electron affinity; IP ionization potential; E_g bandgap, W depletion width).

To overcome this limitation of the photo-induced charge carrier generation, a donor/acceptor (dual molecule) approach has been suggested.[10–13] In general, in such devices, the photocarrier generation is enhanced by using a second, charge generation sensitizing component. For example, for a device consisting of a composite thin film with a conjugated polymer/fullerene mixture, the efficiency of photogeneration of charges is near 100 %. In such a single composite photoactive film a "bulk heterojunction" is formed between the electron donors and acceptors (Fig. 3). An extensive discussion of this concept will be in Section 3 below.

2.2. Heterojunction Diodes

Considering the energy band diagram of a bilayer in Figure 4, the heterojunction formed between (for example) a conjugated polymer and C_{60} should have rectifying current–voltage characteristics even using the same metal contact on both sides (analogous to a p–n junction). One bias direction of such a device (electron injection on the semiconducting polymer side or hole injection on C_{60}) is energetically unfavorable. This polarity of the device results in very low current densities. On the other hand, electron injection onto C_{60} or hole injection into the semiconducting polymer is energetically favorable. This polarity of the device results in relatively high current densities. Thus, devices of organic semiconductors using two layers with different electronic band structures as illustrated in Figure 4 have rectifying diode characteristics. A photophysical interaction between the two molecular units (photo-induced electron transfer) happens at the interface and gives rise to photocurrents as well as a PV effect. In that sense the essential difference between the linear heterojunction of two organic thin films displayed in Figure 4 and the "bulk heterojunction" displayed in Figure 3 is the effective interaction area between the donor and acceptor components: in the linear heterjunction device it is the geometrical interface, in bulk heterojunction it is the entire volume of the composite layer. This results in an enhancement of short circuit photocurrent for several orders of magnitude making the bulk heterojunction approach quite attractive.[11,12]

3. Conjugated Polymers as Photoexcited Donors

Many conjugated polymers (see examples in Table 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 lived charge separation was based on the stability of the photo-induced 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 describe the photo-induced electron transfer from the conjugated polymer donor onto an acceptor moiety as "photodoping".

Independently, Sariciftci et al. and Yoshino et al. reported studies on the photophysics of mixtures of conjugated polymers with fullerenes.[10,14–22] The observations clearly evidenced an ultrafast, reversible, metastable photo-induced electron transfer from conjugated polymers onto Buckminsterfullerene in solid films. A schematic description of this phenomenon is displayed in Figure 3 and Figure 4. Using this molecular effect at the interface of bilayers consisting of a semiconducting polymer (poly((2-methoxy-5-(2′-ethylhexoxy)-*p*-phenylene) vinylene), hereafter referred to as MEH–PPV), and C_{60} films, diodes with rectification ratios on the order of 10^4 and a PV effect[11,23] were made. Significant improvement of the relatively low charge collection efficiency of the donor/acceptor (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] In parallel, the groups of Heeger in Santa Barbara and Friend in Cambridge developed an approach using acceptor-type conjugated polymers in an interpenetrating polymer–polymer composite with MEH–PPV, yielding polymeric PV devices with efficiencies comparable to fullerene mixed devices.[13,24]

3.1. Ultrafast Photo-induced Electron Transfer from Conjugated Polymers onto C_{60}

The linear optical absorption spectrum of a MEH–PPV/C_{60} film is a simple superposition of the two components without any indication of states below the π–π^* gap of the conducting
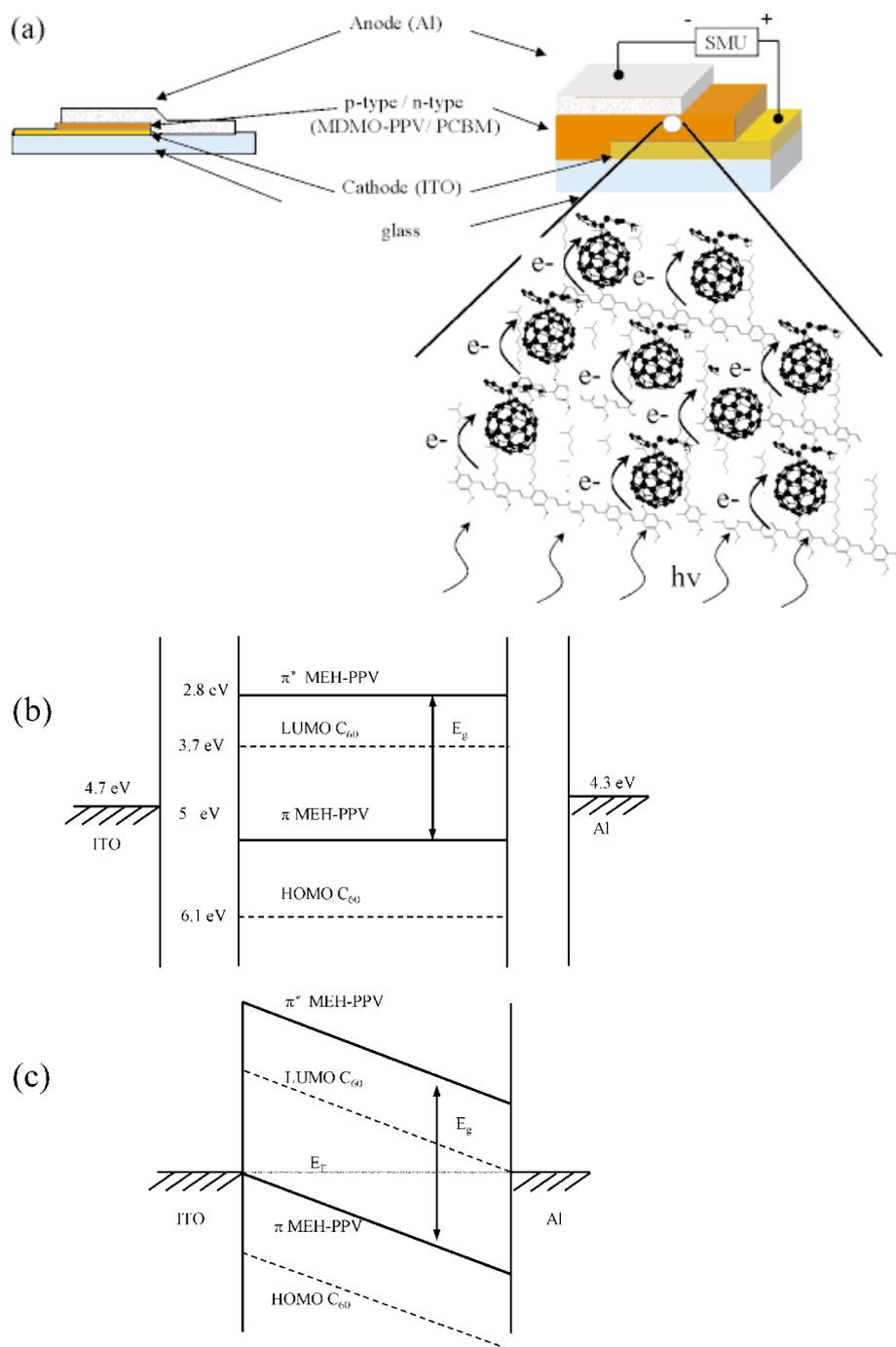
Fig. 3. Formation of a bulk heterojunction and subsequent photo-induced electron transfer inside such a composite formed from the interpenetrating donor/acceptor network plotted with the device structure for such a kind of junction (a). The diagrams with the energy levels of a MDMO–PPV/C_{60} bulk heterojunction 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.

polymer as might arise from interaction between the two materials in the ground state.

The strong luminescence of MEH–PPV was, however, quenched by a factor in excess of 10^3.[10] The luminescence decay time was reduced from $\tau_o = 550$ ps to $\tau_{rad} \ll 60$ ps (the instrumental resolution) indicating the existence of a rapid quenching process; e.g., sub-picosecond electron transfer.[14] The strong quenching of the luminescence of another conjugated polymer, P3OT, reported by Morita et al.[19] was also consistent with efficient photo-induced electron transfer. Thus, the quenching of luminescence was observed in a number of conjugated polymers in composites with fullerenes, indicating this to be a general phenomenon for the non-degenerate ground state conjugated polymers.[25] This confirmed that photo-induced electron transfer occurs in a timescale sufficiently fast to quench the radiative relaxation of the conjugated polymer excited state.

Photo-induced absorption detected magnetic resonance (PIADMR) experiments were performed in conjugated polymer/C_{60} composites giving evidence for a complete quenching of the MEH–PPV triplet–triplet absorption signal at 1.35 eV. Instead a strong spin = 1/2 signal dominated the PIADMR spectrum, indicating charged polarons as photoexcitations on the polymer donor.[18] This confirmed that the photo-induced
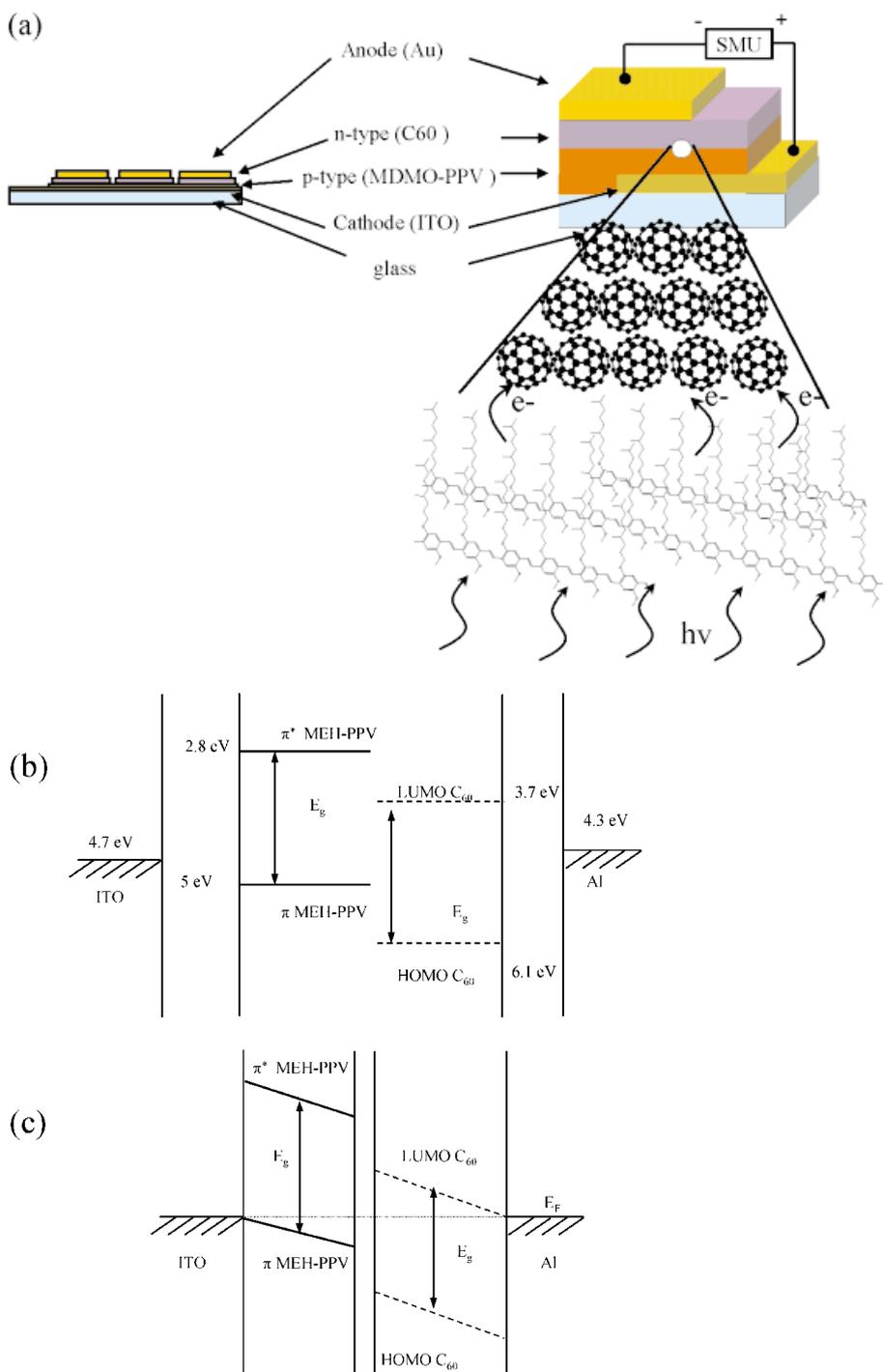
Fig. 4. Schematic diagram of a bilayer and subsequent photo-induced electron transfer at the interface of the two layers with the device structure for such a kind of junction (a). The diagrams with the energy levels of a MDMO–PPV/C_{60} system (as an example) under flat band conditions (b) and under short circuit conditions (c) do not take into account possible interfacial layers at the metal/semiconductor interface.

electron transfer occurs on a time scale sufficiently fast to quench the intersystem crossing to the triplet state.

Using sub-ps photo-induced absorption (PIA) studies[15,26,27] ultrafast (<1 picosecond) formation of the polarons was demonstrated.

Very recently the forward transfer of the photoexcited electrons from conjugated polymer donors onto 1-(3-methoxycarbonyl)-propyl-1-1-phenyl-(6,6)C_{61} (PCBM) acceptors was resolved by pump-probe experiments with an unprecented time resolution of 10 fs.[28] In these studies, the relaxation of the

photo-induced excitations on the polymer chain switched from radiative (intense stimulated emission in pristine polymer, $\Delta T > 0$) to non-radiative (electron transfer in composites, PIA, $\Delta T < 0$) upon mixing PCBM into the polymer matrix. This experimental setup allowed to time-resolve the photo-induced electron transfer time with ~40 fs after an initial relaxation (Kasha relaxation). As a consequence of the resonant excitation of the conjugated polymer by a sub-10 fs laser pulse, the phonon modes which are strongly coupled to the π-electron excitations were directly observed as coherent oscillations

within the pump probe experiment. By Fourier transforming the oscillatory decay of the time dependent signal the resonant/non-resonant Raman spectrum of the conjugated polymer was reproduced. Furthermore, by adding PCBM to the conjugated polymer matrix these vibrational oscillations were quenched nearly completely indicating a rapid depopulation of the excited state on the conjugated polymer due to the electron transfer. These results demonstrated a direct competition of photo-induced electron transfer with vibrational oscillationson the conjugated polymer donor indicating a photo-induced electron transfer rate of $>10^{13}$ s^{-1} ($\tau_{ct} < 100$ fs).

As such this photo-induced electron transfer is indeed ultrafast, resulting in a quantum yield of photo-induced charge generation of 100 %.

The time-resolved transient photocurrent (PC) of MEH–PPV/C$_{60}$ composites with different C$_{60}$ content[29] shows an increase of initial photocurrent by an order of magnitude upon admixture of 1 % of C$_{60}$. This increase of the photocarrier generation efficiency was accompanied by the successive increase in lifetime of the photocarriers upon adding more and more C$_{60}$. Thus, the ultrafast photo-induced electron transfer from the semiconducting polymer to C$_{60}$ not only enhances the charge carrier generation in the host polymer but also serves to prevent recombination by separating the charges and stabilizing them.[29]

Definitive evidence of charge transfer and long-lived charge separation was obtained from light induced electron spin resonance (LESR) experiments.[10] Figure 5 shows the integrated ESR signal upon illuminating the MDMO–PPV/PCBM (where MDMO stands for poly(2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-
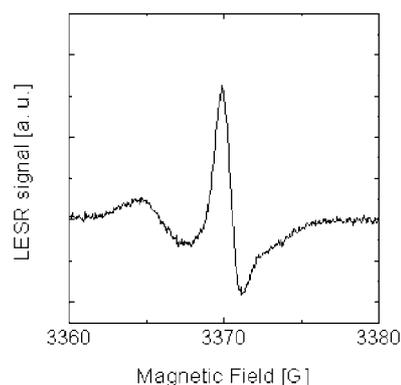
Fig. 5. Integrated light-induced electron spin resonance spectra of MDMO–PPV/ PCBM upon successive illumination with 2.41 eV argon ion laser. (Reproduced from [31] with permission of the American Physical Society.)

phenylene vinylene)) composites with light of $h\nu = E_{\pi-\pi*}$ where $E_{\pi-\pi*}$ is the energy gap of the conjugated polymer (donor). Two photo-induced 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 PCBM$^-$ anion.[30] The saturation behavior of the LESR of conjugated polymer cation signal indicates a different relaxation mechanism compared to the fullerene radical anion signal which is not saturating at all.[31] We can safely conclude from these studies that the photo-induced radicals in these polymer/fullerene composites are independent from each other and dissociated completely.

4. Towards Improved Efficiency Organic Photovoltaic Cells

The use of organic bilayers with photo-induced electron transfer at the interface has been investigated heavily during the last couple of decades (for a summary see the literature[11,32–35]). Tang demonstrated PV activity in small molecular bilayers which were vacuum deposited.[33] In this pioneering work Tang used a vacuum evaporated copper-phtalocyanine (250 Å)/perylene derivative (450 Å) system sandwiched between In$_2$O$_3$ and silver electrodes, with a white light PV power conversion efficiency of around 1 %.

Extensive literature exists on the fabrication of solar cells based on small molecular dyes as well as donor–acceptor systems.[36,37] Inorganic oxide semiconductors also were used to facilitate electron transfer from organic dyes onto inorganic nanoparticles to achieve charge separation and PV conversion.[38,39] Yamashita and co-workers reported a bilayer photodiode based on the organic donor tetrathiafulvalene (TTF) and C$_{60}$.[40] A recent approach to enhance the PV properties of organic solar cells by sensitization with fullerenes was introduced by Meissner et al.[41–44] and is displayed in Figure 6. The performance of a zinc-phthalocyanine (ZnPc)/N,NM'-dimethyl-perylene-3,4,9,10-tetracarboxylic diimide (MPP) bilayer device
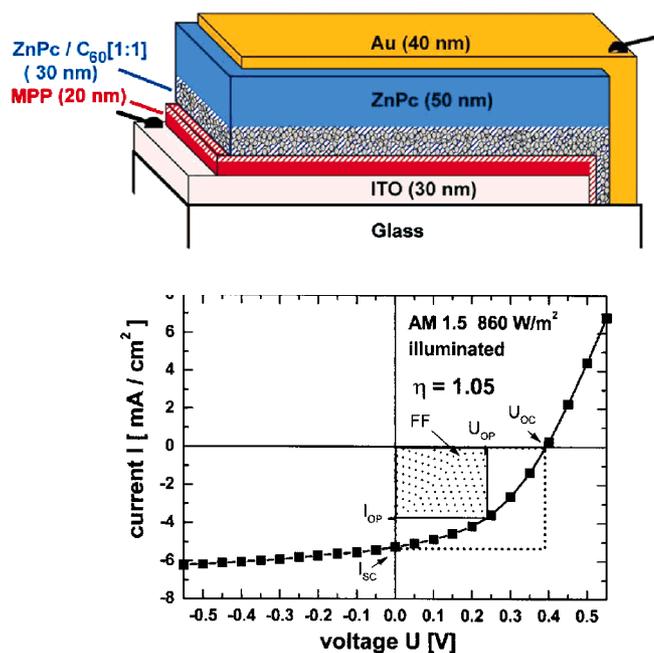
Fig. 6. Schematic drawing of a small molecular solar cell with a sensitizing region of a mixed ZnPc + C$_{60}$ layer embedded between MPP and ZnPc layers and its current/voltage characteristics. Electrodes used are Al and ITO.

was significantly enhanced by inserting a 30 nm thick C$_{60}$–ZnPc composite layer between the ZnPc (50 nm) and the MPP (20 nm).[42] These devices delivered a short circuit current of 5.26 mA/cm^2 under 860 W/m^2 AM 1.5 solar simulators, an open circuit voltage of 0.39 V. Together with a fill factor of 0.45 the overall power efficiency was calculated as 1.05 %. For PV cells made with bilayers of conjugated polymer and C$_{60}$,

monochromatic energy efficiencies as high as 1 % and incident photon to converted electron (IPCE) efficiencies as high as 15 % were measured.[45,46]

The findings for the different bilayer systems investigated so far can be summarized the following way: although the quantum efficiency for photo-induced charge separation is near unity for a D/A pair, the energy conversion efficiency in a bilayer heterojunction device is limited:

● Due to the molecular nature of the heterojunction, efficient charge separation occurs only close to the D/A interface, either within the exciton diffusion path or within the space charge region; thus, photoexcitations created far from the D/A junction recombine prior to diffusing to the heterojunction.

● Since charge separation is located to a rather small region of the photoactive device, the PV conversion efficiency is limited by the amount of photons absorbed within this region and materials with high molar absorption coefficients are required. Further increase of the layer thickness of the single components would reduce the efficiency by the increased series resistance.

4.1. The "Bulk Heterojunction" Concept

Before analyzing results from donor/acceptor bulk heterojunction solar cells based on conjugated polymer/fullerene composites, relevant results from single layer semiconducting polymer devices with asymmetric contacts (a low work function metal on one side and a high work function metal on the opposite side, a MIM "tunneling injection diode") are discussed; such devices have been described by Parker.[5] A schematic cross-sectional band diagram of such devices is displayed in Figure 7. In forward bias, tunneling injection diodes exhibit relatively high efficiency electroluminescence, which is promising for flat panel and/or flexible, large area display applications. In reverse bias, on the other hand, the devices exhibit a strong photoresponse with a quantum yield >20 % (el/ph at –10 V reverse bias).[6,47] Devices based on derivatives of polythiophene exhibited even better photoresponse (80 % el/ph at –15 V), competitive with ultraviolet (UV) sensitized Si photodiodes.[6,47] A PV response was observed under zero bias conditions.[6,47] The charge carrier concentration in these undoped, pristine materials is sufficiently low in dark so that the semi-

conducting layer (several hundred nanometers) is fully depleted; there is negligible band bending at the metal–polymer interface. Note, however, that the mobility of injected charge carriers is not symmetric; in most conjugated polymers, the electron mobility is lower than the hole mobility. Upon photo-induced charge carrier generation, an additional effect may become representative. For low charge carrier density materials photodoping may be sufficient in these materials to lead to interface effects such as photo-induced band bending or photo-induced space charge regions. Such effects are typical for organic semiconductors.[41,42] The exact nature of this band bending and barrier creation at the interfaces under light illumination will be an important parameter for optimizing the solar cell performance in these devices.

For PV cells made with 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 PV 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 "bulk D/A heterojunction" material. If the D/A networks in a device are bicontinuous, as shown schematically in Figure 3, the collection efficiency can be equally efficient.

It is important to note, that the idealized schematic description in Figure 3 is by far not realistic in any actual composite sample studied here. As shown below using atomic force microscopy (AFM) pictures, it is rather a disordered, juxtaposition of islands of its two components. In addition, it is well known that polymer blends most often tend to cleave into separate phases rather than form one uniform medium. Decreasing the size of the islands results directly in increase of the effective contact area between the two components.

Important progress has been made toward creating "bulk D/A heterojunction" materials.[12,13,24,50] 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, I_{sc} = 0.5 mA/cm^2 under 20 mW/cm^2 monochromatic illumination, approximately two orders of magnitude higher than that of pure MEH–PPV tunnel diodes as well as of the MEH–PPV/C$_{60}$ heterojunction device as described in the previous section. Uniform films with even higher concentrations of the PCBM were cast from 1,2-dichlorobenzene solutions containing up to 1:4 weight ratio MEH–PPV/PCBM. The efficiencies of the devices are nearly independent of the incident illumination intensity.

The groups of Friend in Cambridge and Heeger in Santa Barbara also simultaneously made a PV bulk heterojunction using two different conjugated polymers.[13,24,50] Both approaches use MEH–PPV as donor conjugated poly-
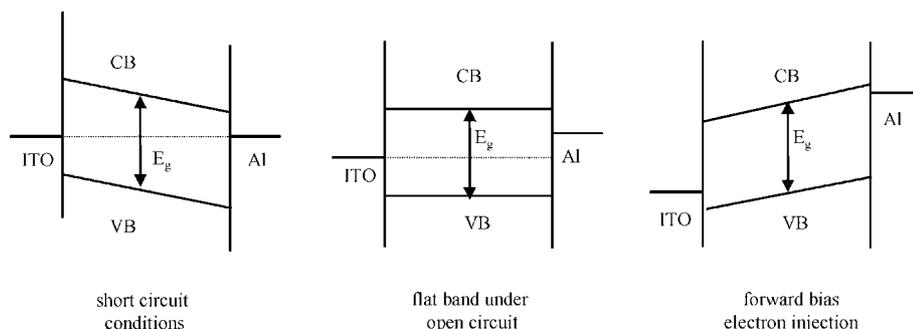
Fig. 7. Schematic band diagrams for single layer conjugated polymer devices at various values of forward bias. Forward bias is defined with respect to ITO. (Reproduced with permission of WILEY-VCH from reference [35]).

mer 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 lowest unoccupied molecular orbital (LUMO) level of this derivative relative to unsubstituted one.[51] This lower LUMO of the high electron affinity material, on one side 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 PV cells[50] using different stoichiometry of two laminated layers, creating a gradient for hole conducting and electron conducting components in the bulk heterojunction.

4.2. Flexible, Large Area, Plastic Solar Cells

To fully utilize the potential of the conjugated polymers as plastic photoactive materials as well as to investigate the device technology problems of up-scaling, we produced at the University of Linz, large-area (6 cm × 6 cm and in a later stage 10 cm × 15 cm) PV elements on flexible ITO coated plastic (PET) substrates. The picture of such an element is shown in Figure 8 while its *I/V* characteristics are plotted in Figure 9. The approach used was the bulk heterojunction formed in the solid state composites of conjugated polymers with fullerene derivatives. The schematic
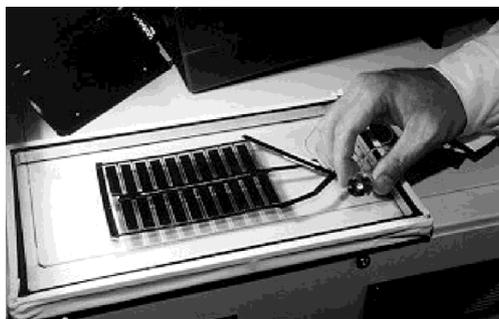
Fig. 8. Picture of a large area plastic solar cell running a small motor.
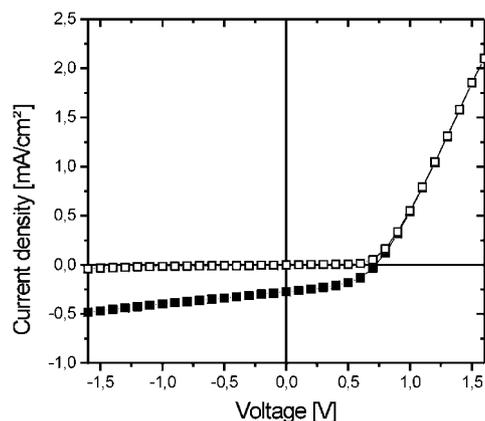
Fig. 9. *I/V* behavior of a 10 cm × 15 cm MDMO–PPV/PCBM solar cell with an active area of 50 cm^2 under light (■) and in the dark (□). Illumination is provided by white light from a fluorescence tube with an intensity of 6 mW/cm^2.

cross section of such devices is displayed in Figure 3. The characterization of these devices in comparison with the small area devices (0.1 cm^2) revealed clearly that the up-scaling to large area flexible plastic solar cells can be achieved with acceptable loss of device efficiency. Large area devices with AM 1.5 simulated efficiencies around 2 % can be routinely fabricated.

The comparison of lifetimes of such a large area PV cell (fabricated in air and under ambient conditions without precaution towards dust free and/or oxygen free conditions), unprotected or protected with a special coating, clearly show that the protection against air and oxygen increases the lifetime considerably (Fig. 10). Further 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 11 clearly shows the enhancement of the stability of the conjugated polymer/PCBM composite compared to the conjugated
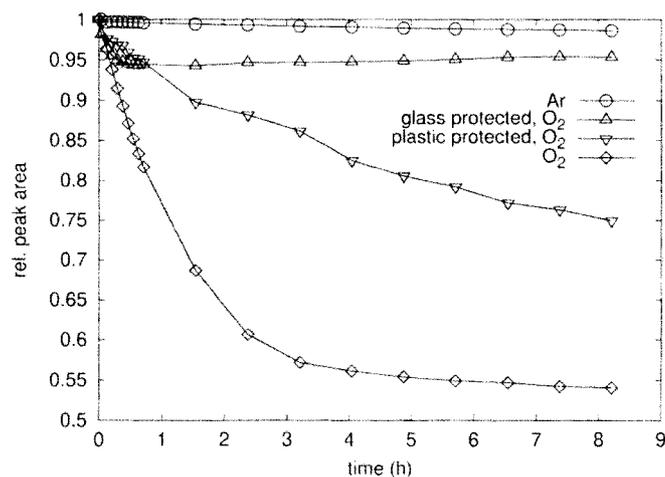
Fig. 10. Time dependence of the changes of one specific absorption band (1506 cm^{-1}) of MDMO–PPV under oxygen, argon, and oxygen protected with plastic foil, oxygen protected with glass plate during controlled degradation tests (reproduced with permission of WILEY-VCH from reference [35]).
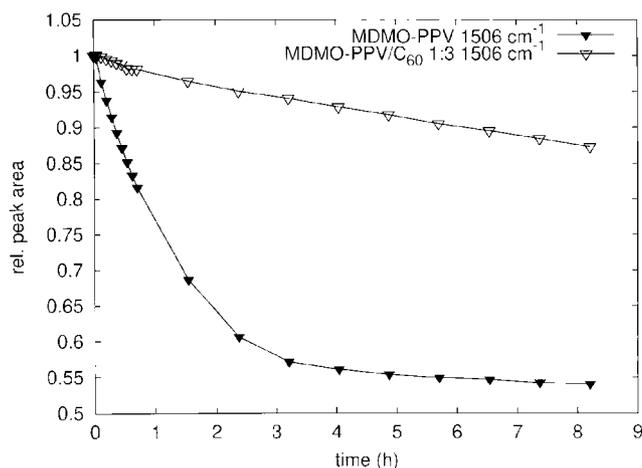
Fig. 11. Time dependence of specific absorption bands. MDMO–PPV (1506 cm^{-1}) (▼), 1:3 mixture of MDMO–PPV/C$_{60}$ at the MDMO–PPV band at 1506 cm^{-1} (▽) during controlled degradation test (reproduced with permission of WILEY-VCH from reference [35]).

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 itself is increased upon adding the C_{60} to it. This is proposed to originate from the photostabilizing effect of the fullerenes because of the ultrafast photo-induced electron transfer:

- 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 highest occupied molecular orbital, HOMO, level) are both very high, it might immediately lead to direct electrochemical interactions with the ambient air humidity, etc. The ultrafast electron transfer from this LUMO level of the conjugated polymer onto the LUMO of C_{60} (or hole transfer from the HOMO level of C_{60} 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.

- The intersystem crossing of the polymer (or the fullerene) produces triplet excited states and these may in return 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 eliminating the conjugation. By the ultrafast photo-induced electron transfer the intersystem crossing to the triplet state is also completely quenched as shown above.

5. Improving the Efficiency of Plastic Solar Cells

Recently we have demonstrated that 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 PV devices originates from improved mobility of the charge carriers.[54,55]

Figure 12 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 as solvent. To compare the impact of these different morphologies on the PV device performance, solar cells were fabricated in an identical manner except for the choice of solvent (either toluene or chlorobenzene) used for spin-coating the active layer. A plot of the current density versus voltage for the two devices is shown in Figure 13. The active area of these high efficiency devices is 7.5 mm^2. The open-circuit voltages of the cells are almost identical (0.82 V). However, the chlorobenzene-based device exhibits a more than two-fold increase in the short-circuit current density as compared to the toluene-based device (5.25 versus 2.33 mA/cm^2). As shown in Figure 14a, the optical absorption spectra of the active layer films are nearly identical, except for a small red-shift in the MDMO–PPV absorption (425–575 nm) in the chlorobenzene-cast film, as expected for the increased effective conjugation length. Figure 14b shows the external quantum efficiency, or IPCE ratio, as a function of
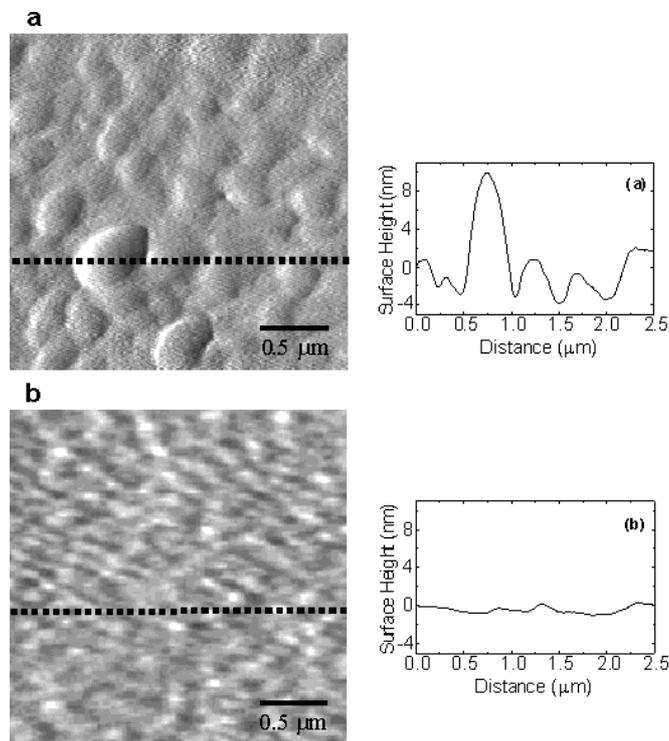
Fig. 12. AFM images showing the surface morphology of MDMO–PPV/PCBM (1:4 by wt.) blend films with a thickness of approximately 100 nm and the corresponding cross sections. a) Film spin-coated from a toluene solution. b) Film spin-coated from a chlorobenzene solution. The images show the first derivative 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 dotted line.
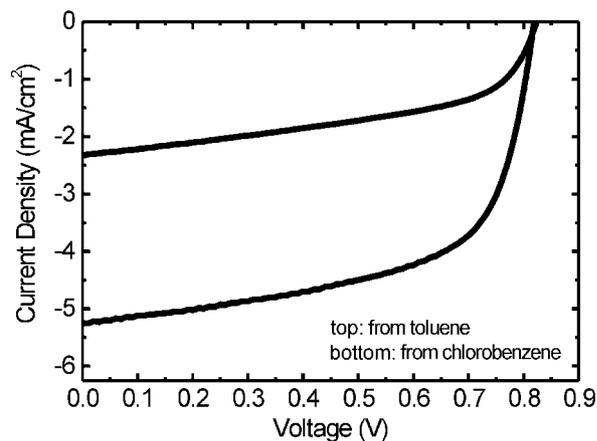
Fig. 13. Characteristics for devices with an active layer that is spin-coated from a toluene solution (top): J_{sc} = 2.33 mA/cm^2, V_{oc} = 0.82 V, FF = 0.50, $\eta_{AM1.5}$ = 0.9 %; and from a chlorobenzene solution (bottom): J_{sc} = 5.25 mA/cm^2, V_{oc} = 0.82 V, FF = 0.61, $\eta_{AM1.5}$ = 2.5 %. Data is for 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.

wavelength, indicating that the charge carrier collection is a sensitive function of the morphology. The increase in efficiency relies on an increase of charge carrier mobility as observed by field-effect mobility measurements of the single components as well as of the mixtures processed form the different solvents.[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]
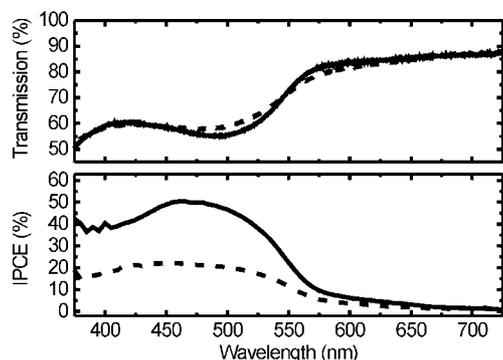
Fig. 14. a) Optical absorption spectra of 100 nm thick MDMO–PPV/PCBM (1:4 by wt.) films spin-coated onto glass substrates from either toluene (broken line) or chlorobenzene (solid line) solutions. b) IPCE spectra for PV devices using these films as the active layer.

The fill factor (FF) of solar cells is determined by

$$FF = I_{mpp}V_{mpp}/I_{sc}V_{oc} \tag{1}$$

where I_{mpp} and V_{mpp} are the current and the voltage in the maximum power point of the I/V curve in the 4th quadrant. In general, a large serial resistance as well as a too small parallel resistance (shunt) tend to reduce the FF. From LEDs, interface layers like LiF or CsF and even SiO_x are well known to reduce the interface barrier for electron injection at the cathode, if they are evaporated between the photoactive material and an Al electrode.[58] Figure 15 shows this enhancement of the diode properties of a MDMO–PPV/PCBM solar cell due to such an interfacial layer. The short circuit current is left almost
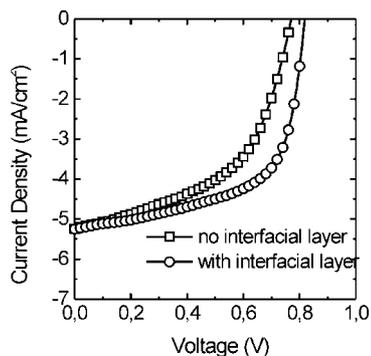
Fig. 15. I/V curve in the 4th quadrant for a plastic solar cell with and without an interfacial layer of LiF beneath the Al electrode, illuminated with 80 mW/cm^2 simulated AM 1.5 radiation.

unchanged and only a small increase in the open circuit voltage is observed (from 780 to 820 mV) due to the interfacial layer. The fill factor, FF, is increased from 0.5 to 0.62 by dropping down the serial resistance of the devices from ~200–400 Ω to ~20–50 Ω.

The light absorption of the device was measured (using a reflection geometry) to be less than 55 % at 460 nm. This yields an internal quantum efficiency, or absorbed photon to converted electron, greater than 85 %. Since the J_{sc} of the devices was measured to have a linear dependence on the incident light intensity for values up to 80 mW/cm^2, monochromatic power

conversion efficiencies can be calculated from the IPCE data (Fig. 14b). Assuming $V_{oc} = 0.82$ V and FF = 0.61 for all incident wavelengths a power conversion efficiency of 9.5 % at 488 nm for the chlorobenzene-based device is obtained.

One of the limiting parameters in plastic solar cells is their mismatch to the solar spectrum. Typically, conjugated polymers such as MDMO–PPV, used for PVs have their peak absorption around 500 nm, which is clearly offset to the maximum in the photon flux of the sun, which peaks around 700 nm. 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. Figure 16 shows the spectrally resolved photocurrent for a photodiode from low bandgap polymer (poly-(thiophene–pyrrole–thiophene–benzothiadiazole)
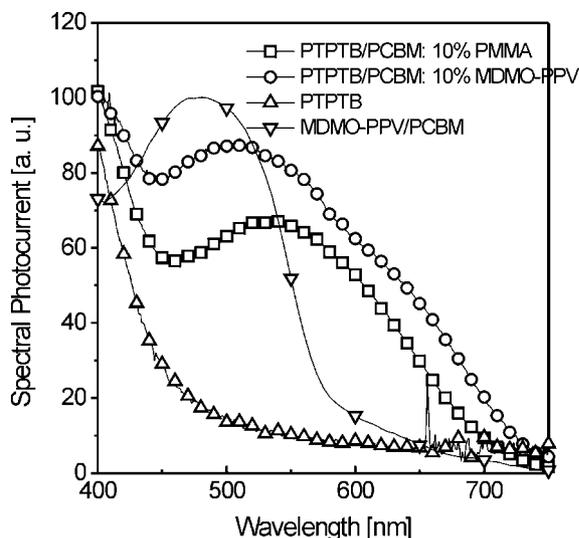
Fig. 16. Spectrally resolved photocurrent of a photodiode, where the active layer, either a low bandgap polymer PTPTB, or PTPTB/PCBM/PMMA or PTPTB/PCBM/MDMO–PPV or MDMO–PPV/PCBM is sandwiched between ITO/PEDOT and Al. Data were first calibrated to the response of a calibrated Si diode and then normalized to their response at 400 nm.

(PTPTB) see Table 1) with and without PCBM. Spectra are normalized to their peak values. While the photocurrent generation for the pristine PTPTB device has the maximum at low wavelengths with a small tail extending to the infrared (IR), the PTPTB/PCBM/PMMA (PMMA = poly(methyl-methacrylate)) device shows efficient charge carrier generation in the region from 500–700 nm, resembling the absorption profile of the polymer.[55,59] PMMA was used to improve the film quality. For a device with MDMO–PPV instead of PMMA as host polymer, the spectral photocurrent is observed to show contributions from both polymers. The photocurrent of a MDMO–PPV/PCBM device is plotted as reference. This demonstration shows the easy production of multiple bandgap solar cells.

6. Outlook and Strategies

Further optimization of device performance can be achieved by optimization of the device physics:

Table 1. Abbreviation and structure of common conjugated polymers as well as acceptor type molecules.

MDMO-PPV

MEH-PPV

MEH-CN-PPV

P3OT

POPT

PTPTB

C60

PCBM
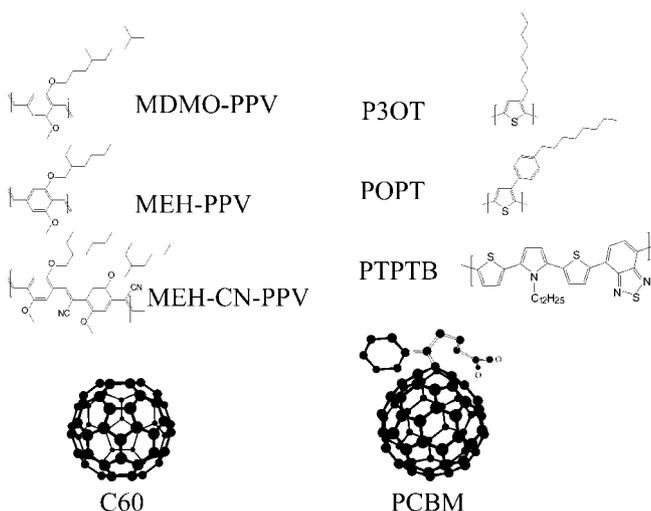
- Optimize the choice of metallic electrodes to achieve good ohmic contacts on both sides for collection of the oppositely charged photocarriers.
- Optimize the choice of the D/A pair (the energetics determine the open circuit potential). In addition, the bandgap of the semiconducting polymer should be chosen for efficient harvesting of the solar spectrum.
- Optimize the network morphology of the phase-separated composite material for enhanced transport and carrier generation. The absorption and the mobility of the charge carriers within the different components of the bulk heterojunction have to be maximized.

In organic PV elements generally two different tasks are to be clearly distinguished: The photo-induced 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.

In this millennium, PV energy conversion will gain in momentum. This clean and regenerative energy source should be utilized by exploiting all possible mechanisms, materials, and devices. This work summarizes the progress in a special section of PV energy conversion: i.e., organic, bulk heterojunction solar cells. With ~3 % power conversion efficiency already having been demonstrated, with large potential for improvement, this approach represents a viable route to realizing large-area "plastic solar power conversion technology".

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