Conjugated polymer/ fullerene based organic solar cells

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Conjugated polymers are increasingly used for the fabrication of electronic and optoelectronic devices like light emitting diodes (LEDs) and photovoltaic (PV) elements. The breakthrough in realising a promisingly efficient conversion of solar energy into electrical energy has been achieved by using blends of soluble electron-donor type conjugated polymers with fullerenes as electron-acceptor, transporting component. This "bulk heterojunction" approach suggests the preparation of intrinsically bipolar materials as a way to control both electronic and morphological properties at once.

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1. Introduction

The development of new exciting concepts in organic semiconductors opened up a viable way for the use of organic materials like fullerenes[1-8] and conjugated polymers[9-12] in application fields traditionally reserved to inorganic semiconductors and metals. For instance, polymeric displays based on LEDs are nowadays entering the display market.[13-16]

Furthermore, since the discovery of a photo induced electron transfer from non-degenerate ground-state conjugated polymers to fullerenes,[17,18] these materials are considered for the cost effective fabrication of flexible large-area solar cells and photodetectors.[19,20]

Organic solar cells of the first generation were *p/n*-heterojunction diodes, consisting of an electron-donor molecule (*p*-type component) thin film and an acceptor molecule (*n*-type component) thin film sandwiched between metal contacts. The flat heterojunction of two organic thin films gives rise to rectification behaviour as well as photocurrent and PV effects.[21-27] However, in this type of devices, the effective interaction between the electron-donor and the electron-acceptor components is limited to the flat geometrical interface. As such, rather low short circuit photocurrent density (J_{SC}) values were obtained. An encouraging breakthrough in realising higher efficient photo energy conversion has been achieved by direct mixing of a soluble *p*-type conjugated polymer and C_{60}, or other fullerene derivatives, as *n*-type component (Fig. 1).[27,28] Effective interaction between the donor and the acceptor components within these "bulk-heterojunction" solar cells can take place in the entire device's volume. Therefore, a more efficient charge generation results in dramatically enhanced short circuit J_{SC} values and in turn in much more efficient PV devices. However, the performance of "bulk-heterojunction" solar cells is still affected by critical factors:

• the compatibility between the conjugated polymer and the fullerene components plays a crucial role in determining the final morphology of the blend. Phase separation and clustering of fullerene can occur, reducing the effective donor/acceptor interfacial area as compared to the ideal value.[29]

• Moreover, in this device architecture, a balanced transport of both photo generated electrons and holes would be highly important. For an efficient transport of holes trough the donor polymer matrix and of electrons trough the acceptor fullerene phase, a truly bicontinuous interpenetrating network is required. Clustering effects, leading to a "void" between *p*- as well

as *n*-type domains are, obviously, dramatically affecting the transport of charges.[29] It is therefore intriguing to think of single materials with intrinsic donor-acceptor properties as well as capable of both electron and hole transport (*p/n*-type material). Even though the search for other electron accepting components alternative to fullerenes has been pursued,[31-36] the results so far obtained indicates fullerenes as specially interesting functional materials.[27,29,37,38]

2. Ultrafast photo induced electron transfer from conjugated polymers onto fullerenes

Most of non-degenerate ground-state conjugated polymers in their photo excited states (electrons promoted to the antibonding π^* band) are electron donors. The stability of the photo induced quasi-particles on conjugated polymers (e.g. photo generated radical-ions such as polarons)[39] suggested their use in combination with electron acceptor molecules. The radical-cations (positive polarons) resulting from an electron transfer from the polymer backbone onto the acceptor molecules are known to be stable, delocalised and mobile charge carriers as shown by chemical oxidative doping (*p*-doping) studies and conductivity measurements.[40] The outstanding electron-accepting properties of fullerene C_{60} suggested the investigation of its behaviour in conjunction with conjugated polymers. Sariciftci et al. and Morita et al. have independently reported the spectroscopic and photo physical properties of blends composed of poly((2-methoxy-5-(2'-ethylhexoxy)-p-phenylene) vinylene) or poly(3-octylthiophene) (hereafter called MEH-PPV and P3OT, respectively, see Chart) and C_{60}.[17,18] The electronic absorption spectrum of MEH-PPV/C_{60} composites turned out to be a simple superposition of the absorption spectra of the single components. Therefore, no indication of electronic states within the π-π^* gap of the conjugated polymer, as expected from a ground-state interaction between the donor and the acceptor, was found. However, the luminescence of MEH-PPV was quenched in these composites by a factor larger than 1000.[17] The luminescence decay time was reduced from 550 ps to a value less than 60 ps, indicating the

existence of a sub-picosecond electron transfer as quenching process.[41] Morita et al. also reported a quenching of the conjugated polymer luminescence in P3OT/C_{60} composites.[18] The same behaviour was observed later in a number of conjugated polymer/fullerene composites, and, as such, it can be regarded as a general phenomenon for non-degenerate ground-state conjugated polymers in combination with fullerenes. Very recently, the transfer of electrons from photo excited conjugated polymers onto 1-(3-methoxycarbonyl)-propyl-1-1-phenyl-(6,6)C_{61} (PCBM, see Chart) has been studied by pump-probe measurements with the unprecedented time resolution of 10 fs.[42] These studies showed that the photo induced state relaxation on the polymer chain switches from a radiative process in pristine polymers to a non-radiative one when PCBM is added. The experimental set-up allowed to time-resolved the photo induced electron transfer time with about 40 fs after an initial Kasha relaxation.[42] This high rate results in a very efficient electron transfer, with a quantum yield that approaches to unity. Time-resolved transient photocurrent studies on MEH-PPV/C_{60} composites with different C_{60} percentage contents showed that the photo induced electron transfer from conjugated polymers onto fullerenes not only enhances the number of the charge carriers photo generated in the host polymeric matrix, but also stabilises them preventing their recombination.[43] Finally, a direct and definitive evidence for an electron transfer from the photo excited conjugated polymers onto fullerenes, leading to long-living charged states, was obtained by steady-state light induced electron spin resonance (LESR) experiments. Fig. 2 displays the integrated LESR signal recorded upon illumination of MDMO-PPV/PCBM composites (MDMO-PPV stands for poly((2-methoxy-5-(3,7-dimethyloctyloxy)-*p*-phenylene) vinylene), see Chart). Two light induced electron spin resonance signals can be resolved: one at g = 2.0026, assigned to radical-cations (positive polarons) on the conjugated polymer backbone and one at g = 1.9997, assigned to PCBM$^{\bullet-}$ radical-anions.[44,45]

The long-living nature of the charge carriers photo generated within conjugated polymer/fullerene composites allows their collection at electrodes via diffusion as well as field induced migration and their use to provide electrical power to an external circuit. As such, these materials are rather attractive for PV solar energy conversion, and have been used for the fabrication of plastic solar cells as described in the next section.

3. "Bulk-heterojunction" plastic solar cells

In this section, we introduce plastic solar cells based on the "bulk-heterojunction" approach with the aim to elucidate the relationship between the morphology of the photoactive layer and the device's performance. A general and updated overview on organic, plastic PV is given by Ref. 27. A discussion on the working principle of conjugated polymer/fullerene "bulk-heterojunction" solar cells, and specifically on the origin of their open circuit voltage (V_{OC}), can be found in Ref.s 37 and 46.

Extensive literature exists on the realisation of photovoltaic elements based on small organic molecules.[21-24] Fullerene C_{60} has been used also to enhance the PV response of these flat *p/n*-heterojunctions, and a power efficiency as high as 1.05% was obtained.[25,26] For PV cells fabricated as bilayers of conjugated polymers and C_{60}, monochromatic energy efficiencies of 1% and incident photon to converted electron (IPCE) efficiencies of 15% were measured.[47,48] Although, as mentioned above, the internal quantum efficiency of photo induced charge separation is almost 100% for a donor/acceptor pair, the power conversion efficiency of these devices is limited by interconnected factors:

• charge separation occurs only at the flat geometrical interface, within the exciton diffusion length. Photo excitations created far away from the heterojunction undergo recombination prior to reach the electrodes;

• only a small fraction of incident photons is absorbed near the heterojunction interface.

To overcome these problems, "bulk-heterojunction" solar cells, whose photoactive layer consists of a conjugated polymer/fullerene blend, have been designed.[27,28] The photoactive blend is typically sandwiched between indium tin oxide/poly(ethylenedioxythiophene):poly(styrene sulphonate) (ITO/PEDOT:PSS) and Al as positive and negative electrodes, respectively.[27] The cross-section of this type of devices as well as the distribution of the conjugated polymer chains and fullerene molecules within the "bulk-heterojunction" are sketched schematically in Fig. 1. If both the donor and the acceptor networks are continuously interconnected, the collection of positive and negative photo carriers can be equally efficient. Yu et al. have obtained, using the "bulk-heterojunction" formed in a solid MEH-PPV/PCBM composite as photoactive layer, short circuit currents of 0.5 mA cm^{-2} under 20 mW cm^{-2} monochromatic illumination.[28] This value was approximately two orders of magnitude larger than those given by pure MEH-PPV devices or by the MEH-PPV/C$_{60}$ bilayer heterojunction mentioned above.[27]

Besides small-area (0.1 cm^2) testing devices, technologically more interesting up scaled large-area (15 cm × 10 cm) PV elements on flexible plastic substrates were produced as well.[27] A large-area solar cells is shown in Fig. 3 while its current voltage (*I/V*) characteristics are plotted in Fig. 4. For these devices the "bulk-heterojunction" approach introduced above was used, by mixing MDMO-PPV and PCBM (Fig. 1).[27] The comparison of these devices with the small-area solar cells on rigid substrate clearly showed that up scaling to large-area flexible devices is possible, giving routinely efficiencies as high as 2% under AM1.5 illumination.

3.1. Improving the efficiency of "bulk-heterojunction" solar cells

Recently, it has been demonstrated that the efficiency of "bulk-heterojunction" plastic solar cells can be improved effectively by manipulating the *morphology* within the photoactive blend.[29] It is very important to note that the ideal schematic sketch given by Fig. 1 is by far not realistic in any actual composite. Composites are juxtapositions of domains with different composition. Fig. 5 shows images of the surfaces of MDMO-PPV/PCBM blends spin-coated from toluene solution (a) and chlorobenzene solutions (b), respectively, obtained by atomic force microscopy (AFM). The images show that a more homogenous mixing of the two components is obtained when chlorobenzene is used as processing solvent. Very recent morphological studies, done by comparing AFM surface images and cross-sectional transmission electron microscopy (TEM) images, clearly confirm this observation.[49] To study the impact of these two highly different morphologies to the PV device performance, solar cells were fabricated under identical conditions except for the choice of the solvent. The *I/V* curves recorded for the two types of devices are plotted in Fig. 6 (active area of 7.5 mm^2). As can be seen the open circuit photovoltages are almost identical while the device cast from chlorobenzene solution exhibits more than a twofold enhancement in the J_{SC} as compared to the device fabricated from toluene solution (5.25 versus 2.33 mA cm^{-2}). This high J_{SC} value, combined with a fill factor (FF) as high as 0.61, results in a power efficiency η of 2.5% under AM1.5 illumination.[50] This is the highest efficiency so far reported for plastic solar cells. The optical absorption spectra of the active layer are nearly identical in the two cases, while the IPCE efficiency of the device made from chlorobenzene is higher all over the absorption spectrum. As such, the difference in the device efficiencies must be related to the different morphologies shown by Fig. 5. Shrinking each of the interpenetrating two phases' domain size below 500 nm leads to a larger donor-acceptor interfacial contact area and also decreases the spatial separation between fullerene domains. Indeed, the increase in efficiency relies also on the increased mobility of the charge carriers of both signs, as indicated by field-effect

measurements on the single components as well as on the composite, spun-cast from different solvents.[51]

4. Conclusions and perspectives

Preparation and properties of a novel class of solar cells using conjugated polymers and fullerenes, have been reviewed. These materials consist of a hole conducting, conjugated backbone (*p-cable*) with mixed/or covalently bound fullerene moieties (*n-cable*).

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 photo carriers,

ii.)   Optimize the choice of the donor/acceptor pair (the energetics determine the open circuit potential). In addition, the band gap of the semiconducting polymer should be chosen for efficient harvesting of the solar spectrum.

iii.) Optimize the network morphology of the phase separated composite material for enhanced transport and carrier generation. The absorption as well as the mobility of the charge carriers within the different components of the bulk heterojunction has to be maximized.

In organic photovoltaic 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.*

Acknowledgements

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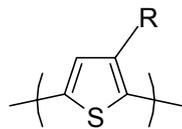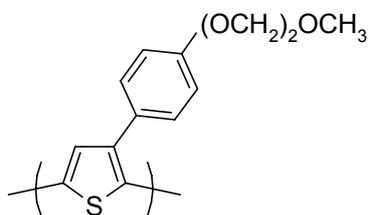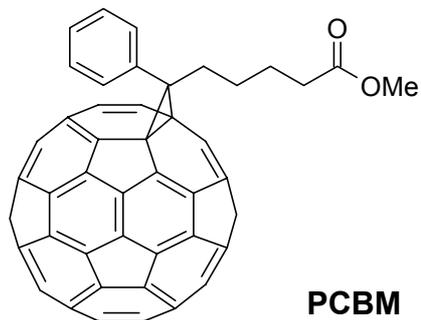
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MEH-PPV

MDMO-PPV

(OCH$_2$)$_2$OCH$_3$

PEOPT

OMe
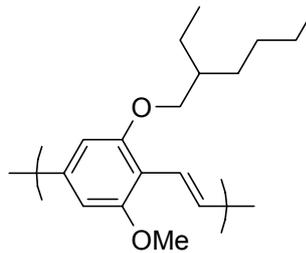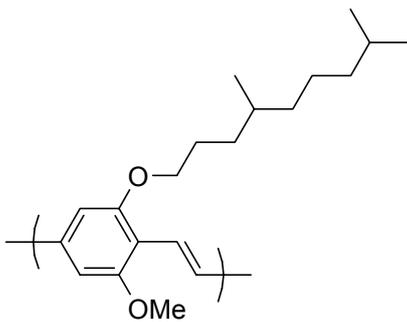
PCBM

CHART

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Captions to figures

Fig. 1: Schematic representation of a "bulk-heterojunction" photovoltaic device (reproduced from 27 with permission of WILEY-VCH).

Fig. 2: Integrated LESR spectrum of a MDMO-PPV/PCBM composite upon successive illumination with 2.41 eV argon ion laser (reproduced from 45 with the permission of the American Physical Society).

Fig. 3: Picture of a large area flexible plastic solar cell (reproduced with permission of WILEY-VCH).

Fig. 4: *I/V* behaviour of a 15 cm × 10 cm MDMO-PPV/PCBM "bulk-heterojunction" solar cell, with active area of 50 cm^2 under light (black squares) and in the dark (open squares). Illumination was provided by a white-light fluorescence tube with intensity of 6 mW cm^{-2} (reproduced from 26 with permission of WILEY-VCH).

Fig. 5: AFM images showing the surfaces morphology of MDMO-PPV/PCBM (1:4 -w.) blend films with thickness of ca. 100 nm and the corresponding cross-section. **a)** Film spun-cast from solution in toluene. **b)** Film spun-cast from solution in chlorobenzene. The images show the first derivative of the actual surface heights. The cross sections of the true surface heights were taken horizontally from the points indicated by the dotted lines (reproduced from 27 with permission of VILEY-VCH).

Fig. 6: Current voltage characteristics for MDMO-PPV/PCBM devices with active layer spun-cast from 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 chlorobenzene solution (bottom): J_{SC} = 5.25 mA cm^{-2}, V_{OC} = 0.82 V, FF =

0.61, $\eta_{AM1.5}$ = 2.5 %. Data are for devices illuminated with an intensity of 80 mW cm^{-2}, with

an AM1.5 spectral mismatch factor of 0.753. Temperature of the devices during

measurements was 50 °C (reproduced from 27 with permission of WILEY-VCH).

Anode (Al)

p-type / n-type
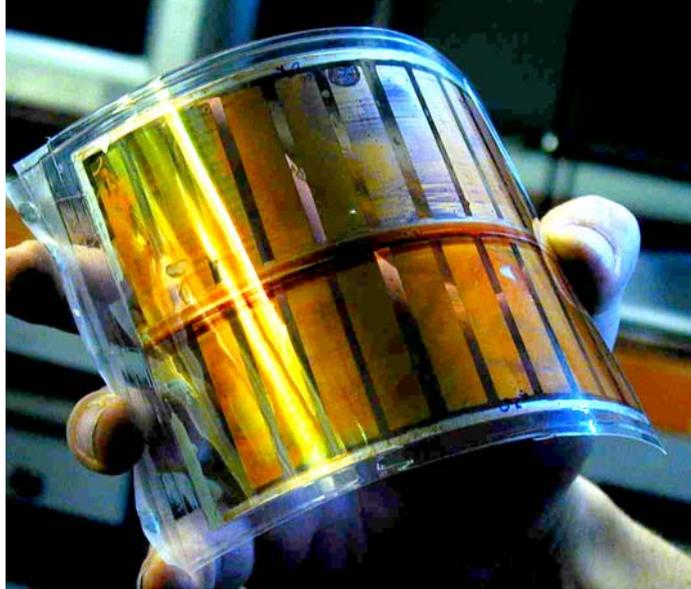(MDMO-PPV/ PCBM)

Cathode (ITO)

glass

SMU

e-

hv
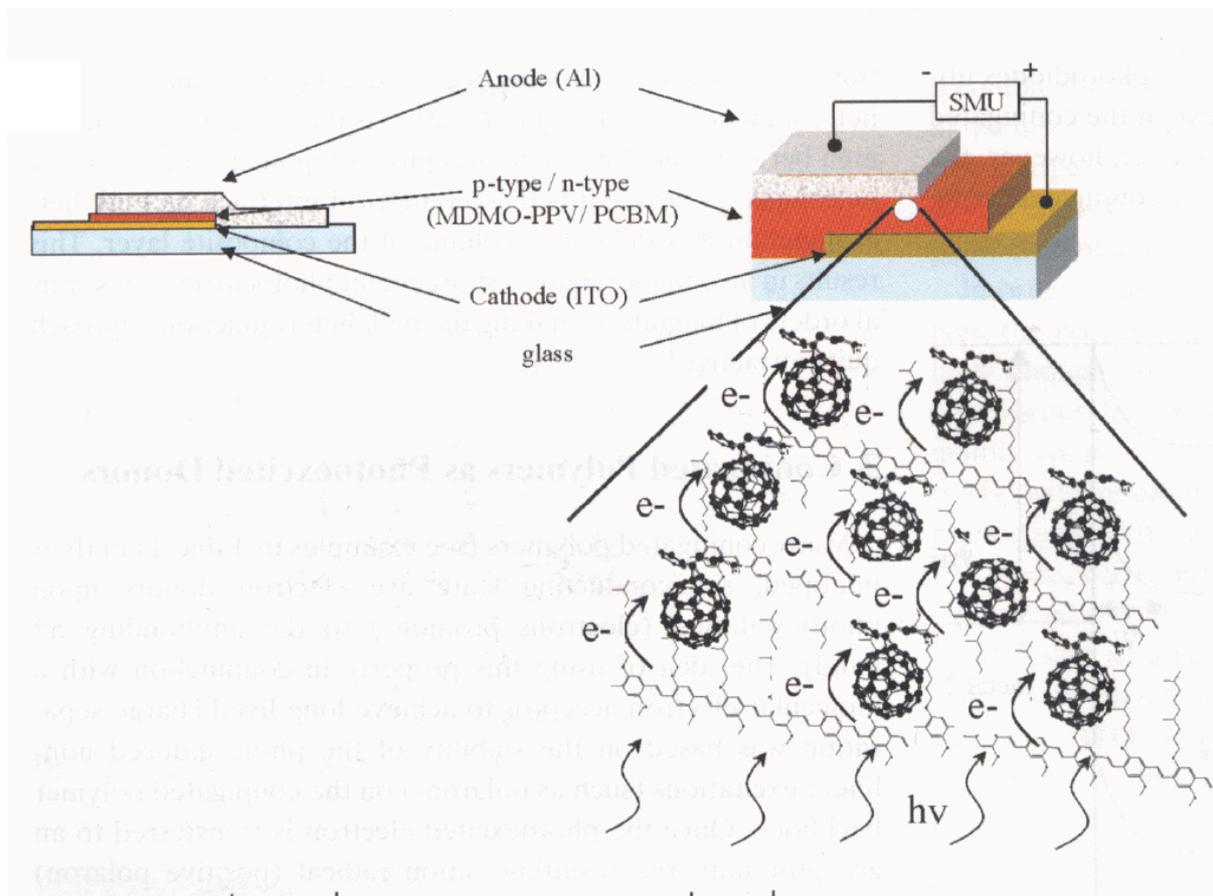
Fig. 1

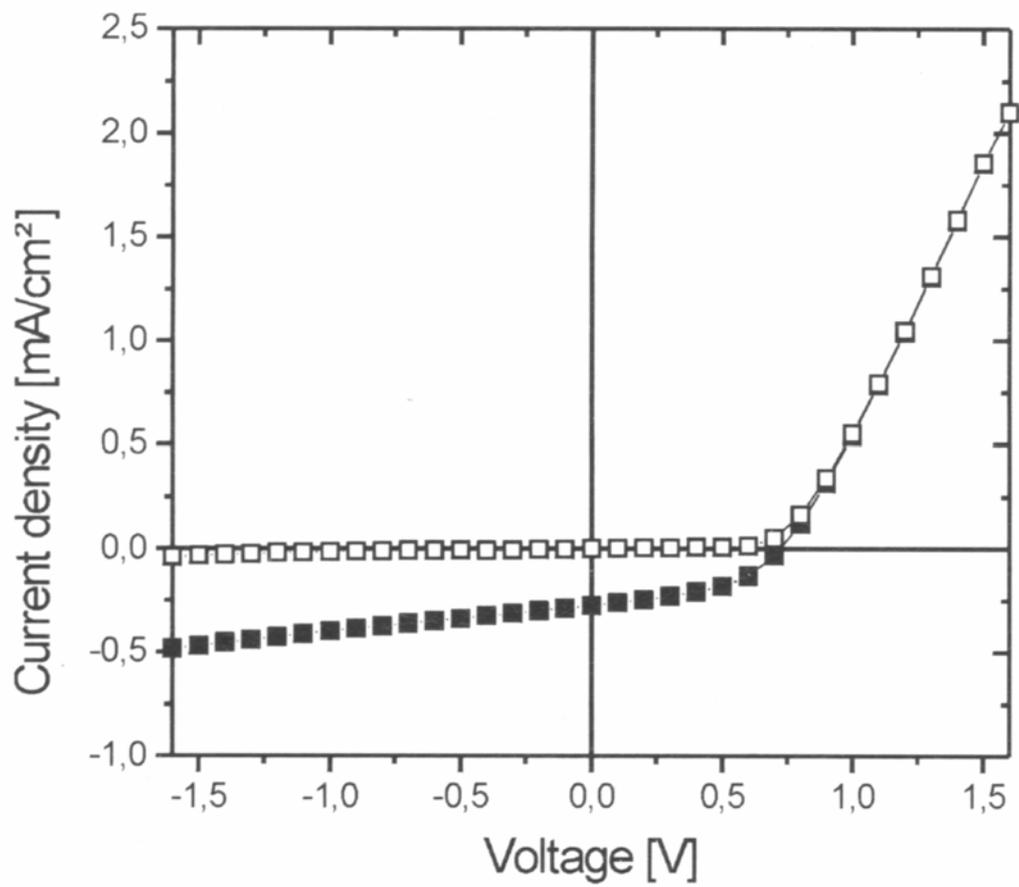**A. Cravino and N. S. Sariciftci**
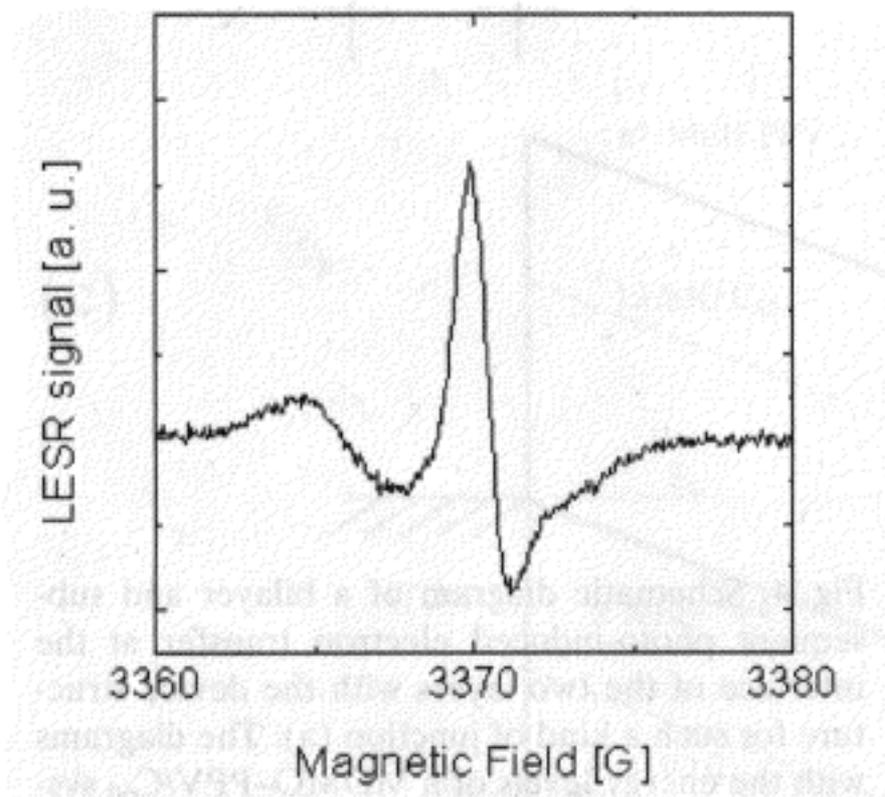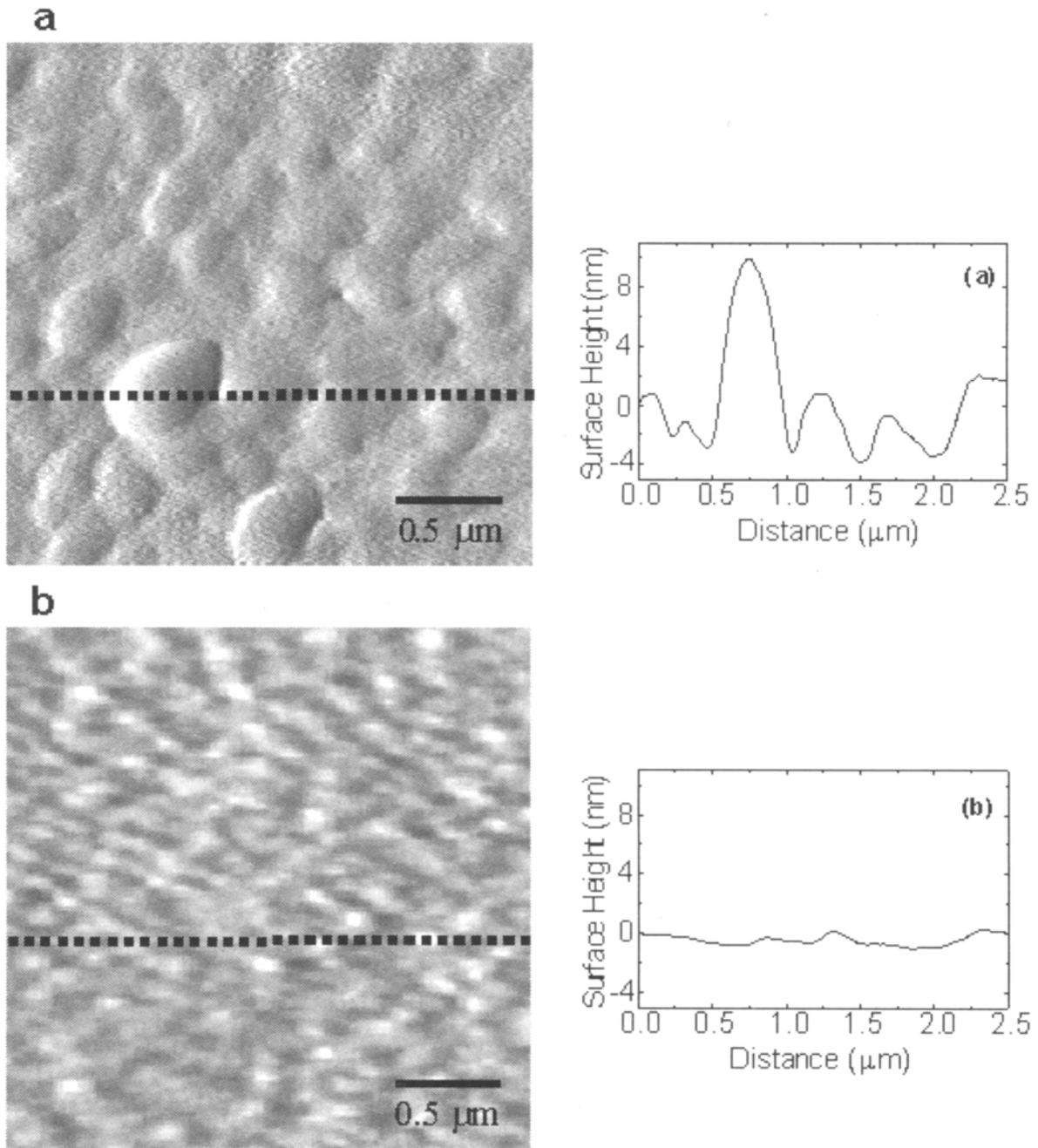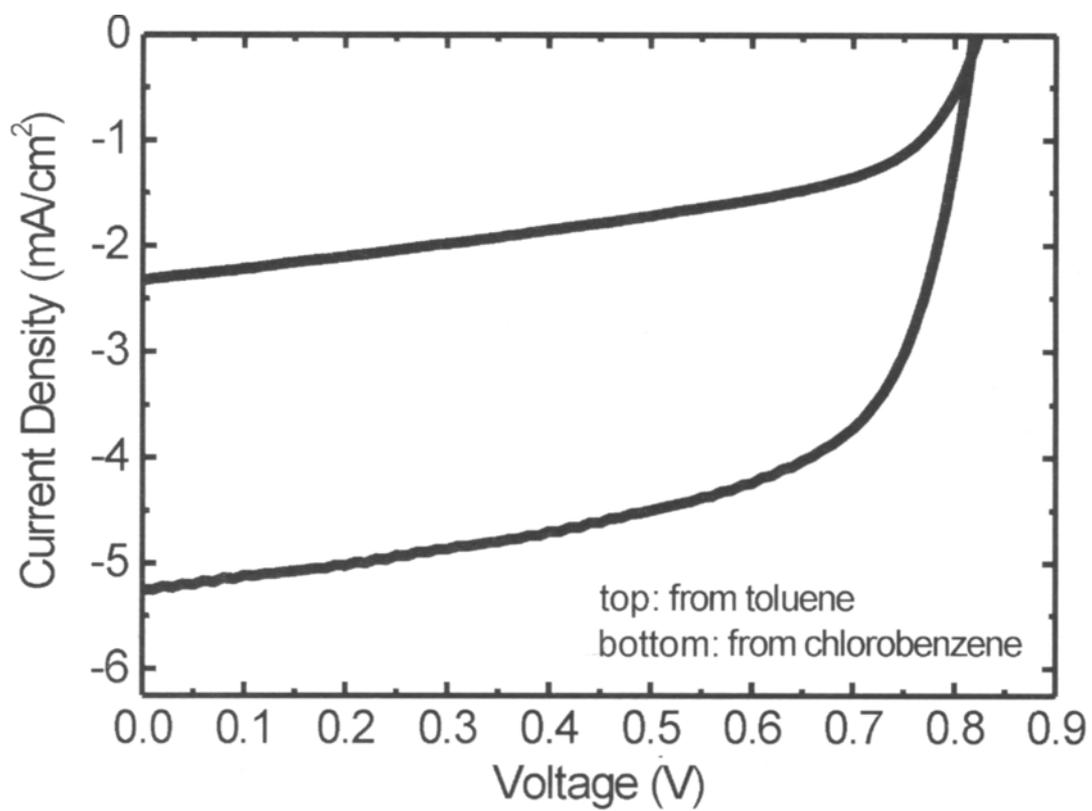
Fig. 2

A. Cravino and N. S. Sariciftci

Fig. 3

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Fig. 4

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Fig. 5

A. Cravino and N. S. Sariciftci

Fig. 6

A. Cravino and N. S. Sariciftci