

DOI: 10.1002/adfm.200600859

Polyterthiophenes as Donors for Polymer Solar Cells**

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Thiophene-containing polymers blended with fullerenes have recently demonstrated impressively high photovoltaic efficiencies. One drawback of this class of polymers is their relatively low ionization potential, which leads to rather low open-circuit voltages. Polyterthiophenes belong to a material class that has recently captured a large amount of interest for polymer electronic applications because of its excellent transport properties. Because of the slightly lower ionization potential, this material class appears more attractive for photovoltaic applications than polythiophenes. In this work, the photovoltaic performance of bulk heterojunction solar cells from polyterthiophene/fullerene composites is discussed and compared to the polymer/fullerene blend morphology.

1. Introduction

The advancement of organic solar cells^[1–4] is creating a huge demand for improved materials, especially smaller bandgap polymers with excellent transport properties. These efforts are primarily driven by the desire to develop a new generation of photovoltaic products, based on using conjugated polymers as active layers.

Critical factors in this development are the power efficiency as well as the device lifetime. In a recent paper we discussed the importance of a polymer's ionization potential and its linear correlation to the open-circuit voltage (V_{oc}).^[5] In parallel, stability studies on poly(3-hexylthiophene) (P3HT) transistors^[6,7] have shown that materials with ionization potentials in this range (4.5–5.0 eV) are susceptible to oxidative doping, and therefore transistors exposed to ambient atmosphere will, over time, p-dope because of interacting with oxygen.^[7,8] For early organic photovoltaic (OPV) applications oxygen stability will be a critical issue. Although there is evidence that such doping may be reversible in the dark either by treating it with a reducing agent or applying a vacuum,^[9] the combination of light and oxygen, in particular, can cause irreversible damage to a conjugated polymer backbone.^[10] Even under the assumption that a flexible barrier encapsulation provides sufficient stability, en-

hanced oxygen stability will ease production and reduce overall product costs. There is a strong desire, therefore, to prepare polymers with lower-lying highest occupied molecular orbital (HOMO) energy levels than poly(3-alkylthiophenes) that are capable of higher V_{oc} s. Consequently, a class of terthiophene polymers, illustrated in Figure 1a, are highly promising, because the unsubstituted thiophene twists slightly out of plane, perturbing the planarity of the backbone and lowering the HOMO energy level compared to P3HT.^[11,12] As a prototype candidate to investigate the photovoltaic properties of polyterthiophenes, a hexyl substituted polyterthiophene that is chemically and structurally the closest to P3HT, was chosen.

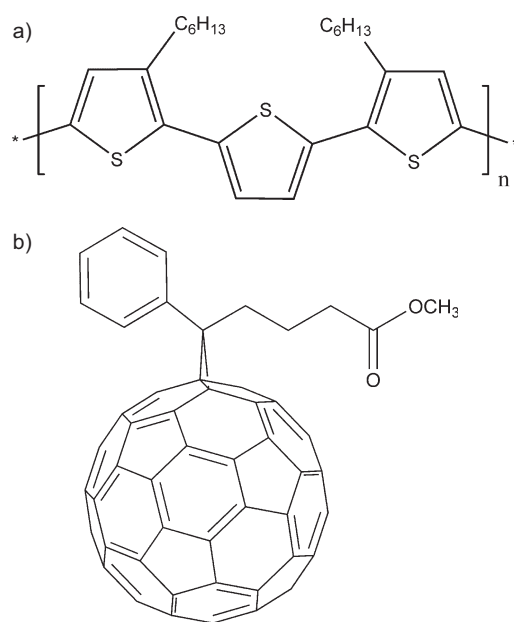


Figure 1. Chemical structure of a) poly-2,2':5',2'':-(3,3'')-dihexyl-terthiophene) (C6-TT) and b) [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM).

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[**] The authors (at Konarka) acknowledge the European Commission for funding from the Molycell project. Further, the authors gratefully acknowledge support from TU Ilmenau (T. Erb and G. Gobsch) for support with X-Ray investigations.

2. Results and Discussion

The materials under investigation are shown in Figure 1. The polymer poly(2,2':5',2''-3,3''-dihexyl-terthiophene) (C6-TT) was synthesized by using Stille copolymerization as previously reported,^[13] and had an M_w of 42000 g mol⁻¹, and M_n of 20000 g mol⁻¹ as determined by using gel-permeation chromatography (GPC) against polystyrene standards. PCBM ([6,6]-phenyl-C₆₁-butyric acid methyl ester) with a purity of 99.5 % was used as the acceptor.

Figure 2a–d summarizes the electro-optical properties of pristine C6-TT. Pristine C6-TT shows a pronounced shoulder at 600 nm indicative of aggregation, followed by a trailing edge in the near-IR part, which results in an optical bandgap of approximately 1.9 eV. Bandgap data from electrochemical measurements differ from the optical bandgap, with the HOMO and the lowest unoccupied molecular orbital (LUMO) determined to be -5.25 eV and -3.05 eV, respectively, yielding an electrochemical bandgap of ca. 2.2 eV. As expected, the HOMO of C6-TT is shifted to lower values relative to P3HT^[14] (not shown in these plots), by approximately 100–150 mV.

The transport properties of C6-TT were studied by using organic field-effect transistor (OFET) measurements in a bottom-gate bottom-contact configuration and the saturated field-effect hole mobility was determined to be 3×10^{-2} cm² V⁻¹ s⁻¹. Though 1,2-dichlorobenzene (*o*-DCB) was used as a solvent, device performance is comparable to results recently reported

for chloroform.^[11,12] Obviously, the choice of solvents has little influence on the supramolecular organization of the polymer. High mobility values are essential for good photovoltaic performance. Mobility values above 10⁻³ cm² V⁻¹ s⁻¹ are regarded^[5] as one of the necessary requirements to guarantee recombination-free operation of photovoltaic devices.

The material parameters of C6-TT are summarized in Table 1. Table 1 also presents the calculation of the maximum efficiency one would expect for a material with the HOMO and

Table 1. Material parameters of C6-TT. The efficiency is predicted, based on the HOMO, optical bandgap, and mobility data according to a model presented in reference [14].

HOMO [eV]	LUMO [eV]	E _g , opt [eV]	Mobility [cm ² V ⁻¹ s ⁻¹]	Predicted Voc [V]	Calc. max. efficiency [%]
-5.25	-3.05	1.9	3×10^{-2}	0.7–0.8	≥5%

the bandgap of C6-TT. The efficiency value was calculated using a recently suggested model^[15] and is an upper limit for the maximum-expected performance of the polymer. The maximum V_{oc} was calculated from the built-in potential V_{bi} , which is the difference between the HOMO of the C6-TT and the LUMO of PCBM, as shown in Figure 3b. Following previous studies,^[5] V_{bi} can be converted into V_{oc} by the subtraction of ca. 0.2 V. For efficiency calculations the optical bandgap needs to be considered for the determination of the short-circuit current.

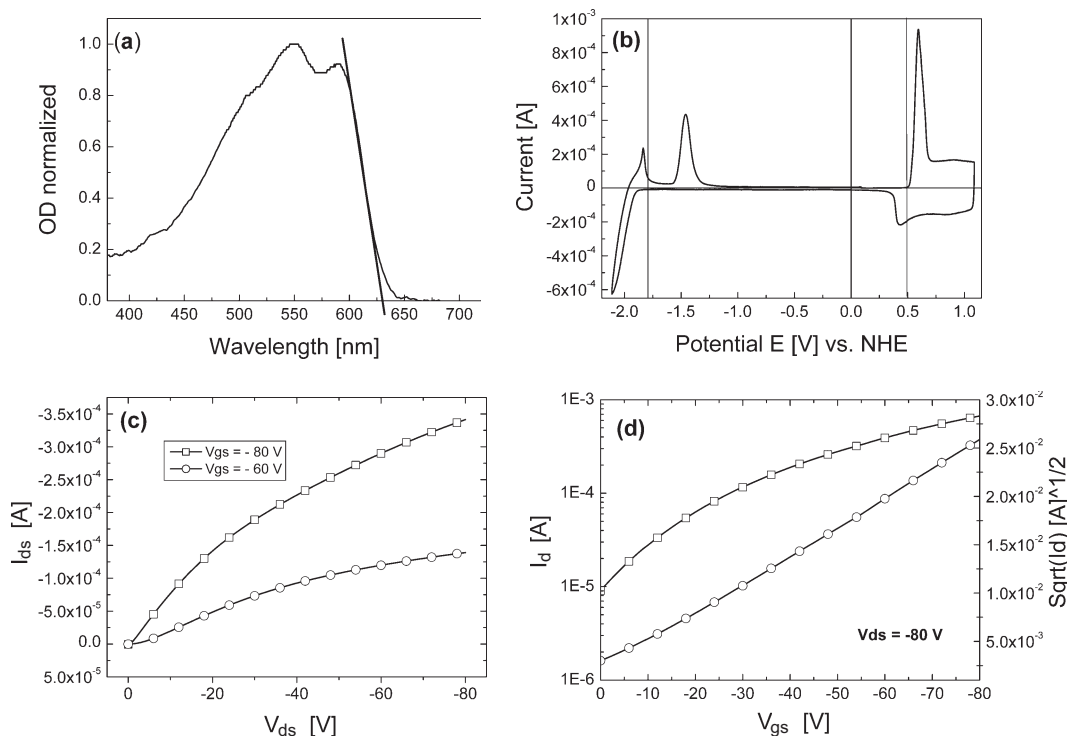


Figure 2. a) The optical absorption spectrum of poly-2,2':5',2''-(3,3''-dihexyl-terthiophene) (C6-TT) film (optical bandgap 1.9 eV). b) Cyclic voltammetry (CV) measurements of C6-TT film (electrochemical bandgap around 2.2 eV). The HOMO level is at 5.25 eV, and the LUMO level is at 3.05 eV. c) Drain–source current (I_{ds})–drain–source voltage (V_{ds}) characteristics. d) Drain current (I_d)–gate–source voltage (V_{gs}) characteristics. The mobility was calculated from the saturation regime with 3×10^{-2} cm² V⁻¹ s⁻¹.

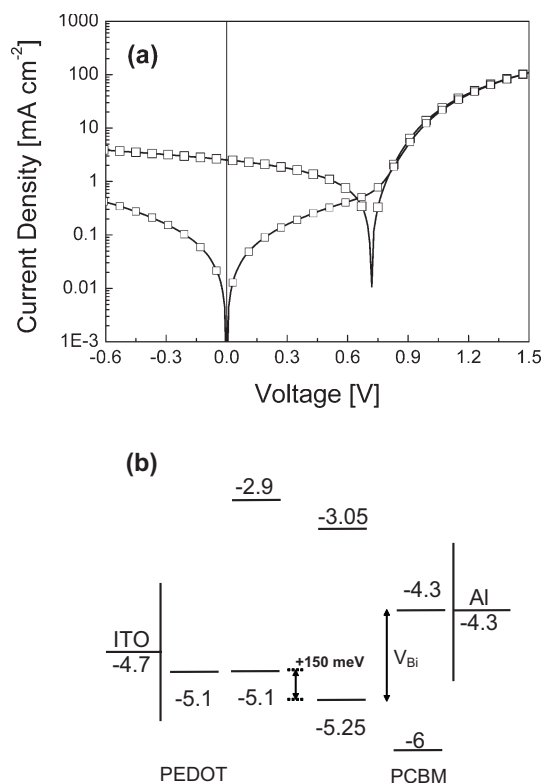


Figure 3. a) j - V characteristics of an ITO-PEDOT-C6-TT/PCBM-LiF/Al device illuminated with 100 mW cm^{-2} white light (AM 1.5 conditions). This particular device gave a V_{oc} of 0.75 V, short circuit current (J_{sc}) of 2.5 mA cm^{-2} , fill factor (FF) of 0.34, and a power efficiency of 0.6%. The highest efficiencies for C6-TT are in the 1% range. Higher efficiencies of over 2% have been observed for terthiophenes with longer alkyl side chains and will be described in more detail elsewhere. b) The energy levels of the bulk heterojunction solar cell, with HOMO/LUMO values given in electron volts for C6-TT and PCBM relative to P3HT. The 150 meV lower HOMO level of C6-TT compared to P3HT predicts higher V_{oc} s for terthiophene-based devices. All polymer/fullerene levels were determined in the same way, by using CV.

During device manufacture, the processing conditions, that is, the blading conditions and the temperature treatment, were varied from batch to batch to provide a broader parameter range in layer thickness and drying conditions. Figure 3a shows a typical current-density-voltage (j - V) curve of a C6-TT/PCBM device under illumination and in the dark. In accordance to the expectations from electrochemical data a V_{oc} as high as 700 mV was observed for individual devices. Aside from the V_{oc} , the other device parameters are below expectations and do not come close to matching the performance of P3HT/PCBM. In particular, the short-circuit current is a factor 2–3 lower than expected for a polymer with a bandgap of 1.9 eV.

From the high mobility values (Table 1, Fig. 2c and d) we can exclude any transport limitations caused by improper carrier transport of one of the pristine components. Nonoptimal segregation of the two components is of course a strong possibility and it has been frequently observed that the blended composites have inferior transport properties compared to the

pristine one.^[16] However, the high chemical and structural similarity between P3HT and C6-TT does not necessarily imply that addition of PCBM impacts C6-TT in a similar way to P3HT. Nevertheless, we verified the assumption by analyzing the device j - V characteristics based on an extended one-diode model recently published^[15,17] and found ideality factors in the order of two or higher. In combination with the lower photo-generation rate (i.e., the photocurrent) the j - V analysis suggests poor phase separation in the C6-TT/PCBM blends. From the magnitude of the photocurrent, the j - V characteristics, and the power efficiency, C6-TT/PCBM devices behave similarly to unannealed P3HT/PCBM devices. The thermal-annealing process in P3HT/PCBM devices^[18] has been studied in detail^[19–21] and is now well understood. Thermal treatment of P3HT/PCBM devices induces a morphological change of the blend. At elevated temperatures between 100°C and 150°C (note, the precise temperature depends on the viscosity and T_g of the polymer and, as such, on the molecular weight) the polymer backbone starts to soften, giving more freedom for PCBM molecules to diffuse within the more flexible polymer matrix. During this process, PCBM starts to aggregate leaving behind “pristine” polymer domains, which, after cooling, can pack together and post-crystallize.^[1,19] Such an optimized phase morphology with better defined polymer and fullerene domains shows significantly reduced recombination of Langevine type^[22] and thus higher short-circuit currents and better fill factors. Increasing the annealing temperature for P3HT fullerene blends up to 200°C further increases the pristine polymer domains within the blend and supports further aggregation of PCBM, which results in the formation of needlelike PCBM crystals.^[23]

The j - V analysis is in agreement with the assumption that C6-TT/PCBM devices behave like not-fully-annealed P3HT/PCBM devices. Even at elevated temperatures PCBM does not seem to start diffusing within the C6-TT network, although the melting point of C6-TT, which was determined by using differential scanning calorimetry, is shifted by approximately 20°C (depending on the molecular weight of the particular polymer) to lower temperatures. After heating the fullerene-blended terthiophene films to 240°C , no formation of fullerene aggregates was observed under the thermomicroscope. Figure 4b shows a microscopy image of a 240°C annealed C6-TT-fullerene film. No needlelike PCBM crystals were observed, in strong contrast to P3HT-fullerene film annealed in the same way, as shown in Figure 4d.

Though preliminary, the structural analysis of C6-TT provides a good indication of the conformational limitations of C6-TT/PCBM blends. The centrosymmetric C6-TT shown in Figure 1a has, similar to regioregular P3HT,^[24] a highly crystalline morphology.^[25] Figure 5a and c show the X-ray diffraction (XRD) spectra recorded in grazing-incidence geometry of the two pristine polymers. Both polymers show a pronounced (100) reflection that originates from the lamellar backbone planes of polymer crystallites with a -axis orientation (polymer backbone parallel and alkyl side chains perpendicular to the substrate). By calculating the a -axis distances using the Bragg equation, the interlamellar backbone distance along the side-

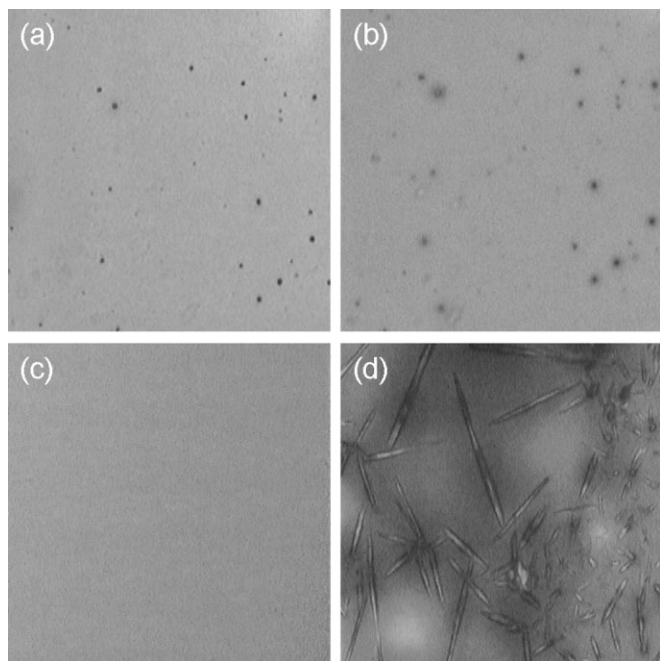


Figure 4. Microscopy images of C6-TT not-annealed (a) and annealed at 240 °C (b) are compared with P3HT/PCBM not-annealed (c) and annealed at 240 °C (d).

chain direction is reduced for C6-TT (1.4 nm) compared to P3HT (1.6 nm). As expected, annealing of the pristine polymer films did not significantly change the number and size of the polymer crystallites. As reported in the literature^[19] the addition of fullerene to a P3HT system causes a dramatic reduction of polymer crystallinity (depending on the molecular weight of the polymer and the boiling point of the solvent used) but an appropriate thermal-annealing enhances the degree of crystallinity significantly, as shown in Figure 5b. No sign of crystallinity is observed for the fullerene-blended terthiophene system, which correlates to a highly disturbed polymer morphology. Thermal-annealing processes at various temperatures (up to 240 °C) did not convert the amorphous polymer system into a crystalline one. The presence of fullerene completely suppresses the crystallization of terthiophene. In addition, fullerene diffusion seems to be strongly suppressed, even under thermal treatments.

Adjacent thiophene rings on the polymer chain are oriented in a coplanar conformation, thus allowing a good overlap of the π -conjugated system along the length of the backbone. Unlike P3HT, in which the side-chain density within an individual polymer chain is too high to allow interchain side-chain interdigitation, the C6-TT polymer can adopt a conformation (shown in Fig. 6) in which interdigitation is possible because of the free volume around the backbone. A necessary prerequisite of 3D

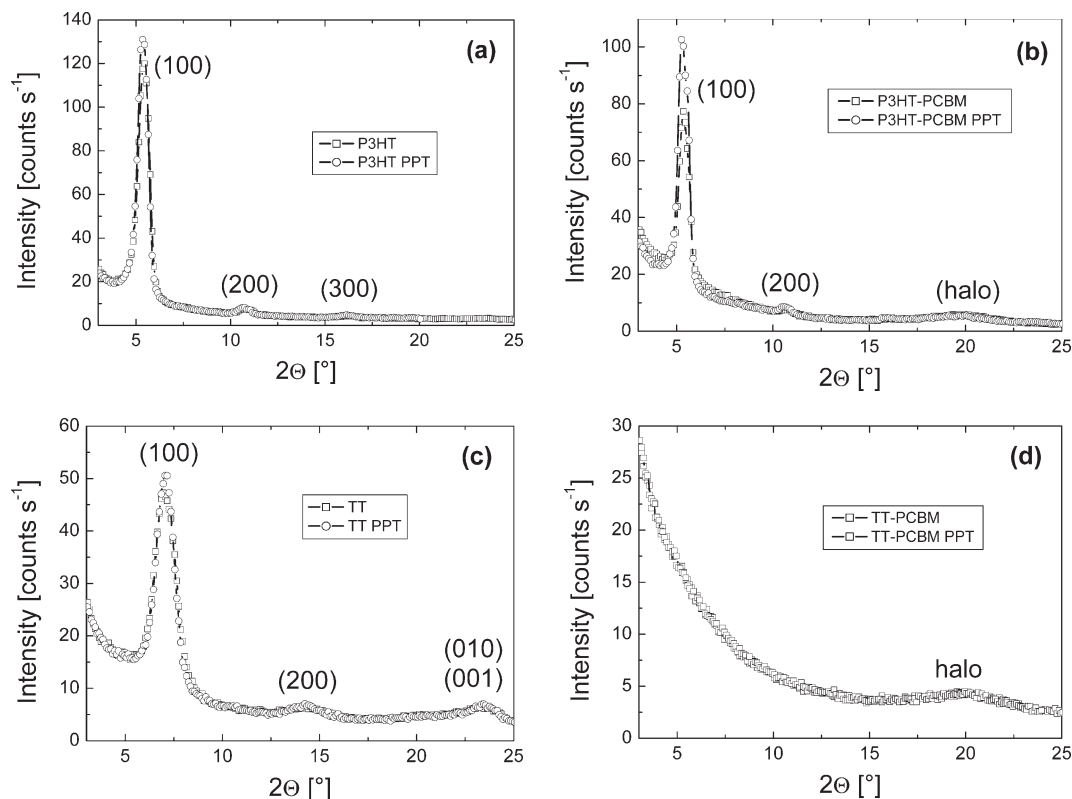


Figure 5. Diffractometry images of thin films of pristine P3HT (a), P3HT-PCBM blend (b), pristine C6-TT (c), and C6-TT blended with fullerene (d). PPT indicates the thermal-annealing of the particular sample.

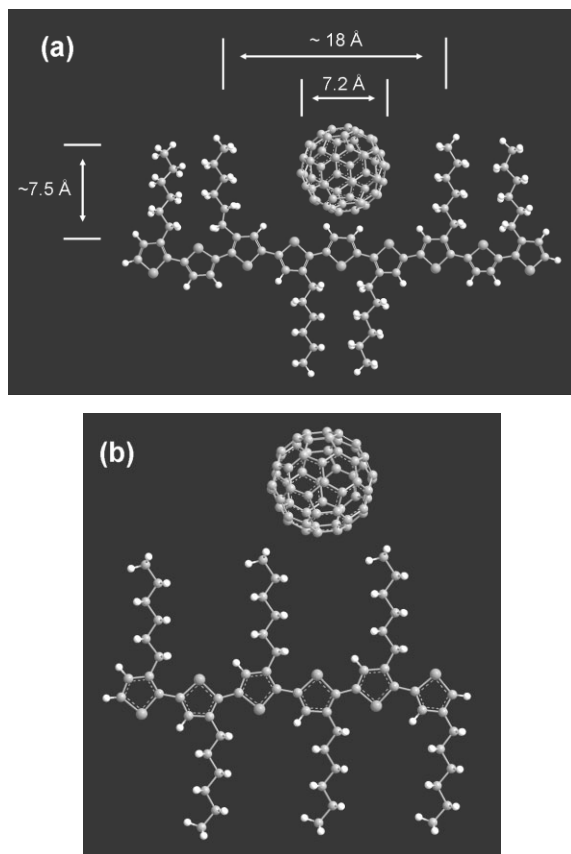


Figure 6. a) This scheme illustrates why the post-treatment process, which is well known for P3HT systems, does not work for the investigated terthiophene systems. The nonfunctionalized fullerene with a diameter of about 7.2 Å can potentially fit into the side-chain gap of about 18 Å × 7.5 Å. It seems that the fullerene is caged by the surrounding alkyl side chains and even at high temperatures that significantly soften the polymer matrix, the fullerenes diffusion is completely suppressed. b) This scheme of P3HT/C60 shows that there is no possibility for the discussed kind of fullerene caging; polymer aggregation is not hindered because of this.

ordering for this polymer is that the regularly spaced side chains extend from the backbone with the planar main chains oriented cofacially with respect to neighboring chains. This, allows a high degree of interdigitization within each polymer layer. However, if one or more fullerenes fit into the regular side-chain spacing, as suggested in Figure 6a, cofacial packing of parallel chains will be strongly suppressed. Comparing the distance of the side-chain spacing calculated from the model (18 Å) to the fullerene diameter, it appears that fullerenes can occupy the free volume between the alkyl-chain pairs, thus suppressing the aggregation of the C6-TT in strong contrast to P3HT as shown in Figure 6b. Fullerenes that are blended with P3HT do not hinder the polymer aggregation like in terthiophene blends. If that rather simple morphology picture is valid, one would expect that the addition of fullerenes can successfully suppress the otherwise strong crystallization of the pristine polymer.^[12] The $\theta/2\theta$ angular scan for a C6-TT/PCBM blend (Fig 5d) shows no signature of C6-TT crystals in contrast to the pristine C6-TT film, which is a strong argument in favor of the morphology hypothesis.

3. Conclusions

We have investigated the photovoltaic properties of a novel thiophene-based polymer, C6-TT, which has promising electro-optical material properties. Most interestingly, this polymer benefits from a small distortion between the thiophene units along the backbone, which effectively lowers the HOMO by ca. 150 meV compared to the HOMO of P3HT and indeed, higher V_{oc} s are observed. The chemical and structural proximity of C6-TT compared to the well-investigated P3HT gave rise to the expectation, that the photovoltaic performance of C6-TT will be qualitatively similar. However, the observed short-circuit current and the fill factor are significantly lower, strongly limited by a suboptimal mixing of the polymer with the fullerene. Preliminary morphology investigations suggest that fullerenes successfully suppress crystallization in terthiophenes, and a simple morphological picture to explain the findings is given. Further investigations are currently being carried out to better understand the phase morphology of fullerene/polyterthiophene blends. Having understood the limitations of the C6-TT/PCBM composites allows us to suggest suitable measures for modifying this promising class of materials for photovoltaic operation. Primarily, modification of the alkyl side chains in such a way that they better fill the intermediate space around the centrosymmetric thiophene appears promising. In parallel, alternative fullerenes with more bulky side chains are a logical approach.

4. Experimental

The electrochemical properties of the polymer were studied by using cyclic voltammetry (CV) on thin films at room temperature in a glove-box under an argon atmosphere. The oxidation onset potentials were determined as the position where the oxidation current starts to differ from the baseline and corrected versus a normal hydrogen electrode (NHE) using a vacuum level -4.75 eV for NHE.

Thin-film OFETs were fabricated under dry nitrogen on a thermally grown silicon oxide (SiO₂) insulating layer and Au source/drain electrodes from 1 wt % *o*-DCB solutions.

Photovoltaic devices were fabricated on glass/ITO substrates covered with a 100 nm layer of PEDOT:PSS (Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate); HC Starck). Photovoltaic layers, consisting of a C6-TT polymer and the methanofullerene PCBM in 1:1 weight ratios were dissolved between 2–4 wt % in *o*-DCB and deposited by doctor blading [26] with a typical film thickness of 250 nm. The LiF/Al (0.6:80 nm) metal electrode was thermally deposited; devices were characterized at 25 °C under AM 1.5 conditions (mismatch ca. 0.98).

The transport properties have been investigated by means of a bottom-gate OFET produced in a nitrogen atmosphere by coating the polymer layers on 230 nm SiO₂ dielectric, thermally grown on N+Si, used as gate electrode; and sputtered gold as source and drain electrodes. Source and drain contacts were patterned using conventional photolithography to obtain a fingered layout with a channel width of $W = 10$ mm and a channel length of 10 μm. Before active layer coating the SiO₂ surface was treated with hexamethyldisilazane (HMDS), to improve the film adhesion and formation. The OFET transfer characteristics were measured in a nitrogen atmosphere by using an Agilent 4155C parameter analyzer.

X-ray diffraction measurements were carried out with a Philips X'Pert-Pro diffractometer. To increase the effective X-ray path length, the thin films were studied in grazing-incidence diffraction geometry.

The radiation used was a monochromatic Cu K α beam with a wavelength of $\lambda = 0.154$ nm.

Received: September 18, 2006

Revised: December 13, 2006

Published online: April 12, 2007

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