Photovoltaic and photophysical properties of a novel bis-3-hexylthiophene substituted quinoxaline derivative

Serap Günes [a,b,*], Derya Baran [c], Görkem Günbas [c], Funda Özyurt [c], Anita Fuchsbauer [a], Niyazi Serdar Sariciftci [a], Levent Toppare [c]

[a] Linz Institute for Organic Solar Cells (LIOS), Johannes Kepler University Linz, Physical Chemistry, Altenberger Strasse 69, A-4040 Linz, Austria
[b] Yildiz Technical University, Faculty of Arts and Science, Department of Physics, Davutpasa Campus, 34210 Esenler, Istanbul, Turkey
[c] Middle East Technical University, Faculty of Arts and Science, Department of Chemistry, 06531 Ankara, Turkey

ABSTRACT

We report on the photophysical properties and photovoltaic performance of a polythiophene derivative, poly-2,3-bis(4-tert-butylphenyl)-5,8-bis(4-hexylthiophen-2-yl)quinoxaline (PHTQ) as an electron donor in bulk heterojunction solar cells blended with the acceptor 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-methanofullerene (PCBM). Devices were composed of PHTQ and varying amounts of PCBM (1:1, 1:2, 1:3, 1:4 w-w ratio). The components were spin cast from ortho-dichlorobenzene (ODCB) and characterized by measuring current–voltage characteristics under simulated AM 1.5 conditions. Efficiencies up to 0.3% have been reached. Incident photon to current efficiency (IPCE) is reported and the nanoscale morphology was investigated with atomic force microscopy (AFM). Photoinduced absorption spectroscopy confirms the photoinduced charge transfer in such donor acceptor blends.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The realization of photoinduced charge transfer from a conjugated polymer poly [2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) to fullerenes (C_{60}) induced large efforts in fabrication of organic solar cells [1]. Despite the high efficiencies of above 20% achieved by monocrystalline silicon solar cells, their production cost and energy consumption during fabrication are quite high. Therefore, the need to develop inexpensive renewable energy sources is evident. New approaches towards stable, low cost, and efficient photovoltaic devices are indeed the high priority [2–5].

Polymers belong to an important material class, which entered nearly every aspects of modern society. The possibility of chemically manipulating the material properties of polymers (plastics) combined with a variety of easy and cheap processing techniques in large-scale production have made polymer-based materials attractive [6–8]. The flexibility, low density (light weight), partial optical transparency, low cost fabrication, easy integration in a wide variety of devices and their tuneable physical/chemical properties are the advantages of organic "plastic" solar cells over that of conventional silicon solar cells.

An organic solar cell consists of two organic materials one of which is an electron donor (p-type) and the other is an acceptor (n-type). Bulk heterojunction solar cells are composed of blends of donor and acceptor materials, yielding a photoactive layer of nanoscale p–n junctions, where photoinduced charge transfer takes place [9]. Organic solar cells based on bulk heterojunction concept have efficiencies up to 5% [10–12] and theoretical studies predict that 10% efficiencies are within the achievable range [13–15]. Derivatives of phenylene vinylene backbones such as poly(2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene) (MDMO-PPV) and thiophene chains such as poly(3-hexylthiophene) (P3HT) have been widely used as donor materials, whereas the fullerene derivative 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-methanofullerene (PCBM) has been employed as an electron acceptor material in organic solar cells [16–19].

Poly(3-alkylthiophenes) (P3ATs) have been found to be a class of conjugated polymers with good solubility and processability [19]. Regioregular poly(3-alkylthiophenes) (RR-P3AT)-based polymer:fullerene bulk heterojunction solar cells have been widely used in bulk heterojunction solar cells [10,12,20,21].

In this report, we have studied a novel thiophene-based conjugated polymer, namely poly-2,3-bis(4-tert-butylphenyl)-5,8-bis(4-hexylthiophen-2-yl)quinoxaline (PHTQ) as an electron donor in bulk heterojunction solar cells, where it was blended
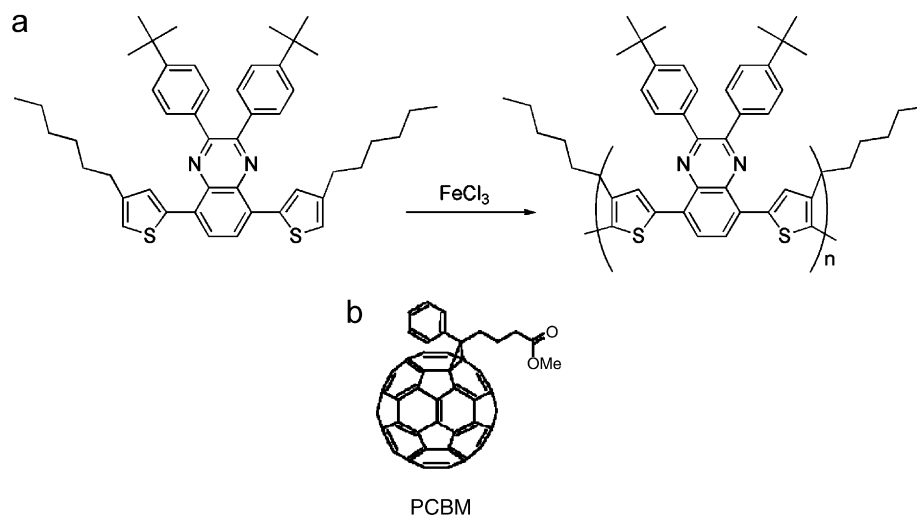
Fig. 1. The structural formula of PHTQ and PCBM.

with the acceptor 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-methanofullerene (PCBM) (see Fig. 1).

PHTQ is easy to synthesize in high yields and large amounts with good solubility in common organic solvents such as chloroform, chlorobenzene and toluene. A simple oxidizing agent like $FeCl_3$ was employed for the synthesis of the corresponding polymer. The band gap of PHTQ was estimated to be 1.8 eV, which was calculated from the onset of the $\pi \to \pi^*$ transition. The donor–acceptor type polymer, PHTQ, reveals a much lower band gap than 3-hexylthiophene, since bond alternation is greatly reduced by donor–acceptor effect.

The synthesis and application of low band gap polymers, which absorb light above 600 nm in organic solar cells, have been reported by several groups [21–28]. A band gap is defined as the difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels in polymers. Low band gap polymers are defined as a polymer with a band gap of approximately lower than 2 eV [25]. One of the limiting parameters in plastic solar cells is the mismatch of their absorption to the terrestrial solar spectrum [28]. The optical band gap of the generally used conjugated polymers in organic solar cells has values around 2.0–2.2 eV, which is not optimized with respect to the solar emission, which has the maximum photon flux around 1.8 eV [28]. The use of low band gap polymers with band gaps around 1.8 eV expands the spectral region of bulk heterojunction solar cells and is a viable route to enhance the number of photons absorbed [28]. In our study, as can be seen from Fig. 2 the PHTQ polymer absorbs light at wavelengths higher than 600 nm due to the estimated low band gap of 1.8 eV.

Previously [29] the polymer was also studied for its electrochromic properties. It revealed multichromism with three distinctive colors (red–purple, green and gray) upon successive doping where this polymer was also found to be solution processable. The polymer also revealed a very high optical contrast of 50% in the NIR region during electrochromic experiments, meaning that the solution processable PHTQ can be a choice for NIR device applications. The electrochromic switching times of the polymer were calculated to be less than 2 s both in visible and in NIR regions (Fig. 3) [29].

This multifunctionality served by PHTQ makes this material potentially interesting and opens up ways in constructing devices by making use of this property in one device configuration.

Here, we report on the performance of bulk heterojunction photovoltaic devices prepared by blending PHTQ and PCBM.
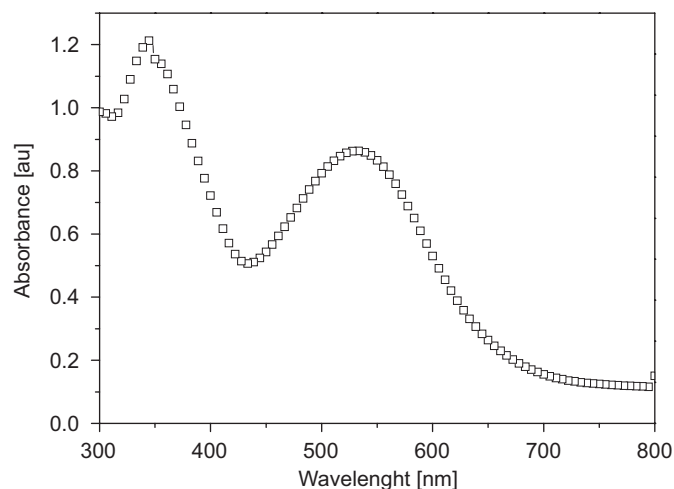

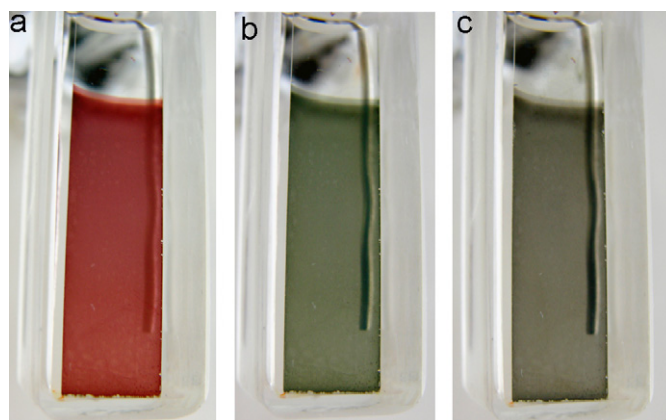**Fig. 2.** Optical absorption spectrum of PHTQ.

Fig. 3. Electrochromism of PHTQ: (a) reduced state, (b) oxidized state and (c) further oxidized state [29].

2. Experimental

For the synthesis, 2,1,3,-benzothiadiazole was brominated in high yields from a mixture of HBr/Br_2 mixture and subsequently

reduced by excess amount of $NaBH_4$ in ethanol to give 3,6-dibromo-1,2-phenylenediamine as pale yellow solid. Condensation reaction of 3,6-dibromo-1,2-phenylenediamine and 1,2-bis(4-tert-butylphenyl)ethane-1,2-dione was performed in ethanol to afford 2,3-bis(4-tert-butylphenyl)-5,8-dibromoquinoxaline. The organotin compound was synthesized by lithiation of an equal molar of 3-hexylthiophene, which was followed by the addition of tributyltin chloride in the corresponding mixture. The Stille coupling reaction of 2,3-bis(4-tert-butylphenyl)-5,8-dibromoquinoxaline with tributyl(4-hexylthiophen-2-yl)stannane was achieved in anhydrous THF in the presence of catalytic amount of Pd(PPh3)2Cl2. The reaction proceeded quite nicely to yield the title compound HTQ in satisfactory yields.

A typical oxidative polymerization of HTQ was achieved using iron (III) chloride in a mixture of nitromethane and chloroform. After the addition of $FeCl_3$ the solution turned into a dark green solution immediately. The solution was stirred for 4 h at room temperature. We extracted the resulting solution with H_2O many times. Then washed with methanol and filtered and dedoped with a hydrazine solution to yield a saturated red color polymer with high solubility in common organic solvents. The molecular weight of the polymer was measured by gel permeation chromatography (GPC) using Polymer Laboratories GPC 220.

For cyclic voltammetry anodic electropolymerization of the monomer was performed in dichloromethane (DCM) acetonitrile (MeCN) mixture (5/95, v/v) with 0.1 M $TBAPF_6$ supporting electrolyte. A platinum foil, platinum wire and Ag wire were used as the working, counter and pseudo-reference electrodes, respectively. The polymer coated on Pt electrode was swept between -0.5 and 1.4 V and the corresponding p-doping processes were examined.

For photoinduced absorption studies drop cast pristine PHTQ and PHTQ/PCBM blend films were mounted into a cryostat and held at liquid nitrogen temperature. The vacuum during the measurements was $< 10^{-6}$ mbar. The excitation source for the PIA measurements was a Coherent Verdi V2 laser operating at $\lambda = 532$ nm and an intensity of 150 mW. The pump beam was modulated by a mechanical chopper (Stanford SR 540) with a frequency of 218 Hz. PIA measurements were carried out by probing the absorption of light from a tungsten halogen lamp during the laser excitation. The transmission T and the photo-induced changes in the transmission ΔT were recorded by a Si–InGaAsSb detector and a lock in amplifier.

For solar cell preparation, as substrates, glass sheets of 1.5×1.5 cm^2 covered with ITO, from Merck KG Darmstadt, were used with an ITO thickness of about 120 nm and sheet resistance $< 15 \Omega$ cm^{-2}. The ITO was patterned by etching with an acid mixture of $HCl:HNO_3:H_2O$ (4.6:0.4:5) for 30 min. The part of the substrate, which forms the contact, is covered with a scotch tape to prevent etching. The tape was removed after etching and the substrate was then cleaned using acetone and iso-propanol in an ultrasonic bath.

An aqueous solution of poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonate) (PEDOT:PSS) was spin coated on the glass–ITO substrate, and dried under a dynamic vacuum.

The blends for the active layer with 1:1, 1:2, 1:3 or 1:4 (w:w) ratios of PHTQ/PCBM was prepared by dissolving 5 mg of PHTQ and 10 mg of PCBM (in the case of 1:2)/ml of dichlorobenzene (DCB) and stirring at 50 °C overnight . For the top electrodes, 0.6 nm of lithium fluoride (LiF) and 100 nm of aluminum (Al) were thermally evaporated.

All current–voltage (I–V) characteristics of the PV devices were measured using a Keithley SMU 236 under nitrogen in a dry glove box. A Steuernagel solar simulator for AM1.5 conditions was used as the excitation source with an input power of 100 mW/cm^2 white-light illumination, which was calibrated using a standard crystalline silicon diode. The solar cells were illuminated through the ITO side.

UV–vis absorption spectra of the solid thin films were obtained using Varian Carry spectrophotometer. Thin films for UV–vis measurements were spin cast on glass from ortho-dichlorobenzene (ODCB) solutions containing 5 mg of PHTQ and 10 mg of PCBM (in the case of 1:2)/ml.

The spectrally resolved photocurrent was measured with an EG&G Instruments 7260 lock-in amplifier. The samples were illuminated with monochromatic light of a Xenon lamp. The incident photon to current efficiency (% IPCE) was calculated according to the following equation:

$$IPCE\,(\%) = \frac{I_{sc}1240}{P_{in}\lambda_{incident}},$$

where I_{sc} ($\mu A/cm^2$) is the measured current under short-circuit conditions of the solar cell.

P_{in} (W/m^2) is the incident light power, measured with a calibrated silicon diode, and λ (nm) is the incident photon wavelength.

Atomic force microscopy (AFM) studies were performed using Digital Instruments DIMENSION 3100 in the tapping mode.

3. Results and discussion

The chemical structure of the monomer and corresponding polymer are shown in Fig. 1. The monomer bears two hexyl groups on thiophene rings and t-butyl groups on the pendant phenyl rings. These groups are responsible for the good solubility of the polymer in common organic solvents. The polymer reveals two absorption bands (see Fig. 2) centered at 345 and 538 nm, which are responsible for the red–purple color in the undoped, semiconducting state. The molecular weight of the polymer was determined by GPC. PHTQ has an M_n of 26,951, M_w of 56.892 and an HI of 2.11, which corresponds to a nearly an average of 40 repeating units per chain in the polymer structure.

The PL quenching studies indicate a photoinduced charge transfer from PHTQ to PCBM (see Fig. 4).

The HOMO and LUMO levels of PHTQ were determined using cyclic voltammetry data. The onset values for oxidation and reduction were determined at +580 and -1070 mV vs. NHE, respectively. This leads to an electrochemical bandgap E_g of 1.65 eV. Assuming a value of -4.75 eV vs. vacuum level for the NHE, the band edges for the HOMO and the LUMO can be
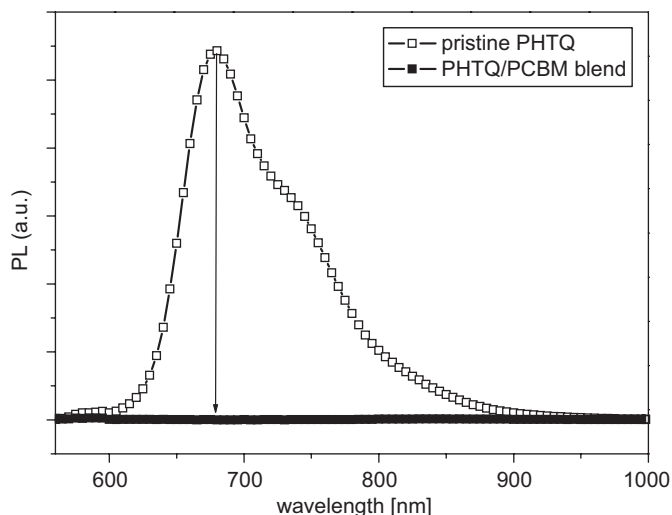

Fig. 4. PL quenching of PHTQ after blending with PCBM.

estimated at −5.8 and −3.1 eV. The band energies of PCBM were estimated to be −6.1 and −3.75 for HOMO and LUMO, respectively [30]. It was shown in literature that at least 0.3–0.4 eV offset between LUMO of the donor and LUMO of the acceptor is necessary to make sure an effective charge transfer from the photoexcited polymer to PCBM [28,31]. In our case, the LUMO of the PHTQ lies higher than LUMO of PCBM.

The PIA spectra are depicted in Fig. 5. The PIA spectrum of pristine PHTQ film shows a maximum peak at approximately 1.13 eV. The features around 2 eV are residual uncompensated photoluminescence. The modulation frequency dependence at the peak wavelength is in the range between 20 and 3600 Hz and the life time was calculated to be 20 μs (see Eqs. (2) and (3)) with a dispersivity factor of alpha of around 0.8 (see Eq. (1)) [32]. In general, the dependence of the PIA signal on the modulation frequency can be used to estimate the recombination time of the species. The frequency response of the signal is given by the following formula (see Eqs. (1)–(3)):

$$R(\omega) = \frac{R_0}{1 + (i\varpi\tau)^{\alpha}} \tag{1}$$

$$X = R_0 \frac{1 + (\varpi\tau)^{\alpha} \cos(\pi\alpha/2)}{1 + 2(\varpi\tau)^{\alpha} \cos(\pi\alpha/2) + (\varpi\tau)^{2\alpha}} \tag{2}$$

$$Y = R_0 \frac{(\varpi\tau)^{\alpha} \cos(\pi\alpha/2)}{1 + 2(\varpi\tau)^{\alpha} \cos(\pi\alpha/2) + (\varpi\tau)^{2\alpha}} \tag{3}$$

$R(\omega)$ is the complex frequency response, R_0 is the steady-state response, τ is the mean lifetime and α is the dispersion factor. The dispersion factor describes the lifetime distribution. It can vary

between 0, meaning the broadest distribution and 1, meaning a homogenous distribution.

To get the information the experimental results were fitted with the second equation (for in-phase signal) and the third equation above (for out of phase signal) simultaneously. Form this fit we can derive the mean lifetime τ and the dispersive factor α. The in-phase signal X decreases with ω, whereas Y shows a maximum.

Additionally, the dependence of the PIA signal upon increasing the laser pump power, I, shows a power law dependence I^k with $k = 0.63$. The PIA of the PHTQ/PCBM blend shows absorption features at 0.5, 2.2, 1.4 eV and as well as a second absorption arising below 0.57 eV. The peak at 0.57 eV can be assigned to low-energy PIA and the one at 1.4 eV to a high-energy PIA of charged polarons [33]. The negative peak at around 2.2 eV is assigned to photobleaching of the linear absorption. The modulation frequency dependence for the two features at 0.57 and 1.4 eV were done separately (see Fig. 5c and d). For the peak at 1.4 eV a mean lifetime of 0.24 ms with a broad distribution ($\alpha = 0.6$) was found (see Fig. 6a). The low-energy peak shows a much weaker dependence on the modulation frequency. The lifetime in this case is around 17 ms, with a dispersive factor of around 0.4 (see Fig. 6b). The in-phase signal and the out of phase signal do not intersect, which is an indication for a weaker dependence. The pump power dependence shows nearly a square root dependence ($k = 0.5$), indicating a bimolecular recombination.

In summary, for pristine films of PHTQ, a single PIA peak at 1.13 eV was found from the PIA measurements. Such PIA is commonly assigned to triplet–triplet absorption.

After blending with the electron acceptor PCBM, the PL is quenched (see Fig. 4) and two PIA peaks are observed at 0.57 and
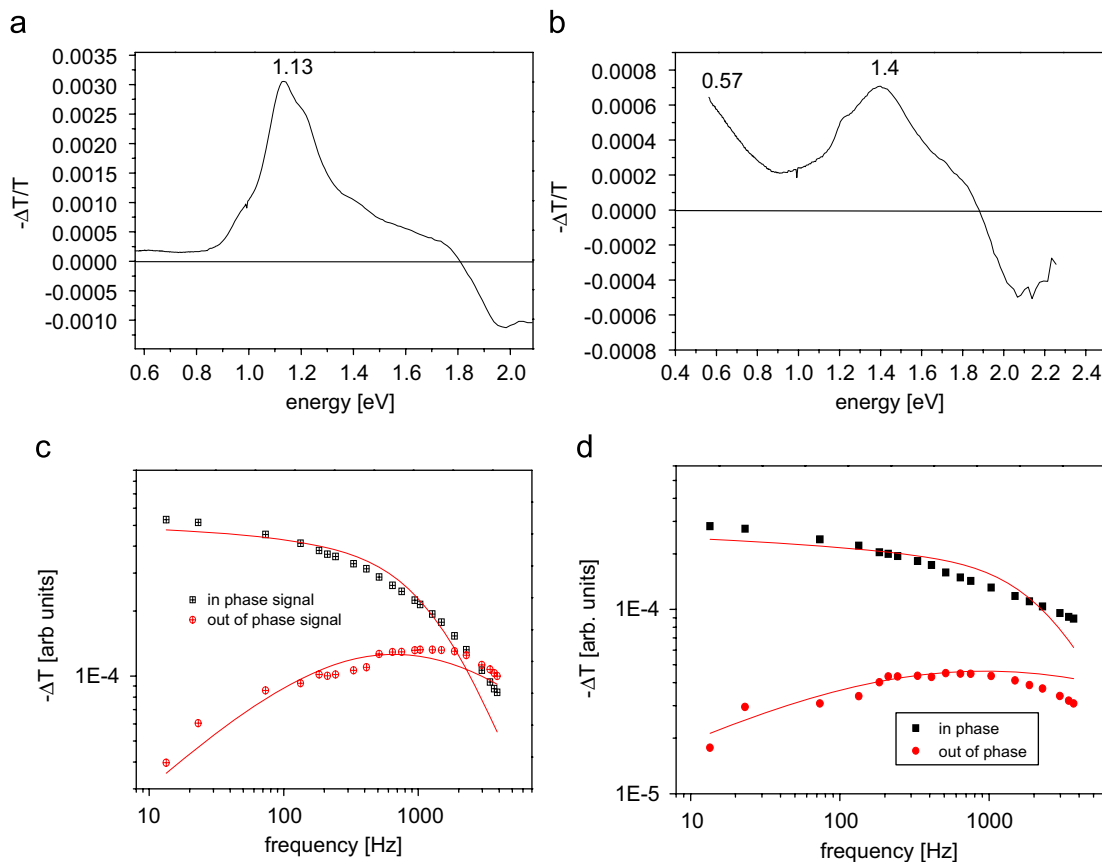

Fig. 5. Photoinduced absorption spectra of (a) pristine PHTQ films and (b) PHTQ/PCBM blend films. (c) Modulation frequency dependence of 1.4-eV blend signal and (d) modulation frequency dependence of 0.57-eV blend signal.

1.4 eV. Such PIA spectra with two photoinduced transitions in the bandgap are commonly assigned to polaronic charge carriers on a conjugated polymer [34].

PHTQ was used as a possible electron donor material in bulk heterojunction solar cell. It has been shown in literature that the solar cells can be optimized using several parameters such as spin coating from different solvents [35,36], varying the polymer to PCBM ratio [37], changing the metal contacts [38] and post production treatment [39]. We have studied the effects of polymer to PCBM ratio, spin coating from different solvents and post production treatment. Varying these parameters did not significantly affect the efficiency of the PHTQ/PCBM solar cells. Our observation was that the best PHTQ-based bulk heterojunction device was composed of 0.5% PHTQ in DCB and two equivalents (by weight) of PCBM. These devices gave a power conversion efficiency of 0.3% under simulated AM 1.5 conditions. Although we have not performed systematic study on the stability of the devices, all the devices investigated in this study showed similar
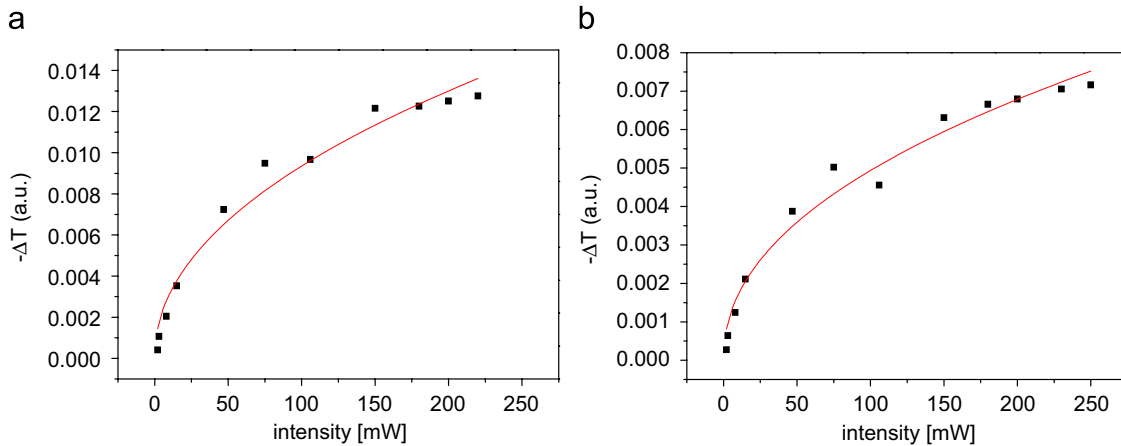

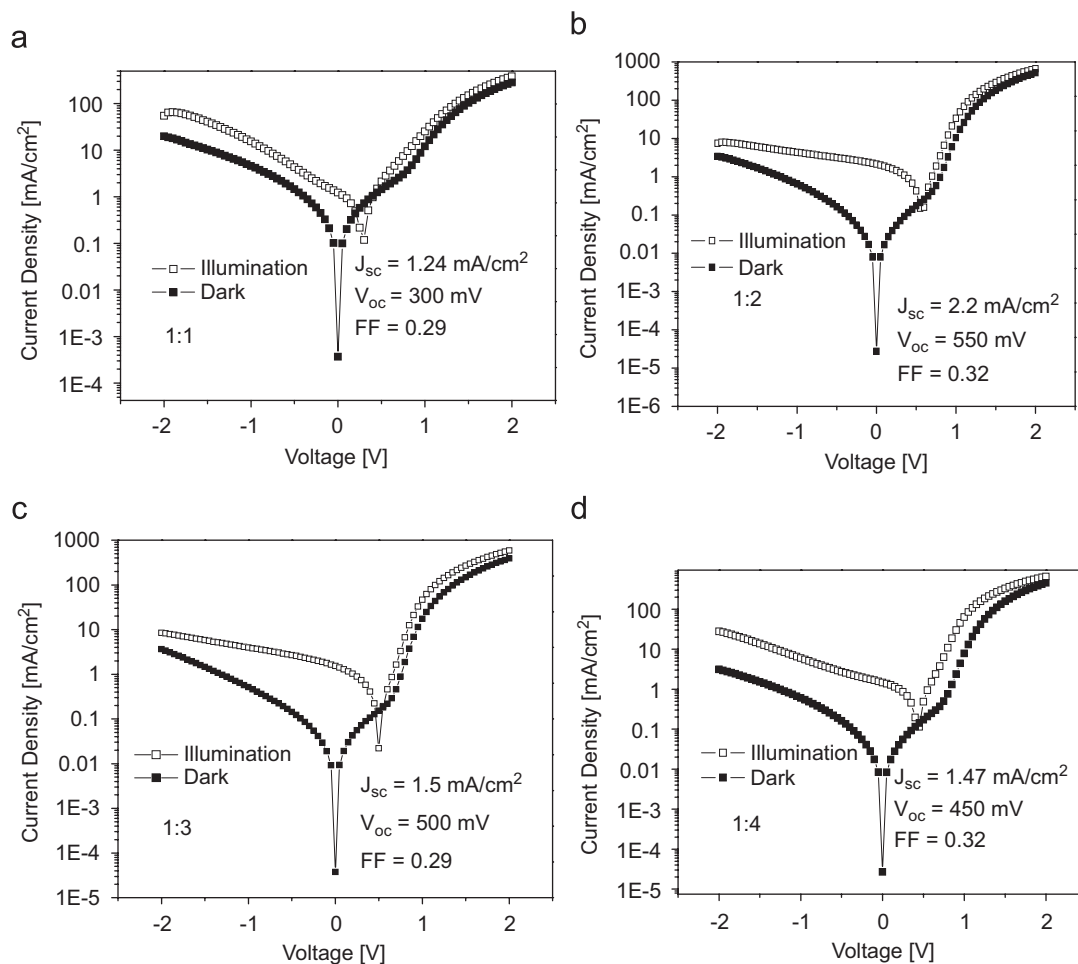Fig. 6. The pump power dependence of the PIA (a) peak at 1.4 eV and (b) peak at 0.57 eV.

Fig. 7. Current–voltage (I–V) characteristics of solar cells comprising PHTQ/PCBM blends: (a) 1:1 ratio, (b) 1:2 ratio, (c) 1:3 ratio and (d) 1:4 ratio.

current–voltage values after several subsequent measurements on the solar simulator, which were characterized under nitrogen atmosphere in a glove box as previously mentioned.

The I–V characteristic curves in dark and under illumination of PHTQ/PCBM, (1:1,1:2, 1:3 and 1:4 w:w) blend are shown in Fig. 7.

Although there are still discussions on the nature of V_{oc} in literature, V_{oc} is known to be directly related to the difference between the HOMO of the donor and the LUMO of the acceptor [13]. In this study, the V_{oc} of the devices was found to be 0.5 V. The fill factor of the device also plays an important role in the overall low efficiency of the cell; the value 0.32 here is low and indicates parallel shunts and series resistances. It has been demonstrated that the improvement of the charge transport of the donor/acceptor polymer composite as well as engineering of the contacts can increase the fill factor of solar cells [38,40].

The behavior of solar cells can better be analyzed via understanding the nanomorphology of the active layer [3,10,12,16,18]. The challenge in bulk heterojunction solar cells is to organize donor and acceptor materials in a nanometer scale. On one hand their interfacial area is maximized [3,41,42], while typical dimensions of phase separation are within the exciton diffusion length (in the order of 10 nm). On the other hand, continuous, preferably undisturbed pathways for transport of charge carriers to the electrodes must be ensured [43].

To correlate the morphology of the solar cells to the photovoltaic performance, we performed an AFM study on the PHTQ/PCBM blends. Fig. 8 shows the images obtained by AFM for PHTQ/PCBM films for four different compositions (1:1, 1:2, 1:3, 1:4) spin cast from ODCB.

As seen from the figures, PHTQ/PCBM films prepared from 1:2 and 1:3 ratio indicate rather smooth surfaces. Although the films prepared from 1:1 and 1:4 ratios also reveal smooth surfaces, the grains on the surface of the films (1:1 ratio) and the holes on the surface of the films (1:4 ratio) might be attributed to the film formation problems, which might explain the efficiency problem for the solar cells prepared using these ratios. AFM images a small part of the film. However, the features on each film for (1:1, 1:2, 1:3 and 1:4) were general and quite reproducible. As previously discussed, 1:2 and 1:3 ratios gave the best solar cell performance.
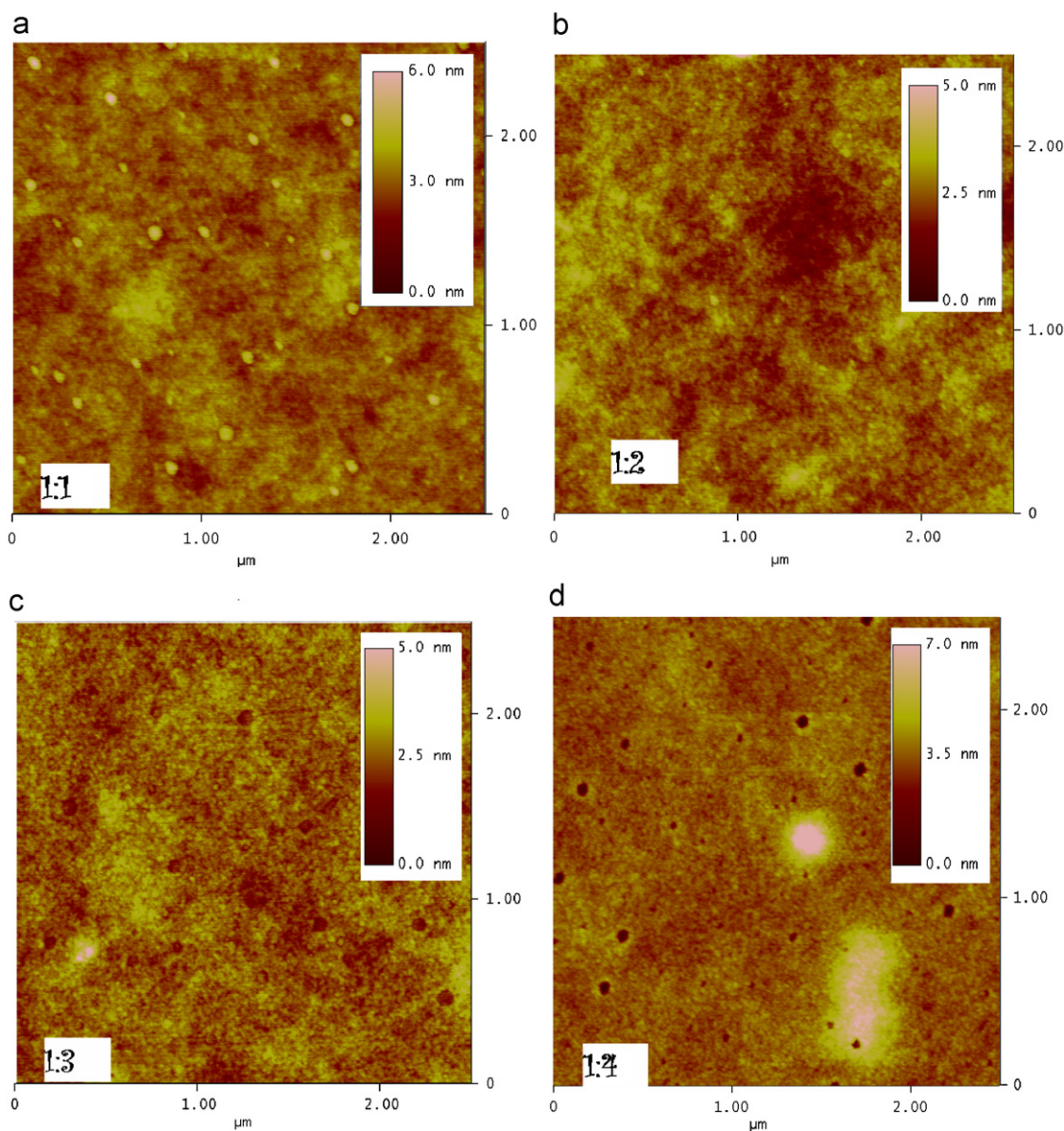

Fig. 8. AFM images of PHTQ/PCBM blends spin cast from dichlorobenzene: (a) 1:1, (b) 1:2, (c) 1:3 and (d) 1:4 ratios.
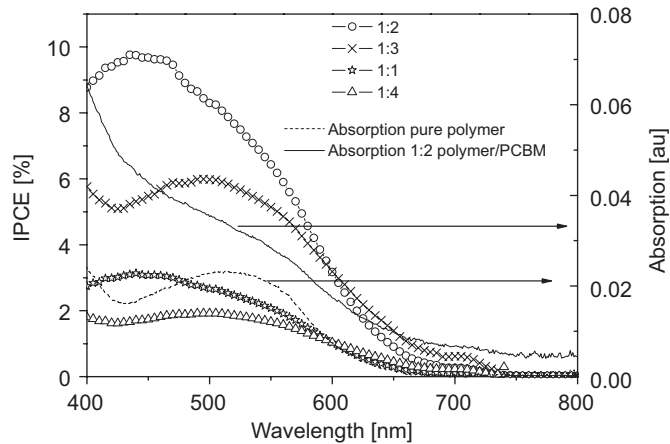
Fig. 9. IPCE (left scale) spectra of the solar cells (PHTQ/PCBM blends) and absorption (right scale) of the pure polymer and the PHTQ/PCBM blend films spin cast from ortho-dichlorobenzene.

Comparing the spectral response of the solar cells and the optical absorption spectra of the components of the devices, information on the charge-generation mechanism can be obtained.

It is used to obtain information on the number of photons of different energy that contributes to charge generation in the solar cell [44]. Fig. 9 shows the IPCE obtained for 1:1, 1:2, 1:3 and 1:4 ratios.

The % IPCE plot exhibits a maximum photocurrent contribution of ca. 10% at around 450 nm. It is noted that the spectrum lies over a wide range of wavelengths, 350–650 nm. It can be clearly seen that optical absorption and IPCE spectra both match.

4. Conclusions

We have studied the performance of PHTQ/PCBM bulk heterojunction solar cells. The polymer has a band gap of 1.8 eV as measured by optical absorption spectroscopy and cyclic voltammetry. The luminescence quenching and the PIA spectra of the PHTQ/PCBM confirm charge transfer. The IPCE spectrum covers the absorption range of PHTQ showing photoactivity of the polymer in combination with the fullerene acceptor. The preliminary efficiency (0.3%) is still not as high as P3HT devices. Further optimization is needed to fully utilize the potential of this novel polythiophene derivative. The number of the thiophene units in the copolymer affects the band gap [26,27]. The materials with four thiophenes might decrease the band gap and the absorption profile might be seriously red shifted. The effect of the number of thiophene units on the band gap will be the subject of the future work.

Acknowledgments

References

[1] N.S. Sariciftci, L. Smilowitz, A.J. Heeger, F. Wudl, Photoinduced electron transfer from conducting polymers onto buckminsterfullerene, Science 258 (1992) 1474.

[2] C.W. Tang, Two layer organic photovoltaic cell, Appl. Phys. Lett. 48 (1986) 183.

[3] X. Yang, J. Loos, S.C. Veenstra, W.J.H. Verkees, M. Wienk, J.M. Kroon, M.H.J. Michels, R.A.J. Janssen, Nanoscale morphology of high-performance polymer solar cells, Nanoletters 5 (2005) 579.

[4] F. Krebs, H. Spanggard, Significant improvement of polymer solar cell stability, Chem. Mater. 17 (2005) 5235.

[5] F. Krebs, K. Norrman, Analysis of failure mechanism for a stable organic photovoltaic during 10,000 h of testing, Prog. Photovoltaic: Res. Appl. 15 (2007) 697.

[6] H. Spangaard, F. Krebs, A brief history of the development of organic and polymeric photovoltaics, Sol. Energy Mater. Sol. Cells 83 (2004) 125.

[7] C. Lungenschmied, G. Dennler, H. Neugebauer, N.S. Sariciftci, M. Glaathar, T. Meyer, A. Meyer, Flexible, long-lived, large-area, organic solar cells, Sol. Energ. Mat. Sol. C. 91 (2007) 379.

[8] F.C. Krebs, H. Spanggard, T.J. Kjaer, M. Biancardo, J. Alstup, Large area plastic solar cell modules, Mater. Sci. Eng. B 138 (2007) 106.

[9] C.J. Brabec, N.S. Sariciftci, J.C. Hummelen, Plastic solar cells, Adv. Funct. Mater. 11 (2001) 15.

[10] W. Ma, C. Yang, X. Gong, K. Lee, A.J. Heeger, Thermally stable, efficient polymer solar cells with nanoscale control of the interpenetrating network morphology, Adv. Funct. Mater. 15 (2005) 1617.

[11] J.Y. Kim, K. Lee, N. Coates, D. Moses, T.Q. Nguyen, M. Dante, A.J. Heeger, Efficient tandem polymer solar cells fabricated by all solution processing, Science 317 (2007) 222.

[12] G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Marioty, K. Emery, Y. Yang, High efficiency solution processable polymer photovoltaic cells by self-organization of polymer blends, Nat. Mater. 4 (2005) 864.

[13] M. Scharber, D. Müchlbacher, M. Koppe, P. Denk, C. Waldauf, A.J. Heeger, C. Brabec, Design rules for donors in bulk heterojunction solar cells-towards 10% energy-conversion efficiency, Adv. Mater. 18 (2006) 789.

[14] L.A. Koster, V.D. Mihailetchi, P.W. Blom, Ultimate efficiency of polymer/fullerene bulk heterojunction solar cells, Appl. Phys. Lett. 88 (2006) 093511-1.

[15] S. Forrest, The limits to organic photovoltaic cell efficiency, MRS Bull. 30 (2005) 28.

[16] S. Shaheen, C. Brabec, N.S. Sariciftci, F. Padinger, J.C. Hummelen, 2.5% efficient organic plastic solar cells, Appl. Phys. Lett. 78 (2001) 841.

[17] D. Chirvaze, Z. Chiguvare, M. Knipper, J. Parisi, V. Dyakonov, Temperature dependent characteristics of poly(3-hexylthiophene)-fullerene based heterojunction organic solar cells, J. Appl. Phys. 93 (2003) 3376.

[18] D. Chirvaze, J. Parisi, J.C. Hummelen, V. Dyakonov, Influence of nanomorphology on the photovoltaic action of polymer-fullerene composites, Nanotechnology 15 (2004) 1317.

[19] M. Allbrahim, O. Ambacher, S. Sensfuss, G. Gobsch, Effect of solvent improvement and annealing on the performance of solar cells based on poly(3-hexylthiophene):fullerene, Appl. Phys. Lett. 86 (2005) 201120.

[20] L. Campos, A. Mozer, S. Günes, C. Winder, H. Neugebauer, N.S. Sariciftci, B.C. Thompson, B.D. Reeves, C.R.G. Grenier, J.R. Reynolds, Photovoltaic activity of a PolyProDOT derivative in a bulk heterojunction solar cell, Sol. Energy Mater. Sol. Cells 90 (2006) 3531.

[21] L. Campos, A. Tontcheva, S. Günes, G. Sönmez, H. Neugebauer, N.S. Sariciftci, F. Wudl, Extended photocurrent spectrum of a low band gap polymer in a bulk heterojunction solar cell, Chem. Mater. 17 (2005) 4031.

[22] E. Perzon, X. Wang, S. Admassic, O. Inganaes, M.R. Andersson, An alternating low band gap polyfluorene for optoelectronic devices, Polymer 47 (2006) 4261.

[23] A. Cravino, M. Loi, M. Scharber, C. Winder, H. Neugebauer, P. Denk, H. Meng, Y. Chen, F. Wudl, N.S. Sariciftci, Spectroscopic properties of PEDOTEHIITN, a novel soluble low band gap polymer, Synth. Met. 137 (2003) 1435.

[24] M. Wienk, M. Struijk, R. Janssen, Low band gap polymer bulk heterojunction solar cells, Chem. Phys. Lett. 422 (2006) 488.

[25] E. Bundgaard, F. Krebs, Low band gap polymers for organic photovoltaics, Sol. Energy Mater. Sol. Cells 91 (2007) 954.

[26] E. Bundgaard, F. Krebs, Low band gap conjugated polymers based on thiophene, benzathiadiazole and benzobis(thiadiazole), Macromolecules 39 (2006) 2823.

[27] E. Bundgaard, F. Krebs, Large area photovoltaics based on low band gap copolymers of thiophene and benzothiadiazole or benzo-bis(thiadiazole), Sol. Energy Mater. Sol. Cells 91 (2007) 1019.

[28] C. Winder, G. Matt, J.C. Hummelen, R.A.J. Janssen, N.S. Sariciftci, C. Brabec, Sensitization of low bandgap polymer bulk heterojunction solar cells, Thin Solid Films 403–404 (2002) 373.

[29] Funda Özyurt, E. Görkem Günbaş, Asuman Durmuş, Levent Toppare, Processable and multichromic polymer of bis-3-hexylthiophene substituted 4-tert-butylphenyl quinoxaline, Org. Electron. 9 (2008) 296.

[30] B.C. Thompson, Y.G. Kim, J.R. Reynolds, Spectral broadening in MEH-PPV:PCBM-based photovoltaic devices via blending with a narrow band gap cyanovinylene–dioxythiophene polymer, Macromolecules 38 (2005) 5359.

[31] A.J. Mozer, P. Denk, M.C. Scharber, H. Neugebauer, N.S. Sariciftci, P. Wagner, L. Lutsen, D. Vanderzande, Novel regiospecific MDMO-PPV copolymer with improved charge transport for bulk heterojunction solar cells, J. Phys. Chem. B 108 (2004) 5235.

[32] O. Epshtein, G. Nakhmanovich, Y. Eichen, E. Ehrenfreund, Dispersive dynamics of photoexcitations in conjugated polymers by photomodulation spectroscopy, Phys. Rev. B 63 (2001) 125206.

[33] R.A.J. Janssen, D. Moses, N.S. Sariciftci, Electron and energy transfer processes of photoexcited oligothiophenes onto tetracyanoethylene and C_{60}, J. Chem. Phys. 101 (1994) 9519.

[34] C. Winder, N.S. Sariciftci, Low bandgap polymers for photon harvesting in bulk heterojunction solar cells, J. Mater. Chem. 14 (2004) 1077.

[35] J. Liu, Y. Shi, Y. Yang, Solvation-induced morphology effects on the performance of polymer-based photovoltaic devices, Adv. Funct. Mater. 11 (2001) 420.

[36] C.Y. Yang, A.J. Heeger, Morphology of composites of semiconducting polymers mixed with C_{60}, Synth. Met. 83 (1996) 85.

[37] J.K.J. van Duren, X. Yang, J. Loos, C.W.T. Bulle-Lieuwma, A.B. Sieval, J.C. Hummelen, R.A.J. Janssen, Relating the morphology of poly(p-phenylene vinylene)/methanofullerene blends to solar-cell performance, Adv. Funct. Mater. 14 (2004) 425.

[38] C.J. Brabec, A. Cravino, D. Meissner, N.S. Sariciftci, M.T. Rispens, L. Sanchez, J.C. Hummelen, T. Fromherz, The influence of materials work function on the open circuit voltage of plastic solar cells, Thin Solid Films 403–404 (2002) 368.

[39] F. Padinger, R. Rittberger, N.S. Sariciftci, Effects of post production treatment on plastic solar cells, Adv. Funct. Mater. 13 (2003) 85.

[40] C. Arndt, U. Zhokhavets, G. Gobsch, C. Winder, C. Lungenschmied, N.S. Sariciftci, Investigation of excited states in polymer/fullerene solar cells by means of photoinduced reflection-/absorption spectroscopy, Thin Solid Films 451–452 (2004) 60.

[41] M.T. Rispens, A. Meetsma, R. Rittberger, C.J. Brabec, N.S. Sariciftci, J.C. Hummelen, Influence of solvent on the crystal structure of PCBM and the efficiency of MDMO-PPV:PCBM 'plastic' solar cells, Chem. Commun. 17 (2003) 2116.

[42] M. Wienk, J.M. Kroon, W.J.H. Verhees, J.C. Hummelen, P.A. Vanhal, J. Janssen, Efficient methano[70]fullerene/MDMO-PPV bulk heterojunction photovoltaic cells, J. Angew. Chem. Int. Ed. 42 (2003) 3371.

[43] C.J. Brabec, C. Winder, N.S. Sariciftci, J.C. Hummelen, A. Dhanabalan, P.A. Van Hal, R.A.J. Janssen, A low-bandgap semiconducting polymer for photovoltaic devices and infrared emitting diodes, Adv. Funct. Mater. 12 (2002) 709.

[44] J. Rostalski, D. Meissner, Monochromatic versus solar efficiencies of organic solar cells, Sol. Energy Mater. Sol. Cells 61 (2000) 87.