High Open-Circuit Voltage Poly(ethynylene bithienylene):Fullerene Solar Cells

Jens Cremer,† Peter Bäuerle,*,† Martijn M. Wienk,‡ and René A. J. Janssen*,‡

Department of Organic Chemistry II (Organic Materials and Combinatorial Chemistry), University of Ulm, Albert-Einstein-Allee 11, D-89081 Ulm, Germany, and Molecular Materials and Nanosystems, Eindhoven University of Technology and Dutch Polymer Institute, P.O. Box 513, NL-5600 MB Eindhoven, The Netherlands

Received August 26, 2006
Revised Manuscript Received November 6, 2006

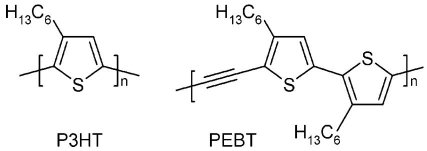

Figure 1. Structures of P3HT and PEBT.

Thin film polymer solar cells offer the prospect of combining easy, solution-based processing and low-temperature manufacturing in combination with good efficiencies. In recent years, bulk heterojunction solar cells based on blends of regioregular poly(3-hexylthiophene) (P3HT, Figure 1) as p-type material and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) as n-type material have been studied intensively.[1−9] The performance of these devices reaches 4−5% in simulated solar light. One of the crucial factors that contributes to the high efficiency of P3HT:PCBM photovoltaic cells is the intrinsic tendency of P3HT to self-organize in a lamellar microstructure. This enhances the charge-carrier mobility and shifts the absorption spectrum to longer wavelengths.[10]

One of the attractive advantages of P3HT:PCBM solar cells is the high external quantum efficiency (EQE) of 60−70% over almost the entire absorption band of P3HT and the correspondingly large short-circuit current density (J_{SC}) under AM1.5 illumination. The energy conversion efficiency of P3HT:PCBM cells is rather limited by the poor coverage of the absorption spectrum of P3HT with the solar spectrum and by a low open-circuit voltage ($V_{OC} \approx 0.6$ V). Considering that only photons with energy higher than the optical band gap of P3HT (1.9 eV) are absorbed, this V_{OC} implies an energy loss of at least 1.3 eV per absorbed photon. This loss is caused by the energy released in the electron transfer from P3HT to PCBM (∼0.9 eV) and by subsequent potential losses when collecting the charges at the electrodes (∼0.4 V).[11,12] Because V_{OC} originates from the energy difference between the HOMO level of the p-type polymer and the LUMO level of n-type fullerene,[13] the open-circuit voltage and possibly the power conversion efficiency can be enhanced by lowering the HOMO energy of the polymer. In fact, for poly(*p*-phenylene vinylene)s[14] and an alternating copolymer with fluorene (APFOs),[15] the open circuit voltages are between 0.80 and 1.05 V as a result of their lower HOMO levels. When the HOMO level is lowered and the optical band gap maintained, the LUMO level shifts correspondingly and care must be taken that photoinduced electron transfer is still exergonic. The ∼0.9 eV energy loss in the charge transfer seems to be in excess of the minimal requirement for efficient operation, and hence, reducing the HOMO level of P3HT by changing its structure may improve the performance of these devices.

Band gap and energy level engineering is one of the attractive features of polymer semiconductors. We conjectured that appealing photovoltaic properties may arise from polymers that are structurally close to P3HT, but have a lower HOMO level. Whereas the energy levels of polythiophenes can be modified by introducing different substitutents on the backbone,[16] an interesting, but less explored, way is incorporating electron-withdrawing ethynylene units into the polymer backbone.[17−19] Here, we show that alternating ethynylene and 4,3′-dihexyl-2,2′-bithien-5,5′-diyl along the chain as in PEBT (Figure 1) lowers the HOMO energy level by 0.3 eV compared to P3HT and that when implemented in bulk heterojunction devices with PBCM, PEBT exhibits

---

* Corresponding author. E-mail: peter.baeuerle@uni-ulm.de (P.B.); r.a.j.janssen@tue.nl (R.A.J.J.).
† University of Ulm.
‡ Eindhoven University of Technology.

(1) Schilinsky, P.; Waldauf, C.; Brabec, C. J. *Appl. Phys. Lett.* **2002**, *81*, 3885.
(2) Padinger, F.; Rittberger, R. S. Sariciftci, N. S. *Adv. Funct. Mater.* **2003**, *13*, 85.
(3) Yang, X.; Veenstra, S. C.; Verhees, W. J. H.; Wienk, M. M.; Janssen, R. A. J.; Kroon, J. M.; Michels, M. A. J.; Loos, J. *Nano Lett.* **2005**, *5*, 579.
(4) Kim, Y.; Choulis, S. A.; Nelson, J.; Bradley, D. D. C.; Cook, S.; Durrant, J. R. *Appl. Phys. Lett.* **2005**, *86*, 063502.
(5) Reyes-Reyes, M.; Kim, K.; Carroll, D. L. *Appl. Phys. Lett.* **2005**, *87*, 083506.
(6) Ma, W.; Yang, C.; Gong, X.; Lee, K.; Heeger, A. J. *Adv. Funct. Mater.* **2005**, *15*, 1617.
(7) Li, G.; Shrotriya, V.; Huang, J.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. *Nat. Mater.* **2005**, *4*, 864.
(8) Kim, Y.; Cook, S.; Tuladhar, S. M.; Choulis, S. A.; Nelson, J.; Durrant, J. R.; Bradley, D. D. C.; Giles, M.; Mcculloch, I.; Ha, C.-S.; Ree, M. *Nat. Mater.* **2006**, *5*, 197.
(9) Mihailetchi, V. D.; Xie, H.; de Boer, B.; Koster, L. J. A.; Blom, P. W. M. *Adv. Funct. Mater.* **2006**, *16*, 699.
(10) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; de Leeuw, D. M. *Nature* **1999**, *401*, 685.
(11) Michailetchi, V. D.; Blom, P. W. M.; Hummelen, J. C.; Rispens, M. T. *J. Appl. Phys.* **2003**, *94*, 6849.
(12) Scharber, M. C.; Mühlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. J. *Adv. Mater.* **2006**, *18*, 789.
(13) Gadisa, A.; Svensson, M.; Andersson, M. R.; Inganäs, O. *Appl. Phys. Lett.* **2004**, *84*, 1609.
(14) Shaheen, S. E.; Brabec, C. J.; Sariciftci, N. S.; Padinger, F.; Fromherz, T.; Hummelen, J. C. *Appl. Phys. Lett.* **2001**, *78*, 841.
(15) Svensson, M.; Zhang, F.; Veenstra, S. C.; Verhees, W. J. H.; Hummelen, J. C.; Kroon, J. M.; Inganäs, O.; Andersson, M. R. *Adv. Mater.* **2003**, *15*, 988.
(16) Greve, D. R.; Apperloo, J. J.; Janssen, R. A. J. *Eur. J. Org. Chem.* **2001**, 3437.
(17) Hoppe, H.; Egbe, D. A. M.; Mühlbacher, D.; Sariciftci, N. S. *J. Mater. Chem.* **2004**, *14*, 3462.
(18) Egbe, D. A. M.; Nguyen, L. H.; Mühlbacher, D.; Hoppe, H.; Schmidtke, K.; Sariciftci, N. S. *Thin Solid Films* **2006**, *511−512*, 486.
(19) Egbe, D. A. M.; Nguyen, L. H.; Carboniier, B.; Mühlbacher, D.; Sariciftci, N. S. *Polymer* **2005**, *46*, 9585.

10.1021/cm0620180 CCC: $33.50

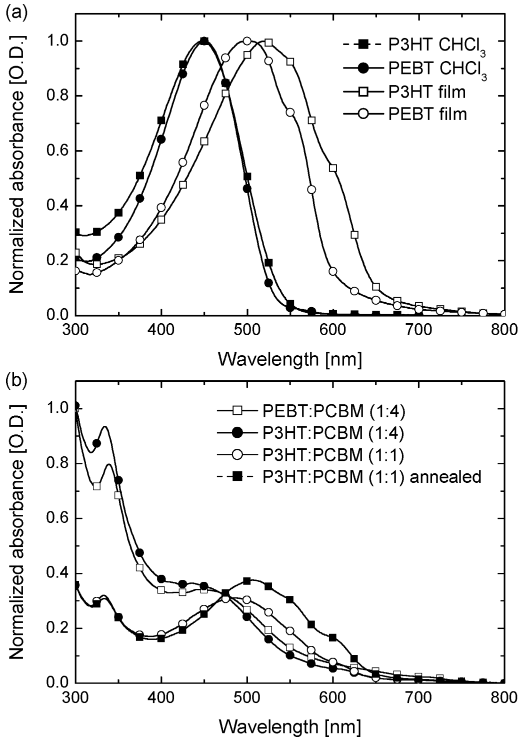

Figure 2. Normalized UV−vis spectra of (a) PEBT and P3HT in chloroform and in thin films (spin-coated from 10 mg/mL toluene solutions at 2000 rpm) on glass, and (b) thin films of PEBT:PCBM and P3HT:PCBM on glass.

the expected increase in open-circuit voltage to values slightly over 1.0 V.

PEBT was synthesized from the 4,3′-dihexyl-5-ethynyl-5′-iodo-2,2′-bithiophene monomer via a palladium catalyzed Shonogashira polymerization, providing molecular weights of $M_n = 23\,500$ g/mol and $M_\mathrm{w} = 34\,800$ g/mol, $D = 1.5$) as determined by GPC at 30 °C in chloroform vs polystyrene standards.[20,21] The UV−vis absorption spectra of PEBT and P3HT[22] ($M_n = 13\,500$ g/mol, $M_\mathrm{w} = 35\,000$ g/mol, $D = 2.6$) in chloroform are very similar, with $\pi-\pi^*$ absorption bands that maximize at 451 and 448 nm, respectively (Figure 2). Apparently, the introduction of ethynylene groups into the backbone of P3HT affects the optical transitions only marginally. In thin films, the absorption spectra of PEBT and P3HT exhibit partly resolved vibrational fine structure and show a significant red shift of the $\pi-\pi^*$ transition (Figure 2) that is due to planarization of the π-system and interchain interactions induced by aggregation and crystallization.[23] The red shift is stronger for P3HT ($\Delta\lambda_\mathrm{max} = 71$ nm) than for PEBT ($\Delta\lambda_\mathrm{max} = 50$ nm). As a result, the onset of the absorption is at a higher wavelength for P3HT (650 nm) than for PEBT (600 nm), resulting in a higher optical band gap of 2.06 eV for PEBT compared to that of P3HT (1.90 eV).

Cyclic voltammograms (0.785 mm^2 Pt working electrode, Ag/AgCl reference electrode, and Pt wire counter electrode) of PEBT and P3HT dissolved in dichloromethane with tetrabutylammonium hexafluorophosphate (n-Bu$_4$NPF$_6$) as the supporting salt revealed broad oxidation waves. For P3HT, the onset of the oxidation wave is at +0.10 V (vs Fc/Fc$^+$), whereas the oxidation onset for PEBT is at +0.40 V and significantly higher. The 0.3 eV lowering of the HOMO level of PEBT compared to P3HT is due to the electron-withdrawing ethynylene units in the chain.

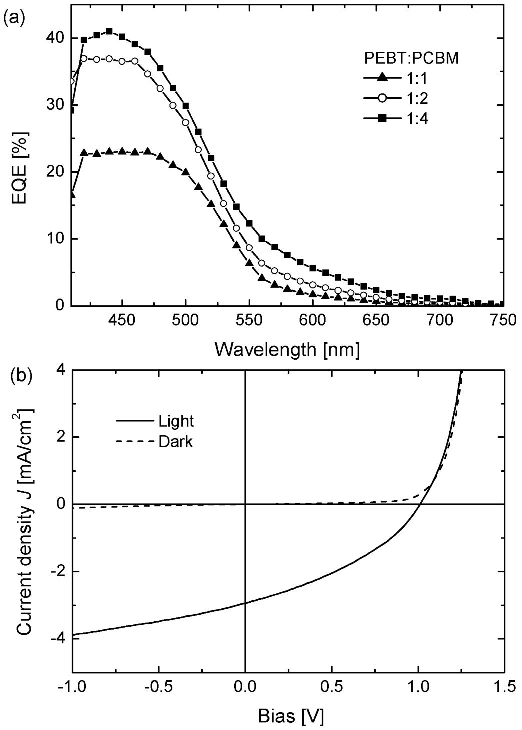

Figure 3. (a) EQE spectra of PEBT:PCBM solar cells for different compositions of the active layer. (b) $J-V$ characteristics of the best performing photovoltaic device fabricated PEBT:PCBM (1:4 w/w) in the dark and under 75 mW/cm^2 illumination. All measurements were performed in an inert atmosphere.

The optical and electrochemical data thus indicate that the ethynylene units in PEBT cause a lowering of the HOMO by 0.3 eV and an increase in the optical band gap by ~0.15 eV (in thin films) compared to P3HT. Moreover, the red shift in the absorption spectra reveals a tendency for PBEBT to form aggregated structures, albeit somewhat less than for P3HT.

Photovoltaic cells (active area 0.1 cm^2) were made by spin-coating mixtures of PEBT and PCBM (from Solenne B.V.) in different weight ratios from chlorobenzene solution on prepatterned ITO(14 Ω/□)/glass substrates covered with PEDOT:PSS (poly(3,4-ethylenedioxythiophene):polystyrene sulfonate, EL grade, from H.C. Starck) as the transparent high-work-function front electrode. The back electrode of LiF (<1 nm) and Al (100 nm) was made by thermal evaporation in a vacuum at 5×10^{-6} mbar. The thickness of the active layer was 80−100 nm for all devices.

The spectral response of the PEBT:PCBM devices reveals a considerable EQE in the wavelength range between 400 and 550 nm (Figure 3a). Devices with a 1:4 blend of PEBT and PCBM exhibit EQE = 42% at 450 nm. For the 1:2 blend, the EQE is somewhat lower, with a maximum of 37% at 450 nm, whereas the 1:1 blend reveals considerably de-

---

(20) Cremer, J. Ph.D. Thesis, University of Ulm, Ulm, Germany, 2005.

(21) Schikora, M.; Cremer, J.; Wienk, M. M.; Janssen, R. A. J.; Bäuerle, P. To be submitted.

(22) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. J. *Org. Chem.* **1993**, *58*, 904.

(23) Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J.; Wudl, F. *J. Polym. Sci., Part B: Polym. Phys.* **1987**, *25*, 1071.

Table 1. Photovoltaic Properties of PEBT:PCBM and P3HT:PCBM Devices

	w/w	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	EQE (%)	λ (nm)	η (%)	ref
PEBT	1:1[b]	1.84[a]	1.03	0.28	24	470	0.53	
	1:2[b]	2.62[a]	1.01	0.34	37	450	0.90	
	1:4[c]	3.1[a]	1.01	0.36	42	450	1.13	
P3HT	1:1	7.2[a]	0.62	0.61	57	500	2.7	3
	1:0.8	9.5[d]	0.63	0.68			5.0	6
	1:1	10.6[e]	0.61	0.67	63	500	4.4	7

[a] From convolution of the EQE and AM1.5 spectra. [b] Spin-coated from a 1 wt % chlorobenzene solution. [c] Spin-coated from a 1.5 wt % chlorobenzene solution. [d] AM1.5 at 80 mW/cm^2. [e] AM1.5 at 100 mW/cm^2.

creased efficiencies with a maximum of 24% at 470 nm. Convolution of the spectral response with the solar AM1.5G spectrum (100 mW/cm^2) gives an estimate for the short-circuit current density under solar irradiation. The device based on a 1:1 blend of PEBT and PCBM has $J_{SC} = 1.8$ mA/cm^2. The current density increases to $J_{SC} = 2.6$ mA/cm^2 for a 1:2 blend and reaches $J_{SC} = 3.1$ mA/cm^2 for the 1:4 mixture (Table 1).

As expected from the spectral response, the short-circuit current densities obtained from $J-V$ measurements of the same devices under illumination with a tungsten halogen lamp (75 mW/cm^2 after filtering by a Schott KG1 IR filter and a GG420 UV filter) also increase with more PCBM in the blend. However, the open-circuit voltage, V_{OC} is invariably high under these conditions and is independent of the amount of PCBM used in the photoactive layer (Table 1). For each composition, we find $V_{OC} > 1.0$ V, which is 0.35−0.40 V higher than the V_{OC} of the best P3HT:PCBM devices.[1−9] This result was anticipated and is consistent with the lower-lying HOMO of PEBT in comparison to P3HT. The increase in V_{OC} for PBET compared to P3HT is larger than the increase found for arylene vinylene/ethynylene polymers.[17−19] On the other hand, relatively low fill factors FF of 0.28−0.38 limit the overall performance of the PEBT:PCBM devices. The low FF may indicate poorly balanced charge transport.[24] Figure 3b displays the $J-V$ characteristic of the best PEBT:PCBM device, with $V_{OC} = 1.0$ V and FF $= 0.36$. Combined with the current density calculated from the spectral response (3.12 mA/cm^2), a power conversion efficiency of $\eta = 1.1\%$ is estimated.

A closer inspection of the EQE spectra reveals that the maximum response of the PEBT:PCBM blend does not match the thin film absorption spectrum of pure PEBT with its maximum at 501 nm, but rather corresponds to the absorption of PEBT in solution that maximizes at 450 nm. Correspondingly, the UV−vis spectrum of the mixed PEBT:PCBM film (Figure 2b) exhibits a band at 450 nm, with a tail to higher wavelengths and a band at 330 nm of PCBM. The absence of a red-shifted absorption for the PEBT:PCBM layer compared to a film of pure PEBT (Figure 2a) indicates that the formation of polymer aggregates is inhibited in the mix. Hence, the lower short-circuit currents of the PEBT:PCBM devices compared to the best P3HT:PCBM cells is partially due to the blue-shifted absorption in the blend.[1−9] In addition, the absence of aggregates or crystallites of PEBT in the blend with PCBM is expected to hamper the hole carrier mobility, which limits the fill factor.

It is instructive to compare the behavior of PEBT to that of P3HT in blends with PCBM. At the same 1:4 weight ratio, the absorption spectrum of a P3HT:PCBM blend is almost identical to that of PEBT:PCBM (Figure 2b), showing no or little aggregation. Only at higher polymer content (e.g., 1:1 w/w) is aggregation of P3HT observed that is further enhanced upon thermal annealing (Figure 2b), providing the 4−5% power conversion efficiency (which is not obtained at a 1:4 ratio). Annealing does not enhance polymer aggregation in P3HT:PCBM (1:4 w/w) layers or in PEBT:PCBM (1:1, 1:2, and 1:4 w/w) layers. Even annealing up to 120 °C gave only minor changes in the absorption spectra and no improvement in device performance. This demonstrates that subtle differences in the tendency to form aggregates can have a strong effect on the power conversion efficiency. The reasons for the different crystallization behavior of PBET compared to P3HT are not fully understood at the moment, but we speculate that it could be due to a less-efficient lamellar packing of chains induced by the ethynyl bonds.

In conclusion, PEBT was synthesized to improve the open-circuit voltage of P3HT:PCBM bulk heterojunction photovoltaic cells. Having $V_{OC} = 1.01$ V, PEBT:PCBM devices indeed give a significant (0.4 V) improvement with respect to P3HT:PCBM solar cells ($V_{OC} = 0.62$ V). The power conversion efficiency $\eta = 1.1\%$, however, is lower compared to $\eta = 4-5\%$ for the best P3HT:PCBM devices (Table 1). In contrast to P3HT, PEBT does not aggregate in mixed films with PCBM, as inferred from the lack of a red shift in the absorption spectrum in the blend. This limits the number of absorbed photons and likely causes a lower mobility for the photogenerated holes. As a consequence, the short-circuit current and fill factor of these PEBT:PCBM devices is limited. This study demonstrates that to improve on P3HT:PCBM devices, the challenge is not only to design polymers that have better optimized energy levels but also to create polymers that are able to form aggregated, partly crystalline structures when mixed with PCBM.

Acknowledgment. We thank the German Ministry for Education and Research (BMBF Netzwerk “Polymere Solarzellen”) for funding. J.C. thanks the “Fonds der Chemischen Industrie” and the German Ministry for Education and Research (BMBF) for a Kekulé-Grant. The work of M.M.W. is part of the research of the Dutch Polymer Institute (DPI #324).

CM0620180

---

(24) Mihailetchi, V. D.; Wildeman, J.; Blom, P. W. M. *Phys. Rev. Lett.* **2005**, *94*, 126602.