

Photoconductivity of a Low-Bandgap Conjugated Polymer**

By Cesare Soci, In-Wook Hwang, Daniel Moses, Zhengguo Zhu, David Waller, Russel Gaudiana, Christopher J. Brabec, and Alan J. Heeger*

The photoconductive properties of a novel low-bandgap conjugated polymer, poly[2,6-(4,4-bis-(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)], PCPDTBT, with an optical energy gap of $E_g \sim 1.5$ eV, have been studied. The results of photoluminescence and photoconductivity measurements indicate efficient electron transfer from PCPDTBT to PCBM ([6,6]-phenyl-C₆₁ butyric acid methyl ester, a fullerene derivative), where PCPDTBT acts as the electron donor and PCBM as the electron acceptor. Electron-transfer facilitates charge separation and results in prolonged carrier lifetime, as observed by fast ($t > 100$ ps) transient photoconductivity measurements. The photoresponsivities of PCPDTBT and PCPDTBT:PCBM are comparable to those of poly(3-hexylthiophene), P3HT, and P3HT:PCBM, respectively. Moreover, the spectral sensitivity of PCPDTBT:PCBM extends significantly deeper into the infrared, to 900 nm, than that of P3HT. The potential of PCPDTBT as a material for high-efficiency polymer solar cells is discussed.

1. Introduction

In the last few years, research has focused on the need to improve the power-conversion efficiency of polymer-based photovoltaics to a level where the cost per generated power would be suitable for commercialization. Bulk heterojunction materials comprised of bicontinuous networks of donor and acceptor components, sandwiched between electrodes with different work functions (typically indium tin oxide and a lower work function metal, e.g., Al), have yielded the best results. In such structures, ultrafast photoinduced charge transfer occurs at the interface between the polymer (as donor) and the fullerene (as acceptor) and results in charge separation and the generation of positive and negative charge carriers that are transported and collected at the opposite electrodes. The carrier collection is driven by the internal field created by the different work functions of the two electrodes in the metal/insulator/metal

configuration. Using this approach, power-conversion efficiencies approaching 5% have been recently demonstrated by using poly(3-hexylthiophene) (P3HT, Fig. 1a) and [6,6]-phenyl-C₆₁ butyric acid methyl ester (PCBM, Fig. 1b).^[1]

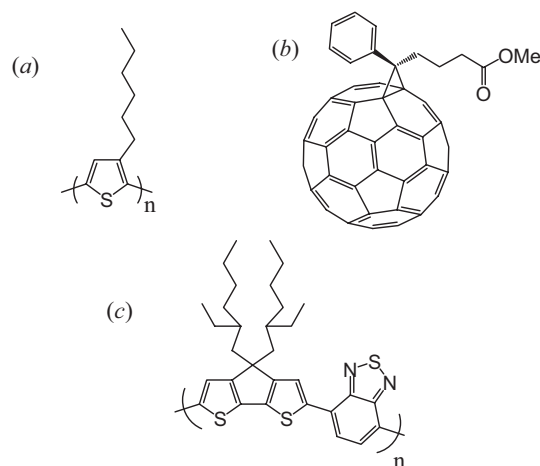


Figure 1. Molecular structures of a) P3HT, b) PCBM, and c) PCPDTBT.

The power-conversion efficiency of organic solar cells depends on a number of factors, including photon absorption and charge-carrier photogeneration (separation) and transport. The conjugated polymers that have shown the highest power-conversion efficiencies are the poly(*p*-phenylene vinylene)s (PPVs) and the polythiophenes (PTs),^[2,3] with absorption spectra that onset at approximately 2 and 1.8 eV, respectively. Although promising results have been demonstrated, the absorption spectra of these semiconducting polymers have poor overlap with the solar emission spectrum, which peaks at ca. 2.5 eV but extends deep into the infrared. The quest for

[*] Prof. A. J. Heeger, Dr. C. Soci, Dr. I.-W. Hwang, Dr. D. Moses

Center for Polymers and Organic Solids
University of California at Santa Barbara
Santa Barbara, CA 93106-5090 (USA)
E-mail: ajhe@physics.ucsb.edu

Dr. Z. Zhu, Dr. D. Waller, Dr. R. Gaudiana
Konarka Technologies, Inc.
116 John Street, Lowell, MA 01852 (USA)

Dr. C. J. Brabec
Konarka Austria Forschungs und Entwicklungs GmbH
Altenbergerstrasse 69, 4040 Linz (Austria)

[**] Research at UCSB was supported by a grant from Konarka Technologies, Inc., and by the AirForce Office of Scientific Research (Charles Lee, Program Officer). The assistance of Dr. Alexander Mikhailovsky in photoluminescence measurements is gratefully acknowledged. We also thank Wanli Ma, Dr. Jin Young Kim and Dr. Cuiying Yang for the useful discussions.

higher solar-cell efficiency, therefore, has focused on the synthesis of new materials in which the optical bandgap is engineered to improve the harvesting of light from the sun.^[4–6] Two factors constrain the design of low-bandgap polymers:

- The difference between the energy of the highest occupied molecular orbital (HOMO) of the polymer donor and the energy of the lowest unoccupied molecular orbital (LUMO) of the fullerene acceptor (for PCBM, $E_{\text{LUMO}} = 4.2\text{--}4.3$ eV) limits the open-circuit voltage (V_{oc}) of the photovoltaic cell;
- In order to obtain efficient charge transfer, the LUMO level of the polymer donor must be energetically higher than the LUMO level of the fullerene acceptor. A similar relation holds for the position of the HOMO level of the donor relative to that of the acceptor.

The combination of these restrictions with the spectral distribution of the solar irradiance leads to an optimum energy gap of $E_{\text{g}} \sim 1.5$ eV. Low-bandgap semiconducting polymers can be obtained by the synthesis of copolymers made of alternating electron-rich and electron-deficient units. Following this synthetic strategy, low-bandgap conjugated polymers such as PTPTB, a polythiophene–benzothiadiazole copolymer ($E_{\text{g}} \sim 1.6$ eV)^[7–10] or PFDTBT, a polyfluorene–benzothiadiazole copolymer ($E_{\text{g}} = 1.9$ eV),^[11,12] have recently been demonstrated. Composites of these copolymers with PCBM have shown improved photon harvesting and efficient photogeneration of charge-separated states; the best solar-cell energy-conversion efficiencies reported so far (1% for PTPTB:PCBM^[9] and 2.2% for PFDTBT:PCBM composites^[11]) are promising, yet still significantly lower than those obtained from P3HT:PCBM bulk heterojunction devices. The limiting factor in photovoltaic devices based on these low-bandgap polymers appeared to be the low fill factor rather than the open-circuit voltage, which in both cases remained high ($V_{\text{OC}} = 1.04$ V in PFDTBT-based cells and $V_{\text{OC}} = 0.72$ V in PTPTB-based cells) despite the lowering of the bandgap.

Here we present the results of studies of the novel low-bandgap polythiophene–benzothiadiazole copolymer, poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT), with an optical energy gap of $E_{\text{g}} \sim 1.46$ eV; the molecular structure of PCPDTBT is shown in Figure 1c.

The optical, charge-photogeneration, and charge-transport properties of PCPDTBT were investigated through measurements of absorbance, photoluminescence (PL), and both steady-state and fast ($t > 100$ ps) transient photoconductivity (PC). These data were compared to those of P3HT obtained in side-by-side measurements. We find that the photophysics of PCPDTBT and PCPDTBT:PCBM bulk heterojunction composites are very similar to those of P3HT and the corresponding P3HT:PCBM composites. The combination of the superior transport properties of polythiophene-based materials and the better match of the spectral response to the solar emission spectrum, as exhibited by PCPDTBT, implies that when fully optimized, PCPDTBT:fullerene bulk heterojunction devices should achieve photovoltaic efficiencies well above 5%.

2. Results and Discussion

The absorption spectrum of a thin PCPDTBT film is shown in the lower panel of Figure 2. From the onset of the absorbance, the optical gap of PCPDTBT is estimated to be $E_{\text{g}} \sim 1.46$ eV

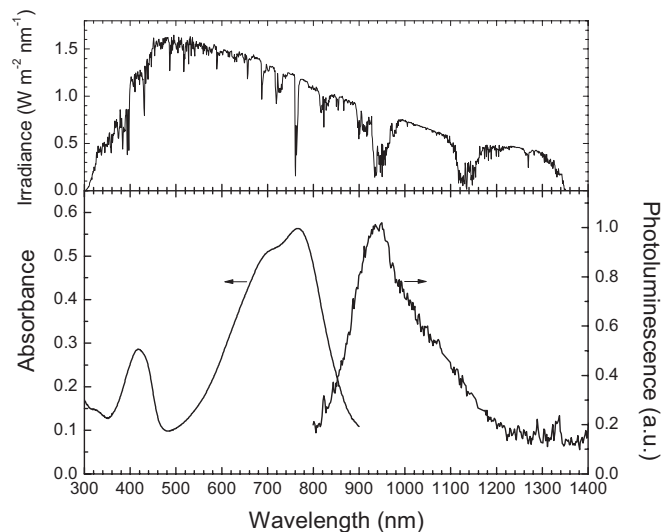


Figure 2. Upper panel: reference AM 1.5 solar spectrum (spectral irradiance of the sun on the earth's surface under illumination at 45°, AM: air mass). Lower panel: absorption (left) and photoluminescence (right) spectra of PCPDTBT.

($\lambda = 850$ nm). The absorption peak is located at $\lambda \sim 768$ nm, considerably red-shifted relative to the absorption peak measured in *ortho*-dichlorobenzene solution (at $\lambda \sim 730$ nm, not shown); this may be indicative of interchain interactions as well as planarization/extension of the conjugated segments occurring in the solid state. For comparison, the reference AM 1.5 solar spectrum (spectral irradiance of the sun on the earth's surface under illumination at 45°, AM: air mass)^[13] is shown in the upper panel of Figure 2. Assuming total absorption at photon energies above the absorption edge, we estimate that the use of PCPDTBT enables the collection of ca. 64% of the available solar photon flux, thus considerably reducing the spectral mismatch typical of higher-bandgap polymers such as P3HT (maximum photon collection ca. 46%). This translates to a potential increase in solar-cell efficiency of approximately a factor of two compared to P3HT-based devices.^[14]

The PL spectrum of a thick (ca. 2 μm) film of PCPDTBT is also shown in the lower panel of Figure 2. The PL spectrum peaks in the near-IR (NIR) ($\lambda \sim 950$ nm), which may be also of interest for the fabrication of IR emitters (e.g., light-emitting diodes) for telecommunication purposes.^[9] The PL intensity in PCPDTBT is quite low compared to other emissive polymers (e.g., the PPVs), a result that might indicate efficient charge-carrier photogeneration. The shape of the PL spectrum on the high-energy side is affected by self-absorption in the thick polymer film. Thinner films show an additional PL peak at $\lambda \sim 880$ nm (not shown), from which a Stokes shift of approximately 100 nm can be deduced. Addition of 50% w/w PCBM

to the PCPDTBT polymer films resulted in total quenching (i.e., by a factor greater than 50) of the PL emission. Energy transfer can be ruled out, as the singlet excited state of PCBM at 1.76 eV is higher than the bandgap of PCPDTBT, ca. 1.46 eV. Thus, the total quenching of the PL is attributed to photoinduced charge transfer and charge separation.

Figure 3 shows the steady-state PC spectra of pristine PCPDTBT (upper panel) and of a PCPDTBT:PCBM blend (lower panel), together with their optical absorption. Addition

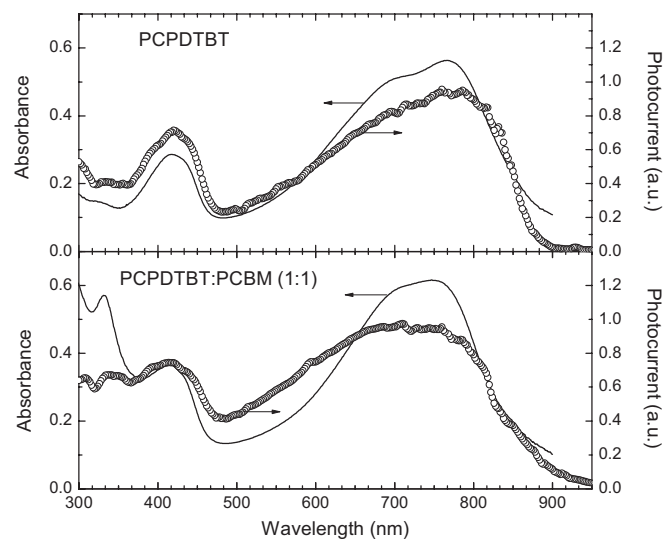


Figure 3. Steady-state photocurrent spectra of PCPDTBT (upper panel) and PCPDTBT:PCBM (lower panel), compared to their absorption spectra.

of PCBM does not significantly alter the absorption properties of PCPDTBT; the new spectral feature that appears in the spectrum of the blend at about 350 nm originates from PCBM. In both pristine PCPDTBT and the PCPDTBT:PCBM bulk heterojunction composite, the photocurrent action spectra show an onset that coincides with that of the optical absorption. The PC is strongly sensitized in the PCPDTBT:PCBM composite; an increase of about two orders of magnitude is obtained in annealed samples after addition of PCBM to PCPDTBT (Fig. 4, upper panel). This is typical of polymer:fullerene composites where electron transfer from the polymer donor to the fullerene acceptor occurs, thus increasing the yield of charge-carrier photogeneration and preventing geminate carrier recombination.^[15] For comparison, we have measured the steady-state photocurrent of P3HT and of P3HT:PCBM blends (Fig. 4, lower panel). The photoresponsivity values (i.e., photocurrent per watt of incident radiation at $F = 2.5 \times 10^4 \text{ V cm}^{-1}$, where F is the applied electric field) of PCPDTBT (PCPDTBT:PCBM) is comparable to that of P3HT (P3HT:PCBM). Note, however, that the photoconductive response of PCPDTBT extends significantly to the low-energy side of the spectrum of P3HT (the shaded area in Fig. 4 indicates the difference between the photocurrent onsets), consistent with the smaller bandgap of PCPDTBT.

In order to further investigate the intrinsic transport properties of PCPDTBT and P3HT, and in particular the effect of

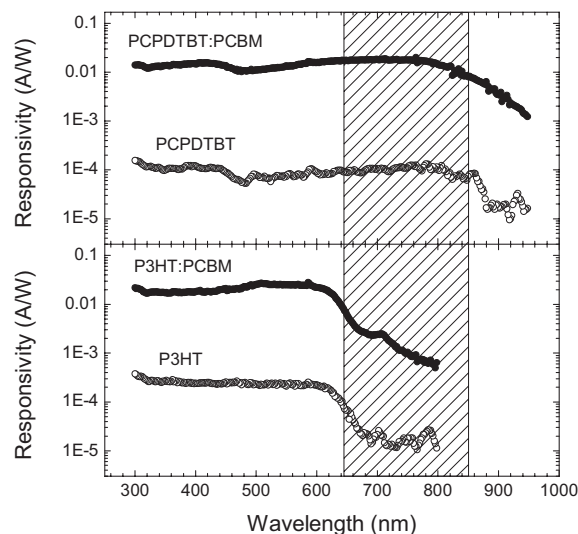


Figure 4. Upper panel: photoresponsivity of PCPDTBT (○) and PCPDTBT:PCBM (●). Lower panel: photoresponsivity of P3HT (○) and P3HT:PCBM (●).

charge transfer on the carrier lifetime in polymer:fullerene composites, we have carried out fast ($t > 100 \text{ ps}$) transient photocurrent measurements. Charge-carrier photogeneration and recombination in the pristine polymers (both in P3HT and PCPDTBT) occur on a timescale faster than the temporal resolution of our measuring system (ca. 100 ps), and therefore could not be resolved. The peak intensity of the resolution-limited transient PC traces of the pristine polymers, however, increases significantly (approximately tenfold) after addition of PCBM. Moreover, the transient PC decays of polymer:fullerene blends show a long-lived “tail” that is consistent with ultrafast charge transfer and the consequent increase of the carrier lifetime.^[15]

The normalized transient PC waveforms obtained from the PCPDTBT:PCBM and P3HT:PCBM bulk heterojunction composites are shown in Figure 5. The photocurrent decay profiles

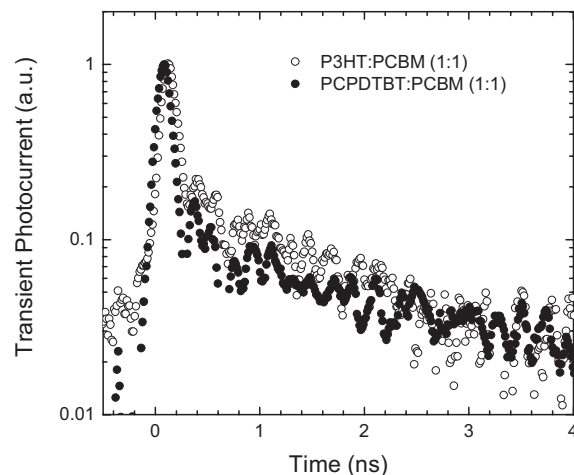


Figure 5. Transient photocurrent decay of P3HT:PCBM (○) and PCPDTBT:PCBM (●).

in the two systems are almost identical; the carrier lifetime deduced from the transient PC data is $\tau \sim 1.5$ ns, somewhat shorter than in PPV-derivative:fullerene bulk heterojunction materials.^[15] This could be due to the higher charge-carrier mobility in P3HT (or PCPDTBT), which might result in faster carrier recombination. In all cases the peak transient PC was linearly dependent on applied electric field and the excitation intensity.

The results of PL quenching, PC sensitization, and increased carrier lifetime strongly indicate a highly efficient charge-transfer reaction occurring in PCPDTBT:PCBM composites. Thus, we expect that the favorable optoelectronic properties of PCPDTBT, combined with its wide spectral responsivity, would allow the realization of efficient photovoltaic devices. Power-conversion efficiencies as high as 3.5% have been obtained in PCPDTBT:PCBM bulk heterojunction solar cells, limited by the rather low fill factor of the devices ($FF < 50\%$).^[16] Comprehensive studies of the device performance are underway with the goal of optimizing the photovoltaic efficiency.

3. Summary and Conclusions

Optical and charge-transport properties of the novel low-bandgap conjugated polymer PCPDTBT have been studied. PCPDTBT exhibits optical absorption and photoconductive response over a wide spectral range, from 850 to 300 nm, which makes it suitable for efficient light harvesting and charge-carrier extraction in polymer-based photovoltaic cells. The data indicate efficient charge transfer and charge separation in PCPDTBT:PCBM bulk heterojunction composites: the electron transfer to the fullerene acceptor favors charge separation and prevents geminate recombination of charge carriers in the polymer, considerably prolonging the carrier lifetime. The results are in every respect similar to those obtained from the well-known P3HT:PCBM bulk heterojunction material system.

In particular, the photoresponsivity of PCPDTBT:PCBM composites is approximately 100-fold higher than that of pristine PCPDTBT.

We conclude that when used as the active component in PCPDTBT:PCBM bulk heterojunction devices, PCPDTBT provides an opportunity for achieving high power-conversion efficiency in polymer photovoltaics through improved solar-light harvesting.

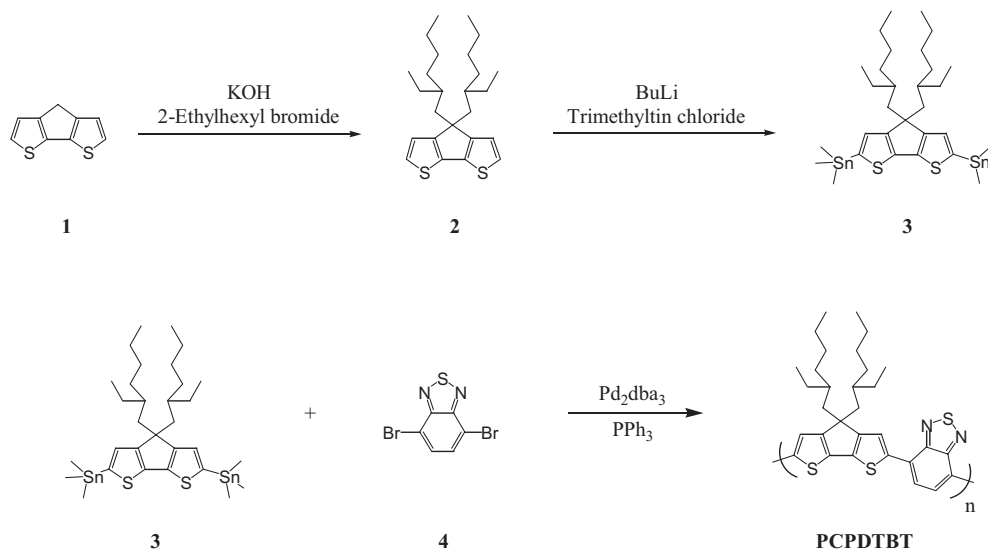
4. Experimental

PCPDTBTB was synthesized according to Scheme 1. 4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (**1**) [17] was alkylated to form 4,4-bis-(2-ethyl-hexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (**2**), which was then converted to 4,4-bis(2-ethyl-hexyl)-2,6-bis-trimethylstannanyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (**3**). Stille coupling of the bisstannane with 4,7-dibromo-2,1,3-benzothiadiazole (**4**) afforded PCPDTBTB. Further details of the synthesis will be provided in a separate publication [18].

The PCPDTBTB used in the current experiments was purified by preparative gel-permeation chromatography (GPC) and had a number-averaged molecular weight of 50 kDa ($1 \text{ Da} = 1.66 \times 10^{-27} \text{ kg}$), a weight-averaged molecular weight of 79 kDa, and a polydispersity index of 1.6, as determined by GPC based on polystyrene standards.

Cyclic voltammetry measurements of PCPDTBT indicated an energy of -5.1 to -5.3 eV for the HOMO [16], slightly dependent on the polymer molecular weight. The energy of the HOMO level of PCPDTBT is comparable to that of P3HT ($E_{\text{HOMO}} = -5.15$ eV), consistent with the almost identical V_{oc} measured with PCPDTBT:PCBM and P3HT:PCBM bulk heterojunction solar cells. Based on the optical energy gap of $E_{\text{g}} \sim 1.5$ eV, the LUMO in PCPDTBT lies between -3.6 and -3.8 eV, significantly higher than the LUMO level of PCBM ($E_{\text{LUMO}} = -4.2$ to -4.3 eV). Electron-transfer reaction from PCPDTBT to PCBM is therefore expected to be favored.

Samples were prepared in a nitrogen glove-box with oxygen count of ~ 1.5 ppm. P3HT and P3HT:PCBM (1:1) blend were dissolved in chlorobenzene (1 wt %), while PCPDTBTB and PCPDTBTB:PCBM (1:1) blend were dissolved in *ortho*-dichlorobenzene (1 wt %). Thin polymer films were obtained by spin-casting the polymer solutions on quartz or alumina substrates at 1000 rpm. The samples were thermally annealed in a vacuum chamber at 150°C for 30 min.



Scheme 1. Synthesis of PCPDTBTB. BuLi: butyllithium; Pd₂dba₃: tris(dibenzylideneacetone)dipalladium; PPh₃: triphenylphosphine.

The absorption spectra were recorded by an automatic, dual-beam spectrometer (Shimadzu UV-2401 PC) while the photoluminescence spectra by a fluorimeter (Photon Technology International) equipped with a xenon lamp. The samples were excited by monochromatic light ($\lambda = 750$ nm) at an incidence angle of ca. 45° and the emitted photoluminescence was collected at ca. 45° , dispersed by a monochromator, and recorded by a liquid-nitrogen-cooled Ge detector (Edinburgh Instruments).

For photoconductivity measurements, polymer films were deposited on alumina substrates and metallic (Au) electrodes were thermally evaporated onto the film surface. The contacts formed a fast microstrip transmission line (Auston switch) [19] with a gap between the electrodes of 100 μm , which allowed both steady-state and transient measurements with temporal resolution as high as 100 ps. Photocurrent transients were generated by pulsed-laser photoexcitation under an applied electric field ($F \sim 1 \times 10^4$ V cm^{-1}) and the photocurrent waveforms were recorded by a Boxcar integrator (EG&G PAR 4400). The laser pulses (100 fs duration, 1 KHz repetition rate) were produced by a Ti:sapphire system (SpectraPhysics), where an optical parametric amplifier (OPA) was used to tune the excitation wavelength to near the polymer absorption maxima (570 and 720 nm for P3HT and PCPDTBTB, respectively). The laser pulse intensity was $I \sim 1 \times 10^{-4}$ J cm^{-2} . Steady-state photoconductivity measurements were carried out by the conventional modulation technique and recorded by a lock-in amplifier; the light source was a xenon lamp and the light-modulation frequency was $\nu = 166$ Hz. The applied electric field was $F = 1.5 \times 10^4$ V cm^{-1} . The data were normalized by the measuring system response obtained after each run with a calibrated Si photodiode. All measurements were performed in vacuum ($P < 10^{-4}$ Torr (1 Torr \approx 133 Pa)).

Received: March 2, 2006

Revised: April 28, 2006

Published online: January 26, 2007

- [1] W. Ma, C. Yang, X. Gong, K. Lee, A. J. Heeger, *Adv. Funct. Mater.* **2005**, *15*, 1617.
- [2] G. Li, V. Shrotriya, Y. Yao, Y. Yang, *J. Appl. Phys.* **2005**, *98*, 43 704.
- [3] F. Padinger, R. S. Rittberger, N. S. Sariciftci, *Adv. Funct. Mater.* **2003**, *13*, 85.
- [4] J. Roncali, *Chem. Rev.* **1997**, *97*, 173.
- [5] C. Winder, N. S. Sariciftci, *J. Mater. Chem.* **2004**, *14*, 1077.
- [6] M. R. Andersson, O. Thomas, W. Mammo, M. Svensson, M. Theander, O. Inganäs, *J. Mater. Chem.* **1999**, *9*, 1933.
- [7] A. Dhanabalan, J. K. J. van Duren, P. A. van Hal, J. L. J. van Dongen, R. A. J. Janssen, *Adv. Funct. Mater.* **2001**, *11*, 255.
- [8] J. K. J. van Duren, A. Dhanabalan, P. A. van Hal, R. A. J. Janssen, *Synth. Met.* **2001**, *121*, 1587.
- [9] C. J. Brabec, C. Winder, N. S. Sariciftci, J. C. Hummelen, A. Dhanabalan, P. A. van Hal, R. A. J. Janssen, *Adv. Funct. Mater.* **2002**, *12*, 709.
- [10] C. Winder, G. Matt, J. C. Hummelen, R. A. J. Janssen, N. S. Sariciftci, C. J. Brabec, *Thin Solid Films* **2002**, *403*, 373.
- [11] M. Svensson, F. Zhang, S. C. Veenstra, W. J. H. Verhees, J. C. Hummelen, J. M. Kroon, O. Inganäs, M. R. Andersson, *Adv. Mater.* **2003**, *15*, 988.
- [12] K. G. Jespersen, W. J. D. Beenken, Y. Zaushitsyn, A. Yartsev, M. Andersson, T. Pullerits, V. Sundstrom, *J. Chem. Phys.* **2004**, *121*, 12 613.
- [13] ASTM G-173-03, *Terrestrial Reference Spectra for Photovoltaic Performance Evaluation*, American Society for Testing and Materials (ASTM) International, West Conshohocken, PA.
- [14] Note that the relevant gauge for solar-cell efficiency is the solar photon flux that peaks at ca. 1.8 eV, rather than the solar photon energy flux shown in the upper panel of Figure 2.
- [15] C. H. Lee, G. Yu, D. Moses, K. Pakbaz, C. Zhang, N. S. Sariciftci, A. J. Heeger, F. Wudl, *Phys. Rev. B: Condens. Matter Mater. Phys.* **1993**, *48*, 15 425.
- [16] D. Mühlbacher, M. Scharber, M. Morana, Z. Zhu, D. Waller, R. Gaudiana, C. Brabec, *Adv. Mater.* **2006**, *18*, 2884.
- [17] P. Coppo, D. C. Cupertino, S. G. Yeates, M. L. Turner, *Macromolecules* **2003**, *36*, 2705.
- [18] Z. Zhu, D. Waller, R. Gaudiana, M. Morana, D. Mühlbacher, M. Scharber, C. Brabec, *Macromolecules*, in press.
- [19] D. H. Auston, *IEEE J. Quantum Electron.* **1983**, *19*, 639.