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Extended Photocurrent Spectrum of a Low Band Gap Polymer in a Bulk Heterojunction Solar Cell

Luis M. Campos,[†] Ana Tontcheva,[†] Serap Günes,[‡]
Gursel Sonmez,[†,§] Helmut Neugebauer,[‡]
N. Serdar Sariciftci,[‡] and Fred Wudl*,[†]

Department of Chemistry & Biochemistry and Exotic Materials Institute, University of California, Los Angeles, California 90095-1569. Linz Institute for Organic Solar Cells (LIOS) Physical Chemistry, Johannes Kepler University Linz, Altenbergerstrasse 69, A-4040 Linz, Austria, and Faculty of Engineering and Natural Sciences, Sabanci University, Orhanli, 34956 Tuzla, Istanbul, Turkey

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The discovery of the photoinduced charge transfer from a semiconducting polymer to C_{60} aroused an interest to develop solar cells based on organic materials.[1] Several device architectures to incorporate the materials have been explored,[2] and those based on the bulk heterojunction concept are promising due to the power conversion efficiencies up to >3% recently accomplished.[3,4] In bulk heterojunction solar cells, an active layer is sandwiched between the electrodes. The active layer is composed of an intimate mixture of donor and acceptor molecules, creating nanoscale heterojunctions where the charge transfer takes place.[5] For devices composed of semiconducting polymer−fullerene blends, the polymer absorbs the light and transfers an electron from its excited state to the fullerene. The driving force is provided by a built-in potential. The holes are transported along the backbone of the polymer while the electrons move by a hopping mechanism through the fullerene network. An intrinsic field gradient in the active layer is achieved by choosing electrodes with different work functions, such as indium tin oxide (ITO) and aluminum.[6] A critical factor for improving the efficiency of solar cells is to match the photon flux spectrum from the sun with the absorption of the donor/acceptor blend. The solar emission spectrum ranges from <350 to >1500 nm with a maximum flux around 700 nm.[7] Nonetheless, the best bulk heterojunction devices currently available are only active for wavelengths ranging from 350 to 650 ($\lambda_{\max} \sim 530$ nm).[8] Low band gap polymers ($E_g < 1.8$ eV) are an alternative for better harvesting of the solar spectrum.[9,10] Here, we present the photovoltaic (PV) activity and extended photocurrent spectrum of a low band gap polymer, containing a thieno(3,4-b)pyrazine core (Scheme 1, PB3OTP), in a blend with a fullerene acceptor. These PV devices can generate electrons over a wide range of wavelengths that expand into the near-infrared. We show that such blends are promising for the development of organic solar cells due to the remarkable harvest of the solar spectrum.[7]

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* To whom correspondence should be addressed. E-mail: wudl@chem.ucla.edu.

[†] University of California.

[‡] Johannes Kepler University Linz.

[§] Sabanci University.

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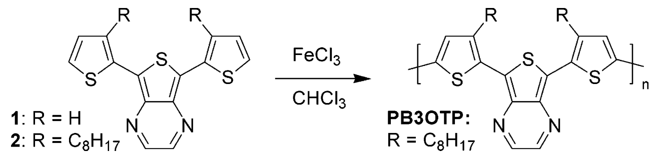
Scheme 1



1: R = H
2: R = C_8H_{17}
PB3OTP: R = C_8H_{17}

The monomer **1** has been previously synthesized by Kitamura et al. and polymerized electrochemically.[11] We have modified the monomer to **2** by attaching octyl groups at the 3 position of the thiophene moiety to increase its solubility. The polymerization was carried out with $FeCl_3$ by a previously published procedure[12] to obtain poly[5,7-bis-(3-octylthiophen-2-yl)thieno{3,4-b}pyrazine] (PB3OTP). The resulting polymer had an average molecular weight of 1.63 kg/mol (polydispersity index, PDI = 1.853) obtained by gel permeation chromatography.[13]

The PV devices were prepared by spin coating the blend from a solution in chlorobenzene onto a poly(3,4-ethylenedioxythiophene) (PEDOT)/poly(styrenesulfonate) (PSS) covered glass−ITO substrate to achieve a layered structure of glass−ITO/PEDOT−PSS/active layer/LiF/Al. The metal electrodes were deposited under vacuum.[14] The active layer was composed of a varied weight-to-weight (w/w, 1:1, 1:2, 1:3, 1:4) mixture of PB3OTP and the soluble fullerene derivative 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-methanofullerene[15] (PCBM). The device that gave the best results contained a ratio of 1:1 PB3OTP/PCBM in the active layer.

The UV−vis spectrum of the pristine polymer and the PB3OTP/PCBM (1:1) blend in thin films is shown in Figure 1. The polymer alone exhibits a significant absorption into the near-IR region due to its low band gap (optical band gap = ca. 1.3 eV). Cyclic voltammetry of an electrochemically polymerized PB3OTP gave a value of 1.45 eV (Supporting Information, Figure S1). PB3OTP exhibits a very wide absorption range, from 300 to 980 nm, with a λ_{max} at 730 nm (Figure 1). The absorption peak of the blend at 330 nm corresponds to PCBM.

Photocurrent measurements show that the blend is capable of generating electrons nearly over the range of absorbed photons by the pristine polymer. The incident photon to current efficiency (IPCE), or external quantum efficiency, spectrum spans from 300 to 900 nm and has a blue-shifted (compared to the absorption spectrum in Figure 1) λ_{max} at 660 nm, with a peak value slightly over 6% (see Figure 2). The overlaid IPCE spectrum with the photon flux of a solar simulator under air mass (AM) 1.5 conditions shows great overlap, especially around the peak of the photon flux (700 nm).

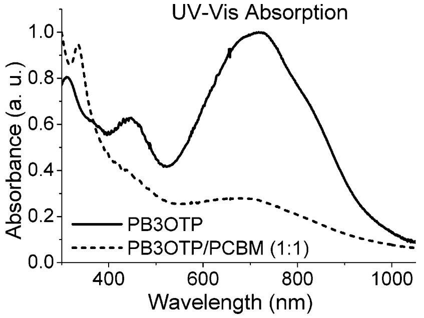


Figure 1. Normalized UV−vis absorption of the pristine polymer (solid line), PB3OTP, and a blend of PB3OTP/PCBM (1:1, w/w, dashed line), in thin films spin-cast from chlorobenzene onto glass. The λ_{onset} = 980 nm corresponds to a band gap of 1.3 eV.

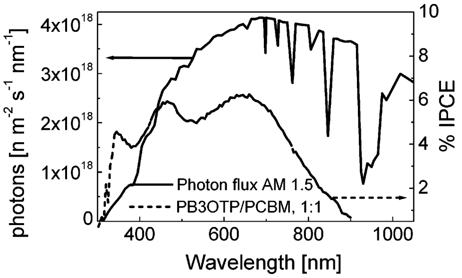


Figure 2. Percent IPCE spectrum (dashed line) overlaid with the solar simulator spectrum (AM 1.5 conditions, solid line). The graphs show a great overlap between the photon emission of the sun and the photocurrent spectrum of the blend.

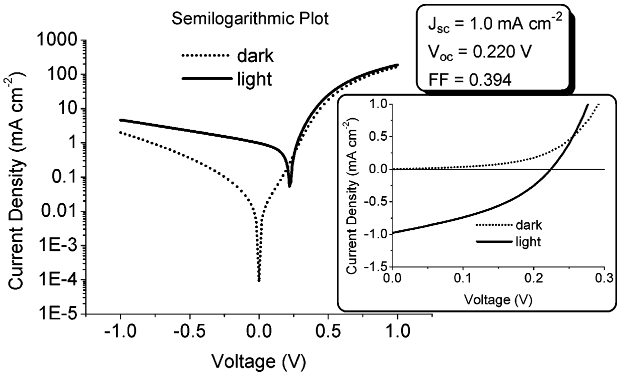


Figure 3. Current−voltage (*I*−*V*) characteristics of the PB3OTP/PCBM (1:1) blend solar cells in the dark and under white light illumination (AM 1.5 conditions) shown in semilogarithmic plot and regular forms.

The *I*−*V* characteristic plot of the solar cell based on the 1:1 PB3OTP/PCBM blend is shown in Figure 3. The bulk heterojunction device under white light illumination (100 mW cm^{-2}) has a short circuit current density (J_{sc}) of 1.0 mA cm^{-2}, an open circuit voltage (V_{oc}) of 0.220 V, and a fill factor (FF) of 0.394. The low rectification ratio of approximately 10^2 can be attributed to the rather poor film formation of the active layer (diode, "dark" curve). It may be possible that the low molecular weight of the polymer and spin casting from chlorobenzene leads to very thin films (60−90 nm thick). In comparison to the low band gap polyfluorene/PCBM solar cell reported by Wang et al.,[10] the short circuit current achieved by the PBO3TP/PCBM blend is much higher (nearly double). However, the overall efficiency of the device is mainly hindered by very low V_{oc}. Generally, V_{oc} is a measure of the difference between the oxidation potential of the donor (PB3OTP) and the reduction potential of the acceptor (PCBM).[4,16] Thus, raising the highest occupied molecular orbital (HOMO) closer to the lowest

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Table 1. Solar Cell Characteristics: Current Density (J_{sc}), Open Circuit Voltage (V_{oc}), and FF, Varying the PB3OTP/PCBM Ratio

PB3OTP/PCBM (w/w ratio)	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF
1:1	0.977	0.220	0.394
1:2	0.478	0.160	0.368
1:3	0.348	0.160	0.348
1:4	0.320	0.160	0.322

unoccupied molecular orbital (LUMO) of PCBM diminishes the value of V_{oc}.

Increasing the concentration of PCBM in the blend has a strong effect on J_{sc} and the FF, while the V_{oc} drops to a constant value after the addition of more than 50% PCBM (Table 1).[17] van Duren et al. have shown that saturating the active layer with PCBM leads to a decrease in the J_{sc} due to phase separation.[18] However, atomic force microscopy (AFM) images show a very smooth surface with no notable phase separation in all the blends and a height scale of 5 nm (see Supporting Information, Figure S4). Furthermore, the appearance of a number of pinholes seems to increase as the PCBM concentration increases and the IPCE also shows bleaching of the 660 nm band. Consequently, the J_{sc} and FF may be affected by the increased resistance in the blend or an increased charge recombination due to the excessive presence of PCBM in close proximity with the polymer.[19] The J_{sc} and FF values in the 1:1 blend are satisfactory, but further work needs to be done to optimize the device.

In summary, we have reported the broad IPCE spectrum and PV characteristics of a modified low band gap polymer. Attaching the octyl side chains increased the polymer solubility in common organic solvents for its processability in bulk heterojunction solar cells. Blending PB3OTP with PCBM in a 1:1 ratio leads to an active layer that absorbs photons to generate current from 300 to 900 nm, with a peak in the red region at 660 nm. Such remarkable harvest of the solar spectrum shows that low band gap polymers are an attractive approach for the development of plastic solar cells.

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Supporting Information Available: Additional information regarding the synthesis of PB3OTP, cyclic voltammetry, device fabrication, and AFM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Devices composed of 2:1 PB3OTP/PCBM gave a high J_{sc} value of 1.118 but extremely low values for the V_{oc} (0.070 V) and FF (0.253) due to the formation of extremely thin films.

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