

A Thieno[3,4-*c*]pyrrole-4,6-dione-Based Copolymer for Efficient Solar Cells

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Polymer bulk heterojunction (BHJ) solar cells offer great opportunities as renewable energy sources because of their unique features such as low-cost production, low weight, and mechanical flexibility.¹ Although such solar cells have witnessed significant advances during the past few years,² the efficiency, stability, processability, and fabrication cost still need to be improved for large-scale production and commercialization.³ Both materials and device designs play important roles in realizing such applications.

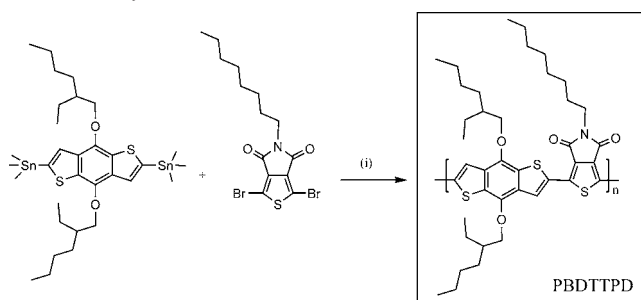
In BHJ devices using 6,6-phenyl-C61-butyric acid methyl ester (PC₆₁BM) as the acceptor, a desirable processable polymer donor should exhibit not only a band gap between 1.2 and 1.9 eV with broad absorption to maximize sunlight absorption but also a highest occupied molecular orbital (HOMO) energy level between -5.2 and -5.8 eV and a lowest unoccupied molecular orbital (LUMO) energy level between -3.7 and -4.0 eV to ensure efficient charge separation while maximizing the open-circuit voltage (V_{oc}). In addition, good hole mobility is also needed to allow adequate charge transport.⁴

Use of donor-acceptor structures has become an efficient strategy for obtaining low-band-gap polymers and modulating their electronic properties.⁵ For photovoltaic applications, 2,1,3-benzothiadiazole (BT) and 4,7-dithien-2-yl-2,1,3-benzothiadiazole (DTBT) were shown to be good electron acceptors and have been copolymerized with various electron donors, including fluorenes,^{6a} carbazoles,^{6b} dibenzosiloles,^{2c} dithienosiloles,^{6c} ladder oligo-*p*-phenylenes,^{6d} and cyclopenta[2,1-*b*:3,4-*b'*]dithiophene,^{2a} leading to polymer BHJ solar cells with power conversion efficiencies (PCEs) of up to 6.1%.^{2d} In the last year, copolymers based on electron-donating benzodithiophenes (BDTs) have also demonstrated great potential for application in organic photovoltaics.⁷ For instance, Yu and co-workers^{7d} have recently designed a series of copolymers with optimized electronic and optical properties that led to PCEs as high as 7.4%.

Taking into account all these recent results and in search of new electron-withdrawing comonomers, we became interested in the thieno[3,4-*c*]pyrrole-4,6-dione (TPD) unit.⁸ Its relatively simple, compact, symmetric, and planar structure could be beneficial for electron delocalization when it is incorporated into various conjugated polymers. On this basis, it seemed likely to promote intrachain and interchain interactions along and between coplanar polymer chains, and its relatively strong electron-withdrawing effect should therefore lead to low HOMO and LUMO energy levels, which are desired in order to increase V_{oc} in BHJ solar cells. Finally, the simple introduction of different alkyl side chains on the pyrrole ring should improve the solubility and processability of the resulting copolymers. Despite these promising features, to the best of our knowledge, TPD-containing polymers have never been investigated for applications in "plastic" electronics.

To shed light on the potential of the TPD unit for photovoltaic applications, a new copolymer combining BDT and TPD units, PBDTTPD (as illustrated in Scheme 1), was designed, synthesized, and characterized. Our first results demonstrate that the TPD building block could become a strategic choice for achieving low-band-gap polymers for the development of highly efficient solar cells.

Scheme 1. Synthesis and Structure of PBDTTPD^a



^a Reaction conditions: Pd₂(dba)₃, P(*o*-tolyl)₃, toluene, 110 °C, 48 h, 98% yield.

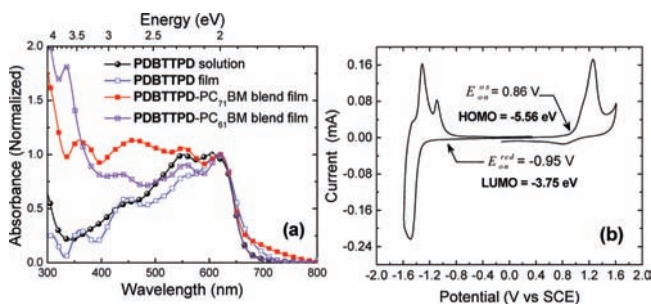


Figure 1. (a) UV-vis-NIR absorption spectra of PBDTTPD in dilute chloroform (●) and in films cast without blending (□), with blended PC₇₁BM (■), and with blended PC₆₁BM (⊗) on a glass/ITO/PEDOT:PSS substrate. (b) Cyclic voltammogram (50 mV s⁻¹) of a PBDTTPD film cast on a platinum wire in Bu₄NBF₄/CH₃CN.

As described in Scheme 1, PBDTTPD was synthesized from Stille coupling between 2,6-bis(trimethyltin)-4,8-di(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene^{7a} and 1,3-dibromo-5-octylthieno[3,4-*c*]pyrrole-4,6-dione^{8c} using Pd₂(dba)₃/P(*o*-tolyl)₃ as the catalyst. PBDTTPD is readily soluble in chloroform, *o*-dichlorobenzene (ODCB), or 1,2,4-trichlorobenzene (TCB) upon heating. Number-average (13 kDa) and weight-average (34 kDa) molecular weights were obtained from high-temperature size-exclusion chromatography (SEC) using TCB at 140 °C as the eluent. The presence of branched side chains on the BDT unit enhanced the solubility of the resulting polymers, while linear alkoxy side chains led to low-molecular-weight polymers with limited processability. In

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contrast, long, linear alkyl side chains on the TPD unit gave polymers with better properties in comparison with branched alkyl side chains. PBDTTPD is thermally stable up to 380 °C and shows a glass transition at 138 °C.

The optical and electrochemical properties were also analyzed. As shown in Figure 1a, PBDTTPD and a PBDTTPD:PC₇₁BM blended film show a broad absorption in the UV–vis range with an absorption onset at 685 nm. The optical band gap obtained from the polymer film absorption edge is 1.8 eV. Interestingly, the UV–vis absorption of PBDTTPD in solution is very similar to that obtained in the solid state, indicating a similar rigid-rod conformation in both states. The HOMO and LUMO energy levels of the polymer were measured by cyclic voltammetry (CV), as shown in Figure 1b. The energy levels of the HOMO and LUMO were estimated to be at -5.56 and -3.75 eV, respectively, on the basis of the onset of the oxidation and reduction currents.⁹ The electrochemical band gap (1.81 eV) is in good agreement with the optical bandgap.

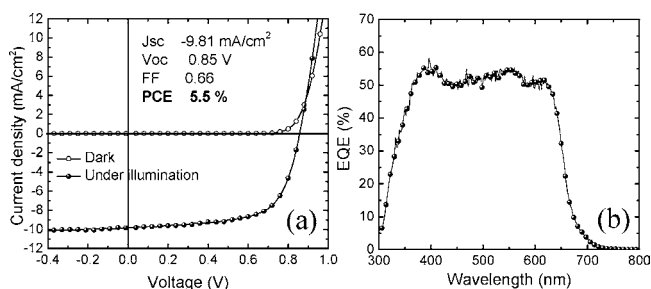


Figure 2. (a) J – V curve for a PBDTTPD-based solar cell device under an illumination of AM 1.5 G, 100 mW/cm². (b) EQE of the PBDTTPD:PC₇₁BM BHJ solar cell.

The photovoltaic properties of PBDTTPD were investigated using [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) as the acceptor in BHJ devices with a general structure of ITO/PEDOT:PSS/PBDTTPD:PC₇₁BM/LiF/Al, where poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was used to facilitate hole extraction and lithium fluoride (LiF) was used for hole blocking and electron extraction purposes. PC₇₁BM was chosen as the acceptor because it has electronic properties similar to those of PC₆₁BM but increased absorption in the visible region from 440 to 530 nm.¹⁰ The active area of the devices was 1.0 cm², since it is known that efficiencies obtained on areas smaller than 0.2–0.3 cm² may become strongly size-dependent.¹¹ Details concerning device fabrication and characterization are provided in the Supporting Information. Figure 2 shows a typical current density–voltage (J – V) curve and the external quantum efficiency (EQE) of a polymer solar cell device with a PBDTTPD:PC₇₁BM weight ratio of 1:2 and an active-layer thickness of 90 nm. The device demonstrated a short-circuit current density (J_{sc}) of 9.81 mA/cm², a V_{oc} of 0.85 V, and a fill factor (FF) of 0.66. The resulting PCE thus reached 5.5%. The device showed a relatively high photoconversion efficiency over the wavelength range 380–630 nm, with monochromatic EQE values of 50–55%. The J_{sc} calculated by integrating the EQE curve with an AM1.5G reference spectrum indicates that a measurement error of $\sim 5\%$ exists in the corresponding J_{sc} value obtained from the J – V measurements due to the spectral mismatch of the solar simulator.

In conclusion, a new low-band-gap thieno[3,4-*c*]pyrrole-4,6-dione-based copolymer, PBDTTPD, has been designed and synthesized. Preliminary experiments on a PBDTTPD-based solar cell

device with an active device area of 1.0 cm² have demonstrated a PCE of 5.5% in air. It is important to note that further improvements are possible through different device configurations such as annealing, solvents, additives, electrodes, acceptors, etc. More importantly, this work shows for the first time that the thieno[3,4-*c*]pyrrole-4,6-dione (TPD) unit and related derivatives can be efficiently utilized to tailor the optical and electronic properties of conjugated polymers and may therefore become quite simple and useful comonomers for the future design of electroactive and photoactive polymers for photovoltaic devices and for many other applications in plastic electronics.

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Supporting Information Available: Experimental details; synthesis of the monomers and polymer; instrumentation; fabrication details and characterization procedures for the PSC devices; and figures showing thermogravimetric analysis, differential scanning calorimetry, and X-ray diffraction data for PBDTTPD. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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