

Synthesis of a Low Band Gap Polymer and Its Application in Highly Efficient Polymer Solar Cells

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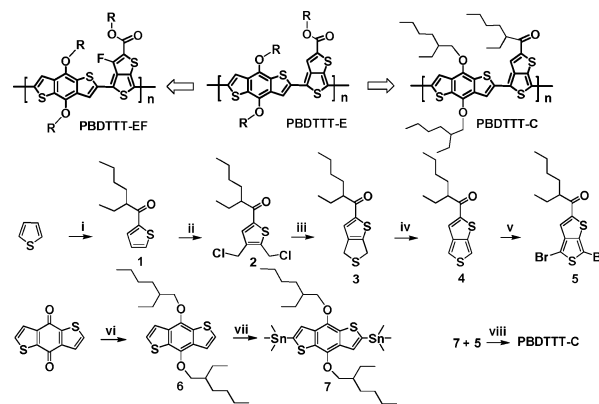
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Recently, polymer solar cells (PSCs) have attracted much attention due to the broad range of small and large area applications, which will benefit from its unique features such as being flexible, lightweight, and colorful.¹ Bulk heterojunction polymer solar cells² have been proven to be the most successful device structure for OPV so far. Stability and a large scale process are of great importance and have attracted much attention,³ and also, great efforts have been made to improve the power conversion efficiency (PCE) of polymer solar cells by using new active layer materials.⁴ In the past three years, several new polymers have been reported which have exhibited very promising properties in polymer solar cell application. For example, to improve the absorption of sunlight, side-chain conjugated polythiophenes (PTs) were prepared. Compared with poly(3-hexylthiophene) (P3HT), PTs with conjugated side chains exhibited a broader response range to the solar irradiation spectrum resulting in a 38% improvement of PCE.⁵ Since the photon flux of the solar irradiation has a peak at 680 nm,⁶ various low band gap materials have been designed and used in PSCs to harvest more sunlight. For instance, the PSCs based on two representative low band gap conjugated polymers, PCPDTBT⁷ and PSBTBT,⁸ exhibited a higher short circuit current (J_{sc}) due to their broad absorption, and accordingly PCEs over 5% have been obtained. It is commonly accepted that the open circuit voltage (V_{oc}) of a bulk heterojunction PSC is proportional to the difference between the HOMO of the electron donor material and LUMO of the electron acceptor material.⁹ Since PCE is the product of J_{sc} , V_{oc} , and fill factor (FF), pursuing a higher V_{oc} by using electron donor materials with a deeper HOMO level is an effective approach to achieving a higher PCE. For example, several deep-HOMO conjugated polymers like BisDMO-PFDTBT,¹⁰ PSiFDBT,¹¹ and PCDTBT¹² have been applied in PSCs, and high PCEs of ~5–6% have been achieved along with a high V_{oc} of ~0.9–1.0 V. However these are polymers with the bandgap similar to that of P3HT. To achieve the maximum potential, an ideal conjugated polymer for PSCs should not only have a low band gap but also a deeper HOMO level.

Recently, benzo(1,2-*b*:4,5-*b'*)dithiophene (BDT) based materials exhibited very promising properties in organic electronic devices, especially in polymer solar cells.^{6,13a,b} As reported, the band gap of the BDT-based polymers can be effectively tuned from 2.1 to 1.1 eV by copolymerizing with different aromatic units, and the HOMO level of the polymers can be successfully adjusted from –5.2 to –4.6 eV. As a result, V_{oc} values of the PSCs based on these polymers are in the range of 0.22–0.75 V, which indicates that photovoltaic properties of this kind of polymers are tunable by introducing suitable functional groups as substituents.^{6a} Y. Liang

Scheme 1. Structure of Three PBDTTT-Based Polymers and Synthesis Route of One of the Polymers, PBDTTT-C^a



^a (i) 2-Ethylhexanoyl chloride, $AlCl_3$, DCM, 10 °C. (ii) $CICH_2OCH_3$, $TiCl_4$, 0 °C, 1 h; then 50 °C, 6 h. (iii) Na_2S , methanol, reflux, 1 h. (iv) See ref 13a. (v) NBS, DMF, inert atmosphere, 20 min. (vi) See ref 6a. (vii) butyllithium, THF, ambient temperature, 1 h; then trimethyltin chloride, ambient temperature, 1 h. (viii) See ref 6a.

et al. reported a poly(4,8-bis-alkyloxybenzo(1,2-*b*:4,5-*b'*)dithiophene-2,6-diyl-alt-(alkyl thieno(3,4-*b*)thiophene-2-carboxylate)-2,6-diyl) (PBDTTT-E as shown in Scheme 1) based device which exhibited very promising photovoltaic properties, including a high J_{sc} and FF. However, the V_{oc} of this device was only ~0.6 V, which was the limiting factor of the device's PCE.^{13a}

It is commonly known that alkoxy groups have much stronger electron donating effects than alkyl ones. Conjugated polymers with alkoxy groups as a substituent usually exhibit higher HOMO levels than their alkyl-substituted counterparts. For example, the HOMO level of poly(3-alkylthiophene)s (P3AT) is typically approximately –5.0 eV, and the HOMO level of poly(3-alkoxythiophene) (P3AOT) is approximately –4.5 eV.¹⁴ The difference between P3AT's HOMO and PCBM's LUMO is 0.8 eV, while that difference of P3AOT and PCBM is only 0.3 eV. As a result, the V_{oc} of P3AT/PCBM-based PSC is ~0.6 V, while the V_{oc} of P3AOT/PCBM-based PSC is lower than 0.1 V.¹⁴ These observations suggest that it is possible to further reduce the HOMO level of PBDTTT-E by removal of the oxygen atom on the ester group in the thieno(3,4-*b*)thiophene units, and accordingly a ketone-substituted polymer, namely PBDTTT-C, was designed as shown in Scheme 1. Although the fluorine atom effectively reduced the HOMO level of PBDTTT-based polymers, like PBDTTT-EF in Scheme 1, the synthesis of PBDTTT-EF is quite tedious and costly.^{13b} In this article, the effective method to synthesize PBDTTT-C not only reduces the synthesis process (and thus cost) but also results in a polymer which exhibits very promising polymer solar cell performance. The combination of an efficient synthesis method for a PBDTTT-based

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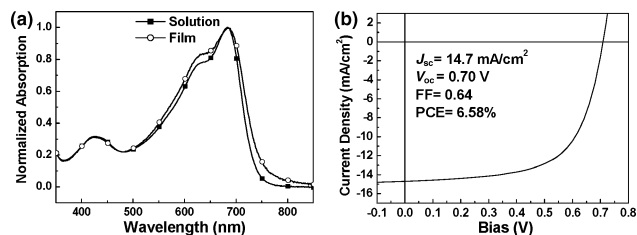


Figure 1. (a) Absorption spectra of PBDTTT-C as film and in chloroform solution. (b) J - V curve of PBDTTT-C/PC₇₀BM based solar cell device under illumination of AM 1.5 G, 100 mW/cm².

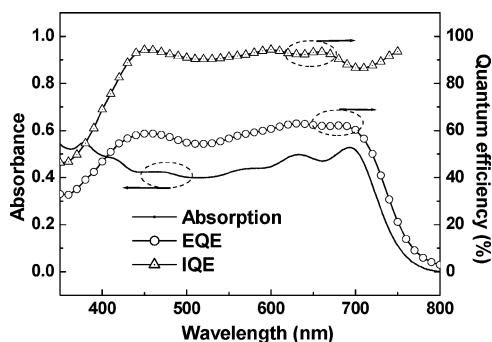


Figure 2. External quantum efficiency (EQE), Internal quantum efficiency (IQE), and absorption curves of PBDTTT-C/PC₇₀BM based solar cell device.

polymer and promising solar cell performance shows strong potential of the new polymer for use in PSC manufacturing.

Absorption spectra of PBDTTT-C in the solid state and in chloroform solution are shown in Figure 1a. The optical band gap of PBDTTT-C in the solid state was calculated from the absorption edge and found to be ~ 1.61 eV. The value is consistent with other PBDTTT-based polymers reported previously,^{13a,b} which means the replacement of ester by keton almost has no influence on the band gap for this kind of polymers. Electrochemical cyclic voltammetry (CV) was also performed to determine the HOMO level of the conjugated polymers. HOMO and LUMO levels of the polymers can be obtained by the reported method.¹⁵ Its HOMO and LUMO were -5.12 and -3.55 eV, respectively.

Polymer solar cells were fabricated using the polymer as an electron donor material and (6,6)-phenyl-C71-butyric acid methyl ester (PC71BM) as an electron acceptor material. The device structure is ITO/PEDOT-PSS/Polymer:PC71BM/Ca/Al. Hole mobilities are 2×10^{-4} cm²/V s for the device. The J - V curve of the fabricated PBDTTT-C/PC₇₁BM device is shown in Figure 1b, where V_{oc} is 0.70 V, 0.12 V higher than that of the PBDTTT-E/PC₇₁BM-based device,^{13a} but it is similar with the fluorine substituted PBDTTT, which is 0.74 V as reported.^{13b} The average PCE obtained from more than 200 devices reached 6.3%. The champion result reached 6.58%, with a V_{oc} of 0.70 V, a J_{sc} of 14.7 mA/cm², and an FF of 0.64, which is the highest value so far for polymer solar cells. The external quantum efficiency (EQE) curve of the PBDTTT-C-based device was shown in Figure 2. The J_{sc} calculated from the integral of EQE curves is 14.1 mA/cm² which is very consistent with the J_{sc} value obtained from the J - V measurement

system (3% error). The reflective absorption spectrum of the complete device was measured using a Cary 50 UV-vis spectrometer. The internal quantum efficiency (IQE) of PBDTTT-C-based device was then calculated using EQE and absorption data. The result is shown in Figure 2. In almost the whole response range, i.e., 400 to 750 nm, the IQE of the PBDTTT-C-based device averaged at $\sim 95\%$, which implied that charge separation, transportation, and collection of the device are quite efficient and photons absorbed by the active layer efficiently convert into electricity.

In conclusion, the HOMO level of the PBDTTT-based polymer was successfully reduced by introducing the ketone group in place of the ester group. The average PCE of the PBDTTT-based devices reached 6.3% with a champion PCE result of 6.58%. Due to its highly efficient photovoltaic performance and more feasible synthesis approach, PBDTTT-C has the potential to be successfully applied in the large-scale manufacturing¹⁶ of polymer solar cells.

Supporting Information Available: Experimental details of the synthesis of the polymer, device fabrication, and characterization of the polymer solar cells (i.e., measurements and instruments used). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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