Solar Cells

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A Polybenzo[1,2-*b*:4,5-*b*′]dithiophene Derivative with Deep HOMO Level and Its Application in High-Performance Polymer Solar Cells**

Lijun Huo, Jianhui Hou, Shaoqing Zhang, Hsiang-Yu Chen, and Yang Yang**

Although there is a consensus on the development of solar energy as a green energy resource, the importance of development of the polymer solar cell (PSC) has only been realized in recent years owing to its advantages of low cost and flexibility in large-area applications.[1] Bulk heterojunction (BHJ) type polymer solar cells now play a leading role in realizing high power conversion efficiency (PCE). The development of new polymer materials to further improve the efficiencies of BHJ-type PSCs will accelerate their commercial application. At present, P3HT-PCBM-based PSCs (P3HT = poly(3-hexylthiophene), PCBM = methanofullerene (6,6)-phenyl-C_{61}-butyric acid methyl ester) have exhibited high efficiencies of 4–5%. However, the narrow absorption spectrum of P3HT in 300–650 nm is one of the main hindrances to the further improvement of the efficiencies of P3HT-based devices. To overcome this problem, some low-band-gap polymer materials as donors have been synthesized successfully and applied to photovoltaic devices. Large short-circuit current density (J_{sc}) and higher efficiencies have been demonstrated using this strategy.[2] In spite of the high J_{sc} achievable with low-band-gap polymers, the device performance suffers owing to the low open-circuit voltage (V_{oc}) of 0.5–0.7 V. According to published models and experimental results, the V_{oc} of a PSC is closely related to the offset between energy levels of the highest occupied molecular orbital (HOMO) of the donor and lowest unoccupied molecular orbital (LUMO) of the acceptor.[3] Thus, to enhance the open-circuit voltage of these devices, some building blocks with lower-lying HOMOs should be introduced in donor molecules to lower their HOMO levels.

Polyfluorene and its derivatives are a well-known class of wide-band-gap organic semiconducting materials. Many donor polymers containing fluorene on the main chain were reported to show lower HOMO levels and correspondingly exhibited higher open-circuit voltages. However, the wider band gaps of these polymers resulted in lower values of J_{sc} and consequently lower efficiencies. To enhance the efficiency, there is a need for a low-band-gap polymers that can have a high V_{oc}. Few polymers with high open-circuit voltages (above 0.8 V) and consequently high PCEs (above 5%) have been reported to date, except for two kinds of polymers, poly[(2,7-silafluorene)-*alt*-(4,7-di-2-thienyl-2,1,3-benzothiadiazole)] (PSiFDBT) and poly[*N*-9″-heptadecanyl-2,7-carbazole-*alt*-5,5-(4′,7′-di-2-thienyl-benzothiadiazole) (PCDTBT), both of which contain a fluorene unit in the polymer main chain.[4,5] Considering the similarity in the molecular structures of PSiFDBT and PCDTBT with analogous fluorene units in both of their main chains, it is necessary to explore new molecular structures with favorable characteristics for higher open-circuit voltages and conversion efficiencies.

Recently, some benzo[1,2-*b*:4,5-*b*′]dithiophene-containing polymers were applied to field-effect transistor (FET) and PSC devices (Table 1).[2d,e,6,7] A high mobility of 0.15–0.25 $cm^2V^{-1}s^{-1}$ was achieved owing to the relatively large and planar molecular structure of the thiophene derivative, which would help promote cofacial π–π stacking, thus benefiting charge transport. Given its symmetrical planar structure and higher mobility, the incorporation of a low-band-gap unit into the benzo[1,2-*b*:4,5-*b*′]dithiophene unit could potentially result in a red-shifted absorption. A more appropriate energy level could be obtained by fine tuning of molecular structures for photovoltaic applications.

Table 1: Photovoltaic data of the high-performance PSCs based on several donor materials with deep HOMO levels.

Polymer	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]	Ref.
PBDTTT-CF[a]	0.76	15.2	66.9	7.73[b]	[2e]
PSiFDBT	0.90	9.55	50.7	5.40[c]	[4]
PCDTBT	0.88	10.60	66.0	6.10[b]	[5]
PBDTTBT	0.92	10.70	57.5	5.66[b]	this work

[a] PBDTTT-CF = poly[4,8-bis(2-ethylhexyloxy)-benzo[1,2-*b*:4,5-*b*′]dithiophene-2,6-diyl-*alt*-(4-octanoyl-5-fluoro-thieno[3,4-*b*]thiophene-2-carboxylate)-2,6-diyl]. [b] $PC_{71}BM$ was used as the acceptor. [c] $PC_{61}BM$ was used as the acceptor.

Herein we report the benzo[1,2-*b*:4,5-*b*′]dithiophene derivative PBDTTBT (Scheme 1), which exhibits high V_{oc} and PCE values. It would thus be a promising candidate for high-efficiency PSCs. The synthesis of the polymer is described in Scheme 2 (see also the Experimental Section). First, to ensure good solubility, four octyl chains were

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[*] Dr. L. Huo, Dr. J. Hou, Prof. Dr. Y. Yang
Department of Materials Science and Engineering
University of California, Los Angeles
Los Angeles, CA 90095 (USA)
Fax: (+1) 310-206-7353
E-mail: yangy@ucla.edu

Dr. J. Hou, S. Zhang, Dr. H. Chen
Solarmer Energy Inc., El Monte, CA 91731 (USA)
Fax: (+1) 626-456-8082
E-mail: jianhuih@solarmer.com

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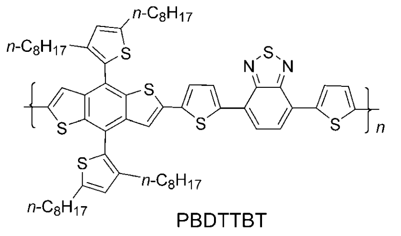
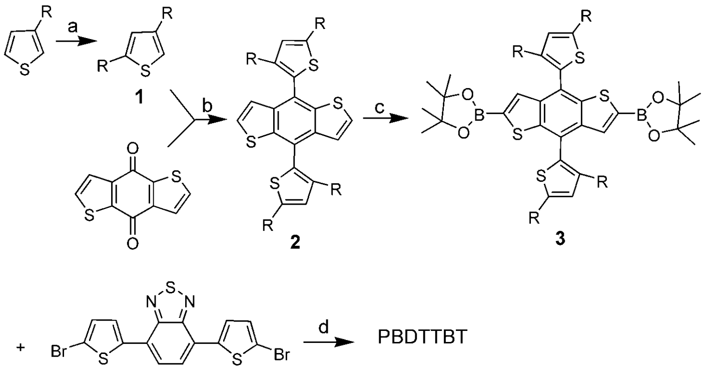


Scheme 1. Molecular structure of PBDTTBT.

symmetrically added to benzo[1,2-*b*:4,5-*b*′]dithiophene by the linkage of thienylene to give **2**. 4,7-Bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5′-diyl (**3**) was copolymerized with benzo[1,2-*b*:4,5-*b*′]dithiophene to lower the band gap. The new polymer poly{4,8-bis(2,5-dioctyl-2-thienyl)-benzo[1,2-*b*:4,5-*b*′]dithiophene-*alt*-[4,7-bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5′-diyl]} (PBDTTBT) was prepared by Suzuki coupling in good yield. PBDTTBT is soluble in common organic solvents, and the number average molecular weight (M_n) is 27.4 kDa, with a polydispersity index (PDI) of 1.8. Thermogravimetric analysis showed an excellent thermal stability with a decomposition temperature of 337 °C without the protection of an inert atmosphere.

As shown in Figure 1 a, PBDTTBT shows three absorption bands in the range 300–700 nm both in chloroform and as a solid film. The main absorption peak of PBDTTBT is located at approximately 581 nm in solution. However, this peak is red-shifted to 596 nm in solid films and showed a stronger shoulder at 627 nm, which could be attributed to a more aggregated configuration in the solid state. The absorption edges of 695 and 708 nm in solution and the solid film correspond to optical band gaps (E_g^{opt}) of 1.78 and 1.75 eV for PBDTTBT, respectively.



Scheme 2. Synthesis route of the polymer PBDTTBT. R = n-C_8H_{17}. a) *n*-Butyllithium, −78 °C, 2 h, then n-$C_8H_{17}Br$, 14 h; b) *n*-butyllithium, THF, 0 °C, then 50 °C, 2 h; benzo[1,2-*b*:4,5-*b*′]dithiophen-4,8-dione, 50 °C, 1 h, then $SnCl_2$, HCl; c) *n*-butyllithium, THF, ambient temperature, 2 h; then borolane, ambient temperature, 6 h; d) [Pd(PPh_3)$_4$], toluene, reflux, 18 h.

Cyclic voltammetry (CV) was used to measure oxidation and reduction potentials. PBDTTBT presents one reversible p-doping ($E_{ox} = 0.51$ V vs. ferrocene/ferrocenium (Fc/Fc^+)) and one irreversible n-doping ($E_{red} = -1.36$ V vs. Fc/Fc^+) process (Figure 1 b). The HOMO (−5.31 eV) and LUMO (−3.44 eV) of PBDTTBT could be calculated from these electrochemical results. Compared to the HOMO of P3HT (−5.0 eV), that of PBDTTBT is 0.3 eV lower and is analogous to those of poly[(9,9-dialkylfluorene)-2,7-diyl-*alt*-(4,7-bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5′-diyl] (PFDTBT), PSiFDBT, and PCDTBT (−5.5 eV, −5.39 eV, and −5.5 eV, respectively), which means a higher V_{oc} could be expected, because V_{oc} is linearly correlated with the difference of the HOMO of the donor and the LUMO of the acceptor.[3a] Furthermore, the electrochemical band gap of PBDTTBT ($E_g^{ec} = 1.87$ eV) is well matched with its optical band gap ($E_g^{opt} = 1.75$ eV) within the experimental error.

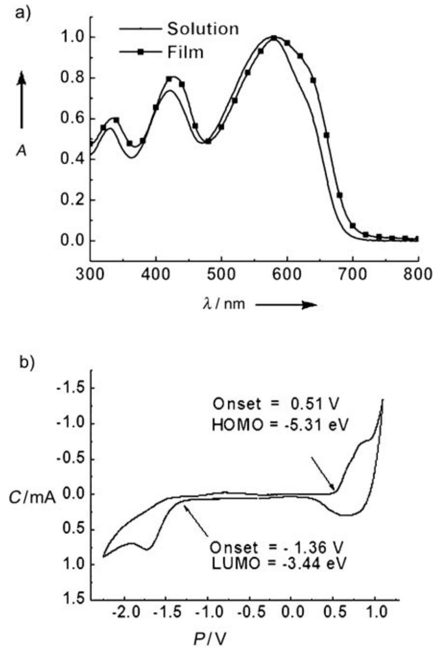


Figure 1. a) Absorption spectra of PBDTTBT as a film and in chloroform solution. b) Cyclic voltammograms of PBDTTBT films on a platinum electrode in 0.1 mol L^{-1} Bu_4NPF_6, CH_3CN solution.

To further explore the photovoltaic properties of PBDTTBT, solar cell devices were fabricated. Figure 2 a presents a typical *J–V* curve of the device. PCEs up to 5.66 % were obtained from the PBDTTBT-based device, with a V_{oc} of 0.92 V, a J_{sc} of 10.7 mA cm^{-2}, and an fill factor (FF) of 57.5 %, which is one of the highest PCEs for single-active-layer PSCs. The higher V_{oc} agrees well with the low-lying HOMO level calculated from electrochemical results. It is worth noting that the high performance of PBDTTBT solar cells was obtained without the need for extra treatments such as annealing or additive addition. There should be more space to improve the performances with development of new processing techniques. The internal quantum efficiency (IQE) and external quantum efficiency (EQE) of the device are shown in Figure 2 b. It is apparent that the device exhibits a very high IQE above 80 % with a broad response from 300 to 700 nm, which validates the

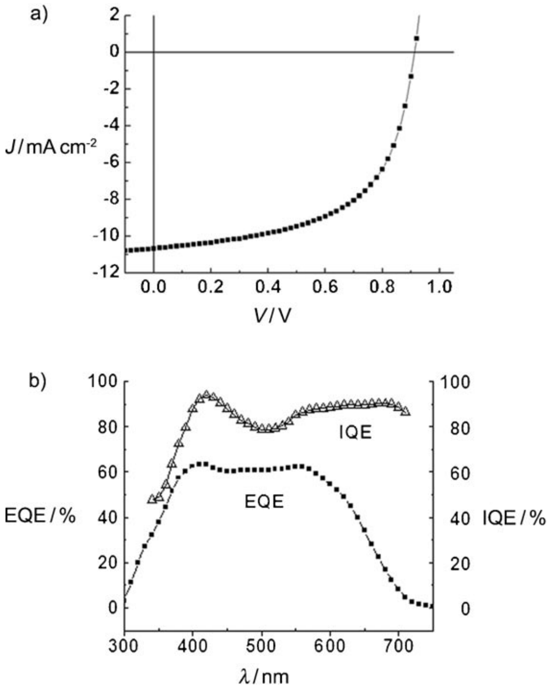


Figure 2. a) *J–V* curve of a PBDTTBT/$PC_{70}BM$-based solar cell device under illumination of AM1.5G, 100 mWcm^{-2}. b) External quantum efficiency (EQE) and internal quantum efficiency (IQE) of a PBDTTBT/$PC_{70}BM$-based solar cell device.

efficient photon conversion properties of this system. Such a broad response above 50% EQE has seldom been reported. Such high EQE values are the main contribution behind the high J_{sc}. Additionally, when $PC_{61}BM$ was used instead of $PC_{71}BM$, the J_{sc} of the device decreased owing to the narrower absorption band of $PC_{61}BM$ than $PC_{71}BM$.

In conclusion, we have reported a new benzo[1,2-*b*:4,5-*b*′]dithiophene-containing polymer PBDTTBT that exhibited a PCE of up to 5.66% under AM1.5G 100 mWcm^{-2} illumination. The higher V_{oc} of 0.92 V from PBDTTBT-based device originates from the lower HOMO level of the polymer and the higher IQE (above 80%) and the EQE response value beyond 50% in a wide spectral range are the main contributions to high J_{sc}. These results indicate that PBDTTBT is a promising polymer donor material for application in polymer solar cells.

Experimental Section

Instruments and measurements: The absorption spectra were obtained from a Varian Cary 50 UV/Vis spectrophotometer. The current–voltage (*J–V*) curves were obtained by a Keithley 2400 source-measure unit. The photocurrent was measured under illumination using a solar simulator [ThermoOriel 150W solar simulator (AM1.5G)], and the light intensity was calibrated with a Newport 818T-10 thermopile detector. To ensure accuracy, the simulated light-source and device area were calibrated by the method in our previous work.[9] The EQE measurements of the encapsulated devices were performed in air [PV Measurements Inc., Model QEX7]. The internal quantum efficiency (IQE) of the device was calibrated according to the our previous work.[10] Cyclic voltammetry was conducted with a Pt disk coated with the polymer film, a Pt wire, and a Ag electrode as working electrode, counter electrode, and reference electrode, respectively, in a 0.1 molL^{-1} tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution; a trace amount of ferrocene was used as reference material.

Device fabrication: Polymer solar cell devices with the structure ITO/PEDOT-PSS/polymer:$PC_{70}BM$(1:2, w/w)/Ca/Al were fabricated as follows: After spin-coating a 30 nm layer of poly(3,4-ethylene dioxythiophene):poly(styrenesulfonate) onto a precleaned indium tin oxide (ITO) coated glass substrate, the polymer/PCBM blend solution was spin-coated. Typical concentration of the polymer/$PC_{70}BM$ (1:2, w/w) blend solution for spin-coating the active layer was 10 mgmL^{-1}, and dichlorobenzene was used as solvent. To optimize device performance, different donor/acceptor (D/A) weight ratios (1:1 to 1:4) were used during the device fabrication process. However, it was found that the 1:2 D/A ratio gave the best device performance. The thickness of the active layer was approximately 80 nm.

1: Under the protection of argon, *n*-butyllithium (2.88 M, 28.1 mL) was added dropwise to 3-octylthiophene (14.45 g, 73.7 mmol) in THF (150 mL) at −78 °C over about 2 h, then the mixture was stirred for 1 h at −78 °C. The cooling bath was removed and the mixture was stirred for another 1 h at room temperature. 1-Bromooctylane (21.23 g, 110 mmol) was injected in one portion at room temperature; then the solution was stirred overnight. After 14 h the reaction was stopped and water (100 mL) was added, and the mixture was extracted with diethyl ether twice. After removing the solvent, the residual oil was distilled in high vacuum to obtain **1** as a colorless liquid (13.07 g, yield 57.4%). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 6.69$ (s, 1H), 6.63 (s, 1H), 2.81 (t, 2H), 2.54 (t, 2H), 1.70 (m, 4H), 1.35 (m, 20H), 0.91 ppm (t, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 145.59$, 142.90, 125.43, 117.08, 31,92, 31.74, 30.47, 29.76, 29.45, 29.32, 22.72, 14.13 ppm.

2: Under the protection of argon, *n*-butyllithium (2.88 M, 7.64 mL) was added dropwise to **1** (6.20 g, 20 mmol) in THF (16 mL) at 0 °C; then the mixture was warmed up to 50 °C and stirred for 2 h. Subsequently, 4,8-dehydrobenzo[1,2-*b*:4,5-*b*′]dithiophene-4,8-dione (1.1 g, 5 mmol) was added, and the mixture was stirred for 1 h at 50 °C. After cooling down to ambient temperature, $SnCl_2 \cdot 2H_2O$ (9.0 g, 40 mmol) in 10% HCl (16 mL) was added, and the mixture was stirred for an additional 1.5 h and poured into ice water. The mixture was extracted by diethyl ether twice, and the combined organic phase was concentrated to obtain raw **2**. Further purification was carried out by column chromatography using petroleum ether as eluent to obtain pure **2** as a light yellow liquid (1.76 g, yield 44.1%). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.39$ (d, 2H), 7.24 (d, 2H), 6.80 (s, 2H), 2.86 (t, 4H), 2.39 (t, 4H), 1.75 (m, 8H), 1.36 (br, 40H), 0.92–0.81 ppm (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 145.79$, 141.24, 141.05, 140.09, 137.72, 130.27, 127.36, 125.72, 123.76, 31.84, 31.50, 30.37, 29.38, 29.21, 29.11, 22.66, 14.12 ppm.

3: Under the protection of argon, *n*-butyllithium (2.88 M, 2.48 mL) was added dropwise to **2** (2.60 g, 3.24 mmol) in THF (35 mL) at room temperature and stirred for 2 h at 50 °C. Then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.5 g, 8.1 mmol) was added in one portion at room temperature. After 6 h, the reaction was stopped and water (120 mL) was added, and then the mixture was extracted by diethyl ether twice. After removing the solvent, the residue was purified by column chromatography with petroleum ether/ethyl acetate (10:1) as eluent to obtain pure **3** as a yellow, sticky liquid (2.61 g, yield 76.2%). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.79$ (s, 2H), 6.75 (s, 2H), 2.82 (m, 4H), 2.36 (m, 4H), 1.75 (m, 8H), 1.34–1.27 (br, 64H), 0.91–0.81 ppm (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta =$ 145.79, 143.77, 141.40, 141.20, 139.53, 133.39, 129.94, 125.60, 124.56, 84.42, 31.83, 31.53, 30.34, 29.39, 29.26, 29.14, 24.73, 22.66, 14.14 ppm.

4,7-Di(2-bromothien-5-yl)-2,1,3-benzothiadiazole and 4,8-dehydrobenzo[1,2-*b*:4,5-*b*′]dithiophene-4,8-dione were synthesized according to the reported method.[7,8]

Polymerization to PBDTTBT: 4,7-Di(2-bromothien-5-yl)-2,1,3-benzothiadiazole (160 mg, 0.35 mmol) and **3** (369 mg, 0.35 mmol) were dissolved in 15 mL toluene with sodium carbonate (1 M, 3 mL). The mixture was purged with argon for 10 min, then [Pd(PPh$_3$)$_4$] (15 mg) was added. After being purged with argon for 20 min, the reaction was heated to 110 °C for 18 h under argon atmosphere. Then, the mixture was cooled to room temperature, and the polymer was precipitated by addition of 100 mL methanol and filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction with methanol, hexane, and chloroform. The polymer recovered from chloroform was purified by preparative gel permeation chromatography. Then, the product was dried under vacuum for 1 day to recover the target polymer PBDTTBT as a dark solid.(yield 34 %, M_n = 27.4 K, PDI = 1.8). ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.99–6.81 (m, 10 H), 2.91 (br, 4 H), 2.39 (br, 4 H), 1.80 (m, 8 H), 1.48–1.26 (m, 40 H), 1.07–0.75 ppm (m, 12 H). Calcd for $C_{64}H_{78}N_2S_7$: C 69.89, H 7.15, N 2.55; found: C 68.97, H 7.12, N 2.51.

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