Novel Benzo[1,2-*b*:4,5-*b′*]dithiophene–Benzothiadiazole Derivatives with Variable Side Chains for High-Performance Solar Cells

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Polymer solar cells (PSCs) have attracted considerable attention because of their advantages of low cost, light weight, and flexibility in large area applications by ink-jet printing and roll-to-roll solution processes.[1] The concept of bulk heterojunction (BHJ) has improved the power conversion efficiencies (PCEs) of the PSCs significantly by blending electron-donating conjugated polymers and electron-accepting fullerene derivatives (such as [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) and [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$)).[2] In the past few years, regioregular poly(3-hexylthiophene) (P3HT) and $PC_{61}BM$ based PSCs were taken as standard BHJ devices with high efficiencies of 4–5%.[3] However, the improvement of PCEs was limited in these devices by their low open circuit voltages (V_{oc}) and narrow absorption spectra. Aiming at achieving broader absorption, higher hole mobility, and more suitable energy levels, low bandgap (LBG) conjugated polymers were developed rapidly to be the alternatives of P3HT with efficiency values over 7%.[1c,1d,4]

Previous work has verified that V_{oc} is directly proportional to the difference between the highest occupied molecular orbital (HOMO) energy level of a conjugated polymer and the lowest unoccupied molecular orbital (LUMO) energy level of a fullerene derivative.[5] So lowering of the HOMO level of a donor will result in a high V_{oc} efficiently. At the same time, a small bandgap is necessary to increase the short circuit current (J_{sc}). In order to obtain high PCEs, the ideal bandgaps of electron-donating polymers should be 1.2–1.8 eV with HOMOs of –5.2 to –5.8 eV and LUMOs of –3.7 to –4.0 eV.[6] Our previous work has described that the HOMO and LUMO energy levels depend on the electronic states of the donor (D)[7] and acceptor (A) moieties[8] in D–A systems. Therefore, we designed low bandgap (LBG) conjugated copolymers with desired deep HOMO and LUMO energy levels by incorporating more electron-rich donors and electron-deficient acceptors. Herein, we report the synthesis of two D–A alternating copolymers, PBDT-OBT and PBDT-FBT, by polymerizing modified benzo[1,2-*b*:4,5-*b′*]dithiophene (BDT) and benzothiadiazole (BT) as the D and A segments, respectively (**Scheme 1**a). BDT has a large and planar molecular structure by fusing a benzene with two flanking thiophene units. Some BDT-containing copolymers show great potential in PSCs with enhanced mobilities and high PCEs surpassing 7% attributable to efficient cofacial π–π stacking.[1d,9] Among the variety of electron deficient acceptors, BT has attracted much attention for its special property of controlling the energy levels for D–A conjugated copolymers.[1b,1e,10] High performance PSCs were achieved by blending BT-based copolymers and fullerene derivatives, such as benzo[1,2-*b*:4,5-*b′*]dithiophene-BT, cyclopenta[2,1-*b*;3,4-*b′*]dithiophene-BT, dithienosilole-BT, dithieno[3,2-*b*:2′,3′-*d*]pyrrole-BT, carbazole-BT, and indolo[3,2-*b*]carbazole-BT alternating copolymers.[1b,1e,10] Here, we attached thiophene groups to the phenyl ring of BDT to afford a more electron-rich donor giving rise to a lower HOMO level. On the other hand, the BT unit as acceptor was also modified here with alkyloxy (a slightly more electron-rich) and fluorine (electron-deficient) moieties. Since the introduction of a fluorine atom leads to a more delocalized LUMO wave function, it can lead to a lower LUMO level to achieve higher J_{sc} and PCE.[1d,11,12] The photovoltaic properties of the prepared copolymers were investigated in typical BHJ devices using $PC_{71}BM$ as the acceptor. High PCEs of 5.64% and 6.21% were obtained for PBDT-OBT and PBDT-FBT, respectively.

The synthesis of monomers **1**, **2**, **3**, and **4** was modified from the reported procedures[1e,10e,11] (see the Supporting Information). The copolymers were synthesized by a Stille coupling reaction using $Pd_2(dba)_3/P(o\text{-tolyl})_3$ as catalyst in good yields as shown in Scheme 1b (see the Experimental Section). Crude copolymers were purified by extracting with methanol, hexane, and chloroform, respectively. The chloroform solution was concentrated and the product reprecipitated in methanol several times to give the resulting copolymers. Gel permeation chromatography analysis showed that both copolymers had high molecular weights. Thermogravimetric analysis also showed that these copolymers with the decomposition temperatures of 342 and 367 °C for PBDT-OBT and PBDT-FBT, respectively, had good thermal stability for application in PSCs and other optoelectronic devices of light emitting diodes and field effect transistors.

The UV-vis absorption spectra of the copolymers in chloroform solution and thin solid films are shown in **Figure 1**a. Both polymers showed relatively similar absorption curves with two absorption bands observed commonly from D–A conjugated copolymers. The main absorption peaks are located at about 574

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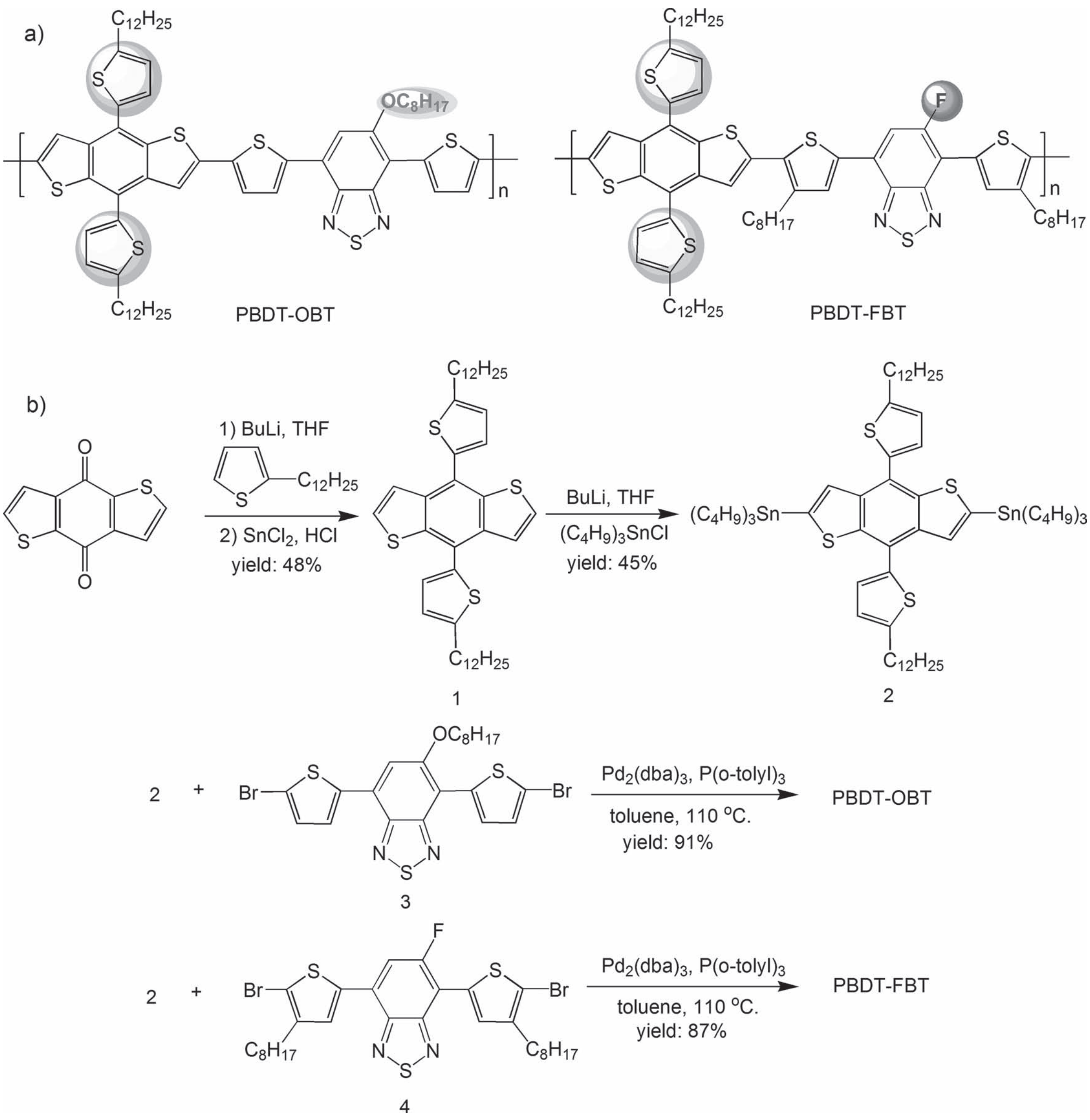

Scheme 1. a) Molecular structures of PBDT-OBT and PBDT-FBT. b) Synthesis routes of the copolymer PBDT-OBT and PBDT-FBT.

and 581 nm in solution for PBDT-OBT and PBDT-FBT, respectively, which are attributed to the intramolecular charge transfer interaction in D–A systems. However, the absorption spectra become broader in solid films with two absorption bands like their solution bands, that peaked at about 604 and 621 nm for PBDT-OBT and PBDT-FBT, respectively. The large red-shifts of

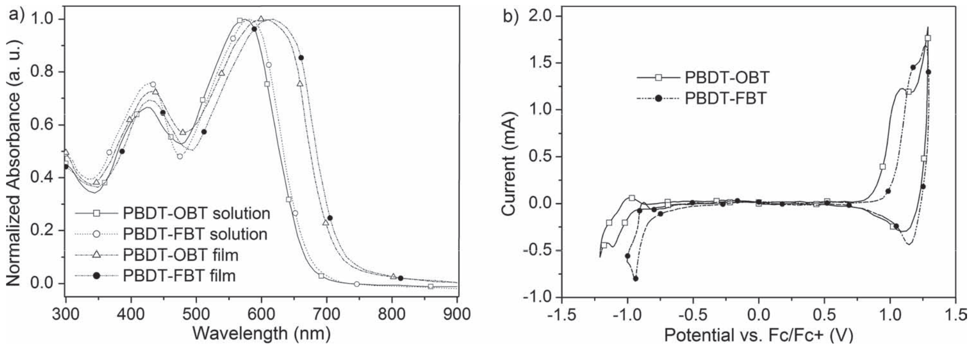

Figure 1. a) UV-vis absorption spectra of PBDT-OBT and PBDT-FBT in chloroform solution and in solid films. b) Electrochemical cyclic voltammetry curves of PBDT-OBT and PBDT-FBT.

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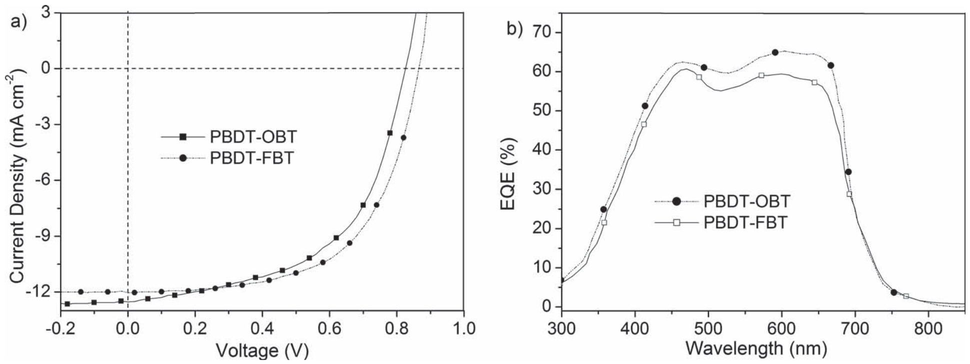

Figure 2. a) Current density–voltage (*J*–*V*) curves of copolymer/PC$_{71}$BM based solar cells under AM 1.5 G illumination, 100 mW cm^{-2}. b) External quantum efficiency (EQE) curves of copolymer/PC$_{71}$BM based solar cell devices.

30 and 40 nm indicate more planar polymer chain structures and more effective interchain π–π stacking in the solid state. The optical bandgaps of PBDT-OBT and PBDT-FBT were 1.67 and 1.63 eV determined from the onsets of the UV-vis absorption in solid films.

The HOMO and LUMO energy levels of these polymers were measured by cyclic voltammetry (CV). The method was described in our previous work.[8c] The energy level of the Ag/AgCl reference electrode (calibrated against the FC/FC$^+$ redox system) was 4.40 eV below the vacuum level.[8c] Calculated from the onset potentials of the oxidation and reduction curves (shown in Figure 1b), the HOMO and LUMO levels of PBDT-OBT and PBDT-FBT were –5.32 and –3.58 eV, and –5.41 and –3.72 eV, respectively. The HOMO levels are analogous to those of BDT-based LBG polymers (–5.30 to –5.50 eV), which can be expected to achieve high V_{oc} in PSCs according to the linear correlation of the difference of the HOMO of the donor and the LUMO of the accepter.[5,8b] These polymers are also expected to be more stable than P3HT (–5.0 eV) because of their deeper HOMO levels.[1e] The thiophene side units and alkyloxy groups can slightly lower the HOMO levels of the polymers around the corresponding ideal energy level of –5.4 eV.[1f] It is interesting to note that the electron-deficient fluorine groups substantially lower both the HOMO and LUMO levels. Compared with PBDT-OBT, a lower ΔHOMO of 0.09 eV and ΔLUMO of 0.14 eV was achieved by the introduction of fluorine atoms, which indicated that PBDT-FBT would be a promising photovoltaic material with high efficiency. The result agrees well with the report that the incorporation of fluorine is effective to control the HOMO and LUMO energy levels as described in Yu's previous work.[12] The electrochemical bandgaps were also calculated to be 1.74 and 1.69 eV for PBDT-OBT and PBDT-FBT, respectively.

Table 1. Photovoltaic properties of PBDT-OBT and PBDT-FBT based BHJ solar cell devices with a copolymer/PC$_{71}$BM (1:2, w/w) blend in chlorobenzene.

Copolymer	Thickness [nm]	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF [%]	PCE$_{max}$ (PCE$_{average}$) [%]
PBDT-OBT	90	12.53	0.82	54.9	5.64 (5.50)
PBDT-FBT	95	12.05	0.86	59.9	6.21 (6.08)

To investigate the photovoltaic properties of these polymers, BHJ devices were fabricated with a typical configuration of ITO/PEDOT:PSS/copolymer:PC$_{71}$BM/Ca/Al. Here, ITO, PEDOT, and PSS refer to indium tin oxide, poly(3,4-ethylenedioxythiophene), and polystyrene sulfonic acid, respectively. **Figure 2**a shows the typical current density–voltage (*J*–*V*) characteristics. The device data are summarized in **Table 1**. A PCE of 5.64% was achieved from a PBDT-OBT based device with a V_{oc} of 0.82 V, a J_{sc} of 12.53 mA cm^{-2}, and a fill factor (FF) of 54.9%. When PBDT-FBT with deep HOMO and LUMO levels was used in BHJ devices, an improved V_{oc} and FF were obtained, giving rise to a higher PCE of 6.21%. The theoretical maximum J_{sc} of a device is largely dependent on the bandgap of the conjugated polymer.[2b,13] As investigated above, PBDT-FBT has a relatively lower bandgap, which allows a higher J_{sc} in the devices. However, the J_{sc} in the PBDT-FBT based device is slightly smaller than that of PBDT-OBT. The reason can mainly be attributed to the alkyl side chains of the thiophene rings near the BT group which increase the solubility of the copolymer, but to twist the aromatic rings to increase the distance between polymer chains and thus affects the packing status. The external quantum efficiency (EQE) of the BHJ devices was measured to test the accuracy of the above investigation, and the EQE curves are shown in Figure 2b. All the devices showed a high incident PCE with a broad response from 300 to 750 nm. The J_{sc} calculated by integrating the EQE curves with a AM1.5G reference spectrum match the *J*–*V* measurements within 5% error. The EQE for the PBDT-FBT based device decreases slightly compared with that of PBDT-OBT because the effective chromophore density in the solid film state is lower in the case of PBDT-FBT due to the presence of the alkyl side chains, which do not contribute to harvesting energy from sunlight and packing the polymer mainchains. This also agrees well with the result of a lower J_{sc} observed for the PBDT-FBT based device. The surface morphology of a blended film of copolymer and PC$_{71}$BM was studied by atomic force microscopy (AFM). As shown in Figure S1 (Supporting Information) the film from PBDT-OBT with PC$_{71}$BM shows less roughness with an average roughness (R_a) of 1.86 nm. However, the film from PBDT-FBT and PC$_{71}$BM shows clear domains with a higher R_a of 2.30, which is helpful for charge separation, and thus improves the FF of the device.

In conclusion, we have reported two novel LBG copolymers that incorporate modified BDT and BT as donor and acceptor moieties. The attached thiophene side chains on the phenyl ring of BDT were designed to afford a more electron-rich donor to lower HOMO levels. On the other hand, the BT unit as acceptor was also modified with alkyloxy and fluorine moieties. The resulting copolymers showed the desired deep HOMO and LUMO energy levels allowing a high V_{oc} and J_{sc}. The photovoltaic properties of the prepared copolymers were investigated in typical BHJ devices using $PC_{71}BM$ as the acceptor with high PCEs of 5.64 and 6.21%. Therefore, these copolymers are promising donor materials for application in polymer solar cells.

Experimental Section

Materials and Instruments: All reagents were purchased from Aladdin Co., Alfa Aesar Co., and Aldrich Chemical Co., and used without further purification. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer with *d*-chloroform as the solvent and tetramethylsilane as the internal standard. The elemental analysis was performed on a Thermo Electron SPA Flash EA1112 series analyzer. Cyclic voltammetry measurements were made on an CHI660 potentiostat/galvanostat electrochemical workstation at a scan rate of 50 mV s^{-1}, with a platinum wire counter electrode and a Ag/AgCl reference electrode in an anhydrous and nitrogen-saturated 0.1 mol L^{-1} acetonitrile solution of tetrabutylammonium perchlorate. The copolymers were coated onto the platinum plate working electrodes from dilute chloroform solutions. UV-vis spectra were obtained on a Carry 300 spectrophotometer. Thermogravimetric analysis was conducted on a TA Instrument Model SDT Q600 simultaneous TGA/DSC analyzer at a heating rate of 10 °C min^{-1} and under a N_2 flow rate of 90 mL min^{-1}.

Device Fabrication: Polymer solar cells were fabricated with ITO glass as an anode, Ca/Al as a cathode, and a blend film of the copolymer and $PC_{71}BM$ as a photosensitive layer. After spin-coating a 30 nm layer of PEDOT:PSS onto the precleaned ITO substrate, the photosensitive layer was subsequently prepared by spin-coating a blend solution of the copolymer and $PC_{71}BM$ (w/w) in chlorobenzene on the ITO/PEDOT:PSS electrode with a typical concentration of 10 mg mL^{-1}. Different donor and acceptor weight ratios (1:1 to 1: 4) were used to optimize the BHJ device performance. In this work, a donor and acceptor ratio of 1:2 was found to obtain the best performance for these two copolymer-based devices. The current–voltage (*I*–*V*) characterization of the devices was carried out on a computer-controlled Keithley 236 Source Measurement system. A solar simulator was used as the light source, and the light intensity was monitored by a standard Si solar cell. The thickness of films was measured using a Dektak 6 M surface profilometer.

PBDT-OBT: 4,7-Bis(5-bromothiophen-2-yl)-5-octyloxy-benzo[1,2,5] thiadiazole (**3**) (210.5 mg, 0.5 mmol) and monomer **2** (317 mg, 0.25 mmol) were dissolved in 15 mL of toluene. The solution was flushed with argon for 10 min, and then Pd_2dba_3 (9.2 mg, 2 mol%) and $P(o\text{-tolyl})_3$ (16.36 mg, 8%) were added into the flask. The flask was purged three times with successive vacuum and argon filling cycles. The polymerization reaction was heated to 110 °C, and the mixture was stirred for 48 h under argon atmosphere. 2-Tributylstannyl thiophene (20 μL) was added to the reaction. After two hours, 2-bromothiophene (6.3 μL) was added. The mixture was stirred overnight to complete the end-capping reaction. The mixture was cooled to room temperature and poured slowly in 350 mL of methanol. The precipitate was filtered and washed with methanol and hexane in a soxhlet apparatus to remove the oligomers and catalyst residue. Finally, the polymer was extracted with chloroform. The solution was condensed by evaporation and precipitated into methanol. The polymer was collected as a dark purple solid with a yield of 91% (508 mg). ^1H NMR (400 MHz, $CDCl_3$, δ): 7.99–7.96 (m, 4H), 7.36–7.19 (m, 3H), 6.98–6.69 (m, 4H), 4.23 –3.98 (t, 2H), 2.85–2.76 (m, 4H), 1.78–1.19 (m, 52H), 0.98–0.80 (br, 9H). Anal. calcd for $(C_{64}H_{78}N_2S_7O)_n$: C 69.90, H 7.05, N 2.51, S 20.11; found: C 68.95, H 7.09, N 2.46, S 20.23. M_n = 19.2 kDa; M_w = 40.90 kDa; PDI = 2.13.

PBDT-FBT: PBDT-FBT was synthesized from monomers 2 and 4 as a dark purple solid with a yield of 87% according to the method of PBDT-OBT described above. ^1H NMR (400 MHz, $CDCl_3$, δ): 8.21–8.14 (m, 4H), 7.42–7.20 (m, 3H), 7.06–6.75 (m, 2H), 3.21–3.15 (m, 4H), 2.92–2.83 (m, 4H), 1.80–1.22 (m, 64H), 1.02–0.78 (br, 12H). Anal. calcd for $(C_{72}H_{93}N_2S_7F)_n$: C 70.31, H 7.62, N 2.28, S 18.25; found: C 70.02, H 7.58, N 2.31, S 18.33. M_n = 22.7 kDa; M_w = 58.6 kDa; PDI = 2.58.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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