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Synthesis and Photovoltaic Properties of a Copolymer of Benzo[1,2-b:4,5-b′]dithiophene and Bithiazole

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In the past few years, bulk-heterojunction polymer solar cells (PSCs) have attracted much attention because of their advantages of low cost, easy fabrication, light weight, and the capability to fabricate flexible large-area devices.[1,2] In typical PSCs, conjugated polymers and fullerene derivatives function as the electron-donor and electron-acceptor materials, respectively. Poly(3-hexylthiophene) (P3HT) is the most representative donor and [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{60}BM$) is the most popular acceptor material, and the power conversion efficiency (PCE) of the PSCs based on P3HT/$PC_{60}BM$ has reached over 4%.[3] Nevertheless, the higher HOMO energy level (ca. −4.76 eV[4]) of P3HT results in lower open-circuit voltage (V_{oc}) (ca. 0.6 V) of the PSCs based on P3HT/$PC_{60}BM$ and thus limits the photovoltaic performance of the devices. Therefore, new conjugated polymers with deeper HOMO energy level are pursued in recent years for improving the V_{oc} of the PSCs.

One feasible approach to drop down the HOMO energy level is to design alternating donor−acceptor copolymers, where suitable donor and acceptor units can provide a deeper HOMO energy level. And in the meantime the absorption spectra of the copolymers can be red-shifted by the charge-transfer absorption of the D−A structure, which is also preferred for high-efficiency polymer photovoltaic materials. In recent years, various D−A copolymers have been successfully synthesized and used for the PSCs.[5−8] Especially, copolymers containing benzo[1,2-b:4,5-b′]dithiophene (BDT) as the donor unit have exhibited outstanding photovoltaic properties for the applications in PSCs.[9−14] For instance, the PSCs based on poly(DBT-thieno[3,4-b]thiophene) derivatives can achieve high power conversion efficiency (PCE) higher than 7% with a higher V_{oc} of 0.76 V.[10b]

In our previous work, we synthesized a series of D−A copolymers based on bithiazole (BTz) as acceptor unit for the photovoltaic application and attained relatively higher PCE of 2.86%,[15] which indicates that bithiazole is a good acceptor unit. So in this Communication, we synthesized a new D−A copolymer PBDTBTz (Scheme 1) by copolymerizing the BDT donor unit and the BTz acceptor unit for the application as donor material in PSCs. PBDTBTz shows a deeper HOMO energy level at −5.15 eV. The PCE of the PSC based on PBDTBTz as donor and [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{70}BM$) as acceptor reached 3.82% with $V_{oc} = 0.86$ V under the illumination of AM1.5, 100 mW cm$^{−2}$.

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PBDTBTz was synthesized by the Stille coupling reaction using Pd (PPh$_3$)$_4$ as the catalyst (see Scheme 1). The copolymer has good solubility in common organic solvents such as chloroform, toluene, chlorobenzene, and so on. The weight-average molecular weight (M_w) of PBDTBTz is 6.4K with a polydispersity index (PDI) of 1.95.

The thermal stability was analyzed by thermogravimetric analysis (TGA). The TGA analysis reveals that the onset temperature with 5% weight loss of PBDTBTz is 249 °C, as shown in Figure S1 in the Supporting Information. This indicates that the thermal stability of the copolymer is good enough for the application in optoelectronic devices.
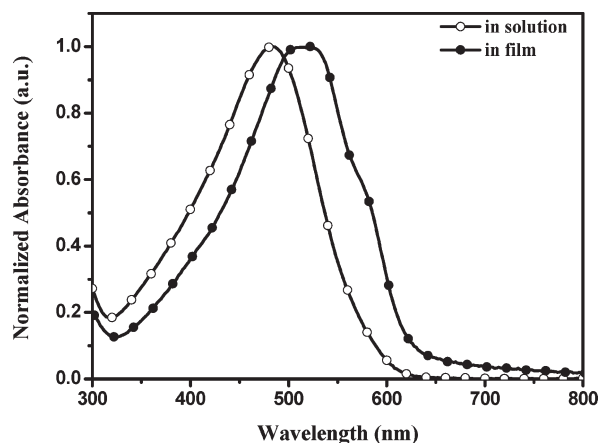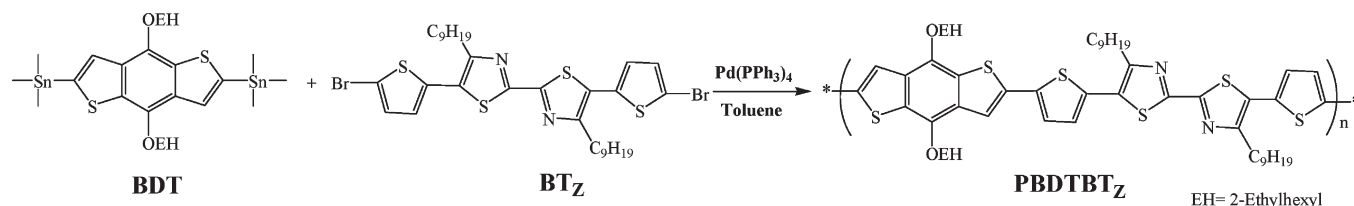
Figure 1 shows the absorption spectra of PBDTBTz in dilute chloroform solution and in solid film. The polymer solution shows an absorption spectrum with the absorption maximum at 480 nm. The absorption spectrum of the polymer film displays an absorption peak at 530 nm, red-shifted by 50 nm in comparison with the polymer solution, indicating strong intermolecular interaction in the polymer film. The shape of the absorption peak of PBDTBTz film is similar to that of poly(3-hexylthiophene) (P3HT) film with a little blue shift than P3HT. The optical band gap of PBDTBTz deduced from the absorption edge (ca. 630 nm) of the polymer film is 1.97 eV.

To investigate the molecular organization, the XRD pattern of the thin film of PBDTBTz on the silicon substrate was measured, as shown in Figure S2 in the Supporting Information. There are two peaks in the XRD pattern: one is a small and sharp peak at small angle of $2\theta = 5.0°$, and another is a broad peak centered at $2\theta = 24−25°$. These two peaks reveal that the intermolecular lamellar d-spacing and the $\pi−\pi$ stacking distance are 17.6 Å ($2\theta = 5.0°$) and 3.6 Å ($2\theta = 24−25°$), respectively. The intermolecular lamellar d-spacing was assigned to the interchain spacing between polymer main chains, where the alkyl substituents were segregated as reported for similar π-conjugated polymers with long side chains.[16,17] In comparison with regioregular P3HT where the lamellar d-spacing is 16.4 Å and $\pi−\pi$ stacking distance is 3.8 Å,[18] the lamellar d-spacing of 17.6 Å is larger and $\pi−\pi$ stacking distance of 3.6 Å is a little smaller for PBDTBTz. It suggests that the π-conjugated polymers containing thiazole units had a stronger tendency to form the face-to-face stacking than those containing thiophene units.[16]

Electrochemical cyclic voltammetry was performed for determining the HOMO and LUMO energy levels of the conjugated polymers.[19] As shown in the cyclic voltammogram of PBDTBTz (see Figure 2), the onset reduction potential (φ_{red}) is −1.76 V vs Ag/Ag$^+$, while the onset oxidation potential (φ_{ox}) is 0.44 V vs Ag/Ag$^+$. The HOMO and LUMO energy levels as well as the energy gap (E_g^{EC}) of the polymer were −5.15, −2.95, and 2.2 eV, respectively, calculated from φ_{ox} and φ_{red}.[4,20] The HOMO energy level of the polymer is significantly deeper than that (−4.76 eV)[4] of P3HT. The deeper HOMO level at −5.15 eV for the polymer implies that the polymer could be more stable against oxidization, which will enhance the device stability. And the deeper HOMO level provide a higher V_{oc} for the PSCs with the polymer as donor, since V_{oc} of PSCs is related to the difference of the LUMO of the acceptor and the HOMO of the donor.[21]

The hole mobility of PBDTBTz was measured to be 6.84 × 10$^{−4}$ cm^2 V$^{−1}$ s$^{−1}$ by the space-charge-limited current (SCLC)

Scheme 1. Synthesis and Molecular Structure of PBDTBTz

EH= 2-Ethylhexyl

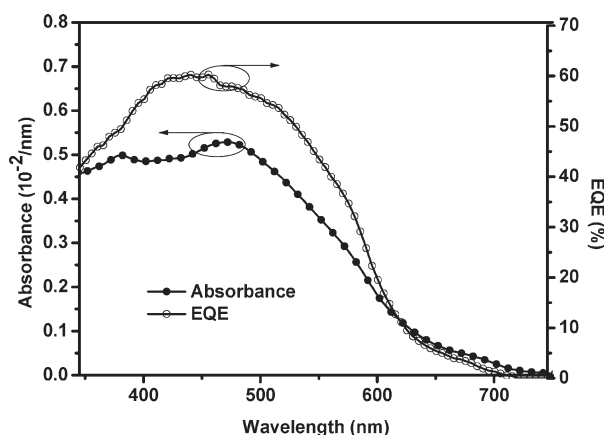
Figure 1. Optical absorption spectra of PBDTBTz in chloroform solution and film state.
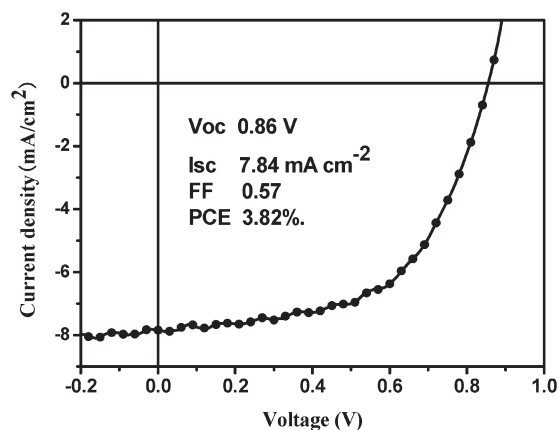
Figure 3. $I-V$ curve of the polymer solar cell based on PBDTBTz: $PC_{70}BM$ = 1:1 (w/w) under the illumination of AM 1.5, 100 mW cm^{-2}.
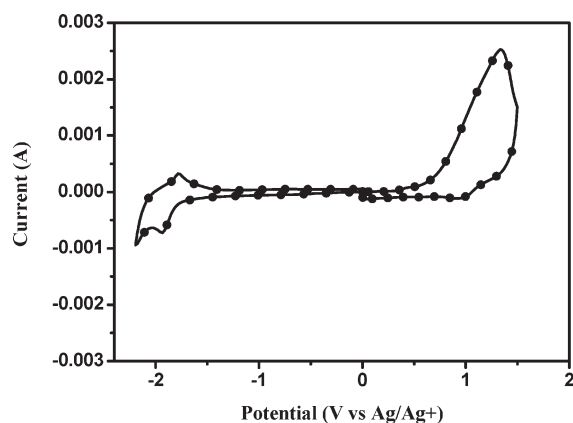
Figure 2. Cyclic voltammogram of PBDTBTz film on a platinum electrode measured in 0.1 mol L^{-1} Bu$_4$NPF$_6$ acetonitrile solution at a scan rate of 100 mV s^{-1}.

Figure 4. External quantum efficiency (EQE) and absorption spectrum of the PSC based on PBDTBTz/PC$_{70}$BM.

method (see Supporting Information for details), indicating that PBDTBTz possesses good hole transporting property owing to its rigid and coplanar structure.

Photovoltaic properties of PBDTBTz were investigated by fabricating the PSCs based on PBDTBTz as donor and PC$_{70}$BM as acceptor with the device structure of ITO/PEDOT: PSS/PBDTBTz:PC$_{70}$BM (1:1, w:w)/Al. The current density−voltage characteristic of the device under the illumination of AM1.5, 100 mW cm^{-2} is shown in Figure 3. The PSC based on PBDTBTz showed a V_{oc} of 0.86 V, I_{sc} of 7.84 mA cm^{-2}, and FF of 0.57, leading to a power conversion efficiency (PCE) of 3.82%. The high V_{oc} of 0.86 V of the PSC should benefit from the lower HOMO energy level of PBDTBTz because V_{oc} is proportional to the difference between the lowest unoccupied molecular orbital (LUMO) level of the acceptor and the HOMO level of the donor.[21,22]

The external quantum efficiency (EQE) of the PSC based on PBDTBTz: PC$_{70}$BM (1:1, w/w) and the absorption spectrum

of the blend film of PBDTBTz: PC$_{70}$BM (1:1, w/w) are shown in Figure 4. Comparing the absorption spectrum of the bend film with that of pure PBDTBTz film (Figure 1), significant increase of the absorbance in the wavelength range of 350−500 nm was observed owing to the absorption of PC$_{70}$BM. The device shows rather efficient photoconversion efficiency between 350 and 600 nm with the maximum EQE value as high as 60.2% at the wavelength of ca. 450 nm. The morphology of the blend film of PBDTBTz and PC$_{70}$BM was observed by atomic force microscopy (AFM) (see Figure S3 in the Supporting Information). The film shows small roughness with a R_a of 0.61 nm and no significant aggregation, suggesting that the polymer is highly compatible with PC$_{70}$BM molecules.

In summary, we have synthesized a new D−A copolymer PBDTBTz containing benzo[1,2-*b*:4,5-*b'*]dithiophene donor unit and bithiazole acceptor unit by the Pd-catalyzed Stille-coupling method. The absorption spectra, electronic energy

Communication

levels, and photovoltaic properties of the copolymer were characterized. PBDTBTz shows a lower HOMO energy level at -5.15 eV with an absorption spectrum similar to P3HT. The PCE of the PSC based on PBDTBTz:$PC_{70}BM$ (1:1, w/w) reached 3.82% with $I_{sc} = 7.84$ mA cm^{-2}, $V_{oc} = 0.86$ V, and FF = 0.57, under the illumination of AM1.5, 100 mW cm^{-2}. These results indicate that PBDTBTz is a promising donor material for the application in polymer solar cells.

Experimental Section. *Materials.* All chemicals and solvents were reagent grades and purchased from Aldrich, Alfa Aesar, and TCI Chemical Co. The following compounds were synthesized according to the procedure in the literature: 2,2′-dibromo-5,5′-dithienyl-4,4′-dinonyl-2,2′-bithiazole[23] and 2,7-bis(trimethyltin)-4,5-bis(2-ethylhexyl)benzo[2,1-b:4,5-b′]-dithiophene.[9−11]

Synthesis of PBDTBTz. 2,2′-Dibromo-5,5′-dithienyl-4,4′-dinonyl-2,2′-bithiazole (772 mg, 0.5 mmol), 2,7-bis(trimethyltin)-4,5-bis(2-ethylhexyl)benzo[2,1-b:4,5-b′]dithiophene (742 mg, 1 mmol), and dry toluene (15 mL) were added to a 50 mL two-neck round-bottom flask. The reaction container was purged with N_2 for 20 min to remove O_2, and then Pd (PPh$_3$)$_4$ (20 mg) was added. After another flushing with N_2 for 20 min, the reactant was heated to reflux for 12 h. The reactant was cooled down to room temperature, poured into MeOH (200 mL), and then filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction with methanol, hexane, and chloroform. Polymer was recovered from the chloroform fraction by rotary evaporation as solid. The polymer was purified by chromatography on silica gel with chloroform as the eluent, and the polymer solution was concentrated and was poured into MeOH. After that, the precipitates were collected and dried under vacuum overnight. Yield: 510 mg (50%). GPC: $M_w = 6.4K$; $M_n = 3.3K$; $M_w/M_n = 1.95$. ^{1}H NMR (CDCl$_3$, 400 MHz), δ (ppm): 7.41−7.11 (m, 6H), 4.14 (s, 4H), 2.91 (s, 4H), 1.85−1.34 (m, 46H), 0.88.0−0.79 (m, 18H).

Measurements and Characterization. All new compounds were characterized by ^{1}H NMR spectroscopy performed on a Bruker DMX-400 spectrometer. For the ^{1}H NMR measurements, CDCl$_3$ was used as the solvent. Chemical shifts in the NMR spectra were reported in ppm relative to the singlet at 7.26 ppm for CDCl$_3$. The molecular weight of the polymer was measured by gel permeation chromatography (GPC), and polystyrene was used as a standard. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7. Mass spectra were obtained with a Shimadzu QP2010 spectrometer. UV−vis absorption spectra were obtained on a Hitachi U-3010 spectrometer. Fluorescence spectra were obtained on a Hitachi F-4500 spectrometer. The X-ray diffraction (XRD) pattern was recorded by a Rigaku D/max-2500 diffractometer operated at 40 kV voltage and a 200 mA current with Cu Kα radiation. The sample for XRD measurements is prepared by spin-coating the chlorobenzene solution of the polymer on the wafer silicon. Cyclic voltammetry (CV) was performed on a Zahner IM6e electrochemical workstation with a three-electrode system in a solution of 0.1 M Bu$_4$NPF$_6$ in acetonitrile at a scan rate of 100 mV s^{-1}. The polymer film was coated on a Pt plate electrode (1.0 cm^2) by dipping the electrode into the corresponding solution and then drying. A Pt wire was used as the counter electrode, and Ag/Ag$^+$ was used as the reference electrode.

Device Fabrication and Characterization of PSCs. PSCs were fabricated with ITO glass as a positive electrode, Al as a negative electrode, and the blend film of the polymer/fullerene between them as a photosensitive layer. The ITO glass was precleaned and modified by a thin layer of PEDOT:PSS which was spin-cast from a PEDOT:PSS aqueous solution

(Clevious P VP AI 4083, H.C. Stark, Germany) on the ITO substrate, and the thickness of the PEDOT:PSS layer is about 60 nm. The photosensitive layer was prepared by spin-coating a blend solution of polymers and $PC_{70}BM$ in o-dichlorobenzene on the ITO/PEDOT:PSS electrode. Then the Al cathode was deposited on the polymer layer by vacuum evaporation under 3×10^{-4} Pa. The thickness of the photosensitive layer is ca. 90 nm, measured on an Ambios Tech. XP-2 profilometer. The effective area of one cell is 4 mm^2. The current−voltage (I−V) measurement of the devices was conducted on a computer-controlled Keithley 236 source measure unit. A xenon lamp with AM1.5 filter was used as the white light source, and the optical power at the sample was around 100 mW cm^{-2}.

Supporting Information Available: TGA, XRD of PBDTBTz, AFM height image of PBDTBTz/$PC_{70}BM$ (1:1, w/w) composite film and the hole mobility measurement. This material is available free of charge via the Internet at http://pubs.acs.org.

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