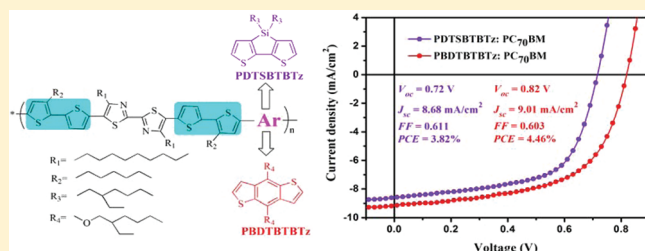


Photovoltaic Performance Improvement of D–A Copolymers Containing Bithiazole Acceptor Unit by Using Bithiophene Bridges

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Supporting Information

ABSTRACT: Two bithiophene-bridged D–A copolymers, PDTSBTBTz and PBDTBTBTz, based on bithiazole acceptor unit and dithienosilole (DTS) or benzodithiophene (BDT) donor unit, were synthesized by the Pd-catalyzed Stille-coupling reaction. The two copolymers exhibit good thermal stability, strong absorption in the visible region, and relatively lower HOMO energy level at ca. -5.10 eV. The hole mobilities of PDTSBTBTz and PBDTBTBTz measured by SCLC method are 1.85×10^{-3} and 1.77×10^{-3} $\text{cm}^2/(\text{V s})$, respectively. Power conversion efficiency (PCE) of the polymer solar cell (PSC) based on PDTSBTBTz:PC₇₀BM (1:1, w/w) was 3.82% with $J_{\text{sc}} = 8.68$ mA/cm^2 , $V_{\text{oc}} = 0.72$ V, and FF = 0.611, under the illumination of AM1.5, 100 mW/cm^2 . In contrast, the PCE of the PSC based on PBDTBTBTz:PC₇₀BM (1:1, w/w) reached 4.46% with $J_{\text{sc}} = 9.01$ mA/cm^2 , $V_{\text{oc}} = 0.82$ V, and FF = 0.603. These results indicate that bithiophene-bridged D–A copolymers are promising photovoltaic donor materials for the application in PSCs.



INTRODUCTION

Polymer solar cells (PSCs) have attracted considerable attention in recent years for their advantages over inorganic solar cells, such as easy fabrication, light weight, flexibility, low cost, and so forth.^{1–4} The bulk heterojunction (BHJ) PSCs have played a leading role in realizing high efficiency by forming a donor–acceptor bicontinuous interpenetrating network of a conjugated polymer donor and soluble fullerene derivative (such as [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₀BM) or [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₀BM)) acceptor.⁵ The key issue in the studies of PSCs is the design and synthesis of high efficiency donor and acceptor photovoltaic materials.^{1–4,6} For the conjugated polymer donor materials, broad absorption spectra, higher hole mobility, and relatively lower HOMO energy level are key points for realizing high efficiency. One of the most popular approaches is to design and synthesize donor–acceptor (D–A) low-bandgap copolymers.^{7–22}

Among the various donor (electron-rich) moieties used in the D–A copolymer photovoltaic materials, dithienosilole (DTS) and benzodithiophene (BDT) are currently two of the most preferred donor units because of their good electron-donating properties, rigid coplanar structure with stronger π – π intermolecular interactions, and the possibility of side-chain manipulation for suitable solubility (or processability).^{1,12,13,20–23} The PSCs based on the DTS- or BDT-containing polymers as donor and PC₇₀BM as acceptor showed high power conversion efficiency up to 6–7%.^{1,21,23c}

In our previous work, we have synthesized two D–A copolymers PDTSBTz (which is P3 in ref 24a) and PBDTBTz (ref 24b) (see Scheme 1) based on bithiazole (BTz) as acceptor unit and dithienosilole (DTS) or benzodithiophene (BDT) as donor unit with thiophene π -bridges between the donor and acceptor units. The two polymers exhibited hole mobilities of 3.07×10^{-4} and 6.84×10^{-4} $\text{cm}^2/(\text{V s})$, respectively, and the polymer solar cell based on these two polymers showed PCE of 2.86% and 3.82%, respectively. In order to attain more extended copolymers,²⁵ here we synthesized two bithiophene (BT)-bridged D–A copolymers, PDTSBTBTz and PBDTBTBTz, based on bithiazole as acceptor unit (compound 3 in Scheme 2) and DTS or BDT as donor unit by Stille-coupling reaction. The two copolymers exhibit broad absorption, relatively lower HOMO energy level at ca. -5.10 eV and higher hole mobilities of ca. 1.8×10^{-3} $\text{cm}^2/(\text{V s})$. PCE of the PSCs based on PDTSBTBTz and PBDTBTBTz reached 3.82% and 4.46%, respectively. These results indicate that the bithiophene-bridged D–A copolymers are promising photovoltaic donor materials for the application in PSCs.

RESULTS AND DISCUSSION

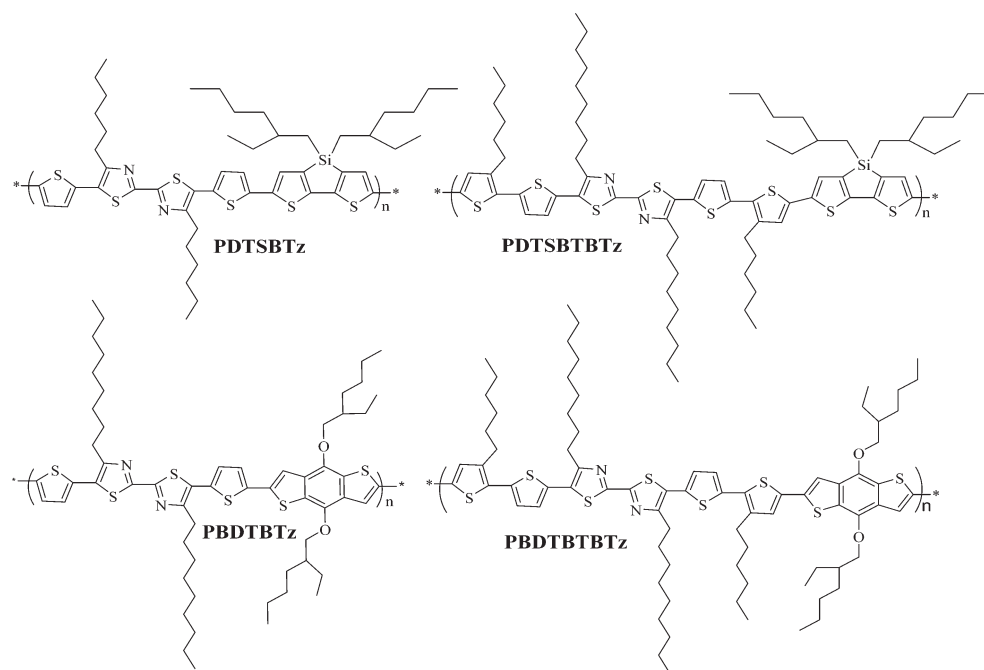
Synthesis and Thermal Stability. The general synthetic strategy for monomer 3 and polymers is outlined in Scheme 2.

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Scheme 1. Molecular Structures of Thiophene-Bridged D–A Copolymers PDTSBTz and PBDTBTz and Bithiophene-Bridged D–A Copolymers PDTSBTBTz and PBDTBTBTz



The alternative copolymers of PDTSBTBTz and PBDTBTBTz were synthesized by Stille-coupling reaction. The two copolymers have good solubility in common organic solvents such as chloroform, toluene, and chlorobenzene. Molecular weights and polydispersity indices (PDIs) of the polymers were determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration, and the results are listed in Table 1. The number-average molecular weights (M_n) of PDTSBTBTz and PBDTBTBTz are 9.1 and 8.6 K, respectively. Although the molecular weights are relatively low, they are higher than those of the corresponding thiophene-bridged D–A copolymers PDTSBTz^{24a} and PBDTBTz.^{24b}

Thermal stability of the polymers was investigated with thermogravimetric analysis (TGA), as shown in Figure 1. The TGA analysis reveals that the onset temperatures with 5% weight loss (T_d) of PDTSBTBTz and PBDTBTBTz are 425 and 343 °C, respectively. In comparison, T_d of PDTSBTz is 368 °C^{24a} and that of PBDTBTz is 317 °C.^{24b} Obviously, the thermal stability of the bithiophene-bridged D–A copolymers is better than that of the corresponding thiophene-bridged copolymers.

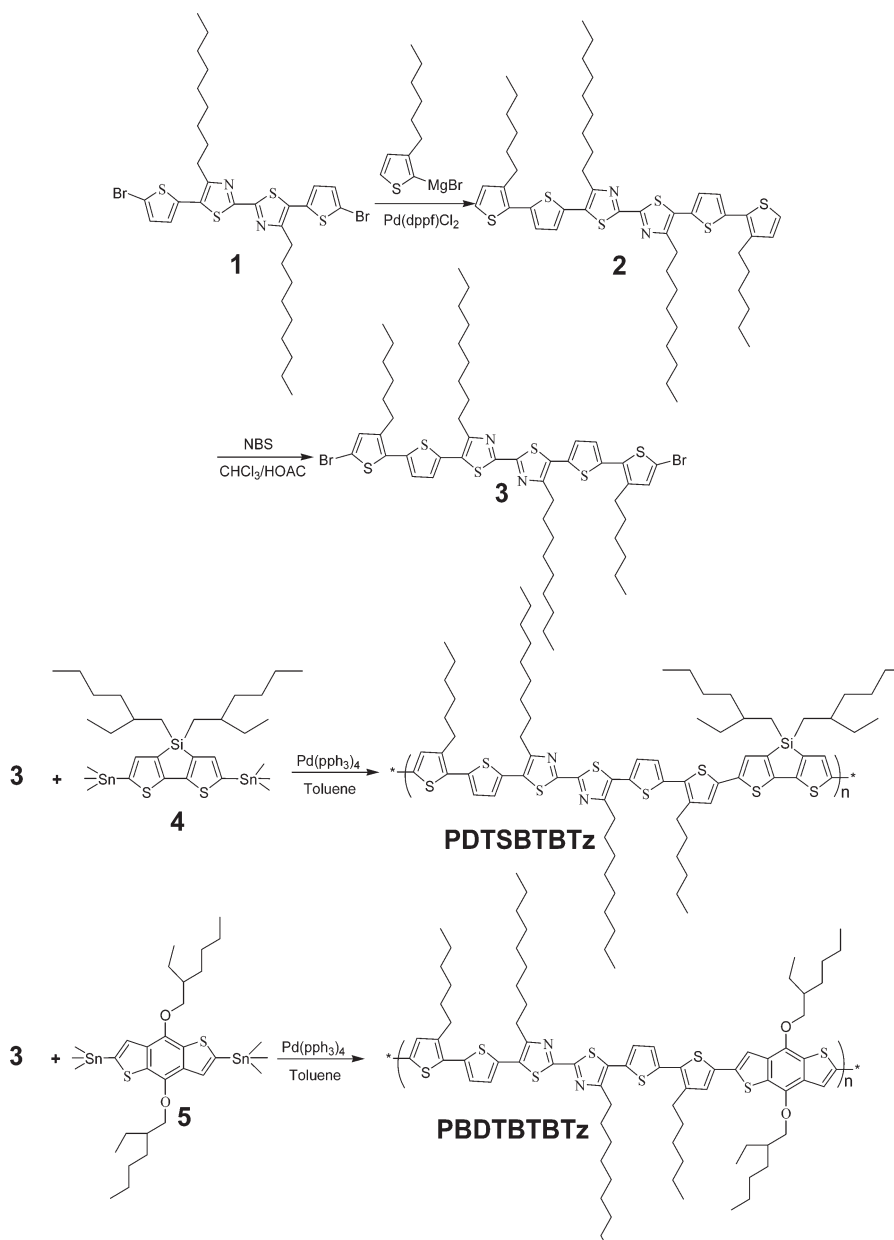
Absorption Spectra. Figure 2 shows the ultraviolet–visible (UV–vis) absorption spectra of the polymer dilute solutions in chloroform and films spin-coated on quartz substrates. The detailed absorption data, including absorption maximum wavelength of the polymer solutions and films, the absorption edge (onset wavelength of the absorption peak, λ_{onset}) of the polymer films, and the optical bandgap deduced from the absorption edges, are summarized in Table 2. PDTSBTBTz and PBDTBTBTz solutions in CHCl₃ show similar absorption spectra with the absorption maxima at 485 and 490 nm, respectively. Compared with the absorption spectra of the polymer solutions, the absorption maxima of PDTSBTBTz and PBDTBTBTz films red-shifted by 65 and 45 nm, respectively, which indicates that there was strong π – π stacking and interchain interaction in

PDTSBTBTz and PBDTBTBTz films. In addition, the absorption spectra of PBDTBTBTz and PDTSBTBTz films exhibited an apparent shoulder peak similar to that of poly(3-hexylthiophene) (P3HT), which means that there was good alignment in the polymer chains. Interestingly, the shoulder peaks of PDTSBTBTz and PBDTBTBTz films are stronger than those of their corresponding thiophene-bridged D–A copolymers PDTSBTz and PBDTBTz films,²⁴ indicating that the bithiophene bridges between the DTS or BDT donor unit and the bithiazole acceptor unit in PDTSBTBTz and PBDTBTBTz benefitted the π – π stacking and ordered aggregation of the polymer main chains. The absorption edges (λ_{edge}) of the two polymer films are 655 nm for PDTSBTBTz and 630 nm for PBDTBTBTz, from which the optical bandgaps (E_g^{opt}) of the polymers can be calculated according to $E_g^{\text{opt}} = 1240/\lambda_{\text{edge}}$. The E_g^{opt} values of PDTSBTBTz and PBDTBTBTz are 1.89 and 1.96 eV, respectively.

X-ray Diffraction. Figure 3 shows the X-ray diffraction (XRD) patterns of the copolymers PDTSBTBTz and PBDTBTBTz. There are a sharp peaks in the XRD pattern of PDTSBTBTz at small angle of $2\theta = 5.11^\circ$ with $d_1 = 17.3$ Å. While in the XRD pattern of PBDTBTBTz, these are only a weak peak in the low-angle region ($d_1 = 17.8$ Å). The peaks correspond to the distance between main chains of the conjugated polymers separated by the alkyl side chains.²⁶ In comparison with regioregular P3HT where the lamellar d -spacing is 16.4 Å,²⁷ the copolymers have larger lamellar d -spacing. It is obvious that the packing of polymer chains for PDTSBTBTz is tighter than that of PBDTBTBTz.

Electrochemical Properties. The electrochemical cyclic voltammetry was performed for determining the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the conjugated polymers.²⁸ Figure 4 shows the cyclic voltammograms of the PDTSBTBTz

Scheme 2. Synthetic Route for Monomer 3 and Copolymers



and PBDTBTBTz films on Pt disk electrode in 0.1 mol/L Bu₄NPF₆ acetonitrile solution. The onset reduction potentials (φ_{red}) of PDTSBTBTz and PBDTBTBTz are -1.79 and -1.77 V vs Ag/Ag⁺, respectively, while the onset oxidation potentials (φ_{ox}) are 0.36 and 0.41 V vs Ag/Ag⁺, respectively. HOMO and LUMO energy levels of the polymers were calculated according to the equations²⁹ $\text{HOMO} = -e(\varphi_{\text{ox}} + 4.71)$ (eV) and $\text{LUMO} = -e(\varphi_{\text{red}} + 4.71)$ (eV). The results of the electrochemical measurements are listed in Table 2. The LUMO energy levels of PDTSBTBTz and PBDTBTBTz are -2.92 and -2.94 eV, respectively, and the HOMO energy levels of PDTSBTBTz and PBDTBTBTz are -5.07 and -5.12 eV, respectively. The relatively lower HOMO energy level of the copolymers is beneficial to the better stability of the polymers against oxidation and higher open circuit voltage (V_{oc}) of the PSCs based on the polymers as donor.¹⁵

Hole Mobility. Hole mobility is another important parameter for the conjugated polymer donor photovoltaic materials. Here we measured the hole mobility of the copolymers PDTSBTBTz and PBDTBTBTz by space-charge limit current (SCLC) method using a device structure of ITO/PEDOT:PSS/polymer/Au. For the hole-only devices, SCLC is described by³⁰

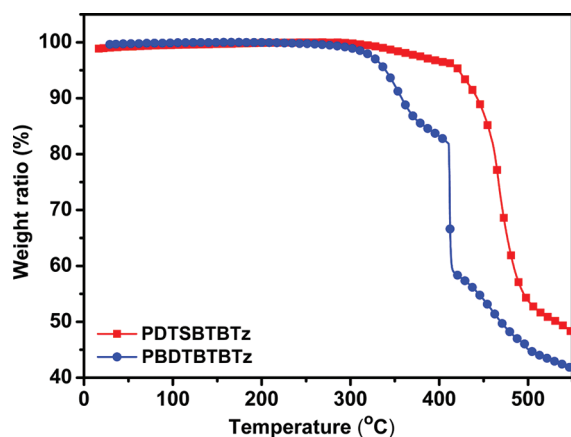
$$J \cong (9/8)\epsilon\epsilon_0\mu_0 V^2 \exp(0.89\sqrt{V/E_0 L})/L^3 \quad (1)$$

where ϵ is the dielectric constant of the polymer, ϵ_0 is the permittivity of the vacuum, μ_0 is the zero-field mobility, E_0 is the characteristic field, J is the current density, L is the thickness of the blended films, $V = V_{\text{appl}} - V_{\text{bi}}$, V_{appl} is the applied potential, and V_{bi} is the built-in potential which results from the difference in the work function of the anode and the cathode (in this device structure, $V_{\text{bi}} = 0.2$ V). The results are plotted as $\ln(JL^3/V^2)$ vs

Table 1. Molecular Weights and Thermal Properties of the Polymers

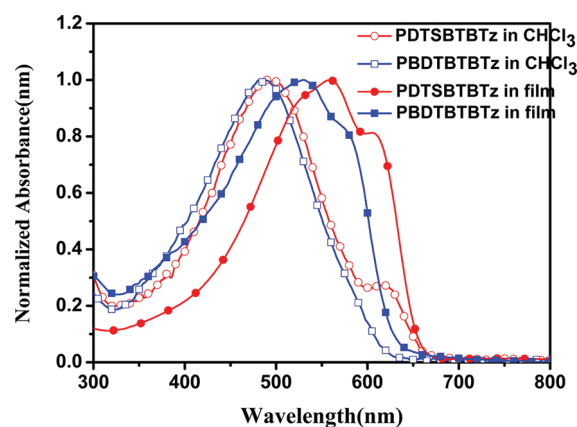
polymers	M_w	M_n	PDI ^a	T_d (°C) ^a
PDTSBTBTz	14.7K	9.1K	1.61	425
PBDTBTBTz	12.6K	8.6K	1.46	343

^a The 5% weight-loss temperatures under inert atmosphere.

**Figure 1.** TGA plots of the copolymers with a heating rate of 10 °C/min under an inert atmosphere.

(V/L)^{0.5} (as shown in Figure 5). According to eq 1 and Figure 5, the hole mobilities obtained are 1.85×10^{-3} and 1.77×10^{-3} cm²/(V s) for PDTSBTBTz and PBDTBTBTz, respectively. The hole mobilities of the corresponding thiophene-bridged copolymers PDTSBTz and PBDTBTz are 3.07×10^{-4} and 6.84×10^{-4} cm²/(V s), respectively.²⁴ Obviously, the hole mobility of the bithiophene-bridged copolymers PDTSBTBTz and PBDTBTBTz is improved over that of their corresponding thiophene-bridged copolymers, and the higher hole mobility of the bithiophene-bridged D–A copolymers should be beneficial for the application as photovoltaic donor materials in PSCs.

Photovoltaic Properties. To investigate and compare the photovoltaic properties of the two copolymers, bulk heterojunction PSC devices with a configuration of ITO/PEDOT:PSS/copolymer:PC₇₀BM (1:1 w/w)/Ca/Al were fabricated. Figure 6 shows the J – V curves of the PSCs under the illumination of AM1.5, 100 mW/cm². The corresponding open-circuit voltage (V_{oc}), short-circuit current (J_{sc}), fill factor (FF), and power conversion efficiency (PCE) of the devices are summarized in Table 3. The photovoltaic properties of the corresponding thiophene-bridged D–A copolymers PDTSBTz and PBDTBTz are also listed in Table 3 for comparison. The PSCs based on the blend of PDTSBTBTz or PBDTBTBTz and PC₇₀BM (1:1 w/w) exhibited higher V_{oc} of 0.72 and 0.82 V, respectively. When increasing PC₇₀BM content to the weight ratio of the polymer to PC₇₀BM of 1:2, the J_{sc} and FF values of devices slightly decreased, which could be ascribed to the reduction of the absorption of the active layer and an unbalanced charge transporting properties between holes and electrons due to the high PC₇₀BM content.³¹ The best device based on PDTSBTBTz showed a V_{oc} of 0.72 V, a J_{sc} of 8.68 mA/cm², and a FF of 0.611, leading to a PCE of 3.82%. The maximum PCE of the PSC based on PBDTBTBTz reached 4.46% with a V_{oc} of 0.82 V, a J_{sc} of 9.01 mA/cm², and a FF of 0.603. In

**Figure 2.** Optical spectra of copolymers in CHCl₃ and in films.

comparison with the PCE of 2.86%^{24a} for PDTSBTz and 3.82%^{24b} for PBDTBTz, the power conversion efficiency of the bithiophene-bridged D–A copolymers is improved significantly over that of their corresponding thiophene-bridged copolymers. The better photovoltaic performance of the bithiophene-bridged copolymers could be ascribed to their higher hole mobilities mentioned above.

Figure 7 demonstrates the external quantum efficiency (EQE) curves of the PSCs based on the two copolymers. The EQE curve of the PSC based on PDTSBTBTz:PC₇₀BM (1:1 w/w) covers a broad wavelength range from 350 to 700 nm with the maximum EQE value of 59.5% at ca. 550 nm and a platform from 450 to 570 nm. In contrast, the EQE curve of the PSC based on PBDTBTBTz:PC₇₀BM (1:1 w/w) exhibits a higher EQE value of 71.1% at 500 nm. The higher EQE values of the PSC based on PBDTBTBTz agree with the higher J_{sc} of the PSC device mentioned above.

In order to understand the effect of morphology of the photoactive layers on the photovoltaic performance of the polymer solar cells, the morphological structures of the blend films of polymer: PC₇₀BM was analyzed by tapping mode atom force microscopy (AFM) measurements (as shown in Figure S1 in Supporting Information). It is clear that the film of 1:1 blends of polymer and PC₇₀BM have better interpenetrating network than that of 1:2 blend of polymer and PC₇₀BM which is beneficial to the exciton dissociation and charge carriers transport. This is consistent with the higher performance of polymer solar cells based on the blend of polymer and PC₇₀BM with weight ratio of 1:1.

CONCLUSION

We have synthesized two new D–A copolymers PDTSBTBTz and PBDTBTBTz by the Pd-catalyzed Stille-coupling reaction. The copolymers contain dithienosilole (DTS) or benzodithiophene (BDT) donor unit, bithiazole (BTz) acceptor unit, and bithiophene (BT) bridges between them. PDTSBTBTz and PBDTBTBTz exhibit stronger interchain interaction, lower HOMO energy level at -5.07 and -5.12 eV, and higher hole mobility of 1.85×10^{-3} and 1.77×10^{-3} cm²/(V s), respectively. The PCE of the PSC based on PDTSBTBTz:PC₇₀BM (1:1, w/w) was 3.82% with $J_{sc} = 8.68$ mA/cm², $V_{oc} = 0.72$ V, and FF = 0.611, and the PCE of the PSC based on PBDTBTBTz:PC₇₀BM (1:1, w/w) reached 4.46% with $J_{sc} = 9.01$ mA/cm², $V_{oc} = 0.82$ V, and FF = 0.603, under the illumination of AM1.5, 100 mW/cm². These results indicate that the bithiophene-bridged D–A

Table 2. Optical and Electrochemical Properties of the Polymers

polymers	UV-vis absorption spectra				cyclic voltammetry		
	solution ^a		film ^b		p-doping	n-doping	E_g^{EC} (eV)
	λ_{max} (nm)	λ_{max} (nm)	λ_{onset} (nm)	E_g^{opt} (eV) ^c			
PDTSBTBTz	490	560	655	1.89	0.36/−5.07	−1.79/−2.92	2.15
PBDTBTBTz	485	530	630	1.96	0.41/−5.12	−1.77/−2.94	2.18

^a Measured in chloroform solution. ^b Cast from chloroform solution. ^c Bandgap estimated from the onset wavelength (λ_{edge}) of the optical absorption: $E_g^{opt} = 1240/\lambda_{edge}$.

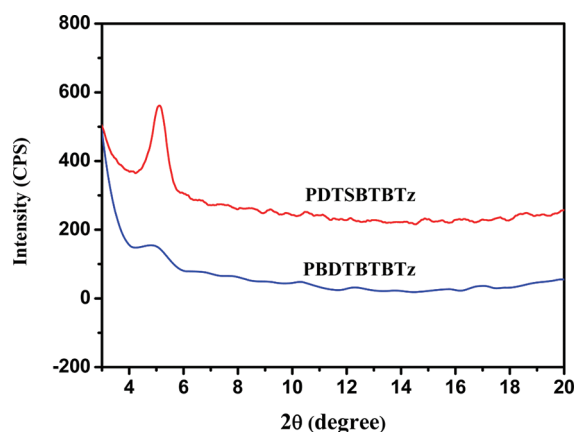
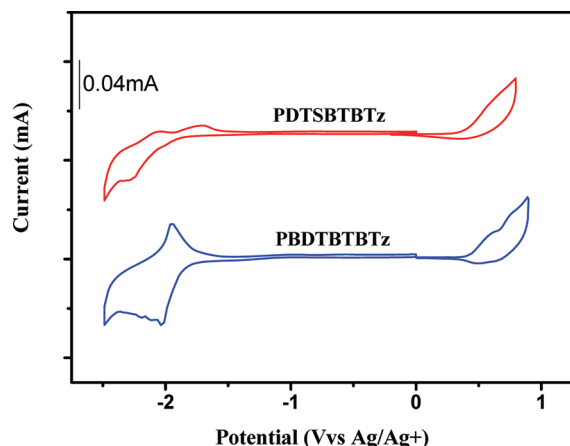


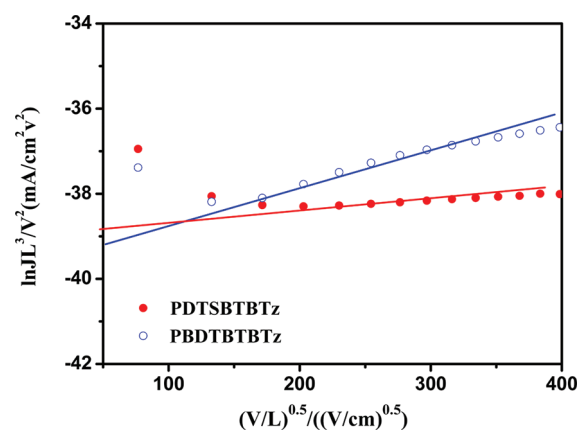
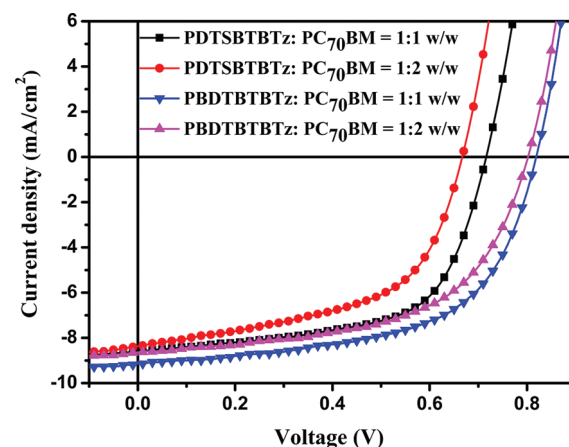
Figure 3. X-ray diffraction patterns of copolymer films.

Figure 4. Cyclic voltammograms of the copolymer films on a platinum electrode measured in 0.1 mol/L Bu₄NPF₆ acetonitrile solutions at a scan rate of 100 mV/s.

copolymers are promising photovoltaic donor materials for the application in PSCs.

EXPERIMENTAL SECTION

Materials. All chemicals and solvents were reagent grades and purchased from Aldrich, Alfa Aesar, and TCI Chemical Co. Toluene, tetrahydrofuran, and diethyl ether were distilled to keep anhydrous before use. The other solvents were degassed by nitrogen for 1 h prior to use, unless otherwise stated.

Figure 5. $\ln(JL^3/V^2)$ vs $(V/L)^{0.5}$ plots of the polymers for the measurement of hole mobility by the SCLC method.Figure 6. I – V curves of the PSCs based on PDTSBTBTz:PC₇₀BM or PBDTBTBTz:PC₇₀BM with different weight ratios under the illumination of AM 1.5, 100 mW/cm².

Measurements and Characterization. All new compounds were characterized by ¹H NMR spectroscopy performed on a Bruker DMX-400 spectrometer. For the ¹H NMR measurements, CDCl₃ was used as the solvent. Chemical shifts in the NMR spectra were reported in ppm relative to the singlet at 7.26 ppm for CDCl₃. The molecular weight of the polymers 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

Table 3. Photovoltaic Properties of the PSCs Based on Copolymers:PC₇₀BM with Different Weight Ratios, under the Illumination of AM1.5, 100 mW/cm²

active layer	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	PCE (%)
PDTSBTBTz:PC ₇₀ BM = 1:1	0.72	8.68	0.611	3.82
PDTSBTBTz:PC ₇₀ BM = 1:2	0.67	8.28	0.555	3.08
PBDTBTBTz:PC ₇₀ BM = 1:1	0.82	9.01	0.603	4.46
PBDTBTBTz:PC ₇₀ BM = 1:2	0.80	8.61	0.576	3.97
PDTSBTz:PC ₇₀ BM = 1:1 ^a	0.68	7.85	0.535	2.86
PBDTBTz:PC ₇₀ BM = 1:1 ^b	0.86	7.84	0.57	3.82

^aThe data from ref 24a. ^bThe data from ref 24b.

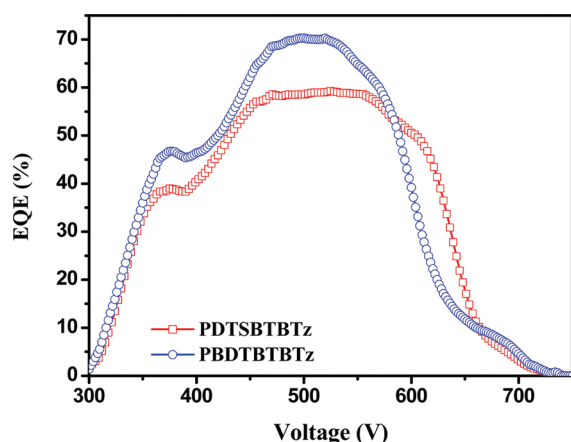


Figure 7. EQE curves of the PSCs based on PDTSBTBTz:PC₇₀BM or PBDTBTBTz:PC₇₀BM (1:1 w/w).

absorption spectra were obtained on a Hitachi U-3010 spectrometer. Cyclic voltammetry was performed on a Zahner IM6e electrochemical workstation with a three-electrode system in a solution of 0.1 M Bu₄NPF₆ in acetonitrile at a scan rate of 50 mV/s. The polymer films were coated on a Pt plate electrode by dipping the electrode into the corresponding solutions 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 Polymer Solar Cells. Polymer solar cells (PSCs) were fabricated with PEDOT:PSS modified ITO glass as a positive electrode, Ca/Al as negative electrode, and the blend film of the polymer/PC₇₀BM between them as a photosensitive layer. A thin layer of PEDOT:PSS was spin-cast on precleaned ITO-coated glass from a PEDOT:PSS aqueous solution at 2000 rpm and dried subsequently at 150 °C for 20 min to give a film with a thickness of 40 nm. Then 1:1 or 1:2 w/w blends of polymer and PC₇₀BM at 10 mg/mL (according to the polymer weight) were dissolved in *o*-dichlorobenzene with heating at 70 °C for at least 3 h until all the solids dissolved completely and then stirring for more than 5 h at room temperature. The photosensitive layer was spin-coated onto the PEDOT:PSS layer at 1000 rpm. Then a 10 nm of calcium and a 80 nm of aluminum were deposited on the polymer layer as the cathode at a pressure of 3×10^{-5} Pa. The thickness of the photosensitive layer is ca. 100 nm, measured on an Ambios Tech. XP-2 profilometer. The effective area of one cell is 4 mm². 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 100 mW/cm². The external quantum efficiency (EQE) was measured using a Stanford Research Systems model SR830 DSP lock-in amplifier

coupled with a WDG3 monochromator and a 500 W xenon lamp. The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell. All the measurements were performed under ambient atmosphere at room temperature.

Synthesis. The synthetic routes of the monomer and polymers are shown in Scheme 2. Compounds **1**,^{32–34} **4**,^{13a} and **5**^{22,23} were synthesized according to the procedure in the literature. The detailed synthetic processes are as follows.

5,5'-Bis(3'-hexyl-2,2'-bithiophen-5-yl)-4,4'-dinonyl-2,2'-bithiazole (2). To a suspension of magnesium (0.96 g, 40.0 mmol) in anhydrous diethyl ether (40 mL), a solution of 2-bromo-3-hexylthiophene (7.9 g, 32.0 mmol) in anhydrous diethyl ether (150 mL) was added dropwise. The Grignard reagent prepared was then added dropwise to an ice-cooled suspension of compound **1** (5.92 g, 8.00 mmol) and Pd(dppf)Cl₂ (200 mg) in anhydrous diethyl ether (100 mL). The reaction mixture was stirred for 6 h at room temperature. It was then hydrolyzed with a saturated aqueous ammonium chloride solution and followed by the addition of diethyl ether. The red layer was washed three times with water (200 mL) and dried over sodium sulfate. After the removal of solvent, recrystallization from hexane gave the red solid with a yield of 82% (6.0 g). ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.21 (d, 2H), 7.14 (d, 2H), 7.09 (d, 2H), 6.95 (t, 2H), 2.99 (t, 4H), 2.72 (t, 4H), 2.01–1.26 (m, 42H), 0.88 (m, 12H).

5,5'-Bis(5'-bromo-3'-hexyl-2,2'-bithiophen-5-yl)-4,4'-dinonyl-2,2'-bithiazole (3). Compound **2** (3.66 g, 4.00 mmol) was dissolved in a mixture of chloroform (50 mL) and acetic acid (10 mL). NBS (1.50 g, 8.42 mmol) was then added to the solution which was then stirred for 1 h in the dark. The precipitate in the reaction mixture was filtered, washed with methanol, and dried to produce a red solid with a yield of 90% (3.87 g). ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.14 (d, 2H), 7.09 (d, 2H), 6.95 (t, 2H), 2.99 (t, 4H), 2.72 (t, 4H), 2.01–1.26 (m, 42H), 0.88 (m, 12H). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 157.80, 154.88, 140.89, 136.13, 133.31, 132.93, 131.52, 127.71, 127.49, 126.86, 111.43, 77.46, 77.36, 77.15, 76.83, 32.05, 31.77, 30.69, 29.71, 29.67, 29.60, 29.47, 29.43, 29.28, 22.83, 22.74, 14.25, 14.21. Anal. Calcd (%) for C₅₂H₇₀Br₂N₂S₆: C, 58.08; H, 6.56; N, 2.61; Br, 14.86; S, 17.89. Found: C, 58.11; H, 6.58; N, 2.67; Br, 14.80; S, 17.82. MALDI-TOF: *m/z* = 1075.

Synthesis of Polymer PDTSBTBTz. Compound **3** (537.5 mg, 0.5 mmol), compound **4** (372 mg, 0.5 mmol), and dry toluene (12 mL) were added to a 50 mL two-neck round-bottom flask. The reaction container was purged with argon for 20 min to remove O₂, and then Pd(PPh₃)₄ (15 mg) was added. After another flushing with argon for 20 min, the reactant was heated to reflux for 10 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 this, the precipitates were collected and dried under vacuum overnight. Yield: 399 mg (60%). GPC: *M*_w = 14.7K; *M*_n = 9.1K; *M*_w/*M*_n = 1.61. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.14 (m, 8H), 3.62 (d, 2H), 1.89 (m, 1H), 1.29 (m, 36H), 0.87 (m, 12H). Anal. Calcd (%) for C₇₆H₁₀₆N₂S₈Si: C, 68.52; H, 8.02; N, 2.10. Found: C, 68.41; H, 7.88; N, 2.67.

Synthesis of Polymer PBDTBTBTz. PBDTBTBTz are synthesized according to the same procedure as that for the synthesis of PDTSBTBTz with monomer **5** was used instead of monomer **4**. Yield: 475 mg (70%). GPC: *M*_w = 12.6K; *M*_n = 8.6K; *M*_w/*M*_n = 1.46. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.79 (m, 4H), 7.22 (m, 4H), 3.62 (d, 2H), 1.89 (m, 1H), 1.29 (m, 36H), 0.87 (m, 12H). Anal. Calcd (%) for C₇₈H₁₀₄N₂O₂S₈: C, 68.52; H, 8.02; N, 2.10. Found: C, 68.41; H, 7.88; N, 2.67.

■ ASSOCIATED CONTENT

S Supporting Information. Figure S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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