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# Poly(thieno[3,2-*b*]thiophene-*alt*-bithiazole): A D–A Copolymer Donor Showing Improved Photovoltaic Performance with Indene-C<sub>60</sub> Bisadduct Acceptor

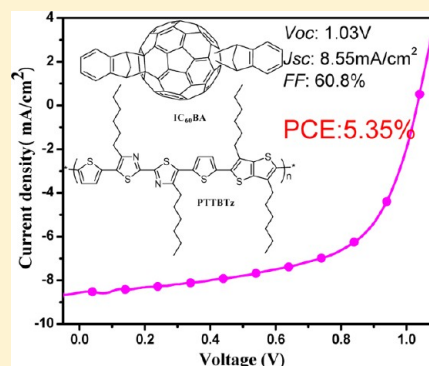
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## S Supporting Information

**ABSTRACT:** A new D–A copolymer, poly(thieno[3,2-*b*]thiophene-*alt*-bithiazole) (PTTBTz), based on thieno[3,2-*b*]thiophene donor unit and bithiazole acceptor unit, was synthesized by the Pd-catalyzed Stille-coupling reaction for the application as donor material in polymer solar cells (PSCs). PTTBTz film possesses high thermal stability with 5% weight-loss temperature at 450 °C, a lower-lying HOMO energy level at –5.20 eV, a higher hole mobility of  $6.45 \times 10^{-3} \text{ cm}^2/(\text{V s})$ , and a crystalline structure. Photovoltaic performance of the polymer was investigated with [6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>70</sub>BM) or indene-C<sub>60</sub> bisadduct (ICBA) as acceptor and with 3% DIO additive. The power conversion efficiency (PCE) of the PSC based on PTTBTz:ICBA (1:1 w/w) reached 5.35% with a high  $V_{oc}$  of 1.03 V, a  $J_{sc}$  of 8.55 mA/cm<sup>2</sup>, and an FF of 0.608, whereas the PCE of the PSC based on PTTBTz:PC<sub>70</sub>BM (1:1 w/w) was 4.57% with a  $V_{oc}$  of 0.82 V, a  $J_{sc}$  of 9.89 mA/cm<sup>2</sup>, and an FF of 0.563, under the illumination of AM1.5, 100 mW/cm<sup>2</sup>.

PTTBTz is one of the D–A copolymers that shows better photovoltaic performance with ICBA as acceptor than PC<sub>70</sub>BM. PTTBTz/ICBA could be a promising front active layer for high-efficiency tandem PSC because of its high  $V_{oc}$ .



## 1. INTRODUCTION

In recent years, polymer solar cells (PSCs) have attracted considerable attention because of their advantages of low cost, easy fabrication, lightweight, and capability to be fabricated into flexible large-area devices.<sup>1–5</sup> Bulk heterojunction (BHJ) structure utilizing a conjugated polymer as donor and fullerene derivatives [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>60</sub>BM) or [6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>70</sub>BM) as acceptor now plays a leading role in realizing high power conversion efficiency (PCE) of the PSCs. The key issue in the studies of PSCs is to increase the PCE of the devices. The factors that determine the PCE of the PSCs are the open-circuit voltage ( $V_{oc}$ ), short-circuit current density ( $J_{sc}$ ), and fill factor (FF).  $V_{oc}$  is proportional to the difference between the lowest unoccupied molecular orbital (LUMO) of the acceptor and the highest occupied molecular orbital (HOMO) of the donor.<sup>6</sup> Therefore, lower HOMO of the donor and higher LUMO of the acceptor will lead to higher  $V_{oc}$  of the PSCs. The  $J_{sc}$  is tightly related to the absorption and charge carrier mobility of the photovoltaic materials, and FF is influenced by the charge carrier mobility of the photoactive layer. Therefore, higher charge carrier mobility will benefit to larger  $J_{sc}$  and higher FF.<sup>7</sup> To design and synthesize donor–acceptor (D–A) copolymers has been proven to be one of the most successful strategy to extend the visible absorption and decrease the HOMO energy level of conjugated polymers,<sup>2,3,8–17</sup> and with this strategy the PCE of the PSCs based on new D–A copolymers as donor has recently reached up to 7 to 8%.<sup>15–17</sup>

Bithiazole (BTz) is an electron-deficient unit containing two electron-withdrawing nitrogen of imine ( $C=N$ ).<sup>18</sup> The BTz unit could lead to lower HOMO energy level of its copolymers, which is desirable for increasing  $V_{oc}$  in PSCs.<sup>19–21</sup> It also possesses a relatively simple coplanar structure similar to bithiophene. For the donor unit in the D–A copolymers, thieno[3,2-*b*]thiophene (TT) unit has a rigid and coplanar fused ring and ensures a highly extended  $\pi$ -electron system and strong  $\pi$  stacking. Therefore, TT unit has attracted much interest in the construction of high-performance organic/polymer semiconductors for the applications in optoelectronic devices.<sup>22–27</sup> The field-effect hole mobility of a conjugated polymer containing TT unit in the polymer main chain reached as high as  $1.95 \text{ cm}^2/\text{V s}$ .<sup>27</sup> The PSCs based on a D–A copolymer with TT as donor unit exhibited a high PCE over 5%.<sup>26,27</sup> In this work, we designed and synthesized a new D–A copolymer based on BTz and TT units, poly(thieno[3,2-*b*]thiophene-*alt*-bithiazole) (PTTBTz). (See Scheme 1.) PTTBTz shows an ordered structure, higher hole mobility, and similar absorption spectrum as that of P3HT but relatively lower HOMO energy level. The PSC based on PTTBTz:PC<sub>70</sub>BM (1:1 w/w) demonstrated a PCE of 4.57% with a  $V_{oc}$  of 0.82 V, a  $J_{sc}$  of 9.89 mA/cm<sup>2</sup>, and an FF of 0.563, under the illumination of AM1.5, 100 mW/cm<sup>2</sup>.

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Scheme 1. Molecular Structure and the Synthetic Route of PTTBTz

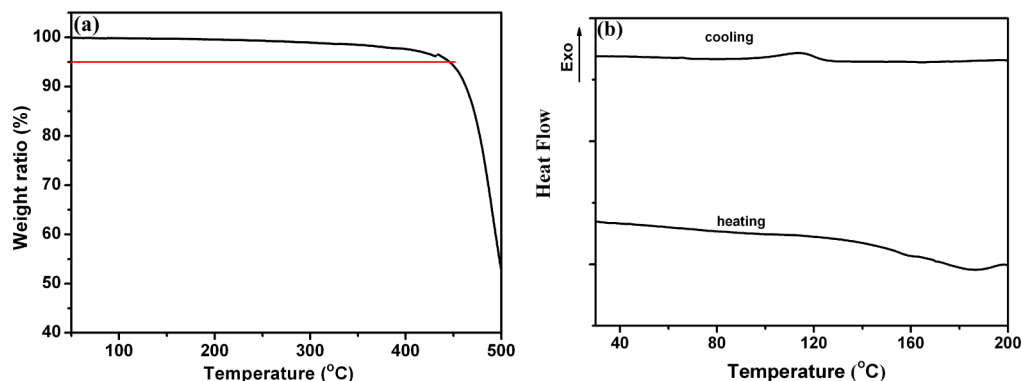
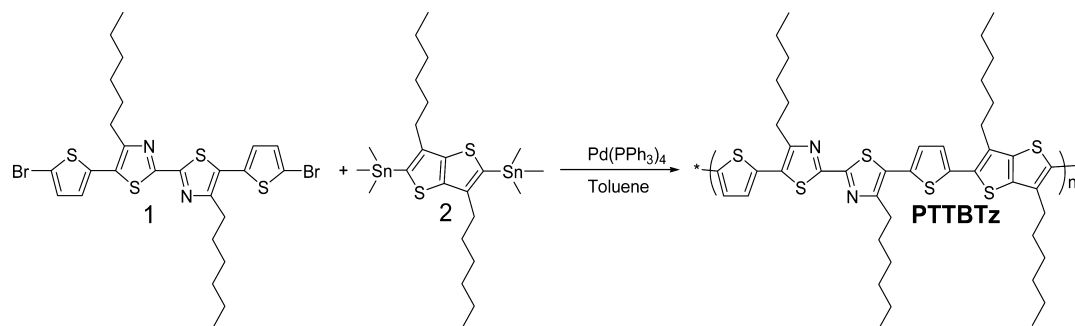


Figure 1. (a) TGA plots with a heating rate of 10 °C/min and (b) DSC thermograms of PTTBTz under an inert atmosphere.

A new fullerene derivative, indene- $C_{60}$  bisadduct (ICBA) with a LUMO energy level of  $-3.74$  eV, which is  $0.17$  eV upshifted from that of  $PC_{60}BM$ , was reported by our group.<sup>28</sup> By using ICBA as acceptor instead of  $PC_{60}BM$ , the  $V_{oc}$  of the PSCs based on P3HT as donor increased from  $0.58$  to  $0.84$  V, so that the PCE of the device increased from  $3.8$  to  $6.5\%$ .<sup>29</sup> Then, ICBA, as a promising new acceptor, has been successfully used in PSCs with polythiophene derivatives and has shown better photovoltaic performance than that of  $PC_{60}BM$ ,<sup>30,31</sup> but the application of ICBA in the PSCs with D–A copolymers as donor is mostly not successfully. Only recently, Jenekhe et al. reported a D–A copolymer of dithionosilole and thiazolothiazole showing improved PCE of  $5.36\%$  with ICBA as acceptor in comparison with a PCE of  $3.61\%$  with  $PC_{60}BM$  as acceptor.<sup>32</sup> Interestingly, our new D–A copolymer PTTBTz also showed better photovoltaic performance when ICBA was used as acceptor instead of  $PC_{70}BM$ . PCE of the PSC based on PTTBTz as donor and ICBA as acceptor reached  $5.35\%$  with a high  $V_{oc}$  of  $1.03$  V, under the illumination of AM1.5G,  $100$  mW/cm<sup>2</sup>. The results are very important for understanding the applicability of the new acceptor ICBA for the D–A copolymer photovoltaic donor materials to get higher  $V_{oc}$  and further improved efficiency.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** All chemicals and solvents were reagent grades and purchased from Aldrich, Alfa Aesar, and TCI Chemical, respectively. 5,5'-Bis(5-bromothiophen-2-yl)-4,4'-dihexyl-2,2'-bithiazole<sup>21a</sup> (1) and (3,6-dihexylthieno[3,2-*b*]thiophene-2,5-diyl)bis(trimethylstannane)<sup>25</sup> (2) were synthesized according to the procedure reported in the literatures, and ICBA was synthesized according to the procedure reported in the literature.<sup>28</sup>

**2.2. Synthesis of PTTBTz.** PTTBTz was synthesized by Stille coupling reaction using  $Pd(PPh_3)_4$  as the catalyst, as shown in Scheme 1. The detailed synthetic processes are as follows. Compound 1 (317

mg,  $0.5$  mmol), Compound 2 (329 mg,  $0.5$  mmol), and dry toluene ( $15$  mL) were added to a  $50$  mL two-necked round-bottomed flask. The reaction container was purged with argon for  $20$  min to remove  $O_2$ , and then  $Pd(PPh_3)_4$  ( $20$  mg) was added. After another flushing with argon for  $20$  min, the reactant was heated to reflux for  $10$  h. The reactant was cooled to room temperature and poured in MeOH ( $200$  mL), 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 and purified by chromatography on silica gel with chloroform as the eluent, and the polymer solution was concentrated and was poured in MeOH. After this, the precipitates were collected and dried under vacuum overnight. Yield:  $200$  mg ( $50\%$ ). GPC:  $M_w = 6.73$  K;  $M_n = 4.2$  K;  $M_w/M_n = 1.60$ .  $^1H$  NMR ( $400$  MHz,  $CDCl_3$ ,  $\delta$ ):  $7.21$  (s, 4H),  $3.02$ – $2.73$  (m, 8H),  $1.47$ – $1.27$  (m, 32H),  $0.92$  (m, 12H).

**2.3. Measurements and Characterization.** All new compounds were characterized by  $^1H$  NMR spectroscopy performed on a Bruker DMX-400 spectrometer. In the  $^1H$  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 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 absorption spectra were obtained on a Hitachi U-3010 spectrometer. Cyclic voltammetry (CV) was performed on a Zahner IM6e electrochemical workstation with a three-electrode system in a solution of  $0.1$  M  $Bu_4NPF_6$  in acetonitrile at a scan rate of  $100$  mV/s. The polymer film was 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. Thin-film X-ray diffraction (XRD) was recorded on a Bruker D8 Discover thin-film diffractometer with  $Cu K\alpha$  radiation ( $\lambda = 1.54056$  Å) operated at  $40$  keV and  $40$  mA. The morphology of blend film was observed by an atomic force microscope (AFM) (NanoMan VS, Veeco, USA) in tapping mode. Transmission

electron microscopy (TEM) was performed using a JEOL 2200FS instrument at 160 kV accelerating voltage.

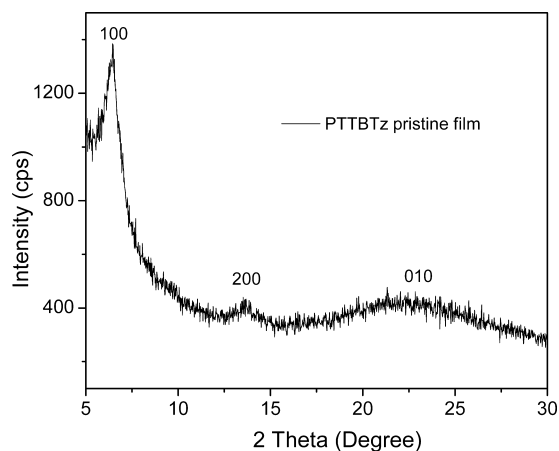
**2.4. Device Fabrication and Characterization of Polymer Solar Cells.** PSCs were fabricated with ITO glass as a positive electrode, Ca/Al as a negative electrode, and the blend film of the polymer/PC<sub>70</sub>BM or polymer/ICBA between them as a photosensitive layer. The ITO glass was precleaned 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 was about 35 nm. The photosensitive layer was prepared by spin-coating a blend solution of polymers and PC<sub>70</sub>BM in *o*-dichlorobenzene on the ITO/PEDOT: PSS electrode. Then, the Ca/Al cathode was deposited on the polymer layer by vacuum evaporation under  $4 \times 10^{-4}$  Pa. The thickness of the photosensitive layer was ca. 100 nm, measured on an Ambios Tech. XP-2 profilometer. The effective area of one cell was 4 mm<sup>2</sup>. 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/cm<sup>2</sup>.

### 3. RESULTS AND DISCUSSION

**3.1. Synthesis and Thermal Properties.** PTTBTz was synthesized by Stille coupling reaction using Pd(PPh<sub>3</sub>)<sub>4</sub> as the catalyst. The polymer has good solubility in common organic solvents such as chloroform, toluene, chlorobenzene, *o*-dichlorobenzene, and so on. The number-average molecular weight (*M<sub>n</sub>*) of PTTBTz is 6.73 K with a polydispersity index (PDI) of 1.60.

Thermal stability of the polymer was investigated with TGA. The TGA result (see Figure 1a) reveals that the onset temperatures with 5% weight-loss (*T<sub>d</sub>*) of PTTBTz is 450 °C. This indicates that the thermal stability of PTTBTz is very good for the application in optoelectronic devices. To investigate possible crystallization in the copolymer films, the differential scanning calorimetry (DSC) was measured, as shown in Figure 1b. There is an apparent exothermic peak at 115 °C for PTTBTz indicating that there is some local crystallization in the polymer films.

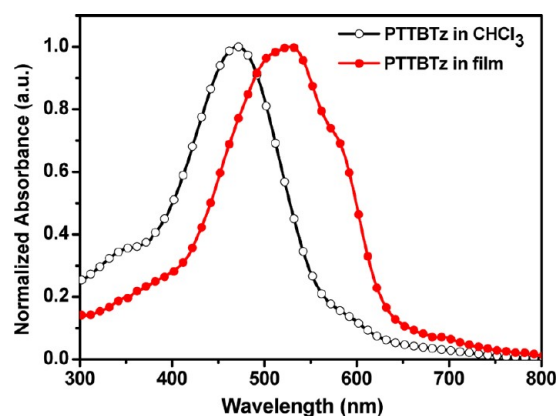
**3.2. X-ray Diffraction.** To investigate further the crystalline property of PTTBTz, we measured the grazing-incidence XRD pattern of the polymer film, as shown in Figure 2. The XRD pattern of the pristine polymer film exhibits three diffraction peaks at  $2\theta = 6.45$ , 13.63, and 21.96°, respectively. The (100) and (200) diffraction peaks for PTTBTz are at 6.45 and 13.63°,



**Figure 2.** X-ray diffraction pattern of the pristine PTTBTz film drop-cast onto a Si substrate.

respectively, indicating an ordered structure along with a *d* spacing of 13.68 Å that can be ascribed to the interchain distance separated by the alkyl side chains. The interchain *d* spacing of 13.68 Å is smaller than that (ca. 16 Å)<sup>33</sup> of regioregular poly(3-hexylthiophene) (P3HT), which indicates more densely packed side chains in PTTBTz than in P3HT. The broad feature at 21.96°, corresponding to a distance of 4.02 Å, can be assigned to the facial  $\pi$ – $\pi$  stacking between polymer backbones. The results indicate that PTTBTz possesses ordered polymer chains and densely packed side chains, which should be beneficial to higher hole mobility and better photovoltaic performance of the polymer.

**3.3. Absorption Spectra.** Figure 3 shows the ultraviolet–visible (UV–vis) absorption spectra of the polymer dilute



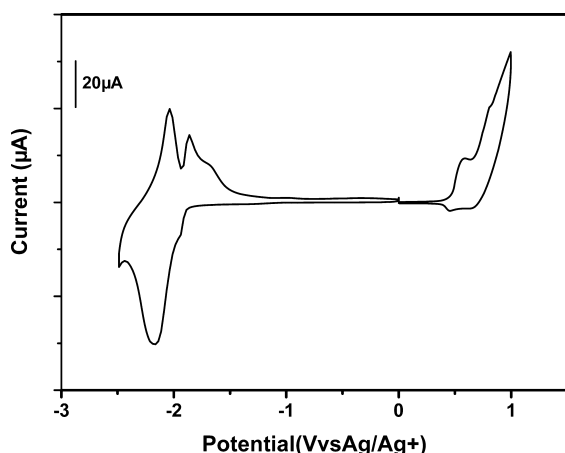
**Figure 3.** Absorption spectra of PTTBTz in chloroform solution and in solid film.

solution in chloroform and film spin-coated on quartz substrate. In solution, the polymer exhibited an absorption peak at 471 nm, which we assign to internal charge transfer between the TT donor unit and the BTz acceptor unit. The absorption maximum of the polymer film appeared at 532 nm; a significant red shift of 61 nm relative to that in solution, indicating that considerably strong intermolecular interactions existed in the solid film. Additionally, a vibronic shoulder at 573 nm implies an ordered arrangement of PTTBTz in the solid film, with strong  $\pi$ – $\pi$  stacking between the polymeric backbones, a feature that also appears in regioregular P3HT. The optical bandgap of PTTBTz, estimated from the onset wavelength (ca. 660 nm) of main absorption band of the polymer film, was 1.89 eV, which is similar to that of P3HT (1.91 eV).<sup>34</sup>

**3.4. Electrochemical Properties.** Electrochemical CV was performed for determining the HOMO and LUMO energy levels of the conjugated polymers.<sup>35</sup> As shown in the CV of PTTBTz (see Figure 4), the onset reduction potential ( $\varphi_{\text{red}}$ ) is –1.81 V versus Ag/Ag<sup>+</sup>, and the onset oxidation potential ( $\varphi_{\text{ox}}$ ) is 0.49 V versus Ag/Ag<sup>+</sup>. The HOMO and LUMO energy levels as well as the electrochemical band gap ( $E_{\text{g}}^{\text{EC}}$ ) of the polymer are –5.20, –2.90, and 2.20 eV, respectively, calculated from  $\varphi_{\text{ox}}$  and  $\varphi_{\text{red}}$ .<sup>36</sup> The HOMO energy level of PTTBTz is ca. 0.3 eV down-shifted in comparison with that (–4.9 eV)<sup>37</sup> of P3HT, which is beneficial to a higher *V<sub>oc</sub>* for the PSCs with the polymer as donor because *V<sub>oc</sub>* of PSCs is related to the difference of the LUMO of the acceptor and the HOMO of the donor.<sup>6</sup>

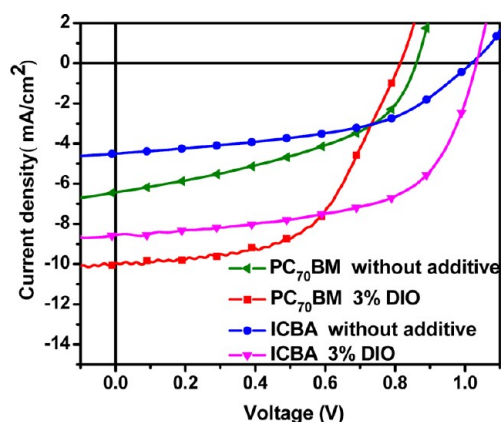
**3.5. Photovoltaic Properties.** Photovoltaic properties of PTTBTz were investigated by fabricating the PSCs based on





**Figure 4.** Cyclic voltammogram of PTTBTz film on a platinum electrode measured in 0.1 mol/L Bu<sub>4</sub>NPF<sub>6</sub> acetonitrile solution at a scan rate of 100 mV/s.

PTTBTz as donor and PC<sub>70</sub>BM or ICBA<sup>28</sup> as acceptor with the device structure of ITO/PEDOT:PSS/PTTBTz: acceptors/Ca/Al. Here ICBA was used as acceptor in the PSC to investigate the suitability of the new acceptor with the D–A copolymer donor. Figure 5 shows the current density–voltage



**Figure 5.** *I*–*V* curves of the polymer solar cells based on PTTBTz:PC<sub>70</sub>BM and PTTBTz:ICBA (1:1 w/w) with or without DIO additive under the illumination of AM 1.5, 100 mW cm<sup>−2</sup>.

characteristic of the device under the illumination of AM1.5, 100 mW cm<sup>−2</sup>, and Table 1 lists the photovoltaic performances of the PSCs based on PTTBTz as donor and PC<sub>70</sub>BM or ICBA as acceptor. PC<sub>70</sub>BM is a widely used acceptor, and the PSC based on PTTBTz:PC<sub>70</sub>BM 1:1 (w/w) demonstrated a *V*<sub>oc</sub> of 0.86 V, *J*<sub>sc</sub> of 6.43 mA cm<sup>−2</sup>, and FF of 0.445, leading to a PCE

**Table 1.** Photovoltaic Performances of the PSCs Based on PTTBTz As Donor and PC<sub>70</sub>BM or ICBA As Acceptor with Donor/Acceptor Weight Ratio of 1:1, under the Illumination of AM1.5G, 100 mW/cm<sup>2</sup>

active layer	<i>V</i> <sub>oc</sub> (V)	<i>J</i> <sub>sc</sub> (mA/cm <sup>2</sup> )	FF	PCE (%)
PTTBTz:PC <sub>70</sub> BM <sup>a</sup>	0.86	6.43	0.445	2.46
PTTBTz:PC <sub>70</sub> BM <sup>b</sup>	0.82	9.89	0.563	4.57
PTTBTz:ICBA <sup>a</sup>	1.02	4.50	0.487	2.23
PTTBTz:ICBA <sup>b</sup>	1.03	8.55	0.608	5.35

<sup>a</sup>Without DIO. <sup>b</sup>With 3% DIO.

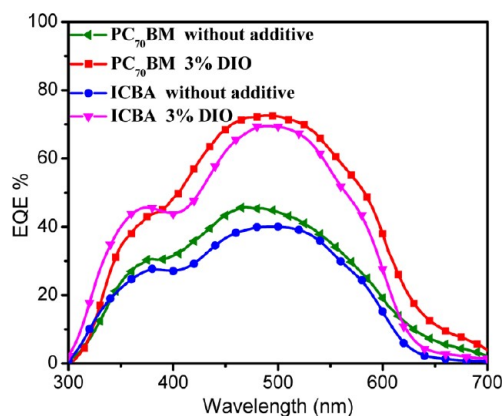
of 2.17%. After using 3% 1,8-diiodooctane (DIO) additive treatment, *J*<sub>sc</sub> and FF of the device based on PTTBTz:PC<sub>70</sub>BM (1:1, w/w) further increased to 9.89 mA cm<sup>−2</sup> and 0.563, respectively, and the PCE reached 4.57%. The PSC based on PTTBTz:ICBA (1:1 w/w) shows an even higher *V*<sub>oc</sub> of 1.02 V, a *J*<sub>sc</sub> of 4.50 mA cm<sup>−2</sup>, and an FF of 0.487, leading to a PCE of 2.23%, which is almost the same as that of the device with PC<sub>70</sub>BM as acceptor. With 3% DIO additive treatment, a high PCE of 5.35% was achieved with a *V*<sub>oc</sub> of 1.03 V, *J*<sub>sc</sub> of 8.55 mA cm<sup>−2</sup>, and an FF of 0.608, respectively. Obviously, the photovoltaic performance is improved greatly by using the 3% DIO additive for both PSCs with PC<sub>70</sub>BM and ICBA as acceptors. Most importantly, the PCE of the PSC with ICBA as acceptor is significantly higher than that of the PSC with PC<sub>70</sub>BM as acceptor for the D–A copolymer of PTTBTz. This is the second D–A copolymer besides the D–A copolymer of dithionosilole and thiazolothiazole<sup>32</sup> that shows much higher PCE with ICBA as acceptor than that with PC<sub>70</sub>BM as acceptor, although ICBA greatly improves the photovoltaic performance of the PSCs based on P3HT<sup>30</sup> and some other polythiophene derivatives<sup>31</sup> than PC<sub>60</sub>BM. Probably, the crystalline structure and relatively higher LUMO energy level of PTTBTz play important role in the high photovoltaic performance of the D–A copolymer blended with the new acceptor ICBA. In considering the similar absorption spectra of PTTBTz and P3HT and the high *V*<sub>oc</sub> of the PSC-based PTTBTz, PTTBTz could be a promising front-layer donor material instead of P3HT in tandem PSCs.

It should be mentioned that the photovoltaic properties reported above are from the PSCs without thermal annealing. Actually, the thermal annealing on the PSCs in the temperature range from 80 to 120 °C for 10 min influenced the photovoltaic performance very little or decreased the photovoltaic performance a little, as shown in Figures S1 and S2 and Tables S1 and S2 in the Supporting Information.

In addition, it deserves to notice that although the new acceptor ICBA improves the photovoltaic performance of P3HT greatly, only very few D–A copolymers<sup>32</sup> show better photovoltaic performance with the acceptor of ICBA than PCBM (PC<sub>60</sub>BM or PC<sub>70</sub>BM). The reasons could be as follows: (1) PCBM is crystalline material but ICBA is amorphous. If the D–A copolymer is amorphous, when it is blended with PCBM the nanoscaled interpenetration network could be formed due to the crystalline aggregation of PCBM, but if the amorphous polymer is blended with the amorphous ICBA, then it will be difficult for the separate aggregation of the donor and acceptor to form the nanoscaled interpenetrating network. (2) The LUMO energy level (−3.74 eV<sup>28</sup>) of ICBA is ca. 0.17 eV up-shifted from that of PCBM; if the LUMO energy level of the D–A copolymer is low, the smaller LUMO energy level difference between the D–A copolymer donor and the ICBA acceptor will decrease the efficiency of the exciton dissociation on the interface of the donor and acceptor, so that it decreases *J*<sub>sc</sub> and PCE of the PSCs. The success of the D–A copolymer PTTBTz here with ICBA acceptor could be benefitted from its crystalline structure and relatively higher-lying LUMO energy levels (−2.90 eV as mentioned above). Anyway, we need more knowledge and polymer examples for understanding what kind of D–A copolymers will show further improved photovoltaic performance with ICBA as acceptor than PCBM. Probably, we also need to look for new solvent additive to improve the interpenetrating network morphology

of the blend films of the D–A copolymers and ICBA in the PSCs.

The external quantum efficiency (EQE) of the PSCs based on PTTBTz:acceptors (1:1 w/w) with and without DIO additive is shown in Figure 6. The maximum EQE values of the



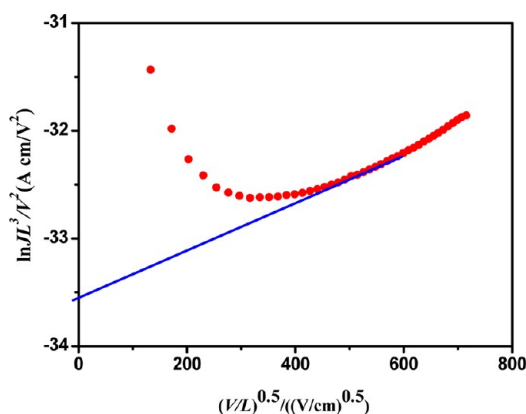
**Figure 6.** EQE of the PSCs based on PTTBTz:PC<sub>70</sub>BM and PTTBTz:ICBA (1:1 w/w) with or without DIO additive.

PSC with PC<sub>70</sub>BM and ICBA as acceptor were 46 and 39% respectively without using DIO additive, and it increased to 73 and 68%, respectively, with 3% DIO additive. The EQE results agree well with the  $J_{sc}$  of the corresponding PSCs mentioned above.

**3.6. Hole Mobility.** Hole mobility is an important parameter for the conjugated polymer donor photovoltaic materials. Here we measured the hole mobility of PTTBTz by space-charge limited current (SCLC) method by using a hole-only device structure of ITO/PEDOT:PSS/polymer/Au. For the hole-only devices, SCLC is described by<sup>38</sup>

$$J \cong (9/8)\epsilon\epsilon_0\mu_0 V^2 \exp(0.89\sqrt{V/E_0L})/L^3 \quad (1)$$

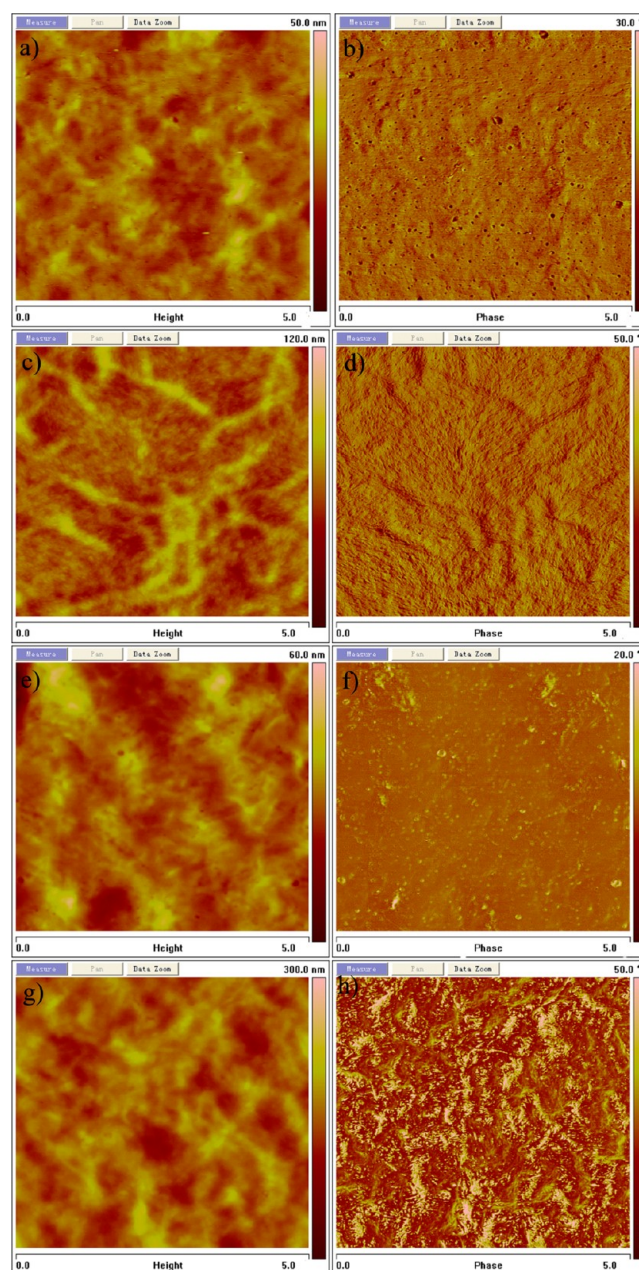
where  $\epsilon$  is the dielectric constant of the polymer,  $\epsilon_0$  is the permittivity of the vacuum,  $\mu_0$  is the zero-field mobility,  $E_0$  is the characteristic field,  $J$  is the current density,  $L$  is the thickness of the blended films layer,  $V = V_{\text{appl}} - V_{\text{bi}}$ ,  $V_{\text{appl}}$  is the applied potential, and  $V_{\text{bi}}$  is the built-in potential that results from the difference in the work function of the anode and the cathode (in this device structure,  $V_{\text{bi}} = 0.2$  V). Figure 7 shows the  $\ln(JL^3/V^2)$  versus  $(V/L)^{0.5}$  plot for the hole mobility measure-



**Figure 7.**  $\ln(JL^3/V^2)$  versus  $(V/L)^{0.5}$  plot of PTTBTz for the measurement of hole mobility by the SCLC method.

ment of PTTBTz. According to eq 1, the hole mobility of PTTBTz was calculated to be  $6.45 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .

**3.7. Morphology.** To understand the effect of 3% DIO additive, we investigated the morphology of the blend films by AFM (as shown in Figure 8). It can be seen that with 3% DIO



**Figure 8.** AFM topography images (a,c,e,g) and phase contrast images (b,d,f,h) of PTTBTz:PC<sub>70</sub>BM (1:1) films without DIO (a,b) and with 3% DIO (c,d) and PTTBTz:ICBA (1:1) films without DIO (e,f) and with 3% DIO (g,h).

treatment the blend film demonstrated more uniform structure and better interpenetrating network than that of the film without DIO treatment. Two features are observed from the comparison: (i) From the height images, the surface processed with DIO is significantly rougher than that without using the solvent additive, with root-mean-square surface roughness of 8.5 nm for the PTTBTz:PC<sub>70</sub>BM (1:1) film with DIO additive (Figure 8c) compared with 3.3 nm for the PTTBTz:PC<sub>70</sub>BM



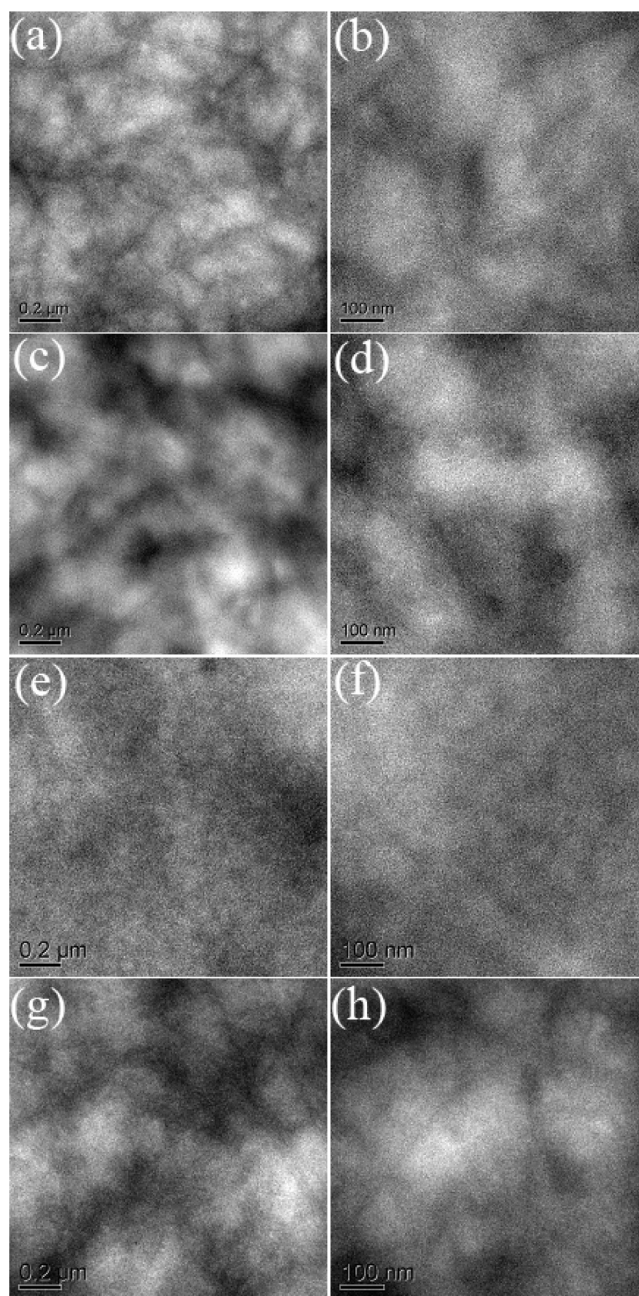
(1:1) film without DIO (Figure 8a) or 20.4 nm for the PTTBTz:ICBA (1:1) film with DIO additive (Figure 8g) compared with 5.1 nm for the PTTBTz:ICBA (1:1) film without DIO (Figure 8e). Islands and valleys are apparent after adding DIO. It has been reported that a rough surface is a “signature” of high-efficiency PSCs in the treatment of both “thermal annealing”<sup>39</sup> and “solvent annealing”.<sup>40</sup> (ii) From the phase images, in the films with the additive, ordered crystalline domains of polymer are clearly visible, but they are absent in the films without the additive. This suggests that ordered chain alignment is achieved when using DIO as solvent additive. As a result, the device performance was greatly improved. These results proved that morphology control by using additive is an effective way to improve the performance of PSCs.

For further confirming the ordered structure induced by the DIO additive, we measured the absorption spectra of the blend films of PTTBTz:PC<sub>70</sub>BM and PTTBTz:ICBA (1:1 w/w) with or without DIO additive, as shown in Figure S3 in the Supporting Information. It can be seen that the absorbance of the blend films with DIO additive is more enhanced than that without DIO additive, which is consistent with the improved ordered structure of the blend films by DIO additive.

Actually, AFM can only probe the surface of active layer. To probe further the morphology throughout the entire film, TEM was used to obtain a real-space image of the phase-separated morphology of the polymer-fullerene blends with or without 3% DIO, as shown in Figure 9. The most pronounced feature of the films with DIO additive compared with that without DIO (Figure 9b,d,f,h) is the appearance of dark clusters in the film and high contrast of these clusters to the background. These clusters are reminiscent of TEM images by Yang et al.,<sup>41</sup> in which PC<sub>70</sub>BM-rich domains were developed during the annealing step. Similar to Yang’s work, the dark regions in Figure 9a are attributed as PC<sub>70</sub>BM clusters. Obviously, the DIO additive helped the formation of appropriate aggregation of the fullerene acceptors, which is beneficial to the improvement of the photovoltaic performance of the PSCs. Our results agree with the literature reports that DIO helps to increase the fullerene domain sizes and morphology of the blend films processed with additives showed larger scaled phase separation than that of the blend film without additive.<sup>42–44</sup>

#### 4. CONCLUSIONS

We synthesized a new D–A copolymer (PTTBTz) containing thienothiophene donor unit and bithiazole acceptor unit, by the Pd-catalyzed Stille-coupling method, for the application as donor materials in PSCs. PTTBTz film shows a similar absorption band and a higher hole mobility of  $6.45 \times 10^{-3} \text{ cm}^2/\text{V s}$  as that of P3HT, but with ca. 0.3 eV lower-lying HOMO energy level at  $-5.20 \text{ eV}$ . The photovoltaic performance of the polymer was improved significantly by using DIO additive and using ICBA as acceptor. The PCE of the PSC based on PTTBTz:PC<sub>70</sub>BM (1:1 w/w) reached 4.57% with  $J_{sc} = 9.89 \text{ mA/cm}^2$ ,  $V_{oc} = 0.82 \text{ V}$ , and FF = 0.563, and the PSC based on PTTBTz:ICBA (1:1 w/w) demonstrated a higher PCE of 5.35% with a high  $V_{oc}$  of 1.03 V, a  $J_{sc}$  of  $8.55 \text{ mA/cm}^2$ , and an FF of 0.608, under the illumination of AM1.5,  $100 \text{ mW/cm}^2$ . These results indicate that PTTBTz is a promising donor material for the application in tandem PSCs, and the new acceptor ICBA could also be used as an efficiency acceptor in the PSCs based on crystalline D–A copolymer donors.



**Figure 9.** TEM images of PTTBTz:PC<sub>70</sub>BM (1:1 w/w) films (a–d) without DIO (a,b) and with 3%DIO (c,d) and PTTBTz:ICBA (1:1 w/w) films (e–h) without DIO (e,f) and with 3%DIO (g,h).

#### ■ ASSOCIATED CONTENT

##### Supporting Information

*I*–*V* curves and photovoltaic performances of the PSCs based on PTTBTz:ICBA and PTTBTz:PC<sub>70</sub>BM and absorption spectra of blend films. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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##### Notes

The authors declare no competing financial interest.

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