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Thiophene-Fused Benzothiadiazole: A Strong Electron-Acceptor Unit to Build D–A Copolymer for Highly Efficient Polymer Solar Cells

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(5) Supporting Information

ABSTRACT: A novel strong electron-acceptor, thieno[2,3-*f*]-2,1,3-benzothiadiazole-6-carboxylate (BTT), was first designed and synthesized. By introducing two thienyl groups into BTT and then copolymerizing with thienyl group substituted benzo[1,2-b:4,5-b']dithiophene (BDTT) unit, a low band gap D–A copolymer (PBTT-TBDTT) was obtained. Compared with its polymer analogue (PBT-TBDTT) with benzothiadiazole (BT) as an acceptor, PBTT-TBDTT exhibits stronger intramolecular charge transfer. Thus, it shows much broader absorption covering almost the whole visible light region (in the range of 300–850 nm) and narrower optical band gap around 1.45 eV with a large IP (ionization potential) at 5.35 eV. The maximum efficiency of PBTT-TBDTT based device reaches 6.07% which is much higher than that of PBT-TBDTT (3.24%), indicating that BTT unit is a promising electron-accentor mojety



indicating that BTT unit is a promising electron-acceptor moiety to construct low band gap D–A copolymers for PSCs with high photovoltaic performances.

INTRODUCTION

Sunlight is a renewable and unlimited energy. The utilization of photovoltaic devices to harvest solar energy and generate electricity is a promising way to solve the problem of energy shortage in the future. In recent years, polymer solar cells (PSCs) have drawn much attention for their lightweight, lowcost, solution-processability to form large-area and flexible devices.¹ And a number of excellent conjugated polymers with PCEs > 8% have been reported.²⁻⁶ In order to harvest the maximum photon flux for polymers, a narrow band gap that absorbs a wide portion of solar spectrum, in particular photon absorption in the near-infrared region is needed. It has been proven that combination of an electron-rich donor (D) unit and an electron-deficient acceptor (A) unit is a powerful strategy in designing narrow band gap conjugated polymers.⁷ Thus, seeking novel efficient donor and acceptor units to develop well-performed p-type conjugated polymers is of great importance in bulk-heterojunction (BHJ) solar cells. So far, a variety of good donor moieties have been designed such as oligothiophene,⁸ carbazole,⁹ benzo[1,2-b:4,5-b']dithiophene (BDT),¹⁰ and dithienosilole (DTS).¹¹ However, excellent electron-accepting moieties such as diketopyrrolopyrrole (DPP) and theinopyrazine enabling polymers to absorb wavelengths over 800 nm remain relatively less.¹²

Due to its planar and rigid geometry, 2,1,3-benzothiadiazole (BT) is regarded to be one of the most classical electrondeficient acceptor units used in PSCs. However, despite its high

absorption coefficient the D-A copolymers containing BT unit commonly show a band gap from 1.7 to 1.9 eV, which were not optimal for efficient sunlight harvesting due to its relatively weak electron-withdrawing capability. In addition, the rigid structure of BT unit without alkyl chain generally leads to low molecular weight and poor solubility of the polymers based on it. This can affect the device fabrication and of course the performance of PSC devices. Thus, further structural modification is necessary for the BT unit to reach better device performance. Until now, much work has been done on this and great achievements have been obtained. Thiadiazole, quinoxaline, and triazole, for example, had been fused on the 5 and 6 positions of BT unit, respectively, affording the corresponding acceptors of benzobisthiadiazole,¹³ [1,2,5]thiadiazolo[3,4-g] quinoxaline,¹⁴ and [1,2,5]thiadiazolo[3,4-f]benzotriazole.¹⁵ These acceptors exhibited much stronger electron withdrawing ability than BT, which could potentially reduce the band gap of resultant polymers. However, the strong electron affinity of the acceptor units affected the charge separation efficiency between the resultant polymer and the fullerene derivative (such as PC₆₁BM, (6,6)-phenyl-C₆₁ butyric acid methyl ester, or PC71BM, (6,6)-phenyl-C71 butyric acid methyl ester, etc.) in the PSCs, thus leading to poor device

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performances despite of their dramatically lowered band gap. Therefore, to develop new acceptors, it is critical to find a balance between the electron affinity and the band gap to match the electron-donating material for PSCs application.

Here, we adopted an approach to increase the quinoid population by fusing a thiophene ring on the BT unit (Figure 1). The BT unit is an aromatic heterocyclic compound



Figure 1. Aromatic and quinoid resonance forms of BTT and BT for comparison.

constituted of a six-member ring of benzene unit fused an adjacent five-member ring of thiadiazole unit on its 2 and 3 positions. The six-member ring connected in the backbone has even higher aromaticity than the five-member ring, so BT unit is even more likely to adopt an aromatic form, and consequently, the polymers with BT unit have relatively larger band gap.^{7a} Generally, the stabilized electronic quinoid state can lead to a lower band gap that had been proven by Wudl and his co-workers.¹⁶ Thus, reducing the aromaticity of benzene group in the BT unit via the structural modification will allow it a greater tendency to adopt the quinoid form through π electron delocalization. Recently, Yu and co-workers had developed thieno [3,4-b]-thiophene (TT) unit by fusing a thiophene ring with the thiophene ring connected in the backbone, which successfully promoted quinoid population of the thiophene unit, thereby reduced the bandgap of polymers.¹⁷ This inspired us to design a new acceptor based on BT unit. It can be expected that fusing a thiophene ring on the 5 and 6 positions of BT unit will stabilize its quinoid structure and further reduce its band gap.

In this work, we presented the design and synthesis of a new strong electron-acceptor, namely, thieno[2,3-f]-2,1,3-benzothiadiazole-6-carboxylate (BTT, see Scheme 1). In this acceptor, the additional carboxyl group moiety was introduced to further lower the HOMO energy level of BTT unit and stabilize the quinoid structure. Meanwhile, introducing a long alkyl chain in the ester could provide unique opportunity to incorporate a solubilizing alkyl side-chain without disturbing the planarity of polymer backbone. BTT is expected to be a stronger acceptor and a more π -extended aromatic ring as compared to BT. Thus, the incorporation of BTT into the polymer main chain could lead to a deeper HOMO energy level and smaller band gap (E_{α}) . Additionally, it can also enhance intermolecular interactions and thereby promote a strong $\pi - \pi$ stacking of polymeric backbones benefiting from the more rigid structure.

Scheme 1. Synthesis of Monomer M1, M3, and polymers PBTT-TBDTT and PBT-TBDTT a



"Reagents and conditions: (a) NBS, Ac_2O , 120 °C, 99.7%; (b) NBS, BPO, 80 °C, 48.2%; (c) urotropin, HAc, H₂O, HCl(aq), 130 °C, 29.8%; (d) ethyl 2-mercaptoacetate, K₂CO₃, CuO, 80 °C, 98%; (e) LiOH·H₂O, HCl(aq), 96%; (f) 2-butyloctan-1-ol, DCC, DMAP, 46%; (g) SnCl₂·2H₂O, 75 °C; (h) Br₂, SOCl₂, Et₃N, 60 °C; (i) 2tributylstannanylthiophene, Pd(PPh₃)₄, 110 °C, 87%; (j) NBS, 74%; (k) NBS, 86%; (l) Pd(PPh₃)₄, toluene, 110 °C; (m) Pd(PPh₃)₄, toluene, 110 °C.

EXPERIMENTAL SECTION

The synthetic procedures of BTT, PBT-TBDTT, and PBTT-TBDTT are described in the Supporting Information (SI). Scheme 1 shows the synthetic routes and approaches used for them.

As can be seen, compound 1 was synthesized by bromination of 5-methyl-2-nitroaniline after protecting of the amino group. Then the benzylic bromination of 1 was implemented to yield compound 2. The key intermediate 3 was obtained via Sommelet reaction in the presence of urotropin. Compound 4 was easily synthesized by using ethyl mercaptoacetate with compound 3. The hydrolysis of compound 4 afforded a carboxylic acid derivative 5. Then the alkylation of 5 yielded 6. Compound 6 was reduced by SnCl₂ and then reacted with Br₂ and SOCl₂ to give a benzothiadiazole derivative 8. BTT-T (9) was obtained by Stille coupling of compound 8 with 2tributylstannanylthiophene. Bromination of 9 with NBS gave 4,8-di(5-bromothiophen-2-yl) thieno[2,3-f]-2,1,3-benzothiadiazole-6-carboxylate (M1) as the monomer.

The PBTT-TBDTT copolymer was obtained via Stille coupling reaction of M1 with M2 (2,6-bis(trimethyltin)-4,8-

di(5-(2-butyloctyl)thiophen-2-yl)-benzo[1,2-b:4,5-b'] dithiophene). The numerable average molecular weight (M_n) reached 58 kDa with polydispersity index (PDI) of 2.8. In addition, the polymer, PBT-TBDTT as a compared analogue was also obtained with M_n of 14 kDa and PDI of 6.2. Both polymers are soluble in common organic solvents such as chloroform, toluene, chlorobenzene, and THF. Moreover, owing to the introduction of a branched long-chain alkyl group into BTT unit, PBTT-TBDTT showed much larger molecular weight and better solubility than PBT-TBDTT. This was beneficial for the performance of the devices.¹⁸ The thermal gravimetrical analysis (TGA) (see Supporting Information Figure S1) indicated that the polymers are much stable up to 380 °C.

RESULTS AND DISSCUSSION

In order to have a better knowledge of BTT, the physicolchemical properties of the monomer units, BT-T and BTT-T (see Scheme 1), were discussed. Figure 2 shows their



Figure 2. UV–vis absorption spectra of BT-T and BTT-T in chloroform solution (the line with symbols) and thin film spun from chloroform (the full line and the dush line). The concentration of both monomers in chloroform was 1×10^{-5} mol⁻¹ L⁻¹.

UV-vis absorption spectra. Obviously, BTT-T displays much higher absorption coefficient of 7.1 \times 10⁴ M⁻¹ cm⁻¹ in the high-energy band around 310 nm, which is over 2-fold than that of BT-T. In the low-energy band from 350 to 650 nm, they give the almost equivalent absorption coefficients of about 1.6 × 10⁴ M⁻¹cm⁻¹. Moreover, BTT-T shows much more redshifted absorption than BT-T. The maximum absorption of BTT-T at 504 nm in chloroform is 62 nm longer than that of BT-T, which can be attributed to the extension of conjugated backbone and stability of quinoid structure through fusing a thiophene ring with an electron accepting ester group. This indicates that BTT unit possesses much stronger electron withdrawing ability than BT. The absorption and emission spectra for BTT-T in different solvents were also measured (See Supporting Information Table S2 and Figures S2 and S3). As can be seen, the polarity of the solvents exerts little influence on the UV-vis absorption. However, the bathochromism for the photoluminescence is observed as the polarity of the solvent increases. Although the solvachromism is not much significant, the large Stokes shift (over 100 nm) is observed for BTT-T at different solvents. This implies that the long wavelength absorption is mainly attributed to the strong ICT. This phenomenon is much similar to some BT derivatives, such as BT-T.^{19,20}

In addition, the much red-shifted absorption is observed in the film state for both monomer units. Especially, in the film state, the ICT absorption of BTT-T appeared a strong shoulder peak at 543 nm, indicating a better molecular ordering. $E_{\rm g}$ values of BTT-T and BT-T determined from the absorption onset are 1.97 and 2.23 eV, respectively. The BTT-T unit possessed a much narrower optical band gap. This is fairly consistent with the results obtained from the cyclic voltammetry (see Supporting Information Figure S4). These results imply that BTT can be acted as a better electronacceptor to build low band gap conjugated copolymers for PSCs.

UV-vis absorption spectra and energy level diagram of the polymers, PBTT-TBDTT and PBT-TBDT, were displayed in Figure 3. The comparisons of their optical and electrical



Figure 3. (a) UV–vis absorption spectra of PBT-TBDTT and PBTT-TBDTT in chloroform solution (the line with symbols) and thin films spun from chloroform (the full line and the dush line). (b) Energy level diagram of the active layer components.

characteristics are provided in Table 1. As shown, the solution absorption spectra of PBT-TBDTT and PBTT-TBDTT display the maximum intramolecular charge transfer (ICT) peak at 615 and 690 nm, respectively, with a similar absorption coefficient of $4.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. In the film state, the maximum absorption of PBT-TBDTT changes barely while PBTT-TBDTT shows a small red-shift of 22 nm. For PBT-TBDT, it shows a pronounced shoulder peak at around 662 nm in the longer wavelength region, indicating the presence of the tight intermolecular packing.

When compared to PBT-TBDTT, PBTT-TBDTT exhibits a broader absorption spectra and a great red-shift over 70 nm in the film state. This can be attributed to the extended π -conjugated and strongly quinoid structure of BTT unit that can be expected to improve the overall PCE of the device. The

polymers	$M_{\rm n}~({\rm kDa})$	PDI	λ_{\max}^{soln} (nm)	$\lambda_{\max}^{\text{film}}$ (nm)	$IP(CV) (eV)^a$	$EA(CV) (eV)^a$	$E_{\rm g}~({\rm eV})^b$	$E_{\rm g}^{\rm opt}({\rm eV})^c$
PBT-TBDTT	14	6.2	427, 615, 662	429, 613, 662	5.18	3.06	2.12	1.70
PBTT-TBDTT	58	2.8	439, 690	447, 712	5.35	3.39	1.96	1.45

^{*a*}Ionization potential (IP) and electron affinity (EA) were determined from the CV using the onset of oxidation (E_{ox} onset) and the onset of reduction (E_{red} onset) of thin films spun from chloroform on platinum electrode in acetonitrile solution with 0.1 M *n*-Bu₄NPF₆ and caculated by the formulas IP (eV) = e (E_{ox} onset + 4.8) and EA (eV) = e (E_{red} onset + 4.8). ${}^{b}E_{g}$ were obtained by E_{g} = IP – EA. ^{*c*}The optical band gaps E_{g}^{opt} were estimated from the absorption edges of thin film spectra.

optical band gaps estimated from the absorption edges of thin film spectra are 1.70 and 1.45 eV for PBT-TBDTT and PBTT-TBDTT, respectively. Interestingly, the optical band gap obtained for PBTT-TBDTT is actually very close to ideal donor polymer (1.5 eV) for PSCs as proposed by Fréchet,²¹ indicative of the great potential of the BTT unit as strong acceptor to construct narrow band gap polymers. Cyclic voltammetry (CV) was used to investigate the electrochemical properties of the polymers and estimate their ionization potentials (IP) and electron affinities (EA) (see Supporting Information Figure S5). The optical and electrical properties of the polymers are summarized in Table 1. PBTT-TBDTT shows a larger IP at 5.35 eV compared to 5.18 eV for PBT-BDTT, this may be benefitial for the open circuit voltage $(V_{\rm OC})$ of the device.²² In addition, the EA value of the former is also increased by 0.33 eV when compared to the latter. The observable increment of both EA and IP makes BTT a stronger acceptor used in PSCs. The band gaps (E_{α}) determined from the CV were 2.12 and 1.96 eV for PBT-TBDTT and PBTT-TBDTT, respectively. The corresponding values were larger than the ones estimated from the absorption edges of thin film spectra. This is caused by the reason that the electron and hole remain electrostatically bound to one another in the excited state (contrary to the ionized state).²³

Polymer solar cells were fabricated from PBT-TBDTT or PBTT-TBDTT as the donating material and (6,6)-phenyl-C₇₁butyric acid methyl ester (PC₇₁BM) as the accepting material with a general device structure of ITO/PEDOT-PSS/ polymer:PC₇₁BM/Ca (20 nm)/Al (90 nm),²⁴ where the active layer was spin-coated from o-dichlorobenzene solution. Besides, PBTT-TBDTT with higher molecular-weight ($M_n = 73$ kDa, PDI = 1.8) and lower molecular-weight ($M_n = 49$ kDa, PDI = 2.1) were also synthesized and discussed in BHJ solar cell devices to study the influence of molecular weight on the device performance. To balance the absorbance and the charge transporting network of the photoactive layer, the weight ratios of polymer and PC₇₁BM were varied from 1:1 to 1:3. Clearly, the 1:2 weight ratio seems to be the optimal ratio (see Supporting Information Figure S6).

The current density-voltage (J-V) curves of the PSC devices based on PBTT-TBDTT/PC₇₁BM (1:2, w/w) under the illumination of AM1.5G, 100 mW cm⁻² are displayed in Figure 4 and the corresponding results are summarized in Table 2. For the higher molecular-weight PBTT-TBDTT (M_n = 73 kDa), the PCE reached 5.10 ± 0.35% (PCE_{max} = 5.45%) with an open circuit voltage (V_{OC}) of 0.75 ± 0.01 V, a short-circuit current density (J_{SC}) of 12.63 ± 0.40 mA cm⁻² and a fill factor (FF) of 53.0 ± 3.5%. With the decreasing of M_n from 73 kDa, 58 kDa to 49 kDa, the corresponding PCE of the devices dropped from 5.10 ± 0.35%, 4.50 ± 0.21% to 2.50 ± 0.23%. Lower M_n leads to poor device performance, this is in accordance with the result that has been reported.¹⁸ Despite the highest PCE value for the highest M_n sample, its poor



Figure 4. J-V curves of the polymer solar cells based on PBTT-TBDTT with different Mn under illumination of AM1.5G, 100 mW cm⁻².

solubility makes the processing of the PBTT-TBDTT/PC₇₁BM film more challenging. A long-time (12 h) and high-temperature (110 °C) stirring process of the PBTT-TBDTT/PC₇₁BM solution (8 mg/mL for PBTT-TBDTT) are needed before use. This makes the deposition of the active layer tedious. Specially, the poor solubility of this high M_n sample ($M_n = 73$ kDa) makes its device performance sensitive to its concentration. At a higher polymer donor concentration of 10 mg/mL, the device showed inferior device performance (see Supporting Information Figure S6). Thus, in the following study, only the 58 kDa M_n sample was used to optimize the morphology for a better device performance. Also for a better understanding of the thiophene fusing effect on the photovoltaic properties, the optimized device performance of its polymer analogue PBT-TBDTT was also provided.

Figure 5a shows the I-V curve of the champion PSC based on PBTT-TBDTT/PC₇₁BM when 1,8-diiodooctane (DIO, 5% v/v) was added as a solvent additive together with the PBT-TBDTT/PC71BM champion device. The corresponding IPCE (incident-photon-to-electron conversion efficiency) spectra are displayed in Figure 5b. The optimal photovoltaic parameters of the devices are summarized in Table 3. The primary optimized solar cell device based on PBT-TBDTT/PC71BM exhibits a $V_{\rm OC}$ of 0.68 ± 0.01 V, a $J_{\rm SC}$ of 8.25 ± 0.20 mA cm⁻², a fill factor (FF) of 54.0 \pm 2.5% and an overall PCE of 3.10 \pm 0.14% $(PCE_{max} = 3.24\%)$, while the corresponding values of PBTT-TBDTT/PC₇₁BM based device are 0.70 \pm 0.001 V, 13.15 \pm 0.25 mA cm⁻², 63.0 \pm 1.5% and 5.90 \pm 0.17 (PCE_{max} = 6.07%) under the same device fabrication conditions except for a DIO additive (5% v/v). The better device performance of PBTT-TBDTT over that of PBT-TBDTT clearly suggested that the as-developed BTT acceptor unit is better than the widely used BT acceptor unit to construct high efficiency conjugated polymers.

Table 2. Summary of	f the Photovoltaic	Characteristics f	for PBTT-TBDTT	with I	Different Molecula	r Weight"
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$M_{\rm n}~({\rm kDa})$	$V_{\rm oc}$ (V)	$J_{\rm sc}$ (mA cm ⁻²)	FF (%)	PCE (PCE_{max}) (%)
49	0.75 ± 0.01	635 ± 0.35	530 ± 25	$250 \pm 0.23(2.73)$
58	0.75 ± 0.01	9.60 ± 0.30	63.0 ± 1.9	450 ± 0.21 (471)
73	0.75 ± 0.01	12.63 ± 0.40	53.0 ± 3.5	$5.10 \pm 0.35(5.45)$
75	0.75 ± 0.01	12.05 ± 0.10	55.0 <u>+</u> 5.5	5.10 ± 0.55 (5.15)

^aDevice average values and standard deviation are based on more than 10 devices. The best efficiencies are given in parentheses.



Figure 5. (a) J-V curves of the champion polymer solar cells based on PBT-TBDTT and PBTT-TBDTT under illumination of AM1.5G, 100 mW cm⁻². (b) IPCE curves of the corresponding polymer solar cells.

DIO is commonly used as a solvent additive in PSCs to improve the device performances owing to its high boil point and good solubility for fullerene aggregates. In this work, we used DIO to optimize the morphology of PBTT-TBDTT based device. This additive was also used in PBT-TBDTT based device, unfortunately, no better device performance was achieved. For PBTT-TBDTT based device, the influence of additive concentration on device fabrication is described in the Supporting Information (Table S1). The effect of DIO additive is clearly visualized from atomic force microscopy (AFM) images in Figure 6. Without DIO, the composite film exhibits microscale phase separation with a root-mean-square (RMS) value of 1.70 nm, suggesting poor dispersion of PC₇₁BM in the polymer matrix. In contrast, nanomorphology with a RMS



Figure 6. Tapping mode AFM topography images $(5 \times 5 \ \mu m^2)$ of the composite films of (a) PBTT-TBDTT without DIO (b) PBTT-TBDTT with DIO. Roughness measurement of the surface (RMS) values are given to describe the smooth level of the morphology.

value of 1.40 nm is clearly visible for the film with 5% DIO additive. The bicontinuous network with nanoscale phase separation improved the exciton dissociation and carrier collection efficiency, thus leading to an increase in the short-circuit current density as well as the device efficiency.

Notably, the $V_{\rm OC}$ of PBTT-TBDTT without DIO is about 0.75 \pm 0.01 V, that is ca. 0.07 V higher than that of PBT-TBDTT (0.68 \pm 0.01 V). This is well in agreement with the result from CV study, in which PBTT-TBDTT has lower IP than PBT-TBDTT. However, the adding DIO additive seems to be unfavorable for the $V_{\rm OC}$ of the PSCs based on PBTT-TBDTT. A drastic decrease from 0.75 \pm 0.01 V (without DIO) to 0.70 \pm 0.01 V (with IDO) is observed. As reported in some references,²⁵ the blend morphology has quite a large effect on $V_{\rm OC}$. Accompanied with the change of morphology, interfacial energy, exciton stabilization and dissociation along with carrier recombination dynamics can also influence the $V_{\rm OC}$. Here, these factors are possible reasons related to the decreased $V_{\rm OC}$ value for PBTT-TBDTT with DIO as additive.

Hole mobility of two polymers (PBTT-TBDTT and PBT-TBDTT) was measured by space charge limit current (SCLC) method. PBTT-TBDTT demonstrated an relatively high hole mobility of 2.00 \times 10⁻⁴ cm² V⁻¹ s⁻¹ (see Supporting Information Figure S7), which is two times higher than that of PBT-TBDTT (8.89 \times 10⁻⁵ cm² V⁻¹ s⁻¹). The higher mobility of PBTT-TBDTT is benefited from its more planar conjugated structure as compared to PBT-TBDTT. This facilitates improved carrier collection efficiency and can partly account for the higher FF and J_{SC} values for PBTT-TBDTT. In the IPCE spectra, PBTT-TBDTT exhibits a much broader photon response range from 300 to 900 nm with relatively high values above 50%. This leads to an enhanced I_{SC} for PBTT-TBDTT. For PBT-TBDTT, the IPCE spectra only showed a response range from 300 to 700 nm with values below 40%. Besides the higher hole-mobility of PBTT-TBDTT, its planar

Table 3. Summary of the Photovoltaic Characteristics for the Polymers of PBT-TBDTT and PBTT-TBDTT $(M_n = 58 \text{ kDa})^a$

polymer	D/A	DIO (%)	$V_{\rm oc}$ (V)	$J_{\rm sc}~({\rm mA~cm^{-2}})$	FF (%)	PCE (PCE _{max}) (%)
PBT-TBDTT	1:2	0	0.68 ± 0.01	8.25 ± 0.20	54.0 ± 2.5	$3.1 \pm 0.14 (3.24)$
PBTT-TBDTT	1:2	5	0.70 ± 0.01	13.15 ± 0.25	63.0 ± 1.5	$5.9 \pm 0.17 (6.07)$

^aDevice average values and standard deviation are based on more than 10 devices. The best efficiencies are given in parentheses.

structure resulted lower reorganization energies can also partly account for its relatively higher IPCE value.²⁶ Thus, benefiting from broader absorption, lager IP and more planar structure, PBTT-TBDTT exhibited enhanced $J_{\rm SC}$ and $V_{\rm OC}$ values and spontaneously resulted in an overall improvement of the PCE of the device.

In organic solar cells, the energy loss (ΔE) under one sun equivalent light intensity can be quantified by the difference between eV_{OC} and the lowest-component optical bandgap (E_{opt}) : $\Delta E = E_{opt} - eV_{OC}$.²⁷ With the fact of the optical band gap of fullerene acceptor is 1.70 eV, here E_{opt} means the optical band gap of PBTT-TBDTT (1.45 eV). Thus, the calculated energy loss of 0.75 eV is approaching 0.70 eV considered as the minimal for charge generation in PSCs. Compared to the optical band gap, the lower ΔE obtained implies that V_{OC} was optimized with PC₇₁BM as acceptor. Recently, Janssen's result suggested a slightly increase in photon energy loss can lead to a higher quantum efficiency for charge generation, indicative of a large room for further enhancing the efficiency by slightly turning the donor–acceptor coupling.²⁸

CONCLUSIONS

In conclusion, thieno [2,3-f]-2,1,3-benzothiadiazole-6-carboxylate (BTT) was first designed and synthesized as a strong electron acceptor and introduced to polymer solar cells to form a novel D-A copolymer with efficient device performance and compared with the traditional benzothiadiazole (BT) based analogue. By the incorporation of the strong electronwithdrawing BTT unit, a polymer with large IP (ionization potential) and good solubility was obtained. The polymer presented a narrow optical band gap around 1.45 eV and broad absorption spectra in the visible and near-infrared region. The maximum PSC device based on PBTT-TBDTT reached more enhanced PCE of 6.07% than that of PBT-TBDTT, implying that BTT will be acted as a novel promising building block developed for organic semiconducting materials. Much work has been done to tailor and optimize the molecular structure by simply adjusting the thiadiazole and thienyl group and further studies are under way.

ASSOCIATED CONTENT

Supporting Information

Experimental details of the synthesis of the polymers, details of the thermal and electrochemical properties, efficient devices fabrication, and characterization of the polymer solar cells. 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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