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# Dialkylthio Substitution: An Effective Method to Modulate the Molecular Energy Levels of 2D-BDT Photovoltaic Polymers

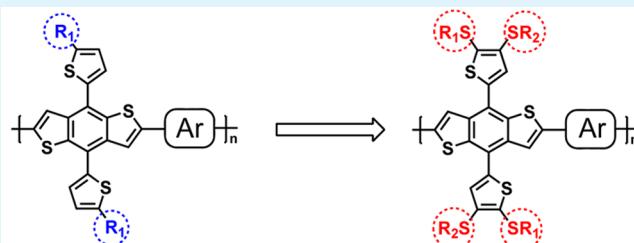
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Supporting Information

**ABSTRACT:** Dialkylthio-substituted thienyl-benzodithiophene (BDT-DST) was designed and synthesized as a building block to modulate the molecular levels of the conjugated polymers, and three copolymers named PDST-BDD, PDST-TT and PDST-DPP were prepared and applied in polymer solar cells (PSCs). Theoretical calculations and electrochemical cyclic voltammetry (CV) measurement suggested that the dialkylthio group could decrease the molecular energy levels of the resulting polymers distinctly. The open-circuit voltage ( $V_{OC}$ ) of PSC devices based on PDST-BDD, PDST-TT, and PDST-DPP are as high as 1.0, 0.98, and 0.88 V, respectively, which are  $\sim 0.15$  V higher than those of the corresponding alky-substituted analogues. Moreover, the influence of the dialkylthio group on the absorption spectra, crystalline properties, hole mobilities, and blend morphologies of the polymers was also investigated. The results indicate that the dialkylthio substitution is an effective method to modulate the molecular energy levels and that the BDT-DST unit has potential for constructing high-efficiency photovoltaic polymers.

**KEYWORDS:** conjugated polymer, polymer solar cell, photovoltaic polymer, molecular energy levels, dialkylthio substitution



**Enhancement of  $V_{OC}$ : 0.14 V - 0.2 V**

## INTRODUCTION

Conjugated polymers have been successfully used as the semiconductors in organic electronic devices like organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic photovoltaic (OPV).<sup>1–6</sup> Unlike the devices based on conventional inorganic semiconductors, the performances of the organic electronic devices are associated with the  $\pi$  electron behaviors of organic semiconductors. Therefore, the modulation of the  $\pi$  orbits of conjugated polymers has become an important topic in the field of organic semiconductors. For instance, the mobility of an organic semiconductor can be tuned by changing the electron transfer integral and reorganization energy, which highly depend on the electron density distributions and energy levels of the highest occupied molecular orbit (HOMO) of and/or the lowest unoccupied molecular orbit (LUMO);<sup>7</sup> for OPV devices, the three key parameters including open circuit voltage ( $V_{OC}$ ), short circuit current density ( $J_{SC}$ ), and fill factor (FF) are all closely correlated to the HOMO and LUMO levels of the photovoltaic materials used in their photoactive layers.<sup>8–19</sup> Therefore, several strategies have been exploited to manipulate the molecular energy levels of conjugated polymers.

Generally,  $V_{OC}$  of the polymer–fullerene solar cells is directly proportional to the gap between the HOMO level of the polymer donor and the LUMO level of the PCBM used in their photoactive layers.<sup>20,21</sup> Hence, the decrease of the HOMO level of the conjugated polymer is beneficial for the enhancement of

$V_{OC}$ .<sup>22–31</sup> Several molecular design strategies have been developed to tune the HOMO levels of conjugated polymers. For example, changing the steric hindrance of the conjugated backbones<sup>26,32,33</sup> or introducing functional groups with varied electronegativity like ester,<sup>23</sup> carbonyl,<sup>34</sup> and fluorine<sup>28</sup> could affect the HOMO levels of the polymers. When alky chains were introduced onto the different positions of the thienyl-substituted benzodithiophene (BDT-T), the HOMO levels of the copolymers based on BDT-T and 4,7-bis-thienylbenzothiadiazole (DTBT) could be tuned from –5.09 to –5.31 eV<sup>26</sup> by the varied steric hindrance of the alkyl side chains; when three “F” atoms were introduced to the copolymers based on BDT-T and thieno[3,4-*b*]thiophene (TT), the HOMO levels were decreased from –4.90 to –5.20 eV and thus the power conversion efficiency (PCE) could be improved from 4.5 to 8.6%.<sup>28</sup> Benefiting from the deep HOMO levels, the PCEs of the devices based on PTB7,<sup>35</sup> PTB7-Th<sup>36</sup> and PBDT-TS1<sup>37</sup> have reached over 10%; however, their  $V_{OC}$  were still relatively low (around 0.8 V). Hence, developing new methods for reducing the HOMO levels is still

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crucial for the improvement of photovoltaic properties of the conjugated polymers.

Recently, alkylthio groups have been utilized in molecular design of organic photovoltaic materials.<sup>38–43</sup> For instance, when the homopolymer based on alkylthio substituted BDT (S-BDT) was applied in PSC, the  $V_{OC}$  of the device reached 0.99 V,<sup>38</sup> a small molecule DR3TSBDT based on the S-BDT unit also achieved an impressive PCE of 9.9% with a  $V_{OC}$  of 0.91 V.<sup>40</sup> Alkylthio groups were also used to modify the BDT-T units, and the resulting polymer yielded a high  $V_{OC}$  of 0.84 V, which was a remarkable  $V_{OC}$  for the PBDT-TT polymers;<sup>44</sup> moreover, for the PBDT-TT-based polymer with linear alkylthio groups, a high PCE of 10.2% with a  $V_{OC}$  of 0.84 V was obtained.<sup>12</sup> Overall, the results demonstrated that although the applications of alkylthio groups show great potentials in molecular design of the PBDT-TT polymers, the  $V_{OC}$  of the corresponding devices are still not as high as that obtained from the homopolymer based on alkylthio substituted BDT or the small molecular DR3TSBDT. Moreover, to gain further understanding of the effect of alkylthio group is an interesting and also a very important topic for molecular design of conjugated polymers.

In this work, a dialkylthio substituted thiényl-benzodithiophene (BDT-DST) unit was designed and synthesized. This new building block was copolymerized with 1,3-bis(thiophen-2-yl)-5,7-bis(2-ethylhexyl)benzo-[1,2-c:4,5-c']dithiophene-4,8-dione (BDD), TT and 2,5-dialkyl-3,6-dithiophene-2-ylidopyrrolo[3,4-c]pyrrole-1,4-dione (DPP) units, respectively, and three new copolymers named as PDST-BDD, PDST-TT and PDST-DPP as shown in Scheme 1 were prepared. The new

polymers based on BDT-T units, and it can be potentially used in other low  $V_{OC}$  polymer systems.

## RESULTS AND DISCUSSION

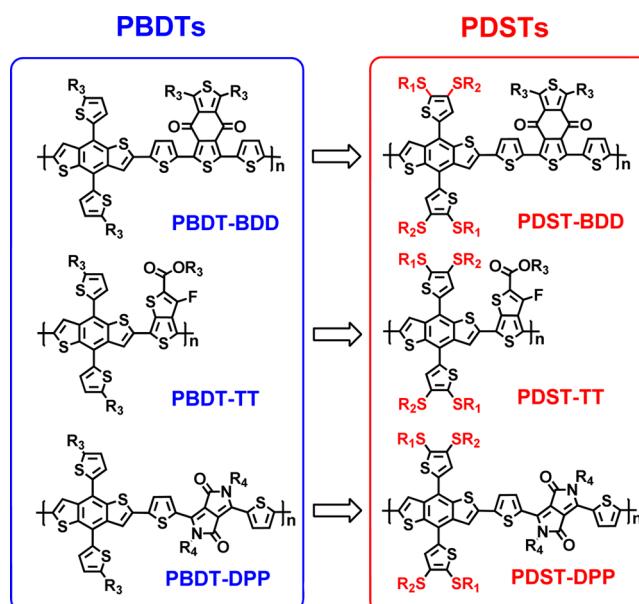
**Synthesis.** The synthetic routes of BDT-DST unit and the three new polymers are demonstrated in Scheme 2. Starting with 3-bromothiophene, the first alkylthio group was introduced onto the 2-position of thiophene; then, the 5-position of the thiophene unit was protected by the trimethylsilyl group. The second alkylthio group was introduced with a yield of 95%. After removal of the trimethylsilyl group, the dialkylthio substituted thiophene unit was introduced onto the BDT unit via the similar method as reported in our previous work.<sup>45</sup> The three polymers, PDST-BDD, PDST-TT, and PDST-DPP, were prepared through a Stille coupling reaction. The detailed synthetic procedures are given in the Experimental Section. Gel permeation chromatography (GPC) was used to determine the molecular weights of the new polymers by using chloroform as the eluent and monodispersed polystyrene as the standard at room temperature. The number-average molecular weights ( $M_n$ ) of PDST-BDD, PDST-TT, and PDST-DPP are 53, 12, and 95 K with polydispersity index (PDI) of 1.73, 2.76, and 2.32, respectively. As shown in Figure 1, thermogravimetric analysis (TGA) was used to evaluate the thermal stability of the polymers, and the thermal decomposition temperature ( $T_d$ ) at 5% weight loss of the three polymers are all above 350 °C.

**Absorption Spectra.** The absorption spectra of the three new polymers and their counterparts based on BDT-T are shown in Figure 2, and the detailed parameters are collected in Table 1. The absorption peaks of PDST-BDD, PDST-TT and PDST-DPP are located at 600, 685, and 773 nm, respectively, and in comparison with their counterparts based on BDT-T, the absorption spectra of the new polymers are slightly blue-shifted. In detail, compared to PBDT-BDD, the absorption peak and edge of PDTS-BDD were blue-shifted by ~20 nm; for PDTS-TT, the absorption peak and edge were blue-shifted by ca. 17 nm compared to PBDT-TT; and in comparison with PBDT-DPP, PDTS-DPP showed the minimum blue shift (3 nm for the absorption peak). Moreover, the optical band gaps of PDTS-BDD, PDTS-TT and PDTS-DPP are 1.83, 1.63, and 1.46 eV, respectively, and these values are all slightly larger than those of their counterparts. The blue shift of absorption spectrum of the PDSTS should be ascribed to the larger steric hindrance effect caused by the side chains on the polymers,<sup>26</sup> which is consistent with the theoretical calculation results.

**Molecular Energy Levels.** Theoretical calculation was performed to investigate the influence of the dialkylthio groups on the molecular energy levels and geometries of the polymers by employing the density functional theory (DFT) with the B3LYP/6-31G\*\* basis set (Gaussian 09).<sup>46</sup> Herein, the molecular structures of the polymers were simplified to dimer and the alkyls were replaced by methyl groups to reduce the cost of calculation. The frontier molecular orbitals, optimized geometries and energy levels the polymers are summarized in Table 2. Clearly, the three new polymers show much deeper HOMO and LUMO levels than their counterparts based on BDT-T. Moreover, the dihedral angles of  $\theta_1$  and  $\theta_2$  in the new polymers are larger than those in the analogue polymers, implying that the BDT-DTS units show different steric hindrance in polymer compared to the BDT-T units.

Electrochemical cyclic voltammetry (CV) was used to determine the HOMO and LUMO levels of the new polymers

**Scheme 1. Molecular Structures of PDSTs and PBDTs**



polymers showed much lower HOMO levels than the analogue polymers based on alkylthio-substituted BDT, i.e. PBDT-BDD, PBDT-TT and PBDT-DPP as shown in Scheme 1. The PSC devices based on the PDST-BDD, PDST-TT and PDST-DPP gave remarkable  $V_{OC}$  values of 1.0, 0.98, and 0.88 V, respectively, which were all the highest values for the devices based on the similar backbone conjugated polymers. The results indicated that the use of dialkythio group is a very effective method to reduce the HOMO levels of the conjugated

Scheme 2. Molecular Structures and Synthetic Routes of the Polymers

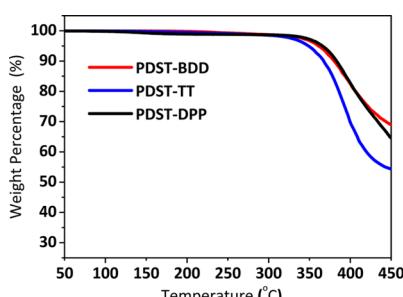
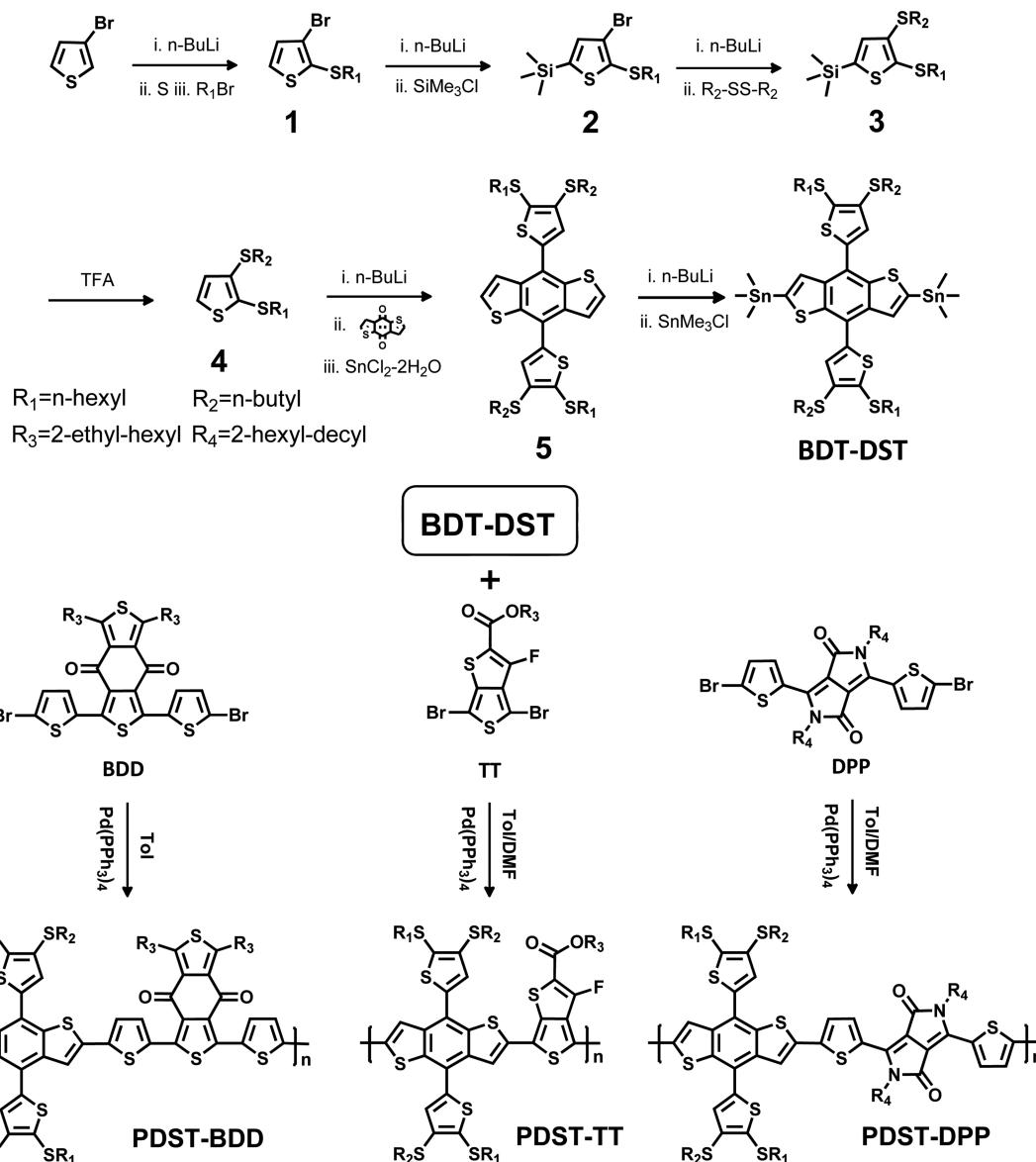
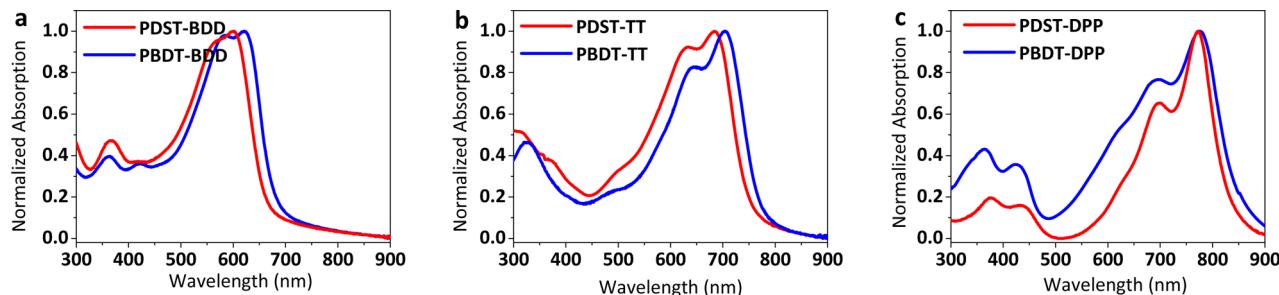


Figure 1. TGA plots of the polymers under a nitrogen atmosphere with a heating rate of 10 °C/min.

and their counterparts. As shown in Figure 3, the three new polymers show higher n- and p-doping potentials than their counterparts. According to the equation of  $\text{HOMO} = -e(\varphi_{\text{OX}} + 4.80)$  (eV),<sup>37</sup> the HOMO levels of the polymers were calculated and listed in Table 1. From PBDT-BDD to PDTBDD and from PBDT-TT to PDTS-TT, the HOMO levels are downshifted for more than 0.2 eV; from PBDT-DPP to PDTS-

DPP, the HOMO levels are downshifted for 0.13 eV. Clearly, the molecular energy levels obtained from the CV measurements are coincident with the results obtained from the theoretical calculations.

**X-ray Diffraction (XRD) Analysis.** XRD measurement was performed to investigate the impact of the dialkylthio groups on interchain packing properties of the polymers. As shown in Figure 4, for PDST-BDD and PBDT-BDD films, (100) and (010) diffraction singles could be observed clearly; the distances of laminar packing of PDST-BDD and PBDT-BDD are 18.1 and 18.7 Å, respectively, and the  $\pi-\pi$  stacking distances of them are 3.79 and 3.64 Å. The different laminar packing distances of the two polymers should be ascribed to the varied lengths of the alkyl chains in the polymers, and the larger  $\pi-\pi$  stacking distance in PDST-BDD than in PBDT-BDD indicates the dialkylthio group has stronger steric hindrance for the intermolecular  $\pi-\pi$  stacking. PDST-TT and PBDT-TT films show similar (010) diffraction peaks, suggesting these two polymers have same  $\pi-\pi$  stacking distances. For PDST-DPP and PBDT-DPP films, the former shows much weaker laminar



**Figure 2.** Absorption spectra of the PBDTs and PDSTs in thin solid films: (a) PBDT-BDD and PDST-BDD, (b) PBDT-TT and PDST-TT, (c) PBDT-DPP and PDST-DPP.

**Table 1. Optical and Electrochemical Parameters of the PDSTs and PBDTs**

polymers	$\lambda_{\text{max}}$ film (nm)	$E_g^{\text{opt}}$ (eV)	HOMO (eV)	HOMO <sup>a</sup> (eV)	$\mu_{\text{hole}}$ ( $\text{cm}^2/(\text{V s})$ )
PDST-BDD	600	1.83	-5.52	-5.01	$1.28 \times 10^{-3}$
PBDT-BDD	620	1.80	-5.30	-4.87	$2.71 \times 10^{-3}$
PDST-TT	685	1.63	-5.50	-5.13	$2.36 \times 10^{-4}$
PBDT-TT	702	1.58	-5.29	-4.93	$4.89 \times 10^{-3}$
PDST-DPP	773	1.46	-5.47	-4.84	$3.86 \times 10^{-4}$
PBDT-DPP	776	1.45	-5.34	-4.73	$1.35 \times 10^{-3}$

<sup>a</sup>Results of theoretical calculation by density functional theory (DFT).

packing but enhanced  $\pi-\pi$  stacking effect than the latter. Overall, the XRD results indicate that the introduction of dialkylthio has different influence on the interchain packing effect for the three polymer systems.

**Hole Mobility.** In order to investigate the influence of the dialkylthio group on the transport properties of carriers, the hole mobilities of PDSTs and PBDTs were measured in parallel by Space-Charge-Limited-Current (SCLC) method.<sup>47</sup> A hole only device structure of ITO/PEDOT:PSS/Polymer/Au was adopted here. The hole mobilities of the three pairs of polymers were calculated from Figure S2 and the results are listed in Table 1. For PDST-BDD, PDST-TT and PDST-DPP, the hole mobilities are  $1.28 \times 10^{-3}$ ,  $2.36 \times 10^{-4}$ , and  $3.86 \times 10^{-4} \text{ cm}^2/(\text{V s})$ , respectively, which are all lower than that of the counterparts based on BDT-T.

**Photovoltaic Properties.** PSC devices with a structure of ITO/PEDOT:PSS/Polymer:PC<sub>71</sub>BM/Mg/Al were fabricated to investigate the photovoltaic properties of the three new polymers. The same device fabrication conditions as those for making the devices based on the analogue polymers<sup>48–50</sup> were used to fabricate the PSCs: the donor/acceptor weight ratios are 1:1, 1:1.5, and 1:2 for PDST-BDD:PC<sub>71</sub>BM, PDST-TT:PC<sub>71</sub>BM, and PDST-DPP:PC<sub>71</sub>BM, respectively, and the mixture of chlorobenzene and 3% (v/v) 1,8-diiodooctane (DIO) was used as the processing solvent for spin-coating. The current–voltage ( $J-V$ ) curves are demonstrated in Figure 5 and the corresponding device parameters are collected in Table 3. The PSC device based on PDST-BDD:PC<sub>71</sub>BM shows a high  $V_{\text{OC}}$  of 1.0 V, which is 0.14 V higher than that of the PBDT-BDD-based PSC. The device of PDST-TT:PC<sub>71</sub>BM shows a  $V_{\text{OC}}$  of 0.98 V, which is the highest value for the PSC devices based on the polymers with BDT and TT backbones. A  $V_{\text{OC}}$  of 0.88 V was obtained from the PDST-DPP:PC<sub>71</sub>BM-based device, which is 0.15 V higher than the device based on PBDT-

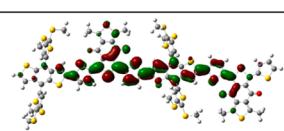
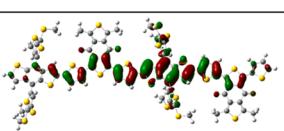
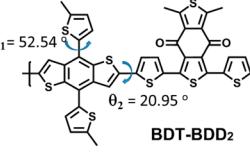
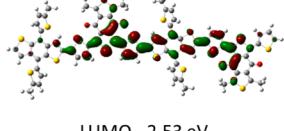
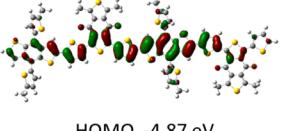
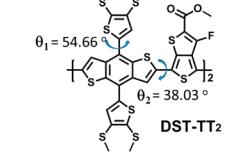
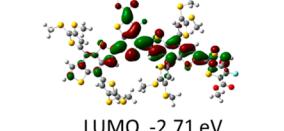
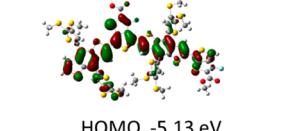
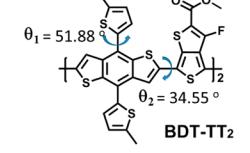
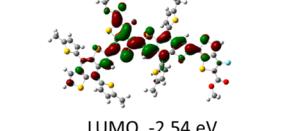
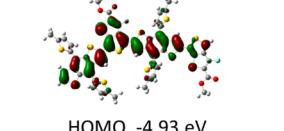
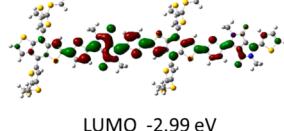
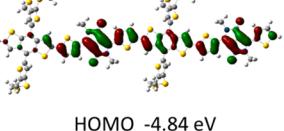
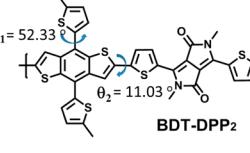
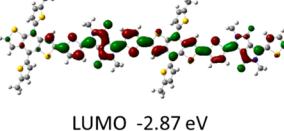
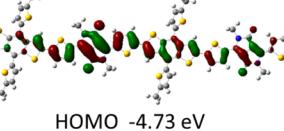
DPP:PC<sub>71</sub>BM and also the highest one for the devices based on DPP-based polymers. However, because the devices based on the three new polymers showed comparatively lower  $J_{\text{SC}}$  and FF, their PCEs are still lower than the PSCs based on their counterparts. Because the FF is primarily depressed by the carrier recombination, the decreased FF of PSC devices might be due to the relatively low hole mobilities of PDSTs, which may cause stronger bimolecular recombination in device.<sup>51,52</sup> On the other hand, from the point of view of molecular design and device physics, the length of the alkyls and the device fabrication conditions for the new polymers have not been fully optimized, which may be another reason for the low PCEs of the devices. However, the photovoltaic results clearly demonstrate that the polymers based on DST unit show great potential in achieving high  $V_{\text{OC}}$  in device.

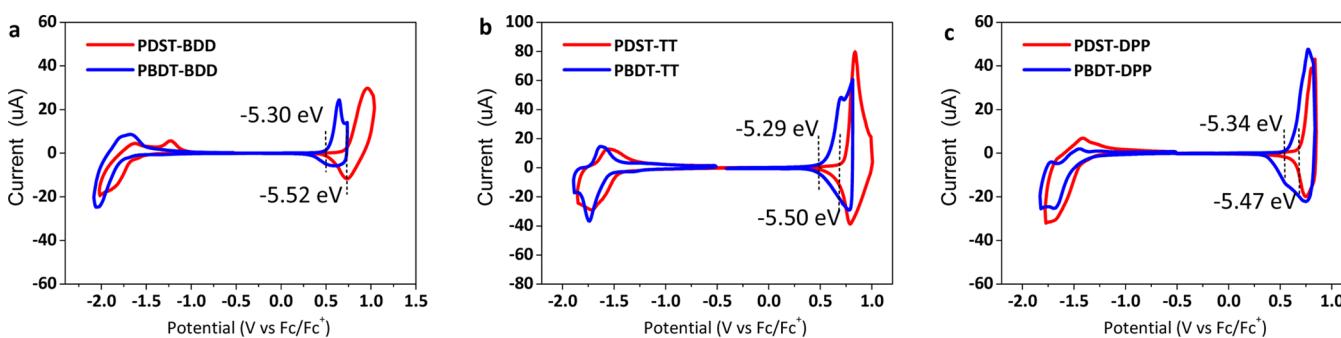
**Morphology.** The surface and bulk morphologies of the blends of polymer:PC<sub>71</sub>BM were respectively studied by atomic force microscopy (AFM) and transmission electron microscopy (TEM). As shown in Figure 6a–c, the mean square surface roughness ( $R_q$ ) of the blends films of PDST-BDD:PC<sub>71</sub>BM, PDST-TT:PC<sub>71</sub>BM and PDST-DPP:PC<sub>71</sub>BM are 0.58, 1.91, and 2.46 nm, respectively. All the films show similar phase separation features to the blend films based on their corresponding BDT-T polymers,<sup>48–50</sup> as illustrated in Figure 6d–f. In addition, as can be clearly observed in TEM images (Figure 6g–6i), both of the PDST-BDD:PC<sub>71</sub>BM and PDST-TT:PC<sub>71</sub>BM films showed uniform and relatively small domains with the length scale of a few tens of nanometers. For PDST-DPP:PC<sub>71</sub>BM film, long fibril domains can be clearly observed, which is a typical character for copolymer based on DPP moiety.<sup>50,52</sup> As a result, the morphological details of BDT-DST polymers exhibited favorable phase separation as well as the previous reported BDT-T polymers with the identical backbones, which revealed that nanoscale morphology is not the main reason for the relatively low efficiency of PDST cases.

## CONCLUSION

In summary, a new conjugated building block, dialkylthio-substituted BDT-T, was designed for the first time and three new polymers were synthesized. The theoretical calculation and CV measurements demonstrated that the HOMO levels of PDST-BDD, PDST-TT, and PDST-DPP are all much deeper than that of the analogue polymers based on BDT-T. Absorption spectra for the polymers are slightly blue-shifted by introducing the DST units and also their crystallinity in thin film can be affected. The  $V_{\text{OC}}$  of PSC devices based on PDST-BDD:PC<sub>71</sub>BM, PDST-TT:PC<sub>71</sub>BM, and PDST-DPP:PC<sub>71</sub>BM are as high as 1.0, 0.98, and 0.88 V, respectively, which are the

**Table 2. Electron Density Distributions and Molecular Energy Levels of the Polymers Calculated by DFT with the B3LYP/6-31G\*\* Basis**

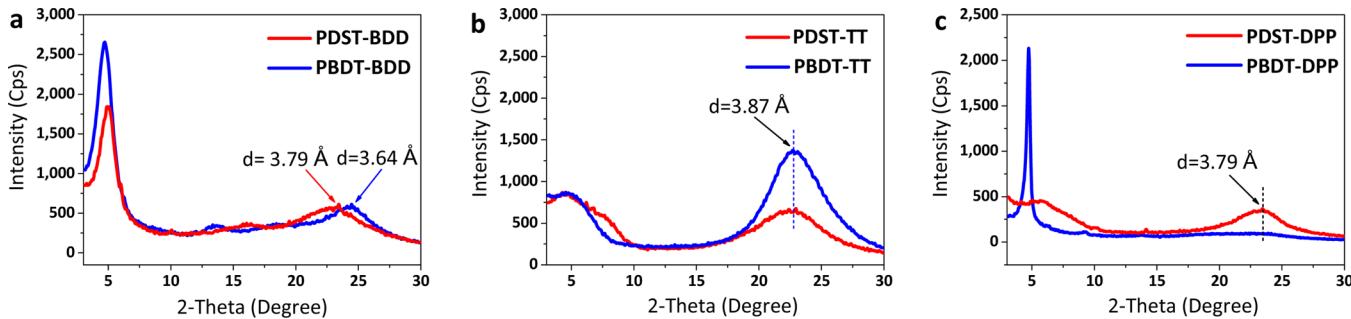
Polymer	LUMO	HOMO
DST-BDD <sub>2</sub>  $\theta_1 = 53.38^\circ$ $\theta_2 = 22.98^\circ$	 LUMO -2.65 eV	 HOMO -5.01 eV
BDT-BDD <sub>2</sub>  $\theta_1 = 52.54^\circ$ $\theta_2 = 20.95^\circ$	 LUMO -2.53 eV	 HOMO -4.87 eV
DST-TT <sub>2</sub>  $\theta_1 = 54.66^\circ$ $\theta_2 = 38.03^\circ$	 LUMO -2.71 eV	 HOMO -5.13 eV
BDT-TT <sub>2</sub>  $\theta_1 = 51.88^\circ$ $\theta_2 = 34.55^\circ$	 LUMO -2.54 eV	 HOMO -4.93 eV
DST-DPP <sub>2</sub>  $\theta_1 = 54.73^\circ$ $\theta_2 = 13.68^\circ$	 LUMO -2.99 eV	 HOMO -4.84 eV
BDT-DPP <sub>2</sub>  $\theta_1 = 52.33^\circ$ $\theta_2 = 11.03^\circ$	 LUMO -2.87 eV	 HOMO -4.73 eV



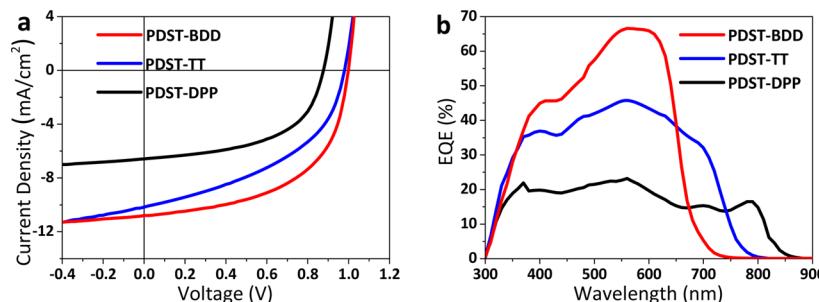
**Figure 3.** CV plots of the polymers in thin films measured in 0.1 M  $\text{Bu}_4\text{NPF}_6$  acetonitrile solution at a scan rate of 50 mV/s: (a) PBDT-BDD and PDST-BDD, (b) PBDT-TT and PDST-TT, (c) PBDT-DPP and PDST-DPP.

highest values for the PSC devices based on the polymers with similar backbones. Overall, this work provides a new and

effective method to reduce HOMO and LUMO levels for the BDT-based polymers, which can be potentially employed to



**Figure 4.** XRD patterns of the PDSTs and PBDTs films on si substrates: (a) PBDT-BDD and PDST-BDD, (b) PBDT-TT and PDST-TT, (c) PBDT-DPP and PDST-DPP.



**Figure 5.** (a)  $J$ - $V$  and (b) EQE curves of the PDST-based solar cell devices.

**Table 3. Photovoltaic Parameters of PSC Devices Based on the Polymers/PC71BM**

polymers	$V_{OC}$ (V)	$J_{SC}$ ( $\text{mA}/\text{cm}^2$ )	FF (%)	PCE (%)
PDST-BDD	1.00	10.80	55.1	5.95
PBDT-BDD <sup>a</sup>	0.86	10.68	72.3	6.67
PDST-TT	0.98	10.15	45.0	4.48
PBDT-TT <sup>a</sup>	0.78	16.86	68.2	9.00
PDST-DPP	0.88	6.59	54.1	3.14
PBDT-DPP <sup>a</sup>	0.73	8.44	68.0	4.23

<sup>a</sup>Data collocated from refs 48–50.

design new polymers with high  $V_{OC}$  and thus high photovoltaic performance.

## EXPERIMENTAL SECTION

**Materials.** The monomers, TT, BDD, DPP as well as the polymer PBDT-TT and the PC<sub>71</sub>BM were obtained from Solarmer Material Inc. The polymers PBDT-BDD<sup>48</sup> and PBDT-DPP<sup>50</sup> were synthesized according the reported literatures. Fresh tetrahydrofuran (THF) was obtained through distillation, dried over the Na/benzophenone. Other chemicals, solvents, and materials used in this work were all commercial available and used as received.

**Synthesis.** *3-Bromo-2-(hexylthio)thiophene (Compound 1).* Under the protection of argon, 10 mL of lithium diisopropylamide (LDA) (2.0 M, 20 mmol) was added dropwise to the solution of 3-bromothiophene (4.89 g, 30 mmol) in distilled THF (60 mL) at 0 °C. After 2 h of stirring, the sulfur powder (0.77 g, 24 mmol) was added into the reaction and stirred for 1 h. Then the 1-bromohexane (4.95 g, 30 mmol) was injected into the reaction and stirred overnight. Water (50 mL) was added to quench the reaction, and the mixture was extracted by diethyl ether. The solvent was removed by rotary evaporation. Four grams (14.34 mmol, yield 72%) of compound 1 was obtained by distillation. GC-MS:  $m/z$  = 280.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$  (ppm):  $\delta$  7.29 (d, 1H),  $\delta$  6.99 (d, 1H),  $\delta$  2.82 (t, 2H),  $\delta$  1.56 (m, 2H),  $\delta$  1.37 (m, 2H),  $\delta$  1.25 (m, 4H),  $\delta$  0.86 (m, 3H).

*(4-Bromo-5-(hexylthio)thiophen-2-yl)trimethylsilane (compound 2).* To a solution of compound 1 (2.79 g, 10 mmol) in THF (20 mL) was added dropwise LDA (6 mL, 12 mmol) at -78 °C under the protection of argon. After 0.5 h of stirring, we added trichloromethylsilane (1.63 g, 15 mmol) and stirred for 0.5 h. Then the cooling bath was removed and the reactant was stirred overnight. The reaction was quenched by water and the reactant was extracted by diethyl ether for three times, and the organic layers were collected and then concentrated. The crude product was purified by silica gel column chromatography using petroleum ether as the eluent; 3.16 g of compound 2 was obtained, yield 90%. GC-MS:  $m/z$  = 352.

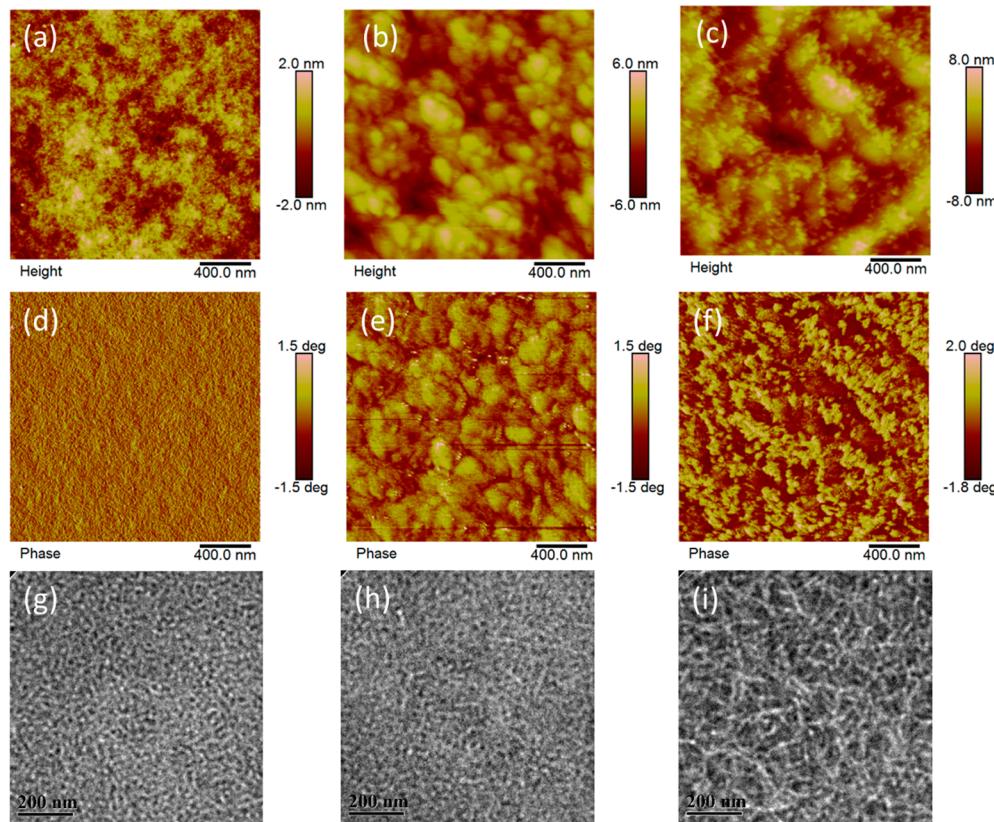
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$  (ppm):  $\delta$  7.09 (s, 1H),  $\delta$  2.85 (t, 2H),  $\delta$  1.61 (m, 2H),  $\delta$  1.40 (m, 2H),  $\delta$  1.26 (m, 4H),  $\delta$  0.87 (m, 3H),  $\delta$  0.30 (s, 9H).

*(4-(Butylthio)-5-(hexylthio)thiophen-2-yl)trimethylsilane (Compound 3).* Under the protection of argon, 3 mL of *n*-butyllithium (2.5 M, 7.5 mmol) was added dropwise to the solution of compound 2 (2.11 g, 6 mmol) in THF (20 mL) at -78 °C. After 0.5 h of stirring at low temperature, 1,2-dibutyldisulfane (1.6 g, 9 mmol) was injected into the reaction and stirred for 0.5 h. Water was then added into the reaction, and the mixture was extracted by diethyl ether. The combined organic layers were concentrated and purified by flash silica gel column chromatography with petroleum ether as eluent; 2.05 g of compound 3 was obtained as yellow oil (5.7 mmol, yield 95%). GC-MS:  $m/z$  = 360.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$  (ppm):  $\delta$  7.07 (s, 1H),  $\delta$  2.85 (m, 4H),  $\delta$  1.58 (m, 4H),  $\delta$  1.40 (m, 4H),  $\delta$  1.27 (m, 4H),  $\delta$  0.84 (m, 6H),  $\delta$  0.30 (s, 9H).

*3-(Butylthio)-2-(hexylthio)thiophene (Compound 4).* To a solution of compound 3 (2.05 g, 5.7 mmol) in THF (30 mL) was added 2 mL of trifluoroacetic acid (TFA) and it was stirred for 2 h. The mixture was then extracted by water and diethyl ether. After the combined organic layer was concentrated, 1.44 g of pure compound 4 (5 mmol, yield 88%) was obtained by silica gel column chromatography with petroleum ether as the eluent. GC-MS:  $m/z$  = 288.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$  (ppm):  $\delta$  7.28 (d, 1H),  $\delta$  6.97 (d, 1H),  $\delta$  2.81 (m, 4H),  $\delta$  1.56 (m, 4H),  $\delta$  1.38 (m, 4H),  $\delta$  1.26 (m, 4H),  $\delta$  0.85 (s, 6H).



**Figure 6.** AFM and TEM images of the PDSTs/PC<sub>71</sub>BM: (a–c) AFM height images of PDST-BDD/PC<sub>71</sub>BM, PDST-TT/PC<sub>71</sub>BM, and PDST-DPP/PC<sub>71</sub>BM; (d–f) AFM phase images of PDST-BDD/PC<sub>71</sub>BM, PDST-TT/PC<sub>71</sub>BM, and PDST-DPP/PC<sub>71</sub>BM; (g–i) TEM images of PDST-BDD/PC<sub>71</sub>BM, PDST-TT/PC<sub>71</sub>BM, and PDST-DPP/PC<sub>71</sub>BM.

**4,8-Bis(4-(butylthio)-5-(hexylthio)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (Compound 5).** Under protection of argon, 2 mL of *n*-butyllithium (2.5 M, 5 mmol) was added into the solution of compound 4 (1.15 g, 4 mmol) in distilled THF (20 mL) at 0 °C. After 10 min of stirring at 0 °C, the mixture was warmed to 50 °C and stirred for another 0.5 h. The mixture was then removed from the oil bath, and benzo[1,2-b:4,5-b']dithiophene-4,8-dione (0.44 g, 2 mmol) was added into the flask at room temperature and stirred for 1 h. Ten minutes later, the reaction was warmed to 50 °C again and stirred for 1 h. After cooling to the room temperature, a solution of SnCl<sub>2</sub>·2H<sub>2</sub>O (3.16 g, 14 mmol) in 10% HCl was added and stirred for another 2 h. The mixture was extracted by water and diethyl ether and concentrated by rotary evaporation, then the raw product was purified by column chromatography with petroleum ether as the eluent; 1.14 g of compound 5 (1.5 mmol, yield 75%) was obtained as sticky yellow oil.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (ppm): δ 7.62 (d, 2H), δ 7.50 (d, 2H), δ 7.36 (s, 2H), δ 2.95 (t, 8H), δ 1.68 (m, 8H), δ 1.47 (m, 8H), δ 1.32 (m, 8H), δ 0.88 (m, 12H).

**(4,8-bis(4-(Butylthio)-5-(hexylthio)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (BDT-DST).** At –78 °C, *n*-butyllithium (1.5 mL, 3.75 mmol) was added dropwise into the solution of compound 5 (1.14 g, 1.5 mmol) in THF (10 mL) under the protection of argon. After reaction for 1 h at this temperature, 4.5 mL of trimethyltin chloride solution (1.0 M, 4.5 mmol) was added and stirred for 0.5 h. The cooling bath was removed, and the mixture was stirred for another 2 h before being quenched by water. The mixture was extracted by diethyl ether, and the combined organic layers were concentrated and purified by recrystallization. The pure BDT-DST (1.1 g, 1 mmol) was obtained as a yellow solid.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (ppm): δ 7.67 (s, 2H), δ 7.38 (s, 2H), δ 2.94 (m, 8H), δ 1.69 (m, 8H), δ 1.47 (m, 8H), δ 1.31 (m, 8H), δ 0.87 (m, 8H), δ 0.51 (t, 18H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz), δ (ppm): 143.37, 143.25, 141.41, 137.21, 136.77, 132.51, 130.63, 130.02, 121.65, 37.54, 34.57, 31.84, 31.44, 29.41, 28.34, 22.56, 21.96, 14.07, 13.76, –8.28.

**Synthesis of the Polymers.** DST (0.3 mmol) and an equal quantity of BDD, TT, or DPP were dissolved in 8 mL of toluene (addition of 1.5 mL of DMF for TT and DPP), and the flask was flushed with argon for 5 min before 15 mg of Pd(PPh<sub>3</sub>)<sub>4</sub> was added. The mixture was flushed with argon for another 15 min, after which the reaction mixture was placed in 110 °C and stirred for 20 h. After cooling to ambient temperature, the polymer was precipitated by addition of 100 mL of methanol. The polymer was collected by filtration and extracted by methanol, hexanes and chloroform, successively, via Soxhlet extractor. The polymer solution in chloroform was precipitated from a large amount of methanol, and the polymer was collected by filtration with a yield about 50%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) spectra of PDST-BDD, PDST-TT and PDST-DPP are provided in the Supporting Information.

**PDST-BDD:** Calcd for C<sub>72</sub>H<sub>86</sub>O<sub>2</sub>S<sub>12</sub>: C 63.20, H 6.34. Found: C 63.28, H 6.87.

**PDST-TT:** Calcd for C<sub>53</sub>H<sub>65</sub>FO<sub>2</sub>S<sub>10</sub>: C 59.29, H 6.10. Found: C 58.97, H 6.14.

**PDST-DPP:** Calcd for C<sub>84</sub>H<sub>118</sub>N<sub>2</sub>O<sub>2</sub>S<sub>10</sub>: C 66.88, H 7.88, N 1.86. Found: C 66.82, H 7.94, N 1.82.

**Instruments and Measurements.** NMR spectra were obtained from a Bruker AVANCE 400 MHz spectrometer at room temperature. Gel permeation chromatography (GPC) was used to estimate the molecular weights and polydispersity (PDI) of the polymers by using polystyrene as standard and chloroform as eluent at room temperature. Elemental analysis results were recorded on a flash EA1112 analyzer. Absorption spectra of polymers were taken on a Hitachi U-3100 UV-vis spectrophotometer. The electrochemical molecular levels were measured on a CHI650D Electrochemical Workstation, in which glassy carbon, platinum wire, and Ag/Ag<sup>+</sup> electrode were used as working electrode, counter electrode, and reference electrode,

respectively, and 0.1 M tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ) acetonitrile solution was used as electrolyte solution. XRD measurement was conducted on a Rigaku D/max 2500 X-ray diffractometer by using thick polymer films drop coated from chloroform solutions. Density–voltage ( $J$ – $V$ ) measurement were performed under 100 mW/cm<sup>2</sup> standard AM 1.5 G spectrum, and a Class AAA solar simulator along with a NIM calibrated KG3-filtered reference cells were used to get reliable results.<sup>53</sup> An integrated IPCE system, QE-R3011 (Enli Technology Co. Ltd., Taiwan), was used to obtain the EQE spectra. The AFM images were obtained from a Nanoscope V AFM on tapping mode, and the bright-field TEM images were obtained from a JEOL 2200FS instrument with an accelerating voltage of 160 kV.

**Fabrication of the PSC Devices.** A device structure of ITO/PEDOT:PSS/polymer:acceptor/Mg/Al was used to evaluate the photovoltaic performance of the polymers, and the devices fabricated under the following conditions: first, the ITO glasses were cleaned by a surfactant scrub, deionized water, acetone, and isopropanol, successively. The ITO glasses went through 15 min of UV-ozone treatment before 35 nm thick of PEDOT:PSS was spin-coated. The ITO substrate was then dried for 15 min at 150 °C. Blend solutions of PDST-BDD/PC<sub>7.1</sub>BM (1:1), PDST-TT/PC<sub>7.1</sub>BM (1:1.5), or PDST-DPP/PC<sub>7.1</sub>BM (1:2) (10 mg/mL for PDST-BDD and PDST-TT, 8 mg/mL for PDST-DPP, based on polymer weight concentration) in chlorobenzene and 3% (v/v) of DIO were spin-coated on PEDOT:PSS. Then 60  $\mu\text{L}$  of methanol was spin-coated on the active layer to remove the residual additives.<sup>54</sup> In the end, 20 nm of Mg and 80 nm of Al were deposited onto the active layer under high vacuum, forming a working area of 4.15 mm<sup>2</sup>. The spin-coating of PEDOT:PSS was performed in a fume hood, and the other processes were all conducted in a glovebox of nitrogen atmosphere.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acsmami.5b07311](https://doi.org/10.1021/acsmami.5b07311).

Absorption spectra of PBDTs and PDSTs in chloroform solutions, mobility measurement plots, and NMR spectra of the intermediates and the polymers ([PDF](#))

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### Notes

The authors declare no competing financial interest.

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