# Macromolecules

# Fluorene Side-Chained Benzodithiophene Polymers for Low Energy Loss Solar Cells

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**S** Supporting Information

**ABSTRACT:** Here we design and synthesize one novel fluorene side-chained benzodithiophene (BDT) monomer for polymer solar cells (PSCs) donor. By copolymerizing this monomer with 4,7-di(thiophen-2-yl)-2,1,3-benzothiadiazole (DTBT) or 4,7-di(4-(2-ethylhexyl)-2-thienyl)-5,6-difluoro-2,1,3-benzothiadiazole (DT*ff*BT), two donor-acceptor (D-A) conjugated polymers PFBDT-DTBT and PFBDT-DT*ff*BT are prepared. PSCs are prepared with these polymers as donor and PC<sub>71</sub>BM as acceptor. The maximum power conversion efficiency (PCE) of the two polymers PFBDT-DTBT and PFBDT-DT*ff*BT based PSCs is 7.13% ( $V_{\rm OC}$  = 0.90 V,  $J_{\rm SC}$  = 13.26 mA cm<sup>-2</sup>, and FF = 0.598) and 7.33% ( $V_{\rm OC}$  = 0.96 V,  $J_{\rm SC}$  = 13.24 mA cm<sup>-2</sup>, and FF = 0.577). The UV-vis absorption and electrochemical cyclic voltammetry test results show that F atoms in



DT*ff*BT unit present an obvious influence on intermolecular effect and molecular energy levels of polymers. Furthermore, the energy loss of two PSCs devices in this work is confirmed to be 0.78 and 0.71 eV, lower than most results based on BDT PSCs devices, which is critical to obtain high PCE PSCs devices with a decent trade-off between  $J_{SC}$  and  $V_{OC}$ .

## INTRODUCTION

Polymer solar cells (PSCs) have received significant attention due to the potential for the fabrication of light-weight, largearea, and flexible light harvesting devices through low-cost solution processing.<sup>1-6</sup> Among them, bulk heterojunction (BHJ) solar cells based on the blend of donor and acceptor materials have been proved to be one of the most efficient structures, and the power conversion efficiency (PCE) with fullerene acceptors has achieved over 10% in both single- and multijunction cells.<sup>7–10</sup> However, the classical fullerene acceptors (for example, PC71BM: [6,6]-phenyl-C71-butyric acid methyl ester) still have intrinsic drawbacks including the relatively narrow absorption region and low molar extinction coefficients, which would cause inefficient harvesting of solar energy. Therefore, the basic optoelectronic properties of donor materials are important and mostly determine photocurrent and photovoltaic efficiencies of polymer solar cells.

D–A conjugated polymers including electron-rich and -deficient units along the polymer backbones have been intensively investigated for the convenience of tuning band gap and energy levels through the intramolecular charge transfer (ICT) effect.<sup>11,12</sup> However, the design of efficient donor materials is still a challenging task because it should

achieve a good balance among all the photovoltaic parameters including open circuit voltage  $(V_{OC})$ , short circuit current density  $(J_{SC})$ , and fill factor (FF), which are directly proportional to power conversion efficiency (PCE =  $J_{SC}$  ×  $V_{\rm OC} \times FF/P_{\rm in}$ ), where  $P_{\rm in}$  is the input light power. Benzo[1,2b:4,5-b']dithiophene (BDT) is one of the most ideal electronrich units for efficient D-A polymers due to its rigid conjugated planarity and suitable electron-donating ability.<sup>13–16</sup> Yu's group first reported efficiency polymer PTB7 based on BDT unit as donor material. The PSCs devices based on PTB7 and PC71BM exhibited excellent photovoltaic property with PCE up to 7.4%.<sup>17</sup> Furthermore, Li and Hou developed twodimensional (2D) conjugated polymers with  $\pi$ -conjugated groups as side chains of BDT unit instead of alkoxy chains to modify the absorption spectra and molecular energy levels, which successfully enhanced the  $J_{SC}$  and  $V_{OC}$  simultaneously.<sup>18–20</sup> Various  $\pi$ -conjugated substitutions with different electronic properties and steric effect have been investigated as BDT side chains, and some efficient D-A polymers (for

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#### Scheme 1. Synthetic Routes of PFBDT-DTBT and PFBDT-DTffBT Polymers



example, PTB7-Th and PBDB-T) were obtained with PCEs exceeding 10% in fullerene and fullerene-free based solar cells.<sup>21–25</sup> The results reveal that the varieties of  $\pi$ -conjugated substitutions in BDT side chains present a significant influence in optoelectronic properties of the resulted D–A polymers and photovoltaic efficiencies of PSCs.

As we all know, the fluorene unit has usually been used as electron-donating moiety to design D-A conjugated polymers due to its rigidity, high hole mobility, and highly conjugated structures.<sup>26,27</sup> Andersson's group introduced the fluorene unit to design donor materials of PSCs.<sup>28</sup> The resulting polymer PFDTBT exhibited good efficiency with PCE of 2.2%. Next, Andersson reported a series of D-A materials based on fluorene with different alkyl and alkoxy side chains with PCE up to 3.5%.<sup>29</sup> In order to improve the solubility and aggregation properties of polymers, Hou synthesized the D-A copolymer PFDTBT and BisDMO-PFDTBT with the PCE of 4.5% and 3.5%, respectively.<sup>30</sup> Woo also brought the fluorene unit into the backbone of highly crystallized polymers to disrupt partially the interchain organizations of excessive aggregation and improved the PCE from 2.6% to 6.6%.<sup>31</sup> Besides, the derivatives of fluorene (including PFN and PFN-Br) were wildly used as interface materials in PSCs field.<sup>32-34</sup> However, to the best of our knowledge, the fluorene unit is generally widely used as the electron-rich unit to construct the polymer backbone, and the photovoltaic polymers with fluorene unit as side chains have not been reported. Considering the excellent property of fluorene unit in polymer backbones, we are attracted by its potential application when it is used as  $\pi$ conjugated side chains of D-A polymers.

In this work, we design and synthesized two D-A conjugated polymers based on novel electron-donating 2D BDT unit with fluorene as the conjugated side chains and electron-withdrawing units 4,7-di(thiophen-2-yl)-2,1,3-benzothiadiazole (DTBT) and 4,7-di(4-(2-ethylhexyl)-2-thienyl)-5,6-difluoro-2,1,3-benzothiadiazole (DTffBT). The results show that F atoms in DTffBT unit present an obvious influence on intermolecular effect and molecular energy levels of polymers. BHJ-PSCs were fabricated with PC71BM as the acceptor material. PSCs devices based on PFBDT-DTBT show the best PCE up to 7.13%, with  $V_{OC}$  = 0.90 V,  $J_{SC}$  = 13.26 mA cm<sup>-2</sup>, and FF = 0.598. Meanwhile, devices based on PFBDT-DTffBT show largely enhanced  $V_{\rm OC}$  (0.96 V) and the best PCE up to 7.33% without any additives or annealing process. Molecular conformations, photophysical/electrochemical properties, and film morphology of blend films were systematically investigated to reveal the structure-property relationships. This work suggests that fluorene moiety is a promising  $\pi$ -conjugated side chain group attached in BDT for the construction of efficient D-A conjugated photovoltaic polymers.

# RESULTS AND DISCUSSION

**Synthesis and Characterization.** The structure and synthetic routes of D–A polymers are outlined in Scheme 1. The fluorene-substituted BDT monomer was designed as electron-donating moiety (D), and DTBT and DT*ff*BT are selected as two electron-withdrawing moieties (A). These two polymers PFBDT–DTBT and PFBDT–DT*ff*BT were prepared by Stille polymerization in the presence of  $Pd_2(dba)_3$  and  $P(o-tolyl)_3$  as catalyst and ligand, respectively. The thermal

	Table 1.	Decompositi	on Temperatu	re, Molecular	Weight, C	ptical Pro	perties, and	Frontier	Energy	Levels of P	olymers
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				$\lambda_{\max}$ (r	nm)				
polymers	$T_{\rm d} (^{\circ}{\rm C})^{a}$	$M_{\rm n}~({\rm kDa})$	PDI	solution	film	$E_{g}^{opt} (eV)^{b}$	$HOMO^{cv} (eV)^{c}$	$LUMO^{cv} (eV)^{c}$	$E_{g}^{cv} (eV)^{c}$
PFBDT- DTBT	371	45.1	1.59	607	645	1.71	-5.41	-3.60	1.81
PFBDT–DT <i>ff</i> BT	392	57.1	1.09	588	602	1.79	-5.82	-3.70	2.12
				636	648				

<sup>a</sup>Measured under N<sub>2</sub> atmosphere. <sup>b</sup>Calculated based on the onset of thin films absorption spectra. <sup>c</sup>Calculated from cyclic voltammograms.



Figure 1. (a) UV-vis absorption spectra of PFBDT-DTBT and PFBDT-DT*ff*BT in dilute *o*-DCB solutions and thin films. (b) Temperaturedependent absorption spectra of PFBDT-DT*ff*BT in dilute *o*-DCB solutions.



Figure 2. (a) Cyclic voltammograms of polymers on glassy carbon electrodes in 0.1 M  $Bu_4NPF_6-CH_3CN$  at a scan rate of 100 mV s<sup>-1</sup>. (b) Energy level diagrams of the materials in this work.

stabilities of the polymers were determined by thermogravimetric analysis (TGA) in a nitrogen atmosphere at a heating rate of 10 °C min<sup>-1</sup>. The TGA curves are shown in Figure S1, and data were collected in Table S1. TGA plots reveal that polymers PFBDT-DTBT and PFBDT-DTffBT exhibit good thermal stability with decomposition temperatures  $(T_d)$  371 and 392 °C at 5% weight loss under nitrogen, respectively, which indicates that the thermal stability of the polymers is good enough for PSCs applications. The number-average molecular weight  $(M_n)$  and polydispersity index (PDI =  $M_w$ /  $M_{\rm p}$ ) were measured by gel permeation chromatography (GPC) using tetrahydrofuran (THF) as the eluent and polystyrenes as the internal standards, and the data are collected in Table 1. As Table 1 indicates, polymer PFBDT-DTffBT shows higher  $M_{\rm p}$ and more favorable polydispersity index (1.09), suggesting more orderly polymer backbones which should benefit the charge transport of PSCs devices.

**Photophysical Properties.** The optical absorption spectra of polymers in dilute *o*-DCB solutions and thin films are shown

in Figure 1a, and the relevant data are summarized in Table 1. The two polymers show similar spectra profiles with broad absorption from 350 to 730 nm covering most of visible spectrum, with two distinct absorption bands at 380-480 and 480-730 nm in solutions and films. The peaks at 380-480 nm are probably corresponding to the  $\pi - \pi^*$  transition, and the major peaks at 480-730 nm should be attributed to the strong intermolecular charge transfer (ICT) effect between the donor and acceptor moieties. Moreover, the UV-vis spectra in thin films are red-shifted compared to those of solutions, which is attributed to the enhanced intermolecular interactions in the solid state. Nevertheless, there are still some differences between polymer PFBDT-DTBT and PFBDT-DTffBT. The absorption spectra of PFBDT-DTffBT in solution and thin film exhibit obvious hypochromatic shift compared to those of PFBDT-DTBT. Analogous results were observed in other fluorine-substituted oligomers and polymers.<sup>35</sup> Different from PFBDT-DTBT, the absorption spectra of PFBDT-DTffBT exhibit strong shoulder peaks at 636 nm in solution



Figure 3. Theoretically calculated molecular conformations, corresponding torsion angles and distributions of frontier energy levels of two polymers. Long alkyl chains were replaced by methyl groups.

Table 2. Photovoltaic Performance of Devices Based on PFBDT–DTBT and PFBDT–DTffB	Table	e 2	2. ]	Photovoltai	: Pe	erformance	of	Devices	Based	on	PFBDT-	-DTBT	and	PFBDT	'-I	)T/	fI	3T
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polymer/acceptor	w/w	$V_{\rm OC}$ (V)	$J_{\rm SC}~({\rm mA~cm^{-2}})$	FF	PCE (%) <sup>a</sup>	$E_{\rm loss}~({\rm eV})$				
PFBDT-DTBT/PC71BM	1:1	0.91	10.63	0.444	4.29 (3.86)	0.76				
PFBDT-DTBT/PC71BM	1:2	0.88	13.69	0.566	6.82 (6.22)	0.79				
PFBDT-DTBT/PC71BM	1:2.5	0.90	13.26	0.598	7.13 (7.07)	0.78				
PFBDT-DTBT/PC71BM	1:3	0.90	11.85	0.617	6.58 (6.14)	0.77				
PFBDT-DTffBT/PC71BM	1:1	0.98	11.69	0.478	5.47 (5.37)	0.69				
PFBDT-DTffBT/PC <sub>71</sub> BM	1:1.5	0.96	13.24	0.577	7.33 (7.15)	0.71				
PFBDT-DTffBT/PC71BM	1:2	0.97	11.51	0.521	5.81 (5.54)	0.70				
The data were based on more than 10 devices and were provided in "highest (average)" format.										

(648 nm in film state) which are directly correlated with polymer aggregation in solution and film state, indicating an improved intermolecular interaction from C-F dipole effect in the DTffBT moiety.<sup>22,36,37</sup> The temperature-dependent absorption spectra arranging from 0 to 100 °C of PFBDT-DTffBT in dilute solution were investigated to further understand the formation of polymer aggregates. As Figure 1b shows, when the solution is heated from 0 to 100 °C, the shapes of the aggregation peak at 648 nm decreased step by step during the heating process. More importantly, the shoulder peak can be detected even at 100 °C, which indicates that the aggregation of PFBDT-DTffBT was strong even at high temperature (100 °C). Furthermore, the optical band gap  $(E_{\alpha}^{opt})$  of polymers PFBDT–DTBT and PFBDT–DTffBT are determined to be 1.71 and 1.79 eV from the onset of the absorption spectra in the thin film states according to  $E_g^{opt}$  =  $1240/\lambda_{onset}$ .

**Electrochemical Properties.** The oxidation and reduction potentials of the polymers were determined by cyclic voltammetry (CV) with the polymer coated on glassy carbon electrodes.<sup>38</sup> In order to obtain the oxidation and reduction potentials of the polymer, the reference electrode was calibrated using ferrocene/ferrocenium (Fc/Fc<sup>+</sup>), which had a redox potential with an absolute energy level of 0.40 eV in a vacuum. CV curves of polymers are shown in Figure 2a. The HOMO and LUMO energy levels were calculated from their onset oxidation potential ( $\varphi_{ox}$ ) and onset reduction potential ( $\varphi_{red}$ ) according to the empirical equation HOMO =  $-(\varphi_{ox} + 4.80 - 0.40)$  (eV) and LUMO =  $-(\varphi_{red} + 4.80 - 0.40)$  (eV). The HOMO/LUMO energy levels of polymers PFBDT–DTBT

and PFBDT–DT*ff*BT are calculated to be -5.41 eV/-3.60 eV, and -5.82 eV/-3.70 eV, respectively, and the relevant data are summarized in Table 1. The deep HOMO energy level of PFBDT–DT*ff*BT would help to obtain a high  $V_{\text{OC}}$  in polymer solar cells. Moreover, as shown in Figure 2b, the gap of HOMO and LUMO levels ( $\Delta$ HOMO and  $\Delta$ LUMO) between polymers and PC<sub>71</sub>BM are both larger than 0.3 eV, which is essential to yield a sufficient driving force for exciton separation in BHJ solar cells.

Molecular Conformation Study. To further understand the influence of fluorene unit in BDT and F atoms in DTffBT moiety on the polymer backbone conformations, quantumchemical calculations (based on density functional theory, B3LYP/6-31G) were performed for the repeat unit of two polymers. The 2-ethylhexyl alkyl chains in BDT units were replaced by a methyl group to reduce the calculation time. From Figure 3 we can see that the bulky fluorene units in BDT produce a large dihedral angle over 58° for two polymers. This highly twisting side groups are beneficial to improve the solubility of polymers and may induce decreased  $\pi$ -orbital overlap between side groups and polymer backbones. Nevertheless, it is clearly observed that both of two polymers exhibit favorable planarity along polymer backbone, which will benefit the charge transport in PSCs active layer. Moreover, the planarity of PFBDT-DTffBT is better than PFBDT-DTBT for the construction of weak noncovalent interactions between S and F atoms in the DTffBT moiety. As a result, polymer PFBDT-DTffBT will possess enhanced intermolecular interactions, which would probably be one reason for the raised aggregation peaks in absorption spectra. From the



Figure 4. (a) J-V curves of polymer/PC71BM solar cells under optimal weight ratio. (b) EQE curves of the corresponding solar cells.

distributions of electron density, both polymers show a delocalized HOMO which is equally distributed over both the donor and acceptor parts of D–A polymer. However, the LUMO energy levels are almost localized on the acceptor units. Moreover, we can see from Figure 3 that polymer PFBDT–DTffBT exhibits deeper frontier energy levels, which is consistent with the results form CV measurement. And we also have calculated the structure of PFBDT–DTffBT and PFBDT–DTffBT with the orientation of two thiophenes in different sides as shown in Figure S2 (Supporting Information), which show similar results as thiophenes in the same sides (Figure 3).

Photovoltaic Properties. Single BHJ-PSCs were fabricated with a configuration of indium tin oxide (ITO)/poly(3,4ethylenedioxythiophene)polystyrenesulfonate (PEDOT:PSS)/ polymers:PC71BM/Ca/Al. The donor-acceptor weight ratio was screened from 1:1 to 1:3. The current density-voltage (*J*-V) curves at different D/A ratios under AM 1.5G (100 mW cm<sup>-2</sup>) illumination are shown in Figure S3, and the device parameters are summarized in Table 2. As Table 2 shows, the optimal donor-acceptor weight ratio of PFBDT-DTBT/  $PC_{71}BM$  is 1:2.5, with PCE up to 7.13% and  $V_{OC} = 0.90 V$ ,  $J_{SC}$ = 13.26 mA cm<sup>-2</sup>, and FF = 0.598. For the devices based on polymer PFBDT-DTffBT, the optimal donor-acceptor weight ratio is proved to be 1:1.5, with PCE up to 7.33% and  $V_{\rm OC} = 0.96$  V,  $J_{\rm SC} = 13.24$  mA cm<sup>-2</sup>, and FF = 0.577. The J-V curves under optimal weight ratio are displayed in Figure 4a. Notably, two PSCs devices exhibit close short-circuit current densities and fill factors, while devices based on PFBDT-DTffBT exhibit significantly enhanced open-circuit voltage near 1.0 V. This should be attributed to its deep HOMO energy levels. To further optimize the solar cells performances, 1,8-diiodooctane (DIO) additive and ITIC acceptor based devices were also systematically investigated. The detailed device performance is summarized in Tables S2 and S3, and the I-V curves are shown in Figures S4 and S5. Unfortunately, they do not show positive improvement.

The corresponding external quantum efficiencies (EQEs) of the PSCs were measured and are shown in Figure 4b. Two devices demonstrate broad photo response in 300–750 nm with the maximum value up to 80% at around 500 nm. Obviously, devices based on PFBDT–DT*ff*BT reveal improved EQE response at 500–670 nm, owing to the strong aggregation peak in absorption spectra. Furthermore, the calculated  $J_{SC}$  for PFBDT–DTBT and PFBDT–DT*ff*BT based devices shows consistent well with the results from J– V measurement. Heterojunction Morphology Studies. Atomic force microscopy (AFM) and transmission electron microscopy (TEM) (Figure 5 and Figure S6) were applied to investigate



**Figure 5.** AFM height (a)  $(5 \ \mu m \times 5 \ \mu m)$  and phase (b)  $(5 \ \mu m \times 5 \ \mu m)$  images of the PFBDT–DTBT:PC<sub>71</sub>BM (1:2.5, w/w) blend films; AFM height (c)  $(5 \ \mu m \times 5 \ \mu m)$  and phase (d)  $(5 \ \mu m \times 5 \ \mu m)$  images of the PFBDT–DT*ff*BT:PC<sub>71</sub>BM (1:1.5, w/w) blend films.

the morphology of blend films. From Figure 5, we can see that both films of PFBDT-DTBT/PC71BM and PFBDT-DTffBT/PC71BM display uniform and fine nanoscale structures. As shown in Figure 5, the root-mean-square (RMS) roughness of PFBDT-DTBT:PC71BM and PFBDT-DTffBT:PC<sub>71</sub>BM are 0.35 and 0.98 nm, respectively. The difference of RMS is probably attributed to the stronger molecular interaction and aggregation ability. However, in the TEM of blend films (Figure S6), we do not observe this aggregation. We propose it may be related to the miscibility between donors and acceptors as well as the film forming mechanism of BHJ structure. Furthermore, some small holes can be observed in two blend films, which is preferable neither for efficient exciton dissociation nor for balanced charge transport. And the defects in blend films should be blamed partially for the low fill factors of two PSCs devices (see Table 2).

Table 3.	Comparison	of Photovoltaic	<b>Properties</b> and	d Energy Los	s of Polymer	s in Analogues
				<i>a</i> ,	,	

polymers/acceptor	$V_{\rm OC}$ (V)	$J_{\rm SC}~({\rm mA~cm^{-2}})$	FF	PCE (%)	$E_{\rm loss}~({\rm eV})$	ref
PFBDT-DTBT/PC71BM	0.90	13.26	0.598	7.13 (7.07)	0.78	this work
PFBDT-DTffBT/PC71BM	0.96	13.24	0.577	7.33 (7.15)	0.71	this work
PBDTB-DTffBT/PC <sub>71</sub> BM	0.85	12.72	0.621	6.71 (6.58)	0.82	21
P3TBDT-DTBT/PC71BM	0.78	8.83	0.520	3.57 (3.51)	0.89	22
PBDT <sub>ODO</sub> -DTBT/PC <sub>71</sub> BM	0.72	11.16	0.620	4.98 (4.90)	0.95	40
PBDT <sub>THO</sub> -DTBT/PC <sub>71</sub> BM	0.68	8.45	0.565	3.24 (3.10)	0.77	41
PBDT <sub>TEH</sub> -DHffBT/PC <sub>71</sub> BM	0.68	11.87	0.552	4.46 (4.35)	0.99	42
$PBDTT_{TEH}-DT_{EH}ffBT/PC_{71}BM$	0.76	13.17	0.619	6.20 (6.03)	0.91	42

**Energy Loss Analysis.** The high  $V_{\rm OC}$  of PFBDT–DT*ff*BT based device would afford a reduced energy loss ( $E_{\rm loss}$ ), which is defined as  $E_{\rm loss} = E_{\rm g} - eV_{\rm OC}$ , where  $E_{\rm g}$  is the lowest optical band gap between donor and acceptor materials.<sup>39</sup> In this work,  $E_{\rm g}$  is defined to be 1.67 eV from the onset absorption of PC<sub>71</sub>BM film at 743 nm (see Figure S7). The  $E_{\rm loss}$  values of PFBDT–DT*ff*BT based device are calculated to be 0.69–0.71 eV, smaller than most of the reported fullerene based PSCs and approaching the empirically low threshold of 0.6 eV (see Tables 2 and 3). The decreased energy loss is critical to afford an ideal trade-off between  $V_{\rm OC}$  and  $J_{\rm SC}$  and strengthen these two parameters simultaneously for high photovoltaic performance.

#### CONCLUSIONS

In this work, a novel fluorene side-chained BDT unit is design and synthesized. By copolymerizing with DTBT or DTffBT unit, high open circuit voltage and low energy loss PSCs donor materials are obtained. Polymer PFBDT–DTffBT shows enhanced PCE (7.33%) and  $V_{\rm OC}$  (0.96 V) than polymer PFBDT–DTBT PCE (7.13%) and  $V_{\rm OC}$  (0.90 V) due to the F induced low HOMO energy level. Furthermore, the fluorene side-chained polymers show low energy loss (0.78 and 0.71 eV) compared with analogues in the literature which contributes to the overall improved photovoltaic performances. The results in this work exhibit that fluorene moiety is a promising  $\pi$ conjugated side chain group attached in BDT for the construction of efficient D–A conjugated photovoltaic polymers and low energy loss PSCs devices.

#### EXPERIMENTAL SECTION

**Materials and Characterization.** Acceptor materials  $PC_{71}BM$  and monomers (2BrDTBT and 2BrDTffBT) are purchased from Solarmer Materials Inc. All solvents and reagents were purchased from Alfa Aesar, Aladdir, and TCI Inc. and utilized directly unless stated otherwise. Toluene or tetrahydrofuran (THF) was distilled from sodium with benzophenone as an indicator, and *N*,*N*-dimethylformamide (DMF) was distilled from CaH<sub>2</sub> under an argon atmosphere before use. The characterization techniques used in this work are collected in the Supporting Information.

**Synthesis.** *Synthesis of* **2**. The synthetic procedures start with the commercially available **1**. **1** (10.0 g, 41 mmol) in 50% aqueous NaOH solution (50 mL) and 3-(bromomethyl)heptane (44.42 g, 230 mmol) dissolved in DMSO (85 mL) were stirred at room temperature. After tetrabutylammonium bromide (1.0 g) was added to the mixture, the mixture was stirred vigorously at 60 °C for 5 h. After the reaction mixture was allowed to cool to room temperature, it was extracted with petroleum ether. The organic phase was washed with water for three times and dried over anhydrous sodium sulfate. After removing the solvent by rotary evaporator, a yellow transparent liquid was collected by distillation under reduced pressure. It was purified by column chromatography on silica gel with petroleum ether as the eluent to afford **2** as oil (yield: 71.75%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.65 (d, *J* = 7.3 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.50 (dd, *J* = 6.4,

1.5 Hz, 1H), 7.44 (dd, J = 8.0, 1.5 Hz, 1H), 7.37–7.33 (m, 1H), 7.31 (d, J = 7.3 Hz, 1H), 7.28 (d, J = 7.2 Hz, 1H), 2.00–1.91 (m, 4H), 0.92–0.67 (m, 22H), 0.51 (m, 6H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):  $\delta$  151.75, 148.96, 139.25, 128.76, 126.30, 125.90, 125.84, 123.07, 123.04, 123.00, 119.86, 118.64, 54.08, 43.33, 33.56, 32.60, 26.97, 26.03, 21.71, 13.03, 9.33.

Synthesis of 3. Under the protection of argon, n-butyllithium (9.38 mL,15 mmol) was added to 2 (7.042 g,15 mmol) in dry THF (30 mL) at -78 °C and stirred for 2 h. Subsequently, dihydrobenzo[1,2-b:4,5b']dithiophene-4,8-dione (1.1 g, 5 mmol) was added at -78 °C and stirred for 1 h.Then the mixture solution was warmed to room temperature and stirred overnight. SnCl<sub>2</sub> (11.28 g, 50 mmol) in 15% HCl (65 mL) was added, and the mixture was heated to 70 °C and stirred further for 6 h. 10 mL of ice water was added, and the mixture as extracted by petroleum ether. The extract was washed with water for three times and dried over anhydrous sodium sulfate. After removing the solvent by the rotary evaporator, the residue was purified by column chromatography on silica gel with petroleum ether as the eluent to afford 3 as light yellow solids (yield: 50.37%). <sup>1</sup>H NMR (600 MHz,  $CDCl_3$ ):  $\delta$  7.89 (d, J = 7.7 Hz, 2H), 7.78 (d, J = 7.4 Hz, 2H), 7.74-7.63 (m, 4H), 7.42 (d, J = 7.3 Hz, 2H), 7.39-7.35 (m, 4H), 7.34-7.26 (m, 4H), 2.11-1.97 (m, 8H), 1.03-0.69 (m, 44H), 0.69-0.52 (m, 24H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 140.44, 140.21, 137.60, 135.71, 135.37, 130.32, 126.26, 124.84, 124.50, 122.22, 121.65, 121.59, 119.56, 119.40, 119.33, 118.00, 109.01, 108.08, 47.03, 37.11, 31.09, 30.82, 30.76, 29.30, 28.96, 28.65, 28.48, 28.22, 25.89, 25.68, 25.66, 21.62, 21.57, 13.08.

Synthesis of 4. Under the protection of argon, n-butyllithium (5.18 mL, 3.23 mmol) was added to 3 (1.16 g, 1.19 mmol) in dry THF (40.0 mL) at -78 °C for 1 h. Then the mixture solution was warmed to room temperature and stirred for 1 h. Then SnMe<sub>3</sub>Cl (4.20 mL, 4.20 mmol) was added at -78 °C. The mixture was stirred overnight. 10 mL of ice water was added, and the mixture was extracted by petroleum ether. After the solvent was removed, the raw product was purified by recrystallization from acetone, and a light yellow solid 4 could be received (yield: 45.79%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$ 7.92-7.89 (m, 2H), 7.79 (d, J = 7.6 Hz, 4H), 7.63 (m, 2H), 7.42 (d, J = 6.4 Hz, 2H), 7.36 (d, I = 7.4 Hz, 4H), 7.32 (d, I = 7.3 Hz, 2H), 2.12-1.97 (m, 8H), 1.13-0.70 (m, 44H), 0.62 (m, 24H), 0.38-0.26 (m, 18H). <sup>13</sup>C NMR (151 MHz,  $CDCl_3$ ):  $\delta$  151.56, 151.30, 151.03, 141.24, 141.21, 141.15, 141.05, 138.56, 130.83, 129.65, 128.47, 126.94, 126.75, 125.34, 124.18, 120.05, 119.86, 55.26, 55.17, 55.09, 45.41, 45.31, 34.83, 34.10, 28.72, 27.50, 22.91, 22.86, 14.18, 10.87, -8.31, -8.32

Synthesis of Polymers PFBDT–DTBT and PFBDT–DTffBT. In a 25 mL flask, 4 (192.97 mg, 0.15 mmol) and 2BrDTBT (68.73 mg, 0.15 mmol) or 2BrDTffBT (74.13 mg, 0.15 mmol),  $Pd_2(dba)_3$  (2.06 mg, 0.0022 mmol), and tri(o-tolyl)phosphine (4.1 mg, 0.0134 mmol) were added under argon. After the addition of dry toluene (8.0 mL), the mixture was heated to 110 °C for 24 h. After cooling to room temperature, the mixture was poured into methanol. The precipitate was collected and filtered into a Soxhlet funnel successively with methanol, acetone, and hexane. The residue was collected and dried overnight under vacuum to afford polymers.

Polymer PFBDT–DTBT was obtained as a black solid (yield: 57%).  $M_n$  (GPC, THF, 40 °C) = 45.1 kDa, PDI = 1.59. Decomposition temperature (N<sub>2</sub>, 5% weight loss): 371 °C. <sup>1</sup>H

NMR (400 MHz, 1,2-dichlorobenzene- $d_4$ , 100 °C):  $\delta$  8.16 (m), 7.91 (br), 7.45 (br), 7.32 (br), 3.34–3.26 (m), 2.11 (br), 1.59 (m), 1.26–0.92 (br), 0.73–0.66 (m).

Polymer PFBDT–DTffBT was obtained as black solid (yield: 61%).  $M_n$  (GPC, THF, 40 °C) = 57.1 kDa, PDI = 1.09. Decomposition temperature (N<sub>2</sub>, 5% weight loss): 392 °C. <sup>1</sup>H NMR (400 MHz, 1,2-dichlorobenzene- $d_4$ , 100 °C): δ 7.97 (br), 7.77 (br), 7.61 (br), 7.46 (br), 7.31 (br), 3.34–3.26 (m), 2.14 (br), 1.26 (m), 0.98 (br), 0.73–0.66 (br).

# ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.7b00998.

General information, TGA analysis, calculated molecular orbitals, details of the PSCs fabrication and performance data,  $^{1}$ H NMR and  $^{13}$ C NMR spectra (PDF)

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#### Notes

The authors declare no competing financial interest.

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