# Macromolecules

# Synthesis and Photovoltaic Properties of Copolymers Based on Benzo[1,2-*b*:4,5-*b*']dithiophene and Thiophene with Different Conjugated Side Groups

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**ABSTRACT:** Three novel copolymers (**PT-ID**, **PT-DTBT**, and **PT-DTBTID**) of benzo[1,2-*b*:4,5-*b'*]dithiophene and thiophene with different conjugated side groups (1,3-indanedione (**ID**), 4,7-dithien-5-yl-2,1,3-benzodiathiazole (**DTBT**), and **DTBT-ID**) were synthesized and developed for polymer solar cell applications. The effects of the different conjugated side groups on the thermal, photophysical, electrochemical and photovoltaic properties of these copolymers were investigated. As the length of the conjugated side groups increased, the absorption of the UV–vis region in solution was



red-shifted. By changing the different side groups, the energy levels and band gaps of the resulted copolymers were effectively tuned. The three copolymers exhibit deep HOMO energy level and relatively high open-circuit voltage ( $V_{oc}$ ). Bulk heterojunction solar cells with these copolymers as electron donors and (6,6)-phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM) as an electron acceptor exhibit power conversion efficiencies of 2.48%, 4.18% and 1.16% for **PT-ID**, **PT-DTBT**, and **PT-DTBTID**, respectively.

# INTRODUCTION

Polymer solar cells (PSCs) have attracted considerable attention in recent years due to their potential for low cost, lightweight, and good compatibility with the roll-to-roll process for making flexible large area devices.<sup>1-3</sup> So far, the most successful polymer solar cells are bulk heterojunction (BHJ) devices,<sup>4-7</sup> which use a phase separated blend of organic electron donor and acceptor components, where the conjugated polymer is often used as the donor and the fullerene derivative is used as the acceptor.<sup>8</sup> It has been realized that an ideal polymer donor in PSCs should exhibit broad absorption with high absorption coefficient in the visible region, high hole mobility, suitable energy level matching with the fullerene acceptor, and appropriate compatibility with the fullerene acceptor to form nanoscale bicontinuous interpenetrating network.9 Optimizing the properties of the polymer donor will offer higher short-circuit current density  $(J_{sc})$ , open-circuit voltage  $(V_{oc})$ , fill-factor (FF), and power conversion efficiency (PCE) of the PSCs.

One feasible approach toward broadening the absorption spectrum and tuning the energy levels is to design alternating donor-acceptor (D-A) copolymers, in which the hybridization of the highest occupied molecular orbital (HOMO) located on the donor moiety with the lowest unoccupied molecular orbital (LUMO) located on the acceptor moiety provides a means of narrowing the band gap and tuning the

HOMO and LUMO energy levels of the conjugated polymers.<sup>10,11</sup> Among these main chain D–A copolymers, it has been demonstrated that benzo(1,2-b:4,5-b') dithiophene (BDT) is the most potential and effective electron-rich donor unit.<sup>12</sup> In the past two years, a series of new D–A low band gap polymers based on BDT have been reported. For example, the solar cells based on a BDT copolymer PBDTTT have achieved a series of high PCE values in the range of 5–7%.<sup>9,13</sup> Although main chain D–A copolymers have been witnessed great success for achieving high performance PSCs, they may suffer from lower hole mobility due to the influence of the acceptor units on the polymer main chain.<sup>14</sup>

A new family of polymers with conjugated side groups or side chains has been developed by several research groups, including ours.<sup>8,15,16</sup> This type of polymers features high hole mobility benefiting from the overlapping of the conjugated side chain interactions with the conjugated main chains, and broad absorption spectra deriving from both the main chains and the conjugated side chains, thus demonstrated prominent device performances in PSCs.<sup>15</sup> Here, we designed and synthesized three copolymers **PT-ID**, **PT-DTBT**, **PT-DTBTID** (as shown in Figure 1) based on BDT and thiophene with different

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Figure 1. Molecular structures of PT-ID, PT-DTBT, and PT-DTBTID.

Scheme 1. Synthetic Routes of the Monomers and the Corresponding Copolymers



conjugated side groups. In order to broaden the absorption spectra of the  $\pi$ -conjugated polymers, 1,3-indanedione (ID) and 4,7-dithien-5-yl-2,1,3-benzodiathiazole (DTBT) as electron-deficient units are to be introduced into side chains of PT-ID and PT-DTBT, respectively. Furthermore, a long side chain (DTBT-ID) composed of DTBT and ID is introduced to form the polymer PT-DTBTID. These conjugated side groups attached to the main chains via vinylene groups. The vinylene linkage serves to enhance coplanarity of the polymer backbone and extend the  $\pi$ -conjugation by further eliminating torsional strains between the main chain and electron-deficient side groups, leading to a lower optical band gap and tunable frontier molecular orbital energy levels. The effects of the conjugated side groups on the thermal, photophysical, electrochemical, and photovoltaic properties of the copolymers were investigated in detail.

### RESULTS AND DISCUSSION

**Synthesis and Chemical Characterization.** Synthetic routes of the monomers and copolymers are shown in Scheme 1. The crucial monomer M4 was synthesized by the reported method.<sup>17</sup> The monomer M1 was obtained by

bromination of thiophene-3-carbaldehyde with NBS under argon atmosphere. The important intermediate, monomer M2, was synthesized from compounds 2 and 3 in a moderate yield (65%) according to the Wittig-Horner reaction, and purified using a silica gel column with an ether/dichloromethane (1/1,v:v) eluent. The aldehyde-functionalized monomer M3 was prepared by Vilsmeier-Haack formylation of M2 under a mild condition.<sup>18</sup> The precursor polymers PT-CHO and PT-DTBTCHO were synthesized by the Stille coupling reaction. Two target copolymers, PT-ID and PT-DTBTID, were obtained by the Knoevenagel condensation between the aldehydefunctionalized precursor polymers (PT-CHO and PT-DTBTCHO) and 1,3-indanedione in yields of 49% and 46%, respectively. The other target copolymer PT-DTBT was directly synthesized by the Stille coupling reaction between the monomer M2 and M4. The chemical structures of the copolymers were verified by <sup>1</sup>H NMR and elemental analysis. The complete disappearance of the aldehyde proton signals at 10.19 for PT-CHO and 10.10 ppm<sup>10,19</sup> for PT-DTBTCHO, and the appearance of olefinic proton signals at 8.75 for PT-ID and 8.72 ppm for PT-DTBTID confirm the efficient conversion reaction of the aldehyde and the successful preparation of target copolymers. **PT-ID**, **PT-DTBT**, and **PT-DTBTID** exhibit good solubility in common organic solvents such as CHCl<sub>3</sub>, THF, CH<sub>2</sub>Cl<sub>2</sub> and chlorobenzene at room temperature. Table 1 summarized the polymerization results

Table 1. Molecular Weights and Thermal Properties of Copolymers

copolymers	yield (%)	$M_{\rm n}~({\rm kg~mol^{-1}})^a$	PDI	$T_{g} (^{\circ}C)^{b}$	$T_{\rm d} (^{\circ}{\rm C})^c$
PT-ID	49	12.1	2.2	160	321
PT-DTBT	78	20.2	2.6	155	368
PT-DTBTID	46	12.5	1.8	165	301

<sup>a</sup>Determined by GPC in THF based on polystyrene standards. <sup>b</sup>Determined by DSC at scan rate of 20 °C/min under nitrogen. <sup>c</sup>Decomposition temperature, determined by TGA in nitrogen, based on 5% weight loss.

and thermal properties of the copolymers. The number-average molecular weight  $(M_n)$  of PT-CHO and PT-DTBTCHO are 11.6 and 11.4 kg mol<sup>-1</sup> with polydispersity index (PDI) of 1.66 and 2.00, respectively. The  $M_n$  of the target copolymers **PT-ID** (12.1 kg mol<sup>-1</sup>) and **PT-DTBTID** (12.5 kg mol<sup>-1</sup>) show a slight increase than those of PT-CHO and PT-DTBTCHO due to the reaction between of 1,3-indanedione and aldehyde group.

**Thermal Properties.** The thermal properties of the target copolymers were obtained by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements. As shown in Figure 2 and Table 1, the TGA curves



Figure 2. TGA curves of copolymers at scan rate of 20  $^{\circ}C/min$  under nitrogen atmosphere.

reveal that the degradation temperatures  $(T_d)$  of 5% weight loss of **PT-ID**, **PT-DTBT**, and **PT-DTBTID**, are 321, 368, and 301 °C, respectively. And the glass transition temperatures  $(T_g)$ are 160, 155, and 165 °C for **PT-ID**, **PT-DTBT**, and **PT-DTBTID**, respectively (Figure 3). We have also measured the DSC curves at different scan rates, and no crystallization or melting peaks are observed upon further heating beyond the  $T_g$ . The results indicate that these copolymers are amorphous. It is clear that the introduction of 1,3-indanedione group in the side chains of the conjugated polymers improves the glass transition temperature. The good thermal stability of the copolymers retards the deformation of the polymer morphology and the degradation of the active layer at elevated temperatures, which are desirable for polymers in PSCs applications.<sup>20</sup>



Figure 3. DSC curves of copolymers collected at a scan rate of 20  $^{\circ}\text{C}/\text{min}.$ 

Photophysical Properties. The photophysical properties of the copolymers were investigated by UV-vis and fluorescence spectroscopy. The correlative data of the copolymers are summarized in Table 2. Figure 4 gives the UV-vis absorption spectra of PT-ID, PT-DTBT, and PT-DTBTID in diluted CHCl<sub>3</sub> solution. All copolymers show two distinct absorption bands. The first absorption bands with the absorption maxima ( $\lambda_{s,max}$ ) at 423 nm for PT-ID, 390 nm for PT-DTBT and 387 nm for PT-DTBTID can be identified with a delocalized excitonic  $\pi - \pi^*$  transition and the second absorption bands of them with  $\lambda_{s,max}$  at 565, 504, and 526 nm, respectively, can be attributed to a localized transition between donor-acceptor charge transfer states.<sup>21,22</sup> PT-DTBTID exhibits the broader absorption which derived from the ICT interaction between the main chain and the conjugated side chains.<sup>23</sup> Obviously, the ICT interactions of the PT-DTBTID are progressively enhanced due to the increase of the electron affinity of the DTBTID group.<sup>10</sup> In comparison with the absorption spectra of the polymer solutions, the absorption spectra of the films are broadened and the peaks are red-shifted. This phenomenon results from the enhanced interchain interaction in the solid films, which is probably related to the increased extent of  $\pi - \pi$  stacking of the backbones and increased polarizability of the film, or both.<sup>24–26</sup> The optical band gaps ( $E_{g}^{opt}$ ) of **PT-ID**, **PT-**DTBT and PT-DTBTID are 1.75, 1.92, and 1.66 eV, respectively, calculated from the onset of the film absorptions.

The photoluminescence (PL) spectra of copolymers in the diluted CHCl<sub>3</sub> solution are shown in Figure 5. The copolymers are excited at the wavelength corresponding to the two  $\lambda_{s,max}$ . For example, PT-DTBT exhibits the same PL spectra when it is excited at 390 and 504 nm, respectively, which indicates that there is a thorough intramolecular energy transfer of the excitons from the conjugated side chains to the main chains. This phenomenon ensures that all photons absorbed by the copolymers are useful for the photovoltaic conversion.<sup>27</sup> In CHCl<sub>3</sub> solution, **PT-ID** exhibits a maximum emission peak ( $\lambda_{fmax}$ ) at 663 nm. With **DTBT** and **DTBTID** as the conjugated side groups, the  $\lambda_{f,max}$ of PT-DTBT (682 nm) and PT-DTBTID (705 nm) are redshifted by 19 and 42 nm, respectively, compared with that of PT-ID. All the results clearly indicate that the photophysical properties of these copolymers could be tuned by changing conjugated side groups.

Electrochemical Properties. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular

Table 2. Optica	l and Electroc	hemical Propertie	s of the	Three Copo	lymers
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	solution $\lambda_{ m s}$	$_{s,max} (nm)^a$	abs (	(nm)				
copolymers	abs	PL	film $\lambda_{f,max}(nm)$	film $\lambda_{edge}(nm)$	$E_{\rm g}^{\rm opt} ({\rm eV})^b$	HOMO (eV)	LUMO (eV)	$E_g^{ec}$ (eV)
PT-ID	423	663	443	707	1.75	-5.22	-3.40	1.82
PT-DTBT	504	682	517	644	1.92	-5.44	-3.44	2.00
PT-DTBTID	526	705	534	748	1.66	-5.25	-3.54	1.71

<sup>a</sup>Measured in chloroform solution. <sup>b</sup>Band gap estimated from the optical absorption band edge of the films.



Figure 4. UV-vis absorption spectra of the copolymers in chloroform solutions and in the film states.



Figure 5. Photoluminescence spectra of copolymers in the CHCl<sub>3</sub> solution.

orbital (LUMO) energy levels of the conjugated polymers are important parameters in the design of optoelectronic devices, and they can be estimated from the onset oxidation and reduction potentials of cyclic voltammogram (CV).<sup>28</sup> Figure 6 shows the CV curves of the three copolymers and that of ferrocene for potential calibration. The redox potential of ferrocene is 0.51 V vs SCE. On the basis of 4.8 eV below vacuum for the energy level of Fc/Fc<sup>+</sup>, the HOMO and LUMO energy levels of as well as the electrochemical energy gaps ( $E_g^{ec}$ ) of copolymers were calculated according to the following equations:

HOMO = 
$$-e(E_{ox} + 4.29)$$
 (eV)  
LUMO =  $-e(E_{red} + 4.29)$  (eV)  
 $E_{\sigma}^{ec} = e(E_{ox} - E_{red})$  (eV)

The onset potentials for oxidation  $(E_{ox})$  were observed to be 0.93, 1.15, and 0.96 V for **PT-ID**, **PT-DTBT**, and



Figure 6. Cyclic voltammograms of the polymer films on platinum electrode in 0.1 mol/L  $Bu_4NPF_6$  acetonitrile solution.

PT-DTBTID, respectively. On the other hand, the onset potentials for reduction  $(E_{\rm red})$  of them were found to be -0.89, -0.85, and -0.75 V, respectively. Accordingly, the HOMO energy levels of PT-ID, PT-DTBT, and PT-DTBTID, are -5.22, -5.44, zand -5.25 eV, respectively. Regarding the threshold HOMO energy level for air stable conjugated polymers being estimated to be -5.2 eV,<sup>29,30</sup> the deep HOMO levels of the three copolymers with acceptor groups (DTBT, ID, and DTBTID) should be beneficial to their chemical stability in ambient conditions. In addition, the deep HOMO levels of the copolymers are desirable for higher open-circuit voltage  $(V_{oc})$  of the PSCs with copolymers as donor materials<sup>31</sup> because the  $V_{ac}$ is usually proportional to the difference between the HOMO energy level of the donor and the LUMO energy level of the acceptor. The HOMO energy level of PT-DTBT is ~0.2 eV lower than those of PT-ID and PT-DTBTID, predicting that **PT-DTBT** would achieve the highest  $V_{ac}$  value. On the other hand, a donor polymer intended for use with a soluble fullerene acceptor (e.g., PC<sub>61</sub>BM) should have a LUMO offset of approximately 0.3–0.4 eV relative to  $PC_{61}BM (-4.2 \text{ eV})^{32,33}$ for the effective charge transfer. The LUMO levels of PT-ID, PT-DTBT, and PT-DTBTID are -3.40, -3.44, and -3.54 eV, respectively, which imply an effective charge transfer could occur from the copolymers to PC<sub>61</sub>BM.<sup>34</sup> The electrochemically estimated band gaps of the copolymers are 1.71-2.00 eV and they are different from corresponding optical band gaps  $(E_g^{opt})$ , but within the range of error (0.2-0.5 eV).<sup>35</sup> Furthermore, compared with PT-ID, the lower LUMO energy levels of polymers PT-DTBT and PT-DTBTID should be a result of the extension of  $\pi$ -electron delocalization in the polymer backbone.<sup>36</sup> In a word, with the increase the length of conjugated side chains, the LUMO energy levels of the three copolymers are lowered gradually.

**Photovoltaic Properties.** In order to investigate whether the conjugated side groups of the three copolymers make a contribution to the photoelectric conversion in the PSCs, the bulk heterojunction PSC devices based on the blend of the copolymers and  $PC_{61}BM$  have been fabricated. The structure of fabricated devices is ITO/PEDOT:PSS/polymer:PC<sub>61</sub>BM-(1:4,w/w)/Ca/Al. Figure 7 shows the current–voltage (*J*–*V*)



Figure 7. J-V curves of the photovoltaic cells based on PT-ID, PT-DTBT, and PT-DTBTID under the illumination of AM 1.5, 100 mW/cm<sup>2</sup>.

curves of the PSCs based on the three copolymers. The photovoltaic parameters of the PSCs are summarized in Table 3. Under standard global AM 1.5 solar condition, the

Table 3. Photovoltaic Properties and Mobility of PT-ID, PT-DTBT, and PT-DTBTID

copolymers/PC <sub>61</sub> BM (1:4, w/w)	$V_{\rm oc} \ ({ m V})$	$J_{\rm sc}$ (mA/cm <sup>2</sup> )	FF	PCE (%)	mobility (cm <sup>2</sup> /V S)
PT-ID	0.71	7.19	0.49	2.48	$6 \times 10^{-5}$
PT-DTBT	0.81	12.65	0.41	4.18	$3.2 \times 10^{-3}$
PT-DTBTID	0.62	4.67	0.40	1.16	$3 \times 10^{-5}$

photovoltaic cells based on PT-DTBT exhibit better photovoltaic performance ( $J_{sc} = 12.65 \text{ mA/cm}^2$ ,  $V_{oc} = 0.81 \text{ V}$ , FF = 0.41, and PCE = 4.18%) than **PT-ID** based device  $(J_{sc} = 7.19)$  $mA/cm^2$ ,  $V_{oc} = 0.71$  V, FF = 0.49, and PCE = 2.48%) and PT-**DTBTID** based device  $(J_{sc} = 4.67 \text{ mA/cm}^2, V_{oc} = 0.62 \text{ V}, FF =$ 0.40, and PCE = 1.16%). In comparison with **PT-ID**, the better overlap of the absorption spectrum of PT-DTBT with the solar spectrum can account for the increase in  $J_{sc}$  as revealed by incidentphoton-to-current efficiency (IPCE) spectra (Figure 8). On the other hand, the PCE based on PT-DTBTID is considerably lower than those of PT-ID and PT-DTBT, despite the fact that the absorption spectrum of PT-DTBTID better match the solar spectrum in comparison with the other two. That is because the electron deficient nature of the DTBTID group provides a wider photo responsive range (Figure 8), but it can also act as a trapping site, inhibiting electron transfer from the main chain to the acceptor and as a result to produce low IPCE values and poor photovoltaic performance for PT-DTBTID.37 In addition, the bulky side chain (DTBTID) of the PT-DTBTID leads to a significant decrease in  $J_{sc}$ , consequently, a decrease in the PCE of the solar cell. PT-DTBT with DTBT as the side chains shows the highest PCE due to the highest  $J_{sc}$  and  $V_{oc}$ . Therefore, the side group DTBT seems to be better than ID, and ID seems to be better than DTBTID.



Figure 8. IPCE of the polymer solar cells based on PT-ID, PT-DTBT, and PT-DTBTID.

To further understand the cause of variation in solar cell performance, the hole mobility of these copolymers was measured using the OTFT technique under the same conditions. The mobility values of the copolymers are listed in Table 3. **PT-DTBT** with the DTBT side chain demonstrated a relatively high hole mobility of  $3.2 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> which is two order higher than those of **PT-ID** ( $6 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) and **PT-DTBTID** ( $3 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) (Table 3). Furthermore, the hole mobility of **PT-ID** is double of **PT-DTBTID**. Therefore, the high hole mobility of the **PT-DTBT** further clearly explain why the photovoltaic properties of the **PT-DTBT** are better than those of **PT-ID** and **PT-DTBTID**.

## CONCLUSION

In summary, three novel alternating copolymers based on benzo 1,2-b:4,5-b' dithiophen and thiophene with different conjugated side groups have been successfully synthesized and characterized. The three copolymers show good solubility and film-forming ability. Through manipulating the length of the acceptor groups attached at the conjugated side chains of the copolymers, the photophysical and electrochemical properties of the copolymers are effectively tuned. The best power conversion efficiency of the PSCs based on **PT-DTBT**/PC<sub>61</sub>BM (1:4, w/w) reached to 4.18% under the illumination of AM1.5, 100 mW cm<sup>-2</sup>. The broad absorption spectrum, deep HOMO level and the noticeably high hole mobility of **PT-DTBT** contribute to the outstanding  $J_{sc}$ ,  $V_{oc}$  as well as the high device efficiency.

# EXPERIMENTAL SECTION

**Materials and Characterization.** All the chemicals were purchased from Alfa Aesar or Shanghai Medical Company (China). THF and toluene were refluxed over sodium and benzophenone, then distilled prior to use. DMF was dried and distilled under reduced pressure. All other commercially available materials were used as received unless noted otherwise. Column chromatography was carried out on silica gel (merck, 200–300 mesh)

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured with Bruker AVANCE 400 spectrometer. FT-IR spectra were obtained on Perkin-Elmer Spectra One. UV–vis spectra and photoluminescence (PL) spectra of the copolymers were measured on Perkin-Elmer Lamada 25 spectrometer and Perkin-Elmer LS-50 luminescence spectrometer, respectively. Molecular mass was determined by matrix assisted laser desorption-ionization time-of-flight mass spectrometer, The elemental analysis of all monomers and copolymers were performed with

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an Elementar Vario EL III element analyzer for C, H, and S determination. Thermogravimetric analyses (TGA) were performed under nitrogen at a heating rate of 20 °C/min with Netzsch TG 209 analyzer, and differential scanning calorimetric measurement (DSC) was recorded with TA DSCQ10 instrument at a heating rate of 20 °C/min. The average molecular weight and polydispersity index (PDI) of the copolymers were determined using Waters 1515 gel permeation chromatography (GPC) analysis with THF as eluent and polystyrene as standard. Cyclic voltammetry (CV) was conducted on an electrochemistry workstation (CHI660A, Chenhua Shanghai) with the polymer film on Pt plate as the working electrode, Pt slice as the counter electrode, and saturated calomel electrode (SCE) as a reference electrode in a 0.1 M tetran-butylammonium hexafluorophosphate acetonitrile solution at a scan rate of 50 mV/s.

Fabrication and Characterization of Polymer Solar Cells. The photovoltaic cells were constructed in the traditional sandwich structure through several steps. The ITO coated glass substrates were cleaned by successive ultrasonic treatment in acetone and isopropyl alcohol, then treated with a nitrogen-oxygen plasma oven for 5 min. Poly(3,4-ethylene dioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, from Bayer AG) was spin-coated from an aqueous solution on a cleaned indium tin oxide (ITO) glass substrate giving a thickness of about 40 nm as measured by Ambios Technology XP-2 surface profilometer, then it was dried at 150 °C for 15 min. Subsequently, the photoactive layer was prepared by spin-coating the dichlorobenzene solution of polymer:PC60BM (1:4, w/w) with the polymer concentration of 6 mg/mL on the top of the PEDOT:PSS layer and the thickness of the active layers of ca. 80 nm, and then annealed at 150 °C for 5 min in a nitrogen-filled glovebox. Finally, the substrates were transferred into an evaporator and pumped down to  $5 \times 10^{-4}$  Pa. to deposit 10 nm of Ca and 100 nm of aluminum cathodes, producing an active area of 4 mm<sup>2</sup> for each cell. Current density-voltage (J-V) characteristics were measured by a Keithley 2602 Source Meter under 100 mW cm<sup>-2</sup> irradiation using a 500W Xe lamp equipped with a global AM 1.5 filter for solar spectrum simulation, and the incident light intensity was calibrated using a standard Si solar cell. The measurement of monochromatic incident photon-to-current conversion efficiency (IPCE) was performed using a Zolix DCS300PA Data acquisition system.

**OTFTs Device Fabrication.** OTFTs fabricated on OTS-modified  $SiO_2/Si$  substrates. OTFT devices were fabricated in a top-contact configuration. Before the deposition of organic semiconductors, octyltrichlorosilane (OTS) treatment was performed on the gate dielectrics which were placed in a vacuum oven with OTS at a temperature of 120 °C to form an OTS self-assembled monolayer. Then the polymer thin films were spin-coated on the OTS modified  $SiO_2/Si$  substrates from the chloroform solutions, followed by Au deposition through a shadow mask to define the source and drain electrodes. The OTFTs characteristics of the devices were determined at room temperature in air by using a Keithley 4200 SCS. The mobility of the devices was calculated in the saturation regime. The equation is listed as follows:

$$I_{DS} = (W/2L)C_{i}\mu(V_{GS} - V_{th})^{2}$$

Here W/L is the channel width/length,  $C_i$  is the insulator capacitance per unit area, and  $V_{\rm GS}$  and  $V_{\rm th}$  are the gate voltage and threshold voltage, respectively.

Synthesis of the Monomers and Copolymers. The synthetic routes of the monomers and copolymers are shown in Scheme 1. 4,7-Bis(4-hexylthiophen-2-yl)benzo[1,2,5]thiadiazole (1),<sup>38</sup> (2,5-dibromothiophen-3-ylmethyl) phosphonic acid diethyl ester (3),<sup>39</sup> and 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b']-dithiophene (M4),<sup>17</sup> were synthesized according to already published procedures. The detailed synthetic procedures of other compounds are as follows.

**2,5-Dibromothiophene-3-carbaldehyde (M1).** *N*-Bromosuccinimide (NBS) (5.337 g, 30 mmol) was dissolved in 35 mL of anhydrous DMF. The mixture was added dropwise to a mixture of thiophene-3-carbaldehyde (1.68 g, 15 mmol) in anhydrous DMF (15 mL) in the dark. The resulting solution was stirred at room temperature under argon overnight. Then, the organic material was extracted with dichloromethane and washed with water. After the solvent was removed, the crude product was purified on silica gel chromatography using a petroleum ether/dichloromethane mixture (3:1 by volume) as eluent. A light yellow solid was obtained. Yield: 2.82 g (70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ /ppm): 9.82 (s, 1H), 7.36 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ /ppm): 183.04, 139.37, 128.70, 124.03, 113.34.

3-Hexyl-5-(7-(4-hexylthiophen-2-yl)benzo[1,2,5]thiadiazol-4-yl)thiophene-2-carbaldehyde (2). The compound 2 was synthesized by the Vilsmeier reaction. To the mixture of compound 1 (2.4 g, 5.1 mmol) in dichloroethane (25 mL) and anhydrous DMF (0.4 mL, 5.1 mmol) was added dropwise under nitrogen atmosphere, then POCl<sub>3</sub> (0.48 mL, 5.1 mmol) was added slowly. The mixture was stirred at 85 °C for 12 h. Then the mixture was cooled to room temperature, 30 mL of water was added to quench the reaction. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. After the solvent was removed, the crude product was purified on silica gel chromatography using a petroleum ether/dichloromethane mixture (1:1 by volume) as eluent. An orange solid was obtained. Yield: 1.78 g (70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ/ppm): 10.12 (s, 1H), 8.08 (s, 1H), 8.06 (s, 1H), 7.99 (d, 1H, J = 7.64 Hz), 7.89 (d, 1H, J = 7.60 Hz), 7.11 (s, 1H), 3.06 (t, 2H, J = 7.66 Hz), 2.72 (t, 2H, J = 7.62 Hz), 1.72–1.83 (m, 4H), 1.44– 1.36 (m, 12H), 0.96 (m, 6H).

(E)-4-(5-(2-(2,5-dibromothiophen-3-yl)vinyl)-4-hexylthiophen-2-yl)-7-(4-hexylthiophen-2-yl)benzo[1,2,5]thiadiazole (M2). Compound 2 (0.497 g, 1 mmol) and 3 (0.39 g, 1 mmol) were dissolved in THF (20 mL) and the solution was stirred at room temperature for 30 min under nitrogen atmosphere. Then potassium tertbutoxide (0.13 g, 1.15 mmol) was dissolved in THF (20 mL) and added dropwise to the solution. The reaction mixture was stirred for 5 h at room temperature, and then heated to 50  $^\circ C$  for 12 h. After cooling to room temperature, the reaction mixture was extracted with dichloromethane and washed with dilute aqueous HCl solution. The organic phase was dried over anhydrous MgSO4, and then the solvent was removed by rotary evaporation. The crude product was purified on silica gel chromatography using a petroleum ether/dichloromethane mixture (1:1 by volume) as eluent. A red solid was obtained. Yield: 0.48 g (65%). FT-IR (KBr, cm<sup>-1</sup>): 938 (trans-vinylene). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ/ppm): 8.01 (s, 1H), 7.98 (s, 1H), 7.86 (d, 2H, J = 1.44 Hz), 7.22 (s, 1H), 7.12 (d, 1H, J = 15.96 Hz), 7.07 (s, 1H), 6.90 (d, 1H, J = 15.96 Hz), 2.70 (m, 4H), 1.72-1.71 (m, 4H), 1.42-1.36 (m, 12H), 0.93-0.92 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ /ppm): 152.63, 143.39, 143.37, 139.03, 137.39, 136.92, 130.55, 129.15, 127.31, 126.32, 125.47, 122.57, 121.69, 119.50, 111.91, 109.72, 31.68, 30.64, 29.01, 22.59, 14.02. Anal. Calcd for  $C_{32}H_{34}Br_2N_2S_4{:}$  C, 52.31; H, 4.66; N, 3.81; S, 17.46. Found: C, 53.26; H, 5.19; N, 3.80; S, 17.31. MALDI–TOF MS (C<sub>32</sub>H<sub>34</sub>Br<sub>2</sub>N<sub>2</sub>S<sub>4</sub>), m/z: calcd, 734.000; found, 733.905.

(E)-5-(7-(5-(2-(2,5-Dibromothiophen-3-yl)vinyl)-4-hexylthiophen-2-yl)benzo[1,2,5]thiadiazol-4-yl)-3-hexylthiophene-2carbaldehyde (M3). By following a similar method, as for compound 2, monomer M3 was synthesized from anhydrous DMF (0.80 mL, 10.2 mmol), POCl<sub>3</sub> (0.94 mL, 10.0 mmol) and monomer M2 (0.743 g, 1 mmol). The crude product was purified on silica gel chromatography using a petroleum ether/dichloromethane mixture (3:1 by volume) as eluent. A black red solid was obtained. Yield: 0.32 g (40%). FT-IR (KBr, cm<sup>-1</sup>): 1657 ( $v_{C=0}$ ), 929 (*trans*-vinylene). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ /ppm): 10.12 (s, 1H), 8.09 (s, 1H), 8.04 (s, 1H), 7.99 (d, 1H, J = 7.60 Hz), 7.90 (d, 1H, J = 7.56 Hz), 7.23 (s, 1H), 7.11 (d, 1H, J = 15.88 Hz), 6.91 (d, 1H, J = 15.76 Hz), 3.06 (t, 2H, J = 7.48 Hz), 2.76 (t, 2H, J = 7.42 Hz), 1.81-1.69 (m, 4H), 1.56-1.27 (m, 12H), 0.930-0.927 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ/ppm): 181.98, 153.27, 147.38, 143.48, 139.05, 138.00, 137.52, 136.81, 131.41, 130.57, 127.26, 124.98, 122.35, 119.99, 112.03, 31.47, 28.96, 22.55, 14.00. Anal. Calcd for C<sub>33</sub>H<sub>34</sub>Br<sub>2</sub>N<sub>2</sub>OS<sub>4</sub> C, 51.92; H, 4.46; N, 3.67; S, 16.78. Found: C, 52.42; H, 4.72; N, 3.44; S, 15.74. MALDI-TOF MS (C<sub>33</sub>H<sub>34</sub>Br<sub>2</sub>N<sub>2</sub>OS<sub>4</sub>) m/z: calcd, 762.700; found 761.951.

2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2**b:4,5-b']dithiophene (M4).** M4 were synthesized according to already published procedures<sup>17</sup> with a yield of 75%. <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ ,  $\delta/ppm$ ): 7.55 (s, 2 H), 4.23–4.22 (d, 4 H, J = 4.52 Hz), 1.85-1.71 (m, 2 H), 1.65-1.29 (m, 16 H), 1.08-0.98 (m, 12 H), 0.48 (s, 18 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ/ppm): 143.3, 140.3, 133.8, 132.9, 128.0, 75.66, 40.72, 30.58, 29.26, 23.95, 23.14, 14.12, 11.32. MALDI-TOF MS (m/z): calcd, 772.160; found, 772.130.

Synthesis of the Precursor Polymer PT-CHO. M1 (67.25 mg, 0.25 mmol) and M4 (193 mg, 0.25 mmol) were dissolved in 20 mL of toluene, and the solution was flushed with argon for 15 min; then, 30 mg of  $Pd(PPh_3)_4$  was added into the solution. The mixture was again flushed with argon for 30 min. The polymerization was carried out at 110 °C for 3 days. Finally, the reaction mixture was cooled to room temperature and slowly added to methanol (120 mL). The precipitate was collected by filtration from methanol and further purified by Soxhlet extraction with methanol, hexane, and chloroform in sequence. The chloroform fraction was evaporated by rotary evaporation. The final product was obtained as a green solid and dried under vacuum for 24 h. Yield: 152 mg (60%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ/ppm): 10.19 (br, 1H), 7.41-7.35 (br, 3H), 4.08 (br, 4H), 1.82–1.57 (br, 18H), 1.23–0.96 (br, 12H). Anal. Calcd for  $(C_{31}H_{38}O_3S_3)_n$ : C, 67.10; H, 6.91; N, 0; S, 17.33. Found: C, 66.07; H, 6.92; N, 0.084; S, 17.22.

Synthesis of the Copolymer PT-ID. The compound was synthesized according to procedures similar to reported in the literature.<sup>40</sup> A mixture of PT-CHO (0.120 g, 0.21 mmol of basic units) and 1,3-indanedione (0.306 g, 2.1 mmol) in 10 mL of chloroform was stirred for 0.5 h, then 0.5 mL pyridine was added. The mixture solution was stirred for 24 h at room temperature, after which the resulting mixture was poured into methanol and the precipitate was filtered. The precipitate was purified by Soxhlet extraction with methanol, hexane and chloroform in sequence. The chloroform fraction was evaporated by rotary evaporation. The final product was obtained as a black solid and dried under vacuum for 24 h. Yield: 72 mg (49%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ/ppm): 8.75 (br, 1H), 7.98-7.97 (d, 2H), 7.84-7.82 (d, 2H), 7.76-7.12 (br, 3H), 4.37-4.04 (br, 4H), 1.81-1.01 (br, 30H). Anal. Calcd for  $(C_{40}H_{42}O_4S_3)_n$ : C, 70.28; H, 6.15; N, 0.00; S, 14.05. Found: C, 66.56; H, 6.12; N, 0.09; S, 12.84.

Synthesis of the Copolymer PT-DTBT. By following the similar method used for PT-CHO, PT-DTBT was synthesized with monomer M2 (0.193 g, 0.25 mmol) and M4 (0.1835 g, 0.25 mmol). The final product was obtained as a green solid. Yield: 0.2 g (78%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ/ppm): 8.08-7.12 (br, 10H), 4.26-4.23 (br, 4H), 2.67-2.63 (br, 4H), 1.37-0.94 (br, 52H). Anal. Calcd for (C58 H<sub>70</sub>N<sub>2</sub>O<sub>2</sub>S<sub>6</sub>)<sub>n</sub>: C, 68.32; H, 6.92; N, 2.75; S, 18.87. Found: C, 67.73; H, 7.79; N, 2.63; S, 19.08.

Synthesis of the Precursor PT-DTBTCHO. By following the similar method as for PT-CHO, PT-DTBTCHO was synthesized with M3 (0.229 g, 0.30 mmol) and M4 (0.231 g, 0.30 mmol)). The final product was obtained as a green solid. Yield: 0.32 g (70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ/ppm): 10.10–10.06 (br, 1H), 8.11–7.01 (br, 9H), 4.25 (br, 4H), 2.98-2.26 (br, 4H), 1.70-0.92 (br, 52H). Anal. Calcd for (C<sub>59</sub>H<sub>70</sub>N<sub>2</sub>O<sub>3</sub>S<sub>6</sub>)<sub>n</sub>: C, 67.64; H, 6.75; N, 2.67; S, 18.36. Found: C, 67.08; H, 7.28; N, 2.69; S, 18.29.

Synthesis of the Polymer PT-DTBTID. By following the similar method as for PT-ID, PT-DTBTID was synthesized with PT-DTBTCHO (0.12 g, 0.117 mmol of basic units) and 1,3-indanedione (0.178 g, 1.17 mmol)). The final product was obtained as a black purple solid. Yield: 62 mg (46%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ/ppm): 8.72 (s, 1H), 8.06-7.27 (br, 13H), 4.35-4.21 (br, 4H), 2.97-2.44 (br, 4H), 2.17-2.13 (m, 2H), 1.68-1.01 (br, 50H). Anal. Calcd for (C<sub>68</sub>H<sub>74</sub>N<sub>2</sub>O<sub>4</sub>S<sub>6</sub>)<sub>n</sub>: C, 69.46; H, 6.36; N, 2.38; S, 16.36. Found: C, 67.28; H, 7.07; N, 2.28; S, 15.36.

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#### Notes

The authors declare no competing financial interest.

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