

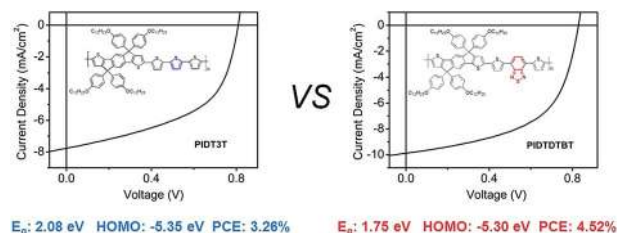
## PAPER

# 1

## Benzothiadiazole – an excellent acceptor for indacenodithiophene based polymer solar cells

5 Deyu Liu, Liang Sun, Zhengkun Du, Manjun Xiao, Chuantao Gu, Ting Wang, Shuguang Wen, Mingliang Sun\* and Renqiang Yang\*

10 Indacenodithiophene is copolymerized with di-2-thienyl-2',1',3'-benzothiadiazole or terthiophene. The reason why the benzothiadiazole based polymer shows high PCE is discussed.



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# Benzothiadiazole – an excellent acceptor for indacenodithiophene based polymer solar cells

Cite this: DOI: 10.1039/c4ra06967f

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Two tetradodeoxyphenyl-substituted indacenodithiophene (IDT) based polymers, PIDT3T and PIDTDTBT, were achieved by copolymerizing IDT with terthiophene (3T) or di-2-thienyl-2',1',3'-benzothiadiazole (DTBT). Although these two polymers show significantly different UV-vis absorption spectra and band gaps (2.08 eV and 1.75 eV), the HOMO levels (−5.35 eV and −5.30 eV) of these polymers are almost the same. Polymer solar cells (PSCs) based on polymers with the benzothiadiazole (BT) unit show relatively high short-circuit current density ( $J_{sc}$ ) due to the relatively wide and high photo-electronic response and high hole mobility. Thanks to the four long aryl side chains on IDT, the polymer thin film shows an amorphous nature, and the AFM root-mean-square roughness (RMS) value of the polymer/PCBM blend film is only around 0.3 nm which can contribute to the homogenous bulk heterojunction structures without significant phase separation. Finally, decent power conversion efficiency (PCE) of 4.52% is achieved by the benzothiadiazole based polymer and PC<sub>71</sub>BM composite. By comparison study, we demonstrate why BT is an excellent acceptor unit for indacenodithiophene-based PSCs.

Received 11th July 2014  
Accepted 14th August 2014

DOI: 10.1039/c4ra06967f

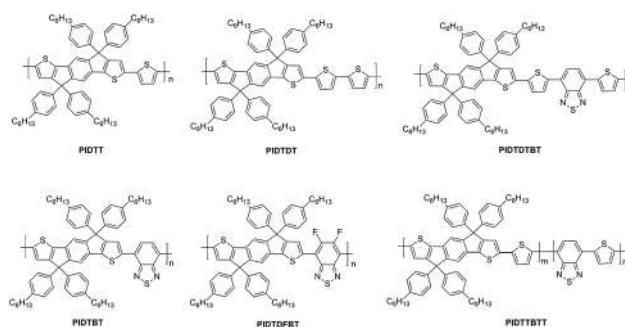
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## 1. Introduction

Polymer solar cells (PSCs) have attracted increasing interest due to their potential for fabrication of light-weight, large-area, and flexible light-harvesting devices through low-cost solution processing.<sup>1–7</sup> With prolonged effort, the PCE of PSCs has already exceeded 10%.<sup>8</sup> PSCs usually adopt a bulk-heterojunction (BHJ) structure, where a photoactive layer consists of an interpenetrating network of  $\pi$ -conjugated polymer donors and soluble fullerene or nanocrystal acceptors.<sup>9</sup> Because donor polymer can harvest most of the solar energy, more efforts have been focused on developing conjugated polymers with small band gap and proper energy levels that can be used as a donor material to complement fullerene-based acceptors.<sup>10–14</sup>

Among different donor materials, indacenodithiophene (IDT) based conjugated polymers have attracted much attention in optoelectronic devices.<sup>15–17</sup> In IDT, the rigid ring unit could enhance both the degree of conjugation<sup>18</sup> and the co-planarity of the molecular backbones. A series of polymers based on IDT, BT and thiophene have been synthesized (Scheme 1).<sup>16,19–24</sup> The highest PCE reached 7% based the corresponding PSCs.<sup>25</sup> Jen *et al.* studied several high performance D–A polymers based on

IDT and different acceptor units.<sup>26–29</sup> The IDT-based polymers have presented pretty high mobility and the appropriate optical properties, which can facilitate the charge transport simultaneously enhance the absorption of sunlight and subsequently lead to high  $J_{sc}$  of PSCs devices.<sup>30</sup> Therefore, both thiophene and BT are promising building blocks for IDT-based polymers. Among these materials, IDT and di-2-thienyl-2',1',3'-benzothiadiazole (DTBT) based high performance polymer solar cells showed PCE up to 6%.<sup>24</sup> In general, the strategy to improve the PCE of solar cells devices is to adjust band gap of polymers.<sup>31,32</sup> Low band gap could enhance the absorption at long wavelengths. However, usually lowering the band gap will lead to the change of the HOMO level, which could reduce  $V_{oc}$  of the devices. Increasing  $J_{sc}$  and keeping high  $V_{oc}$  is a contradiction, but IDT and di-2-thienyl-2',1',3'-benzothiadiazole (DTBT) based polymer



Scheme 1 Molecular structures of IDT-based polymers.

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solar cells can show high  $J_{sc}$  resulting from wide absorption and acceptable  $V_{oc}$  resulting from deep HOMO energy level.<sup>24</sup>

Typically, the side chain of IDT based polymer was hexyl, and molecular weights ( $M_n$ ) of polymers (Scheme 1) were exhibited to be in the range of 15–25 K.<sup>16,19–24</sup> Longer side chains on the donor can produce better solubility of the polymer and intermediate oligomers, which may potentially lead to higher molecular weight.<sup>33</sup> On the other hand, long side chains could reduce the tendency for crystallization to help to obtain the complete non-crystalline materials, which could avoid considering that crystallinity impacts on spectral red shift and mobility in polymer solar cells study. Especially in chemical structure comparison study, long sided chained polymer is favorite.

Here, we synthesized a new tetra-dodeoxyphenyl long chain substituted indacenodithiophene (IDT) derivative and used it as a building unit for polymers. Two IDT-based copolymers P1DT3T and P1DTDTBT (Scheme 2) with different building blocks were prepared by Stille polycondensation, and their thermal, optical, electrochemical and photovoltaic properties were investigated. Thanks to the long dodecyl chain, P1DT3T and P1DTDTBT showed high molecular weights (Table 1). Especially, P1DT3T showed one of the highest molecular weights of 61.7 K in IDT based polymers. Compared with P1DT3T polymer, the benzothiadiazole unit in P1DTDTBT polymer was introduced to lower the band gap and increase the absorption. Fortunately, the introduction of BT could lower the band gap and increase  $J_{sc}$  effectively, while the HOMO level did not changed. Thanks to the amorphous nature of these polymers, the comparison of two polymers is completely due to difference of the thiophene and the BT in the middle of other units. In this paper, by comparison study we demonstrate why BT is an excellent acceptor unit for indacenodithiophene-based PSCs.

## 2. Results and discussion

### 2.1. Synthesis of monomers and polymers

The synthetic routes of the monomer (IDT) and the copolymer are depicted in Scheme 3. The synthesis of the indacenodithiophene (IDT) was generally based on the previous literature.<sup>34</sup> The TMS groups on compound 1 (Scheme 3) were introduced to facilitate the later intramolecular cyclization reactions. Two polymers, P1DT3T and P1DTDTBT, were synthesized by using palladium-catalyzed Stille coupling copolymerization of IDT with 3T and DTBT.<sup>35</sup> The structures of two polymers were confirmed by <sup>1</sup>H NMR spectroscopy. Both polymers showed good solubility in common organic solvents, such as chloroform, toluene and chlorobenzene, due to the four dodecyloxyphenyl side chains in the IDT repeat unit. The



Scheme 2 Molecular structures of P1DT3T and P1DTDTBT.

Table 1 Molecular weights and thermal properties of P1DT3T and P1DTDTBT

Polymers	$M_n$	$M_w$	PDI	$T_d$ (°C)
P1DT3T	61.7 K	62.6 K	1.01	374
P1DTDTBT	35.1 K	44.3 K	1.26	422

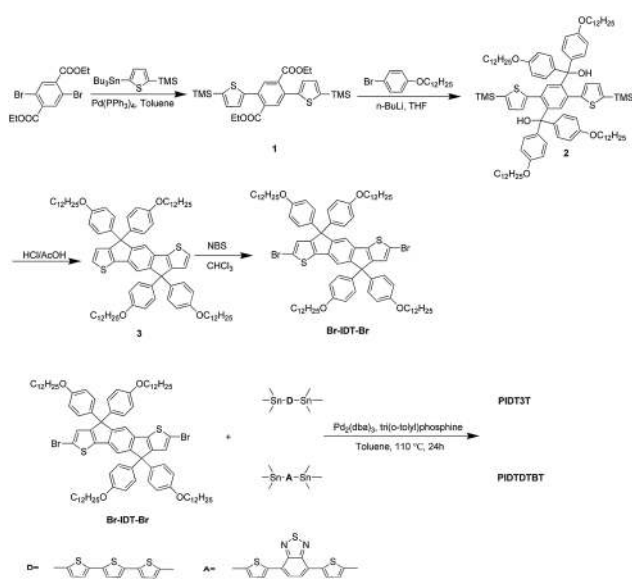
number-average molecular weight ( $M_n$ ) and polydispersity index (PDI) were measured by gel permeation chromatography (GPC) using THF as the eluant and polystyrenes as the internal standards, and the results were listed in Table 1. The  $M_n$  of P1DT3T and P1DTDTBT are 61.7 K and 35.1 K, respectively. Molecular weights of the copolymers are relatively high, probably due to the good solubility of IDT monomer with long side chains.

### 2.2. Thermal analysis

The thermal properties of the polymers were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), as shown Fig. 1. DSC thermogram didn't show apparent thermal transitions for P1DT3T and P1DTDTBT polymer, implying their amorphous nature. The TGA analysis reveals that the onset temperature with 5% weight-loss ( $T_d$ ) of P1DT3T and P1DTDTBT are 374 °C and 422 °C, respectively. DTBT unit has higher thermal stability than 3T unit,<sup>36,37</sup> which results in higher thermal stability of P1DTDTBT polymer. This indicates that the thermal stability of the polymers is good enough for PSCs applications.

### 2.3. Optical properties

The UV-vis absorption spectra of P1DT3T and P1DTDTBT in chloroform solution and in thin film are shown in Fig. 2, respectively, and the corresponding absorption properties are



Scheme 3 Synthetic routes of the IDT monomer and the IDT-based copolymers.

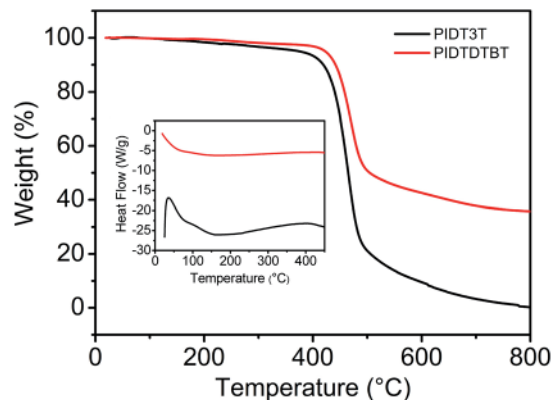


Fig. 1 TGA of the polymers with a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  under an inert atmosphere (inset: DSC thermogram of the polymers).

summarized in Table 2. PIDs3T exhibited one absorption band due to the  $\pi\text{-}\pi^*$  transition with the absorption maximum at 516 nm. PIDTDTBT exhibited two absorption bands due to the  $\pi\text{-}\pi^*$  transition and the intramolecular charge transfer with the absorption maximum at 450 nm and 606 nm in chloroform solution. In the thin film, both polymers exhibit a red-shift in the absorption maximum and onset, which is attributed to solid state packing effects. Compared the absorption in thin film with that in solution, PIDTDTBT polymer exhibits a greater red-shift compared to PIDs3T, which is attributed to more effective  $\pi\text{-}\pi$  stacking.<sup>38,39</sup> PIDTDTBT polymer shows more planar polymer structure and packs better than PIDs3T. The optical band gaps ( $E_g^{\text{opt}}$ ) of PIDs3T and PIDTDTBT were estimated to be 2.08 eV and 1.75 eV according to  $E_g^{\text{opt}} = 1240/\lambda$ . Due to the introduction of BT unit, the band gap of PIDTDTBT was obviously lowered compared with PIDs3T. The lower band gap of PIDTDTBT should be beneficial to its application as donor material in PSCs.

#### 2.4. Electrochemical properties

The electrochemical cyclic voltammetry (CV) was performed for determining the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy

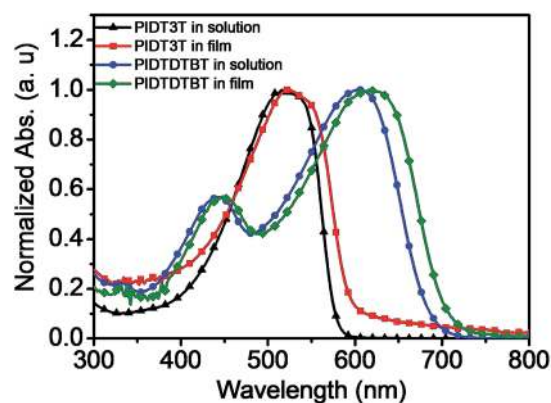


Fig. 2 Normalized absorption spectra of the PIDs3T and PIDTDTBT in chloroform solution and in thin film.

levels of the conjugated polymers.<sup>40</sup> Fig. 3 shows the cyclic voltammogram (CV) properties of the polymers. A three electrode cell consisting of a glassy carbon working electrode, a platinum wire counter electrode and a saturated calomel reference electrode has been used. The potentials were internally calibrated using the  $\text{Fc}/\text{Fc}^+$  redox couple. The redox potential of the  $\text{Fc}/\text{Fc}^+$  internal reference is found to be 0.43 V vs. SCE. According to the empirical equation,

$$\text{HOMO} = -(E_{\text{ox}} + 4.4) \text{ (eV)}$$

$$\text{LUMO} = -(E_{\text{re}} + 4.4) \text{ (eV)}$$

The results of the electrochemical properties are listed in Table 2. Compared with PIDs3T, the LUMO energy levels of PIDTDTBT decreased significantly due to the electron-withdrawing ability of the acceptor unit, but the HOMO energy levels of the polymer changed little, which is possibly due to similar oxidation potential of 3T and DTBT. These two polymers show deep HOMO energy levels ( $\sim -5.3$  eV), which is desirable for good stability in the air and high open circuit voltage ( $V_{\text{oc}}$ ) in PSCs.

#### 2.5. Photovoltaic properties

To investigate and compare the photovoltaic properties of the polymers, bulk heterojunction PSCs devices with a configuration of ITO/PEDOT:PSS/polymer:PC<sub>61</sub>BM/Ca/Al were fabricated by the method of solution processing as our previous work.<sup>41–43</sup> And then, we further optimized the device performances using PC<sub>71</sub>BM acceptor with device configuration ITO/PEDOT:PSS/polymer:PC<sub>71</sub>BM(1 : 3)/Ca/Al. Fig. 4 exhibits the  $J\text{-}V$  curves of the PSCs under illumination of AM 1.5G,  $100\text{ mW cm}^{-2}$ . Table 3 summarized the detailed device performances. Finally, the best solar cell obtained from PIDs3T:PC<sub>71</sub>BM (1 : 3) showed a PCE of 3.26% with an  $V_{\text{oc}}$  of 0.81 V, a  $J_{\text{sc}}$  of  $7.75\text{ mA cm}^{-2}$ , and a FF of 51.93% and PIDTDTBT showed a PCE of 4.52% with an  $V_{\text{oc}}$  of 0.83 V, a  $J_{\text{sc}}$  of  $9.85\text{ mA cm}^{-2}$ , and a FF of 53.26% at the same condition. The  $V_{\text{oc}}$  of two polymers based PSCs devices was almost the same due to the similar HOMO level. Compared to the PIDs3T, PIDTDTBT showed higher  $J_{\text{sc}}$  value, which may be originated from the relatively lower band gap and stronger  $\pi\text{-}\pi$  stacking interaction. The external quantum efficiency (EQE) curves of the devices based on PIDs3T:PC<sub>71</sub>BM and PIDTDTBT:PC<sub>71</sub>BM (1 : 3) are shown in Fig. 5. The EQE value of PIDTDTBT is higher than that of PIDs3T in most parts of spectra (320–700 nm) and the maximum value reaches 61%. It indicates that PIDTDTBT has good photo response among the absorption range. The calculated current density from the EQE measurement were  $7.66$  and  $9.74\text{ mA cm}^{-2}$ , respectively for PIDs3T and PIDTDTBT, which agree well with the  $J_{\text{sc}}$  ( $7.75\text{ mA cm}^{-2}$  for PIDs3T and  $9.85\text{ mA cm}^{-2}$  for PIDTDTBT) obtained from the  $J\text{-}V$  measurements (Fig. 6).

Mobility measurements via space charge limited current (SCLC) method<sup>40</sup> disclose a hole mobility of  $2.35 \times 10^{-4}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  for the PIDTDTBT:PC<sub>71</sub>BM device, higher than that of the PIDs3T:PC<sub>71</sub>BM device ( $1.31 \times 10^{-4}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ ). This could be a potential reason that PIDTDTBT:PC<sub>71</sub>BM device exhibits larger  $J_{\text{sc}}$  and FF than PIDs3T:PC<sub>71</sub>BM device.

Table 2 Optical and electrochemical properties of the polymers

Polymer	$\lambda_{\max}$ solution (nm)	$\lambda_{\max}$ film (nm)	$E_g^{\text{opt}}$ film (eV)	$E_g^{\text{cv}}$ (eV)	HOMO (eV)	LUMO (eV)
PIDT3T	516	522	2.08	1.8	-5.35	-3.55
PIDTDTBT	606	622	1.75	1.6	-5.30	-3.70

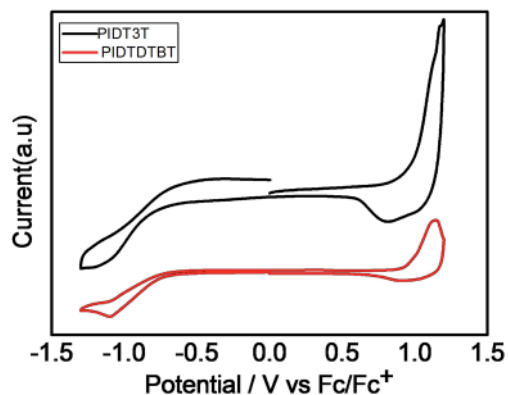
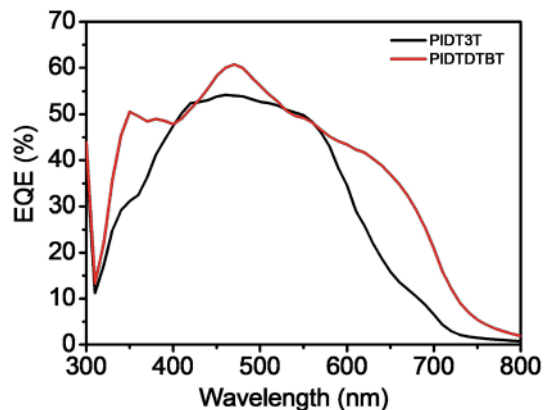
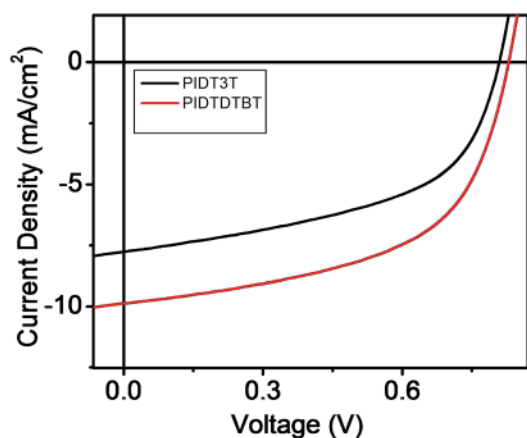


Fig. 3 Cyclic voltammogram of PIDT3T and PIDTDTBT.

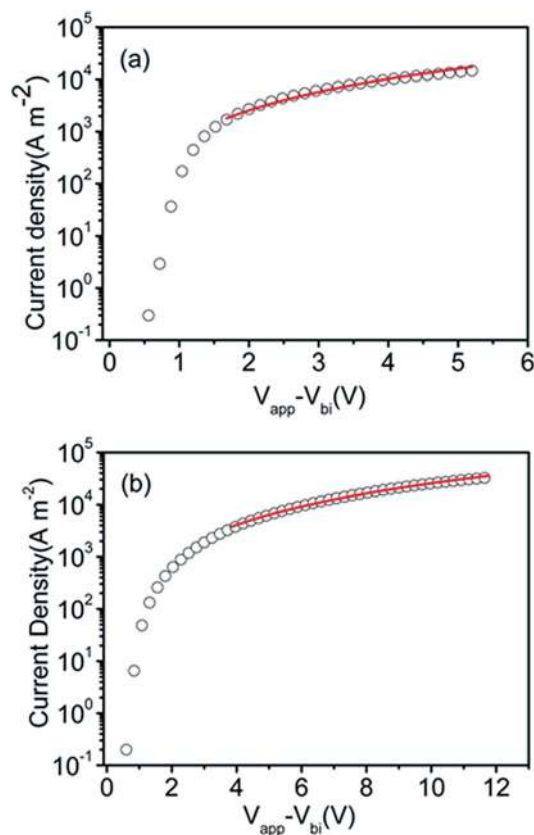
Fig. 5 EQE curves of the PSCs based on the blend of PIDT3T or PIDTDTBT/PC<sub>71</sub>BM.Fig. 4  $J$ - $V$  curves of the PSCs based on the blend of PIDT3T or PIDTDTBT/PC<sub>71</sub>BM under the illumination of AM 1.5G, 100 mW cm<sup>-2</sup>.Table 3 Solar cells devices performance of PIDT3T and PIDTDTBT<sup>a</sup>

Polymers/acceptor	$V_{oc}/V$	$J_{sc}/\text{mA cm}^{-2}$	FF/(%)	PCE/(%)
PIDT3T/PC <sub>61</sub> BM	0.81	5.06	49.7	2.03
PIDT3T/PC <sub>71</sub> BM	0.81	7.75	51.93	3.26
PIDTDTBT/PC <sub>61</sub> BM	0.85	7.13	58.48	3.56
PIDTDTBT/PC <sub>71</sub> BM	0.83	9.85	55.26	4.52

<sup>a</sup> The active layers were annealed at 150 °C for 10 min.

## 2.6. Morphological characterization

Atomic force microscopy (AFM) was used to investigate the morphology of the two polymers: PC<sub>71</sub>BM blend films annealed at 150 °C. The height images and phase images of the blends are

Fig. 6 Current density ( $J$ )-voltage ( $V$ ) curves for PIDT3T based device (a) and PIDTDTBT based device (b) (the symbols are experimental data for transport of hole, and the red line is fitted according to the space-charge-limited-current model).



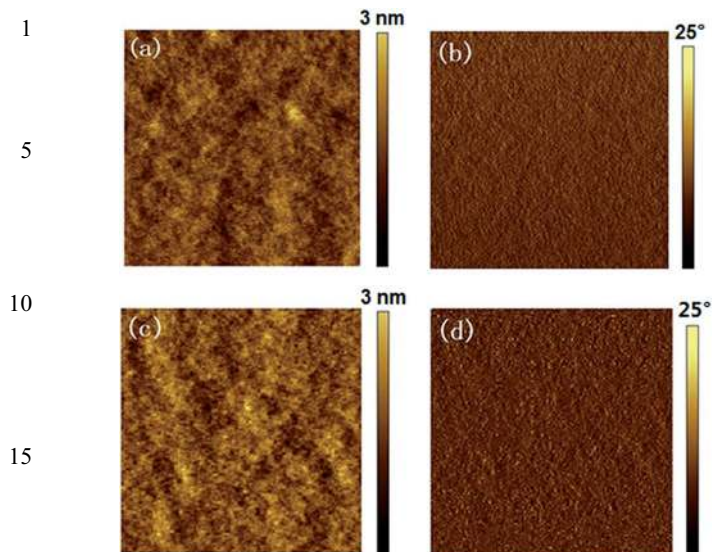


Fig. 7 AFM height (a) and phase (b) images of the PIDT3T:PC<sub>71</sub>BM (1 : 3) blend films annealed at 150 °C; AFM height (c) and phase (d) images of the PIDTDTBT:PC<sub>71</sub>BM (1 : 3) blend films annealed at 150 °C (all the images are 4 μm × 4 μm).

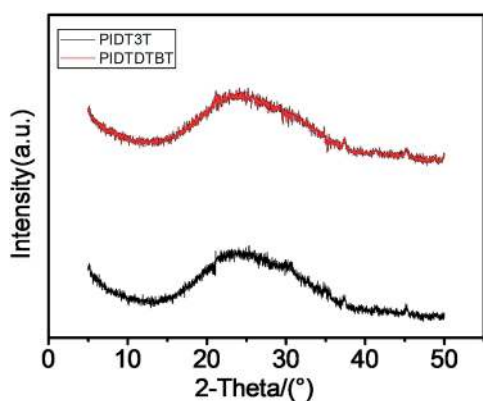


Fig. 8 X-ray diffraction (XRD) pattern of the PIDT3T and the PIDTDTBT.

shown in Fig. 7. The blend films of PIDT3T and PIDTDTBT with PC<sub>71</sub>BM showed surface roughness with root-mean-square (RMS) of 0.343 nm and 0.328 nm, respectively. Although with a smooth surface morphology of the active layer, the device based on PIDT3T has a lower  $J_{sc}$  value than PIDTDTBT which can be attributed to its lower EQE value. The crystallinity of the polymer films was investigated using XRD pattern, as shown in Fig. 8. There are no peaks observed for these polymers in XRD test, indicating their amorphous nature.

### 3. Conclusions

We have successfully synthesized two indacenodithiophene-based polymers PIDT3T and PIDTDTBT. Thanks to the long side chain, the polymers show high (up to 6.0 K) molecule weight with narrow PDI and amorphous nature

(no crystallization). Although these two polymers show significantly different UV-vis absorption spectrum and band gap (2.08 eV and 1.75 eV), the HOMO levels (−5.35 eV and −5.30 eV) are almost the same. PSCs based on these two materials show almost the same  $V_{oc}$  (around 0.8 V) due to the same HOMO level. PSCs based on PIDTDTBT with benzothiadiazole unit show relatively high  $J_{sc}$  and FF due to the relatively wide and high photo-electronic response and high hole mobility. Our comparison study shows that BT is a good acceptor unit in IDT polymer backbone which does broad absorption to increase  $J_{sc}$  of PSCs devices without lowering  $V_{oc}$  of the device due to proper HOMO levels.

## 4. Experimental

### 4.1. Materials

All chemicals, unless otherwise specified, were commercial grade and used as received. Toluene and THF were freshly distilled from sodium and benzophenone ketyl under nitrogen prior to use. 5-(Trimethylsilyl)-2-(tri-*n*-butylstannyl)thiophene, 4-dodecyloxy-1-bromobenzene, 2,5''-bis(trimethylstannyl)-5,2',5',2''-terthiophene were synthesized as reported in the literature.<sup>44–47</sup>

### 4.2. Instruments and measurements

Nuclear magnetic resonance (NMR) spectra were taken on a Bruker AVANCE-III 600 Spectrometer. High resolution mass spectra (MS) were recorded under APCI mode on a Bruker Maxis UHRTOF spectrometer. All GPC analyses were made using tetrahydrofuran (THF) as eluant and polystyrene standard as reference. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) measurements were performed on STA-409 at a heating rate of 10 °C min<sup>−1</sup>. UV-vis absorption spectrum was measured with a Hitachi U-4100 spectrophotometer. The organic molecule films on quartz used for absorption spectral measurement were prepared by spin-coating their chloroform solutions. Cyclic voltammetry (CV) was performed using a CHI660D electrochemical workstation with a glassy carbon working electrode, a saturated calomel reference electrode (SCE) and a platinum wire counter electrode at a scan rate of 100 mV s<sup>−1</sup>. Tetrabutylammonium phosphorus hexafluoride (Bu<sub>4</sub>NPF<sub>6</sub>, 0.1 M) in acetonitrile was used as the supporting electrolyte. Surface roughness and morphology of thin films were characterized by atomic force microscopy (AFM) on an Agilent 5400 working at the tapping mode. X-ray diffraction (XRD) pattern were recorded on a Bruker D8 Advance.

### 4.3. Fabrication and characterization of organic solar cells

Photovoltaic devices were fabricated on pre-patterned indium tin oxide (ITO) coated glass substrates with a layered structure of ITO/PEDOT:PSS/donor:acceptor/Ca(10 nm)/Al(100 nm). The ITO coated glass substrates were cleaned in ultrasonic bath in acetone, toluene, methanol and isopropyl alcohol sequentially. And then, oxygen plasma treatment was made for 20 min, spin-coated with PEDOT:PSS at 5000 rpm, and dried under argon for 20 min at 120 °C. The photosensitive layer was prepared by spin-coating a blend solution of the polymers and PC<sub>61</sub>BM (PC<sub>71</sub>BM)

with a weight ratio of 1:3 in deoxygenated anhydrous *o*-dichlorobenzene at 2000 rpm on the ITO/PEDOT:PSS substrate and then annealed at 150 °C for 10 min in a glove box. The thickness of active layer films measured by a Dektak 150 profilometer is around 100 nm. Finally, Ca (10 nm) and aluminum (100 nm) were thermally evaporated at a vacuum of  $\sim 2 \times 10^{-4}$  Pa on top of active layer. The photovoltaic performance was measured under illumination at 100 mW cm<sup>-2</sup> AM 1.5 G irradiation using a Xe arc lamp in an argon atmosphere (<0.1 ppm H<sub>2</sub>O and O<sub>2</sub>), and the current density–voltage (*J*–*V*) curves was obtained by Keithley 2400. The external quantum efficiency (EQE) was obtained by a source meter, silicon photodiode and a computer-controlled light source–monochromator–lock-in system.

#### 4.4. Synthesis

**4.4.1. Diethyl-1,4-bis(5-trimethylsilylthiophen-2-yl)-2,5-benzene-dicarbonate (1).** Diethyl-2,5-dibromoterephthalate (3.04 g, 8 mmol), 5-(trimethylsilyl)-2-(tri-*n*-butylstannyl)-thiophene (8.91 g, 20 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (462 mg, 0.4 mmol) were mixed in toluene (60 ml) under nitrogen atmosphere. The mixture was heated to reflux for 48 h. After cooled to room temperature, it was poured into water and extracted with ethyl acetate. The combined extracts were dried over Na<sub>2</sub>SO<sub>4</sub> and filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography over silica gel, eluting with petroleum ether and ethyl acetate (v/v, 10/1) to give (1) as a white solid (1.29 g, 31%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ (ppm) 7.81 (s, 2H), 7.18 (d, *J* = 3.4 Hz, 2H), 7.14 (d, *J* = 3.4 Hz, 2H), 4.21 (q, *J* = 7.1 Hz, 4H), 1.13 (t, *J* = 7.1 Hz, 6H), 0.34 (s, 18H).

**4.4.2. 4,9-Dihydro-4,4,9,9-(*p*-dodeoxyphenyl)-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene (3).** To a solution of 4-dodeoxy-1-bromobenzene (6.14 g, 18 mmol) in THF (10 ml) at –78 °C, *n*-BuLi (11.25 ml, 18 mmol, 1.6 M in hexane) was added, and the mixture was kept at –78 °C for 1 h, then a solution of compound (1) (1.06 g, 2 mmol) in THF (5 ml) was added slowly. The mixture was stirred at room temperature overnight and then poured into water and extracted with chloroform. The combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub> and filtered, and the solvent was removed under reduced pressure. The resulting solid was washed with hexanes to give (2) as a white solid crude product. The white product was then directly dissolved in acetic acid (25 ml) and 1 ml of concentrated hydrochloric acid was added to the solution. The mixture was stirred at 80 °C for 2 h. After pouring into water, the mixture was extracted with chloroform. The combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub> and filtered, and the solvent was removed under reduced pressure. The resulting solid was washed with water, an aqueous sodium carbonate solution, and methanol to give (3) as a yellow solid (1.28 g, 51%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ (ppm) 7.38 (s, 2H), 7.23 (d, *J* = 4.9 Hz, 2H), 7.14 (dd, *J* = 6.9 Hz, 8H), 6.96 (d, *J* = 4.9 Hz, 2H), 6.76 (d, *J* = 8.4 Hz, 8H), 3.89 (t, *J* = 6.5 Hz, 8H), 1.73 (m, 8H), 1.41 (m, 8H), 1.35–1.20 (m, 64H), 0.87 (t, *J* = 7.0 Hz, 12H).

**4.4.3. 2,7-Dibromo-4,9-dihydro-4,4,9,9-(*p*-dodeoxyphenyl)-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene (Br-IDT-Br).** To a solution of 3 (1.27 g, 1 mmol) dissolved in chloroform (25 ml), NBS was added (391 mg, 2.2 mmol). The mixture was stirred under dark at room temperature overnight and extracted with chloroform and water. The combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub> and filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography over silica, eluting with petroleum ether to give the monomer as a yellow solid (1.35 g, 92%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ (ppm) 7.28 (s, 2H), 7.10 (d, *J* = 8.8 Hz, 8H), 6.96 (s, 2H), 6.77 (d, *J* = 8.9 Hz, 8H), 3.90 (t, *J* = 6.5 Hz, 8H), 1.74 (m, 8H), 1.42 (m, 8H), 1.35–1.20 (m, 64H), 0.88 (t, *J* = 7.0 Hz, 12H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ (ppm) 158.20, 155.13, 152.86, 141.14, 135.89, 134.90, 128.91, 125.92, 117.05, 114.30, 113.81, 67.96, 62.71, 31.92, 29.66, 29.63, 29.60, 29.58, 29.40, 29.35, 29.29, 26.08, 22.69, 14.13. MS (MALDI-TOF): calcd for C<sub>88</sub>H<sub>120</sub>Br<sub>2</sub>O<sub>4</sub>S<sub>2</sub> [M]<sup>+</sup>, 1464.6974; found: 1464.7075.

**4.4.4. Synthesis of PIDT3T.** To a 25 ml flask, 2,7-dibromo-4,9-dihydro-4,4,9,9-(*p*-dodeoxyphenyl)-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene (254 mg, 0.2 mmol), 2,5''-bis(trimethylstannyl)-5,2',5',2''-terthiophene (115 mg, 0.2 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (5.5 mg, 0.006 mmol), and tri(*o*-tolyl)phosphine (11 mg, 0.036 mmol) were added under nitrogen protection. After the addition of toluene (5 ml), the mixture was heated to 110 °C and maintained at the same temperature for 24 h. After cooling to room temperature, the mixture was poured into methanol. The precipitate was collected and purified by column chromatography over silica using chloroform as the eluant. After removing the solvent, the resulting red solid was dissolved into a small amount of chloroform and then poured methanol again. The product was collected and dried overnight under vacuum with the yield 81% for PIDT3T as a red solid. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ (ppm) 7.34 (s, 2H), 7.18–6.80 (m, 24H), 3.91 (br, 8H), 1.75 (br, 8H), 1.42 (br, 8H), 1.35–1.20 (m, 64H), 0.87 (t, *J* = 7.0 Hz, 12H). GPC (THF at room temp.): *M*<sub>n</sub> = 61.7 K, *M*<sub>w</sub> = 62.6 K, PDI = 1.01.

**4.4.5. Synthesis of PIDTDTBT.** To a 25 ml flask, 2,7-dibromo-4,9-dihydro-4,4,9,9-(*p*-dodeoxyphenyl)-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene (254 mg, 0.2 mmol), 4,7-di(2-trimethylstannylthiophen-5-yl)-2,1,3-benzothiadiazole (125 mg, 0.2 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (5.5 mg, 0.006 mmol) and tri(*o*-tolyl)phosphine (11 mg, 0.036 mmol) were added under nitrogen protection. The other procedures are just as PIDT3T. The product was obtained with the yield 63% for PIDTDTBT as a dark-blue solid. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ (ppm) 8.01–7.84 (m, 4H), 7.38 (br, 2H), 7.23–6.81 (m, 20H), 3.92 (br, 8H), 1.75 (br, 8H), 1.43 (br, 8H), 1.37–1.20 (m, 64H), 0.86 (t, *J* = 7.0 Hz, 12H). GPC (THF at room temp.): *M*<sub>n</sub> = 35.1 K, *M*<sub>w</sub> = 44.3 K, PDI = 1.26.

## Acknowledgements

The authors are deeply grateful to the National Natural Science Foundation of China (Project no. 21274134, 21202181, 51303197 and 51173199), New Century Excellent Talents in University (NCET-11-0473), and Qingdao Municipal Science and Technology Program (13-1-4-200-jch) for financial support.



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