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# Single-strand and ladder-type polymeric acceptors based on regioisomerically-pure perylene diimides towards all-polymer solar cells

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## HIGHLIGHTS

• Regioisomerically-pure 1,7-DBPDIs lead to single-strand polymers (PrPDIT) with molecular weight distribution as low as 1.08.

• Ladder-type polymers (FPrPDIT) were synthesized by the quantitative yield cyclization of PrPDIT.

• Both PrPDIT and FPrPDIT are excellent acceptors with highest power conversion efficiency of 5.95% in all-polymer solar cells.

## ARTICLEINFO

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## ABSTRACT

Since dibromo perylene diimides (DBPDIs) contain two isomers that are difficult to separate, isomeric effect on properties and applications of PDI polymers has been rarely studied. Few ladder-type polymers have been used in organic solar cells. Herein, single-strand polymers (PrPDIT) were synthesized by the polymerization of regioisomerically-pure 1,7-dibromo-PDIs (1,7-DBPDIs) and 2,5-bis(trimethylstannyl)thiophene. Furthermore, ladder-type polymers (FPrPDIT) were obtained by the highly efficient photo-induced cyclization of polymers PrPDIT. The effects of isomers and molecular weight on the absorption, electrochemistry, thermal stability, and photovoltaic application of polymers were studied. Pure 1,7-DBPDIs lead to polymers with molecular weight distribution as low as 1.08. These polymers with strong absorption in 300–700 nm, low-lying lowest unoccupied molecular orbital (LUMO) energy levels around -4.0 eV and high thermal stability could be excellent electron acceptors. Regioisomerically-pure polymers demonstrate better photovoltaic performance than that of mixed ones. The highest power conversion efficiency (PCE) of all-polymer solar cells based on PrPDIT and FPrPDIT is up to 5.95% and 4.52% respectively.

#### 1. Introduction

Aiming for efficient solar-to-electricity conversion, bulk heterojunction organic solar cells (BHJOSCs) have attracted more and more attention because of light-weight, flexible, and low-cost devices [1–11]. Electronic donors and acceptors are both essential in BHJOSCs. Compared to the prosperity and excellence of donor materials, electron acceptors lag obviously [12–20]. Widely used fullerene acceptors (such as PC<sub>61</sub>BM, PC<sub>71</sub>BM) have disadvantages of difficult modification, high cost, and weak absorption [21–24]. Thus, much effort has been focused on non-fullerene organic acceptors in the past several years, and they show diverse and precise molecular structures, strong absorption, and tunable energy levels [25–31]. All-polymer solar cells (all-PSCs) are focused recently, because polymeric semiconductors exhibit excellent flexibility, film forming ability, mechanical strength, and charge transport [32–34]. Perylene diimides (PDIs) and naphthalene diimides (NDIs) are two promising building blocks to construct polymeric acceptors [35–42]. Polymeric PDIs have been widely reported for their advantages of suitable lowest unoccupied molecular orbital (LUMO) energy levels, high stability, and strong absorption [43–46]. Since dibromo perylene diimides (DBPDIs, Fig. 1) contain two isomers of 1,6-dibromo PDIs (1,6-DBPDIs) and 1,7dibromo PDIs (1,7-DBPDIs) which are difficult to separate, pure major isomer 1,7-DBPDIs are rarely used to construct conjugated polymers. Different configurations of isomers result in polymers with different arrangement and charge transport, which has significant effect on their

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Fig. 1. Structures of 1,7-DBPDI&1,6-DBPDI, PrPDIT, FPrPDIT, and optimized geometry of FPrPDIT.



Scheme 1. Synthetic route of PrPDIT, FPrPDIT, and FPDI-Th. a) 1) KOH, H<sub>2</sub>O, 70 °C, 60 min; 2) TBAB, 1-butyl bromide, 100 °C, 5 h, 92%; b) Br<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, rt, 12 h; c) CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>CN, rt, recrystallization, 46%; d) ClSO<sub>3</sub>H, rt, 4 h, quantitative yield; e) alkyl amine, NMP, AcOH, 80 °C, 40 min, 57%; f) 2,5bis(trimethylstannyl)thiophene,

Pd<sub>2</sub>(dba)<sub>3</sub>, P(o-tolyl)<sub>3</sub>, toluene, 110 °C, 48 h, 78%; g) 2,5-bis(trimethylstannyl) thiophene, Pd(PPh<sub>3</sub>)<sub>4</sub>, toluene, 110 °C, 12 h, 91%; h) I<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>,  $h\nu$ , rt, 2 h, quantitative yield; i) I<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>,  $h\nu$ , rt, 10 h, quantitative yield.



photovoltaic application [47]. Dahui Zhao and Jian Pei et al. reported a regioisomerically-pure polymeric acceptor based on 1,7-DBPDIs and bithiophene, and it reached the highest power conversion efficiency (PCE) of 2.17%, and the regioisomerically-pure polymer shows improved device performance compared to the irregular ones [44]. So it is necessary to study this isomeric effect.

Ladder-type semiconductor polymers in which conjugated cores are connected by double bonds or aromatic rings have large rigid skeletons, which lead to free intramolecular electron communication, unique packing and special applications [48]. Ladder-type polymers with perfect structures are rare due to synthetic difficulty. In single-strand PDI polymers, PDIs and neighboring aromatic ring such as benzene, thiophene, and thieno[3.2-b]thiophene could be cvclized by the dehvdrogenation reaction, which lead to ladder-type polymers [49-54]. However, quantitative cyclization is essential to ensure flawless structures. Xiao et al. synthesized planar ladder-type polymers based on PDIs and thieno[3,2-b]thiophene through a highly efficient photo-induced cyclization [48]. However, they show limited solubility due to strong intermolecular interaction. Furthermore, their isomeric effect was not considered, and they did not exhibit any performance in photovoltaic application. Herein, we are interested in single-strand and ladder-type polymers based on regioisomerically-pure PDIs and thiophene, and they show twisted well-defined structures (Fig. 1), good solubility, and excellent photovoltaic application.

Interestingly, when pure 1,7-DBPDIs were used for polymerization, two fractions of PrPDIT (Fig. 1) with different molecular weight and narrow molecular weight distribution (as low as 1.08) could be obtained through the simple column separation. Molecular weight and isomeric effect have little influence on the absorption and energy levels of these polymers, while they show different performance in photovoltaic application. Ladder-type polymer of FPrPDIT (Fig. 1) was synthesized by the quantitative yield cyclization of polymer PrPDIT. All-PSCs based on these polymers achieved highest PCE of 5.95% without adding any additives or post-treatment.

## 2. Results and discussion

## 2.1. Synthesis

As shown in Scheme 1, key intermediate 1,7-DBPDIs were synthesized in five steps from commercial available perylene-3,4,9,10-tetracarboxylic dianhydride (1) according to literature method [43,55]. Some improvement was made as following. 1) Regioisomerically-pure **3a** could be obtained directly after the evaporation of 10 mL mixed solvent(CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN = 1:2, v/v)gradually, and the purity was characterized by <sup>1</sup>H NMR, while recrystallization for 2–3 times were required in literature method. 2) Compound **4** was obtained quantitatively by the hydrolysis of **3a** in chlorosulfonic acid, while *p*toluenesulfonic acid was used in the literature method, which had a complicated post-treatment.

Single-strand polymer PrPDIT was prepared via a Stille polymerization reaction using Pd<sub>2</sub>(dba)<sub>3</sub>/P(o-tolyl)<sub>3</sub> as the catalyst. 1,7-Dibromo-*N*, *N'*-bis(2-octyldodecyl)-3,4,9,10-perylene diimides (1,7-DBPDIs) with bulky side chains were adopted to make target polymers soluble. Molecular weight of polymers could be adjusted by the reaction time. Notably, when the 1,7-DBPDIs were used, two fractions with different molecular weight are easily separated through simple gel column chromatography, and the molecular weight distribution is as low as 1.08. As shown in Table 1, polymerization of 1,7-DBPDI for 48 h lead to mixed polymers, and two polymers of PrPDIT with different molecular weight ( $M_n = 6.3$  KDa and 8.4 KDa) and low molecular distribution ( $M_w/M_n = 1.08$  and 1.28) were isolated conveniently through a silica gel column.

The molecular weight distribution of regioisomerically-pure polymers (PrPDIT) was much lower than that of mixed polymers (PPDIT). For example, the distribution of regioisomerically-pure polymer PrPDIT  $(M_n: 6.3 \text{ KDa})$  is as low as 1.08, while that of PPDIT  $(M_n: 6.9 \text{ KDa})$  is 1.78, as determined by gel permeation chromatography (GPC) using THF as the eluent.

As shown in Scheme 1, to get well-defined ladder-type FPrPDIT, a highly efficient cyclization of single-strand PrPDIT is necessary. A model compound FPDI-Th was synthesized under different conditions. With optimized reaction condition of photo-induced cyclization, the precursor compound PDI-Th could be converted into FPDI-Th quantitatively in the presence of catalytic amount  $I_2$ . PDI-Th tends to decompose in the solvent under ambient condition, and it leads to a complicated mixture in the absence of catalyst  $I_2$ .

Single-strand PrPDIT could be converted into ladder-type FPrPDIT gradually under irradiation of a xenon lamp HSX-F300 (350-780 nm) in CH<sub>2</sub>Cl<sub>2</sub>, and the process can be tracked by UV–Visible absorption. The absorption of reaction mixture was recorded after removing catalyst I2 by aqueous Na<sub>2</sub>SO<sub>3</sub>. As shown in Fig. 2, the absorption of starting polymer hypsochromic shifted gradually in the reaction process in 2.5 h. The solution color changed from purple dark into red, which was consistent with the reaction process of model compound. FPrPDIT was characterized by high temperature NMR. Single-strand PrPDIT showed clear NMR response at room temperature, while ladder-type FPrPDIT gave low-field signal only at high temperature, because the rigid core limits the free rotation of the molecule. <sup>1</sup>H NMR signal of protons at thienyl group ( $\delta$  = 7.4 ppm) disappeared after cyclization, and a broad peak ( $\delta$  = 9.0–7.6 ppm) was observed in <sup>1</sup>H NMR of FPrPDIT (see Supporting Information). Due to bulky alkyl chains and twisted conjugated cores, target polymers FPrPDIT as the red solid showed good solubility in common solvents like CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, THF, and toluene.

## 2.2. Optical and electrochemical properties

The absorption of these compounds in solution and thin film were characterized. All the polymers in this study show strong absorption in the range of 300–700 nm (Fig. 3a and b). Their solid absorption has slight hypsochromic shift by 5–10 nm compared to their solution absorption because of stronger aggregation in solid state. Polymers with different molecular weights show different solid absorption due to their different aggregation and packing in solid state.

As shown in Fig. 3a, solution absorption of ladder-type FPrPDIT hypsochromic shifted by about 25 nm compared to that of single-strand PrPDIT, which agrees with the model compound [24]. The optical band gap of FPrPDIT is about 0.2 eV higher than that of PrPDIT (Table 1), because LUMO energy levels keep consistent, while the highest occupied molecular orbital (HOMO) energy levels decline after cyclization, which is confirmed by the theoretical calculation (see Supporting Information). The extinction coefficients ( $\varepsilon$ ) of FPrPDIT in 300–550 nm are obviously higher than those of single-strand polymers, and the ladder-type polymers show clear absorption fine structure, which is the reflection of their special rigid core. The optical data of these polymers were summarized in Table 1.

To study electrochemistry property of these compounds, their redox properties in the solid state were measured by the cyclic voltammetry (CV). All of them showed a semi-reversible reduction peak indicating their ability to accept at least one electron, and no oxidation peak was observed. The LUMO energy levels were estimated based on the assumption that the energy level of Fc/Fc<sup>+</sup> is -4.8 eV relative to vacuum [56,57]. As shown in Table 1, these polymers have similar LUMO energy levels in the range of  $-3.96 \sim -4.03 \text{ eV}$ , the reason is that the first electron-accepting position is at the oxygen atom in the carbonyl group due to its strong electron-withdrawing property, and there is little energy difference on the carbonyl groups among these polymers [58].

The target polymers PrPDIT, FPrPDIT, and PPDIT exhibit excellent thermal stability, and the 5% weight loss temperatures (Td) are 435, 440, and 431 °C respectively, which is confirmed by thermogravimetric analysis (TGA, Fig. S2) in the air.

#### Table 1

Optical, electrochemical, and molecular weight data of polymers.

Polymers ( <i>M</i> <sub>n</sub> )	λ (nm) Solution Fil	m	$\varepsilon_{\max}^{a}$ (M <sup>-1</sup> cm <sup>-1</sup> )	$E_{\rm g}^{\rm b}$ (eV)	LUMO (eV)	M <sub>n</sub> <sup>°</sup> ∕KDa	$M_{\rm w}/M_{\rm n}^{\rm c}$
PrPDIT (4.3 KDa) <sup>d</sup>	542	537	15900	1.71	-4.00	4.3	1.14
PrPDIT (5.1 KDa) <sup>e</sup>	556	551	15400	1.71	-4.01	5.1	1.24
PrPDIT (6.3 KDa) <sup>f</sup>	538	527	15500	1.78	- 3.96	6.3	1.08
PrPDIT (8.4 KDa) <sup>g</sup>	553	548	15000	1.71	-4.01	8.4	1.28
PPDIT (6.9 KDa) <sup>h</sup>	553	547	15600	1.72	-4.01	6.9	1.78
PPDIT (8.0 KDa) <sup>i</sup>	554	546	15800	1.74	-4.02	8.0	1.51
FPrPDIT (6.3 KDa)	513	510	23400	1.96	-4.03	6.3	1.08

 $^a\,$  The molar extinction coefficient at  $\lambda_{max}$  in solution.

<sup>b</sup> Optical band gap.

<sup>c</sup>  $M_{\rm n}$ ,  $M_{\rm w}$ , and  $M_{\rm w}/M_{\rm n}$  were determined by GPC on the basis of polystyrene calibration.

<sup>d</sup> The first and

e second fraction of gel column, reaction lasted for 30 h.

 $^{\rm f}\,$  The first and

<sup>g</sup> second fraction of gel column, reaction last for 48 h.

<sup>h</sup> Reaction last for 30 h.

<sup>i</sup> Reaction lasted for 48 h.



Fig. 2. The absorption of polymer  $\mbox{PrPDIT}$  in  $\mbox{CHCl}_3$  with different irradiation time.

## 2.3. Photovoltaic properties

To evaluate the photovoltaic properties of these electron acceptors, all-PSCs with the structure of ITO/ZnO/donor:acceptor/MoO<sub>3</sub>/Ag were fabricated. The PTB7-Th (structure is in Fig. S3) was selected as the donor, because it has matched energy levels (Fig. S4) and complementary absorption (Fig. S5) with those of target polymers. Table S1 shows the device properties of PTB7-Th:FPrPDIT ( $M_n$ : 6.3 KDa) with different donor:acceptor ratios, and the optimal weight ratio is 1:1. The detailed device parameters at different concentration were shown in Table S2, and the best concentration is 16 mg mL<sup>-1</sup>. The detailed

Table 2

Photovoltaic properties of the all-PSCs based on different acceptors with D/A ratio of 1:1.

Acceptor $(M_n)$	$V_{\rm oc}$ (V)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	FF (%)	PCE <sub>max</sub> (%)	PCE <sub>avg</sub> <sup>d</sup> (%)
PrPDIT (4.3 KDa)	0.73	12.00	58.49	5.16	$\begin{array}{r} 4.95 \ \pm \ 0.21 \\ 4.76 \ \pm \ 0.16 \\ 5.78 \ \pm \ 0.17 \\ 4.44 \ \pm \ 0.14 \\ 4.28 \ \pm \ 0.08 \\ 3.82 \ \pm \ 0.10 \\ 4.11 \ \pm \ 0.11 \\ 4.36 \ \pm \ 0.16 \end{array}$
PrPDIT (5.1 KDa)	0.73	12.34	54.47	4.92	
PrPDIT (5.3 KDa)	0.74	14.01	57.23	5.95	
PrPDIT (6.3 KDa)	0.74	11.53	53.37	4.58	
PPDIT (6.4 KDa)	0.75	10.88	53.50	4.36	
PPDIT (6.9 KDa)	0.74	10.22	51.73	3.93	
PPDIT (6.3 KDa)	0.76	12.22	45.34	4.21	
FPrPDIT (6.3 KDa) <sup>c</sup>	0.77	11.81	49.83	4.52	

 $^{\rm a}$  Under the illumination of AM 1.5G, 100 mW cm $^{-2};$   $^{\rm b}$  The film thickness of around 100 nm ( $\pm$ 10 nm) was determined by AFM;  $^{\rm c}$  1% DIO was used as the additive;  $^{\rm d}$  The average PCE are calculated from 10 devices.

performances at different amounts of DIO were shown in Table S3, and the optimized amount of DIO is 1%. Therefore, above optimized conditions were adopted in the following device fabrication.

Table 2 shows parameters of solar cells fabricated at above optimal conditions. Compared to mixed PPDIT, regioisomerically-pure PrPDIT shows higher short-circuit current density ( $J_{sc}$ ), fill factor (FF), and PCE, which may be assigned to regular packing of the former polymers. Molecular weight of single-strand polymers has little influence on the device performance, and PrPDIT with  $M_n$  of 6.3 KDa gave the best PCE of 5.95%, so it was selected to prepare ladder-type polymers. Single-strand polymers with higher FF,  $J_{sc}$ , and PCE have better photovoltaic performance than ladder-type ones, which is caused by different



Fig. 3. Absorption of polymers (a) in CHCl<sub>3</sub> ( $1 \times 10^{-5}$  M) and (b) in solid state.



Fig. 4. (a) J - V curves and (b) EQE spectra of solar cells based on PTB7-Th:PrPDIT and PTB7-Th:FPrPDIT.

morphology of active layers. Upon adding 1% DIO, PCE of ladder-type FPrPDIT increased to 4.52% due to the improved morphology. While single-strand polymers were insensitive to any solvent additives, they are excellent polymeric acceptors for additive-free solar cells.

The external quantum efficiency (EQE) was measured to examine the spectral response in the solar cells. As shown in Fig. 4b, these devices show strong photoresponse in the broad range of 300–800 nm, which indicates that both the absorption of PTB7-Th and PrPDIT/ FPrPDIT have significant contribution to the photocurrent. The highest EQE for PTB7-Th:PrPDIT and PTB7-Th:FPrPDIT devices are 57% and 50% respectively, located at 695 nm. Specifically, the photon responses between 300 and 600 nm are mainly contributed by PrPDIT or FPrPDIT, while PTB7-Th provides the dominant role from 600 to 800 nm. Compared to FPrPDIT, PrPDIT shows higher PCE, which is consistent with its higher EQE.

To understand charge transport properties of all-PSCs based on PrPDIT and FPrPDIT, their charge carrier mobilities were measured by the space-charge-limited-current (SCLC) method. The typical *J-V* curves of the hole-only and electron-only devices are shown in Fig. S7. The calculated hole and electron mobilities are  $5.72 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $6.69 \times 10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for PTB7-Th:PrPDIT blend film, and they are  $7.58 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $1.61 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for PTB7-Th:PrPDIT (Table S4). The electron mobility of ladder-type polymer FPrPDIT is higher than single-strand polymer PrPDIT.

Atomic force microscopy (AFM) and transmission electron microscopy (TEM) were used to study the morphology of active layers. As shown in Fig. 5, the surface roughness of the PTB7-Th:PrPDIT and PTB7-Th:FPrPDIT films show similar root-mean-square (RMS) as 3.03 and 2.57 nm. Blend film of PTB7-Th:PrPDIT shows better



Fig. 5. AFM images of PTB7-Th:PrPDIT and PTB7-Th:FPrPDIT film.

interpenetrating networks. The ideal morphology with a donor:acceptor interpenetrating network could promote exciton dissociation and charge transport, which is beneficial for achieving good performance in all-PSCs. Combining AFM and TEM images (Fig. S8), blend film of PTB7-Th:FPrPDIT shows larger domain size in phase separation. Too large domain size hampered efficient charge separation and exciton generation, which lead to its lower  $J_{sc}$  and PCE in solar cells.

Further studies on the basic operational mechanism were performed to obtain the photo-generated current density ( $J_{\rm ph} = J_{\rm L} \cdot J_{\rm D}$ ,  $J_{\rm L}$ : current density under illumination;  $J_{\rm D}$ : current density in the dark) versus effective voltage ( $V_{\rm eff} = V_0$ - $V_a$ ,  $V_0$ : the voltage when  $J_{\rm ph}$  is zero;  $V_a$ : applied voltage) curves of devices based on PTB7-Th:PrPDIT and PTB7-Th:FPrPDIT, as shown in Fig. 6a [59–61].

The exciton dissociation probability ( $P_{diss}$ ) of devices based on PTB7-Th:PrPDIT and PTB7-Th:FPrPDIT under the short circuit condition are 64% and 50%, respectively. The  $P_{diss}$  of PTB7-Th:PrPDIT is higher than that of PTB7-Th:FPrPDIT, which is consistent with the superior photovoltaic performance of the former device. The  $J_{sc}$  of optimal all-PSCs under different light intensities (P) were also measured: the relationship between  $J_{sc}$  and P can be described as  $J_{sc} \propto P^S$  [62]. The light intensity dependence curve based on  $J_{sc}$  was shown in Fig. 6b, and the scaling factor (S) value of devices based on PTB7-Th:PrPDIT and PTB7-Th:FPrPDIT are 0.95 and 0.90, respectively. Therefore, all these devices exhibited reduced bimolecular recombination, which are beneficial to achieve high  $J_{sc}$  and high FF.

#### 3. Conclusion

Regioisomerically-pure 1,7-DBPDIs lead to high performance conjugated polymers with molecular weight distribution as low as 1.08. Ladder-type polymers of FPrPDIT were synthesized by quantitative yield cyclization of regioisomerically-pure polymer PrPDIT. These polymers with strong absorption, low-lying LUMO energy levels, and high thermal stability are excellent polymeric acceptors. Compared to mixed polymers, regioisomerically-pure ones show higher  $J_{sc}$ , FF, and PCE. Molecular weight of single-strand polymers has a little influence on the device performance, and PrPDIT with  $M_n$  of 6.3 KDa gave the best PCE of 5.95%. Single-strand polymers have better photovoltaic performance than ladder-type ones, because the former lead to better morphology. Thus, pure 1,7-DBPDIs are important in the construction of high performance polymeric semiconductors, and twisted conjugated ladder-type polymers with perfect structures are promising acceptors.

#### 4. Experimental section

#### 4.1. Materials

Known compound PDI-Th, FPDI-Th, **3a**, **4**, and polymer PPDIT were synthesized according to literature method [43,63,64], and the detailed



Fig. 6. (a) Photocurrent versus effective voltage plots and (b) light intensity dependence of short circuit intensity curves of polymer PrPDIT and FPrPDIT.

procedure is in Supporting Information. All the chemicals were obtained commercially and used without further purification.

#### 4.2. Characterization

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured on a NMR spectrometer. Absorption spectra were recorded on a PerkinElmer lambda 750 spectrophotometer. TGA measurements were performed using a TGA Mettler-Toledo Gmbh under flowing air at a heating rate of 10 K·min<sup>-1</sup>. Atomic force microscopy (AFM) images were obtained using a NanoMan VS microscope in the tapping mode. The thickness of the active layer of the device was measured via a VeecoDektak 150 surface profiler. TEM images of blend films were acquired by a JEOL 2200FS transmission electron microscopy with 200 kV accelerating voltage.

## 4.3. Synthesis of polymer PrPDIT

1,7-Dibromo-*N*, *N'*-bis-(2-octyl dodecyl)-3,4,9,10-perylene diimides (1,7-DBPDIs, 700 mg, 0.63 mmol), 2,5-bis (trimethylstannyl) thiophene (258 mg, 0.63 mmol), catalyst of Pd<sub>2</sub>(dba)<sub>3</sub> (23 mg, 0.025 mmol), P(o-tolyl)<sub>3</sub> (77 mg, 0.25 mmol), and 20 mL toluene were mixed and stirred at 110 °C for 48 h under argon. The crude polymer was precipitated from the solution by adding it to excess methanol, and the dried polymer was purified through silica gel column with eluent of CHCl<sub>3</sub>. The first fraction was precipitated from methanol to obtain PrPDIT ( $M_n$ : 6.3 KDa, 148 mg, 22.1%), and the second fraction PrPDIT ( $M_n$ : 6.3 KDa, 389 mg, 58.0%) was dark purple solid. PrPDIT ( $M_n$ : 6.3 KDa)  $M_n = 6.3$  KDa,  $M_w/M_n = 1.08$ ; PrPDIT ( $M_n$ : 8.4 KDa)  $M_n = 8.4$  KDa,  $M_w/M_n = 1.28$ .<sup>1</sup>H NMR (400 MHz, C<sub>2</sub>Cl<sub>4</sub>D<sub>2</sub>)  $\delta$  8.97–8.16 (m, 6H), 7.43 (m, 2H), 4.08 (m, 4H), 1.97 (m, 2H), 1.16 (m, 64H), 0.78 ppm (m, 12H).

#### 4.4. Synthesis of polymer PPDIT

(1,7&1,6)-DBPDI (260 mg, 0.23 mmol), 2,5-bis (trimethylstannyl) thiophene (96 mg, 0.23 mmol), catalyst Pd<sub>2</sub>(dba)<sub>3</sub> (9 mg, 0.01 mmol), P (o-tolyl)<sub>3</sub> (31 mg, 0.10 mmol), and 10 mL toluene were mixed and stirred at 110 °C for 48 h under argon. The crude polymer was precipitated from the solution by adding it to excess methanol, and the dried polymer was purified through silica gel column with eluent of CHCl<sub>3</sub>. PPDIT ( $M_n$ : 8.0 KDa) was obtained (193 mg, 78%) as dark purple solid. PPDIT ( $M_n$ : 8.0 KDa)  $M_n = 8.0$  KDa,  $M_w/M_n = 1.51.^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.92–8.23 (m, 6H), 7.36 (m, 2H), 4.11 (m, 4H), 1.99 (m, 2H), 1.44–1.00 (m, 64H), 0.78 ppm (m, 12H).

#### 4.5. Synthesis of polymer FPrPDIT

The polymer PrPDIT (50 mg),  $I_2$  (5 mg, 0.02 mmol), and 300 mL  $CH_2Cl_2$  were mixed and stirred at room temperature and irradiated with

a xenon lamp HSX-F300 (350–780 nm) for 10 h. The reaction mixture was washed with saturated Na<sub>2</sub>SO<sub>3</sub> solution to remove I<sub>2</sub>. Next, the polymer was precipitated from methanol to obtain FPrPDIT (49 mg, quantitative yield) as dark red solid. <sup>1</sup>H NMR (400 MHz, C<sub>2</sub>Cl<sub>4</sub>D<sub>2</sub>)  $\delta$  9.00–7.61 (m, 4H), 4.20–3.70 (m, 4H), 2.10 (m, 2H), 1.30 (m, 64H), 0.86 ppm (m, 12H).

#### 4.6. All-polymer solar cell fabrication

Organic photovoltaic (OPV) devices were fabricated with an inverted structure of ITO/ZnO/active layer/MoO<sub>3</sub>/Ag. The conductive ITO substrates were sequentially cleaned with ultrasonication in detergent, water, acetone, and isopropanol. After drying the ITO substrates and treating the surface with UV ozone for 20 min, the ZnO precursor solution was prepared by dissolving 0.5 g of zinc acetate dihydrate (Zn (CH3COO)2·2H2O, 99.9%) in 5 mL 2-methoxyethanol (CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OH, 99.8%), and 138 µL ethanolamine (NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH, 99.8%). The ZnO precursor was spun-coated at 4000 r.p.m. for 1 min onto the ITO surface. After being baked at 200 °C for 60 min in air, the substrates were transferred into a nitrogen-filled glove box. Then the active layers were spun-coated from solutions of donor: acceptor (1:1 w/ w) in chlorobenzene with a total concentration of  $16 \text{ mg mL}^{-1}$ . To ensure the donor polymer soluble, active solutions were heated at 70 °C for 12 h prior to spin coating in a glovebox. MoO<sub>3</sub> (7 nm) and Ag (90 nm) were deposited by thermal evaporation under a vacuum chamber to complete the device fabrication. The effective area of one cell was 0.04 cm<sup>2</sup>. The current-voltage (J-V) characteristics were measured by a Keithley 2400 Source Meter under simulated solar light  $(100 \text{ mW cm}^{-2}, \text{ AM } 1.5 \text{ G}, \text{ Abet Solar Simulator Sun 2000})$ . The incident photon-to-electron conversion efficiency (IPCE) spectra were detected on an IPCE measuring system (Oriel Cornerstone monochromator equipped with Oriel 70613NS QTH lamp). All the measurement was performed at room temperature under nitrogen atmosphere.

#### **Conflicts of interest**

The authors declare no competing financial interest.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2018.12.041.

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