

# Diketopyrrolopyrrole Polymers with Thienyl and Thiazolyl Linkers for Application in Field-Effect Transistors and Polymer Solar Cells

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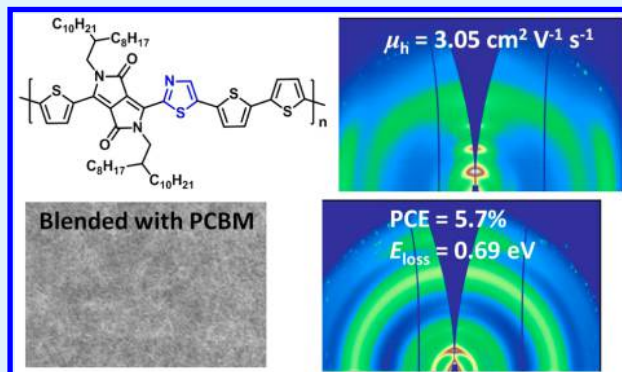
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## Supporting Information

**ABSTRACT:** Conjugated polymers consisting of diketopyrrolopyrrole (DPP) units have been successfully applied in field-effect transistors (FETs) and polymer solar cells (PSCs), while most of the DPP polymers were designed as symmetric structures containing identical aromatic linkers. In this manuscript, we design a new asymmetric DPP polymer with varied aromatic linkers in the backbone for application in FETs and PSCs. The designation provides the chance to finely adjust the energy levels of conjugated polymers so as to influence the device performance. The asymmetric polymer exhibits highly crystalline properties, high hole mobilities of  $3.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  in FETs, and a high efficiency of 5.9% in PSCs with spectra response from 300 to 850 nm. Morphology investigation demonstrates that the asymmetric polymer has a large crystal domain in blended thin films, indicating that the solar cell performance can be further enhanced by optimizing the microphase separation. The study reveals that the asymmetric design via adjusting the aromatic linkers in DPP polymers is a useful route toward flexible electronic devices.

**KEYWORDS:** conjugated polymer, field-effect transistors, polymer solar cells, diketopyrrolopyrrole, crystalline, asymmetric polymer



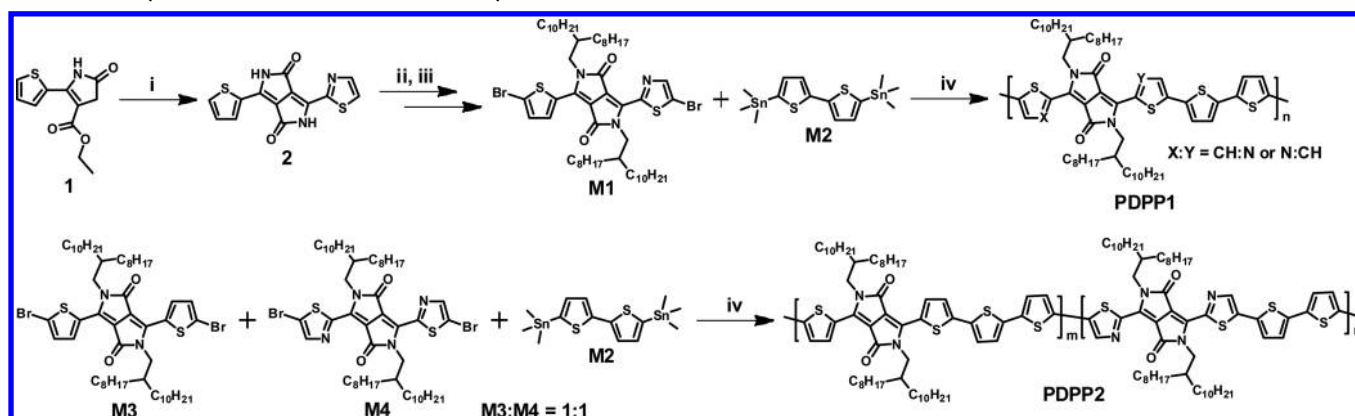
## INTRODUCTION

Semiconducting polymers containing diketopyrrolopyrrole (DPP) units have been successfully applied into field-effect transistors (FETs)<sup>1,2</sup> and polymer solar cells (PSCs)<sup>3,4</sup> in recent years. Electron-deficient DPP units are used to construct polymers with near-infrared (NIR) spectra, which is helpful for harvesting more photons from sunlight in solar cells.<sup>5</sup> Small band gap DPP polymers also desire low-lying lowest unoccupied molecular orbital (LUMO) levels approaching  $-4.0 \text{ eV}$  and high-lying highest occupied molecular orbital (HOMO) levels, which is beneficial for charge (hole and electron) injection processes between the polymers and the gold electrode in FETs.<sup>6,7</sup> Combined with the good crystalline properties originated from the fused bislactam rings of the DPP core, DPP polymers have high carrier mobilities in FET devices, including p-type,<sup>8–13</sup> n-type,<sup>14–16</sup> and ambipolar properties.<sup>17–22</sup> Low-lying LUMO levels also reduce the LUMO offset between DPP polymers and fullerene derivatives so as to lower the energy loss ( $E_{\text{loss}}$ ) and potentially enhance the solar cells performance.<sup>23–27</sup> DPP polymers-based PSCs have gained power conversion efficiencies (PCEs)  $> 9\%$ ,<sup>28</sup> indicating their large potential to realize high-performance solar cells.

DPP polymers consist of a DPP core alternated with  $\pi$ -conjugated segments, in which the aromatic substituent is required as the linker because of the synthetic nature of DPP monomers. In the early period of research about DPP compounds, phenyl rings are usually introduced as the linkers due to easy preparation.<sup>29,30</sup> However, it was found that the dihedral angle between benzene and the DPP core is close to  $30^\circ$ ,<sup>31</sup> seriously disturbing the  $\pi$ -conjugation of the polymer backbone and resulting in a low performance in transistors and solar cells.<sup>32–34</sup> The dihedral angle can be significantly reduced by using thienyl units as linkers, which also represent the most successful strategy for designing DPP polymers.<sup>15</sup> Other aromatic substituents, such as thienothiophene,<sup>35,36</sup> pyridine,<sup>15,37,38</sup> furan,<sup>39,40</sup> selenophene,<sup>41,42</sup> and thiazole,<sup>23,43,44</sup> can be introduced as linkers into the DPP polymer for adjusting the energy levels, absorption spectra, and crystalline properties. For instance, the thiazolyl linkers with the electron-deficient imine nitrogens ( $\text{C}=\text{N}-\text{C}$ ) can provide the DPP

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Scheme 1. Synthetic Procedures and the Polymer Structures of PDPP1 and PDPP2<sup>a</sup>

<sup>a</sup>(i) Sodium/FeCl<sub>3</sub>, thiazole-2-carbonitrile, 120 °C; (ii) Cs<sub>2</sub>CO<sub>3</sub>, 18-crown-6, 2-octyldodecyl bromide, 120 °C; (iii) Br<sub>2</sub>; (iv) Pd<sub>2</sub>(dba)<sub>3</sub>/PPh<sub>3</sub>, 115 °C.

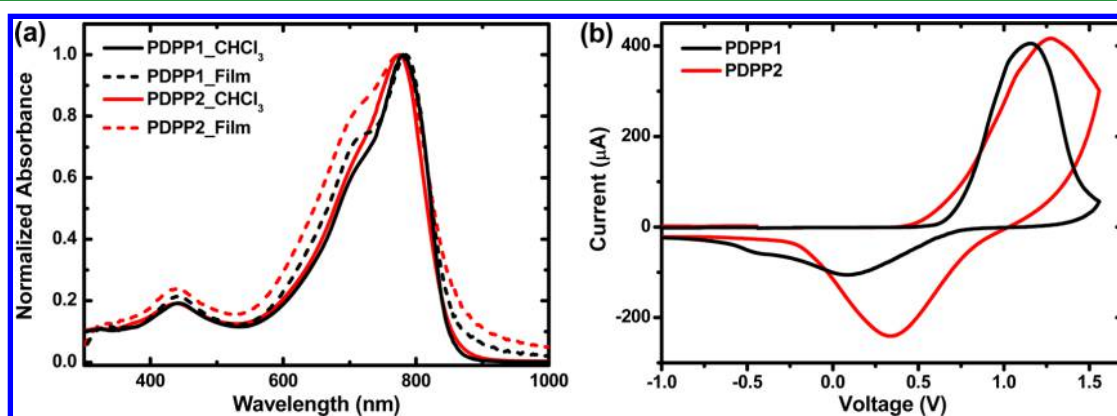


Figure 1. (a) Optical absorption and (b) CV spectra of PDPP1 and PDPP2. Potential vs Fc/Fc<sup>+</sup>.

Table 1. Molecular Weight and Optical and Electrochemical Properties of the Polymers PDPP1 and PDPP2

| polymer | $M_n$ (kg mol <sup>-1</sup> ) | PDI  | solution                     |                               |            | film                         |                               |            | $E_{\text{HOMO}}^a$ (eV) | $E_{\text{LUMO}}^b$ (eV) |
|---------|-------------------------------|------|------------------------------|-------------------------------|------------|------------------------------|-------------------------------|------------|--------------------------|--------------------------|
|         |                               |      | $\lambda_{\text{peak}}$ (nm) | $\lambda_{\text{onset}}$ (nm) | $E_g$ (eV) | $\lambda_{\text{peak}}$ (nm) | $\lambda_{\text{onset}}$ (nm) | $E_g$ (eV) |                          |                          |
| PDPP1   | 75.4                          | 1.57 | 780                          | 848                           | 1.46       | 785                          | 853                           | 1.45       | -5.48                    | -4.03                    |
| PDPP2   | 118.4                         | 1.75 | 774                          | 849                           | 1.46       | 774                          | 867                           | 1.43       | -5.36                    | -3.93                    |

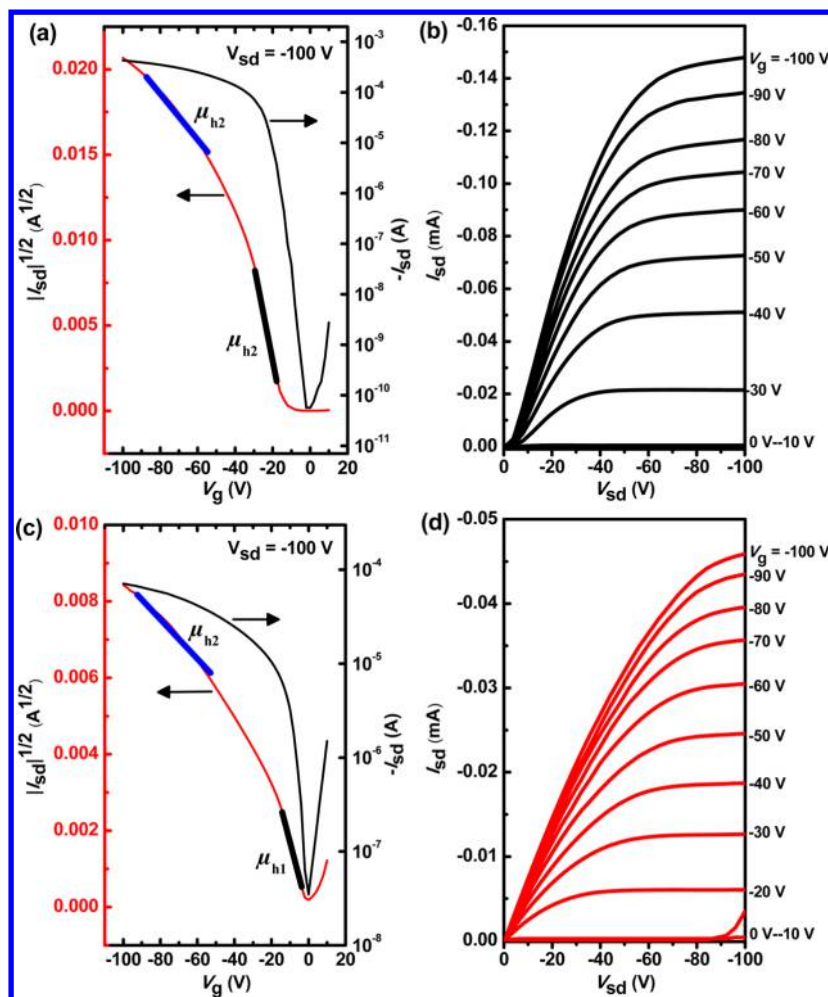
<sup>a</sup>Using a work function of -4.8 eV for Fc/Fc<sup>+</sup>. <sup>b</sup>Calculated as  $E_{\text{HOMO}} + E_g^{\text{film}}$ .

polymers with deep HOMO and LUMO levels, resulting in high ambipolar and n-type charge transport in FETs.<sup>45</sup> Thiazolyl-based DPP polymers can act as electron donor in fullerene-based cells to realize low  $E_{\text{loss}}$  below 0.6 eV<sup>23</sup> or as electron acceptor to replace fullerene derivatives.<sup>44,46</sup>

Most of the DPP polymers contain the same aromatic linkers along the conjugated backbone. In our recent work, we designed two asymmetric DPP polymers with different linkers, such as thiophene with thienothiophene or 3-methylthiophene. We found the polymers had good solubility in nonchlorinated solvents while keeping good crystalline properties. When fabricating from nonchlorinated solvents, these polymers had high mobilities of 12.5 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in FETs and PCEs of 6.5% in solar cells.<sup>10</sup> The results encourage us to further explore the asymmetric polymers.

Herein, a new DPP polymer PDPP1 with thienyl and thiazoyl units as linkers was designed and synthesized for application in organic electronic devices. A random copolymer PDPP2 was prepared from the symmetric DPP monomers for comparison (Scheme 1). The design motivation is that the

introduction of thiophene and thiazole with distinct electronic properties into conjugated polymers will allow tuning the energy levels of the polymers so as to have an impact on the device performance. The asymmetric PDPP1 was found to desire energy levels lying between the symmetric polymers and provided a high mobility of 3.05 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in FETs. Solar cells by using PDPP1 as donor exhibit a PCE of 5.9% with an  $E_{\text{loss}}$  of 0.69 eV. On the basis of the photovoltaic performance of symmetric, asymmetric, and random copolymers, we can study the relation between quantum efficiencies and  $E_{\text{loss}}$  in the range of 0.55–0.80 eV. Furthermore, by systematically studying the microphase separation of blending thin films based on PDPP1 and PDPP2, we find that PDPP1 shows large domain size. This indicates that asymmetric DPP polymers can provide better PCEs if the domain size can be reduced in order to improve the exciton diffusion efficiency in bulk–heterojunction systems.



**Figure 2.** (a and c) Transfer fitting from different gate voltage region for PDPP1 ( $\mu_{h1}$  from  $-20$  to  $-30$  V and  $\mu_{h2}$  from  $-50$  to  $-90$  V) and for PDPP2 ( $\mu_{h1}$  from  $-5$  to  $-15$  V and  $\mu_{h2}$  from  $-50$  to  $-90$  V) and (b and d) output curves from FETs: (a and b) for PDPP1; (c and d) for PDPP2. Thin films were prepared from  $\text{CHCl}_3/\text{o-DCB}$  (10%) solution.

**Table 2.** Hole Mobilities of the DPP Polymers in FET Devices<sup>a</sup>

| polymer | $\mu_{h1}$ ( $\mu_{h2}$ ) ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ ) | $V_T$ (V) | $I_{on}/I_{off}$ | (100)    |              |               | (010)    |              |               |
|---------|-------------------------------------------------------------------------|-----------|------------------|----------|--------------|---------------|----------|--------------|---------------|
|         |                                                                         |           |                  | $d$ (nm) | CL (IP) (nm) | CL (OOP) (nm) | $d$ (nm) | CL (IP) (nm) | CL (OOP) (nm) |
| PDPP1   | 3.05 (0.15)                                                             | $-15.6$   | $8 \times 10^6$  | 2.1      | 8.6          | 17.3          | 0.37     | 4.0          | 2.6           |
| PDPP2   | 0.32 (0.024)                                                            | $-1.75$   | $2 \times 10^3$  | 2.1      |              | 17.7          | 0.37     | 4.0          | 2.6           |

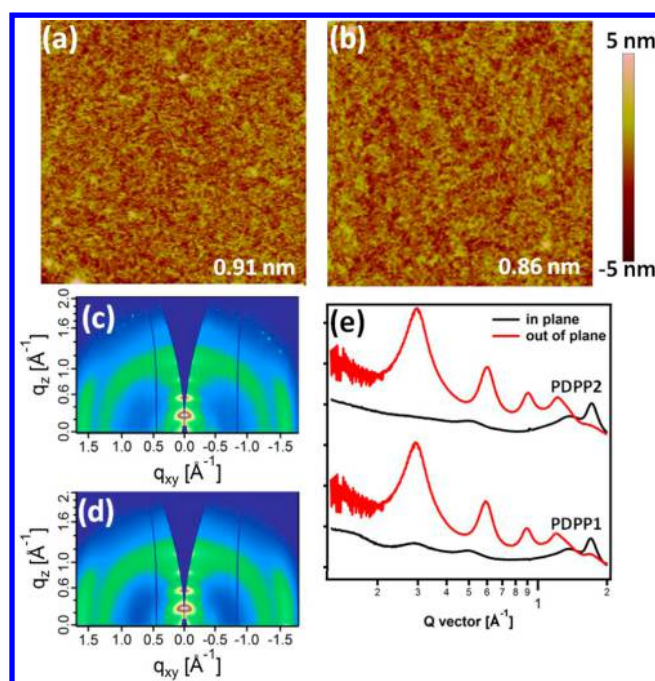
<sup>a</sup>The parameters from 2D-GIWAXS were also included. CL: coherence length. IP: in-plane. OOP: out-of-plane.

## RESULTS AND DISCUSSION

**Synthesis and Characterization.** The synthetic routes for the DPP compounds are shown in Scheme 1. The asymmetric monomer **M1** was prepared from the thiophene-contained precursor **1**.<sup>47</sup> The asymmetric compound **2** was prepared by using thiazole-2-carbonitrile, followed by N-alkylation and bromination to yield the monomer **M1**. By using Stille polymerization with  $\text{Pd}_2(\text{dba})_3/\text{PPh}_3$  catalyst, the polymer PDPP1 can be obtained. The random copolymer PDPP2 was prepared by using the same polymerization condition, in which the dibromo monomers **M3** and **M4** with a ratio of 1:1 were copolymerized with the bisstannyl-bithiophene **M2**. Both of the DPP polymers show good solubility in chloroform ( $\text{CHCl}_3$ ) but have low solubility in *o*-dichlorobenzene (*o*-DCB) and toluene. This is different from our previous observation for the asymmetric DPP polymers that can be well dissolved in

toluene.<sup>10</sup> Gel permeation chromatography (GPC) by using *o*-DCB as eluent at  $140^\circ\text{C}$  was used to determine the molecular weight of the polymers (Figure S1, Supporting Information, SI). The asymmetric polymer PDPP1 exhibits a high number-average molecular ( $M_n$ ) of  $75.4 \text{ kg mol}^{-1}$  with a polydispersity index (PDI) of 1.57, while the random copolymer PDPP2 has a  $M_n$  of  $118.4 \text{ kg mol}^{-1}$ . High molecular weight in these polymers is beneficial for realizing higher performance organic electronic devices.

**Optical and Electrochemical Properties.** Absorption spectra of the polymers are presented in Figure 1. The two polymers exhibit NIR absorption spectra with the same optical band gap ( $E_g = 1.46 \text{ eV}$ ) in  $\text{CHCl}_3$  solution (Table 1). The polymer thin films have a slightly red-shifted absorption with  $E_g$  of 1.45 and 1.43 eV for PDPP1 and PDPP2. It has been reported that the DPP polymer with symmetric linkers, such as PDPP4T<sup>48</sup> with thienyl units and PDPP2Tz2T<sup>23</sup> with thiazoyl



**Figure 3.** (a and b) AFM height images ( $3 \times 3 \mu\text{m}^2$ ), (c and d) 2D-GIWAXS patterns, and (e) out-of-plane and in-plane cuts: (a and c) PDPP1; (b and d) PDPP2. RMS roughness is also included in a and b.

units (Figure S2), showed an  $E_g$  of 1.43 and 1.47 eV. The polymers with asymmetric or random structures had similar absorption spectra as their symmetric analogs.

Cyclic voltammetry (CV) was used to determine the energy levels of the polymers (Figure 1b and Table 1). The HOMO and LUMO levels of the asymmetric polymer PDPP1 are  $-5.48$  and  $-4.03$  eV, which are enhanced to  $-5.36$  and  $-3.93$  eV for PDPP2. We also measured the energy levels of PDPP4T and PDPP2Tz2T by using the same method, as summarized in Figure S3. The HOMO and LUMO levels of PDPP4T are  $-5.23$  and  $-3.8$  eV, which are significantly reduced to  $-5.61$  and  $-4.14$  eV for PDPP2Tz2T. Therefore, the energy levels of PDPP1 can be finely tuned to lie between PDPP4T and PDPP2Tz2T. We also analyze the molecular geometries of the polymer segments via density functional theory calculations (Figure S4), indicating that the asymmetric PDPP1 segment has a slightly lower dihedral angle compared to that of random copolymer PDPP2 segment. Calculated HOMO and LUMO levels of the PDPP1 segment are also slightly deep as compared to the PDPP2 segment, which is consistent with the CV measurement.

**Field-Effect Transistors.** Charge transport properties of the polymers were determined by using FET devices with a bottom gate-bottom contact (BGBC) configuration. The polymers were dissolved in  $\text{CHCl}_3/\text{o-DCB}$  (10%) to prepare thin films via spin coating. The detailed charge mobilities related to annealing temperature are summarized in Table S1. The asymmetric DPP polymer has a high hole mobility of  $3.05$

$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$  with a threshold voltage ( $V_T$ ) of  $-15.6$  V and an on/off ratio of  $8 \times 10^6$  (Figure 2 and Table 2). The hole mobility was reduced to  $0.32 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  for PDPP2. In addition, both of the polymers also perform n-type transport, but the electron mobilities are relatively low with  $0.003$  and  $0.023 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  for PDPP1 and PDPP2 (Figure S5). The hole mobilities over the high gate voltage regime (from  $-50$  to  $-90$  V) were also calculated as suggested in the literature (Figure 2).<sup>49</sup> PDPP1 provided a high hole mobility of  $0.15 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  compared to  $0.024 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  for PDPP2-based FETs (Table 2). We also fabricated FETs based on PDPP4T and PDPP2Tz2T, providing mobilities of  $6.20$  and  $0.54 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  (Figure S6 and Table S2). Therefore, PDPP1 has similar charge transport properties with PDPP4T, but random polymer PDPP2 exhibits obviously poor hole mobilities compared to its analogy. Interestingly, we observe a large  $V_T$  in PDPP1- and PDPP2Tz2T-based FET devices (Table 2 and Table S2), which may originate from the high charge injection barrier from the HOMO levels of the polymers ( $-5.48$  and  $-5.61$  eV) and work function of the Au electrode ( $-5.1$  eV).<sup>6</sup>

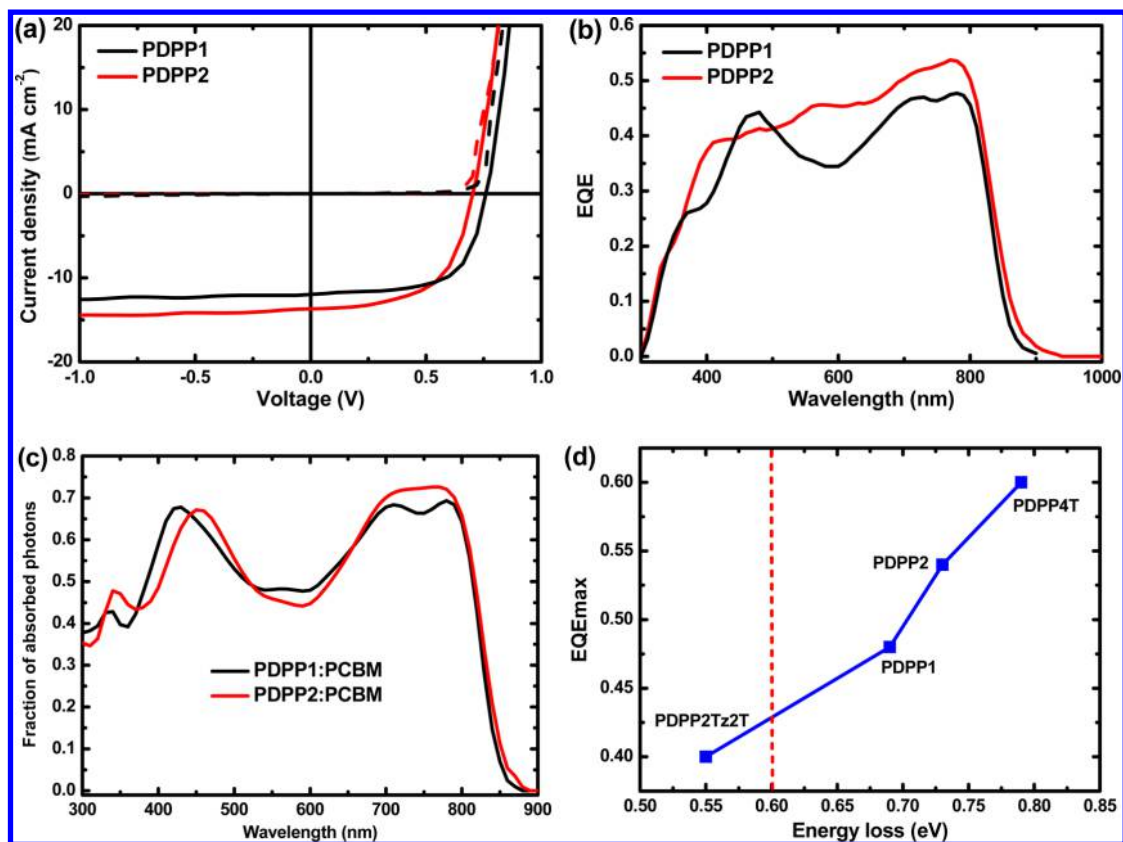
It is interesting to study the different hole mobilities in asymmetric and random copolymers. From the atom force microscopy (AFM) images smooth surface can be observed with similar roughness, and it is hard to get the clue from this measurement (Figure 3a and 3b). Highly crystalline properties can be observed for both of the polymers from 2D grazing-incidence wide-angle X-ray scattering (2D-GIWAXS) measurement, as evidenced from the high ordered ( $h00$ ) diffraction peaks in the out-of-plane direction. The lamellar stacking distance calculated from (100) diffraction peaks is  $2.1$  nm for PDPP1 and PDPP2, representing the distance induced by the alkyl side chains (Table 2). The diffraction peaks (010) for both of the polymers can also be observed in the in-plane directions, with an estimated distance of  $0.37$  nm. The results indicate that PDPP1 and PDPP2 have preferentially “edge-on” configurations. We further analyze the coherence length (CL) that is related to the crystalline size of the polymers, as summarized at Table 2. Both PDPP1 and PDPP2 have similar a coherence length of lamellar and  $\pi$ - $\pi$  stacking, although PDPP1 shows weak lamellar stacking at the in-plane direction. From AFM and 2D-GIWAXS measurement we cannot explain the different mobility in PDPP1- and PDPP2-based FETs. Some studies reveal that the noncrystalline region in a polymer thin film determined the charge transport compared to the crystalline region with well-aligned  $\pi$ -stacking microstructure. In the noncrystal region, partially short-range intermolecular aggregation will be helpful for charge hopping via polymer chains, which can explain some unusual high mobility in amorphous conjugated polymers.<sup>50,51</sup> Compared to the random copolymer PDPP2, the asymmetric PDPP1 may have better aggregation in noncrystalline regions so as to provide higher mobility. Unfortunately, we have no further evidence and technique to confirm this speculation.

**Polymer Solar Cells.** PSCs based on the polymers as donor and a fullerene derivative phenyl- $\text{C}_{71}$ -butyric acid methyl ester

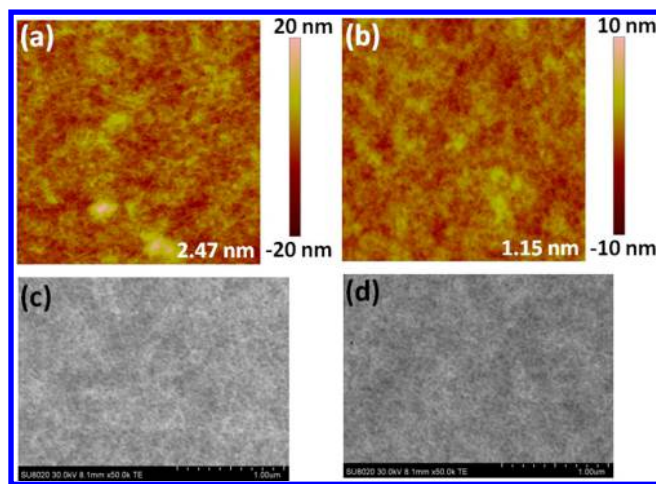
**Table 3.** Characteristics of Optimized Polymer:[70]PCBM (1:2) Cells

| polymer | solvent                            | thickness (nm) | $J_{sc}^a$ ( $\text{mA cm}^{-2}$ ) | $V_{oc}$ (V) | FF   | PCE <sup>a</sup> (%) | $E_{loss}^b$ (eV) |
|---------|------------------------------------|----------------|------------------------------------|--------------|------|----------------------|-------------------|
| PDPP1   | $\text{CHCl}_3/\text{DIO}$ (2.5%)  | 75             | 12.0                               | 0.76         | 0.65 | 5.9                  | 0.69              |
| PDPP2   | $\text{CHCl}_3/\text{o-DCB}$ (10%) | 90             | 13.7                               | 0.70         | 0.59 | 5.7                  | 0.73              |

<sup>a</sup>EQE spectrum was used to calculate  $J_{sc}$  with the AM1.5G spectrum. <sup>b</sup> $E_{loss} = E_g - eV_{oc}$ .



**Figure 4.** (a)  $J$ - $V$  plots in the dark (dashed lines) and under white light illumination (solid lines). (b) EQE of the optimized polymer:[70]PCBM solar cells. (c) Fraction of photons absorbed in the photoactive layers (75 and 90 nm for PDPP1- and PDPP2-based cells). Average IQE for PDPP1- and PDPP2-based cells can be calculated as 0.72 and 0.81. (d) Maximum EQE within the polymer absorption band vs the energy loss. Lines are guides to the eye.



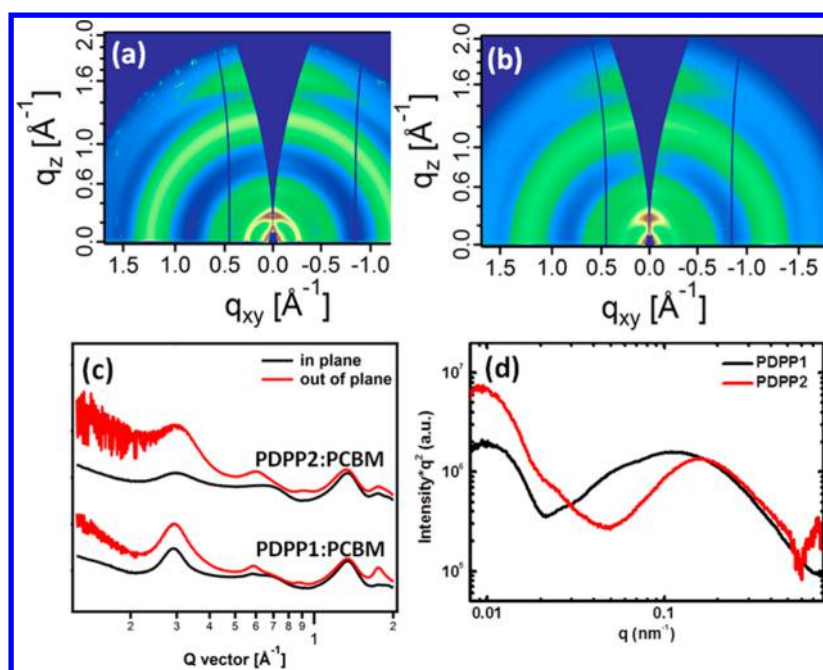
**Figure 5.** (a and b) AFM height images ( $3 \times 3 \mu\text{m}^2$ ) and (c and d) TEM images of the polymer:[70]PCBM (1:2) thin films: (a and c) PDPP1; (b and d) PDPP2. RMS roughness is 2.47 and 1.15 nm for a and b.

([70]PCBM) as electron acceptor were prepared. The solar cells use an inverted configuration with ITO/ZnO and MoO<sub>3</sub>/Ag as electron and hole transport electrode. The photoactive layers were solution processed from CHCl<sub>3</sub> solution, in which the additive, donor/acceptor ratio, and thickness were carefully optimized, as summarized in Tables S3–S6.

Asymmetric polymer PDPP1 has the best PCE of 5.9% together with a short-circuit current density ( $J_{sc}$ ) of 12.0 mA

cm<sup>-2</sup>, open-circuit voltage ( $V_{oc}$ ) of 0.76 V, and fill factor (FF) of 0.65. The random copolymer PDPP2 has a PCE of 5.7% with a high  $J_{sc}$  of 13.7 mA cm<sup>-2</sup>, a relatively low  $V_{oc}$  of 0.70, and a FF of 0.59. The  $V_{oc}$ s of PDPP1 and PDPP2 lie between the solar cells based on PDPP4T ( $V_{oc}$  of 0.64 V)<sup>48</sup> and PDPP2Tz2T ( $V_{oc}$  of 0.92 V),<sup>23</sup> resulting in a high energy loss ( $E_{loss}$ ) of 0.69 and 0.73 eV (Table 3). The high  $J_{sc}$  of PDPP2 is also consistent with the high external quantum efficiency (EQE) with the maximum EQE above 0.5, while PDPP1-based cells have a relatively low EQE with a maximum EQE of 0.48. We also measure the fraction of absorption photons in blended thin films based on PDPP1 and PDPP2 (Figure 4c), indicating that both thin films have similar absorption. By using the simulated  $J_{sc}$  as shown in Figure S7a we can calculate the average internal quantum efficiencies (IQE) as 0.72 and 0.81 for PDPP1- and PDPP2-based cells. This is consistent with the EQE results. It should be noted that when we calculate the IQE vs wavelength, an unusual spectral response between 550 and 700 nm for PDPP2:PCBM thin film was observed (Figure S7b), which may be due to strong light scattering in this film.

The relation between  $E_{loss}$  and EQE based on PDPP1, PDPP2, and their analogs PDPP4T and PDPP2Tz2T is analyzed, as shown in Figure 4d. A clear trend that high EQE is obtained with increased  $E_{loss}$  can be observed in the range from 0.55 and 0.80 eV. This is similar to the previous observation in DPP polymer solar cells.<sup>52</sup> However, this is a passive result since high EQE at low  $E_{loss}$  is of paramount importance for efficient solar cells.<sup>53</sup> Therefore, we intend to study the microphase separation in PDPP1- and PDPP2-based



**Figure 6.** (a and b) 2D-GIWAXS images of the polymer:PCBM thin films. (c) Out-of-plane and in-plane cuts. (d) R-SoXS scattering profiles at 284.2 eV of the polymers blended with PCBM. (a) PDPP1 and (b) PDPP2. Fabrication for the blended thin films is summarized at Table 3.

**Table 4. Crystallographic Parameters of the Polymer:PCBM Thin Films<sup>a</sup>**

|            | (100)    |              |               | (010)    |              |               | domain size (nm) | relative domain purity |
|------------|----------|--------------|---------------|----------|--------------|---------------|------------------|------------------------|
|            | $d$ (nm) | CL (IP) (nm) | CL (OOP) (nm) | $d$ (nm) | CL (IP) (nm) | CL (OOP) (nm) |                  |                        |
| PDPP1:PCBM | 2.1      | 12.6         | 11.6          | 0.36     | 0.8          | 4.3           | 62 and 27        | 1                      |
| PDPP2:PCBM | 2.1      | 7.1          | 7.7           | 0.36     | 3.2          | 2.9           | 20               | 1                      |

<sup>a</sup>OOP: out-of-plane. IP: in-plane. CL: coherence length.

photoactive layers and try to find out if it is possible to further enhance the EQE in solar cells.

We study the microphase separation of blended thin films by AFM and transmission electron microscopy (TEM) images. The fibrillar structures on the surface of PDPP1:PCBM thin films can be clearly observed (Figure 5a and 5b), which is further confirmed by TEM images. PDPP2-based thin films also show fiber-like structures, but the diameter of the fiber is smaller than that in PDPP1-based thin films. Large fibrillar structures can provide a separate channel for charge transport, explaining the high FF in PDPP1-based cells. However, this also has an adverse effect on exciton diffusion into the donor/acceptor interface due to the short lifetime of exciton, resulting in low photocurrent. A similar effect has also been observed in the literature.<sup>54</sup>

2D-GIWAXS and resonant soft X-ray scattering (R-SoXS) were further used to study the microstructure of blended thin films, as shown in Figure 6. Incorporating PCBM into the thin films, the crystal process of PDPP1 and PDPP2 was disturbed. Different from the “edge-on” orientation, PDPP1 and PDPP2 in blended thin films exhibit mixed orientation with “edge-on” and “face-on” arrangements. The CL of the lamellar and  $\pi$ - $\pi$  stacking is also calculated as shown in Table 4. PDPP1:PCBM films have a large CL of lamellar stacking of alkyl side chains, which is similar to the large fibrillar structures in TEM images. We also observe that PDPP1-based films show  $\pi$ - $\pi$  stacking in the out-of-plane direction with a CL of 4.3 nm, while the CL is 0.8 nm in the in-plane direction. For comparison, PDPP2:PCBM films show a similar CL of 3.2 and 2.9 nm in

the two directions. This indicates that PDPP1 in blended thin films has a more “face-on” constituent, which will be helpful for charge transport. R-SoXS measurement can further study the noncrystalline region of blended thin films, as shown in Figure 6d. Although both blended thin films have a similar domain purity, PDPP1:PCBM films have much a higher domain size of 62 and 27 nm with two peaks, while the domain size of PDPP2:PCBM films is 20 nm. TEM, 2D-GIWAXS, and R-SoXS results confirm that PDPP1 has a large domain size in blended thin films, which is not helpful for exciton diffusion processes. Therefore, we speculate that by further improving the microphase separation of the PDPP1:PCBM system, such as via tuning the chemical structures, enhancing the molecular weight, or optimizing the device fabrication condition, PDPP1-based solar cells can achieve better PCEs via enhancing EQE.

## CONCLUSION

In conclusion, an asymmetric DPP polymer flanked with thienyl and thiazoyl linkers was explored for application in organic electronic devices, in which a random copolymer was developed for comparison. The asymmetric DPP polymer shows similar absorption spectra as random copolymer but has deep-lying energy levels. The asymmetric DPP polymers show a high mobility of  $3.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  in FETs, while the random copolymer exhibits a relatively low mobility of  $0.32 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . Although the two polymers provide similar PCEs in solar cells, the asymmetric polymer shows a high FF of 0.66 with a low  $J_{sc}$ . The finely tuned energy levels of symmetric, asymmetric, and random polymers also provide us the opportunity to study the

relation between  $E_{\text{loss}}$  and quantum efficiency. Further investigation reveals that both asymmetric and random polymers have good crystalline properties in pure and blended thin films, but the asymmetric polymer has a large domain size in blended thin films, explaining the relatively low photocurrent. The results indicate that our design by incorporating different aromatic linkers into the polymer backbone is an efficient method to adjust the energy levels and provide interesting properties in devices.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b06967.

Materials and measurements, synthesis of the monomers and polymers, GPC, CV of PDPP4T and PDPP2Tz2T, DFT calculations, FETs, solar cells results, fraction of photons absorbed in the photoactive layers, and NMR spectra (PDF)

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### Notes

The authors declare no competing financial interest.

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