



Letter

Enhancing the performance of non-fullerene solar cells with polymer acceptors containing large-sized aromatic units



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ABSTRACT

In this work, we develop four diketopyrrolopyrrole-based polymer acceptors for application in polymer-polymer solar cells. The polymer acceptors contain different-sized aromatic units, from small thiophene to benzodithiophene and large alkylthio-benzodithiophene units. Although the polymer acceptor with large-sized groups shows small LUMO offset and low energy loss when blended with the donor polymer PTB7-Th, the corresponding solar cells can achieve a high power conversion efficiency (PCE) of 3.1% due to high photocurrent. In contrast, the polymer acceptor with small thiophene units only provides a low PCE of 0.14% in solar cells. These results indicate that polymer acceptors with large-sized aromatic units can be potentially used into high performance non-fullerene solar cells.

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Since poly(phenylene vinylene)s based donor/acceptor heterojunction solar cells were reported at 1995 [1,2], polymer-polymer solar cells that use conjugated polymers both as electron donor and electron acceptor have been intensively studied in the last decades [3–5]. The power conversion efficiencies (PCEs) over 8% have been achieved, partially due to the vast amount of polymer donors and acceptors developed in recent years [6–10]. The PCEs are still relatively low compared to fullerene-based [11] or non-fullerene small molecules-based solar cells with PCEs around 12% [10,12–17], remaining much room to be improved. Conjugated polymers with long conjugated backbone show structural complexity due to the strong intra- and inter-molecular interaction. Therefore, bulk-heterojunction (BHJ) systems based on binary conjugated polymers show complicate micro-phase separation that relates to charge generation in solar cells [18]. It is a challenging task to design conjugated polymer acceptors in order to understand

the relation between chemical structures and BHJ morphology, consequently realizing high performance polymer-polymer solar cells.

Conjugated polymers with different-sized alternating building blocks, such as small thiophene, medium benzothiophene and large benzodithiophene (BDT), exhibit distinct photovoltaic performance due to their aggregated properties. For example, a diketopyrrolopyrrole (DPP) based conjugated polymer containing BDT units show low solubility compared to its analogical polymer copolymerized with thiophene [19]. As a result, DPP-BDT based polymer as electron donor was found to form small fibrillar structures (diameter < 10 nm) when blended with a fullerene derivative, resulting in a PCE of 6.9% in solar cells due to efficient exciton diffusion into the interface of donor/acceptor. In contrast, thiophene-contained polymer exhibited large fibrillar structures (diameter ~ 30 nm) in blended thin films and showed PCEs below 5% in solar cells. The size of aromatic units can be further extended by using two-dimensional strategy, which has been widely used to design conjugated polymers as electron donor [20,21]. By attaching alkylthiophene units onto BDT, BDT-polymers show the advantage of aligned energy levels, broad absorption and orientated self-assembly (such as ordered π - π stacking), and hence provide high

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photocurrent and PCEs in solar cells [17,20,22–25]. The two-dimensional structures were also used to design non-fullerene small molecules, such as a well-known acceptor ITIC developed by Zhan et al. with a large indacenodithiophene central unit [26]. This ensured ITIC to have large π -conjugated units for charge transportation and highly steric hindrance to prevent self-aggregation, partially explaining high performance ITIC-based solar cells [15]. From these aspects, we speculate that conjugated polymer acceptors bearing large copolymerized groups can improve the device performance in polymer-polymer solar cells, but they have been rarely reported [27,28].

In this work, we are interested with exploring conjugated polymer acceptors containing different-sized aromatic units and studying their effect on the photovoltaic performance. The polymer acceptors consist of DPP as core and electron-negative thiazole as bridges in order to reduce the frontier energy levels [29]. The aromatic units, from thiophene to BDT, alkylthiophene-BDT and alkylthiophene-BDT [30,31], were incorporated into the polymers, as shown in Fig. 1. These polymers perform near-infrared absorption spectra and low-lying energy levels. The polymers as electron acceptor were applied into polymer solar cells, in which P1 showed the lowest PCEs of 0.14%, but P2, P3 and P4 with large-sized aromatic units exhibited PCEs of 1.1%, 2.4% and 3.1%. The results confirm that the design by introducing large aromatic units into polymer acceptors is an efficient way to improve the photovoltaic performance of polymer-polymer solar cells.

The DPP-polymers P1-P4 were synthesized via Stille polymerization by using $Pd_2(dbu)_3/Ph_3P$ as catalyst and toluene/DMF as solvent. P1 and P2 were prepared according to the literature [32,33]. Synthetic procedures of P3 and P4 were shown in Scheme S1, Supporting Information (SI). Thiazole-bridged DPP monomers bear different side chains, such as 2'-butyloctyl (BO) for P3, 2'-octyldodecyl for P1 and P4 and 2'-decyltetradecyl for P2. It is worth noting that when using short BO or 2'-hexyldecyl side chains, the polymer P4 is completely insoluble in $CHCl_3$ or chlorobenzene, indicating that P4 with alkylthiol groups has strong aggregation tendency. All the polymers showed good solubility in $CHCl_3$. The molecular weight of the polymers was determined by using gel permeation chromatography (GPC) measurement under a high temperature of 140 °C, as shown in Figs. S1–2 (SI) and the data was summarized at Table 1. The polymers showed high weight average molecular weight (M_w) of 169–324 kg mol^{−1}, in which the polydispersity index (PDI) of P3 and P4 was relatively high (7.5 and 5.8). This is possibly due to small molecular weight fractions (Fig. S1-2, SI).

Optical absorption spectra of P1-P4 and the donor polymer PTB7-Th [34] in thin films were shown in Fig. 2 and the data was summarized at Table 1. These polymers performed near-infrared absorption with optical band gap (E_g) of 1.44–1.61 eV. The polymer P1 with small thiophene unit exhibited broad absorption in the range of 300–900 nm, while P2 – P4 with large-sized aromatic units performed blue-shifted absorption.

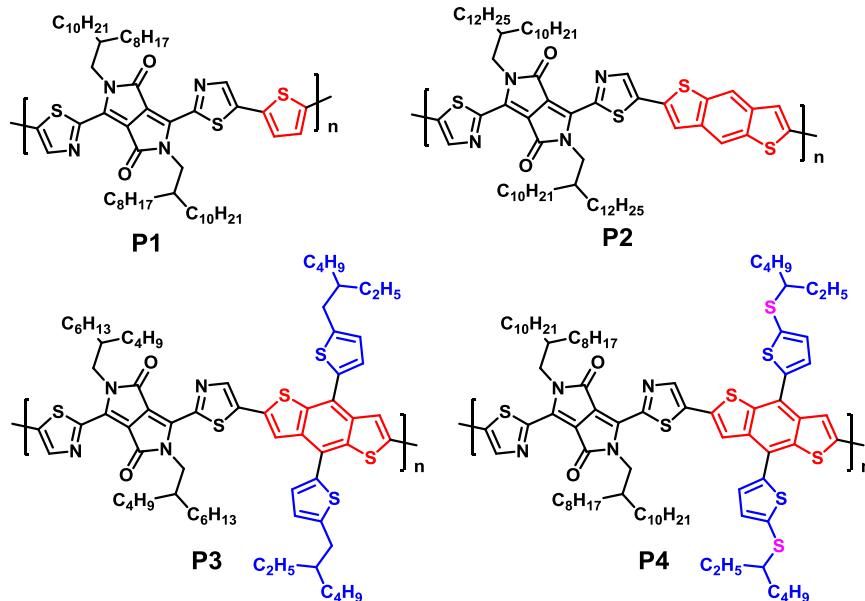


Fig. 1. Chemical structures of the conjugated polymer acceptors P1 – P4 in this work.

Table 1

Optical and electrochemical properties of the DPP polymers.

Polymer	M_w^a (kg mol ^{−1})	PDI	E_g^{film} (eV)	E_{HOMO}^b (eV)	E_{LUMO}^c (eV)	ΔE_{HOMO}^d (eV)	ΔE_{LUMO}^e (eV)
PTB7-Th	—	—	1.61	−5.40	−3.97	—	—
P1	207	2.8	1.44	−5.70	−4.26	0.30	0.47
P2	324	3.8	1.53	−5.71	−4.18	0.31	0.39
P3	256	7.5	1.53	−5.69	−4.16	0.29	0.37
P4	169	5.8	1.58	−5.67	−4.09	0.27	0.3

^a Determined with GPC at 140 °C using *o*-DCB as the eluent.

^b Determined using a work function value of −4.8 eV for Fc/Fc^+ .

^c Determined as $E_{\text{HOMO}} + E_g^{\text{film}}$.

^d $\Delta E_{\text{HOMO}} = E_{\text{HOMO}}(\text{PTB7-Th}) - E_{\text{HOMO}}(\text{polymer})$.

^e $\Delta E_{\text{LUMO}} = E_{\text{LUMO}}(\text{PTB7-Th}) - E_{\text{LUMO}}(\text{polymer})$.

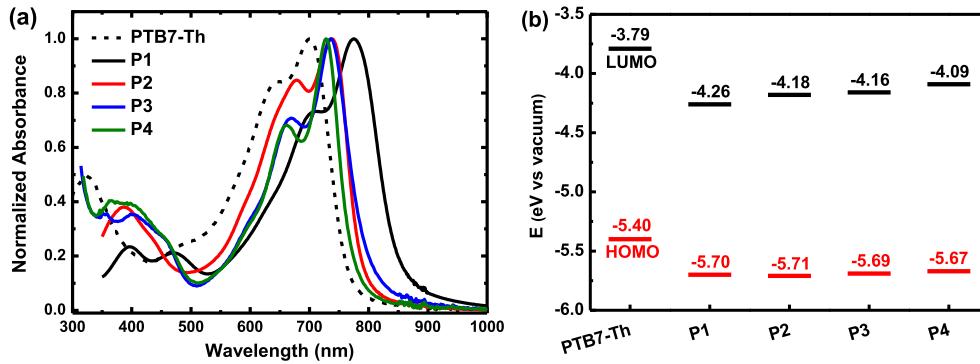


Fig. 2. (a) Absorption spectra and (b) energy levels of the thiazole-DPP polymers and PTB7-Th in solid state films.

The frontier energy levels of PTB7-Th and P1-P4 were determined by cyclic voltammetry (CV) measurements, as shown in Fig. S3 (SI), Fig. 2b and Table 1. The highest occupied molecular orbital (HOMO) levels were calculated from the oxidation potential (E_{ox}) of $I-V$ plots (Figs. S3 and SI) and the lowest unoccupied molecular orbital (LUMO) levels were calculated by using $E_{\text{HOMO}} + E_g$ (Table 1). The polymer P1 showed deep HOMO and LUMO levels of -5.70 eV and -4.26 eV, while the energy levels of P2-P4 were shifted to high-lying positions. The polymer P4 with electron-donating alkylthio-thiophene units had HOMO and LUMO levels of -5.67 eV and -4.09 eV. The energy offset between PTB7-Th and DPP-polymer acceptor was also calculated, in which HOMO offsets (ΔE_{HOMO}) were around 0.3 eV and LUMO offsets (ΔE_{LUMO}) were 0.3 – 0.47 eV. Interestingly, PTB7-Th:P1 has the highest LUMO offset of 0.47 eV, which is reduced to 0.3 eV for PTB7-Th:P4 (Table 1). Since it was believed that ΔE_{LUMO} is the driving force for exciton dissociation into free charges, the high ΔE_{LUMO} in PTB7-Th:P1 was presumably helpful for charge separation and improving performance [35]. However, P1-P4 as electron acceptor performed reversible photovoltaic performance, as discussed in the following section.

The DPP-polymer acceptors P1-P4 with PTB7-Th as electro donor were applied into BHJ solar cells by using inverted device configuration. The photoactive layers were solution-processed from CHCl_3 solution, in which the amount of additive 1-chloronaphthalene (1-CN), the ratio of donor to acceptor and the thickness were carefully optimized. The detailed device fabrication condition, photovoltaic performance and the statistic parameters were summarized in SI, Tables S1–S8. The optimized device performance was shown in Fig. 3 and their photovoltaic parameters were summarized at Table 2.

Table 2

Solar cell parameters of optimized inverted solar cells of PTB7-Th:Thiazole-DPP polymer.

Acceptor	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)	PCE ^a (%)	E_{loss} ^b (eV)
P1 ^c	0.66	0.71	0.29	0.14	—	0.73
P2 ^d	3.2	0.95	0.36	1.1	0.88	0.58
P3 ^e	6.4	0.99	0.37	2.4	2.2	0.54
P4 ^f	7.5	0.94	0.45	3.1	3.0	0.64

^a J_{sc} calibrated from EQE spectrum for PCEs.

^b $E_{\text{loss}} = E_g - qV_{\text{oc}}$.

^c PTB7:P1 with ratio of 2:1 was spin-coated from CHCl_3 :3% 1-CN with thickness of 70 nm.

^d PTB7:P2 with ratio of 1:1 was spin-coated from CHCl_3 :3% 1-CN with thickness of 90 nm.

^e PTB7:P3 with ratio of 1:1 was spin-coated from CHCl_3 with thickness of 90 nm.

^f PTB7:P4 with ratio of 3:1 was spin-coated from CHCl_3 :3% 1-CN with thickness of 60 nm.

PTB7-Th:P1 cells with the highest LUMO offset of 0.47 eV exhibit the lowest PCE of 0.14% due to low short-circuit current density (J_{sc}) of 0.66 mA cm^{-2} , a low open-circuit voltage (V_{oc}) of 0.71 and a low fill factor (FF) of 0.29 . The polymer P2 with BDT units showed an enhanced PCE of 1.1% with $J_{\text{sc}} = 3.2 \text{ mA cm}^{-2}$, a high V_{oc} of 0.95 and FF of 0.36 . The PCE was further increased to 2.4% by using the polymer acceptor P3 with alkylthiophene-BDT, with $J_{\text{sc}} = 6.4 \text{ mA cm}^{-2}$, $V_{\text{oc}} = 0.99$ and FF = 0.37 . The highest PCE of 3.1% could be obtained in PTB7-Th:P4 solar cells due to high $J_{\text{sc}} = 7.5 \text{ mA cm}^{-2}$ and a high FF of 0.45 .

The distinct $J_{\text{sc},\text{s}}$ in these cells can be reflected by their external quantum efficiencies (EQEs) (Fig. 3b). EQE of PTB7-Th:P1 cells is too low to be detected by the instrument. P2-P4 based cells showed photo-response from 300 nm to 800 nm, in which the maximum

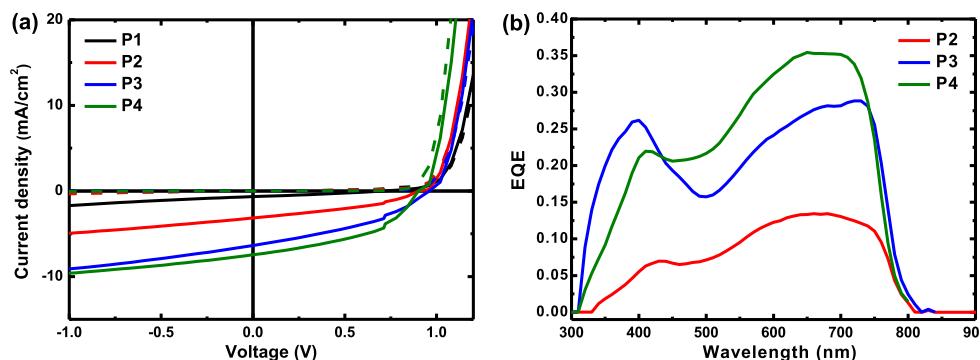


Fig. 3. (a) $J-V$ characteristics in dark (dashed lines) and under simulated AM1.5G illumination (solid lines) of optimized solar cells of PTB7-Th with Thiazole-DPP polymer P1-P4. (b) EQE of the same devices. EQE of PTB7-Th:P1 cells was too small to be detected.

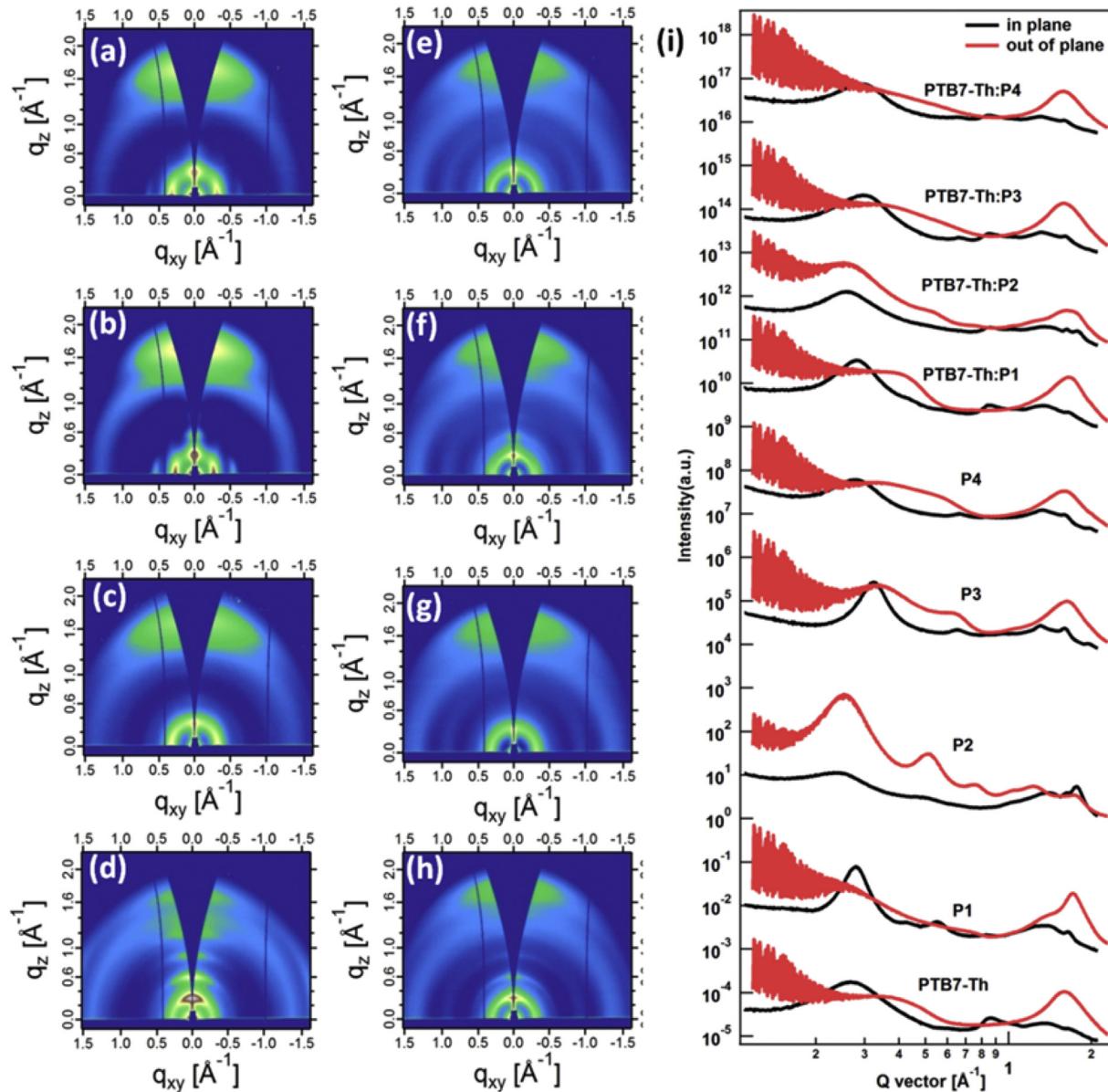


Fig. 4. GIWAXS images of (a–d) the pure polymers and (e–h) blended thin films. (a,e) P1, (b,f) P2, (c,g) P3 and (d,h) P4. (i) the in plane and out of plane cuts of the corresponding GIWAXS patterns. The solution-processed condition for the pure and blended thin films was identical with that of solar cells as summarized at Table 2.

EQE was enhanced from 0.1 to 0.25 and 0.35 in these cells. In addition, V_{oc} s of the cells are consistent with the LUMO levels of the acceptor, in which deep LUMO levels (such as P1) contributed to low V_{oc} (Note: in PTB7-Th:P4 cells, V_{oc} has small variation concerning its highest LUMO level) [36]. The energy loss (E_{loss}) of the cells by using E_g and eV_{oc} were also calculated, as summarized at Table 2 [33]. PTB7-Th:P1 cells had E_{loss} of 0.73 eV, which reduced to 0.58 eV, 0.54 eV and 0.64 eV in P2–P4 based cells. In general, low E_{loss} means low driving force for charge separation, causing poor solar cells performance. However, we observed high PCEs with low E_{loss} in these polymer-polymer solar cells. Similar trend can also be observed in other solar cells when using a wide band gap polymer PBDB-T [37] (Figs. S4 and SI) as electron donor, as summarized in Fig. S5 and Table S9. P1 and P2 based solar cells show poor PCEs, while PBDB-T:P3 exhibited a PCE of 0.60%. Solar cells based on PBDB-T:P4 provided the highest PCEs of 1.88%.

The unusually high PCEs under small LUMO offset and E_{loss} in these polymer-polymer solar cells intrigue us to study the charge

transport and morphology in binary polymer systems. We apply space charge limited current (SCLC) measurement to calculate the hole and electron mobilities in solar cells, as shown in Fig. S6 and Tables S10 and SI. The hole and electron mobilities were firstly dropped from P1 to P2 based solar cells, and then increased in P3 and P4 based solar cells. The ratio of hole to electron mobilities showed the trend of enhancement from 1.3 for P1 based cells to 25.1 for P4 based cells. However, this is inconsistent with the improved J_{sc} and FF in these cells, since it has been recognized that high ratio of hole to electron mobilities is detrimental for charge separation due to charge recombination. The surface of blended thin films was investigated by atomic force microscopy (AFM), but they didn't show distinct micro-phase separation on the surface (also with small variation in roughness, as shown in Figs. S7 and SI). Finally, we performed grazing incidence wide-angle X-ray scattering (GIWAXS) to study the crystalline properties of the pure polymer and blended thin films, as shown in Fig. 4 and Figs. S8 and SI. PTB7-Th performed typical “face-on” orientation with (100)

diffraction peak at in-plane direction and (010) diffraction peak at out-of-plane direction (Figs. S8 and SI). Similarly, P1, P3 and P4 also desired “face-on” orientation, but P2 showed typical “edge-on” orientation with (h00) diffraction peak at out-of-plane direction and (010) diffraction peak at in-plane direction. The blended thin films of PTB7-Th:DPP-polymer showed similar “face-on” orientation with PTB7-Th. The diffraction patterns for all these blended thin films seem to be identical to their pure donor and acceptor (except P2), so it is difficult to correlate the crystalline properties from GIWAXS to the device performance in solar cells. The GIWAXS results also reveal that PTB7-Th and DPP-polymers have low miscibility (as confirmed by the similar crystal structure in pure and blended thin films), resulting in inefficient exciton diffusion and poor performance compared to other polymer acceptors, such as naphthalene diimide [38]. Therefore, we speculate that designing new DPP-polymer acceptors with large aromatic units will be a possible way to enhance the miscibility of polymer-polymer systems.

In conclusion, four thiazole-based DPP-polymers were developed as electron acceptors for polymer-polymer solar cells, in which aromatic units with different size, such as small thiophene and large two-dimensional BDT, were selected as copolymerized units. The polymer acceptors with large aromatic units show small LUMO offset and low energy loss when blended with PTB7-Th as electron donor, but PCEs can be enhanced to 3.1%. In contrast, the polymer acceptor with small thiophene only provided a very low PCE of 0.14% in solar cells. The reason for high PCEs based on large-sized DPP polymers with small LUMO offset is still unclear, although some advanced techniques such as SCLC, AFM and GIWAXS have been applied to study the morphology of blended thin films. Our results reveal that large-sized polymer acceptors can be potentially used to realize high performance polymer-polymer solar cells.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.orgel.2017.05.011>.

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