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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.

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 alkylthiothiophene-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 untis 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 $Pd_2(dba)_3/PPh_3$ 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.

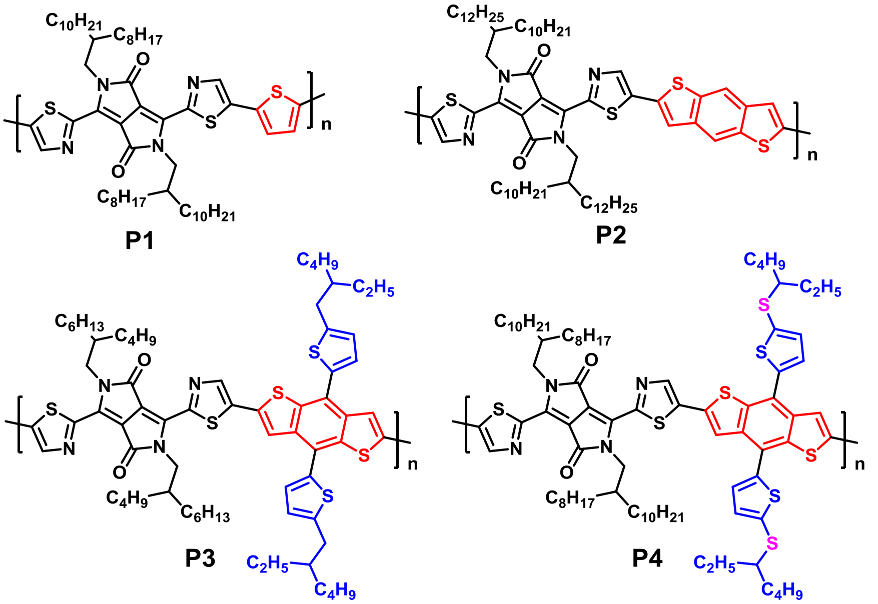

Fig. 1. Chemical structures of the conjugated polymer acceptors **P1** – **P4** in this work.

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 $E_{HOMO} + E_g^{film}$.
[d] $\Delta E_{HOMO} = E_{HOMO}$ (PTB7-Th) − E_{HOMO} (polymer).
[e] $\Delta E_{LUMO} = E_{LUMO}$ (PTB7-Th) − E_{LUMO} (polymer).