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# A lactam building block for efficient polymer solar cells†

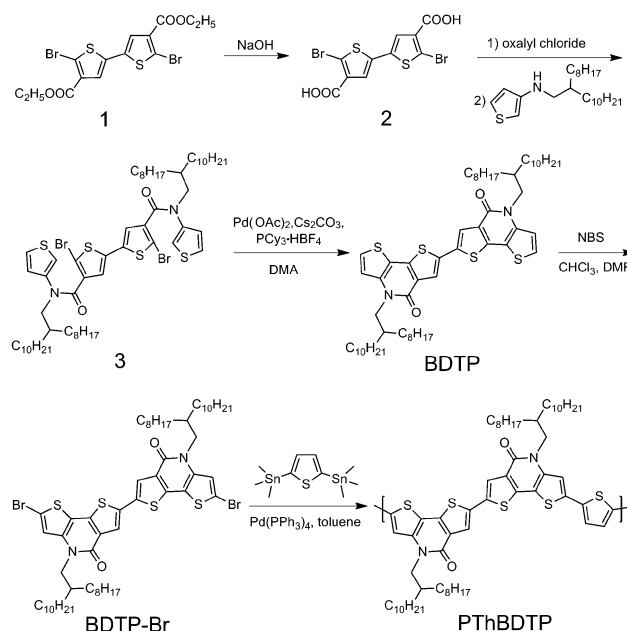
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A new lactam acceptor unit, [7,7'-bidithieno[3,2-*b*:2',3'-*d*]pyridine]-5,5'-(4*H*,4'*H*)-dione (BDTP), was developed. A D–A copolymer PThBDTP using BDTP as the acceptor unit and thiophene as the donor unit was synthesized. PThBDTP:PC<sub>71</sub>BM solar cells gave a decent PCE of 9.13% with a *V*<sub>oc</sub> of 0.96 V. PThBDTP is one of the few D–A copolymers with PCEs of over 9%.

Polymer solar cells (PSCs) have many advantages, such as solution processing, flexibility and lightweight.<sup>1</sup> Power conversion efficiencies (PCEs) for a single PSC have reached 10.8%,<sup>2</sup> shedding light on its potential for future commercialization. The D–A structure is a general structure employed for developing highly efficient donor materials, which contain alternating electron donating (D) and electron-accepting (A) units in the backbone. Many efforts have been devoted to design high-performance D and A units. Some electron-accepting units, such as diketopyrrolopyrrole,<sup>3</sup> thieno[3,4-*c*]pyrrole-4,6-dione,<sup>4</sup> isoindigo,<sup>5</sup> and bithiophene imide,<sup>6</sup> have been used and the corresponding D–A copolymers gave PCEs of over 8%. Imide and lactam moieties show unique functions: (1) they possess strong electron-withdrawing ability for tuning energy levels and bandgaps; (2) alkyl side chains can be introduced facilely to endow monomers and polymers with good solubility; (3) imide and lactam units can fuse thiophene rings to make symmetrical acceptor units with two free  $\alpha$  positions on thiophenes, which can be brominated facilely to give monomers.<sup>7</sup> Recently, we developed a series of D–A copolymers using a pentacyclic acceptor unit, thieno[2',3':5,6]-pyrido[3,4-*g*]thieno[3,2-*c*]isoquinoline-5,11(4*H*,10*H*)-dione (TPTI).<sup>8</sup>

PThTPTI/PC<sub>71</sub>BM solar cells produced a PCE of 7.8%.<sup>8a</sup> Being inspired by the promising results, we designed a new lactam acceptor unit, [7,7'-bidithieno[3,2-*b*:2',3'-*d*]pyridine]-5,5'-(4*H*,4'*H*)-dione (BDTP) (Scheme 1), and based on this A unit a new D–A copolymer PThBDTP was synthesized. Optimized PThBDTP/PC<sub>71</sub>BM solar cells gave a decent PCE of 9.13%. The thermal, optical, and electrochemical properties, mobility, crystallinity, molecular stacking mode and morphology of the active layer were studied.

BDTP possesses two lactam moieties and four thiophene rings, and can be regarded as a derivative of TPTI by replacing benzene with 2,2'-bithiophene. 2,2'-Bithiophene has a rigid and coplanar structure and can endow BDTP with high hole mobility.<sup>9</sup> However, introducing a bithiophene unit into the polymer backbone reduces the solubility.<sup>10</sup> By introducing two octyldodecyl side chains on nitrogen atoms of BDTP, the target



Scheme 1 Synthetic route to PThBDTP.

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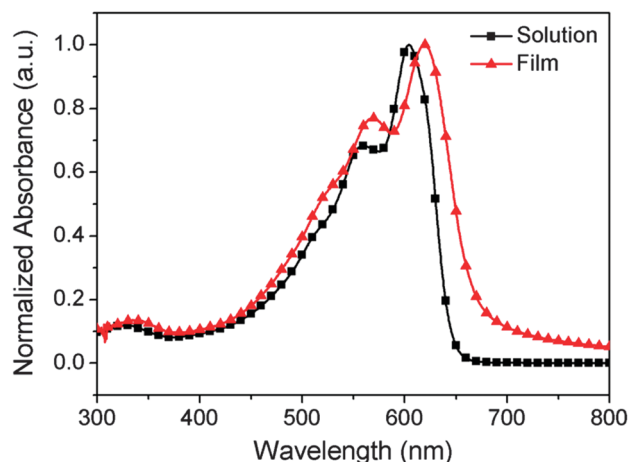


Fig. 1 Absorption spectra of PThBDTP in chloroform and as a film.

copolymer PThBDTP shows good solubility in common organic solvents, such as toluene, chloroform, chlorobenzene, and *o*-dichlorobenzene (ODCB). The synthetic routes for the monomer and PThBDTP are illustrated in Scheme 1. The starting material diethyl 5,5'-dibromo-[2,2'-bithiophene]-4,4'-dicarboxylate<sup>11</sup> was hydrolysed to obtain compound 2, which reacted with oxalyl chloride and *N*-(2-octyldodecyl)thiophen-3-amine successively to give compound 3 in 83% yield. BDTP was obtained by intramolecular coupling reaction using Pd(OAc)<sub>2</sub> as the catalyst in 56% yield. In the <sup>1</sup>H NMR spectrum, two double peaks of H on thiophenes certify the structure of BDTP (Fig. S1, ESI†). Bromination of BDTP afforded the monomer BDTP-Br in 62% yield. PThBDTP was synthesized *via* copolymerization of BDTP-Br with 2,5-bis(trimethylstannyl)thiophene through the Stille coupling reaction using Pd(PPh<sub>3</sub>)<sub>4</sub> as the catalyst. The copolymer was purified *via* Soxhlet extraction using methanol, hexane and chloroform as eluents successively, and the chloroform fraction was precipitated to obtain purple PThBDTP in 83% yield. The number-average molecular weight (*M*<sub>n</sub>) and the polydispersity index (PDI) of PThBDTP are 89.8 kDa and 2.94, respectively. PThBDTP shows excellent thermal stability with a *T*<sub>d</sub> of 439 °C (Fig. S3, ESI†).

PThBDTP shows two absorption peaks in solution and in the solid state (Fig. 1). The maximum absorption for PThBDTP solution and the film are located at 604 and 620 nm, respectively. The redshift results from better  $\pi$ - $\pi$  stacking in the solid state. The optical band gap of PThBDTP is 1.86 eV, which is calculated from the film absorption onset at 667 nm. A cyclic voltammogram of the polymer is shown in Fig. S4 (ESI†) and all potentials were corrected against the Fc/Fc<sup>+</sup> redox couple. The onset potentials for oxidation ( $E_{\text{ox}}^{\text{on}}$ ) and for reduction ( $E_{\text{red}}^{\text{on}}$ ) of PThBDTP are 0.72 and -2.06 V, respectively. The HOMO and LUMO energy levels for PThBDTP are -5.52 eV and -2.74 eV, respectively, according to the empirical formulae: HOMO =  $-(E_{\text{ox}}^{\text{on}} + 4.8)$  eV, LUMO =  $-(E_{\text{red}}^{\text{on}} + 4.8)$  eV.<sup>12</sup> The low HOMO energy level endows PThBDTP with good oxidation-resistance and provides solar cells with a high  $V_{\text{oc}}$ .<sup>7,13</sup>

Solar cells with a conventional structure of ITO/PEDOT:PSS/PThBDTP:PC<sub>61</sub>BM/Ca/Al were first investigated. The best devices were obtained after optimizations, having a D-A ratio of 1 : 1 (w/w),

Table 1 Performance data of PThBDTP/PCBM solar cells

| Cell type    | Acceptor            | $V_{\text{oc}}$ [V] | $J_{\text{sc}}$ [mA cm <sup>-2</sup> ] | FF [%] | PCE <sup>a</sup> [%] |
|--------------|---------------------|---------------------|--|--------|----------------------|
| Conventional | PC <sub>61</sub> BM | 0.96                | 10.76                                  | 61.0   | 6.30 (6.12)          |
|              | PC <sub>71</sub> BM | 0.98                | 11.56                                  | 70.1   | 7.94 (7.60)          |
| Inverted     | PC <sub>71</sub> BM | 0.96                | 12.59                                  | 75.5   | 9.13 (8.98)          |

<sup>a</sup> Data in parentheses stand for the average PCEs of 10 cells.

an active layer thickness of 150 nm and by adding 3 vol% 1,8-diiodooctane (DIO) into ODCB solution. A PCE of 6.30% was obtained with a  $V_{\text{oc}}$  of 0.96 V, a  $J_{\text{sc}}$  of 10.76 mA cm<sup>-2</sup>, and a FF of 61.0% (Table 1). In order to further improve the device performance, PC<sub>71</sub>BM was used. PC<sub>71</sub>BM has better absorption in the visible region because of its relatively low symmetry.<sup>14</sup> After optimizations, the best devices gave a PCE of 7.94% with an enhanced  $J_{\text{sc}}$  of 11.56 mA cm<sup>-2</sup> and a better FF of 70.1%. The external quantum efficiency (EQE) spectra suggest a higher photocurrent for PThBDTP/PC<sub>71</sub>BM cells.  $J_{\text{sc}}$  calculated from the EQE spectra is 11.06 mA cm<sup>-2</sup>, which is close to  $J_{\text{sc}}$  obtained from *J*-*V* measurements (Fig. 2).

The PThBDTP/PC<sub>71</sub>BM blend film with DIO has a RMS roughness of 1.06 nm, which is smoother than that of the film without DIO, which has a roughness of 1.75 nm (Fig. 3).

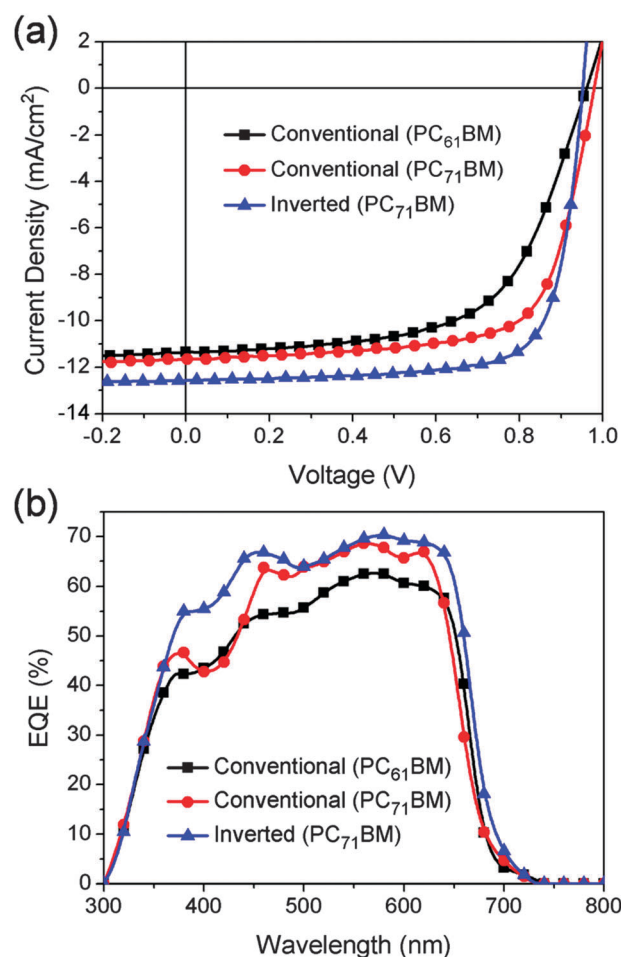


Fig. 2 *J*-*V* curves (a) and EQE spectra (b) of PThBDTP/PCBM solar cells.

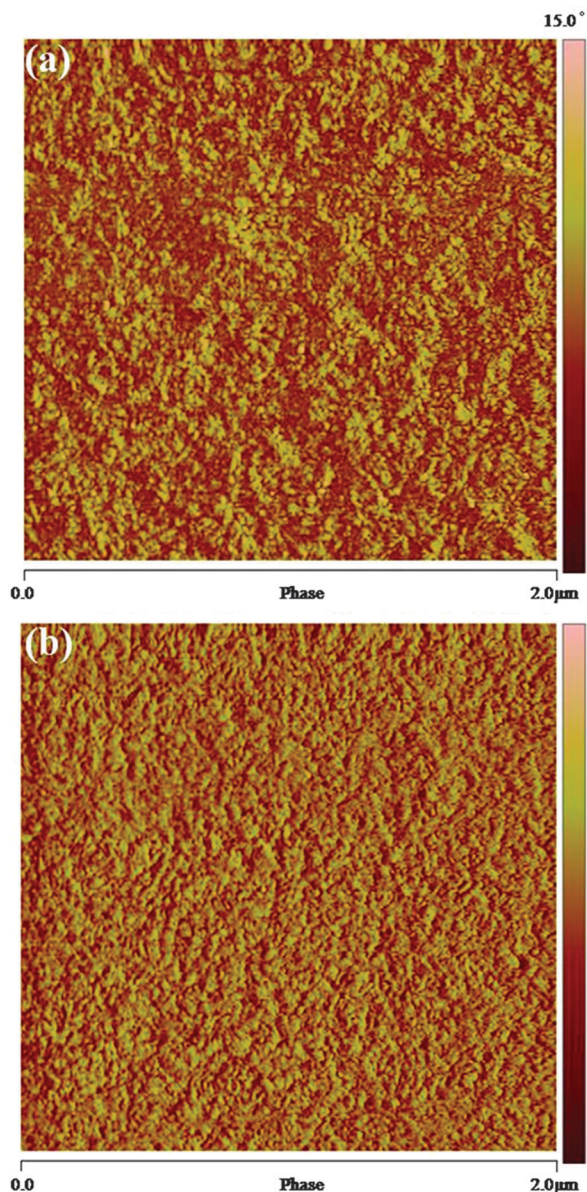


Fig. 3 AFM phase images of PThBDTP:PC<sub>71</sub>BM blend films. (a) without DIO; (b) with 3% DIO.

The distribution of two phases gets more even, producing more D/A interfaces for exciton dissociation. The diameter of typical earthworm-like domains is about 12 nm, which is comparable to the typical exciton diffusion lengths of 10–20 nm in organic semiconductors.<sup>15</sup> Hole and electron mobilities for PThBDTP/PC<sub>71</sub>BM blend films were evaluated using the space-charge limited current (SCLC) method (Fig. S6 and S7, ESI†). The hole mobilities of the blend film without or with DIO are  $2.24 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $1.61 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , respectively. The electron mobility increases from  $4.84 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  to  $1.41 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  after adding 3% DIO, getting closer to the hole mobility. The significantly enhanced electron mobility by adding DIO made charge carrier transport in the active layer more balanced, thus leading to higher  $J_{\text{sc}}$  and FF.<sup>8a</sup> DIO might inhibit PC<sub>71</sub>BM to form large and isolated aggregates,

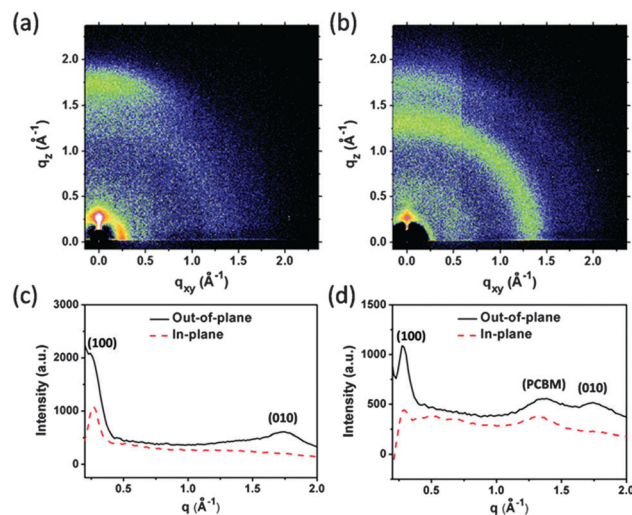


Fig. 4 Two-dimensional GIWAXS patterns of the pure PThBDTP film (a) and the PThBDTP:PC<sub>71</sub>BM blend film (b); GIWAXS out-of-plane and in-plane profiles of the pure PThBDTP film (c) and the PThBDTP:PC<sub>71</sub>BM blend film (d).

and promote the formation of a continuous 3D electron-transport network, which enhances electron mobility remarkably.

Inverted solar cells with a structure of ITO/ZnO/PThBDTP:PC<sub>71</sub>BM/MoO<sub>3</sub>/Ag were fabricated to further improve device performance. The optimized cells (D/A = 1 : 1.2) gave a PCE of 9.13% with a  $V_{\text{oc}}$  of 0.96 V, a  $J_{\text{sc}}$  of  $12.59 \text{ mA cm}^{-2}$ , and a FF of 75.5% (Fig. 2a). The inverted cells showed a higher EQE than the conventional cells, and EQE values are over 60% at 424–651 nm with a maximum of 70.4% (Fig. 2b). The EQE enhancement of the inverted cells mainly results from the higher transmittance of ZnO.<sup>16</sup> The integrated current for the inverted cell from the EQE spectrum is  $12.00 \text{ mA cm}^{-2}$ , which is consistent with the  $J_{\text{sc}}$  ( $12.59 \text{ mA cm}^{-2}$ ) from  $J$ - $V$  measurements. To further understand polymer chain packing, a GIWAXS study on pure polymer and PThBDTP/PC<sub>71</sub>BM blend films was performed. The peaks at  $q_{010} \approx 1.74 \text{ \AA}^{-1}$  (out-of-plane direction) for both pure and blend films are assigned to  $\pi$ - $\pi$  stacking (Fig. 4), which correspond to a  $3.61 \text{ \AA}$   $d$ -spacing. In the PThBDTP/PC<sub>71</sub>BM blend film, the face-on orientation and  $d_{\pi-\pi}$  of the polymer were maintained, and the active layer possesses decent hole mobility,<sup>17</sup> thus producing a high PCE.

In summary, a highly efficient D-A copolymer PThBDTP consisting of a new lactam unit BDTP as the acceptor unit and thiophene as the donor unit was developed. Conventional and inverted solar cells based on the PThBDTP:PC<sub>71</sub>BM blend gave decent PCEs up to 7.94% and 9.13%, respectively. An EQE of over 60% was obtained at the 424–651 nm region for the inverted cells. Further application of this high-performance D-A copolymer in different device configurations, such as tandem cells, to get a higher PCE is ongoing.

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