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A facilely synthesized lactam acceptor unit for high-performance polymer donors†

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An aromatic lactam acceptor unit, [2,2′-bidithieno[3,2-*b*:2′,3′-*d*]pyridine]-5,5′(4*H*,4′*H*)-dione (BDTP$_i$), was developed for making D–A copolymer donors. Two D–A copolymers, PThBDTP$_i$ and PSeBDTP$_i$, gave power conversion efficiencies (PCEs) of 8.11% and 6.50%, respectively, when using PC$_{71}$BM as the acceptor.

Polymer solar cells (PSCs) have attracted great interests due to the advantages of lightweight, flexibility and roll-to-roll fabrication.[1] The power conversion efficiencies (PCEs) for single-junction PSCs have exceeded 12%.[2] Developing donor–acceptor (D–A) copolymer donors is an effective way to obtain efficient solar cells.[3] Polycyclic aromatic building blocks are favorable for constructing high-performance D–A copolymers since the extended π-conjugation of these units can improve the light-harvesting capability and the hole mobility of the materials.[4] The tricyclic lactam unit, dithieno[3,2-*b*:2′,3′-*d*]pyridin-5(4*H*)-one (DTP), has emerged as a promising acceptor unit for D–A copolymers. Yu *et al.* reported the first DTP copolymer, which gave a PCE of 5.33%.[5] By copolymerizing DTP with BDTT and IDT units, Yang *et al.* obtained wide-bandgap D–A copolymers, which afforded PCEs of 6.84% and 7.33%, respectively.[6] By linking two DTPs *via* "C7" position, we obtained a lactam unit, BDTP (Fig. 1). The BDTP-based D–A copolymers gave decent PCEs up to 9.13%.[7] These results demonstrated the potential of DTP copolymers. Developing new DTP-based D–A copolymers is highly desirable. Here, we report a new lactam acceptor unit, BDTP$_i$, by linking two DTPs *via* "C2" position (Fig. 1). Different from the tedious synthesis of BDTP (8 steps from commercially available starting compounds), the synthesis of BDTP$_i$ is simplified (only 4 steps from starting compounds). Two BDTP$_i$-based copolymers, PThBDTP$_i$ and PSeBDTP$_i$, were prepared and used as the donor materials for PSCs. PThBDTP$_i$:PC$_{71}$BM solar cells gave a decent PCE of 8.11%.

The synthetic routes for BDTP$_i$ monomer and the copolymers are shown in Scheme 1. DTP was prepared according to literature.[6] The mono-bromination of DTP by NBS took place at "C7" rather than "C2", producing DTP-Br in 85% yield. The high regioselectivity was confirmed by heteronuclear multiple bond correlation (HMBC) spectrum of DTP-Br (Fig. S3†). The proton near bromine (7.63 ppm peak) correlates with the carbonyl carbon (157.57 ppm peak), thus ruling out "C2" bromination. The regioselective bromination implies that "C7" presents higher electron density. The resonance structure of DTP could make "C7" to possess negative charge. A Pd-catalyzed dehydrogenative dimerization linked two DTP-Br *via* "C2", producing BDTP$_i$ monomer in 31% yield.[8] Finally, the copolymerization of BDTP$_i$ monomer with 2,5-bis(trimethylstannyl)thiophene or 2,5-bis(trimethylstannyl)selenophene *via* Stille coupling gave PThBDTP$_i$ or PSeBDTP$_i$ in 97% and 88% yield, respectively. The number-average molecular weights (M_n) for PThBDTP$_i$ and PSeBDTP$_i$ are 46.3 kDa and 56.7 kDa, with PDI of 2.07 and 1.74, respectively. The decomposition temperature (T_d, 5% wt loss) for PThBDTP$_i$ and PSeBDTP$_i$ are 405 °C and 424 °C, respectively, indicating their good thermal stability.

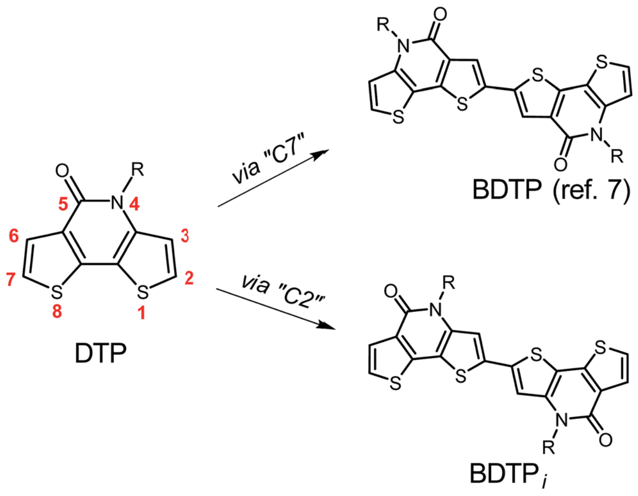

Fig. 1 Chemical structures for DTP, BDTP and BDTP$_i$.

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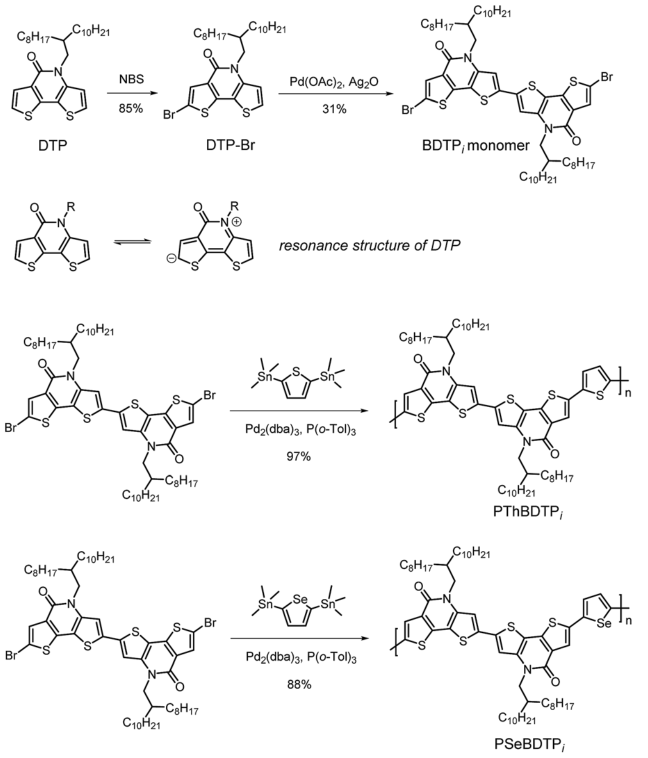

Scheme 1 Synthetic routes for BDTP$_i$ monomer and the copolymers.

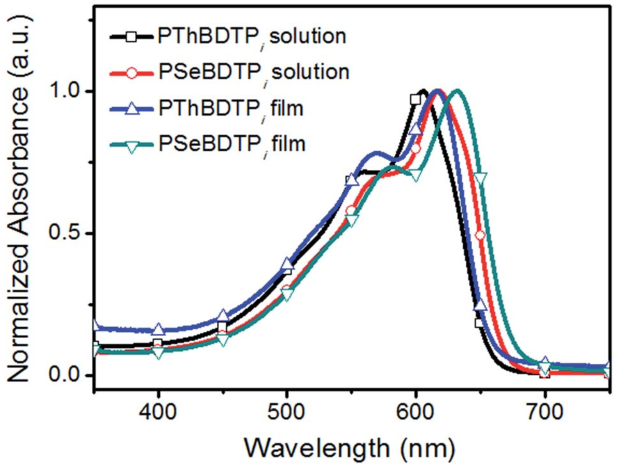

Fig. 2 Absorption spectra for PThBDTP$_i$ and PSeBDTP$_i$ in solution and as films.

The absorption spectra for PThBDTP$_i$ and PSeBDTP$_i$ in solution and as films are shown in Fig. 2 and the optical data are listed in Table 1. In solution, PThBDTP$_i$ and PSeBDTP$_i$ show absorption peaks at 605 nm and 618 nm, respectively. For the films, the peaks shift to 616 nm and 632 nm, respectively. The optical bandgaps (E_g^{opt}) for PThBDTP$_i$ and PSeBDTP$_i$ are 1.88 eV and 1.85 eV, respectively. The smaller bandgap of PSeBDTP$_i$ results from the reduced aromaticity of selenophene.[9] The HOMO and LUMO energy levels for PThBDTP$_i$ and PSeBDTP$_i$ were calculated from the onset potentials of oxidation (E_{ox}^{on}) and reduction (E_{red}^{on}), respectively (Fig. S9†).[10] PThBDTP$_i$ and PSeBDTP$_i$ exhibit deep HOMO levels of −5.47 eV and −5.44 eV, respectively, and similar LUMO levels of −3.00 eV and −2.99 eV, respectively. Deep HOMO leads to high V_{oc} for solar cells.[11] The energy level diagram for PThBDTP$_i$, PSeBDTP$_i$ and PC$_{71}$BM is presented in Fig. 3.

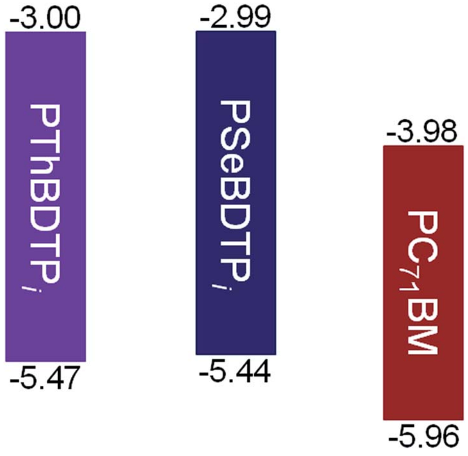

Fig. 3 The energy level diagram for PThBDTP$_i$, PSeBDTP$_i$ and PC$_{71}$BM.

The photovoltaic performance for PThBDTP$_i$ and PSeBDTP$_i$ was evaluated by studying the inverted solar cells with a structure of ITO/ZnO/polymer:PC$_{71}$BM/MoO$_3$/Ag.[12] The *J*–*V* curves and external quantum efficiency (EQE) spectra for the solar cells are shown in Fig. 4. The performance data are listed in Table 2. A mixed solvent of chloroform : chlorobenzene (3 : 2) was used to dissolve PThBDTP$_i$:PC$_{71}$BM blend. The best PThBDTP$_i$:PC$_{71}$BM cells gave a PCE of 8.11%, with a V_{oc} of 0.95 V, a J_{sc} of 12.13 mA cm^{-2} and a FF of 70.5%. These cells have a D/A ratio of 1 : 2 (w/w), an active layer thickness of 92 nm and 0.5% (v/v) 1,8-diiodooctane (DIO) as the additive (Tables S1–S3†). PSeBDTP$_i$:PC$_{71}$BM cells were made by using chlorobenzene as the solvent and the best cells gave a PCE of 6.50%, with a V_{oc} of 0.91 V, a J_{sc} of 10.32 mA cm^{-2} and a FF of 69.6%. These cells have a D/A ratio of 1 : 2 (w/w), an active layer thickness of 104 nm and 1% (v/v) DIO as the additive (Tables S4–S6†). Compared with PSeBDTP$_i$ cells, PThBDTP$_i$ cells gave higher V_{oc} because of the deeper HOMO level of PThBDTP$_i$. PThBDTP$_i$ cells produce a higher J_{sc} than PSeBDTP$_i$ cells, and the

Table 1 Optical and electrochemical data for the polymers

Polymers	λ_{sol} [nm]	λ_{film} [nm]	λ_{on} [nm]	$E_g^{opt\,a}$ [eV]	E_{ox}^{on} [V]	E_{red}^{on} [V]	HOMO^b [eV]	LUMO^c [eV]	$E_g^{ec\,d}$ [eV]
PThBDTP$_i$	605	616	658	1.88	0.67	−1.80	−5.47	−3.00	2.47
PSeBDTP$_i$	618	632	671	1.85	0.64	−1.81	−5.44	−2.99	2.45

[a] $E_g^{opt} = 1240/\lambda_{on}$. [b] HOMO = $-(E_{ox}^{on} + 4.8)$. [c] LUMO = $-(E_{red}^{on} + 4.8)$. [d] E_g^{ec} = LUMO − HOMO.

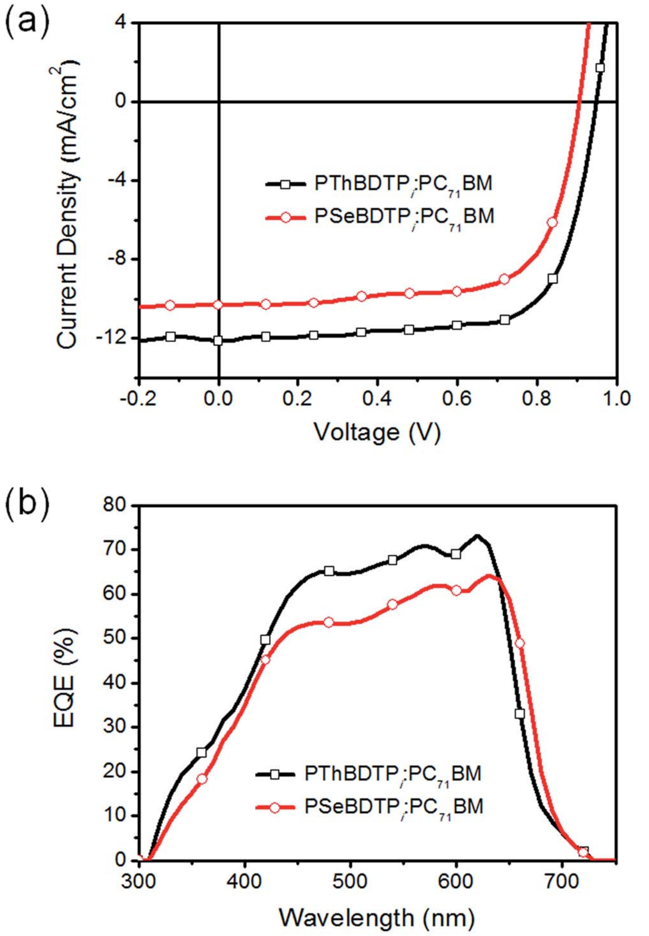

Fig. 4 *J*–*V* curves (a) and EQE spectra (b) for polymer:PC$_{71}$BM solar cells.

higher EQE of PThBDTP$_i$ cells at 310–640 nm also confirms this. The higher J_{sc} might result from better charge transporting capability of PThBDTP$_i$. According to space charge limited current (SCLC) measurements, the hole mobilities for PThBDTP$_i$ and PSeBDTP$_i$ are 2.60×10^{-4} cm^2 V^{-1} s^{-1} and 1.70×10^{-4} cm^2 V^{-1} s^{-1}, respectively (Fig. S10†). The XRD pattern for PThBDTP$_i$ film presents a stronger (010) peak, which corresponds to a π–π stacking distance of 3.60 Å, while PSeBDTP$_i$ possesses a π–π stacking distance of 3.78 Å (Fig. 5). The smaller π–π stacking *d*-spacing for PThBDTP$_i$ might be due to the smaller volume of sulfur atom. The smaller π–π stacking *d*-spacing favors hole transport. This could explain the higher hole mobility of PThBDTP$_i$ and also the higher photocurrent from PThBDTP$_i$ cells.

Table 2 Performance data for polymer:PC$_{71}$BM solar cells

Polymer	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
PThBDTP$_i$	0.95	12.13 (11.20)[a]	70.5	8.11 (7.93)[b]
PSeBDTP$_i$	0.91	10.32 (10.15)	69.6	6.50 (6.29)

[a] The data in the parentheses are integrated current density from EQE spectra. [b] The data in the parentheses are averages for 10 cells.

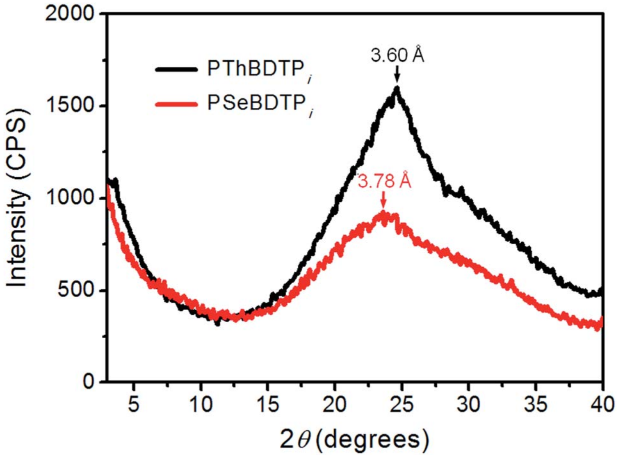

Fig. 5 XRD patterns for PThBDTP$_i$ and PSeBDTP$_i$ films.

PThBDTP$_i$:PC$_{71}$BM and PSeBDTP$_i$:PC$_{71}$BM solar cells without DIO gave low PCEs of 2.55% and 2.56%, respectively, presenting low J_{sc} and FF. DIO can effectively dissolve fullerene aggregates and promote fullerene's mixing with polymer to form 3D charge-transport channels. More D/A interfaces could promote exciton dissociation and produce high photocurrent. PThBDTP$_i$:PC$_{71}$BM and PSeBDTP$_i$:PC$_{71}$BM blend films with DIO show fine and clear nano-structures (Fig. S11†), and this ideal morphology is always favourable for improving J_{sc} and FF of bulk heterojunction solar cells.

Conclusions

In summary, an aromatic lactam acceptor unit, BDTP$_i$, was developed. By using this unit, two D–A copolymers, PThBDTP$_i$ and PSeBDTP$_i$, were synthesized. PThBDTP$_i$:PC$_{71}$BM solar cells gave a decent PCE of 8.11%. The facile synthesis and good performance of BDTP$_i$ copolymers suggest that BDTP$_i$ is a promising building block for developing high-performance materials for polymer solar cells.

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