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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 PC₇₁BM 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:PC₇₁BM 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)sephenophene *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.

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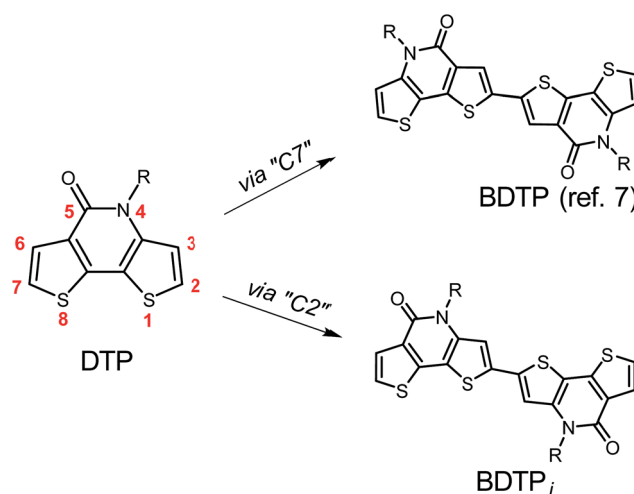
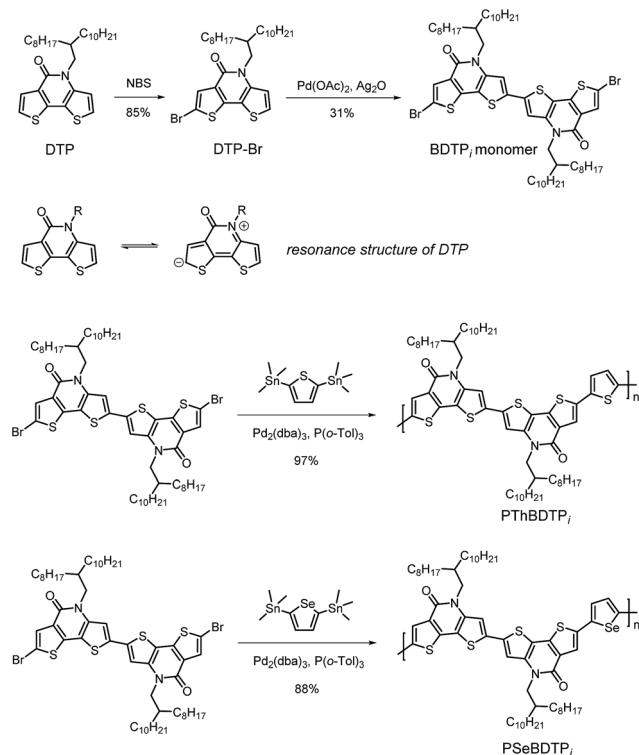
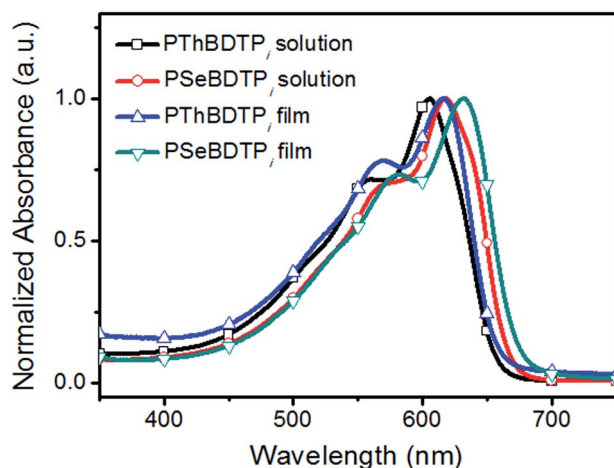


Fig. 1 Chemical structures for DTP, BDTP and BDTP_i.



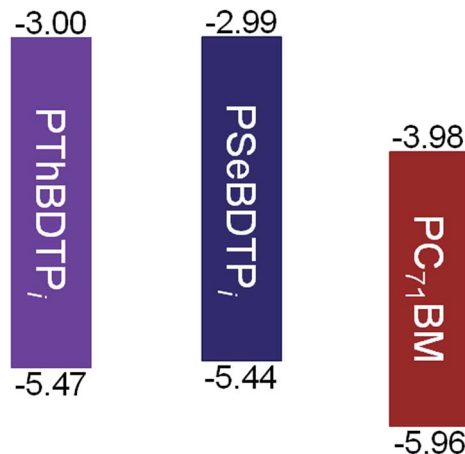
Scheme 1 Synthetic routes for BDTP_i monomer and the copolymers.Fig. 2 Absorption spectra for PThBDTP_i and PSeBDTP_i in solution and as films.

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

Table 1 Optical and electrochemical data for the polymers

Polymers	λ_{sol} [nm]	λ_{film} [nm]	λ_{on} [nm]	$E_{\text{g}}^{\text{opta}}$ [eV]	$E_{\text{ox}}^{\text{on}}$ [V]	$E_{\text{red}}^{\text{on}}$ [V]	HOMO ^b [eV]	LUMO ^c [eV]	$E_{\text{g}}^{\text{ecd}}$ [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

$$^a E_{\text{g}}^{\text{opt}} = 1240/\lambda_{\text{on}}. \quad ^b \text{HOMO} = -(E_{\text{ox}}^{\text{on}} + 4.8). \quad ^c \text{LUMO} = -(E_{\text{red}}^{\text{on}} + 4.8). \quad ^d E_{\text{g}}^{\text{ec}} = \text{LUMO} - \text{HOMO}.$$

Fig. 3 The energy level diagram for PThBDTP_i, PSeBDTP_i and PC₇₁BM.

peaks at 605 nm and 618 nm, respectively. For the films, the peaks shift to 616 nm and 632 nm, respectively. The optical bandgaps ($E_{\text{g}}^{\text{opt}}$) 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 ($E_{\text{ox}}^{\text{on}}$) and reduction ($E_{\text{red}}^{\text{on}}$), 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 PC₇₁BM is presented in Fig. 3.

The photovoltaic performance for PThBDTP_i and PSeBDTP_i was evaluated by studying the inverted solar cells with a structure of ITO/ZnO/polymer:PC₇₁BM/MoO₃/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:PC₇₁BM blend. The best PThBDTP_i:PC₇₁BM 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:PC₇₁BM 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



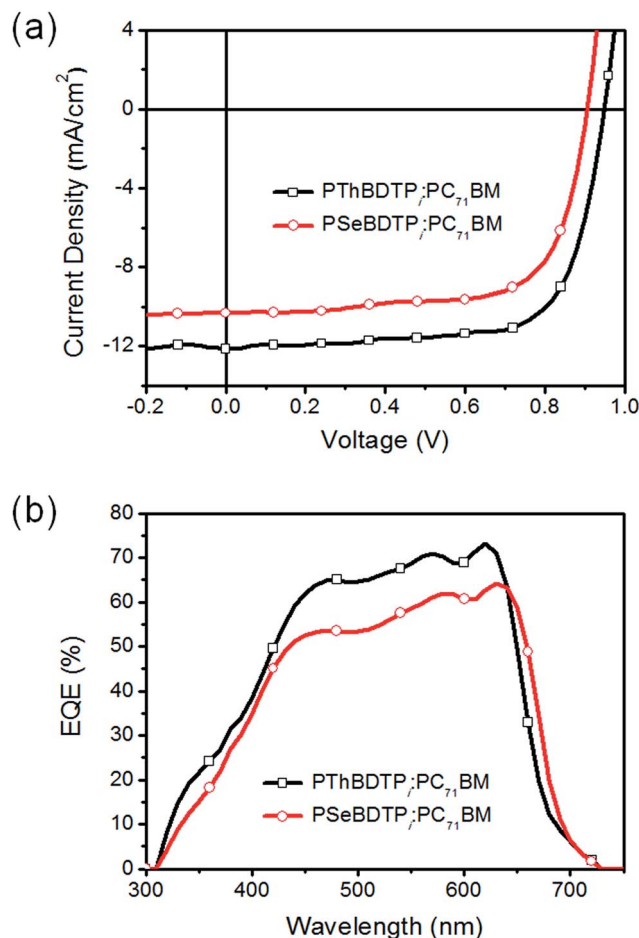


Fig. 4 J - V curves (a) and EQE spectra (b) for polymer:PC₇₁BM solar cells.

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 $2.60 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $1.70 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, 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:PC₇₁BM 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.

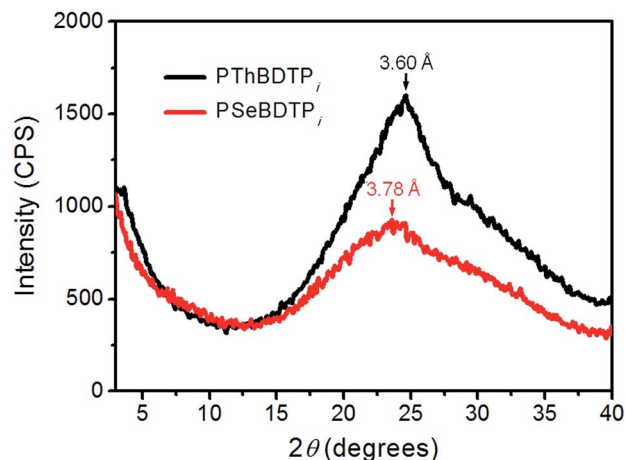


Fig. 5 XRD patterns for PThBDTP_i and PSeBDTP_i films.

PThBDTP_i:PC₇₁BM and PSeBDTP_i:PC₇₁BM 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:PC₇₁BM and PSeBDTP_i:PC₇₁BM 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:PC₇₁BM 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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