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A heptacyclic acceptor unit developed for D–A copolymers used in polymer solar cells†

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Thiophene rings in the pentacyclic unit TPTI were replaced with thieno[3,2-*b*]thiophene moieties to produce a new fused-ring acceptor unit TTP. A D–A copolymer PBDTTTP was synthesized *via* copolymerizing TTP and benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT). PBDTTTP possessed an optical bandgap of 2.11 eV, a deep HOMO level of –5.43 eV, and partial crystallinity. PBDTTTP:PC₇₁BM solar cells gave a PCE of 5.53%, and the maximum V_{oc} reached 1 V.

Fused-ring units as building blocks have been used to develop highly efficient D–A copolymers for bulk heterojunction (BHJ) solar cells due to their unique advantages such as extended conjugation length, reduced bandgap, enhanced light-absorbance, stronger interchain interactions, and high charge carrier mobility.¹ Replacing thiophene with thieno[3,2-*b*]thiophene (TT) is an effective approach to develop new fused-ring units (Fig. 1).² TT can promote polymer packing and improve charge carrier mobility.^{2a} Durrant *et al.* reported a new donor unit dithienogermolodithiophene (DTTG), in which two TT units are connected through a dialkylgermanium unit. pDTTG-TPD:PC₇₁BM solar cells exhibit efficiencies up to 7.2%.^{2b} Hou *et al.* developed a two-dimensional donor unit DTBDT, and its copolymer PDT-S-T gives a higher PCE (7.79%) than polymer PBDTTT-S-T (5.93%).^{2c} Jen and Cheng independently reported a new heptacyclic ladder-type donor unit IDTT *via* replacing the terminal thiophenes of IDT with TT. The IDTT building block endows D–A copolymers with extended conjugation length, better light-harvesting capability, enhanced charge mobilities and better photovoltaic performance.^{2a,d} In addition, TT can also be used as a π -bridge, which used to be thiophene, furan or selenophene.³ The above mentioned approach is rarely used to develop new fused-ring acceptor units as far as we know. Recently, we have developed a series of lactam acceptor units and their copolymers show

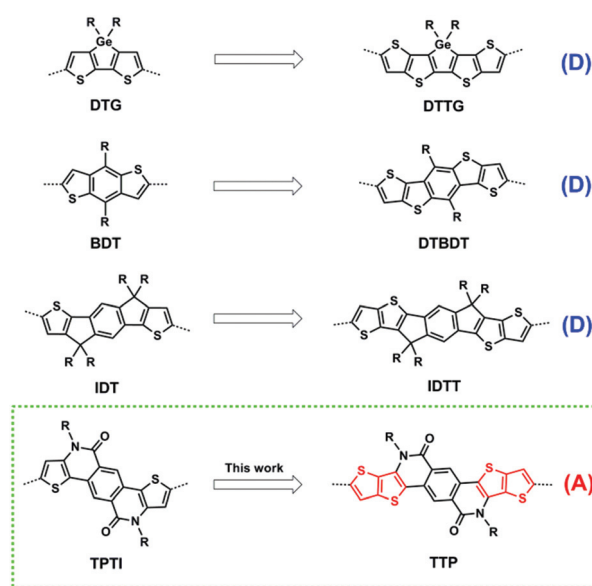


Fig. 1 Fused-ring units developed by replacing thiophene with thieno[3,2-*b*]thiophene. D and A stand for donor and acceptor units, respectively.

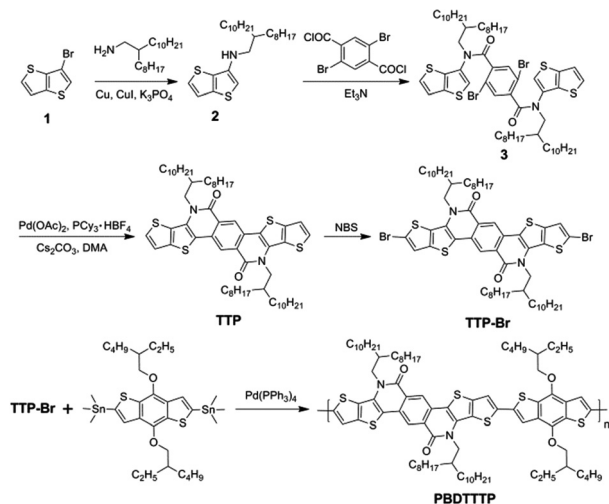
good photovoltaic performance.⁴ PThTPTI consisting of thieno[2',3':5,6]pyrido[3,4-*g*]thieno[3,2-*c*]isoquinoline-5,11(4*H*,10*H*)-dione (TPTI) and thiophene afforded efficiencies up to 9.20%.^{4b} In this work, two thiophenes at the end of TPTI were replaced by TT to produce a new heptacyclic acceptor unit thieno[2'',3'':4',5']thieno[2',3':5,6]pyrido[3,4-*g*]thieno[2',3':4,5]-thieno[3,2-*c*]isoquinoline-1,8(2*H*,9*H*)-dione (TTP, Fig. 1). The centrosymmetric TTP contains seven fused aromatic rings with two TTs, one benzene, and two pyridones. The D–A copolymer PBDTTTP was synthesized by copolymerizing TTP with benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT). PBDTTTP possesses a deep HOMO level and an optical bandgap of 2.11 eV. The PBDTTTP:PC₇₁BM solar cells gave a PCE of 5.53%, which is higher than that of its analogue PBDTTPTI.⁵

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Scheme 1 Synthetic route to PBDTTTP.

The synthetic route to **PBDTTTP** is depicted in Scheme 1. The commercially available 3-bromothiopheno[3,2-*b*]thiophene (**1**) reacted with 2-octyldodecan-1-amine to produce *N*-(2-octyldodecyl)thieno[3,2-*b*]thiophen-3-amine (**2**). Compound **2** reacted with 2,5-dibromoterephthaloyl dichloride to afford compound **3**. The Pd-catalyzed intramolecular coupling reaction of **3** produced **TTP**, which was brominated with NBS to give monomer **TTP-Br**. The chemical structure of **TTP-Br** was confirmed by ^1H NMR (Fig. S2†) and mass spectroscopy. **TTP-Br** shows poor solubility in chloroform, and the ^{13}C NMR spectrum cannot be obtained. 4,8-Bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene was chosen as the donor unit. Stille coupling of **TTP-Br** and distannyl BDT produced the target copolymer **PBDTTTP**. The polymer was purified by Soxhlet extraction using methanol, hexane and chloroform successively. **PBDTTTP** was soluble in chloroform, chlorobenzene, *o*-dichlorobenzene, and other common organic solvents. The number-average molecular weight (M_n) of **PBDTTTP** was 69.3 kDa with a polydispersity index (PDI) of 4.00, estimated by gel permeation chromatography (GPC) using THF as the eluent. As determined by thermogravimetric analysis (TGA) (Fig. S3†), the decomposition temperature (T_d) of **PBDTTTP** is 329 °C, suggesting its good thermal stability for photovoltaic application.

The optical properties of **PBDTTTP** were studied by UV-vis absorption spectroscopy. The **PBDTTTP** solution and thin film show similar absorption spectra with two peaks (Fig. 2). The strongest absorption peaks appear at 553 and 556 nm, and the second peaks at 512 and 514 nm, respectively. From solution to solid state, the red shift is ~3 nm. Aggregation might also exist in solution. The optical bandgap for **PBDTTTP** is 2.11 eV, which is larger than that of the pentacyclic **TPTI** analogue **PBDTTPTI** (2.03 eV).⁵ From **TPTI** to **TTP**, the conjugation system was extended, while the absorption spectrum shows a blue shift. The aromatic feature for the copolymer might get stronger when extending the **TPTI** unit to the **TTP** unit.^{6,7}

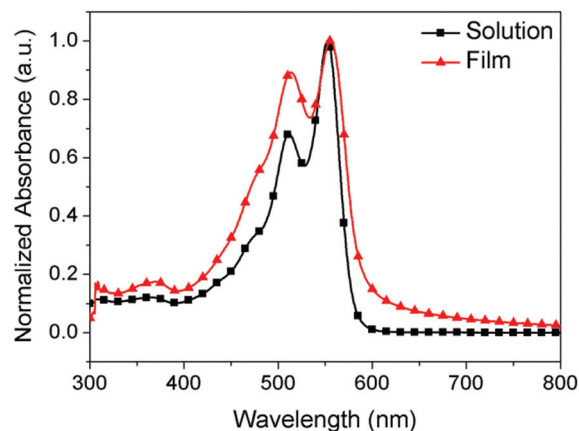


Fig. 2 Absorption spectra for PBDTTTP in chloroform and solid state.

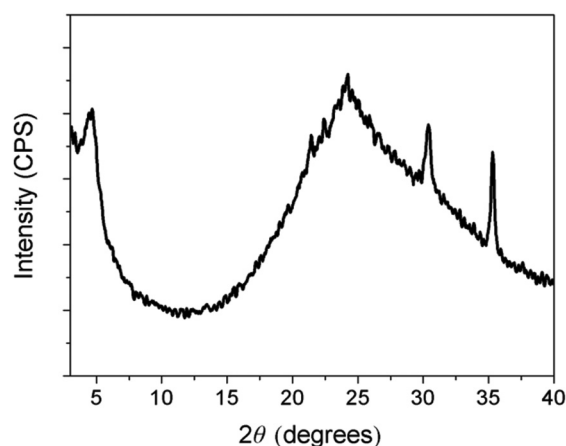


Fig. 3 XRD pattern for the PBDTTTP film on ITO glass.

X-ray diffraction (XRD) pattern of the pure polymer film is shown in Fig. 3. The two peaks at 4.62° and 24.25° correspond to an interlayer *d*-spacing of 19.11 Å and a π - π stacking *d*-spacing of 3.67 Å, respectively. The peak at 4.62° indicates that **PBDTTTP** is partially crystalline, which is necessary for high hole mobility. The cyclic voltammogram of the polymer thin film was measured (Fig. S4†). **PBDTTTP** has an oxidation onset potential ($E_{\text{ox}}^{\text{on}}$) of 0.63 V and a reduction onset potential ($E_{\text{red}}^{\text{on}}$) of -2.20 V, and the HOMO and LUMO energy levels are determined to be -5.43 eV and -2.60 eV, respectively. The deep HOMO level favours the device to produce a high open-circuit voltage (V_{oc}).⁸

To evaluate the photovoltaic properties of **PBDTTTP**, solar cells with a structure of ITO/PEDOT:PSS/**PBDTTTP**:PC₇₁BM/Ca/Al were fabricated. After systematic optimization, the best device had a D/A ratio of 1 : 1 (w/w), an active layer thickness of 149 nm, with 3 vol% 1,8-diiodooctane (DIO) in chlorobenzene. DIO is widely used in polymer:fullerene solar cells, and it can inhibit fullerene to form large aggregates and increase the D-A interfaces in the active layers, thus increasing the photocurrent

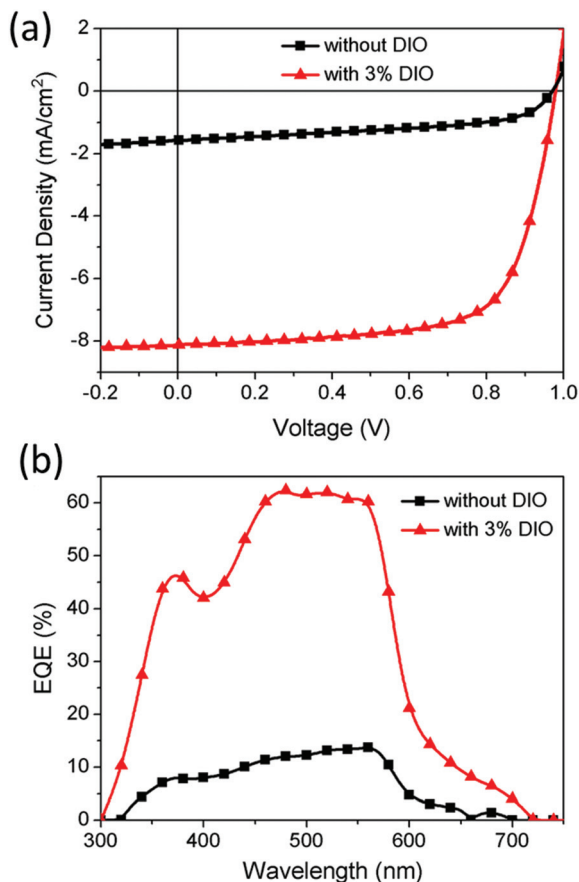


Fig. 4 J–V curves (a) and EQE spectra (b) for PBDTTTP:PC₇₁BM solar cells.

Table 1 Performance data for PBDTTTP:PC₇₁BM solar cells

DIO [vol%]	V _{oc} [V]	J _{sc} [mA cm ⁻²]	FF [%]	PCE [%]
0	0.97	1.53	52.1	0.80
1	0.96	7.88	68.3	5.18
3	0.98	8.12	69.5	5.53
5	1.00	7.92	65.8	5.22

and improving photovoltaic performance. Solar cells without DIO exhibited a very low PCE of 0.80% with a small J_{sc} of 1.53 mA cm⁻² (Fig. 4a and Table 1). After adding 1 vol% DIO, the efficiency increased over five times to 5.18% with a higher J_{sc} of 7.88 mA cm⁻² and a higher FF of 68.3%. Devices with 3 vol% DIO gave the highest PCE of 5.53% with a V_{oc} of 0.98 V, a J_{sc} of 8.12 mA cm⁻², and a FF of 69.5%. This efficiency is higher than that of the TPTI analogue PBDTTPTI (5.30%).⁵ The significant improvements in J_{sc} were confirmed by EQE spectra (Fig. 4b). Solar cells without DIO show EQE below 14% in the range of 300–750 nm with an integrated current of 1.57 mA cm⁻². After adding 3 vol% DIO, the EQE soared to 60% in the range of 460–558 nm with an integrated current of 7.81 mA cm⁻².

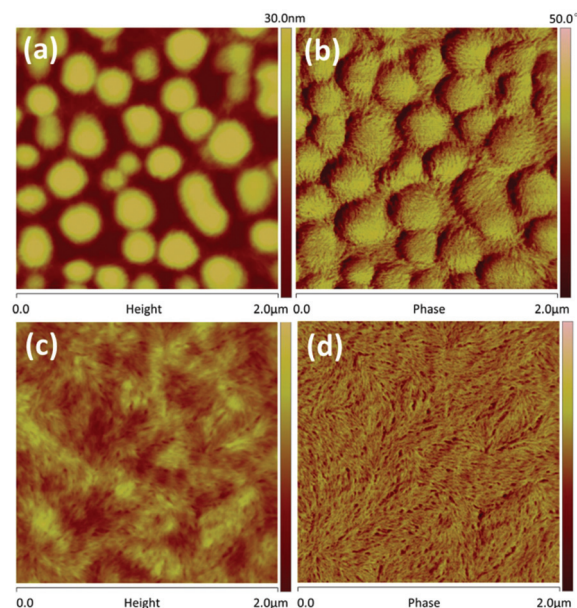


Fig. 5 AFM height (left) and phase (right) images for PBDTTTP:PC₇₁BM blend films. (a) and (b), without DIO; (c) and (d), with 3% DIO.

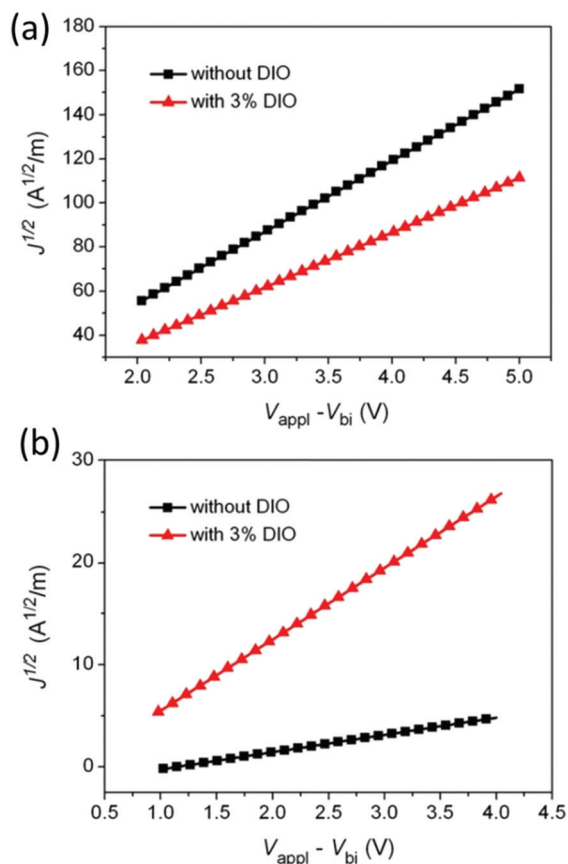


Fig. 6 $J^{1/2}$ -V plots for hole-only (a) and electron-only (b) devices based on PBDTTTP:PC₇₁BM blend films without or with 3% DIO (in the dark).

Morphologies for **PBDTTTP**:PC₇₁BM blend films were studied by atomic force microscopy (AFM) (Fig. 5). The film without DIO exhibited large fullerene domains with diameters of a few hundred nanometers, while the film with 3 vol% DIO became uniform and showed fine nano-structures, which might provide more D–A interfaces for producing a high photocurrent. Charge carrier mobilities for the blend films were measured by the space charge limited current (SCLC) method (Fig. 6). The electron mobilities for **PBDTTTP**:PC₇₁BM blend films without or with 3 vol% DIO are 1.86×10^{-6} and $3.19 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. This suggests that DIO addition can significantly increase electron mobility. On the other hand, the hole mobilities for the blend films without or with 3 vol% DIO are 6.85×10^{-4} and $4.03 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. With DIO, hole/electron mobilities in the active layer are more balanced, leading to higher J_{sc} and FF.

Conclusions

As an extension of our previous work on a pentacyclic acceptor unit **TPTI**, a new heptacyclic acceptor unit **TTP** was developed by replacing the terminal thiophene rings of **TPTI** with thieno-[3,2-*b*]thiophenes. Its D–A copolymer **PBDTTTP** has partial crystallinity and a deep HOMO level of -5.43 eV . **PBDTTTP**:PC₇₁BM solar cells gave a PCE of 5.53% with a high V_{oc} of 0.98 V. Using **TTP** to construct more efficient D–A copolymers is ongoing in our lab.

Acknowledgements

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