

A pentacyclic aromatic lactam building block for
efficient polymer solar cells†Cite this: *Energy Environ. Sci.*, 2013, **6**,
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A D–A conjugated polymer (PThTPTI) was developed by using a brand new pentacyclic aromatic lactam acceptor unit (TPTI). PThTPTI possesses good light absorption, thermal stability, and a deep HOMO level. PThTPTI/PC₇₁BM cells afford an outstanding PCE up to 7.80%, with high V_{oc} (0.87 V), J_{sc} (13.69 mA cm^{−2}) and FF (65.6%), and over 70% EQE in the range of 435–640 nm.

The great consumption of fossil fuels forces human beings to put more efforts on research and development of renewable energy. Solar energy is the most abundant renewable energy source, which can be converted to electricity by photovoltaic devices like silicon solar cells. However, the high-cost and brittle solar cells based on inorganic semiconductors are not the most ideal and final solution for solar energy conversion. During the last 18 years, polymer solar cells (PSCs) based on a blend of a conjugated polymer donor and a fullerene acceptor have attracted great interest due to their unique advantages like low cost, lightweight, flexibility, and roll-to-roll fabrication.¹ The power conversion efficiency (PCE) is rapidly advancing and is close to that of the amorphous silicon solar cells.^{2,3}

Low bandgap donor–acceptor (D–A) conjugated polymers have been widely used in PSCs for achieving high PCE due to their superior sunlight harvesting capability and good mobilities. Among numerous D–A conjugated polymers, the polymers containing polycyclic conjugated building blocks are of particular interest due to their distinctive structures and decent performance in PSCs. These fused-ring building blocks include polyarenes, polycyclic heteroaromatic compounds, and ladder-type compounds, which were reported by Ko,⁴ Hsu,⁵ Jen,⁶ Yu,⁷

Broader context

Solar energy is the most abundant renewable energy source on earth. Taking solar energy and using it will greatly reduce our reliance on fossil fuels and will be beneficial to the global environment. The most direct way to utilize solar energy is transforming sunlight into electricity by solar cells. Traditional solar cells based on inorganic semiconductors can give high power conversion efficiency but with high cost. Polymer solar cells (PSCs) have attracted great interest due to their unique advantages like low cost, lightweight, flexibility, and roll-to-roll fabrication. The power conversion efficiency (PCE) of PSCs has exceeded 10% recently. Donor–acceptor (D–A) conjugated polymers have been widely used for achieving highly efficient PSCs. Studies on fused-ring D–A polymers to date have focused on developing polycyclic donor units; the development of new polycyclic acceptor units is rare. In this work, we designed and synthesized a novel pentacyclic aromatic lactam acceptor unit, TPTI, and applied it for developing a D–A polymer PThTPTI, which demonstrates outstanding performance in PSCs.

McCulloch,⁸ Zheng,⁹ and others.¹⁰ Up to 7.6% PCE was obtained from the corresponding solar cells.^{7b} The superiority of polycyclic conjugated building blocks in PSCs originates from these features: first, their extended conjugation systems facilitate π -electron delocalization through the polymer backbone, reducing the bandgap and enhancing light-absorbance of the materials;^{4,5a} second, their molecular planarity favors cofacial π – π stacking of polymer chains in film, improving the charge carrier mobility.^{5a,11} Studies on fused-ring D–A polymers to date have focused on developing polycyclic donor units; the development of new polycyclic acceptor units is rare.^{10d} Recently, McCulloch *et al.* reported the synthesis of D–A polymers based on two distinctive tricyclic lactam acceptor units, benzodipyrrolidone (BP) and dihydropyrroloindoleone (DPID), which render the copolymers with narrow bandgaps, deep HOMO levels, and high charge carrier mobility. These polymers showed good performance in both organic field-effect transistors (OFETs) and PSCs.¹² Being inspired by these results, we expected that polycyclic aromatic lactams with more fused-rings could be promising acceptor units for high-performance D–A

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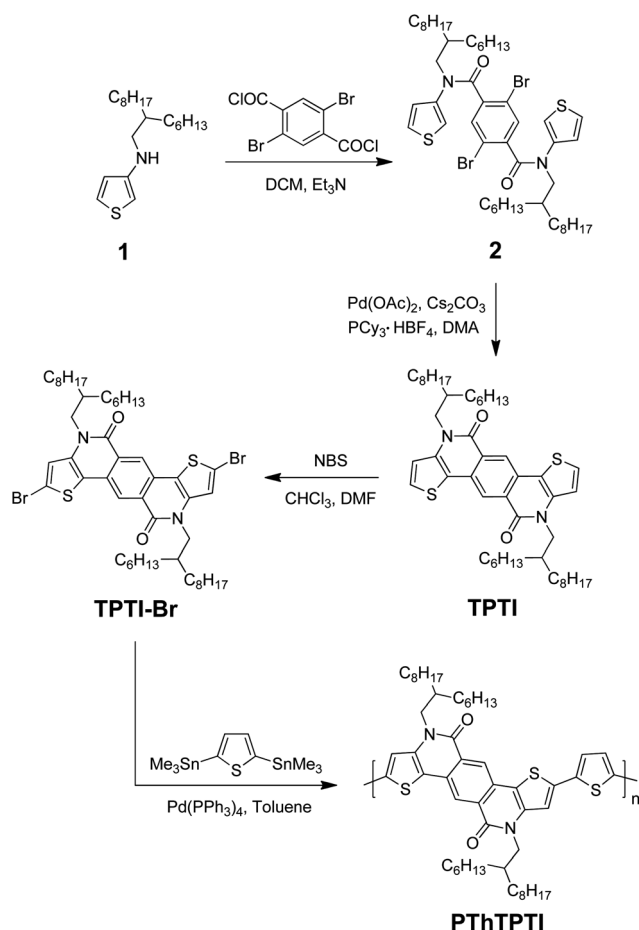
polymers. Here we report the synthesis of a pentacyclic aromatic lactam acceptor unit, thieno[2',3':5,6]pyrido[3,4-g]thieno[3,2-c]-isoquinoline-5,11(4*H*,10*H*)-dione (TPTI), and the resulting D-A conjugated polymer PThTPTI (Scheme 1). Solar cells based on PThTPTI/PC₇₁BM blends exhibit outstanding performance with a PCE of 7.80%, which is among the highest PCEs reported for single polymer solar cells.

The centrosymmetric TPTI contains five fused aromatic rings with two thiophenes at the end, one benzene at the center, and two pyridones connecting thiophene and benzene. The two electron-withdrawing lactam moieties endow TPTI with electron affinity and offer the sites for introducing alkyl chains to guarantee good solubility of the materials. The synthesis of TPTI started from the reaction of *N*-(2-hexyldecyl)thiophen-3-amine (**1**) with 2,5-dibromoterephthaloyl dichloride, which afforded bis-amide **2** in 72% yield. Pd-catalyzed intramolecular cyclization transformed **2** to TPTI in 57% yield.¹³ NOE spectra of TPTI indicate that the cyclization selectively took place between the C–H bond at C2 of thiophene and the C–Br bond of benzene (Fig. S3†). Bromination of TPTI afforded the monomer TPTI-Br in 91% yield. Copolymerization of TPTI-Br and 2,5-bis(trimethylstannyl)thiophene through Stille coupling gave D-A polymer PThTPTI in 93% yield. The purple PThTPTI possesses good solubility in common organic solvents and outstanding thermostability up to 434 °C (Fig. S6†). Gel

permeation chromatography (GPC) experiments indicate that PThTPTI has a number-average molecular weight (M_n) of 28.5 kDa, with a polydispersity index (PDI) of 2.2.

The absorption spectra of PThTPTI are shown in Fig. 1. The absorption maxima of PThTPTI in chloroform and in film are 583 nm and 623 nm, respectively. A 40 nm red shift in film indicates the enhanced interchain π – π stacking in the solid state. The absorption onset of PThTPTI in film is located at 666 nm, corresponding to an optical bandgap of 1.86 eV. The electrochemical properties of PThTPTI were studied by the cyclic voltammetry (CV) method (Fig. S7†). The onset oxidation and reduction potentials (E_{ox}^{on} and E_{red}^{on}) of PThTPTI are 0.62 V and –2.03 V, respectively, corresponding to a HOMO energy level of –5.42 eV and a LUMO energy level of –2.77 eV estimated from empirical equations.¹⁴ The –5.42 eV HOMO level of PThTPTI is close to an ideal HOMO level, which may lead to high V_{oc} .^{1b,15} PThTPTI shows a moderate bandgap among the reported D-A polymers.^{10b,15}

Solar cells with a conventional device configuration of ITO/PEDOT:PSS/PThTPTI:PC₇₁BM/Ca/Al were firstly investigated. The optimized device afforded a PCE of 7.21%, with a V_{oc} of 0.92 V, a J_{sc} of 12.47 mA cm^{–2}, and a FF of 62.8%. The best device had a D-A ratio of 1 : 1 (w/w), an active layer thickness of 180 nm, a 3 vol% 1,8-diiodooctane (DIO) additive, and took no thermal annealing (see the ESI†). Solvent additives have been frequently used to adjust the nanoscale morphology of the active layer. High boiling point additives like DIO can selectively dissolve fullerene aggregates and promote fullerene intercalation into polymer domains, thus optimizing the domain size and D-A interface.¹⁶ In our case, the DIO additive plays a crucial role in device performance improvement. As shown in Fig. 2 and Table 1, the device without DIO gave a much lower PCE of 1.09%, with a low J_{sc} of 2.11 mA cm^{–2} and a low FF of 55.4%. External quantum efficiency (EQE) spectra indicate that the EQE is below 10% for the device without DIO, while over 60% EQE can be obtained in the range of 360–650 nm for the device with 3 vol% DIO. These results suggest that DIO can effectively enhance the photocurrent probably by improving the morphology of the active layer. This hypothesis is verified by atomic force microscopy (AFM) and transmission electron microscopy (TEM). AFM images show the morphology of the



Scheme 1 Synthetic route for PThTPTI.

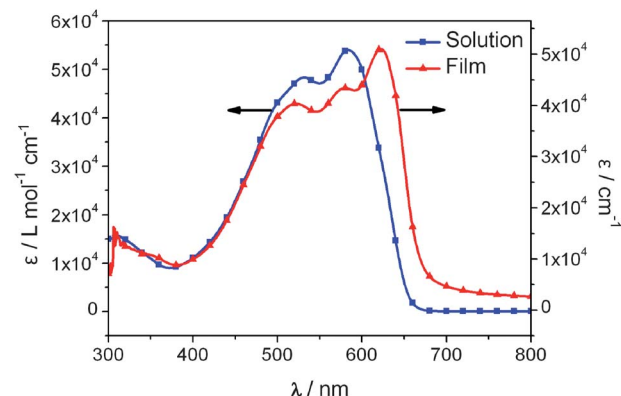


Fig. 1 UV/Vis absorption spectra of PThTPTI in chloroform and in film.

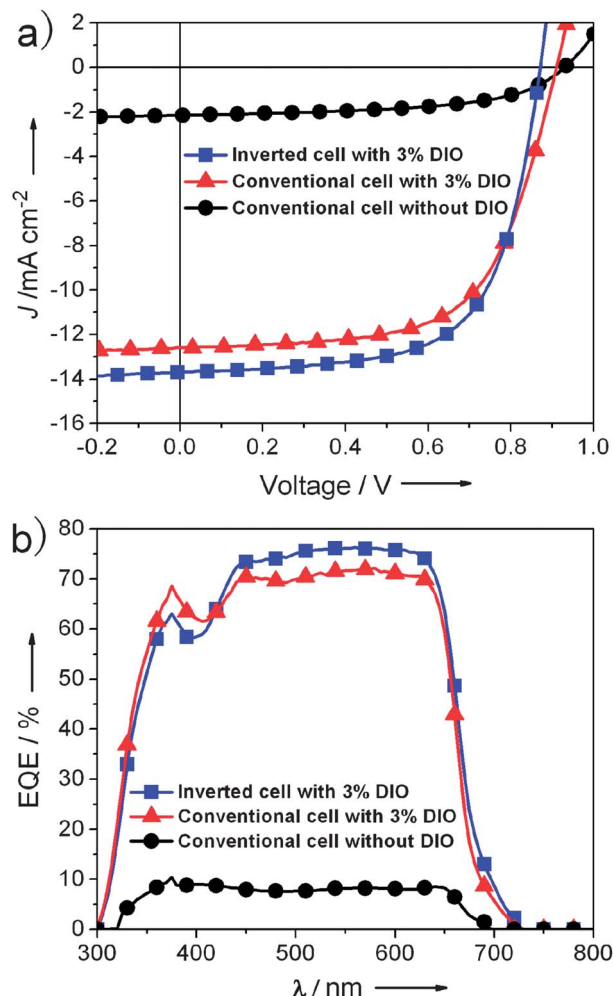


Fig. 2 (a) J - V curves of PThTPTI/PC₇₁BM solar cells; (b) EQE spectra.

Table 1 Performance data for PThTPTI/PC₇₁BM (1 : 1, w/w) solar cells

Device type	DIO [v/v]	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
Conventional	Without	0.93	2.11	55.4	1.09
	3%	0.92	12.47	62.8	7.21
Inverted	3%	0.87	13.69	65.6	7.80

film surface. They indicate that the film without DIO shows large domains dispersed in the film, while the film with 3 vol% DIO shows fine structures (Fig. 3a and b). The TEM image indicates that the large domains are fullerene domains (dark regions), which disperse in a polymer matrix (bright regions) (Fig. 3c).¹⁷ In contrast, the film with DIO is quite uniform without large aggregates (Fig. 3d). The significantly increased D-A interfaces induced by the additive favor effective exciton dissociation and lead to much higher J_{sc} and FF.

Solar cells with an inverted configuration of ITO/ZnO/PThTPTI:PC₇₁BM/MoO₃/Ag were also fabricated.¹⁸ Under the same optimized conditions for conventional cells, inverted cells showed a superior PCE of 7.80%, with an enhanced J_{sc} of 13.69 mA cm⁻² and a better FF of 65.6%. The devices gave over

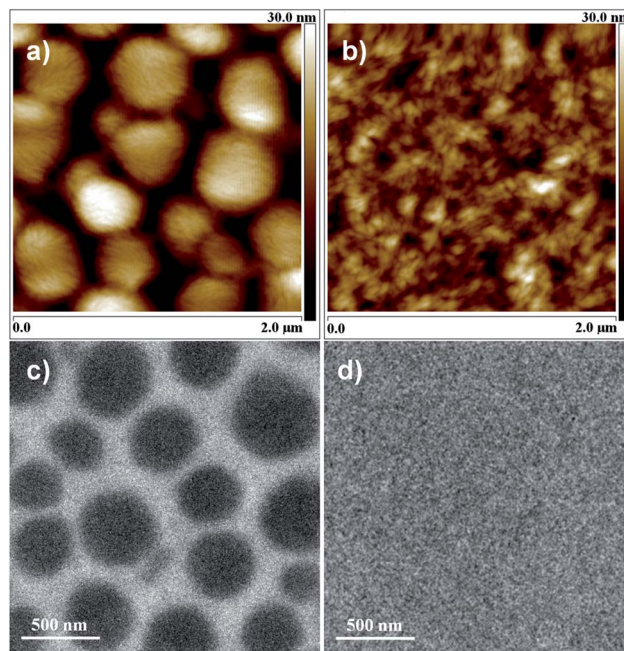


Fig. 3 AFM height images (top) and TEM images (bottom) of PThTPTI/PC₇₁BM blend films without DIO (a and c) and with 3 vol% DIO (b and d).

70% EQE in the range of 435–640 nm. The average integrated current from the EQE curve is 13.21 mA cm⁻², which is consistent with the J_{sc} value from J - V measurements. The integrated currents of those conventional cells are also consistent with the corresponding J_{sc} values, suggesting that J - V measurements in this work are reliable. High J_{sc} and FF obtained in both conventional and inverted cells suggest good charge carrier mobility of PThTPTI. The hole and electron mobilities of PThTPTI:PC₇₁BM blend films with and without an additive were measured by the space-charge limited current (SCLC) method (Fig. S8 and S9†). The hole mobilities of the films with and without DIO are 1.07×10^{-3} and 1.40×10^{-3} cm² V⁻¹ s⁻¹, respectively, indicating good hole-transporting properties of PThTPTI. The film with DIO shows much higher electron mobility, 7.88×10^{-4} cm² V⁻¹ s⁻¹, than that of the film without DIO, 7.10×10^{-5} cm² V⁻¹ s⁻¹. The significantly enhanced electron mobility by using additive leads to more balanced charge carrier transport in the active layer, thus improving the FF. The XRD pattern of the as-cast PThTPTI film shows two distinct diffraction peaks at $2\theta = 4.3^\circ$ and 24.9° , respectively (Fig. S10†). The strong peak at 4.3° corresponds to an interlayer d -spacing of 20.53 Å, while the peak at 24.9° corresponds to a d -spacing of 3.58 Å for π - π stacking. XRD results suggest that polymer PThTPTI is partially crystalline, which accounts for its good mobility.¹⁹

In summary, a highly efficient D-A conjugated polymer PThTPTI based on a novel pentacyclic aromatic lactam acceptor unit TPTI has been developed for organic solar cell applications. PThTPTI/PC₇₁BM solar cells afforded outstanding PCEs up to 7.80%, with a V_{oc} of 0.87 V, a J_{sc} of 13.69 mA cm⁻², and a FF of 65.6%, suggesting that TPTI is a promising building block for developing high performance D-A polymers. To the best of our

knowledge, PThTPTI is among the best donor materials with a moderate bandgap, which can be useful for further development of tandem solar cells.

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