

An efficient selenophene-containing conjugated copolymer for organic solar cells†

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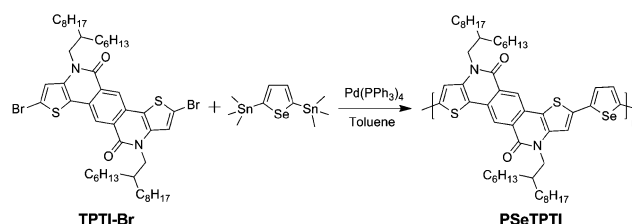
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A D–A polymer, **PSeTPTI**, was developed by copolymerizing a pentacyclic acceptor unit TPTI with a selenophene unit. **PSeTPTI** possesses a narrow optical bandgap, a low-lying HOMO energy level, and a high hole mobility of $0.26 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. **PSeTPTI/PC₇₁BM** solar cells demonstrate a PCE of 6.04%, which is the highest efficiency for the conjugated copolymers using selenophene as the donor unit.

Polymer solar cells (PSCs) with great commercialization potential show unique advantages, such as solution processing, lightweight, and flexibility.¹ To date, power conversion efficiencies (PCEs) of single and tandem PSCs have reached 9.2%² and 10.6%,³ respectively. D–A conjugated copolymers have been widely used to obtain efficient solar cells. An outstanding D–A copolymer should possess: (1) low bandgap for harvesting more photons; (2) low-lying HOMO level for high open-circuit voltage (V_{oc}); (3) high hole mobility for high photocurrent and fill factor (FF); (4) good solubility for facile solution processing and favourable nano-morphology. Polycyclic aromatic donor and acceptor building blocks function very well in PSCs since their extended conjugation can effectively reduce bandgap, enhance light absorbance, and improve charge carrier mobility.⁴ Recently, we developed a highly efficient D–A polymer **PThTPTI** using a pentacyclic aromatic lactam unit, thieno[2',3':5,6]pyrido[3,4-g]thieno[3,2-c]isoquinoline-5,11(4*H*,10*H*)-dione (TPTI), as the acceptor unit. **PThTPTI/PC₇₁BM** solar cells afforded a PCE of 7.8%.⁵ **PThTPTI** is among the best donor materials. However, **PThTPTI** exhibited relatively narrow absorption spectra with a moderate optical bandgap of 1.86 eV, which limited the absorption in long-wavelength region. One approach to broaden absorption spectra and reduce bandgap is to replace thiophene unit with selenophene unit. Compared with

thiophene, the reduced aromaticity of selenophene increases the ground state quinoid resonance of the polymer, and selenophene-containing polymers possess enhanced planarity, extended conjugation length, and reduced bandgaps.⁶ Besides, selenium is more polarizable than sulfur, Se...Se interactions favor interchain charge hopping and enhance hole mobility.⁷ Selenophene was used in D–A copolymers as a donor unit,⁸ a π -bridge,⁹ or part of the donor unit or acceptor unit.¹⁰ In this work, we synthesized **PSeTPTI** based on TPTI acceptor unit and selenophene donor unit (Scheme 1). **PSeTPTI** exhibited good thermal stability, broad absorption, low optical bandgap, and high hole mobility of $0.26 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. **PSeTPTI/PC₇₁BM** solar cells afforded a PCE of 6.04%. To the best of our knowledge, this is the highest efficiency for D–A copolymers using selenophene as the donor unit (Table 1).

The synthesis of compound TPTI-Br is described in the literature.⁵ Target polymer **PSeTPTI** was synthesized through Stille reaction of TPTI-Br and 2,5-bis(trimethylstannyl)selenophene.

Scheme 1 Synthesis of **PSeTPTI**.Table 1 Performance data for **PSeTPTI:PC₇₁BM** (1 : 1, w/w) solar cells under AM 1.5G illumination (100 mW cm^{-2})

DIO [vol%]	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
3	0.85	11.10	64	6.04
Without	0.89	1.95	64	1.12

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selenophene in toluene at 115 °C. The crude product was purified by Soxhlet extraction using methanol, hexane, and chloroform in sequence. The chloroform fraction was added into methanol to obtain **PSeTPTI** as dark blue solid in 97% yield. The chemical structure of **PSeTPTI** was confirmed by ^1H NMR and elemental analysis. **PSeTPTI** is highly soluble in common organic solvents, such as toluene, chloroform, chlorobenzene, and *o*-dichlorobenzene. From gel permeation chromatography (GPC) against polystyrene standards in THF eluent, the number-average molecular weight (M_n) and the polydispersity index (PDI) of the polymer are 34.9 kDa and 3.51, respectively. **PSeTPTI** shows good thermal stability with a decomposition temperature T_d of 417 °C (5% wt loss) (Fig. S1†).

As shown in Fig. 1, **PSeTPTI** exhibits two absorption peaks at 548 and 602 nm in chloroform solution. The film absorption peak at 638 nm originates from interchain π - π stacking. The absorption onset for **PSeTPTI** film is 701 nm, corresponding to an optical bandgap of 1.77 eV, which is narrower than that of its analogue **PThTPTI** (1.86 eV).^{6,9b} The electrochemical property of **PSeTPTI** film was studied by cyclic voltammetry (CV) and all potentials were calibrated against Fc/Fc^+ redox couple. As shown in Fig. S2†, the oxidation onset potential ($E_{\text{ox}}^{\text{on}}$) and the reduction onset potential ($E_{\text{red}}^{\text{on}}$) of **PSeTPTI** are 0.61 and -1.92 V, respectively. According to the empirical formulae: $\text{HOMO} = -(E_{\text{ox}}^{\text{on}} + 4.8)$ eV, $\text{LUMO} = -(E_{\text{red}}^{\text{on}} + 4.8)$ eV,¹¹ the HOMO and LUMO energy levels of the polymer are calculated to be -5.41 and -2.88 eV, respectively. Compared with **PThTPTI**, **PSeTPTI** possesses similar HOMO energy level and lower LUMO energy level.^{10b} V_{oc} is proportional to the difference between the HOMO energy level of donor materials and the LUMO energy level of acceptor materials.¹² Deep HOMO energy level should render **PSeTPTI** high V_{oc} and good stability against oxidation.^{9b} The electrochemical bandgap of **PSeTPTI** is 2.53 eV, 0.76 eV higher than the optical bandgap, which results from the interface barrier between polymer films and electrode surface.¹³

Solar cells with a structure of ITO/PEDOT:PSS/**PSeTPTI**:PC₇₁BM/Ca/Al were fabricated to evaluate the photovoltaic performance of **PSeTPTI**. After optimization, solar cells with a D-A ratio of 1 : 1 (w/w), an active layer thickness of 140 nm, and

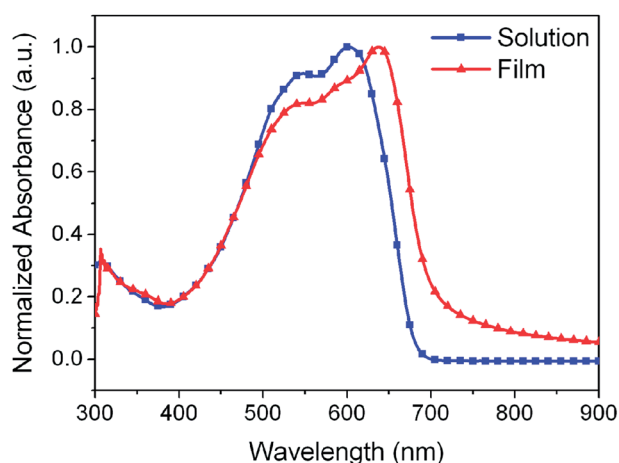


Fig. 1 Absorption spectra for **PSeTPTI** in chloroform and as thin films.

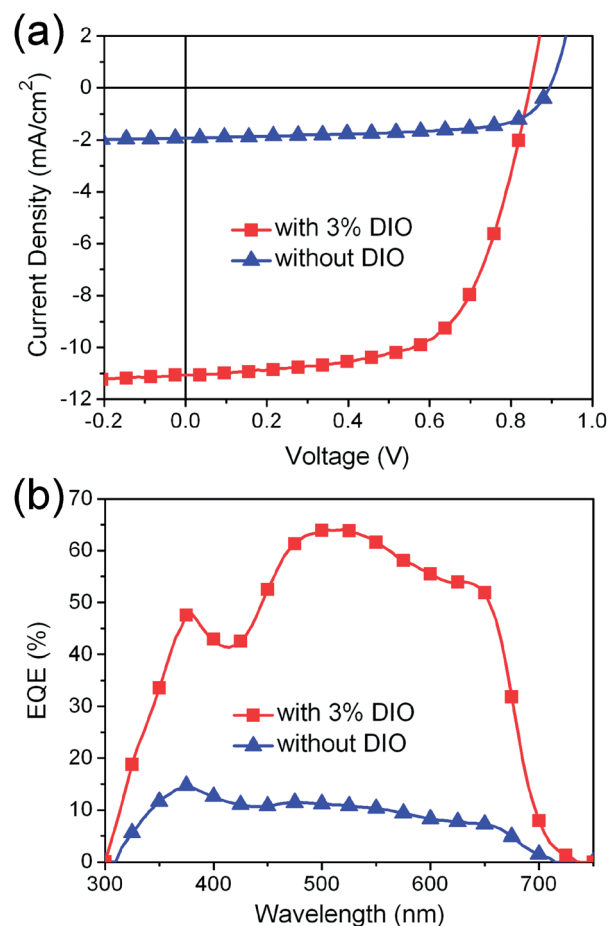


Fig. 2 (a) J - V curves for **PSeTPTI**/PC₇₁BM solar cells; (b) EQE spectra.

3 vol% 1,8-diiodooctane (DIO) gave the best result (see ESI†). The best device afforded a PCE of 6.04%, with a V_{oc} of 0.85 V, a J_{sc} of 11.10 mA cm^{-2} , and a FF of 64%. DIO addition greatly increases photocurrent by reducing domain size and increasing D-A interfaces in the active layer.¹⁴ External quantum efficiency (EQE) spectra indicate that the device with 3 vol% DIO exhibits much higher EQE values than the device without DIO. The integrated currents from EQE curves for the devices without and with DIO are 1.87 and 10.61 mA cm^{-2} , respectively, which consist with the J_{sc} values from J - V measurements (Fig. 2).

Bottom-gate and bottom-contact organic field-effect transistors (OFETs) were fabricated to explore the charge-transporting property of **PSeTPTI** film. As shown in Fig. 3, the devices show p -type behavior with typical transfer and output curves. **PSeTPTI**-based OFET exhibited a high hole mobility of $0.26 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with a large on/off current ratio of 1.89×10^8 and a low threshold voltage of -6.51 V. In the annealing temperature range of 20–160 °C, the polymer showed similar mobility (Fig. S3†). The high mobility of **PSeTPTI** accounts for its good J_{sc} and FF in solar cells. X-ray diffraction (XRD) pattern of **PSeTPTI** films shows two diffraction peaks at $2\theta = 4.46^\circ$ and 25.12° , respectively (Fig. S4†). The primary peak at 4.46° corresponds to an interlayer d -spacing of 19.80 \AA , and the peak at 25.12° corresponds to a d -spacing of 3.54 \AA for π - π stacking. The lamellar structures existing in **PSeTPTI** film lead to its high mobility.

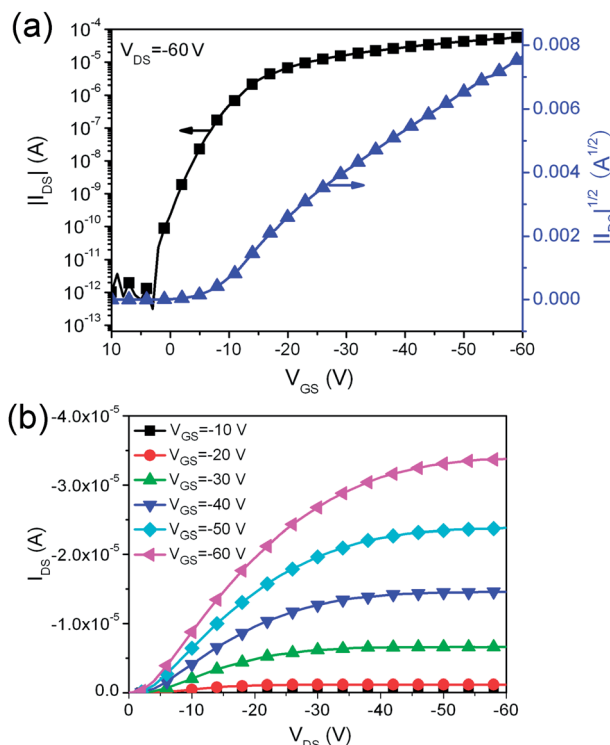


Fig. 3 (a) Transfer and (b) output curves for PSeTPTI-based OFETs. Device dimension: channel length (L) = 50 μm ; channel width (W) = 1400 μm .

In summary, a D–A conjugated polymer, **PSeTPTI**, based on a pentacyclic acceptor unit, TPTI, and selenophene donor unit, was developed. The optical bandgap of **PThTPTI** was decreased successfully by replacing thiophene unit with selenophene unit. **PSeTPTI** possesses good solubility, excellent thermal stability, narrow optical bandgap, low-lying HOMO energy level, and high mobility. **PSeTPTI**/PC₇₁BM solar cells demonstrate a PCE of 6.04%, which is the highest efficiency for the D–A copolymers using selenophene as the donor unit.

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