

Supporting Information

An efficient selenophene-containing conjugated copolymer for organic solar cells

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1. General characterization

All reagents were purchased from Alfa Aesar Co., Aladdin Co., J&K Co. and other commercial suppliers. ^1H and ^{13}C NMR spectra were measured with a Bruker Avance-400 spectrometer. Absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Gel permeation chromatography (GPC) measurements were performed on a Waters 1515 series GPC coupled with UV-vis detector using tetrahydrofuran as eluent and polystyrenes as standards. Thermogravimetric analysis was measured by a Perkin-Elmer Diamond TG/DTA thermal analyzer under nitrogen. Cyclic voltammetry was conducted on a Shanghai Chenhua CHI620D voltammetric analyzer under argon in an anhydrous acetonitrile solution of tetra-*n*-butylammonium hexafluorophosphate (0.1 M). A glassy-carbon electrode was used as the working electrode, a platinum-wire was used as the counter electrode, and a Ag/Ag⁺ electrode was used as the reference electrode. **PSeTPTI** was coated on the surface of glassy-carbon electrode and all potentials were corrected against Fc/Fc⁺. X-ray diffraction (XRD) of thin films was performed in the reflection mode using Cu K α radiation (40 kV, 200 mA) on a 2 kW Rigaku D/max-2500 X-ray diffractometer.

2. Device fabrication and measurements

Solar cells

Patterned ITO glass with a sheet resistance of 15 Ω sq⁻¹ was ultrasonically cleaned using detergent, distilled water, acetone, isopropanol sequentially and then given UV-ozone treatment. A 30 nm thick poly(3,4-ethylenedioxythiophene)-polystyrenesulfonate (PEDOT:PSS, CleviosTM P VP Al 4083) layer was formed on ITO substrates by spin coating an aqueous dispersion onto ITO glass (4000 rpm for 30 s). PEDOT:PSS coated substrates were dried at 150 °C for 10 min. A **PSeTPTI/PC₇₁BM** blend (1:1 w/w, 16 mg/mL) in a mixed solvent (CB/CF, 4/1, v/v) with 3 vol% DIO was spin-coated onto PEDOT:PSS layer (1200 rpm for 60 s). The thicknesses of the active layers (130-140 nm) were measured by KLA Tencor D-120 profilometer. Finally, Ca (~10 nm) and Al

(~100 nm) were thermally evaporated under a shadow mask (pressure ca. 10^{-4} Pa). The effective area for the devices is 4 mm^2 . J - V curves were measured with a computerized Keithley 2420 SourceMeter. Device characterization was done in air using a Xenon-lamp-based solar simulator (Newport, Oriel 91159A, 150 W, AM 1.5G, 100 mW/cm^2). The illumination intensity of solar simulator was determined using a monocrystalline silicon solar cell (Oriel 91150, $2 \times 2 \text{ cm}$) calibrated by NREL. The external quantum efficiency (EQE) was measured by a QE-R3011 measurement system (Enli Technology, Inc.).

Organic field-effect transistors

Organic field-effect transistors (OFETs) were fabricated using bottom-gate and bottom-contact geometry. Heavily doped silicon wafers with a 300 nm thick SiO_2 (10 nF/cm^2) served as the bottom gate electrode and dielectric layer, respectively. Au source/drain electrodes (30 nm thick) were sputtered and patterned by a lift-off technique. The device channel lengths varied from 5 to $50 \mu\text{m}$, and the channel width was maintained at 1.4 mm . SiO_2 surface was treated with octadecyltrichlorosilane (OTS) at $120 \text{ }^\circ\text{C}$ in a vacuum oven. Then the substrates were rinsed successively with heptane, ethanol, and chloroform, keeping a self-assembled OTS monolayer. **PSeTPTI** in a mixed solvent (CB/CF, 4/1, v/v, 10 mg/mL) was spin-coated onto the substrates (2000 rpm for 60 s). The devices were annealed at different temperatures for 10 minutes. OFET characterization was performed using a Keithley 4200 system. All the spin coating, annealing, and characterization were conducted in a N_2 glovebox.

The field-effect mobility was calculated using the following equation:

$$I_{DS} = \left(\frac{WC_i}{2L} \right) \mu (V_{GS} - V_T)^2$$

where I_{DS} is the drain-source current, W and L are the channel width ($1400 \mu\text{m}$) and length ($50 \mu\text{m}$), respectively, C_i is the capacitance per unit area for the insulation layer (SiO_2 , 10 nF/cm^2), μ is the field-effect mobility, V_{GS} and V_T are the gate and threshold voltages, respectively. μ was calculated from the linear fit of $(I_{DS})^{1/2}$ vs V_{GS} . V_T was estimated as the X-intercept of the linear section of $(I_{DS})^{1/2}$ - V_{GS} plot.

3. Synthetic procedures

All reactions dealing with air- or moisture-sensitive compounds were carried out using standard Schlenk techniques. 2,8-Dibromo-4,10-bis(2-hexyldecyl)thieno[2',3':5,6]pyrido[3,4-g]thieno[3,2-c]isoquinoline-5,11(4*H*,10*H*)-dione (**TPTI-Br**)¹ and 2,5-bis(trimethylstannyl)selenophene² were prepared according to literatures.

Poly{2,5-selenophene-alt-2,8-(4,10-bis(2-hexyldecyl))thieno[2',3':5,6]pyrido[3,4-g]thieno[3,2-c]isoquinoline-5,11(4*H*,10*H*)-dione} (PSeTPTI). TPTI-Br (127 mg, 0.14 mmol) and 2,5-bis(trimethylstannyl)selenophene (62 mg, 0.14 mmol) were dissolved in 20 mL toluene, and the solution was flushed with argon for 15 min, then 9 mg Pd(PPh₃)₄ was added into the solution. The mixture was flushed again with argon for 20 min. The reaction solution was heated to reflux for 24 h. Then the solution was cooled to room temperature and added dropwise into 150 mL methanol. The precipitate was collected and further purified by Soxhlet extraction using methanol, hexane, and chloroform in sequence. The chloroform fraction was concentrated and added dropwise into methanol. Subsequently, the precipitate was collected and dried under vacuum overnight to give **PSeTPTI as a dark blue solid (120 mg, 97%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 7.98 (br, 2H), 6.35 (br, 4H), 4.87 (br, 4H), 1.51-0.86 (br, 62H). Elemental analysis (%) calcd for C₅₂H₇₂N₂O₂S₂Se: C, 69.38; H, 8.06; N, 3.11. Found: C, 68.51; H, 8.07; N, 2.97.**

4. TGA

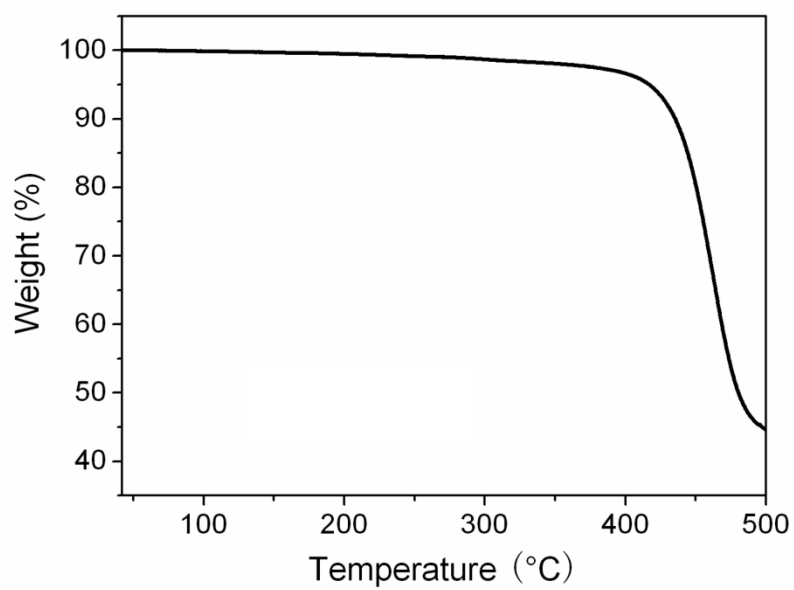


Figure S1 TGA curve of **PSeTPTI**.

5. CV

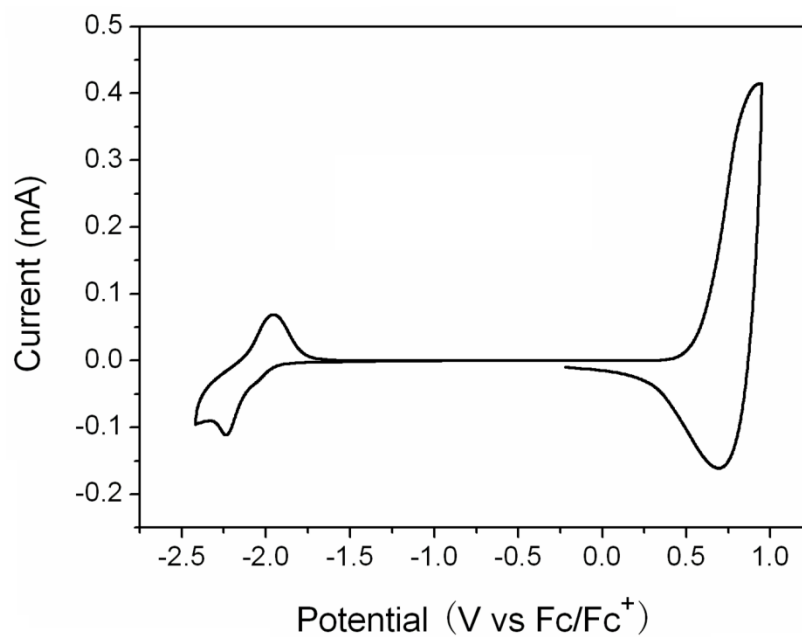


Figure S2 Cyclic voltammogram of **PSeTPTI**.

6. Device optimization

Table S1 Optimization of the D/A ratio for **PSeTPTI:PC₇₁BM** solar cells^a.

D:A	V_{oc}	J_{sc}	FF	PCE
[w/w]	[V]	[mA/cm ²]	[%]	[%]
1:0.8	0.84	11.19	55	5.16
1:1.0	0.84	11.00	62	5.72
1:1.2	0.84	10.38	61	5.31
1:1.4	0.83	10.31	60	5.14
1:1.6	0.82	9.67	60	4.79
1:1.8	0.80	8.83	57	4.02

^a Blend solution: 16 mg/mL in a mixed solvent (CB/CF, 4/1, v/v) with 3 vol% DIO; spin-coating: 1000 rpm for 60 s.

Table S2 Optimization of the active layer thickness for **PSeTPTI:PC₇₁BM** solar cells^a.

Thickness	V_{oc}	J_{sc}	FF	PCE
[nm]	[V]	[mA/cm ²]	[%]	[%]
182	0.83	11.57	55	5.29
168	0.83	11.43	60	5.70
155	0.85	11.21	62	5.89
139	0.85	11.10	64	6.04
126	0.86	10.35	62	5.52

^a D/A ratio: 1:1, w/w; blend solution: 16 mg/mL in a mixed solvent (CB/CF, 4/1, v/v) with 3 vol% DIO.

7. OFET measurements

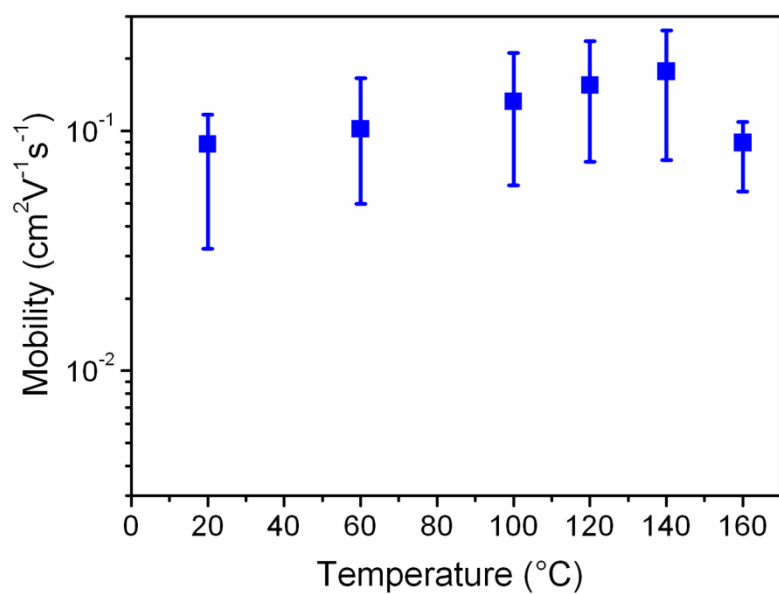


Figure S3 Effect of annealing temperature on hole mobility of **PSeTPTI**.

8. XRD

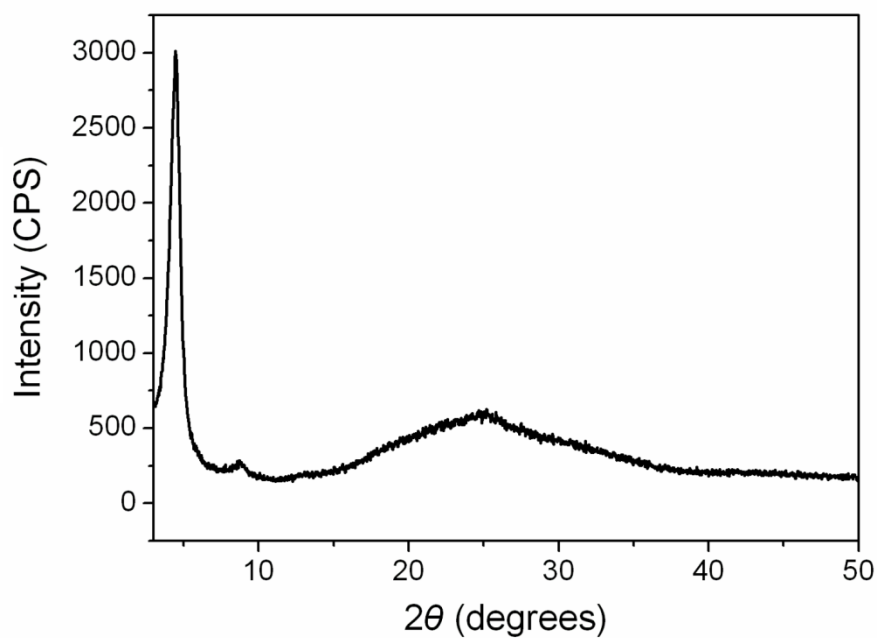


Figure S4 XRD pattern for as-cast **PSeTPTI** film.

References

- [1] J. Cao, Q. Liao, X. Du, J. Chen, Z. Xiao, Q. Zuo and L. Ding, *Energy Environ. Sci.*, 2013, **6**, 3224.
- [2] (a) S. Haid, A. Mishra, C. Urich, M. Pfeiffer and P. Bäuerle, *Chem. Mater.*, 2011, **23**, 4435; (b) S. Haid, A. Mishra, M. Weil, C. Urich, M. Pfeiffer and P. Bäuerle, *Adv. Funct. Mater.*, 2012, **22**, 4322.