Supporting Information for:

High-Performance Solution-Processed Non-Fullerene Organic Solar Cells based on Selenophene-Containing Perylene Bisimide Acceptor

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Methods

Materials: PDBT-T1 was synthesized according to our previous report[1]. All chemicals and solvents were purchased from commercial suppliers and used without further purification unless otherwise specified.

Solar cell fabrication and testing: Solar cells were fabricated in a conventional device configuration of ITO/PEDOT:PSS/blend/Ca/Al. ITO substrates were cleaned with detergent, ultrasonicated in deionized water, acetone and isopropanol, subsequently dried in an oven overnight. The glass substrates were treated by UV-Ozone for 20min before use. PEDOT:PSS (Heraeus Clevios P VP A 4083) was spin cast from aqueous solution at 4000 rmp for 40s, and then dried at 140 °C for 10 min in air. PDBT-T1 and SdiPBI-Se was co-dissolved in chlorobenzene with different mass ratios and DIO concentrations (PDBT-T1 concentration is fixed at 8mg/mL). The blend solution was spin cast at 1200 rmp for 40s on top of PEDOT:PSS layer followed by annealed at 100 °C for 5 min in a glove box filled with N_2. A thin Ca layer (10 nm) and Al layer (100 nm) were sequentially evaporated through a shadow mask under vacuum of 5×10^{-6} Pa. The active area is 4.50 mm^2. During the measurement, an aperture with the area of 3.14 mm^2 was used. The optimal blend thickness was ~110 nm, measured on a Bruker Dektak XT profilometer. Current density-voltage *(J-V)* curves were measured in a Keithley 2400 Source Measure Unit. Photocurrent was measured in an Air Mass 1.5 Global (AM 1.5 G) solar simulator (Class AAA solar simulator, Model 94063A, Oriel) with an irradiation intensity of 100 mW cm^{-2}, which was measured by a calibrated silicon solar cell and a readout meter (Model 91150V, Newport). IPCE spectra were performaed in a QEX10 Solar Cell IPCE measurement system (PV measurements, Inc.). Except for the deposition of the PEDOT:PSS layers, all the fabrication processes were carried out inside a controlled atmosphere of nitrogen dry glovebox.

GIWAXS Characterization. GIWAXS measurements were accomplished at PLS-II 9A U-SAXS beamline of the Pohang Accelerator Laboratory in Korea. X-rays coming from the in-vacuum undulator (IVU) were monochromated (E_k = 11.065 KeV, wavelength λ = 1.10994 Å) using a Si(111) double crystal monochromator and focused both horizontally and vertically at the sample position (450 (H) × 60 (V) μm^2 in FWHM @ sample position) using K-B type mirrors system. The GIWAXS sample stage was equipped with a 7-axis motorized stage for the fine alignment of sample, and the incidence angle of X-ray beam was set to be 0.12°-0.14° for PDBT-T1, SdiPBI-Se polymer films and blended films. GIWAXS patterns were recorded with a 2D CCD detechtor (Rayonix SX165) and X-ray irradiation time was 6-9 s, dependent on the saturation level of the detector. Diffraction angles were calibrated using a sucrose standard (Monoclinic, P21, a = 10.8631 Å, b = 8.7044 Å, c = 7.7624 Å, β = 102.938°) and the sample-to-detector distance was ≈ 231 mm. Samples for GIWAXS measurements were prepared by spin-coating PDBT-T1, SdiPBI-Se and blend solutions on top of the Si substrates.

TAS measurements. TAS system is described in our previous publications[2-4], however the pump beam is altered to go through an optical parametric amplifier (Spectra Physics OPA 800) instead of a frequency doubling crystal to produce either 488 nm or 643 nm femtosecond pulses (pulse width 150 fs). The pump intensity can be varied in the range of 1-90 $\mu J/cm^2$. Thin film samples were kept in a cryostat chamber (Janis ST-100) with a vacuum level of ~4×10^{-6} mbar at room temperature.

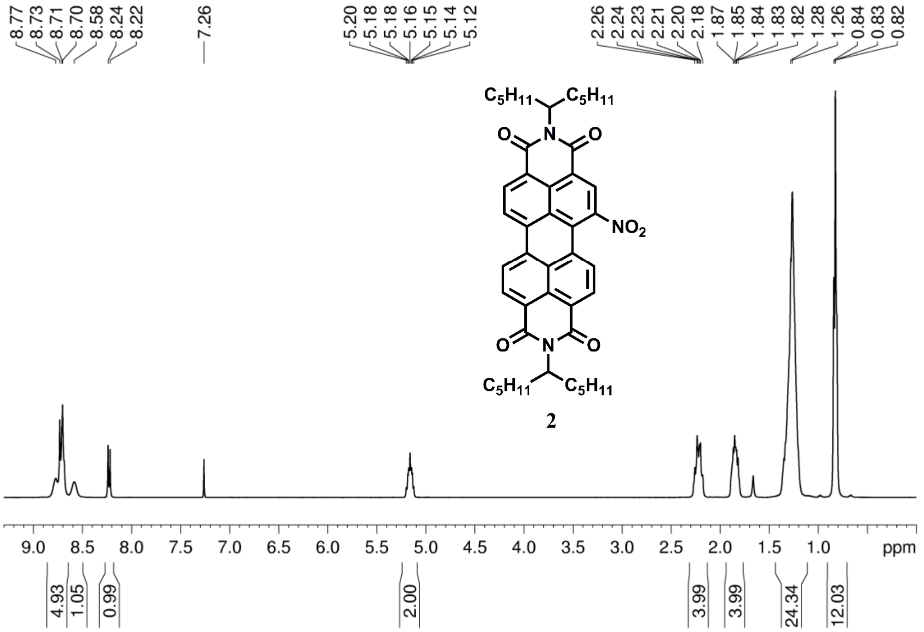
Synthesis of SdiPBI-Se

1-nitroperylene bisimide (2): A solution of perylene bisimide (**1**, 1g, 1.43 mmol) in CH_2Cl_2 was cooled in ice bath. Then a diluted solution of fuming nitric acid (3ml) in CH_2Cl_2 (5ml) was added drop by drop over a period of 15min. The reaction mixture was stirred at 0 °C for additional 2h. Next, the cooled mixture was poured into methanol and the precipitate was collected by vacuum filtration, washed with water, dried and purified by column chromatography on silica gel (petroleum ether /CH_2Cl_2, 1:1 v/v) to afford compound **2** as an dark red solid (1.06g, 98 %) . ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.77-8.70 (m, 5H), 8.58 (s, 1H), 8.24-8.22 (d, *J* = 8.0 Hz, 1H), 5.20-5.12 (m, 2H), 2.26-2.18 (m, 4H), 1.87-1.82 (m, 4H), 1.28-1.26 (m, 24H), 0.84-0.82 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.91, 162.87, 147.71, 135.49, 132.94, 131.60, 129.50, 129.37, 129.12, 127.92, 127.53, 126.65, 126.47, 124.47, 124.01, 55.26, 54.97, 32.28, 32.19, 31.70, 31.67, 26.58, 26.56, 22.69, 22.52, 22.35, 14.00; HRMS (MALDI(N), 100%): calcd (%) for $C_{46}H_{53}N_3O_6$: 743.39399; found, 743.39401.

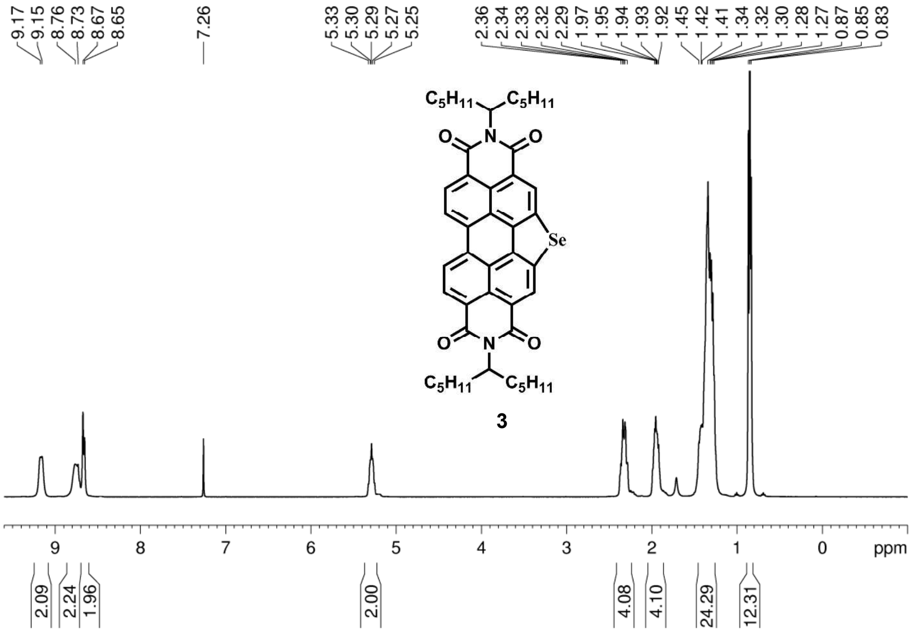
[1,12-*b*,*c*,*d*]selenophene perylene bisimide (3): Selenium (8.74 mmol) was dissolved in *N*-methylpyrrolidone (NMP, 35 mL, 70°C), then 1-nitroperylene bisimide **2** (650mg,0.874mmol) was added under argon. The mixture was heated to 190 °C with vigorous stirring for 3 h until the starting material could not be detected by TLC. Upon cooling to room temperature, the reaction mixture was poured into 1L of 2 M HCl, then the precipitate was collected by vacuum filtration, washed with water, dried, and purified by column chromatography on silica gel (petroleum ether /CH_2Cl_2, 1:1 to 1:2 v/v) to give **3**. Yellow-brown needle; yield: 542mg, 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.17-9.15 (sd, *J* = 8.0 Hz, 2 H), 8.76-8.73 (sd, *J* = 12.0 Hz, 2 H), 8.67-8.65 (d, *J* = 8.0 Hz, 2 H), 5.33-5.25 (m, 2 H), 2.36-2.29 (m, 4 H), 1.97-1.92 (m, 4 H), 1.45-1.27 (m, 24 H), 0.87-0.83 (m, 12 H); ^{13}C NMR (100 MHz, CDCl3): δ = 164.95, 164.68, 163.81, 140.36, 133.96, 133.04, 130.00, 129.35, 126.57, 126.34, 125.41, 124.16, 122.81, 121.85, 55.02, 32.44, 31.80, 31.72, 26.77, 26.62, 22.61, 22.52, 14.04; HRMS (MALDI (N), 100%): calcd (%) for $C_{46}H_{52}N_2O_4Se$: 776.31028; found, 776.31000.

[1,12-*b*,*c*,*d*]selenophene-6-bromoperylene bisimide (4): A mixture of **3** (1g) and bromine (18.66 g, 0.116 mol) in 60 mL of dichloromethane was stirred at room temperature in a closed round-bottom flask for 5h. The excess of bromine was removed by air bubbling, and the solvent was removed under vacuum. The crude product was purified by silica gel column chromatography with petroleum ether /CH_2Cl_2 as an eluent (1:1) to give **4**. Red solid; yield: 1.06g, 96%. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 9.88-9.86 (d, *J* = 8.0 Hz, 1 H), 9.09 (s, 2 H), 8.86 (s, 1 H), 8.65 (s, 1 H), 5.32-5.27 (m, 2 H), 2.36-2.31 (m, 4 H), 2.00-1.96 (m, 4 H), 1.47-1.31 (m, 24 H), 0.89-0.86 (m, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.24, 163.26, 140.34, 139.61, 137.64, 132.80, 132.48, 132.17, 130.44, 129.10, 126.74, 126.10, 125.73, 124.95, 124.34, 122.62, 122.00, 120.74, 55.28, 55.10, 32.42, 32.36, 31.82, 31.80, 31.72, 26.85, 22.66, 14.08; HRMS (MALDI (N), 100%): calcd (%) for $C_{46}H_{51}BrN_2O_4Se$: 854.22059; found, 854.21992.

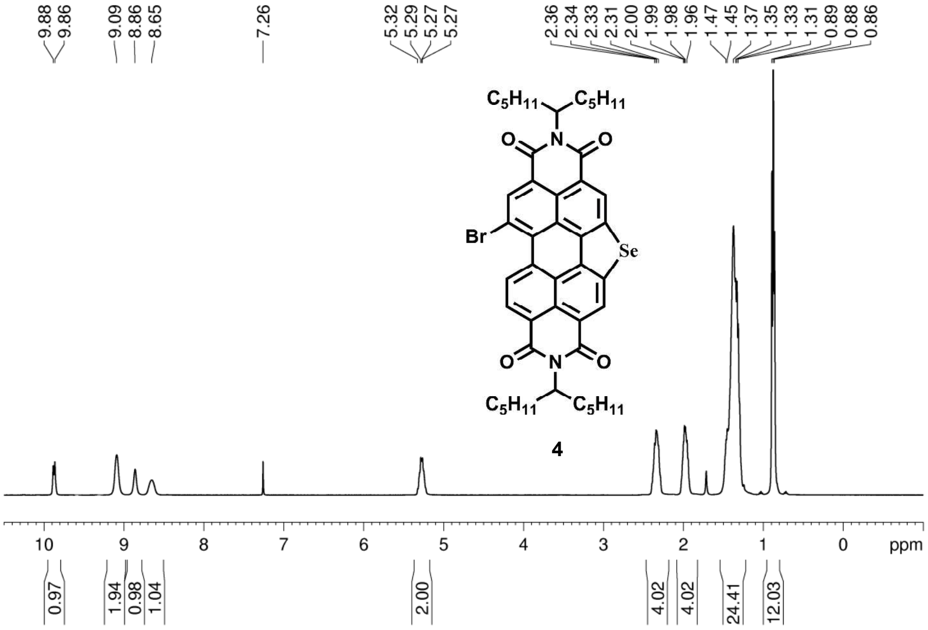
SdiPBI- Se (5): A Schlenk flask was charged with **4** (350mg), zinc powder (157mg, 2.4 mmol), tris(dibenzylideneacetone)dipalladium(0) (46mg, 0.05mmol) and dry DMF (60 ml) under argon. The mixture was heated to 55 ºC with vigorous stirring for 1 h. The cooled mixture was poured into water, and the precipitate was collected by vacuum filtration, washed with water, dried, and purified by column chromatography on silica gel with petroleum ether/CH_2Cl_2 (2:1 to 1:1) as an eluted to afford **5**. Orange solid; yield: 278mg, 87.6%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.61-9.56 (d, *J* = 20.0 Hz, 2 H), 9.47-9.41 (d, *J* = 24.0 Hz, 2 H), 8.72-8.68 (d, *J* = 16.0 Hz, 2 H), 8.25-8.23 (d, *J* = 8.0 Hz, 2 H), 8.19-8.15 (m, 2 H), 5.31-5.10 (m, 4 H), 2.23-2.20 (m, 8 H), 1.96-1.79 (m, 8 H), 1.27 (m, 48 H), 0.83-0.77 (m, 24 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.04, 164.35, 163.86, 163.23, 141.46, 140.81, 134.77, 134.43, 133.50, 132.27, 131.09, 130.47, 129.75, 129.11, 126.80, 126.74, 126.64, 126.63, 125.59, 123.47, 122.48, 55.25, 54.89, 32.55, 32.28, 31.74, 31.65, 26.69, 26.50, 22.53, 22.46, 14.02, 13.94; HRMS (MALDI(N), 100%): calcd (%) for $C_{92}H_{102}N_4O_8Se_2$: 1550.60654; found, 1550.60703.



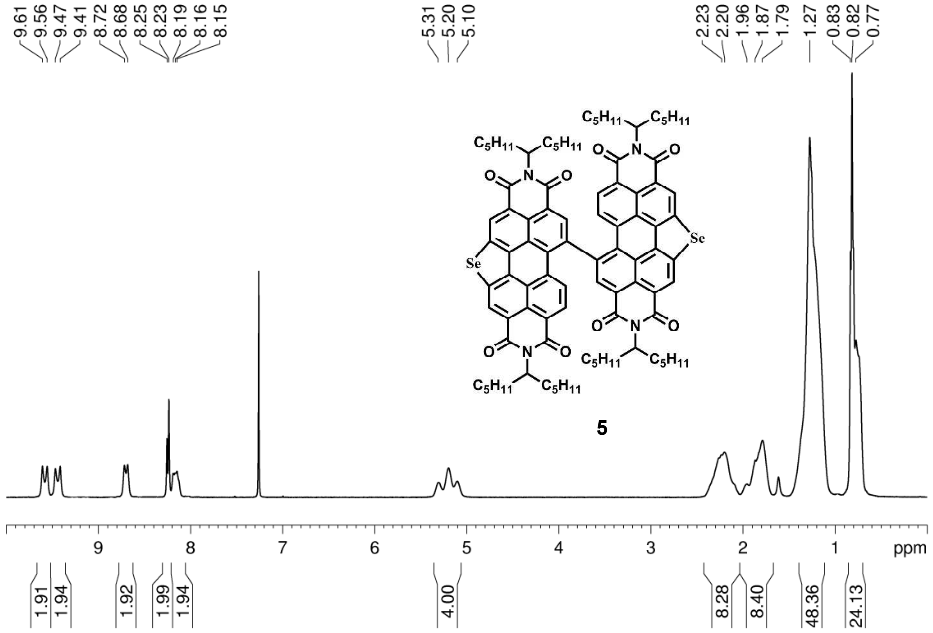
^{1}H NMR Spectrum of **2**.



^{1}H NMR Spectrum of **3**.



^{1}H NMR Spectrum of **4**.



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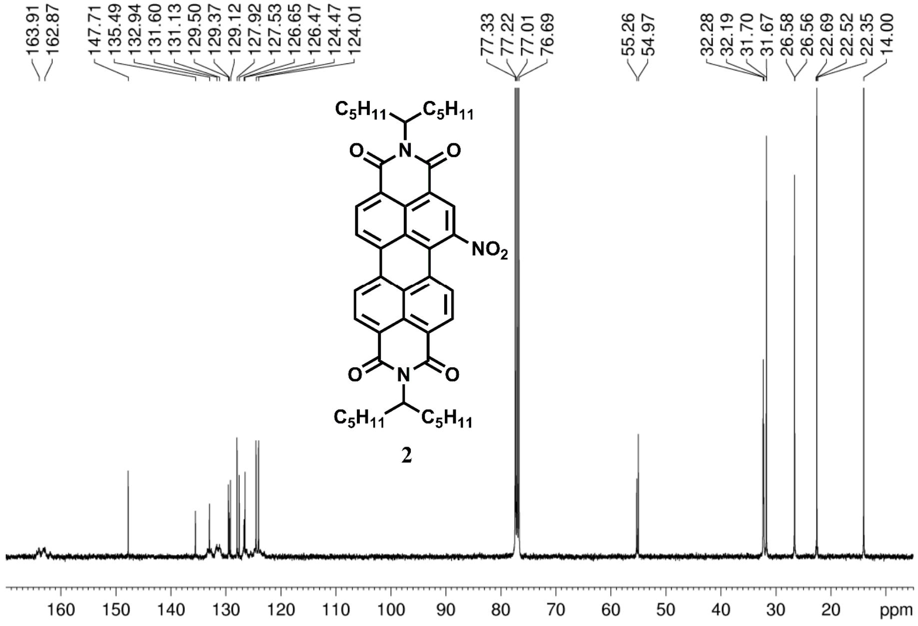
^{1}H NMR Spectrum of **5**.



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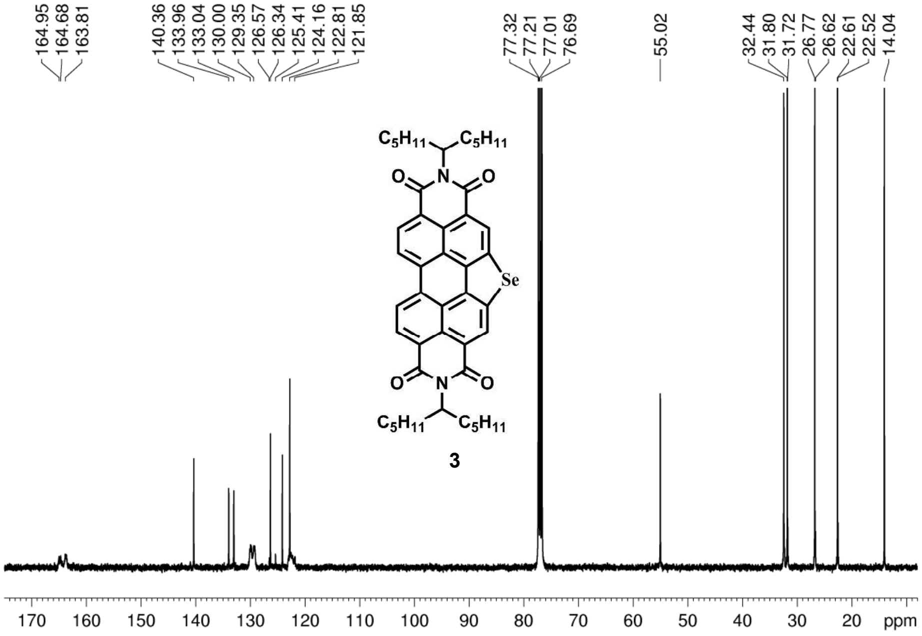
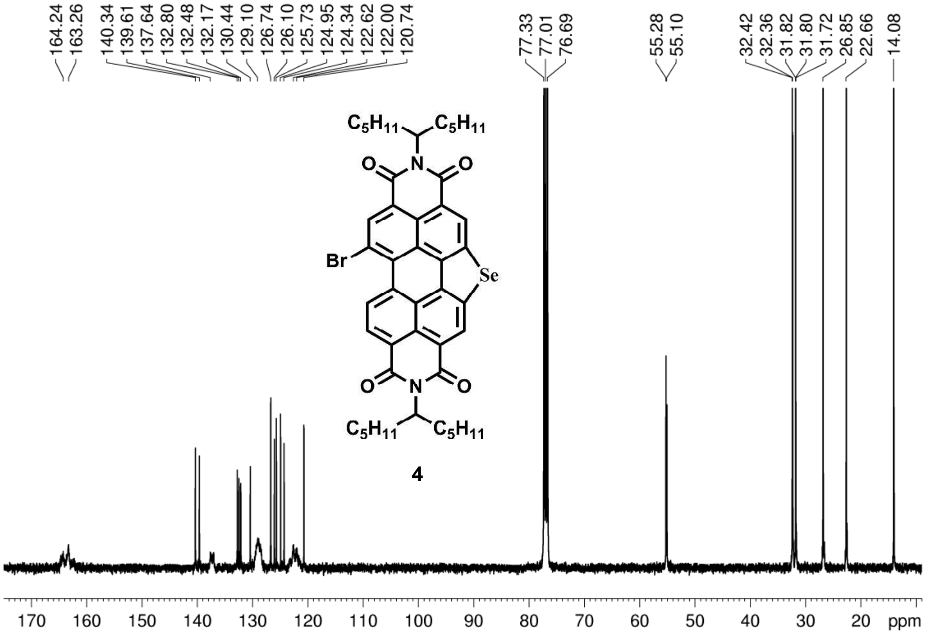
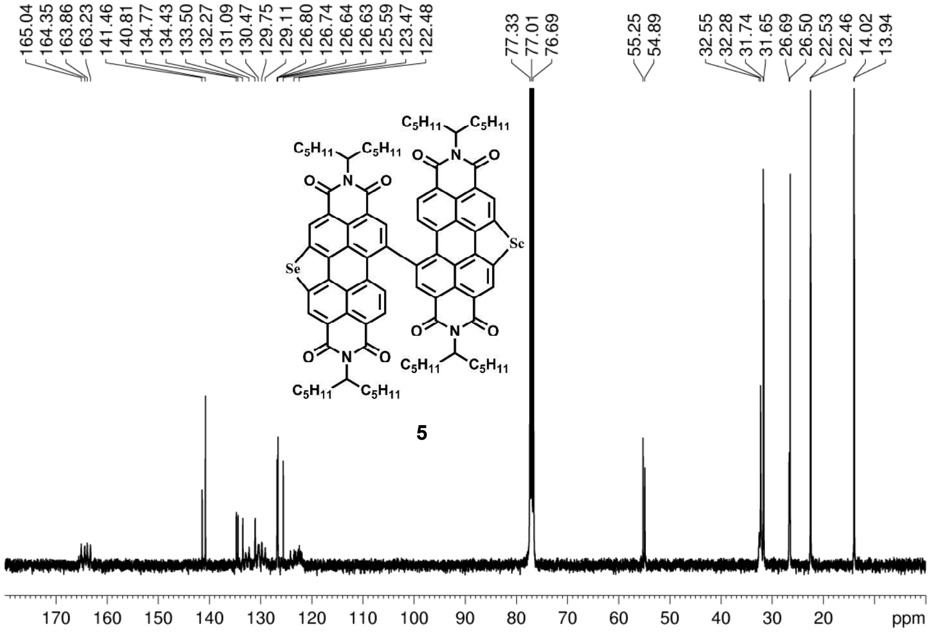
^{13}C NMR Spectrum of **2**.



^{13}C NMR Spectrum of **3**.



^{13}C NMR Spectrum of **4**.



^{13}C NMR Spectrum of **5**.

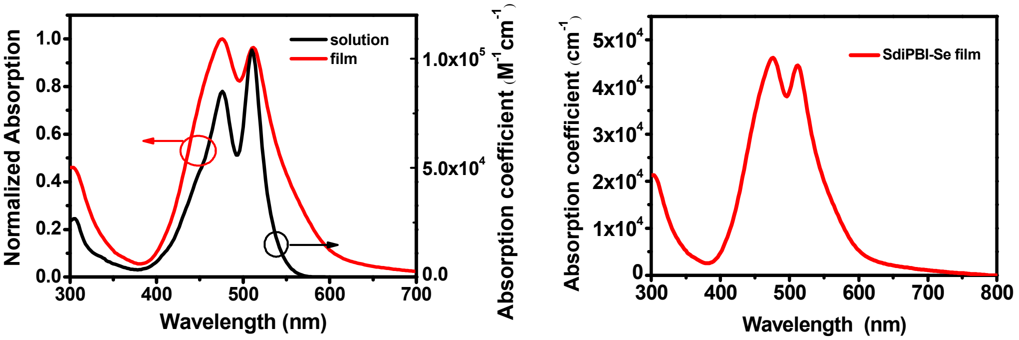


Figure S1. UV-vis absorption spectra of SdiPBI-Se in solution and solid state.

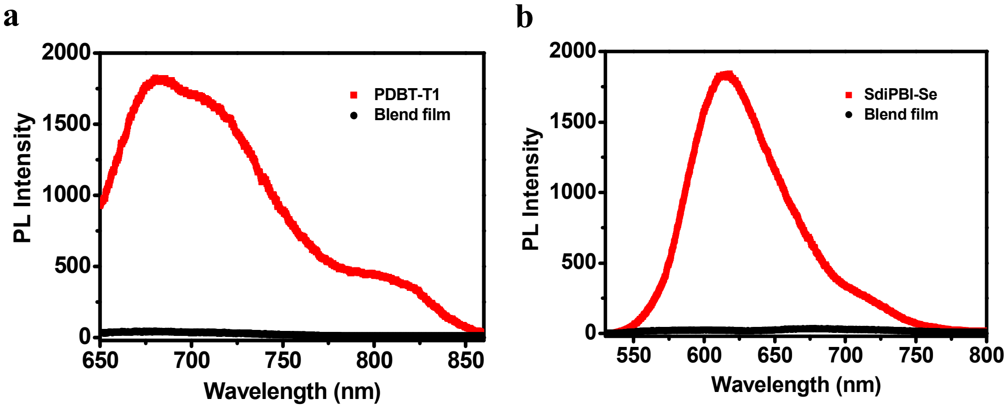


Figure S2. The photoluminescent properties of (a) PDBT-T1 (excitation at 648 nm) and (b) SdiPBI-Se (excitation at 522 nm) and PDBT-T1:SdiPBI-Se blend films (1:1, w/w) (excitation at 648 and 522 nm, respectively).

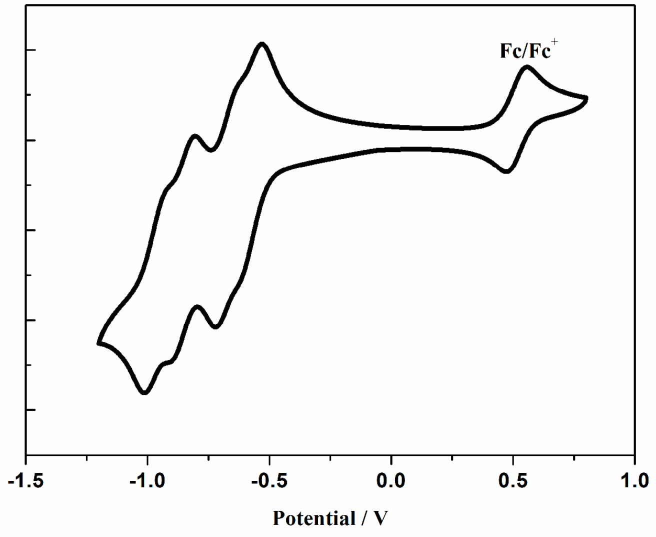


Figure S3. Cyclic voltammograms of SdiPBI-Se in solution.

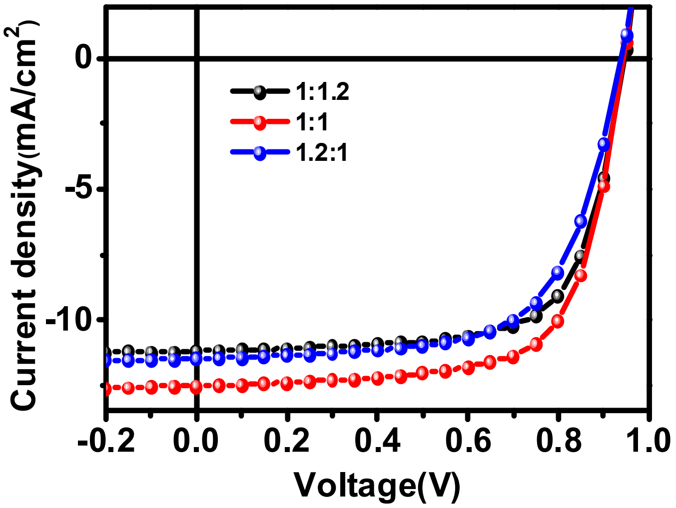


Figure S4. *J-V* curves of non-fullerene solar cells with different PDBT-T1:SdiPBI-Se blend ratios (0.25% DIO).

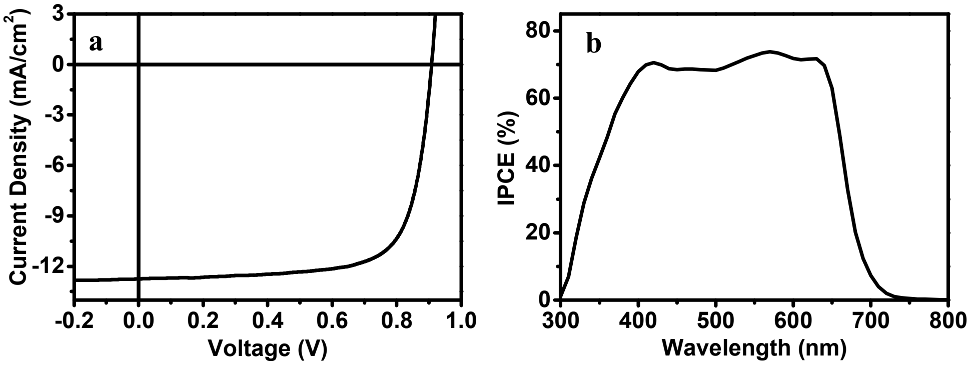


Figure S5. (a) *J-V* curves of PDBT-T1:PC$_{70}$BM solar cells with 3% DIO (CB as the host solvent) and (b) the corresponding IPCE spectra. The device shows a high PCE of 8.47%, with V$_{oc}$ of 0.91 V, J$_{sc}$ of 12.75 mA cm^{-2} and FF of 73.1%.

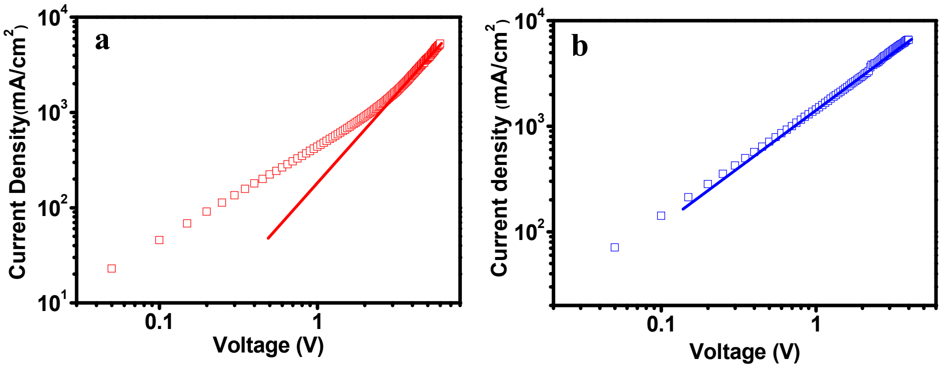


Figure S6. The experimental current density-applied voltage (*J*-*V*) characteristics for (a) hole-only device, and (b) electron-only device for PDTB-TI:SdiPBI-Se blend films. The hole mobility was calculated to be 3.6 × 10^{-3} cm^2 V^{-1} s^{-1} and the electron mobility is 4.8 ×10^{-3}cm^2 V^{-1} s^{-1}.

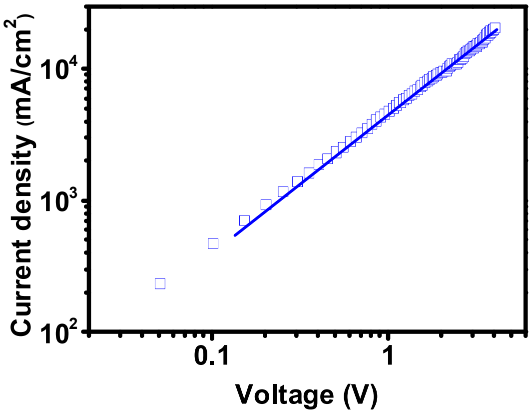


Figure S7. The experimental current density-applied voltage (*J*-*V*) characteristics for SdiPBI-Se neat film.

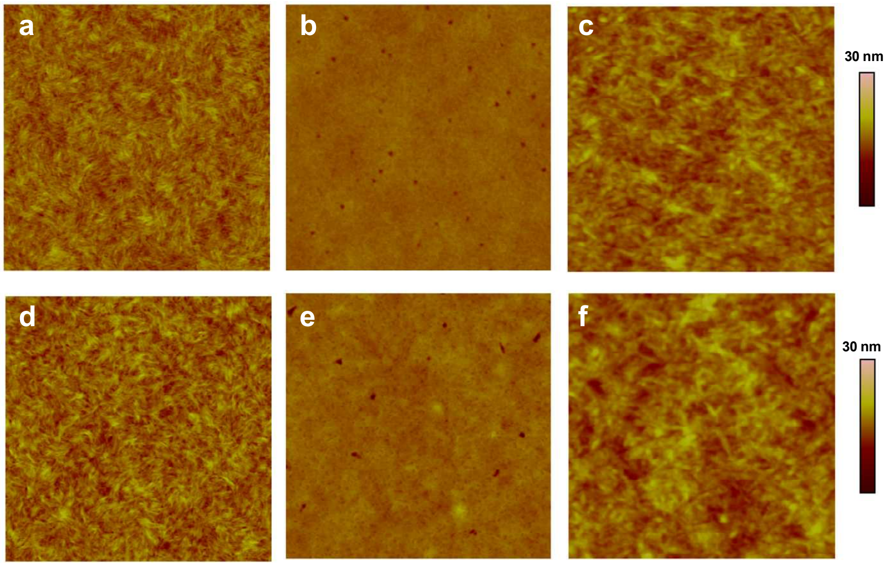


Figure S8. AFM height images (2 × 2 μm) of PDBT-T1 neat film without (a) and with (d) 0.25% DIO, SdiPBI-Se neat film without (b) and with (e) 0.25% DIO, PDBT-T1:SdiPBI-Se blend film without (c) and with (f) 0.25% DIO.

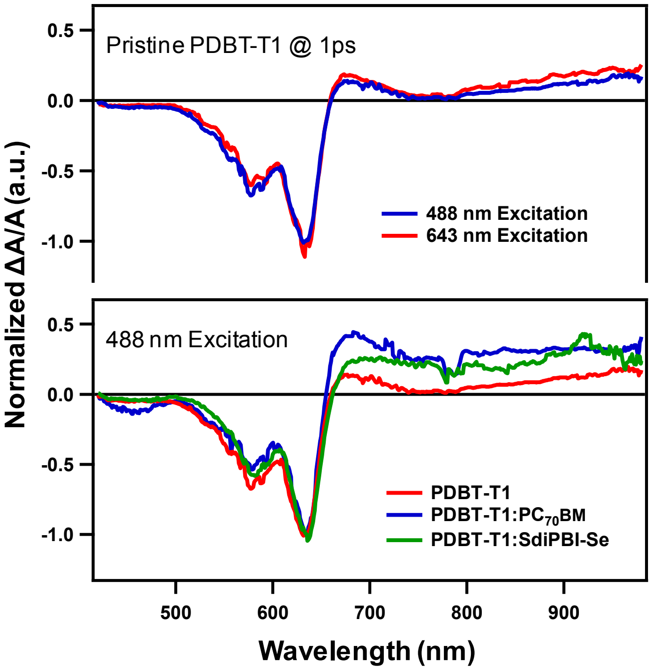


Figure S9. The TAS spectra comparison at delay time of 1 ps and excitation wavelength of 488 nm or 643 nm for pristine PBDT-T1, PBDT-T1:SDiPBI-Se and PBDT-T1: PC$_{70}$BM thin films.

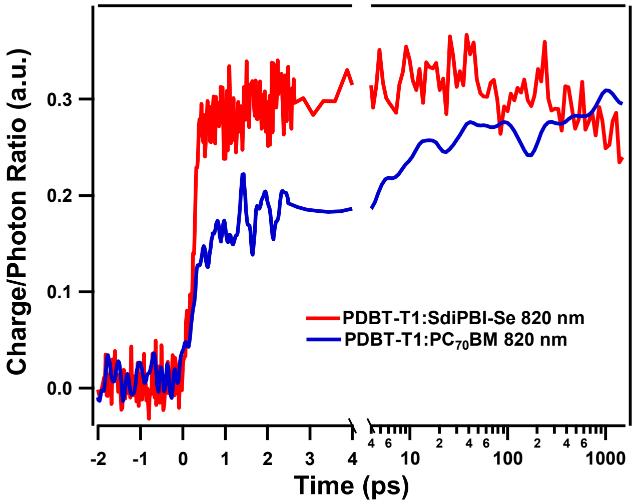


Figure S10. Charge population dynamics of PBDT-T1:SdiPBI-Se and PBDT-T1:PC$_{70}$BM thin films at excitation intensity of 3 μJ/cm^2 (charge absorption signal at 820 nm normalized by photobleaching peak intensity)

Table S1. Summary of device parameters of PDBT-T1:SdiPBI-Se solar cells with 0.25% DIO additive with different blend ratios under simulated AM 1.5G (100 mW cm^{-2}).

D/A ratio	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE[a] (%)
1:1.2	0.943±0.001	11.09±0.11	69.5±0.2	7.27±0.09
1:1	0.947±0.009	12.48±0.09	69.7±0.8	8.23±0.08
1.2:1	0.940±0.001	11.28±0.16	66.0±0.6	6.98±0.06

[a] The average PCE value was calculated from six devices for each condition.

Table S2. Summary of device parameters of PDBT-T1:SdiPBI-Se solar cells with different active layer thicknesses under simulated AM 1.5G (100 mW cm^{-2}).

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm2]	FF [%]	PCE[a] [%]
110	0.947±0.009	12.48±0.09	69.7±0.8	8.23±0.08
130	0.938±0.004	12.62±0.03	67.8±0.1	8.03±0.04
150	0.936±0.004	12.35±0.14	67.6±0.2	7.81±0.08
170	0.932±0.003	12.24±0.07	63.2±0.2	7.21±0.07

[a] The average PCE value was calculated from six devices for each condition.

References

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