Supporting Information

A Selenophene Substituted Double-cable Conjugated Polymer Enables Efficient Single-Component Organic Solar Cells

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1. Materials and measurements

The synthetic procedures were performed under argon atmosphere. Commercial chemicals (from Energy Chemical, sigma-Aldrich, TCI, Innochem and JK Chemical) were used as received. The polymer PBDBPBI-Se was synthesized by the route as Scheme 1 shows, compound M1 and M3 were prepared according to literature procedures[1, 2]. The double-cable polymer PBDBPBI-S and donor polymer PBDB-S and PBDB-Se were prepared by the literature.[3]

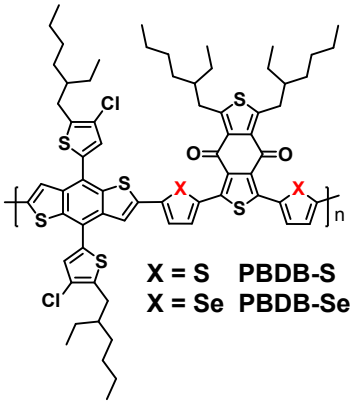

Figure S1. Chemical structures of the donor polymer PBDB-S and PBDB-Se.

^{1}H-NMR and ^{13}C-NMR spectra were recorded at 400 MHz and 100 MHz on a Bruker AVANCE spectrometer with tetramethylsilane (TMS) as the internal standard. The Molecular weight was determined with GPC at 140 °C on a PL-GPC 220 system using a PL-GEL 13 μm Olexis column and *o*-DCB as the eluent against polystyrene standards. The two-dimensional (2D) GIWAXS/MAXS experiments were carried out on a GANESHA 300XL+ system from JJ X-ray in the X-ray lab at DSM Materials Sciences Center (DMSC). The instrument is equipped with a Pilatus 300K detector, with pixel size of 172 μm × 172 μm. The X-ray source is a Genix 3D Microfocus Sealed Tube X-Ray Cu-source with integrated Monochromator (multilayer optic "3D version" optimized for SAXS) (30 W). The wavelength used is λ = 1.5418 Å. The detector moves in a vacuum chamber with sample-to-detector distance varied between 0.115 m and 1.47 m depending on the configuration used, as calibrated by using silver behenate (d_{001} = 58.380 Å). The minimized background scattering plus high-performance detector allows for a detectable q-range varying from 3 $\times 10^{-3}$ to 3 Å^{-1} (0.2 to 210 nm). The sample was placed vertically on the goniometer and tilted to a

glancing angle of 0.2° with respect to the incoming beam. A small beam was used to get a better resolution. The primary slits have a size of 0.3 (horizontal) × 0.5 mm (vertical), and the guard slits have a size of 0.1 (horizontal) × 0.3 (horizontal) mm. The accumulation time was 6 h for each measurement. GIMAXS scattering curves (at Yoneda maximum) were obtained by using SAXSGUI program.

2. Synthesis of the monomer and polymer

((5-(5,7-bis(2-ethylhexyl)-4,8-dioxo-3-(5-(trimethylstannyl)selenophen-2-yl)-4H,8H-benzo[1,2-c:4,5-c']dithiophen-1-yl)selenophen-2-yl)dimethylstannyl)methylium (M2)

1,3-bis(2-ethylhexyl)-5,7-di(selenophen-2-yl)-4H,8H-benzo[1,2-c:4,5-c']dithiophene-4,8-dione **(M1)** (272 mg, 0.387 mmol) was dissolved in dry tetrahydrofuran under an inert atmosphere. The solution was cooled down to -78°C by using a liquid ethyl alcohol and then freshly made LDA (0.97 mmol in THF) was added drop-wise. The reaction was stirred at -78 °C for 1h and trimethyltinchloride [$(CH_3)_3SnCl$, 1.16 mmol, 1 M in THF] was subsequently added. The mixture was stirred at room temperature overnight. The reactant was quenched by water, then extracted by diethyl ether (200 mL) and dried over anhydrous Na_2SO_4. After removing solvent, the crude product was purified by recrystallization using ethyl alcohol to obtain **M2** (210 mg, yield 52.7%) as orange solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.03 (d, 2H), 7.54 (d, 2H), 3.32 (t, 4H), 1.78 (s, 2H), 1.36 (m, 16H), 0.97-0.90 (m, 12H), 0.51-0.33 (t, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 178.0, 153.0, 142.5, 137.5, 133.6, 133.1, 41.2, 33.7, 32.9, 28.9, 26.1, 23.0, 14.2, 10.9, 1.0, 0, -7.9. HRMS (MALDI-TOF) m/z: $[M]^+$, Calcd for $C_{40}H_{56}O_2S_2Se_2Sn_2$: 1033.019135, found: 1033.016784.

PBDBPBI-Se

To a degassed solution of monomer **M2** (15.71 mg, 15.27 μmol), **M3** (35.74 mg, 15.27 μmol) in toluene (4 mL) and DMF (0.4 mL), $Pd_2(dba)_3$ (0.42 mg, 0.46 μmol) and PPh_3 (0.48 mg, 1.83 μmol) were added. The mixture was stirred at 115 °C for 24

h, after which it was precipitated in methanol and filtered through a Soxhlet thimble. The polymer was extracted with acetone, hexane, dichloromethane and 1,1,2,2-tetrachloroethane. The solvent was evaporated and the polymer was precipitated in acetone. The polymer was collected by filtering over a 0.45 μm PTFE membrane filter and dried in a vacuum oven to yield PBDBPBI-Se (40.2 mg, 91.36%) as a dark solid. GPC (*o*-DCB, 140 °C): M_n = 47.1 kg mol^{-1}, M_w = 82.4 kg mol^{-1} and PDI = 1.75.

3. OFETs

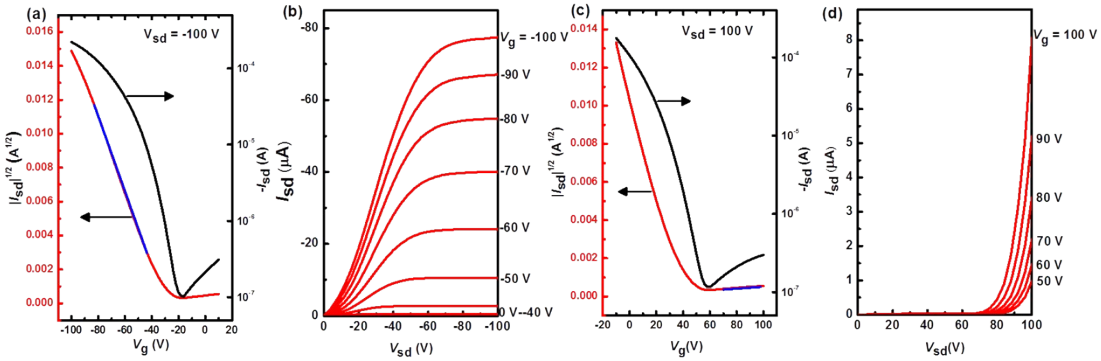

Figure S2. (a, c) Transfer and (b, d) output curves obtained from BGBC FET devices based on PBDBPBI-Se thin films fabricated from *o*-DCB after thermal annealed at 280 °C. The blue lines in the figures were used to calculate (a) hole and (c) electron mobilities.

4. Single-component organic solar cells

Table S1. Characteristics of PBDBPBI-Se based solar cells spin coated from different solution, thickness and different thermal annealing temperature (10 min).

Solvent	TA [°C]	Thickness [nm]	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF	PCE [%]
o-DCB	r. t.	65	5.08	0.90	0.31	1.44
o-DCB/DIO (0.5%)	r. t.	65	5.27	0.92	0.32	1.56
o-DCB/DIO (1%)	r. t.	65	4.39	0.93	0.30	1.23
o-DCB/DIO (0.5%)	r. t.	65	5.27	0.92	0.32	1.56
o-DCB/DIO (0.5%)	150	70	5.67	0.90	0.32	1.64
o-DCB/DIO (0.5%)	230	70	12.68	0.84	0.58	6.25
o-CB/DIO (0.5%)	280	70	12.34	0.80	0.56	5.51

o-CB/DIO (0.5%)	230	80	12.82	0.84	0.55	5.99
o-CB/DIO (0.5%)	230	70	12.68	0.84	0.58	6.25
o-CB/DIO (0.5%)	230	60	11.58	0.84	0.61	5.92
o-CB/DIO (0.5%)	230	50	11.08	0.84	0.63	5.82

Table S2. Photovoltaic performances of 8 devices based on PBDBPBI-Se fabricated from *o*-DCB/DIO (0.5%) without thermal annealing.

No.	J_{sc} [mA/cm^2]	V_{oc} [V]	FF	PCE [%]
1	5.39	0.91	0.34	1.65
2	5.27	0.92	0.32	1.56
3	5.30	0.92	0.32	1.54
4	5.26	0.92	0.32	1.55
5	5.28	0.92	0.32	1.55
6	5.43	0.92	0.33	1.62
7	5.41	0.92	0.33	1.62
8	5.05	0.91	0.33	1.51
average	5.30±0.11	0.92±0.004	0.33±0.007	1.58±0.05

Table S3. Photovoltaic performances of 8 devices based on PBDBPBI-Se fabricated from *o*-DCB/DIO (0.5%) and thermal annealed at 230 °C for 10 min.

No.	J_{sc} [mA/cm^2]	V_{oc} [V]	FF	PCE [%]
1	11.75	0.85	0.61	6.05
2	12.83	0.84	0.56	6.07
3	12.79	0.83	0.57	6.01
4	12.93	0.83	0.57	6.12
5	12.68	0.84	0.58	6.25
6	12.69	0.84	0.58	6.22
7	12.58	0.84	0.58	6.12
8	12.61	0.84	0.58	6.15
average	12.61±0.34	0.84±0.01	0.58±0.01	6.12±0.08

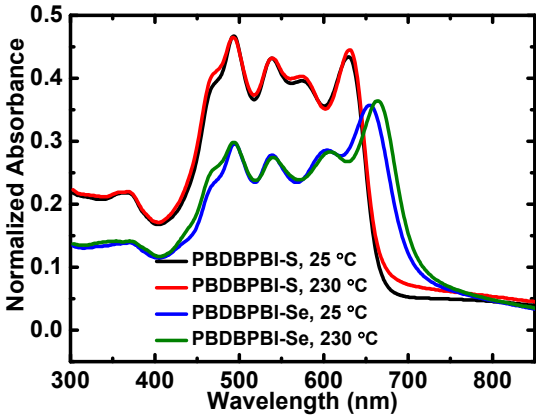

Figure S3. Absorption spectra of the polymer thin films annealed at different temperature.

5. NMR of the compounds and the polymer

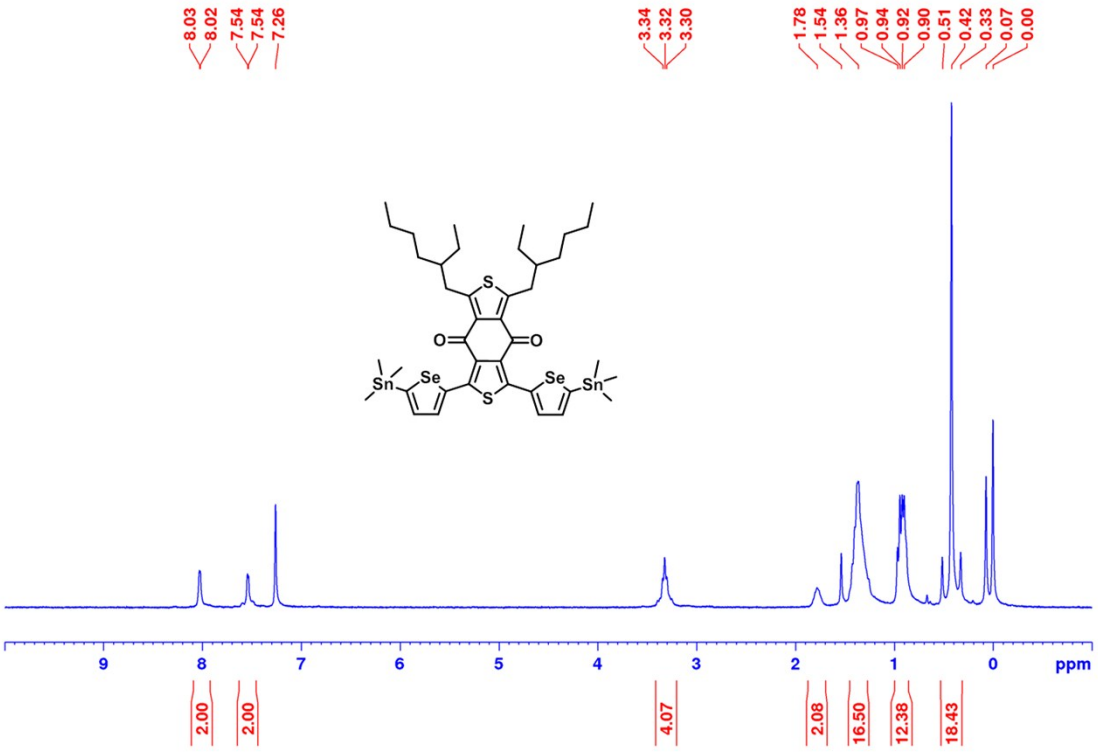

Figure S4. ^{1}H-NMR of the compound M2 recorded in $CDCl_3$.

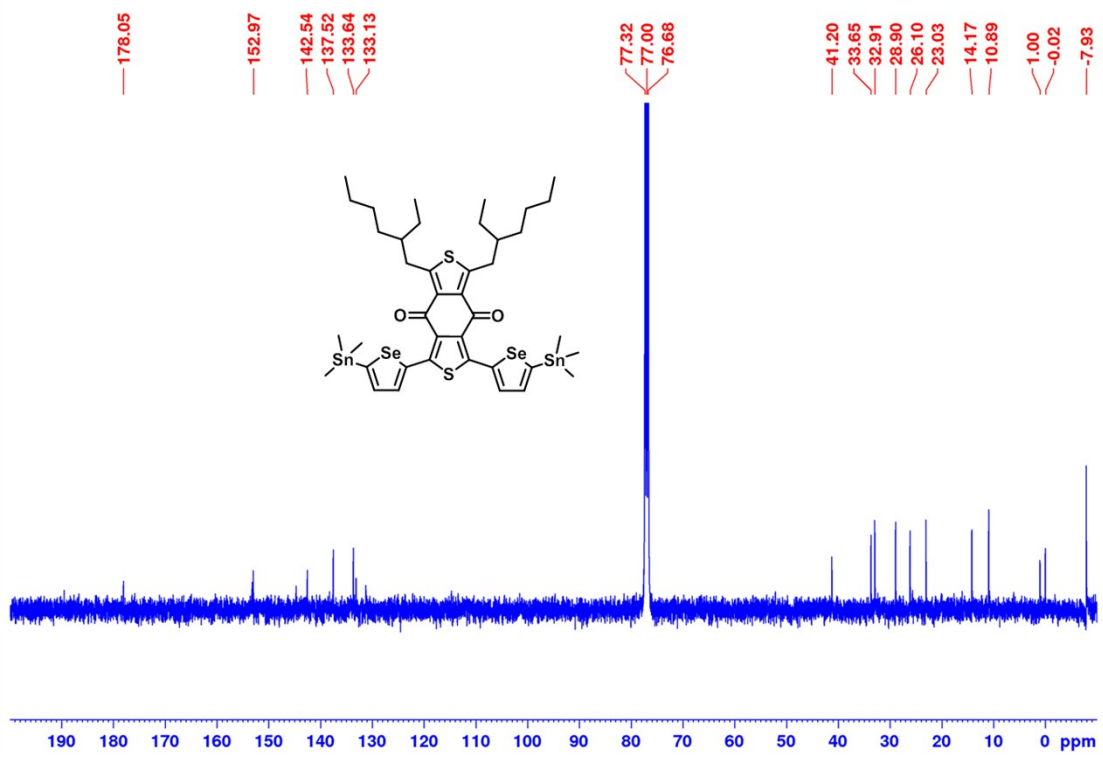

Figure S5. ^{13}C-NMR of the compound **M2** recorded in $CDCl_3$.

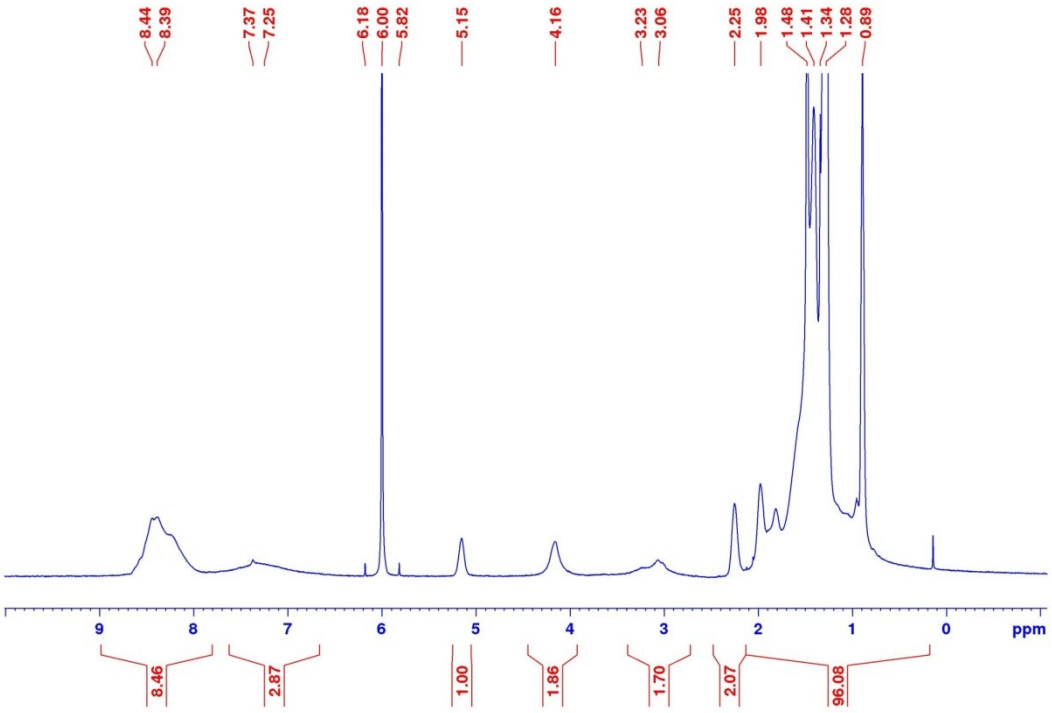

Figure S6. ^{1}H-NMR of PBDBPBI-Se r recorded at 100 °C with 1,1,2,2-tetrachloroethane-d_2 as the solvent.

6. References

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2. G. Feng, J. Li, F. J. M. Colberts, M. Li, J. Zhang, F. Yang, Y. Jin, F. Zhang, R. A. J. Janssen, C. Li and W. Li, *J. Am. Chem. Soc.*, 2017, **139**, 18647-18656.
3. S. Zhang, Y. Qin, J. Zhu and J. Hou, *Advanced Materials*, 2018, **30**, 1800868.