

Supporting information

A small molecule donor containing non-fused ring core for all-small-molecule organic solar cells with high efficiency over 11%

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Experimental Section

Chemicals. The chemical raw materials were purchased from Aldrich, TCI Chemical, J&K and Alfa Aesar, respectively, which are reagent grades and used without further purification.

Synthesis of P2TBR-CHO. To a two-necked round-bottomed flask were added compound **1** (300 mg, 0.40 mmol), compound **2** (140 mg, 0.17 mmol), and toluene (15 ml). The mixture was deoxygenated with argon for 15 min, and then Pb(PPh₃)₄ (11.83 mg, 0.010 mmol) was added. The mixture was refluxed for 48 h and then

cooled to room temperature. 10 ml of aqueous KF solution (0.1 g ml^{-1}) was added and stirred at room temperature overnight to remove the tin impurity. 100 ml of water was added and the mixture was extracted with CH_2Cl_2 ($3 \times 100 \text{ ml}$). The organic phase was dried over anhydrous MgSO_4 . After removing the solvent, the solid P2TBR-CHO (230 mg, yield 79%) was purified by silica gel column chromatography using petroleum ether and dichloromethane as eluent. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ): 10.03 (s, 2H), 8.30 (s, 2H), 7.71 (s, 2H), 7.51-7.50 (d, $J=4 \text{ Hz}$, 2H), 7.36-7.35 (d, $J=4 \text{ Hz}$, 2H), 7.32 (m, 4H), 7.24 (s, 2H), 6.95-6.94 (d, $J=4 \text{ Hz}$, 4H), 4.03-4.02 (m, $J=4 \text{ Hz}$, 4H), 2.90 (m, 8H), 1.88-1.87 (m, 2H), 1.72-1.71 (m, 8H), 1.38 (m, 44H), 1.00-0.89 (m, 36H). MALDI-TOF MS (m/z) for $\text{C}_{100}\text{H}_{122}\text{O}_4\text{S}_{10}$, Calcd: 1707.66, Found: 1706.62. Anal. Calcd for $\text{C}_{100}\text{H}_{122}\text{O}_4\text{S}_{10}$ (%): C, 70.29. H, 7.20; Found (%): C, 69.08; H, 7.39.

Synthesis of P2TBR. To a two-necked round-bottomed flask were added P2TBR-CHO (171 mg, 0.10 mmol), 3-ethylrhodanine (161 mg, 1.0 mmol) and chloroform (15 ml). The mixture was deoxygenated with argon gas for 15 min. Three drops of pyridine were added at the room temperature. Then the mixture was placed in an oil bath at $65 \text{ }^\circ\text{C}$ and stirring for 12 h under argon gas. After cooling to room temperature, the mixture was precipitated into methanol and filtered through a Buchner funnel, and the solid was washed by methanol. Then the solid product of P2TBR (152 mg, yield 76%) was purified by silica gel column chromatography using petroleum ether and dichloromethane as eluent. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ): 7.91 (s, 2H), 7.87 (s, 2H), 7.67 (s, 2H), 7.50-7.49 (d, $J=4 \text{ Hz}$, 2H), 7.33 (m, 4H), 7.29-7.28 (d, $J=4 \text{ Hz}$, 2H), 7.21 (s, 2H), 6.96-6.95 (d, $J=4 \text{ Hz}$, 4H), 4.14-4.13 (m, $J=4 \text{ Hz}$, 4H), 4.02 (m, 4H), 2.94-

2.90 (m, 8H), 1.88 (m, 2H), 1.73 (m, 8H), 1.38 (m, 20H), 1.28-1.25 (t, $J=12$ Hz, 6H), 1.00 (m, 24 H), 0.95 (m, 18H), 0.89 (m, 18H). ^{13}C -NMR (100 MHz, CDCl_3 , δ): 192.38, 167.13, 149.42, 146.67, 146.34, 145.93, 141.96, 140.36, 140.21, 139.16, 138.83, 137.66, 136.80, 136.18, 135.78, 131.75, 128.16, 128.06, 126.18, 126.03, 125.65, 125.20, 123.44, 123.28, 122.48, 118.37, 111.46, 71.48, 41.48, 41.44, 39.91, 34.38, 34.30, 32.58, 32.51, 30.76, 29.24, 28.96, 28.92, 25.78, 25.74, 24.25, 23.08, 23.05, 14.22, 14.20, 14.11, 12.28, 11.44, 10.98, 10.91. MALDI-TOF MS (m/z) for $\text{C}_{110}\text{H}_{132}\text{N}_2\text{O}_4\text{S}_{14}$, Calcd: 1993.63, Found: 1992.58. Anal. Calcd. for $\text{C}_{110}\text{H}_{132}\text{N}_2\text{O}_4\text{S}_{14}$ (%): C, 66.22; H, 6.67; N, 1.40. Found (%): C, 64.53; H, 6.06; N, 1.61.

Instruments and measurements. ^1H NMR and ^{13}C NMR spectra were measured in CDCl_3 on an Agilent arx-400 spectrometer. Mass spectra were obtained with a Shimadzu QP2010 spectrometer. Elemental analysis was carried out on a flash EA1112 analyzer. UV-Vis absorption spectra were measured by an Agilent Carry-5000 UV-Vis spectrophotometer. Electrochemical cyclic voltammetry (CV) was taken on a Zahner Ennium IM6 electrochemical workstation with a three-electrode system in 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solutions at a scan rate of 100 mV/s. The three-electrode system included glassy carbon disk, Pt wire and Ag/AgCl electrode, as the working electrode, counter electrode and reference electrode, respectively. The potential of the Ag/AgCl reference electrode was internally calibrated by using the ferrocene/ferrocenium redox couple (Fc/Fc^+), and the Ag/AgCl reference electrode possesses an energy level at -4.38 eV. The atomic force microscopy (AFM) measurement of the surface

morphology of samples was conducted on a Dimension 3100 (Veeco) Atomic Force Microscope in the tapping mode. Transmission electron microscopy (TEM) was performed using a Tecnai G2 F20 S-TWIN instrument at 200 kV accelerating voltage, where the P2TBR:IDIC films were prepared by the following processing techniques for the TEM measurement: The P2TBR:IDIC films were spin-cast on the ITO/PEDOT:PSS substrates, and then the resulting substrates with the P2TBR:IDIC films were submerged in deionized water to make these P2TBR:IDIC films float onto the water/air interface, and finally the floated P2TBR:IDIC films were picked up on unsupported 200 mesh copper grids.

Device Fabrication and characterization. Organic solar cells were fabricated with a conventional device structure of ITO/PEDOT:PSS/P2TBR:IDIC/ZnO/Al. The patterned indium tin oxide (ITO)-coated glass substrate (10-15 Ω /sq) was cleaned by a surfactant scrub and then underwent a wet-cleaning process inside an ultrasonic bath, beginning with deionized water followed by acetone and isopropanol. After UV-ozone treating for 20 min, a 30 nm thick poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Bayer Baytron 4083) anode buffer layer was spin-cast onto the ITO substrate and then dried by baking in an oven at 150 °C for 15 min. The active layer was then deposited on top of the PEDOT:PSS layer by spin-coating a 7 mg/ml chloroform (CF) solution (dissolved 5 h under 40 °C) of P2TBR:IDIC (w:w, 1:1). In the case of the devices using solvent vapor annealing (SVA) treatment, carbon disulfide (CS₂) was added to the solutions before using. The thickness of the active layers was controlled by adjusting the spin

speed during the spin-coating process and measured by a KLA Tencor D-100 (KLA-Tencor Inc.) profilometer. The ZnO was deposited on the active layer at 2000 rpm for 60 s. At last, 80 nm Al layer was successively deposited in vacuum onto the active layer at a pressure of *ca.* 4×10^{-4} Pa and through a shadow mask to determine the active area of the devices ($\sim 2 \times 2$ mm²). The current-voltage (*J-V*) measurement of the devices was conducted on a computer-controlled Keithley 2450 Source Measure Unit. The power conversion efficiencies of the OSCs were measured under an illumination of AM 1.5 G (100 mW/cm²) using a SS-F5-3A (Enli Technology Co. Ltd.) solar simulator (AAA grade, 50 × 50 mm² photobeam size). A 2 × 2 cm² monocrystalline silicon reference cell (SRC-00019) was purchased from Enli Technology Co., Ltd. Mask made by laser beam cutting technology with a defined area of 4 mm² was used to determine the effective area for accurate measurement. All the measurements with mask or without mask gave consistent results with relative errors within 2%. EQE measurements were performed at Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology Co. Ltd.). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell. GIWAXS measurements were performed at beamline 7.3.3 at the Advanced Light Source (ALS). Samples were prepared on a Si substrate under the same conditions as those used for device fabrication. The 10 KeV X-ray beam was incident at a grazing angle of 0.12°-0.16°, which maximized the scattering intensity from the samples. The scattered x-rays were detected using a Dectris Pilatus 2M photon counting detector. RSoXS transmission measurements were performed at beamline 11.0.1.2 at the Advanced Light Source

(ALS). Samples for R-SoXS measurements were prepared on a PSS modified Si substrate under the same conditions as those used for device fabrication, and then transferred by floating in water to a 1.5 mm \times 1.5 mm, 100 nm thick Si₃N₄ membrane supported by a 5 mm \times 5 mm, 200 μ m thick Si frame (Norcada Inc.). 2-D scattering patterns were collected on an in-vacuum CCD camera (Princeton Instrument PI-MTE). The sample detector distance was calibrated from diffraction peaks of a triblock copolymer poly(isoprene-*b*-styrene-*b*-2-vinyl pyridine), which has a known spacing of 391 Å. The beam size at the sample is approximately 100 μ m by 200 μ m.

Computation details. Density functional theory (DFT) calculations were performed with the Gaussian 09 program, using the B3LYP functional. All-electron double- ξ valence basis sets with polarization functions 6-31G (d, p) were used for all atoms. Geometry optimizations were performed with full relaxation of all atoms in gas phase without solvent effects. Vibration frequency calculation was performed to check that the stable structures had no imaginary frequency. Charge distribution of the molecules was calculated by Mulliken population analysis.

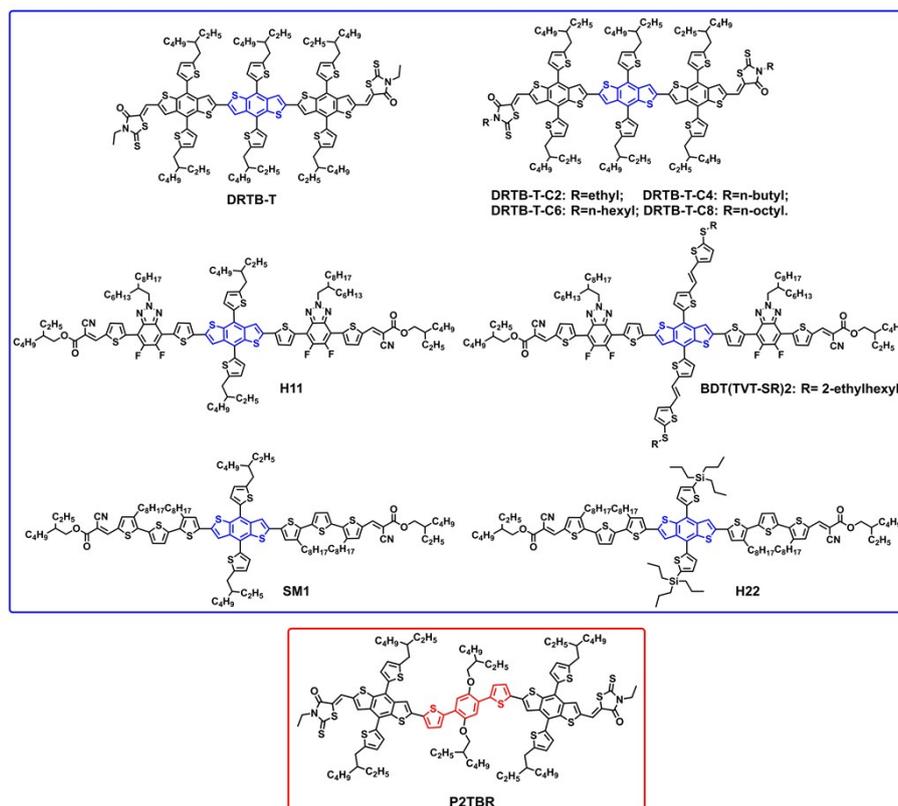


Fig. S1 The structure of small molecule donors with PCEs over 9% in SM-OSCs and the structure of P2TBR.

Table S1. Photovoltaic performance of high efficient nonfullerene all-small-molecule organic solar cells (PCE > 9%).

Donor	Acceptor	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	Ref.
DRTB-T	IDIC	0.98	14.25	65	9.08	[35]
DRTB-T-C2	IT-4F	0.893	16.66	64	9.52	[42]
DRTB-T-C4	IT-4F	0.909	18.27	68	11.24	[42]
DRTB-T-C6	IT-4F	0.929	17.92	63	10.52	[42]
DRTB-T-C8	IT-4F	0.928	16.15	61	9.14	[42]
H11	IDIC	0.977	15.21	65.46	9.73	[36]
BDT(TVT-SR) ₂	IDIC	0.98	15.92	71.15	11.10	[43]
SM1	IDIC	0.905	15.18	73.55	10.11	[37]
H22	IDIC	0.942	15.38	71.15	10.29	[28]
P2TBR	IDIC	0.94	17.5	70.1	11.5	This work

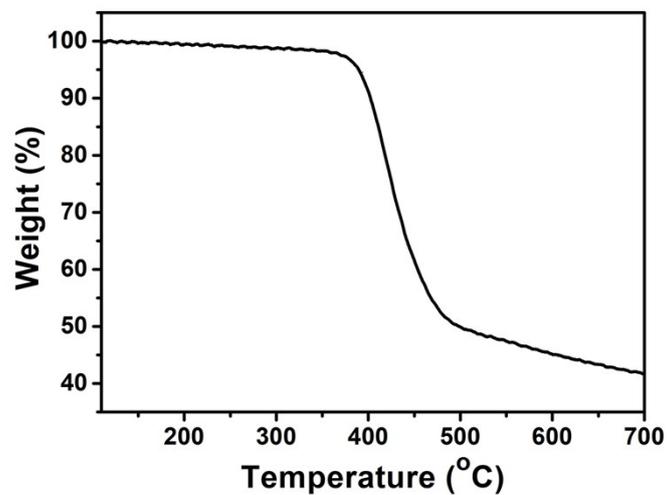


Fig. S2 TGA plot of P2TBR with a heating rate of 10 °C/min under an inert atmosphere.

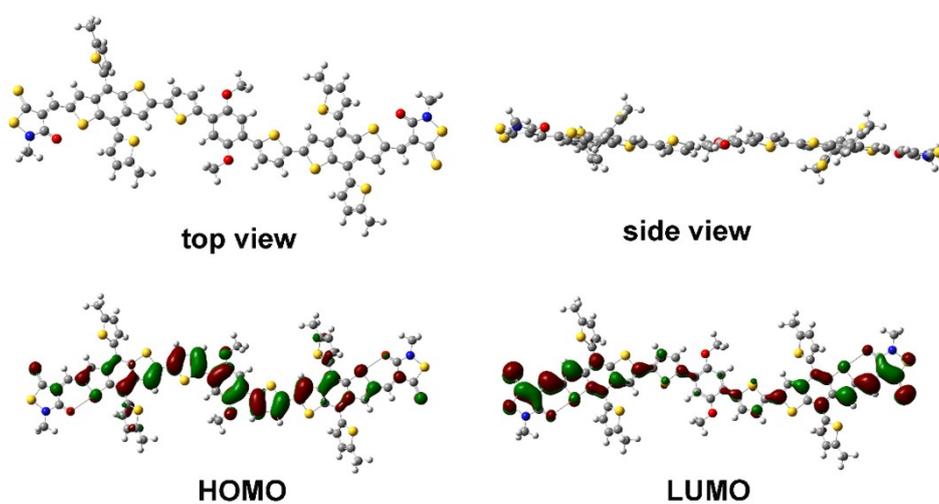


Fig. S3 Optimized geometry of *n*-OS donor P2TBR by DFT calculation: top view and side view, and the HOMO and LUMO electron distribution.

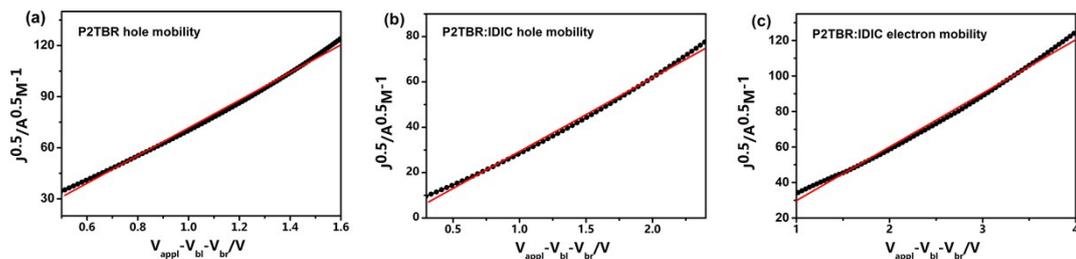


Fig. S4 The J - V curves of (a) and (b) the hole-only devices with the structure of ITO/PEDOT:PSS/P2TBR or P2TBR:IDIC/MoO₃/Al, and (c) the electron-only devices with the structure of ITO/ZnO/P2TBR:IDIC/Ca/Al according to the SCLC model.

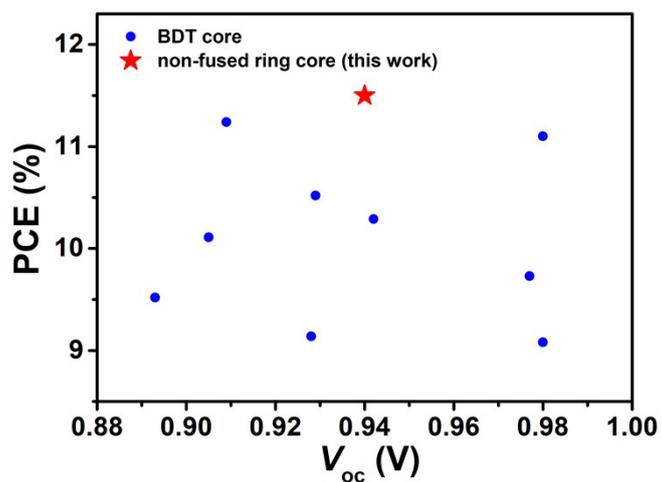


Fig. S5 The PCE- V_{oc} relationship of P2TBR and the other high efficiency small molecule donors in SM-OSCs with PCEs over 9%.