Supporting Information for

Introducing Identical Benzodithiophene Donor Unit for Polymer Donor and Small-molecule Acceptor to Unveil the Relationship of Molecule Structure and Photovoltaic Performance of Non-Fullerene Organic Solar Cells

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Characterization

The ¹H NMR and ¹³C NMR spectra were measured on Bruker 400 MHz spectrometer. Mass spectra were measured on an AB Sciex MALDI-TOF/TOF Mass Spectrometer using MALDI mode. The UV-Vis absorption spectra were recorded on the PerkinElmer Lambda 750s spectrophotometer. The cyclic voltammetry was recorded with a computer controlled PP211 electrochemical workstation using polymer films on platinum electrode (1.0 cm²) as the working electrode, a platinum wire as the counter electrode and Ag/AgCl (0.1 M) as the reference electrode in an anhydrous and argon-saturated solution of 0.1 M of tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile at a scanning rate of 20 mV·s⁻¹. Electrochemical onsets were determined at the position where the current starts to differ from the baseline. Thermogravimetric analysis (TGA) was conducted on a Perkin-Elmer TGA-7 with a heating rate of 20 K/min under nitrogen. The thickness of active layer was measured on a Bruker DektakXT profilometer.

Solar cell fabrication and characterization. Solar cells were fabricated in a conventional device configuration of ITO/PEDOT:PSS/active layers/ZrAcAc/Al. The ITO substrates were first scrubbed by detergent and then sonicated with deionized water, acetone and isopropanol subsequently, and dried overnight in an oven. The glass substrates were treated by UV-Ozone for 30 min before use. PEDOT:PSS (Heraeus Clevios P VP AI 4083) was spin-cast onto the ITO substrates at 4000 rpm

for 30 s, and then dried at 150 °C for 15 min in air. The PBDB-T-SF:ITIC-SF blends (1:1 weight ratio) were dissolved in chloroform (the total concentration of blend solutions were 16 mg mL⁻¹ for all blends), and stirred overnight on a hotplate at 40 °C in a nitrogen-filled glove box. The blend solution was spin-cast at 2700 rpm. A thin zracac layer was coated on the active layer. was coated on the active layer, followed by the deposition of Al (100 nm) (evaporated under 5×10^{-5} Pa through a shadow mask). The optimal active layer thickness measured by a Bruker Dektak XT stylus profilometer was about 100 nm. The current density-voltage (J - V) curves of all encapsulated devices were measured using a Keithley 2400 Source Meter in air under AM 1.5G (100 mW cm⁻²) using a Newport solar simulator. The light intensity was calibrated using a standard Si diode (with KG5 filter, purchased from PV Measurement to bring spectral mismatch to unity). Optical microscope (Olympus BX51) was used to define the device area (5.9 mm²). EQEs were measured using an Enlitech QE-S EQE system equipped with a standard Si diode. Monochromatic light was generated from a Newport 300 W lamp source.

SCLC measurements. The electron and hole mobility were measured by using the method of space-charge limited current (SCLC) for electron-only devices with the structure of ITO/ZnO/active layer/Zracac/Al and hole-only devices with the structure of ITO/MoO_x/active layers/MoO_x/Al. The charge carrier mobility was determined by fitting the dark current to the model of a single carrier SCLC according to the equation: $J = 9\varepsilon_0\varepsilon_{\rm r}\mu V^2/8d^3$, where J is the current density, d is the film thickness of the active layer, μ is the charge carrier mobility, $\varepsilon_{\rm r}$ is the relative dielectric constant of the

transport medium, and ε_0 is the permittivity of free space. $V = V_{app} - V_{bi}$, where V_{app} is the applied voltage, V_{bi} is the offset voltage. The carrier mobility can be calculated from the slope of the $J^{1/2} \sim V$ curves.

Atomic force microscopy (AFM). AFM images were obtained by using a Dimension Icon AFM (Bruker) in a tapping mode.

GIWAXS characterization. The grazing incidence X-ray scattering (GIWAXS) measurement was carried out with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and a Pilatus3R 300K detector. The incident angle was 0.2°. The samples for GIWAXS measurements were fabricated on silicon substrates using the same recipe for the devices.



Fig. S1. TGA curves of ITIC-SF.



Fig. S2. DSC thermograms of neat ITIC2, ITIC-S and ITIC-SF.



Fig. S3. Cyclic voltammograms for ITIC-SF.



Fig. S4. *J* - *V* characteristics in dark for electron-only devices based on ITIC2, ITIC-S and **ITIC-SF**.





Fig. S5. *J* - *V* characteristics in dark for (a) hole-only and (b) electron-only devices based on PBDB-T-SF:ITIC2, PBDB-T-SF:ITIC-S and PBDB-T-SF:ITIC-SF blends.



Fig. S6. AFM height images (a - c scale bar: 400 nm) and phase images (d - f scale bar: 400 nm): (a, d) PBDB-T-SF:ITIC2, (d, e) PBDB-T-SF:ITIC-S and (c, f) PBDB-



Fig. S7. 2D GIWAXS patterns of pure PBDB-T-SF, ITIC2, ITIC-S and **ITIC-SF** films and the corresponding GIWAXS intensity profiles along the in-plane (dotted line) and out-of-plane (solid line) directions.



Fig. S8. The fitting profile shapes of ITIC2 and ITIC-S pure films.

Samples	100			010		
	Position/Å ⁻¹	d-spacing/Å	CCL/Å	Position/Å ⁻¹	d-spacing/Å	CCL/Å
PBDB-T-SF	0.268	23.4	51.9	1.70	3.69	16.6
ITIC2	0.316	19.9	40.6	1.57	4.00	7.57
ITIC-S	0.319	19.7	34.4	1.53	4.11	11.3
ITIC-SF	0.343	18.3	32.5	/	/	/
PBDB-T- SF: ITIC2	0.283	22.2	60.2	1.71	3.67	17.9
PBDB-T- SF: ITIC-S	0.282	22.3	58.6	1.71	3.67	13.9
PBDB-T- SF: ITIC-SF	0.284	22.1	71.5	1.73	3.63	17.5

 Table S1. Relative data of pure and blend films obtained from GIWAXS

 measurement.

Synthesis

Unless stated otherwise, all the solvents and chemical reagents were obtained commercially and used without further purification. **Scheme S1** shows the synthetic route to ITIC-SF. Compound ITIC2, ITIC-S and PBDB-T-SF were synthesized according to previously published procedures, respectively.[1, 2]



Scheme S1 Molecular structure of PBDB-T-SF.



Compound **1** (2.51 g, 2.50 mmol) ethyl 2-bromothiophene-3-carboxylate (1.76 g, 7.50 mmol), Pd(PPh₃)₄ (173.22 mg, 0.149mmol) and toluene (25 mL) was heated in a 110°C bath for 12 hours under the protection of an argon atmosphere. The reaction S-12

mixture was cooled to at room temperature, after dichloromethane/water extraction, the organic layer was dried over anhydrous MgSO₄ then filtered. After solvent evaporate from filtrate, the residue was purified by silica gel (200 – 300 mesh) column chromatography. Using dichloromethane/petroleum ether (1:4) as the eluent, 1.30 g (yield 53%) of target product was obtained as yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 7.91 (s, 1H), 7.54 (d, 1H), 7.31 (d, 1H), 7.24 (d, 1H), 4.31 (s, 2H), 2.88 (d, 2H), 1.59 (s, 1H), 1.54 – 1.38 (m, 5H), 1.28 (d, 9H), 0.90 ppm (s, 7H); ¹³C NMR (100 MHz, CDCl₃) δ 162.74, 159.99, 157.39, 139.70, 139.02, 138.92, 136.56, 136.38, 130.79, 129.78, 125.52, 124.53, 123.09, 118.55, 118.28, 115.20, 115.00, 60.97, 42.80, 39.32, 32.01, 28.73, 25.23, 22.90, 14.09, 10.73 ppm; HRMS (MALDI-TOF) *m/z*: [M + H]⁺ calcd for C₄₈H₅₂F₂O₄S₈ 986.2; found, 986.9.

Synthesis of compound 3



Compound **2** (1.3 g, 1.32 mmol) and THF (47 mL) were stirred together in a 250 mL round bottom flask at rt under the protection of argon. A THF solution (35 mL) of fresh 4-hexylphenyl-1-magnesium bromide which prepared from magnesium turnings (381mg, 15.9 mmol) and 1-bromo-4-hexylbenzene (3.81 g, 15.9 mmol) was added S-13

dropwise to the mixture. The mixture was stirred for 14 hour at 70°C. The reaction mixture was cooled to at room temperature and 30 mL saturated NH₄Cl aqueous solution was added to it. After dichloromethane/water extraction, the organic layer was dried over anhydrous MgSO₄ then filtered. After solvent evaporate from filtrate, the yellow residue was added into a 250 mL round bottom flask. Toluene (50 mL) and Amberlyst 15 (3 g) were added under the protection of an argon atmosphere. The mixture was stirred for 15 h at 110°C. The reaction mixture was cooled to at room temperature and filtered. After solvent evaporate from filtrate, the residue was purified by silica gel (200 – 300 mesh) column chromatography. Using petroleum ether as the eluent, 0.90 g (yield 45%) of target product was obtained as light yellow solid. ¹H NMR (400 MHz, CD₂Cl₂) δ 7.16 (d, 1H), 7.00 (d, 5H), 6.83 (d, 1H), 5.94 (d, 1H), 2.73 (s, 2H), 2.57 (d, 3H), 1.61 (d, 4H), 1.33 (s, 15H), 0.93 ppm (d, 9H); ¹³C NMR (100 MHz, CD₂Cl₂) δ 165.08, 158.98, 156.42 – 156.35, 149.95, 148.50, 141.73, 141.62, 141.46, 141.26, 136.36, 136.30, 135.95, 135.91, 128.63, 128.27, 127.98, 123.49, 122.28, 120.52, 120.26, 62.98, 42.89, 39.15, 35.39, 31.97, 31.86, 31.76, 31.73, 31.50, 31.44, 29.65, 29.13, 29.07 - 29.04, 28.99, 28.80, 28.72, 25.20, 25.08, 22.99, 22.61, 14.00 - 13.77, 10.52, 0.73 ppm; HRMS (MALDI-TOF) m/z: [M + H^{+} calcd for $C_{92}H_{108}F_{2}S_{8}$ 1506.6; found, 1506.3.

Synthesis of compound 4



Compound 4 was synthesized by two steps: firstly, anhydrous DMF (1.19 mL, 12.75 mmol) was added to a 25 mL round bottom flask at rt under the protection of argon. then POCl₃ (1.5 mL, 19.5 mmol) was added slowly with a syringe at 0°C. The mixture was stirred at room temperature for 30 min. Secondly, compound 4 (885mg, 0.564 mmol) and 1,2-dichloroethane (20 mL) were stirred together in a 50 mL round bottom flask at rt under nitrogen atmosphere. The mixture was stirred for 14 h at 85°C. The reaction mixture was cooled to at room temperature, then the reaction mixture was extracted with CH₂Cl₂ and water. After solvent evaporate from filtrate, the residue was purified by silica gel (200 – 300 mesh) column chromatography. Using dichloromethane/petroleum ether (1:3) as the eluent, 665 mg (yield 74%) of target product was obtained as orange solid. ¹H NMR (400 MHz, CD₂Cl₂) δ 9.68 (s, 1H), 7.46 (s, 1H), 7.01 (s, 10H), 5.97 (d,1H), 2.74 (s, 3H), 2.59 (s, 6H), 1.61 (s, 7H), 1.52 – 1.42 (m, 6H), 1.32 (s, 27H), 1.01 – 0.76 ppm (m, 18H); ¹³C NMR (100 MHz, CD₂Cl₂) & 182.34, 149.94, 146.46, 142.31, 142.01, 141.36, 131.00, 130.39, 128.50, 128.25, 127.96, 42.78, 39.18, 35.39, 31.92, 31.83, 31.69, 31.41, 29.08, 28.92, 25.23 -25.17, 25.09, 22.96, 22.55, 13.97 - 13.90, 13.85, 10.57, 10.52 - 10.49 ppm; HRMS

(MALDI-TOF) m/z: $[M + H]^+$ calcd for C₉₄H₁₀₈F₂O₂S₈ 1562.6; found, 1562.6.



Synthesis of compound 5

Compound 4 (217 mg, 0.138 mmol) and 1,1-dicyanomethylene-3-indanone (188 mg, 0.971 mmol), chloroform (50 mL) and pyridine (1.0 mL) were stirred together in a 100 mL round bottom flask at rt under the protection of argon. Then, the reaction was placed in an oil bath at 70°C and stirred for 12 h. The reaction mixture was cooled to room temperature, the mixture was poured into methanol (200 mL) and filtered. The residue was purified by silica gel (200 - 300 mesh) column chromatography. Using dichloromethane/petroleum ether (1:2) as the eluent, 240 mg (yield 90%) of target product was obtained as dark blue solid. ¹H NMR (400 MHz, CDCl₃) δ 8.70 (s, 1H), 8.63 (d, 1H), 7.85 (d, 1H), 7.70 (t, 2H), 7.42 (s, 1H), 7.10 - 6.84 (m, 8H), 5.99 (s, 1H), 2.78 (d, 2H), 2.58 (s, 4H), 1.61 (s, 5H), 1.52 – 1.43 (m, 3H), 1.32 (s, 17H), 0.96 (s, 5H), 0.88 ppm (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 175.72, 165.70, 160.10, 155.96, 151.89, 142.45, 142.08, 141.37, 139.87, 137.97, 137.61, 137.30 - 137.21, 136.78, 135.03, 134.34, 128.68, 128.34, 128.00, 125.21, 123.70, 118.89 - 118.88, 114.52, 110.09 - 109.88, 43.20 - 43.05, 39.29, 35.56, 32.07, 31.76, 31.32, 29.14, 28.99, 28.84, 28.79 - 28.75, 25.27, 23.01, 22.59, 14.08, 10.84 ppm; HRMS

(MALDI-TOF) m/z: [M + H]⁺ calcd for C₁₁₈H₁₁₆F₂N₂O₂S₈ 1914.6; found, 1914.0.

¹H NMR of 2 in CDCl₃ (400MHz)



¹³C NMR of 2 in CDCl₃ (100MHz)



¹H NMR of 3 in CD₂Cl₂ (400MHz)



¹³C NMR of 3 in CD₂Cl₂ (100MHz)



¹H NMR of 4 in CD₂Cl₂ (400MHz)



¹³C NMR of 4 in CD₂Cl₂ (100MHz)



¹H NMR of 5 in CDCl₃ (400MHz)





¹³C NMR of 5 in CDCl₃ (100MHz)



References

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