### **Supporting Information**

## A nonfullerene acceptor utilizing a novel asymmetric multifused-ring

## core unit for highly efficient organic solar cells

Chao Li<sup>‡a</sup>, Yuanpeng Xie<sup>‡a</sup>, Bingbing Fan<sup>a</sup>, Guangchao Han<sup>b</sup>, Yuanping Yi <sup>\*b</sup> and Yanming Sun<sup>\*a</sup>

<sup>a</sup> Heeger Beijing Research and Development Center, School of Chemistry and Environment, Beihang University, Beijing 100191, China. E-mai: sunym@buaa.edu.cn

<sup>b</sup> Beijing National Laboratory for Molecular Science, Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China. E-mai: ypyi@iccas.ac.cn

- S1.1 Materials
- S1.2 Measurements
- S1.3 Organic Solar Cells Fabrication and Characterization
- S1.4 Space-Charge Limited Current Measurement
- S1.5 Figures and Tables
- S1.6 Reference

### S1.1 Materials

All the chemicals and solvents were purchased from commercial sources and used without further purification unless otherwise stated. Tetrahydrofuran was freshly distilled from sodium/benzophenoneketyl prior to use. All the reactions were performed under nitrogen atmosphere unless otherwise noted. tributyl(thieno[3,2-b]thiophen-2-yl)stannane<sup>1</sup> was prepared according to the reported method.

Synthesis of diethyl 2-bromo-5-(thiophen-2-yl)terephthalate (1): Diethyl 2,5dibromoterephthalate (10 g, 26.31 mmol ), tributyl(thiophen-2-yl)stannane (9.82 g, 26.31 mmol) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.37 g, 0.53 mmol) were dissolved in anhydrous toluene (150 mL) under nitrogen atmosphere. The resulting solution was stirred at 90°C for 6 h. After cooling down to room temperature, the reaction mixture was poured into water (100 mL) and extracted with dichloromethane for three times. The combined organic layers were dried over anhydrous MgSO<sub>4</sub> and filtered. The filtrate was concentrated under vacuum and purified by column chromatography on silica gel with petroleum ether: ethyl acetate (9:1) as an eluent to give the title compound as colorless liquid (4.24 g, 42 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.98 (s, 1 H), 7.85 (s, 1H), 7.38 (m, 1H), 7.06 (m, 2H), 4.46-4.38 (q, 2H), 4.25-4.17 (q, 2H), 1.44-1.38 (t, 3H), 1.18-1.13 (t, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 166.53, 165.25, 139.78, 135.32, 134.91, 134.51, 133.46, 133.28, 127.40, 127.13, 126.67, 120.57, 62.12, 61.87, 14.20, 13.80. GCMS m/z cald. for (C<sub>16</sub>H<sub>15</sub>BrO<sub>4</sub>S):381.99. Found: 384.

Synthesis of diethyl 2-(thieno[3,2-b]thiophen-2-yl)-5-(thiophen-2-yl)terephthalate (2): Diethyl 2-bromo-5-(thiophen-2-yl)terephthalate (1) (2.2 g, 5.74 mmol),tributyl(thieno[3,2-b]thiophen-2-yl)stannane (4.92 g, 11.48 mmol) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.4 g, 0.57 mmol) were dissolved in anhydrous toluene (100 mL) under nitrogen atmosphere. The resulting solution was stirred at 110°C overnight. After cooling down to room temperature, the reaction mixture was poured into water (100 mL) and extracted with dichloromethane for three times. The combined organic layers were dried over anhydrous MgSO<sub>4</sub> and filtered. The filtrate was concentrated under vacuum and purified by column chromatography on silica gel with petroleum ether: dichloromethane (1:1) as an eluent to give the title compound as a light yellow solid (2.18 g, 86 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.86 (d, 2H), 7.40 (d, 2H), 7.28 (s, 2H), 7.12-7.07 (m, 2H), 4.27-4.19 (m, 4H), 1.18-1.10 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 167.62, 167.55, 142.14, 140.41, 139.89, 139.37, 134.16, 134.06, 133.76, 133.51, 132.01, 131.97, 127.42, 127.36, 127.09, 126.63, 119.45, 119.24, 61.79, 61.74, 13.86, 13.86. GCMS m/z cald. for (C<sub>22</sub>H<sub>18</sub>O<sub>2</sub>S<sub>3</sub>):442.04. Found: 442.

Synthesis of **TPTT**: To a stirring solution of 1-bromo-4-hexylbenzene (6.54 g, 27.11 mmol) in dry THF (120 mL) at -78°C was added dropwise n-BuLi (10.8 mL, 27.11 mmol) under nitrogen atmosphere. After being kept stirring at at -78°C for 1.5 h, a solution of compound 2 (2 g, 4.52 mmol) in dry THF (15 mL) was added dropwise within 15 mins, then the resulting mixture was warmed to room temperature and stirred ovenight. After the reaction was finished, the reaction mixture was poured into water and extracted with dichloromethane for three times. The combined organic phases was dried over with anhydrous MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude product was charged into 250 mL flask, and acetic acid (100 mL) and concentrated H<sub>2</sub>SO<sub>4</sub> (1 mL) were added in sequence, then the reaction mixture was stirred at 120°C for 3 h under nitrogen atmosphere. After cooling to room temperature, the reaction mixture was poured into water and extracted with dichloromethane. Then the conbined organic extracts were washed with water, dried with anhydrous MgSO<sub>4</sub>, filtered, and the solvent was removed under reduced pressure. The obtained crude product was further purified by column chromatography on silica gel with petroleum ether: dichloromethane (20:1) as an eluent to afford a novel asymmetrical fused-ring building block as yellowish brown liquid (0.92 g, 21 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 7.49 (s, 1H), 7.43 (s, 1H), 7.28-7.23 (m, 3H), 7.18-7.15 (d, 8H), 7.07-7.04 (d, 8H), 7.00 (d, 1H), 2.58-2.51 (t, 8H), 1.57-1.53 (m, 8H), 1.34-1.25 (m, 24H), 0.86 (t, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 156.00, 153.62, 153.05, 145.89, 143.34, 142.04, 141.70, 141.56, 141.44, 141.23, 140.42, 135.80, 135.46, 133.83, 128.42,

128.33, 128.09, 127.94, 127.55, 126.26, 123.17, 120.36, 117.27, 117.18, 62.96, 62.72, 35.62, 31.76, 31.75, 31.37, 31.31, 29.75, 29.19, 22.63, 14.14. HR-MS (MALDI-TOF) m/z cald. for (C<sub>66</sub>H<sub>74</sub>S<sub>3</sub>): 962.50. Found: 962.3.

Synthesis of TPTT-CHO: Under the protection of nitrogen, n-BuLi (1.26 mL, 3.16 mmol) was added dropwise to a stirring solution of compound 3 (0.76 g, 0.79 mmol) in dry THF (40 mL) at -78°C. After being kept stirring at -78 °C for 1.5 h, the reaction mixture was stirred at room temperature for another 1 h, which was then cooled to -78 °C again and stirred for 10 mins, then N-Formylpiperidine(0.54 g, 4.73 mmol) was added to the reaction mixture using a syringe, and the reaction mixture was allowed to warm to room temperature and stirred overnight. The resulting mixture was poured into water, followed by extraction with dichloromethane. The combined organic layers were dried with anhydrous MgSO<sub>4</sub> and the solvent was removed in vacuo to give crude product, which was futher purified by column chromatography on silica gel with petroleum ether: dichloromethane (1:1) as an eluent to afford a bright yellow solid (0.62 g, 77 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 9.89 (s, 1H), 9.82 (s, 1H), 7.94 (s, 1H), 7.66 (s, 1H), 7.65 (s, 1H), 7.54 (s, 1H), 7.16-7.07 (m, 16H), 2.60-2.53 (t, 8H), 1.58-1.54 (m, 8H), 1.29 (m, 24H), 0.86 (t, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 182.86, 156.70, 155.19, 154.63, 150.67, 149.22, 147.02, 146.13, 144.62, 142.40, 142.16, 141.94, 140.72, 140.17, 139.09, 137.17, 135.25, 131.98, 129.75, 128.76, 128.63, 127.81, 127.71, 118.90, 118.27, 63.14, 62.98, 35.57, 31.72, 31.70, 31.33, 31.26, 29.13, 22.60, 22.59, 14.10. HR-MS (MALDI-TOF) m/z cald. for (C<sub>68</sub>H<sub>74</sub>O<sub>2</sub>S<sub>3</sub>): 1018.49. Found: 1019.5.

Synthesis of **TPTT-IC**: Under nitrogen atmosphere, compound 4 (100 mg, 0.098 mmol), 1,1-dicyanomethylene-3-indanone (114 mg, 0.588 mmol) and chloroform (30 mL) was added to 50 mL round bottom flask. After the reaction mixture was stirred at room temperature for 10 mins, pyridine (0.5 mL) was then added. The reaction mixture was allowed to stirred at 65°C overnight. After removal of solvent of reaction mixture,

methanol was added and the precipitate was collected by filtration to get crude product, which was futher purified by column chromatography on silica gel with petroleum ether: dichloromethane (1:1.5) as an eluent to afford a dark-red solid (86 mg, 64 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.89 (s, 1H), 8.87 (s, 1H), 8.68-8.67 (m, 2H), 8.20 (s, 1H), 7.92-7.90 (m, 2H), 7.89-7.88(m, 6H), 7.77 (s, 1H), 7.23-7.10 (m, 16H), 2.60-2.55(t, 8H), 1.62-1.57(m, 8H), 1.29-1.25 (m, 24H),0.87-0.85 (t, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 188.43, 188.15, 160.37, 160.29, 159.28, 157.74, 156.42, 156.17, 155.69, 152.52, 148.10, 146.92, 143.88, 142.56, 142.36, 141.16, 140.40, 140.02, 139.96, 139.85, 139.47, 138.90, 138.50, 138.20, 138.15, 136.89, 136.86, 136.78, 136.00, 135.25, 135.18, 134.53, 134.50, 128.93, 128.77, 127.84, 127.75, 125.34, 123.78, 122.97, 122.16, 119.73, 118.81, 114.65, 114.63, 114.59, 114.53, 69.60, 69.18, 63.26, 63.01, 35.63, 35.59, 31.73, 31.35, 31.27, 29.73, 29.35, 29.17, 29.13, 22.61, 14.12. HR-MS (MALDI-TOF) m/z cald. for (C<sub>92</sub>H<sub>82</sub>N<sub>4</sub>O<sub>2</sub>S<sub>3</sub>): 1370.56. Found: 1371.8.

#### S1.2 Measurements

Nuclear magnetic resonance spectra (NMR), which were recorded on a Bruker Avance 300 spectrometer, were obtained in deuterated chloroform (CDCl<sub>3</sub>) with TMS as the internal reference. UV–vis–NIR absorption spectra were measured on a Hitachi (model U-3010) UV–vis spectrophotometer. Mass spectra were recorded on GSMS-QP2010 SE and using Bruker Daltonics Biflex III MALDI-TOF Analyzer in the MALDI mode, respectively. Cyclic voltammetry (CV) measurements were carried out under nitrogen at a scan rate of 100 mV s<sup>-1</sup> using a Zahner IM6e Electrochemical workstation. A platinum plate as a working electrode, a platinum wire as a counter electrode, a saturated Ag/AgCl electrode as a reference electrode and 0.1 M tetra-n-butylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) in anhydrous acetonitrile solution were employed as a supporting electrolyte and Ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) was used as an internal standard. The HOMO and LUMO energy level could be calculated from the following equations: HOMO =  $-(E_{red}^{onset} + 4.37)$  eV, where  $E_{ox}^{onset}$  and  $E_{red}^{onset}$  were the onset oxidation potential and onset

reduction potential relative to Ag/AgCl, respectively. Atomic force microscopy (AFM) measurements were carried out using a Dimension Icon AFM (Bruker) in the tapping mode. Transmission electron microscopy (TEM) measurements were performed on a JEOL JEM-1400 transmission electron microscope.

#### S1.3 Organic Solar Cells Fabrication and Characterization

Nonfullerence organic solar cells with invented device architecture of ITO/ZnO/ PBT1-C:TPTT-IC (ITIC)/MoO<sub>3</sub>/Ag were fabricated according to the following procedure: the ITO-coated glass substrates were firstly cleaned by ultrasonic treatment in detergent deionized water, acetone and isopropyl alcohol for 30 minutes each. After drying for one night, ZnO precursor solution was spin coated at 4000 rpm and the ZnO layer was annealed at 200 °C for 15 min in the ambient atmosphere. PBT1-C: TPTT-IC (ITIC) at the weight ratio of 1:1, at an overall concentration of 15 mg/ml with 0.5 v% DIO, was spin cast on the top of ZnO to form the active layer. Films were allowed to heat at 100 °C for 10 min under the inert atmosphere to drive off residual solvent. The MoO<sub>3</sub> were deposited by sequential thermal evaporation of 7 nm followed by 90 nm of Ag. Current density-voltage (J-V) characteristics were measured using a Keithley 2400 Source Measure Unit. The currents were measured under 100 mW/cm<sup>2</sup> simulated 1.5 Global (AM 1.5 G) solar simulator (Enli Technology Co., Ltd, SS-F5-3A). The light intensity was calibrated by a standard Si solar cell (SRC-2020, Enli Technology Co., Ltd). IPCE spectra were recorded by using a QEX10 Solar Cell IPCE measurement system (PV Measurements, Inc.).

#### S1.4 Space-Charge Limited Current Measurement

The electron mobility and hole mobility were evaluated by space charge limited current (SCLC) method by fabricating electron-only devices with a structure of ITO/ZnO/film/ZrAcac/Al and hole-only devices with a structure of ITO/PEDOT:PSS/ film/MoO<sub>3</sub>/Ag, respectively, The J–V curves of devices were fitted by using the Mott–Gurney equation:  $J = 9\epsilon_0\epsilon_r\mu V^2/8L^3$ , where J is the current density,  $\epsilon_0$  is the permittivity of free space,  $\epsilon_r$  is the permittivity of the active layer,  $\mu$  is the hole mobility or electron mobility,  $V=V_{app} - V_{bi}$ , where  $V_{app}$  is the applied voltage,  $V_{bi}$  is the offset voltage ( $V_{bi}$  is 0 V here). and L is the film thickness of active layer. The eletron mobility or hole

mobility could be calculated from the slope of the J<sup>0.5</sup>-V curve.

### S1.5 Figures and Tables



**Figure S1.** Optimized geometries of (a) TPTT-IC and (b) ITIC dimer by DFT calculations. The permanent dipole moment ( $\mu$ ) of TPTT-IC and intermolecular binding energy of ITIC dimer are inserted.



Figure S2. Absorption spectra of TPTT-IC and ITIC in chloroform solution.



Figure S3. Electrochemical cyclic voltammetry curves of Fc/Fc<sup>+</sup>, TPTT-IC and ITIC.

 Table S1. Optical and electrochemical properties of TPTT-IC.

Acceptors	λ <sub>max</sub> <sup>a</sup> (nm)	λmax <sup>b</sup> (nm)	λ <sub>onset</sub> <sup>b</sup> (nm)	Eg <sup>opt</sup> c (eV)	E <sub>ox</sub> (eV)	E <sub>red</sub> (eV)	E <sub>HOMO</sub> (eV)	E <sub>LUMO</sub> (eV)
TPTT-IC	668	692	758	1.63	1.41	-0.42	-5.78	-3.95
ITIC	678	703	773	1.60	1.34	-0.40	-5.71	-3.97

<sup>a)</sup> In CHCl<sub>3</sub> solution; <sup>b)</sup> In thin film drop cast from CHCl<sub>3</sub> solution; <sup>c)</sup> Estimated from empirical formula:  $E_g^{opt} = 1240 / \lambda_{onset}$ .



**Figure S4.** The histogram of PCEs measurements for 30 PBT1-C:ITIC (a) and PBT1-C:TPTT-IC (b) devices.



Figure S5. Operational stability of PBT1-C:ITIC and PBT1-C:TPTT-IC devices.



Figure S7. J<sup>0.5</sup>-V curves of the eletron-only devices based on pure TPTT-IC and ITIC.



**Figure S8. (a)** J<sup>0.5</sup>-V curves of the hole-only device based on PBT1-C:TPTT-IC and PBT1-C:ITIC blend film and **(b)** J<sup>0.5</sup>-V curves of the electron-only device based on PBT1-C:TPTT-IC and PBT1-C:ITIC blend film.

Active layer	Hole mobility ( $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ )	Electron mobility $(10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$		
TPTT-IC		4.3±0.5		
ITIC		2.8±0.4		
PBT1-C:TPTT-IC	5.1±0.3	3.23±0.3		
PBT1-C:ITIC	4.9±0.2	2.85±0.2		

**Table S2.** Charge transpot properties of TPTT-IC, ITIC and PBT1-C:TPTT-IC blend

 film

 Table S3. Optimization of DIO content for PBT1-C:TPTT-IC inverted solar cells.

DIO (v %)	$J_{\rm sc}$ (mA cm <sup>-2</sup> )	J <sub>sc,cal</sub> (mA cm <sup>-2</sup> )	V <sub>oc</sub> (V)	FF (%)	PCE <sup>a)</sup> (%)
0	12.9±0.5	12.81	0.98±0.01	56.2±1.2	7.1 (7.3)
0.25	13.0±0.3	13.81	0.97±0.01	67.5±1.8	9.2 (9.3)
0.5	15.0±0.6	14.82	0.96±0.01	69.5±2.1	10.0 (10.3)
0.75	14.4±0.5	14.50	0.95±0.005	68.7±2.3	9.4 (9.7)

a) Average values with standard deviation were obtained from 10 devices.

Thickness (nm)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	$J_{\rm sc,cal}$ (mA cm <sup>-</sup> <sup>2</sup> )	V <sub>oc</sub> (V)	FF (%)	PCE <sup>a)</sup> (%)
89	14.5±0.2	14.23	0.95±0.01	67.0±2.0	9.2 (9.6)
103	15.5±0.4	15.01	0.96±0.01	69.4±1.4	10.3 (10.5)
112	14.7±0.3	14.52	0.95±0.01	66.6±2.1	9.3 (9.5)

**Table S4.** Optimization of the active layer thickness for PBT1-C:TPTT-IC inverted solar cells.

a) Average values with standard deviation were obtained from 10 devices.



**Figure S7. (a)** AFM height of optimal PBT1-C:TPTT-IC blend film , **(b)** AFM phase of optimized PBT1-C:TPTT-IC blend film, **(c)** AFM height of optimal PBT1-C: ITIC

blend film and (d) AFM phase of optimized PBT1-C:ITIC blend film The scan size of the AFM images is  $2\times 2 \mu m$ .



**Fig. S8** <sup>1</sup>H NMR spectrum of compound **1** 

Figure S9. <sup>13</sup>C NMR spectrum of compound 1



Figure S11. <sup>13</sup>C NMR spectrum of compound 2



Figure S13. <sup>13</sup>C NMR spectrum of TPTT



Figure S15. <sup>13</sup>C NMR spectrum of TPTT-CHO



Figure S17. <sup>13</sup>C NMR spectrum of TPTT-IC







Figure S19. GCMS spectrum of compound 2



Figure S20. HR-MS spectrum of TPTT



Figure S21. HR-MS spectrum of TPTT-CHO



Figure S22. HR-MS spectrum of TPTT-IC



# S1.6 Reference

1. Y. Cai, X. Zhang, X. Xue, D. Wei, L. Huo and Y. Sun, *Journal of Materials Chemistry C*, 2017, **5**, 7777-7783.