

## Electronic Supplementary Information (ESI)

### **Development of naphtho[1,2-*b*:5,6-*b'*]dithiophene based novel small molecules for efficient bulk-heterojunction organic solar cells**

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## 1. General Instrumentation

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a JEOL FT-NMR (400MHz and 100 MHz) spectrophotometer using chloroform-d ( $\text{CDCl}_3$ ) as solvent. Chemical shifts were reported as  $\delta$  values (ppm) relative to tetramethylsilane (TMS) as internal standards. Elemental analyses were carried out using CE Instruments Flash EA 1112 series. The UV-vis absorption spectra were obtained using a Shimadzu UV-2550 spectrophotometer. Photoluminescence (PL) spectra of films or solutions in chlorobenzene were obtained using a FP-6500 (JASCO). Cyclic voltammetry (CV) measurements were performed on a VersaSTAT3 (METEK), using a solution of tetrabutylammonium hexafluorophosphate ( $\text{n-Bu}_4\text{NPF}_6$ ) (0.10M) in acetonitrile, under argon, at a scan rate of  $50 \text{ mVs}^{-1}$  at room temperature. A Pt wire and Ag/Ag $^+$  were used as the counter and reference electrodes, respectively. The surface morphology was measured using an Atomic Force Microscope (AFM, Digital Instruments, Tapping mode).

## 2. Material Synthesis

All chemicals and solvents were reagent grades and purchased from Aldrich, Fluka, TCI, Lancaster Chemical Co. Toluene, Chlorobenzene, Tetrahydrofuran, and diethyl ether were distilled over sodium/benzophenone to keep anhydrous before use. Chloroform was purified by refluxing with calcium hydride and then distilled. Naphtho[1,2-b:5,6-b']dithiophene<sup>1</sup> (NDT) (**7**) and 4-bromobenzo[c]-[1,2,5]thiadiazole<sup>2</sup> (**12**) were prepared according to literature procedures.

### (i) Synthesis of 2,7-Bis(trimethylstannyl)naphtho[1,2-b:5,6-b']dithiophene (**8**)

To a solution of NDT **7** (0.5 g, 2.08 mmol) in THF (20 mL), TMEDA (0.68 mL, 4.57 mmol) was added at  $-50^\circ\text{C}$  under stirring, and then 1.6 M n-butyllithium in hexane (4.57 mmol, 2.85 mL) was added dropwise at  $-78^\circ\text{C}$ . The solution was stirred at  $-78^\circ\text{C}$  for 30 minutes and subsequently refluxed for 2 h under  $\text{N}_2$  atmosphere. Then the reaction mixture was cooled to  $-78^\circ\text{C}$ , and trimethyl tin chloride in THF (1.04 mL, 5.0 mmol) was added in one portion. The reaction mixture was warmed to room temperature and was stirred for 6 h. The reaction was quenched with 20 mL of water and the compound was extracted with dichloromethane. The organic layer was washed twice with 20 mL brine and dried with anhydrous  $\text{MgSO}_4$ . Finally the

residue obtained after removing the solvent was recrystallized from acetone to yield 0.82 g (70 %) of **8** as white solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ: 7.56 (s, 2H, ArH), 7.92 (d, 2H, ArH), 8.05 (d, 2H, ArH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm), 0.47 (s, 18H, Sn(CH<sub>3</sub>)). δ: 143.3, 138.7, 138.5, 133.2, 125.4, 121.9, 121.4. **Elemental analysis:** Calculated for C<sub>20</sub>H<sub>24</sub>S<sub>2</sub>Sn<sub>2</sub>: C, 42.44 %; H, 4.27%; S, 11.33%. Found: C, 42.51 %; H, 4.19%; S, 11.39%.

### (ii) Synthesis of 2,7-bis(3-decylthiophene-2-yl) naphtho[1,2-b:5,6-b']dithiophene (**9**)

In a 50 mL flame-dried two neck flask fitted with condenser, 2,7-bis(trimethylstannyl)naphtho[1,2-b:5,6-b']dithiophene (**8**) (2.0 g, 3.53 mmol), 2-bromo-3-decylthiophene (2.67 g, 8.82 mmol, 2.5 eq.), and dichlorobis-(triphenylphosphine)palladium(II) (118 mg, 0.17 mmol) were added and subjected to three vacuum/argon fill cycles. Argon degassed chlorobenzene (20 mL) were added and the mixture was stirred for 20 min under argon. The reaction mixture was heated to reflux for 24 h and was monitored by TLC. After completion of the reaction, the reaction was quenched with 20 mL of water and the compound was extracted with dichloromethane. The organic layer was washed twice with 20 mL brine and dried with anhydrous MgSO<sub>4</sub>. Dichloromethane was removed under reduced pressure. The resulting crude product was purified by column chromatography eluting with hexane to afford compound **9** (1.52 g, 63 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ: 8.01 (d, 2H, ArH), 7.88 (d, 2H, ArH), 7.46 (s, 2H, ArH), 7.25 (s, 2H, ArH), 6.99 (d, 2H, ArH), 2.89 (t, 4H), 1.75-1.65 (m, 4H), 1.42-1.27 (m, 28 H), 0.85 (t, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm) δ: 140.95, 138.60, 137.77, 135.95, 130.44, 125.81, 124.89, 123.67, 122.72, 121.54, 32.13, 31.13, 30.96, 29.85, 29.83, 29.75, 29.69, 29.56, 22.89, 14.32. **Elemental analysis:** Calculated for C<sub>42</sub>H<sub>52</sub>S<sub>4</sub>, C, 73.63%; H, 7.65%; S, 18.72%. Found: C, 73.56%; H, 7.79%; S, 18.65%.

### (iii) Synthesis of 2,7-bis(3-decylthiophene-2-yl) naphtho[1,2-b:5,6-b']dithiophene distanane (**10**)

2,7-bis(3-decylthiophene-2-yl) naphtho[1,2-b:5,6-b']dithiophene distanane (**10**) was prepared similar to the method reported for the compound **8**. Briefly, to a solution of **9** (0.5 g, 0.88 mmol) in THF (20 mL), TMEDA (0.29 mL, 1.94 mmol) was added at -50 °C under stirring,

and then 1.6 M n-butyllithium in hexane (1.94 mmol, 1.20 mL) was added dropwise at  $-78\text{ }^{\circ}\text{C}$  under  $\text{N}_2$  atmosphere. After 30 min, the solution was refluxed for 2 h. The reaction mixture was cooled to  $-78\text{ }^{\circ}\text{C}$ , and trimethyl tin chloride in THF (0.44 mL, 2.4 mmol) was added in one portion. The reaction mixture was warmed to room temperature and was stirred for 6 h. The reaction was quenched with 20 mL of water and the compound was extracted with dichloromethane. The organic layer was washed twice with 20 mL brine and dried with anhydrous  $\text{MgSO}_4$ . The residue obtained after removing the solvent was recrystallized from acetone to yield 0.45 g (62%) of **10** as yellow solid.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 8.00 (d, 2H, ArH), 7.86 (d, 2H, ArH), 7.44 (s, 2H, ArH), 7.06 (s, 2H, ArH), 2.94 (t, 4H), 1.77-1.69 (m, 4H), 1.44-1.24 (m, 28 H), 0.88 (t, 6H), 0.50 (s, 18H,  $\text{Sn}(\text{CH}_3)_3$ ).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz, ppm)  $\delta$ : 141.78, 138.52, 138.26, 137.69, 137.58, 136.21, 135.98, 125.53, 122.83, 122.42, 121.24, 31.91, 30.88, 29.67, 29.63, 29.61, 29.46, 29.35, 29.24, 22.67, 14.11. **Elemental analysis**: Calculated for  $\text{C}_{48}\text{H}_{68}\text{S}_4\text{Sn}_2$ , C, 57.04%; H, 6.78%; S, 12.69%. Found: C, 57.12%; H, 6.82%; S, 12.63%.

#### (iv) BNB (**1**)

In a 50 mL flame-dried two neck flask, 2,7-bis(3-decylthiophene-2-yl) naphtho[1,2-b:5,6-b']dithiophene distanane (**10**) (0.20 g, 0.20 mmol), 4-bromobenzo[c]-[1,2,5]thiadiazole (**12**) (0.10 g, 0.5 mmol),  $\text{Pd}_2(\text{dba})_3$  (9 mg, 5 mol %) and  $\text{P}(o\text{-Tolyl})_3$  (6 mg, 10 mol %) were added and subjected to three vacuum / argon fill cycles. Argon degassed chlorobenzene (8 mL) were added and the mixture was stirred for additional 20 min flushing argon. The reaction mixture was heated to reflux for 24 h and was monitored by TLC. After completion of the reaction, water was added to quench the reaction and the organic layer was extracted with dichloromethane. Dichloromethane was removed under reduced pressure. The resulting crude product was purified by column chromatography eluting with hexane/ $\text{CH}_2\text{Cl}_2$  (5:1) to afford target compound **1** (0.12 g, 68 %).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 7.99 (d, 2H, ArH), 7.97 (d, 2H, ArH), 7.88 (d, 2H, ArH), 7.86 (d, 2H, ArH), 7.47 (d, 2H, ArH), 7.45 (s, 2H, ArH), 7.07 (s, 2H, ArH), 2.89 (t, 4H), 1.77 (m, 4H), 1.54-1.25 (m, 28 H), 0.87 (t, 6H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz, ppm)  $\delta$ : 147.40, 141.28, 137.52, 132.16, 130.60, 129.85, 129.36, 125.50, 125.15, 124.94, 123.35, 123.13, 122.74,

122.39, 121.32, 31.93, 30.60, 29.77, 29.68, 29.54, 29.38, 22.69, 14.12. **Elemental analysis:** Calculated for C<sub>54</sub>H<sub>56</sub>N<sub>4</sub>S<sub>6</sub>, C, 68.03%; H, 5.92%; S, 20.18%. Found: C, 68.12%; H, 5.84%; S, 20.27%.

**(v) [4-(7-Bromo-benzo[1,2,5]thiadiazol-4-yl)-phenyl]-diphenyl-amine (15)**

To a mixture of 4,7-dibromobenzo[c]-[1,2,5]thiadiazole **14** (0.5 g, 1.7 mmol), **N,N**-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline **13** (0.49 g, 1.7 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.1 g, 0.08 mmol) under N<sub>2</sub> atmosphere, 9.0 mL of degassed toluene and 3.0 mL of degassed 2M K<sub>2</sub>CO<sub>3</sub> (aq) were added and the resulting solution was vigorously stirred and heated at reflux for 24 h. When the reaction was completed, water was added to quench the reaction. The product was extracted with diethyl ether. The organic layer was collected, dried over anhydrous MgSO<sub>4</sub> and evaporated under reduced pressure. The resulting crude product was adsorbed on silica gel and purified by column chromatography using hexane/CH<sub>2</sub>Cl<sub>2</sub> mixture (4:1) as eluent to give **15** (0.42 g, 54 %) as dark yellow solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ: 7.05 (t, 2H), 7.15-7.19 (m, 6H), 7.25-7.30 (m, 4H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.78-7.80 (d, 1H), 7.89 (d, *J* = 7.2 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm) δ: 153.95, 147.48, 132.34, 129.88, 129.82, 129.38, 129.33, 127.39, 127.28, 125.02, 124.87, 123.49, 122.92, 112.170. **Elemental analysis:** Calculated for C<sub>24</sub>H<sub>16</sub>BrN<sub>3</sub>S, C, 62.89%; H, 3.52%; S, 7.00%. Found: C, 62.94%; H, 3.59%; S, 6.88%.

**(iv) TBNBT (2)**

In a 50 mL flame-dried two neck flask, 2,7-bis(3-decylthiophene-2-yl) naphtho[1,2-b:5,6-b']dithiophene distanane (**10**) (0.20 g, 0.20 mmol) and [4-(7-Bromo-benzo[1,2,5]thiadiazol-4-yl)-phenyl]-diphenyl-amine (**10**) (0.23 g, 0.5 mmol, 2.5 eq.), (9 mg, 5 mol %) and P(*o*-Tolyl)<sub>3</sub> (6 mg, 10 mol %) were added and subjected to three vacuum / argon fill cycles. Argon degassed chlorobenzene (8 mL) were added and the resulting solution was degassed for another 20 min under argon. The mixture was heated to reflux for 24 h. The reaction was quenched with water and extracted with dichloromethane. Dichloromethane was removed under reduced pressure. The resulting crude product was purified by column chromatography eluting with hexane/CH<sub>2</sub>Cl<sub>2</sub> (5:1) to afford target compound **2** (0.19 g, 72 %).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, ppm) δ: 7.97 (d, 2H), 7.93 (d, 2H), 7.85 (d, 2H), 7.78-7.80 (m, 2H), 7.64 (d, 4H), 7.49 (s, 2H), 7.25-7.30 (m, 8H), 7.16-7.19 (m, 12H), 7.08 (d, 2H), 7.05 (t, 4H) 2.95 (t, 4H), 1.80 (m, 4H), 1.53-1.25 (m, 28 H), 0.86 (t, 6H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz, ppm) δ: 147.40, 141.28, 137.52, 132.16, 130.60, 129.85, 129.36, 125.5, 125.15, 124.95, 123.36, 123.13, 122.74, 122.39, 121.32, 31.93, 30.60, 29.77, 29.68, 29.54, 29.38, 22.689. **Elemental analysis:** Calculated for C<sub>90</sub>H<sub>82</sub>N<sub>6</sub>S<sub>6</sub>, C, 75.06%; H, 5.74%; S, 13.36%. Found: C, 75.13%; H, 5.69%; S, 13.33%.

### 3. OFET device fabrication and characterization

OFET devices were fabricated in a bottom-contact geometry (channel length,  $L = 12 \mu\text{m}$ , width,  $W = 120 \mu\text{m}$ ). A heavily n-doped silicon wafer with a 300 nm thermal silicon dioxide (SiO<sub>2</sub>) layer was used as the substrate/gate electrode, with the top SiO<sub>2</sub> layer serving as the gate dielectric. The SiO<sub>2</sub> surface of the wafer substrate was first cleaned with piranha solution (H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub>) at 130 °C for 20 min, and the cleaned wafer was immersed in a solution of 1.0 mM octyltrichlorosilane (OTS-8) in toluene at room temperature for 2 h under nitrogen. The semiconductor layer was spin-coated at 2000 rpm from a 0.5 wt% chlorobenzene solution, to a thickness of 70 nm. Subsequently, a series of gold source/drain electrode pairs were deposited by vacuum evaporation through a shadow mask. Silicon oxide on the backside of the silicon wafer of the TFT device was removed with HF to provide a conductive gate contact. All device fabrication procedures and measurements were carried out in air at room temperature.

### 4. Photovoltaic device fabrication and characterization

The organic photovoltaic cells were prepared on commercial ITO-coated glass substrate with the sandwiched structure of glass/ITO/PEDOT:PSS/BNB or TBNBT:PC<sub>71</sub>BM/LiF/Al with an active area of 9 mm<sup>2</sup>. Prior to use, the patterned ITO glass was cleaned with deionized water, acetone, and isopropyl alcohol using ultrasonication, followed by treatment with UV and O<sub>3</sub>. The PEDOT:PSS (AI 4083, H. C. Starck) was spin-coated (2600 rpm, 40 s) onto the ITO glass with a thickness of 40 nm and dried at 140 °C for 20 min. A blend of BNB or TBNBT and [6,6]-phenyl-C<sub>71</sub> butyric acid methyl ester (PCBM) (Nano-C, USA) with different weight ratios (from 1:1 to 1:4 w/w) was solubilized overnight in chlorobenzene (CB), filtered through a 0.45- $\mu\text{m}$  poly(tetrafluoroethylene) (PTFE) filter and subsequently spin-coated at 1000-3000 rpm for 60 s

(thickness ~ 75-55 nm) onto the PEDOT: PSS layer of the ITO. The resulting films were dried RT for 20 min under nitrogen and then under vacuum at room temperature for 12 h. The devices were completed by deposition of a 0.5-nm layer of LiF and a 120-nm Al layer. The current–voltage ( $J$ – $V$ ) characteristics of the photovoltaic devices were measured in the dark and under white light illumination at AM 1.5 G using a solar simulator (Newport) and 100 mW/cm<sup>2</sup> conditions, adjusted with a standard PV reference (2 cm×2 cm), amono-crystalline silicon solar cell (calibrated at NREL, Colorado, USA) with a Keithley 2400 source-measure unit. The external quantum efficiency (EQE) was determined using a Polaronix K3100 spectrometer.

S8

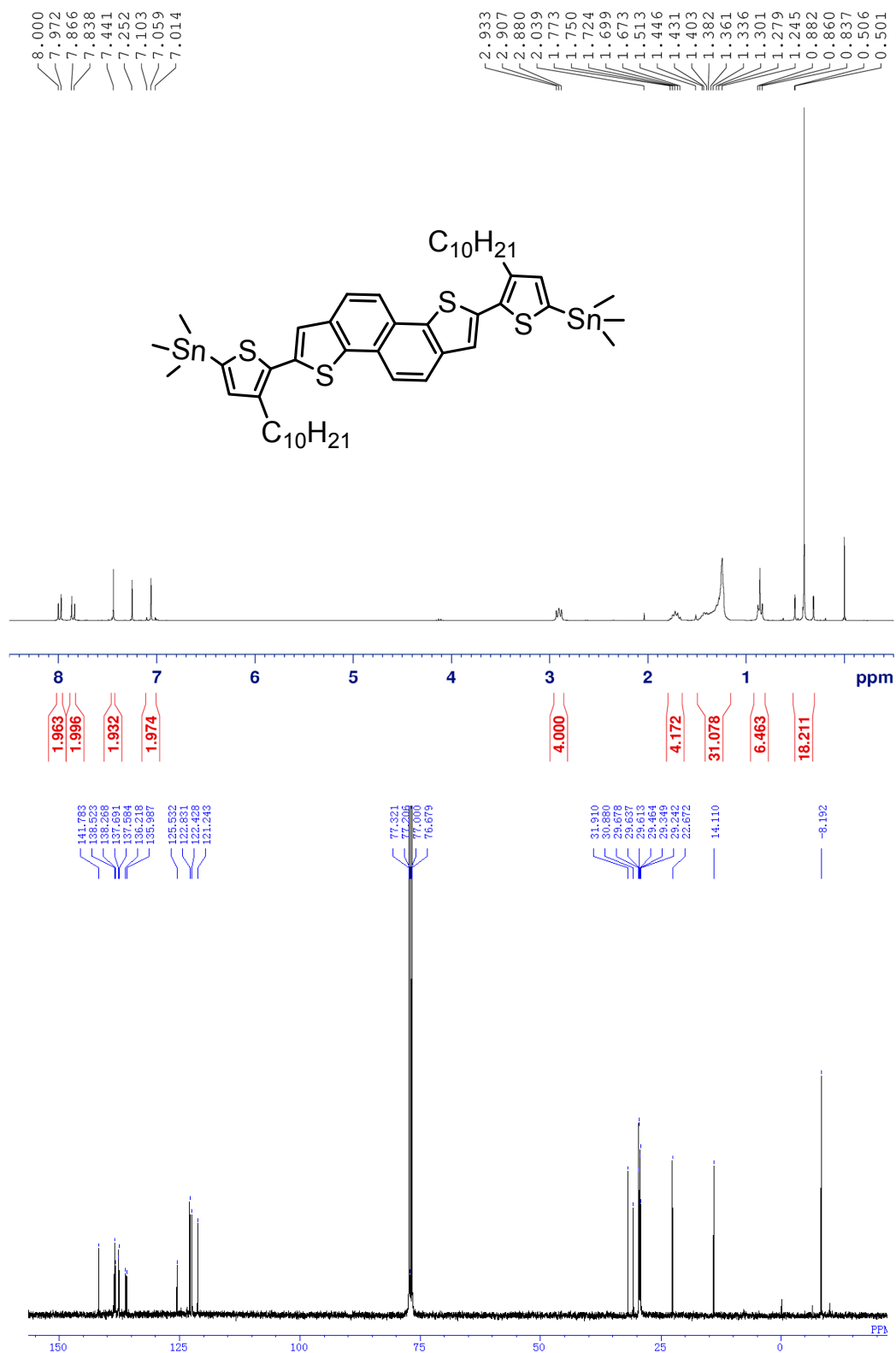


Fig. S1 <sup>1</sup>H-NMR and <sup>13</sup>C NMR spectra of compound 10



S9

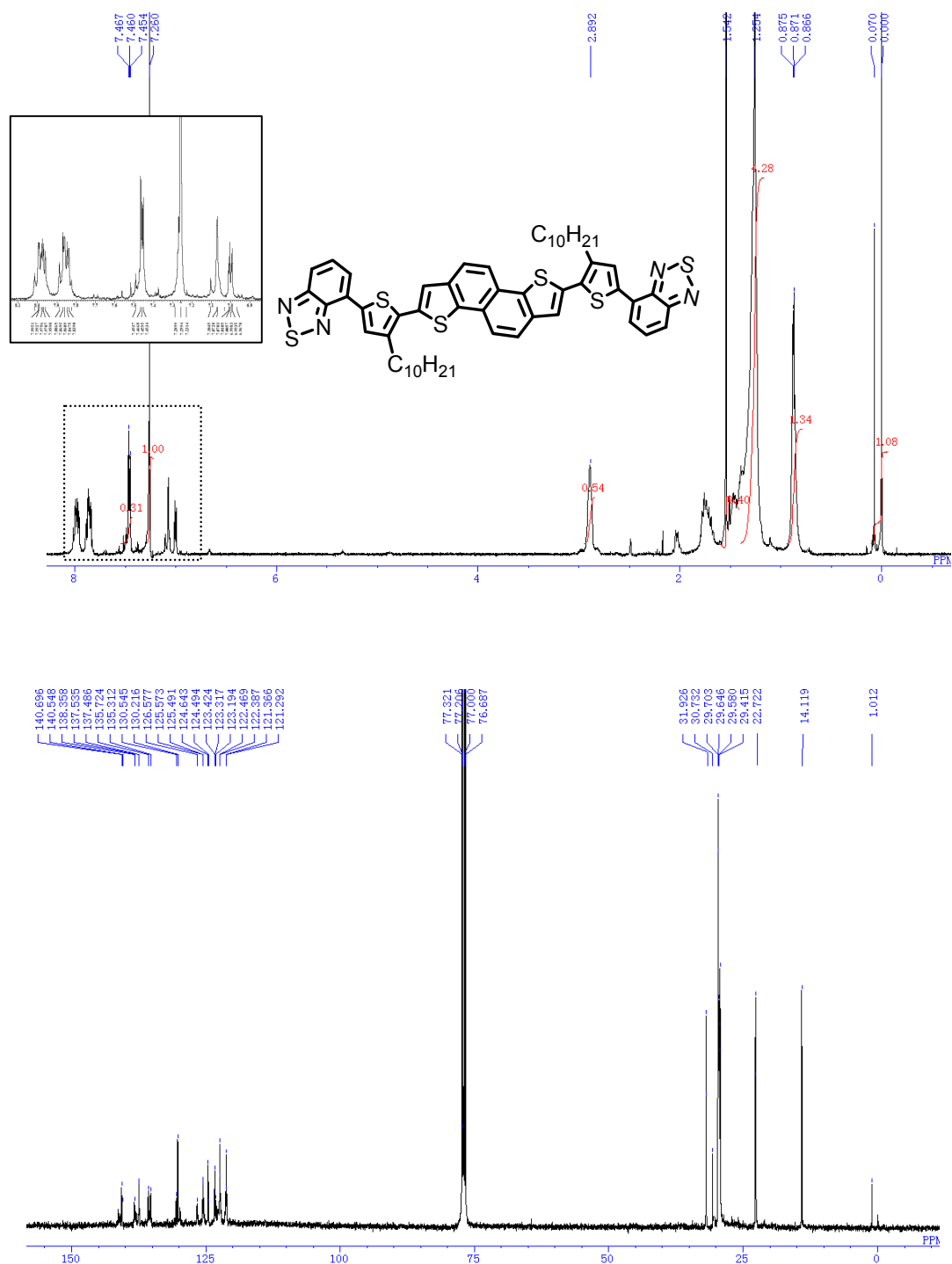


Fig. S2 <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of BNB (1)

S10

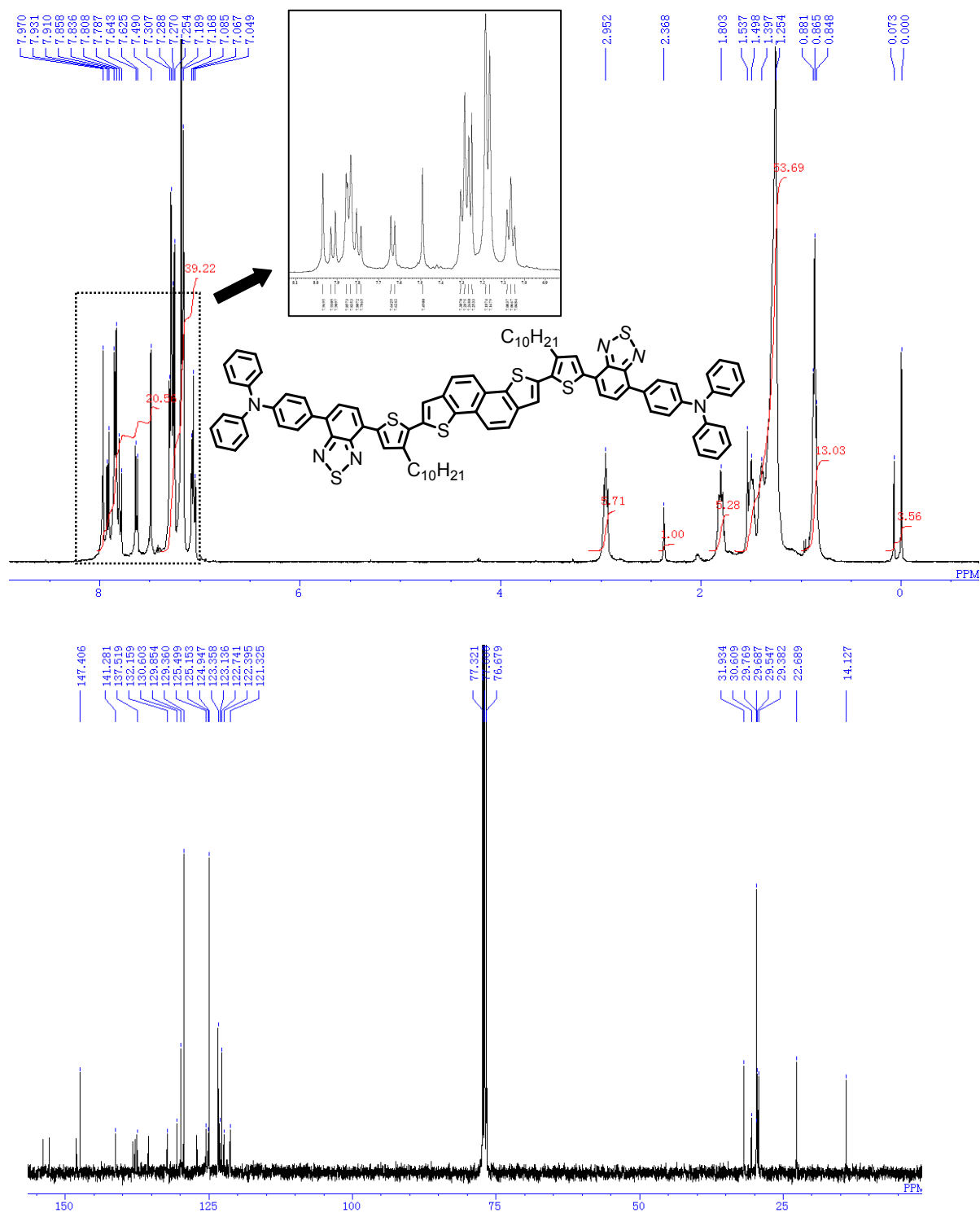
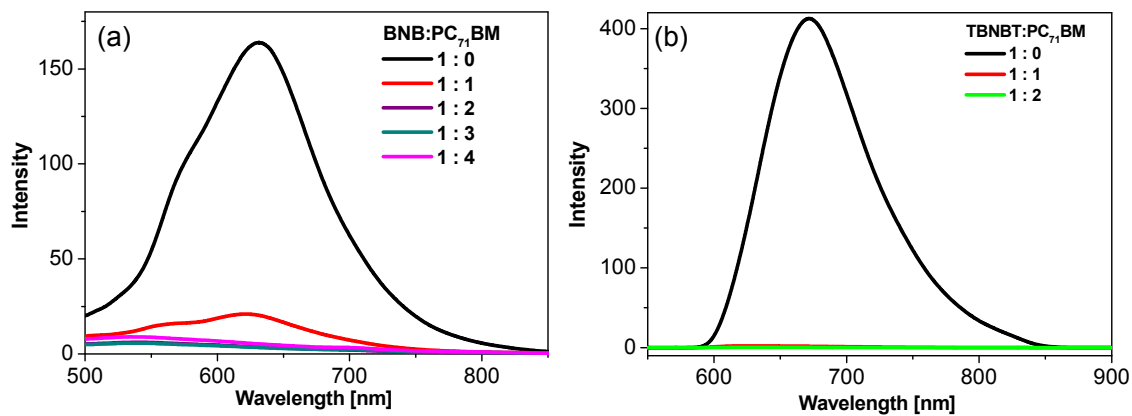
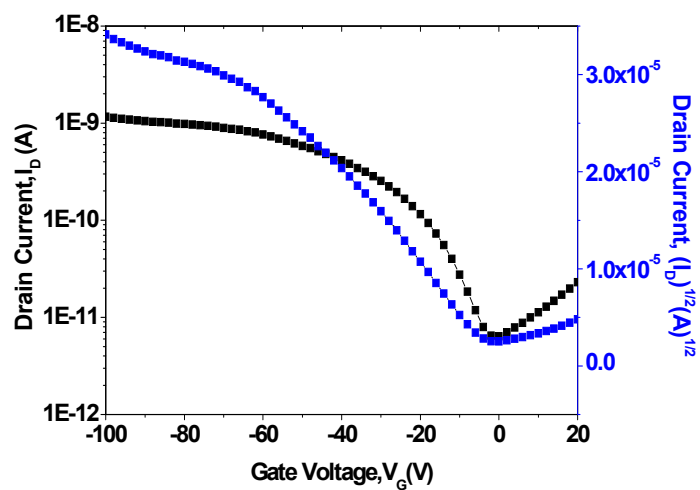


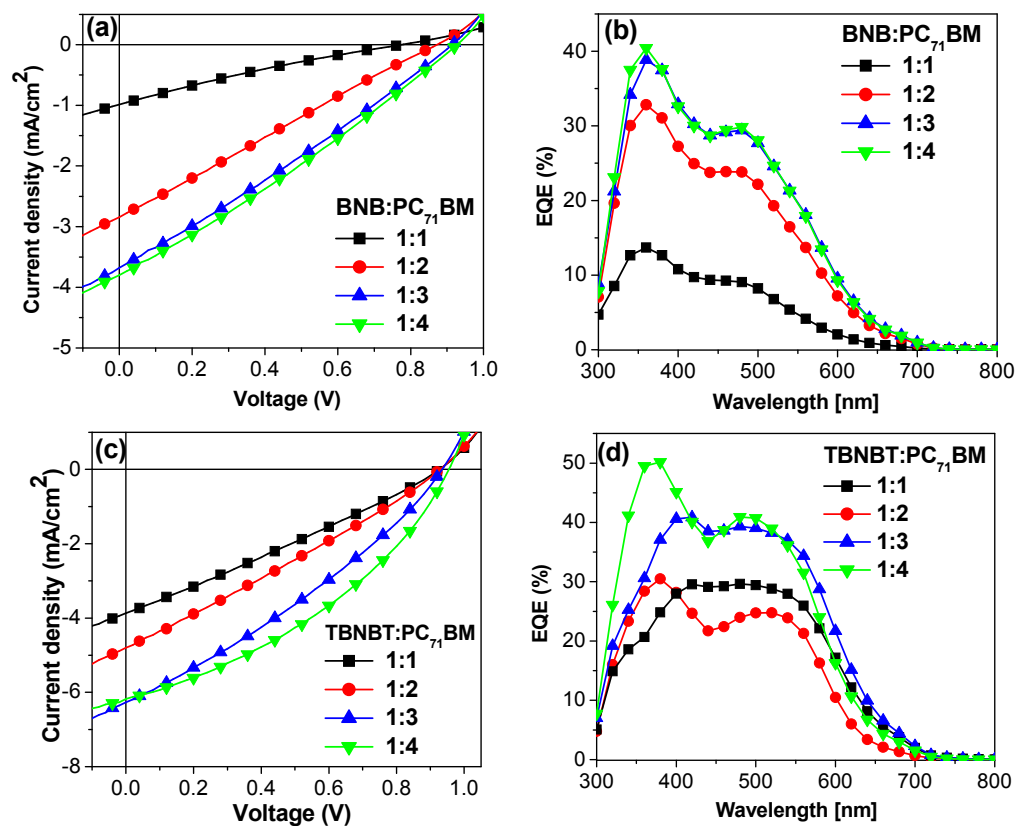
Fig. S3 <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of TBNBT (2)



**Fig. S4** PL spectra of (a) **BNB** and **BNB/PC<sub>71</sub>BM**-blended film and (b) **TBNBT** and **TBNBT/PC<sub>71</sub>BM**-blended film.



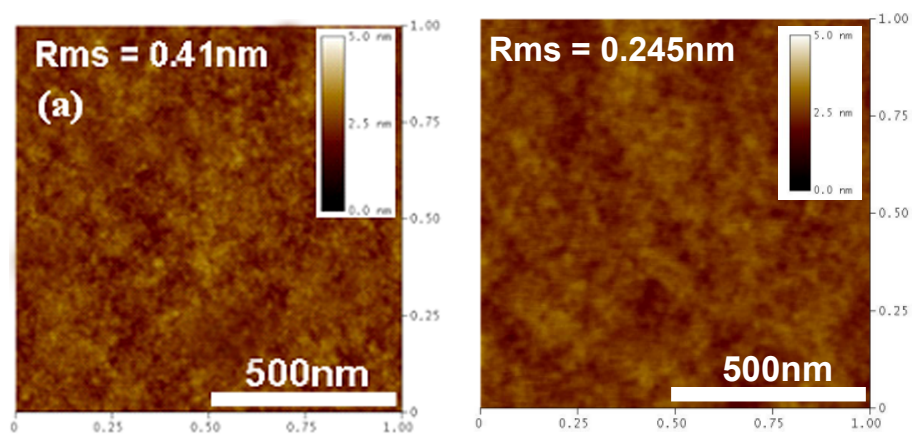
**Fig. S5** Transfer characteristics curves at constant  $V_D = -60$  V for an OFET devices with **TBNBT**.



**Fig. S6** *J-V* curve for small molecules: PC<sub>71</sub>BM solar cell devices at various ratios in CB under an illumination of AM 1.5G, 100 mW/cm<sup>2</sup>.

**Table 2.** Summary of device parameters at various small molecules/PC<sub>71</sub>BM compositions blended in CB.

Small molecules	Active layer	$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (V)	FF	PCE (%)
BNB	1:1	0.99	0.77	0.21	0.16
	1:2	2.85	0.87	0.25	0.61
	1:3	3.67	0.91	0.27	0.92
	1:4	3.79	0.93	0.28	0.98
TBNBT	1:1	3.87	0.93	0.27	0.98
	1:2	4.80	0.93	0.27	1.22
	1:3	6.27	0.94	0.31	1.82
	1:4	6.18	0.95	0.37	2.20



**Fig. S7** AFM height images of (a) **BNB:PC<sub>71</sub>BM** (1:4 w/w) and (b) **TBNBT:PC<sub>71</sub>BM** (1:4 w/w) films as-cast in chlorobenzene.

## References

1. S. Shinamura, E. Miyazaki and K. Takimiya, *J. Org. Chem.* 2010, **75**, 1228.
2. J. C. Bijleveld, M. Shahid, J. Gilot, M. M. Wienk and R. A. J. Janssen, *Adv. Funct. Mater.*, 2009, **19**, 3262.