

## Supporting Information

### Asymmetrical Small Molecule Acceptor Enabling Non-fullerene Polymer Solar Cell with Fill Factor Approaching 79%

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### General information

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of all compounds were recorded on a Bruker Advanced II (400 MHz) spectrometer using *d*-chloroform as solvent. The high resolution mass spectra (HRMS) were recorded on Thermo Scientific LTQ Orbitrap XL using ESI, and matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS) were performed on 5800 MALDI-TOF/TOF mass spectrometry (AB SCIEX, USA) in positive mode. UV-vis spectra were measured using a Shimadzu UV-2700 recording spectrophotometer. Cyclic voltammetry (CV) measurements of SMAs thin films were conducted on a CHI voltammetric analyzer in acetonitrile solution with 0.1 M tetrabutylammonium hexafluorophosphate (*n*-Bu<sub>4</sub>NPF<sub>6</sub>) as supporting electrolyte at room temperature by using a scan rate of 100

mV s<sup>-1</sup> and conventional three-electrode. Atomic force microscopy (AFM) images were obtained by using a NanoMan VS microscope in the tapping-model. The geometries of single and dimer molecules were optimized at B3LYP/def2-SVP level with RIJCOSX<sup>1</sup> approximation using ORCA 4.0 program<sup>2</sup> where the long alkyl chain was simplified to be methyl. Grimme's D3 dispersion correction with Becke-Johnson damping<sup>3</sup> and Grimme's geometrical counterpoise correction (gCP)<sup>4</sup> were used during the optimization. The wave functions were obtained using Gaussian09 program at B3LYP/6-31G(d,p) level. The transfer integral and electron density overlap integral were evaluated by J-from-g03 and Multiwfn<sup>5</sup> program, respectively.

## Synthesis

Diethyl 2,5-dibromoterephthalate, thiophene, thieno[3,2-*b*]thiophene, dithieno[3,2-*b*:2',3'-*d*]thiophene, 1-bromo-4-hexylbenzene, bis(triphenylphosphine)palladium(II) dichloride (Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>), polymer donor of PBDB-T and all solvent were purchased from commercial sources. 2-(5/6-methyl-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (DCI-M) were synthesized according to reported method.<sup>6</sup> Tetrahydrofuran (THF) was further dried by using potassium sodium alloy under refluxing condition.



stirring solution of thiophene (1.50 g, 17.86 mmol) in dry THF (25 ml) was added dropwise a 2.38 M (titrated with 4-biphenylmethanol in our laboratory) solution of *n*-butyllithium (*n*-BuLi) in hexane (7.5 ml, 17.86 mmol) at -35°C under argon atmosphere. After one hour, a solution of anhydrous zinc chloride (2.39 g, 17.86 mmol) in dry THF (30 ml) was added dropwise to the resulting solution within 10 mins, and then the mixture was allowed to stir at -35°C for another one hour. Diethyl 2,5-dibromoterephthalate (compound **1**) (6.75 g, 17.86 mmol) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (627 mg, 0.893 mmol) were added into the solution of thiophen-2-ylzinc(II) chloride under the protection of argon, and then the mixture was refluxed with a refluxing device for 12 hours. After cooling to room temperature, water was added and the mixture was extracted with dichloromethane and washed with water, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by silicon chromatography using petroleum ether/ ethyl acetate (12:1 v/v) as eluent to get the product as a pale yellow oil (3.4 g, 50%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ (ppm): 7.99 (s, 1H), 7.85 (s, 1H), 7.40 (dd, *J*<sub>1</sub> = 1.6 Hz, *J*<sub>2</sub> = 4.4 Hz, 1H), 7.06-7.08 (m, 2H), 4.43 (q, *J* = 7.2 Hz, 2H), 4.22 (q, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>), δ (ppm): 166.58, 165.29, 139.79, 135.30, 134.93, 134.48, 133.49, 133.29, 127.42, 127.13, 126.69, 120.61, 62.16, 61.91, 14.21, 13.81; MS *m/z*: [M] calcd. for C<sub>16</sub>H<sub>15</sub>BrO<sub>4</sub>S, 381.99; found, 382.00.

*Synthesis of diethyl 2-(thieno[3,2-*b*]thiophen-2-yl)-5-(thiophen-2-yl)terephthalate (compound **3**):* To a stirring solution of thieno[3,2-*b*]thiophene (1.2 g, 8.64 mmol) in dry THF (20 ml) was added dropwise a 2.38 M solution of *n*-BuLi in hexane (3.6 ml,

8.64 mmol) at -35°C under argon atmosphere. After one hour, a solution of anhydrous zinc chloride (1.16 g, 8.64 mmol) in dry THF (20 ml) was added dropwise to the resulting solution within 10 mins, and then the mixture was allowed to stir at -35°C for another one hour. Compound **2** (3.0 g, 7.85 mmol) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (275 mg, 0.393 mmol) were added into the solution of thieno[3,2-*b*]thiophene-2-ylzinc(II) chloride under the protection of argon, and then the mixture was refluxed with a refluxing device for 12 hours. After cooling to room temperature, water was added and the mixture was extracted with dichloromethane and washed with water, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by silicon chromatography using petroleum ether/dichloromethane (3:1 v/v) as eluent to get the product as a yellow solid (2.85 g, 82%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ (ppm): 7.86 (s, 1H), 7.84 (s, 1H), 7.39-7.41 (m, 2H), 7.26-7.28 (m, 2H), 7.08-7.12 (m, 2H), 4.20-4.26 (m, 4H), 1.11-1.18 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>), δ (ppm): 167.66, 167.59, 142.13, 140.39, 139.87, 139.35, 134.13, 134.03, 133.76, 133.51, 132.01, 131.97, 127.43, 127.35, 127.07, 126.63, 119.45, 119.22, 61.81, 61.76, 13.86, 13.84; MS *m/z*: [M] calcd. for C<sub>22</sub>H<sub>18</sub>O<sub>4</sub>S<sub>3</sub>, 442.04; found, 442.20.

#### *Synthesis*

*of*

#### ***4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-*b*]thiophene-alt-***

***[5,6-*d*]thieno[3,2-*b*]thiophene (compound 4)***: To a stirring solution of compound **3** (800 mg, 1.81 mmol) in dry THF (30 ml) under argon condition was added dropwise (4-hexylphenyl)magnesium bromide which was prepared from 1-bromo-4-hexylbenzene (6.54 g, 27 mmol) and magnesium (715 mg, 30 mmol) in

THF (15 ml). Then the mixed solution was heated to reflux for 16h. After cooling to room temperature, the solution was poured into water and extracted with ethyl acetate, then washed with saturated salt water several times and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent under reduced pressure, the crude product was obtained and then used in the next step without further purification. The crude product was dissolved in chloroform/glacial acetic acid (5:1 v/v), and 1 ml concentrated sulfuric acid in 5 ml glacial acetic acid was dropwise added into the solution, then the mixture was refluxed for 30 min. After cooling to room temperature, the mixture was extracted with dichloromethane and washed with water. The collected organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by column chromatography on silica gel using a mixture solvent as eluent (petroleum ether/dichloromethane, v/v = 15/1) to give a yellow solid (627 mg, 36%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ (ppm): 7.49 (s, 1H), 7.43 (s, 1H), 7.23-7.25 (m, 3H), 7.17 (d, *J* = 8.4 Hz, 8H), 7.07 (d, *J* = 8.4 Hz, 8H), 7.00 (d, *J* = 4.8 Hz, 1H), 2.52-2.57 (m, 8H), 1.54-1.58 (m, 8H), 1.28 (m, 24H), 0.83-0.88 (m, 12H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>), δ (ppm): 156.06, 153.69, 153.11, 145.94, 143.40, 142.14, 141.77, 141.65, 141.51, 141.29, 140.51, 135.89, 135.55, 133.88, 128.52, 128.43, 128.17, 128.02, 127.67, 126.36, 123.23, 120.44, 117.35, 117.27, 63.04, 62.80, 35.71, 31.86, 31.84, 31.49, 31.42, 29.29, 22.73, 14.26; MALDI-TOF-MS *m/z*: [M] calcd. for C<sub>66</sub>H<sub>74</sub>S<sub>3</sub>, 962.50, found 962.36.

*Synthesis*

*of*

***4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-b]thiophene-alt-***

**[5,6-*d*]thieno[3,2-*b*]thiophene-dicarbaldehyde (compound 5):** To a dry 100 mL two-necked round bottom flask, 20 mL anhydrous *N,N*-dimethylformamide (DMF) was added, and the solution was cooled to 0°C and stirred when 4 mL phosphorous oxychloride (POCl<sub>3</sub>) was added by syringe under argon protection. The mixture kept at 0°C for 1.5h, and then compound 4 (600 mg, 0.62 mmol) in dry 1, 2-dichloroethane (30 mL) was added. Then, the mixture solution was allowed to reflux overnight. After cooling to room temperature, 100 mL water was added, then the mixture was extracted with dichloromethane (DCM), and the organic layer was collected, washed with water and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using a mixture solvent as eluent (petroleum ether/dichloromethane, v/v = 3/2) to give a yellow solid (483 mg, 77%). <sup>1</sup>H NMR (400 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), 7.08-7.16 (m, 16H), 2.57 (q, *J*<sub>1</sub> = 7.6 Hz, *J*<sub>2</sub> = 15.2 Hz, 8H), 1.58 (m, 8H), 1.28-1.31 (m, 24H), 0.85-0.87 (m, 12H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>), δ (ppm): 182.96, 156.70, 155.18, 154.61, 150.72, 149.26, 146.99, 146.12, 144.59, 142.42, 142.19, 141.96, 140.73, 140.17, 139.11, 137.19, 135.25, 132.07, 129.87, 128.79, 128.66, 127.82, 127.72, 118.93, 118.29, 63.13, 62.98, 35.60, 35.59, 31.74, 31.72, 31.38, 31.31, 29.17, 29.15, 22.64, 22.62, 14.15, 14.14; HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd. for C<sub>68</sub>H<sub>75</sub>O<sub>2</sub>S<sub>3</sub><sup>+</sup>, 1019.49237, found 1019.49304.

**Synthesis of *IDT6CN-M*:** To a 100 mL round bottom flask, compound 6 (250 mg, 0.245 mmol), DCI-M (205 mg, 0.982 mmol), chloroform (40 mL) were added under

argon protection and stirred for a while when pyridine (1 ml) was added. The mixture was kept stirring at 70°C for 12 h. After removal of chloroform of reaction mixture under reduced pressure, 100 ml methanol was added and the precipitate was collected by filtration. The residue was purified by column chromatography on silica gel using a mixture solvent as eluent (petroleum ether/dichloromethane, v/v = 1/1) to give a dark solid (274 mg, 80%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ (ppm): 8.85 (s, 1H), 8.83 (s, 1H), 8.56 (d, *J* = 8.0 Hz, 1H), 8.47 (s, 1H), 8.19 (d, *J* = 5.6 Hz, 1H), 7.79-7.81 (m, 1H), 7.76 (m, 1H), 7.68 (m, 2H), 7.58 (s, 1H), 7.52-7.55 (m, 2H), 7.10-7.22 (m, 16H), 2.53-2.60 (m, 14H), 1.61 (m, 8H), 1.29-1.35 (m, 24H), 0.84-0.89 (m, 12H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>), δ (ppm): 188.58, 188.33, 188.21, 187.95, 160.54, 160.49, 160.44, 160.39, 158.92, 158.81, 157.59, 156.29, 155.57, 152.24, 148.01, 146.91, 146.82, 146.73, 146.61, 146.37, 146.31, 143.74, 142.51, 142.32, 141.10, 140.45, 140.35, 139.78, 139.22, 138.96, 138.17, 138.06, 137.88, 137.69, 137.62, 137.24, 137.20, 136.53, 136.18, 136.11, 135.99, 135.62, 135.54, 134.77, 134.74, 128.91, 128.75, 127.84, 127.75, 125.67, 125.28, 124.09, 123.71, 123.47, 123.43, 122.70, 122.64, 119.66, 118.74, 114.85, 114.77, 114.66, 114.60, 69.28, 68.86, 68.71, 68.29, 63.22, 62.97, 35.63, 35.59, 31.74, 31.38, 31.30, 29.19, 29.14, 22.62, 14.15; MALDI-TOF-MS *m/z*: [M] calcd. for C<sub>94</sub>H<sub>86</sub>N<sub>4</sub>O<sub>2</sub>S<sub>3</sub>, 1398.59, found 1398.69. Anal. calcd (%) for (C<sub>94</sub>H<sub>86</sub>N<sub>4</sub>O<sub>2</sub>S<sub>3</sub>): C, 80.65; H, 6.19; N, 4.00; S, 6.87; found: C, 80.43; H, 6.23; N, 4.12; S, 6.56.

*Synthesis of diethyl 2-bromo-5-(thieno[3,2-*b*]thiophen-2-yl)terephthalate (compound 6):* To a stirring solution of thieno[3,2-*b*]thiophene (1.50 g, 10.72 mmol)



in dry THF (25 ml) was added dropwise a 2.38 M (titrated with 4-biphenylmethanol in our laboratory) solution of *n*-butyllithium (*n*-BuLi) in hexane (4.5 ml, 10.72 mmol) at -35°C under argon atmosphere. After one hour, a solution of anhydrous zinc chloride (1.44 g, 10.72 mmol) in dry THF (20 ml) was added dropwise to the resulting solution within 10 mins, and then the mixture was allowed to stir at -35°C for another one hour. Diethyl 2,5-dibromoterephthalate (compound **1**) (4.05 g, 10.72 mmol) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (376 mg, 0.536 mmol) were added into the solution of thieno[3,2-*b*]thiophene-2-ylzinc(II) chloride under the protection of argon, and then the mixture was refluxed with a refluxing device for 12 hours. After cooling to room temperature, water was added and the mixture was extracted with dichloromethane and washed with water, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by silicon chromatography using petroleum ether/ ethyl acetate (10:1 v/v) as eluent to get the product as an yellow solid (1.92 g, 41%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ (ppm): 8.01 (s, 1H), 7.91 (s, 1H), 7.39 (d, *J* = 5.2 Hz, 1H), 7.25-7.27 (m, 2H), 4.42 (q, *J*<sub>1</sub> = 6.8 Hz, *J*<sub>2</sub> = 14.0 Hz, 2H), 4.22 (q, *J*<sub>1</sub> = 7.2 Hz, *J*<sub>2</sub> = 14.4 Hz, 2H), 1.41 (t, 3H), 1.13 (t, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>), δ (ppm): 166.42, 165.20, 141.36, 139.91, 139.32, 135.22, 135.10, 134.54, 133.60, 133.38, 127.54, 121.01, 119.42, 119.38, 62.22, 62.04, 14.22, 13.84. HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd. for C<sub>18</sub>H<sub>16</sub>BrO<sub>4</sub>S<sub>2</sub><sup>+</sup>, 438.96679, found 438.96634.

*Synthesis of diethyl 2-(dithieno[3,2-*b*:2',3'-*d*]thiophen-2-yl)-5-(thieno[3,2-*b*]thiophen-2-yl)terephthalate (compound **7**):* To a stirring solution of dithieno[3,2-*b*:2',3'-*d*]thiophene (886 mg, 4.52

mmol) in dry THF (20 ml) was added dropwise a 2.38 M solution of *n*-BuLi in hexane (1.9 ml, 4.52 mmol) at -35°C under argon atmosphere. After one hour, a solution of anhydrous zinc chloride (605 mg, 4.52 mmol) in dry THF (20 ml) was added dropwise to the resulting solution within 10 mins, and then the mixture was allowed to stir at -35°C for another one hour. Compound **6** (1.8 g, 4.11 mmol) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (145 mg, 0.206 mmol) were added into the solution of dithieno[3,2-*b*:2',3'-*d*]thiophen-2-ylzinc(II) chloride under the protection of argon, and then the mixture was refluxed with a refluxing device for 12 hours. After cooling to room temperature, water was added and the mixture was extracted with dichloromethane and washed with water, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by silicon chromatography using petroleum ether/dichloromethane (2:1 v/v) as eluent to get the product as an yellow solid (1.55 g, 68%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ (ppm): 7.91 (s, 2H), 7.41 (d, *J* = 1.2 Hz, 1H), 7.40 (d, *J* = 1.2 Hz, 1H), 7.27-7.32 (m, 4H), 4.23-4.29 (m, 4H), 1.16 (q, *J*<sub>1</sub> = 7.2 Hz, *J*<sub>2</sub> = 13.2 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>), δ (ppm): 167.45, 141.96, 141.48, 141.46, 140.52, 139.96, 139.39, 134.15, 134.01, 133.88, 133.48, 132.21, 132.09, 127.47, 126.49, 120.80, 120.71, 119.46, 119.34, 61.94, 61.91, 13.94, 13.88. HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd. for C<sub>26</sub>H<sub>19</sub>O<sub>4</sub>S<sub>5</sub><sup>+</sup>, 554.98814, found 554.98814.

### *Synthesis*

*of*

**4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-*b*]thiophene[3,2-*b*]thiophene-alt-[5,6-*d*]dithieno[3,2-*b*:2',3'-*d*]thiophene (compound 8):** To a stirring solution of compound **7** (600 mg, 1.08 mmol) in dry THF (30 ml) under argon

condition was added dropwise (4-hexylphenyl)magnesium bromide which was prepared from 1-bromo-4-hexylbenzene (3.90 g, 16.2 mmol) and magnesium (428 mg, 17.8 mmol) in THF (9 ml). Then the mixed solution was heated to reflux for 16h. After cooling to room temperature, the solution was poured into water and extracted with ethyl acetate, then washed with saturated salt water several times and dried with anhydrous  $\text{Na}_2\text{SO}_4$ . After removal of the solvent under reduced pressure, the crude product was obtained and then used in the next step without further purification. The crude product was dissolved in chloroform/glacial acetic acid (5:1 v/v), and 1 ml concentrated sulfuric acid in 5 ml glacial acetic acid was dropwise added into the solution, then the mixture was refluxed for 30 min. After cooling to room temperature, the mixture was extracted with dichloromethane and washed with water. The collected organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated. The residue was purified by column chromatography on silica gel using a mixture solvent as eluent (petroleum ether/dichloromethane, v/v = 10/1) to give a yellow solid (325 mg, 28%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 7.51 (s, 2H), 7.27-7.30 (m, 4H), 7.18-7.21 (m, 8H), 7.10 (d,  $J$  = 8.4 Hz, 8H), 2.53-2.57 (m, 8H), 1.55-1.59 (m, 8H), 1.27-1.43 (m, 24H), 0.83-0.87 (m, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 158.52, 158.18, 158.08, 153.30, 153.24, 153.12, 147.37, 147.16, 146.32, 146.14, 146.09, 145.96, 143.27, 141.84, 141.77, 141.63, 141.58, 141.41, 141.28, 141.10, 140.88, 140.64, 140.51, 140.35, 140.22, 140.14, 140.01, 136.21, 136.04, 135.63, 134.79, 133.82, 133.03, 132.87, 132.22, 130.24, 129.33, 128.73, 128.47, 128.44, 128.21, 128.15, 128.11, 126.37, 126.26, 126.11, 120.40, 116.93, 116.84, 116.68, 63.06, 63.03, 62.99,

42.36, 35.65, 35.53, 31.94, 31.77, 31.47, 31.45, 31.36, 29.24, 29.17, 22.66, 14.18.

HRMS (ESI) m/z:  $[M + H]^+$  calcd. for  $C_{70}H_{75}S_5^+$ , 1075.44669, found 1075.44643.

### *Synthesis*

*of*

***4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-b]thiophene[3,2-b]thiophene-alt-[5,6-d]dithieno[3,2-b:2',3'-d]thiophene-dicarbaldehyde (compound 9)***: To a dry 100 mL two-necked round bottom flask, 10 ml anhydrous *N,N*-dimethylformamide (DMF) was added, and the solution was cooled to 0°C and stirred when 2 ml phosphorous oxychloride ( $POCl_3$ ) was added by syringe under argon protection. The mixture kept at 0°C for 1.5h, and then compound 4 (300 mg, 0.28 mmol) in dry 1, 2-dichloroethane (20 ml) was added. Then, the mixture solution was allowed to reflux overnight. After cooling to room temperature, 100 ml water was added, then the mixture was extracted with dichloromethane (DCM), and the organic layer was collected, washed with water and dried with anhydrous  $Na_2SO_4$ . After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using a mixture solvent as eluent (petroleum ether/dichloromethane, v/v = 1/1) to give a yellow solid (230 mg, 73%).  $^1H$  NMR (400 MHz,  $CDCl_3$ ),  $\delta$  (ppm): 9.91 (s, 1H), 9.89 (s, 1H), 7.94 (s, 1H), 7.86 (s, 1H), 7.61 (s, 1H), 7.60 (s, 1H), 7.10-7.20 (m, 16H), 2.56 (t,  $J$  = 7.6 Hz, 8H), 1.55-1.62 (m, 8H), 1.28-1.35 (m, 24H), 0.85-0.88 (m, 12H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ),  $\delta$  (ppm): 182.92, 182.74, 154.65, 154.18, 149.64, 147.85, 146.44, 145.59, 144.28, 143.26, 142.36, 141.62, 141.19, 140.51, 140.29, 139.30, 139.28, 138.72, 136.70, 136.04, 132.89, 130.13, 129.91, 128.76, 128.69, 127.95, 127.86, 117.90, 117.57, 63.20, 63.12,

35.61, 31.72, 31.31, 29.18, 22.61, 14.13.

*Synthesis of **IDT8CN-M***: To a 100 ml round bottom flask, compound 6 (200 mg, 0.177 mmol), DCI-M (147 mg, 0.708 mmol), chloroform (40 ml) were added under argon protection and stirred for a while when pyridine (1 ml) was added. The mixture was kept stirring at 70°C for 12 h. After removal of chloroform of reaction mixture under reduced pressure, 100 ml methanol was added and the precipitate was collected by filtration. The residue was purified by column chromatography on silica gel using a mixture solvent as eluent (petroleum ether/dichloromethane, v/v = 1/1) to give a dark solid (203 mg, 76%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ (ppm): 8.87 (d, *J* = 2.8 Hz, 1H), 8.82 (s, 1H), 8.52 (t, *J* = 8.4 Hz, 0.8 H), 8.45 (d, *J* = 7.6 Hz, 1.2H), 8.18 (d, *J* = 6.0 Hz, 1H), 7.90 (d, *J* = 9.6 Hz, 1H), 7.78 (t, *J* = 7.2 Hz, 1.2H), 7.69 (d, *J* = 7.6 Hz, 0.8H), 7.64 (s, 2H), 7.50-7.53 (m, 1H), 7.46-7.49 (m, 1H), 7.12-7.26 (m, 16H), 2.49-2.60 (m, 14H), 1.55-1.63 (m, 8H), 1.28-1.35 (m, 24H), 0.86 (t, *q* = 6.4 Hz, 8H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>), δ (ppm): 188.60, 188.34, 188.22, 187.97, 160.48, 160.42, 160.25, 155.64, 154.73, 152.80, 148.41, 147.91, 147.32, 147.02, 146.90, 146.79, 146.31, 146.25, 145.62, 145.50, 143.34, 142.56, 142.54, 142.47, 140.40, 139.41, 139.08, 139.03, 138.11, 137.87, 137.69, 137.26, 137.18, 137.13, 136.86, 136.68, 136.24, 135.51, 134.71, 134.65, 133.45, 128.88, 128.80, 127.95, 127.91, 125.61, 125.23, 124.06, 123.70, 123.63, 123.08, 122.93, 122.89, 118.36, 117.94, 114.74, 114.69, 69.16, 68.98, 68.56, 68.42, 63.24, 63.22, 35.65, 35.62, 31.74, 31.72, 31.32, 29.25, 29.18, 22.63, 22.62, 22.59, 22.11, 14.15, 14.14. MALDI-TOF-MS *m/z*: [M] calcd. for C<sub>98</sub>H<sub>86</sub>N<sub>4</sub>O<sub>2</sub>S<sub>5</sub>, 1510. 54, found 1510.33. Anal. calcd (%) for

(C<sub>98</sub>H<sub>86</sub>N<sub>4</sub>O<sub>2</sub>S<sub>5</sub>): C, 77.84; H, 5.73; N, 3.71; S, 10.60; found: C, 77.67; H, 5.88; N, 3.43; S, 10.38.

### **Devices fabrication and characterization**

Polymer solar cells (PSCs) devices using IDT6CN-M or IDT8CN-M as electron acceptors and PBDB-T as electron donor were fabricated with a structure of ITO/PEDOT:PSS/active layer/ZrAcAc/Al. The patterned ITO-coated glass was scrubbed by detergent and then cleaned inside an ultrasonic bath by using deionized water, acetone, and isopropyl alcohol sequentially and dried overnight in an oven. Before use, the glass substrates were treated in a UV-Ozone Cleaner for 20 min to improve its work function and clearance. The IDT6CN-M (or IDT8CN-M) and PBDB-T (weight ratio of 1:1) were dissolved in chloroform with 0.5 % DIO addition, then the mixture was stirred overnight at room temperature to obtain a blend solution with a total concentration of 16 mg/mL. A thin PEDOT: PSS (Heraeus Clevios P VP A 4083) layer (40 nm) was spin-coated onto the ITO substrates and then dried at 150 °C for 10 min in air. The PEDOT:PSS coated ITO substrates were fast transferred to a N<sub>2</sub> filled glove-box for further processing. The blend solution was spin-cast on the top of PEDOT: PSS layer at 2000 rpm for 40 s. Then it was annealed at 100 °C for 5 min. Subsequently, the active layer coated substrates were quickly transferred to a glove-box integrated thermal evaporator for electrode deposition. A thin ZrAcAc layer (10 nm) and Al layer (100 nm) were sequentially evaporated under vacuum of  $5 \times 10^{-5}$  Pa through a shadow mask. The active area of each device was 3.14 mm<sup>2</sup> controlled

by a shadow mask. The optimal blend thickness measured on a Bruker Dektak XT stylus profilometer was about 105 nm. The current-voltage ( $J$ - $V$ ) characteristic curves of all packaged devices were measured by using a Keithley 2400 Source Meter in air. Photocurrent was measured under AM 1.5G (100 mW cm<sup>-2</sup>) using a Newport solar simulator in an Air. The light intensity was calibrated using a standard Si diode (with KG5 filter, purchased from PV Measurement) to bring spectral mismatch to unity. EQEs were measured using an Enlitech QE-S EQE system equipped with a standard Si diode. Monochromatic light was generated from a Newport 300W lamp source.

### **SCLC measurements**

The electron-only SCLC devices were a stack of ITO/ZnO/active layer/ZrAcAc/Al, and the hole-only devices were a stack of ITO/V<sub>2</sub>O<sub>5</sub>/active layer/V<sub>2</sub>O<sub>5</sub>/Al. The electron-only and hole-only SCLC devices fabrication processing methods are same with those for solar cell. The charge carrier mobility was determined by fitting the dark current to the model of a single carrier SCLC according to the equation:

$$J = \frac{9\varepsilon_0\varepsilon_r\mu V^2}{8L^3}$$

where  $J$  is the current density,  $L$  is the film thickness of the active layer,  $\mu$  is the charge carrier mobility,  $\varepsilon_r$  is the relative dielectric constant of the transport medium, and  $\varepsilon_0$  is the permittivity of free space.  $V = V_{\text{app}} - V_{\text{bi}}$ , where  $V_{\text{app}}$  is the applied voltage,  $V_{\text{bi}}$  is the offset voltage. The carrier mobility can be calculated from the slope of the  $J^{1/2} \sim V$  curves.

## **OFET fabrication and characterization**

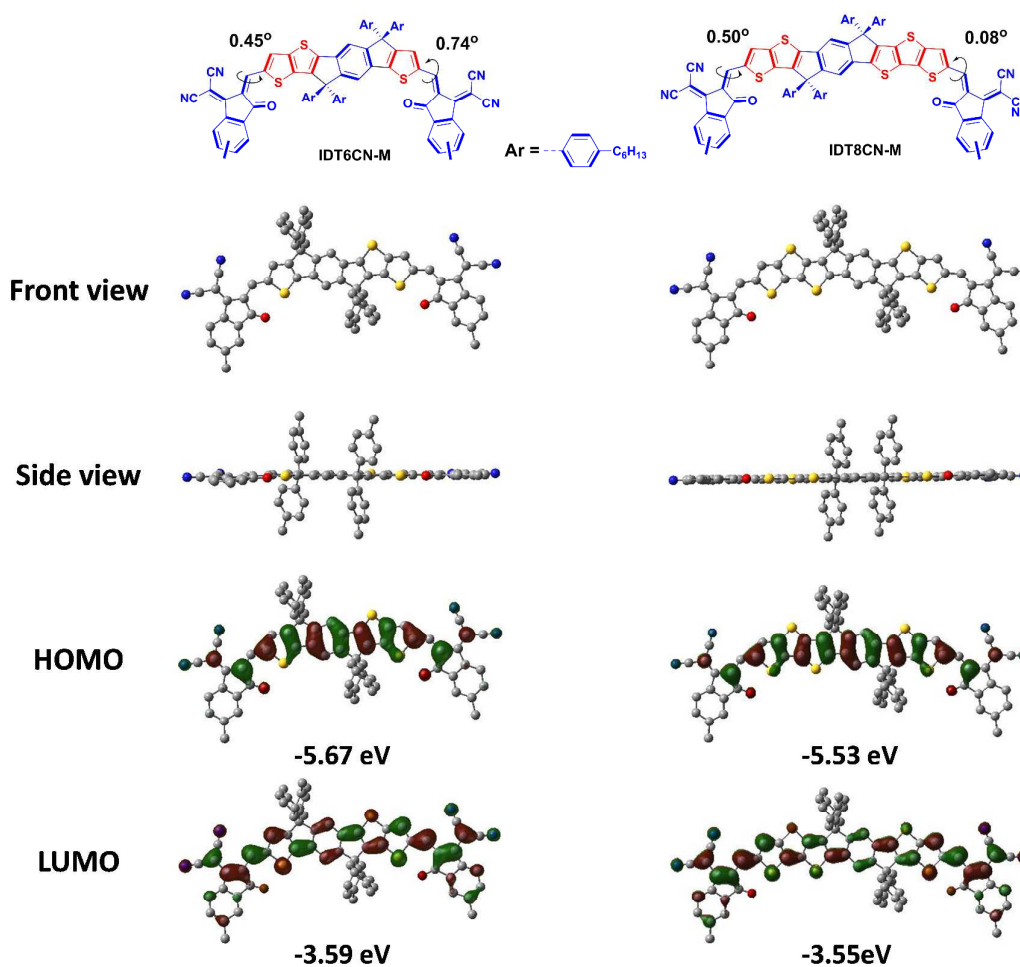
Organic field-effect transistors (OFETs) devices in a top-gate bottom-contact configuration were fabricated on Corning glass substrate. The source-drain gold electrodes (gold/titanium, 30 nm/5 nm) were prepared through a photolithography technique. Polar SMAs of IDT6CN-M or IDT8CN-M in  $\text{CHCl}_3$  solution with a concentration of  $10 \text{ mg mL}^{-1}$  was spin-cast on top of Au-coated Corning glass substrate at a spin coating rate of 2500 rpm, and then the samples were annealed at  $120^\circ\text{C}$  for 5 min. A Cytop layer (300 nm) was acted as the dielectric layer. The aluminum (Al) gate electrodes (thickness  $\sim 80 \text{ nm}$ ) were evaporated through a shadow mask onto the surface of the Cytop gate dielectric. Electrical characterization of OFET devices used a Keithley 4200 SCS semiconductor parameter analyzer. All measurements were performed under an inert nitrogen atmosphere.

## **GIWAXS and RSoXS measurements**

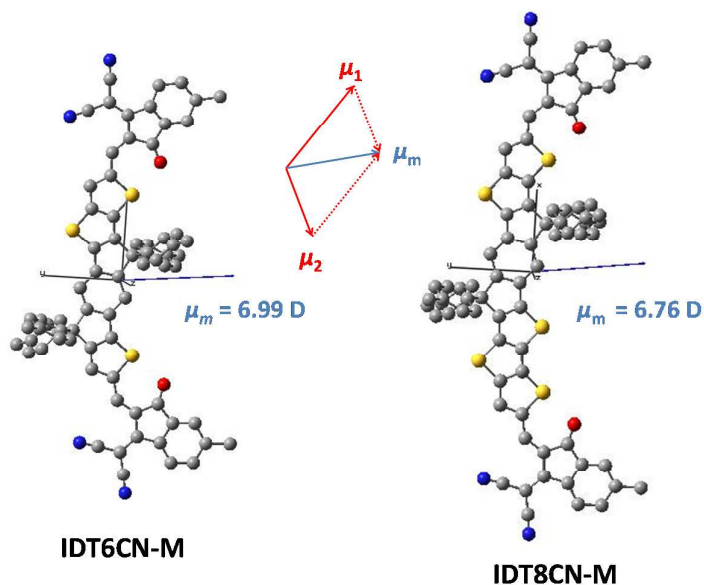
All the tested samples were fabricated under the same condition of best-performance devices on the cleaned Si substrates. GIWAXS measurement was performed at beamline 7.3.3 at the Advanced Light Source of Lawrence Berkeley National Lab (LBNL). The 10 K eV X-ray beam was incident at a grazing angle of  $0.12^\circ - 0.16^\circ$  to obtain optimal signal-to-background ratio. The scattered X-ray signals were detected by using a Dectris Pilatus 2M photon counting detector. The whole experiments were carried out in helium atmosphere. RSoXS measurement was carried out at beamline 11.0.1.2 at the Advanced Light Source of LBNL. Samples for RSoXS measurement



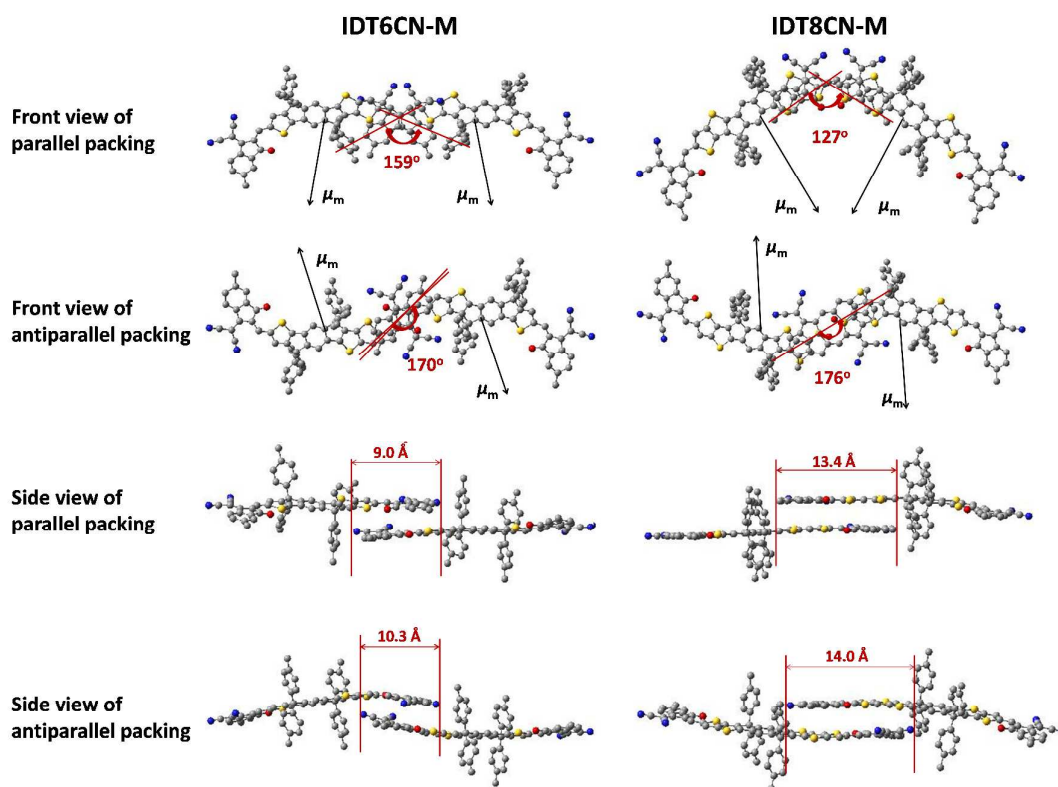
were transferred by floating in water to a 1.5 mm x 1.5mm, 100 nm thick Si<sub>3</sub>N<sub>4</sub> membrane supported by a 5 mm x 5 mm, 200 µm thick Si frame (Norcada Inc.). 2D scattering patterns were collected on an in-vacuum CCD camera (Princeton Instrument PI-MET). The sample detector distance was 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 µm by 200 µm.



**Figure S1.** The DFT calculation results of IDT6CN-M and IDT8CN-M single molecules.

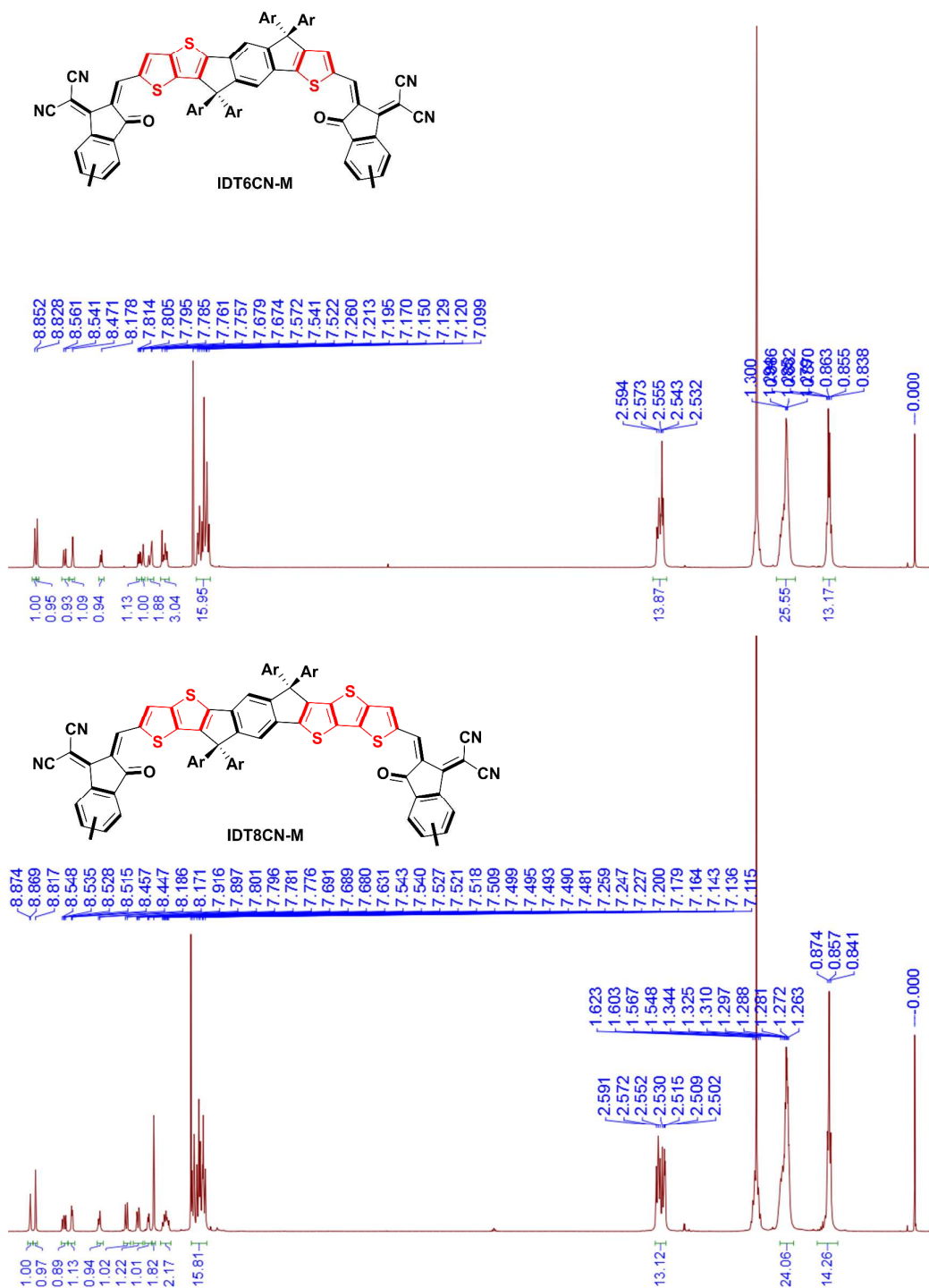


**Figure S2.** The size and orientation of dipole moments of IDT6CN-M and IDT8CN-M.

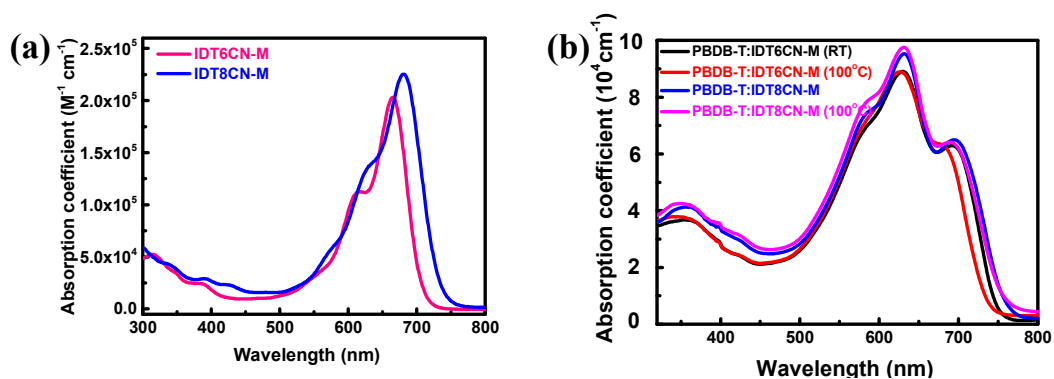


**Figure S3.** The results of theoretical simulations of IDT6CN-M and IDT8CN-M

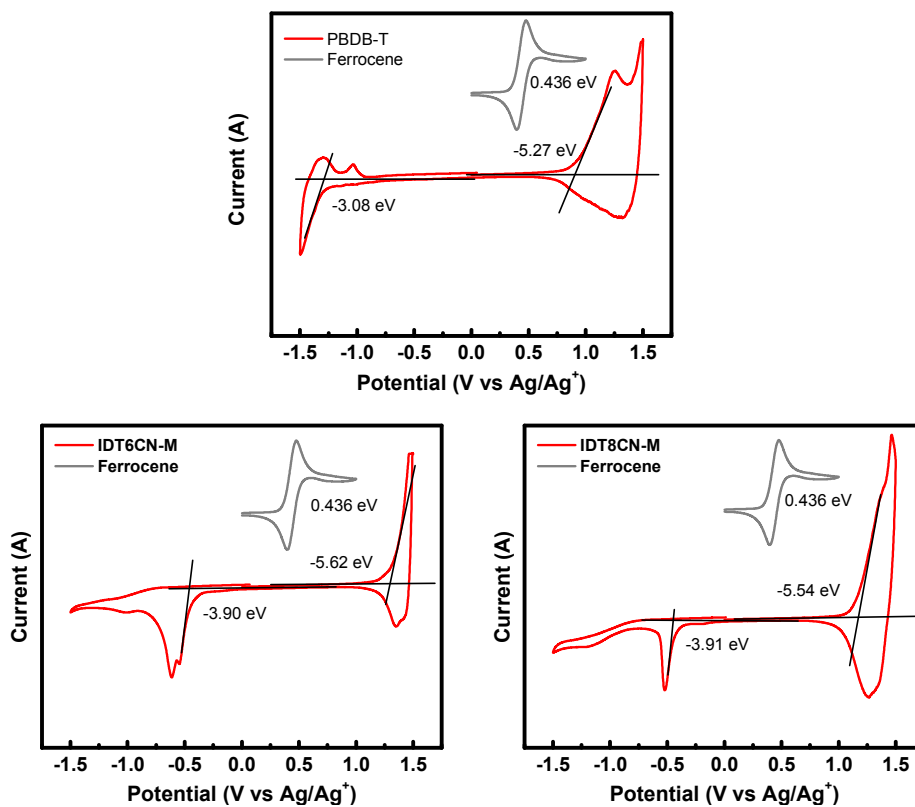
dimer molecules.



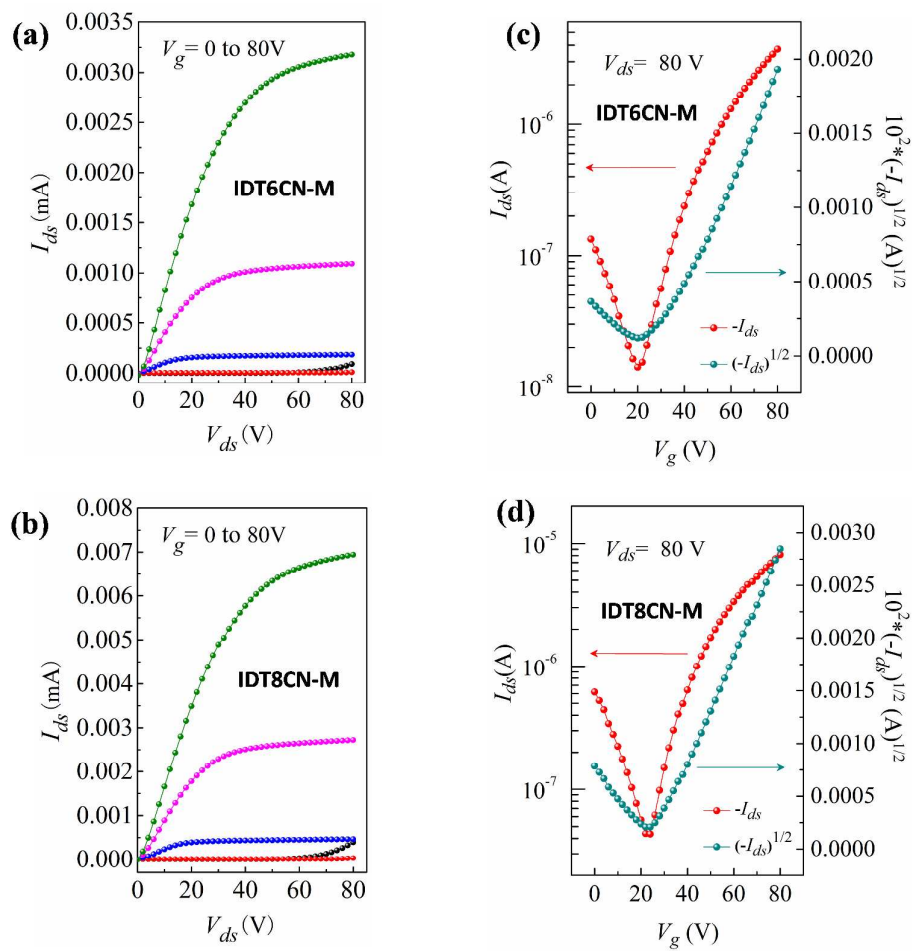
**Figure S4.** The <sup>1</sup>H-NMR spectra of two asymmetrical SMAs after one week continuous illumination under a 100 W LED lamp.



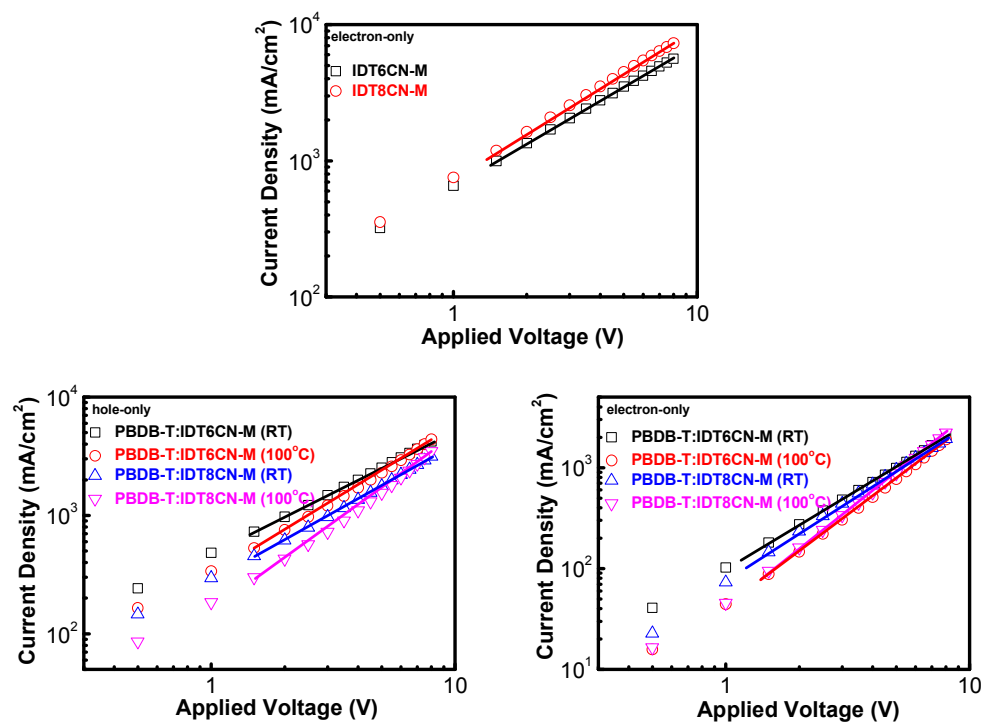
**Figure S5.** a) Molar absorption coefficient spectra of IDT6CN-M and IDT8CN-M in chloroform solution. b) Absorption coefficient spectra of PBDB-T:IDT6CN-M and PBDB-T:IDT8CN-M blend films before and after annealing.



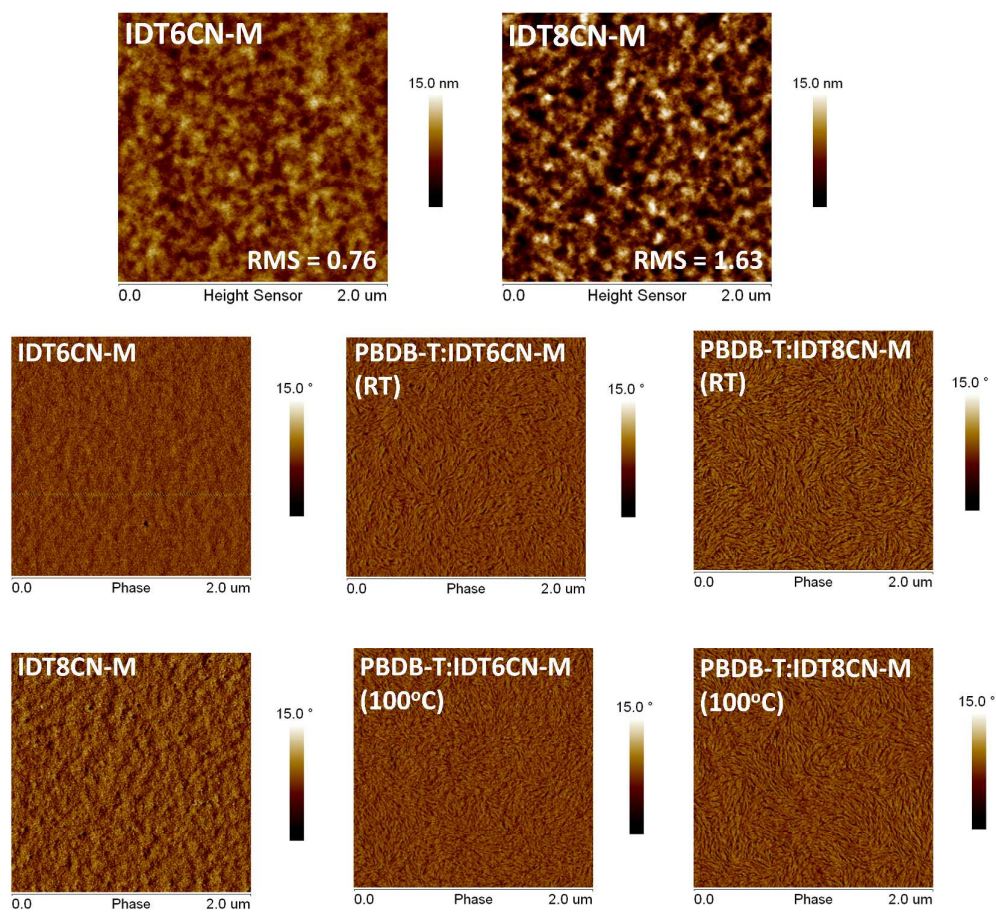
**Figure S6.** The CV plots of PBDB-T, IDT6CN-M and IDT8CN-M.



**Figure S7.** The output curves of OFETs: a) IDT6CN-M and b) IDT8CN-M. The Transfer characteristics of OFETs: c) IDT6CN-M and d) IDT8CN-M.

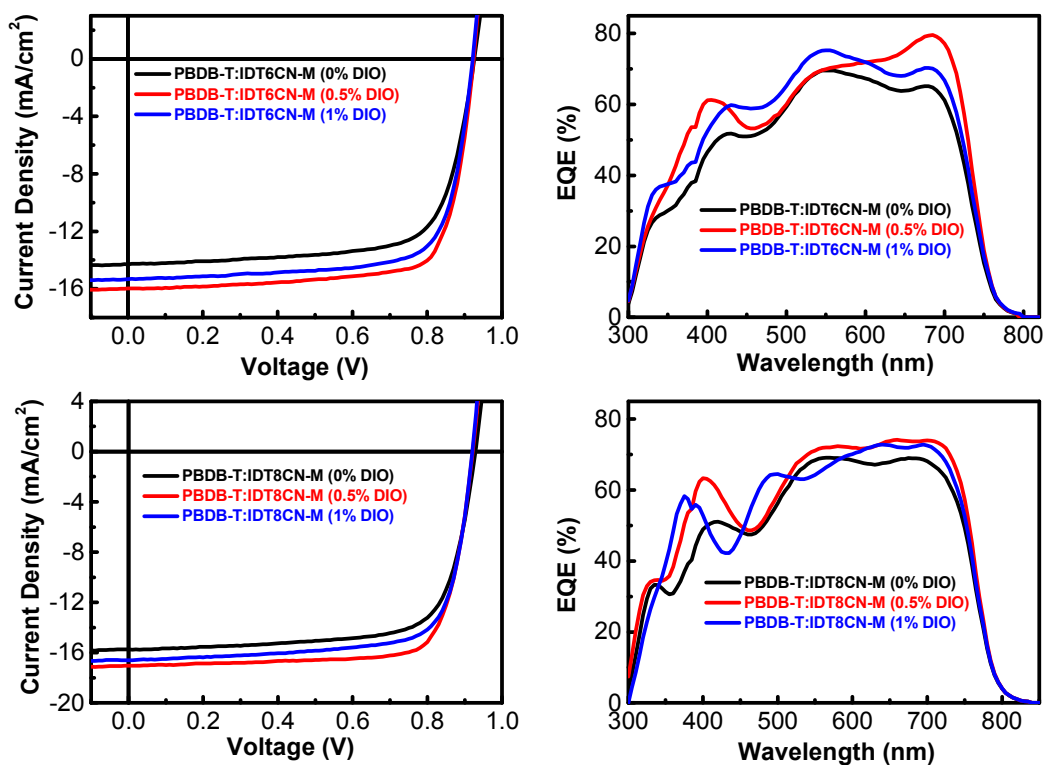


**Figure S8.** The electron and hole mobilities of IDT6CN-M and IDT8CN-M based neat and blend films.

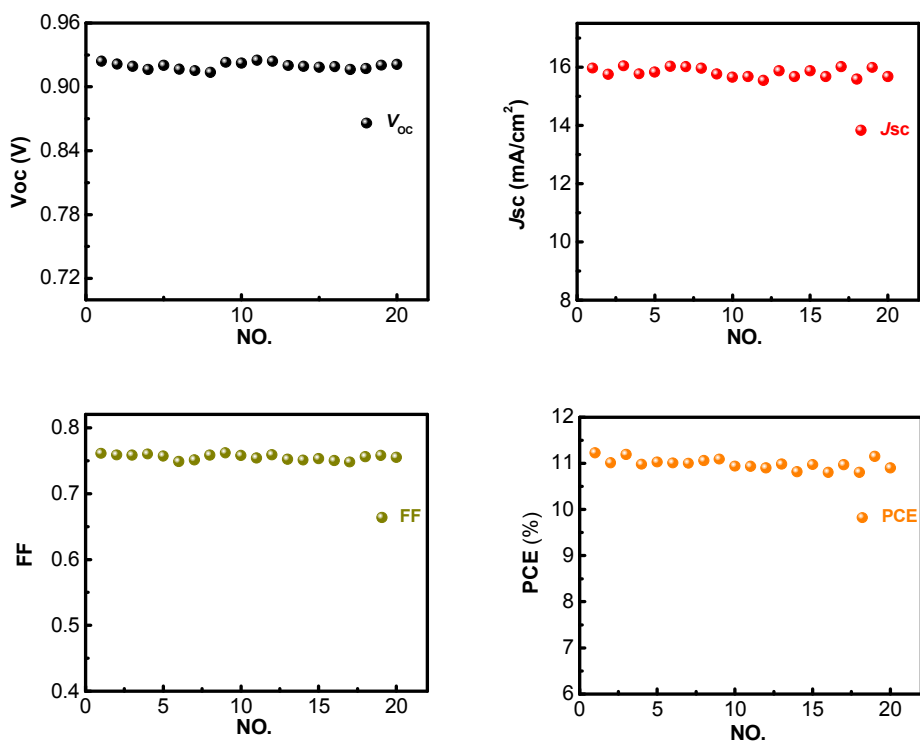


**Figure S9.** The AFM height sensor images and phase images of IDT6CN-M and IDT8CN-M neat and blend films.



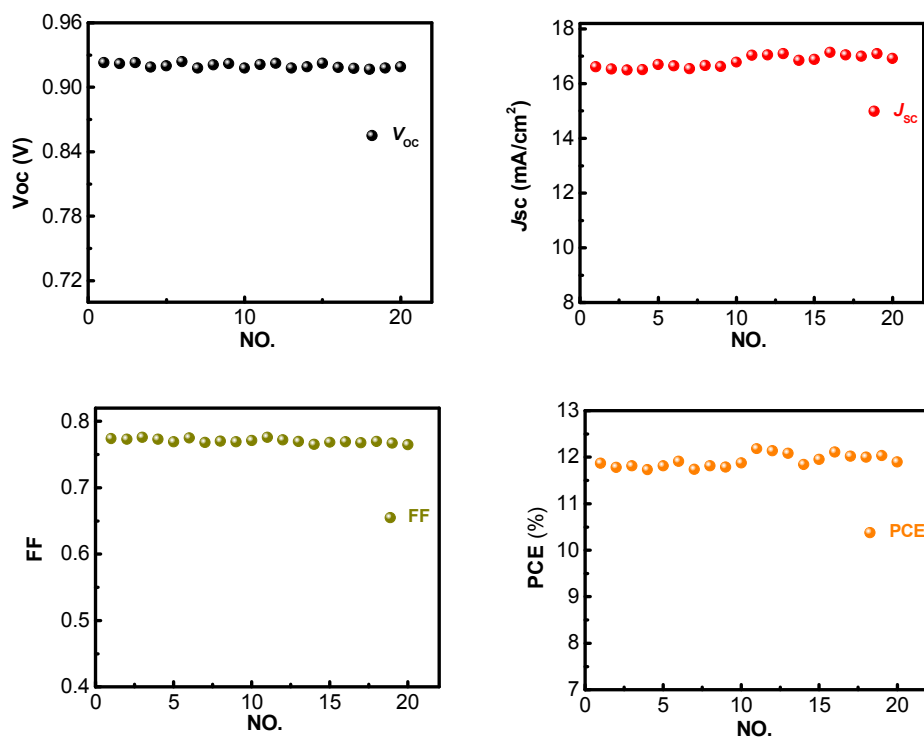


**Figure S10.** The  $J-V$  curves and EQE spectra of PBDB-T:IDT6CN-M and PBDB-T:IDT8CN-M based PSCs with different DIO addition.

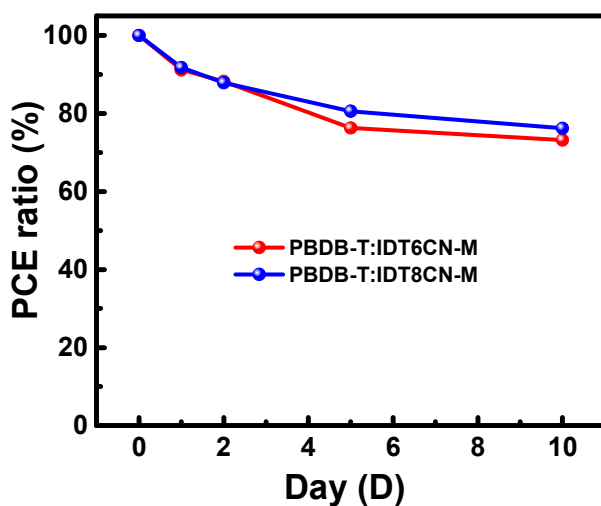




**Figure S11.** The detailed photovoltaic parameters of typical 20 devices based on PBDB-T:IDT6CN-M annealed at 100°C and with 0.5% DIO addition.



**Figure S12.** The detailed photovoltaic parameters of typical 20 devices based on PBDB-T:IDT8CN-M annealed at 100°C and with 0.5% DIO addition.



**Figure S13.** The stability of two asymmetrical SMAs-based conventional PSCs packaged and stored in air.

**Table S1.** Morphological parameters obtained from RSoXS and GIWAXS.

Samples	RSoXS		(100)			(010)		
	Domain size <sup>a)</sup>	Domain	location	<i>d</i> -spacing <sup>c)</sup>	CL <sup>d)</sup>	location	<i>d</i> -spacing <sup>c)</sup>	CL <sup>d)</sup>
	(nm)	purity <sup>b)</sup>	(Å <sup>-1</sup> )	(Å)	(Å)	(Å <sup>-1</sup> )	(Å)	(Å)
IDT6CN-M			0.27	23.19	82.1	1.80	3.47	25.5
IDT8CN-M			0.29	21.58	109.9	1.82	3.45	26.8
PBDB-T:IDT6CN-M (RT)	25.08	0.95	0.30	20.75	83.6	1.80	3.48	23.7
PBDB-T:IDT6CN-M (100°C)	23.29	1.00	0.30	20.85	100.3	1.80	3.49	24.6
PBDB-T:IDT8CN-M (RT)	27.32	0.82	0.29	21.47	82.3	1.80	3.48	22.1
PBDB-T:IDT8CN-M (100°C)	23.83	0.92	0.29	21.63	102.1	1.78	3.54	24.6

<sup>a)</sup>Calculated from  $d = \pi/q$ , where  $q$  is the location of maximum peak of RSoXS profile.

<sup>b)</sup>Integrated area of RSoXS profile. <sup>c)</sup>Calculated from  $d = 2\pi/q$ , where  $q$  is the location of the (100) or (010) diffraction peak. <sup>d)</sup>Obtained from Scherrer equation:  $CL = 2\pi K/\Delta q$ , where  $\Delta q$  is the full-width at the half-maximum of the peak and K is the Scherrer factor.

**Table S2.** The key parameters of PBDB-T:IDT6CN-M and PBDB-T:IDT8CN-M based PSCs with different DIO addition and annealed at 100°C under illumination of AM 1.5 G at 100 mW cm<sup>-2</sup>.

Active layer	DIO (%)	V <sub>oc</sub> (V)	J <sub>sc</sub> <sup>a)</sup> (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
PBDB-T:IDT6CN-M	0	0.926	14.30 (13.95)	71.7	9.50
	0.5	0.924	15.97 (15.64)	76.1	11.23
	1	0.921	15.35 (15.28)	74.1	10.47
PBDB-T:IDT8CN-M	0	0.928	15.74 (15.39)	72.7	10.63
	0.5	0.921	17.04 (16.65)	78.9	12.43
	1	0.920	16.61 (16.12)	74.3	11.35

<sup>a)</sup>The values in bracket are integrated J<sub>sc</sub> from EQE spectra.

**Table S3.** Comparison of FFs between this work and reported high-performance OSCs (with FF >75%).

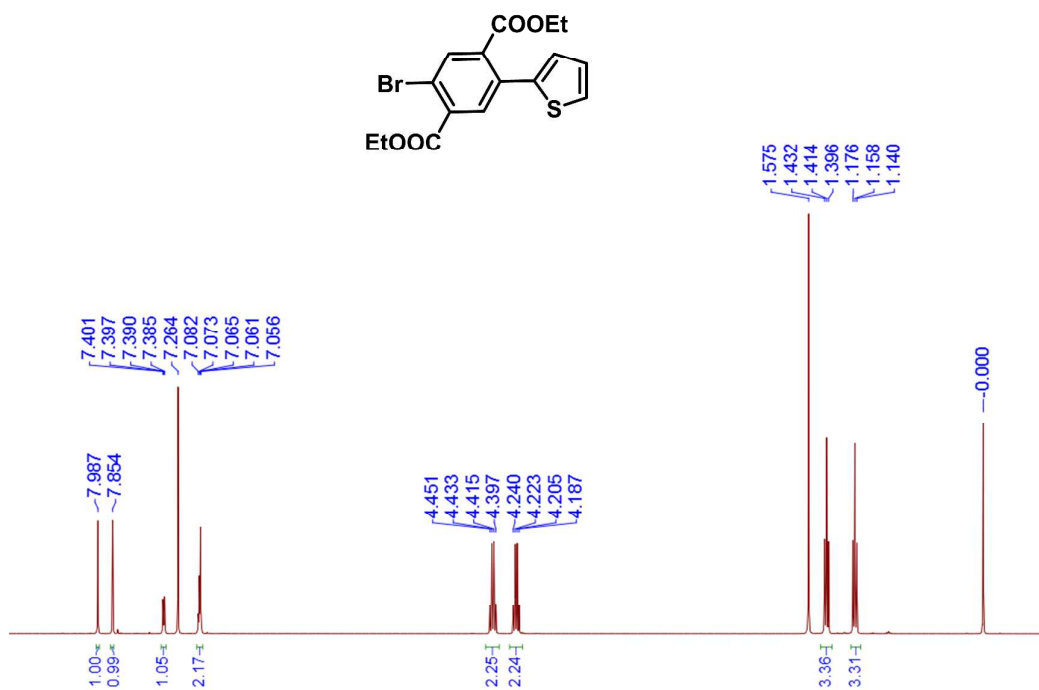
Active layer	FF (%)	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	PCE (%)	Ref.
<b>PBDB-T:IDT8CN-M</b>	<b>78.9</b>	<b>0.920</b>	<b>17.11</b>	<b>12.43</b>	<b>this work</b>
<b>PBDB-T:IDT6CN-M</b>	<b>76.1</b>	<b>0.924</b>	<b>15.97</b>	<b>11.23</b>	<b>this work</b>
PTPD3T:PC <sub>71</sub> BM	79.6	0.795	12.5	7.9	7
PBTI3T:PC <sub>71</sub> BM	77.8	0.850	12.8	8.66	7
PBDF-T1:PC <sub>71</sub> BM	77.4	0.92	13.28	9.43	8
PBT1-C:PC <sub>71</sub> BM	80.5	0.94	13.21	10	9
PBT1-C:ITCPTC	78.5	0.95	17.02	12.7	9
PBDB-TF:IDTN	78	0.946	16.58	12.2	10
PBDB-T-2Cl:IT-4F	77	0.86	21.80	14.4	11
P2:IT-4F	76	0.900	20.73	14.2	12
PTZ1:IDIC	76.2	0.92	16.4	11.5	13
PBDB-TF:IT-4F	77	0.87	20.38	13.7	14
PBDB-T:F-Br	76	0.87	18.22	12.05	15

**Table S4.** Key photovoltaic parameters calculated from the  $J_{ph}$ - $V_{eff}$  curves of PBDB-T:IDT6CN-M and PBDB-T:IDT8CN-M based devices before and after annealing.

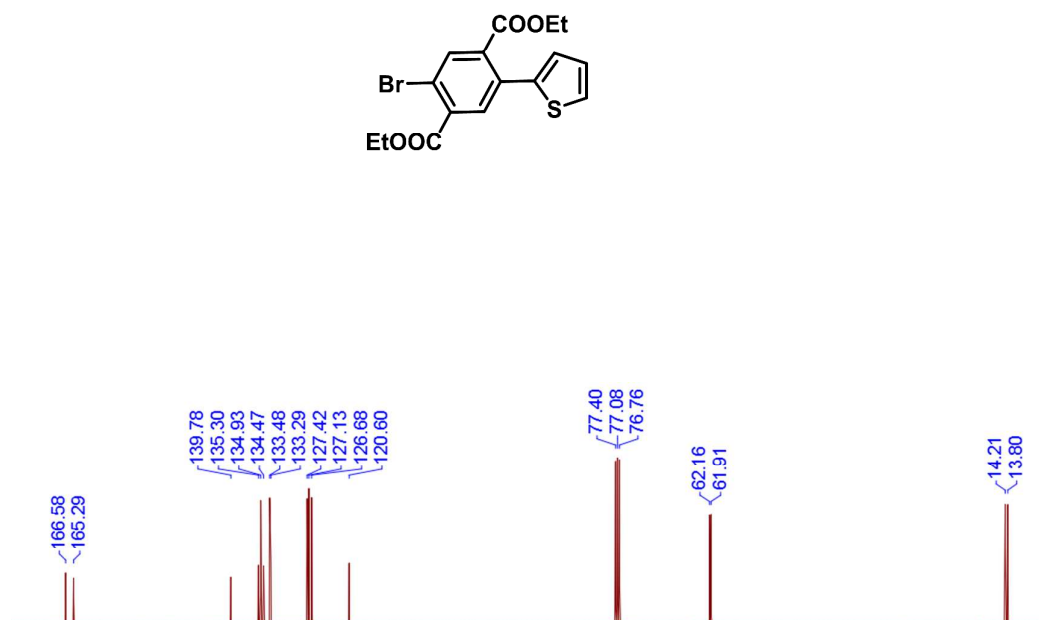
Active layer	$J_{sat}^a)$ (mA cm <sup>-2</sup> )	$J_{ph}^b)$ (mA cm <sup>-2</sup> )	$J_{ph}^c)$ (mA cm <sup>-2</sup> )	$J_{ph}^b)/J_{sat}$ (%)	$J_{ph}^c)/J_{sat}$ (%)
PBDB-T:IDT6CN-M (RT)	15.67	14.90	12.95	95.1	82.6
PBDB-T:IDT6CN-M (100°C)	16.50	15.97	14.34	96.8	86.9
PBDB-T:IDT8CN-M (RT)	16.91	16.10	14.01	95.2	82.8
PBDB-T:IDT8CN-M (100°C)	17.74	17.11	15.93	96.4	89.8

<sup>a)</sup> $J_{sat}$  is the  $J_{ph}$  under condition of  $V_{eff} = 2.0$  V, <sup>b)</sup>The  $J_{ph}$  under short circuit condition.

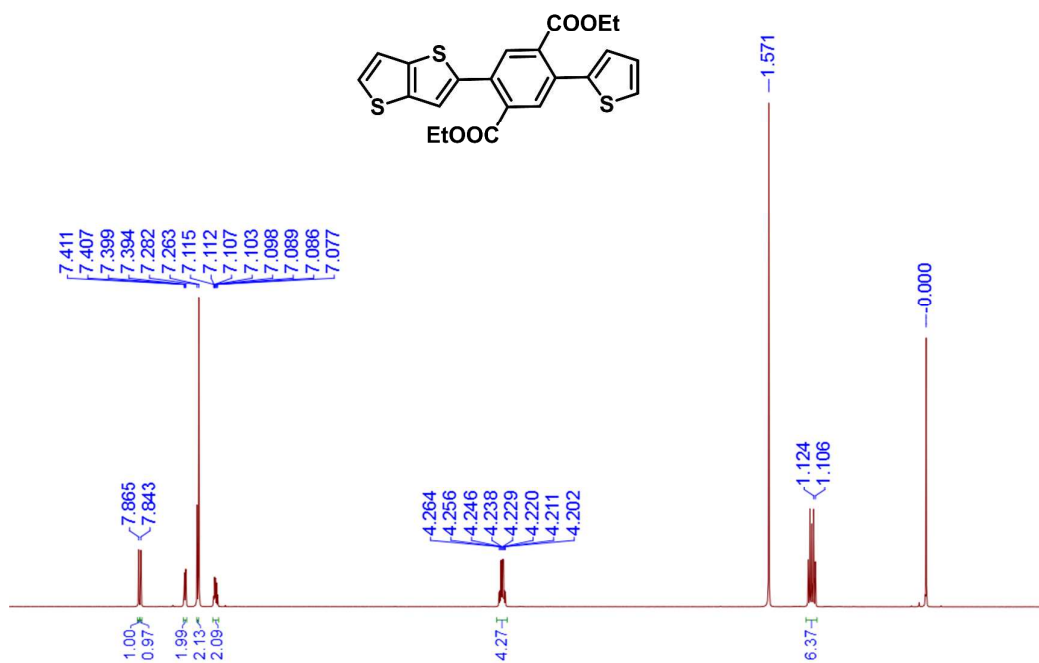
<sup>c)</sup>The  $J_{ph}$  under maximum power output condition.



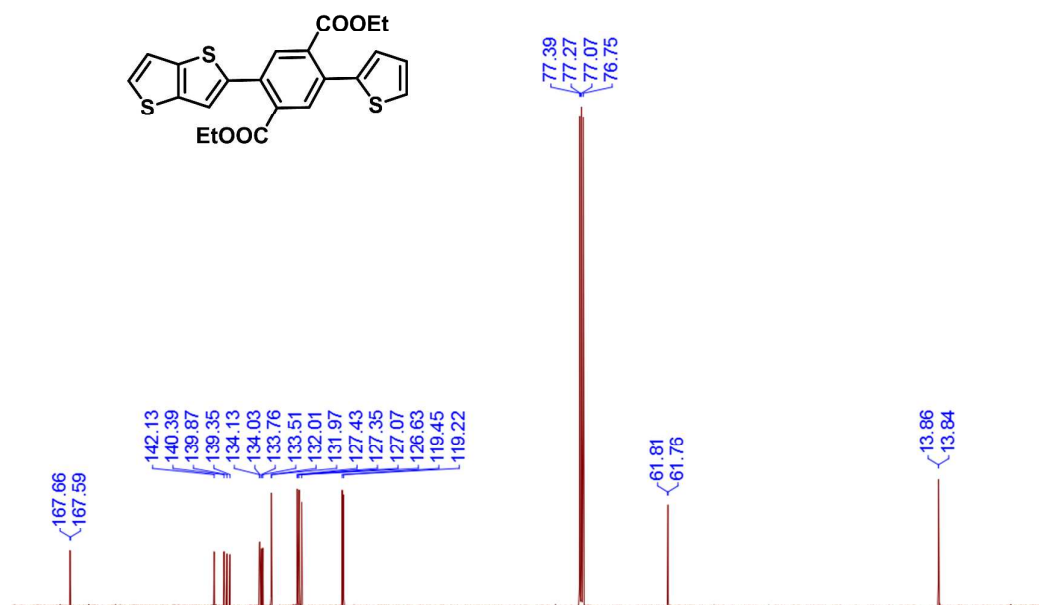
**Figure S14.** The  $^1\text{H}$  NMR spectrum of compound **2** in  $\text{CDCl}_3$ .



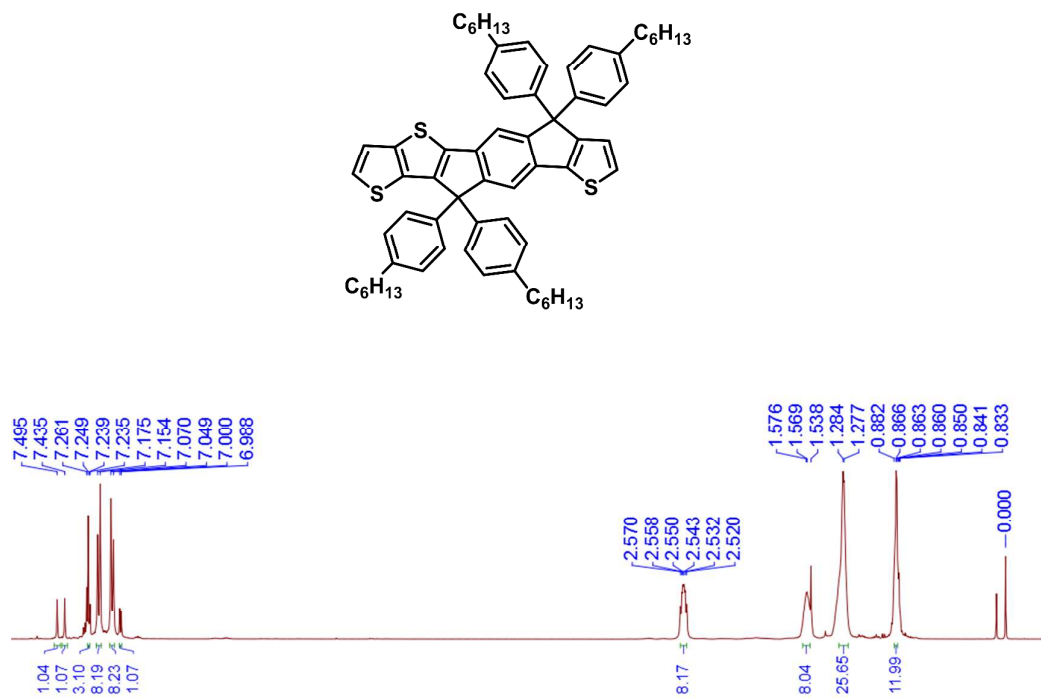
**Figure S15.** The  $^{13}\text{C}$  NMR spectrum of compound **2** in  $\text{CDCl}_3$ .



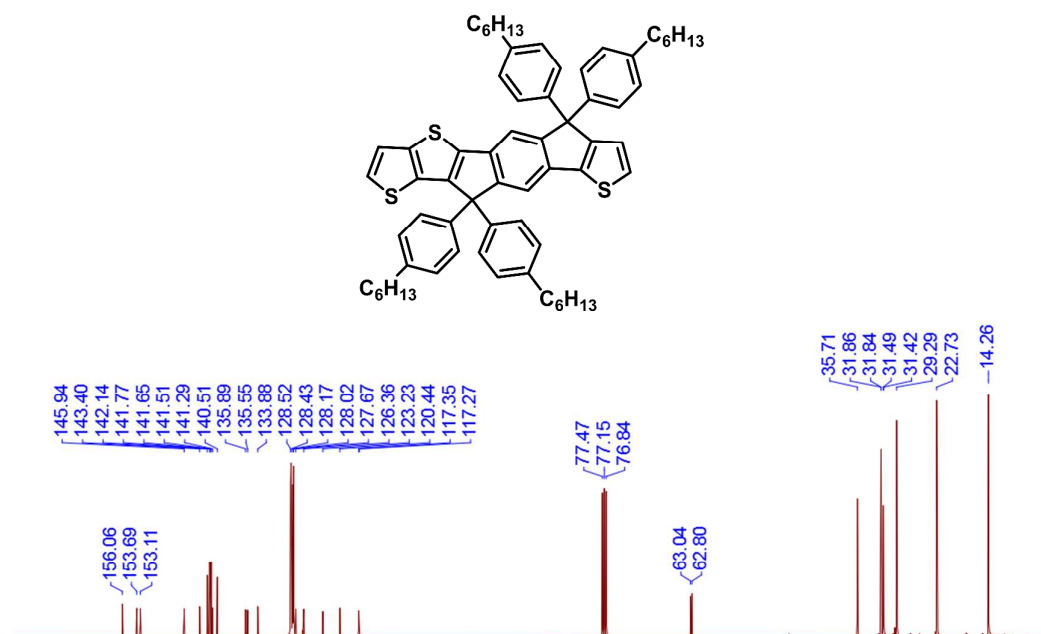
**Figure S16.** The <sup>1</sup>H NMR spectrum of compound **3** in CDCl<sub>3</sub>.



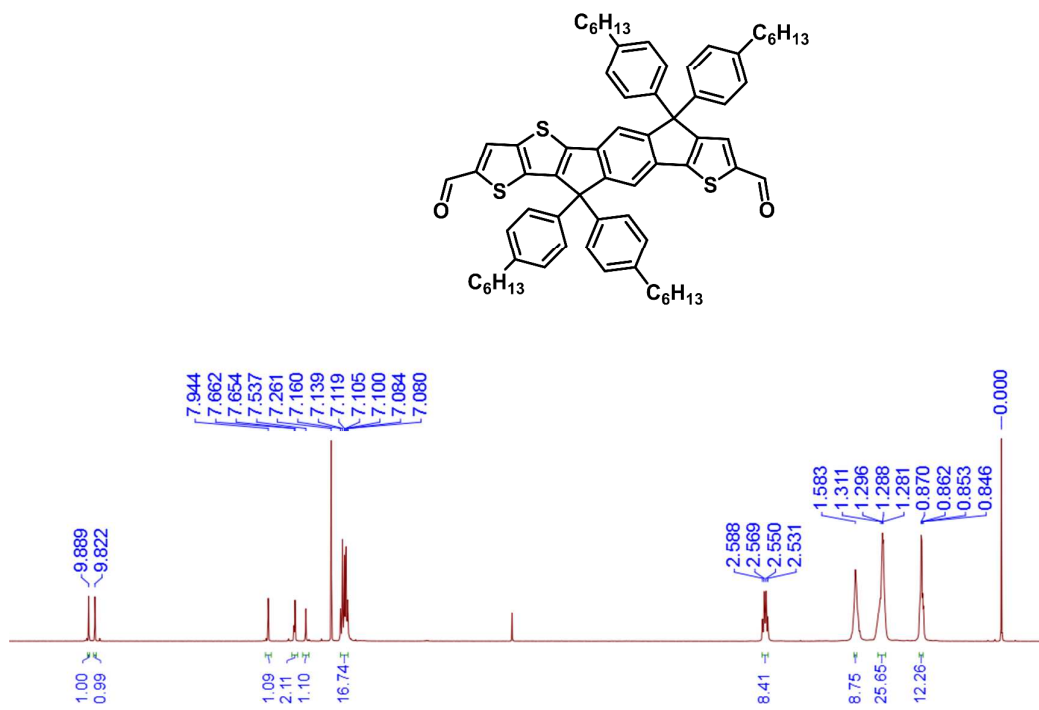
**Figure S17.** The <sup>13</sup>C NMR spectrum of compound **3** in CDCl<sub>3</sub>.



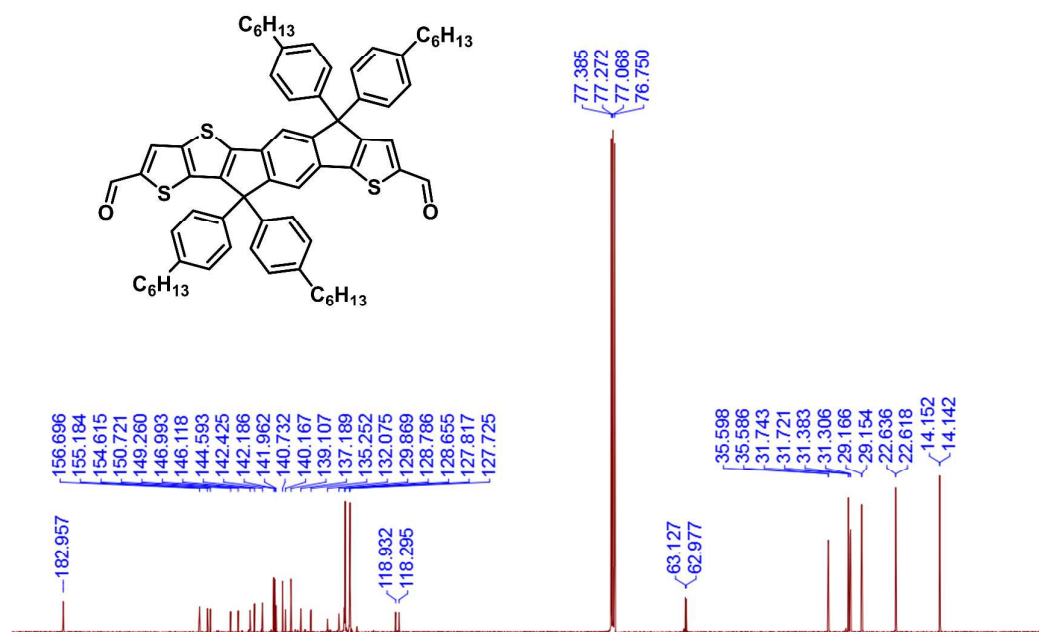
**Figure S18.** The  $^1\text{H}$  NMR spectrum of compound 4 in CDCl<sub>3</sub>.



**Figure S19.** The  $^{13}\text{C}$  NMR spectrum of compound 4 in CDCl<sub>3</sub>.



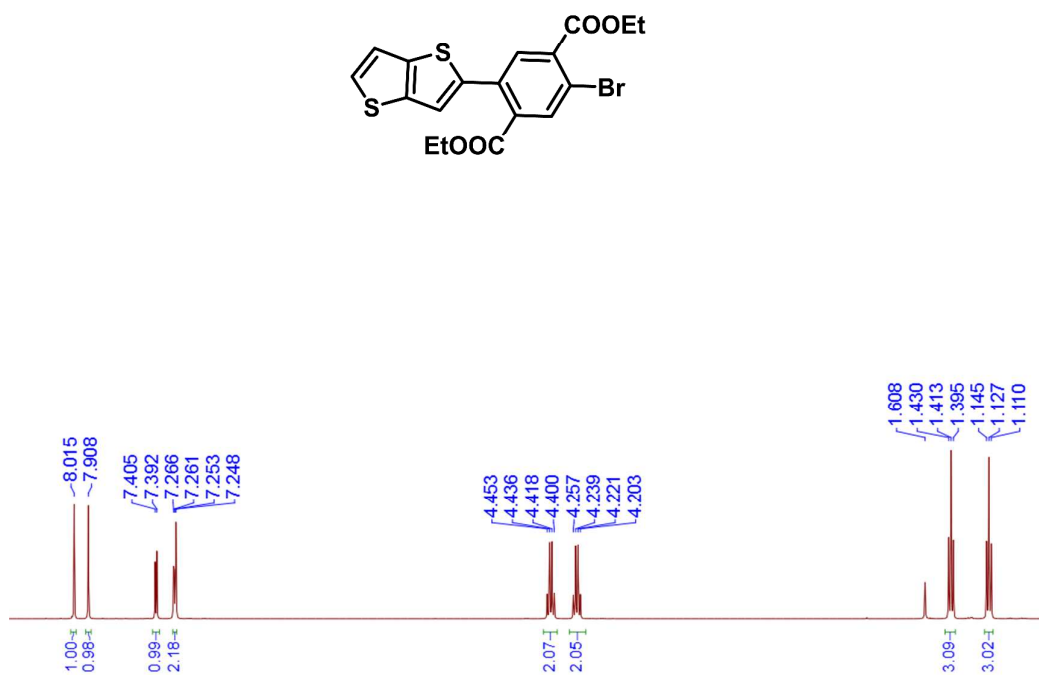
**Figure S20.** The  $^1\text{H}$  NMR spectrum of compound **5** in  $\text{CDCl}_3$ .



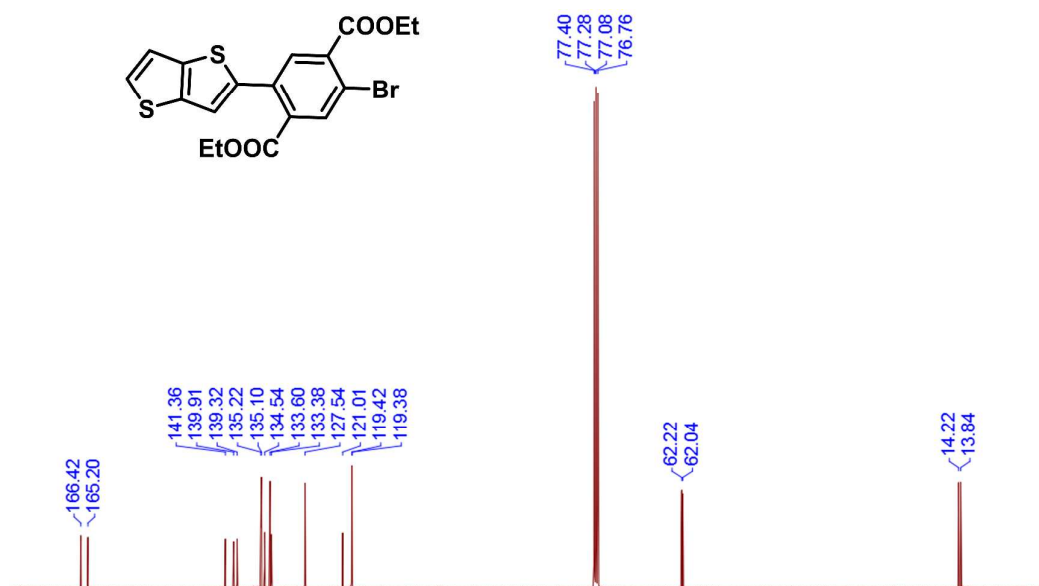
**Figure S21.** The  $^{13}\text{C}$  NMR spectrum of compound **5** in  $\text{CDCl}_3$ .



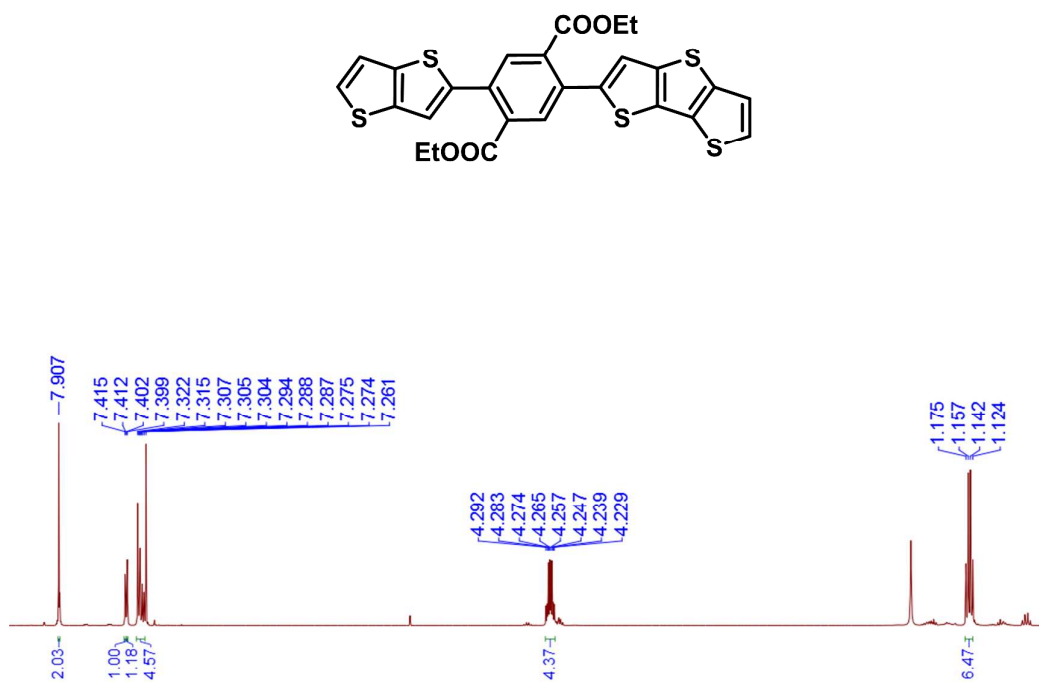




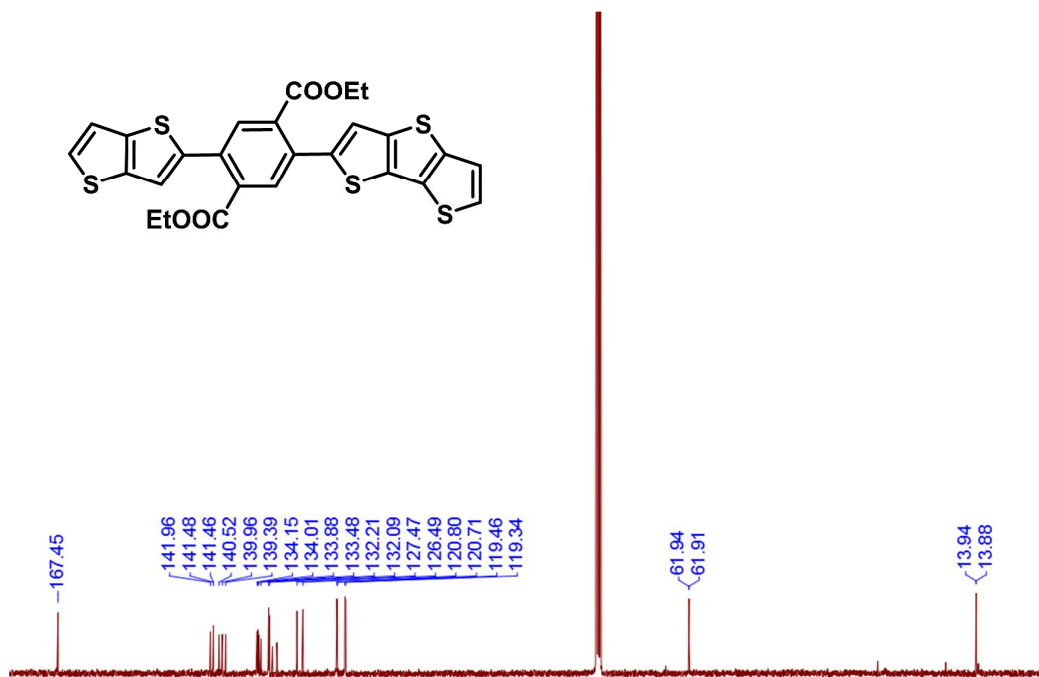
**Figure S24.** The <sup>1</sup>H NMR spectrum of compound **6** in CDCl<sub>3</sub>.



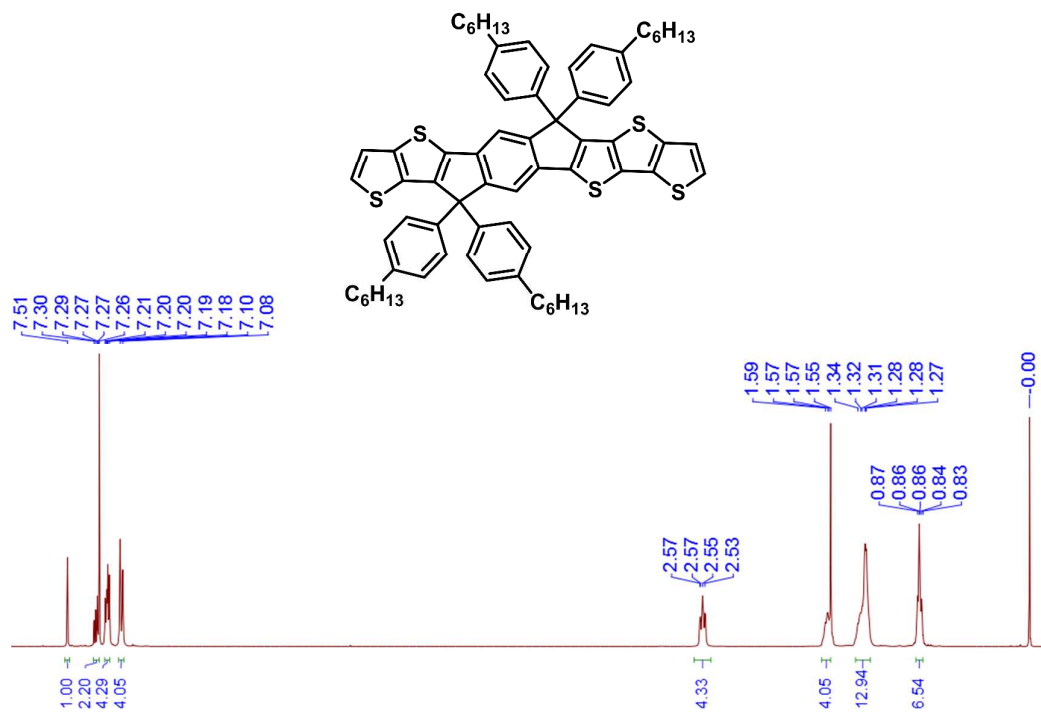
**Figure S25.** The <sup>13</sup>C NMR spectrum of compound **6** in CDCl<sub>3</sub>.



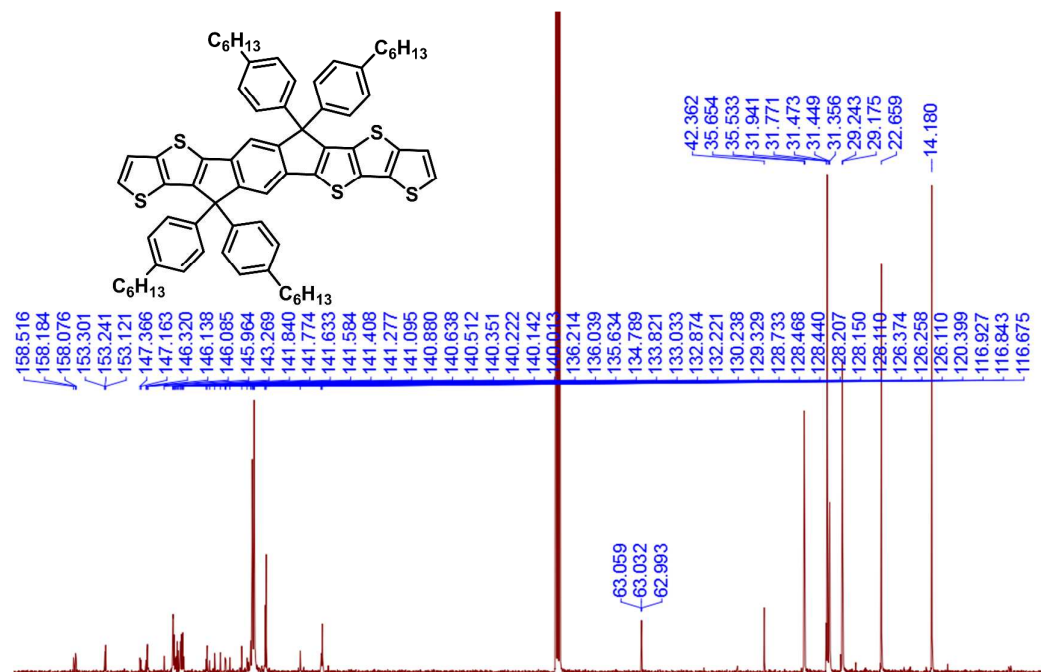
**Figure S26.** The <sup>1</sup>H NMR spectrum of compound 7 in CDCl<sub>3</sub>.



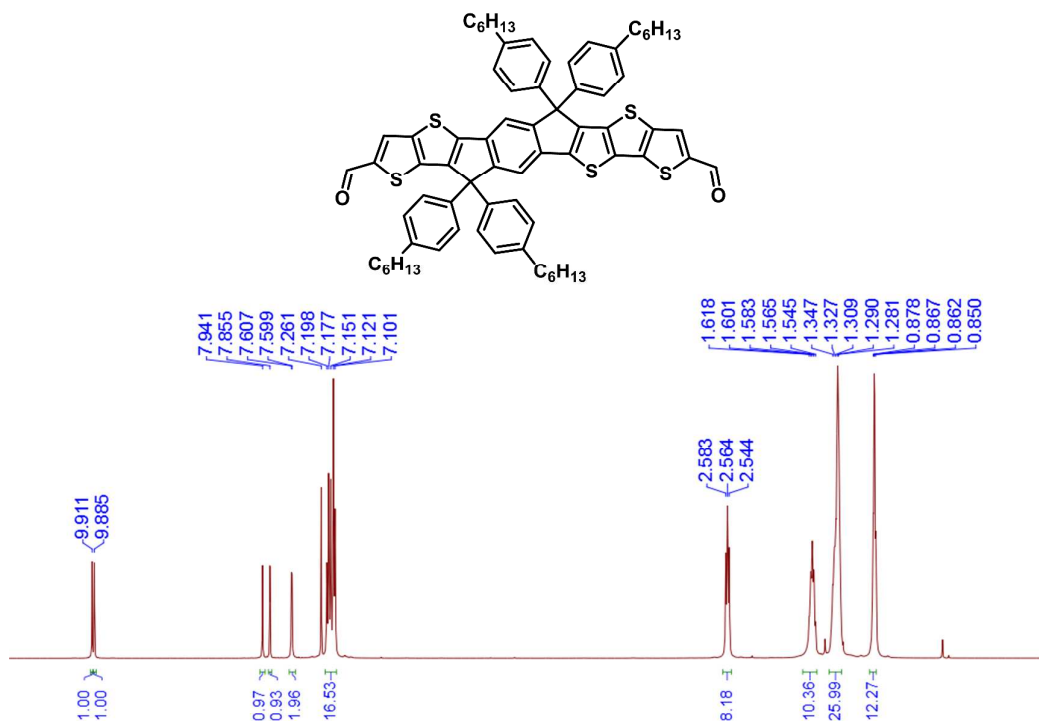
**Figure S27.** The <sup>13</sup>C NMR spectrum of compound 7 in CDCl<sub>3</sub>.



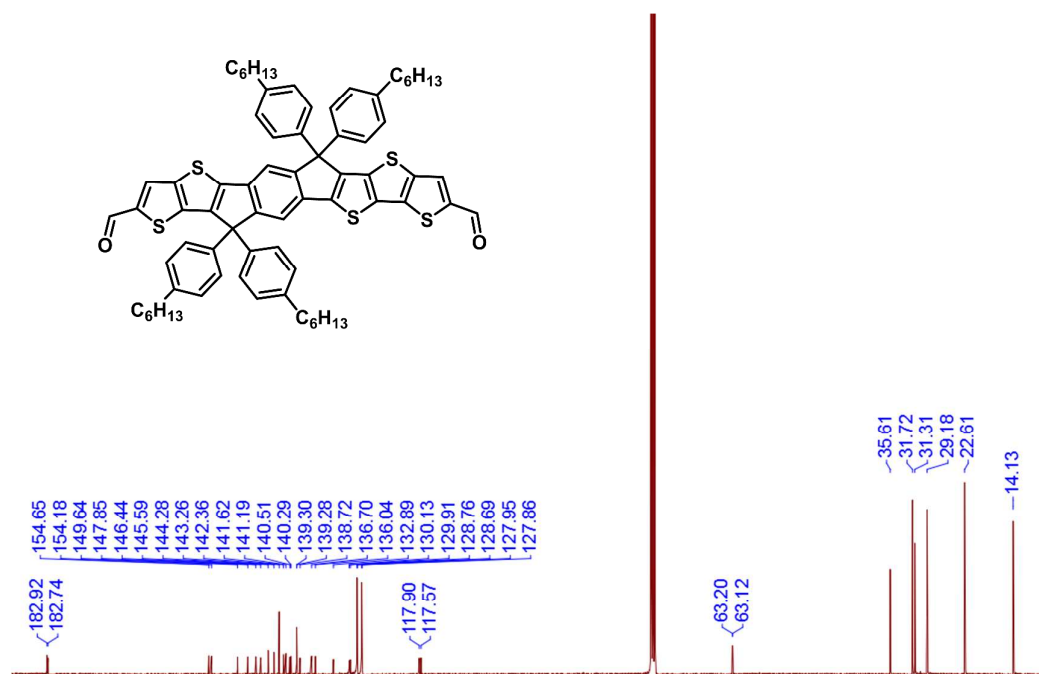
**Figure S28.** The <sup>1</sup>H NMR spectrum of compound **8** in CDCl<sub>3</sub>.



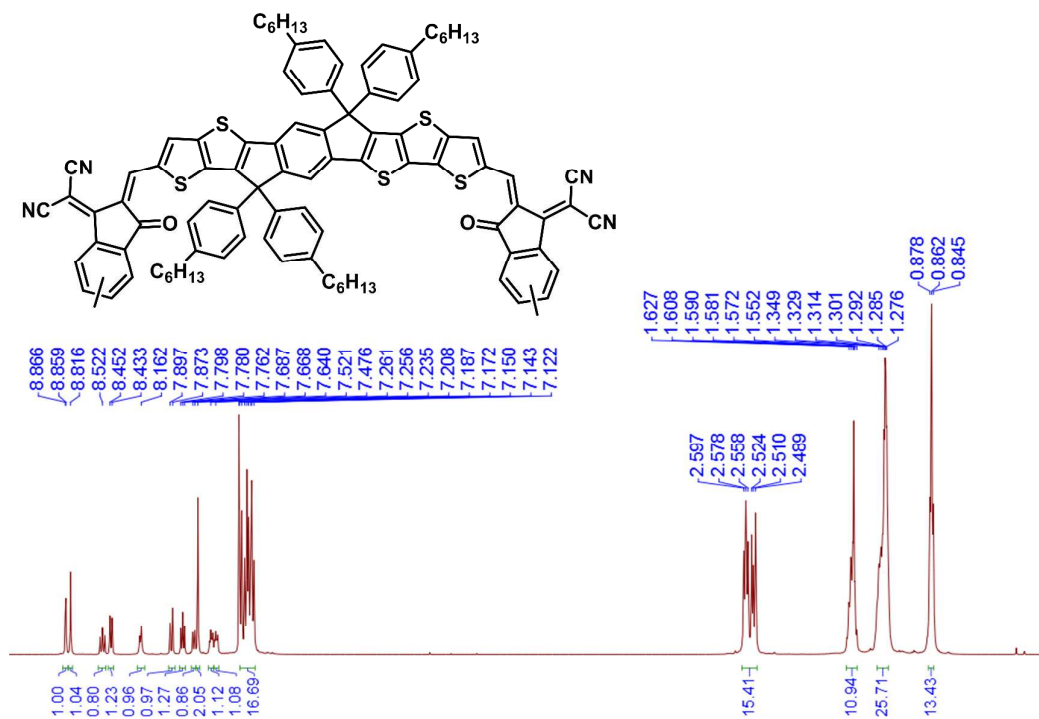
**Figure S29.** The <sup>13</sup>C NMR spectrum of compound **8** in CDCl<sub>3</sub>.



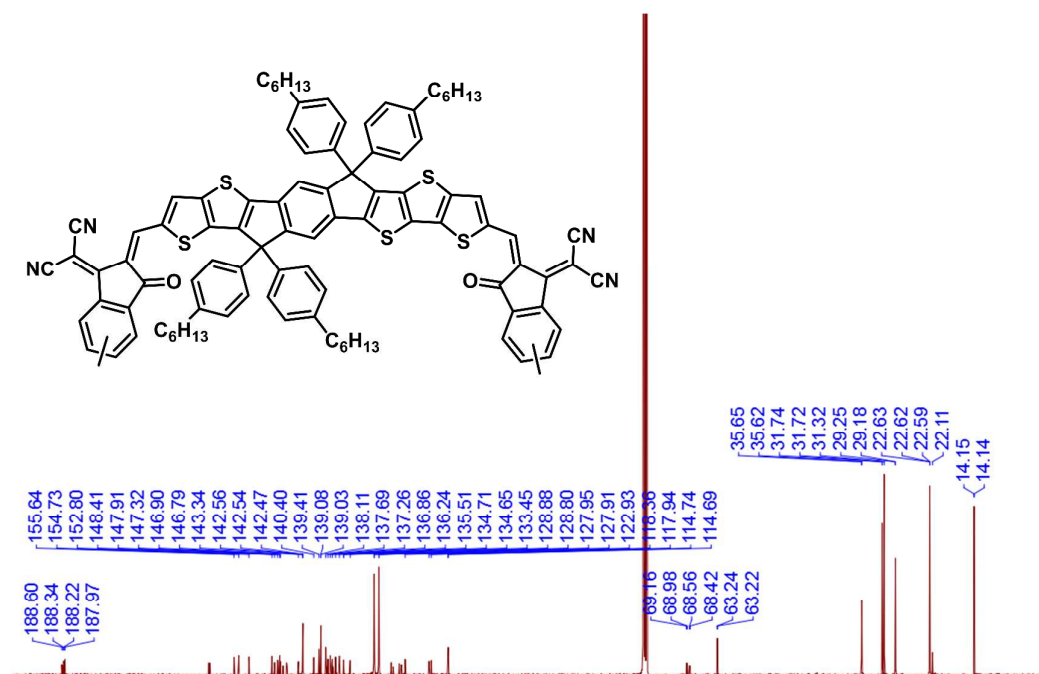
**Figure S30.** The  $^1\text{H}$  NMR spectrum of compound **9** in  $\text{CDCl}_3$ .



**Figure S31.** The  $^{13}\text{C}$  NMR spectrum of compound **9** in  $\text{CDCl}_3$ .



**Figure S32.** The <sup>1</sup>H NMR spectrum of IDT8CN-M in CDCl<sub>3</sub>.



**Figure S33.** The <sup>13</sup>C NMR spectrum of IDT8CN-M in CDCl<sub>3</sub>.

## Reference

- (1) Neese, F.; Wennmohs, F.; Hansen, A.; Becker, U. *Chem. Phys.* **2009**, 356, 98.
- (2) Neese, F.; *WIREs Comput. Mol. Sci.* **2012**, 2, 73.
- (3) Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comput. Chem.* **2011**, 32, 1456.
- (4) Kruse, H.; Grimme, S. *J. Chem. Phys.* **2012**, 136, 154101.
- (5) Lu, T.; Chen, F. *J. Comput. Chem.* **2012**, 33, 580.
- (6) Li, S.; Ye, L.; Zhao, W.; Zhang, S.; Mukherjee, S.; Ade, H.; Hou, J. *Adv. Mater.* **2016**, 28, 9423.
- (7) Guo, X.; Zhou, N.; Lou, S. J.; Smith, J.; Tice, D. B.; Hennek, J. W.; Ortiz, R. P.; Navarrete, J. T. L.; Li, S.; Strzalka, J.; Chen, L. X.; et al. *Nat. Photonics* **2013**, 7, 825-833.
- (8) Huo, L.; Liu, T.; Fan, B.; Zhao, Z.; Sun, X.; Wei, D.; Yu, M.; Liu, Y.; Sun, Y. *Adv. Mater.* **2015**, 27, 6969-6975.
- (9) Liu, T.; Huo, L.; Chandrabose, S.; Chen, K.; Han, G.; Qi, F.; Meng, X.; Xie, D.; Ma, W.; Yi, Y.; et al. *Adv. Mater.* **2018**, 30, 1707353.
- (10) Li, S.; Ye, L.; Zhao, W.; Liu, X.; Zhu, J.; Ade, H.; Hou, J. *Adv. Mater.* **2017**, 29, 1704051.
- (11) Zhang, S.; Qin, Y.; Zhu, J.; Hou, J. *Adv. Mater.* **2018**, 30, 1800868.
- (12) Li, S.; Ye, L.; Zhao, W.; Yan, H.; Yang, B.; Liu, D.; Li, W.; Ade, H.; Hou, J. *J. Am. Chem. Soc.* **2018**, 140, 7159-7167.
- (13) Guo, B.; Li, W.; Guo, X.; Meng, X.; Ma, W.; Zhang, M.; Li, Y. *Adv. Mater.* **2017**, 29, 1702291.

- (14) Li, W.; Ye, L.; Li, S.; Yao, H.; Ade, H.; Hou, J. *Adv. Mater.* **2018**, 30, 1707170.
- (15) Wang, Y.; Zhang, Y.; Qiu, N.; Feng, H.; Gao, H.; Kan, B.; Ma, Y.; Li, C.; Wan, X.; Chen, Y. *Adv. Energy Mater.* **2018**, 8, 1702870.