

## Supporting Information

### Fused or Unfused? Two-dimensional Non-fullerene Acceptors for Efficient

### Organic Solar Cells

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**1. Materials:** The main materials in the experiment were purchased from commercial businesses and were used without further purification. The reactions and manipulations were carried out under argon atmosphere with the use of standard Schlenk techniques. Toluene and THF were distilled from sodium benzophenone.

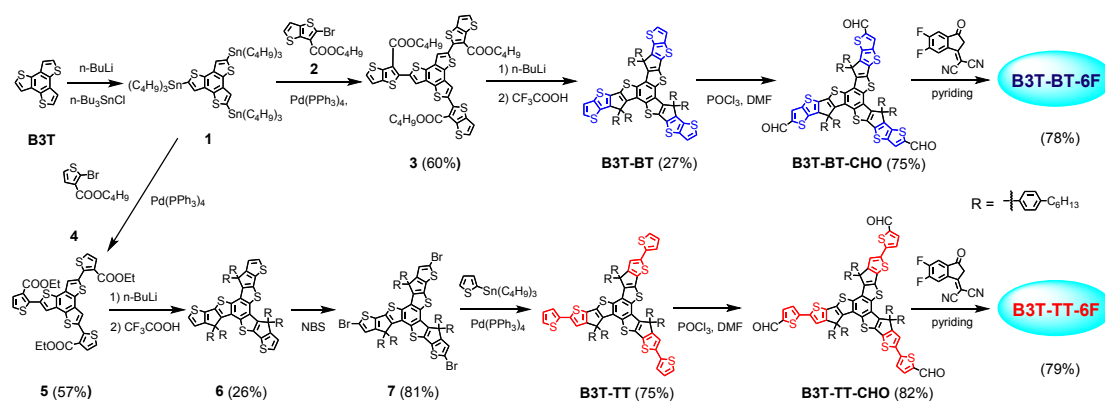
**2. Measurements:** Bruker AV400 Spectrometer were applied to obtain  $^1\text{H}$  NMR spectra and  $^{13}\text{C}$  NMR spectra. Varian 7.0T FTMS was connected to achieve the HRMS data. JASCO V-570 UV-vis spectrophotometer was used to obtain the UV-vis spectra. Thermogravimetric analysis (TGA) was measured by using a Netzsch Model STA409PC instrument under purified nitrogen gas flow with a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$ . Cyclic voltammogram (CV) was employed to evaluate the energy levels with a Model IMP2014 microcomputer-based electrochemical analyzer at a scan rate of  $50\text{ mV/s}$ . By the use of versatile calculation formula that assuming the absolute energy level of  $\text{FeCp}_2^{+/0}$  to be  $4.8\text{ eV}$  below vacuum :  $E_{HOMO} = -e[E_{OX} + (4.8 - E_{Fc})]eV$ ;  $E_{LUMO} = -e[E_{red} + (4.8 - E_{Fc})]eV$ , where  $E_{ox}$  and  $E_{red}$  were measured by the use of a standard

three-electrode electrochemical cell in acetonitrile solution containing 0.1 M tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ) at room temperature under nitrogen atmosphere in thin films, and  $E_{Fc}$  was 0.42 eV in this work which refers to the half-wave potential of redox couple ( $\text{Fc}/\text{Fc}^+$ ). Space charge limited current (SCLC) was used to measure the hole and electron mobilities. Atomic force microscopy (AFM) images were recorded in tapping mode on a Bruker MultiMode 8 atomic force microscope. Transmission electron microscopy (TEM) images were recorded on a JEM1011 transmission electron microscope with accelerating voltage of 100 KV and camera length of 160 cm. The current density–voltage ( $J$ – $V$ ) curves and steady-state power output were recorded by using a Keithley 2400 source-measurement unit under AM 1.5 G illumination with the light intensity of  $100 \text{ mW cm}^{-2}$  using a SS-F5-3A (Enli tech) solar simulator. The light intensity was calibrated by a certified silicon diode and the simulator irradiance was characterized by a calibrated spectrometer. The external quantum efficiency (EQE) was collected by using a QE-R Solar Cell Spectral Response Measurement System (Enli Technology Co., Ltd., Taiwan). (GIWAXS) measurement was performed at MetalJet-D2, Excillum on the wavelength of 0.134144 nm with Xeuss 2.0. All samples were deposited on the silicon and were irradiated at a fixed X-ray incident angle of  $0.2^\circ$  with an exposure time of 1800 s.

**3. Device Fabrication and characterization:** the devices were fabricated by using an inverted structure of ITO/ZnO/active layers/ $\text{MoO}_3$ /Ag. The indium tin oxide (ITO)-coated glass substrates were cleaned by ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol. A 40 nm thick layer of ZnO was deposited by

spin-coating ZnO precursor solution on the top of the ITO glass substrates at 3000 rpm for 40 s. Then baked at 200 °C in air for 60 min. Subsequently, the active layer was spin-coated from donor (10 mg/mL) and acceptor (15 mg/mL) in chlorobenzene solution at 1500 rpm for 40 s for PBDB-T: B3T-TT-6F with 0.6% DIO then annealed at 120°C for 5 min .The PBDB-T: B3T-BT-6T film from donor (10 mg/mL) and acceptor (12 mg/mL) with 0.7% DIO in chlorobenzene solution at 1500 rpm for 60 s on the ZnO substrate, followed by vacuum poling of one hour in vacuum chamber. MoO<sub>3</sub> (~10 nm) and Ag (~100 nm) was successively evaporated onto the active layer through a shadow mask (pressure ca. 10<sup>-4</sup> Pa). The effective area for the devices is 0.1 cm<sup>2</sup> defined by mask.

#### 4. Synthesis



**Scheme S1.** Synthetic routes of of **B3T-TT-6F** and **B3T-BT-6F**

**Synthesis of compound 1:** BTT (0.40 g, 1.62 mmol) was dissolved in 30 mL anhydrous THF, n-butyllithium (n-BuLi) (3.9 mL, 2.5M) was added to the solution under an argon atmosphere at 0°C, and the mixture was allowed to stir at 0°C for 2 h, chlorotributyltin (2.6 mL, 9.72 mmol) was added dropwise to the solution, after 2 hours at 0 °C the reaction was warmed to room temperature and stirred for another 2 hours. The reaction

was quenched with water, the aqueous layer was extracted with petroleum ether (3 x 50 mL), the combined organic layer was washed with brine (100 mL), dried over Na<sub>2</sub>SO<sub>4</sub> then evaporated under vacuum to give the crude product. The crude product was used without any further purification <sup>[1]</sup>.

**Synthesis of compound 3:** Stannyl crude derivative **1** (1.80 g 1.62 mmol) and Thieno[3,2-b]thiophene bromo-ester **2** (1.84 g, 5.83 mmol) were added to a 100 mL three neck round-bottom flask, 40 mL toluene and 5 mL DMF were added. The mixture was purged with argon for 5 min, and Pd(PPh<sub>3</sub>)<sub>4</sub> (93.6 mg, 0.08 mmol) was added under N<sub>2</sub>. The reaction mixture was stirred at 110 °C overnight. Then toluene was removed in vacuo, and then residue was extracted with dichloromethane and washed with water. The organic layer was collected and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and concentration, the product was purified by column chromatography using hexane /dichloromethane (4:1) as an eluent to give a light yellow solid (0.93 g, 60%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (ppm): δ 7.98 (s, 3H), 7.46 (d, *J* = 5.3 Hz, 3H), 7.20 (d, *J* = 5.3 Hz, 3H), 4.39 (t, *J* = 6.6 Hz, 6H), 1.84-1.76 (m, 12H), 0.84 (t, *J* = 6.6 Hz, 9H).; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz), δ (ppm): 153.21, 149.55, 142.04, 141.27, 139.56, 136.68, 134.16, 133.39, 131.82, 129.81, 129.29, 128.23, 125.64, 120.00, 63.50, 35.53, 31.66, 31.05, 29.01, 26.91, 22.56, 14.02. (MALDI-TOF): calc for C<sub>45</sub>H<sub>36</sub>O<sub>6</sub>S<sub>9</sub> [M<sup>+</sup>], 999.99; found: 1000.01.

**Synthesis of compound 5:** Compound **5** was prepared with a method similar to that described for compound **2**. Yield: 57%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (ppm): 7.81 (d, *J* = 7.2 Hz, 3H), 7.40 (d, *J* = 7.2 Hz, 3H), 7.13 (s, 3H), 4.16 (d, *J* = 7.4 Hz, 6H), 1.55

(m, 6H), 1.20 (m, 9H), 0.80 (m, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 163.15, 142.45, 133.52, 130.81, 128.84, 124.82, 123.96, 77.48, 77.17, 76.85, 64.91, 30.69, 29.76, 19.29, 13.76. MS (MALDI-TOF): calcd for  $\text{C}_{39}\text{H}_{36}\text{O}_6\text{S}_6$   $[\text{M}]^+$ , 792.084; found: 792.044.

**Synthesis of B3T-BT:** To a solution of 1-bromo-4-hexylbenzene (2.40 g, 10 mmol) in THF (30 mL) at  $-78\text{ }^\circ\text{C}$  was added n-BuLi (4.0 mL, 2.5 M in hexane), the mixture was kept at  $-78\text{ }^\circ\text{C}$  for 0.5 h, and a solution of compound 5 (0.9 g, 0.9 mmol) in THF (20 mL) was added slowly. After addition, the mixture was kept to stir at  $-78\text{ }^\circ\text{C}$  for 0.5 h, and stirred at room temperature for another two hours, water was added and the organic layer was extracted with ethyl acetate (3 x 50 mL) The combined organic phase was dried over  $\text{Na}_2\text{SO}_4$ . Yellow oil crude was obtained and was used without further purification. The crude product 5 was dissolved in 100 mL anhydrous 1,2-dichloroethane (DCE), the mixture was purged with argon for 15 min, and two point of  $\text{CF}_3\text{COOH}$  was added under  $\text{N}_2$ . The reaction mixture was stirred at  $60\text{ }^\circ\text{C}$  for 2 h, then DCE was removed in vacuo, and the residue was purified by column chromatography using hexane /dichloromethane (16:1) as an eluent to give B3T-BT core (400 mg) as a yellow solid, gave a total yield of 27% for the two steps.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz),  $\delta$  (ppm):  $\delta$  7.51 (d,  $J = 8.3$  Hz, 12H), 7.22 (q,  $J = 5.3$  Hz, 6H), 7.09 (d,  $J = 8.3$  Hz, 12H), 2.59-2.51 (m, 12H), 1.58-1.53 (m, 12H), 1.30-1.20 (m, 36H), 0.79 (t,  $J = 6.9$  Hz, 18H).;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz),  $\delta$  (ppm): 141.04, 140.59, 128.44, 128.40, 127.76, 127.73, 116.76, 97.94, 71.18, 63.25, 39.48, 35.57, 31.75, 31.35, 31.32, 30.68, 29.18, 29.15,

29.11, 23.85, 23.00, 22.60, 14.11, 11.25. (MALDI-TOF): calc for C<sub>105</sub>H<sub>108</sub>S<sub>9</sub> [M<sup>+</sup>], 1656.59; found: 1656.82.

**Synthesis of compound 6:** Compound **6** was prepared with a method similar to that described for compound B3T-BT. Yield: 26%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ (ppm): 7.43 (d, *J* = 7.9 Hz, 12H), 7.10 (d, *J* = 4.9 Hz, 3H), 7.06 (d, *J* = 8.1 Hz, 12H), 6.98 (d, *J* = 5.0 Hz, 3H), 2.56 (t, *J* = 7.8 Hz, 12H), 1.57 (p, *J* = 7.7, 7.2 Hz, 12H), 1.40-1.17 (m, 36H), 0.96-0.74 (m, 18H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>), δ (ppm): 163.16, 149.99, 141.67, 139.04, 135.60, 134.68, 131.97, 129.90, 129.39, 128.02, 126.42, 122.83, 63.13, 35.52, 31.69, 31.10, 29.69, 29.05, 22.57, 14.04. MS (MALDI-TOF): calcd for C<sub>99</sub>H<sub>108</sub>S<sub>6</sub> [M]<sup>+</sup>, 1490.693; found: 1490.743.

**Synthesis of compound 7:** B3T (0.20 g, 0.134 mmol) was dissolved in 30 mL anhydrous CHCl<sub>3</sub>, N-Bromosuccinimide (79.6 mg, 0.59 mmol) was added under an argon atmosphere at 0°C, the mixture was stirred at this temperature under dark for 5 h, CHCl<sub>3</sub> was removed in vacuo, and the residue was purified by column chromatography using hexane as an eluent to give compound **7** as a yellow solid (185 mg, 81%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (ppm): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (ppm): 7.53 (d, *J* = 7.9 Hz, 12H), 7.23 (d, *J* = 7.9 Hz, 12H), 7.14 (s, 3H), 2.73 (t, *J* = 7.8 Hz, 12H), 1.73 (t, *J* = 7.6 Hz, 12H), 1.42 (q, *J* = 9.5, 8.6 Hz, 40H), 1.02 (dt, *J* = 25.2, 6.5 Hz, 18H).; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>), δ (ppm): 161.69, 149.28, 142.05, 138.65, 134.92, 134.71, 132.08, 129.69, 129.26, 129.20, 128.66, 128.18, 125.73, 112.80, 63.72, 35.59, 35.51, 31.93, 31.75, 31.73, 31.70, 31.67, 31.11, 29.70, 29.66, 29.36, 29.07, 26.91, 22.69,

22.65, 22.60, 22.57, 14.12, 14.09, 14.06. (MALDI-TOF): calc for C<sub>99</sub>H<sub>107</sub>Br<sub>3</sub>S<sub>6</sub> [M]<sup>+</sup>, 1724.425; found: 1726.0133.

**Synthesis of B3T-TT:** B3T-T-Br (0.20 g 0.115 mmol) and (2-Thienyl)tributylstannane (0.26 g, 0.69 mmol) were added to a 100 mL three neck round-bottom flask, 30 mL toluene and 4 mL DMF were added. The mixture was purged with argon for 5 min, and Pd(PPh<sub>3</sub>)<sub>4</sub> (13 mg, 0.011 mmol) was added under N<sub>2</sub>. The reaction mixture was stirred at 110 °C overnight. Then toluene was removed in vacuo, and then residue was extracted with dichloromethane and washed with water. The organic layer was collected and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and concentration, the product was purified by column chromatography using hexane /dichloromethane (32:1) as an eluent to give a yellow solid (0.15 g, 75%) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (ppm): 7.36 (d, *J* = 8.0 Hz, 12H), 7.04-6.97 (m, 18H), 6.96 (s, 3H), 6.85 (dd, *J* = 5.1, 3.6 Hz, 3H), 2.48 (t, *J* = 7.7 Hz, 12H), 1.49 (dd, *J* = 11.0, 5.0 Hz, 12H), 1.33 (s, 2H), 1.27-1.07 (m, 40 H), 0.81-0.65 (m, 18H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>), δ (ppm): 163.55, 149.69, 141.86, 138.98, 138.96, 137.91, 135.20, 133.52, 132.08, 129.79, 129.38, 128.12, 127.74, 124.06, 123.06, 119.40, 63.46, 35.53, 31.70, 31.13, 29.08, 26.89, 22.59, 14.07. (MALDI-TOF): calc for C<sub>111</sub>H<sub>116</sub>S<sub>9</sub> [M]<sup>+</sup>, 1736.656; found: 1737.045.

**Synthesis of B3T-BT-CHO:** POCl<sub>3</sub> 0.1mL was added to the solution of DMF 2.00 mL and DCE 5 mL, the mixture was stirred at room temperature for 0.5 h [2]. A solution of B3TTT (0.20 g, 0.12 mmol) in DCE (20 mL) under N<sub>2</sub>. After being stirred at 60 °C for 12 h, the mixture was poured into ice water (100 mL), neutralized with saturated CH<sub>3</sub>COONa aq, and then extracted with dichloromethane. The combined organic layer

was washed with water and brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After filtration and concentration, the product was purified by column chromatography using hexane/dichloromethane (4:1) as an eluent to give an orange solid (156 mg, 75%)  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz),  $\delta$  (ppm):  $\delta$  9.86 (s, 3H), 7.89 (s, 3H), 7.48 (d,  $J = 7.2$  Hz, 12H), 7.11 (d,  $J = 7.2$  Hz, 12H), 2.57 (d,  $J = 6.4$  Hz, 12H), 1.56 (dd,  $J = 11.0, 5.0$  Hz, 12H), 1.25 (d,  $J = 16.3$  Hz, 40 H), 0.60-0.72 (m, 18H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz),  $\delta$  (ppm): 182.64, 153.14, 152.25, 143.43, 143.37, 142.73, 141.13, 139.54, 138.97, 133.96, 132.89, 129.64, 129.45, 129.08, 128.54, 63.63, 35.49, 31.62, 31.00, 29.66, 28.98, 22.63, 22.53, 14.07, 13.98. (MALDI-TOF): calc for  $\text{C}_{90}\text{H}_{110}\text{O}_4\text{S}_4$  [ $\text{M}^+$ ], 1740.58; found: 1740.75.

**Synthesis of B3T-TT-CHO:** B3T-TT-CHO was prepared with a method similar to that described for B3TTT-CHO. Yield: 82%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz),  $\delta$  (ppm): 9.82 (s, 3H), 7.62 (d,  $J = 4.0$  Hz, 3H), 7.46 (d,  $J = 7.9$  Hz, 12H), 7.26 (d,  $J = 3.3$  Hz, 3H), 7.18 (d,  $J = 4.0$  Hz, 3H), 7.13 (d,  $J = 7.9$  Hz, 12H), 4.16 (t,  $J = 7.1$  Hz, 4H), 2.60 (t,  $J = 7.7$  Hz, 12H), 2.07 (s, 6H), 1.60 (p,  $J = 7.7, 7.3$  Hz, 12H), 1.42-1.17 (m, 40H), 0.93-0.73 (m, 18H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 182.18, 171.13, 163.95, 150.93, 147.59, 142.22, 140.98, 138.53, 137.48, 137.34, 136.52, 134.50, 133.18, 129.68, 129.26, 128.26, 123.28, 121.48, 63.49, 60.36, 35.48, 31.65, 31.09, 29.64, 29.02, 22.55, 21.01, 14.15, 14.03. (MALDI-TOF): calc for  $\text{C}_{111}\text{H}_{114}\text{O}_3\text{S}_9$  [ $\text{M}^+$ ], 1820.64; found: 1820.54.

**Synthesis of B3T-BT-6F:** B3T-BT-CHO (0.100 g, 0.05 mmol) and 2-(3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (0.112 g, 0.51 mmol) were dissolved in 30



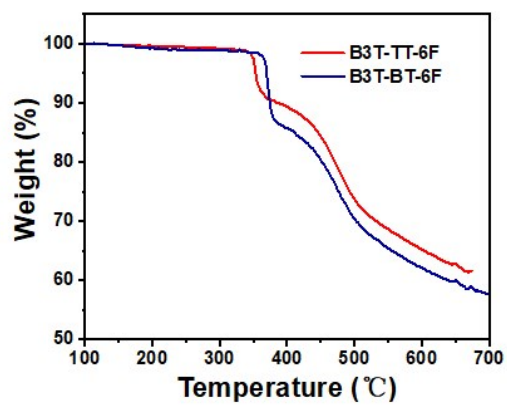
mL anhydrous  $\text{CHCl}_3$ , 0.1 mL pyridine was added under an argon atmosphere at room temperature, the mixture was stirred at 65 °C under dark for overnight.<sup>[2]</sup> The mixture was poured into ethanol and filtered, then the solid was washed by menthol, and the residue was purified by column chromatography using  $\text{CHCl}_3$  as an eluent to give B3T-BT-6F (93 mg, 78%) as a dark blue solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz),  $\delta$  (ppm): 8.82 (s, 3H), 8.55 (dd,  $J = 9.7, 6.6$  Hz, 3H), 8.22 (s, 3H), 7.73 (t,  $J = 7.5$  Hz, 3H), 7.53 (d,  $J = 8.2$  Hz, 12H), 7.16 (d,  $J = 8.2$  Hz, 12H), 2.57 (m, 10H), 1.62-1.56 (s, 21H), 1.24 (m, 38H), 0.76 (m, 16H), 0.04 (d,  $J = 28.0$  Hz, 30H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz),  $\delta$  (ppm): 185.50, 158.62, 156.82, 154.27, 153.75, 148.90, 146.48, 144.78, 142.32, 138.24, 138.21, 137.50, 135.89, 135.39, 128.63, 128.46, 128.44, 124.72, 123.88, 120.14, 116.99, 114.65, 114.50, 112.37, 77.60, 64.29, 39.58, 35.56, 31.74, 31.41, 29.75, 29.14, 29.12, 28.66, 23.13, 23.04, 22.62, 14.13, 10.75. HRMS (MALDI):  $\text{C}_{144}\text{H}_{114}\text{F}_6\text{N}_6\text{O}_3\text{S}_9$  calc. for 2379.065, found 2379.155.

**Synthesis of B3T-TT-6F:** B3T-TT-6F was prepared with a method similar to that described for B3T-BT-6F. Yield: 79%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz),  $\delta$  (ppm):  $\delta$  8.80 (s, 3H), 8.54 (dd,  $J = 10.0, 6.4$  Hz, 3H), 7.73 (d,  $J = 4.3$  Hz, 3H), 7.68 (t,  $J = 7.5$  Hz, 3H), 7.46-7.41 (m, 12H), 7.27 (s, 3H), 7.13 (d,  $J = 8.0$  Hz, 12H), 2.59 (t,  $J = 7.7$  Hz, 12H), 1.58 (m, 15H), 1.36-1.15 (m, 37H), 0.80 (d,  $J = 6.8$  Hz, 15H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz),  $\delta$  (ppm): 186.12, 161.30, 158.58, 157.26, 154.15, 150.00, 148.03, 145.78, 142.46, 140.83, 139.16, 137.93, 135.35, 134.33, 128.67, 128.52, 128.49, 126.42, 125.96, 118.96, 116.89, 114.83, 114.69, 77.89, 64.41, 40.11, 35.53, 31.73, 31.39, 29.90,

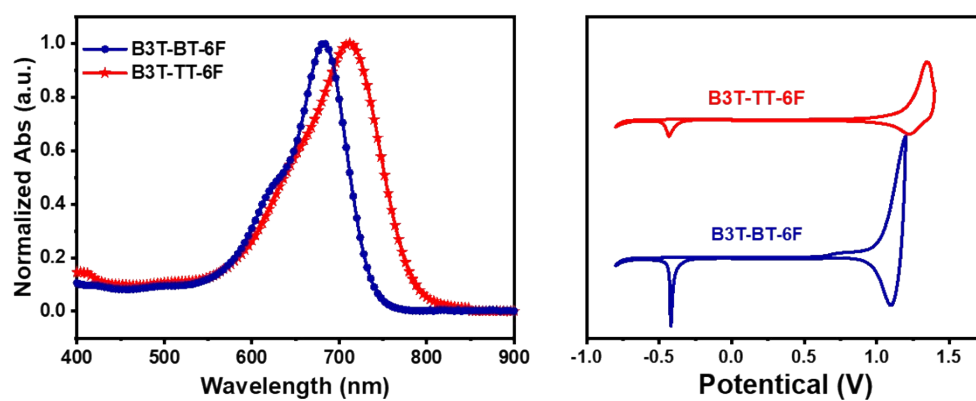
29.13, 29.09, 28.75, 23.29, 23.01, 22.61, 14.14, 14.12, 10.80. HRMS (MALDI):

$C_{150}H_{122}F_6N_6O_3S_9$  calc for. 2456.697 found 2456.799.

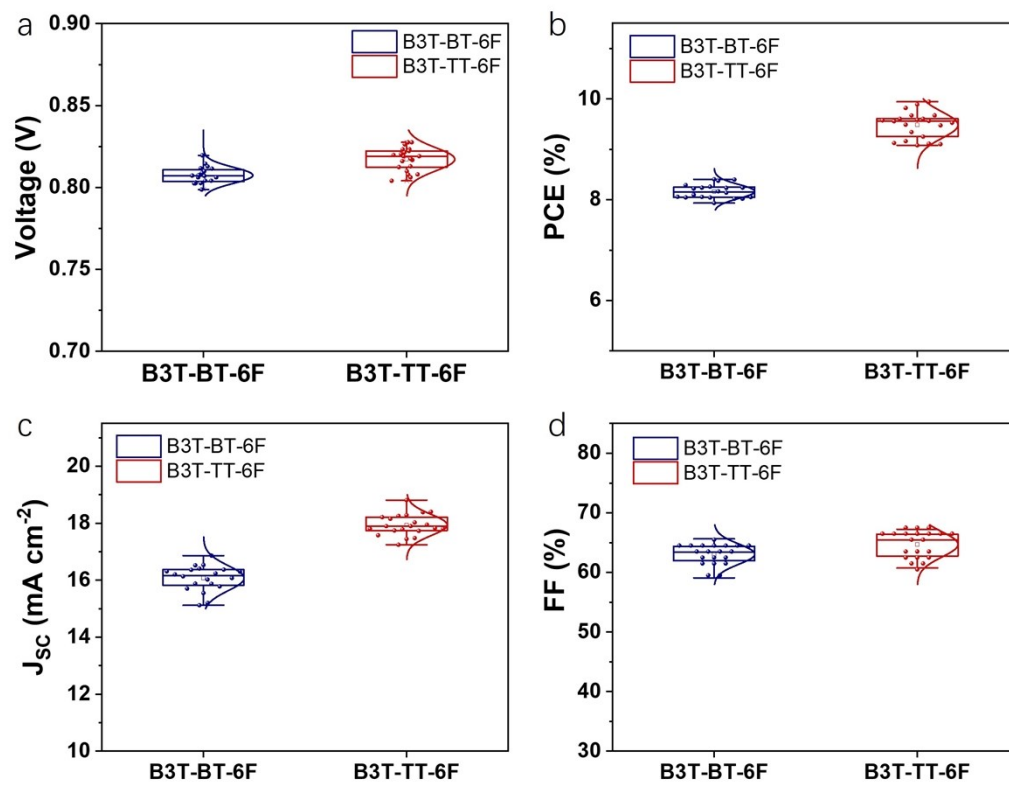
## 5. Supporting Figures



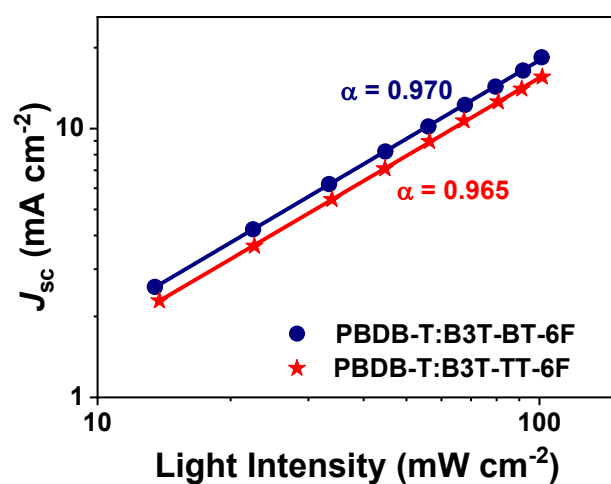
**Figure S1.** Thermogravimetric analysis plot of B3T-TT-6F and B3T-BT-6F.



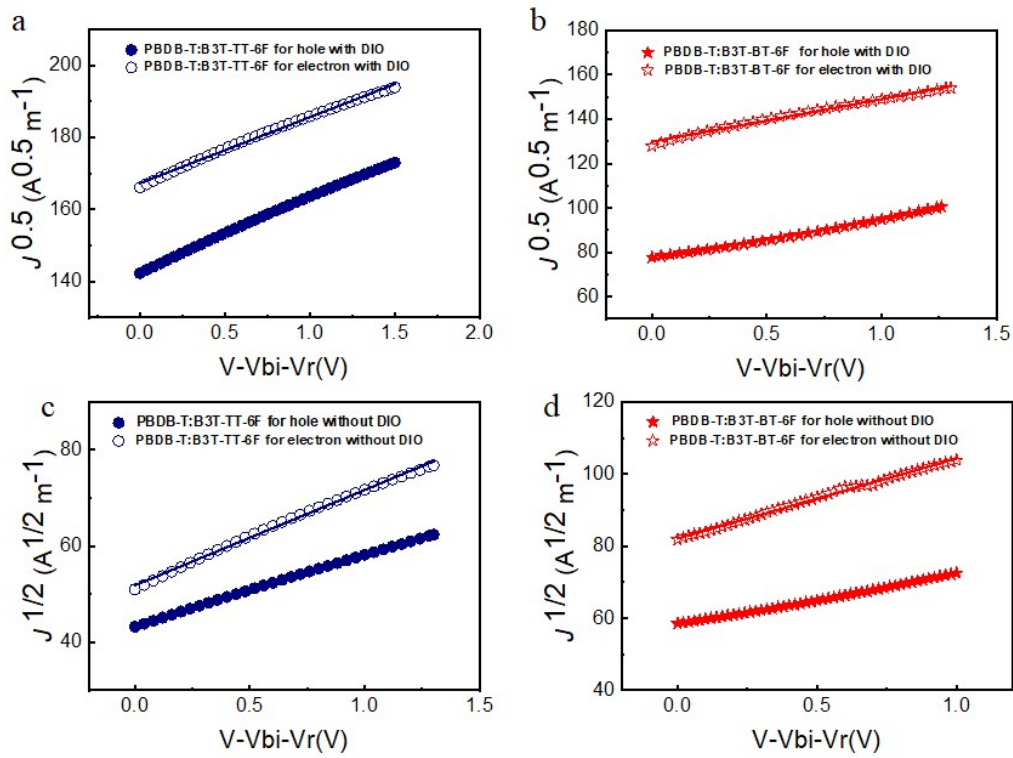
**Figure S2.** (a) Normalized absorption spectra of B3T-TT-6F and B3T-BT-6F in chloroform solutions. (b) Cyclic voltammogram (CV) curves of B3T-TT-6F and B3T-BT-6F in thin films.



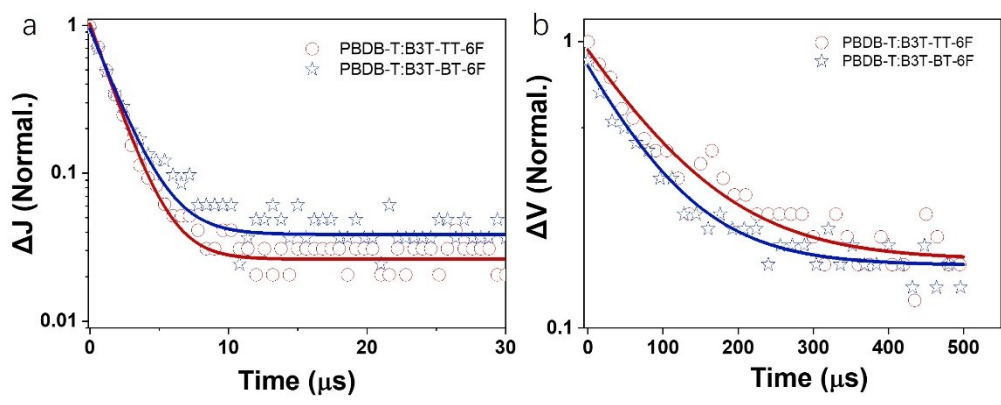
**Figure S3.** Statistical distribution of photovoltaic parameters of 20 devices based on B3T-TT-6F and B3T-BT-6F.



**Figure S4.**  $J_{sc}$  values of B3T-TT-6F and B3T-BT-6F based devices versus light intensity on a double-logarithmic scale.

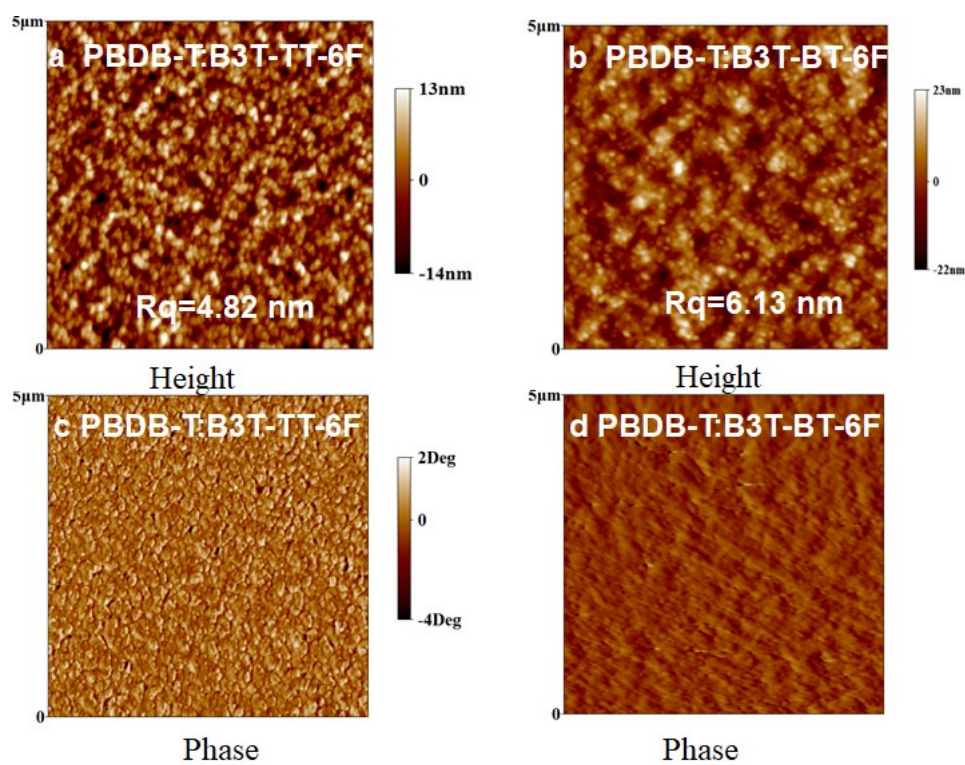


**Figure S5.**  $J^{0.5}$ - $V$  plots for the hole-only and electron-only devices based on PBDB-T: B3T-TT-6F (a) with DIO and (c) without DIO, PBDB-T: B3T-BT-6F (b) with DIO and (d) without DIO. The solid lines represent the fit using a model of single carrier SCLC with field-independent mobility.

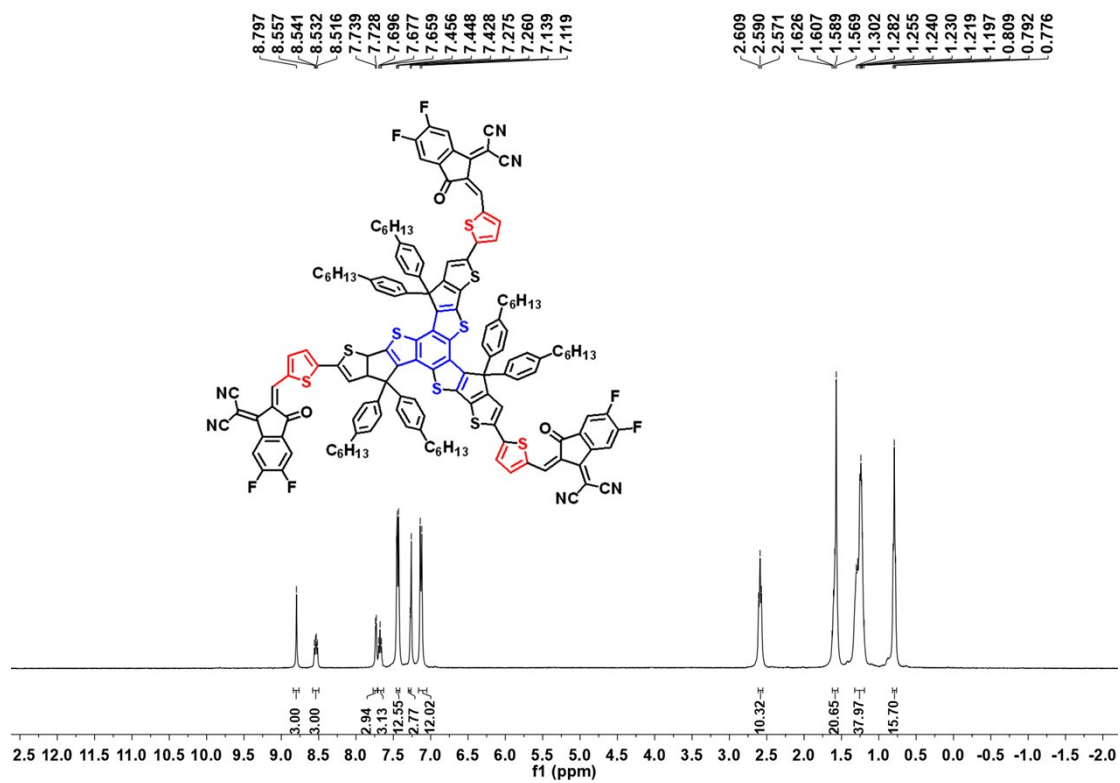


**Figure S6.** Transient photocurrent and transient photovoltage decay curves of corresponding devices under light condition.





**Figure S7.** Tapping mode AFM height images ( $5 \mu\text{m} \times 5 \mu\text{m}$ ) for PBDB-T: NFAs blend films. a) PBDB-T: B3T-TT-6F blend film; b) PBDB-T: B3T-BT-6F blend film. AFM phase images for PBDB-T: acceptors blend films: c) PBDB-T: B3T-TT-6F blend; d) PBDB-T: B3T-BT-6F blend.



**Figure S8.** <sup>1</sup>H NMR spectra of compound B3T-TT-6F at 300K in CDCl<sub>3</sub>.

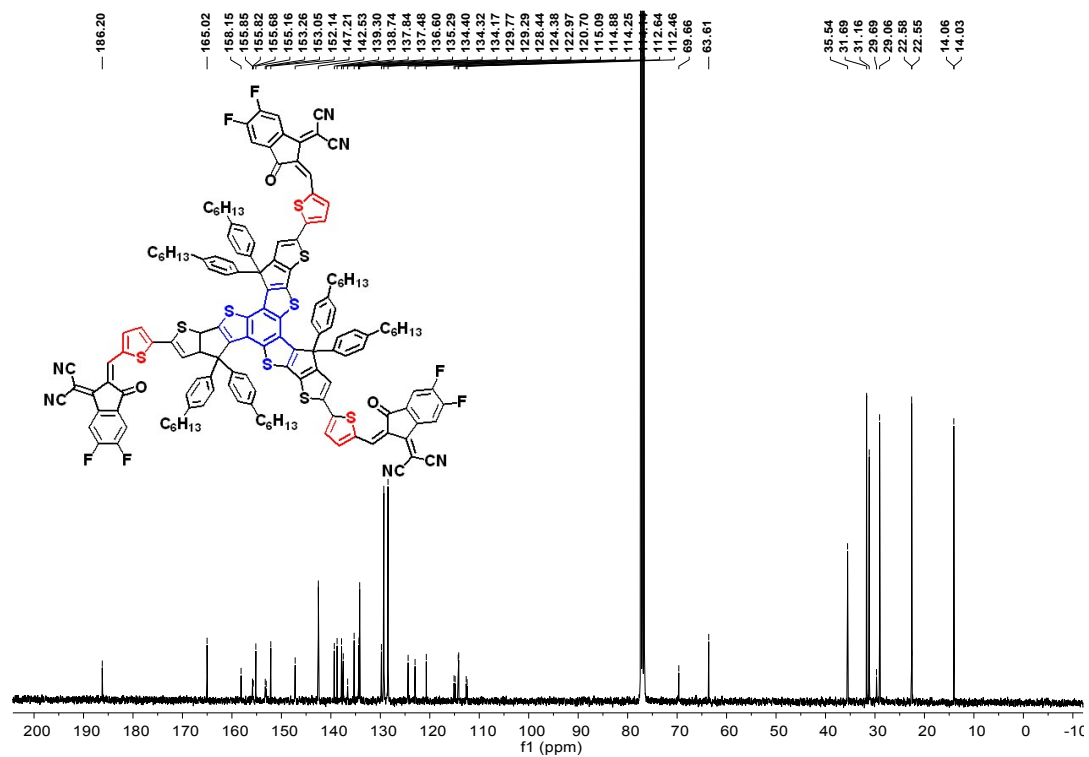
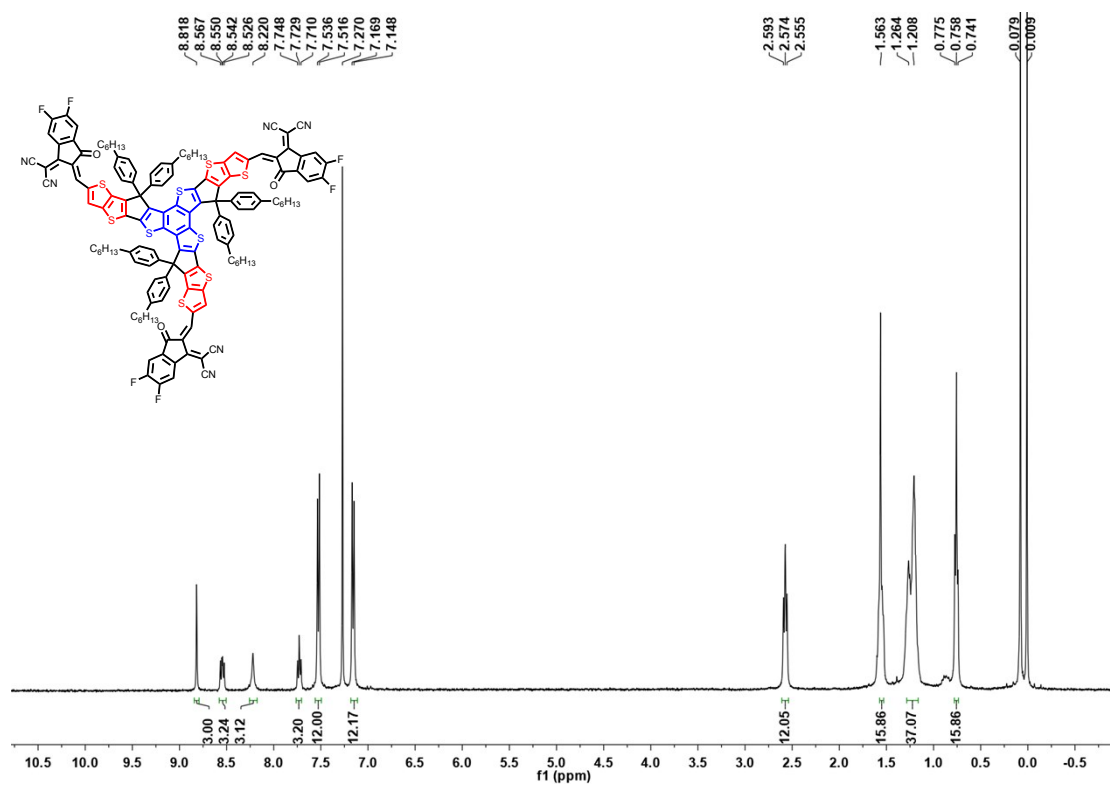
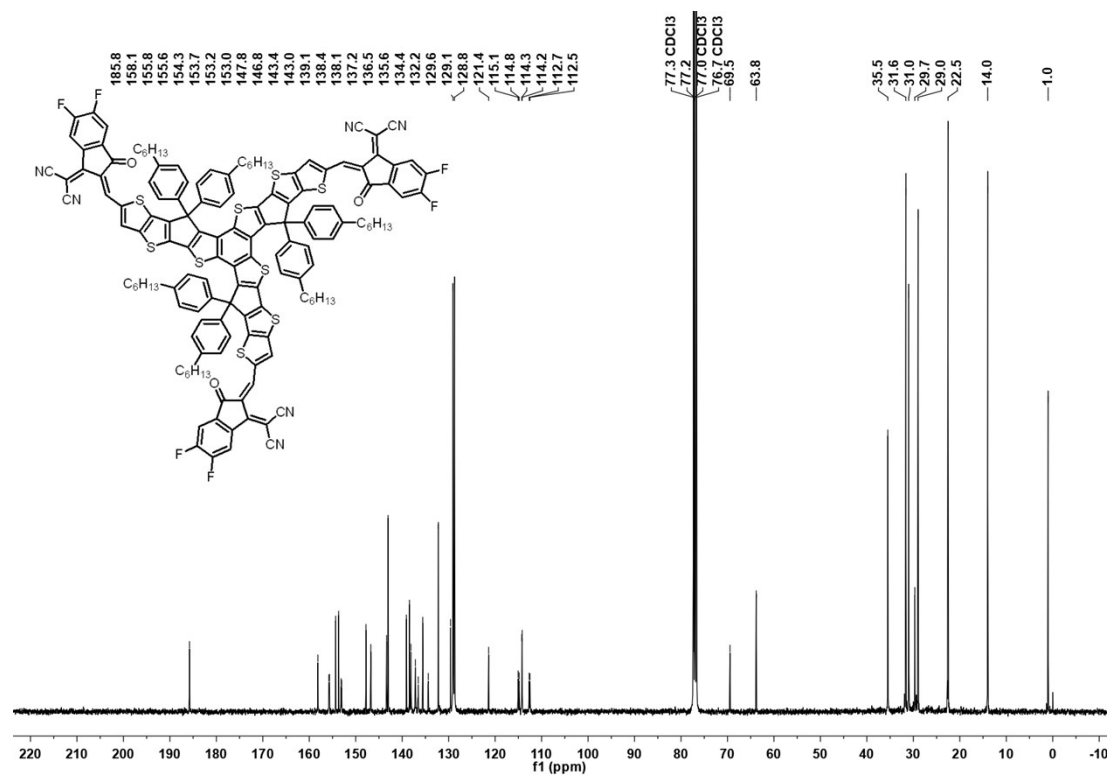


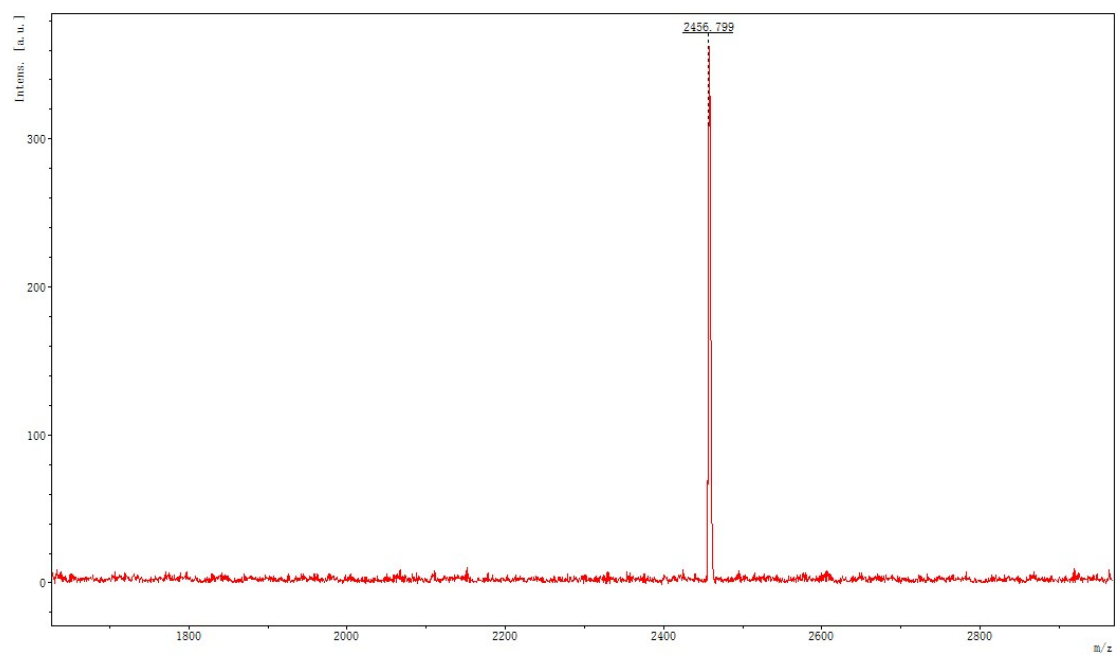
Figure S9.  $^{13}\text{C}$  NMR spectra of compound B3T-TT-6F at 300K in  $\text{CDCl}_3$ .



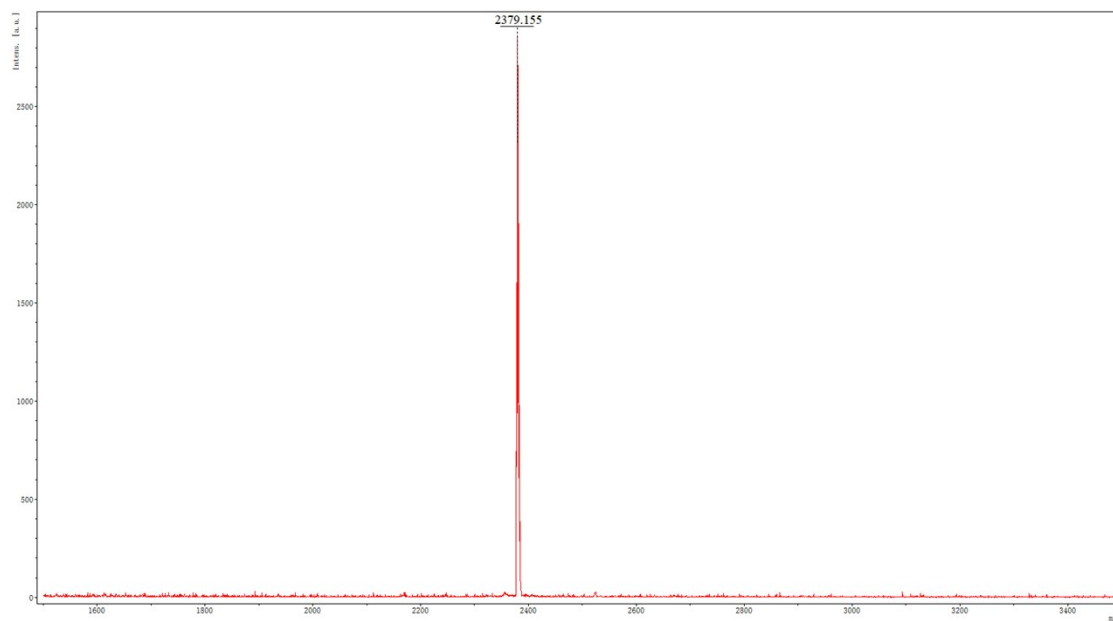
**Figure S10.**  $^1\text{H}$  NMR spectra of compound B3T-BT-6F at 300K in  $\text{CDCl}_3$ .



**Figure S11.**  $^{13}\text{C}$  NMR spectra of compound B3T-BT-6F at 300K in  $\text{CDCl}_3$ .



**Figure S12.** MS (MALDI-TOF) spectra of B3T-TT-6F



**Figure S13.** MS (MALDI-TOF) spectra of B3T-BT-6F.

## Supporting Tables

**Table S1.** The basic properties of the NFA materials.

Compound	T <sub>d</sub> °C	Solution		Film		HOMO	LUMO	E <sub>g</sub> <sup>CVb)</sup> (eV)	
		$\lambda_{max}$	$\lambda_{onset}$	$\lambda_{max}$	$\lambda_{onset}$				E <sub>g</sub> <sup>opt a)</sup> (eV)
		(nm)	(nm)	(nm)	(nm)				
B3T-TT-6F	365	712	784	755	856	1.45	-5.42	-4.04	1.38
B3T-BT-6F	346	682	740	721	808	1.53	-5.62	-4.03	1.59

<sup>a)</sup> E<sub>g</sub><sup>opt</sup> was calculated from the onset absorption of film,  $E_g^{opt} = 1240/\lambda_{onset}$ . <sup>b)</sup> E<sub>g</sub><sup>CV</sup> = E<sub>HOMO</sub> - E<sub>LUMO</sub>.

**Table S2.** Photovoltaic performance of OSCs based on PBDB-T-B3T-based blend films with different D: A ratio under illumination of AM 1.5 G, 100 mW cm<sup>-2</sup>.

Acceptor	D: A (w/w)	V <sub>OC</sub>	J <sub>SC</sub>	FF	PCE
		(V)	(mA cm <sup>-2</sup> )	(%)	(%)
B3T-TT-6F	1:1.2	0.81	14.68	56.25	6.69
	1:1.5	0.82	15.84	57.35	7.43
	1:1.7	0.79	15.24	53.41	6.43
B3T-BT-6F	1:1	0.77	14.64	53.31	6.04
	1:1.2	0.78	13.97	59.15	6.48
	1:1.5	0.77	14.81	55.41	6.33



**Table S3.** Photovoltaic performance of OSCs based on PBDB-T-B3T-based blend films with different DIO contents under illumination of AM 1.5 G, 100 mW cm<sup>-2</sup>.

Acceptor	DIO	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
B3T-TT-6F	0	0.82	15.84	57.35	7.43
	0.5	0.80	15.45	58.52	7.28
	0.6	0.82	16.70	56.86	8.27
	0.6+(TA) <sup>a)</sup>	0.82	18.28	66.41	9.94
	0.7	0.81	16.18	62.28	8.20
B3T-BT-6F	0	0.78	13.97	59.15	6.48
	0.5	0.79	15.40	58.56	7.12
	0.7	0.807	16.53	63.48	8.40
	1	0.74	15.58	61.21	7.02

<sup>a)</sup> Thermal annealing of active layer