

## Supporting Information

### **Bithiazole-based A- $\pi$ -A'- $\pi$ -A-type completely non-fused small-molecule acceptors for efficient organic solar cells**

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## **Experimental section**

### **1. Instruments and measure methods**

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured with Bruker AVANCE 400 spectrometer. Molecular mass was determined by flight mass spectrometry (MALDITOF MS) using a Bruker Aupoflex-III mass spectrometer. Ultraviolet-visible (UV-vis) absorption spectra were measured on Perkin Elmer Lamada 25 spectrometer with a dilute CHCl<sub>3</sub> solution or as a solid film casted from chlorobenzene. Photoluminescence (PL) spectrum was carried out on Edinburgh Instrument FLS 980. Thermal gravimetric analysis (TGA) was performed under nitrogen at a heating rate of 20 °C min<sup>-1</sup> with TGA Q50 analyzer. Differential scanning calorimetry (DSC) analysis was measured on a DSC instrument (DSC Q10) in a temperature range from 25 to 280 °C under N<sub>2</sub> with a heating rate of 10 °C min<sup>-1</sup>. The ground-state geometries of the three molecules were optimized by density functional theory (DFT) at the RB31YP/6-311G level. All calculations were performed in the gas phase and with Gaussian 09 program. Cyclic voltammetry (CV) was measured on a

31 electrochemistry work station (CHI830B, Chenhua Shanghai) with a Pt slice electrode (coated with a small  
32 acceptor film), a Pt ring, and a Ag/AgCl electrode as the working electrode, the auxiliary electrode and the  
33 reference electrode respectively, in a 0.1 M tetrabutylammonium hexafluorophosphate acetonitrile solution.  
34 The potentials were calibrated using a ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple as an internal standard,  
35 whose redox potential is supposed at -4.8 eV relative to zero vacuum level. The HOMO/LUMO energy  
36 levels were obtained from the equation  $\text{HOMO/LUMO} = -(E_{\text{ox/red}} - E_{\text{Fc/Fc}^+} + 4.8)$  (eV), where the redox  
37 potential ( $E_{\text{Fc/Fc}^+}$ ) of Fc/Fc<sup>+</sup> was determined to be 0.43 V versus Ag/AgCl in this study. Therefore, the above  
38 equation can be simplified as  $\text{HOMO/LUMO} = -(E_{\text{ox/red}} + 4.37)$  (eV). Atomic force microscopy (AFM)  
39 measurement was carried out on a Digital Instruments Veeco Nanoscopy V using a tapping mode. Contact  
40 angles were measured with a contact angle meter (JC2000D1). The solution of each pure organic material  
41 was spin-coated on cleaned ITO substrates. Droplets of two different liquids, water and ethylene glycol (EG)  
42 were cast onto the pure organic films with the drop size kept at 1  $\mu\text{L}$  per drop. Contact angle images were  
43 taken at 4 s after the whole droplet was deposited onto the sample surface. At least 3 independent  
44 measurements were performed for each single liquid. Grazing incidence wide angle X-ray scattering  
45 (GIWAXS) measurement was conducted at the beamline of 7.3.3 at the Advanced Light Source (ALS).  
46 Samples were prepared on Si/PEDOT:PSS substrates using identical blend solutions and conditions as those  
47 used in device fabrication. The CCL was calculated according to the formula:  $\text{CCL} = 2\pi K/\Delta q$ , where  $K$  and  
48  $\Delta q$  are the shape factor ( $K = 0.9$ ) and the full-width at half-maximum (FWHM) of the diffraction peak,  
49 respectively.

## 50 2. Materials synthesis and structural characterization

51 *Synthesis of compound 2a.* Under an Ar atmosphere, compound **1a** (5.23 g, 21.0 mmol), dithiooxamide  
52 (1.2 g, 10.0 mmol) and absolute ethanol (50 mL) were added a 100 mL round bottom flask. Then, the  
53 reaction mixture was heated up to 70 °C and stirred for 6h. After that the reaction mixture was allowed to  
54 drop to room temperature and extracted with dichloromethane. The organic layer was washed several times  
55 with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removing the solvent, the product (compound **2a**) was  
56 obtained as a light yellow solid (3.70 g, yield 89%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ /ppm): 6.94 (s, 2H), 2.82-  
57 2.78 (t,  $J = 8.0$  Hz, 4H), 1.75-1.71 (m, 4H), 1.35-1.22 (m, 24H), 0.89-0.85 (t,  $J = 8$  Hz, 6H).

58 *Synthesis of compound 2b.* This compound was obtained according to the similar process with compound  
59 **2a** except for the replacement of compound **1a** with **1b**. Finally, compound **2b** was obtained as a yellow oil  
60 (2.70 g, yield 75%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ /ppm): 7.26 (s, 2H), 6.63 (s, 2H), 2.87-2.83 (t,  $J = 8.0$  Hz,  
61 4H), 2.73-2.72 (d,  $J = 4$  Hz, 4H), 1.77-1.58 (m, 6H), 1.43-1.26 (m, 28H), 0.93-0.89 (t,  $J = 8.0$  Hz, 18H).

62 *Synthesis of compound 3a.* Under an Ar atmosphere, compound **2a** (2.10 g, 5.00 mmol) and CH<sub>3</sub>COOH  
63 (15 mL) were slowly added a 50 mL round bottom flask. Then, 1.80 g NBS (10.1 mmol) dissolved in 15 mL

64 DMF was dropwise added into this solution under 0 °C. After that the reaction mixture was allowed to rise  
65 to room temperature and stirred for 4h under darkness. The reaction residue was filtered to obtain solid,  
66 which was further recrystallized with dichloromethane/*n*-hexane to obtain a white solid as compound **3a**  
67 (2.40 g, yield 83%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ/ppm): 2.75-2.71 (t, *J* = 8.0 Hz, 4H), 1.71-1.67 (m, 4H),  
68 1.32-1.25 (m, 24H), 0.89-0.85 (t, *J* = 8.0 Hz, 6H).

69 *Synthesis of compound 3b.* Under an Ar atmosphere, compound **2b** (1.81 g, 2.50 mmol) and CH<sub>3</sub>COOH  
70 (15 mL) were slowly added a 50 mL round bottom flask. Then, 0.899 g NBS (5.05 mmol) dissolved in 15  
71 mL DMF was dropwise added into this solution under 0 °C. After that the reaction mixture was allowed to  
72 rise to room temperature and stirred for 4h under darkness. The reaction was quenched with water and  
73 extracted with dichloromethane. The organic layer was washed several times with water and dried over  
74 anhydrous Na<sub>2</sub>SO<sub>4</sub>. Finally, the pure compound **3b** was obtained as a yellow oil (1.88 g, yield 85%) through  
75 silica gel column chromatography with petroleum ether as an eluent. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ/ppm):  
76 6.67 (s, 2H), 2.75-2.73 (d, *J* = 8.0 Hz, 4H), 2.69-2.65 (t, *J* = 8.0 Hz, 4H), 1.59-1.56 (m, 6H), 1.40-1.26 (m,  
77 28H), 0.92-0.85 (m, 18H).

78 *Synthesis of compound 4a.* Under an Ar atmosphere, compound **3a** (1.74 g, 3.00 mmol), 2-(4-(2-  
79 ethylhexyl)thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.89 g, 9.00 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (65 mg),  
80 K<sub>2</sub>CO<sub>3</sub> (2.48 g), H<sub>2</sub>O (9 mL) and two drops of trioctylmethylammonium chloride were added into a 100 mL  
81 round bottom flask. The reaction mixture was carried out vacuuming and backfilling with argon three times  
82 before the addition of dry toluene (25 mL). The resultant mixture was heated slowly to 110 °C and stirred  
83 for 48 h. The reaction mixture was allowed to reduce to room temperature and extracted with  
84 dichloromethane. The organic layer was washed several times with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>.  
85 After the removal of solvent, compound **4a** was obtained as a yellow oily liquid (1.85 g, yield 76%) after the  
86 crude produce was subjected to silica gel column chromatography using petroleum ether as an eluent. <sup>1</sup>H  
87 NMR (400 MHz, CDCl<sub>3</sub>, δ/ppm): 7.00 (s, 2H), 6.93 (s, 2H), 2.95-2.91 (t, *J* = 8.0 Hz, 4H), 2.56-2.55 (d, *J* =  
88 4.0 Hz, 4H), 1.80-1.76 (m, 4H), 1.58-1.55 (m, 2H), 1.32-1.27 (m, 40H), 0.92-0.88 (m, 18H).

89 *Synthesis of compound 4b.* This compound was synthesized according to the similar process as compound  
90 **4a** except for the replacement of **3a** with **3b** (1.88 g, 2.13 mmol). Finally, the pure compound **4b** was  
91 obtained as a yellow liquid (2.11 g, yield 89%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ/ppm): 6.89 (s, 2H), 6.82 (s,  
92 2H), 6.66 (s, 2H), 2.76-2.75 (d, *J* = 4.0Hz, 4H), 2.47-2.45 (d, *J* = 4.0 Hz, 4H), 2.37-2.33 (t, *J* = 8.0 Hz, 4H),  
93 1.62-1.60 (m, 2H), 1.47-1.18 (m, 50H), 0.93-0.82 (m, 30H).

94 *Synthesis of compound 5a.* To a dry 100 mL round bottom flask, compound **4a** (0.809 mg, 1.00 mmol),

95 dried DMF (4 mL) and dry 1,2-dichloroethane (15 mL) were added under an argon atmosphere. The solution  
96 was cooled to 0 °C and 2.3 mL of POCl<sub>3</sub> was added slowly. After stirring for 1 h at room temperature, the  
97 reaction mixture was allowed to warmed up to 90 °C and stirred for 12 h. After cooling to room temperature,  
98 the reaction mixture was poured into saturated CH<sub>3</sub>COONa aqueous solution and extracted with  
99 dichloromethane. The combined organic phase was washed with water and the crude product was purified  
100 via silica gel column chromatography with petroleum ether/dichloromethane as an eluent to afford  
101 compound **5a** as an orange-red solid (718 mg, 83%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ/ppm): 10.02 (s, 2H),  
102 7.06 (s, 2H), 3.00-2.96 (t, *J* = 8.0 Hz, 4H), 2.88-2.86 (d, *J* = 8.0 Hz, 4H), 1.83-1.77(m, 4H), 1.64-1.63 (d, *J* =  
103 4 Hz, 2H), 1.37-1.26 (m, 40H), 0.93-0.85 (m, 18H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ/ppm): 181.89, 158.50,  
104 156.91, 152.53, 141.37, 138.26, 130.82, 127.35, 41.63, 32.71, 32.53, 31.91, 30.84, 29.56, 29.51, 29.47,  
105 29.33, 29.27, 28.83, 25.71, 22.99, 22.71, 14.16, 14.12, 10.83. MS (MALDI-TOF, *m/z*) C<sub>50</sub>H<sub>76</sub>N<sub>2</sub>O<sub>2</sub>S<sub>4</sub>:  
106 calculated: 865.410; found: 865.487.

107 *Synthesis of compound 5b.* This compound was synthesized according to the similar process as  
108 compound **5a** except for the replacement of **4a** with **4b** (2.11 g, 1.90 mmol). Finally, the pure compound **4b**  
109 was obtained as a yellow oily liquid (1.98 g, yield 89%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ/ppm): 9.94 (s, 2H),  
110 6.92 (s, 2H), 6.69 (s, 2H), 2.79-2.76 (m, 8H), 2.36-2.32 (t, *J* = 8.0 Hz, 4H), 1.71 (s, 2H), 1.63-1.60 (m, 6H),  
111 1.56-1.17 (m, 44H), 0.93-0.79 (m, 30H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ/ppm): 181.85, 157.95, 151.89,  
112 147.65, 146.58, 143.64, 140.90, 138.74, 131.65, 131.08, 127.45, 124.84, 41.46, 41.27, 34.22, 32.47, 32.37,  
113 31.60, 30.13, 29.15, 29.09, 28.86, 28.80, 25.59, 25.48, 23.05, 22.97, 22.59, 14.22, 14.13, 10.87, 10.77. MS  
114 (MALDI-TOF, *m/z*) C<sub>68</sub>H<sub>100</sub>N<sub>2</sub>O<sub>2</sub>S<sub>6</sub>: calculated (M + H)<sup>+</sup>: 1170.920; found: 1171.558.

115 *Synthesis of CBTz-2F.* Under an argon atmosphere, compound **5a** (138 mg, 0.16 mmol), IC-2F (74 mg,  
116 0.32 mmol), toluene (20 mL), 0.2 mL acetic anhydride and 0.1 mL boron trifluoride ether were added into a  
117 50 mL round bottom flask. Reaction was performed at 60 °C for 1 h. The reaction droplets were added into  
118 methanol and **CBTz-2F** was obtained as blue solid powder (189 mg, yield 92%) by filter. <sup>1</sup>H NMR (400 MHz,  
119 CDCl<sub>3</sub>, δ/ppm): 9.02 (s, 2H), 8.60-8.56 (t, *J* = 8.0 Hz, 2H), 7.75-7.71 (t, *J* = 8.0 Hz, 2H), 7.24 (s, 2H), 3.15-  
120 3.11 (t, *J* = 8.0 Hz, 4H), 2.93-2.92 (d, *J* = 4.0 Hz, 4H), 1.91-1.87 (m, 4H), 1.72 (m, 2H), 1.55-1.27 (m, 40H),  
121 0.93-0.85(m, 18H). MS (MALDI-TOF, *m/z*) C<sub>74</sub>H<sub>80</sub>F<sub>4</sub>N<sub>6</sub>O<sub>2</sub>S<sub>4</sub>: calculated:1288.516; found: 1289.876.  
122 Notably, the <sup>13</sup>C NMR spectrum of this compound was not obtained due to the poor solubility in chloroform.

123 *Synthesis of TBTz-2F.* This compound was synthesized according to the similar procedure of **CBTz-2F**  
124 using compound **5b** (117 mg, 0.1 mmol) and IC-2F (46 mg, 0.2 mmol) as reactants. Finally, **TBTz-2F** was

125 obtained as blue-black solid power (143 mg, yield 90%) after purification. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  
126 δ/ppm): 8.92 (s, 2H), 8.54 (dd, *J* = 12 Hz, *J* = 8 Hz, 2H), 7.69-7.65 (t, *J* = 8.0 Hz, 2H), 6.96 (s, 2H), 6.75 (s,  
127 2H), 2.83-2.80 (m, 8H), 2.42-2.38 (t, *J* = 8.0 Hz, 4H), 1.65-1.62 (m, 2H), 1.54-1.48 (m, 6H), 1.35-1.18 (m,  
128 44H), 0.93-0.77 (m, 30H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ/ppm): 185.32, 160.56, 159.14, 158.85, 149.17,  
129 146.65, 146.61, 143.70, 134.67, 133.50, 131.40, 130.38, 127.50, 125.30, 121.54, 115.05, 114.83, 114.55,  
130 114.26, 112.80, 112.61, 41.77, 41.21, 34.33, 34.15, 32.42, 32.18, 31.61, 30.22, 29.72, 29.26, 29.05, 28.90,  
131 28.69, 25.45, 25.28, 23.06, 23.00, 22.60, 14.20, 14.14, 14.11, 10.85, 10.62. MS (MALDI-TOF, *m/z*)  
132 C<sub>92</sub>H<sub>104</sub>F<sub>4</sub>N<sub>6</sub>O<sub>2</sub>S<sub>6</sub>: calculated: 1592.648; found: 1594.050.

133 *Synthesis of TBTz-2Cl*. This compound was synthesized according to the similar procedure of **CBTz-**  
134 **2F** using compound **5b** (117 mg, 0.10 mmol) and IC-2Cl (52.6 mg, 0.2 mmol) as reactants. Finally, **TBTz-**  
135 **2Cl** was obtained as blue-black solid power (151 mg, yield 91%) after purification. <sup>1</sup>H NMR (400 MHz,  
136 CDCl<sub>3</sub>, δ/ppm): 8.94 (s, 2H), 8.77 (s, 2H), 7.93 (s, 2H), 6.96 (s, 2H), 6.75 (s, 2H), 2.83-2.78 (m, 8H), 2.42-  
137 2.38 (t, *J* = 8.0 Hz, 4H), 1.70-1.62 (m, 2H), 1.59-1.50 (m, 6H), 1.35-1.16 (m, 44H), 0.93-0.77(m, 30H). <sup>13</sup>C  
138 NMR (100 MHz, CDCl<sub>3</sub>, δ/ppm): 185.42, 160.80, 159.03, 158.89, 149.31, 146.98, 146.72, 143.77, 139.72,  
139 139.51, 138.47, 136.10, 135.26, 133.80, 131.49, 130.45, 127.52, 126.95, 125.29, 125.22, 121.53, 114.63,  
140 114.25, 41.78, 41.19, 34.35, 34.14, 32.41, 32.17, 31.62, 30.23, 29.27, 29.05, 28.89, 28.68, 25.44, 25.27,  
141 23.08, 23.00, 22.61, 14.22, 14.15, 14.13, 10.86, 10.62. MS (MALDI-TOF, *m/z*) C<sub>92</sub>H<sub>104</sub>Cl<sub>4</sub>N<sub>6</sub>O<sub>2</sub>S<sub>6</sub>:  
142 calculated: 1658.527; found: 1656.857.

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### 144 3. Preparation and performance test of OSCs

145 The OSC devices with a conventional architecture of ITO/PEDOT:PSS/PM6:SMA/PFN-Br/Ag were  
146 fabricated and characterized in an N<sub>2</sub>-filled glovebox, where BTz-based molecules were used as SMAs. The  
147 indium tin oxide (ITO) patterned glass was cleaned with ultrasonic treatment in detergent, deionized water,  
148 acetone, ethanol, and isopropyl alcohol sequentially, and dried in an ultraviolet-ozone chamber for 15 min.  
149 A PEDOT:PSS hole transport layer was deposited onto the cleaned ITO substrates via spin-coating at 3500  
150 rpm, followed by TA at 150 °C for 15 min. Subsequently, the PEDOT:PSS-coated substrates were  
151 transferred to the nitrogen-filled glovebox. The polymer donor (PM6) and acceptor materials with different  
152 feed ratios dissolved in chloroform and stirred at for 30 min before being spin-coated onto the PEDOT:PSS-  
153 coated substrates. Notably, the additive (CN or DIO or 2-MN) was added into the donor:acceptor mixed  
154 solution and thermally annealed (110 °C for 10 min) for the spin-coated active layer was performed if  
155 necessary. Next, an electron transport layer composed of PFN-Br (0.5 mg mL<sup>-1</sup> in methanol) was spin-

156 coated onto the active layers at 3500 rpm. Finally, Ag electrodes (~100 nm) were deposited via thermal  
 157 evaporation under vacuum (~10<sup>-4</sup> Pa) using a shadow mask to define the active area. The active area of the  
 158 devices was defined by a shadow mask. The thicknesses of the active layer were controlled by varying the  
 159 spin-coating speed and measured on an Ambios Technology XP-2 surface profilometer. Photovoltaic  
 160 performance of solar cells was tested under illumination condition with an AM 1.5G (100 mW cm<sup>-2</sup>), and  
 161 the current density-voltage (*J-V*) characteristics were measured by a computer controlled Keithley 2602  
 162 Source Meter. The device area was determined as 0.038 cm<sup>2</sup>. The incident light intensity was calibrated  
 163 using a standard Si solar cell. The external quantum efficiency (EQE) was measured by using a Solar Cell  
 164 Spectral Response Measurement System QE-R3011 (Enli Technology Co., Ltd.). The light intensity at each  
 165 wavelength was calibrated by a standard single-crystal Si solar cell.

#### 166 4. Measurement of charge mobility

167 The charge mobility was measured by the space charge-limited current (SCLC) method with a hole only  
 168 device configuration (ITO/PEDOT:PSS/active layer/MoO<sub>3</sub>/Al) for hole mobility and an electron only device  
 169 configuration (ITO/ZnO/active layer/PFN-Br/Al) for electron mobility. Both hole and electron mobilities  
 170 were extracted by fitting measured *J-V* curves using the empirical Mott-Gurney formula in single carrier  
 171 SCLC device with the equation of  $\ln(JL^3/V^2) \approx 0.89(1/E_0)^{0.5} (V/L) + \ln(9\epsilon_0\epsilon_r\mu/8)$ .

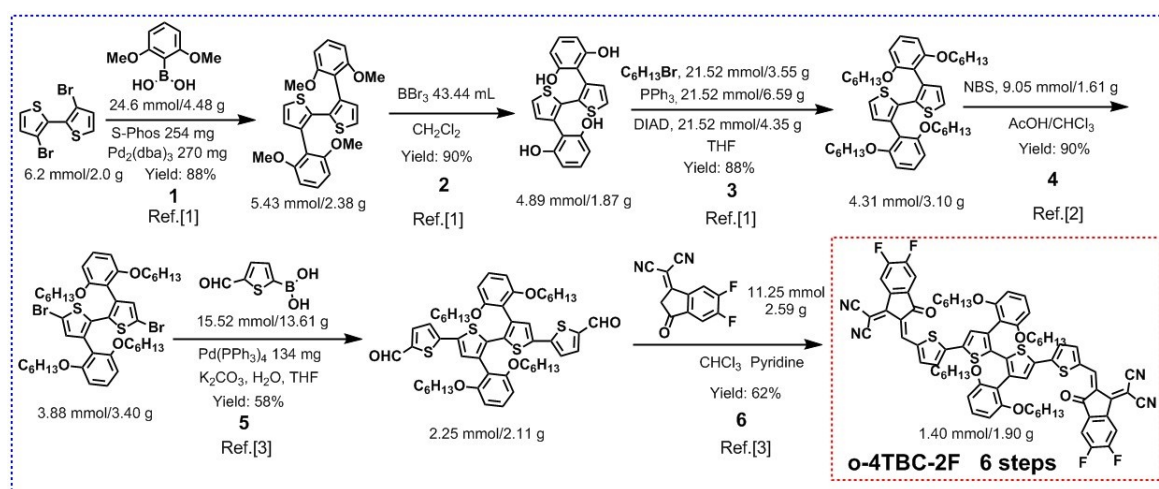
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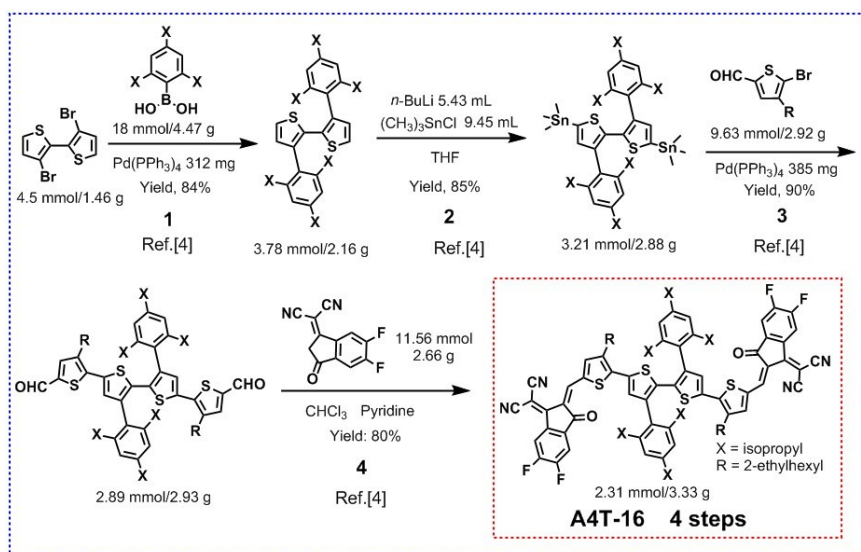
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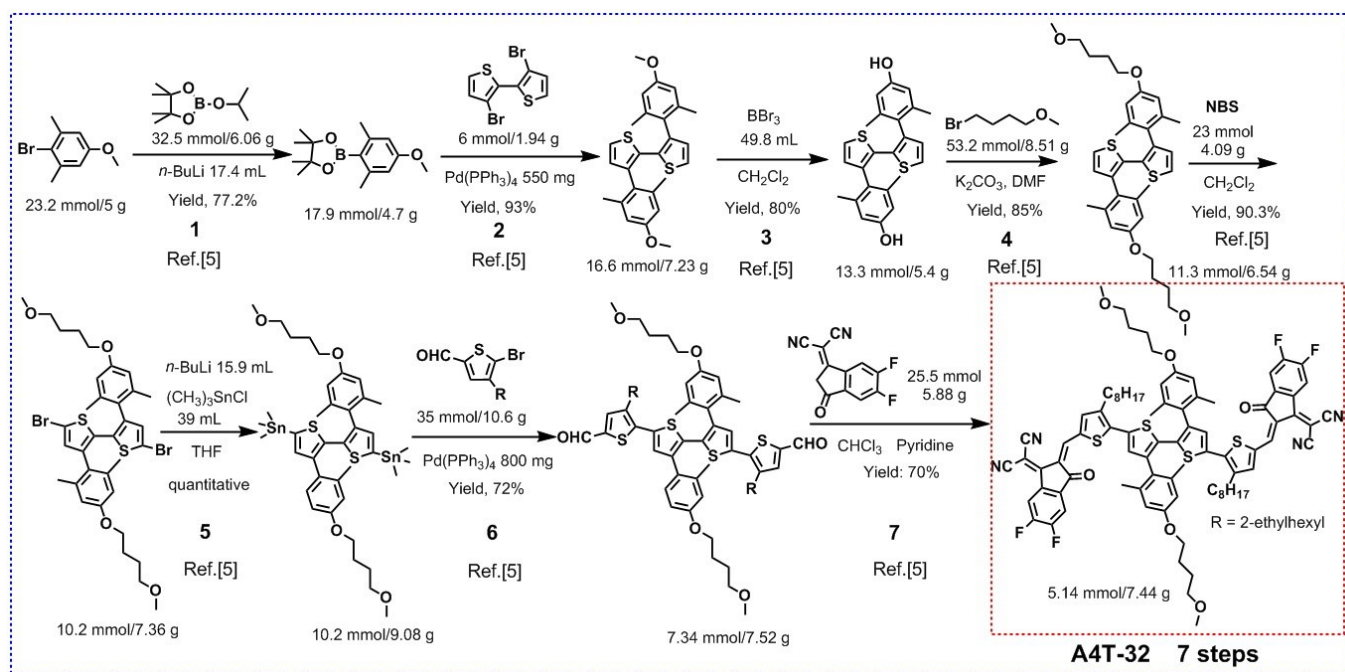
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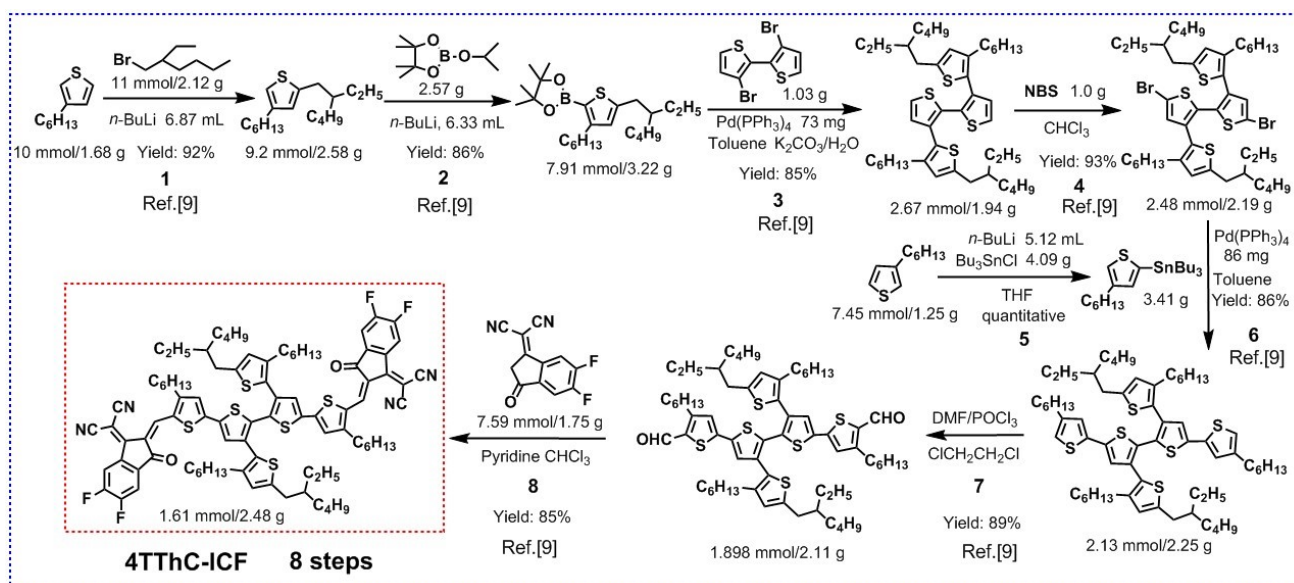
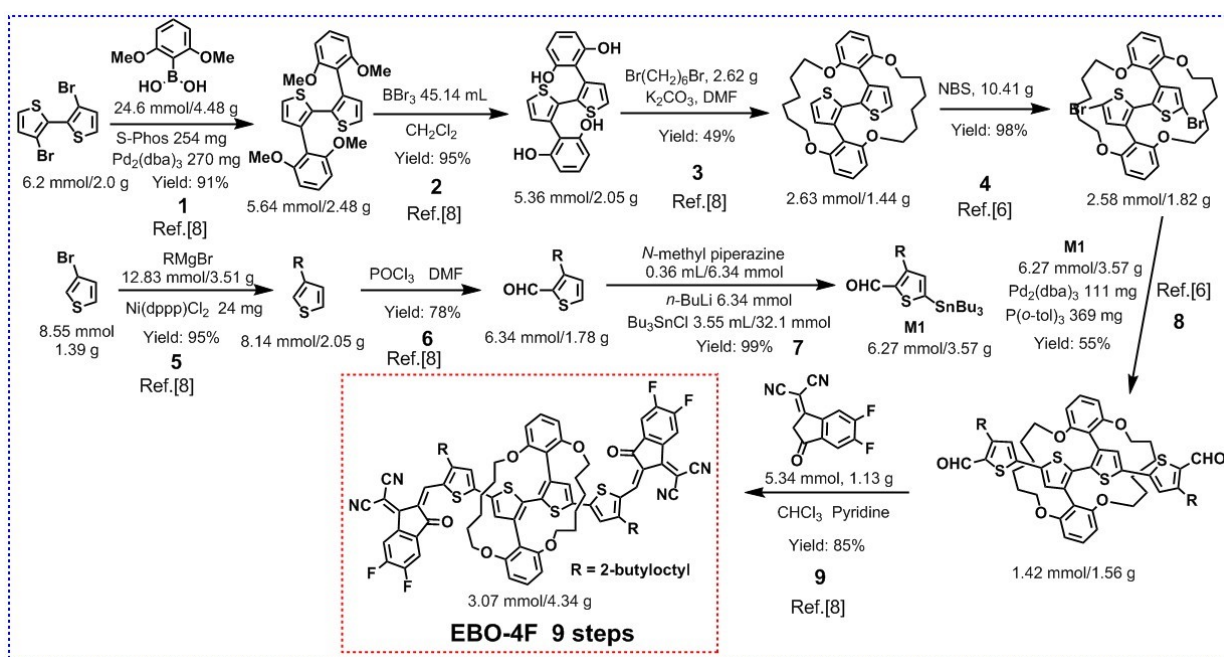
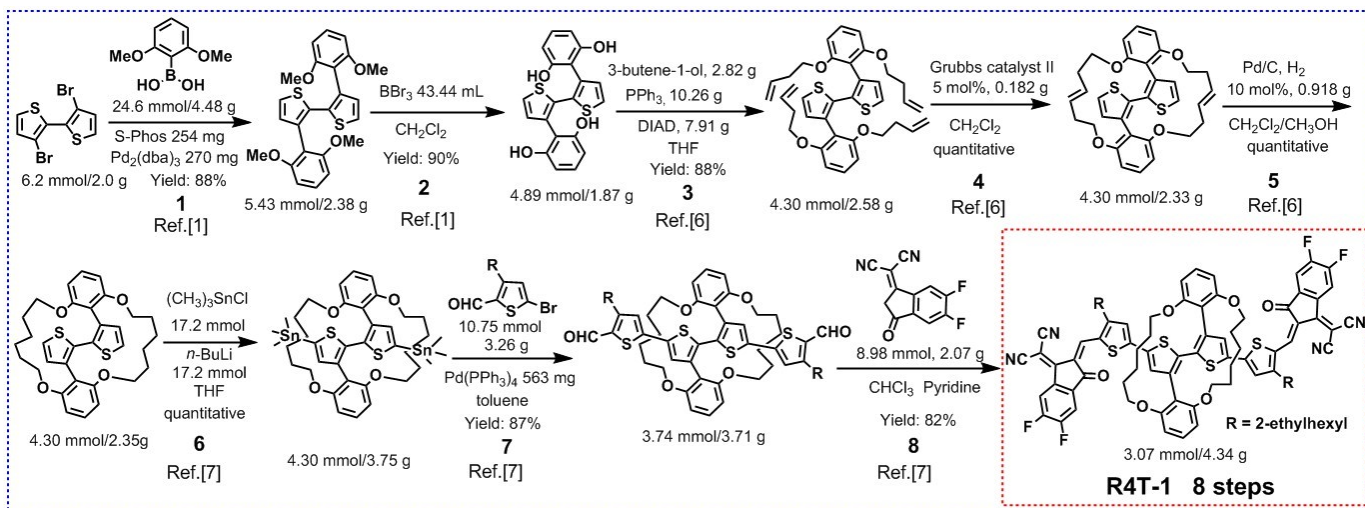
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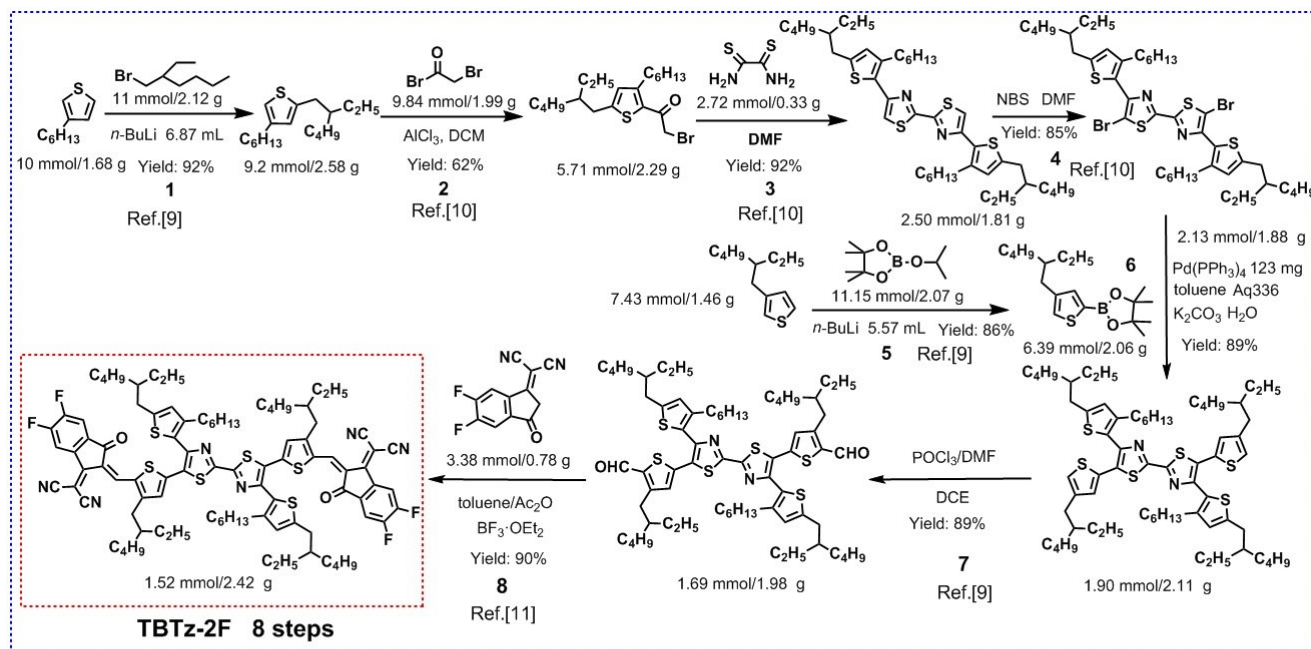
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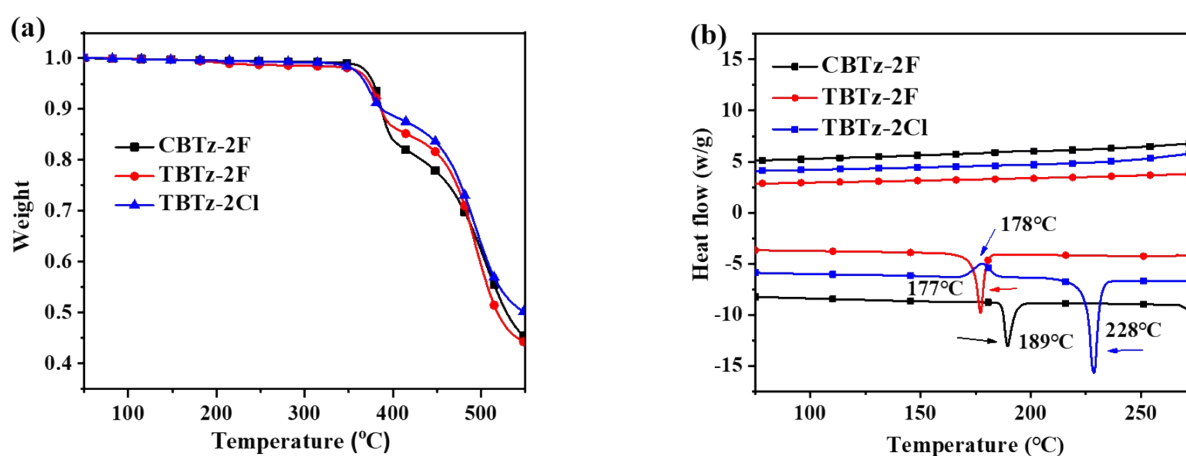


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195 **Fig. S1** The detailed synthetic route and the yield of each step of representative high-performance  
 196 tetrathiophene-based CNF-SMAs with different side chains and **TBTz-2F**. Note that the initial raw materials  
 197 here are defined as one can be bulkily purchased in hectograms or kilograms (excluding the common  
 198 organic and inorganic solvents). To ensure the accuracy of statistical data, each step of synthesis is referred  
 199 to designated references. The yield of each step is prioritized from the reference which provides synthetic  
 200 details of the related SMAs. Moreover, the references are preferred to the work that firstly reported the  
 201 corresponding CNF-SMAs. In addition, the quantity of reactants including catalyst in each steps is scaled up  
 202 or down according to the feed ratio in the corresponding references.

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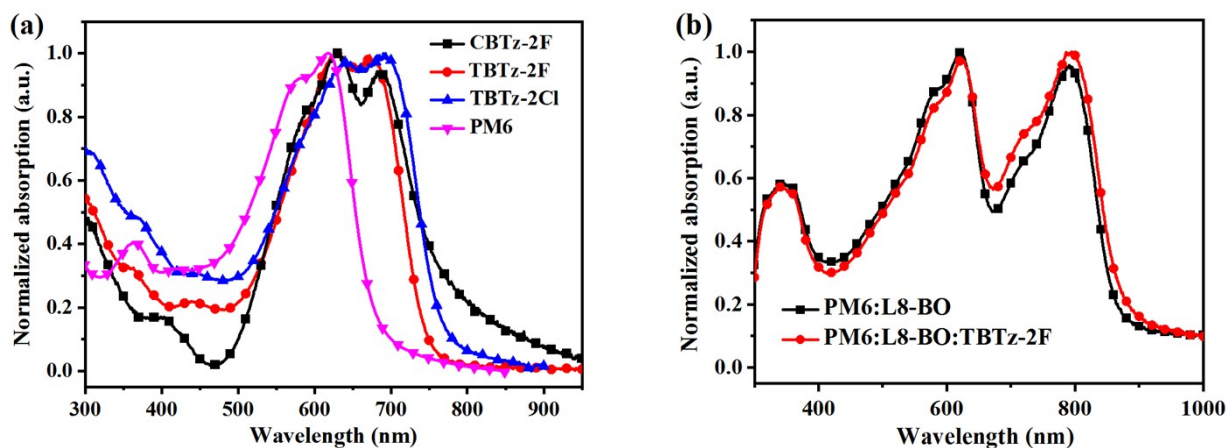
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**Fig. S2** (a) TGA and (b) DSC plots of **CBTz-2F**, **TBTz-2F**, and **TBTz-2Cl**.

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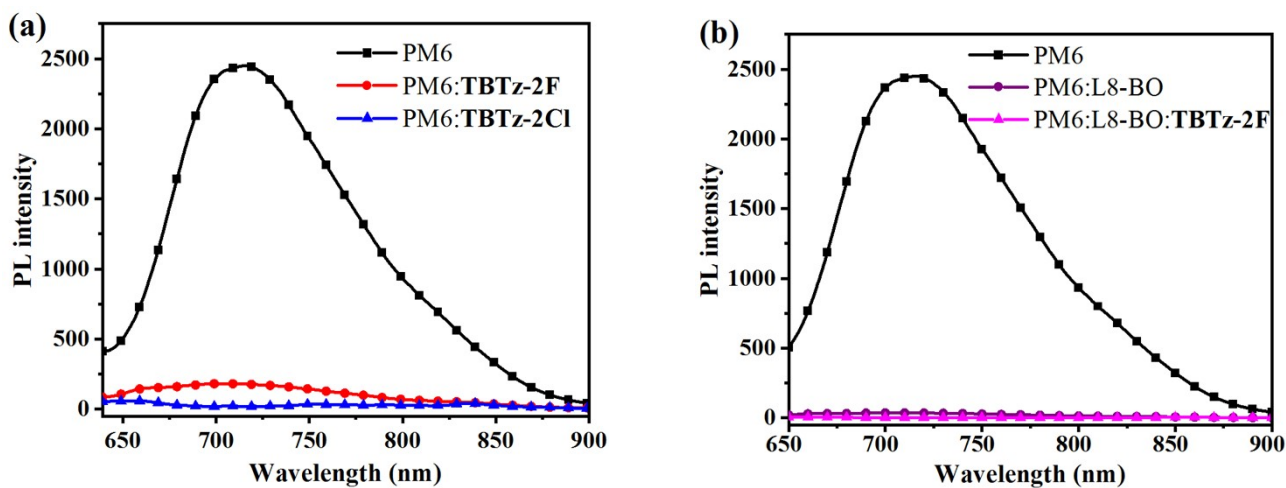
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211 **Fig. S3** Normalized UV-vis absorption spectra of (a) the pure thin film of CBTz-2F, TBTz-2F, TBTz-2Cl  
 212 and PM6; (b) the blend film of PM6:L8-BO and PM6:L8-BO:TBTz-2F.

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215 **Fig. S4** (a) PL spectra of the pure PM6 and PM6:SMA-based blend films; (b) PL spectra of the pure PM6  
 216 film and PM6:L8-BO, PM6:L8-BO:TBTz-2F-based blend films.

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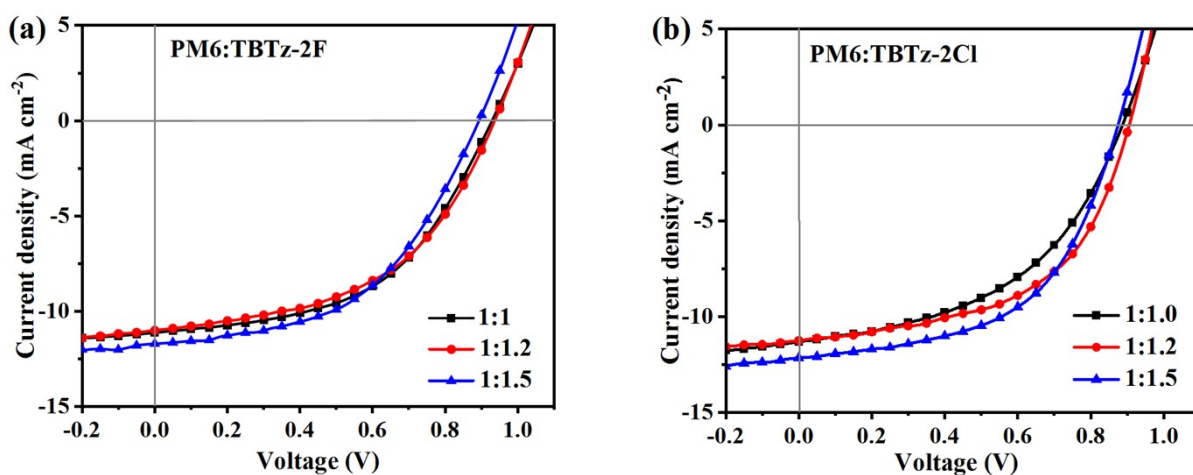
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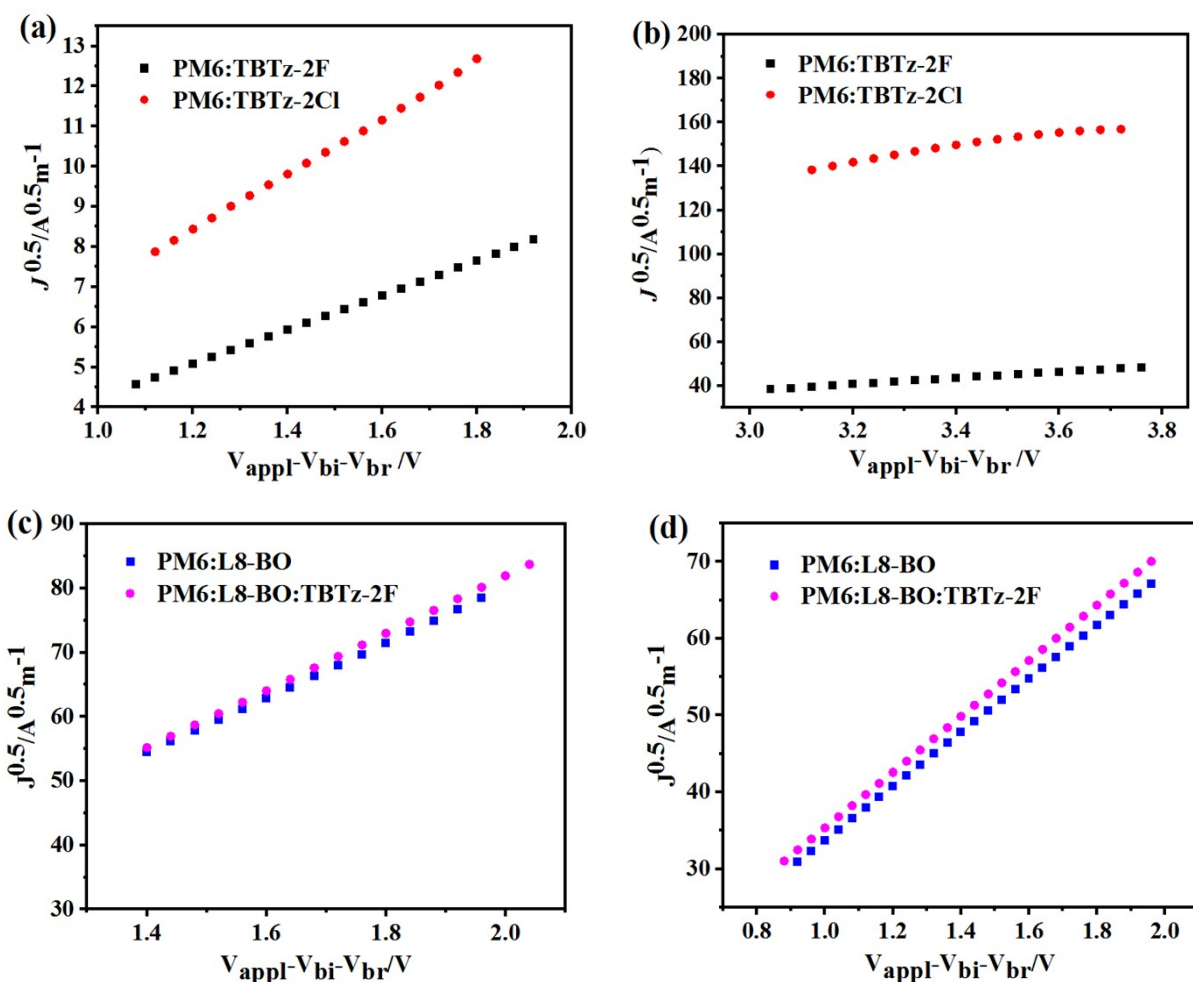


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228 **Fig. S5** The  $J$ - $V$  plots of (a) PM6:TBTz-2F and (b) PM6:TBTz-2Cl-based OSCs fabricated with different  
229 donor:acceptor ratios.

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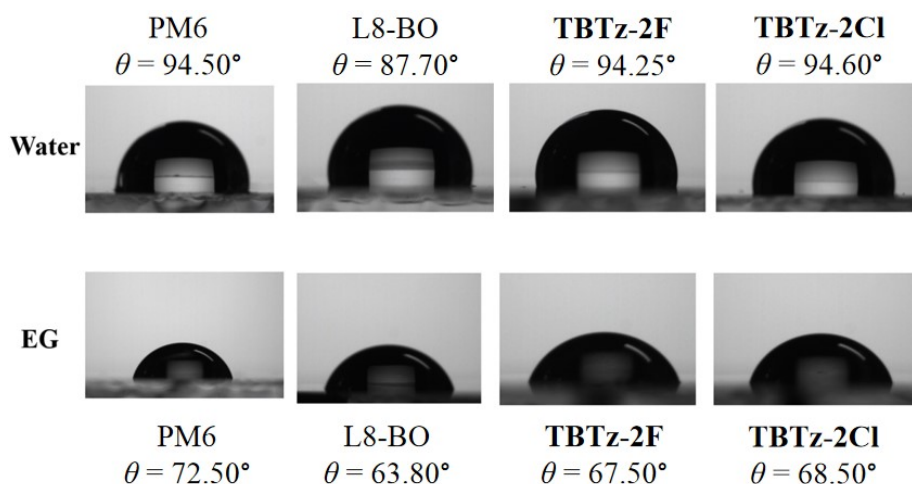
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234 **Fig. S6** The  $J^{0.5}$ - $V$  plots of the electron mobilities (a), (c) and hole mobilities (b), (d) of the binary and  
235 ternary devices by using SCLC method.

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**Fig. S7** Contact angle images and data of water and EG on the pure film of PM6 and three SMAs.

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**Table S1** The MOC evaluation of typically efficient 4T-based CFN-SMAs (PCE over 10%) and **TBTz-2F**.<sup>a</sup>

<b><i>o</i>-4TBC-2F</b>			
Reagent	Quantity	Unit (source) <sup>b,c</sup> (By Feb. 2026)	Cost (¥)
3,3'-dibromo-2,2'-bithiophene	2.0 g	1245 ¥/25 g (J&K)	99.6
2,6-bis(methoxy)phenylboronic acid	4.48 g	587 ¥/25 g (J&K)	105.2
S-Phos	254 mg	5096 ¥/10 g (J&K)	129.4
Pd <sub>2</sub> (dba) <sub>3</sub>	270 mg	1791 ¥/5 g (J&K)	96.7
BBr <sub>3</sub> (1 M)	43.44 mL	895 ¥/100 mL (TCI)	388.8
C <sub>6</sub> H <sub>13</sub> Br ( $\rho=1.176$ g/mL)	3.55 g	148 ¥/500 g (Macklin)	1.1
PPh <sub>3</sub>	6.59 g	300 ¥/500 g (Aladdin)	4.0
DIAD	4.35 g	218 ¥/500 g (J&K)	1.9
NBS	1.61 g	100 ¥/500 g (Macklin)	0.8
(5-formylthiophen-2-yl)boronic acid	13.61 g	1167 ¥/100 g (Aladdin)	158.8
Pd(PPh <sub>3</sub> ) <sub>4</sub>	134 mg	950 ¥/5 g (J&K)	5.1
5,6-difluoro-3-(dicyanomethylidene)indan-1-one	2.59 g	2500 ¥/5 g (Derthon Optoelectronic Mater. Sci. Tech. Co. Ltd)	1290
<b>Overall Cost</b>	1.90 g		2281.4 <b>(1200.7/g)</b> <b>(\$174.3/g)</b>
<b>A4T-16</b>			
Reagent	Quantity	Unit (source) <sup>b,c</sup> (By Feb. 2026)	Cost (¥)
3,3'-dibromo-2,2'-bithiophene	1.46 g	1245 ¥/25g (J&K)	72.7
2,4,6-trimethylbenzeneboronic acid	4.47 g	1327 ¥/25 g (J&K)	23.3

Pd(PPh <sub>3</sub> ) <sub>4</sub>	312+385 mg	950 ¥/5 g (J&K)	132.4
<i>n</i> -BuLi (1.6 M)	5.43 mL	560 ¥/500 mL (Macklin)	6.1
(CH <sub>3</sub> ) <sub>3</sub> SnCl (1 M)	9.45 mL	4940 ¥/800 mL (J&K)	58.4
5-bromo-4-(2-ethylhexyl)thiophene-2-carbaldehyde	2.92 g	4100 ¥/5 g (HWRK CHEM)	2394.4
5,6-difluoro-3-(dicyanomethylidene)indan-1-one	2.66 g	2500 ¥/5 g (Derthon Optoelectronic Mater. Sci. Tech. Co. Ltd)	1330
<b>Overall Cost</b>	3.33 g		4017.3 <b>(1206.4/g)</b> <b>(\$175.1/g)</b>

#### A4T-32

Reagent	Quantity	Unit (source) <sup>b,c</sup> (By Feb. 2026)	Cost (¥)
2-bromo-5-methoxy-1,3-dimethylbenzene	5 g	3402 ¥/500 g (Macklin)	34
2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane	6.06 g	488 ¥/500 g (Macklin)	5.9
<i>n</i> -BuLi (1.6 M)	17.4+15.9 mL	560 ¥/500 mL (Macklin)	37.3
3,3'-dibromo-2,2'-bithiophene	1.94 g	1245 ¥/25g (J&K)	96.6
Pd(PPh <sub>3</sub> ) <sub>4</sub>	550+800 mg	950 ¥/5 g (J&K)	256.5
BBr <sub>3</sub> (1 M)	49.8 mL	895 ¥/100 mL (TCI)	445.7
1-bromo-4-methoxybutane	8.51 g	1204 ¥/100 g (Macklin)	102.5
NBS	4.09 g	100 ¥/500 g (Macklin)	0.8
(CH <sub>3</sub> ) <sub>3</sub> SnCl (1 M)	39 mL	4940 ¥/800 mL (J&K)	240.8
5-bromo-4-(2-ethylhexyl)thiophene-2-carbaldehyde	10.6 g	4100 ¥/5 g (HWRK CHEM)	5692
5,6-difluoro-3-(dicyanomethylidene)indan-1-one	5.88 g	2500 ¥/5 g (Derthon Optoelectronic Mater. Sci. Tech. Co. Ltd)	2940
<b>Overall Cost</b>	7.44 g		9852.1 <b>(1324.2/g)</b> <b>(\$192.2/g)</b>

#### EBO-4F

Reagent	Quantity	Unit (source) <sup>b,c</sup> (By Feb. 2026)	Cost (¥)
3,3'-dibromo-2,2'-bithiophene	2.0 g	1245 ¥/25 g (J&K)	99.6
2,6-bis(methoxy)phenylboronic acid	4.48 g	587 ¥/25 g (J&K)	105.2
S-Phos	254 mg	5096 ¥/10 g (J&K)	129.4
Pd <sub>2</sub> (dba) <sub>3</sub>	270 + 111 mg	1791 ¥/5 g (J&K)	136.5
BBr <sub>3</sub> (1 M)	45.14 mL	895 ¥/100 mL (TCI)	404.0
1,6-dibromohexane	2.62 g	155 ¥/5 g (Macklin)	14.0
NBS	10.41 g	100 ¥/500 g (Macklin)	2.1
3-bromothiophene	1.39 g	847 ¥/500 g (Aladdin)	2.4
(2-ethylhexyl)magnesium bromide (1 M)	12.83 mmol	702 ¥/100 mL (J&K)	90.1
Ni(dppp)Cl <sub>2</sub>	24 mg	120 ¥/25 g (Aladdin)	0.1
N-methyl piperazine	0.36 mL	188 ¥/500 mL (Macklin)	0.1
<i>n</i> -BuLi (1.6 M)	6.34 mL	560 ¥/500 mL (Macklin)	7.1
(Bu) <sub>3</sub> SnCl (ρ = 1.2 g/mL)	3.55 mL	480 ¥/500 g (Macklin)	2.8
P( <i>o</i> -tol) <sub>3</sub>	369 mg	100 ¥/25 g (Aladdin)	1.5
5,6-difluoro-3-(dicyanomethylidene)indan-1-one	1.13 g	2500 ¥/5 g (Derthon Optoelectronic	565

		Mater. Sci. Tech. Co. Ltd)	
<b>Overall Cost</b>	4.34 g		1560 <b>(359.4/g)</b> <b>(\$226.5/g)</b>

#### R4T-1

Reagent	Quantity	Unit (source) <sup>b,c</sup> (By Feb. 2026)	Cost (¥)
3,3'-dibromo-2,2'-bithiophene	2.0 g	1245 ¥/25 g (J&K)	99.6
2,6-bis(methoxy)phenylboronic acid	4.48 g	587 ¥/25 g (J&K)	105.2
S-Phos	254 mg	5096 ¥/10 g (J&K)	129.4
Pd <sub>2</sub> (dba) <sub>3</sub>	270 mg	1791 ¥/5 g (J&K)	96.7
BBr <sub>3</sub> (1 M)	43.44 mL	895 ¥/100 mL (TCI)	388.8
3-butene-1-ol ( $\rho = 0.838$ g/mL)	2.82 g	579 ¥/100 mL (Macklin)	19.5
PPh <sub>3</sub>	10.26 g	300 ¥/500 g (Aladdin)	6.2
DIAD	7.91 g	218 ¥/500 g (J&K)	3.4
Grubbs catalyst II	0.182 g	1079 ¥/5 g (Macklin)	39.3
Pd/C catalyst	0.918 g	3900 ¥/50 g (J&K)	71.6
(CH <sub>3</sub> ) <sub>3</sub> SnCl (1 M)	17.2 mL	4940 ¥/800 mL (J&K)	106.2
<i>n</i> -BuLi (1.6 M)	17.2 mL	560 ¥/500 mL (Macklin)	19.2
Pd(PPh <sub>3</sub> ) <sub>4</sub>	563 mg	950 ¥/5 g (J&K)	107
5-bromo-4-(2-ethylhexyl)thiophene-2-carbaldehyde	4.06 g	4100 ¥/5 g (HWRK CHEM)	3329.2
5,6-difluoro-3-(dicyanomethylidene)indan-1-one	2.07 g	2500 ¥/5 g (Derthon Optoelectronic Mater. Sci. Tech. Co. Ltd)	1035
<b>Overall Cost</b>	4.34g		5556.4 <b>(1280.3/g)</b> <b>(\$185.9/g)</b>

#### 4TThC-ICF

Reagent	Quantity	Unit (source) <sup>b,c</sup> (By Feb. 2026)	Cost (¥)
3-hexylthiophene	1.68+1.25 g	1634 ¥/100 g (Aladdin)	47.9
2-ethylhexyl bromide	2.12 g	146 ¥/500 g (Macklin)	0.62
<i>n</i> -BuLi (1.6 M)	6.87+6.33+5.1mL	560 ¥/500 mL (Macklin)	20.5
2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane	2.57 g	488 ¥/500 g (Macklin)	2.5
3,3'-dibromo-2,2'-bithiophene	1.03 g	1245 ¥/25 g (J&K)	51.3
Pd(PPh <sub>3</sub> ) <sub>4</sub>	73 + 86 mg	950 ¥/5 g (J&K)	30.2
NBS	1.0 g	100 ¥/500 g (Macklin)	0.2
chlorotributyltin	4.09 g	480 ¥/500 g (Macklin)	3.9
5,6-difluoro-3-(dicyanomethylidene)indan-1-one	1.75 g	2500 ¥/5 g (Derthon Optoelectronic Mater. Sci. Tech. Co. Ltd)	875
<b>Overall Cost</b>	2.48 g		1031.6 <b>(416.0/g)</b> <b>(\$60.4/g)</b>

#### TBTz-2F

Reagent	Quantity	Unit (source) <sup>b,c</sup> (By Feb. 2026)	Cost (¥)
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3-hexylthiophene	1.68 g	1634 ¥/100 g (Aladdin)	27.5
2-ethylhexyl bromide	2.12 g	146 ¥/500 g (Macklin)	1.3
<i>n</i> -BuLi (1.6 M)	6.87+5.57 mL	560 ¥/500 mL (Macklin)	13.9
bromoacetyl bromide	1.99 g	260 ¥/500 g (Aladdin)	1.0
dithiooxamide	0.33 g	2088 ¥/25 g (Macklin)	27.6
2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane	2.07 g	488 ¥/500 g (Macklin)	2.0
3-(2-ethylhexyl)thiophene	1.46 g	2188 ¥/50 g (Macklin)	63.9
Pd(PPh <sub>3</sub> ) <sub>4</sub>	123 mg	950 ¥/5 g (J&K)	23.4
NBS	0.9 g	100 ¥/500 g (Macklin)	0.18
5,6-difluoro-3-(dicyanomethylidene)indan-1-one	0.78 g	2500 ¥/5 g (Derthon Optoelectronic Mater. Sci. Tech. Co. Ltd)	390
<b>Overall Cost</b>	2.42 g		550.8 <b>(227.6/g)</b> <b>(\$79.9/g)</b>

244 <sup>a</sup> Here, the reactants shown in **Fig. S1** are taken into account, excluding organic solvents, inorganic substances (acids,  
245 bases and salt), solvents for post-treatment, water, electricity, rent and labor costs.

246 <sup>b</sup> The prices were obtained from some famous vendors, including J&K, Aladdin, Macklin, Derthon Optoelectronic  
247 Mater. Sci. Tech. Co. Ltd et al.

248 <sup>c</sup> The maximum package scales of some raw materials, including 3,3'-dibromo-2,2'-bithiophene, 2,6-  
249 bis(methoxy)phenylboronic acid, (5-formylthiophen-2-yl)boronic acid, 2,4,6-trimethylbenzeneboronic acid, 5,6-  
250 difluoro-3-(dicyanomethylidene)indan-1-one, Pd(PPh<sub>3</sub>)<sub>4</sub>, Pd(OAc)<sub>2</sub>, Pd<sub>2</sub>(dba)<sub>3</sub>, Ni(dppp)Cl<sub>2</sub>, dithiooxamide, 5-bromo-  
251 4-(2-ethylhexyl)thiophene-2-carbaldehyde and 2-bromo-5-methoxy-1,3-dimethylbenzene are limited to 5 g or 25 g.  
252 Thus, their units are determined based on the maximum package scale.

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254 **Table S2** The PCE, synthesis steps, and MOC values of some efficient 4T-based CFN-SMAs and **TBTz-2F**  
255 in this work.

CFN-SMAs	PCE (%) <sup>a</sup>	Step <sub>b</sub>	MOC <sup>c</sup> (¥/g)	Refs.
<b><i>o</i>-4TBC-2F</b>	10.26	6	1200.7 (\$174.3)	[3]
<b>A4T-16</b>	15.2	4	1206.4 (\$175.1)	[4]
<b>A4T-32</b>	15.9	7	1324.2 (\$192.2)	[5]
<b>R4T-1</b>	15.1	8	1300.6 (\$188.8)	[6]
<b>EBO-4F</b>	18.04	9	359.4 (\$52.2)	[8]
<b>4TThC-ICF</b>	11.03	8	416.0 (\$60.4)	[9]
<b>TBTz-2F</b>	19.15 (ternary)	8	227.6 (\$33.0)	This work

256 <sup>a</sup> Paired polymer donors including PBDB-T, PM6, etc; <sup>b</sup> The synthesis routes of the acceptors are started with the rule  
257 that the raw materials are commercially available in hectograms or kilograms (excluding the catalysts); <sup>c</sup> MOC:  
258 material-only cost, which is the cost of the raw materials used for acceptor synthesis.

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262 **Table S3** Photovoltaic properties of the binary OSCs based on these BTz-based CNF-SMAs under different  
 263 fabricated conditions.<sup>a</sup>

Active layer	TA (°C)	Additive (vol %)	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
PM6:CBTz-2F	-	0.5% CN	0.596	1.01	27.6	0.17
PM6:CBTz-2F	100	0.5% CN	0.761	1.54	29.3	0.34
PM6:TBTz-2F	-	-	0.933	10.11	46.2	4.36
PM6:TBTz-2F	100	-	0.934	10.31	47.6	4.59
PM6:TBTz-2F	100	0.5% CN	0.932	9.78	47.2	4.31
PM6:TBTz-2F	100	0.5% 2-MN	0.948	10.33	50.7	4.97
PM6:TBTz-2Cl	-	-	0.915	9.39	44.0	3.78
PM6:TBTz-2Cl	100	-	0.894	10.72	48.3	4.63
PM6:TBTz-2Cl	100	0.5% 2-MN	0.896	9.40	40.4	3.40
PM6:TBTz-2Cl		0.5% CN	0.911	11.21	54.5	5.57
PM6:TBTz-2Cl	100	0.5% CN	0.908	11.51	55.1	5.76

264 <sup>a</sup> The devices were prepared with the donor:SMA blend ratio of 1:1 (by weight).

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267 **Table S4** Photovoltaic properties of PM6:TBTz-2F and PM6:TBTz-2Cl-based OSCs with various  
 268 donor:acceptor ratios.<sup>a</sup>

Active layer	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
PM6:TBTz-2F = 1:1.0	0.929	11.13	50.7	5.25
PM6:TBTz-2F = 1:1.2	0.936	11.01	49.5	5.10
PM6:TBTz-2F = 1:1.5	0.893	11.71	49.6	5.19
PM6:TBTz-2Cl = 1:1.0	0.908	11.51	55.1	5.76
PM6:TBTz-2Cl = 1:1.2	0.906	11.25	53.2	5.42
PM6:TBTz-2Cl = 1:1.5	0.875	12.15	53.9	5.73

277 <sup>a</sup> The devices were prepared with TA treatment at 100 °C for 10 min and 0.5 vol% 2-MN and 0.5 vol% CN  
 278 as the additive for TBTz-2F and TBTz-2Cl, respectively.

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282 **Table S5** Photovoltaic properties of **TBTz-2F**- and **TBTz-2Cl**-based ternary OSCs with various feed ratios.<sup>a</sup>

Active layer	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
PM6:L8-BO: <b>TBTz-2F</b> =1:1.2:0	0.885	26.96	77.6	18.52
PM6:L8-BO: <b>TBTz-2F</b> =1:1.2:0.05	0.888	27.68	77.9	19.15
PM6:L8-BO: <b>TBTz-2F</b> =1:1.2:0.1	0.879	13.92	76.3	18.45
PM6:L8-BO: <b>TBTz-2Cl</b> =1:1.2:0.05	0.894	26.73	73.1	17.47
PM6:L8-BO: <b>TBTz-2Cl</b> =1:1.2:0.1	0.891	27.21	68.7	16.88

283 <sup>a</sup> The devices were prepared with TA treatment at 100 °C for 10 min and 0.25 vol% DIO as the additive.

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285 **Table S6** Summary of contact angles ( $\theta$ ), surface energies ( $\gamma$ ) and Flory-Huggins interaction parameters ( $\chi$ ).

Material	$\theta_{Water}$ (°)	$\theta_{EG}$ (°)	$\gamma$ (mJ cm <sup>-2</sup> )	$\chi_{PM6:B}$ ( <i>k</i> )	$\chi_{L8-BO:B}$ ( <i>k</i> )
PM6	94.50	72.50	22.64	-	-
L8-BO	87.70	63.80	26.29	0.136	-
<b>TBTz-2F</b>	94.25	67.50	27.19	0.208	0.0076
<b>TBTz-2Cl</b>	94.60	68.50	26.21	0.131	-

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288 **Table S7** GIWAXS parameters, including the positions,  $d$ -spacing ( $d_{\pi-\pi}$  and  $d_1$ ), FWHM, and CCL of the  
289 (010) and (100) peaks of the binary and ternary blend films.

Blend films	Out-Of-plane (OOP)				In-plane (IP)			
	$\pi$ - $\pi$ stacking cell long axis (010)				Unit cell long axis (100)			
	$q_z$ [Å <sup>-1</sup> ]	$d_{\pi-\pi}$ [Å]	FWHM [Å <sup>-1</sup> ]	CCL [Å]	$q_{xy}$ [Å <sup>-1</sup> ]	$d_1$ [Å]	FWHM [Å <sup>-1</sup> ]	CCL [Å]
PM6: <b>TBTz-2F</b>	1.719	3.655	0.255	24.65	0.303	20.77	0.062	100.98
PM6: <b>TBTz-2Cl</b>	1.705	3.685	0.253	24.83	0.294	21.37	0.073	85.81
PM6:L8-BO	1.721	3.652	0.334	18.32	0.297	21.13	0.130	48.22
PM6:L8-BO: <b>TBTz-2F</b>	1.681	3.738	0.218	28.86	0.287	21.89	0.096	65.72

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