

## Electronic Supplementary Information

### Mapping Polymer Donors with a Non-fused Acceptor Possessing

### Outward Branched Alkyl Chains for Efficient Organic Solar Cells

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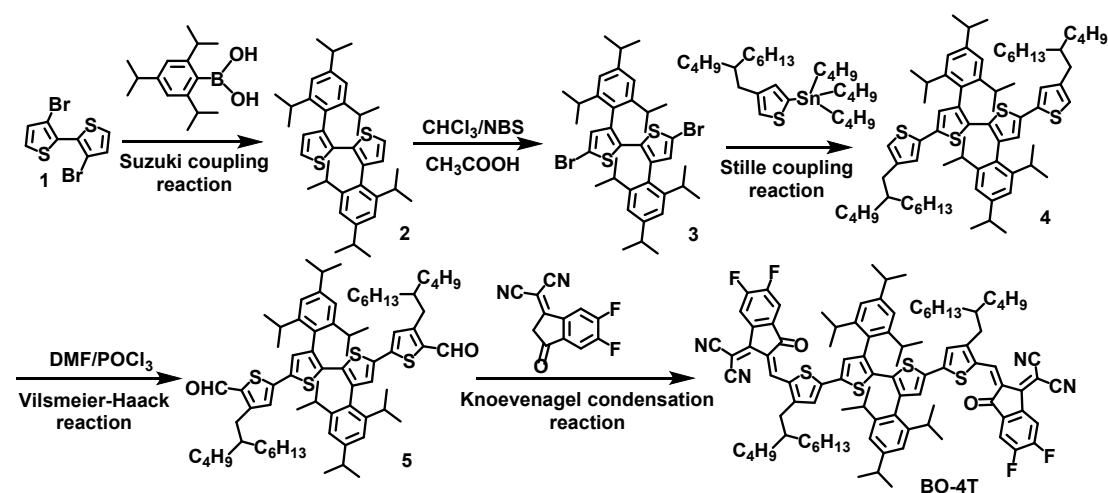
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# 1. Materials and methods

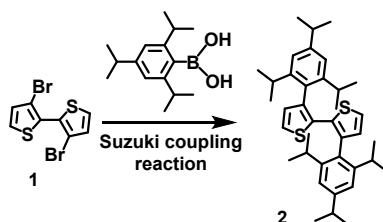
## Materials

All reagents and solvents, unless otherwise specified, were purchased from commercial sources and were used without further purification. **D18**, **PM6**, **PBDB-T**, **J52** and **PDINN** were purchased from Solarmer Material Inc.

## Synthesis of BO-4T

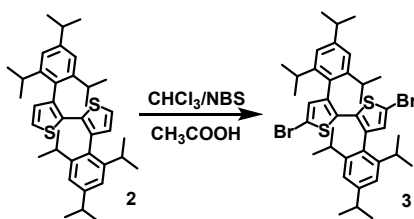


Scheme S1 Synthetic route for BO-4T.



3,3'-bis(2,4,6-triisopropylphenyl)-2,2'-bithiophene (Compound 2)

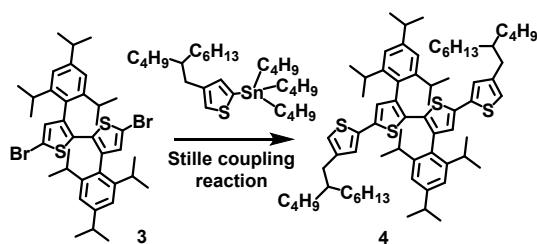
3,3'-dibromo-2,2'-bithiophene (2.52 g, 7.78 mmol), (2,4,6-triisopropylphenyl)boronic acid (7.72 g, 31.1 mmol) and K<sub>2</sub>CO<sub>3</sub> (6.09 g, 54.3 mmol) were dissolved into the solution of tBuOH (38 mL) and dimethoxyethane (95 mL), then the mixture was frozen by liquid nitrogen, after vacuum and Ar circulated for three times. Pd(PPh<sub>3</sub>)<sub>4</sub> (0.539 g, 0.47 mmol) was added in, followed by another three times of the former circulation. The mixture was refluxed at 90 °C for 96 h. Using water to wash the crude product and dichloromethane to obtain the organic phase. After removing the solvent, silica gel column chromatography was used to purify the product with petroleum ether as the eluent, yielding a white solid of compound **2** (3.67 g, 83%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ): 7.09 (s, 4H), 7.00 (d, *J* = 4.1 Hz, 2H), 6.70 (d, *J* = 4.1 Hz, 2H), 3.05-2.94 (m, 2H), 2.68-2.58 (m, 4H), 1.35 (d, *J* = 5.5 Hz, 12H), 1.08 (dd, *J* = 5.5, 9.4 Hz, 24H).



5,5'-dibromo-3,3'-bis(2,4,6-triisopropylphenyl)-2,2'-bithiophene (Compound **3**)

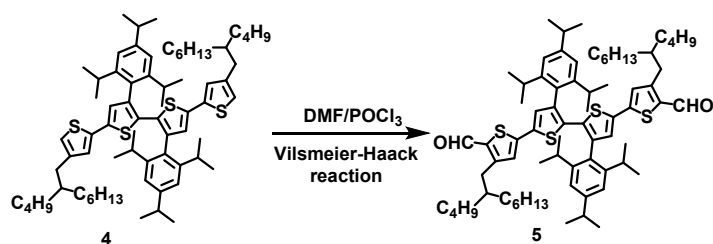
Compound **2** (300 mg, 0.53 mmol) was dissolved into the solution of chloroform (20 mL) and acetic acid (2 mL), then N-bromosuccinimide (234 mg, 1.31 mmol) was added in batches under stirring. After stirring at room temperature for 2 h, silica gel column chromatography was used to purify the product with petroleum ether as the eluent, yielding a yellow solid of compound **3** (355 mg, 92%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ):

7.10 (s, 4H), 6.64 (s, 2H), 3.03-2.95 (m, 2H), 2.65-2.55 (m, 4H), 1.35 (d,  $J = 5.5$  Hz, 12H), 1.10 (dd,  $J = 5.5, 13.2$  Hz, 24H).



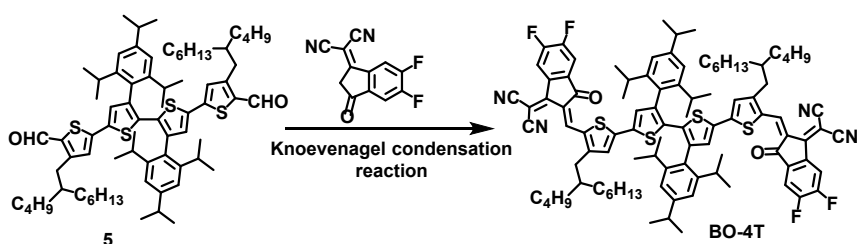
4,4'''-bis(2-butyl-octyl)-3''',4'-bis(2,4,6-triisopropylphenyl)-2,2':5',2'':5'',2'''-  
quaterthiophene (Compound 4)

Compound **3** (300 mg, 0.41 mmol) and tributyl(4-(2-butyl-octyl)thiophen-2-yl)stannane (490 mg, 0.91 mmol) were dissolved into the solution of Toluene (30 mL) and N, N-dimethylformamide (DMF, 3 mL), then the mixture was frozen by liquid nitrogen, after vacuum and Ar circulated for three times, Pd(PPh<sub>3</sub>)<sub>4</sub> (23.7 mg, 0.02 mmol) was added in, followed by another three times of the former circulation. The mixture was refluxed at 110 °C for 12 h. After cooling to room temperature (r.t.), silica gel column chromatography was used to purify the product with the mixture of petroleum ether and dichloromethane (1:1, v/v) as the eluent, yielding an orange solid of compound **4** (360 mg, 82%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ): 7.14 (s, 4H), 6.81 (s, 2H), 6.67 (s, 2H), 6.64 (s, 2H), 3.05-2.98 (m, 2H), 2.75-2.68 (m, 4H), 2.44-2.41 (m, 4H), 1.38 (d,  $J = 5.5$  Hz, 14H), 1.29-1.24 (m, 26H), 1.15-1.04 (m, 28H), 0.91-0.85 (m, 14H).



4,4'''-bis(2-butyl-1-octyl)-3'',4'-bis(2,4,6-triisopropylphenyl)-[2,2':5',2'':5'',2'''-quaterthiophene]-5,5'''-dicarbaldehyde (Compound **5**)

To a Schlenk tube under Ar atmosphere at 0 °C, 1 mL DMF and 0.8 mL POCl<sub>3</sub> were injected successively. After being stirred for 0.5 h at 0 °C, compound **4** (200 mg, 0.19 mmol) was added into the reaction system through 1,2-dichloroethane (10 mL) as the solvent. The mixture was refluxed at 80 °C for 10 h. After cooling to r.t., the mixture was extracted with a syringe and injected into a NaHCO<sub>3</sub> aqueous solution dropwise, then stirred for another 8 h. Using water to wash the crude product and dichloromethane to obtain the organic phase. After removing the solvent, silica gel column chromatography was used to purify the product with the mixture of petroleum ether and dichloromethane (1:1, v/v) as the eluent, yielding an orange solid of compound **5** (182 mg, 85%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ): 9.91 (s, 2H), 7.17 (s, 4H), 7.03 (s, 2H), 6.68 (s, 2H), 3.07-3.00 (m, 2H), 2.76 (d, *J* = 5.72 Hz, 4H), 2.67-2.60 (m, 4H), 1.41-1.36 (m, 14H), 1.30-1.25 (m, 28H), 1.13-1.05 (m, 26H), 0.91-0.84 (m, 14H).



2,2'-((2Z,2'Z)-((4,4''-bis(2-butyloctyl)-3'',4'-bis(2,4,6-triisopropylphenyl)-[2,2':5',2'':5'',2''-quaterthiophene]-5,5''-diyl)bis(methaneylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (**BO-4T**)

To a Schlenk tube were added compound **5** (60 mg, 0.053 mmol), 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (30 mg, 0.24 mmol) and CHCl<sub>3</sub> (30 mL). Then 0.5 mL pyridine was added drop by drop. The mixture was refluxed at 70 °C for 24 h. After cooling to r.t., silica gel column chromatography was used to purify the product with the mixture of petroleum ether and dichloromethane (1:2, v/v) as the eluent, yielding a black solid of compound **BO-4T** (76.5 mg, 93%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ): 8.90 (s, 2H), 8.57-8.49 (m, 2H), 7.66-7.59 (m, 2H), 7.32 (s, 2H), 7.22 (s, 4H), 6.84 (s, 2H), 3.13-3.03 (m, 2H), 2.86-2.78 (m, 4H), 2.69-2.56 (m, 4H), 1.46-1.39 (m, 12H), 1.35-1.18 (m, 34H), 1.15-1.09 (m, 24H), 0.91-0.84 (m, 12H).

<sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) (ppm): δ 185.74, 162.12, 151.48, 151.23, 147.66, 140.97, 136.02, 135.01, 134.66, 134.54, 132.06, 129.90, 129.47, 126.93, 121.97, 119.98, 114.89, 114.53, 105.26, 68.80, 40.49, 37.11, 34.88, 34.77, 33.04, 32.69, 31.84, 30.92, 29.63, 28.56, 26.39, 25.10, 24.54, 23.38, 23.01, 22.67, 14.12.

MS (MALDI-TOF): Calcd for C<sub>96</sub>H<sub>106</sub>F<sub>4</sub>N<sub>4</sub>O<sub>2</sub>S<sub>4</sub> (M<sup>+</sup>): 1552.16, Found: 1551.66.

### **<sup>1</sup>H NMR spectra and MALDI-TOF MS spectra**

<sup>1</sup>H NMR spectra were obtained on a Bruker Avance III 500 (500 MHz) nuclear magnetic resonance (NMR) spectroscope. MALDI-TOF MS spectra were measured on the Bruker Ultraflex MALDI.

## Cyclic Voltammetry and UV-vis Absorption Tests

Cyclic voltammetry (CV) was done on a CHI600A electrochemical workstation by utilizing the acetonitrile solution of 0.1 mol/L tetrabutylammoniumhexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ). The CV curves were recorded versus the potential of SCE, which was calibrated by the ferrocene-ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) redox couple (4.8 eV below the vacuum level). Then LUMO and HOMO levels were calculated by the equation of  $E_{\text{LUMO/HOMO}} = -e (E_{\text{red/ox}} + 4.41)$  (eV). UV-vis absorption spectra were measured on a Shimadzu UV-1800 spectrophotometer.

## Device Fabrication

Organic solar cells (OSCs) were fabricated on glass substrates commercially pre-coated with a layer of indium tin oxide (ITO), constructing the inverted structure of ITO/PEDOT:PSS/Active Layer/PDINN/Ag. Before fabrication, the substrates were pre-cleaned in an ultrasonic bath of detergent, deionized water, acetone and isopropanol consecutively, and then treated in an ultraviolet ozone generator for 15 min. After that, a thin layer PEDOT:PSS (Baytron P AI4083) was spin coated onto the substrates at 4500 rpm (~20 nm thick) for 30 s and annealed at 150 °C for 20 min. The substrates were put into glovebox. All of the active layers were spin coated from chloroform solution and the detailed fabrication conditions were summarized in **Table S1**. After that, the PDINN film was deposited as the cathode buffer layer by the spin-coating of a solution of 1.0 mg/mL PDINN in methanol with 3500 rpm. Finally, the Ag (120 nm)

electrode was deposited by thermal evaporation, and the devices were completed with an active area of 0.06 cm<sup>2</sup>.

### ***J-V* and EQE Measurement**

The current density-voltage (*J-V*) curves of OSCs were performed on a Enlitech SS-X50 solar simulator under the condition of AM 1.5 G illumination, whose light intensity was calibrated by a standard Si solar cell at 100 mW cm<sup>-2</sup>. The EQE data were measured by a Solar Cell Spectral Response Measurement System (RE-R, Enlitech). All of the devices mentioned were tested by a shadow mask with an area of 0.0473 cm<sup>2</sup>.

### **SCLC Measurement**

The charge carrier mobilities of the Donor:Acceptor films were measured using the space charge limited current (SCLC) method. Electron-only devices were fabricated in a structure of ITO/ZnO/Active Layer/PDINN/Ag whereas Hole-only devices utilizing the structure of ITO/PEDOT:PSS/Active Layer/MoO<sub>3</sub>/Ag. The device characteristics were extracted by modeling the dark current under forward bias the SCLC expression described by the Mott-Gurney Law:

$$J = \frac{9}{8} \epsilon_r \epsilon_0 \mu \frac{V^2}{L^3} \quad (1)$$

Here,  $\epsilon_r \approx 3.5$  is the average dielectric constant of the blend film,  $\epsilon_0$  is the permittivity of the free space,  $\mu$  is the carrier mobility,  $L$  is the thickness of the film, and  $V$  is the applied voltage.



### **GIWAXS Characterization**

GIWAXS measurements were conducted at a Xeuss 3.0 SAXS/WAXS laboratory beamline at Vacuum Interconnected Nanotech Workstation (Nano-X) in China with  $K\alpha$  X-ray of Cu source (operated at 50kV, 0.06 mA, 1.542 Å). GIWAXS patterns were recorded by a two dimensional X-ray detector (Eiger2 R 1M, Dectris). The incident angle was set to 0.18 degree.

### **AFM measurement**

AFM images were obtained on a VeecoMultiMode atomic force microscopy in the tapping mode.

## 2. Supporting figures

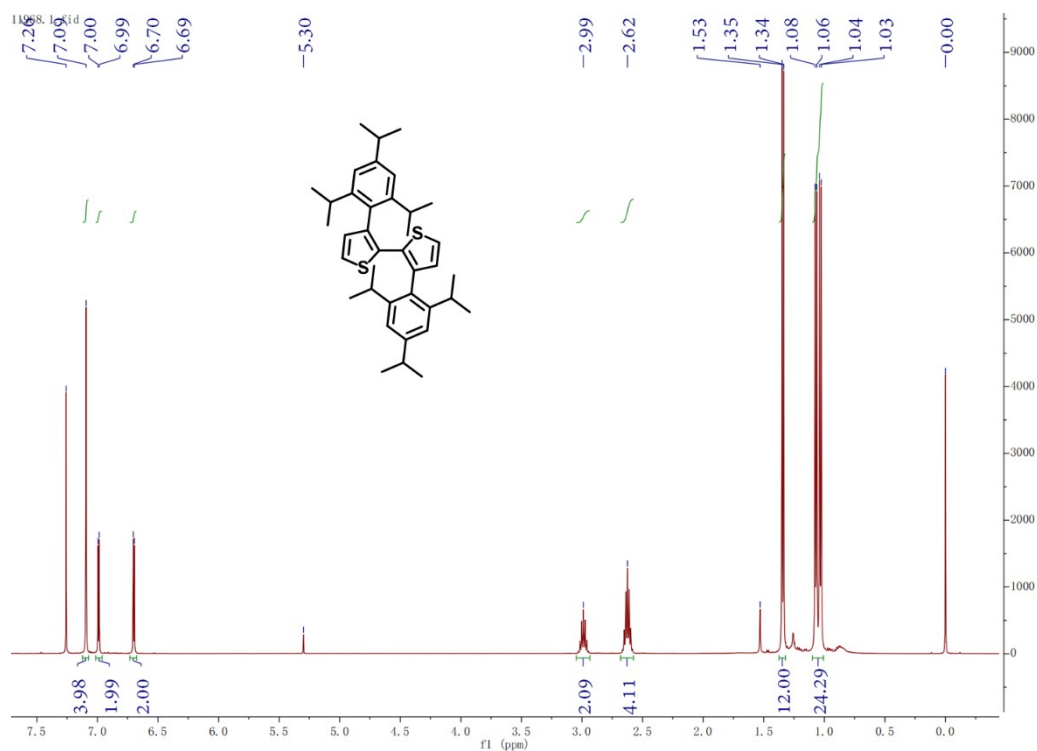


Fig. S1 <sup>1</sup>H NMR spectrum of compound 2.

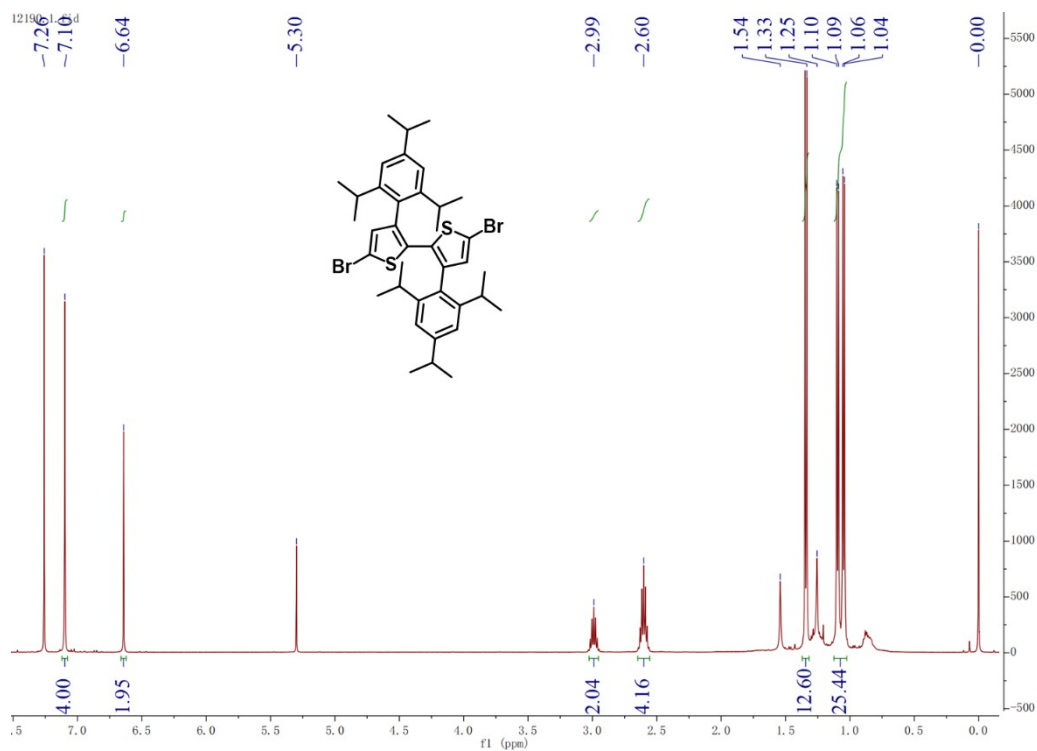
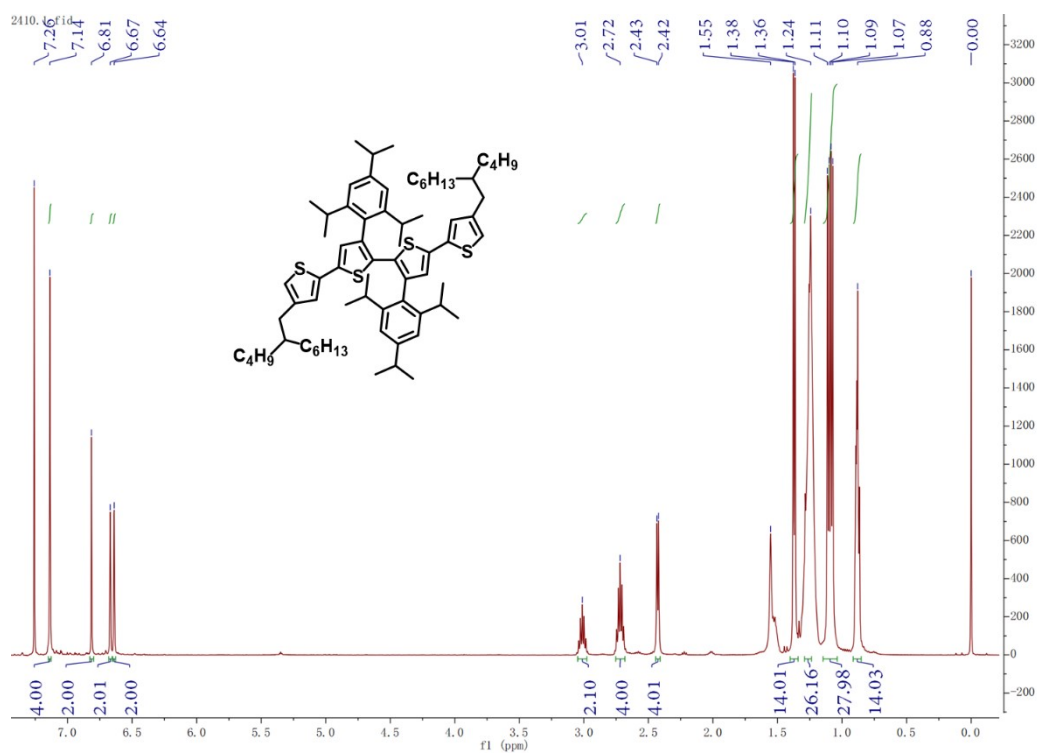
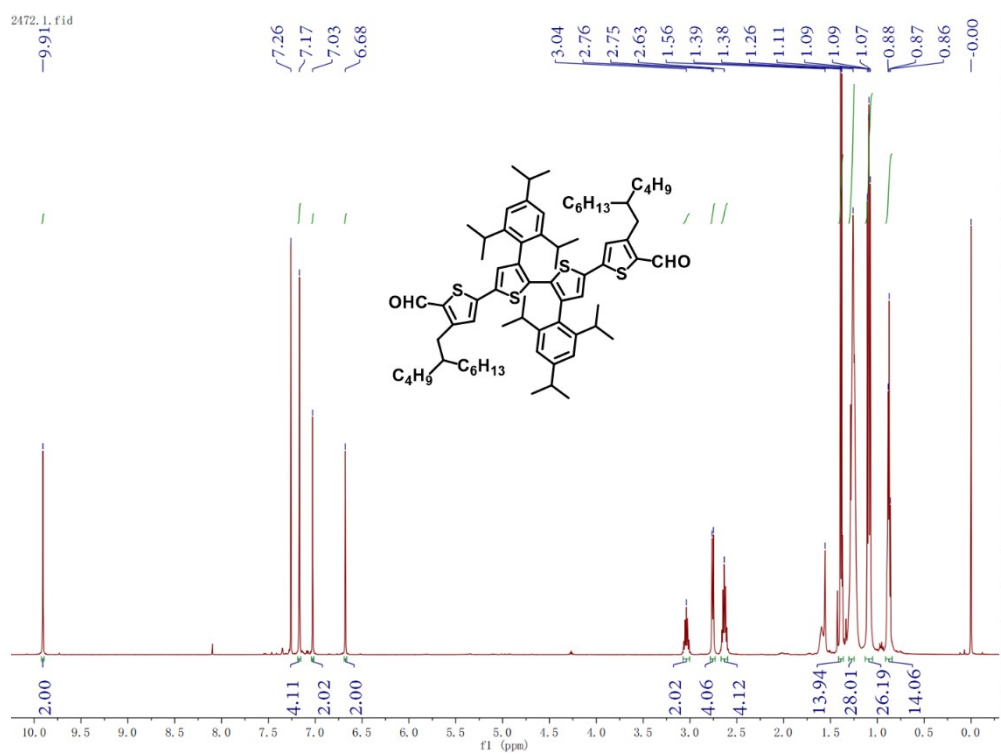


Fig. S2 <sup>1</sup>H NMR spectrum of compound 3.



**Fig. S3** <sup>1</sup>H NMR spectrum of compound 4.



**Fig. S4** <sup>1</sup>H NMR spectrum of compound 5.

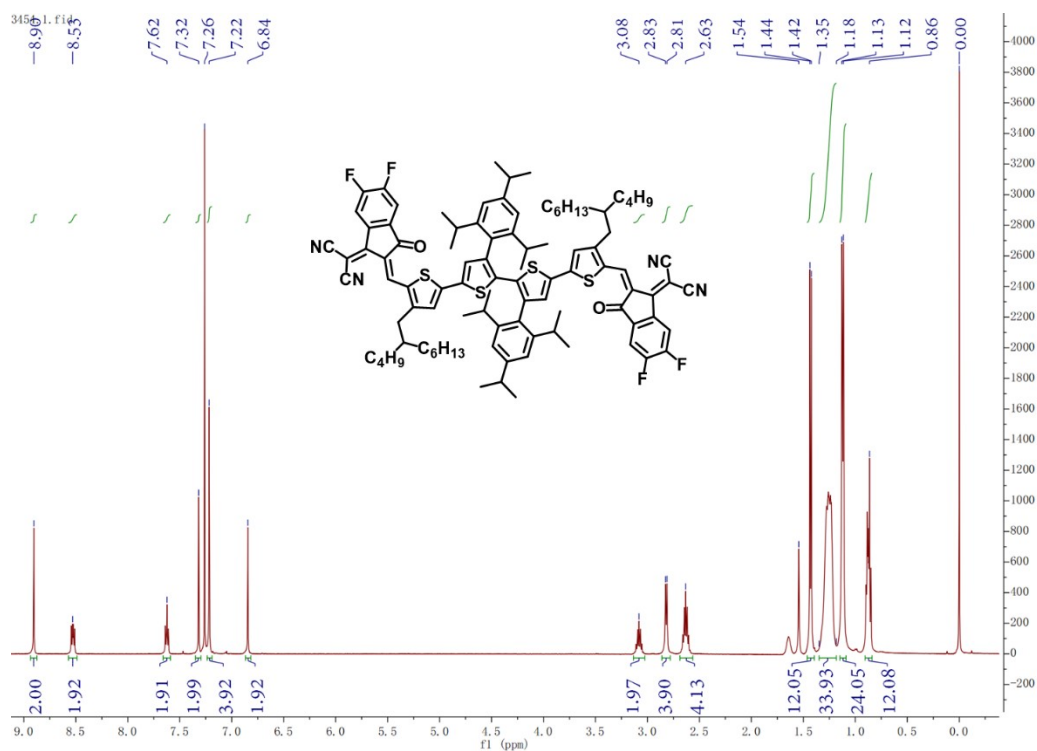


Fig. S5 <sup>1</sup>H NMR spectrum of compound BO-4T.

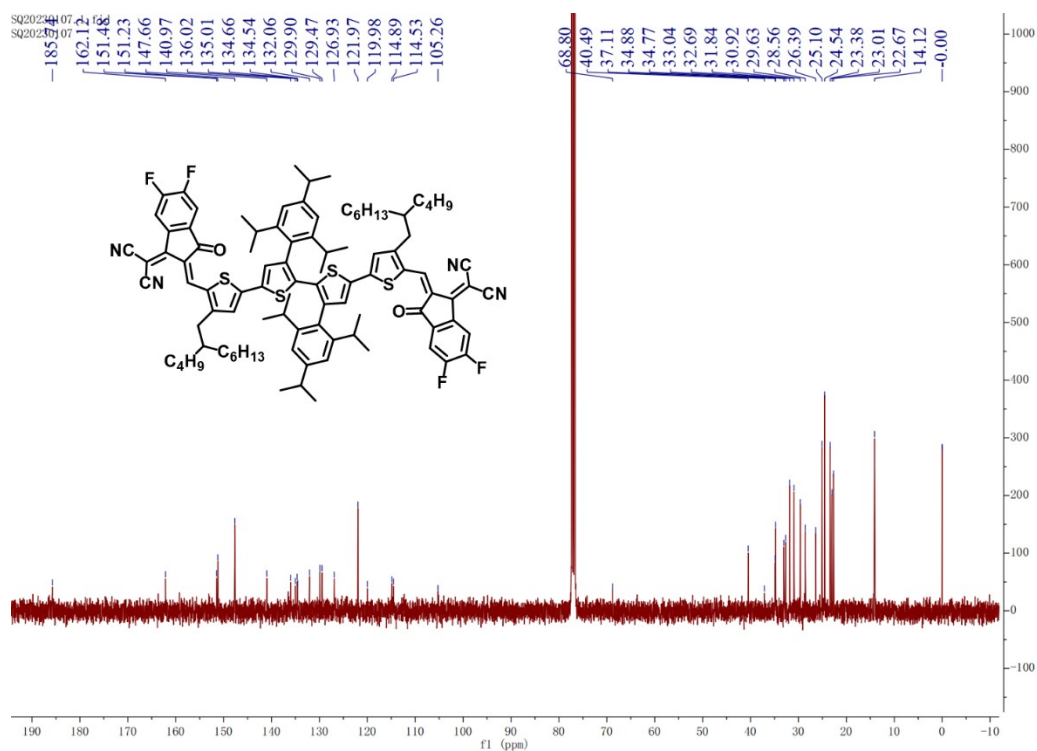
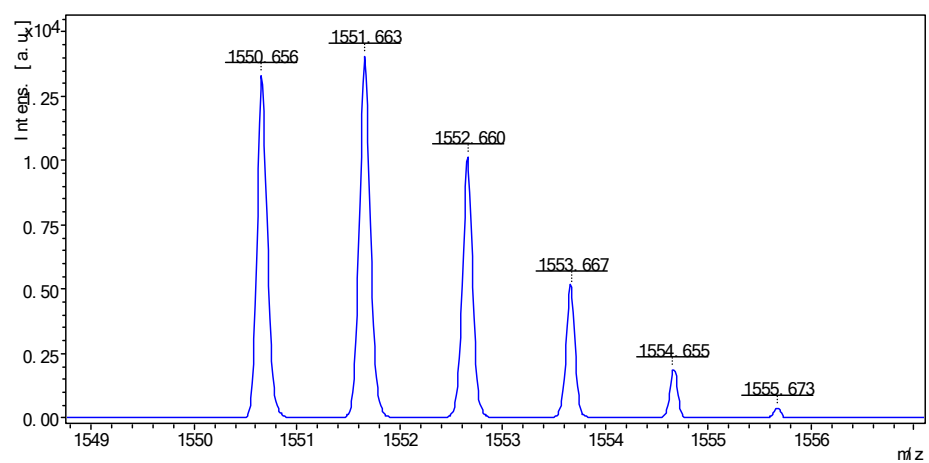
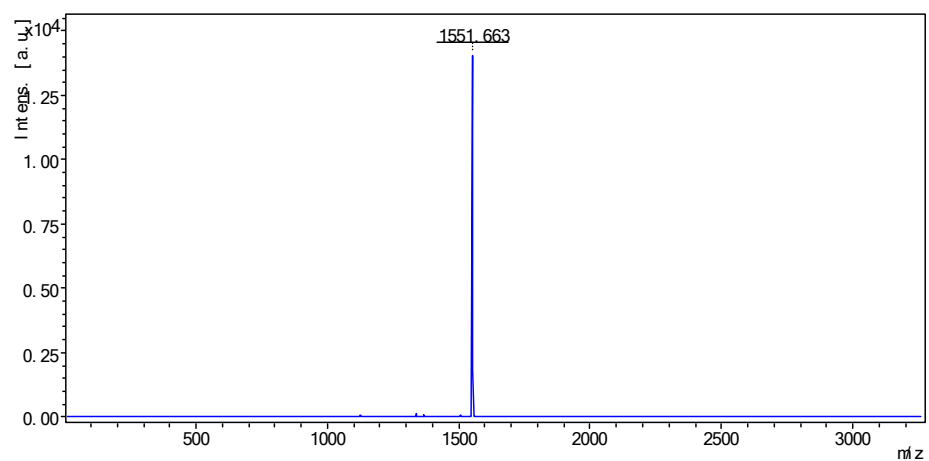
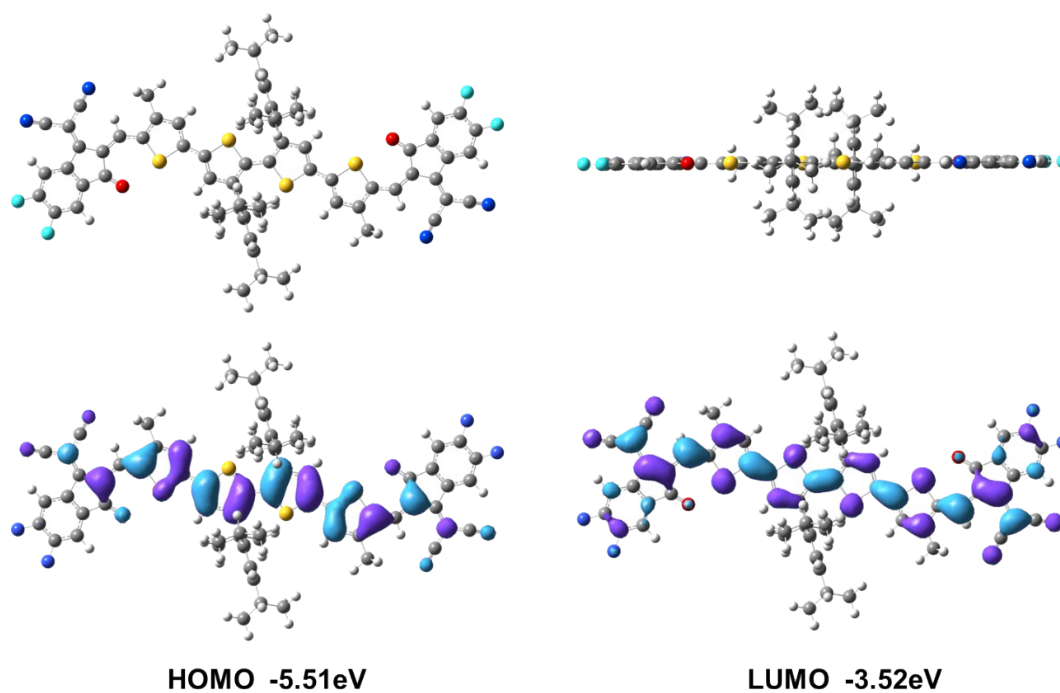


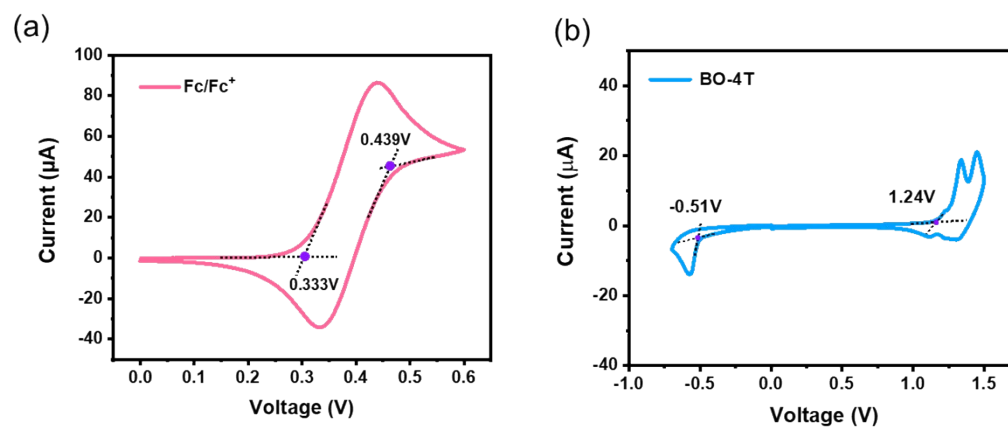
Fig. S6 <sup>13</sup>C NMR spectrum of compound BO-4T.



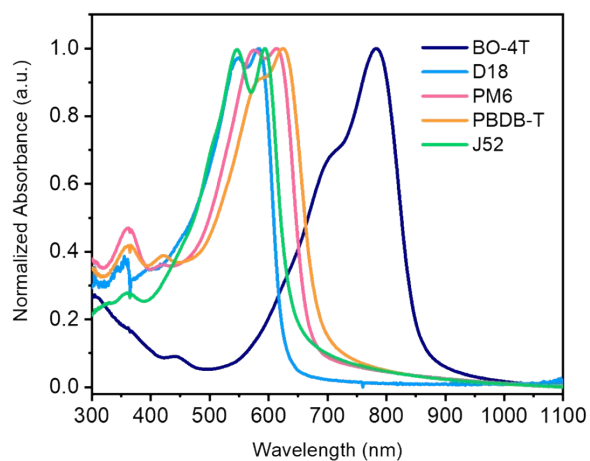
**Fig. S7** The high-resolution mass spectra of BO-4T.



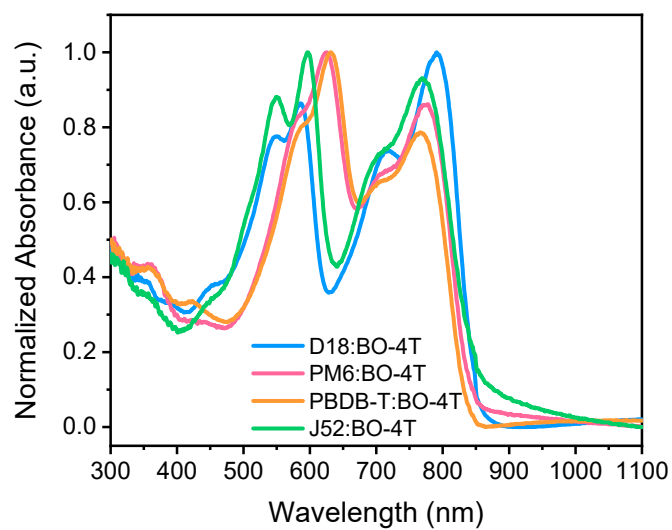
**Fig. S8** Simulated molecular geometries and frontier molecular orbitals by DFT calculation for BO-4T.



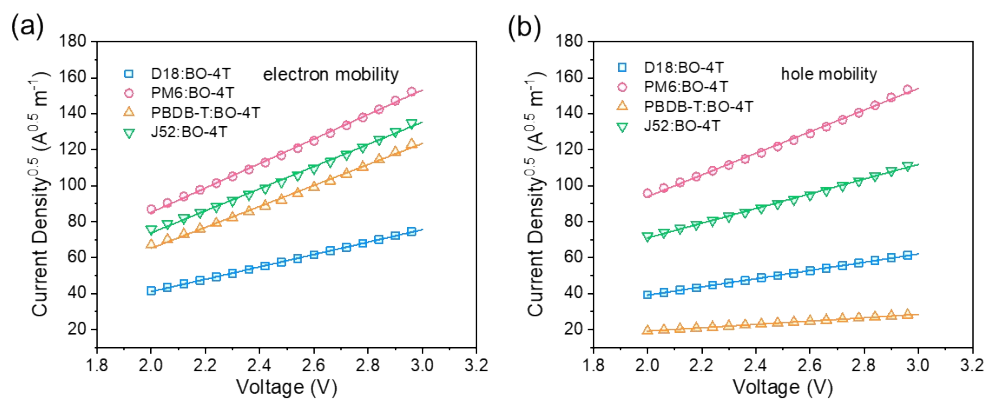
**Fig. S9** Cyclic voltammograms of (a) Fc/Fc<sup>+</sup> and (b) BO-4T.



**Fig. S10** UV-vis absorption spectrum of the pristine films.



**Fig. S11** UV-vis absorption spectrum of the blend films.



**Fig. S12** (a)  $J^{0.5}$ - $V$  curves of the electron-only devices based on D18:BO-4T, PM6:BO-4T, PBDB-T:BO-4T and J52:BO-4T blend films. (b)  $J^{0.5}$ - $V$  curves of the hole-only devices based on D18:BO-4T, PM6:BO-4T, PBDB-T:BO-4T and J52:BO-4T blend films.



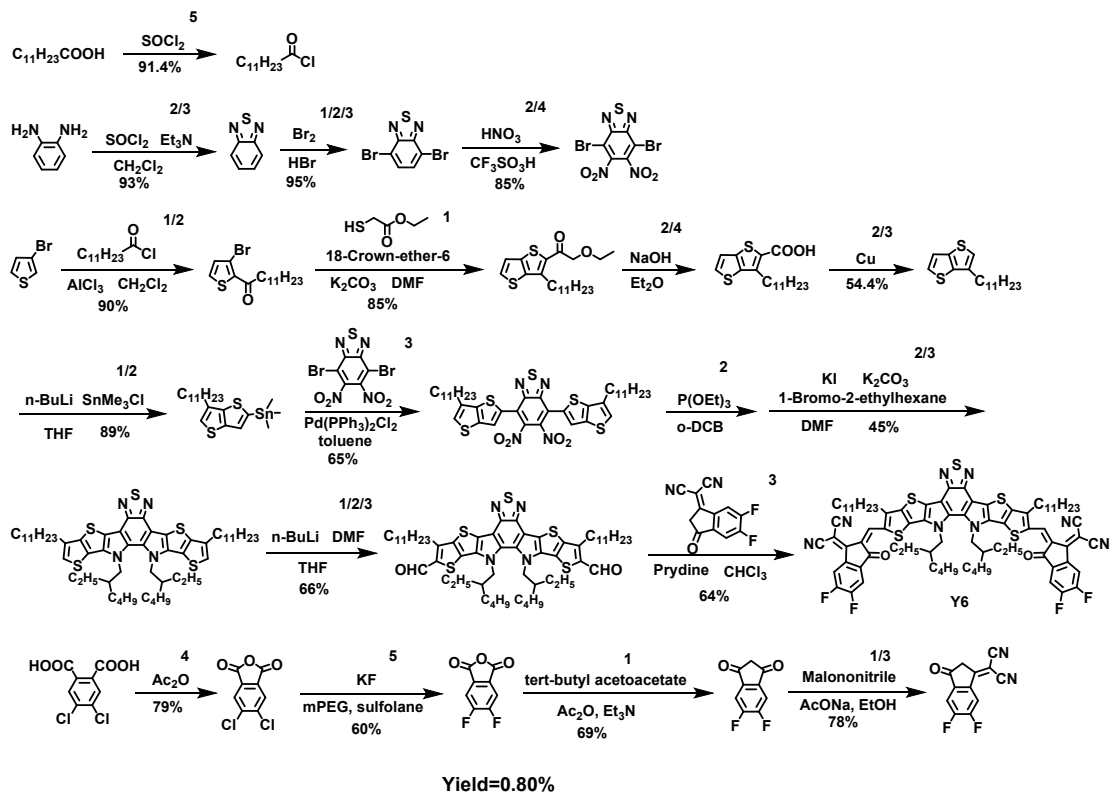
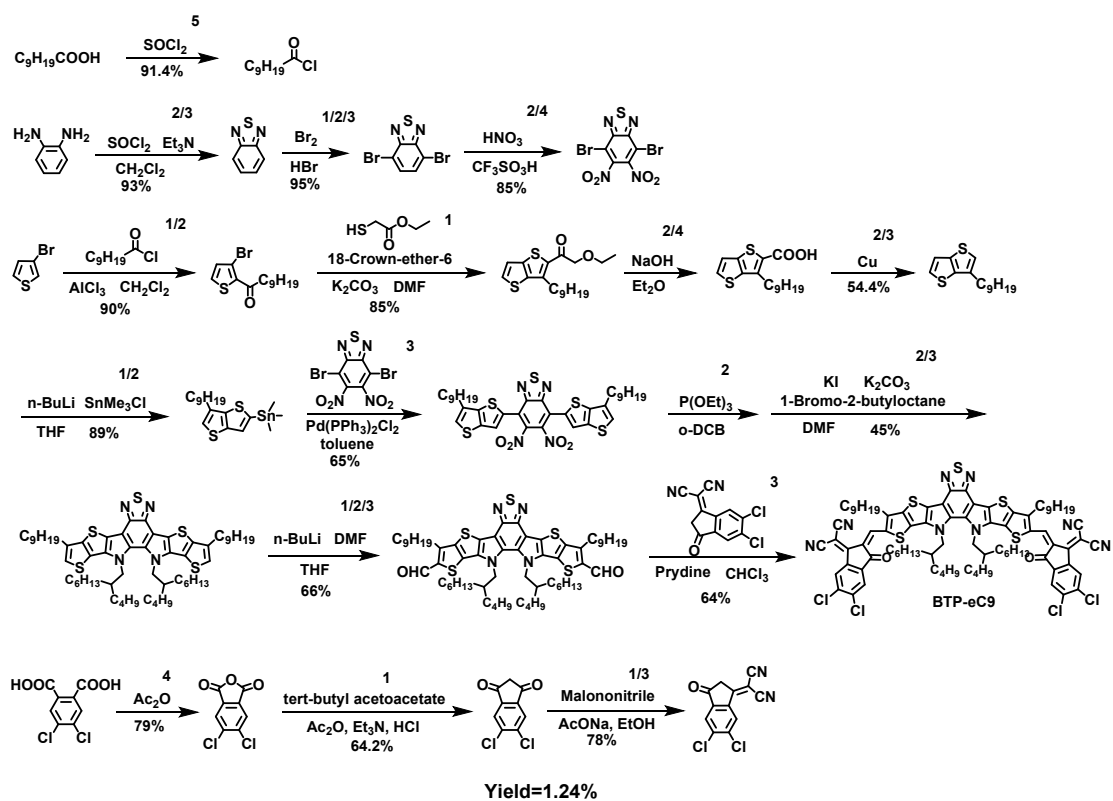
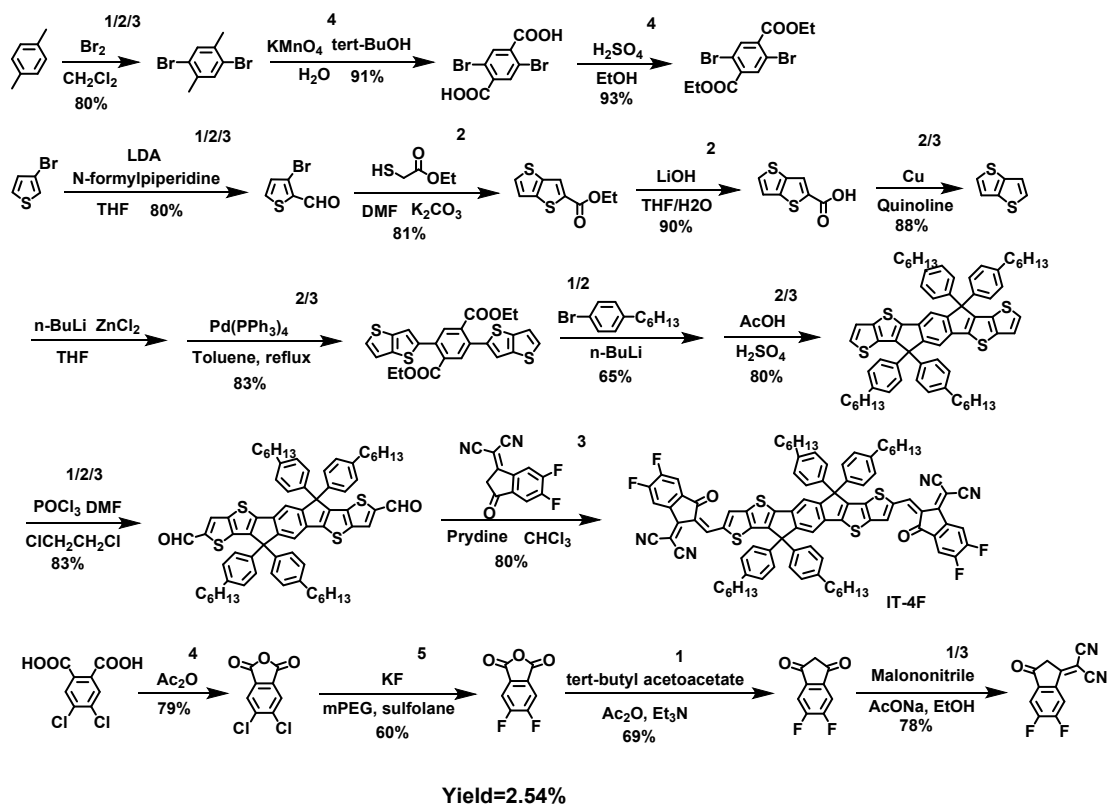


Fig. S13 Synthetic routes of Y6.



**Fig. S14** Synthetic routes of BTP-eC9.



**Fig. S15** Synthetic routes of IT-4F.

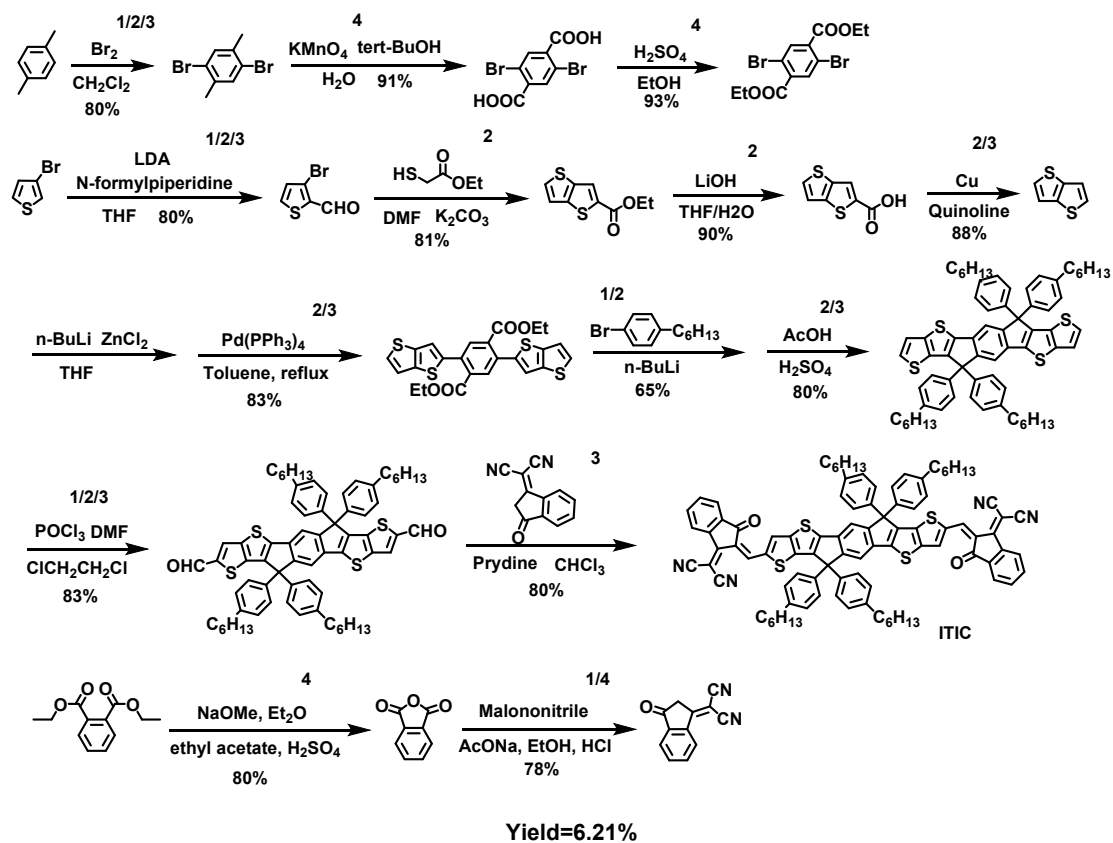


Fig. S16 Synthetic routes of ITIC.

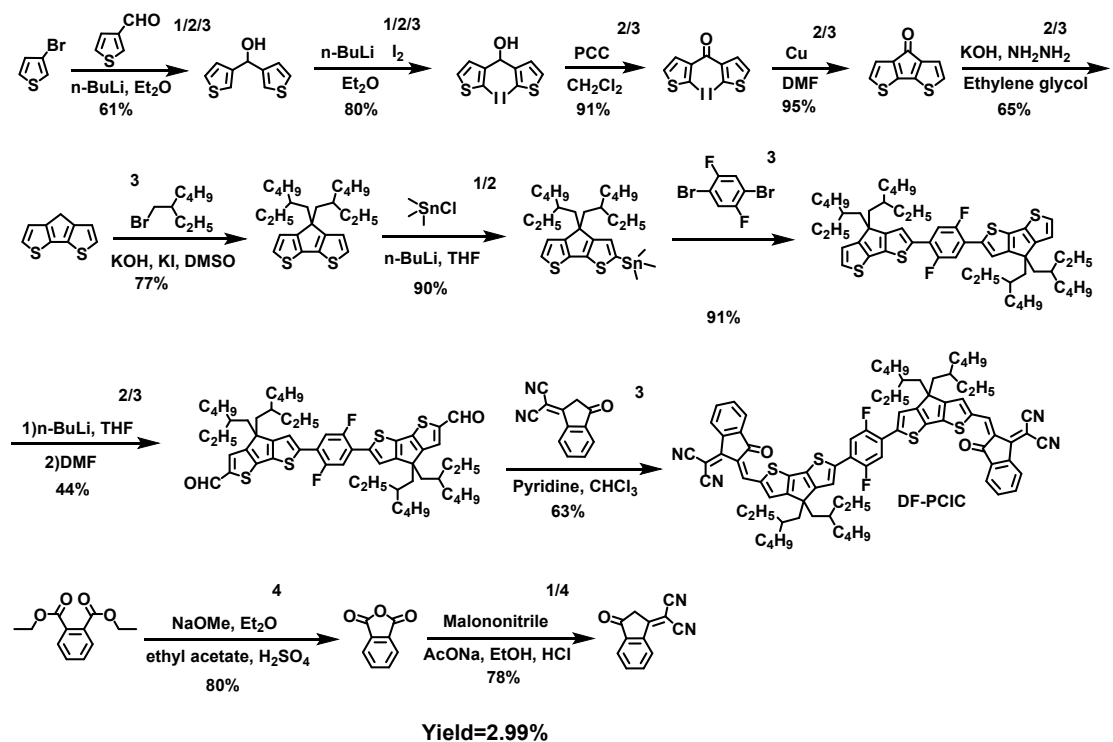
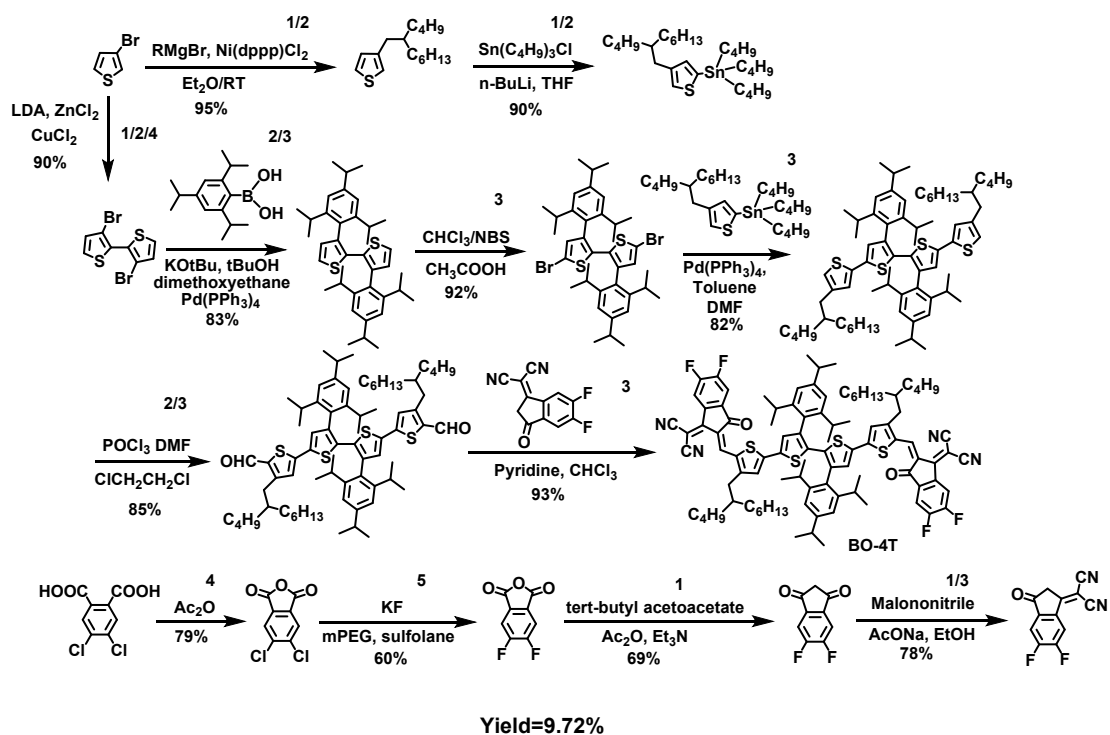


Fig. S17 Synthetic routes of DF-PCIC.



**Fig. S18** Synthetic routes of BO-4T.

### 3. Supporting tables

**Table S1.** Device fabrication conditions.

Active Layer	D:A	Additive	Concentration	Speed	Annealing
D18:BO-4T	1:1.2	0.25% DIO	15.4 mg/mL	3500 rpm	100°C 8min
PM6:BO-4T	1:1.2	0.25% DIO	17.6 mg/mL	3000 rpm	80°C 8min
PBDB-T:BO-4T	1:1.2	0.5% CN	17.6 mg/mL	3000 rpm	80°C 8min
J52:BO-4T	1:1.2	0.5% CN	17.6 mg/mL	2500 rpm	80°C 8min

**Table S2.** Synthetic parameters of acceptors.

Acceptor	NSS	RY	NCC	NUO	NHC	SC index %	PCE %	FOM	Ref
Y6	18	125	8	30	50	99.20	15.7	15.83	1
BTP-eC9	17	80.65	8	29	47	93.84	17.8	18.97	2
IT-4F	17	39.37	8	27	44	88.47	13.0	14.69	3
ITIC	15	16.1	7	25	39	76.20	6.80	8.92	4
DF-PCIC	12	33.44	9	22	30	74.03	10.14	13.70	5
BO-4T	12	10.29	6	19	31	61.64	14.33	23.25	This work

The synthetic complexity (SC) value involves five parameters: (1) the number of synthetic steps (NSS), (2) the reciprocal yields of the acceptor (RY), (3) the number of unit operations required for the isolation/purification of the acceptor (NUO), (4) the number of column chromatographic purifications required by the acceptor (NCC), and (5) the number of hazardous chemicals used for preparation (NHC).

The SC is calculated according to the following equation:<sup>6</sup>

$$SC = 35 \frac{NSS}{NSS_{\max}} + 25 \frac{\log(RY)}{\log(RY_{\max})} + 15 \frac{NUO}{NUO_{\max}} + 15 \frac{NCC}{NCC_{\max}} + 10 \frac{NHC}{NHC_{\max}} \quad (2)$$

In order to compare acceptor molecules with different synthesis complexity and efficiency, a cost-performance figure-of-merit (cp-FOM) are defined as followed:<sup>7</sup>

$$FOM = PCE/SC \quad (3)$$

According to **Table S2**, values used for the normalization:  $NSS_{\max} = 18$ ;  $RY_{\max} = 125$ ;  $NUO_{\max} = 30$ ;  $NCC_{\max} = 9$ ;  $NHC_{\max} = 50$ .

**Table S3.** Detailed Data of GIWAXS Characterization.

System	In plane		Out of plane			
	$Q/\text{\AA}^{-1}$	$D/\text{\AA}$	$Q/\text{\AA}^{-1}$	$D/\text{\AA}$	FWHM	CL/ $\text{\AA}$
BO-4T	0.238	26.4	1.88	3.34	0.201	34.7
	0.452	13.9	1.73	3.63	0.544	12.8
PM6:BO-4T	0.276	22.8	1.83	3.43	0.239	29.2
			1.69	3.72	0.753	9.30
D18:BO-4T	0.268	23.4	1.84	3.41	0.250	27.9
			1.52	4.13	0.369	18.9
PBDB-T:BO-4T	0.330	19.0	1.84	3.41	0.281	24.8
			1.62	3.88	0.609	11.5
J52:BO-4T	0.277	22.7	1.84	3.41	0.240	29.1
			1.74	3.61	0.682	10.2

#### 4. Supporting References

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