

Supporting Information

A Non-fullerene Electron Acceptor with Benzotrithiophene and π - Extension Terminal Group for Development of High-Efficiency Organic Solar Cells

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1. General Measurements

NMR spectra of ^1H NMR and ^{13}C NMR were recorded on Bruker AVANCE 500 NMR spectrometer with tetramethylsilane (TMS) as the internal reference. MALDI-TOF spectra were measured by a Bruker BIFLEX III mass spectrometer. Thermogravimetric (TG) measurements were carried out with a NETZSCH (TG209F3) apparatus at a heating rate of $20\text{ }^\circ\text{C min}^{-1}$ in nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements were performed on a NETZSCH (DSC200F3) apparatus under a nitrogen atmosphere. The samples were placed in lidded $40\text{ }\mu\text{L}$ Al pans and thermally cycled two times with a heating/cooling rate of $10/20\text{ }^\circ\text{C min}^{-1}$ for the first cycle and a heating/cooling rate of $10/40\text{ }^\circ\text{C min}^{-1}$ for the second cycle, respectively. UV-vis absorption spectrums were recorded on a SHIMADZU UV-3600 spectrophotometer. Photoluminescence was measured with a SHIMADZU RF-5301PC fluorimeter. The ground state geometry of molecular was optimized by using the Density Functional Theory (DFT) method at a B3LYP/6-31 G (d, p) level. All the calculations of the acceptor molecules were performed using the Gaussian 16 package. Cyclic voltammetry (CV) measurements were carried out on a CHI660A electrochemical workstation at a scan rate of 100 mV s^{-1} by using a platinum electrode as counter electrode, a saturated calomel electrode as reference electrode, and nitrogen-saturated 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile as electrolyte. The ferrocene/ferrocenium (Fc/Fc^+) was used as a reference and the potential was 0.39 V .

The E_{HOMO} and E_{LUMO} were caculated according to equations:

$$E_{\text{HOMO}} = -e[E_{\text{ox}} + \left(4.8 - \frac{F_c}{F_c^+}\right)] \quad \text{and} \quad E_{\text{LUMO}} = -e[-E_{\text{red}} + \left(4.8 - \frac{F_c}{F_c^+}\right)]. \quad \text{Atomic force}$$

microscopy (AFM) characteristics were carried out on a NanoMan VS microscope in the tapping mode. High-resolution transmission electron microscopy (TEM) images were obtained from a JEM-2100F instrument. Grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were performed on a Xenocs Xeuss 2.0 system with an Excillum MetalJet-D2 X-ray source at 70.0 kV, 2.8570 mA, and a wavelength of 1.34144 Å. The sample to detector distance was ~218.18 mm and the incidence angle was 0.20°. Scattering images were recorded using a DECTRIS PILATUS3 R 1M area detector with a pixel size of 0.172 mm by 0.172 mm. Samples were prepared by spin-coating neat non-fused FEA or blend solutions on PEDOT:PSS/silicon wafer substrates.

Transient Photocurrent and Transient Photovoltage Measurements: The transient photocurrent (TPC) characteristics of devices were measured by applying 500 nm laser pulses with a pulse width of 120 fs and a low pulse energy to the short-circuit current devices in dark. The laser pulses were generated from optical parametric amplifier (TOPAS-Prime) pumped by a mode-locked Ti: sapphire oscillator seeded regenerative amplifier with a pulse energy of 1.3 mJ at 800 nm and a repetition rate of 1 kHz (Spectra Physics Spitfire Ace). The charge extraction time was extracted from the fitting line of the TPC signal with equation: $\delta I = A \exp(t/T)$, where A is a constant that fits to the peak high, t is time, and T is the charge extraction time constant.

Hole-only devices (ITO/PEDOT:PSS/Active Layer/MoO₃/Ag) and electron-only devices (ITO/ZnO/Active Layer/PFN-Br/Ag) were fabricated to evaluate the hole and electron mobilities (μ_h and μ_e) of blend films by the space-charge limited current

(SCLC) model. The mobilities were determined by fitting the dark current based on a single-carrier SCLC model, which is described by the following equation:

$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu_0 \frac{V^2}{d^3}$, where J is the current, μ_0 is the carrier mobility, ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity of the material, d is the thickness of the active layer, and V is the effective voltage. The effective voltage (V_{eff}) was obtained by subtracting the built-in voltage ($V_{bi}=0$) and the voltage drop ($V_s=10 \times I$, where the value 10 is the resistance of MoO₃ and I is the current of the devices in this work) from the applied voltage (V_{appl}), that is: $V_{eff} = V_{appl} - V_{bi} - V_s$.

2. Device Fabrication and Characterization

Organic solar cells (OSCs) were fabricated with a conventional structure of ITO/PEDOT:PSS/Active Layer/PFN-Br/Ag. The OSCs were prepared by the following procedures. The indium tin oxide (ITO) patterned glass substrate was firstly cleaned with ultrasonic treatment in detergent, deionized water, acetone, ethanol, and isopropyl alcohol sequentially, and dried in an ultraviolet-ozone chamber for 20 min. PEDOT:PSS solution filtered with a 0.45 μm PES filter was then spin-coated on the pre-cleaned ITO substrate at 3500 rpm for 30 s to obtain a film with thickness of ~ 40 nm, followed by baking at 150 $^{\circ}\text{C}$ for 15 min in air. Afterwards, the substrates were transferred into a nitrogen (N_2) protected glove-box for further fabrication processes. The active layers was prepared by spin coating PBDB-T:A (weight ratio 1:1.50) in CB solution on the obtained substrates with a final layer thicknesses of about 100 nm, which was then thermally treated at 100 $^{\circ}\text{C}$ for 10 minutes in a nitrogen atmosphere. Thereafter, a 5 nm PFN-Br layer was obtained by spin-coating PFN-Br/methanol

solution onto the abovementioned active layer. Finally, Ag electrode with a thickness of 100 nm was thermally deposited on the as prepared device through a shadow mask using a vacuum evaporator system under 10^{-7} Pa. The resultant active area of the device was 0.04 cm^2 .

The current–voltage (J – V) characteristics were measured on a computer-controlled Keithley 2400 source meter under 1 sun, AM 1.5 G spectra from a class solar simulator (Taiwan, Enlitech), and the light intensity was 100 mW cm^{-2} as calibrated by a China General Certification Center certified reference monocrystal silicon cell (Enlitech). Before the J – V test, a physical mask of an aperture with a precise area of 0.04 cm^2 was used to define the device area. The external quantum efficiency (EQE) data were recorded with a QE-R3011 test system from Enli technology company (Taiwan).

3. Materials and Synthesis

4,7-Dibromo-5,6-dinitrobenzo[*c*][1,2,5]thiadiazole, 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (IC-2F), and 2-(6,7-difluoro-3-oxo-2,3-dihydro-1H-cyclopenta-*[b]*naphthalen-1-ylidene) malononitrile (NC-2F) were purchased from Derthon Optoelectronic Materials Science Technology. Other raw materials and all reagents using in the work were purchased from Energy Chemistry and Aladdin commercial sources and directly used without further purification. All reactions were carried out under the atmosphere without oxygen and water. Compounds from 1 to 5 were synthesized according to the previously reported procedure.^{1,2}

Synthesis 1-(2,8-bis(4,4-bis(2-butyloctyl)-4H-cyclopenta[2,1-*b*:3,4-*b'*])dithiophen-2-yl)-3b,6a-dihydrobenzo[1,2-*b*:3,4-*b'*:6,5-*b''*]trithiophen-5-yl)-2-butyloctan-1-

one (compound 6). Under nitrogen atmosphere, the crude product compound 4 (2.00 g, 3.40 mmol), compound 5 (8.20 g, 10.2 mmol), and Pd(PPh₃)₂Cl₂ (0.48 g, 0.68 mmol) were separately added in 250 mL flask with 80 mL anhydrous THF. The mixture was stirred at 80 °C for 24 h. After cooling to room temperature, the reaction mixture was extracted with DCM (50 mL) and washed with H₂O for three times. Thereinto, the organic phase was dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure. Finally, the crude product was purified by column chromatography on silica gel to get the product as red solid (3.77 g, 76% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.75 (s, 1H), 7.60 (s, 1H), 7.24-7.18 (m, 4H), 6.99-6.94 (m, 2H), 3.49-3.39 (m, 1H), 2.06-1.80 (m, 8H), 1.62 (s, 4H), 1.41-1.20 (m, 8H), 1.14-0.81 (m, 72H), 0.79-0.64 (m, 30H). ¹³C NMR (126 MHz, CDCl₃) δ 198.7, 158.4, 158.3, 158.2, 143.2, 138.1, 138.0, 137.9, 137.7, 136.5, 136.0, 135.8, 135.4, 134.2, 132.2, 132.0, 131.5, 131.4, 129.5, 126.9, 125.5, 125.4, 122.5, 122.4, 120.7, 120.6, 116.8, 116.6, 53.9, 48.6, 44.6, 43.8, 42.4, 41.4, 40.4, 39.0, 38.8, 35.2, 35.1, 35.0, 34.8, 34.7, 33.7, 33.2, 32.9, 32.0, 31.9, 31.7, 31.6, 30.0, 29.6, 29.4, 29.1, 28.7, 28.6, 27.8, 26.9, 26.7, 26.4, 25.3, 23.0, 22.9, 22.8, 22.7, 22.6, 22.2, 20.7, 20.5, 20.2, 19.2, 18.8, 14.9, 14.4, 14.3, 14.1, 14.0, 12.0, 11.4. HR-MS (MALDI-TOF) m/z calcd. for (C₉₀H₁₃₄OS₇): 1454.48. Found: 1454.30.

Synthesis **6,6'-(5-(2-butyloctanoyl)-3b,6a-dihydrobenzo[1,2-b:3,4-b':6,5-b'']trithiophene-2,8-diyl)bis(4,4-bis(2-butyloctyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-carbaldehyde) (compound 7).** Compound 6 (2.00 g, 0.1.63 mmol) was dissolved in 20 ml dimethylformamide (DMF) in a degassed two-neck round-

bottom flask. The mixture was stirred at room temperature for 30 min. Afterwards, 1 mL phosphorus oxychloride (POCl_3) was dropwise added in the mixture at 0 °C. The mixture was then stirred at the room temperature for 30 min. The reaction was carried out at 90 °C for 12 hours. After cooling to room temperature, the solution was extracted with DCM (3×30 mL) and washed with H_2O (3×50 mL). Thereafter, the organic phase was dried over MgSO_4 and the solvent was removed under reduced pressure. Finally, the crude product was purified by column chromatography on silica gel (PE:DCM = 2:1) to get the product as red solid (1.66 g, 80% yield). ^1H NMR (500 MHz, CDCl_3) δ 9.87 (d, $J = 1.8$ Hz, 2H), 8.35 (s, 1H), 7.86 (s, 1H), 7.71 (s, 1H), 7.60 (s, 2H), 7.29 (s, 2H), 3.43 (t, $J = 5.2$ Hz, 1H), 1.99 (d, $J = 4.3$ Hz, 8H), 1.87 (dd, $J = 14.2, 8.6$ Hz, 2H), 1.63 (s, 4H), 1.43-0.81 (m, 78H), 0.79-0.60 (m, 30H). ^{13}C NMR (126 MHz, CDCl_3) δ 198.7, 182.5, 182.4, 162.7, 162.5, 162.4, 158.0, 157.9, 147.1, 143.8, 143.6, 140.6, 140.2, 137.4, 137.2, 136.5, 136.3, 134.4, 132.5, 132.3, 131.8, 130.6, 130.1, 126.7, 124.5, 124.0, 120.5, 119.1, 118.4, 118.2, 54.5, 48.7, 43.7, 35.3, 35.1, 34.9, 34.8, 34.5, 33.9, 33.2, 31.9, 31.7, 31.6, 31.5, 31.4, 30.3, 30.2, 30.0, 29.7, 29.6, 29.5, 29.4, 28.7, 28.6, 27.8, 26.4, 23.0, 22.8, 22.7, 22.6, 14.1, 14.0, 14.9. HR-MS (MALDI-TOF) m/z calcd. for ($\text{C}_{92}\text{H}_{134}\text{O}_3\text{S}_7$): 1510.49. Found: 1510.31.

Synthesis of compound BTTBo-4F. Compound 7 (0.20 g, 0.13 mmol) and IC-2F (0.12 g, 0.52 mmol) were dissolved in the mixture of chloroform and anhydrous pyridine (20 mL, v/v, 20/0.1) in a degassed two-neck round-bottom flask. The reaction was carried out at 60 °C for 12 hours. After removal of solvent under vacuum, the product was purified by flash chromatography with the eluent of dichloromethane/hexanes=2/1. The

resultant material was further purified by recrystallization chloroform/methanol (v/v = 1/5) before device application, to obtain a black solid (0.18 g, 82% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.90 (s, 1H), 8.81 (s, 1H), 8.45 (s, 1H), 8.35-8.25 (m, 2H), 7.87 (s, 1H), 7.72 (s, 2H), 7.64 (d, *J* = 7.3 Hz, 1H), 7.58 (s, 1H), 7.56-7.50 (m, 1H), 7.40 (d, *J* = 7.3 Hz, 2H), 3.48 (d, *J* = 5.9 Hz, 1H), 2.08 (dd, *J* = 17.7, 12.4 Hz, 8H), 1.97-1.87 (m, 2H), 1.69 (dd, *J* = 13.0, 7.0 Hz, 2H), 1.40-0.74 (m, 110H). ¹³C NMR (126 MHz, CDCl₃) δ 198.2, 185.9, 185.4, 166.2, 166.0, 159.7, 158.1, 157.8, 157.5, 155.3, 153.2, 153.1, 144.6, 144.2, 143.8, 139.6, 139.4, 138.3, 137.9, 137.7, 137.4, 137.3, 137.1, 136.3, 136.0, 134.6, 134.3, 132.5, 131.8, 130.4, 126.3, 120.7, 120.7, 119.6, 119.4, 119.3, 118.7, 114.9, 114.6, 114.4, 112.4, 112.2, 68.1, 67.7, 54.5, 54.4, 48.8, 43.8, 43.7, 35.3, 35.1, 35.0, 34.8, 34.2, 33.0, 32.6, 32.0, 31.9, 31.7, 29.9, 29.6, 29.5, 28.6, 28.5, 27.7, 26.4, 26.3, 26.2, 23.0, 22.90, 22.7, 22.6, 14.2, 14.1, 14.0. HR-MS (MALDI-TOF) *m/z* calcd. for (C₁₁₆H₁₃₈F₄N₄O₃S₇): 1934.80. Found: 1934.22.

Synthesis of compound BTTBo-4FN. Compound 7 (0.20 g, 0.13 mmol) and NC-2F (0.15 g, 0.52 mmol) were dissolved in the mixture of chloroform and anhydrous pyridine (20 mL, v/v, 20/0.1) in a degassed two-neck round-bottom flask. The reaction was carried out at 65 °C for 12 hours. After removal of solvent under vacuum, the product was purified by flash chromatography with the eluent of dichloromethane/hexanes=2/1. The resultant material was further purified by recrystallization chloroform/methanol (v/v = 1/5) before device application, to obtain a black solid (0.23 g, 85% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.95 (d, *J* = 27.7 Hz, 4H), 8.36-8.14 (m, 3H), 7.90-7.51 (m, 8H), 7.36 (d, *J* = 7.3 Hz, 2H), 3.47 (d, *J* = 5.5

Hz, 1H), 2.02 (d, $J = 76.6$ Hz, 10H), 1.71 (s, 2H), 1.43-0.65 (m, 110H). ^{13}C NMR (126 MHz, CDCl_3) δ 198.31, 187.5, 166.4, 166.3, 159.8, 158.3, 153.4, 151.0, 144.6, 144.2, 140.4, 138.4, 137.3, 137.0, 136.3, 135.3, 134.5, 133.3, 132.5, 130.3, 126.4, 125.3, 123.0, 121.9, 120.5, 116.5, 116.0, 115.3, 66.3, 54.4, 48.9, 43.8, 35.1, 34.8, 34.2, 33.1, 32.8, 31.9, 31.8, 30.0, 29.7, 28.6, 28.5, 27.8, 26.4, 26.3, 23.1, 23.0, 22.7, 22.7, 14.2, 14.1, 14.0. HR-MS (MALDI-TOF) m/z calcd. for $(\text{C}_{124}\text{H}_{142}\text{F}_4\text{N}_4\text{O}_3\text{S}_7)$: 2034.92. Found: 2037.44.

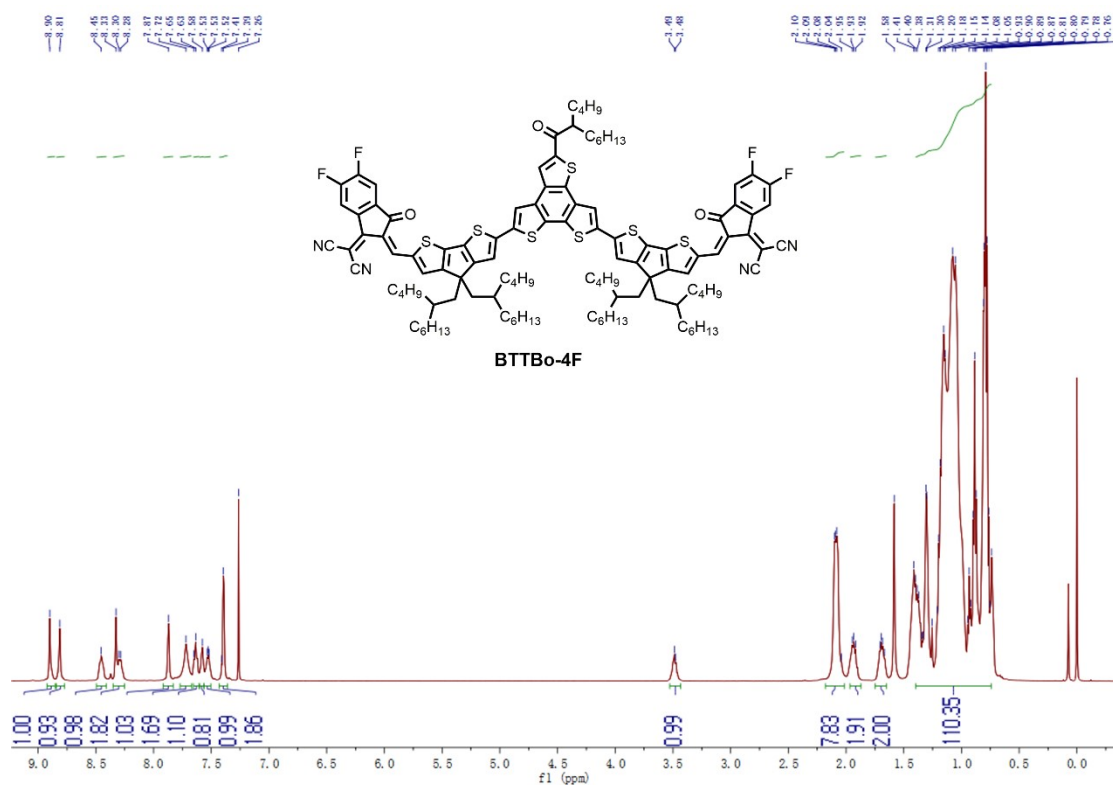


Fig. S1 ^1H -NMR (500 MHz) spectrum of **BTTBo-4F**.

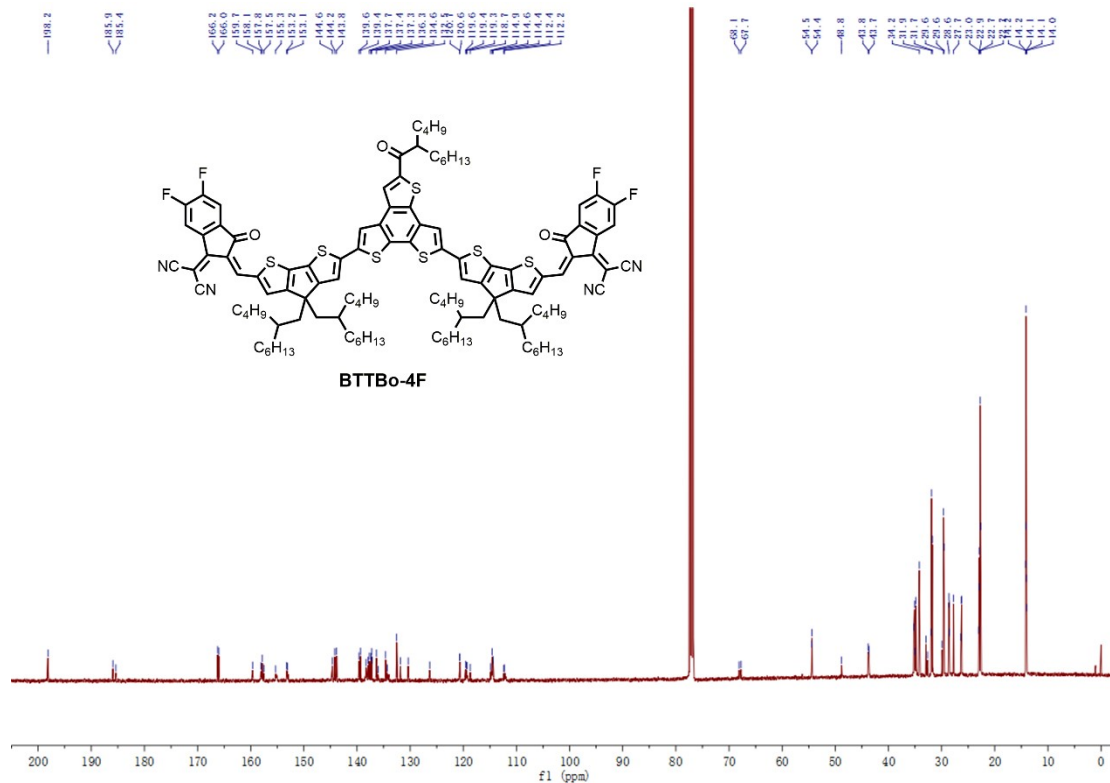


Fig. S2 ^{13}C -NMR (126 MHz) spectrum of BTTBo-4F.

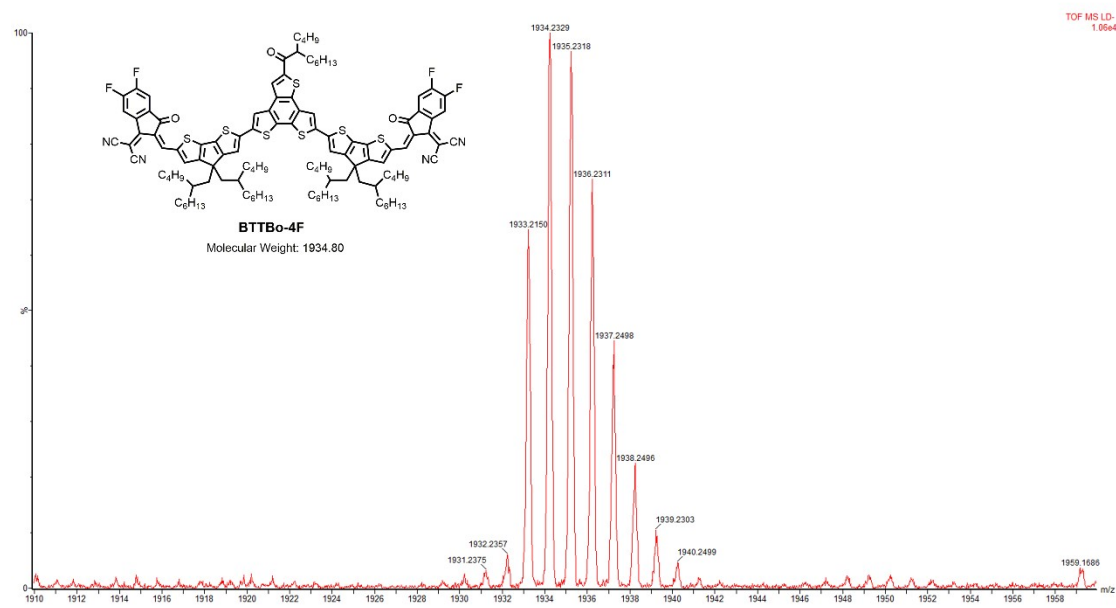


Fig. S3 The high-resolution mass spectrum (MALDI-TOF) of BTTBo-4F.

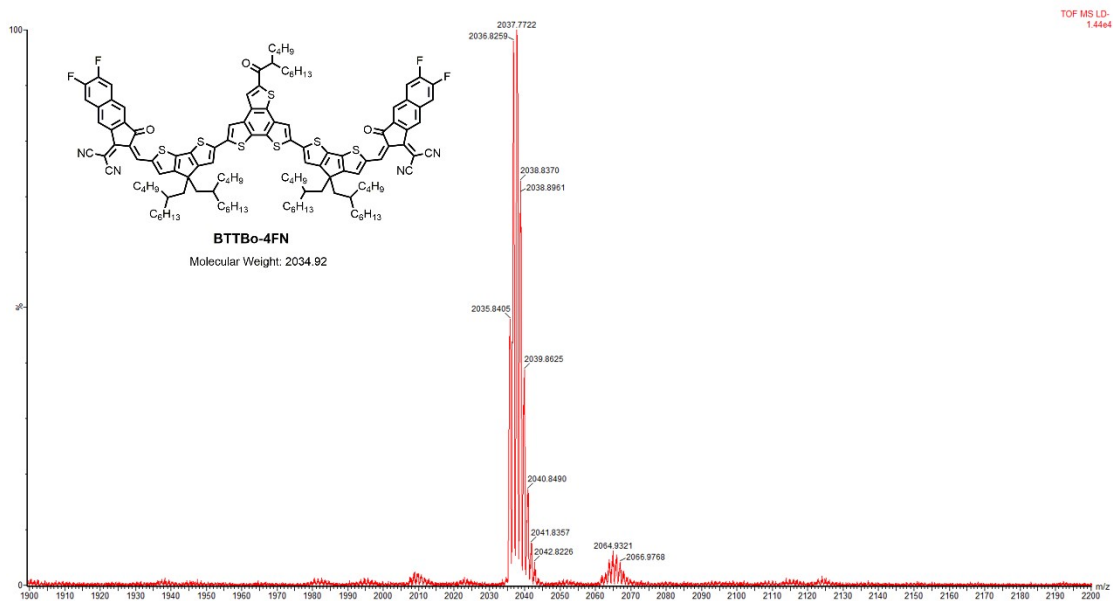


Fig. S6 The high-resolution mass spectrum (MALDI-TOF) of BTTBo-4FN.

4. Thermal Properties

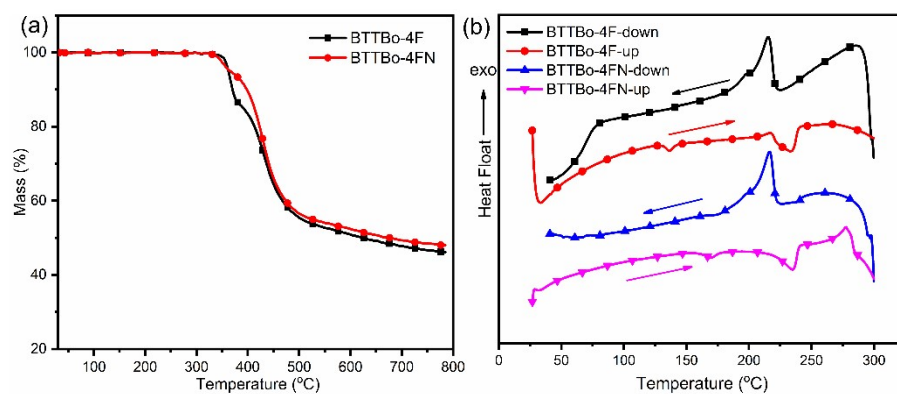


Fig. S7 (A) TG curves of BTTBo-4F and BTTBo-4FN; (B) DSC curves of BTTBo-4F and BTTBo-4FN with a heating/cooling rate of 10/20 °C min⁻¹.

5. DFT calculation

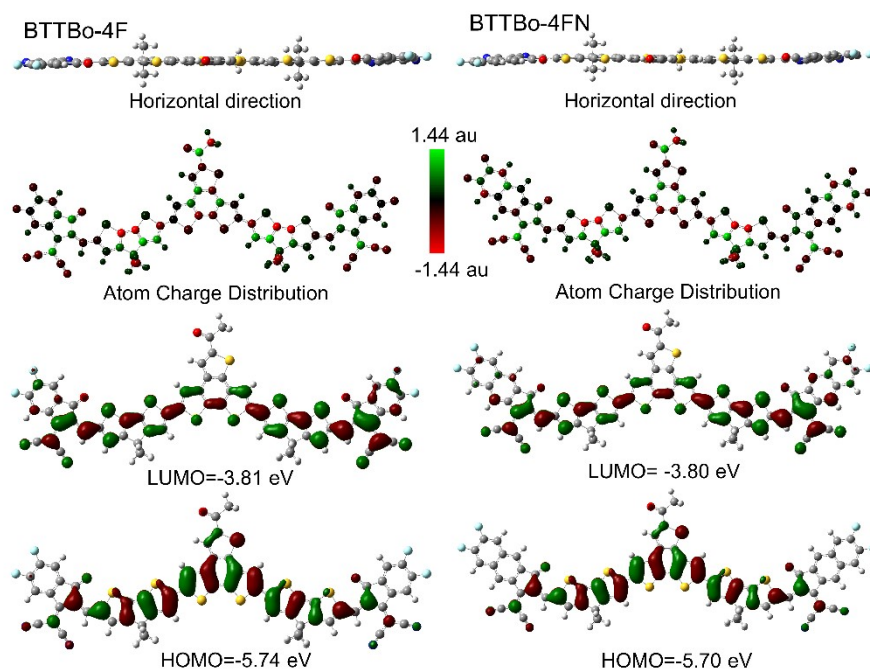


Fig. S8 Optimized geometry, atom charge distribution and energy levels of BTTBo-4F and BTTBo-4FN calculated by the DFT calculation.

6. Hole and Electron Mobility

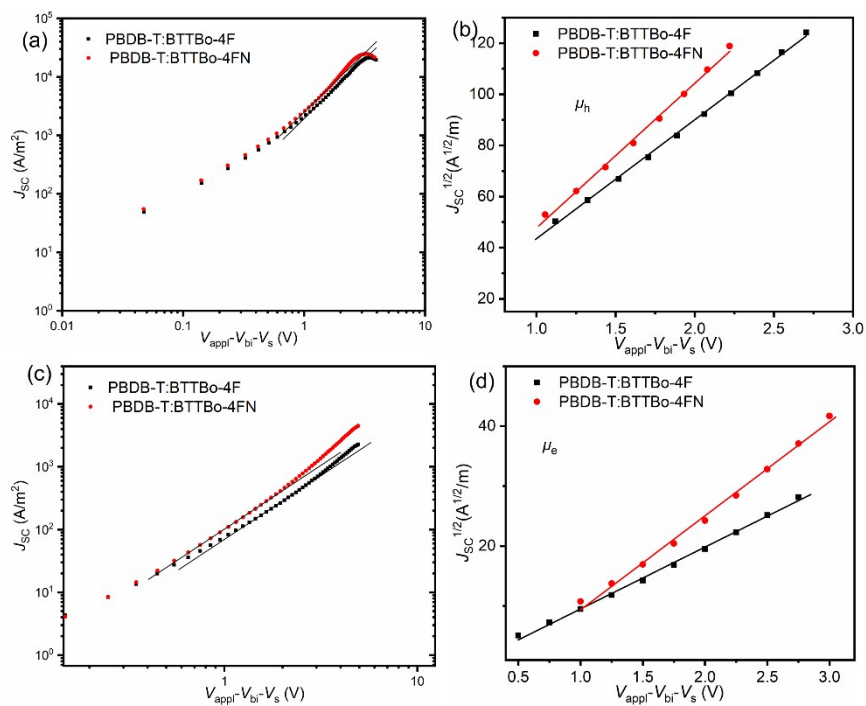


Fig. S9 (a) J - V characteristics of hole-only PBDB-T:NFEA blend devices; (b) $J^{1/2}$ - V characteristics of hole-only PBDB-T:NFEA blend devices; (c) J - V characteristics of electron-only device based on PBDB-T:NFEA blend films; (d) $J^{1/2}$ - V characteristics of electron-only device based on PBDB-T:NFEA blend films.

7. Film Microstructure and Morphology

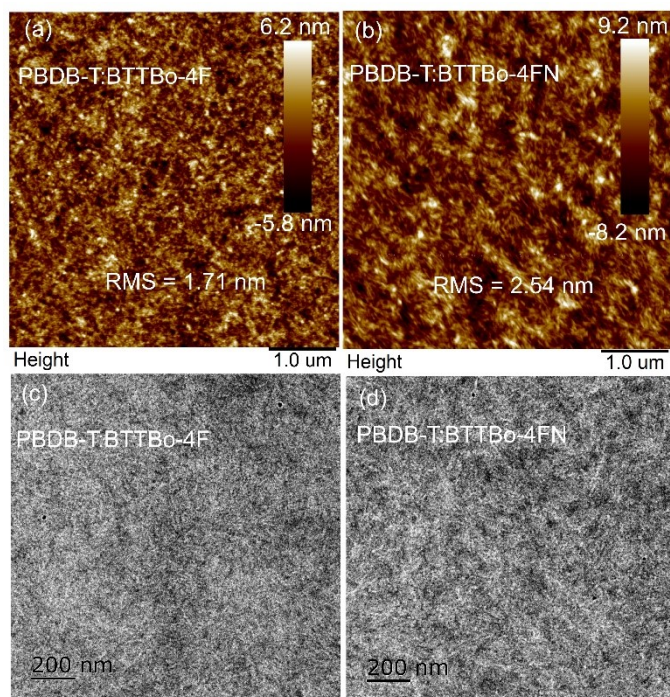


Fig. S10. (a, b) AFM height images (5×5 μm) and (c, d) TEM images of the blend films.

8. Device data

Table S1. Device structure: Glass/ITO/PEDOT:PSS/ PBDB-T (7mg/mL in CB):A/PFN-Br/Ag with 0.5% CN and thermal annealing 100 °C for 10 min.

A	D:A	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	PCEs(%)	PCE _{max}
	1:1.20	0.84±0.00	13.99±0.17	49.78±0.13	5.48±0.07	6.55
BTTBo-4F	1:1.50	0.85±0.00	14.52±0.16	60.98±3.23	7.51±0.53	8.07
	1:1.70	0.83±0.00	12.62±0.18	59.91±2.06	6.30±0.30	6.60
	1:1.20	0.84±0.00	18.61±0.91	69.47±0.99	10.84±0.49	11.09
BTTBo-4FN	1:1.50	0.84±0.00	19.40±0.11	68.72±0.21	11.14±0.06	11.26
	1:1.70	0.84±0.00	19.00±0.57	67.22±0.65	10.68±0.25	10.95

Table S2. Device structure: Glass/ITO/PEDOT:PSS/PBDB-T(7mg/mL in CB):A /PFN-Br /Ag with 0.5% CN and thermal annealing 100 °C for 10 min.

D:A	Rotate speed (r/s)	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	PCEs(%)	PCE _{max}
PBDB-T:BTTBo-4F(1:1.50)	1500	0.85±0.00	14.51±0.18	60.63±0.21	7.48±0.10	7.57
	1800	0.85±0.00	14.52±0.16	60.98±3.23	7.51±0.53	8.07
	2000	0.85±0.00	14.93±0.21	64.09±0.62	8.14±0.13	8.27
	2200	0.85±0.00	14.68±0.08	61.33±1.20	7.65±0.11	7.76
	2500	0.85±0.00	14.44±0.12	59.59±1.15	7.28±0.13	7.40
PBDB-T:BTTBo-4FN(1:1.50)	1500	0.83±0.00	19.04±0.10	66.22±1.18	10.53±0.25	10.76
	1800	0.84±0.00	19.40±0.11	68.72±0.21	11.14±0.06	11.26
	2000	0.84±0.00	19.62±0.21	69.33±2.70	11.46±0.38	11.60
	2200	0.84±0.00	19.42±0.17	69.47±0.29	11.39±0.06	11.49
	2500	0.84±0.00	19.04±0.06	69.83±0.53	11.22±0.13	11.34

9. Reference

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2. Z. Yao, Y. Li, S. Li, J. Xiang, X. Xia, X. Lu, M. Shi and H. Chen, *ACS Appl. Energy Mater.*, 2020, **4**, 819-827.