

Electronic supplementary information for

**Fully-unfused electron acceptors based on steric boron
dipyrromethene (BODIPY) core for organic solar cells**

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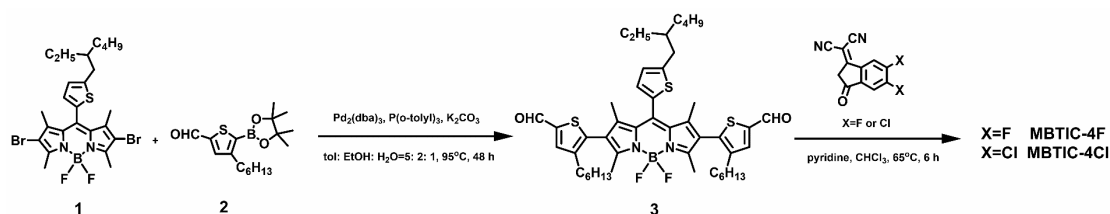
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General Information of Synthesis Procedures

All the solvent were commercially available and used without further purification. BODIPY dibromide 2,8-dibromo-10-(5-(2-ethylhexyl)thiophen-2-yl)-5,5-difluoro-1,3,7,9-tetramethyl-5*H*- $\lambda^4,5\lambda^4$ -dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine was purchased from WuXi AppTec (Wuhan) Co. 4-hexyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene-2-carbaldehyde, terminal groups 2-(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile and 2-(5,6-dichloro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile were purchased from SunaTech (Suzhou, China). Polymer donor PBDB-T was purchased from Zhiyan Chemical Co. (Nanjing, China).



Scheme S1. Synthetic routes of BODIPY-cored FUEAs.

Synthesis of Intermediate 3:

A mixture of compound 1 (300 mg, 0.50 mmol), compound 2 (403 mg, 1.25 mmol) and K_2CO_3 (690 mg, 5 mmol) was dissolved into a mixed solution of toluene/EtOH/ H_2O (10/4/2 mL) under nitrogen protection. After that, $\text{Pd}_2(\text{dba})_3$ (64 mg) and $\text{P}(o\text{-tolyl})_3$ (20 mg) were added into the mixture. Then the mixture was deoxygenated with nitrogen purging for 20 minutes. The reaction mixture was stirred at 95°C for 48 hours. After cooling to room temperature, the crude product was diluted in dichloromethane and washed with brine for 3 times. The organic phase was dried by magnesium sulphate and the solvent was removed under reduced pressure. After that, the crude product was purified by silica gel column chromatography (eluent: dichloromethane/petroleum ether (3:1, v/v)). The product obtained as a red oil with yield of around 70% (300 mg).

^1H NMR (400 MHz, CDCl_3 , δ ppm) :9.86 (s, 2H), 7.67 (d, $J = 1.2$ Hz, 2H), 6.86 (dd, $J_1 = 21.2$ Hz, $J_2 = 3.6$ Hz, 2H), 2.82 (d, $J = 6.8$ Hz, 2H), 2.46 (s, 6H), 2.38 (q, $J = 8.8$ Hz, 4H), 1.62 (d, $J = 4.0$ Hz, 1H), 1.51 (d, $J = 6.8$ Hz, 3H), 1.27-1.20 (m, 24H), 0.89-0.83 (m, 15H).

Synthesis of MBTIC-4F:

A mixture of compound **3** (100 mg, 0.12 mmol), 2-(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (IC-2F) (113 mg, 0.48 mmol), pyridine (1 mL) and anhydrous chloroform (10 mL) were stirred at reflux for 6 hours under a nitrogen atmosphere. After cooling to room temperature, the crude product was diluted in dichloromethane and washed with brine for 3 times. The organic phase was dried by magnesium sulphate and the solvent was removed under reduced pressure. After that, the crude product was further purified by silica gel column chromatography (eluent: dichloromethane/petroleum ether (3:1, v/v)). The product obtained as green solid with yield of 60% (91 mg).

¹H NMR (400 MHz, CDCl₃, δ ppm): 8.85 (d, *J* = 1.6 Hz, 2H), 8.56 (q, *J* = 6.4 Hz, 2H), 7.80 (d, *J* = 2.4 Hz, 2H), 7.72-7.67 (m, 2H), 6.89 (dd, *J*₁ = 26.4 Hz, *J*₂ = 4.4 Hz, 2H), 2.83 (d, *J* = 6.0 Hz, 2H), 2.52 (s, 6H), 2.43 (q, *J* = 7.6 Hz, 4H), 1.61 (s, 7H), 1.32-1.23 (m, 23H), 0.90-0.84 (m, 13H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 185.85, 185.79, 158.64, 158.63, 156.13, 155.78, 153.49, 153.47, 153.36, 153.33, 148.01, 147.96, 147.91, 146.67, 146.58, 144.87, 144.77, 142.81, 142.76, 138.38, 138.34, 136.81, 136.79, 136.77, 136.62, 136.55, 134.71, 134.64, 133.07, 131.29, 131.26, 127.84, 127.82, 126.13, 126.09, 124.97, 122.46, 122.40, 115.26, 115.04, 114.05, 113.92, 113.91, 113.04, 112.87, 70.97, 41.71, 41.61, 33.96, 32.28, 31.58, 30.34, 28.94, 28.92, 28.89, 28.83, 28.78, 28.37, 25.54, 25.52, 23.08, 22.64, 14.21, 14.18, 14.14, 13.66, 12.56, 12.54, 10.94, 10.91, 10.89.

MS (MALDI-TOF) (*m/z*): Calcd. for C₇₁H₆₅BF₆N₆O₂S₃ [M⁺]: 1254.43; found: 1253.86. Anal. Calcd. for C₇₁H₆₅BF₆N₆O₂S₃: C 67.93, H 5.22, B 0.86, F 9.08, N 6.69, O 2.55, S 7.66; found: C 67.59, H 5.77, N 6.25, S 7.70.

Synthesis of MBTIC-4Cl:

A mixture of compound **3** (100 mg, 0.12 mmol), 2-(5,6-dichloro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (IC-2Cl) (127 mg, 0.48 mmol), pyridine (1 mL) and anhydrous chloroform (10 mL) were stirred at reflux for 6 hours under a nitrogen atmosphere. After cooling to room temperature, the crude product was diluted in

dichloromethane and washed with brine for 3 times. The organic phase was dried by magnesium sulphate and the solvent was removed under reduced pressure. After that, the crude product was purified by silica gel column chromatography (eluent: dichloromethane/petroleum ether (3:1, v/v)). The product obtained as purple-black solid with yield of 58% (92 mg).

^1H NMR (400 MHz, CDCl_3 , δ ppm): 8.87 (d, $J = 1.6$ Hz, 2H), 8.79 (s, 2H), 7.97 (d, $J = 4.0$ Hz, 2H), 7.81 (d, $J = 2.4$ Hz, 2H), 6.89 (dd, $J_1 = 26.4$ Hz, $J_2 = 3.2$ Hz, 2H), 2.83 (d, $J = 6.0$ Hz, 2H), 2.52 (s, 6H), 2.44-2.37 (m, 4H), 1.61 (s, 7H), 1.32-1.22 (m, 23H), 0.90-0.84 (m, 13H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 185.92, 185.86, 158.49, 158.46, 155.78, 148.51, 148.45, 147.97, 147.93, 146.86, 146.85, 146.75, 144.99, 144.89, 142.80, 142.77, 140.12, 140.10, 139.93, 139.92, 139.00, 138.96, 138.60, 138.59, 137.03, 136.98, 136.82, 136.81, 136.09, 136.08, 133.09, 131.27, 131.24, 127.16, 125.54, 125.51, 124.97, 122.46, 122.41, 114.02, 113.98, 71.12, 71.09, 41.71, 41.62, 33.96, 32.28, 31.63, 31.58, 30.34, 28.94, 28.92, 28.89, 28.83, 28.79, 28.38, 25.55, 25.53, 25.52, 23.08, 23.07, 22.65, 14.21, 14.19, 14.15, 13.67, 12.58, 12.57, 10.95, 10.92, 10.90.

MS (MALDI-TOF) (m/z): Calcd. for $\text{C}_{71}\text{H}_{65}\text{BCl}_4\text{F}_2\text{N}_6\text{O}_2\text{S}_3$ [M^+]: 1318.31; found: 1319.73.

Anal. Calcd. for $\text{C}_{71}\text{H}_{65}\text{BCl}_4\text{F}_2\text{N}_6\text{O}_2\text{S}_3$: C 64.55, H 4.96, B 0.82, Cl 10.73, F 2.88, N 6.36, O 2.42, S 7.28; found: C 64.71, H 4.82, N 6.07, S 7.03.

Characterizations

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DMX-400 spectrometer. Elemental analysis of different terpolymers was performed on a Vario EL III micro analyzer. Thermogravimetric analysis (TGA) was conducted through a METTLER TOLEDO TGA2 instrument. The thermal stability of the samples was determined by measuring their weight loss at a heating rate of $10^\circ\text{C min}^{-1}$ from 25 to 500°C using 3 mg sample under a nitrogen atmosphere. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit at a heating rate of $10^\circ\text{C min}^{-1}$ from 25 to 350°C , under argon. Ultraviolet-visible (UV-vis) absorption spectra of solution in chloroform and thin film on a quartz substrate were measured using Shimadzu UV-2500 recording spectrophotometer. The simulated chemical geometry of the

polymer monomers was conducted using the Gaussian 09 program package at B3LYP/(def2svp) level. The electrochemical cyclic voltammetry was conducted on a CHI voltammetric analyzer, in a 0.1 mol L⁻¹ acetonitrile solution of tetrabutylammonium hexafluorophosphate (*n*-Bu₄NPF₆) at a potential scan rate of 100 mV s⁻¹. The conventional three electrode configuration consists of a platinum working electrode, a platinum wire counter electrode, and an Ag/AgCl wire pseudo-reference electrode. The samples were coated on the platinum sheet of working electrode. The reference electrode was checked versus ferrocenium-ferrocene (Fc⁺/Fc) as internal standard as recommended by IUPAC (the vacuum energy level: 24.8 eV). All the solutions were deaerated by bubbling nitrogen gas for a few minutes prior to the electrochemical measurements. HOMO energy levels were calculated from the equation of $E_{\text{HOMO}} = -(4.80 + E_{\text{ox}})$ eV, and LUMO from $E_{\text{LUMO}} = -(4.80 + E_{\text{re}})$ eV. Photoluminescence spectra were carried out using Edinburgh FLS980 spectrophotometer. *J-V* curves of PSCs were measured on a computer-controlled Keithley 2400 Source Measure Unit. Oriel Sol3A Class Solar Simulator (model, Enlitech SS-F5-3A) with a 450 W xenon lamp and an air mass 1.5 filter was used as the light source. The light intensity was calibrated to 100 mW cm⁻² by a silicon reference cell. EQE spectra was measured by Solar Cell Spectral Response Measurement System QE-R3-011 (Enli Technology, Taiwan). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell. The contact angle measurements were performed through KRUSS DSA1005 contact angle analyzer. Distilled deionized water and diiodomethane were employed as probe liquids. The surface energy was calculated via Owens-Wendt model. Blend film morphologies were characterized via Bruker Dimension ICON atomic force microscopy.

Fabrication of Photovoltaic Devices

OSCs in inverted structure of ITO/ZnO/active layer/MoO₃/Ag were fabricated. ITO (patterned indium tin oxide) glass was cleaned in an ultrasonic bath with acetone and isopropanol solvents, and treated in an ultraviolet-ozone chamber for 30 min. ZnO was deposited through spin-coating onto ITO glass at 4000 rpm followed by

thermal treatment at 200°C for 1 h. The thickness of ZnO layer was calculated as 35 nm. Afterwards, the active layer was spin-coated. Finally, a layer of *ca.* 8 nm MoO₃ and then a Ag layer of *ca.* 100 nm were evaporated subsequently under high vacuum (*approx.* 8×10⁻⁵ Pa). The fabricating processes for both of OSCs based on MBTIC-4F and MBTIC-4Cl were identical. PBDB-T:FUEAs (1:1.5, w/w) with total concentration of 12 mg mL⁻¹ mixed in chloroform solution were spin-coated at 1600 rpm to form active layers. 0.75 vol% of 1-chloronaphthalene (1-CN) was employed as solvent additive. After spin-coating, the active layers were baked at 130°C for 10 min. The thickness of active layers and buffer layers was measured with stylus profiler (KLA Tencor P-7). For blend films based on MBTIC-4F and MBTIC-4Cl, the thicknesses were both detected at around 110 nm, respectively.

Hole- and Electron-Only Devices for SCLC Measurements

Hole and electron mobility were measured using the space charge limited current (SCLC) method. The hole-only devices with the device structure of ITO/PEDOT:PSS/active layer/Au were used to measure the hole mobility and the electron-only devices were fabricated with the configuration of ITO/ZnO/active layer/PDINO/Al. And the processing details of blend films were same with the fabricating conditions of OSCs. The hole and electron mobilities were calculated by Mott-Gurney equation.

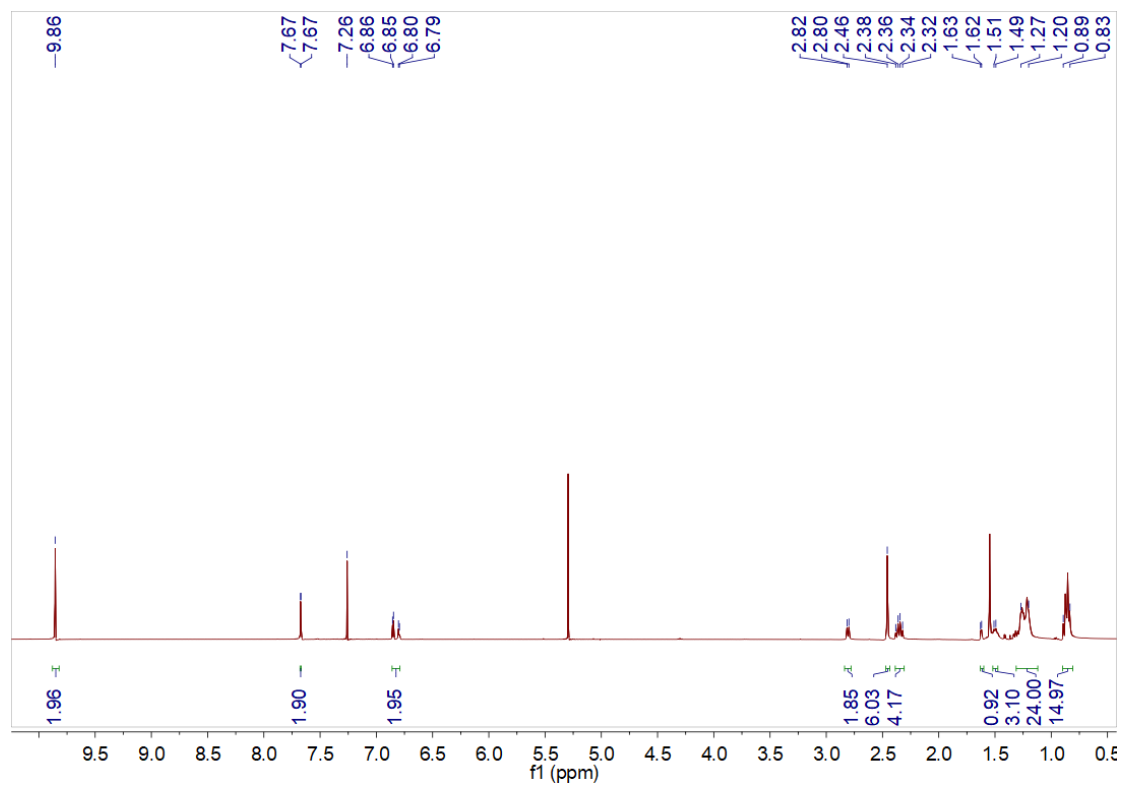


Figure S1. ^1H NMR spectrum of dialdehyde intermediate (CDCl_3 , 400 MHz).

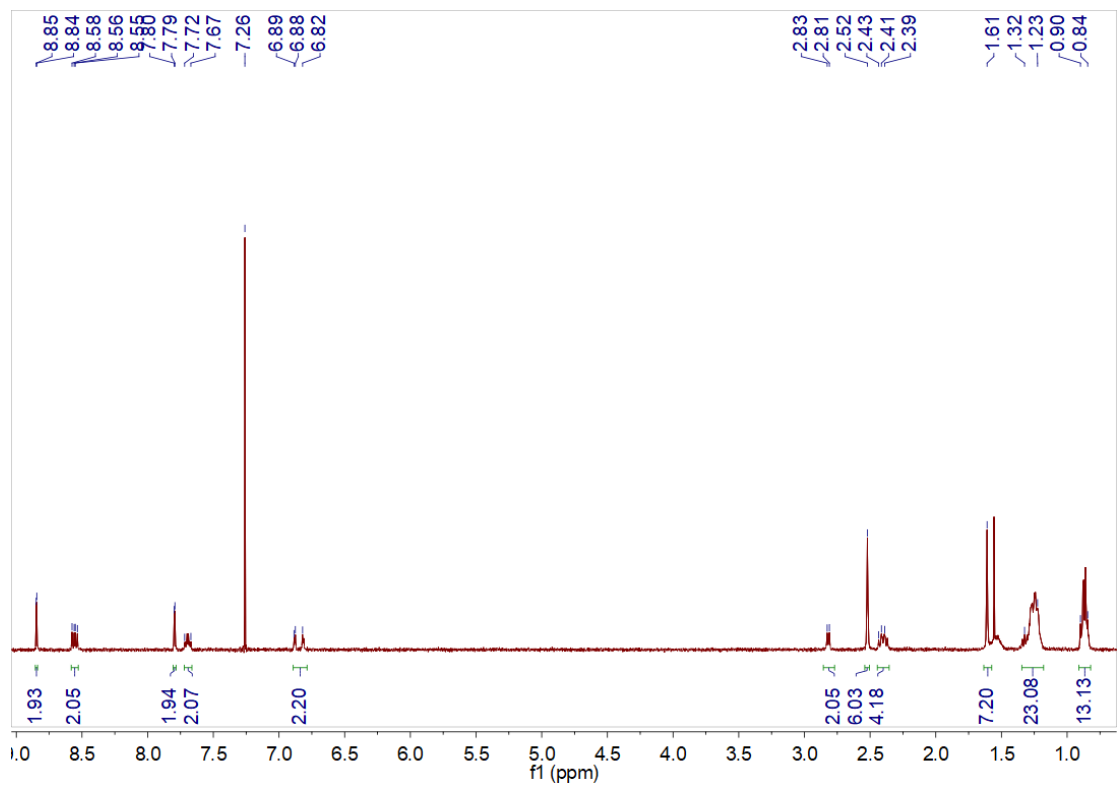


Figure S2. ^1H NMR spectrum of MBTIC-4F (CDCl_3 , 400 MHz).

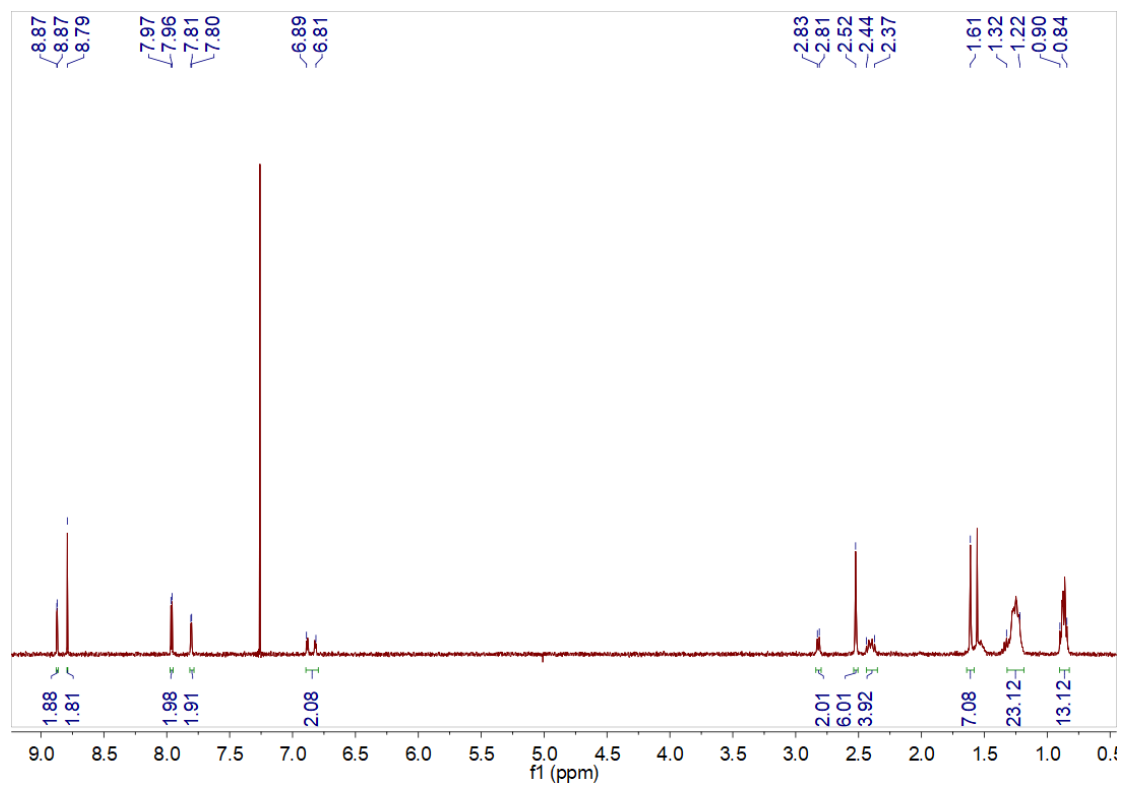


Figure S3. ^1H NMR spectrum of MBTIC-4Cl (CDCl_3 , 400 MHz).

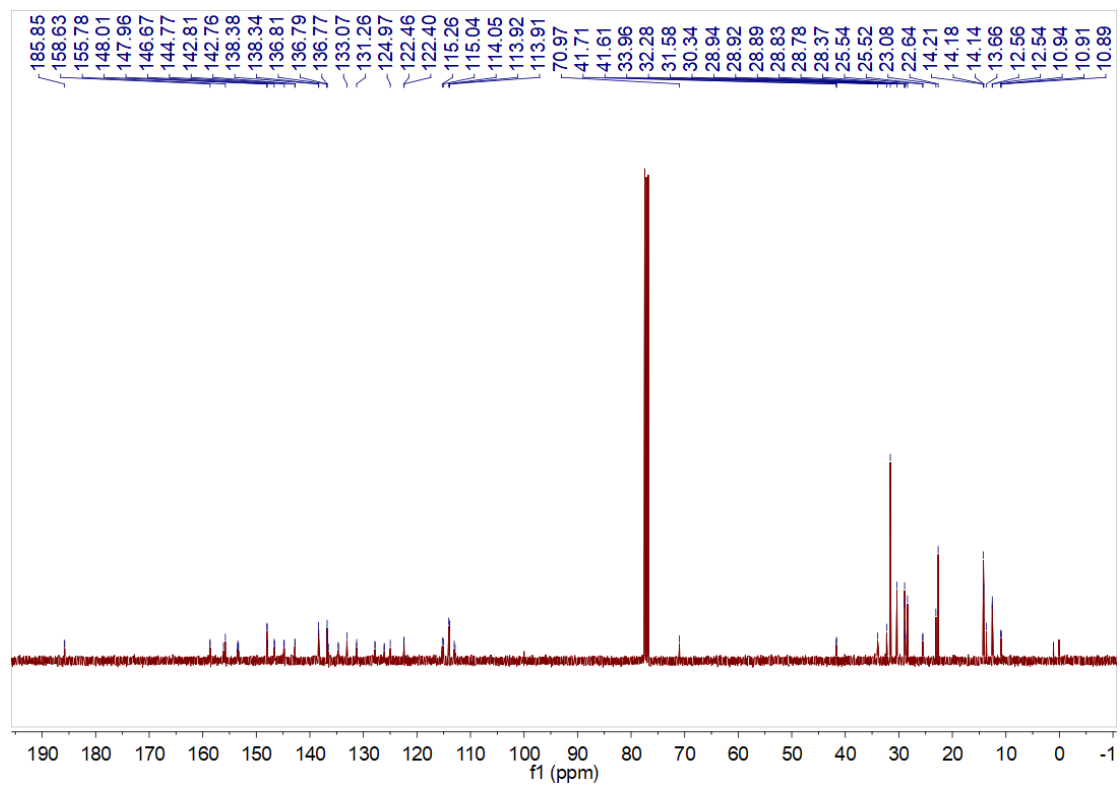


Figure S4. ^{13}C NMR spectrum of MBTIC-4F (CDCl_3 , 400 MHz).

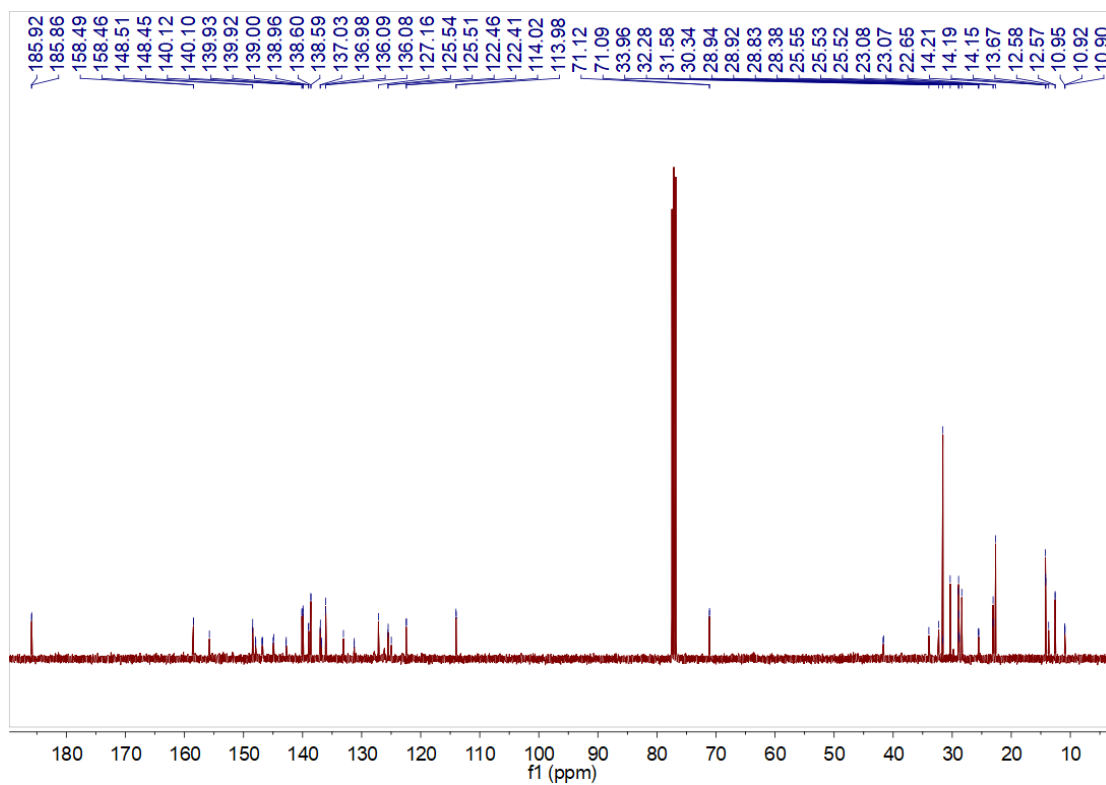


Figure S5. ^{13}C NMR spectrum of MBTIC-4Cl (CDCl_3 , 400 MHz).

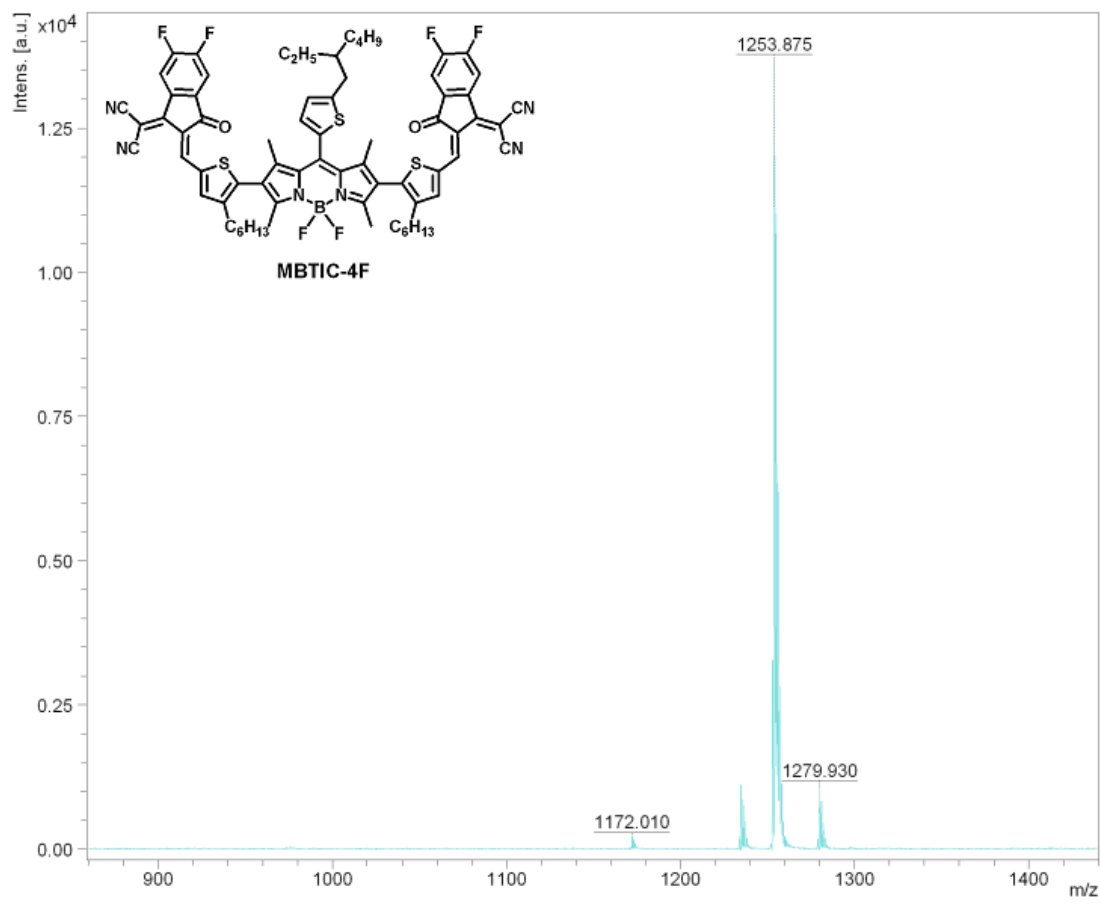


Figure S6. MALDI-TOF mass spectrum of MBTIC-4F.

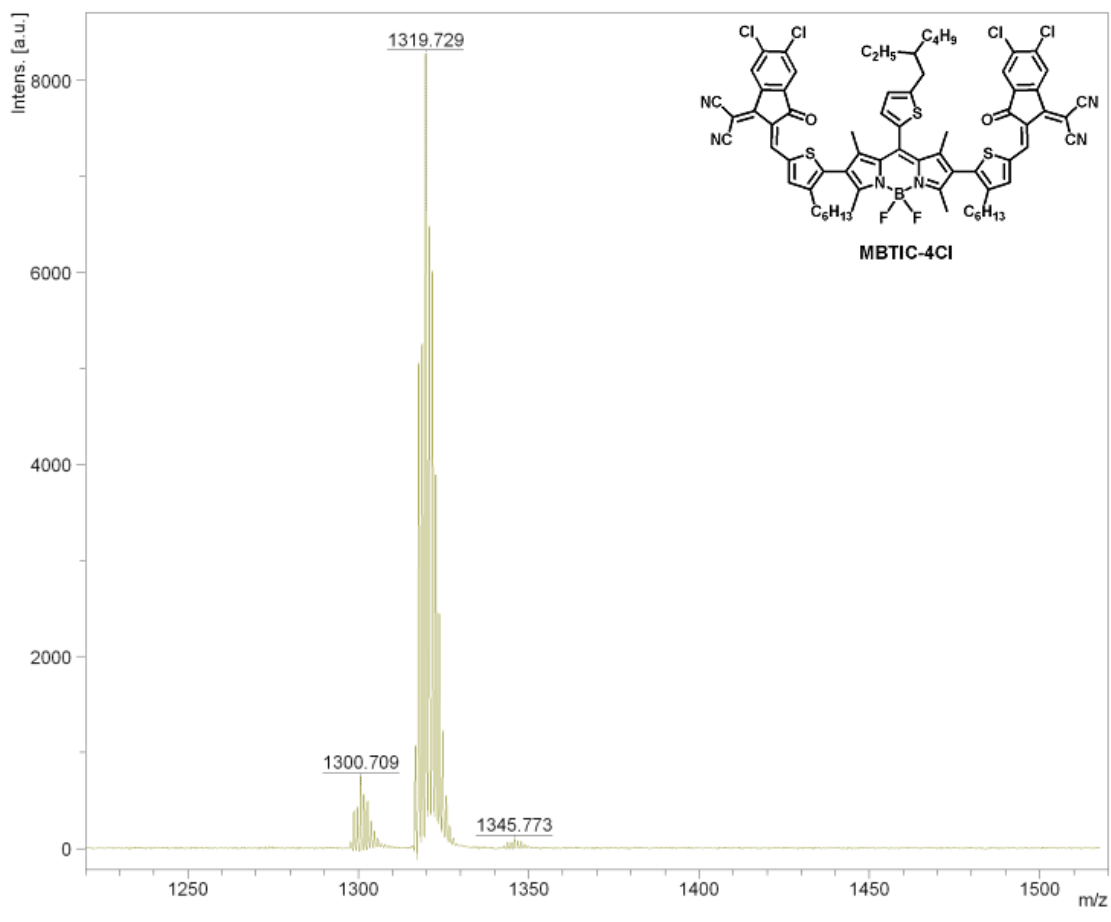


Figure S7. MALDI-TOF mass spectrum of MBTIC-4Cl.

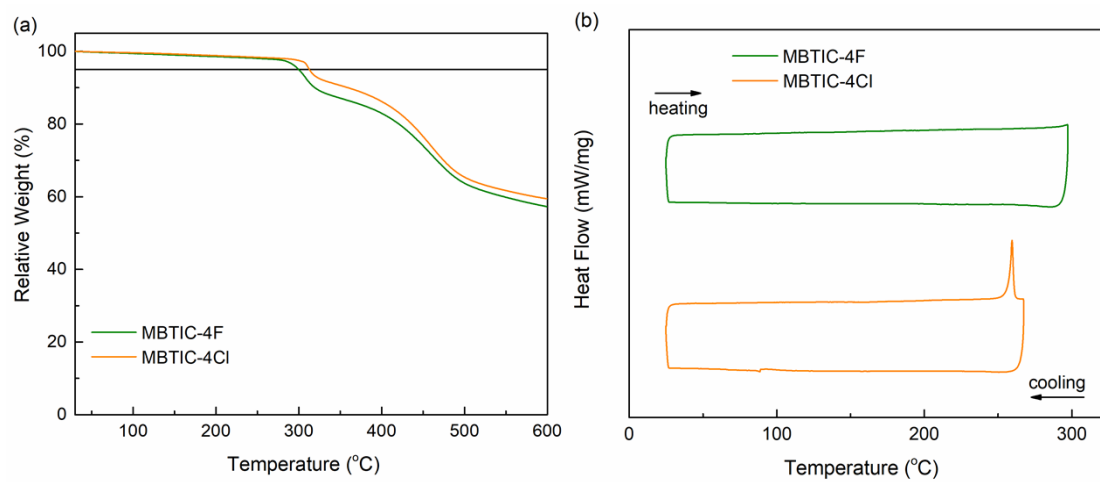


Figure S8. TG (a) and DSC (b) curves of FUEAs.

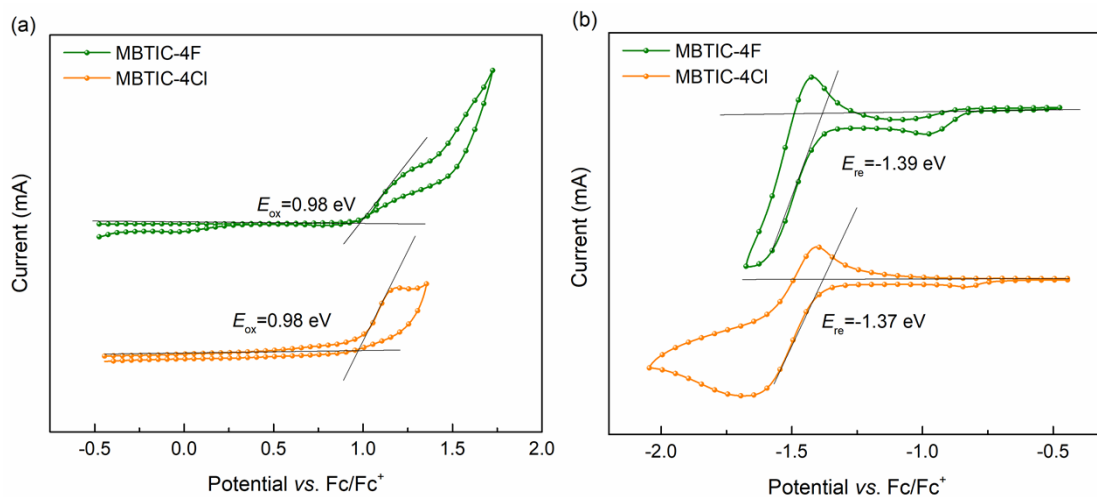


Figure S9. CV curves of FUEAs.

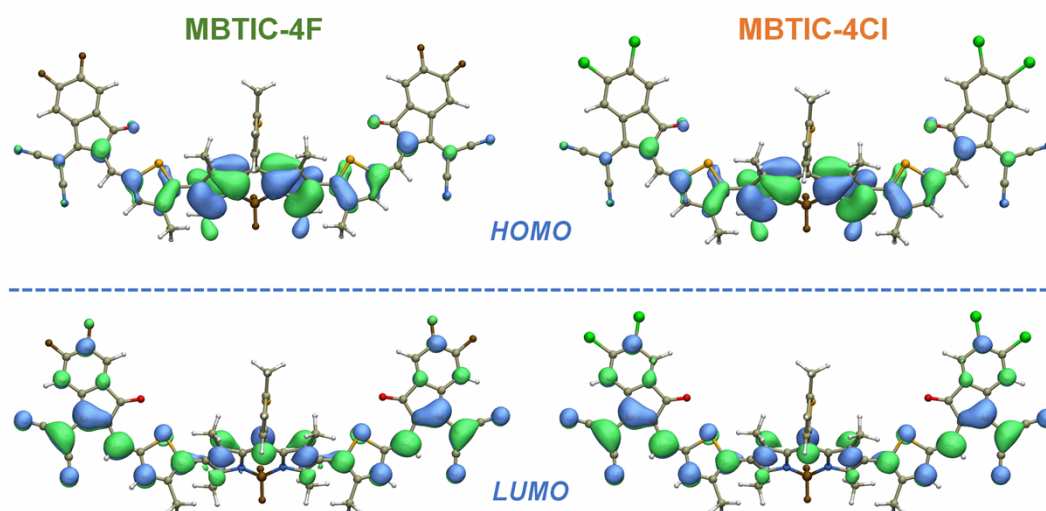


Figure S10. Simulated molecular frontier orbital distributions of FUEAs from DFT calculation.

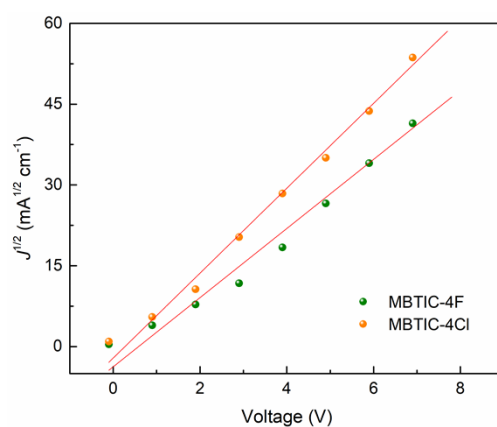


Figure S11. $J^{1/2}$ - V plots fitted by SCLC method of electron-only devices based on FUEAs neat films.

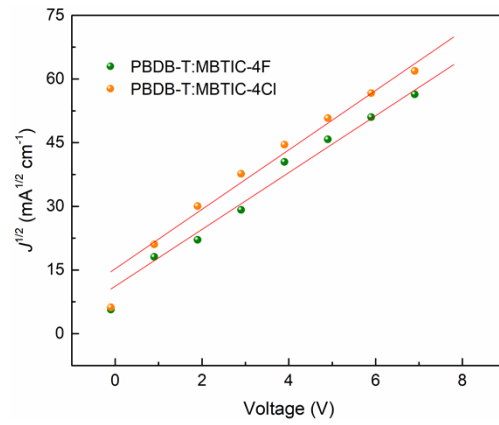


Figure S12. $J^{1/2}$ - V plots fitted by SCLC method of hole-only devices based on FUEAs blend films.

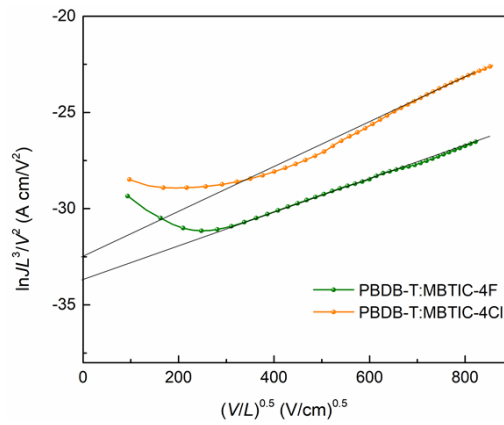


Figure S13. J - V curves fitted by SCLC method of electron-only devices based on FUEAs blend films.

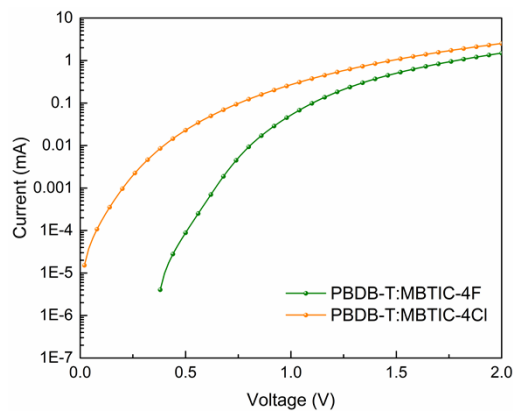


Figure S14. Forward-bias dark current curves of the corresponding devices.

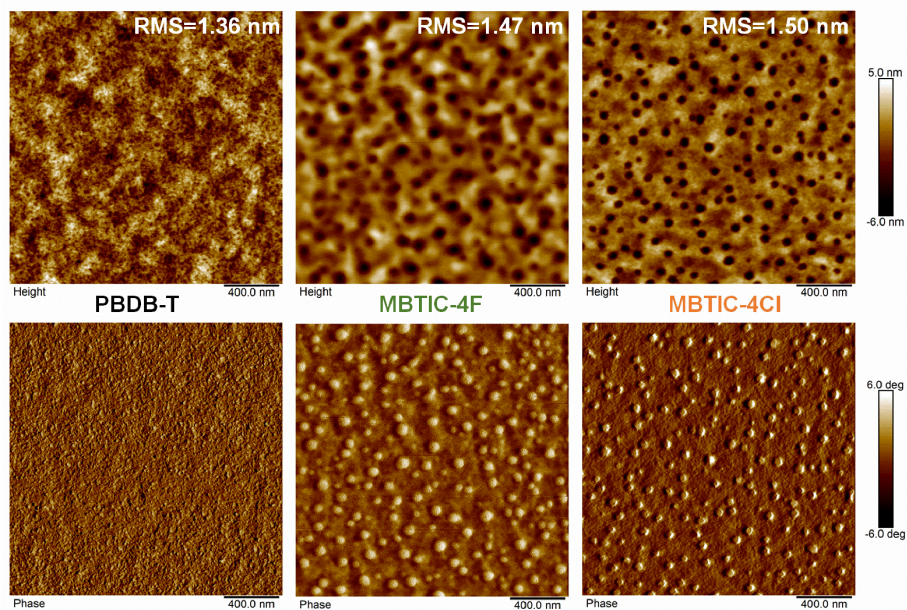


Figure S15. AFM height (top) and phase (bottom) patterns ($2\ \mu\text{m}\times 2\ \mu\text{m}$) of different neat films and the corresponding RMS values.

Table S1. Key parameters from contact angle measurement.

Film surface	ϑ_{water} [°]	ϑ_{oil} [°]	γ [mN m ⁻¹]	χ^{a}	$\gamma_{\text{donor:acceptor}}^{\text{b}}$ [mN m ⁻¹]
PBDB-T	98.4	47.5	35.88	-	-
MBTIC-4F	106.8	49.3	34.71	0.01	0.021
MBTIC-4Cl	103.3	36.5	41.40	0.21	0.47

^a Flory-Huggins interaction parameters between FUEAs and polymer PBDB-T.

^b Interfacial surface energy in different donor:acceptor pairs calculated from interfacial tension equation.