Electronic supplementary information for

Estimating donor:acceptor compatibility for polymer solar cells through non-fused ring acceptors with benzoxadiazole core and different halogenated terminal groups

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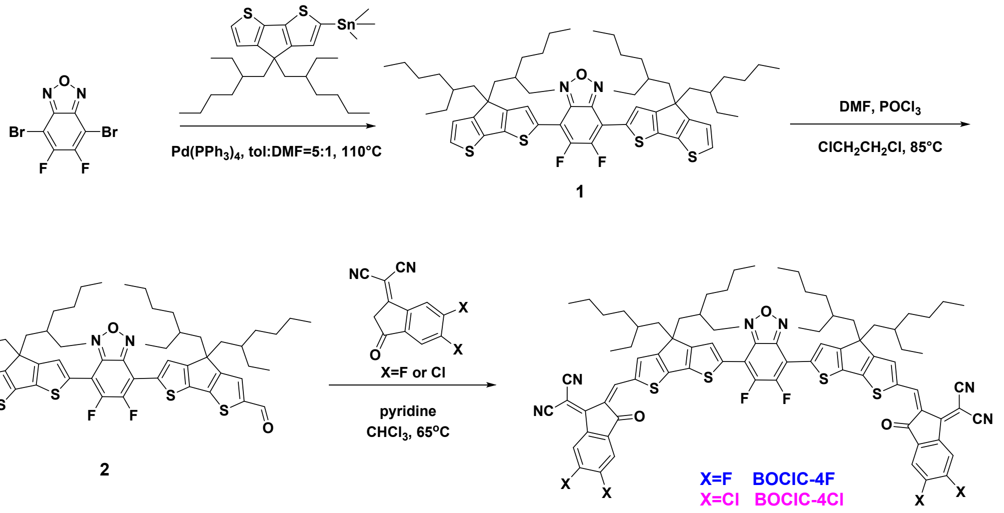
Materials and characterizations

All solvents were commercially available and used without further purification. PBDB-T and PM6 were purchased from Zhiyan Technology Co., Ltd (Nanjing, China) and Vizu Chem Co., Ltd (Shanghai, China), respectively.

^{1}H NMR spectra was measured on a BRUKER AVANCE spectrometer. Elemental analysis was performed on a Vario EL III microanalyzer. Mass spectra was measured through Bruker Daltonics BIFLEX III matrix-assisted laser desorption ionization time-of-flight mass spectrometer (MALDI-TOF). 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 electrochemical cyclic voltammetry was conducted on a CHI voltammetric analyzer, in a 0.1 mol L^{-1} acetonitrile solution of tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6) 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 $E_{\mathrm{HOMO}}=-(4.80+E_{\mathrm{onset(ox)}})$ eV, and LUMO from $E_{\mathrm{LUMO}}=-(4.80+E_{\mathrm{onset(re)}})$ 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 energies were calculated via Owens-Wendt model. Blend film morphologies were characterized via Bruker Dimension ICON atomic force microscopy.



Scheme S1. Synthetic routes of BOCIC-4F and BOCIC-4Cl.

Synthesis of BOCIC-4F and BOCIC-4Cl

The synthetic routes for the non-fused ring electron acceptors (NFREAs) of BOCIC-4F and BOCIC-4Cl were depicted in **Scheme S1**. (4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b*']dithiophen-2-yl)trimethylstannane was synthesized according to the literature. 4,7-dibromo-5,6-difluorobenzo[*c*][1,2,5]oxadiazole was purchased commercially.

Synthesis of 4,7-bis(4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b*']dithiophen-2-yl)-5,6-difluorobenzo[*c*][1,2,5]oxadiazole (Compound 1):

In a two-neck bottle, (4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b*']dithiophen-2-yl)trimethylstannane (1.00 g, 1.81 mmol) and 4,7-dibromo-5,6-difluorobenzo[*c*][1,2,5]oxadiazole (220 mg, 0.72 mmol) were dissolved in anhydrous toluene/DMF (*N*,*N*-dimethylformamide) (25 mL/5 mL) under nitrogen atmosphere. Then $Pd(PPh_3)_4$ was added into the mixture, and the mixture was further deoxygenated with nitrogen for 10 minutes. After that, the solution was stirred at 110°C for 6 hours. The reaction was quenched by adding KF aqueous solution and extracted with brine/dichloromethane. The organic layer was dried through $MgSO_4$

and the solvent was removed under reduced pressure. Then, the crude product was purified via silica gel column chromatography with dichloromethane/petroleum ether (1:3, v/v) as eluent. After drying under vacuum, the product obtained as red oil with yield of 55% (550 mg). ^{1}H NMR (400 MHz, $CDCl_3$), *δ* (TMS, ppm): 8.21 (t, *J* = 8 Hz 2H), 7.27 (d, *J* = 4 Hz, 2H), 7.00 (dd, *J* = 8Hz, 4 Hz, 2H), 2 (m, 8H), 0.97-0.85 (m, 36H), 0.75-0.70 (m, 12H), 0.63-0.59 (m, 12H).

Synthesis of 6,6'-(5,6-difluorobenzo[*c*][1,2,5]oxadiazole-4,7-diyl)bis(4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b*']dithiophene-2-carbaldehyde) (Compound 2): In a 50 mL Schlenk bottle, 5 mL anhydrous DMF was added and purged with nitrogen for 3 times. Then 1 mL $POCl_3$ was added into DMF and stirred at 0°C for 2 h. Compound 1 (600 mg, 0.63 mmol) in dichloroethane (15 mL) was added into the solution and heated at 85°C overnight. After cooling down to room temperature, the reaction mixture was added into saturated $NaHCO_3$ solution (70 mL) drop by drop. After that, the resulting mixture was extracted through brine/dichloromethane and the organic layer was dried over $MgSO_4$. By concentrating under reduced pressure, the crude conduct was further purified through silica gel column chromatography by using dichloromethane/petroleum ether (3:1, v/v) as eluent. The product was afforded as dark-red solid after drying under vacuum with a yield of 73% (440 mg). ^{1}H NMR (400 MHz, CDCl3), δ (TMS, ppm): 9.88 (s, 2H), 8.27 (m, 2H), 7.63 (m, 2H), 2.08-1.94 (m, 8H), 0.97-0.95 (m, 36H), 0.73-0.61(m, 24H).

Synthesis of BOCIC-4F:

Compound 2 (300 mg, 0.3 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (IC-2F, 400 mg, 1.80 mmol) was dissolved into 20 mL anhydrous $CHCl_3$ in a two-neck bottle. The mixture was further deoxygenated with purging nitrogen for 10 minutes and then 1 mL anhydrous pyridine was added. Then, the mixture was reflux at 65°C for 4 hours. After cooling down to room temperature, the crude product was diluted in dichloromethane and washed with brine for 3 times. The organic phase was dried through $MgSO_4$ and the solvent was removed under reduced pressure. After that, the residue was purified by silica gel column chromatography with dichloromethane/petroleum ether (2:1, v/v) as eluent. The crude compound was further recrystallized with $CHCl_3$/methanol to afford BOCIC-4F (150 mg, 35%) as dark-blue solid. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.93 (s, 2H), 8.55 (s, 2H), 8.36 (s, 2H), 7.71 (s, 4H), 2.07(s, 8H), 0.99(m, 36H), 0.74-0.63 (m, 24H). ^{13}C NMR (101 MHz): 139.42 (s), 138.20–138.00 (m), 137.06 (s), 100.00 (s), 77.58–77.16 (m), 77.10 (s), 76.79 (s), 76.35 (s), 28.54 (d, *J*=6.8 Hz), 27.39 (s), 22.87 (d, *J*=1.5 Hz), 14.28–13.95 (m), 10.84–10.34 (m). MALDI-TOF (m/z): M^+ calculated at 1436.49, found at 1436.5; Anal. Calcd for $C_{82}H_{78}F_6N_6O_3S_4$: C 68.50, H 5.47, N 5.85, S 8.92; found: C 68.18, H 5.80, N 5.49, S8.64.

Synthesis of BOCIC-4Cl:

The synthetic procedure of BOCIC-4Cl was similar with BOCIC-4F by using Compound 2 (300 mg, 0.3 mmol) and 2-(5,6-dichloro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (IC-2Cl, 460 mg, 1.80 mmol) as raw materials. BOCIC-4Cl was produced as dark-blue solid with a yield of 30% (150 mg). ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.95 (s, 2H), 8.77 (s, 2H), 8.35 (m, 2H), 7.96 (s, 2H), 7.71(s, 2H), 2.07(m, 8H), 0.98-0.94 (m, 24H), 0.73-0.61 (m, 24H). ^{13}C NMR (101 MHz): 139.42 (s), 138.20–138.00 (m), 137.06 (s), 100.00 (s), 77.58–77.16 (m), 77.10 (s), 76.79 (s), 76.35 (s), 28.54 (d, *J*=6.8 Hz), 27.39 (s), 22.87 (d, *J*=1.5 Hz), 14.28–13.95 (m), 10.84–10.34 (m). MALDI-TOF (m/z): M^+ calculated at 1500.37, found at 1500.4; Anal. Calcd for $C_{82}H_{78}Cl_4F_2N_6O_3S_4$: C 65.50, H 5.23, N 5.59, S 8.53; found: C 65.18, H 4.90, N 5.90, S5.59.

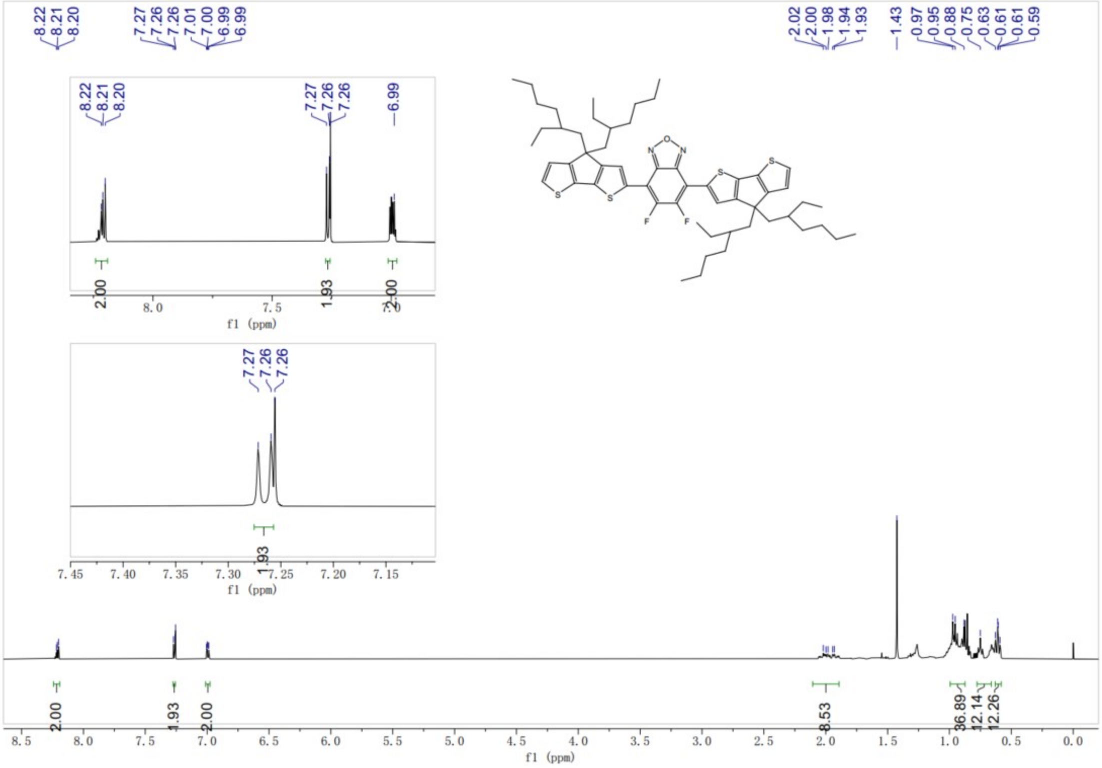


Figure S1. ^{1}H NMR spectrum of intermediate 1.

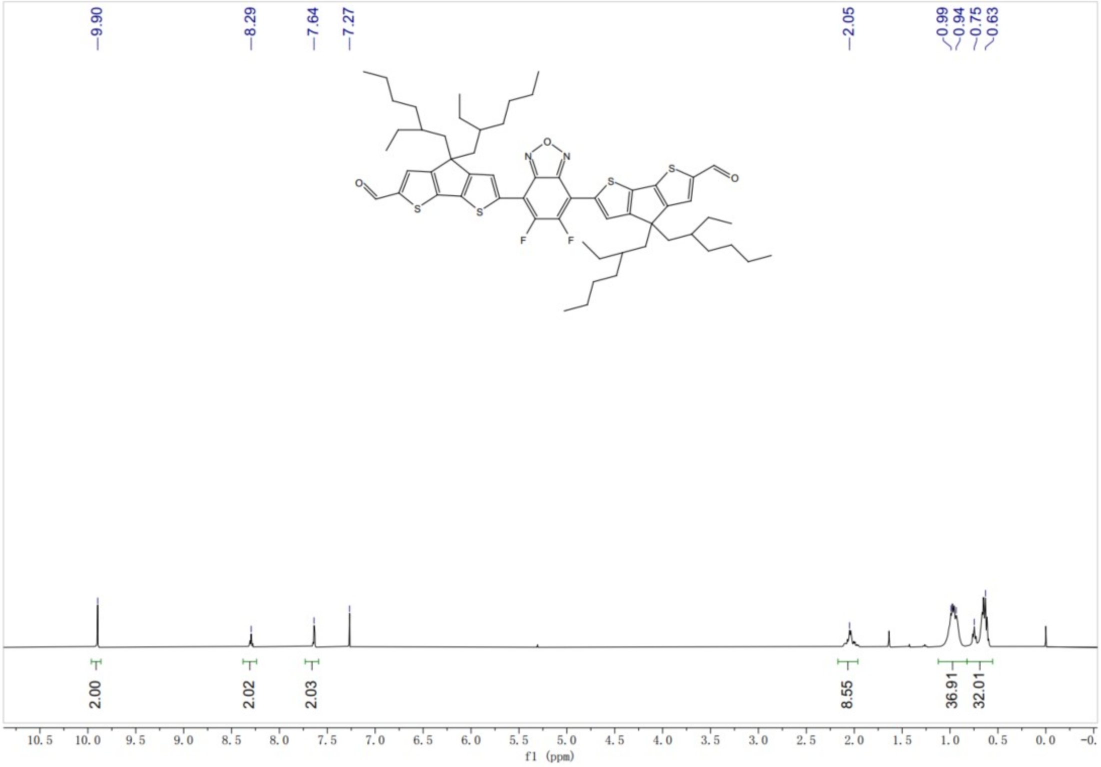


Figure S2. ^{1}H NMR spectrum of intermediate 2.

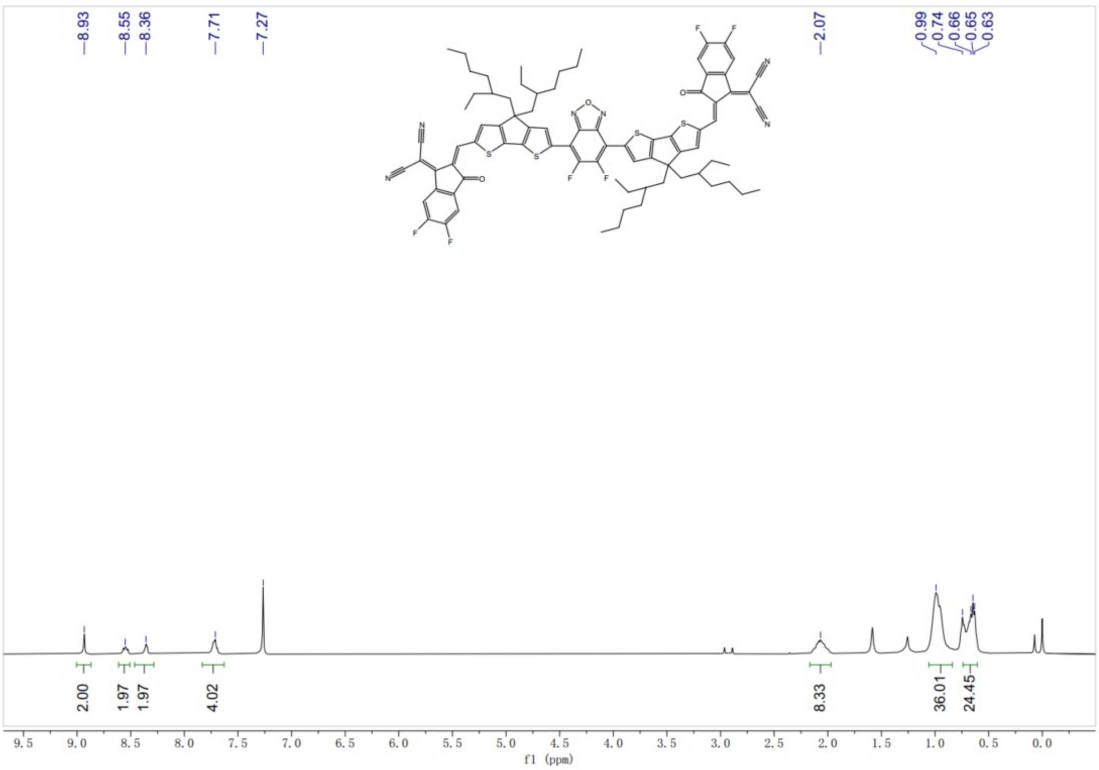


Figure S3. ^{1}H NMR spectrum of BOCIC-4F.

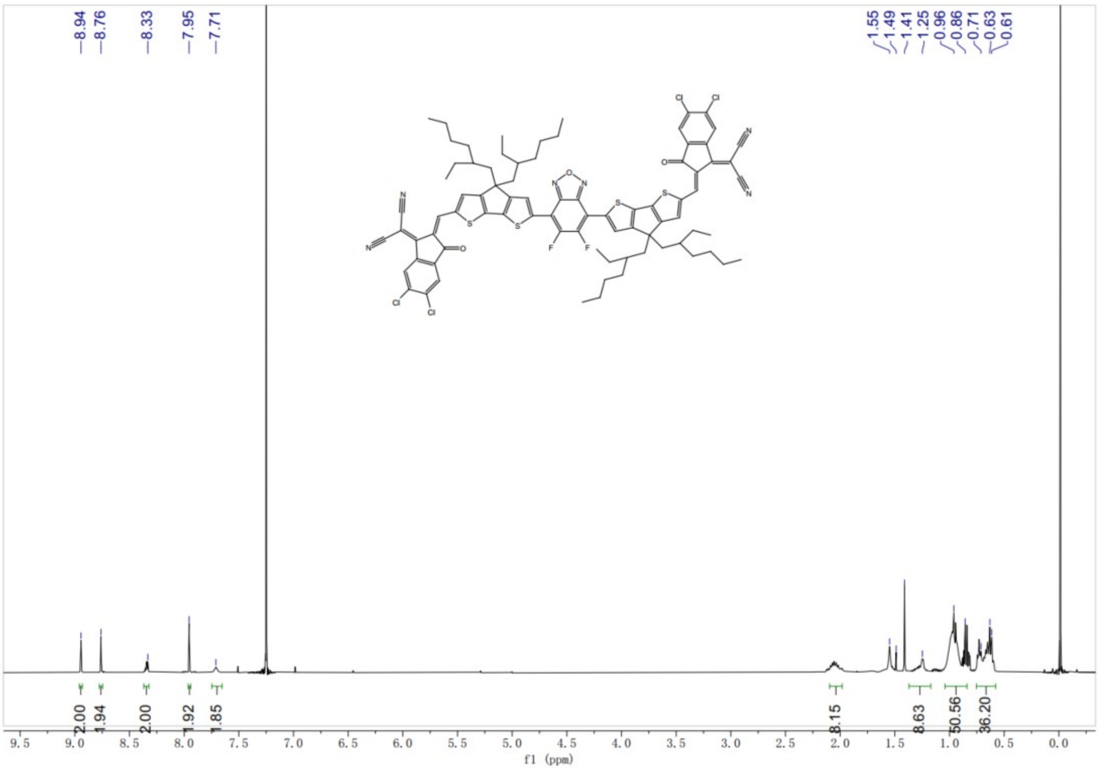


Figure S4. ^{1}H NMR spectrum of BOCIC-4Cl.

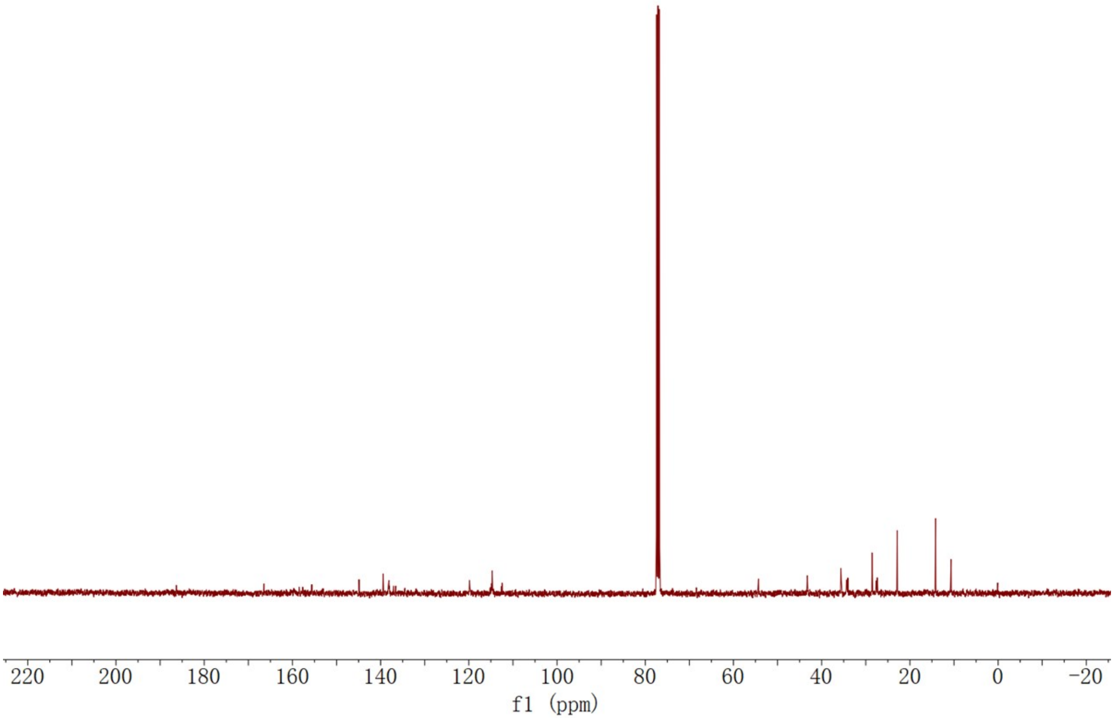


Figure S5. ^{13}C NMR spectrum of BOCIC-4F.

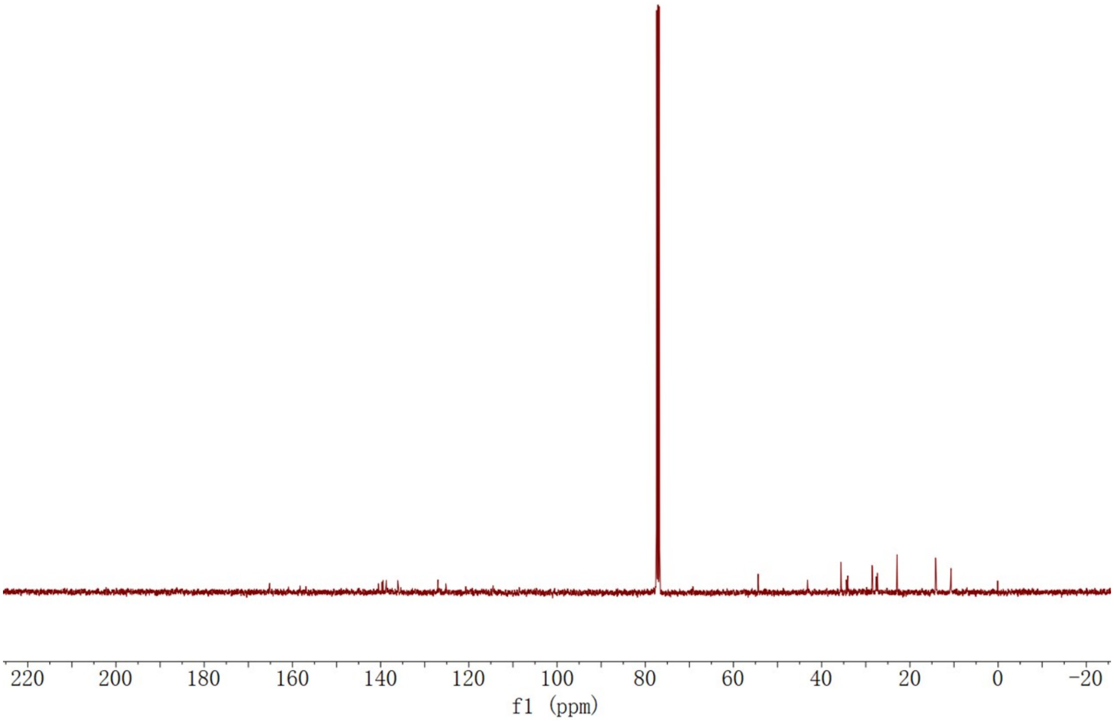


Figure S6. ^{13}C NMR spectrum of BOCIC-4Cl.

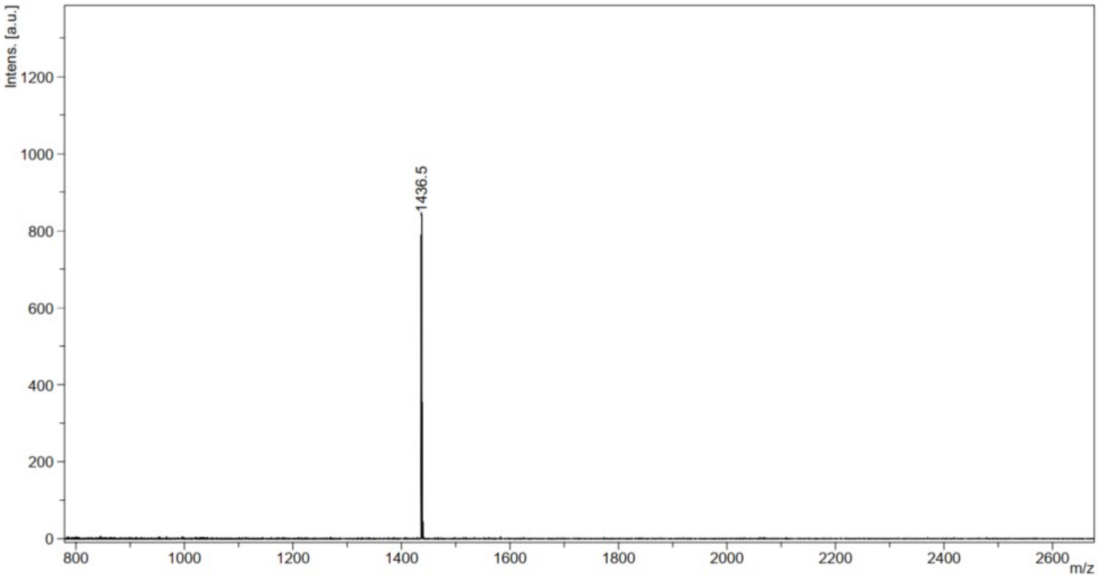


Figure S7. MALDI-TOF MS spectrum of BOCIC-4F.

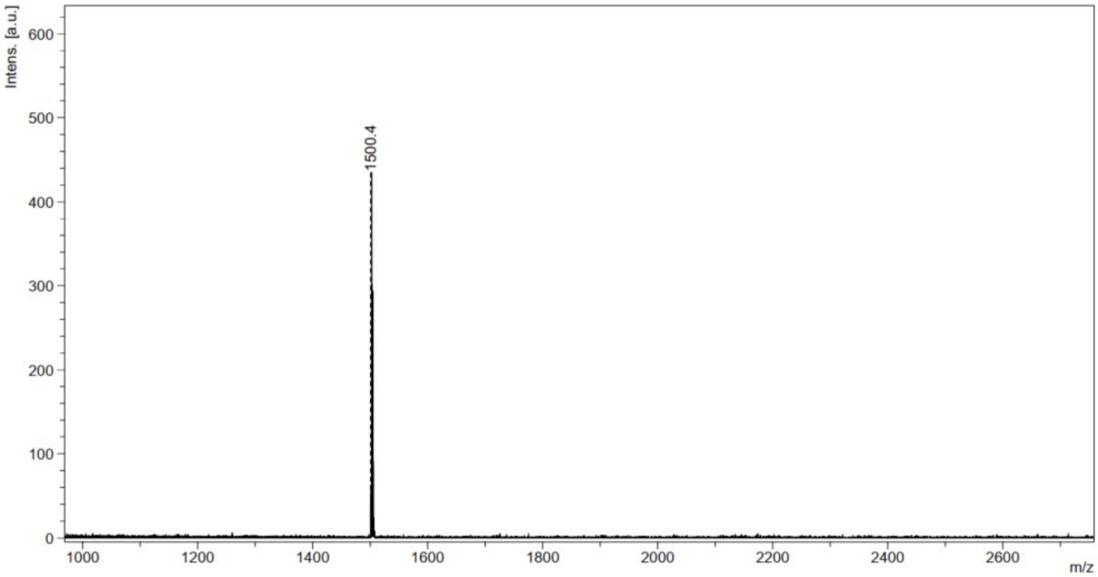


Figure S8. MALDI-TOF MS spectrum of BOCIC-4Cl.

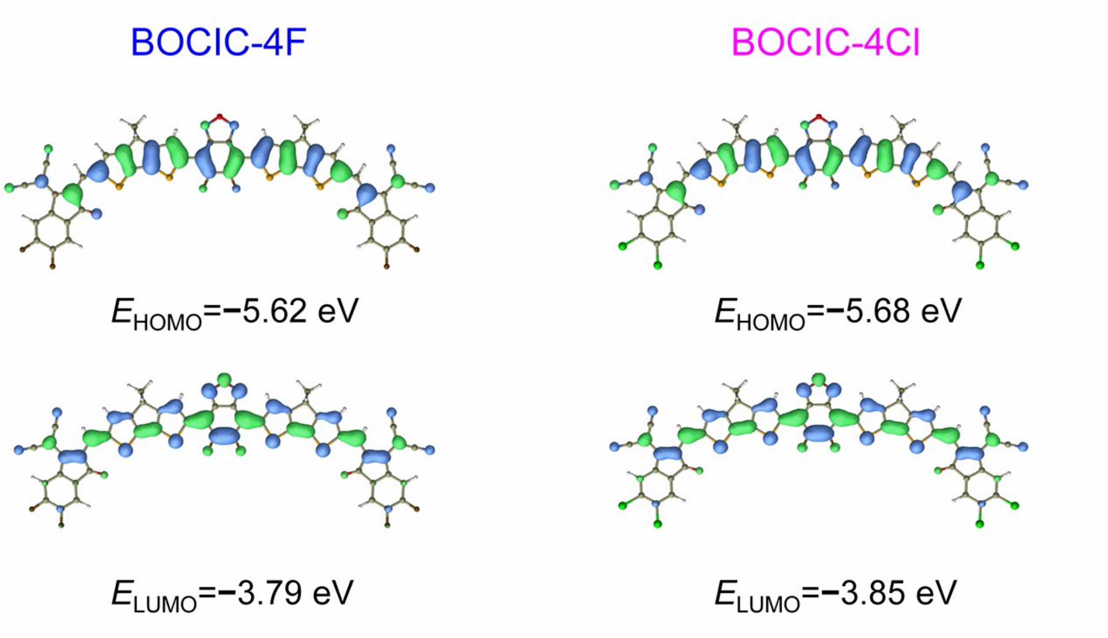


Figure S9. Simulated frontier molecular orbitals of BOCIC-4F and BOCIC-4Cl.

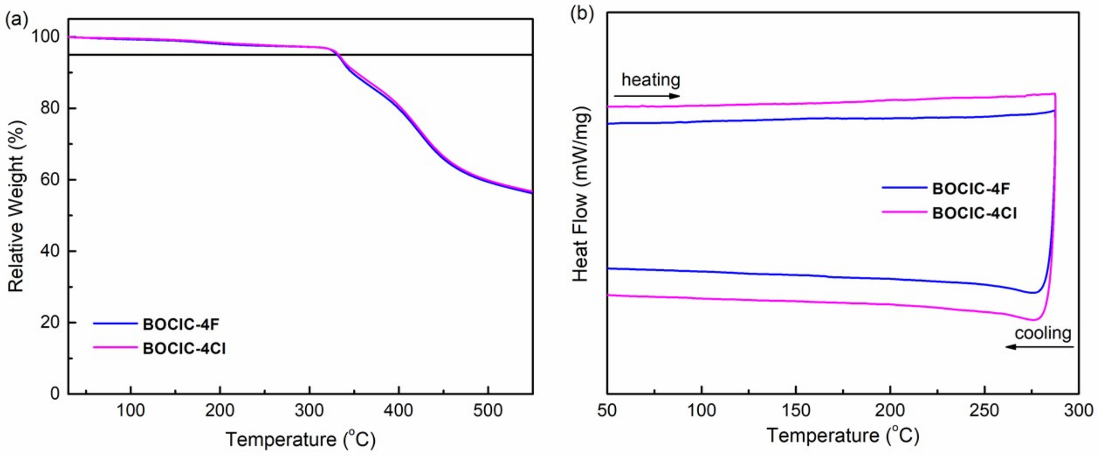


Figure S10. TGA (a) and DSC (b) curves of the NFREAs.

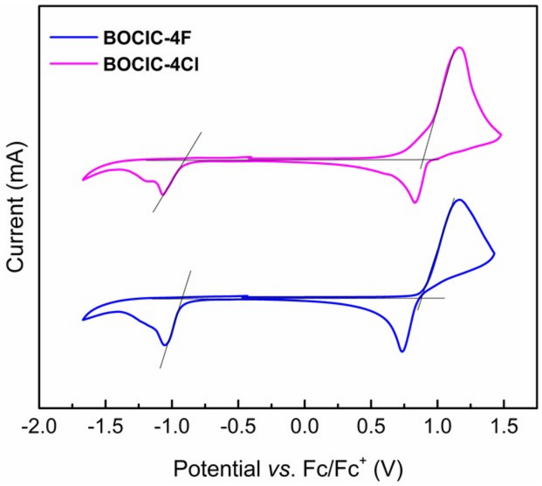


Figure S11. CV curves of the NFREAs.

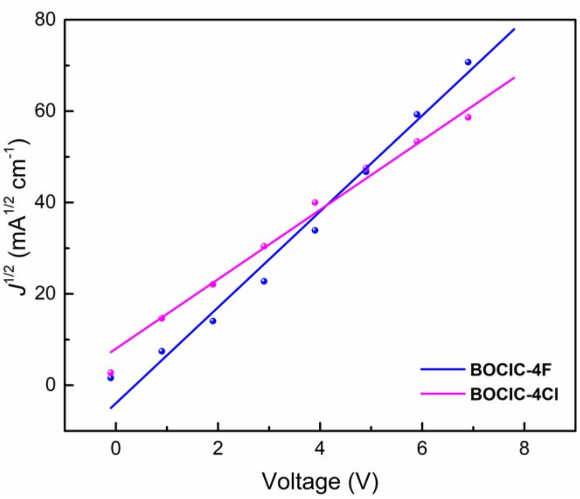


Figure S12. $J^{1/2}$-V curves of electron-only devices based on NFREAs neat films fitted by SCLC method.

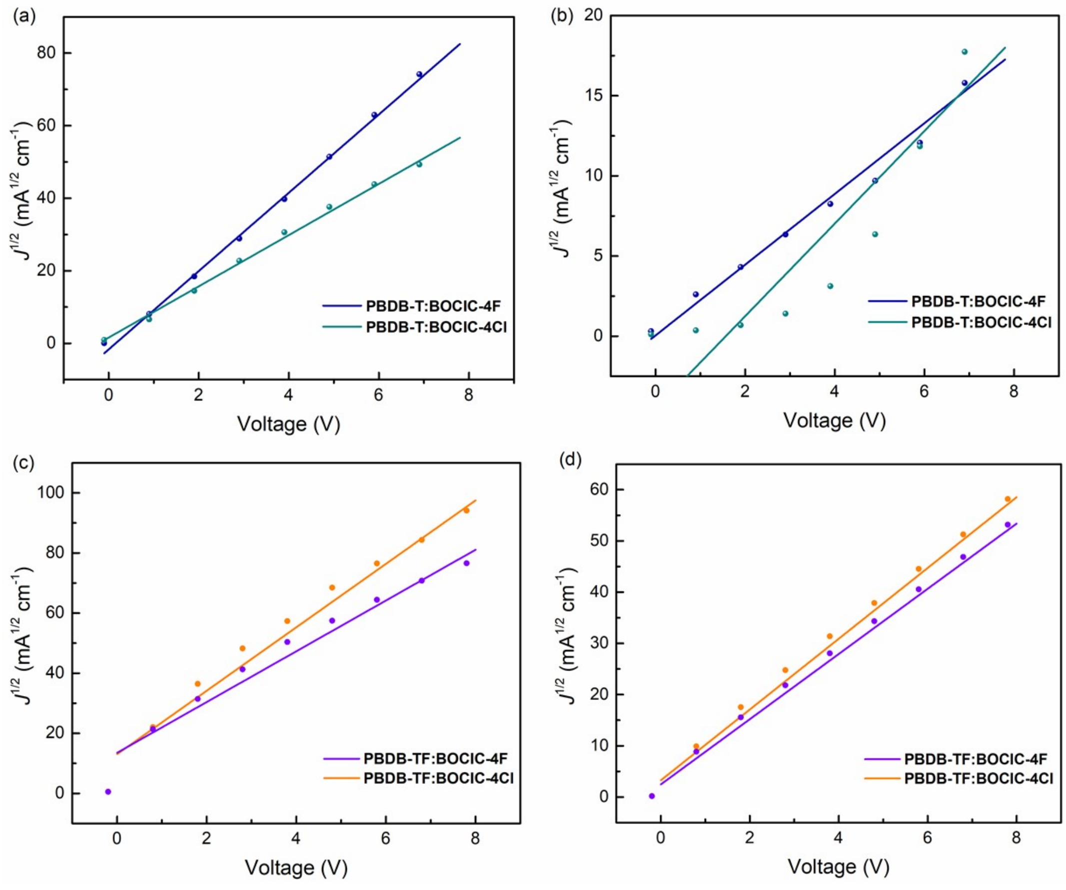


Figure S13. $J^{1/2}$-V curves fitted by SCLC method for hole-only devices based on PBDB-T:NFREAs (a), PBDB-TF:NFREAs (c) and electron-only devices based on PBDB-T:NFREAs (b) and PBDB-TF:NFREAs (d), respectively.

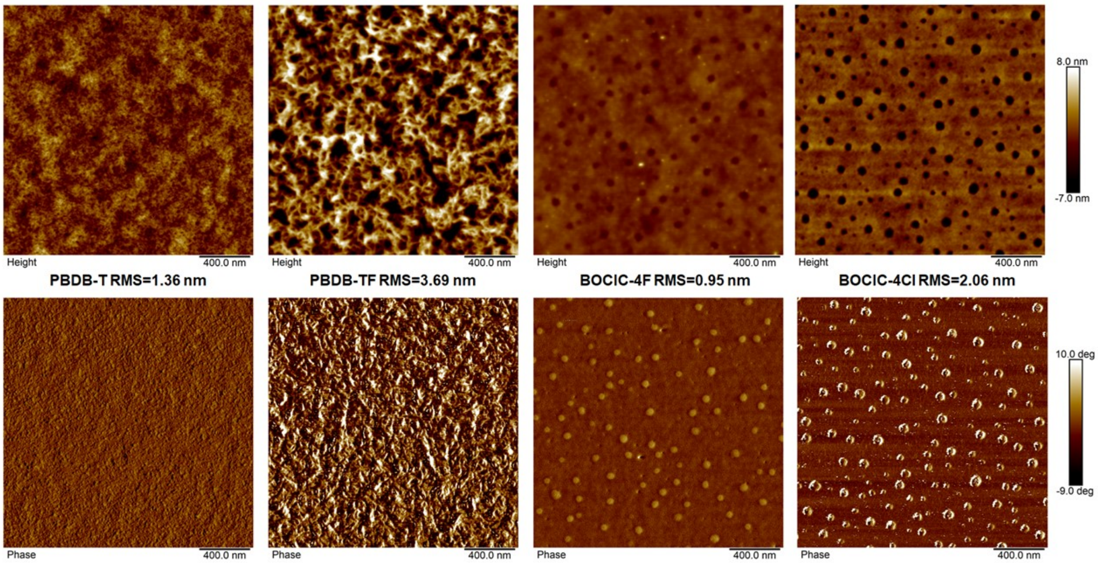


Figure S14. AFM height (top) and phase (bottom) patterns (2×2 μm^2) of different neat films.

Table S1. Key parameters of contact angle measurements.

film surface	ϑ_{water} [°]	ϑ_{DIM} [°]	γ_d [mN m^{-1}]	γ_p [mN m^{-1}]	γ [mN m^{-1}]
PBDB-T	98.4	47.5	35.66	0.20	35.86
PBDB-TF	102.7	53.2	32.47	0.06	32.53
BOCIC-4F	101.2	42.9	38.12	0.005	38.13
BOCIC-4Cl	105.4	37.3	40.94	0.19	41.13