Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Over 14% Efficiency Nonfullerene All-Small-Molecule Organic Solar Cells Enabled by Improving the Ordering of Molecular Donor via Side-Chains Engineering

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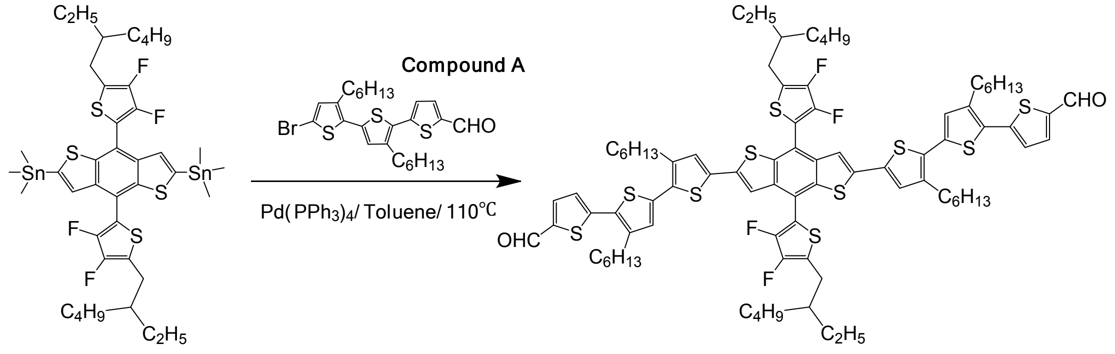
Experimental section

Materials: compound 1, compound A, compound C, Y6, N3 were purchased from Solarmer Materials Inc. Toluene, piperidine, chloroform were commercially available from China National Medicines Corporation Ltd. Pd(PPh$_3$)$_4$ was obtained from Energy Chemical. All the solvents, materials were used without further purification. PEDOT:PSS (Clevios P VP 4083) was obtained from J&K Chemicals Inc. The indium-doped tin oxide (ITO)-coated glass (1.1 mm thick, ≤15Ω/square) were purchased from Wuhu Token Sciences Company.

Synthesis route: the synthesis route of BT-2F exhibited as follows.



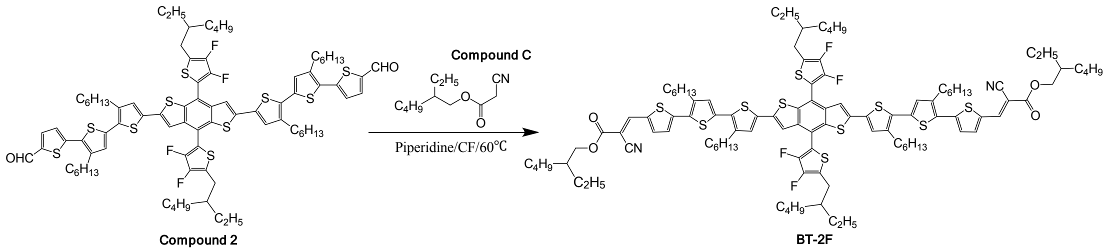
Compound 1

Compound 2

Scheme S1 The synthetic route of compound 2

Synthesis of compound 2: compound 1 (0.10g, 0.102mmol), compound A (0.16g, 0.307mmol) and Pd(PPh$_3$)$_4$ (15mg) were added to a flask with three necks under nitrogen, then the toluene (25ml) was injected. After stirring at 110°C for 12 hours, the mixture was quenched with water, extracted with CHCl$_2$ (100ml×3). The organic layer dried over anhydrous MgSO$_4$. After removal of the solvent, the residue was purified by silica gel chromatography (dichloromethane: hexane=2: 1) to give a red solid (0.12g, 76%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.88 (d, *J* = 1.2 Hz, 2H), 7.70 (dd, *J* = 4.0, 1.9

Hz, 2H), 7.34 (d, J = 1.9 Hz, 1H), 7.22 (d, J = 3.9 Hz, 2H), 7.11 (s, 2H), 7.03 – 6.98 (m, 3H), 2.82 (d, J = 7.0 Hz, 6H), 1.80 – 1.63 (m, 11H), 1.58 (s, 2H), 1.52 – 1.29 (m, 39H), 1.05 – 0.85 (m, 24H). ^{19}F NMR (377 MHz, $CDCl_3$): δ -130.40 (dd, J = 13.6, 8.0 Hz), -140.13 (d, J = 13.7 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): δ 182.56, 146.13, 146.00, 142.58, 142.28, 142.19, 141.24, 141.19, 139.30, 138.34, 137.89, 136.84, 136.11, 135.80, 135.16, 134.97, 130.96, 129.70, 129.35, 129.22, 129.18, 128.94, 128.85, 126.86, 125.94, 125.85, 118.39, 77.34, 77.23, 77.03, 76.71, 40.54, 32.51, 31.66, 30.39, 30.24, 30.09, 29.80, 29.64, 29.26, 28.85, 25.92, 23.02, 22.61, 14.18, 14.08, 10.88, 0.00. m/z:1534.47 (M^+).



Scheme S2 The synthetic route of BT-2F

Synthesis of BT-2F: compound 2 (0.10g, 0.065mmol), compound C (0.5g, 2.53mmol), and 10 drops piperidine were dissolved in $CHCl_3$, then mixture was degassed 6 times with nitrogen. After stirring at 60°C over night, the mixture was quenched with water, extracted with $CHCl_2$ (100ml×3). The organic layer dried over anhydrous $MgSO_4$. After removing the solvent, the residue was purified by silica gel chromatography (dichloromethane: hexane=2: 1) to give a red solid (0.11g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 2H), 7.78 (d, J = 4.1 Hz, 2H), 7.38 (s, 2H), 7.28 (s, 4H), 7.16 (s, 2H), 7.06 (s, 2H), 4.31 – 4.16 (m, 4H), 2.93 – 2.76 (m, 13H), 1.81 – 1.65 (m, 10H), 1.58 –

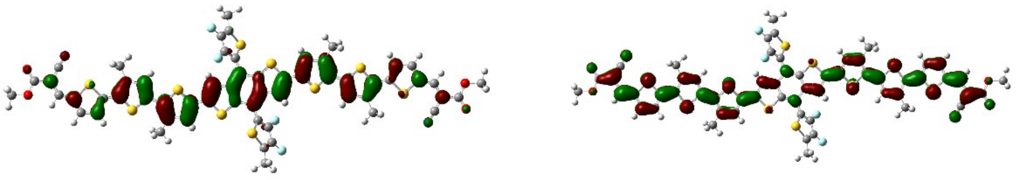
1.28 (m, 40H), 1.06 – 0.88 (m, 32H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -130.40 (d, J = 13.7 Hz), -140.12 (d, J = 13.7 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.15, 146.20, 145.68, 142.91, 141.27, 139.27, 138.24, 137.80, 136.21, 135.02, 134.84, 130.93, 129.58, 129.27, 128.81, 126.11, 121.69, 118.40, 115.93, 97.75, 77.32, 77.01, 76.69, 68.79, 40.53, 38.82, 32.53, 31.65, 30.34, 30.30, 30.22, 30.11, 30.00, 29.71, 29.27, 29.23, 28.93, 28.85, 25.92, 23.78, 23.01, 22.94, 22.60, 22.58, 14.16, 14.07, 14.02, 11.01, 10.87.m/z:1892.73 (M^+).

Characterization and measurements

The absorption profile, DSC curve of BTEC-2F, 2D GIWAX images of BTEC-2F and BTEC-2F:Y6, 1D GIWAX plots data of BTEC-2F, BTEC-2F:Y6 are obtained from our previous work, reference 31. Absorption profile of neat Y6 film, PL of BTEC-2F and BTEC-2F:Y6, AFM, TEM images, carrier mobility and EQE profile of BTEC-2F:Y6 are remeasured in this work. Chemical structure of obtained small molecules and other products were identified by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR (Bruker Avance DPX-300). Spectrophotometer (Perkin-Elmer Lambda 950) was employed to measure the UV-vis absorption spectrums. Photoluminescence spectroscopy was recorded on a fluorescence spectrometer (FL3-111, Horiba). Cyclic voltammetry was obtained from an electrochemical workstation (CHI660C). Surface morphology and phase diagram were performed by Veeco Dimension 3100V atomic force microscope. The GIWAXS was measured in National Center for Nanoscience and Technology. Keithley 2440 sourcemeter with a solar simulator (Newport-Oriel® Sol3A 450W) were used to do the current-voltage (J-V) (under AM 1.5 G irradiation) and electrical conductivity test (under dark), and the simulated solar light was calibrated by a standard Si solar cell. A solar cell QE tester (QE-R, Enli Technology Co., Ltd) calibrated with a 75W xenon lamp source standard probe was be utilized to obtain the external quantum efficiency (EQE) spectrums.

Device fabrication and characterization.

The devices were fabricated with a structure of ITO/PEDOT:PSS/SM-D:A/PDINO/Al. The ITO glass was cleaned with sequential ultrasonication in a distilled water, acetone and isopropanol. Then, the ITO glass was treated in an ultraviolet ozone box for 20 minutes. Subsequently, PEDOT:PSS aqueous solution (Clevios P VP 4083) was spin-coated on the treated ITO substrates at 3000 rpm for 1 min and annealed at 130 °C for 10min. Then, the substrates were transferred into a nitrogen-filled glove box. A chloroform solution (20mg/ml, D/A=1:1) containing mixture of a small molecule donor and Y6/N3 was spin-coated on the PEDOT: PSS layer at 2000 rpm for 1min and then thermal annealing at 100 °C for 10min. Subsequently, PDINO was spin-coated on the active layer at 3000 rpm for 1min. Finally, Al was deposited about 100nm under the pressure of 3×10^{-5} Pa. Photovoltaic properties of the devices were measured under simulated solar light (100 mW cm^{-2} AM 1.5G) provided by a Newport-Oriel® Sol3A 450W solar simulator, and device area is 4 mm^2.

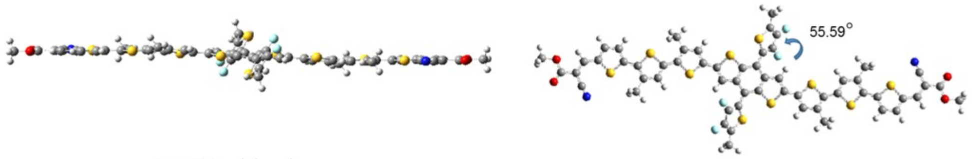


HOMO: -5.123 eV

LUMO: -2.861 eV

Fig

ure S1 HOMO/LUMO distribution of BT-2F obtained from DFT results



BT-2F side view

BT-2F over view

Figure S2 Side view and over view of BT-2F.

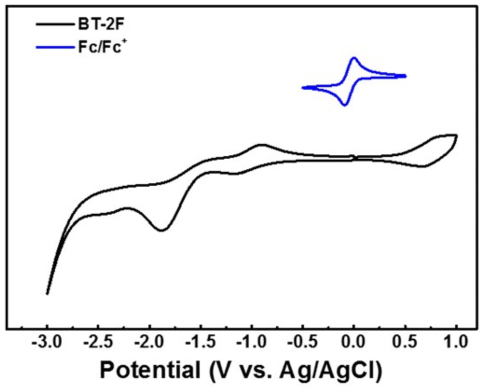


Figure S3 CV cures of BT-2F

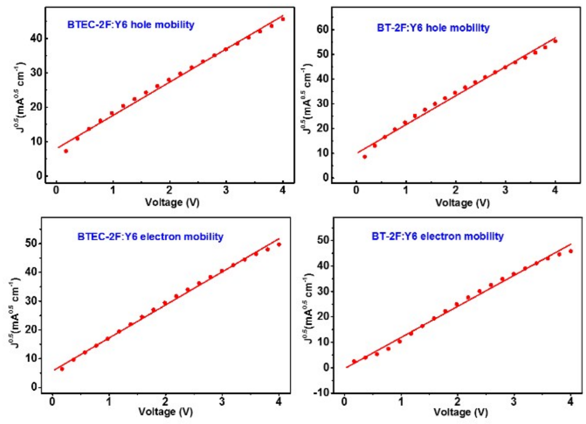


Figure S4 Carrier mobility curves measured by SCLC method

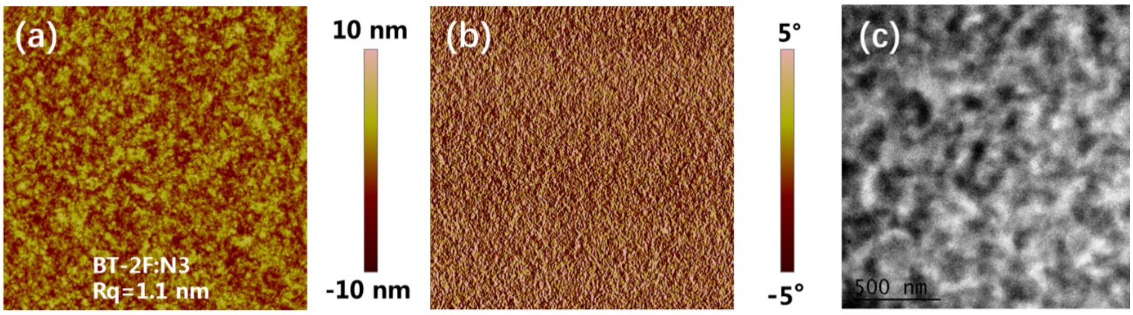


Figure S5 (a) AFM height images of BT-2F:N3, (b) AFM phase image, (c) TEM image

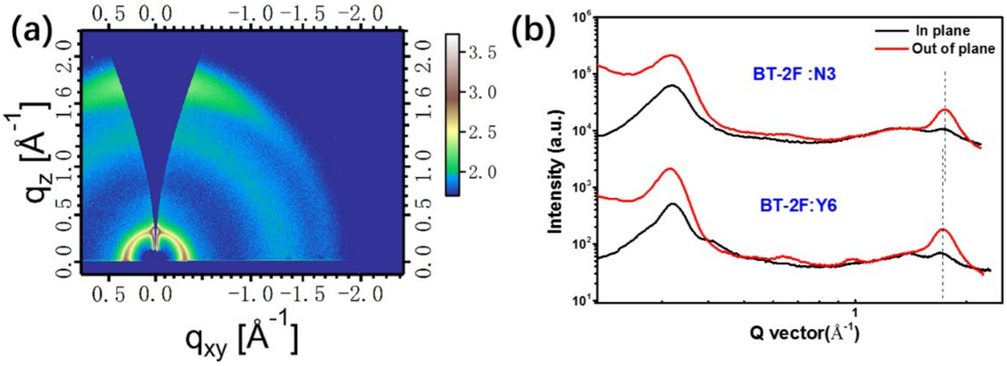


Figure S6 (a) 2D GIWAX image of the blend film for BT-2F:N3 (b) 1D plots extracted from Figure S5a and Figure 5d.

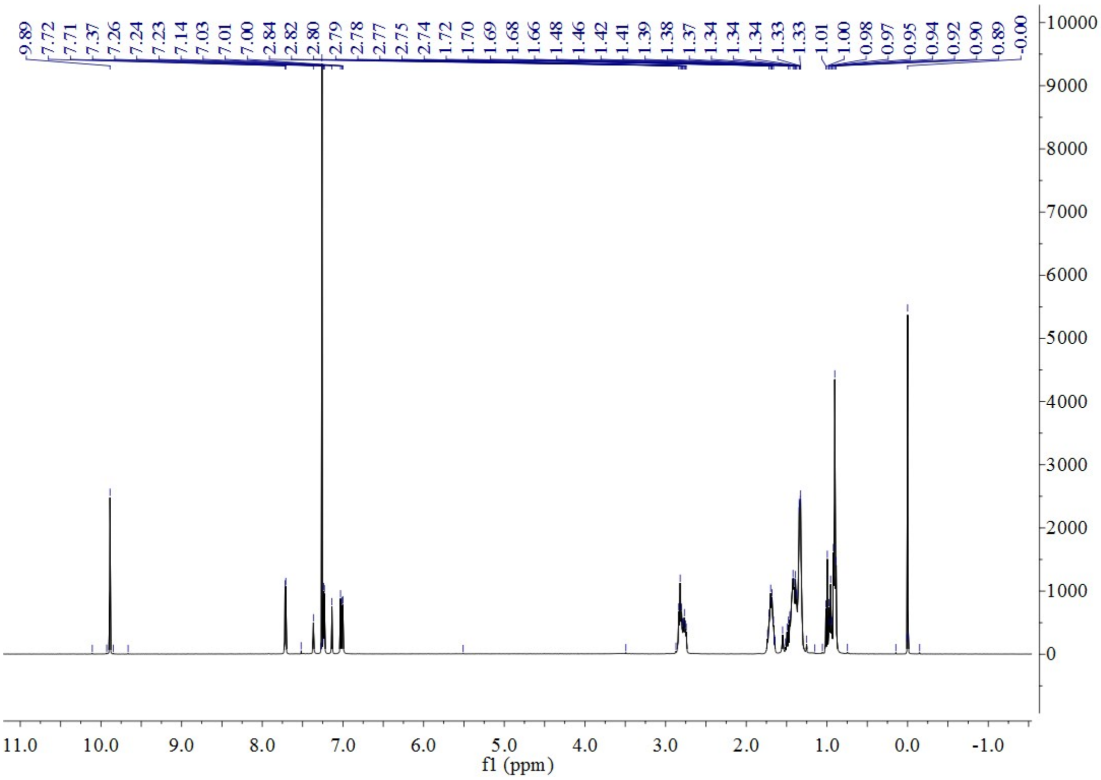


Figure S7 ^{1}H NMR spectrum of compound 2**.**

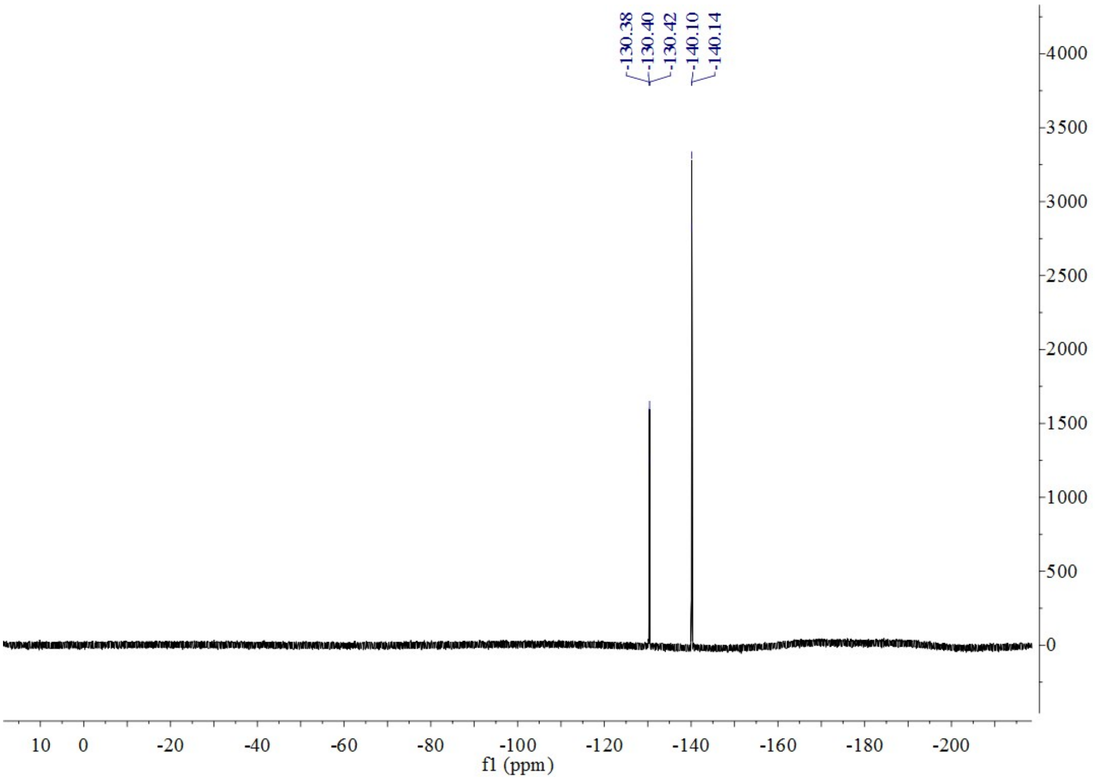


Figure S8 ^{19}F NMR spectrum of compound 2**.**

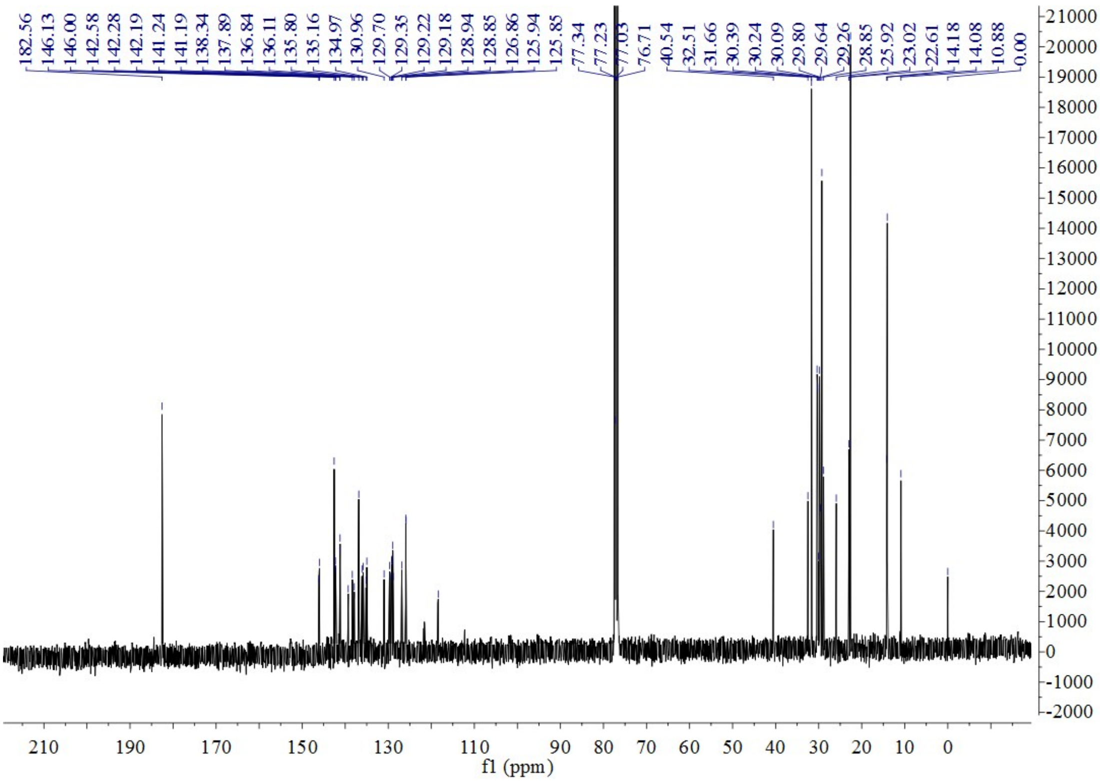


Figure S9 ^{13}C NMR spectrum of compound 2.

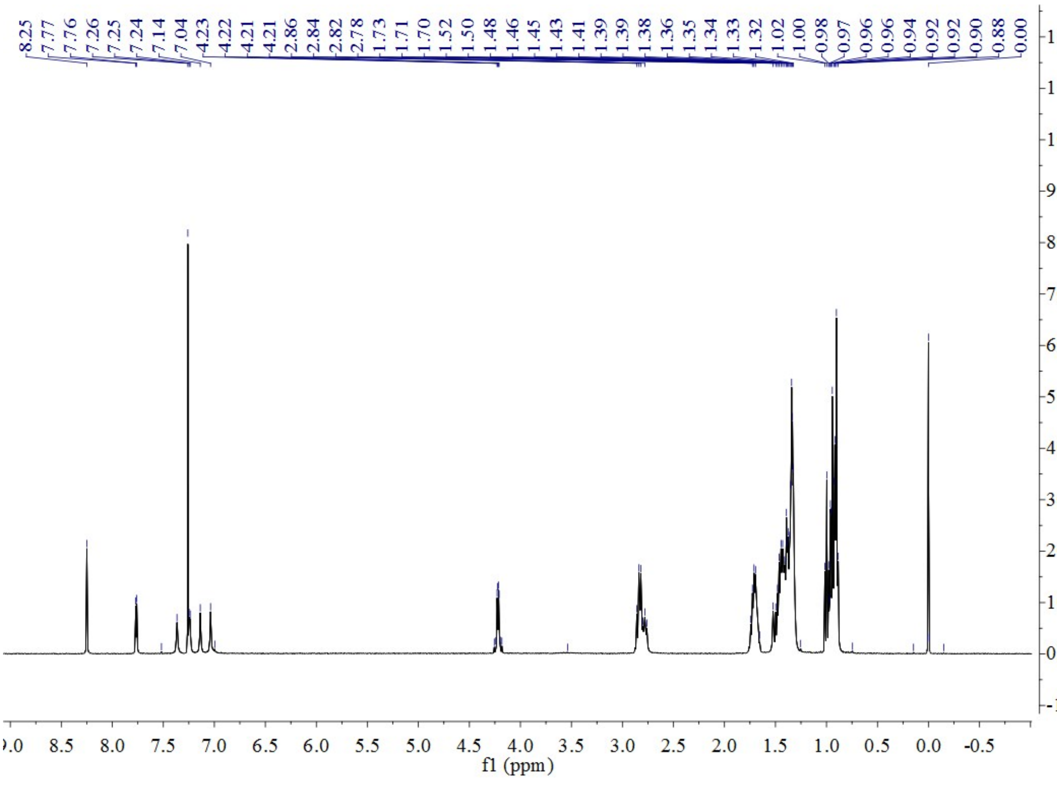


Figure S10 ^{1}H NMR spectrum of BT-2F**.**

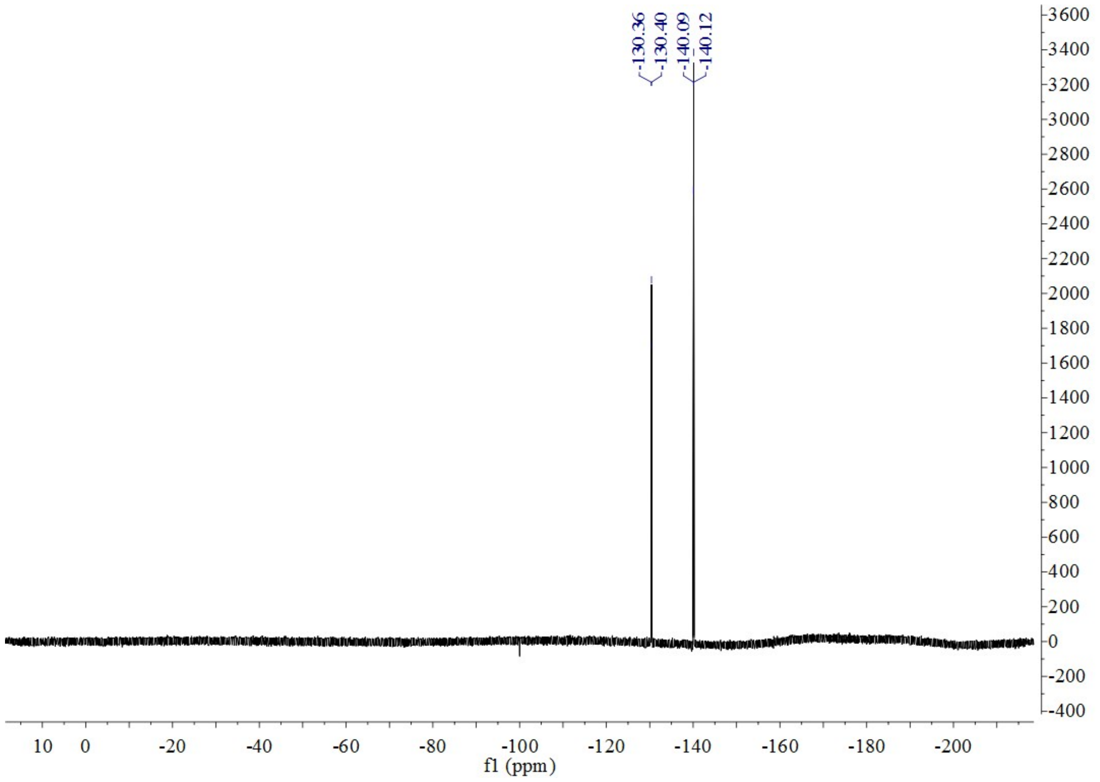


Figure S11 ^{19}F NMR spectrum of BT-2F.

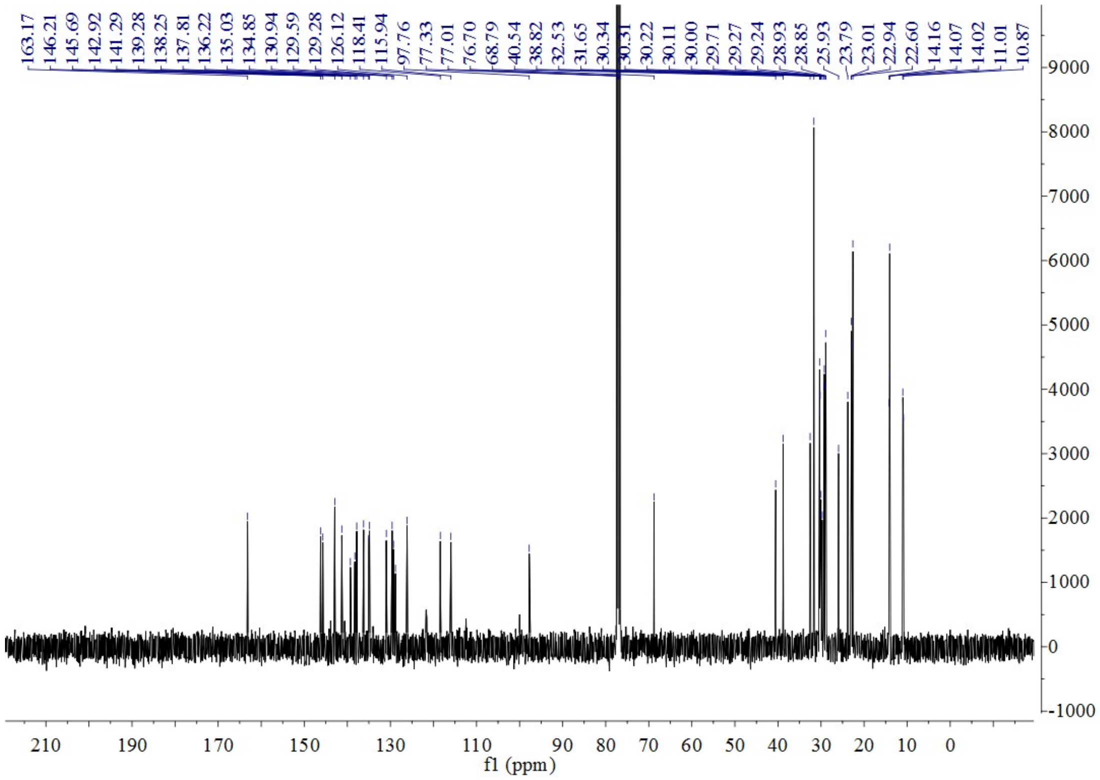


Figure S12 ^{13}C NMR spectrum of BT-2F.