Supporting Information

An oxygen heterocycle-fused fluorene based non-fullerene acceptor for high efficiency organic solar cells

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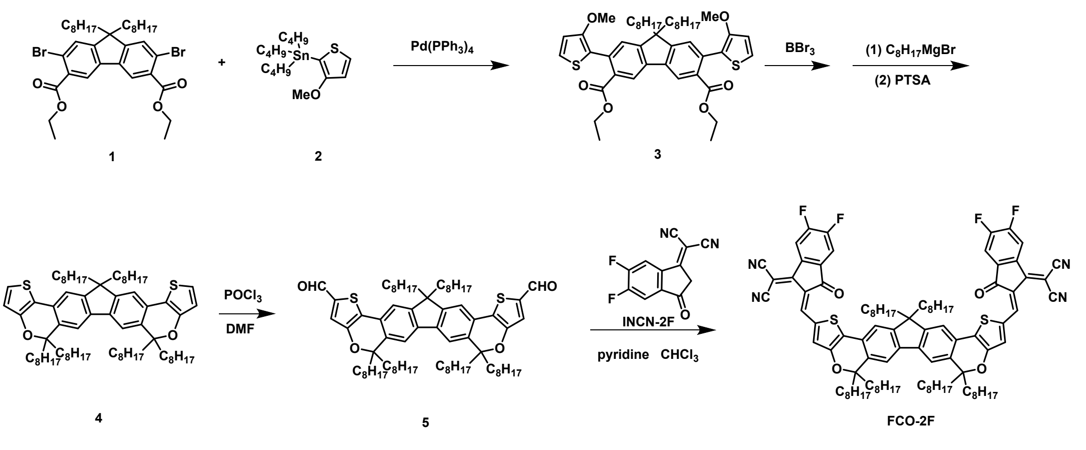
Experimental Section

Materials and synthesis. All reactions and manipulations were carried out under argon atmosphere with the use of standard Schlenk techniques. All starting materials were purchased from commercial suppliers and used without further purification unless indicated otherwise. Polymer donor PM6 was purchased from Solarmer Material (Beijing) Inc. Diethyl 2,7-dibromo-9,9-dioctyl-9*H*-fluorene-3,6-dicarboxylate was synthesized according to the literatures.[1]



Scheme S1. Synthetic Route of FCO-2F.

Synthesis of Compound 3. A solution of diethyl 2,7-dibromo-9,9-dioctyl-9*H*-fluorene-3,6-dicarboxylate (0.8 g, 1.16 mmol) and tributyl(3-methoxythiophen-2-yl)stannane (1.07 g, 2.66 mmol) in toluene：DMF (5:1, 120 mL) and was degassed twice with argon. Then $Pd(PPh_3)_4$ (0.067 g, 0.058 mmol) was added and the mixture was stirred at 120 °C for 24 h under argon, after which the mixture was poured into water (100 mL), and extracted with dichloromethane (100 mL × 2). The organic layer was then dried over anhydrous Na_2SO_4. The solvent was removed and the crude product was purified by column chromatography to obtain a yellow solid (0.39 g, 45%).

^1H NMR (400 MHz, $CDCl_3$): δ 8.15 (s, 2H), 7.37 (s, 2H), 7.27 (d, *J* = 5.5 Hz, 2H), 6.91 (d, *J* = 5.5 Hz, 2H), 4.29 (q, *J* = 7.1 Hz, 4H), 3.80 (s, 6H), 1.98-1.94 (m, 4H), 1.27-1.04 (m, 30H), 0.81 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.79, 153.98, 153.51, 139.29, 131.48, 131.34, 126.15, 123.02, 121.73, 119.43, 116.46, 61.04, 58.57, 55.94, 40.06, 31.77, 29.96, 29.22, 29.15, 23.85, 22.60, 14.09, 14.03. MS (MALDI-TOF): calcd for $C_{45}H_{58}O_6S_2$ [M^+] 758.37; found: 758.88.

Synthesis of Compound 4. Compound 3 (0.49 g, 0.64 mmol) was dissolved in 50 mL dry CH_2Cl_2 and the reaction mixture was cooled down to -78°C. Then 3.23 mL BBr_3 (1.0 M solution in CH_2Cl_2) was added slowly, afterwards the reaction mixture was stirred at room temperatue for 12 h. After that, the reaction was quenched by water and extracted with CH_2Cl_2. After dried over anhydrous Na_2SO_4, the precipitation was dissolved in 50 mL dry THF and 3.2 mL octylmagnesium bromide (2.0 M solution in diethyl ether) was added at -78°C. Then the reaction was stirred at room temperatue for 12 h, and the mixture was extracted with CH_2Cl_2 (100 mL × 3) and water (100 mL). The organic layer was dried over anhydrous Na_2SO_4, and after removal of the solvent, the crude product was dissolved in 50 mL toluene, and reacted with *p*-toluenesulfonic acid (0.26 g, 1.36 mmol) at 110°C for 12 h. The mixture was extracted with CH_2Cl_2 and water, dried over anhydrous Na_2SO_4, and was was purified by silica gel chromatography using petroleum ether as eluent, yielding a solid product 4 (0.50 g, 73%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (s, 2H), 7.09 (s, 2H), 7.05 (d, *J* = 5.2 Hz, 2H), 6.70 (d, *J* = 5.3 Hz, 2H), 2.10-2.03 (m, 4H), 1.96-1.90 (m, 8H), 1.26-1.22 (m, 72H), 0.87-0.84 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.10, 150.24, 139.52, 132.63, 127.52, 121.90, 119.28, 115.40, 115.35, 115.23, 85.83, 54.79, 39.55, 39.13, 38.91, 32.06, 31.99, 31.96, 30.12, 30.06, 29.84, 29.62, 29.59, 29.40, 29.36, 29.29, 29.21, 28.09, 26.56, 26.43, 23.85, 23.10, 22.83, 22.78, 22.74, 20.29, 19.18, 14.11. MS (MALDI-TOF): calcd for $C_{71}H_{110}O_2S_2$ [M$^+$] 1058.79; found: 1058.43.

Synthesis of Compound 5. $POCl_3$ (0.26 mL) was added drop by drop to DMF (3 mL) at 0°C under the protection of argon and then stirred at room temperature for 5 h to gain the Vilsmerier reagent. The Vilsmerier reagent was added into a 1,2-dichloroethane (50 mL) solution of compound 2 (0.5 g, 0.47 mmol). The above reaction mixture was stirred at room atmosphere for 1 h and then heated to 80 °C for 12 hours. The mixture was quenched with CH_3COONa (aq), and then extracted with dichloromethane (50 mL × 2). The combined organic layer was dried over anhydrous Na_2SO_4 and purified by silica gel after removal of solvent, yielding a yellow solid (0.45 g, 85%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.82 (s, 2H), 7.33 (s, 2H), 7.29 (s, 2H), 7.26 (s, 2H), 2.10-2.02 (m, 4H), 1.99-1.92 (m, 8H), 1.26-1.08 (m, 72H), 0.85-0.79 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 181.02, 151.25, 149.96, 140.31, 136.99, 133.44, 125.45, 125.41, 125.37, 115.80, 114.89, 85.40, 54.01, 38.93, 38.82, 30.90, 30.82, 30.77, 28.87, 28.80, 28.72, 28.67, 28.50, 28.42, 28.22, 28.18, 28.13, 22.81, 22.74, 21.71, 21.64, 21.61, 13.12, 13.07, 13.03. MS (MALDI-TOF): calcd for $C_{73}H_{110}O_4S_2$ [M^+] 1114.78; found: 1115.00.

Synthesis of Compound FCO-2F. Under the protection of argon, compound 5 (230 mg, 0.21 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (166.1 mg, 0.72 mmol) was dissolved in dry chloroform (50 mL), followed by the addition of pyridine (0.5 mL). After stirring at room temperature for 12 h, the mixture was poured into water and then extracted with $CHCl_3$ (50 mL × 2). The organic layer was dried over anhydrous Na_2SO_4 for 3 h. After removal of solvent, the crude product was purified by silica gel, and then recrystallized from $CHCl_3$ and methanol to give FCO-2F as a dark blue solid (0.16 g, 51%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (s, 2H), 8.55 (dd, J = 9.4, 6.6 Hz, 2H), 7.71 (t, J = 7.3 Hz, 2H), 7.52 (s, 2H), 7.47 (s, 2H), 7.35 (s, 2H), 2.07-1.96 (m, 12H), 1.25-1.09 (m, 72H), 0.85-0.75 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 186.16, 158.08, 155.84, 155.70, 153.76, 153.22, 151.64, 142.58, 137.51, 136.71, 136.22, 136.10, 134.52, 134.47, 133.18, 133.10, 126.69, 121.58, 117.93, 116.31, 115.13, 114.91, 114.25, 114.10, 112.64, 112.46, 86.67, 69.88, 55.47, 40.45, 40.12, 31.79, 31.74, 29.82, 29.70, 29.39, 29.20, 23.88, 23.71, 22.61, 22.59, 14.07, 14.03. HR-MS: calcd for $C_{97}H_{114}F_4N_4O_4S_2$ $[M]^+$ 1538.8212; found: 1538.8201.

Measurements and Instruments. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AV400 Spectrometer. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry were performed on a Bruker Autoflex III instrument. Varian 7.0T FTMS was used to achieve the HR-MS data. UV-vis spectra were obtained with a Cary 5000 Spectrophotometers. Cyclic voltammogram (CV) was performed with a LK2010 Microcomputerbased Electrochemical Analyzer. Thermogravimetric analyses (TGA) were carried out on a NETZSCH STA 449 F5 Jupiter instrument under a purified nitrogen gas. The heating rate is a 10 °C min^{-1} heating rate. The current density-voltage (*J-V*) curves of photovoltaic devices were obtained by a Keithley 2400 source-measure unit. The photocurrent was measured under simulated illumination of 100 mW cm^{-2} with AM1.5G irradiation using a xenon-lamp-based solar simulator [Oriel 96000] in an argon-filled glove box. External quantum efficiency values (EQEs) of the encapsulated devices were obtained with a halogen-tungsten lamp, monochromator, optical chopper, and lock-in amplifier in air and the photon flux was determined by a calibrated silicon photodiode. Atomic force microscopy (AFM) images were performed using in tapping mode on a Bruker MutiMode 8 atomic force microscope. Transmission electron microscopy (TEM) was performed on a Philips Technical G2 F20 at 200 kV. The GIWAXS (grazing incidence wide angle X-ray scattering) samples were prepared on ZnO-coated Si substrates using the same preparation conditions as for devices. SCLC was uesd to measure hole and electron mobilities, using a diode configuration of ITO/PEDOT:PSS/active layer/Au for hole and glass/ZnO/active layer/Al for electron by taking the dark current density in the range of 0–8 V and fitting the results to a space charge limited form.

Fabrication of OPV devices. The photovoltaic devices were fabricated with a structure of indium tinoxide (ITO)/ZnO/PFN-Br/ donor:acceptor /MoO_x/Ag. The ITO-coated glass substrates were cleaned by ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 minutes each time and subsequently dried by a nitrogen flow. A 30 nm thick layer of ZnO precursor solution was spin-coated (3000 rpm) onto the ITO surface. After baked at 200 °C for 60 min, the substrates were transferred into an argon-filled glove box. A thin film of PFN-Br was spin-coated on ZnO. Subsequently, the active layer was spin-coated from blend chlorobenzene solutions and then MoOx (~6 nm) and Ag (~70 nm) was successively evaporated onto the active layer through a shadow mask.

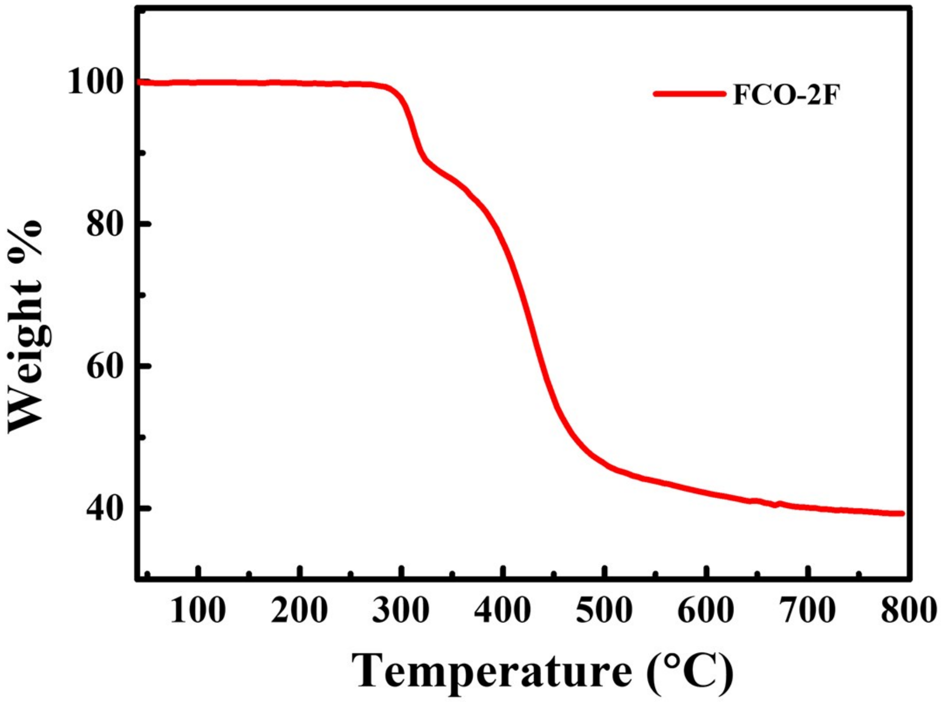


Fig. S1 TGA curve of FCO-2F with a heating rate of 10 °C/min under N_2 atmosphere.

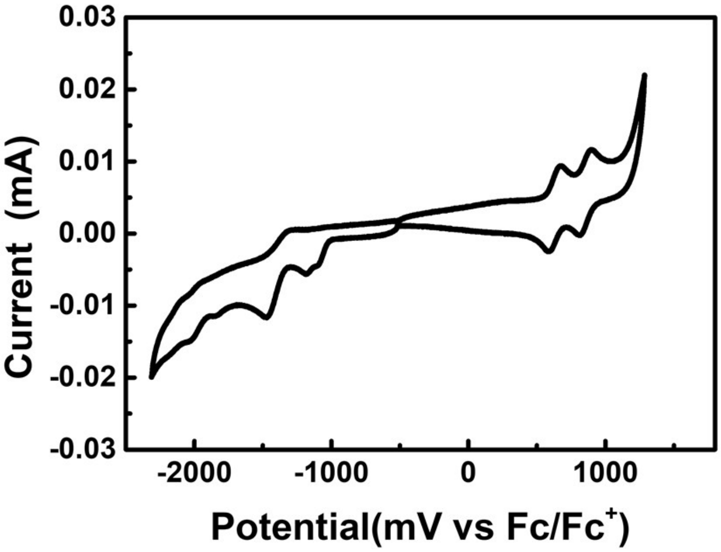


Fig. S2 Cyclic voltammogram of FCO-2F in dichloromethane solution with 0.1 mol L^{-1} n-Bu_4NPF_6 at a scan rate of 100 mV s^{-1}.

Table S1. Photovoltaic performance of the solar cells based on PM6:FCO-2F blend films with weight ratios (w:w) under illumination of AM 1.5 G, 100 mW cm^{-2}.

D:A	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
1:0.8	0.92	19.03	0.66	11.53
1:1	0.92	19.45	0.66	11.77
1:1.2	0.92	19.74	0.64	11.62

Table S2. Photovoltaic performance of the solar cells based on PM6:FCO-2F (1:1, w/w) blend films with different TA temperature under illumination of AM 1.5 G, 100 mW cm^{-2}.

TA temperature (°C)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
As-cast	0.92	19.45	0.66	11.77
120	0.89	20.90	0.72	13.36
140	0.88	19.72	0.74	12.73

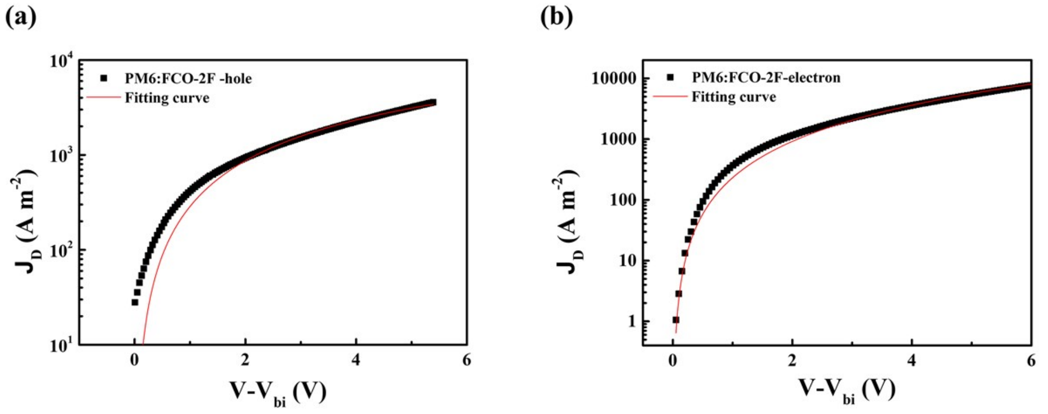


Fig. S3 The current-density-voltage (*J-V*) plots for hole-only and electron-only devices based on PM6:FCO-2F.

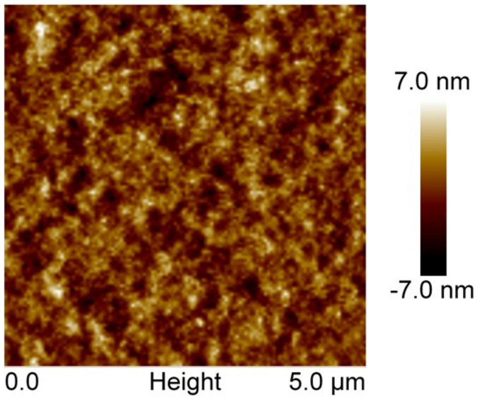


Fig. S4 AFM image for PBDB-T:F-H blend film.

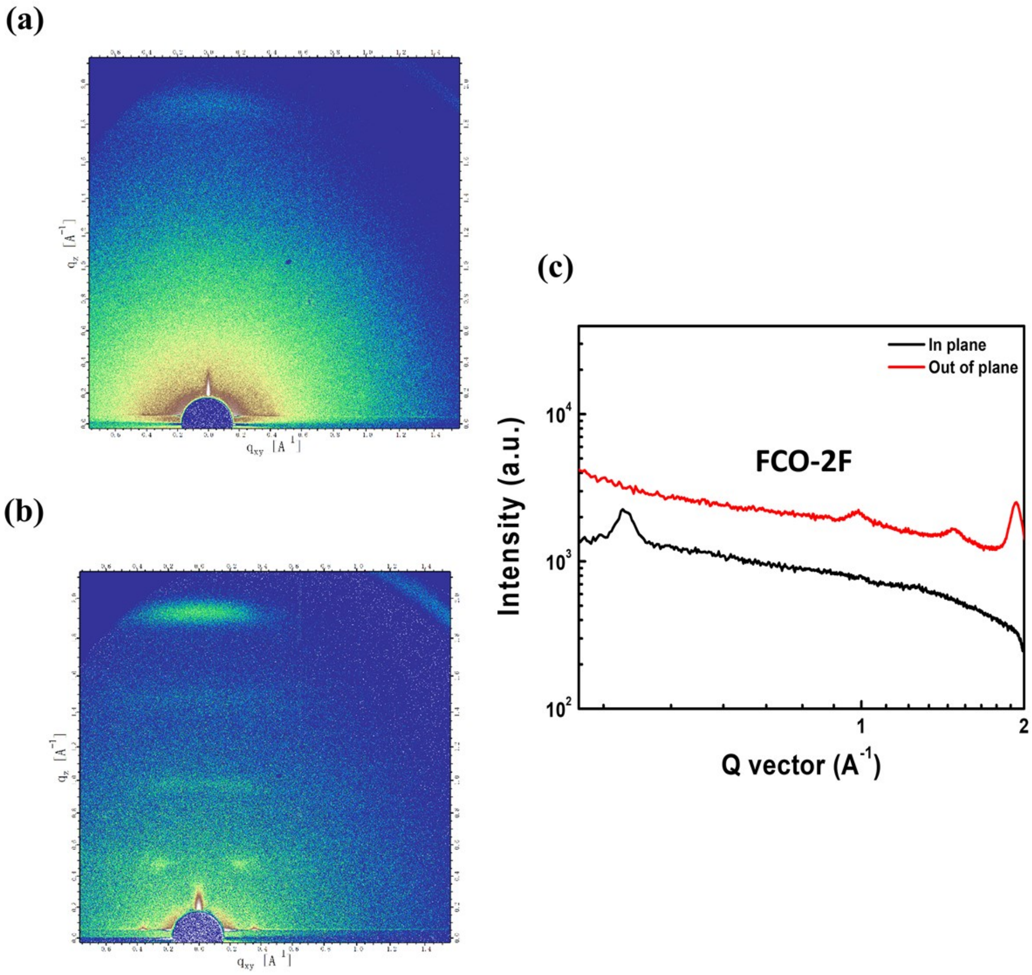


Fig. S5 GIWAXS pattern for (a) FCO-2F pristine film, (b) FCO-2F film after TA. (c) In-plane and Out-of -plane line cuts of the GIWAXS patterns for the corresponding pure films after TA.

NMR and MS spectra of FCO-2F.

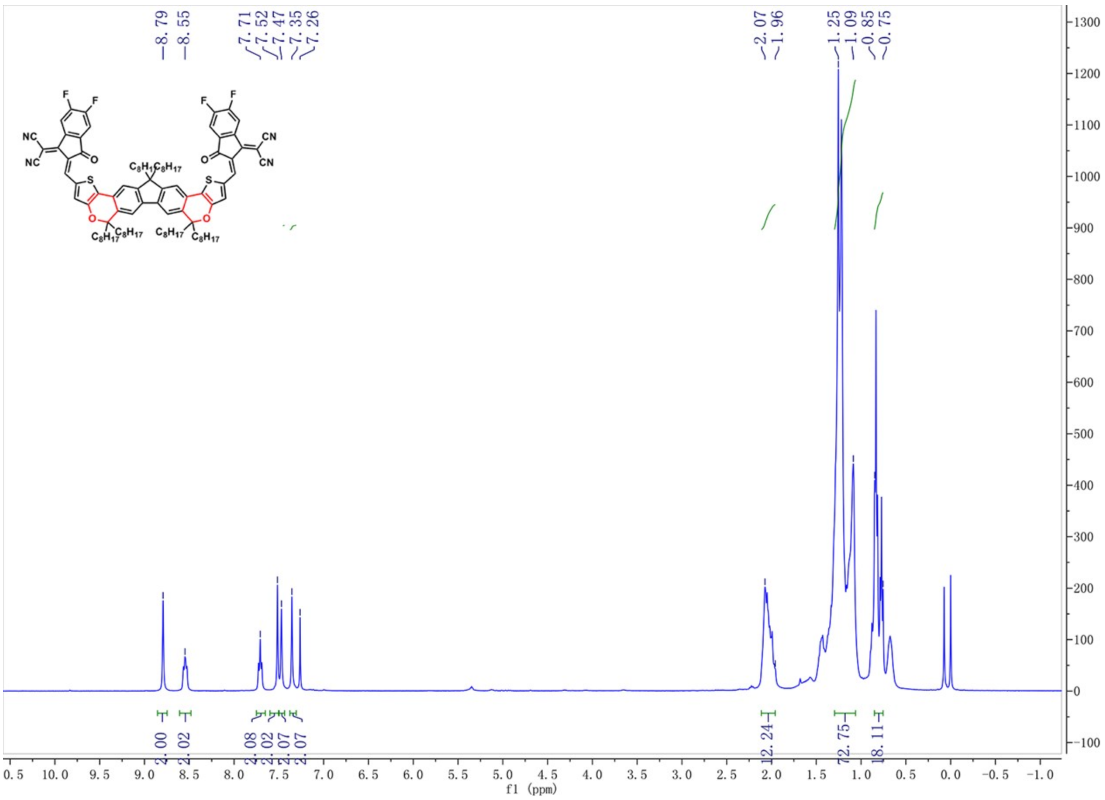


Fig. S6 ^{1}H NMR spectra of compound FCO-2F in $CDCl_3$.

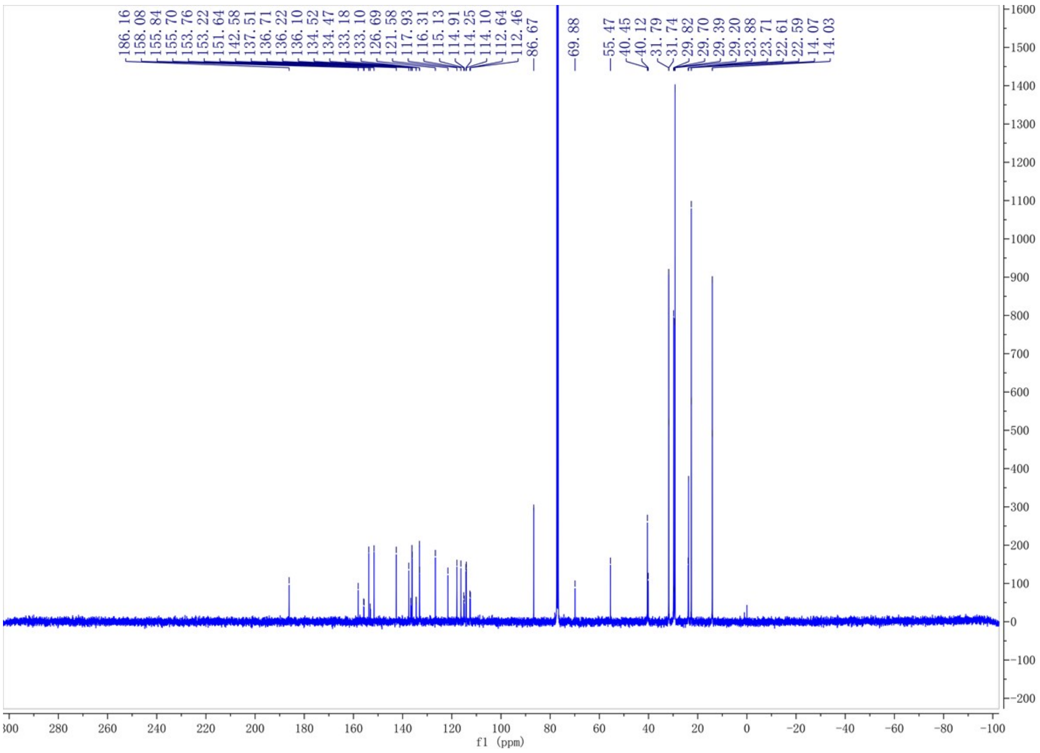


Fig. S7 ^{13}C NMR spectra of compound FCO-2F in $CDCl_3$.

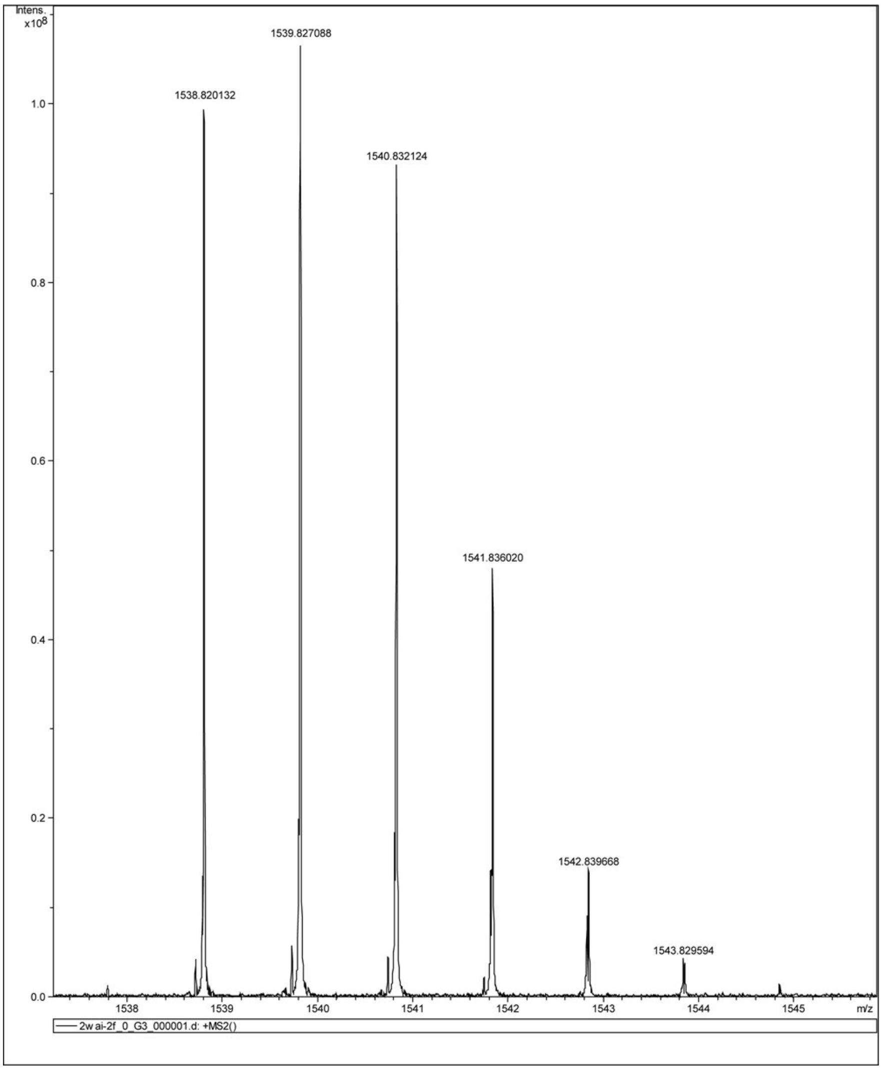


Fig. S8 HR-MS plots of compound FCO-2F.

References

1 B. Kobin, L. Grubert, S. Blumstengel, F. Henneberger and S. Hecht, *J. Mater. Chem.*, 2012, **22**, 4383-4390.