# Electronic Supplementary Information

## Rational and effective design of nonfullerene acceptors guided by a semi-empirical model for organic solar cell with efficiency over 15%

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### 1. Semi-empirical model analysis for PCE prediction

For the semi-expirical analysis based on a single cell, the fundamental assumptions are made as follows:

1) An internal quantum efficiency (IQE) of 100% is considered for the whole absorption wavelengths.[1]
2) EQE is assumed to be same in the whole absorption range with given values 65-85% and *FF* is assumed to be 0.8.
3) In the discussion as follows, the optical gap of the subcell $E_g$ ( = $1240/\lambda_{onset}$) is defined as the narrower optical gaps of the donor-acceptor couples.[2]

Based on above assumptions, the photovoltaice parameters $V_{oc}$ and $J_{sc}$ of a single cell is obtained as follows:

1) For a single cell with absorption onset $\lambda$, the $J_{sc}$ of the cell could be obtained from equation 1 (Eq. 1).

$$J_{SC} = \int_{300}^{\lambda} \frac{q\lambda}{hc} \cdot E(\lambda) \cdot EQE(\lambda) \cdot d\lambda \qquad (1)$$

where E($\lambda$) is the spectral irradiance in AM 1.5G, $\lambda$ is the absorption onset of the cell, $h$ is Planck's constant, $c$ is the speed of light and $q$ is the elementary charge.

2) The $V_{oc}$ of the cell is determined by the following Eq. 2.[2]

$$V_{\mathrm{OC}} = \frac{1}{q}(E_g - E_{loss}) = \frac{1}{q}(\frac{1240}{\lambda} - E_{loss}) \tag{2}$$

The $E_{\mathrm{loss}}$ are assumed to be 0.4-0.8 eV according to overall reported values.[3]

So for the single cell, the PCE can be calculated from the Eq. 3 under AM 1.5G light illumination.

$$\begin{aligned} PCE(\%) &= V_{OC} \cdot J_{SC} \cdot FF / P_{in} \\ &= \frac{1}{q}(\frac{1240}{\lambda} - E_{loss})\int_{300}^{\lambda} \frac{q\lambda}{hc} \cdot E(\lambda) \cdot EQE(\lambda) \cdot d\lambda \cdot FF / P_{in} \end{aligned} \tag{3}$$

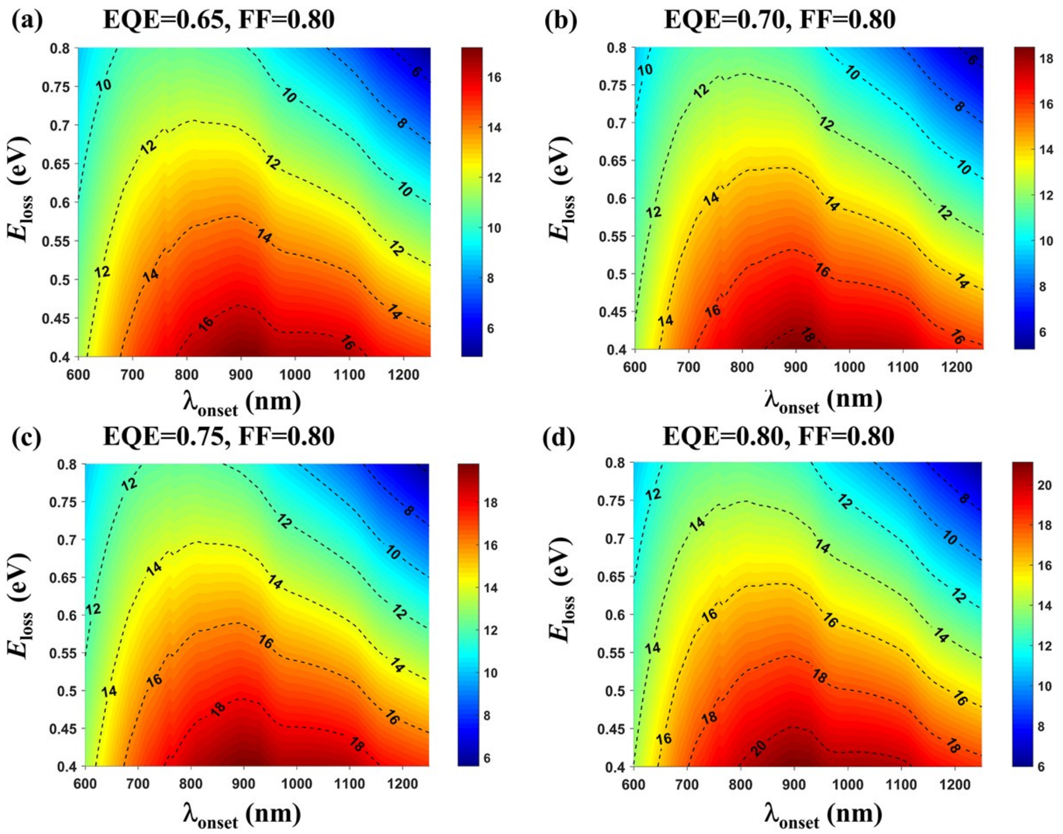
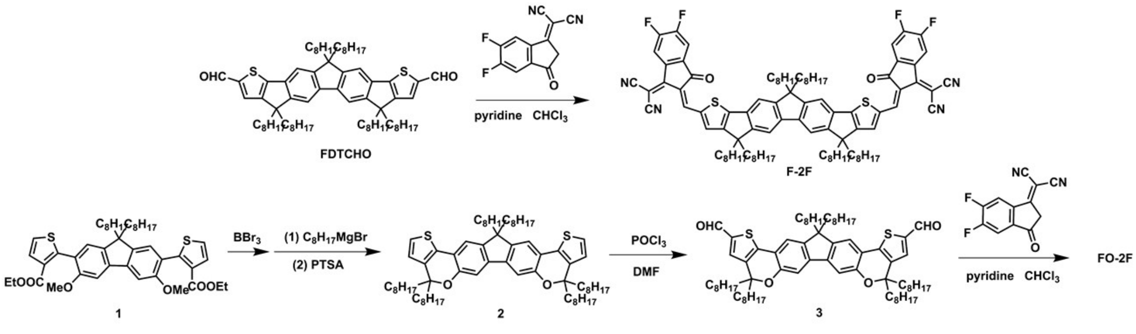


**Fig. S1** Predicted PCEs of a single solar cell based on semi-empirical analysis under AM1.5G. (A-D) PCEs versus $E_{loss}$ and $\lambda_{onset}$, with assuming FF of 0.80 and the EQE with value of (a)0.65 (b)0.70 (c)0.75 (d)0.80.

## 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. FDTCHO was synthesized according to our previous report method.[4] 2,7-dibromo-3,6-dimethoxy-9,9-dioctyl-9*H*-fluorene were synthesized according to the literatures.[5]



**Scheme S1**. Synthetic Route of F-2F and FO-2F.

***Synthesis of Compound F-2F***. Under the protection of argon, FDTCHO (65 mg, 0.06 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (48.3 mg, 0.21 mmol) was dissolved in dry chloroform (30 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 $CHCl_3$ (30 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 F-2F as a dark blue solid (41 mg, 45.3%).

$^1$H NMR (400 MHz, $CDCl_3$): δ 8.98 (s, 2H), 8.54 (m, 2H), 7.74 (s, 2H), 7.70 (m, 4H), 7.64 (s, 2H), 2.13-2.04 (m, 8H), 2.00-1.92 (m, 4H), 1.20-1.07 (m, 72H), 0.81-0.77 (m, 18H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ 185.96, 163.05, 158.68, 157.05, 156.61, 155.72, 153.13, 153.07, 152.99, 152.48, 142.76, 140.27, 138.77, 136.58, 134.51, 120.27, 116.38, 115.06, 114.63, 114.55, 112.63, 112.45, 68.72, 54.76, 54.26, 40.41, 39.15, 31.73, 29.95, 29.19, 24.49, 23.90, 22.57, 14.05.

HR-MS: calcd for $C_{97}H_{114}F_4N_4O_2S_2$ $[M]^+$, 1506.8314; found: 1506.8303.

***Synthesis of Compound 1.*** A solution of 2,7-dibromo-3,6-dimethoxy-9,9-dioctyl-9*H*-fluorene (2 g, 3.29 mmol) and ethyl 2-(tributylstannyl)thiophene-3-carboxylate (3.66 g, 8.22 mmol) in 100 mL DMF and was degassed twice with argon. Then $Pd(PPh_3)_4$ (0.19 g, 0.16 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 (0.42 g, 16.8%).

$^1$H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, $J = 5.3$ Hz, 2H), 7.28 (d, $J = 5.3$ Hz, 2H), 7.24 (s, 2H), 7.23 (s, 2H), 4.11 (q, $J = 7.1$ Hz, 4H), 3.88 (s, 6H), 1.93-1.89 (m, 4H), 1.26-1.04 (m, 30H), 0.83-0.79 (m, 6H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ 163.83, 156.51, 146.19, 143.17, 142.38, 130.65, 129.22, 125.34, 124.09, 122.15, 101.93, 60.20, 55.78, 54.31, 40.15, 31.84, 30.03, 29.30, 29.26, 23.83, 22.63, 14.13, 14.03.

MS (MALDI-TOF): calcd for $C_{45}H_{58}O_6S_2$ [$M^+$] 758.37; found: 758.18.

***Synthesis of Compound 2.*** Compound 1 (0.62 g, 0.82 mmol) was dissolved in 50 mL dry $CH_2Cl_2$ and the reaction mixture was cooled down to -78°C. Then 5.72 mL $BBr_3$ (1.0 M solution in $CH_2Cl_2$) was added slowly, and 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 4.1 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). 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 (0.33 g, 1.72 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 purified by silica gel chromatography using petroleum ether as eluent, yielding a solid product 2 (0.42 g, 48.5%).

$^1$H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, *J* = 5.0 Hz, 2H), 7.13 (s, 2H), 7.10 (s, 2H), 6.77 (d, *J* = 5.0 Hz, 2H), 1.93-1.86 (m, 12H), 1.43-1.07 (m, 72H), 0.86-0.77 (m, 18H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ 150.64, 143.04, 140.76, 136.39, 134.85, 132.38, 127.33, 124.63, 124.07, 122.02, 117.43, 115.61, 106.87, 83.03, 53.24, 39.77, 39.47, 33.34, 33.30, 31.19, 31.02, 30.85, 29.47, 29.20, 29.15, 28.66, 28.43, 23.01, 22.93, 21.81, 21.78, 21.64, 13.23.

MS (MALDI-TOF): calcd for $C_{71}H_{110}O_2S_2$ [$M^+$] 1058.79; found: 1058.90.

***Synthesis of Compound 3.*** $POCl_3$ (0.22 mL) was added drop by drop to DMF (2 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 (0.42 g, 0.40 mmol). The above reaction mixture was stirred at room atmosphere for 1 h and then heated to 80 °C for 12 h. The mixture was quenched with $CH_3COONa$ (aq), and then extracted with

$CH_2Cl_2$ (50 mL × 2). The combined organic layer was dried over anhydrous $Na_2SO_4$ and purified by silica gel, yielding a yellow solid (0.28 g, 63.3%).

$^1$H NMR (400 MHz, $CDCl_3$): δ 9.88 (s, 2H), 7.42 (s, 2H), 7.25 (s, 2H), 7.15 (s, 2H), 1.96-1.84 (m, 12H), 1.26-1.08 (m, 72H), 0.86-0.77 (m, 18H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ 181.01, 151.76, 143.74, 142.65, 142.21, 139.87, 137.07, 132.58, 116.65, 116.50, 107.54, 82.57, 53.31, 39.21, 33.13, 30.82, 30.79, 28.88, 28.45, 28.23, 28.20, 22.85, 22.81, 21.64, 13.07.

MS (MALDI-TOF): calcd for $C_{73}H_{110}O_4S_2$ [M+H$^+$] 1115.79; found: 1115.89.

***Synthesis of Compound FO-2F.*** Under the protection of argon, compound 3 (200 mg, 0.18 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (144.4 mg, 0.63 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 FO-2F as a dark blue solid (173 mg, 62.7%).

$^1$H NMR (400 MHz, $CDCl_3$): δ 8.88 (s, 2H), 8.57 (dd, $J$ = 9.7, 6.4 Hz, 2H), 7.72 (t, $J$ = 7.4 Hz, 2H), 7.48 (s, 2H), 7.46 (s, 2H), 7.19 (s, 2H), 2.04-1.87 (m, 12H), 1.26-1.09 (m, 72H), 0.86-0.75 (m, 18H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ 186.26, 158.08, 155.81, 154.10, 153.18, 151.66, 145.55, 145.15, 142.81, 139.79, 137.61, 136.61, 135.41, 134.44, 120.76, 118.45, 117.99, 115.13, 114.91, 114.23, 112.64, 112.46, 108.96, 83.79, 69.67, 54.72, 53.46, 53.39, 40.60, 31.80, 31.74, 29.94, 29.86, 29.79, 29.73, 29.45, 29.39, 29.23, 29.17, 23.94, 23.78, 23.71, 22.64, 22.58, 14.07, 14.01.

HR-MS: calcd for $C_{97}H_{114}F_4N_4O_4S_2$ $[M]^+$ 1538.8212; found: 1538.8200.

***Measurements and Instruments.*** The $^1H$ and $^{13}C$ nuclear magnetic resonance (NMR) spectra were taken 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 at a scan rate of 100 mV/s. 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 /MoOx/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.

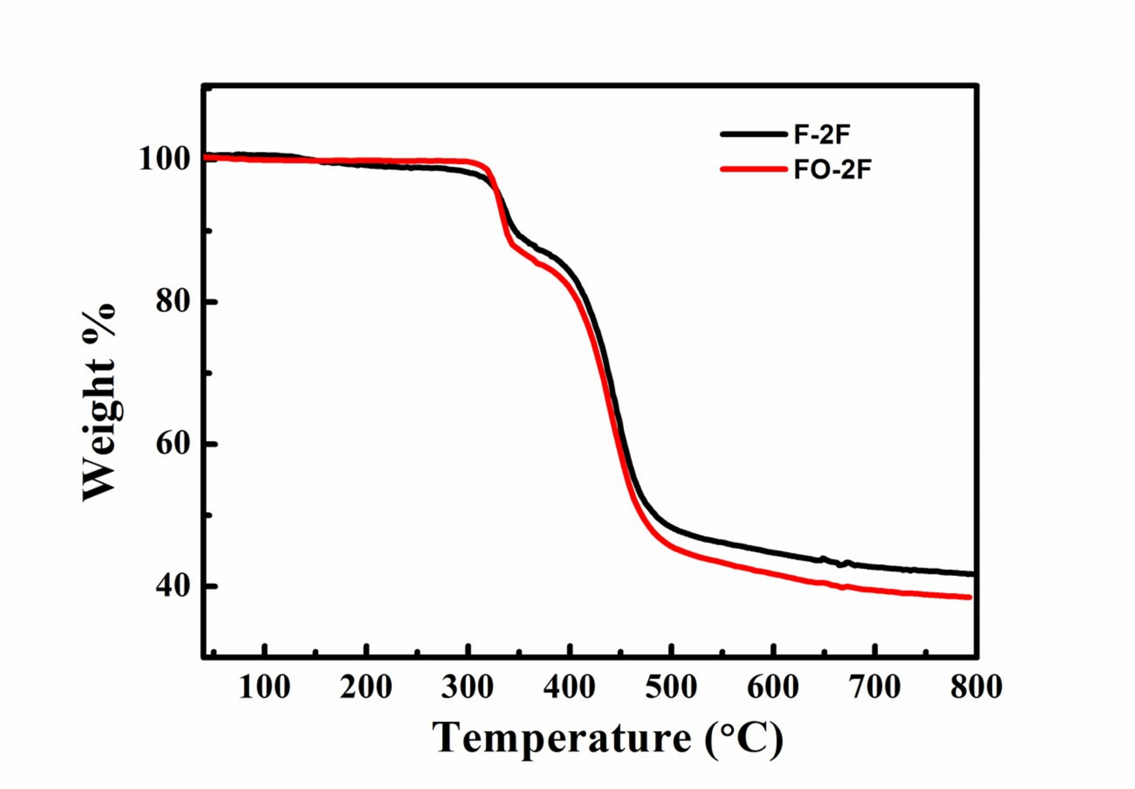


**Fig. S2** TGA curves of F-2F and FO-2F with a heating rate of 10 °C/min under $N_2$ atmosphere.

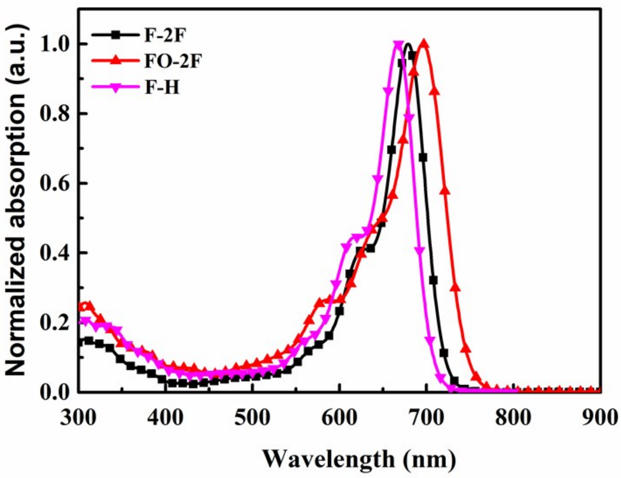


**Fig. S3** Normalized absorption spectra of F-H, F-2F and FO-2F in chloroform solution.

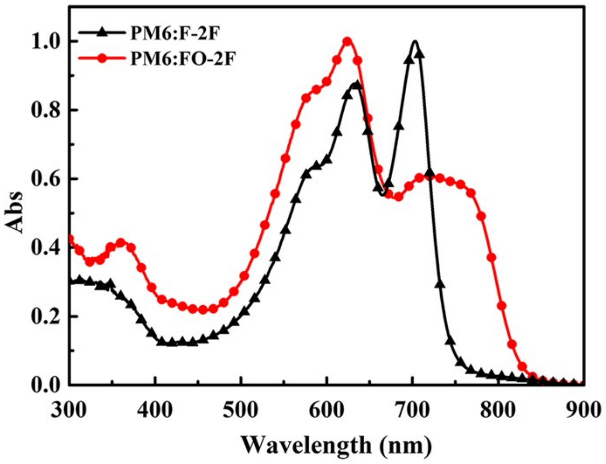


**Fig. S4** Absorption spectra of PM6:F-2F and PM6:FO-2F based blend films.

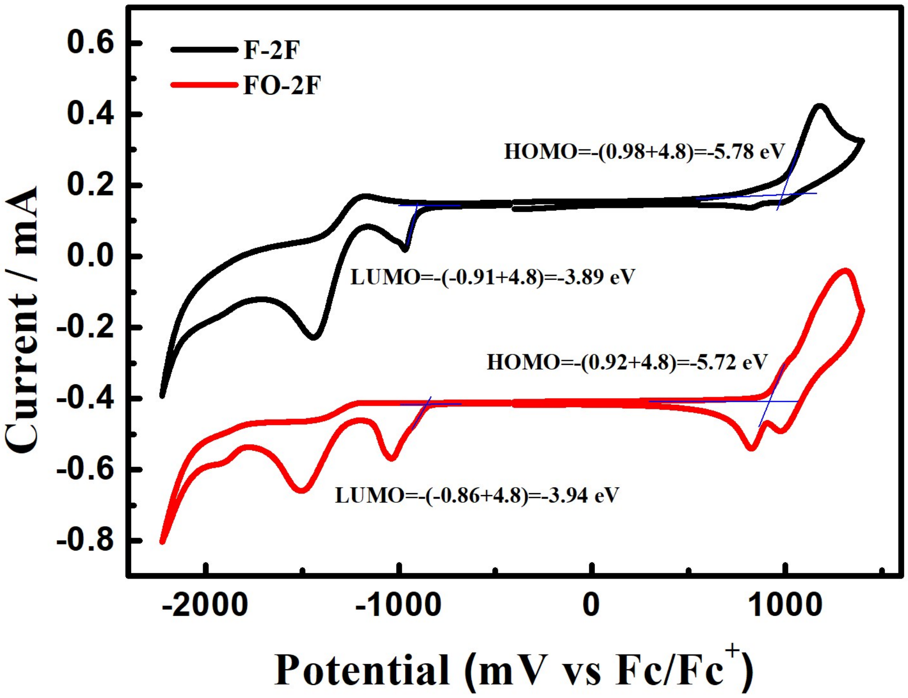


**Fig. S5** Cyclic voltammogram of F-2F and FO-2F film in acetonitrile solution with 0.1 mol $L^{-1}$ $n$-$Bu_4NPF_6$ at a scan rate of 100 mV $s^{-1}$. The HOMO/LUMO energy levels were calculated from the onset oxidation potential and the onset reduction potential vs FC/FC$^+$, using the equation $E_{HOMO} = -(4.80 + E_{onset\ vs\ FC/FC+}{}^{ox})$, $E_{LUMO} = -(4.80 + E_{onset\ vs\ FC/FC+}{}^{re})$.

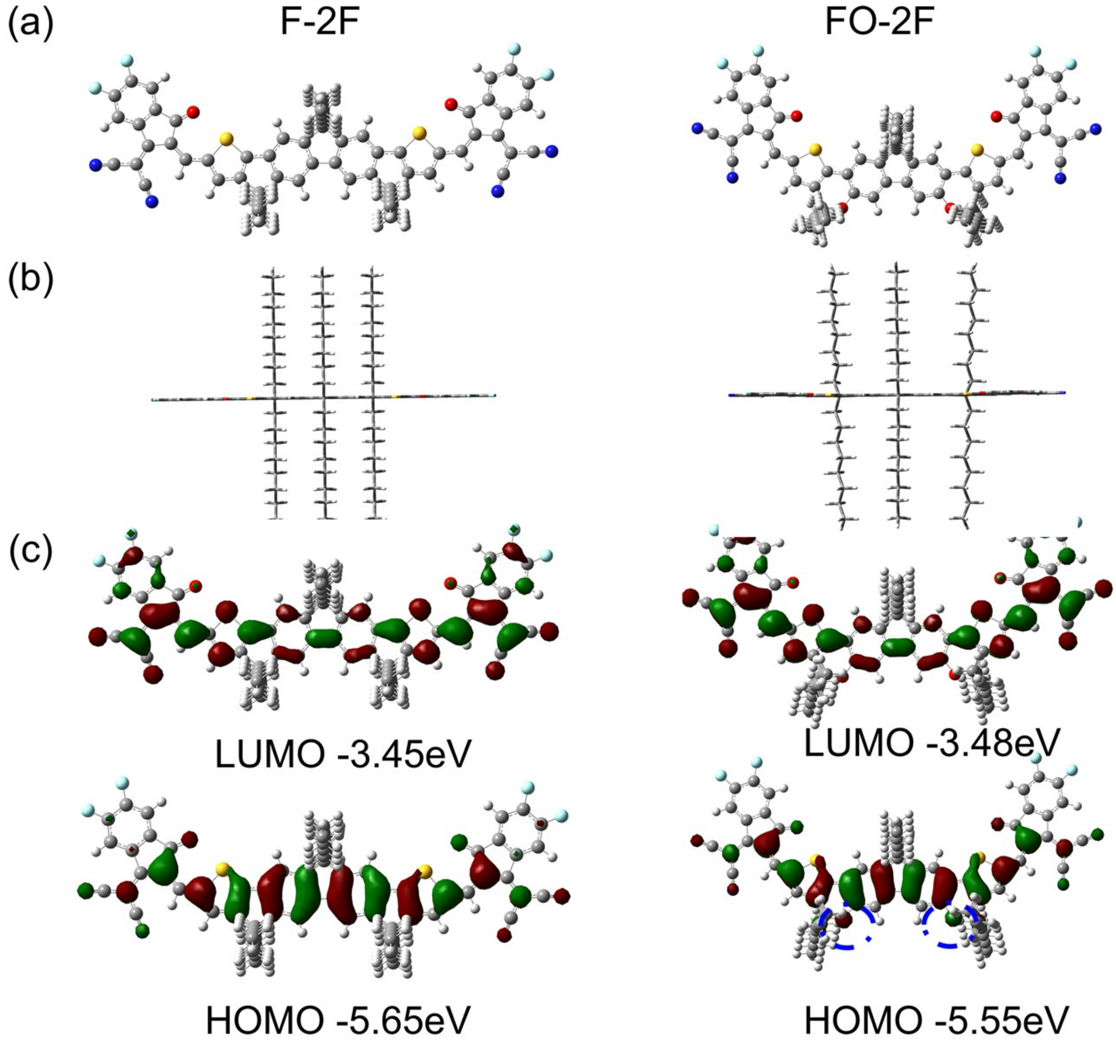


**Fig. S6** The optimized geometries for F-2F and FO-2F from (a) top view and (b) side view. (c) Theoretical density distribution for the frontier molecular orbits of F-2F and FO-2F. All calculations were carried out using Gaussian 16.[6]

**Table S1.** Photovoltaic performance of the solar cells based on PM6:F-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 (%) |
|---|---|---|---|---|
| 0 | 1.019 | 16.29 | 0.672 | 11.15 |
| 110 | 0.943 | 18.29 | 0.734 | 12.66 |
| 120 | 0.941 | 18.54 | 0.741 | 12.93 |
| 130 | 0.949 | 18.20 | 0.681 | 11.75 |
| 140 | 0.944 | 17.08 | 0.663 | 10.70 |

**Table S2.** Photovoltaic performance of the solar cells based on PM6:FO-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 (%) |
|---|---|---|---|---|
| 0 | 0.942 | 18.27 | 0.711 | 12.24 |
| 110 | 0.881 | 21.26 | 0.759 | 14.20 |
| 120 | 0.880 | 21.72 | 0.760 | 14.53 |
| 130 | 0.878 | 22.26 | 0.770 | 15.05 |
| 140 | 0.875 | 22.34 | 0.756 | 14.78 |

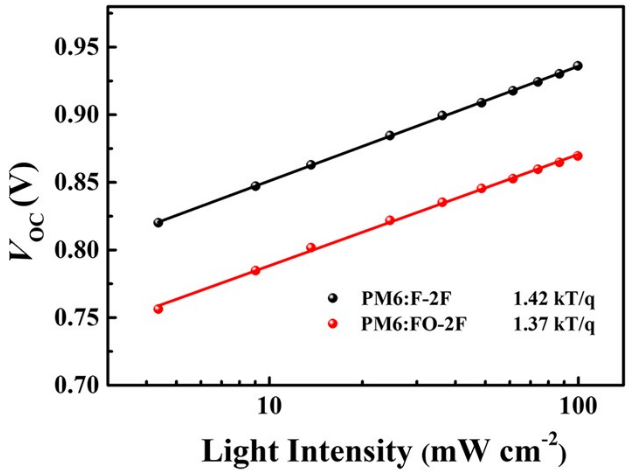


**Fig. S7** $V_{oc}$ as a function of light intensity on a seminatural logarithmic scale for devices based on PM6:F-2F and PM6:FO-2F.

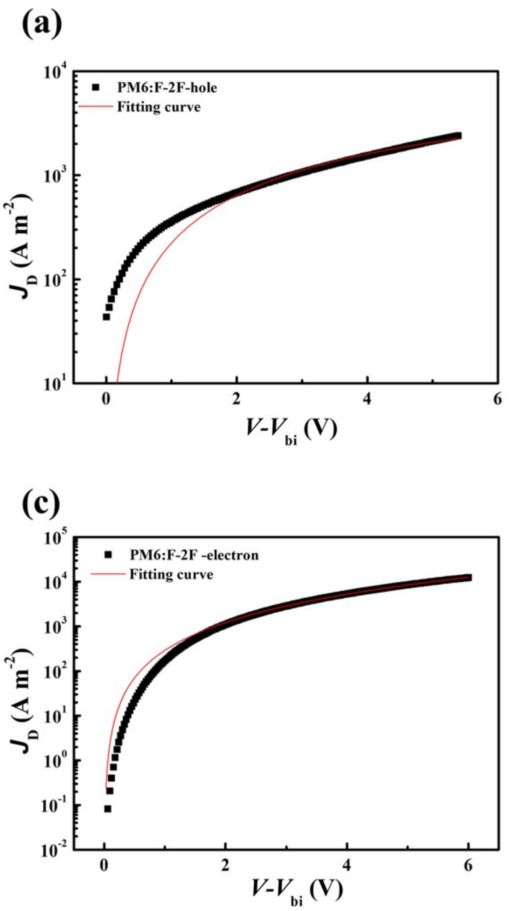


**Fig. S8** The current-density-voltage (*J-V*) plots for hole-only and electron-only devices based on (a,c) PM6:F-2F and (b,d) PM6:FO-2F.

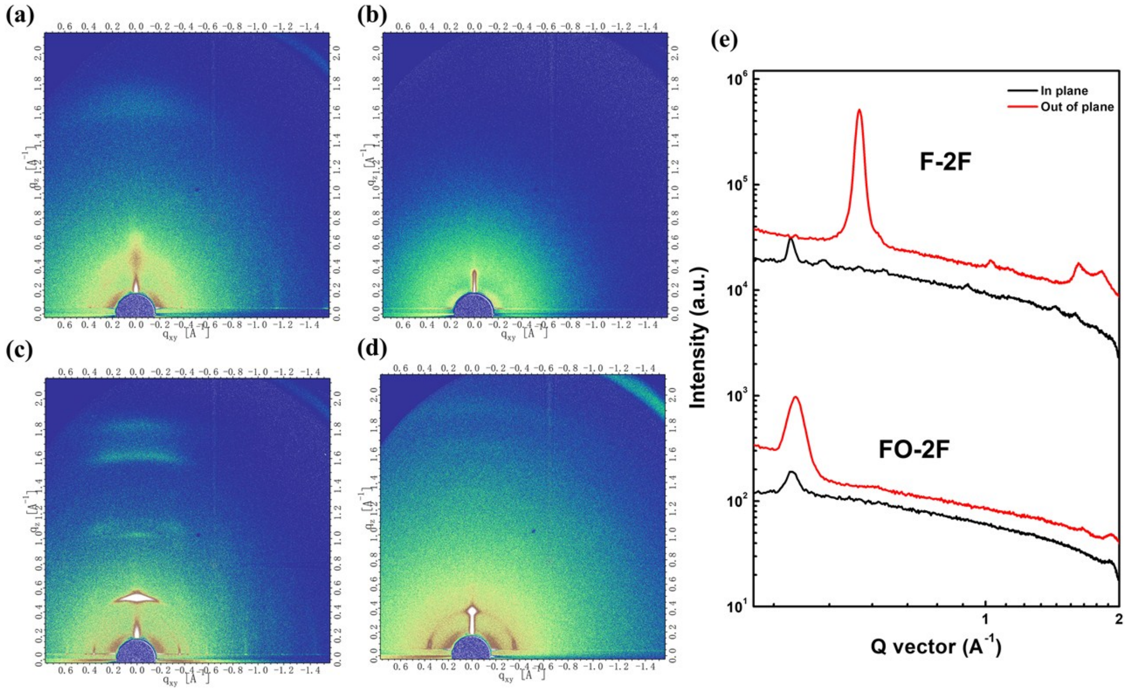


**Fig. S9** GIWAXS pattern for (a) F-2F pristine film, (b) FO-2F pristine film, (c) F-2F film after TA and (d) FO-2F film after TA. (e) In-plane and Out-of -plane line cuts of the GIWAXS patterns for the corresponding pure films after TA.

**Table S3.** Summary of the GIWAXS parameters for PM6:F-2F and PM6:FO-2F films.

| blends | | out-of-plane | | | |
|---|---|---|---|---|---|
| | | q(Å$^{-1}$) | d(Å) | FWHM(Å$^{-1}$) | CCL(Å) |
| PM6:F-2F | (010) stacking | 1.82 | 3.46 | 0.18 | 31.5 |
| | (100) packing | 0.52 | 12.2 | 0.046 | 122.0 |
| PM6:FO-2F | (010) stacking | 1.89 | 3.32 | 0.11 | 49.5 |

**NMR and MS spectra of F-2F and FO-2F**.

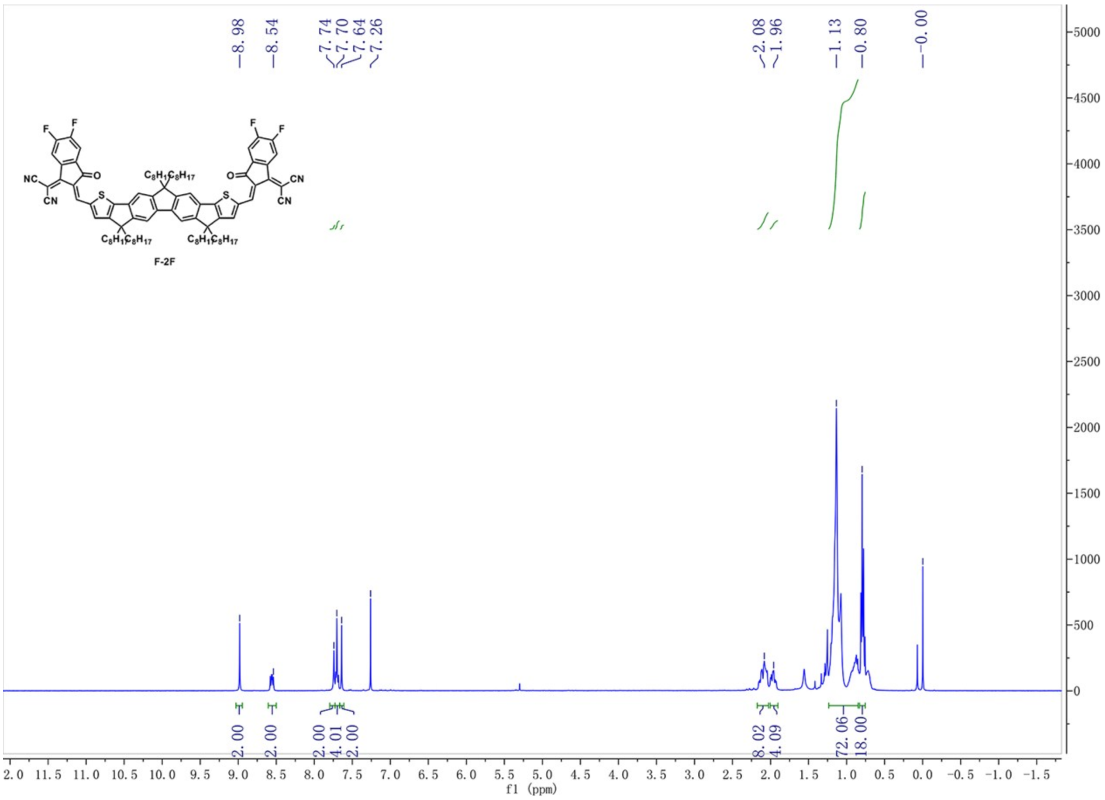


**Fig. S10** $^1$H NMR spectra of compound F-2F in $CDCl_3$.

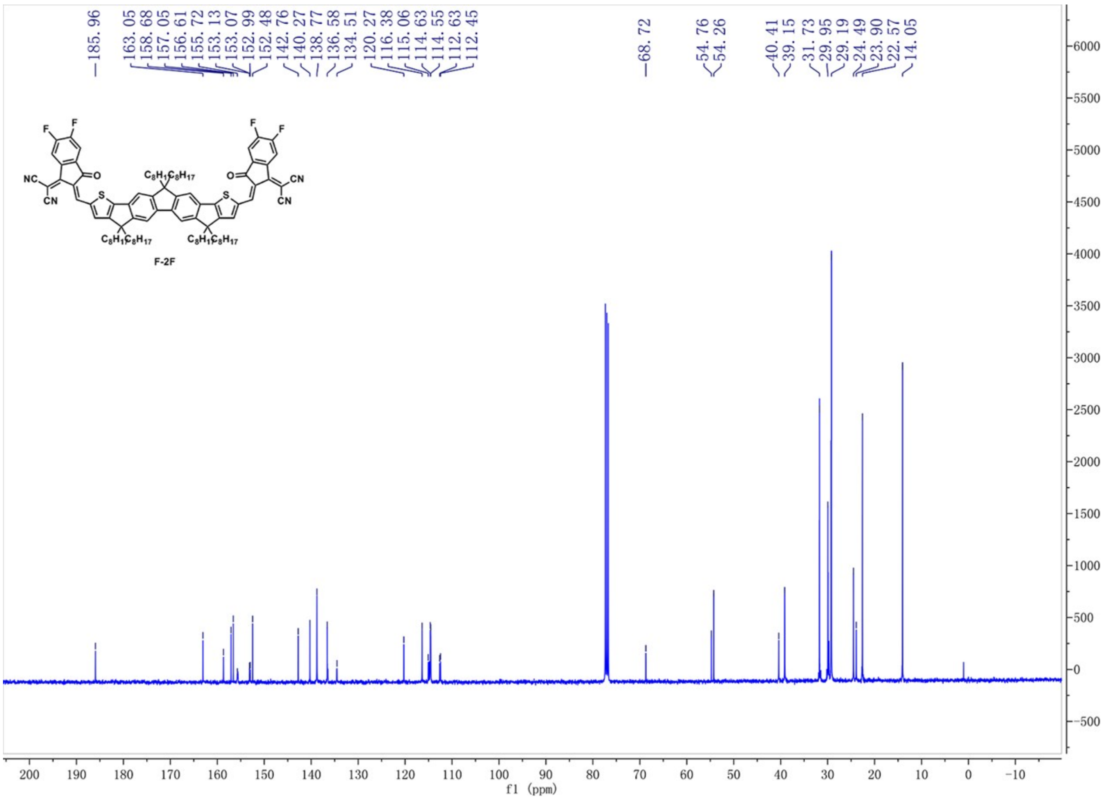


**Fig. S11** $^{13}$C NMR spectra of compound F-2F in CDCl$_3$.

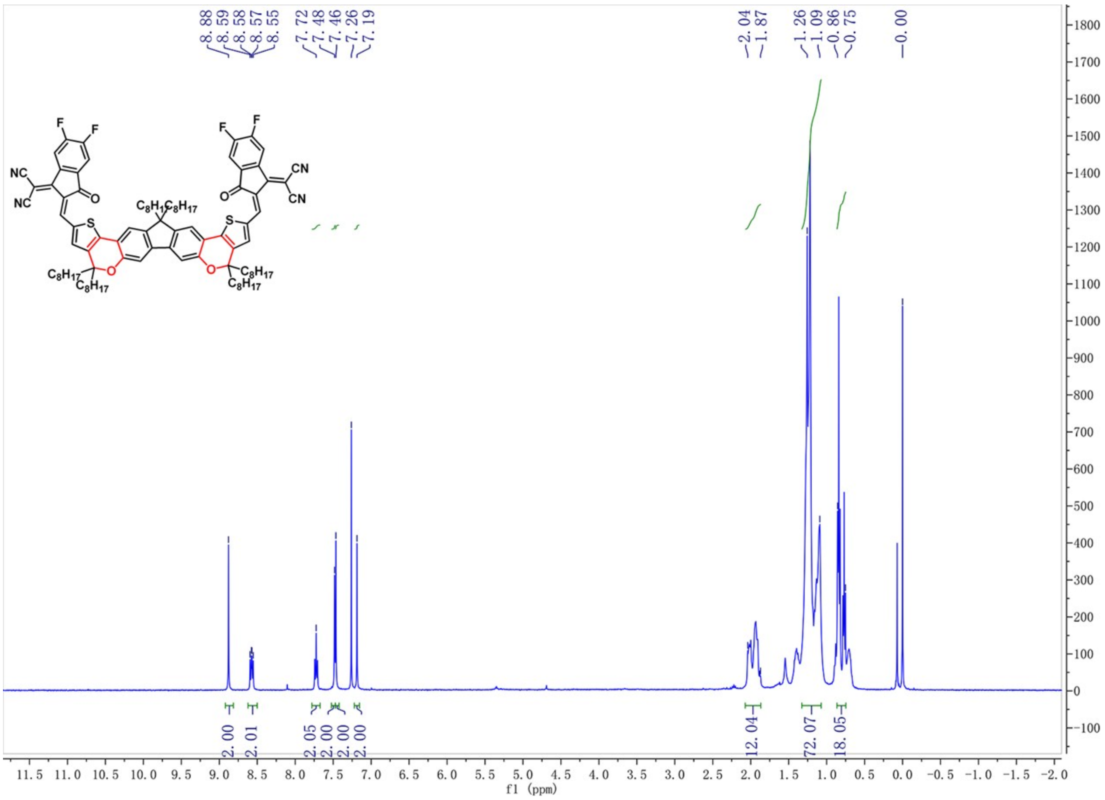


**Fig. S12** $^{1}$H NMR spectra of compound FO-2F in CDCl$_3$.

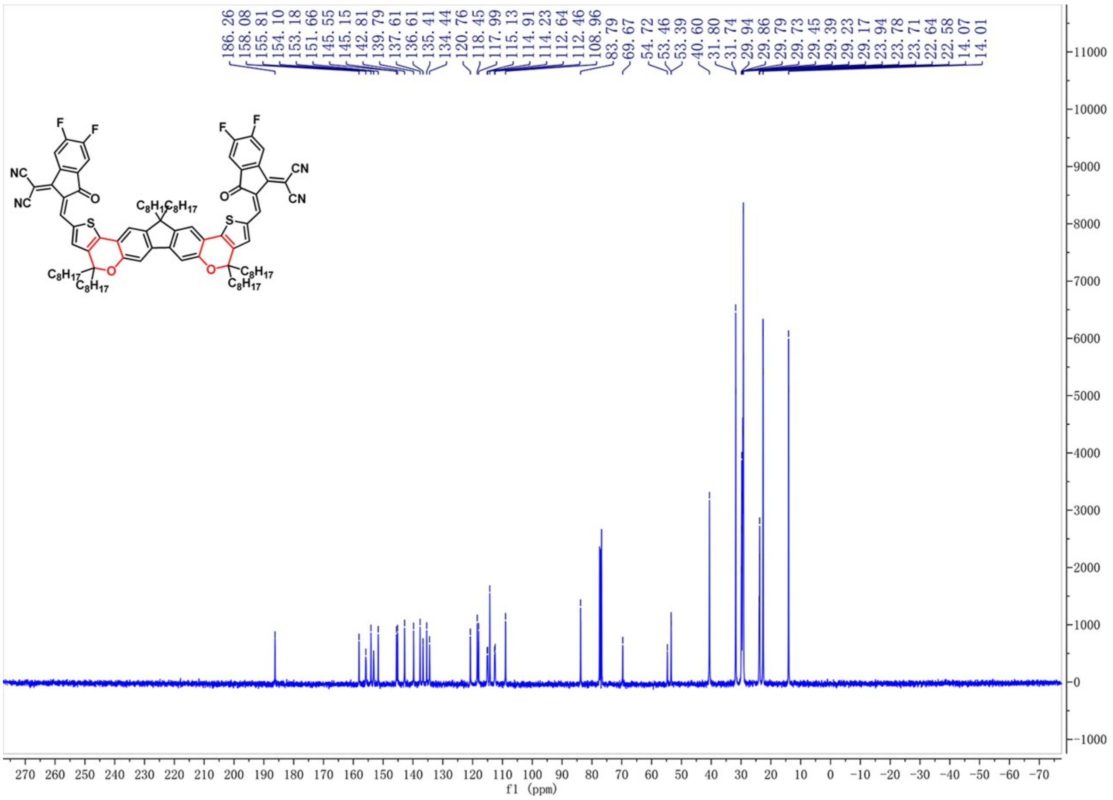


**Fig. S13** $^{13}$C NMR spectra of compound FO-2F in $CDCl_3$.

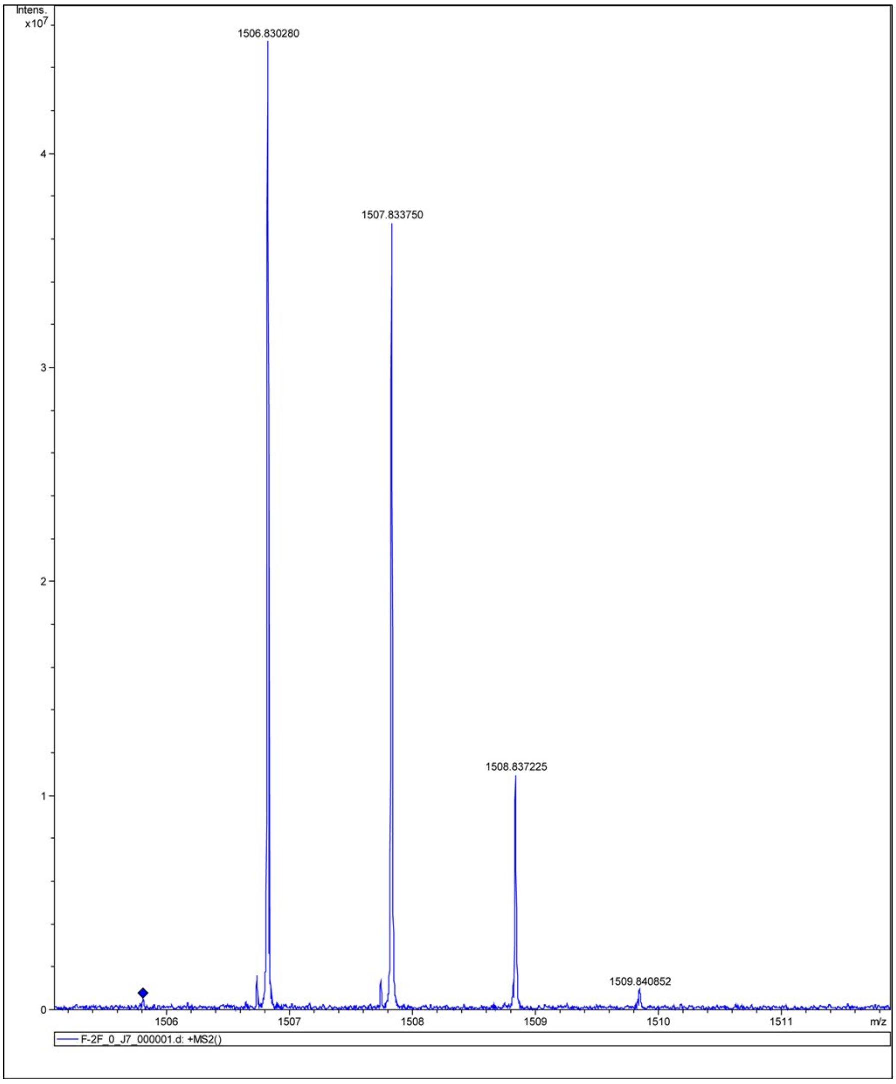


**Fig. S14** HR-MS plots of compound **F-2F**.

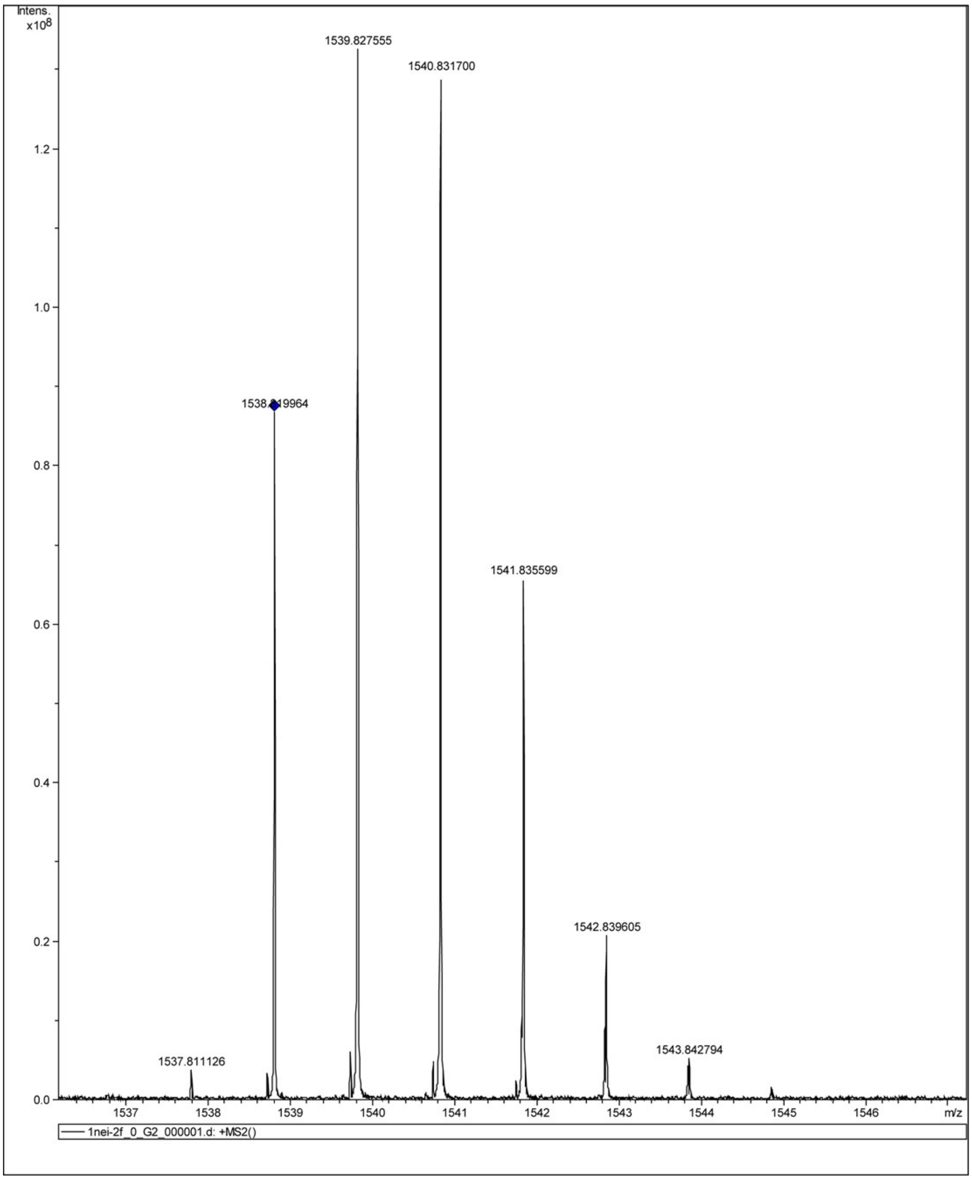


**Fig. S15** HR-MS plots of compound **FO-2F**.

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