

Supporting Information

Completely non-fused ring acceptors with low non-radiative energy loss enabled by end-group modulation

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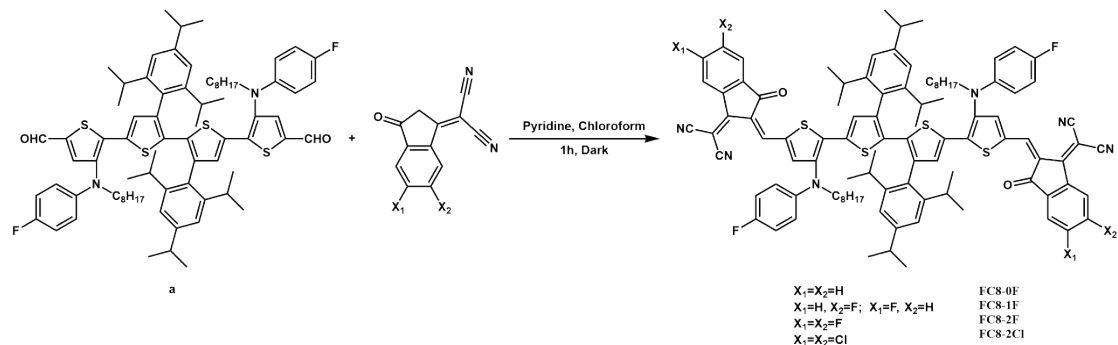
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Materials and Synthesis

Compound a was synthesized according to the literature,^[1] and the synthesis procedure of FC8-0F, FC8-1F, FC8-2F and FC8-2Cl can be concluded in **Scheme 1**.



Scheme 1. The synthesis routes of FC8-0F, FC8-1F, FC8-2F and FC8-2Cl.

Synthetic route of FC8-0F

Compound a (100.1 mg, 0.08 mmol) and 2-(3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (78.7 mg, 0.45 mmol) was dissolved in 10 mL of chloroform, and then 0.25 mL of pyridine was added into the mixture. The reaction was stirred at room temperature for 2 h. The reaction solution was diluted with 20 mL PE and the solution was directly purified by silica gel column using CH_2Cl_2 /PE(1:2 to 1:1) as eluent. The product FC8-0F was obtained as dark green solid (40.21 mg, 31.84%). ¹H NMR (400 MHz, Chloroform-*d*) δ = 8.67 (d, *J* = 9.1 Hz, 2H), 7.88 (d, *J* = 6.9 Hz, 1H), 7.74 (p, *J* = 7.0 Hz, 2H), 7.55 (s, 1H), 7.30 (s, 1H), 7.08 (s, 2H), 6.87 (t, *J* = 8.7 Hz, 2H), 6.38 (dd, *J* = 9.1, 4.2 Hz, 2H), 3.12 (p, *J* = 6.9 Hz, 1H), 2.97 – 2.79 (m, 2H), 2.57 (p, *J* = 6.8 Hz, 2H), 1.48 (d, *J* = 6.9 Hz, 8H), 1.25 (d, *J* = 10.7 Hz, 10H), 1.06 (d, *J* = 6.8 Hz, 6H), 0.93 – 0.57 (m, 9H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 148.97 , 148.43 , 147.36 , 146.60 , 141.51 , 140.06 , 139.23 , 137.14 , 136.77 , 136.67 , 135.27 , 134.57 , 133.17 , 131.56 , 125.33 , 123.85 , 122.86 , 121.80 , 115.66 , 115.36 , 114.75 , 114.65 , 77.22 , 50.94 , 34.25 , 31.79 , 30.76 , 29.41 , 29.33 , 27.08 , 25.99 , 25.22 , 24.15 , 22.93 , 22.62 , 14.11 .

Synthetic route of FC8-1F

Compound a (140.1 mg, 0.11 mmol) and 2-(5-fluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (120.4.9 mg, 0.57 mmol) was dissolved in 10 mL of chloroform, and then 0.2 mL of pyridine was added into the mixture. The reaction was stirred at

room temperature for 0.5 h. The reaction solution was diluted with 20 mL PE and the solution was directly purified by silica gel column using CH₂Cl₂ /PE(1:2 to 1:1) as eluent. The product FC8-1F was obtained as dark green solid (53.5 mg, 29.73%). ¹H NMR (300 MHz, Chloroform-d) δ 8.68 (d, J = 17.9 Hz, 1H), 8.35 (d, J = 8.6 Hz, 1H), 7.87 (dd, J = 8.4, 5.2 Hz, 1H), 7.53 (d, J = 9.4 Hz, 1H), 7.40 (t, J = 7.7 Hz, 1H), 7.32 (s, 1H), 7.07 (s, 2H), 6.84 (s, 2H), 6.37 (dd, J = 8.8, 4.3 Hz, 2H), 3.12 (p, J = 6.8 Hz, 1H), 2.85 (s, 2H), 2.63 – 2.50 (m, 2H), 1.47 (d, J = 6.9 Hz, 8H), 1.26 (s, 10H), 1.05 (d, J = 6.8 Hz, 5H), 0.96 – 0.60 (m, 8H). ¹³C NMR (75 MHz, Chloroform-d) δ 147.35 , 142.99 , 121.83 , 115.69 , 114.69 , 77.22 , 50.95 , 34.25 , 31.79 , 30.77 , 29.40 , 29.33 , 27.07 , 25.99 , 25.22 , 24.15 , 22.92 , 22.62 , 14.11 .

Synthetic route of FC8-2F

Compound a (315.1 mg, 0.26 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (293.9 mg, 1.28 mmol) was dissolved in 15 mL of chloroform, and then 0.2 mL of pyridine was added into the mixture. The reaction was stirred at room temperature for 1h. The reaction solution was diluted with 20 mL PE and the solution was directly purified by silica gel column using CH₂Cl₂ /PE(1:2 to 1:1) as eluent. The product FC8-2F was obtained as dark green solid (316.8 mg, 74.81%). ¹H NMR (300 MHz, Chloroform-d) δ 8.64 (s, 1H), 8.51 (dd, J = 9.9, 6.3 Hz, 1H), 7.63 (t, J = 7.4 Hz, 1H), 7.56 (s, 1H), 7.32 (s, 1H), 7.08 (s, 2H), 6.87 (t, J = 8.5 Hz, 2H), 6.37 (dd, J = 9.2, 4.2 Hz, 2H), 3.12 (p, J = 7.0 Hz, 1H), 2.86 (t, J = 8.2 Hz, 2H), 2.56 (p, J = 6.7 Hz, 2H), 1.59 – 1.38 (m, 9H), 1.26 (s, 10H), 1.06 (d, J = 6.7 Hz, 6H), 0.96 – 0.61 (m, 9H). ¹³C NMR (75 MHz, Chloroform-d) δ 149.28 , 149.10 , 147.34 , 141.88 , 139.52 , 137.49 , 136.83 , 132.98 , 131.86 , 130.43 , 121.87 , 115.71 , 115.41 , 114.83 , 114.72 , 77.21 , 50.96 , 34.24 , 31.78 , 30.78 , 29.39 , 29.32 , 27.07 , 26.01 , 25.21 , 24.14 , 22.92 , 22.61 , 14.10 .

Synthetic route of FC8-2Cl

Compound a (100.2 mg, 0.08 mmol) and 2-(5,6-dichloro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (106.6 mg, 0.41mmol) was dissolved in 10 mL of chloroform, and then 0.2 mL of pyridine was added into the mixture. The reaction was stirred at room temperature for 0.5 h. The reaction solution was diluted with 20 mL PE

and the solution was directly purified by silica gel column using $\text{CH}_2\text{Cl}_2/\text{PE}(1:2 \text{ to } 1:1)$ as eluent. The product FC8-2Cl was obtained as light green solid (30.2 mg, 21.47%). ^1H NMR (300 MHz, Chloroform-*d*) δ 8.75 (s, 1H), 8.67 (s, 1H), 7.89 (s, 1H), 7.57 (s, 1H), 7.34 (s, 1H), 7.08 (s, 2H), 6.87 (t, $J = 8.6$ Hz, 2H), 6.37 (dd, $J = 9.1, 4.3$ Hz, 2H), 3.12 (p, $J = 7.0$ Hz, 1H), 2.95 – 2.73 (m, 2H), 2.66 – 2.39 (m, 2H), 1.48 (d, $J = 6.9$ Hz, 8H), 1.26 (s, 9H), 1.06 (d, $J = 6.7$ Hz, 5H), 0.94 – 0.48 (m, 9H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 149.15 , 147.35 , 142.97 , 142.07 , 139.93 , 139.66 , 139.61 , 138.68 , 137.65 , 137.38 , 135.86 , 133.24 , 132.02 , 130.39 , 126.99 , 125.26 , 121.89 , 115.72 , 115.42 , 114.88 , 114.78 , 114.04 , 70.31 , 51.00 , 34.23 , 31.78 , 30.80 , 29.39 , 29.31 , 27.08 , 26.05 , 25.21 , 24.13 , 22.93 , 22.60 , 14.09 .

Measurements and Instruments

Current density/voltage (J - V) measurements were performed in the AM 1.5G spectrum using an Enlitech SS-F5-3A solar simulator. External quantum efficiency (EQE) spectra were measured using the Enlitech QE-R3011 quantum efficiency measurement system. Photo-carrier extraction by linearly increasing voltage (Photo-CELIV) measurement was conducted using the Fluxim AG Paios all-in-one characterization platform. Sensitive EQE (s-EQE) spectra were recorded using the Enlitech PECT-600 integrated system. Electroluminescence quantum efficiency (EQE_{EL}) spectra were measured using an Enlitech ELCT-3010. The effective voltage is obtained by subtracting the built-in voltage (V_{bi}) from the applied voltage (V_{app}), $V = V_{\text{app}} - V_{\text{bi}}$. ^1H and ^{13}C NMR spectra were recorded with Bruker Fourier 300, Avance 400 and Avance III 400 HD spectrometers. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were acquired on a Bruker Reflex II-TOF spectrometer. Absorption spectra were measured with a Hitachi UH5300 spectrophotometer. Electrochemical cyclic voltammetry (CV) measurements were performed using a standard three-electrode system in 0.1 M Bu₄NPF₆ in MeCN solution, while scanning at 0.1 V s⁻¹ under an argon atmosphere at room temperature using a CH Instruments CHI650D electrochemical workstation rate. Density functional theory (DFT) calculations were performed using Gaussian 09 software. Atomic Force Microscopy (AFM) images were acquired using a Bruker Multimode 8 AFM microscope. Space charge limited current (SCLC) hole and electron mobility equipped with

ITO/PEDOT:PSS/PBDB-TF:Acceptor/Au device structure for hole mobility, and ITO/ZnO/PBDB-TF:Acceptor/Al for electron mobility for the Mott-Gurney equation.

The fabrication of OSCs

OSCs fabricated with a conventional structure of ITO/PEDOT:PSS/PBDB-TF:NFEAs/PFN-Br/Al. The ITO-coated glass was washed with deionized water/detergent, deionized water, acetone and ethanol in sequence for 15 minutes. Later, the ITO-coated glass was treated under the ultraviolet-ozone condition for 20 min. After that, PEDOT:PSS (Heraeus Clevis™ AI 4083) was spin coated onto the glass at 3000 r.p.m for 40 s and processed by thermal annealing at 155 °C for 15 min. To make PBDB-TF dissolved fully, the blends of PBDB-TF: NFEAs (1:1, w/w) was dissolved in chloroform (CF) at a total concentration of 16 mg mL⁻¹ and stirred for 2 hours at 45 °C. Next, adding 0.5 % (v/v) 1,8- diiodooctane (DIO) as additive into the host solution CF prior to the spin-coating treatment. Afterwards, the blend solution was spin-coated and thermal annealed at 100 °C for 10 min. Subsequently, PFN-Br was spin-coated on the active layer at 3000 r.p.m. Finally, the OSC was finished by evaporating 100-nm- thick Al under high vacuum (about 2×10⁻⁴ Pa).

Supporting Figures

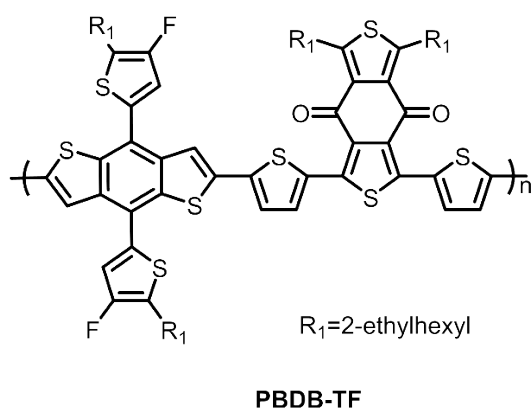


Fig. S1. Chemical structure of the donor PBDB-TF.

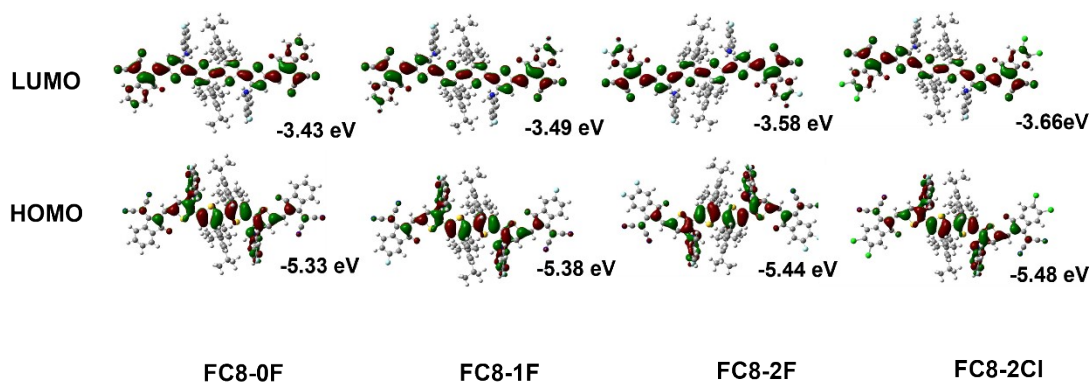


Fig. S2. DFT calculation for simplified models of NFREAs at B3LYP/6-31G (d, p) level.

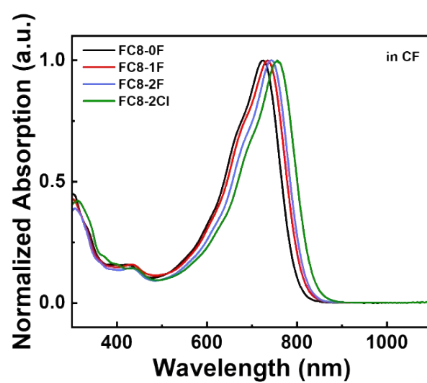


Fig. S3. Normalized UV-Vis absorption spectrum of FC8-0F, FC8-1F, FC8-2F and FC8-2Cl in CF.

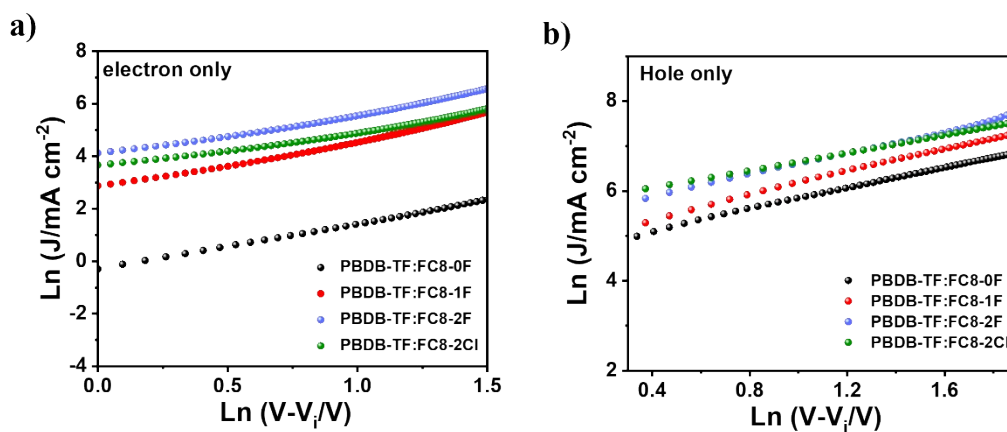


Fig. S4. a) electron mobilities and b) hole mobilities of PBDB-TF:NFREAs blend films.

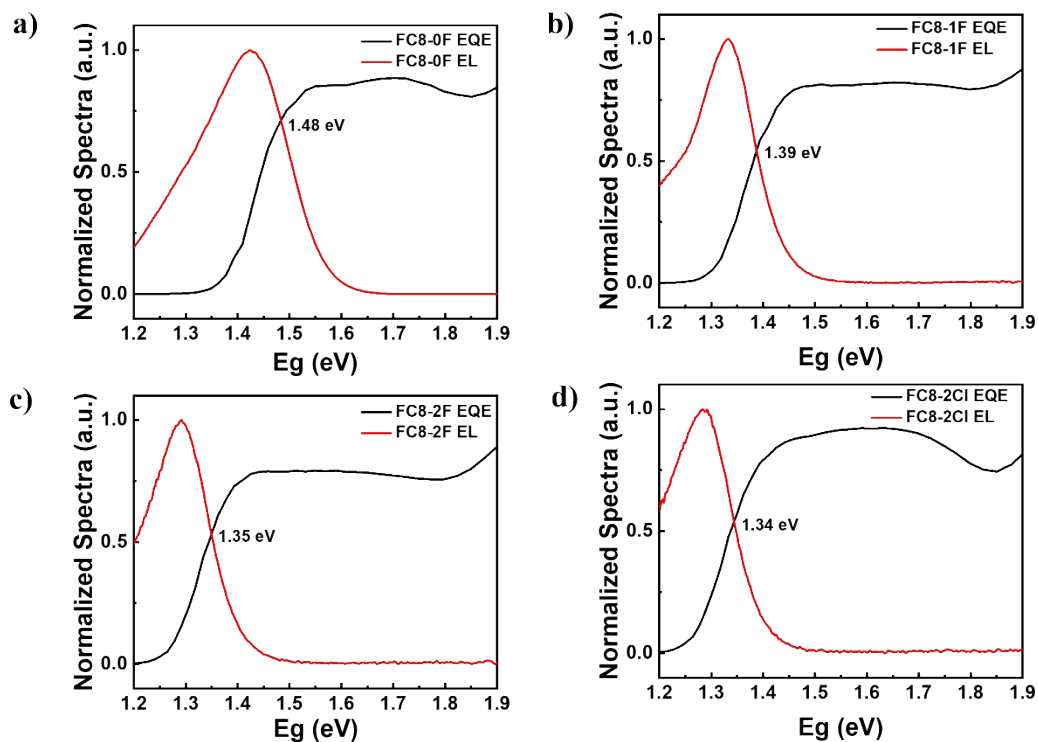


Fig. S5. Normalized EQE and EL spectra for a) PBDB-TF:FC8-0F, b) PBDB-TF:FC8-1F, c) PBDB-TF:FC8-2F and d) PBDB-TF:FC8-2Cl.

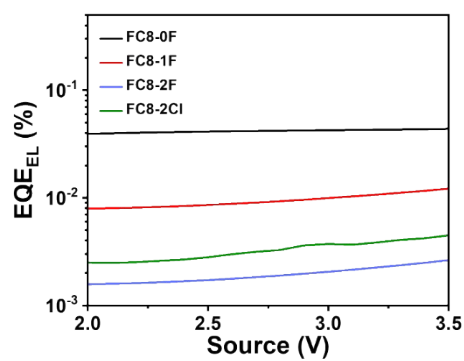


Fig. S6. EQE_{EL} spectrum of PBDB-TF:FC8-0F, PBDB-TF:FC8-1F, PBDB-TF:FC8-2F and PBDB-TF:FC8-2Cl based devices.

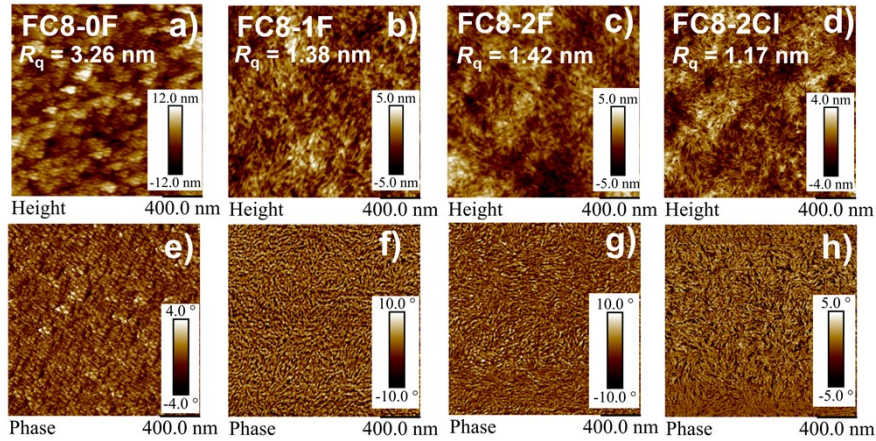


Fig. S7. a-h) AFM height and phase images for PBDB-TF:FC8-0F-, PBDB-TF:FC8-1F-, PBDB-TF:FC8-2F- and PBDB-TF:FC8-2Cl- blend films.

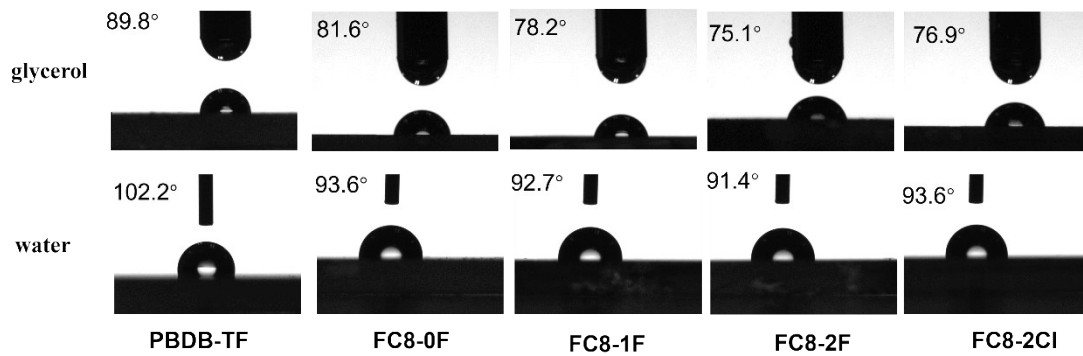


Fig. S8. The contact angles of PBDB-TF, FC8-0F, FC8-1F, FC8-2F and FC8-2Cl on water and glycerol.

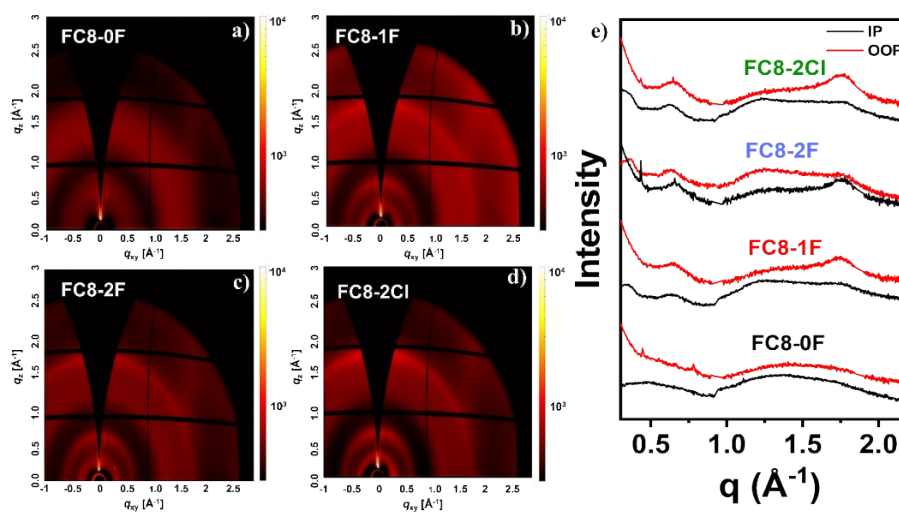


Fig. S9. a-d) 2D GIWAXS patterns for FC8-0F, FC8-1F, FC8-2F and FC8-2Cl pristine films. e) Extracted 1D GIWAXS profiles of the four pristine films.

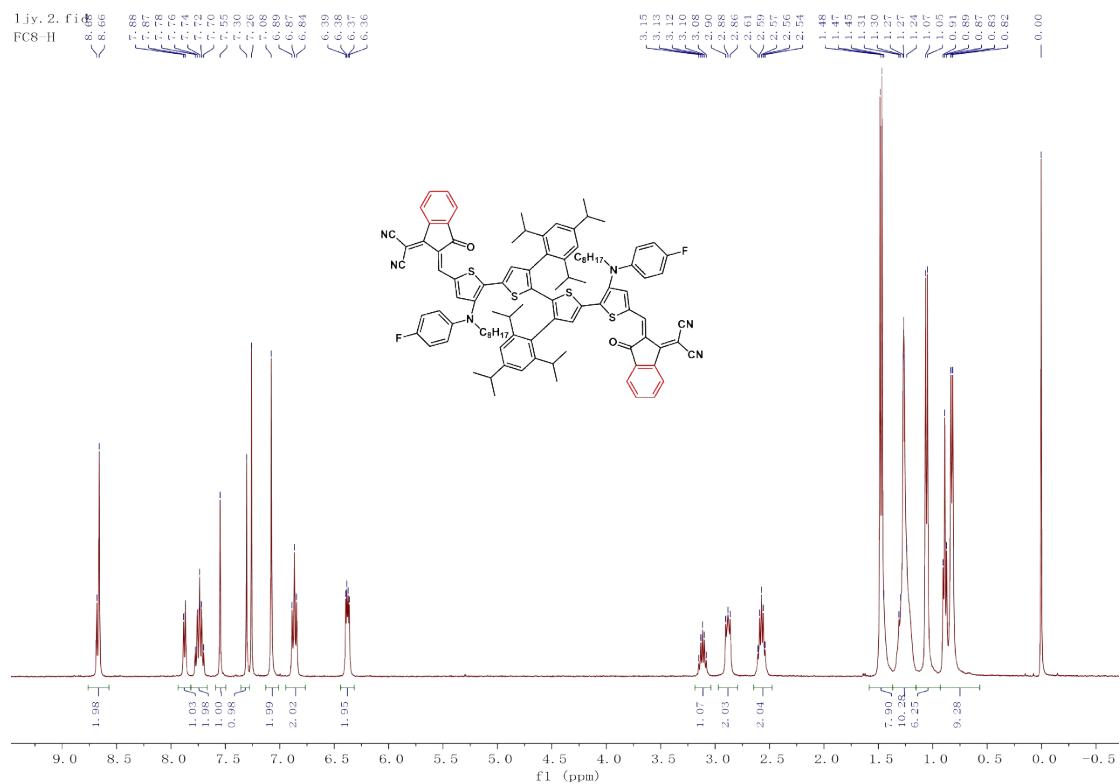


Fig S10. $^1\text{H-NMR}$ spectrum of FC8-0F.

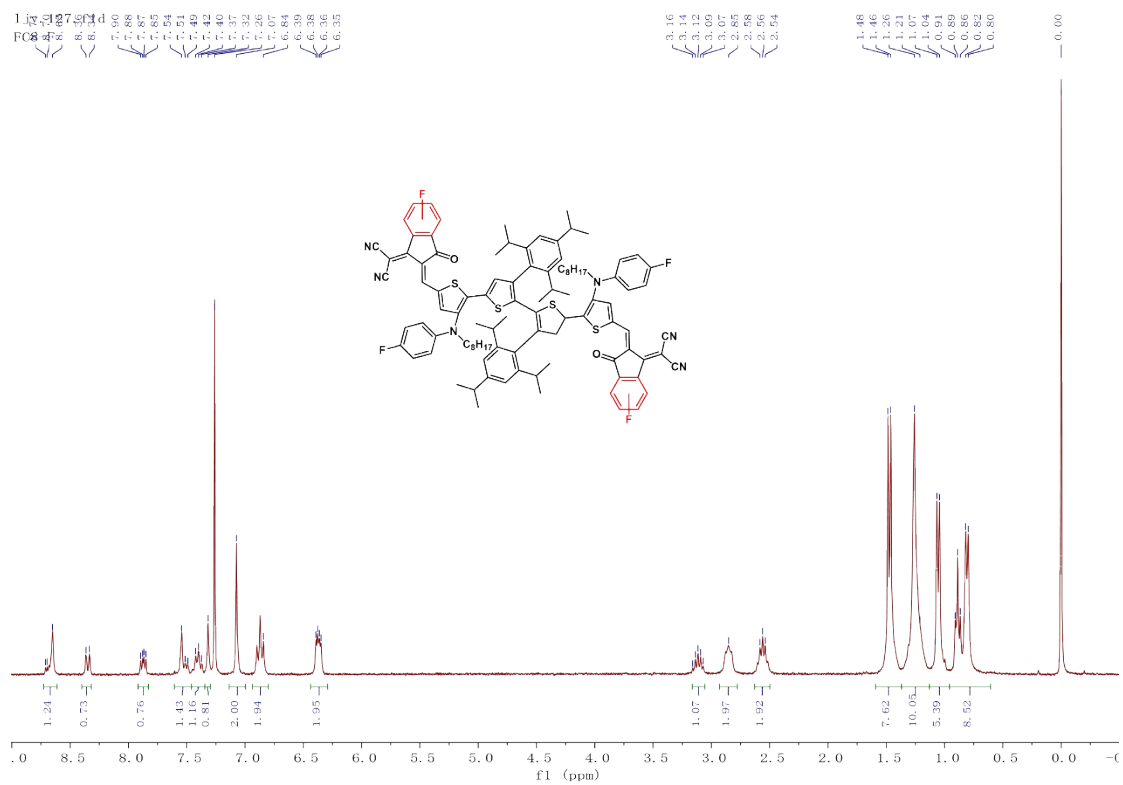


Fig S11. $^1\text{H-NMR}$ spectrum of FC8-1F.

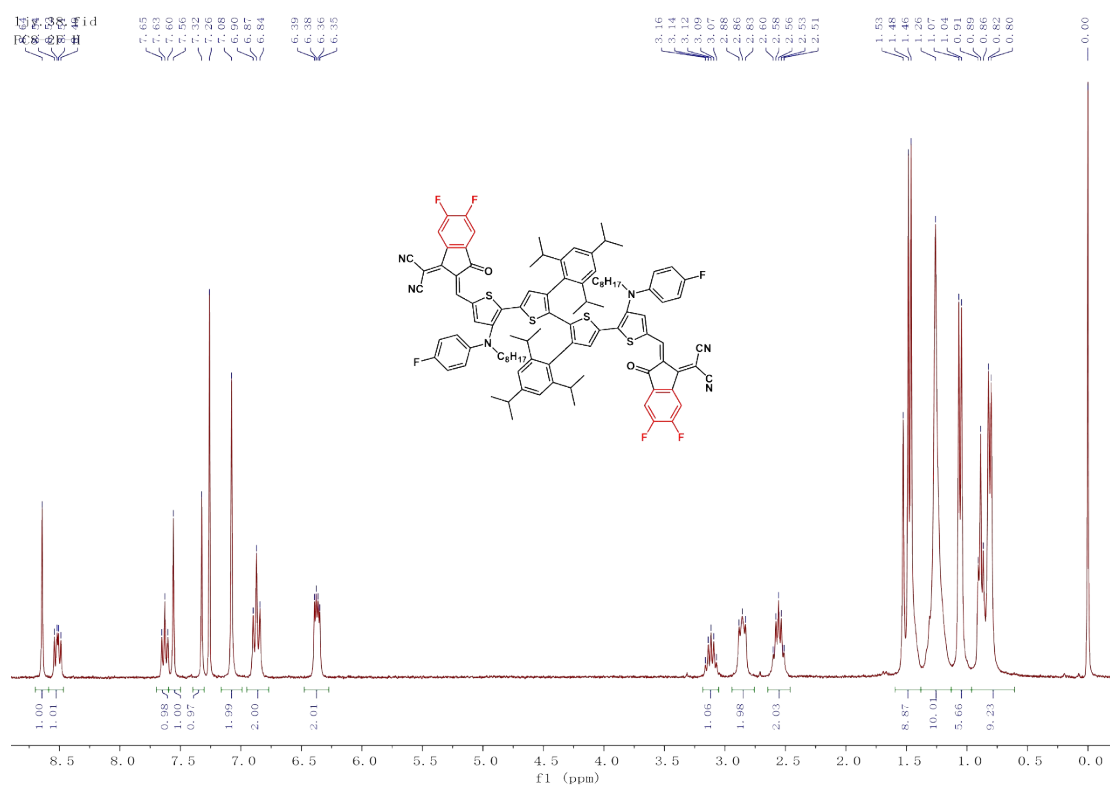


Fig S12. $^1\text{H-NMR}$ spectrum of FC8-2F.

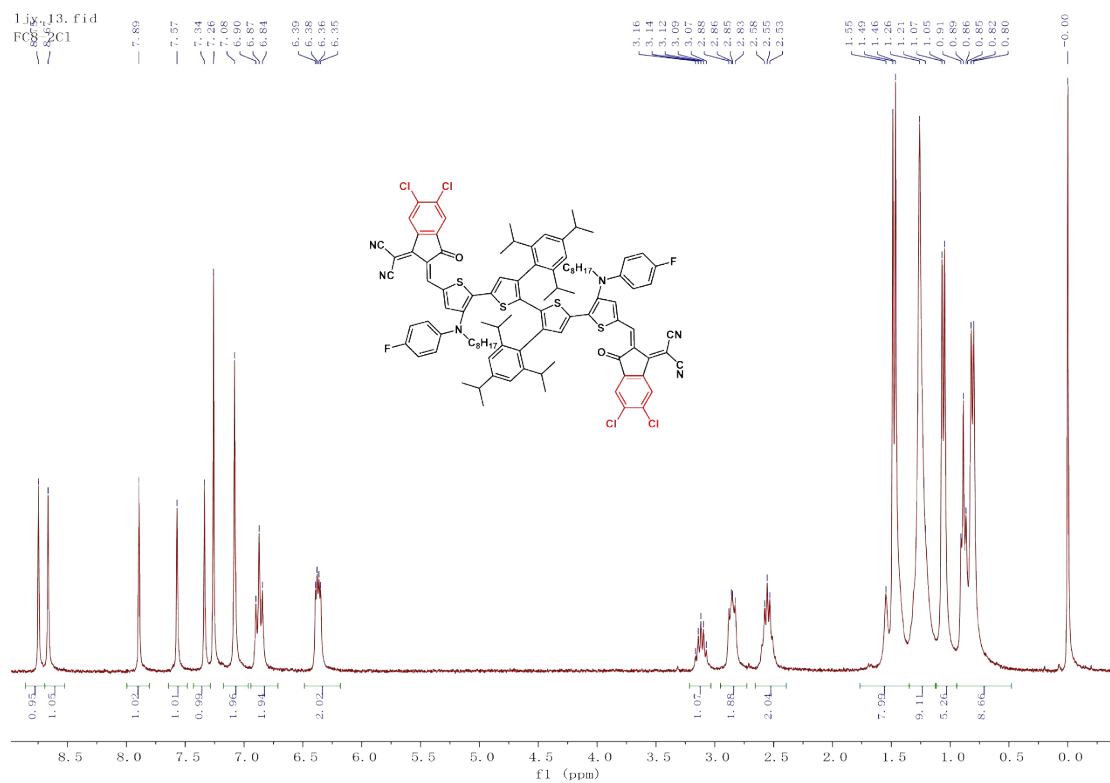


Fig S13. $^1\text{H-NMR}$ spectrum of FC8-2Cl.

Ljy. 117. fid
FC8-0F-C

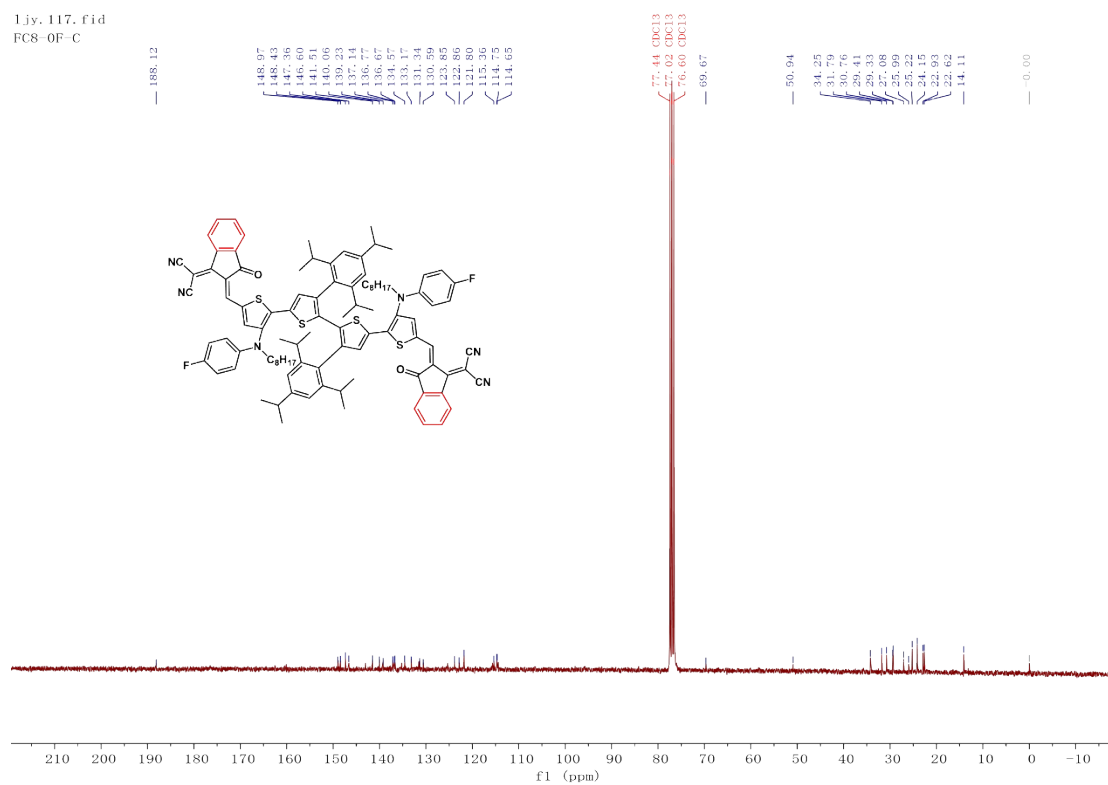


Fig. S14. ^{13}C -NMR spectrum of FC8-0F.

Ljy. 21. fid
FC8-1F-C

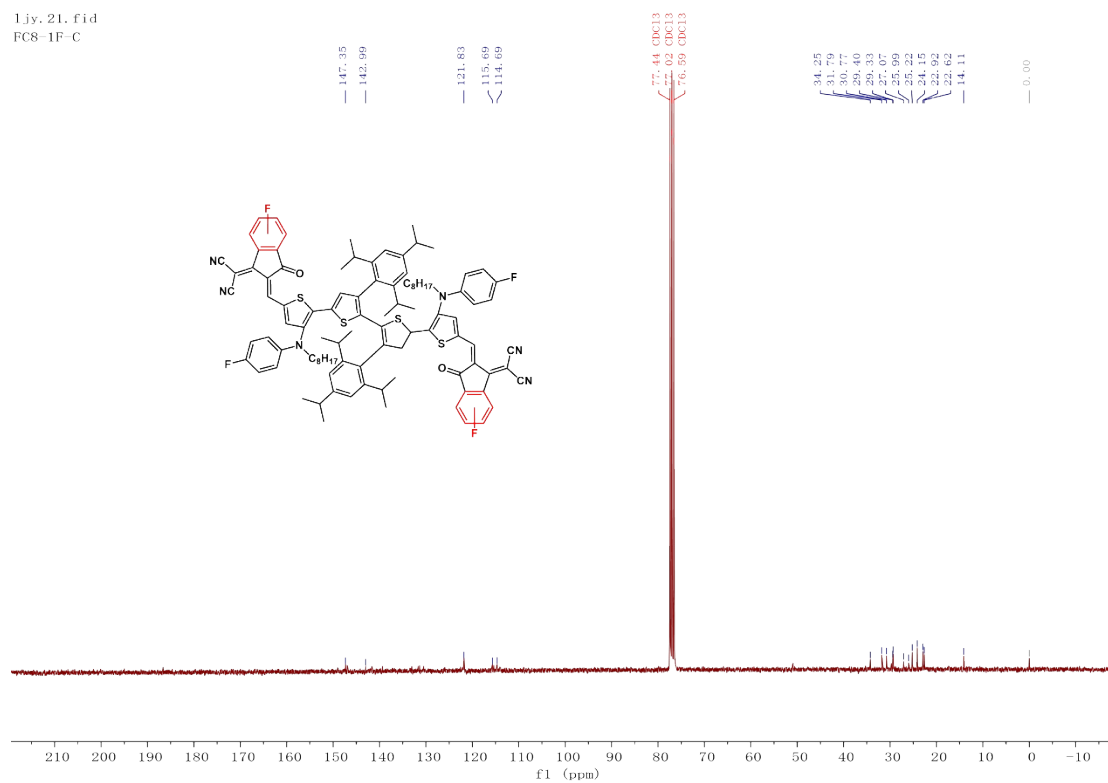


Fig. S15. ^{13}C -NMR spectrum of FC8-1F.

Ljy. 39. fid
FC8-2F-C

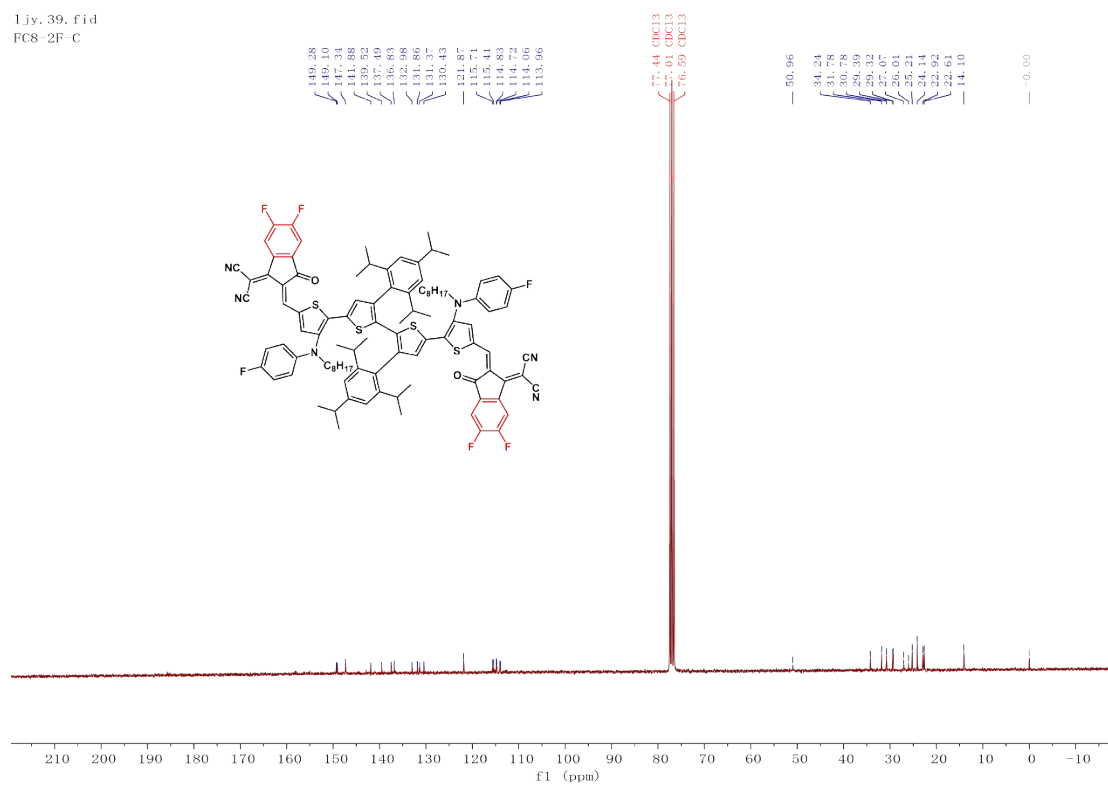


Fig. S16. ¹³C-NMR spectrum of FC8-2F.

Ljy. 65. fid
FC8-2Cl-C

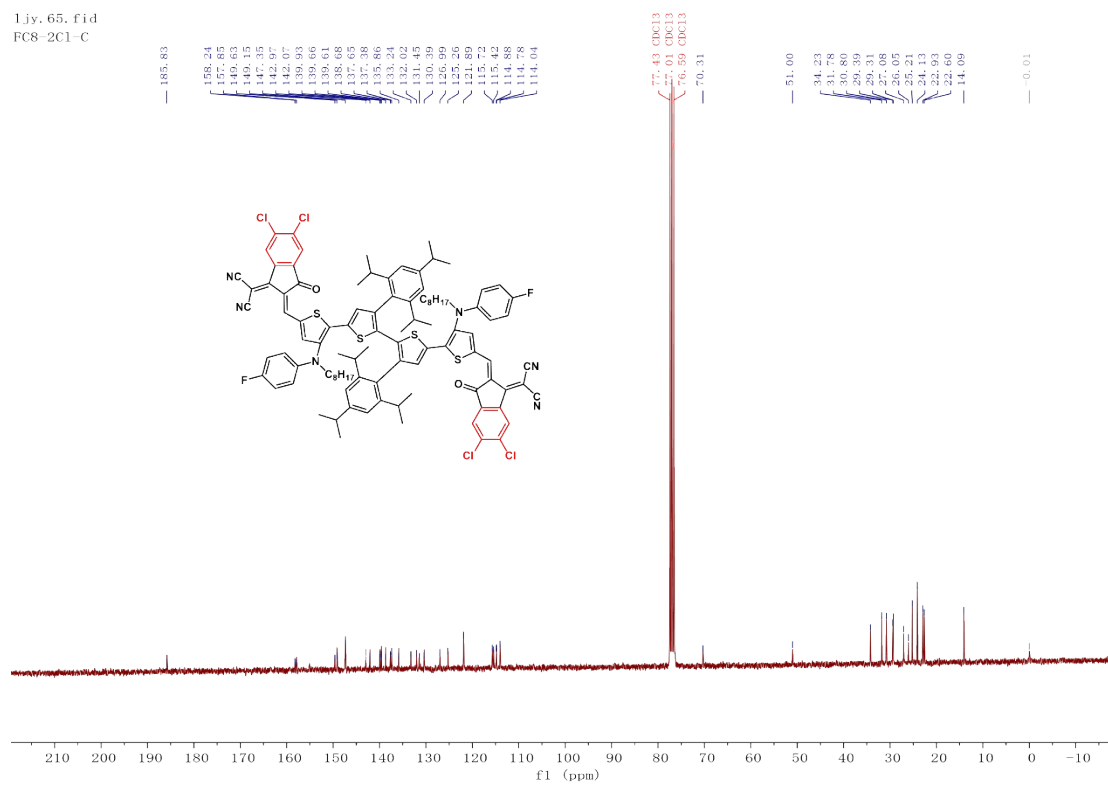


Fig. S17. ¹³C-NMR spectrum of FC8-2Cl.

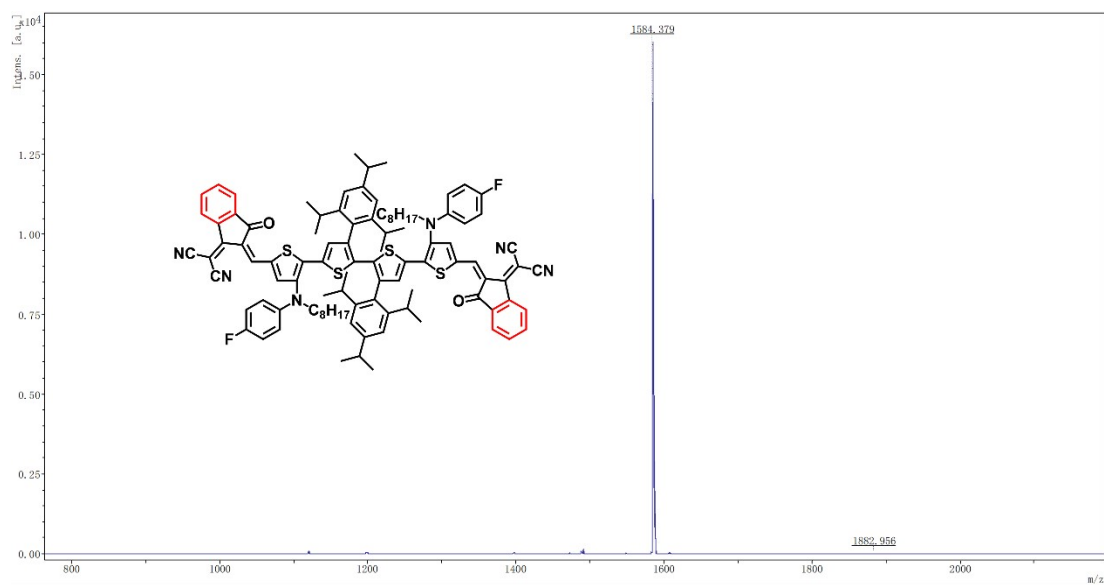


Fig. S18. MALDI-TOF mass spectrum of FC8-0F.

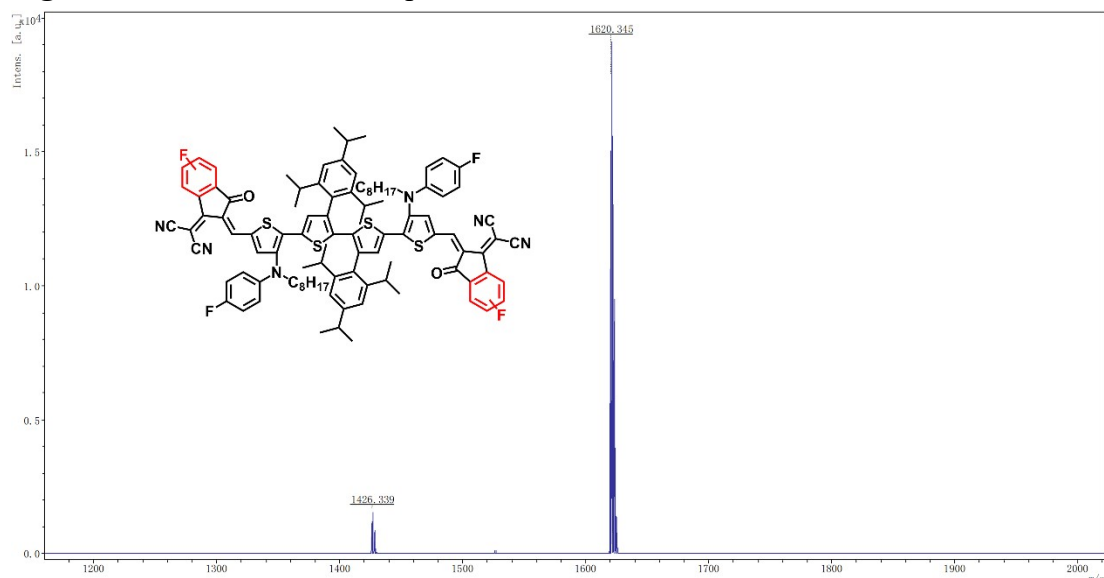


Fig. S19. MALDI-TOF mass spectrum of FC8-1F.

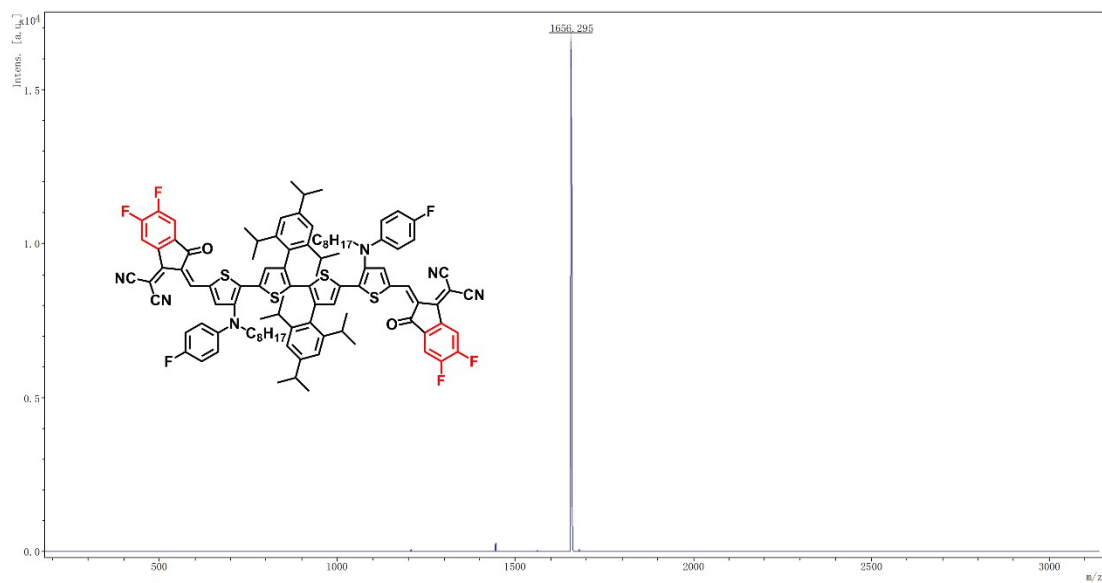


Fig. S20. MALDI-TOF mass spectrum of FC8-2F.

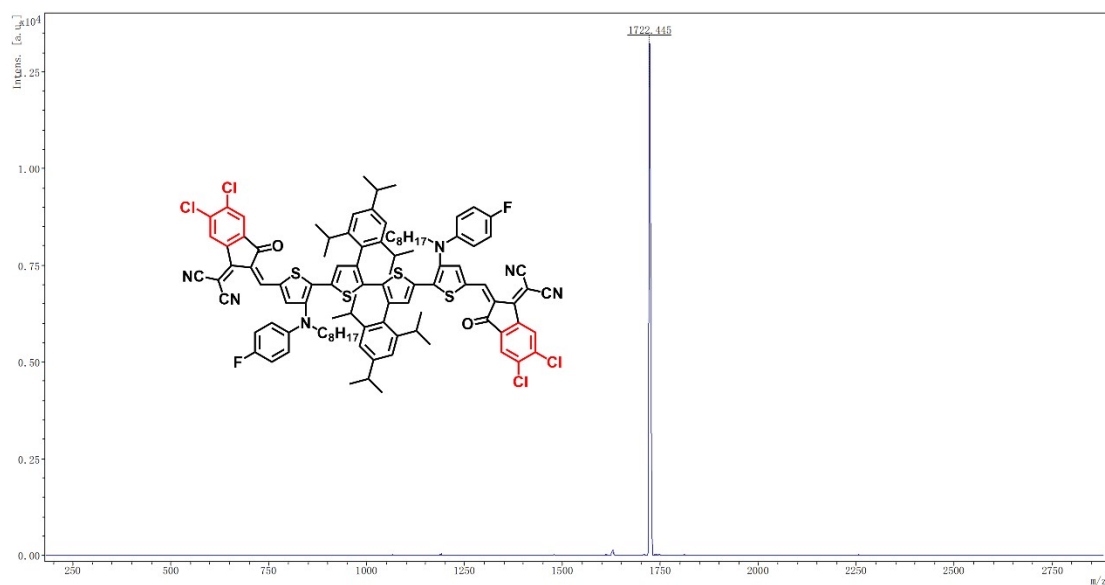


Fig. S21. MALDI-TOF mass spectrum of FC8-2Cl.

Table S1. The devices optimization based on ITO/PEDOT:PSS/PBDB-TF:FC8-2Cl/PFN-Br/Al by different solvents.

Solvent	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
CF	0.753	23.47	71.32	12.61
CB	0.714	17.96	70.22	9.01
Tol	0.715	18.19	71.98	9.36
<i>o</i> -XY	0.708	20.64	71.09	10.40

Table S2. The devices optimization based on ITO/PEDOT:PSS/PBDB-TF:FC8-2Cl/PFN-Br/Al by D/A ratios.

D/A ratio	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
1:0.8	0.751	23.28	71.64	12.52
1:1	0.754	23.00	73.04	12.67
1:1.2	0.749	23.98	69.32	12.46
1:1.5	0.752	23.31	69.44	12.18

Table S3. The devices optimization based on ITO/PEDOT:PSS/PBDB-TF:FC8-2Cl/PFN-Br/Al by different additives.

Additive	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
DIO	0.756	22.92	73.26	12.70
CN	0.741	23.31	70.69	12.20
DPE	0.771	23.73	69.31	12.67

Table S4. The devices optimization based on ITO/PEDOT:PSS/PBDB-TF:FC8-2Cl/PFN-Br/Al by different additive contents.

Additive Content	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
0.2%	0.764	24.26	68.75	12.74
0.5%	0.750	23.99	72.84	13.11
1%	0.748	21.81	72.18	11.78

Table S5. The devices optimization based on ITO/PEDOT:PSS/PBDB-TF:FC8-2Cl/PFN-Br/Al by different annealing conditions.

Annealing condition	V_{OC} [V]	J_{SC} [mA cm ⁻²]	FF [%]	PCE [%]
none	0.767	22.65	66.53	11.55
80°C,10 min	0.768	22.77	67.62	11.83
100°C,10 min	0.756	24.03	73.05	13.28
120°C,10 min	0.760	22.67	69.70	12.00

Table S6. The contact angles of PBDB-TF, FC8-0F, FC8-1F, FC8-2F and FC8-2Cl on water and glycerol.

Material	θ_{water}	θ_{glycerol}	γ (mN m ⁻¹)	χ
FC8-0F	93.6	81.6	22.52	0.19
FC8-1F	92.7	78.2	26.42	0.69
FC8-2F	91.4	75.1	29.95	1.35
FC8-2Cl	93.6	76.9	29.51	1.26
PBDB-TF	102.2	89.8	18.58	-

References

- [1]. J. Li, H. Li, L. Ma, S. Zhang and J. Hou, *Chin. J. Chem.*, 2023, **41**, 424-430.