

Supporting Information

Fused-ring electron acceptors with a macrocyclic side chain

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1. General characterization

¹H and ¹³C NMR spectra were measured on a Bruker Avance-400 spectrometer. Absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Cyclic voltammetry was done by using a Shanghai Chenhua CHI620D voltammetric analyzer under argon in an anhydrous acetonitrile solution of tetra-n-butylammonium hexafluorophosphate (0.1 M). A glassy-carbon electrode was used as the working electrode, a platinum-wire was used as the counter electrode, and a Ag/Ag⁺ electrode was used as the reference electrode. Acceptors were coated onto glassy-carbon electrode and all potentials were corrected against Fc/Fc⁺. AFM was performed on a Multimode microscope (Bruker-M8-HR) by using tapping mode. Single-crystal X-ray diffraction data of MC8-4H was collected on a Bruker D8 VENTURE diffractometer.

2. Synthesis

All reagents were purchased from J&K Co., Aladdin Co., Innochem Co., and other commercial suppliers. Tributyl(6-undecylthieno[3,2-b]thiophene-2-yl)stannane was synthesized according to literature.^[1] All reactions dealing with air- or moisture-sensitive compounds were carried out by using standard Schlenk techniques.

Compound 1. To a mixture of 2,5-dibromoterephthalaldehyde (782 mg, 2.68 mmol), tributyl(6-undecylthieno[3,2-b]thiophene-2-yl)stannane (3.9 g, 6.68 mmol) and Pd(PPh₃)₄ (310 mg, 0.27 mmol) was added DMF (8 mL) under N₂. The mixture was heated to 130 °C and stirred for 1 h. After cooling to room temperature, the reaction mixture was poured into methanol and filtered. The residue was washed with methanol to give **compound 1** as a yellow solid (1.84 g, 95%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 10.34 (s, 2H), 8.22 (s, 2H), 7.30 (s,

2H), 7.10 (s, 2H), 2.77 (t, $J = 7.6$ Hz, 4H), 1.83-1.74 (m, 4H), 1.44-1.24 (m, 32H), 0.88 (t, $J = 6.7$ Hz, 6H). ^{13}C NMR (CDCl_3 , 100 MHz, δ/ppm): 191.02, 141.58, 139.22, 138.07, 137.29, 136.79, 135.10, 130.93, 123.01, 122.83, 31.91, 29.93, 29.65, 29.62, 29.57, 29.40, 29.37, 29.35, 28.64, 22.69, 14.12. MALDI-TOF MS (m/z): $\text{C}_{42}\text{H}_{54}\text{O}_2\text{S}_4$ (M^+) calc. 718.3, found 718.3.

Compound 2. To compound 1 (278 mg, 0.387 mmol) was added phenylmagnesium bromide (3.9 mL, 1.0 M in THF) under N_2 . After stirring for 0.5 h, the reaction mixture was poured into water and extracted with petroleum ether (PE). After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CH_2Cl_2 as eluent to afford the phenylation intermediate as a yellow solid. Then, to a mixture of the above solid (282 mg) and Amberlyst 15 (250 mg) was added dry toluene (100 mL). The mixture was stirred at room temperature for 1.5 h. The mixture was purified via flash column chromatography (silica gel) by using hot CHCl_3 as eluent to give **compound 2** as a yellow solid (270 mg, 83%). ^1H NMR (CDCl_3 , 400 MHz, δ/ppm): 7.41 (s, 2H), 7.36-7.28 (m, 6H), 7.25-7.22 (m, 4H), 6.85 (s, 2H), 5.02 (s, 2H), 2.71 (t, $J = 7.4$ Hz, 4H), 1.80-1.69 (m, 4H), 1.34-1.26 (m, 32H), 0.87 (t, $J = 6.6$ Hz, 6H). ^{13}C NMR data was not acquired due to the low solubility of compound 2. MALDI-TOF MS (m/z): $\text{C}_{54}\text{H}_{62}\text{S}_4$ (M^+) calc. 838.4, found 838.4.

MC8-CHO. To a mixture of compound 2 (258 mg, 0.31 mmol) and $t\text{-BuONa}$ (118 mg, 1.23 mmol) was added dry DMSO (86 mL) under N_2 . After stirring for additional 40 minutes, 1,8-diiodooctane (72 μL , 0.372 mmol) was added. The solution was heated to 80 $^\circ\text{C}$ and stirred for 10 minutes. After cooling to room temperature, the reaction mixture was poured into water and extracted with PE. After removal of the solvent, the mixture was purified via flash column chromatography (silica gel) by using CH_2Cl_2 as eluent to give macrocyclic intermediate MC8 as a green oil. MC8 is not stable under air. To avoid decomposition, the MC8 was quickly mixed with anhydrous DMF (0.1 mL), POCl_3 (0.1 mL) and dichloroethane (4.0 mL) at 0 $^\circ\text{C}$ under N_2 . After stirring at room temperature for 10 minutes, the mixture was heated to 80 $^\circ\text{C}$ and stirred overnight. Then, the solution was cooled to 0 $^\circ\text{C}$, quenched with saturated CH_3COOK (aq) and extracted with CH_2Cl_2 . After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CH_2Cl_2 :PE (1:1) as eluent to give **MC8-CHO** as a yellow sticky solid (65 mg, 21%). ^1H NMR (CDCl_3 , 400 MHz, δ/ppm): 10.02 (s, 2H), 7.48-7.27 (m, 12H), 3.13-3.06 (m, 4H), 2.88-2.83 (m, 2H), 2.47-2.41 (m, 2H), 1.87-1.80 (m, 4H), 1.45-1.26 (m, 32H), 1.13-1.04 (m, 4H), 0.88 (t, $J = 6.8$ Hz, 6H), 0.83-0.77 (m, 2H), 0.48-0.47 (m, 2H), 0.33-0.31 (m, 2H), 0.24-0.11 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz, δ/ppm): 181.86, 155.03, 148.94, 146.84, 146.01, 143.71, 140.99, 138.25, 138.17, 137.58, 128.97, 127.49, 126.47, 117.20, 57.75, 35.35, 31.87, 30.24, 29.58, 29.56, 29.45, 29.29, 28.45, 28.26, 28.13, 25.24, 22.66, 14.10. MALDI-TOF MS (m/z): $\text{C}_{64}\text{H}_{76}\text{O}_2\text{S}_4$ (M^+) calc. 1004.5, found 1004.5.

MC8-4H. To a solution of MC8-CHO (74 mg, 0.074 mmol) and 3-dicycanovinylindan-1-one (72 mg, 0.371 mmol) in chloroform (4 mL) was added pyridine (8 drops). The mixture was heated to reflux and stirred for 80 minutes. The mixture was then purified via column chromatography (silica gel) by using CHCl_3 as eluent to give **MC8-4H** as a black solid (77 mg, 77%). ^1H NMR (CDCl_3 , 400 MHz, δ/ppm): 9.08 (s, 2H), 8.69 (d, $J = 7.1$ Hz, 2H), 7.91-7.83 (m, 2H), 7.76-7.66 (m, 4H), 7.52 (s, 2H), 7.48-7.46 (m, 4H), 7.39 (t, $J = 7.6$ Hz, 4H), 7.33-7.29

(m, 2H), 3.17-3.14 (m, 4H), 2.96-2.92 (m, 2H), 2.57-2.52 (m, 2H), 1.85-1.81 (m, 4H), 1.51-1.47 (m, 4H), 1.38-1.05 (m, 32H), 0.89-0.79 (m, 8H), 0.49-0.47 (m, 2H), 0.36-0.34 (m, 2H), 0.23-0.15 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz, δ/ppm): 188.40, 161.09, 156.37, 152.85, 152.65, 147.56, 145.44, 144.30, 140.62, 139.98, 137.86, 136.84, 135.44, 134.97, 134.64, 134.24, 129.15, 127.71, 126.42, 125.18, 123.54, 121.04, 117.54, 115.32, 114.91, 68.32, 57.90, 35.32, 31.89, 31.08, 29.84, 29.76, 29.62, 29.60, 29.48, 29.38, 29.32, 28.64, 28.27, 25.32, 22.67, 14.11. MALDI-TOF MS (m/z): $\text{C}_{88}\text{H}_{84}\text{N}_4\text{O}_2\text{S}_4$ (M^+) calc. 1356.5, found 1356.6. Single crystals were obtained by slow diffusion of MeOH into the CHCl_3 solution of MC8-4H. Formula: $\text{C}_{89}\text{H}_{85}\text{Cl}_3\text{N}_4\text{O}_2\text{S}_4$ (CHCl_3 is contained in the crystal); formula weight: 1477.19; crystal system: triclinic; space group: P-1; unit cell parameters: $a = 12.9896(13)$ Å, $b = 21.2706(18)$ Å, $c = 29.157(3)$ Å, $\alpha = 78.613(3)^\circ$, $\beta = 80.549(4)^\circ$, $\gamma = 81.194(3)^\circ$, $V = 7729.5(13)$ Å³; temperature for data collection: 170.0 K; $Z = 4$; final R indices [$I > 2\sigma(I)$]: $R_1 = 0.1323$, $wR_2 = 0.3242$; GoF on F^2 : 1.084. The crystallographic data have been deposited in Cambridge Crystallographic Data Centre (CCDC-2241547).

MC8-4F. To a solution of MC8-CHO (38 mg, 0.038 mmol) and DFIC (45 mg, 0.196 mmol) in CHCl_3 (2 mL) was added pyridine (5 drops). The mixture was heated to reflux and stirred for 1 h. The mixture was then purified via column chromatography (silica gel) by using CHCl_3 as eluent to give **MC8-4F** as a black solid (34 mg, 63%). ^1H NMR (CDCl_3 , 400 MHz, δ/ppm): 9.05 (s, 2H), 8.54 (dd, $J = 10.0, 6.5$ Hz, 2H), 7.64 (t, $J = 7.5$ Hz, 2H), 7.53 (s, 2H), 7.48-7.30 (m, 10H), 3.19-3.14 (m, 4H), 2.98-2.93 (m, 2H), 2.57-2.52 (m, 2H), 1.84-1.80 (m, 4H), 1.50-1.47 (m, 4H), 1.37-1.26 (m, 28H), 1.15-1.05 (m, 4H), 0.89-0.82 (m, 8H), 0.49-0.47 (m, 2H), 0.36-0.34 (m, 2H), 0.19-0.17 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz, δ/ppm): 185.96, 158.94, 156.53, 155.69, 153.58, 153.48, 153.07, 147.69, 145.67, 144.88, 140.45, 137.99, 136.60, 135.58, 134.61, 134.41, 129.19, 127.79, 126.40, 120.11, 117.72, 115.01, 114.87, 114.79, 114.50, 112.55, 112.36, 68.80, 57.92, 35.32, 31.89, 31.14, 29.90, 29.77, 29.61, 29.59, 29.46, 29.36, 29.32, 28.62, 28.24, 25.31, 22.67, 14.11. MALDI-TOF MS (m/z): $\text{C}_{88}\text{H}_{80}\text{F}_4\text{N}_4\text{O}_2\text{S}_4$ (M^+) calc. 1428.5, found 1428.6.

MC8-4Cl. To a solution of MC8-CHO (21 mg, 0.02 mmol) and DCIIC (27.4 mg, 0.10 mmol) in CHCl_3 (1 mL) was added pyridine (2 drops). The mixture was heated to reflux and stirred for 1 h. The mixture was then purified via column chromatography (silica gel) by using CHCl_3 as eluent to give MC8-4Cl as a black solid (21 mg, 67%). ^1H NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 400 MHz, δ/ppm): 8.98 (s, 2H), 8.64 (s, 2H), 7.86 (s, 2H), 7.50 (s, 2H), 7.42-7.29 (m, 10H), 3.11-3.09 (m, 4H), 2.84-2.50 (m, 3H), 1.78-1.75 (m, 4H), 1.42-1.40 (m, 4H), 1.29-1.19 (m, 28H), 1.08-0.97 (m, 4H), 0.82-0.79 (m, 9H), 0.41 (br, 2H), 0.26 (br, 2H), 0.11 (br, 2H). ^{13}C NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 100 MHz, δ/ppm): 184.99, 157.97, 155.47, 153.29, 152.90, 146.37, 144.89, 144.33, 139.36, 138.33, 138.07, 137.51, 136.83, 135.04, 134.87, 133.90, 128.24, 126.79, 125.66, 125.38, 124.04, 118.95, 116.73, 114.04, 113.68, 98.44, 67.41, 56.90, 30.88, 30.09, 28.79, 28.60, 28.47, 28.32, 27.56, 24.26, 21.70, 13.23. MALDI-TOF MS (m/z): $\text{C}_{88}\text{H}_{80}\text{Cl}_4\text{N}_4\text{O}_2\text{S}_4$ (M^+) calc. 1494.4, found 1494.4.

3. NMR

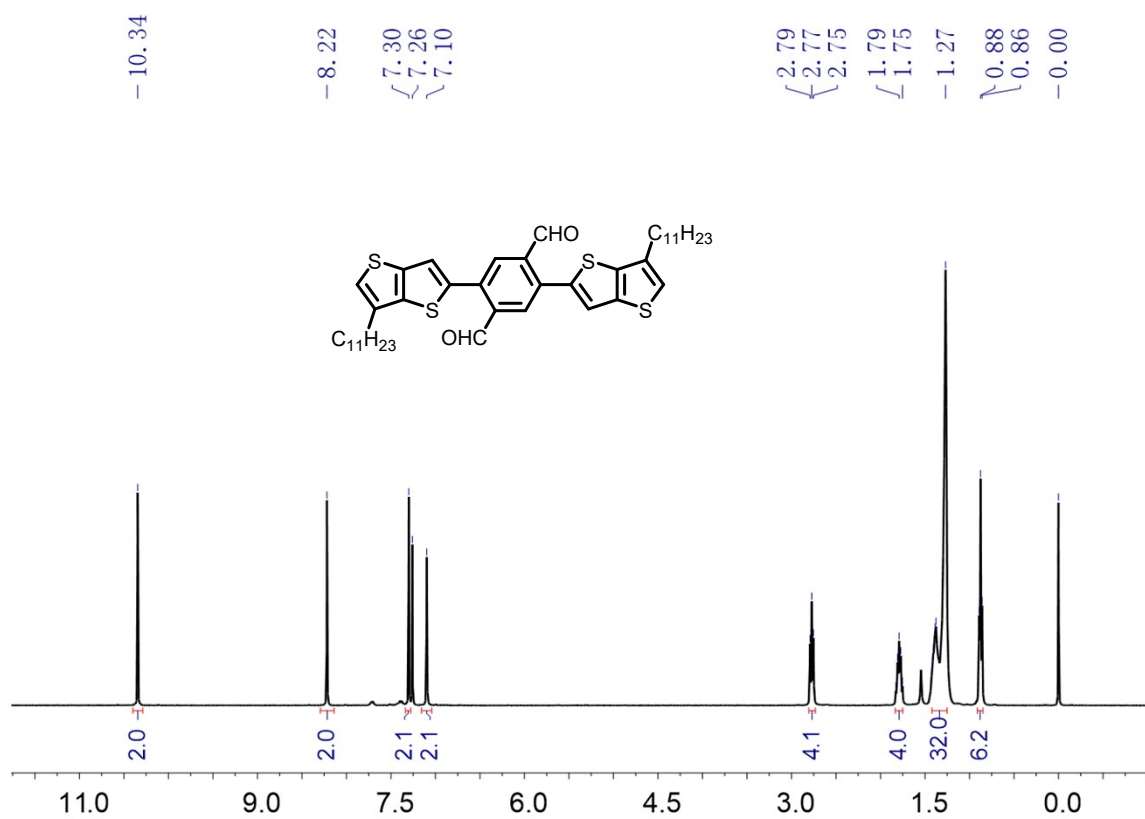


Fig. S1 ¹H NMR spectrum of compound 1.

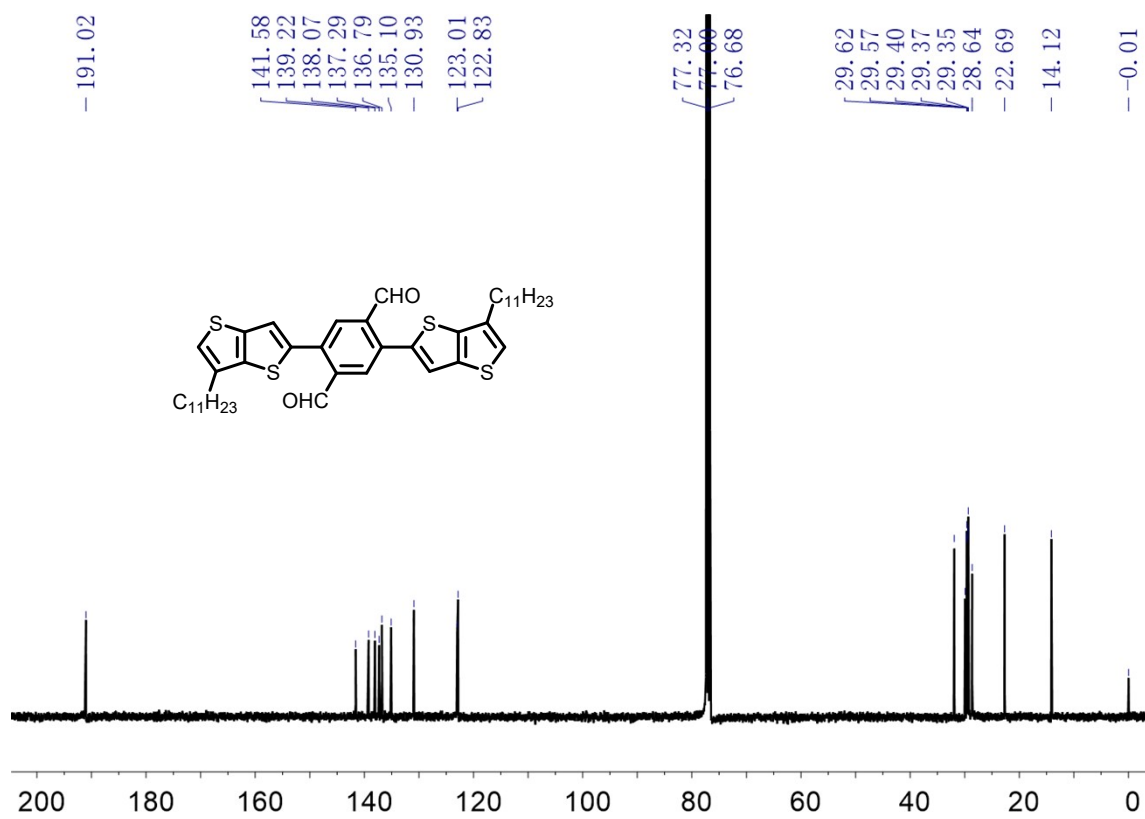


Fig. S2 ¹³C NMR spectrum of compound 1.

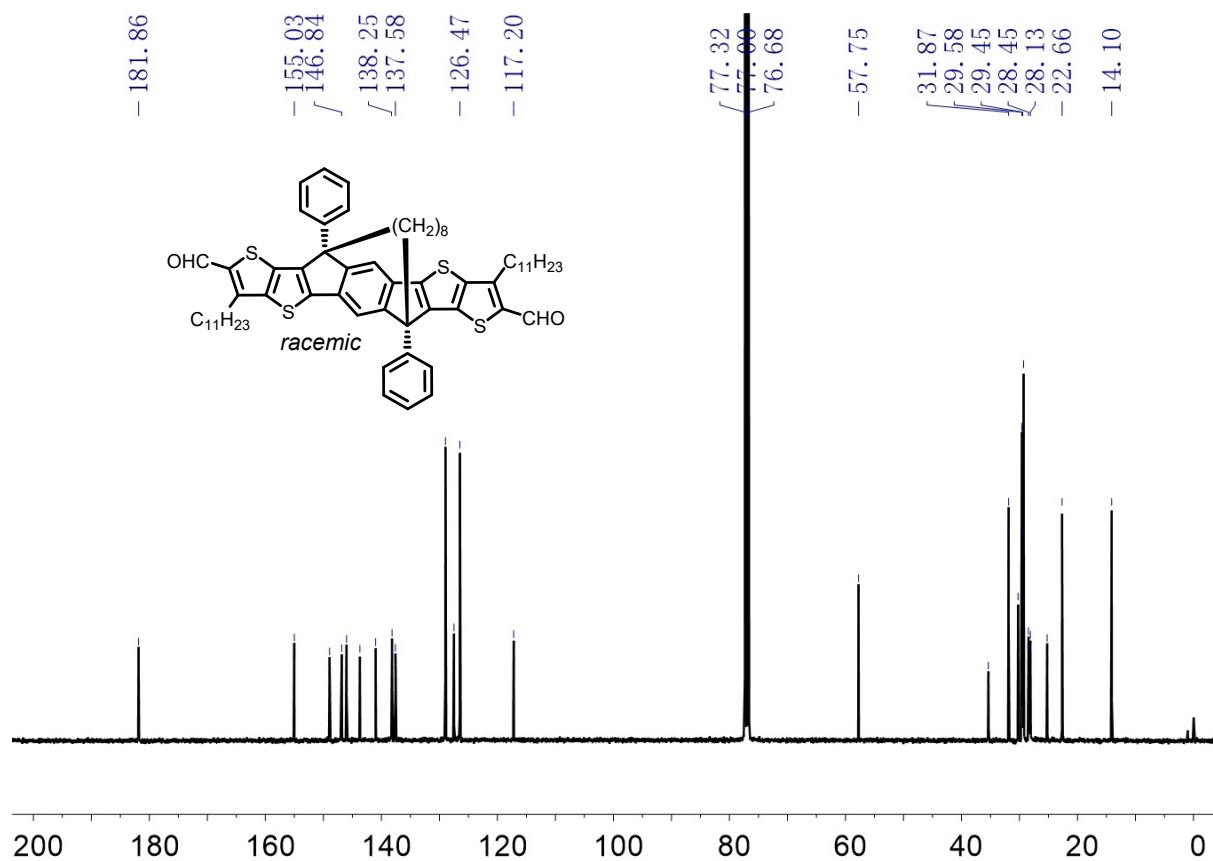


Fig. S5 ^{13}C NMR spectrum of MC8-CHO.

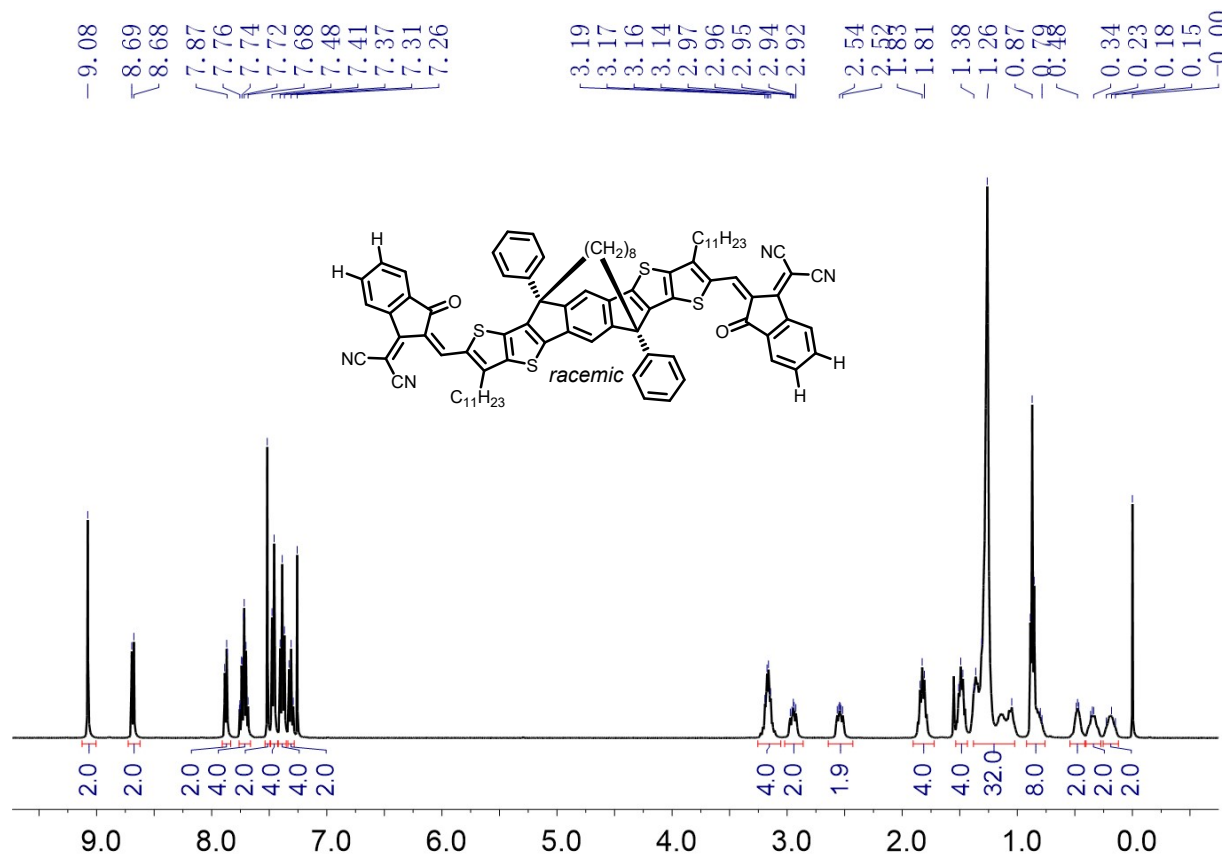


Fig. S6 ^1H NMR spectrum of MC8-4H.

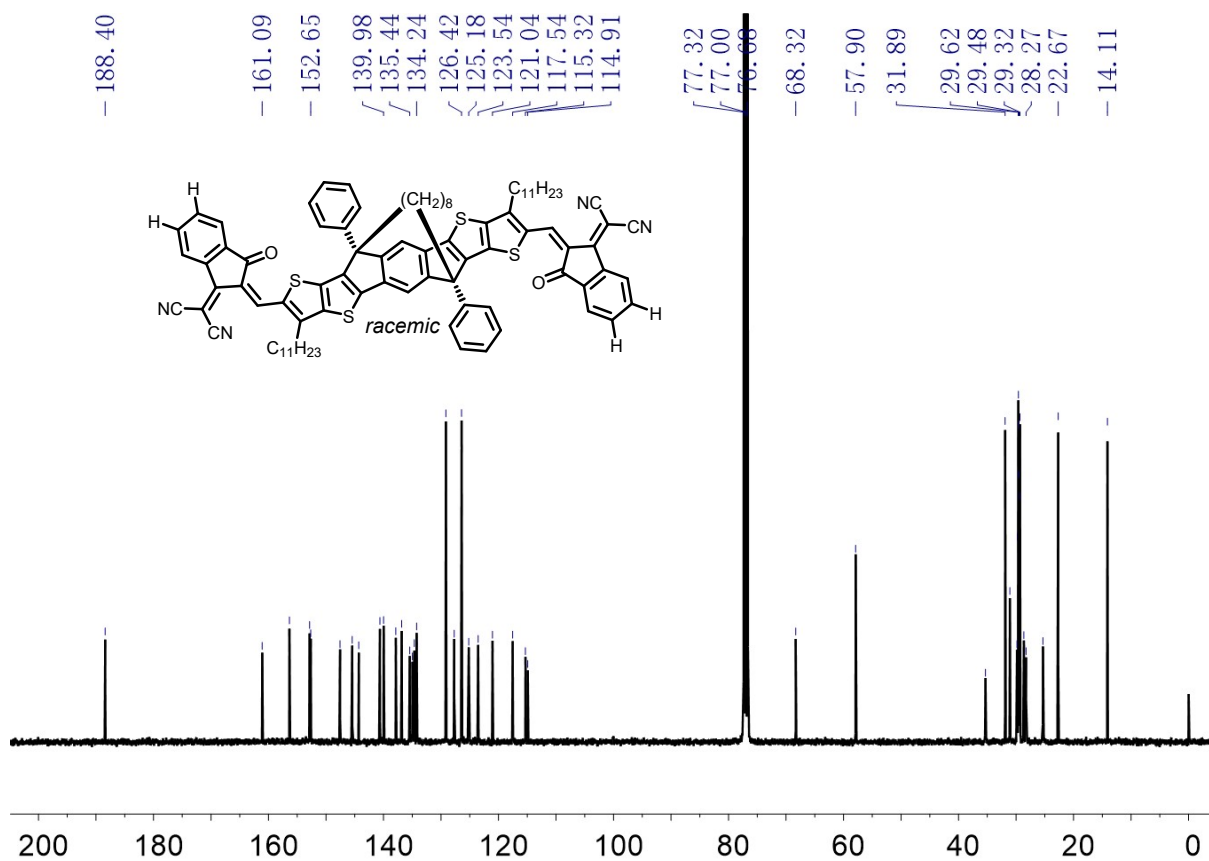


Fig. S7 ¹³C NMR spectrum of MC8-4H.

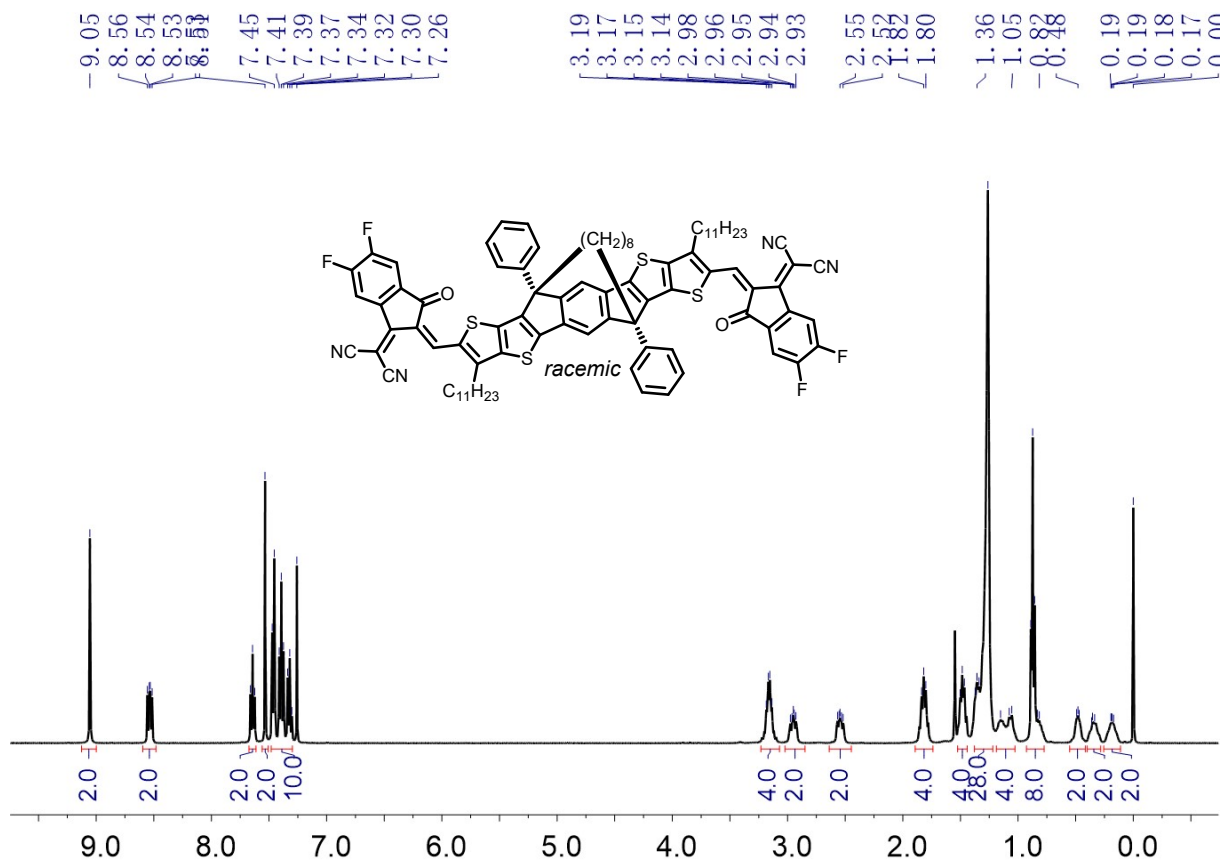


Fig. S8 ¹H NMR spectrum of MC8-4F.

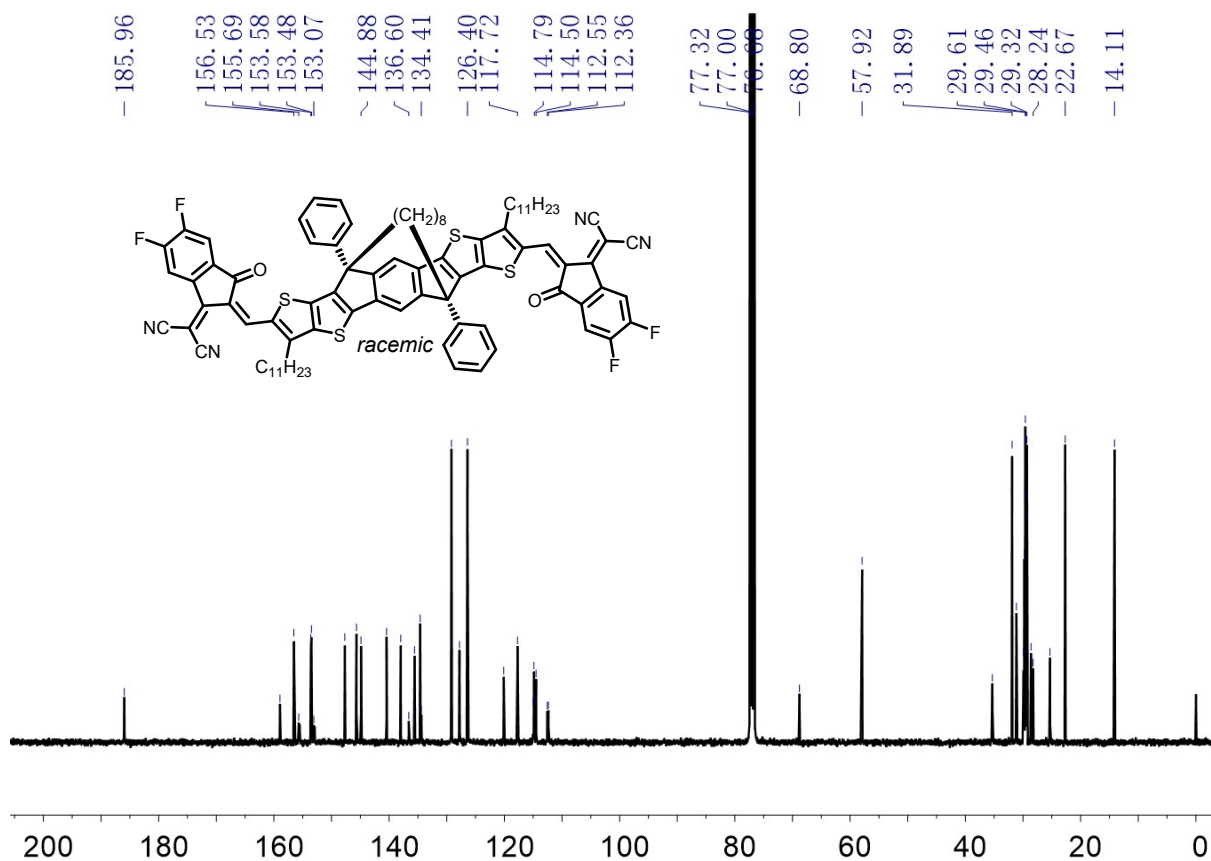


Fig. S9 ^{13}C NMR spectrum of MC8-4F.

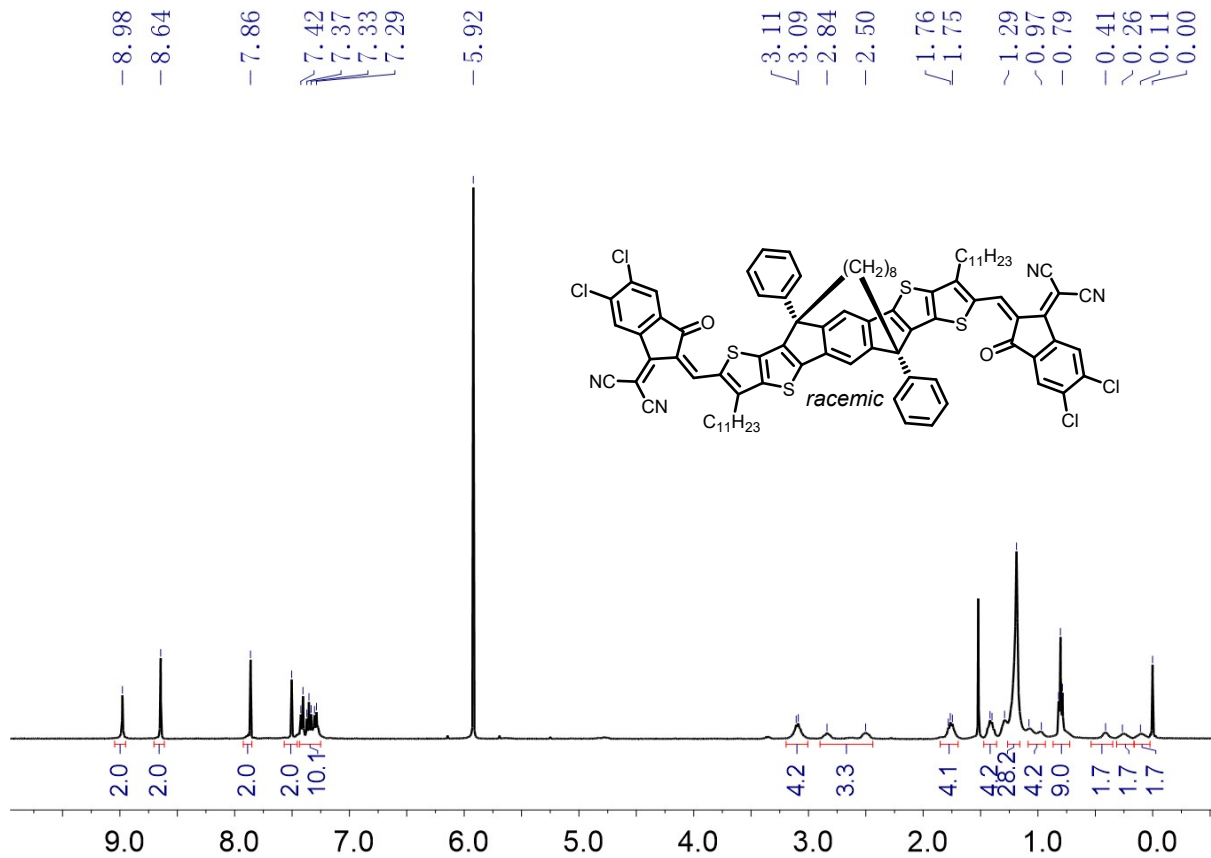


Fig. S10 1H NMR spectrum of MC8-4Cl ($C_2D_2Cl_4$).

4. CV

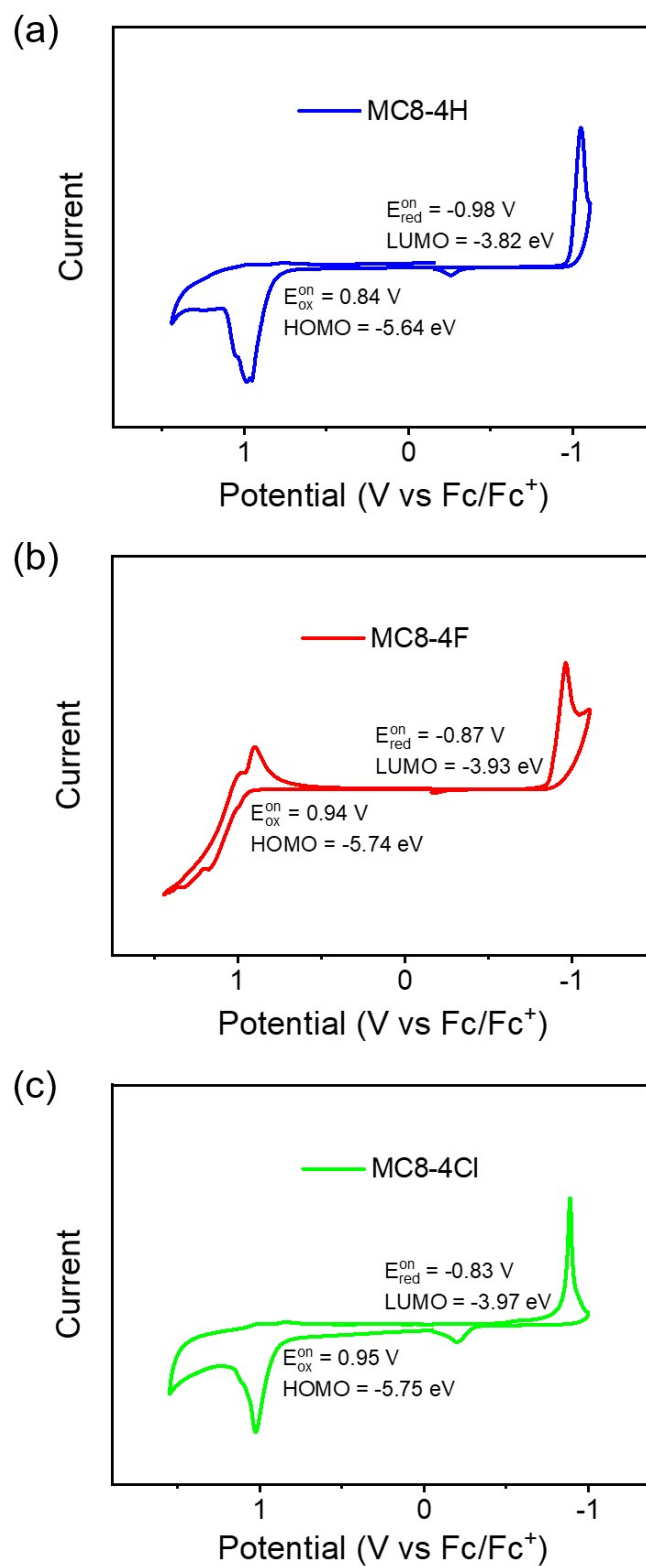


Fig. S12 Cyclic voltammograms for (a) MC8-4H, (b) MC8-4F and (c) MC8-4Cl.

5. DFT

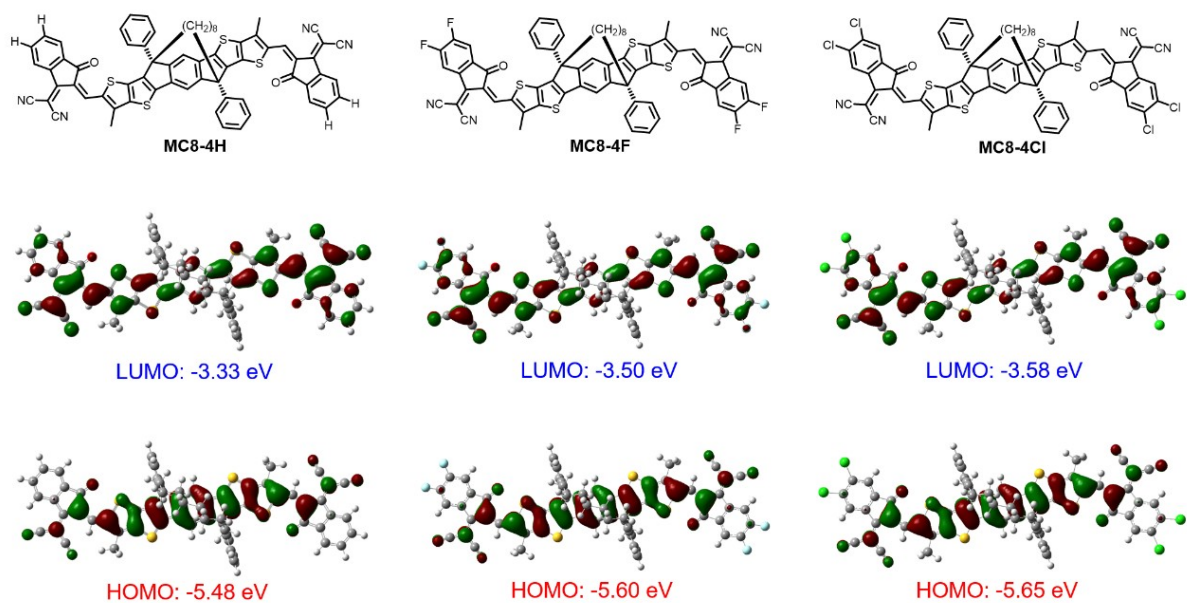


Fig. S13 DFT-predicted HOMO and LUMO levels for MC8-4H, MC8-4F and MC8-4Cl at the B3LYP/6-31G(d) level. Note: the undecyl side chains were replaced by methyl groups for simplification.

6. Device fabrication and measurements

Conventional solar cells

A 30 nm thick PEDOT:PSS (CLEVIOSTM P VP Al 4083 from Heraeus) layer was made by spin-coating an aqueous dispersion onto ITO glass (4000 rpm for 25 s). PEDOT:PSS substrates were dried at 150 °C for 15 min. An active blend solution (L4:acceptor in CF) was spin-coated onto PEDOT:PSS. PDIN (Organtec Co) (2 mg/mL) in MeOH:AcOH (1000:3) was spin-coated onto active layer (5000 rpm for 30 s). Ag (~80 nm) was evaporated onto PDIN through a shadow mask (pressure ca. 10^{-4} Pa). The effective area for the devices is 4 mm². The thicknesses of the active layers were measured by using a KLA Tencor D-120 profilometer. *J-V* curves were measured by using a computerized Keithley 2400 SourceMeter and a Xenon-lamp-based solar simulator (Enli Tech, AM 1.5G, 100 mW/cm²). The illumination intensity of solar simulator was determined by using a monocrystalline silicon solar cell (Enli SRC2020, 2cm×2cm) calibrated by the National Institute of Metrology (NIM). The external quantum efficiency (EQE) spectra were measured by using a QE-R3011 measurement system (Enli Tech).

Hole-only devices

The structure for hole-only devices is ITO/PEDOT:PSS/active layer/MoO₃/Al. A 30 nm thick PEDOT:PSS layer was made by spin-coating an aqueous dispersion onto ITO glass (4000 rpm for 25 s). PEDOT:PSS substrates were dried at 150 °C for 10 min. An active blend in CF was spin-coated onto PEDOT:PSS layer. Finally, MoO₃ (~6 nm) and Al (~100 nm) was successively evaporated onto the active layer through a shadow mask (pressure ca. 10^{-4} Pa). *J-V* curves were measured by using a computerized Keithley 2400 SourceMeter in the dark.

Electron-only devices

The structure for electron-only devices is ITO/ZnO/active layer/PDIN/Al. The ZnO precursor solution was spin-coated onto ITO glass (4000 rpm for 30 s). The films were annealed at 200 °C in air for 20 min. Pure acceptor or an active blend in CF was spin-coated onto ZnO. Al (~100 nm) was successively evaporated onto the active layer through a shadow mask (pressure ca. 10^{-4} Pa). *J-V* curves were measured by using a computerized Keithley 2400 SourceMeter in the dark.

7. Optimization of the performance for L4:acceptor solar cells

Table S1 Optimization of D:A ratio for L4:MC8-4H conventional solar cells.^a

D:A [w:w]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
1:1	1.074	13.79	53.6	7.93 (7.78) ^b
1:1.4	1.080	13.71	57.5	8.51 (8.26)
1:1.8	1.084	13.39	56.9	8.25 (7.98)
1:2.2	1.085	12.85	58.0	8.09 (7.76)

^aBlend solution: 12.5 mg/mL in CF; spin-coating: 5000 rpm for 30 s.

^bData in parentheses stand for the average PCEs for 8 cells.

Table S2 Optimization of active layer thickness for L4:MC8-4H conventional solar cells.^a

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
129	1.072	13.10	52.3	7.35 (7.05) ^b
113	1.078	13.56	55.1	8.06 (7.71)
104	1.080	13.71	57.5	8.51 (8.26)
92	1.083	13.37	58.0	8.39 (8.22)

^aD/A ratio: 1:1.4 (w/w); blend solution: 12.5 mg/mL in CF.

^bData in parentheses stand for the average PCEs for 8 cells.

Table S3 Optimization of DPE content for L4:MC8-4H solar cells.^a

DPE [vol%]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
0	1.080	13.71	57.5	8.51 (8.26) ^b
0.25	1.073	14.59	54.9	8.59 (8.32)
0.5	1.070	14.32	56.4	8.65 (8.46)
0.75	1.051	13.12	53.3	7.36 (7.13)

^aD/A ratio: 1:1.4 (w/w); blend solution: 12.5 mg/mL in CF; spin-coating: 5000 rpm for 30 s.

^bData in parentheses stand for the average PCEs for 8 cells.

Table S4 Optimization of D:A ratio for L4:MC8-4F conventional solar cells.^a

D:A [w:w]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
1:1	0.947	20.06	74.2	14.10 (13.99) ^b
1:1.4	0.950	20.09	74.6	14.24 (14.14)
1:1.8	0.947	20.09	72.7	13.83 (13.50)
1:2.2	0.947	19.86	69.1	12.99 (12.83)

^aBlend solution: 12.5 mg/mL in CF; spin-coating: 5000 rpm for 30 s.

^bData in parentheses stand for the average PCEs for 8 cells.

Table S5 Optimization of active layer thickness for L4:MC8-4F conventional solar cells.^a

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
132	0.945	19.60	70.7	13.10 (12.92) ^b
115	0.946	20.44	72.8	14.07 (13.86)
105	0.950	20.09	74.6	14.24 (14.14)
91	0.953	19.21	75.9	13.89 (13.83)

^aD/A ratio: 1:1.4 (w/w); blend solution: 12.5 mg/mL in CF.

^bData in parentheses stand for the average PCEs for 8 cells.

Table S6 Optimization of DPE content for L4:MC8-4F solar cells.^a

DPE [vol%]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
0	0.950	20.09	74.6	14.24 (14.14) ^b
0.5	0.944	21.22	72.5	14.52 (14.33)
0.75	0.948	21.00	73.7	14.68 (14.48)
1	0.945	20.79	73.0	14.34 (13.96)

^aD/A ratio: 1:1.4 (w/w); blend solution: 12.5 mg/mL in CF; spin-coating: 5000 rpm for 30 s.

^bData in parentheses stand for the average PCEs for 8 cells.

Table S7 Optimization of D:A ratio for L4:MC8-4Cl conventional solar cells.^a

D:A [w:w]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
1:0.6	0.936	18.68	66.7	11.67 (11.55) ^b
1:1.0	0.933	19.11	72.6	12.94 (12.84)
1:1.4	0.929	19.12	72.5	12.87 (12.74)
1:1.8	0.920	18.80	66.2	11.45 (11.31)

^aBlend solution: 11 mg/mL in CF; spin-coating: 4000 rpm for 30 s.

^bData in parentheses stand for the average PCEs for 8 cells.

Table S8 Optimization of active layer thickness for L4:MC8-4Cl conventional solar cells.^a

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
128	0.925	18.88	70.6	12.34 (12.15) ^b
111	0.933	19.11	72.6	12.94 (12.84)
104	0.929	19.07	72.3	12.81 (12.67)
82	0.927	17.68	72.6	11.90 (11.81)

^aD/A ratio: 1:1 (w/w); blend solution: 11 mg/mL in CF.

^bData in parentheses stand for the average PCEs for 8 cells.

Table S9 Optimization of DPE content for L4:MC8-4Cl solar cells.^a

DPE [vol%]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
0	0.933	19.11	72.6	12.94 (12.84) ^b
0.5	0.921	20.40	70.7	13.29 (12.99)
0.75	0.896	20.86	74.2	13.87 (13.52)
1	0.899	19.17	71.5	12.32 (11.99)

^aD/A ratio: 1:1 (w/w); blend solution: 11 mg/mL in CF; spin-coating: 4000 rpm for 30 s.

^bData in parentheses stand for the average PCEs for 8 cells.

8. P_{diss} and P_{coll} for L4:MC8-4H, L4:MC8-4F and L4:MC8-4Cl solar cells

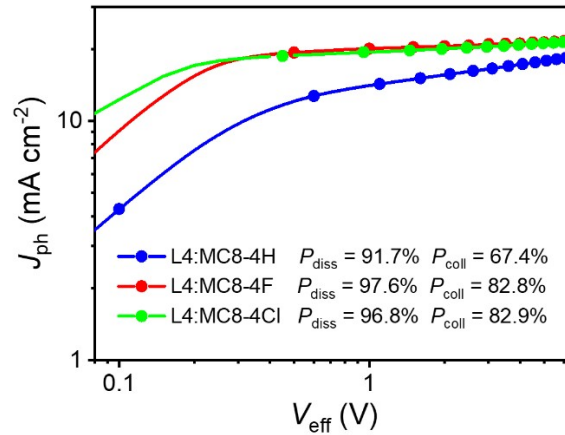


Fig. S14 $J_{\text{ph}}-V_{\text{eff}}$ plots for L4:MC8-4H, L4:MC8-4F and L4:MC8-4Cl solar cells.

9. SCLC measurements

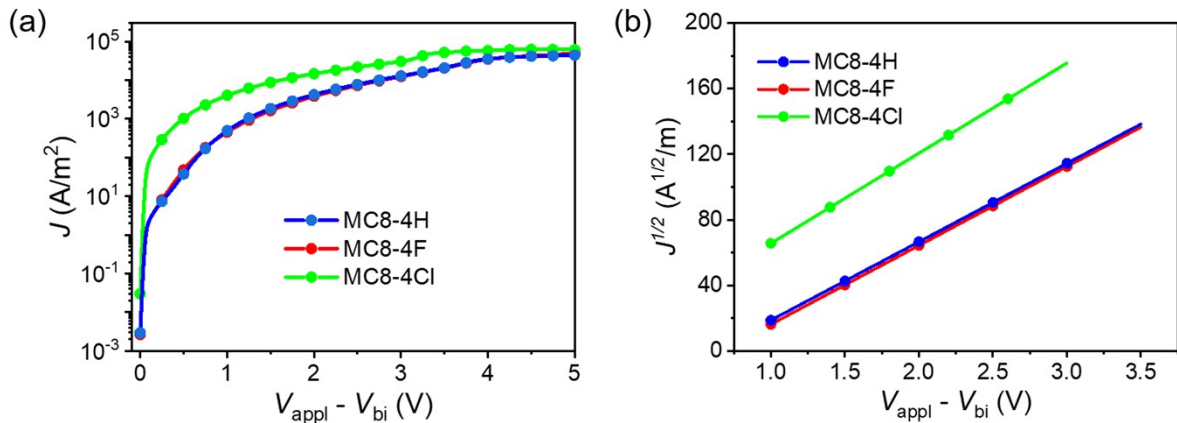


Fig. S15. $J-V$ curves (a) and corresponding $J^{1/2}-V$ plots (b) for the electron-only device (in dark). The thicknesses for MC8-4H, MC8-4F and MC8-4Cl films are 92, 95 and 85 nm, respectively.

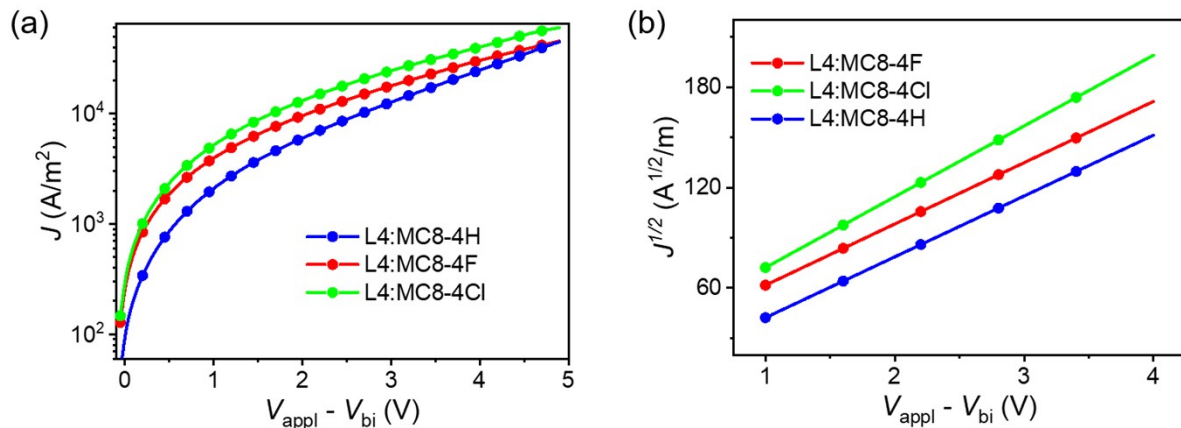


Fig. S16 $J-V$ curves (a) and corresponding $J^{1/2}-V$ plots (b) for the hole-only devices (in dark). The thicknesses for L4:MC8-4H, L4:MC8-4F and L4:MC8-4Cl films are 110, 113 and 101 nm, respectively.

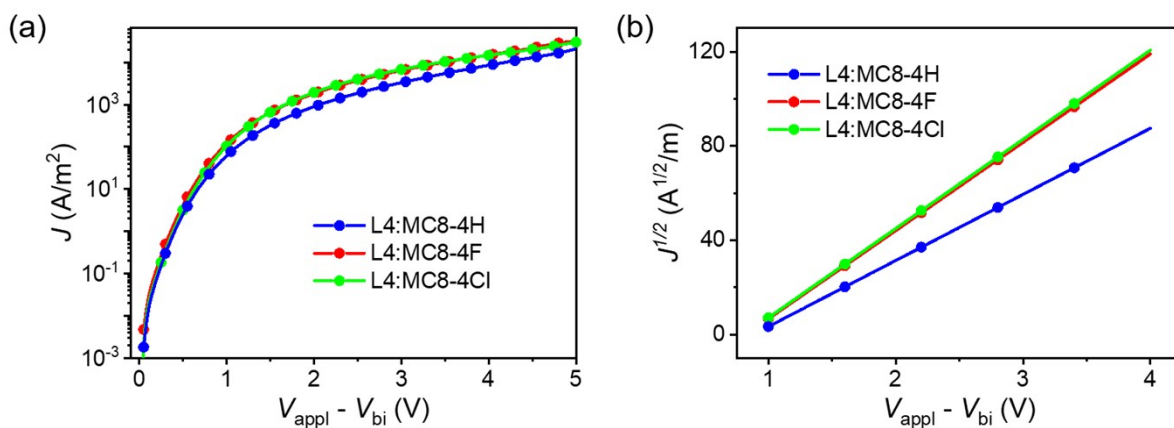


Fig. S17 J - V curves (a) and corresponding $J^{1/2}$ - V plots (b) for the electron-only devices (in dark). The thicknesses for L4:MC8-4H, L4:MC8-4F and L4:MC8-4Cl films are 126, 111 and 108 nm, respectively.

Table S10 Charge carrier mobilities.

Film	μ_{h} [cm ² /Vs]	μ_{e} [cm ² /Vs]	$\mu_{\text{h}}/\mu_{\text{e}}$
MC8-4H	/	5.96×10^{-4}	/
MC8-4F	/	6.64×10^{-4}	/
MC8-4Cl	/	6.22×10^{-4}	/
L4:MC8-4H	5.88×10^{-4}	5.26×10^{-4}	1.12
L4:MC8-4F	6.47×10^{-4}	6.20×10^{-4}	1.04
L4:MC8-4Cl	6.17×10^{-4}	6.03×10^{-4}	1.02

10. Surface free energy measurements

The experiments were performed on a KRUSS DSA100S contact angle goniometer. Droplets of two different liquids, water and ethylene glycol (EG) were cast onto the films with the drop size of 2 μL . Contact angle images were taken at 1 s after the whole droplet was deposited onto the sample surface. The surface free energy of each sample was calculated by:

$$\begin{aligned}\gamma_{\text{water}}(\cos\theta_{\text{water}} + 1) &= 2(\gamma_{\text{sample}}^{\text{d}}\times\gamma_{\text{water}}^{\text{d}})^{1/2} + 2(\gamma_{\text{sample}}^{\text{p}}\times\gamma_{\text{water}}^{\text{p}})^{1/2} \\ \gamma_{\text{EG}}(\cos\theta_{\text{EG}} + 1) &= 2(\gamma_{\text{sample}}^{\text{d}}\times\gamma_{\text{EG}}^{\text{d}})^{1/2} + 2(\gamma_{\text{sample}}^{\text{p}}\times\gamma_{\text{EG}}^{\text{p}})^{1/2} \\ \gamma_{\text{sample}}^{\text{total}} &= \gamma_{\text{sample}}^{\text{d}} + \gamma_{\text{sample}}^{\text{p}}\end{aligned}$$

where θ is the droplet contact angle on the sample film; $\gamma_{\text{sample}}^{\text{total}}$ is the surface free energy of the sample, which is equal to the sum of the dispersion ($\gamma_{\text{sample}}^{\text{d}}$) and polarity ($\gamma_{\text{sample}}^{\text{p}}$) components; $\gamma_{\text{water}} = 72.8 \text{ mJ/m}^2$, $\gamma_{\text{water}}^{\text{d}} = 21.8 \text{ mJ/m}^2$, $\gamma_{\text{water}}^{\text{p}} = 51.0 \text{ mJ/m}^2$, $\gamma_{\text{EG}} = 48.0 \text{ mJ/m}^2$, $\gamma_{\text{EG}}^{\text{d}} = 29.0 \text{ mJ/m}^2$, $\gamma_{\text{EG}}^{\text{p}} = 19.0 \text{ mJ/m}^2$.^[2,3]

Table S11 The contact angles and surface free energy parameters.

Film	Contact Angle ($^{\circ}$)		$\gamma_{\text{sample}}^{\text{d}}$ [mJ/m ²]	$\gamma_{\text{sample}}^{\text{p}}$ [mJ/m ²]	$\gamma_{\text{sample}}^{\text{total}}$ [mJ/m ²]
	Water	Ethylene glycol			
L4	106.4	77.2	27.82	0.04	27.9
MC8-4H	87.9	61.1	24.57	4.17	28.7
MC8-4F	91.8	62.6	28.46	2.10	30.6
MC8-4Cl	89.5	59.3	29.81	2.47	32.3

11. The performance for L4:IDIC, L4:ITIC and L4:IT-4F solar cells

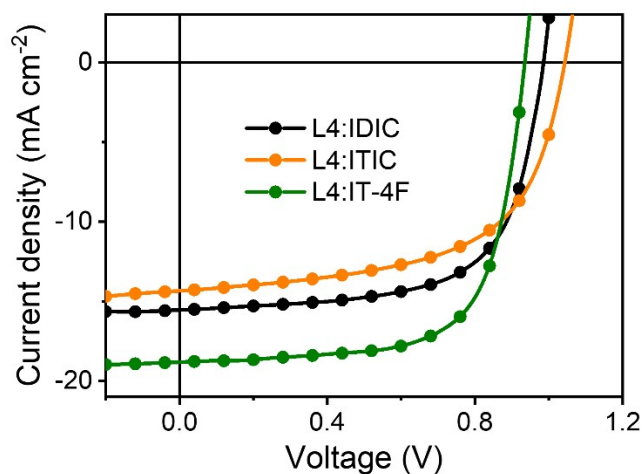


Fig. S18 J - V curves for L4:IDIC, L4:ITIC and L4:IT-4F solar cells.

Table S12 The performance data for L4:IDIC, L4:ITIC and L4:IT-4F solar cells. ^a

Active layer	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
L4:IDIC	0.986	15.54	65.5	10.05 (9.85) ^b
L4:ITIC	1.044	14.35	59.4	8.89 (8.25)
L4:IT-4F	0.935	18.83	68.9	12.13 (11.93)

^aDevice structure: glass/ITO/PEDOT:PSS/L4:acceptor (1:1.4)/PDIN/Ag (80 nm).

^bData in parentheses stand for the average PCEs for 8 cells.

12. The performance for D18:MC8-4F and PM6:MC8-4F solar cells

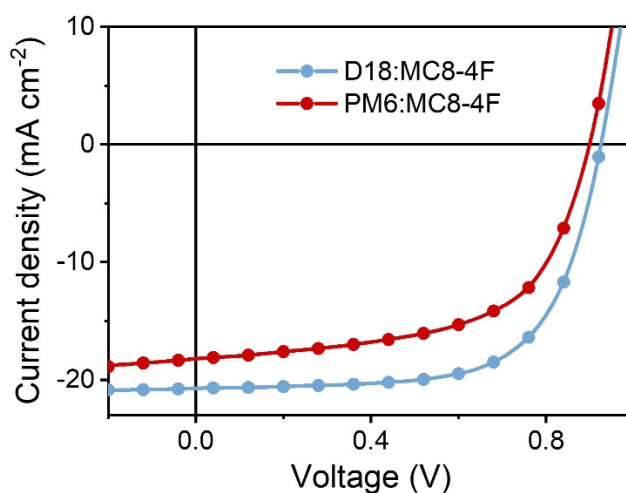


Fig. S19 J - V curves of D18:MC8-4F and PM6:MC8-4F solar cells.

Table S13 The performance data for D18:MC8-4F and PM6:MC8-4F solar cells. ^a

Active layer	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
D18:MC8-4F	0.925	20.73	66.1	12.69 (12.45) ^b
PM6:MC8-4F	0.899	18.21	58.9	9.65 (9.07)

^aDevice structure: glass/ITO/PEDOT:PSS/donor:MC8-4F (1:1.4)/PDIN/Ag (80 nm).

^bData in parentheses stand for the average PCEs for 8 cells.

13. The stability tests for L4:MC8-4H, L4:MC8-4F and L4:MC8-4Cl solar cells

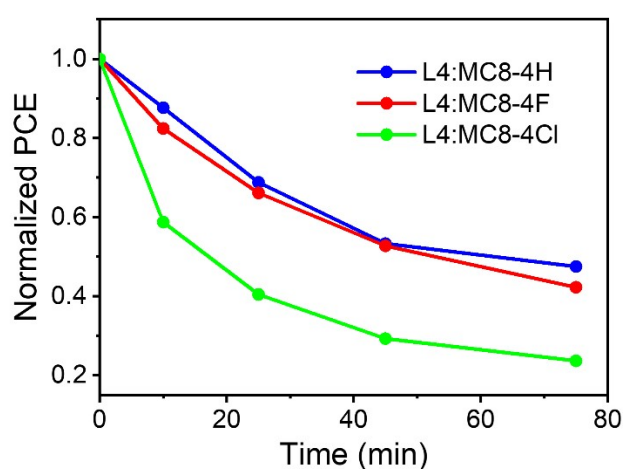


Fig. S20 Thermal stability test (85 °C) for L4:MC8-4H, L4:MC8-4F and L4:MC8-4Cl solar cells.

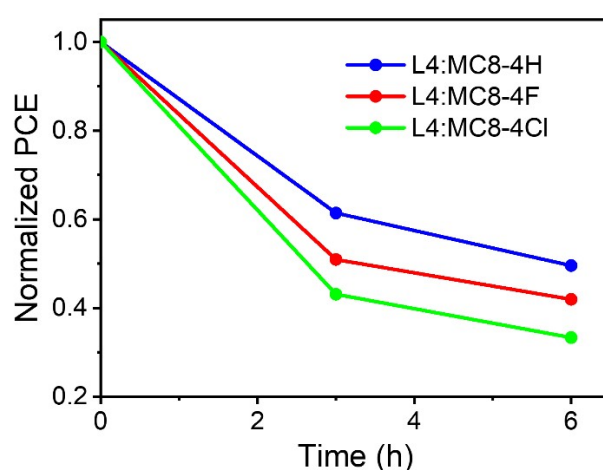


Fig. S21 Light-soaking stability test (1 sun irradiation) for L4:MC8-4H, L4:MC8-4F and L4:MC8-4Cl solar cells.

References

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