Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supporting Information

Optimizing miscibility for enhanced photovoltaic performance of non-fused ring electron acceptors through side-chain engineering

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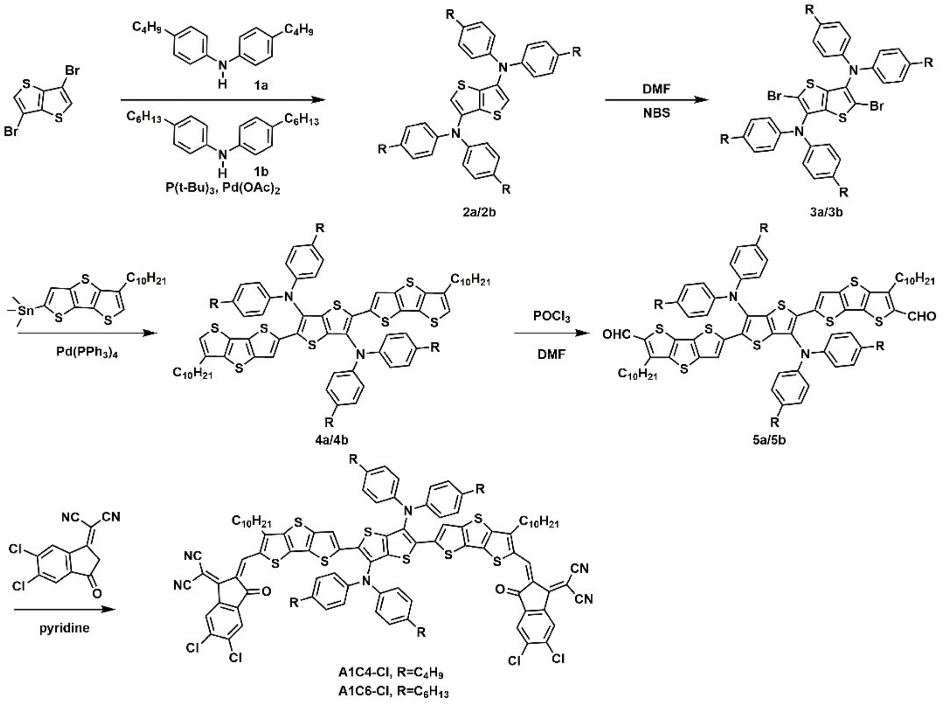
1. General characterization

^1H and ^{13}C NMR spectra were measured on a Bruker Avance-400 spectrometer. Absorption spectra were recorded on a Lambda 950 spectrophotometer (PerkinElmer, U.S.A.). Cyclic voltammetry was done by using a Shanghai Chenhua CHI660C voltammetric analyzer under argon in acetonitrile 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. All potentials were corrected against Fc/Fc^+ (Fc represents ferrocene.). AFM was performed on a Bruker Dimension icon using tapping mode. The *J-V* curves were measured by using a Keithley 2450 source-measure unit in the nitrogen-filled glove box along the reverse scan direction from -0.2 V to 1 V at room temperature. The scan speed and dwell times were fixed at 0.02 V per step and 0 ms, respectively. The photocurrent was measured under AM 1.5G illumination at 100 mW cm^{-2} by using a 3A solar simulator (LSS-55, Lightsky Technology Co., Ltd). Light intensity was calibrated with a standard photovoltaic cell equipped with a KG5 filter (certificated by the National Institute of Metrology). The EQE measurements of devices were carried out in the air with a solar cell spectral response measurement system (LST-QE, Lightsky Technology Co., Ltd). The light intensity at each wavelength was calibrated by a standard single-crystal Si photovoltaic cell.

2. Synthesis

All reagents were purchased from Innochem Co., HWRK Chem Co., SunaTech Inc., and other commercial suppliers, and used as received. The polymer donor, PBDB-T, was purchased from Hyper Inc.. All reactions dealing with air- or moisture-sensitive compounds were carried out using standard Schlenk techniques.



Scheme S1. Synthesis routes of A1C4-Cl/A1C6-Cl.

Compound 1a/1b. Compound **1a** and **1b** were synthesized, according to the reported literatures.[1]

1a: ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.06 (d, *J* = 8.5 Hz, 4H), 6.97 (d, *J* = 8.5 Hz, 4H), 5.55 (s, 1H), 2.58-2.52 (m, 4H), 1.57 (dd, *J* = 6.1, 3.4 Hz, 4H), 1.37 (dt, *J* = 14.9, 7.3 Hz, 4H), 0.93 (t, *J* = 7.3 Hz, 6H).

1b: ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.06 (d, *J* = 8.3 Hz, 4H), 6.97 (d, *J* = 8.1 Hz, 4H), 5.53 (s, 1H), 2.54 (t, *J* = 7.6 Hz, 4H), 1.58 (dd, *J* = 14.8, 7.0 Hz, 4H), 1.37-1.27 (m, 12H), 0.89 (t, *J* = 6.6 Hz, 6H).

Compound 2a/2b. Compound **1a**/**1b** (4.15 g/4.98 g, 14.76 mmol/14.76 mmol), (3,6-dibromothieno[3,2-*b*]thiophene (2.00 g, 6.71 mmol), $Pd(OAc)_2$ (76 mg, 0.34 mmol), P(*t*-Bu)$_3$ (2.75 g, 1.36 mmol) and NaO(*t*-Bu) (2.60 g, 26.84 mmol) were dissolved in dry 1,4-dioxane (20 mL) and stirred at 100 °C overnight. Then the solvent was removed under reduced pressure. The crude product was purified via column chromatography (silica gel) by using petroleum ether/CH_2Cl_2 (5:1, v/v) as eluent to give compound **2a/2b** (3.85 g/4.36 g, 82%/80%) as the dark yellow oil.

2a: ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.11-7.00 (m, 16H), 6.61 (s, 2H), 2.61-2.53 (m, 8H), 1.60 (dd, *J* = 8.2, 2.3 Hz, 8H), 1.36 (dd, *J* = 14.9, 7.4 Hz, 8H), 0.93 (t, *J* = 7.3 Hz, 12H).

2b: ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.05 (q, *J* = 8.7 Hz, 16H), 6.61 (s, 2H), 2.59-2.54 (m, 8H), 1.61 (dd, *J* = 14.3, 7.6 Hz, 8H), 1.34-1.28 (m, 24H), 0.87 (t, *J* = 6.7 Hz, 12H).

Compound 3a/3b. *N*-bromosuccinimide (NBS) (1.07 g/0.92 g, 6.01 mmol/5.19 mmol) in 10 mL of DMF was added dropwise under darkness to a solution of compound **2a**/**2b** (2.00 g/2.00 g, 2.86 mmol/2.47 mmol) in 10 mL of DMF at 0 °C. The mixture was stirred at room temperature for 16 h. Then it was poured into water and extracted with CH_2Cl_2. The organic phase was dried over anhydrous Na_2SO_4 and filtrated. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using petroleum ether/CH_2Cl_2 (7:1, v/v) as eluent to give compound **3a/3b** (2.30 g/2.20 g, 94%/92%) as colorless oil.

3a: ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.09 (d, *J* = 8.4 Hz, 8H), 6.96 (d, *J* = 8.4 Hz, 8H), 2.63-2.56 (m, 8H), 1.65-1.57 (m, 8H), 1.38 (dd, *J* = 14.9, 7.4 Hz, 8H), 0.95 (t, *J* = 7.3 Hz, 12H).

3b: ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.08 (d, *J* = 8.4 Hz, 8H), 6.94 (d, *J* = 8.4 Hz, 8H), 2.60-2.54 (m, 8H), 1.65-1.58 (m, 8H), 1.33-1.27 (m, 24H), 0.88 (t, *J* = 5.2 Hz, 12H).

Compound 4a/4b. Compound **3a/3b** (1.00 g/1.00 g, 1.17 mmol/1.03 mmol), (5-decyldithieno[3,2-*b*:2',3'-*d*]thiophen-2-yl)trimethylstannane (1.40 g/1.23 g, 2.81 mmol/2.47 mmol) and $Pd(PPh_3)_4$ (41 mg/36 mg, 0.04 mmol/0.03 mmol) were dissolved in dry toluene (30 mL) and stirred at 110 °C overnight. Then the solvent was removed under reduced pressure. The crude product was purified via column chromatography (silica gel) by using petroleum ether as eluent to give compound **4a/4b** as the red solid (1.25 g/1.22 g, 78%/80%).

4a: ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.18 (s, 2H), 7.10-7.05 (m, 16H), 6.90 (s, 2H), 2.66 (t, *J* = 7.6 Hz, 4H), 2.57-2.52 (m, 8H), 1.74-1.67 (m, 4H), 1.58 (t, *J* = 4.5 Hz, 8H), 1.34-1.25 (m, 36H), 0.89 (dd, *J* = 11.7, 4.2 Hz, 18H).

4b: ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.19 (s, 2H), 7.07 (q, *J* = 8.8 Hz, 16H), 6.90 (s, 2H), 2.65 (dd, *J* = 16.6, 8.9 Hz, 4H), 2.57-2.48 (m, 8H), 1.73-1.67 (m, 4H), 1.61-1.56 (m, 8H), 1.30-1.24 (m, 52H), 0.88-0.85 (m, 18H).

Compound 5a/5b. $POCl_3$ (1.0 mL) was added to 10.0 mL DMF under nitrogen at 0°C. After stirring for 1 hour, compound **4a/4b** (500 mg/500 mg, 0.37 mmol/0.34 mmol) dissolved in 1,2-dichloroethane (10 mL) was added dropwise to the resulting Vilsmeier reagent. The mixture was stirred at 0°C for 30 minutes and then heated to 85 °C for 24 hours. After cooling to room temperature, saturated sodium bicarbonate solution was added and stirred for 2 hours. The mixture was extracted with CH_2Cl_2. The organic phase was dried over anhydrous Na_2SO_4 and filtrated. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using petroleum ether/CH_2Cl_2 (1:2, v/v) as eluent to give compound **5a/5b** as the orange solid (448 mg/439 mg, 85%/84%).
5a: ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 10.02 (s, 2H), 7.19 (s, 2H), 7.08 (s, 16H), 3.03 (t, *J* = 7.5 Hz, 4H), 2.55 (t, *J* = 7.7 Hz, 8H), 1.80-1.69 (m, 4H), 1.53 (d, *J* = 7.9 Hz, 8H), 1.36-1.22 (m, 36H), 0.88 (q, *J* = 7.2 Hz, 18H).
5b: ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 10.02 (s, 2H), 7.19 (s, 2H), 7.07 (s, 16H), 3.03 (t, *J* = 7.5 Hz, 4H), 2.58-2.50 (m, 8H), 1.80-1.71 (m, 4H), 1.61-1.55 (m, 8H), 1.27 (dd, *J* = 16.5, 12.1 Hz, 52H), 0.86 (q, *J* = 6.8 Hz, 18H).

A1C4-Cl. Compound **5a** (150 mg, 0.11 mmol) and 5,6-dichloro-3(dicyanomethylidene)indan-1-one (84 mg, 0.32 mmol) was dissolved in $CHCl_3$ (20 mL) and stirred at room temperature for 10 min. Then pyridine (0.5 mL) was added. heated to reflux for 1.5 h and then cooled down to room temperature. It was dropped into methanol and filtered to obtain the crude product. The crude product was purified on silica gel chromatography using petroleum ether/CH_2Cl_2 (1:2, v/v) as eluent to give the target compound **A1C4-Cl** as a black solid (173 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 9.04 (s, 2H), 8.75 (s, 2H), 7.90 (s, 2H), 7.19 (s, 2H), 7.13-7.07 (m, 16H), 3.06 (t, *J* = 7.6 Hz, 4H), 2.61-2.54 (m, 8H), 1.77-1.69 (m, 4H), 1.59 (dd, *J* = 15.3, 7.5 Hz, 8H), 1.39-1.22 (m, 36H), 0.89 (dd, *J* = 14.2, 6.8 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$, δ/ppm): 186.01, 158.52, 153.50, 148.06, 144.48, 144.14, 142.76, 142.14, 139.38, 139.05, 138.51, 138.34, 135.87, 135.58, 135.51, 134.62, 133.86, 132.00, 131.31, 129.40, 126.67, 124.87, 121.88, 119.57, 117.53, 114.97, 114.50, 77.20, 68.41, 35.01, 33.52, 31.86, 30.92, 29.82, 29.58, 29.55, 29.44, 29.35, 29.28, 22.66, 22.32, 14.11, 13.99. MALDI-MS (m/z) of $C_{108}H_{102}Cl_4N_6O_2S_8$ for [M^+]: calcd. 1913.46; found: 1913.61.

A1C6-Cl. Compound **5b** (150 mg, 0.10 mmol) and 5,6-dichloro-3(dicyanomethylidene)indan-1-one (79 mg, 0.30 mmol) was dissolved in $CHCl_3$ (20 mL) and stirred at room temperature for 10 min. Then pyridine (0.5 mL) was added. heated to reflux for 1.5 h and then cooled down to room temperature. It was dropped into methanol and filtered to obtain the crude product. The crude product was purified on silica gel chromatography using petroleum ether/CH_2Cl_2 (1:2, v/v) as eluent to give the target compound **A1C6-Cl** as a black solid (174 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 9.04 (s, 2H), 8.74 (s, 2H), 7.90 (s, 2H), 7.18 (s, 2H), 7.13-7.07 (m, 16H), 3.06 (t, *J* = 7.5 Hz, 4H), 2.56 (t, *J* = 7.6 Hz, 8H), 1.77-1.69 (m, 4H), 1.63-1.57 (m, 8H), 1.27 (dd, *J* = 15.8, 9.4 Hz, 52H), 0.85 (q, *J* = 6.7 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$, δ/ppm): 186.04, 158.60, 153.51, 148.05, 144.49, 144.16, 142.76, 142.12, 139.40, 139.07, 138.54, 138.40, 135.91, 135.64, 135.52, 134.63, 133.87, 132.09, 131.34, 129.39, 126.71, 124.89, 121.87, 119.60, 117.51, 114.97, 114.51, 68.42, 35.34, 31.86, 31.70, 31.34, 30.92, 29.82, 29.58, 29.55, 29.44, 29.35, 29.28, 28.97, 22.66, 22.60, 14.10. MALDI-MS (m/z) of $C_{116}H_{118}Cl_4N_6O_2S_8$ for [M^+]: calcd. 2025.58; found: 2025.68.

3. NMR spectra

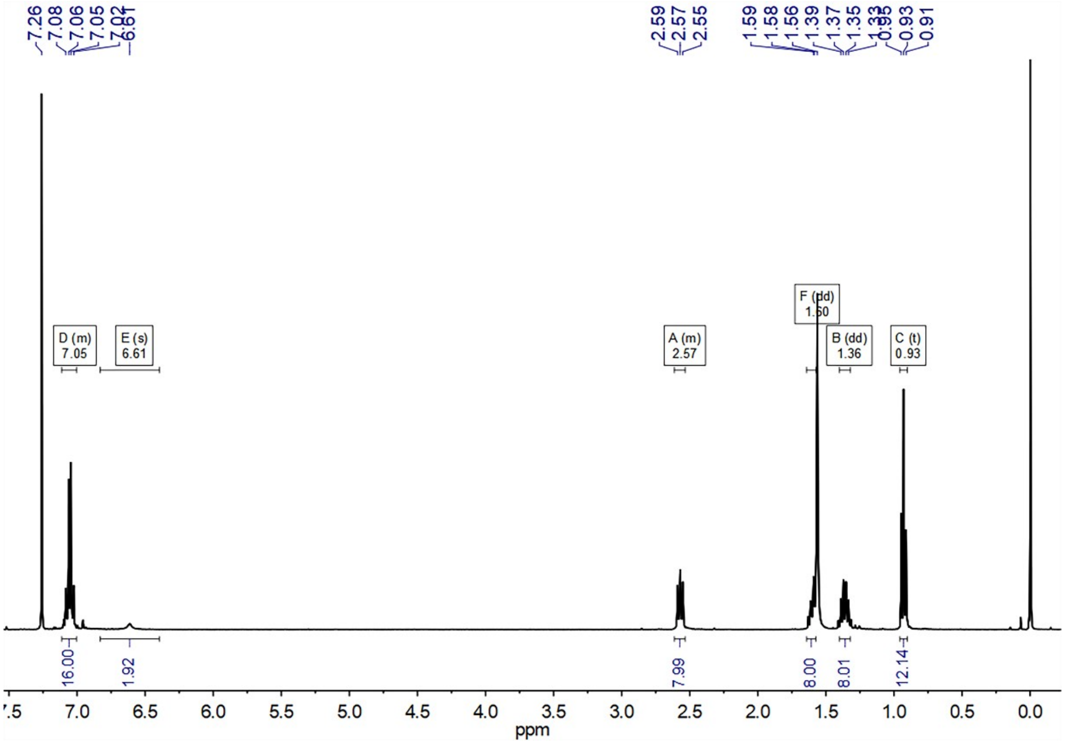


Figure S1. ^{1}H NMR spectrum of **Compound 2a**.

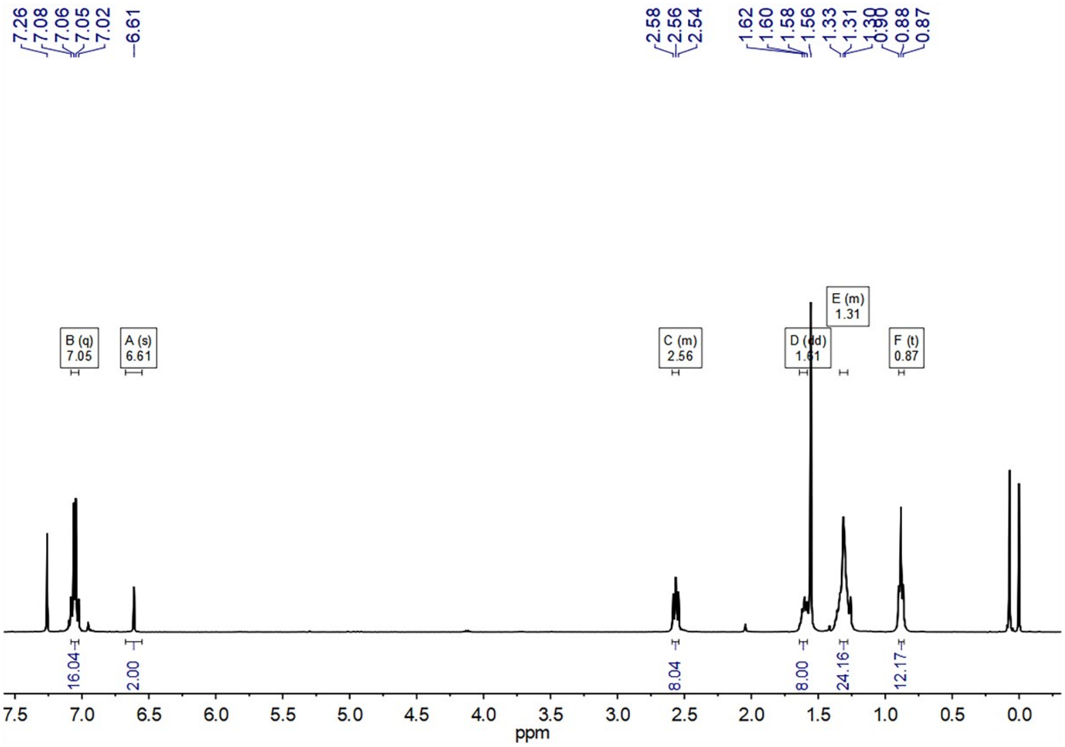


Figure S2. ^{1}H NMR spectrum of **Compound 2b**.

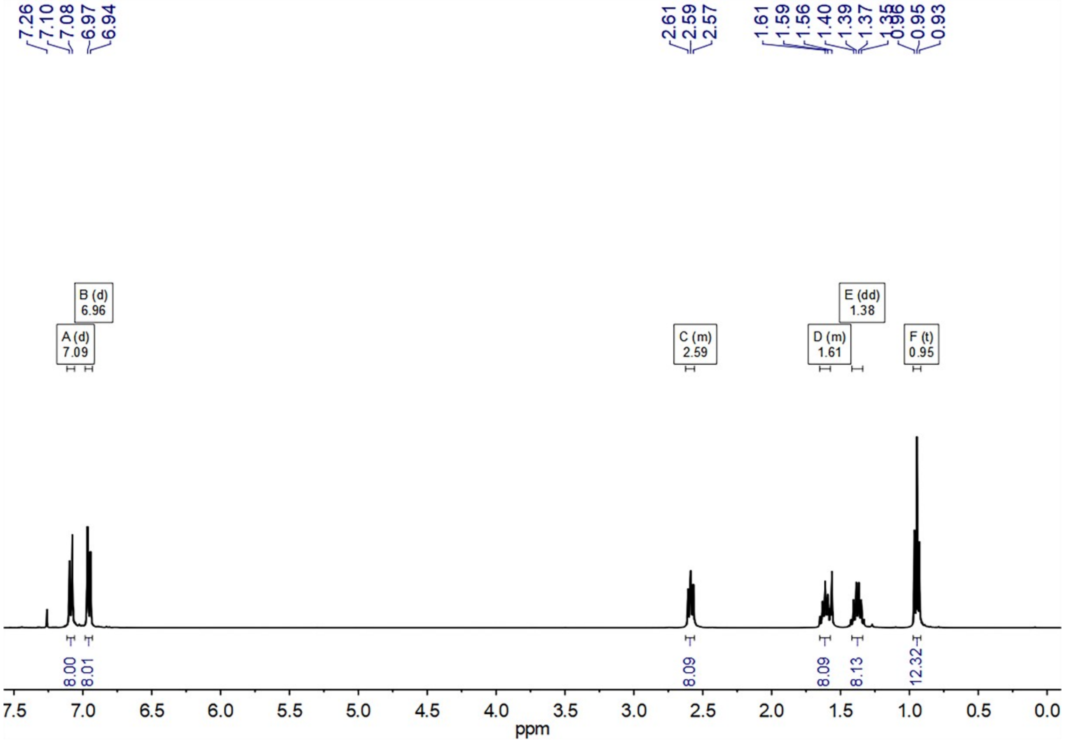


Figure S3. ^{1}H NMR spectrum of **Compound 3a**.

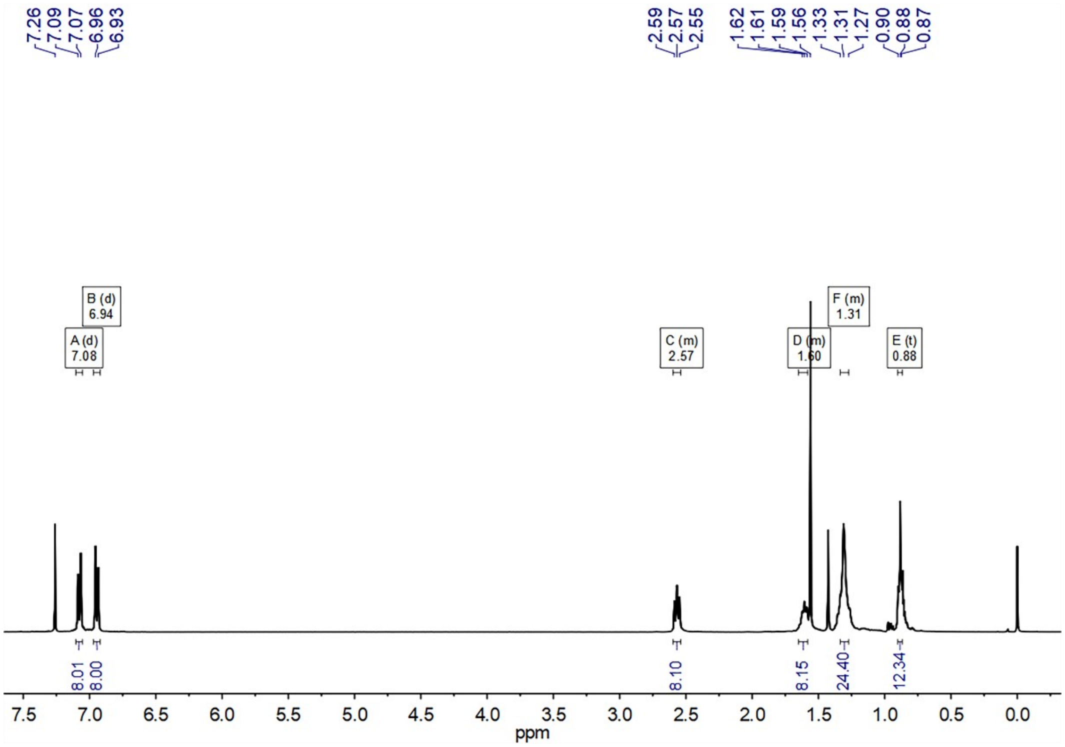


Figure S4. ^{1}H NMR spectrum of **Compound 3b**.

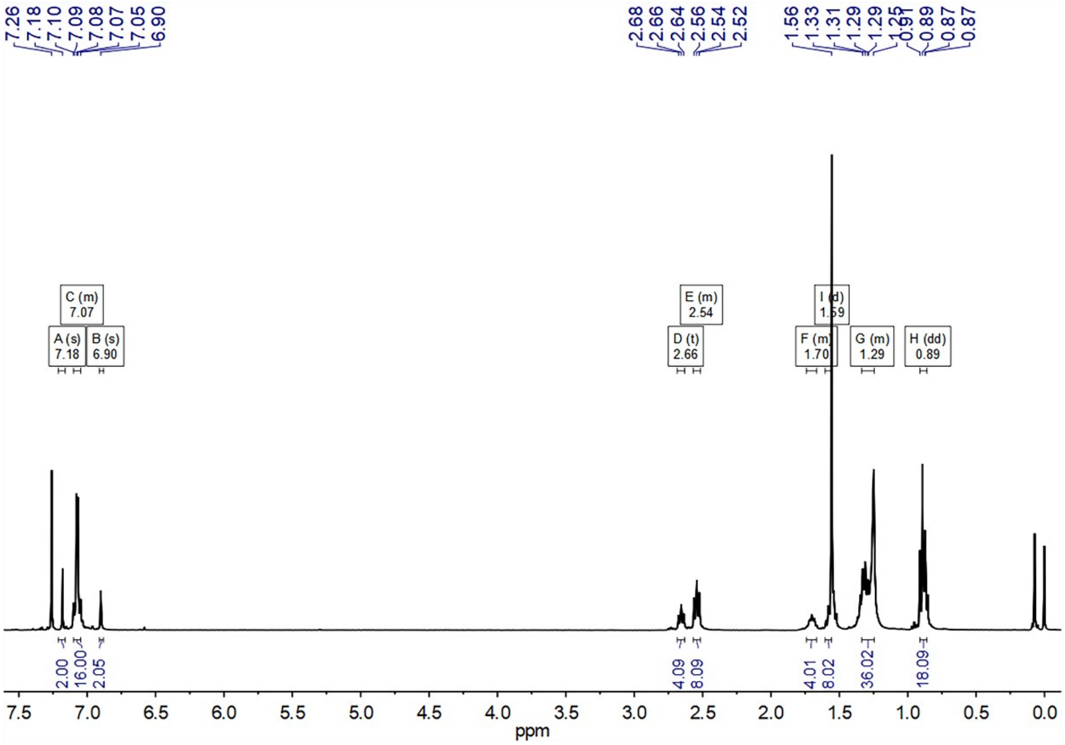


Figure S5. ^{1}H NMR spectrum of **Compound 4a**.

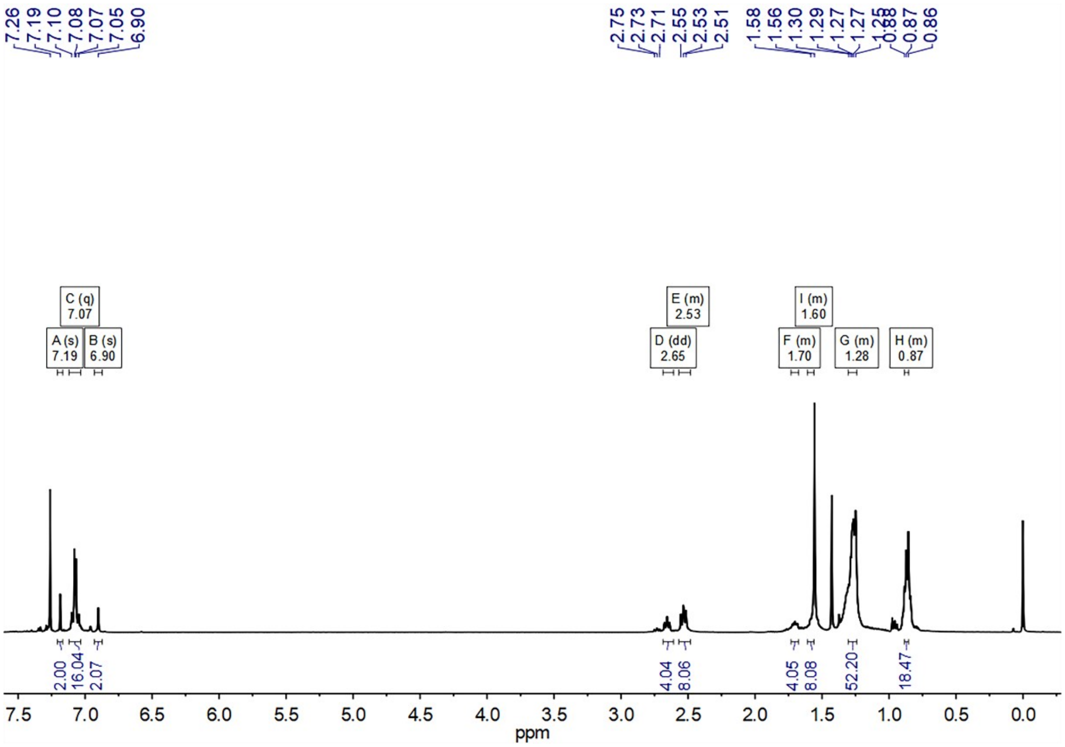


Figure S6. ^{1}H NMR spectrum of **Compound 4b**.

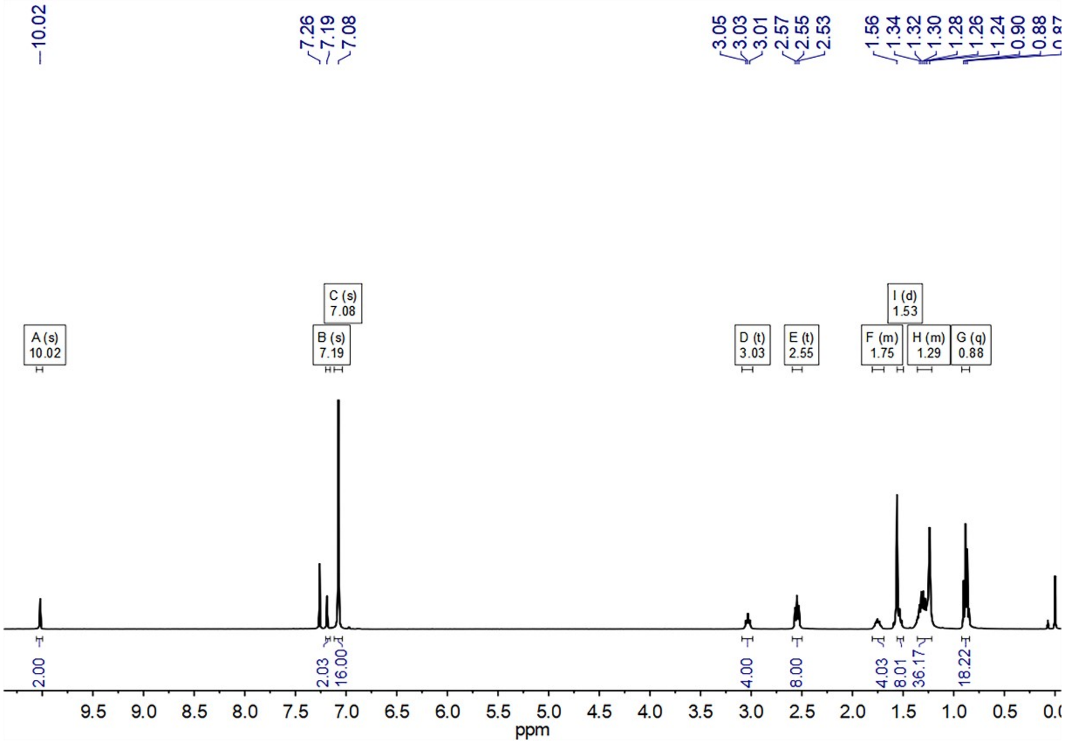


Figure S7. ^{1}H NMR spectrum of **Compound 5a**.

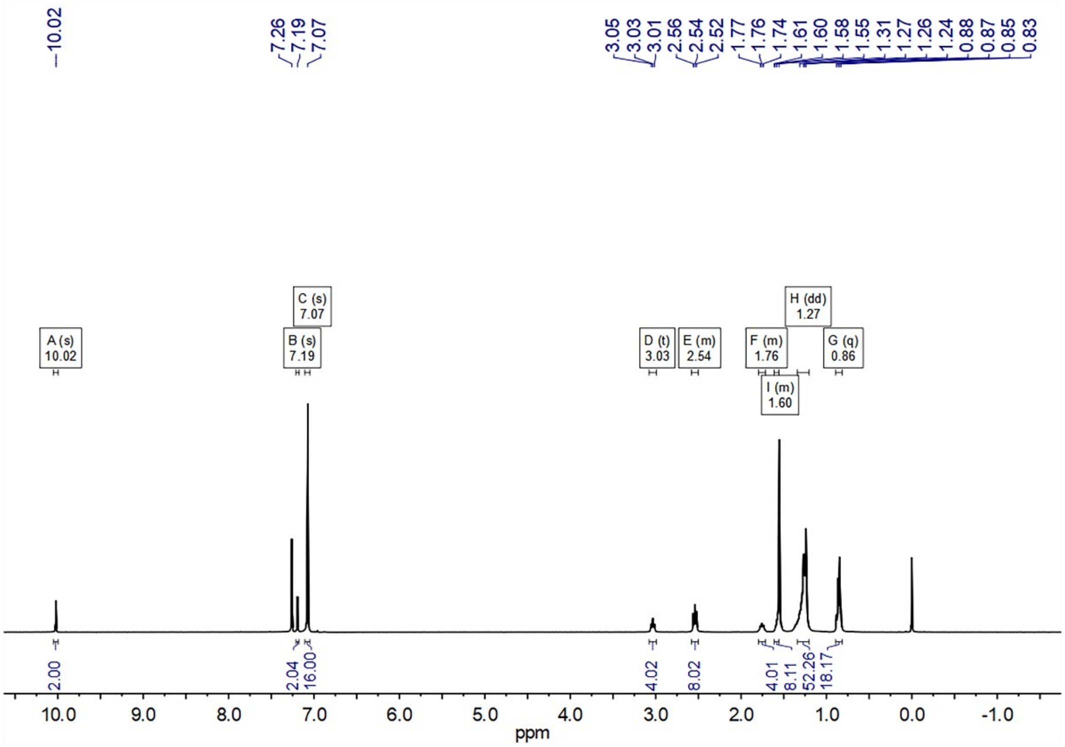


Figure S8. ^{1}H NMR spectrum of **Compound 5b**.

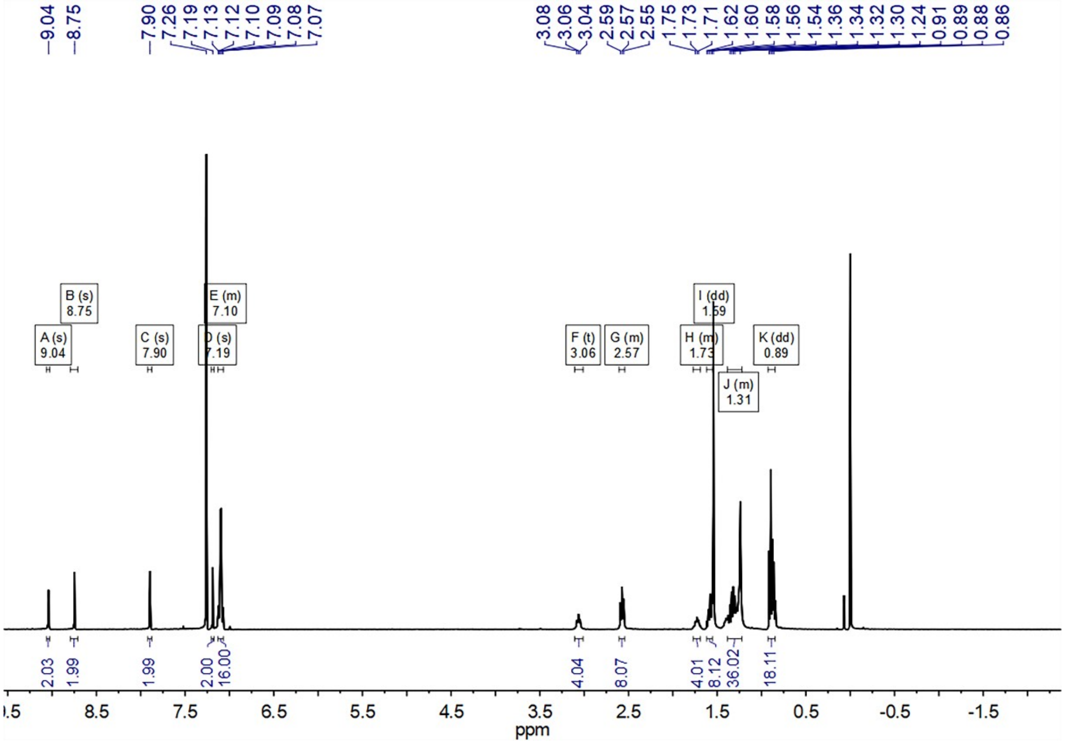


Figure S9. ^{1}H NMR spectrum of **A1C4-Cl**.

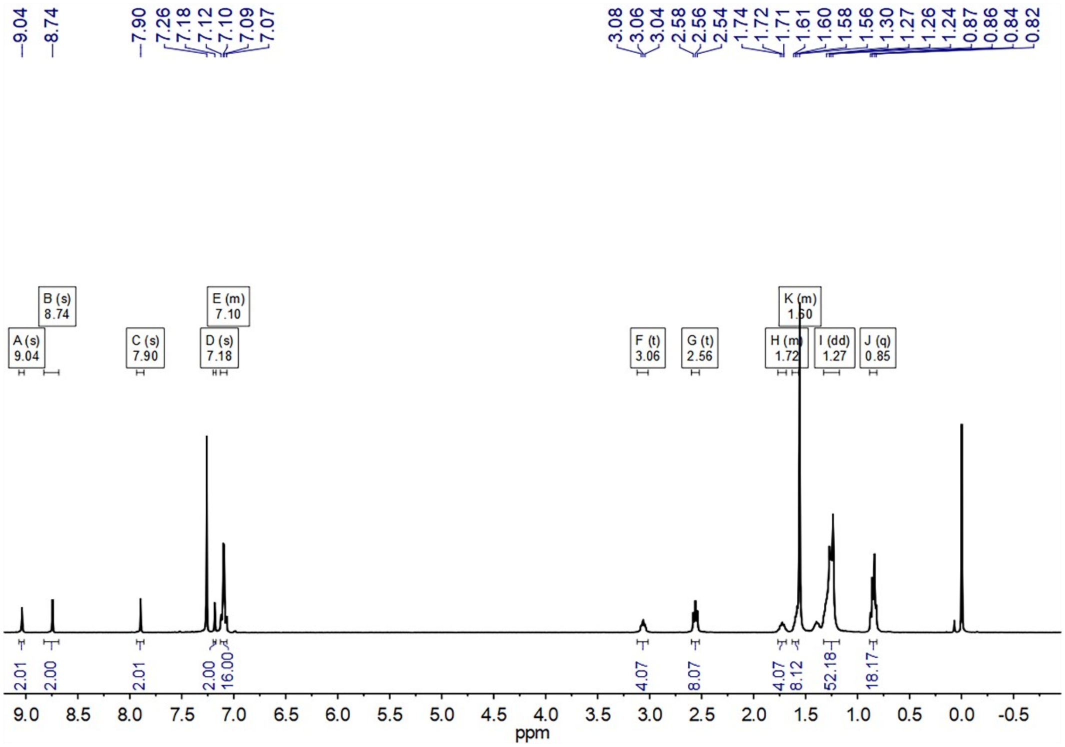


Figure S10. ^{1}H NMR spectrum of **A1C6-Cl**.

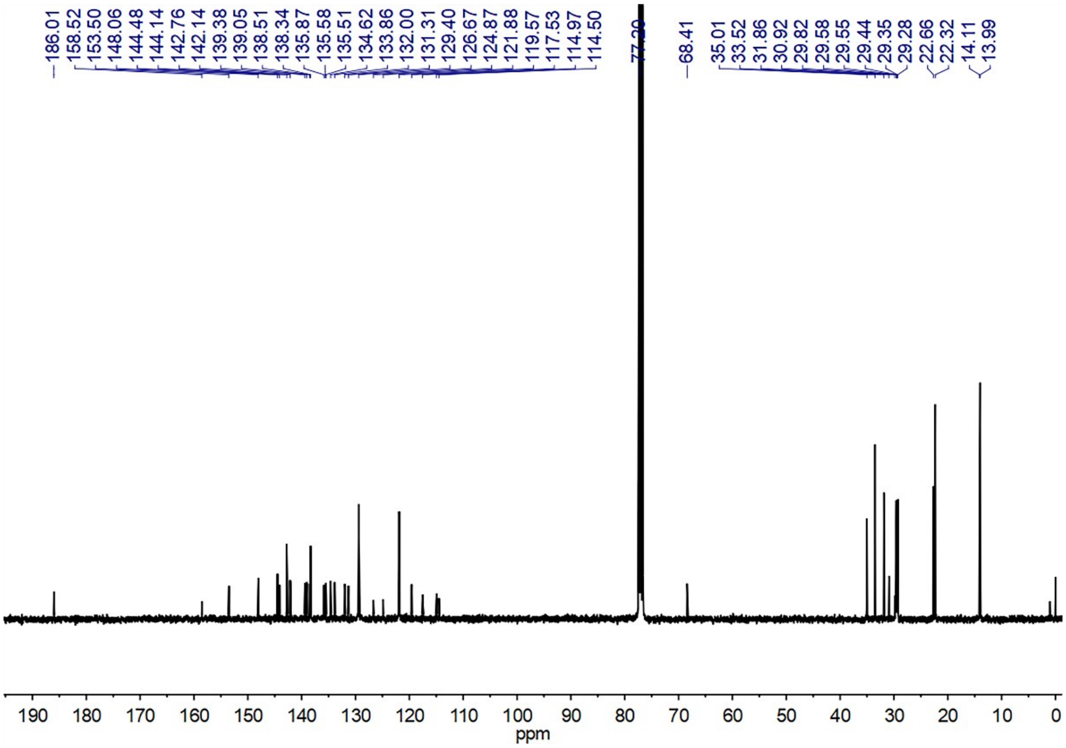


Figure S11. ^{13}C NMR spectrum of **A1C4-Cl**.

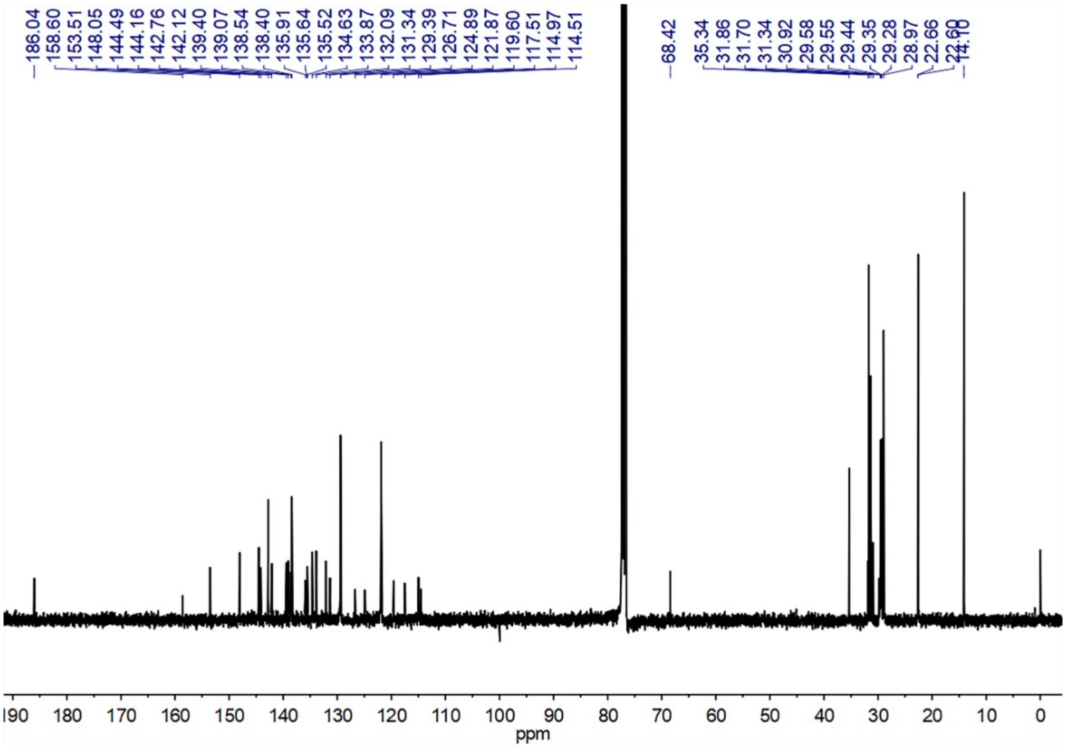


Figure S12. ^{13}C NMR spectrum of **A1C6-Cl**.

4. Mass spectra

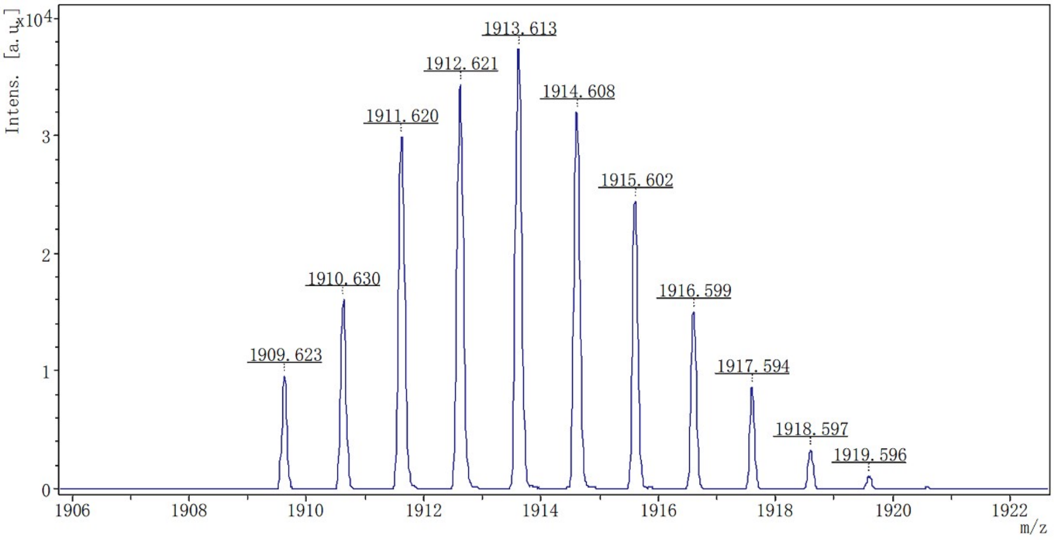


Figure S13. MALDI-MS spectrum of **A1C4-Cl**.

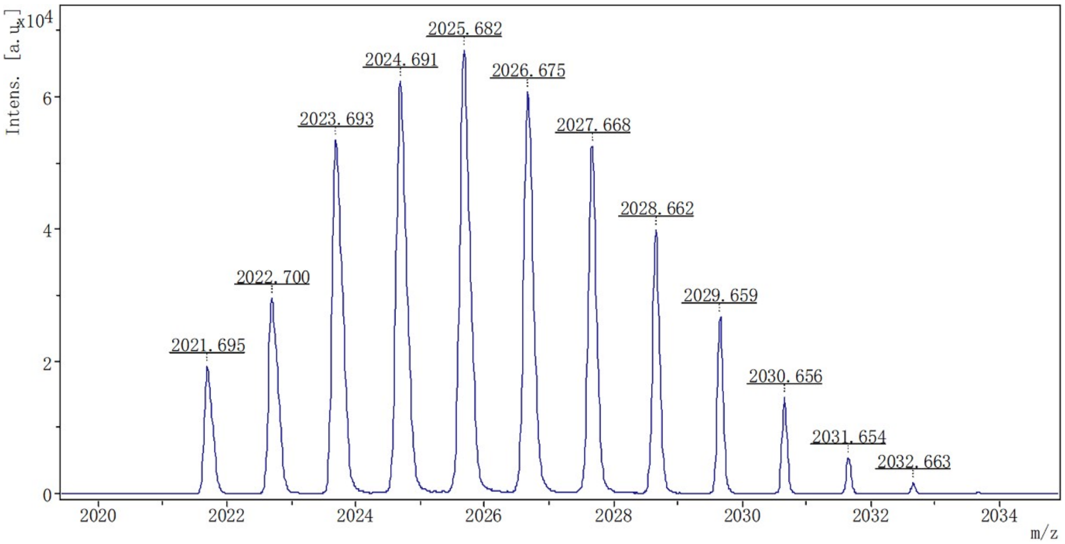


Figure S14. MALDI-MS spectrum of **A1C6-Cl**.

5. Cyclic voltammetry

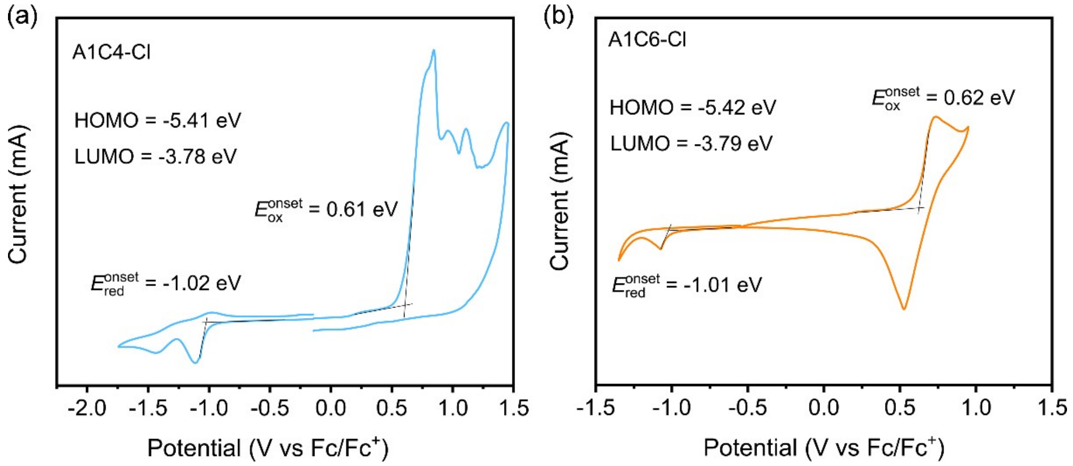


Figure S15. Cyclic voltammograms of (a) A1C4-Cl and (b) A1C6-Cl.

Table S1. Optical and electrochemical data of A1C4-Cl and A1C6-Cl.

	$\lambda_{sol.}$ [nm]	λ_{film} [nm]	λ_{onset} [nm]	E_g^{opt} [eV]^a	E_{ox}^{on}/E_{red}^{on} [V]	HOMO [eV]	LUMO [eV]	E_g^{ec} [eV]^b
A1C4-Cl	742	774	904	1.37	0.61/-1.02	-5.41	-3.78	1.63
A1C6-Cl	743	771	896	1.38	0.62/-1.01	-5.42	-3.79	1.63

$^a E_g^{opt} = 1240/\lambda_{onset}$; HOMO = $-(E_{ox}^{on} + 4.8)$; LUMO = $-(E_{red}^{on} + 4.8)$; $^b E_g^{ec}$ = LUMO-HOMO.

6. Contact angle

According to the contact angles, the surface tension of PBDB-T and NFREAs can be calculated by using the Wu's model:

$$\gamma_{water}(1+\cos\theta_{water}) = \frac{4\gamma_{water}^{d}\gamma^{d}}{\gamma_{water}^{d}+\gamma^{d}} + \frac{4\gamma_{water}^{p}\gamma^{p}}{\gamma_{water}^{p}+\gamma^{p}} \qquad (1)$$

$$\gamma_{GL}(1+\cos\theta_{GL}) = \frac{4\gamma_{GL}^{d}\gamma^{d}}{\gamma_{GL}^{d}+\gamma^{d}} + \frac{4\gamma_{GL}^{p}\gamma^{p}}{\gamma_{GL}^{p}+\gamma^{p}} \qquad (2)$$

$$\gamma^{total} = \gamma^{d} + \gamma^{p} \qquad (3)$$

where γ^{total} is the total surface tension of PBDB-T and NFREAs, γ^{d} and γ^{p} are the dispersion and polar components of γ^{total}, γ_i is the total surface tension of the i material (i = water or glycerol), γ_i^{d} and γ_i^{p} are dispersion and polar components of γ_i, and θ is the contact angle of the droplet (water or glycerol) on PBDB-T or NFREA films.

7. Space charge limited current (SCLC)

Charge carrier mobility was obtained by using SCLC method. The mobility was determined by fitting the dark current to the model of a single charge carrier SCLC, which is described by

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V^2}{d^3}$$

where J is the current density, μ is the zero-field mobility of electron (μ_e) or hole (μ_h), ε_0 is the permittivity of the vacuum, ε_r is the relative permittivity of the material, d is the thickness of the blend film, and V is the effective voltage, $V = V_{appl} - V_{bi}$, where V_{appl} is the applied voltage, and V_{bi} is the built-in potential determined by electrode work function difference.

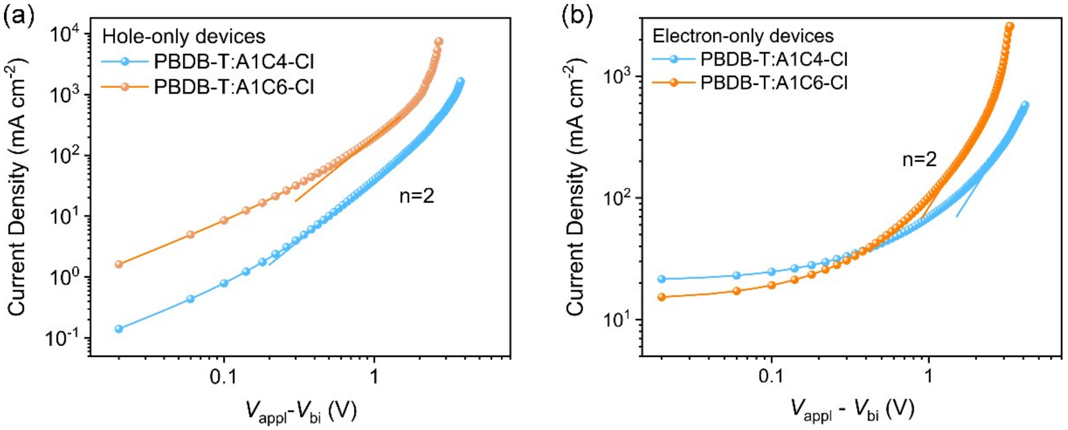


Figure S16. Typical current density-applied voltage semi-log plots for (a) electron-only and (b) hole-only devices based on PBDB-T:A1C4-Cl and PBDB-T:A1C6-Cl blend films under dark. Measured data are shown as symbols, while the solid lines are the best fits to SCLC model. Mobilities were extracted from the fitting.

Table S2. Electron and hole mobilities of PBDB-T:NFREAs based devices.

	μ_h [cm^2 V^{-1} s^{-1}]	μ_e [cm^2 V^{-1} s^{-1}]
PBDB-T:A1C4-Cl	0.56×10^{-4}	0.27×10^{-4}
PBDB-T:A1C6-Cl	6.59×10^{-4}	4.20×10^{-4}

8. Device fabrication and measurements

The PEDOT:PSS layer was deposited onto the ITO glass via spin coating with 4000 rpm for 30 s. The films were annealed under 150 °C in air for 10 min. The PBDB-T:NFREA blend with chloronaphthalene was dissolved in chlorobenzene. The active layer was deposited onto PEDOT:PSS layer via spin coating with 1000 rpm for 60 s in nitrogen glove box. The films were annealed at 100 °C in N_2 for 5 min. Then PDINN in MeOH (1 mg/mL) was deposited onto the active layer with 4000 rpm for 20 s. Ag (~100 nm) was evaporated onto PDINN through a shadow mask (pressure ca. 10^{-4} Pa). The effective device area was 0.04 cm^2. The J-V curves were measured by using a Keithley 2450 source-measure unit. Photocurrent was measured under AM 1.5G illumination at 100 mW/cm^2 by using a 3A solar simulator (LSS-55, Lightsky Technology Co., Ltd). Light intensity is calibrated with a standard photovoltaic cell equipped with a KG5 filter (certificated by the National Institute of Metrology). The thickness of all films was measured by the Bruker Dektak-XT.

Electron-only devices

The structure for electron-only devices is ZnO/active layer/Ca/Al. The ZnO precursor was spin-coated onto ITO glass and annealed at 200 °C in air for 30 min. PBDB-T:NFREA blend in chlorobenzene with additive was spin-coated onto ZnO. Then the film was annealed at 120 °C in N_2 for 15 min. Ca (~15 nm) and Al (~100 nm) were successively evaporated onto the active layer through a shadow mask (pressure ca. 10^{-4} Pa). *J-V* characteristics were measured by using a computerized Keithley 2450 SourceMeter in the dark.

Hole-only devices

The structure for hole-only devices is ITO/PEDOT:PSS/active layer/MoO_3/Al. A ~30 nm thick PEDOT:PSS layer was made by spin coating an aqueous dispersion onto ITO glass (4000 rpm for 30 s). PEDOT:PSS substrates were dried at 150 °C for 10 min. PBDB-T:NFREA blend in chlorobenzene with additive was spin-coated onto PEDOT:PSS layer. Then the film was annealed at 120 °C in N_2 for 15 min. Finally, MoO_3 (~3 nm) and Al (~100 nm) was successively evaporated onto the active layer under a shadow mask (pressure ca. 10^{-4} Pa). *J-V* characteristics were measured by using a computerized Keithley 2450 SourceMeter in the dark.

Reference

[1] Z. Han, C. Zhang, T. He, J. Gao, Y. Hou, X. Gu, J. Lv, N. Yu, J. Qiao, S. Wang, C. Li, J. Zhang, Z. Wei, Q. Peng, Z. Tang, X. Hao, G. Long, Y. Cai, X. Zhang and H. Huang, *Angew. Chem. Int. Ed.*, 2024, **63**, e202318143.