

Carbon-Oxygen-Bridged Hexacyclic Non-fullerene Acceptors with Chlorinated End Groups

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1. Experimental Section

Measurements: ¹H NMR spectra were recorded on Bruker AV 400 MHz spectrometer in CDCl₃ with tetramethylsilane (TMS) as an internal standard. Preparative gel permeation chromatography purification was performed with a JAI LC-9104 recycling preparative high performance liquid chromatography, and the eluent was chloroform. Cyclic voltammetry (CV) measurements were performed on a CHI 660E potentiostat/galvanostat (Shanghai Chenhua Instrumental Co., Ltd. China) to determine the HOMO and LUMO levels of the polymers, in an acetonitrile solution of 0.1 mol·L⁻¹ tetrabutylammonium hexafluorophosphate ([*n*-Bu₄N]⁺ [PF₆]⁻) at a potential scan rate of 100 mV s⁻¹ with an Ag/Ag⁺ reference electrode and a platinum wire counter electrode under an argon atmosphere. Solution and film UV-Vis absorption spectra absorption

spectra were recorded on a Shimadzu UV3600 spectrometer. Thermogravimetric analysis (TGA) plots were measured with a Discovery series instrument under a nitrogen atmosphere at heating and cooling rates of 10 °C/min. Different scanning calorimetry (DSC) measurements were performed on a Discovery series thermal analyzer at a scanning rate of 10 °C/min in N₂. Atom force microscopy (AFM) images were taken on a NanoScopeIIIa controller (Veeco Metrology Group/Digital Instruments, Santa Barbara, CA), using built-in software (version V6.13R1) to capture images. Transmission electron microscopy (TEM) images were acquired using a HITACHI H-7650 electron microscope operating at an acceleration voltage of 100 kV. **PTB7-Th** was purchased from 1-Material Inc. ($M_n=43000$ kDa, $M_w=105700$ kDa and PDI=2.46).

2. Device Fabrication and Testing

The fabrication and measurement methods of OSCs devices are as follows: first of all, a thorough cleaning of the indiumtin oxide (ITO)-coated glass substrate was performed with detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 minutes each. The substrates were subsequently dried in an oven for 1 minute at 80 °C under vacuum. The ITO glass substrates were treated with UV-ozone for 15 minutes and then the sol-gel-derived ZnO films were spin-coated onto the ITO substrates followed by thermal treatment at 200 °C for 30 min. The total concentration of the PTB7-Th:Acceptor (1:1) blend solution for spin-coating was 20 mg mL⁻¹ with chlorobenzene as the processing solvent. The additive, 1,8-diiodooctane (DIO) was added into solution 30 minutes before the spin-coating process. The blend

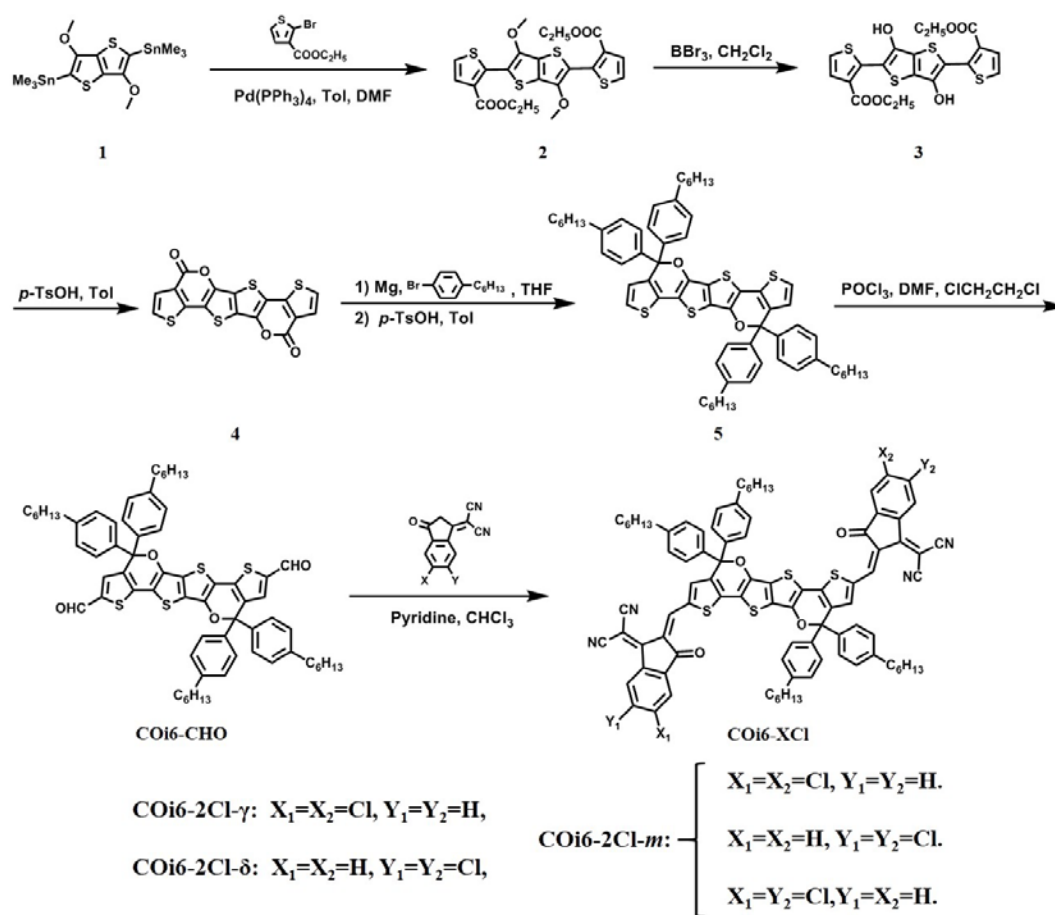
was stirred at room temperature in the glove box overnight. The active layer was spin-coating at 1600 rpm for 45 s to get a neat film, and the active layer thickness is about 100 nm. A 10 nm MoO₃ layer and a 100 nm Ag layer were subsequently evaporated through a shadow mask to define the active area of the devices. The integrated device structure is ITO/ZnO/PTB7-Th: Acceptor/MoO₃/Ag. A solar simulator (Enlitech.Inc) with an AM 1.5G filter was used as a light source to produce an intensity of 100 mW cm⁻² for the illumination of the photovoltaic cells. The light intensity was calibrated by a 2 cm × 2 cm calibrated silicon solar cell with KG-3 visible color filter. A shadow mask with a single aperture (4.15 mm²) was placed onto the devices in order to accurately define the photoactive area. Steady-state current-voltage (J-V) curves were measured by a Keithley 2400 source-measurement unit under AM 1.5 G spectrum from a solar simulator (Enlitech.Inc) calibrated by a silicon reference cell (Hamamatsu S1133 color, with KG-5 visible fiith). The relationship of J_{sc} to the light intensity were measured by steady-state current-voltage measurement, the light intensity was modulated by neutral density filters (NDF) with different values of optical density (OD). The external quantum efficiency (EQE) was measured by a solar cells–photodetector responsibility measurement system (Enlitech.Inc).

Electron-only devices fabrication. Electron-only devices were fabricated with the device structure of ITO/ZnO/PTB7-Th:Acceptor/Ca/Al. The mobilities were determined by fitting the dark current to the model of a single carrier SCLC, which is described by the equation:

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu_h \frac{V^2}{d^3}$$

where J is the current, μ_h is the zero-field mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, d is the thickness of the active layer, and V is the effective voltage.

2. Synthesis



Scheme S1 The synthetic route for **COi6-2Cl- γ** , **COi6-2Cl- δ** and **COi6-2Cl- m** .

Compounds 1-4, **COi6** and **COi6-CHO** were synthesized according to the method reported by Ding's work¹⁻⁵.

COi6-2Cl- γ . To a solution of COi6-CHO (100 mg, 0.095 mmol) in CHCl₃ (20 mL) was added 2-(5-chloro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (IC-Cl- γ , 86.88 mg, 0.38 mmol) and pyridine (0.5 mL) at room temperature. The mixture was heated to reflux for 12 h. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CHCl₃ as eluent to give **COi6-2Cl- γ** as a dark green solid with metallic luster (118 mg, 84%). ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 8.63 (s, 2H), 8.24 (s, 2H), 7.74 (s, 2H), 7.58-7.56 (d, 2H), 7.16-7.13 (m, 18H), 2.60-2.57 (t, 8H), 1.63-1.56 (m, 8H), 1.36-1.27 (m, 24H), 0.89-0.85 (t, 12H). ¹³C NMR (CDCl₃, 400 MHz, δ /ppm): 186.728, 147.919, 144.990, 143.989, 141.439, 139.517, 138.000, 137.578, 137.024, 134.657, 134.368, 128.998, 128.351, 125.947, 123.407, 119.839, 117.056, 114.472, 114.389, 89.243, 68.235, 35.671, 31.697, 31.107, 29.225, 22.625, 14.098. MALDI-TOF MS (m/z): 1478.4306 (M⁺).

COi6-2Cl- δ . To a solution of COi6-CHO (100 mg, 0.095 mmol) in CHCl₃ (20 mL) was added 2-(6-chloro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (IC-Cl- δ , 86.88 mg, 0.38 mmol) and pyridine (0.5 mL) at room temperature. The mixture was heated to reflux for 12 h. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CHCl₃ as eluent to give **COi6-2Cl- δ** as a dark green solid with metallic luster (121 mg, 86%). ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 8.59 (s, 2H), 8.27 (s, 2H), 7.75-7.71 (m, 4H), 7.16-7.08 (m, 18H), 2.60-2.56 (t, 8H), 1.63-1.56 (m, 8H), 1.36-1.29 (m, 24H), 0.89-0.85 (t, 12H). ¹³C NMR (CDCl₃, 400 MHz, δ /ppm): 186.967, 157.970, 147.837, 144.914, 143.977, 141.768, 140.734,

139.484, 136.881, 135.069, 134.559, 134.297, 128.992, 128.312, 125.045, 124.236, 119.803, 117.119, 114.543, 114.231, 89.190, 68.521, 35.669, 31.700, 31.097, 29.234, 22.629, 14.102. MALDI-TOF MS (m/z): 1478.4540 (M^+).

COi6-2Cl-*m*. To a solution of COi6-CHO (100 mg, 0.095 mmol) in CHCl_3 (20 mL) was added IC-Cl-*m* (a mixture of IC-Cl- γ and IC-Cl- δ , 86.88 mg, 0.38 mmol) and pyridine (0.5 mL) at room temperature. The mixture was heated to reflux for 12 h. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CHCl_3 as eluent to give **COi6-2Cl-*m*** as a dark green solid with metallic luster (107 mg, 76%). ^1H NMR (CDCl_3 , 400 MHz, δ/ppm): 8.59 (s, 2H), 8.21 (s, 2H), 7.74-7.72 (m, 3H), 7.57-7.56 (d, 1H), 7.15-7.08 (m, 18H), 2.60-2.56 (t, 8H), 1.63-1.56 (m, 8H), 1.36-1.25 (m, 24H), 0.88-0.85 (t, 12H). MALDI-TOF MS (m/z): 1478.5253 (M^+).

3. NMR

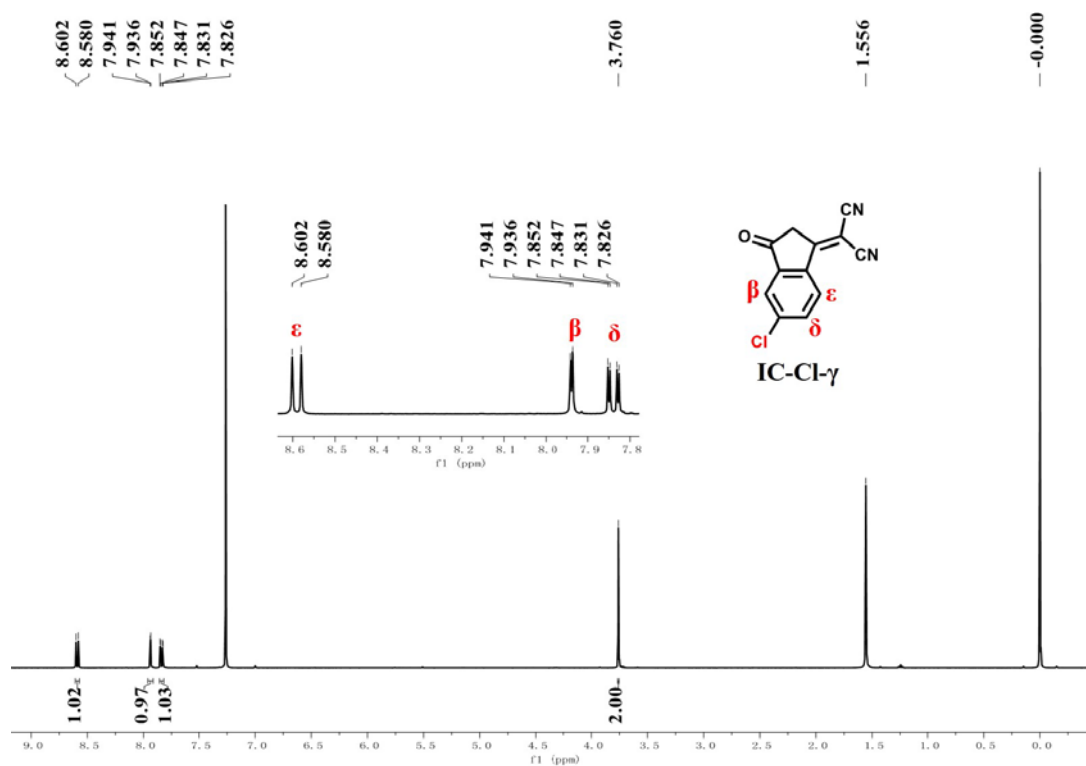


Fig. S1 ^1H NMR spectrum of IC-Cl- γ .

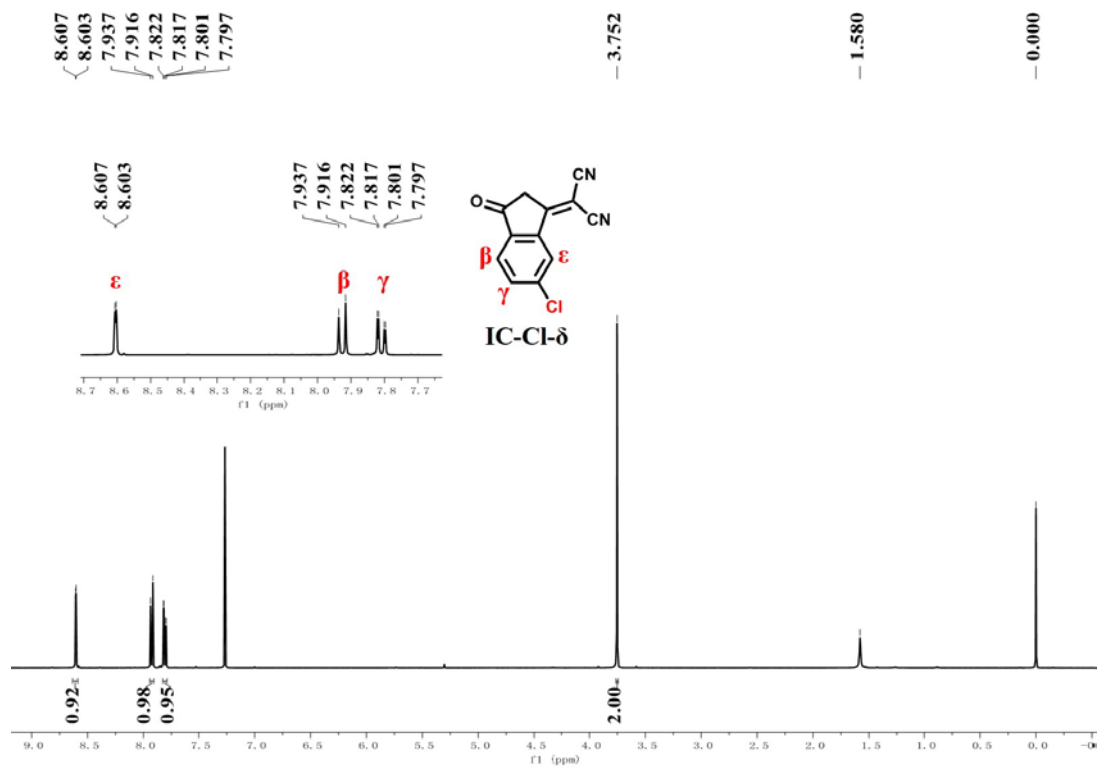


Fig. S2 ^1H NMR spectrum of IC-Cl- δ .

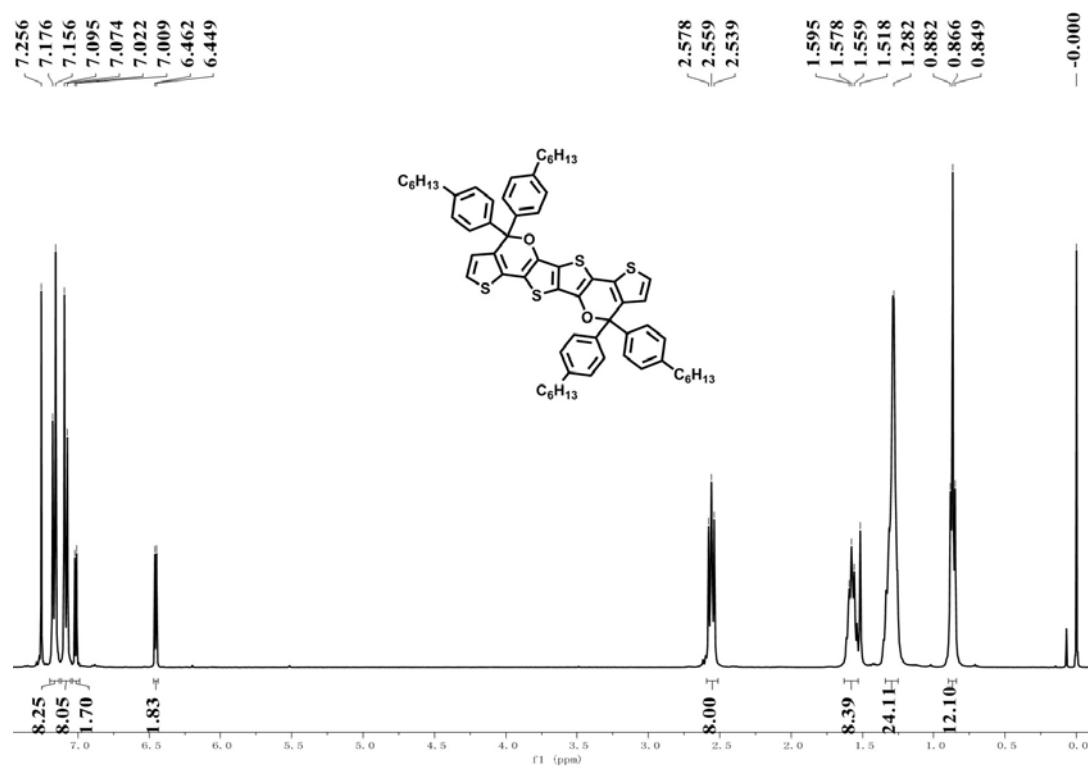


Fig. S3 ¹H NMR spectrum of **COi6**.

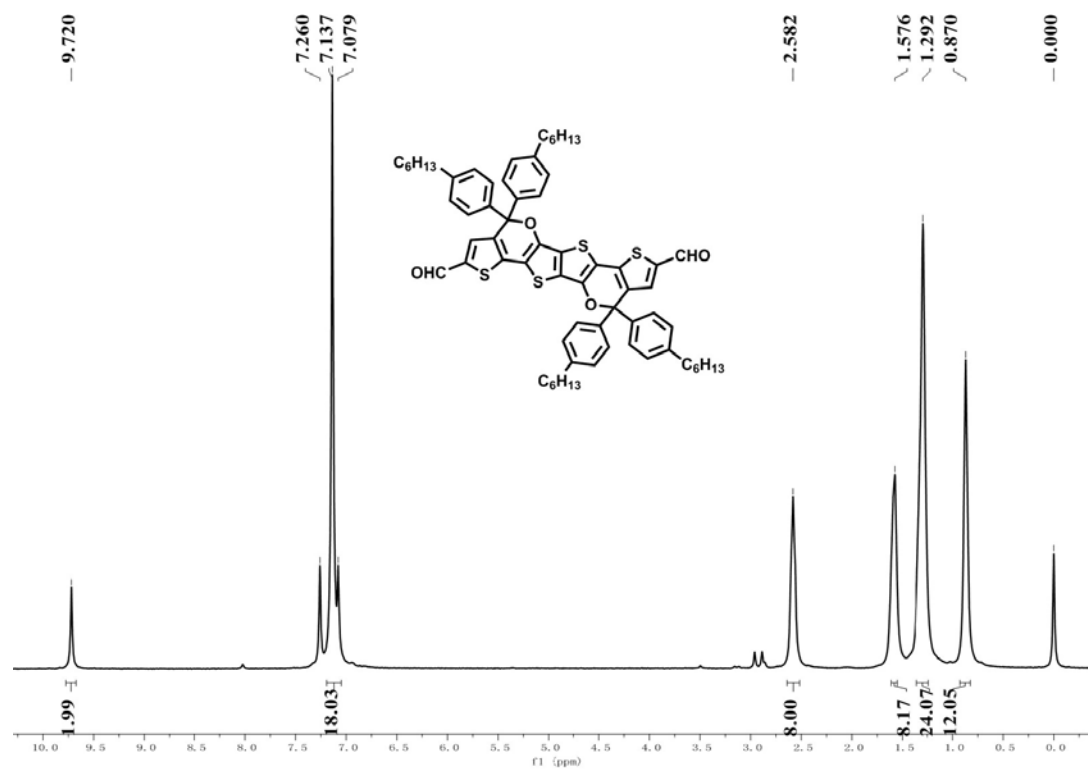


Fig. S4 ¹H NMR spectrum of **COi6-CHO**.

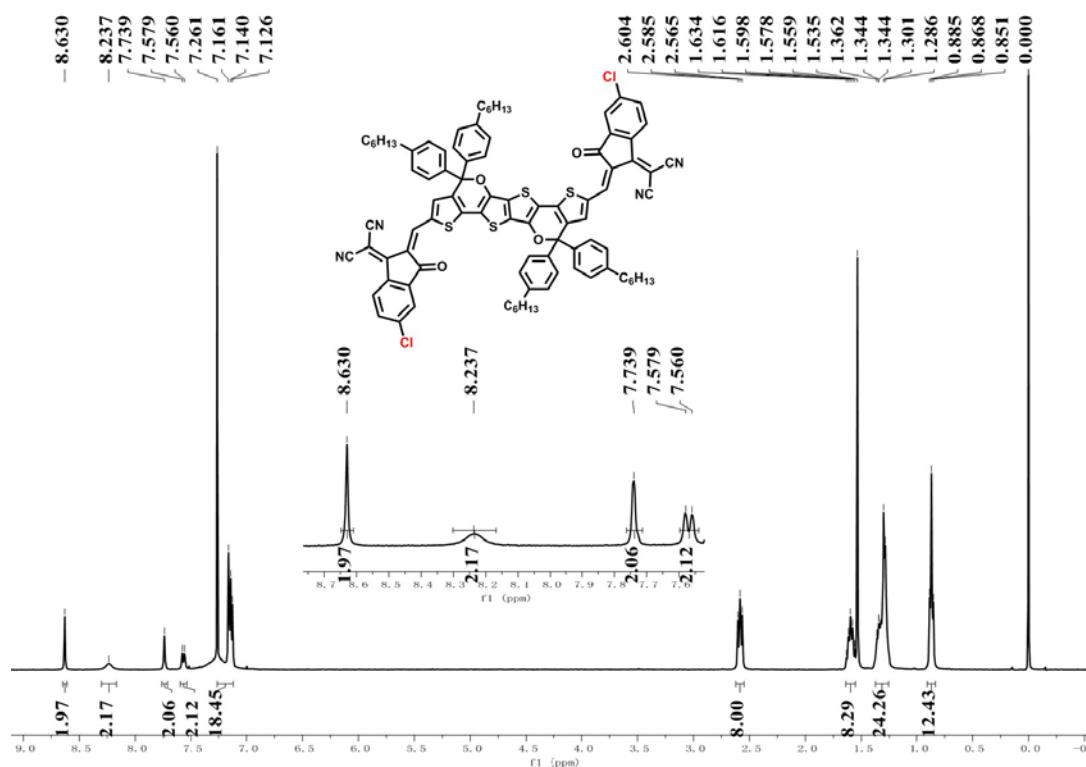


Fig. S5 ¹H NMR spectrum of COi6-2Cl-γ.

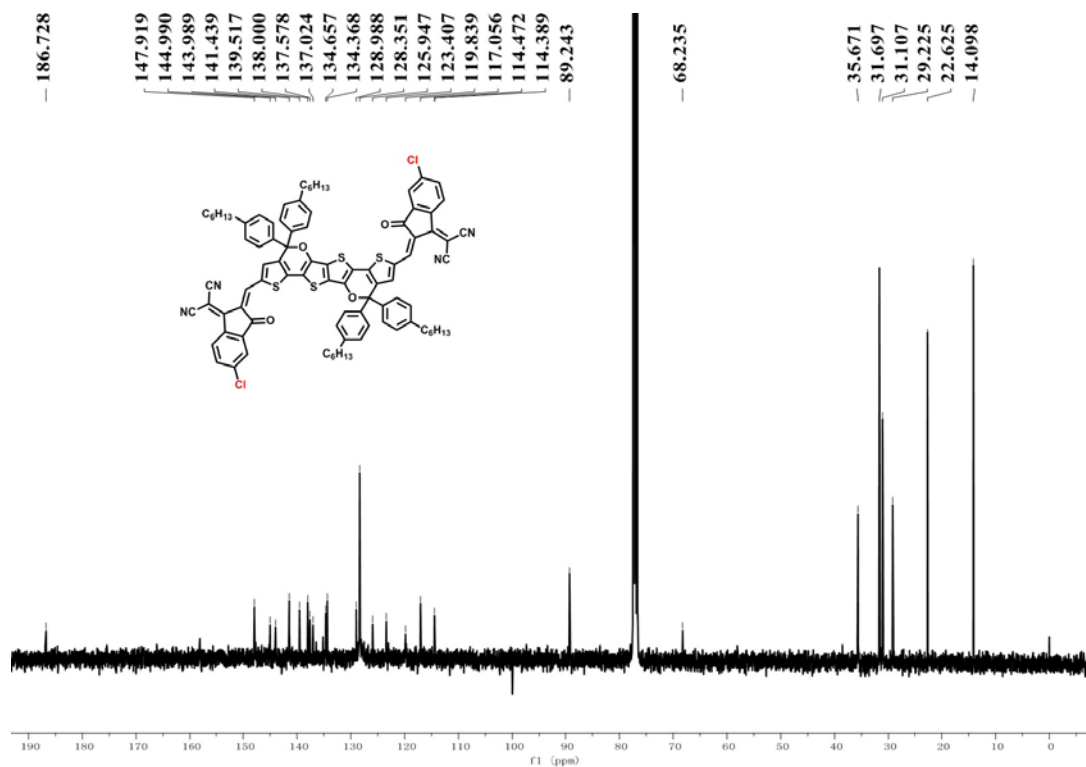


Fig. S6 ¹³C NMR spectrum of COi6-2Cl-γ.

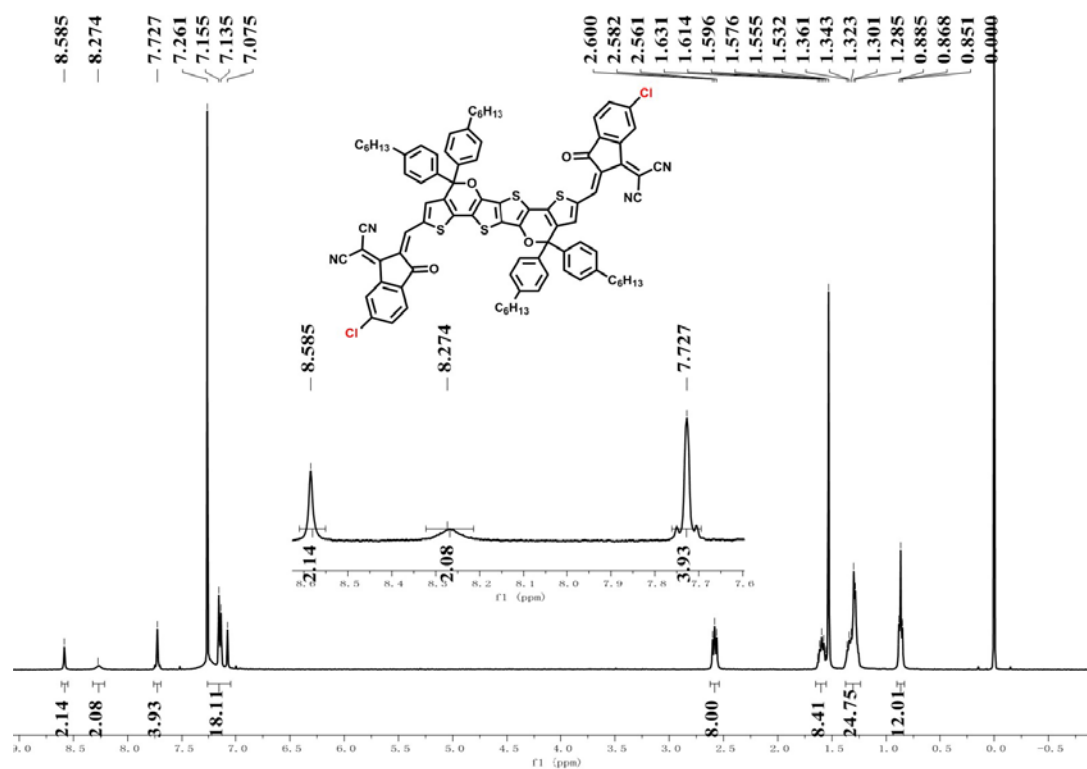


Fig. S7 ¹H NMR spectrum of COi6-2Cl-δ.

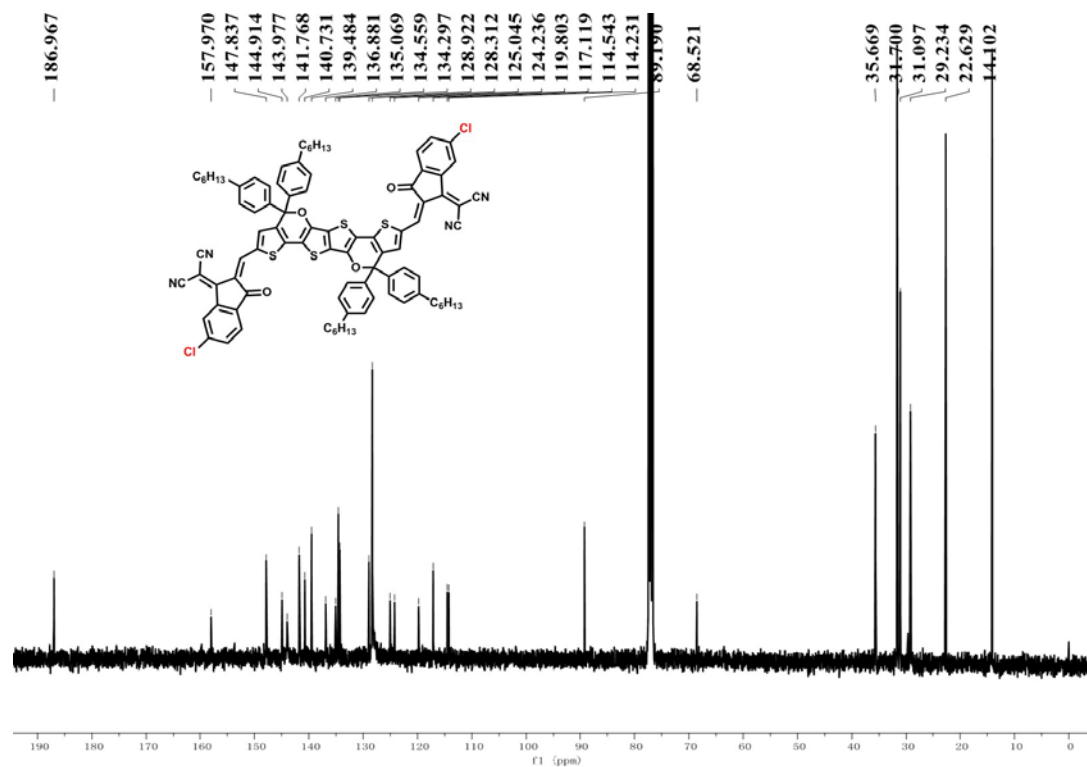


Fig. S8 ¹³C NMR spectrum of COi6-2Cl-δ.

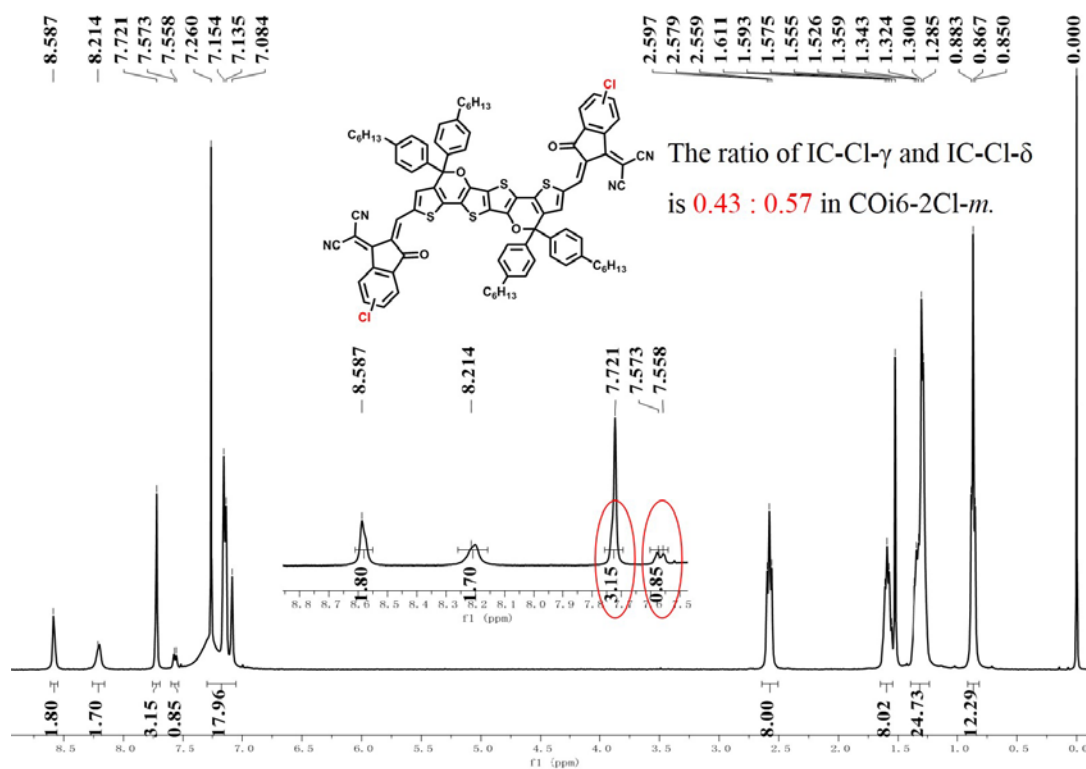


Fig. S9 ^1H NMR spectrum of COi6-2Cl- m .

4. HRMS

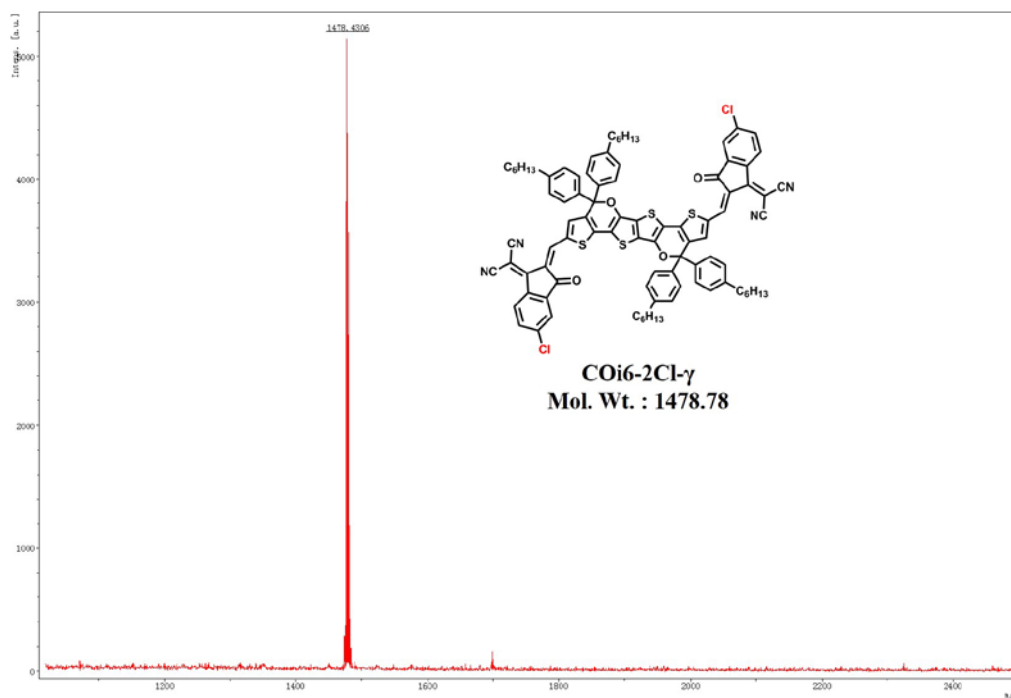


Fig. S10 High-resolution MALDI-TOF mass spectrum for COi6-2Cl- γ .

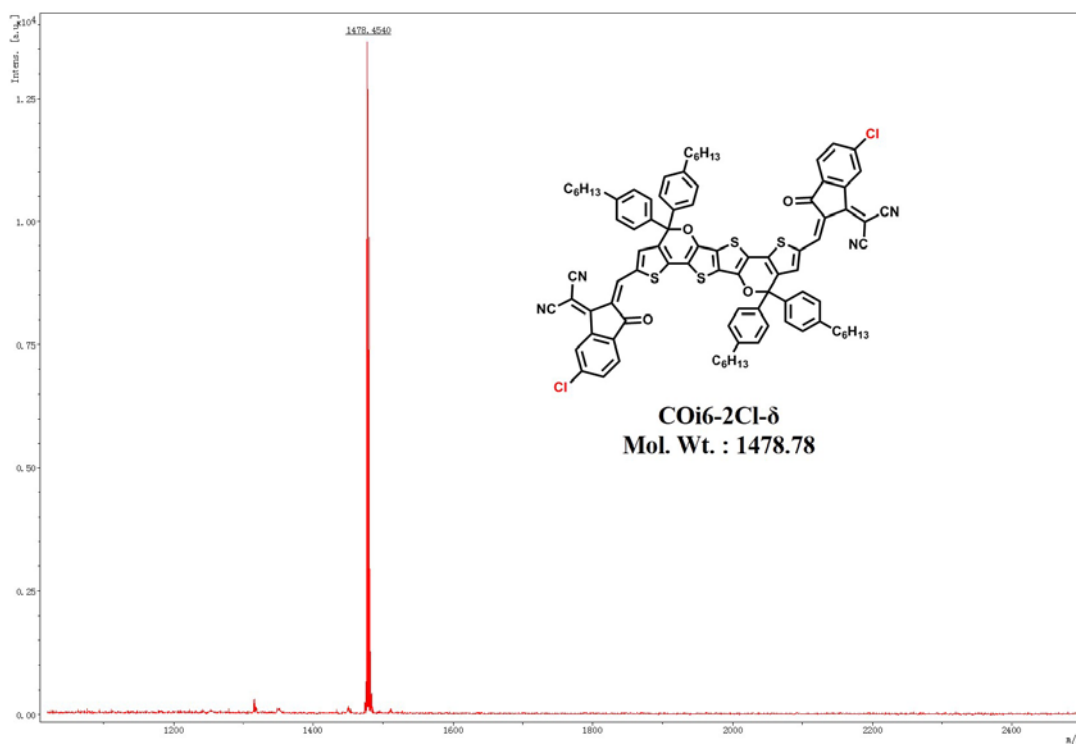


Fig. S11 High-resolution MALDI-TOF mass spectrum for **COi6-2Cl- δ** .

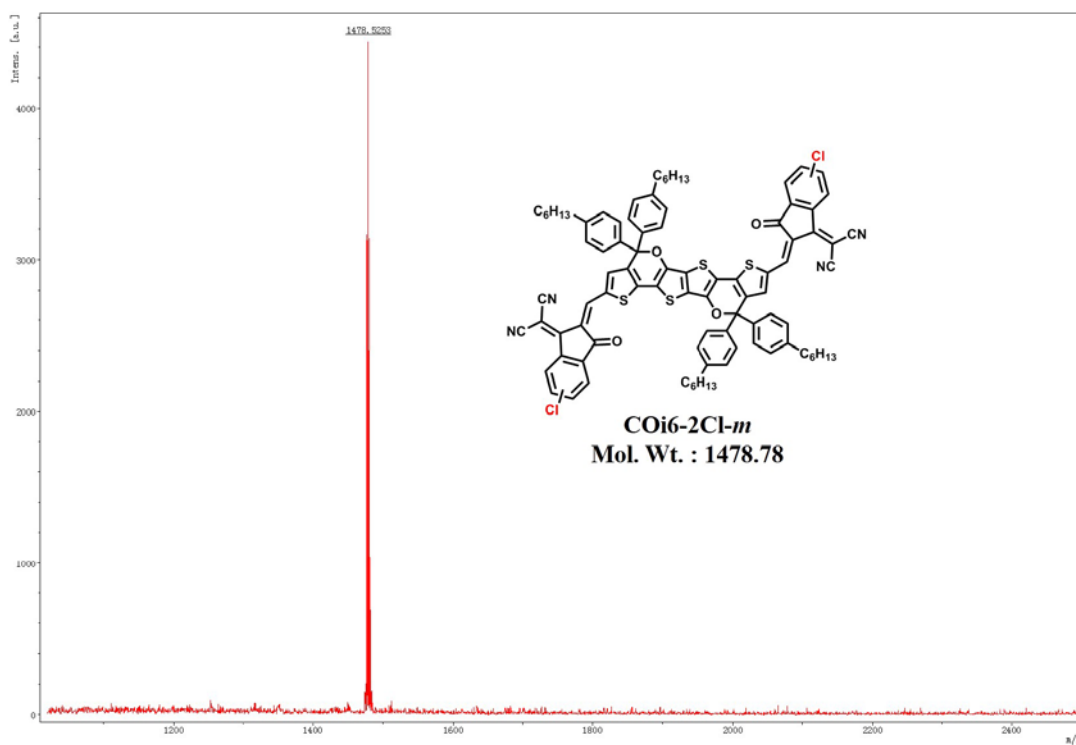


Fig. S12 High-resolution MALDI-TOF mass spectrum for **COi6-2Cl- m** .

5. UV-vis absorption spectra

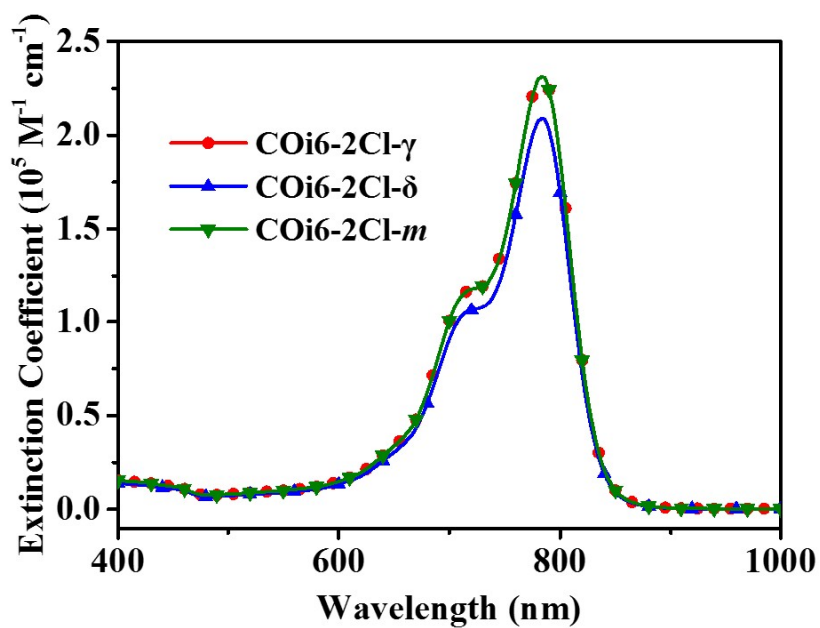


Fig. S13 Absorption spectra of three small molecules in chloroform solution with a concentration of $10^{-5} \text{ mol L}^{-1}$.

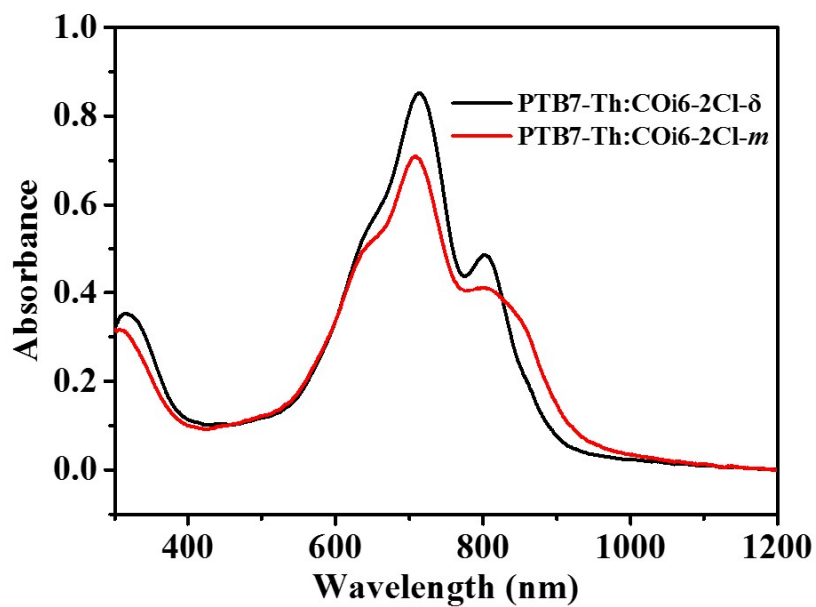


Fig. S14 Normalized UV-vis absorption spectra of PTB7-Th:COi6-2Cl- δ and PTB7-Th:COi6-2Cl- m blended films.

6. Cyclic voltammogram

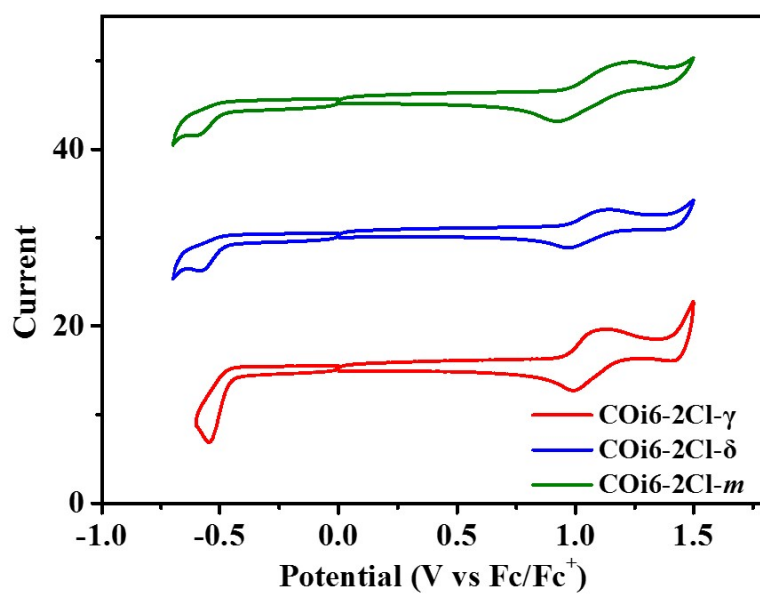


Fig. S15 Cyclic voltammograms for COi6-2Cl- γ , COi6-2Cl- δ and COi6-2Cl- m .

7. TGA and DSC

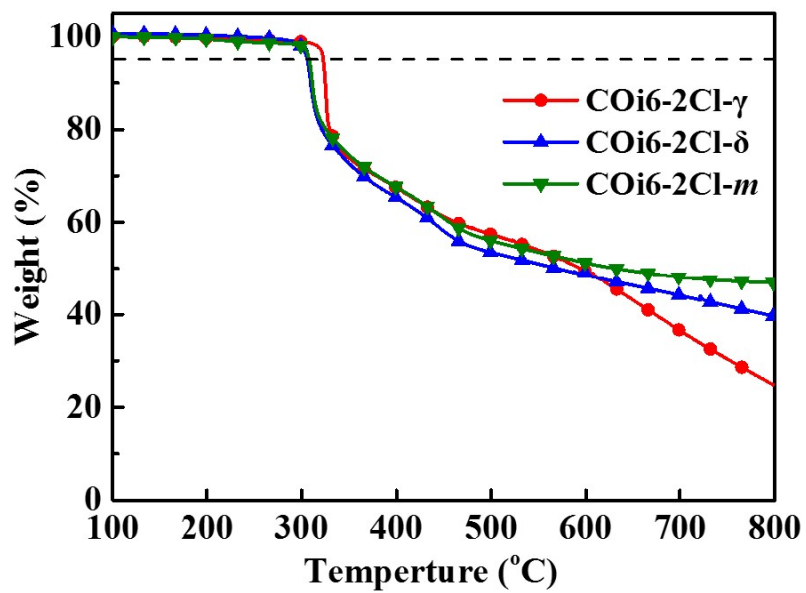


Fig. S16 Thermogravimetric analysis (TGA) of the COi6-2Cl- γ , COi6-2Cl- δ and COi6-2Cl- m .

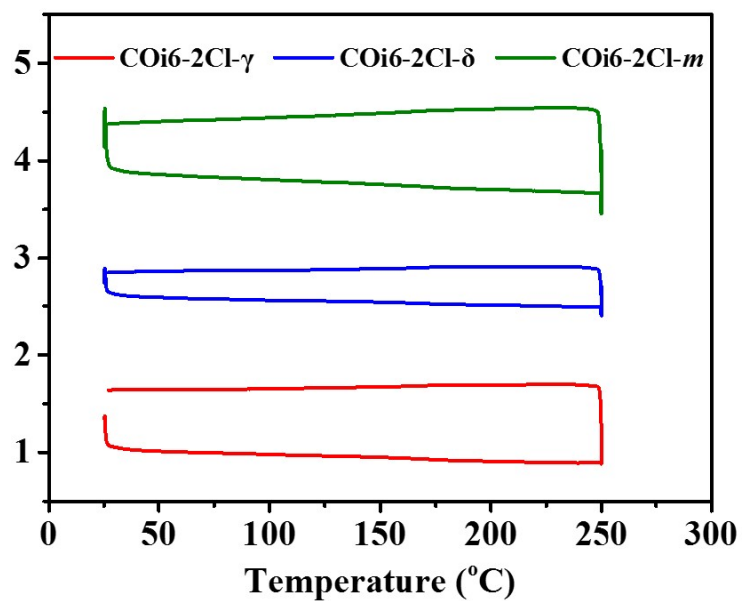


Fig. S6 Differential scanning calorimetry (DSC) of the **COi6-2Cl- γ** , **COi6-2Cl- δ** and **COi6-2Cl- m** .

8. Optimized photovoltaic parameters

Table. S1 Photovoltaic characteristics of the PTB7-Th:COi6-2Cl- γ solar cells with different DIO weight ratio.

PTB7-Th:COi6-2Cl- γ	V_{oc} (V)	J_{sc} (mA cm ²)	FF (%)	PCE (%)
pristine	0.69	18.50	56.45	7.20
0.2% DIO	0.70	18.27	59.79	7.65
0.5% DIO	0.69	20.33	62.84	8.81
0.8% DIO	0.69	20.00	58.99	8.14

Table. S2 Photovoltaic characteristics of the PTB7-Th:COi6-2Cl- δ solar cells with different DIO weight ratio.

PTB7-Th:COi6-2Cl- δ	V_{oc} (V)	J_{sc} (mA cm ²)	FF (%)	PCE (%)
pristine	0.69	15.81	54.45	5.94
0.2% DIO	0.68	20.76	58.73	8.29
0.5% DIO	0.67	20.65	60.81	8.41
0.8% DIO	0.67	20.37	58.91	8.04

Table. S3 Photovoltaic characteristics of the PTB7-Th:COi6-2Cl- m solar cells with different DIO weight ratio.

PTB7-Th:COi6-2Cl- m	V_{oc} (V)	J_{sc} (mA cm ²)	FF (%)	PCE (%)
pristine	0.69	18.67	59.67	7.69
0.2% DIO	0.69	19.21	61.86	8.20
0.5% DIO	0.69	20.78	64.32	9.22
0.8% DIO	0.68	20.80	60.61	8.57

Table. S4 Photovoltaic characteristics of the **PTB7-Th:COi6-2Cl- γ** solar cells with different D/A weight ratio.

PTB7-Th:COi6-2Cl- γ	V_{oc} (V)	J_{sc} (mA cm ²)	FF (%)	PCE (%)
1:0.8	0.68	16.38	54.26	6.04
1:1	0.69	20.33	62.84	8.81
1:1.2	0.69	19.50	62.14	8.36

Table. S5 Photovoltaic characteristics of the **PTB7-Th:COi6-2Cl- δ** solar cells with different D/A weight ratio.

PTB7-Th:COi6-2Cl- δ	V_{oc} (V)	J_{sc} (mA cm ²)	FF (%)	PCE (%)
1:0.8	0.68	16.12	54.26	5.95
1:1	0.67	20.65	60.81	8.41
1:1.2	0.67	19.45	60.18	7.84

Table. S6 Photovoltaic characteristics of the **PTB7-Th:COi6-2Cl- m** solar cells with different D/A weight ratio.

PTB7-Th:COi6-2Cl- m	V_{oc} (V)	J_{sc} (mA cm ²)	FF (%)	PCE (%)
1:0.8	0.68	17.75	57.79	6.98
1:1	0.69	20.78	64.32	9.22
1:1.2	0.69	19.46	62.35	8.37

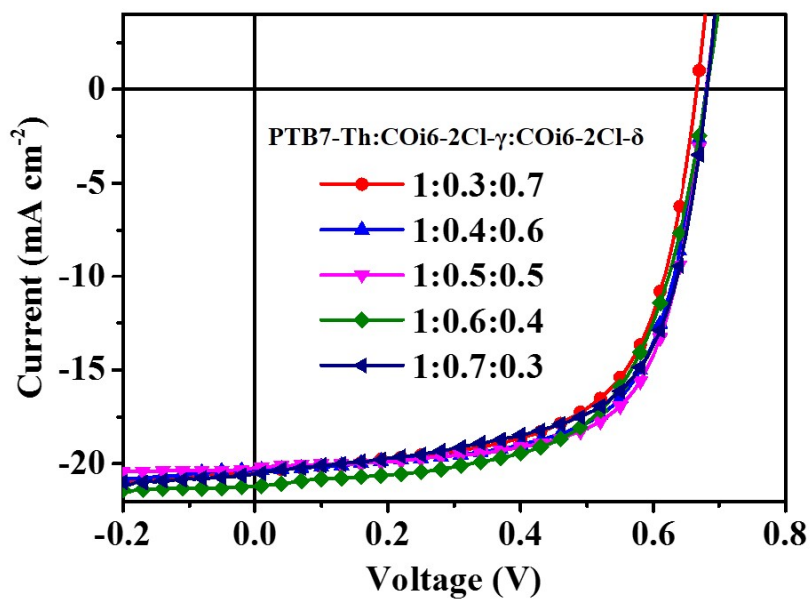


Fig. S7 The J-V characteristics of the ternary cells.

9. Bimolecular recombination

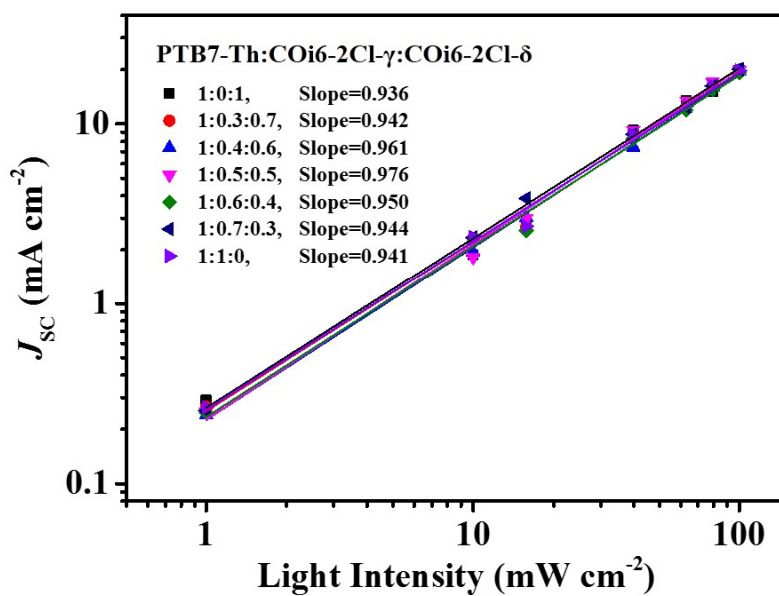


Fig. S8 The J_{sc} versus light intensity of the seven different **PTB7-Th:COi6-2Cl- γ :COi6-2Cl- δ** -based PSCs.

10. Electron mobilities

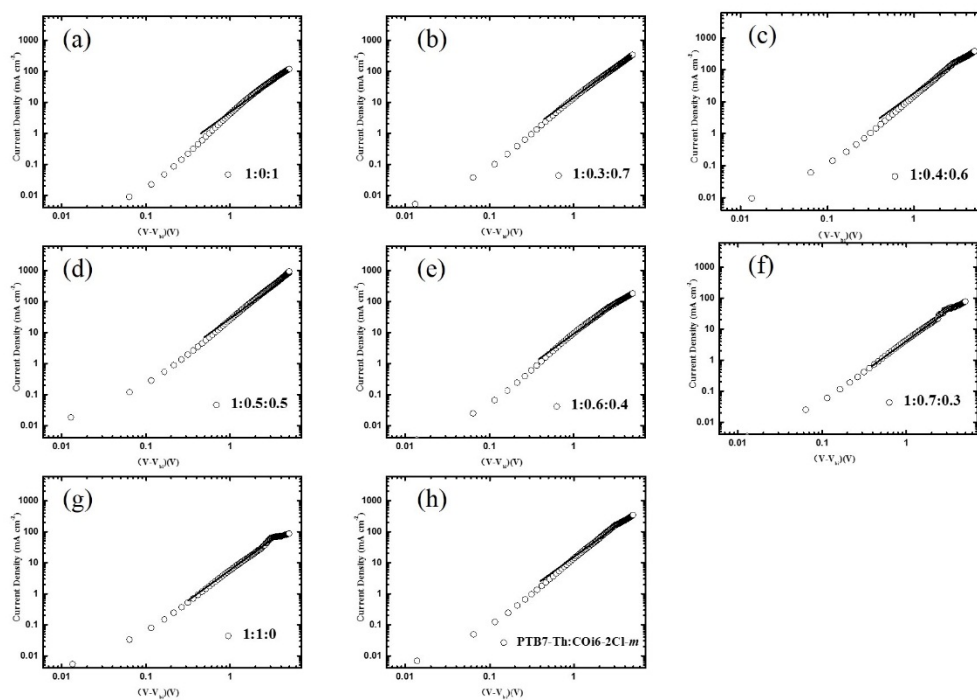


Fig. S20 J-V curves of the electron-only devices for **PTB7-Th:COi6-2Cl-*m*** blend and other seven different ternary blends (**PTB7-Th:COi6-2Cl- γ :COi6-2Cl- δ**).

11. Density functional theory (DFT) calculations

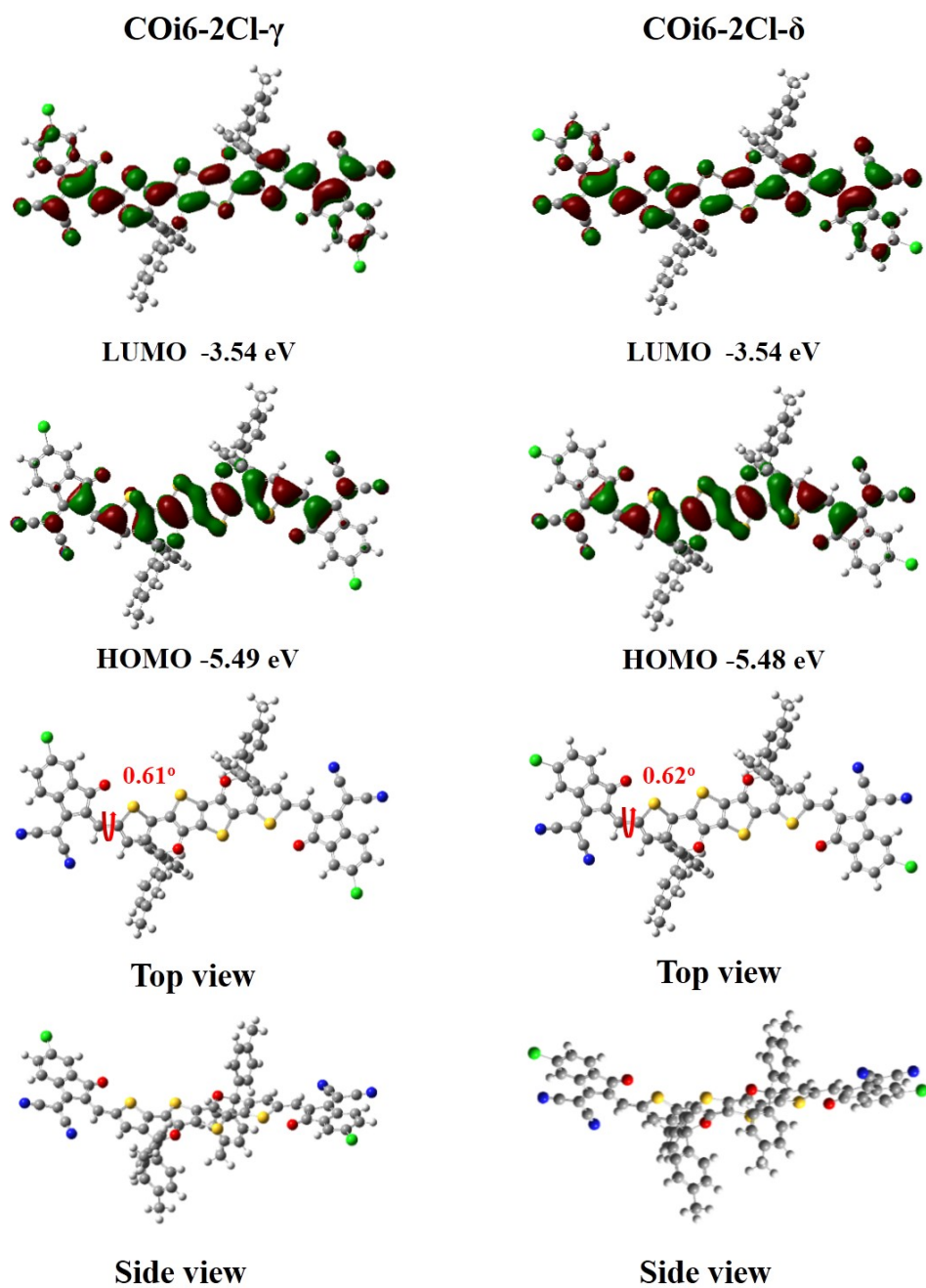


Fig. S21 Molecular geometries, HOMO/LUMO wavefunctions and values of **COi6-2Cl- γ** and **COi6-2Cl- δ** . The alkyl chains were replaced by methyl groups to reduce the computational time within a reasonable range. Note: grey, carbon; red, oxygen; blue, nitrogen; orange, sulphur; green, chlorine.

References

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