

## Supporting Information

### **An Acceptor-Donor-Acceptor Type Non-Fullerene Acceptor with Asymmetric Backbone for High Performance Organic Solar Cells**

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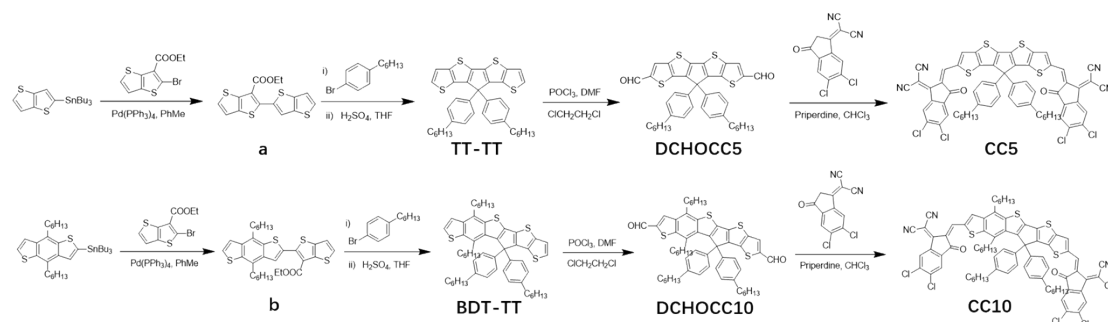
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## 1. Materials and Synthesis

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. Tetrahydrofuran (THF) and toluene were distilled from sodium benzophenone before use, and 1,2-dichloroethane was dried with calcium hydride.



**Figure S1.** Synthetic route of CC5 and CC10.

### *Synthesis of ethyl [2,2'-bithieno[3,2-b]thiophene]-3-carboxylate (compound a)*

Tributyl(thieno[3,2-*b*]thiophen-2-yl)stannane (2.41 g, 5.61 mmol), ethyl 2-bromothiopheno[3,2-*b*]thiophene-3-carboxylate (1.5 g, 5.15 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.60 g, 0.52 mmol) were dissolved in anhydrous toluene (50 mL) under argon atmosphere. The resulting solution was stirred at 100 °C for 10 h. After cooling down to room temperature, the reaction mixture was poured into water (100 mL) and extracted with dichloromethane for three times. The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. The filtrate was concentrated under vacuum and purified by column chromatography on silica gel with petroleum ether: dichloromethane (1:1) as an eluent to obtain target compound **a** as a yellow solid (1.70 g, 94%).

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.80 (s, 1H), 7.49 (d, *J* = 5.3 Hz, 1H), 7.46 (d, *J* = 5.2 Hz, 1H), 7.33 – 7.27 (d, *J* = 4.8 Hz, 1H), 7.26 (d, *J* = 5.3 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 161.85, 145.45, 141.01, 139.23, 135.90, 135.84, 129.2, 128.48, 121.90, 120.49, 119.36, 118.75, 61.26, 14.2.

**MS** (MALDI-TOF): calculated for C<sub>15</sub>H<sub>10</sub>O<sub>2</sub>S<sub>4</sub> [M<sup>+</sup>], 350.50; found:350.13.

### *Synthesis of compound TT-TT*

Step 1: To an argon-filled two-neck flash was added 1-(4-bromophenyl)hexane (1.93 g, 8.00 mmol) and then anhydrous THF (30 mL). The reaction mixture was stirred as -

78 °C for 10 min, and *n*-BuLi (3.33 mL, 2.4 M in hexane) was added slowly to the mixture through funnel. The mixture was stirred at the same temperature for over 2 hours and then an anhydrous THF solution of (a) (0.70 g, 2.00 mmol) was added by syringe. The reaction mixture was allowed to warm to room temperature and stirred overnight. By the completion of the reaction, saturated aqueous NH<sub>4</sub>Cl (50 mL) was added and extracted with EA for three times. The organic layer was washed with water, and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by a rotating evaporator and the residue was used in next step without further purification.

Step 2: The residue was dissolved in THF (100 mL) and conc. H<sub>2</sub>SO<sub>4</sub> (1.2 mL) was added to the mixture. The reaction mixture was stirred and heated to reflux. After 2 hours, the reaction was completed, and then quenched by water (50 mL) and extracted with EA for three times. The organic layer was washed with water, and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by a rotating evaporator and the residue (yellow solid) was used in next step without further purification.

#### *Synthesis of compound DCHOCC5*

A Vilsmeier reagent, which was prepared with POCl<sub>3</sub> (0.50 mL) in DMF (4 mL), was added to a solution of TT-TT (0.60 g, 0.98 mmol) in 1,2-dichloroethane (40 mL) under the protection of argon. After refluxing at 80 °C overnight, the mixture was poured into ice water (100 mL), neutralized with aqueous AcONa, and then extracted with dichloromethane for three times. The combined organic layer was washed with water and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of solvent, the crude product was purified by silica gel to obtain DCHOCC5 (0.55g, 85%) as a red solid.

<sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 9.91 (s, 2H), 7.96 (s, 2H), 7.17 – 7.01 (m, 8H), 2.54 (t, J = 7.9 Hz, 4H), 1.55 (t, J = 7.7 Hz, 4H), 1.34 – 1.22 (m, 12H), 0.90 – 0.82 (t, J = 6.8 Hz, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 182.82, 149.48, 144.63, 144.31, 143.04, 141.65, 139.95, 136.67, 129.73, 129.22, 127.61, 62.58, 35.67, 31.75, 31.31, 29.18, 22.65, 14.17.

MS (MALDI-TOF): calculated for C<sub>39</sub>H<sub>38</sub>O<sub>2</sub>S<sub>4</sub> [M<sup>+</sup>], 666.98; found: 667.04.

#### *Synthesis of CC5*

Under the protection of argon, DCHOCC5 (100 mg, 0.15 mmol) and IC-2Cl (197 mg, 0.75 mmol) was dissolved in a dry CHCl<sub>3</sub> (40 mL) solution, and then pyridine (0.5 mL) was added to the mixture. After stirring at room temperature for 12 h, the mixture

was poured into water and then extracted with  $\text{CHCl}_3$  for three times, the organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  for 0.5 h. After removal of solvent, the crude product was purified by silica gel, and then recrystallized from  $\text{CHCl}_3$  and methanol to give CC5 (132 mg, 76%) as a blue solid.

$^1\text{H NMR}$  (400 MHz, Chloroform- $d$ )  $\delta$  8.79 (s, 2H), 8.68 (s, 2H), 7.96 (s, 2H), 7.89 (s, 2H), 7.24 (m, 8H), 2.63 – 2.54 (t, 4H), 1.66 – 1.51 (m, 4H), 1.39 – 1.18 (m, 12H), 0.87 – 0.75 (t, 6H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  185.95, 157.63, 151.75, 148.08, 147.05, 144.41, 143.59, 140.50, 140.27, 139.93, 138.66, 137.44, 136.17, 135.94, 129.60, 127.84, 127.03, 125.46, 122.52, 114.10, 70.72, 62.86, 53.57, 35.74, 31.82, 31.41, 29.32, 22.72, 14.21.

**HR-FTMS:** calculated for  $\text{C}_{63}\text{H}_{42}\text{Cl}_4\text{N}_4\text{O}_2\text{S}_4$  [ $\text{M}^+$ ], 1157.11; found: 1156.10.

*Synthesis of ethyl 2-(4,8-dihexylbenzo[1,2- $b$ :4,5- $b'$ ]dithiophen-2-yl)thieno[3,2- $b$ ]thiophene-3-carboxylate (compound b)*

Tributyl(4,8-dihexylbenzo[1,2- $b$ :4,5- $b'$ ]dithiophen-2-yl)stannane (2.17 g, 3.35 mmol), ethyl 2-bromothieno[3,2- $b$ ]thiophene-3-carboxylate (0.98 g, 3.35 mmol) and  $\text{Pd}(\text{PPh}_3)_4$  (0.39 g, 0.34 mmol) were dissolved in anhydrous toluene (50 mL) under argon atmosphere. The resulting solution was stirred at 100 °C for 12 h. After cooling down to room temperature, the reaction mixture was poured into water (100 mL) and extracted with dichloromethane for three times. The combined organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and filtered. The filtrate was concentrated under vacuum and purified by column chromatography on silica gel with petroleum ether: dichloromethane (1:1) as an eluent to obtain target compound b as a yellow solid (1.73 g, 91%).

$^1\text{H NMR}$  (400 MHz, Methylene Chloride- $d_2$ )  $\delta$  7.96 (d,  $J$  = 1.4 Hz, 1H), 7.51 (q,  $J$  = 5.8 Hz, 3H), 7.29 (dd,  $J$  = 5.4, 1.4 Hz, 1H), 4.41 (q,  $J$  = 7.1 Hz, 2H), 3.68 (h,  $J$  = 4.6, 4.0 Hz, 2H), 3.19 (dt,  $J$  = 12.6, 7.9 Hz, 4H), 1.95 – 1.73 (m, 4H), 1.64 – 1.19 (m, 13H), 0.90 (t,  $J$  = 6.7 Hz, 6H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.12, 145.47, 141.41, 138.33, 137.81, 136.75, 136.52, 136.05, 133.76, 130.07, 129.50, 128.68, 126.60, 124.81, 122.10, 121.51, 118.90, 61.40, 33.67, 33.56, 31.85, 29.93, 29.81, 29.72, 22.76, 14.40, 14.27.

**MS** (MALDI-TOF): calculated for  $\text{C}_{31}\text{H}_{36}\text{O}_2\text{S}_4$  [ $\text{M}^+$ ], 568.88.; found: 568.03.

### *Synthesis of compound BDT-TT*

Step 1: To an argon-filled two-neck flash was added 1-(4-bromophenyl)hexane (2.50 g, 10.34 mmol) and then anhydrous THF (30 mL). The reaction mixture was stirred at -78 °C for 10 min, and *n*-BuLi (3.90 mL, 2.4 M in hexane) was added slowly to the mixture through funnel. The mixture was stirred at the same temperature for over 2 hours and then an anhydrous THF solution of (b) (1.18 g, 2.07 mmol) was added by syringe. The reaction mixture was allowed to warm to room temperature and stirred overnight. By the completion of the reaction, saturated aqueous NH<sub>4</sub>Cl (50 mL) was added and extracted with EA for three times. The organic layer was washed with water, and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by a rotating evaporator and the residue was used in next step without further purification.

Step 2: The residue was dissolved in THF (100 mL) and conc. H<sub>2</sub>SO<sub>4</sub> (1.2 mL) was added to the mixture. The reaction mixture was stirred and heated to reflux. After 2 hours, the reaction was completed, and then quenched by water (50 mL) and extracted with EA for three times. The organic layer was washed with water, and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by a rotating evaporator and the residue (yellow solid) was used in next step without further purification.

### *Synthesis of compound DCHOCC10*

A Vilsmeier reagent, which was prepared with POCl<sub>3</sub> (0.50 mL) in DMF (4 mL), was added to a solution of BDT-TT (0.46 g, 0.55 mmol) in 1,2-dichloroethane (40 mL) under the protection of argon. After refluxing at 80 °C overnight, the mixture was poured into ice water (100 mL), neutralized with aqueous AcONa, and then extracted with dichloromethane for three times. The combined organic layer was washed with water and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of solvent, the crude product was purified by silica gel to obtain DCHOCC10 (0.43 g, 88%) as a red solid.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 10.12 (s, 1H), 9.84 (s, 1H), 8.16 (s, 1H), 7.86(s, 1H), 7.39 – 7.32 (m, 4H), 7.11 – 7.02 (m, 4H), 3.32 – 3.21 (m, 2H), 2.75 (dd, *J* = 10.5, 6.0 Hz, 2H), 2.53 (dd, *J* = 9.0, 6.7 Hz, 4H), 1.89 (ddt, *J* = 12.6, 8.0, 4.0 Hz, 2H), 1.58 – 1.50 (m, 6H), 1.41 – 1.12 (m, 20H), 0.99 – 0.93 (m, 4H), 0.92 – 0.70 (m, 12H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 184.46, 182.65, 154.51, 153.41, 143.49, 142.97, 142.82, 142.47, 141.95, 141.90, 141.19, 139.17, 134.87, 134.38, 133.82, 133.47, 132.46, 130.37, 129.67, 128.65, 128.38, 64.07, 35.47, 34.56, 33.47, 31.73, 31.67, 31.58, 31.11, 30.17, 30.04, 29.89, 29.09, 29.09, 28.67, 22.84, 22.70, 22.57, 14.20, 14.19, 14.09.

**MS (MALDI-TOF):** calculated for C<sub>55</sub>H<sub>64</sub>O<sub>2</sub>S<sub>4</sub> [M<sup>+</sup>], 885.36; found: 884.20.

### *Synthesis of CC10*

Under the protection of argon, DCHOCC10 (100 mg, 0.11 mmol) and IC-2Cl (145 mg, 0.55 mmol) was dissolved in a dry CHCl<sub>3</sub> (40 mL) solution, and then pyridine (0.5 mL) was added to the mixture. After stirring at room temperature for 12 h, the mixture was poured into water and then extracted with CHCl<sub>3</sub> for three times, the organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> for 0.5 h. After removal of solvent, the crude product was purified by silica gel, and then recrystallized from CHCl<sub>3</sub> and methanol to give CC10(125 mg, 81%) as a blue solid.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 8.98 (s, 1H), 8.81 (s, 1H), 8.75 (s, 1H), 8.72 (s, 1H), 8.35 (s, 1H), 8.04 (s, 1H), 8.01 (s, 1H), 7.99 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 4H), 7.15 (d, *J* = 8.0 Hz, 4H), 3.28 (s, 2H), 2.84 (d, *J* = 7.7 Hz, 2H), 2.56 (t, *J* = 7.8 Hz, 4H), 1.91 (s, 2H), 1.60 – 1.53 (m, 6H), 1.45 – 1.18 (m, 20H), 0.93 – 0.80 (m, 16H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 185.79, 185.37, 158.03, 157.54, 156.20, 155.30, 147.97, 146.88, 146.40, 144.33, 143.00, 142.89, 142.78, 140.75, 140.38, 140.11, 139.92, 139.67, 139.44, 139.01, 138.68, 138.56, 137.72, 137.63, 136.14, 135.86, 135.54, 135.31, 133.96, 133.39, 131.02, 130.03, 129.06, 128.61, 127.11, 126.84, 125.72, 125.29, 124.88, 121.45, 114.28, 113.97, 71.79, 69.82, 64.49, 35.61, 34.28, 33.63, 31.81, 31.69, 31.22, 29.95, 29.83, 29.21, 27.34, 22.94, 22.79, 22.68, 14.36, 14.27, 14.17.

**HR-FTMS:** calculated for C<sub>79</sub>H<sub>68</sub>Cl<sub>4</sub>N<sub>4</sub>O<sub>2</sub>S<sub>4</sub> [M<sup>+</sup>], 1375.48; found: 1374.30.

## **2. Measurements and Instruments.**

<sup>1</sup>H, <sup>13</sup>C NMR spectra were measured using a Bruker AV400 Spectrometer. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry were performed on a Bruker Autoflex III instrument. Fourier transform mass spectrometry (FTMS) with high resolution matrix assisted laser desorption/ionization (HR-MALDI) were performed on a Varian 7.0T FTMS instrument. Ultraviolet-visible (UV-Vis) absorption spectra were measured on a UV-Vis instrument Agilent Cary 5000 UV-vis-NIR spectrophotometer. UV-vis spectra were obtained with a JASCO V-570 spectrophotometer. Cyclic voltammetry (CV) experiments of targeted NF-SMAs thin films were employed to evaluate the energy levels with a LK98B II Microcomputer based Electrochemical Analyzer in acetonitrile solution at room temperature. The experiments were carried out in a conventional three-electrode configuration with a glassy carbon electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a Pt wire as the counter electrode. Tetrabutylammonium phosphorus hexafluoride (Bu<sub>4</sub>NPF<sub>6</sub>, 0.1 M) in anhydrous acetonitrile solution was used as the supporting electrolyte with the scan rate of 100 mVs<sup>-1</sup> under the protection of argon. The energy levels were calculated by the use of versatile calculation formula

(assumed the energy level of  $\text{FeCp}_2^{+/0}$  to be 4.8 eV below vacuum):  $E_{\text{HOMO}} = -e[E_{\text{OX}} + (4.8 - E_{\text{Fc}})]\text{eV}$ ;  $E_{\text{LUMO}} = -e[E_{\text{red}} + (4.8 - E_{\text{Fc}})]\text{eV}$ . CC10:  $E_{\text{Fc}} = 0.41 \text{ V}$ ,  $E_{\text{OX}} = 1.33 \text{ V}$ ,  $E_{\text{red}} = -0.32 \text{ V}$ ;  $E_{\text{HOMO}} = -e[E_{\text{OX}} + (4.8 - E_{\text{Fc}})]\text{eV} = -e[1.33 + (4.8 - 0.41)]\text{eV} = -5.72 \text{ eV}$ ;  $E_{\text{LUMO}} = -e[E_{\text{red}} + (4.8 - E_{\text{Fc}})]\text{eV} = -e[-0.32 + (4.8 - 0.41)]\text{eV} = -4.07 \text{ eV}$ . CC5:  $E_{\text{Fc}} = 0.37 \text{ V}$ ,  $E_{\text{OX}} = 1.32 \text{ V}$ ,  $E_{\text{red}} = -0.34 \text{ V}$ ;  $E_{\text{HOMO}} = -e[E_{\text{OX}} + (4.8 - E_{\text{Fc}})]\text{eV} = -e[1.32 + (4.8 - 0.37)]\text{eV} = -5.75 \text{ eV}$ ;  $E_{\text{LUMO}} = -e[E_{\text{red}} + (4.8 - E_{\text{Fc}})]\text{eV} = -e[-0.34 + (4.8 - 0.37)]\text{eV} = -4.09 \text{ eV}$ . The geometry structures of CC5 and CC10 were optimized by using DFT calculations (B3LYP/6-31G(d,p)). All calculations were carried out using Gaussian 09. Atomic force microscope (AFM) investigation was performed using Bruker MultiMode 8 in tapping mode. The transmission electron microscopy (TEM) investigation was performed on Philips Technical G2 F20 at 200 kV.

### 3. Device Fabrication and Measurements

The OSCs devices were fabricated using an inverted structure of ITO/ZnO/PFN-Br/active layers/ $\text{MoO}_x$ /Ag. The indium tin oxide (ITO)-coated glass substrates were cleaned by ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 min each and subsequently dried by an argon blow. Subsequently, the ZnO was deposited by spin-coating a ZnO precursor solution on the top of the ITO glass substrates at 3000 rpm for 20 s. After being baked at 200 °C in air for 40 min, the ZnO-coated substrates were transferred into an argon-filled glove box. In order to fine-tune the interfacial properties a thin film of PFN-Br was spin-coated on ZnO. Subsequently, the PM6:CC5/CC10 in chlorobenzene (CB) with DIO additive was spin-coated onto PFN-Br layer.  $\text{MoO}_x$  (~6 nm) and Ag (~70 nm) was successively evaporated onto the active layer through a shadow mask (pressure ca.  $10^{-4}$  Pa). The effective area for the devices is 4 mm<sup>2</sup>.

The current density-voltage ( $J$ - $V$ ) curves of photovoltaic devices were obtained by a Keithley 2400 source-measure unit. The photocurrent was measured under AM 1.5G illumination at 100 mW/cm<sup>2</sup> irradiation using an Enli SS-F5-3A solar simulator, calibrated with a standard Si solar cell (made by Enli Technology Co., Ltd., Taiwan, and calibrated report can be traced to NREL). The EQE spectrum was measured using a QE-R Solar Cell Spectral Response Measurement System (Enli Technology Co., Ltd., Taiwan).

### 4. Space Charge Limited Current (SCLC) Measurement

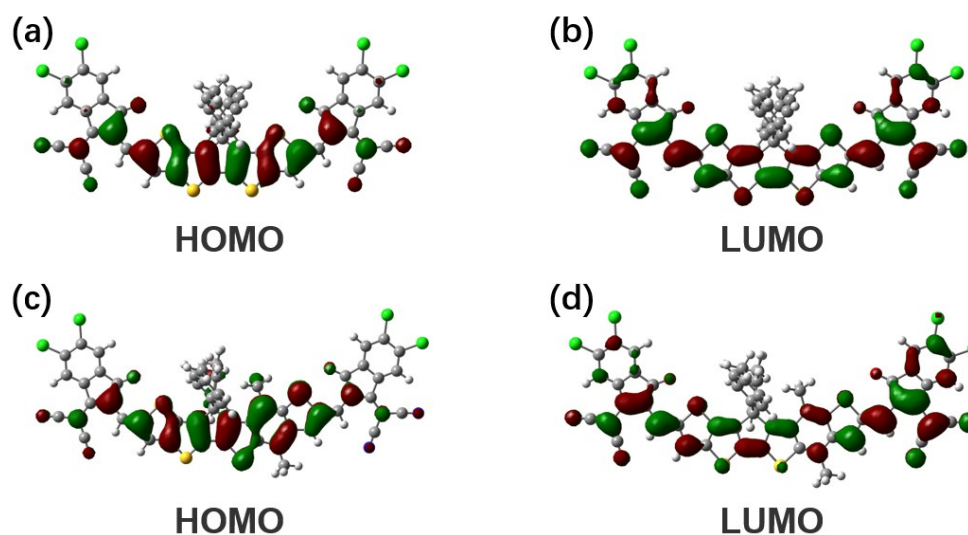
The hole and electron mobility were measured using the space charge limited current (SCLC) method, employing a diode configuration of ITO/PEDOT:PSS/active layer/Au for hole and ITO/ZnO/active layer/Al for electron by taking the dark current

density in the range of 0–6 V and fitting the results to a space charge limited form, where SCLC is described by:

$$J = \frac{9\varepsilon_0\varepsilon_r\mu_0V^2}{8L^3} \exp\left(0.89\beta\sqrt{\frac{V}{L}}\right)$$

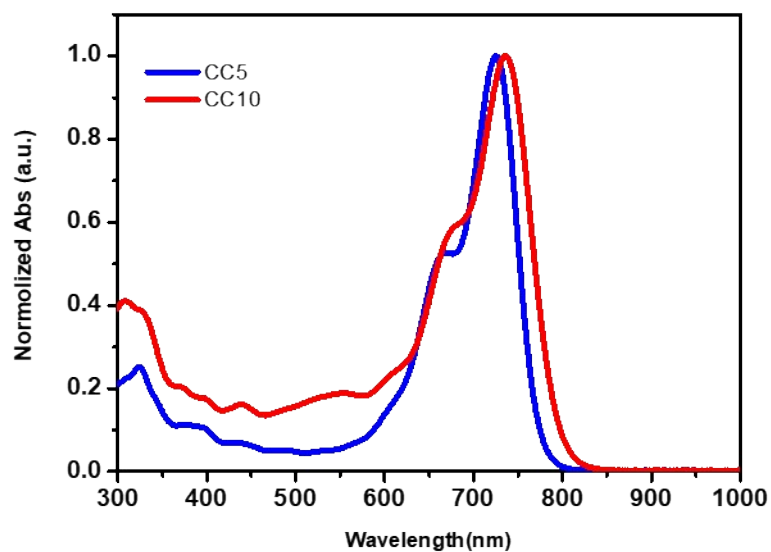
where  $J$  is the current density,  $L$  is the film thickness of the active layer,  $\mu$  is the hole or electron mobility,  $\varepsilon_r$  is the relative dielectric constant of the transport medium,  $\varepsilon_0$  is the permittivity of free space ( $8.85 \times 10^{-12}$  F m<sup>-1</sup>),  $V$  ( $=V_{\text{appl}} - V_{\text{bi}}$ ) is the internal voltage in the device, where  $V_{\text{appl}}$  is the applied voltage to the device and  $V_{\text{bi}}$  is the built-in voltage due to the relative work function difference of the two electrodes.

## 5. Figures and Tables

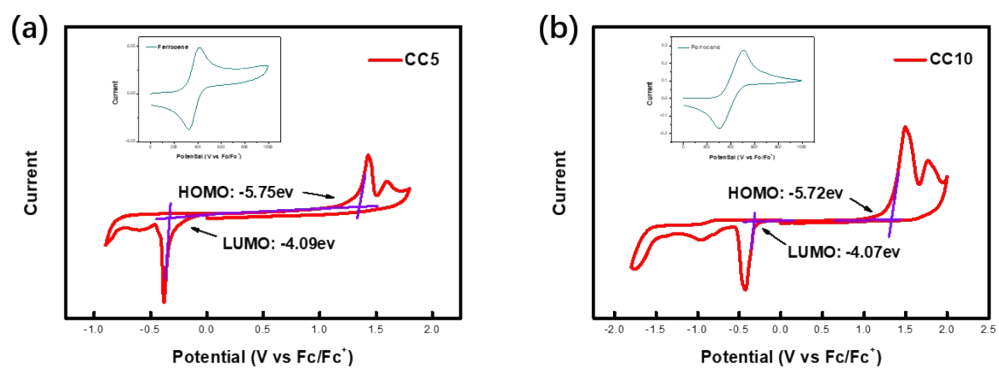


**Figure S2.** Frontier molecular orbitals (HOMO and LUMO) from DFT calculations of CC5(a, b) and CC10 (c, d), respectively.

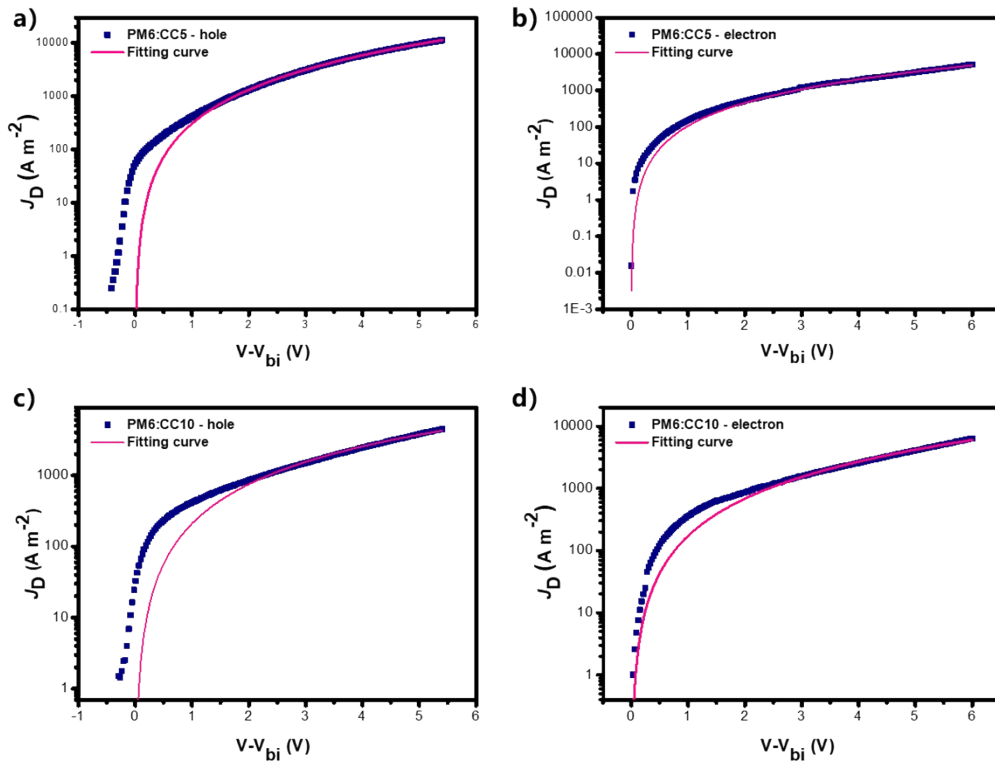




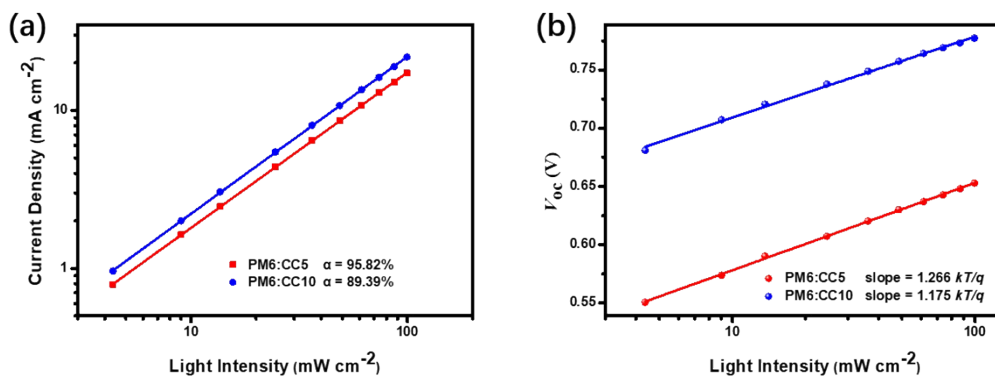
**Figure S3.** Normalized UV-Vis absorption spectra of CC5 and CC10 in chloroform solution.



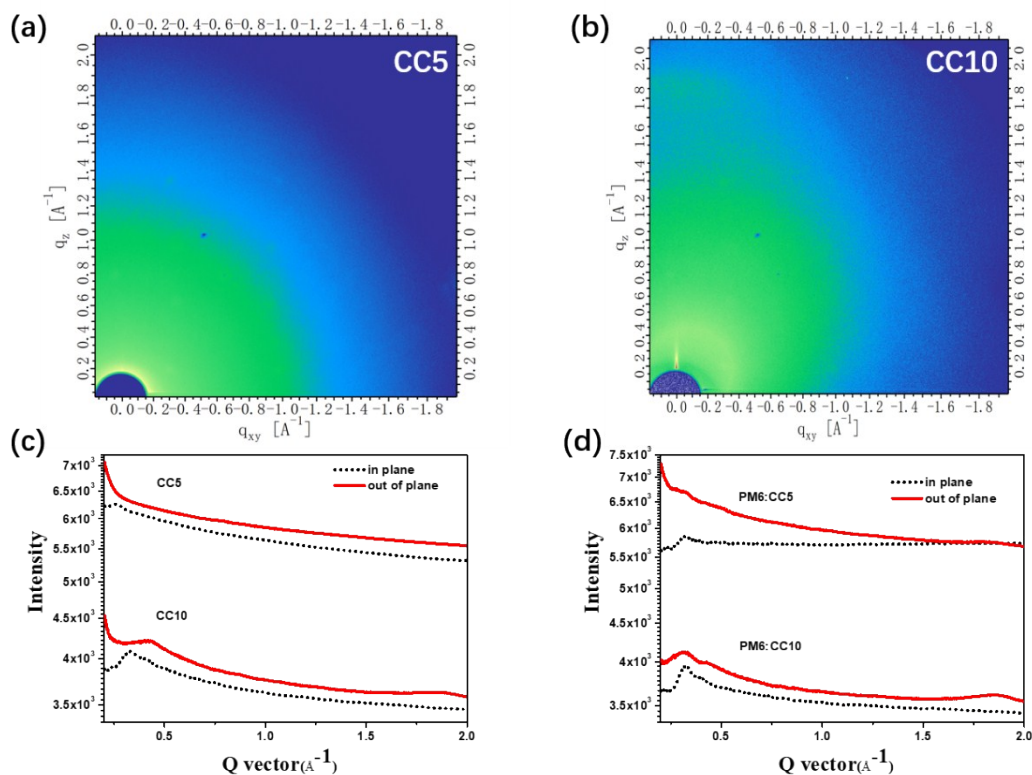
**Figure S4.** Cyclic voltammetry plots of CC5 and CC10 film.



**Figure S5.** (a) Hole-only and (b) electron-only devices based on PM6:CC5 films. (c) Hole only and (d) electron-only devices based on PM6:CC10 films. The solid lines represent the fit using a model of single carrier SCLC with field-independent mobility. The  $J_D$ - $V$  characteristics are corrected for the built-in voltage  $V_{bi}$  that arises from the work function difference between the contacts.



**Figure S6.** (a) Light-intensity dependence of  $J_{sc}$  characteristics, (b) Light-intensity dependence of  $V_{oc}$  characteristic of CC5- and CC10-based devices.



**Figure S7.** 2D GIWAXS patterns for (a) CC5 and (b) CC10 neat films. GIWAXS scattering profiles cut of (c) CC5 and CC10 neat films, (d) PM6:CC5 and PM6:CC10 optimized blend films.

**Table S1.** Photovoltaic performance of the solar cells based on PM6:CC5 with different D:A ratio under illumination of AM 1.5 G,  $100 \text{ mW cm}^{-2}$ .

D:A	$V_{oc}$ (V)	FF	$J_{sc}$ ( $\text{mA cm}^{-2}$ )	PCE (%)
1:0.7	0.700	0.462	-14.68	4.75
1:1	0.692	0.468	-13.44	4.35
1:1.2	0.690	0.462	-13.58	4.33
1:1.5	0.687	0.432	-10.73	3.18

**Table S2.** Photovoltaic performance of the solar cells based on PM6:CC5 (1:0.7, w/w) with different DIO contents under illumination of AM 1.5 G, 100 mW cm<sup>-2</sup>.

V%	$V_{oc}$ (V)	FF	$J_{sc}$ (mA cm <sup>-2</sup> )	PCE (%)
0.3	0.661	0.541	-17.09	6.11
0.5	0.651	0.543	-17.58	6.21
0.7	0.653	0.521	-17.05	5.80

**Table S3.** Photovoltaic performances of the solar cells based on PM6:CC5 with different donor concentration under one sun illumination (AM 1.5 G, 100 mW cm<sup>-2</sup>).

C (mg/ml)	$V_{oc}$ (V)	FF	$J_{sc}$ (mA cm <sup>-2</sup> )	PCE (%)
8	0.651	0.559	-18.98	6.91
9	0.655	0.588	-16.80	6.47
10	0.665	0.488	-15.85	5.14
11	0.662	0.402	-12.77	3.40

**Table S4.** Photovoltaic performance of the solar cells based on PM6:CC10 devices with different D:A ratio under illumination of AM 1.5 G, 100 mW cm<sup>-2</sup>.

D:A	$V_{oc}$ (V)	FF	$J_{sc}$ (mA cm <sup>-2</sup> )	PCE (%)
1:0.5	0.866	0.446	-11.91	4.60
1:0.7	0.851	0.492	-14.76	6.18
1:1	0.831	0.519	-17.40	7.51
1:1.2	0.822	0.530	-17.80	7.75
1:1.5	0.810	0.484	-19.00	7.45

**Table S5.** Photovoltaic performances of the solar cells based on PM6:CC10 with different donor concentration under one sun illumination (AM 1.5 G, 100 mW cm<sup>-2</sup>).

<b>C (mg/ml)</b>	<b><math>V_{oc}</math> (V)</b>	<b>FF</b>	<b><math>J_{sc}</math> (mA cm<sup>-2</sup>)</b>	<b>PCE (%)</b>
9	0.775	0.664	-20.47	10.53
10	0.780	0.619	-21.56	10.41
11	0.772	0.625	-20.95	10.11

**Table S6.** Photovoltaic performance of the solar cells based on PM6:CC10 (1:1.2, w/w) blend films with different DIO contents under illumination of AM 1.5 G, 100 mW cm<sup>-2</sup>.

<b>V%</b>	<b><math>V_{oc}</math> (V)</b>	<b>FF</b>	<b><math>J_{sc}</math> (mA cm<sup>-2</sup>)</b>	<b>PCE (%)</b>
0.9	0.790	0.639	-20.72	10.46
1.1	0.794	0.663	-20.45	10.77
1.3	0.778	0.675	-21.40	11.24
1.5	0.771	0.673	-22.70	11.78
1.7	0.771	0.659	-21.53	10.94
2.0	0.774	0.663	-20.55	10.55

## 6. NMR and Mass Spectra

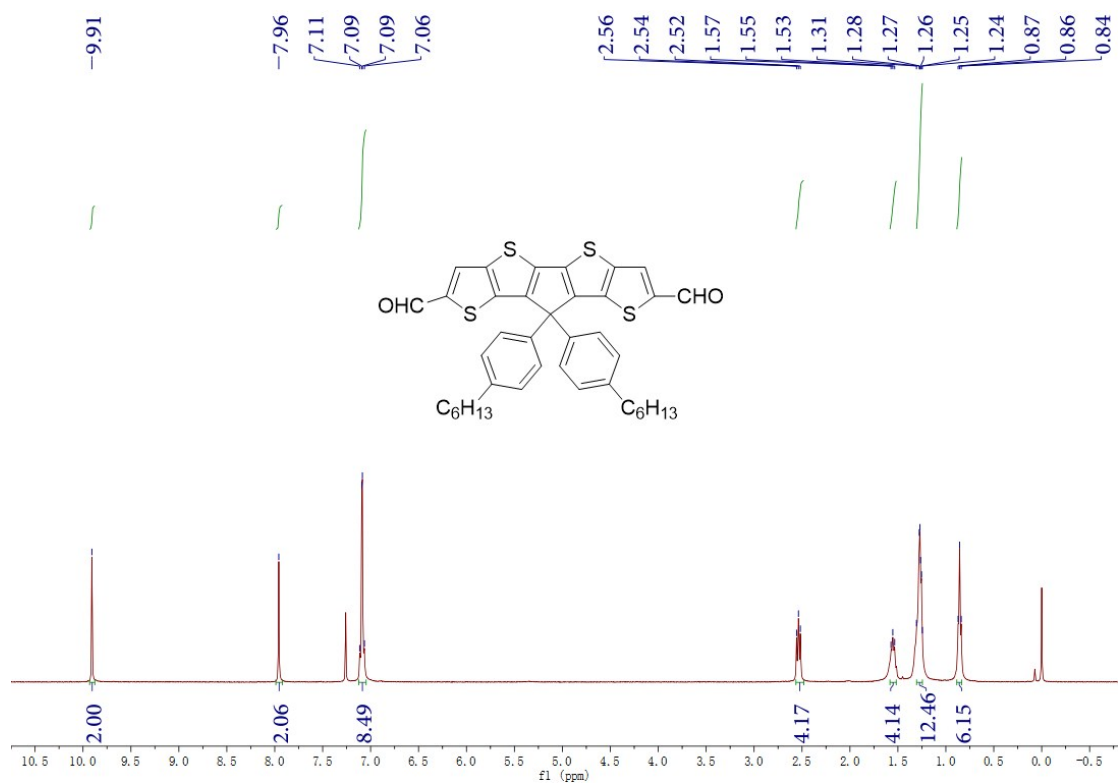


Figure S8. <sup>1</sup>H NMR of DCHOCC5

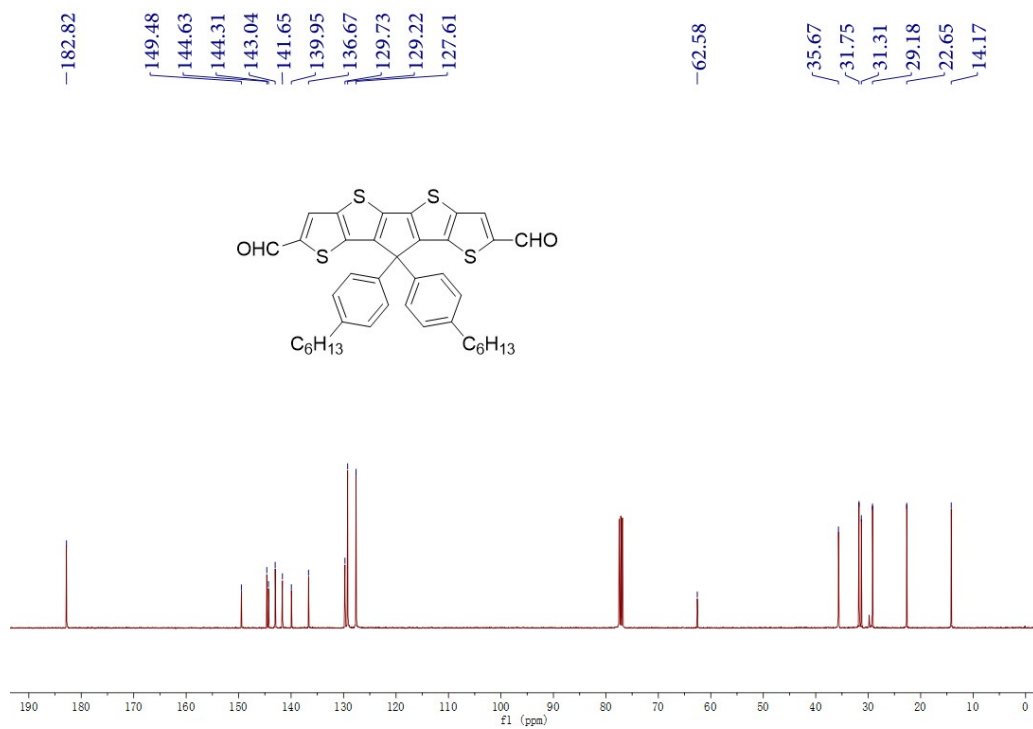


Figure S9. <sup>13</sup>C NMR of DCHOCC5

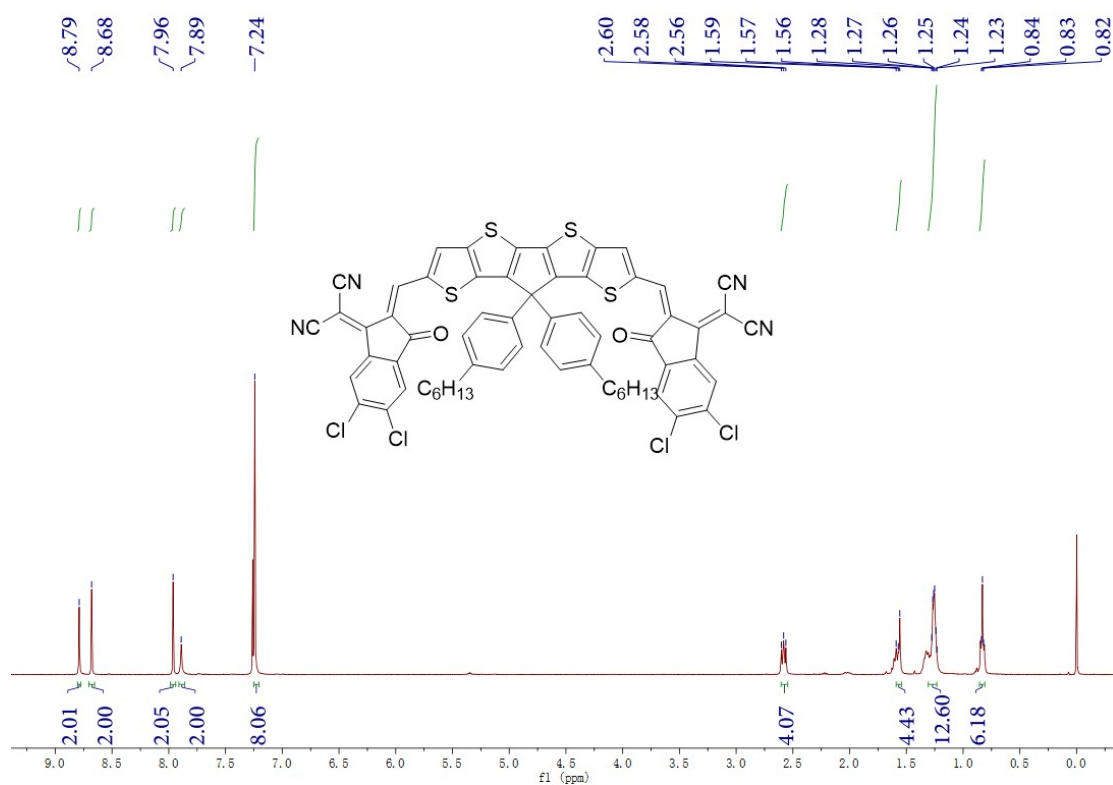


Figure S10. <sup>1</sup>H NMR of CC5

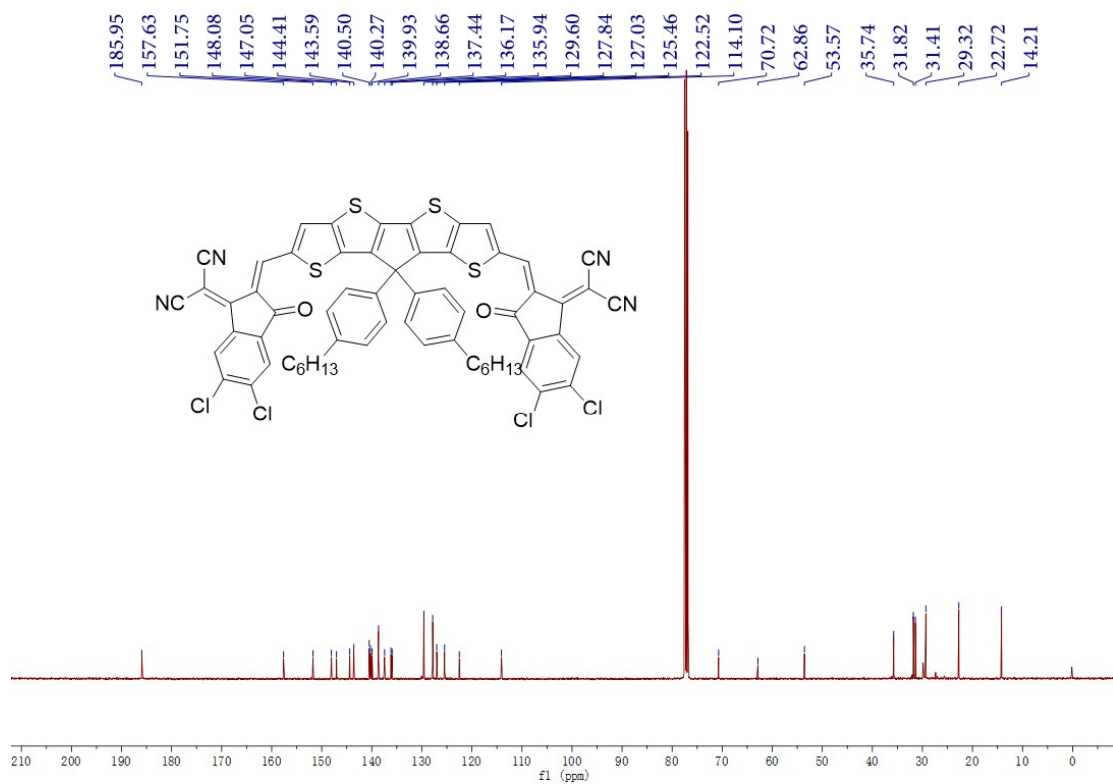


Figure S11. <sup>13</sup>C NMR of CC5

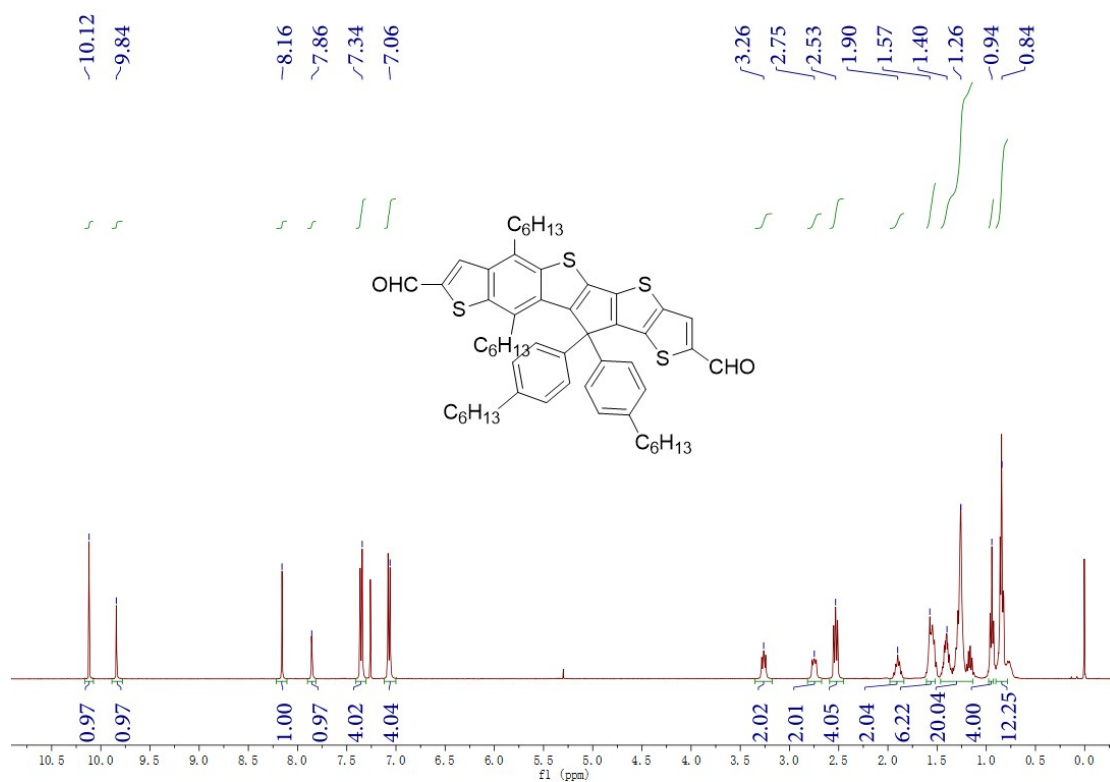


Figure S12. <sup>1</sup>H NMR of DCHOCC10

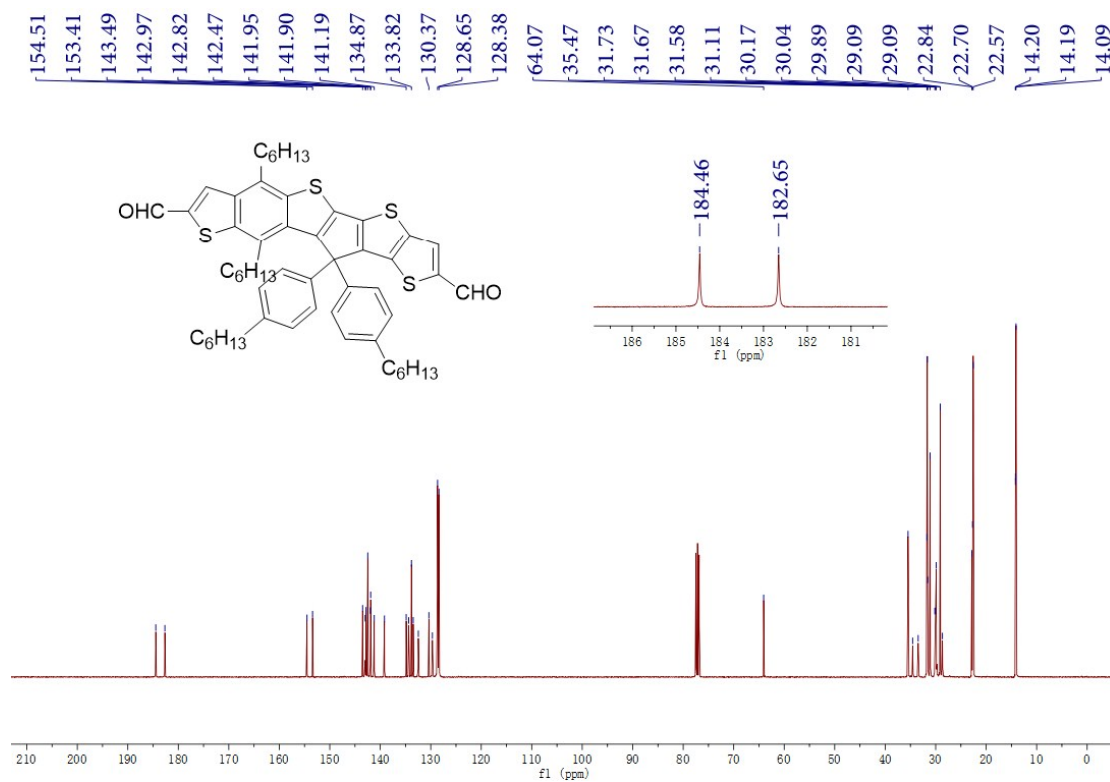


Figure S13. <sup>13</sup>C NMR of DCHOCC10



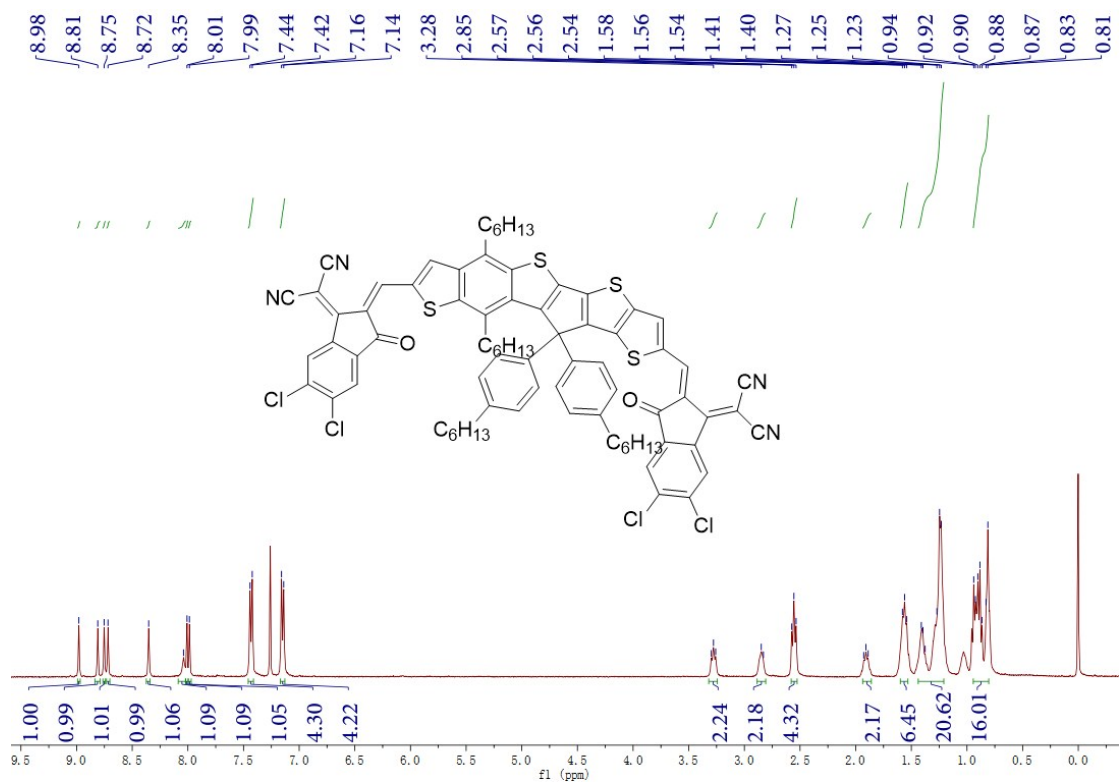


Figure S14.  $^1\text{H}$  NMR of CC10

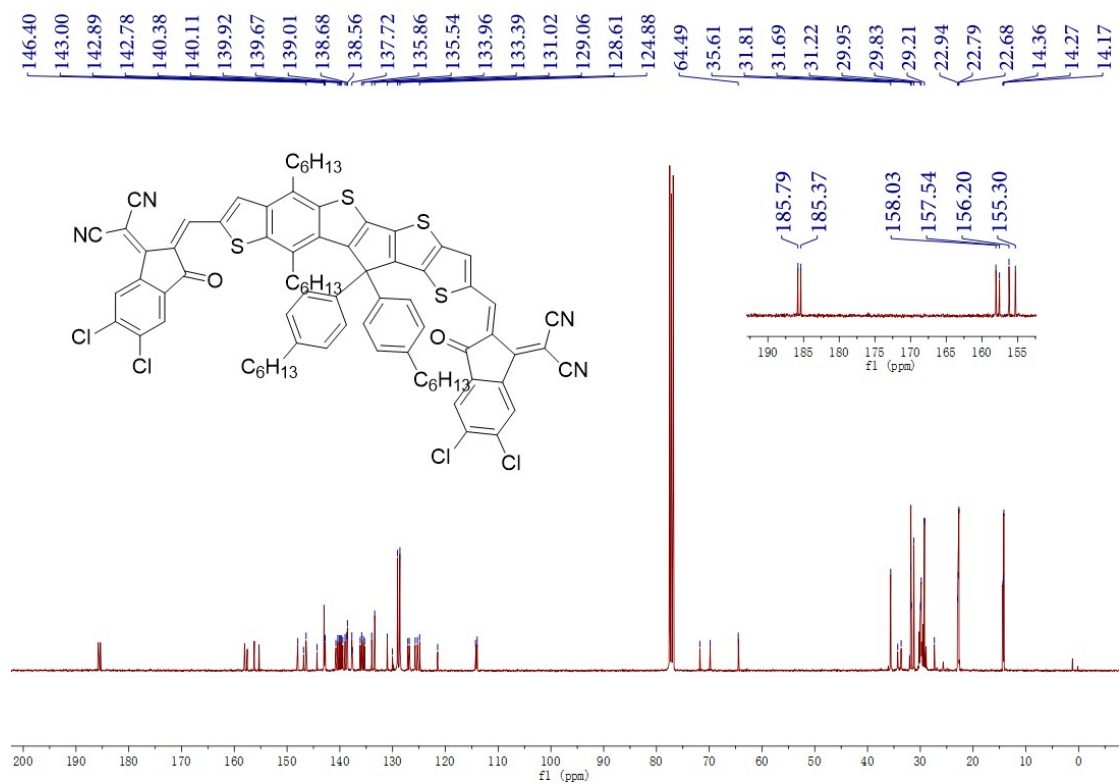
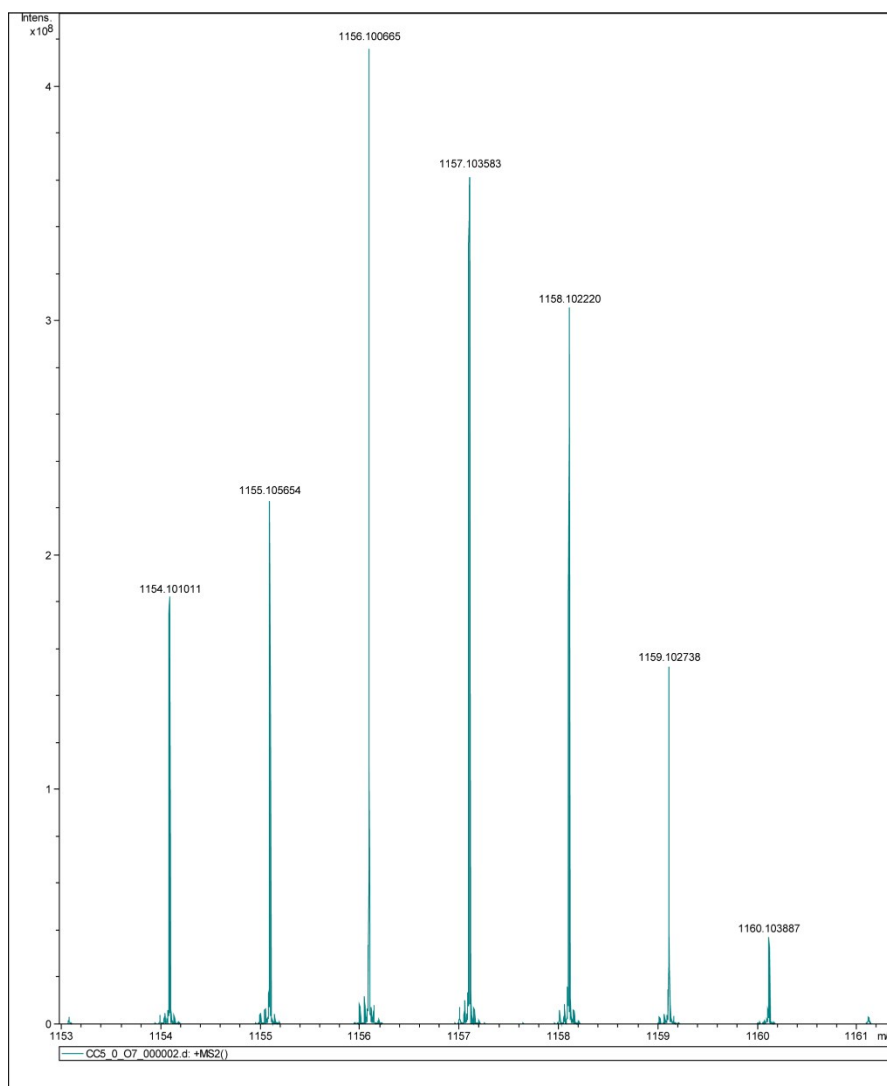
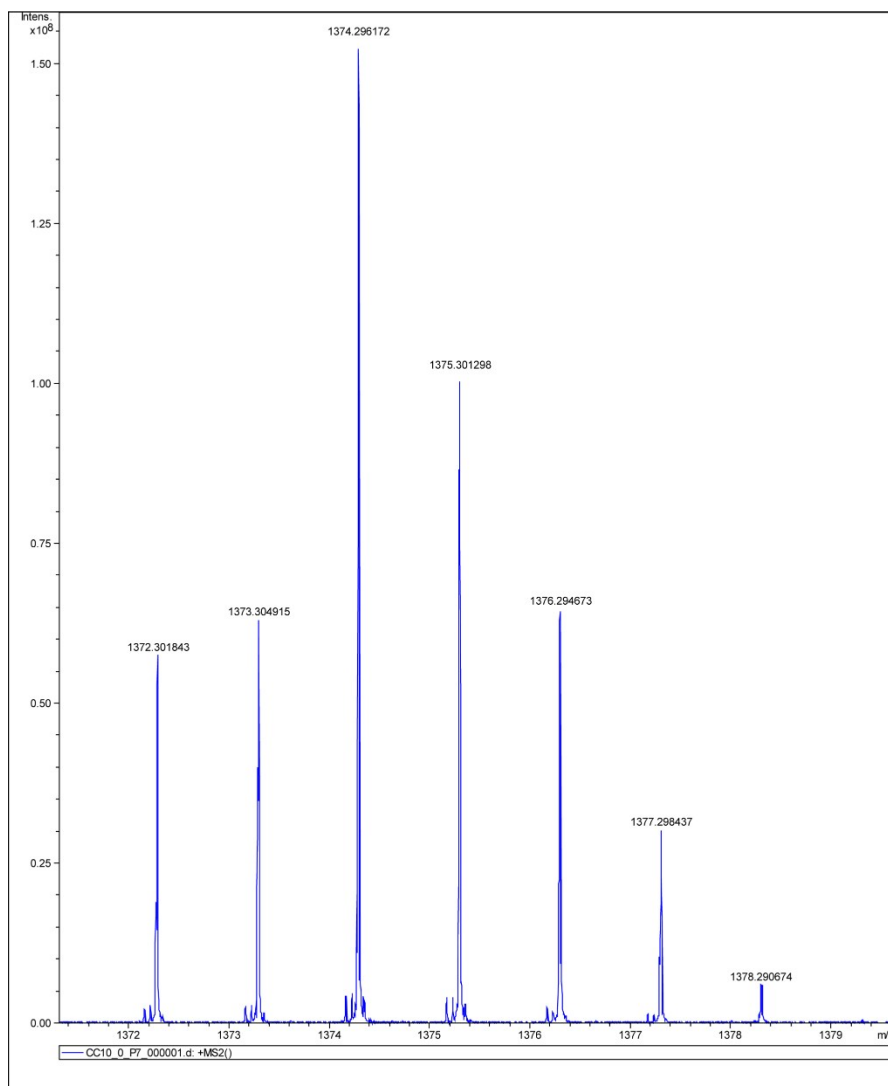


Figure S15.  $^{13}\text{C}$  NMR of CC10



**Figure S16.** HR-FTMS of CC5



**Figure S17.** HR-FTMS of CC10