

## Supplementary information

### **Cis- and Trans-orientation of Benzo[1,2-b:4,5-b']dithiophene-based Isomers in Organic Solar Cells**

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## GENERAL METHODS

**Instruments.**  $^1\text{H}$  NMR spectra were recorded on Bruker AV 400 MHz spectrometer in  $\text{CDCl}_3$  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  $0.1 \text{ mol}\cdot\text{L}^{-1}$  tetrabutylammonium hexafluorophosphate ( $[\text{n-Bu}_4\text{N}]^+ [\text{PF}_6]^-$ ) at a potential scan rate of  $100 \text{ mV s}^{-1}$  with an  $\text{Ag}/\text{Ag}^+$  reference electrode and a platinum wire counter electrode under a argon atmosphere. Solution and film UV-Vis 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  $10 \text{ }^\circ\text{C min}^{-1}$ . Differential scanning calorimetry (DSC) measurements were performed on a Discovery series thermal analyzer at a scanning rate of  $10 \text{ }^\circ\text{C min}^{-1}$  in  $\text{N}_2$ . 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.

**Fabrication and Characterization of OSCs.** The fabrication and measurement methods of OSCs devices are as follows: After a thorough cleaning of the indium-tin oxide (ITO)-coated glass substrate with detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 minutes each and subsequently dried in an oven at 80 °C. 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 PBDB-TF: acceptors (1:1.2) blend solution for spin-coating was 17 mg mL<sup>-1</sup> with chlorobenzene as the processing solvent. The additive, 1, 8-diiiodooctane (DIO) (volume content: 0.5%) 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 3000 rpm for 30 s to get neat film. A 10 nm MoO<sub>3</sub> 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/PBDB-TF: Acceptors/MoO<sub>3</sub>/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<sup>-2</sup> for the illumination of the photovoltaic cells. The light intensity was calibrated by a 2 cm × 2 cm calibrated silicon solar cell with KG-5 visible color filter. A shadow mask 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

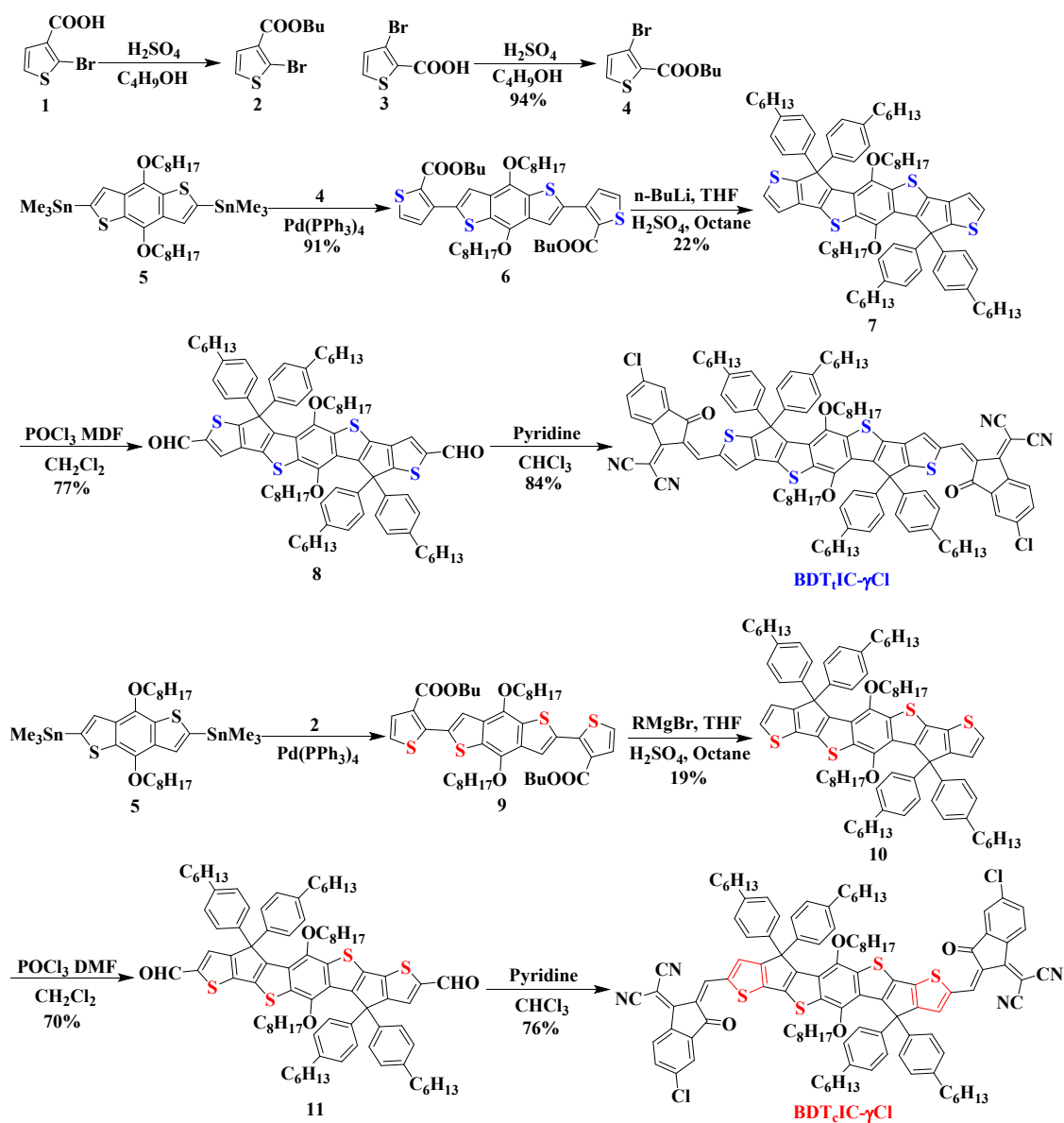
fiith). The relationship of  $J_{sc}$  to the light intensity were measured by steady-state current-voltage measurement, the light intensity was modulated by neutral density filters (NDF) with different values of optical density (OD). The external quantum efficiency (EQE) was measured by a solar cells–photodetector responsibility measurement system (Enlitech.Inc).

**Electron-only and hole-only devices fabrication.** Electron-only devices were fabricated with the device structure of ITO/ZnO/PBDB-TF: Acceptors/PFN-Br/Al, while the hole-only devices were fabricated with the device structure of ITO/PEDOT: PSS/ PBDB-TF: Acceptors /MoO<sub>3</sub>/Ag. The mobilities were determined by fitting the dark current to the model of a single carrier SCLC, <sup>1,2</sup> which is described by the equation:

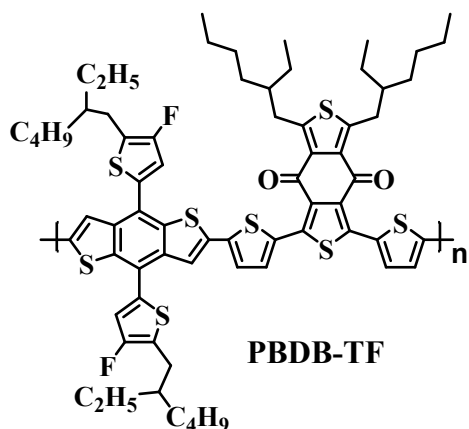
$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu_h \frac{V^2}{d^3}$$

where  $J$  is the current,  $\mu_h$  is the zero-field mobility,  $\epsilon_0$  is the permittivity of free space,  $\epsilon_r$  is the relative permittivity of the material,  $d$  is the thickness of the active layer, and  $V$  is the effective voltage.

## EXPERIMENTAL SECTION



Scheme S1. The synthetic routes of  $\text{BDT}_{11}\text{C-}\gamma\text{Cl}$  and  $\text{BDT}_6\text{C-}\gamma\text{Cl}$ .



**Scheme S2.** The structure of polymer donor PBDB-TF.

**Materials:** Compound **2**, **5**, **9** and IC- $\gamma$ Cl were synthesized according previously reported approaches<sup>3-5</sup>. All the other chemicals were purchased as reagent grade from J&K, Energy, Macklin, and Sigma-Aldrich, and used without further purification. All solvents for reactions were freshly distilled immediately prior to use.

**Compound 4:** 10 g of compound **3** was dissolved in 100 ml n-butanol, then 1 ml H<sub>2</sub>SO<sub>4</sub> was added, the mixture was reacted 12 hours under Argon at 110 °C. The reaction mixture was then cooled to room temperature and then extracted with dichloromethane. The organic layer was washed with brine and dried over MgSO<sub>4</sub>. The crude product was purified by flash column chromatography with dichloromethane as eluent to get the product (12 g, 94.4%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  : 7.43-7.45 (d, 1H), 7.06-7.08 (d, 1H), 1.70-1.74 (m, 2H), 1.41-1.49 (m, 2H), 0.94-0.98 (t, 3H).

**Compound 6:** 1.23 g of compound **4**, 1.2 g compound **5** and 100 mg Pd(PPh<sub>3</sub>)<sub>4</sub> were dissolved in 100 ml Tol and 20 ml DMF, the mixture was reacted 12 hours under

Argon at 130 °C. The reaction mixture was then cooled to room temperature and then extracted with ethyl acetate. The organic layer was washed with brine and dried over MgSO<sub>4</sub>. The crude product was purified by flash column chromatography with dichloromethane: petroleum ether as eluent to get the product (1.1 g, 90.9%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ : 7.95 (s, 1H), 7.52-7.53 (d, 2H), 7.34-7.36 (d, 2H), 4.27-4.32 (m, 8H), 1.86-1.93 (m, 4H), 1.64-1.71 (m, 4H), 1.53-1.61 (m, 4H), 1.28-1.40 (m, 20H), 0.86-0.90 (m, 12H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ: 161.88, 144.37, 139.52, 135.87, 132.12, 131.65, 130.20, 128.59, 122.21, 77.27, 74.12, 65.18, 31.89, 30.67, 30.60, 29.48, 29.34, 26.11, 22.70, 19.23, 14.13, 13.69. MALDI-TOF-MS calcd for C<sub>44</sub>H<sub>58</sub>O<sub>6</sub>S<sub>4</sub> (M<sup>+</sup>): 810.3116, found: 810.2206.

**Compound 7:** 1.5g 1-(4-Bromophenyl)hexane was dissolved in 20 ml THF, 4 ml n-BuLi was added slowly at -78 °C, 500 mg compound 6 was added in one portion after 1h, the reaction mixture was then cooled to room temperature and reacted for 10 h, and then extracted with ethyl acetate. The organic layer was washed with brine and dried over MgSO<sub>4</sub>. The crude product was dissolved in 40 ml octane, and 0.1 ml H<sub>2</sub>SO<sub>4</sub> was added, the mixture was reacted 3 hours at 60 °C. The reaction mixture was then cooled to room temperature and then extracted with ethyl acetate. The organic layer was washed with brine and dried over MgSO<sub>4</sub>. The crude product was purified by flash column chromatography with petroleum ether as eluent to get the product (350 mg, 22.2%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ : 7.24-7.31 (m, 10H), 7.02-7.05 (m, 10H), 3.49 (t, 4H), 2.51-2.57 (m, 8H), 1.54-1.58 (m, 8H), 1.17-1.34 (m, 48H), 0.84-0.94 (m, 18H).

**Compound 8:** 1 ml POCl<sub>3</sub> was added to 5 ml DMF at 0 °C and reacted for 1 h, then the mixture was dropped into 150 mg compound 7 dissolved in 20 ml CH<sub>2</sub>Cl<sub>2</sub> at 0 °C. The reaction mixture was then reacted for 10 h at 40 °C. The reaction mixture was then cooled to room temperature and then extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with brine and dried over MgSO<sub>4</sub>. The crude product was purified by flash column chromatography with dichloromethane: petroleum ether as eluent to get the product (120 mg, 76.6%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ : 9.85 (s, 2H), 7.67 (s, 2H), 7.26-7.28 (m, 8H), 7.05-7.07 (m, 8H), 3.46-3.49 (m, 4H), 2.53-2.56 (t, 8H), 1.53-1.58 (m, 8H), 1.18-1.44 (m, 48H), 0.85-0.94 (m, 18H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ: 182.77, 170.91, 150.51, 147.67, 144.70, 142.07, 139.42, 137.34, 136.90, 133.85, 130.90, 128.66, 128.19, 127.33, 125.70, 77.25, 72.69, 65.23, 35.57, 31.94, 31.74, 31.31, 29.87, 29.61, 29.43, 29.14, 25.64, 22.77, 22.63, 14.19, 14.12. MALDI-TOF-MS calcd for C<sub>86</sub>H<sub>106</sub>O<sub>4</sub>S<sub>4</sub> (M<sup>+</sup>): 1330.6974, found: 1331.6696.

**Compound BDT<sub>4</sub>IC-γCl:** A mixture of compound 8 (100 mg), IC-γCl (70 mg) in chloroform/pyridine (20 ml/0.5 ml) was reacted 10 hours under Argon at 60 °C. The reaction mixture was then cooled to room temperature and then extracted with chloroform. The organic layer was washed with brine and dried over MgSO<sub>4</sub>. The crude product was purified by flash column chromatography with chloroform as eluent and further purified with cycling preparative HPLC to get the product (110 mg, 83.6%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ : 8.90 (s, 2H), 8.60-8.62 (d, 2H), 7.89 (s, 2H), 7.80-7.81 (d, 2H), 7.68-7.71 (dd, 2H), 7.31-7.33 (m, 8H), 7.08-7.10 (m, 8H), 3.49 (m, 4H), 2.53-2.57 (t, 8H), 1.55-1.59 (m, 8H), 1.18-1.36 (m, 48H), 0.85-0.95 (m, 18H).



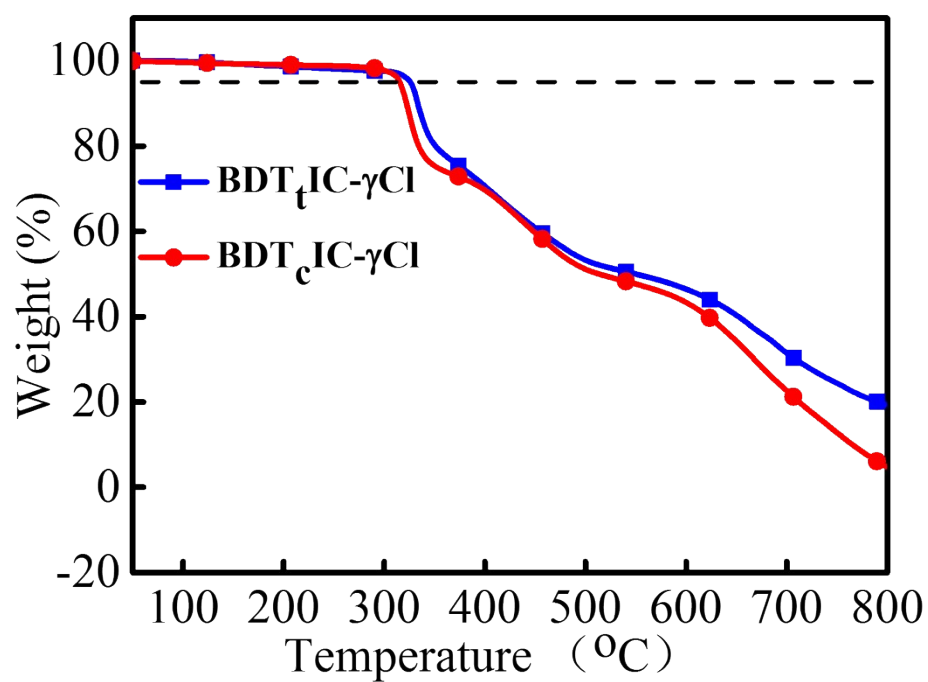
$^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  : 186.64, 180.93, 159.20, 159.15, 151.05, 142.32, 141.95, 141.38, 140.97, 138.78, 138.30, 137.89, 137.04, 136.62, 135.02, 132.65, 128.83, 128.38, 127.44, 126.54, 123.81, 122.10, 114.34, 114.24, 77.29, 72.73, 70.05, 66.12, 35.62, 31.97, 31.76, 31.36, 29.99, 29.75, 29.66, 29.47, 29.16, 25.68, 22.81, 22.65, 14.24, 14.15, 1.07. MALDI-TOF-MS calcd for  $\text{C}_{110}\text{H}_{112}\text{Cl}_2\text{N}_4\text{O}_4\text{S}_4$  (M<sup>+</sup>): 1750.6943, found: 1752.8214.

**Compound 10:** 2.5g 1-(4-Bromophenyl)hexane was dissolved in 4 ml THF and then dropped into 400 mg Mg in 100 ml THF with 2 grains of iodine, the mixture was reacted 4 hours under Argon at 60 °C. The newly prepared Grignard reagent was added to a THF solution of 500 mg compound 9 slowly and reacted 10 hours under Argon at 80 °C, then extracted with ethyl acetate. The organic layer was washed with brine and dried over  $\text{MgSO}_4$ . The crude product was dissolved in 40 ml octane, and 0.1 ml  $\text{H}_2\text{SO}_4$  was added, the mixture was reacted 3 hours at 60 °C. The reaction mixture was then cooled to room temperature and then extracted with ethyl acetate. The organic layer was washed with brine and dried over  $\text{MgSO}_4$ . The crude product was purified by flash column chromatography with petroleum ether as eluent to get the product (300 mg, 19.0%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  : 7.29-7.31 (m, 8H), 7.14-7.17 (d, 2H), 7.01-7.03 (m, 8H), 6.88-6.89 (d, 2H), 3.47-3.51 (t, 4H), 2.52-2.56 (m, 8H), 1.55-1.58 (m, 8H), 1.26-1.34 (m, 48H), 0.86-0.95 (m, 18H).

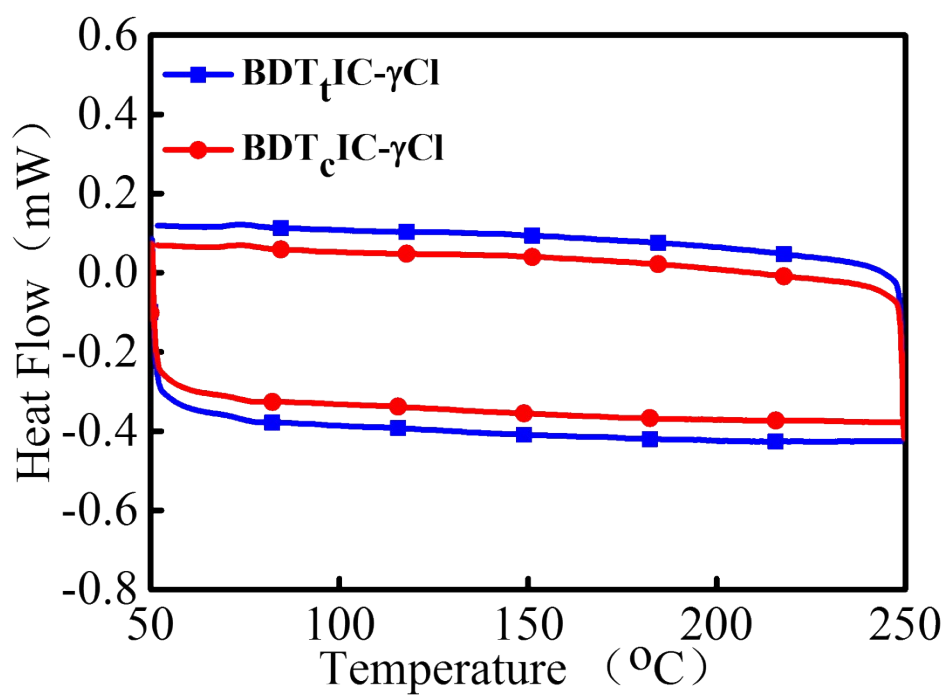
**Compound 11:** 1 ml  $\text{POCl}_3$  was added to 5 ml DMF at 0 °C and reacted for 1 h, then the mixture was dropped into 300 mg compound 7 dissolved in 20 ml  $\text{CH}_2\text{Cl}_2$  at 0 °C. The reaction mixture was then reacted for 10 h at 40 °C. The reaction mixture was

then cooled to room temperature and then extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with brine and dried over  $\text{MgSO}_4$ . The crude product was purified by flash column chromatography with dichloromethane: petroleum ether as eluent to get the product (220 mg, 70.2%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 9.74 (s, 2H), 7.50 (s, 2H), 7.27-7.29 (m, 8H), 7.04-7.06 (m, 8H), 3.51-3.54 (m, 4H), 2.52-2.56 (t, 8H), 1.56-1.60 (m, 8H), 1.19-1.35 (m, 48H), 0.85-0.94 (m, 18H).

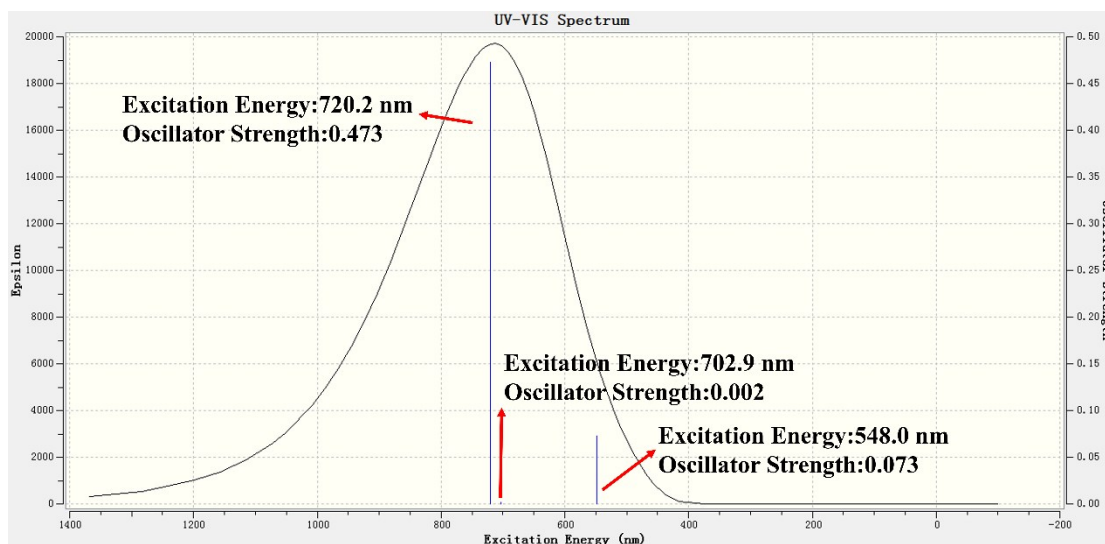
**Compound *BDT<sub>c</sub>IC- $\gamma$ Cl***: A mixture of compound 8 (100 mg), IC- $\gamma$ Cl (70 mg) in chloroform/pyridine (20 ml/0.5 ml) was reacted 10 hours under Argon at 60 °C. The reaction mixture was then cooled to room temperature and then extracted with chloroform. The organic layer was washed with brine and dried over  $\text{MgSO}_4$ . The crude product was purified by flash column chromatography with chloroform as eluent and further purified with cycling preparative HPLC to get the product (100 mg, 76.0%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.81 (s, 2H), 8.58-8.60 (d, 2H), 7.81 (s, 2H), 7.64-7.68 (dd, 2H), 7.52 (s, 2H), 7.26-7.29 (m, 8H), 7.07-7.09 (m, 8H), 3.51-3.55 (m, 4H), 2.54-2.58 (t, 8H), 1.58-1.62 (m, 8H), 1.21-1.39 (m, 48H), 0.85-0.97 (m, 18H).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 187.04, 164.69, 159.11, 159.08, 157.78, 154.87, 146.02, 142.26, 141.01, 140.79, 138.85, 138.77, 138.50, 138.46, 138.26, 137.91, 135.98, 135.75, 134.69, 128.58, 128.34, 126.37, 123.69, 120.77, 114.71, 114.65, 77.27, 73.30, 68.47, 63.92, 35.58, 31.94, 31.74, 31.36, 29.89, 29.62, 29.45, 29.17, 25.68, 22.80, 22.64, 14.23, 14.13. MALDI-TOF-MS calcd for  $\text{C}_{110}\text{H}_{112}\text{Cl}_2\text{N}_4\text{O}_4\text{S}_4$  (M<sup>+</sup>): 1750.6943, found: 1752.9036.



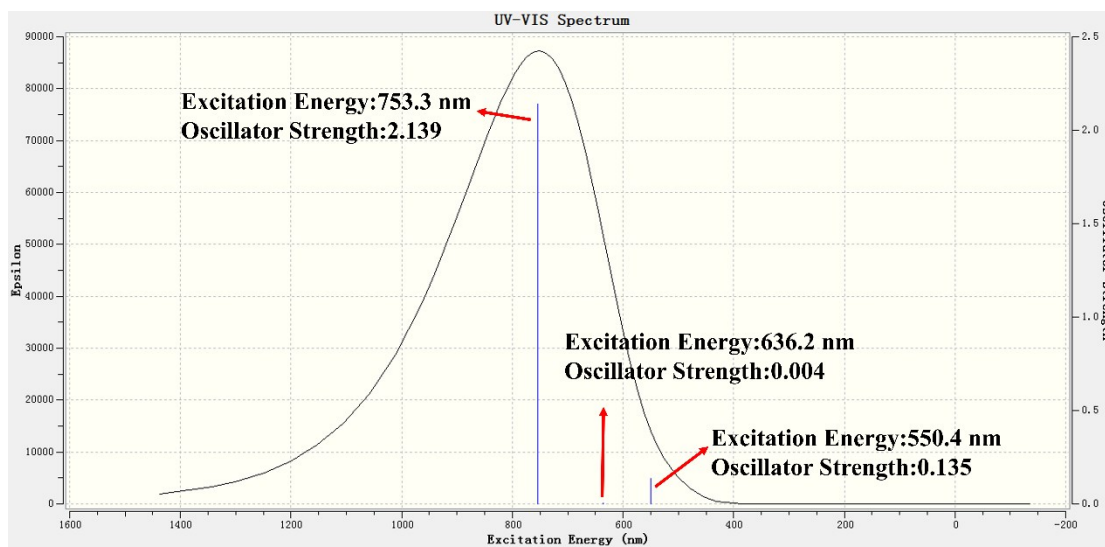
**Figure S1.** Thermogravimetric analysis (TGA) results of  $\text{BDT}_t\text{IC-}\gamma\text{Cl}$  and  $\text{BDT}_c\text{IC-}\gamma\text{Cl}$  with a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  under nitrogen purge.



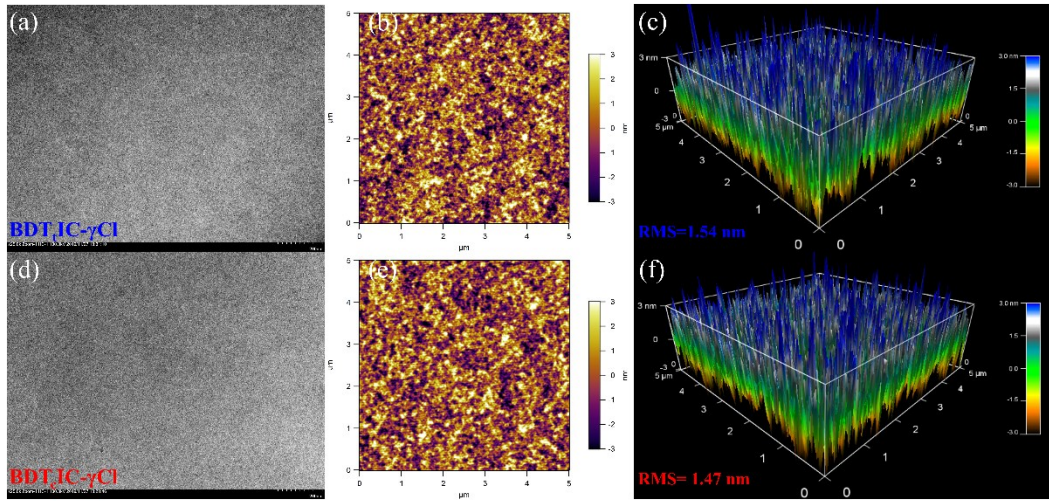
**Figure S2.** Differential scanning calorimetry (DSC) results of two molecules with heating and cooling rates of  $10\text{ }^{\circ}\text{C min}^{-1}$  under nitrogen purge.



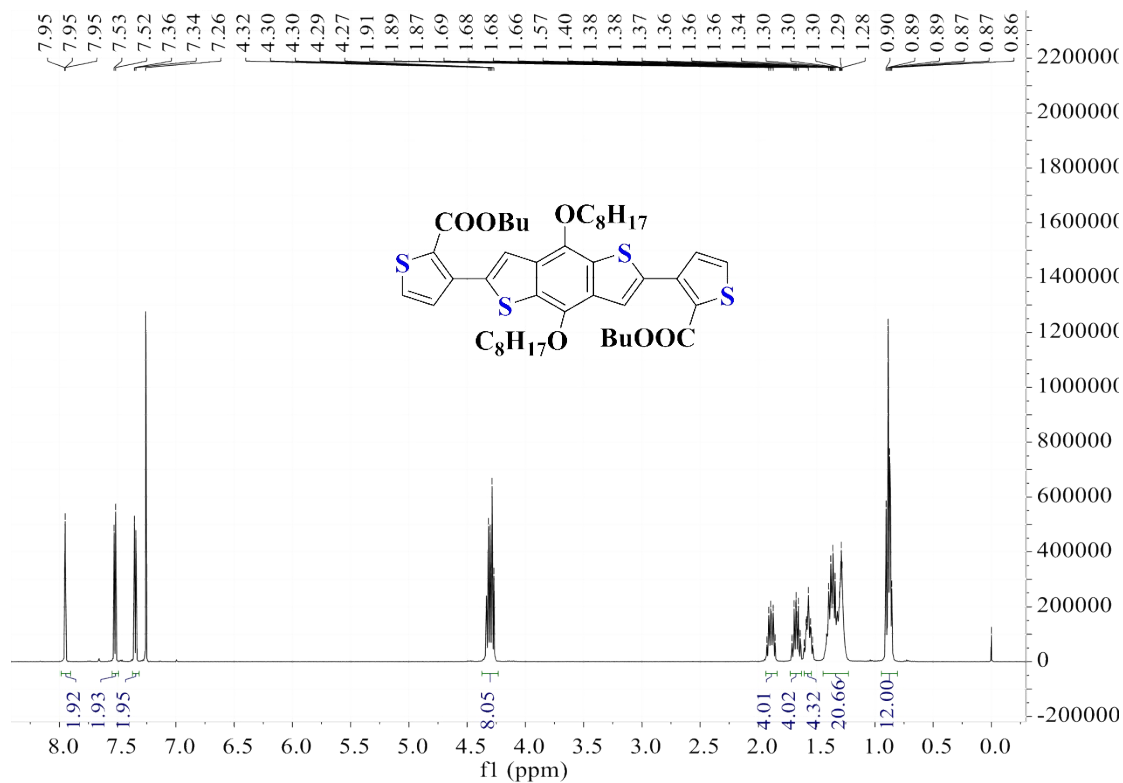
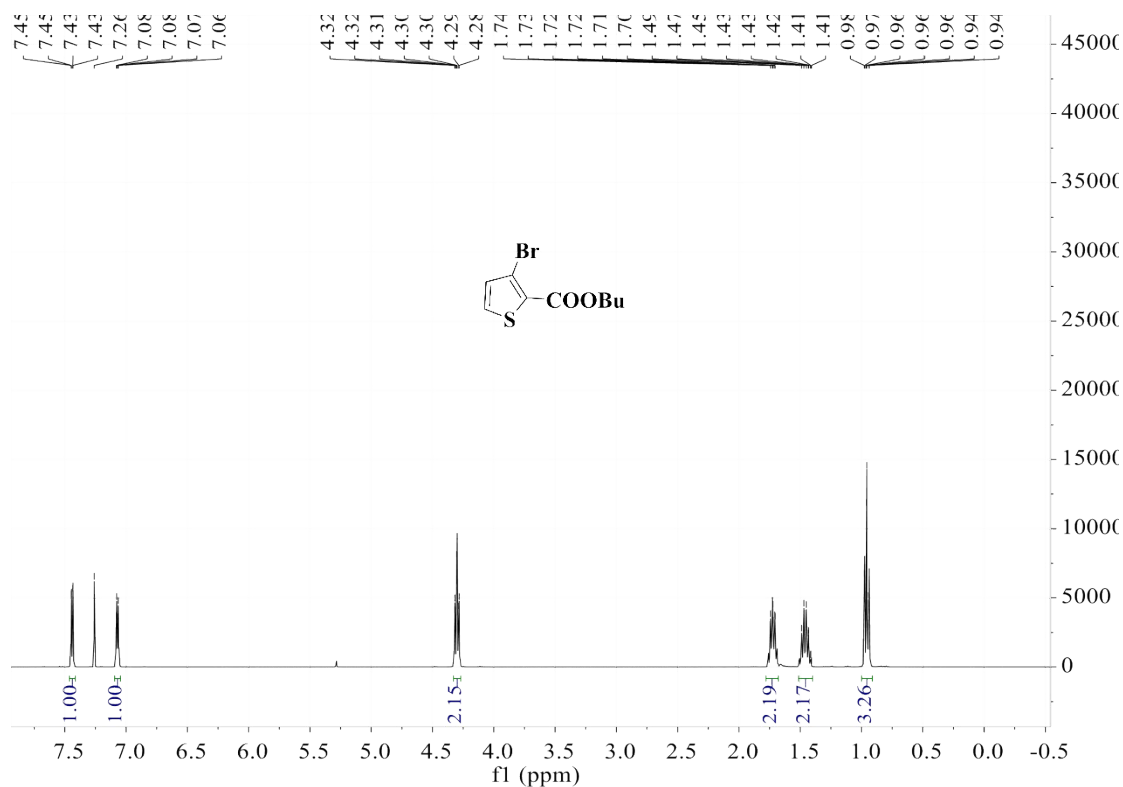
**Figure S3.** The oscillator strengths and simulated excitation energies of  $\text{BDT}_t\text{IC-}\gamma\text{Cl}$  by TD-DFT (B3LYP/6-31G\*) calculation.



**Figure S4.** The oscillator strengths and simulated excitation energies of  $\text{BDT}_c\text{IC-}\gamma\text{Cl}$  by TD-DFT (B3LYP/6-31G\*) calculation.



**Figure S5.** TEM images of (a) **BDT<sub>t</sub>IC-γCl** (d) **BDT<sub>c</sub>IC-γCl**; AFM images of (b) **BDT<sub>t</sub>IC-γCl** (e) **BDT<sub>c</sub>IC-γCl**; 3D AFM images of (c) **BDT<sub>t</sub>IC-γCl** (f) **BDT<sub>c</sub>IC-γCl**.



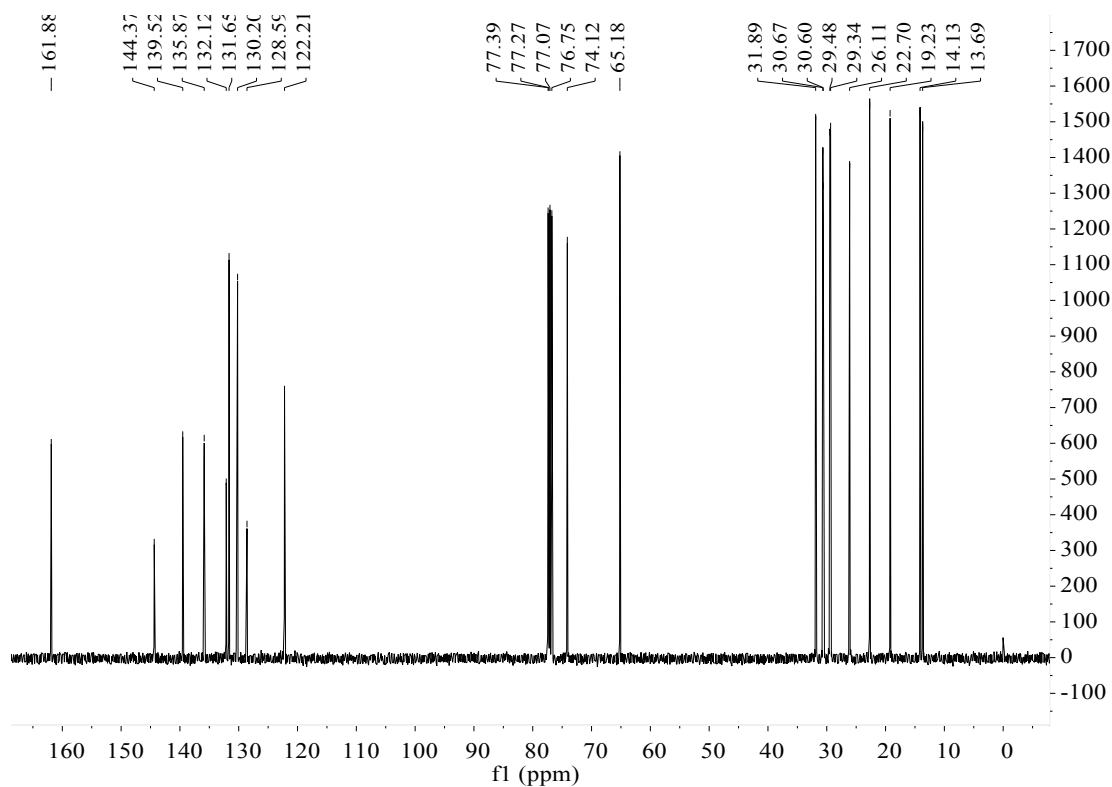


Figure S8.  $^{13}\text{C}$  NMR of compound 6 in  $\text{CDCl}_3$ .

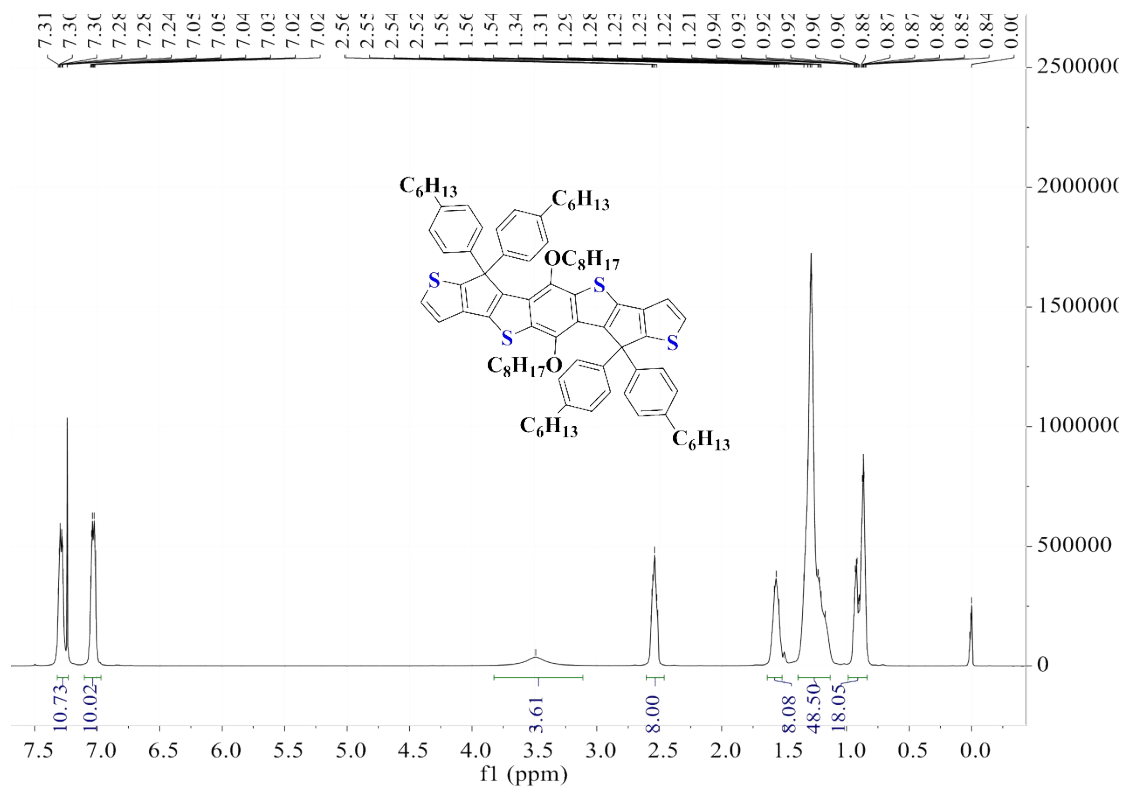


Figure S9.  $^1\text{H}$  NMR of compound 7 in  $\text{CDCl}_3$ .



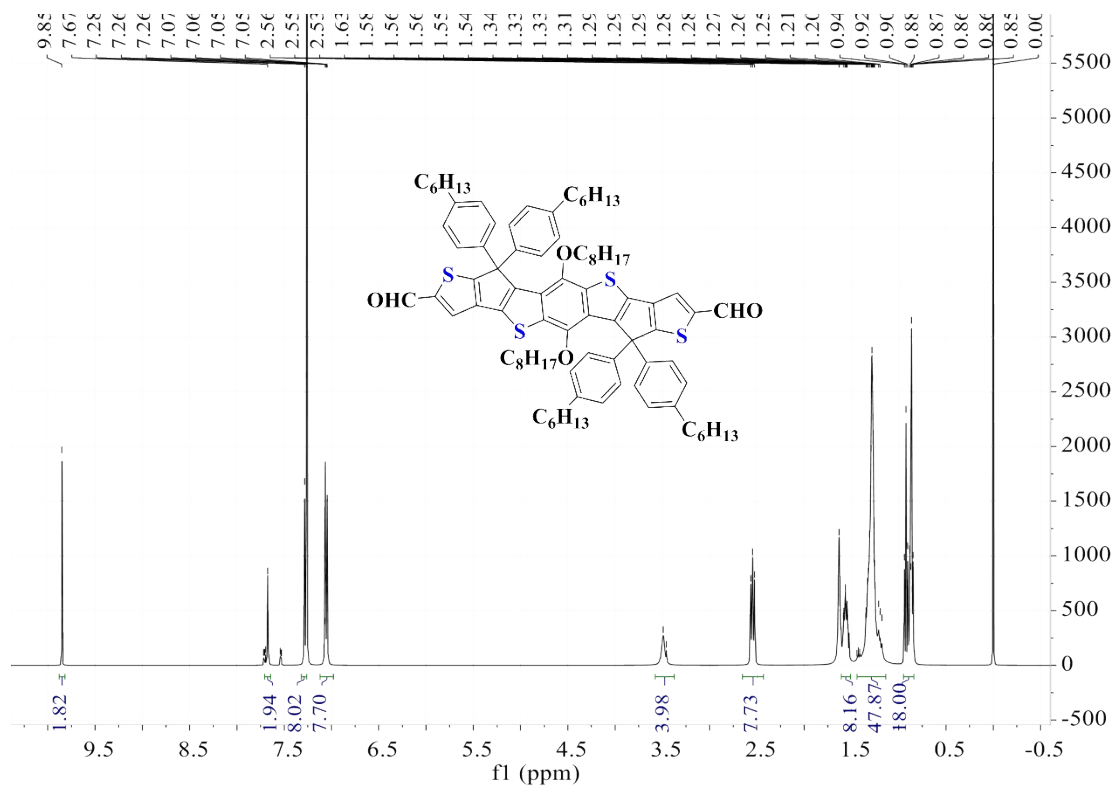


Figure S10. <sup>1</sup>H NMR of compound 8 in CDCl<sub>3</sub>.

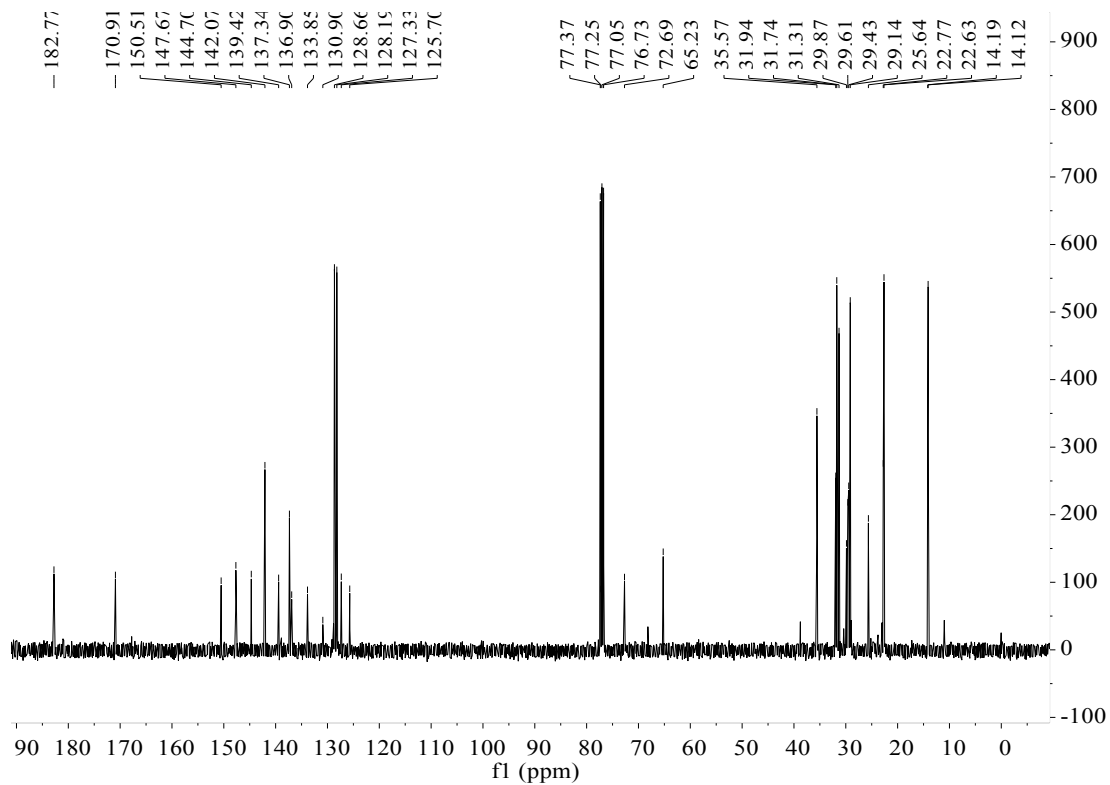


Figure S11. <sup>13</sup>C NMR of compound 8 in CDCl<sub>3</sub>.

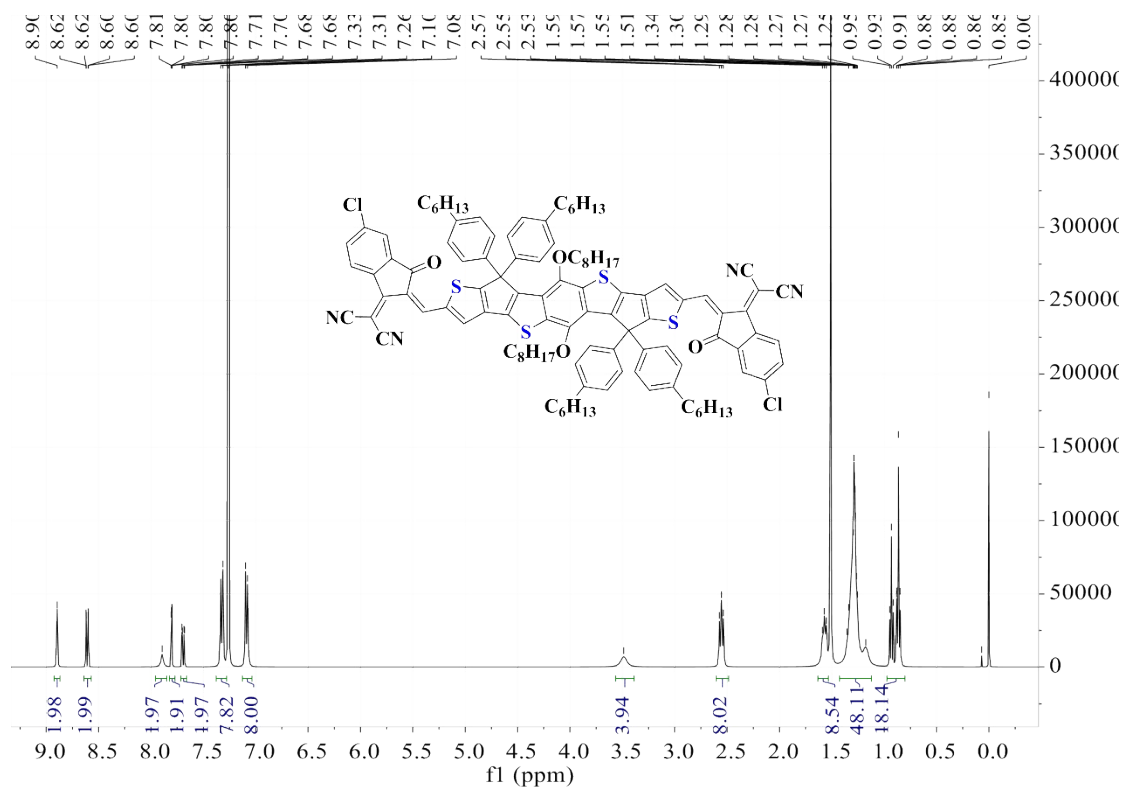


Figure S12.  $^1\text{H}$  NMR of  $\text{BDT}_4\text{IC-}\gamma\text{Cl}$  in  $\text{CDCl}_3$ .

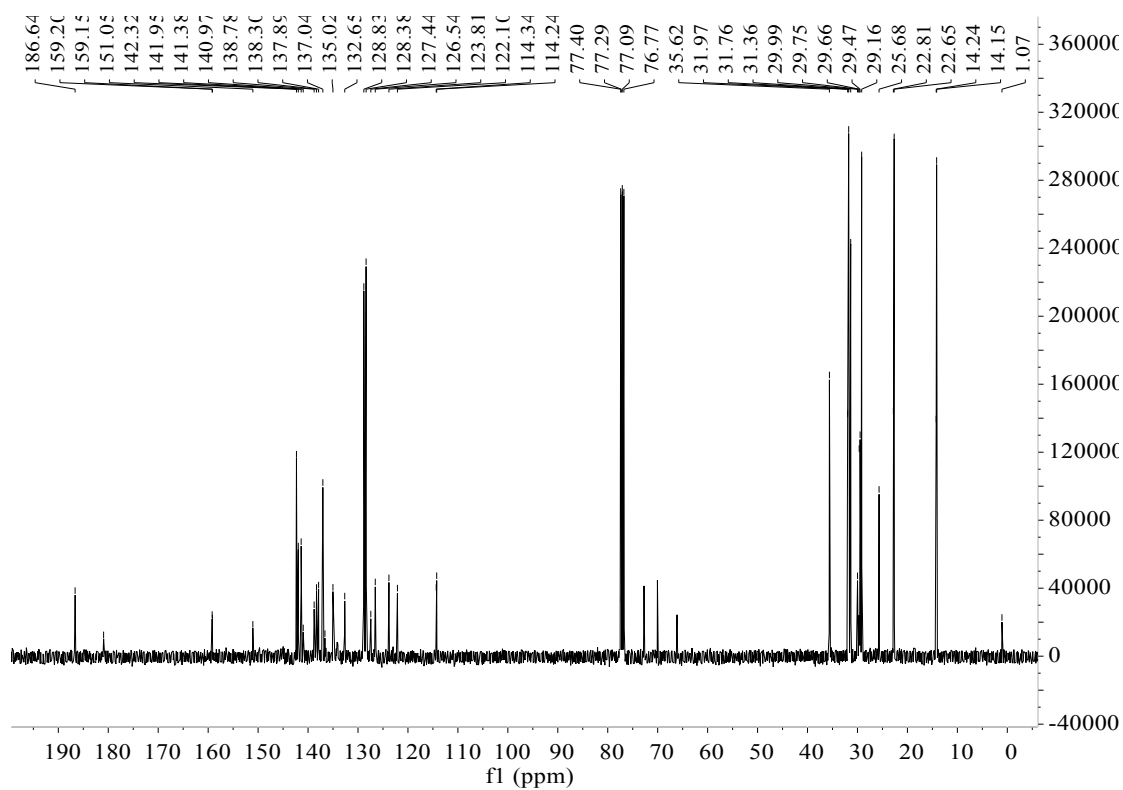


Figure S13.  $^{13}\text{C}$  NMR of  $\text{BDT}_4\text{IC-}\gamma\text{Cl}$  in  $\text{CDCl}_3$ .

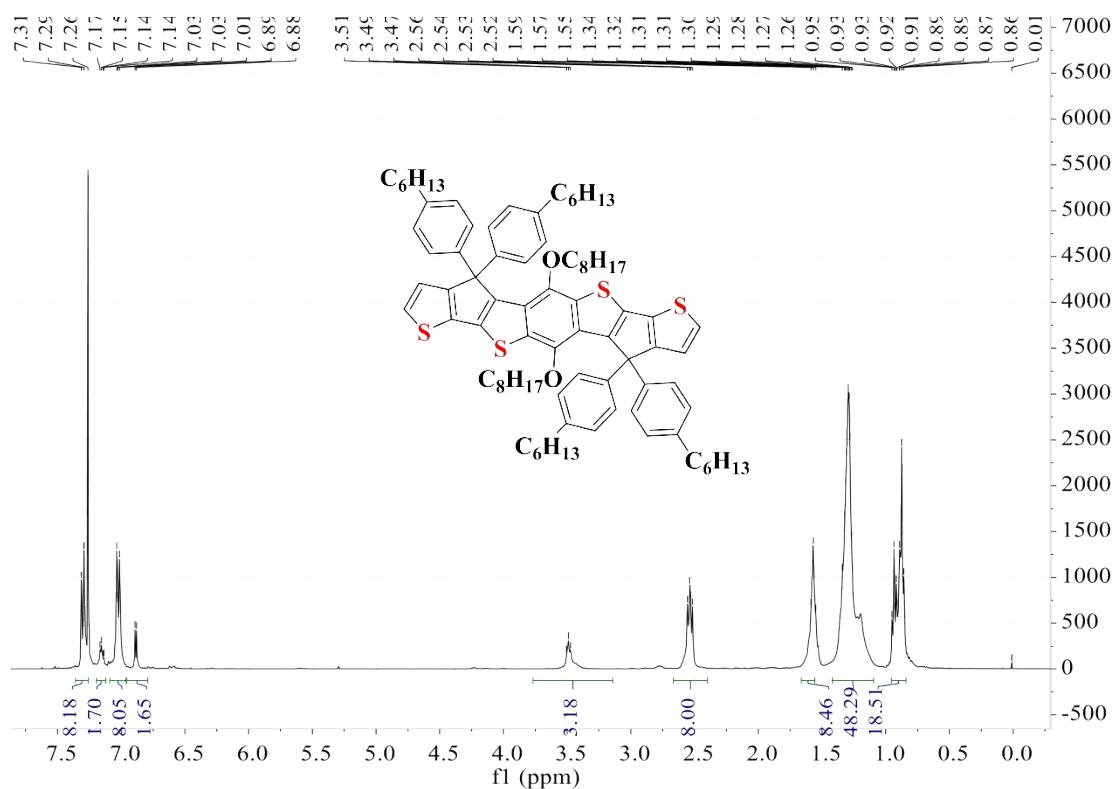


Figure S14.  $^1\text{H}$  NMR of compound 10 in  $\text{CDCl}_3$ .

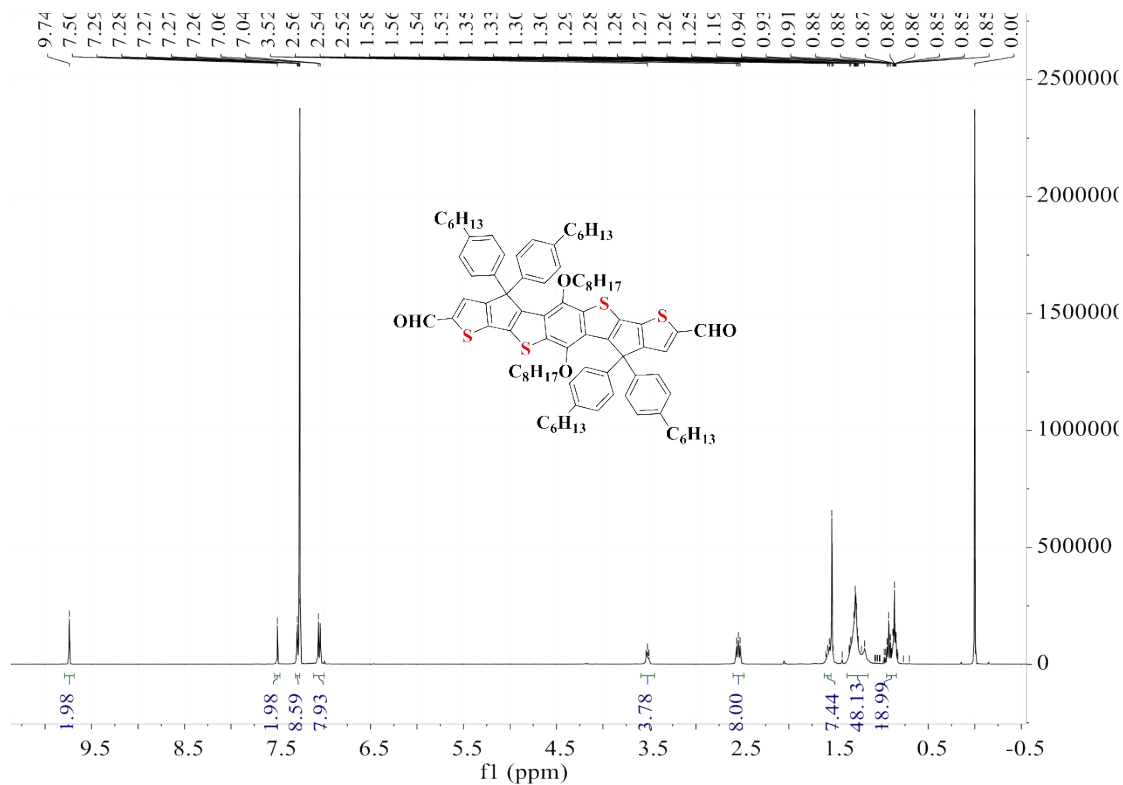


Figure S15.  $^1\text{H}$  NMR of compound 11 in  $\text{CDCl}_3$ .

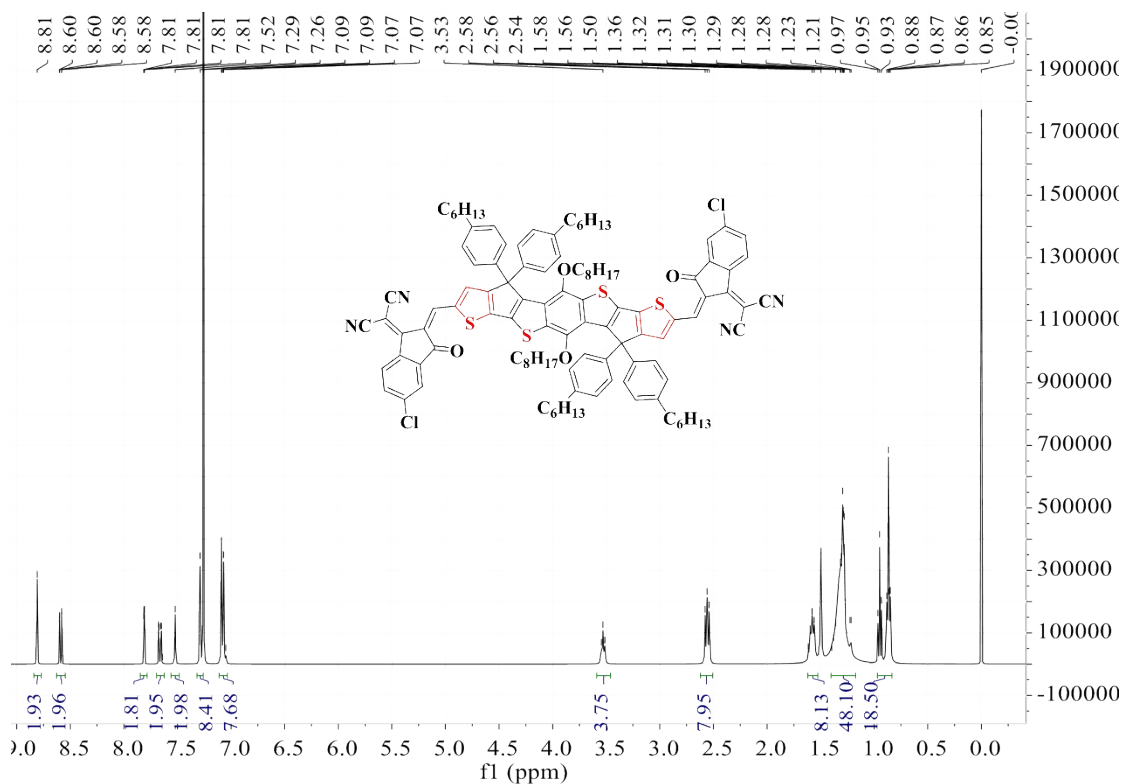


Figure S16.  $^1\text{H}$  NMR of  $\text{BDT}_c\text{IC-}\gamma\text{Cl}$  in  $\text{CDCl}_3$ .

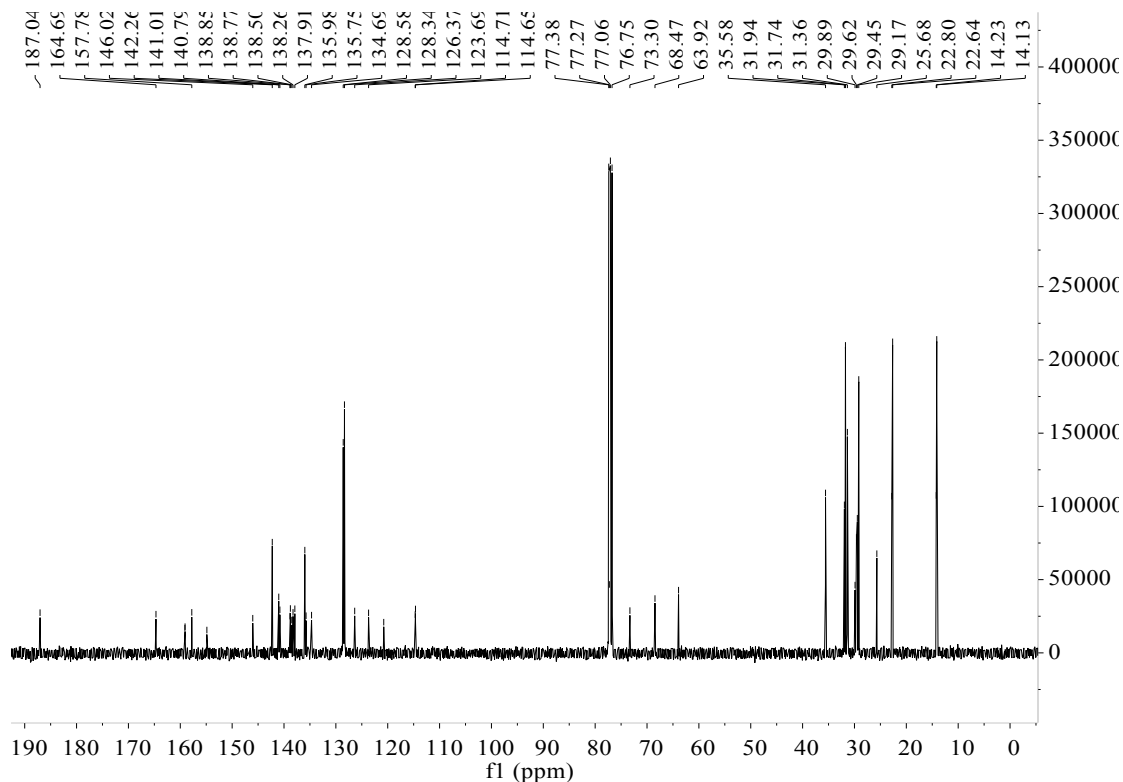
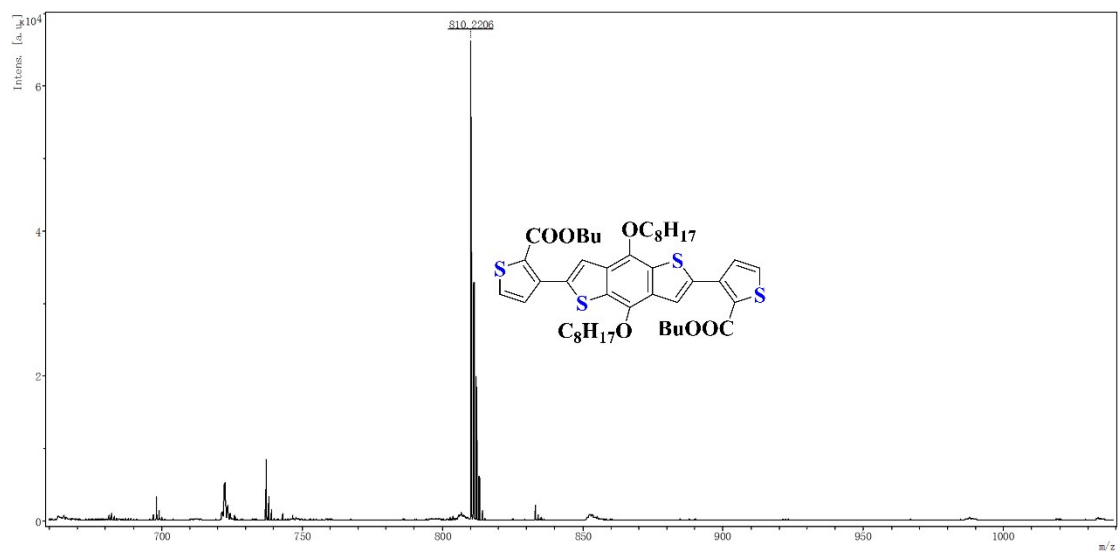
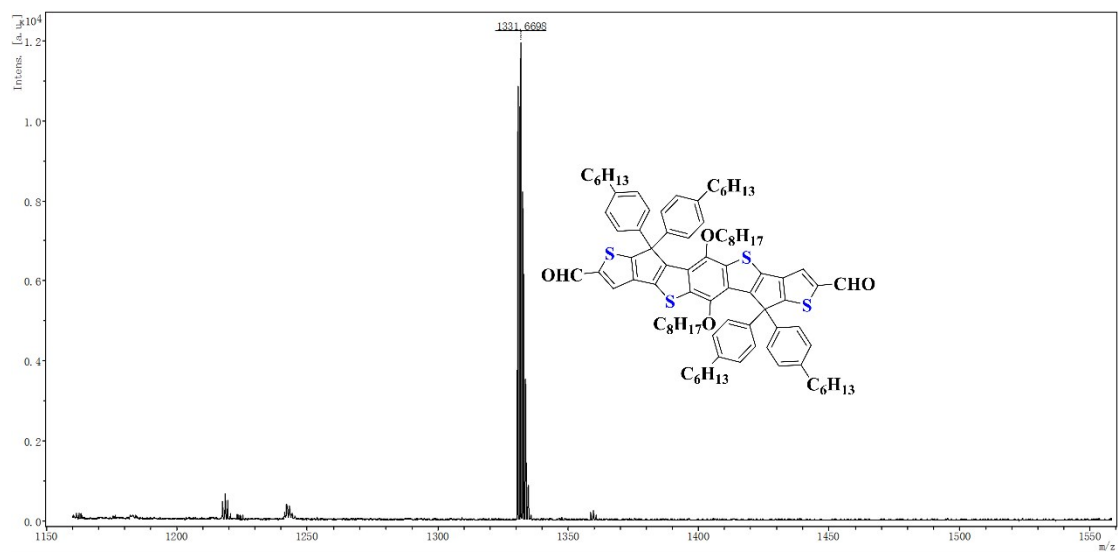


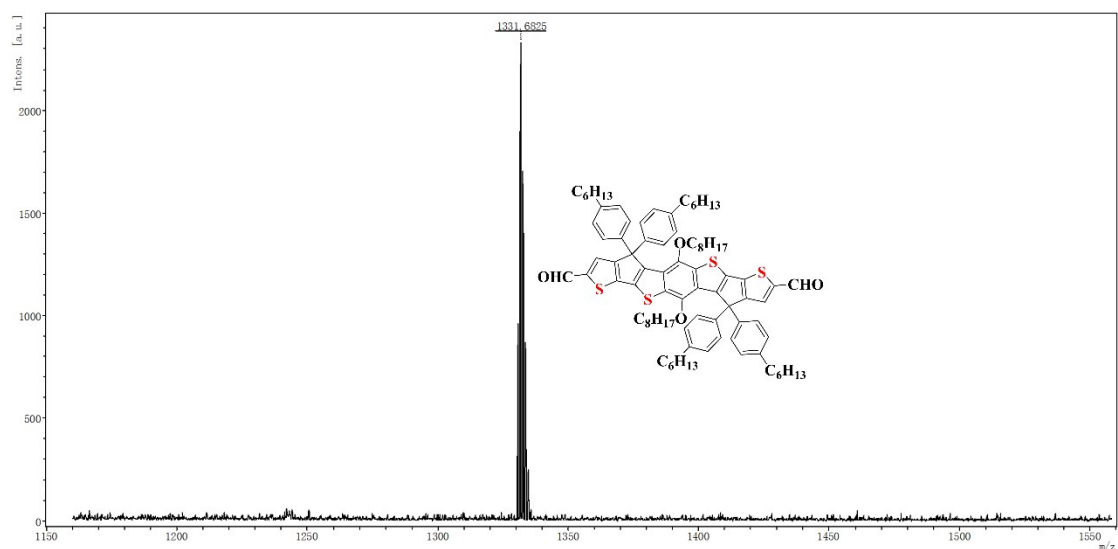
Figure S17.  $^{13}\text{C}$  NMR of  $\text{BDT}_c\text{IC-}\gamma\text{Cl}$  in  $\text{CDCl}_3$ .



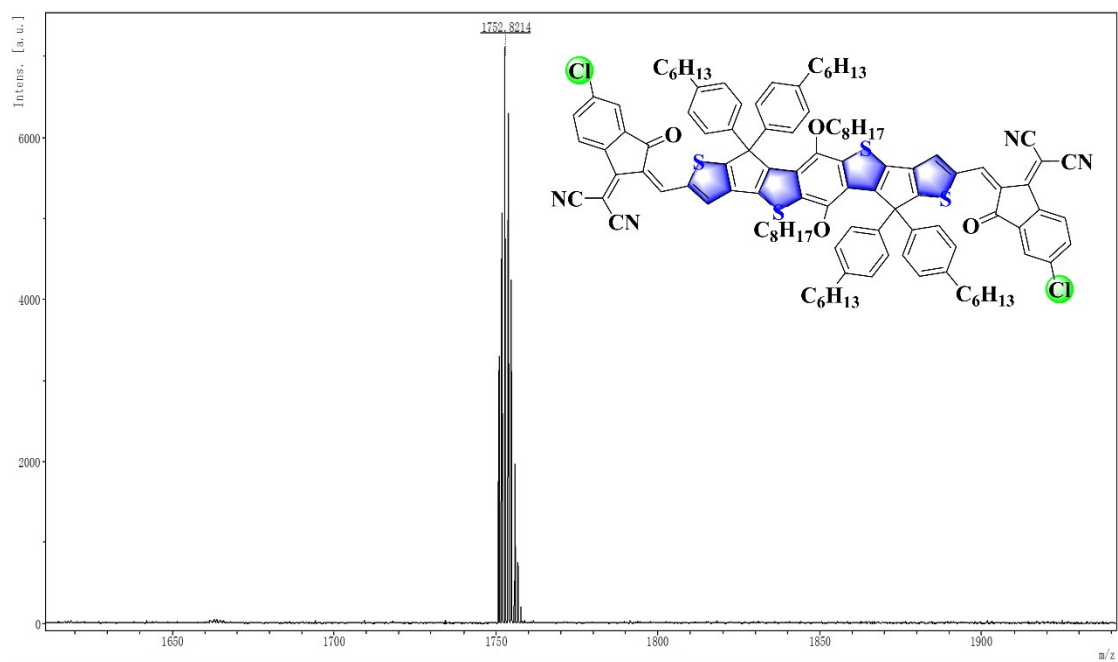
**Figure S18.** The MALDI-TOF figure of compound 6.



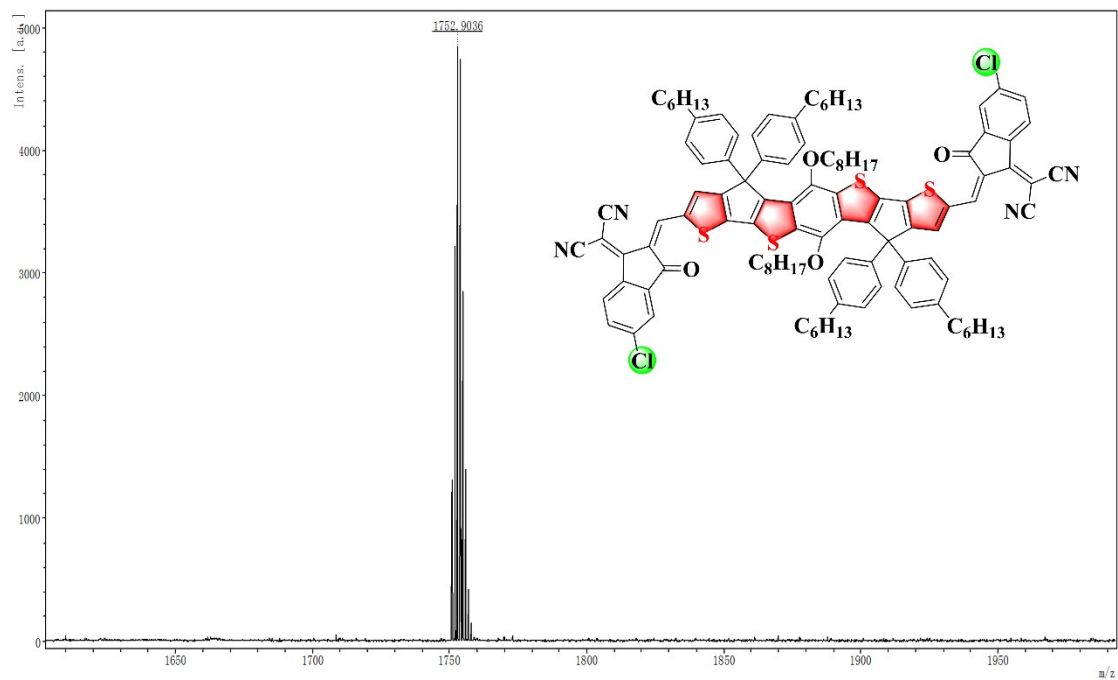
**Figure S19.** The MALDI-TOF figure of compound 8.



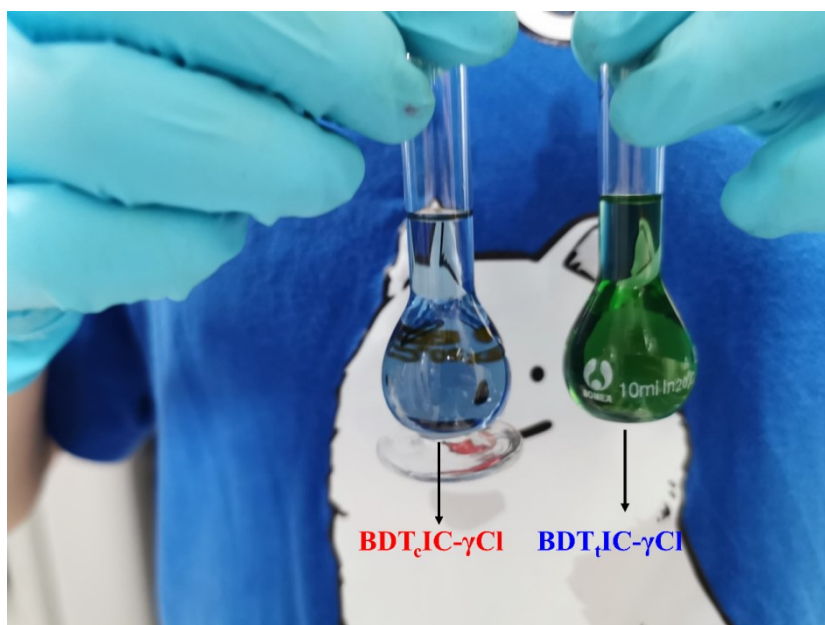
**Figure S20.** The MALDI-TOF figure of compound 11.



**Figure S21.** The MALDI-TOF figure of **BDT<sub>4</sub>IC- $\gamma$ Cl**.



**Figure S22.** The MALDI-TOF figure of  $\text{BDT}_c\text{IC-}\gamma\text{Cl}$ .



**Figure S23.** The solution ( $\text{CHCl}_3$ ) color of  $\text{BDT}_c\text{IC-}\gamma\text{Cl}$  and  $\text{BDT}_c\text{IC-}\gamma\text{Cl}$ .

## Notes and references

1. V. D. Mihailetschi, J. Wildeman, P. W. Blom, space-charge limited photocurrent, *Phys. Rev. Lett.*, 2005, **94**, 126602.
2. P. S. Davids, I. H. Campbell, D. L. Smith, device model for single carrier organic diodes, *J. Appl. Phys.*, 1997, **82**, 6319.
3. Y. Lin, J. Wang, Z. G. Zhang, H. Bai, Y. Li, D. Zhu, X. Zhan, an electron acceptor challenging fullerenes for efficient polymer solar cells, *Adv. Mater.*, 2015, **27**, 1170.
4. H. Lai, H. Chen, J. Zhou, J. Qu, P. Chao, T. Liu, X. Chang, N. Zheng, Z. Xie and F. He, isomer-free: Precise Positioning of Chlorine-Induced Interpenetrating Charge Transfer for Elevated Solar Conversion, *iScience*, 2019, **17**, 302-314.
5. Y. Li, J.-D. Lin, X. Che, Y. Qu, F. Liu, L. S. Liao, S. R. Forrest, High efficiency near-infrared and semitransparent non-fullerene acceptor organic photovoltaic cells, *J. Am. Chem. Soc.*, 2017, **139**, 17114.