

## **Electronic Supplementary Material for:**

### **Alkoxy Substitution on IDT-Series and Y-Series Non-fullerene Acceptors Yielding Highly Efficient Organic Solar Cells**

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## Measurements

**General information:**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AV-400 MHz NMR spectrometer. Chemical shifts are reported in parts per million (ppm,  $\delta$ ).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were referenced to tetramethylsilane (0 ppm) for  $\text{CDCl}_3$ . Mass spectra were collected on a MALDI Micro MX mass spectrometer, or an API QSTAR XL System.

**Optical characterizations:** Film UV-Vis absorption spectra were acquired on a Perkin Elmer Lambda 20 UV/VIS Spectrophotometer. All film samples were spin-cast on ITO substrates. UV-Vis absorption spectra were collected from the solution of three small molecules with a concentration of 0.02 mg/mL in chloroform. A cuvette with a stopper (Sigma Z600628) was used to avoid volatilization during the measurement.

**Electrochemical characterizations:** Cyclic voltammetry was carried out on a CHI610E electrochemical workstation with three electrodes configuration, using Ag/AgCl as the reference electrode, a Pt plate as the counter electrode, and a glassy carbon as the working electrode. 0.1 mol/L tetrabutylammonium hexafluorophosphate in acetonitrile was used as the supporting electrolyte. J71, PM6 and small molecules were drop-cast onto the glassy carbon electrode from chloroform solutions (5 mg/mL) to form thin films. Potentials were referenced to the ferrocenium/ferrocene couple by using ferrocene as external standards in acetonitrile solutions. The scan rate is 100 mV/s. The HOMO energy levels were determined by  $E_{\text{HOMO}} = - [q (E_{\text{re}} - E_{\text{ferrocene}}) + 4.8 \text{ eV}]$ , while the LUMO energy levels were determined by  $E_{\text{LUMO}} = - [q (E_{\text{ox}} - E_{\text{ferrocene}}) + 4.8 \text{ eV}]$ .

**DFT calculations:** The calculations were performed on a Gauss software package on B3LYP/6-31G\* level.

**AFM analysis:** AFM measurements were performed by using a Scanning Probe Microscope Dimension 3100 in tapping mode. All film samples were spin-cast on ITO substrates.

**Device fabrication and characterization:** For IDTN-O and IDTN, OSCs were made with a device structure of ITO (indium tin oxide)/PEDOT: PSS(poly(3,4-ethylenedioxythiophene): poly (styrene sulfonate))/J71: acceptor/ZrAcAc/Al. For Y6-O and Y6, OSCs were made with a device structure of ITO/PEDOT: PSS/PM6: acceptor/PDINO/Al. The patterned ITO-coated glass was scrubbed by detergent and then cleaned inside an ultrasonic bath by using deionized water, acetone, and isopropyl alcohol sequentially and dried overnight in an oven. Before use, the glass substrates were treated in a UV-Ozone Cleaner for 40 min to improve its work function and clearance. A thin PEDOT: PSS (Heraeus Clevios P VPA 4083) layer with a thickness of about 40 nm was spin-coat onto the ITO substrates at 4000 rpm for 40 s, and then dried at 150 °C for 10 min in air. The PEDOT: PSS coated ITO substrates were transferred to a N<sub>2</sub>-filled glove box for further processing. Chloroform was chosen as the solvent, and 1-chloronaphthalene (CN) was chosen as the additive (0.5%, v/v) in Y-series acceptors. The concentration of J71 or PM6 is 8 mg/mL with the weight ratio of J71 or PM6 and acceptors is 1: 1.2. Then the solution was stirred overnight for intensive mixing in a nitrogen-filled glove box. The blend solution was spin-cast on the top of PEDOT: PSS layer at 2500 rpm for 40 s. Then it was annealed at 85 °C for 5 min to remove the solvent. Then, the active layer coated substrates were quickly transferred

to a glove-box integrated thermal evaporator for electrode deposition. ZrAcAc (10 nm) or PDINO (10 nm) and the Al layer (100 nm) were sequentially evaporated under the vacuum of  $5 \times 10^{-5}$  Pa through a shadow mask. The optimal blend thickness measured on a Bruker Dektak XT stylus profilometer was about 100 nm. The current-voltage ( $J$ - $V$ ) characteristic curves of all packaged devices were measured by using a Keithley 2400 Source Meter in air. The photocurrent was measured under AM 1.5G (100 mW  $\text{cm}^{-2}$ ) using a Newport solar simulator in an Air. The light intensity was calibrated using a standard Si diode (with KG5 filter, purchased from PV Measurement) to bring spectral mismatch to unity. EQEs were measured using an Enlitech QE-S EQE system equipped with a standard Si diode. Monochromatic light was generated from a Newport 300W lamp source.

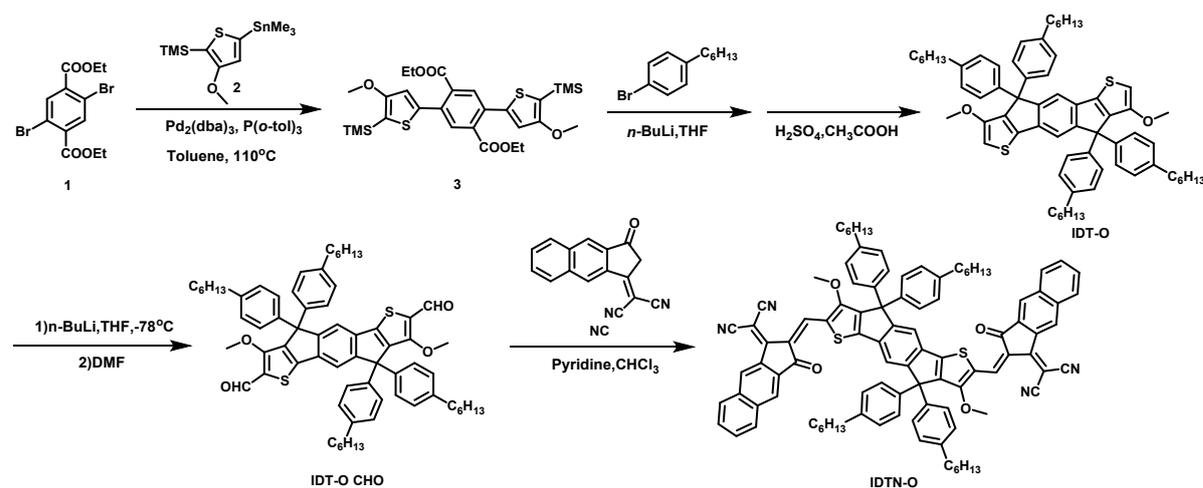
**SCLC measurements:** The electron and hole mobility of IDTN-O, IDTN, Y6-O and Y6 blend films were measured by using the method of space-charge limited current (SCLC). The electron-only SCLC device was a stack of ITO/ZnO/active layer/ ZrAcAc or PDINO/Al, and the hole-only SCLC device was a stack of ITO/PEDOT: PSS/active layer/MoO<sub>3</sub>/Al. The electron-only and hole-only SCLC devices fabricating methods were the same as those for OSCs. The charge carrier mobility was determined by fitting the dark current to the model of a single carrier SCLC according to the equation:  $J=9\varepsilon_0\varepsilon_r\mu V^2/8d^3$ , where  $J$  is the current density,  $d$  is the film thickness of the active layer,  $\mu$  is the charge carrier mobility,  $\varepsilon_r$  is the relative dielectric constant of the transport medium, and  $\varepsilon_0$  is the permittivity of free space.  $V=V_{\text{app}}-V_{\text{bi}}$ , where  $V_{\text{app}}$  is the applied voltage,  $V_{\text{bi}}$  is the offset voltage. The carrier mobility can be calculated from the slope

of the  $J^{1/2} \sim V$  curves.

**GIWAXS characterization:** GIWAXS measurements were performed at beamline 7.3.3 at the Advanced Light Source.<sup>1</sup> Samples were prepared on Si substrates using identical blend solutions like those used in devices. The 10 keV X-ray beam was incident at a grazing angle of  $0.11^\circ - 0.15^\circ$ , which maximized the scattering intensity from the samples. The scattered X-rays were detected using a Dectris Pilatus 2M photon-counting detector. In-plane and out-of-plane sector averages were calculated using the Nika software package.<sup>2</sup> The uncertainty for the peak fitting of the GIWAXS data is  $0.3 \text{ \AA}$ . The coherence length was calculated using the Scherrer equation:  $CL = 2\pi K / \Delta q$ , where  $\Delta q$  is the full-width at half-maximum of the peak and K is a shape factor (0.90 was used here).

## Materials and synthesis

All chemicals, unless otherwise specified, were purchased from Aldrich or other commercial resources and used as received. Compound **1**, Compound **2**, NC and **IDTN** were synthesized according to literature.<sup>3, 4</sup> PM6 (Mn = 24.2 kDa, polydispersity index = 3.6) was purchased from Solarmer Energy Inc. Y6 was synthesized according to literature procedure.<sup>5, 6</sup> Y6-O was synthesized with a similar procedure of Y6. The starting materials of 3-methoxythieno[3,2-b]thiophene are commercially available. Toluene and THF were distilled from sodium benzophenone under nitrogen before use.



**Scheme S1.** The synthetic routes of **IDTN-O**

### Synthesis of compound **3**

To a solution of compound **1** (450.0 mg, 1.02 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (46.8 mg, 0.051 mmol) and P(*o*-tol)<sub>3</sub> (124.2 mg, 0.408 mmol) in toluene (10 mL), compound **2** (1.87 g, 4.08 mmol) was added under N<sub>2</sub>. The reaction mixture was stirred for 12 h at 110 °C. Then, the reaction mixture was cooled to r.t. and poured into an aqueous potassium fluoride. The mixture was extracted with ethyl acetate three times. The combined organic phase

was washed with water followed by brine. Then the solution was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: *n*-hexane: ethyl acetate= 1:1) to get the product as pale yellow solid (493 mg, 55%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ =7.76 (s, 2H), 6.95 (s, 2H), 4.27 (q, 4H, *J*=6.8 Hz), 3.81 (s, 6H), 1.19 (t, 6H, *J*=6.8 Hz), 0.31 (s, 18H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ=168.1, 163.8, 143.9, 133.8, 133.7, 131.3, 117.0, 61.9, 59.0, 14.0, -0.3; MALDI-TOF MS: calcd for C<sub>28</sub>H<sub>28</sub>O<sub>6</sub>S<sub>2</sub>Si<sub>2</sub> (M<sup>+</sup>), 590.1648; found, 590.1671.

#### Synthesis of **IDT-O**

To a solution of 4-hexyl-1-bromobenzene (817 mg, 3.4 mmol) in THF (10 mL) at -78 °C, *n*-butyl lithium (2.0 mL, 1.3 mmol, 1.6 M in hexane) was added under N<sub>2</sub>. The mixture was kept at -78 °C for one hour. Then a solution of compound **3** (370 mg, 0.42 mmol) in THF (10 mL) was added slowly. After the addition, the mixture was stirred at room temperature overnight. Water was added and the mixture was stirred for 5 hours. The mixture was extracted three times with ethyl acetate. The combined organic phase was washed with water followed by brine. Then the solution was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure.

Then the crude was dissolved in CH<sub>3</sub>COOH (30 mL). The concentrated sulfuric acid (0.1 mL) was added dropwise to the solution at 0 °C. Then the solution was heated to 40 °C and stirred for 5 hours. After cooled down to room temperature, the reaction was quenched with water and extracted with ethyl acetate three times. The combined organic phase was washed with water followed by brine. Then the solution was dried

over Na<sub>2</sub>SO<sub>4</sub>. The residue was purified by flash column chromatography (eluent: *n*-hexane: toluene= 10:1) to get the product as pale yellow solid (267 mg, 59%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ =7.36 (s, 2H), 7.24 (d, 8H, *J*=8.0 Hz), 7.07 (d, 8H, *J*=8.0 Hz), 6.17 (s, 2H), 3.73 (s, 6H), 2.60 (t, 8H, *J*=7.6 Hz), 1.62-1.60 (m, 8H), 1.33-1.32 (m, 24H), 0.92 (t, 12H, *J*=6.0 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ=154.3, 153.8, 144.1, 141.4, 140.8, 140.7, 135.5, 128.5, 128.1, 117.1, 88.8, 63.6, 57.5, 35.8, 31.9, 31.5, 29.4, 22.8, 14.3; MALDI-TOF MS: calcd for C<sub>66</sub>H<sub>78</sub>O<sub>2</sub>S<sub>2</sub> (M<sup>+</sup>), 966.5443; found, 966.5469.

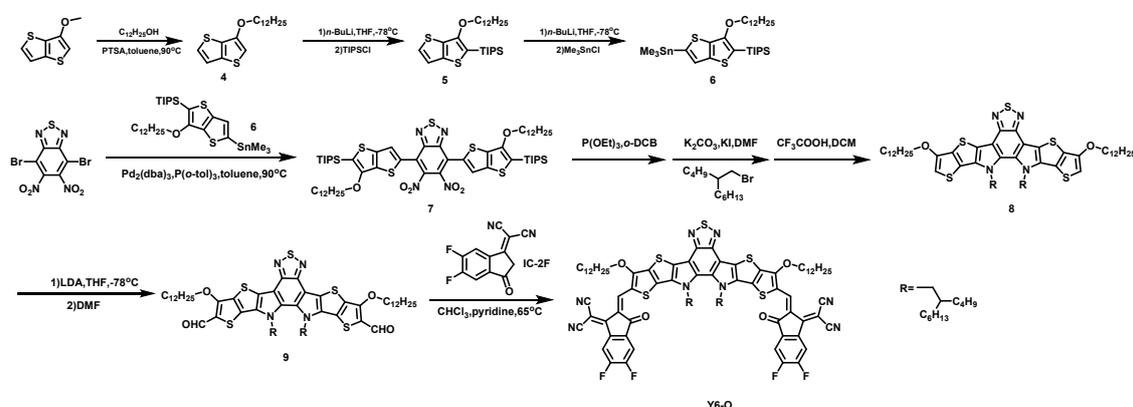
#### Synthesis of **IDT-O CHO**

To a solution of **IDT-O** (60 mg, 0.060 mmol) in THF (10mL), 1.6 M *n*-butyllithium in hexane (0.1 mL, 0.16 mmol) was added dropwise slowly at -78 °C under N<sub>2</sub>. The mixture was stirred at -78 °C for one hour, and then anhydrous DMF (0.4 mL) was added. The mixture was stirred overnight at room temperature. Brine was added and the mixture was extracted with ethyl acetate three times. The combined organic phase was washed with water followed by brine. Then the solution was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: *n*-hexane: CH<sub>2</sub>Cl<sub>2</sub>= 1:1) to get the product as yellow solid (55 mg, 87%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ =10.02 (s, 2H), 7.50 (s, 2H), 7.19 (d, 8H, *J*=8.4 Hz), 3.79 (s, 6H), 2.60 (t, 8H, *J*=7.6 Hz), 1.62 (m, 8H), 1.33 (m, 24H), 0.89 (t, 12H, *J*=6.8 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ=180.3, 159.0, 155.6, 149.1, 146.6, 141.6, 138.2, 135.6, 128.2, 127.7, 127.5, 117.6, 63.2, 63.0, 34.9, 31.1, 30.7, 28.5, 22.0, 13.5; MALDI-TOF MS: calcd for C<sub>68</sub>H<sub>78</sub>O<sub>4</sub>S<sub>2</sub> (M<sup>+</sup>), 1022.5342; found,

1122.5358.

### Synthesis of **IDTN-O**

To a solution of **IDT-O CHO** (60 mg, 0.053 mmol) and **NC** (102 mg, 0.53 mmol) in dry  $\text{CHCl}_3$  (10 mL) was added pyridine (0.1 mL) under  $\text{N}_2$ . The mixture was refluxed for 16 hours and then allowed to cool to room temperature, then the mixture was poured into  $\text{CH}_3\text{OH}$  (100 mL) and filtered, the residue left in filter paper was dissolved by  $\text{CHCl}_3$ . After removing the solvent, the residue was purified using column chromatography on silica gel (eluent: *n*-hexane:  $\text{CH}_2\text{Cl}_2$ = 1:1), yielding a dark blue solid (50 mg, 64%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 9.18 (s, 2H), 9.17 (s, 2H), 8.33 (s, 2H), 8.08 (m, 4H), 7.69 (m, 6H), 7.25 (d, 8H,  $J$ =8.4 Hz), 7.15 (d, 8H,  $J$ =8.4 Hz), 3.54 (s, 6H), 2.61 (t, 8H,  $J$ =7.6 Hz), 1.62-1.57 (m, 8H), 1.30-1.28 (m, 24H), 0.88 (t, 12H,  $J$ =6.8 Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$ =188.7, 164.1, 160.7, 158.8, 158.6, 147.3, 142.7, 138.0, 137.4, 136.2, 135.3, 134.9, 134.8, 133.0, 130.6, 130.2, 129.7, 129.5, 128.7, 128.5, 128.3, 126.8, 124.3, 122.4, 118.9, 115.6, 115.2, 67.0, 64.0, 63.8, 35.5, 31.7, 31.2, 29.0, 22.6, 14.1; MALDI-TOF MS: calcd for  $\text{C}_{100}\text{H}_{90}\text{N}_4\text{O}_4\text{S}_2$  ( $\text{M}^+$ ), 1474.6403; found, 1474.6479.



**Scheme S2.** The synthetic routes of **Y6-O**

#### Synthesis of **compound 4**

To a solution of 3-methoxythieno[3,2-b]thiophene (2 g, 11.75 mmol) and *p*-toluenesulfonic acid (**PTSA**) (223.5 mg, 1.175 mmol) in dry toluene (10 mL), dodecan-1-ol (4.378 g, 23.50 mmol) was added under N<sub>2</sub>. The mixture was refluxed at 90 °C overnight and then allowed to cool to room temperature. After poured into water, it was extracted for three times with ethyl acetate. The combined organic phase was washed with water followed by brine. Then the solution was dried over Na<sub>2</sub>SO<sub>4</sub>. After removing the solvent, the residue was purified using column chromatography on silica gel (eluent: *n*-hexane: CH<sub>2</sub>Cl<sub>2</sub>= 8:1, v/v), yielding a colorless oil (3.11 g, 81%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ= 7.36 (dd, 1H), 7.18 (d, 1H, *J*=5.6 Hz), 6.26 (d, 1H, *J*=1.4 Hz), 4.07 (t, 2H, *J*=6.6 Hz), 1.87-1.80 (m, 2H), 1.51-1.44 (m, 2H), 1.32-1.29 (m, 16H), 0.88 (t, 3H, *J*=6.8 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ= 150.2, 137.2, 130.9, 127.3, 120.3, 98.1, 70.7, 32.1, 29.9-29.4 (m), 26.2, 22.9, 14.3; MALDI-TOF MS: calcd for C<sub>18</sub>H<sub>28</sub>OS<sub>2</sub> (M<sup>+</sup>), 324.1582; found, 324.1589.

#### Synthesis of **compound 5**

To a solution of compound **4** (3.11 g, 9.571 mmol) in THF at -78 °C, 1.6 M *n*-butyl lithium in hexane (6.3 mL, 10.05 mmol) was added dropwise under N<sub>2</sub>. The reaction mixture was stirred for 1h at -78 °C, and then TIPSCl (2.21 g, 11.49 mmol) was added. The mixture was returned to room temperature and stirred overnight. The reaction was quenched with water and extracted with ethyl acetate for three times. The combined organic phase was washed with water followed by brine. Then the solution was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by

flash column chromatography (eluent: *n*-hexane) to get the product as colorless oil (1.83 g, 40%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ= 7.35 (d, 1H, *J*=5.2 Hz), 7.18 (d, 1H, *J*=5.2 Hz), 4.36 (t, 2H, *J*=6.6 Hz), 1.87-1.80 (m, 2H), 1.56-1.34 (m, 21H), 1.20 (d, 18H, *J*=7.4 Hz), 0.95 (t, 3H, *J*=7.0 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ= 155.3, 144.0, 130.3, 127.9, 120.1, 113.8, 71.3, 32.1, 30.2, 29.9-29.5 (m), 26.1, 22.9, 19.0, 18.5, 14.3, 12.3; MALDI-TOF MS: calcd for C<sub>27</sub>H<sub>48</sub>OS<sub>2</sub>Si (M<sup>+</sup>), 480.2916; found, 480.2917.

### Synthesis of **compound 6**

To a solution of compound **5** (1.83 g, 3.808 mmol) in THF at -78 °C, 1.6 M *n*-butyl lithium in hexane (2.6 mL, 4.189 mmol) was added dropwise under N<sub>2</sub>. The reaction mixture was stirred for 1h at -78 °C, and then 1.0 M trimethyltin chloride in THF (4.57 mL, 4.570 mmol) was added. The mixture was returned to room temperature and stirred overnight. The reaction was quenched with an aqueous potassium fluoride and extracted with ethyl acetate for three times. The combined organic phase was washed with water followed by brine. Then the solution was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue as white solid was used directly without further purification. MALDI-TOF MS: calcd for C<sub>30</sub>H<sub>56</sub>OS<sub>2</sub>SiSn (M<sup>+</sup>), 644.2564; found, 644.2542.

### Synthesis of **compound 7**

To a solution of 4,7-dibromo-5,6-dinitrobenzo[*c*][1,2,5]thiadiazole (598.0 mg, 1.558 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (71.3 mg, 0.078 mmol) and P(*o*-tol)<sub>3</sub> (190.0 mg, 0.623 mmol) in toluene (10 mL), compound **5** (2.41 g, 3.740 mmol) was added under N<sub>2</sub>. The reaction mixture was stirred for 12 hours at 90 °C. Then, the reaction mixture was cooled to

room temperature and poured into an aqueous potassium fluoride. The mixture was extracted with ethyl acetate for three times. The combined organic phase was washed with water followed by brine. Then the solution was dried over  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: *n*-hexane:  $\text{CH}_2\text{Cl}_2$ = 8:1, v/v) to get the product as dark purple oil (1.239 g, 67%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  =7.63 (s, 2H), 4.37 (t, 4H,  $J$ =6.4 Hz), 1.85-1.81 (m, 4H), 1.54-1.29 (m, 42H), 1.18 (d, 36H,  $J$ =7.6 Hz), 0.90 (t, 6H,  $J$ =7.0 Hz) ;  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ , ppm):  $\delta$ =155.0, 152.3, 143.9, 142.0, 133.9, 131.2, 124.0, 121.4, 118.6, 71.6, 32.1, 30.2, 29.9-29.5 (m), 26.0, 22.9, 22.9, 19.0, 14.3, 12.3; MALDI-TOF MS: calcd for  $\text{C}_{60}\text{H}_{94}\text{N}_4\text{O}_6\text{S}_5\text{Si}_2$  ( $\text{M}^+$ ), 1182.5315; found, 1182.5319.

### Synthesis of **compound 8**

Compound **7** (295.0 mg, 0.2492 mmol) and triethyl phosphate(5 mL) were dissolved in the odichlorobenzene (*o*-DCB, 10 mL) under nitrogen. After being heated at 180 °C overnight, the solvent was removed to get the crude product.

The red residue was mixed with 1-bromo-2-butyloctane (1.49 g, 5.981 mmol), potassium carbonate (688.8 mg, 4.984 mmol) and potassium iodide (992.8 mg, 5.981 mmol) in DMF (20 mL) under  $\text{N}_2$ . The mixture was refluxed at 80 °C overnight. After cooled down to room temperature, the residue was poured into water and extracted with ethyl acetate three times. The combined organic phase was washed with water followed by brine. Then the solution was dried over  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure.

Then the crude was dissolved in dry  $\text{CH}_2\text{Cl}_2$  (10 mL).  $\text{CF}_3\text{COOH}$  (1 mL) was added to the solution and stirred for 3 hours. After poured into water, it was extracted for three times with chloroform. The combined organic phase was washed with water followed by brine. Then the solution was dried over  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: *n*-hexane:  $\text{CH}_2\text{Cl}_2$  = 3:1, v/v) to get the product as orange oil (104.2 mg, 37%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 6.30 (s, 2H), 4.58 (d, 4H,  $J$  = 7.6 Hz), 4.16 (t, 4H,  $J$  = 6.4 Hz), 2.10-2.06 (m, 2H), 1.92-1.85 (m, 4H), 1.55-1.51 (m, 4H), 1.38-1.26 (m, 36H), 1.02-0.83 (m, 34H), 0.70-0.59 (m, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 151.2, 147.6, 136.9, 132.6, 131.8, 123.0, 122.2, 111.6, 95.8, 70.8, 55.1, 38.7, 32.0, 31.6, 30.4-29.2 (m), 28.0, 27.8, 26.1, 25.3, 25.2, 22.8, 22.7, 22.5, 22.5, 14.2, 14.0, 13.8, 13.77; MALDI-TOF MS: calcd for  $\text{C}_{66}\text{H}_{102}\text{N}_4\text{O}_2\text{S}_5$  ( $\text{M}^+$ ), 1142.6606; found, 1142.6595.

### Synthesis of **compound 9**

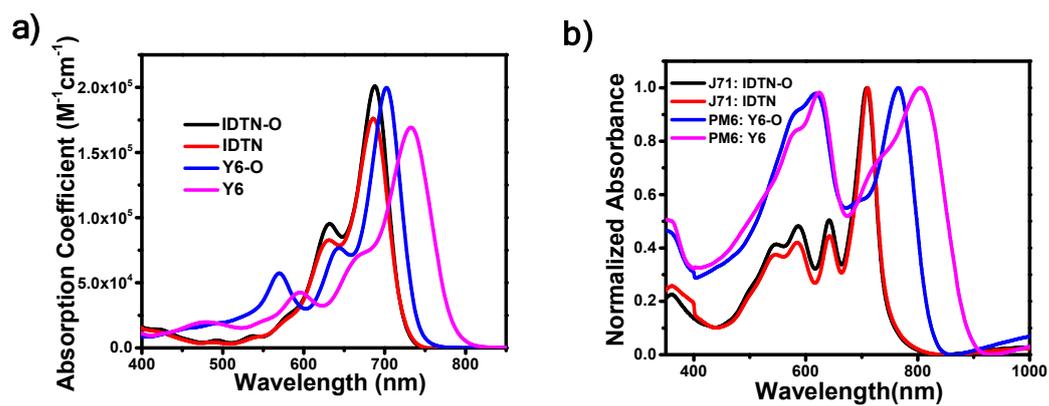
To a solution of compound **8** (104.2 mg, 0.09109 mmol) in THF (10 mL), 2.0 M lithium diisopropylamide in hexane (0.18 mL, 0.3643 mmol) was added dropwise slowly at  $-78$  °C under  $\text{N}_2$ . The mixture was stirred at  $-78$  °C for 1 h, and then anhydrous DMF (0.4 mL) was added. The mixture was stirred overnight at room temperature. Brine was added and the mixture was extracted with ethyl acetate for three times. The combined organic phase was washed with water followed by brine. Then the solution was dried over  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: *n*-hexane:  $\text{CH}_2\text{Cl}_2$  = 1:4, v/v) to get the product as orange solid (100 mg, 95%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 10.10 (s, 2H),

4.68 (t, 4H,  $J = 6.4$  Hz), 4.59 (d, 4H,  $J = 7.6$  Hz), 2.03-2.01 (m, 2H), 1.97-1.90 (m, 4H), 1.59-1.52 (m, 4H), 1.41-1.24 (m, 36H), 1.06-0.81 (m, 34H), 0.69-0.60 (m, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 181.3, 158.8, 147.6, 136.9, 133.3, 130.2, 129.6, 128.2, 122.2, 112.3, 73.5, 55.5, 39.2, 32.1, 31.7, 30.5-29.5$  (m), 28.1, 28.0, 26.0, 25.4, 25.2, 22.9, 22.9, 22.6, 14.3, 14.1, 13.9, 13.8; MALDI-TOF MS: calcd for  $\text{C}_{68}\text{H}_{102}\text{N}_4\text{O}_4\text{S}_5$  ( $\text{M}^+$ ), 1198.6505; found, 1198.6519.

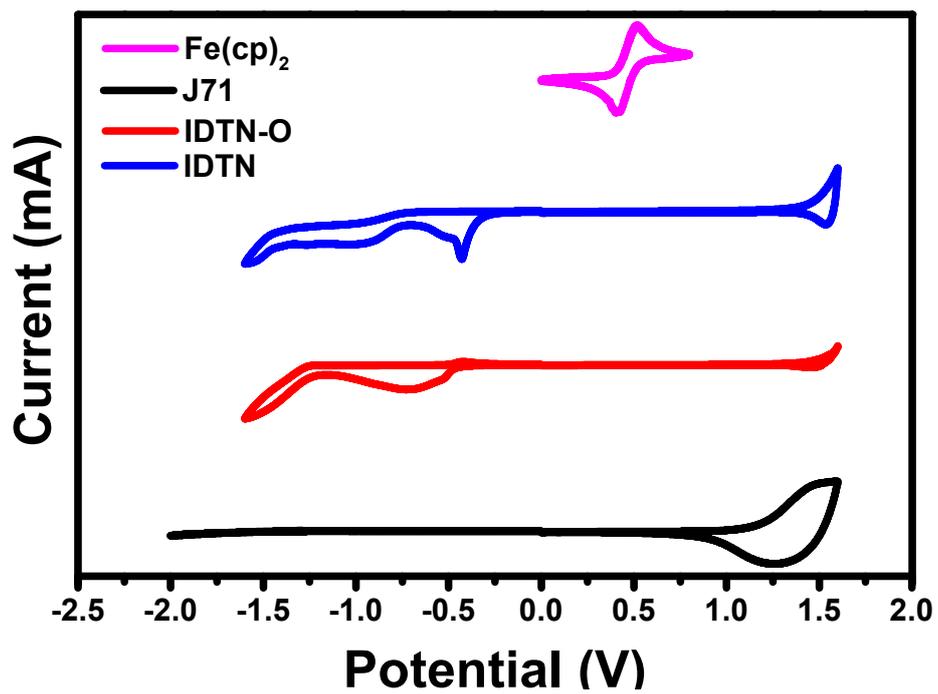
### Synthesis of **Y6-O**

To a solution of compound **9** (42.8 mg, 0.03567 mmol) and 2-(5, 6-difluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene) malononitrile (**IC-2F**) (49.3 mg, 0.2140mmol) in dry  $\text{CHCl}_3$  (10 mL) was added pyridine (0.1 mL) under  $\text{N}_2$ . The mixture was refluxed for 16 hours and then allowed to cool to room temperature, then the mixture was poured into  $\text{CH}_3\text{OH}$  (100 mL) and filtered, the residue left in filter paper was dissolved by  $\text{CHCl}_3$ . After removing the solvent, the residue was purified using column chromatography on silica gel (eluent: *n*-hexane:  $\text{CH}_2\text{Cl}_2 = 1:1$ , v/v), yielding a dark purple solid (37.5 mg, 65%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 9.35$  (s, 2H), 8.54-8.50 (m, 2H), 7.66-7.62 (m, 2H), 4.81 (t, 4H,  $J = 6.4$  Hz), 4.74 (d, 4H,  $J = 6.6$  Hz), 2.10-2.01 (m, 6H), 1.59-1.57 (m, 10H), 1.43-1.25 (m, 32H), 1.05-0.86 (m, 32H), 0.70-0.64 (m, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 186.7, 162.7, 158.8, 155.7, 155.6, 155.6, 153.1, 153.0, 152.9, 147.6, 137.8, 137.4, 137.0, 136.9, 134.6, 134.6, 132.1, 128.4, 120.1, 118.0, 115.3, 115.1, 114.9, 113.3, 112.4, 112.2, 74.4, 67.8, 56.0, 39.5, 32.2, 31.8, 31.8, 30.7, 30.7, 30.6, 30.6, 29.9, 29.8, 29.8, 29.6, 29.6, 29.5, 28.3, 28.1, 26.0, 25.6, 25.5, 23.1, 23.0, 22.9, 22.7, 22.7, 14.3, 14.2, 14.2, 14.0, 14.0$ ; MALDI-

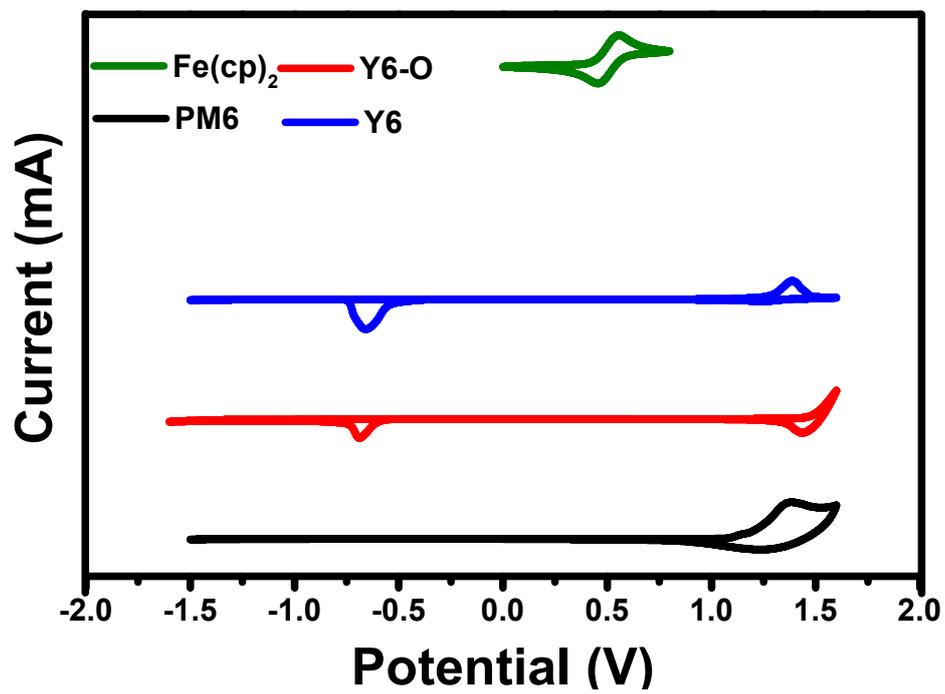
TOF MS: calcd for  $C_9H_{10}F_4N_8O_4S_5 (M^+)$ , 1622.6877; found, 1622.6931.



**Figure S1.** a) Absorption spectra of IDTN-O, IDTN, Y6-O and Y6 in chloroform solution; b) Normalized absorption spectra of J71: IDTN-O, J71: IDTN, PM6: Y6-O and PM6: Y6 blend films.

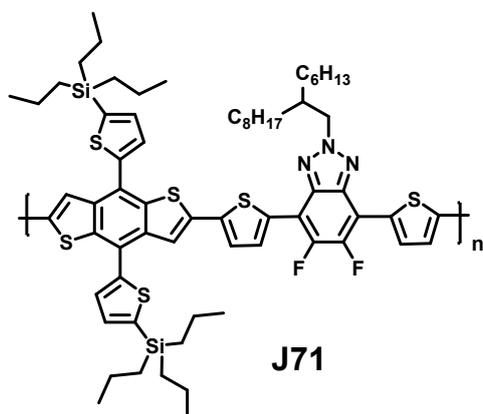


**Figure S2.** The CV plots of J71, IDTN-O and IDTN.

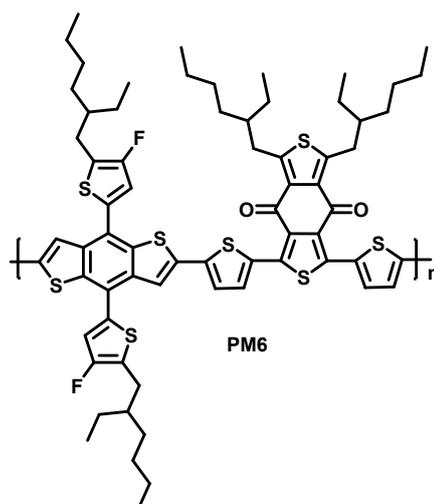


**Figure S3.** The CV plots of PM6, Y6-O and Y6.

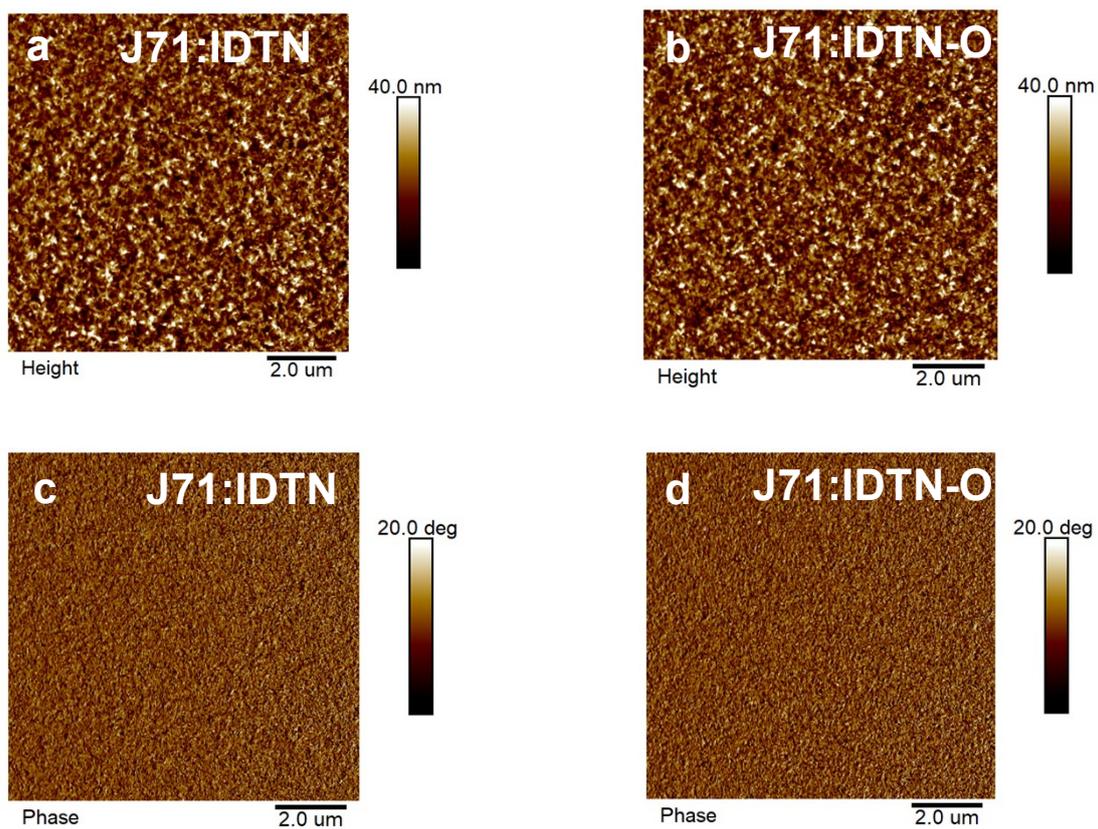
a)



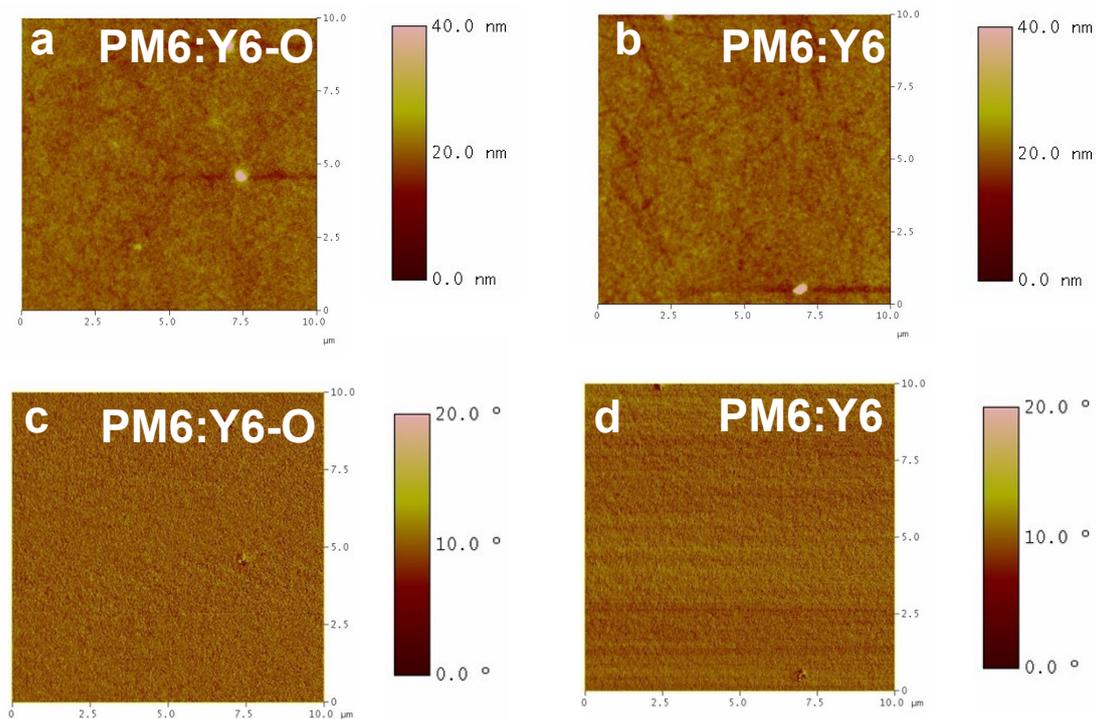
b)



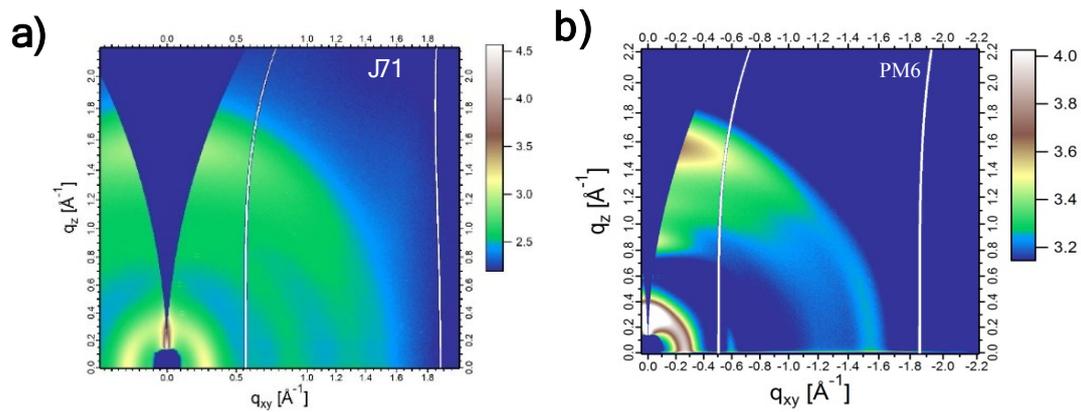
**Figure S4.** Chemical structure of a) J71 and b) PM6.



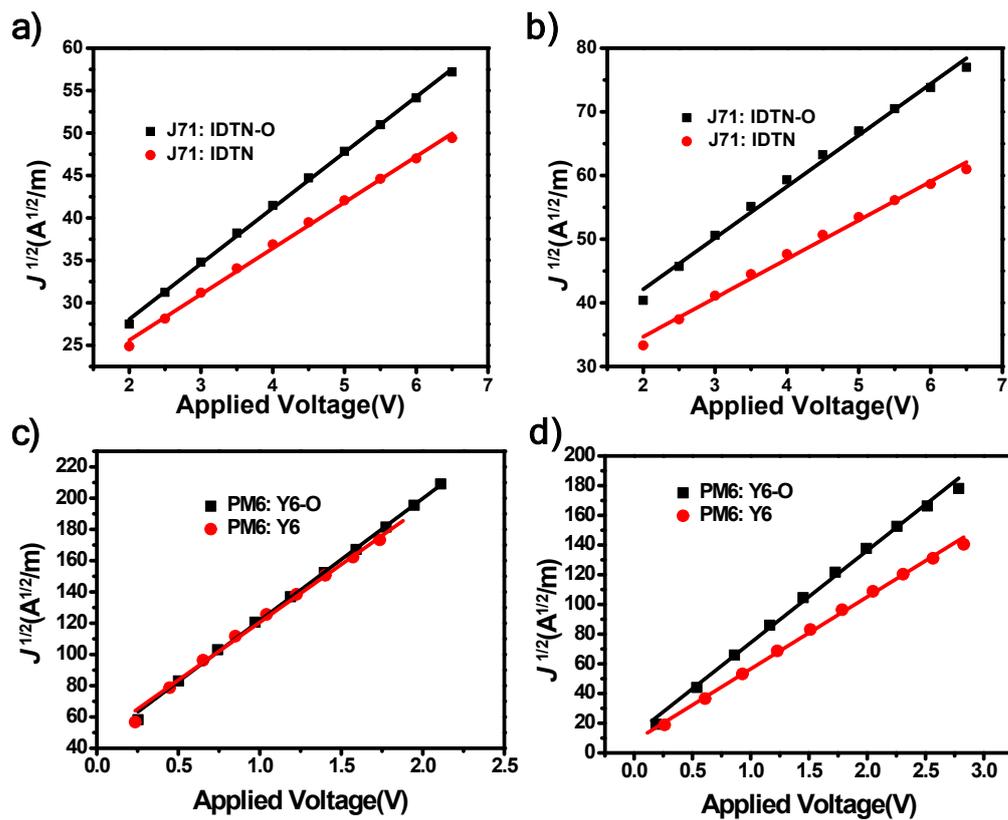
**Figure S5.** The AFM height images ( $10\mu\text{m} \times 10\mu\text{m}$ ): a) a J71: IDTN blend film and b) a J71: IDTN-O blend film; The AFM phase images ( $10\mu\text{m} \times 10\mu\text{m}$ ): c) a J71: IDTN blend film and d) a J71: IDTN-O film.



**Figure S6.** The AFM height images ( $10\mu\text{m} \times 10\mu\text{m}$ ): a) a PM6: Y6-O blend film and b) a PM6: Y6 blend film; The AFM phase images ( $10\mu\text{m} \times 10\mu\text{m}$ ): c) a PM6: Y6-O blend film and d) a J71: Y6 blend film.

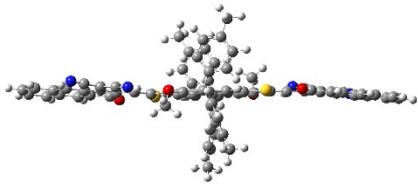
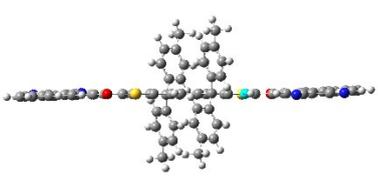
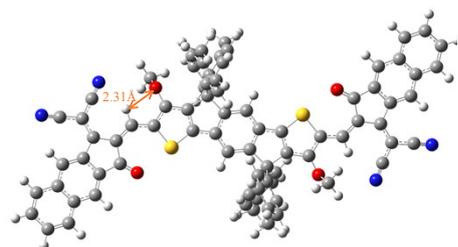
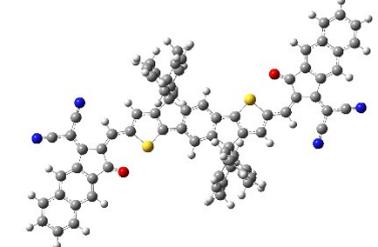
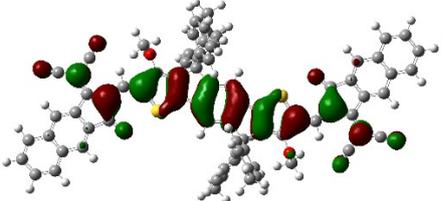
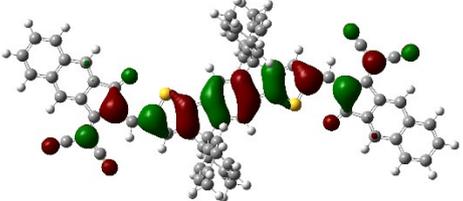
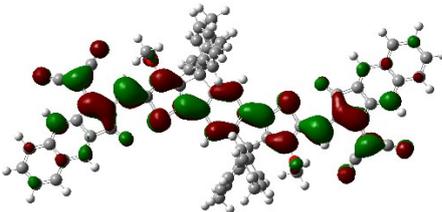
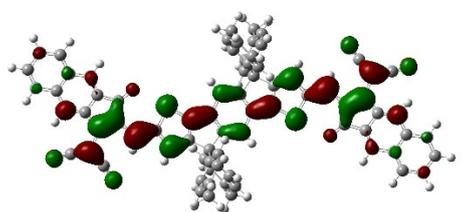
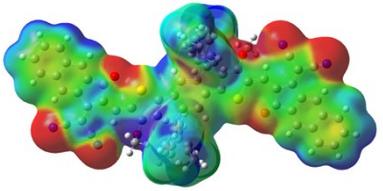
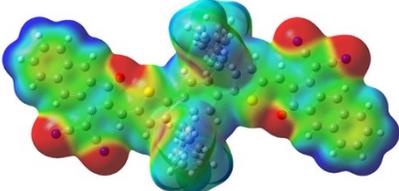


**Figure S7.** 2D-GIWAXS patterns: a) a neat J71 film, b) a neat PM6 film.

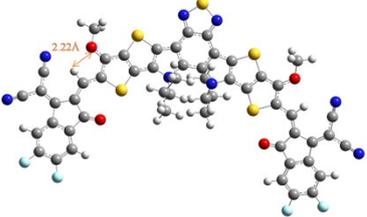
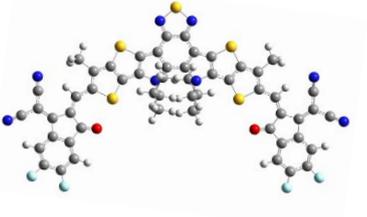
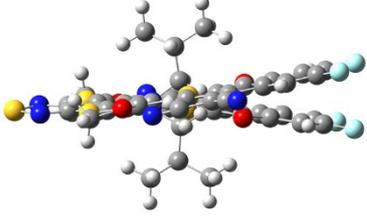
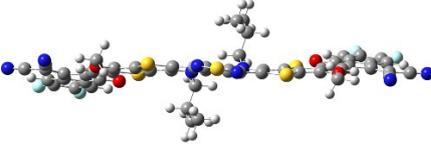
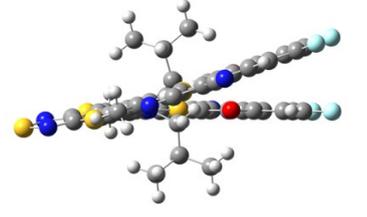
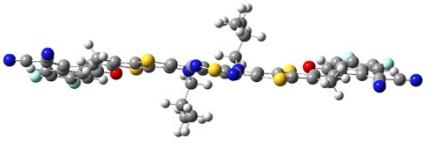
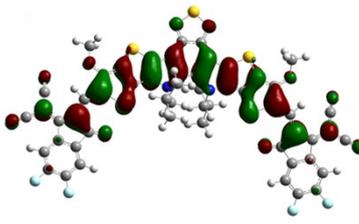
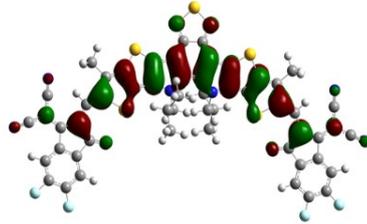
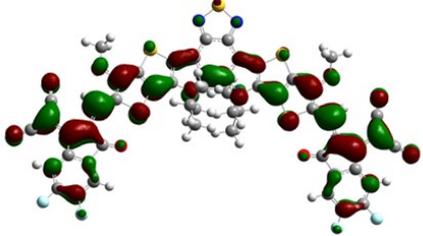
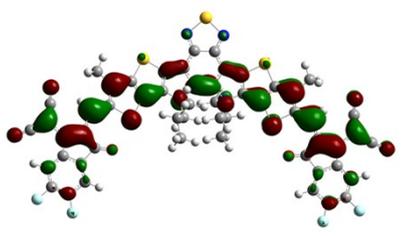


**Figure S8.** a) the hole motilities in J71: IDTN-O and J71: IDTN films; b) the electron motilities in J71: IDTN-O and J71: IDTN films; c) the hole motilities in PM6: Y6-O and PM6: Y6 films; d) the electron motilities in PM6: Y6-O and PM6: Y6 films.

**Table S1.** The DFT calculation results of IDTN-O and IDTN.

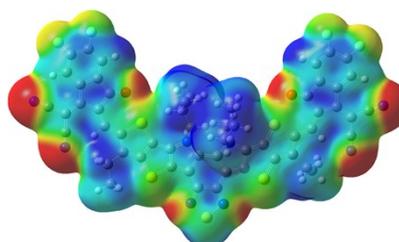
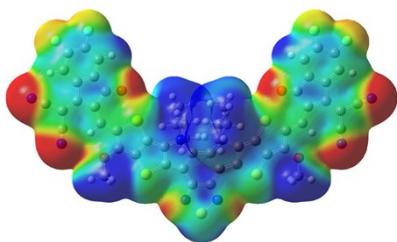
Molecule	IDTN-O	IDTN
Side view		
Top view		
HOMO	 -5.55 eV	 -5.58 eV
LUMO	 -3.35 eV	 -3.41 eV
electronic potential diagram		
Dipole moment (Debye)	0.90	0.04

**Table S2.** The DFT calculation results of Y6-O and Y6.

Molecule	Y6-O	Y6
Top View		
Side View	 	 
HOMO	 -5.90 eV	 -5.89 eV
LUMO	 -3.61 eV	 -3.75 eV

---

**electronic  
potential  
diagram**



---

**Dipole  
moment  
(Debye)**

3.66

1.04

---

**Table S3.** The average values and standard deviations of key parameters of IDTN-O, IDTN, Y6-O and Y6 from 20 devices

Active layer	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF(%)	PCE(%)	PCE(max,%)
<b>J71: IDTN-O</b>	0.90±0.01	17.0±0.2	76.3±0.4	11.7±0.17	12.1
<b>J71: IDTN</b>	0.87±0.01	16.7±0.2	73.3±1.6	10.6±0.17	10.9
<b>PM6: Y6-O</b>	0.95±0.00	22.4±0.1	77.3±0.3	16.4±0.08	16.6
<b>PM6: Y6</b>	0.82±0.00	25.3±0.5	73.4±1.3	15.2±0.44	15.7

**Table S4.** Morphological parameters obtained from 2D-GIWAXS patterns of J71 and PM6.

sample	in plane				out of plane			
	Location/ $\text{\AA}^{-1}$	FWHM	d-spacing/ $\text{\AA}$	CL/ $\text{\AA}$	Location/ $\text{\AA}^{-1}$	FWHM	d-spacing/ $\text{\AA}$	CL/ $\text{\AA}$
J71	0.29	0.119	21.9	50.9	1.65	0.355	3.81	15.9
PM6	0.29	0.086	21.7	65.4	1.65	0.325	3.81	17.4

**Table S5.** Key photovoltaic parameters found from the  $J_{\text{ph}}-V_{\text{eff}}$  curves of IDTN-O, IDTN, Y6-O and Y6 based OCSs.

Active layer	$J_{\text{sat}}^{\text{a}}$ (mA/cm <sup>2</sup> )	$J_{\text{ph}}^{\text{b}}$ (mA/cm <sup>2</sup> )	$J_{\text{ph}}^{\text{c}}$	$J_{\text{ph}}^{\text{b}}/J_{\text{sat}}(\%)$	$J_{\text{ph}}^{\text{c}}/J_{\text{sat}}(\%)$
J71: IDTN-O	18.3	17.2	15.6	93.9	85.2
J71: IDTN	18.2	16.7	15.0	91.7	81.8
PM6: Y6-O	23.6	22.4	20.4	94.9	86.4
PM6: Y6	27.2	25.3	22.8	93.0	83.8

a) The  $J_{\text{ph}}$  when  $V_{\text{eff}}=3.0$  V. b) The  $J_{\text{ph}}$  under short current condition. c) The  $J_{\text{ph}}$  under maximum power output condition.

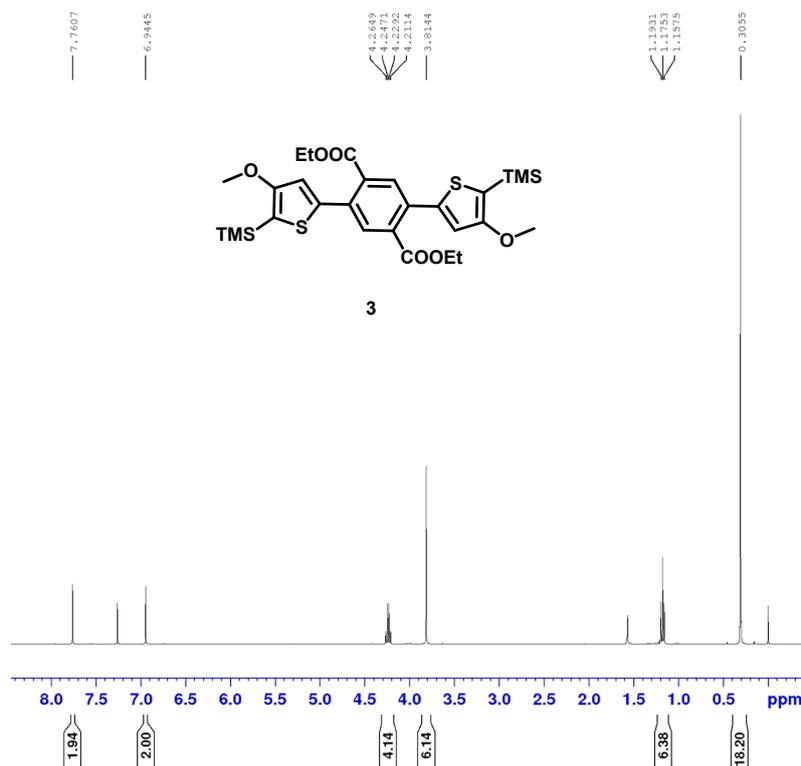


Figure S9. <sup>1</sup>H NMR spectrum of compound 3 (400 MHz, CDCl<sub>3</sub>).

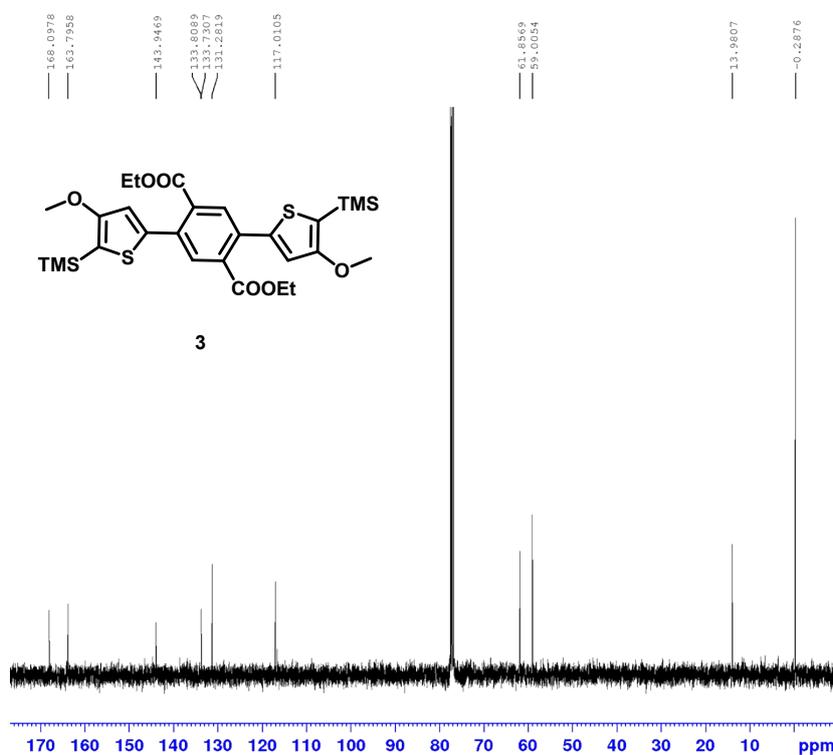
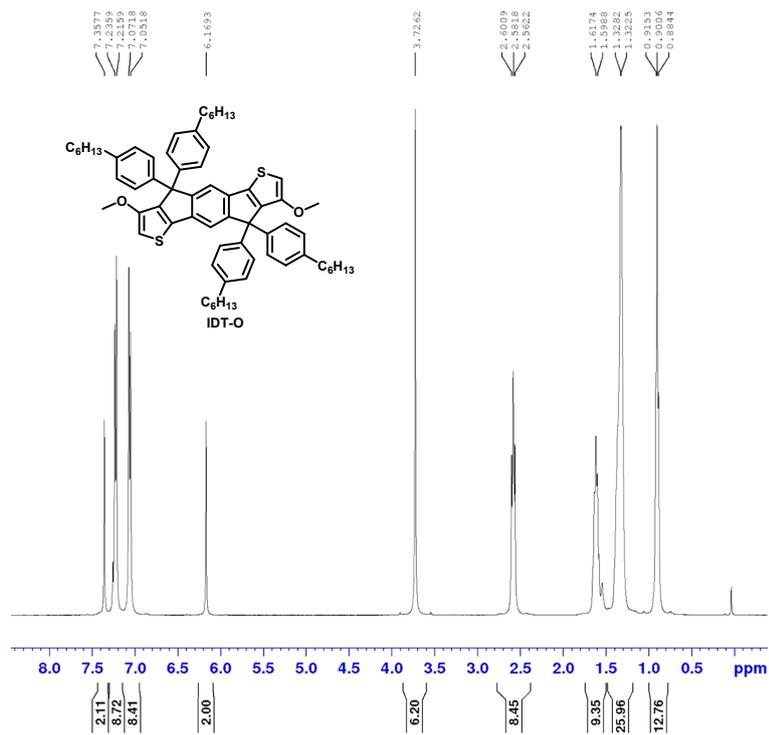
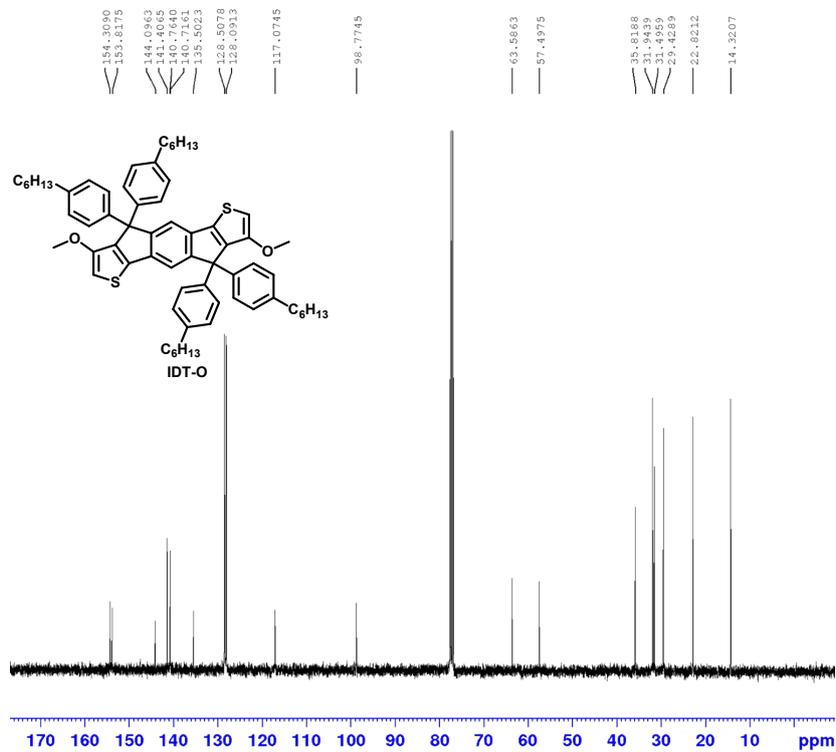


Figure S10. <sup>13</sup>C NMR spectrum of compound 3 (100 MHz, CDCl<sub>3</sub>).



**Figure S11.** <sup>1</sup>H NMR spectrum of IDT-O (400 MHz, CDCl<sub>3</sub>).



**Figure S12.** <sup>13</sup>C NMR spectrum of IDT-O (100 MHz, CDCl<sub>3</sub>).

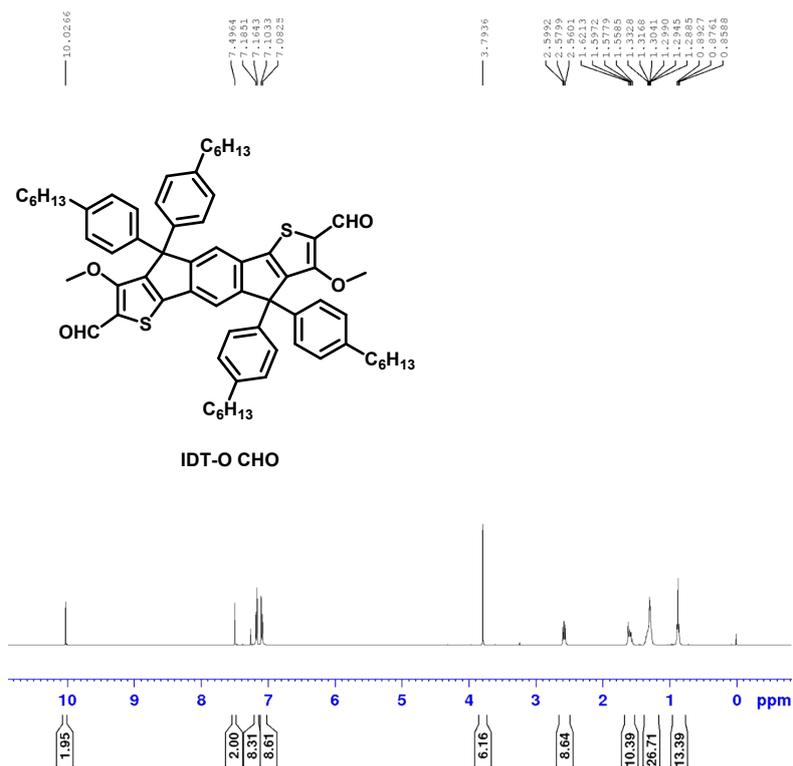


Figure S13. <sup>1</sup>H NMR spectrum of IDT-O CHO (400 MHz, CDCl<sub>3</sub>).

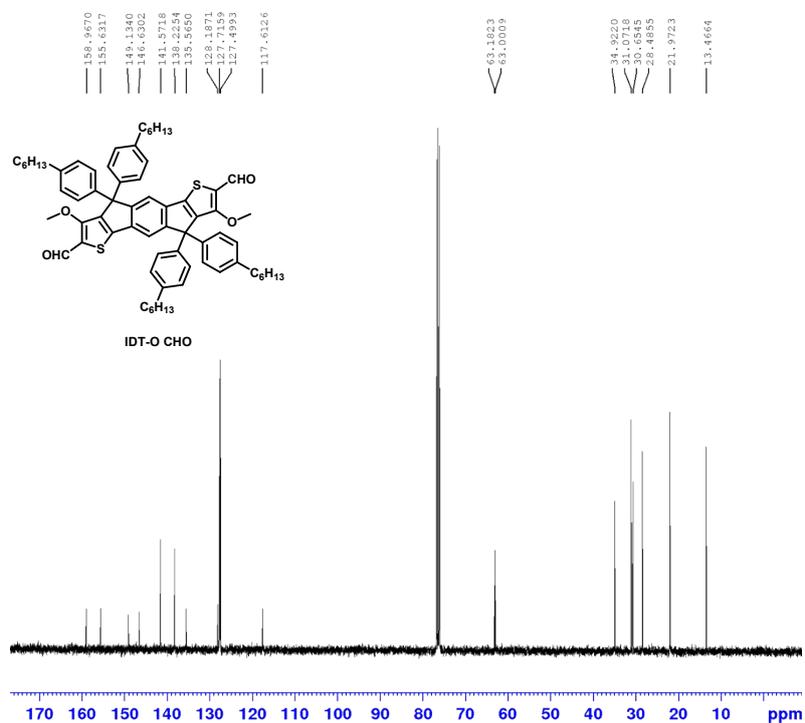
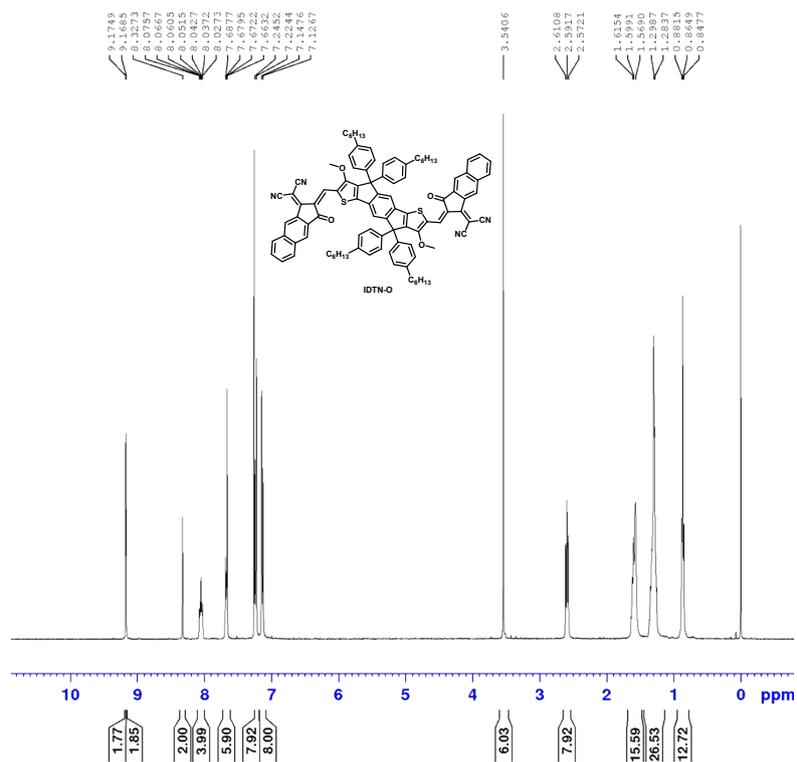
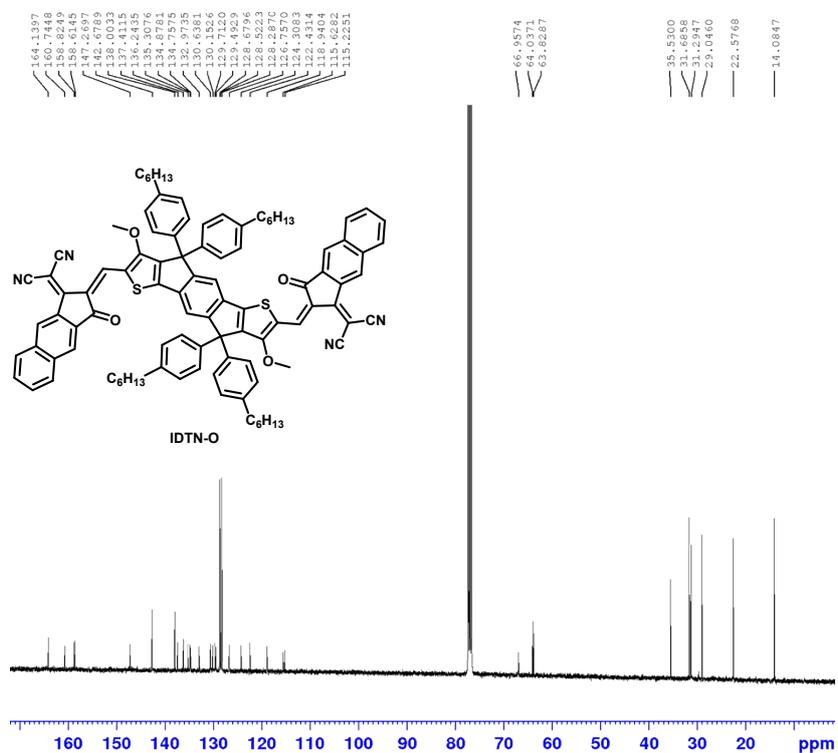


Figure S14. <sup>13</sup>C NMR spectrum of IDT-O CHO (100 MHz, CDCl<sub>3</sub>).



**Figure S15.** <sup>1</sup>H NMR spectrum of IDTN-O (400 MHz, CDCl<sub>3</sub>).



**Figure S16.** <sup>13</sup>C NMR spectrum of IDTN-O (100 MHz, CDCl<sub>3</sub>).

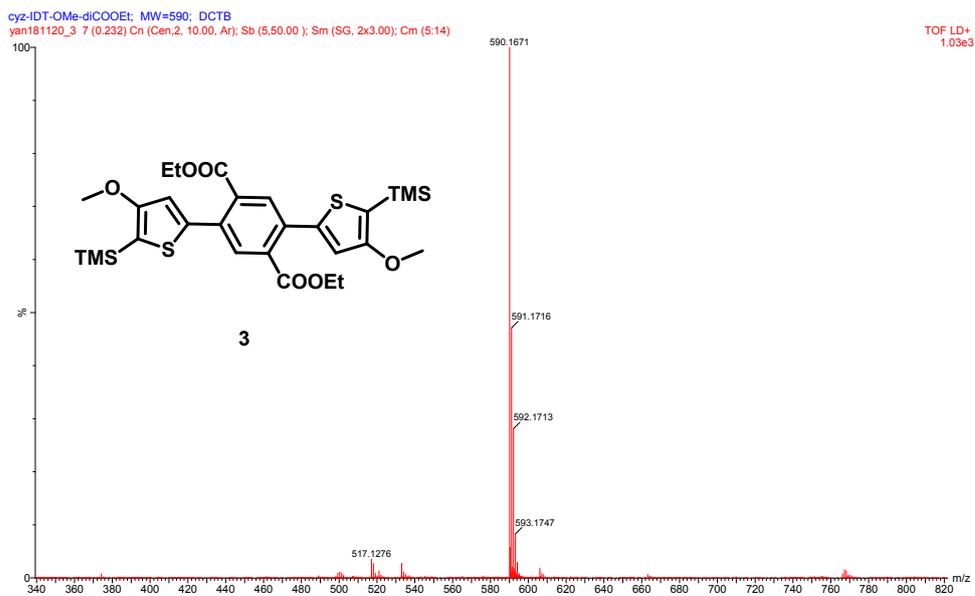


Figure S17. MS spectrum (MALDI-TOF) of compound 3.

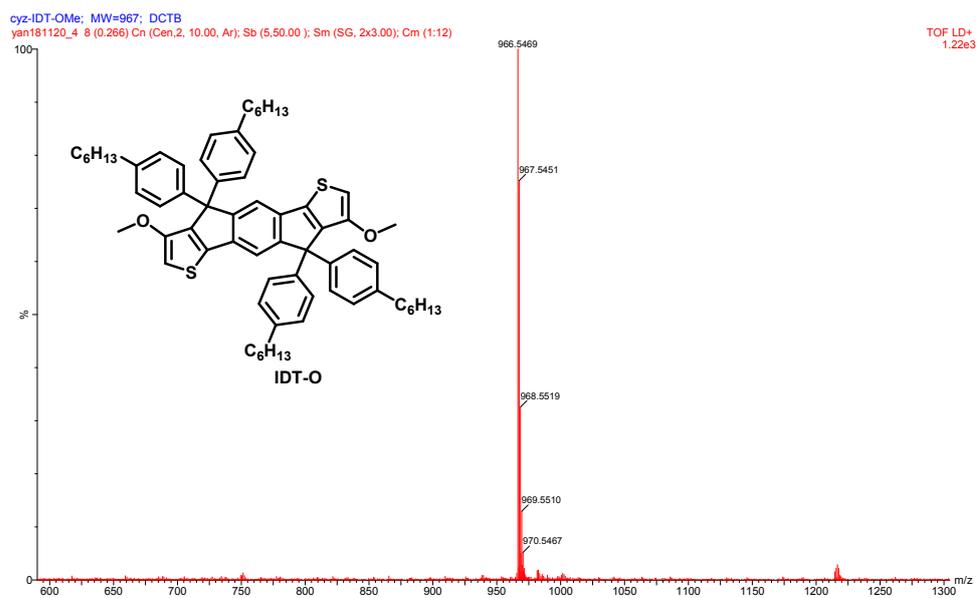


Figure S18. MS spectrum (MALDI-TOF) of IDT-O.



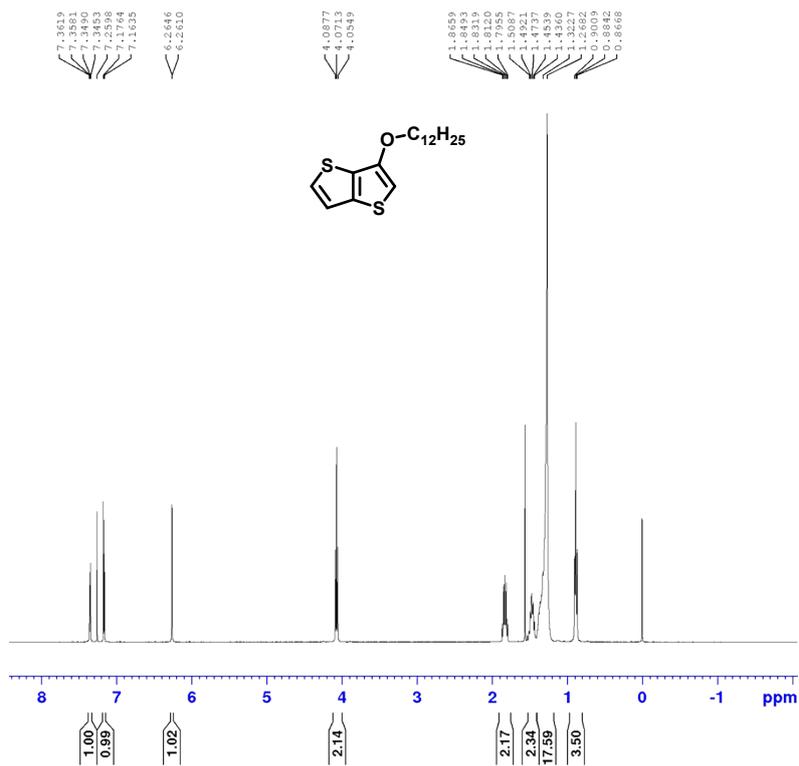


Figure S21. <sup>1</sup>H NMR spectrum of compound 4 (400 MHz, CDCl<sub>3</sub>).

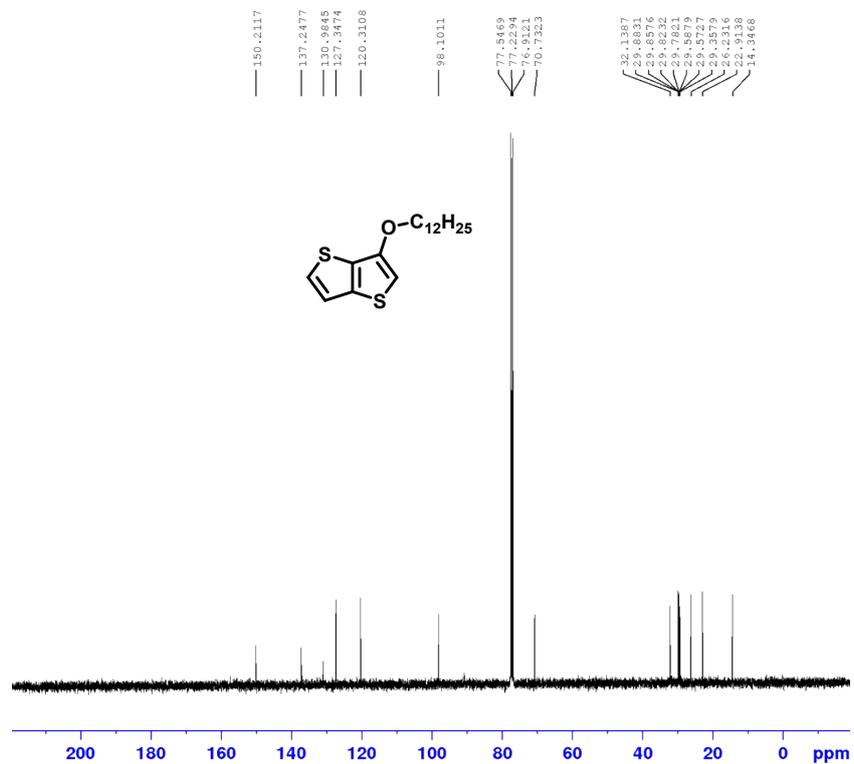
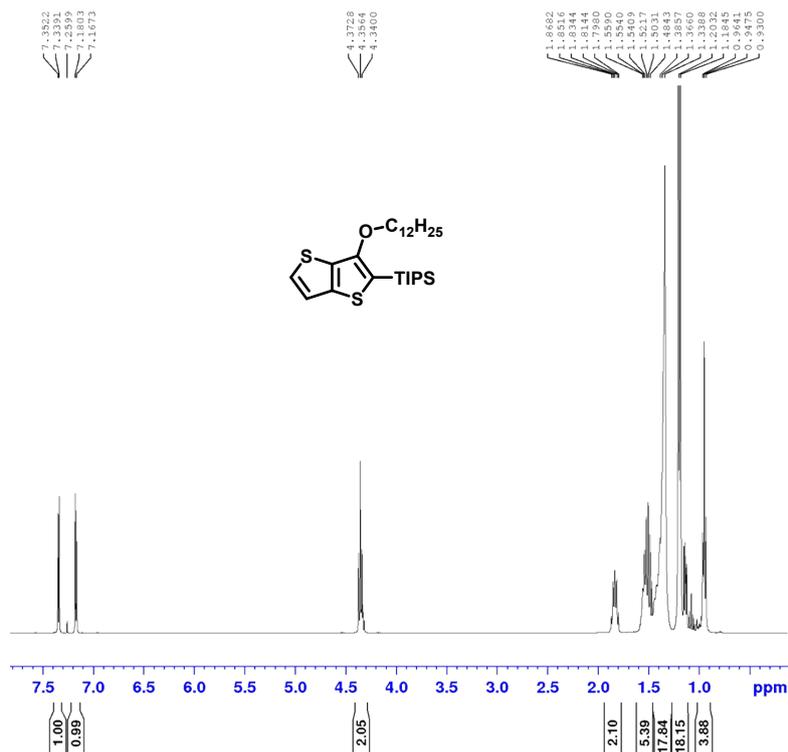
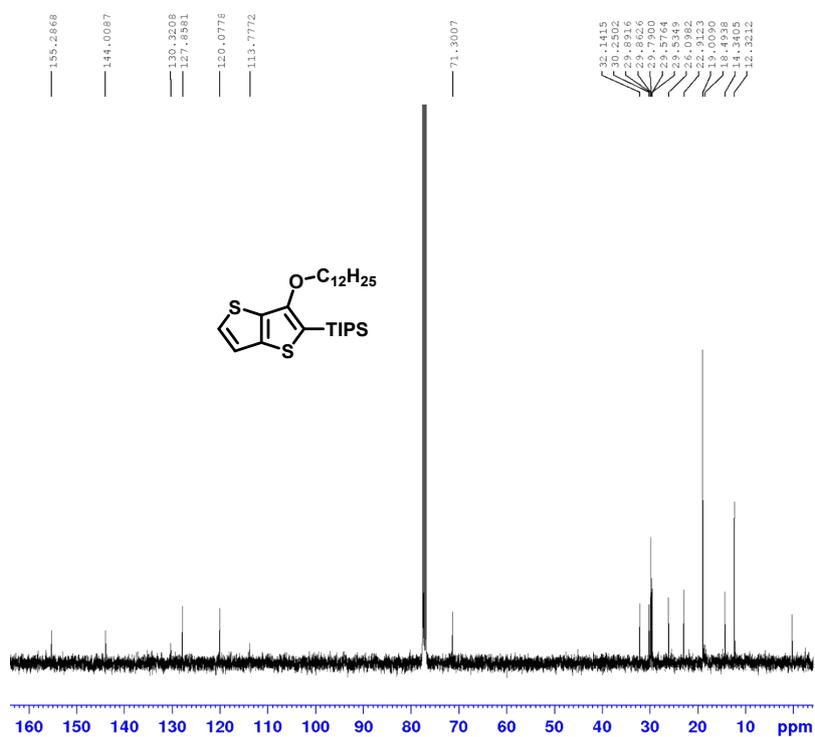


Figure S22. <sup>13</sup>C NMR spectrum of compound 4 (100 MHz, CDCl<sub>3</sub>).



**Figure S23.** <sup>1</sup>H NMR spectrum of compound **5** (400 MHz, CDCl<sub>3</sub>).



**Figure S24.** <sup>13</sup>C NMR spectrum of compound **5** (100 MHz, CDCl<sub>3</sub>).

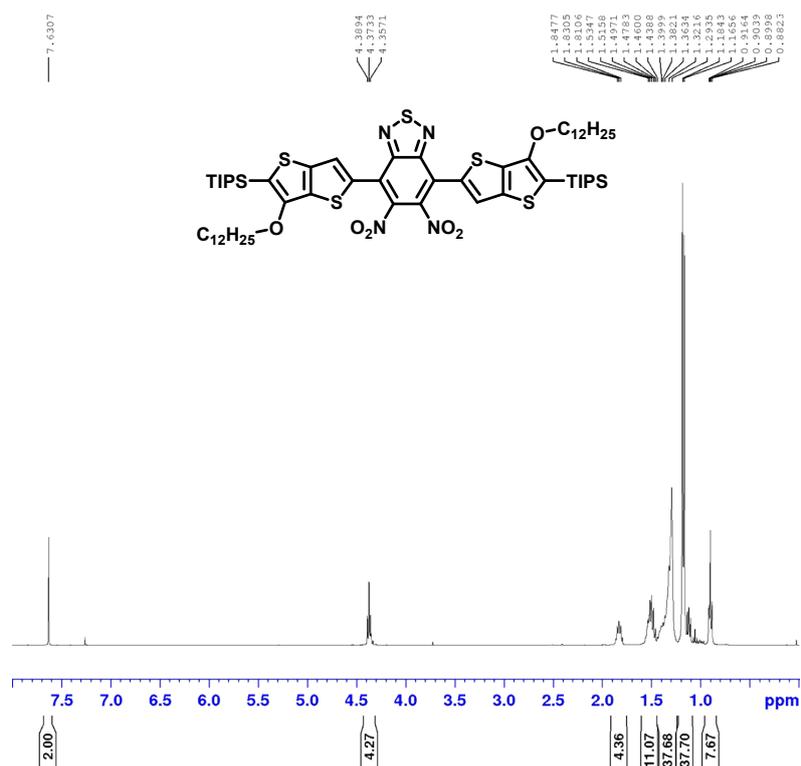


Figure S25. <sup>1</sup>H NMR spectrum of compound 7 (400 MHz, CDCl<sub>3</sub>).

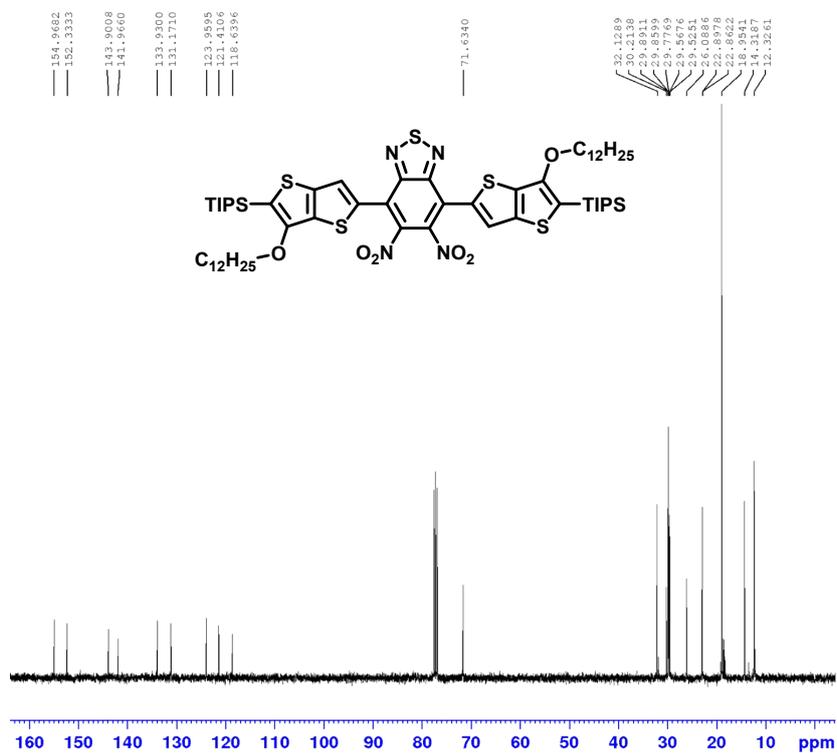


Figure S26. <sup>13</sup>C NMR spectrum of compound 7 (100 MHz, CDCl<sub>3</sub>).









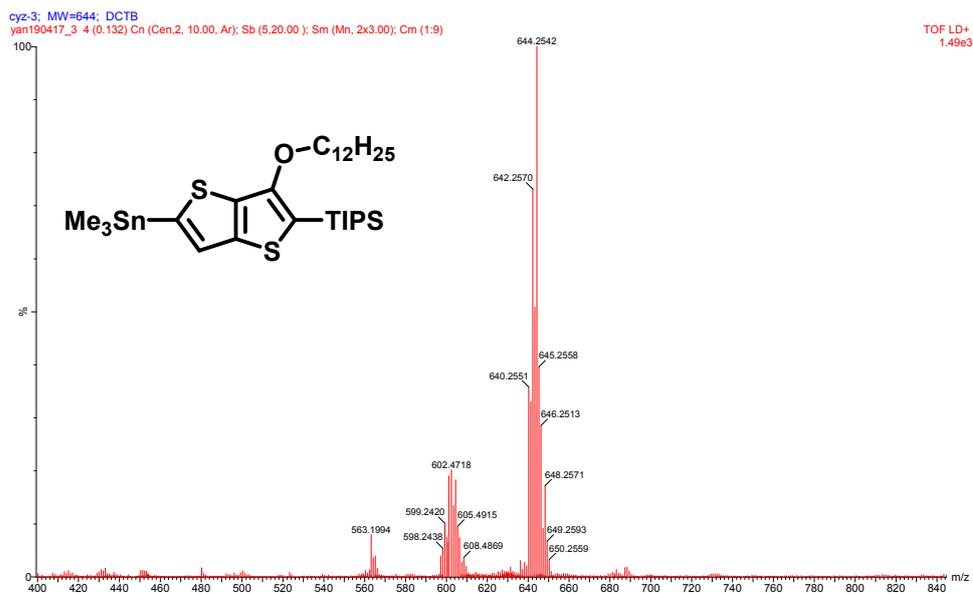


Figure S35. MS spectrum (MALDI-TOF ) of compound 6.

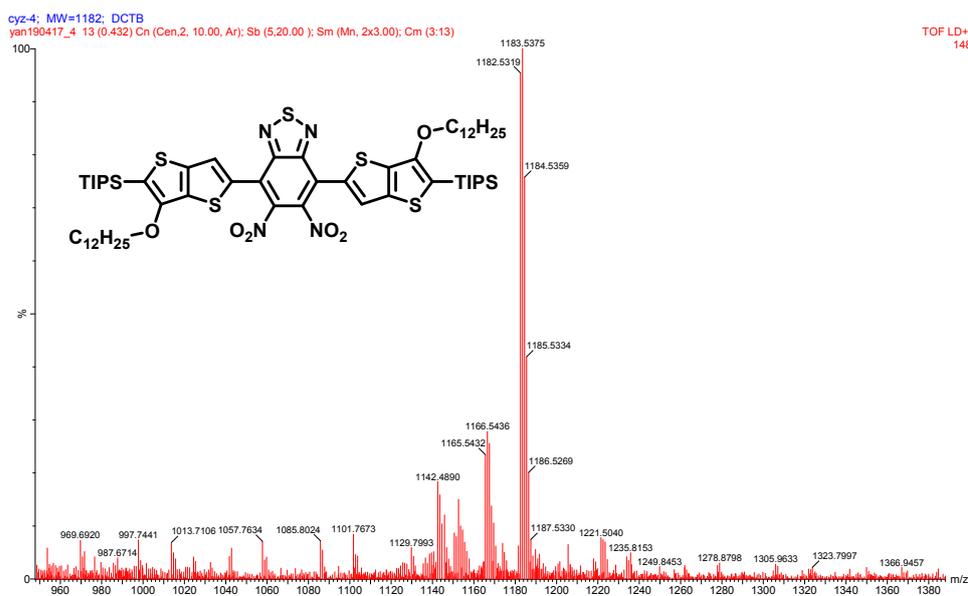
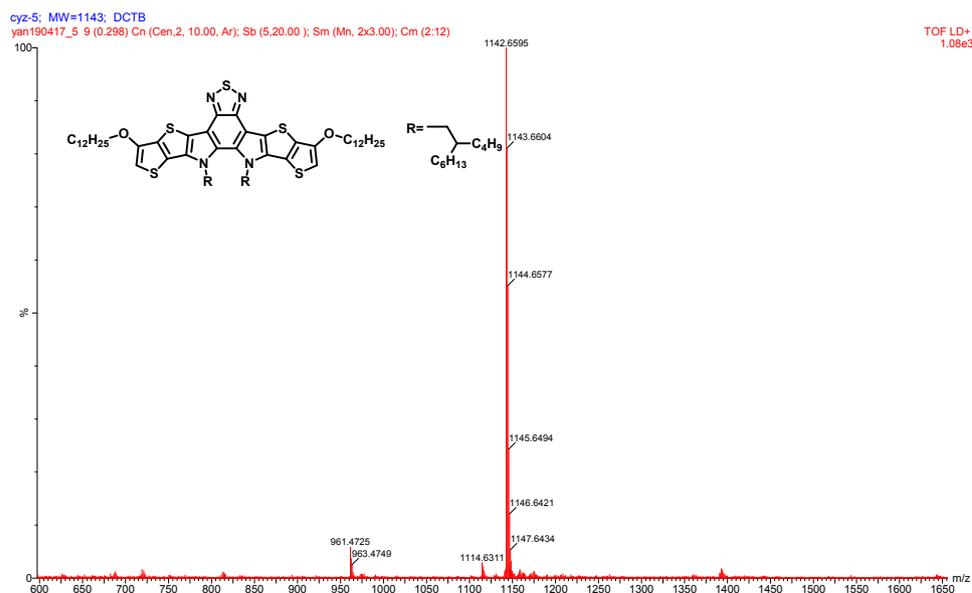
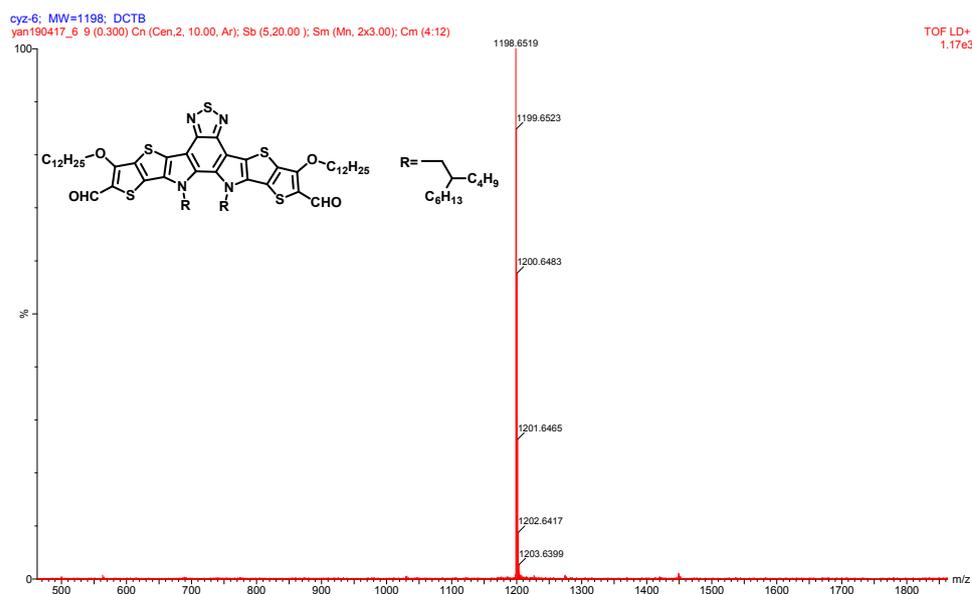


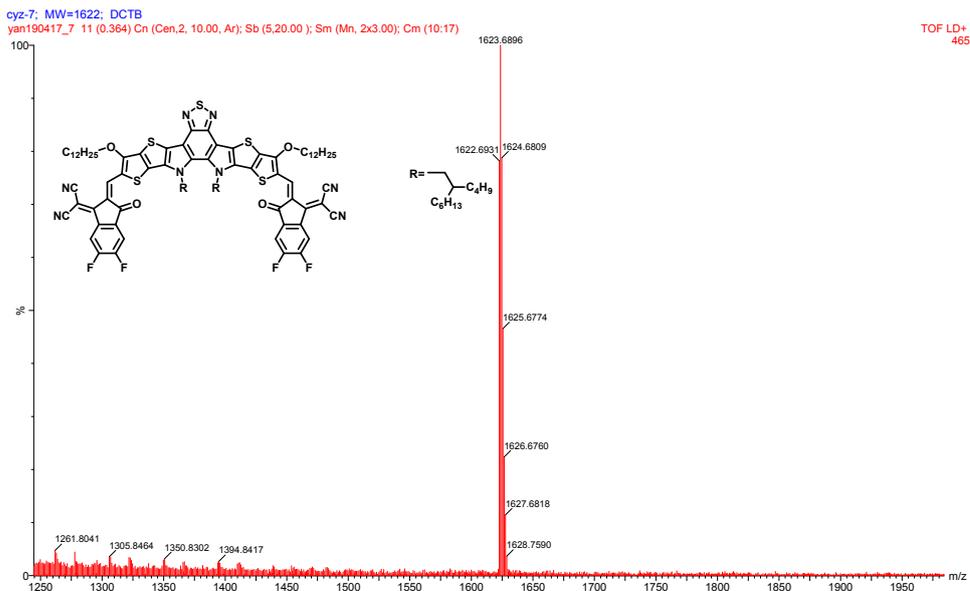
Figure S36. MS spectrum (MALDI-TOF ) of compound 7.



**Figure S37.** MS spectrum (MALDI-TOF ) of compound **8**.



**Figure S38.** MS spectrum (MALDI-TOF ) of compound **9**.



## Reference

1. A. Hexemer, W. Bras, J. Glossinger, E. Schaible, E. Gann, R. Kirian, A. MacDowell, M. Church, B. Rude and H. Padmore, *J. Phys. Conf. Ser.*, 2010, **247**, 012007.
2. J. Ilavsky, *J. Appl. Crystallogr.*, 2012, **45**, 324-328.
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2019, **10**, 570.