

**Incorporation of Alkylthio Side Chains on Benzothiadiazole-based Non-fullerene Acceptors Enables High-performance Organic Solar Cells with over 16% Efficiency**

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**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.

**Materials.** PM6 ( $M_n=24.2$  kDa) was purchased from Solarmer Energy Inc. Tetrahydrofuran was freshly distilled before use from sodium using benzophenone as the indicator. All other reagents and chemicals were purchased from commercial sources and used without further purification.

**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 chloroform solutions of respective small molecules at  $1.0 \times 10^{-5}$  M. 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.  $0.1 \text{ mol L}^{-1}$  tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile was used as the supporting electrolyte. The polymer 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  $100 \text{ mV s}^{-1}$ .

**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.

**Solar cell fabrication and testing.** OSCs were made with a device structure of ITO (indium tin oxide)/PEDOT: PSS(poly(3,4-ethylenedioxythiophene): poly (styrene sulfonate))/PM6: acceptor/ PNDIT-F3N ([9,9-bis(3'-(N,N-dimethylamino)propyl)-

2,7-fluorene)-alt-5,5'-bis(2,2'-thiophene)-2,6-naphthalene-1,4,5,8-tetracarboxylic-N,N'-di(2-ethylhexyl)imide) /Ag. 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 20 min to improve its work function and clearance. A thin PEDOT: PSS (Heraeus Clevis P VPA 4083) layer with a thickness of about 40 nm was spin-coat onto the ITO substrates at 4000rpm for 40 s, and then dried at 150 °C for 15 min in air. The PEDOT: PSS coated ITP substrates were transferred to a N<sub>2</sub>-filled glove box for further processing. The donor: acceptor blends with a weight ratio of 1:1.2 and a total concentration of 16 mg/mL dissolved in chloroform. Then the solution was stirred overnight for intensive mixing in a nitrogen-filled glove box. Then, 0.5% 1-chloronaphthalene was added to the chloroform solution 30 minutes before spin coating. The blend solution was spin-cast on the top of PEDOT: PSS layer immediately after being stirred on a hotplate of 58 °C for 30 minutes at 2500 rpm for 40 s. Then the devices were put into vacuum to remove the additive and annealed at 100 °C for 5 min to facilitate phase separation and morphology optimization. A thin layer of PNDIT-F3N (~10 nm) was cast onto the processed active layer, and the Ag layer (~200 nm) was deposited in a thermal evaporator under 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 100nm. 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 cm<sup>-2</sup>) 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.

**EQE measurements.** 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.

**Hole-mobility measurements.** The hole-mobilities were measured using the space charge limited current (SCLC) method, employing a device architecture of

ITO/PEDOT:PSS/blend film/MoO<sub>3</sub>/Al. The mobilities were obtained by taking current-voltage curves and fitting the results to a space charge limited form, where the SCLC is described by:

$$J = \frac{9\varepsilon_0\varepsilon_r\mu(V_{appl} - V_{bi} - V_s)^2}{8L^3}$$

Where  $\varepsilon_0$  is the permittivity of free space,  $\varepsilon_r$  is the relative permittivity of the material (assumed to be 3),  $\mu$  is the hole mobility and  $L$  is the thickness of the film. Hole mobilities can be found from the plots of  $J^{1/2}$  vs  $V_{appl} - V_{bi} - V_s$ .

**Electron mobility measurements.** The electron mobilities were measured using the SCLC method, employing a device architecture of ITO/ZnO/blend film/Ca/Al. The mobilities were obtained by taking current-voltage curves and fitting the results to a space charge limited form, where the SCLC is described by:

$$J = \frac{9\varepsilon_0\varepsilon_r\mu(V_{appl} - V_{bi} - V_s)^2}{8L^3}$$

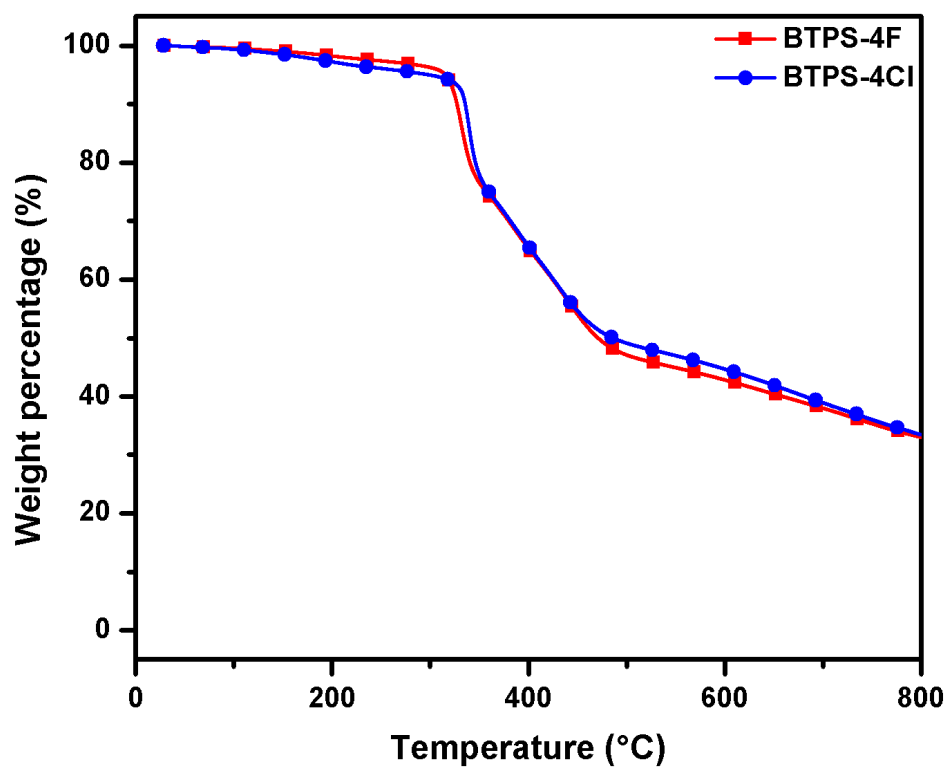
Where  $\varepsilon_0$  is the permittivity of free space,  $\varepsilon_r$  is the relative permittivity of the material (assumed to be 3),  $\mu$  is the hole mobility and  $L$  is the thickness of the film. Electron mobilities from the plots of  $J^{1/2}$  vs  $V_{appl} - V_{bi} - V_s$ .

**GIWAXS characterization.** GIWAXS measurements were performed at beamline 7.3.3 at the Advanced Light Source.<sup>[3]</sup> Samples were prepared on Si substrates using identical blend solutions as those used in devices. The 10 keV X-ray beam was incident at a grazing angle of 0.11° - 0.15°, 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>[4]</sup> The uncertainty for the peak fitting of the GIWAXS data is 0.3 Å. The coherence length was calculated using the Scherrer equation:

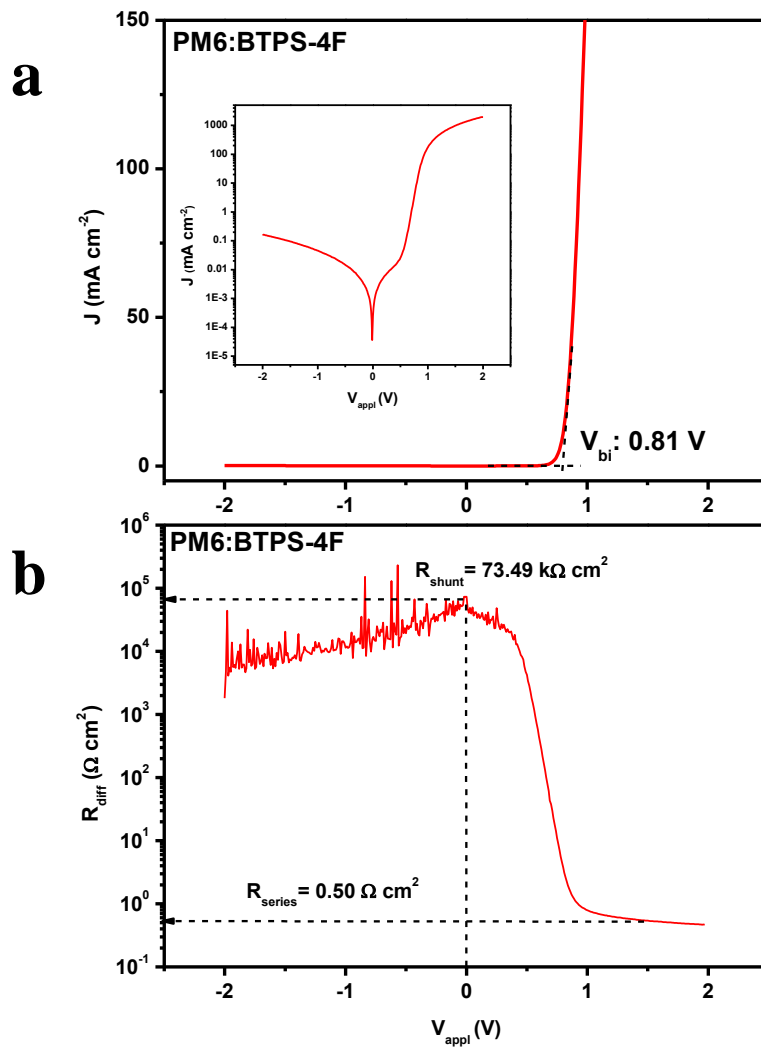
$$L_c = \frac{2\pi K}{\Delta q}$$

**R-SoXS characterization.** R-SoXS transmission measurements were performed at beamline 11.0.1.2 at the Advanced Light Source.<sup>[5]</sup> Samples for R-SoXS measurement were prepared on a PSS modified Si substrate under the same conditions as those used for device fabrication, and then transferred by floating in water to a 1.5 mm × 1.5 mm, 100 nm thick Si<sub>3</sub>N<sub>4</sub> membrane supported by a 5 mm × 5 mm, 200 μm thick Si frame

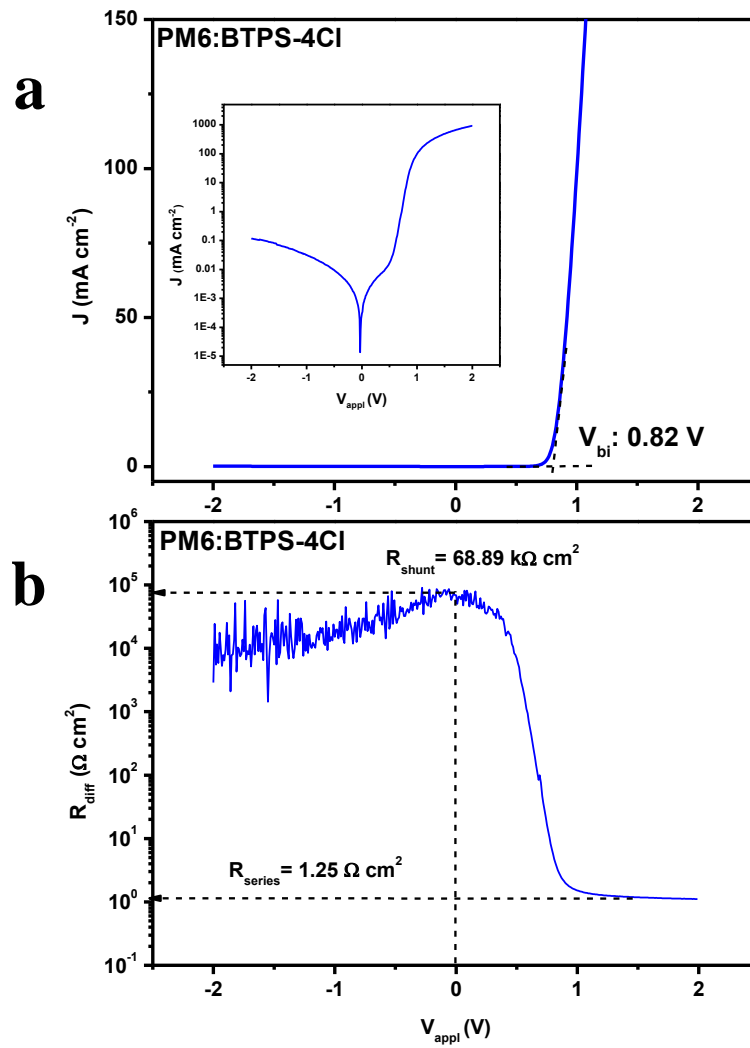
(Norcada Inc.). 2D scattering patterns were collected on an in-vacuum CCD camera (Princeton Instrument PI-MTE). The sample detector distance was calibrated from diffraction peaks of a triblock copolymer poly(isoprene-*b*-styrene-*b*-2-vinyl pyridine), which has a known spacing of 391 Å. The beam size at the sample is approximately 100 μm by 200 μm.



**Figure S1.** Thermogravimetric curves of BTPS-4F and BTPS-4Cl. The thermal degradation temperature ( $T_d$  at 5% weight loss) of BTPS-4F and BTPS-4Cl are 315 °C and 299 °C respectively.

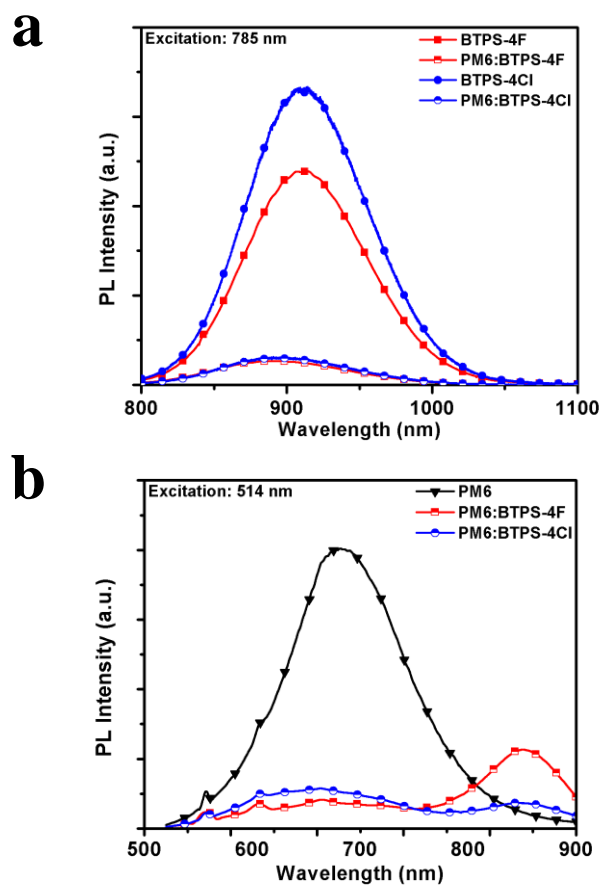


**Figure S2.** (a)  $J$ - $V$  characteristics and (b) differential resistance  $R_{\text{diff}}$  of BTPS-4F-based devices in the dark.



**Figure S3.** (a)  $J$ - $V$  characteristics and (b) differential resistance  $R_{\text{diff}}$  of BTPS-4Cl-based devices in the dark.

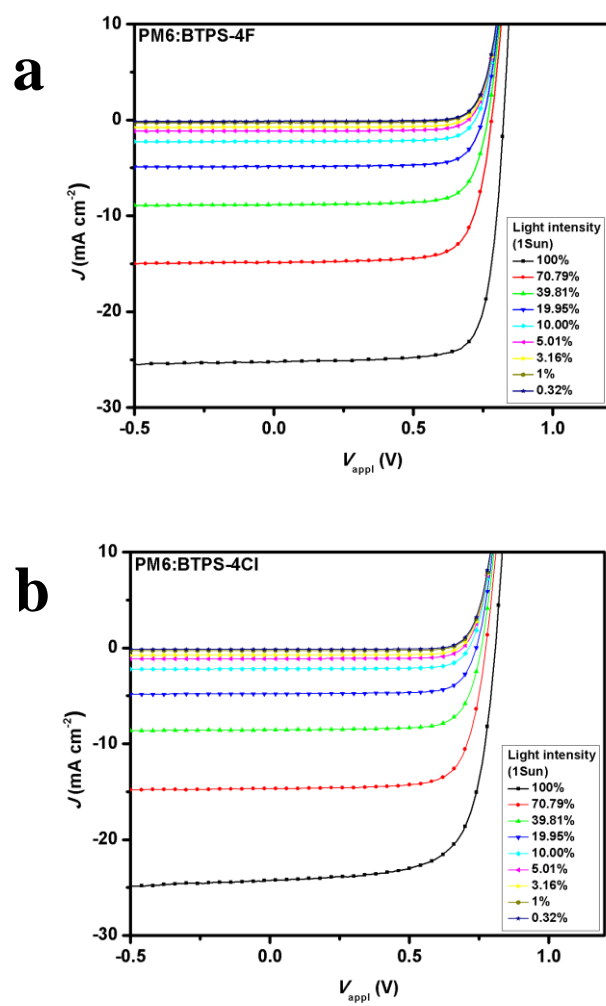




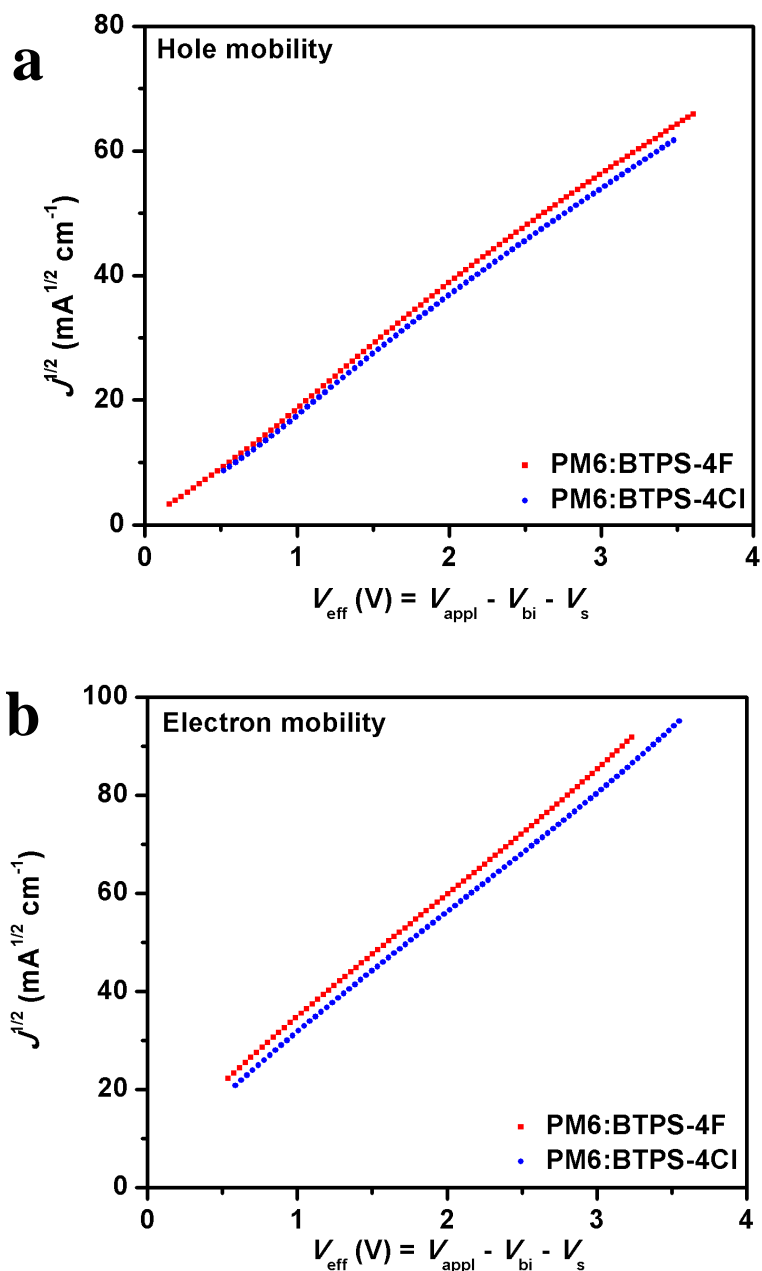
**Figure S4.** Photoluminescence quenching experiments of (a) pure BTPS-4F, pure BTPS-4Cl, PM6:BTPS-4F and PM6:BTPS-4Cl films excited at 785 nm; (b) PM6, PM6:BTPS-4F and PM6:BTPS-4Cl films excited at 514 nm.

**Table S1. Photoluminescence quenching efficiencies**

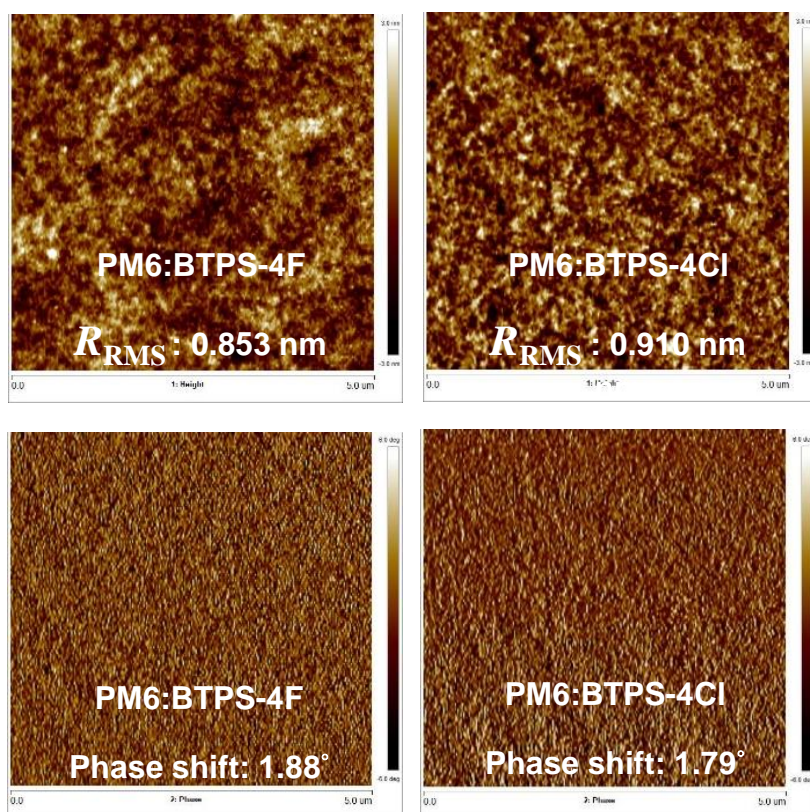
Material	Excited by 785 nm laser	Excited by 514 nm laser
BTPS-4F	0.878	0.865
BTPS-4Cl	0.903	0.778



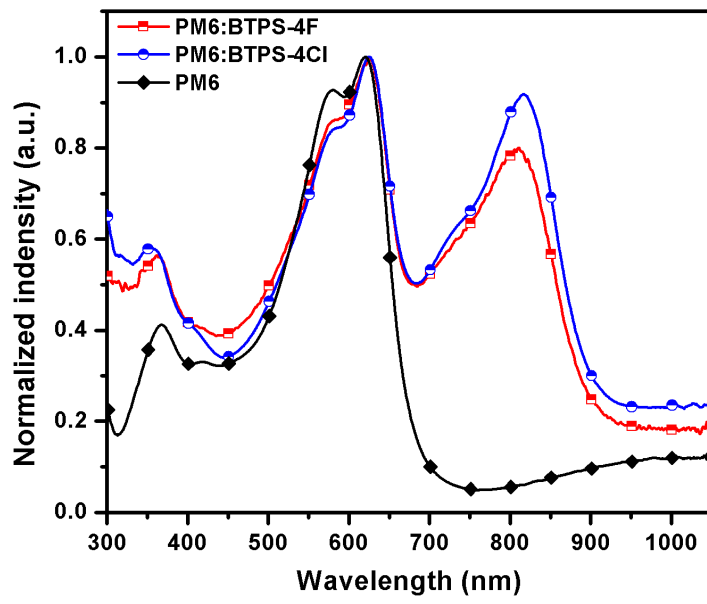
**Figure S5.** Light-intensity-dependent  $J$ - $V$  characteristics of (a) BTSP-4F- and (b) BTSP-4Cl-based devices.



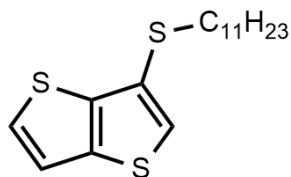
**Figure S6.**  $J^{1/2} \sim V_{\text{eff}}$  characteristics of (a) hole-only devices and (b) electron-only devices based on PM6:BTPS-4F and PM6:BTPS-4Cl. Effective voltage ( $V_{\text{eff}}$ ) is obtained by subtracting built-in voltage ( $V_{\text{bi}}$ ) and voltage drop due to series resistance ( $V_{\text{s}}$ ) from applied voltage ( $V_{\text{appl}}$ ).



**Figure S7.** 5 μm by 5 μm AFM images. Height mode colour bar: ± 3.0 nm, phase mode colour bar: ± 6.0°.

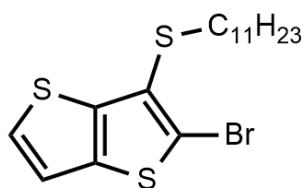


**Figure S8.** UV-vis spectra of PM6:BTTPS-4F, PM6:BTTPS-4Cl and PM6 in thin film states.



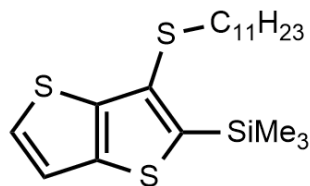
### Synthesis of compound 1

To a solution of 3-bromothieno[3,2-b]thiophene (8.18 g, 4.85 mL, 37.3 mmol) in anhydrous diethyl ether (100 mL) was added *n*-BuLi (20.5 mL, 41.1 mmol, 2 M in hexane) dropwise at -78 °C under N<sub>2</sub>. The mixture was kept at -78 °C for 1 h. Sulphur (1.32 g, 41.1 mmol) was added in 1 portion at 0 °C. The mixture was kept at 0 °C for 1 h. 1-bromoundecane (9.66 g, 9.11 mL, 41.1 mmol) was added slowly at 0 °C. The mixture was stirred overnight. HCl (1 M) was added to quench the reaction. The mixture was extracted with diethyl ether. The combined organic phase was washed with water followed by brine. Then the solution was dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated with reduced pressure. The mixture was purified using column chromatography on silica gel (eluent: n-hexane: CH<sub>2</sub>Cl<sub>2</sub> = 10:1, v/v) to yield a white solid (850 mg, 28.6%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.40 (d, *J* = 5.4 Hz, 1H), 7.25 (d, *J* = 4.5 Hz, 2H), 2.92 (q, *J* = 6.6 Hz, 2H), 1.65 – 1.55 (m, 2H), 1.41 (q, *J* = 6.9 Hz, 2H), 1.25 (d, *J* = 5.3 Hz, 14H), 0.88 (q, *J* = 6.3 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 141.80, 138.75, 127.65, 126.77, 124.21, 120.12, 34.43, 31.93, 29.66, 29.62, 29.60, 29.51, 29.35, 29.16, 28.58, 22.71, 14.15.



### Synthesis of compound 2

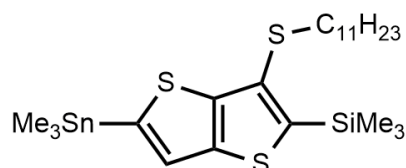
To a solution of compound 1 (2.24 g, 6.89 mmol) in *N,N*-dimethylformamide (5 mL) was added *N*-bromosuccinimide (1.22 g, 6.89 mmol) slowly at 0 °C under ambient conditions. The solution was stirred at room temperature for 3 h. Acetone was added to quench the reaction. The mixture was extracted with diethyl ether. The combined organic phase was washed with water followed by HCl (1 M), then brine. The mixture was purified by flash column chromatography (eluent: n-hexane) to yield a colorless oil (2.75 g, 99%). <sup>1</sup>H NMR (400 MHz, Acetone) δ 7.73 (d, *J* = 5.3 Hz, 1H), 7.42 (d, *J* = 5.3 Hz, 1H), 2.98 (t, *J* = 7.0 Hz, 2H), 1.60 – 1.49 (m, 2H), 1.49 – 1.38 (m, 2H), 1.26 (d, *J* = 6.3 Hz, 14H), 0.91 – 0.83 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 141.77, 136.34, 126.68, 124.88, 119.75, 118.66, 34.43, 31.94, 31.62, 29.98, 29.62, 29.59, 29.51, 29.36, 29.13, 28.46, 22.72, 14.17.



### Synthesis of compound 3

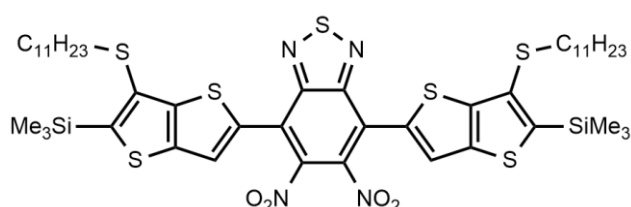
To a solution of compound 2 (320 mg, 0.789 mmol) in anhydrous tetrahydrofuran (10 mL) was added *n*-BuLi (0.35 mL, 0.829 mmol, 2.4 M in hexane) dropwise at -78 °C under N<sub>2</sub>. The mixture was kept at -78 °C for 2 h. Chlorotrimethylsilane (94.2 mg, 0.11

mL, 0.868 mmol) was added dropwise at  $-78\text{ }^{\circ}\text{C}$ . The mixture was stirred overnight. Water was added to quench the reaction. The mixture was extracted with diethyl ether. The combined organic phase was washed with water followed by brine. Then the solution was dried with  $\text{Na}_2\text{SO}_4$  and concentrated with reduced pressure. The mixture was purified using column chromatography on silica gel (eluent: n-hexane) to yield a colorless oil (150 mg, 47.7%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (d,  $J = 5.2$  Hz, 1H), 7.22 (d,  $J = 5.2$  Hz, 1H), 2.95 – 2.87 (m, 2H), 1.66 – 1.53 (m, 2H), 1.36 (dd,  $J = 13.2, 6.4$  Hz, 2H), 1.33 – 1.21 (m, 14H), 0.88 (t,  $J = 6.8$  Hz, 3H), 0.42 (s, 9H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.74, 145.06, 142.72, 129.94, 128.16, 119.89, 34.98, 31.92, 30.09, 29.61, 29.59, 29.51, 29.34, 29.16, 28.86, 22.71, 14.14.



#### Synthesis of compound 4

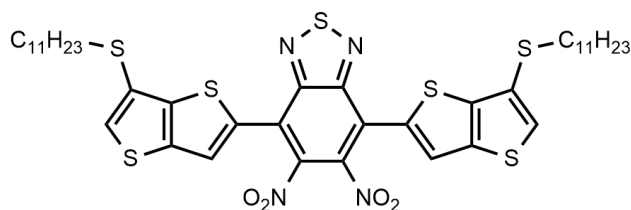
To a solution of compound 3 (62.1 mg, 0.156 mmol) in anhydrous tetrahydrofuran (3 mL) was added *n*-BuLi (0.081 mL, 0.171 mmol, 2 M in hexane) dropwise at  $-78\text{ }^{\circ}\text{C}$  under  $\text{N}_2$ . The mixture was kept at  $-78\text{ }^{\circ}\text{C}$  for 1 h. Trimethyltin chloride (0.171 mL, 0.171 mmol, 1 M in THF) was added dropwise at  $-78\text{ }^{\circ}\text{C}$ . The mixture was stirred overnight. Water was added to quench the reaction. The mixture was extracted with diethyl ether. The combined organic phase was washed with water followed by brine. Then the solution was dried with  $\text{Na}_2\text{SO}_4$  and concentrated with reduced pressure to yield a dark oil (57 mg, 65.4%). The crude product was used in the next step without any further purification.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 (s, 1H), 2.93 (td,  $J = 7.5, 1.0$  Hz, 2H), 1.60 (t,  $J = 7.5$  Hz, 2H), 1.38 (t,  $J = 7.4$  Hz, 2H), 1.24 (s, 14H), 0.88 (dd,  $J = 5.0, 2.1$  Hz, 3H), 0.41 (dd,  $J = 2.7, 0.9$  Hz, 18H).



#### Synthesis of compound 5

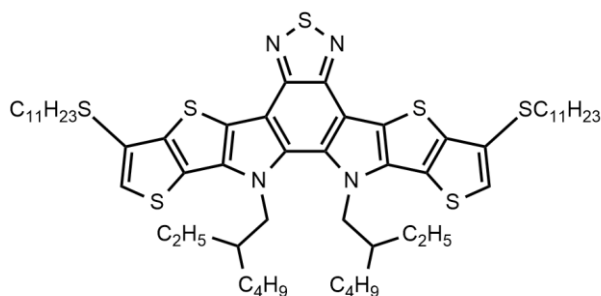
Compound 4 (57 mg, 0.102 mmol), 4,7-dibromo-5,6-dinitrobenzo[*c*][1,2,5]thiadiazole (17.7 mg, 0.0461 mmol), tris(dibenzylideneacetone)dipalladium(0) (2.1 mg, 2.31 nmol) and tri(*o*-tolyl)phosphine (5.61 mg, 18.5 nmol) were dissolved in anhydrous toluene (3 mL) under  $\text{N}_2$ . The mixture was stirred at  $110\text{ }^{\circ}\text{C}$  overnight. Saturated KF aqueous solution was added to quench the reaction. The mixture was extracted with chloroform. The combined organic phase was washed with water followed by brine. Then the solution was dried with  $\text{Na}_2\text{SO}_4$  and concentrated with reduced pressure. The mixture was purified using column chromatography on silica gel (eluent: n-hexane:  $\text{CH}_2\text{Cl}_2 = 5:1$ , v/v) to yield a dark-red oil (44.3 mg, 94.3%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 (s, 2H), 2.98 – 2.90 (m, 4H), 1.70 – 1.58 (m, 4H), 1.41 (s, 4H), 1.26 (d,  $J = 13.1$  Hz,

28H), 0.86 (t,  $J = 7.0$  Hz, 6H), 0.46 (s, 18H).



### Synthesis of compound 6

Compound 5 (110 mg, 0.108 mmol) was dissolved in chloroform (10 mL) under ambient conditions. The mixture was cooled to 0 °C and trifluoroacetic acid (1 mL) was added dropwise. The mixture was warmed to room temperature and stirred for 15 min. Water was added to quench the reaction. The mixture was extracted with chloroform. The combined organic phase was washed with water followed by brine. Then the solution was dried with  $\text{Na}_2\text{SO}_4$  and concentrated with reduced pressure. The mixture was purified using column chromatography on silica gel (eluent: n-hexane:  $\text{CH}_2\text{Cl}_2 = 3:1$ , v/v) to yield a dark-red solid (93.5 mg, 99%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (s, 2H), 7.37 (s, 2H), 2.94 (t,  $J = 7.3$  Hz, 4H), 1.65 (p,  $J = 7.4$  Hz, 4H), 1.42 (p,  $J = 7.1$  Hz, 4H), 1.26 (d,  $J = 5.9$  Hz, 28H), 0.87 (t,  $J = 6.7$  Hz, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  151.93, 145.99, 141.67, 138.78, 131.14, 129.47, 124.75, 123.98, 121.21, 34.64, 31.88, 29.68, 29.60, 29.58, 29.57, 29.49, 29.31, 29.13, 28.56, 22.67, 14.12. **MALDI-TOF MS**: Calculated for  $\text{C}_{40}\text{H}_{50}\text{N}_4\text{O}_4\text{S}_7\text{H}$  (M<sup>-</sup>): 873.1804, Found: 873.1774.

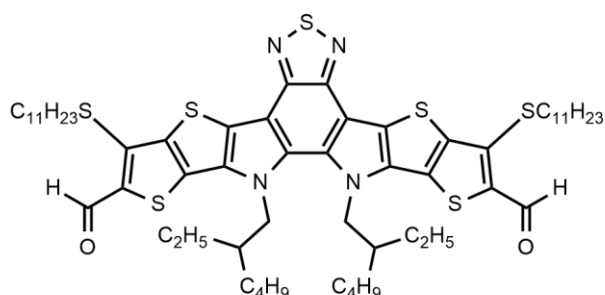


### Synthesis of compound 7

Compound 6 (100 mg, 0.114 mmol) and triphenylphosphine (360 mg, 1.37 mmol) were dissolved in anhydrous 1,2-dichlorobenzene (3 mL) under  $\text{N}_2$ . The mixture was stirred at 160 °C overnight. The mixture was poured to methanol to quench the reaction. The residue was washed with methanol twice by centrifugation (7000 RPM, 3 min) to yield a red solid (91 mg). The crude product (red powder), potassium carbonate (78.8 mg, 0.570 mmol), appropriate alkyl bromide (130 mg, 0.672 mmol) and potassium iodide (30 mg) were dissolved in anhydrous N,N-dimethylformamide (5 mL) under  $\text{N}_2$ . The solution was stirred at 80 °C overnight. Ethyl acetate, water and HCl (1M) were added to quench the reaction. The mixture was extracted with ethyl acetate. The combined organic phase was washed with water followed by brine. Then the solution was dried with  $\text{Na}_2\text{SO}_4$  and concentrated with reduced pressure. The mixture was purified using column chromatography on silica gel (eluent: n-hexane:  $\text{CH}_2\text{Cl}_2 = 3:1$ , v/v) to yield an orange solid (41 mg, 34.6% over 2 steps).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 (s, 2H), 4.67 – 4.49 (m, 4H), 3.04 (t,  $J = 7.3$  Hz, 4H), 2.02 (p,  $J = 6.7$  Hz, 2H), 1.68 (p,  $J = 7.4$  Hz, 4H), 1.44 (t,  $J = 7.3$  Hz, 4H), 1.26 (d,  $J = 8.5$  Hz, 28H), 1.06 (dq,  $J = 12.4, 5.3, 3.6$  Hz, 4H), 0.95 – 0.80 (m, 18H), 0.67 – 0.56 (m, 12H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.62, 144.01, 136.85, 131.53, 126.40, 124.00, 123.86, 123.19, 111.68, 54.98, 39.99,

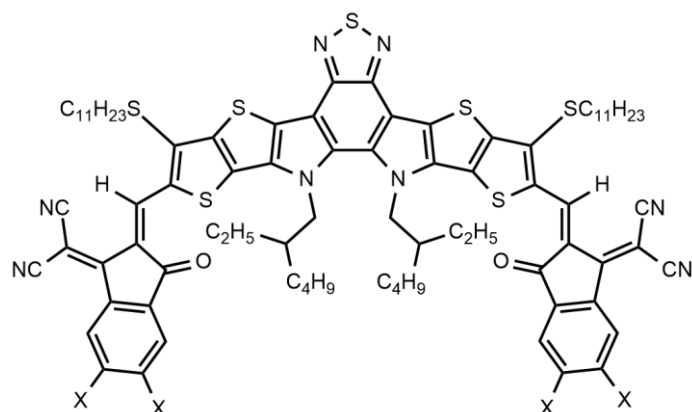


34.51, 31.93, 29.79, 29.62, 29.54, 29.36, 29.20, 28.65, 27.66, 23.11, 22.72, 22.71, 14.15, 13.73, 10.08, 10.06. **MALDI-TOF MS:** Calculated for  $C_{56}H_{82}N_4S_7H$  ( $M^+$ ): 1035.4657, Found: 1035.4654.



### Synthesis of compound 8

Phosphoryl trichloride (0.2 mL) was added dropwise to anhydrous *N,N*-dimethylformamide (1 mL) under  $N_2$  at 0 °C. The mixture was stirred at room temperature for 30 min to generate Vilsmeier agent in situ. In another Schlenk flask, compound 7 was dissolved in 1,2-dichloroethane (5 mL) under  $N_2$ . Vilsmeier agent was added dropwise to the substrate at 0 °C. The reaction mixture was kept at room temperature for 30 min, then heat to 80 °C and stirred overnight. To quench the reaction, let the solution cool down to room temperature then slowly add saturated solution of sodium carbonate. The mixture was stirred at room temperature for 30 min. The mixture was extracted with chloroform. The combined organic phase was washed with water followed by brine. Then the solution was dried with  $Na_2SO_4$  and concentrated with reduced pressure. The mixture was purified using column chromatography on silica gel (eluent: *n*-hexane:  $CH_2Cl_2$  = 1:1, v/v) to yield an orange solid (50 mg, 94.9%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  10.29 (d,  $J$  = 4.9 Hz, 2H), 4.63 (d,  $J$  = 8.3 Hz, 4H), 3.20 (q,  $J$  = 6.6, 5.9 Hz, 4H), 1.99 (q,  $J$  = 7.6, 7.0 Hz, 2H), 1.67 (q,  $J$  = 7.0 Hz, 4H), 1.52 – 1.35 (m, 4H), 1.25 (d,  $J$  = 11.4 Hz, 28H), 1.09 – 0.80 (m, 22H), 0.72 – 0.52 (m, 12H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  183.23, 147.49, 145.56, 140.80, 137.11, 136.58, 132.82, 129.10, 127.33, 112.52, 55.22, 53.46, 40.19, 35.32, 31.90, 31.61, 30.16, 29.59, 29.57, 29.54, 29.49, 29.33, 29.11, 28.49, 27.51, 23.09, 22.69, 14.13, 13.68, 10.08. **MALDI-TOF MS:** Calculated for  $C_{58}H_{82}N_4O_2S_7H$  ( $M^+$ ): 1091.4556, Found: 1091.4556.



### Synthesis of BTPS-4F and BTPS-4Cl

Compound 8, appropriate end groups ( $X = F$  or  $Cl$ ) (5 equivalents) and pyridine (1 mL) were dissolved in anhydrous chloroform (10 mL). The mixture was stirred at 60 °C for 1 h. Without quenching, extraction and concentration, the reaction mixture was purified using column chromatography on silica gel (eluent: *n*-hexane:  $CH_2Cl_2$  = 1:1, v/v). The

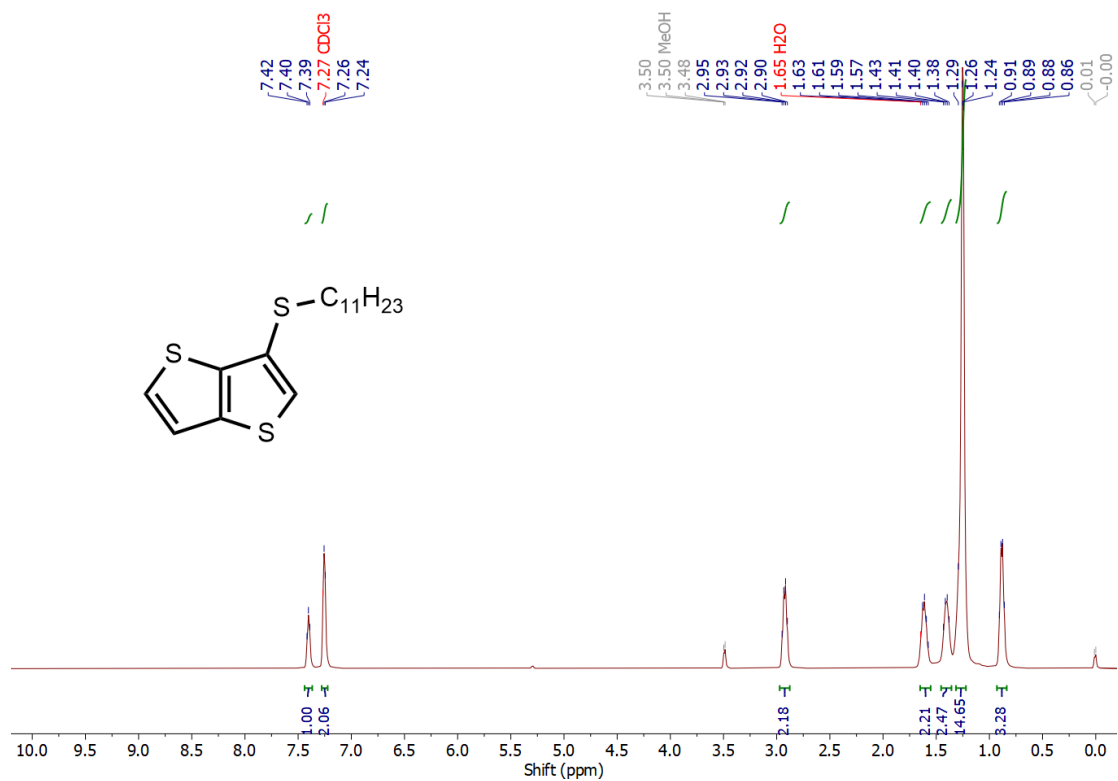
crude product was further purified by recrystallization to yield a dark blue solid.

#### **BTPS-4F**

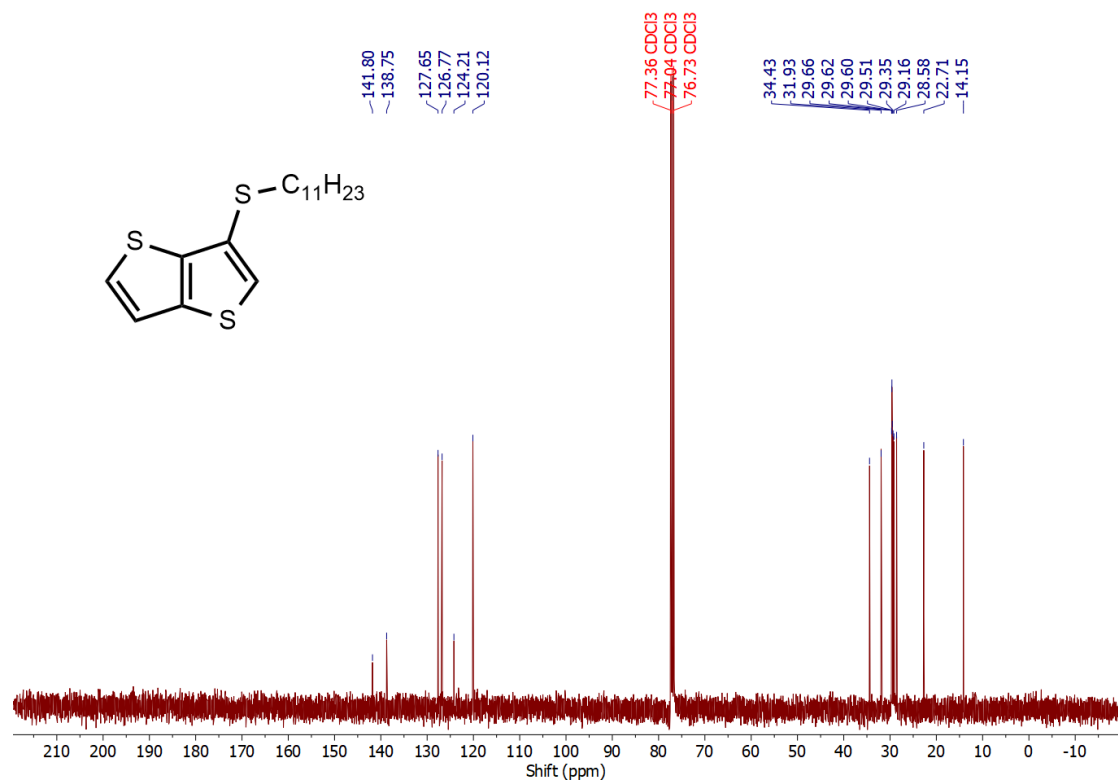
Yield: 50%.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.53 (s, 2H), 8.57 (dd,  $J = 9.9, 6.3$  Hz, 2H), 7.76 (t,  $J = 7.4$  Hz, 2H), 4.81 (d,  $J = 8.2$  Hz, 4H), 3.23 (t,  $J = 7.5$  Hz, 4H), 2.16 (p,  $J = 6.8$  Hz, 2H), 1.71 (t,  $J = 7.6$  Hz, 4H), 1.44 (q,  $J = 7.2$  Hz, 4H), 1.25 (d,  $J = 10.8$  Hz, 32H), 1.14 – 1.02 (m, 12H), 0.86 (t,  $J = 6.7$  Hz, 6H), 0.80 (t,  $J = 7.6$  Hz, 6H), 0.70 (t,  $J = 7.2$  Hz, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  186.11, 158.56, 155.79, 148.18, 147.37, 144.90, 137.49, 136.80, 136.46, 134.61, 133.72, 130.02, 121.42, 115.02, 114.80, 114.56, 114.10, 113.62, 112.76, 112.58, 70.04, 55.71, 40.43, 36.72, 31.88, 30.24, 29.70, 29.58, 29.56, 29.46, 29.32, 29.11, 28.63, 27.66, 23.30, 22.85, 22.65, 14.08, 13.76, 10.31, 10.27. **MALDI-TOF MS**: Calculated for  $\text{C}_{82}\text{H}_{86}\text{F}_4\text{N}_8\text{O}_2\text{S}_7\text{H}$  ( $\text{M}^+$ ): 1515.4928, Found: 1515.4906.

#### **BTPS-4Cl**

Yield: 35%.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.50 (d,  $J = 1.3$  Hz, 2H), 8.75 (d,  $J = 1.3$  Hz, 2H), 7.92 (s, 2H), 4.69 (d,  $J = 7.9$  Hz, 4H), 3.16 (t,  $J = 7.5$  Hz, 4H), 2.01 (s, 2H), 1.68 – 1.60 (m, 4H), 1.37 (s, 4H), 1.16 (d,  $J = 13.2$  Hz, 28H), 1.01 – 0.74 (m, 22H), 0.68 (t,  $J = 7.4$  Hz, 6H), 0.59 (t,  $J = 7.2$  Hz, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  186.20, 158.45, 148.31, 147.39, 145.22, 139.81, 139.34, 138.81, 137.54, 137.04, 137.01, 136.02, 134.92, 133.80, 130.27, 126.89, 125.19, 121.38, 114.60, 114.23, 113.71, 70.13, 55.76, 40.45, 36.74, 31.90, 31.61, 30.26, 29.73, 29.60, 29.59, 29.49, 29.35, 29.14, 28.65, 27.69, 23.34, 22.87, 22.68, 14.15, 14.12, 13.80, 10.36, 10.34, 1.04. **MALDI-TOF MS**: Calculated for  $\text{C}_{82}\text{H}_{86}\text{Cl}_4\text{N}_8\text{O}_2\text{S}_7$  ( $\text{M}^-$ ): 1578.3678, Found: 1578.3678.



**Figure S5.** <sup>1</sup>H NMR spectrum of compound **1** (400 MHz, CDCl<sub>3</sub>).



**Figure S6.** <sup>13</sup>C NMR spectrum of compound **1** (101 MHz, CDCl<sub>3</sub>).

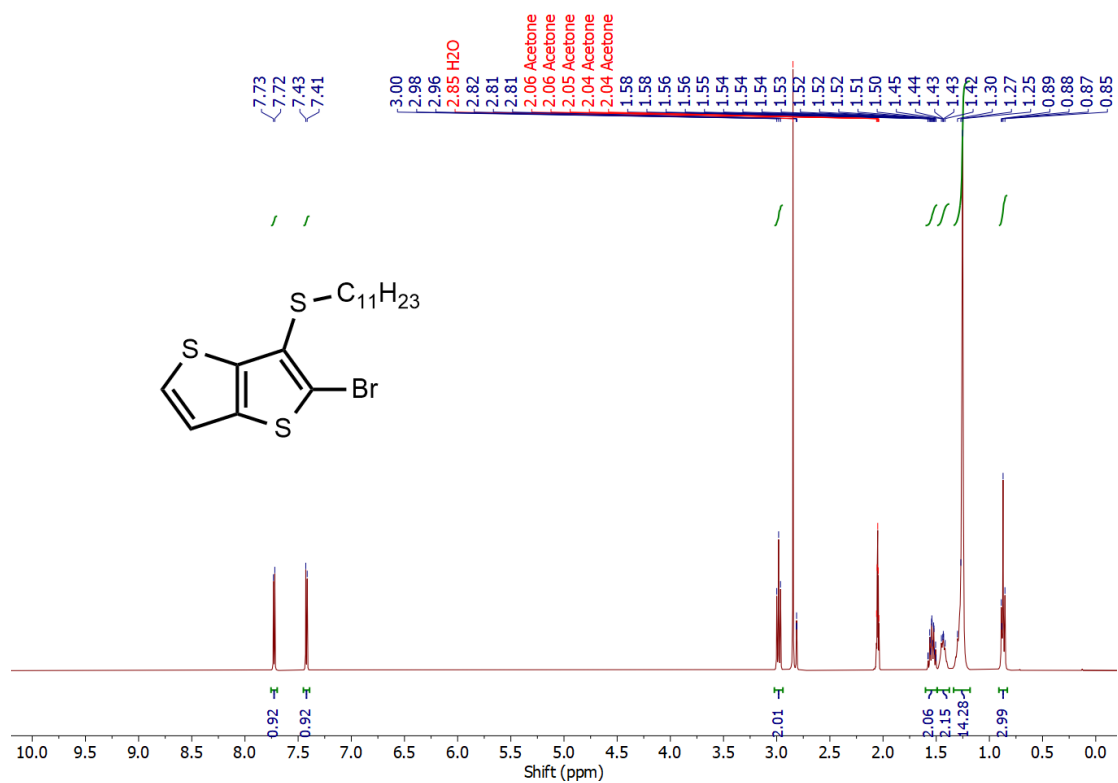


Figure S7. <sup>1</sup>H NMR spectrum of compound **2** (400 MHz, d<sub>6</sub>-acetone).

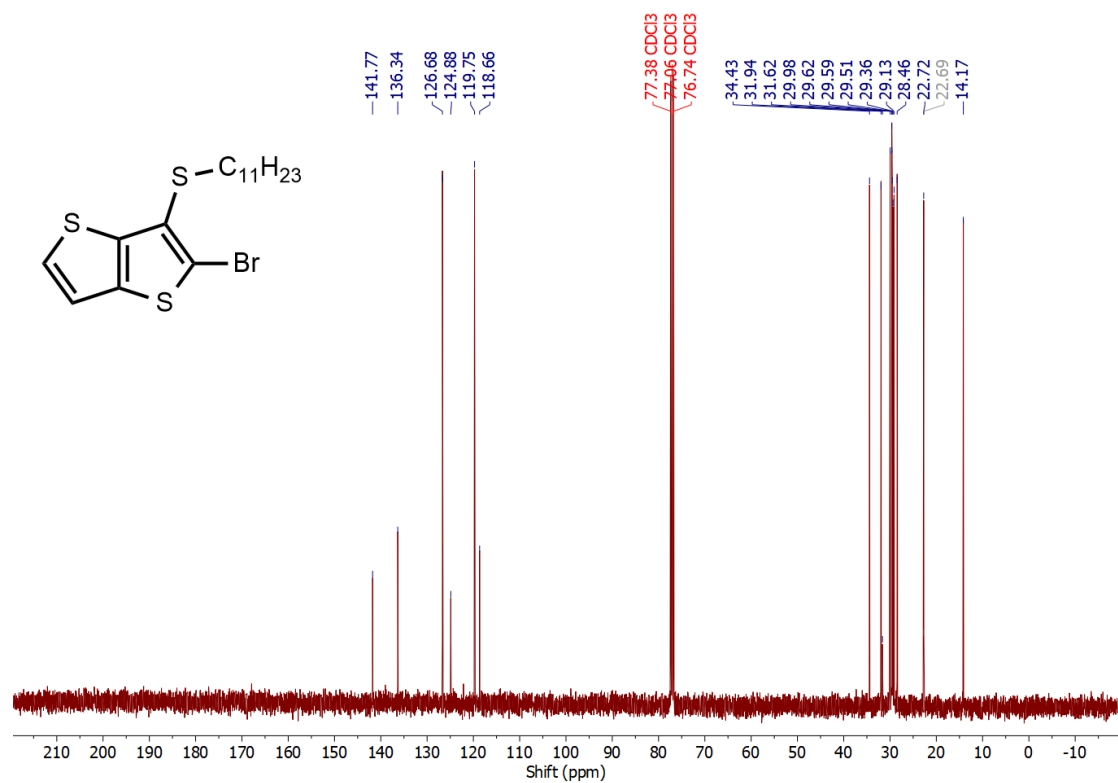
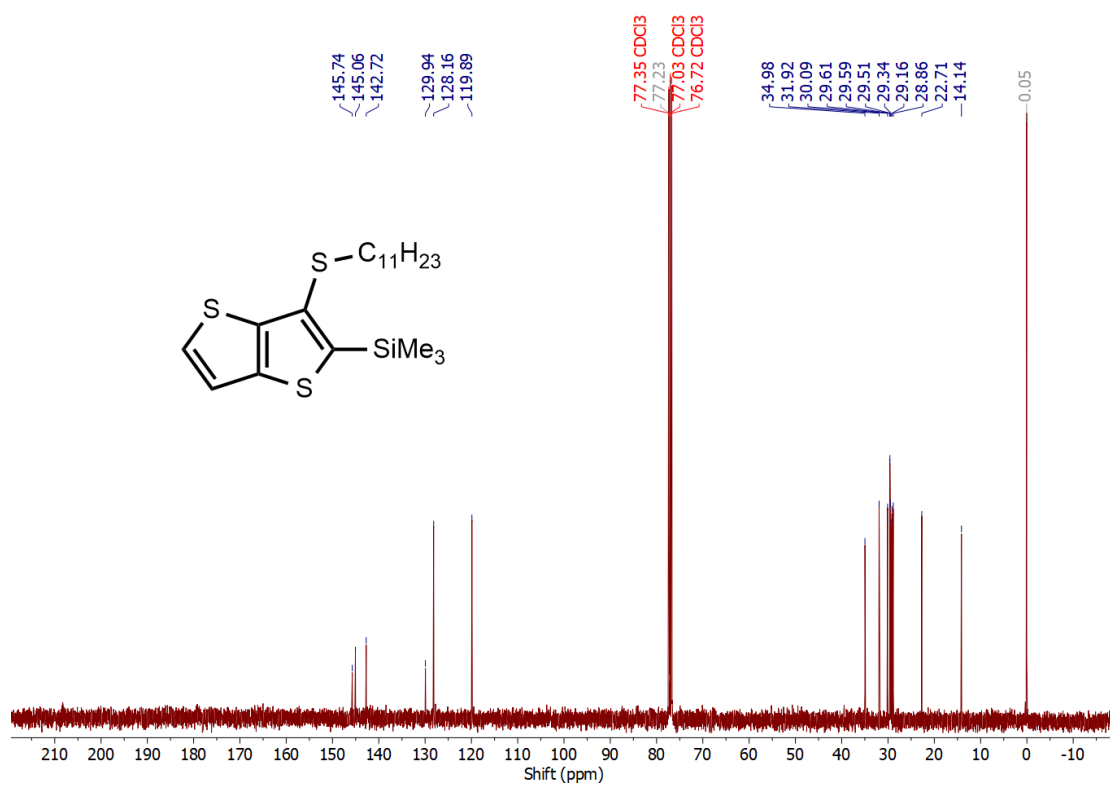
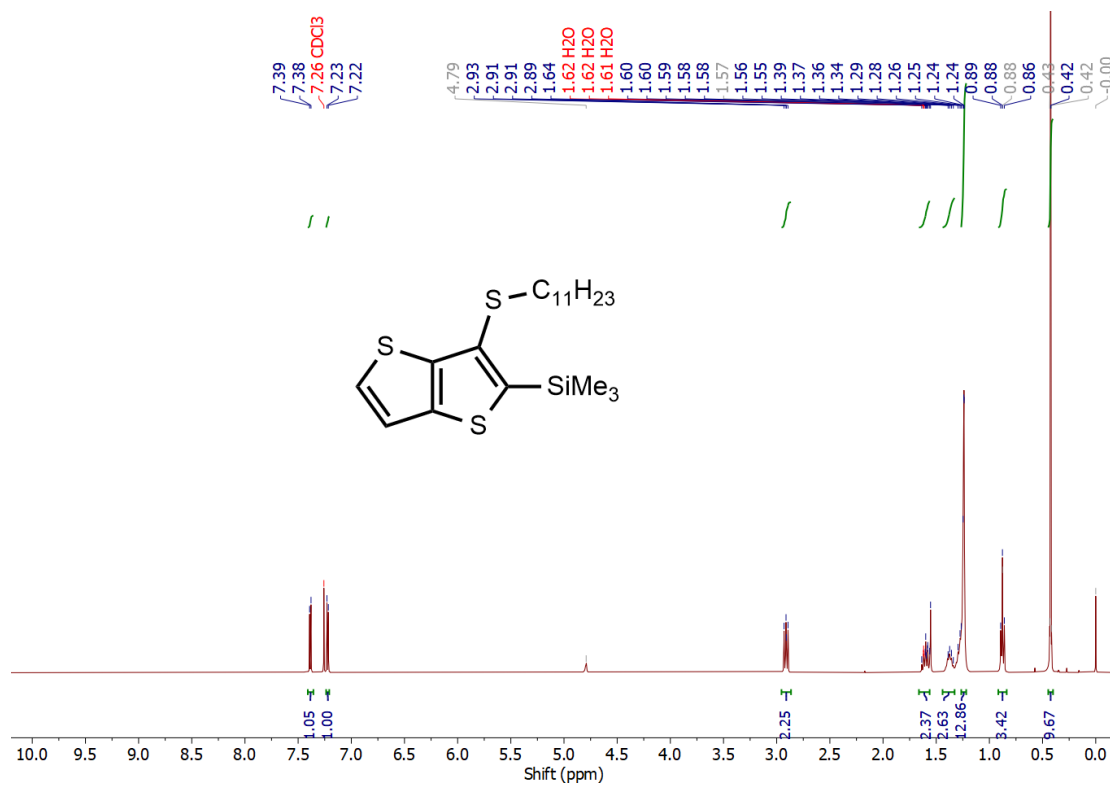


Figure S8. <sup>13</sup>C NMR spectrum of compound **2** (101 MHz, CDCl<sub>3</sub>).



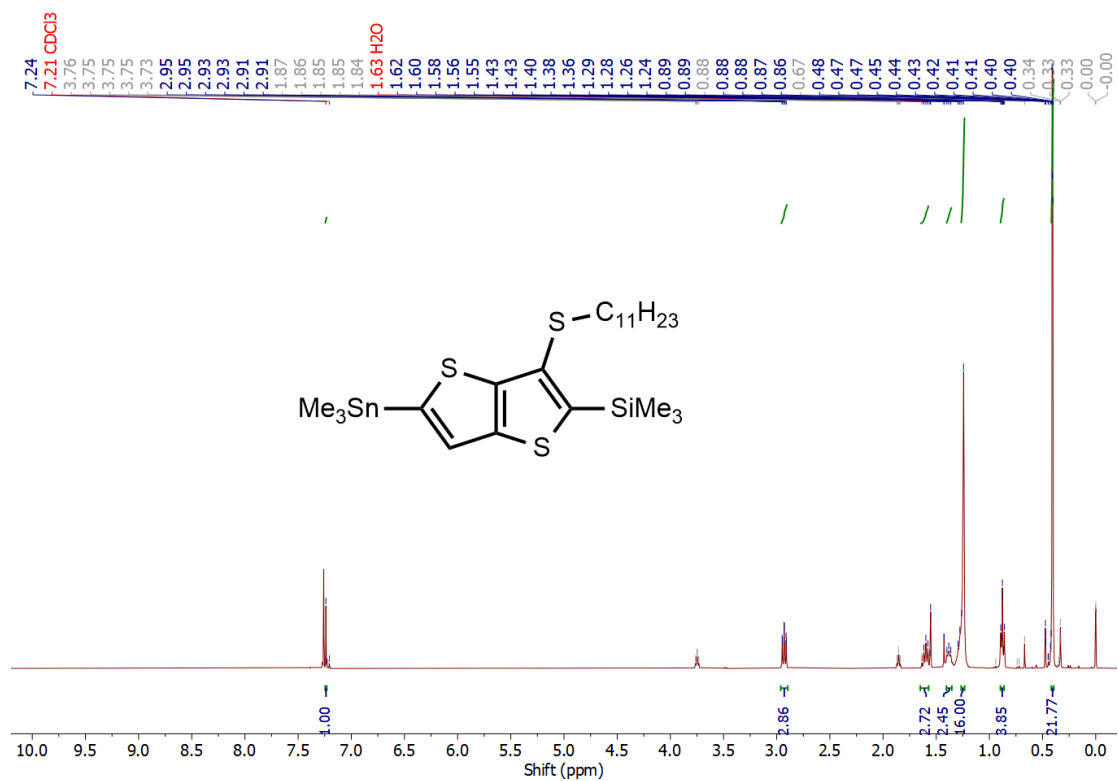


Figure S11. <sup>1</sup>H NMR spectrum of compound 4 (400 MHz, CDCl<sub>3</sub>).

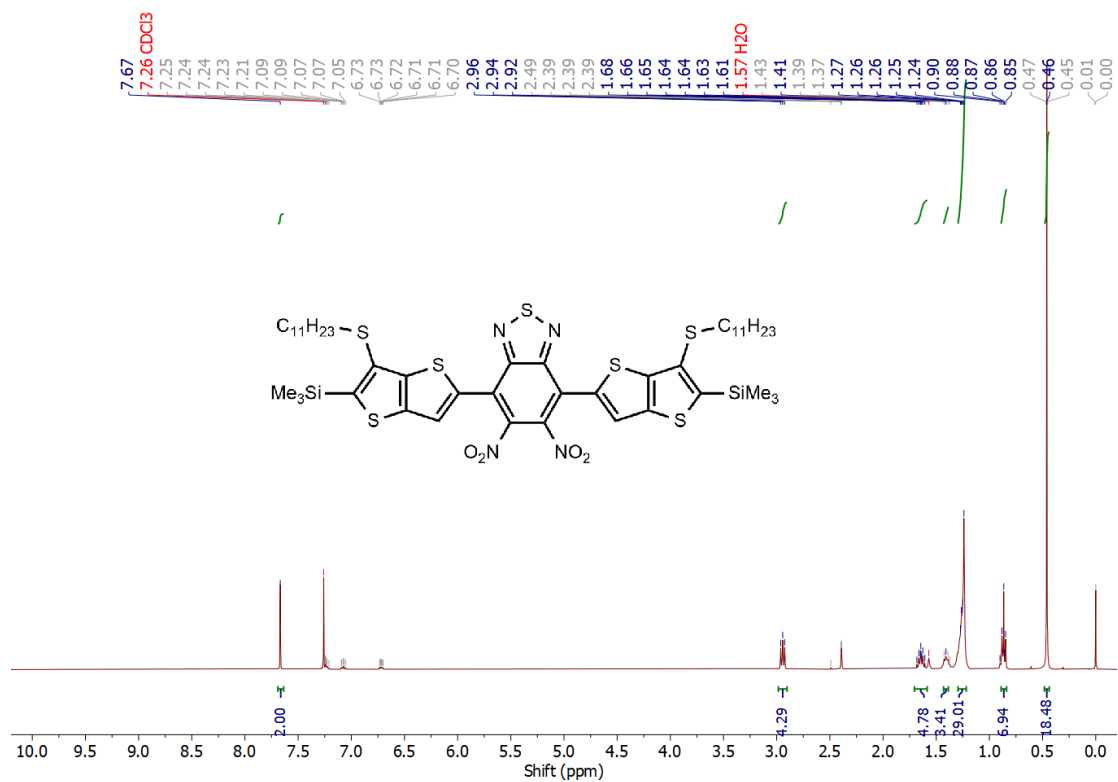
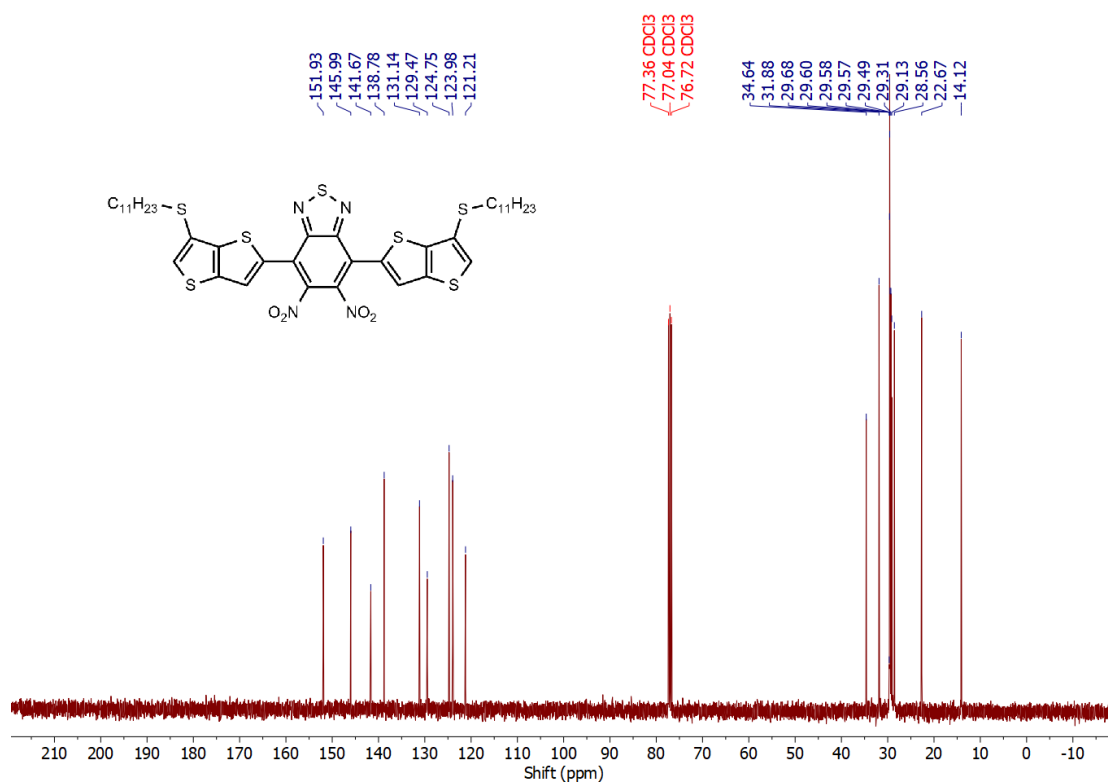
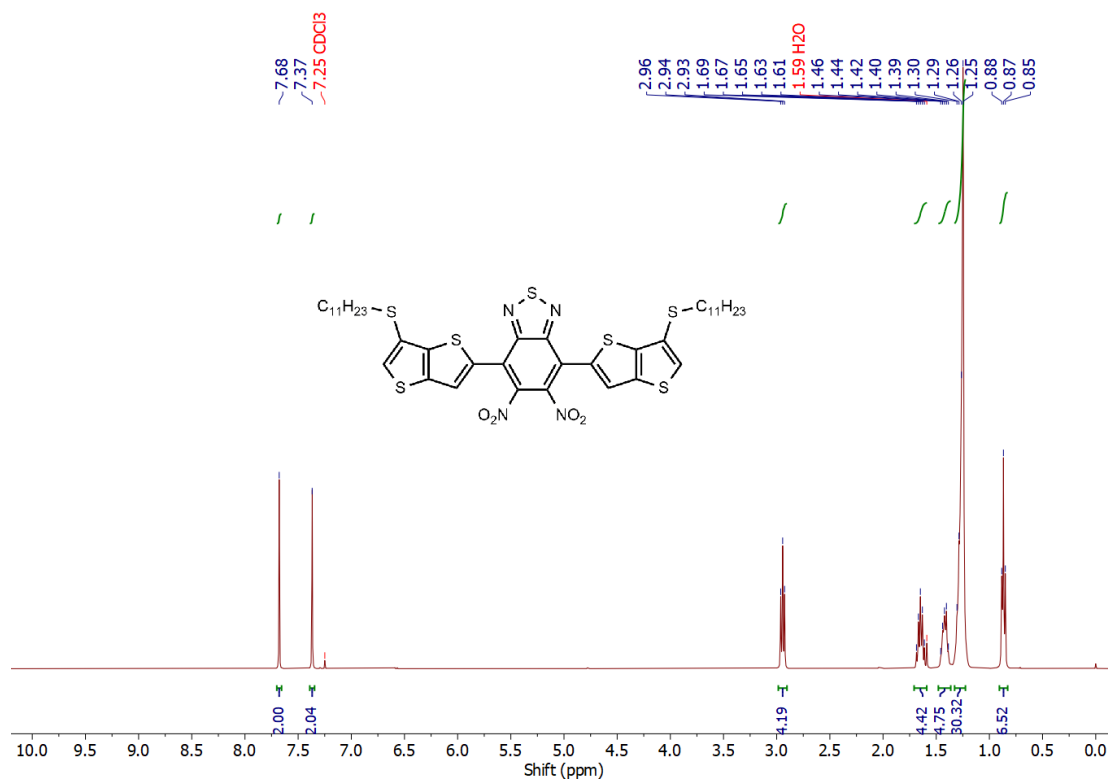


Figure S12. <sup>1</sup>H NMR spectrum of compound 5 (400 MHz, CDCl<sub>3</sub>).



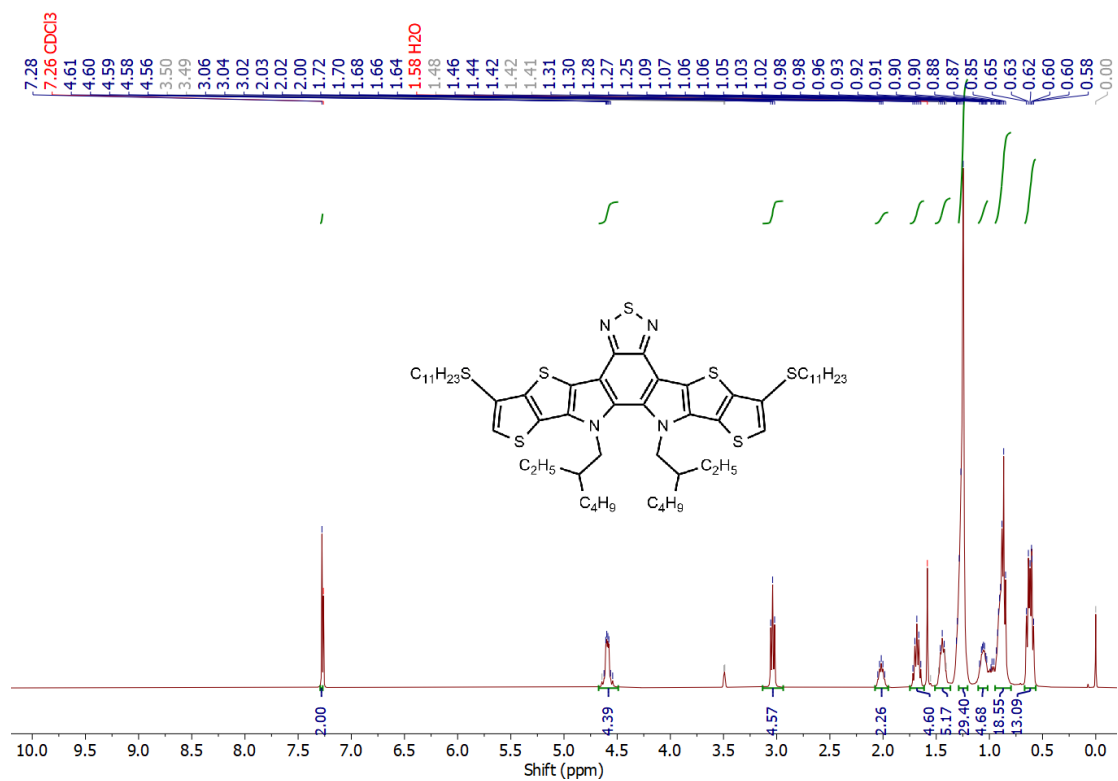


Figure S15. <sup>1</sup>H NMR spectrum of compound 7 (400 MHz, CDCl<sub>3</sub>).

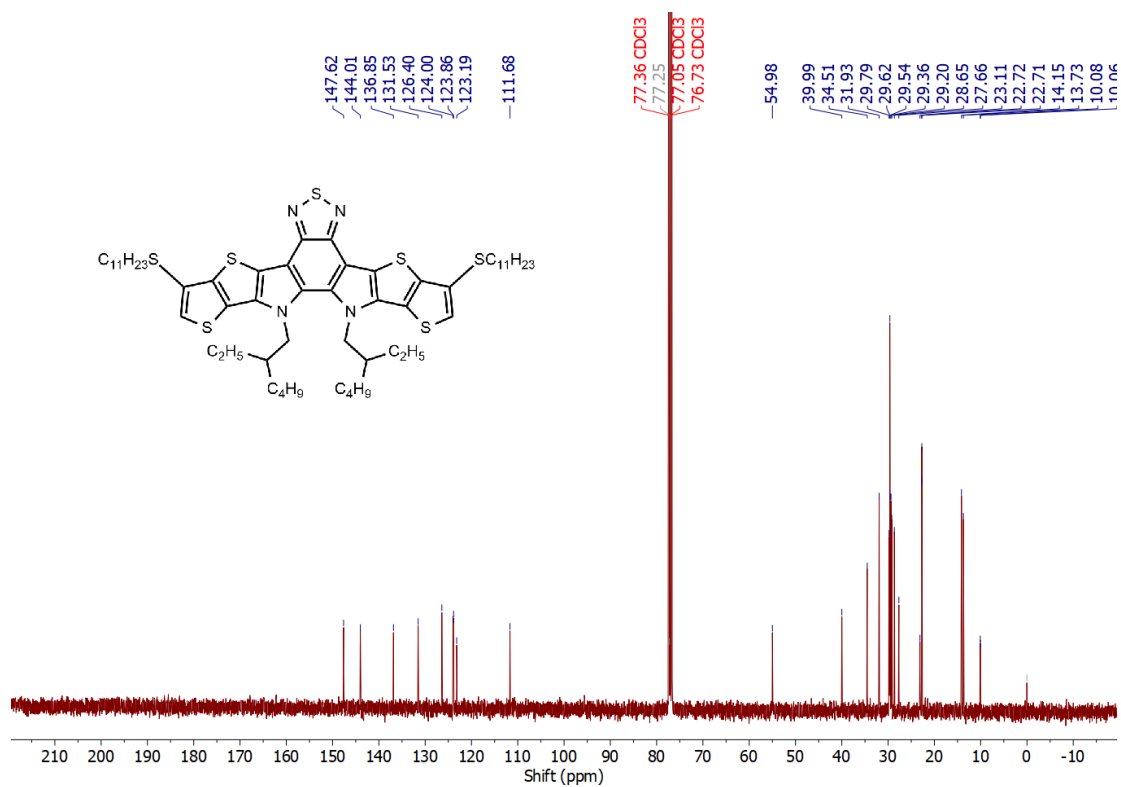
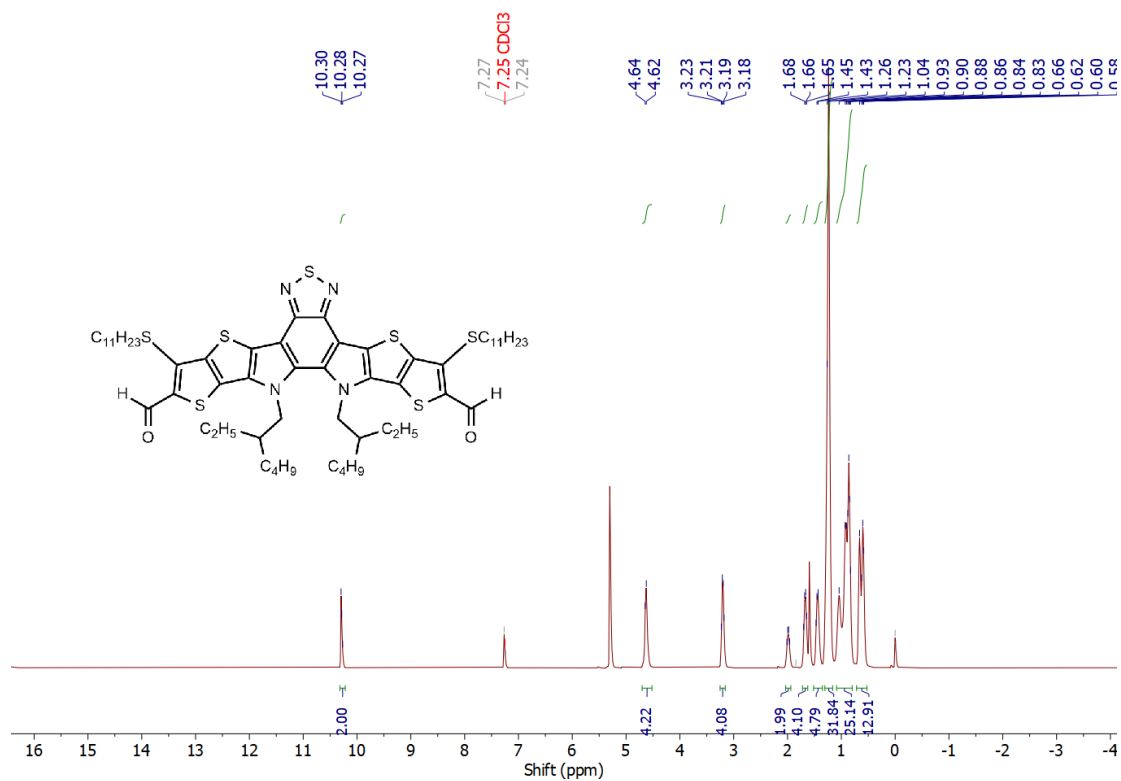
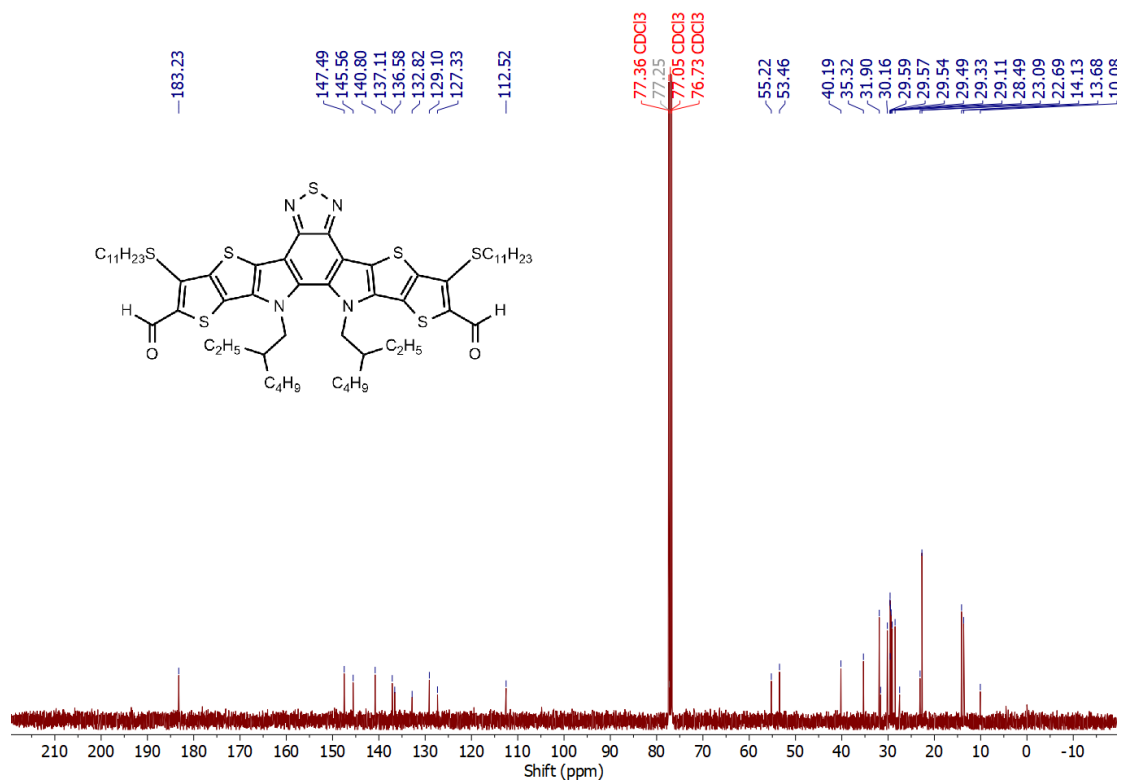


Figure S16. <sup>13</sup>C NMR spectrum of compound 7 (101 MHz, CDCl<sub>3</sub>).

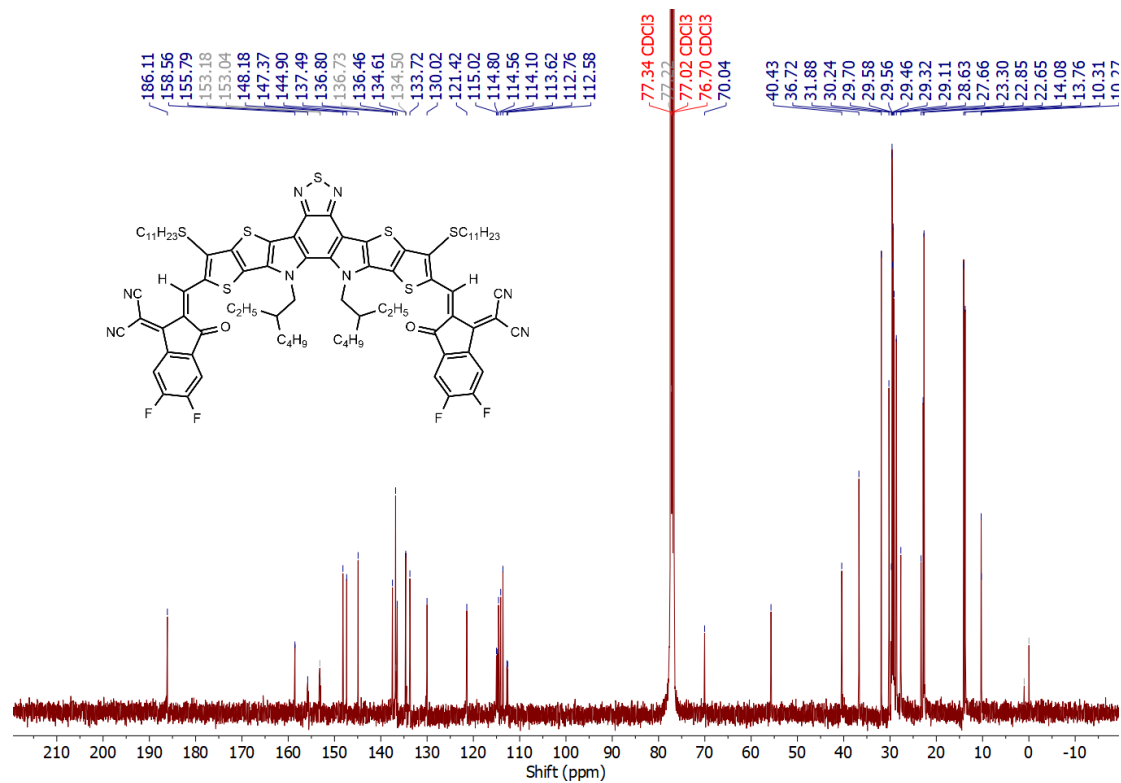
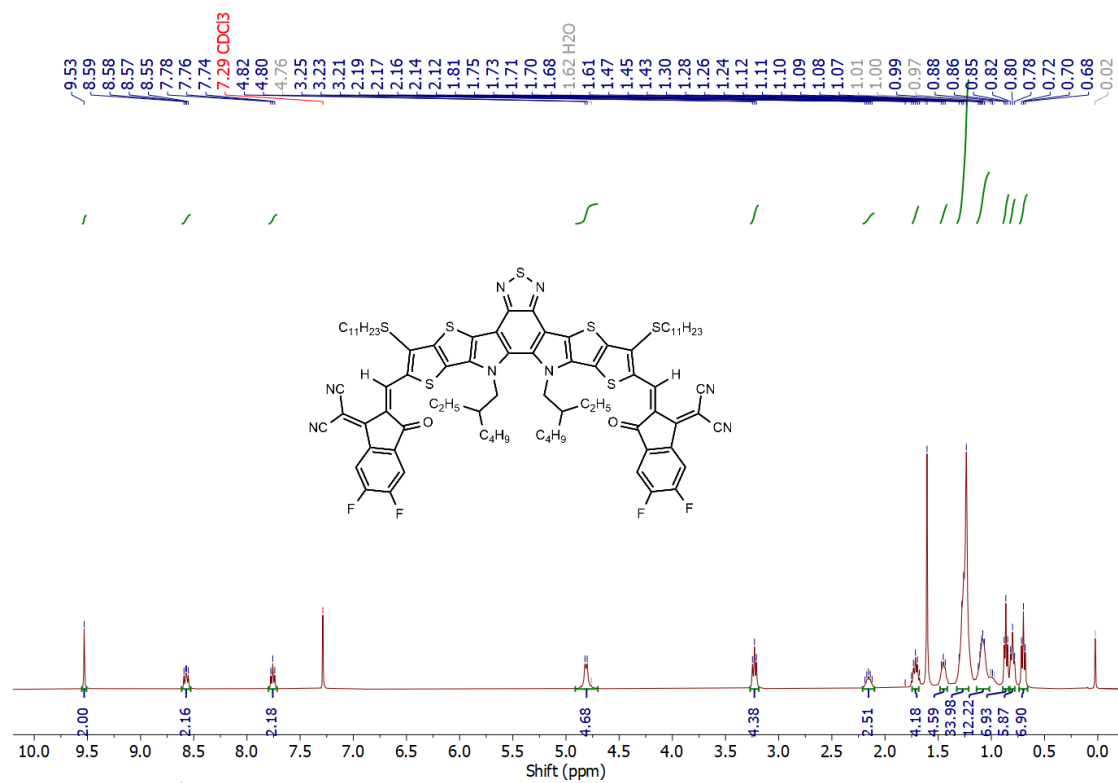




**Figure S17.** <sup>1</sup>H NMR spectrum of compound **8** (400 MHz, CDCl<sub>3</sub>).



**Figure S18.** <sup>13</sup>C NMR spectrum of compound **8** (101 MHz, CDCl<sub>3</sub>).



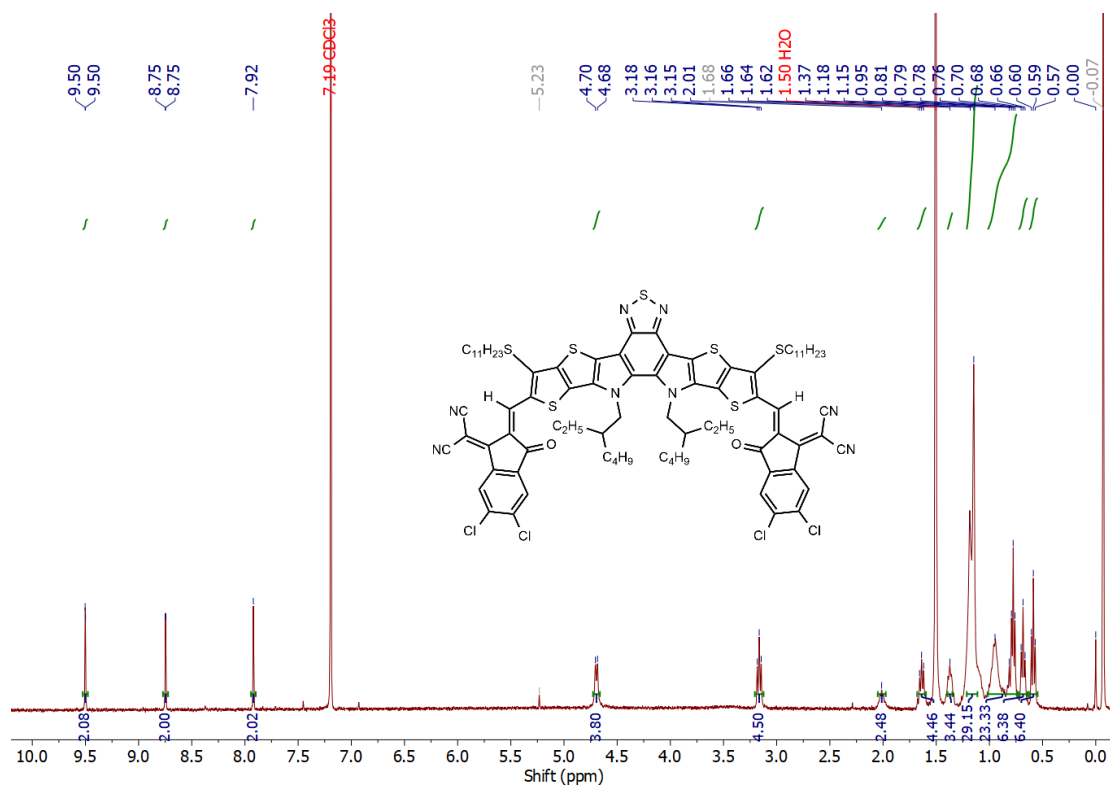


Figure S21. <sup>1</sup>H NMR spectrum of BTPS-4Cl (400 MHz, CDCl<sub>3</sub>).

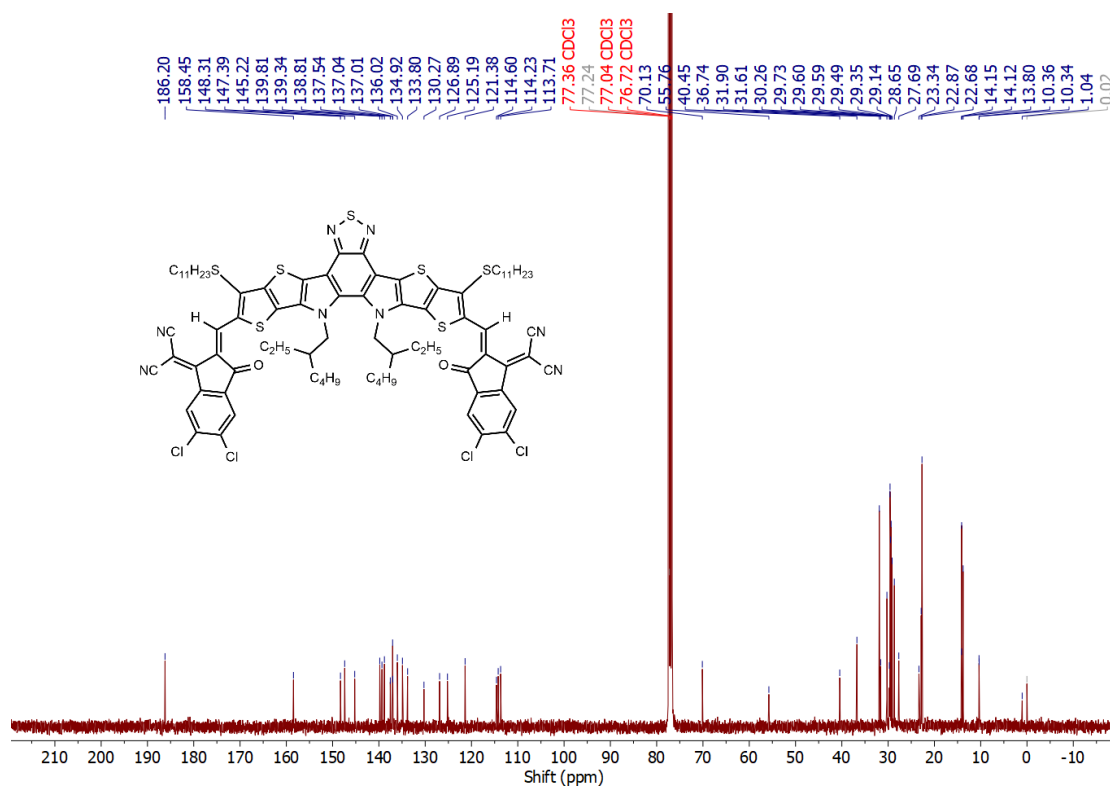


Figure S22. <sup>13</sup>C NMR spectrum of BTPS-4Cl (101 MHz, CDCl<sub>3</sub>).

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