

Electronic Supplementary Information

Backbone-shape engineering of fused-ring electron-deficient molecular semiconductors for unipolar n-type organic transistors: synthesis, conformation changes, and structure–property correlations†

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Instruments and Measurements

Chemical synthesis and characterization: All commercially available solvents, reagents, and chemicals were purchased from Aldrich, TCI and several other reagent companies and used as received without further purification unless otherwise specified. All reactions and manipulations were carried out with the use of standard inert atmosphere and Schlenk techniques. Compound 1, 4, 7, 8, 9, and BTPOCl-c were synthesized according to the literature.^[1-5] ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were measured on a Varian Mercury Plus-400 spectrometer. The splitting patterns were designated as follows: s (singlet); d (doublet); t (triplet); m (multiplet). Deuterated chloroform was used as the solvent. The NMR chemical shifts were reported in ppm (parts per million) relative to the residual solvent peak at 7.26 ppm (chloroform) for the ¹H NMR spectroscopy and 77.6 ppm (chloroform) for the ¹³C NMR spectroscopy. The MALDI-TOF mass spectra were measured by a Bruker autoflex maX MALDI-TOF mass spectrometer.

TGA measurements: TGA measurement was carried out on Mettler STARE (TA Instrument) with a heating ramp of 10 °C min⁻¹ under nitrogen flow.

Optical characterizations: UV-Vis absorption spectra were acquired from PerkinElmer Lambda 750 spectrophotometer. All film samples were spin-cast on glass substrates. All the solution of small molecules were measured with a concentration of 0.02 mg/mL in chloroform.

Electrochemical characterizations: Cyclic voltammetry (CV) measurements of

films were performed under argon atmosphere using a CHI760E voltammetric analyzer with 0.1 M tetra-n-butylammonium hexafluorophosphate ($n\text{Bu}_4\text{NPF}_6$) in acetonitrile as the supporting electrolyte. A platinum disk working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode were employed. The scanning rate was 0.1 V s^{-1} . Films were drop-casted from chloroform solutions of organic molecules on a Pt working electrode (2 mm in diameter). The supporting electrolyte solution was thoroughly purged with argon before all CV measurements. For calibration, the redox potential of ferrocene/ferrocenium (Fc/Fc^+) was measured under the same conditions. It was assumed that the redox potential of Fc/Fc^+ has an absolute energy level of -4.80 eV to a vacuum. 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: All calculations were carried out with Gaussian 16 Rev. B.01. [6]

Geometry optimizations of monomer and dimer were performed using B3LYP functional with D3 dispersion correction with BJ-dumping, basis set 6-31G(d) for all atoms.

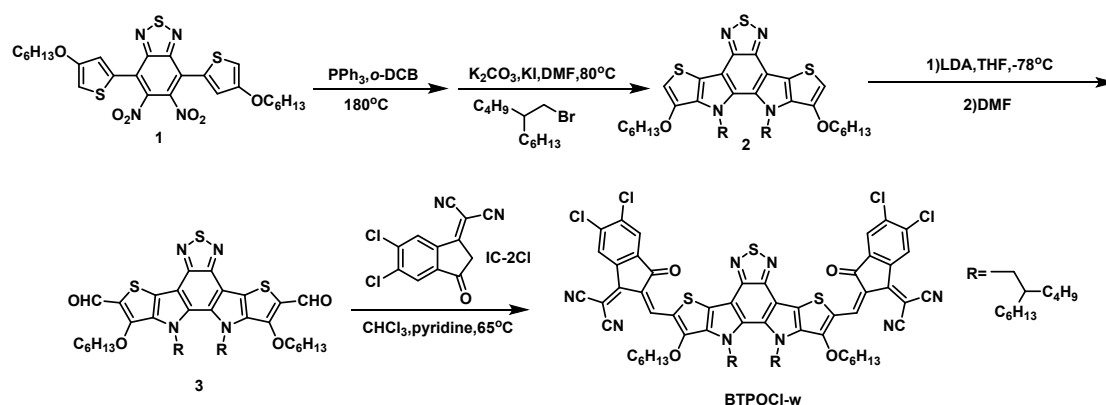
Fabrication of Organic Thin-film Transistors: The top-gate bottom-contact (TGBC) OFET device based on the thin films of small molecules was fabricated to evaluate the charge-transport properties. A metal layer of 30 nm Au was deposited on a cleaned glass plate with thermal evaporation process as source and drain electrodes. Then the substrate was cleaned by sonication in deionized water, acetone and isopropanol for 10 minutes successively and finally was transferred into glove box with nitrogen

atmosphere. The organic semiconductor layers were fabricated with spin-coating process of a 1500 rpm 40 μL 5 mg/mL chloroform solution and annealed at 90 $^{\circ}\text{C}$ for 30 minutes. The dielectric layer was fabricated with spin-coating process of a 1500 rpm 60 μL polymethyl methacrylate (PMMA) butylacetate solution and annealed at 90 $^{\circ}\text{C}$ for 30 minutes, subsequently. Finally, 100 nm Ag layer was deposited on the dielectric layer with thermal evaporation process as gate electrode.

AFM analysis: AFM measurements were performed by using Bruker Dimension® Icon™ in tapping mode. All film samples were spin-cast on glass substrates according to devices fabrication conditions.

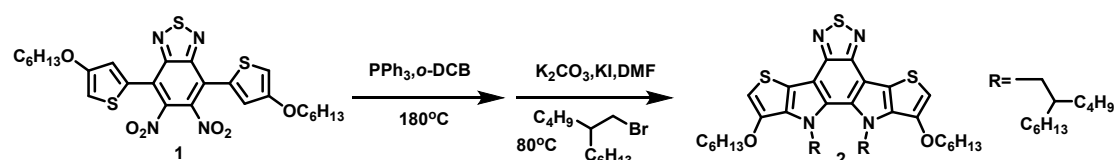
GIWAXS characterization:^[8] GIWAXS experiments was carried out at Shanghai Synchrotron Radiation Facility (SSRF) beamline BL14B/15U.

Measurement of OFET devices: The OFET devices of both film and single crystal was measured in glove box with nitrogen atmosphere. Primarius Technologies FS-pro PDA semiconductor characterization system was utilized to measure the transfer and output curve of OFET. The saturation charge-carrier mobility (μ) was calculated according to the equation: $I_{DS} = (W\mu C_i/2L)(V_G - V_{th})^2$, where the I_{DS} is the source-drain current, W and L are the channel width and length of OFET, C_i is the capacitance per unit area of dielectric and C_i (PMMA) = 3 $\text{nF}\cdot\text{cm}^{-2}$, C_i (SiO₂) = 11.5 $\text{nF}\cdot\text{cm}^{-2}$ in this work according to our measure, V_G and V_{th} are the gate voltage and threshold, respectively.



Scheme S1. The synthetic routes of **BTPOCI-w**.

Synthesis of compound 2:

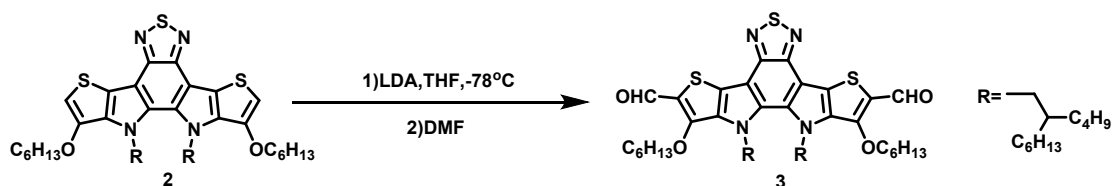


Compound **1** (145.0 mg, 0.246 mmol) and PPh_3 (643.8 mg, 2.46 mmol) were dissolved in the 1,2-dichlorobenzene (*o*-DCB, 10 mL) under nitrogen. After being heated at 180 °C for 3 hrs, the solvent was removed to get the crude product.

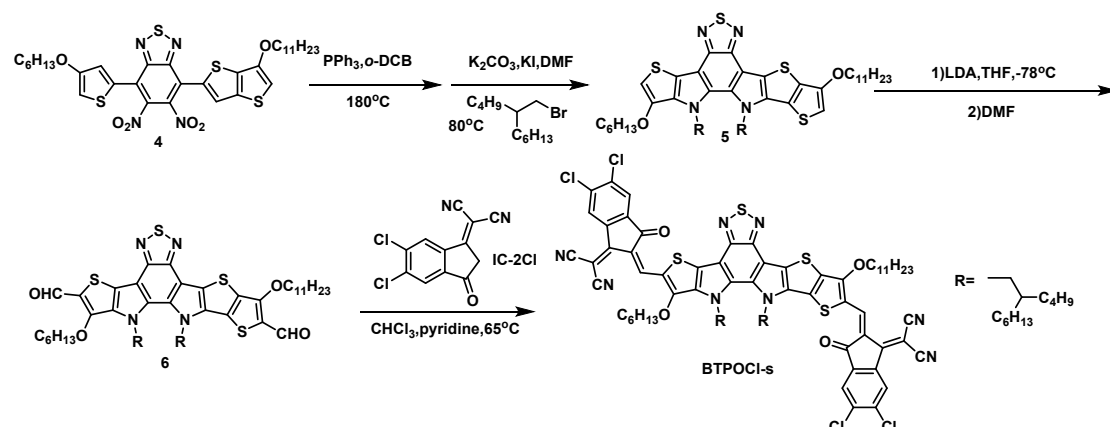
The red residue was mixed with 5-(bromomethyl)undecane (1.468 g, 5.89 mmol), potassium carbonate (678.5 mg, 4.91 mmol) and potassium iodide (978.0 mg, 5.89 mmol) in DMF (10 mL) under N_2 . The mixture was refluxed at 80 °C overnight. After cooled down to room temperature, the residue was poured into 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 Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: *n*-hexane:

CH₂Cl₂ = 3:1, v/v) to get the product as orange oil (56 mg, 26%). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 6.31 (s, 2H), 4.56 (m, 4H), 4.15 (t, 4H, *J* = 6.0 Hz), 1.93-1.88 (m, 6H), 1.56-1.39 (m, 14H), 1.01-0.63 (m, 48H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 147.9, 144.8, 134.9, 134.0, 120.7, 111.0, 98.1, 70.6, 53.7, 39.3, 31.8, 30.4, 30.3, 29.7, 29.6, 26.1, 23.0, 23.0, 22.9, 14.3, 14.2, 14.0, 14.0.

Synthesis of compound 3:

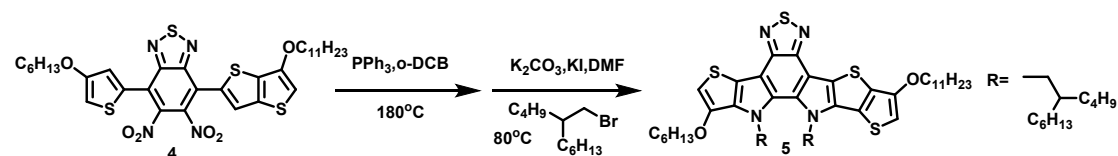


To a solution of compound 4 (56 mg, 0.0649 mmol) in THF (10 mL), 2.0 M lithium diisopropylamide in hexane (0.26 mL, 0.519 mmol) was added dropwise slowly at -78 °C under N₂. The mixture was stirred at -78 °C for 1 h, and then anhydrous DMF (0.26 mL) was added. The mixture was stirred overnight at room 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 Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: CH₂Cl₂) to get the product as orange solid (22.0 mg, 37%). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 10.19 (s, 2H), 4.52-4.49 (m, 8H), 2.01-1.88 (m, 6H), 1.60-1.39 (m, 14H), 1.00-0.63 (m, 48H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 181.5, 150.2, 147.7, 136.3, 136.1, 128.1, 127.8, 112.7, 77.7, 54.0, 39.5, 31.8, 31.8, 30.4, 30.3, 29.6, 25.8, 23.0, 22.9, 22.8, 22.7, 22.7, 14.2, 14.2, 14.0, 13.9.



Scheme S2. The synthetic routes of **BTPOCI-s**.

Synthesis of compound 5 :

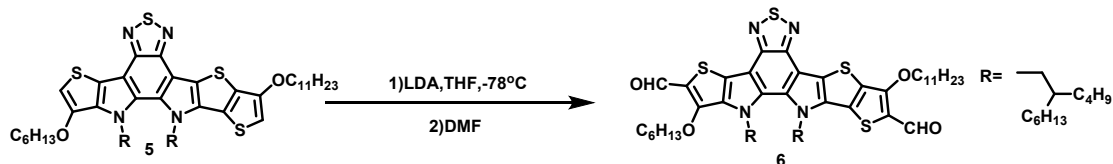


Compound **4** (130.0 mg, 0.182 mmol) and PPh_3 (476.1 mg, 1.82 mmol) were dissolved in the 1,2-dichlorobenzene (*o*-DCB, 10 mL) under nitrogen. After being heated at 180 °C for 3 hrs, the solvent was removed to get the crude product.

The red residue was mixed with 5-(bromomethyl)undecane (1.086 g, 4.36 mmol), potassium carbonate (501.7 mg, 3.63 mmol) and potassium iodide (723.1 mg, 4.36 mmol) in DMF (10 mL) under 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 Na_2SO_4 and concentrated under reduced

pressure. The residue was purified by flash column chromatography (eluent: *n*-hexane: CH₂Cl₂= 4:1, v/v) to get the product as orange oil (65 mg, 34%). ¹H NMR (400 MHz, CDCl₃, ppm): δ= 6.32 (s, 1H), 6.30 (s, 1H), 4.58-4.54 (m, 4H), 4.17-4.14 (m, 4H), 2.07-2.04 (m, 1H), 1.96-1.85 (m, 5H), 1.57-1.52 (m, 4H), 1.43-1.29 (m, 16H), 1.01-0.63 (m, 52H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ= 151.4, 148.0, 147.7, 144.8, 137.0, 135.0, 133.8, 132.7, 132.1, 123.2, 122.4, 120.7, 111.8, 111.0, 98.2, 96.0, 70.9, 70.2, 55.2, 53.7, 39.2, 38.9, 32.1, 31.8, 31.7, 30.6, 30.5, 30.4, 30.3, 29.8, 29.8, 29.8, 29.6, 29.5, 29.4, 28.2, 28.1, 26.2, 26.1, 25.4, 23.0, 23.0, 22.9, 22.9, 22.8, 22.7, 22.6, 14.3, 14.3, 14.2, 14.0, 13.9.

Synthesis of compound 6 :



To a solution of compound 5 (65 mg, 0.0657 mmol) in THF (10 mL), 2.0 M lithium diisopropylamide in hexane (0.27 mL, 0.526 mmol) was added dropwise slowly at $-78\text{ }^{\circ}\text{C}$ under N₂. The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h, and then anhydrous DMF (0.27 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 Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: CH₂Cl₂) to get the product as orange

solid (56.0 mg, 81%). ¹H NMR (400 MHz, CDCl₃, ppm): δ= 10.19 (s, 1H), 10.10 (s, 1H), 4.69 (t, 2H, *J*= 6.0 Hz), 4.57-4.49 (m, 6H), 2.00-1.92 (m, 6H), 1.57-1.28 (m, 20H), 1.01-0.61 (m, 52H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ= 181.5, 181.4, 158.8, 150.3, 147.7, 147.5, 137.1, 136.7, 135.8, 133.0, 130.1, 129.9, 129.0, 128.3, 128.2, 127.6, 122.2, 113.0, 112.0, 73.4, 68.3, 55.2, 54.4, 39.5, 39.2, 38.9, 32.1, 31.7, 31.7, 30.5, 30.4, 30.3, 30.1, 29.8, 29.8, 29.7, 29.5, 29.5, 29.1, 28.0, 26.0, 25.8, 25.3, 23.9, 23.2, 23.0, 22.9, 22.9, 22.8, 22.6, 14.3, 14.2, 14.1, 14.0, 13.9, 13.9.

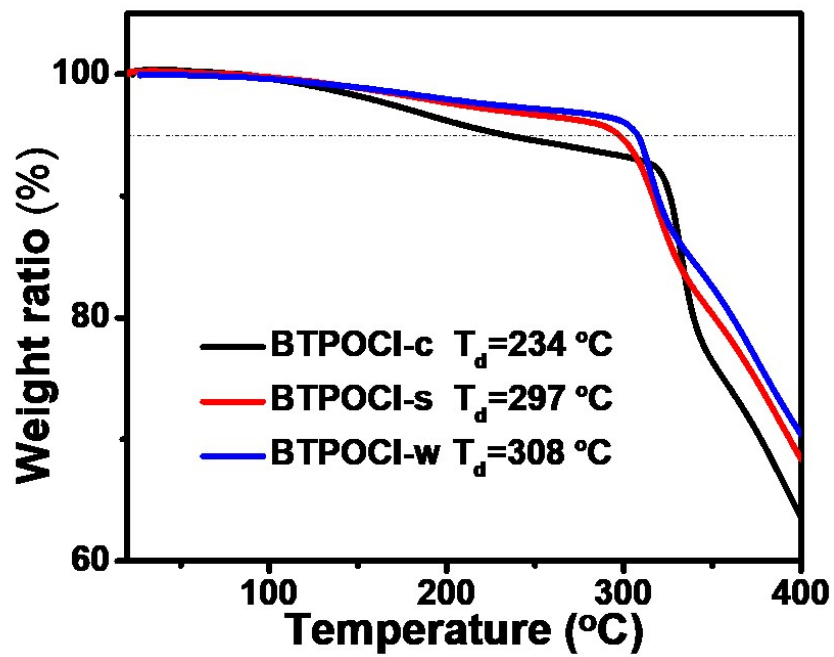


Figure S1. Thermogravimetric analysis (TGA) curves of BTPOCl-w, BTPOCl-s and BTPOCl-c.

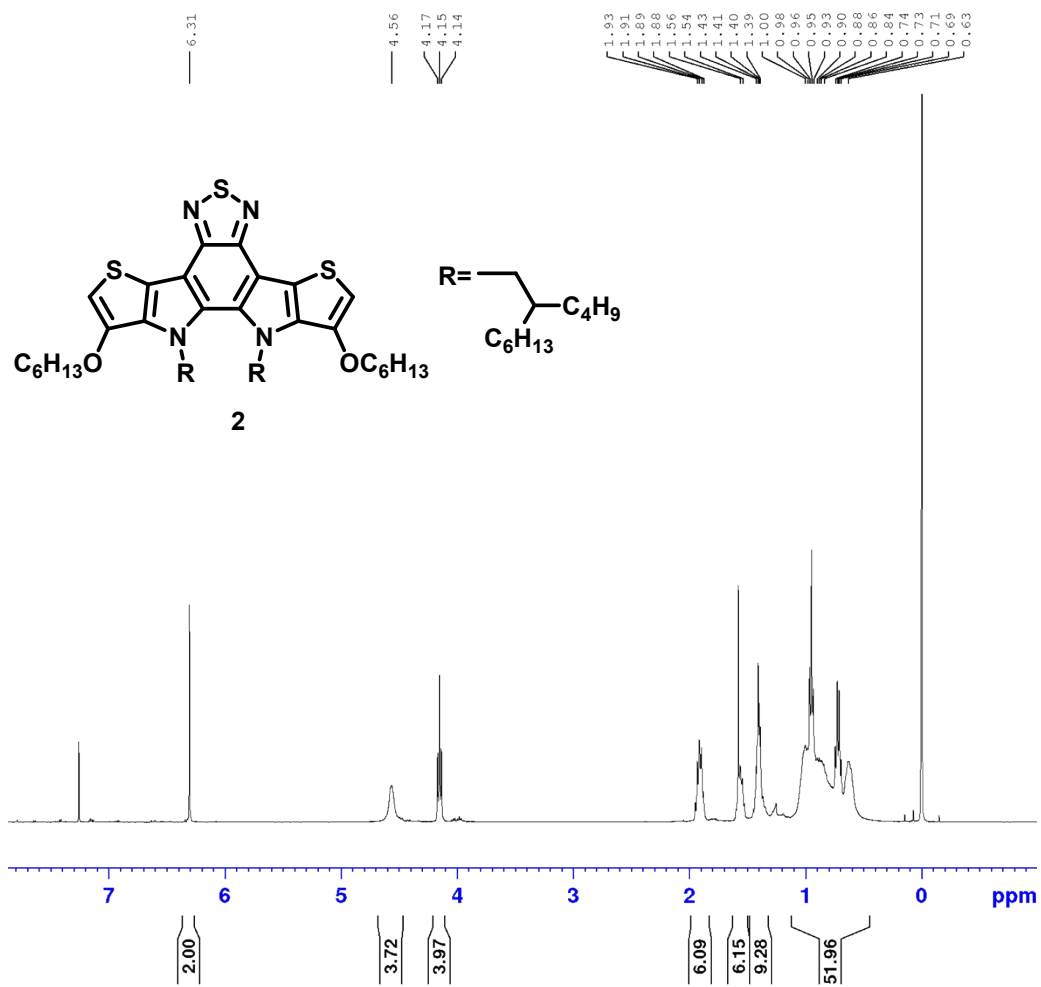


Figure S2 $^1\text{H NMR}$ spectrum of compound 2 (400 MHz, CDCl_3).

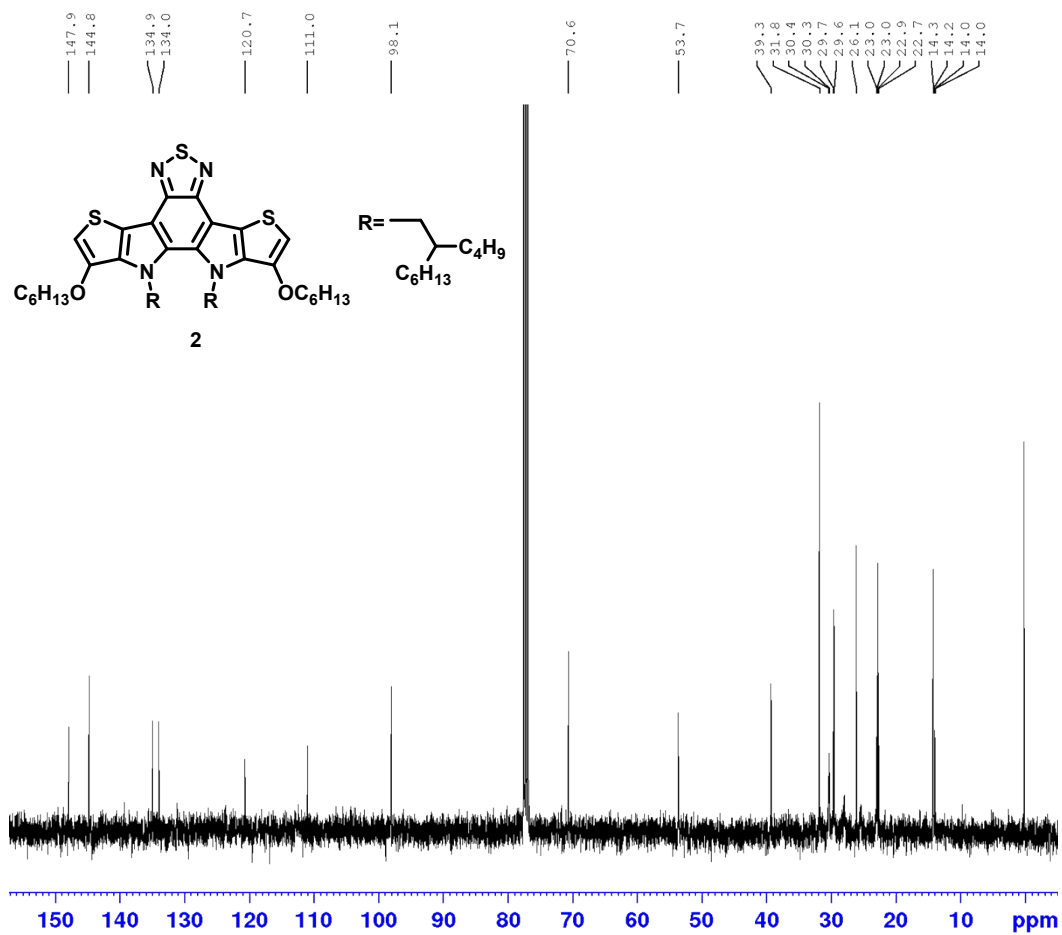


Figure S3 ^{13}C NMR spectrum of compound **2** (100 MHz, CDCl_3).

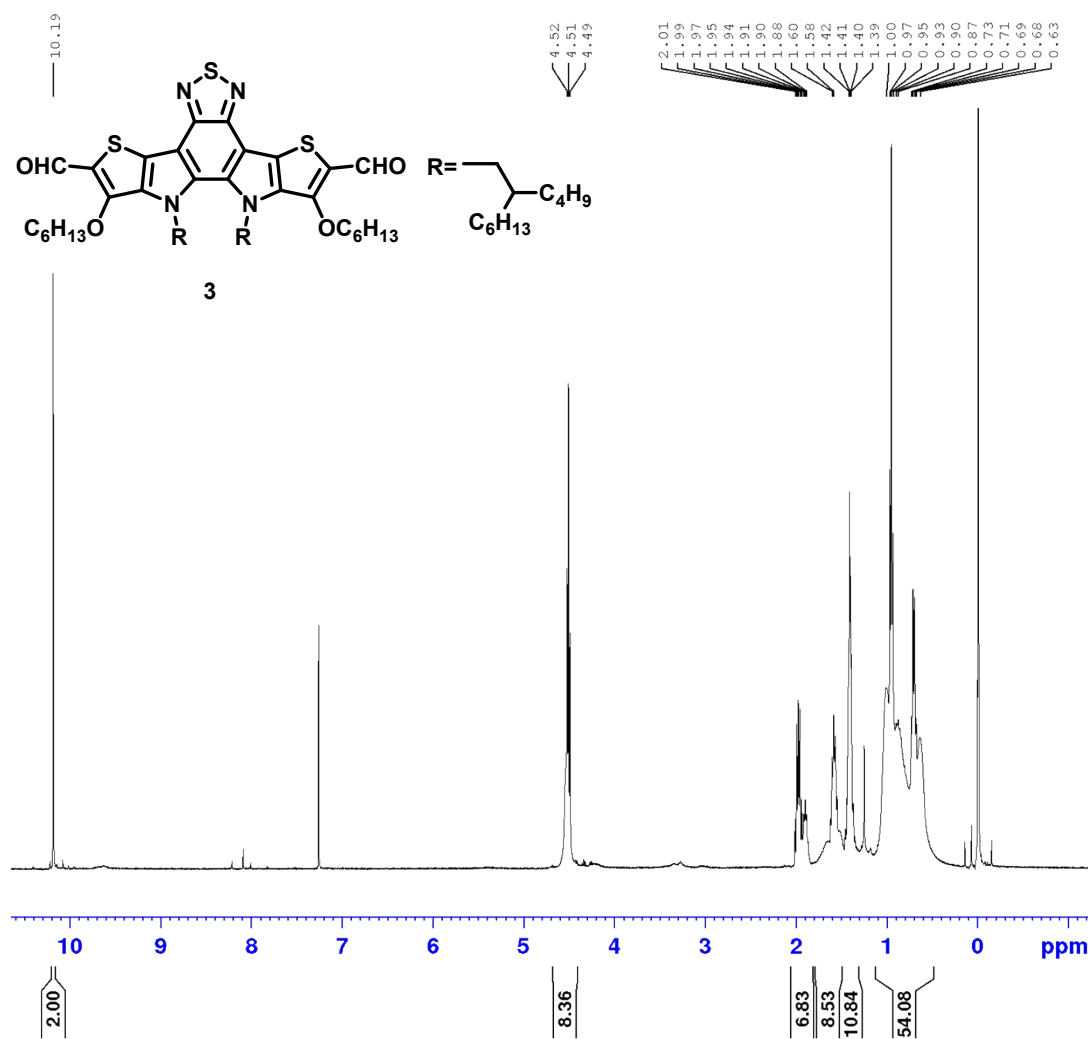


Figure S4 ¹H NMR spectrum of compound **3** (400 MHz, CDCl₃).

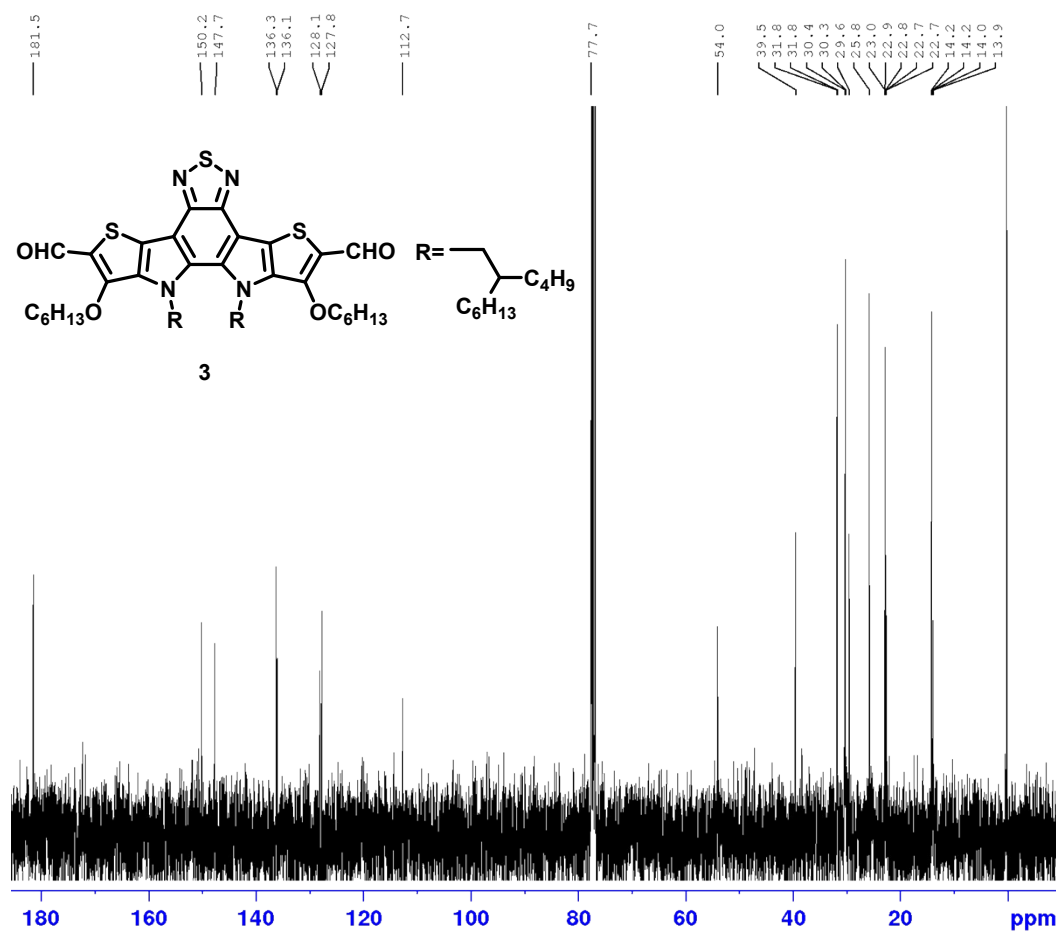


Figure S5 ^{13}C NMR spectrum of compound **3** (100 MHz, CDCl_3).

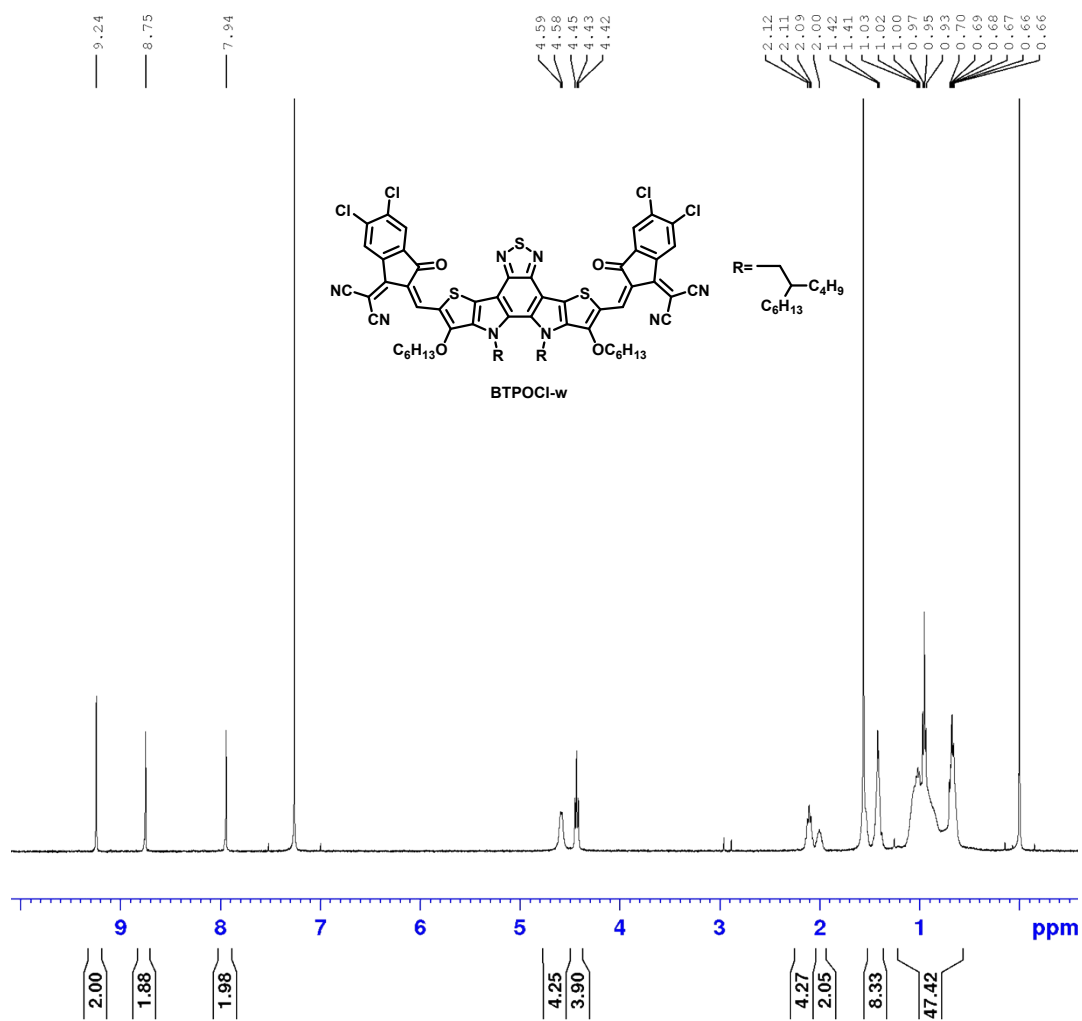


Figure S6 ^1H NMR spectrum of BTPOCI-w (400 MHz, CDCl_3).

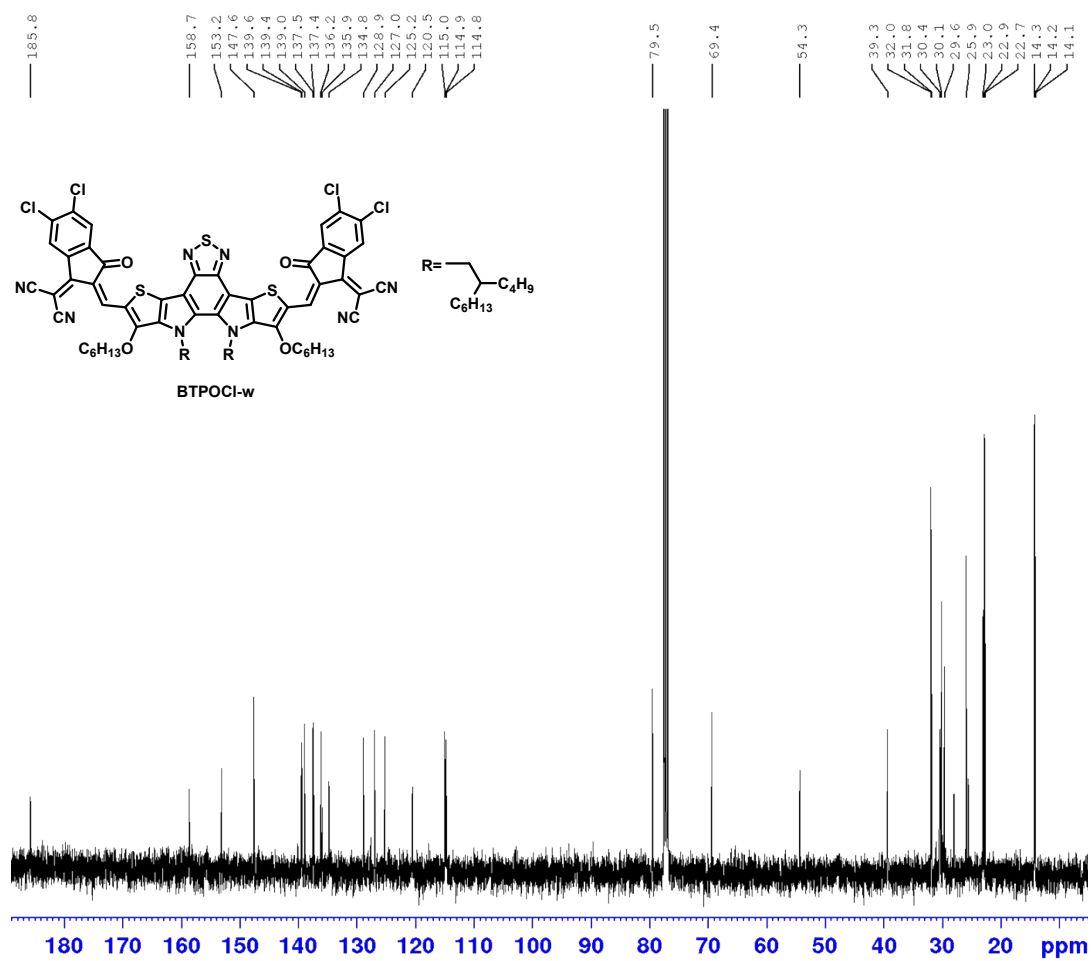


Figure S7 ^{13}C NMR spectrum of BTPOCl-w (100 MHz, CDCl_3).

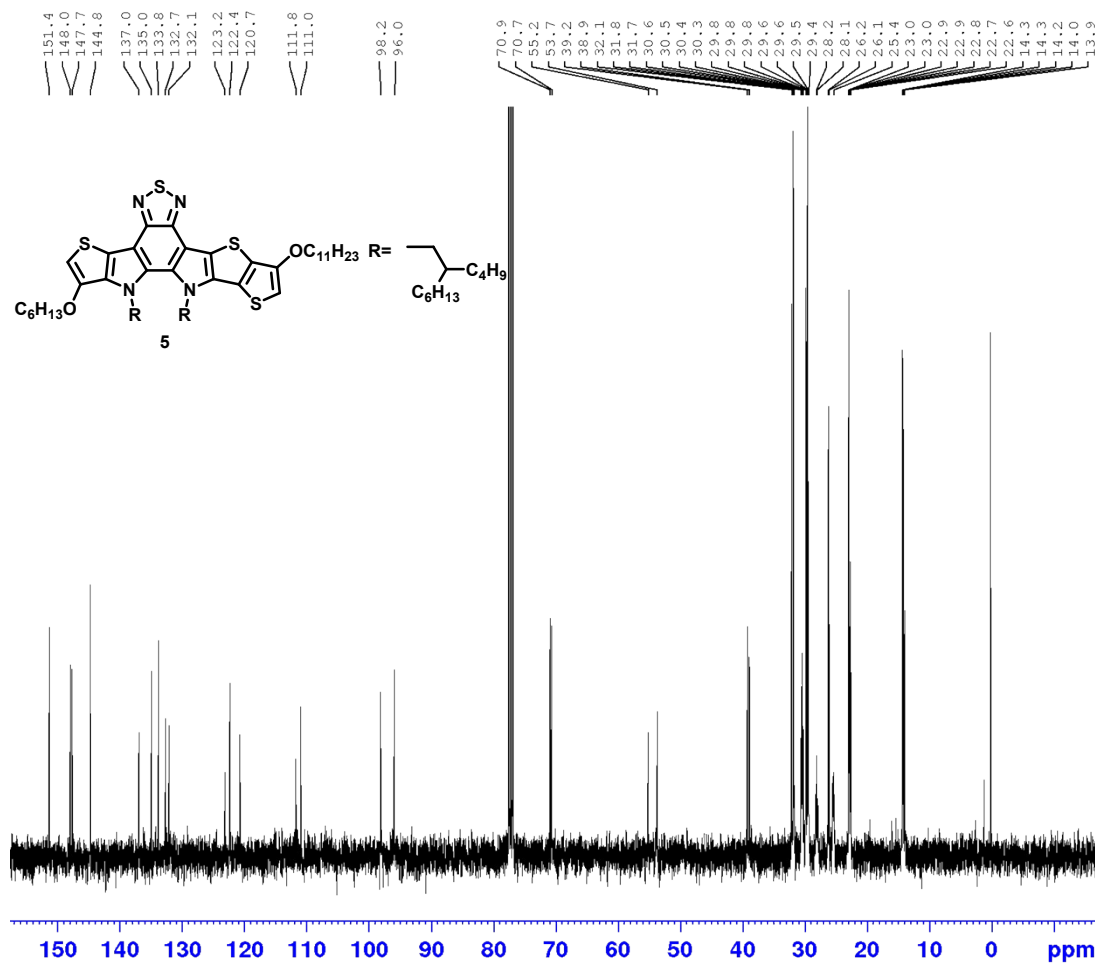


Figure S9 ^{13}C NMR spectrum of compound **5** (100 MHz, CDCl_3).

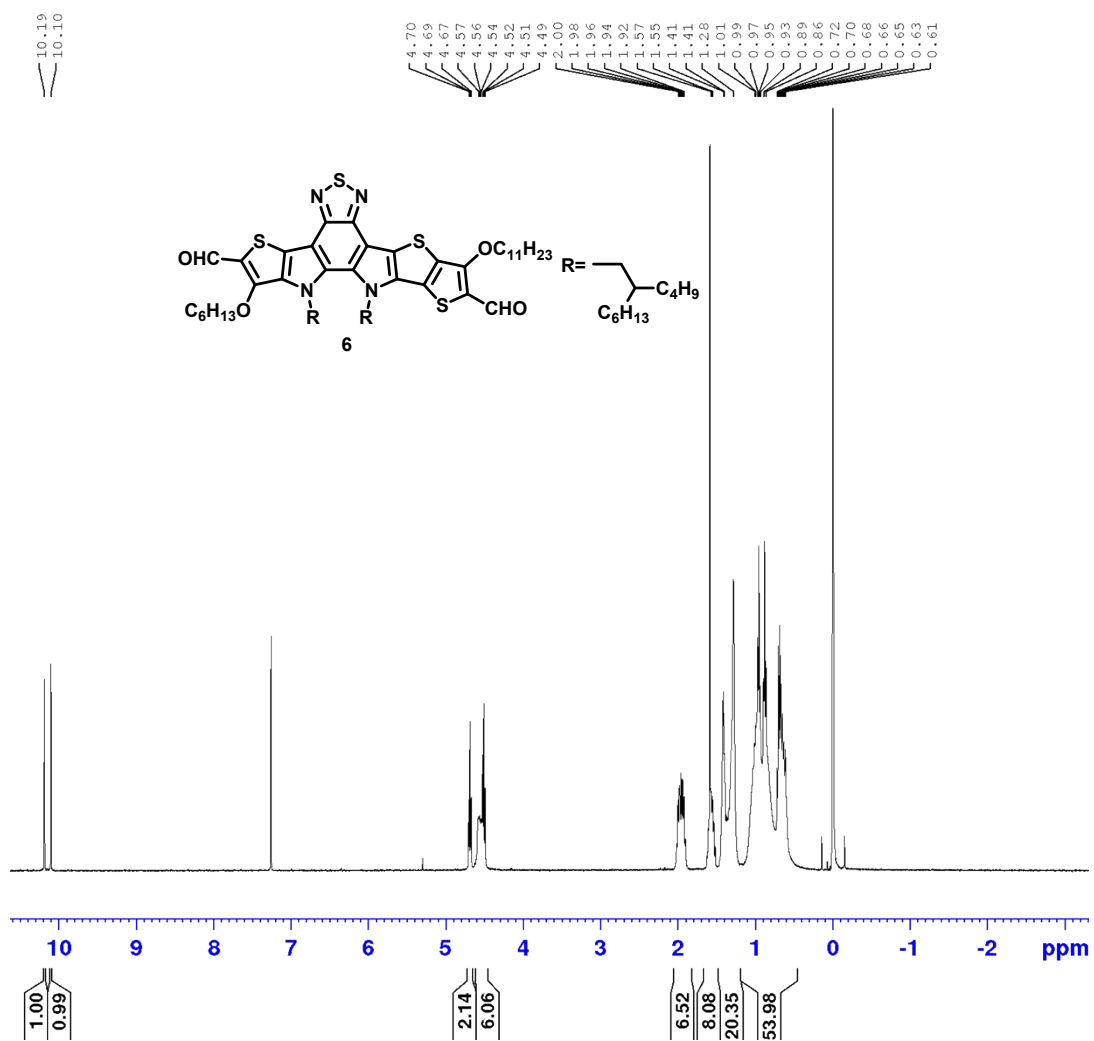


Figure S10 ^1H NMR spectrum of compound **6** (400 MHz, CDCl_3).

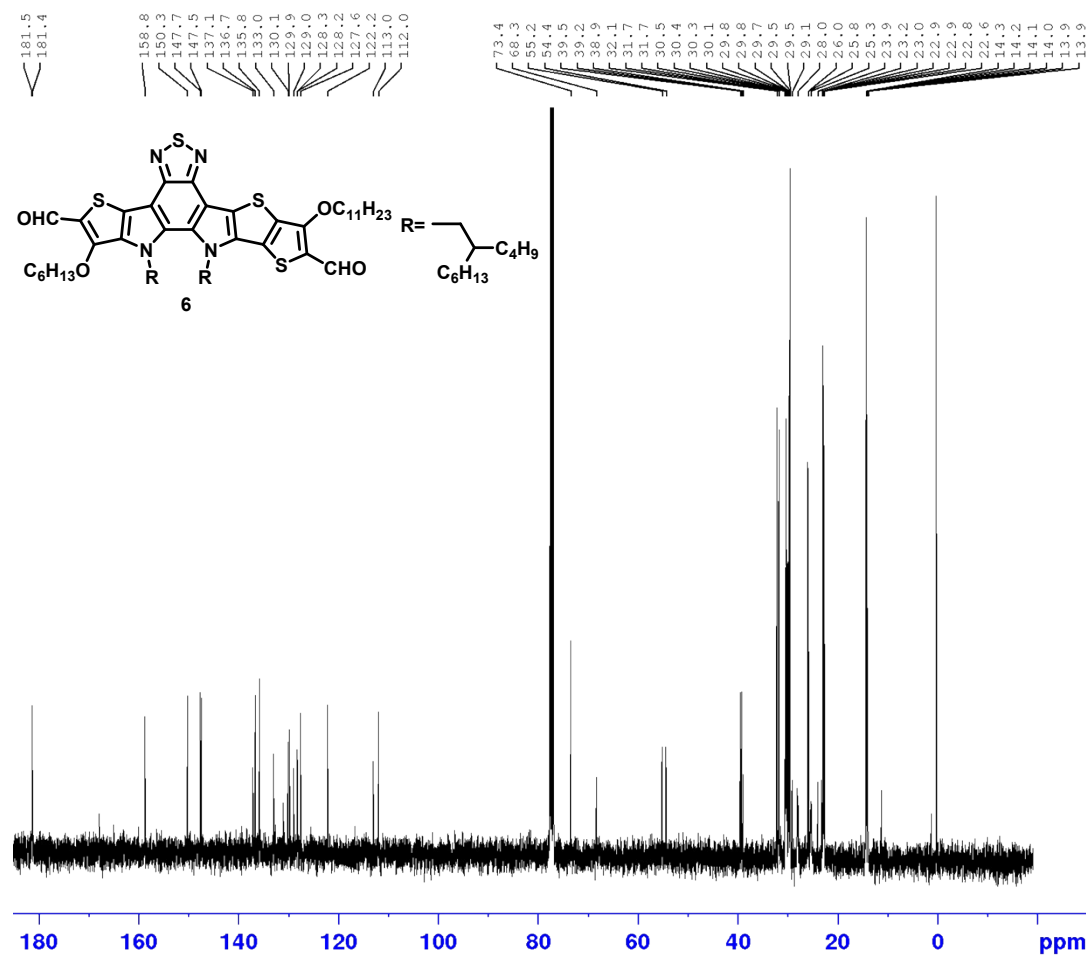


Figure S11 ^{13}C NMR spectrum of compound 6 (100 MHz, CDCl_3).

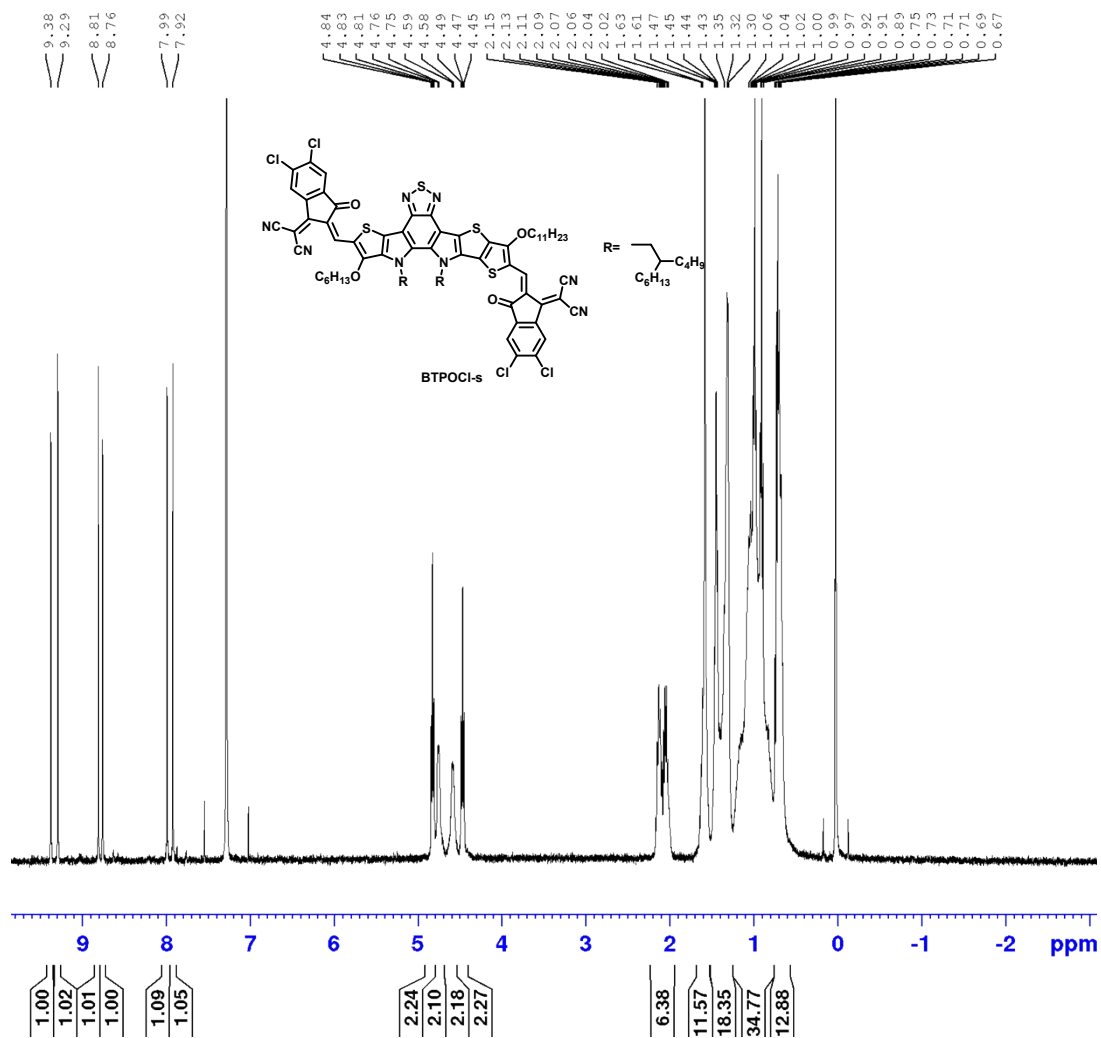


Figure S12 ¹H NMR spectrum of BTPOCl-s (400 MHz, CDCl₃).

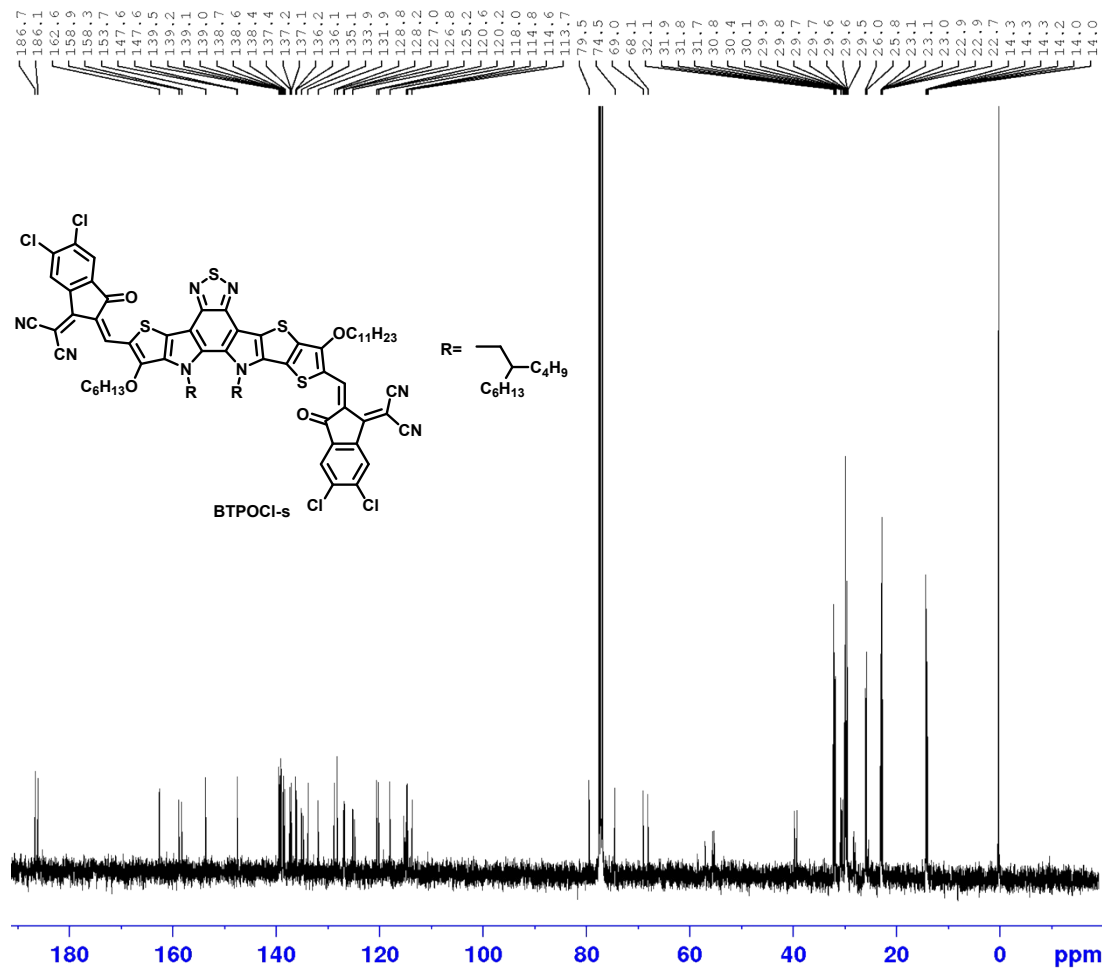


Figure S13 ^{13}C NMR spectrum of BTPOCI-s (100 MHz, CDCl_3).

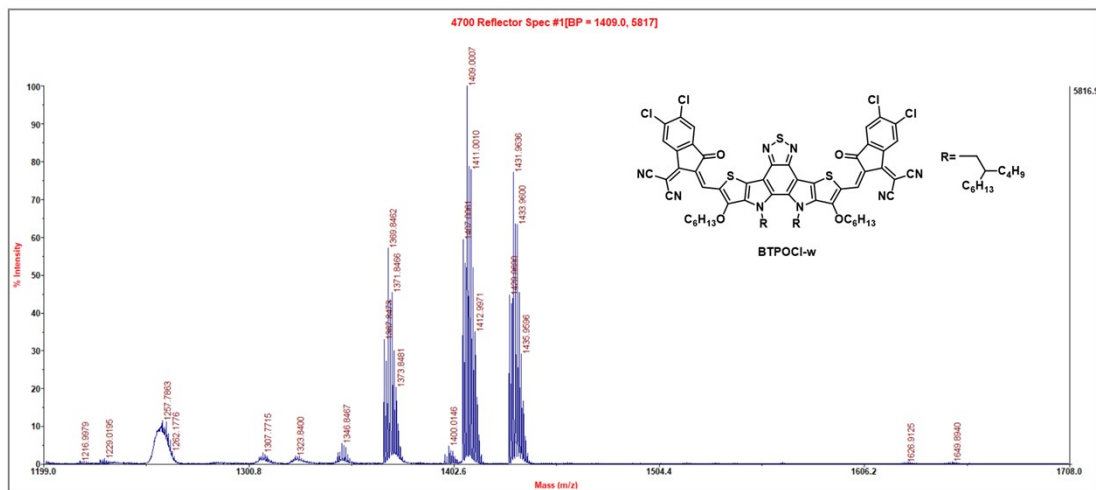


Figure S14 MS spectrum (MALDI-TOF) of BTPOCl-w.

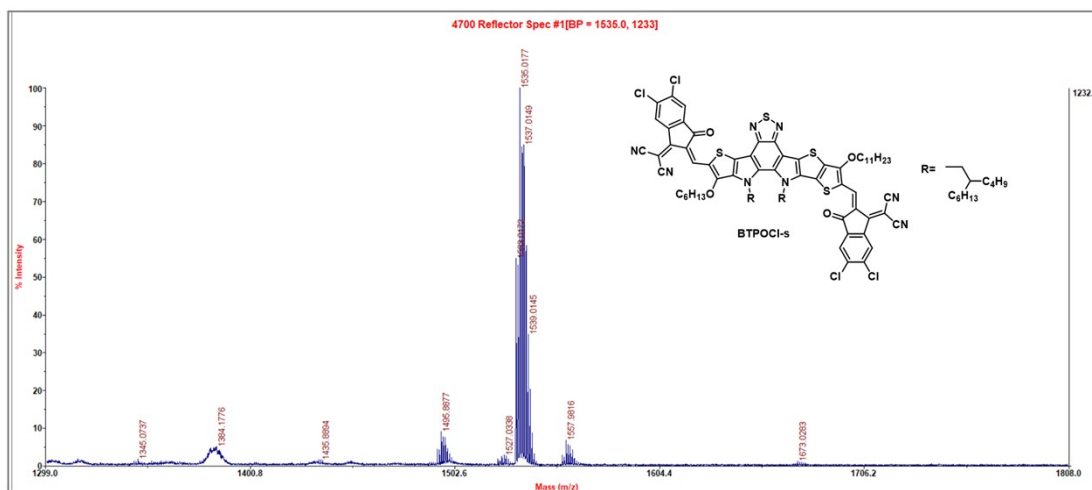


Figure S15. MS spectrum (MALDI-TOF) of BTPOCl-s.

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