

Supporting Information

Side Chain Independent Photovoltaic Performance of Thienopyrroledione Conjugated Donor-Acceptor Polymers

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Materials

All starting materials were purchased from a commercial supplier and were used without further purification. Thiophene-3,4-dicarboxylic acid was purchased from Santa Cruz Biochemicals. Iodomethane, 99%, stab. w/ copper was purchased from Alfa Aesar. Iodopropane, 99%, stab. w/ copper was purchased from Aldrich. 1-bromo-2-methylpropane was purchased from Aldrich. 2-bromomethyl cyclohexane was purchased from Aldrich. Potassium carbonate was purchased from VWR. N,N-dimethylformamide was purchased from EMD Millipore Corporation. N-bromosuccinimide, 99% was purchased from Alfa Aesar. Sulfuric acid, 95-98% was purchased from VWR. 2-octyldodecan-1-ol was purchased from TCI America. Triphenylphosphine was purchased from AK Scientific Inc. 1,2-bis(diphenyl phosphino) ethane nickel (II) chloride, 99% was purchased from STREM Chemicals, Inc. Mg, 99.9+% (trace metal basis), turnings were purchased from Acros Organics. Lithium diisopropyl amine was purchased from Sigma. Trimethyl tin chloride was purchased from TCI America. Pd₂(dba)₃ was purchased from STREM Chemicals, Inc. P(o-tol)₃ was purchased from Oakwood Products, Inc. 2-bromothiophene was purchased from Oakwood Products, Inc. 2-(tri-n-butyl-stannyl thiophene), 97% was purchased from Alfa Aesar. The palladium scavenger (diethyl dithiocarbamic acid diethyl ammonium salt) was purchased from TCI America. 5,5'-bis(trimethylstannyl)-2,2'-bithiophene was synthesized according to a published procedure.¹

Instrument & Measurement Details

The ¹H-NMR spectra of the polymers were obtained on a Bruker 400 MHz NMR instrument in TCE-*d*₂ at 110 °C for at least 256 scans.

Number average molecular mass (*M*_n) and dispersity (*Đ*) were determined by gel permeation chromatography (GPC) using a Tosoh EcoSEC HT GPC Instrument with RI detector. Experiments were run with 1,2,4 trichlorobenzene (TCB) as eluent at 140 °C at a flow rate of 1 mL/min on two sequentially connected 30 x 7.8 mm GMHhr-H(S) TT2 column (Tosoh Bioscience). The instrument was calibrated vs. polystyrene standards (1,390-1,214,000 g/mol), and data were analyzed using EcoSEC High Temperature GPC Workstation Software. To prepare polymer samples for GPC measurements, each polymer was dissolved in HPLC grade TCB at a concentration 1.0 mg/mL and then stirred for at least 3 h at 120 °C prior to filtering through a 0.45 μm PTFE filter.

Differential pulse voltammetry (DPV) was performed in a glove box using a standard three-electrode cell based on a polished and cleaned Pt button working electrode, a Ag/Ag⁺ reference electrode (calibrated vs Fc/Fc⁺ which is taken as -5.12 eV vs vacuum), and a Pt flag counter electrode. Polymer films

were made by drop-casting a polymer solution in chlorobenzene (CB) (1 mg/mL) onto the Pt button and drying in air prior to measurement. Recrystallized TBAPF₆ (0.5 M) in acetonitrile dried in a solvent purification system (SPS) was used as the supporting electrolyte.

Grazing incidence wide angle X-ray scattering (GIWAXS) and grazing incidence small angle X-ray scattering (GISAXS) were performed at the Brookhaven National Laboratory at the 11-BM Complex Materials Scattering (CMS) beamline of the National Synchrotron Light Source II (NSLS-II) with a beam energy of 13.5 keV. The polymer and blend samples were prepared by spin-coating onto silicon wafers in the same manner as described for organic solar cell device preparation. The 2D scattering patterns were collected at an X-ray incidence angle of 0.13° with a Pilatus detector with a pixel size of 172 μm, placed about 250 mm from the sample for GIWAXS and about 3.0 m from the sample for GISAXS. Both datasets were analyzed using the Nika analysis package for Wavemetrics Igor Pro,² while the GISAXS data was additionally processed with the Irena analysis package.³

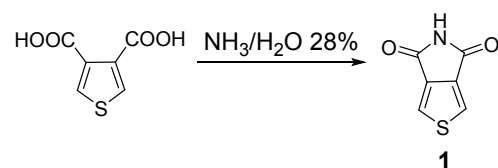
UV-Vis absorption spectra were obtained on a Cary 5000 spectrometer under Cary WinUV control. For thin-film UV-Vis absorption measurements, polymers were spin-coated onto pre-cleaned glass slides from 6 mg/mL solutions in CB. Thickness of the films were obtained with a Bruker DektakXT profilometer.

Differential scanning calorimetry (DSC) was performed using a TA Instruments Q200 DSC with heating and cooling rates of 20 °C/min in hermetically sealed aluminum pans.

S1: Synthetic Methods

Abbreviations: methyl (M), isopropyl (IP), isobutyl (IB), and cyclohexylmethyl (CM).

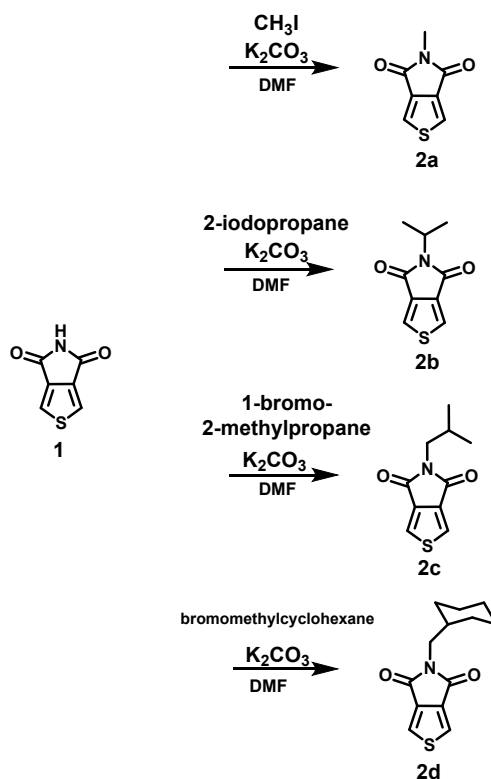
Synthetic Scheme 1



4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (1)⁴: To a 50-mL round bottom flask was added 3,4-thiophene dicarboxylic acid (5.0 g, 29.05 mmol) and water (2-3 mL). Small pieces of glass were added as boiling stones. Concentrated aqueous ammonia (28%/14.8M) (20.75 mL, 290.5 mmol) was added slowly. The flask was heated gently to dissolve the starting material, then to a boil until all water and excess ammonia were driven off. A white, crystalline material remained. A short (3-4") air-condenser was attached to the flask. In a sand bath, the flask was heated to 260-280 °C for 3-4 hours. During this time, the reaction became a homogeneous melt, and product began to sublime to the top of the flask and into the condenser. Heating was continued until all material had sublimed. After cooling, the sublimed material was dissolved into hot acetonitrile and passed through a nylon filter. The solution was dried by rotary evaporation yielding white crystals. The white crystals were added to 50 mL of DI water in a 100-mL round bottom flask. The solution was sonicated for 30 minutes and vacuum filtered to collect the crystals. Drying under high vacuum yielded **1** (1.40 g, 16% yield) as a crystalline beige solid.

^1H NMR (300 MHz, DMSO- d_6): δ 11.26 (bs, 1H), 8.28 (s, 2H).

Synthetic Scheme 2



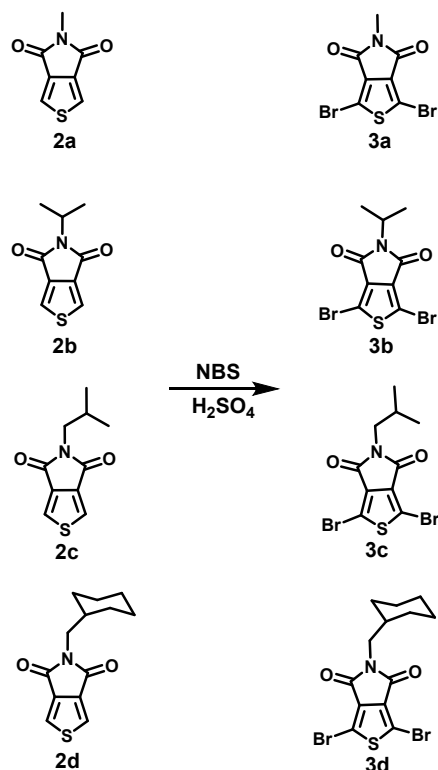
General procedure for reaction of a thiophene imide with an electrophile: To an oven-dried 3-necked round bottom flask, **1** (1.0 eq.) and K_2CO_3 (3.0 eq.) was added, sealed, evacuated, and refilled with argon 3 times. Dry dimethylformamide was added to the flask to form a 0.15 M solution of the thiophene imide. The electrophile (2.0 eq.) was slowly added to the solution, and the solution was allowed to stir at room temperature overnight. The solution was then quenched with ~ 1 mL 1M HCl, poured into a round bottom flask, and concentrated by rotary evaporation. The compound was dissolved in ethyl acetate, gravity filtered through a conical paper funnel, and concentrated by rotary evaporation to remove the remaining salts. Further purification is described separately. Note: compound **2a** was synthesized by literature procedure.^{4,5}

5-isopropyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (2b): 4 mmol scale of **1** with 2-iodopropane as the electrophile. Crude material was subjected to column chromatography (silica gel, 10% EtOAc in hexanes) to give 290 mg (37%) of white crystalline solid **2b**. ^1H NMR (300 MHz, CDCl_3 - d) δ 7.77 (s, 2H), 4.46 (hept, $J=7.1$ Hz, 1H), 1.48 (d, $J=7.1$ Hz, 6H). ^{13}C NMR (175 MHz, Chloroform- d) δ 162.74, 136.86, 125.36, 43.55, 20.09. HRMS (ESI MS) m/z : theor: 196.0427 found: 196.0420.

5-isobutyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (2c): 3.6 mmol scale of **1** with 1-bromo-2-methylpropane as the electrophile. Crude material was subjected to column chromatography (silica gel, 10% EtOAc in hexanes) to give 310 mg (41%) of a white crystalline solid **2c**. ^1H NMR (300 MHz, Chloroform- d) δ 7.81 (s, 2H), 3.44 (d, $J=7.4$ Hz, 2H), 2.17 – 2.01 (m, 1H), 0.93 (d, $J=6.7$ Hz, 6H). ^{13}C NMR (75 MHz, Chloroform- d) δ 162.85, 136.56, 125.60, 45.72, 27.76, 20.15. HRMS (ESI MS) m/z : theor: 210.0583 found: 210.0577.

5-(cyclohexylmethyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (2d): 4.8 mmol scale of **1** with bromomethyl cyclohexane as the electrophile. Crude material was subjected to column chromatography (silica gel, 20% EtOAc in hexanes) to give 887 mg (75%) of a white crystalline solid **2d**. ¹H NMR (300 MHz, Chloroform-*d*) δ 7.79 (s, 2H), 3.44 (d, *J* = 7.2 Hz, 2H), 1.75 – 1.01 (m, 11H). ¹³C NMR (175 MHz, Chloroform-*d*) δ 163.04, 136.73, 125.60, 44.68, 37.00, 30.88, 26.38, 25.81. HRMS (ESI MS) *m/z*: theor: 250.0896 found: 250.0893.

Synthetic Scheme 3



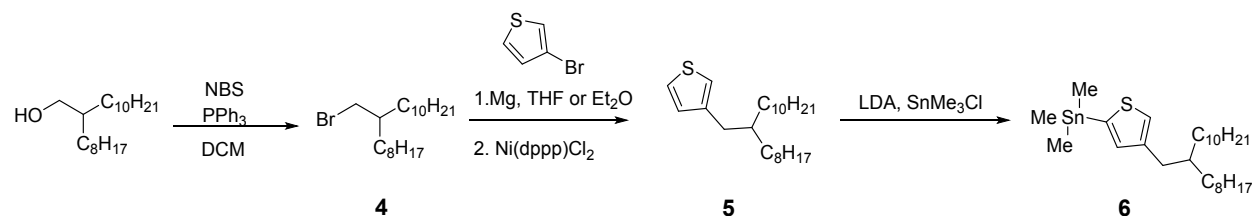
General procedure for substitutional bromination of thiophene imide compounds: To a round bottom flask, the alkylated TPD unit (**2a**, **2b**, **2c**, **2d**) (1.0 eq.), N-bromosuccinimide (4.0 eq.), and concentrated sulfuric acid (0.25M to alkylated imide) was added. The reaction was stirred under an argon atmosphere for 30 minutes at 0 °C, then at least 3 hours at room temperature. The reaction was poured onto a large excess of ice-water. The precipitated solid was collected on a nylon filter then washed with a large excess of DI water. The product was used without further purification. Note: compound **3a** was synthesized by literature procedure.^{1,5}

1,3-dibromo-5-isopropyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (3b): 1.2 mmol scale of **2b** yielded 287 mg (69%) of a powdery beige solid **3b**. ¹H NMR (300 MHz, Chloroform-*d*) δ 4.44 (hept, *J* = 7.0 Hz, 1H), 1.45 (d, *J* = 7.0 Hz, 6H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 160.40, 134.81, 112.83, 44.03, 19.94. HRMS (ESI MS) *m/z*: theor: 351.8637 found: 351.8632.

1,3-dibromo-5-isobutyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (3c): 1 mmol scale of **2c** yielded 253 mg (72%) of a powdery beige solid **3c**. ¹H NMR (300 MHz, Chloroform-*d*) δ 3.42 (d, *J* = 7.3 Hz, 2H), 2.13 – 2.04 (m, 1H), 0.93 (d, *J* = 6.7 Hz, 6H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 160.68, 134.77, 113.13, 46.16, 27.76, 20.24. HRMS (ESI MS) *m/z*: theor: 365.8790 found: 365.8786.

1,3-dibromo-5-(cyclohexylmethyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (3d): 0.64 mmol scale of **2d** yielded 198 mg (76%) of a powdery beige solid **3d**. ¹H NMR (300 MHz, Chloroform-*d*) δ 3.44 (d, *J* = 7.0 Hz, 2H), 1.99 – 0.61 (m, 11H). ¹³C NMR (175 MHz, Chloroform-*d*) δ 160.77, 134.84, 113.11, 45.02, 36.94, 30.88, 26.32, 25.78. HRMS (ESI MS) *m/z*: theor: 427.8912 found: 427.8913.

Synthetic Scheme 4



9-(bromomethyl)nonadecane (4)⁵: An oven-dried 300-mL round bottom flask was sealed and cooled to 0 °C under argon. To this vessel was added 2-octyldodecan-1-ol (20 g, 67 mmol), PPh₃ (28.11 g, 107 mmol), and 100 mL dry DCM. The solution was stirred, and N-bromosuccinimide (17.88 g, 100 mmol) was slowly added to the solution. The reaction was stirred for 12 hours. The compound was purified by column chromatography (silica gel, hexanes) to yield **4** (18.26 g, 89% yield) as a colorless liquid. ¹H NMR (300 MHz, CDCl₃-*d*) δ 3.44 (d, *J* = 4.7 Hz, 2H), 1.61 (s, 1H), 1.28 (s, 32H), 0.93-0.84 (m, 6H).

3-(2-octyldodecyl)thiophene (5)⁵: To an oven-dried, 250-mL round bottom flask was added magnesium (1.82 g, 75.8 mmol). The vessel was flame dried under vacuum to ensure the Mg was dry. To the vessel were added 5 drops of Br₂. The vessel was stirred under vacuum overnight. Dry degassed diethyl ether (50 mL) was added under argon, followed by an addition of iodine (5 mg) dissolved in ~1 mL Et₂O. 0.5 mL of **4** was added dropwise, followed by 3 drops of 1,2 dibromoethane with gentle heat from a heat gun. At this point, an orange to gray color change was observed. The rest of **4**: (total of 18.26 g, 50.52 mmol) was added dropwise to the reaction vessel. NiCl₂(dppp) (40 mg, 0.07 mmol) was added; a yellow color and foaming was observed. The reaction was stirred 5 minutes. 3-Bromothiophene (1.25 mL) was added dropwise followed by NiCl₂(dppp) (23 mg). The 3-bromothiophene and NiCl₂(dppp) step was repeated 4 times. The reaction was stirred overnight at room temperature. The reaction was quenched with water (20 mL) over a period of 1 hour. Concentrated HCl (37%) (10 mL) was added to the reaction over 30 minutes. The reaction was extracted with ether and dried by rotary evaporation. The product was purified by Kugelroher distillation to yield **5** (5.32 g, 47% yield) as a colorless liquid. ¹H NMR (300 MHz, CDCl₃) δ 7.23 (1H, *J* = 4.9, 2.9, dd), 6.91 (2H, *J* = 6.9, 2.0 Hz, dd), 2.57 (2H, *J* = 6.8 Hz, d), 1.61 (1H, s), 1.27 (32H, s), 0.90 (6H, *J* = 6.7 Hz, t).

Trimethyl(4-(2-octyldodecyl)thiophen-2-yl)stannane (6)⁵: In an oven-dried 100-mL round bottom flask, **5** (2.5 g, 6.86 mmol) was dissolved in dry degassed THF [45 mL (0.15 M)] under inert conditions. The vessel was cooled to -78 °C. In an oven-dried 10-mL vial, di-isopropylamine (0.549 mL, 7.55 mmol) was dissolved in 5 mL of dry degassed THF. The vial was cooled to -78 °C. N-Butyllithium (2.875 mL, 7.2 mmol) was added dropwise to the diisopropyl amine solution. This vial was kept at -78 °C for 10 minutes,

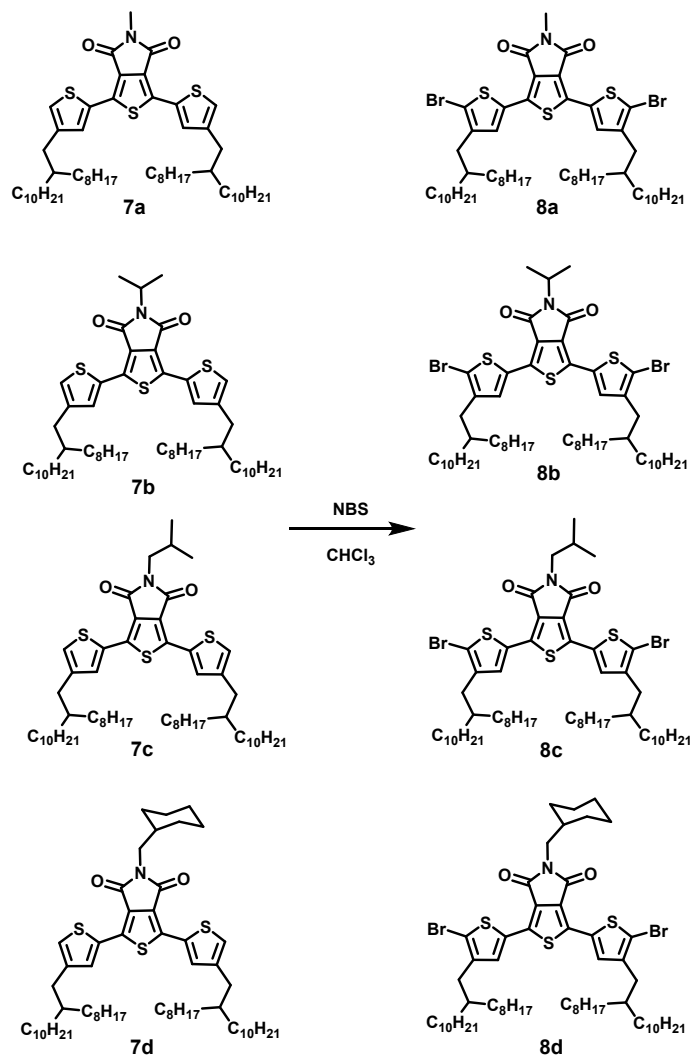
by syringe; the syringe was subsequently rinsed out with the remaining half of the THF. The reaction was refluxed overnight at 70 °C. Further purification is described separately. Note: compound **7a** was synthesized by literature procedure.⁵

5-isopropyl-1,3-bis(4-(2-octyldodecyl)thiophen-2-yl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (7b): A 0.43 mmol scale (**3b**) reaction was purified by column chromatography (silica gel, 5% EtOAc in hexanes) to yield 328 mg (84%) of an orange-yellow waxy solid compound **7b**. ¹H NMR (300 MHz, CDCl₃) δ 7.78 (2H, s), 6.99 (2H, s), 4.52(1H, m), 2.56 (4H, d), 1.65 (2H, s), 1.50 (6H, d), 1.25 (64H, s), 0.90-0.84 (12H, m). ¹³C NMR (75 MHz, Chloroform-*d*) δ 162.70, 143.67, 136.66, 132.08, 131.56, 128.24, 124.47, 43.46, 38.97, 34.97, 33.37, 32.08, 30.16, 29.85, 29.82, 29.79, 29.53, 29.51, 26.70, 22.85, 20.12, 14.27. HRMS (ESI MS) *m/z*: theor: 920.6407 found: 920.6409.

5-isobutyl-1,3-bis(4-(2-octyldodecyl)thiophen-2-yl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (7c): A 0.43 mmol scale (**3c**) reaction was purified by column chromatography (silica gel, 5% EtOAc in hexanes) to yield 300 mg (76%) of an orange-yellow waxy solid compound **7c**. ¹H NMR (300 MHz, CDCl₃) δ 7.82 (2H, s), 7.00 (2H, s), 3.50 (2H, d), 2.57 (4H, d), 2.15 (1H, m), 1.65 (2H, s), 1.25 (64H, s), 1.00-0.84 (18H, m). ¹³C NMR (75 MHz, Chloroform-*d*) δ 163.00, 143.79, 136.94, 132.10, 131.69, 128.06, 124.55, 45.97, 38.98, 35.02, 33.37, 32.09, 30.18, 29.86, 29.83, 29.79, 29.54, 29.51, 27.91, 26.70, 22.86, 20.37, 14.29. HRMS (ESI MS) *m/z*: theor: 934.6580 found: 934.6580.

5-(cyclohexylmethyl)-1,3-bis(4-(2-octyldodecyl)thiophen-2-yl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (7d): A 0.54 mmol scale (**3d**) reaction was purified by column chromatography (silica gel, 10% DCM in hexanes) to yield 310 mg (59%) of an orange-yellow waxy solid compound **7d**. Note: Reaction was run with tetrakis (0.08 eq.), toluene at 110 °C, and 3 equivalents of the stannylated octyl dodecyl thiophene side chain. ¹H NMR (300 MHz, CDCl₃) δ 7.82 (2H, s), 6.98 (2H, s), 3.51 (2H, d), 2.57 (4H, d), 1.85-1.55 (8H, m), 1.25 (64H, s), 1.10-0.99 (3H, m), 0.97-0.80(12H, m). ¹³C NMR (125 MHz, Chloroform-*d*) δ 163.05, 143.80, 136.92, 132.11, 131.69, 128.09, 124.55, 44.80, 38.99, 37.08, 35.04, 33.39, 33.38, 32.09, 31.04, 30.18, 30.17, 29.85, 29.83, 29.79, 29.53, 29.51, 26.69, 26.44, 25.87, 22.85, 14.28. HRMS (ESI MS) *m/z*: theor: 974.6877 found: 974.6879.

Synthetic Scheme 6



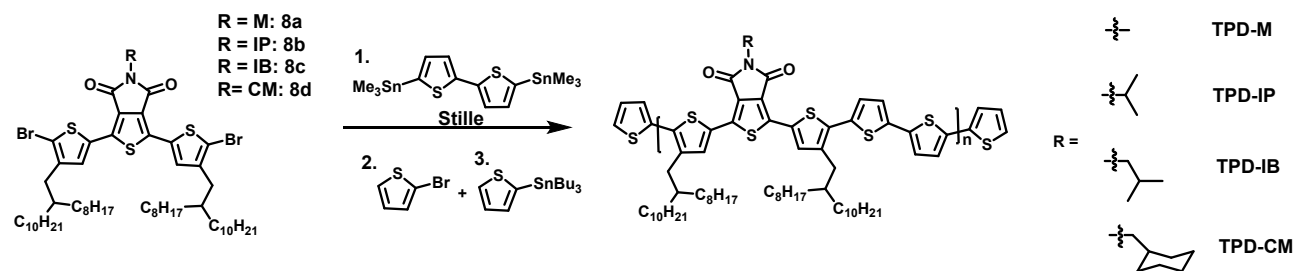
General procedure for bromination of the TPD trimers: The trimers (**7a**, **7b**, **7c**, **7d**) (1.0 eq.), SiO₂ (0.01 eq.), and CHCl₃ (0.05M) were added to a round bottom flask. N-bromosuccinimide (2.5 eq.) was slowly added to the reaction vessel at 0 °C. The reaction was stirred in the dark overnight with an argon line while the reaction vessel was brought to room temperature. The reaction was extracted with H₂O and dried by rotary evaporation. Further purification is described separately. Note: compound **8a** was synthesized by literature procedure.⁵

1,3-bis(5-bromo-4-(2-octyldodecyl)thiophen-2-yl)-5-isopropyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (8b**):** 0.35 mmol scale (**7b**) reaction was purified by column chromatography (silica gel, 25% DCM in hexanes) to yield 371 mg (98%) of a yellow waxy solid **8b**. ¹H NMR (300 MHz, CDCl₃) δ 7.54 (2H, s), 4.50 (1H, m), 2.50 (4H, d), 1.70 (2H, s), 1.50 (6H, d), 1.25 (64H, s), 0.87 (12H, t). ¹³C NMR (75 MHz, Chloroform-*d*) δ 162.46, 142.92, 135.36, 131.81, 130.78, 128.56, 114.27, 43.65, 38.62, 34.23, 33.43, 32.09, 30.16, 29.87, 29.84, 29.83, 29.79, 29.54, 29.53, 26.64, 22.86, 20.11, 14.28. HRMS (ESI MS) *m/z*: theor: 1075.4564 found: 1075.4564.

1,3-bis(5-bromo-4-(2-octyldodecyl)thiophen-2-yl)-5-isobutyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (8c): 0.31 mmol scale (**7c**) reaction was purified by column chromatography (silica gel, 5% EtOAc in hexanes) to yield 331 mg (98%) of a yellow waxy solid **8c**. ¹H NMR (300 MHz, CDCl₃) δ 7.57 (2H, s), 3.46 (2H, m), 2.50 (4H, d), 2.13 (1H, m), 1.70 (2H, s), 1.25 (64 H, s), 1-0.8 (18H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 162.56, 142.80, 135.45, 131.57, 130.66, 128.15, 114.12, 45.83, 38.38, 34.04, 33.18, 31.84, 29.90, 29.60, 29.58, 29.56, 29.52, 29.28, 29.26, 27.67, 26.39, 22.60, 20.11, 14.03. HRMS (ESI MS) *m/z*: theor: 1090.4791 found: 1090.4788.

1,3-bis(5-bromo-4-(2-octyldodecyl)thiophen-2-yl)-5-(cyclohexylmethyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (8d): 0.36 mmol scale (**7d**) reaction was purified by column chromatography (silica gel, 25% DCM in hexanes) to yield 378 mg (93%) of a yellow waxy solid **8d**. ¹H NMR (300 MHz, CDCl₃) δ 7.56 (2H, s), 3.50 (2H, d), 2.51 (4H, d), 1.85-1.55 (8H, m), 1.25 (64H, s), 1.10-0.99 (3H, m), 0.97-0.80 (12H, m). ¹³C NMR (125 MHz, Chloroform-*d*) δ 162.84, 143.02, 135.65, 131.82, 130.87, 128.41, 114.38, 53.58, 44.91, 38.63, 37.09, 34.29, 33.43, 32.09, 31.03, 30.15, 30.14, 29.85, 29.83, 29.81, 29.77, 29.53, 29.51, 26.63, 26.40, 25.85, 22.85, 14.29. HRMS (ESI MS) *m/z*: theor: 1128.6417 found: 1128.6421.

Synthetic Scheme 7



General procedure for Stille copolymerization of TPD polymers: To an oven-dried round bottom flask was added the monomer (**8a**, **8b**, **8c**, **8d**) (1.0 eq.). The vessel was brought into an argon glove box, where 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (1.0 eq.), Pd₂(dba)₃ (0.03 eq.), and P(*o*-tol)₃ (0.12 eq.) was added to the vessel. Dry, degassed toluene (0.05M) was added from the glove box. The flask was equipped with a condenser, sealed, and removed from the glove box. The reaction was stirred for 24 hours at 110 °C; 2-bromothiophene (0.1 mL) was added at this point. 2-(tri-*n*-butyl-stannyl thiophene) (0.1 mL) was added two hours later. A palladium scavenger (0.1 g) was added 2 hours later and allowed to stir an additional hour. After the reaction was cooled to room temperature, the product was purified by soxhlet extraction (solvents used: methanol, acetone, hexane, dichloromethane, chloroform). The specific fraction collected is reported in the individual procedures. Elemental analysis is calculated for the polymer repeat units.

Polymerization for TPD-M: Product in the chloroform fraction was dried by rotary evaporation, dissolved in a small amount of chloroform, precipitated in methanol, and dried by vacuum filtration to yield the polymer TPD-M as a dark blue solid (175 mg, 70% yield). *M_n*: 58 kg/mol, *M_w*: 101 kg/mol, Đ: 1.8 (GPC in 1,2,4-trichlorobenzene vs. polystyrene at 140 °C). ¹H NMR (400 MHz, 1,1,2,2-TCE-*d*₂, 105 °C): δ 7.91 (br, 2H), 7.23 (br, 4H), 3.24 (br, 3H), 2.85 (br, 4H), 1.87 (br, 2H), 1.34 (br, 57H), 0.94 (br, 10H). Anal.

calcd. for $C_{63}H_{93}NO_2S_5$: C (71.74%), H (8.70%), N (1.33%), S (15.20%); Found: C (71.95%), H (8.88%), N (1.38%), S (15.16%).

Polymerization for TPD-IP: Product in the chloroform fraction was dried by rotary evaporation, dissolved in a small amount of chloroform, precipitated in methanol, and dried by vacuum filtration to yield the polymer TPD-IP as a dark blue solid (136 mg, 70% yield). M_n : 36 kg/mol, M_w : 66 kg/mol, \bar{D} : 1.8 (GPC in 1,2,4-trichlorobenzene vs. polystyrene at 140 °C). 1H NMR (400 MHz, 1,1,2,2-TCE- d_2 , 105 °C): δ 7.89 (br, 2H), 7.23 (br, 4H), 4.60 (br, 1H), 2.86 (br, 4H), 1.88 (br, 2H), 1.59 (br, 6H), 1.34 (br, 61H), 0.94 (br, 11H). Anal. calcd. for $C_{65}H_{97}NO_2S_5$: C (72.10%), H (8.84%), N (1.29%), S (14.80%); Found: C (72.80%), H (9.05%), N (1.40%), S (14.85%).

Polymerization for TPD-IB: Product in the chloroform fraction was dried by rotary evaporation, dissolved in a small amount of chloroform, precipitated in methanol, and dried by vacuum filtration to yield the polymer TPD-IB as a dark blue solid (152 mg, 65% yield). M_n : 28 kg/mol, M_w : 40 kg/mol, \bar{D} : 1.4 (GPC in 1,2,4-trichlorobenzene vs. polystyrene at 140 °C). 1H NMR (400 MHz, 1,1,2,2-TCE- d_2 , 105 °C): δ 7.91 (br, 2H), 7.22 (br, 4H), 3.59 (br, 2H), 2.86 (br, 4H), 2.26 (br, 1H), 1.88 (br, 2H), 1.34 (br, 65H), 1.06 (br, 6H), 0.94 (br, 12H). Anal. calcd. for $C_{66}H_{99}NO_2S_5$: C (72.28%), H (8.91%), N (1.28%), S (14.62%).

Polymerization for TPD-CM: Product in the chloroform fraction was dried by rotary evaporation, dissolved in a small amount of chloroform, precipitated in methanol, and dried by vacuum filtration to yield polymer TPD-CM as a dark blue solid (132 mg, 68% yield). M_n : 51 kg/mol, M_w : 80 kg/mol, \bar{D} : 1.6 (GPC in 1,2,4-trichlorobenzene vs. polystyrene at 140 °C). 1H NMR (400 MHz, 1,1,2,2-TCE- d_2 , 105 °C): δ 7.89 (br, 2H), 7.24 (br, 4H), 3.60 (br, 2H), 2.86 (br, 4H), 1.82 (br, 8H), 1.34 (br, 61H), 1.16 (br, 2H), 0.94 (br, 10H). Anal. calcd. for $C_{69}H_{103}NO_2S_5$: C (72.90%), H (8.96%), N (1.23%), S (14.10%); Found: C (72.96%), H (9.04%), N (1.27%), S (14.15%).

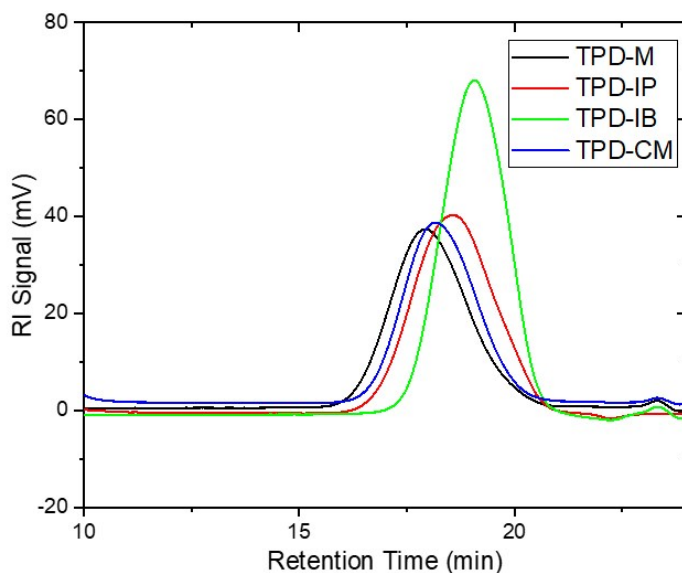
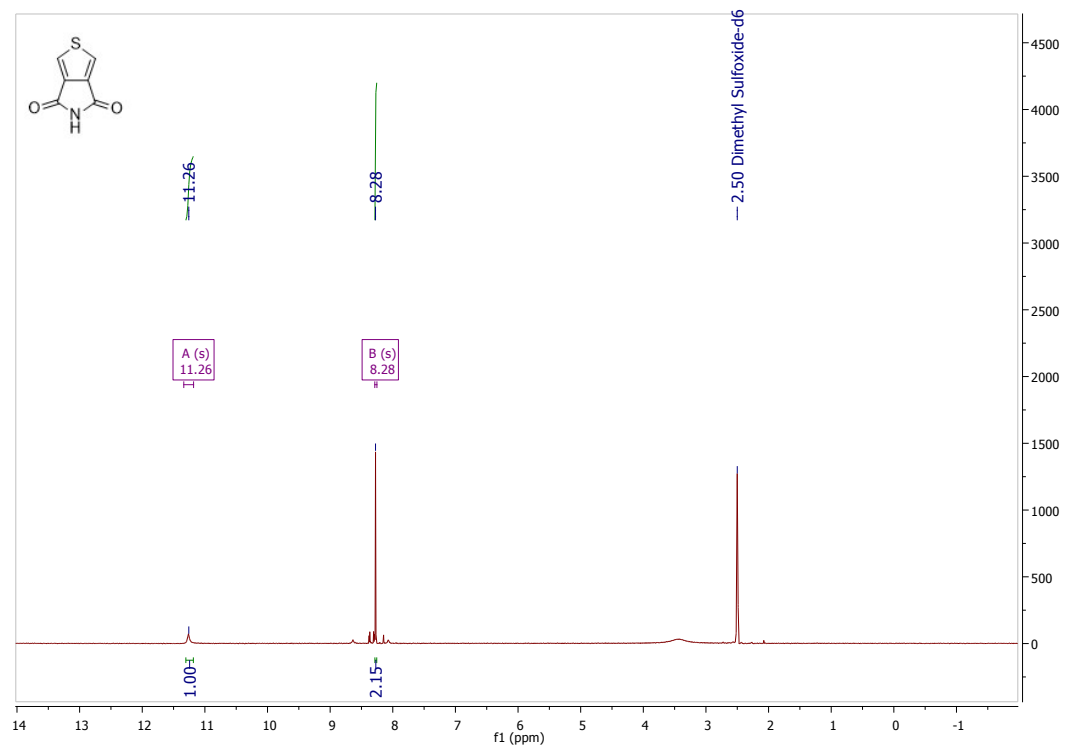
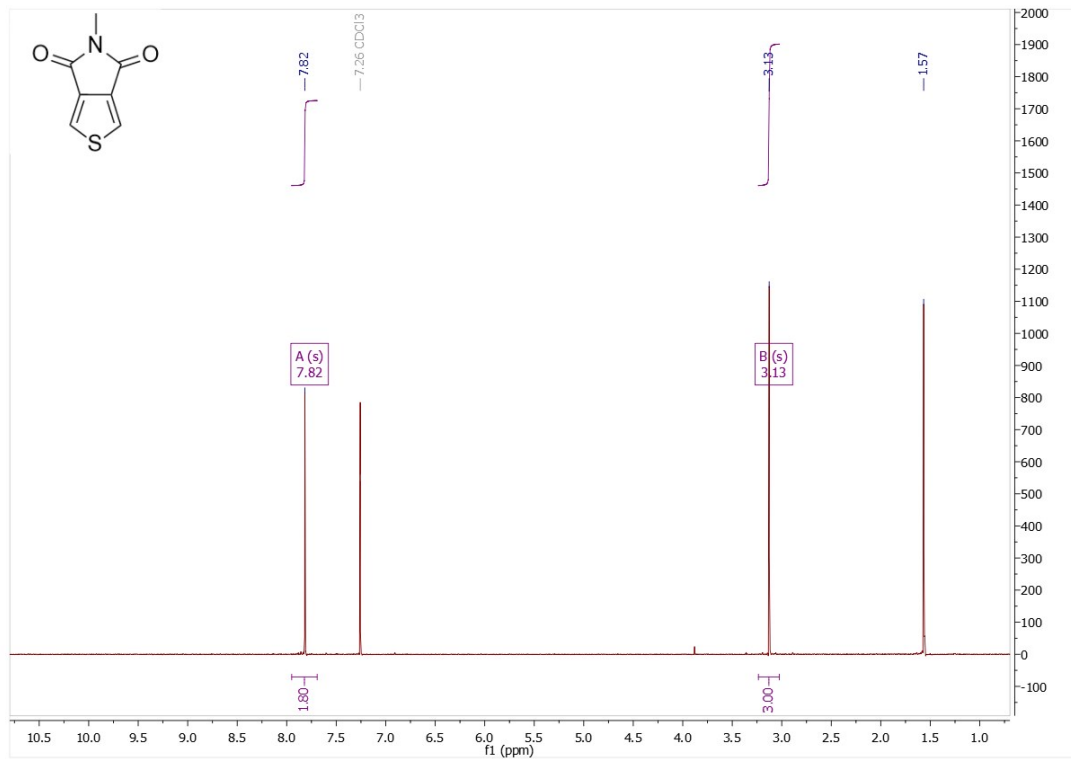


Figure S1. GPC traces of each polymer using the eluent 1,2,4-trichlorobenzene at 140 °C at a flow rate of 1 mL/min.

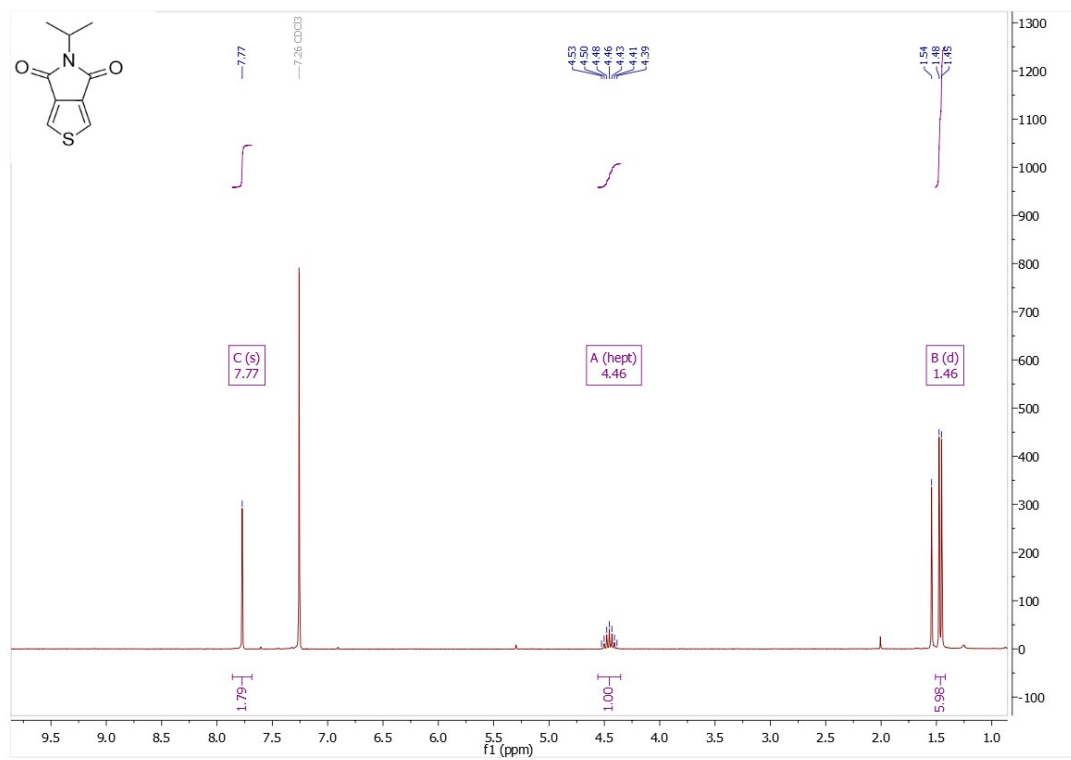
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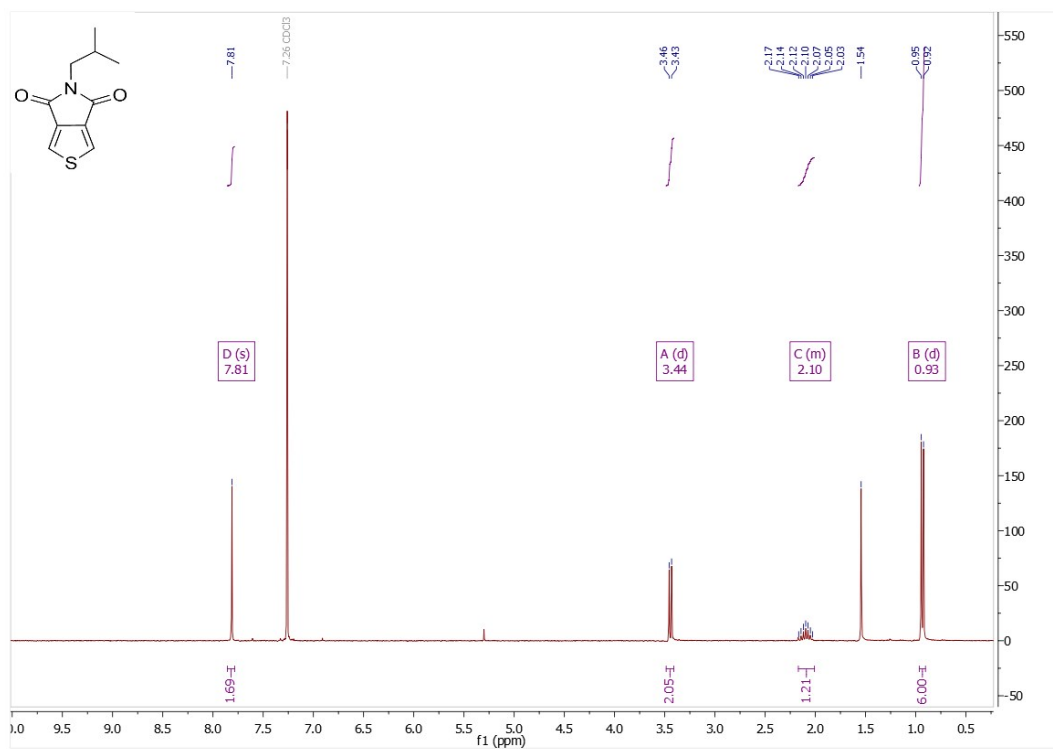
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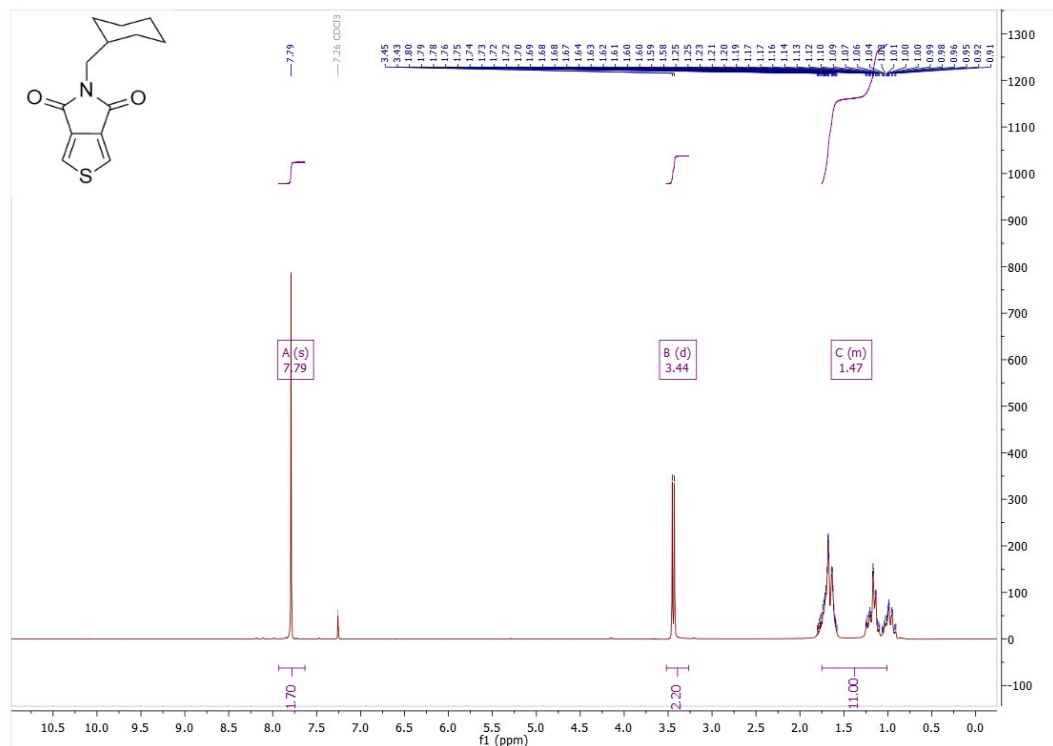
¹H-NMR of 2a CDCl₃-d



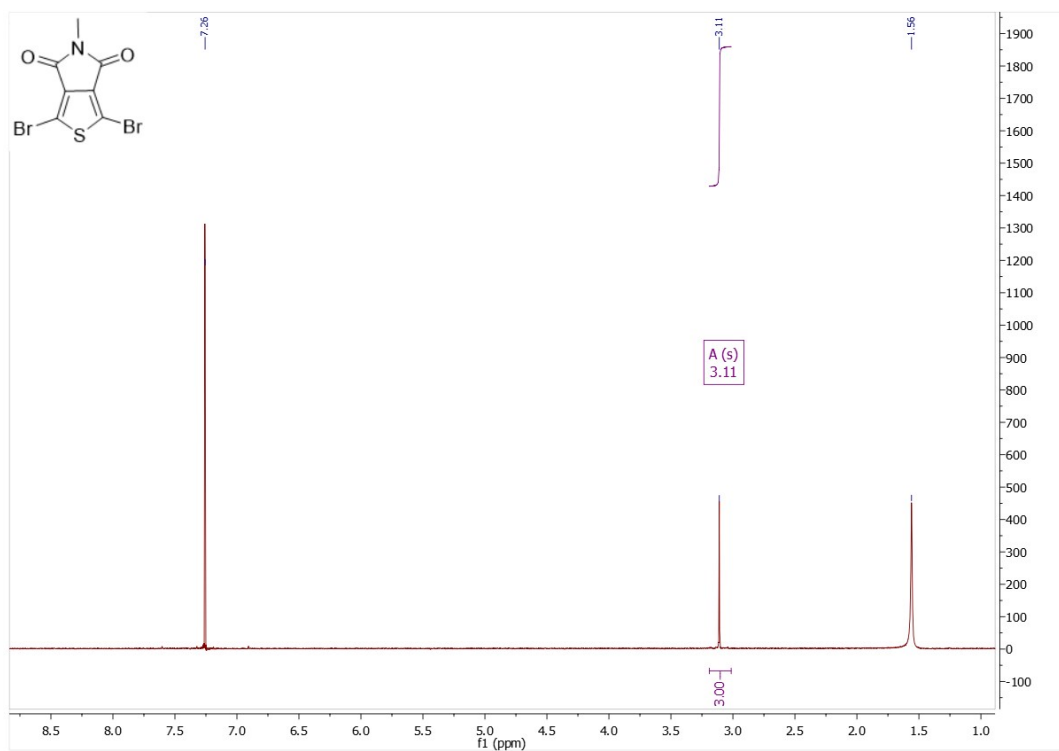
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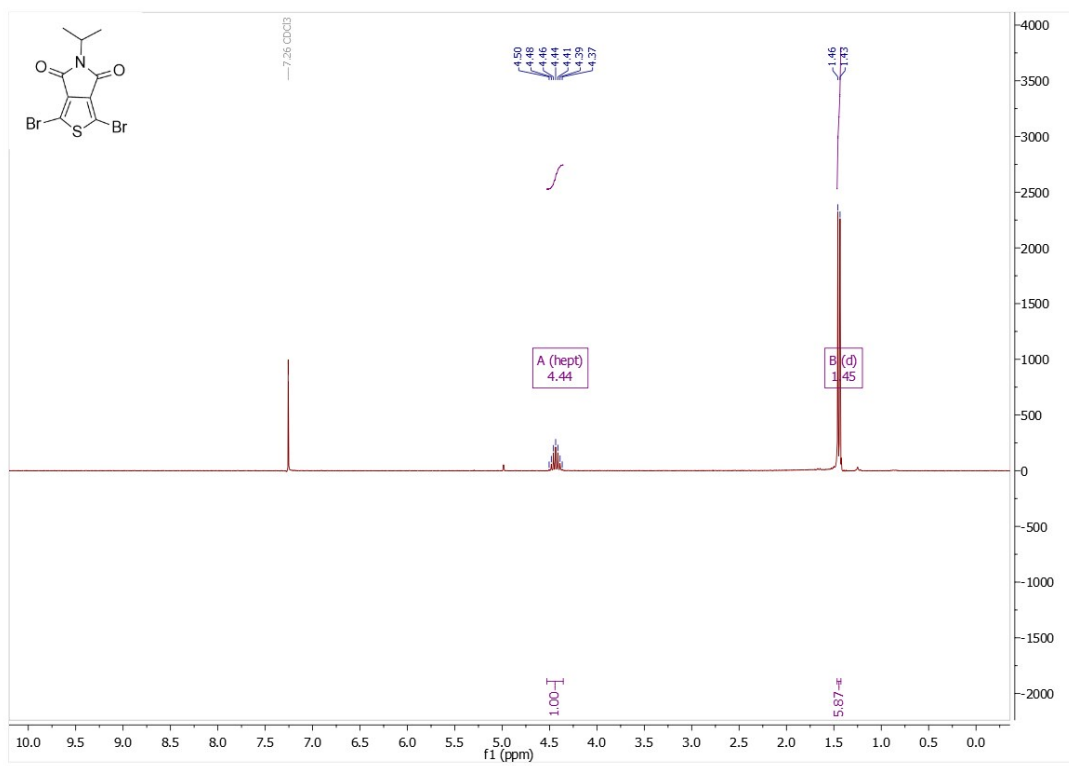
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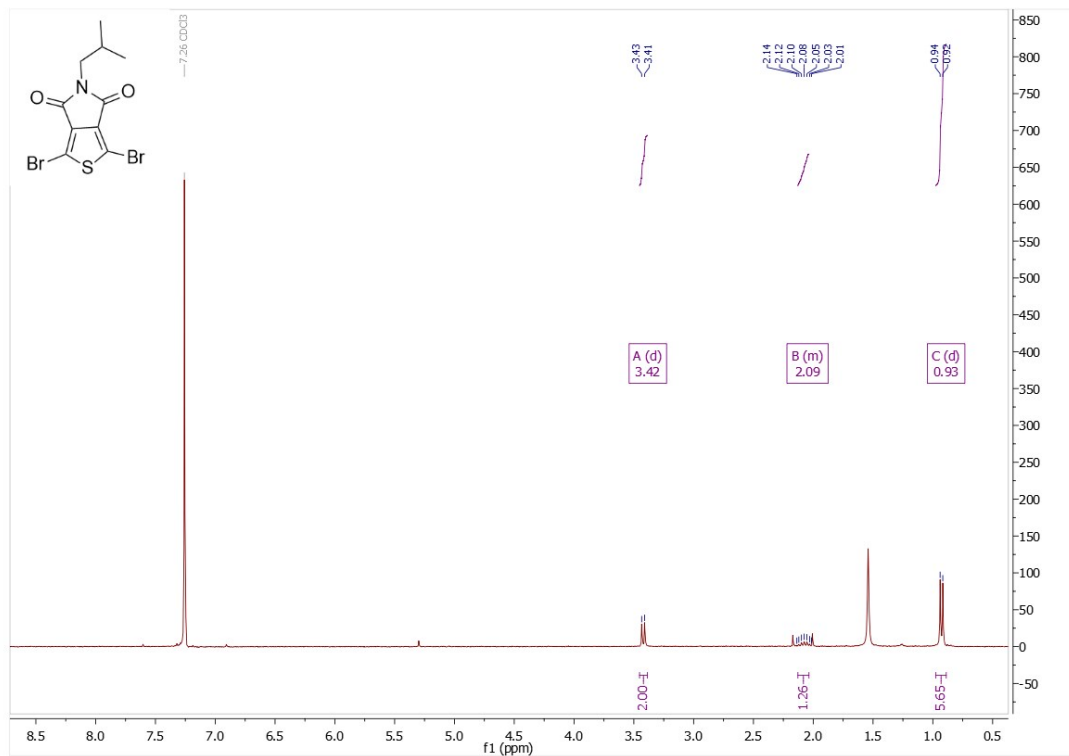
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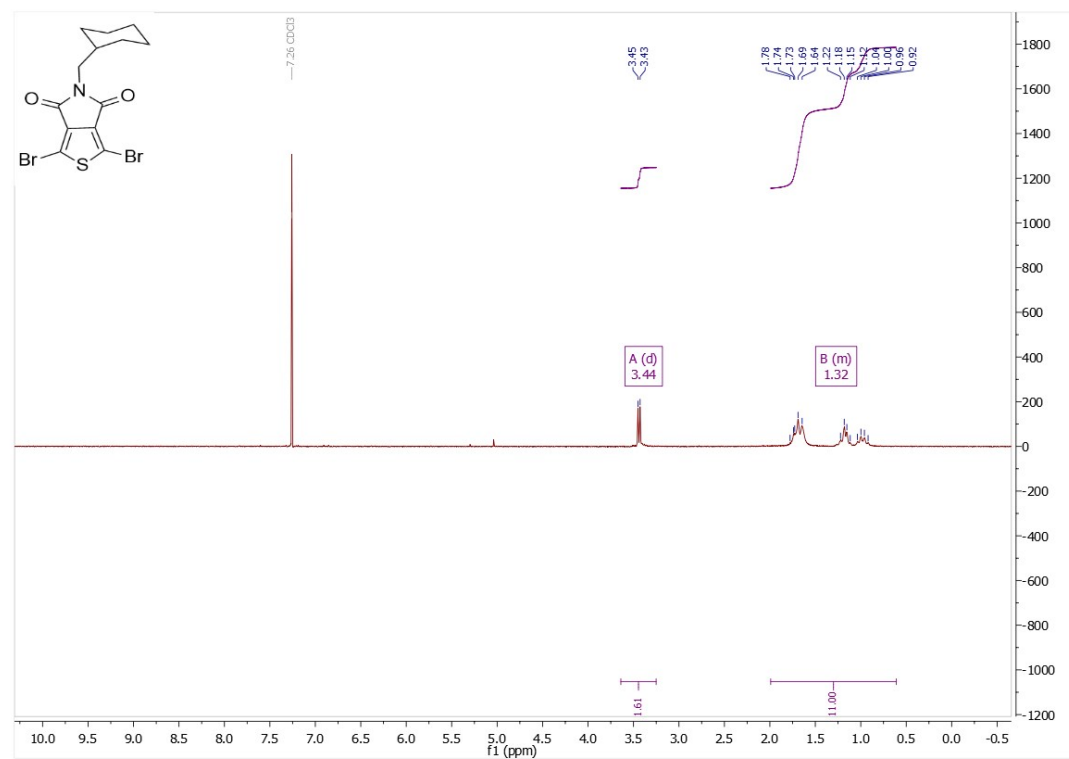
¹H-NMR of 3a CDCl₃-d



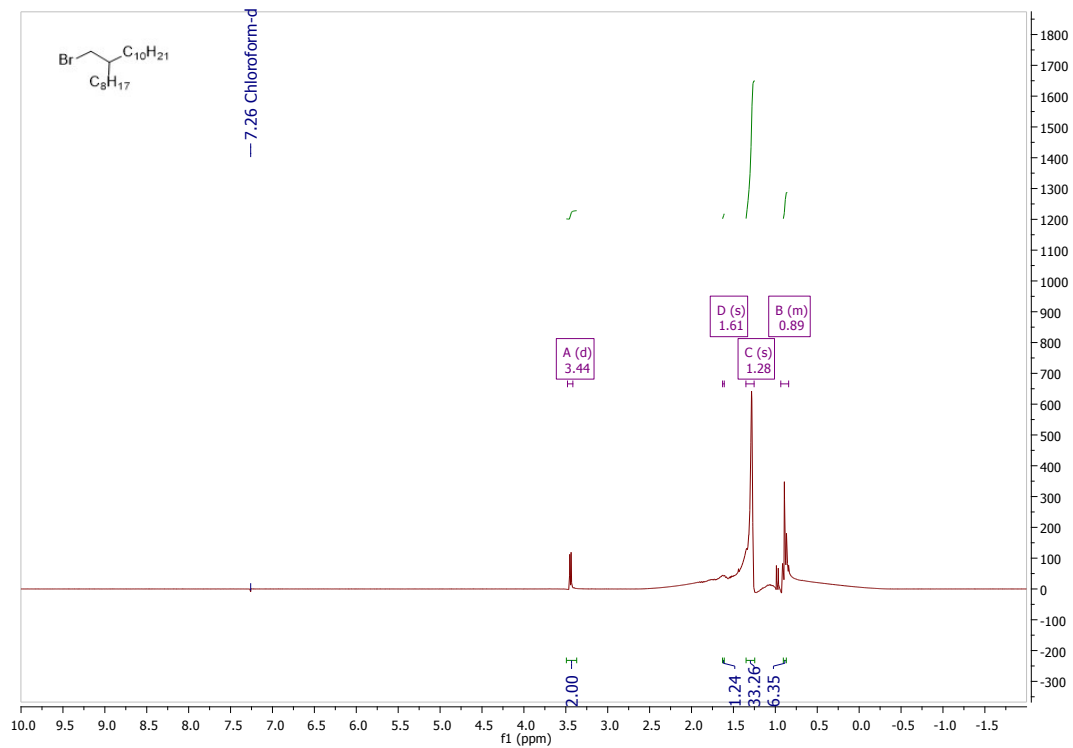
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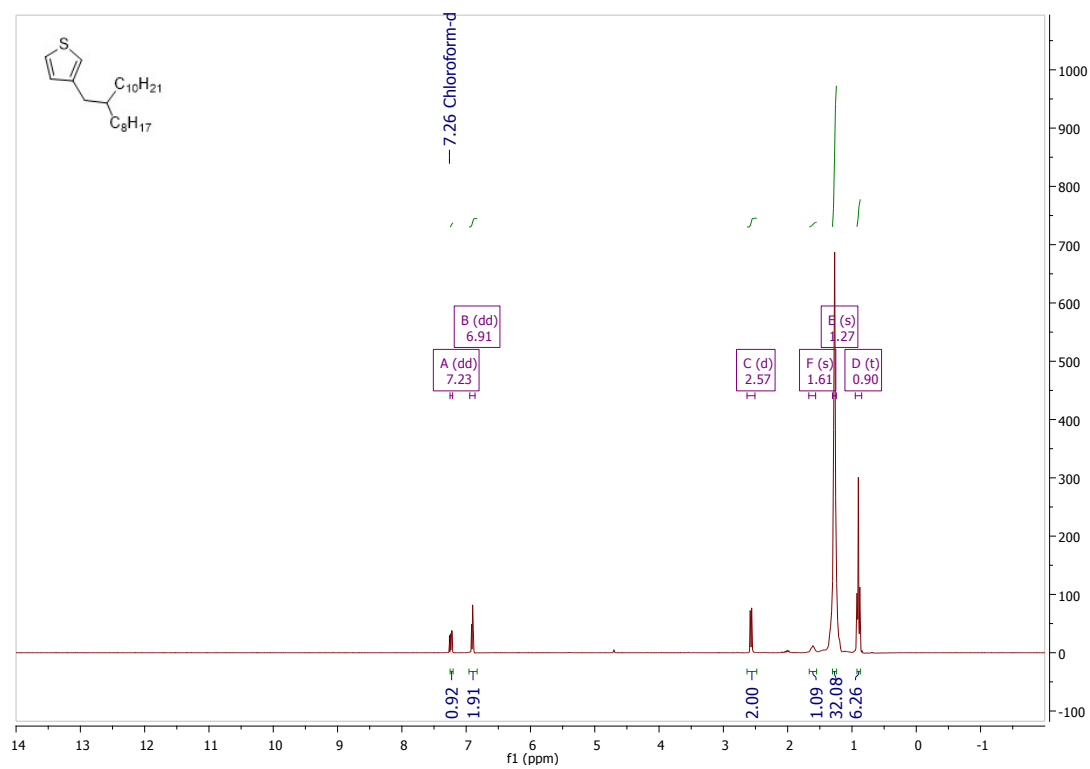
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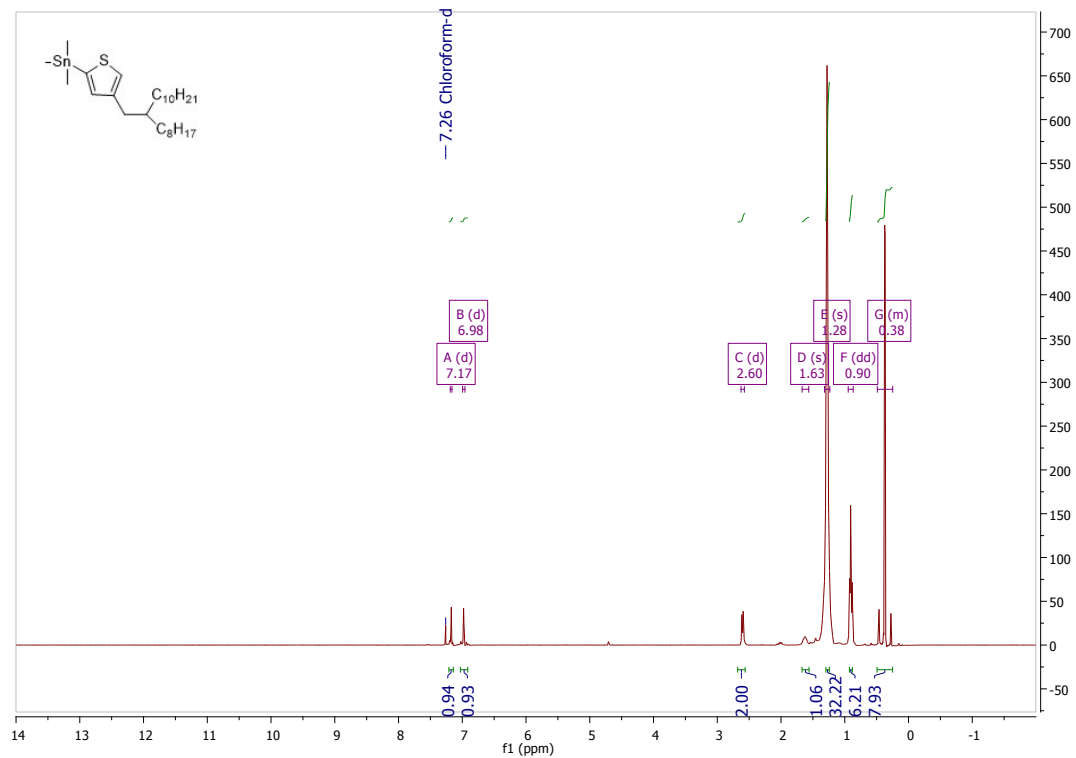
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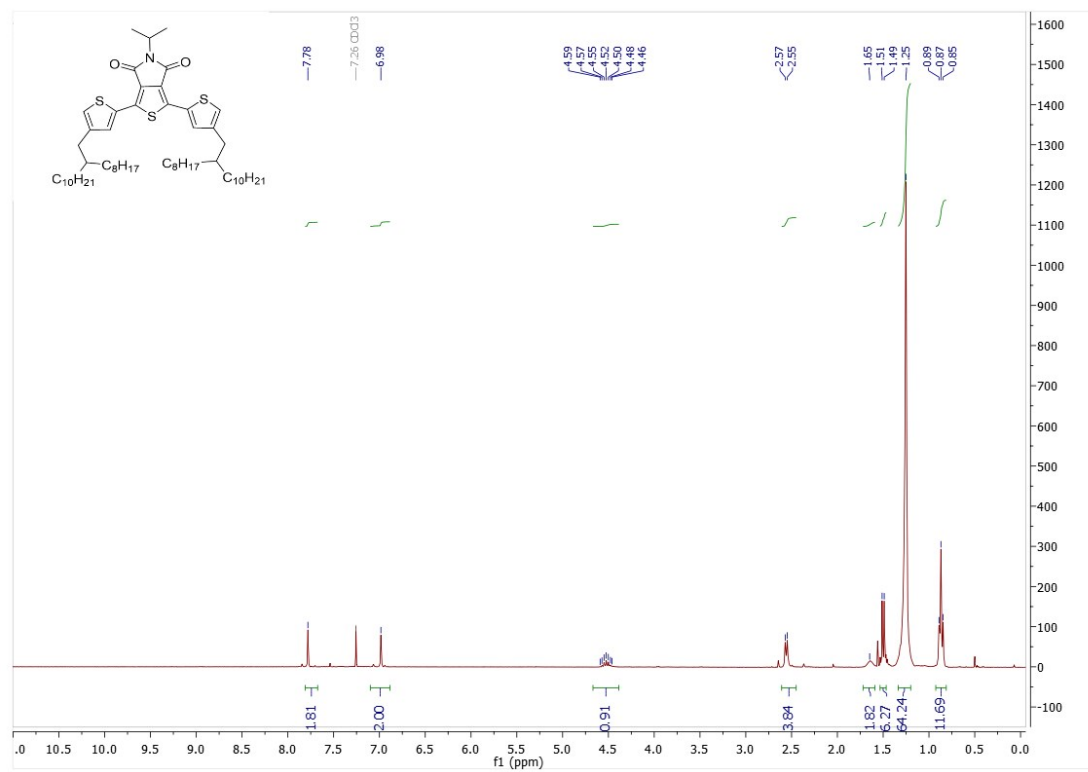
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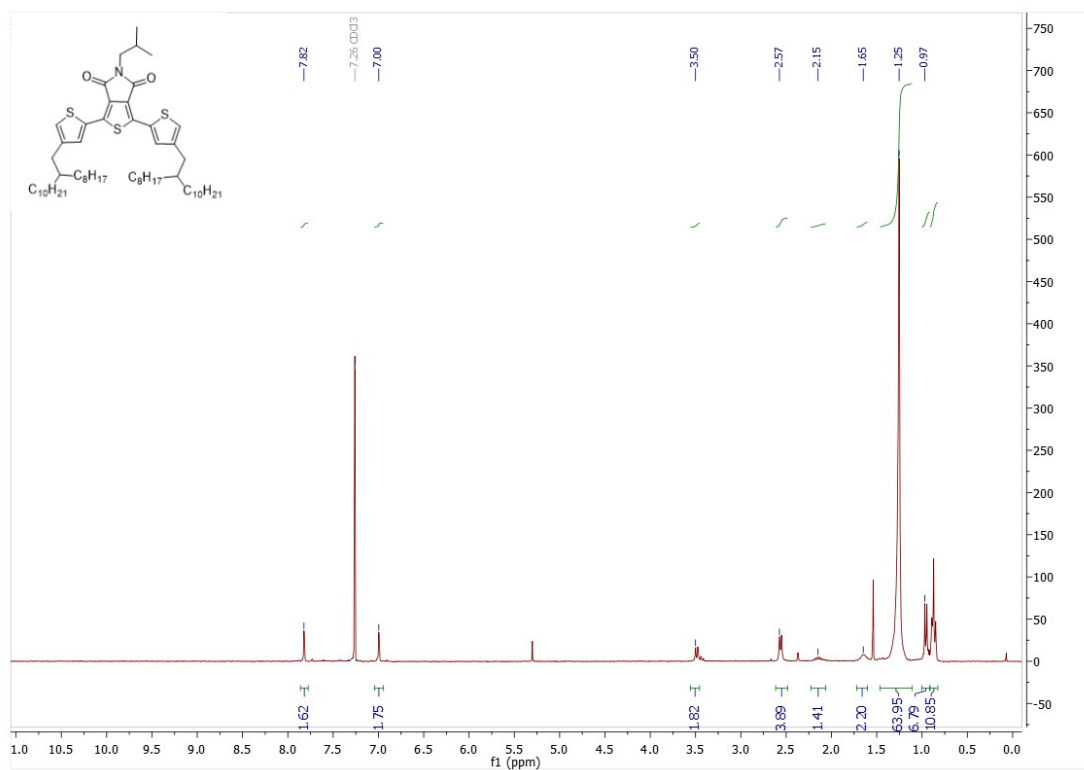
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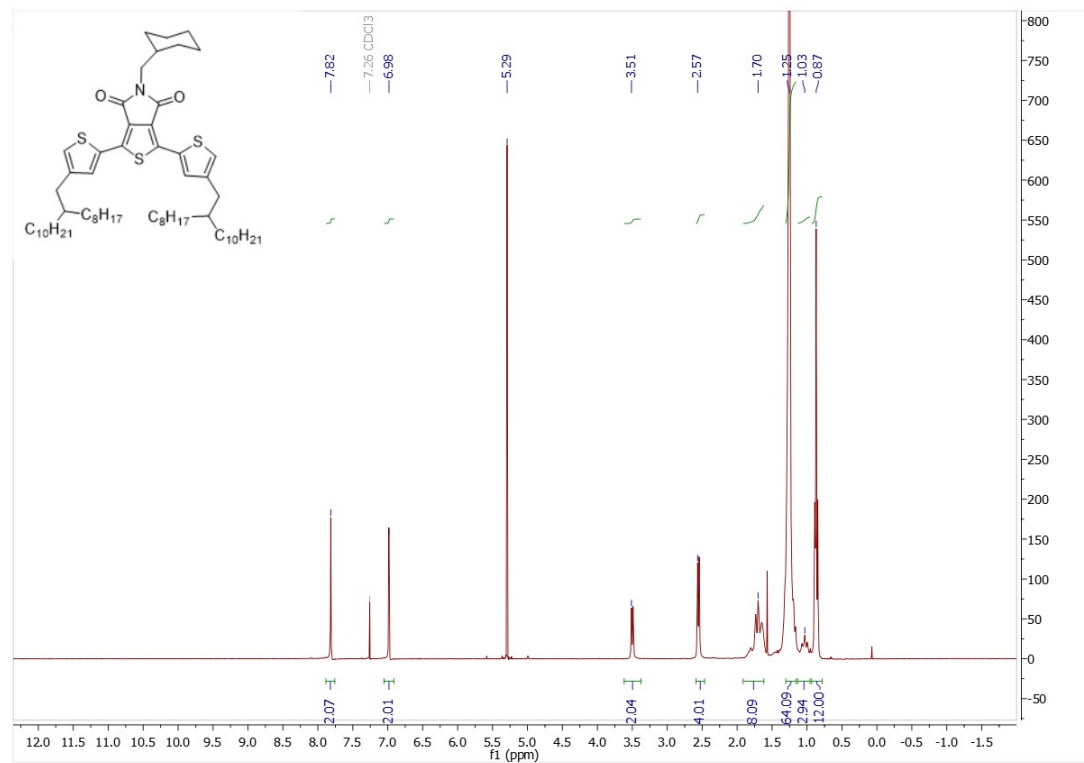
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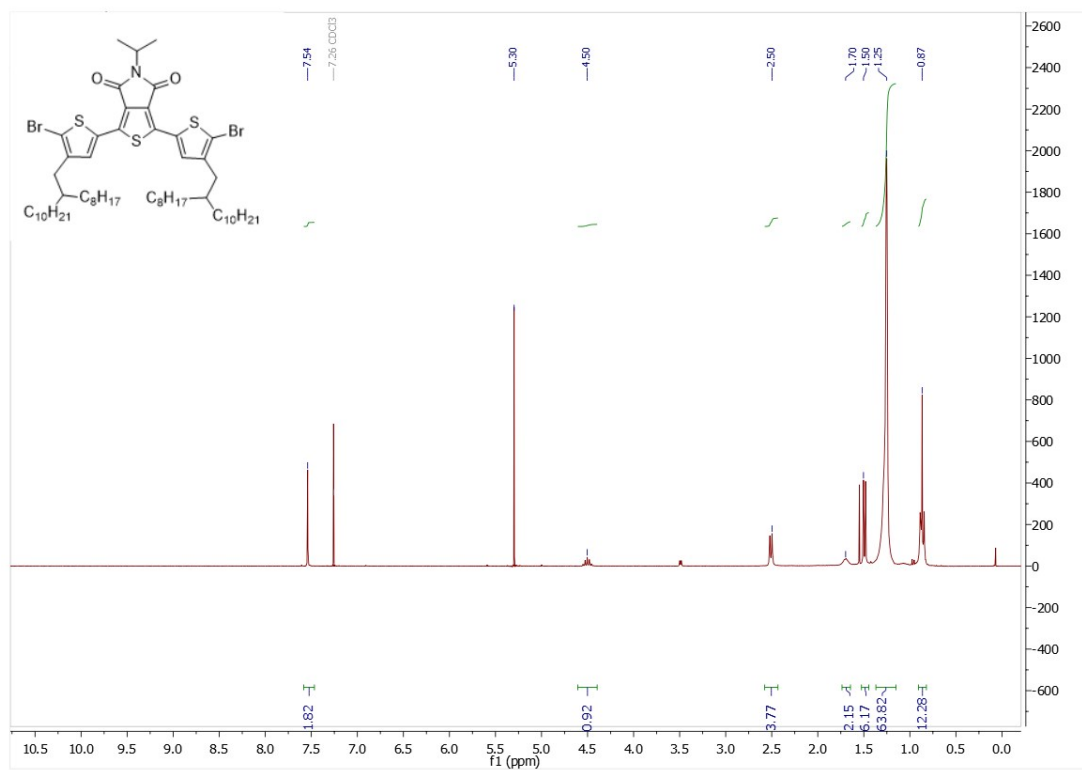
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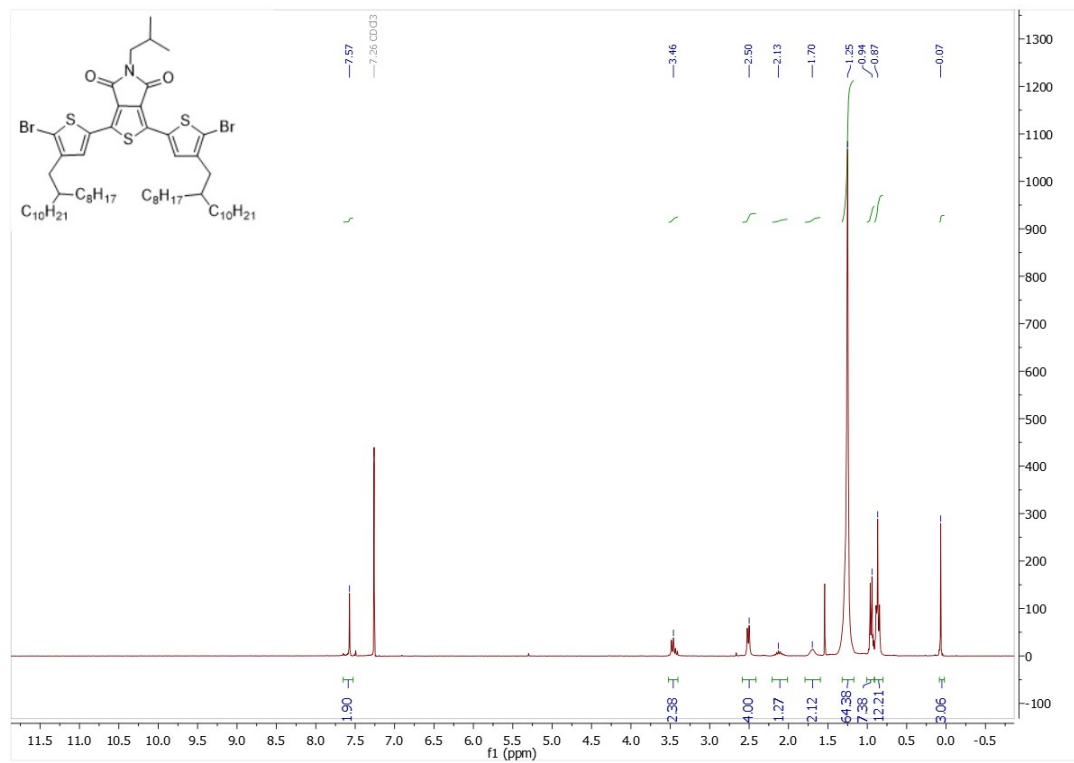
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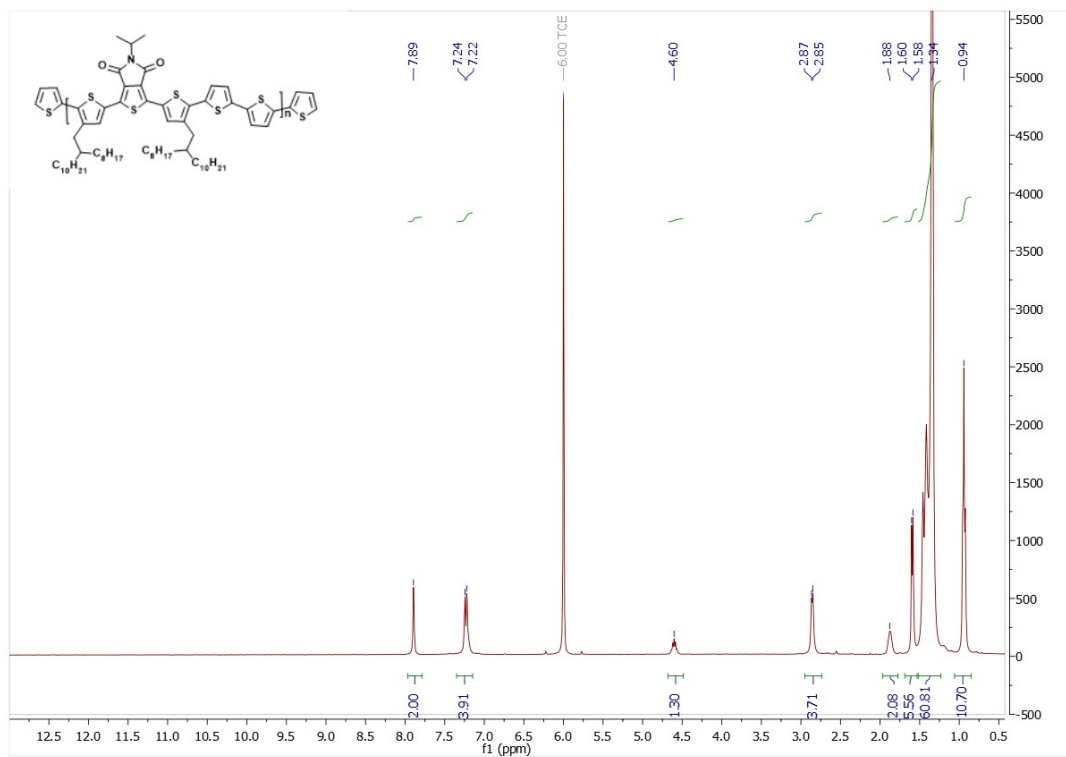
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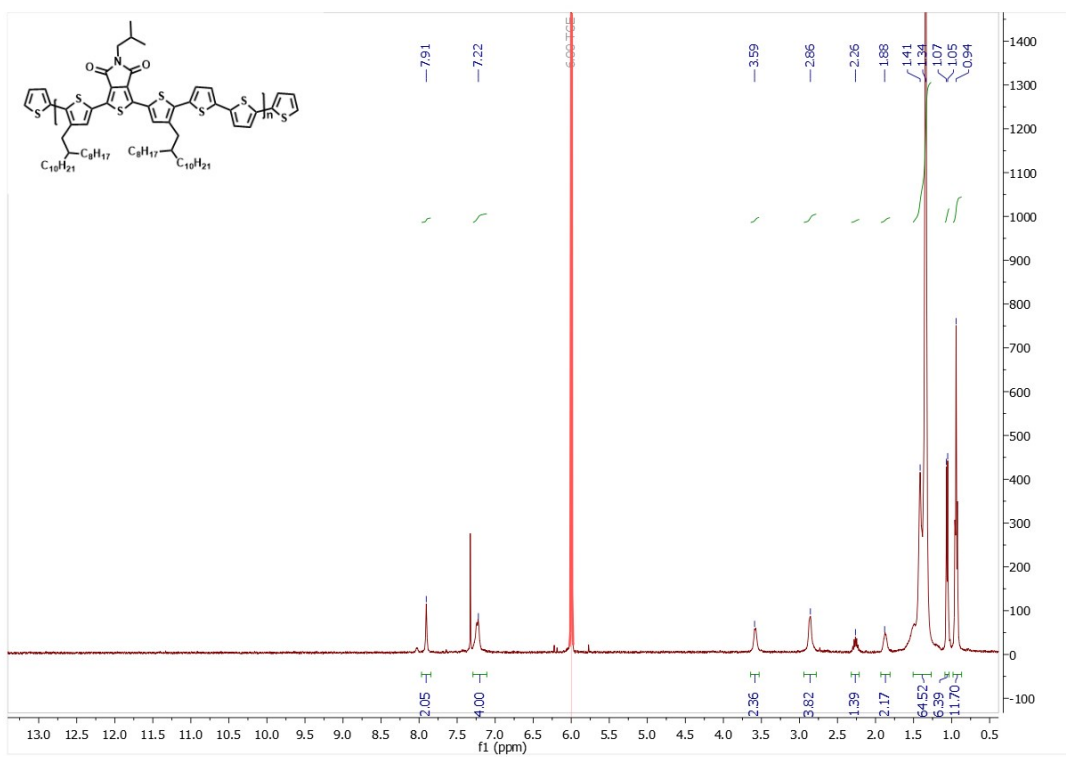
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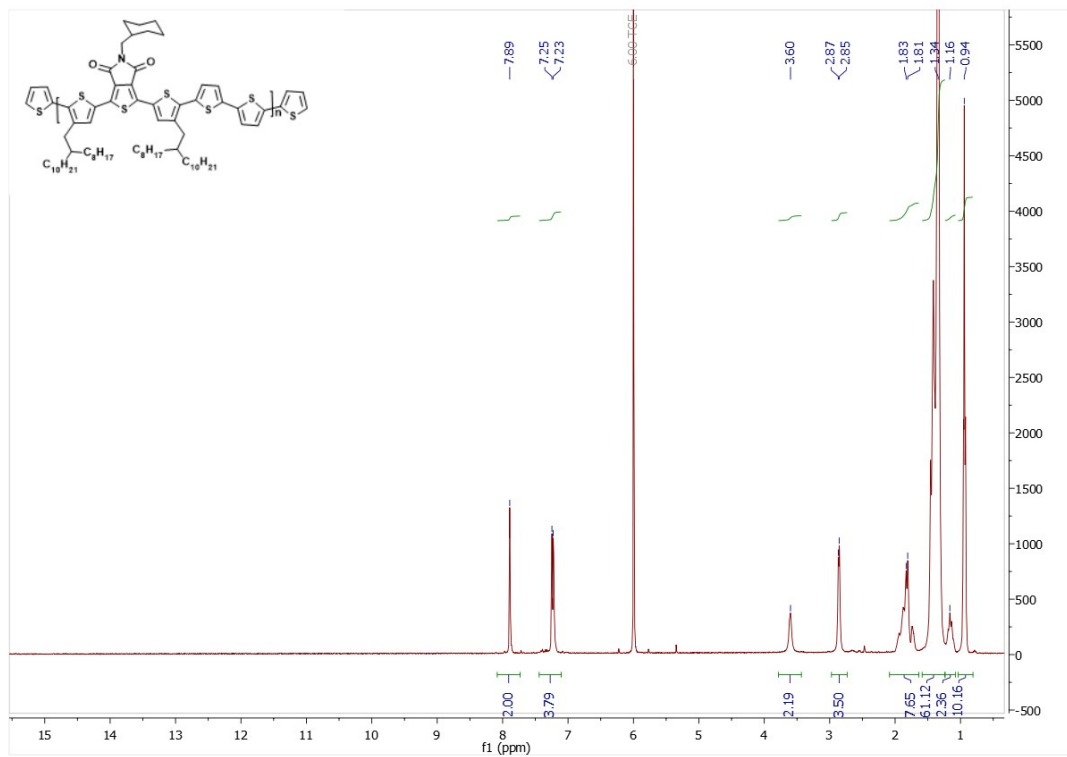
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¹H-NMR of TPD-IP TCE-d₂

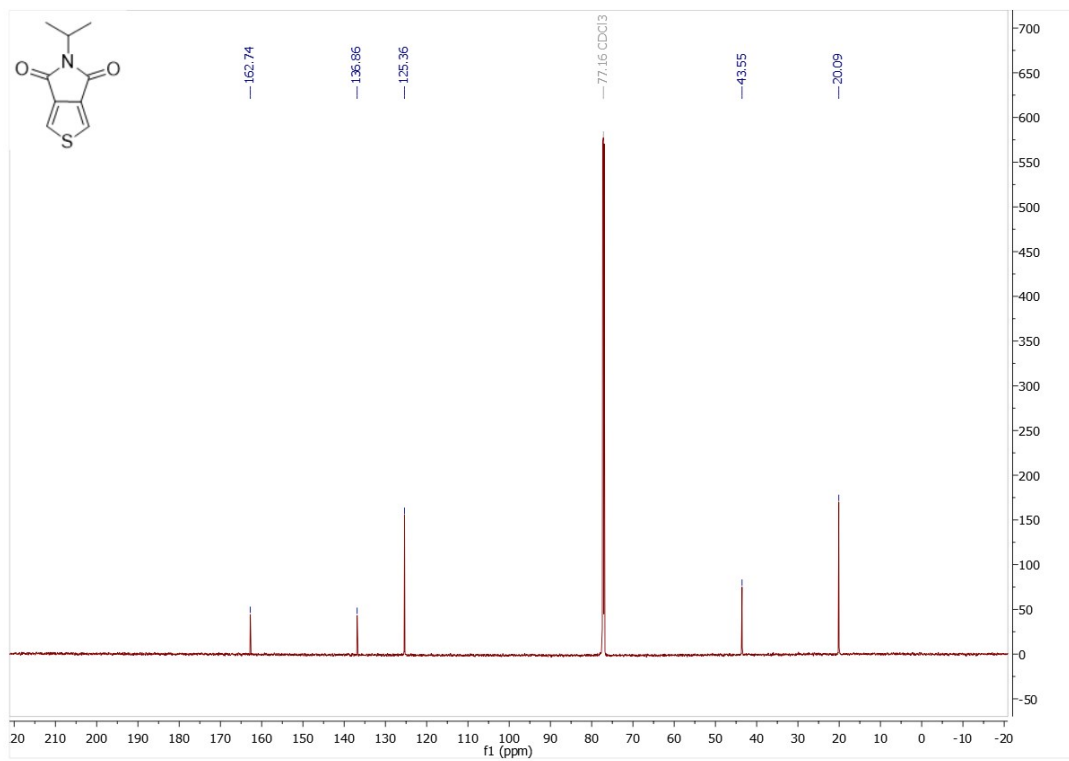


¹H-NMR of TPD-IB TCE-d₂

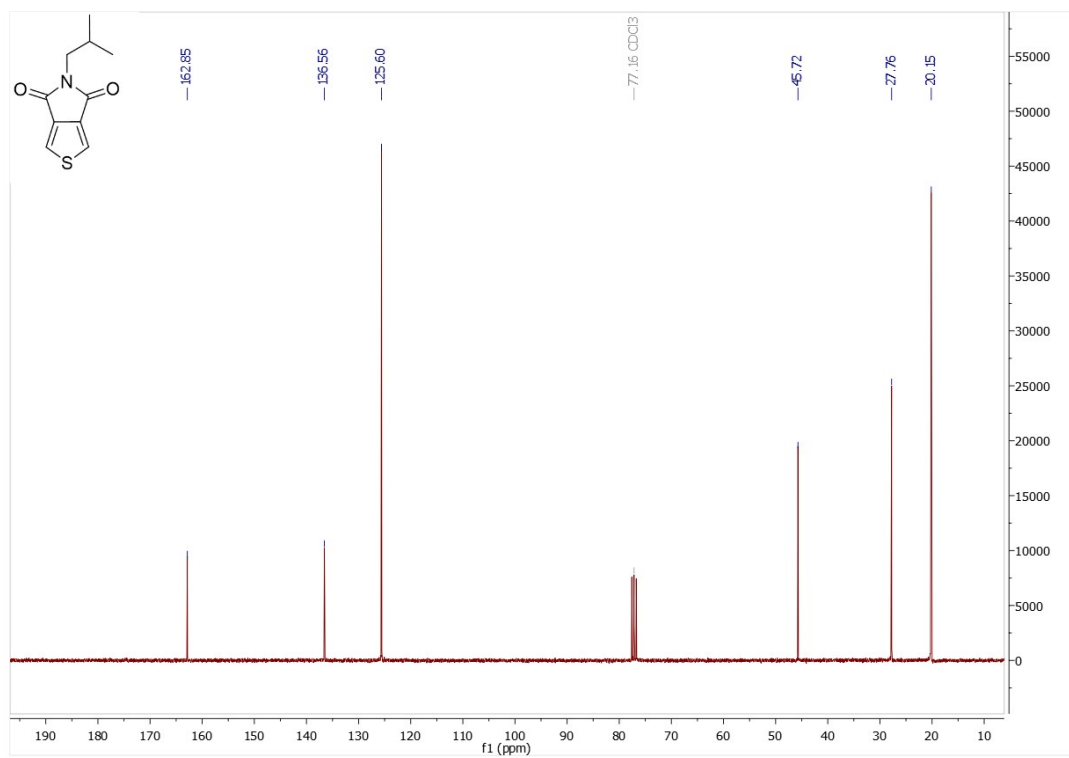


¹H-NMR of TPD-CM TCE-d₂

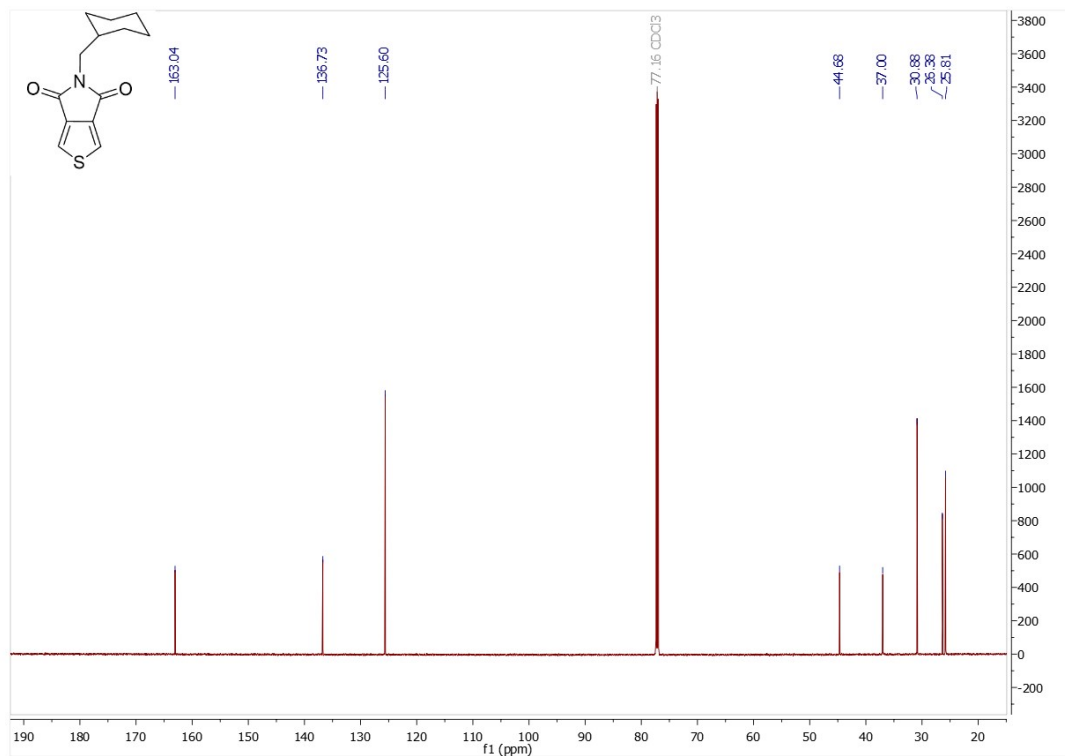
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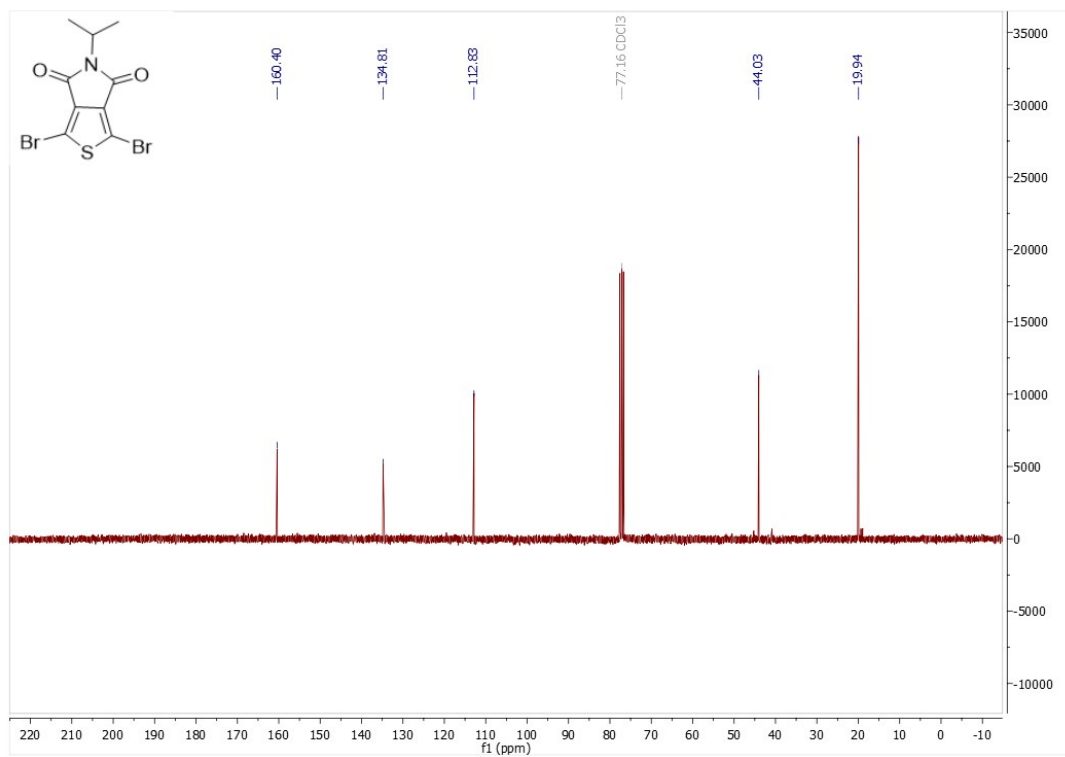
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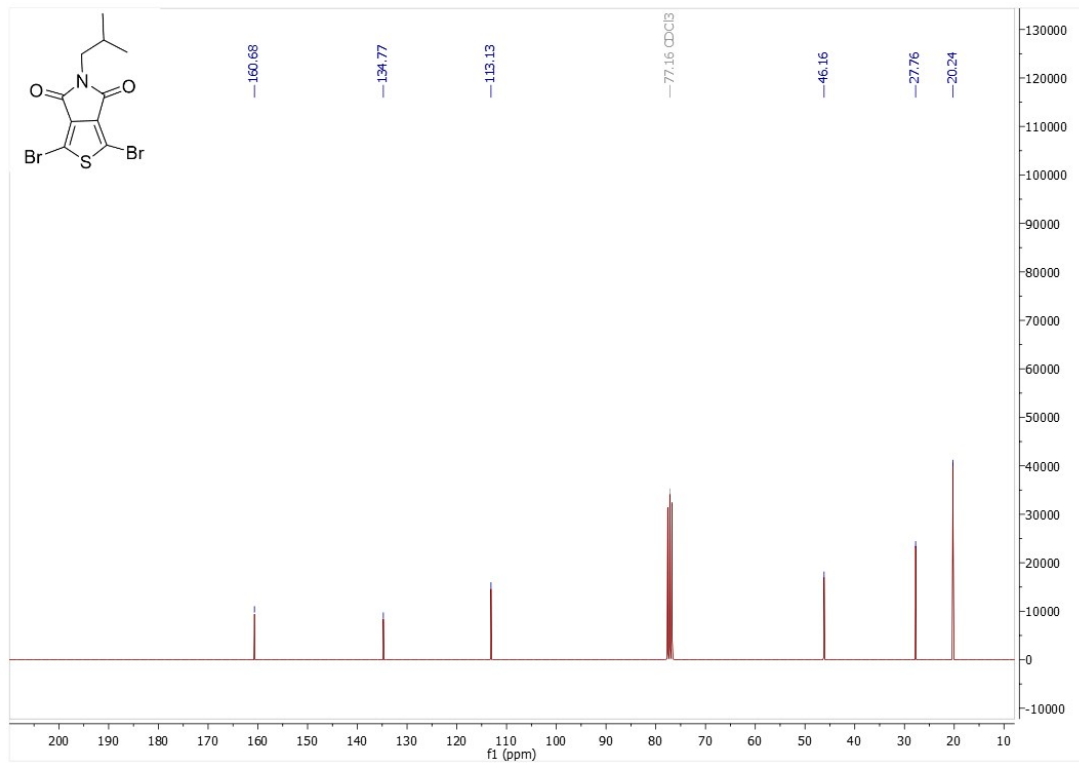
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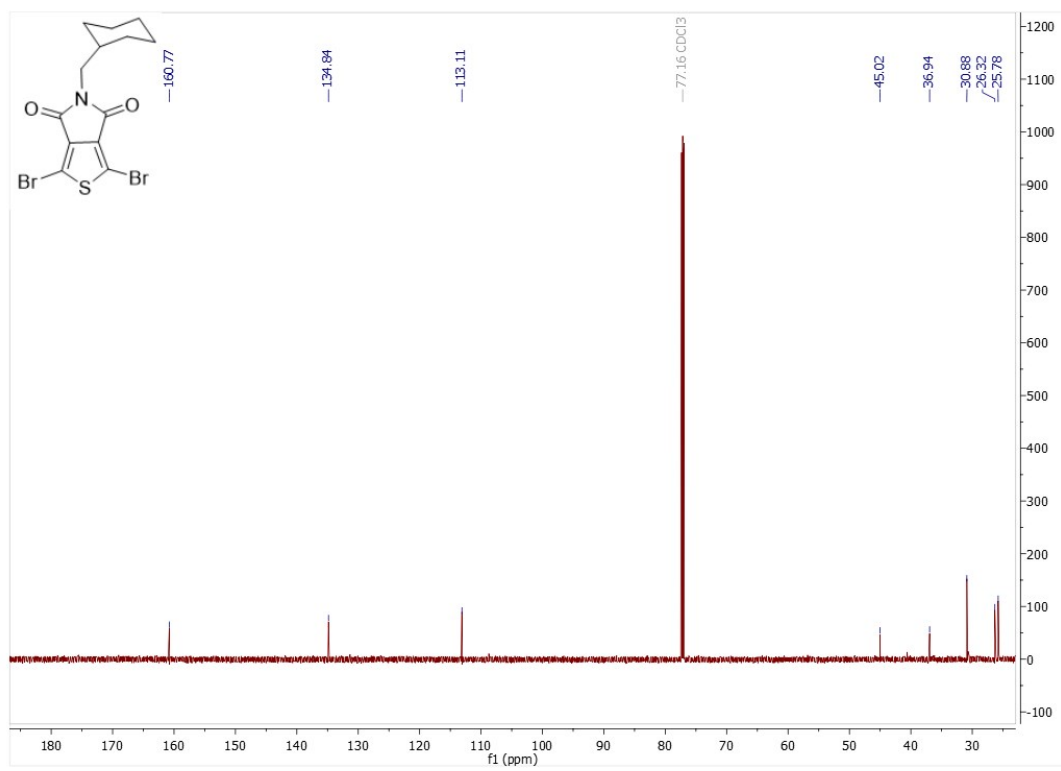
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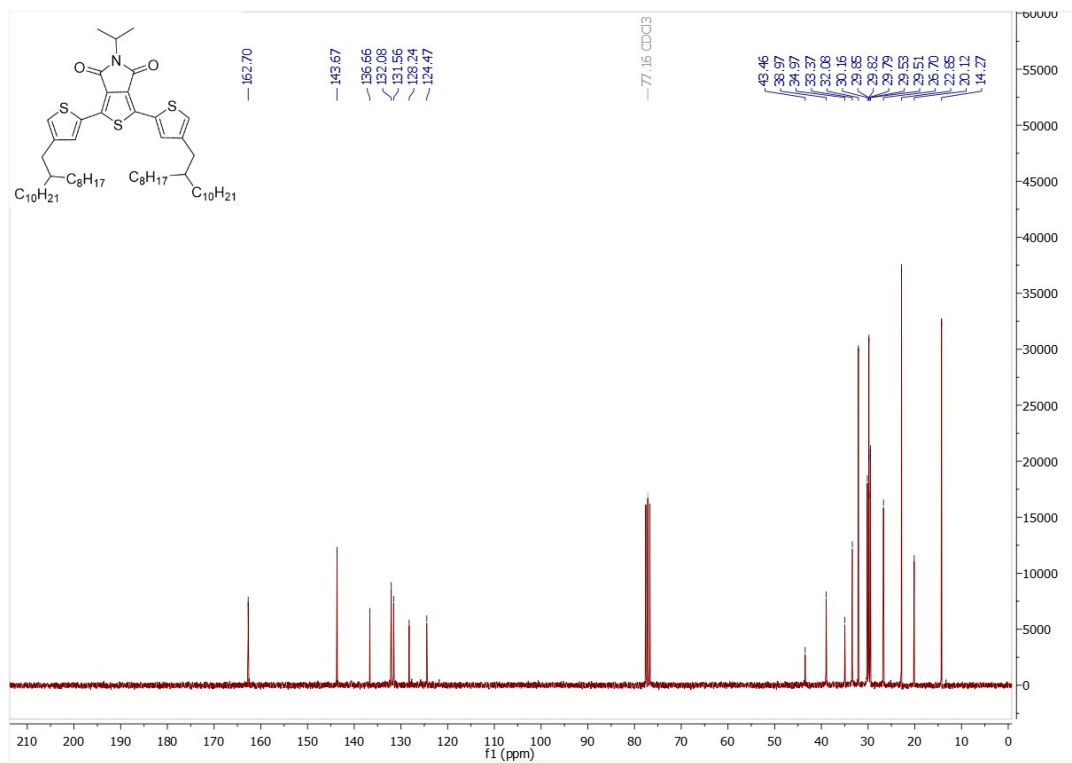
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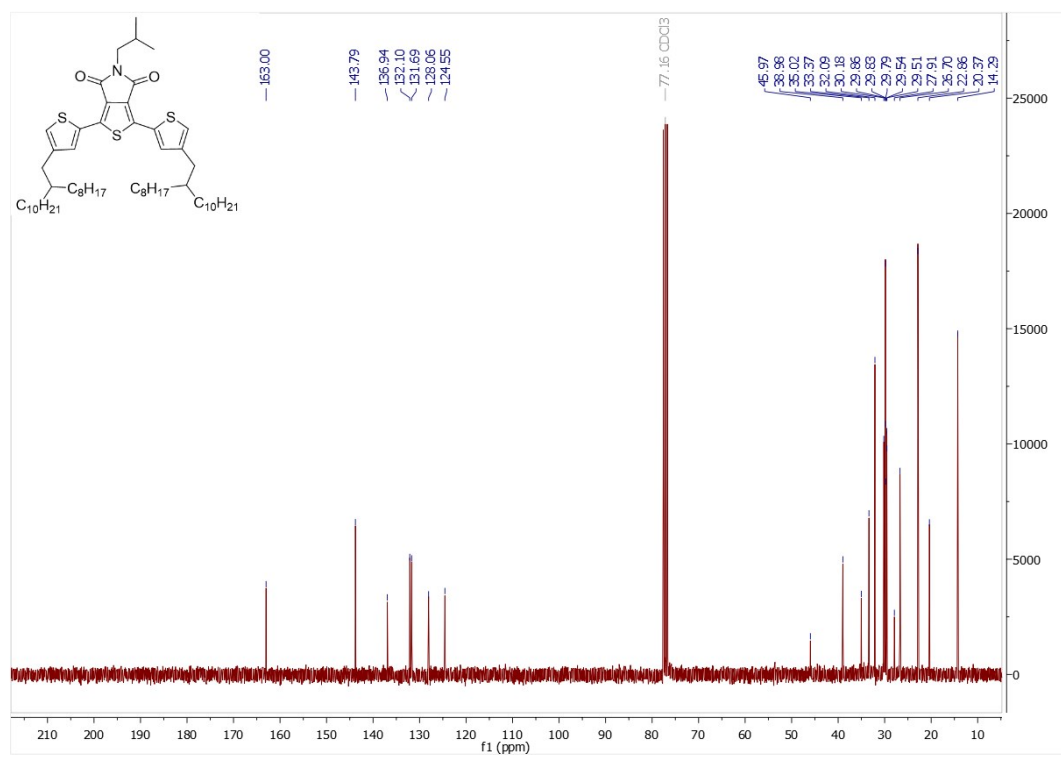
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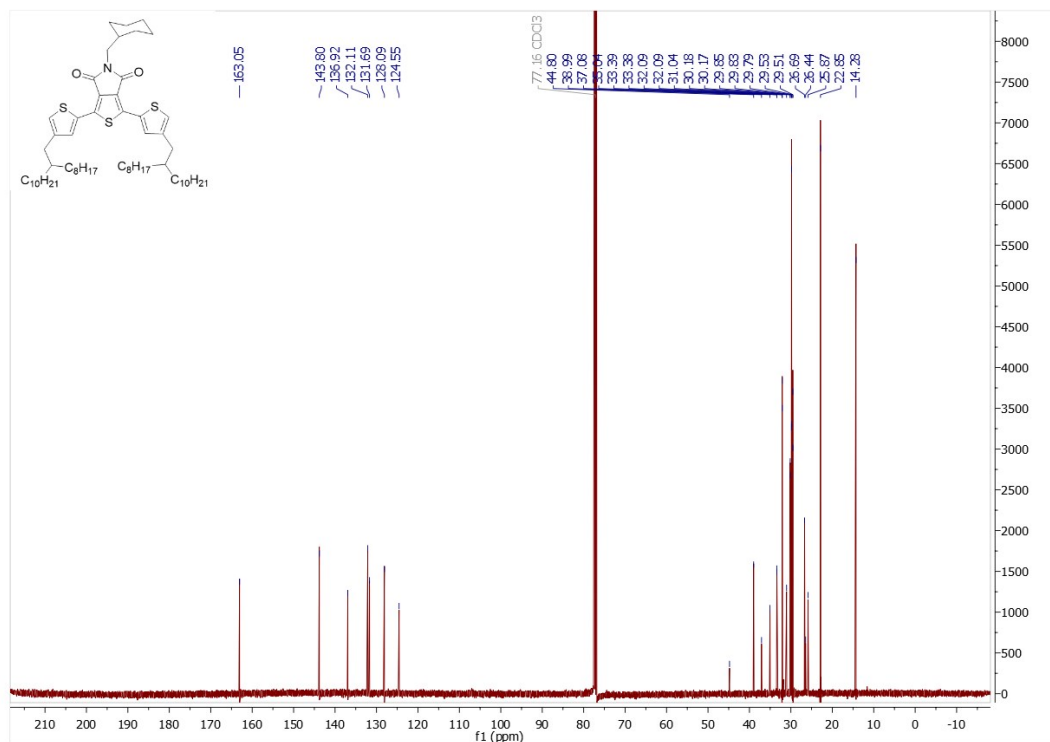
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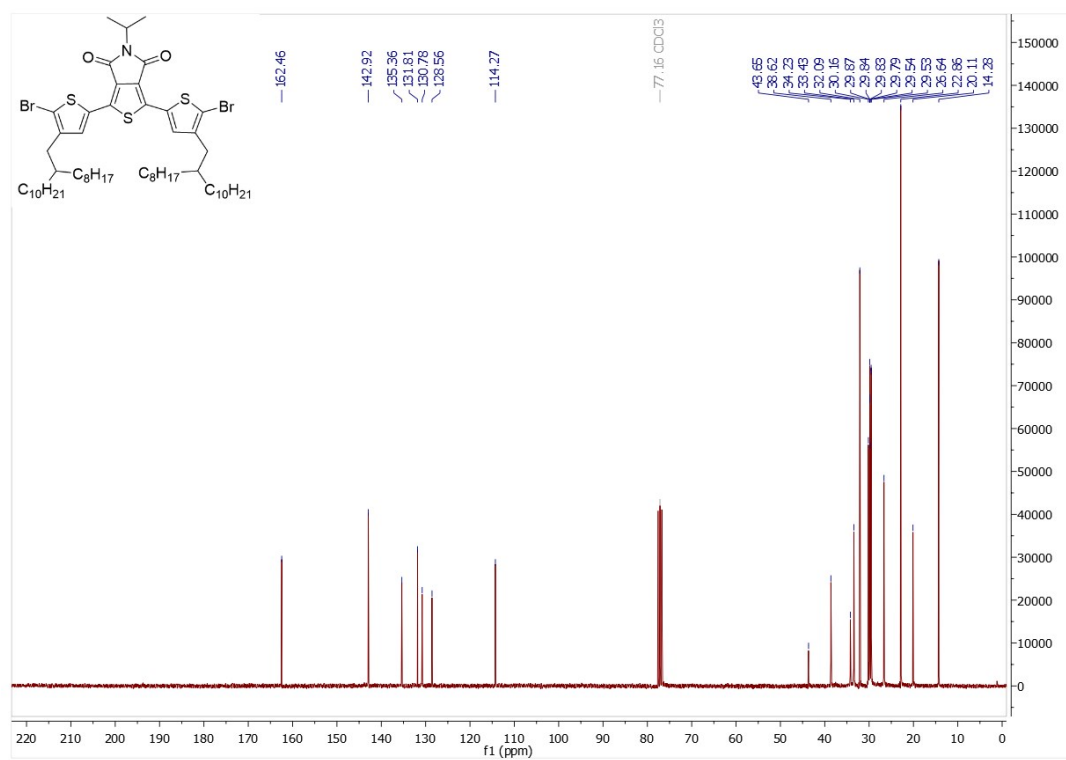
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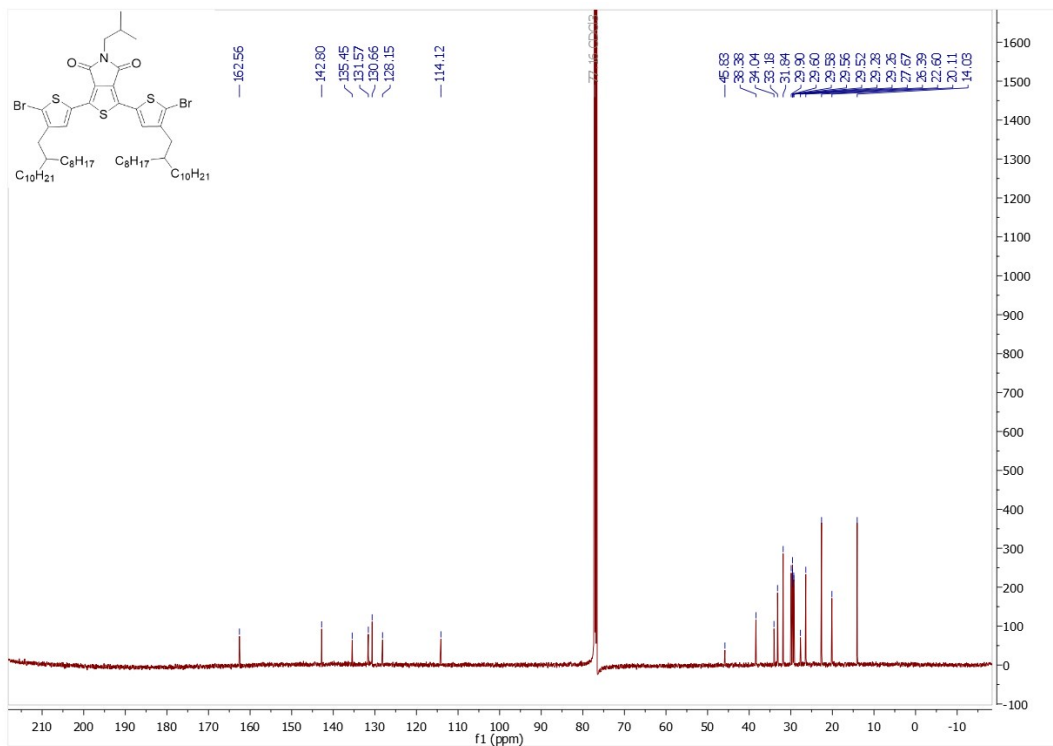
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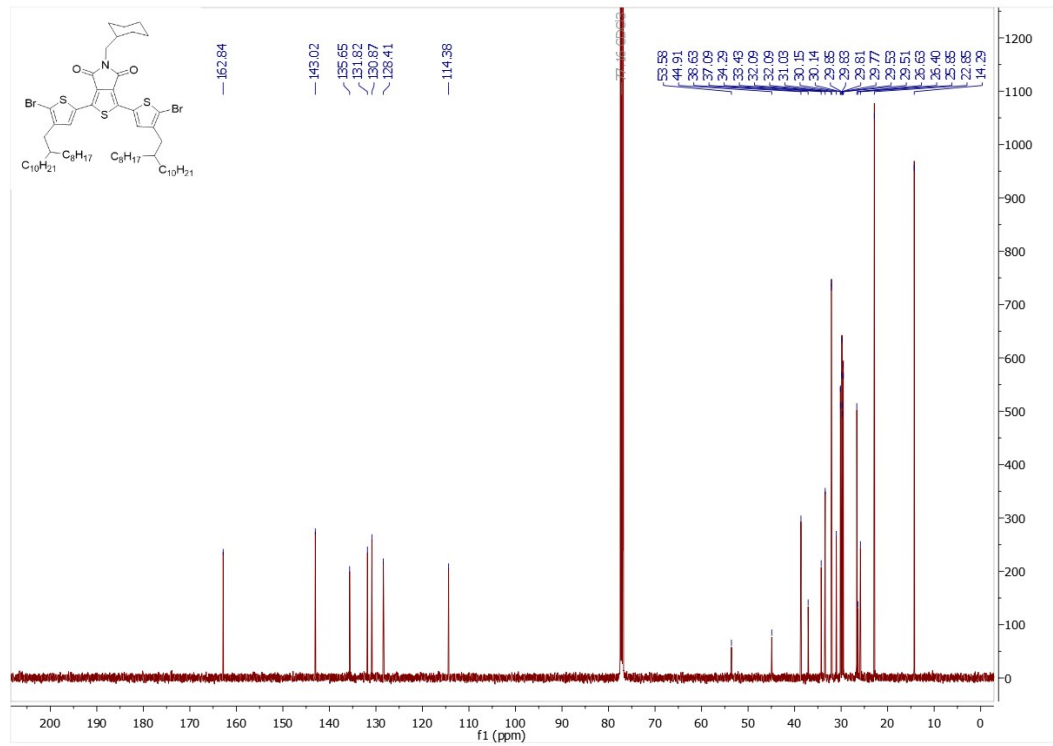
¹³C-NMR of 7d CDCl₃-d



¹³C-NMR of 8b CDCl₃-d



¹³C-NMR of 8c CDCl₃-d



¹³C-NMR of 8d CDCl₃-d

S2: Inverted Organic Solar Cell (OSC) Device Fabrication & Testing

Inverted architecture devices were fabricated with the layered structure of ITO/ZnO/Polymer-Fullerene blend/MoO₃/Ag. ZnO sol-gel was made from a 0.11 M Zn acetate dihydrate (Sigma Aldrich) and 0.11 M ethanolamine (Sigma Aldrich) solution in 2-methoxyethanol (Sigma Aldrich), which was stirred overnight at room temperature and subsequently passed through a 0.45 μm PTFE syringe filter. Patterned ITO coated glass substrates were scrubbed with a solution of sodium dodecyl sulfate (SDS) in Millipore 18.2 MΩ water and sequentially sonicated in the SDS water solution, Millipore water, and finally isopropanol. UV/ozone treatment of the cleaned ITO surfaces was then performed for 10 minutes. The ZnO sol-gel was spin coated in air onto precleaned ITO substrates at 4000 rpm for 30 seconds, and was then annealed in air at 150 °C for 10 minutes on a hotplate, followed by turning off the hotplate and allowing the substrates to gradually cool for another 10 minutes. A polymer-fullerene blend solution was then spun-coated onto the substrate using the following conditions:

A 30 mg/mL solution of a 1:1.2 blend of polymer:PC₇₁BM in 1:1 chlorobenzene:o-dichlorobenzene was stirred overnight at 85 °C. 3% by volume of DIO was added to the solution and allowed to stir for ~30 minutes prior to coating. From the 85 °C solution, films were spin-coated at 500 rpm in a glovebox and a room temperature substrate. To remove the additive from the photoactive layer without disturbing the wet film, the samples were placed in a vacuum chamber with a pressure of 1×10^{-5} mbar for 45 min.

Top contacts of MoO₃ (15 nm) and Ag (160 nm) were evaporated onto the active layer at 10^{-6} torr through a metal mask to obtain complete solar devices with an electrode overlap area of 0.07 cm². Fast drying Ag paint (Ted Pella, 16040-30) was applied to the ITO electrodes to improve contact with the device switch-box. An aperture with area 0.049 cm² was aligned with the electrode overlap area for solar measurements.⁶

OSC devices tested within an argon atmosphere glovebox using AM 1.5G illumination at 100 mW/cm² 22 generated using a Newport Oriel 69907 power supply connected to a 150 W xenon arc lamp (Newport 6255) with collimating lenses in a Newport Oriel 94021A simulator lamp housing calibrated with a reference silicon solar cell. J-V characteristics were recorded with a Keithley 2410 SourceMeter® SMU. Current was measured while a voltage sweep from -1 V to + 1 V was applied to the device under illumination. The resulting current-voltage curve was converted to current density using the known active layer area. From the current density and voltage curve plot the J_{SC}, V_{OC}, FF and PCE% were calculated. Eight devices of each blend were tested to gain an average and standard deviation of solar cell performance.

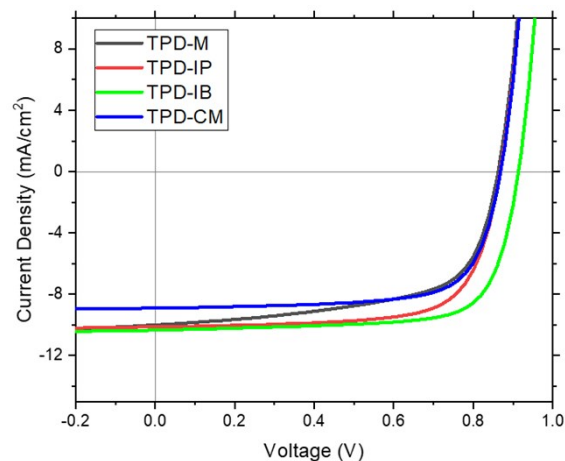


Figure S2. Current density-voltage (J-V) characteristics of polymer solar cells utilizing blends of TPD-M, TPD-IP, TPD-IB, and TPD-CM with PC₇₁BM under illumination (100 mW/cm², AM 1.5G).

S3: External Quantum Efficiency Measurements

External quantum efficiency (EQE) spectra of TPD-M, TPD-IP, TPD-IB, and TPD-CM devices with PC₇₁BM were captured with a Newport EQE/IPCE setup consisting of a Newport 66485 xenon lamp, an Oriel CS26 VIS-NIR 1/4 m monochromator, and a Merlin 70104 Digital Lock-in radiometry detector. The system was calibrated against a Newport 91150V silicon reference cell. Table S1 compares the J_{SC} measured from solar illumination in Figure 3 to the J_{SC} calculated from integrating the EQE curves against the AM 1.5G solar spectrum.

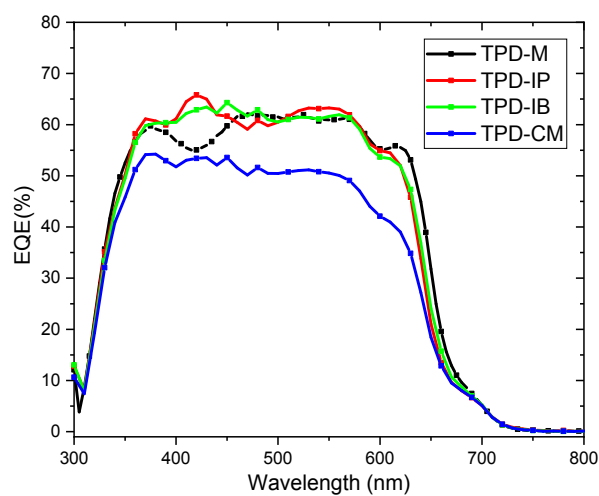


Figure S3. EQE spectra of solar cell devices utilizing TPD-M, TPD-IP, TPD-IB, and TPD-CM.

Table S1. Measured J_{sc} and Integrated J_{sc} .

Blend	J_{sc} measured from solar data (mA/cm ²)	J_{sc} integrated from EQE (mA/cm ²)
TPD-M:PC ₇₁ BM	10.4	10.2
TPD-IP:PC ₇₁ BM	10.6	9.9
TPD-IB:PC ₇₁ BM	10.3	9.9
TPD-CM:PC ₇₁ BM	9.0	8.1

S4: Space-Charge Limited Current (SCLC) Measurements

Mobility of the polymers was measured using a hole-only device configuration of ITO/MoO₃/polymer/MoO₃/Ag in the space-charge-limited regime. After evaporation of 10 nm MoO₃ onto precleaned ITO glass slides, all polymers were spun-coat from an 85 °C solution dissolved in 1:1 chlorobenzene:*o*-dichlorobenzene. Each polymer was spun-coat to three different thicknesses to confirm thickness dependence of $J \sim 1/L^3$. Afterwards, 10 nm MoO₃ followed by 100 nm Ag was evaporated onto the active layer at 10⁻⁶ torr through a metal mask to obtain complete devices with an electrode overlap area of 0.07 cm². Fast drying Ag paint (Ted Pella, 16040-30) was applied to the ITO electrodes to improve contact with the device switch-box. An aperture with area 0.049 cm² was aligned with the electrode overlap area for SCLC measurements. J-V characteristics were recorded with Keithley 2410 SourceMeter® SMU. Resulting J-V curves, mobility fits, and thickness dependence checks are shown below for the four polymers (**Figure S4**).

The current density J in the trap-free space-charge limited-current region can be described by the Mott-Gurney Law⁷:

$$J = \frac{9}{8} \varepsilon \varepsilon_0 \mu \frac{V^2}{L^3} \quad (\text{S4-1})$$

where ε is the dielectric constant of the polymer, ε_0 is the permittivity of free space, μ is the charge carrier mobility, V is the effective voltage (applied voltage minus the built-in voltage), and L is the thickness of the polymer film. Transport in disordered materials is often limited by the presence of shallow traps whose heights are field dependent. As described the Poole-Frenkel effect, trap barrier height decreases in the presence of stronger electric fields.⁷ Taking this dependence into account, the mobility can be calculated as:

$$\mu = \mu_0 \exp(0.891\gamma\sqrt{E}) \quad (\text{S4-2})$$

where μ_0 is the zero-field mobility, γ is the field dependence parameter and E is the electric field through the semiconductor. Substituting equation (S4-2) into equation (S4-1) allows for the determination of mobility from the measured J-V curve of the device through equation (S4-3).

$$J = \frac{9}{8} \varepsilon \varepsilon_0 \mu_0 \exp(0.891 \gamma \sqrt{E}) \frac{V^2}{L^3}$$

(S4-3)

It should be noted in equation S4-3 that $J \sim 1/L^3$, meaning current density will decrease with thicker polymer films. When measuring SCLC mobility, multiple thicknesses of material should be tested to quantify that this relationship holds true in order to determine the accuracy of the measured mobility.

Current was measured while a voltage sweep from 0.01 V to 1 V, 5 V, or 10 V was applied to the device. The resulting current-voltage curve is converted to current density using the known active layer area. Since conjugated polymers can display an SCLC regime at a variety of voltages, and importantly can also break down at varying voltages, it is important to begin testing at lower voltages (1 V) and to scan to increasingly higher voltages. Since $J \sim V^2$ in the SCLC regime as shown in equation S4-3, a slope of 2 will be seen in the log-log plot of the J-V curve within the SCLC regime (indicated by the red lines in **Figure S4**). Voltage

Table S2. SCLC voltage ranges.

Polymers	SCLC voltage ranges (V)
TPD-M	1.23-3.04
TPD-IP	1.52-3.52
TPD-IB	1.17-3.88
TPD-CM	1.18-2.83

ranges at which SCLC regimes are measured are listed below in **Table S2**.

Once an SCLC curve is obtained and the voltage region where the slope is equal to 2 on a log-log plot is identified, the SCLC regime is fit across that voltage range using equation S4-3 to determine the mobility. ε was assumed to be 4 based on values found commonly in other conjugated polymers.⁸ The electric field E was assumed to be the voltage of the sweep V over the film thickness L. Since MoO₃ was used as both interlayers, the built-in voltage across the device V_{bi} was determined to be zero, and Ohmic contacts are assumed. The field dependence variable γ is left as open variable in the fit; these have been calculated and averaged below in **Table S3**. Mobility data (μ_0) was averaged across 8 pixels per device, and then averaged between the three thicknesses.

Table S3. Field dependence variables.

Polymers	γ_1	γ_2	γ_3	γ_{ave}
TPD-M	7.00×10^{-4}	5.00×10^{-4}	4.00×10^{-4}	$(5.33 \pm 1.53) \times 10^{-4}$
TPD-IP	6.00×10^{-4}	4.00×10^{-4}	5.00×10^{-4}	$(5.00 \pm 1.00) \times 10^{-4}$
TPD-IB	6.00×10^{-4}	5.00×10^{-4}	7.00×10^{-4}	$(6.00 \pm 1.00) \times 10^{-4}$
TPD-CM	1.00×10^{-3}	1.00×10^{-3}	8.00×10^{-4}	$(9.33 \pm 1.15) \times 10^{-4}$

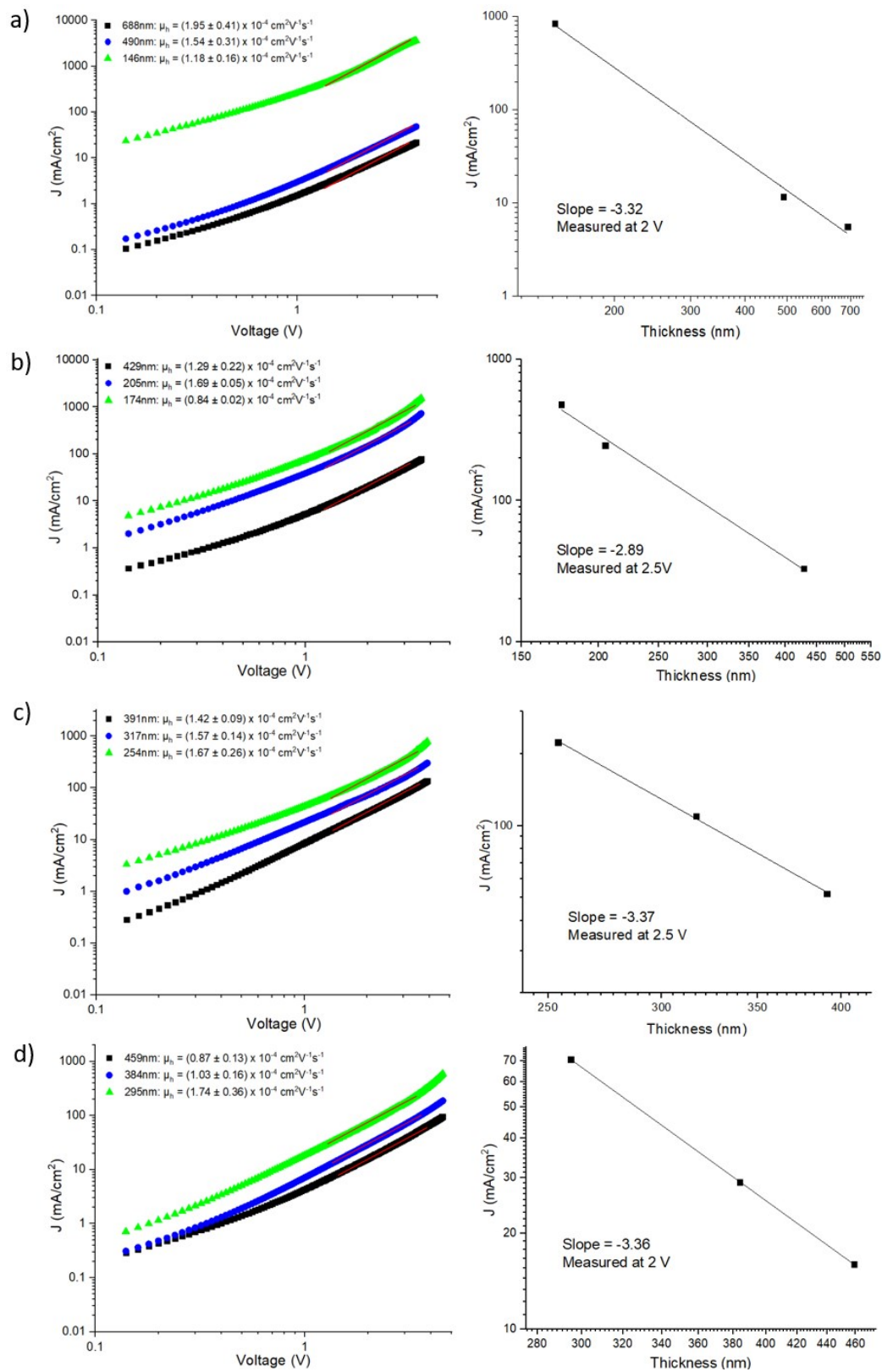


Figure S4. J-V curves, mobility fits, and thickness dependence checks for a) TPD-M, b) TPD-IP, c) TPD-IB, and d) TPD-CM. The red lines in the J-V curves denote the SCLC regime ($J \sim V^2$).

S5: Differential Pulse Voltammetry

We measured the HOMO energy level (E_{HOMO}) and LUMO energy level (E_{LUMO}) of the polymers differential pulse voltammetry (DPV) with Ag/AgNO₃ as the reference electrode. We calculated the HOMO/LUMO energy levels ($E_{\text{HOMO/LUMO}}$) of the polymers from their onset oxidation/reduction potentials according to the equation $E_{\text{HOMO/LUMO}} = -e(E_{\text{ox/red}} \text{ vs Fc/Fc}^+, + 5.12) \text{ eV}$.⁹

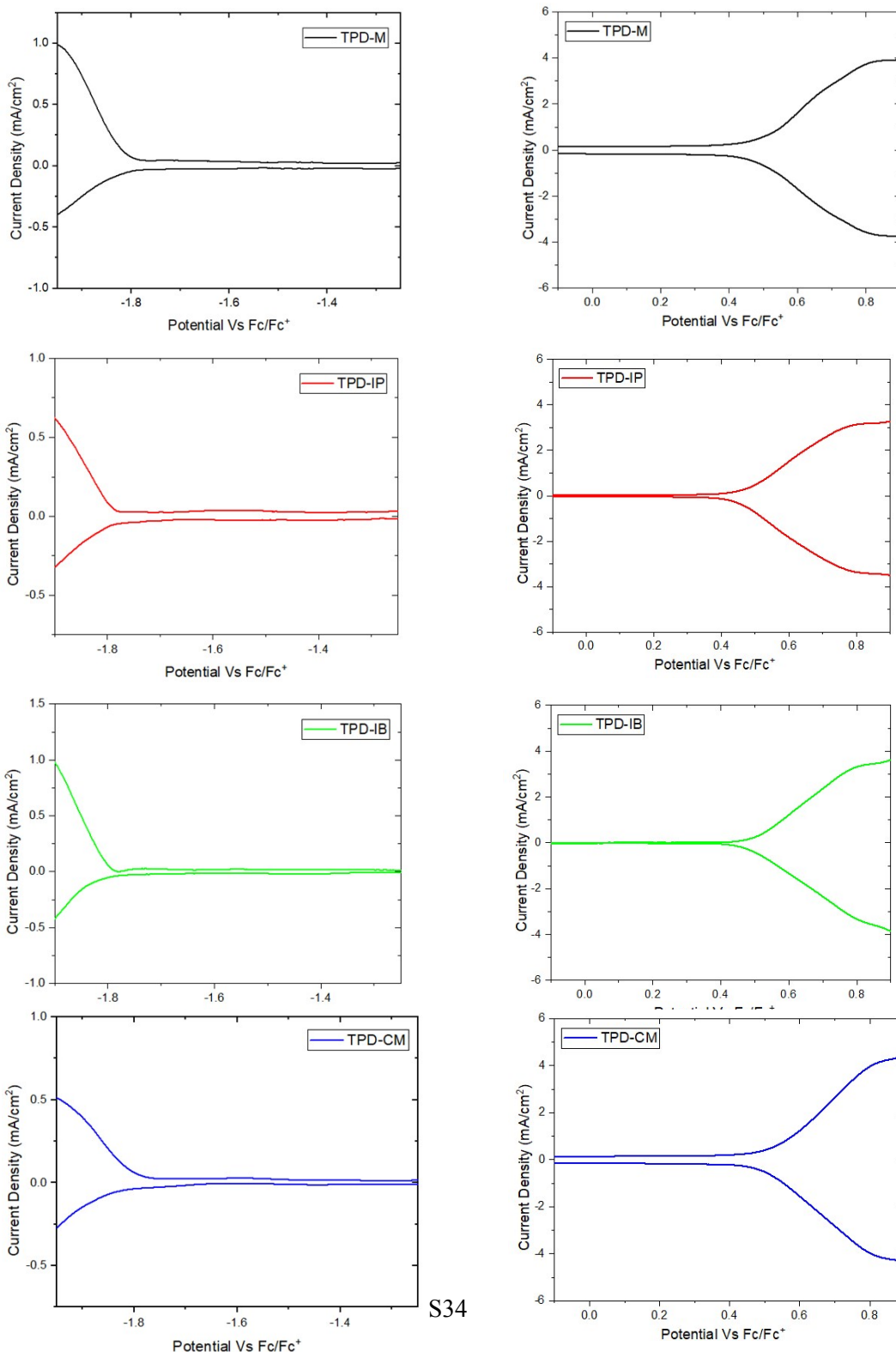


Figure S5. DPV traces for the four polymers versus Fc/Fc⁺. Left column are the reduction traces and the right column are oxidation traces.

Table S4. Calculated onsets and energy levels.

Polymers	E_{onset}^{ox} (V)	E_{onset}^{red} (V)	E_{HOMO} (eV)	E_{LUMO} (eV)
-----------------	---	--	--	--

TPD-M	0.51	-1.81	-5.63	-3.31
TPD-IP	0.46	-1.79	-5.58	-3.33
TPD-IB	0.49	-1.83	-5.61	-3.29
TPD-CM	0.51	-1.82	-5.63	-3.30

S6: GIWAXS/GISAXS Sample Preparation

Sample Preparation

Silicon substrates were scrubbed with a solution of SDS in Millipore 18.2 M Ω water and sequentially sonicated in the SDS solution, pure Millipore water, and finally isopropanol; the substrates were allowed to air-dry completely.

A 25 mg/mL solution of polymer in 1:1 chlorobenzene:o-dichlorobenzene was stirred overnight at 85 °C. From the 85 °C solution, films were spin-coated at 700 rpm in an Ar-filled glovebox and a room temperature substrate. To dry the neat polymer layer without disturbing the wet film, the samples were placed in a vacuum chamber with a pressure of 1×10^{-5} mbar for 45 min.

A 30 mg/mL solution of a 1:1.2 blend of polymer:PC₇₁BM in 1:1 chlorobenzene:o-dichlorobenzene was stirred overnight at 85 °C. 3% by volume of DIO was added to the solution and allowed to stir for ~30 minutes prior to coating. From the 85 °C solution, films were spin-coated at 700 rpm in an Ar-filled glovebox and a room temperature substrate. To remove the additive from the blend layer without disturbing the wet film, the samples were placed in a vacuum chamber with a pressure of 1×10^{-5} mbar for 45 min.

2D GIWAXS Images

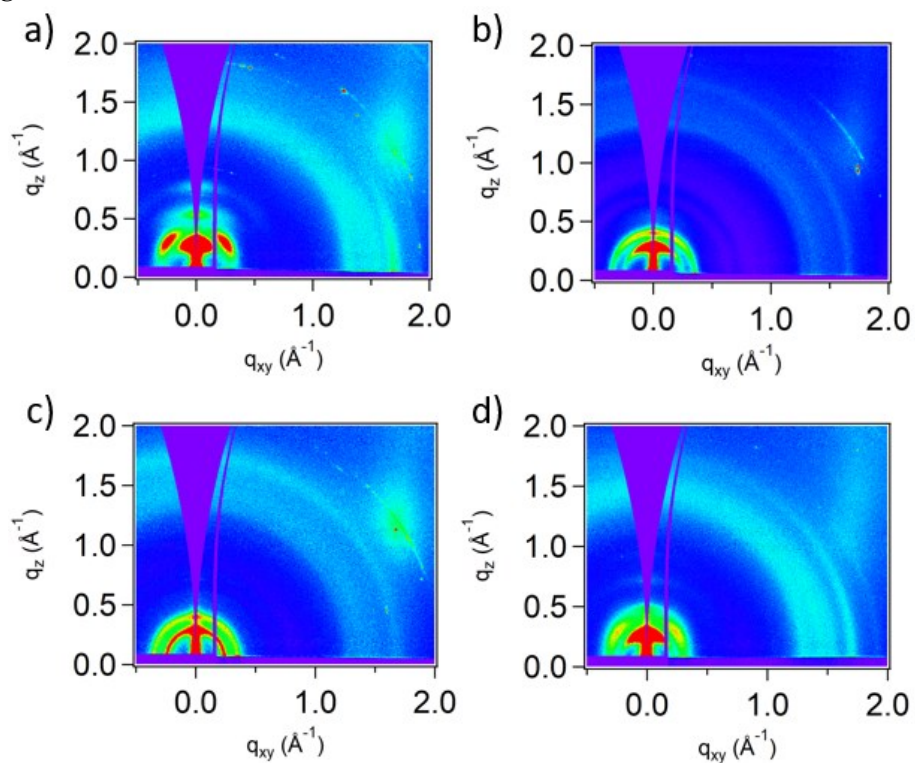


Figure S6. 2D GIWAXS images of pristine polymers: a) TPD-M, b) TPD-IP, c) TPD-IB, d) TPD-CM.

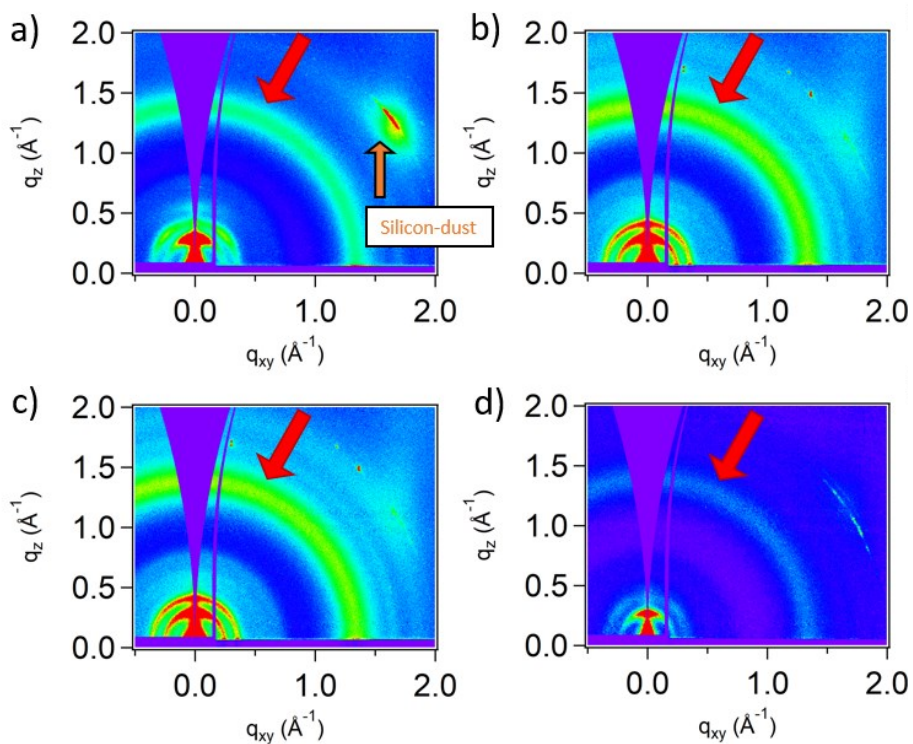


Figure S7. 2D GIWAXS images of polymer:PC₇₁BM blends: a) TPD-M:PC₇₁BM, b) TPD-IP:PC₇₁BM, c) TPD-IB:PC₇₁BM, d) TPD-CM:PC₇₁BM. Red arrows indicate isotropic PC₇₁BM “halo.”

Calculations of lamellar stacking and π - π stacking values

Lamellar stacking spacing using (100) peak and the π - π stacking spacing using (010) peak were calculated from the following relation:

$$q = \frac{2\pi}{d}$$

(S6-1)

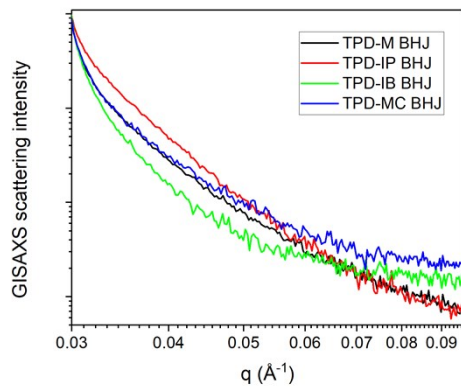


Figure S8. Volume normalized GISAXS scattering intensity for the four blend films.

S7: Temperature dependent solution UV-vis spectroscopy

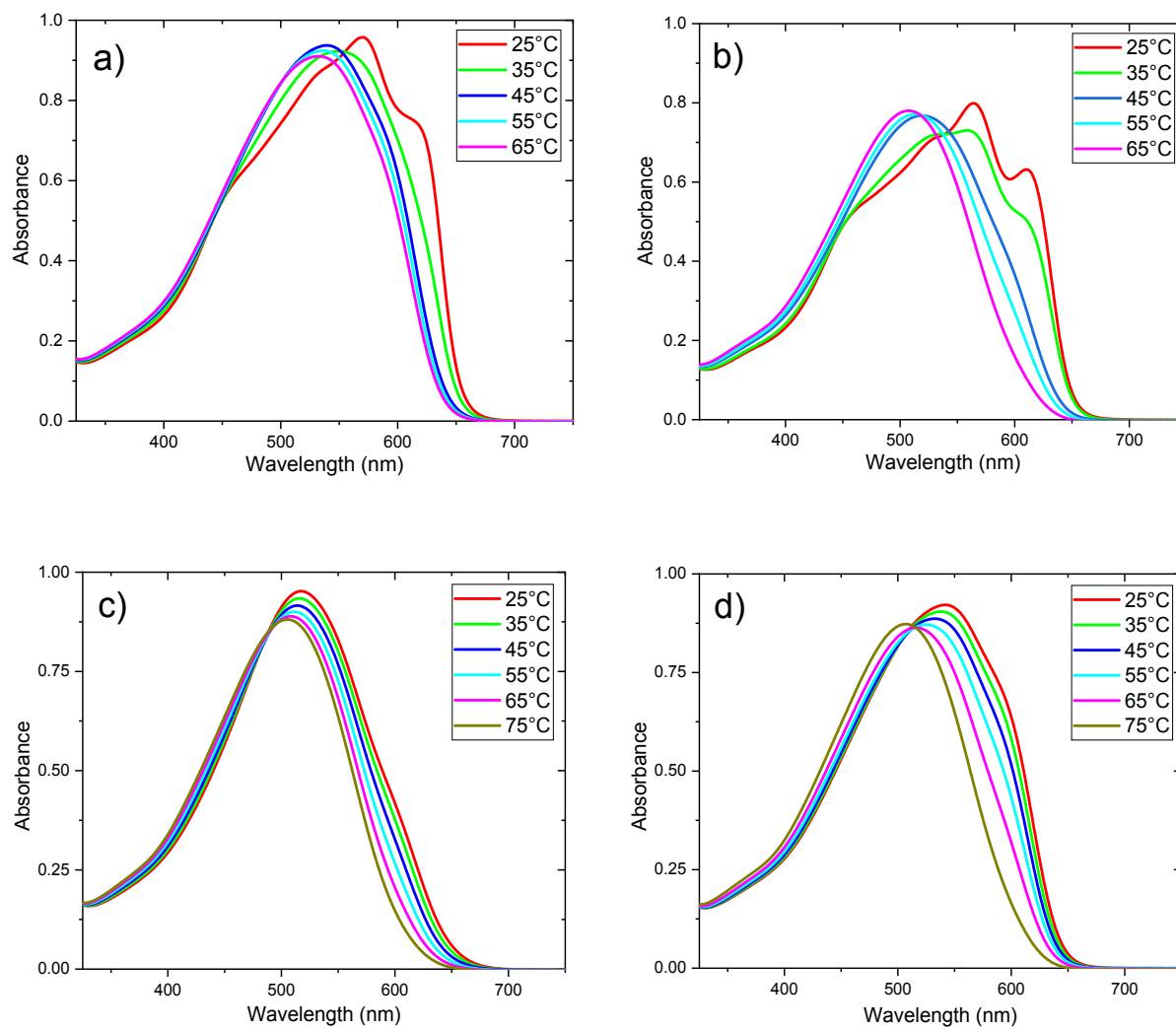


Figure S9. Thermochromism UV-Vis spectra of a) TPD-M, b) TPD-IP, c) TPD-IB, and d) TPD-CM.

S8: Differential Scanning Calorimetry

Sample preparation of neat polymer samples

~0.5 mL of a 7 mg/mL polymer:chlorobenzene 85 °C solution was drop cast onto a room temperature glass substrate (~25 °C) and allowed to dry completely to make a ~3 mg sample. A razor blade was used to scrape the film off the substrate to run the differential scanning calorimetry (DSC) sample.

Sample preparation of polymer:PC₇₁BM blend samples

~0.333 mL of a 30 mg/mL solution of a 1:1.2 blend of polymer:PC₇₁BM in 1:1 chlorobenzene:o-dichlorobenzene was stirred overnight at 85 °C. 3% by volume of DIO was added to the solution and allowed to stir for ~30 minutes prior to coating. From the 85 °C solution, films were drop-cast on a room temperature substrate (~25 °C). To remove the additive from the blend layer without disturbing the wet film, the samples were placed in a vacuum chamber with a pressure of 1×10^{-5} mbar for 45 min. A razor blade was used to scrape the film off the substrate to run the DSC sample (~3 mg).

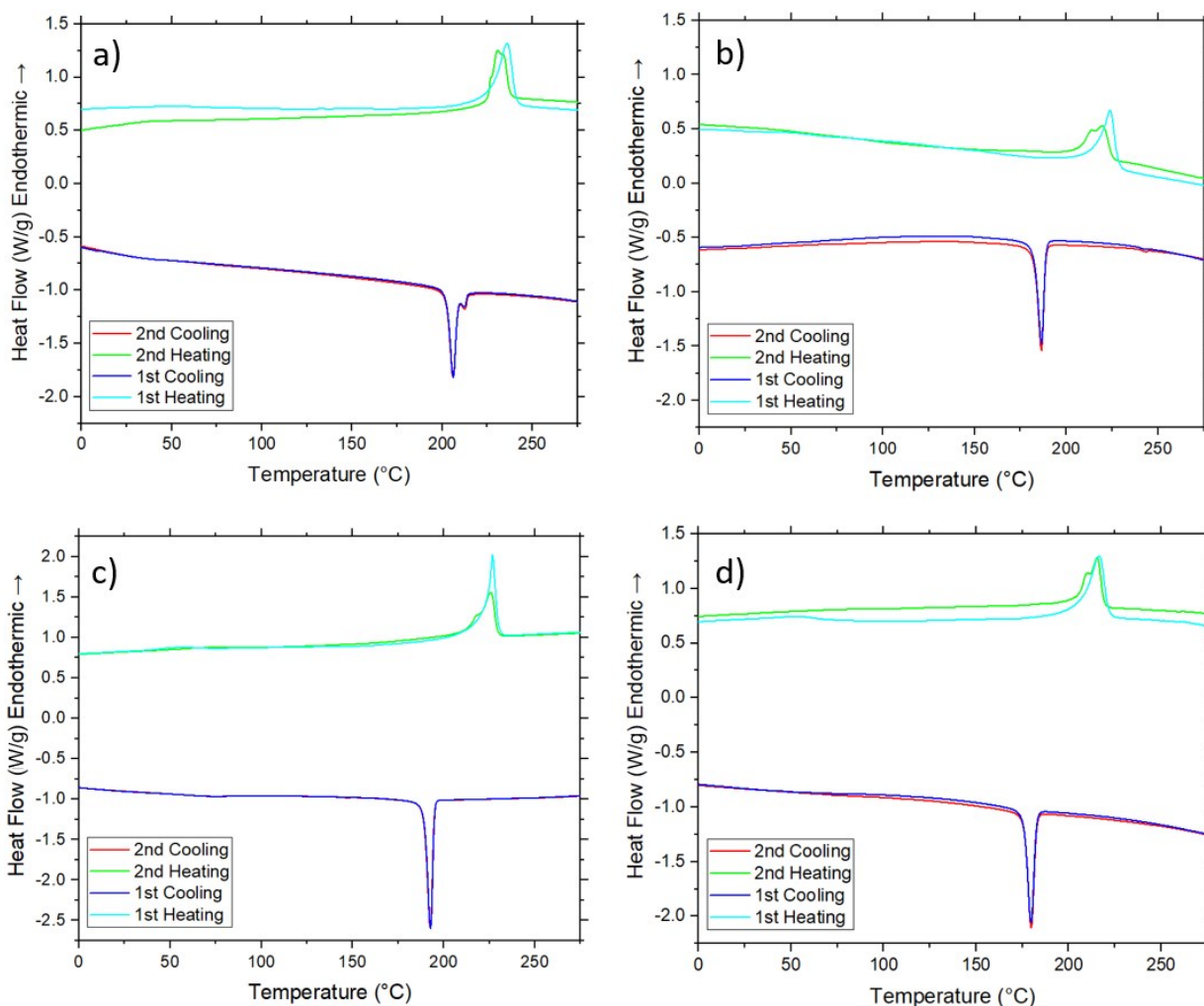


Figure S10. Full DSC Thermograms of a) TPD-M, b) TPD-IP, c) TPD-IB, d) TPD-CM.

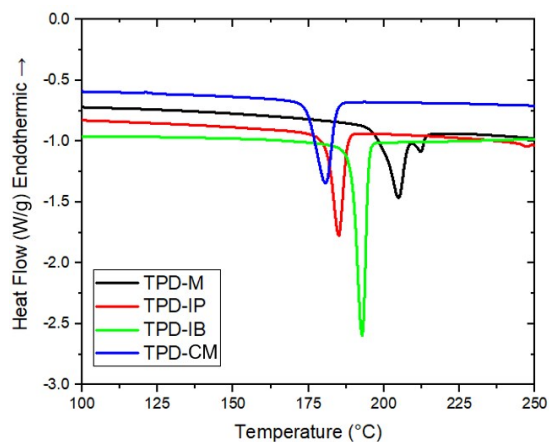


Figure S11. DSC thermograms of the polymers depicting the crystallization transitions (taken from the second cooling curve).

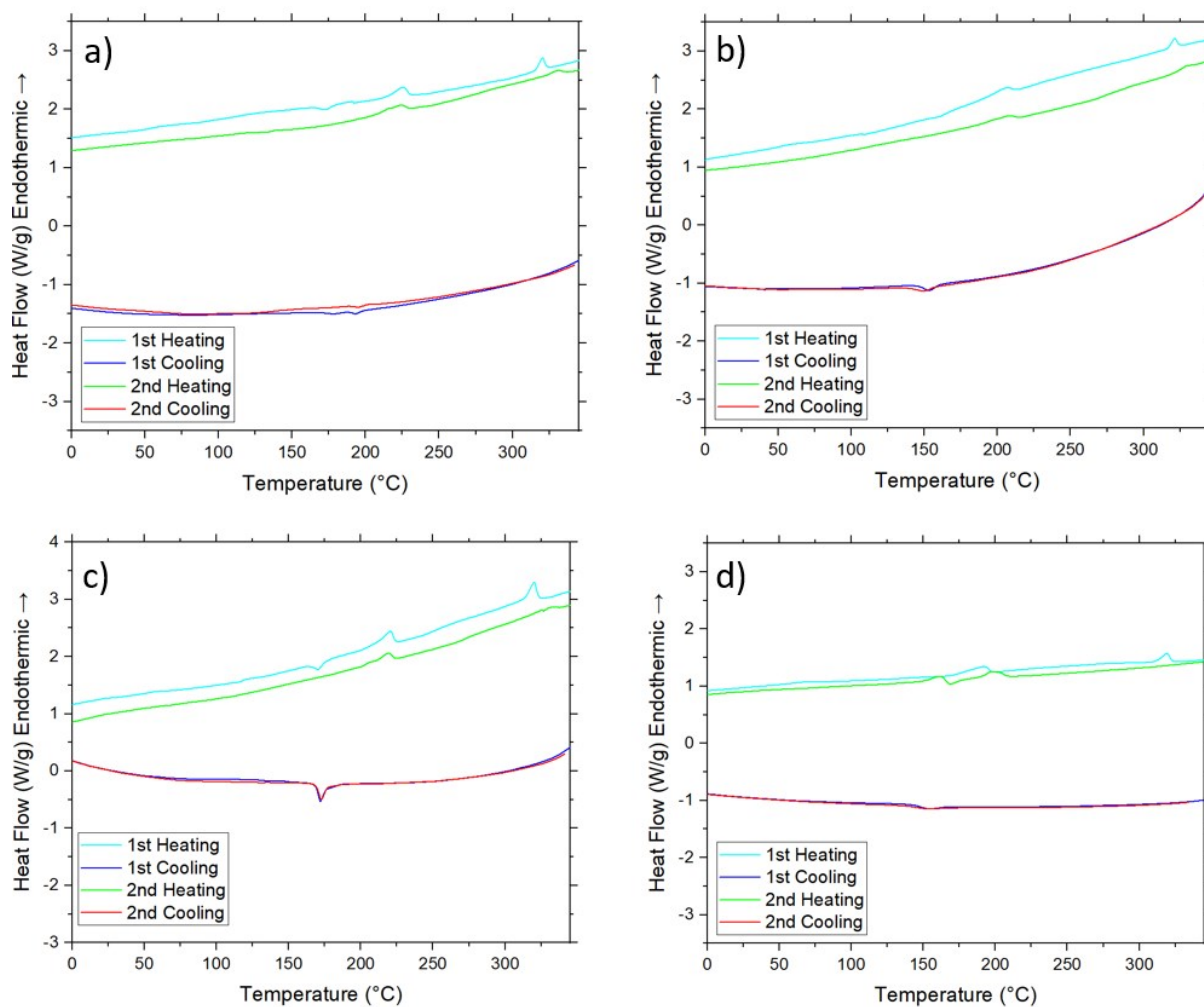


Figure S12. Full DSC Thermograms of polymer:PC₇₁BM blends a) TPD-M:PC₇₁BM, b) TPD-IP:PC₇₁BM, c) TPD-IB:PC₇₁BM, d) TPD-CM:PC₇₁BM.

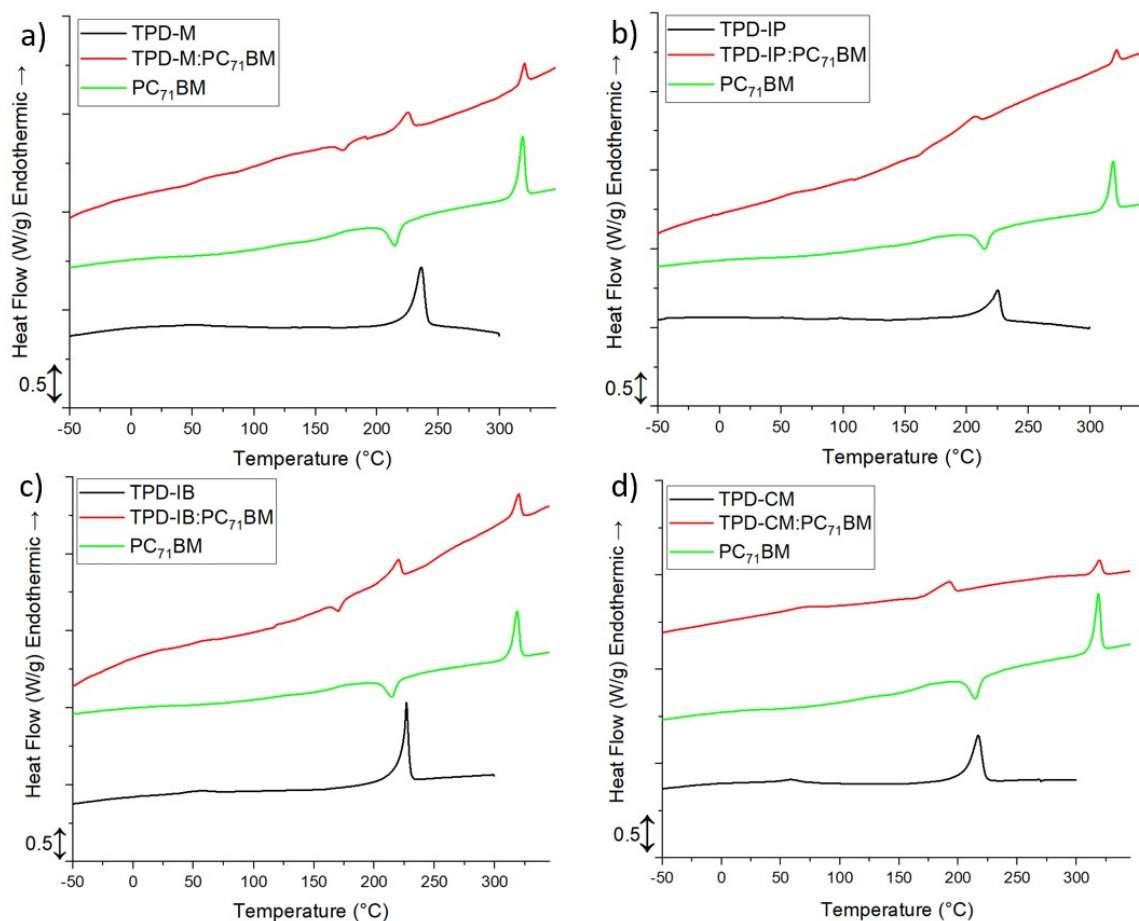


Figure S13. First heating curves of DSC scans of the neat polymer, the polymer:PC₇₁BM blend, and neat PC₇₁BM – a) TPD-M, b) TPD-IP, c) TPD-IB, d) TPD-CM.

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