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Phthalimide-based π-Conjugated Small Molecules with Tailored Electronic Energy Levels for use as Acceptors in Organic Solar Cells

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SUPPORTING INFORMATION

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1. Experimental Details

General Details: Preparations were carried out on a bench top or under an atmosphere of dry, O_2-free N_2 via Schlenk line techniques and/or an Innovative Technology inc. N_2 atmosphere glove box.

Materials: 4-bromo-phthalic anhydride, perylene-3,4,9,10-tetracarboxylic-dianhydride (PDA), naphthalene-1,4,5,8-tetracarboxylic-dianhydride (NDA), dibromoisocyanuric acid, N,N'-dimethylacetamide (DMA), N,N'-dimethylformamide (DMF), toluene, and pivalic acid (PivOH) were purchased from TCI America and were used without further purification. N-Octylamine, 1-ethylpropylamine, bromine, imidazole, 2-tributylstannylthiophene ($SnBu_3$-Th), and 2,5 bis-tributylstannylthiophene ($(SnBu_3)_2$-Th) were purchased from Sigma-Aldrich and were used without further purification. 5,6-difluoro-4,7-dibromo-2,1,3-benzothiadiazole was purchased from One Chemical and used without further purification. Heterogeneous catalyst SilicaCat-DPP® was purchased from Silicycle and used without further purification. Anhydrous Potassium Carbonate (K_2CO_3) was purchased from ACP Chemicals, and after initial usage, was stored in a Gallenkamph Hotbox oven at 100°C. Glacial Acetic Acid (CH_3COOH) was purchased from Fisherbrand and used without further purification. All solvents were purchased from the Dalhousie solvent exchange program and used without further purification, unless otherwise noted.

Nuclear Magnetic Resonance (NMR): ^1H and $\{^1H\}^{13}C$ (NMR) spectroscopy spectra were recorded on either a Bruker Avance-500 MHz spectrometer or a Bruker Avance-300 MHz spectrometer at 300 K. Chemical shifts (in ppm) were referenced to $SiMe_4$. All experiments were performed in deuterated chloroform ($CDCl_3$).

Mass Spectrometry: Mass spectrometry measurements were performed courtesy of Xiao Feng in the Dalhousie University Analytical Laboratory. A Bruker-Daltronics Micro TOF Mass Spectrometer was used. Atmospheric pressure chemical ionization (APCI) or atmospheric pressure photo-ionization (APPI) were used to ionize the samples.

UV-Visible Spectroscopy (UV-vis): All UV-vis spectra were recorded with an Agilent Cary 60 Spectrophotometer at room temperature. All solution UV-vis experiments were run using $CHCl_3$ as a solvent in telfon capped 2 mm quartz cuvettes. Films were prepared by spin-coating solutions from $CHCl_3$ onto glass substrates cut from corning Micro slides (single frosted) at 1000 rpm for 10 seconds.

Differential Scanning Calorimetry (DSC): Differential Scanning Calorimetry was performed on a TA instruments Q-1000 DSC instrument with compressed air as the purging gas. Samples were heated from 50 °C to 300 °C for 3 cycles under air.

Cyclic Voltammetrey (CV): All CV measurements were performed using a BASi Cell Stand instrument and BASi Epsilon EC software. Measurements were performed in a three-electrode, one compartment configuration equipped with a Ag/AgCl electrode, a Pt wire, and a glassy carbon electrode (3 mm diameter) as the pseudo reference, counter

electrode, and working electrode respectively; as well as an N_2 bubbler. Glassy carbon electrodes were polished with alumina. The CV experiments were performed in anhydrous dichloromethane solution ~0.1M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte. All solutions were scanned at 100 mV/s (both with and without a Fc/Fc^+ standard) after being purged with N_2 for one min to agitate the solution and remove water. Under these conditions, a Fc/Fc^+ standard was calibrated to be ~ 0.48 V. Solution CV measurements were carried out with a small-molecule concentration of ~ 1 mg/mL in CH_2Cl_2. The HOMO and LUMO levels were obtained by correlating the onsets ($E_{ox}^{Fc/Fc+}$, $E_{rd}^{Fc/Fc+}$) to the normal hydrogen electrode (NHE), assuming the HOMO of Fc/Fc^+ to be 4.80 eV.[1]

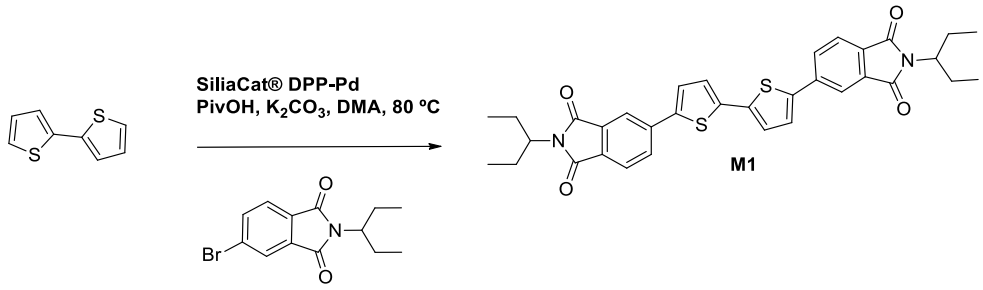
Atomic Force Microscopy: Tapping mode AFM was carried out in air with a Bruker Innova AFM. Sb doped Si tips (Bruker) with a nominal spring constant of 42 N m^{-1}, resonant frequency of 320 kHz, and a tip radius of 10 nm were used. Acquired images of 5 μm × 5 μm were taken with a scan frequency of 1 Hz.

Device Fabrication and Testing: OPV-BHJ devices were fabricated using pre-patterned ITO on glass substrates (Thin Film Devices), which were cleaned by ultrasonication and exposure to UV-ozone immediately prior to use. PEDOT:PSS (Clevios P VP AI 4083) was deposited through a PVDF filter and spin-cast at 5000 RPM and annealed at 140 ºC in air for 10 minutes. Substrates were then transferred to inert atmosphere for the remainder of device fabrication and testing. Solutions of 1:1 donor:acceptor ratio with a total concentration of 20 mg/mL in chlorobenzene (with 0.4 % v/v DIO added to the **DTS(FBTTh$_2$)$_2$** blends) were stirred overnight at 90 ºC, hot-cast through a PTFE filter and spun at 1000 RPM to form the active layers. Active layers were thermally annealed at 70 ºC for 10 minutes prior to vacuum thermal deposition of 8 nm of Ca followed by 100 nm of Al. Device area was 0.11 cm^2. Devices were tested using a Xe source (Sciencetech SS-0.5k) with an illumination intensity of 100 mW/cm^2, calibrated using a calibrated Si photodetector and a KG5 filter (Newport).

Single Crystal X-Ray Diffraction: X-ray crystallographic data collection was carried out using APEX2, cell refinement using SAINT and data reduction using SAINT. Structure identification was completed using SHELXS97. Structure refinement software packages used included SHELXL97 and Olex2.[2] Molecular graphics were created through ORTEP-3 for Windows and POV-Ray for Windows. The Olex2 software package was used to generate angles between planar parts of the molecules using the 'mpln' command. The plane for the NDI core was defined using all 14 carbon atoms in the NDI core. The thiophene ring plane was defined using all 5 atoms in the thiophene ring and the phthalimide plane was defined by using all 8 carbon atoms in the phthalimide unit. Using these planes with the "esd" function in Olex2 allowed for the generation of plane-to-plane angles and distances (**Figure 5** in main body of paper). Th-Phth plane to plane angle: 11.50(8) °. NDI-Th plane to plane angle: 58.10(6) °. Short π-π stacking distance in c-direction: 3.284(4) Å (calculated using Th-Th plane to plane centroid distances). Long π-π stacking distance in c-direction: 5.397(9) Å (using Th-Th plane to plane centroid distances). Angle between oppositely oriented NDI fragments: 82.84(6) °.

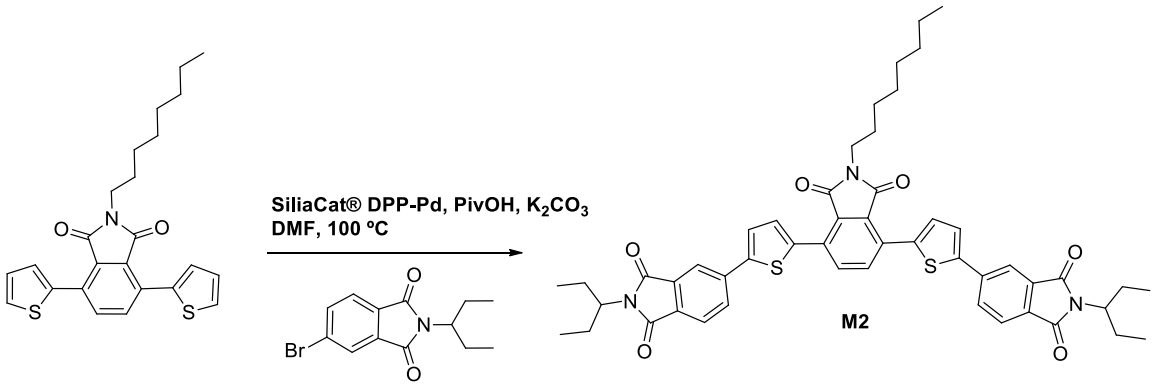
2. Synthesis and Characterization

2.1 Experimental Details for M1-M7



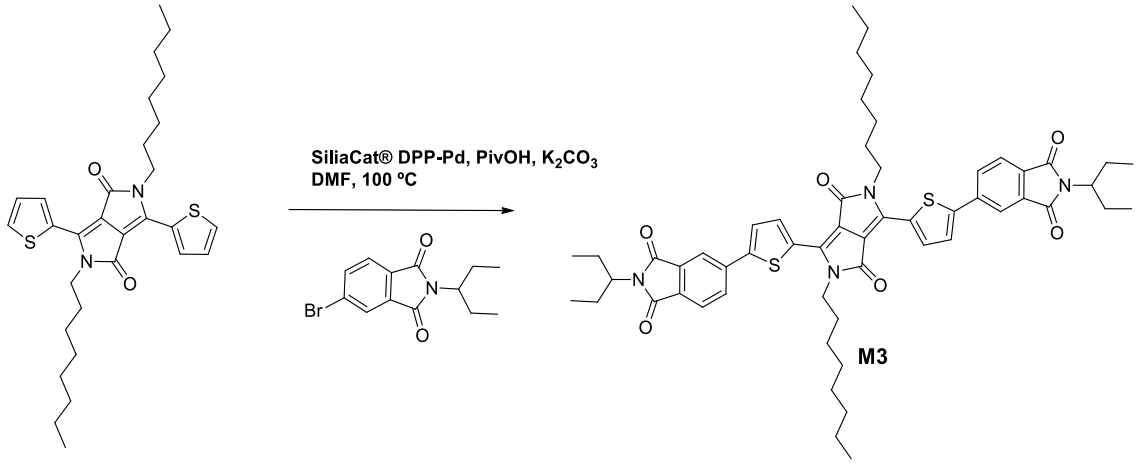
Scheme S1 – Experimental procedure for the Synthesis of **M1**

Synthesis of 5,5'-(1-ethylpropyl-isoindoline-1,3-dione)-bithiophene (M1): A 10-20 mL glass vial was loaded on the bench top with 2,2′-bithiophene (0.1 g, 0.60 mmol), 4-bromo-2-(1-ethylpropyl)phthalimide (0.374 g, 1.26 mmol), potassium carbonate (0.207 g, 1.50 mmol), pivalic acid (0.012 g, 0.12 mmol), SiliaCat® DPP-Pd (0.12 g, 0.03 mmol), and a stir bar. The contents were sealed with a silicone cap and purged with N_2 gas for 5 minutes before the addition of anhydrous DMF (3 mL). The reaction mixture was heated in an oil bath at ~80 ºC. The reaction was allowed to cool to room temperature and subsequently was diluted with ~50 mL of CH_2Cl_2 and was filtered through a short silica plug to isolate the product from the heterogeneous catalyst SiliaCat® DPP-Pd. The filtrate containing product was concentrated under reduced pressure and loaded onto silica gel for purification *via* flash column chromatography with pentane/CH_2Cl_2 as the eluting solvent system. Following the removal of solvent from the product fraction, methanol was added to the solid product and it was collected via filtration using a Buchner funnel. The product was washed with a mixture of methanol/pentane (1:1) and isolated as a bright orange solid. **Yield**: 92 % (330 mg) **^{1}H NMR ($CDCl_3$): δ** 8.04 (m, 2H); 7.92-7.82 (m, 4H); 7.44 (d, 2H, $^3J_{H\text{-}H}$ = 4 Hz); 7.28 (d, 2H, $^3J_{H\text{-}H}$ = 4 Hz); 4.11-4.01 (m, 2H); 2.15-2.00 (m, 4H); 1.88-1.74 (m, 4H); 0.89 (t, 12H, $^3J_{H\text{-}H}$ = 7 Hz).**^{13}C NMR ($CDCl_3$): δ** 168.49; 168.43; 141.44; 139.60; 138.33; 133.06; 130.25; 130.06; 126.23; 125.58; 123.86; 119.71; 55.82; 25.32; 11.19. **MS (APCI-TOF):** *m/z* 597.2 *calcd.* 597.2.



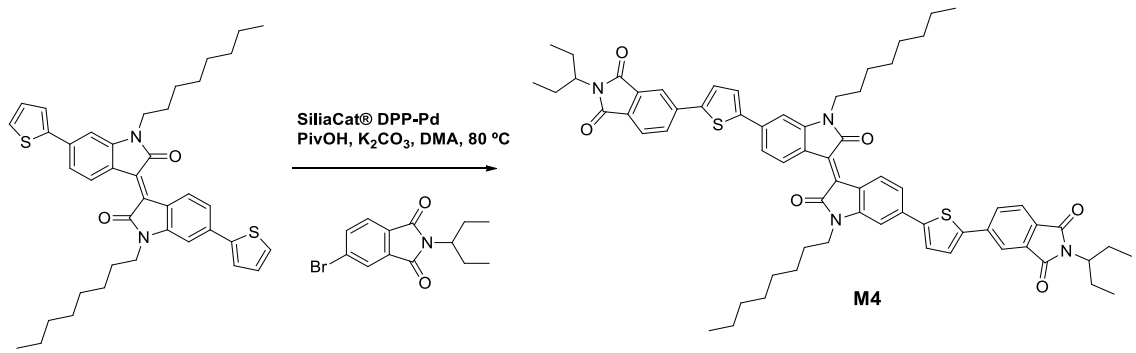
Scheme S2 – Experimental procedure for the Synthesis of **M2**

***Synthesis of 5,5'-(5,5'-(2-octyl-1,3-phthalimide-4,7-diyl)bis(thiophene-5,2-diyl))bis(2-(1-ethylpropyl)phthalimide) (M2)*:** A 2-5 mL glass vial was loaded on the bench top with 2-octyl-3,6-di(thiophen-2-yl)phthalimide (0.190 g, 0.45 mmol), 4-bromo-2-(1-ethylpropyl)phthalimide (0.313 g, 1.1 mmol), pivalic acid (0.017 g, 0.17 mmol), potassium carbonate (0.169 g, 1.2 mmol) and SiliaCat® DPP-Pd (0.100 g, 0.025 mmol). The contents were sealed with a silicone cap and purged with N_2 gas for 5 minutes before the addition of anhydrous DMF (~3 mL). The reaction mixture was heated in an oil bath between 100-105 ºC and monitored by TLC, which showed full conversion of starting material after 5 hours. The reaction was allowed to cool to room temperature and subsequently precipitated into H_2O (~200 mL) and stirred overnight. The solid product was collected via filtration and washed with EtOAc (~250 mL) to isolate the product from the heterogeneous catalyst SiliaCat® DPP-Pd. The filtrate containing product was concentrated under reduced pressure and liquid loaded onto silica for purification via flash column chromatography with CH_2Cl_2 as the eluent. Following the removal of solvent from the product fraction, methanol was added to the solid product and it was collected via filtration using a Buchner funnel. The product was washed with methanol and isolated as a yellow-orange solid. **Yield**: 62 % (238 mg). If necessary the product can also be completely recrystallized when cooled from a heated solution of isopropanol. **^{1}H NMR ($CDCl_3$):** δ 8.12 (s, 2H); 7.99 (d, 4H, $^3J_{H-H}$ = 8 Hz); 7.86 (m, 4H); 7.56 (d, 2H, $^3J_{H-H}$ = 4 Hz); 7.28 (m, 2H); 4.08 (m, 2H); 3.72 (t, 2H); 2.18-2.03 (m, 4H); 1.90-1.81 (m, 4H); 1.76-1.67 (m, 2H); 1.34-1.28 (m, 10H); 0.92 (m, 15H).**^{13}C NMR ($CDCl_3$):** δ 168.51; 168.45; 167.12; 144.18; 139.67; 138.70; 135.53; 133.04; 131.86; 131.68; 130.64; 130.35; 128.28; 125.86; 123.86; 120.03; 55.84; 38.44; 31.78; 29.15; 28.49; 26.99; 25.32; 22.62; 14.07; 11.20. **MS (APCI-TOF):** *m/z* 854.4 *calcd.* 854.4.

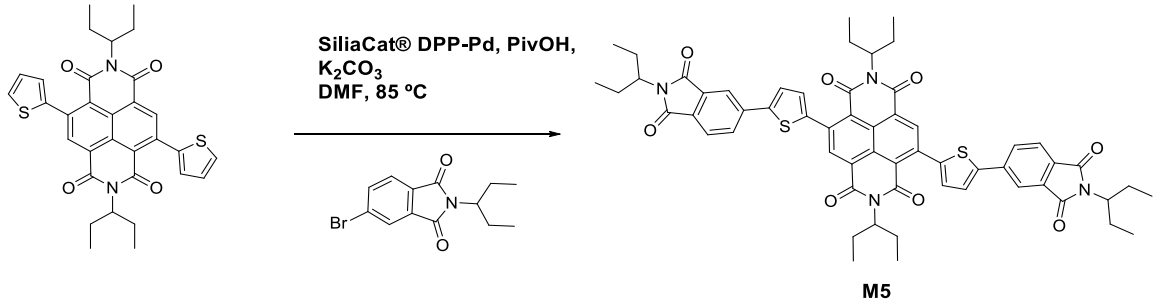


Scheme S3 – Experimental procedure for the Synthesis of **M3**

Synthesis of 3,6-bis-((1-ethylpropyl-4-(thiophen-2-yl)isoindoline-1,3-dione))-2,5-bis-(n-octyl)-2,5-dihydro-pyrrole-1,4-dione (M3): A 2-5 mL glass vial was loaded on the bench top with 3,6-(bis-thiophene-2-yl)-2,5-bis-(n-octyl)-6-(thiophene-2-yl) -2,5-dihydro-pyrrole-1,4-dione (0.165 g, 0.314 mmol), 4-bromo-2-(1-ethylpropyl)phthalimide (0.196 g, 0.66 mmol), potassium carbonate (0.108 g, 0.785 mmol), pivalic acid (0.006 g, 0.063 mmol), and SiliaCat® DPP-Pd (0.063 g, 0.016 mmol). The contents were sealed with a silicone cap and purged with N_2 gas for 5 minutes before the addition of anhydrous DMA (~10 mL). The reaction mixture was heated in an oil bath between 80-85 ºC for 48 hours. The reaction was diluted in dichloromethane and was filtered through a short silica plug to isolate the product from the heterogeneous catalyst SiliaCat® DPP-Pd. The filtrate containing product was concentrated under reduced pressure and loaded onto silica gel for purification via flash column chromatography with Pentane/CH_2Cl_2 as the eluting solvent system. Following the removal of solvent from the product fraction, methanol/water (1:9), was added to the solid product and it was collected via filtration using a Buchner funnel. The product was washed with methanol and isolated as a dark blue solid. **Yield 16%** (47 mg). **^{1}H NMR ($CDCl_3$):** δ 9.00 (d, 2H $^3J_{H\text{-}H}$ = 4 Hz); 8.12-8.10 (m, 2H,); 8.01-7.86 (m, 4H); 7.64 (d, 2H $^3J_{H\text{-}H}$ = 4 Hz); 4.17-4.02 (m, 6H) 2.13-2.00 (m, 4H); 1.84-1.75 (m, 8H); 1.47-1.27 (m, 16H); 0.92-0.84 (m, 18H).**^{13}C NMR ($CDCl_3$):** δ 168.24; 168.19; 161.19; 147.00; 139.34; 138.75; 136.73; 133.12; 131.00; 130.93; 130.73; 126.62; 123.96; 120.28; 108.92; 55.94; 42.39; 31.80; 30.09; 29.24; 29.19; 26.93; 25.30; 22.63; 14.08; 11.10. **MS (APCI-TOF):** *m/z* 955.4. *calcd.* 955.4.

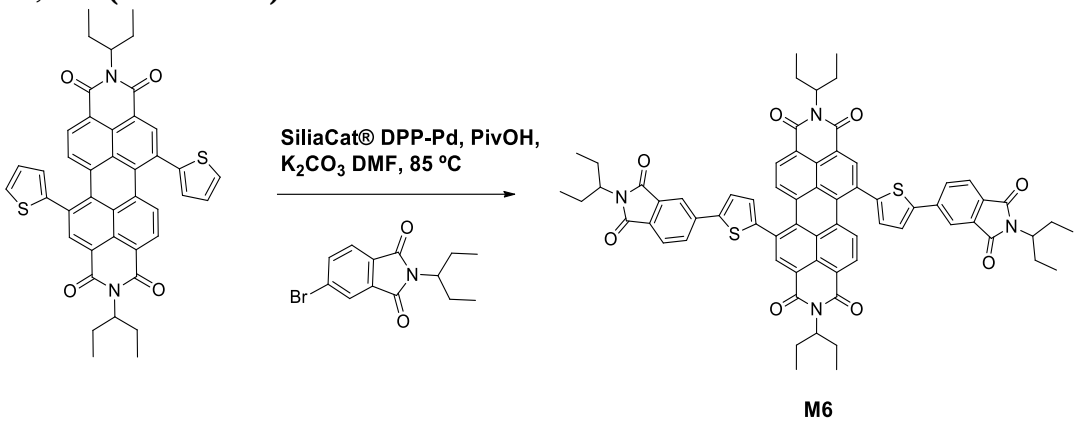


Scheme S4 – Experimental procedure for the Synthesis of **M4**. The synthesis of this small molecule and its precursors was previously reported by our lab group.[3]



Scheme S5 – Experimental procedure for the Synthesis of **M5**.

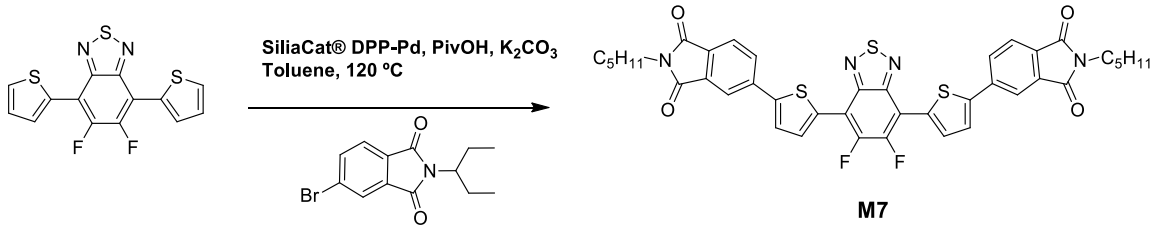
Synthesis of 2,6-(bis-(1-ethylpropyl-4-(thiophen-2-yl)isoindoline-1,3-dione))- N,N-Bis-ethylpropyl naphthalene 1,4,5,8 tetracarboxylic diimide (M5): A 10-20 mL glass vial was loaded on the bench top with 2,6-dithienyl-N,N-bis-ethylpropyl naphthalene 1,4,5,8 tetracarboxylic diimide (200 mg, 0.35 mmol), 4-bromo-2-(1-ethylpropyl)phthalimide (260 mg, 0.88 mmol), potassium carbonate (120 mg, 0.88 mmol), SiliaCat® DPP-Pd (70 mg, 0.018 mmol), pivalic acid (0.011 g, 0.11 mmol) and a stir bar. The vial was then brought inside the glove-box where N,N'-dimethylacetamide (~10 mL) was added as a solvent. The vial was sealed with a Teflon® cap under an atmosphere of N_2. The reaction vial was removed from the glove box and heated in an oil bath at 85 ºC for 48 hours. The reaction was allowed to cool to room temperature and was then diluted with ~100 mL of CH_2Cl_2 and was filtered through a short silica plug to isolate the product from the heterogeneous catalyst SiliaCat® DPP-Pd. The filtrate containing product was concentrated under reduced pressure and loaded onto silica gel for purification via flash column chromatography with pentane/CH_2Cl_2 as the eluting solvent system. Following the removal of solvent from the product fraction, methanol/pentane (1:1), was added to the solid product and it was collected via filtration using a Buchner funnel. The product was washed with methanol and isolated as a dark red solid. **Yield:** 48% (109 mg). **^{1}H NMR ($CDCl_3$): δ** 8.79 (s, 2H); 8.09-8.08 (m, 2H); 7.99-7.84 (m, 4H); 7.57 (d, 2H $^3J_{H-H}$ = 4 Hz); 7.35 (d, 2H, $^3J_{H-H}$ = 4 Hz); 5.02-4.92 (m, 2H); 4.16-4.02 (m, 2H) 2.26-2.01 (m, 8H); 1.97-1.75 (m, 8H); 0.94-0.88 (m, 24H). **^{13}C NMR ($CDCl_3$): δ** 168.53; 168.45; 144.60; 142.68; 139.70; 136.39; 133.03; 130.64; 130.35; 129.82; 127.69; 125.65; 123.86; 120.05; 58.51; 55.85; 25.33; 24.88; 11.30; 11.21; **MS (APPI-TOF):** m/z 1001.2 calcd 1001.2.



Scheme S6 – Experimental procedure for the Synthesis of **M6**.

Synthesis of *1,7-(bis-(1-ethylpropyl-4-(thiophen-2-yl)isoindoline-1,3-dione))- N,N', bis-ethylpropyl-perylene 3,4,9,10 tetracarboxylic diimide (M6)*: A 10-20 mL glass vial was loaded on the bench top with 1,7-dithienyl-N,N-bis-ethylpropyl perylene 1,4,5,8 tetracarboxylic diimide (250 mg, 0.36 mmol), 4-bromo-2-(1-ethylpropyl)phthalimide (224 mg, 0.76 mmol), potassium carbonate (124 mg, 0.9 mmol), pivalic acid (0.007 g, 0.018 mmol), SiliaCat® DPP-Pd (72 mg, 0.018 mmol) and a stir bar. N,N'-dimethylacetamide (~10 mL) was added as a solvent. The vial was sealed with a Teflon® cap and was heated in an oil bath at 85 ºC for 48 hours. The reaction was allowed to cool to room temperature and was then diluted with ~100 mL of CH_2Cl_2 and was filtered through a short silica plug to isolate the product from the heterogeneous catalyst SiliaCat® DPP-Pd. The filtrate containing product was concentrated under reduced pressure and

loaded onto silica gel for purification *via* flash column chromatography with pentane/CH_2Cl_2 as the eluting solvent system. Following the removal of solvent from the product fraction, methanol/water (1:9), was added to the solid product and it was collected via filtration using a Buchner funnel. The product was washed with methanol and isolated as a black solid. **Yield**: 25% (103 mg).** This product was purified multiple times using chromatography and recrystallization techniques, however minor impurities were still visible in the ^{1}H NMR spectra that could not be removed. **^{1}H NMR ($CDCl_3$):** δ 8.72 (s, 2H); 8.28 (s, 4H); 8.05-8.04 (m, 2H); 7.95-7.84 (m, 4H); 7.59 (d, 2H, $^3J_{H-H}$ = 4 Hz); 7.42 (d, 2H, $^3J_{H-H}$ = 4 Hz); 5.09-4.99 (m, 2H); 4.06-4.01 (m, 2H); 2.31-2.16 (m, 4H); 2.13-2.00 (m, 4H); 1.96-1.74 (m, 8H); 0.94-0.87 (m, 24H). **^{13}C NMR ($CDCl_3$):** δ 168.38; 145.30; 144.80; 139.30; 134.32; 133.24; 133.10; 132.42; 130.50; 12 9.84; 129.20; 129.06; 128.38; 126.70; 123.92; 120.02; 57.80; 55.85; 25.32; 25.00; 11.33; 11.18. **MS (APPI-TOF):** *m/z* 1125.3 *calcd.* 1125.3.



Scheme S7 – Experimental procedure for the Synthesis of **M7**.

Synthesis of *5,6-dicyano-4,7-bis-(1-ethylpropyl-4-(thiophen-2-yl)isoindoline-1,3-dione)-2,1,3-benzothiadiazole (M7):* A 10-20 mL glass vial was loaded on the bench top with 5,6-Difluoro-4,7-di(thiophen-2-yl)-2,1,3-benzothiadiazole (4a, 0.100 g, 0.3 mmol), 4-bromo-2-(1-ethylpropyl)phthalimide (0.184 g, 0.62 mmol), potassium carbonate (0.091 g, 0.66 mmol), SiliaCat® DPP-Pd (0.06 g, 0.015 mmol), pivalic acid (0.006 g, 0.06 mmol) and a stir bar. Toluene (~10 mL) was added as a solvent and the vial was sealed with a silicone cap before being heated in an oil bath at 120 ºC for 48h. The reaction was allowed to cool to room temperature and subsequently precipitated into methanol (~100 mL) and stirred for 20 minutes. The solid product was collected by filtration and washed with methanol (~100 mL). The solid was dissolved in dichloromethane and was filtered through a short silica plug to isolate the product from the heterogeneous catalyst SiliaCat® DPP-Pd. The filtrate containing product was concentrated under reduced pressure and loaded onto silica gel for purification via flash column chromatography with pentane/CH_2Cl_2 as the eluting solvent system. Following the removal of solvent from the product fraction, methanol was added to the solid product and it was collected via filtration using a Buchner funnel. The product was washed with methanol and isolated as a red solid. **Yield:** 48 % (109 mg) **^{1}H NMR ($CDCl_3$):** δ 8.30; (d, 2H, $^3J_{H-H}$ = 3Hz); 8.14 (m, 2H); 8.03-7.83 (m, 4H); 7.60 (d, 2H, $^3J_{H-H}$ = 3 Hz); 4.12-4.02 (m, 2H); 2.13-2.03 (m, 4H);1.86-1.78 (m, 4H); 0.90 (t, 12H, $^3J_{H-H}$= 7 Hz).**^{19}F NMR ($CDCl_3$):** δ -126.82 ^{13}C NMR ($CDCl_3$): δ 168.46; 168.40; 139.51; 133.17; 133.04; 130.65; 130.43; 125.61; 123.85; 120.04; 55.85; 25.32; 11.20. **MS (APCI-TOF):** m/z 767.2. calcd. 767.2.

Table S1. Synthesis of Small Molecules **M1-M7**

	Temperature (C)	Solvent	Reaction time (h)	Yield (%)

M1	85	DMF	24	92
M2	100	DMF	24	62
M3	85	DMF	48	16
M4	80	DMA	16	70
M5	85	DMA	48	48
M6	85	DMA	48	25*
M7	120	Tol.	48	48

***** Molecule could not be completely purified, the low yield is due to repeated attempts at purification.

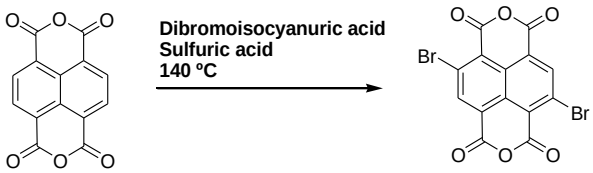
2.2 Experimental Details for the Synthesis of Precursor Materials.

Synthesis of SW-Pt: The synthesis for 4-bromo-N-ethylpropyl-phthalimide was previously reported by our lab group.[3]

Synthesis of 2-octyl-3, 6-di(thiophen-2-yl)phthalimide: The synthesis of 2-octyl-3,6-di(thiophen-2-yl)phthalimide was completed according to literature procedures.[4]

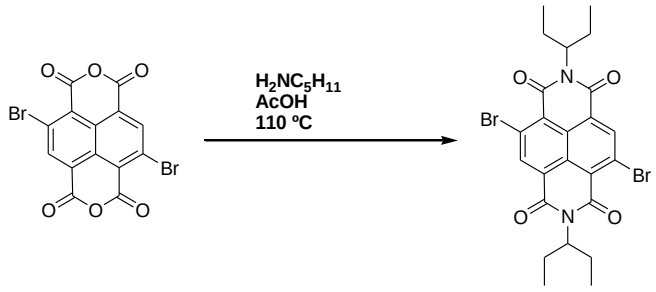
Synthesis of Octyl-DPP: The synthesis of octyl DPP was previously reported by our lab group.[5]

Synthesis of Octyl-Isoindigo: The synthesis of octyl-II was completed as previously reported by our lab group.[3]



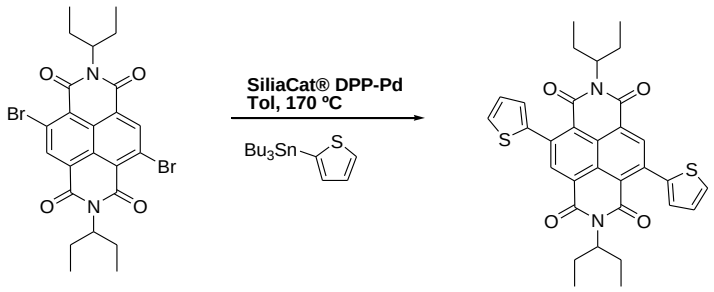
Scheme S8 – Experimental procedure for the Synthesis of **NDA-Br$_2$.**

Synthesis of 2,6-dibromo Naphthalene 1,4,5,8 tetracarboxylic dianhydride (NDA-Br$_2$):
A 50 mL round-bottom flask was loaded on the bench top with naphthalene-1,4,5,8-tetracarboxylic dianhydride (**NDA**, 1.0g, 3.7 mmol) and dibromoisocyanuric acid (2.1 g, 7.5 mmol), Sulfuric acid (conc., ~40 mL) and a stir-bar. The flask was fitted with a reflux condenser and heated to 130-140 ºC using an oil bath for 48 hours. The reaction was allowed to cool to room temperature and was poured into water (~200 mL) containing ice which resulted in the formation of a yellow precipitate. The mixture was stirred in ice water until all the ice had melted and then the yellow precipitate was filtered and washed with distilled water to isolate the product as an off white solid. ^{1}H NMR data for this compound matches that reported in the literature.[6] except in this case there are minor impurities visible in the ^{1}H NMR, likely consisting of mono and un-brominated NDA as well as ring opened (tetracarboxylic acid) NDI derivatives. The impurities could not be separated at this stage and the crude product was used in subsequent reactions. **Yield**: quant. (2.21 g).



Scheme S9 – Experimental procedure for the Synthesis of **NDI-Br$_2$-EP$_2$**

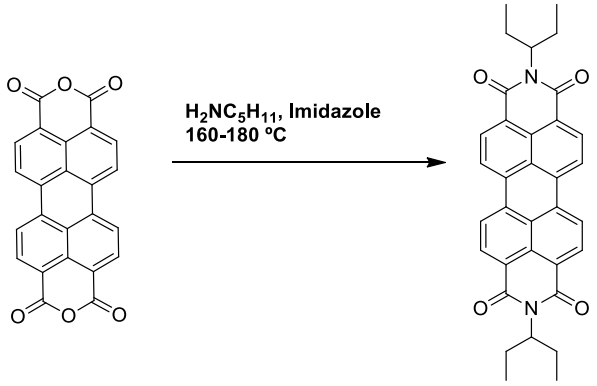
Synthesis of2,6-dibromo-N,N'-bis-(1-ethylpropyl)-naphthalene-1,4,5,8-tetracarboxylic diimide(NDI-Br$_2$-EP$_2$): A 10-20 mL glass vial was loaded on the bench top with 2,6-dibromo naphthalene-1,4,5,8 tetracarboxylic dianhydride (**NDA-Br2**, 1.0 g, 2.3 mmol) and 1-ethylpropylamine, (1.23 g, 14.1 mmol) and a stir-bar. Acetic acid (~10 mL) was added as a solvent. The vial was sealed on the bench-top with a Teflon® cap and the reaction was heated to 120 ºC using an oil bath for 24 hours. The reaction was allowed to cool to room temperature and was poured into approx. 250 mL of water which resulted in the formation of an orange precipitate. The orange precipitate was filtered and washed with ~200 mL distilled water resulting in an orange solid. The crude solid was dissolved in CH_2Cl_2 and passed through a short silica plug, volatiles were removed from the filtrate using a rotary evaporator giving an orange solid. The orange solid was boiled in a small amount of acetone and left in the fridge to cool, yielding a yellow orange solid which was filtered and washed with cold acetone (~10 mL) to give **NDI-Br$_2$-EP$_2$** as a yellow orange solid. Similar to the **NDA-Br$_2$** compound, minor impurities remained, which represented incomplete product formation. Column chromatography using a CH_2Cl_2 gradient was attempted but was unsuccessful in purifying the product. Minor impurities remained in the material which could be seen in the ^{1}H NMR, and the crude product was used in the next stage of the synthesis. **Yield**: 8% (211 mg). **^{1}H NMR ($CDCl_3$):** δ 8.97 (s, 2H); 5.08–4.97 (m, 2H); 2.28–2.13 (m, 4H); 2.02–1.87 (m, 4H); 0.90 (t, 12H, $^3J_{H\text{-}H}$ = 8 Hz).



Scheme S10 – Experimental procedure for the Synthesis of **NDI-EP$_2$-Th$_2$**

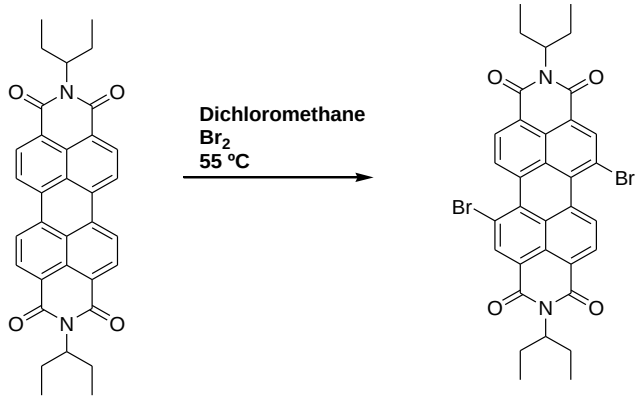
Synthesis of 2,6 dithio-N,N'-bis-(1-ethylpropyl)-naphthalene-1,4,5,8-tetracarboxylic diimide(NDI-EP$_2$-Th$_2$): A 10-20 mL glass vial was loaded on the bench top with 2,6-dibromo-N,N'-bis-(ethylpropyl) naphthalene-1,4,5,8-tetracarboxylic-diimide (**NDI-Br$_2$-EP$_2$**, 208 mg 0.37 mmol), 2-tributylstannyl thiophene (275 mg, 0.74 mmol) and Pd-DPP (296 mg, 0.07 mmol) and a stir bar. Toluene ~10 mL was added as a solvent. The reaction mixture was sealed using a Teflon® cap and heated to 120-130 °C for 3 hours in an oil

bath. After the reaction period, the reaction was diluted with 200 mL of CH_2Cl_2 and slurried with 200 mL of a 1:1 (v:v) mixture of K_2CO_3 and SiO_2 and then filtered through a glass frit. The organic phase was dried over $MgSO_4$, filtered and the solvent removed under reduced pressure using a rotary evaporator to yield a red-orange solid. The red-orange solid was slurried in methanol/water and filtered using a Buchner funnel to give 1,7- dithienyl-N,N-bis-ethylpropyl naphthalene 1,4,5,8 tetracarboxylic diimide as a red-orange solid. The red-orange solid was recrystallized from CH_2Cl_2/methanol layering layering technique, where the product was taken up in a minimal amount of CH_2Cl_2, methanol was carefully layered on top and the recrystallization vessel was set in the fridge overnight, yielding orange needle like crystals of pure 1, 7- dithienyl-N,N-bis-ethylpropyl-naphthalene-1,4,5,8-tetracarboxylic diimide which were filtered using a Buchner funnel and washed with methanol to isolate the product. **Yield**: 75% (158 mg). **^{1}H NMR ($CDCl_3$):** δ 8.73 (s, 2H); 7.55; (dd, 2H, $^3J_{H-H}$ = 5 Hz, 1 Hz); 7.29 (dd, 2H, $^3J_{H-H}$= 5 Hz, 1 Hz); 7.19 (dd, 2H, $^3J_{H-H}$ = 5 Hz, 4 Hz); 4.97 (m, 2H); 2.22-2.11 (m, 4H) 1.91-1.82 (m, 4H); 0.89 (t, 12H, $^3J_{H-H}$ = 8 Hz).



Scheme S11 – Experimental procedure for the Synthesis of **PDI-EP$_2$**

Synthesis of N,N'-bis-1-ethylpropyl-perylene-3,4,9,10-tetracarboxylic diimide (PDI-EP$_2$): A 10-20 mL glass vial was loaded on the bench top with perylene-3,4,9,10-tetracarboxylic-dianhydride (**PDA**, 1.0 g 2.5 mmol) and 1-ethylpropylamine (0.56 g, 6.4 mmol) and a stir bar. The vial was then packed with imidazole, sealed using a Teflon® cap and heated to 120-130 °C for 24 h in an oil bath. After the reaction period, the reaction was extracted using water and dichloromethane (~ 300 mL each). The organic phase was dried over $MgSO_4$, filtered and the solvent removed under reduced pressure using a rotary evaporator. Following the removal of solvent from the product, methanol/water (1:1) was added to the solid and it was collected via filtration using a Buchner funnel. The product was washed with methanol and isolated as a red solid. **Yield**: 70% (950 mg). Spectroscopic data for this compound match the previously reported data in the literature.[7]



Scheme S12 – Experimental procedure for the synthesis of **PDI-EP$_2$-Br$_2$**

Synthesis of 1,7-dibromo-N,N'-bis-1-ethylpropyl-perylene-3,4,9,10-tetracarboxylic diimide (PDI-EP$_2$-Br$_2$): A 250 mL round-bottom flask was loaded on the bench top with N,N'-bis-ethylpropyl-perylene-3,4,9,10-tetracarboxylic-diimide (**PDA-EP$_2$**, 1.5 g, 2.8 mmol) and elemental bromine (23 g, 131 mmol 7.8 mL) and a stir-bar. The flask was fitted with a reflux condenser and was heated to 50-60 °C using an oil bath for 48 hours. The reaction was allowed to cool to room temperature and air bubbling was used to remove excess Br_2. The solvent was removed under reduced pressure using a rotary evaporator and a red solid was obtained, which was then slurried in methanol/water (1:1) and filtered using a Buchner funnel. 1.8 g of a red solid was obtained which contained a mixture of mono-brominated, dibrominated and unbrominated product. Column chromatography was used to separate the dibrominated perylenes from the mixture, a 1:1 mixture of pentane and dichloromethane was used as the eluting solvent system. The dibrominated perylenes elute as the first band during the separation, followed by monobrominated product. 900 mg of dibrominated perylene was recovered from the column (contained a 7:1 mixture of 1,7-dibromoperylene to 1,6-dibromoperylene). These two isomers were inseparable using flash chromatography and so the method of repeated crystallization was used to obtain pure 1,7 dibromoperylene. Adopted from the literature[8], the crystallization procedure involved dissolution of 900 mg of dibromoperylenes into approx. 200 mL of CH_2Cl_2 and carefully layering with approx. 400 mL of methanol in a tall glass beaker and storing in the fridge for two days. After two days, red-needle like crystals had formed and were filtered using a Buchner funnel to isolate the product. Three recrystallizations of this kind were performed in order to isolate pure 1,7-dibromo-N,N', bis-ethylpropyl-perylene-3,4,9,10-tetracarboxylic diimide. ^{1}H NMR spectra of the aromatic region are provided (**Figure S1A**), which show the isolation of 1,7-dibromo-N,N'-bis-ethylpropyl-perylene-3,4,9,10 tetracarboxylic diimide after multiple recrystallizations. **Yield**: 39% (758 mg). Spectroscopic data for this compound match the previously reported data in the literature.[7,8]

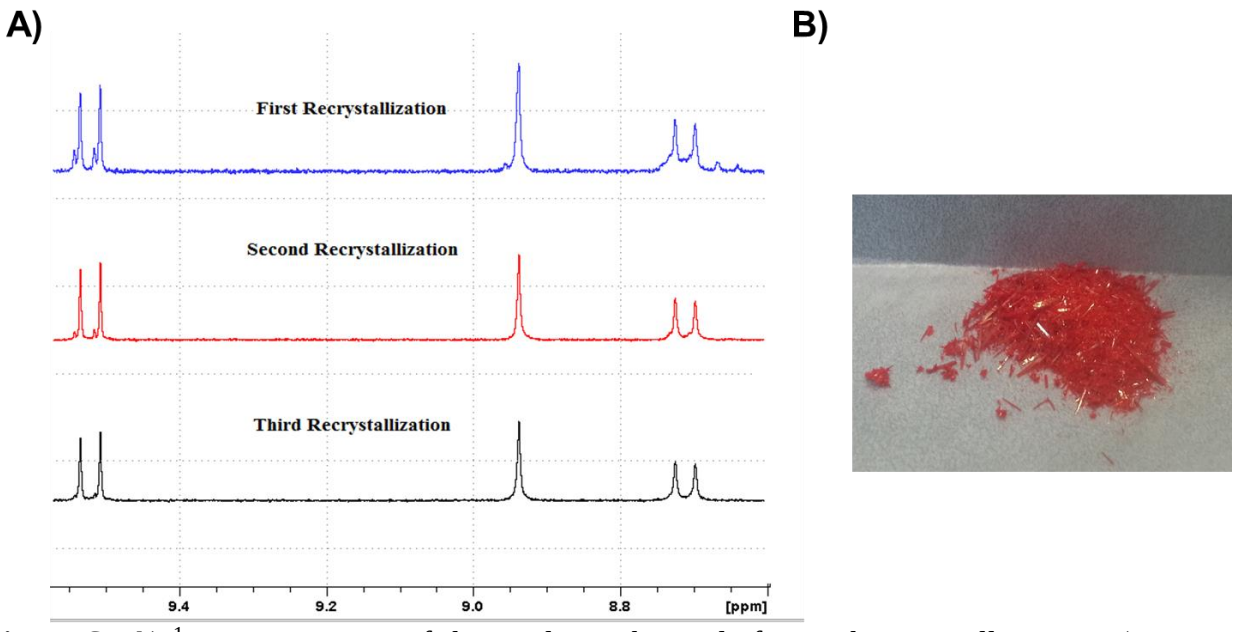
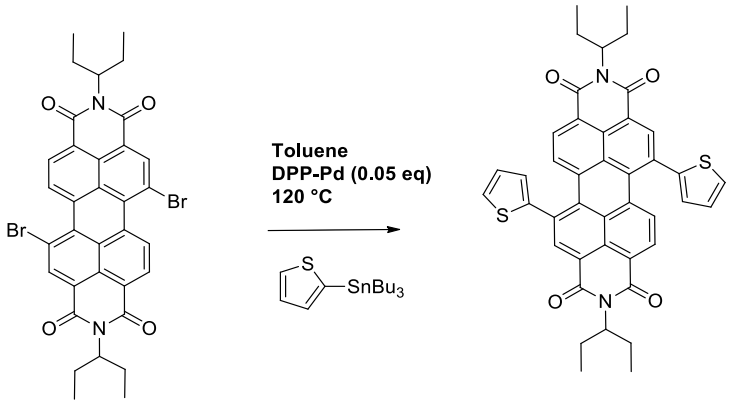


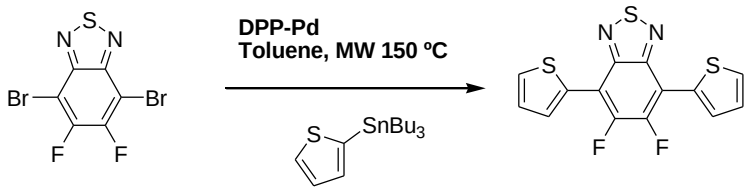
Figure S1.A) ^{1}H NMR spectra of the products obtained after each recrystallization. **B)** Isolated red needle-like crystals of **PDI-EP$_2$-Br$_2$** after 3 sequential CH_2Cl_2/MeOH layering recrystallizations.



Scheme S13 – Experimental procedure for the Synthesis of **PDI-EP$_2$-Th$_2$**

Synthesis of 1,7-dithienyl-N,N-bis-1-ethylpropyl-perylene-1,4,5,8-tetracarboxylic diimide (PDI-EP$_2$-Th$_2$): A 10-20 mL glass vial was loaded on the bench top with 1,7 dibromo-N,N' bis-ethylpropyl-perylene-3,4,9,10-tetracarboxylic-diimide (**PDA-Br$_2$-EP$_2$**, 300 mg 0.44 mmol), 2-tributylstannyl thiophene (352 mg, 0.872 mmol), Pd-DPP (87 mg, 0.022 mmol) and a stir bar. Toluene ~10 mL was used as a solvent. The reaction vial was sealed using a Teflon® cap and heated to 120-130 °C for 1 hour in an oil bath. After the reaction period, the reaction was diluted with 200 mL CH_2Cl_2 and slurried in 200 mL of a 1:1 (v:v) mixture of K_2CO_3:SiO_2 and then filtered through a glass frit. The organic phase was dried over $MgSO_4$, filtered and the solvent removed under reduced pressure using a rotary evaporator. Following the removal of solvent from the product fraction, methanol/water (1:1) was added to the solid product and it was collected via filtration using a Buchner funnel as a purple solid. The purple solid was recrystallized once using a CH_2Cl_2/methanol layering technique, where the product was taken up in a minimal amount

of CH_2Cl_2, methanol was carefully layered on top and the recrystallization vessel was set in the fridge overnight, yielding dark purple crystals. The crystals were filtered using a Buchner funnel and washed with methanol to yield pure 1,7- dithienyl-N,N-bis-ethylpropyl perylene. **Yield:** 81% (246 mg). **^{1}H NMR ($CDCl_3$):** δ 8.67 (s, 2H); 8.23 (d, 2H); 8.08 (d, 2H); 7.50 (dd, 2H, $^3J_{H-H}$ = 5 Hz, 1 Hz); 7.32 (dd, 2H, $^3J_{H-H}$ = 4 Hz , 1 Hz); 7.19 (dd, 4H, $^3J_{H-H}$ = 5 Hz, 3 Hz); 5.07 (m, 4H); 2.30-2.19 (m, 4H); 1.95-1.86 (m, 4H); 0.91 (t, 12H, $^3J_{H-H}$ = 7 Hz).



Scheme S14 – Experimental procedure for the synthesis of **M7.**

Synthesis of 4,7-dithio-5,6-dibromo-2,1,3-benzothiadiazole (Th$_2$-F$_2$BTD A 10-20 mL glass vial was loaded on the bench top with 5,6 difluoro-4,7-dibromo-2,1,3-benzothiadiazole (**Br$_2$-F$_2$BT**, 500 mg, 1.52 mmol), 2-tributylstannyl thiophene (1.13 g, 3.03 mmol), Pd-DPP (122 mg, 0.03 mmol) and a stir bar. Toluene (~10 mL) was added as a solvent. The reaction mixture was sealed using a Teflon® cap and heated to 180 °C for 45 minutes using microwave irradiation. After the reaction period, the reaction was diluted with ~100 mL of CH_2Cl_2 and slurried with ~200 mL of a 1:1 (v:v) mixture of K_2CO_3 and SiO_2 and then filtered through a medium porosity glass frit. The solvent was removed under reduced pressure using a rotary evaporator. Following removal of the solvent from the product, a mixture of methanol/water (1:1) was added to the solid product and it was filtered to give the product as an orange solid. The orange solid was recrystallized from hot iso-propanol and filtered using a Buchner funnel to isolate the product as a bright orange solid. **Yield:** 86% (436 mg). Spectroscopic data match those reported previously in the literature.[9]

3. Solution ^{1}H, ^{13}C & ^{19}F NMR Spectra

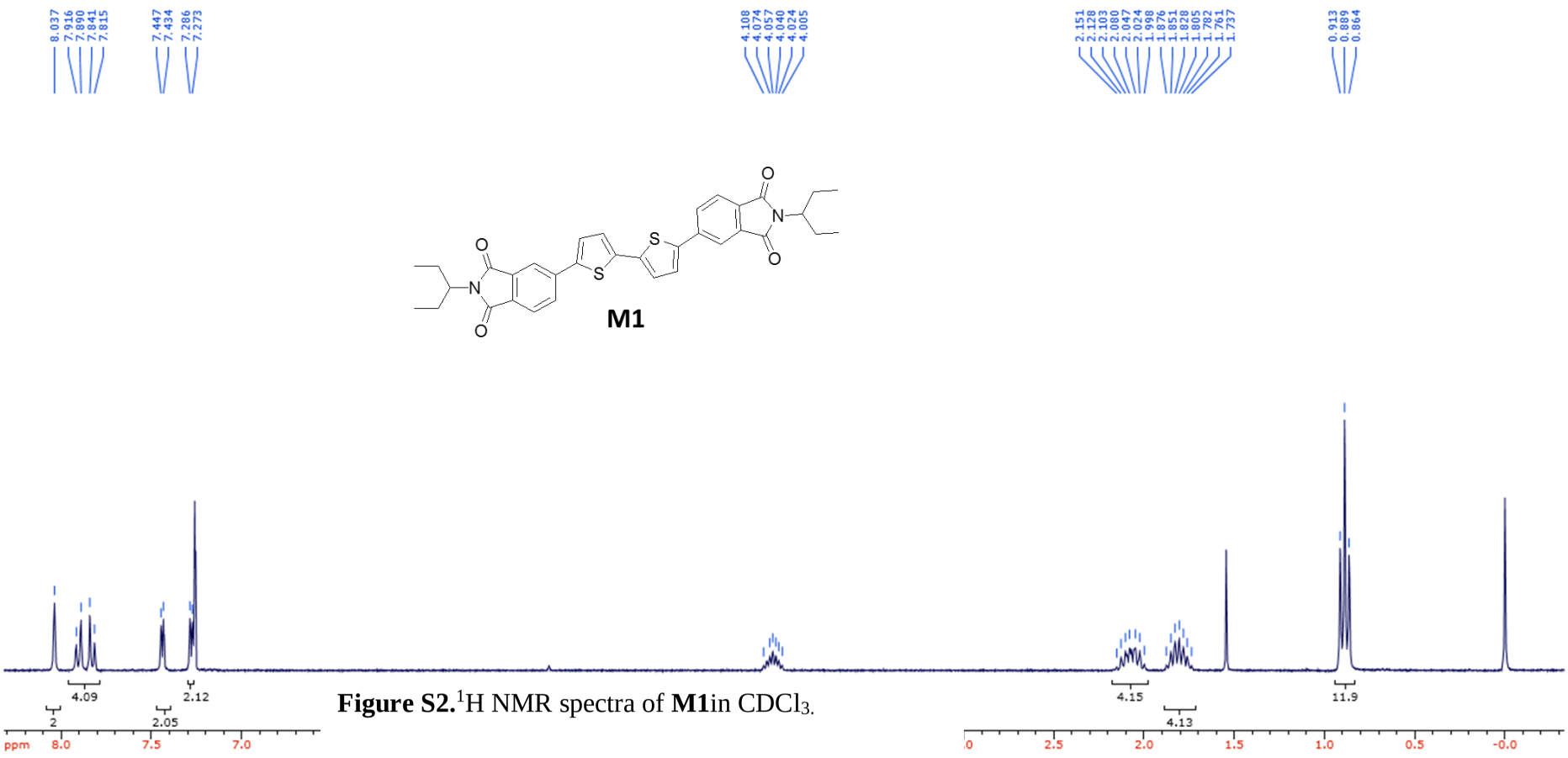


Figure S2. ^{1}H NMR spectra of **M1**in $CDCl_3$.

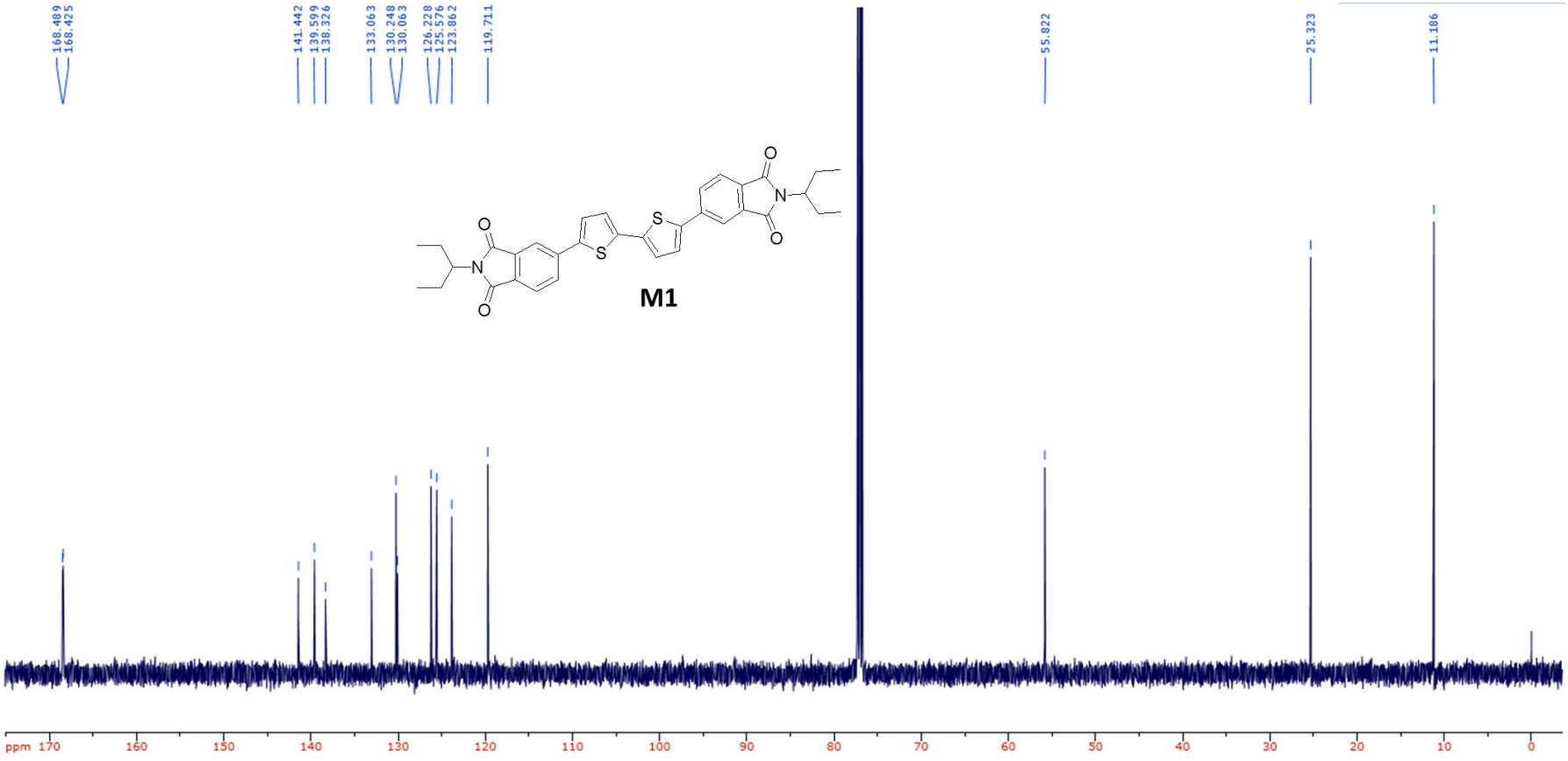


Figure S3. ^{13}C NMR spectra of **M1** in $CDCl_3$

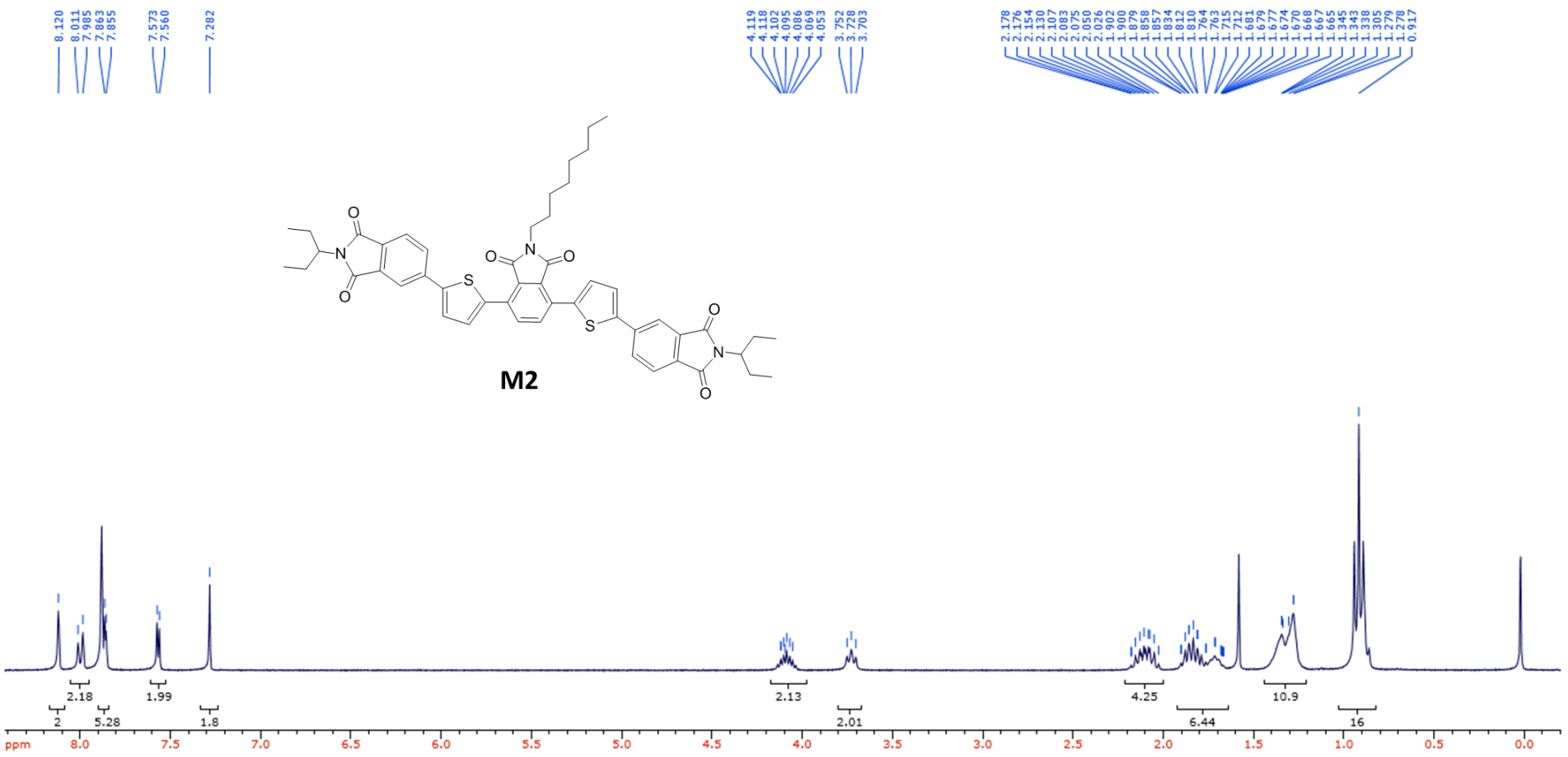


Figure S4.[1]H NMR spectra of **M2**in $CDCl_3$.

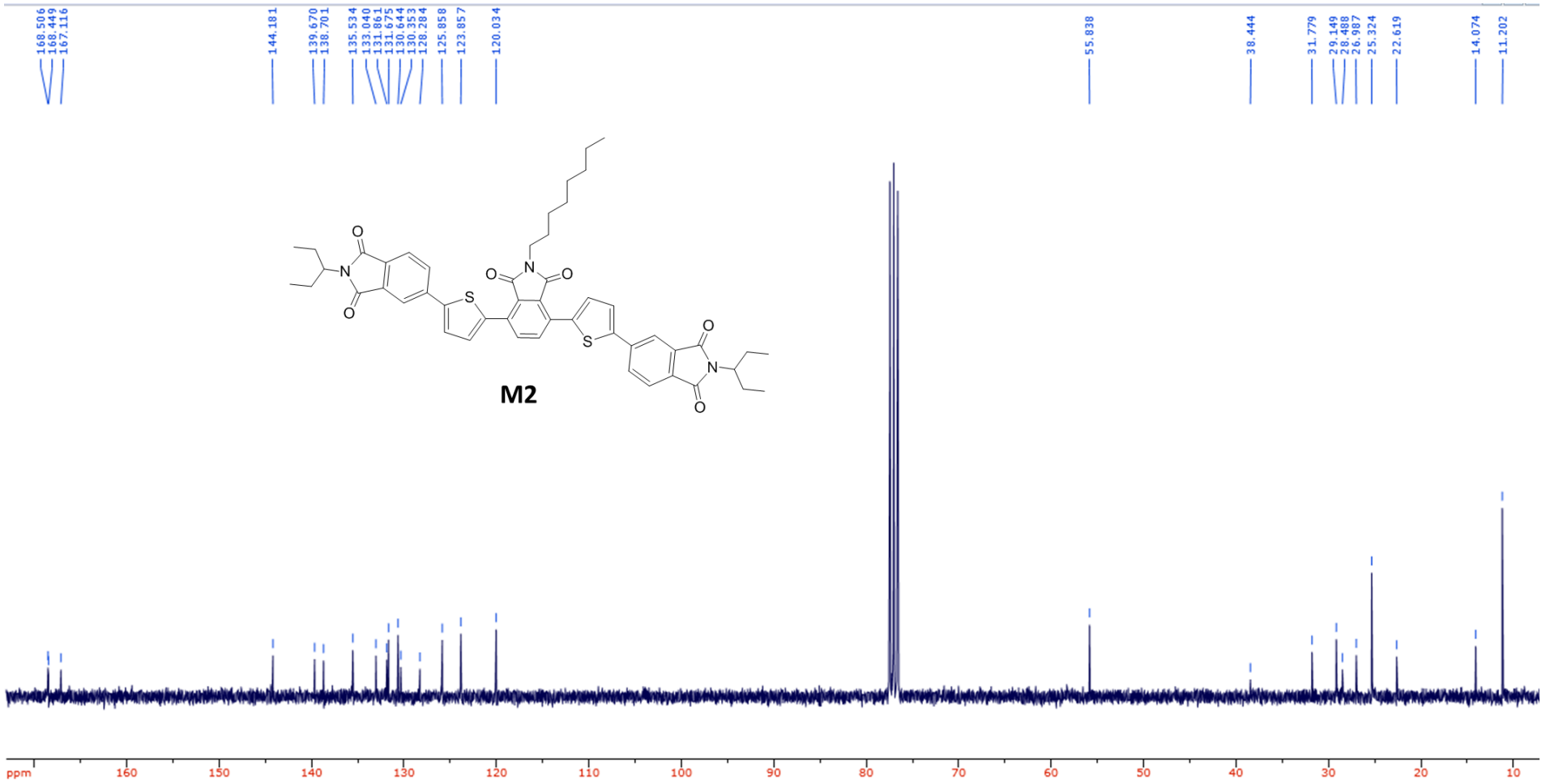


Figure S5. ^{13}C NMR spectra of **M2** in $CDCl_3$.

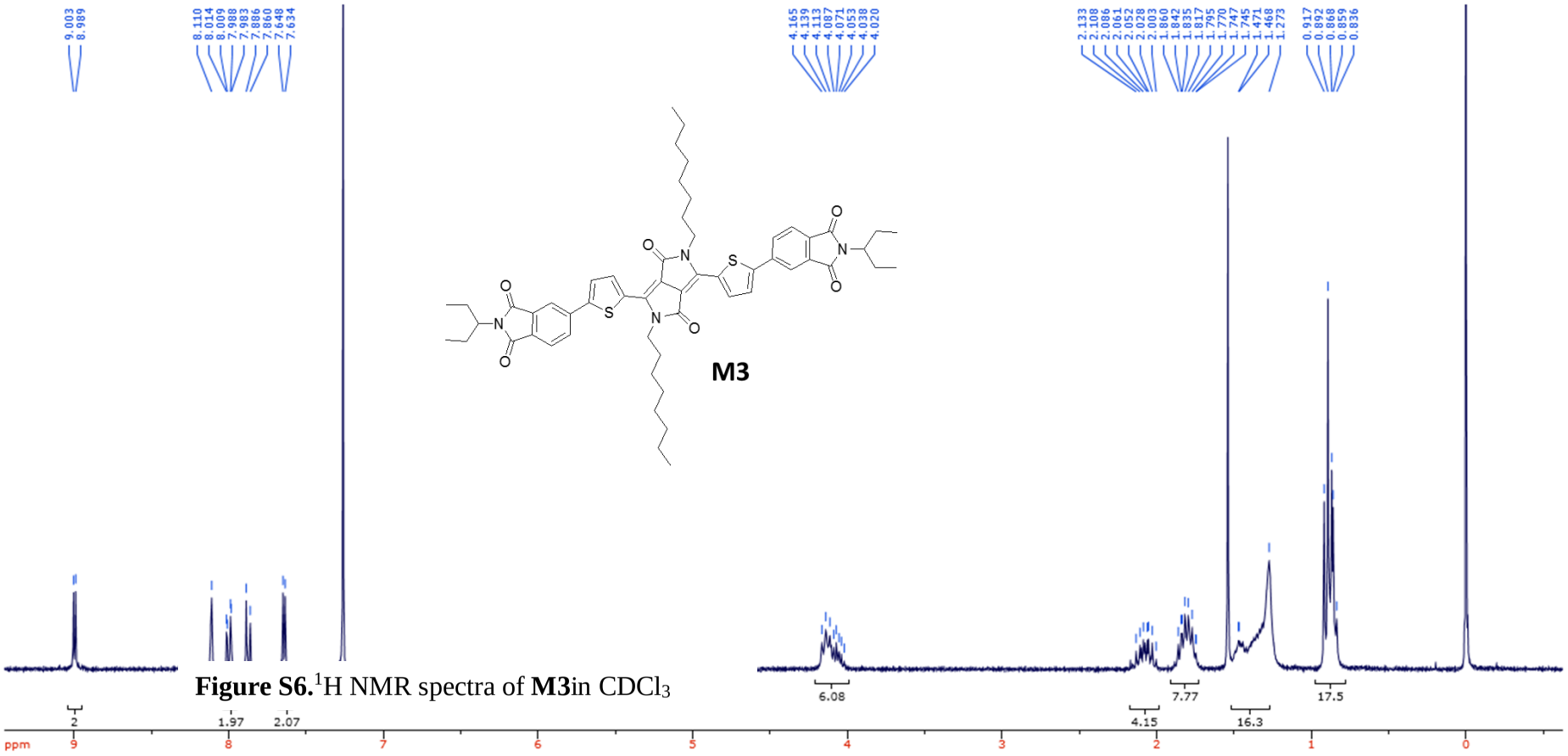


Figure S6. ^{1}H NMR spectra of **M3**in $CDCl_3$

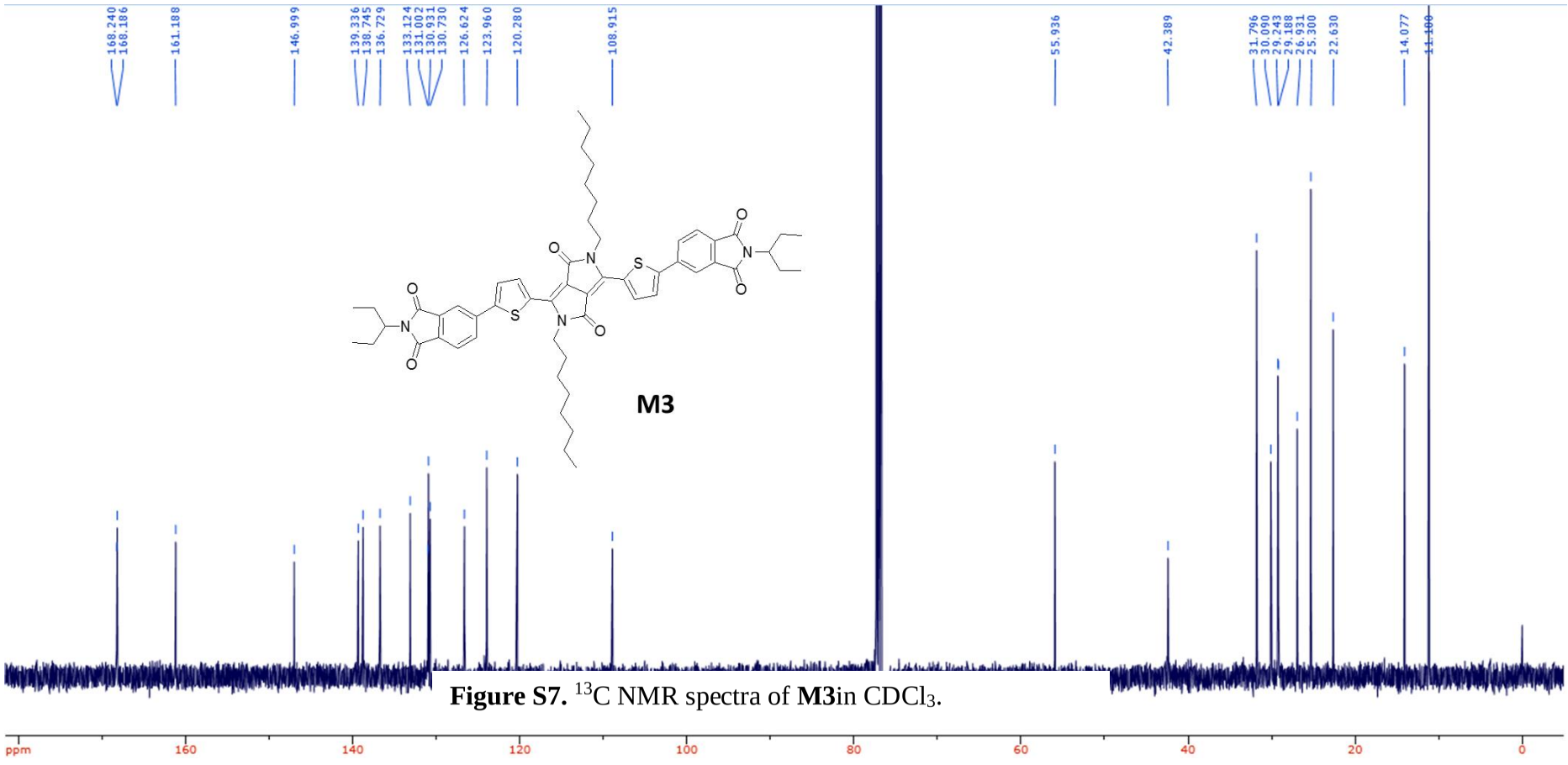


Figure S7. ^{13}C NMR spectra of **M3**in $CDCl_3$.

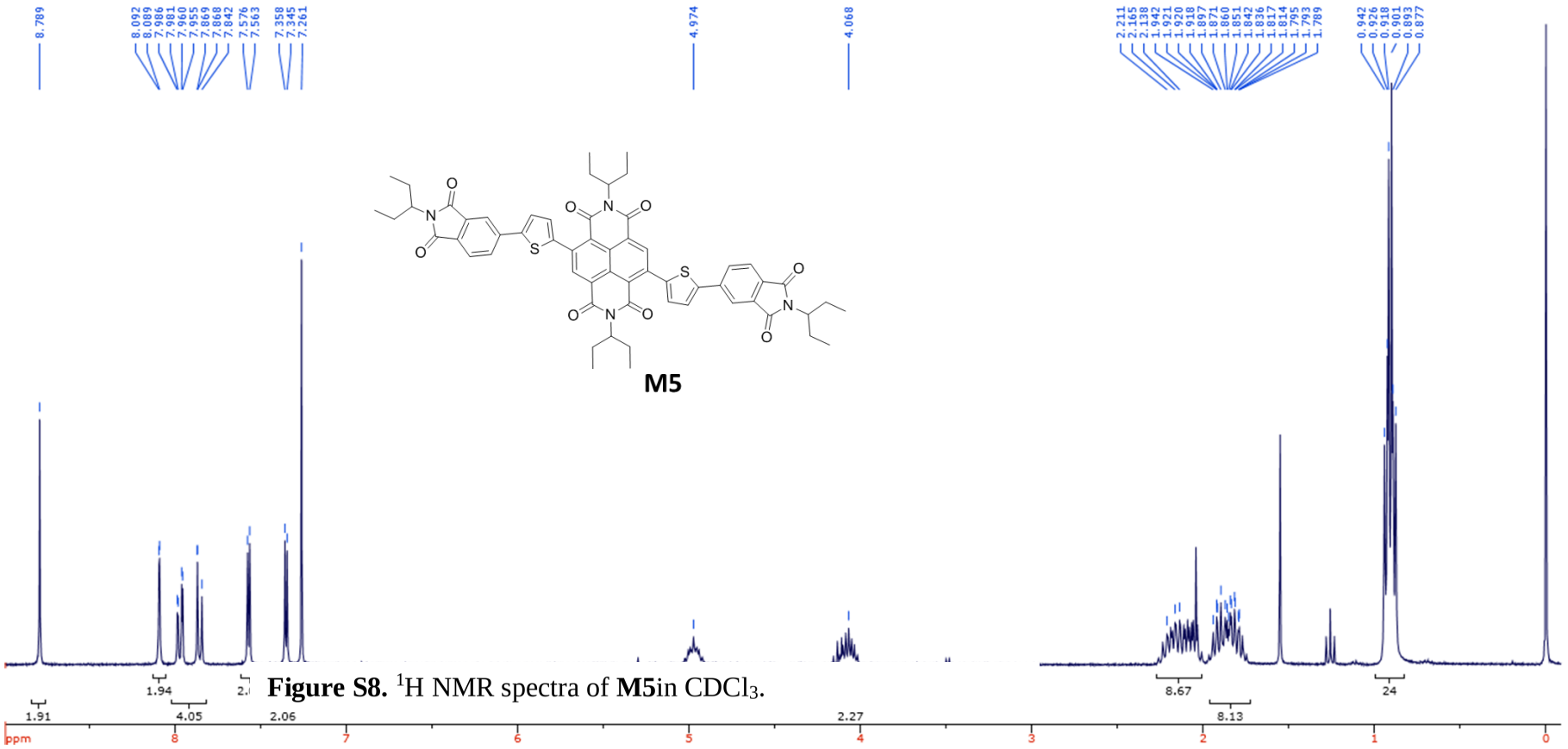


Figure S8. ^{1}H NMR spectra of **M5**in $CDCl_3$.

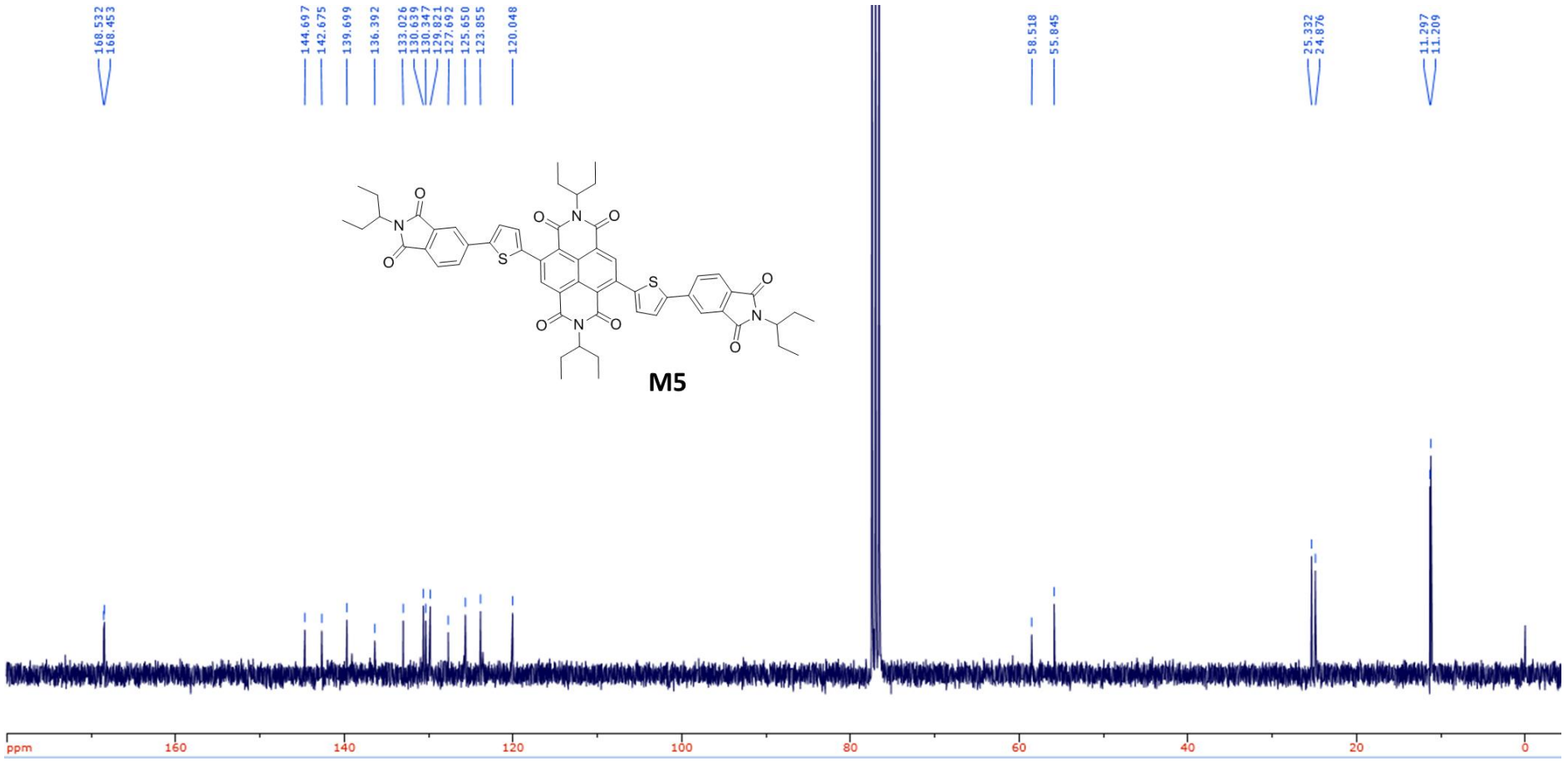


Figure S9. ^{13}C NMR spectra of **M5** in $CDCl_3$.

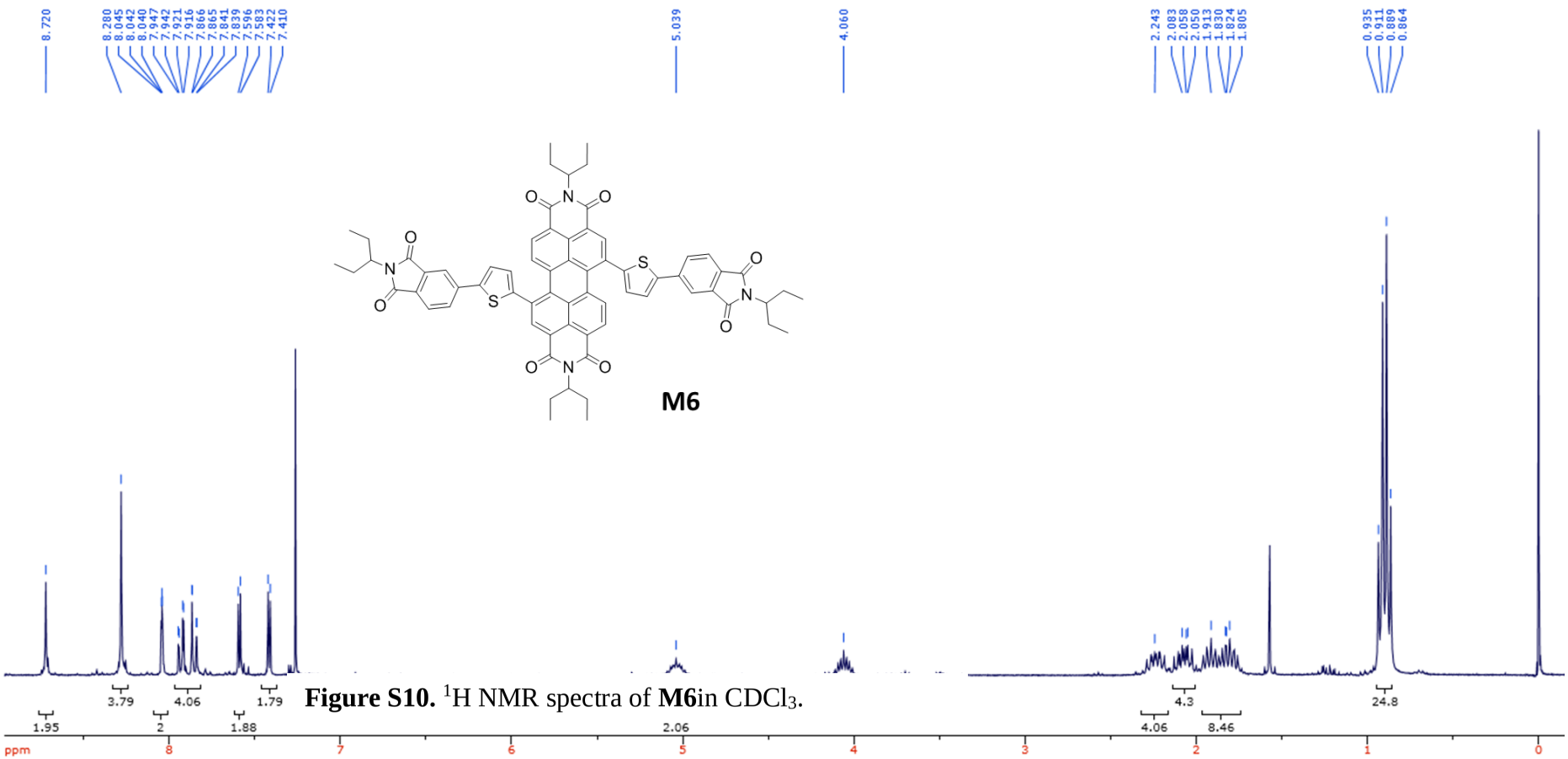


Figure S10. ^{1}H NMR spectra of **M6**in $CDCl_3$.

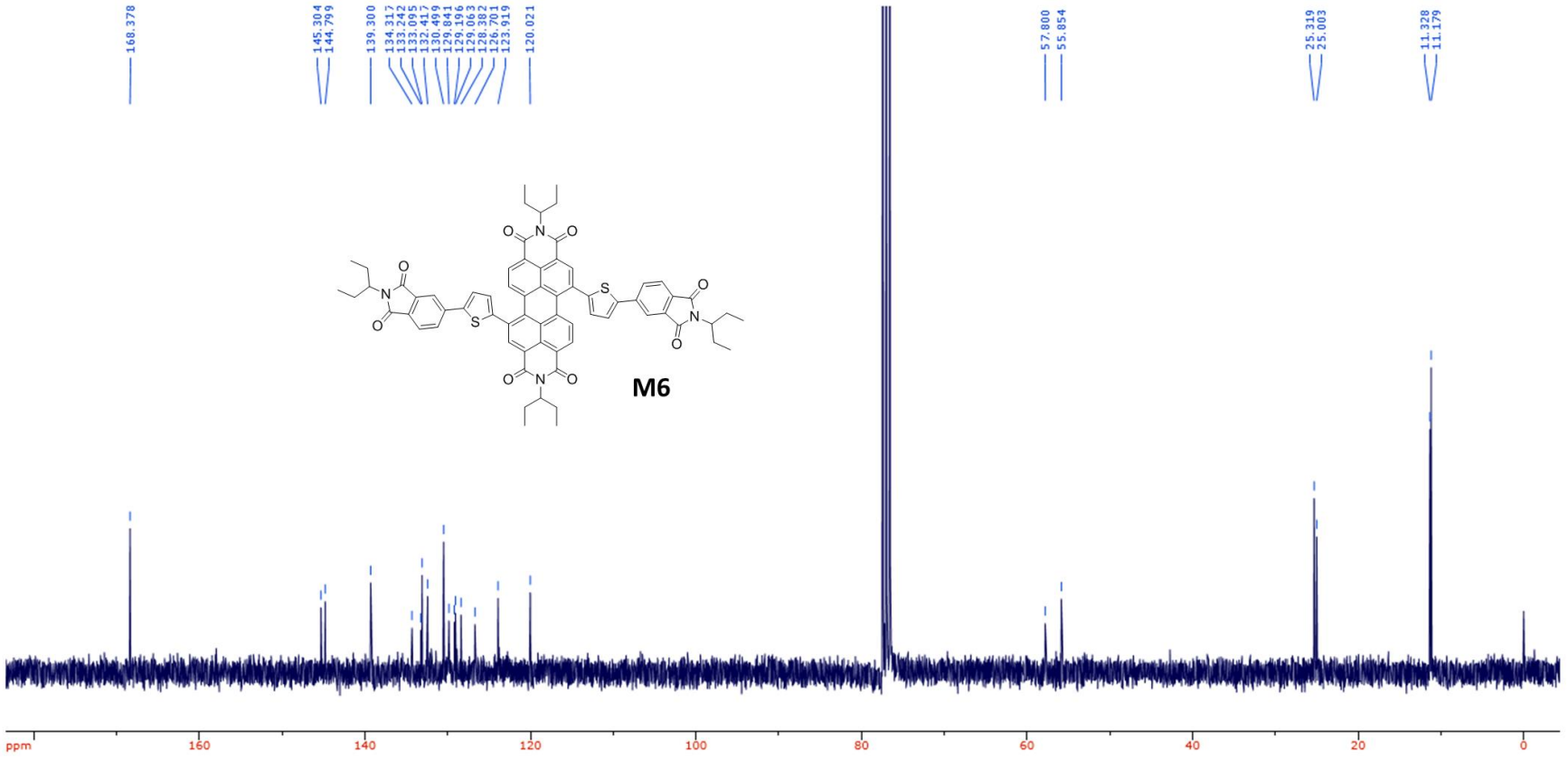


Figure S11. ^{13}C NMR spectra of **M6**in $CDCl_3$.

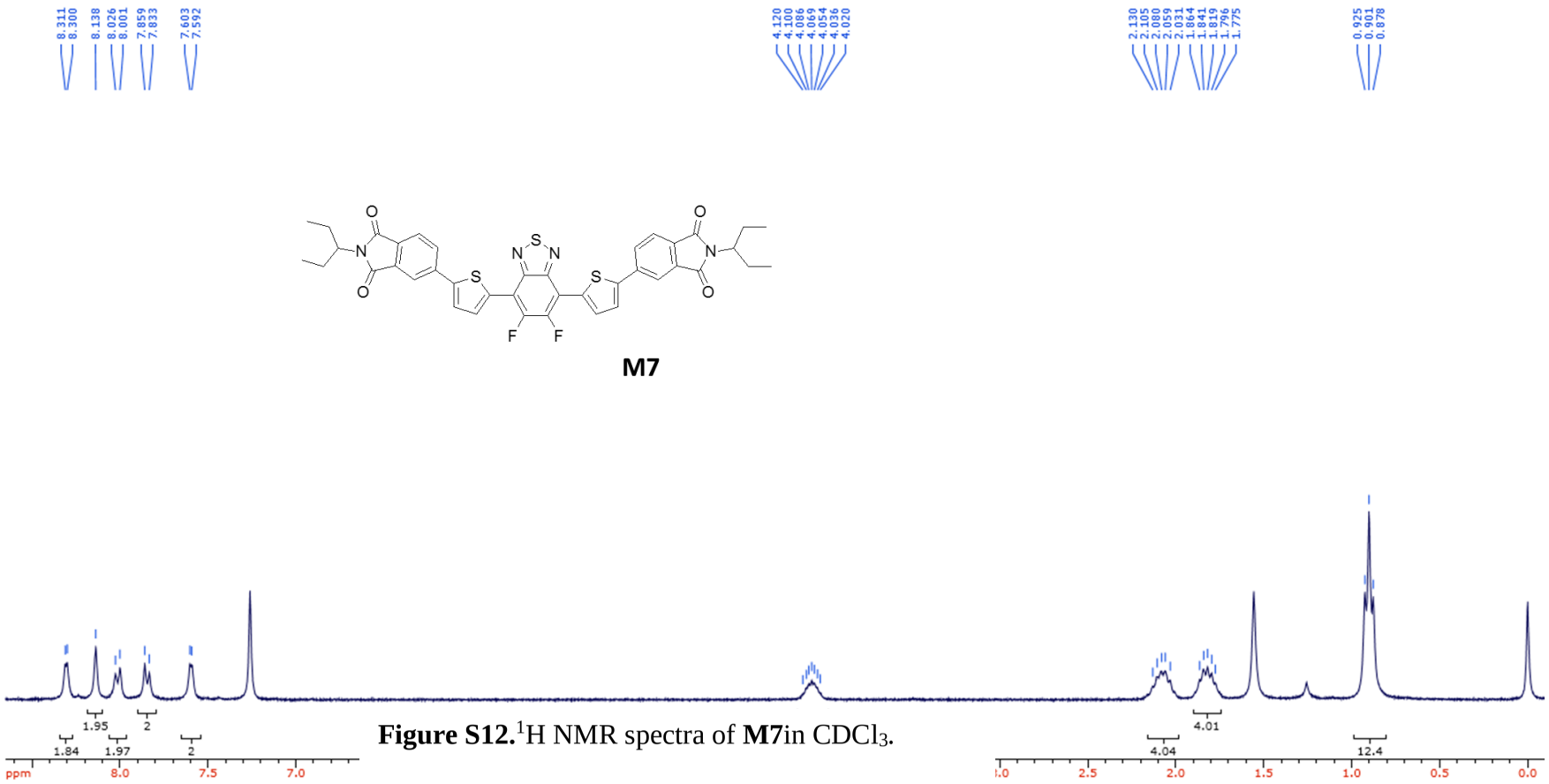


Figure S12.[1]H NMR spectra of **M7**in $CDCl_3$.

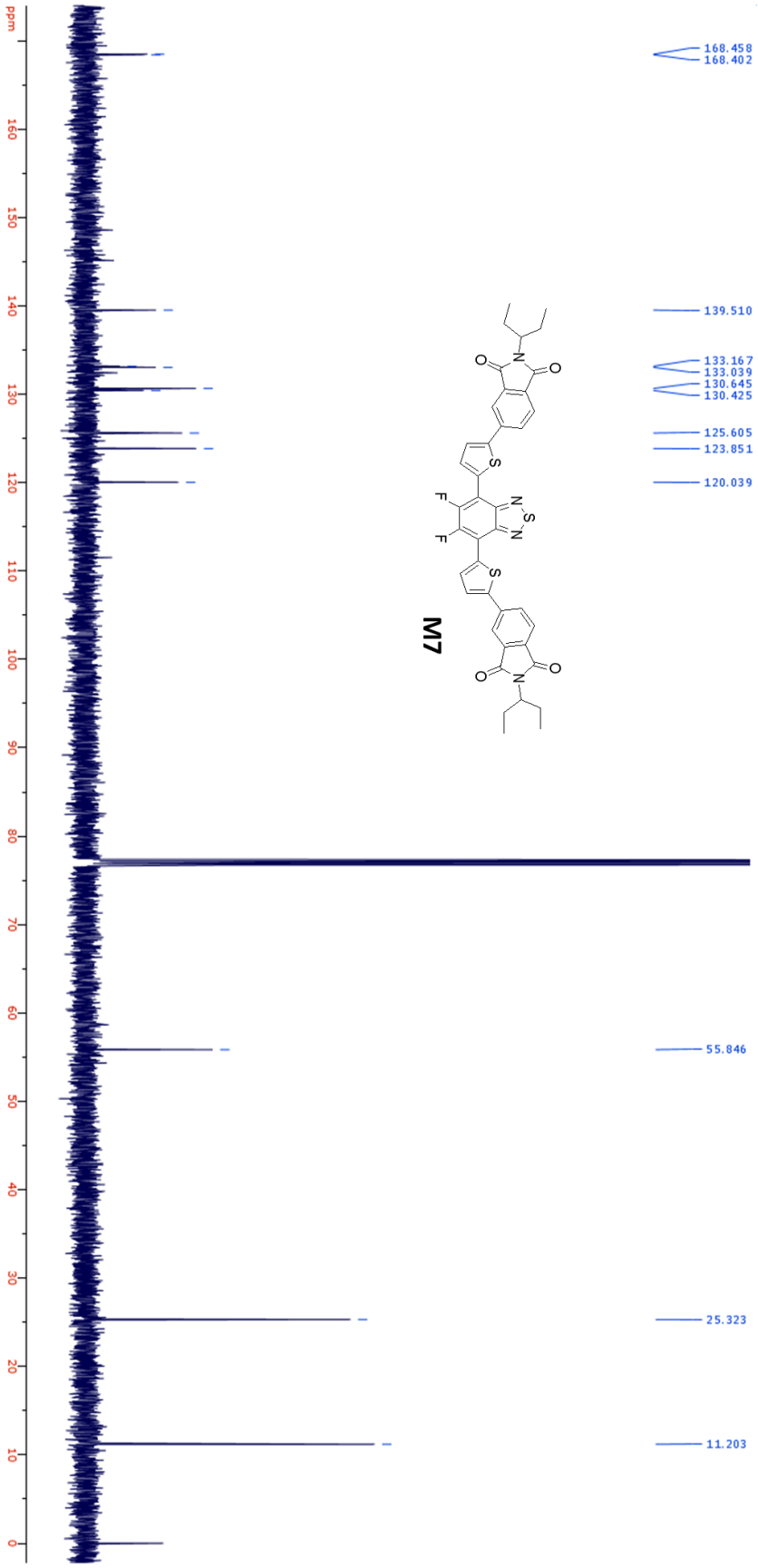


Figure S13. ^{13}C NMR spectra of **M7** in $CDCl_3$.

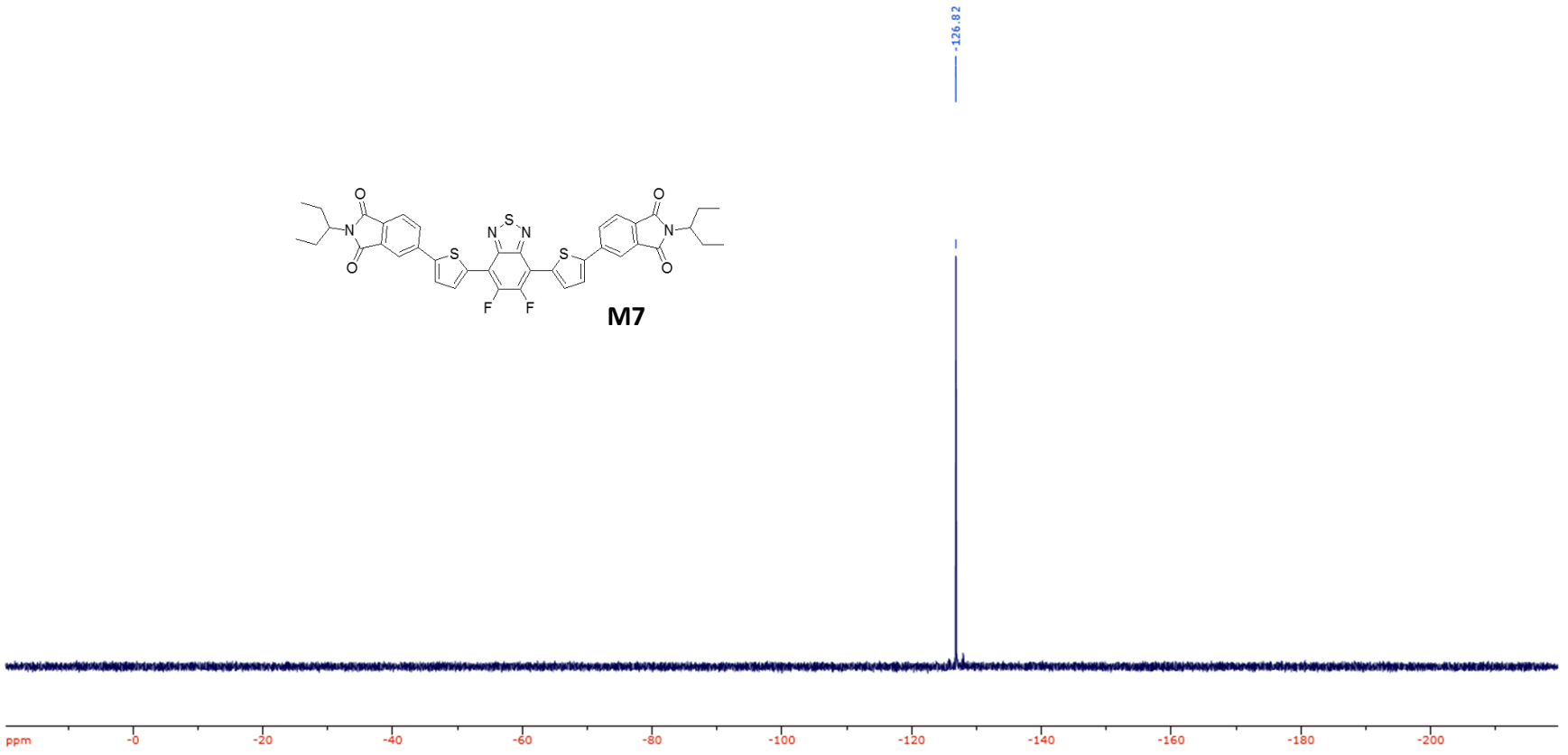


Figure S13. ^{19}F NMR spectra of **M7**in $CDCl_3$.

4. Mass Spectrometry

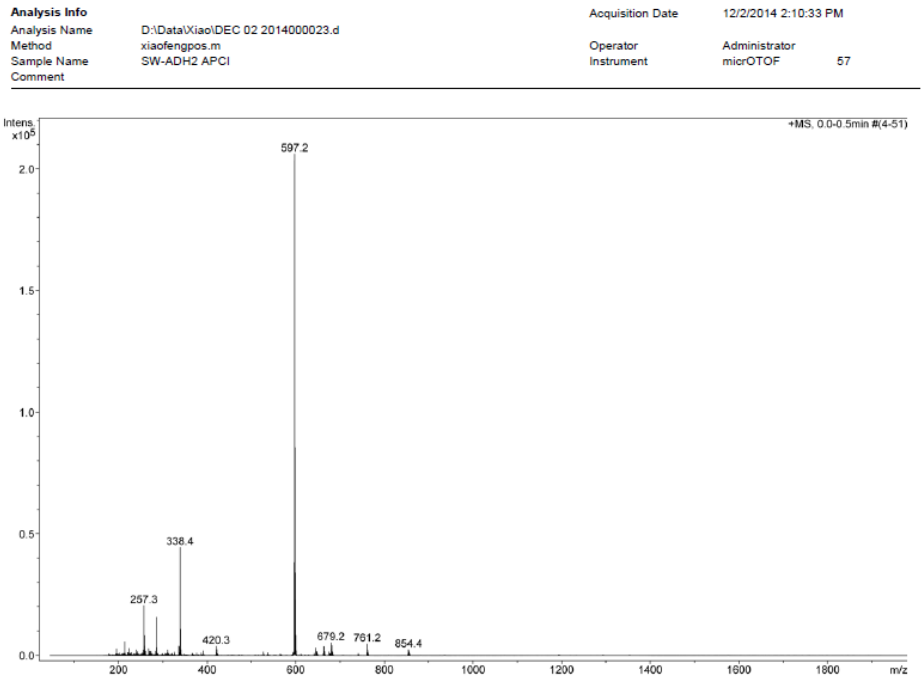


Figure S15. Mass Spectrum (APCI-TOF) obtained from **M1.**

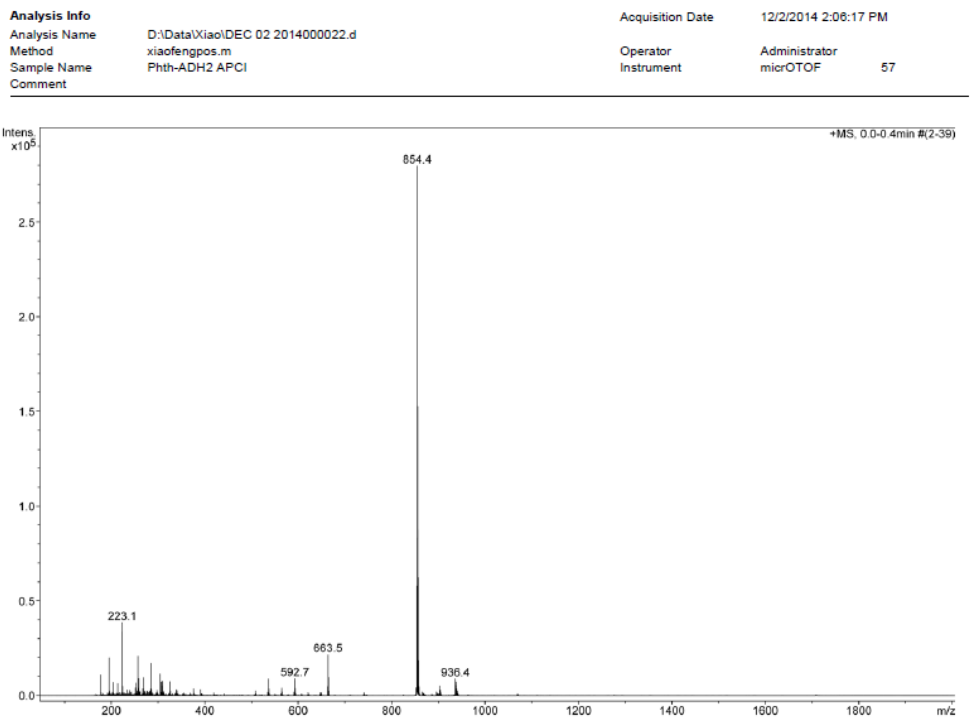


Figure S16. Mass Spectrum (APCI-TOF) obtained from **M2.**

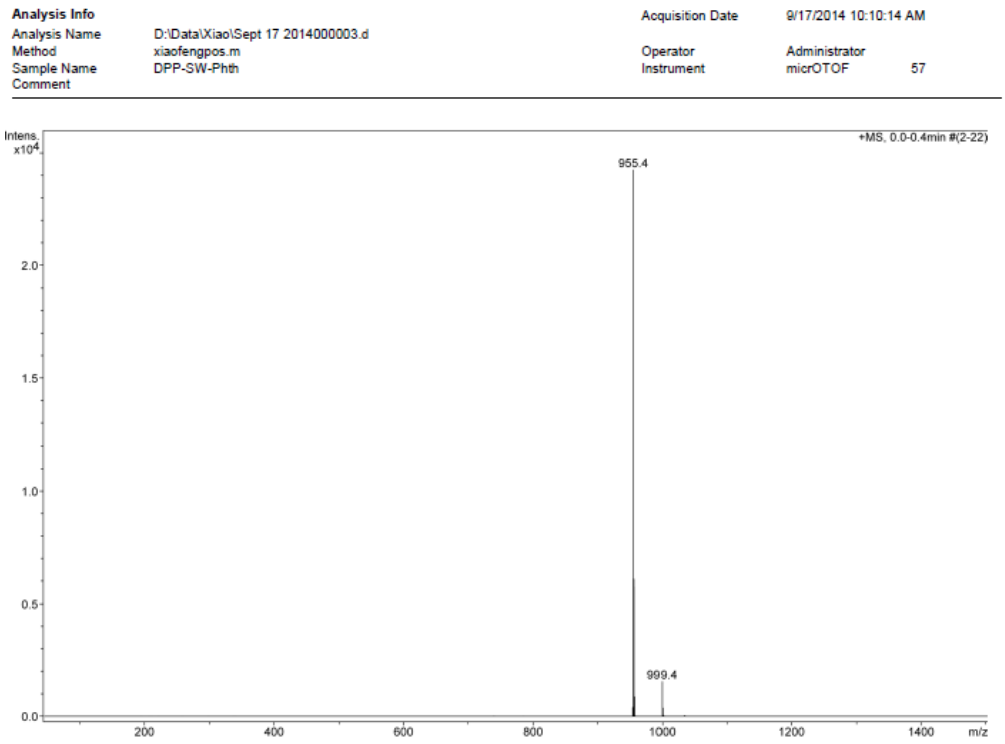


Figure S17. Mass Spectrum (APCI-TOF) obtained from**M3**

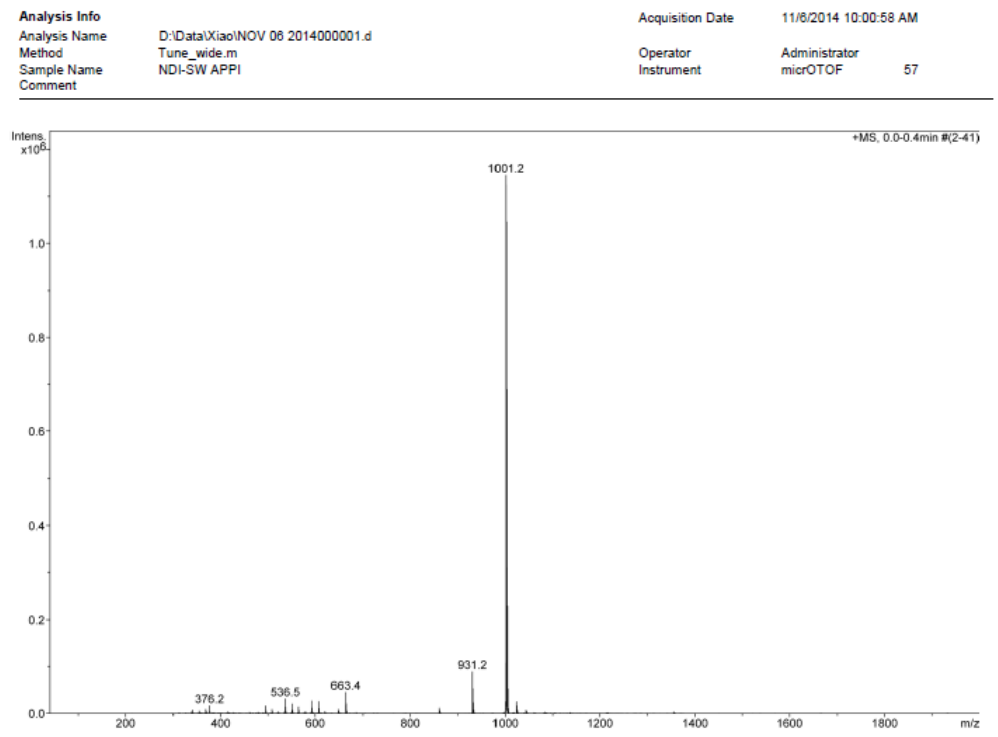


Figure S18. Mass Spectrum (APPI-TOF) obtained from **M5.**

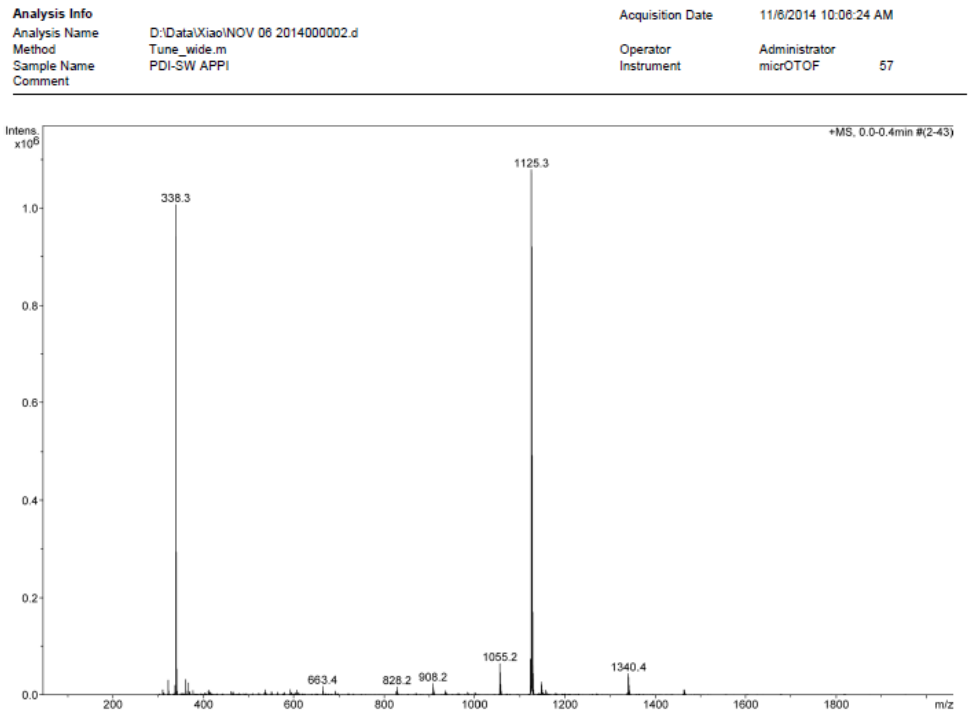


Figure S19. Mass Spectrum (APPI-TOF) obtained from **M6.**

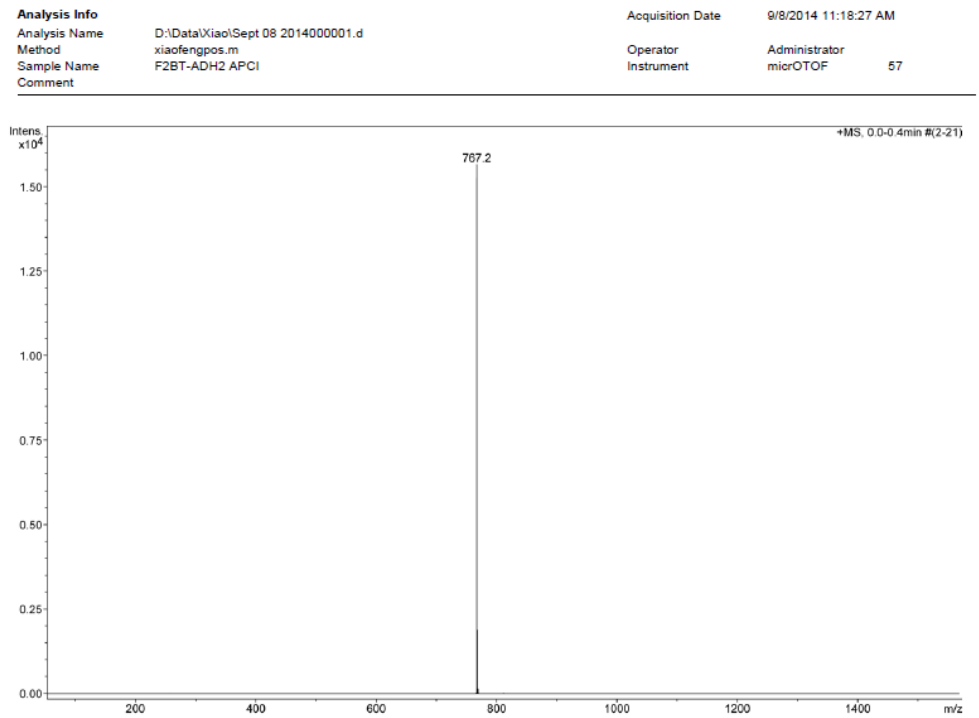


Figure S20. Mass Spectrum (APCI-TOF) obtained from **M7.**

5. Differential Scanning Calorimitrey.

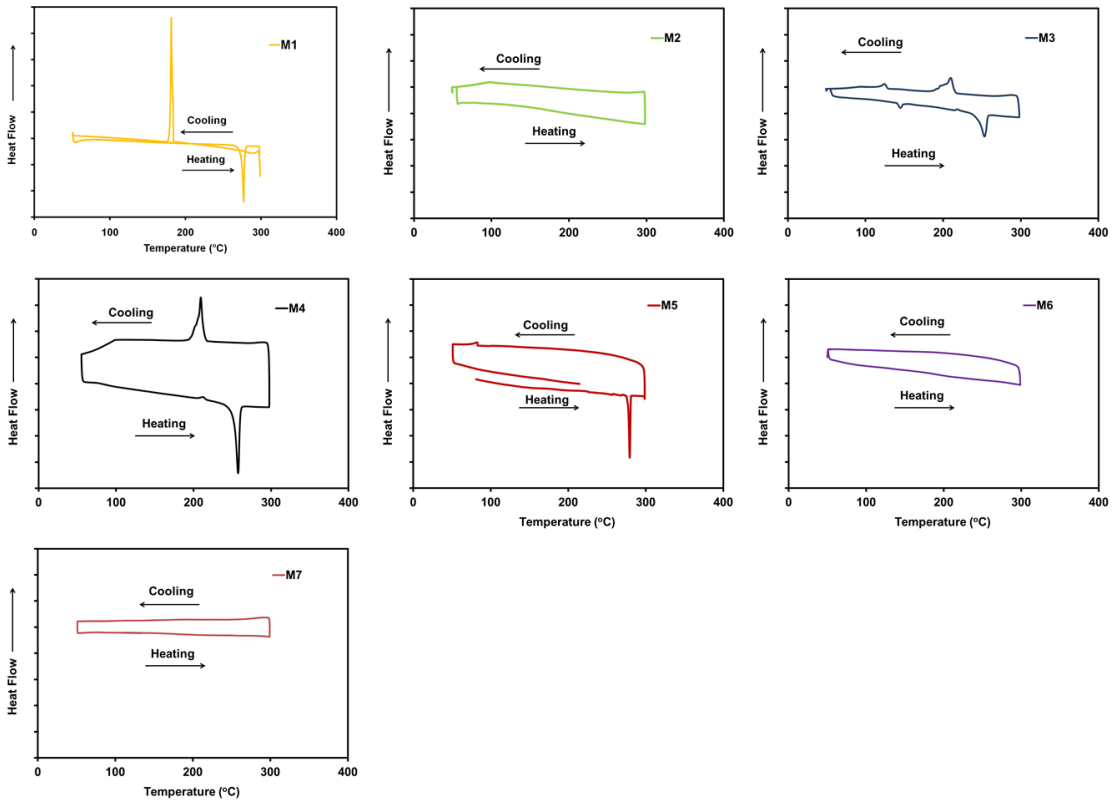


Figure S21. Differential Scanning Calorimitrey plots of **M1**-**M7**, samples were heated from 50 °C to 300 °C for 3 cycles under air (**M1** was run in air and under N_2 with no significant differences, N_2 trace shown)

6. Cyclic Voltammetry

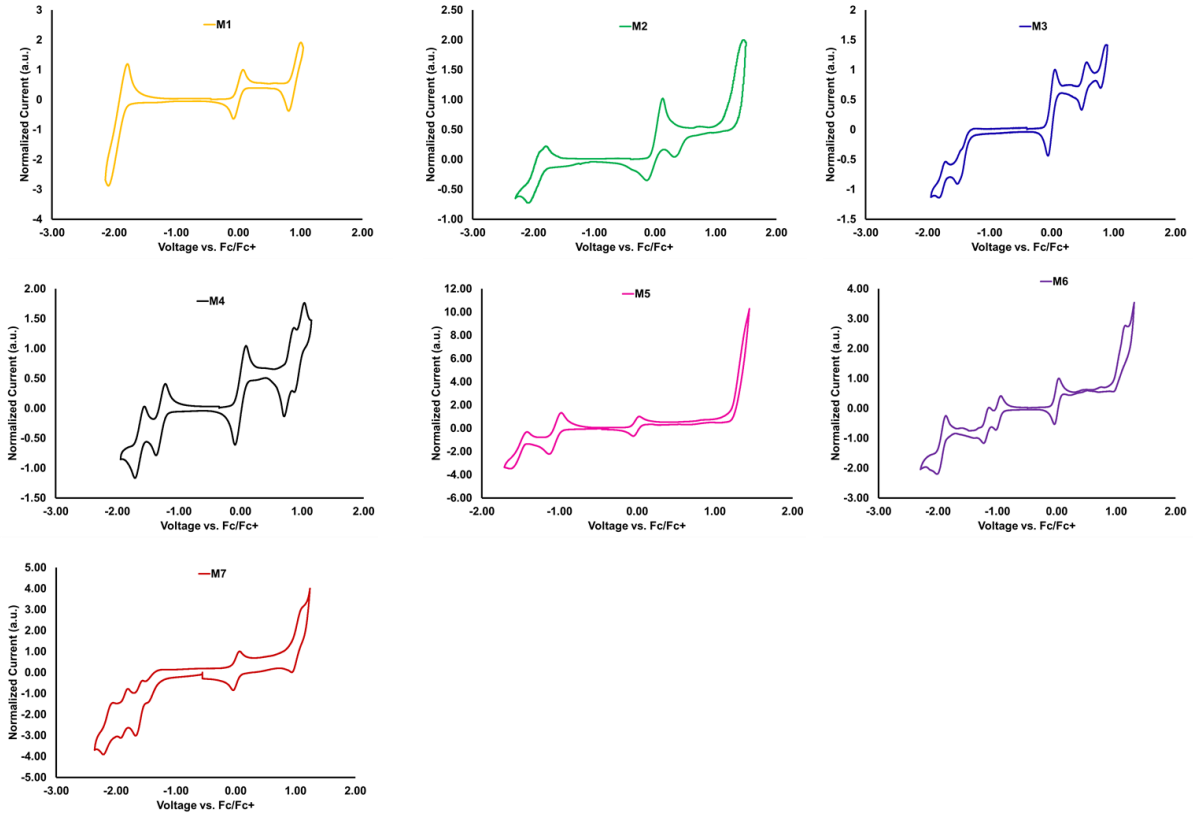


Figure S22. Cyclic voltammetry plots of **M1-M7** in CH_2Cl_2 solution.

Table S2. Tabulated oxidation and reduction potentials for **M1-M7**.

	Onset of Oxidation (V)	Onset of Reduction (V)
M1	0.8	-1.77
M2	1.12	-1.82
M3	0.43	-1.36
M4	0.67	-1.16
M5	1.12	-0.98
M6	0.89	-0.90
M7	0.86	-1.51

7. Ultraviolet Photoelectron Spectroscopy

1 mg mL^{-1} and 2mg mL^{-1} solutions of each compound were spin coated from chlorobenzene at 5000 rpm, to produce films of two different thicknesses on top of polished float glass coated with 80 nm of ITO (Delta Technologies). All films were prepared in air and immediately transferred to the UPS chamber, where they were held under high vacuum for several hours prior to measuring. The UPS analysis chamber was equipped with a hemispherical energy analyzer (Phoibos 150) and was maintained at a base pressure of 10^{-10} mbar. The UPS measurements were carried out using a He I ($h\nu$ = 21.22 eV) source. A sample bias of -3 V was used to measure the onset of photoemission. Reproducibility of UPS spectra between the two film thicknesses was confirmed for each compound.

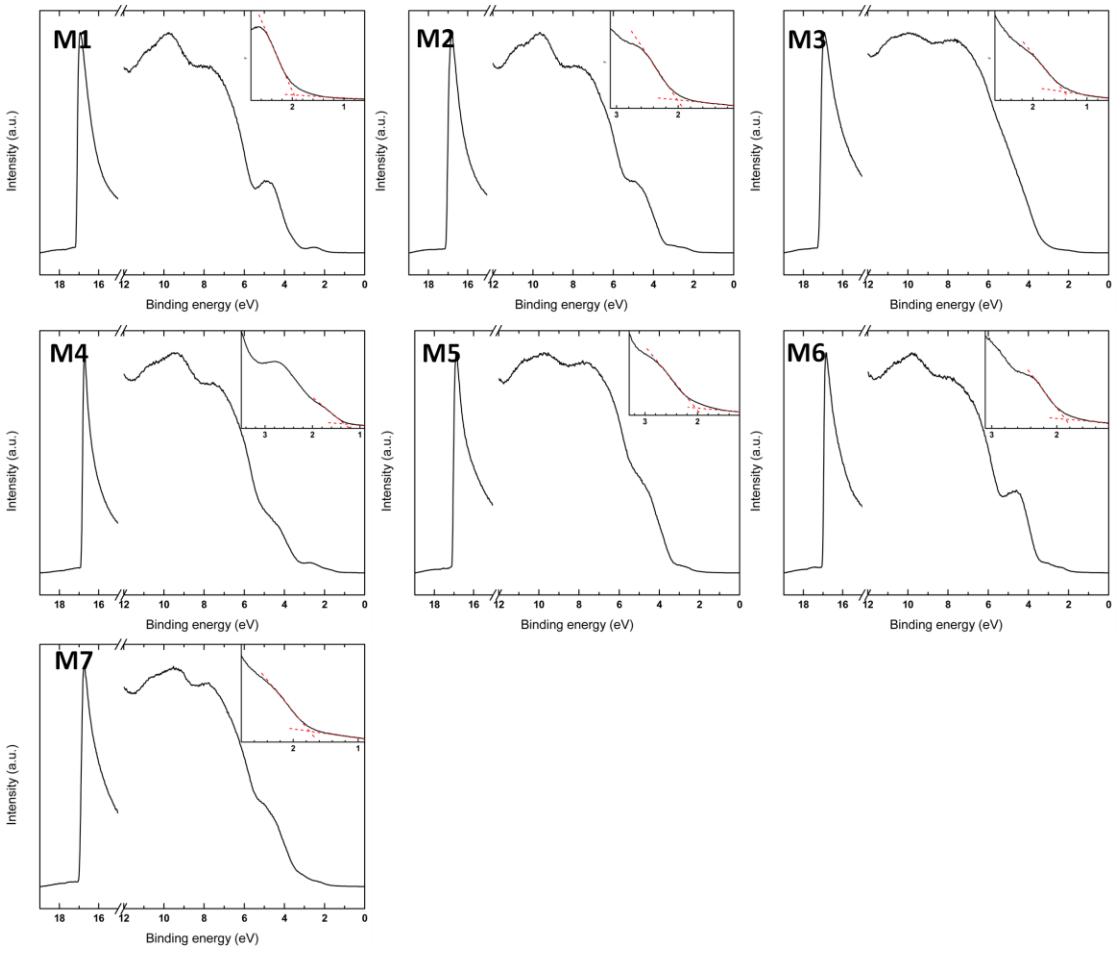


Figure S23. UPS He I spectra (*hv* = 21.22 eV) of molecules **M1** – **M7**.

8. DFT Calculations

Table S3. Dihedral angles from the optimized geometries of **M1**-**M7**. Taken from thiophene-thiophene S-C-C-S angles (S-C-C-C) and thiophene-core angles S-C-C-C. Angles in (°).

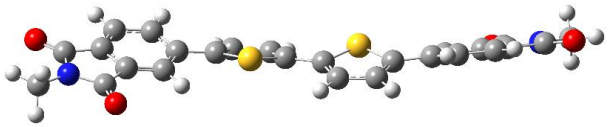
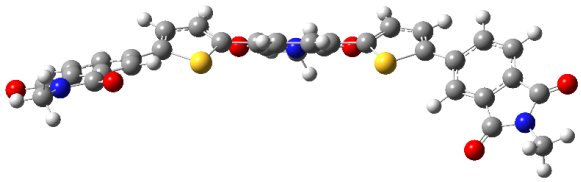
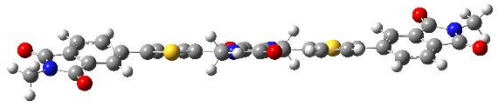
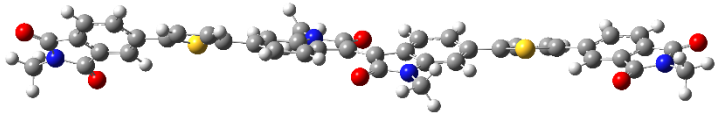
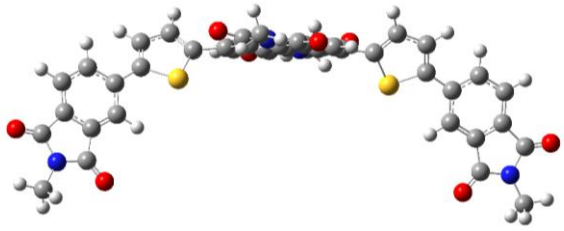
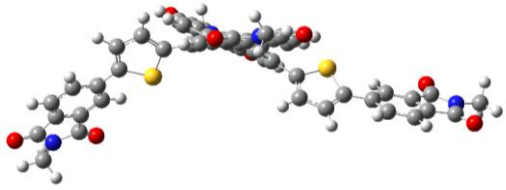
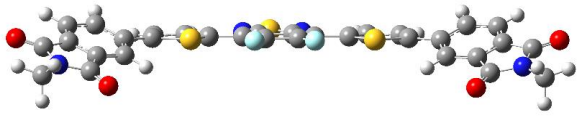
	Angle (thiophene)	**Angle (thiophene-core)**	
M1	-157.9 (22.1)		
M2	-0.04 (-173.4)	-32.9	
M3	-178.6	-179.4	
M4	172.8	21.1	
M5	62.2 (-112.5)	-58.1	
M6	-74.8	-121.7	
M7	1.1	0.3	

Table S4. Calculated electronic energy levels of optimized structures of M1-M7 with B3LYP/6-311+G(d). All energies reported in eV**.**

	M1	**M2**	**M3**	**M4***	**M5**	**M6**	**M7**
LUMO+6	-0.372	-1.057	-0.894	-1.251	-1.703	-1.989	-1.083
LUMO+5	-0.776	-1.592	-1.371	-1.318	-1.892	-2.072	-1.422
LUMO+4	-1.389	-1.845	-1.746	-1.917	-2.138	-2.243	-1.858
LUMO+3	-1.745	-2.351	-2.074	-2.015	-2.283	-2.459	-2.078
LUMO+2	-2.176	-2.697	-2.616	-2.730	-2.746	-2.847	-2.736
LUMO+1	-2.696	-2.926	-2.863	-2.805	-2.769	-2.888	-2.742
LUMO	-2.979	-2.966	-3.420	-3.422	-3.939	-3.939	-3.468
HOMO	-6.029	-6.178	-5.529	-5.769	-6.453	-6.184	-6.016
HOMO-1	-7.228	-6.726	-6.991	-6.255	-6.599	-6.684	-6.849
HOMO-2	-7.595	-7.491	-7.072	-6.613	-7.442	-6.961	-7.563
HOMO-3	-7.719	-7.537	-7.296	-6.640	-7.467	-7.677	-7.581

***** Energies from B3LPY/6-311+G(d) single point energy calculation structure optimized with B3LPY/6-31G(d)

Table S5. Calculated electronic transitions for optimized structures of **M1**-**M7**.

	First excitation			
M1	456.60 nm f=1.0773 HOMO -> LUMO	417.33 nm f=0.0010 HOMO -> LUMO+1	362.70 nm f=0.3523 HOMO -> LUMO+2	
M2	450.50 nm f=0.0985 HOMO -> LUMO+1	436.54 nm f=1.1757 HOMO -> LUMO	319.90 nm f=0.1133 HOMO -> LUMO+4	
M3	628.39 nm f=1.2390 HOMO -> LUMO	521.47 nm f=0.0000 HOMO -> LUMO+1	384.25 nm f=0.5269 HOMO-1 -> LUMO	360.12 nm f=0.1795 HOMO -> LUMO+4
M4	596.09 nm f=1.3224 HOMO -> LUMO	458.80 nm f=0.7466 HOMO-2 -> LUMO	379.28 nm f=0.2115 HOMO-1 -> LUMO+1	
M5	604.47 nm f=0.2747 HOMO -> LUMO	378.69 nm f=0.5782 HOMO -> LUMO+2	376.16 nm f=0.2486 HOMO-1 -> LUMO	330.03 nm f=0.4170 HOMO -> LUMO+4
M6	638.55 nm f=0.3305 HOMO -> LUMO	465.82 nm f=0.2573 HOMO-1 -> LUMO	413.65 nm f=0.3759 HOMO -> LUMO+2	330.66 nm f=0.2779
M7	562.55 nm f=0.8513 HOMO -> LUMO	430.57 nm f=0.4740 HOMO -> LUMO+2	355.74 nm f=0.5031 HOMO -> LUMO+3	309.56 nm f=0.0187 HOMO-6 -> LUMO

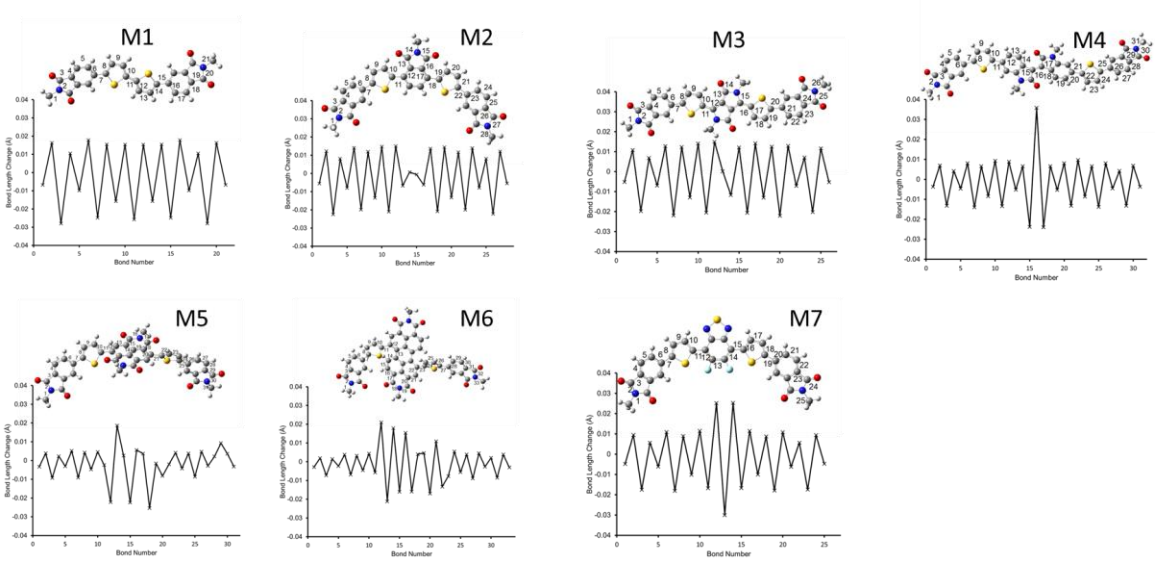


Figure S24. Plots showing changes in bond lengths upon reduction. Change in bond length with reduction was modeled with DFT using B3LYP with the 6-31G(d) basis set. The geometry was optimized with the complexes with a -1 charge doublet state.

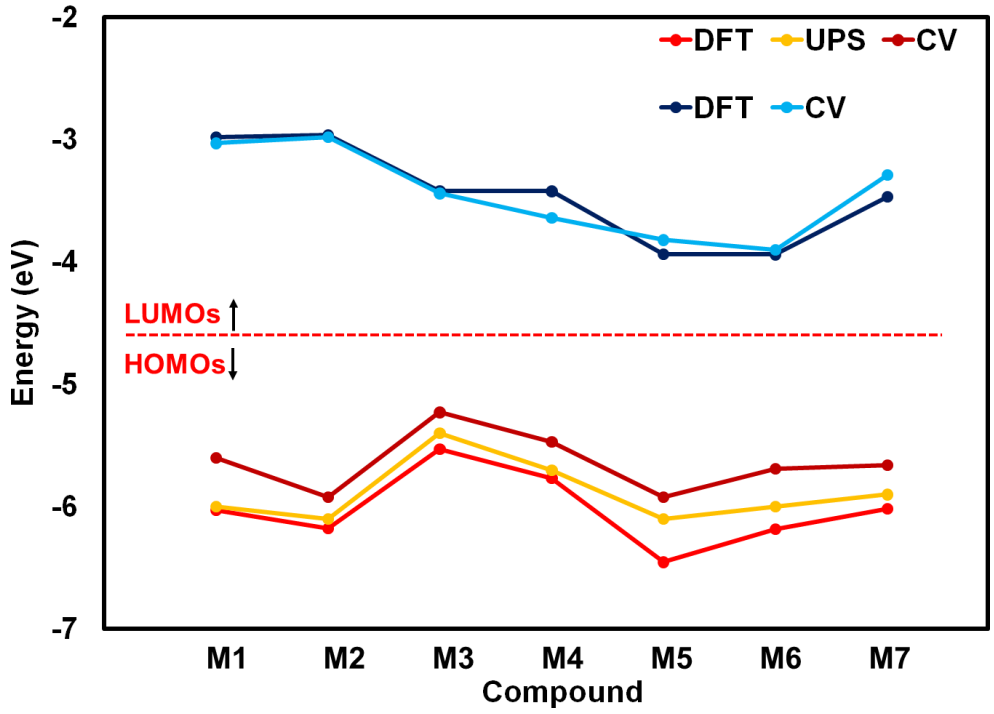
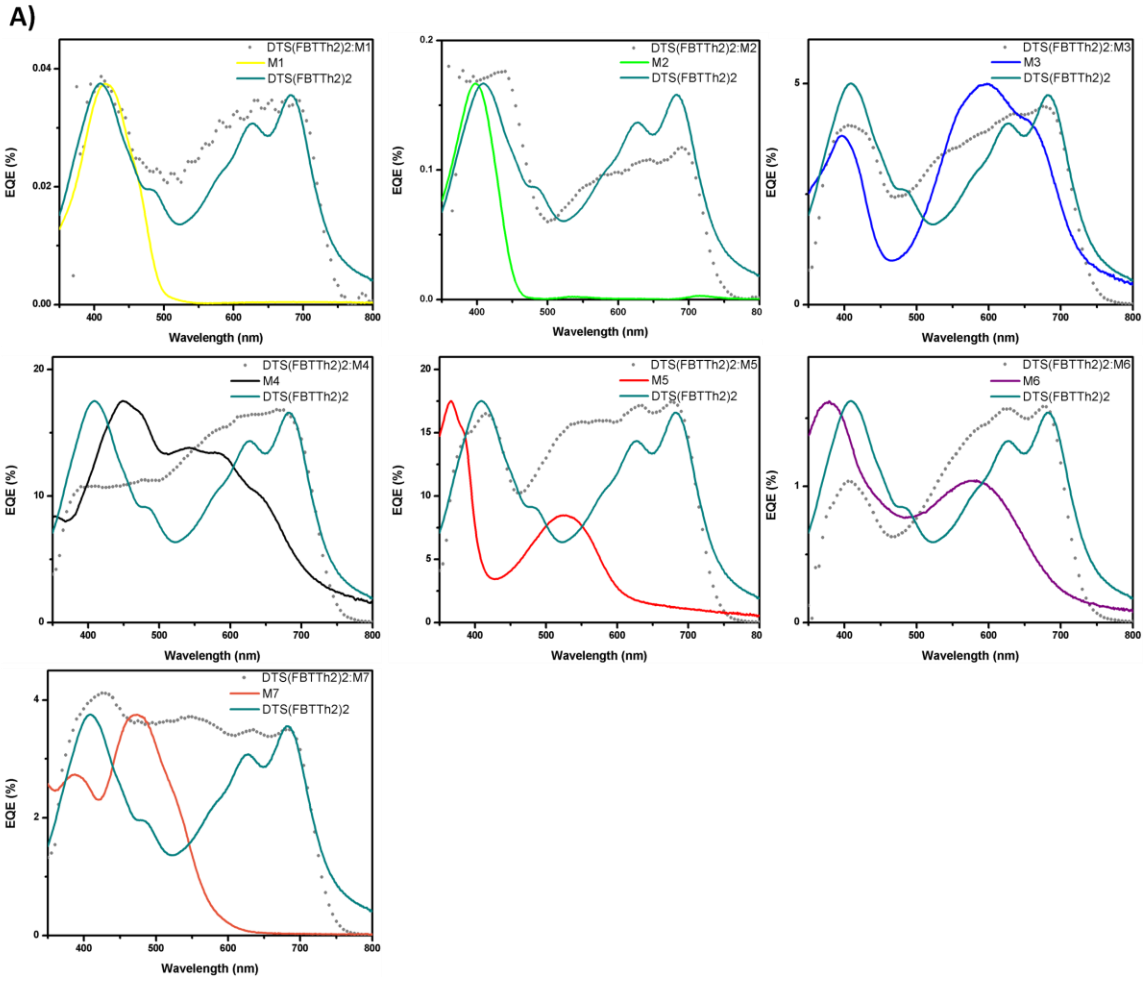


Figure S25. Comparison of frontier energy levels derived using different methods for compounds **M1**-**M7.** Experimentally determined values for IE and EA (determined using

CV and UPS) are compared to the HOMO and LUMO values (obtained using DFT calculations) in order to show a similar trend in energy levels for the molecular series.

9. External Quantum Efficiency Measurements

EQE spectra were recorded using a 150 W Xe source, optical chopper wheel, monochromator (Oriel Cornerstone 260 1/4 m), lock-in amplifier, and a calibrated silicon photodiode (Newport 818-UV-L). Various long-pass filters were used to reduce second order transmission through the monochromator.



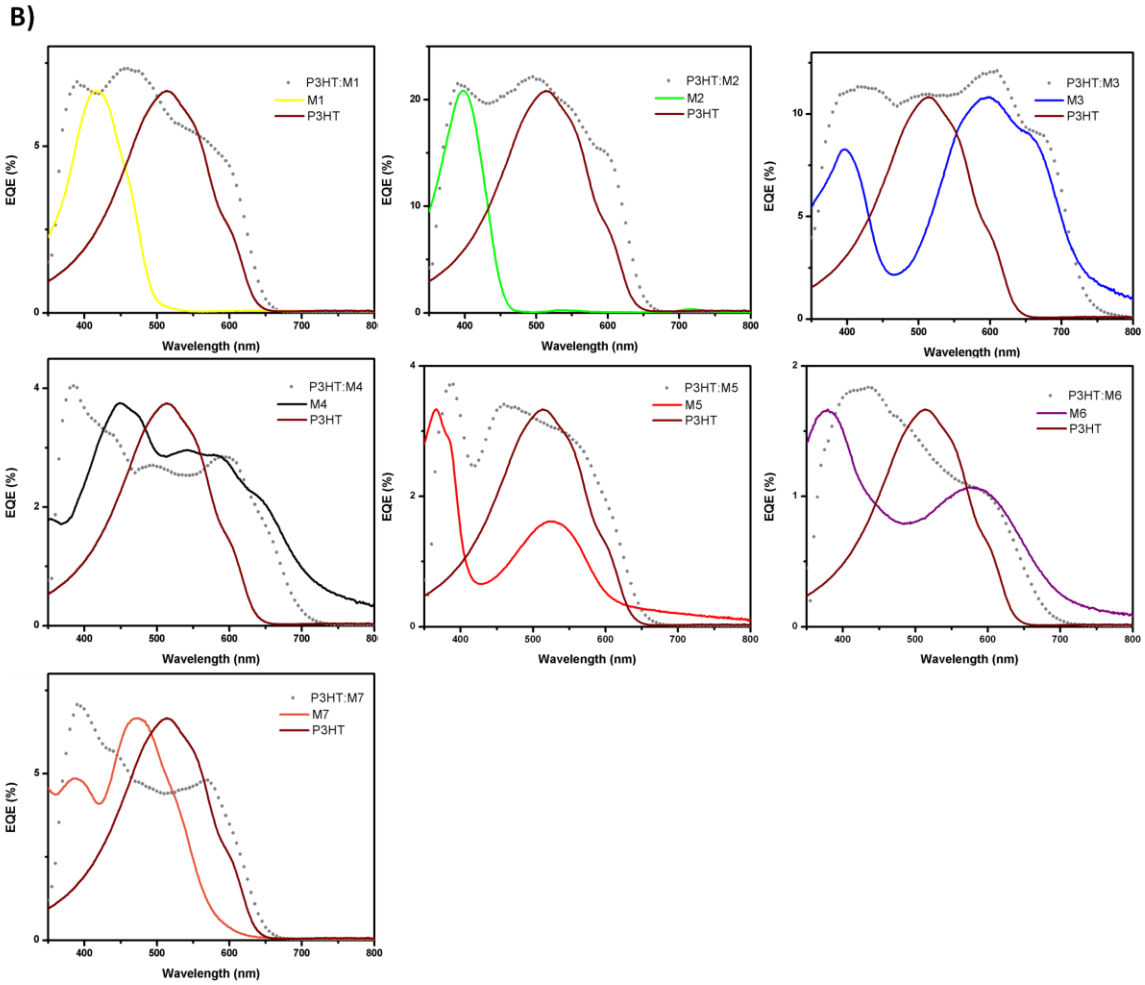


Figure S26. EQE spectra (dotted lines) for **A) DTS(FBTTh$_2$)$_2$**:acceptor and **B) P3HT**:acceptor devices. Normalized absorbance spectra (solid lines) of neat films of each donor and acceptor is shown for reference.

10. Absorbance Spectroscopy

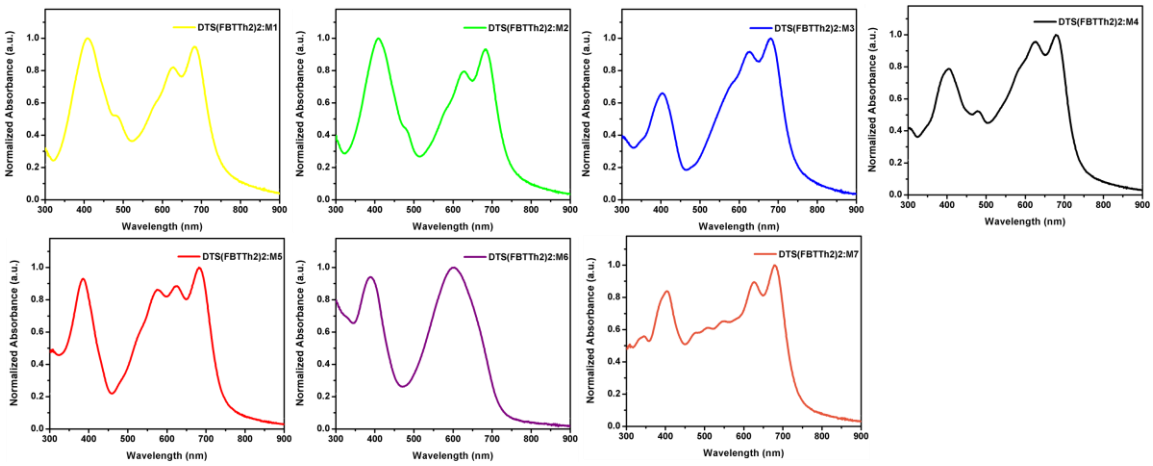


Figure S27. Blend film absorbance spectra of **DTS(FBTTh$_2$)$_2$** with molecules **M1**-**M7**. Films cast from 1:1 weight ratio solutions.

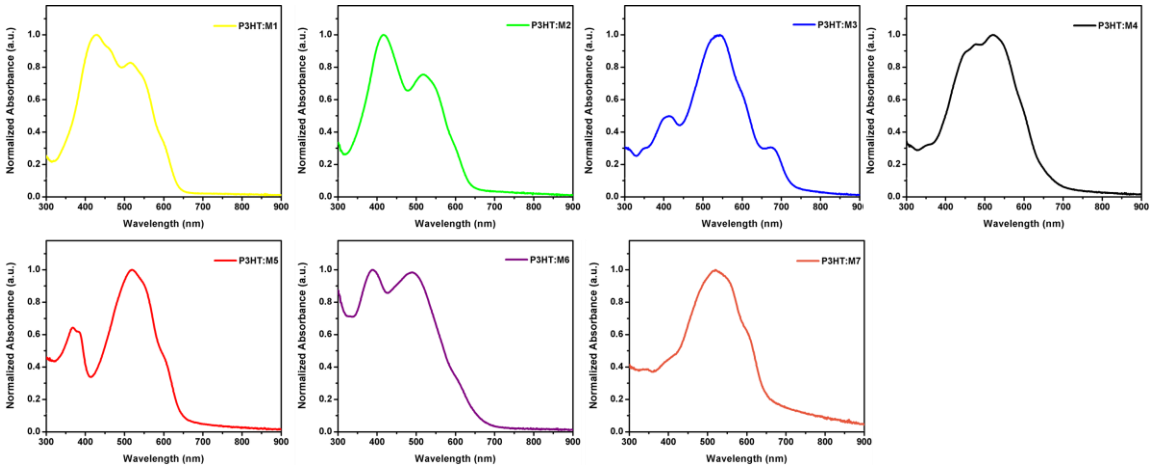


Figure S28. Blend film absorbance spectra of **P3HT** with molecules **M1**-**M7**. Films cast from 1:1 weight ratio solutions.

11. Solar Cell Device Data

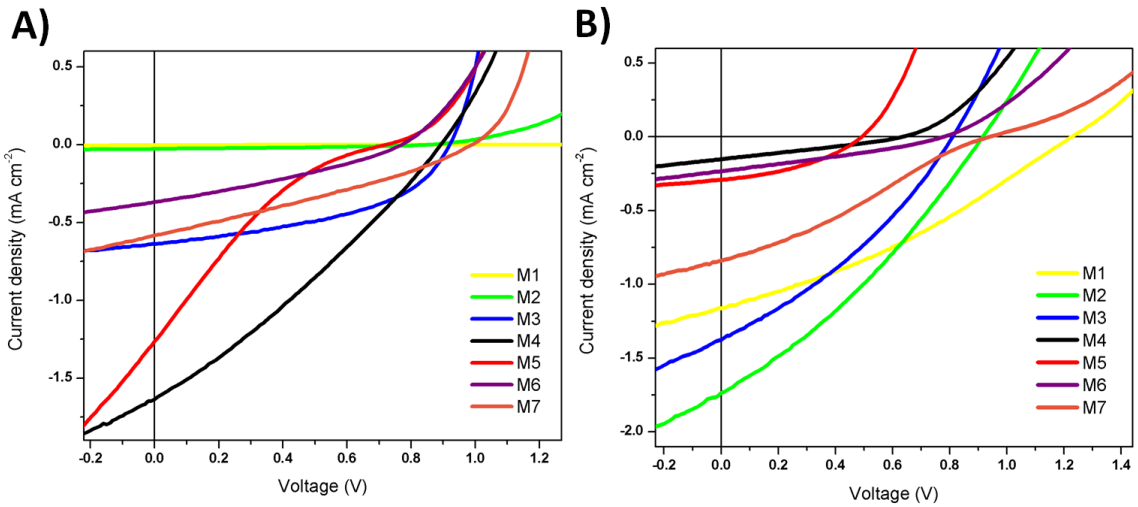


Figure S29. Current density vs voltage curves for **M1-M7** with **A) DTS(FBTTh$_2$)$_2$** and **B) P3HT** as the donor.

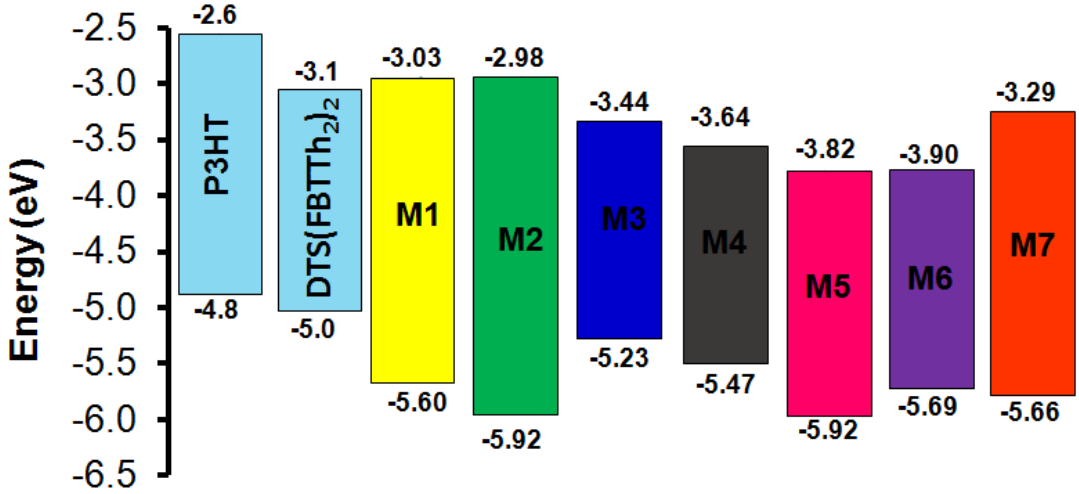


Figure S30. Energy level diagram for **M1-M7**, energy levels for **P3HT** and **DTS(FBTTh$_2$)$_2$** were obtained using CV measurements in our lab, using the same method used for **M1-M7**. It has previously been noted that estimations of frontier orbital energies of molecules or polymers using CV can vary significantly from lab to lab[12] and so for reference the LUMO and HOMO energy levels for **P3HT** and **DTS(FBTTh$_2$)$_2$** taken from the literature are -3.3 eV, -5.1 eV and -3.2 eV and -5.2 eV respectively.[10,11]

10. AFM IMAGES

Tapping mode atomic force microscopy was used to gain insight into the extent of domain separation in each blend film, which could lead to the observed differences in the performance of the devices (*vide supra*). The same device casting conditions were used to characterize blend films of **DTS(FBTTh$_2$)$_2$**and **P3HT** with each molecule. Topographical images of blend films with **DTS(FBTTh$_2$)$_2$** are presented in **Figure S32**. Films of **DTS(FBTTh$_2$)$_2$** and **M1** (**A**) form large needle-like grains on the order of several hundred nanometers, indicating a large degree of phase separation that could be responsible to the poor device performance. **M2** blend films (**B**) show very similar behavior to **M1**, although with larger grains. It is interesting to note the similar composition of **M1** and **M2**, comprised solely of thiophene and phthalimide. The polar imide groups have a strong effect on the solubility of these two molecules, clearly demonstrating a low degree of miscibility with **DTS(FBTTh$_2$)$_2$**. **M3** (**C**) with a DPP core forms smoother blend films than **M1** and **M2**, with pebble-shaped grains on the order of 100 nm, which is consistent with the relatively high performance obtained for devices using **M3**. **M4** (**D**), with an isoindigo core exhibits similar morphology in blend films, albeit with a smaller grain size on the order of 50 nm. The central part of both of these molecules contain two symmetric lactam units with *n*-octyl side chains, however the extended chromophore size of isoindigo compared to DPP may contribute to the higher degree of mixing with **DTS(FBTTh$_2$)$_2$**. Blend films of **M5** (**E**), with an NDI core, exhibit large crystalline peaks protruding from the surface, with a roughness greater than films of **M1** or **M2**. Similar to **M1** and **M2**, **M5** contains a high number of polar imide groups in comparison to lipophilic content. Films of **M6** (**F**), with a PDI core, show a similar needle-like crystalline arrangement with domain sizes in the 50 – 100 nm range. The extension of the conjugated core from NDI (**M5**) to PDI (**M6**) increases the amount of carbon π-π interactions relative to the interactions between polar imide groups, enhancing the miscibility with **DTS(FBTTh$_2$)$_2$** which may explain higher device performance for **M5** vs **M6**. Films of **M7** (**G**), with a F_2BT core, show intimate intermixing with domain sizes on the order of 50 nm, punctuated by dispersed crystalline grains (~150 nm) protruding from the surface. The F_2BT core of **M7**, flanked by two thiophene units, bears the most similar structure to the fluorobenzothiadiazole (FBT) unit of **DTS(FBTTh$_2$)$_2$**, flanked by a thiophene and the thienyl group of dithienosilole (DTS). This similarity in structure may be the cause of the smoother film formation in comparison to **M1**, although further investigation, especially into the nature of the isolated islands, is required. Topographical images of blend films with **P3HT** are presented in **Figure S33**. Films of **P3HT** and **M1** (**A**) form elongated needle-like grains approximately 200 nm in length, with a high degree of lateral coherence between adjacent grain orientations spanning distances of a few microns. Self-assembled long-range ordering of **P3HT** grains has been observed previously in neat films spun on silane treated SiO_2 substrates[13], as well as in pre-cast films of **P3HT** dissolved in molten 1,3,5-trichlorobenzene (TCB) and seeded via TCB needles upon cooling and crystallization.[14] Previous studies on films of *n*-butyl, *n*-hexyl, and *n*-octyl derivatives of **M1** also showed characteristic needle-like crystalline grains,[15] and may be acting is a similar cooperative manner to align the **P3HT** chains. **M2** blend films (**B**) show low surface roughness without any distinct features, apart from a few scattered round grains. **M3** (**C**) showed the largest degree of phase separation and surface

roughness of the **P3HT** blend film series, with domain sizes on the order of 200 nm. **M4**, **M5**, and **M6** blends with **P3HT** (**D**-**F**) all appear as relatively smoother films, with increasingly intimate mixing in going from the isoindigo to the NDI and then to the PDI core. **M7** films (**G**) exhibit pebble-like grains approximately 200 nm in size. Similar features are visible in blend films of **M7** with **DTS(FBTTh$_2$)$_2$** (**Figure S33 G**), which leads to the presumption that crystalline grains of **M7** are embedded in a P3HT matrix. In general, there are distinct differences in the behavior amongst molecules **M1**-**M7** in blending with another small molecule (**DTS(FBTTh$_2$)$_2$**) in comparison to a polymer (**P3HT**). It is expected that subtle chemical interactions that affect the miscibility of the two components in the blend would manifest as large-scale phase separation when two small molecules are mixed, especially in the presence of a high-boiling point additive (DIO), as seen in **Figures S33 A**, **B**, **E**. With the polymer-small molecule blends, large-scale phase separation is expected for the more crystalline small molecules **M1** and **M7**, which lack solubilizing chains on the cores. The surprising result is the blend film of **P3HT** and **M3**, containing a DPP core. The ethylpropyl terminal and *n*-octyl side chains afford **M3** comparable solubility in chlorobenzene to **M4**, however the resultant films are very different.

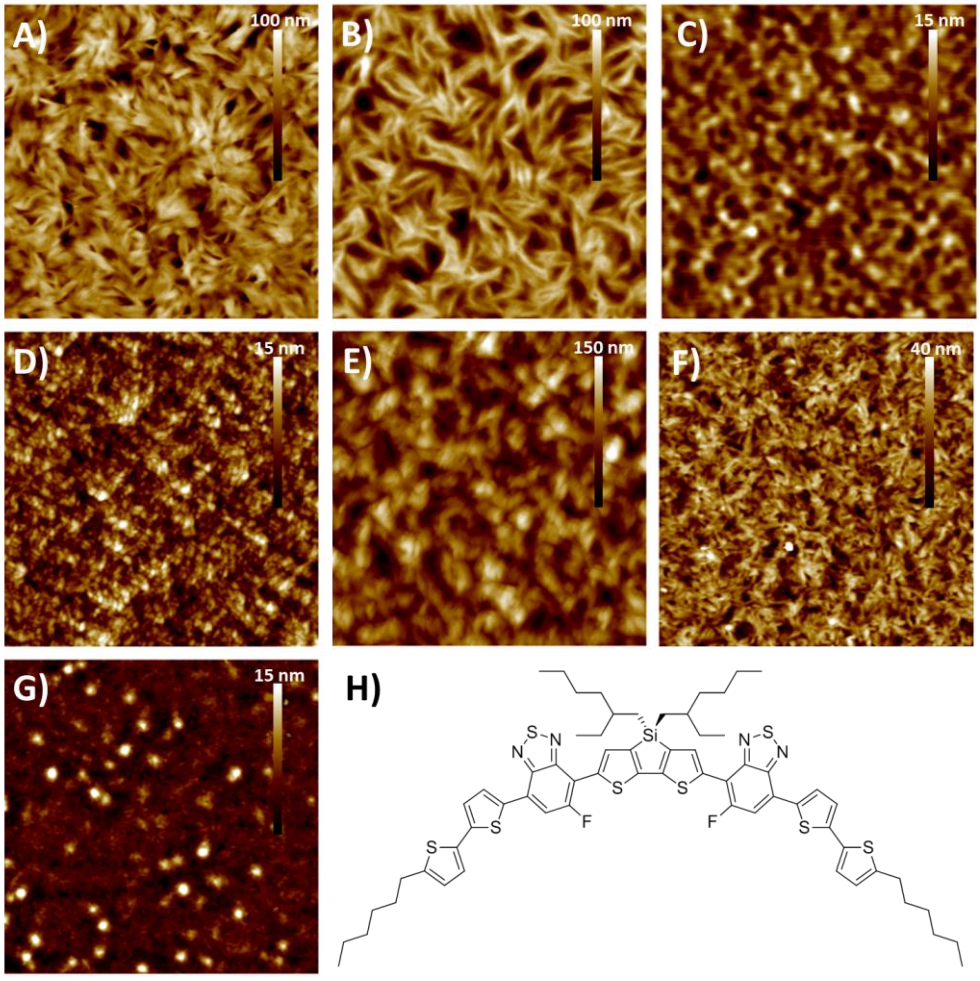


Figure S31: A-G) AFM topography images of blend films of **DTS(FBTTh$_2$)$_2$** and molecules **M1**-**M7**, respectively. AFM image dimensions are 5 μm x 5 μm. **H)** Chemical structure of **DTS(FBTTh$_2$)$_2$**.

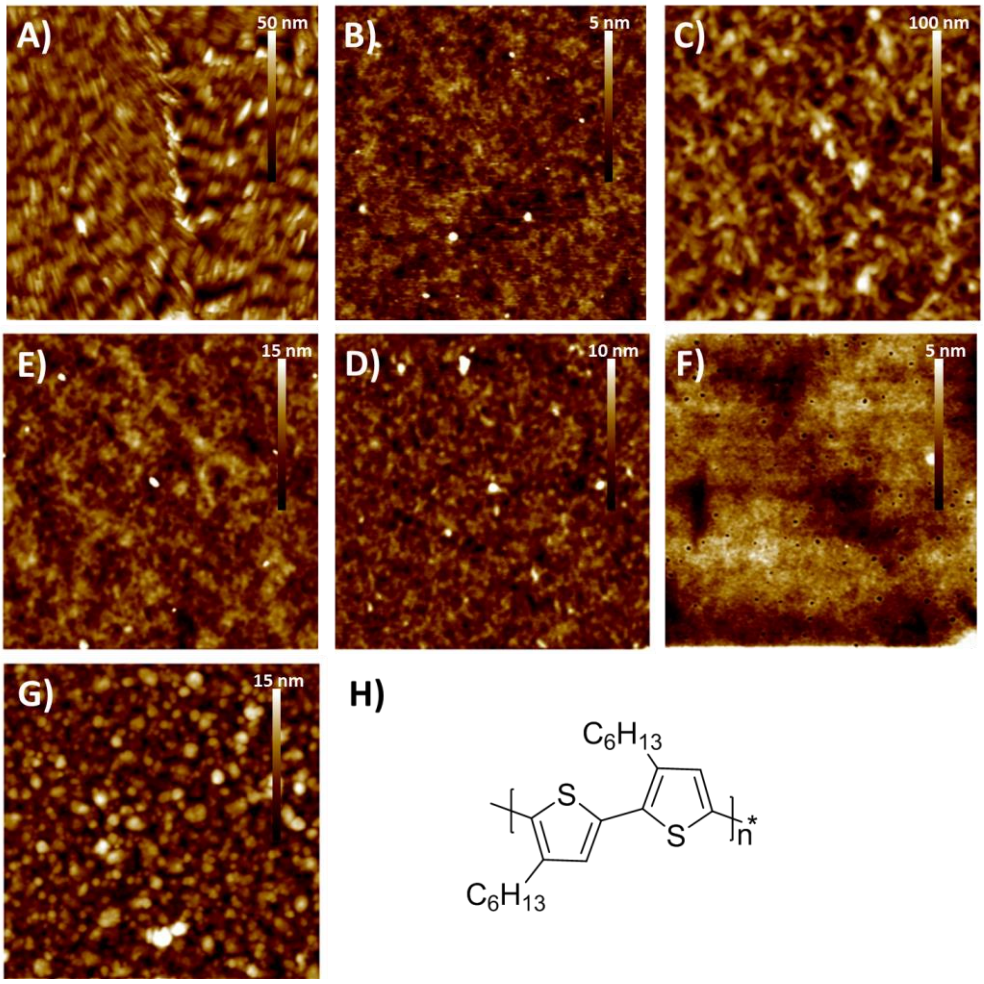


Figure S32: A-G) AFM topography images of blend films of **P3HT**and molecules **M1-M7**, respectively. AFM image dimensions are 5 µm x 5 µm. Chemical structure of **P3HT**.

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