Lewis Acid Adducts of Narrow Bandgap Conjugated Polymers

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Supporting Information

General Data: Preparations were carried out on a bench top or under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and an Vacuum Atmospheres inert atmosphere glove box. Solvents (pentane, toluene, THF, xylenes) were dried over sodium/benzophenone, distilled under vacuum, and stored over molecular sieves (4 Å). Solvents (methylene chloride, chloroform, 1,2-dichlorobenzene (oDCB)) were dried over calcium hydride, distilled under vacuum, and stored over molecular sieves (4 Å). Molecular sieves (4 Å) were purchased from Aldrich Chemical Company and dried at 140 ºC under vacuum for 24 hours prior to use. Deuterated solvents were dried over CaH_2 (CD_2Cl_2, $CDCl_3$, C_6D_5Br) or sodium/benzophenone (C_6D_6) and vacuum distilled prior to use. All reactants and reagents are commerically available and used as recieved unless otherwise noted.

Materials: Compound 4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CDT) was purchased from AstarPharma while 4,7-dibromo-pyridal[2,1,3]thiadiazole ($PTBr_2$) was purchased from WUXI Chemical and purified by flash chromatography (10% Et_3N in $CHCl_3$) and recrystallization (EtOH) prior to use. Compounds 4,4-*bis*(2-ethylhexyl)-2,6-*bis*(trimethylstannyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (5, Me_3Sn-CDT_{EH}-$SnMe_3$)[1] and 4,4-*bis*(hexyl)-2,6-*bis*(trimethylstannyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (Me_3Sn-CDT_{C6}-$SnMe_3$)1 were prepaed by literature methods. Compound 4,4-*Bis*(n-hexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CDT_{C6}),[2] 4,7-dithienyl[1,2,5]thiadiazolo[3,4-c]pyridine (Th-PT-Th),[3] and 4,7-bis(5-bromo-2-thienyl)[1,2,5]thiadiazolo[3,4-c]pyridine (7, BrTh-PT-ThBr),3 were prepared by methods similar to those reported in the literautre. $B(C_6F_5)_3$ (BCF) was purified by treatment with neat Et_3SiH for 5 minutes followed by volatile removal and sublimation at 120°C under vacuum. It is imperative that all Lewis acids be handled using strict ahydrous conditions.

GPC: Gel permeation chromatography (150 °C in 1,2,4-trichlorobenzene) was performed on a Polymer Laboratories PL220 instrument.

NMR: ^{1}H, ^{13}C, ^{11}B, and ^{19}F nuclear magnetic resonance (NMR) spectroscopy spectra were recorded on a Bruker Avance-500 MHz spectrometer at 25°C unless otherwise noted. ^{1}H and ^{13}C NMR spectra are referenced to $SiMe_4$ using the residual solvent peak impurity of the given solvent. ^{11}B and ^{19}F NMR experiments were referenced to $BF_3(OEt_2)$, and $CFCl_3$, respectively. Chemical shifts are reported in ppm and coupling constants in Hz as absolute values. DEPT, ^{1}H-^{1}H, and ^{1}H/^{13}C correlation experiments were completed for assignment of the carbon atoms.

UV-vis-nearIR: UV-visible-nearIR spectroscopy were recored using wither a Beckman Coulter DU 800 series or Perkin Elmer Lambda 750 spectrophotometer at room temperature unless otherwise noted. All solution UV-vis experiments were run under an N_2 atmosphere in telfon capped 1mm quartz cuvettes using 1,2 dichlorobenzene or chlorobeznene as the solvent. ***Oligomers:*** All oligomer solutions for absorption spectroscopy were prepared with a concentration of 2.5 x 10^{-4} M. Oligomer films were prepared by spin casting the appropriate solution (15 mg/mL in toluene) onto a 15mm x 15mm x 2mm quartz substrate at 1000 rpm under an atmosphere of N_2. Solution combinations of oligomers and $B(C_6F_5)_3$ or BBr_3 were prepared by by adding an appropriate molar amount of 0.01 M Lewis acid solution in 1,2-dichlorobezene to a 0.1 mL aliquot of a 0.01 M dichlorobenzene solution of oligomer and diluting to 4 mL to give a solution with a final concetraion of 0.00025 M wrt oligomer. For thin films, 1 molar equivalent of $B(C_6F_5)_3$ in 0.5 mL toluene was added to 0.5 mL of a 2% toluene solution of oligomer in a vial and sealed with a teflon cap. The solution was stirred at room temperature for 1 hour before spin casting thin films on quartz at 1000 rpm. ***Polymers:*** Polymer solutions were prepared with a concentration of 0.25 mg/mL in 1,2-dichlorobezene. Polymer films were prepared by spin casting the appropriate solution (10 mg/mL in chlorobenzene) onto a 15mm x 15mm x 2mm quartz substrate at 2000 rpm under an atmosphere of N_2. For polymer/$B(C_6F_5)_3$ solution UV-vis-NIR absoprption spectroscopy study, solution mixtures were prepared by adding an appropriate weight equivalent of $B(C_6F_5)_3$ in 1,2-dichlorobenzne to a 0.1 mL aliqout of a 1.5 mg/mL polymer solution in 1,2-dichlorobenzne and diluted to 2mL total volume for a final concentration of 0.075 mg/mL wrt polymer. Polymer/ $B(C_6F_5)_3$ thin films were prepared by spin casting the appropriate solution (10 mg/mL in chlorobenzene wrt to polymer with appropriate weight equilvanet of $B(C_6F_5)_3$ added) onto a 15mm x 15mm x 2mm quartz substrate at 2000 rpm under an atmosphere of N_2. Temperature dependant UV-visible-nearIR spectroscopy were obtained by heating the appropraite solutions in 1 cm cuvettes sealed with screw caps, equilibrating for 10 minutes, then obtaining the spectrum. Solutions were heated by placing the cuvettes in a cuvette holder heated via a continous flow of silicon oil.

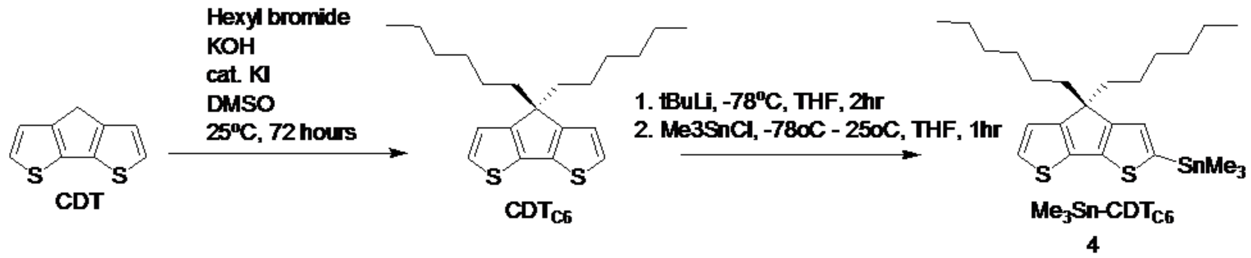
CHN: Combustion analyses were performed by the MSI analytical lab at the University of California, Santa Barbara.

Electrochemistry: All electrochemical measurements were performed using CHI instrument model 730B in a standard three-electrode, one compartment configuration equipped with Ag/AgCl electrode, Pt wire and Glassy carbon electrode (dia. 3 mm), as the pseudo reference, counter electrode and working electrode respectively. Glassy carbon electrodes were polished with alumina. The cyclic voltammetry (CV) experiments were performed in anhydrous acetonitrile (AcCN) or dichloromethane (DCM) solution with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte at scan rate 100 mV/s unless otherwise stated. All electrochemical solutions were purged with dry Ar_2 for 15 minutes at least to deoxygenate the system. Under these conditions, a Fc/Fc$^+$ standard was calibrated to be 0.40 V. A mixture of polymer in dry $CHCl_3$ (~3 mg/mL) was used for preparation films at room temperature. Films were prepared by drop-cast onto Glassy carbon electrode for CV measurement. In solution, monomer concentration was about ~10^{-3} M.

XPS and UPS: For XPS and UPS experiments, a Au film 75nm thick was deposited on a precleaned Si substrate with a thin native oxide. Polymer and oligomer solutions (0.25% chlorobenzene) were then spin-coated at 2000 and 4000 rpm atop a Au film. The total time of spin coating was kept at 60 s for all samples. Film fabrication was done in a N2-atmosphere globe box. To minimize possible influence by exposure to air, the films were then transferred from the N2-atmosphere dry box to the analysis chamber inside an air-free holder. Subsequently, all samples were kept inside a high vacuum chamber overnight, to remove solvent. The XPS and UPS analysis chamber was equipped with a hemispherical electron-energy analyzer (Kratos Ultra Spectrometer), and was maintained at 1.33_10_7 Pa. The XPS was measured using monochromatized Al Ka (hv¼1486.6 eV) excitation, while UPS measurements were carried out using the He I (hv¼21.2 eV) source. The electron energy analyzer was operated at constant pass energy of 20 eV (for XPS) and 10 eV (for UPS). During UPS measurements, a sample bias of 9 V was used in order to separate the sample and the secondary edge for the analyzer. In order to confirm reproducibility of XPS and UPS spectra, we repeated these measurements twice on two sets of samples. UPS measurement require that thin film samples be inserted into a high vacuum chamber for 12 hours. Free $B(C_6F_5)_3$ readily sublimes under vacuum, and therefore to confirm that the Lewis acid remained in the sample, XPS measurements were performed. Signals attributed to fluorine atoms were observed confirming the presence of $B(C_6F_5)_3$. Additionally, no significant signals due to oxygen could be detected, indicating that no hydrolysis reactions are taking place.

Calculations: All calculations were performed using the Gaussian 03 program.[4] Optimized gas-phase structures were obtained using the density functional theory (DFT) method B3LYP[5] in conjunction with 6-31G(d,p) basis set, i.e., B3LYP/6-31G(d,p). California NanoSystems Institute at UCSB is acknowledged for computational resources.

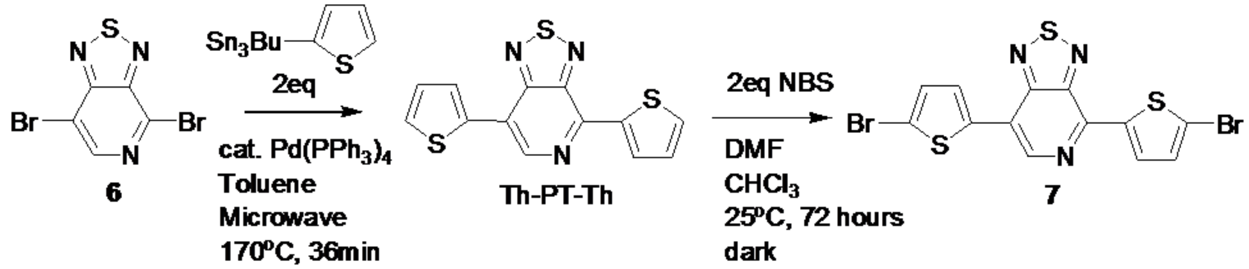
Synthesis:



Synthesis of 4,4-Dihexyl-cyclopenta[2,1-b:3,4-b']dithiophene (CDT$_{C6}$): To a solution of *4H*-Cyclopenta[2,1-b:3,4-b']dithiophene (CDT) (1.63g, 9.14 mmol) in dimethyl sulfoxide (50 mL) was added hexyl bromide (3.1g, 18.9 mmol) and a catalytic amount of potassium iodide (50mg). The mixture was purged with argon for 10 minutes followed by the slow addition of solid potassium hydroxide (2g). The now dark green mixture was stirred in the dark at room temperature for 72 hours. The mixture was then poured into de-ionized water (150 mL) and the organic phase extracted with diethyl ether (4 x 100 mL). The organic phases were collected and washed with brine (100 mL) and a saturated ammonium chloride solution (100 mL). The organic phase was dried over magnesium sulphate, filtered, and concentrated to give the crude product as yellow oil. Purification via flash chromatography with hexanes (monitored at 254 nm, collected at 320 nm) and drying under high vacuum for 48 hours gave pure product as colorless oil. Yield 2.8g (88%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.15 (d, 2H, $^{3}J_{\text{H-H}}$ = 5 Hz), 6.94 (d, 2H, $^{3}J_{\text{H-H}}$ = 5 Hz), 1.84 (m, 4H, C-CH_2), 1.19 (m, 12H, alkyl-CH_2), 0.95 (m, 4H, alkyl-CH_2), 0.82 (m, 6H, alkyl-CH_3).

Synthesis of 5-(trimethylstannyl)-4,4-bis(hexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene (4, Me$_3$Sn-CDT$_{C6}$): A dry three-neck round bottom flask was equipped with a Schlenk adapter, dropping funnel, and rubber septum. Under argon, compound CDT$_{C6}$ (2.80, 8.07 mmol) was dissolved in dry THF (200 mL) and cooled –78 °C using a dry ice/acetone cold bath. A solution of t-butyllithium (1.7 M pentane, 5.22 mL, 8.87 mmol) diluted with dry pentane (30mL) was then added dropwise over 20 minutes via a dropping funnel. The dropping funnel was rinsed with dry pentane (30 mL) to ensure all lithium reagent was transferred to the reaction vessel. The reaction was stirred at –78 °C under argon for 2 hours. A solution of trimethyltin chloride (1.93g, 9.68 mmol) in dry pentane (30 mL) was then added dropwise over 5 minutes via a dropping funnel. The dropping funnel was rinsed with dry pentane (30 mL) to ensure all tin reagent was transferred to the reaction vessel. The reaction was stirred at –78 °C under argon for 1 hour and subsequently warmed to room temperature and stirred for a further 3 hours. The mixture was then poured into de-ionized water (300 mL) and the organic phase extracted with hexanes (3 x 100 mL). The organic phases were collected and washed with de-ionized water (5 x 100 mL), dried over magnesium sulphate, filtered, and concentrated to give the product as yellow oil. Yield 4.05g (98%). **^{1}H NMR** (500 MHz, CDCl$_3$): δ = 7.12 (d, 1H, $^{3}J_{\text{H-H}}$ = 5 Hz), 6.96 (s, 1H), 6.93 (d, 1H, $^{3}J_{\text{H-H}}$ = 5 Hz), 1.82 (m, 4H, C-CH_2), 1.21 (m, 4H, alkyl-CH_2), 1.16 (m, 8H, alkyl-CH_2), 1.00 (m, 4H, alkyl-CH_2), 0.83 (t, 6H, $^{3}J_{\text{H-H}}$ = 7 Hz, alkyl-CH_3), 0.40 (s, d, 9H, $^{2}J_{\text{H-Sn}}$ = 57 Hz, Sn-CH_3). **^{13}C NMR** (500 MHz, CDCl$_3$): δ = 160.69, 158.32, 142.35, 137.60, 136.80, 129.47, 124.26, 122.01 (aromatic *C*), 52.91 (quaternary, bridged C), 37.87, 31.81, 29.95, 24.72, 22.82 (CH$_2$), 14.25 (CH$_3$), 7.84 (s, d, $^1J_{\text{C-Sn}}$ = 362 Hz, Sn-CH$_3$). **^{119}Sn NMR** (500 MHz, CDCl$_3$): δ = -26.7.

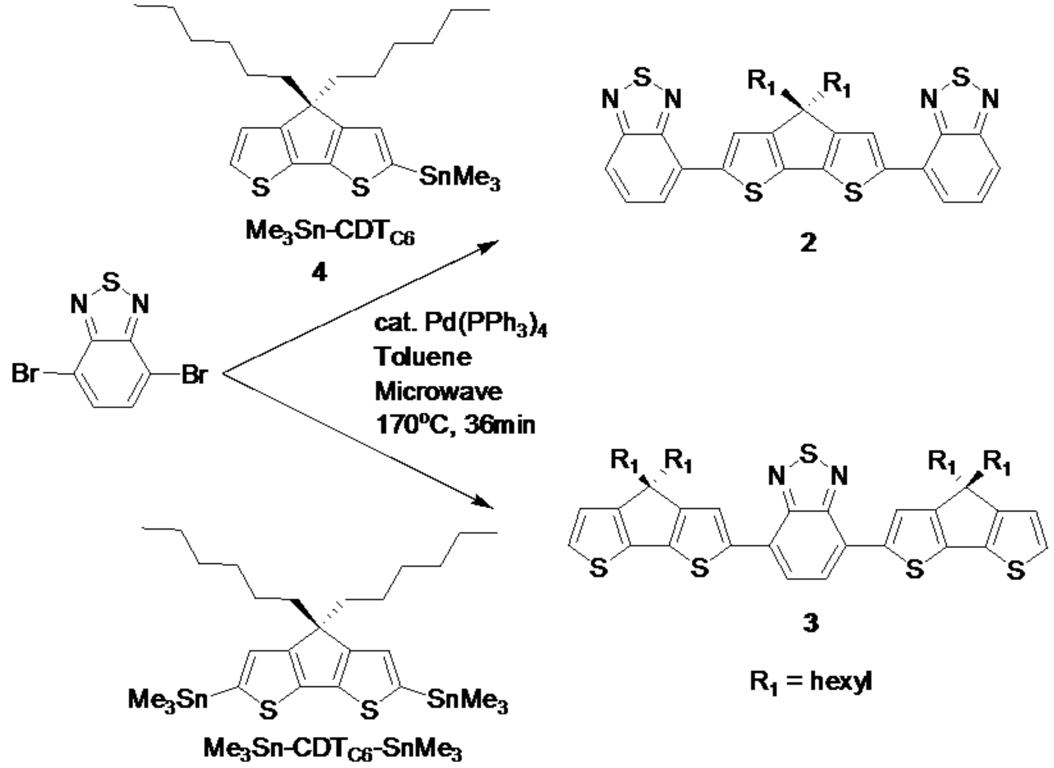
Synthesis of PT acceptor:



Synthesis of ***4,7-dithienyl[1,2,5]thiadiazolo[3,4-***c***]pyridine*** **(Th-PT-Th):** A 5 mL microwave tube was charged with 4,7-dibromo-pyridal[2,1,3]thiadiazole (**6**, $PTBr_2$, 0.556 g, 1.885 mmol), 2-(tributylstannyl)thiophene (Bu_3Sn-Th, 1.477 g, 3.957 mmol), $Pd(PPh_3)_4$ (0.020 g, 0.018 mmol), toluene (3 mL), and sealed with a teflon cap. The reaction mixture was heated to 120°C for 3 minutes, 140°C for 3 minutes, and 170°C for 36 minutes, using a Biotage microwave reactor. Upon cooling, the residue was passed through a short silica plug eluting with methylene chloride (200 mL). All volatiles were removed *in vacuo* to give the crude product as a red solid. The solid was slurried in MeOH (100 mL), sonicated for 10 minutes, and filtered. The solid was washed with copious amounts of MeOH and then dried under vacuum for 24 hours. The product was collected as a bright red solid. Recovered yield: 535 mg (94%). **^{1}H NMR** (CD_2Cl_2): δ 8.81 (s, 1H, PT-C*H*), 8.68 (d, $^3J_{H\text{-}H}$ = 4 Hz, 1H, Th'-C*H*), 8.11 (d, $^3J_{H\text{-}H}$ = 4 Hz, 1H, Th-C*H*), 7.61 (d, $^3J_{H\text{-}H}$ = 5 Hz, 1H, Th'-C*H*), 7.51 (d, $^3J_{H\text{-}H}$ = 5 Hz, 1H, Th-C*H*), 7.27 (dd, $^3J_{H\text{-}H}$ = 4 Hz, $^3J_{H\text{-}H}$ = 4 Hz 1H, Th'-C*H*), 7.23 (dd, $^3J_{H\text{-}H}$ = 4 Hz, $^3J_{H\text{-}H}$ = 4 Hz 1H, Th-C*H*), **^{13}C{^{1}H} NMR** (CD_2Cl_2): 155.50, 148.62, 146.91, 142.53 (s, quaternary), 141.28 (s, PT-*C*H), 137.18 (s, quaternary), 131.97 (s, Th'-*C*H), 131.00 (s, Th'-*C*H), 129.40 (s, Th-*C*H), 128.61 (s, Th-*C*H), 128.38 (s, Th'-*C*H), 127.88 (s, Th-*C*H), 121.00 (s, quaternary). **Anal. Calcd.** for $C_{13}H_7N_3S_3$: C, 51.80; H, 2.34; N, 13.94. Found: C, 51.8; H, 2.40; N, 13.7 %. **UV-vis**: (*o*-DCB) λ_{max} = 302, 470 nm, λ_{onset} = 550 nm, ε = 22150 $cm^{-1}M^{-1}$. **PL**: (*o*-DCB) λ_{max} = 607 nm. **HRMS (EI)** *m/z*, calcd for $C_{13}H_7N_3S_3$ (M^+): 300.98; found: 301.

Synthesis of ***4,7-bis(5-bromo-2-thienyl)[1,2,5]thiadiazolo[3,4-***c***]pyridine*** **(7, Br-Th-PT-Th-Br):** A 250 mL round bottom flask was charged with 4,7-dithienyl[1,2,5]thiadiazolo[3,4-c]pyridine (Th-PT-Th, 0.500 g, 1.662 mmol), *n*-bromosuccinimide (NBS, 0.700 mg, 3.932 mmol), *N-N*-dimethyl formamide (50 mL), chloroform (100 mL), and capped with a rubber septum. The reaction mixture was stirred for 72 hours in the dark. The reaction mixture was precipitated into MeOH (400 mL) and stirred for 1 hour. The precipitate was collected via filtration and washed with copious amounts of MeOH and dried under vacuum for 12 hours. Crude product was purified via flash chromatography (hexanes/methylene chloride) to give pure product as a red solid. Recovered yield: 600 mg (79%). **^{1}H NMR** (CD_2Cl_2): δ 8.80 (s, 1H, PT-C*H*), 8.45 (d, $^3J_{H\text{-}H}$ = 5 Hz, Th'-C*H*), 7.87 (d, $^3J_{H\text{-}H}$ = 5 Hz, 1H, BrTh-C*H*), 7.29 (d, $^3J_{H\text{-}H}$ = 5 Hz, Th'-C*H*), 7.22 (d, $^3J_{H\text{-}H}$ = 5 Hz, Th-C*H*). **Anal. Calcd.** for $C_{13}H_5Br_2N_3S_3$: C, 34.00; H, 1.10; N, 9.15. Found: C, 33.6; H, 1.13; N, 8.86 %. **HRMS (EI)** *m/z*, calcd for $C_{13}H_5Br_2N_3S_3$ (M^+): 456.8; found: 457.

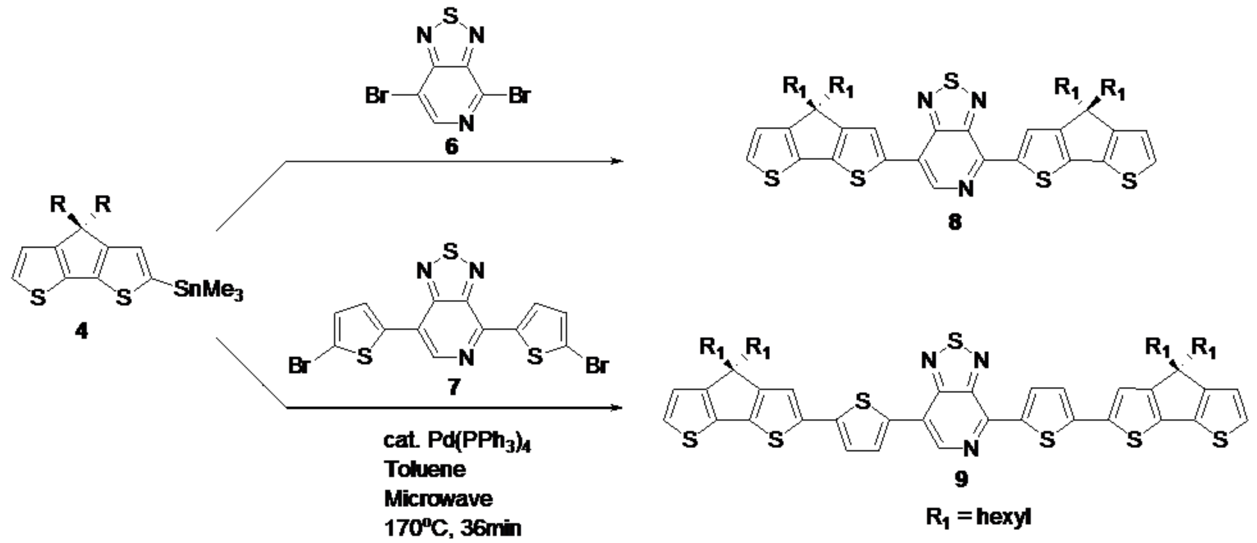
Synthesis of BT small molecules:



Synthesis of 5,5'-*Bis*(benzo[2,1,3]thiadiazole)-4,4-bis(hexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene (2): A 5 mL microwave tube was charged with 4-bromo-benzo[2,1,3]thiadiazole (200 mg, 0.93 mmol), 5,5'*Bis*(trimethylstannyl)-4,4-bis(hexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene ($Me_3Sn-CDT_{C6}-SnMe_3$) (302 mg, 0.45 mmol), $Pd(PPh_3)_4$ (0.010 g, 0.009 mmol), toluene (3 mL), and sealed with a teflon cap. The reaction mixture was heated to 120°C for 3 minutes, 140°C for 3 minutes, and 170°C for 36 minutes, using a Biotage microwave reactor. Upon cooling, all volatiles were removed *in vacuo* to give the crude product as a red solid. The crude product was subjected to flash chromatography on a silica gel column using hexane as the elutent. After removal of the solvent the product was precipitated using methanol (50 mL) and the red solid collected by filtration. Recovered yield: 270 mg (94%). **^{1}H NMR** ($CDCl_3$): δ 8.12 (s, 2H, Th-C*H*)**,** 7.90 (d, $^3J_{H\text{-}H}$ = 8 Hz, 2H, BT-*CH*)**,** 7.88 (d, $^3J_{H\text{-}H}$ = 8 Hz, 2H, BT-*CH*)**,** 7.61 (dd, $^3J_{H\text{-}H}$ = 8 Hz, $^3J_{H\text{-}H}$ = 8 Hz, 2H, BT-*CH*)**,** 2.03 (m, 4H, CH_2), 1.21-1.11 (m, 16H, CH_2), 0.79 (t, 6H, $^3J_{\text{H-H}}$ = 7 Hz, CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$): 160.22, 156.34, 152.55, 139.22, 130.34, 128.88, 124.56, 123.05, 119.87, 38.48, 32.22, 30.32, 25.25, 23.19, 14.36. **Anal. Calcd.** for $C_{33}H_{34}N_4S_4$: C, 64.46; H, 5.57; N, 9.11. Found: C, 64.1; H, 5.53; N, 8.69%. **UV-vis (*o*-DCB)**: λ_{max} = 516 nm, λ_{onset} = 606 nm. **UV-vis (film)**: λ_{max} = 542 nm, λ_{onset} = 640 nm.

Synthesis of {*Bis*(4,4-bis(hexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)}-4,7-benzo[2,1,3]thiadiazole (3): A 5 mL microwave tube was charged with 4,7-dibromo-benzo[2,1,3]thiadiazole ($BTBr_2$, 0.161 g, 0.548 mmol), 5-(trimethylstannyl)- 4,4-bis(hexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene (4, Me_3Sn-CDT, 0.557 g, 1.09 mmol), $Pd(PPh_3)_4$ (0.010 g, 0.009 mmol), toluene (3 mL), and sealed with a teflon cap. The reaction mixture was heated to 120°C for 3 minutes, 140°C for 3 minutes, and 170°C for 36 minutes, using a Biotage microwave reactor. Upon cooling, the residue was passed through a short silica plug eluting with methylene chloride (100 mL). All volatiles were removed *in vacuo* to give the crude product as a purple residue. To the residue was added MeOH (100 mL), the mixture sonicated for 10 minutes, and the MeOH decanted off. The crude product was then subjected to flash chromatography on a silica gel column using a hexane/CH_2Cl_2 gradient. The first fraction was combined and all solvent was removed *in vacuo* to give a purple film. MeOH was added (150 mL), the mixture sonicated for 10 minutes, filtered and dried under vacuum for 12 hours to give the product as a purple solid. Recovered yield: 345 mg (77%). **^{1}H NMR** (CD_2Cl_2): δ 8.05 (s, 2H, benzothiadiazole-C*H*), 7.87 (s, 2H, thiophene-C*H*), 7.27 (d, $^3J_{H\text{-}H}$ = 5 Hz, 2H, thiophene-C*H*), 7.06 (d, $^3J_{H\text{-}H}$ = 5 Hz, 2H, thiophene-C*H*), 1.95 (m, 8H, CH_2), 1.23-1.13 (m, 24H, CH_2), 1.08-1.99 (m, 8H, CH_2), 0.81 (t, 12H, $^3J_{\mathrm{H\text{-}H}}$ = 7 Hz, CH_3). **^{13}C{^{1}H} NMR** (CD_2Cl_2): 159.65, 159.54, 152.97, 140.05, 139.09, 137.10, 126.40 (s, quaternary), 126.34 (s, thiophene-*C*H), 124.76 (s, benzothiadiazole-*C*H), 122.42 (s, thiophene-*C*H), 122.36 (s, thiophene-*C*H), 38.39 (s, C-CH_2), 32.16 (s, alkyl-CH_2), 30.24 (s, alkyl-CH_2), 25.11 (s, alkyl-CH_2), 23.10 (s, alkyl-CH_2), 14.35 (s, alkyl-CH_3). **Anal. Calcd.** for $C_{47}H_{59}N_3S_5$: C, 69.85; H, 7.33; N, 3.39. Found: C, 69.7; H, 7.21; N, 3.58 %. **UV-vis**: ($CHCl_3$) λ_{max} = 378, 568 nm, λ_{onset} = 664 nm, ε = 27790 cm^{-1}M^{-1}. Optical bandgap = 1.87 eV. **HRMS (FAB)** *m/z*, calcd for $C_{47}H_{59}N_3S_5$ (M^+): 824.34; found: 824.

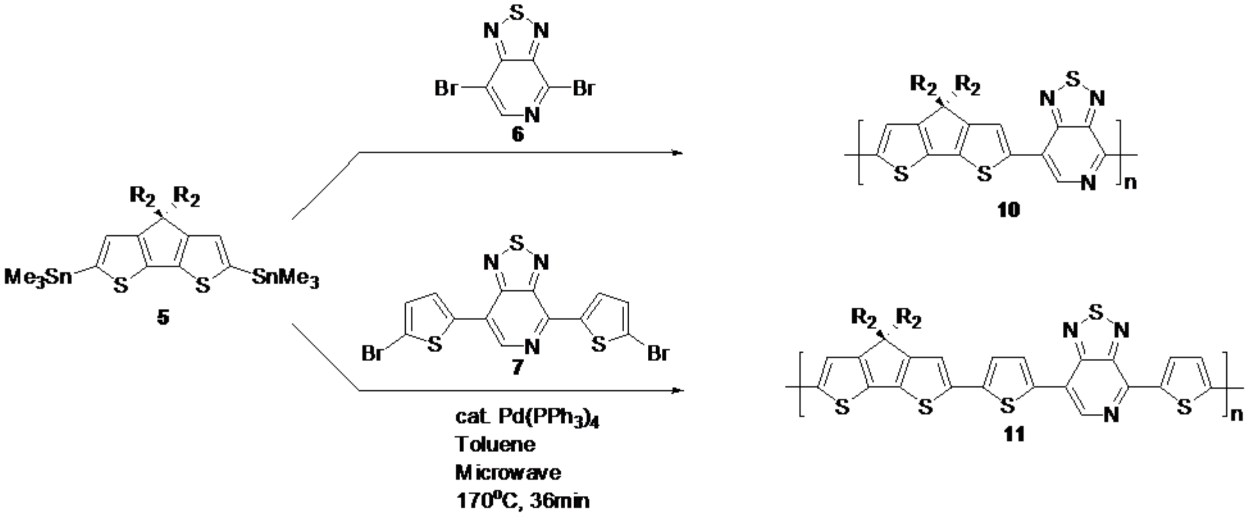
Synthesis of PT small molecules:



Synthesis of {*Bis*(4,4-bis(hexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)}-4,7-pyridal[2,1,3]thiadiazole (8): A 5 mL microwave tube was charged with 4,7-dibromo-pyridal[2,1,3]thiadiazole ($PTBr_2$, 0.250 g, 0.848 mmol), 5-(trimethylstannyl)- 4,4-bis(hexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene (Me_3Sn-CDT, 0.873 g, 1.714 mmol), $Pd(PPh_3)_4$ (0.010 g, 0.009 mmol), toluene (3 mL), and sealed with a teflon cap. The reaction mixture was heated to 120°C for 3 minutes, 140°C for 3 minutes, and 170°C for 36 minutes, using a Biotage microwave reactor. Upon cooling, the residue was passed through a short silica plug eluting with methylene chloride (100 mL). All volatiles were removed *in vacuo* to give the crude product as a blue residue. To the residue was added MeOH (100 mL), the mixture sonicated for 10 minutes, and the MeOH decanted off. The crude product was then subjected to flash chromatography on a silica gel column using a hexane/CH_2Cl_2 gradient. The first fraction was combined and all solvent was removed *in vacuo* to give a blue film. MeOH was added (150 mL), the mixture sonicated for 10 minutes, filtered and dried under vacuum for 12 hours to give the product as a blue solid. Recovered yield: 503 mg (72%). **^{1}H NMR** (CD_2Cl_2): δ 8.78 (s, 1H, PT-C*H*), 8.57 (s, 1H, Th'-C*H*), 8.05 (s, 1H, Th-C*H*), 7.35 (d, $^3J_{H-H}$ = 5 Hz, 1H, Th'-C*H*), 7.28 (d, $^3J_{H-H}$ = 5 Hz, 1H, Th-C*H*), 7.04 (d, $^3J_{H-H}$ = 6 Hz, 1H, Th'-C*H*), 7.01 (d, $^3J_{H-H}$ = 6 Hz, 1H, Th-C*H*), 1.96 (m, 8H, C-CH_2), 1.17 (m, 24H, alkyl-CH_2), 1.03 (m, 8H, alkyl-CH_2), 0.86 (m, 12H, alkyl-CH_3). **^{13}C{^{1}H} NMR** (CD_2Cl_2): 161.11, 160.64, 159.81, 155.21, 148.59, 146.41, 143.06, 142.79 (s, quaternary), 140.32 (s, PT-*C*H),139.33, 137.50, 137.19, 137.03 (s, quaternary), 127.97 (s, Th'-*C*H), 126.65 (s, Th'-*C*H), 126.63 (s, Th-*C*H), 122.63 (s, Th-*C*H), 122.50 (s, Th'-*C*H), 122.43 (s, Th-*C*H), 122.20, 121.07 (s, quaternary), 54.57 (s, quaternary, bridged C'), 54.47 (s, quaternary, bridged C), 38.43 (m, C-CH_2), 32.22 (s, alkyl-CH_2), 30.28 (s, alkyl-CH_2), 25.17 (s, alkyl-CH_2), 23.18 (s, alkyl-CH_2), 14.37 (s, alkyl-CH_3). **Anal. Calcd.** for $C_{47}H_{59}N_3S_5$: C, 68.32; H, 7.20; N, 5.09. Found: C, 68.10; H, 7.25; N, 5.13 %. **UV-vis**: (*o*-DCB) λ_{max} = 386, 618 nm, λ_{onset} = 766 nm, ε = 35440 $cm^{-1}M^{-1}$. **PL**: (*o*-DCB, e600nm) λ_{max} = 745 nm. **MS (FAB)** *m/z*, calcd for $C_{47}H_{59}N_3S_5$ (M^+): 825.33; found: 825.

Synthesis of *Bis*{2-thienyl-(4,4-bis(hexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)}-4,7-pyridal[2,1,3]thiadiazole (9): A 5 mL microwave tube was charged with 4,7-bis(5-bromo-2-thienyl)[1,2,5]thiadiazolo[3,4-c]pyridine (Br-Th-PT-Th-Br, 0.287 g, 0.628 mmol), 5-(trimethylstannyl)- 4,4-bis(hexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene (Me_3Sn-CDT, 0.670 g, 1.316 mmol), $Pd(PPh_3)_4$ (0.020 g, 0.018 mmol), toluene (3 mL), and sealed with a teflon cap. The reaction mixture was heated to 120^{o}C for 3 minutes, 140^{o}C for 3 minutes, and 170^{o}C for 36 minutes, using a Biotage microwave reactor. Upon cooling, the residue was passed through a short silica plug eluting with methylene chloride (400 mL). All volatiles were removed *in vacuo* to give the crude product as a blue-green residue. To the residue was added MeOH (300 mL), the mixture sonicated for 10 minutes, and the MeOH decanted off. The crude product was then subjected to flash chromatography on a silica gel column using a hexane/CH_2Cl_2 gradient. The first fraction was combined and all solvent was removed *in vacuo* to give a blue-green film. MeOH was added (300 mL), the mixture sonicated for 10 minutes, filtered and dried under vacuum for 12 hours to give the product as a purple solid. Recovered yield: 480 mg (77%). **^{1}H NMR** (CD_2Cl_2): δ 8.78 (s, 1H, PT-C*H*), 8.58 (d, $^{3}J_{H-H}$ = 4 Hz, 1H, Th'-C*H*), 8.06 (d, $^{3}J_{H-H}$ = 4 Hz, 1H, Th-C*H*), 7.31 (d, $^{3}J_{H-H}$ = 4 Hz, 1H, Th'-C*H*), 7.29 (s, 1H, CDT'-C*H*), 7.27 (m, 2H, CDT'-C*H*, CDT-C*H*)7.24 (d, $^{3}J_{H-H}$ = 4 Hz, 1H, Th-C*H*), 7.22 (s, 1H, CDT-C*H*), 7.00 (m, 2H, CDT'-C*H*, CDT-C*H*), 1.92 (m, 8H, C-C*H*$_2$), 1.20 (m, 24H, alkyl-C*H*$_2$), 1.05 (m, 8H, alkyl-C*H*$_2$), 0.82 (m, 12H, alkyl-C*H*$_3$). **^{13}C{^{1}H} NMR** (CD_2Cl_2): 159.77, 159.95, 159.60, 159.22, 155.23, 148.66, 145.94, 143.99 (s, quaternary), 140.89 (s, PT-*C*H), 140.83, 140.15, 138.01, 137.21, 137.13, 136.77, 136.70, 135.24 (s, quaternary), 133.47 (s, Th'-*C*H), 129.21 (s, Th-*C*H), 126.56 (s, CDT'-*C*H), 126.19 (s, CDT-*C*H), 124.73 (s, Th'-*C*H), 124.01 (s, Th-*C*H), 122.38 (m, CDT'-*C*H, CDT-*C*H), 120.38 (s, quaternary), 120.28 (s, CDT'-*C*H), 119.62 (s, CDT-*C*H), 54.55 (s, quaternary, bridged C'), 54.42 (s, quaternary, bridged C), 38.38 (m, C-C*H*$_2$), 32.23 (s, alkyl-C*H*$_2$), 30.30 (s, alkyl-C*H*$_2$), 25.13 (s, alkyl-C*H*$_2$), 23.21 (s, alkyl-C*H*$_2$), 14.41 (s, alkyl-C*H*$_3$). **Anal. Calcd.** for $C_{55}H_{63}N_3S_7$: C, 66.69; H, 6.41; N, 4.24. Found: C, 66.0; H, 6.11; N, 4.60 %. **UV-vis**: (*o*-DCB) λ_{max} = 418, 626 nm, λ_{onset} = 768 nm, ε = 37500 cm^{-1} M^{-1}. **PL**: (*o*-DCB, e600nm) λ_{max} = 798 nm. **MS (FAB)** *m/z*, calcd for $C_{55}H_{63}N_3S_7$ (M^{+}): 989.31; found: 990.

Synthesis of PT polymers:



Polymer Synthesis General: The polymers were prepared following a previously reported microwave assisted polymerization technique involving stoichiometric adjustment to optimize molecular weights.**Error! Bookmark not defined.** The stoichiometric adjustment procedure is used to compensate for possible impurities in the distannane monomers as a result of them being viscous oils that are difficult to purify. It was determined for both distannane monomers 1 and 2 that an apparent excess of 5 mol% should be used in polymerizations. Monomer loadings were such that the theoretical yield of copolymer would be ~250 mg. The two monomers were carefully weighed within a tenth of an mg and added to a 2-5 mL microwave tube. The tube was transferred into a glovebox where $Pd(PPh_3)_4$ (~5 mol % relative to Br) and 2 mL of Xylenes were added. The tube was sealed, removed from the glovebox and subjected to the following reaction conditions in a microwave reactor: 100 °C for 1 min, 150 °C for 1 min and 200 °C for 20 min. After this time the reaction was allowed to cool leaving a viscous liquid containing some solid material. The mixture was dissolved in hot 1,2-dichlorobenzene, then precipitated into methanol and collected via filtration. The residual solid was loaded into a cellulose extraction thimble and washed successively with methanol (4 hrs), hexanes (4 hrs), and acetone (2 hrs). The remaining polymer was dried on a high vacuum line overnight.

***Poly[(4,4-bis(2-ethylhexyl)cyclopenta-[2,1-b:3,4-b']dithiophene)-2,6-diyl-alt-([1,2,5]thiadiazolo[3,4-c]pyridine)-4,7-diyl]* (10).**

357.0 mg (0.490 mmol) of $Me_3Sn\text{-}CDT_{EH}\text{-}SnMe_3$, 137.7 mg (0.467 mmol) of Br-PT-Br and 15 mg of $Pd(PPh_3)_4$ were added to the microwave tube and subjected to the procedure outlined above. Batch 1: Yield: 188 mg (75 %), M_n = 16 kg/mol, PDI = 2.0. **Anal. Calcd.** for $C_{32}H_{43}N_3S_3$: C, 67.92; H, 7.66; N, 7.43. Found: C, 65.4; H, 6.63; N, 7.58. ^{1}**H NMR** (C_6D_5Br): δ 8.94 (s, 1H, C*H*), 8.85 (s, 1H, C*H*), 8.33 (s, 1H, C*H*), 2.28 (br m, 4H), 1.19 (br m, 16H), 0.84 (br m, 7H), 0.77 (br m, 7H).^{13}**C{^{1}H} NMR** (C_6D_5Br) partial: 154.7, 148.3, 128.4, 54.4, 43.5, 35.6, 34.5, 28.8, 27.7, 23.1, 14.3, 11.1. **UV-vis**: (*o*-DCB) λ_{max} = 805, 420 nm, λ_{onset} = 890 nm, ε = 45000, 15400 $cm^{-1}M^{-1}$.

Batch 2: M_n = 30 kg/mol, PDI = 2.0

Poly[(4,4-bis(2-ethylhexyl)cyclopenta-[2,1-b:3,4-b']dithiophene)-2,6-diyl-alt-(4',7'-bis(2-thienyl)-[1,2,5]thiadiazolo[3,4-c]pyridine)-5,5-diyl] **(11).**

273.1 mg (0.375 mmol) of $Me_3Sn-CDT_{EH}-SnMe_3$, 164.0 mg (0.357 mmol) of Br-Th-PT-Th-Br and 10 mg of $Pd(PPh_3)_4$ were added to the microwave tube and subject to the procedure outline above. Yield: 220 mg (88 %). M_n = 18 kg/mol, PDI = 2.0. **Anal. Calcd.** for $C_{40}H_{47}N_3S_5$: C, 65.80; H, 6.49; N, 5.76. Found: C, 63.8; H, 5.77; N, 5.77. **^{1}H NMR** (o-$C_6D_4Cl_2$, 400K): δ 8.62 (s, 1H, C*H*), 8.45 (s, 1H, C*H*), 7.96 (s, 1H, C*H*), 7.32 (s, 2H, C*H*), 7.27 (s, 2H, C*H*), 2.01 (br m, 4H), 1.10 (br m, 17H), 0.75 (br m, 13H). **UV-vis**: (*o*-DCB) λ_{max} = 680, 450 nm, λ_{onset} = 855 nm, ε = 38100, 22500 $cm^{-1}M^{-1}$.

General Procedure for BCF reactions

NMR Data:

NMR Characterization of 8-($B(C_6F_5)_3$): A glass NMR tube was charged with $B(C_6F_5)_3$ (0.012 g, 0.023 mmol), **8** (0.020 g, 0.023 mmol) and CD_2Cl_2 (0.75 mL). The resulting blue-green solution was vigorously shaken for 5minutes and the product analyzed via NMR spectroscopy. Spectra at 300K broadened due to equilibrium between free and bound $B(C_6F_5)_3$, Keq (280K) = 1.3 x 10^2 M^{-1}. **^{1}H NMR** (CD_2Cl_2, 300K): δ 8.82 (br, 1H, $\mathrm{C}H$), 8.56 (br, 1H, $\mathrm{C}H$), 8.82 (br, 1H, $\mathrm{C}H$), 8.07 (s, 1H, $\mathrm{C}H$), 7.36 (d, 1H, $^3J_{H-H}$ = 7 Hz, $\mathrm{C}H$), 7.30 (br, 1H, $\mathrm{C}H$), 7.05 (d, 1H, $^3J_{H-H}$ = 5 Hz, $\mathrm{C}H$), 7.03 (d, 1H, $^3J_{H-H}$ = 5 Hz, $\mathrm{C}H$), 1.97 (m, 8H, C-$\mathrm{C}H_2$), 1.21 (m, 24H, alkyl-$\mathrm{C}H_2$), 1.07 (m, 8H, alkyl-$\mathrm{C}H_2$), 0.83 (m, 12H, alkyl-$\mathrm{C}H_3$). **^{19}F NMR** (CD_2Cl_2, 300K): δ -128.2 (br s, 6F, *ortho*-$\mathrm{C_6}F_5$), -143.8 (br s, 6F, *para*-$\mathrm{C_6}F_5$), -160.9 (br s, 6F, *meta*-$\mathrm{C_6}F_5$).

^{1}H NMR (CD_2Cl_2, 230K): δ 9.00 (m, 1H, PT-$\mathrm{C}H$), 8.17 (s, 1H, Th-$\mathrm{C}H$), 7.40 (d, $^3J_{H-H}$ = 5 Hz, 1H, Th-$\mathrm{C}H$), 7.33 (d, $^3J_{H-H}$ = 5 Hz, 1H, Th-$\mathrm{C}H$), 7.02 (m, 2H, Th-$\mathrm{C}H$), 6.83 (s, 1H, Th-$\mathrm{C}H$), 1.89 (m, 4H, C-$\mathrm{C}H_2$), 1.73 (m, 2H, C-$\mathrm{C}H_2$), 1.48 (m, 2H, C-$\mathrm{C}H_2$), 1.23-0.94 (m, 32H, alkyl-$\mathrm{C}H_2$), 0.82 (m, 6H, alkyl-$\mathrm{C}H_3$). 0.76 (m, 6H, alkyl-$\mathrm{C}H_3$). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 230K): 161.1, 160.8, 157.7, 154.5, 153.0 (s, quaternary), 148.8 (dm, *C*F), 147.6 (s, quaternary), 146.8 (dm, *C*F), 142.8, 142.5 (s, quaternary), 136.6 (*C*H), 135.5, 134.2, 133.8 (s, quaternary), 128.9, 128.5, 127.8, 126.4 (*C*H), 124.5, 122.3 (s, quaternary), 122.0 (*C*H), 53.9 (s, quaternary, bridged C), 53.3 (s, quaternary, bridged C), 37.7, 37.6, 35.9, 35.8, 31.9, 31.83, 31.81, 31.4, 29.84, 29.82, 29.79, 24.9, 24.63, 24.56, 24.50, 23.1, 22.90, 22.88, 14.21, 14.19, 14.18, 14.16 (s, alkyl $C\mathrm{H_2}$ and $C\mathrm{H_3}$). **^{11}B {^{1}H} NMR** (CD_2Cl_2, 230K): δ -4 (bs). **^{19}F NMR** (CD_2Cl_2, 230K): δ -125.35 (m, 1F, *ortho*-$\mathrm{C_6}F_5$), -128.43 (m, 1F, $^3J_{\mathrm{F-F}}$ = 22 Hz, *ortho*-$\mathrm{C_6}F_5$), -130.53 (m, 1F, *ortho*-$\mathrm{C_6}F_5$), -132.20 (m, 1F, $^3J_{\mathrm{F-F}}$ = 22 Hz, *ortho*-$\mathrm{C_6}F_5$), -134.62 (m, 1F, $^3J_{\mathrm{F-F}}$ = 22 Hz, *ortho*-$\mathrm{C_6}F_5$), -136.07 (m, 1F, *ortho*-$\mathrm{C_6}F_5$), -154.23 (m, 1F, $^3J_{\mathrm{F-F}}$ = 24 Hz, *para*-$\mathrm{C_6}F_5$), -156.83 (m, 1F, $^3J_{\mathrm{F-F}}$ = 24 Hz, *para*-$\mathrm{C_6}F_5$), -157.73 (m, 1F, $^3J_{\mathrm{F-F}}$ = 24 Hz, *para*-$\mathrm{C_6}F_5$), -161.83 (m, 1F, $^3J_{\mathrm{F-F}}$ = 22 Hz, *meta*-$\mathrm{C_6}F_5$), -162.63 (m, 1F, *meta*-$\mathrm{C_6}F_5$), -164.17 (m, 1F, $^3J_{\mathrm{F-F}}$ = 22 Hz, *meta*-$\mathrm{C_6}F_5$), -164.98 (m, 2F, *meta*-$\mathrm{C_6}F_5$), -165.48 (m, 1F, $^3J_{\mathrm{F-F}}$ = 24 Hz, *meta*-$\mathrm{C_6}F_5$).

NMR Characterization of 9-($B(C_6F_5)_3$): A glass NMR tube was charged with $B(C_6F_5)_3$ (0.012 g, 0.023 mmol), **9** (0.025 g, 0.023 mmol) and CD_2Cl_2 (0.75 mL). The resulting green-blue solution was vigorously shaken for 5minutes and the product analyzed via NMR spectroscopy. Spectra at 300K broadened due to equilibrium between free and bound $B(C_6F_5)_3$, Keq (280K) = 2.8 x10^2 M^{-1}. **^{1}H NMR** (CD_2Cl_2, 230K): δ 9.05 (m, 1H, PT-$\mathrm{C}H$), 7.88 (s, 1H, Th-$\mathrm{C}H$), 7.29 (m, 1H, Th-$\mathrm{C}H$), 7.27 (m, 1H, Th-$\mathrm{C}H$), 7.25 (m, 1H, Th-$\mathrm{C}H$), 7.23 (s, 1H, Th-$\mathrm{C}H$), 7.00 (d, 1H, $^3J_{H-H}$ = 5 Hz, Th-$\mathrm{C}H$), 6.98 (d, 1H, $^3J_{H-H}$ = 5 Hz, Th-$\mathrm{C}H$), 6.96 (d, 1H, $^3J_{H-H}$ = 5 Hz, Th-$\mathrm{C}H$), 6.94 (s, 1H, Th-$\mathrm{C}H$), 6.83 (br s, 1H, Th-$\mathrm{C}H$), 1.84 (m, 8H, C-$\mathrm{C}H_2$), 1.18-1.04 (m, 24H, alkyl-$\mathrm{C}H_2$), 0.95-0.81 (m, 8H, alkyl-$\mathrm{C}H_3$). 0.76 (m, 12H, alkyl-$\mathrm{C}H_3$). **^{11}B {^{1}H} NMR** (CD_2Cl_2, 230K): δ -5 (bs).**^{19}F NMR** (CD_2Cl_2, 230K): δ -125.49 (m, 1F, *ortho*-$\mathrm{C_6}F_5$), -128.79 (br s, 1F, *ortho*-$\mathrm{C_6}F_5$), -130.24 (m, 1F, *ortho*-$\mathrm{C_6}F_5$), -132.24 (m, 2F, *ortho*-$\mathrm{C_6}F_5$), -136.67 (br s, 1F, *ortho*-$\mathrm{C_6}F_5$), -154.46 (m, 1F, *para*-$\mathrm{C_6}F_5$), -157.08 (m, 1F, *para*-$\mathrm{C_6}F_5$), -157.63 (m, 1F, *para*-$\mathrm{C_6}F_5$), -161.80 (m, 1F, *meta*-$\mathrm{C_6}F_5$), -162.96 (m, 1F, *meta*-$\mathrm{C_6}F_5$), -164.27 (m, 1F, *meta*-$\mathrm{C_6}F_5$), -164.68 (m, 2F, *meta*-$\mathrm{C_6}F_5$), -164.88 (m, 1F, $^3J_{\mathrm{F-F}}$ = 24 Hz, *meta*-$\mathrm{C_6}F_5$).

Attempted NMR Characterization of 10-($B(C_6F_5)_3$): A glass NMR tube was charged with $B(C_6F_5)_3$ (0.010 g), **10** (0.025 g, 0.023 mmol) and C_6D_5Br (1 mL) , forming a 2% by weight solution. The resulting green solution was vigorously shaken for 5minutes and the reaction analyzed via NMR spectroscopy. The ^1H NMR spectrum exhibited two significantly broadened aromatic resonances compared to neat **10** solution, while the ^{19}F NMR spectrum showed primary resonances attributed to free $B(C_6F_5)_3$. Upon cooling to 260K, the four broad aromatic resonances could be detected in the ^1H NMR spectrum, while several new small broad resonances emerged in the ^{19}F NMR spectrum. These results indicated that exchange likely exits between free and bound (P2- $B(C_6F_5)_3$ adduct) $B(C_6F_5)_3$ at room temperature, with the unbound form being significantly favored. Upon cooling adduct formation begins to become favored. Unfortunately, due to the fact that P2 is only soluble in halogenated aromatic solvents that freeze below 250K, we were unable to investigate this process further.

Regeneration of oligomers 8 and 9: Recovery of oligomers were identical and thus only the method for one is reported. Solutions of **8-$B(C_6F_5)_3$** were collected into a flask and diluted with excess pyridine to quench all borane. All volatiles were removed *in vacuo*. The resulting solids were slurred in hexanes and the filtered through celite. The precipitate was discarded and the filtrate loaded onto silica and eluted with hexanes via flash chromatography. The hexane fractions absorbing at 365 nm were collected and reduced to give crude **8**. Precipitation in methanol and collection by filtration gave pure **8**, as determined by NMR spectroscopy.

Regeneration of polymers: Recovery of polymers were identical and thus only the method for one is reported. Solutions of **10-$B(C_6F_5)_3$** were collected into a flask and diluted with excess pyridine to quench all borane. The solutions were concentrated under vacuum and methanol (~50 mL per ml of polymer solution) was added resulting in precipitation. The precipitate was collected via filtration and washed with copious amounts of methanol, acetone, and hexanes. Upon drying under high vacuum, **10** was obtained as determined by absorption spectroscopy and elemental analysis.

Calculation of equilibrium constants, Keq for the following equilibrium:

8 **8-B(C$_6$F$_5$)$_3$**

Equilibrium concentrations of **8**, $B(C_6F_5)_3$, and **8**-$B(C_6F_5)_3$ were determined via ^{1}H NMR spectroscopy at 280K. Solutions were generated by adding **8** (0.023 mmol), $B(C_6F_5)_3$ (0.023 mmol), and dry CD_2Cl_2 (0.75mL) to a NMR tube under N_2. The NMR tube was vigorously shaken, inserted into the NMR probe re-cooled to 280K and allowed to equilibrate for 30 minutes. ^{1}H NMR spectra (64 scans, 10 second pulse delay) were collected at 280K. Reliable integration could not be obtained above 280K due to significant line broadening due to chemical exchange. The ratio of free and bound 8 was calculated from the integration of ^{1}H NMR signals for the aromatic PT resonances of each species at 280K. For concentration determination, it was assumed [8] = [$B(C_6F_5)_3$], and that the ^{1}H NMR chemical shift for all PT protons is directly proportional to the mole fraction of the total species present as free or bound **8**. The ratio of **8:8-**$B(C_6F_5)_3$ was determined to be 0.6:1.

	[8] +	$[B(C_6F_5)_3]$ $\rightleftharpoons$	$[8\text{- }B(C_6F_5)_3]$
Initial:	0.31 M	0.031 M	0
Change:	- 0.019 M	- 0.019 M	+ 0.019 M
Final	0.012 M	0.012 M	0.019 M

$$K_{eq} = \frac{[8\text{- }B(C_6F_5)_3]}{[8][\,B(C_6F_5)_3]} = \frac{0.019\text{ M}}{0.012\text{ M}^2} = 1.3 \times 10^2\text{ M}^{-1}$$

A similar method was used to calculate the equilibrium concentrations of **9**, $B(C_6F_5)_3$, and **9**-$B(C_6F_5)_3$. Here the ratio of **9:9-**$B(C_6F_5)_3$ was determined to be 0.4:1. The K_{eq} was calculated to be 2.8×10^2 M^{-1}

NMR spectra:

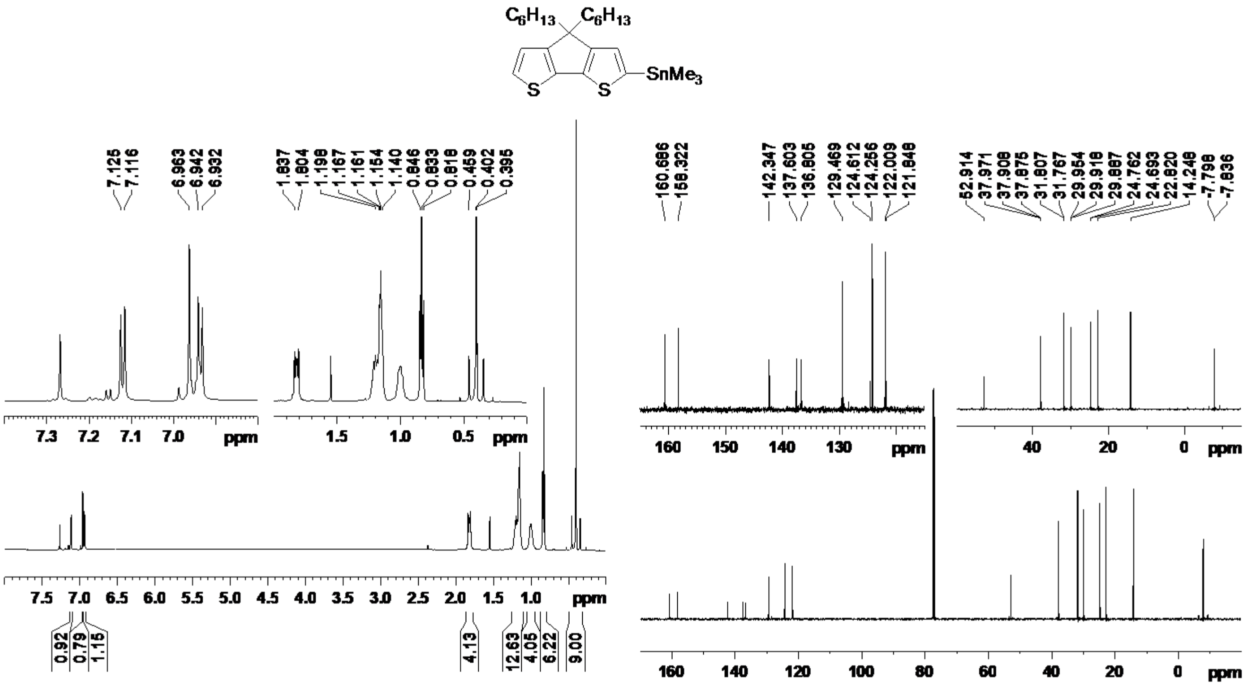


Figure S1. ^1H and ^{13}C NMR spectra of **4** in $CDCl_3$ at 300K. Resonance at 1.5 ppm in ^1H spectrum attributed to water from the solvent.

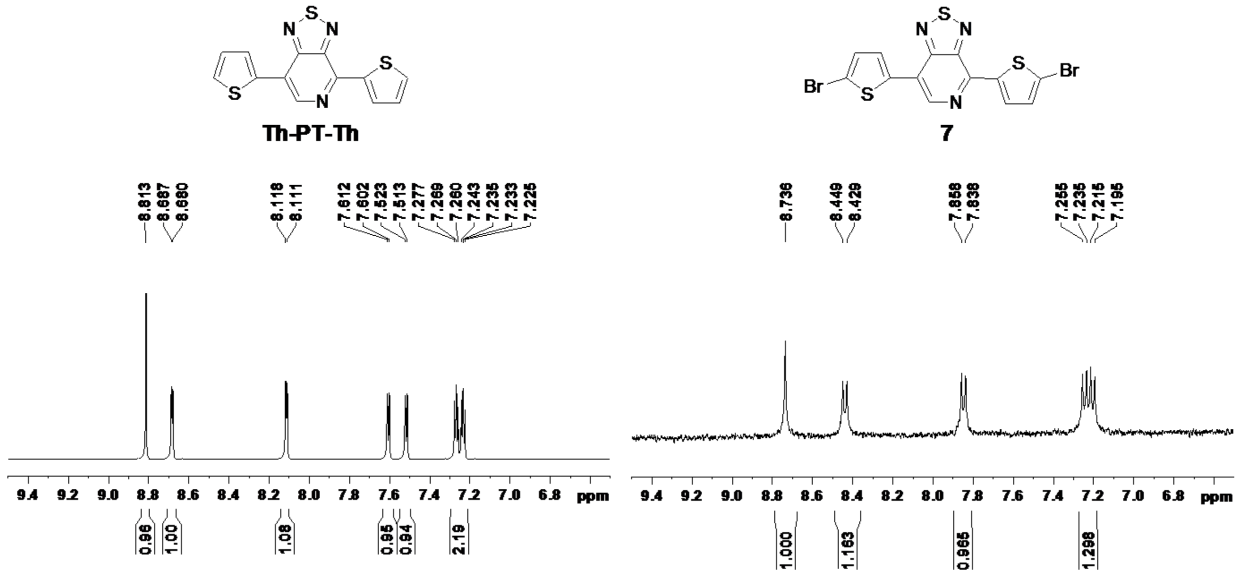


Figure S2. Aromatic region of the ^{1}H NMR spectra of the organic intermediates Th-PT-Th (left) and 7 (right) in CD_2Cl_2 at 300K.

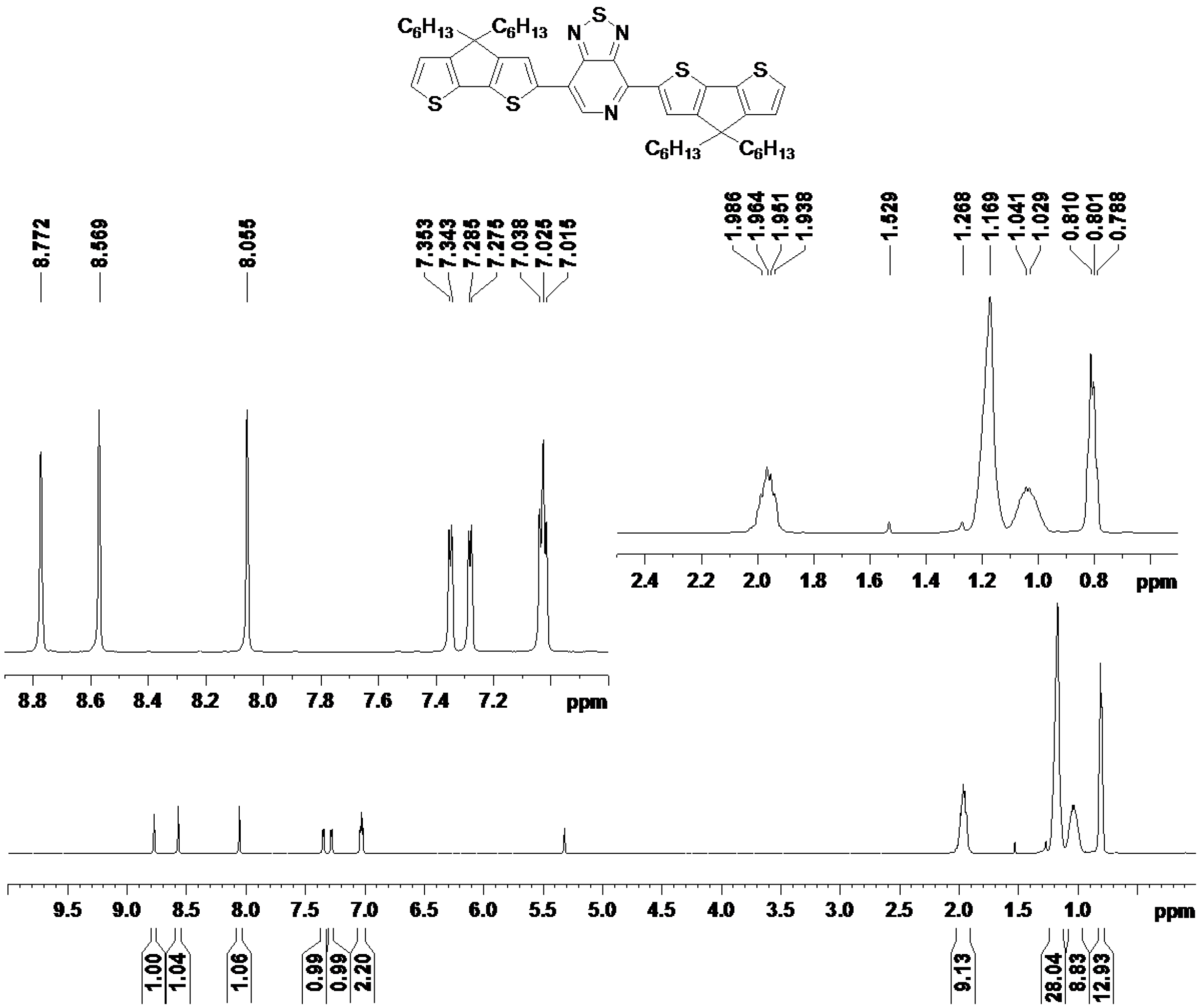


Figure S3 ^{1}H NMR spectra of **8** at 300K in CD_2Cl_2. Aromatic region of ^{1}H NMR spectra exhibits 7 in-equivalent aromatic proton resonances.

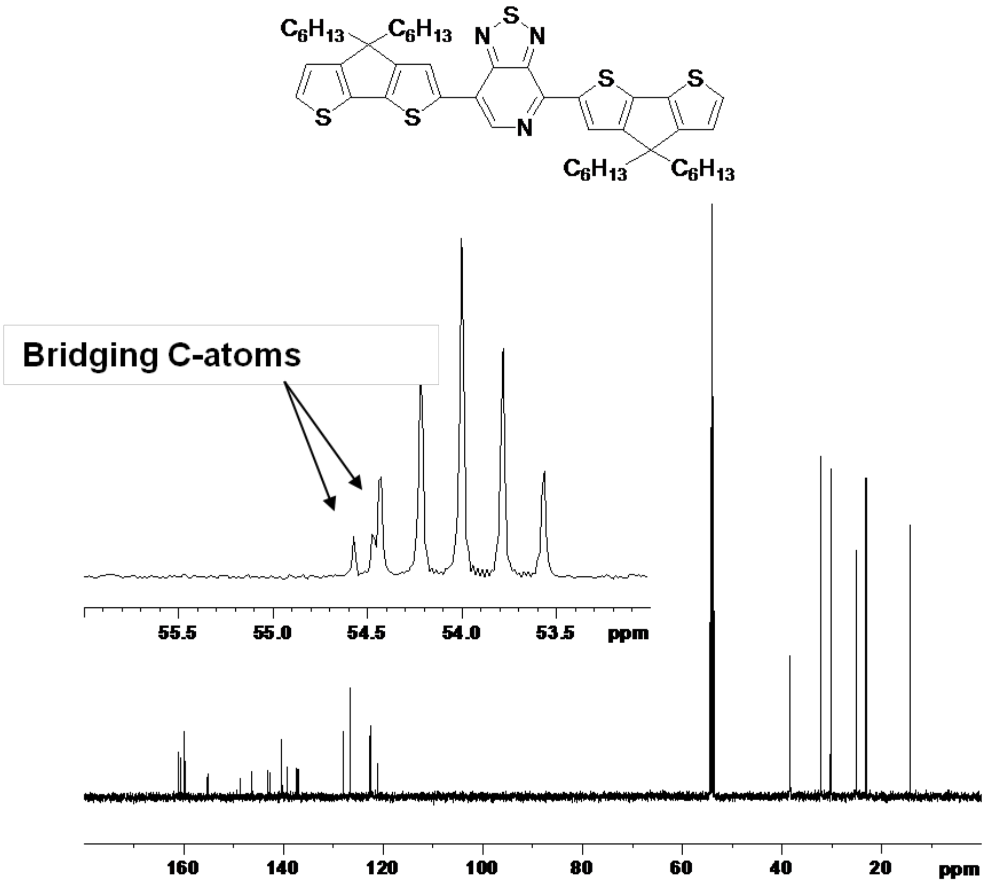


Figure S4. ^{13}C NMR spectra of **8** at 300K in CD_2Cl_2. Two in-equivalent thiophene bridging carbons atoms observed.

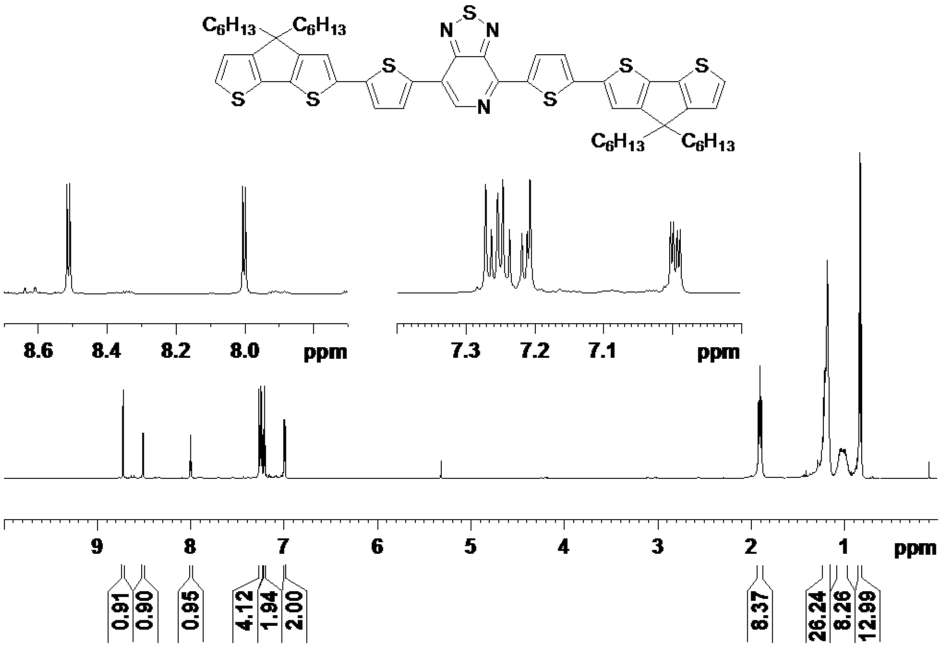


Figure S5. ^{1}H NMR spectra of **9** at 300K in CD_2Cl_2. Aromatic region of ^{1}H NMR spectra exhibits 11 aromatic proton resonances.

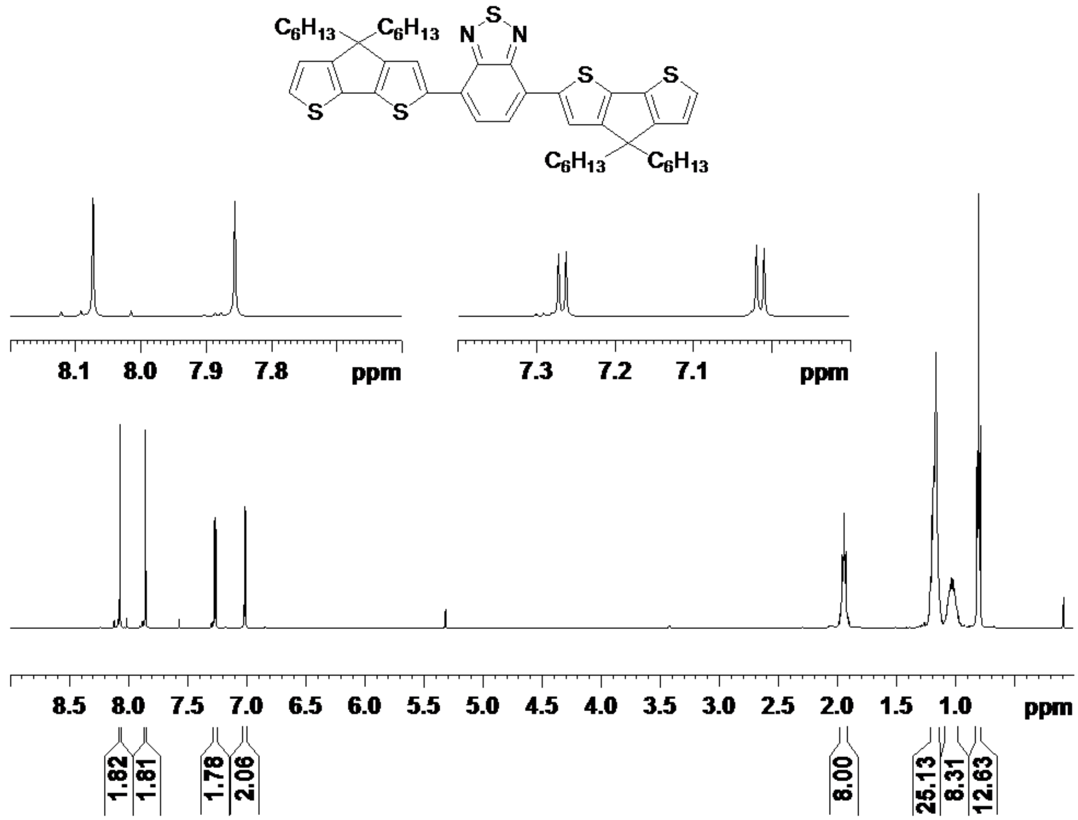


Figure S6. ^{1}H NMR spectra of **3** at 300K in CD_2Cl_2. Aromatic region of ^{1}H NMR spectra exhibits 4 aromatic proton resonances, consistent with a symmetric structure.

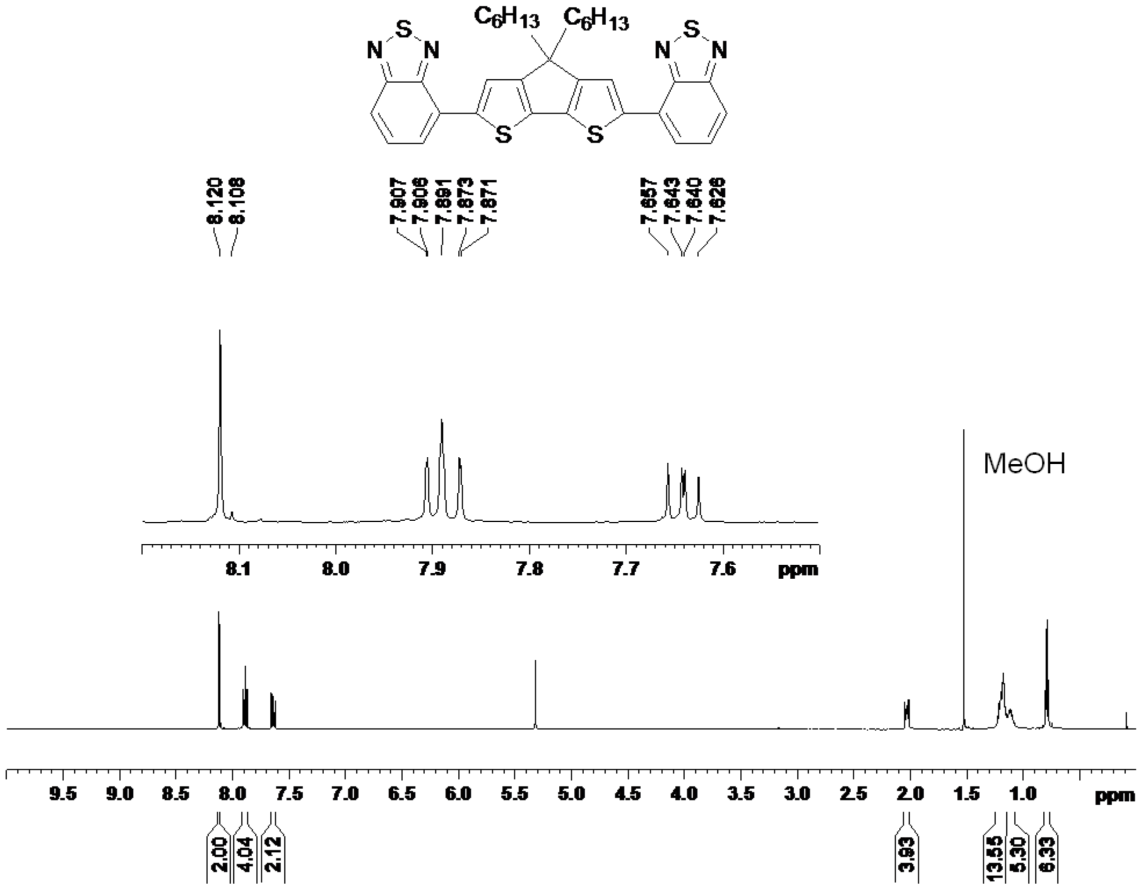


Figure S7. ^{1}H NMR spectra of **2** at 300K in CD_2Cl_2. Aromatic region of ^{1}H NMR spectra exhibits 4 aromatic proton resonances, consistent with a symmetric structure.

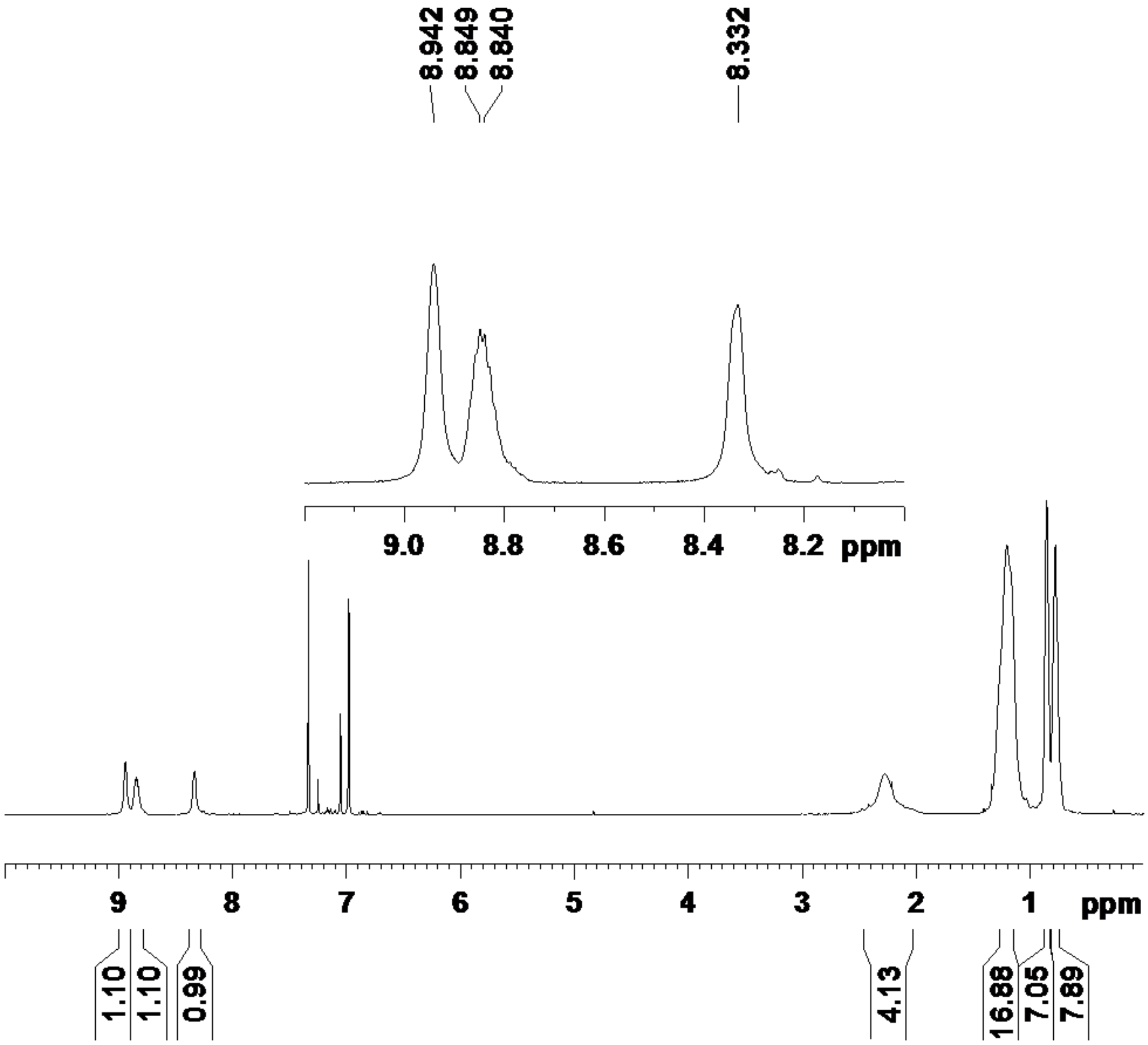


Figure S8. ^{1}H NMR spectra of polymer **10** at 300K in C_6D_5Br. Aromatic region of ^{1}H NMR spectra exhibits 3 aromatic proton resonances.

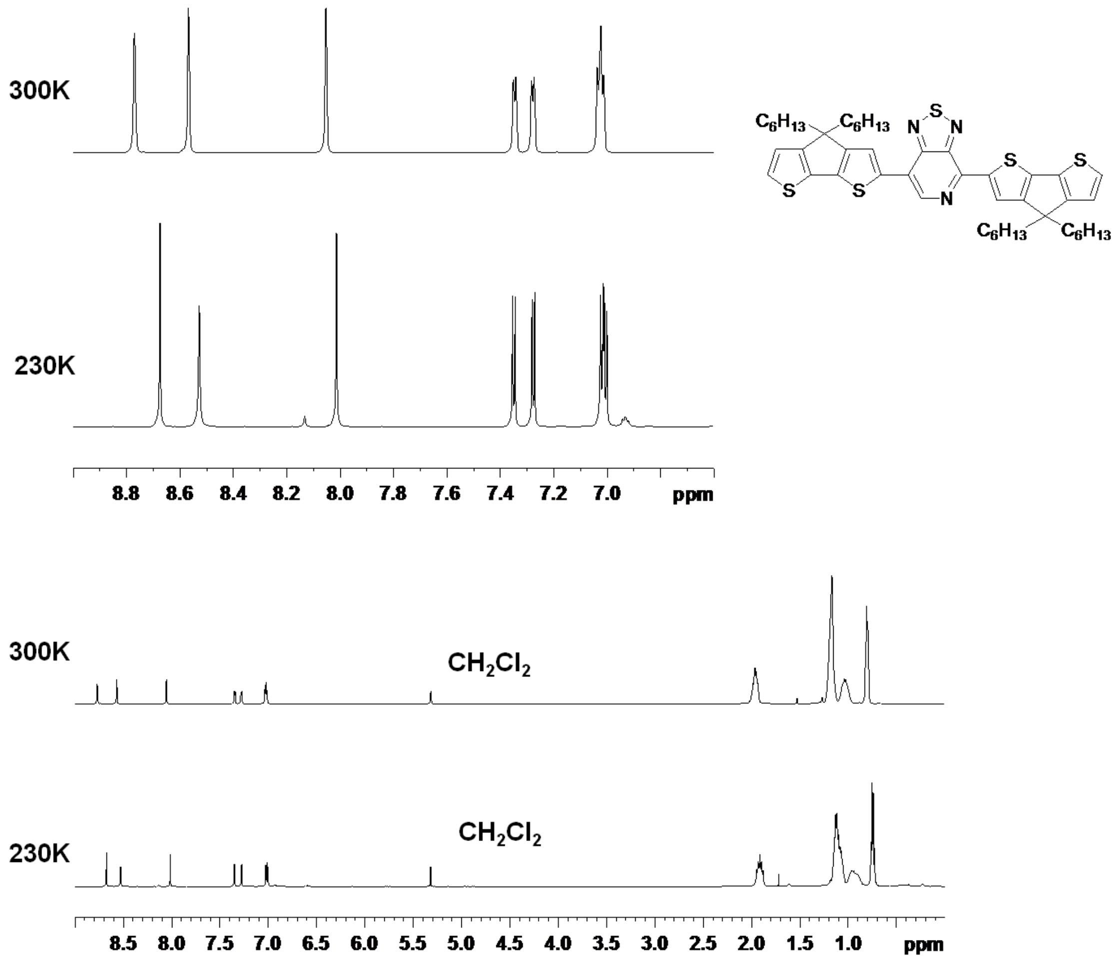


Figure S9. ^{1}H NMR spectra of **8** at 300K and 230K in CD_2Cl_2. Aromatic region of ^{1}H NMR spectrum shown at top. Compound **8** only shows minor temperature dependent ^{1}H NMR spectroscopy.

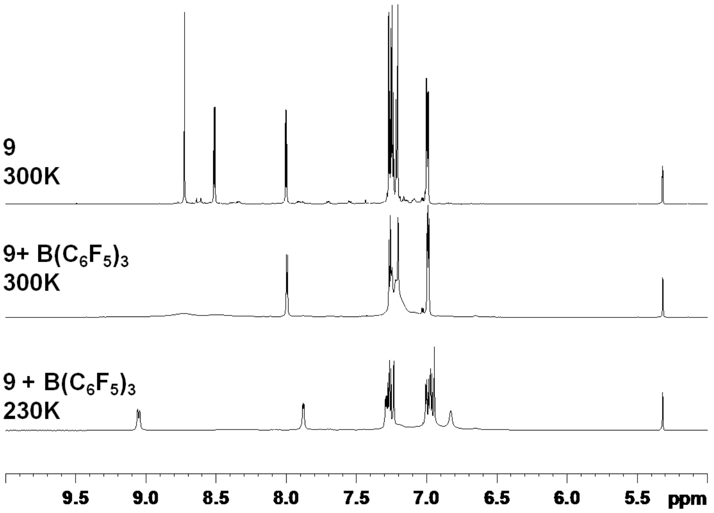


Figure S10. ^{1}H NMR spectra of **9** at 300K and **9** plus 1 eq. of $B(C_6F_5)_3$ at 300K and 230K in CD_2Cl_2 (5.32 ppm). Only aromatic region of ^{1}H NMR spectrum shown.

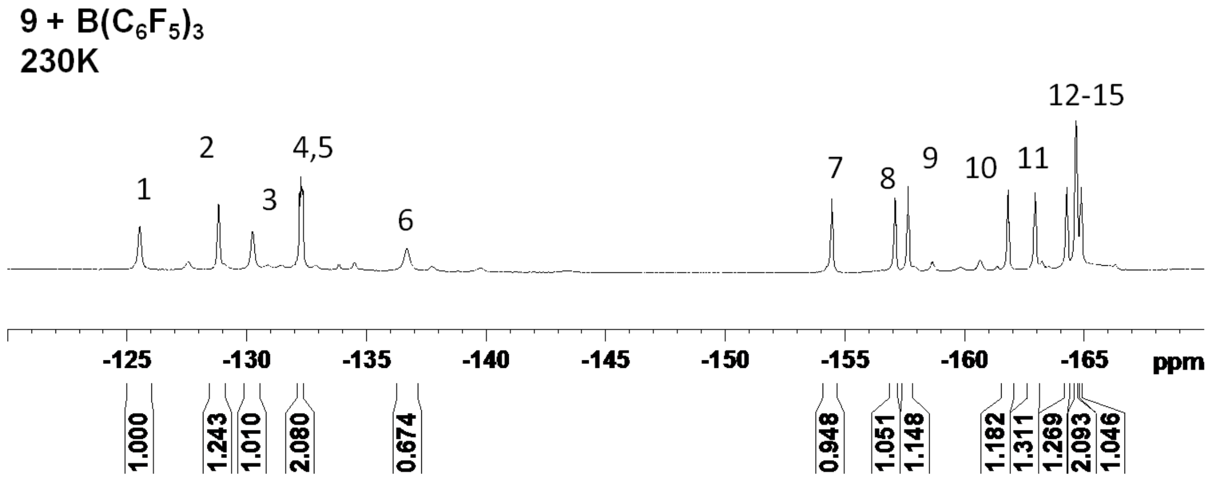


Figure S11. ^{19}F NMR spectra of **9** plus 1 eq. of $B(C_6F_5)_3$ 230K in CD_2Cl_2. Spectrum shows 15 in equivalent F-atoms

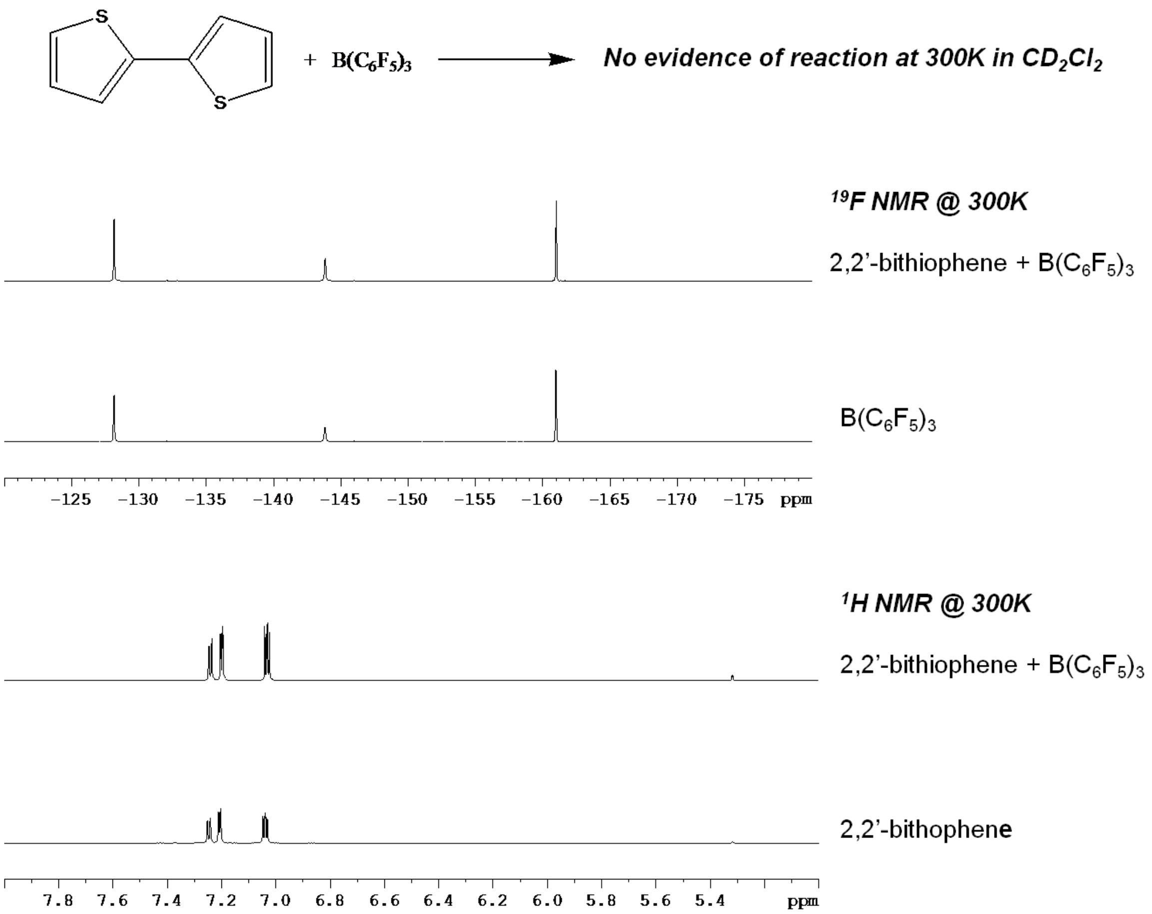


Figure S12. ${}^{19}F$ NMR spectrum of $B(C_6F_5)_3$ at 300K in CD_2Cl_2 solution, ${}^{1}H$ NMR spectrum of 2,2’-bithiophene at 300K in CD_2Cl_2 solution, and the ${}^{19}F$ and ${}^{1}H$ NMR spectra of a equal molar amounts of 2,2’-bithiophene and $B(C_6F_5)_3$ at 300K in CD_2Cl_2 solution.

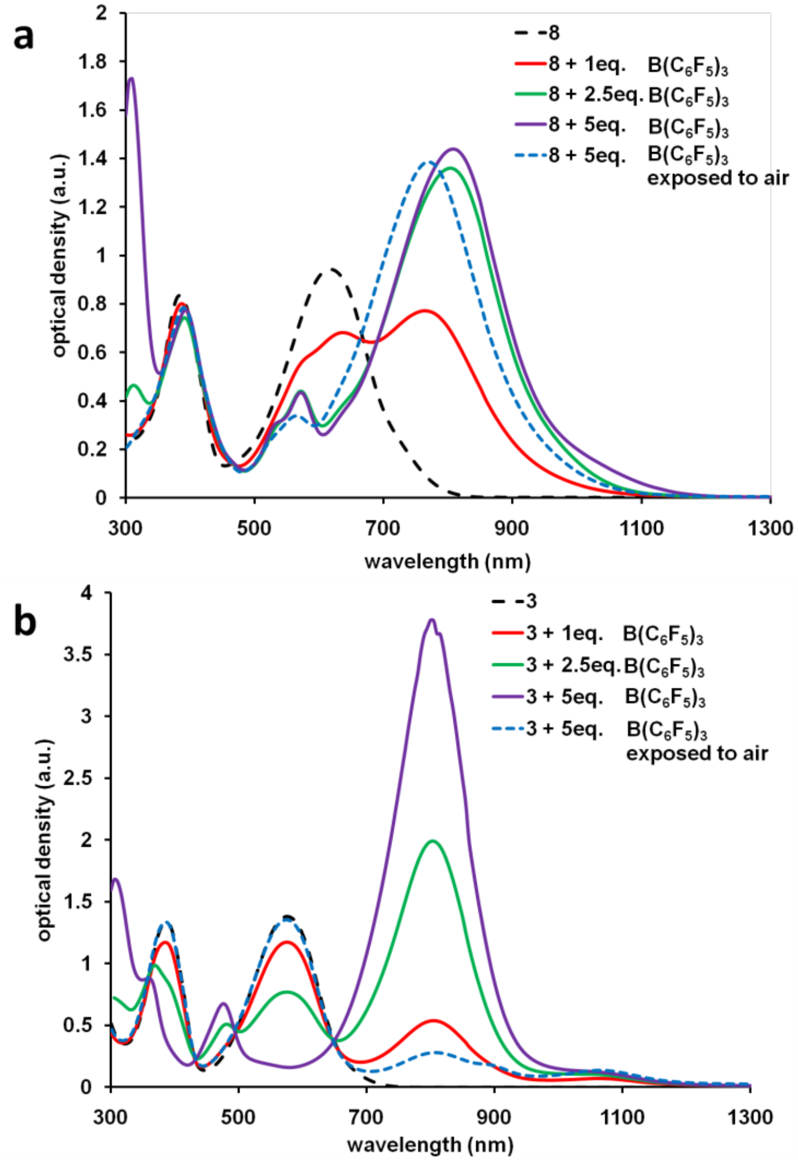


Figure S13. 8 (a) and **3** (b) with varying molar equivalent of $B(C_6F_5)_3$ in 1,2-dichlorobenzne solution at room temperature under N_2 and after exposure to atmosphere for 60 minutes.

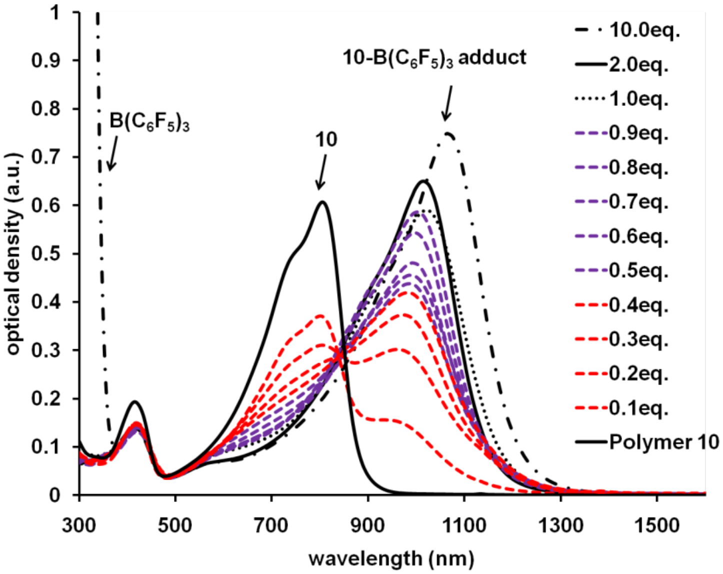


Figure S14. Polymer **10** with varying weight equivalent of $B(C_6F_5)_3$ in 1,2-dichlorobenzne solution at room temperature under N_2.

Electrochemistry:

Table S1 Summary of electrochemical data for 8, 9, 10 and 11.

Materials	E_{onset}[a] (V)	$E_{1/2}$[b] (V)	HOMO (eV)	E_{onset}[c] (V)	$E_{1/2}$[d] (V)	LUMO (eV)	E_g[e](eV)
10 (film)	0.72	0.94	-5.12	-0.70	-1.06	-3.70	1.42
11 (film)	0.62	0.86	-5.02	-0.86	-0.96	-3.54	1.48
8 (sol)	0.66	0.75	-5.06	-0.86	-1.03	-3.54	1.52
9 (sol)	0.67	0.74	-5.07	-0.78	-0.98	-3.62	1.45

a) the oxidation onset potential of material; b) the oxidation redox potential $E_{1/2} = (E_{pa} + E_{pc})/2$; c) the reduction onset potential of material; d) the reduction redox potential $E_{1/2} = (E_{pa} + E_{pc})/2$; e) the band gap was calculated using the onset of the oxidation and reduction potential. f) $E(\text{HOMO}) = -(E_{ox}+4.4)$[eV], $E(\text{LUMO}) = -(E_{red}+4.4)$[eV]. HOMO of F_c^+/F_c taken to be 4.88 eV. $E_{1/2}$ of F_c^+/F_c determined to be 0.48 V.

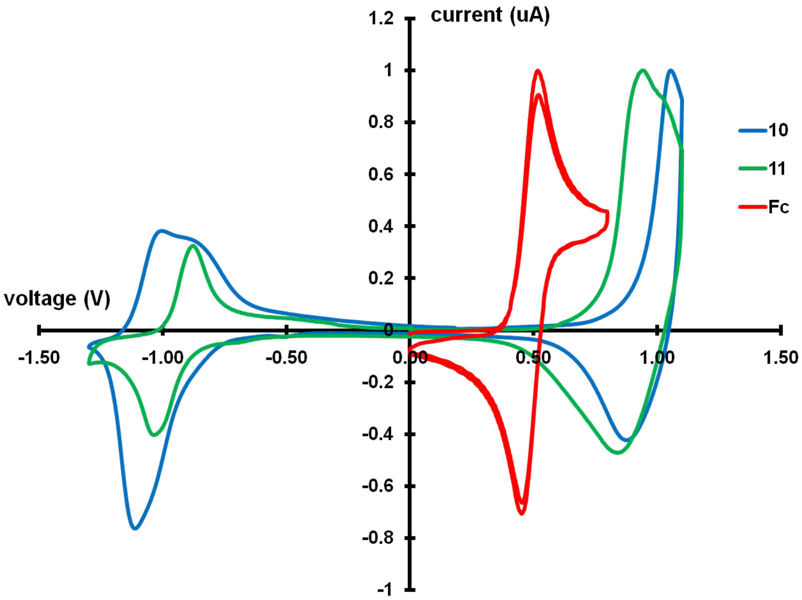


Figure S15. Cyclic voltamagrams for polymers **10** and **11** as thin-films.

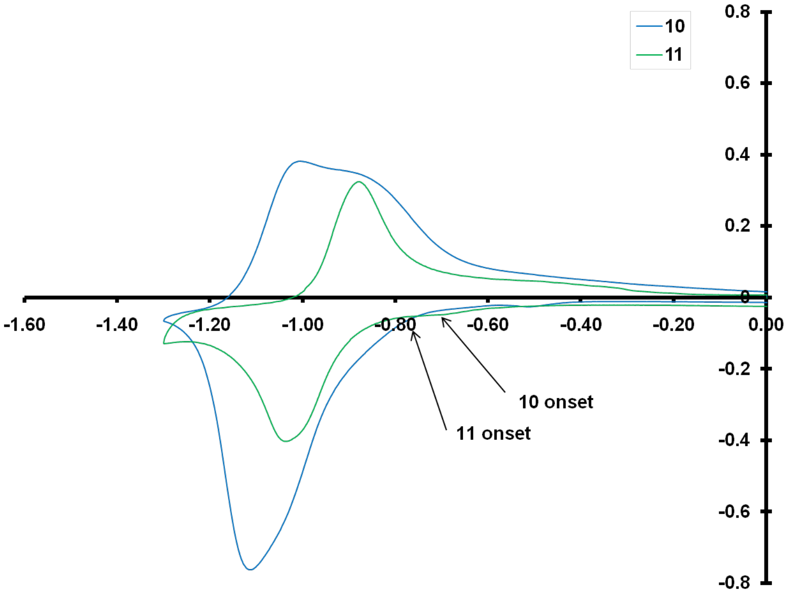


Figure S16. Cyclic voltamagrams for polymers **10** and **11** as thin-films.

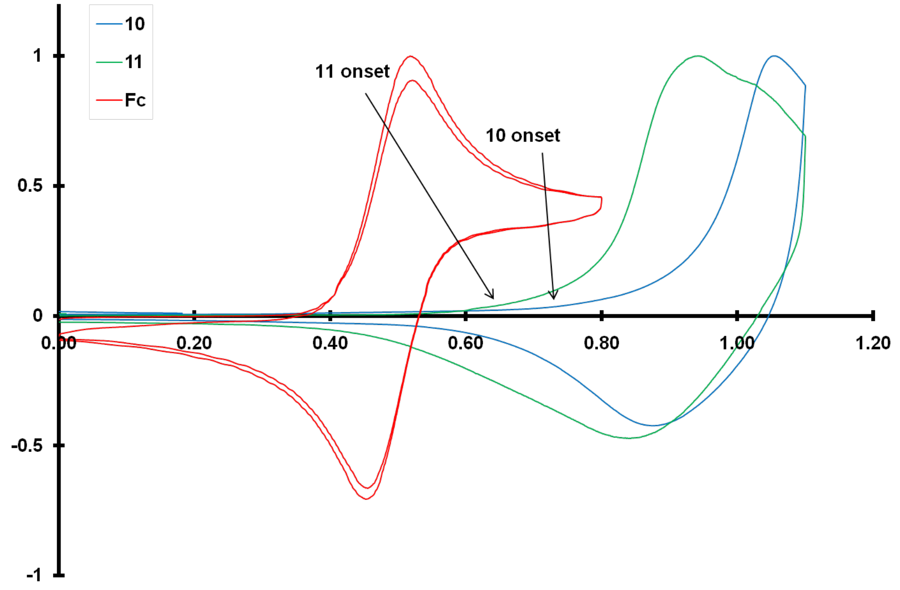


Figure S17. Cyclic voltamagrams for polymers **10** and **11** as thin-films.

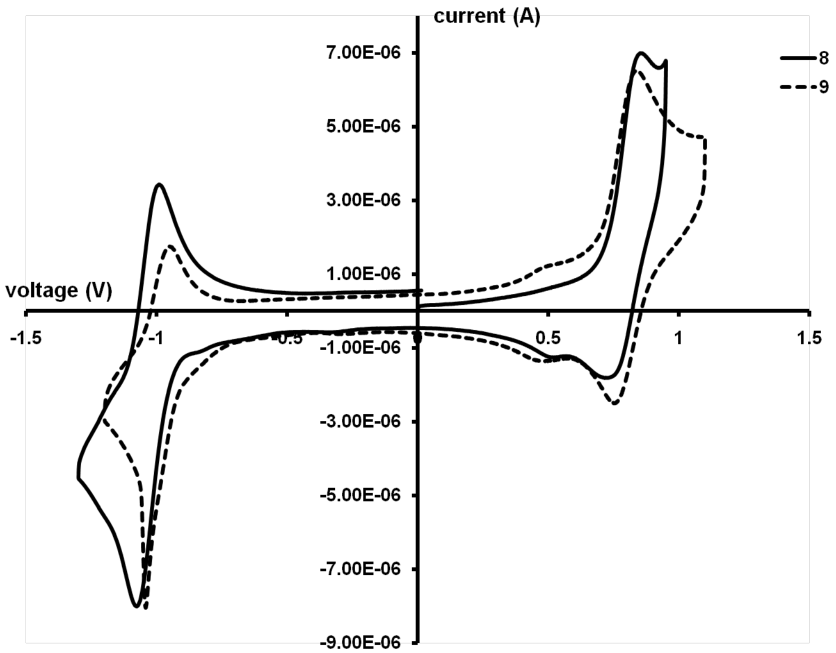


Figure S18. Cyclic voltamagrams for **8** and **9** in solution.

DFT Results

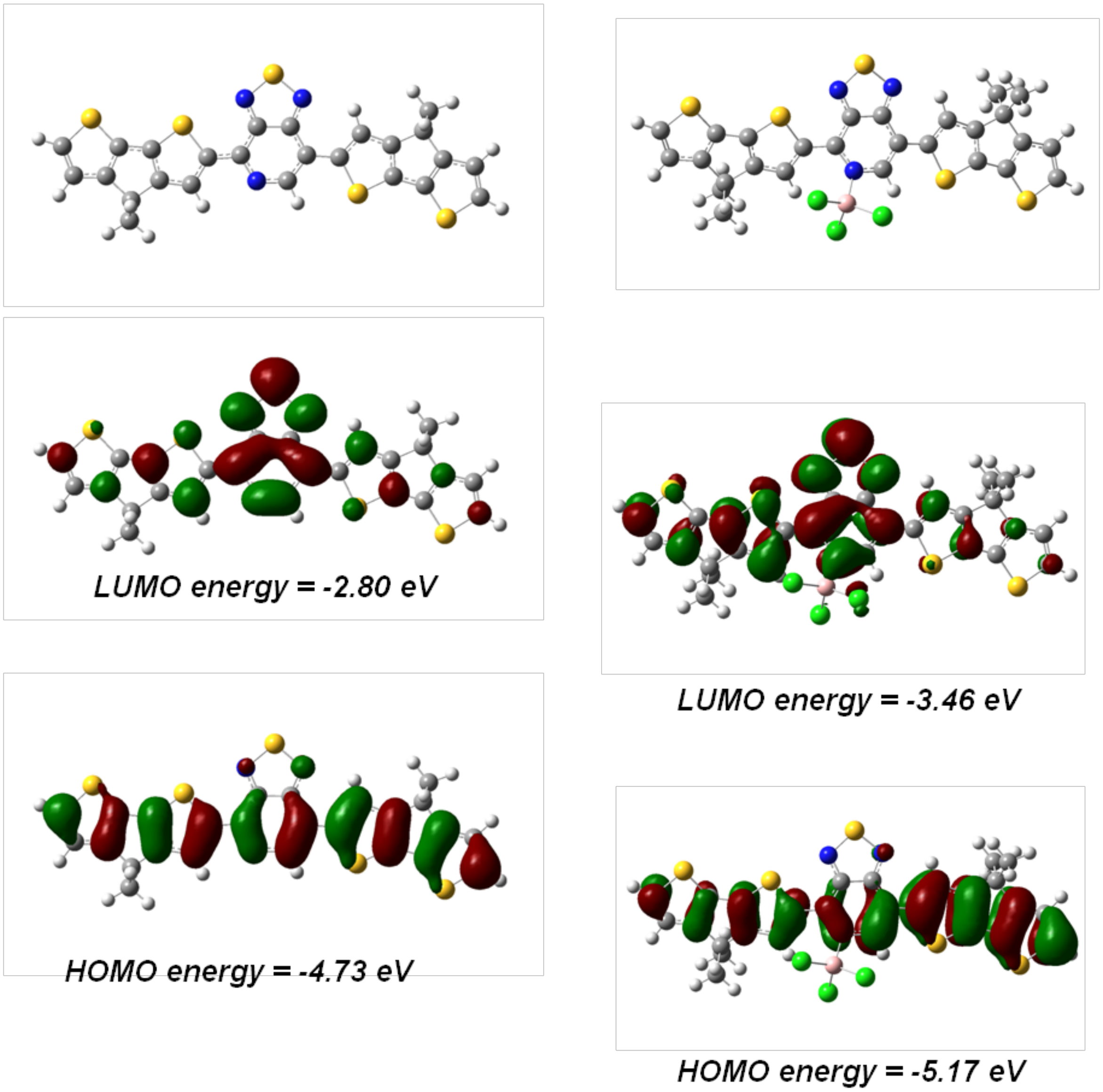


Figure S19. Ground state geometry optimizations **8** (left) and **8**-BCl_3 (right) Methyl groups were used in replace of hexyl side chains on carbon. Carbon: gray, Nitrogen: blue, Sulfur: orange, Boron: pink, Chlorine: green. Optimized structures calculated using DFT at the B3LYP/6-31G(d,p) level of theory.

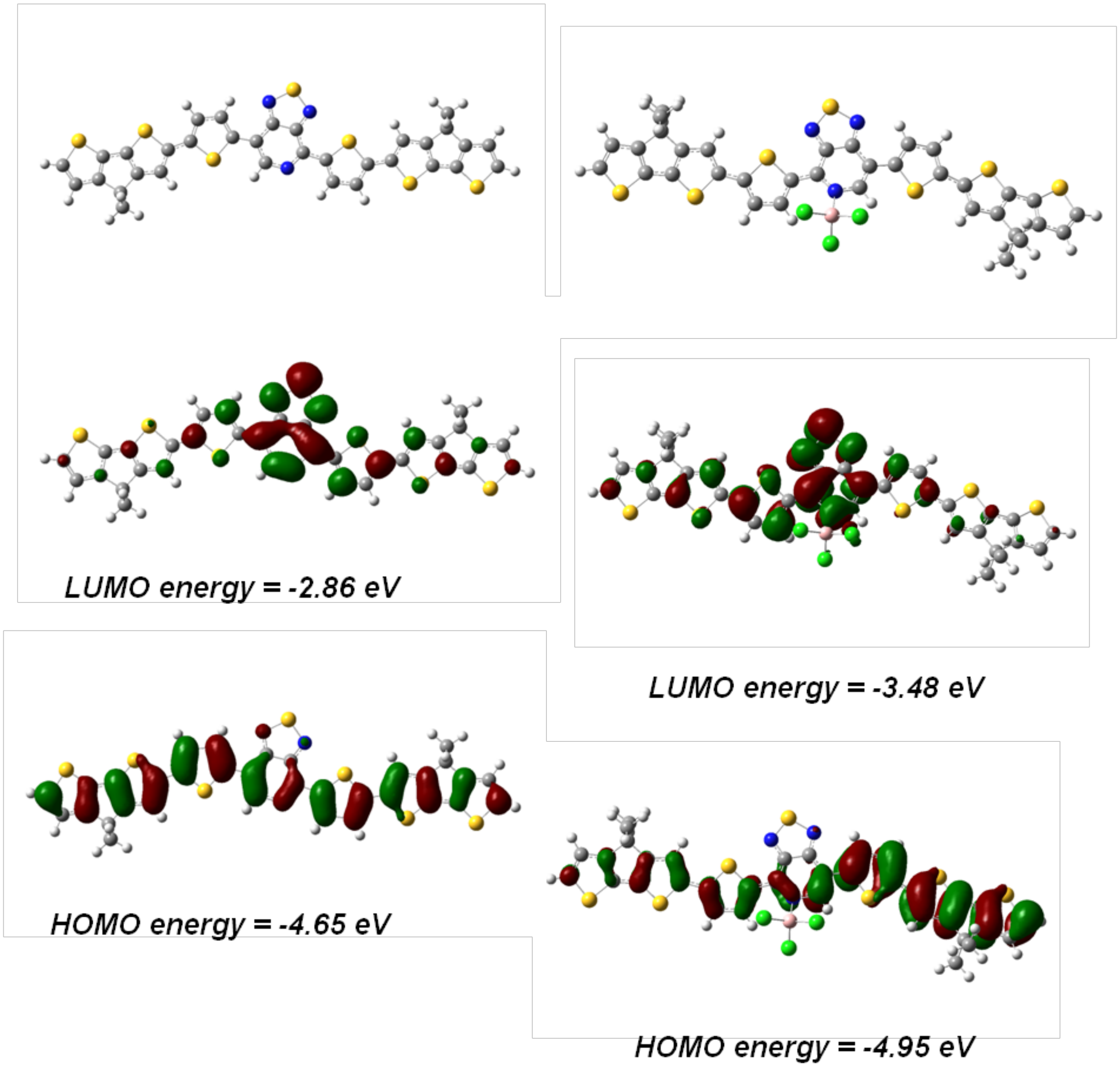


Figure S20. Ground state geometry optimizations **8** (left) and **8**-BCl_3 (right) Methyl groups were used in replace of hexylside chains on carbon. Carbon: gray, Nitrogen: blue, Sulfur: orange. Optimized structures calculated using DFT at the B3LYP/6-31G(d,p) level of theory.

XPS Data:

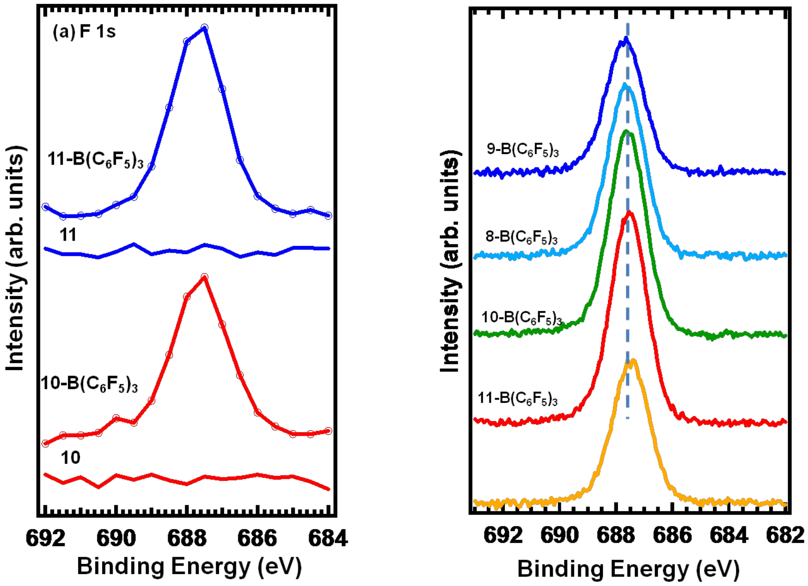


Figure S21. Example data for fluorine (1s) obtained from X-ray photoelectron spectroscopy (XPS) for all polymers and oligomers and their corresponding Lewis acid adducts. This data confirms the incorporation of B(C_6F_5)$_3$ into the oligomer and polymer films.

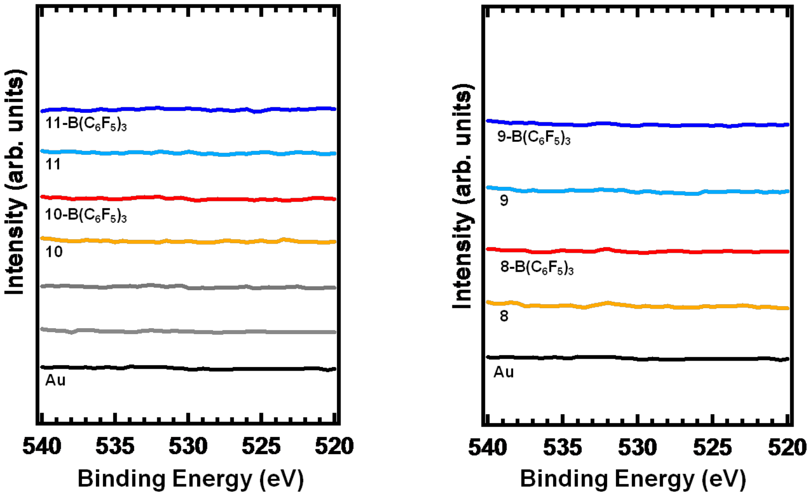


Figure S22. Data for oxygen (1s) obtained from XPS for polymers (left) and oligomers (right) and their corresponding Lewis acid adducts. This data confirms that no hydrolysis of the B-N adducts has occurred in the solid state. Detection of oxygen signals would imply hydrolysis had taken place.

UPS Data:

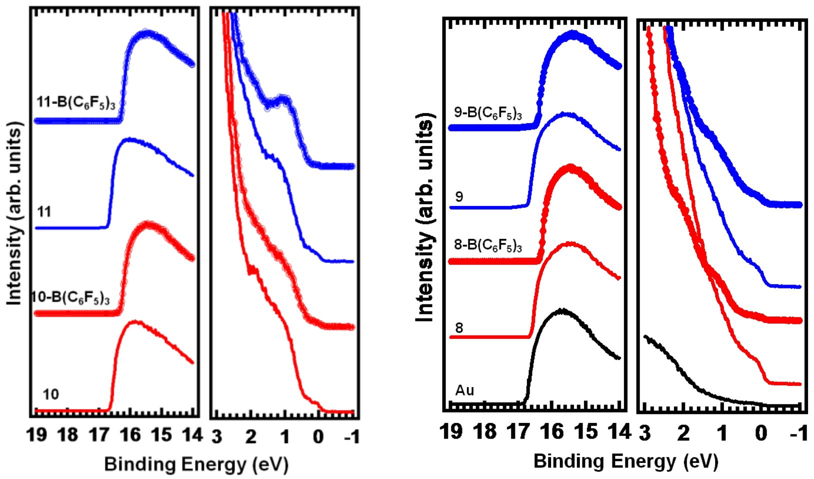


Figure S23. Example data from ultraviolet photoemission spectroscopy (UPS) experiments carried out on polymers 10 and 11 and small molecules 8 and 9 and their corresponding $B(C_6F_5)_3$ adducts.

Full citation for reference 11:

Albota, M.; Beljonne, D.; Bredas, J. L.; Ehrlich, J. E.; Fu, J. Y.; Heikal, A. A.; Hess, S. E.; Kogej, T.; Levin, M. D.; Marder, S. R.; McCord-Maughon, D.; Perry, J. W.; Rockel, H.; Rumi, M.; Subramaniam, C.; Webb, W. W.; Wu, X. L.; Xu, C. *Science* **1998**, *281*, 1653-1656.

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