Supporting Information

Conjugated Polymers Based on 4,10-Bis(thiophen-2-yl)anthanthrone: Synthesis, Characterization and Fluoride-Promoted Photoinduced Electron Transfer

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Experimental

Materials and methods

Chemical reagents were purchased from Sigma-Aldrich Co. Canada, Alfa Aesar Co., TCI America Co. or Oakwood Products Inc. and were used as received. 4,10-dibromoanthanthrone was generously offered by Heubach GmbH as product Monolite Red 316801. The dibrominated monomers were synthesized according to previous literature.[1,2,3,4,5,6] Solvents used for organic synthesis were obtained from Fisher Scientific (except THF from Sigma-Aldrich Co. Canada) and purified with a Solvent Purifier System (SPS) (Vacuum Atmosphere Co., Hawthorne, USA). Other solvents were obtained from Fisher Scientific and were used as received. Toluene and THF used for Stille coupling reactions were degassed 30 minutes prior to use. All anhydrous and air sensitive reactions were performed in oven-dried glassware under positive argon pressure. Analytical thin-layer chromatographies were performed with silica gel 60 F254, 0.25 mm pre-coated TLC plates (Silicycle, Québec, Canada) or basic aluminium oxide 60 F254 TLC (EMD Millipore Corporation). Compounds were visualized using 254 nm and/or 365 nm UV wavelength and/or aqueous sulfuric acid solution of ammonium heptamolybdate tetrahydrate (10 g/100 mL H_2SO_4 + 900 mL H_2O). Flash column chromatographies were performed on 230-400 mesh silica gel R10030B (Silicycle, Québec, Canada) or on Aluminum Oxide Type CG-20 (Sigma-Aldrich). ^{1}H and ^{13}C NMR

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[1] Thiophene, 2,5-dibromo-3-octyl-: D. Hanne et al., *Macromolecules* **2010**, *43*, 10231.

[2] 2,1,3-Benzothiadiazole, 4,7-dibromo-: J. Seonyoung et al., *ACS Appl. Mater. Interfaces* **2014**, *6*, 22884.

[3] 4*H*-Thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione, 1,3-dibromo-5-(2-hexyldecyl)-: A. Najari et al. *Macromol*ecules **2012**, *45*, 1833.

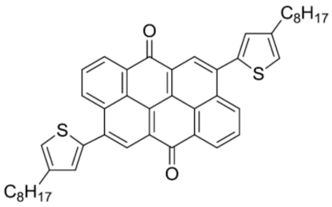
[4] 9*H*-Carbazole, 2,7-dibromo-9-(2-octyldodecyl)-: Müllen et al. *Synthesis* **2003**, *16*, 2470.

[5] Pyrrolo[3,4-*c*]pyrrole-1,4-dione, 3,6-bis(5-bromo-2-thienyl)-2,5-dihydro-2,5-bis(2-octyldodecyl)-: C. Shaoyun et al. *J. Mater. Chem. C* **2014**, *2*, 2183.

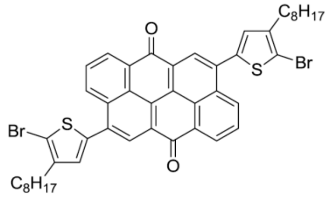
[6] Benzo[1,2-*b*:4,5-*b*']dithiophene, 4,8-bis[(2-ethylhexyl)oxy]- Hong Il, K. et al. *ACS Appl. Mater. Interfaces* **2014**, *6*, 15875.

spectra were recorded on a Varian AS400 apparatus in appropriate deuterated solvent solution at 298 K. Chemical shifts were reported as values (ppm) relative to internal tetramethylsilane or residual solvent peak. Signals are reported as m (multiplet), s (singlet), d (doublet), dd (doublet of doublet), t (triplet), q (quadruplet), h (hexaplet) and br s (broad singlet) and coupling constants are reported in hertz (Hz). High-resolution mass spectra (HRMS) were recorded with an Agilent 6210 Time-of-Flight (TOF) LC-MS apparatus equipped with an ESI or APPI ion source (Agilent Technologies, Toronto, Canada). UV-visible absorption spectra were recorded on a Varian diode-array spectrophotometer (model Cary 500) using 3-mm path length quartz cells. DSC and TGA measurements were done on a Mettler Toledo (DSC 823e and TGA/SDTA851e). GPC analysis was performed using a 2X Mixed BLZ GPC in chloroform. All of the cyclic voltammograms were acquired employing a three-electrodes potentiostat. The potential was referenced to a Ag/AgCl-saturated KCl electrode, and Pt wires were used as the working and counter electrodes. Acetonitrile or Dichloromethane with a supporting electrolyte of Bu_4NPF_6 (0.1 M) was sparged using argon 5 min prior to electrochemical measurements. For calculation of vacuum levels, the potentials were calibrated against a ferrocene/ ferrocenium external standard measured at 0.45 V versus the Ag/AgCl reference electrode.

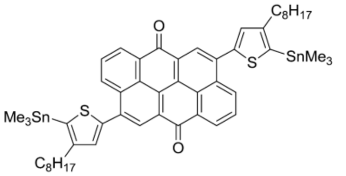
Monomer synthesis



Synthesis of compound 1. A round bottom flask equipped with a magnetic stir bar was charged with dry THF (200 mL), 4,10-dibromoanthanthrone (3.00 g, 6.46 mmol), LiCl (0.137 g, 3.23 mmol) and 4-*n*-octyl-2-thienyltributyltin (7.84 g, 16.2 mmol). The cloudy solution was degassed for 10 min. and $PdCl_2(PPh_3)_2$ (0.227 g, 0.323 mmol) was added. The reaction mixture was heated to reflux for 48h. The reaction was poured in MeOH (200 mL) and then filtrated. The residue was extracted with warm chloroform and the crude product was then purified over a silica gel short plug with chloroform as the eluent to afford compound **1** (2.95 g, 66% yield) as a purple powder. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.77 – 8.69 (m, 4H), 8.52 (s, 2H), 7.87 (dd, *J* = 8.5, 7.3 Hz, 2H), 7.23 (d, *J* = 1.4 Hz, 2H), 7.16 (s, 2H), 2.74 (t, *J* = 7.7 Hz, 4H), 1.74 (p, *J* = 7.5 Hz, 4H), 1.55 (s, 8H), 1.32 (d, *J* = 11.1 Hz, 12H), 0.99 – 0.86 (m, 6H). ^{13}C NMR (126 MHz, $cdcl_3$) δ 182.67, 145.73, 144.14, 139.75, 135.96, 133.90, 132.70, 130.83, 130.42, 129.16, 129.00, 128.97, 127.97, 126.84, 125.53, 122.00, 99.41, 77.26, 77.21, 77.01, 76.75, 46.70, 34.01, 31.93, 30.67, 30.65, 30.63, 29.70, 29.51, 29.48, 29.46, 29.35, 22.71, 21.86, 14.15, 13.63. HRMS (APPI-TOF): m/z calcd for $C_{46}H_{46}O_2S_2$ [M]+: 694.2945, found 694.2993.

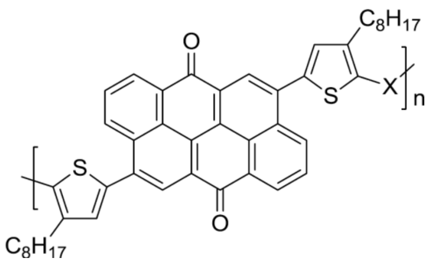


Synthesis of compound 2. A dry round bottom flask equipped with a magnetic stir bar and placed in an ice-water bath was charged with compound **1** (0.800 g, 1.15 mmol), $CHCl_3$ (100 mL), acetic acid (50 mL) and NBS (0.410 g, 2.30 mmol). The reaction was allowed to reach room temperature at stirred overnight. The solvent was removed under vacuo and the crude product was purified by silica gel chromatography with chloroform as the eluent to afford compound **2** (0.798 g, 80% yield) as a red powder. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.59 (dd, *J* = 8.5, 1.2 Hz, 2H), 8.43 – 8.36 (m, 2H), 8.08 (s, 2H), 7.77 (dd, *J* = 8.4, 7.3 Hz, 2H), 7.10 (s, 2H), 2.77 – 2.68 (m, 4H), 1.73 (q, *J* = 7.6 Hz, 6H), 1.50 – 1.35 (m, 8H), 1.32 (s, 10H), 0.94 – 0.86 (m, 6H). ^{13}C NMR (126 MHz, cdcl$_3$) δ 181.83, 143.15, 139.44, 134.85, 133.54, 132.19, 130.79, 130.10, 129.08, 128.69, 128.53, 127.63, 126.52, 125.26, 111.02, 77.26, 77.21, 77.01, 76.75, 31.94, 29.94, 29.81, 29.46, 29.35, 22.72, 22.72, 14.16. HRMS (APPI-TOF): m/z calcd for $C_{46}H_{44}Br_2O_2S_2$ [M+H]+: 851.1188, found 851.1309.



Synthesis of compound 3. A dry round bottom flask equipped with a magnetic stir bar was charged with compound **2** (0.800 g, 0.938 mmol), hexamethylditin (1.23 g, 3.75 mmol) and dry toluene (80 mL). The mixture was degassed for 10 minutes, then $PdCl_2(PPh_3)_2$ (0.033 g, 0.047 mmol) was added and the reaction was heated to 85 °C for 18 h. The reaction mixture was brought to room temperature and diluted with chloroform. The organic layer was washed with water (3x) and dried over Na_2SO_4. Following the removal of the solvent under reduced pressure, the crude product was purified under alumina chromatography using hexanes first as the eluent, and then gradually adding chloroform up to a ratio of 1:1 (hexanes:chloroform) as the eluents to afford compound **3** (0.380 g, 40% yield) as a purple powder. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.61 (dd, *J* = 8.4, 1.3 Hz, 2H), 8.43 (dd, *J* = 7.2, 1.2 Hz, 2H), 8.14 (s, 2H), 7.69 (td, *J* = 10.5, 9.4, 7.6 Hz, 2H), 7.37 (s, 2H), 2.75 (t, *J* = 7.9 Hz, 4H), 1.76 (h, *J* = 7.8, 7.1 Hz, 4H), 1.50 – 1.29 (m, 18H), 0.95 – 0.86 (m, 8H), 0.50 (s, 18H). ^{13}C NMR (101 MHz, cdcl$_3$) δ 212.29, 195.03, 182.14, 168.70, 151.57, 145.38, 135.89, 134.65, 133.79, 132.22, 131.49, 130.53, 128.82, 128.68, 128.61, 127.68, 126.24, 124.98, 109.99, 81.13, 79.22, 77.34, 77.02, 76.70, 49.30, 33.03, 32.36, 31.94, 29.80, 29.63, 29.40, 29.37, 22.72, 14.16, 7.00, -7.68. HRMS (APPI-TOF): m/z calcd for $C_{52}H_{62}S_2Sn_2$ [M-H]-: 1020.2334, found 1020.2187.

General procedure for polymerization by Stille coupling



A dry flask under argon with a magnetic stir bar was charged with compound **3** (0.050 g, 0.049 mmol), dibrominated monomer (0.049 mmol) and dry toluene (5 mL). The mixture was degassed with a flow of N_2 for 10 minutes. $Pd_2(dba)_3$ (2.2 mg, 0.002 mmol), tri(*o*-tolyl)phosphine (3.0 mg, 0.010 mmol) were then added and the reaction mixture was heated at 110°C. Before the reaction was quenched, bromobenzene (16.0 mg, 0.098 mmol) was added as a capping agent and the mixture was heated for 1 h, then trimethyl(phenyl)tin (21 mg, 0.098 mmol) was added and the mixture was heated for an additional hour. Following the completion of the reaction, the mixture was allowed to cool down to room temperature and poured into 100 mL of a 9:1 mixture of methanol and water. The mixture was then filtrated to recover the precipitated polymer. Soxhlet purification with acetone was used to remove low molecular weight materials and catalyst residues. The polymer was then extracted with chloroform and the solvent was reduced under pressure to approximately 20 mL. To remove the remaining catalytic residues, *N*,*N*-diethylphenylazothioformamide (10 mg, 0.049 mmol) was added as a scavenging agent and the mixture was stirred for 1 hour. The mixture was poured in MeOH (100 ml) and the polymer was recovered by filtration.

^{1}H and ^{13}C NMR spectra of compounds 1-3

Figure S1: Compound **1** H^{1}NMR Spectra

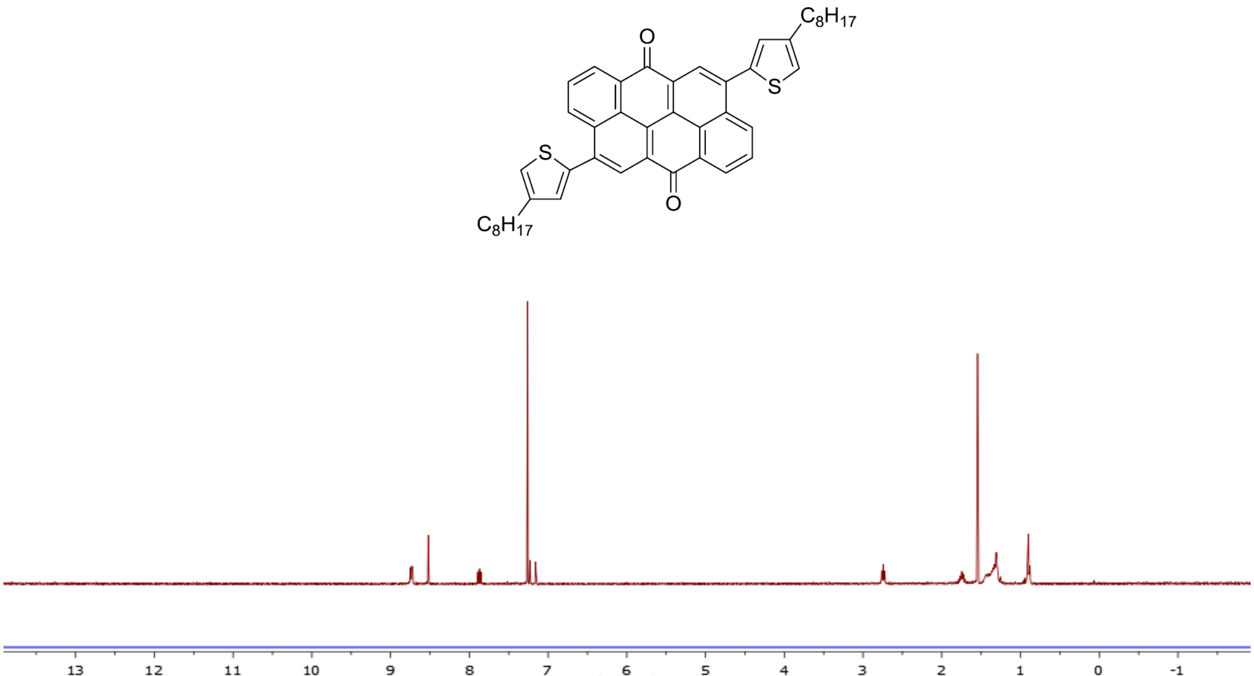


Figure S2: Compound **1** C^{13}NMR Spectra

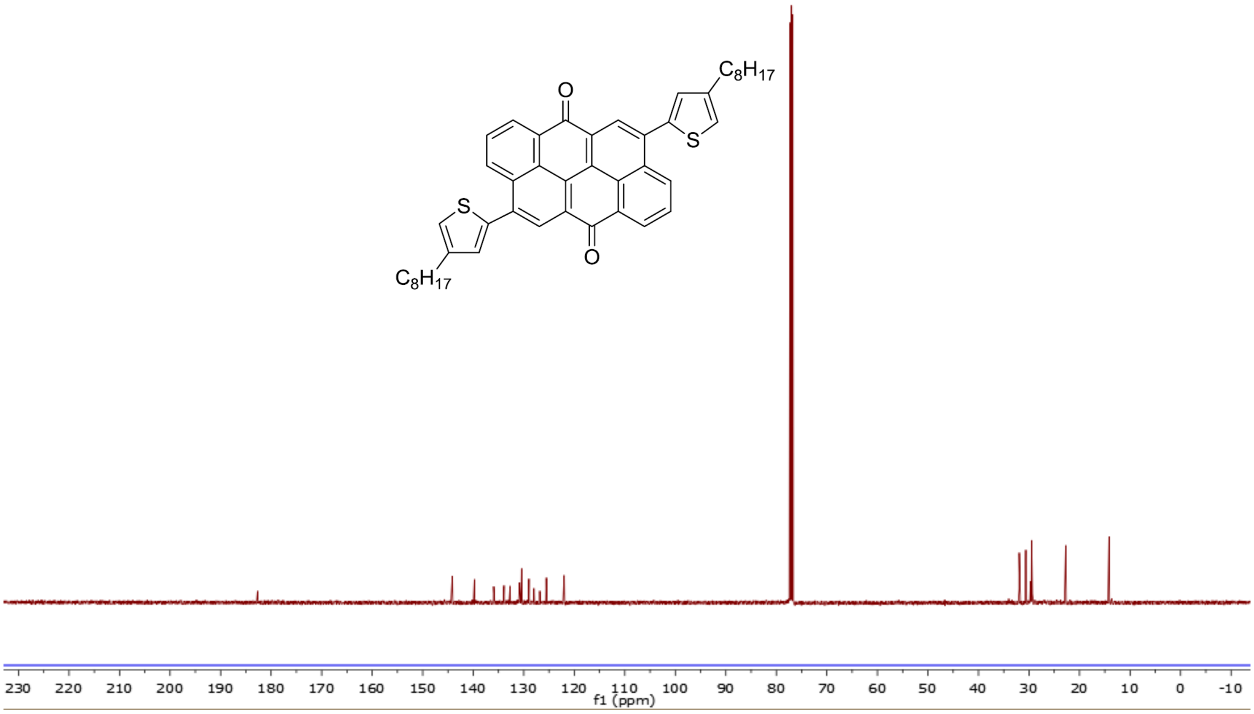


Figure S3: Compound **2** H^1NMR Spectra

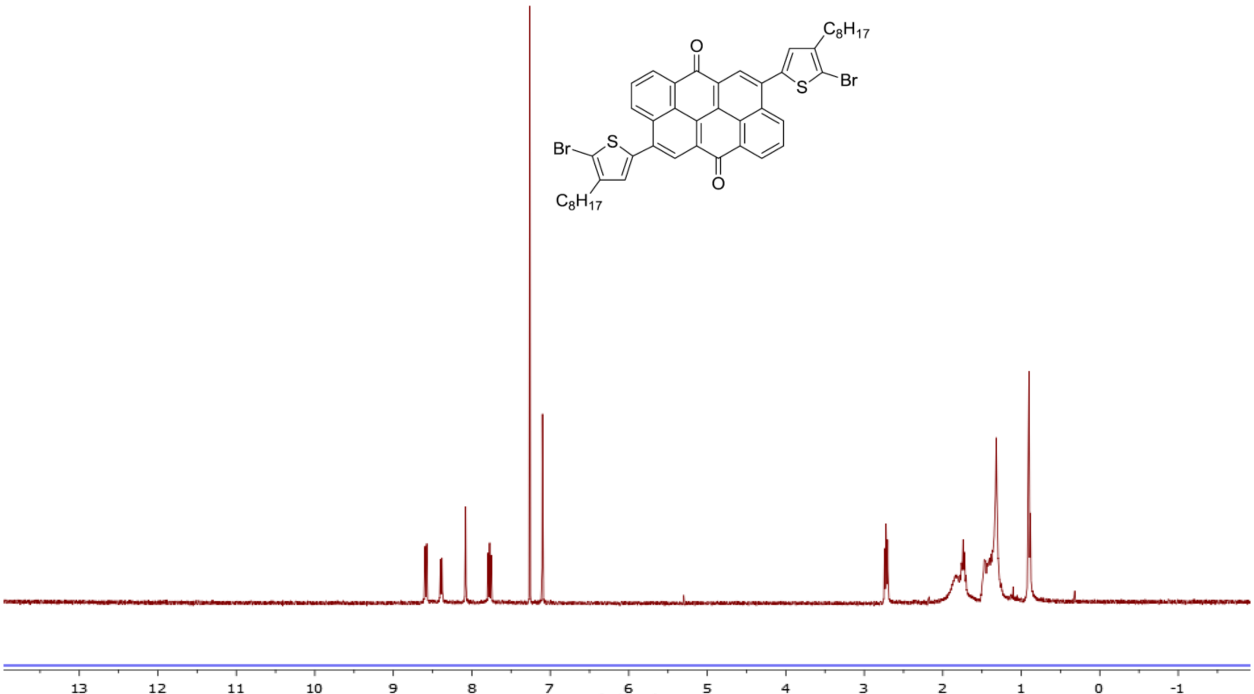


Figure S4: Compound **2** C^{13}NMR Spectra

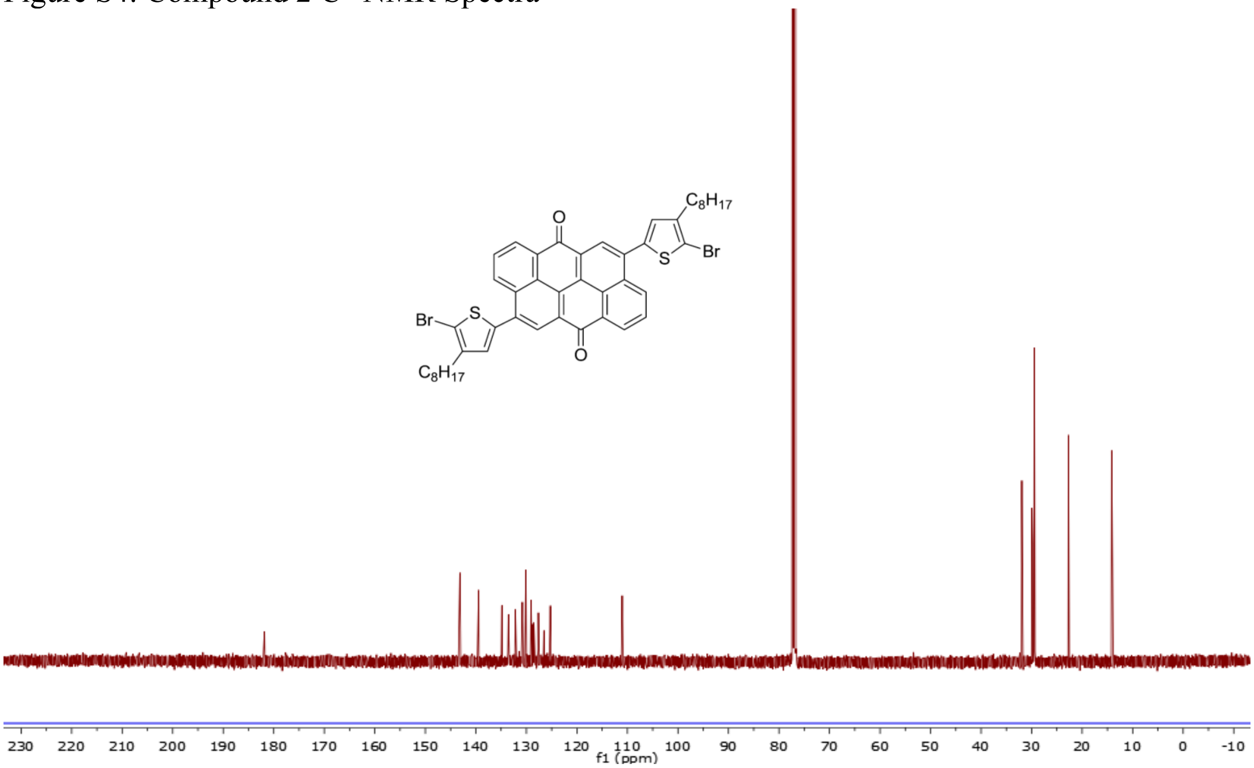


Figure S5: Compound **3** H^{1}NMR Spectra

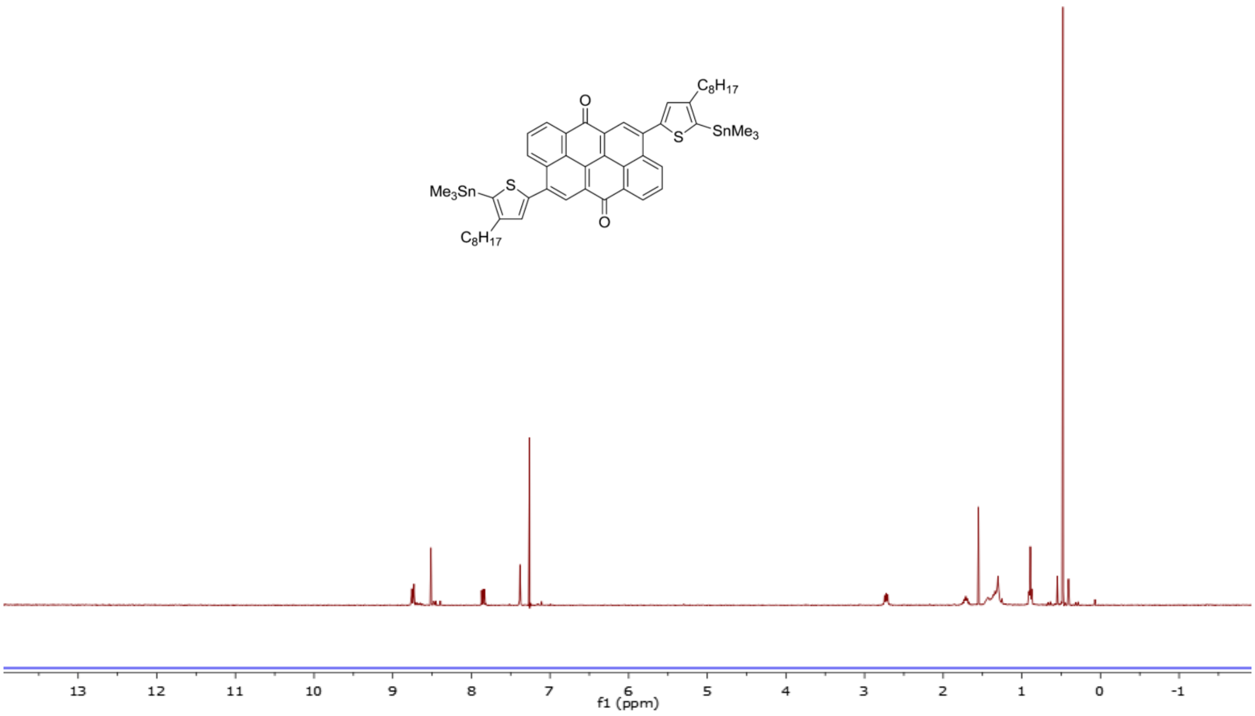
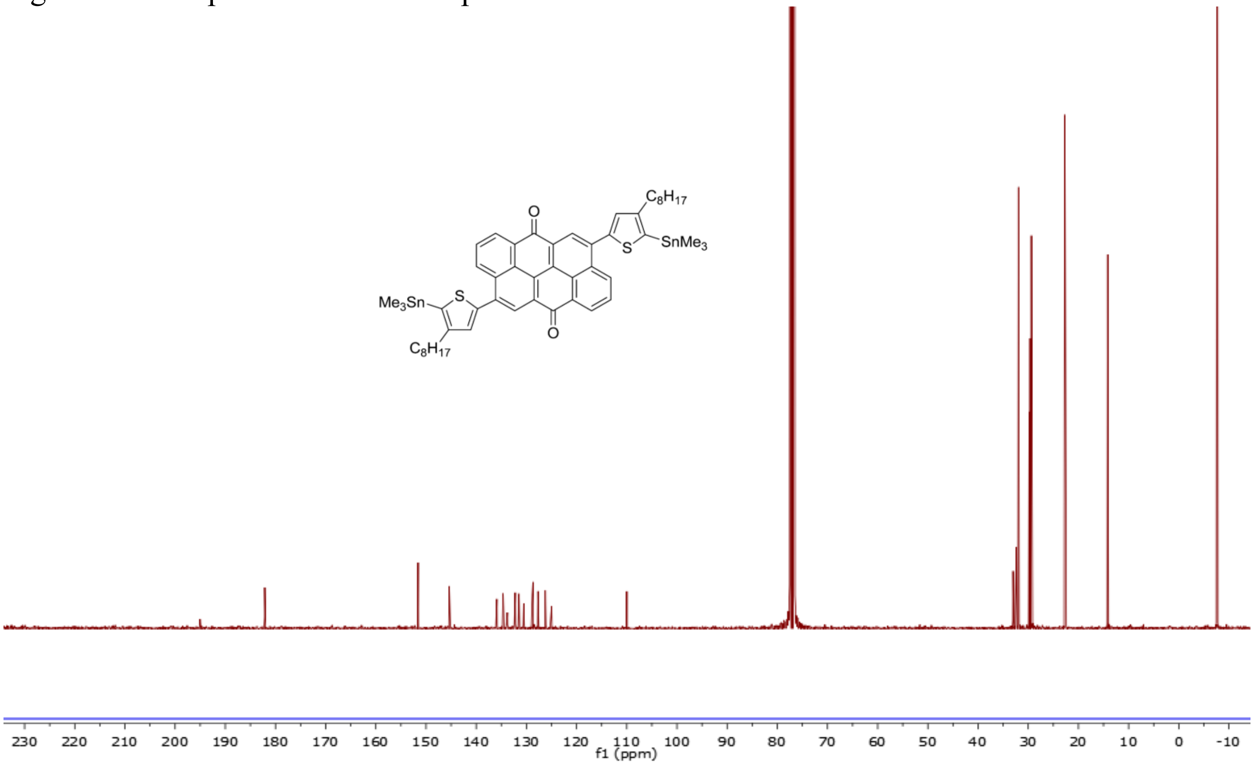


Figure S6: Compound **3** C^{13}NMR Spectra



UV-visible spectra of polymers

Figure S7: UV-Visible Spectra for PTANT series in chloroform solution

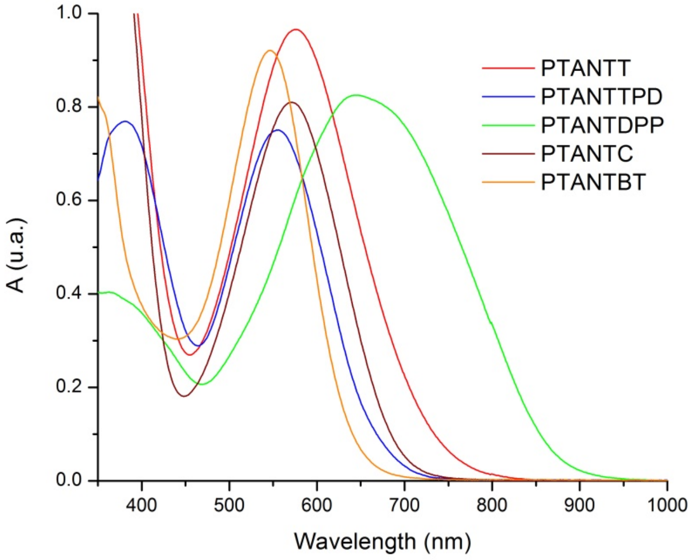
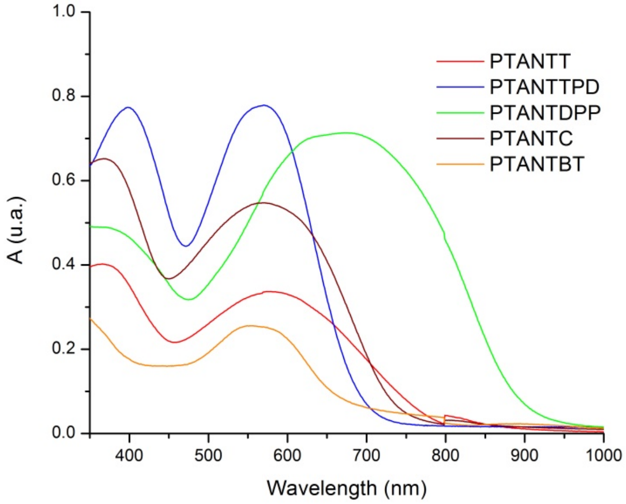


Figure S8: UV-Visible Spectra for PTANT series in solid state



Cyclovoltamograms of polymers

Figure S9: Cyclic Voltammogram of PTANTDPP

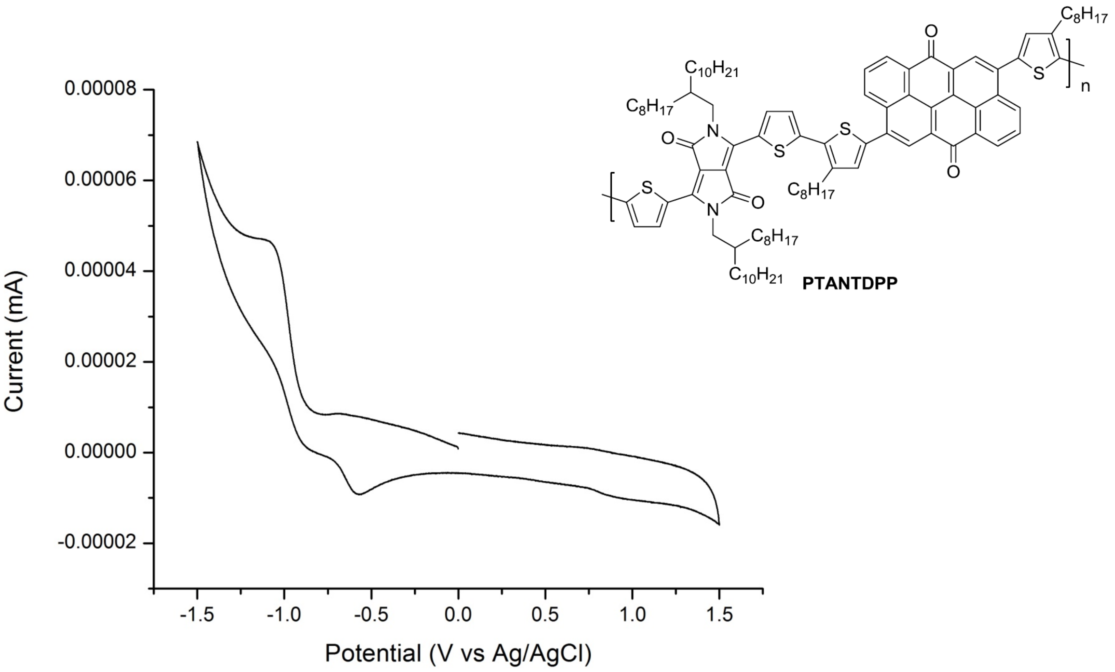


Figure S10: Cyclic Voltammogram of PTANTBT

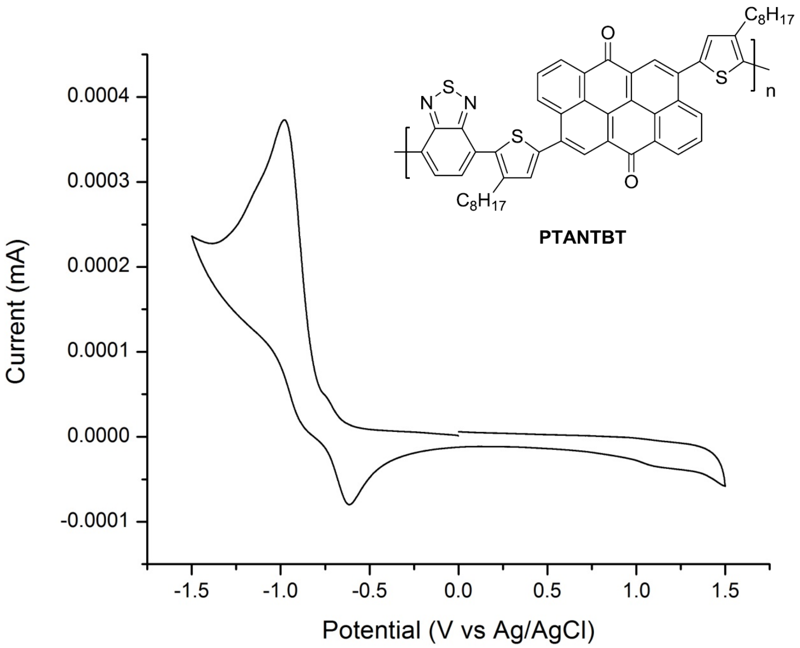


Figure S11: Cyclic Voltammogram of PTANTC

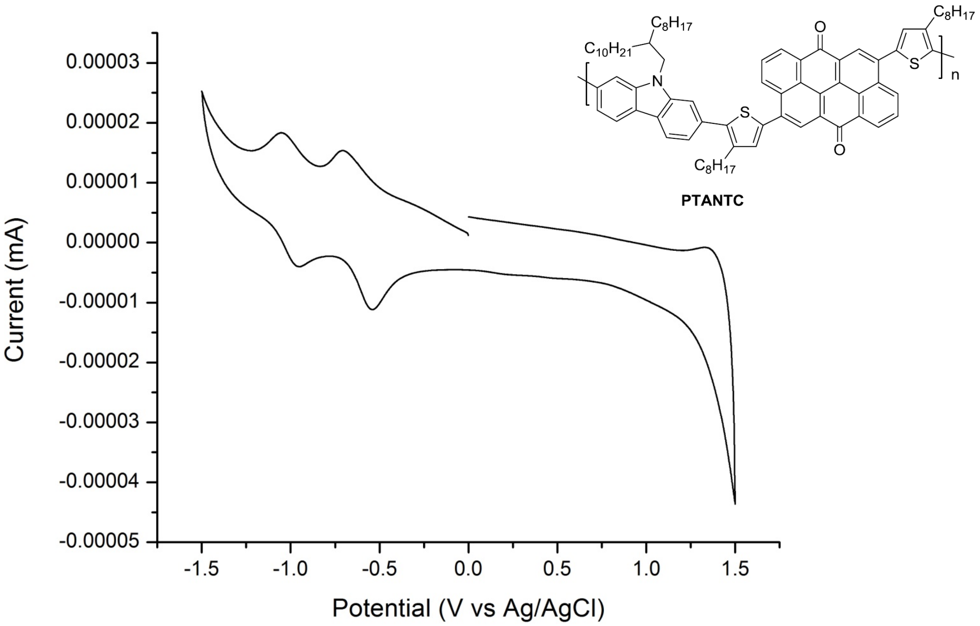


Figure S12: Cyclic Voltammogram of PTANTT

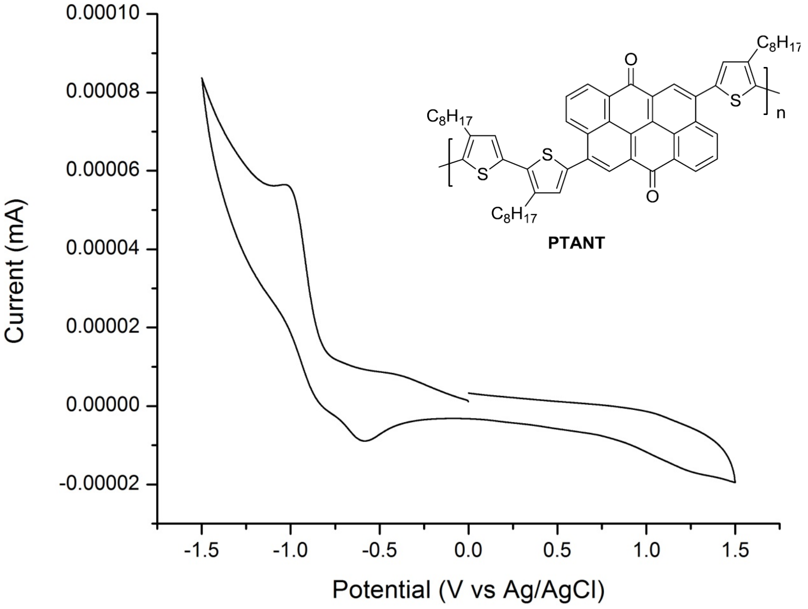
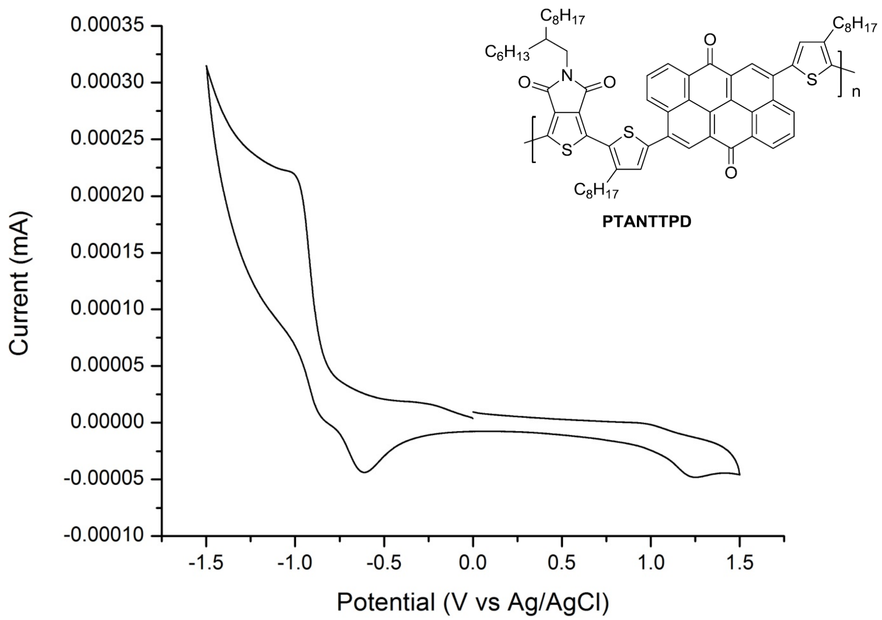
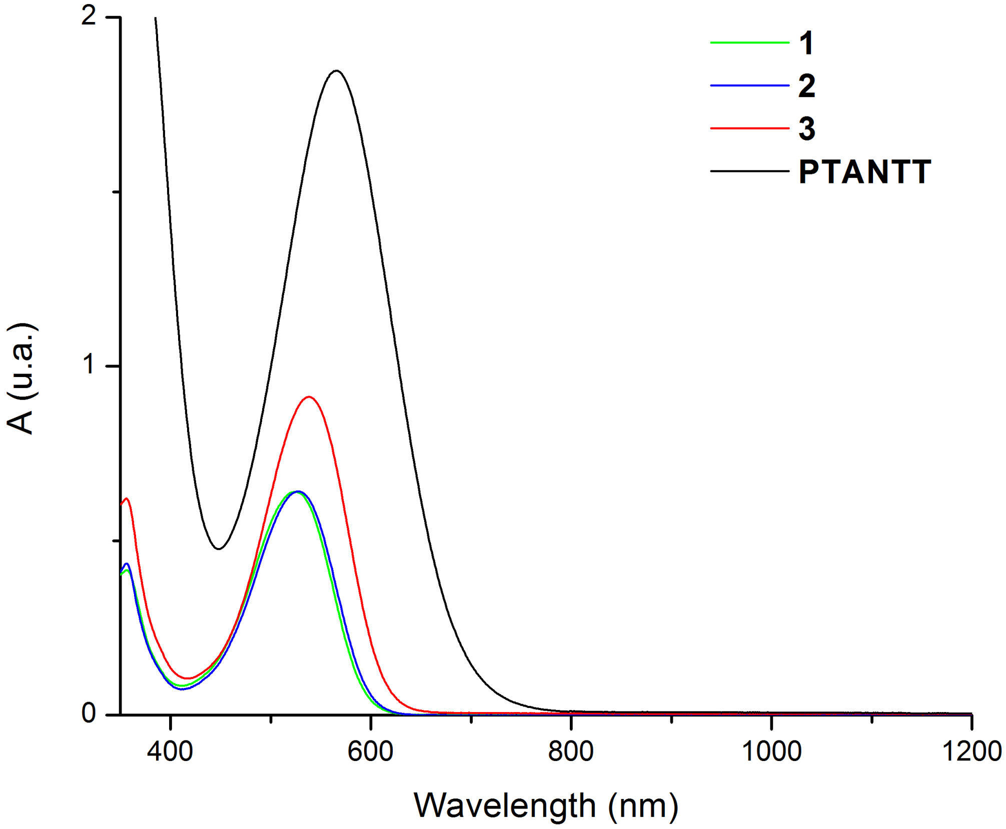


Figure S13: Cyclic Voltammogram of PTANTTPD



UV-visible spectra of monomers

Figure S14: UV-Visible spectra for compound **1**, **2** ,**3** and **PTANTT** in chloroform solution



UV-visible spectra of compound 2 reduction with TBAF, hν

Figure S15: UV-visible spectra of a gradual reduction of coumpound **2** in THF with X eq. of TBAF followed by 10 seconds of hν exposition