Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Anthanthrene as a Large PAH Building Block for the Synthesis of Conjugated Polymers

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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 provided as a courtesy of Heubach GmbH as product Monolite Red 316801. The dibrominated monomer 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 (PhMe) and diisopropylamine (DIPA) used for Castro-Stephen-Sonogashira 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). 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). ^1H and ^{13}C NMR 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) 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 10-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-electrode potentiostat. The potential was referenced to an Ag/AgCl-saturated KCl electrode, and Pt wires were used as the working and counter electrodes. Acetonitrile with a supporting electrolyte of Bu_4NPF_6 (0.1 M) was sparged using argon for 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. An Anton Paar Monowave 300 microwave apparatus with glass vial and IR temperature sensor was used for reaction under microwave.

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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

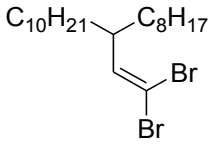
[3] 4*H*-Thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione, 1,3-dibromo-5-(2-hexyldecyl)-: A. Najari *et al. Macromolecules*, 2012, **45**, 1833

[4] 9*H*-Carbazole, 2,7-dibromo-9-(2-octyldodecyl)-: J. Bea, *Kongop Hwahak*, 2013, **24**, 396

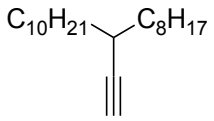
[5] Pyrrolo[3,4-*c*]pyrrole-1,4-dione, 3,6-bis(5-bromo-2-thienyl)-2,5-dihydro-2,5-bis(2-octyldodecyl)-: C. Shaoyun et al. *J. Mater. Chem. C*, 2014, **2**, 2183

[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

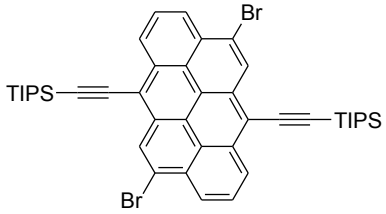
Monomer synthesis



Synthesis of compound 1. A round bottom flask equipped with a magnetic stir bar was charged with dry CH_2Cl_2 (250 mL) and CBr_4 (4.47 g, 13.5 mmol). After dilution of the CBr_4, the temperature was lowered to 0 °C using an ice bath and compound 2-octyldodecanal[7] (2.00 g, 6.75 mmol) was added. PPh_3 (7.08 g, 26.7 mmol) was then added in small portions over 15 minutes and the reaction was stirred for 18 hours. The solvent was removed under reduced pressure and cold ether (50 mL) was added to the crude product. The unreacted PPh_3 excess precipitated and was removed by filtration. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with hexanes as the eluent to afford compound **1** (2.29 g, 75% yield) as a translucent oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.12 (d, J = 9.8 Hz, 1H), 2.38 (s, 1H), 1.41 (m, 2H), 1.28 (m, 30H), 0.90 (t, J = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.77, 87.60, 43.74, 34.52, 31.96, 31.91, 29.78, 29.69, 29.66, 29.60, 29.56, 29.38, 29.35, 27.12, 22.74, 22.71, 14.16, 14.14

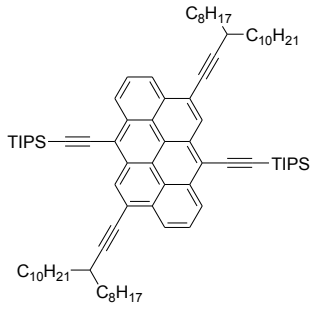


Synthesis of compound 2. A dry round bottom flask equipped with a magnetic stir bar was charged with compound **1** (5.50 g, 12.2 mmol) and dry THF (10 mL) under nitrogen atmosphere. The reaction mixture was cooled to -78 °C using a dry-ice/acetone bath and *n*-butyllithium (2.4 M in hexanes, 15.2 mL, 36.5 mmol) was added dropwise. After stirring for 1.5 hours, the reaction was quenched using water (1 mL) and the solvents were removed under reduced pressure. The reaction mixture was diluted with hexanes, washed with water three times and dried over $MgSO_4$. The solvent was removed under reduce pressure and the crude product was purified by flash chromatography on silica gel with hexanes as the eluent to afford compound **2** (3.52 g, 99% yield) as a colourless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.30 (d, J = 2.2 Hz, 1H), 2.02 (d, J = 2.4 Hz, 1H), 1.43 (q, J = 6.5 Hz, 6H), 1.31 – 1.24 (m, 26H), 0.91 – 0.86 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 88.23, 68.85, 34.99, 31.92, 31.89, 31.51, 29.65, 29.63, 29.59, 29.54, 29.52, 29.35, 29.31, 27.28, 22.68, 22.67, 14.09.



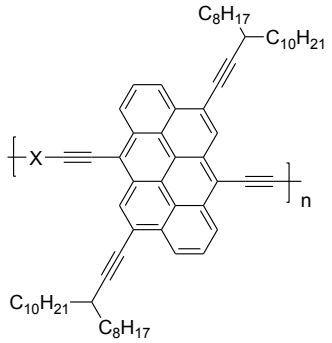
[7] A. Efrem, C.-J. Lim, Y. Lu, S.-C. Ng, *Tetrahedron Lett*. 2015, **55**, 4849

Synthesis of compound 3. A dry round bottom flask equipped with a magnetic stir bar was charged with triisopropylsilylacetylene (2.42 mL, 1.96 g, 10.8 mmol) and dry THF (43 mL) and the reaction mixture was cooled to 0 °C using an ice bath. Then, *n*-butyllithium (2.4 M in hexane, 4.49 mL, 10.8 mmol) was added dropwise over 10 minutes. After stirring for 20 minutes, 4,10-dibromoanthanthrone (Vat Orange 3, 1.00 g, 2.16 mmol) was added and the reaction was allowed to stir overnight before a solution of tin(II) chloride dihydrate (2.79 g, 9.27 mmol) in 2.5 mL of aqueous HCl 3M was added. The mixture was stirred for an additional 20 minutes and poured into MeOH (100 mL). The precipitated crude product was recovered by filtration. Hot chloroform was used to dissolve the crude product and the solution was filtered again and the solvent evaporated. Recrystallization from hexanes afforded compound **3** (0.940 g, 55% yield) as an orange solid: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.23 (s, 2H), 9.19 (d, *J* = 8.2 Hz, 2H), 8.76 (d, *J* = 7.7 Hz, 2H), 8.37 – 8.28 (m, 2H), 1.47 – 1.31 (m, 42H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.42, 130.71, 130.43, 129.91, 127.37, 126.98, 126.29, 125.51, 123.89, 122.82, 120.75, 116.87, 109.20, 105.58, 103.19, 18.98, 11.61. HRMS (APPI-TOF): m/z calcd for $C_{44}H_{50}Br_2Si_2$ [M+H]+: 793.1896, found 793.1852.



Synthesis of compound 4. A dry microwave vial under argon with a magnetic stir bar was charged with compound **3** (0.500 g, 0.629 mmol), dry toluene (8 mL), DIPA (2 mL) and compound **2** (0.552 g, 1.887 mmol) then the mixture was degassed with a flow of N_2 for 10 minutes. $Pd_2(dba)_3$ (14.4 mg, 0.016 mmol), PPh_3 (16.5 mg, 0.063 mmol) and CuI (6.0 mg, 0.031 mmol) were then added and the mixture was heated in the microwave reactor for 1 h at 140 °C. The reaction was allowed to cool to room temperature and was diluted with chloroform, washed with aqueous saturated NH_4Cl solution three times, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel with hexanes as the eluent to afford compound **4** (0.58 g, 76% yield) as a bright orange solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (dd, *J* = 8.2, 1.0 Hz, 2H), 9.04 (s, 2H), 8.81 (dd, *J* = 7.5, 1.0 Hz, 2H), 8.26 (t, *J* = 7.9 Hz, 2H), 2.84 (s, 2H), 1.81 – 1.67 (m, 16H), 1.51 – 1.24 (m, 90H), 0.88 (dt, *J* = 10.0, 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.14, 131.07, 131.04, 130.96, 126.74, 125.99, 124.52, 123.66, 122.42, 121.02, 116.83, 104.80, 104.12, 100.10, 80.11, 35.46, 32.99, 31.82, 31.80, 29.63, 29.61, 29.58, 29.55, 29.54, 29.27, 29.22, 27.64, 22.52, 22.49, 18.87, 13.80, 13.78, 11.74. HRMS (APPI-TOF): m/z calcd for $C_{86}H_{128}Si_2$ [M+H]+: 1217.9633, found 1217.9418.

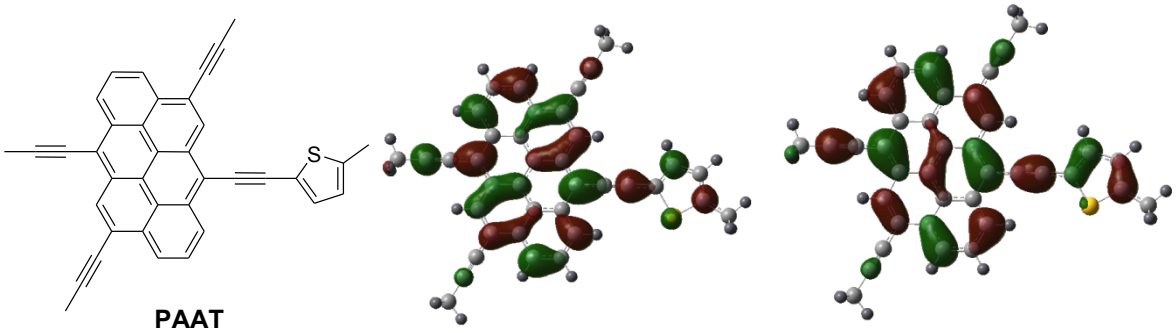
General procedure for polymerization by Castro-Stephen-Sonogashira coupling



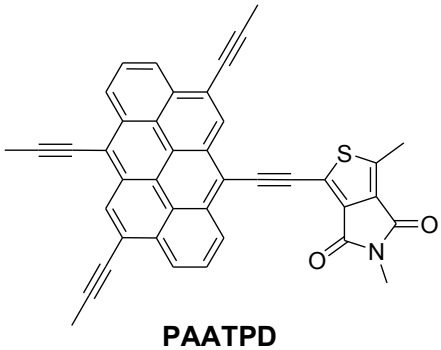
A dry flask under argon with a magnetic stir bar was charged with compound **4** (0.050 g, 0.041 mmol) and dry Toluene (4 mL), TBAF (1.0 M in THF, 0.08 mL, 0.082 mmol) and water (0.05 mL). The reaction was stirred for 5 minutes. DIPA (0.8 mL) (0.041 mmol) and dibromide **X** (0.041 mmol) were added and the mixture was degassed with a flow of N_2 for 10 minutes. $Pd_2(dba)_3$ (1.9 mg, 0.002 mmol), tri(*o*-tolyl)phosphine (2.5 mg, 0.008 mmol) and CuI (0.4 mg, 0.002 mmol) were then succinctly added and the reaction was heated at 110 °C. At the end of the reaction time, bromobenzene (13 mg, 0.082 mmol) was added as a capping agent and the mixture was heated for one hour, then phenylacetylene (8 mg, 0.082 mmol) was added and the mixture was heated for an additional hour. The mixture was allowed to cool down to room temperature and poured into 100 mL of 9:1 solution of methanol and water. The mixture was then filtered to recover the precipitated polymer. Soxhlet extraction with acetone was used to remove low molecular weight materials. The polymer was then extracted with chloroform and the solvent was reduced under pressure to approximately 20 mL. To remove catalytic residues, *N*,*N*-diethylphenylazothioformamide (9 mg, 0.041 mmol) was added as a scavenging agent and the mixture was stirred for 1 hour. Then the mixture was poured in MeOH (100ml) and the polymer was recovered by filtration.

Computational Method: DFT calculations were carried out with Gaussian 09 program suite at the B3LYP/6-311G* level of theory, and the orbital plots are reported at an isovalue of 0.02.

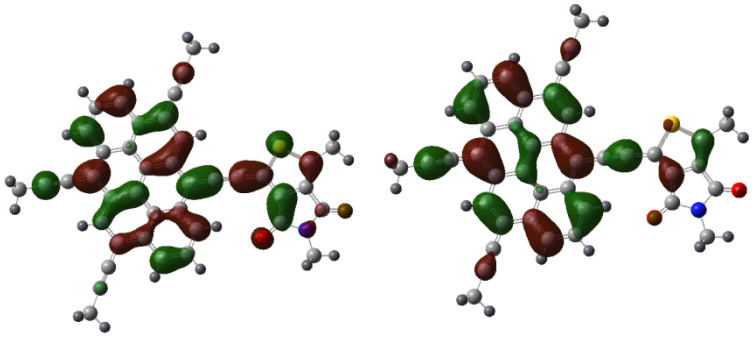
Figure S1: DFT calculated structures and frontier orbitals distribution



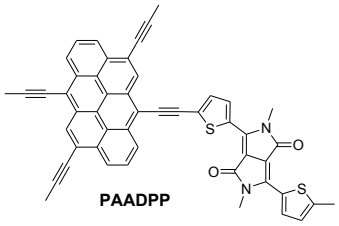
PAAT Energy: -1859.66980344 a.u. LUMO -2.56 eV
HOMO -4.87 eV



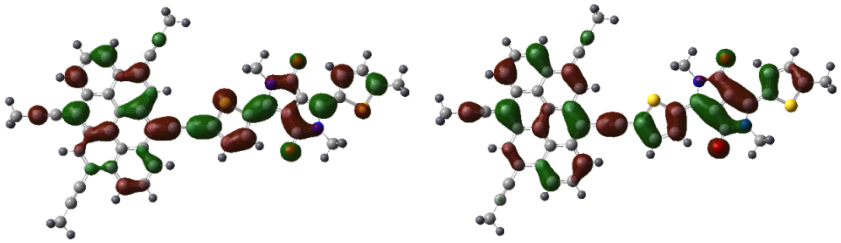
PAATPD



PAATPD Energy: -2179,90780884 a.u. LUMO -2.83eV
HOMO -5,03 eV



PAADPP



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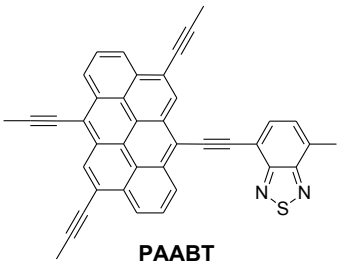
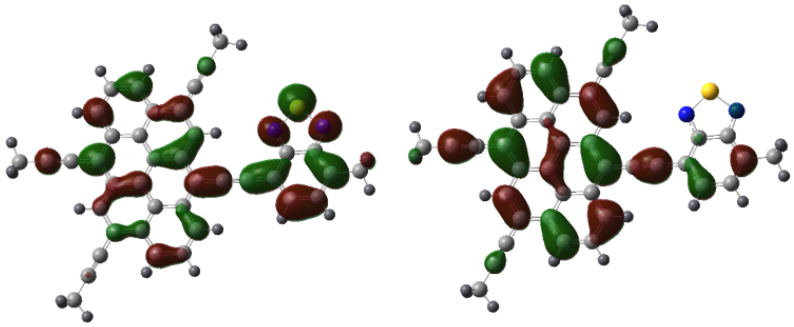


PAABT



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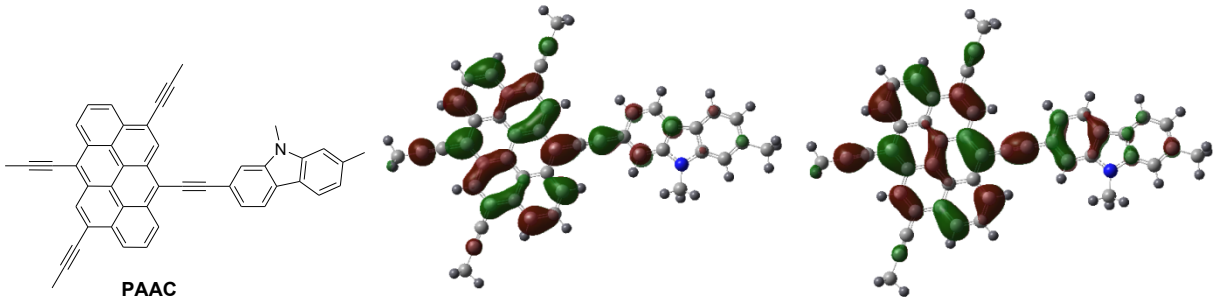

PAAC Energy: -1863.49977500 a.u. LUMO -2.53 eV
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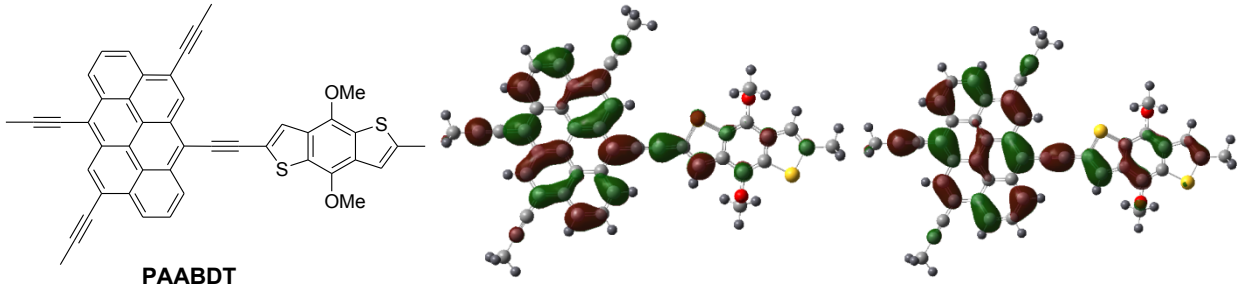

PAABDT Energy: -2716,88492516 a.u LUMO -2.67 eV
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Calculated coordinates

PAAT

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PAATDP

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C	7.53461967	-1.58579136	0.00046872
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C	7.45720622	2.51524357	0.03944616
C	8.70822326	3.21802384	0.03173072
C	9.92871396	2.49905255	0.02880598
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C	6.23650724	4.64297399	0.03797458
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C	0.31813145	-9.97026877	0.23572468
C	-2.20401280	-5.76329789	-0.15646404
C	-0.95646875	-6.47088841	-0.05508185
C	-4.66313751	-4.40244381	-0.35259509
C	-3.45918951	-3.69396693	-0.35572425
C	-2.25177472	-4.35713762	-0.25957437
C	1.57172298	-10.64186963	0.33491710
C	-7.16529252	-5.88240039	-0.34527195
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H	-9.96858482	-4.79696499	-1.51187176
H	-10.22039371	-5.02608989	0.22108290
H	-7.95687433	-13.23055065	0.06155380
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H	1.85935302	-2.34215878	-0.06422076
H	9.05197378	-2.63774457	0.05065127
H	9.80823496	0.80805218	-0.84945179
H	9.77384928	0.82020153	0.91254224
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H	2.73682107	1.09726435	1.08052952
H	2.79954875	-0.53372223	1.80158744
H	4.23496329	0.52569672	1.86062286
H	6.67612663	-5.50107987	-1.87660471
H	8.11565570	-4.44844443	-1.80623323
H	8.16834022	-6.08339012	-1.09347866

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C	-5.85587290	-10.78006056	0.04720939
C	1.29165394	-5.11072861	-0.03849256
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C	2.63704530	-11.20271258	0.42034578
C	3.92885988	-11.86703323	0.52420723
C	-8.22871940	-5.31743087	-0.42712861
C	-9.51735469	-4.64595879	-0.52623377
C	-8.13979418	-12.15218981	0.05195935
C	2.49876309	-4.40106538	-0.02316612
S	4.04453055	-5.28327704	0.01134148
C	4.93329616	-3.77048531	-0.00530110
C	4.05524681	-2.64999775	-0.00806595
C	2.68247594	-3.04314015	-0.03003435
C	6.31631743	-3.63318698	-0.00757369
C	6.85111084	-2.33708138	-0.00297319
C	5.97380666	-1.21777912	-0.00423113
C	4.59242935	-1.35078089	-0.00265440
C	8.23047505	-1.93271881	0.01756980
C	8.41080548	-0.58813189	0.01444341
S	6.87629047	0.29122711	-0.01638217
C	9.69952957	0.17145886	0.03421796
O	3.77316692	-0.24688500	-0.02911178
O	7.13412023	-4.74004005	0.01908418
C	3.36894335	0.22900227	1.26163979
C	7.54066351	-5.21123193	-1.27205578
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H	-2.12332390	-13.91125997	0.40977807
H	-6.80263640	-8.47346382	-0.14948792
H	1.21289281	-8.05442021	0.14138259
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Figure S2: Compound 1 ^{1}H NMR Spectra:

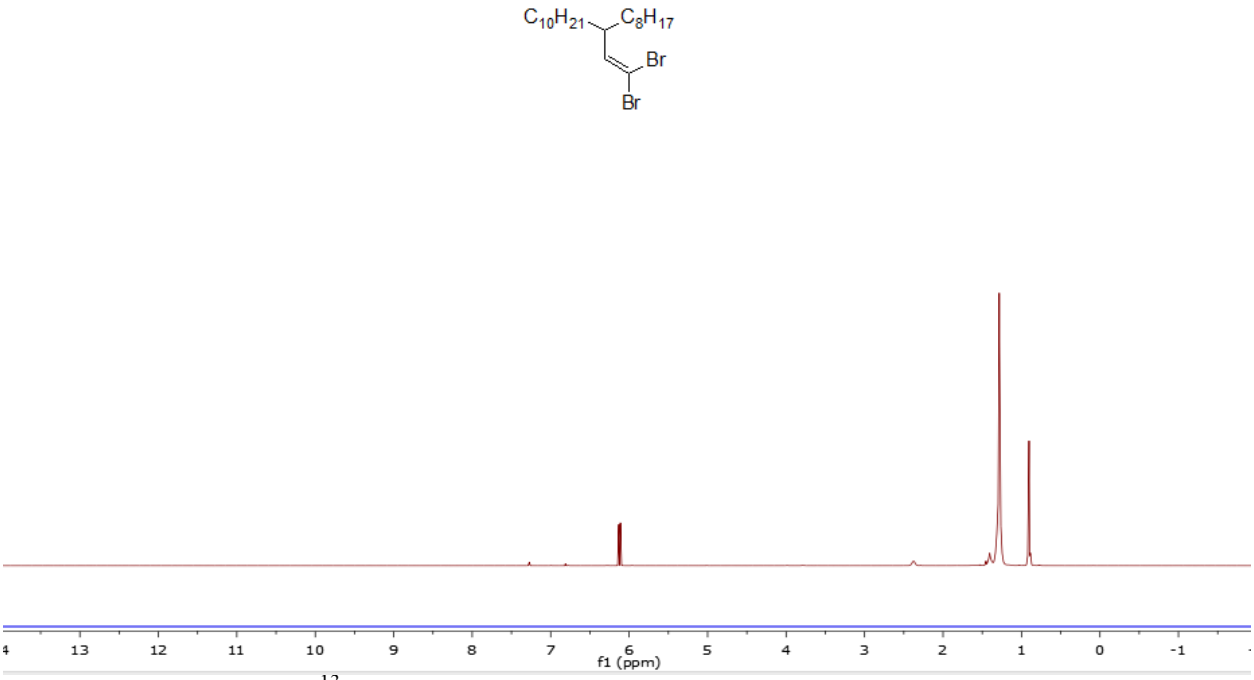

Figure S3: Compound 1 ^{13}C NMR Spectra:

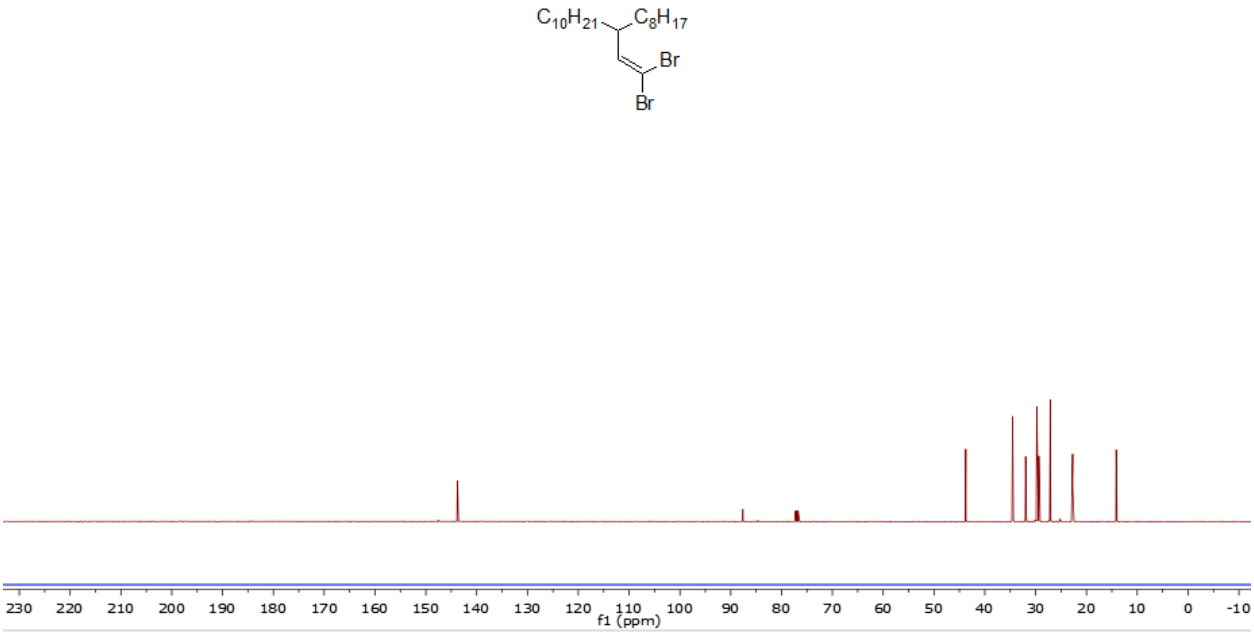

Figure S4: Compound 2 ^{1}H NMR Spectra:

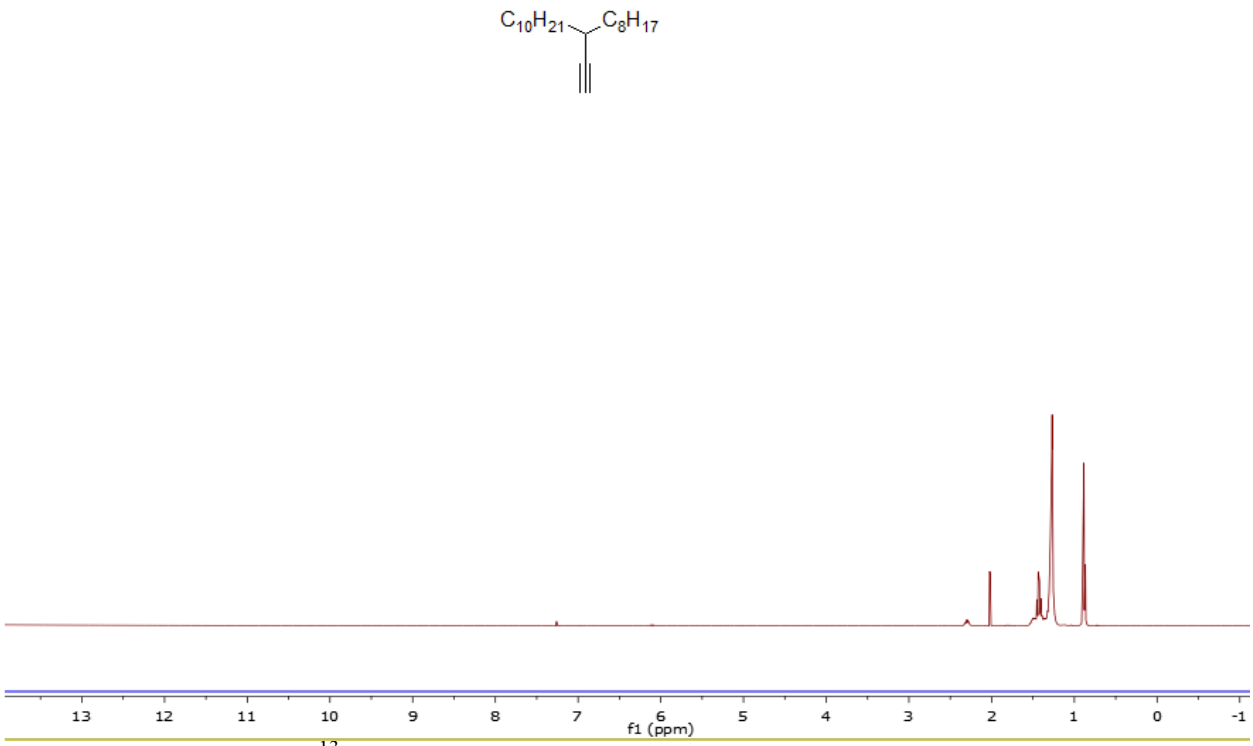

Figure S5: Compound 2 ^{13}C NMR Spectra:

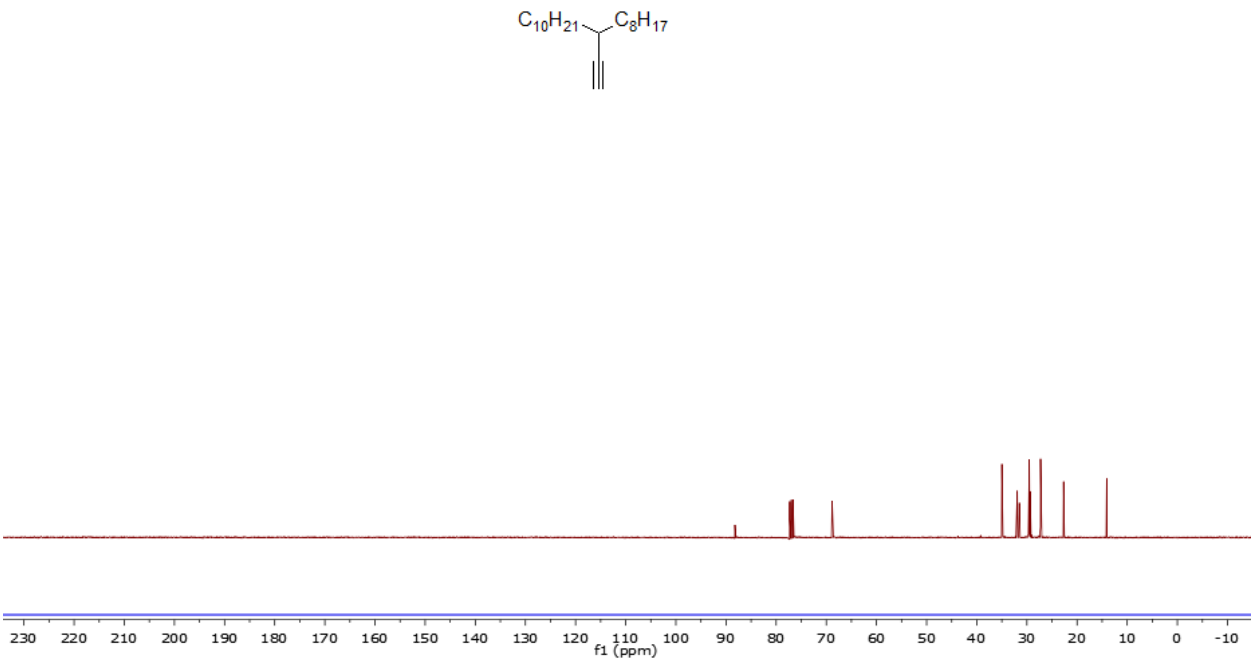

Figure S6: Compound 3 ^{1}H NMR Spectra:

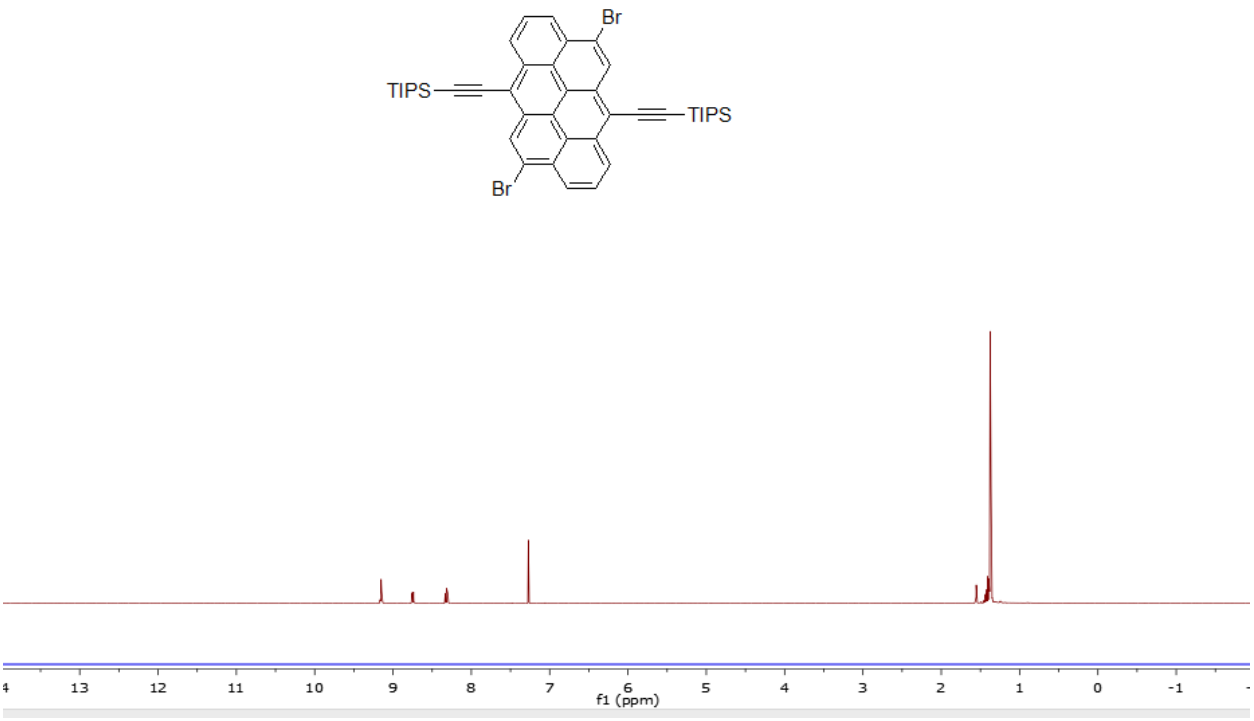

Figure S7: Compound 3 ^{13}C NMR Spectra:

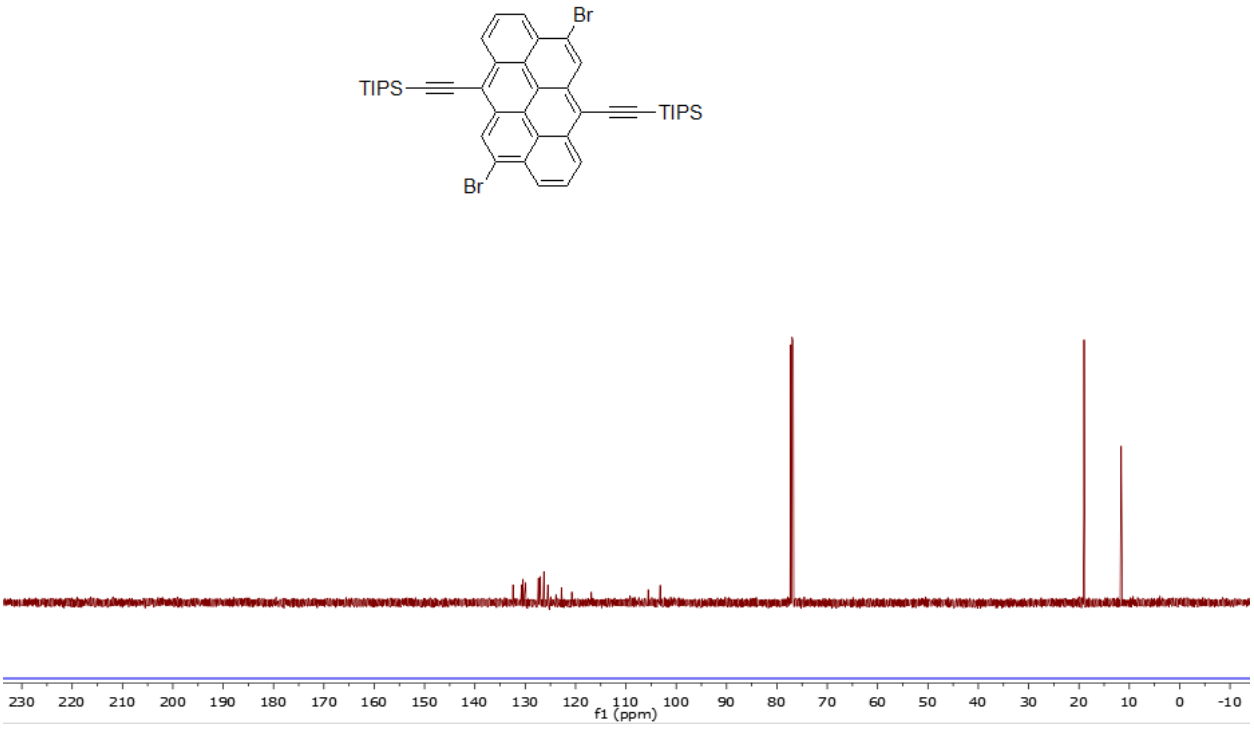

Figure S8: Compound 4 ^{1}H NMR Spectra:

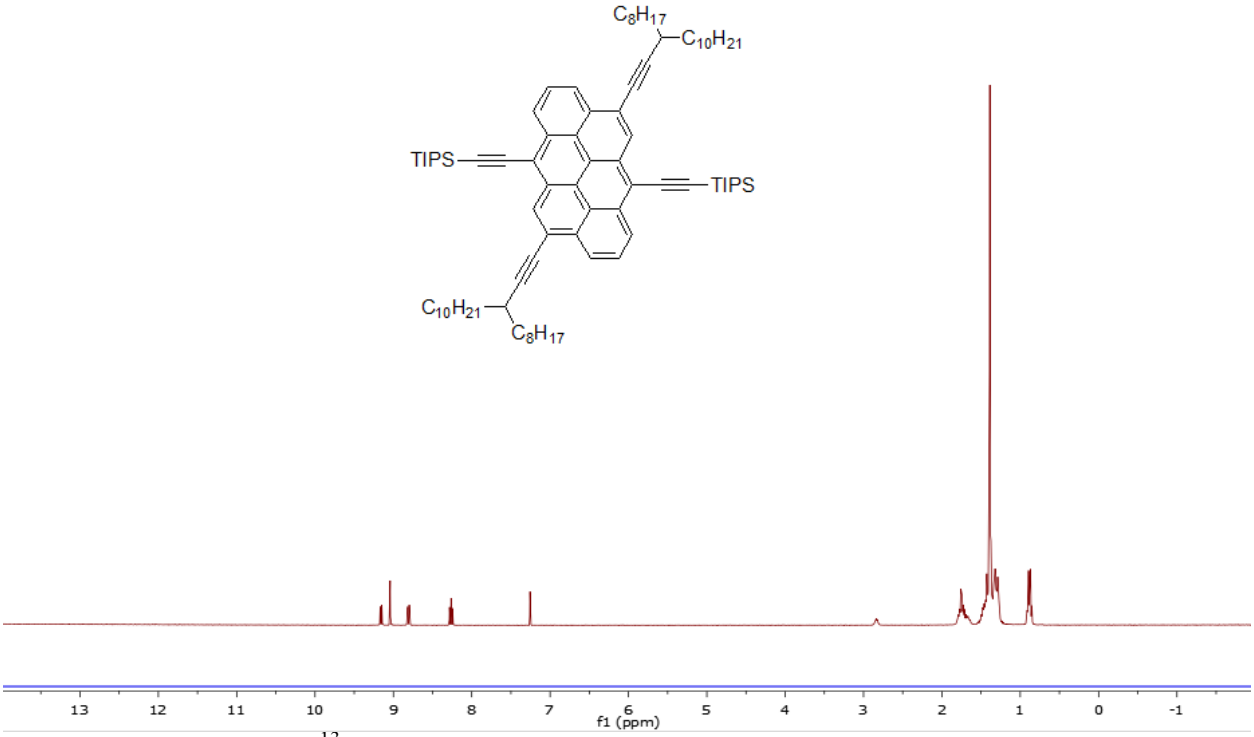

Figure S9: Compound 4 ^{13}C NMR Spectra:

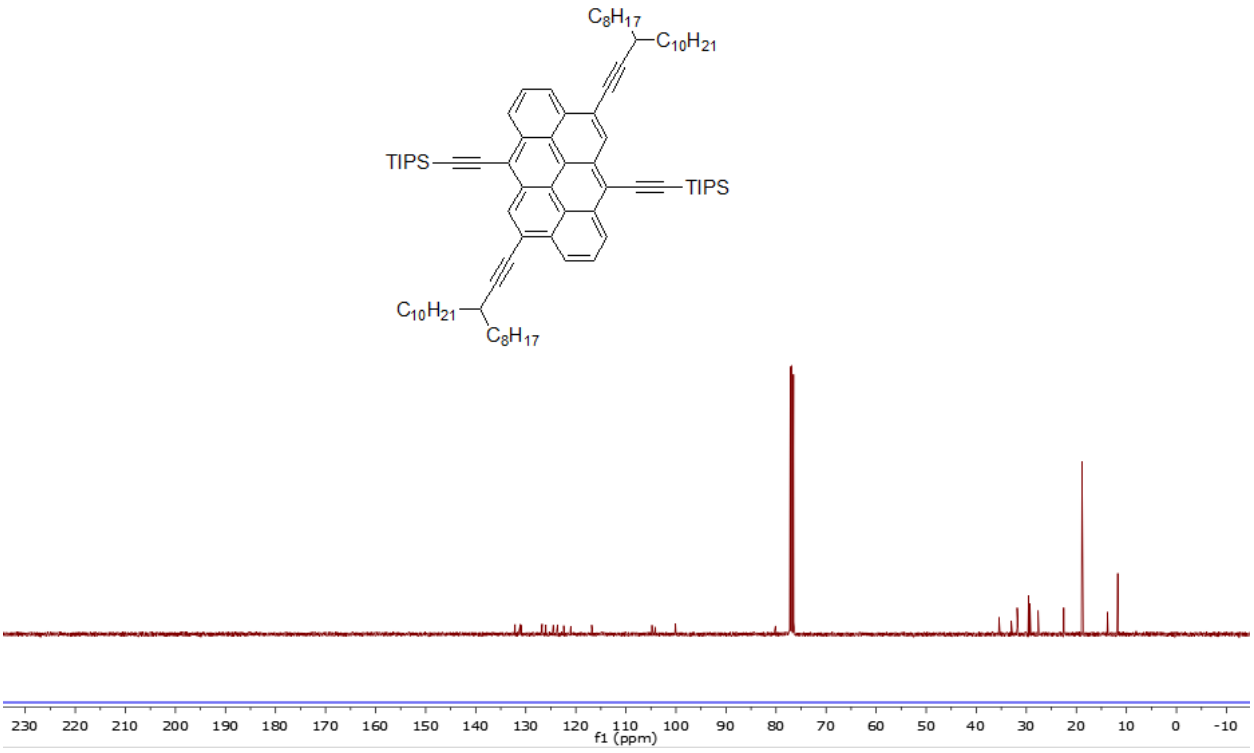

Figure S10: Cyclic Voltammogram of PAAT

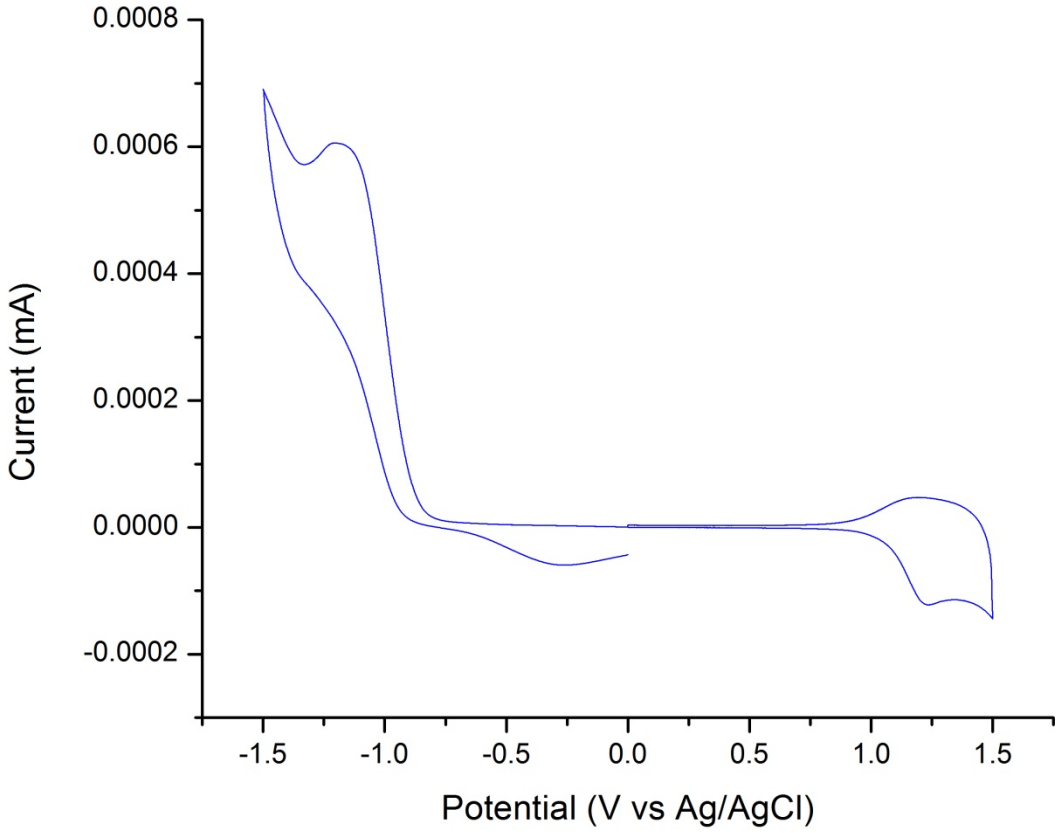

Figure S11: Cyclic Voltammogram of PAABT

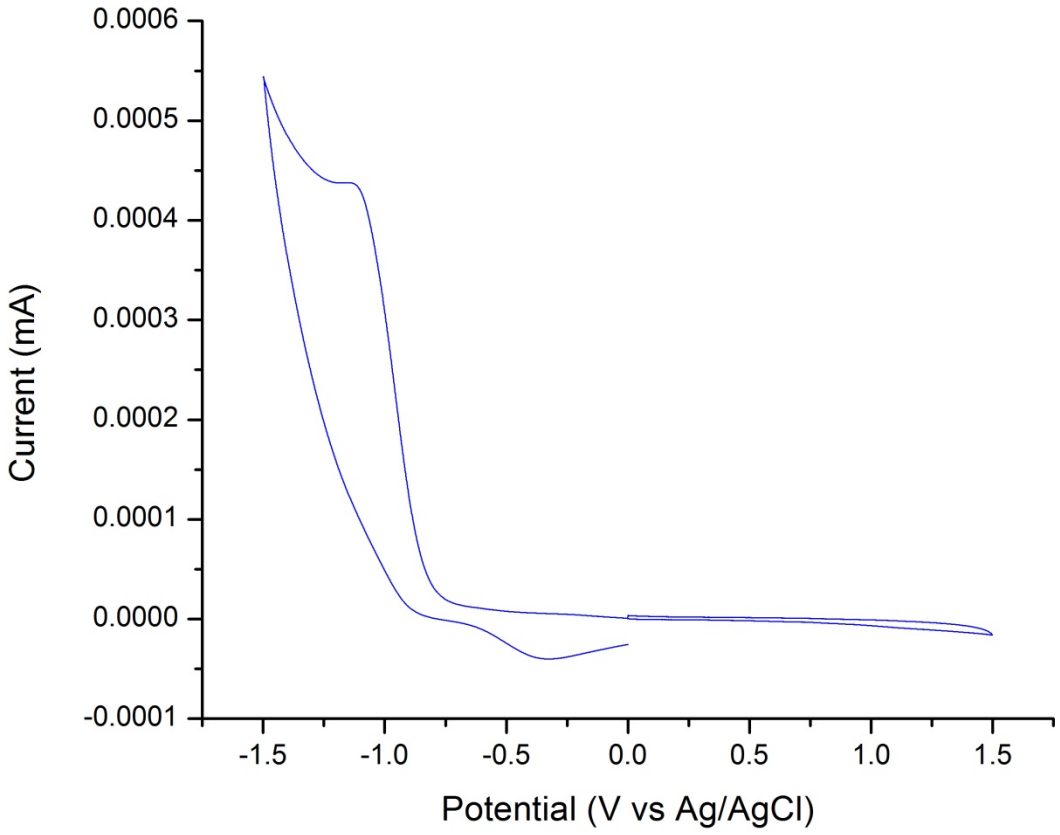

Figure S12: Cyclic Voltammogram of PAATPD

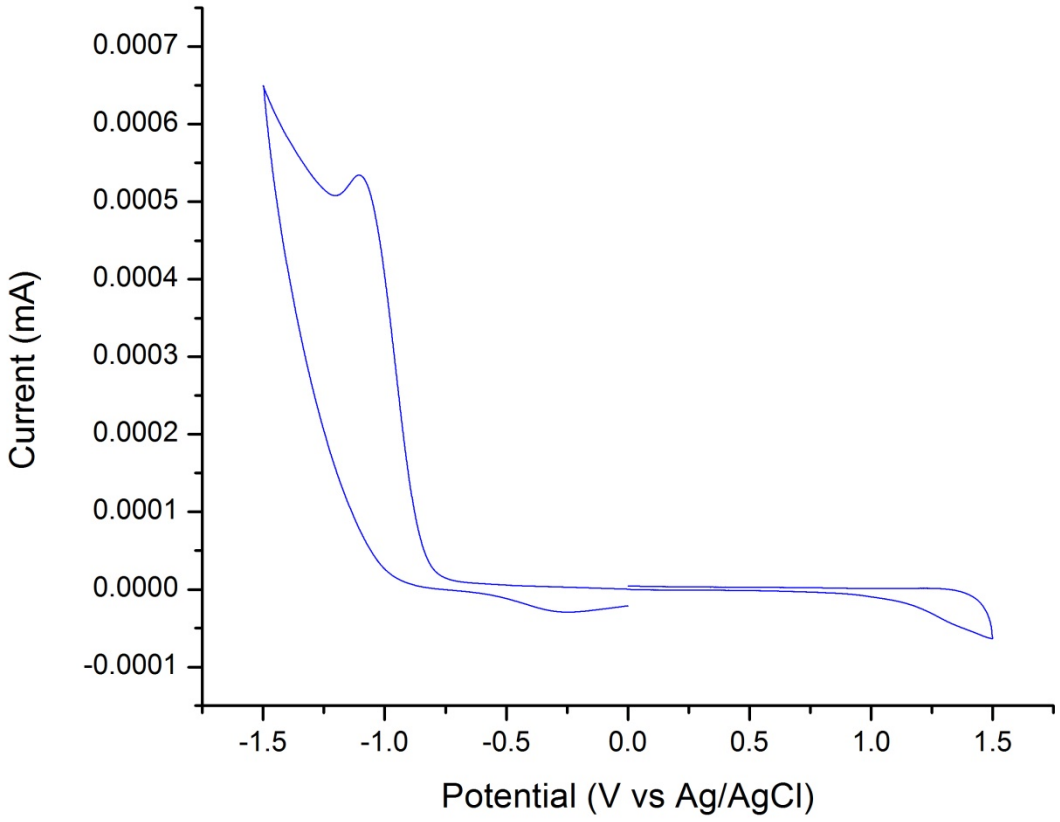

Figure S13: Cyclic Voltammogram of PAAC

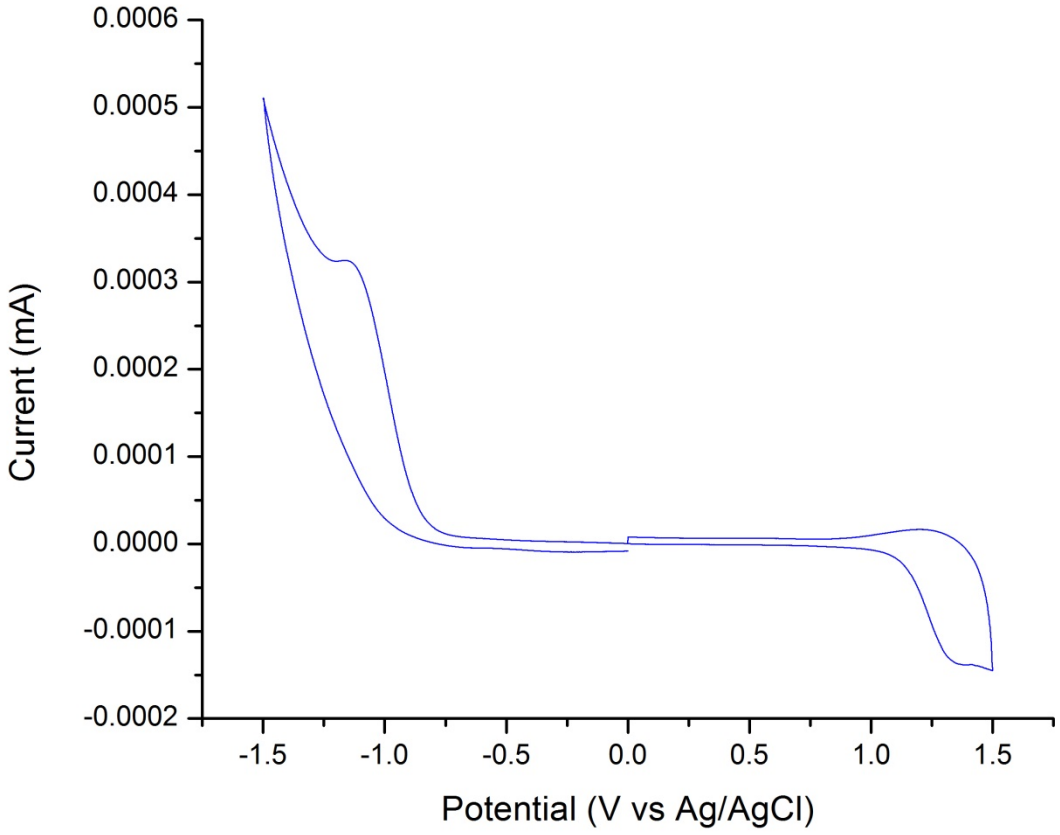

Figure S14: Cyclic Voltammogram of PAADPP

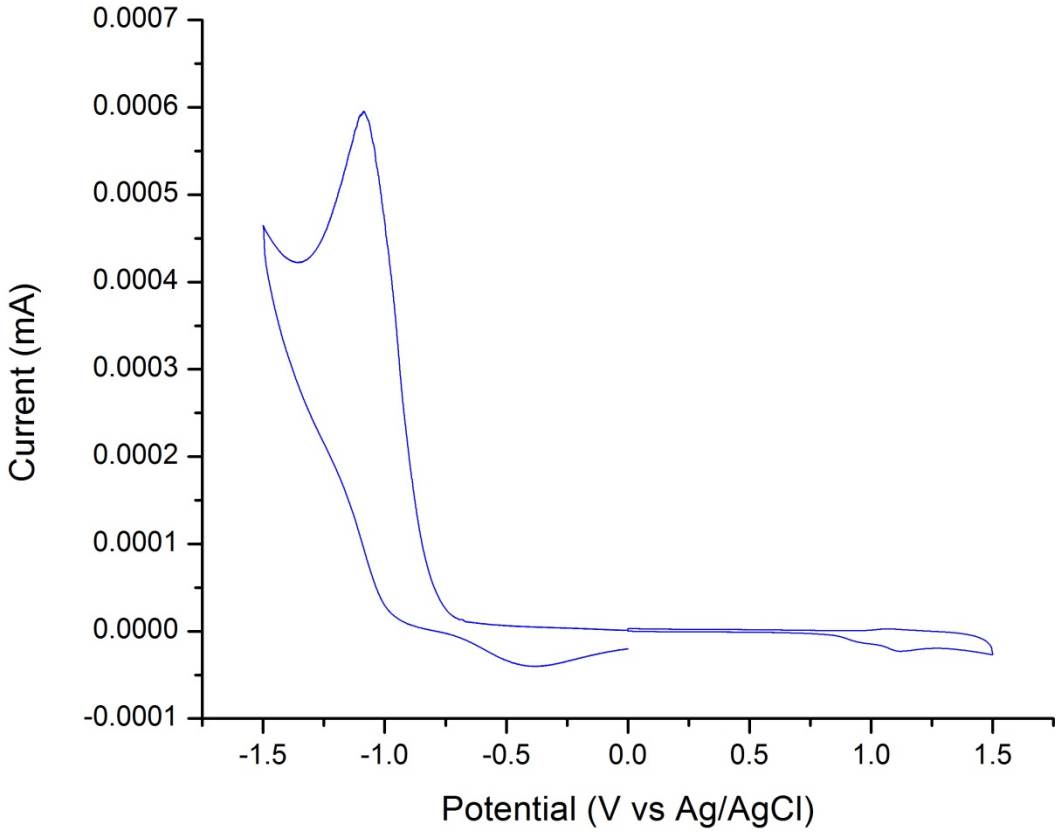

Figure S15: Cyclic Voltammogram of PAABDT

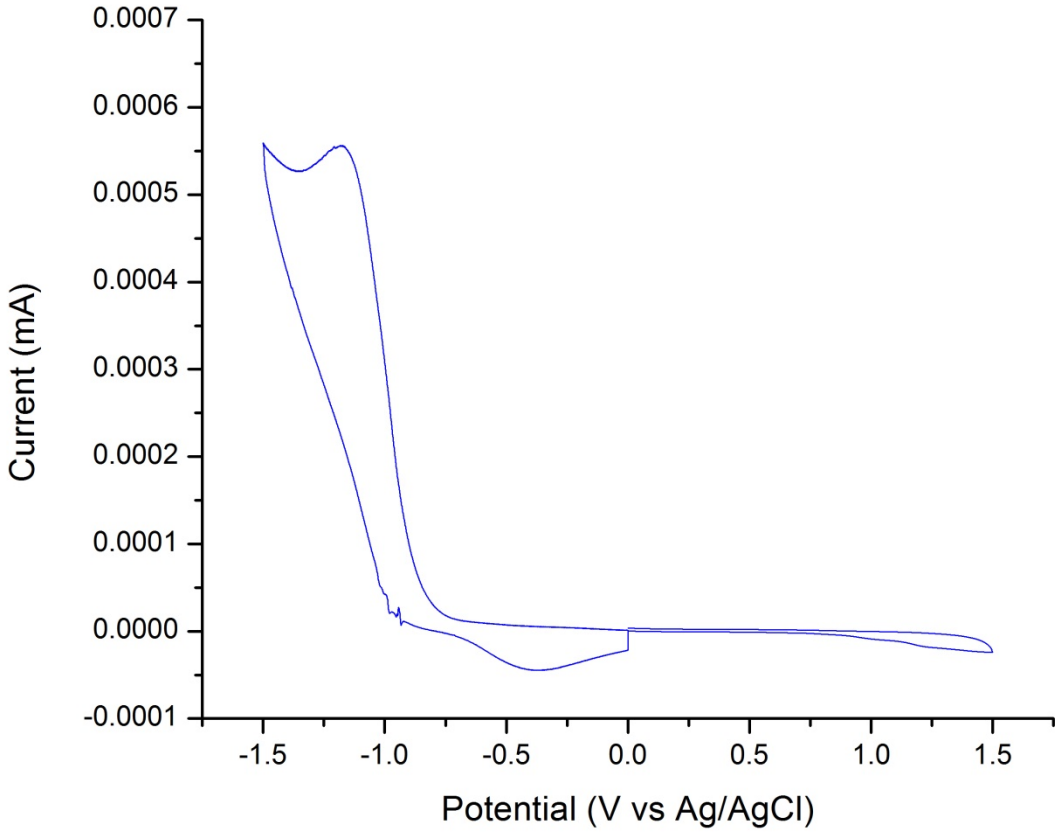

Figure S16: Differential scanning calorimetry measurement of PAADPP

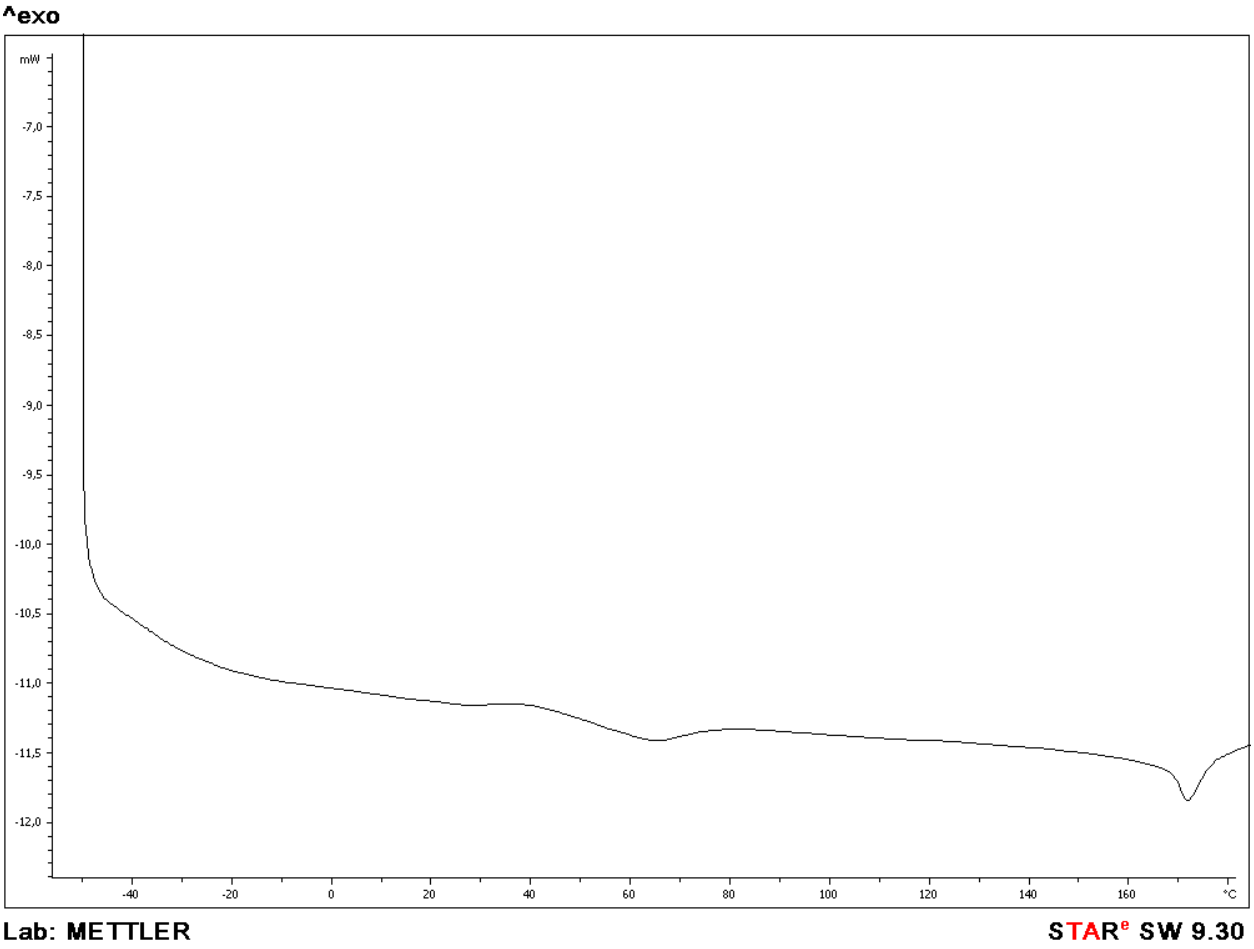

Figure S17: Thermogravimetric Analysis of PAAT

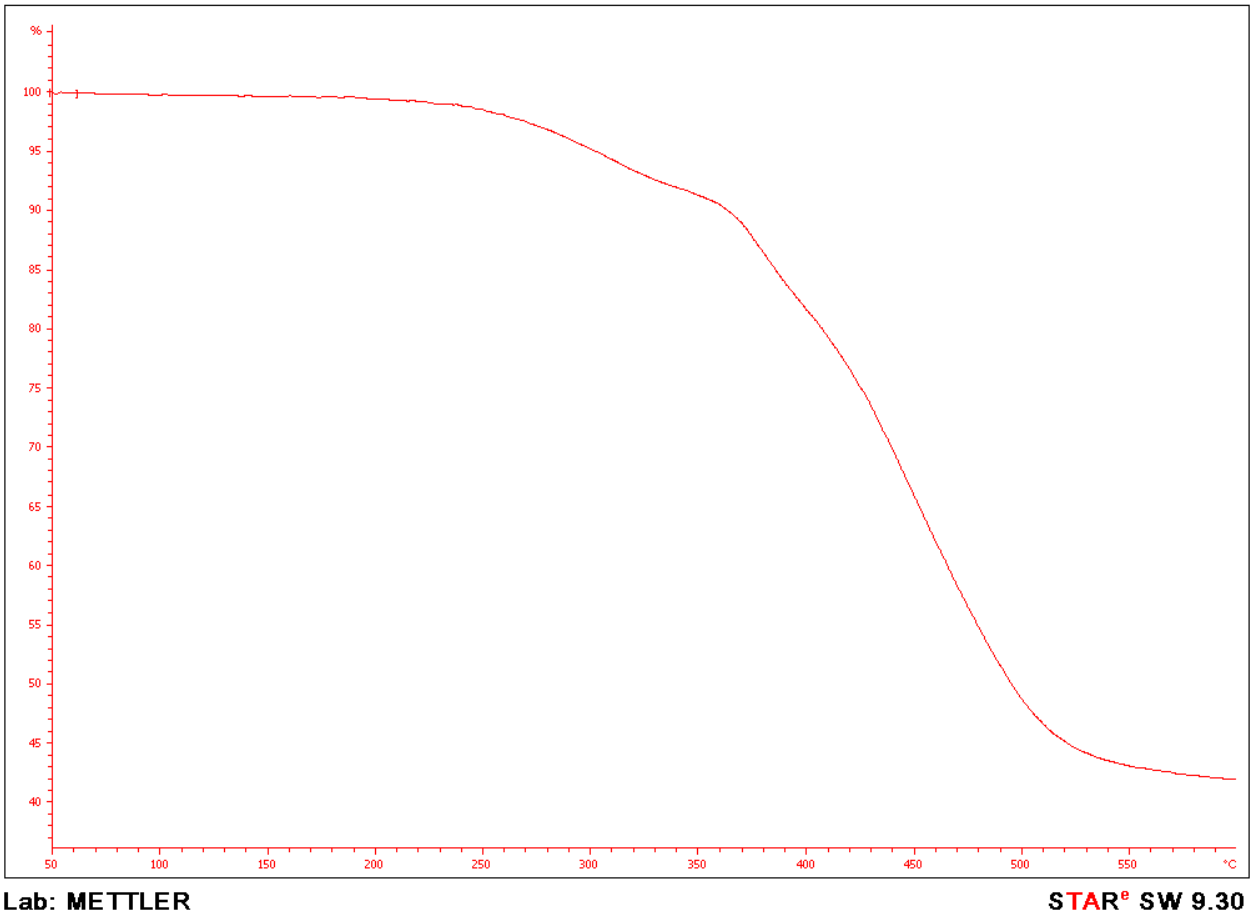

Figure S18: Thermogravimetric Analysis of PAABT

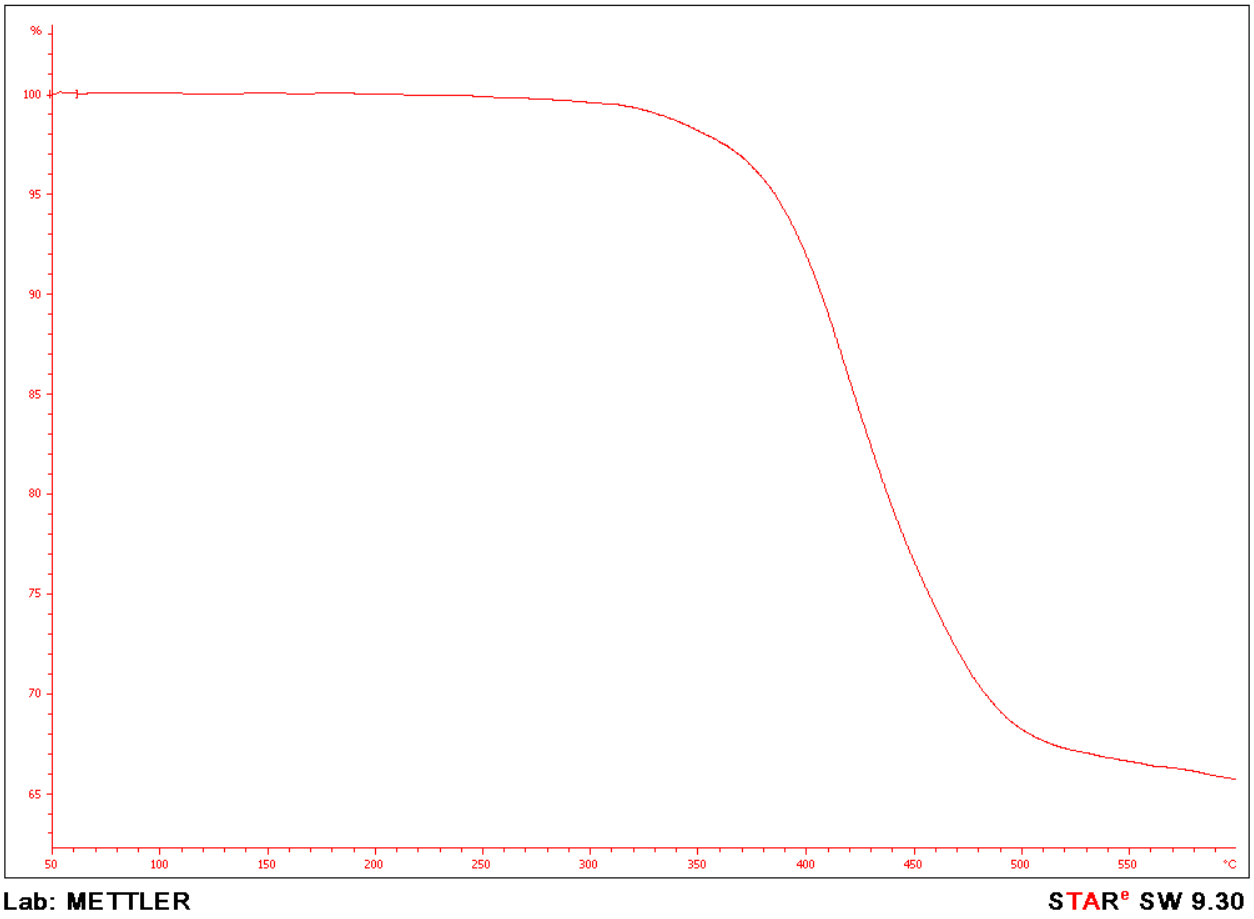

Figure S19: Thermogravimetric Analysis of PAATPD

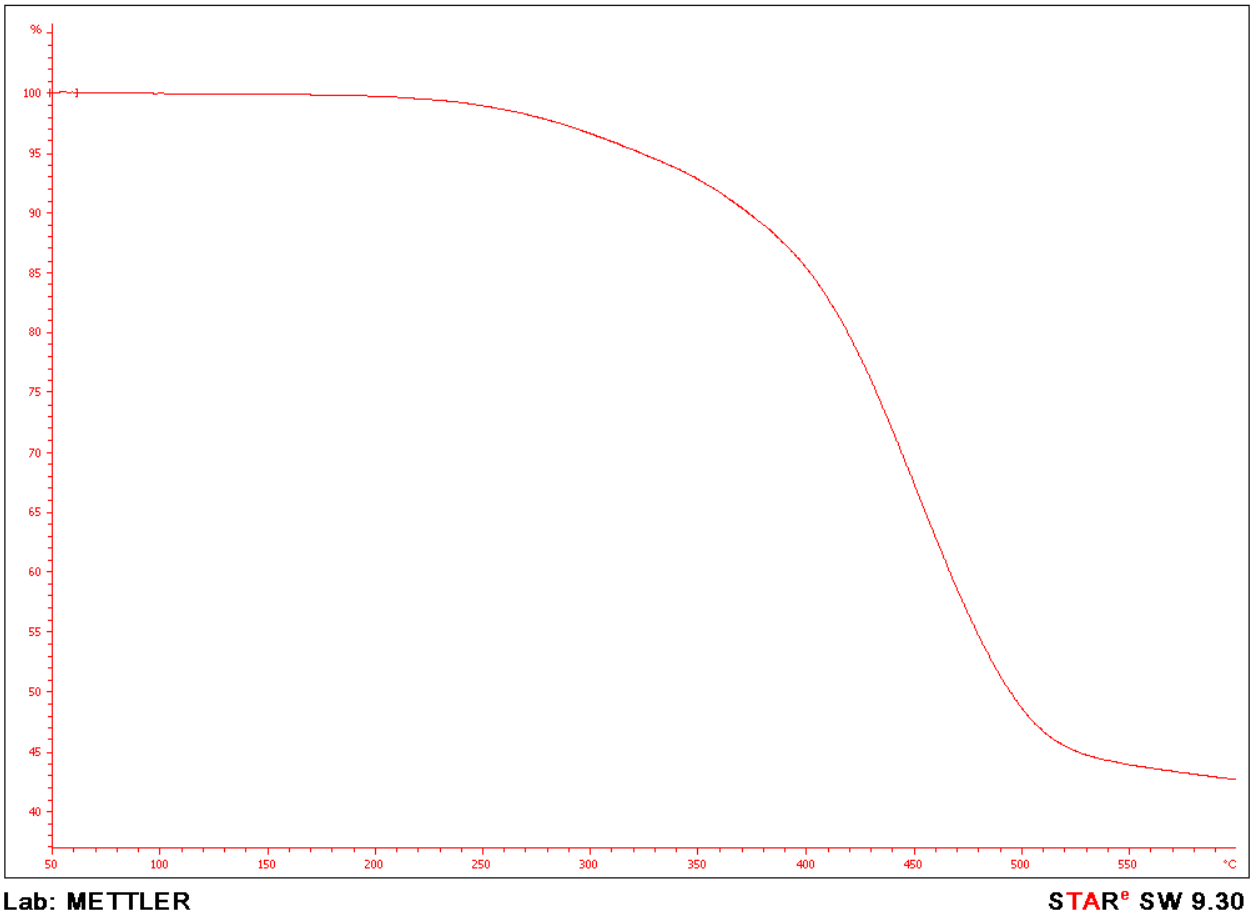

Figure S20: Thermogravimetric Analysis of PAAC

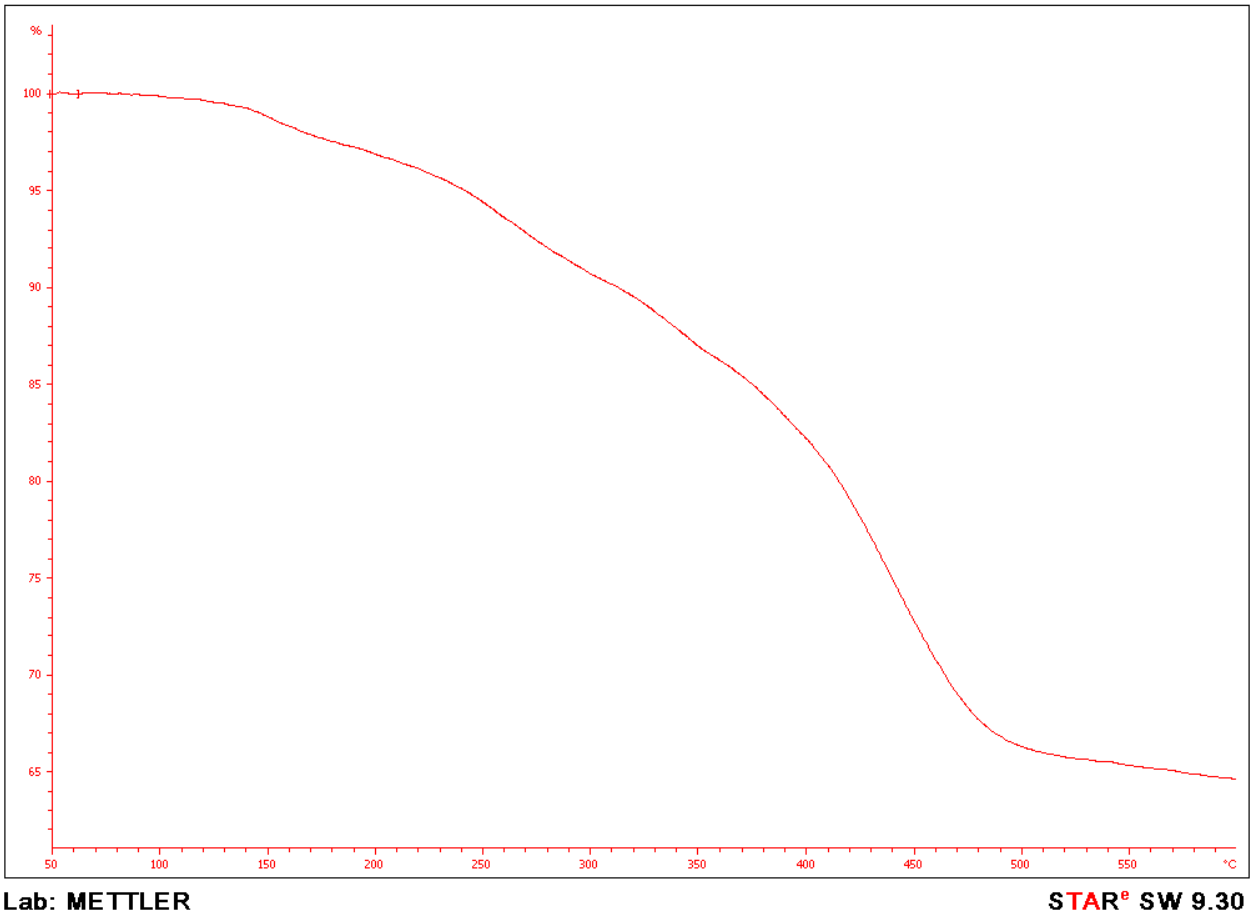

Figure S21: Thermogravimetric Analysis of PAADPP

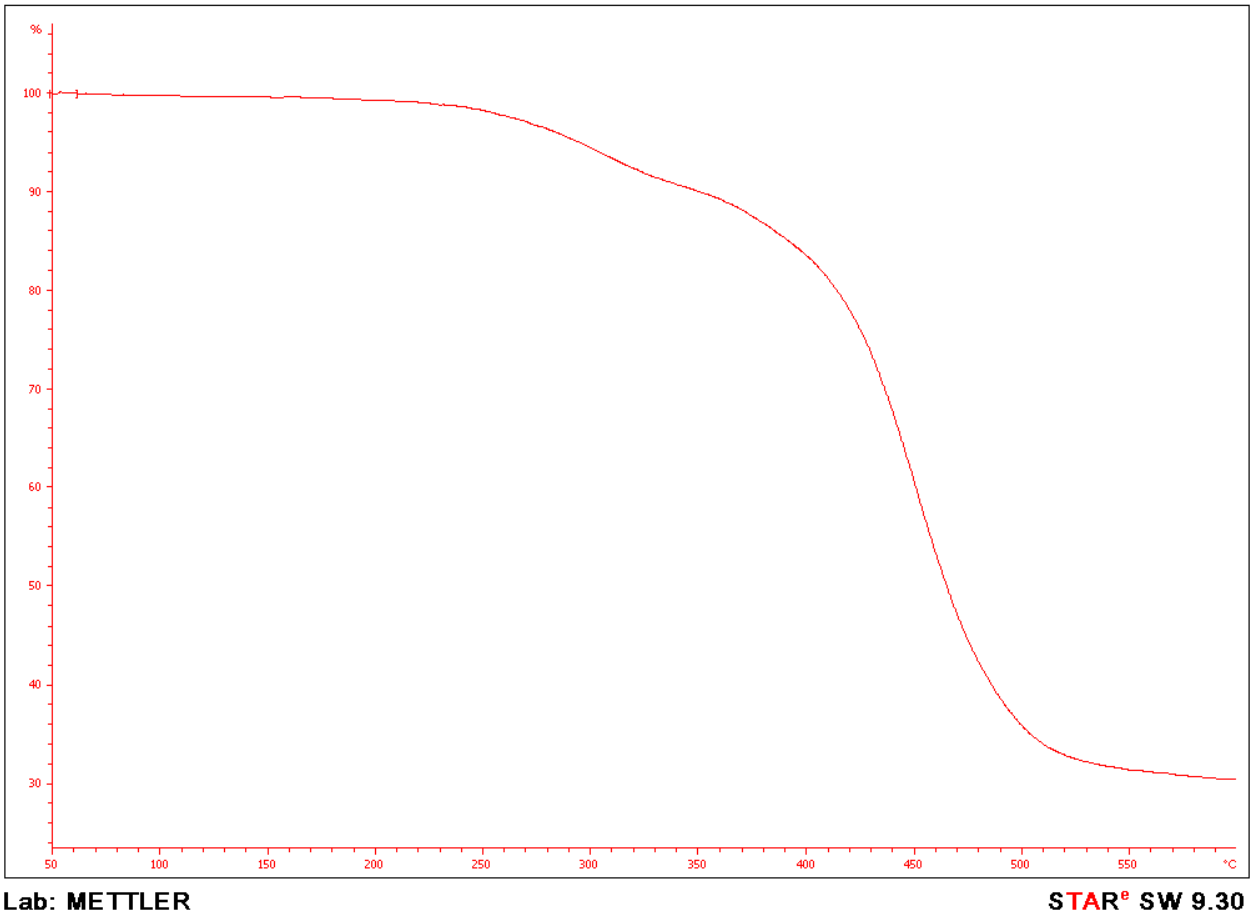

Figure S22: Thermogravimetric Analysis of PAABDT