Supporting information

Synthesis and Properties of 2,6-Azulene-Based Conjugated Polymers and their Applications in Dispersing Single-Walled Carbon Nanotubes

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Apparatus

NMR spectra were recorded using a Varian Inova AS400 spectrometer (Varian, Palo Alto, USA) at 400 MHz or an Agilent DD2 500 MHz. Signals are reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), dt (doublet of triplets), m (multiplet) and coupling constants (*J*) are reported in hertz (Hz). The chemical shifts are reported in ppm (δ) relative to residual solvent peak. High-resolution mass spectra (HRMS) were recorded using an Agilent 6210 time-of-flight (TOF) LCMS apparatus equipped with an ESI and APPI ion source (Agilent Technologies, Toronto, Canada). Number-average (M_n) and weight-average (M_w) molecular weights were obtained by size-exclusion chromatography (SEC) at high temperature using a Tosoh EcoSEC HLC-8321GPC/HT equipped with an RI detector. The column set consists of a TSKgel GMHhr-H(20) HT2, 20 µm, mixed bed, 7.8 mm ID x 30 cm column and a TSKgel GMHhr-H guard column (30 µm, 7.5 mm ID x 7.5). The flow rate was fixed at 1 mL min^{-1} using chloroform ($CHCl_3$) as the eluent. The temperature of the system was set to 40 °C. All the samples were prepared at a nominal concentration of 1.0 mg mL^{-1} in $CHCl_3$. Dissolution was performed using a homemade dry block heater. The sample vials were held at 40 °C with shaking for 1 h for complete dissolution. The solutions were filtered through a 2 mm porous stainless-steel filter used with a 0.40 mm thick glass filter having a 0.7 µm porosity into a 4 mL chromatography vial. A volume of 300 µL of sample solution was injected. The calibration method used to generate the reported data was the classical polystyrene method using polystyrene narrow standards EasiVial PS-H from Agilent which were dissolved in $CHCl_3$. UV-visible spectra of the polymers were recorded on a Varian diode-array spectrophotometer (model Cary 7000) using 10 mm path length quartz cells. Cyclic voltammograms (CVs) were recorded on a Solartron 1287 potentiostat using platinum electrodes at a scan rate of 100 mV s^{-} and an Ag/Ag^+ (0.01 M of $AgNO_3$ in acetonitrile) reference electrode in an anhydrous and argon-saturated solution of 0.1 M of tetrabutylammonium tetrafluoborate (Bu_4NPF_6) in acetonitrile.[1] In these conditions, for a freshly prepared reference electrode, the half-wave oxidation potential ($E_{½}$) of ferrocene should be around 0.091 V versus Ag/Ag$^+$ as reported by Li *and al.*[2] The HOMO and LUMO energy levels are determined from the oxidation and reduction onset.[3,4] The onsets potential (E') are determined at the position where the current starts to differ from the baseline.

$$E_{HOMO} = -\left[\left(E'_{ox\ vs\ Ag/Ag^{+}}\right) - \left(E^{1/2}_{Ferrocene\ vs\ Ag/Ag^{+}}\right) + 4.8\right]$$

$$E_{LUMO} = -\left[\left(E'_{red\ vs\ Ag/Ag^{+}}\right) - \left(E^{1/2}_{Ferrocene\ vs\ Ag/Ag^{+}}\right) + 4.8\right]$$

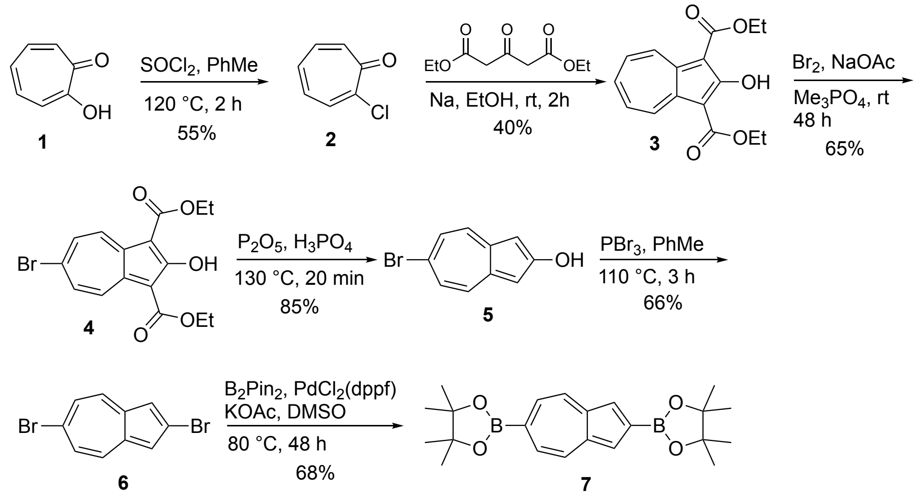
TGA spectra were recorded using a Mettler TGA/SDTA-851e/SF/1100 °C instrument equipped with a MT1 model balance. The balance was protected with a constant flow of PP nitrogen at a flow of 20 mL/min. 2 mg of samples were weight and heated from 50 °C to 550 °C at 10 °C/min. Elemental analysis was performed using a Flash 2000 CHNS Analyzer and a TDC detector from Thermo Scientific. L-Cystine and Sulfinamide were used as standards and were purchased from Fisher Scientific and Carlo Erba, respectively. The CHNS/NCS Multiseparation Column (PTFE, 6x5 mm Flash) was used for the analysis. The column temperature was 65°C and the combustion temperature was 950°C.

General Methods

Chemical reagents were purchased from Sigma-Aldrich Co. Canada, A2B, TCI America Co. or Oakwood Products Inc. and used as received, except for the tropolone that was recrystallized in petroleum ether (PE) first. Solvents used for organic synthesis were purchased from Fisher Chemical Co., EMD Millipore Co. and CFS Chemical Co. as HPLC grade. These solvents were degassed, dried and purified with a Solvent Purifier System (SPS) (Vacuum Atmosphere Co., Hawthorne, USA). All anhydrous and air-sensitive reactions were performed in oven-dried glassware under a positive stream of nitrogen.

Analytical thin layer chromatographies were performed on silica gel 60 F254, 0.25 mm pre-coated TLC plates (Silicycle, Québec, Canada). Compounds were revealed by a 254 nm and/or 365 nm UV wavelength and/or aqueous K_2CO_3 and NaOH solution of potassium permanganate. Flash column chromatographies were performed with 230-400 mesh silica gel R10030B (Silicycle, Québec, Canada). Azulene was prepared with a slightly modified procedure from literature and other monomers where prepared according to literature.[5–8]

Experimental section



Compound 2 (2-chlorocyclohepta-2,4,6-trien-1-one)

Tropolone (5.00 g, 41.0 mmol) was dissolved in toluene (125 mL) and thionyl chloride (4.5 mL, 61 mmol, 1.5 eq) was then added to the solution, producing a white precipitate of tropolone hydrogen chloride that dissolved after heating under reflux for 2 h, affording a dark-red solution. Excess thionyl chloride and toluene were removed by distillation and the brown residue was first washed with petroleum ether (PE) and then purified by column chromatography on silica with PE:AcOEt (1:5) before being recrystallized in hexanes to afford yellow crystals (3.17 g, 55%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 9.4, 0.8 Hz, 1H), 7.23 – 7.20 (m, 2H), 7.08 (dddd, *J* = 10.9, 6.5, 2.8, 0.8 Hz, 1H), 6.96 – 6.91 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.32, 149.27, 138.79, 135.79, 135.63, 134.16, 131.52. HRMS (ESI$^+$): calculated for C_7H_5ClO $(M+H)^+$ 141.0102, found 141.0116.

Compound 3 (diethyl 2-hydroxyazulene-1,3-dicarboxylate)

Sodium (4.00 g, 171 mmol, 12.0 eq) was added to absolute ethanol (120 mL). To this solution was added diethylacetone-1,3-dicarboxylate (4.34 g, 21.4 mmol, 1.5 eq), giving a pale-yellow solution. Then, a solution of compound **2** (2.00 g, 14.3 mmol, 1.0 eq) in absolute ethanol (6 mL) was added, resulting in a deep red solution. The mixture was stirred at 20 °C for 2 h. Water (150 mL) was added and the orange sodium salt was collected before it was redissolved in glacial acetic acid (25 mL) and diluted with water (70 mL). The mixture was extracted three times with dichloromethane and the combined organic layers were washed with brine, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by recrystallization in hexanes to afford orange crystals (1.65 g, 40%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.78 (s, 1H), 9.40 – 9.35 (m, 2H), 7.75 – 7.68 (m, 3H), 4.52 (q, *J* = 7.2 Hz, 4H), 1.50 (t, *J* = 7.1 Hz, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.28, 143.38, 136.19, 134.77, 132.48, 60.56, 14.59. HRMS (ESI$^+$): calculated for $C_{16}H_{16}O_5$ $(M+H)^+$ 289.1071, found 289.1065.

Compound 4 (diethyl 6-bromo-2-hydroxyazulene-1,3-dicarboxylate)

A solution of compound **3** (1.50 g, 5.20 mmol, 1.0 eq), anhydrous NaOAc (0.43 g, 5.20 mmol, 1.0 eq), and bromine (1.66 g, 10.4 mmol, 0.54 mL, 2.0 eq) in trimethyl phosphate (40 mL) was stirred for 16 hours at 50 °C. The reaction mixture was poured into 10% NH_4Cl and the precipitate was collected by filtration. The filtrate was extracted three times with toluene, washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by recrystallization in AcOEt:MeOH to afford orange crystals (1.54 g, 65%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.72 (s, 1H), 9.07 (d, *J* = 11.0 Hz, 2H), 8.01 – 7.95 (m, 2H), 4.52 (q, *J* = 7.1 Hz, 4H), 1.49 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.24, 141.61, 135.40, 132.81, 102.67, 60.80, 14.54. HRMS (APPI$^+$): calculated for $C_{16}H_5BrO_5$ $(M+H)^+$, not found.

Compound 5 (6-bromoazulen-2-ol)

P_2O_5 (23.20 g, 81.7 mmol, 30.0 eq) was dissolved in 85 % w/w aqueous H_3PO_4 (27 mL) and heated at 130 °C for 10 min. Then, compound **4** (1.00 g, 2.72 mmol, 1.0 eq) was added and the mixture was stirred at 130 °C for 30 min. After cooling at room temperature, the solution was carefully poured into ice water (500 mL) and extracted three times with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using hexanes:AcOEt as the eluent to afford a dark red powder (0.51 g, 85%).

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 11.23 (s, 1H), 7.81 (d, *J* = 10.5 Hz, 2H), 7.48 (d, *J* = 10.5 Hz, 2H), 6.80 (s, 2H). ^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 169.06, 139.09, 129.05, 127.13, 126.61, 105.90. HRMS (APPI$^+$): calculated for $C_{10}H_7BrO$ $(M+H)^+$ 222.9753, found 222.9771.

Compound 6 (2,6-dibromoazulene)

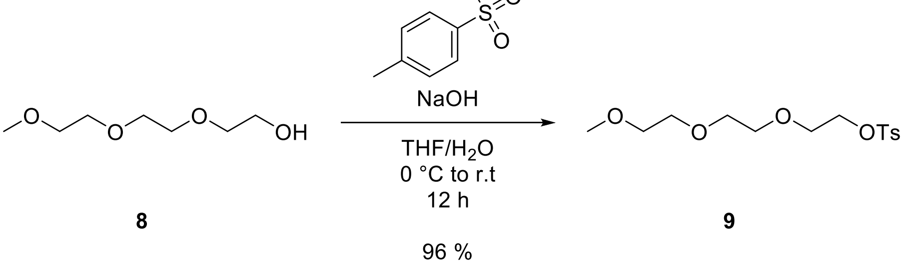
Compound **5** (1.00 g, 4.48 mmol, 1.0 eq) was dissolved in dry toluene (56 mL), then PBr_3 (3.64 g, 1.28 mL, 13.5 mmol, 3.0 eq) was added dropwise. The mixture was stirred at 110 °C for 3 h. The mixture was poured into ice water (500 mL) and the aqueous phase was extracted three times with ethyl acetate. The combined organic layers were washed with water (140 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica with petroleum ether to give a dark violet powder (0.84 g, 66%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (dt, *J* = 10.4, 0.8 Hz, 2H), 7.58 (dt, *J* = 10.3, 0.7 Hz, 2H), 7.37 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.43, 134.45, 133.19, 128.29, 128.05, 120.72. HRMS (APPI$^+$): calculated for $C_{10}H_6Br_2$ $(M+H)^+$ 284.8909, found 284.8906.

Compound 7 (2,2'-(azulene-2,6-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane))

Compound **6** (4.00 g, 14.0 mmol, 1.0 eq), KOAc (8.24 g, 83.9 mmol, 6.0 eq), bis(pinacolato)diboron (21.3 g, 83.9 mmol, 6.0 eq) and $PdCl_2$(dppf) (1.02 g, 1.34 mmol, 0.1 eq) were dissolved in dry DMSO and stirred 2 days at 80 °C. The mixture was then filtrated over Celite® and water was added to the filtrate. The aqueous phase was extracted three times with AcOEt and the combined organic layers were washed with water and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The resulting solid was recrystallized in isopropanol twice to afford greenish blue crystals (3.62 g, 68%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 9.9 Hz, 2H), 7.74 (s, 2H), 7.67 (d, *J* = 9.6 Hz, 2H), 1.40 (d, *J* = 5.3 Hz, 24H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.77, 137.08, 128.47, 124.57, 84.59, 83.77, 24.93 (d, *J* = 3.1 Hz). HRMS (ESI$^+$): calculated for $C_{22}H_{30}B_2O_4$ $(M+H)^+$ 381.2411, found 381.2411.



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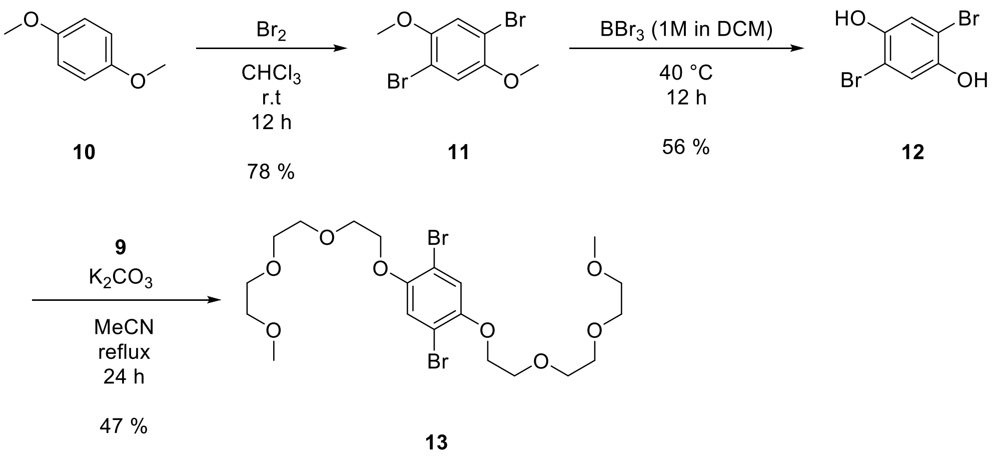
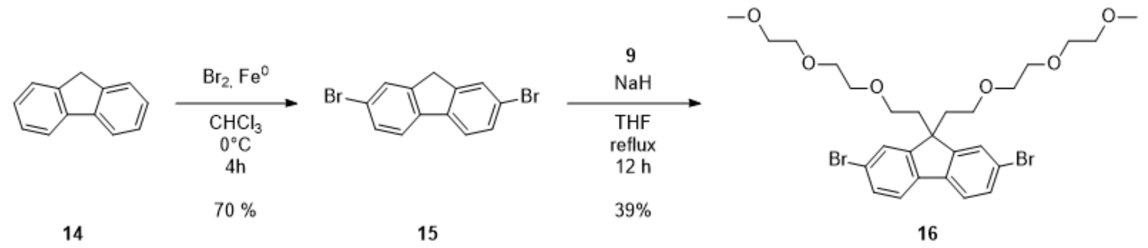
Compound 9 (2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate)

Compound **8** (10 g, 60 mmol, 1.0 eq) was dissolved in THF (30 mL) and the resulting solution was cooled in a water-ice bath. To this solution, sodium hydroxide (7.30 g, 183 mmol, 3.0 eq) in water (30 mL) was added, followed by *p*-tosyl chloride (15.1 g, 79.2 mmol, 1.3 eq) in THF (20 mL) over 30 min. Then, the mixture was allowed to warm at room temperature and stirred overnight. After completion of the reaction, the organic layer was collected and the aqueous layer was extracted twice with diethyl ether. The combined organic layers were washed with 10% sodium hydroxide solution, followed by water and brine. The organic phase was dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure to provide the desired product as a colorless viscous liquid (18.15 g, 95%).

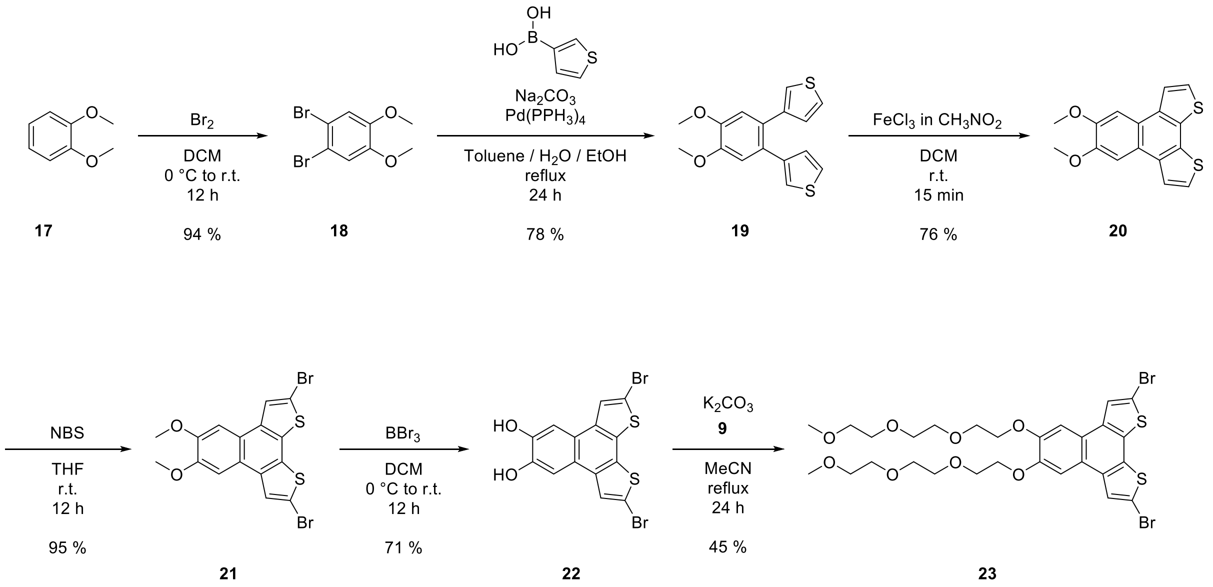
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 8.3 Hz, 2H), 7.34 (dq, J = 8.0, 0.7 Hz, 2H), 4.19 – 4.13 (m, 3H), 3.76 – 3.72 (m, 2H), 3.70 – 3.67 (m, 2H), 3.62 – 3.59 (m, 3H), 3.59 (s, 4H), 3.54 – 3.51 (m, 3H), 3.37 (s, 4H), 2.45 (d, J = 0.9 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.79, 132.98, 129.82, 127.98, 71.89, 70.73, 70.55, 70.53, 68.66, 67.97, 59.03, 25.60, 21.64. HRMS (APPI$^+$): calculated for $C_{14}H_{22}O_6S$ $(M + H)^+$ 319.1210, found 319.1253.



Compound **13** was obtained following reported procedure[8]



Compound **16** was obtained following reported procedure[6]



Compound 21 (2,9-dibromo-5,6-dimethoxynaphtho[2,1-b:3,4-b']dithiophene)

Synthesis up to compound **20** was synthesized following reported literature.[7] *N*-bromosuccinimide (NBS) (2.17 g, 13.4 mmol, 2 eq) in dichloromethane (50 mL) was added to a solution of compound **20** (2.00 g, 6.66 mmol) in dichloromethane (200 mL) under nitrogen and the mixture was stirred at room temperature for 12 h. After aqueous sodium thiosulfate ($Na_2S_2O_3$) was added to the mixture, the organic layer was collected and the aqueous layer was extracted three times with AcOEt. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure to provide the desired product (2.90 g, 95%). The product was pure enough to be used without further purification.

1H NMR (500 MHz, $CDCl_3$) δ 7.80 (s, 2H), 7.45 (s, 2H), 4.08 (s, 6H). 13C NMR (126 MHz, $CDCl_3$) δ 149.15, 133.55, 130.35, 125.33, 121.58, 112.31, 104.20, 56.01, 29.57. HRMS (APPI$^+$): calculated for $C_{16}H_{10}Br_2O_2S_2$ $(M+H)^+$ 456.8562, found 456.8535.

Compound 22 (2,9-dibromonaphtho[2,1-*b*:3,4-*b'*]dithiophene-5,6-diol)

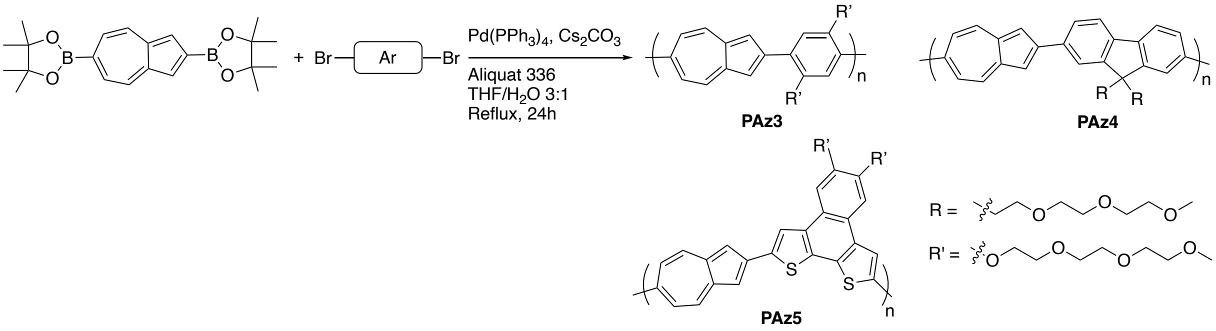
Compound **21** (1.00 g, 2.18 mmol, 1.0 eq) was dissolved in dry dichloromethane (90 mL) and the solution was cooled at -78 °C. BBr_3 (10.9 mL, 5.0 eq, 1M in CH_2Cl_2) was added dropwise. The resulting mixture was allowed to warm at room temperature and the resulting solution was stirred overnight. Diethyl ether was added and the solution was washed with water, saturated $NaHCO_3$ solution and brine, dried over Na_2SO_4 and concentrated under vacuum. The crude product was then washed with a small amount of AcOEt and filtered to afford the desire compound as a green powder (0.66 g, 71%).

^{1}H NMR (500 MHz, acetone-d_6) δ 8.07 (s, 2H), 7.80 (s, 2H). ^{13}C NMR (126 MHz, acetone-d_6) δ 170.01, 148.60 – 143.51 (m), 134.13, 129.10, 121.94, 111.31, 108.27, 59.64, 19.93, 13.61. HRMS (APPI$^+$): calculated for $C_{14}H_6Br_2O_2S_2$ $(M+H)^+$ 428.8249, found 428.8203.

Compound 23 (2,9-dibromo-5,6-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)naphtho[2,1-*b*:3,4-*b'*]dithiophene)

A solution of compound **22** (0.20 g, 0.46 mmol, 1.0 eq) and K_2CO_3 (0.26 g, 1.86 mmol, 4.0 eq) in acetonitrile (4 mL) was heated to reflux under nitrogen for 30 min. Then, a solution of compound **9** (0.44 g, 1.39 mmol, 3.0 eq) in acetonitrile (1 mL) was added dropwise to the mixture and the resulting solution was heated to reflux for an additional 24 h. The reaction mixture was then cooled at room temperature, filtered and the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel using AcOEt as the eluent to give the desired compound as a yellow liquid (0.15 g, 45%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (s, 2H), 7.59 (s, 2H), 4.37 (dd, J = 5.5, 4.5 Hz, 4H), 4.02 – 3.96 (m, 4H), 3.84 – 3.79 (m, 4H), 3.75 – 3.70 (m, 4H), 3.70 – 3.65 (m, 4H), 3.58 – 3.53 (m, 4H), 3.38 (d, J = 0.8 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.95, 133.66, 130.45, 125.47, 121.98, 112.30, 107.09, 71.95, 70.99, 70.76, 70.60, 69.76, 68.84, 59.05. HRMS (ESI$^+$): calculated for $C_{28}H_{34}Br_2O_8S_2$ $(M+H)^+$ 721.0135, found 720.9941.



General procedure for polymerization

A dry flask equipped with magnetic stir bar was charged with 1.0 eq of compound **7** and 1.0 eq. of the corresponding dibrominated monomer, Cs_2CO_3 (4.0 eq) and $Pd(PPh_3)_4$ (1.2% mol). The vessel was put under vacuum for one hour and purged three times with nitrogen. In a separated flask, a mixture of THF:H_2O (3:1) (0.2M) and Aliquat 336 (0.03 eq) was degassed with nitrogen for 1 hour before being added to the first flask. The mixture was then stirred at reflux for 24 hours. The reaction was cooled at room temperature and the polymer was precipitated in cold hexanes. The precipitate was filtered under vacuum and washed with hexanes, methanol and acetone using a Soxhlet apparatus. The polymer was then collected with using a Soxhlet in $CHCl_3$. The solution was concentrated under reduced pressure and the polymer was precipitated in cold hexanes and dried to give the desired polymers 86, 25 and 10 % yield for **Paz3**, **Paz4** and **Paz5**, respectively.

NMR SPECTRA

Compound 2 : (2-Chlorocyclohepta-2,4,6-trien-1-one)

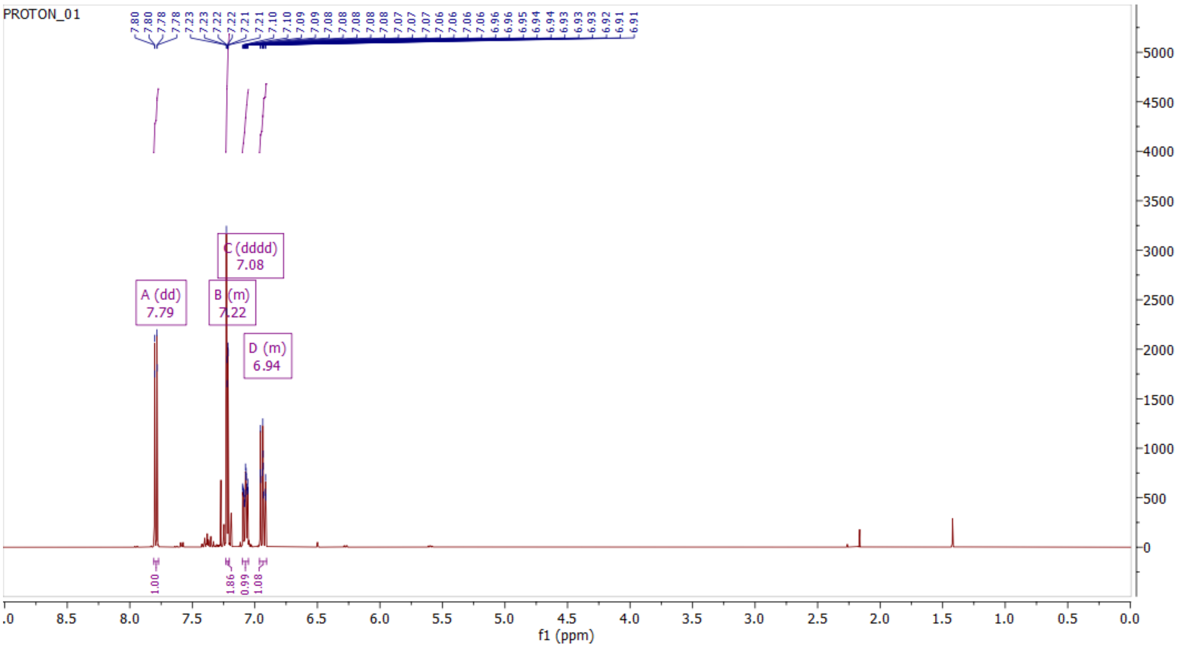


Figure S1: ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

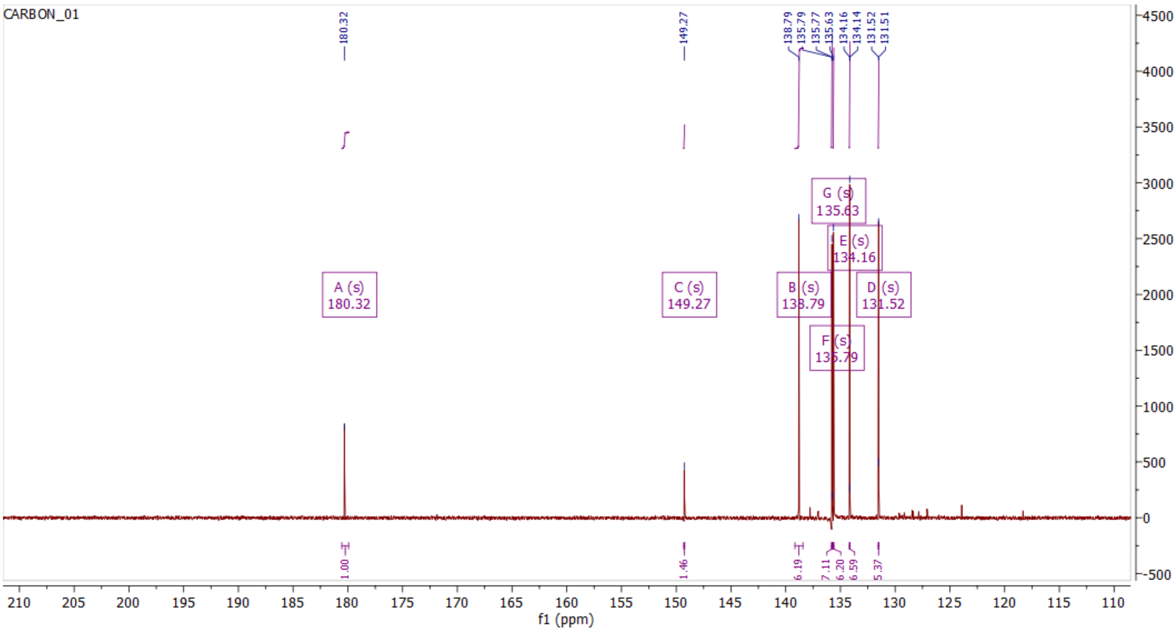


Figure S2: ^{13}C NMR spectrum of compound **2** in $CDCl_3$.

Compound 3: diethyl 2-hydroxyazulene-1,3-dicarboxylate

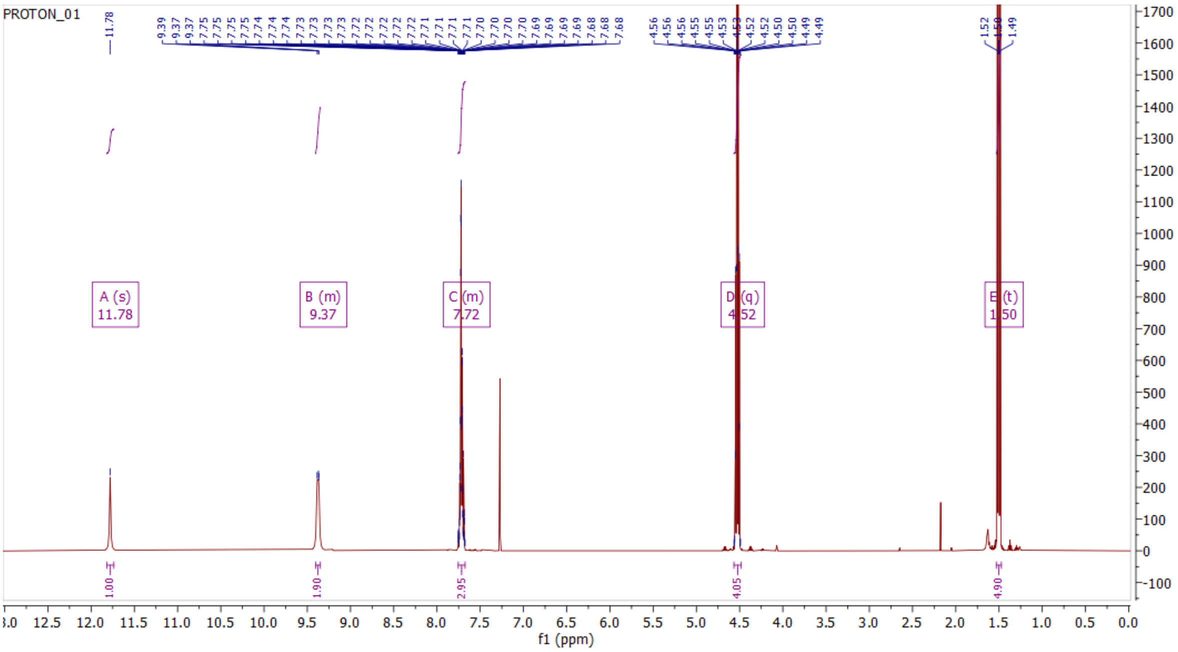


Figure S3: ^{1}H NMR spectrum of compound **3** in CDCl$_3$.

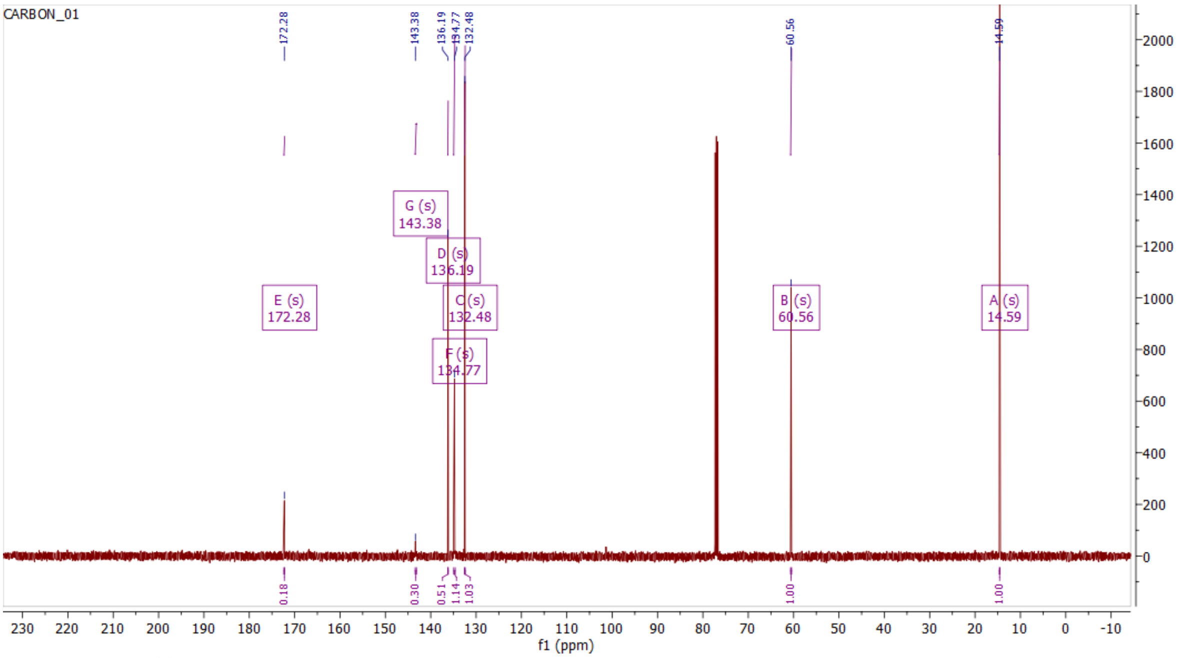


Figure S4: ^{13}C NMR spectrum of compound **3** in CDCl$_3$.

Compound 4: diethyl 6-bromo-2-hydroxyazulene-1,3-dicarboxylate

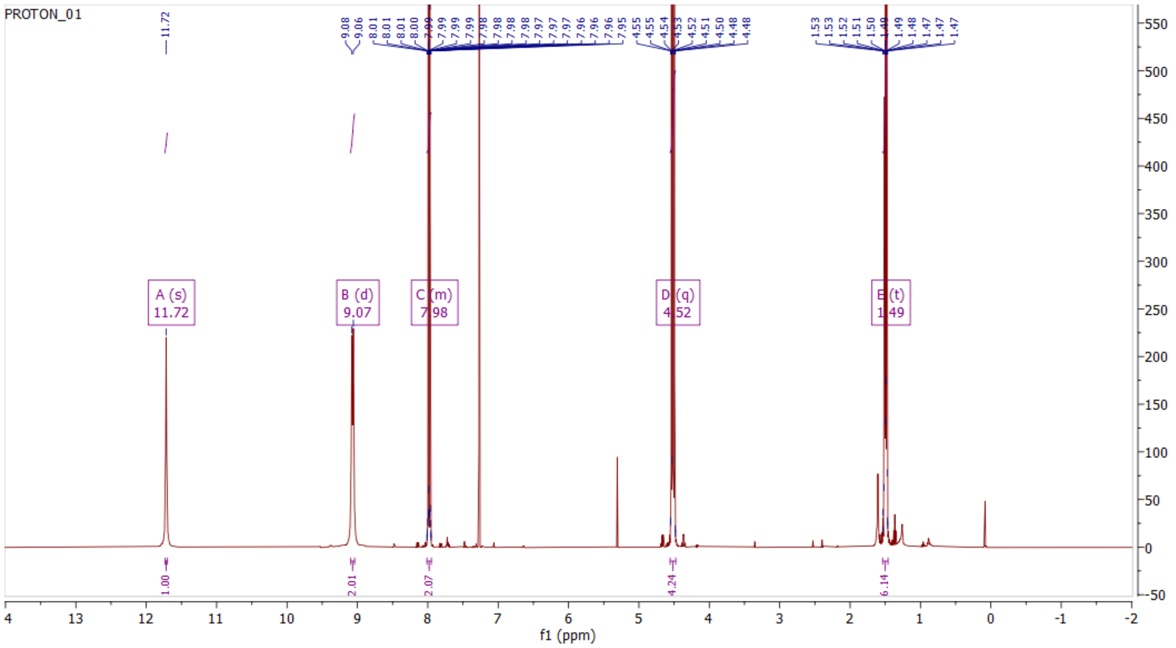


Figure S5: ^{1}H NMR spectrum of compound **4** in $CDCl_3$.

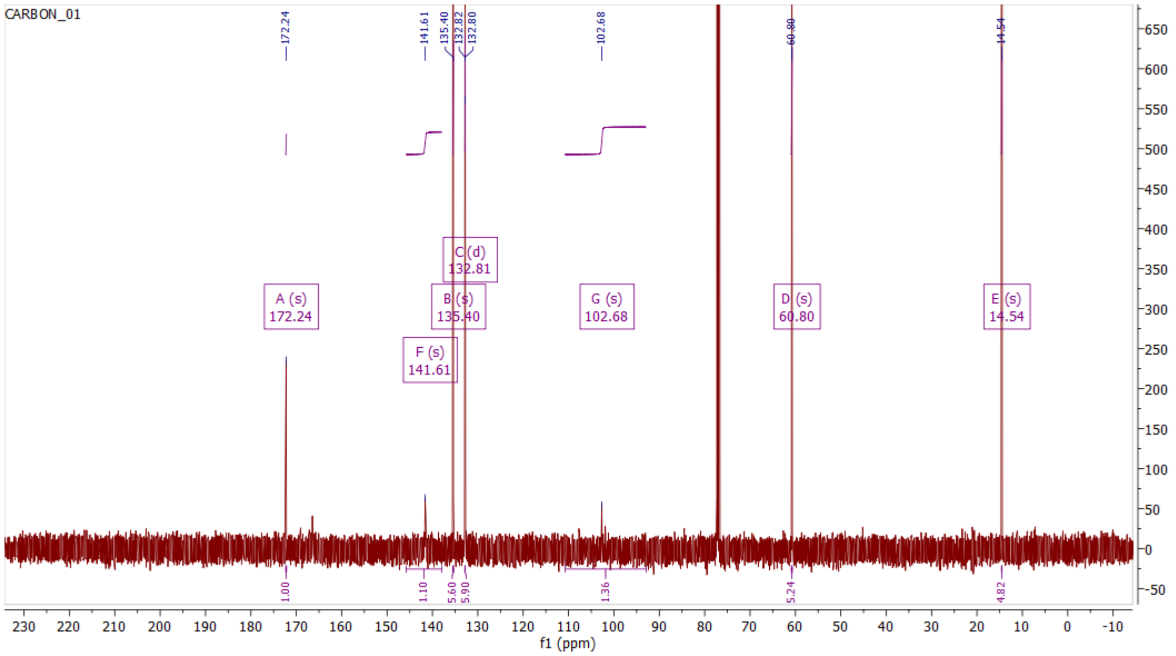


Figure S6: ^{13}C NMR spectrum of compound **4** in $CDCl_3$.

Compound 5: 6-bromoazulen-2-ol

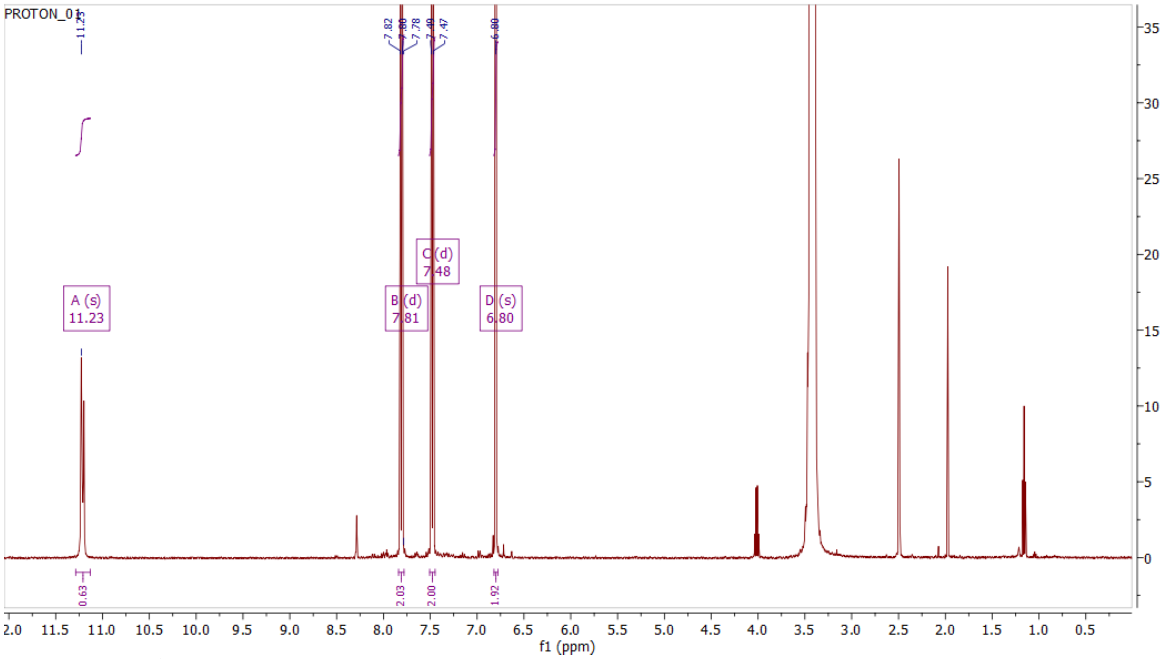


Figure S7: ^{1}H NMR spectrum of compound **5** in DMSO-d_6.

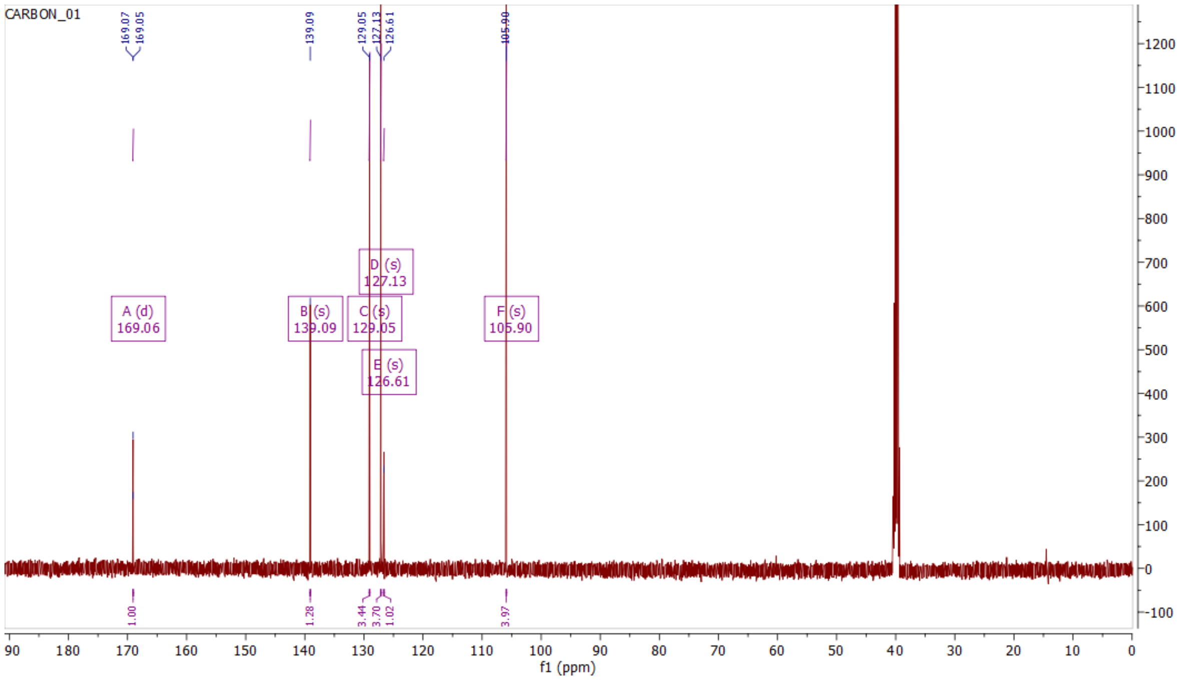


Figure S8: ^{13}C NMR spectrum of compound **5** in DMSO-d_6.

Compound 6: 2,6-dibromoazulene

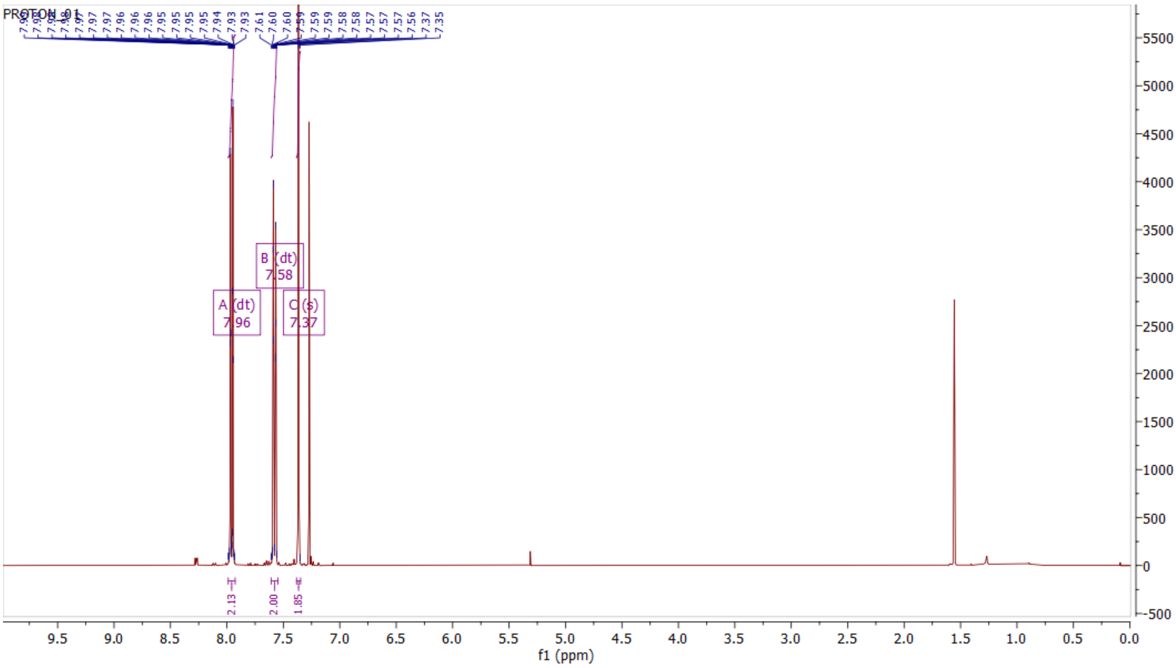


Figure S9: ^{1}H NMR spectrum of compound **6** in $CDCl_3$.

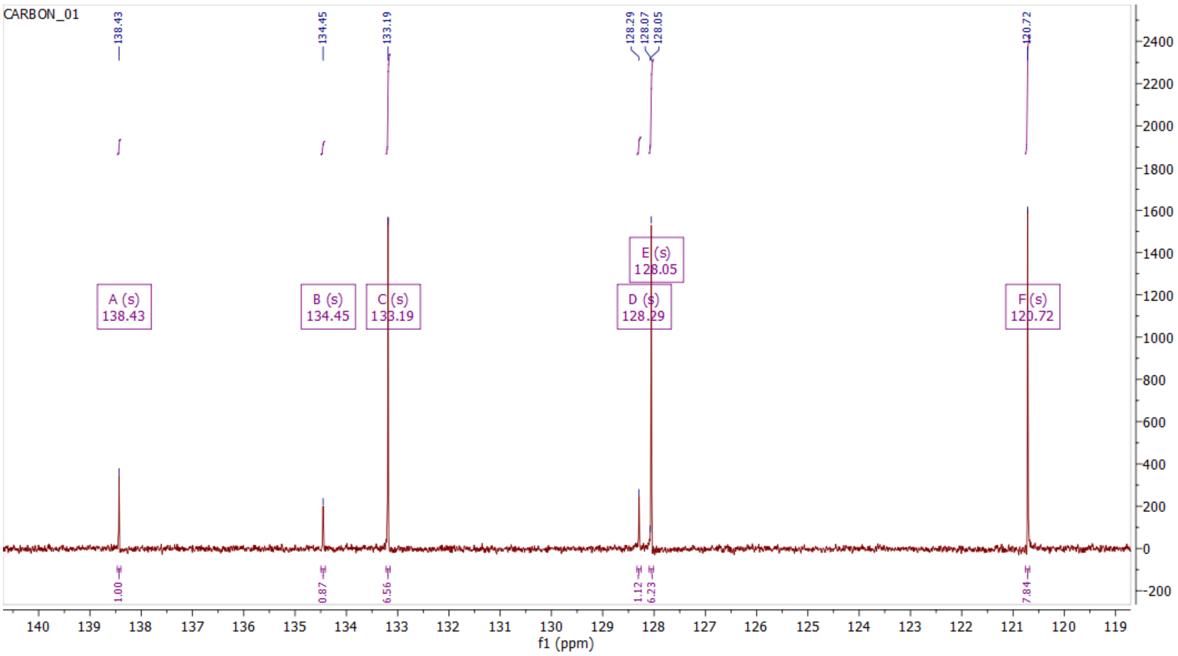


Figure S10: ^{13}C NMR spectrum of compound **6** in $CDCl_3$.

Compound 7: 2,2'-(Azulene-2,6-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)

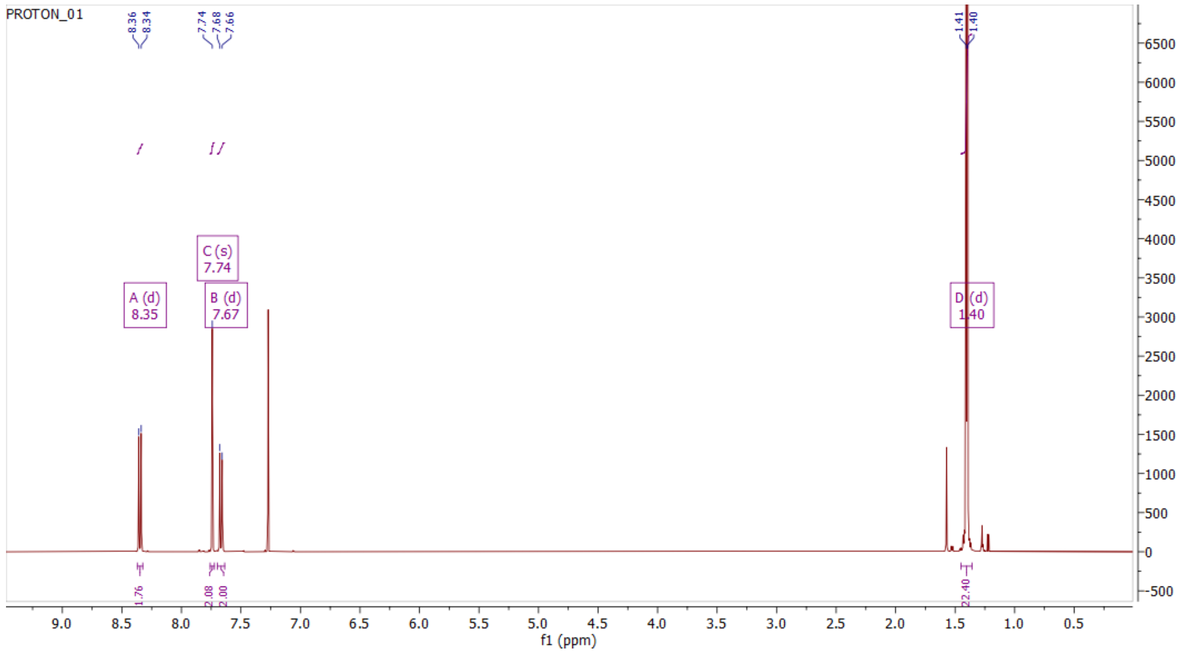


Figure S11: ^{1}H NMR spectrum of compound **7** in $CDCl_3$.

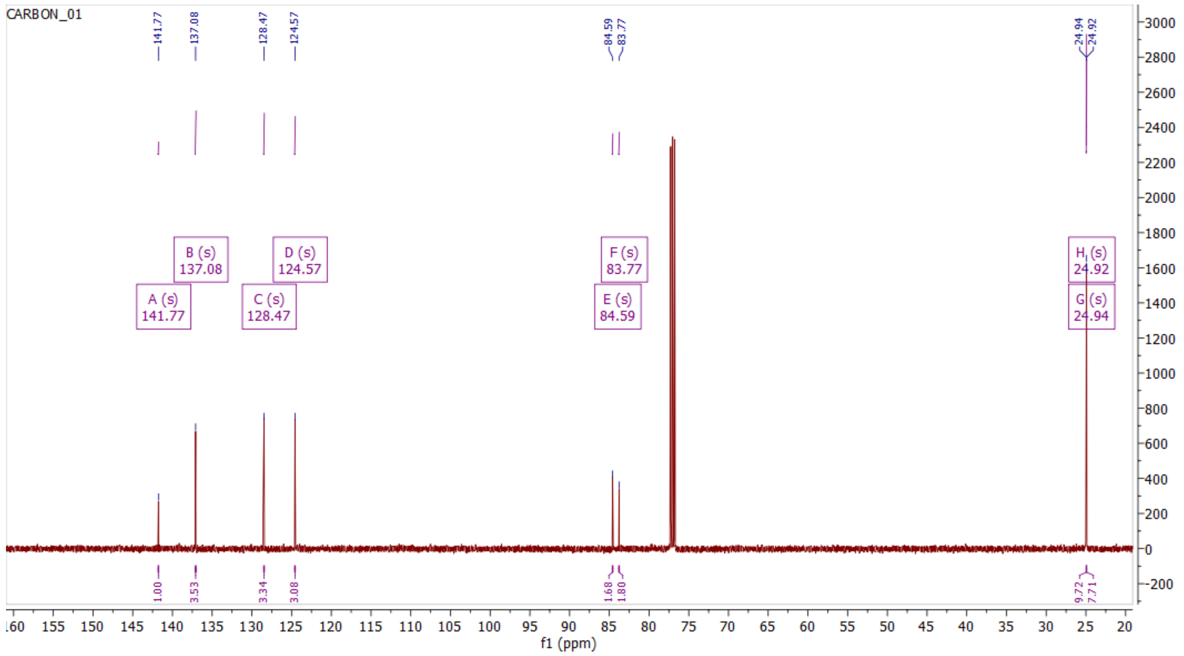


Figure S12: ^{13}C NMR spectrum of compound **7** in $CDCl_3$.

Compound 9: 2-(2-(2-Methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate

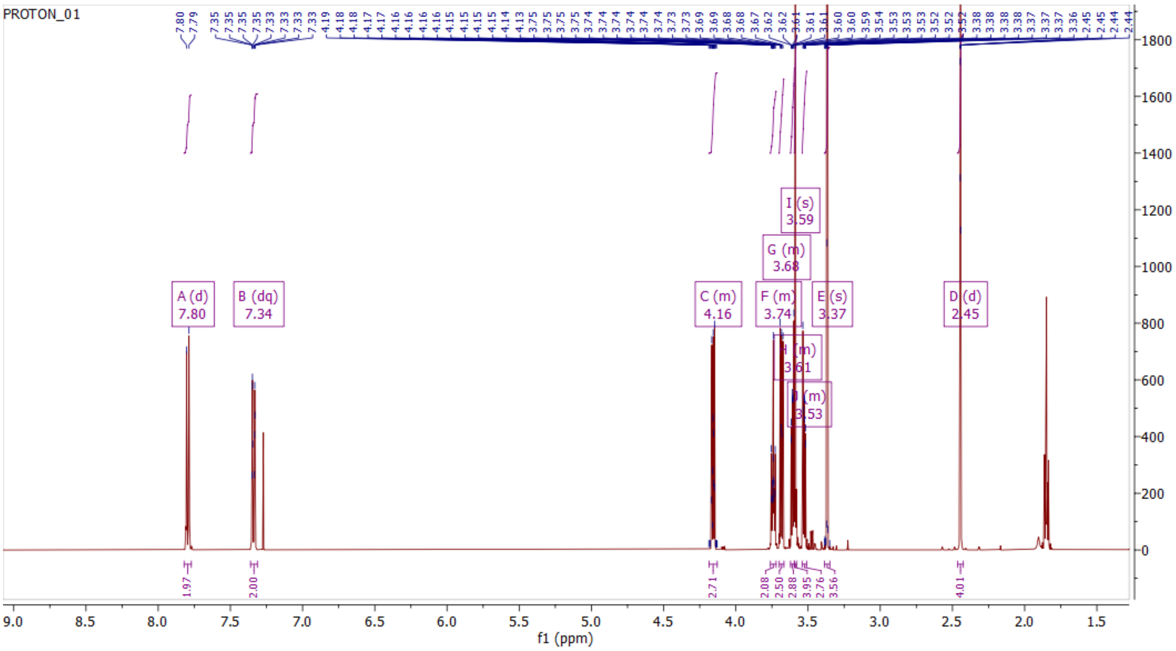


Figure S13: ^{1}H NMR spectrum of compound **9** in CDCl$_3$.

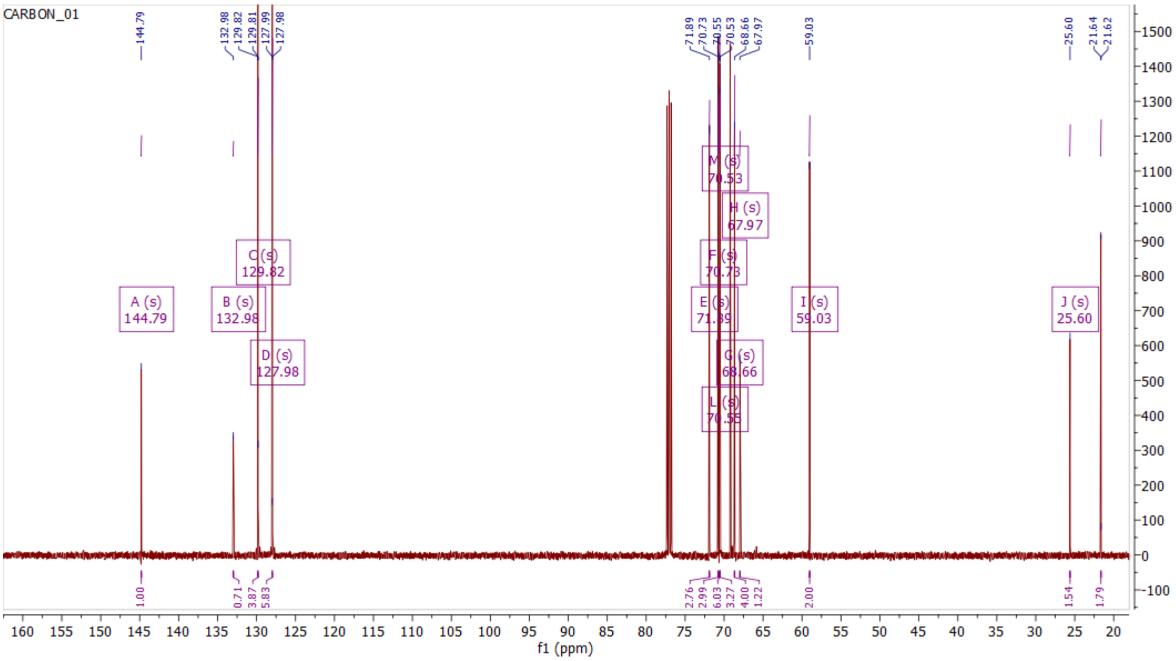


Figure S14: ^{13}C NMR spectrum of compound **9** in CDCl$_3$.

Compound 13: 1,4-dibromo-2,5-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene

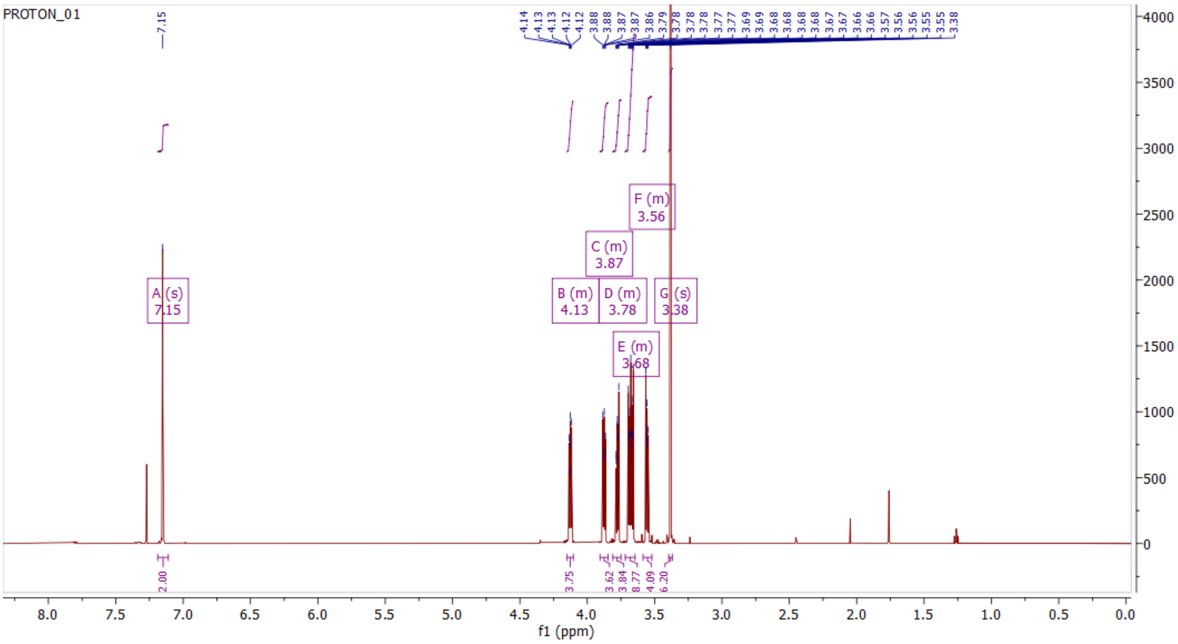


Figure S15: ^{1}H NMR spectrum of compound **13** in $CDCl_3$.

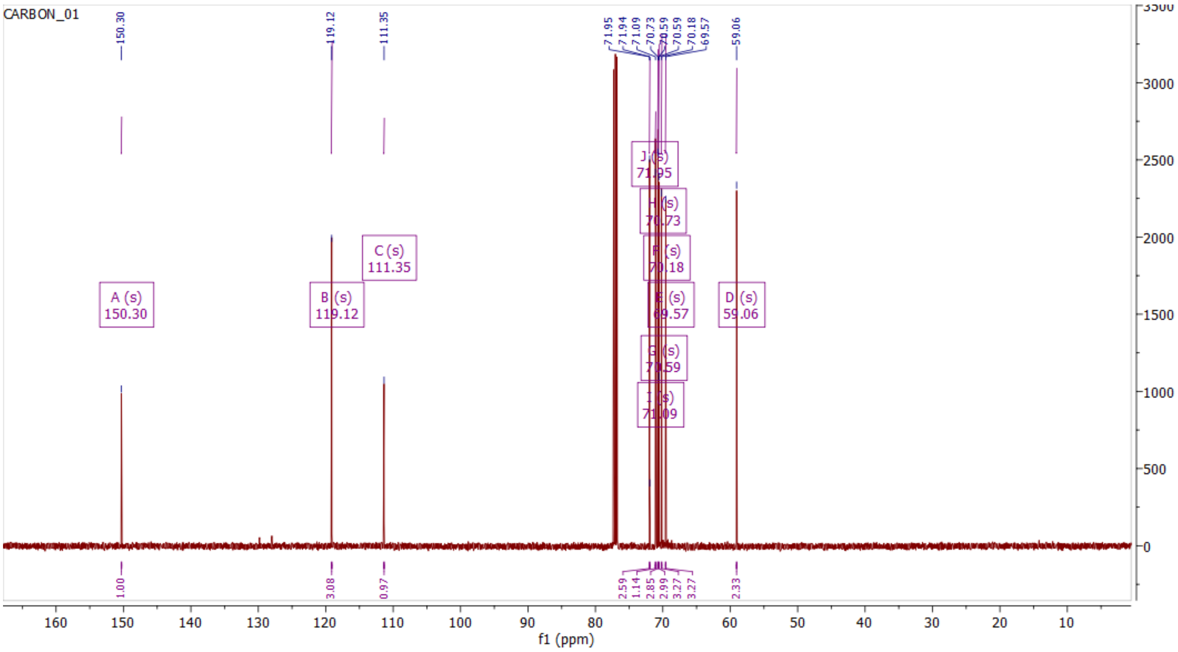


Figure S16: ^{13}C NMR spectrum of compound **13** in $CDCl_3$.

Compound 16: 2,7-Dibromo-9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-9H-fluorene

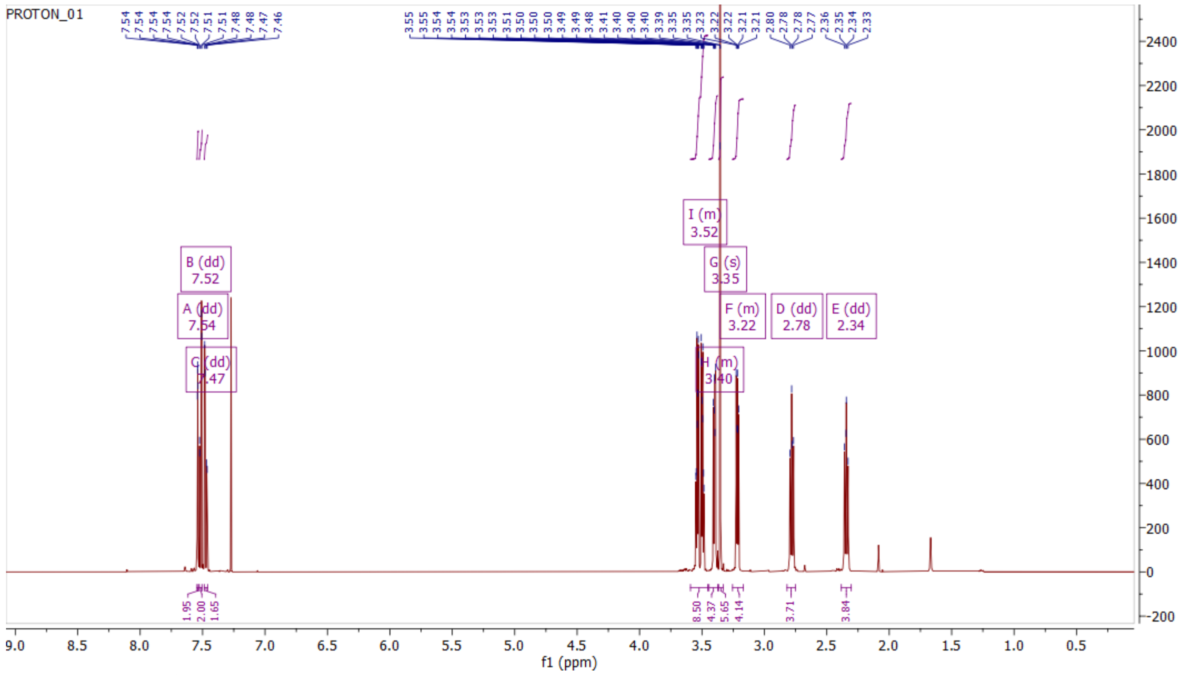


Figure S17: ^{1}H NMR spectrum of compound **16** in CDCl$_3$.

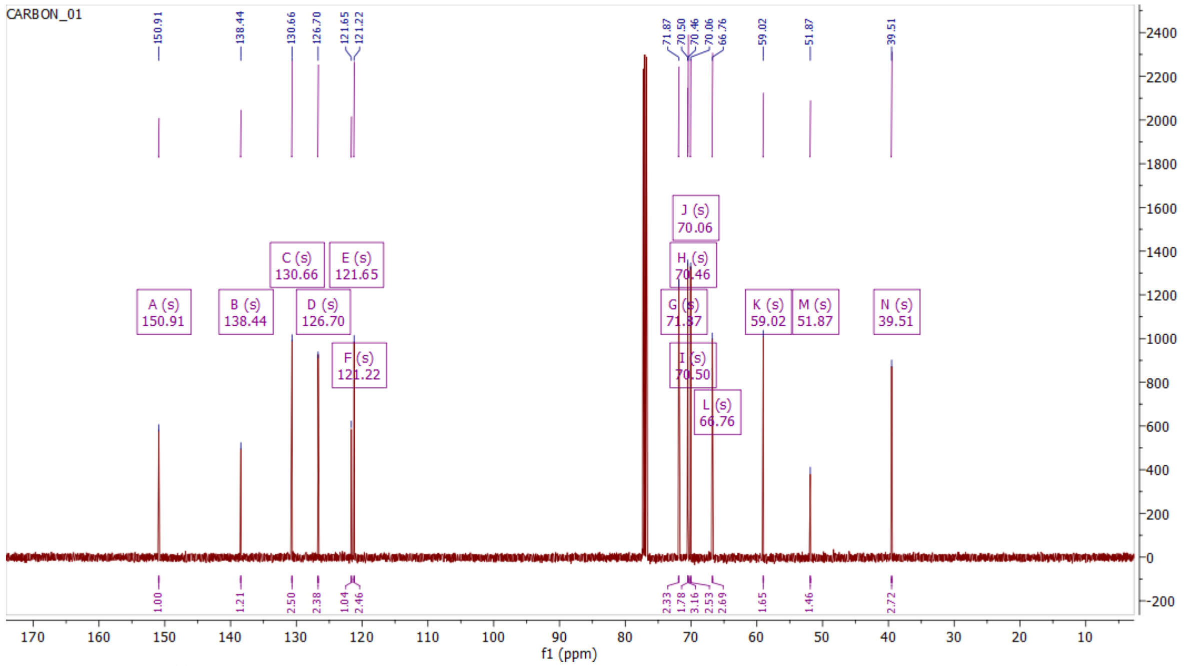


Figure S18: ^{13}C NMR spectrum of compound **16** in CDCl$_3$.

Compound 19: 3,3'-(4,5-Dimethoxy-1,2-phenylene)dithiophene

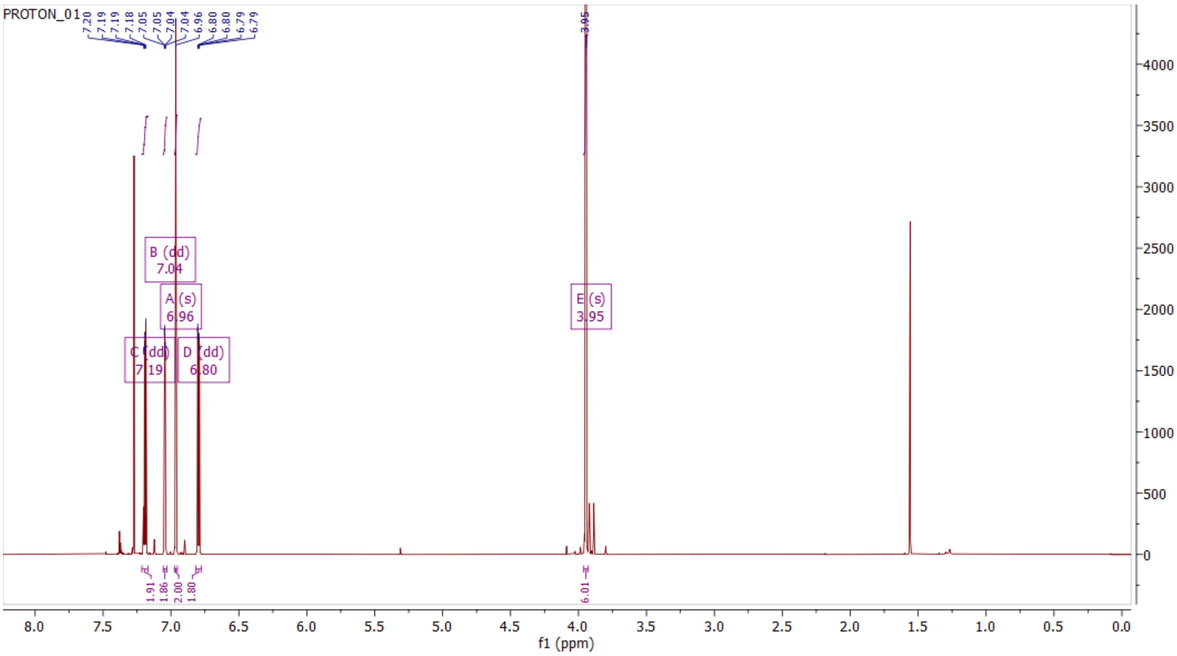


Figure S19: ^{1}H NMR spectrum of compound **19** in $CDCl_3$.

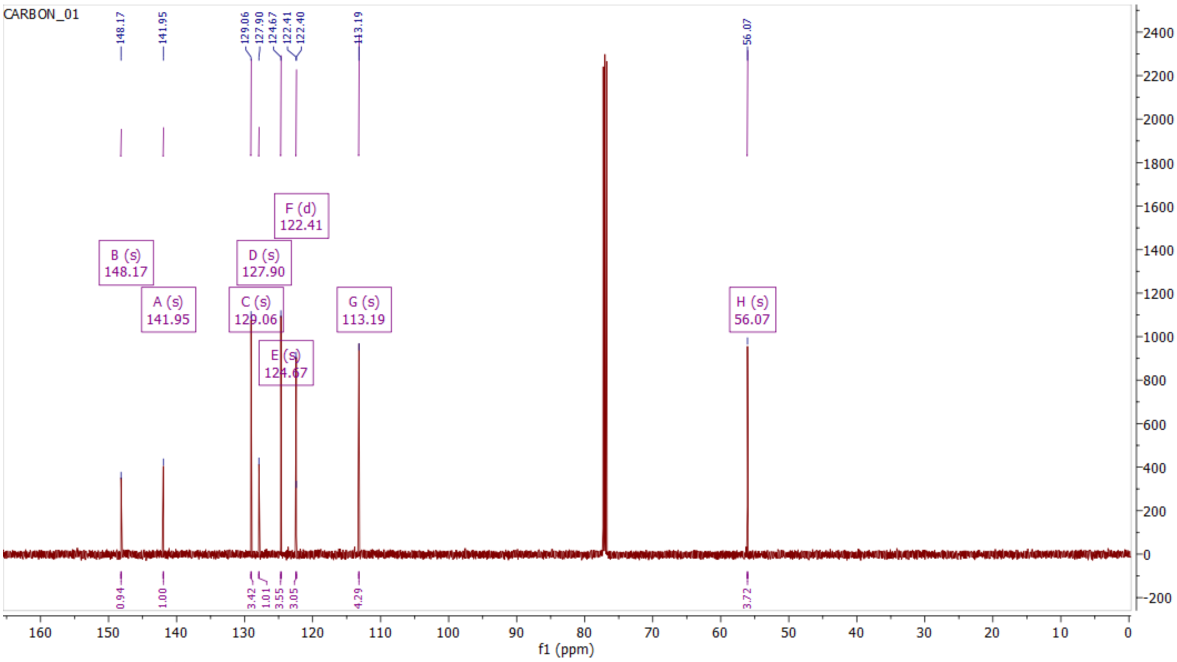


Figure S20: ^{13}C NMR spectrum of compound **19** in $CDCl_3$.

Compound 20: 5,6-Dimethoxynaphtho[2,1-*b*:3,4-*b'*]dithiophene

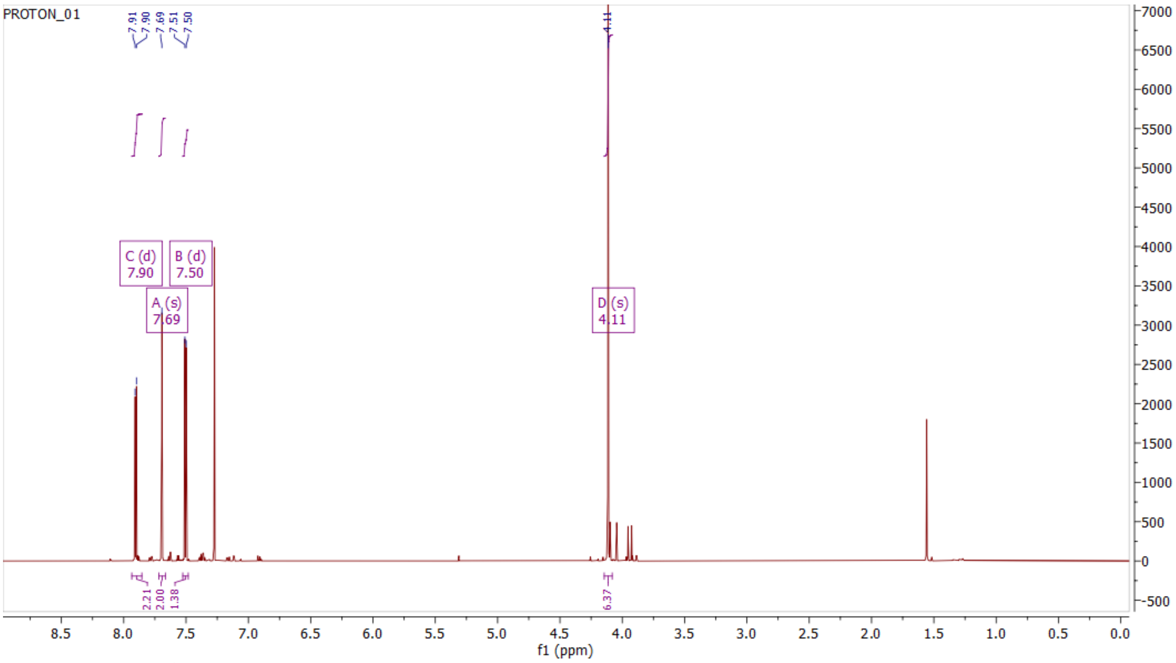


Figure S21: ^{1}H NMR spectrum of compound **20** in $CDCl_3$.

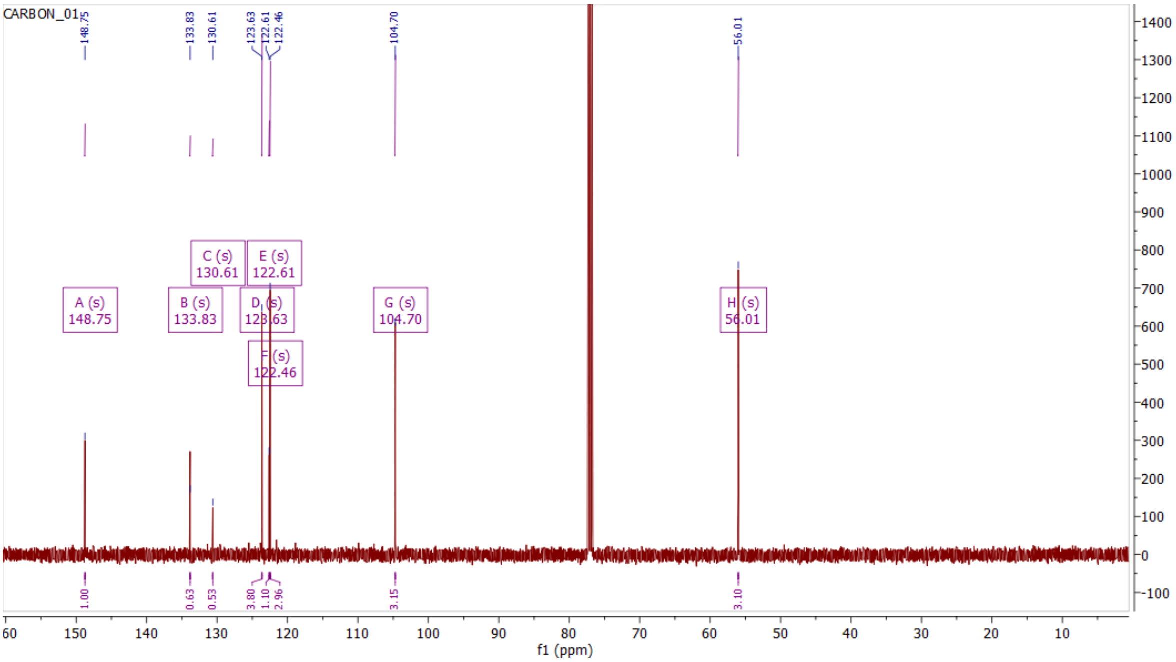


Figure S22: ^{13}C NMR spectrum of compound **20** in $CDCl_3$.

Compound 21: 2,9-dibromo-5,6-dimethoxynaphtho[2,1-*b*:3,4-*b′*]dithiophene

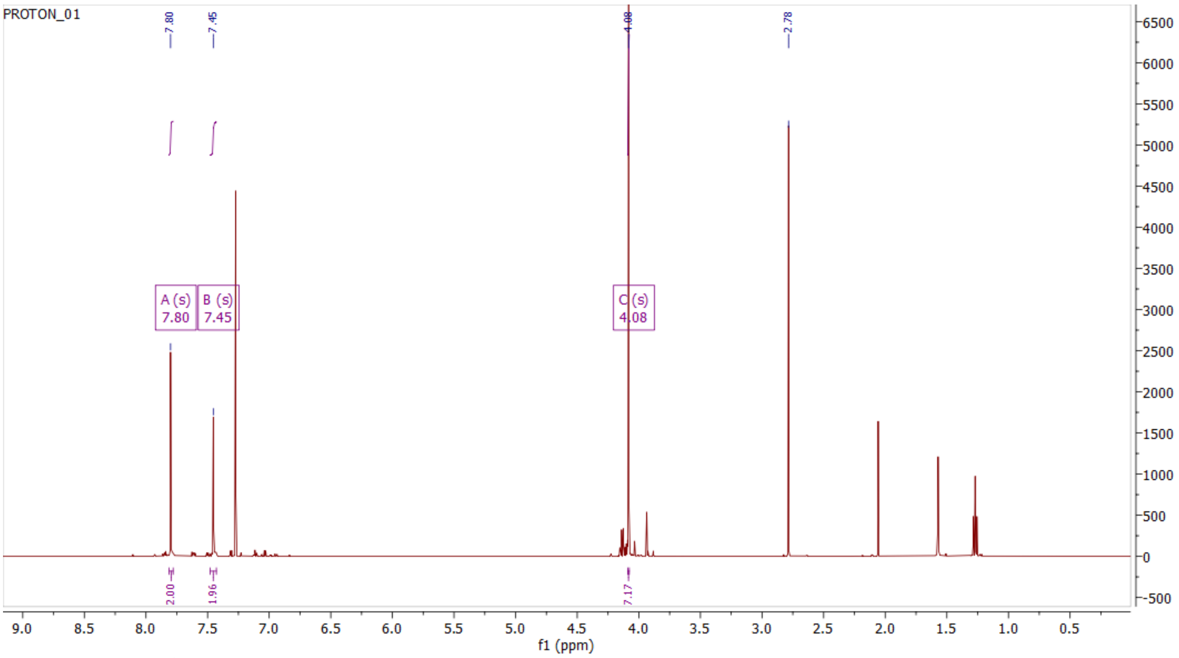


Figure S23: ^{1}H NMR spectrum of compound **21** in $CDCl_3$.

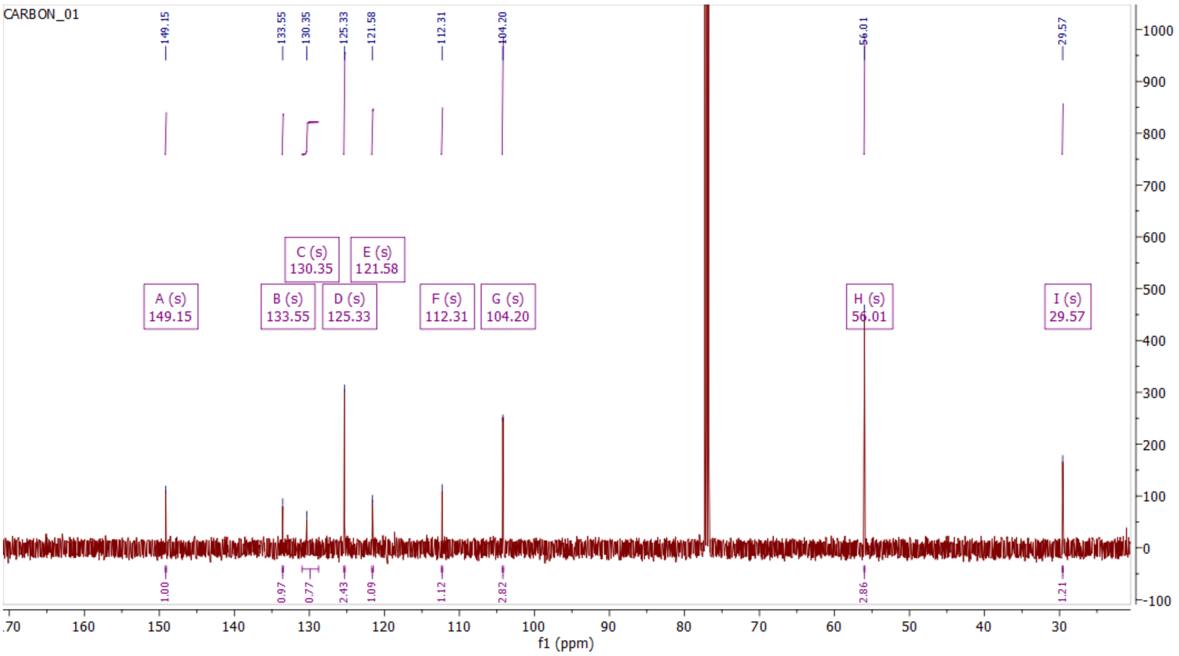


Figure S24: ^{13}C NMR spectrum of compound **21** in $CDCl_3$.

Compound 22: 2,9-dibromonaphtho[2,1-*b*:3,4-*b'*]dithiophene-5,6-diol

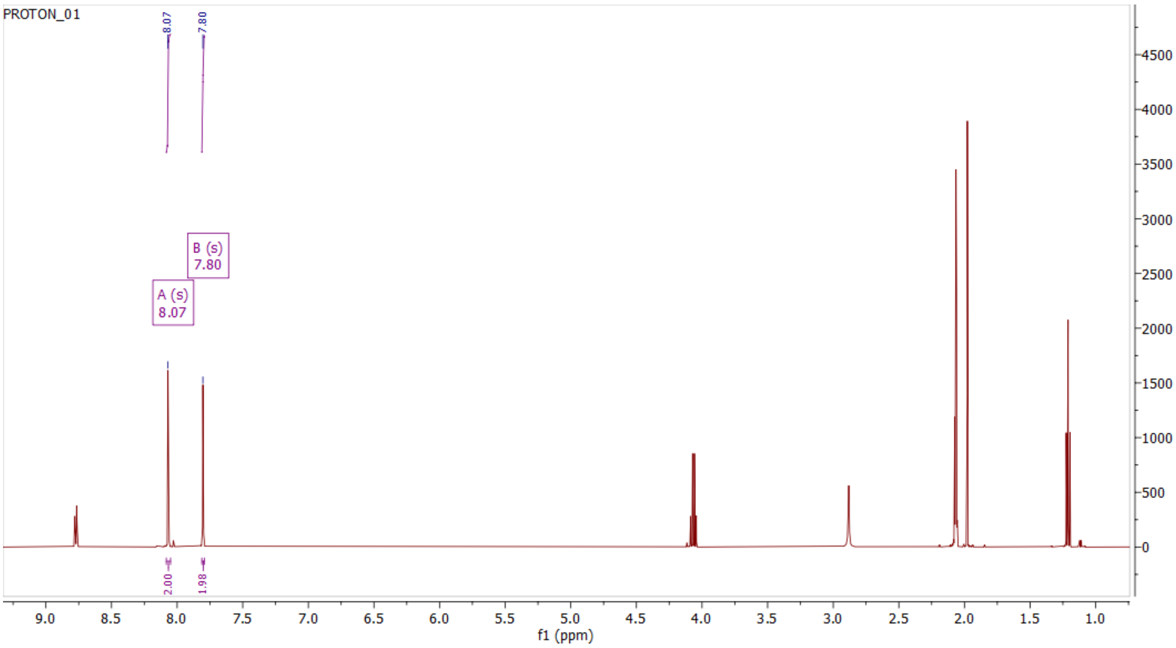


Figure S25: ^{1}H NMR spectrum of compound **22** in acetone-*d*.

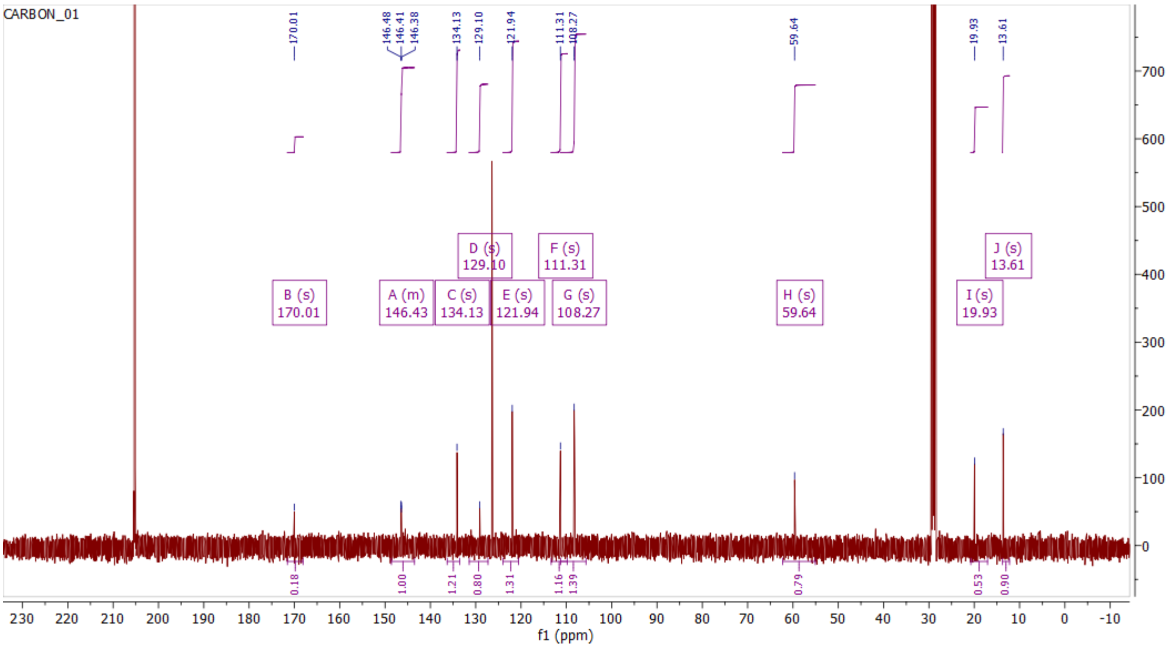


Figure S26: ^{13}C NMR spectrum of compound **22** in acetone-*d*.

Compound 23: 2,9-Dibromo-5,6-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)naphtho[2,1-*b*:3,4-*b′*]dithiophene

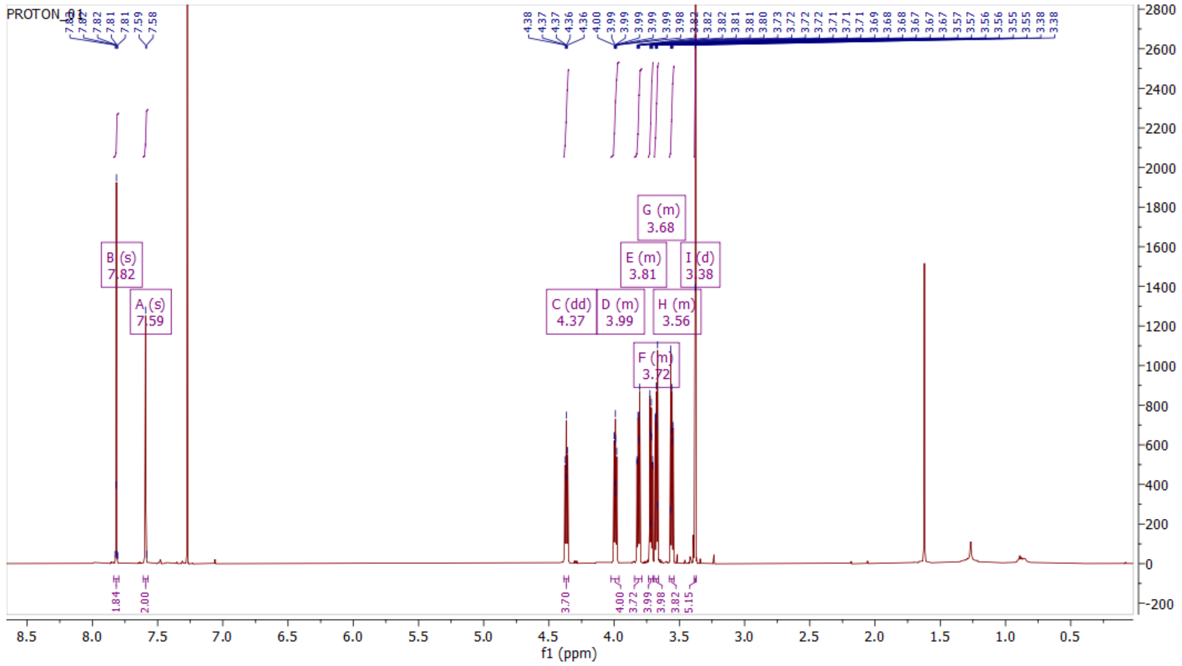


Figure S27: ^{1}H NMR spectrum of compound **23** in CDCl$_3$.

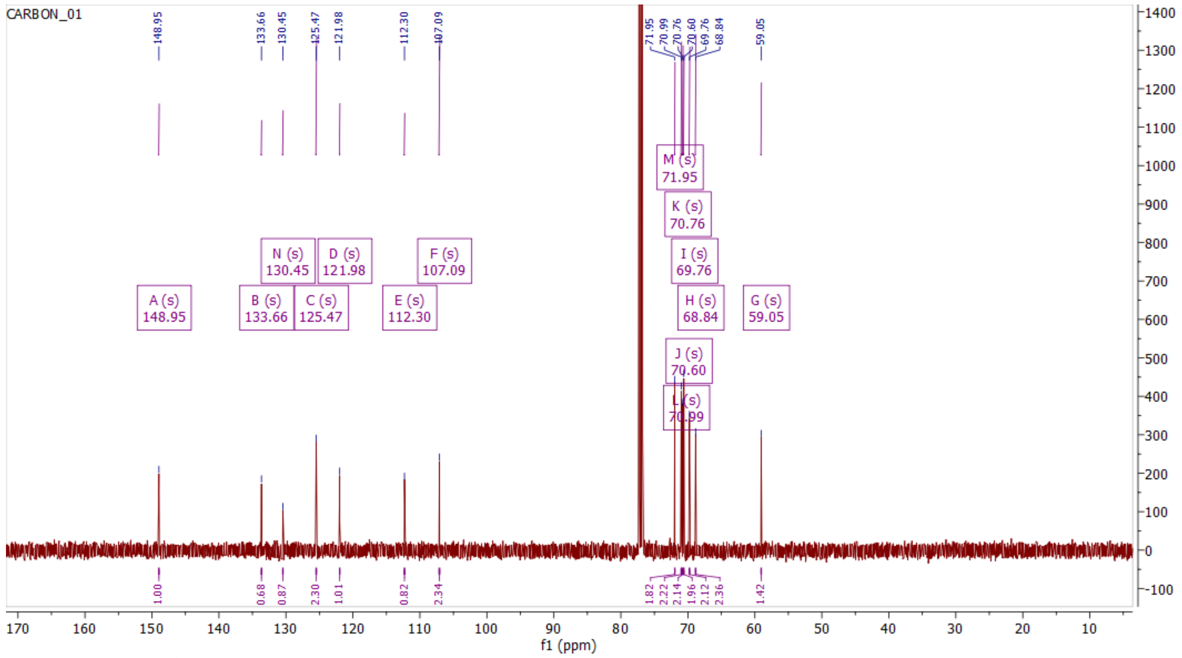


Figure S28: ^{13}C NMR spectrum of compound **23** in CDCl$_3$.

Size-Exclusion chromatography

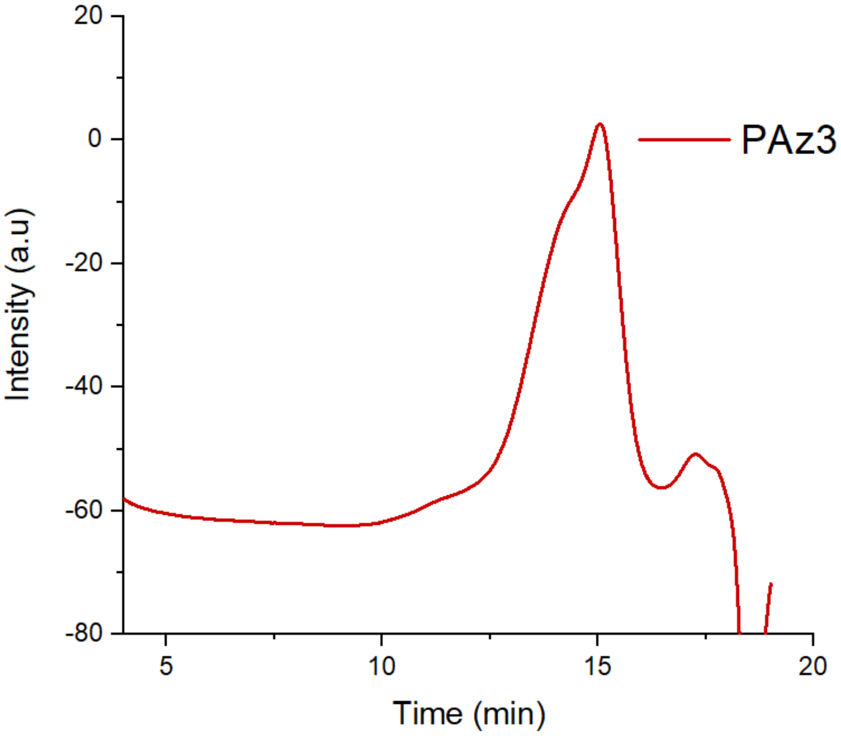


Figure S29: Size exclusion chromatography traces for polymer **Paz3** (M_n: 19 kg·mol^{-1}, M_w: 52 kg·mol^{-1}, polydispersity index ($Đ$): 2.7, X_n: 32

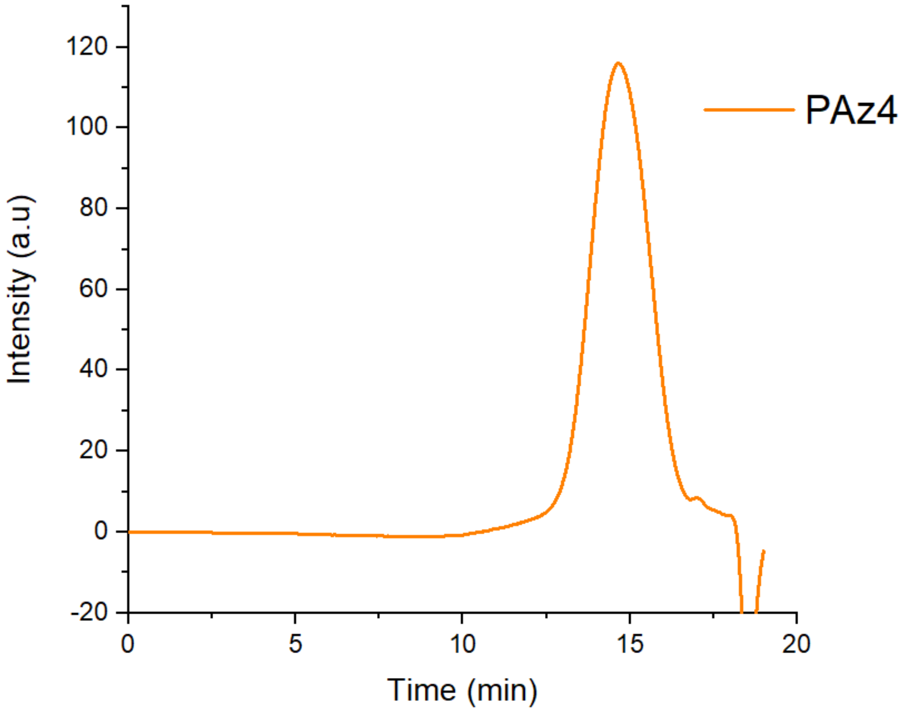


Figure S30: Size exclusion chromatography traces for the soluble fraction of polymer **Paz4** (M_n: 12 kg·mol^{-1}, M_w: 44 kg·mol^{-1}, polydispersity index ($Đ$): 3.7, X_n: 20

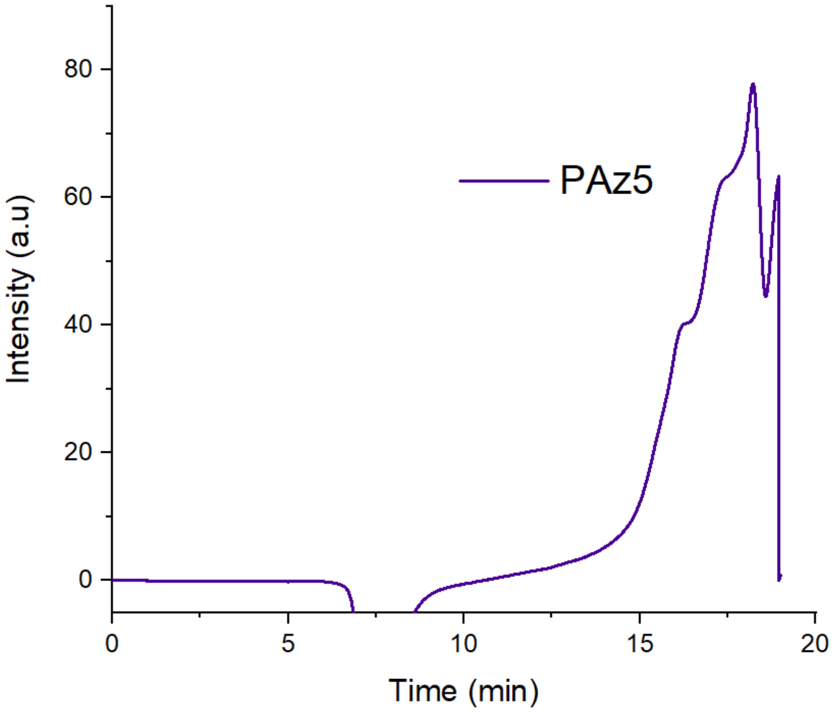


Figure S31: Size exclusion chromatography traces for the soluble fraction of polymer **Paz5** (M_n: N/A, M_w: 5 N/A, polydispersity index (*Đ*): N/A, X_n: N/A

Thermogravimetric Analysis

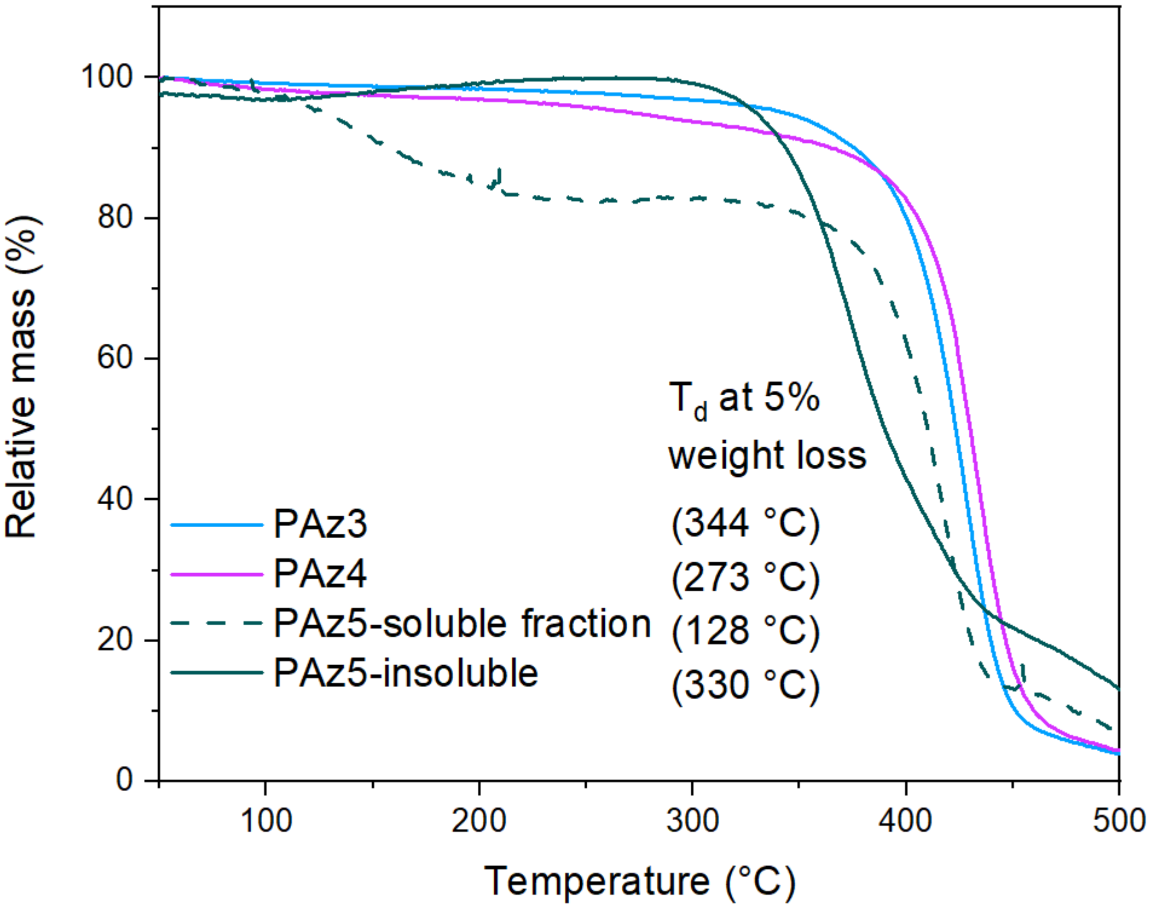


Figure S32: Thermogravimetric analysis curves for polymers **Paz3**, **Paz4 and Paz5.** The early weight loss for **PAz5** below 250 °C can be attributed either to the presence of residual solvent left in the sample or the presence of smallest chains. Insoluble fraction of **Paz5** collected after Soxhlet extraction allowed the measurement.

Differential Scanning Calorimetry

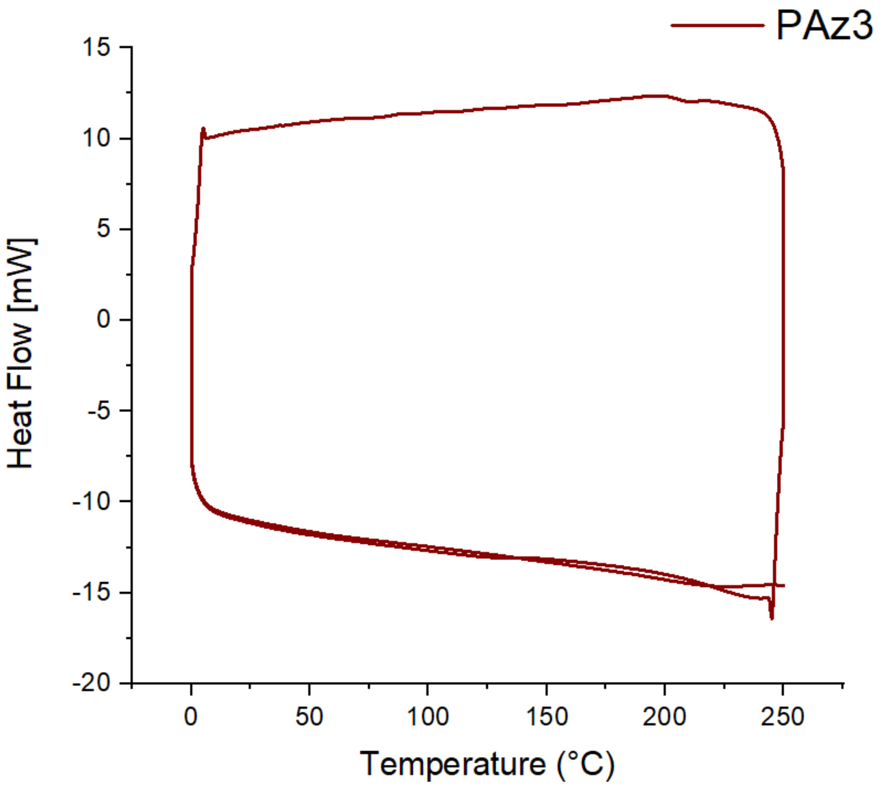


Figure S33: Differential scanning calorimetry plots of polymer **PAz3**

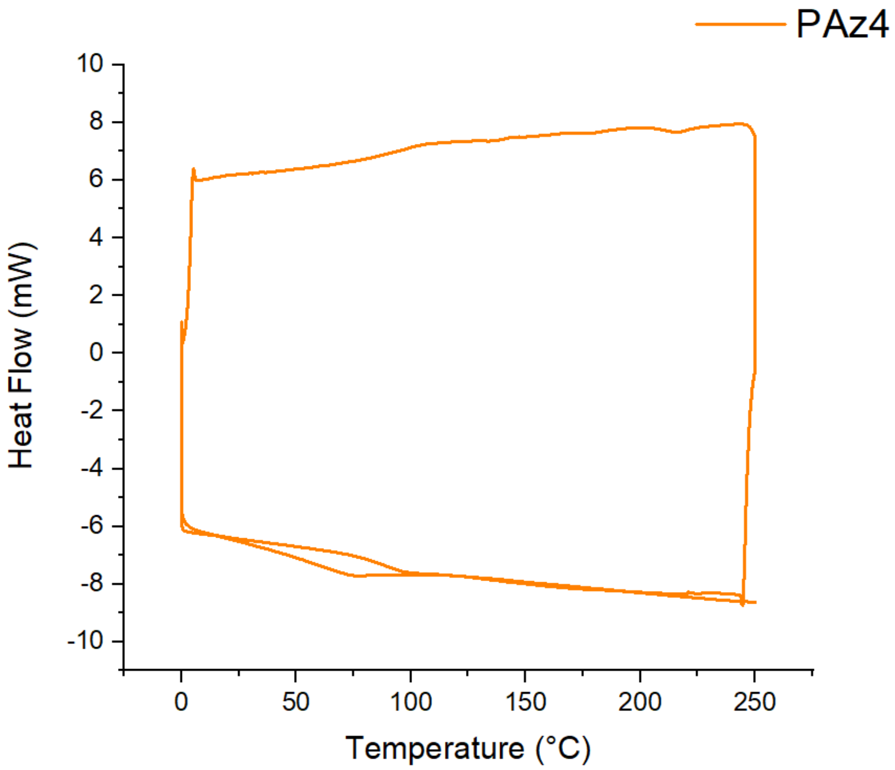


Figure S34: Differential scanning calorimetry plots of polymer **Paz4**

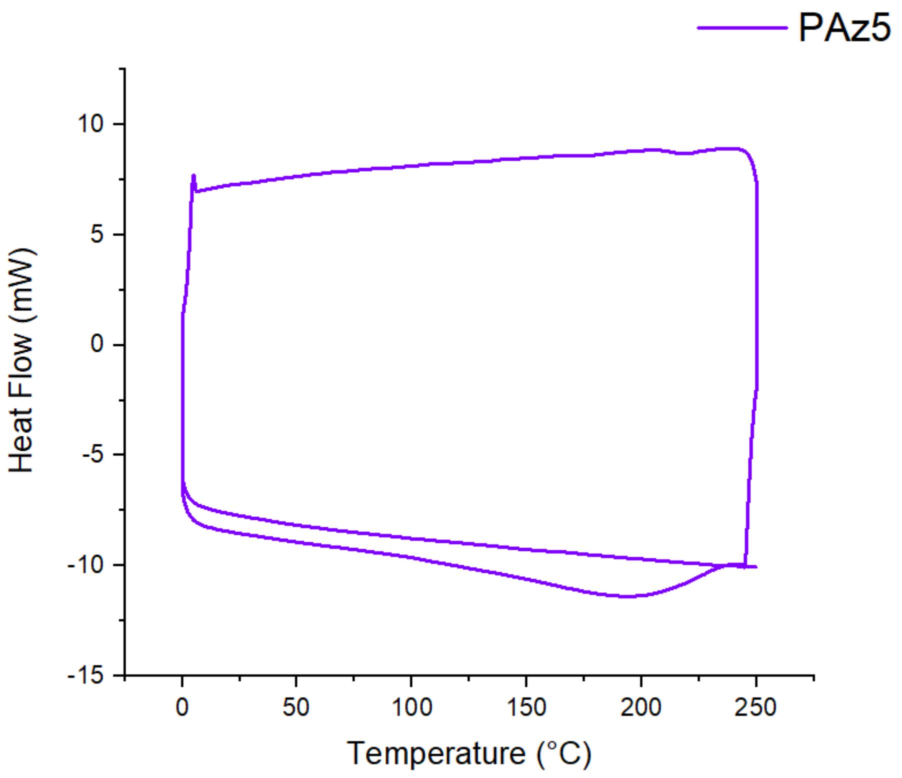


Figure S35: Differential scanning calorimetry plots of polymer **Paz5**

Cyclic Voltammetry

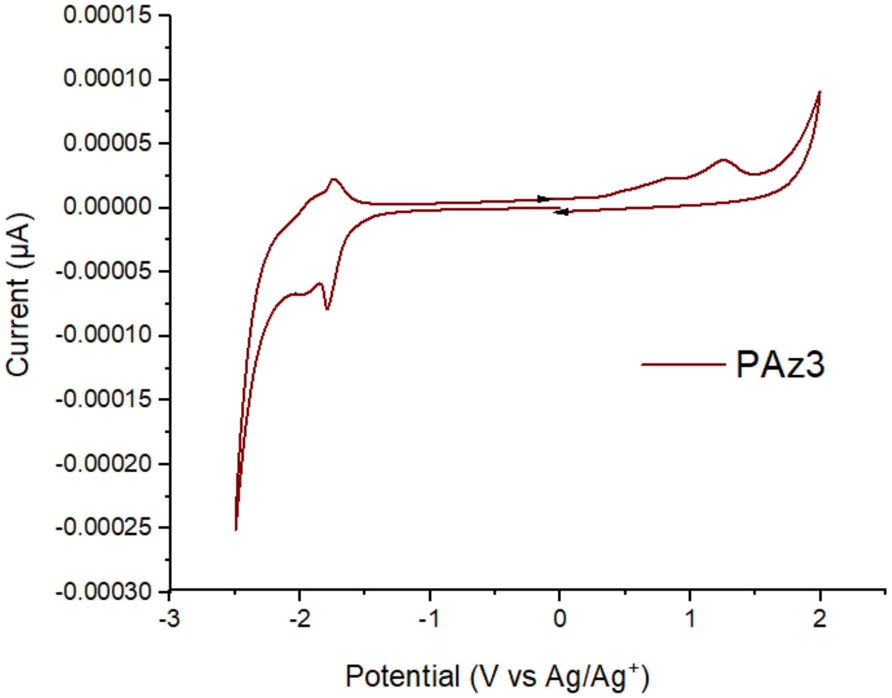


Figure S36: Cyclic voltammetry of **Paz3** (thin-film on a Pt electrode) in acetonitrile solution with 0.1M [Bu_4N][PF_6] as the supporting electrolyte with a scan r ate of 100 mV·s^{-1}.

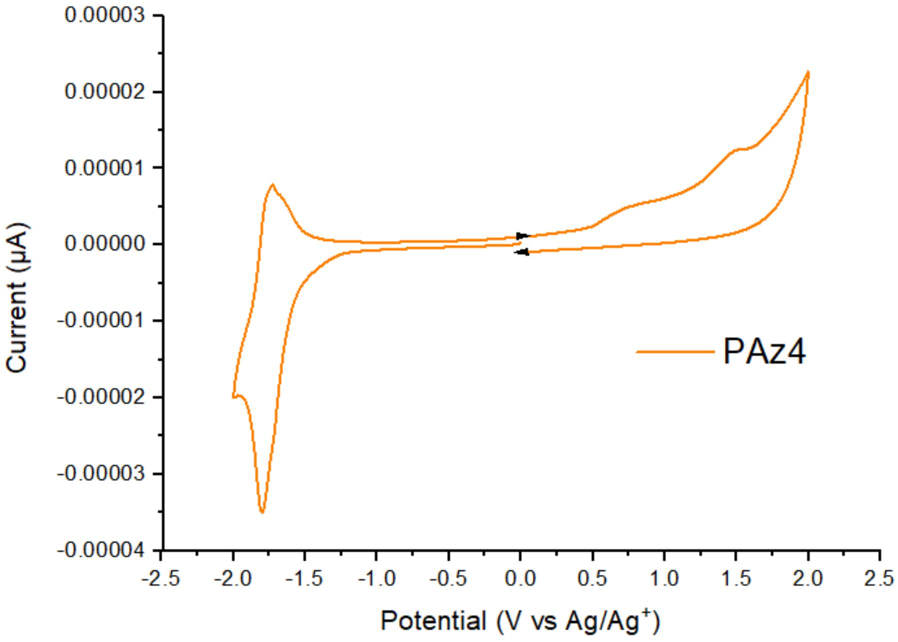


Figure S37: Cyclic voltammetry (thin-film on a Pt electrode) of **Paz4** in acetonitrile solution with 0.1M [Bu_4N][PF_6] as the supporting electrolyte with a scan rate of 100 mV·s^{-1}.

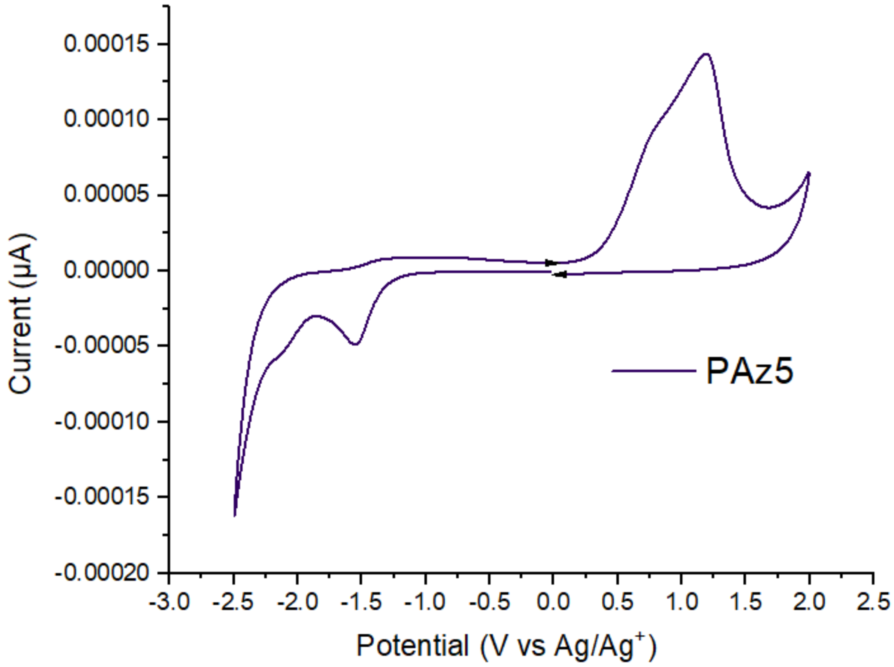


Figure S38: Cyclic voltammetry (thin-film on a Pt electrode) of **Paz5** in acetonitrile solution with 0.1M [Bu_4N][PF_6] as the supporting electrolyte with a scan rate of 100 mV·s^{-1}.

UV-Vis Absorption Spectroscopy

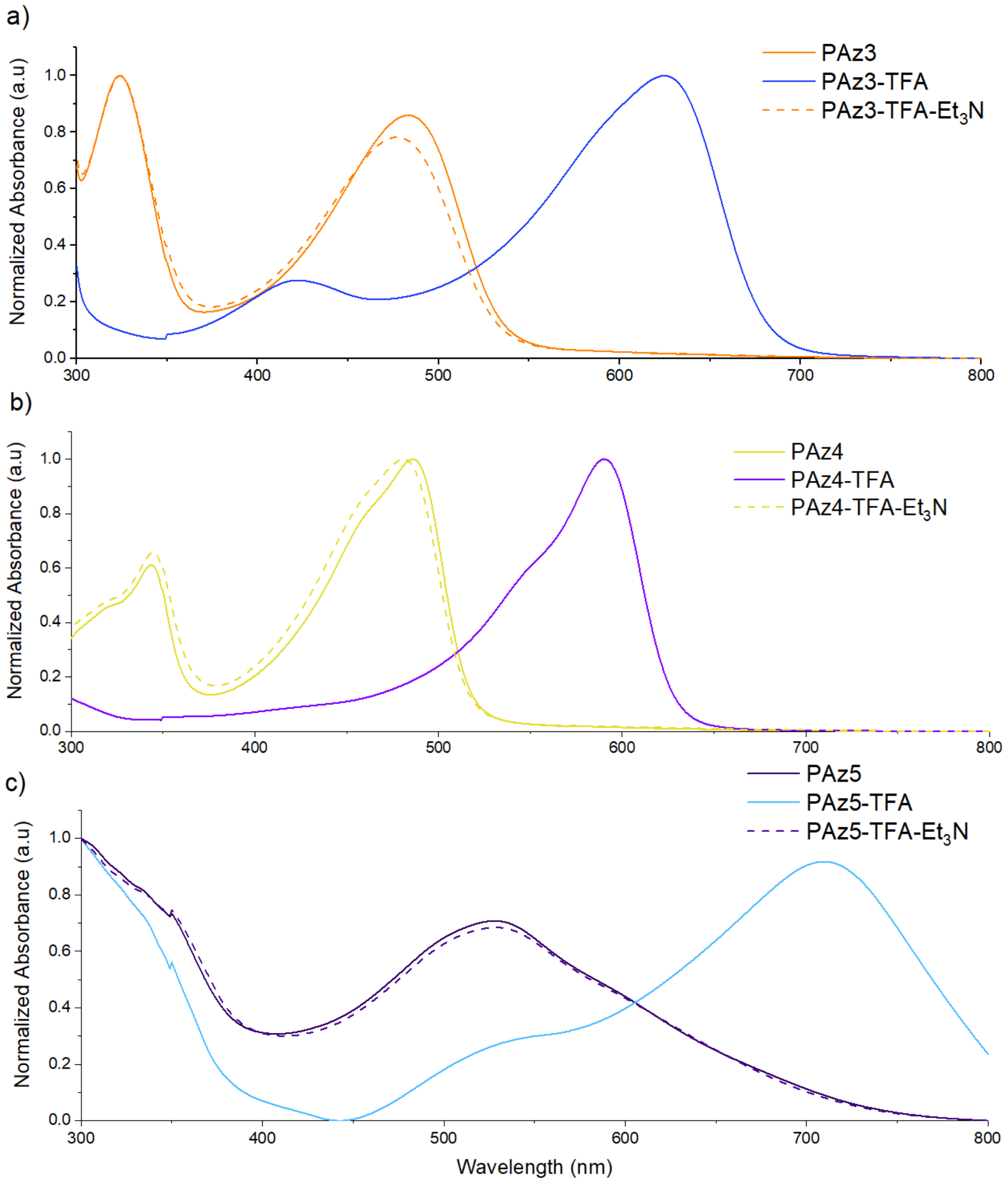


Figure S39: a) Normalized UV-Vis absorption spectra of **Paz3** in neutral state in solution of $CHCl_3$ (orange line), upon addition of TFA (blue line) and upon addition of NEt_3 (dashed orange line). b) Normalized UV-Vis absorption spectra of **Paz4** in neutral state in solution of $CHCl_3$ (yellow line), upon addition of TFA (purple line) and upon addition of NEt_3 (dashed yellow line). c) Normalized UV-Vis absorption spectra of **Paz5** in the neutral state in solution of $CHCl_3$ (purple line), upon addition of TFA (blue line) and upon addition of NEt_3 (dashed purple line).

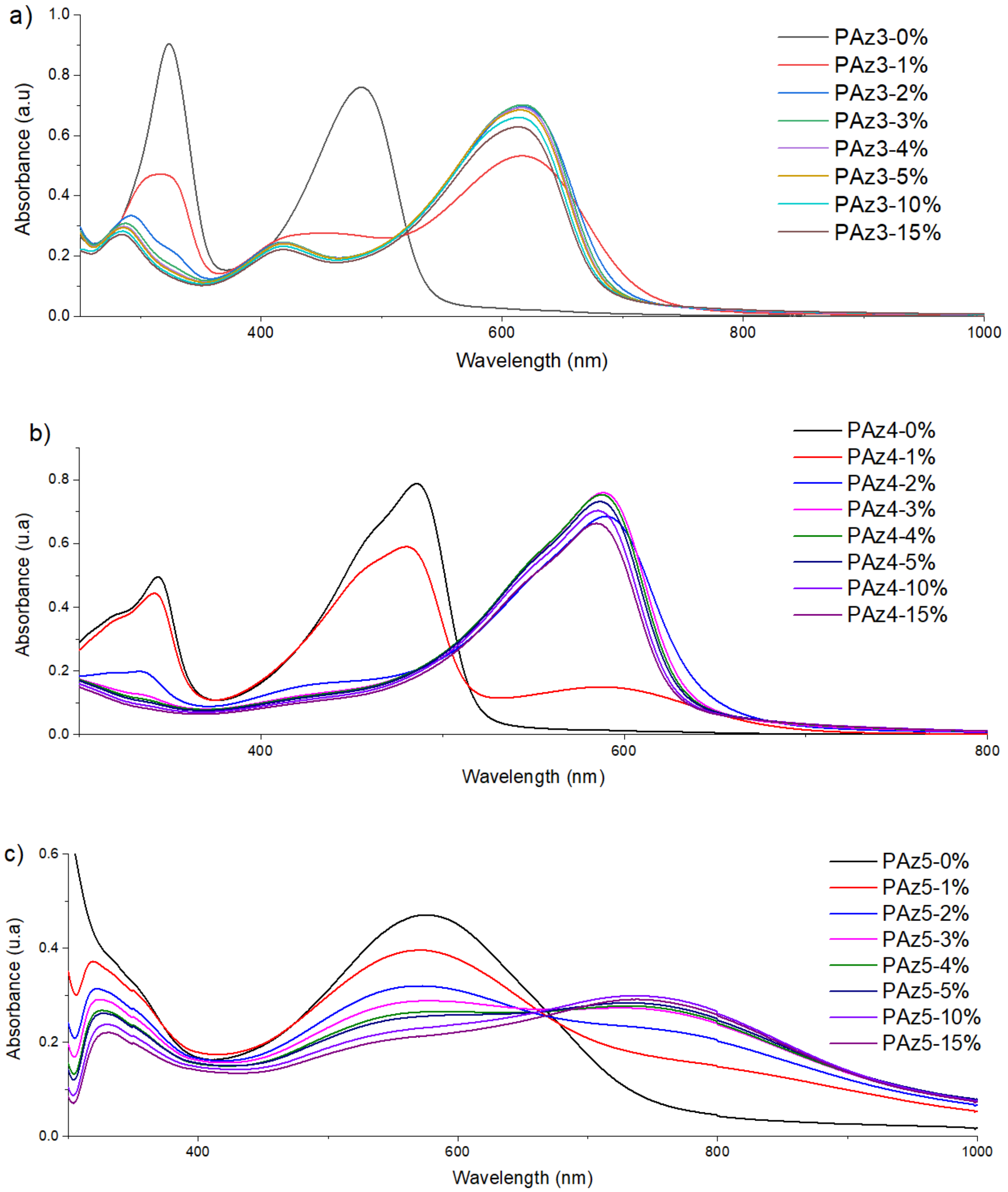


Figure S40: a) Absorbance of **Paz3** in $CHCl_3$ with the addition of % TFA. b) Absorbance of **Paz4** in $CHCl_3$ with the addition of % TFA. c) Absorbance of **Paz5** in $CHCl_3$ with the addition of % TFA

UV-vis Spectroelectrochemistry

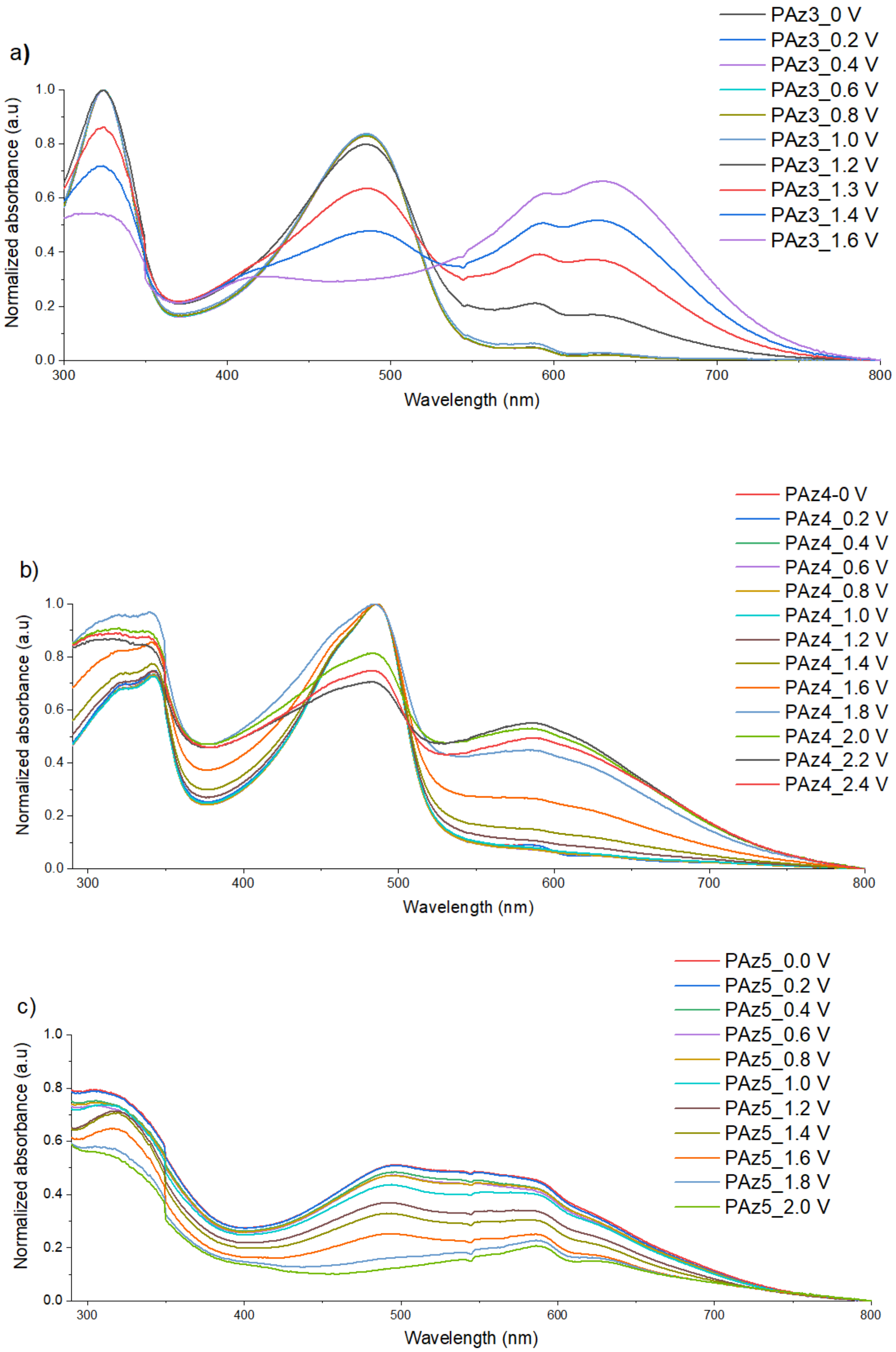


Figure S41: a) Absorbance of **Paz3** in $CHCl_3$ with increasing voltage b) Absorbance of **Paz4** in $CHCl_3$ with increasing voltage. c) Absorbance of **Paz5** in $CHCl_3$ with increasing voltage

^{1}H NMR of borylated moieties

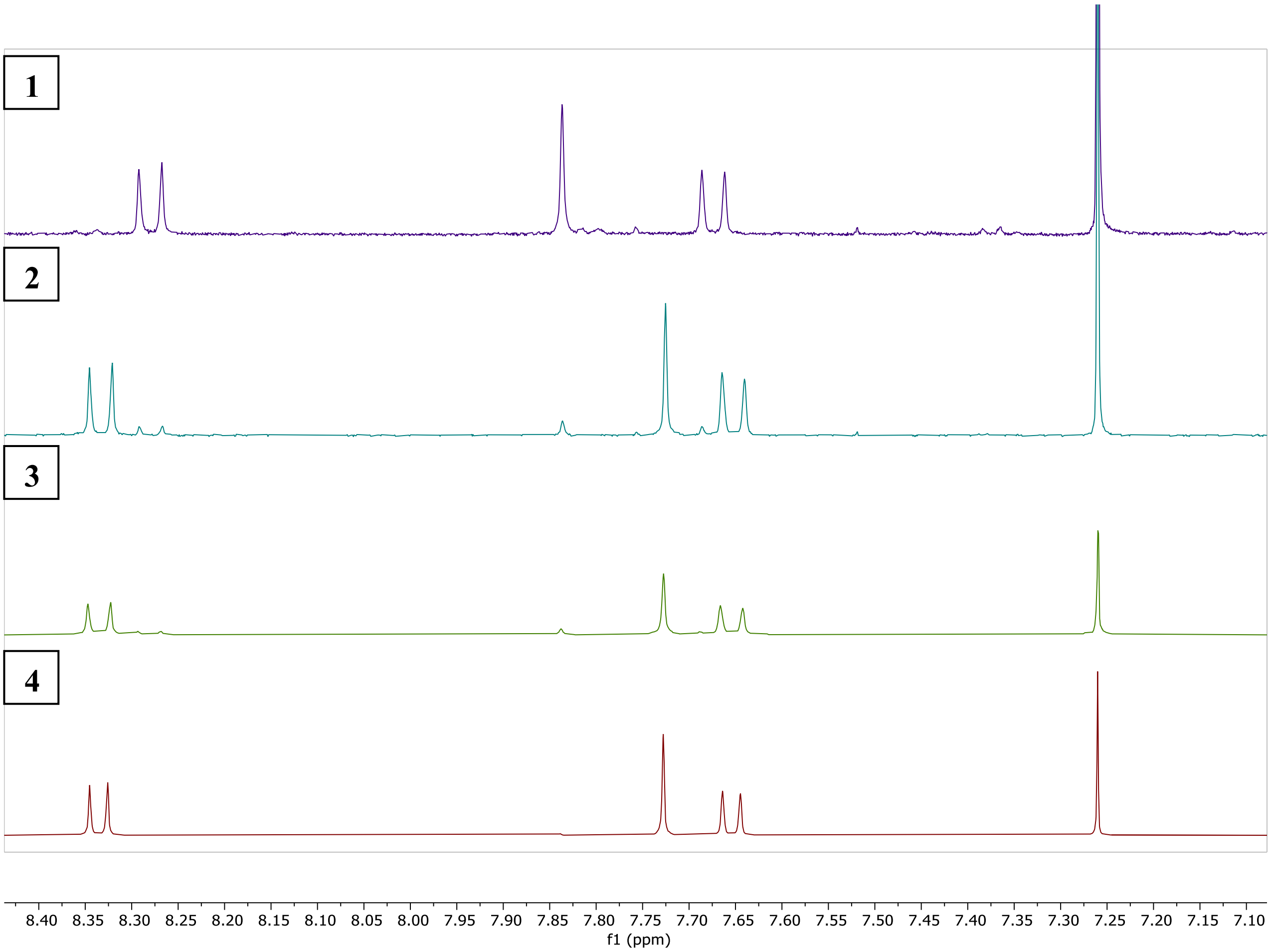


Figure S42: Comparison of ^{1}H NMR spectra of entries 1 to 4 of Table 1.

DFT calculations

Table S1. Dihedral angles between the azulene and the comonomers at the 7-membered ring junction (θ_7) and at the 5-membered ring junction (θ_5) as calculated by DFT calculations for **Paz3**, **Paz4** and **Paz5**

Entry	Polymer	θ_5 (°)	θ_7 (°)	HOMO (eV)	LUMO (eV)
1	**Paz3**	26.2	52.2	-4.88	-1.78
2	**Paz4**	21.8	42.4	-5.18	-2.10
3	**Paz5**	01.5	30.0	-5.13	-2.41

SWNT dispersion protocol

RN120 CNTs were purchased from Raymor Industries Inc. Dispersions of CNTs were prepared with a 20 mL vial charged with 0.5 mg·mL^{-1} of polymer, 0.5 mg·mL^{-1} of CNTs and 10 mL of solvent ($CHCl_3$). The resulting suspensions were pre-sonicated at room temperature for 1 minutes in a standard Branson® 2510 sonicator bath, followed by ultrasonication with a Q700 sonicator from Qsonica, equipped with a 6.4 mm microtip. The suspension was sonicated at 50% of its maximum power for 30 minutes in an ice-water bath with two seconds on and two seconds off. The dispersion was then centrifuged at 13000 rpm for 30 minutes before the supernatant was carefully collected using a pipette.

Raman analyses were conducted with a confocal Raman Senterra II (Bruker Optics Inc. Milton, ON) with x50 lens, analyses were performed at 785 nm.

XRF analysis

Table S2. Mass % of all metal impurities in RN-120 crude CNT and Paz3- Paz4-SWCNT

	RN-120 mass%	**PAz3-CNT mass%**	**PAz-CNT mass%**
C	87.9994	99.2153	99.5108
Al	0.0119	0.00661	--
Si	0.025	0.00287	0.0066
P	0.0049	0.00149	0.0193
S	0.0934	0.00181	0.0473
Cl	--	0.01392	0.2495
K	--	0.0017	0.0017
Ca	0.0443	0.00158	0.0699
Cr	--	5.3E-4	0.0421
Fe	2.5362	4.4E-4	0.0278
Co	1.7945	8.7E-4	0.0067
Ni	6.2917	7.0E-04	0.015
Zn	--	5.3E-4	--
Br	--	3.4E-4	0.0017
Cu	0.0345	--	--
Pd	--	8.3E-4	0.0016
Mn	0.0688	--	--
Y	0.0325	--	--
La	1.0626	--	--

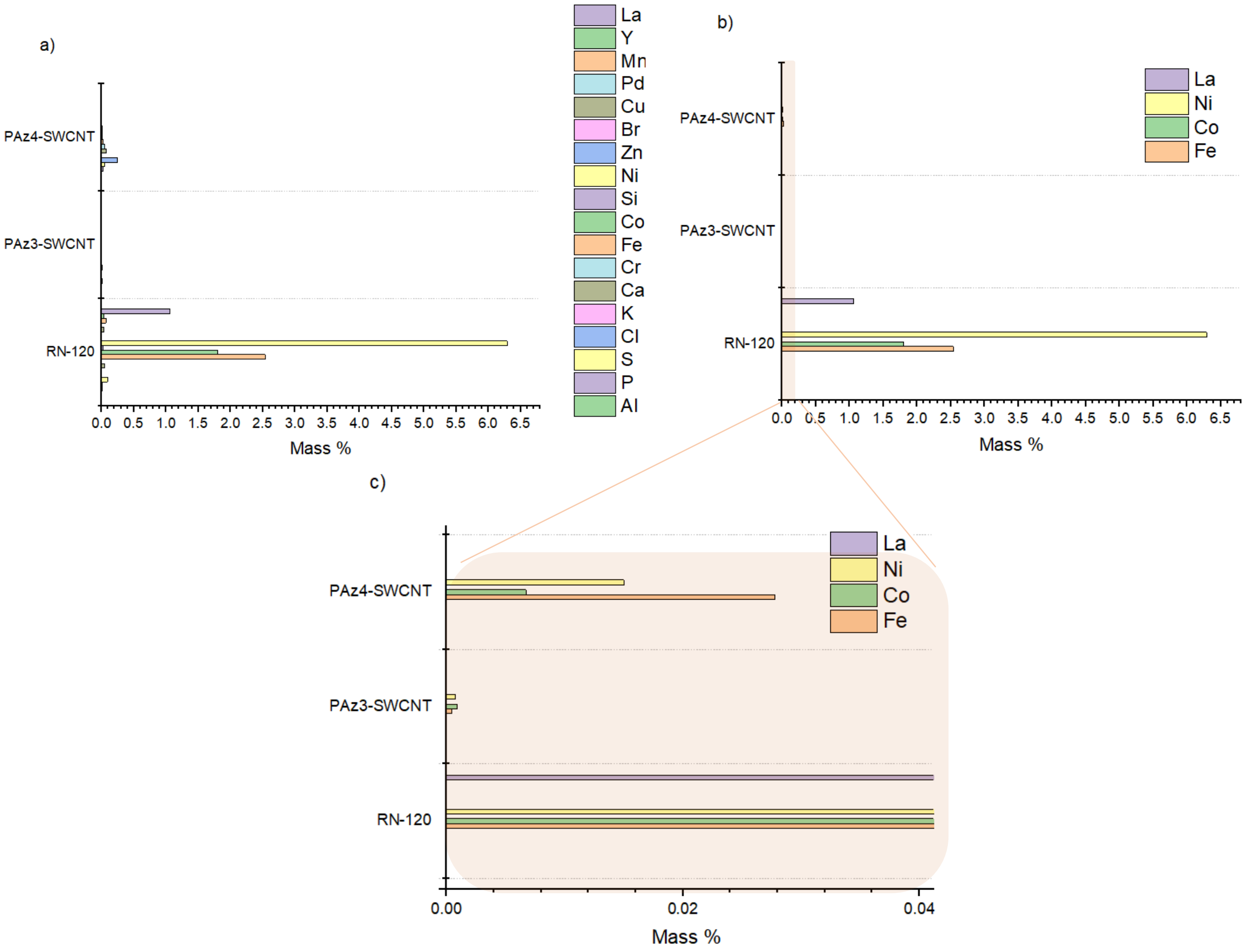


Figure S43: Comparison between RN-120, Paz3- Paz4-SWCNT for: (a) All metal impurities. (b) and (c) La, Ni, Co, Fe.

Conductivity measurement

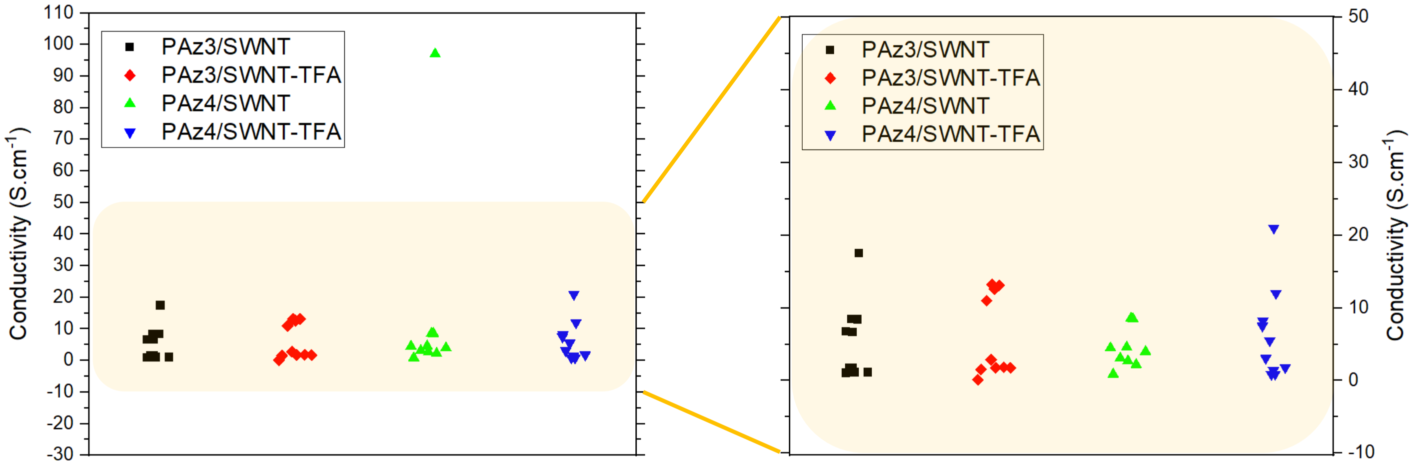


Figure S44: Conductivity of **PAz**/SWNT with and without TFA

Table S3. Conductivity values for 10 measurements of Paz3/SWNT with and without TFA

Entry	**Neutral**		**Doped**	
	Conductivity (S·cm^{-1})	**Sheet Resistance (Ω/□)**	**Conductivity (S·cm^{-1})**	**Sheet Resistance (Ω/□)**
1	8.47	54	13.20	34
2	17.60	38	13.10	34
3	8.55	54	12.60	36
4	1.79	257	1.83	247
5	1.80	255	11.00	42
6	1.21	382	0.11	4200
7	1.12	431	1.75	260
8	6.74	68	1.75	260
9	6.81	67	1.50	300
10	1.20	396	2.86	158
Average	**5.53**	**200**	**5.97**	**557**
Standard deviation	**5.28**	**162**	**5.67**	**1285**

Table S4. Conductivity values for 10 measurements of **Paz4**/SWNT with and without TFA. Conductivity value at neutral state for entry 1 was removed from calculations because of the huge gap with other values.

Entry	**Neutral**		**Doped**	
	Conductivity ($S{\cdot}cm^{-1}$)	**Sheet Resistance (Ω/□)**	**Conductivity ($S{\cdot}cm^{-1}$)**	**Sheet Resistance (Ω/□)**
1	97.00	2	7.50	31
2	2.70	85	1.40	159
3	4.60	30	12.00	19
4	8.60	24	21.00	12
5	8.50	26	3.07	75
6	2.20	105	8.20	28
7	4.50	51	1.80	154
8	3.10	74	5.49	42
9	4.00	57	0.87	266
10	0.87	264	0.85	273
Average	**4.34**	**72**	**6.22**	**106**
Standard deviation	**2.66**	**74**	**6.40**	**101**

Elemental Analysis

Samples were prepared by adding 0.8 to 1.2 mg of the sample to an aluminum capsule. **Paz5** was analyzed once with the soluble fraction extracted via Soxhlet extraction using $CHCl_3$ and three times with the non-soluble fraction recovered after Soxhlet extraction. **Paz3** and **Paz4** were analyzed three times each.

The results are presented in the table below.

Table S5. %N, %C and %H of standards, Paz3, Paz4 and Paz5

Sample	Mass (mg)	%N	%C	%H
Standard SFA	1.471	16.2	42.2	4.8
PAz3-A	1.503	< 0.5	67.6	7.3
PAz3-B	1.488	< 0.5	67.4	7.3
PAz3-C	1.568	< 0.5	67.2	7.3
Standard Cystine	1.428	11.5	30.0	5.4
Standard SFA	1.469	16.1	42.1	5.0
PAz4-A	0.972	< 0.5	76.1	7.4
PAz4-B	0.961	< 0.5	75.4	7.4
PAz4-C	1.185	< 0.5	75.9	7.1
PAz5-Soluble	1.012	< 0.5	63.8	6.0
PAz5-Unsoluble-A	0.992	0.7	63.1	5.9
PAz5-Unsoluble-B	0.933	0.7	64.9	6.0
PAz5-Unsoluble-C	1.018	0.7	64.9	6.0
Standard Cystine	1.532	11.6	30.3	5.4
Standard SFA	1.582	16.2	42.1	4.9
Theorical value of standard (Cystine)	-	**11.66**	**29.99**	**5.03**
Theorical value of standard (Sulphanilamide)	-	**16.27**	**41.85**	**4.68**
ND < 0.5 %				

Calculated values for Paz3 are 68.16 %C, 7.63 %H. Average Measured values are 67.40 %C, 7.30 %H.

Calculated values for Paz4 are 76.00 %C, 7.58 %H. Average Measured values are 75.80 %C, 7.30 %H.

Calculated values for Paz5 are 66.06 %C, 6.13 %H, (9.28%S). Average Measured values are 64.15%C, 5.97%H.

References

(1) Simonet, J.; Rault-Berthelot, J. Electrochemistry: A Technique to Form, to Modify and to Characterize Organic Conducting Polymers. *Prog. Solid State Chem.* **1991**, *21* (1), 1–48. https://doi.org/10.1016/0079-6786(91)90005-K.

(2) Sun, Q.; Wang, H.; Yang, C.; Li, Y. Synthesis and Electroluminescence of Novel Copolymers Containing Crown Ether Spacers. *J. Mater. Chem.* **2003**, *13* (4), 800–806. https://doi.org/10.1039/b209469j.

(3) Bard, A. J.; Faulkner, L. R. Electrochemical Methods: Fundamentals and Applications, 2nd Edition. In *Electrochemical Methods: Fundamentals and Applications, 2nd Edition*; Wiley: New York, NY, 2000.

(4) Thompson, B. C.; Kim, Y.-G.; Reynolds, J. R. Spectral Broadening in MEH-PPV:PCBM-Based Photovoltaic Devices via Blending with a Narrow Band Gap Cyanovinylene−Dioxythiophene Polymer. *Macromolecules* **2005**, *38* (13), 5359–5362. https://doi.org/10.1021/ma0505934.

(5) Gao, H.; Ge, C.; Hou, B.; Xin, H.; Gao, X. Incorporation of 1,3-Free-2,6-Connected Azulene Units into the Backbone of Conjugated Polymers: Improving Proton Responsiveness and Electrical Conductivity. *ACS Macro Lett.* **2019**, *8* (10), 1360–1364. https://doi.org/10.1021/acsmacrolett.9b00657.

(6) Bura, T.; Ziessel, R. Design, Synthesis and Redox Properties of a Fluorene Platform Linking Two Different Bodipy Dyes. *Tetrahedron Lett.* **2010**, *51* (21), 2875–2879. https://doi.org/10.1016/j.tetlet.2010.03.095.

(7) Keshtov, M. L.; Kuklin, S. A.; Godovskii, D. Yu.; Konstantinov, I. O.; Krayushkin, M. M.; Peregudov, A. S.; Khokhlov, A. R. Synthesis and Optical and Electrochemical Properties of 5,6-Bis[9-(2-Decyltetradecyl)-9H-Carbazol-3-Yl]Naphtho[2,1-b:3,4-

b’]Dithiophene as a Promising Building Block for Photovoltaic Applications. *Dokl. Chem.* **2016**, *467* (1), 94–99. https://doi.org/10.1134/S0012500816030022.

(8) Ding, Z.; Li, H.; Gao, W.; Zhang, Y.; Liu, C.; Zhu, Y. Detection of Picric Acid by Terpy-Based Metallo-Supramolecular Fluorescent Coordination Polymers in Aqueous Media. *Chin. J. Chem.* **2017**, *35* (4), 447–456. https://doi.org/10.1002/cjoc.201600885.