

SUPPORTING INFORMATION

Synthesis of an Azulene-Containing Graphene Nanoribbon

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Table of Content

Apparatus	3
Chemicals.....	4
Experimental Section	4
NMR Spectroscopy	9
UV-Visible Spectroscopy	16
Cyclic Voltammetry.....	17
IR Spectroscopy	18
SEC Profiles and Data Summary.....	19
Conductivity.....	19
References	22

Apparatus

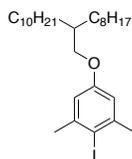
A Varian Inova AS400 spectrometer (Varian, Palo Alto, USA) operating at 400 MHz and an Agilent DD2 500 MHz were employed for conducting all NMR analyses. All peaks are expressed using a ppm scale (δ) and identified as m (multiplet), s (singlet), d (doublet), t (triplet), and dd (doublet of doublets). They are reported in reference to the residual solvent peak. The coupling constant (J) values are presented in hertz (Hz). UV-visible spectrums were obtained using 10 mm path length quartz cells on a Varian diode-array spectrophotometer (Cary 7000 model). For coated electrode, a Solartron 1287 potentiostat was utilized to perform cyclic voltammetry. Platinum wires were utilized as electrodes at a scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$. Ag/Ag^+ (0.01 M AgNO_3 in acetonitrile) in an anhydrous and nitrogen-purged solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in dry acetonitrile was used as the reference electrode. For in solution cyclic voltammetry, IKA Electrochemistry Kit ElectraSyn 2.0 Package was utilized. Platinum wires were utilized as electrodes at a scan rate of 100 and $50 \text{ mV}\cdot\text{s}^{-1}$. Ag/Ag^+ (0.01 M AgNO_3 in CH_2Cl_2) in an anhydrous and nitrogen-purged solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in dry CH_2Cl_2 was used as the reference electrode. Number average (M_n) and weight average (M_w) molecular weights were determined using size-exclusion chromatography (SEC) under high-temperature conditions ($135 \text{ }^\circ\text{C}$) using a Tosoh EcoSEC HLC-8321GPC/HT system equipped with an RI detector. The column set consisted of a TSKgel GMHhr-H(20) HT2, $20 \text{ }\mu\text{m}$, mixed bed, $7.8 \text{ mm ID} \times 30 \text{ cm}$ column, and a TSKgel GMHhr-H guard column ($30 \text{ }\mu\text{m}$, $7.5 \text{ mm ID} \times 7.5 \text{ cm}$). The flow rate was maintained at 1 mL min^{-1} using 1,2,4-Trichlorobenzene (TCB) as the eluent, with the system temperature set at $135 \text{ }^\circ\text{C}$. All samples were prepared at a nominal concentration of 1.0 mg mL^{-1} in TCB. Dissolution was performed using a custom-made dry block heater. The sample vials were incubated at $100 \text{ }^\circ\text{C}$

with agitation for 1 hour to ensure complete dissolution. The solutions were then filtered through a 2 mm porous stainless-steel filter in conjunction with a 0.40 mm thick glass filter with a porosity of 0.7 μm , into a 4 mL chromatography vial. A 300 μL volume of the sample solution was injected. The calibration method employed to generate the reported data was the traditional polystyrene method using narrow polystyrene standards EasiVial PS-H from Agilent, which were dissolved in CHCl_3 . A FT-IR ABB MB-3000 was used to record infrared spectra. Raman analyses were conducted with a confocal Raman Senterra II (Bruker Optics Inc. Milton, ON) with x50 lens at 532 nm. The thickness of polymer **3** and **ANR** films were determined with DektakXT from Bruker with a Stylus 5 μm tips. Conductivity was measured using a four-point probe from Ossila.

Chemicals

Chemical reagents were used as received and were ordered from Sigma–Aldrich Co. Canada and Oakwood Products Inc. Compound **1** was synthesized as previously reported.¹

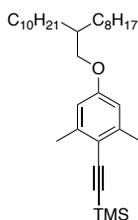
Experimental Section



Compound 4: To a solution containing 4-iodo-3,5-dimethylphenol (9.92 g, 40.0 mmol) in 120 mL of tetrahydrofuran (THF), triphenylphosphine (12.6 g, 48.0 mmol), diisopropyl azodicarboxylate (DIAD) (8.7 g, 48.0 mmol, 10 mL) and 2-octyldodecanol (14.32 g, 48.0 mmol, 12 mL) were added. The resulting mixture was stirred at room temperature for 14 hours. Then, the mixture was neutralized with water and extracted with dichloromethane (DCM). The organic

layer was washed with brine, dried using anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, hexanes as the eluent) to afford the desired compound as a colorless liquid (6.2g, 29%).

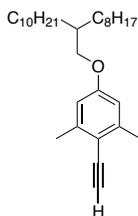
^1H NMR (500 MHz, CDCl_3) δ = 6.69 – 6.65 (m, 2H), 3.79 (d, J = 5.6 Hz, 2H), 2.44 (s, 6H), 1.75 (t, J = 6.1 Hz, 1H), 1.47 – 1.23 (m, 38H), 0.94 – 0.85 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ = 159.0, 142.7, 113.5, 96.6, 70.8, 38.0, 34.5, 32.0, 32.0, 31.4, 30.1, 29.7, 29.7, 29.7, 29.7, 29.4, 29.4, 26.9, 22.8, 22.7, 14.2. HRMS (ESI $^+$): m/z calcd for $\text{C}_{28}\text{H}_{49}\text{OI}$: 528.2823; found: 528.2815 $[\text{M}]^+$, diff = 1.42 ppm.



Compound 5: A degassed mixture of compound **4** (5.28 g, 10.0 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (115 mg, 0.1 mmol) and CuI (38 mg, 0.2 mmol) in toluene (40 mL) and diisopropylamine (DIPA) (10 mL) was combined with a solution of trimethylsilylacetylene (1.50 g, 2.17 mL, 15.0 mmol) in toluene (40 mL) and triethylamine (10 mL). The resulting mixture was refluxed for 18 hours. Then, the mixture was cooled to room temperature and diluted with CH_2Cl_2 (50 mL). The resulting mixture was washed with 10% aqueous NH_4OH , water and brine. The organic phase was dried using MgSO_4 , filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, hexanes as the eluent) to afford the desired compound as a pale-yellow oil (4.3 g, 86%).

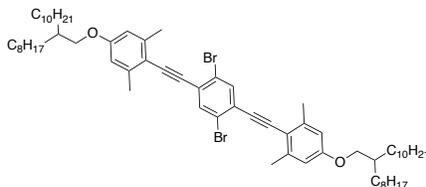
^1H NMR (500 MHz, CDCl_3) δ = 6.63 – 6.59 (m, 2H), 3.84 (d, J = 5.7 Hz, 2H), 2.45 (q, J = 0.7 Hz, 6H), 1.79 (t, J = 6.1 Hz, 1H), 1.51 – 1.25 (m, 31H), 0.93 (td, J = 7.0, 0.9 Hz, 6H), 0.33 – 0.25 (m, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ = 158.9, 142.3, 115.1, 112.9, 103.2, 100.6, 70.7, 38.0,

32.0, 32.0, 31.4, 30.0, 29.7, 29.7, 29.7, 29.6, 29.4, 29.4, 26.9, 22.7, 22.7, 21.3, 14.2, 0.3. HRMS (ESI⁺): m/z calcd for C₃₃H₅₈OSi: 499.4290; found: 499.4318 [M+H]⁺, diff = 5.61 ppm.



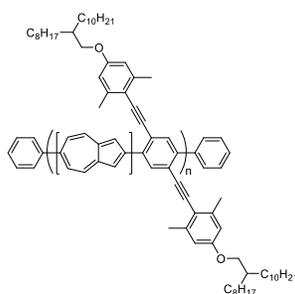
Compound 6: A solution of compound **5** (5.00 g, 10.0 mmol) in methanol (30 mL) was treated with K₂CO₃ (13.11 g, 95.0 mmol). The reaction mixture was stirred for 18 hours at room temperature. After the solvent was removed under reduced pressure, the resulting residue was filtered through a Celite pad using hexanes as the eluent (80 mL). The filtrate was then evaporated under reduced pressure and the crude product was purified by column chromatography (silica gel, hexanes as the eluent) to afford the desired compound as a white waxy solid (3.87 g, 91%).

¹H NMR (500 MHz, CDCl₃) δ = 6.60 (s, 2H), 3.81 (d, *J* = 5.6 Hz, 2H), 3.42 (d, *J* = 1.4 Hz, 1H), 2.43 (s, 6H), 1.75 (q, *J* = 6.0 Hz, 1H), 1.49 – 1.19 (m, 38H), 0.89 (t, *J* = 6.8 Hz, 7H). ¹³C NMR (126 MHz, CDCl₃) δ = 159.1, 142.6, 114.0, 113.0, 83.6, 81.5, 70.7, 38.0, 32.0, 32.0, 31.4, 30.1, 29.8, 29.7, 29.7, 29.7, 29.4, 29.4, 26.9, 22.8, 22.7, 21.2, 14.2. HRMS (ESI⁺): m/z calcd for C₃₀H₅₀O: 426.3862; found: 426.3829 [M]⁺, diff = 7.76 ppm.



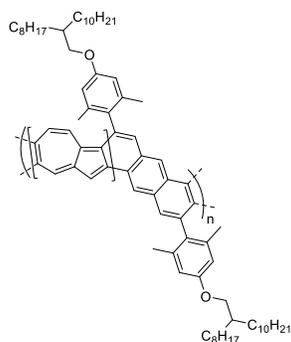
Compound 2: A mixture of compound **6** (2.44 g, 5.0 mmol), 1,4-dibromo-2,5-diiodobenzene (4.267 g, 10.0 mmol), Pd(PPh₃)₂Cl₂ (115 mg, 0.1 mmol), and CuI (38 mg, 0.2 mmol) was added to a dry and degassed flask filled with THF (25 mL) and diisopropylamine (DIPA) (5 mL). The reaction mixture was heated to 60 °C and stirred for 15 hours. The mixture was cooled to room temperature and filtered through the pad of silica. The residue was diluted with CH₂Cl₂ (50 mL) and the resulting mixture was washed with 10% aqueous NH₄OH, water and brine. The organic phase was dried using MgSO₄, filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, hexanes/DCM 9/1 as the eluent) to afford the desired compound as a pale-yellow solid (4.3 g, 86%).

¹H NMR (500 MHz, CDCl₃) δ = 7.75 (s, 2H), 6.65 (d, *J* = 0.9 Hz, 4H), 3.84 (d, *J* = 5.6 Hz, 4H), 2.54 (s, 12H), 1.77 (q, *J* = 6.0 Hz, 3H), 1.50 – 1.20 (m, 79H), 0.90 (td, *J* = 7.0, 1.1 Hz, 12H). ¹³C NMR (126 MHz, CDCl₃) δ = 159.6, 142.8, 135.7, 126.6, 122.9, 114.2, 113.2, 95.1, 93.8, 70.7, 37.9, 31.9, 31.3, 30.0, 29.7, 29.7, 29.7, 29.6, 29.4, 29.4, 26.8, 22.7, 21.6, 14.2. HRMS (ESI⁺): *m/z* calcd for C₆₆H₁₀₀O₂Br₂ : 1082.6090; found: 1082.6108 [M]⁺, diff = 1.65 ppm.



Compound 3: A dry flask equipped with magnetic stir bar was charged with compound **1** (0.073 g, 0.19 mmol, 1.0 eq), compound **2** (0.208 g, 0.19 mmol, 1.0 eq), Cs₂CO₃ (0.250 g, 0.76 mmol, 4.0 eq) and Pd(PPh₃)₄ (0.003 g, 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:H₂O (3:1) (0.2M) and

Aliquat 336 (0.002 g, 0.006 mmol, 0.03 eq) was degassed with nitrogen for 1 hour before being added to the first flask. The mixture was then stirred at 80 °C for 72 hours. Bromobenzene (0.200 mL, 1.9 mmol, 10 eq) was added to the reaction and the reaction was stirred for an additional 4 hours before the addition of phenylboronic acid (0.234 g, 1.9 mmol, 10 eq). After another 4 hours, the mixture was cooled at room temperature and the polymer was precipitated in cold MeOH. The precipitate was filtered under vacuum and washed with methanol, acetone and hexanes using a Soxhlet apparatus. The polymer was then collected from the hexanes fraction and the solution was concentrated under reduced pressure. The polymer was precipitated in cold MeOH and dried under vacuum to give the desired polymers as a brown powder (0.134 g, 58 %).



ANR: 3 (0.050 g, 0.042 mmol, 1 eq) and nitrogen-purged dichloromethane (10 mL) were added to a round bottom flask under nitrogen. The mixture was purged three times with nitrogen and cool down to 0 °C. Methanesulfonic acid (MSA, 0.5 mL, 7.6 mmol, 180 eq) was added dropwise and the mixture was allowed to warm to room temperature for 1 hour. The reaction was quenched with aqueous NaHCO₃ and the solvent was removed under reduced pressure. The crude product was filtrated from the remaining aqueous mixture and washed with water 3 times to afford the desired compound as a red solid (0.050 g, 99 %).

NMR Spectroscopy

Compound 4:

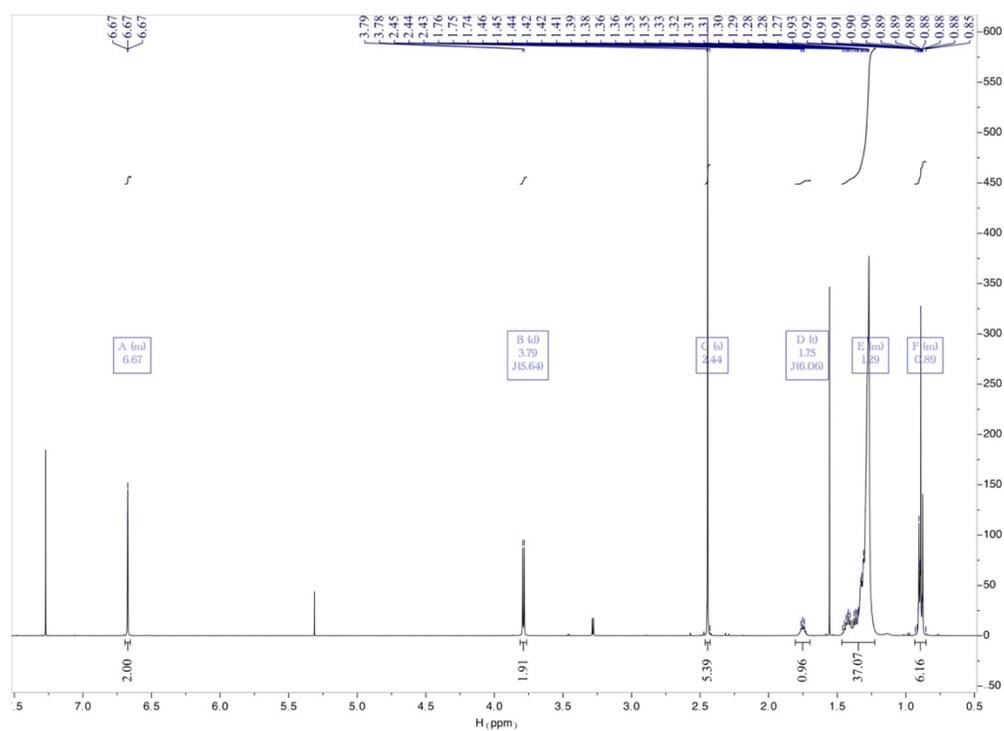


Fig. S1: ^1H NMR spectrum of compound 4 in CDCl_3 at 500 MHz

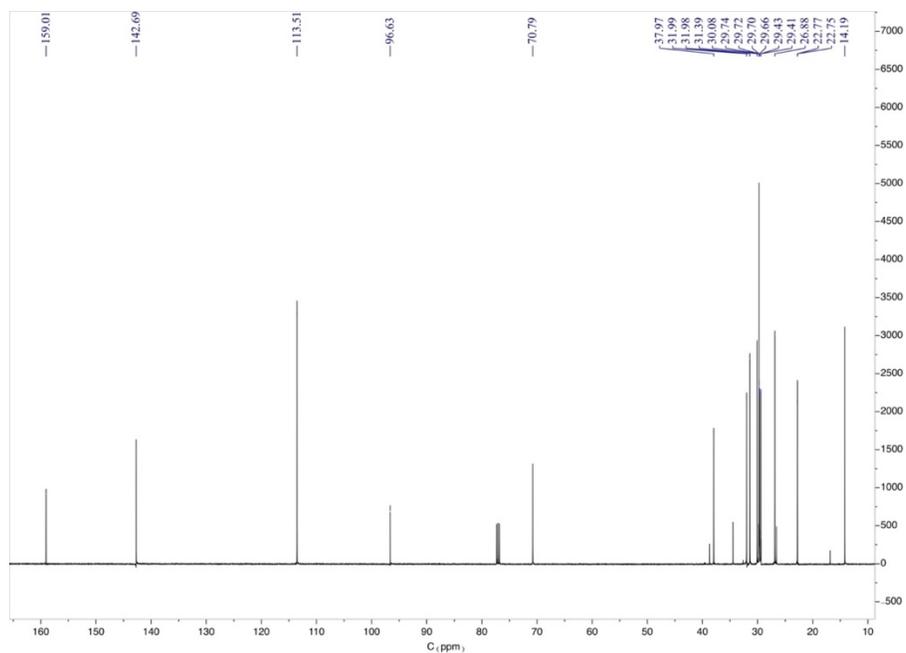


Fig. S2: ^{13}C NMR spectrum of compound **4** in CDCl_3 at 126 MHz

Compound 5:

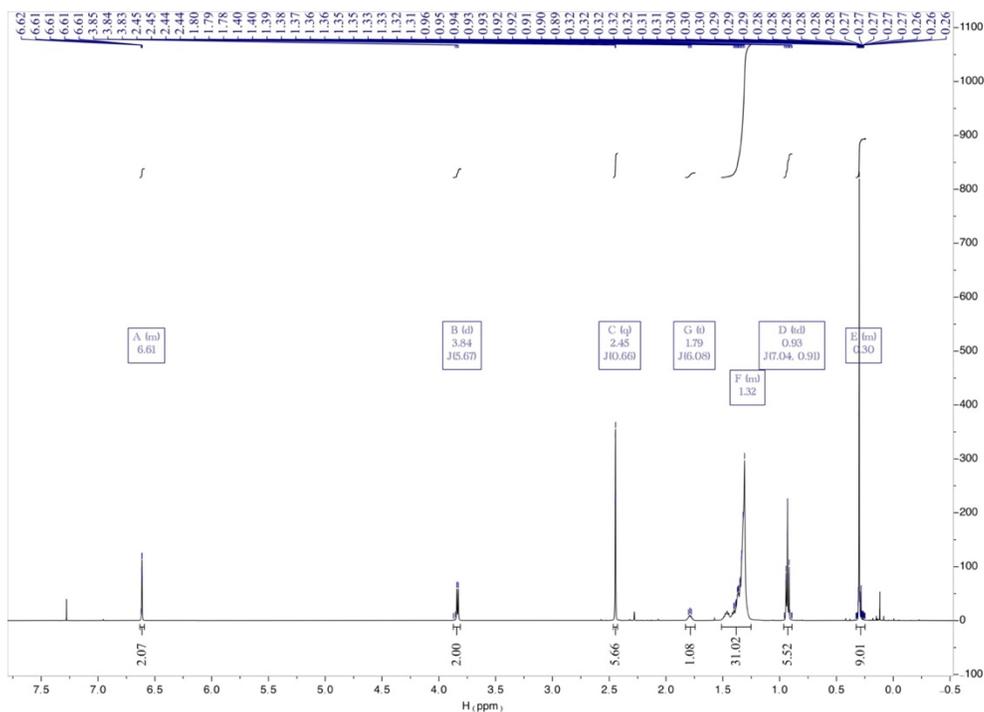


Fig. S3: ^1H NMR spectrum of compound **5** in CDCl_3 at 500 MHz

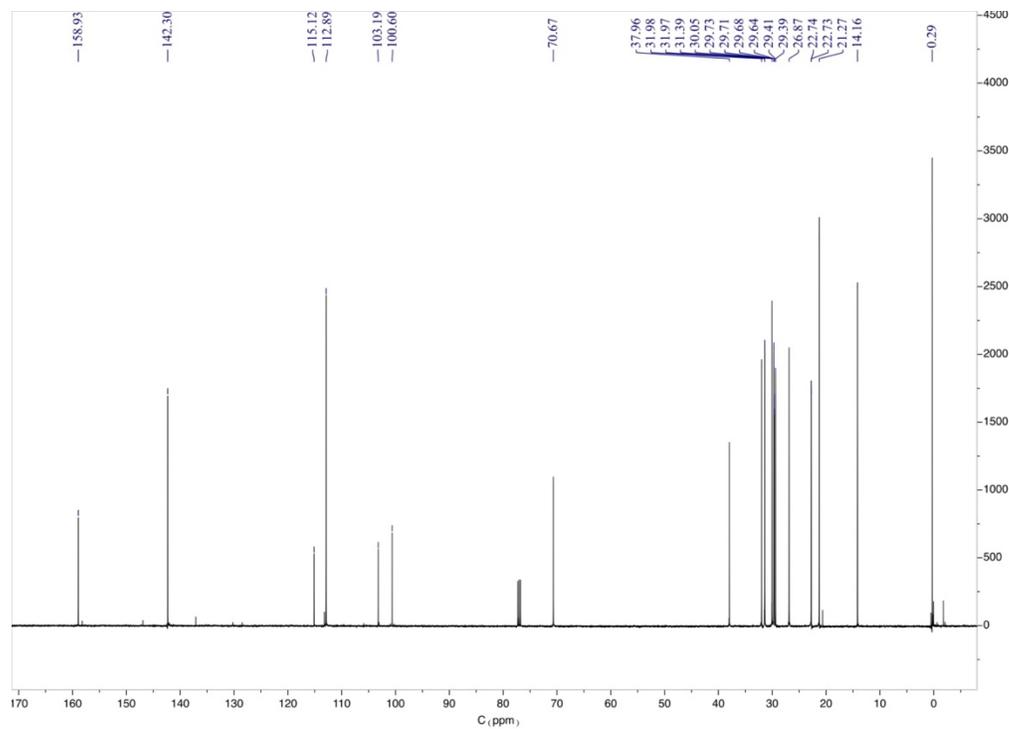


Fig. S4: ^{13}C NMR spectrum of compound **5** in CDCl_3 at 126 MHz

Compound **6**:

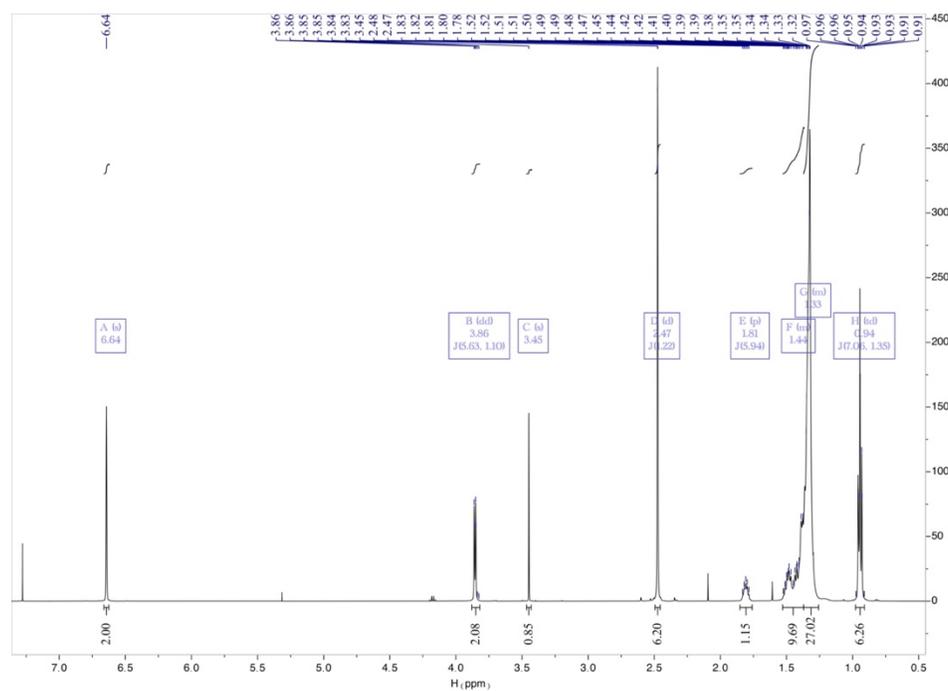


Fig. S5: ^1H NMR spectrum of compound **6** in CDCl_3 at 500 MHz

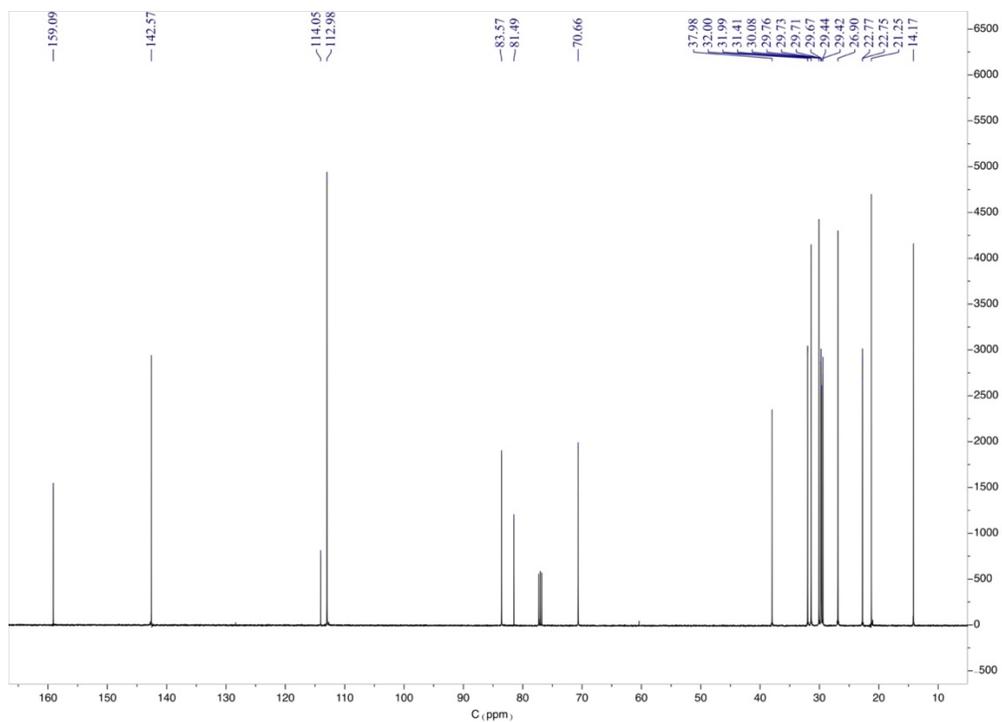


Fig. S6: ^{13}C NMR spectrum of compound **6** in CDCl_3 at 126 MHz

Compound 2:

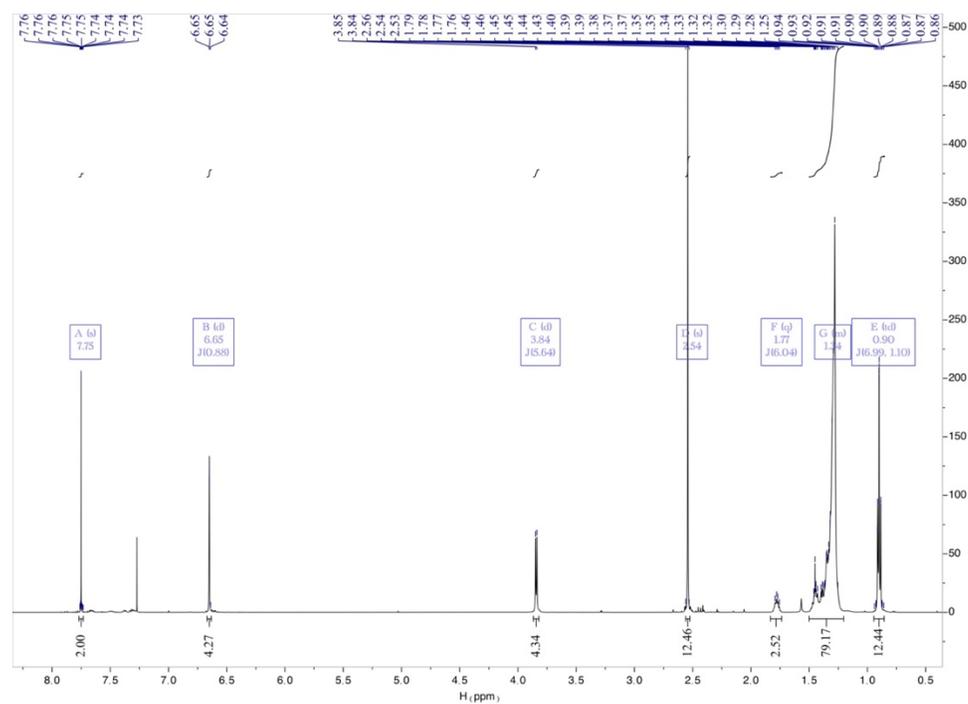


Fig. S7: ^1H NMR spectrum of compound **2** in CDCl_3 at 500 MHz

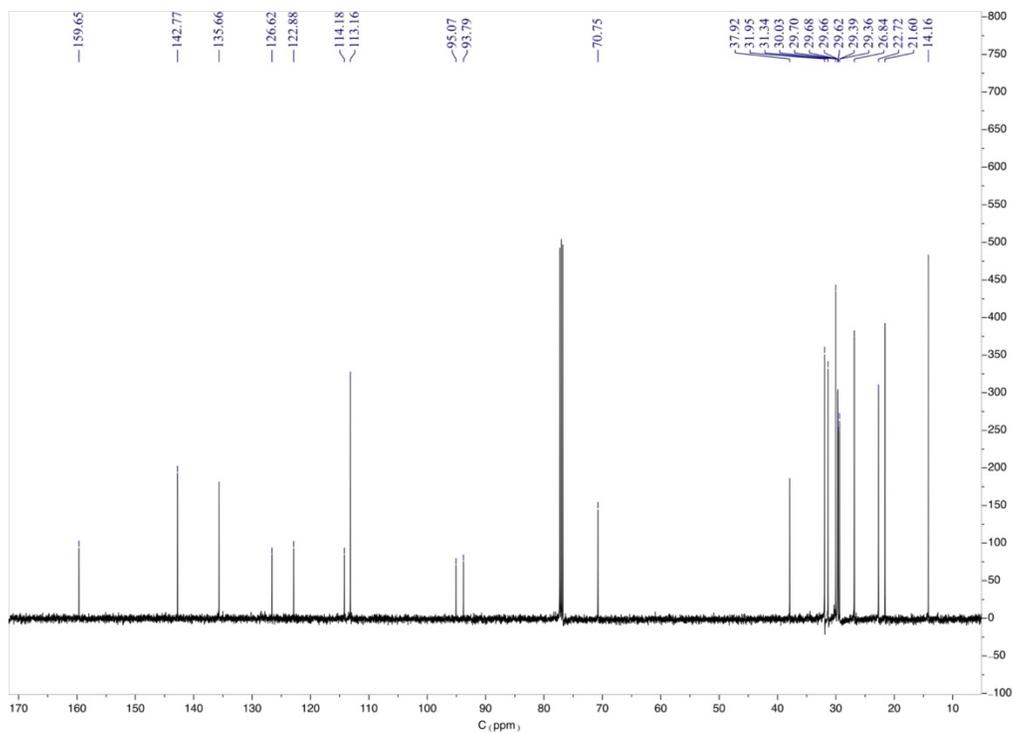


Fig. S8: ^{13}C NMR spectrum of compound **2** in CDCl_3 at 126 MHz

Compound 3:

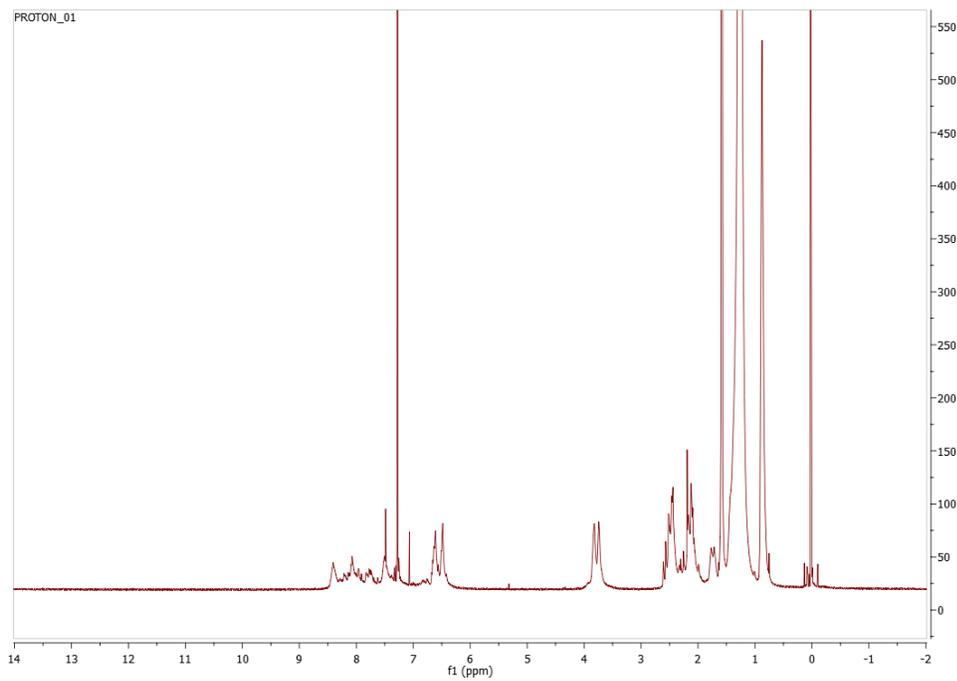


Fig. S9: ^1H NMR spectrum of compound **3** in CDCl_3 at 400 MHz

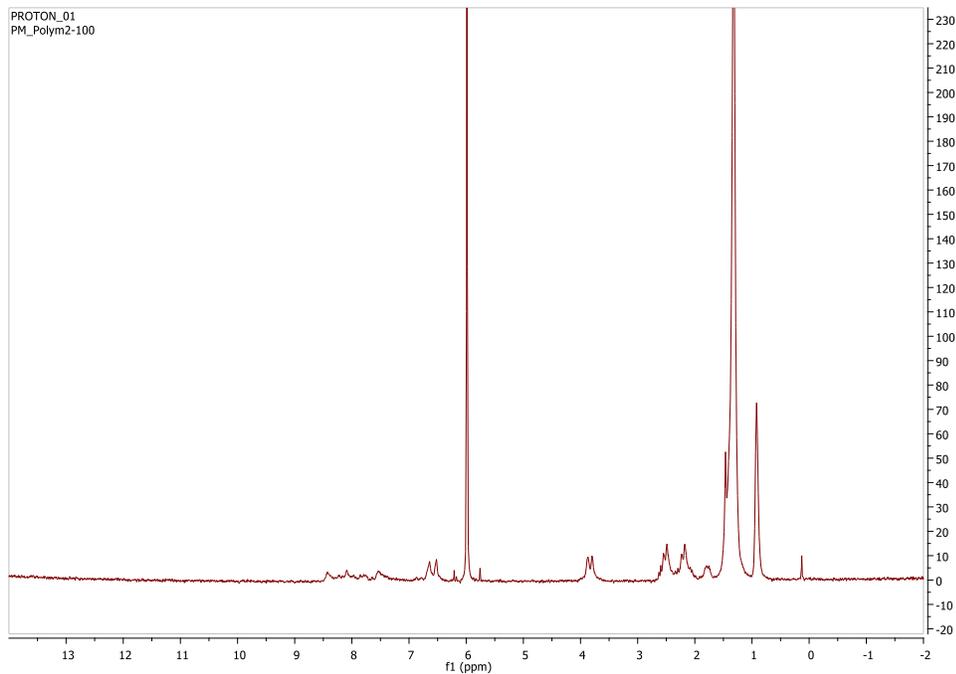


Fig. S10: ¹H NMR spectrum of compound **3** in C₂D₂Cl₃ at 100 °C and 400 MHz

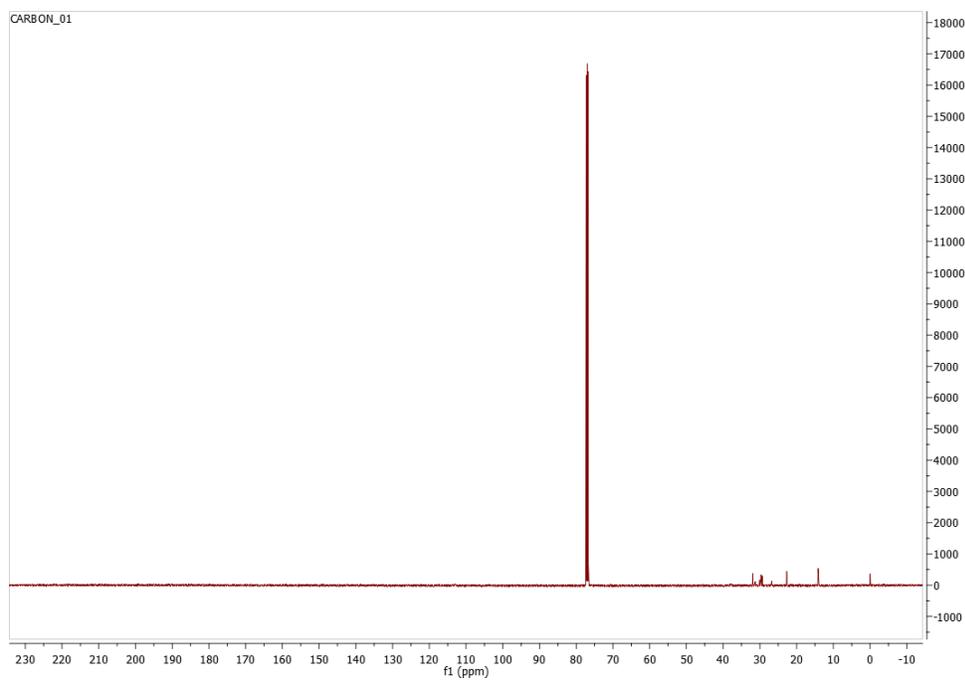


Fig. S11: ¹³C NMR spectrum of compound **3** in CDCl₃ at 500 MHz

ANR:

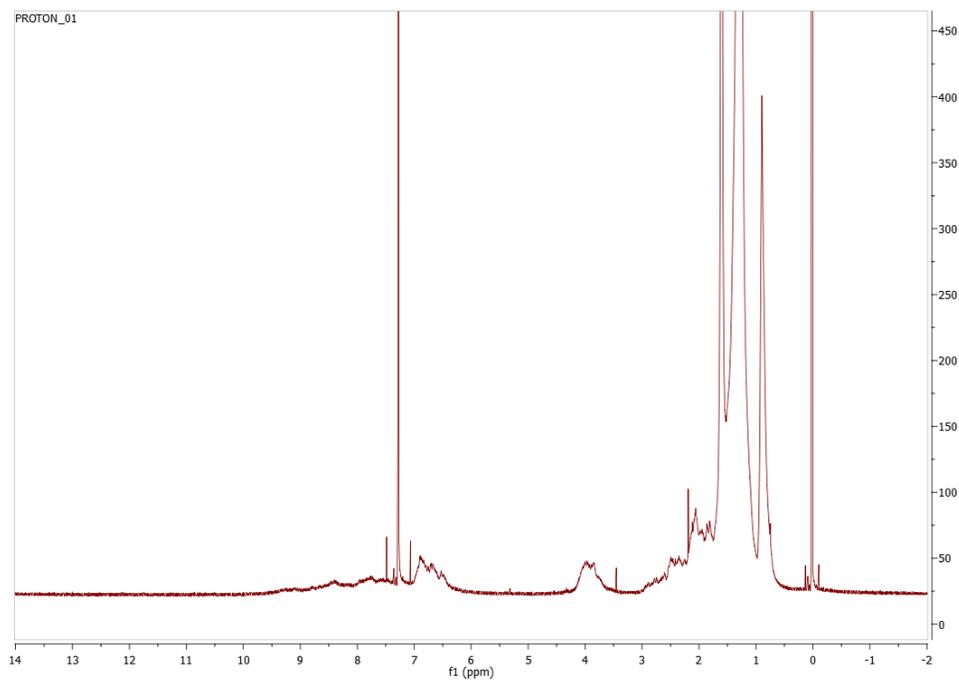


Fig. S12: ¹H NMR spectrum of compound ANR in CDCl₃ at 400 MHz

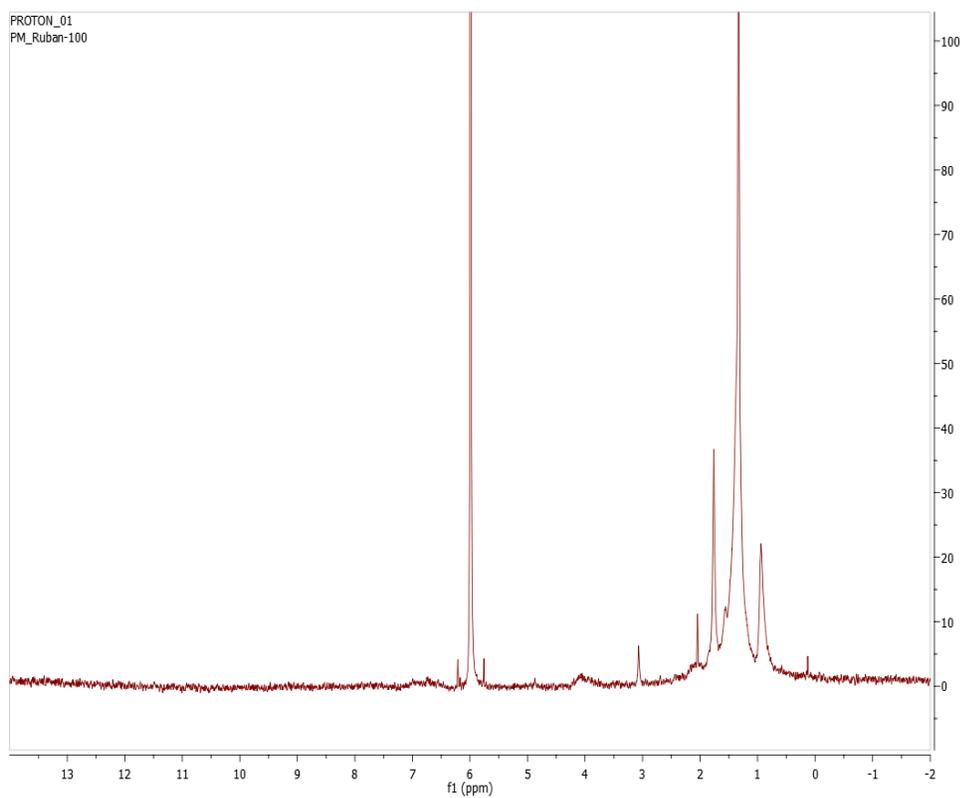


Fig. S13: ^1H NMR spectrum of compound ANR in $\text{C}_2\text{D}_2\text{Cl}_3$ at 100 °C and 400 MHz

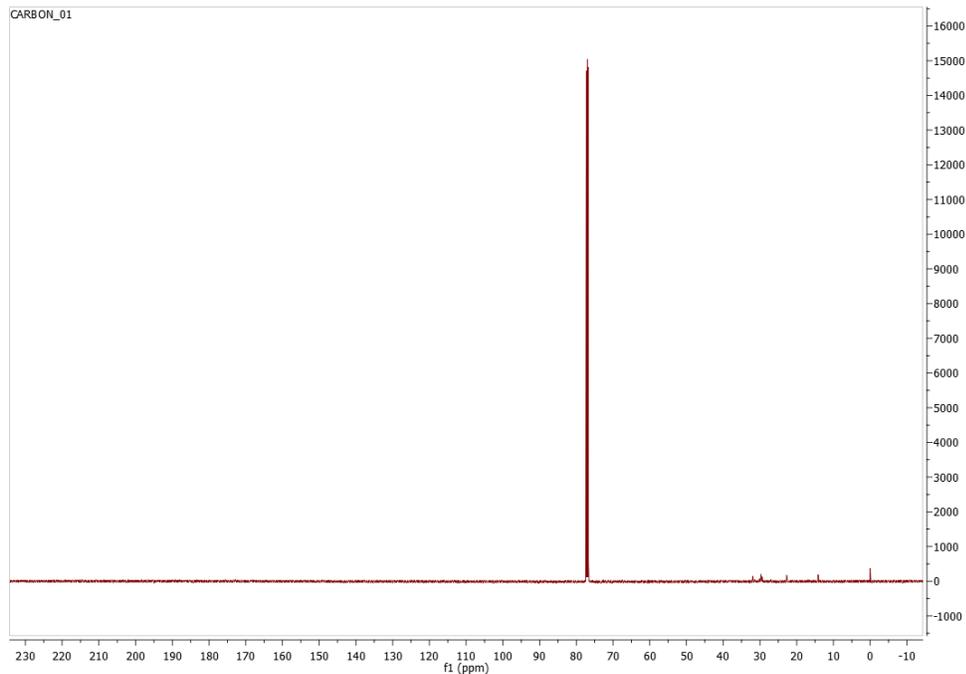


Fig. S14: ^{13}C NMR spectrum of compound ANR in CDCl_3 at 500 MHz

UV-Visible Spectroscopy

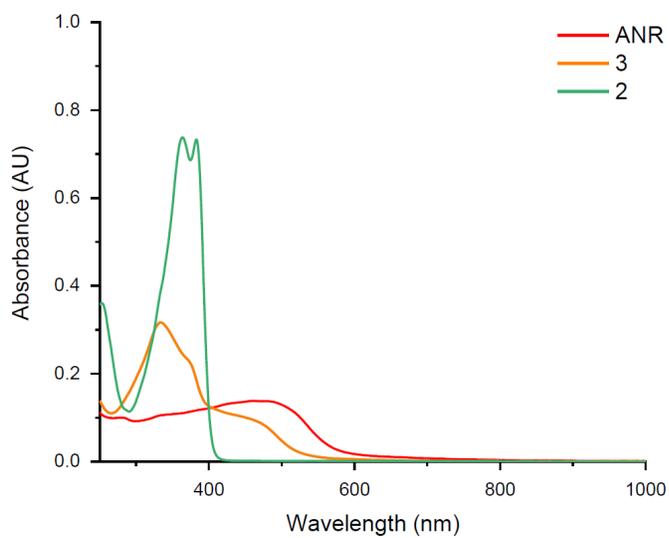


Fig. S15: Comparison of the UV-visible absorption spectrum of monomer **2**, polymer **3** and ANR in CH₂Cl₂.

Cyclic Voltammetry

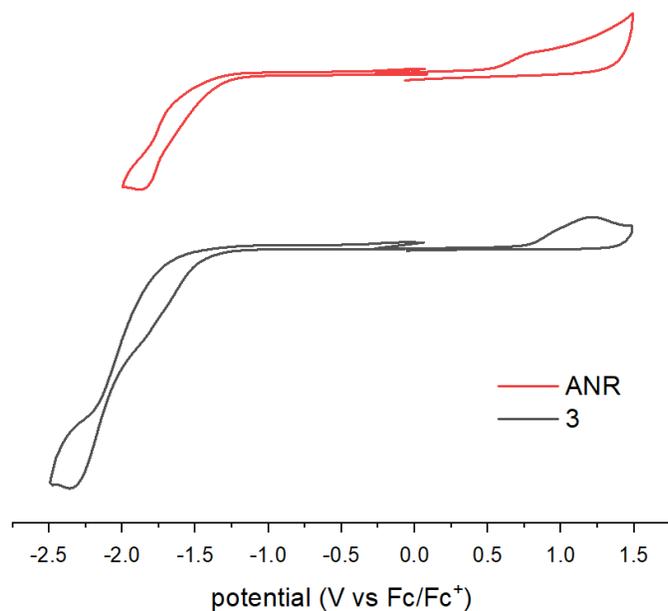


Fig. S16: Cyclic voltammetry of **3** and ANR thin film deposited on a Pt electrode in acetonitrile solution with 0.1M [Bu₄N][PF₆] as the supporting electrolyte with a scan rate of 100 mV·s⁻¹.

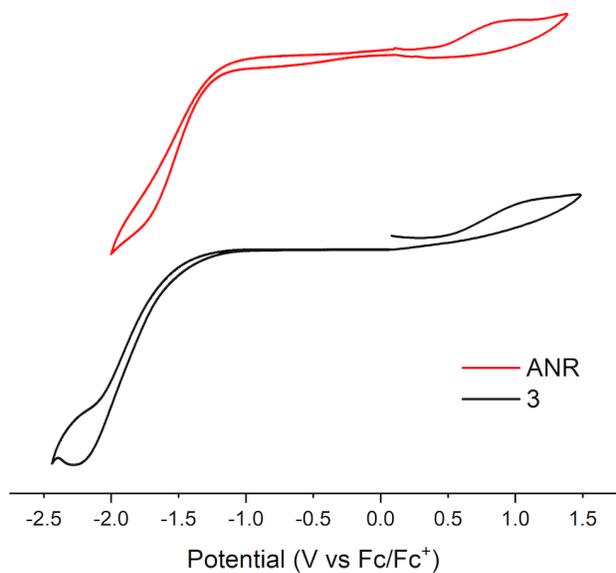


Fig. S17: Cyclic voltammetry of **3** and **ANR** with Pt electrode in CHCl_2 solution with 0.1M $[\text{Bu}_4\text{N}][\text{PF}_6]$ as the supporting electrolyte with a scan rate of $50 \text{ mV}\cdot\text{s}^{-1}$.

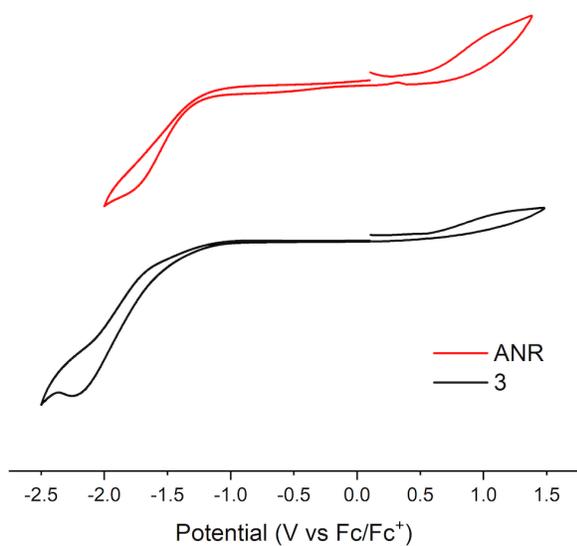


Fig. S18: Cyclic voltammetry of **3** and **ANR** with Pt electrode in CHCl_2 solution with 0.1M $[\text{Bu}_4\text{N}][\text{PF}_6]$ as the supporting electrolyte with a scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$.

IR Spectroscopy

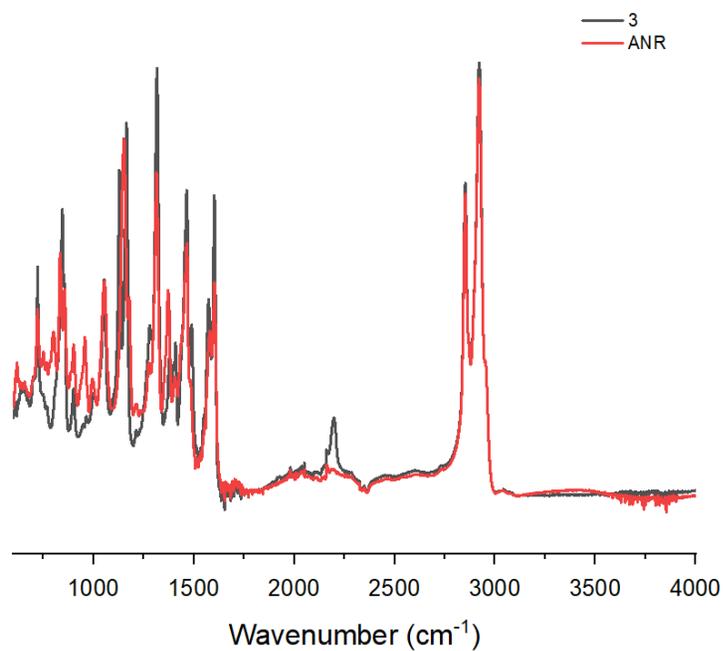


Fig. S19: IR spectrum of **3** and **ANR**

SEC Profiles and Data Summary

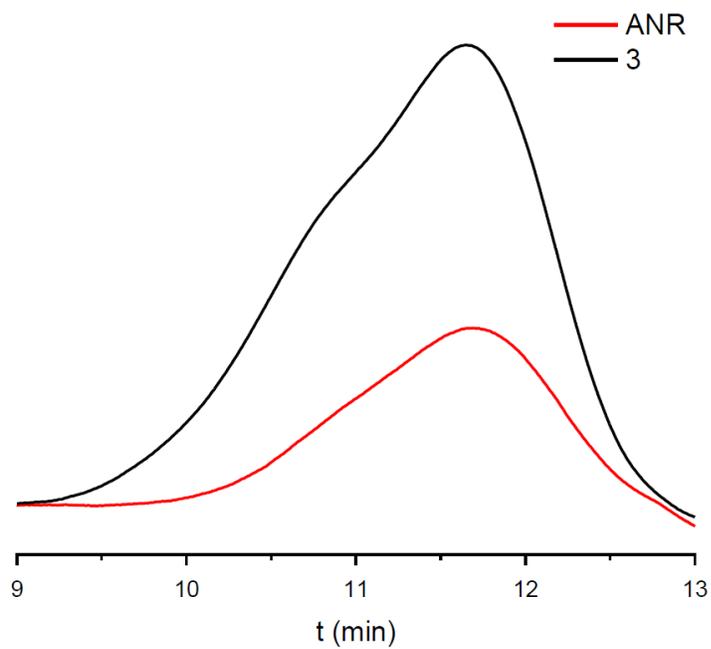


Fig. S20: SEC spectrum of **3** and **ANR**

Table S1: SEC data of **3** and **ANR**

	M_n ($\text{g}\cdot\text{mol}^{-1}$)	M_w ($\text{g}\cdot\text{mol}^{-1}$)	M_w/M_n
3	15,800	41,500	2.6
ANR	9,900	28,900	2.9

Conductivity

Table S2: Thickness values determined by Dektak measurements for polymer **3** and **ANR** films.

Films-1 were prepared by dropcast and dried on a hot plate. Films-2 were prepared by dropcast and dried in an oven. Films-3 were prepared by spin-coating.

	Thickness (μm)					
	3-Film-1	3-Film-2	3-Film-3	ANR-Film-1	ANR-Film-2	ANR-Film-3
1	11.7	8.9	4.2	33.7	3.5	0.2
2	11.6	8.8	4.1	20.6	2.0	0.3
3	11.6	8.9	4.1	25.3	6.6	0.1
4	11.7	7.9	4.3	39.2	2.6	0.3
5	11.6	9.1	4.2	31.2	4.2	0.5
Average	11.6	8.7	4.2	29.3	3.8	0.3

Table S3: Conductivity values determined by the four-point probe method for polymer **3** and **ANR** films doped with TFA vapor for 5 minutes. The measurements were made under ambient conditions. Entry 1 has only one value due to an extensive exposition to the TFA vapor (4h) that partially transformed polymer **3** to **ANR**.

	Conductivity ($\text{S}\cdot\text{cm}^{-1}$)					
	3-Film-1	3-Film-2	3-Film-3	ANR-Film-1	ANR-Film-2	ANR-Film-3
1	6.5E-06	8.6E-06	1.1E-04	1.0E-04	2.9E-04	4.5E-04
2	N/A	6.6E-06	1.4E-04	3.6E-05	2.9E-04	2.8E-04
3	N/A	7.0E-05	5.4E-05	1.5E-05	1.2E-04	2.7E-04

4	N/A	1.0E-05	4.1E-05	8.0E-05	1.0E-03	3.9E-04
5	N/A	4.1E-05	3.2E-05	9.1E-06	2.1E-03	2.1E-04
6	N/A	3.7E-05	2.6E-05	1.1E-05	1.3E-04	1.2E-02
7	N/A	2.7E-05	2.2E-05	4.2E-06	3.0E-04	2.1E-04
8	N/A	2.8E-05	2.1E-05	4.2E-06	3.5E-04	2.6E-04
9	N/A	2.5E-05	1.9E-05	5.6E-06	1.1E-03	2.9E-04
10	N/A	1.9E-05	1.8E-05	4.1E-06	3.8E-04	2.4E-04
Average	6.46E-06	2.7E-05	4.9E-05	2.7E-05	6.1E-04	1.5E-03

Table S4: Conductivity values determined by the four-point probe method for ANR films doped with TFA vapor for 4 h. The measurements were made under ambient conditions.

	Conductivity (S.cm⁻¹)		
	ANR-Film-1	ANR-Film-2	ANR-Film-3
1	1.1E-04	1.0E-04	1.1E-03
2	8.7E-05	1.0E-04	1.1E-03
3	6.2E-05	1.0E-04	1.1E-03
4	5.5E-05	1.5E-04	1.1E-03
5	3.8E-05	1.3E-04	1.3E-03
6	3.4E-05	1.0E-04	1.2E-03
7	3.3E-05	1.0E-04	1.2E-03
8	3.0E-05	1.7E-04	1.1E-03
9	2.9E-05	1.3E-04	1.1E-03
10	2.7E-05	1.1E-04	1.1E-03
Average	5.0E-05	1.2E-04	1.1E-03

References

- (1) Chamelot, G.; Idir, M.; Leclerc, M.; Morin, J.-F. Synthesis and Properties of 2,6-Azulene-Based Conjugated Polymers and Their Applications in Dispersing Single-Walled Carbon Nanotubes. *Polym. Chem.* **2023**, *14*, 1206–1212.