

# Electronic Supplementary Material

## Chevron-type graphene nanoribbons with a reduced energy band gap: Solution synthesis, scanning tunneling microscopy and electrical characterization

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### 1 Experimental section

#### 1) General

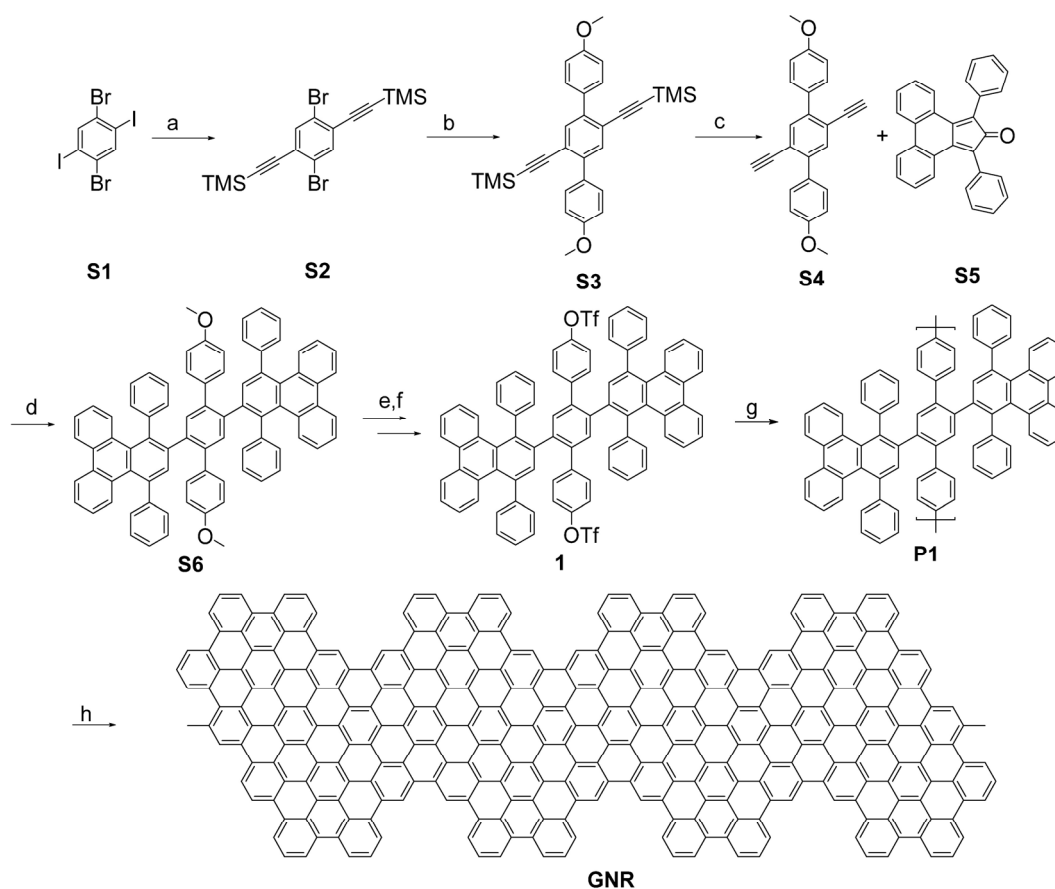
All manipulations of air- and/or water-sensitive compounds were carried out under a nitrogen atmosphere using standard Schlenk or glovebox techniques. All solvents and reagents were purchased from commercial sources and used as received unless otherwise noted. <sup>1</sup>H NMR and <sup>13</sup>C NMR were recorded with a Bruker FT-NMR spectrometer 400 (400 MHz, <sup>1</sup>H at 400 MHz, <sup>13</sup>C at 101 MHz). Chemical shifts are reported in parts per million (ppm,  $\delta$ ), downfield from tetramethylsilane (TMS,  $\delta = 0.00$  ppm) and are referenced to residual solvent (CDCl<sub>3</sub>,  $\delta = 7.26$  ppm (<sup>1</sup>H) and 77.00 ppm (<sup>13</sup>C)), multiplicity (br = broad; s = single, m = multiplet). FTIR spectra were recorded on a Nicolet 380 spectrometer using neat thin film technique. Measurements with a scan number of 32 were recorded for each sample and the background was subtracted.

Size-exclusion chromatography for polymer molecular weight and molecular weight distribution analysis (based on polystyrene standard) was carried out with an Agilent 1260 GPC/SEC System (RI detector). Agilent PLgel 5  $\mu$ m Mixed-D 300 x 7.5 mm with a PLgel 5  $\mu$ m 50 x 7.5 mm guard column eluted with THF. Flow rate was 1.0 mL/min and the temperature of the column was maintained at 30 °C. The data were analyzed using Cirrus GPC/SEC software.

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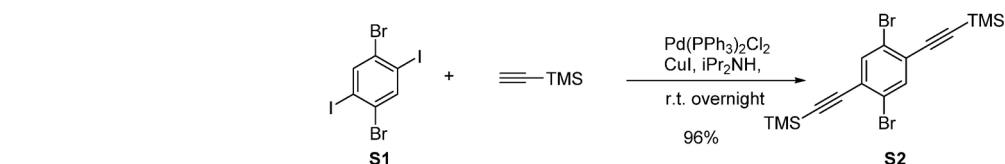
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Scheme S1. Scheme of the GNR synthesis

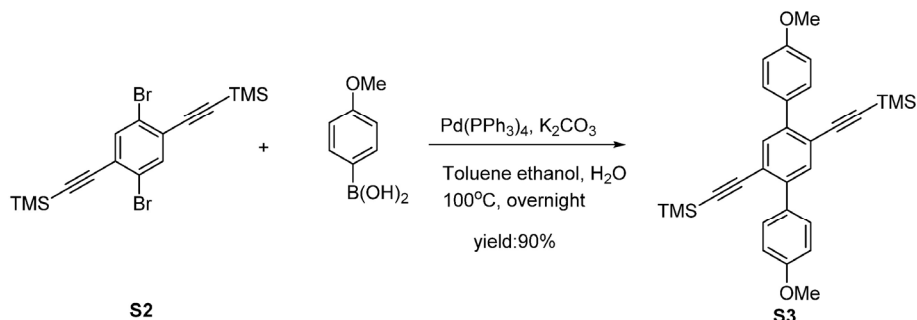


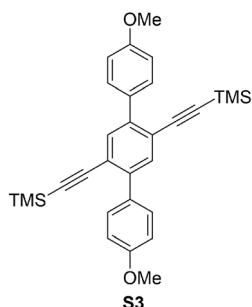
Reagents and conditions: a). Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI, iPr<sub>2</sub>NH, ethynyltrimethylsilane, r.t. overnight, 96%. b). (4-Methoxyphenyl) boronic acid, K<sub>2</sub>CO<sub>3</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub>, toluene/ethanol/water, overnight, 90%. c). K<sub>2</sub>CO<sub>3</sub>, DCM, overnight, 97%. d). Ph<sub>2</sub>O, refluxing for 4 hrs, 90%. e). BBr<sub>3</sub>, DCM, -78°C to r.t., overnight, 85%; f). Pyridine, (Tf)<sub>2</sub>O, DCM, r.t. overnight, 68%. g). Ni(COD)<sub>2</sub>, 2,2'-Bipyridine, 1,5-cyclooctadiene(COD), DMF and toluene, 80°C, 3 days, 89%. h) FeCl<sub>3</sub>, CH<sub>3</sub>NO<sub>2</sub>, DCM, 2 days, 90%.

## 2) Synthesis of molecular precursor 1



Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (280 mg, 0.4 mmol), CuI (120 mg, 0.8 mol) and 1,4-dibromo-2,5-diiodobenzene (1.93 g, 3.96 mmol) were mixed with 30 mL of diisopropylamine at room temperature. After the mixture was cooled down to 0 °C for 10 min, ethynyltrimethylsilane (1.68 mL, 11.8 mmol) was added. The resulting mixture was warmed to room temperature and stirred overnight. After the solvents were removed by rotary evaporation, the crude product was purified by silica gel chromatography with hexanes as eluent, affording compound **S2** as a yellow solid (1.62 g, 96%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.69 (s, Ar-H, 2H), 0.30 (s, 18 H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): 136.5, 126.6, 123.8, 103.1, 101.5, -0.1 ppm. FTIR (KBr): 2955, 2916, 2849, 2156, 1574, 1462, 1384, 1249, 1063, 891, 843, 761, 631 cm<sup>-1</sup>.

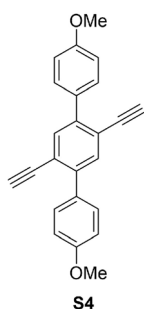
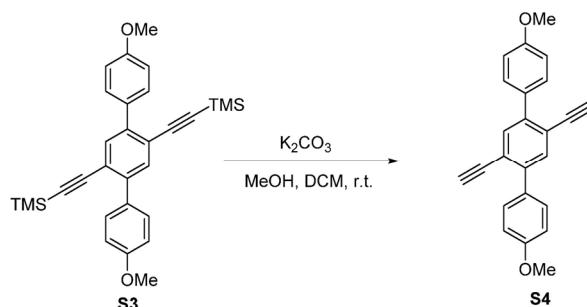




(4-Methoxyphenyl) boronic acid (0.684 g, 4.5 mmol), S2 (0.642 g, 1.5 mmol),  $K_2CO_3$  (1 g, 7.5 mmol) and Tetrakis(triphenylphosphine)palladium ( $Pd(PPh_3)_4$ ) (345 mg) were mixed in a solution of toluene/ethanol/water (20 mL/2 mL/2 mL). Then, the mixture was degassed by a freeze-pump three times. The orange mixture was heated to 100 °C and stirred overnight. After cooling down to room temperature, 50 mL of DCM and 50 mL of water were added. The aqueous phase was extracted with DCM ( $3 \times 20$  mL). The combined organic phase was washed with brine and water, dried over anhydrous Magnesium sulfate. After removal of the solvents by rotary evaporation, the crude product was purified by silica gel chromatography using Hexanes/DCM as eluent, affording the compound S3 as a yellow powder (651 mg) with 90% yield.  $^1H$  NMR (400 MHz,  $CDCl_3$ ): 7.61 (d,  $J = 4$  Hz, Ar-H, 4H), 7.58 (s, Ar-H, 2H), 6.95 (d,  $J = 4$  Hz, Ar-H, 4H), 3.87 (s,  $OCH_3$ , 6H), 0.17 (s, TMS-H, 18H) ppm.  $^{13}C$  NMR (101 MHz,  $CDCl_3$ ): 159.3, 141.7, 134.1, 131.6, 130.4, 121.5, 113.3, 104.6, 99.2, 55.4, -0.3 ppm.

MALDI-MS for  $C_{30}H_{34}O_2Si_2$  [M]: 482.209. Found: 482.210.

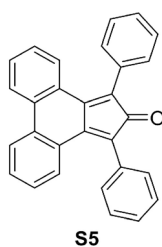
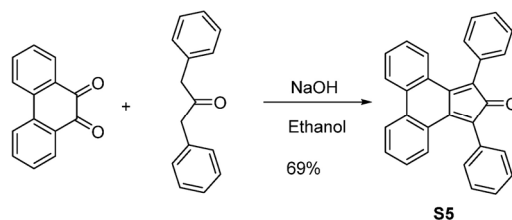
FTIR (KBr): 2959, 2914, 2837, 2155, 1609, 1578, 1520, 1484, 1443, 1382, 1291, 1244, 1178, 1112, 1049, 1027, 907, 841, 759, 732, 648  $cm^{-1}$ .



**S3** (172 mg, 0.36 mmol) and  $K_2CO_3$  (200 mg, 1.43 mmol) was mixed with 2 mL of DCM and 2 mL of methanol. The mixture was stirred at room temperature overnight, and then poured into 50 mL of water. The aqueous phase was extracted with DCM ( $3 \times 20$  mL), and the organic layer was washed with water and dried over magnesium sulfate. After the solvents were removed by rotary evaporation, the pure product **S4** was obtained as a white solid (118 mg) with 97% yield.  $^1H$  NMR (400 MHz,  $CDCl_3$ ): 7.60 (m, Ar-H, 6H), 7.01 (m, Ar-H, 4H), 3.89 (m,  $-OCH_3$ , 6H), 3.17 (s,  $\equiv C-H$ , 2H) ppm.  $^{13}C$  NMR (101 MHz,  $CDCl_3$ ): 159.4, 142.1, 134.8, 131.3, 130.3, 120.9, 113.5, 82.8, 81.5, 55.3 ppm.

MALDI-MS for  $C_{24}H_{18}O_2$  [M]: 338.131. Found: 338.130.

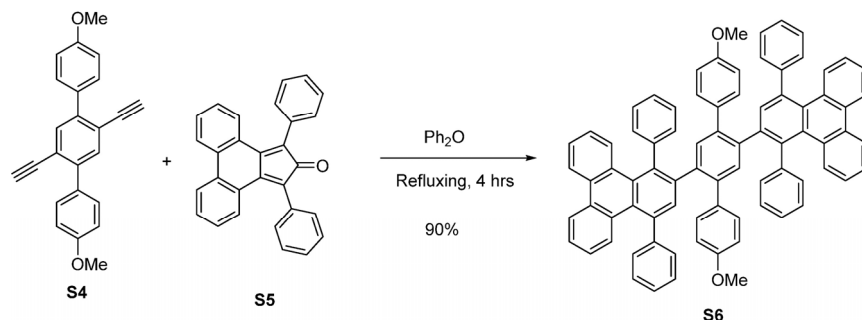
FTIR (KBr): 2961, 2914, 2847, 2272, 1606, 1577, 1519, 1438, 1374, 1288, 1243, 1177, 1024, 920, 829, 668  $cm^{-1}$ .

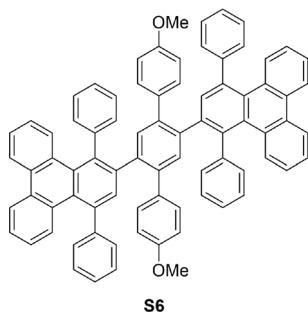


Compound **S5** was prepared following the known procedure [1] with modifications. An ethanol solution of NaOH (734 mg, 18.3 mmol) was added slowly to a suspension of 9,10-phenanthrenequinone (1.91 g, 9.18 mmol) and diphenylacetone (2.12 g, 10.1 mmol) in 50 ml of ethanol. The dark solution was stirred at room temperature for 10 min and refluxed for 5 min. Next, the solution was cooled down in an ice-bath. The precipitate was collected and rinsed with ethanol. After being dried in vacuum, **S5** was obtained as a black solid (2.42 g) with 69% yield.  $^1H$  NMR (400 MHz,  $CDCl_3$ ): 7.83 (d,  $J = 8$  Hz, 2H), 7.57 (d,  $J = 8$  Hz, 2H), 7.47-7.40 (m, 10H), 7.31 (m, 2H), 6.97 (t, 2H) ppm.  $^{13}C$  NMR (101 MHz,  $CDCl_3$ ): 200.2, 148.3, 133.6, 132.3, 131.4, 130.0, 129.0, 128.6, 128.3, 128.1, 124.5, 123.1 ppm.

MALDI-MS for  $C_{29}H_{18}O$  [M]: 382.136. Found: 383.143.

FTIR (KBr): 2912, 2854, 1698, 1594, 1441, 1302, 959, 904, 803, 765, 752, 727, 717, 695, 668  $cm^{-1}$ .

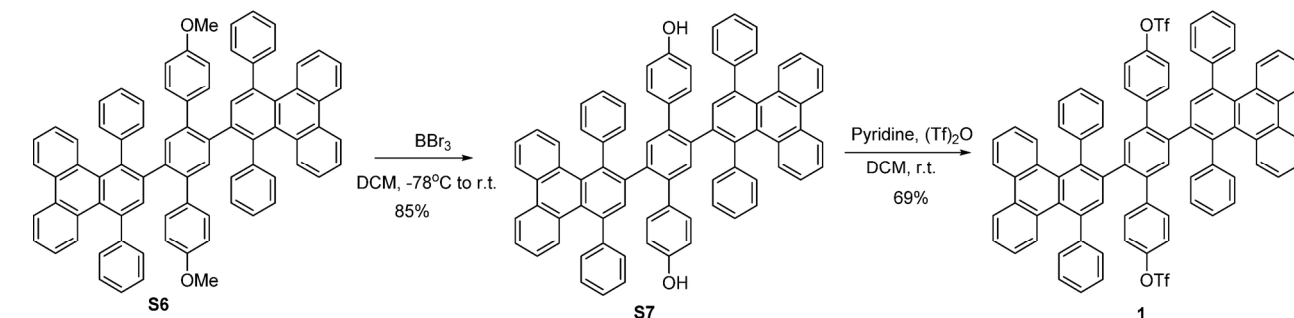




A mixture of **S4** (109 mg, 0.32 mmol) and **S5** (370 mg, 0.97 mmol) in phenyl ether (0.5 ml) was stirred and refluxed for 4 hours. The reaction was monitored by TLC. After cooling down to room temperature, the crude product was purified by column chromatography with hexane/DCM (4/1) as eluent. Compound **S6** was isolated as a yellow solid with 90% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.45(dd, 4H), 7.83(d,  $J=8\text{Hz}$ , 2H), 7.80(s, 2H), 7.52-7.32 (m, 19H), 7.25(t, 3H), 7.18(t, 3H), 7.01 (t, 3H), 6.86 (br, 2H), 6.66 (d,  $J=8\text{Hz}$ , 4H), 6.48 (d,  $J=8\text{Hz}$ , 4H), 6.14(s, 2H), 3.64 (s,  $-\text{OCH}_3$ , 6H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ): 158.3, 144.4, 141.5, 139.8, 139.0, 138.8, 138.3, 136.6, 133.8, 133.4, 132.8, 132.3, 131.6, 131.5, 131.0, 130.5, 130.3, 130.2, 130.0, 129.9, 129.2, 127.3, 126.7, 126.4, 126.2, 125.6, 125.2, 123.3, 113.3, 55.3 ppm.

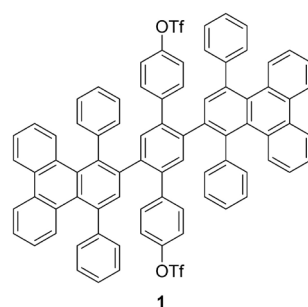
MALDI-MS for  $\text{C}_{80}\text{H}_{54}\text{O}_2[\text{M}]$ : 1046.412. Found: 1046.409.

FTIR (KBr): 3056, 3026, 2916, 2852, 1691, 1666, 1597, 1493, 1441, 1246, 1177, 906, 757, 727, 699  $\text{cm}^{-1}$ .



To a solution of **S6** (244 mg, 0.23 mmol) in anhydrous DCM (10 mL) at  $-78^\circ\text{C}$ ,  $\text{BBr}_3$  (0.11 mL, 1.2 mmol) was added dropwise. Then, the mixture was allowed to warm to room temperature and stirred overnight. After that, the reaction was quenched with water. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate ( $2 \times 10$  mL). After the solvents were removed by rotary evaporation, the crude product was purified by flash chromatography with hexanes and EtOAc as eluent to afford **S7** (176 mg) as a yellow powder with 85% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.42 (dd, 4H), 7.77(d,  $J=8\text{Hz}$ , 2H), 7.74 (s, 2H), 7.53-7.35 (m, 18H), 7.25-7.18 (m, 4H), 7.13(t, 3H), 6.96 (t, 2H), 6.83(br, 2H), 6.55 (d,  $J=8\text{Hz}$ , 4H), 6.36 (d,  $J=8\text{Hz}$ , 4H), 6.10 (s, 2H), 4.39 (s,  $-\text{OH}$ , 2H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ): 154.2, 144.4, 141.4, 139.6, 138.9, 138.8, 138.2, 136.6, 133.7, 133.2, 132.9, 132.3, 131.5, 131.4, 131.0, 130.5, 130.2, 130.1, 130.0, 129.9, 129.1, 128.9, 128.3, 127.3, 126.7, 126.4, 126.2, 125.6, 125.1, 123.2, 114.6 ppm. MALDI-MS for  $\text{C}_{78}\text{H}_{49}\text{O}_2[\text{M}-\text{H}]$ : 1018.38. Found: 1017.30.

FTIR (KBr): 3405, 3058, 3032, 2949, 2919, 2845, 1611, 1522, 1493, 1440, 1383, 1259, 1171, 908, 834, 758, 728, 699  $\text{cm}^{-1}$ .



To a solution of **S7** (176 mg 0.18 mmol) and pyridine (0.16 mL, 2 mmol) in dry DCM (10 mL) at  $0^\circ\text{C}$ , trifluoromethanesulfonic anhydride (0.33 mL, 1.96 mmol) was added dropwise under nitrogen. The reaction was allowed to warm to room temperature and stirred overnight. The resulting mixture was diluted with EtOAc (20 mL). The organic layer was separated and washed with 1M HCl(aq) (10 mL), water and brine, dried over  $\text{Na}_2\text{SO}_4$ . After removal of the solvents, the crude product was purified by flash chromatography with hexanes/EtOAc, affording the compound **1** as a white solid (160 mg) with 69% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.46 (dd, 4H), 7.84 (d,  $J=8\text{Hz}$ , 2H), 7.77 (s, 2H), 7.55-7.34 (m, 19H), 7.28 (m, 3H), 7.20 (t, 3H), 7.03 (t, 2H), 6.89-6.81 (m, 11H), 6.09 (m, 2H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ): 148.2, 144.1, 141.1, 140.0, 139.4, 138.6, 138.4, 138.1, 136.2, 133.6, 133.2, 132.8, 132.3, 131.6, 131.5, 130.8, 130.6, 130.5, 130.3,

130.2, 129.8, 129.7, 129.1, 127.4, 126.9, 126.5, 126.4, 125.6, 125.1, 123.3, 123.2, 120.6, 120.5, 120.1, 117.0 ppm.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ): -73.04 ppm.

FTIR (KBr): 3058, 3024, 2924, 2849, 1598, 1492, 1423, 1248, 1212, 1181, 1139, 884, 758, 728, 699  $\text{cm}^{-1}$ .

### 3) Synthesis of polymer precursor

Bis(1,5-cyclooctadiene)nickel(0) (43 mg, 0.16 mmol), 2,2'-bipyridyl (24 mg, 0.16 mmol), and 1,5-cyclooctadiene (17 mg, 0.16 mmol) were mixed into anhydrous dimethylformamide(DMF) (1 ml) in an 8 mL of vial. The mixture was heated to  $60^\circ\text{C}$  for 30 min. After that, the molecular precursor **1** (0.1 g, 0.08 mmol) in anhydrous toluene (3 ml) was added. The reaction was heated to  $80^\circ\text{C}$  for three days. Then, the reaction was allowed to cool down to room temperature. The dark mixture was poured into 20 mL of methanol to precipitate the polymer and stirred for 2 hours. The solid was filtered and washed with methanol and acetone. After being dried under vacuum, the polymer precursor was isolated as a yellow solid (68 mg) with 89% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ): 8.33 (br, 4H), 7.65-6.62 (m, 42H), 5.96 (br, 2H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ): 144.3 141.3, 139.3, 138.9, 138.3, 136.5, 133.8, 133.6, 132.2, 131.5, 130.9, 130.4, 130.2, 129.9, 129.1, 128.9, 127.3, 126.6, 126.3, 125.4, 125.1, 123.2, 120.6 ppm.

GPC:  $M_n = 5240$  Da,  $M_w = 35978$  Da, PDI = 6.87

FTIR(KBr): 4048, 3082, 3057, 3027, 2924, 2847, 1598, 1477, 1440, 1424, 1213, 1140, 1005, 968, 953, 886, 822, 727, 699  $\text{cm}^{-1}$ .

#### 4) Synthesis of GNR

Polymer precursor **P1** (40 mg, 0.041 mmol) in dichloromethane (100 ml) was degassed with nitrogen bubbling for 15 min. Then, iron(III) chloride (138 mg, 0.85 mmol) in nitromethane (2 ml) was added to the yellow solution. The black solution was stirred for two days with nitrogen bubbling. Next, the reaction mixture was filtered, washed with methanol and acetone to obtain GNR as a black solid with 90% yield.

FTIR(KBr): 2917, 2850, 1578, 1420, 1303, 1205, 1133, 775, 750, 698  $\text{cm}^{-1}$ .

## 2 Supporting figures

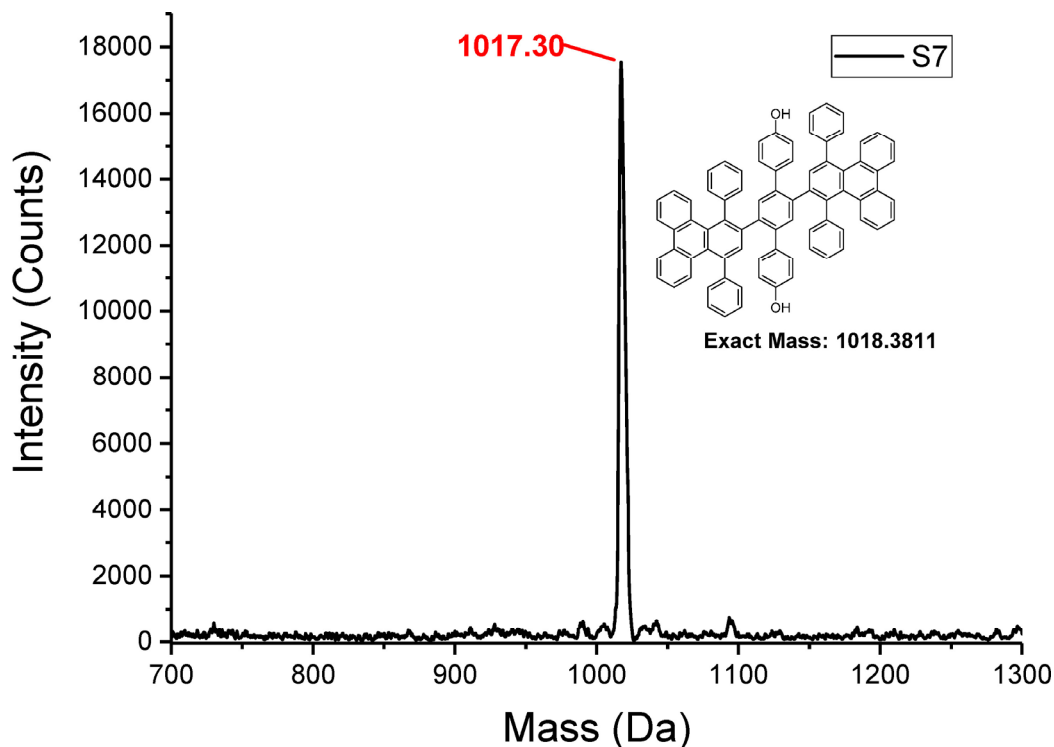


Figure S1 MALDI spectrum of S7 (Reflection mode, matrix: DHB).

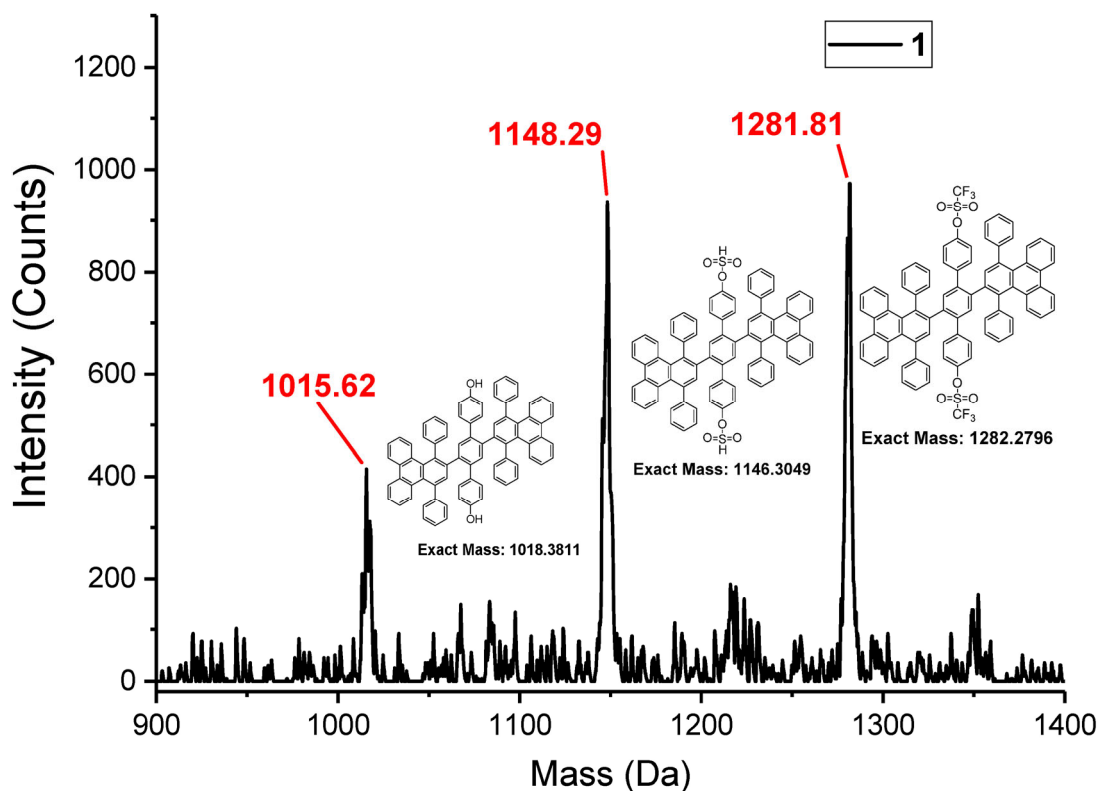
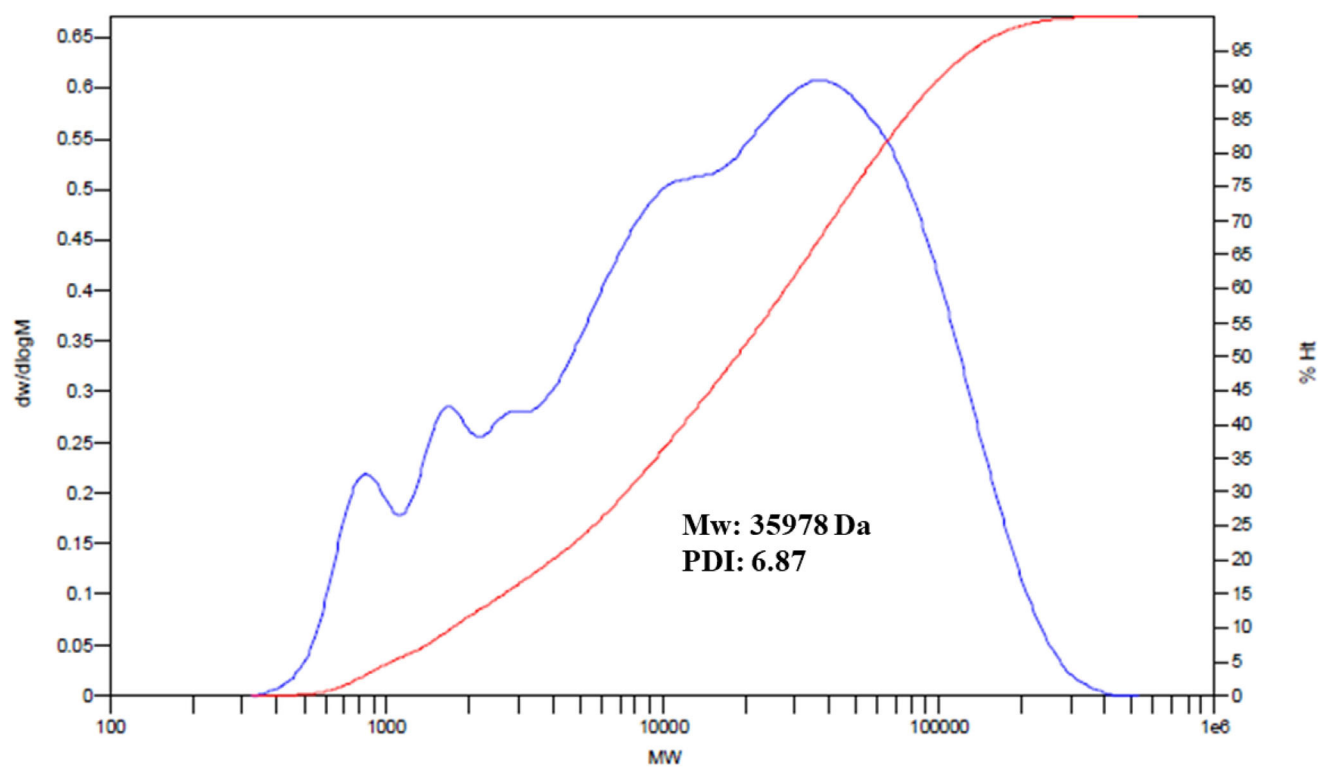
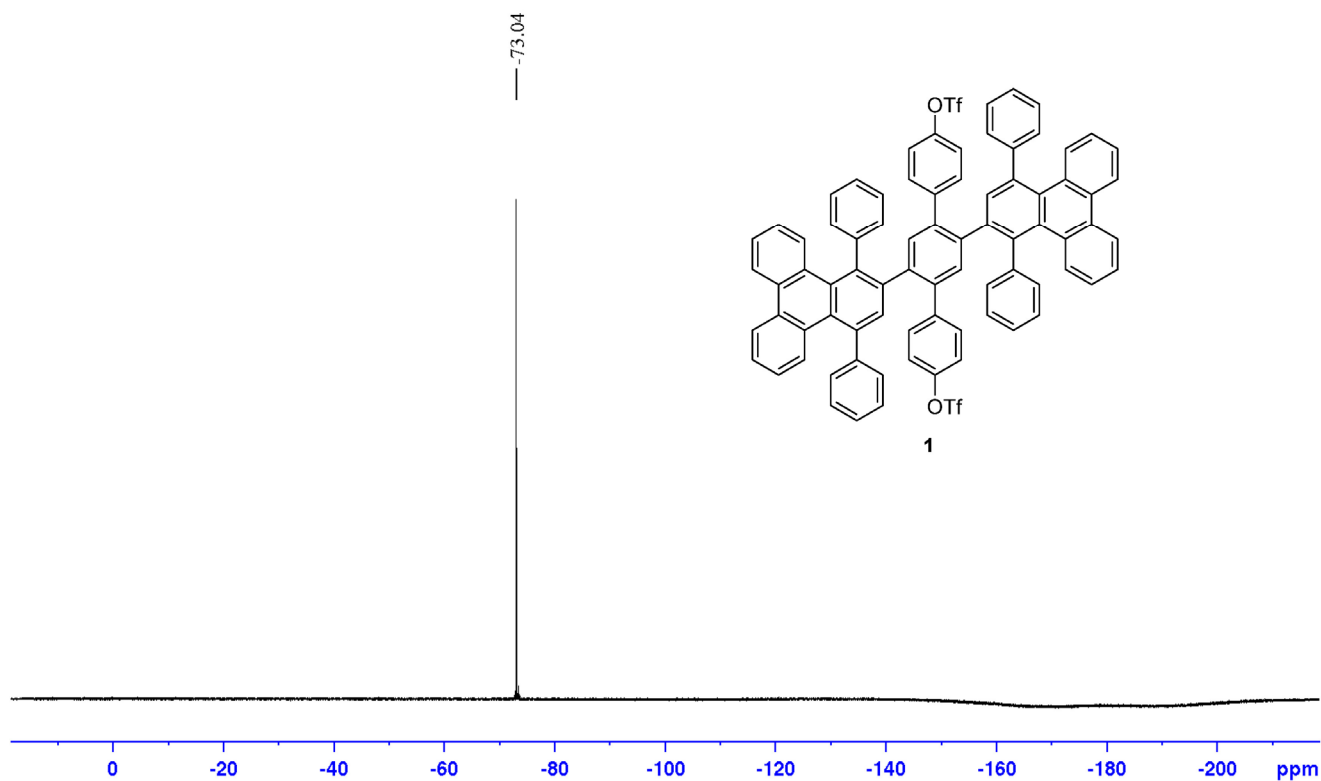
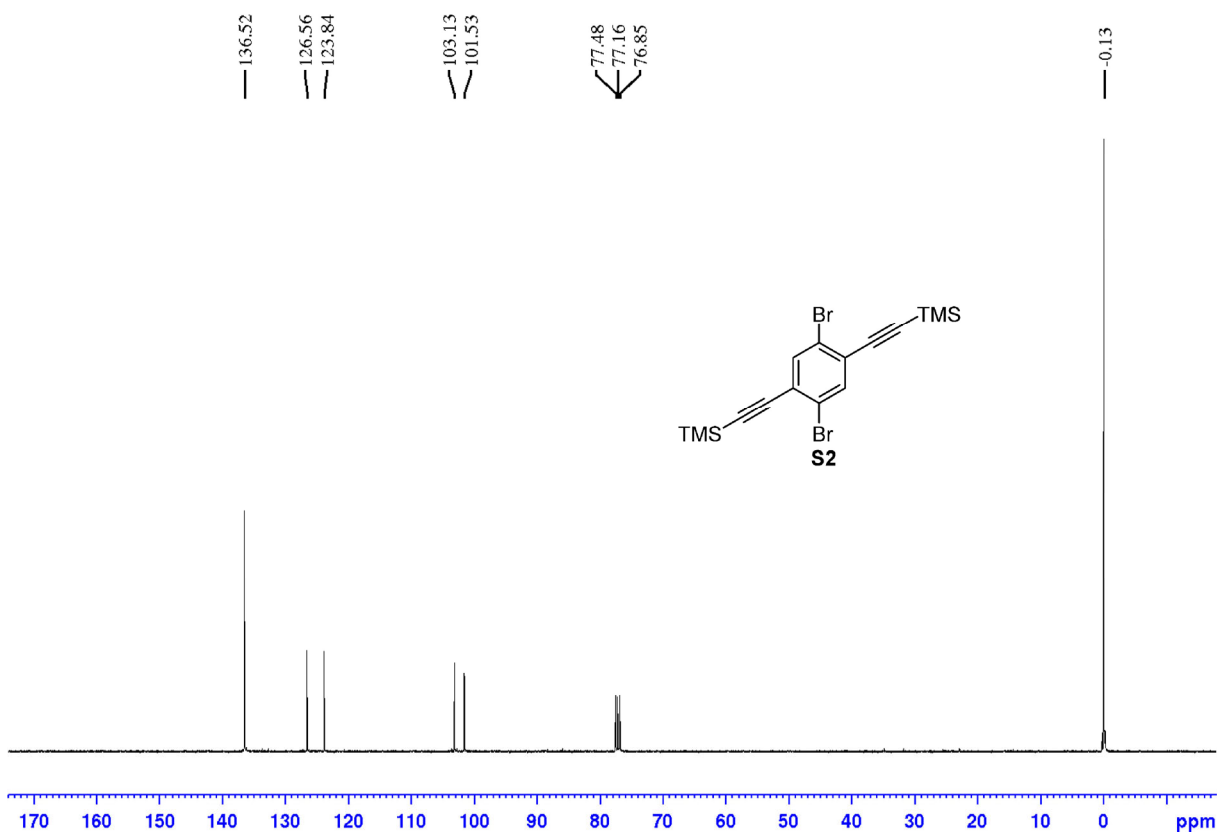
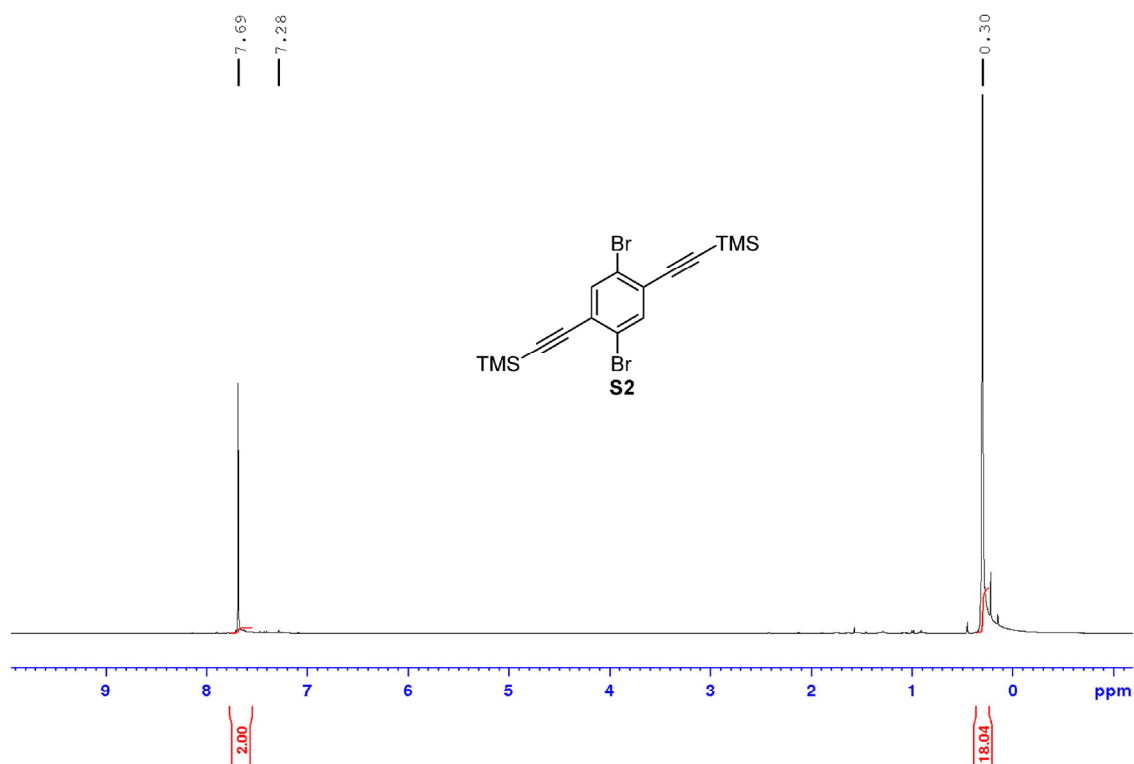
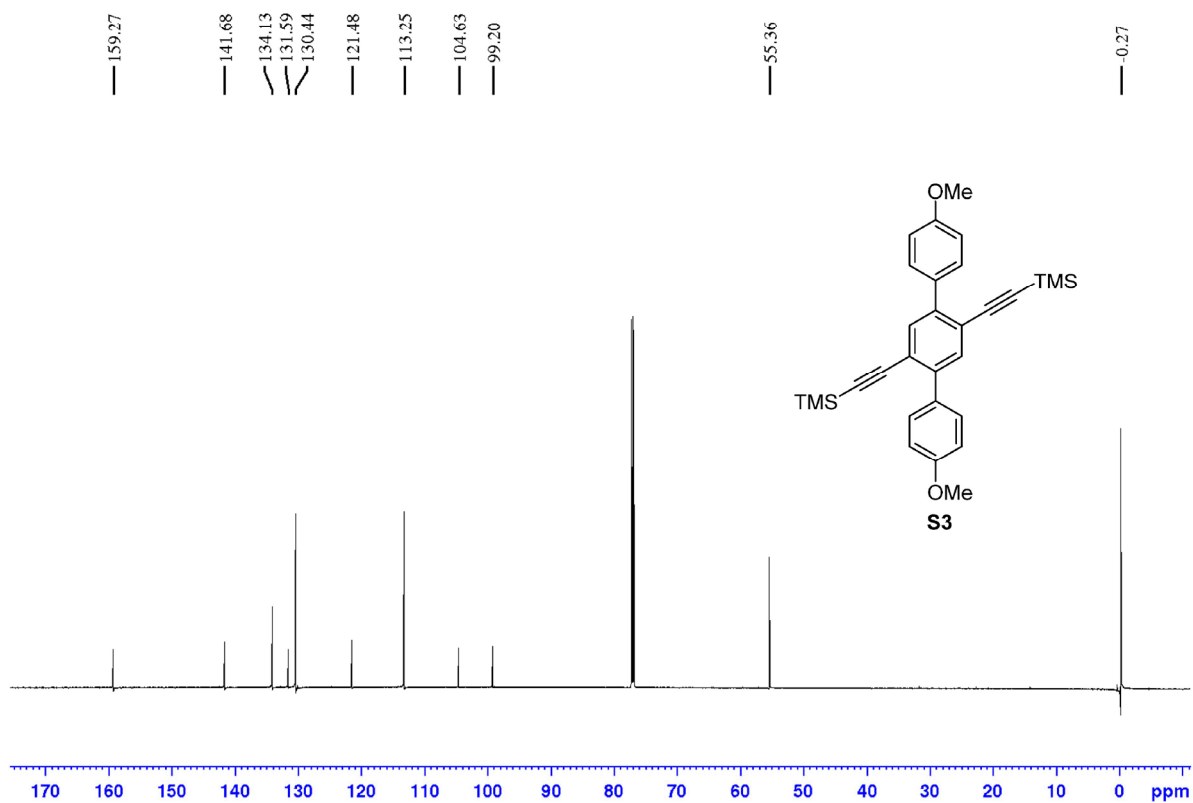
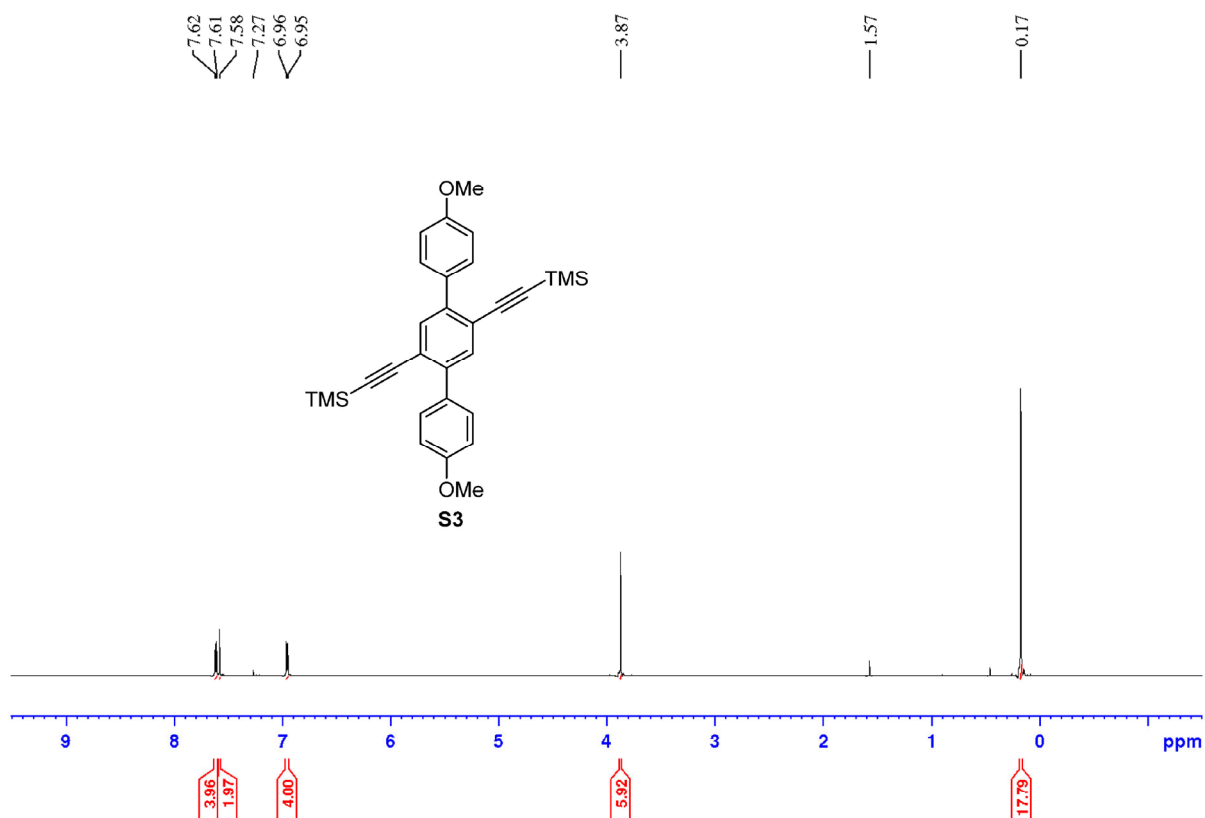


Figure S2 MALDI spectrum of 1 (Reflection mode, matrix: DHB).

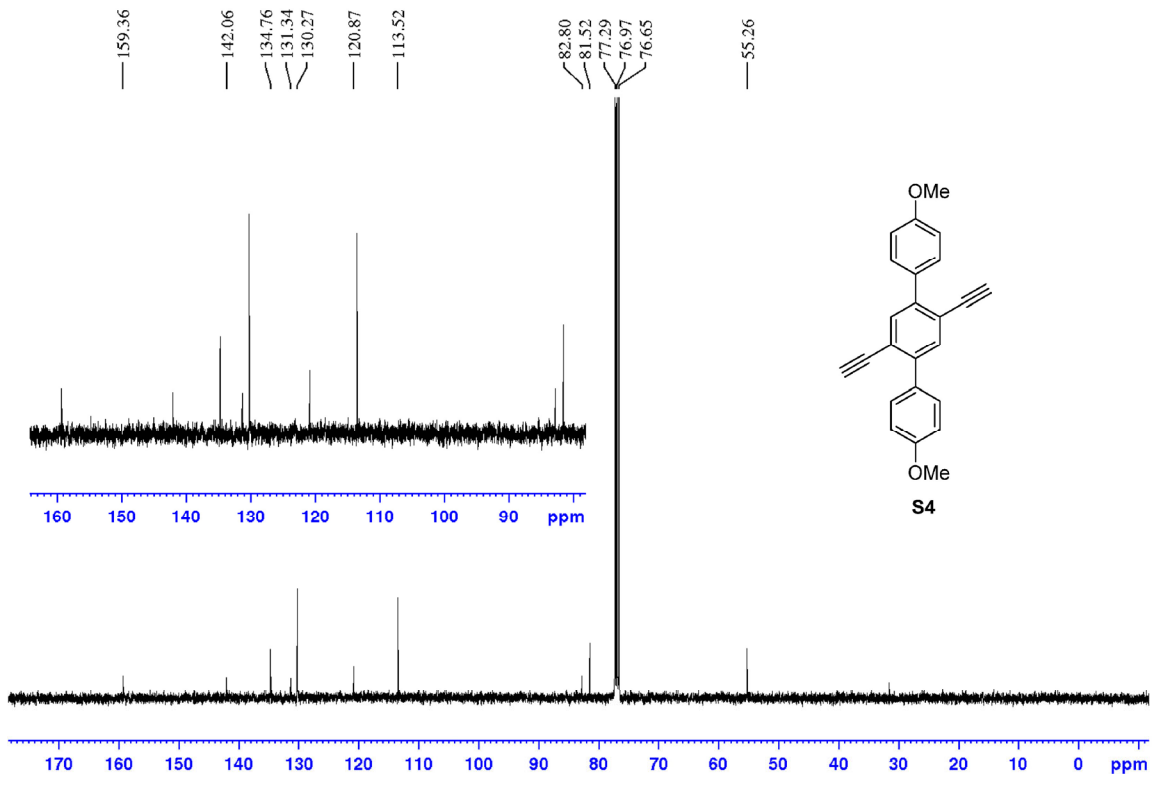
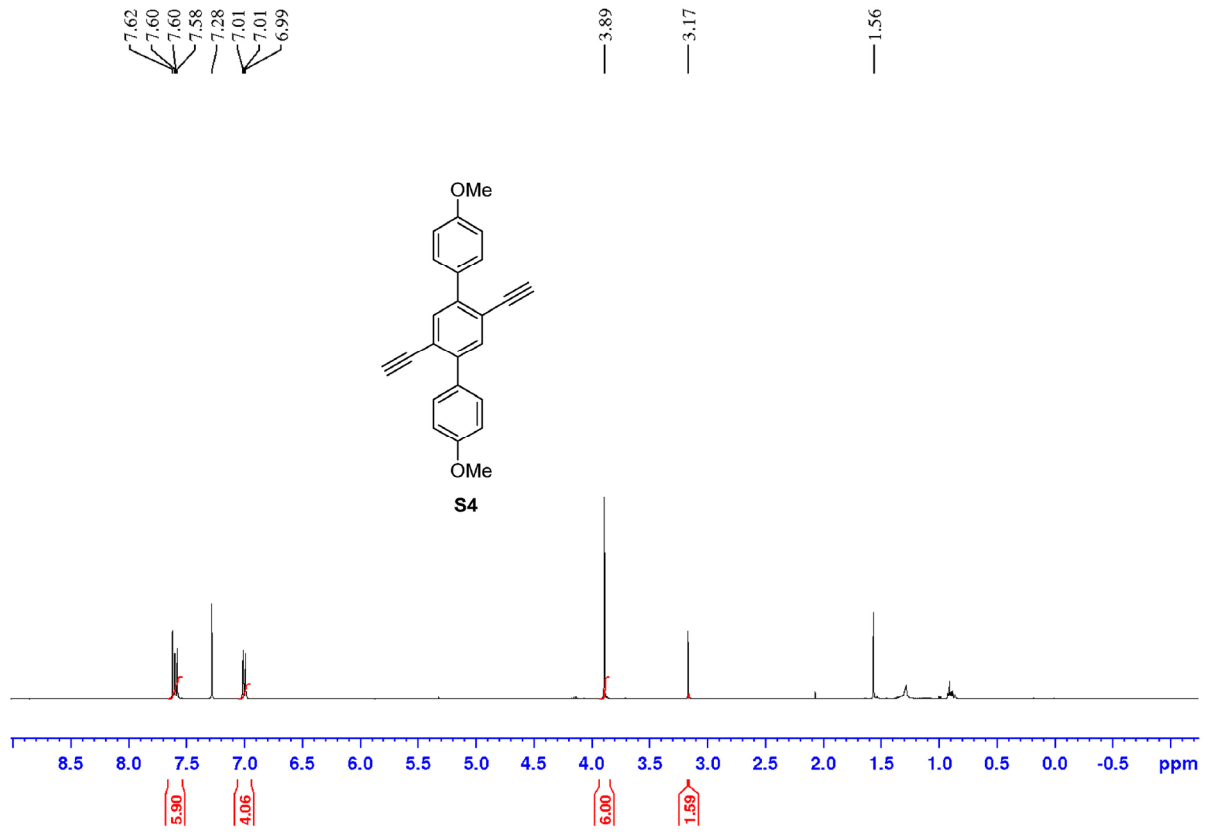


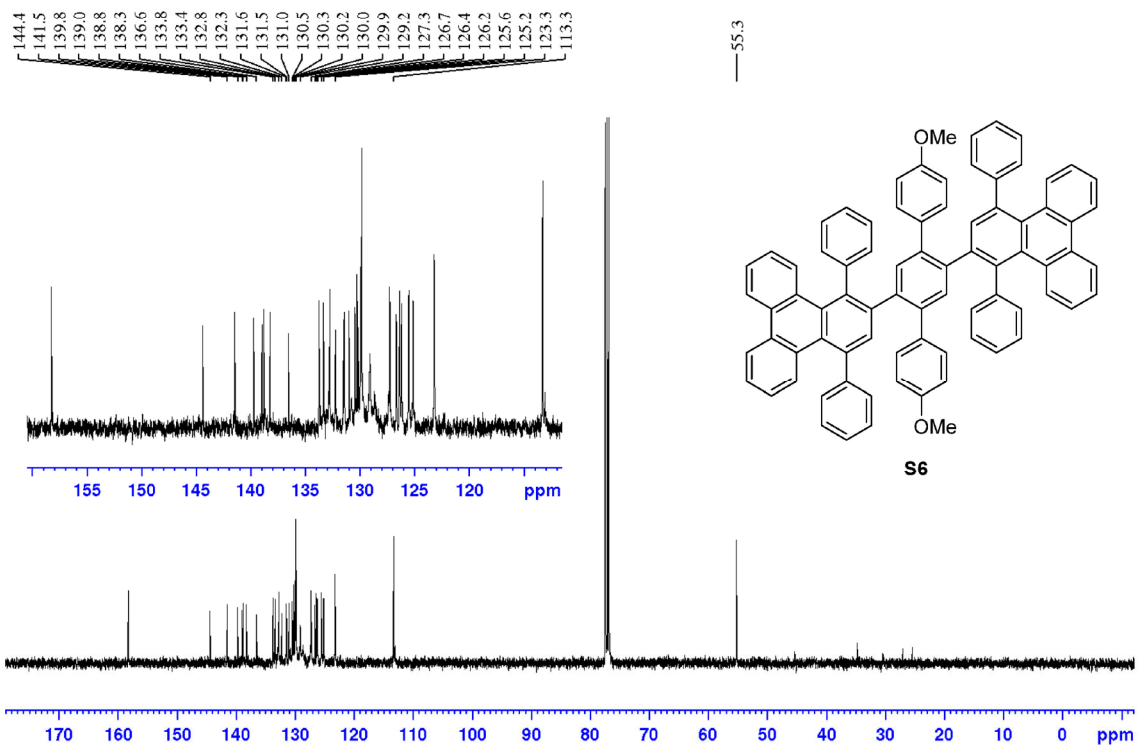
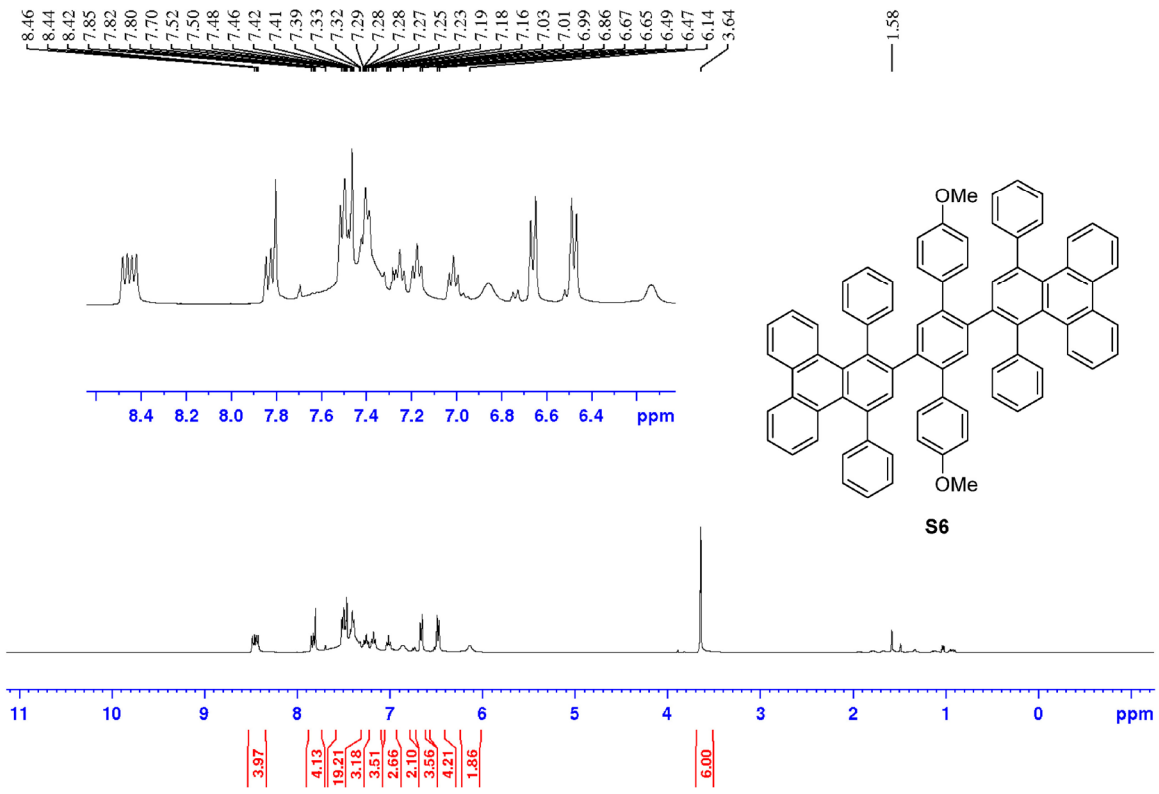
$^1\text{H}/^{13}\text{C}$  NMR Spectra

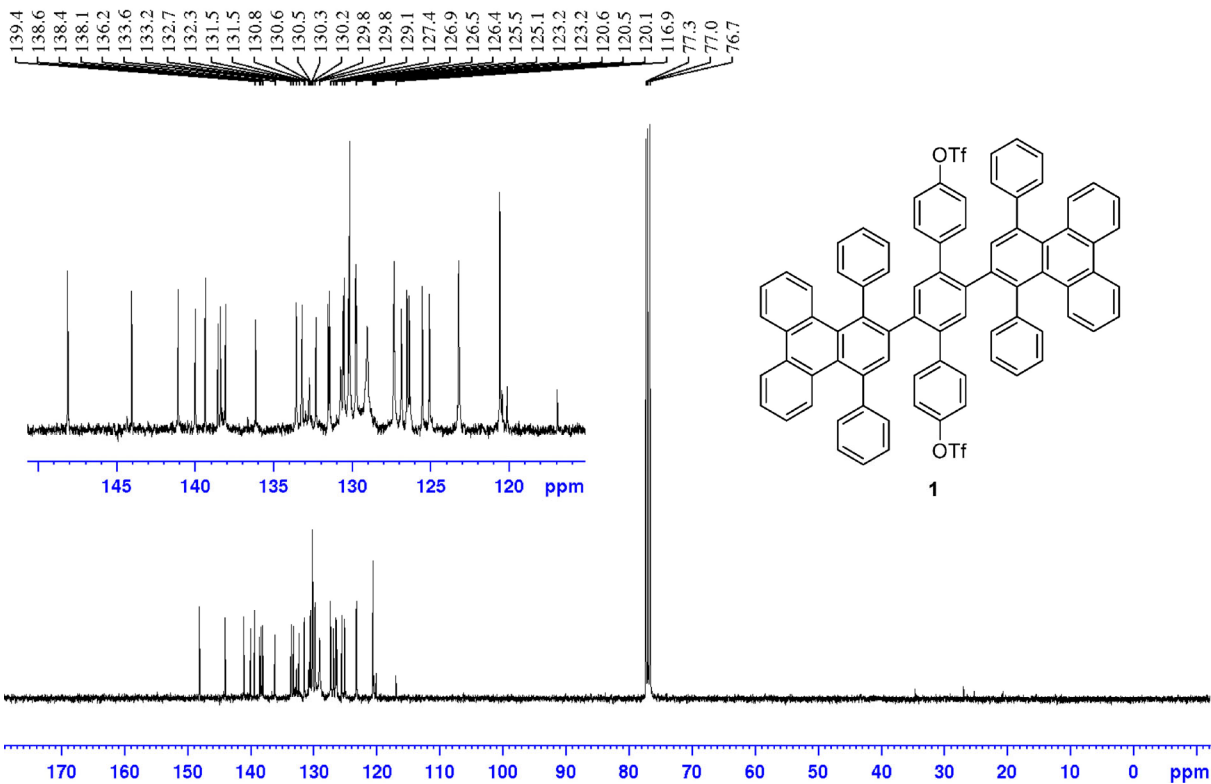
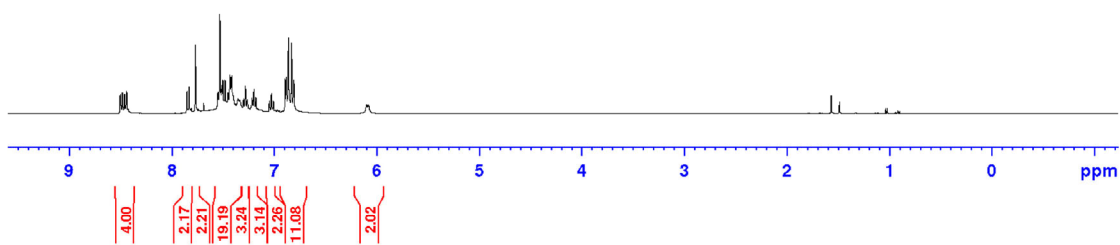
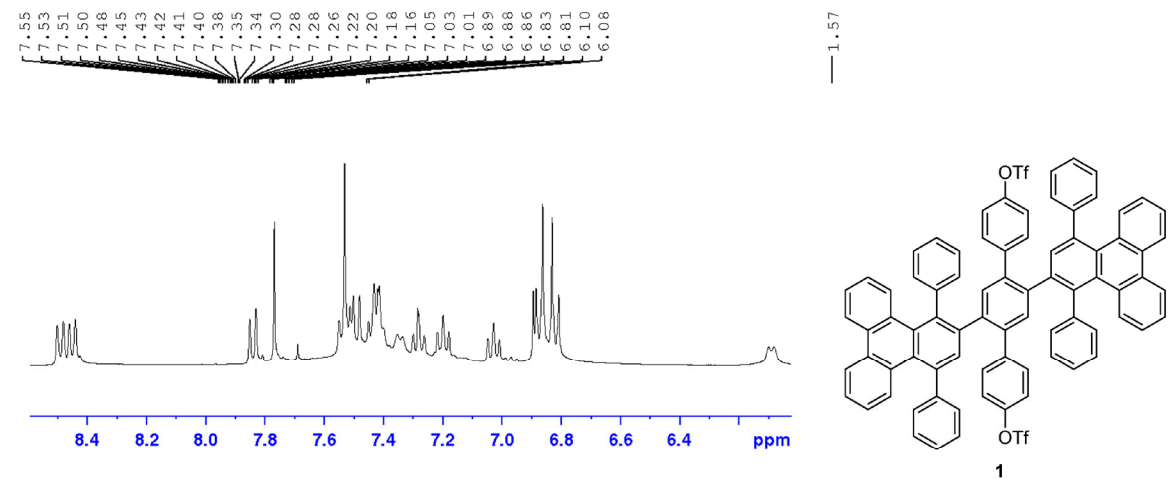


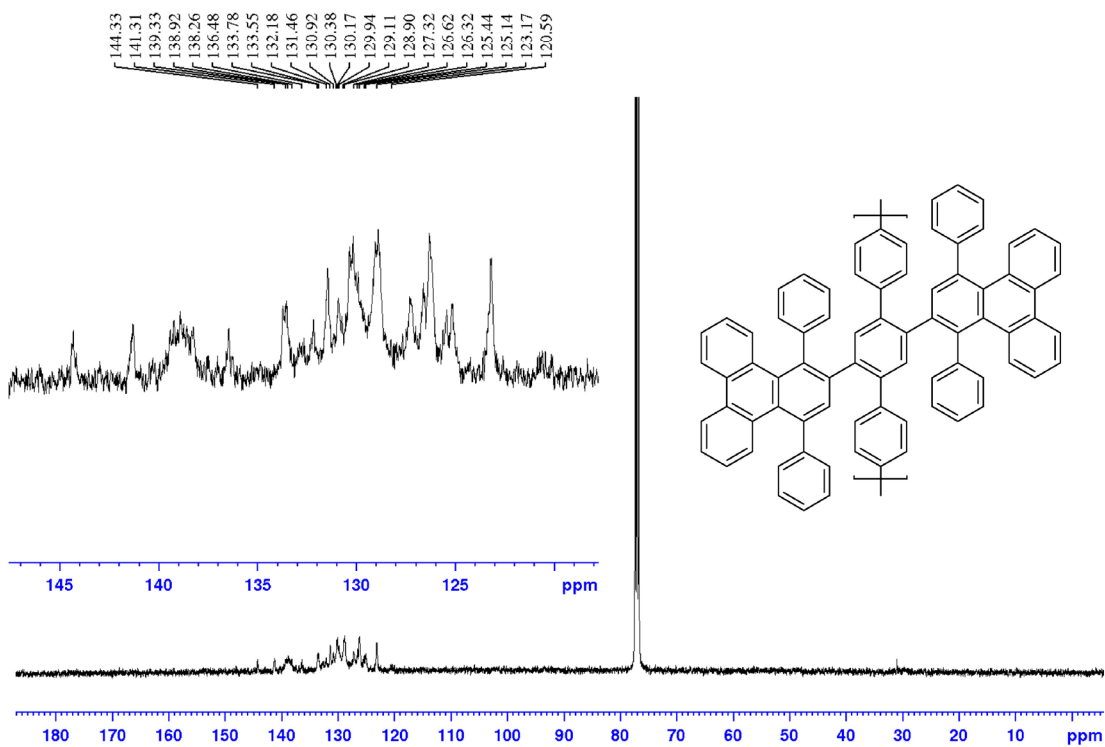
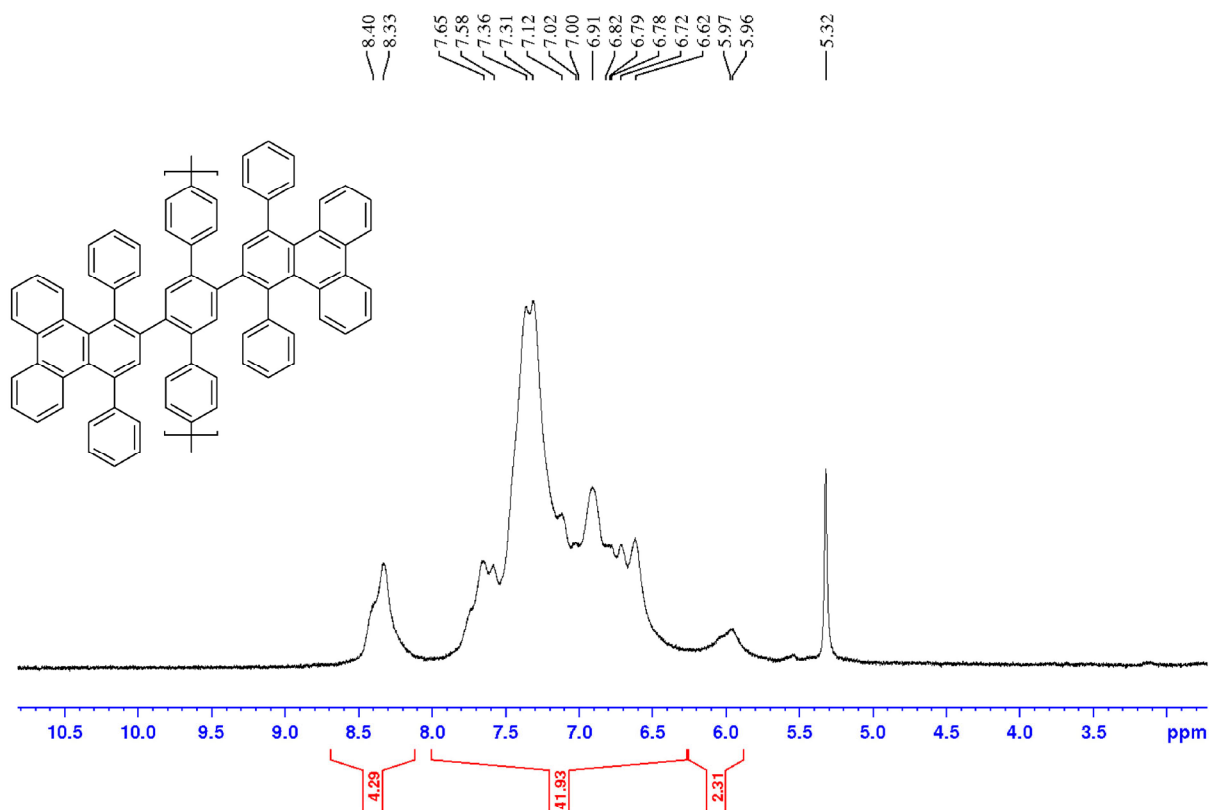


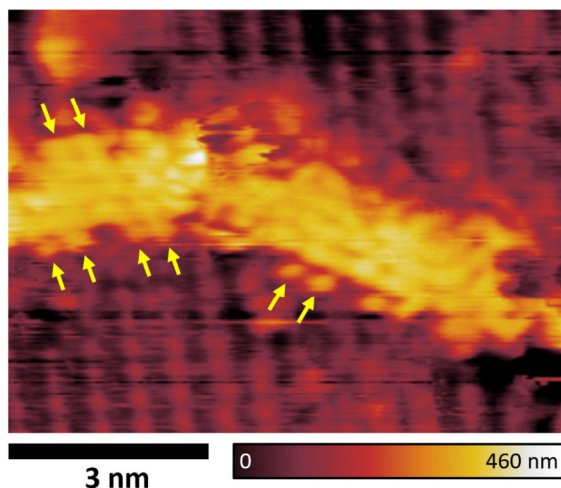




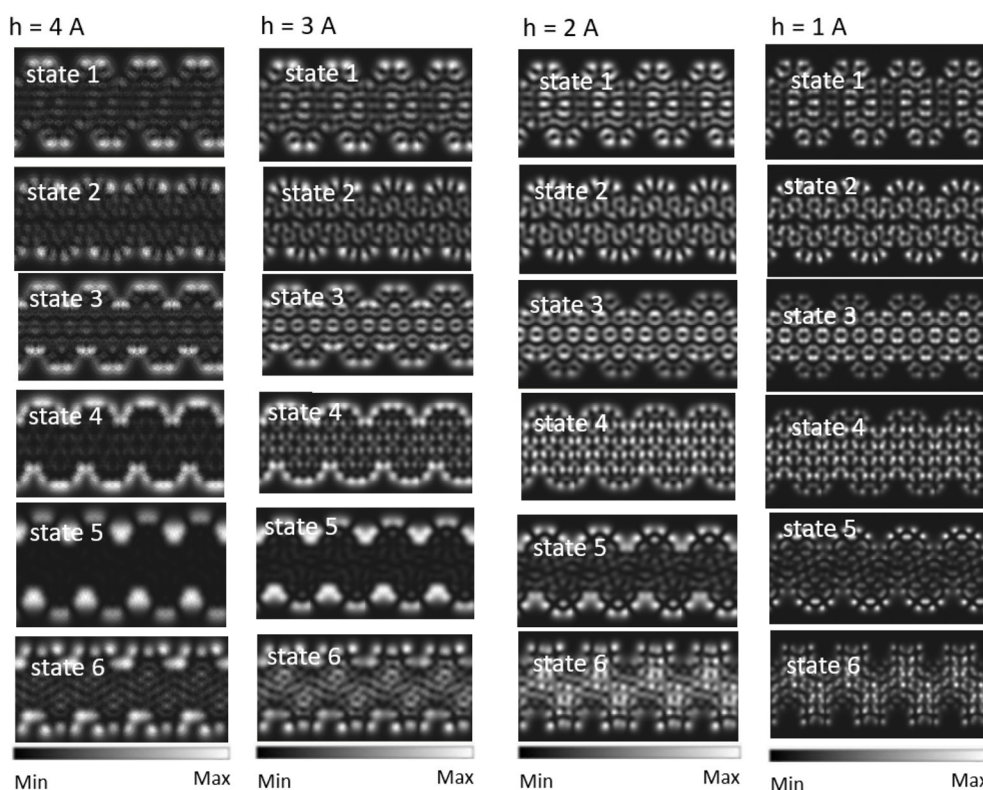




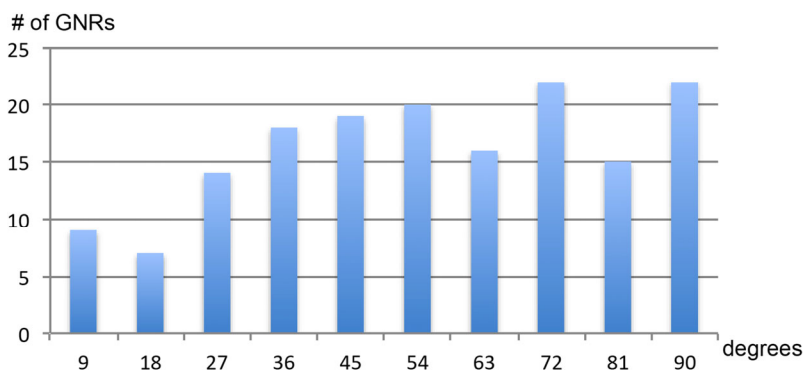




**Figure S5** STM topographic image of a kinked GNR or a pair of touching GNRs on InAs(110) scanned with a sample bias of +2 V and tunneling current of 30 pA. The paired protrusions showed on GNRs' edges by yellow arrows correspond to the two extra benzene rings at each elbow of a ribbon.

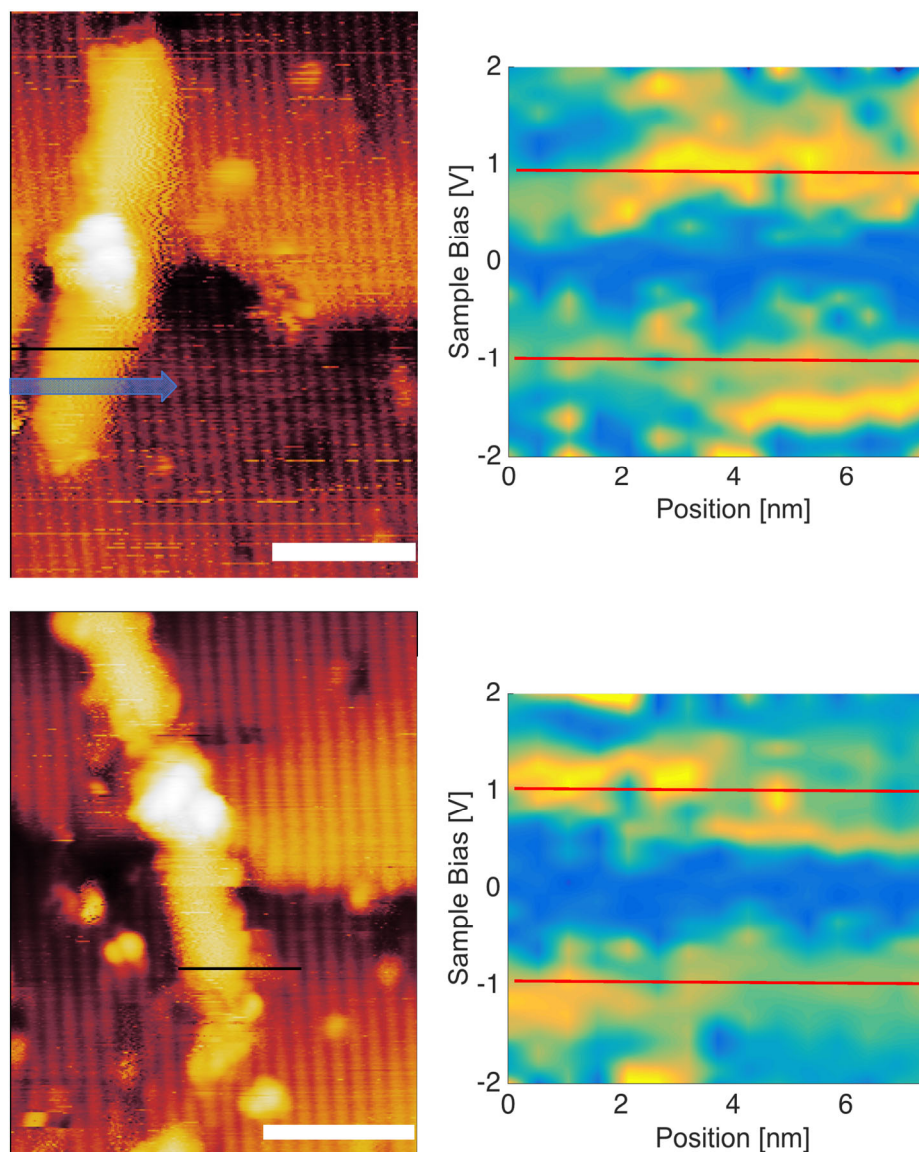


**Figure S6** DFT modeling and spatial mappings of the local density of states of an infinitely long GNR with tip-ribbon distances of 4 Å to 1 Å above the GNR. The closer to the GNR surface, the weaker the edge states' intensity, and stronger the center states' intensity, which indicates a difference in the decay length between the edge and center states.

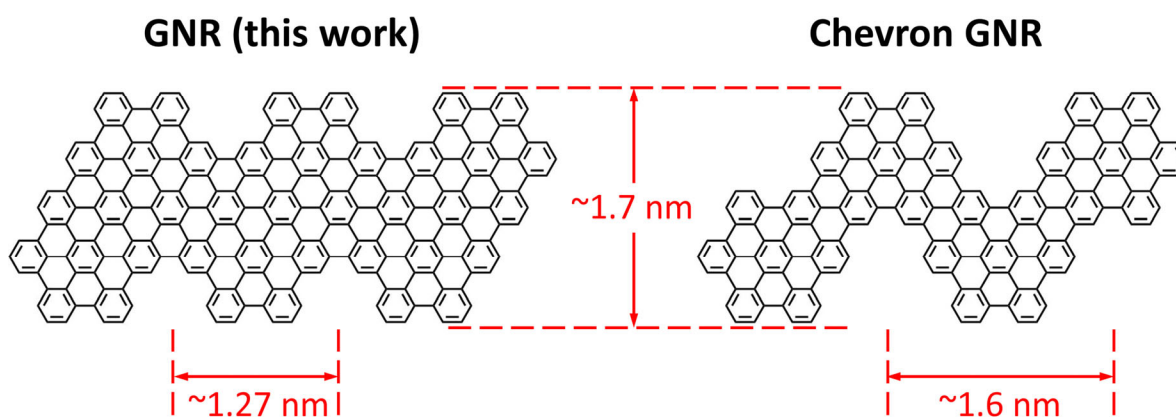


**Figure S7** Histogram showing the number of GNRs observed in STM images versus their orientations relative to InAs(110) substrate: 0 degrees represents the GNRs longitudinal axis parallel to the As dimer row direction and 90 degrees represents the perpendicular case.





**Figure S8** An example of a GNR that was pushed by the STM tip (in the direction indicated by the arrow) with the corresponding STS spectra taken across the GNR (black lines), both before and after the manipulation. After the ribbon rotation, there was no significant change in the  $dI/dV$  map.



**Scheme S2** Comparison of the GNR synthesized in this work and the chevron GNR. The ribbons have the same widths of about 1.7 nm measured across the GNR longitudinal axis, but different periodicities. The GNR synthesized in this work also has less developed concave regions along the edges compared to the chevron GNR.

### Supporting Reference

- [1] Clevenger, R. G.; Kumar, B.; Menuey, E. M.; Lee, G.-H.; Patterson, D.; Kilway, K. V. A superior synthesis of longitudinally twisted acenes. *Chemistry – A European Journal* **2018**, *24*, 243-250.