Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Information

Band Structure Modulation by Methoxy-Functionalization of Graphene Nanoribbons

by

Alicia Götz,[a,b,c,#] Xiao-Ye Wang,[a,d,#] Alice Ruini,[e,f] Wenhao Zheng,[a] Paniz Soltani,[a] Robert Graf,[a] Alexander Tries,[a] Juan Li,[g] Carlos-Andres Palma,[g] Elisa Molinari,[e,f] Michael Ryan Hansen,[h] Hai I. Wang,[a,*] Deborah Prezzi,[f,*] Klaus Müllen,[a,b,*] and Akimitsu Narita[a,c,*]

[a]Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

[b]Department of Chemistry, Johannes Gutenberg University Mainz, Duesbergweg 10-14, 55128 Mainz, Germany

[c]Organic and Carbon Nanomaterials Unit, Okinawa Institute of Science and Technology Graduate University, 1919-1 Tancha, Onna-son, Okinawa 904-0495, Japan

[d]State Key Laboratory of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China

[e]Dipartimento di Scienze Fisiche, Informatiche e Matematiche, Università di Modena e Reggio Emilia, 41125 Modena, Italy

[f]Istituto Nanoscienze, CNR, via G. Campi 213/a, 41125, Modena, Italy

[g]Institute of Physics, Chinese Academy of Sciences, 100190, Beijing, China

[h]Institute of Physical Chemistry, Westfälische Wilhelms-Universität Münster, Corrensstr. 28/30, 48149 Münster, Germany

*Address correspondence to wanghai@mpip-mainz.mpg.de; deborah.prezzi@nano.cnr.it; muellen@mpip-mainz.mpg.de; narita@mpip-mainz.mpg.de

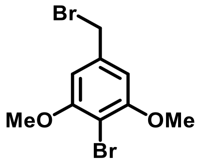
Table of Contents

1. General methods and materials

All chemicals were purchased from commercial sources and used without further purification unless otherwise stated. All reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under argon. Preparative column chromatography was performed on silica gel from Macherey Nagel with a grain size of 0.063–0.200 mm or 0.04–0.063 mm. Analytical thin layer chromatography (TLC) was performed on silica gel coated substrates Alugram Sil G/UV$_{254}$. Solution NMR spectra were measured on Bruker AVANCE 300 MHz and 500 MHz spectrometers, and referenced to residual signals of the deuterated solvent. Abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet. High resolution mass spectrometry (HRMS) was taken on a SYNAPT G2 Si high resolution time-of-flight (TOF) mass spectrometer (Waters Corp., Manchester, UK) by matrix-assisted laser desorption/ionization (MALDI). MALDI-TOF MS analysis of polyphenylene precursor **8** was performed on a SYNAPT G2 Si high resolution time-of flight (TOF) mass spectrometer (Waters Corp., Manchester, UK), using trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix. Atmospheric pressure chemical ionization (APCI) MS was recorded with atmospheric pressure solids analysis probe (ASAP) using an Advion expression compact mass spectrometer (CMS). Analytical size exclusion chromatography (SEC) was performed on an SDV PSS GPC columns using tetrahydrofuran (THF) as eluent at a temperature of 303 K. Absorbance was determined on a UV S-3702 detector (SOMA) at a fixed wavelength of 270 nm. The samples were referenced with respect to standard polystyrene (PS) as well as poly(*para*-phenylene) (PPP) calibration curves. UV–vis absorption spectra were recorded at room temperature on a Perkin-Elmer Lambda 900 spectrophotometer. Photoluminescence spectrum was recorded at room temperature on a J&M TIDAS FL3095SL spectrofluorometer. For the spectroscopic measurements, GNR samples were dispersed in tetrahydrofuran (THF) by using sonication (30 min) in a Bandelin Sonorex RK 102 H ultrasonicator followed by filtration through polytetrafluoroethylene (PTFE) syringe filters with 5 µm pores. Infrared spectra were measured on a Nicolet 730 FT-IR spectrometer equipped with an attenuated total reflection (ATR) setup. The solid or powder samples were placed on the diamond crystal and pressed on it with a stamp. Spectra were recorded with a scan number of 128 for each sample and the background was subtracted. The Raman spectrum was measured with a Bruker RFS 100/S Raman spectrometer, which is equipped with several excitation lines in the visible and near-IR range. The melting points were determined on a Büchi hot stage apparatus B-545 and are uncorrected.

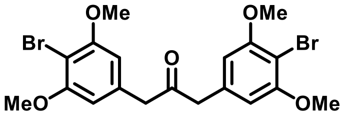
2. Synthetic procedures

2-Bromo-5-(bromomethyl)-1,3-dimethoxybenzene (2)



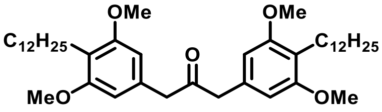
To a solution of 4-bromo-3,5-dimethoxybenzylbromide (**1**) (9.24 g, 40.0 mmol, 1.0 eq) in dichloromethane (250 mL) was added phosphorous tribromide (9.5 mL, 93.0 mmol, 2.3 eq) under stirring. After stirring overnight at room temperature, the reaction was quenched with a saturated aqueous solution of sodium bicarbonate and extracted three times with dichloromethane. The combined organic layers were dried over magnesium sulphate, and concentrated *in vacuo*. Purification by silica gel column chromatography (eluent: 50% dichloromethane/hexane) yielded the title compound as colorless crystals (12.4 g, 84%): Mp: 84.0-84.4°C, ^{1}H NMR (300 MHz, DMSO-d_6) $\delta = 6.00$ (s, 2H), 3.82 (s, 2H), 2.98 (s, 6H), ^{13}C NMR (75 MHz, CD_2Cl_2) $\delta = 157.41, 138.74, 105.63, 101.03, 56.68, 33.70$; HRMS (MALDI-TOF, positive) *m/z*: Calcd for $C_9H_{10}Br_2O_2$ 307.9048; Found 307.9034 $[M]^+$.

1,3-Bis(4-Bromo-3,5-dimethoxyphenyl)propane-2-one (3)



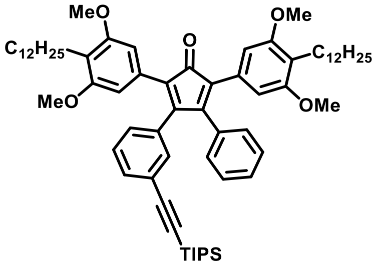
2-Bromo-5-(bromomethyl)-1,3-dimethoxybenzene (**2**) (2.0 g, 6.4 mmol, 1.0 eq) and *N*-benzyl-*N*,*N*-triethylammonium chloride (44.1 mg, 0.193 mmol, 0.03 eq) were dissolved in dry dichloromethane (10 mL). Sodium hydroxide (1.11 g, 27.7 mmol, 4.3 eq) was dissolved in 1 mL of water and added to the mixture. After degassing, the solution was heated to 40 °C, and then iron pentacarbonyl (669 mg, 3.42 mmol, 0.53 eq) was added slowly over 5 min. After stirring overnight, the residues of sodium hydroxide were neutralized by 2 M HCl, and the reaction mixture was extracted with dichloromethane. The combined organic layers were washed with water three times and dried over sodium sulphate. After evaporation of the solvent, the purification by silica gel column chromatography (eluent: 30% dichloromethane/hexane) gave the title compound as a colorless solid (300 mg, 23%): Mp >165 °C (decomposition): ^{1}H NMR (300 MHz, CD_2Cl_2) $\delta = 6.34$ (s, 4H), 3.83 (s, 12H), 3.72 (s, 4H), ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 204.42, 156.93, 133.99, 105.74, 56.18, 49.17$; HRMS (MALDI-TOF, positive) *m/z*: Calcd for $C_{19}H_{20}Br_2O_5$ 485.9677; Found: 485.9677 $[M]^+$.

1,3-Bis(4-Dodecyl-3,5-dimethoxyphenyl)propane-2-one (4)



9-Borabicyclo[3.3.1]nonane (9-BBN, 0.5 M in THF, 6.1 mL 3.1 mmol, 3 eq) and 1-dodecene (515 mg, 3.06 mmol, 3 eq) were dissolved in THF (5 mL). The solution was degassed for 30 min and stirred overnight. 1,3-Bis(4-bromo-3,5-dimethoxyphenyl)propan-2-one (**3**) (498 mg, 1.02 mmol, 1 eq), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (Sphos, 20.9 mg, 0.051 mmol, 5 mol%) and palladium(II) acetate (11.5 mg, 0.051 mmol, 5 mol%) were dissolved in degassed THF (25 mL), and potassium phosphate (866 mg, 4.08 mmol, 4 eq) in water (2 mL) was added. The reaction mixture was degassed, and then the separately prepared solution of alkyl borane was added. After stirring at 80 °C for 21 hours, the mixture was extracted with dichloromethane. The combined organic layers were dried over sodium sulphate and evaporated. Purification by silica gel column chromatography (eluent: 10% ethyl acetate/hexane) yielded the title compound as a colorless solid (600 mg, 90%): ^{1}H NMR (300 MHz, CD_2Cl_2) δ = 6.29 (s, 4H), 3.74 (s, 12H), 3.67 (s, 4H), 2.56 (t, J = 7.5 Hz, 4H), 1.47 - 1.18 (m, 40H), 0.88 (t, J = 6.9 Hz, 6H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ = 206.01, 158.82, 133.01, 118.32 105.49, 55.96, 49.37, 29.70, 23.08, 14.25; HRMS (MALDI-TOF, positive) *m/z*: Calcd for $C_{43}H_{70}O_5$ 666.5223; Found 666.5226 $[M]^+$.

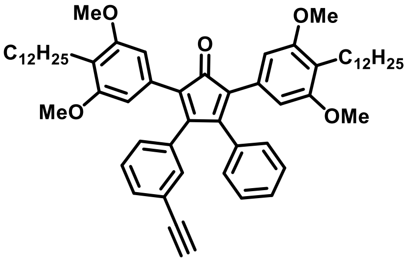
2,5-Bis(4-dodecyl-3,5-dimethoxyphenyl)-3-phenyl-4-{3-(triisopropylsilylethynyl) phenyl}cyclopenta-2,4-dien-1-one (6)



To a degassed solution of 1,3-bis(4-dodecyl-3,5-dimethoxyphenyl)propane-2-one (**4**) (700.0 mg, 1.05 mmol, 1 eq) and 1-phenyl-2-{3-(triisopropylsilylethinyl)phenyl}ethan-1,2-dione (**S5**)[1] (809 mg, 1.11 mmol, 1.06 eq) in *tert*-butanol was added a solution of tetrabutylammonium hydroxide in methanol (40%, 55 mg, 0.21 mmol, 0.2 eq). After stirring at 80 °C for 40 min, the reaction was quenched by the addition of 2 M hydrochloric acid, and the mixture was extracted three times with dichloromethane. The combined organic layers were washed three times with brine, dried over sodium sulphate, and evaporated. Purification by silica gel column chromatography (eluent: 25% dichloromethane/hexane) gave the title compound as a purple sticky oil. (514 mg, 72%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.32 (d, J = 7.6

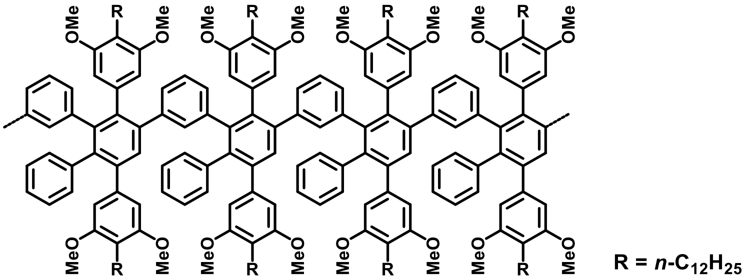
Hz, 1H), 7.27 – 7.21 (m, 3H), 7.18 – 7.12 (m, 2H), 7.05 – 7.01 (m, 2H), 7.0 (d, *J* = 7.7 Hz, 1H), 6.48 (s, 2H), 6.47 (s, 2H), 3.59 (s, 6H), 3.54 (s, 6H), 2.58 - 2.50 (m, 4H), 1.32 - 1.22 (m, 40H), 1.12 (s, 18H), 0.91 (t, *J* = 6.7 Hz, 9H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ = 200.93, 158.16, 158.04, 154.73, 153.38, 134.09, 133.78,131.81, 130.20, 129.57, 129.42, 128.80, 128.55, 125.81, 106.73, 106.19, 106.13, 91.75, 55.82, 32.30, 32.09, 29.73, 23.06, 18.73, 14.27, 11.61; HRMS (MALDI-TOF, positive) *m*/*z*: Calcd for $C_{68}H_{96}O_5Si$ 1020.7027; Found 1020.7013 [M]$^+$.

2,5-Bis(4-dodecyl-3,5-dimethoxyphenyl)-3-(3-ethynylphenyl)-4-phenylcyclopenta-2,4-dien-1-one (7)



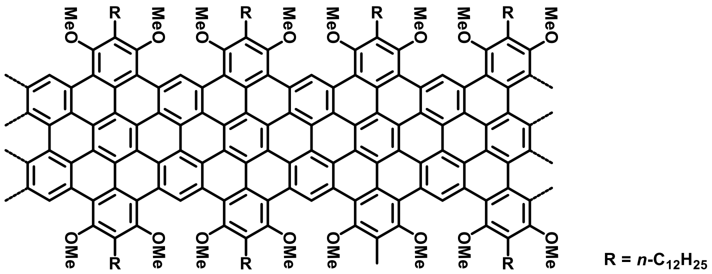
To a solution of 2,5-bis(4-dodecyl-3,5-dimethoxyphenyl)-3-phenyl-4-{3-(triisopropylsilyl ethynyl)phenyl}cyclopenta-2,4-dien-1-one (**6**) (266 mg, 0.26 mmol, 1.0 eq) in dichloromethane (15 mL) a solution of tetra-*n*-butylammonium fluoride (1 M, 0.27 mL, 0.27 mmol, 1.1 eq) was added dropwise. After stirring at room temperature for 20 min, water was added to the reaction mixture. The suspension was extracted three times with dichloromethane. The combined organic layers were dried over magnesium sulphate and the product was purified by silica gel column chromatography (eluent: 25% dichlormethane/hexane) to give the title compound as purple oil (200 mg, 93%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ = 7.40 (d, *J* = 7.8 Hz, 1H), 7.33 – 7.14 (m, 3H), 7.12 – 6.93 (m, 5H), 6.48 (s, 4H), 3.59 (s, 6H), 3.56 (s, 6H), 3.09 (s, 1H), 2.64 – 2.51 (m, 4H), 1.38 – 1.20 (m, 40H), 0.92 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ = 200.85, 158.17, 154.60, 153.37, 132.94, 132.19, 129.19, 128.57, 125.79, 106.18, 77.96, 55.79, 32.31, 30.10, 30.04, 23.19, 14.25; APCI-MS *m*/*z*: Calcd for $C_{59}H_{76}O_5$ 864.57, Found 864.59 [M]$^+$.

Polyphenylene precursor 8



A degassed solution of monomer **7** (140 mg, 0.5 mM) in diphenyl ether (0.28 mL) was refluxed for 36 h using a heating mantle. The completion of the reaction was indicated by the disappearance of the purple color of **7**, turning to pale yellow. After cooling down to room temperature, methanol was added to precipitate the crude polymer, which was collected by filtration with a membrane filter. The crude polymer was fractionated by preparative SEC (Japan Analytical Industry JAIGEL-1H+2H, eluent: chloroform, 3.0 mL/min) to remove small-molecular-weight oligomers, affording polyphenylene precursor **8** as a pale yellow solid (123 mg, 90%). FTIR (powder): 2921, 2851, 1604, 1577, 1455, 1405, 1233, 1186, 1132, 914, 895, 833, 793, 699, 647 cm^{-1}

GNR-OMe 9



Polyphenylene precursor **8** (20.0 mg, 24 µmol) was dissolved in unstabilized dichloromethane (125 mL) and degassed by argon bubbling for 15 min. A suspension of iron(III) chloride (325 mg, 202 µmol, 7 eq for one hydrogen) in nitromethane (2 mL) was then added. After stirring at room temperature for 42 h under continuous bubbling with argon presaturated with dichloromethane, the reaction was quenched by addition of methanol to form bluish black precipitates. The precipitates were collected by filtration with a membrane filter, washed with methanol and tetrahydrofuran, and then sonicated for 30 min in tetrahydrofuran (50 mL). This process was repeated again to give GNR-OMe **9** (17.6 mg, 97%). FTIR (powder): 2918, 2848, 1594, 1,530, 1450, 1331, 1271, 1118, 1043, 995, 855, 719 cm^{-1}; Raman (powder, 532 nm): 1313, 1589, 2647, 2899, 3169 cm^{-1}.

3. First principles simulations

	m^*_{v2}	m^*_{v1}	m^*_{c1}	m^*_{c2}
GNR-H	-0.539	-0.279	+0.317	+1.963
GNR-OMe	-0.535	-0.257	+0.2713	+0.792

Table S1. DFT effective masses of charge carriers for the frontier bands.

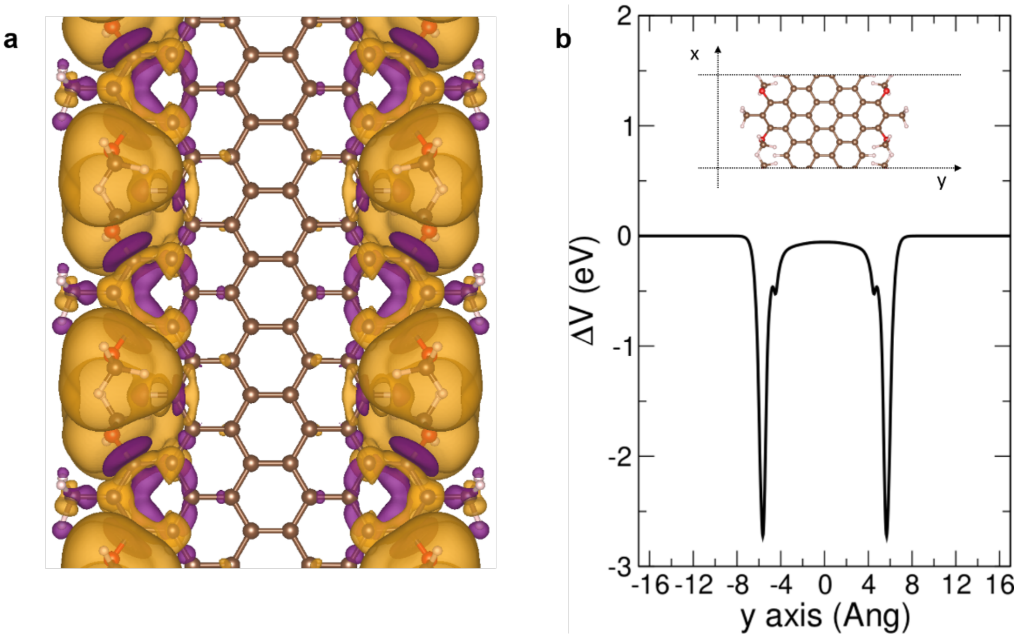


Figure S1. (a) Differential charge density $\Delta\rho = \rho_{OMe} - \rho_H$, with positive and negative contributions in orange and violet, respectively; isosurface value set to 0.001. (b) Electrostatic potential variation $\Delta V - V_{OMe} - V_H$ along the GNR width (y axis), after averaging along x and z. Both panels clearly show that the charge redistribution is strongly localized at the edges.

4. SEC and MALDI-TOF analysis

Linear-mode MALDI-TOF MS analyses of polyphenylene precursor **8** before the fractionation by SEC showed a regular mass pattern up to *m*/*z* = ca. 10000 with an interval of 838, which agreed with the molecular weight of one repeating unit of approximately 837 (Figure S2). It should be noted that the highest *m*/*z* detected in this measurement does not correspond to the largest polymers in the sample, considering the limitation of the MALDI-TOF MS analysis for high-molecular-weight polymers with a broad molecular weight distribution.[2, 3]

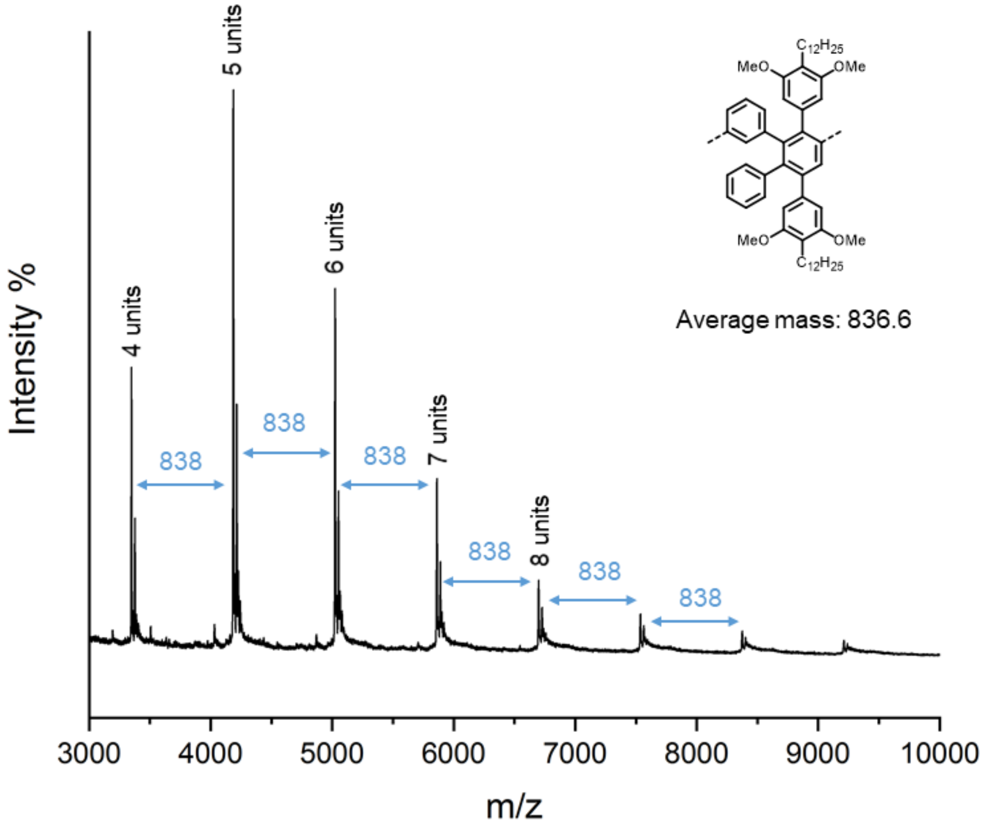


Figure S2. Linear-mode MALDI-TOF MS spectrum of polyphenylene precursor **8** (matrix: DCTB).

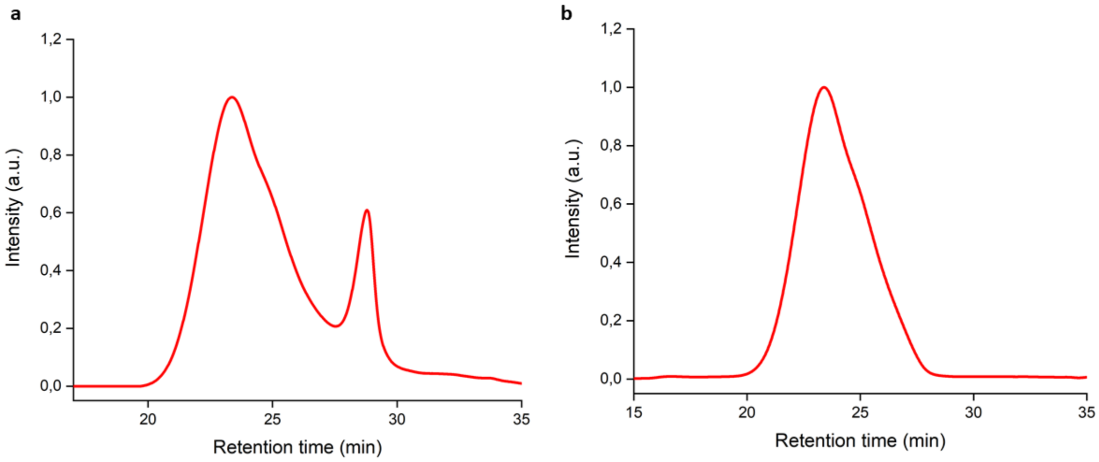


Figure S3. Normalized SEC profiles of polyphenylene precursor **8** (eluent: THF, 1.0 mL/min, UV detector) **a**, before and **b**, after the fractionation by the preparative SEC.

5. FT-IR and Raman spectra

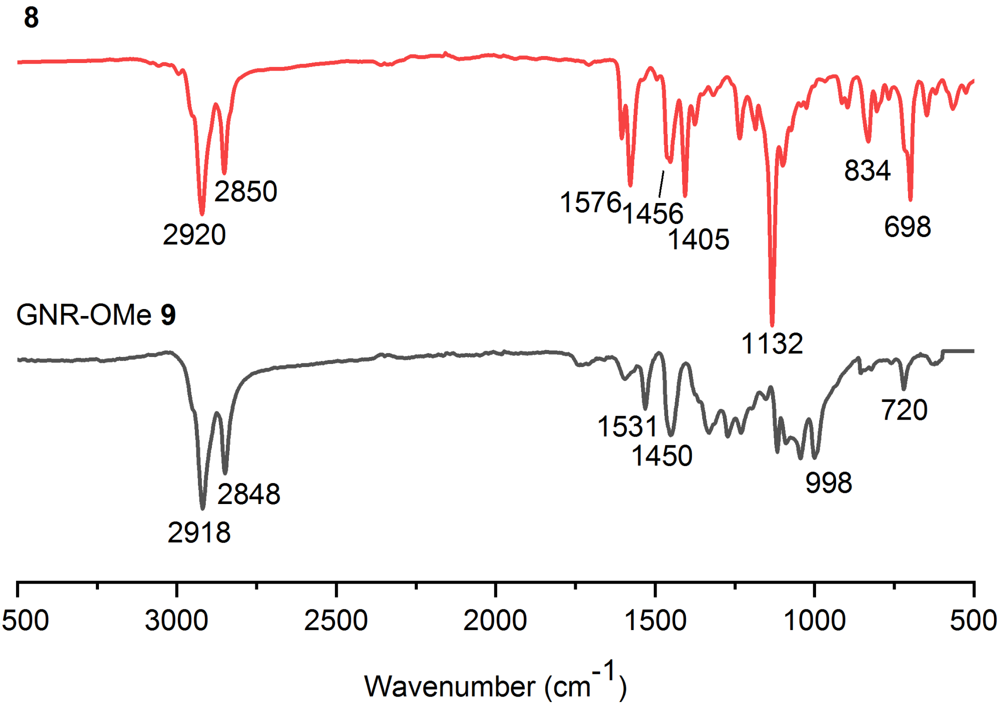


Figure S4. FT-IR spectra of polyphenylene precursor **8** and GNR-OMe **9**.

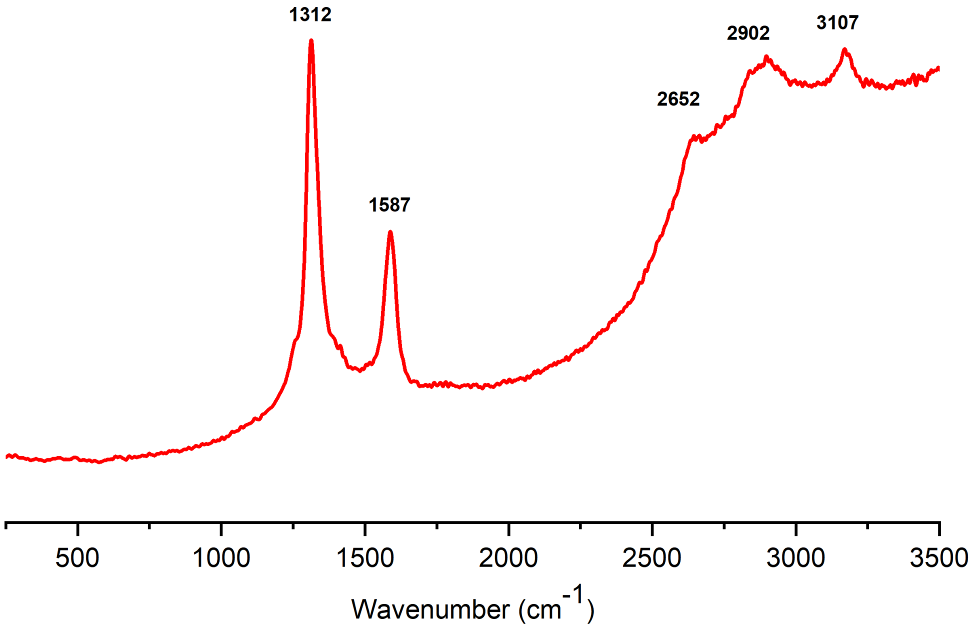


Figure S5. Raman spectrum of GNR-OMe **9** measured with laser power below 0.1 mW (powder, 532 nm).

6. Scanning tunneling microscopy

Au(111) on mica was purchased from Georg Albert PVD (Silz, Germany), Ar sputtered for 30 min and annealed to 400 °C for 5 min. A speckle of molecular powder was added to 1,2,4-trichlorobenzene (Sigma-Aldrich) followed by 3 hours ultrasonic treatment. The freshly sputtered annealed Au(111) surface was submerged in the dispersion for 10 to 30 s, and then in electronic grade isopropanol (Sigma-Aldrich) and blown dry with nitrogen. The sample was immediately measured with a Brucker MultiMode© scanning tunneling microscope, employing a Pt/Ir or W tip under ambient conditions.

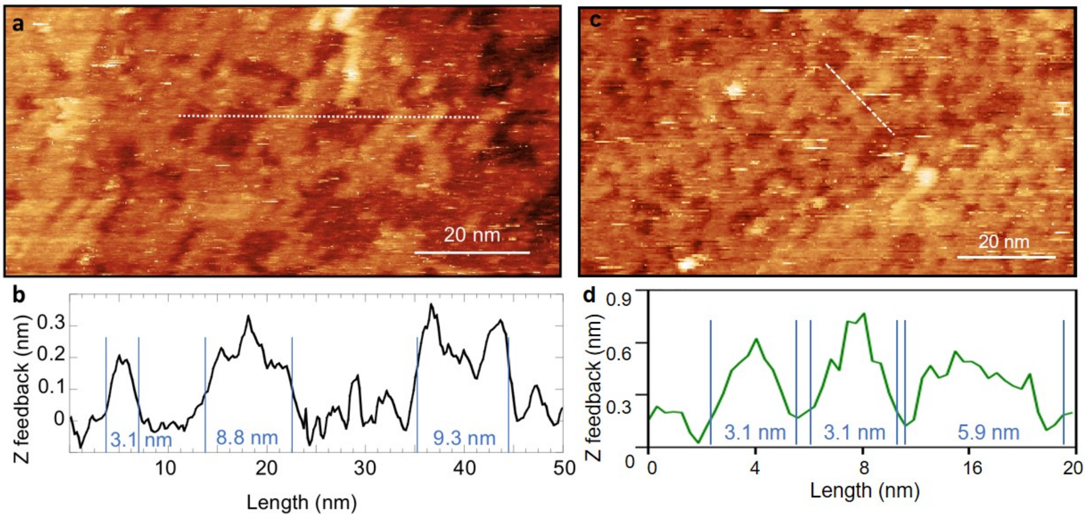


Figure S6. (a,c) Scanning tunnelling microscopy of multilayer self-assembly of GNR-OMe **9** on Au(111) deposited by submersing the substrate in dispersion of **9** in 1,2,4-trichlorobenzene. I_t = 300 pA, V_s = 2 V. (b,d) Height profile of the cross-section in (a) and (c). The average ribbon width is estimated as (3.0±0.1) nm from the eleven elongated structures which appear to align on top of the multilayer.

7. NMR spectroscopic data

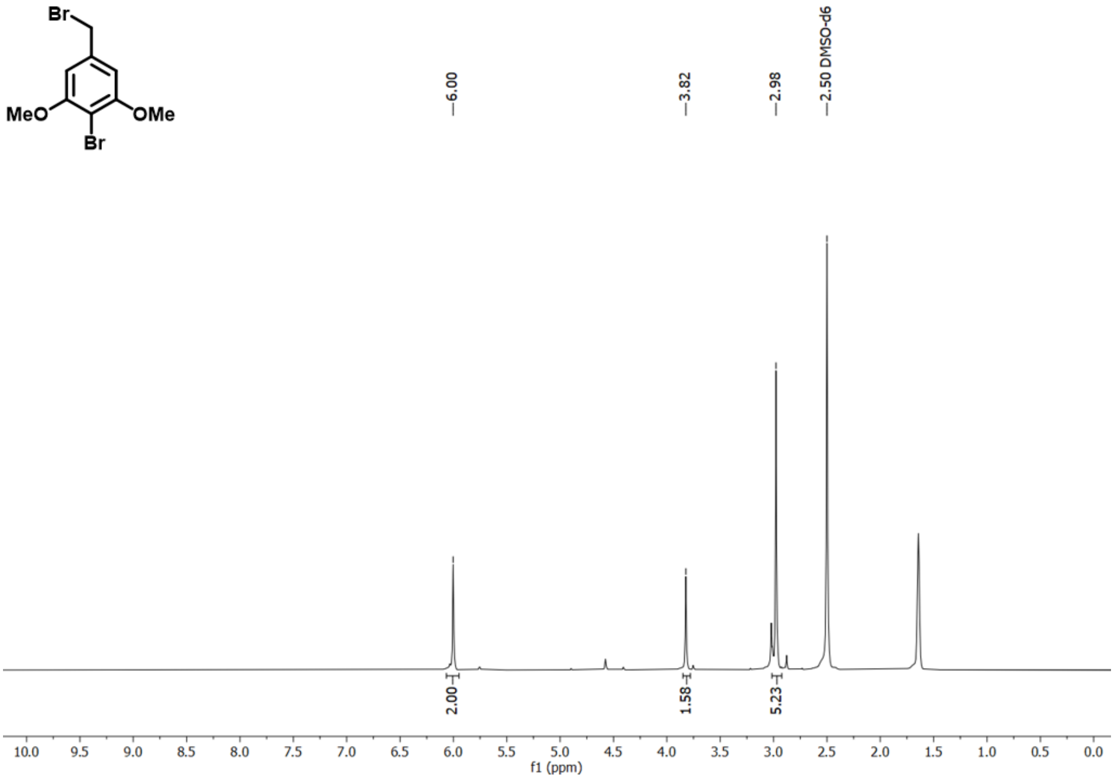


Figure S7. ^{1}H NMR spectrum of compound **2** (300 MHz, DMSO-d_6).

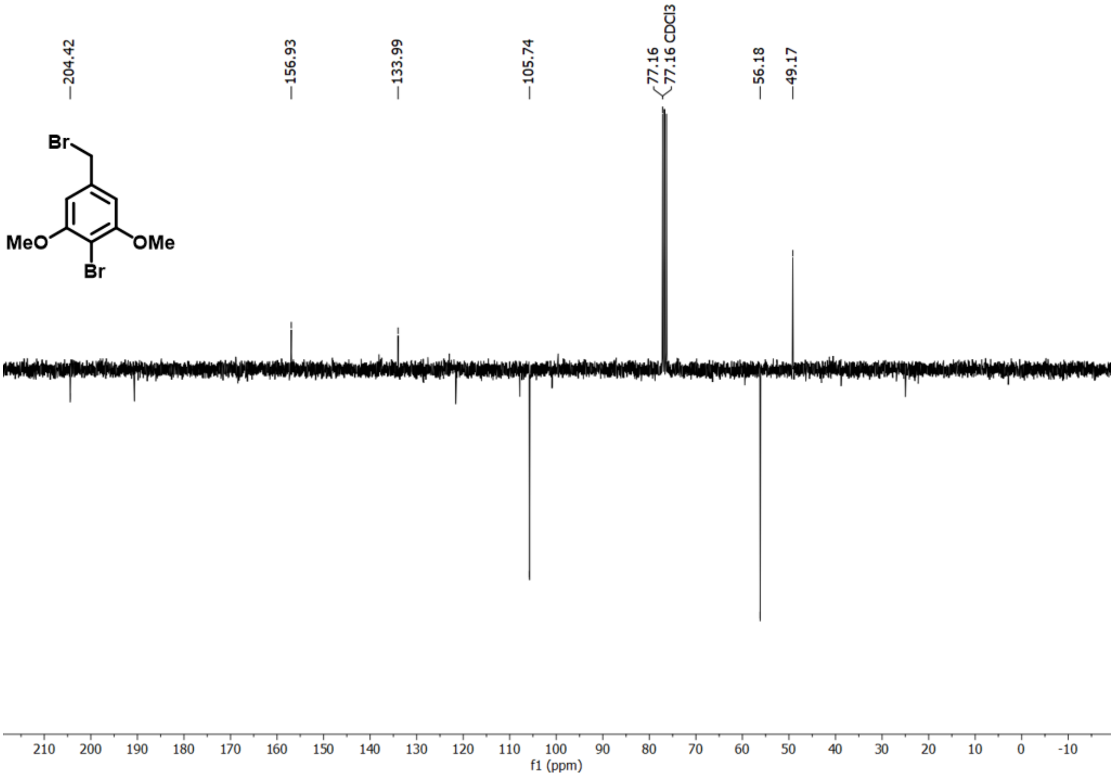


Figure S8. ^{13} C APT NMR spectrum of compound **2** (75 MHz, DMSO-d_6).

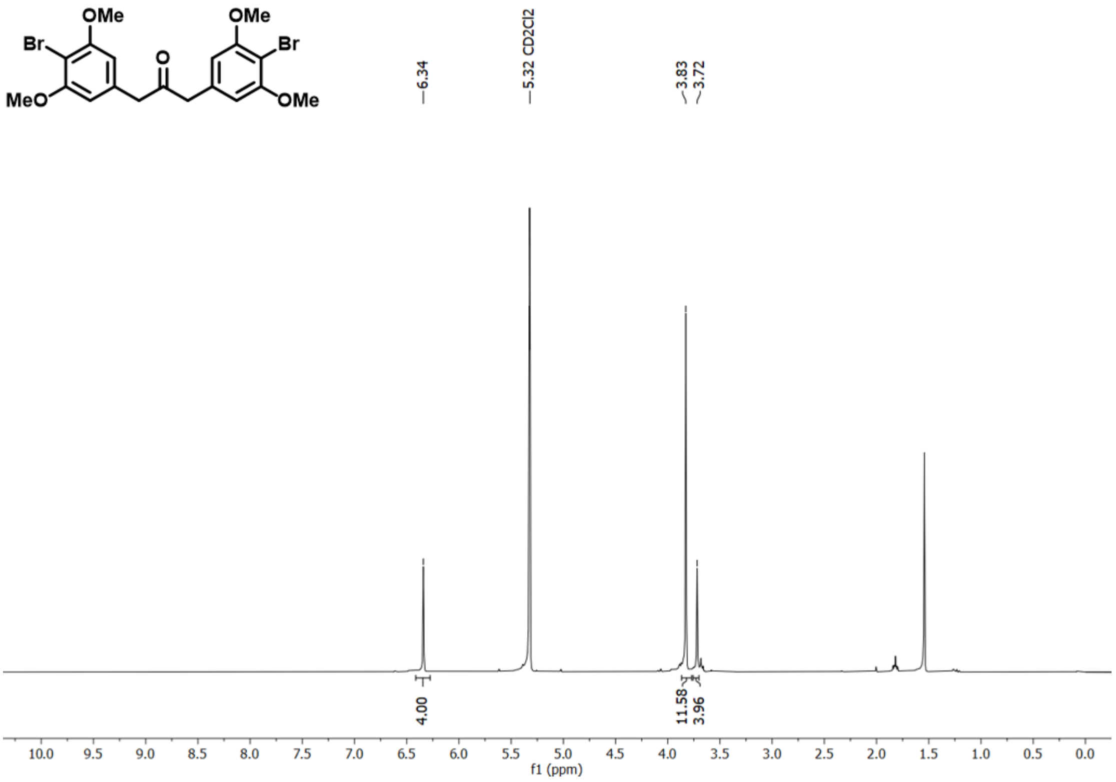


Figure S9. ^{1}H NMR spectrum of compound **3** (300 MHz, CD_2Cl_2).

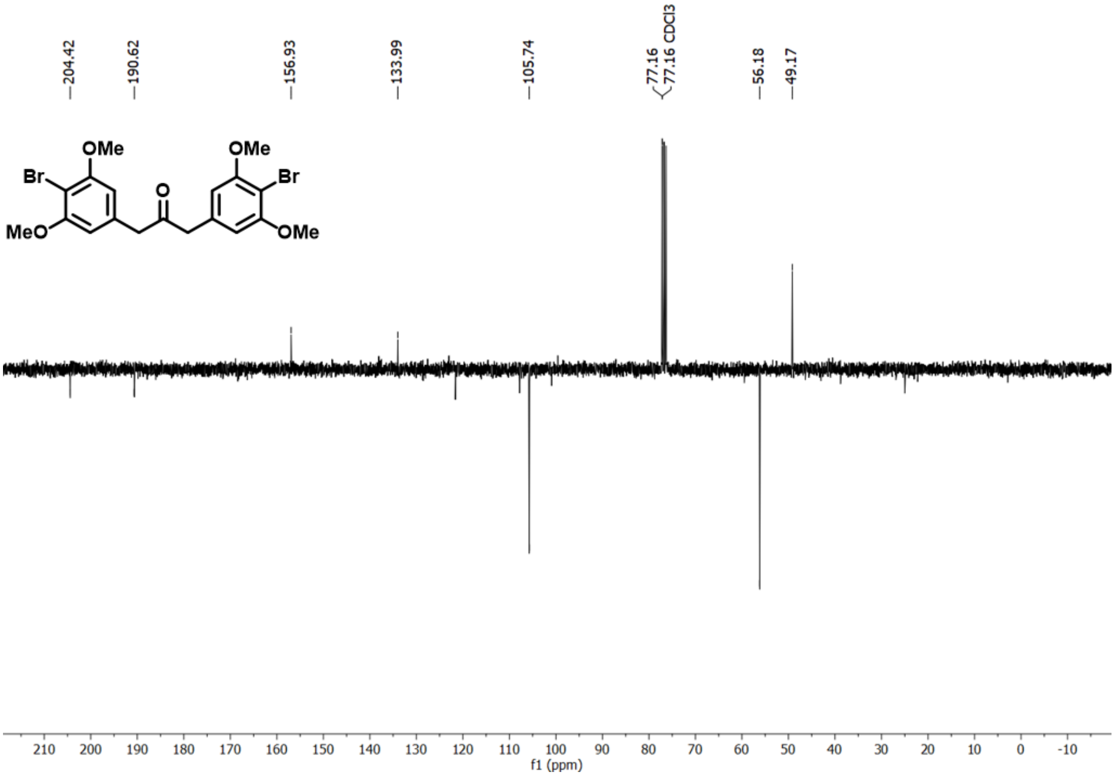


Figure S10. ^{13}C APT NMR spectrum of compound **3** (75 MHz, $CDCl_3$).

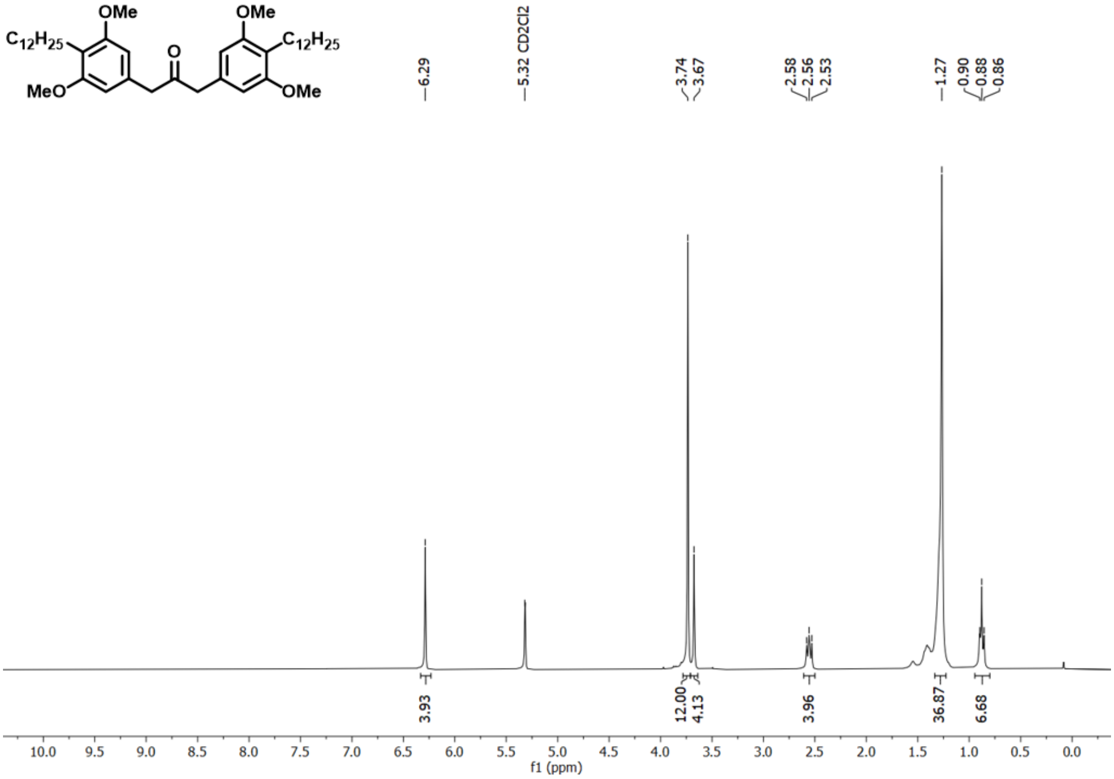


Figure S11. ^{1}H NMR spectrum of compound **4** (300 MHz, CD_2Cl_2).

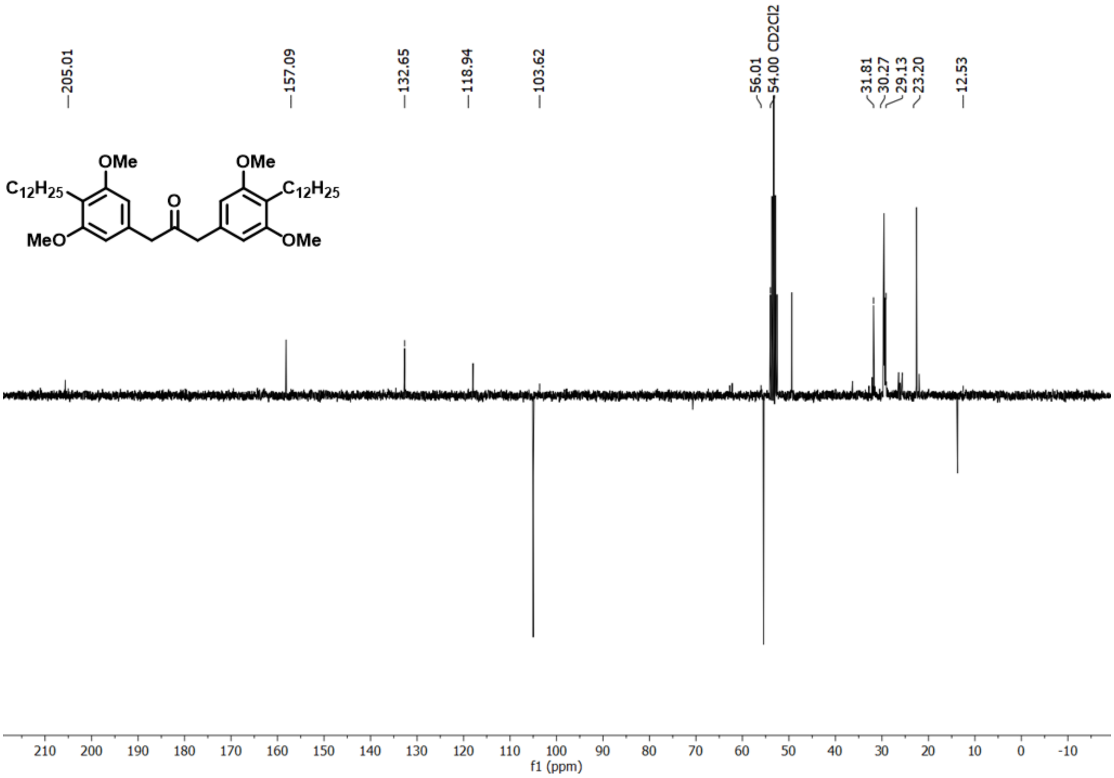


Figure S12. ^{13}C APT NMR spectrum of compound **4** (75 MHz, CD_2Cl_2).

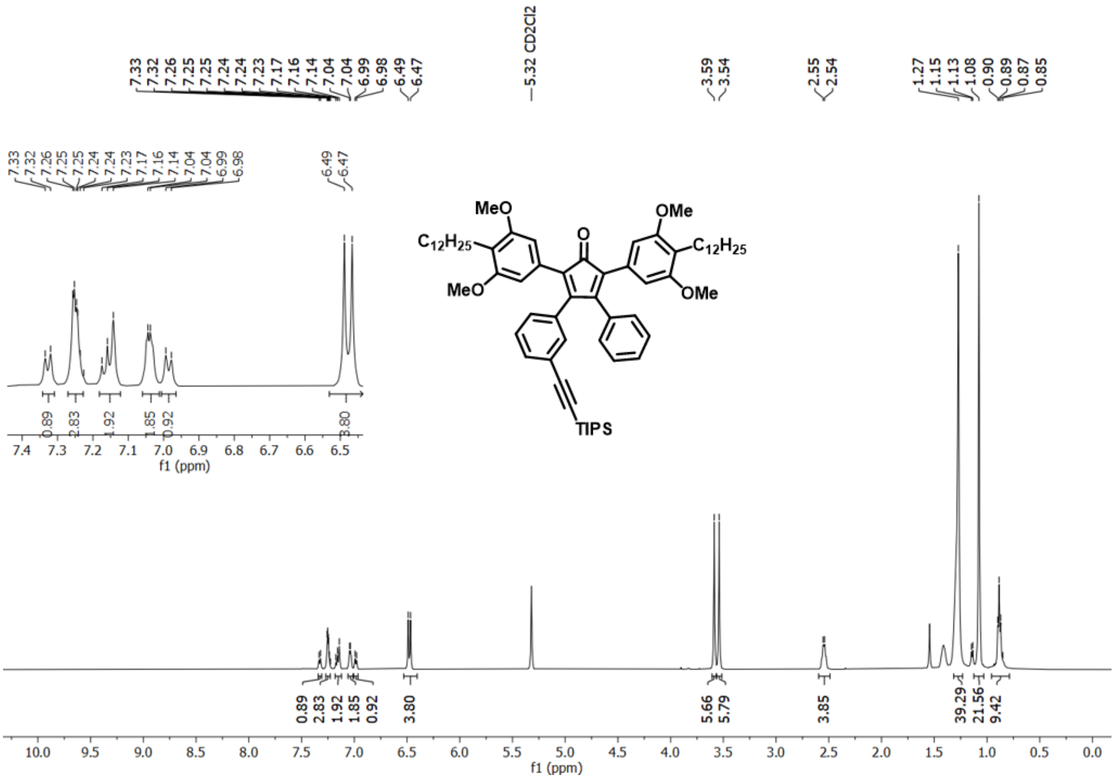


Figure S13. ^{1}H NMR spectra of compound **6** (75 MHz, CD_2Cl_2).

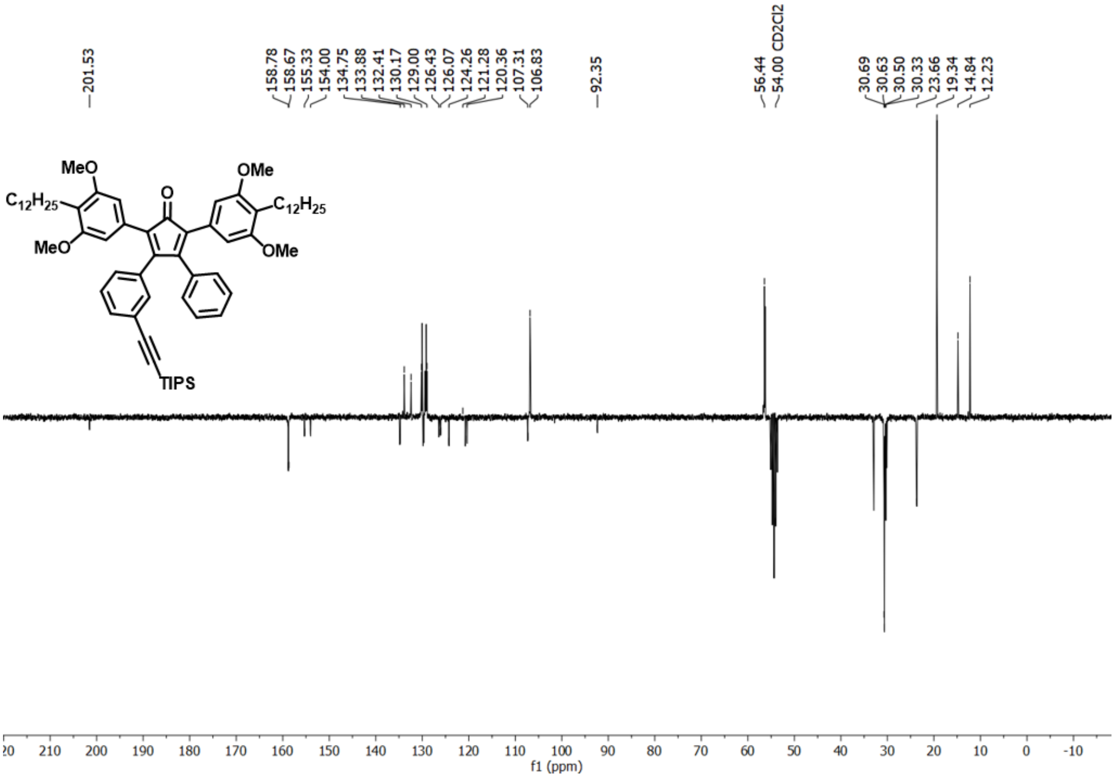


Figure S14. ^{13}C APT NMR spectrum of compound **6** (75 MHz, CD_2Cl_2).

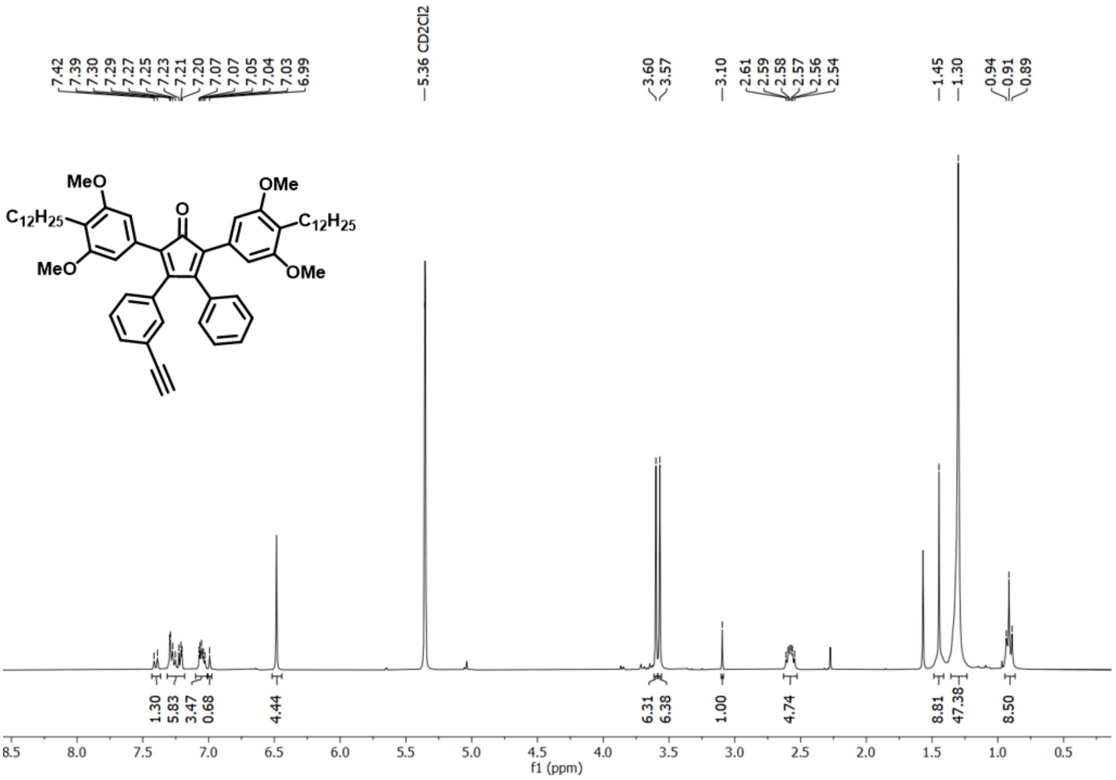


Figure S15. ^{1}H NMR spectrum of compound **7** (300 MHz, CD_2Cl_2).

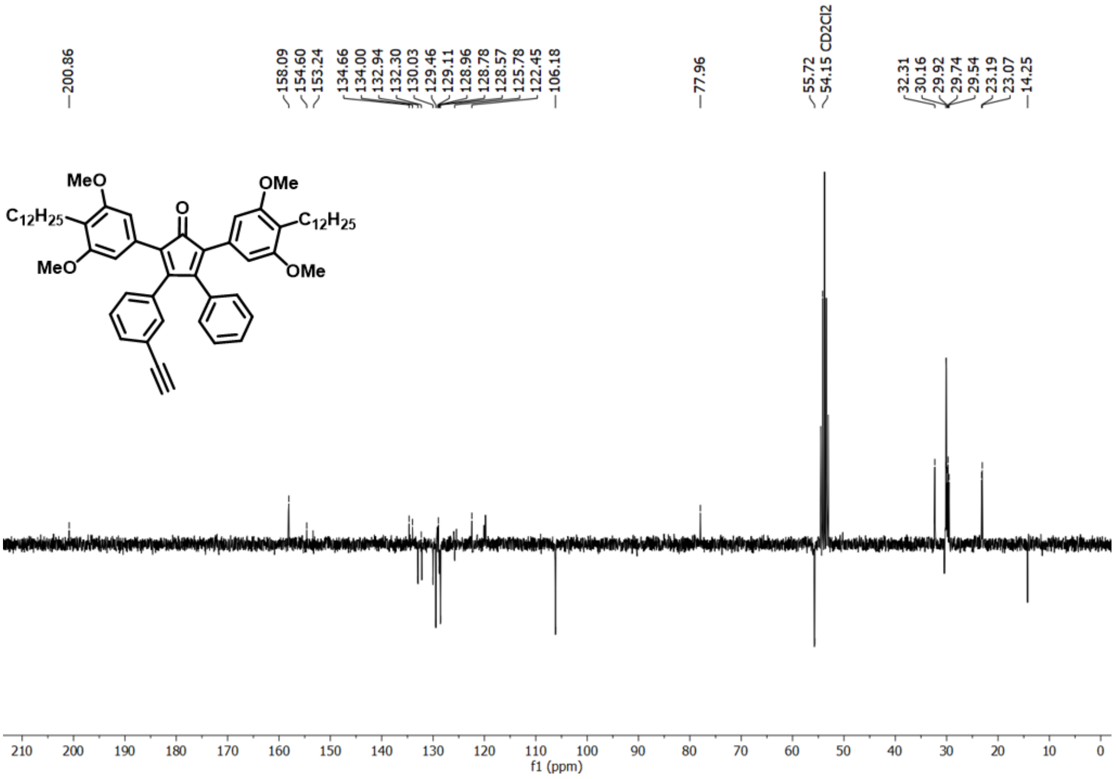


Figure S16. ^{13}C APT NMR spectrum of compound **7** (75 MHz, CD_2Cl_2).

8. References

1. Y.-Z. Tan, B. Yang, B., K. Parvez, A. Narita, S. Osella, D. Beljonne, X. Feng, K. Müllen, *Nat. Commun.* 2013, **4**, 2646.
2. M. G. Schwab, A. Narita, Y. Hernandez, T. Balandina, K. S. Mali, S. De Feyter, X. Feng, X., K. Müllen, *J. Am. Chem. Soc.,* 2012, **134**, 18169-18172.
3. L. Dössel, L. Gherghel, X. Feng, K. Müllen, *Angew. Chem. Int. Ed.,* 2011, **50**, 2540-2543.