

Supporting Information

Morphological Changes in the Self-Assembly of a Radial Oligo-Phenylene Ethyne Amphiphilic System

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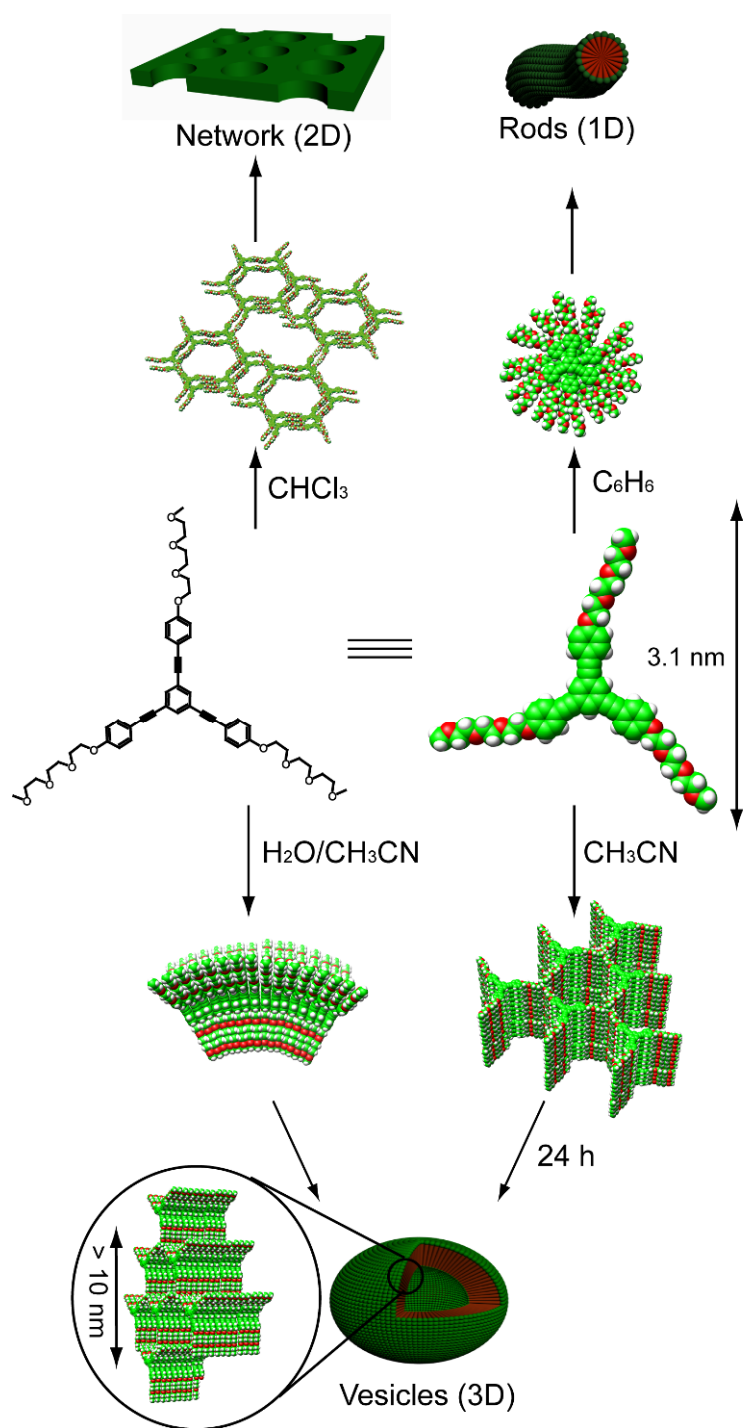
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Scheme S1. Chemical structure of **1** and cartoon representation of its proposed self-assembly in different solvents.

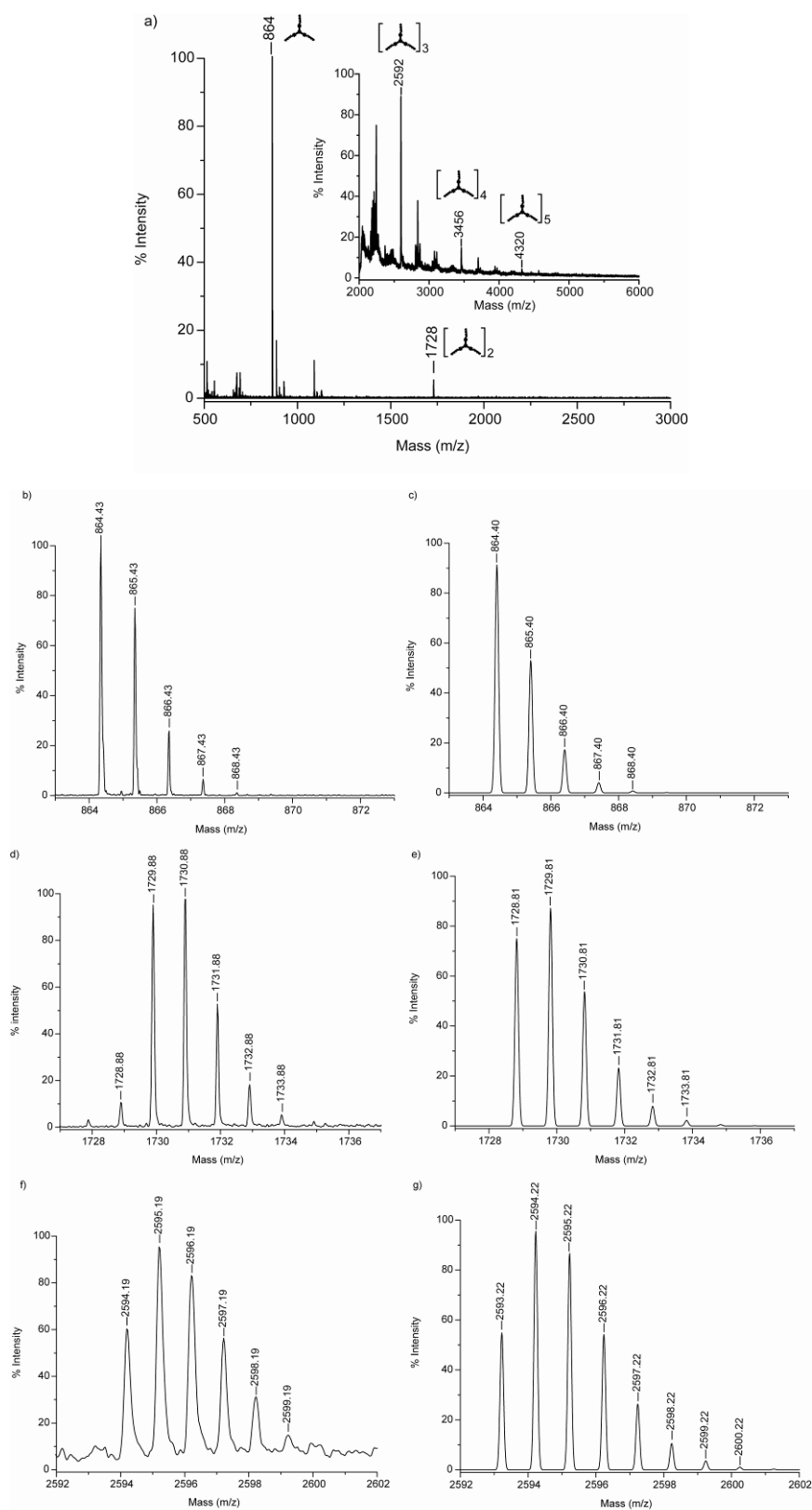


Figure S1. a) MALDI-TOF (ditranol) mass spectrum of amphiphile **1**. The inset shows the formation of aggregates in the gas phase. Measured (left) and calculated (right) isotopic distribution of **1** (b, c), its dimer (d, e) and trimer (f, g) in positive, reflector MALDI-TOF spectrum in ditranol as matrix.

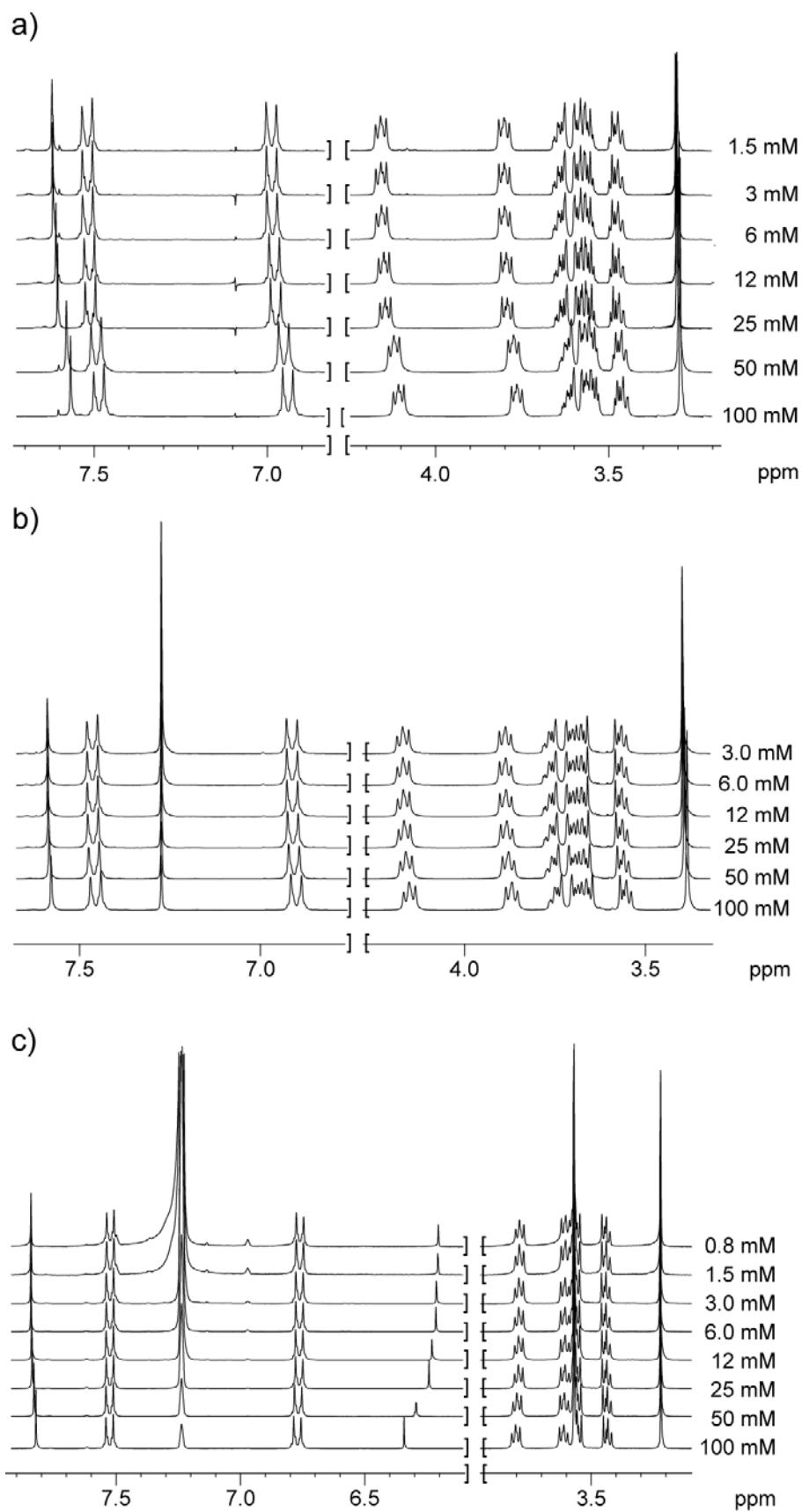


Figure S2. Partial ^1H NMR spectra (300 MHz, 298 K) of **1** at different concentrations (a) in CD_3CN , (b) in CDCl_3 , and (c) in C_6D_6 .

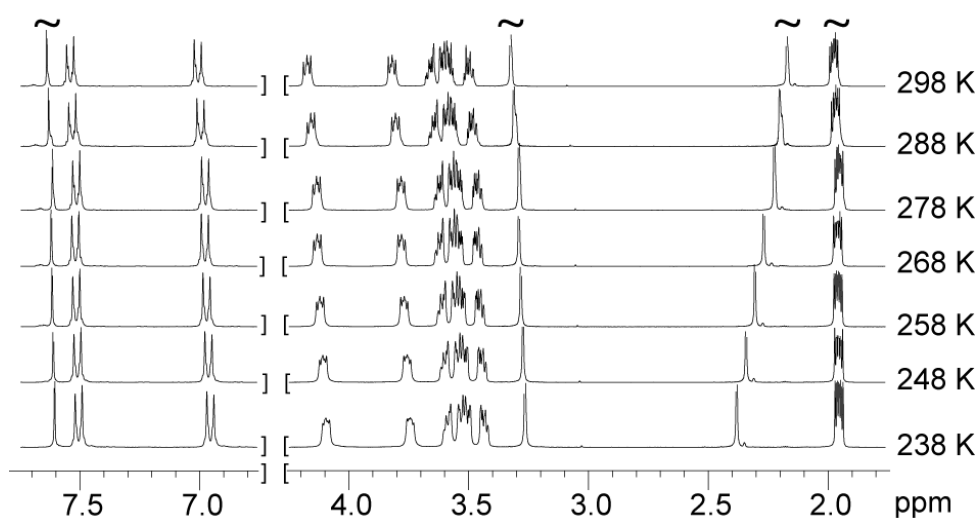


Figure S3. Partial variable temperature ^1H NMR (298-238 K, 4 mM, CD_3CN , 300 MHz) spectra of **1**.

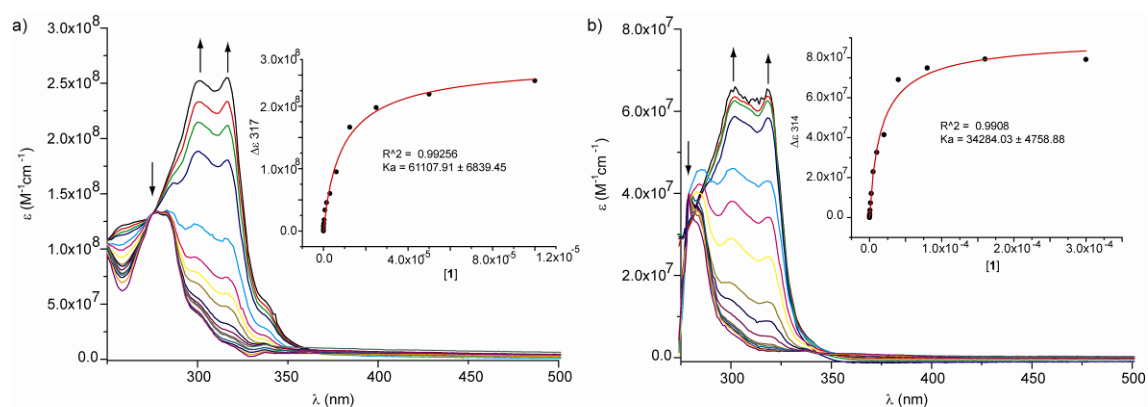


Figure S4. Concentration dependent UV-Vis absorption spectra of **1** in CHCl_3 (a) and C_6H_6 (b) (298 K, 3×10^{-4} to 9×10^{-9} M). Arrows indicate the direction of change with increasing concentration. The inset in a) and b) shows the fit of $\Delta\epsilon$ at 317 and 314 nm, respectively, to the isodesmic model (see: Würthner, F.; Thalacker, C.; Diele, S.; Tschierske, C. *Chem. Eur. J.* **2001**, *7*, 2245-2253).

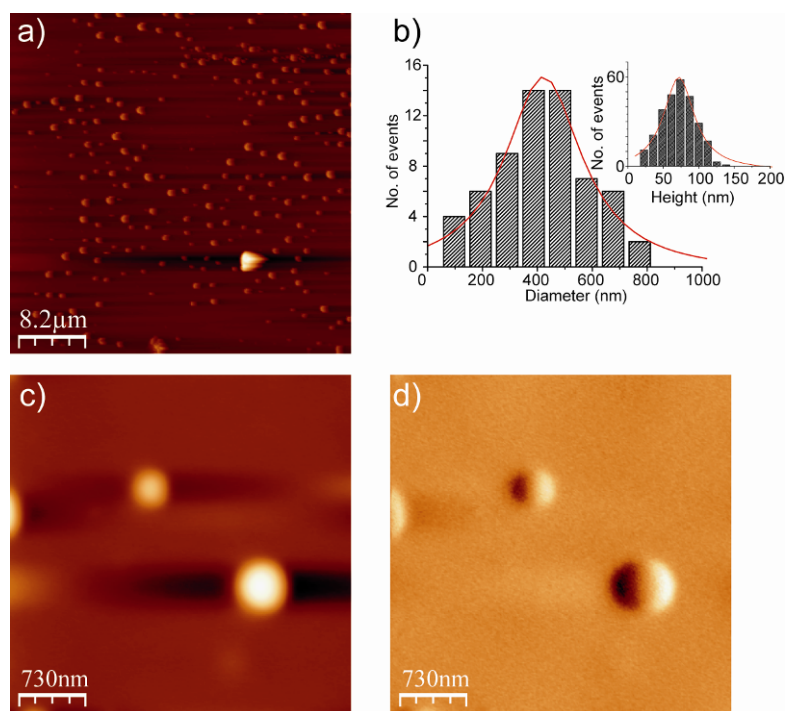


Figure S5. Tapping-mode AFM images (air, 298 K) of a drop-cast of a 1:1 H₂O/MeCN mixture ($\sim 10^{-6}$ M) of **1** on mica. (a) Large size (50 x 50 μm) image (Z scale = 200 nm); (b) diameter and height histograms (Lorentzian fit, $R^2 = 0.97$) after the tip broadening correction; (c, d) height and phase images of an expanded area (Z scale = 80 nm).

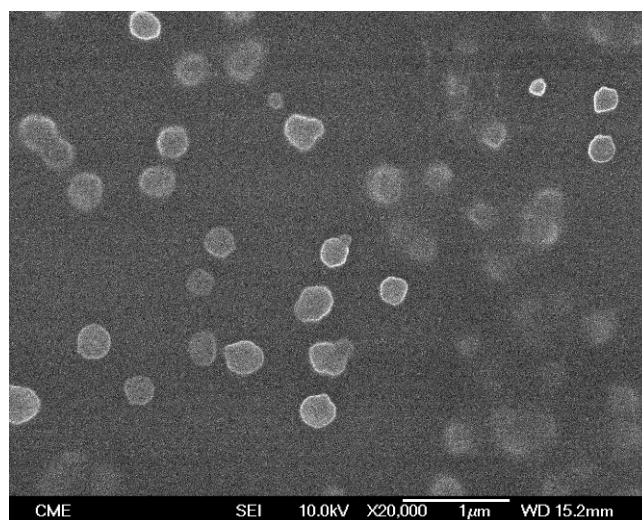


Figure S6. SEM image (298 K) of a drop-cast of a mixture acetonitrile/H₂O (1/1) of **1** ($\sim 1 \times 10^{-4}$ M) on glass plate.

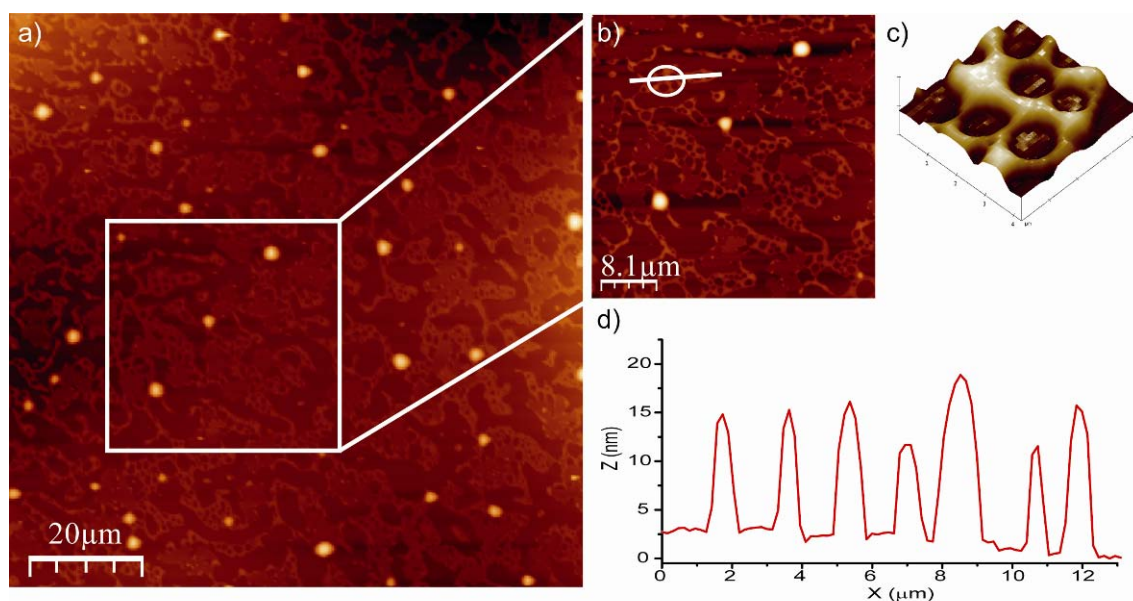


Figure S7. Tapping-mode AFM images (air, 298 K) of a drop-cast of a freshly prepared MeCN solution ($\sim 10^{-6}$ M) of **1** on mica. Large size (100 x 100 μm , Z scale = 120 nm) (a) and (50 x 50 μm , Z scale = 90 nm) (b) images; (c) 3D image of the encircled (white circle in b) area; (d) height profile of selected region (white line).

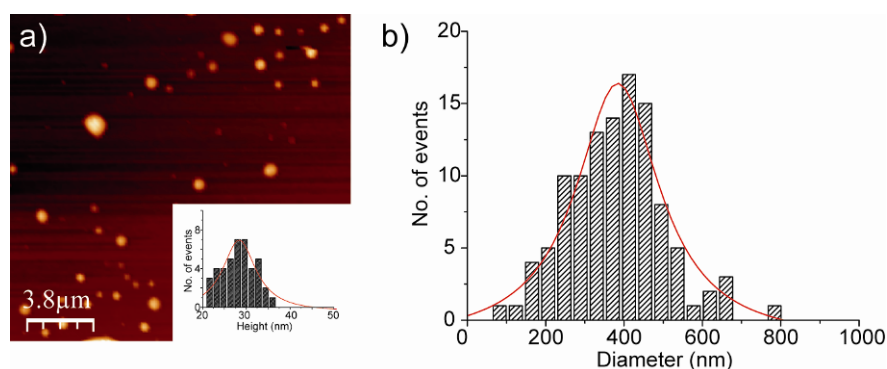


Figure S8. (a) Tapping-mode AFM image (air, 298 K, Z scale = 100 nm) of **1** ($\sim 10^{-6}$ M in MeCN) upon aging the sample onto mica. The inset show the height histogram and the corresponding Lorentzian fit. (a) Diameter histogram after the tip broadening correction and the corresponding Lorentzian fit ($R^2 = 0.94$).

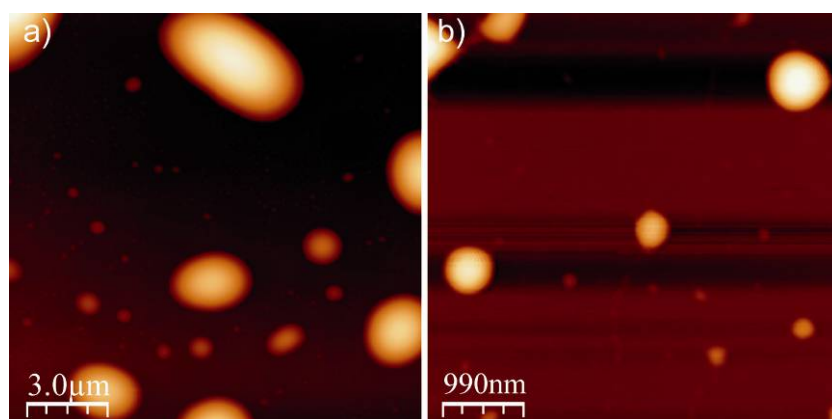


Figure S9. Tapping-mode AFM images (air, 298 K) of a drop-cast of a 1:1 H₂O/MeCN mixture at $\sim 10^{-4}$ M (Z scale = 120 nm)(a) and $\sim 10^{-7}$ M (100 nm) (b) of **1** on mica.

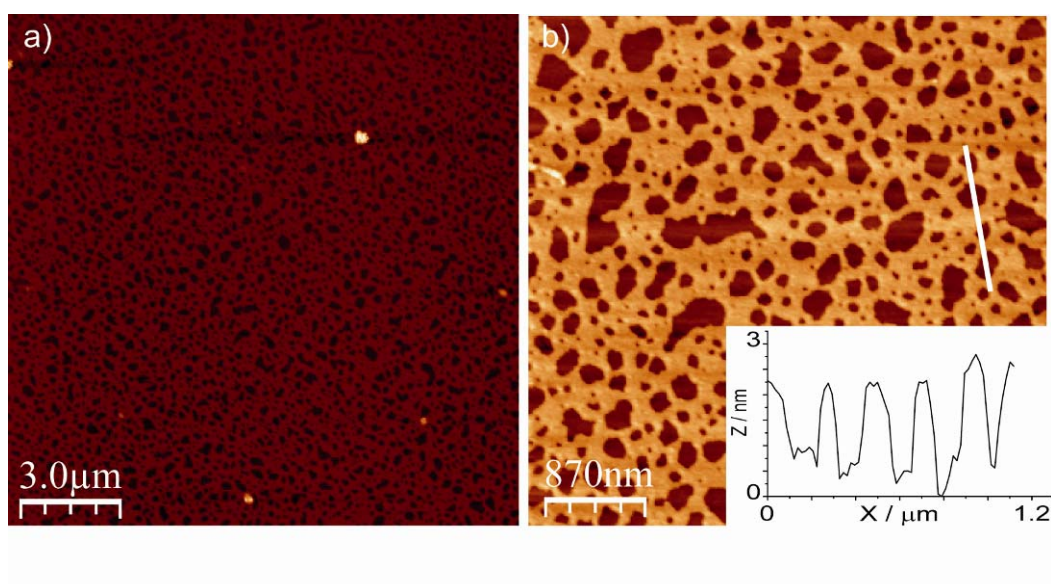


Figure S10. Tapping-mode AFM images (air, 298 K, Z scale = 50 nm for a, and Z scale = 7 nm for b) of a drop-cast of a chloroform solution of **1** on mica. The inset in (b) shows the height profile of the selected area (white line)

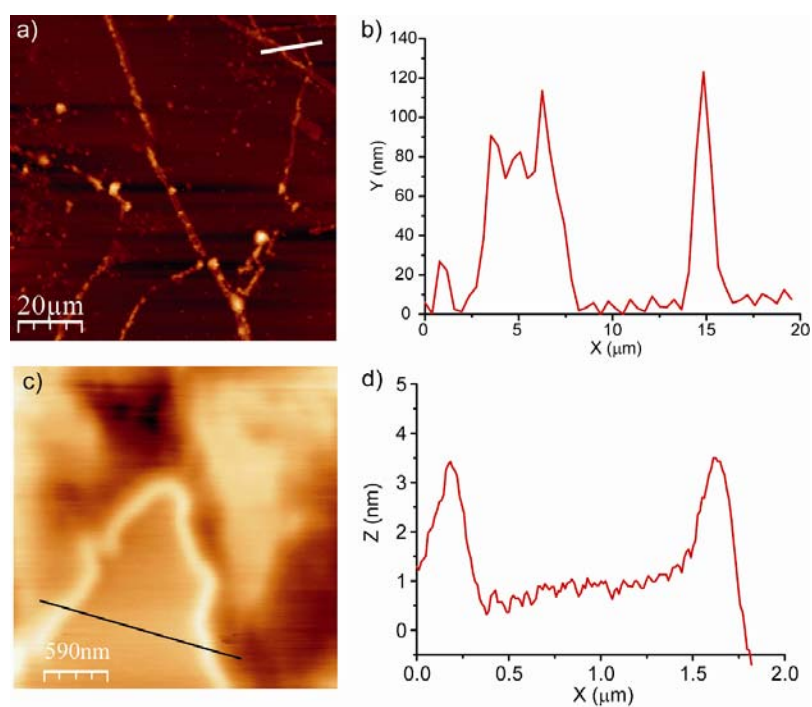


Figure S11. a) and c) Tapping-mode AFM images (air, 298 K, 10^{-6} M, Z scale = 350 for a; Z scale = 10 nm for c) of a drop-cast of a benzene solution of **1** on mica; b) and d) Profiles of the selected rods formed.

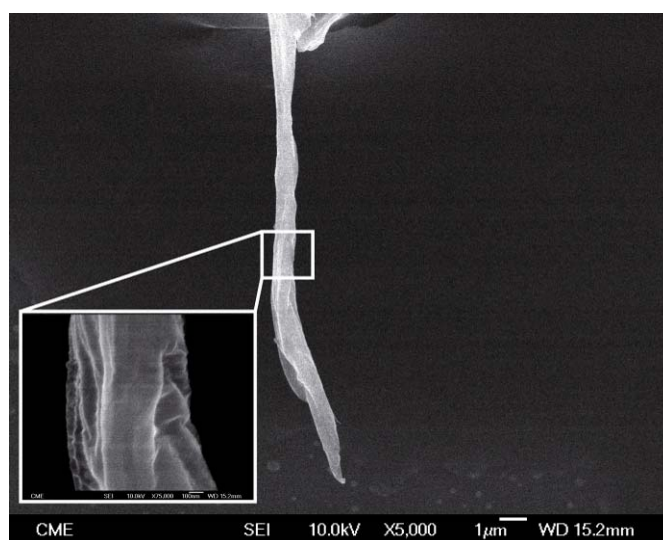
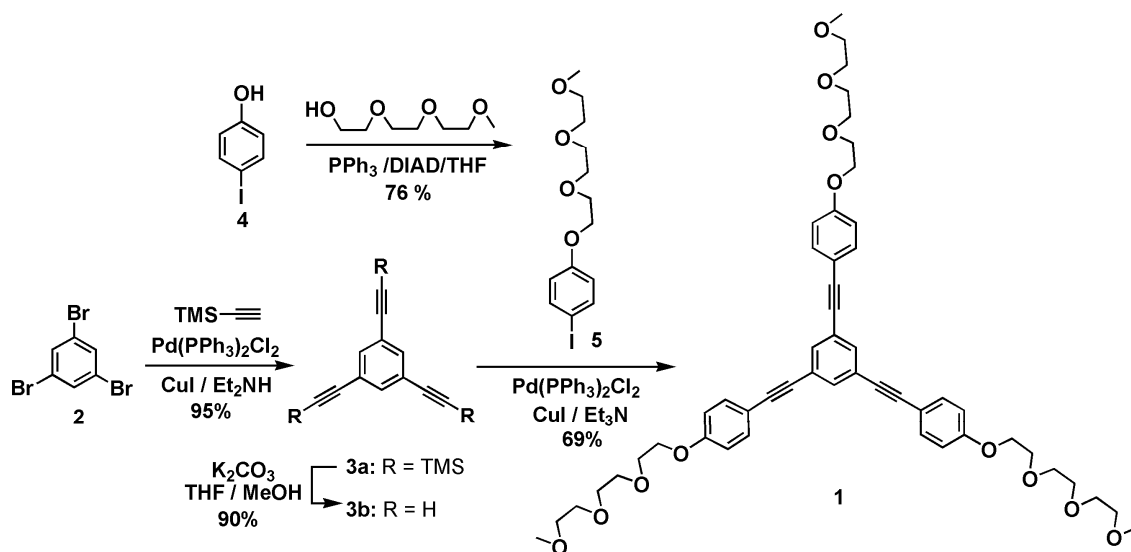


Figure S12. SEM image (298 K) of a drop-cast of a benzene solution of **1** ($\sim 1 \times 10^{-4}$ M) on glass plate.

2. Experimental Section

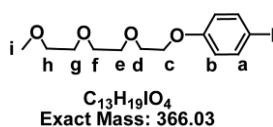
General. All solvents were dried according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. Flash chromatography was performed using silica gel (Merck, Kieselgel 60, 230-240 mesh or Scharlau 60, 230-240 mesh). Analytical thin layer chromatography (TLC) was performed using aluminum coated Merck Kieselgel 60 F254 plates. NMR spectra were recorded on a Bruker Avance 300 (^1H : 300 MHz; ^{13}C : 75 MHz) spectrometer at 298 K using partially deuterated solvents as internal standards. Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. FT-IR spectra were recorded on a Bruker Tensor 27 (ATR device) spectrometer. UV-Vis spectra were recorded on a Varian Cary 50 spectrophotometer. Matrix Assisted Laser Desorption Ionization (coupled to a Time-Of-Flight analyzer) experiments (MALDI-TOF) were recorded on a Bruker REFLEX spectrometer. Dynamic Light Scattering measurements were carried out on an ALV GSC08 correlator working in a cross-correlation mode with an Ar^+ laser operating at $\lambda = 514.5$ nm. The output signals were obtained with backscatter detection at an angle of 30° and processed with a digital correlator that computed intensity-intensity autocorrelation of the scattered light. Measurements were made in a 1-cm path-length round quartz cell maintained at 298 K. Solution samples were filtered through nylon Acrodisc syringe filters (Pall Life Sciences) with 0.2- μm pore size. Atomic Force Microscopy was performed on a SPM Nanoscope IIIa multimode microscope working on tapping mode with a RTESPA tip (Veeco) at a working frequency of ~ 235 kHz. SEM images were obtained from on a JEOL JSM 6335F microscope working at 10kV. Fluorescence images were recorded on a Leica TCE SP2 confocal microscope. TEM measurements were performed on a JEOL 2000-FX electron microscope, operating at an acceleration voltage of 200 kV.

3. Synthetic details and characterization



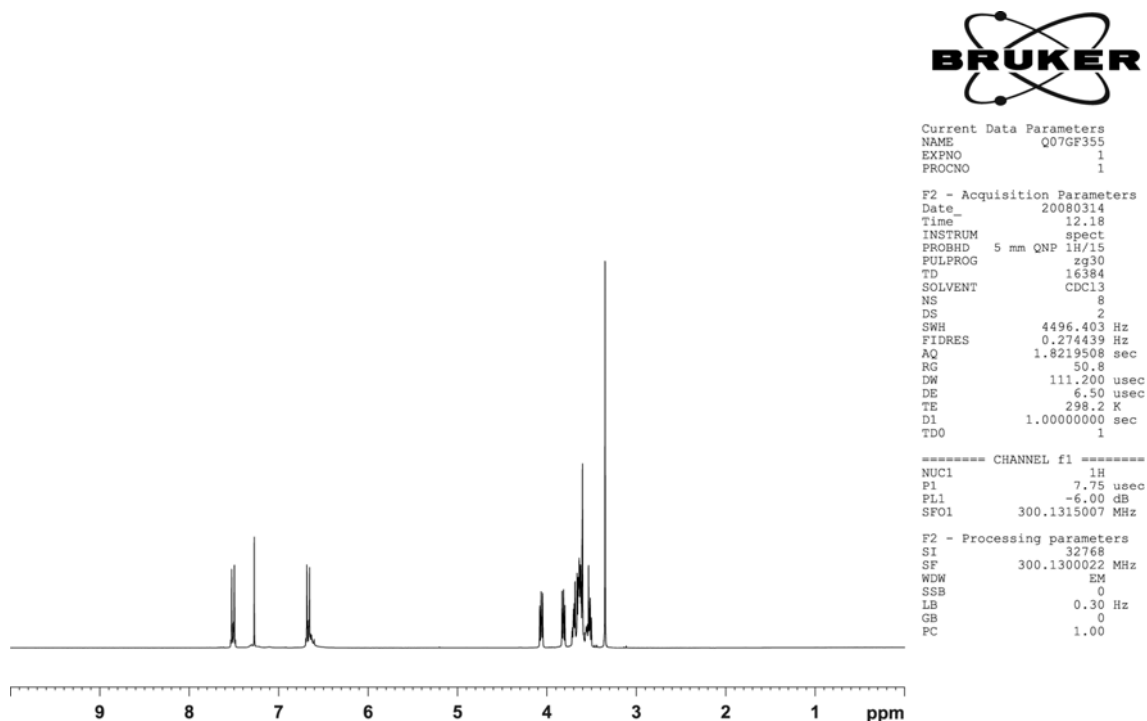
Compounds **3a**, and **3b** were prepared according to previously reported synthetic procedures (see W. Uhl, H. R. Bock, F. Breher, M. Claesener, S. Haddadpour, B. Jasper, A. Hepp, *Organometallics* **2007**, *26*, 2363-2369) and showed identical spectroscopic properties to those reported therein.

Compound 5

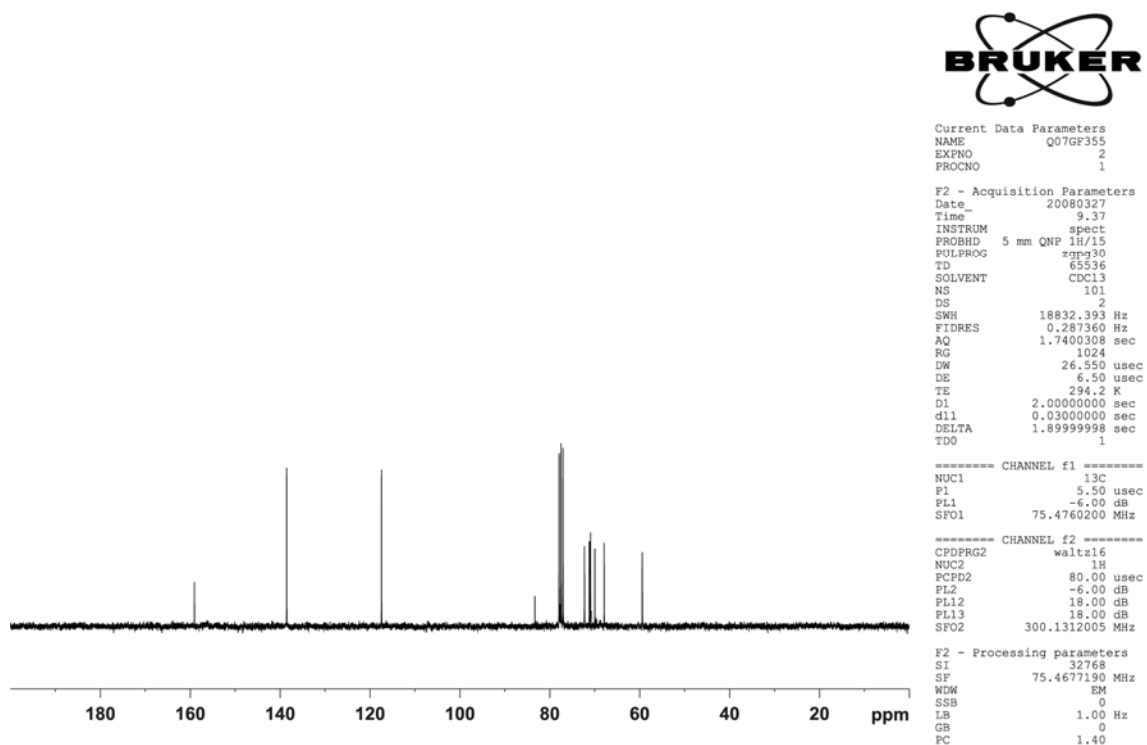


Diisopropyl azodicarboxylate (DIAD) (7.66 g, 37.91 mmol) was added portionwise to a previously cooled solution (0 °C) of iodophenol (5.56 g, 25.27 mmol) and triethylene glycol monomethyl ether (4.98 g, 30.31 mmol) in dry THF (50 mL) under argon atmosphere. The mixture was allowed to warm up to room temperature and stirred overnight. After evaporation of the solvent under reduced pressure the triphenylphosphine oxide generated in the reaction was precipitated with a diethyl ether/hexane mixture (1:1) and the liquid residue was purified by column chromatography (silica gel, hexane:diethyl ether 1:2) affording **5** as a yellow oil (7.00 g, 76%). ¹H NMR (CDCl₃, 300 MHz) δ 7.51 (2H, H_a, d, J = 9Hz), 6.67 (2H, H_b, d, J = 9Hz), 4.06 (2H, H_c, t, J = 4.7 Hz), 3.81 (2H, H_d, t, J = 4.7 Hz), 3.71-3.68 (2H, H_e, m), 3.66-3.50 (6H, H_{f+g+h}, m), 3.34 (3H, H_i, s); ¹³C NMR (CDCl₃, 75Mz) δ 159.1, 138.5, 117.4, 83.3,

72.3, 71.2, 71.0, 70.9, 70.0, 67.9, 59.4; FTIR (neat) 635, 696, 821, 945, 999, 1107, 1176, 1244, 1282, 1351, 1453, 1485, 1572, 1586, 1730, 2875 cm^{-1} ; ESI-MS m/z $[M^+]=366$.

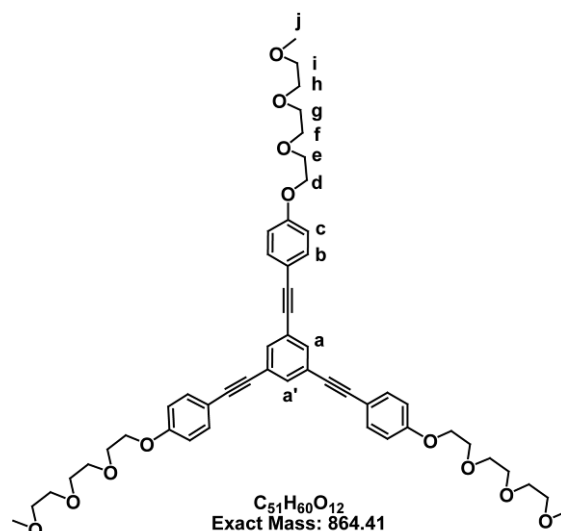


^1H NMR (CDCl_3 , 300 MHz, 298 K) of compound 5



^{13}C NMR (CDCl_3 , 75 MHz, 298 K) of compound 5

Compound 1

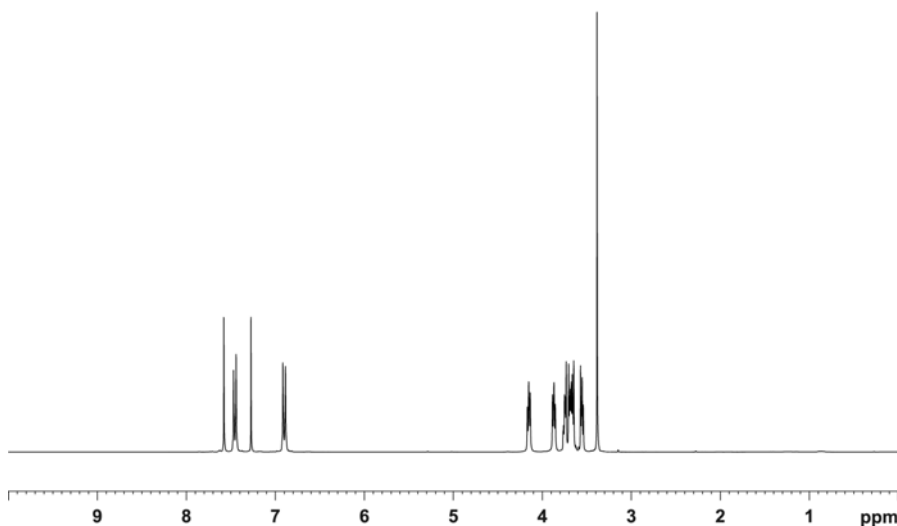


Compound **5** (2.68 g, 7.33 mmol), bis-(triphenylphosphine)-palladium(II)-chloride (0.12 g, 0.17 mmol) and copper (I) iodide (0.04 g, 0.20 mmol) were dissolved in triethylamine (50 mL). The mixture was subjected to several vacuum/argon cycles and compound **3b** (0.50 g, 3.33 mmol) was added. The mixture was heated at 70 °C for 2 hours and then was allowed to warm up until room temperature and stirred overnight. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (silica gel, $CHCl_3/EtOH$ 20:1) affording **1** as a brown oil (2.00 g, 69%); 1H NMR ($CDCl_3$, 300 MHz) δ 7.58 (3H, H_a , s), 7.45 (6H, H_b , d, $J = 9$ Hz), 6.91 (6H, H_c , d, $J = 9$ Hz), 4.15 (6H, H_d , t, $J = 6$ Hz), 3.87 (6H, H_e , t, $J = 6$ Hz), 3.76-3.54 (24H, $H_{f+g+h+i}$, m); 3.39 (9H, H_j , s); ^{13}C NMR ($CDCl_3$, 75Mz) δ 159.5, 133.8, 133.5, 124.6, 115.5, 115.1, 90.8, 87.2, 72.3, 71.2, 71.1, 71.0, 70.0, 67.9, 59.5; 1H NMR (C_6D_6 , 300MHz) δ 7.84 (2H, H_a , s), 7.55 (6H, H_b , d, $J = 9$ Hz), 6.79 (6H, H_c , d, $J = 9$ Hz), 6.36 (1H, $H_{a'}$, s), 3.81-3.78 (6H, H_d , m), 3.62-3.59 (6H, H_e , m), 3.56-3.53 (18H, $H_{f+g+h+i}$, m), 3.45-3.41 (6H, H_j , m), 3.21 (9H, s); ^{13}C NMR (C_6D_6 , 75Mz) δ 159.8, 134.1, 133.7, 125.3, 115.8, 115.2, 91.6, 87.7, 77.9, 72.5, 71.3, 71.2, 71.1, 69.9, 67.8, 58.8; FTIR (neat) 642, 681, 734, 832, 876, 947, 1059, 1108, 1175, 1248, 1289, 1415, 1485, 1508, 1578, 1605, 2209, 2877, 3051 cm^{-1} ; MALDI-TOF-MS m/z 864.4. HRMS: calcd. for $C_{51}H_{60}O_{12}$ [M], 864.40851; found, 864.40793.



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PROCNO   1

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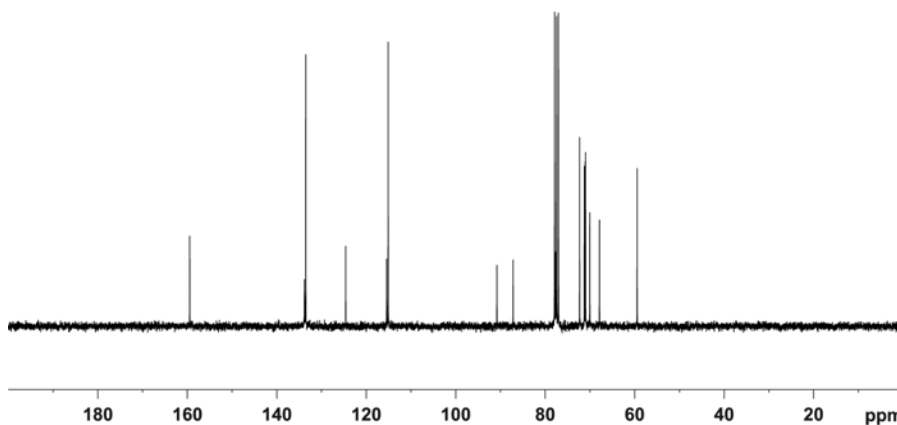
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^1H NMR (CDCl_3 , 300 MHz, 298 K) of compound **1**



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^{13}C NMR (CDCl_3 , 75 MHz, 298 K) of compound **1**

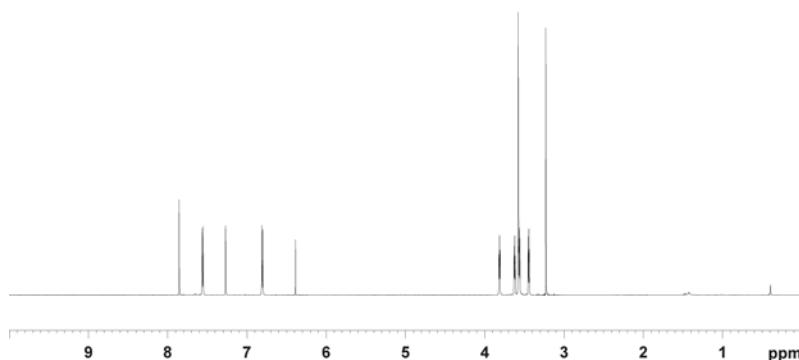


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^1H NMR (C_6D_6 , 300 MHz, 298 K) of compound **1**



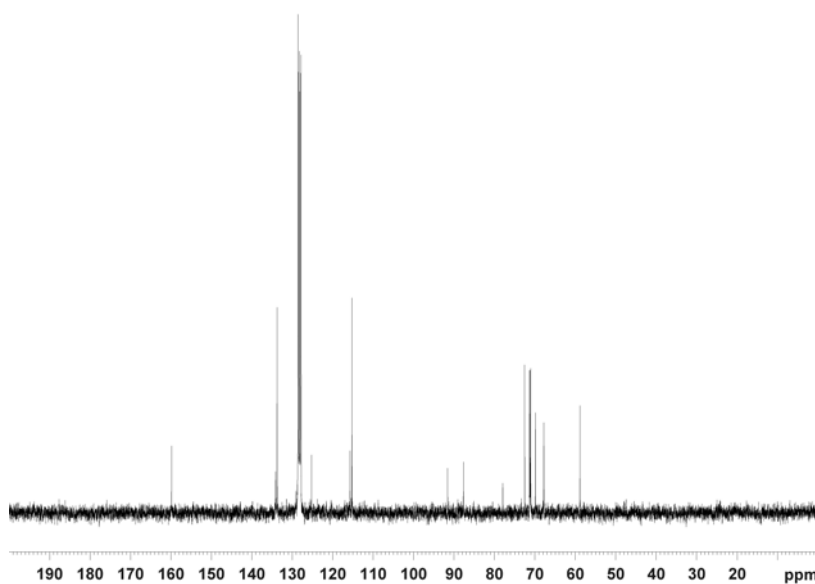
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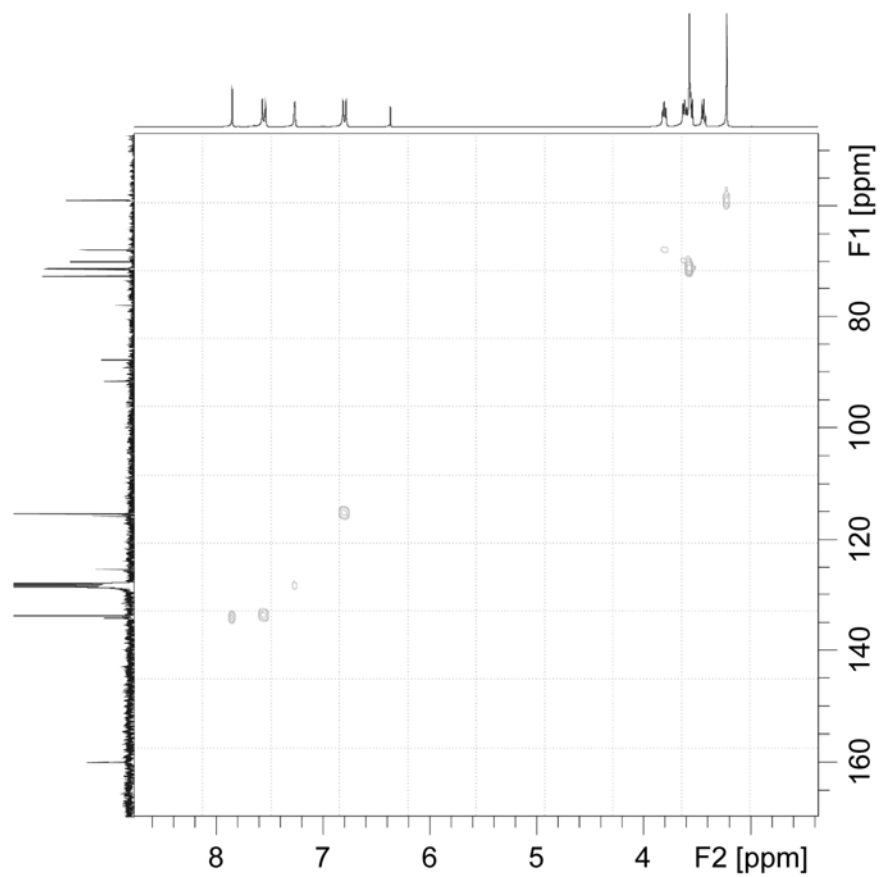
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^{13}C NMR (C_6D_6 , 75 MHz, 298 K) of compound **1**



^1H , ^{13}C -HMQC spectrum (C_6D_6 , 298 K) of compound **1**.

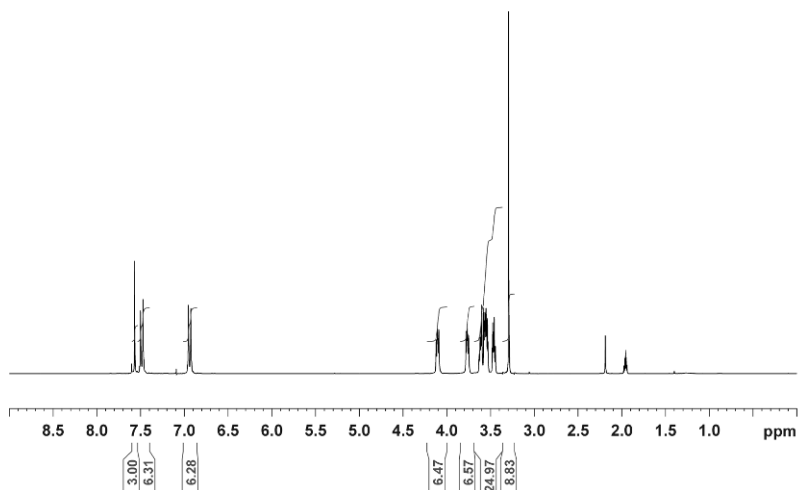


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TE         295.2 K
D1         1.00000000 sec
TDO        1

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F2 - Processing parameters
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¹H NMR (CD₃CN, 300 MHz, 298 K) of compound 1

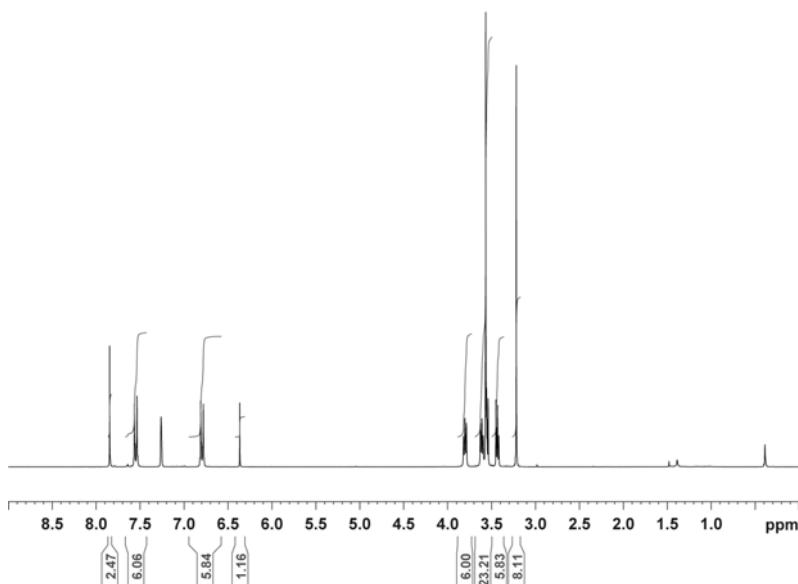


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FIDRES     0.274439 Hz
AQ         1.8219508 sec
RG         114
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TE         294.2 K
D1         1.00000000 sec
TDO        1

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PL1       -6.00 dB
SFO1      300.1315007 MHz

F2 - Processing parameters
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SSB         0
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¹H NMR (C₆D₆, 300 MHz, 298 K) of compound 1