A Fishing Rod-like Conjugated Polymer Bearing Pillar[5]arenes

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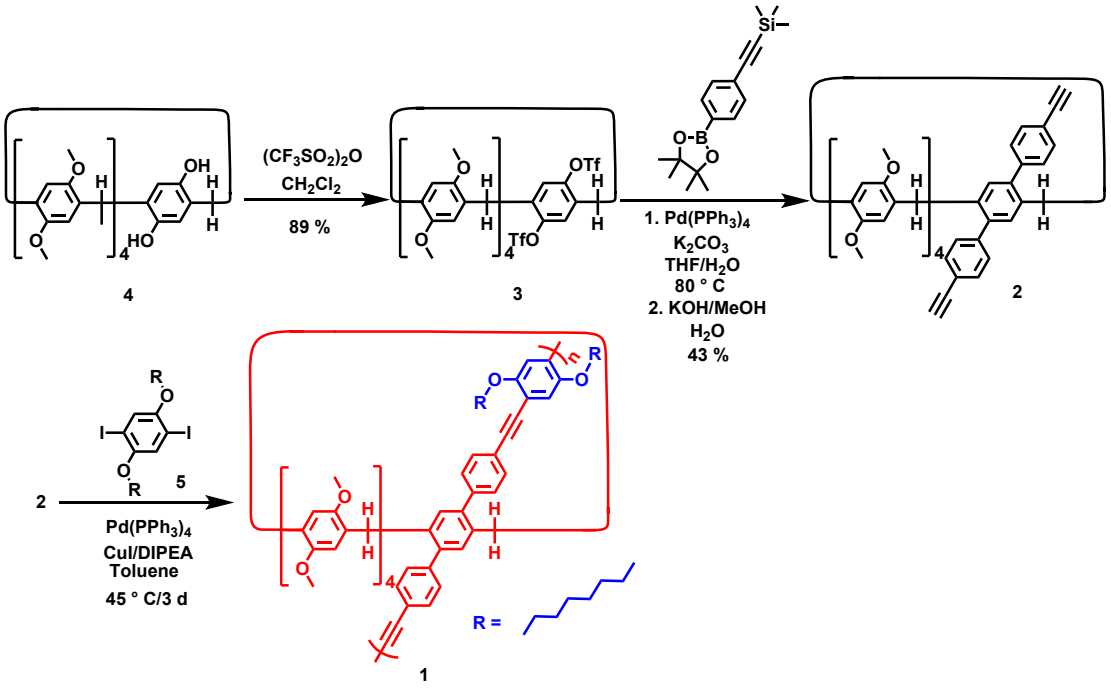
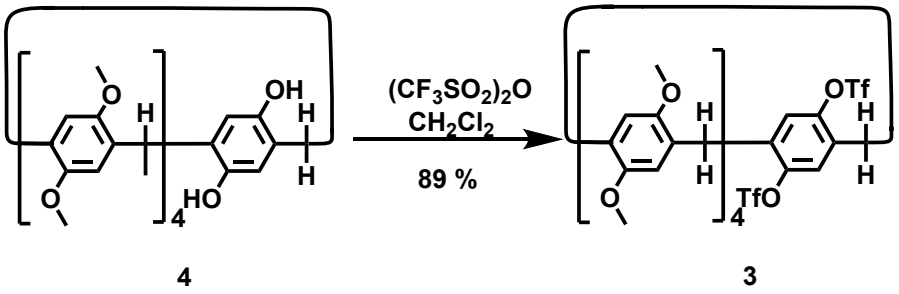
1. Materials and methods

All the reactants were purchased from commercial resources. ^{1}H, ^{13}C and 2D NMR spectra were recorded on Bruker AMX250, and AMX500 NMR spectrometers using the residual proton of the solvent or the carbon signal of the deuterated solvent as an internal standard. MALDI-TOF mass spectra were measured using a Bruker Reflex II, which was calibrated against poly(ethylene glycol) (3000 g/mol). Samples for MALDI-TOF MS were prepared by mixing the analyte with the matrix (DCTB) in chloroform in a ratio of 1:50. All reported MALDI-TOF MS measurements were within the experimental error, characteristicfor the applied technique. The high resolution mass spectrometry was performed on an ESI-Q-TOF system (maXis, BrukerDaltonics, Germany). Solution UV-vis absorption and emission spectra were recorded at room temperature on a Perkin-Elmer Lambda 100 spectrophotometer and J&M TIDAS spectrofluorometer, respectively. Crystal-structure determinations were carried out on a Nonius KCCD diffractometer with graphite monochromated Mo K radiation. The structures were solved by direct methods (SHELXS-97). Size exclusion chromatography (SEC) was performed in THF at room temperature using PSS SECcurity pump, SDV GPC columns with 500 Å, 104, and 106Å porosities (PSS, Mainz), UV SECcurity VWD (at 254 nm) and Shodex RI 101 refractive index detectors.

2. Synthetic route



3. Synthesis of ***3*** [S1,S2]



Trifluoromethanesulfonic anhydride (12 mL) was added dropwise to a mixture of **4** [S1] (3.00 g, 4.14 mmol) and C_5H_5N (dry, 6 mL) in CH_2Cl_2 (dry, 20 mL), cooled to 0°C and then allowed to stir at room temperature for 12 h. The reaction mixture was poured into cold water. The organic phase was washed with water, and was concentrated under vacuum and subjected to silica gel chromatography (petroleum ether/dichloromethane: 1/1) to give **3** as a white powder (2.96 g, 68%). ^{1}H NMR (250 MHz, chloroform-*d*, room temperature) δ (ppm): 7.74 (d, J = 8.3 Hz, 4H), 7.31 (d, J = 8.3 Hz, 4H), 4.10 (t, J = 5 Hz, 4H), 3.63 (t, J = 5 Hz, 4H), 3.55 (d, J = 10.2 Hz, 16H), 2.39 (s, 6H).

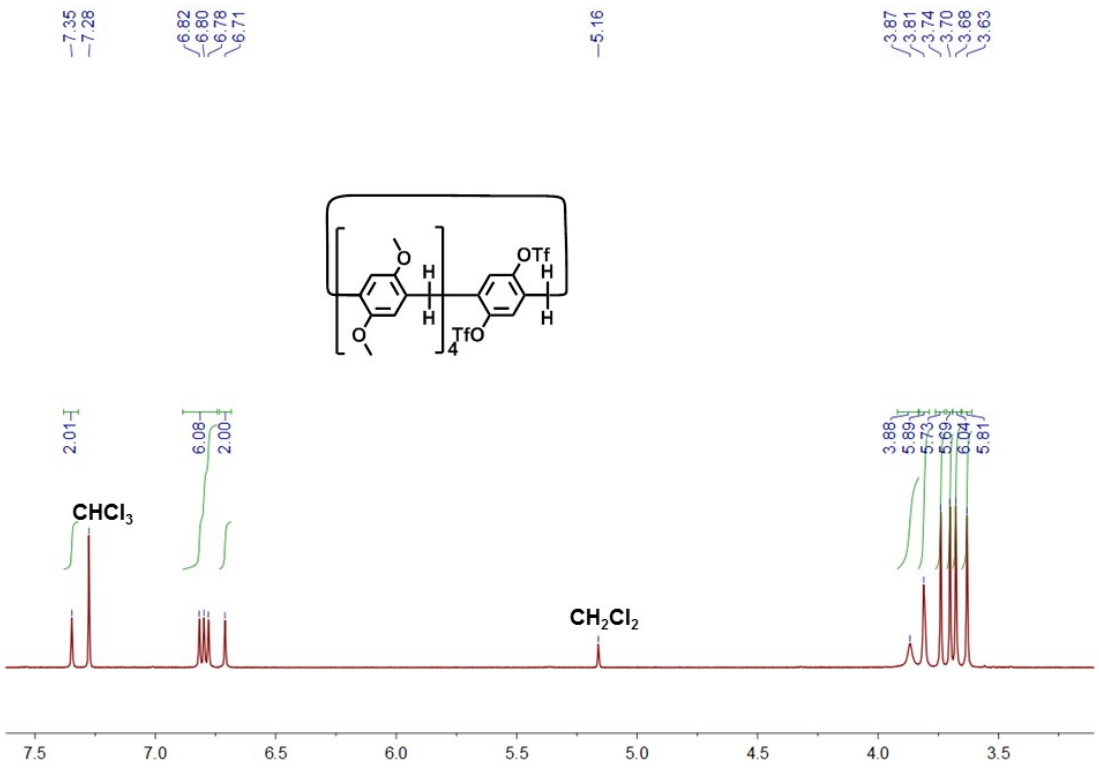
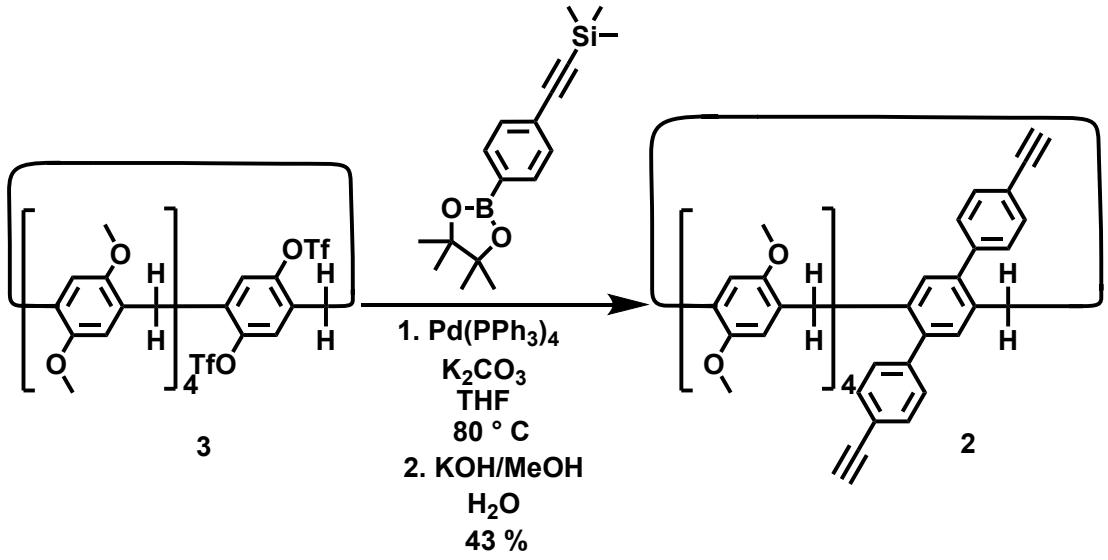


Figure S1. ^{1}H NMR spectrum (250 MHz, chloroform-*d*, room temperature) of **3**.

4. Synthesis of ***2***



$Pd(PPh_3)_4$ (22 mg, 0.0315 mmol) was added to a mixture of **3** (0.207 g, 0.21 mmol), 4-(methoxycarbonyl)phenylboronic acid (0.218 g, 1.00 mmol) and 2 M aqueous (5.00 mL) in THF (25.0 mL). The mixture was stirred at 80°C for 24 h. The solvent was removed under vacuum. The residue was diluted with CH_2Cl_2 (50 mL).The solution

was washed with H_2O (2 x 50 mL) and brine (100 mL), and dried (Na_2SO_4), concentrated under vacuum, and subjected to silica gel chromatography (CH_2Cl_2/petroleum ether: 1/4) to give the intermediate as a white solid (113 mg, 52 %). The white solid (113 mg, 0.109 mmol) was dissolved in CH_2Cl_2/methanol (*v*/*v*= 1/1, 10.0 mL). 1 M KOH (1.00 mL) was added. And the mixture was stirred at room temperature for 5 h. The solvent was removed under vacuum. The residue was crystallized from CH_2Cl_2/methanol to give compound **2** (80.5 mg, 83%) as colorless needles. ^{1}H NMR (250 MHz, chloroform-*d*, room temperature) δ (ppm): 7.33 (s, 2H), 7.30 (s, 2H), 6.92 (s, 2H), 6.88 (d, J = 3.2 Hz, 4H), 6.78 (s, 2H), 6.73 (s, 2H), 6.53 (s, 2H), 5.92 (s, 2H), 3.88 (m, 4H), 3.75 (m, 6H), 3.72 (s, 6H), 3.59 (s, 6H), 3.42 (s, 6H), 3.31 (s, 6H), 3.12 (s, 2H). ^{13}C NMR (250 MHz, chloroform-*d*, room temperature) δ (ppm): 150.99, 150.95, 150.85, 150.61, 142.75, 139.91, 136.61, 131.75, 131.68, 129.12, 129.06, 128.95, 128.58, 128.54, 127.65, 120.15, 114.26, 114.04, 113.93, 113.90, 83.73, 56.08, 56.00, 55.65, 55.53, 33.67, 29.89, 29.50. MALDI-TOF: m/z 890.05 $[M]^+$ HRMS: (m/z): calcd for [M + Na]$^+$: 913.3711 ; found 913.3722.

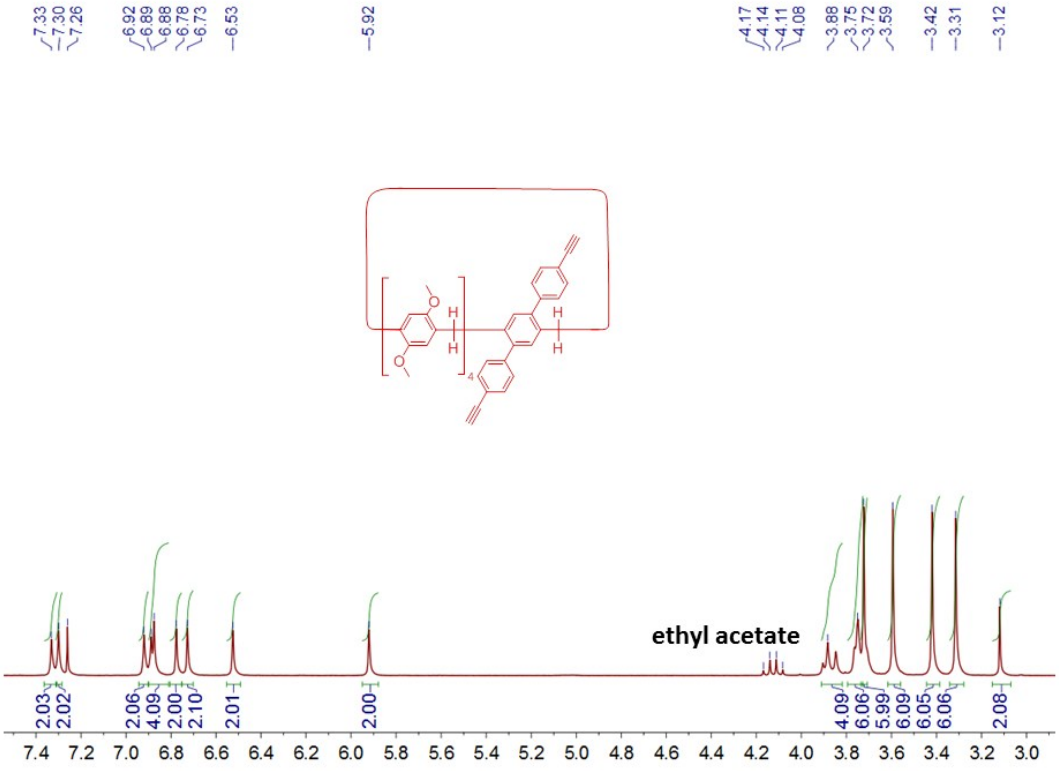


Figure S2. ^{1}H NMR spectrum (250 MHz, chloroform-*d*, room temperature) of **2**.

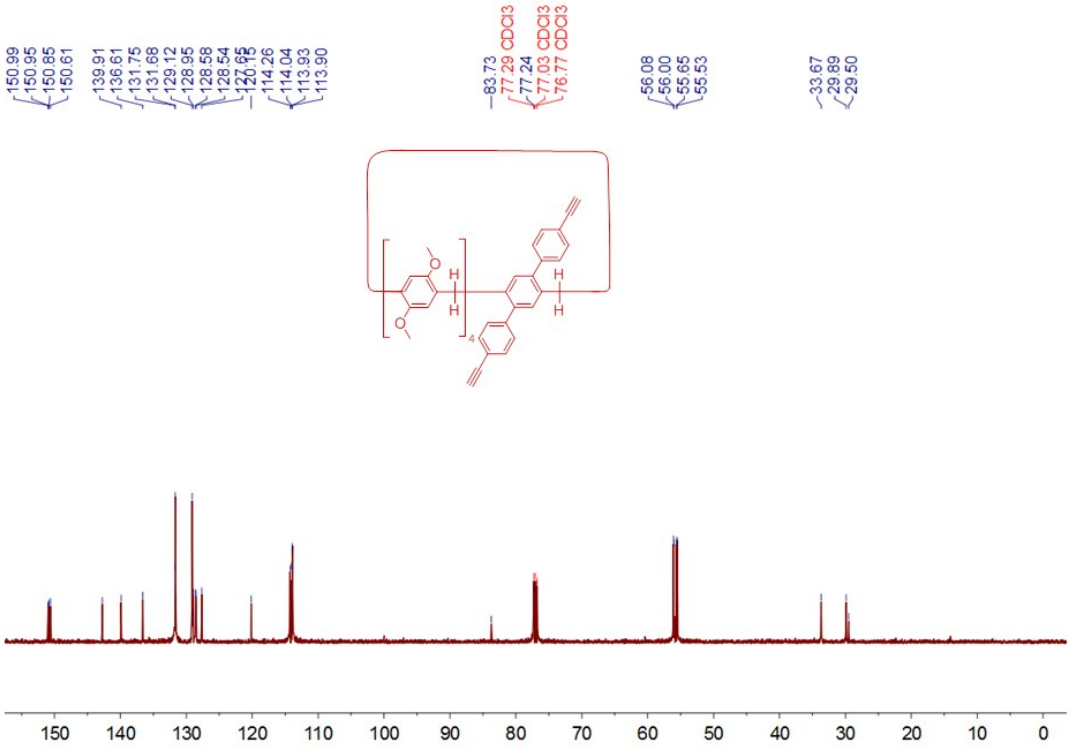


Figure S3. ^{13}C NMR spectrum (250 MHz, chloroform-*d*, room temperature) of **2**.

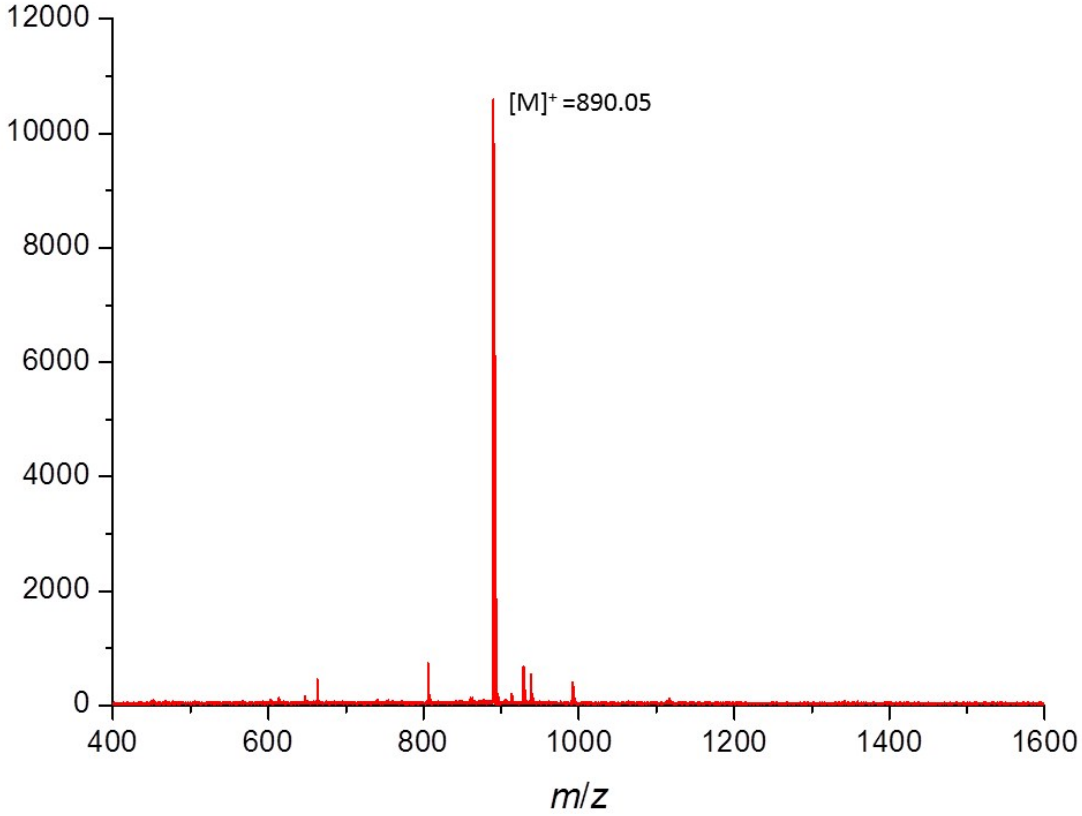


Figure S4. MALDI-TOF mass spectrum of **2**.

5. 2D NMR Spectroscopy of Compound ***2***

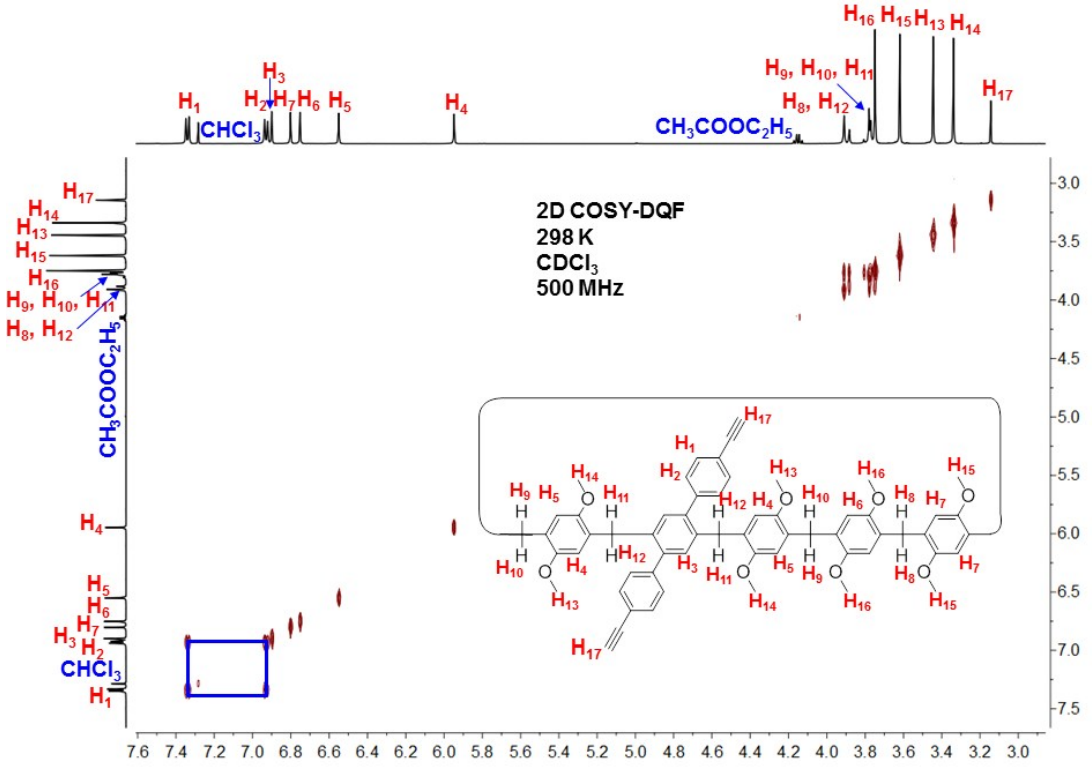


Figure S5. 2D COSY-DQF NMR (500 MHz, chloroform-*d*, 298K) of **2**.

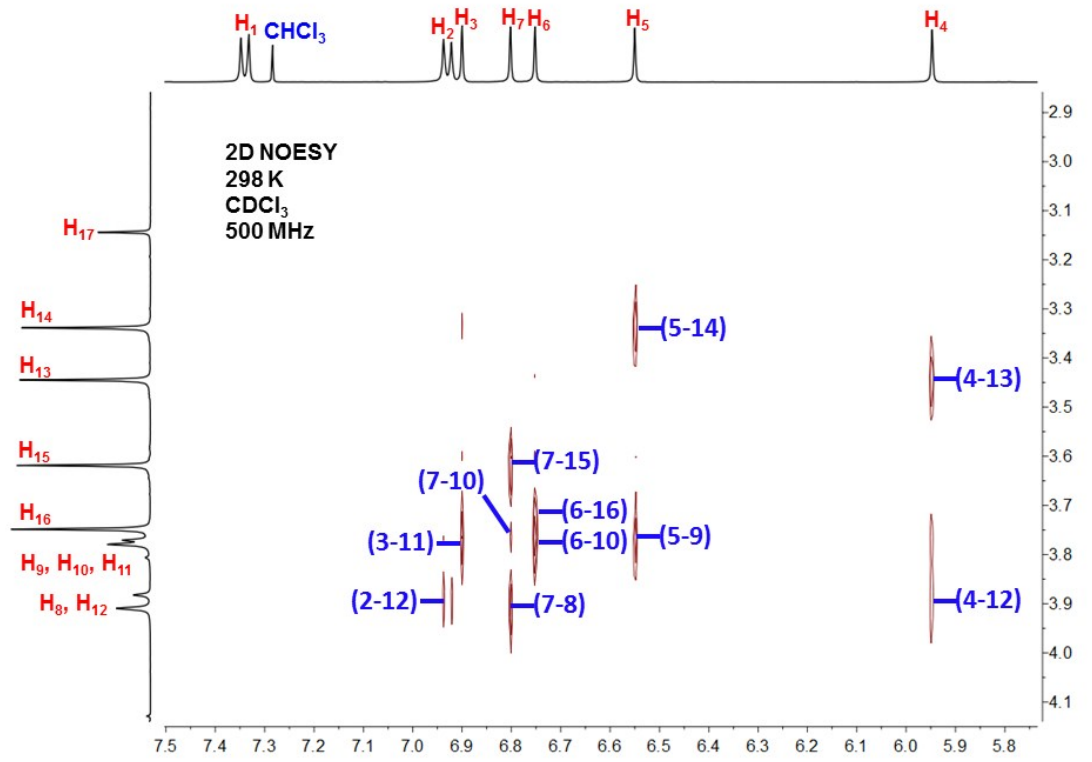


Figure S6. 2D NOESY NMR (500 MHz, chloroform-*d*, 298K) of **2**.

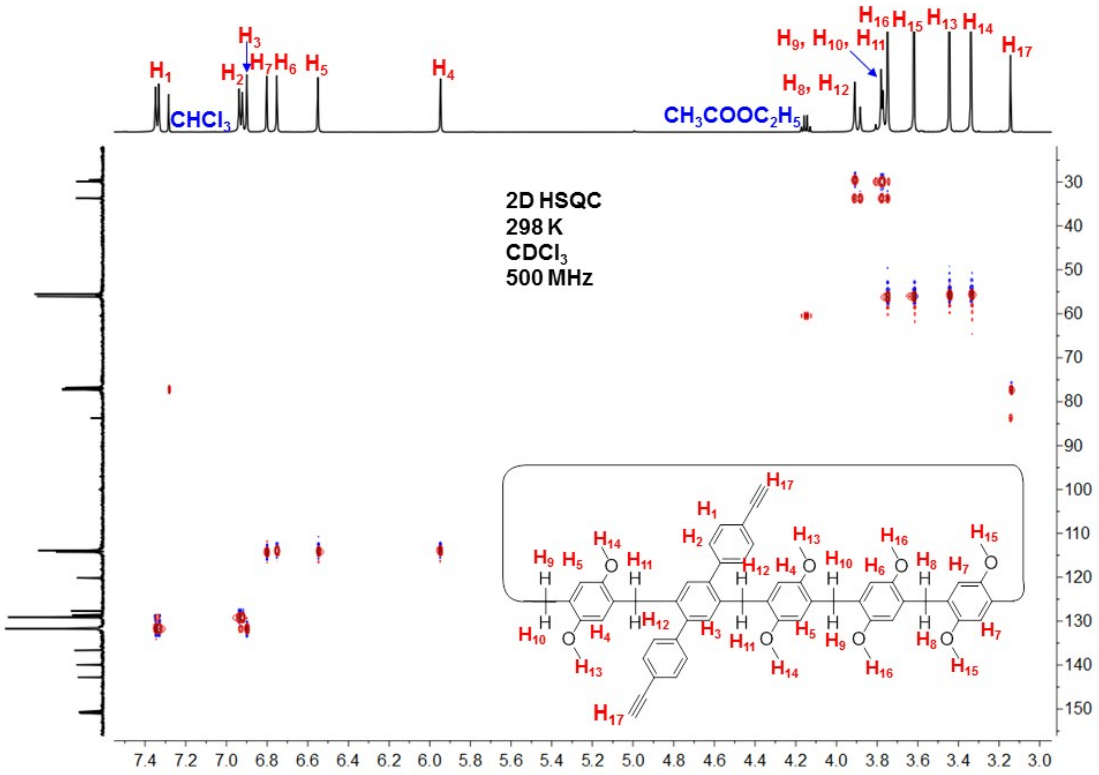
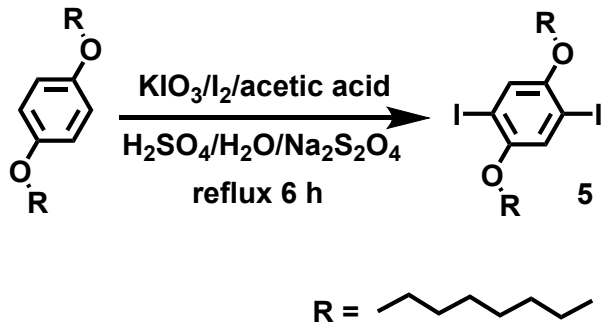


Figure S7. $^{1}H - {}^{13}C$ 2D HSQCNMR (500 MHz, chloroform-*d*, 298K) of **2**.

6. Single -Crystal X-Ray Crystallography of ***2***

Crystal Parameters. $[C_{59}H_{54}O(CH_2Cl_2)]$, *FW* 975.95, Colorless block (0.3 × 0.3 × 0.3 mm^3). Monoclinic, C2/c, a = 12.0691(8), b = 21.1780(13), c = 20.7260(12) Å, α= 90.00, β= 105.081(5), γ= 90.00º, V = 5115.1(5) $Å^3$, Z = 4, T = 213(2) K, ρ_{calc} = 1.267 g/cm3, μ = 0.183 mm^{-1}. Of a total of 16370 reflections which were collected, 6284 were unique (Rint = 0.052). Final R1(F2> 2σF2) = 0.0584 and wR2 = 0.1774. Goodness-of-fit (F_2) = 1.045. CCDC 1456830.

7. Synthesis of ***5***[S3]



1,4-Bis(octyloxy)benzene (4.78 g, 14.3 mmol), KIO_3 (1.22 g, 5.7 mmol) and I_2 (4.00 g, 15.8 mmol) were combined in 150 mL of acetic acid, 1.5 mL of H_2SO_4, and 15 mL

of H_2O. The mixture was refluxed for 6 h and then 20% aqueous $Na_2S_2O_4$ was added until the brown iodine color was gone. The precipitate was collected, rinsed with cold EtOH, and recrystallized twice from EtOH/$CHCl_3$ to yield 80% of analytically pure material (2.42 g). ^{1}H NMR (250 MHz, chloroform-*d*, room temperature) δ (ppm): 7.17 (s, 2H), 3.92 (t, J = 6.4 Hz, 4H), 1.85–1.74 (m, 4H), 1.52–1.43(m, 4H), 1.42 – 1.22 (m, 16H), 0.89 (t, J = 7.5 Hz, 4H).

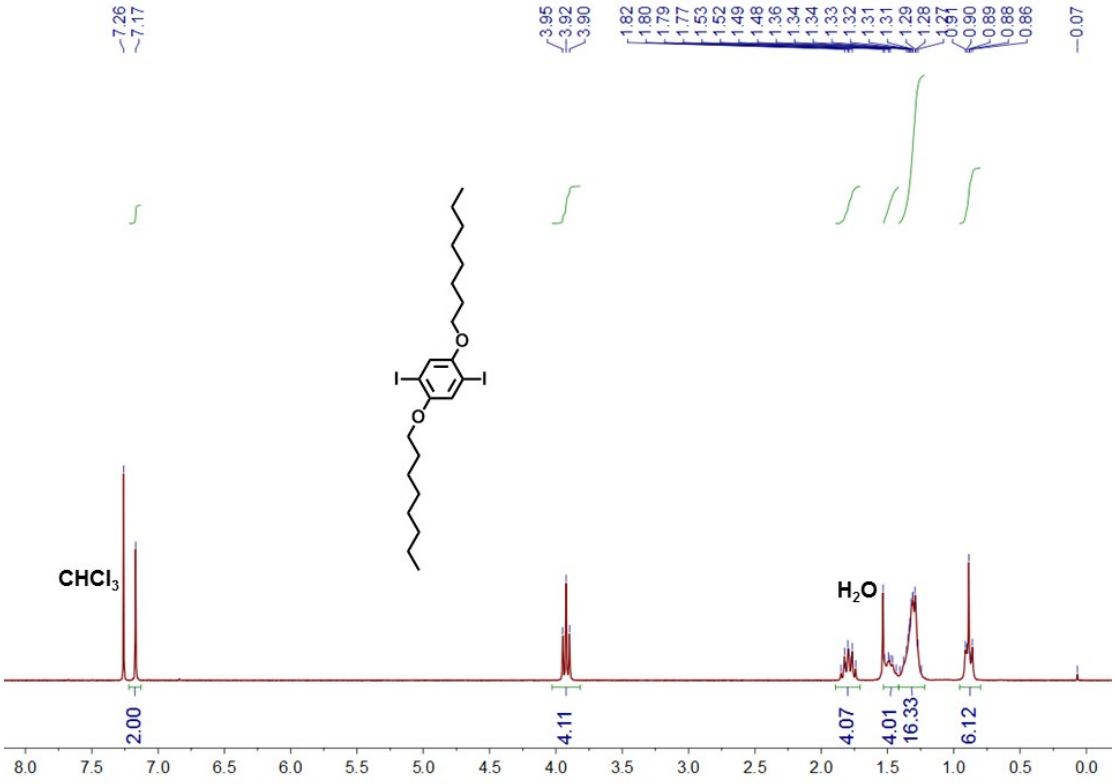
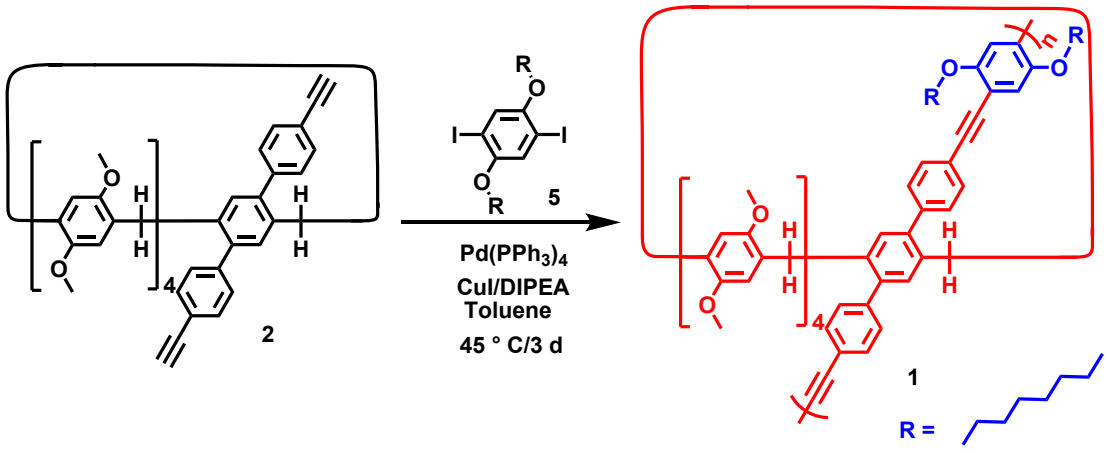


Figure S8. ^{1}H NMR spectrum (250 MHz, chloroform-*d*, room temperature) of **5**.

8. *Synthesis of **1***



To an oven-dried 10-mL Schlenk flask, 0.0197 g of diiodo **5** (0.0168 mmol, 1.00 equiv) and 0.031 g (0.0168 mmol, 1.03 equiv) of monomer **2** were added under argon. And 0.000390 g CuI (5 mol%), 0.00118 Pd(0)$[P(Ph)_3]_4$ (3mol%), 1.5 mL of toluene, and 0.5 mL diisopropylamine were added and the reaction was heated to 45 ºC for 3 d. Upon cooling, the reaction was extracted into dichloromethane. The organic layer was washed with aqueous ammonium chloride, dilute hydrochloric acid, and brine. The organic layer was dried with sodium sulfate and removed. The crude polymer was dissolved in a minimal amount of dichloromethane and precipitated into a rapidly stirring excess of methanol and the solid was collected by filtration. This process was repeated twice to obtain 0.040 g **1** as a white powder in 94 % yield. ^{1}H NMR (250 MHz, chloroform-*d*, room temperature) δ (ppm): 7.40 (d, J = 9.0 Hz, 4H), 7.09 (s, 2H), 6.96 (s, 6H), 6.81 (s, 2H), 6.74 (s, 2H), 6.55 (s, 2H), 5.97 (s, 2H), 4.11 (t, J = 6.3 Hz, 4H), 3.93 – 3.69 (m, 16H), 3.62 (s, 6H), 3.43 (s, 6H), 3.36 (s, 6H), 1.92 (t, J = 7.5 Hz, 4H), 1.41–1.25 (m, 20H), 0.87 (d, J = 5.0 Hz, 6H). GPC (THF, 30 °C, Polystyrene standards as calibrant): M_w = 61469; M_n = 16074; PDI = 3.82.

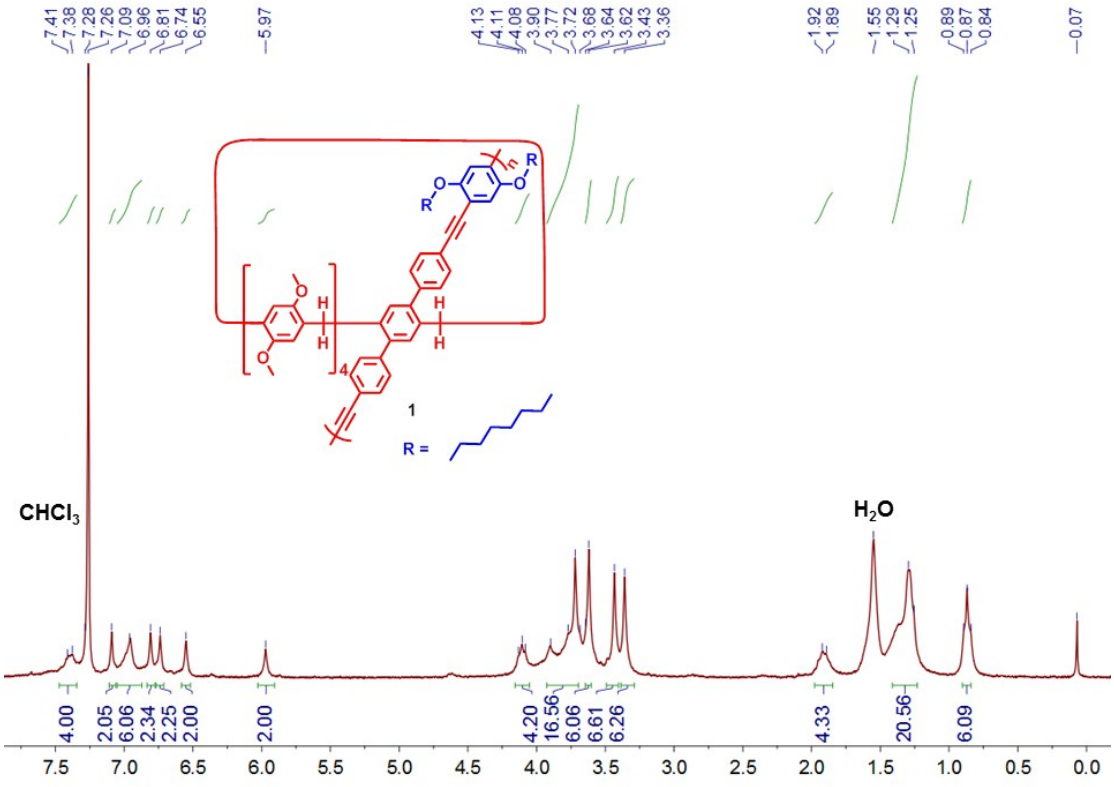


Figure S9. ^{1}H NMR spectrum (250 MHz, chloroform-*d*, room temperature) of **1**.

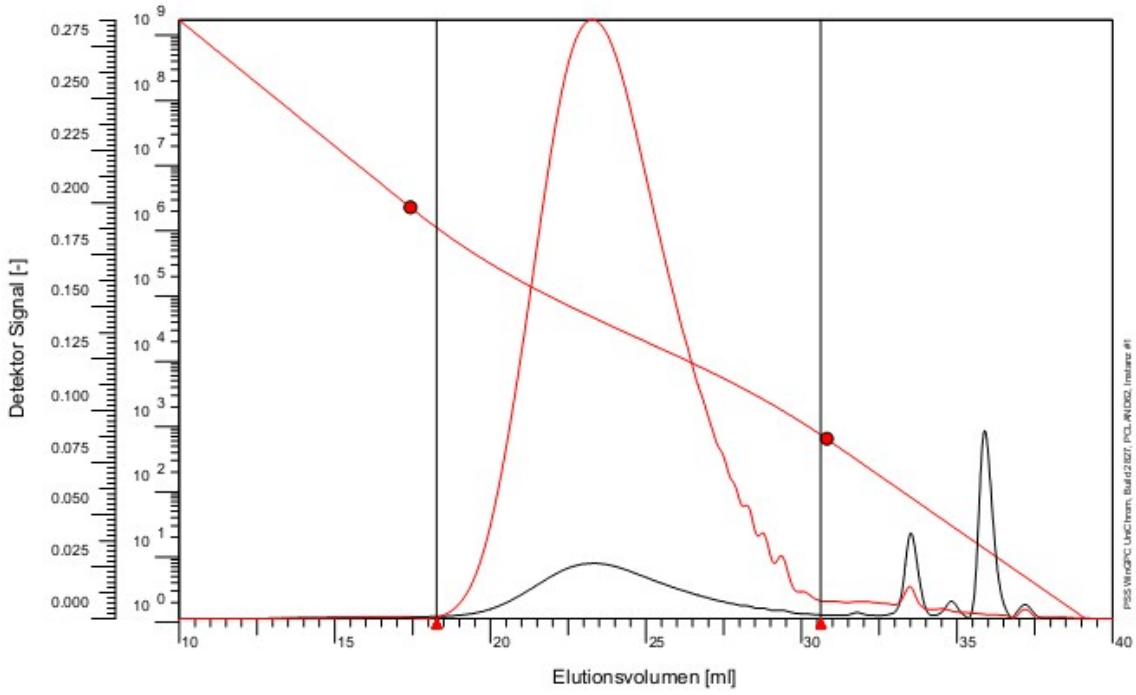


Figure S10. GPC traces of **1** (red line; THF eluent, calibrated against polystyrene standards).

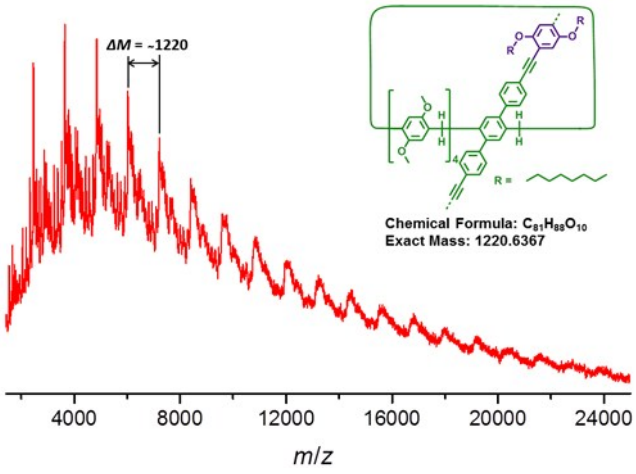


Figure S11. MALDI-TOF mass spectrum of 1 (matrix: DCTB).

References:

S1. C. Han, Z. Zhang, G. Yu and F. Huang, *Chem. Commun.* 2012, **48**, 9876–9878.

S2. N. L. Strutt, D. F. Jimenez, J. Iehl, M. B. Lalonde, R. Q. Snurr, O. K. Farha, J. T. Hupp, J. F. Stoddart, *J. Am. Chem. Soc.* **2012**, *134*, 17436− 17439.

S3. T. M. Swager, C. J. Gil, M.S. Wrighton, *J. Phys. Chem.* **1995**, *99*, 4886–4893.