Electronic Supplementary Material (ESI) for RSC Advances

A pillar[2]arene[3]hydroquinone which can self-assemble to a molecular zipper in the solid state

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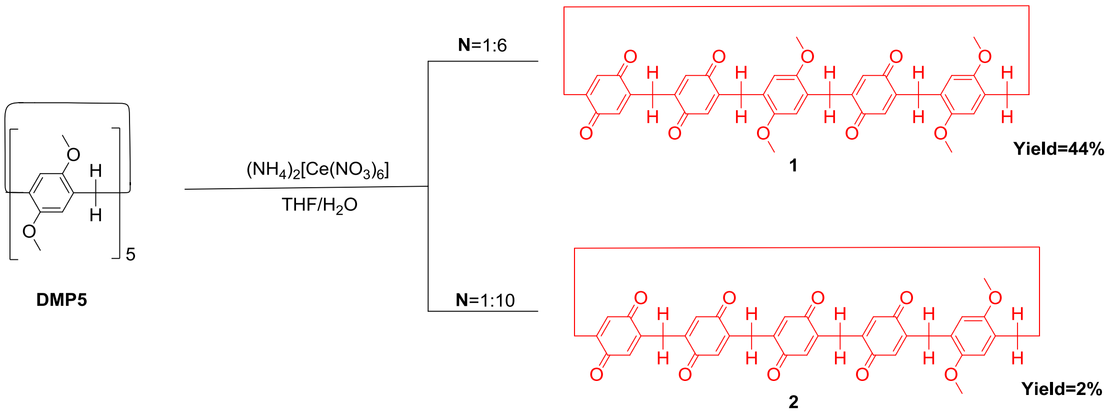
Electronic Supplementary Information

1. Materials and Methods:

1,4-dimethoxypillar[5]arene (DMP5) was synthesized according to literature procedures. All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. NMR spectra were recorded with a Bruker Advance DMX 400 spectrophotometer or a Bruker Advance DMX 500 spectrophotometer with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. The variable-temperature NMR experiment was carried out on Mercury NMR 300 MHZ. The cyclic voltammetry was carried out on a CHI650D potentiosat connected with a classical three-electrode electrochemical cell. Low-resolution electrospray ionization (LRESI) mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. High-resolution mass spectrometry experiments were performed with a Bruker Daltonics Apex III spectrometer or with a Bruker 7-Tesla FT-ICR mass spectrometer equipped with an electrospray source (Billerica, MA, USA). The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus.

*2. Synthesis of **1** and **2***



N means the molar ratio of DMP[5]/$(NH_4)_2[Ce(NO_3)_6]$

Scheme S1. Synthesis of **1** and **2**.

A solution of DMP5 (2.54 g, 3.38mmol) in THF (300 mL) was stirred in a 500 mL round–bottom flask while an aqueous solution $(NH_4)_2[Ce(NO_3)_6]$ (11.12g, 20.28mmol) was added dropwise. The mixture was stirred at room temperature for 24 h. The organic solvent was removed and water layer was extracted by dichloromethane (50 mL × 3). The combined organic phase was washed with water (100 mL) and saturated NaCl solution (100 mL), and dried over anhydrous Na_2SO_4. After being filtered and evaporated, the residue was purified by chromatography on silica gel (petroleum ether/dichloromethane, *v*/*v* 1:1 → 0:1) to obtain red solid **1** (0.99g, 44%). However, in this reaction condition, **2** is in a trace amount. Therefore, when the molar ratio of DMP[5]/($(NH_4)_2[Ce(NO_3)_6]$) increased up to 10 (DMP[5]: 2.50g), the yield of **2** (35mg) improved to 2%. **1** M.p. 202.4–203.3°C, **2** M.p. 86.2-87.5°C. The ^{1}H NMR spectrum of **1** is shown in Fig. S1. ^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ (ppm): 6.81 (s, 2H), 6.76 (br, 4H), 6.74 (s, 2H), 6.63(s, 2H), 3.80 (s, 2H), 3.78 (s, 6H), 3.76 (s, 6H), 3.62 (br, 8H), 3.47 (s, 2H). The ^{13}C NMR spectrum of **1** is shown in Fig. S2. ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ (ppm): 188.44, 187.64, 187.45, 151.04, 150.97, 146.75, 146.27, 143.10, 135.29, 133.39, 133.34, 124.93, 124.40, 114.23, 113.87, 55.98, 55.83, 27.97, 27.63, 25.83. The LRESIMS of **1** is shown in Fig. S3. LRESIMS: *m*/*z* 682.7[M + Na]$^+$ (100%), 660.7[M + H]$^+$ (25%). HRESIMS: *m*/*z* calcd for [M+Na]$^+$ $C_{39}H_{32}O_{10}Na^+$, 683.1888, found 683.1878, error 1.41 ppm. The ^{1}H NMR spectrum of **2** is shown in Fig. S4. ^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ (ppm): 6.82(s, 2H), 6.78(s, 2H), 6.76(s, 2H), 6.72(s, 2H), 6.67(s, 2H), 3.79(s, 6H), 3.64(s, 4H), 3.48(br, 6H). The ^{13}C NMR spectrum of **2** is shown in Fig. S5. ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ (ppm): 185.53, 185.45, 184.69, 184.53, 149.06, 145.02, 141.84, 141.48, 141.05, 133.56, 133.39, 131.35, 122.81, 112.10, 54.07, 25.92, 24.61, 24.20. The LRESIMS of **2** is shown in Fig. S6. LRESIMS: *m*/*z* 631.2 [M + H]$^+$ (100%). HRESIMS: *m*/*z* calcd for [M+Na]$^+$ $C_{37}H_{26}O_{10}Na^+$, 653.1418, found 653.1403, error 2.29 ppm.

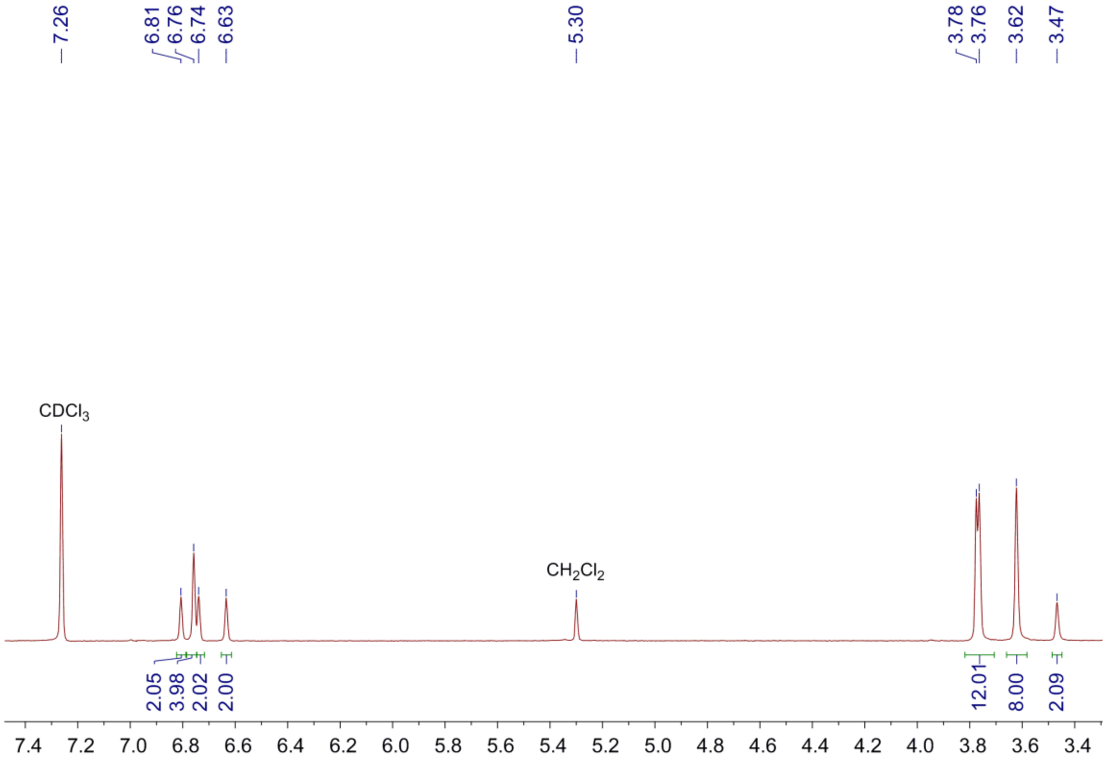


Fig. S1 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of **1**.

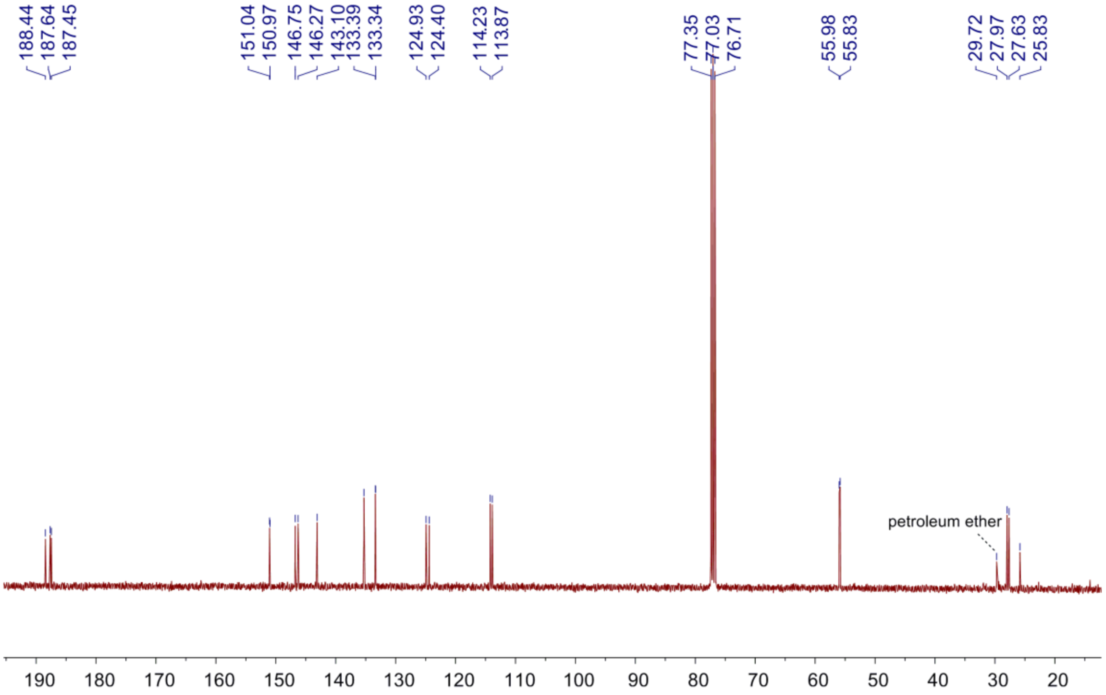


Fig. S2 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) of **1**.

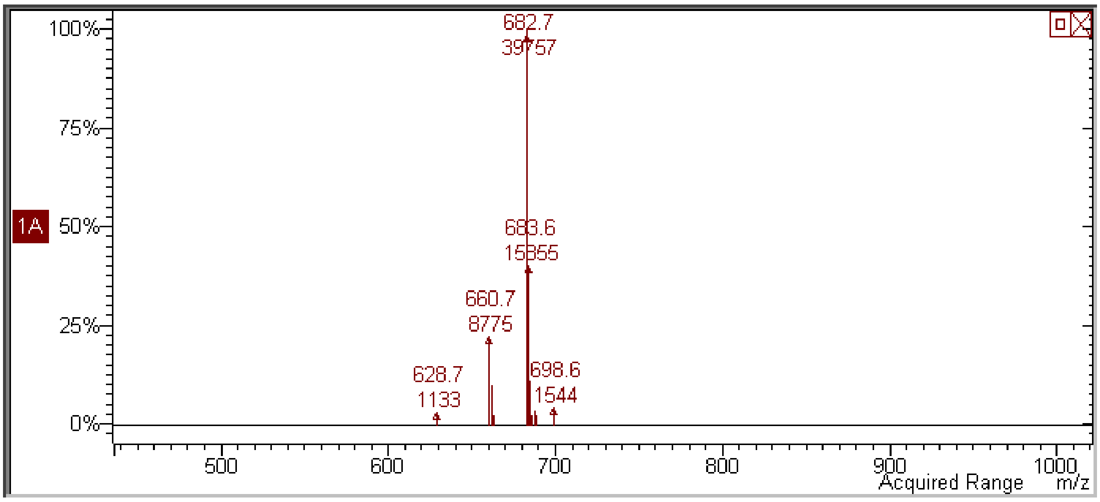


Fig.S3 Positive electrospray ionization mass spectrum of **1**.

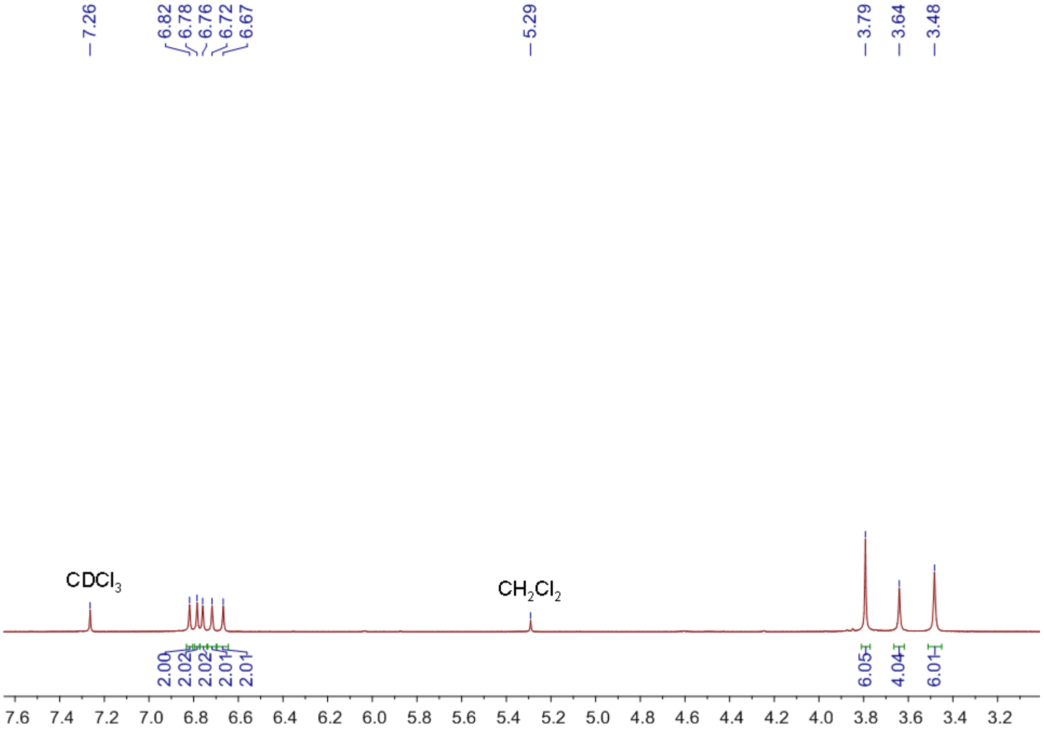


Fig. S4 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of **2**.

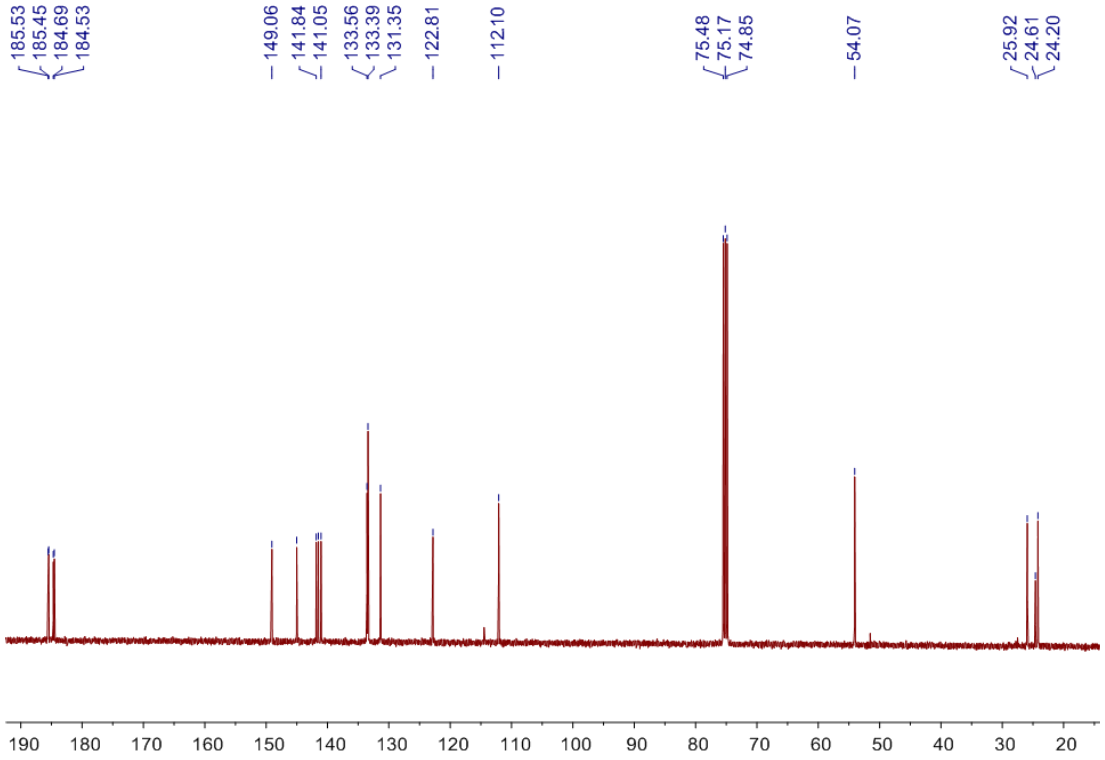


Fig. S5 ^{13}C NMR spectrum (100 MHz, CDCl$_3$, room temperature) of **2**.

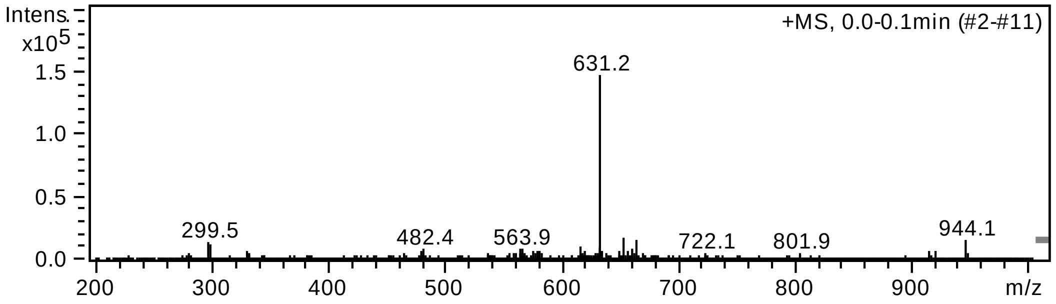
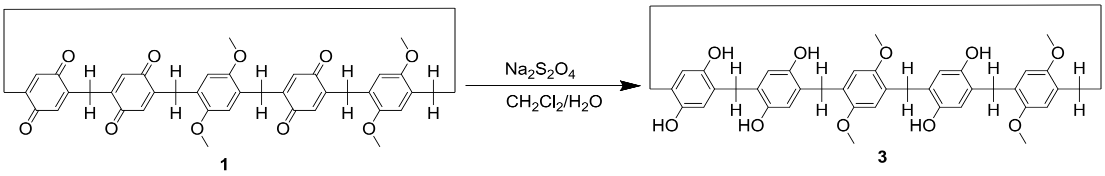


Fig.S6 Positive electrospray ionization mass spectrum of **2**.

3. *Synthesis of **3***



Scheme S2. Synthesis of **3**.

A solution of **1** (110 mg, 0.175 mmol) in CH_2Cl_2 (100 ml) was stirred in a 250 mL round–bottom flask while an aquous solution $Na_2S_2O_4$ (1.77g, 10.17 mmol) was added. The mixture was stirred roughly at room temperature for 1.0 h. The white products partly dissolved out from CH_2Cl_2. Then added 10mL water to the solution. The water layer was extracted by CH_2Cl_2 several times until the organic layer was clear and the white solid was not observed. After being spin dried and vacuum drying, **3** was obtained as a white solid quantitatively (111 mg). M.p. ＞250℃. The ^{1}H NMR spectrum of **3** is shown in Fig. S7. ^{1}H NMR (400 MHz, DMSO-d_6, room temperature) δ (ppm): 8.35(s, 2H), 8.24(s, 2H), 8.23(s, 2H), 6.91(s, 2H), 6.85(s, 2H), 6.61(s, 2H), 6.59(s, 2H), 6.58(s, 2H), 3.67(br, 12H), 3.54(br, 8H), 3.44(s, 2H). The ^{13}C NMR spectrum of **3** is shown in Fig. S8. ^{13}C NMR (100 MHz, DMSO-d_6, room temperature) δ (ppm): 149.62, 149.61, 146.39, 146.37, 146.10, 128.04, 128.02, 126.44, 126.26, 126.19, 117.62, 117.49, 117.21, 113.74, 113.39, 55.65, 28.98, 28.74, 28.45. The LRESIMS of **3** is shown in Fig. S9. LRESIMS: *m*/*z* 665.6 $[M - H]^+$ (100%). HRESIMS: *m*/*z* calcd for $[M - H]^+$ $C_{39}H_{37}O_{10}^+$, 665.2392, found 665.2424, error -4.75 ppm.

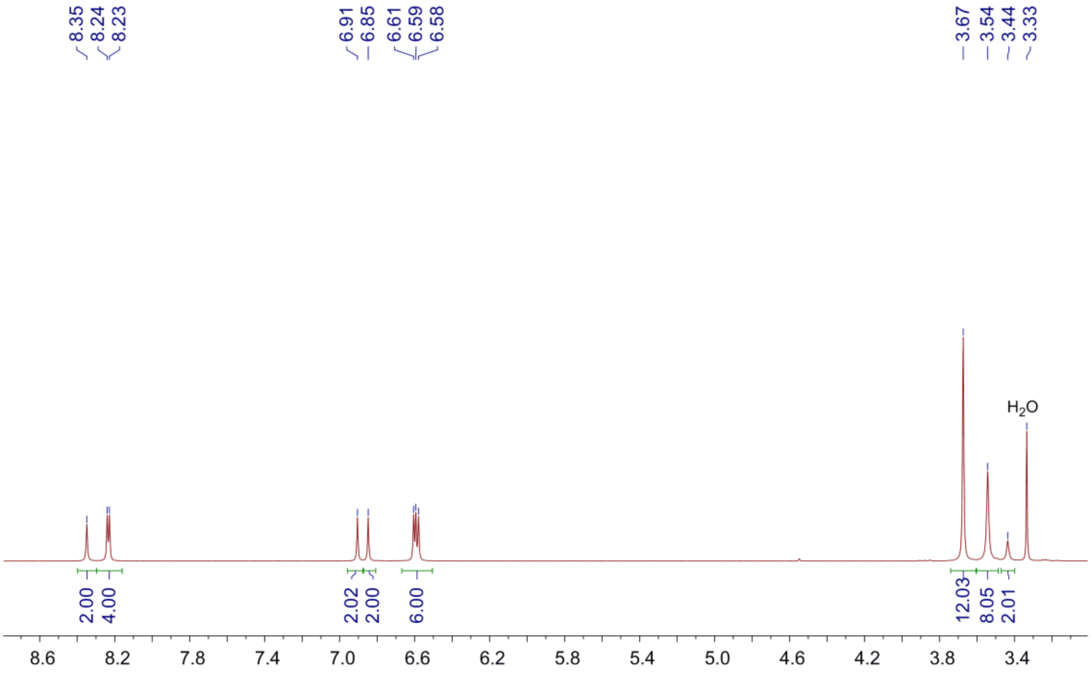


Fig. S7 ^{1}H NMR spectrum (400 MHz, DMSO-d_6, room temperature) of **3**.

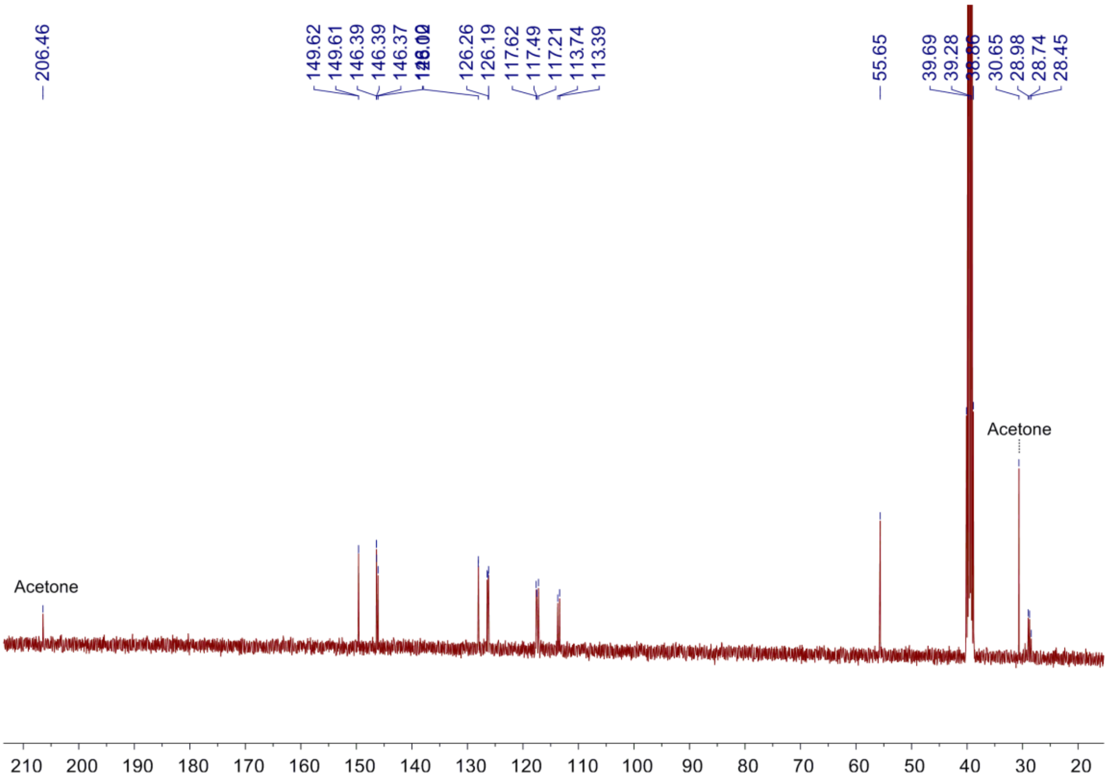


Fig. S8 ^{13}C NMR spectrum (100 MHz, DMSO-d_6, room temperature) of **3**.

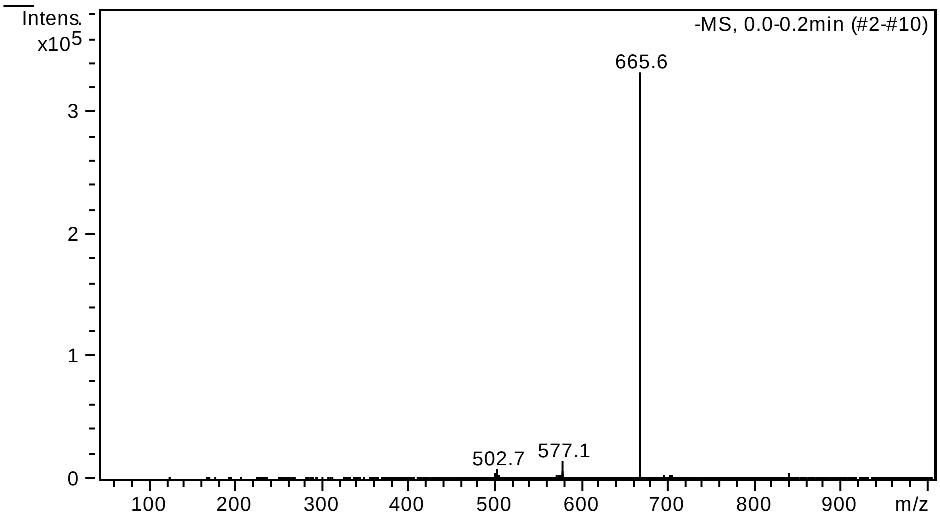
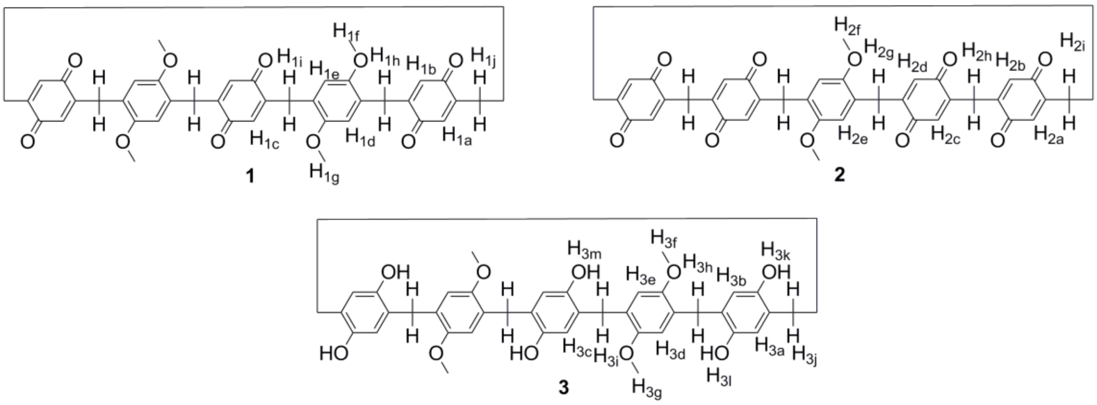


Fig.S9 Negative electrospray ionization mass spectrum of **3**.

4. *Partial ^{1}H NMR spectra of **1**, **2** and **3***



Scheme S3. Chemical structures of ***1*, *2*, *3***.

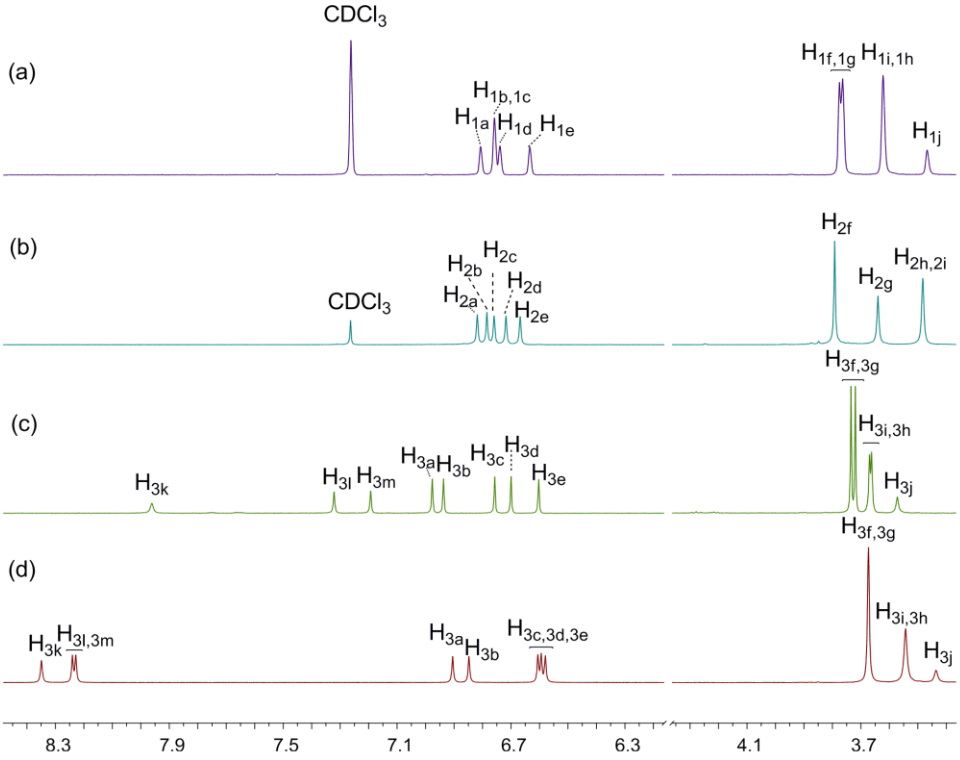


Fig.S10 Partial ^{1}H NMR spectra (400 MHz, 20 °C) of (a) **1**; (b) **2**; (c) **3**; (d) **3**. (a) and (b) in $CDCl_3$, (c) in acetone-d_6, (d) in DMSO-d_6.

5. *X-ray crystal data of **1**, **2** and **3***

Crystal data of ***1***: red, $C_{40}H_{34}Cl_2O_{10}$, *FW* 745.57, monoclinic, space group *P 21/n*, $a = 11.5284(2)$, $b = 15.3983(3)$, $c = 20.2646(4)$ Å, $\alpha = 90.00°$, $\beta = 91.7392(17)$ °, $\gamma = 90.00°$, $V = 3595.67(11)$ Å^{3}, $Z = 4$, $D_c = 1.377$ g cm^{-3}, $T = 170(2)$ K, $\mu = 2.129$ mm^{-1}, 18937 measured reflections, 6408 independent reflections, 473 parameters, 0 restraints, $F(000) = 1552$, $R_1 = 0.0644$, $wR_2 = 0.1695$ (all data), $R_1 = 0.0580$, $wR_2 = 0.1623$ [$I > 2\sigma(I)$], max. residual density 1.175e•Å^{-3}, and goodness-of-fit (F^2) = 1.074. CCDC 938940.

Crystal data of **2**: red, $C_{43}H_{35}N_3O_{10}$, *FW* 753.74, monoclinic, space group *P 21/c*, a = 12.0359(3), b = 21.1081(5), c = 14.8313(4) Å, α = 90.00°, β = 98.540(3)°, γ = 90.00°, V = 3726.19(16) $Å^3$, Z = 4, D_c = 1.344 g cm^{-3}, T = 170(2) K, μ = 0.799 mm^{-1}, 13643 measured reflections, 6549 independent reflections, 510 parameters, 0 restraints, $F(000)$ = 1576, R_1 = 0.0714, wR_2 = 0.1761 (all data), R_1 = 0.0580, wR_2 = 0.1618 [$I > 2\sigma(I)$], max. residual density 1.158e•$Å^{-3}$, and goodness-of-fit (F^2) = 1.036. CCDC 938941.

Crystal data of **3**: colorless, $C_{45}H_{50}O_{12}$, *FW* 782.85, Triclinic, space group *P-1*, a = 10.3617(4), b = 12.5519(7), c = 17.8498(9) Å, α = 70.793(5)°, β = 86.489(4)°, γ = 66.809(4)°, V = 2008.92(17) $Å^3$, Z = 2, D_c = 1.294 g cm^{-3}, T = 170(2) K, μ = 0.769 mm^{-1}, 15832 measured reflections, 7117 independent reflections, 528 parameters, 0 restraints, $F(000)$ = 832, R_1 = 0.0665, wR_2 = 0.1763 (all data), R_1 = 0.0581, wR_2 = 0.1642 [$I > 2\sigma(I)$], max. residual density 0.468e•$Å^{-3}$, and goodness-of-fit (F^2) = 1.033. CCDC 938943.

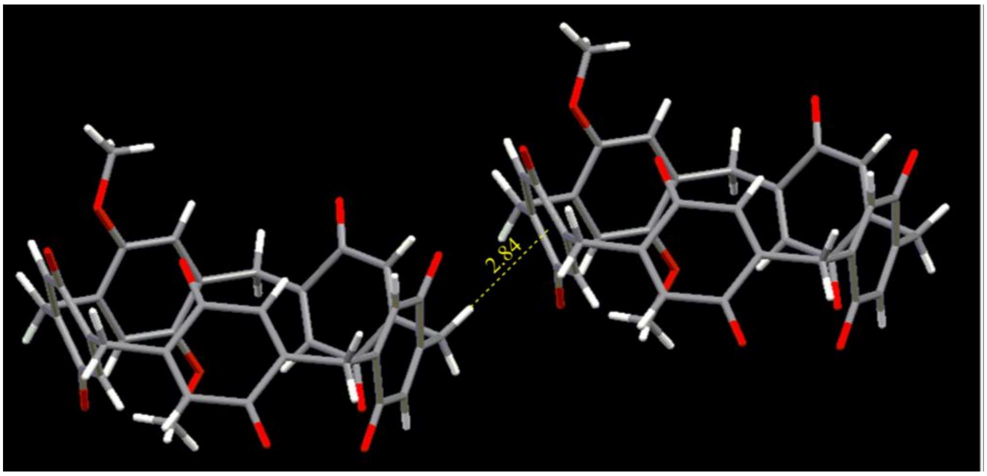


Fig. S11 A capped-stick views of the crystal structures of **2**. Carbon atoms are black, hydrogen atoms are white, oxygen atoms are red. The yellow dotted line denotes C-H···π interactions. (C-H···π: 2.84 Å).

6. *Cyclic voltammogram of* **3**

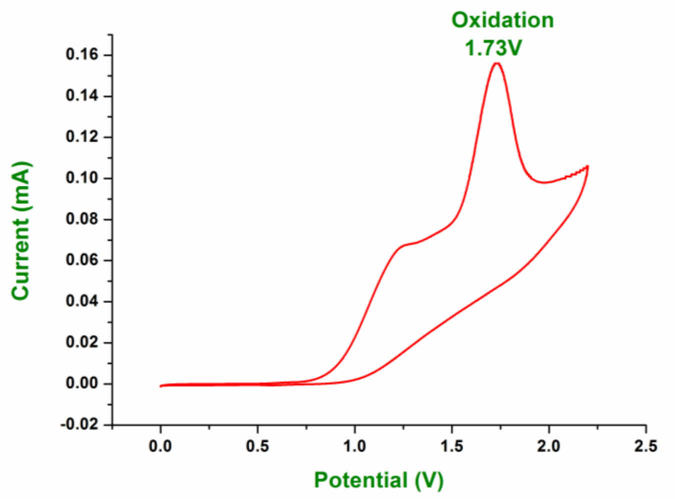


Fig. S12 Cyclic voltammogram of **3** (0.5 mM) in mixed solutions ($CHCl_3/CH_3CN$ = 5:1, *v*/*v*, containing 0.1 M $TBAClO_4$) at a scan rate of 5 mV/s using tin doped indum oxide as working electrode.

7. Different views of molecular zipper

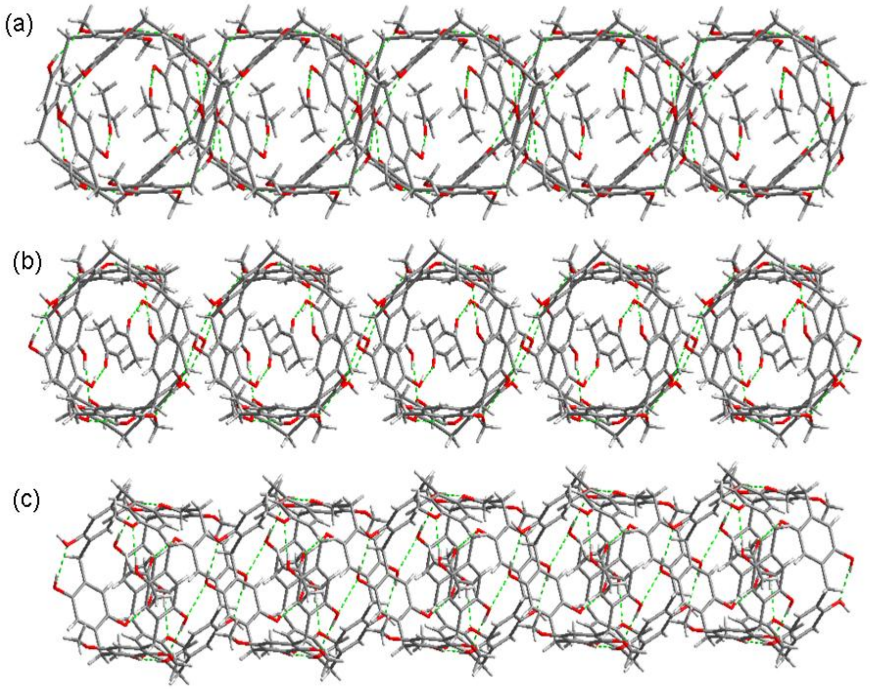


Fig. S13 Different views of molecular zipper (a), (b), (c). The irrelevant solvent molecules were omitted for clarity. Carbon atoms are dark grey, hydrogen atoms are light-grey, and oxygen atoms are red. The bright green dotted line denotes the hydrogen bonds.