Chemical-responsive control of the lower critical solution temperature behavior by pillar[10]arene-based host−guest interactions

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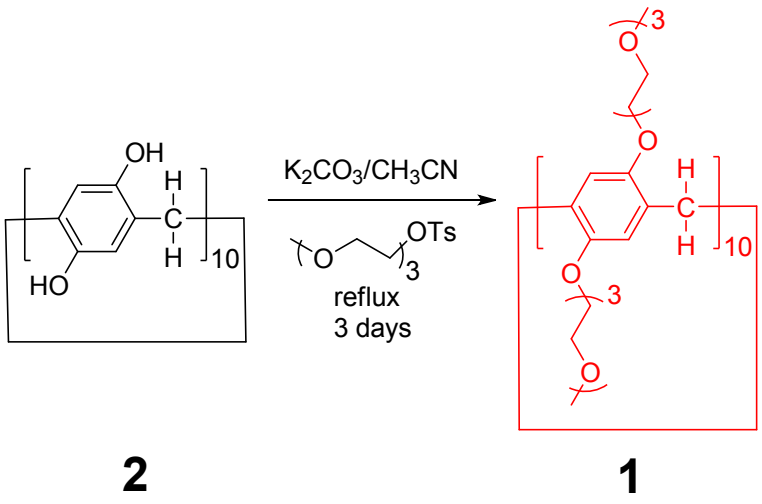
Electronic Supplementary Information (10 pages)

1. Materials and methods:

Pillar[10]arene **2**[S1] was synthesized according to a literature procedure. Solvents were either employed as purchased or dried according to procedures described in the literature. ^{1}H NMR spectra were collected on a temperature-controlled 400 MHz spectrometer. ^{13}C NMR spectra were recorded on a Bruker AVANCE DMX-500 spectrometer at 125 MHz. 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. UV-vis spectroscopy was performed on a Shimadzu UV-2550 instrument at room temperature. Isothermal titration calorimetric (ITC) measurements were performed on a VP-ITC micro-calorimeter (Microcal, USA).

*2. Synthetic route to pillar[10]arene **1***



2 **1**

Scheme S1 Synthetic route to pillar[10]arene **1**.

*3. Synthesis of pillar[10]arene **1***

per-Hydroxylated pillar[10]arene **2** (0.25 g, 0.21 mmol)[S1] was dissolved in CH_3CN (50 mL). K_2CO_3 (0.85 g, 6.2 mmol) was added and the reaction mixture was stirred. Then triethylene glycol monomethyl ether mono-*p*-tosylate (1.98 g, 6.2 mmol)

was added and the reaction mixture was stirred under N_2 at reflux for 3 days. The solvent was evaporated and the residue was dissolved in CH_2Cl_2. The resultant solution was washed with H_2O and brine. The organic phase was collected, dried over anhydrous Na_2SO_4 and concentrated to give a crude liquid. Column chromatography (silica gel; CH_2Cl_2 : CH_3OH = 20 : 1) afforded a light yellow liquid (174 mg, 20%). The ^1H NMR spectrum of pillar[10]arene **1** is shown in Figure S1. ^1H NMR (400 MHz, $CDCl_3$, room temperature) δ (ppm): 6.65 (s, 20H), 3.94 (t, J = 8.0 Hz, 40H), 3.81 (s, 20H), 3.71 (t, J = 8.0 Hz, 40H), 3.65-3.55 (m, 120H), 3.50-3.45 (m, 40H), 3.32 (s, 60H) The ^{13}C NMR spectrum of pillar[10]arene **1** is shown in Figure S2. ^{13}C NMR (125 MHz, $CDCl_3$, room temperature) δ (ppm): 150.68, 127.93, 115.18, 71.88, 70.47, 70.33, 69.94, 68.48, 58.88, 29.75. LRESIMS: m/z 2090.1 $[M + H + K]^{2+}$ (100%). HRMALDIMS: m/z calcd. for $[M + H + K]^{2+}$ $C_{210}H_{341}O_{80}K$, 2090.1270, found 2090.1240.

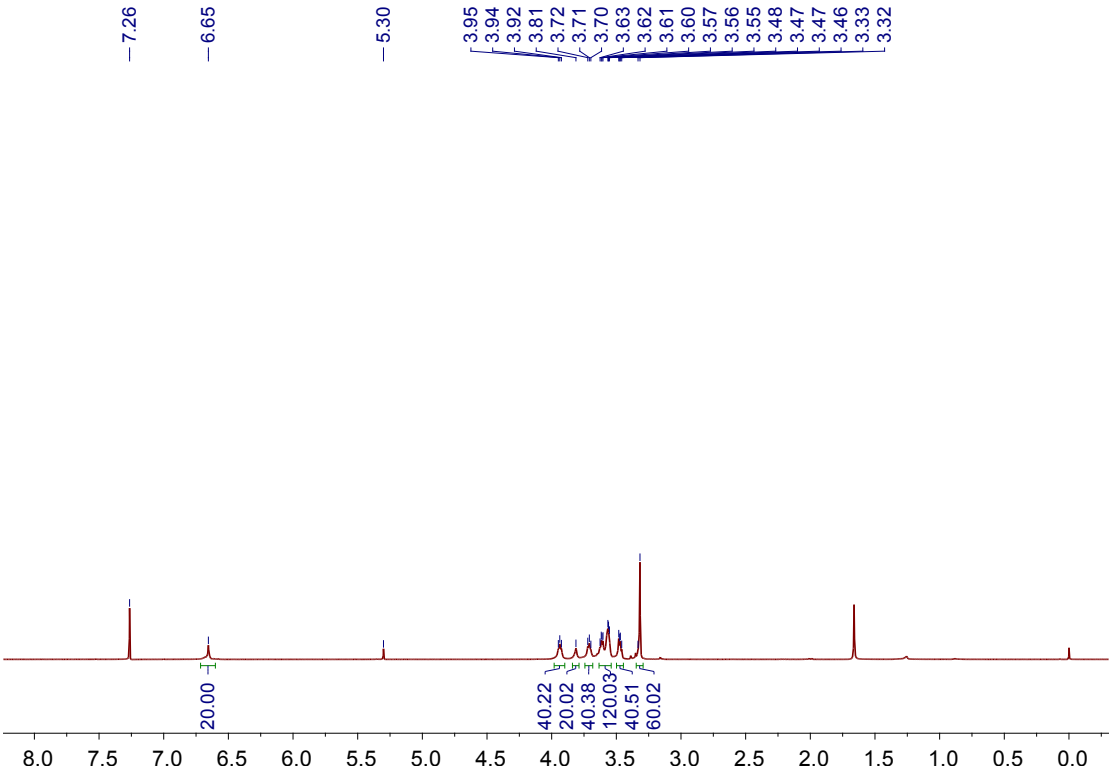


Fig. S1 ^1H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of pillar[10]arene **1**.

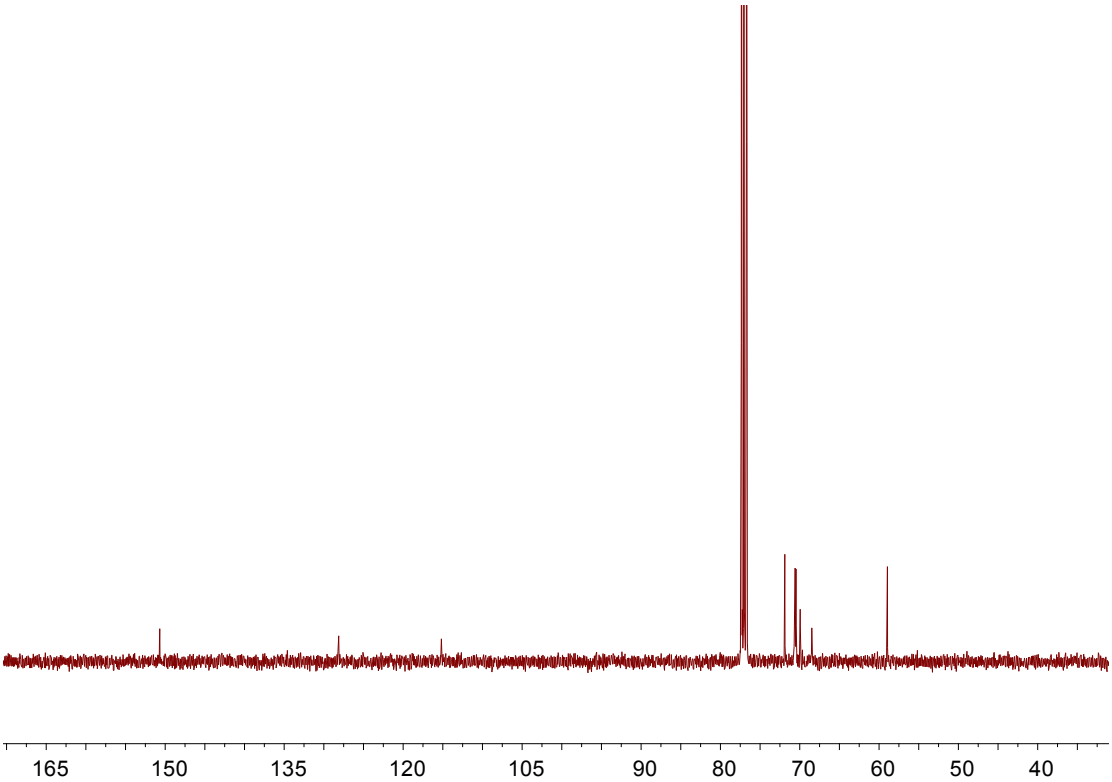


Fig. S2 ^{13}C NMR spectrum (125 MHz, $CDCl_3$, room temperature) of pillar[10]arene **1**.

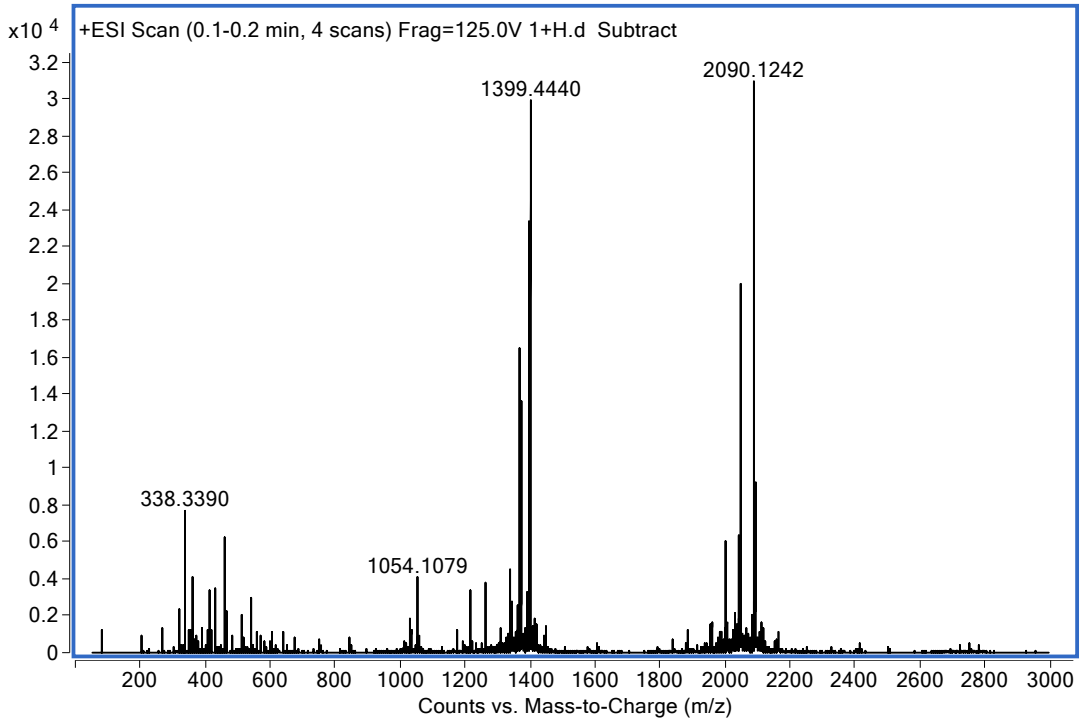


Fig. S3 LRESI mass spectrum of pillar[10]arene **1**. Assignment of the main peak: *m*/*z* 2090.1242 $[M + K]^+$ (100%).

*4. Stoichiomestry and association constant determination for the complexation between **1** and **G***

Isothermal titration calorimetric measurements were performed on a VP-ITC micro calorimeter (Microcal, USA), which is composed of a reference cell and a sample cell of 1.43 mL. Stock solutions of host (0.100 mM, 10.0 mL) and guest (2.00 mM, 5.00 mL) in water were prepared using volumetric glassware. Before each titration, all the solutions were degassed and kept constant temperature. In a typical run, a 250 μL syringe was full of guest (2.00 mM) and the cell was loaded with host (0.100 mM, 1.43 mL). The titration of the host with the guest was carried out at 298 K with a constant rate of 307 rpm, 29 injections of 3.3 μL, a time interval of 240 s and a duration of 2 s per μL. The enthalpy change per mole of each added **G** in the sample cell was recorded continuously. The control titrations of **G** into water were also completed under the same conditions. The enthalpy changes of the titrations of the blank test were subtracted from the original titration. All the data were analyzed with Microcal Origin 7.0 software provided by the manufacturer. The final integration data obtained from the titration were fitted by the one set of binding site model

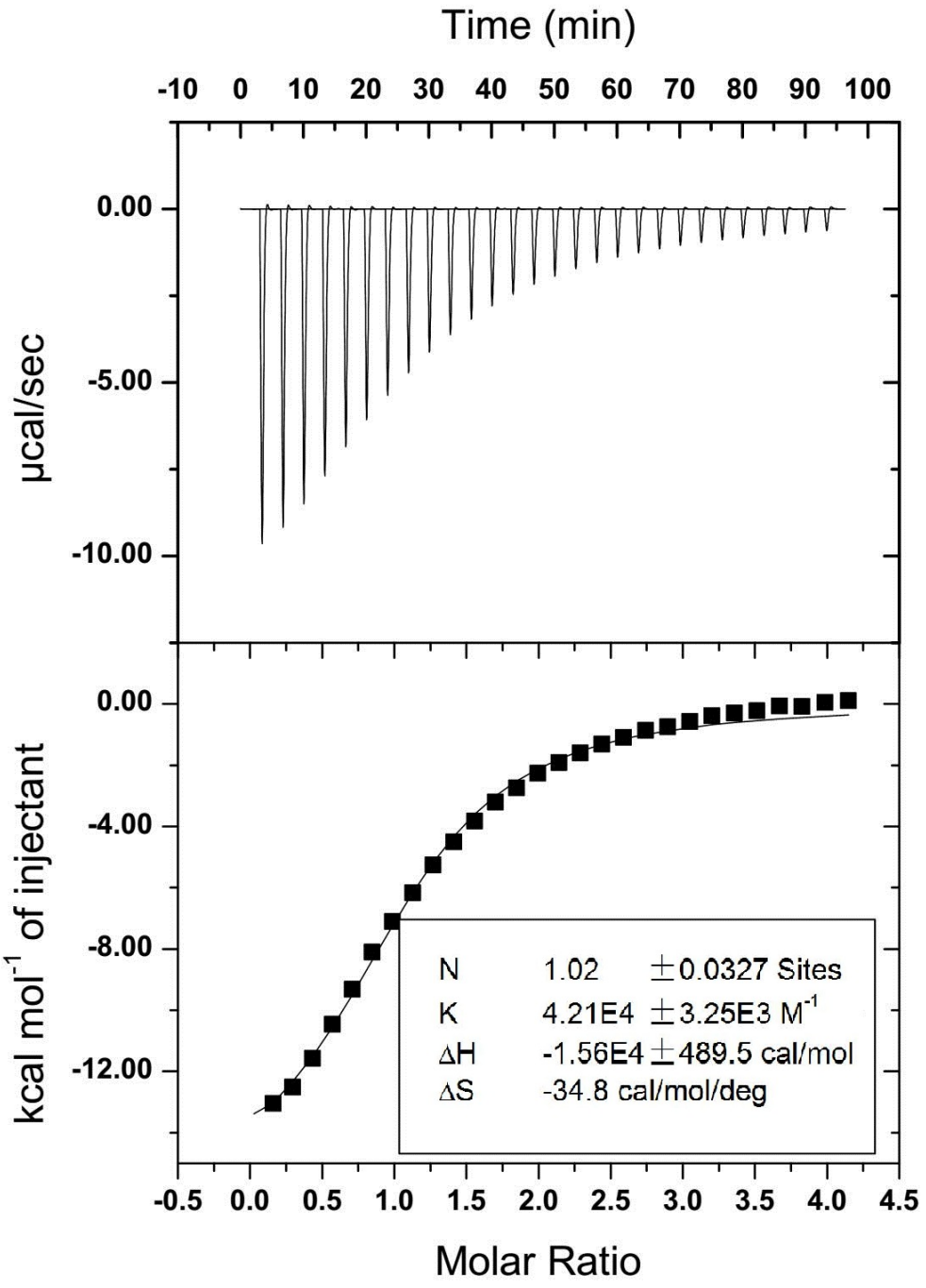


Fig. S4 Titration of **1** (0.100 mM) with **G** (2.00 mM) in water at 298 K.

*5. UV-vis spectroscopy investigation of the complexation between **1** and **G** in acetonitrile*

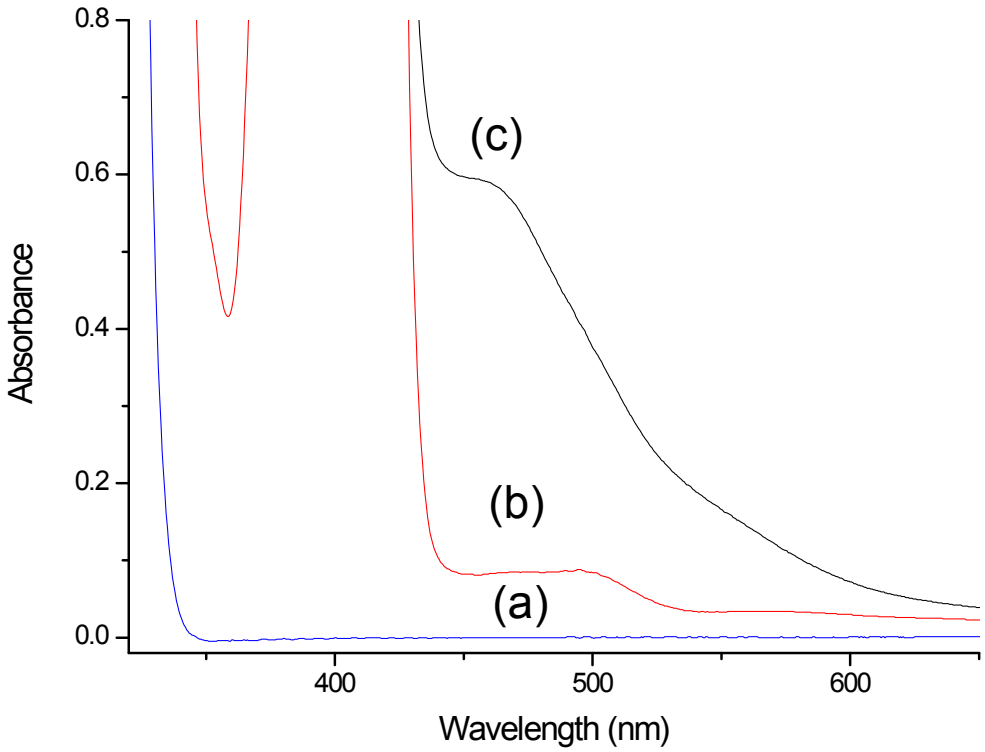


Fig. S5 UV-vis spectra of (a) 1.00×10^{-3} M **1**, (b) 1.00×10^{-3} M **G**, and (c) 1.00×10^{-3} M **1** with equimolar **G** in water at room temperature.

6. Temperature dependence of light transmittance of an aqueous solution of **1** (2.00 mM) upon addition of G (0−3.20 mM) on heating.

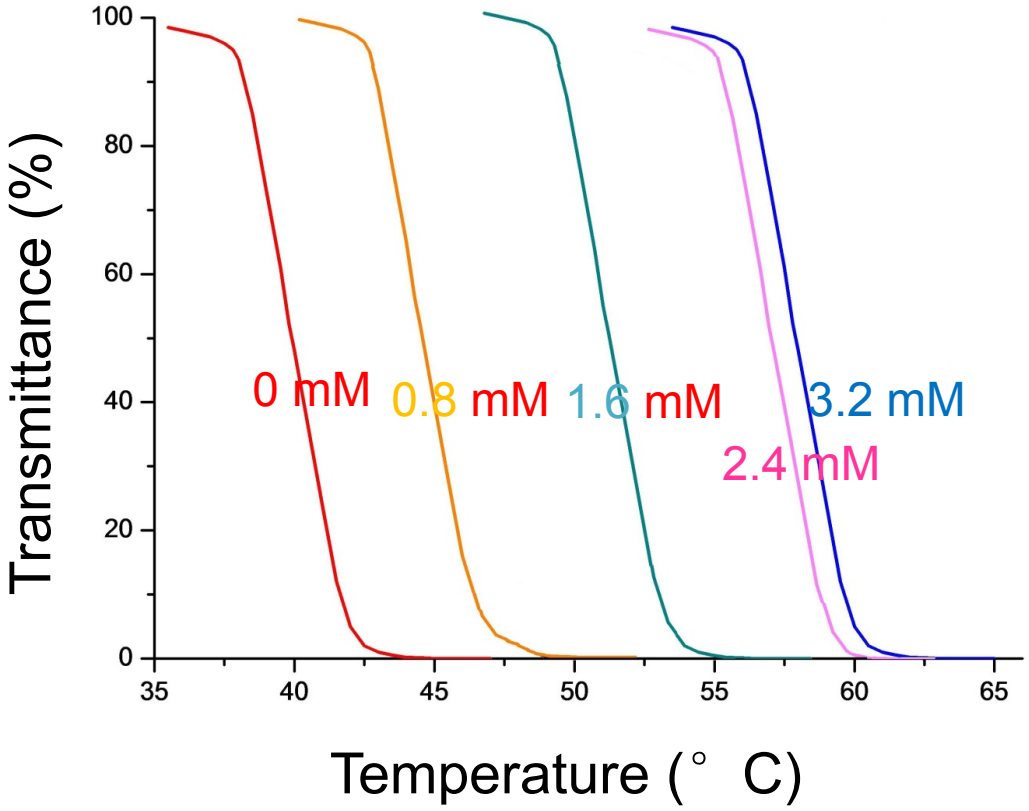


Fig. S6 Temperature dependence of light transmittance of an aqueous solution of **1** (2.00 mM) upon addition of G (0−3.20 mM) on heating.

7. The host–guest complexation between 1 and G

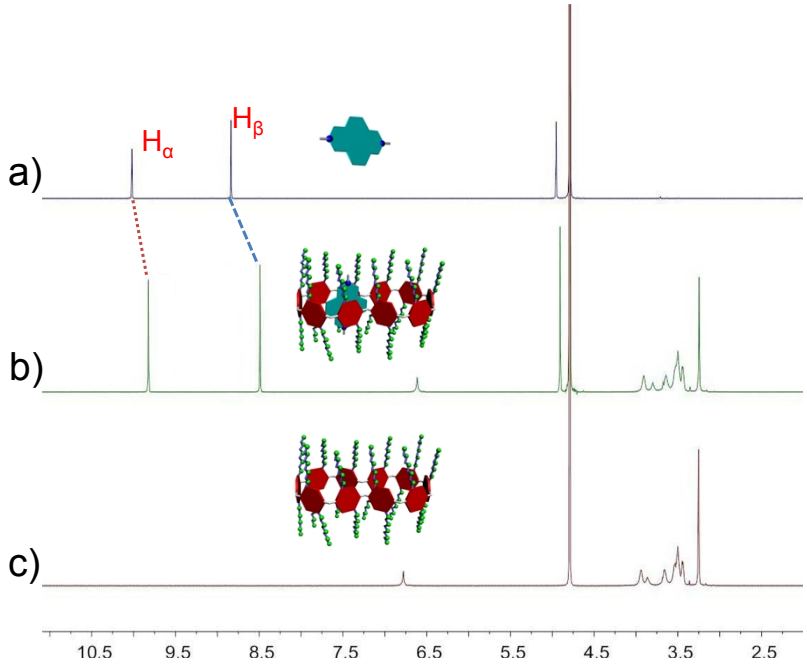


Fig. S7 Partial ^{1}H NMR spectra (400 MHz, D_2O, 25 °C): (a) 1.00 mM **G**; (b) 1.00 mM **1** and 1.00 mM **G**; (c) 1.00 mM **1**.

References:

S1. J. Yang, X. Chi, Z. Li, G. Yu, J. He, Z. Abliz, N. Li and F. Huang, *Org. Chem. Front.*, 2014, **1**, 630.