Electronic Supplementary Material (ESI) for ChemComm.

A Cu^{2+} specific metallohydrogel: preparation, multi-responsiveness and pillar[5]arene-induced morphology transformation

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Electronic Supplementary Information (13 pages)

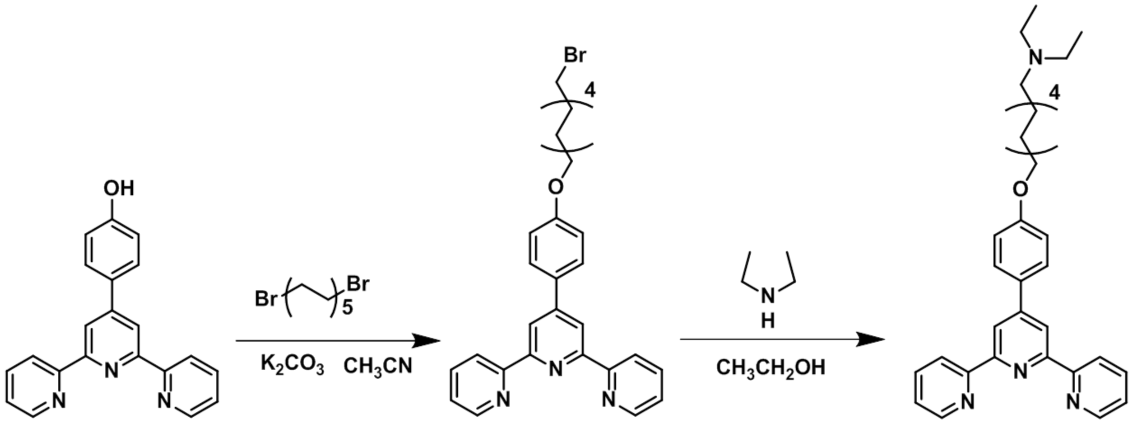
1. Materials and methods

All reagents including model compound **M1** 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. Water-soluble pillar[5]arene was prepared according to a published procedure.[S1] ^{1}H NMR and ^{13}C HMR spectra were recorded with a Bruker Avance DMX 400 spectrophotometer using the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Low-resolution electrospray ionization mass spectra were recorded with a Bruker Esquire 3000 Plus spectrometer. High-resolution mass spectrometry experiments were performed with IonSpec 4.7 Tesla FTMS. Transmission electron microscopy investigations were carried out on a HITACHI HT-7700 instrument. Scanning electron microscopy investigations were carried out on a HITACHI SU-8010 instrument. UV-Vis spectra were taken on a PerkinElmer Lambda 35 UV-Vis spectrophotometer.

*2. Syntheses of compound **1** and model compound **M2***

*2.1 Synthesis of compound **1***

Scheme S1. Synthetic route to **1**.



1

4-([2,2':6',2''-terpyridin]-4'-yl)phenol (3.25 g, 10 mmol) and potassium carbonate (5.52 g, 40 mmol) was added to a solution of 1,10-dibromodecane (6.00 g, 20 mmol) in ethanol (350 mL) under vigorous stirring. The mixture was refluxed at 80 ℃ for 16 hours. After removal of the inorganic salt, the solvent was evaporated and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 10:1) to give the crude product as a white solid. A mixture of the crude product with excess diethylamine (30 equiv) were dissolved in ethanol and refluxed for 24 h. The solvent was evaporated, and the residue was poured into a NaOH solution (1.00 M, 400 mL) and stirred. The solution was extracted with ethyl acetate (3 × 100 mL), and the organic phase was obtained. The oil yellow liquid was isolated after evaporation of the solution as the crude product, which was distilled in vacuo to give **1** as a solid. The yield of **1** was 87%. The ^1H NMR spectrum of **1** is shown in Fig. S1. ^1H NMR (400 MHz, chloroform-*d*, 293 K) δ (ppm): 1.04–1.08 (t, J = 8 Hz, 6H), 1.26–1.31 (m, 14H), 1.41–1.49 (m, 4H), 1.79–1.86 (m, 2H), 2.39–2.43 (t, J = 8 Hz, 2H), 2.50–2.55 (m, 4H), 4.01–4.05 (t, J = 8 Hz, 2H), 7.01–7.03 (d, 2H), 7.37–7.34 (m, 2H), 7.90–7.86 (m, 4H), and 8.66–8.74 (m, 6H). The ^{13}C NMR spectrum of **1** is shown in Fig. S2. ^{13}C NMR (100 MHz, chloroform-*d*, 293 K) δ (ppm): 160.14, 156.44, 155.83, 149.84, 149.11, 136.86, 130.48, 128.49, 123.75, 121.38, 118.25, 114.86, 76.70, 68.15, 52.96, 46.85, 29.63, 29.57, 29.54, 29.41, 29.28, 27.74, 26.85, 26.06, 11.57. LRESIMS is shown in Fig. S3: *m*/*z* 537.4 [**1** + H]$^+$. HRESIMS is shown in Fig. S4: *m*/*z* calcd for [**1** + H]$^+$ $C_{35}H_{45}N_4O^+$, 537.3588; found 537.3578; error – 1.9 ppm.

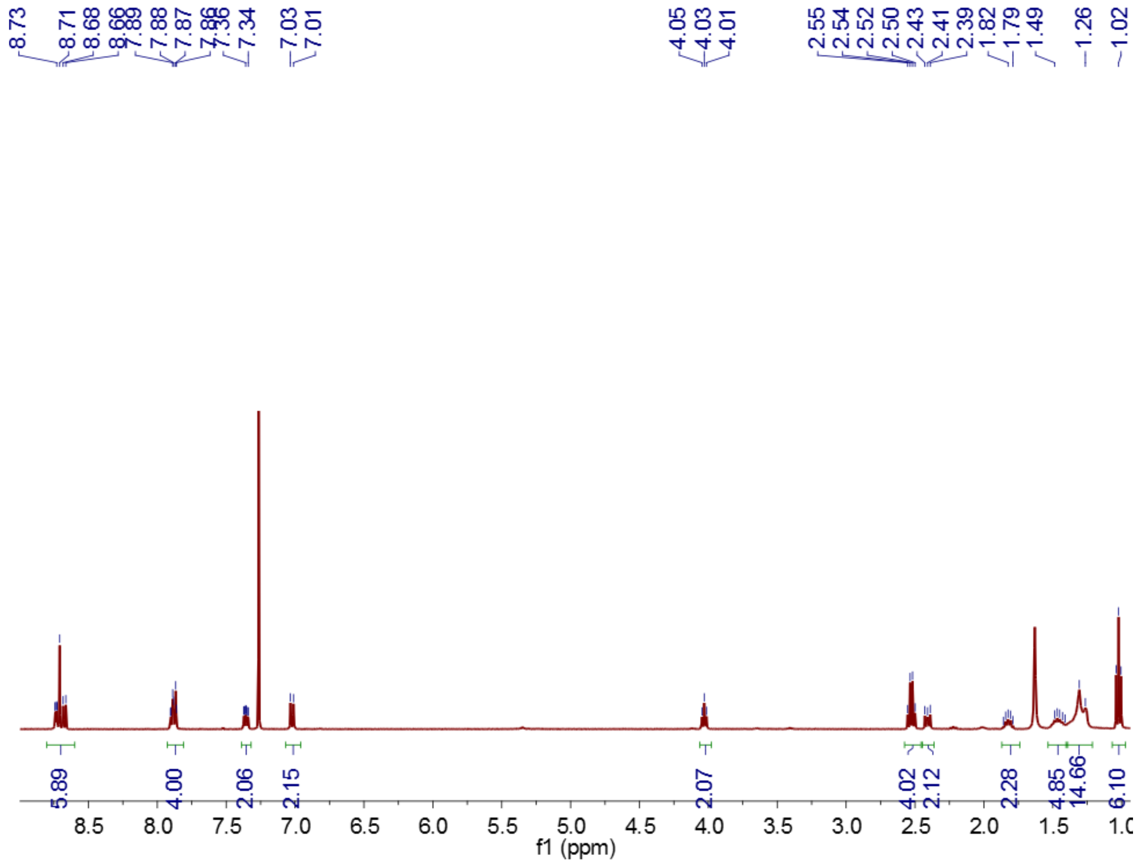


Fig. S1 ^{1}H NMR spectrum (400 MHz, chloroform-*d*, 293K) of **1**.

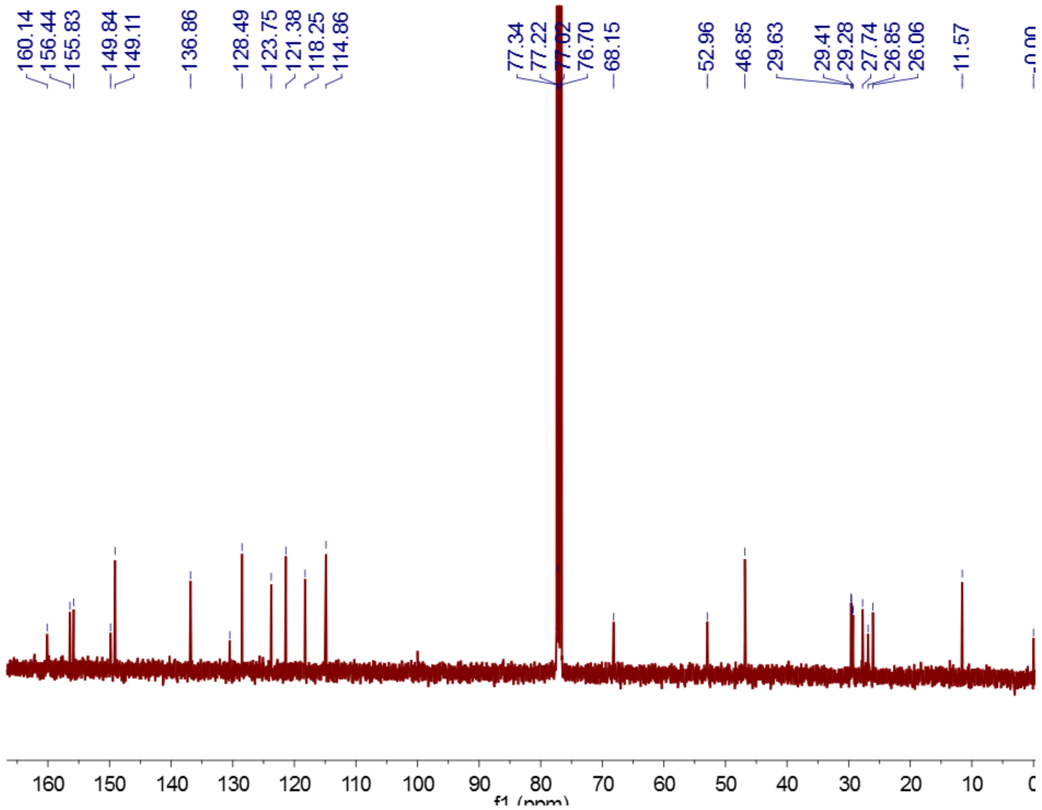


Fig. S2 ^{13}C NMR spectrum (100 MHz, chloroform-*d*, 293K) of **1**.

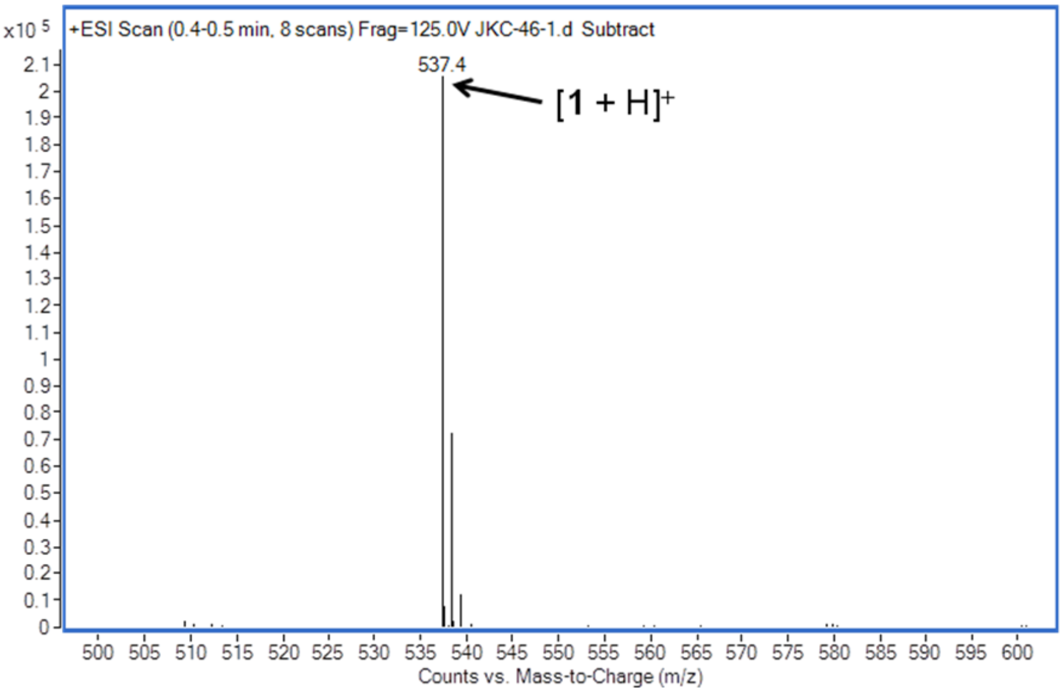


Fig. S3 Electrospray ionization mass spectra of **1**.

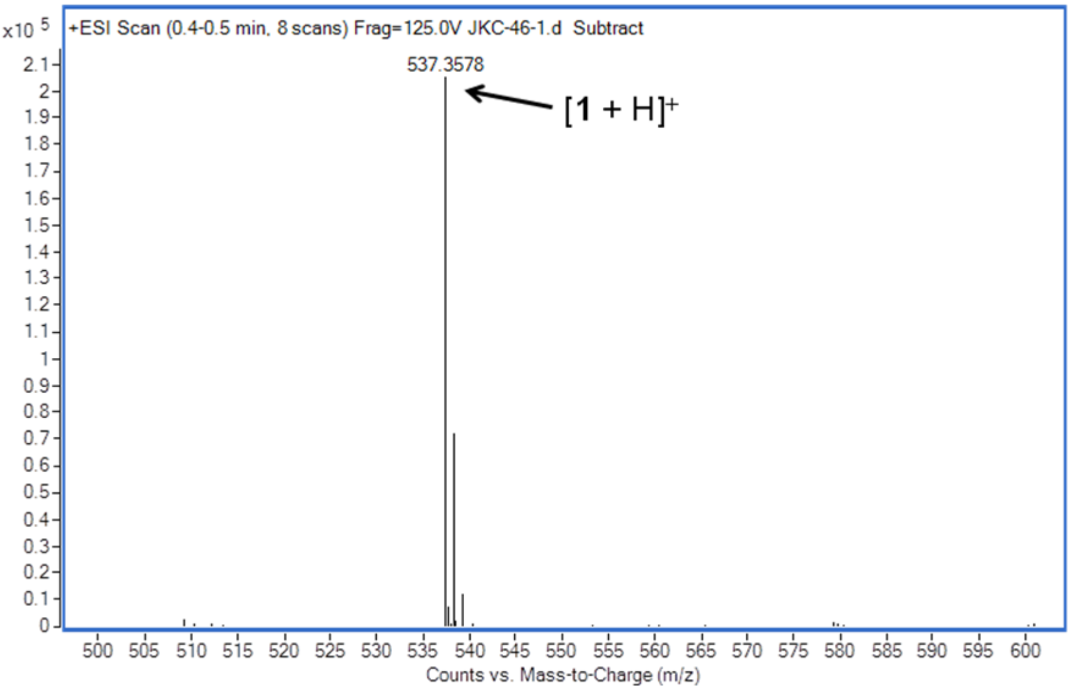
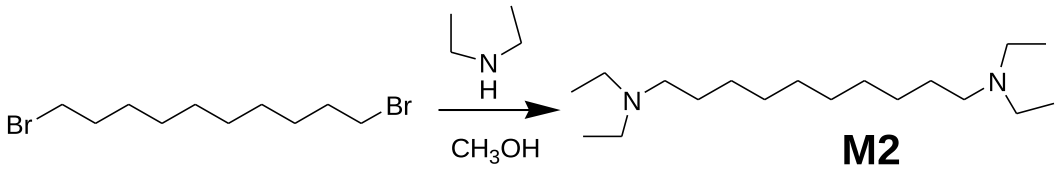


Fig. S4 High resolution electrospray ionization mass spectra of **1**.

*2.2 Synthesis of model compound **M2***

Scheme S2. Synthetic route to **M2**.



A mixture of 1,10-dibromodecane (3.00 g, 10.0 mmol) with excess diethylamine (30 equiv) were dissolved in ethanol and refluxed for 24 h. The solvent was evaporated, and the residue was poured into a NaOH solution (1.00 M, 400 mL) and stirred. The solution was extracted with ethyl acetate (3 × 50 mL), and the organic phase was obtained. The yellow liquid was isolated after evaporation of the solution as the crude product, which was distilled in vacuo to give **M2** as yellow liquid. The yield of **M2** was 88%. The ^{1}H NMR spectrum of **M2** is shown in Fig. S5. ^{1}H NMR (400 MHz, chloroform-*d*, 293 K) δ (ppm): 2.54–2.49 (m, 4H), 2.39 (t, J = 8 Hz, 4H), 1.45–1.42 (m, 4H), 1.28 (s, 12H), 1.02 (t, J = 6 Hz, 12H). The ^{13}C NMR spectrum of **M2** is shown in Fig. S6. ^{13}C NMR (100 MHz, chloroform-*d*, 293 K) δ (ppm): 55.06, 52.97, 46.84, 30.95, 29.63, 29.59, 29.74, 26.91, 11.62. LRESIMS is shown in Fig. S7: m/z 285.2 [**M2** + H]$^+$. HRESIMS m/z calcd for **M2** $C_{18}H_4N_2$, 284.3191; found 284.3187; error −1 ppm.

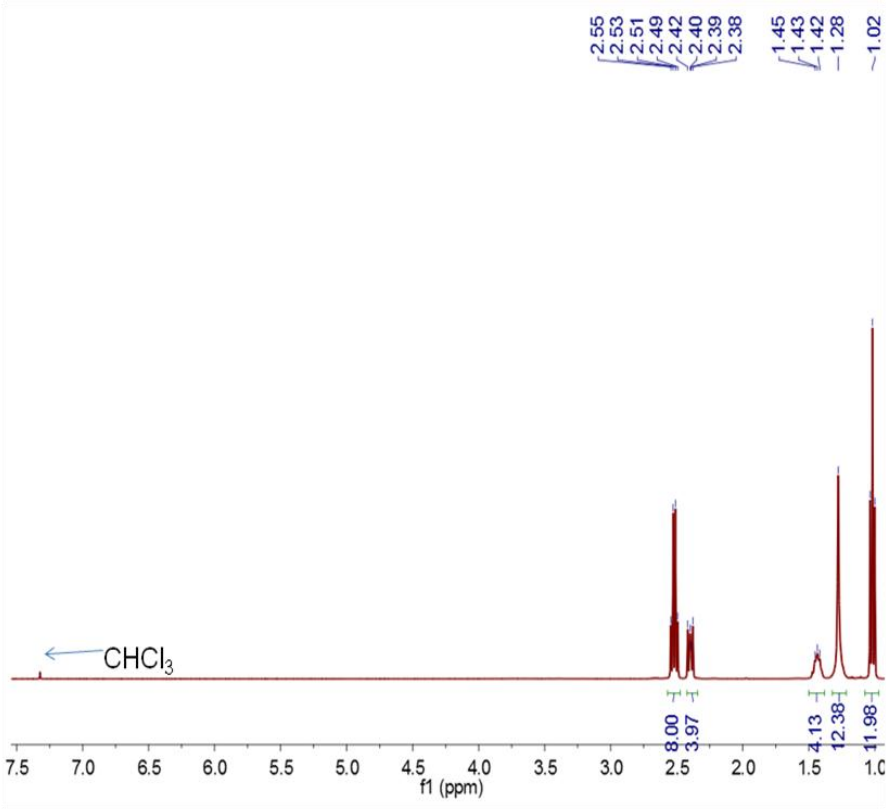


Fig. S5 ^{1}H NMR spectrum (400 MHz, chloroform-*d*, 293 K) of **M2**.

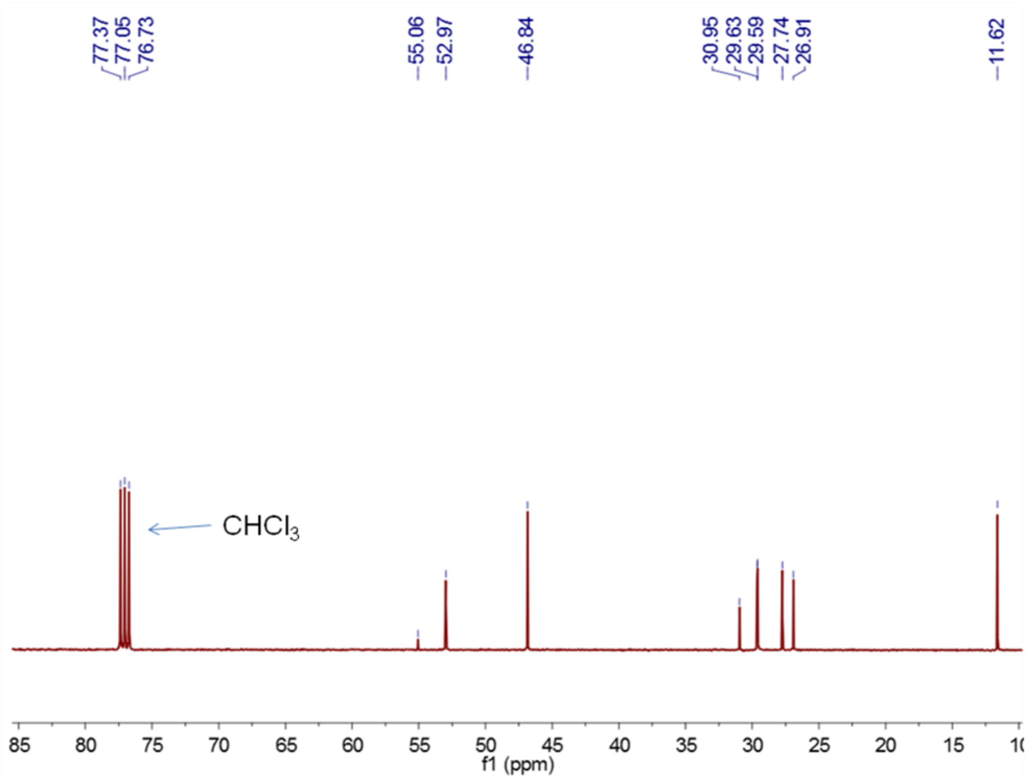


Fig. S6 ^{13}C NMR spectrum (100 MHz, chloroform-*d*, 293 K) of **M2**.

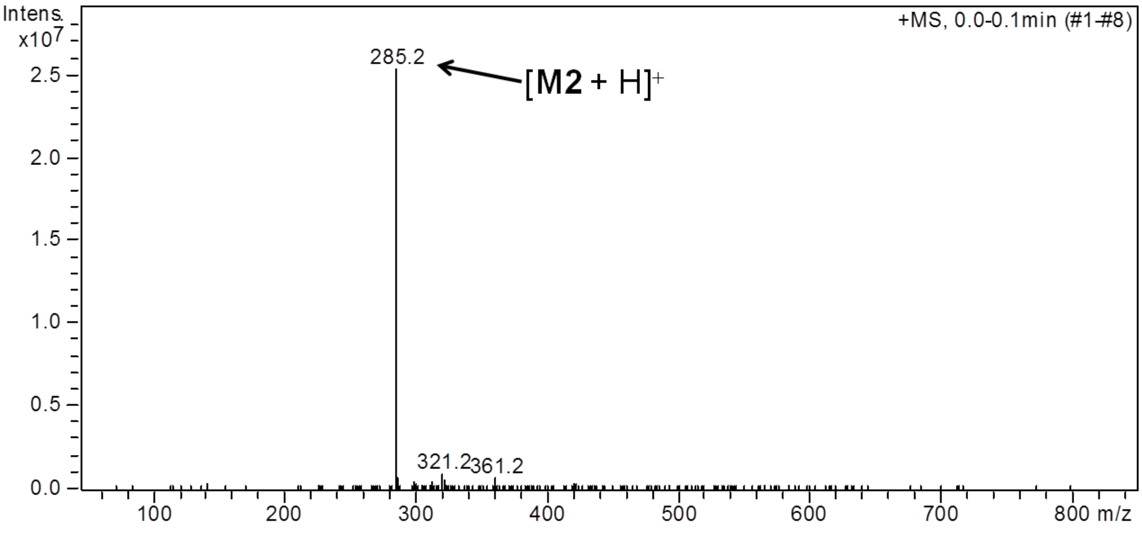


Fig. S7 Electrospray ionization mass spectrum of **M2**.

*3. UV-Vis studies of **1** before and after slightly acidification in water*

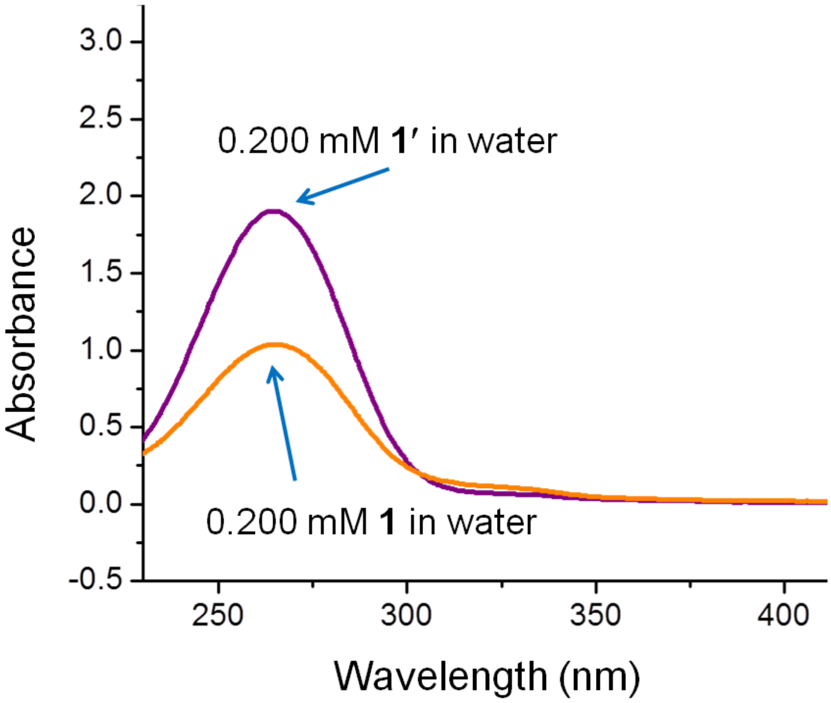


Fig. S8 UV−Vis spectra of 0.200 mM **1** and **1′** in water.

4. TEM and SEM images of ***1′*** *in water*

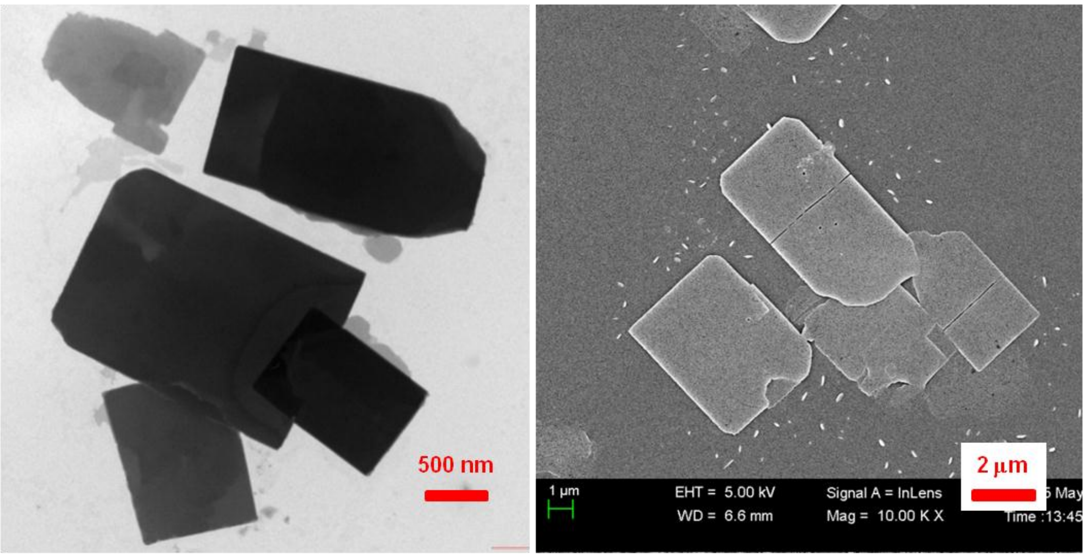


Fig. S9 (a) TEM and (b) SEM images of the brick-like structures formed by **1′** (0.200 mM) in water.

5. Gelation study of the metallogel:

5.1 Gelation study of the metallogel with Cu^{2+} in presence of other metal ions:

To a stock solution of **1′** (800 μL, 0.25 mM) taken in a test bottle, a mixture of 100 μL of M^{2+} (0.200 mM Cd^{2+}/Zn^{2+}/Ni^{2+}/Ca^{2+}/Rh^{2+}/Fe^{2+}/Mg^{2+}/Co^{2+}/Mn^{2+}) and 100 μL of $CuCl_2$ (0.200 mM in H_2O) was added and allowed to stand after gentle shaking. It was observed that most of the metal ions disturbed the gelation while the presence of Ca^{2+} resulted in a partial gel.

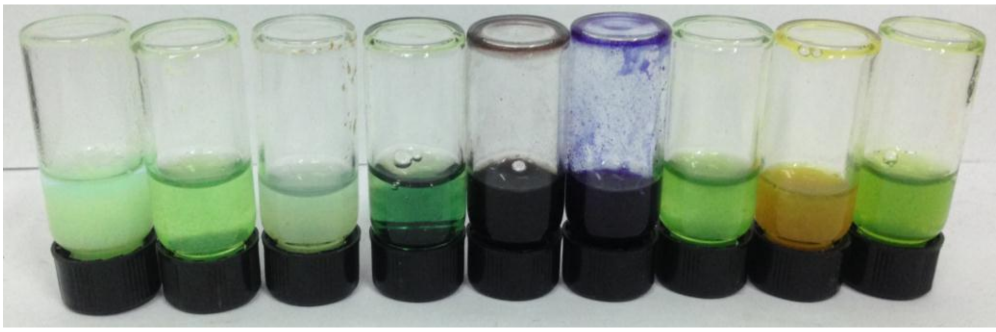


Fig. S10 From left to right: 0.200 mM of **1′** in presence of 0.200 mM (chloride salt of) Cd^{2+}/Cu^{2+}, Zn^{2+}/Cu^{2+}, Ni^{2+}/Cu^{2+}, Ca^{2+}/Cu^{2+}, Rh^{2+}/Cu^{2+}, Fe^{2+}/Cu^{2+}, Mg^{2+}/Cu^{2+}, Co^{2+}/Cu^{2+}, and Mn^{2+}/Cu^{2+}.

5.2 Gelation study of the metallogel in the presence of Cu^{2+} with other counter anions:

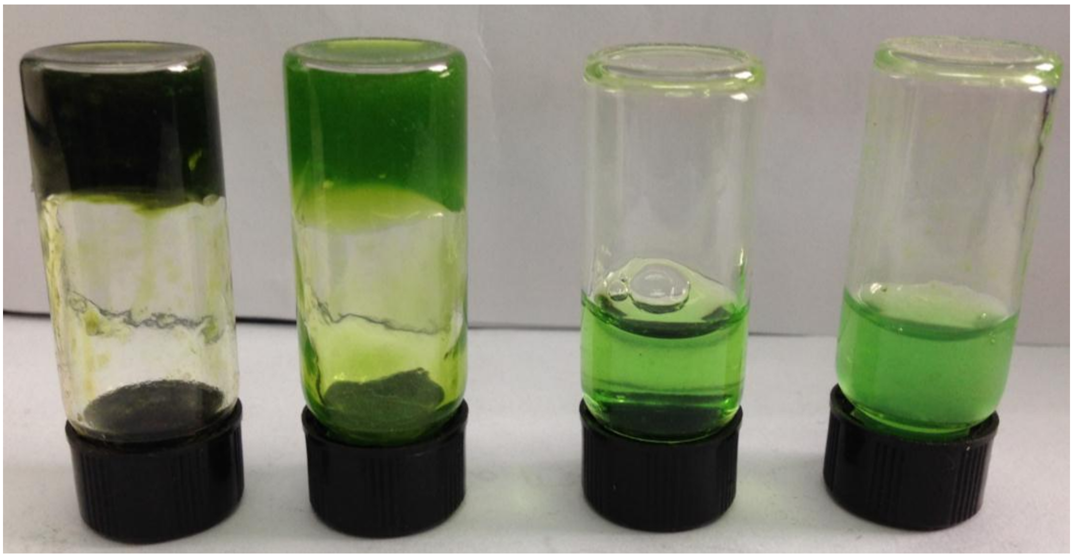


Fig. S11 From left to right: 0.200 mM of **1′** in presence of 0.200 mM $CuBr_2$, CuI_2, $Cu(OAc)_2$ and $CuSO_4$.

6. *Host–guest complexation between **WP5** and model compounds **M1H** and **M2H***

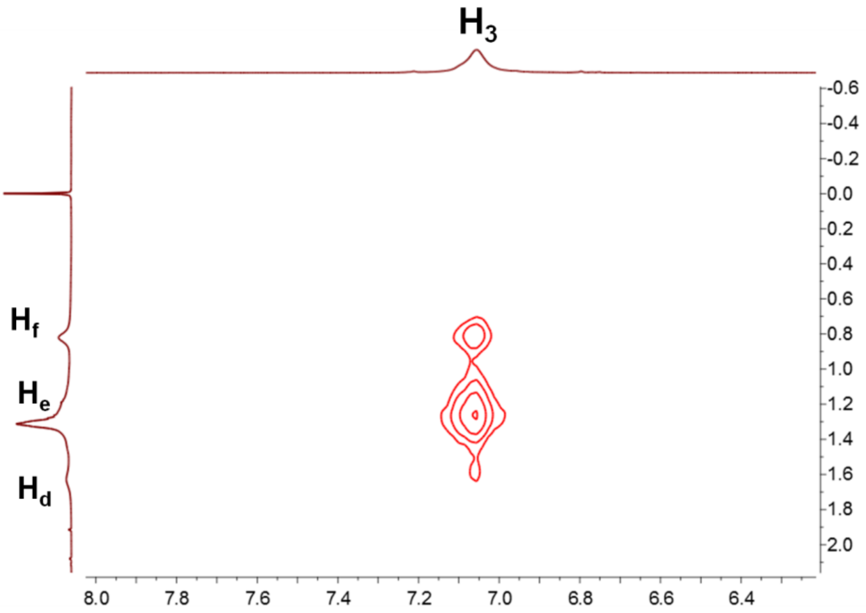


Fig. S12 2D NOESY NMR (500 MHz, D_2O, 293 K) spectrum of a solution of **WP5** (5.00 mM) and **M1H** (5.00 mM).

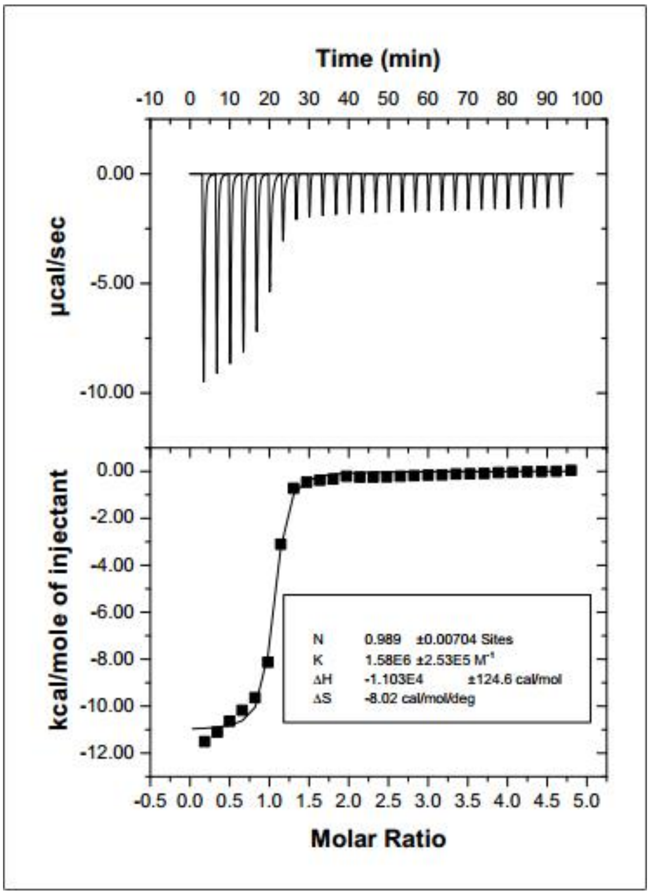


Fig. S13 Microcalorimetric titration of **M1H** with **WP5** in water at 298.15 K. (Top) Raw ITC data for 29 sequential injections (10 µL per injection) of an **M1H** solution (2.00 mM) into a **WP5** solution (0.100 mM). (Bottom) Net reaction heat obtained from the integration of the calorimetric traces.

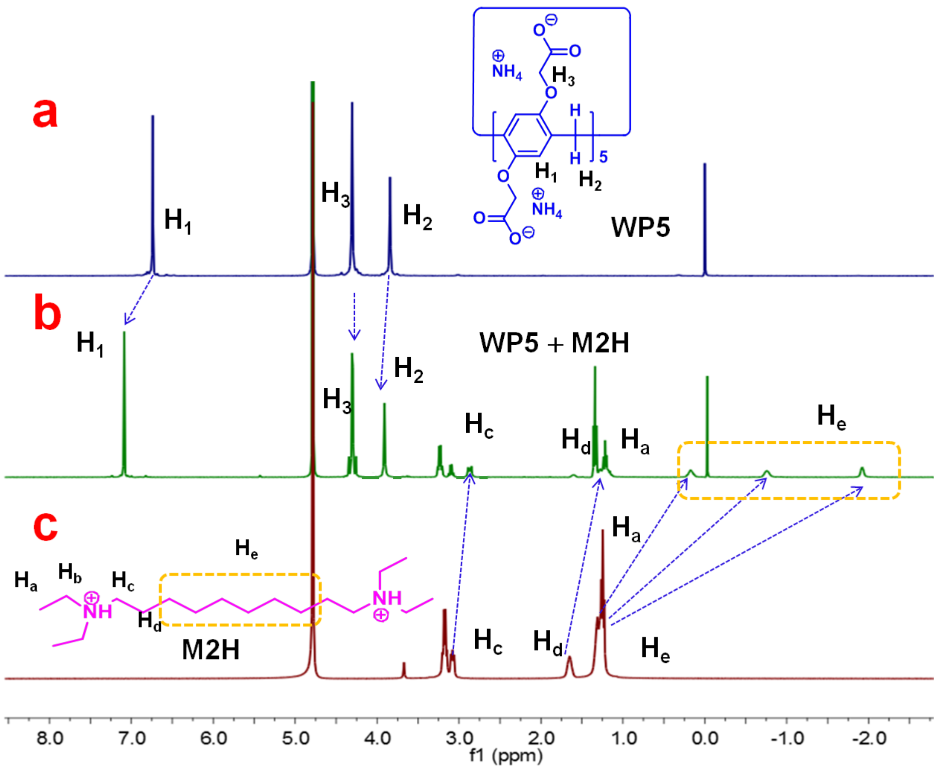


Fig. S14 Partial ^{1}H NMR spectra (400 MHz, D_2O, room temperature): (a) **WP5** (2.00 mM); (b) **WP5** (2.00 mM) and **M2H** (6.00 mM); (c) **M2H** (2.00 mM).

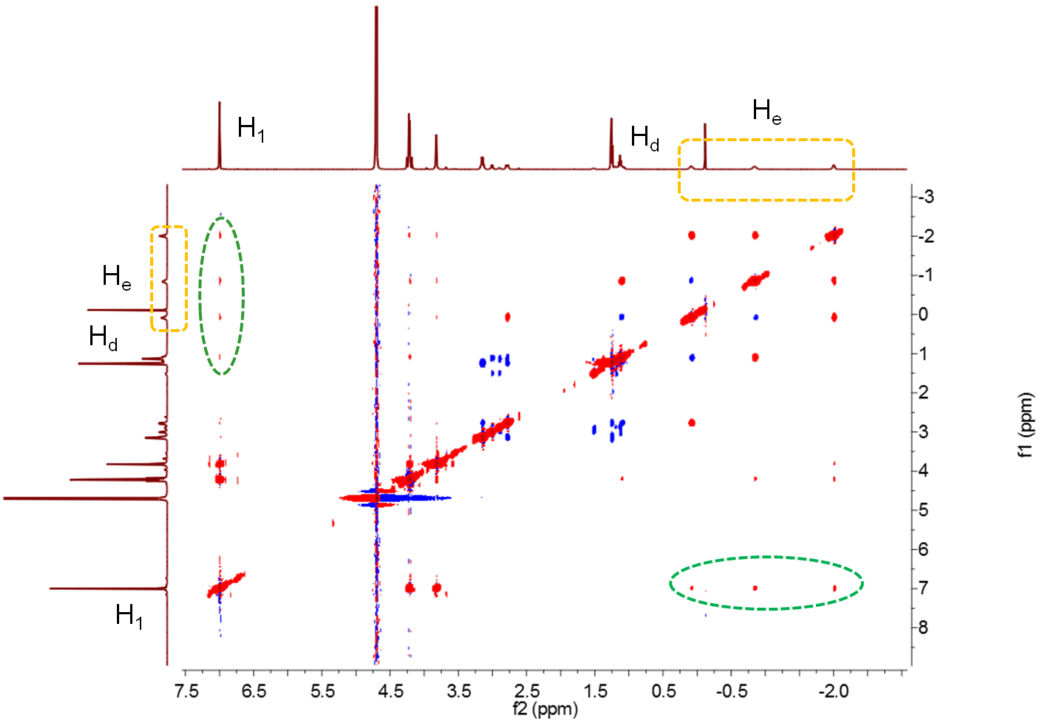


Fig. S15 2D NOESY NMR (500 MHz, D_2O, 293 K) spectrum of a solution of **WP5** (5.00 mM) and **M2H** (5.00 mM).

References:

S1. (*a*) Y. Yao, X. Chi, Y. Zhou and F. Huang, *Chem. Sci.*, 2014, **5**, 2778; (*b*) P. Wang, Z. Li and X. Ji, *Chem. Commun.*, 2014, **50**, 13114.