

Dual-responsive [2]pseudorotaxane on the basis of a pH-sensitive pillar[5]arene and its application in the fabrication of metallosupramolecular polypseudorotaxane

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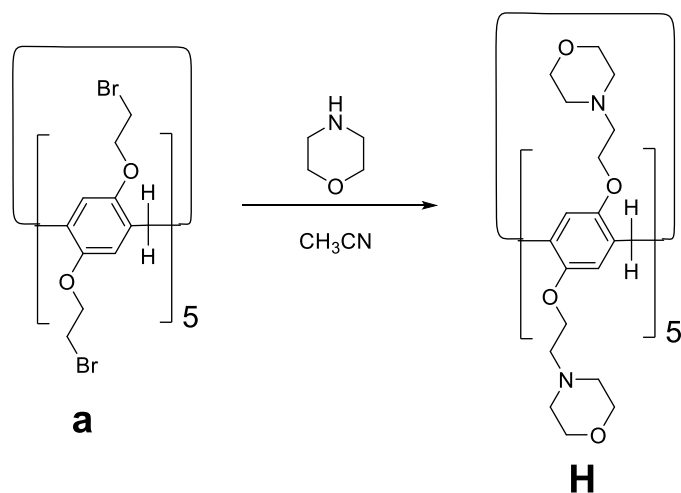
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1. *Materials and methods*

Compound **a**^{S1} was prepared according to published procedures. Compound *trans*-**G** were commercially available. 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 Avance DMX 400 spectrophotometer or a Bruker Avance DMX 500 spectrophotometer or a Bruker Avance DMX 600 spectrophotometer. Low-resolution electrospray ionization mass spectra were recorded with a Bruker Esquire 3000 Plus 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 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. Scanning electron microscopy was carried out on a JEOL 6390LV instrument. The crystal structures were solved by SHELXS-97^{S2} and refined by SHELXL-97.^{S3} UV-vis spectra were taken on a Perkin-Elmer Lambda 35 UV-vis spectrophotometer.

2. Synthetic routes for **H**



Scheme S1 Synthetic routes for **H**.

3. Synthesis of **H**

Compound **H** (1.00 g, 0.595 mmol) and Morpholine (1.05 g, 12.0 mmol) were added to acetonitrile (50.0 mL). The solution was refluxed overnight. Then the crude product was purified by a silica gel column using dichloromethane as eluent. (0.535 g, 35 %). Mp: 108.2–110.4 °C. The ^1H NMR spectrum of **1** is shown in Fig. S1. ^1H NMR (400 MHz, CDCl_3 , 298 K) δ (ppm): 6.85 (s, 10H), 4.14–4.09 (m, 10H), 3.98–3.92 (m, 10H), 3.75–3.73 (t, $J = 8.0$ Hz, 50H), 2.88–2.75 (m, 20H), 2.62–2.61 (d, $J = 4.0$ Hz, 40H). The ^{13}C NMR spectrum of **1** is shown in Fig. S2. ^{13}C NMR (125 MHz, CDCl_3 , 298 K) δ (ppm): 149.89, 128.75, 115.51, 66.98, 58.23, 54.27, 29.44. LRESIMS is shown in Fig. S3: m/z 1743.4 corresponding to $[\text{M} + \text{H}]^+$, m/z 1766.4 corresponding to $[\text{M} + \text{H} + \text{Na}]^+$, m/z 1782.5 corresponding to $[\text{M} + \text{H} + \text{K}]^+$. HRESIMS: m/z calcd for $[\text{M} + \text{H}]^+$ $\text{C}_{95}\text{H}_{141}\text{O}_{20}\text{N}_{10}$, 1742.0323, found 1742.0318, error -0.3 ppm.

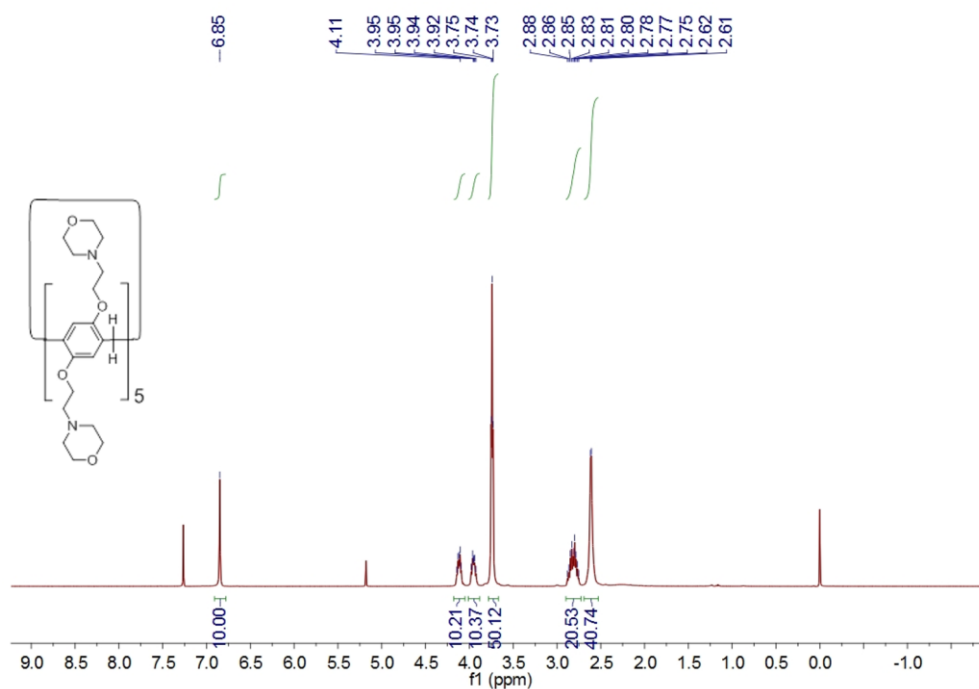


Figure S1. ¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **H**.

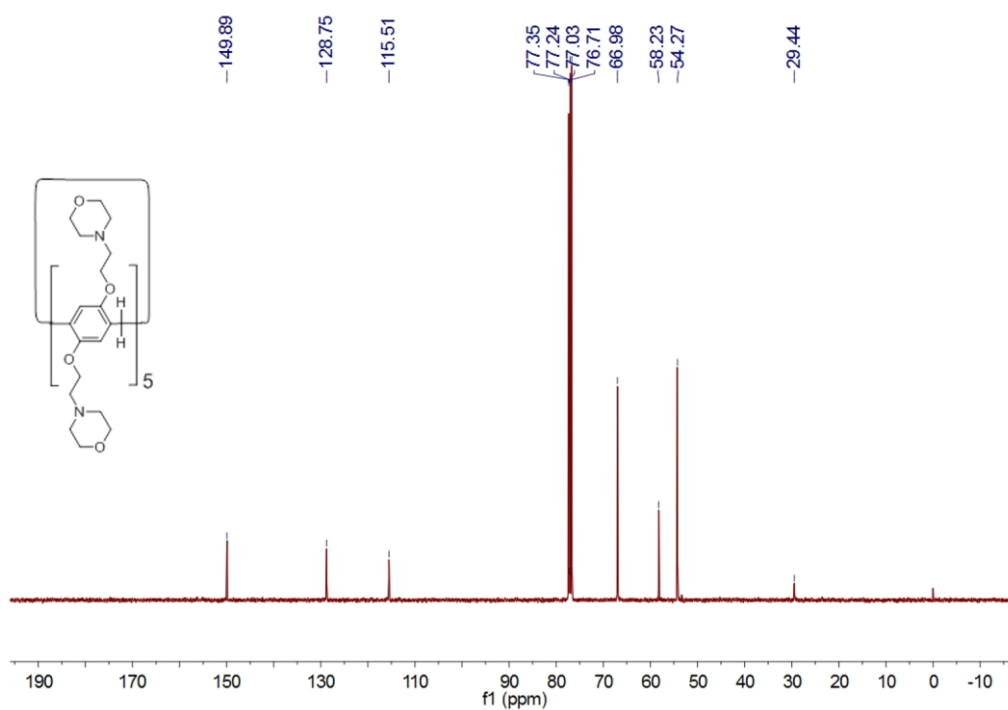


Figure S2. ¹³C NMR spectrum (100 MHz, CDCl₃, 298K) of **H**.

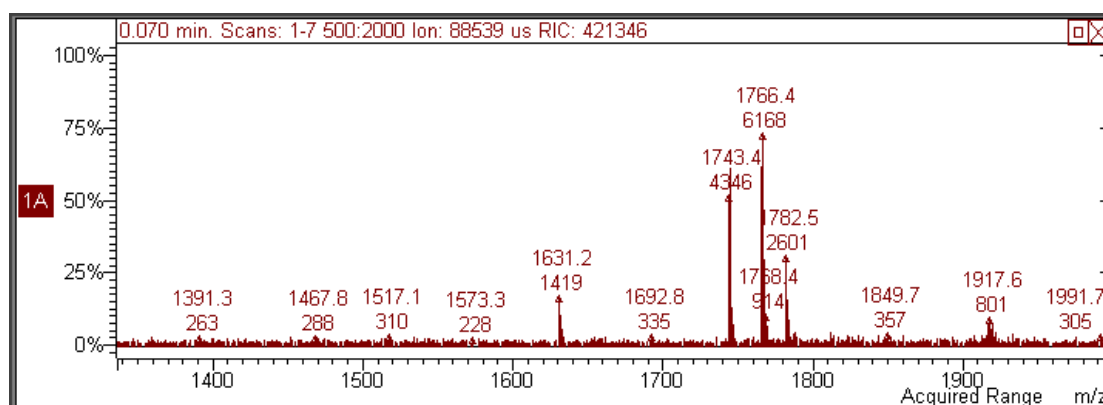


Figure S3. Electrospray ionization mass spectrum of **H**. The peaks at m/z 1743.4 corresponding to $[M + H]^+$, m/z 1766.4 corresponding to $[M + H + Na]^+$, m/z 1782.5 corresponding to $[M + H + K]^+$ were clearly observed.

4. X-ray crystal data of **H** acetoneitrile

Crystal data of **H** acetoneitrile: colourless, $C_{97}H_{140}N_{11}O_{20}$, FW 1780.62, triclinic, space group $P\bar{1}$, $a=14.961(3)$, $b=16.550(3)$, $c=21.063(4)$, $\alpha=101.77(3)$, $\beta=92.13(3)$, $\gamma=103.45(3)$, $V = 4946.0(17) \text{ \AA}^3$, $Z = 2$, $D_c = 1.196 \text{ g cm}^{-3}$, $T = 293 \text{ K}$, $\mu = 0.084 \text{ mm}^{-1}$, 17444 measured reflections, 17175 independent reflections, 1182 parameters, 207 restraints, $F(000) = 1918.84$, $R_1 = 0.1059$, $wR_2 = 0.2437$ (all data), $R_1 = 0.0174$, $wR_2 = 0.2069$ [$I > 2\sigma(I)$], max. residual density $1.34 \text{ e}\cdot\text{\AA}^{-3}$, and goodness-of-fit (F^2) = 1.088. CCDC-1586691.

5. pH-Sensitive property of **H**

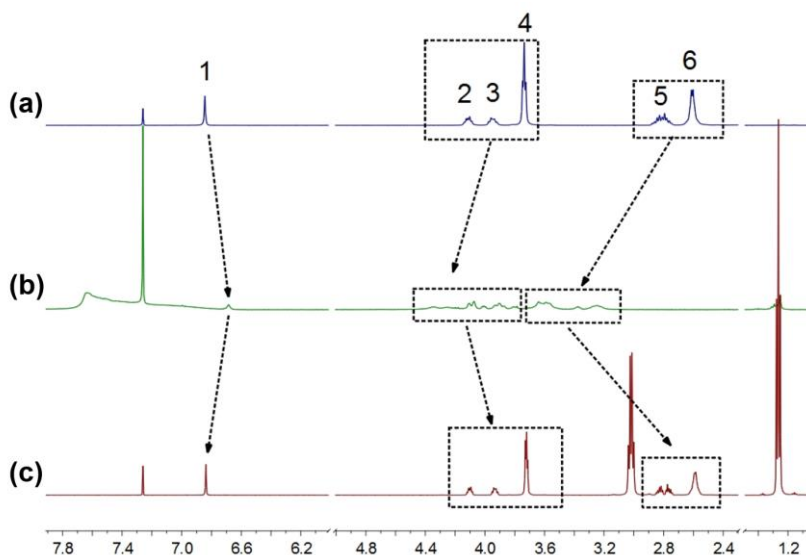


Figure S4. 1H NMR spectra (400 MHz, $CDCl_3$, room temperature): (a) **H** (5.00 mM) (b) after addition of 2 μ L of trifluoroacetyl acid to a; (c) after addition of 4 μ L of triethylamine to b.

6. Variable-temperature ^1H NMR spectra of $\text{H} \rightleftharpoons \text{trans-G}$

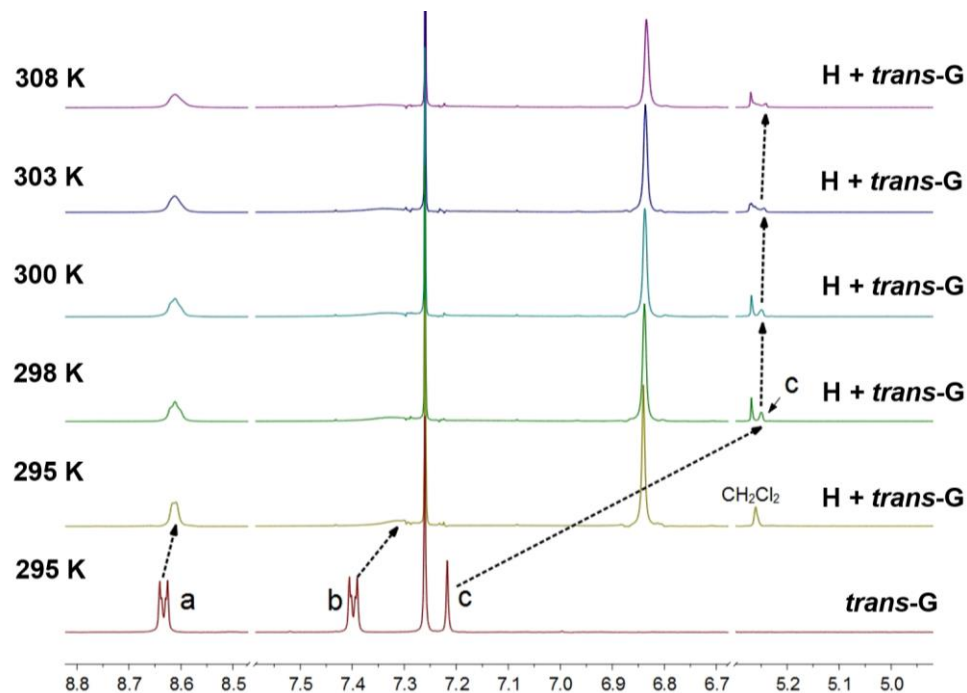


Figure S5. Variable-temperature ^1H NMR spectra (600 MHz, CDCl_3 ,) of an equimolar solution of **H** and **trans-G** (5.00 mM).

7. Partial 2D NOESY spectra of an equimolar solution of $\text{H} \rightleftharpoons \text{trans-G}$

2D NOESY NMR experiment was employed to study the relative positions of the components in complex $\text{H} \rightleftharpoons \text{trans-G}$. NOE correlation signals were observed between proton H_a of **trans-G** and protons H_2 , H_4 , H_5 and H_6 of **H** (Figure. S5, A, B, C and D), between proton H_b of **trans-G** and protons H_2 and H_3 of **H** (Figure S5, E and F).

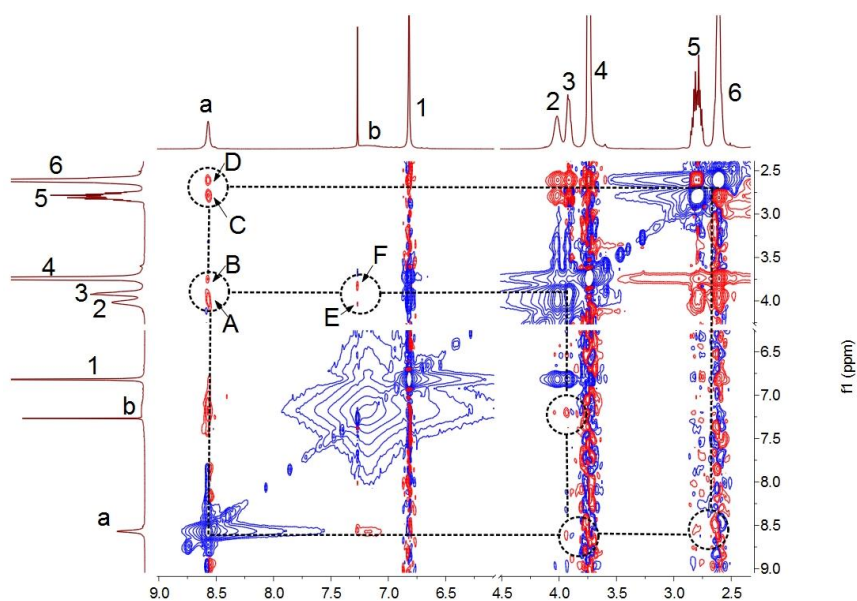


Figure S6. Partial 2D NOESY spectra of an equimolar mixture **trans-G** and **H** (10.0 mM) (500 MHz, CDCl_3 , room temperature).

8. The determination of the association constant of complex **H**–*trans*-**G** by ^1H NMR titration experiments

To determine the stoichiometry and association constant between **H** and *trans*-**G**, ^1H NMR titration was done with solutions which had a constant concentration of **H** (1.00 mM) and different concentrations of *trans*-**G**. By a non-linear curve-fitting method, the association constant between the **H** and *trans*-**G** was calculated. By a mole ratio plot, a 1:1 stoichiometry was obtained for this system.

The non-linear curve-fitting was based on the equation:

$$\Delta\delta = (\Delta\delta_{\infty}/[\text{G}]) (0.5[\text{H}]_0 + 0.5([\text{G}] + 1/K_a) - (0.5([\text{H}]_0^2 + (2[\text{H}]_0(1/K_a - [\text{G}]) + (1/K_a + [\text{G}])^2)^{0.5})) \quad (\text{Eq. S1})$$

wherein $\Delta\delta$ is the chemical shift change of H_2 on **H** at $[\text{H}]_0$, $\Delta\delta_{\infty}$ is the chemical shift change of H_2 when the host is completely complexed, $[\text{H}]_0$ is the fixed initial concentration of the host, and $[\text{G}]$ is the varying concentration of **G**.

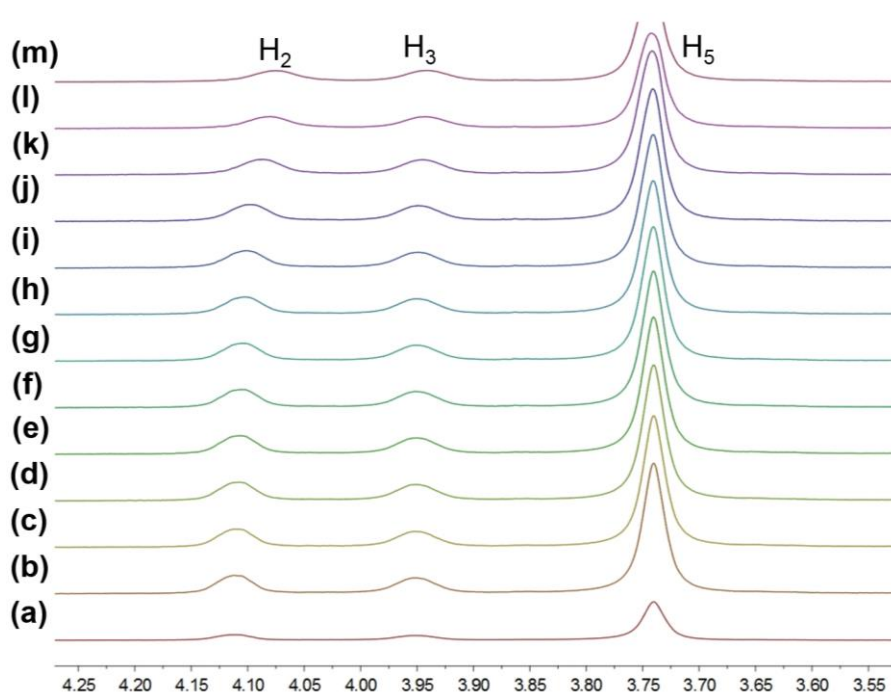


Figure S7. Partial ^1H NMR spectra (600 MHz, CDCl_3 , room temperature) of **H** at a concentration of 1.00 mM with different concentrations of *trans*-**G**: (a) 0.00 mM; (b) 0.0990 mM; (c) 0.196 mM; (d) 0.385 mM; (e) 0.566 mM; (f) 0.826 mM; (g) 1.07 mM; (h) 1.38 mM; (i) 1.67 mM; (j) 2.31 mM; (k) 4.12 mM; (l) 5.24 mM; (m) 5.23 mM; (n) 6.30 mM.

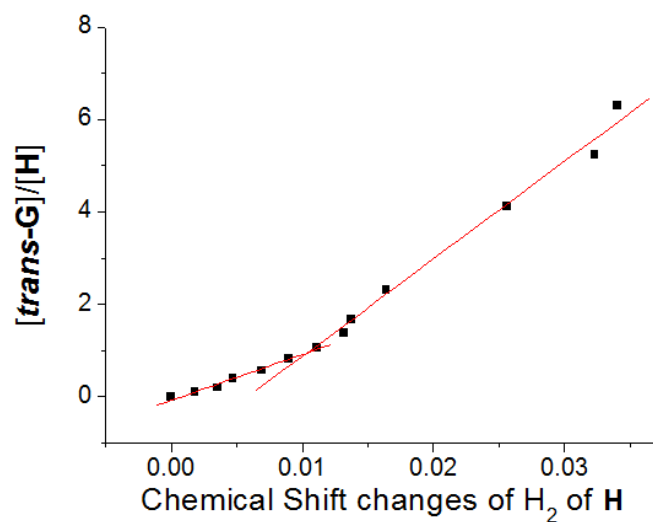


Figure S8. Mole ratio plot for the complexation between **H** and *trans-G*, indicating a 1:1 stoichiometry.

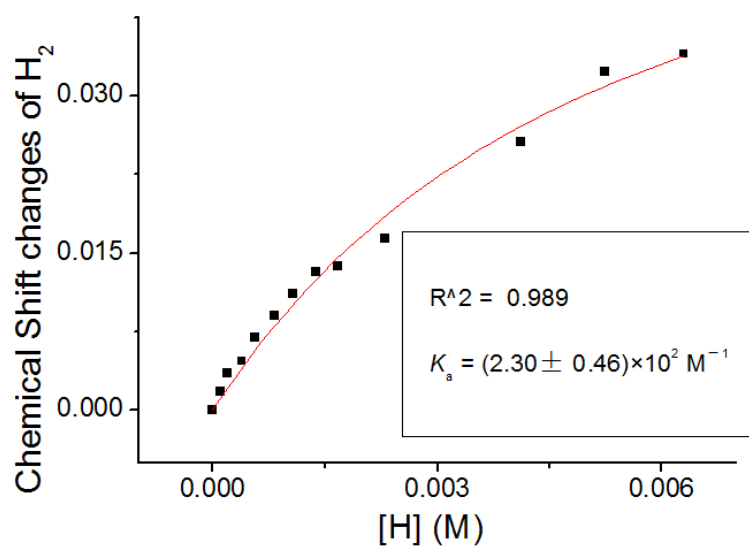


Figure S9. The chemical shift changes of H₂ on **H** upon addition of *trans-G*. The red solid line was obtained from the non-linear curve-fitting using Eq. S1.

9. UV-vis absorption spectra of **H** and *trans*-**G**

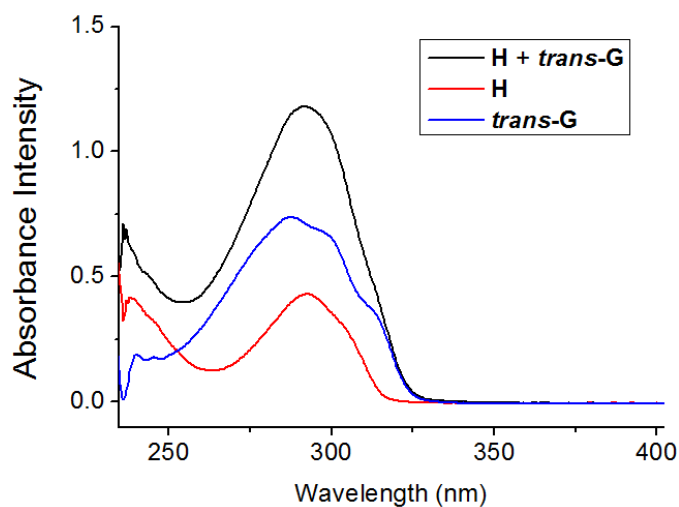


Figure S10. UV-vis absorption spectra of **H** (2.00×10^{-4} M), **H** with *trans*-**G** (2.00×10^{-4} M for both) and *trans*-**G** (5.00×10^{-5} M) in chloroform.

10. UV-vis absorption spectroscopy experiments of photo-responsive ability of *trans*-**G** and **H** \rightleftharpoons *trans*-**G**

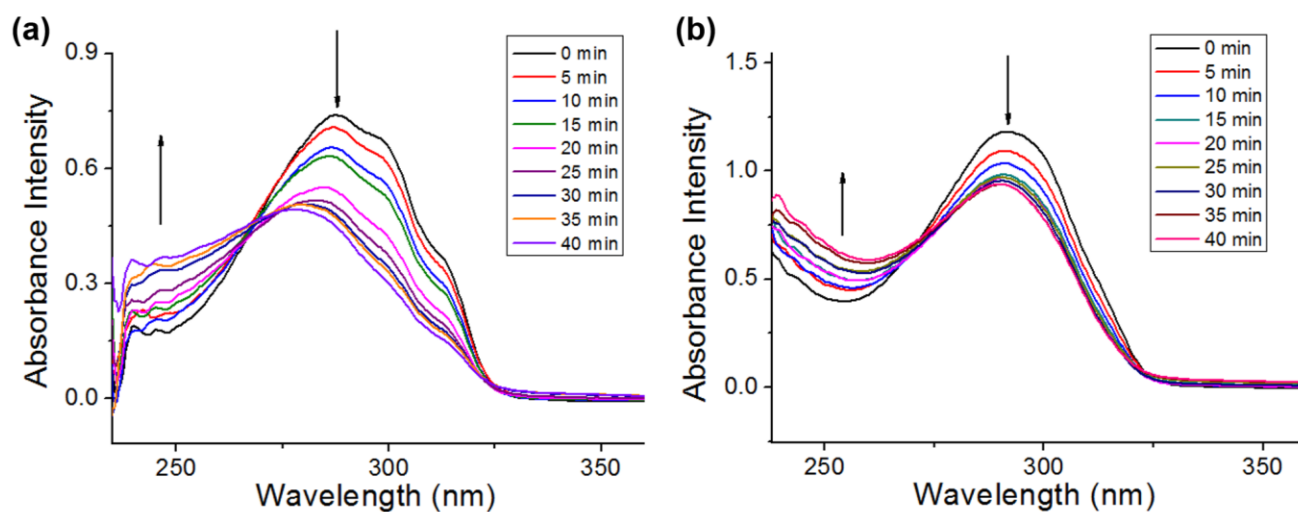


Figure. S11 UV-vis spectra of 2.00×10^{-4} M *trans*-**G** (initial and after irradiation with UV light irradiation and then after irradiation with UV light at 254 nm) and solution of equimolar 2.00×10^{-4} M *trans*-**G** and **H** (initial, after irradiation with UV light at 365 nm, and then after irradiation with UV light at 254 nm) in chloroform.

11. UV-vis absorption spectroscopy of $H\text{-}trans\text{-G}$ -based metallosupramolecular polypseudorotaxane

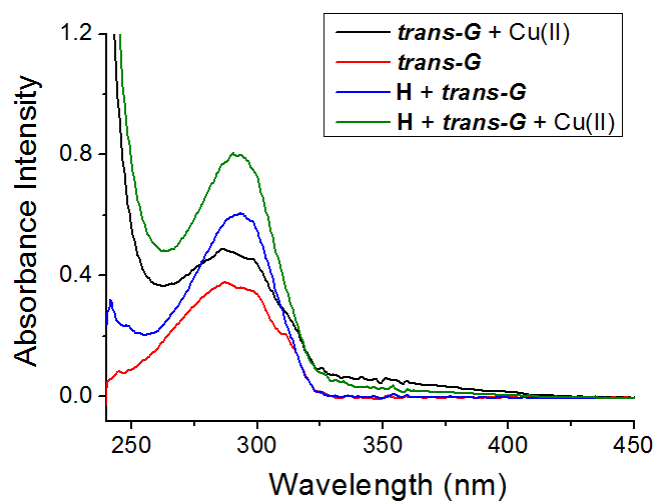


Figure S12. UV-vis spectra of *trans-G*, $H\text{-}trans\text{-G}$, *trans-G* + Cu(II) and $H\text{-}trans\text{-G}$ + Cu(II) (2.00×10^{-4} M) in chloroform.

12. ^1H NMR spectroscopy experiments of pH-responsive property of $H\text{-}trans\text{-G}$ -based metallosupramolecular polypseudorotaxane

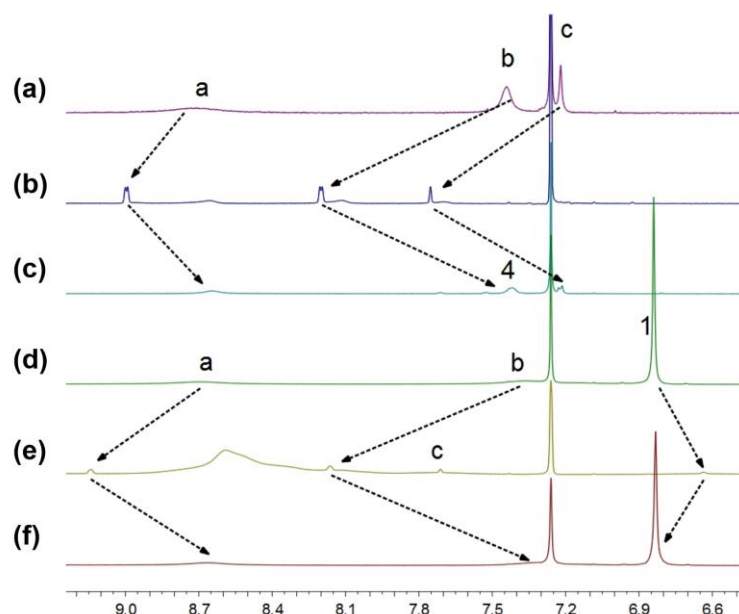


Figure S13 Partial ^1H NMR spectra (400 MHz, CDCl_3 , room temperature): (a) *trans-G* and Cu(II) (5.00 mM); (b) after addition of 0.5 μL of trifluoroacetyl acid to a; (c) after further addition of 1.0 μL of triethylamine to b; (d) $H\text{-}trans\text{-G}$ -based metallosupramolecular polymer (5.00 mM); (e) after addition of 2.5 μL of trifluoroacetyl acid to d; (f) after further addition of 5.0 μL of triethylamine to e.

13. ^1H NMR spectroscopy experiments of photo-responsive property of $\text{H}\rightarrow\text{trans-G}$ -based metallosupramolecular polypseudorotaxane

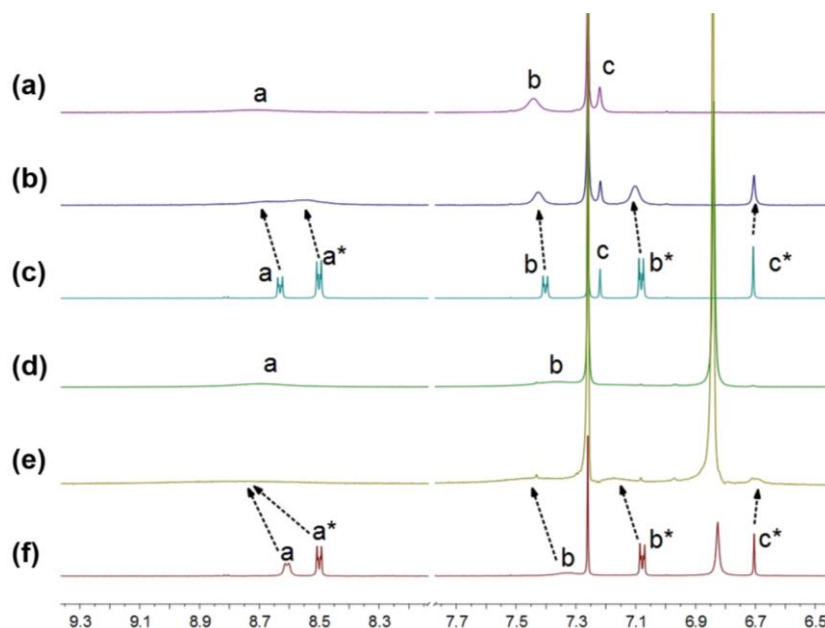


Figure S14 Partial ^1H NMR spectra (400 MHz, CDCl_3 , room temperature): (a) trans-G -based Cu(II) coordinate polymer; (b) after irradiation with UV light at 365 nm of a; (c) trans-G (5.00 mM) after irradiation with UV light at 365 nm; (d) $\text{H}\rightarrow\text{trans-G}$ -based metallosupramolecular polymer; (e) after irradiation with UV light at 365 nm of e; (f) $\text{H}\rightarrow\text{trans-G}$ (5.00 mM) after irradiation with UV light at 365 nm.

References:

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