Electronic Supplementary Material (ESI) for RSC Advances.

A multiple-responsive water-soluble [3]pseudorotaxane constructed by pillar[5]arene-based molecular recognition and disulfide bond connection

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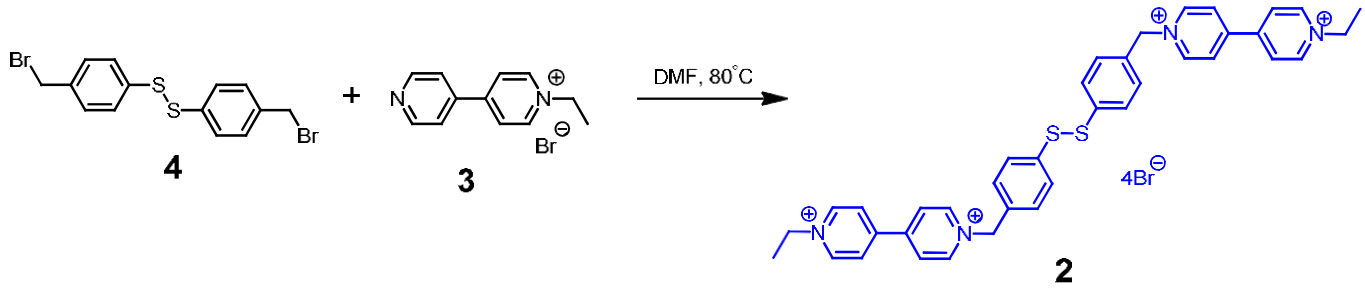
Electronic Supplementary Information (7 pages)

1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Compounds **3**,[S1] **4**[S2] and **1**[S3] were synthesized by published literature procedures. ^{1}H NMR spectra were collected on a temperature-controlled 400 MHz or 500 MHz spectrometer. ^{13}C NMR spectra were recorded on a Bruker AVANCE DMX-400 or DMX-500 spectrometer. Low-resolution electrospray ionization mass spectra (LRESI-MS) 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 electrospray ionization mass spectra (HRESI-MS) were obtained on 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 compound **2***



A mixture of **4** (200 mg, 0.498 mmol) and **3** (788 mg, 2.99 mmol) was added to DMF (50 ml) under the protection of N_2 and the solution was stirred at 80 °C for 24 hours. After cooling, the precipitate was collected by filtration. The precipitate was washed by CH_3CN for three times and dried to give a light yellow power (381 mg, 82 %). Mp: > 250 °C. The ^{1}H NMR spectrum of **2** is shown in Fig. S1. ^{1}H NMR (400 MHz, D_2O, 298 K) δ (ppm): 9.10 (d, *J* = 5.4 Hz, 8H), 8.50 (d, *J* = 6.7 Hz, 8H), 7.66 (d, *J* = 8.4 Hz, 4H), 7.46 (d, *J* = 8.4 Hz, 4H), 5.88 (s, 4H), 4.73 (m, 4H), 1.66 (m, 6H). The ^{13}C NMR spectrum of **2** is shown in Fig. S2. ^{13}C NMR (600 MHz, D_2O, 298K) δ (ppm): 153.11, 152.27, 148.06, 147.82, 140.98, 134.02, 132.83, 130.59, 129.75, 129.59, 66.70, 60.30, 18.19. LRESIMS of **2** is shown in Fig. S3: *m*/*z* 122.0236 $[M - Br + 6H]^{7+}$ (100%). HRESIMS: *m*/*z* calcd for $[M - Br]^+$ $C_{38}H_{38}Br_3N_4S_2^+$, 851.0083; found 851.0088; error 0.59 ppm.

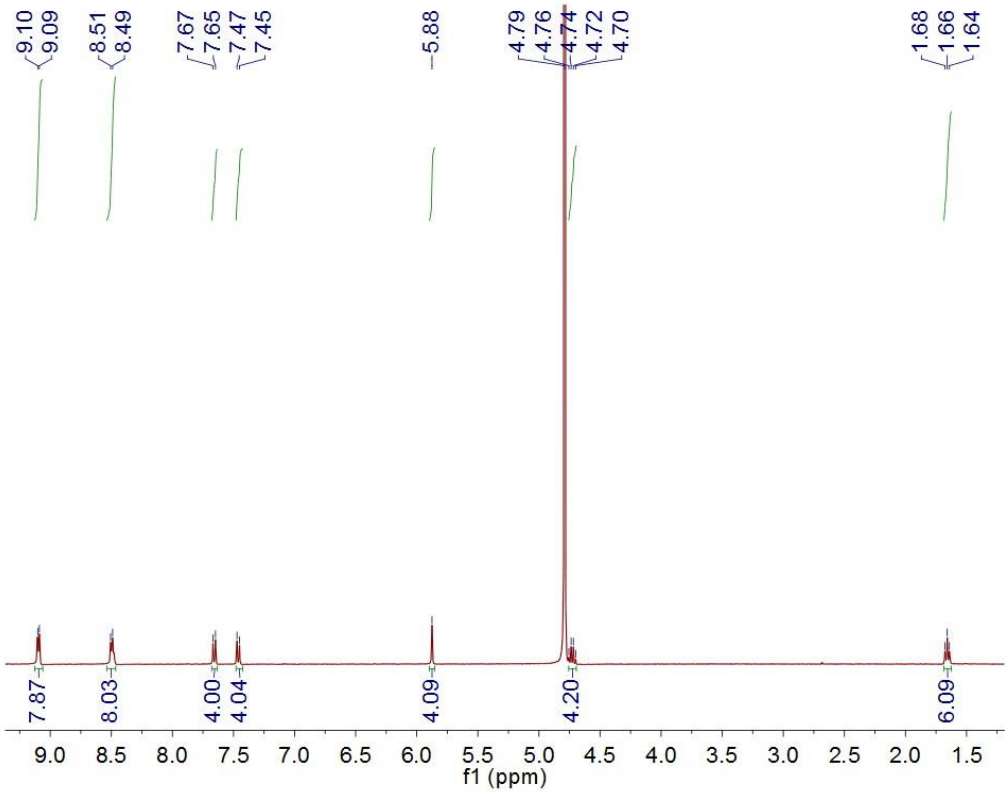


Fig. S1 ^{1}H NMR spectrum (400 MHz, D_2O, 298K) of **2**.

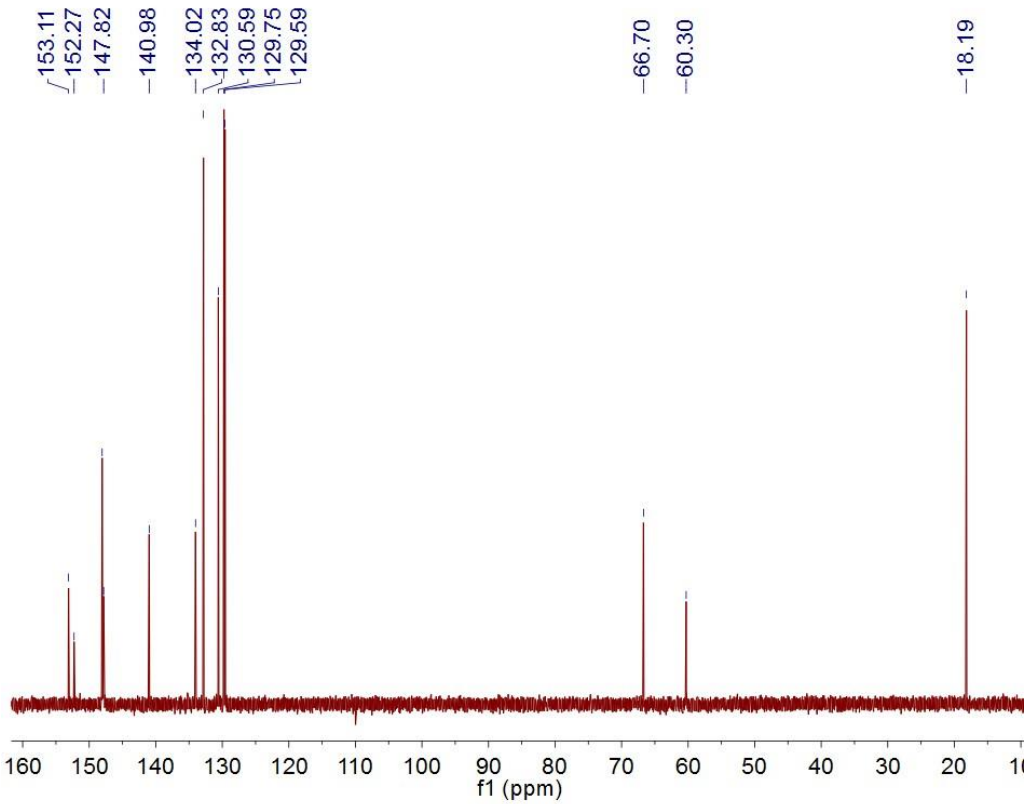


Fig. S2 ^{13}C NMR spectrum (600 MHz, D_2O, 298K) of **2**.

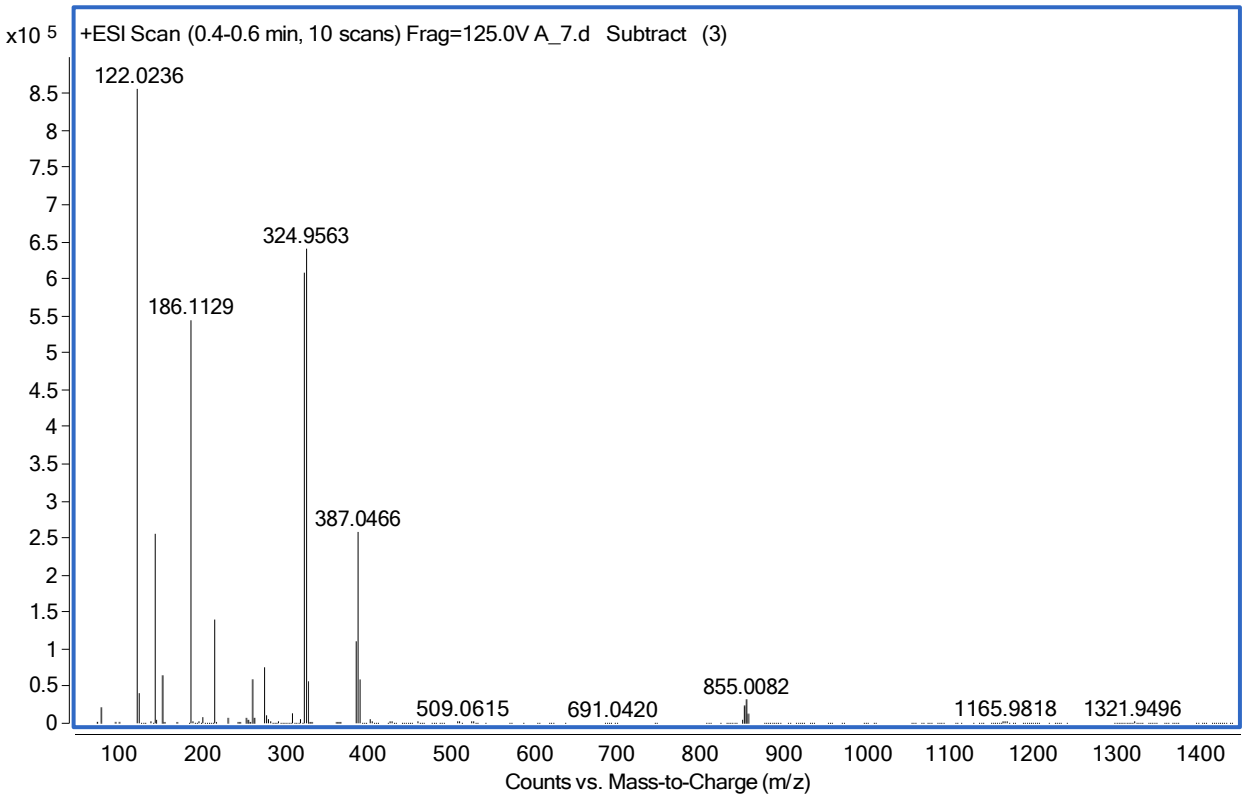


Fig. S3 LRESI mass spectrum of **2**.

*3. Proton NMR spectra of **1***

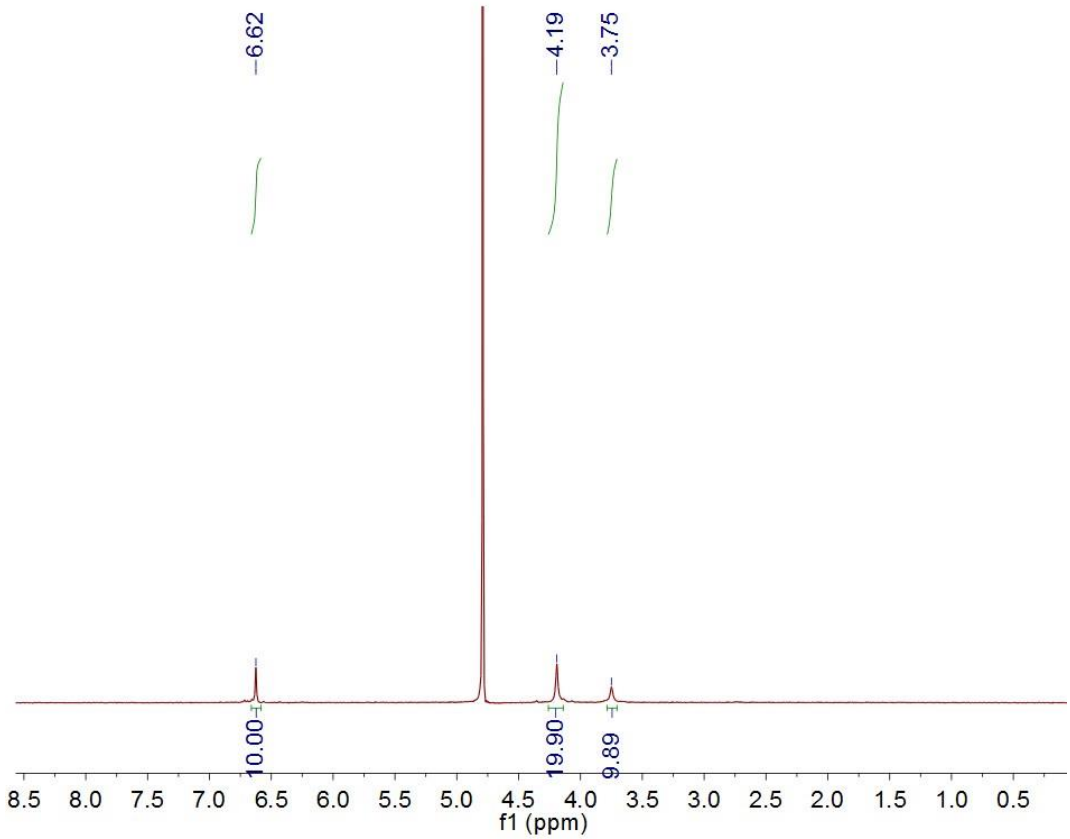


Fig. S4 ^{1}H NMR spectrum (400 MHz, D_2O, 298K) of **1**.

*4. Electrospray ionization mass spectrum of **1** ⊃**2** in H_2O*

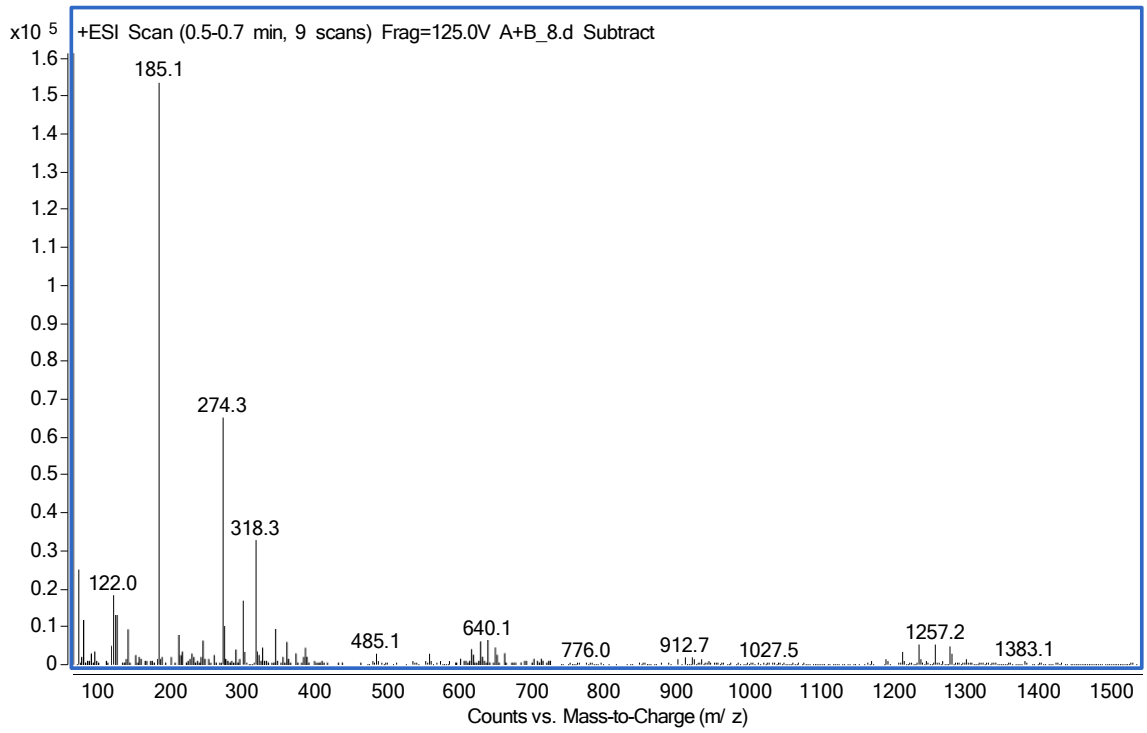


Fig. S5 Electrospray ionization mass spectrum of **1** ⊃ **2** in H_2O. The peak at *m/z* 185.1 corresponding to [**1** + 2**2** –19 NH_4 + Na]$^{18-}$ was clearly observed.

*5. Mole ratio plot for **1** and **2***

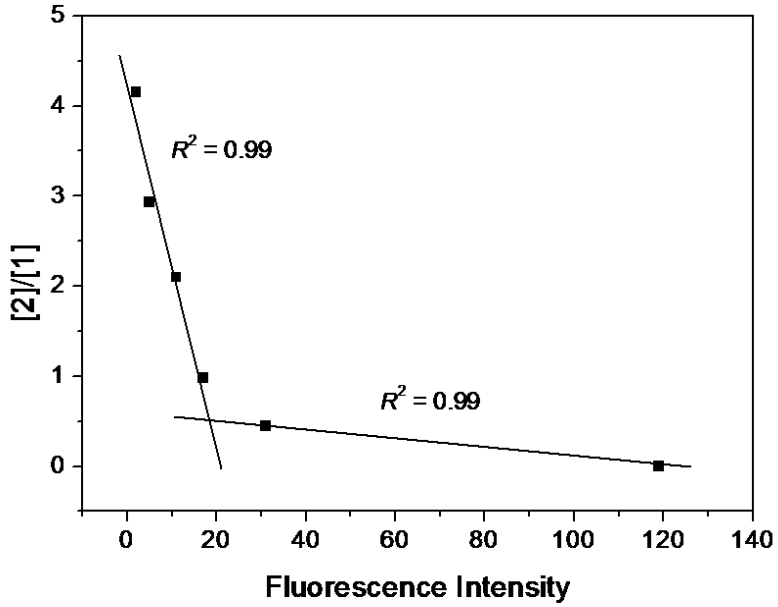


Fig. S6 Mole ratio plot for **1** and **2**, indicating a 2:1 stoichiometry.

6. The pH-responsiveness experiment of the [3]pseudorotaxane

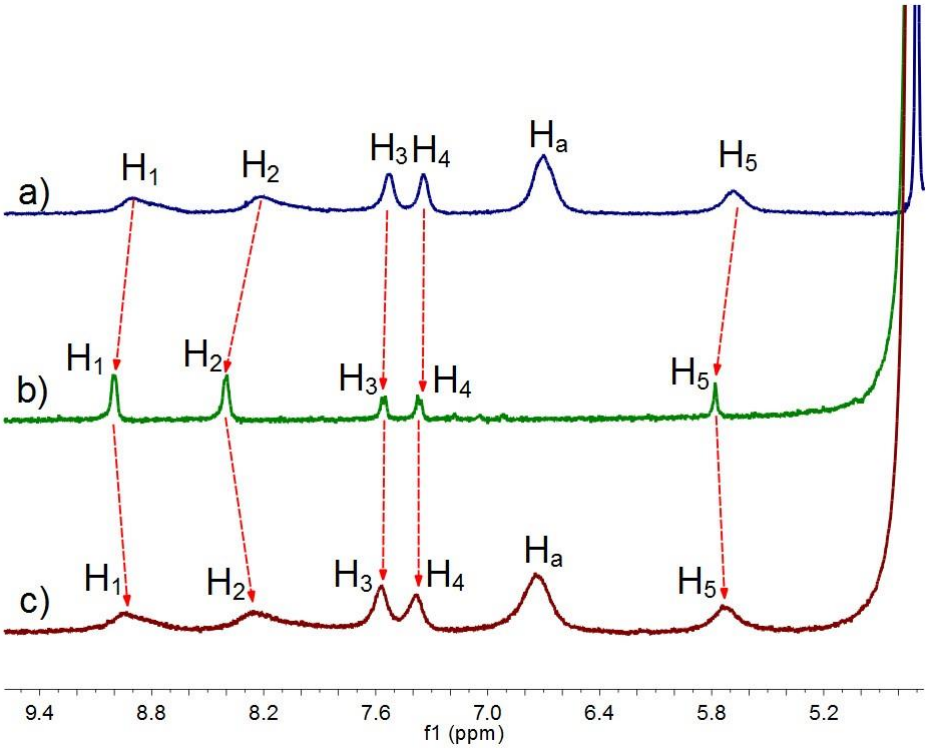


Fig. S7 Partial ^{1}H NMR spectra (500 MHz, D_2O, 298 K): a) a solution of 5.00 mM **1** and 2.50 mM **2**; (b) after adding 10.0 µL aqueous DCl solution (20 %) to a; (c) after adding 5.0 µL aqueous NaOD solution (30 %) to b.

7. The redox responsiveness experiment of the [3]pseudorotaxane

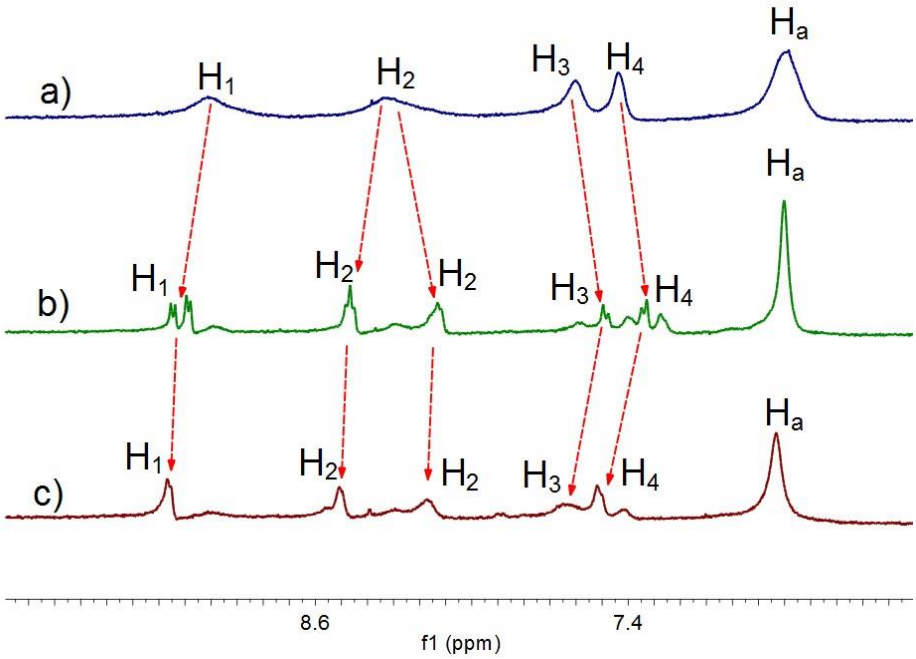


Fig. S8 Partial ^{1}H NMR spectra (500 MHz, D_2O, 298 K): a) a solution of 5.00 mM **1** and 2.50 mM **2**; b) after addition of 2.31 mg (1.5 equiv.) of GSH to a; c) after addition of 0.75 μL (1.5 equiv.) of H_2O_2 to b.

8. The photo responsiveness experiment of the [3]pseudorotaxane

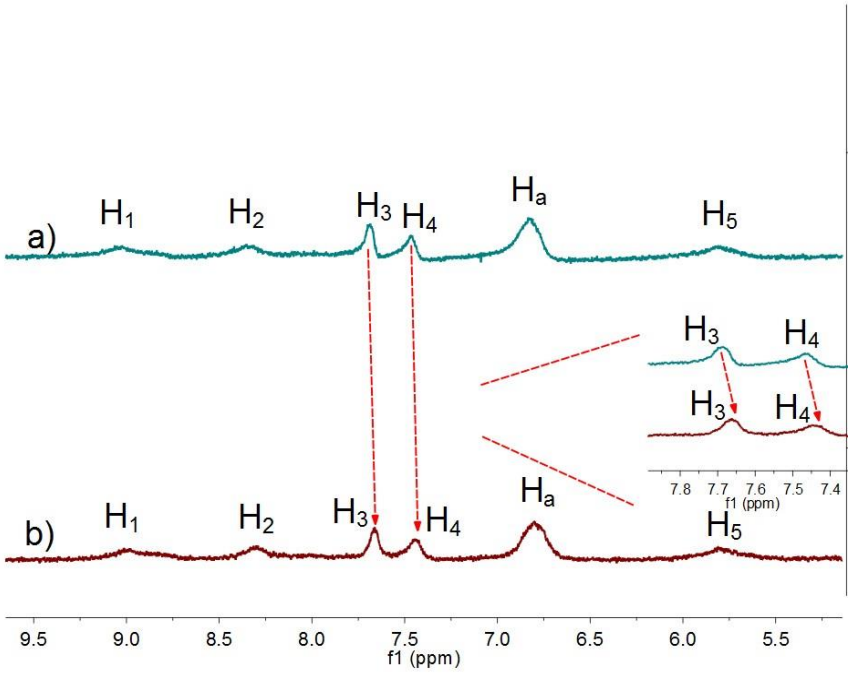


Fig. S9 Partial ^{1}H NMR spectra (500 MHz, D_2O, 298 K): a) a solution of 5.00 mM **1** and 2.50 mM **2**; b) after irradiated by UV at 265nm for 10 hours.

*9. Job plot of **1** □ **2***

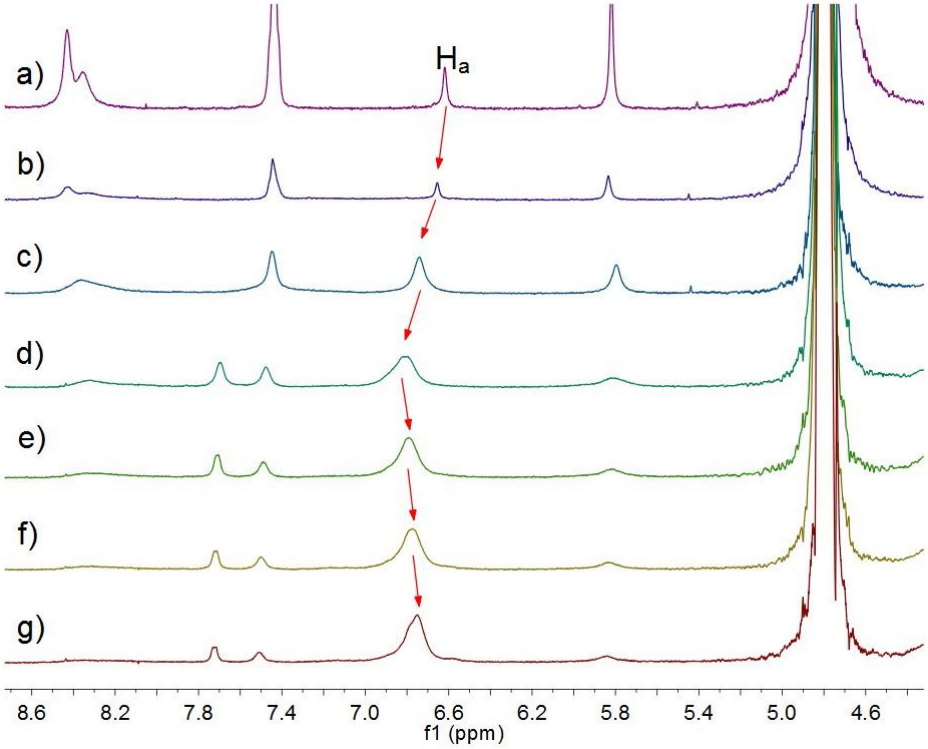


Fig. S10 Partial ^{1}H NMR spectra (400 MHz, D_2O, 298K) of different ratios between **1** and **2**: a) 1 : 3; b) 1 : 2; c) 1 : 1; d) 2 : 1; e) 3 : 1; f) 4 : 1; g) 5 : 1. $[\mathbf{1}]_0 + [\mathbf{2}]_0 = 2.00$ mM.

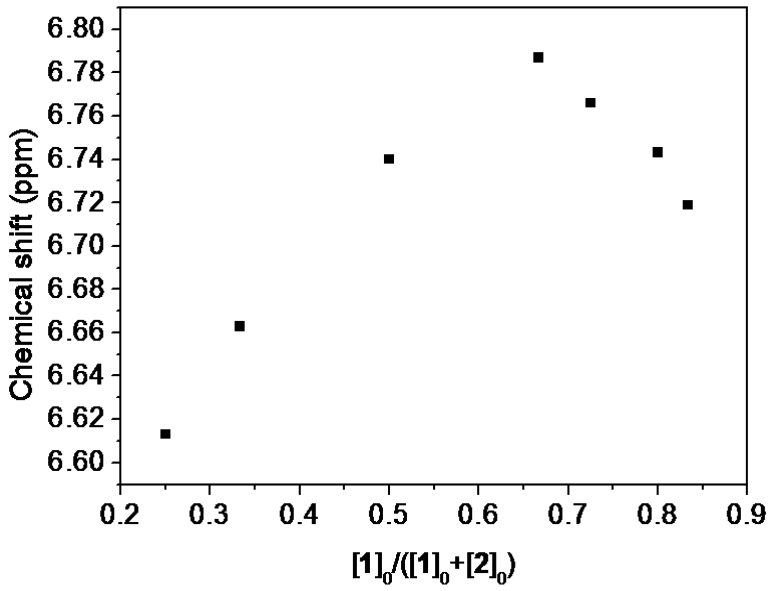


Fig. S11 Job plot showing the 2:1 stoichiometry of the complex between **1** and **2** in D_2O using proton NMR data for H_a of **1**. $[\mathbf{1}]_0 + [\mathbf{2}]_0 = 2.00$ mM.

10. Determination of association constants of ***1*** □ **2**

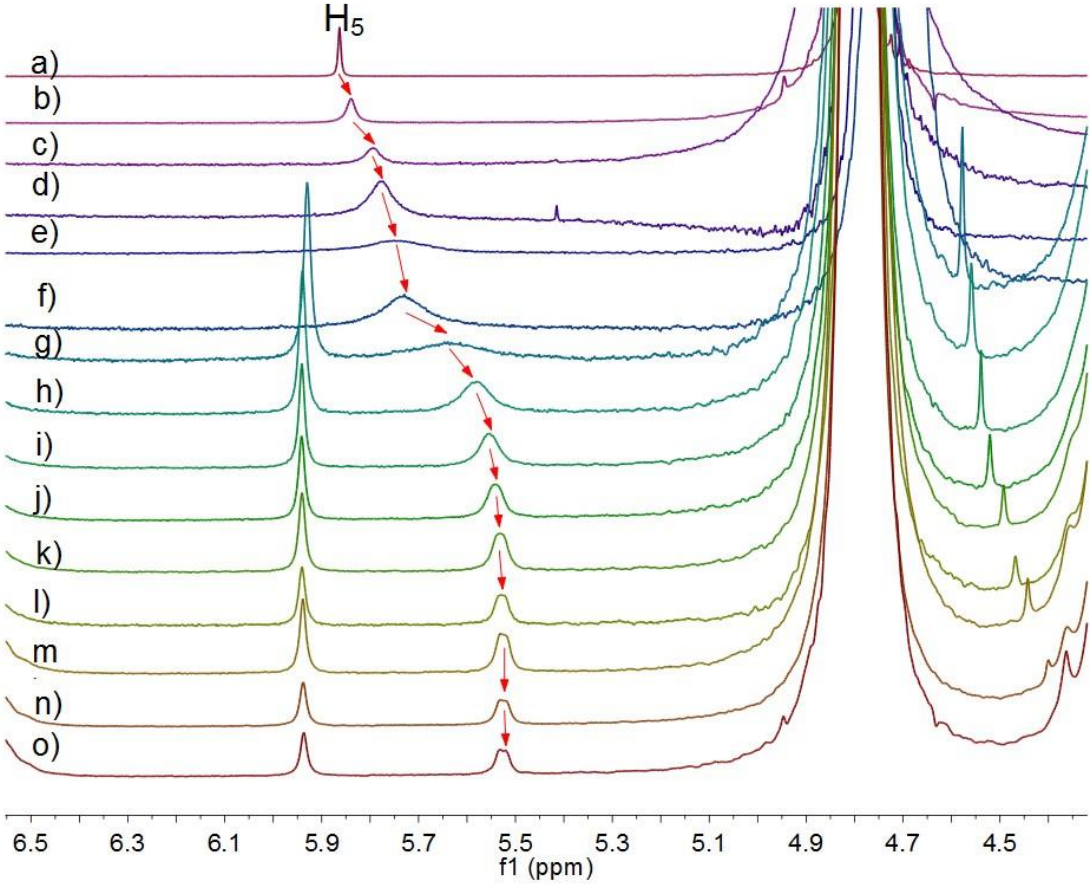
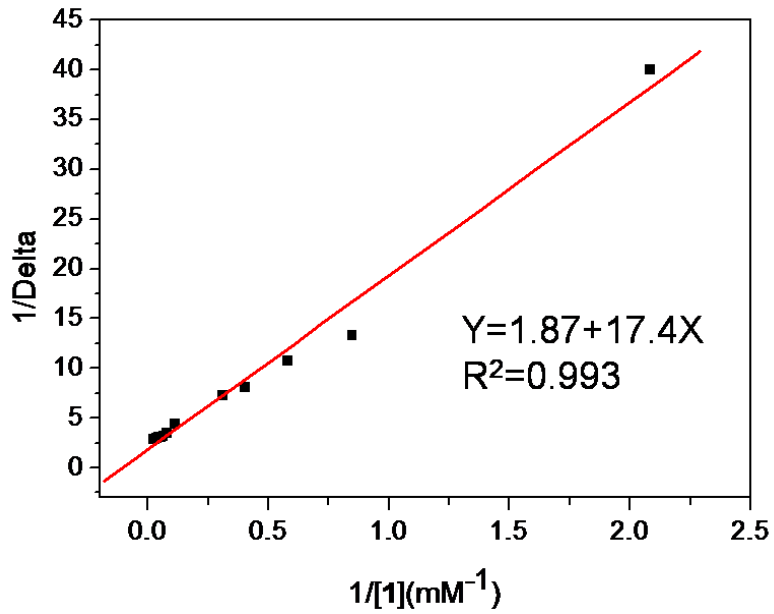


Fig. S12 Partial ^{1}H NMR spectra (400 MHz, D_2O, 298K) of **2** at the concentration of 1.50 mM upon addition of **1**: (a) 0.00 mM, (b) 0.480 mM, (c) 0.950 mM, (d) 1.72 mM, (e) 2.48 mM, (f) 3.22 mM, (g) 8.70 mM, (h) 12.3 mM, (i) 15.6 mM, (j) 18.6 mM, (k) 22.9 mM, (l) 26.7 mM, (m) 30.1 mM, (n) 35.6 mM, (o) 40.0 mM.

Treatment of chemical shifts of H_5 on **2** by Benesi-Hildebrand method[S4] and Scatchard plot[S5] method.

(a)



(b)

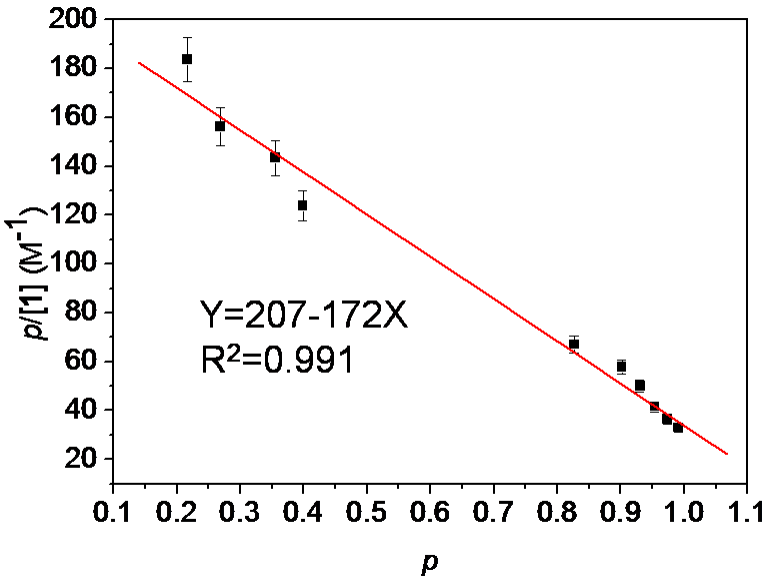


Figure S13. (a) BenesiHildebrand plot for complexation of host **1** with guest **2**. Δ_0, the difference in δ values for H_5 of **2** in the uncomplexed and fully complexed species, was determined as the y-intercept of a plot of $\Delta = \delta - \delta_u$ versus $1/[\mathbf{1}]_0$ in the high initial concentration range of **1**; $\Delta_0 = 1/1.87 = 0.535$ ppm. (b) p = fraction of paraquat units bound. $p = \Delta/\Delta_0$; Δ is the observed chemical shift change relative to uncomplexed species. Error bars in $p/[\mathbf{1}]_{uc}$: ±0.04. The linear nature of this plot demonstrated that the complexation between **1** and **2** was statistical, that is, the two paraquat units binding sites behaved independently. From the intercept and the slope of the Scatchard plot, the average association constant (K_{av}) was determined to be 1.89 (± 0.2) × 10^2 M^{-1} for **1** ⊃ **2**. Since K_1/K_2 = 4:1 for statistical systems (K_1 = [**1** ⊃ **2**]/{[**1**][**2**]} and K_2 = [$\mathbf{1}_2$ ⊃ **2**]/{[**1** ⊃ **2**][**1**]}), K_1 and K_2 were calculated to be 3.02 (± 0.3) × 10^2 M^{-1} and 0.76 (± 0.1) × 10^2 M^{-1}, respectively.

*11. The pH-responsiveness experiment of the guest **2** alone*

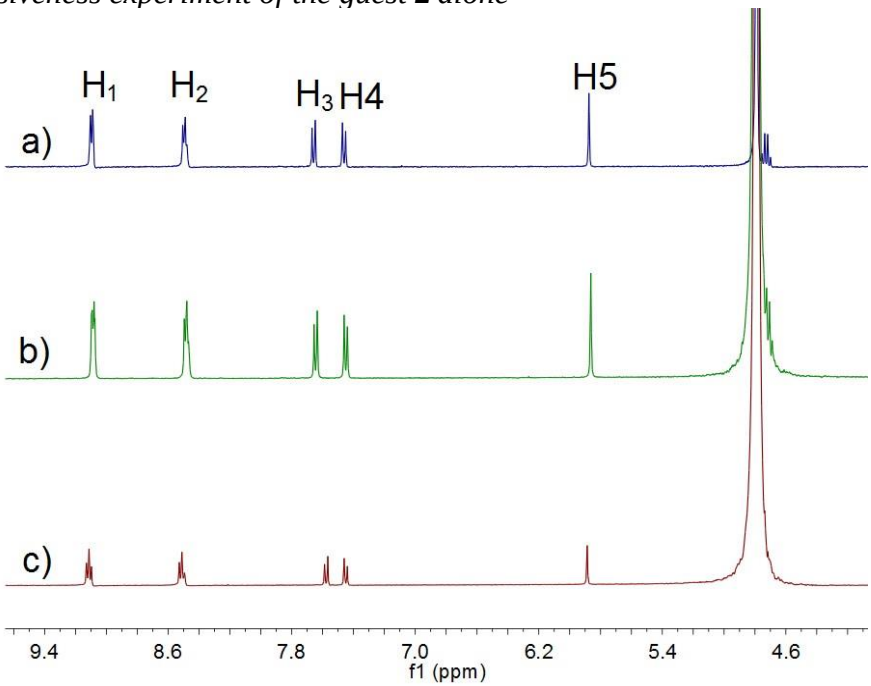


Figure S14. Partial ^{1}H NMR spectra (500 MHz, D_2O, 298 K): a) a solution of 2.50 mM **2**; (b) after adding 10.0 μL aqueous DCl solution (20 %) to a; (c) after adding 5.0 μL aqueous NaOD solution (30 %) to b. There is no change of chemical shift and the guest **2** have no pH-responsiveness. Therefore, the effect of the guest **2** on the pH-responsiveness experiment of the [3]pseudorotaxane was excluded.

*12. The cartoon schematic of the expected effect of breaking and forming the disulfide bond on guest **2** in pseudorotaxane formation*

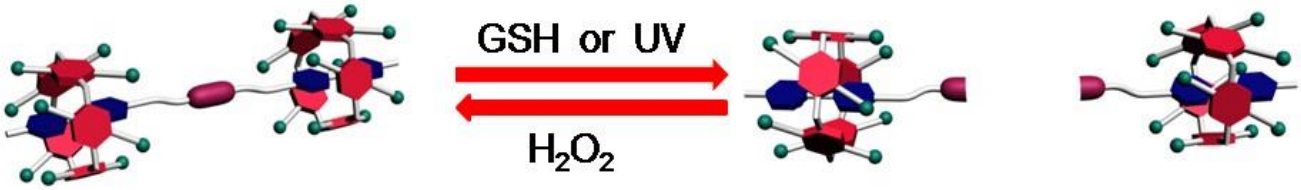


Figure S15. The cartoon schematic of the expected effect of breaking and forming the disulfide bond on guest **2** in pseudorotaxane formation.

References:

S1. F. Campus, P. Bonhote, M. Gratzel, S. Heinen and L. Walder, *Sol. Energy Mater. Sol. Cells.*, 1999, **56**, 281–297.

S2. F. Dumur, V. Roubaud, E. Dumas and C. R. Mayer, *Synlett*, 2010, **16**, 2477–2481.

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S4. H.A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703–2707.

S5. A. G. Marshall, *Biophysical Chemistry*; J. Wiley and Sons: New York, 1978; pp 70–77. D. M. Freifelder, *Physical Biochemistry*; W. H. Freeman and Co.: New York, 1982; pp 659–660. K. A. Connors, *Binding Constants*; J. Wiley and Sons: New York, 1987; pp 78–86.