

# A multi-responsive cross-linked supramolecular polymer network constructed by mussel yield coordination interaction and pillar[5]arene-based host-guest complexation

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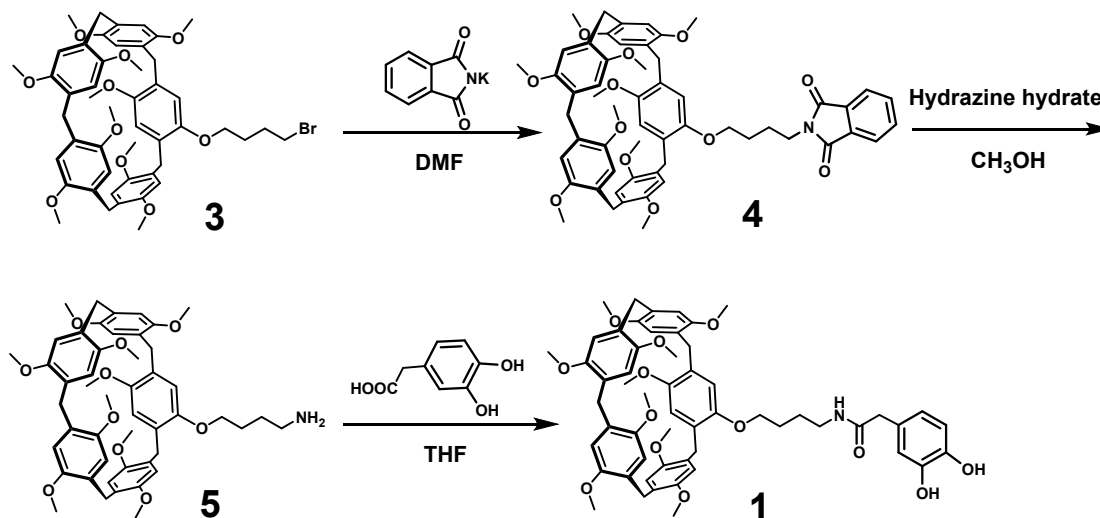
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## ***1. Materials and instrumentations***

All reagents were commercially available and used as supplied without further purification. The compounds **2**, **3**, **4**, **5** were prepared according to previous work.<sup>S1,S2</sup> <sup>1</sup>H NMR spectra, <sup>13</sup>C NMR spectra, NOESY and DOSY were recorded with an Agilent 600 MHz DirectDrive2 with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. UV-vis spectra was taken on a PerkinElmer Lambda 35 UV-vis spectrophotometer. 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 spectrometric experiment was performed with a Bruker 7-Tesla FT-ICR mass spectrometer equipped with an electrospray source (Billerica, MA, USA). Scanning electron microscopy (SEM) investigations were carried out on a JEOL 6390LV instrument. SEM samples were prepared at relative dilute concentration via the vacuum freeze-drying methodology. Rheological behavior of the supramolecular gel-like was analyzed by using an ARG-2 rheometer (TA Instruments, USA). The disc-shaped gel-like with thickness of 1 mm and diameter of 20 mm adhered to the plates and was surrounded by silicone oil. Frequency sweeps were performed to the sample with strain amplitude of 0.05%.

## 2. Synthesis of compound 1



**Scheme S1** The synthetic route to compound 1.

The compounds **4** were prepared according to previous work.<sup>S1</sup> The <sup>1</sup>H NMR spectrum of **4** is shown in Fig. S1. <sup>1</sup>H NMR spectrum of **4** (600 MHz, 298 K) in CDCl<sub>3</sub> δ (ppm): 7.77–7.79 (m, 2 H), 7.64–7.67 (m, 2 H), 6.64–6.71 (m, 10 H), 3.78–3.81 (t, *J* = 9 Hz, 2 H), 3.67–3.73 (m, 12 H), 3.56–3.59 (m, 24 H), 3.53 (s, 3 H), 1.83–1.89 (m, 2 H), 1.74–1.79 (m, 2 H). The <sup>13</sup>C NMR spectrum of **4** is shown in Fig. S2. <sup>13</sup>C NMR spectrum of **4** (150 MHz, 298 K) in CDCl<sub>3</sub> δ (ppm): 167.4, 149.6, 148.8, 132.9, 131.0, 127.1, 122.2, 113.8, 112.9, 66.7, 59.4, 54.8, 51.6, 36.8, 28.6, 26.2, 24.6, 20.0, 13.1. LRESIMS is shown in Fig. S3: *m/z* 955.24 [M + NH<sub>4</sub>]<sup>+</sup>.

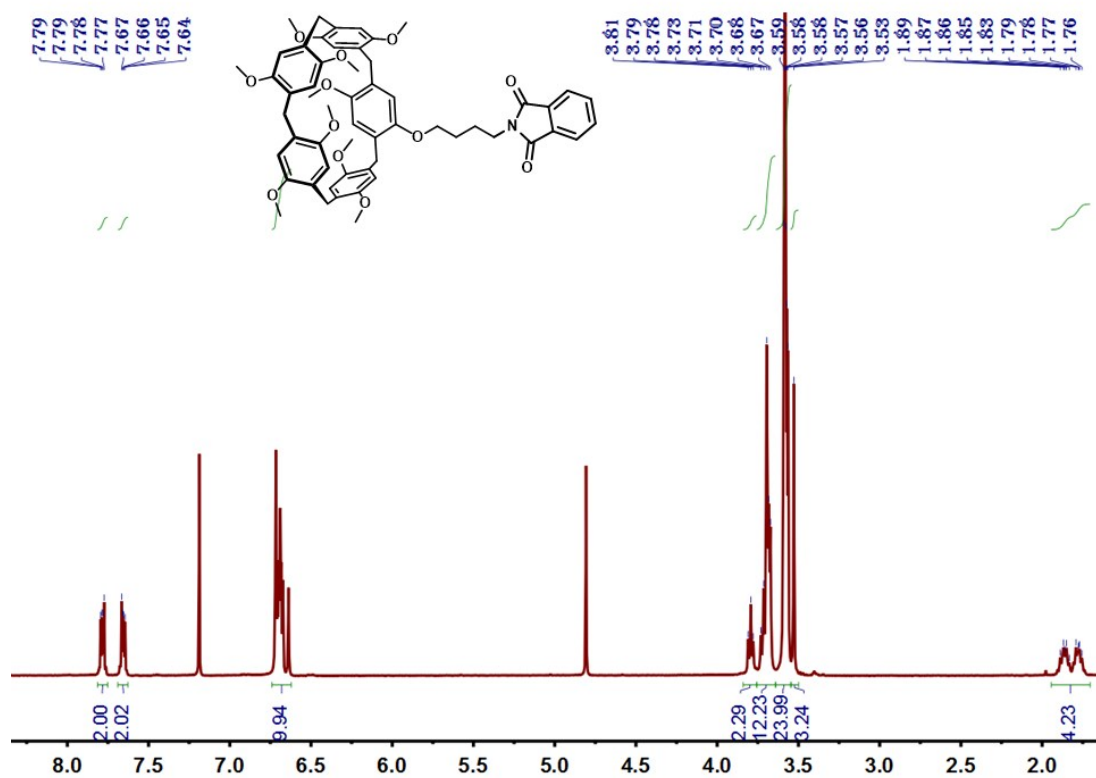


Fig. S1  $^1\text{H}$  NMR spectrum (600 MHz,  $\text{CDCl}_3$ , 298 K) of 4.

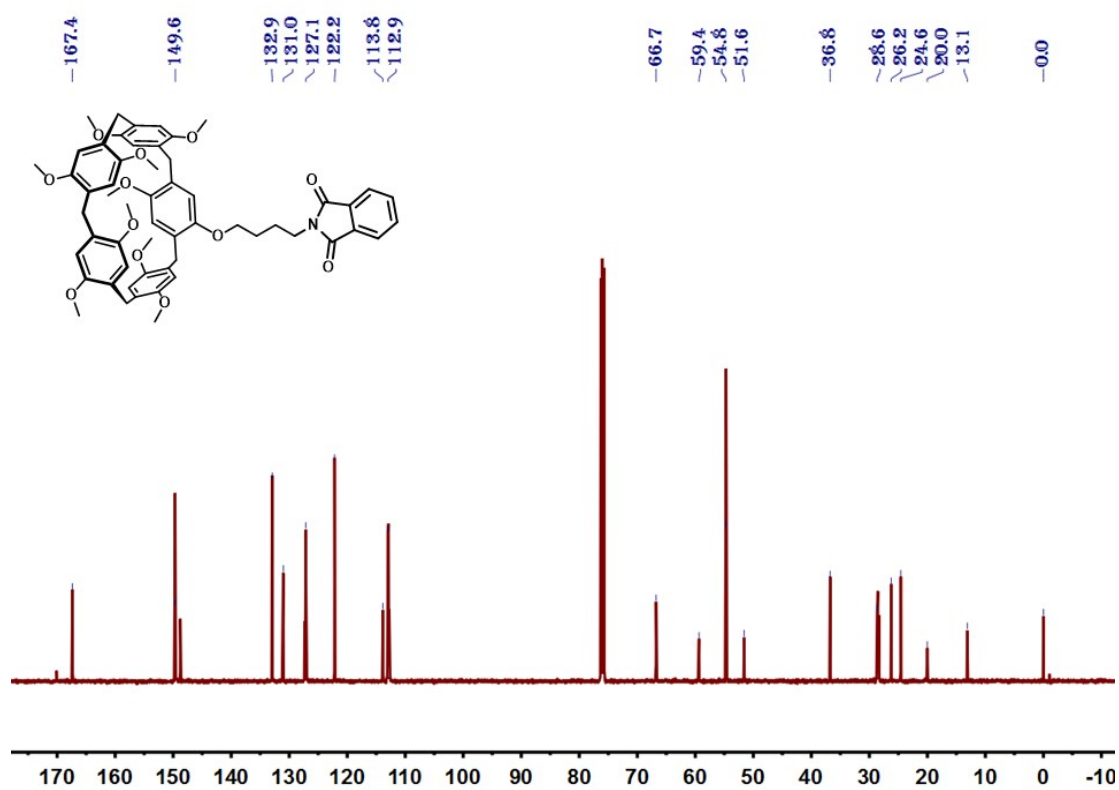
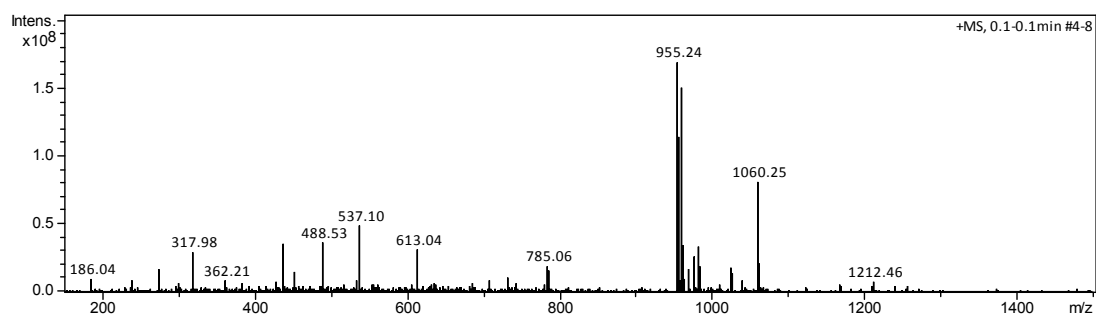
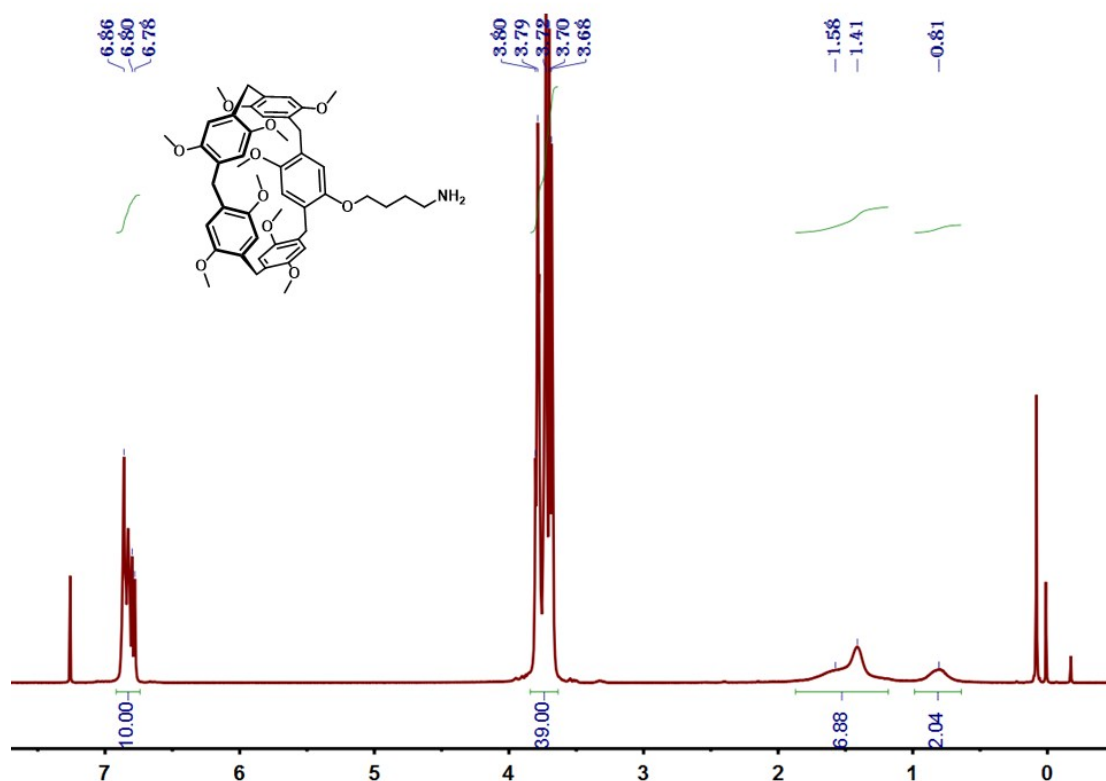


Fig. S2  $^{13}\text{C}$  NMR spectrum (150 MHz,  $\text{CDCl}_3$ , 298 K) of 4.



**Fig. S3** LRESIMS spectrum of **4** in  $\text{CHCl}_3$ .

The compounds **5** were prepared according to previous work.<sup>S1</sup> The  $^1\text{H}$  NMR spectrum of **5** is shown in Fig. S4.  $^1\text{H}$  NMR spectrum of **5** (600 MHz, 298 K) in  $\text{CDCl}_3$   $\delta$  (ppm): 6.78–6.86 (m, 10 H), 3.68–3.80 (m, 39 H), 1.24–1.74 (m, 4 H), 0.81 (s, 2 H). The  $^{13}\text{C}$  NMR spectrum of **5** is shown in Fig. S5.  $^{13}\text{C}$  NMR spectrum of **5** (150 MHz, 298 K) in  $\text{CDCl}_3$   $\delta$  (ppm): 153.4, 152.6, 130.8, 117.6, 116.9, 110.0, 71.0, 58.6, 32.4, 29.5. LRESIMS is shown in Fig. S6:  $m/z$  808.63  $[\text{M} + \text{H}]^+$ .



**Fig. S4**  $^1\text{H}$  NMR spectrum (600 MHz,  $\text{CDCl}_3$ , 298 K) of **5**.

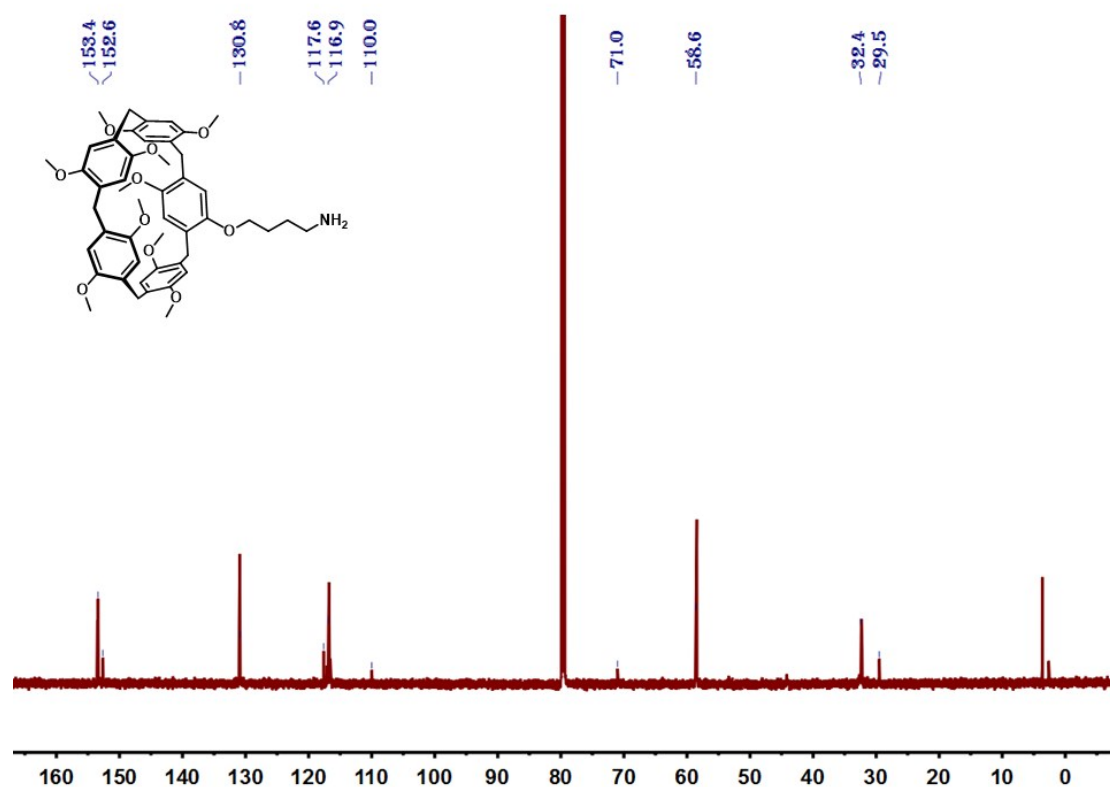


Fig. S5  $^{13}\text{C}$  NMR spectrum (150 MHz,  $\text{CDCl}_3$ , 298 K) of **5**.

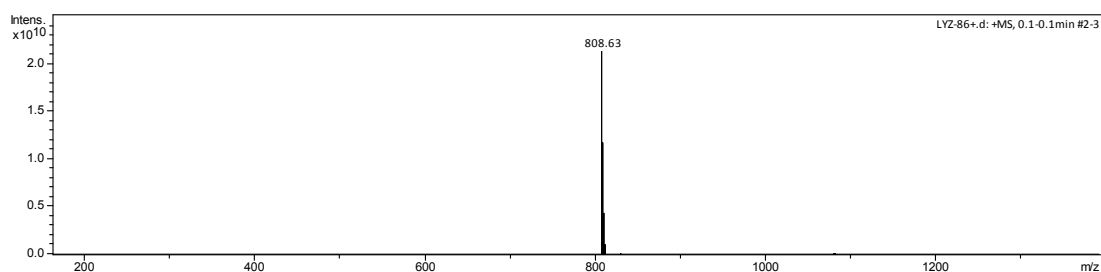
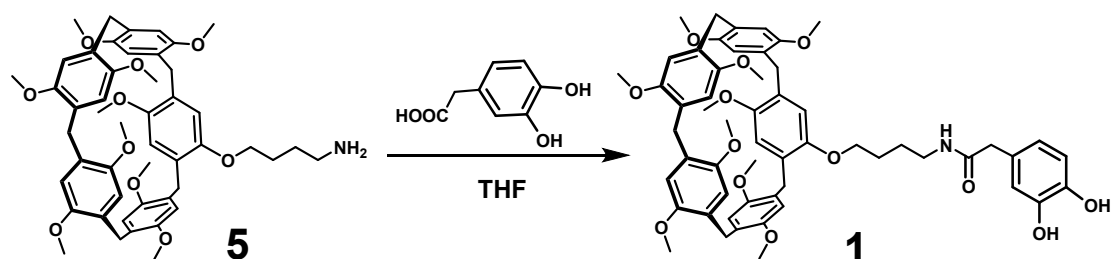


Fig. S6 LRESIMS spectrum of **5** in  $\text{CHCl}_3$ .



Synthesis of compound **1**: A mixture of compound **5** (2.12 g, 2.58 mmol), DOPAC (650 mg, 3.87 mmol), EDC (520 mg, 2.71 mmol) and DMAP (catalytic amount) was stirred at room temperature in dry THF (200 ml) for 24 hours. After the solid was

filtered off, the solvent was concentrated by rotary evaporation. The crude product was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) and washed three times with H<sub>2</sub>O (50 mL). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated to afford a brown solid, which was further purified by column chromatography using dichloromethane/methanol (*v* : *v* = 20:1). The fractions containing the product were concentrated to give **1** as a white solid.

The <sup>1</sup>H NMR spectrum of **1** is shown in Fig. S7. <sup>1</sup>H NMR spectrum of **1** (600 MHz, 298 K) in CDCl<sub>3</sub> δ (ppm): 6.71–6.75 (m, 10 H), 6.66–6.67 (m, 2 H), 6.53–6.54 (d, *J* = 6 Hz, 1 H), 6.36–6.39 (m, 1 H), 3.76–3.78 (t, *J* = 6 Hz, 2 H), 3.68–3.73 (m, 12 H), 3.60–3.63 (m, 24 H), 3.57 (s, 3 H), 3.18–3.21 (t, *J* = 9 Hz, 2 H), 1.67–1.72 (m, 2 H), 1.59–1.63 (m, 2 H). The <sup>13</sup>C NMR spectrum of **1** is shown in Fig. S8. <sup>13</sup>C NMR spectrum of **1** (150 MHz, 298 K) in CDCl<sub>3</sub> δ (ppm): 171.8, 149.9, 148.7, 143.7, 142.9, 127.3, 125.3, 120.2, 114.9, 114.0, 112.9, 66.9, 55.2, 54.8, 51.9, 42.0, 38.6, 28.7, 26.0, 25.4. LRESIMS is shown in Fig. S9: *m/z* 958.54 [M + H]<sup>+</sup>. *m/z* calcd for [M + H]<sup>+</sup> C<sub>56</sub>H<sub>64</sub>NO<sub>13</sub><sup>+</sup>, 958.4378; found 958.4265, error –1ppm.

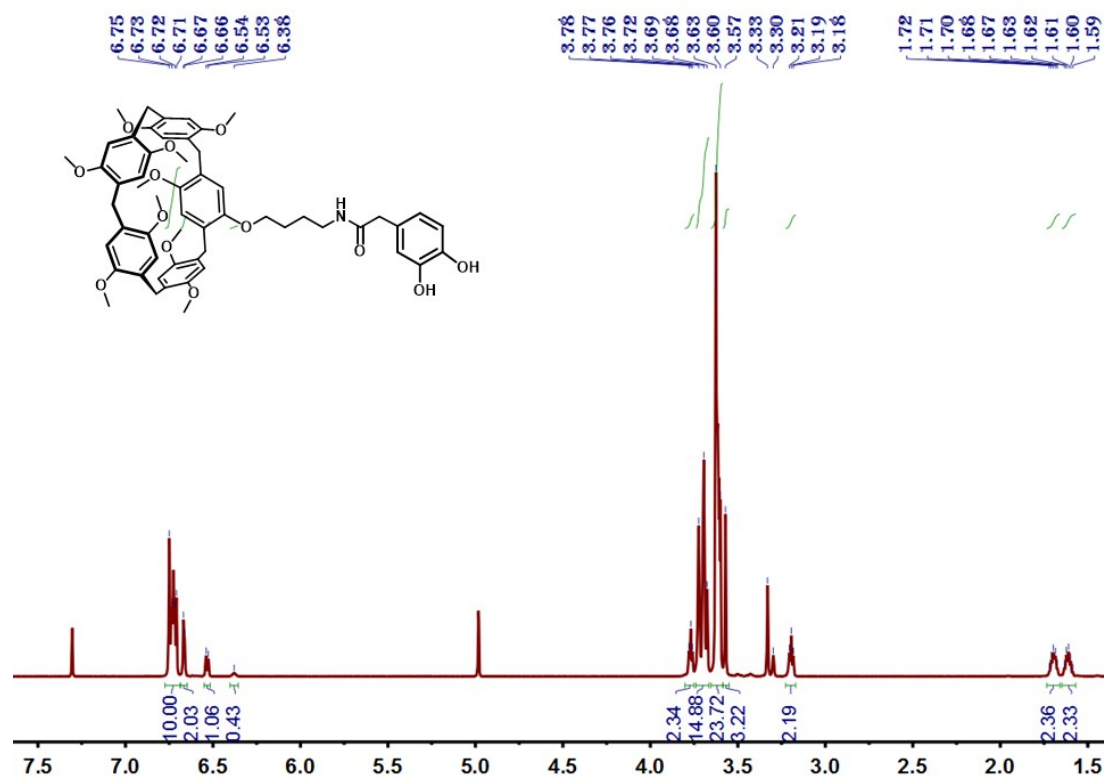
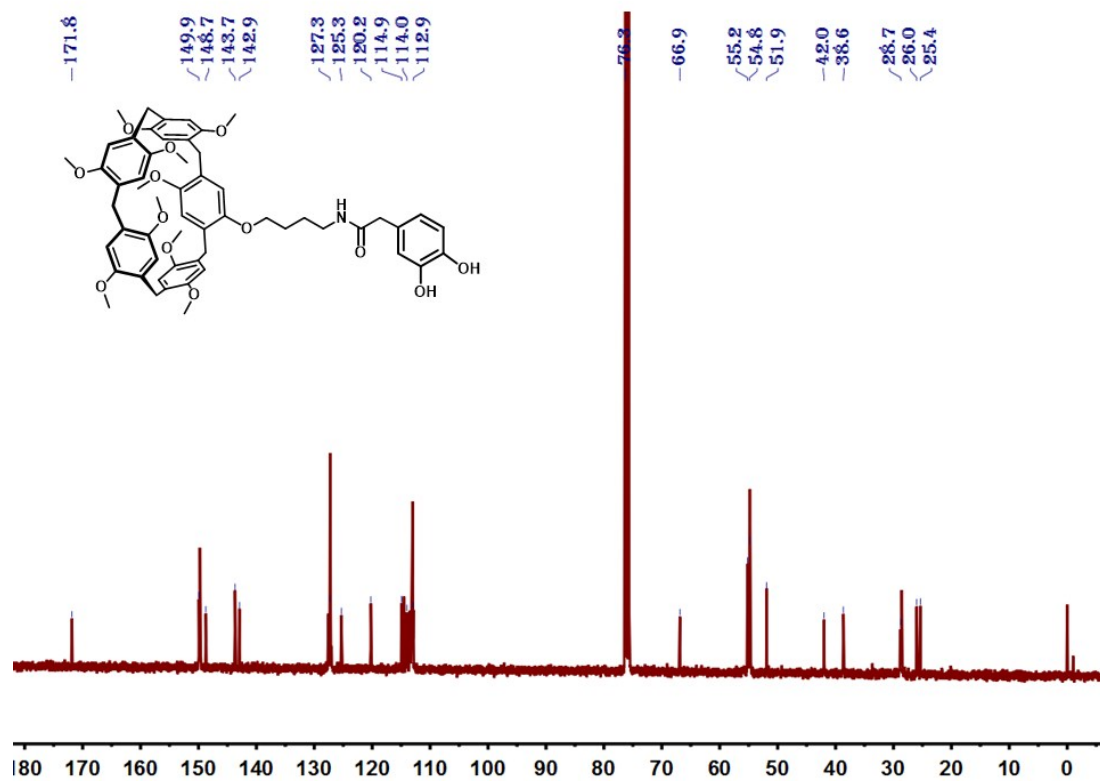
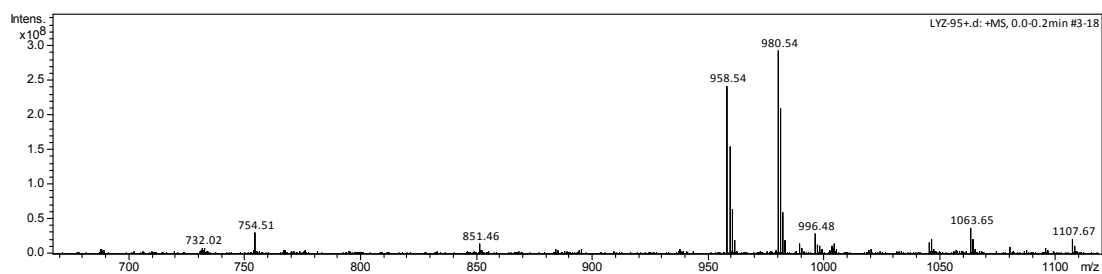


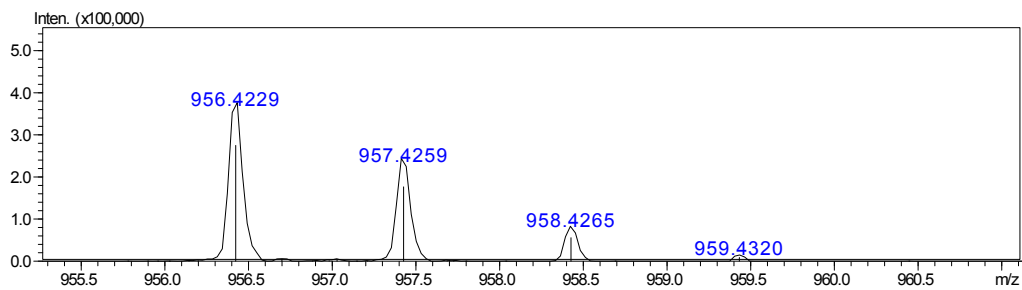
Fig. S7 <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>, 298 K) of **1**.



**Fig. S8**  $^{13}\text{C}$  NMR spectrum (150 MHz,  $\text{CDCl}_3$ , 298 K) of **1**.



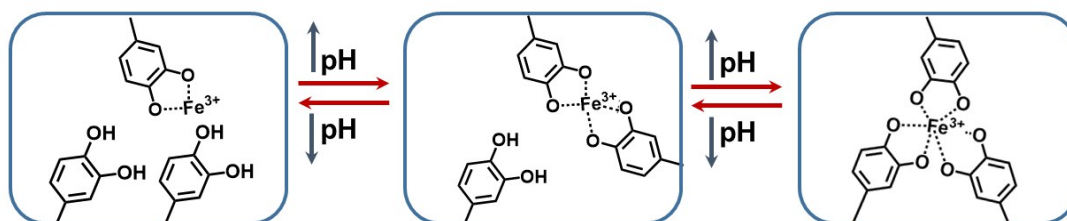
**Fig. S9** LRESIMS spectrum of **1** in  $\text{CHCl}_3$ .



**Fig. S10** HRESIMS spectrum of **1** in  $\text{CHCl}_3$ .

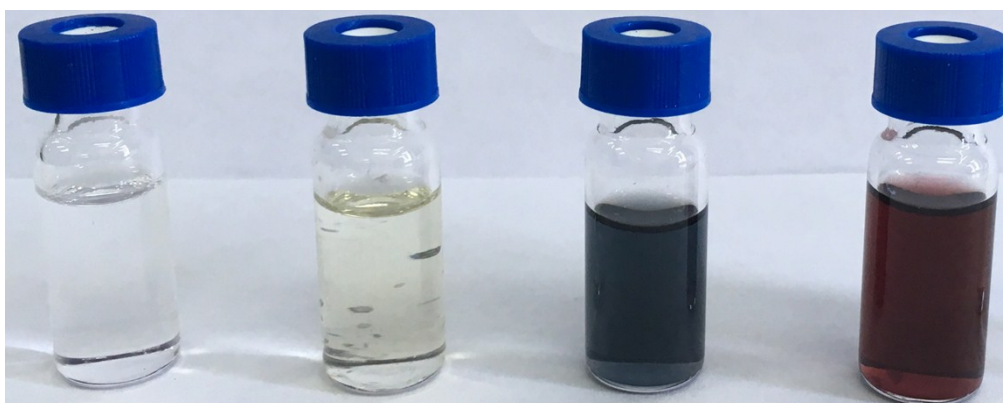


### 3. pH-dependent catechol-Fe<sup>3+</sup> coordination



Scheme S2 pH-dependent catechol-Fe<sup>3+</sup> coordination.

### 4. Photographs of colour changes of pH-dependent catechol-Fe<sup>3+</sup> coordination



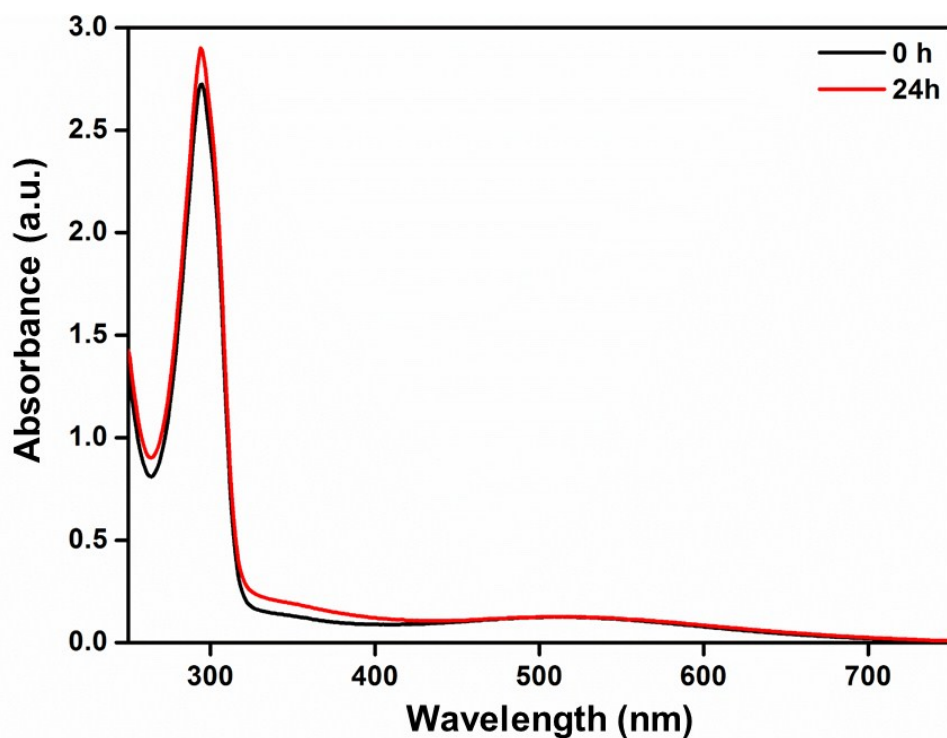
**Fig. S11** Photographs of colour changes of each swatch at different equivalent of MeONa compared with **1** (left to right): 1.00 mM **1**; 1.00 mM **1** and 1/3 equivalent of Fe(SO<sub>3</sub>CF<sub>3</sub>)<sub>3</sub>; 1.00 mM **1**, 1/3 equivalent of Fe(SO<sub>3</sub>CF<sub>3</sub>)<sub>3</sub> and 1.00 equivalent of MeONa; 1.00 mM **1**, 1/3 equivalent of Fe(SO<sub>3</sub>CF<sub>3</sub>)<sub>3</sub> and 4.00 equivalents of MeONa.

### 5. The diffusion coefficient *D* of pH-dependent catechol-Fe<sup>3+</sup> coordination

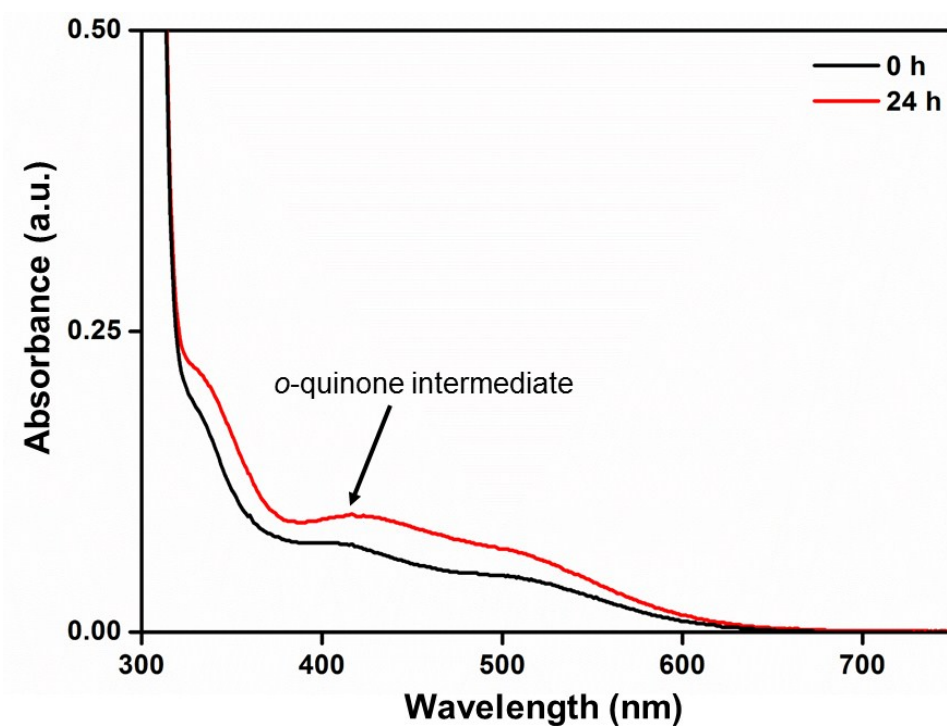
Base/Compound <b>1</b> (molar ratio)	0	1.0	4.0
<i>D</i> /10 <sup>-9</sup> m <sup>2</sup> s <sup>-1</sup>	16.7	13.2	9.2

**Fig. S12** The diffusion coefficient *D* (600 MHz, 298 K) in CDCl<sub>3</sub>/CD<sub>3</sub>OD (*v* : *v* = 10 : 1) of mixtures of 5.00 mM **1**, 1/3 equivalent of Fe(SO<sub>3</sub>CF<sub>3</sub>)<sub>3</sub> with different ratio of MeONa compared with **1**: 0 equivalent; 1.00 equivalent; 4.00 equivalents.

6. The stability of tri-catechol- $\text{Fe}^{3+}$  complex and compound 1

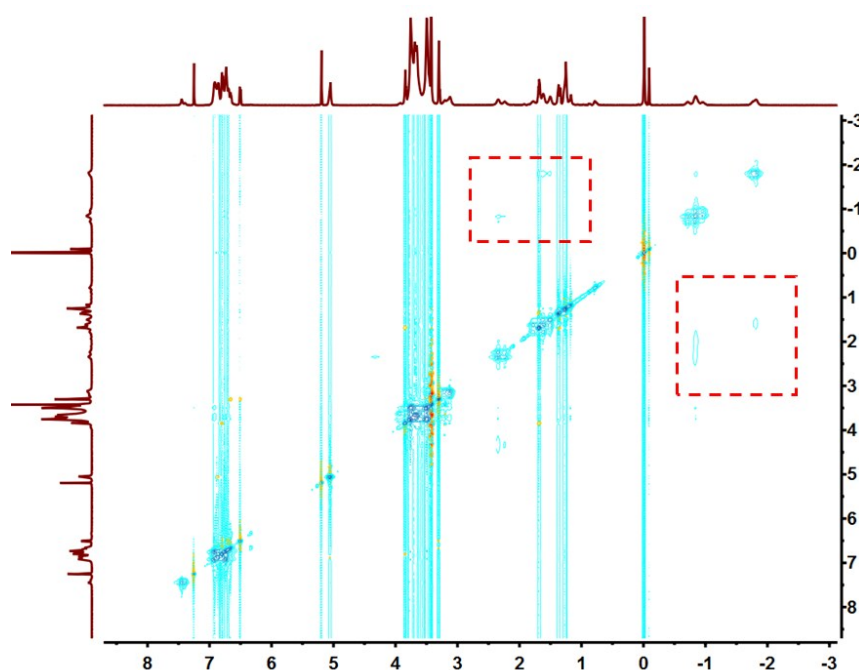


**Fig. S13** Time-dependent UV-vis spectra of tri-catechol- $\text{Fe}^{3+}$  complex (0.10 mM **1**, 1/3 equivalent of  $\text{Fe}^{3+}$  and 4.00 equivalents of MeONa) in  $\text{CHCl}_3/\text{CH}_3\text{OH}$  ( $v : v = 10 : 1$ ).



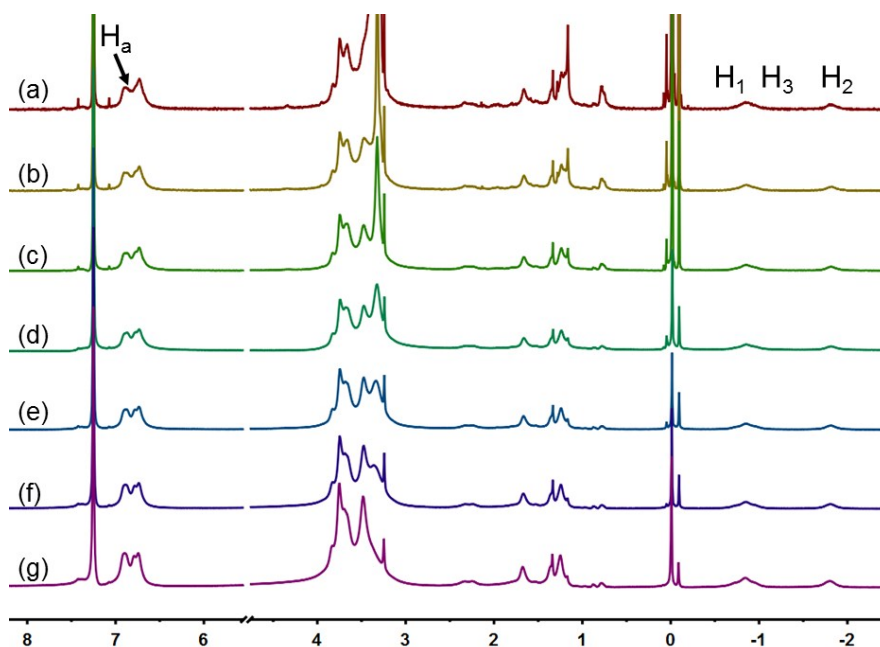
**Fig. S14** Time-dependent UV-vis spectra of 0.10 mM compound **1** with 4.00 equivalent of MeONa in  $\text{CHCl}_3/\text{CH}_3\text{OH}$  ( $v : v = 10 : 1$ ).

## 7. 2D NOESY NMR spectra of a mixture of 1 and 2



**Fig. S15** 2D NOESY NMR spectrum (600 MHz, 298 K) in CDCl<sub>3</sub>/CD<sub>3</sub>OD ( $\nu : \nu = 10 : 1$ ) of 10.0 mM **1** and 5.00 mM **3**.

## 8. Concentration-variant <sup>1</sup>H NMR spectra of 1·Fe<sup>3+</sup>·2



**Fig. S16** Partial <sup>1</sup>H NMR spectra (600 MHz, 298 K) of mixtures of **1**·Fe<sup>3+</sup>·**2** at different concentrations of host molecule **1** in CDCl<sub>3</sub>/CD<sub>3</sub>OD ( $\nu : \nu = 10 : 1$ ): (a) 2.00 mM; (b) 5.00 mM; (c) 10.0 mM; (d) 20.0 mM; (e) 30.0 mM; (f) 40.0 mM; (g) 50.0 mM.

9. Concentration-variant 2D DOSY NMR spectra of  $1 \cdot \text{Fe}^{3+} \cdot 2$

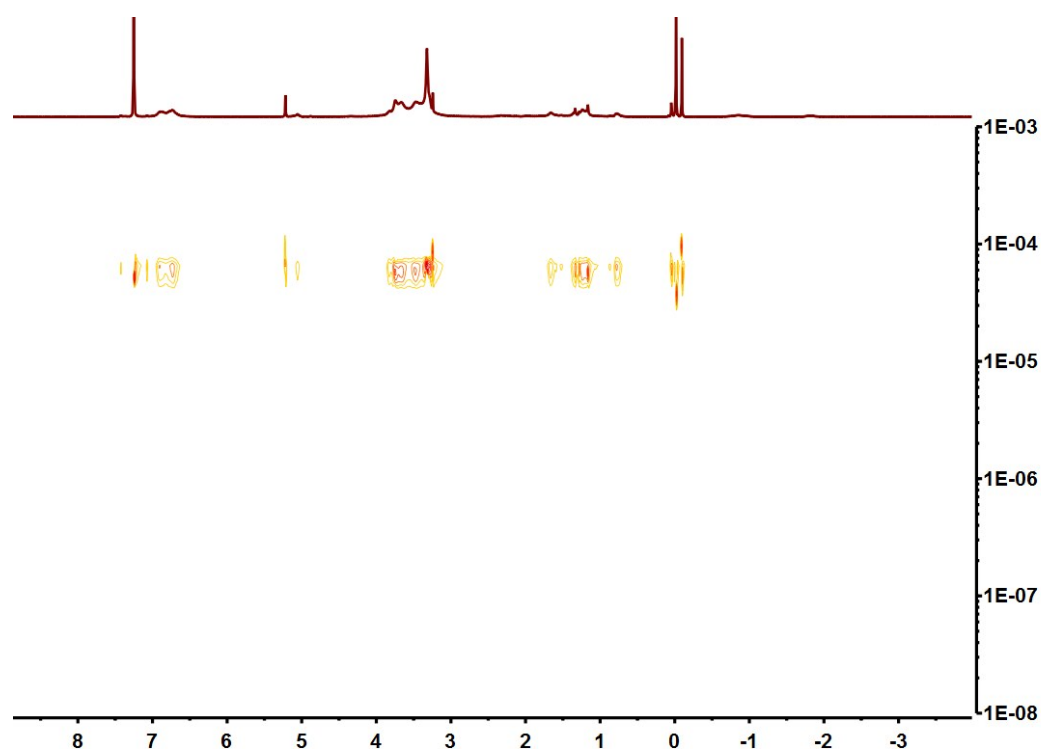


Fig. S17 2D DOSY NMR spectrum (600 MHz, 298 K) of  $1 \cdot \text{Fe}^{3+} \cdot 2$  at 5.00 mM **1** in  $\text{CDCl}_3/\text{CD}_3\text{OD}$  ( $\nu : \nu = 10 : 1$ ).

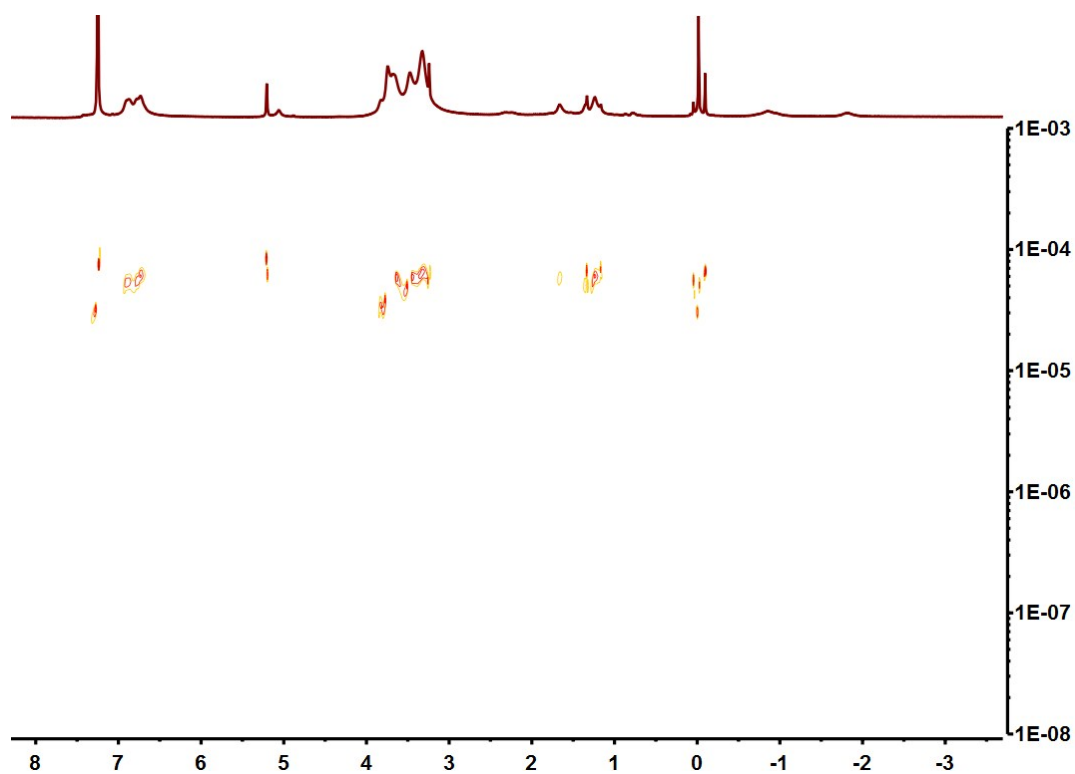
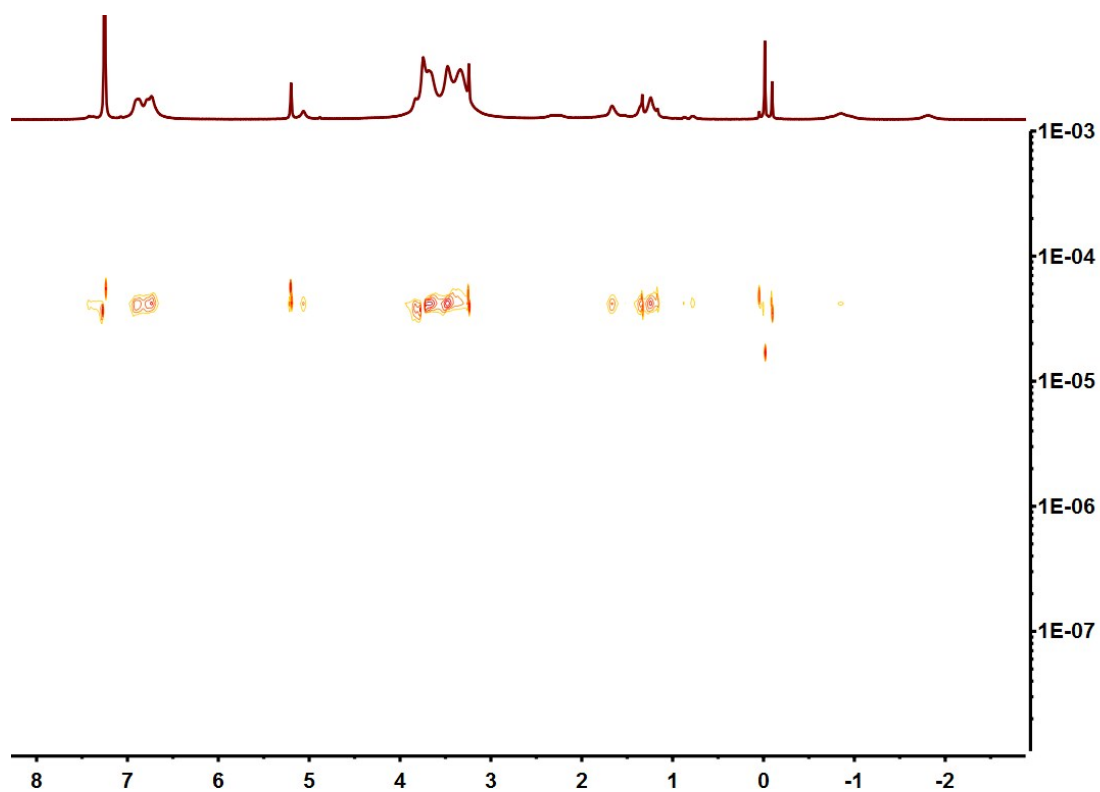
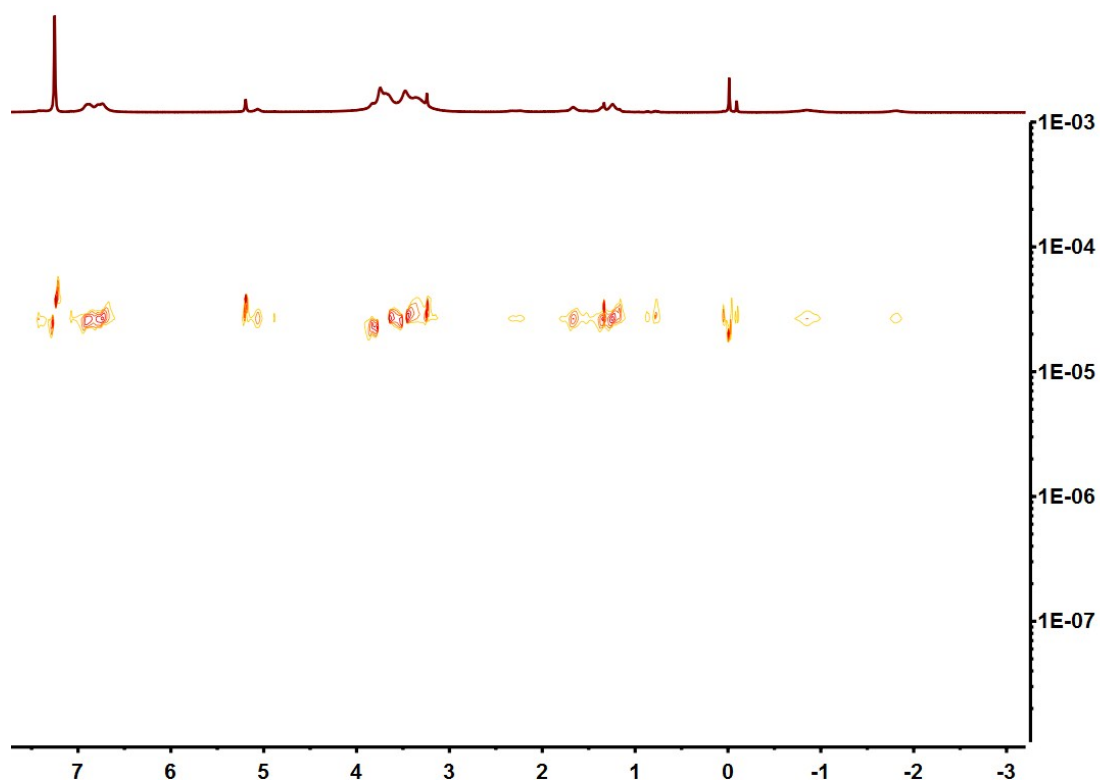


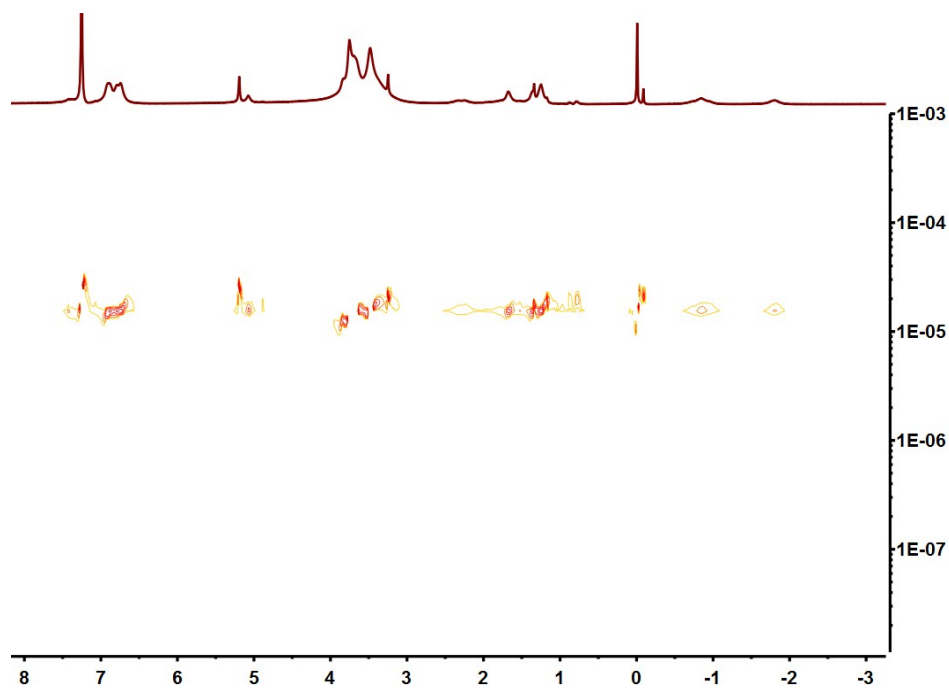
Fig. S18 2D DOSY NMR spectrum (600 MHz, 298 K) of  $1 \cdot \text{Fe}^{3+} \cdot 2$  at 20.0 mM **1** in  $\text{CDCl}_3/\text{CD}_3\text{OD}$  ( $\nu : \nu = 10 : 1$ ).



**Fig. S19** 2D DOSY NMR spectrum (600 MHz, 298 K) of  $1 \cdot \text{Fe}^{3+} \cdot 2$  at 30.0 mM **1** in  $\text{CDCl}_3/\text{CD}_3\text{OD}$  ( $v : v = 10 : 1$ ).

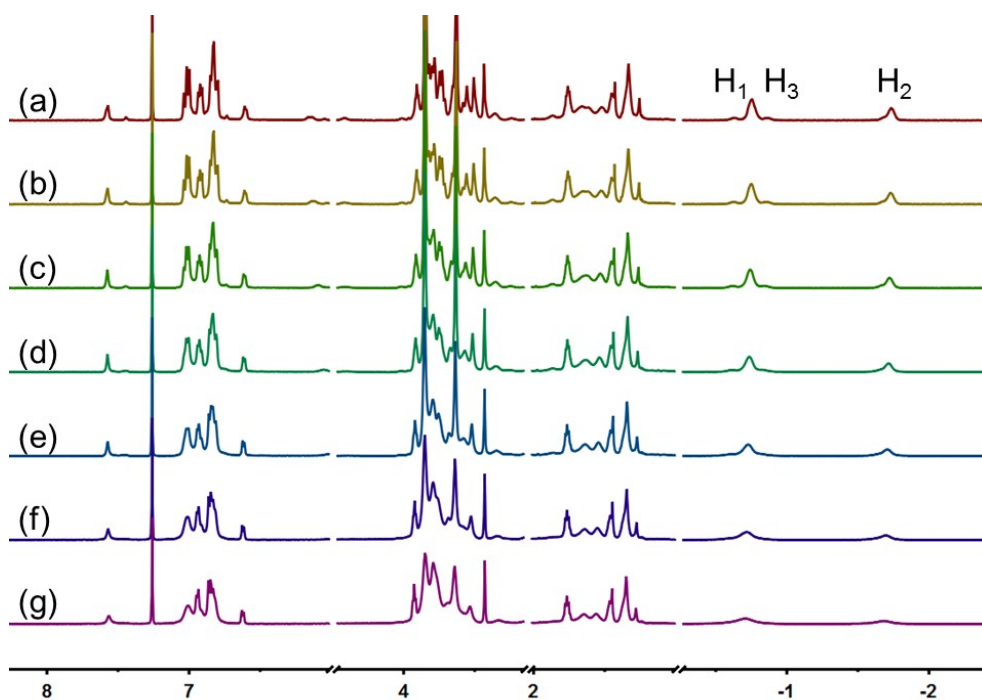


**Fig. S20** 2D DOSY NMR spectrum (600 MHz, 298 K) of  $1 \cdot \text{Fe}^{3+} \cdot 2$  at 40.0 mM **1** in  $\text{CDCl}_3/\text{CD}_3\text{OD}$  ( $v : v = 10 : 1$ ).



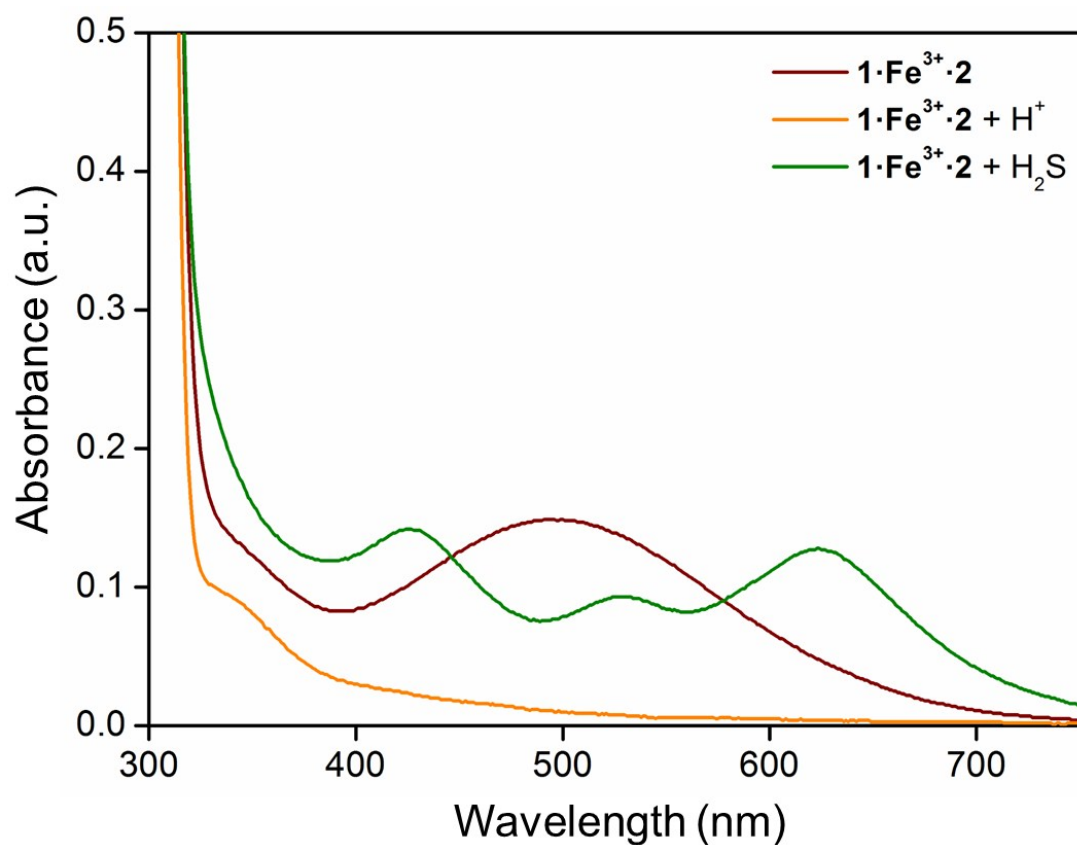
**Fig. S21** 2D DOSY NMR spectrum (600 MHz, 298 K) of  $1 \cdot \text{Fe}^{3+} \cdot 2$  at 50.0 mM **1** in  $\text{CDCl}_3/\text{CD}_3\text{OD}$  ( $v : v = 10 : 1$ ).

**10. The temperature-variant NMR experiments of a mixture of 1 and 2**



**Fig. S22**  $^1\text{H}$  NMR spectra (600 MHz) of a 1:2 molar ratio mixture of **2** and **1** at 5.00 mM **1** in  $\text{CDCl}_3/\text{CD}_3\text{OD}$  ( $v : v = 10 : 1$ ) at various temperatures: (a) 298 K; (b) 303 K; (c) 308 K; (d) 313 K; (e) 318 K; (f) 323 K; (g) 328 K.

### 11. The pH and H<sub>2</sub>S responsivenesses of the 1·Fe<sup>3+</sup>·2



**Fig. S23** UV-vis spectra of 1·Fe<sup>3+</sup>·2 at 0.10 mM 1, 1·Fe<sup>3+</sup>·2 at 0.10 mM 1 after adding 4.00 equivalents of H<sup>+</sup>, 1·Fe<sup>3+</sup>·2 at 0.10 mM 1 after blowing H<sub>2</sub>S into the solution in in CDCl<sub>3</sub>/CD<sub>3</sub>OD ( $\nu : \nu = 10 : 1$ ), respectively.

### 12. References

- S1. L. Shao, J. Yang and B. Hua, *Polym. Chem.*, 2018, **9**, 1293–1297.
- S2. B. Shi, K. Jie, Y. Zhou, D. Xia and Y. Yao, *Chem. Commun.*, 2015, **51**, 4503–4506.