

Electronic Supplemmetary Information

A novel supramolecular system with multiple fluorescent states constructed by orthogonal self-assembly

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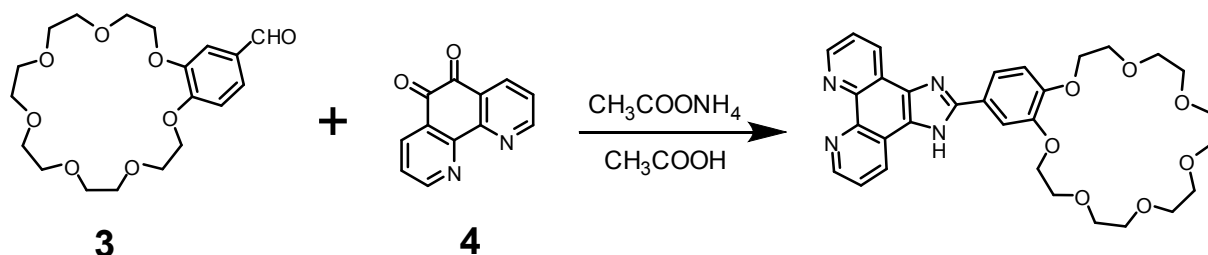
Table of Contents

Materials and methods	S2
Synthesis of compound 1	S3
Partial NOESY NMR spectrum of 1 + 2	S5
Partial ^1H NMR spectra of 1 + 2 and 1 + 2 + Zn^{2+}	S6
Partial DOSY NMR spectra of 1, 1 + 2, 1 + 2 + Zn^{2+}	S6
SEM and pictures of the gel	S8
Variable temperature partial ^1H NMR spectra of 1 + 2 + Zn^{2+}	S8
SI References	S9

Materials and methods

Compounds 2^{S1} and 3^{S2} were synthesized according to the literature procedures. All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to the procedures described in the literature. NMR spectra were recorded with a Bruker Avance DMX 500 spectrophotometer with the use of deuterated solvent as the lock and the residual solvent or TMS as the internal reference. 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. Scanning electron microscopy (SEM) investigations were carried out on a JEOL 6390LV instrument. Dynamic light scattering (DLS) was carried out on a Malvern Nanosizer S instrument at room temperature. The fluorescence experiments were conducted on a RF-5301 spectrofluorophotometer (Shimadzu Corporation, Japan).

Synthesis of compound 1



Scheme S1. Synthetic route of **1**.

A mixture of 1,10-phenanthroline-5,6-dione (compound **4**, 1.05 g, 5.0 mmol), corresponding compound **3** (1.92 g, 5.0 mmol), ammonium acetate (3.1 g, 40.0 mmol) and acetic acid (20 mL) was refluxed under nitrogen in an oil bath. After 5 h, the mixture was cooled and filtered, and then separated by chromatography to give a yellow powder of **1** (2.44 g, 85%). The ^1H NMR spectrum of **1** is shown in Figure S1. ^1H NMR (400 MHz, DMSO, 298 K) δ (ppm): 9.03 (d, $J = 1.6$ Hz, 2H), 8.93 (d, $J = 3.0$ Hz, 2H), 7.87-7.85 (m, 4H), 7.20 (d, $J = 3.4$ Hz, 1H), 4.25–4.20 (m, 4H), 3.85–3.81 (m, 4H), 3.67-3.64 (m, 4H), 3.59-3.58 (m, 4H), 3.55-3.51 (m, 8H). The ^{13}C NMR spectrum of **1** is shown in Figure S2. ^{13}C NMR (100 MHz, DMSO, 298 K) δ (ppm): 150.72, 149.58, 148.22, 147.63, 143.44, 129.55, 122.77, 119.49, 113.13, 111.18, 70.31, 70.26, 70.23, 70.16, 70.13, 69.88, 68.93, 68.85, 68.56, 68.34. RESIMS is shown in Figure S3: m/z 575.6 $[\text{M} + \text{H}]^+$, m/z 597.7 $[\text{M} + \text{Na}]^+$, m/z 613.6 $[\text{M} + \text{K}]^+$.

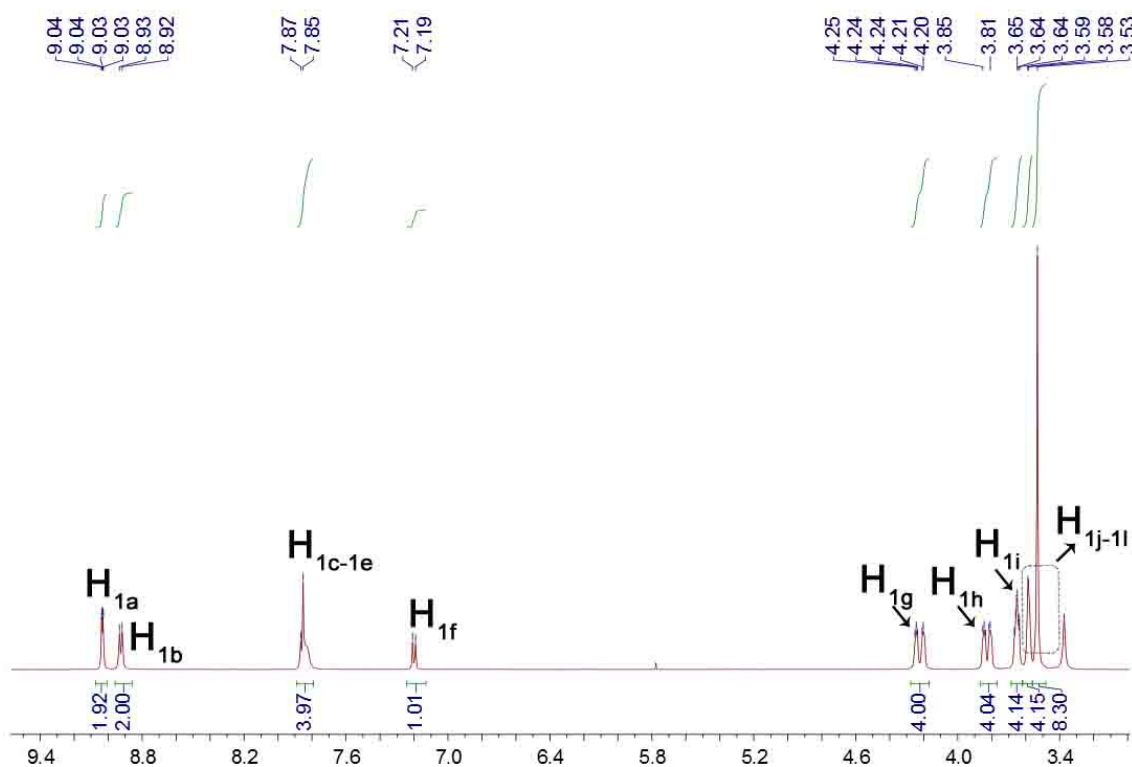


Figure S1. ¹H NMR spectrum (500 MHz, DMSO, 298 K) of **1**.

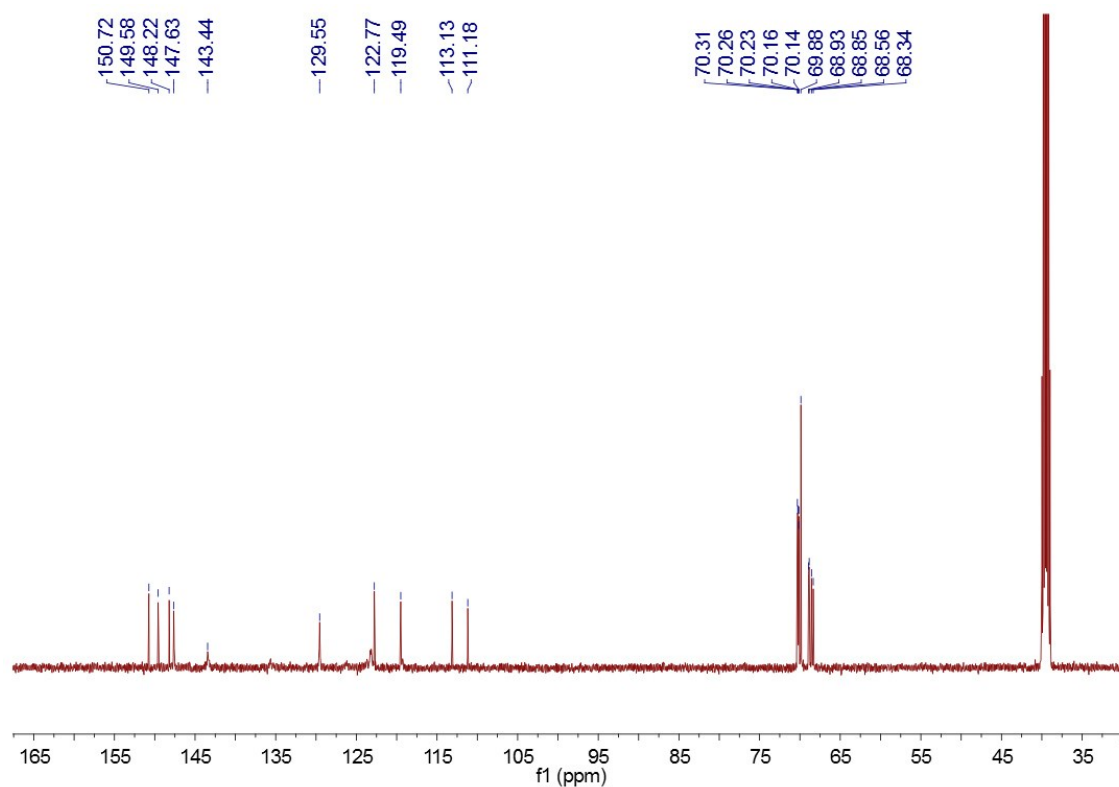


Figure S2. ¹³C NMR spectrum (125 MHz, DMSO, 298 K) of **1**.

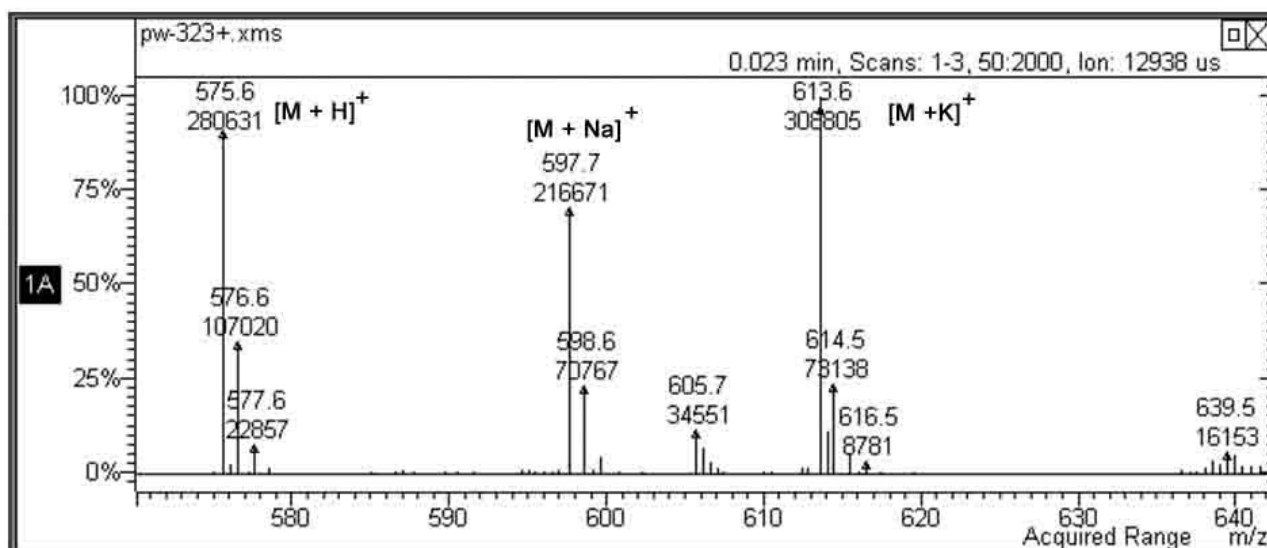


Figure S3. LRESI mass spectrum of 1.

Partial NOESY NMR spectrum of 1 + 2

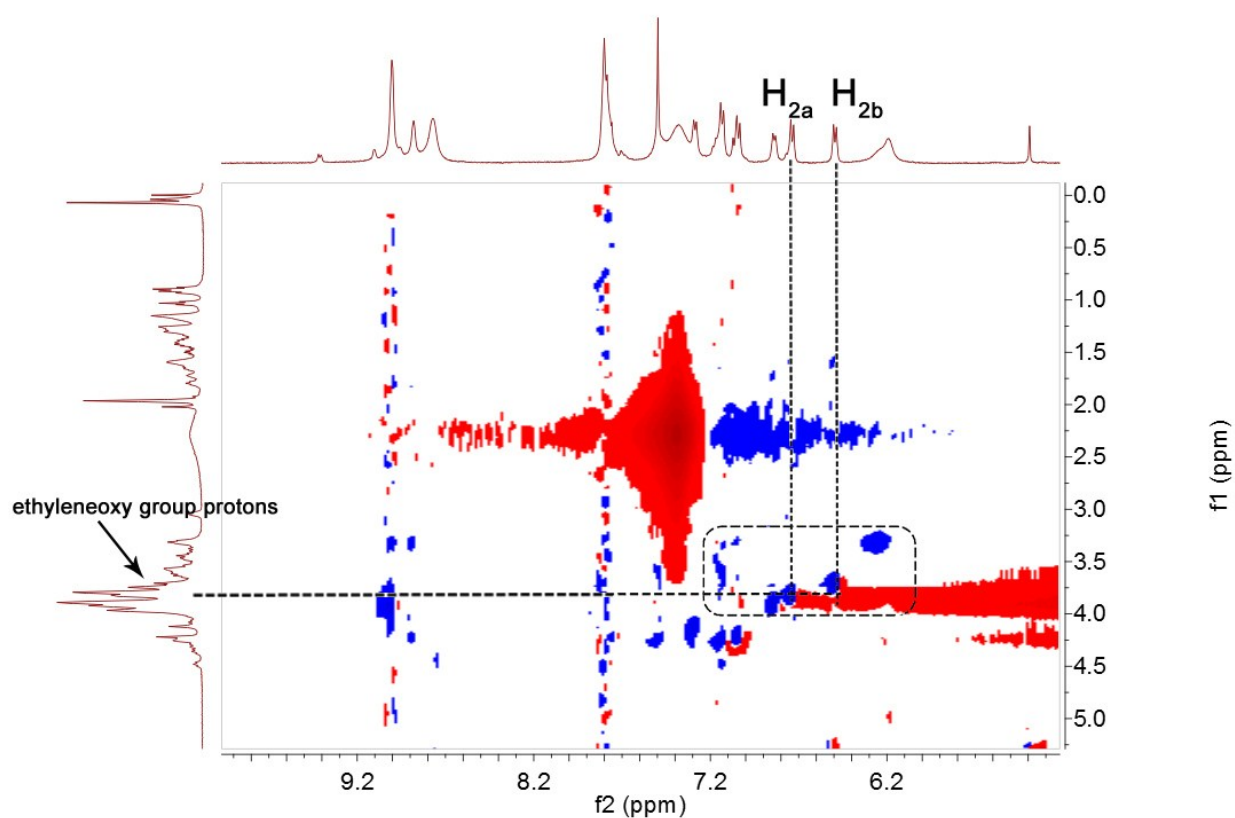


Figure S4. NOESY NMR spectrum (500 MHz, DMSO, 298 K) of 1 + 2 at 60.0 mM.

Partial ^1H NMR spectra of **1** + **2** and **1** + **2** + Zn^{2+}

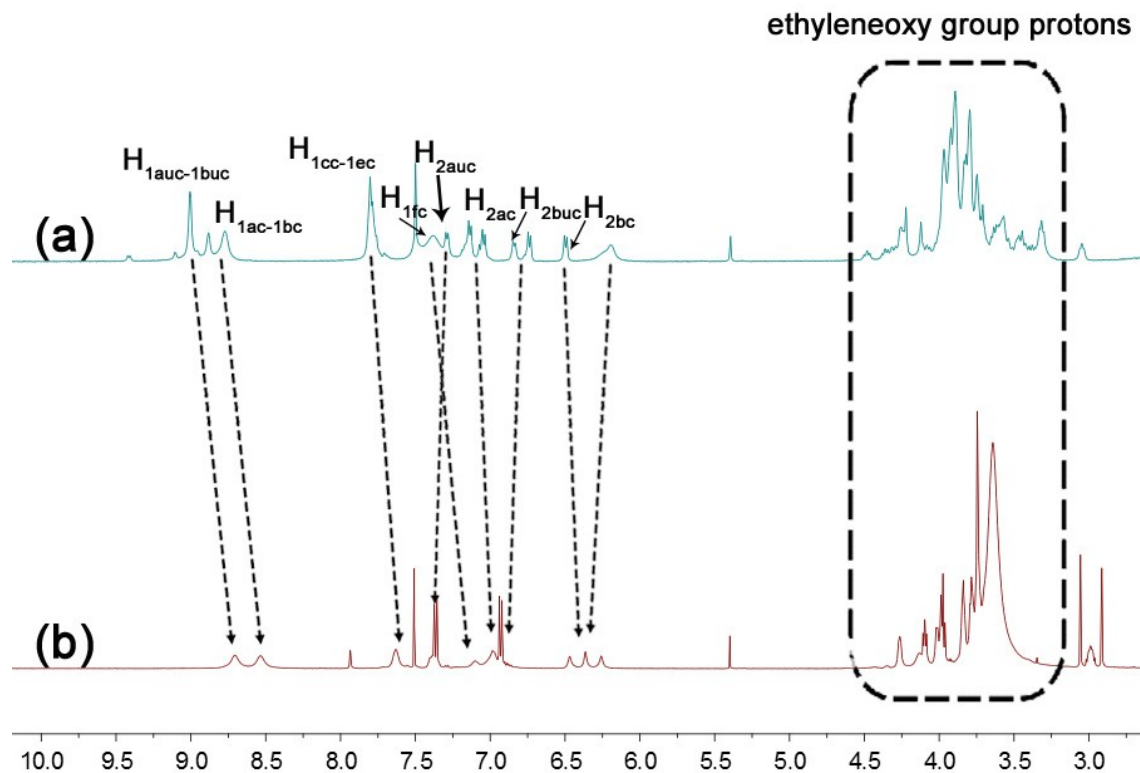


Figure S5. ^1H NMR spectrum (500 MHz, $\text{CDCl}_3/\text{CD}_3\text{CN}$ (1:1), 298 K) of (a) **1** + **2** and (b) **1** + **2** + Zn^{2+} .

Partial DOSY NMR spectra of **1**, **1** + **2**, **1** + **2** + Zn^{2+}

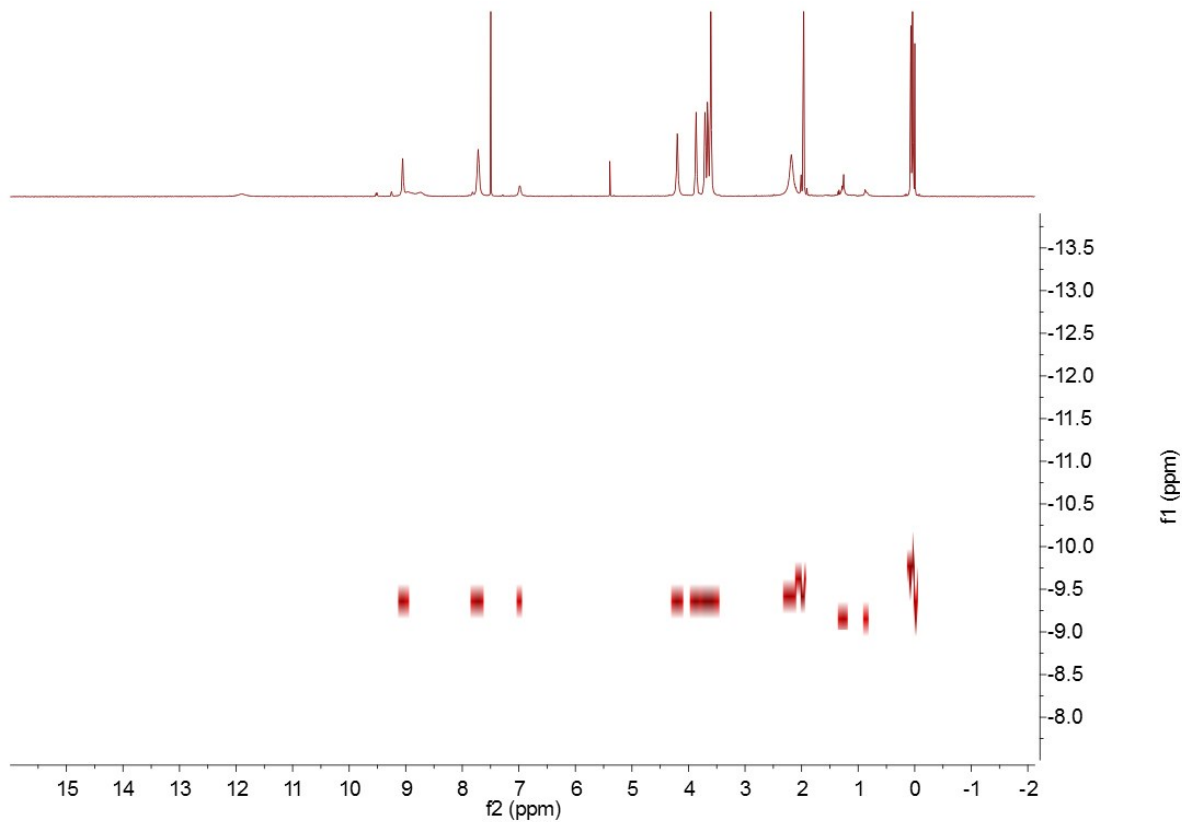


Figure S6. DOSY NMR spectrum (500 MHz, $\text{CDCl}_3/\text{CD}_3\text{CN}$ (1:1), 298 K) of **1** at 15.0 mM.

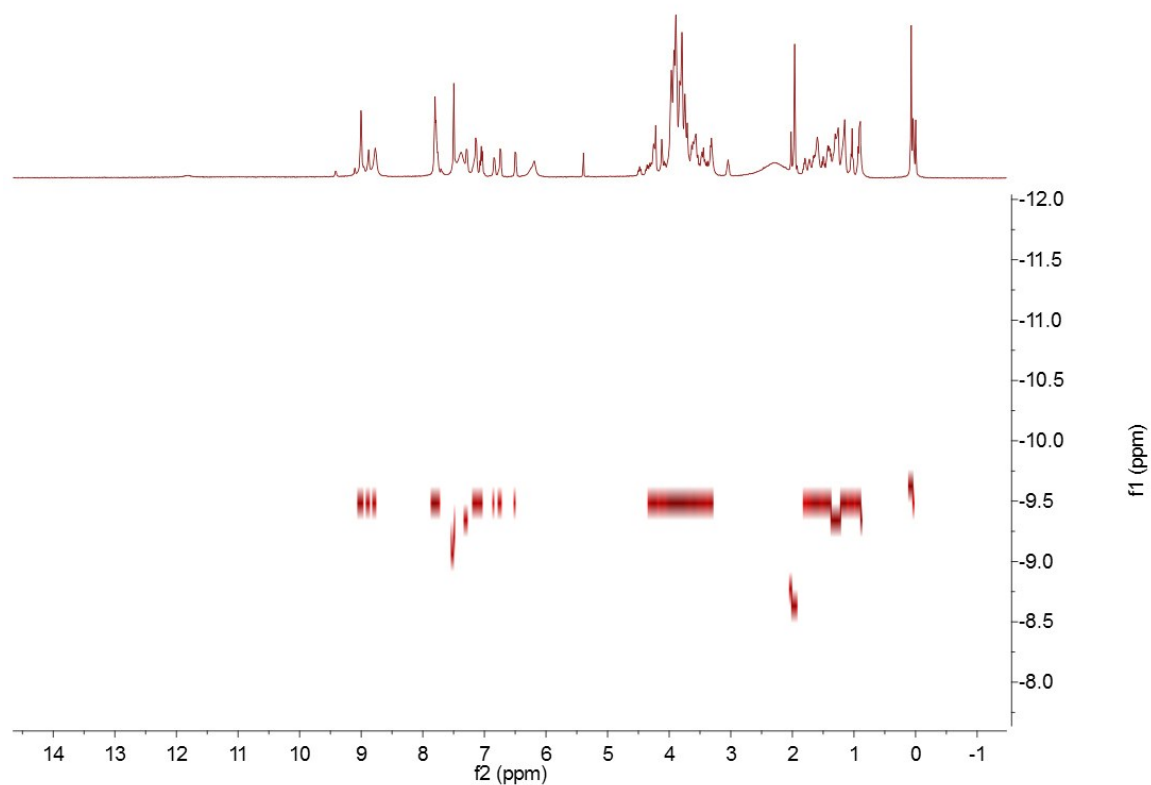


Figure S7. DOSY NMR spectrum (500 MHz, $\text{CDCl}_3/\text{CD}_3\text{CN}$ (1:1), 298 K) of **1** + **2** at 15.0 mM.

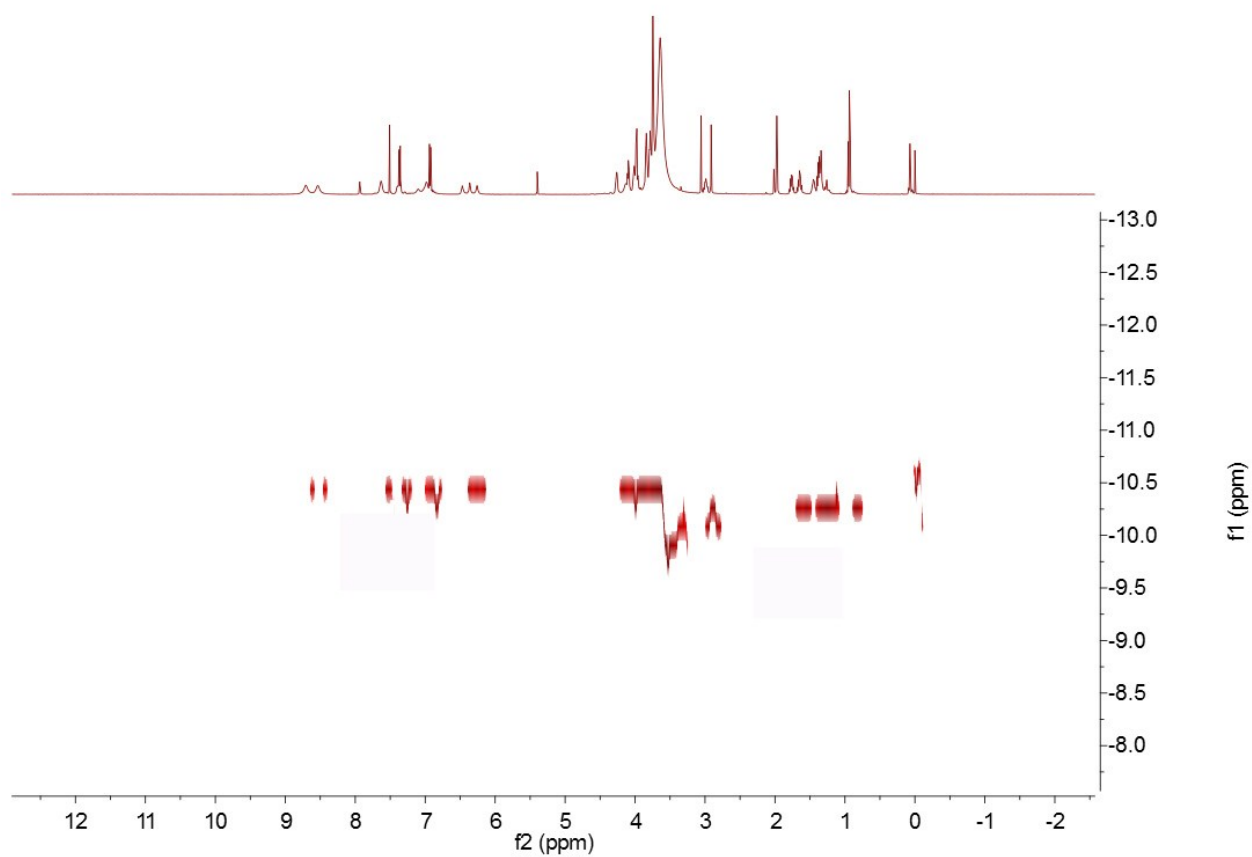


Figure S8. DOSY NMR spectrum (500 MHz, $\text{CDCl}_3/\text{CD}_3\text{CN}$ (1:1), 298 K) of **1** + **2** + Zn^{2+} at 15.0 mM.

SEM and pictures of the gel

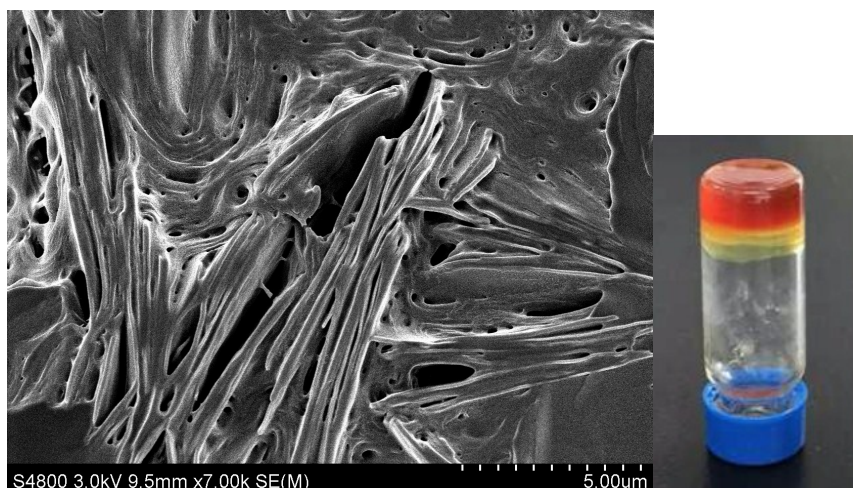


Figure S9. SEM image of the polymeric aggregates prepared from self-assembly of **1** + **2** + Zn^{2+} .

Variable temperature partial ^1H NMR spectra of **1** + **2** + Zn^{2+}

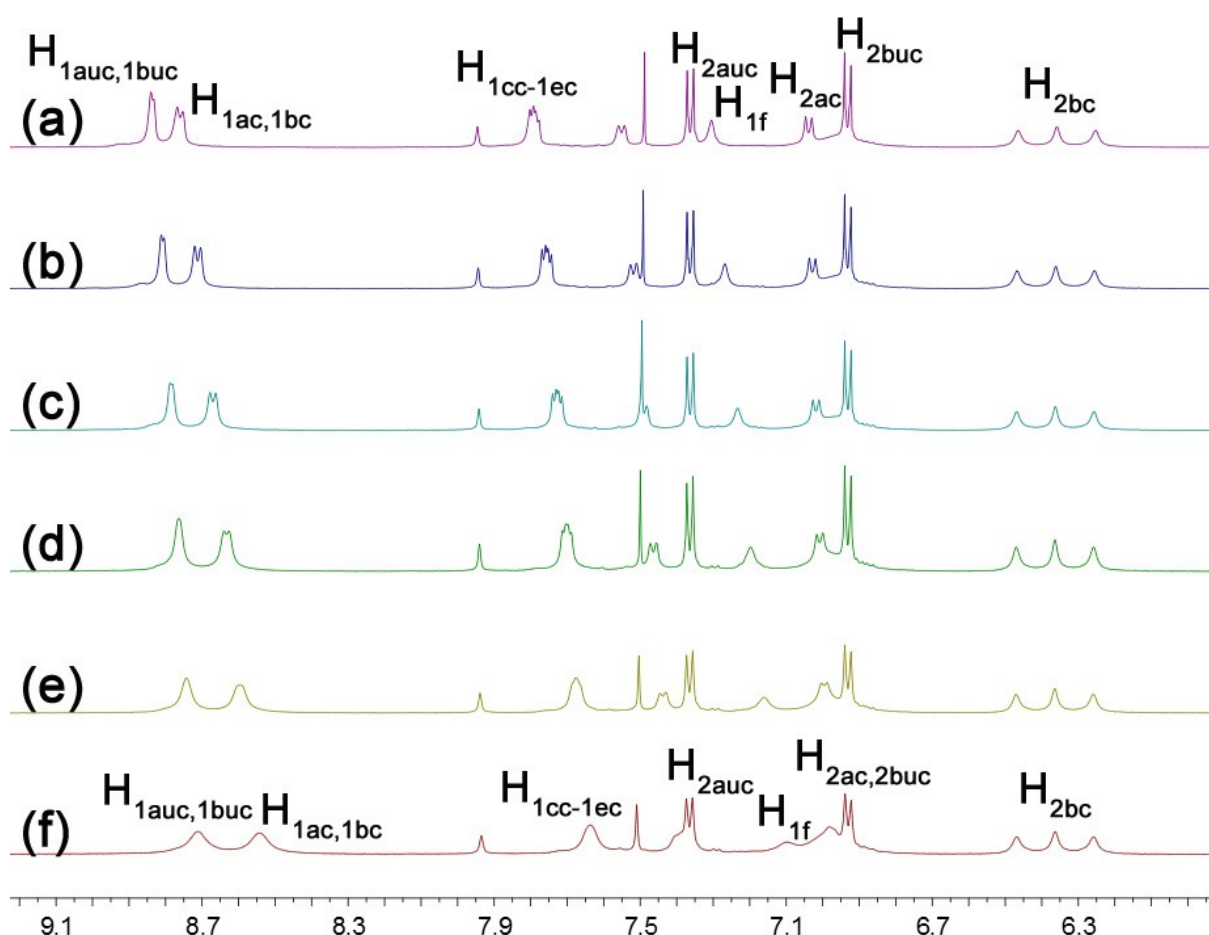


Figure S10. Variable temperature partial ^1H NMR spectra of **1** + **2** + Zn^{2+} (100 mM, 500 MHz, $\text{CDCl}_3/\text{CD}_3\text{CN}$ (1:1)): a) 273 K, b) 283 K, c) 293 K, d) 303 K, e) 313 K, f) 323 K.

SI References

- S1. Z. Zhang, Y. Luo, J. Chen, S. Dong, Y. Yu, Z. Ma and F. Huang, *Angew. Chem., Int. Ed.*, 2011, **50**, 1397–1401.
- S2. M. Xue, Y. Yang, X. Chi, Z. Zhang and F. Huang, *Acc. Chem. Res.* 2012, **45**, 1294–1308.