

A responsive supramolecular metallogel constructed by coordination-driven self-assembly of a crown ether-based [3]pseudorotaxane and diplatinum(II) acceptor

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1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Compounds **1**,^{S1} **2**,^{S2} and **3**^{S3} were synthesized by published literature procedures. NMR spectra were recorded with a Bruker Avance DMX 500 spectrophotometer with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. UV-vis spectroscopy was performed on a Shimadzu UV-2550 instrument at room temperature. Dynamic light scattering (DLS) was carried out on a Malvern Nanosizer S instrument at room temperature. Scanning electron microscopy (SEM) investigations were carried out on a JEOL 6390LV instrument.

2. ^1H NMR spectra of **1** and **2**

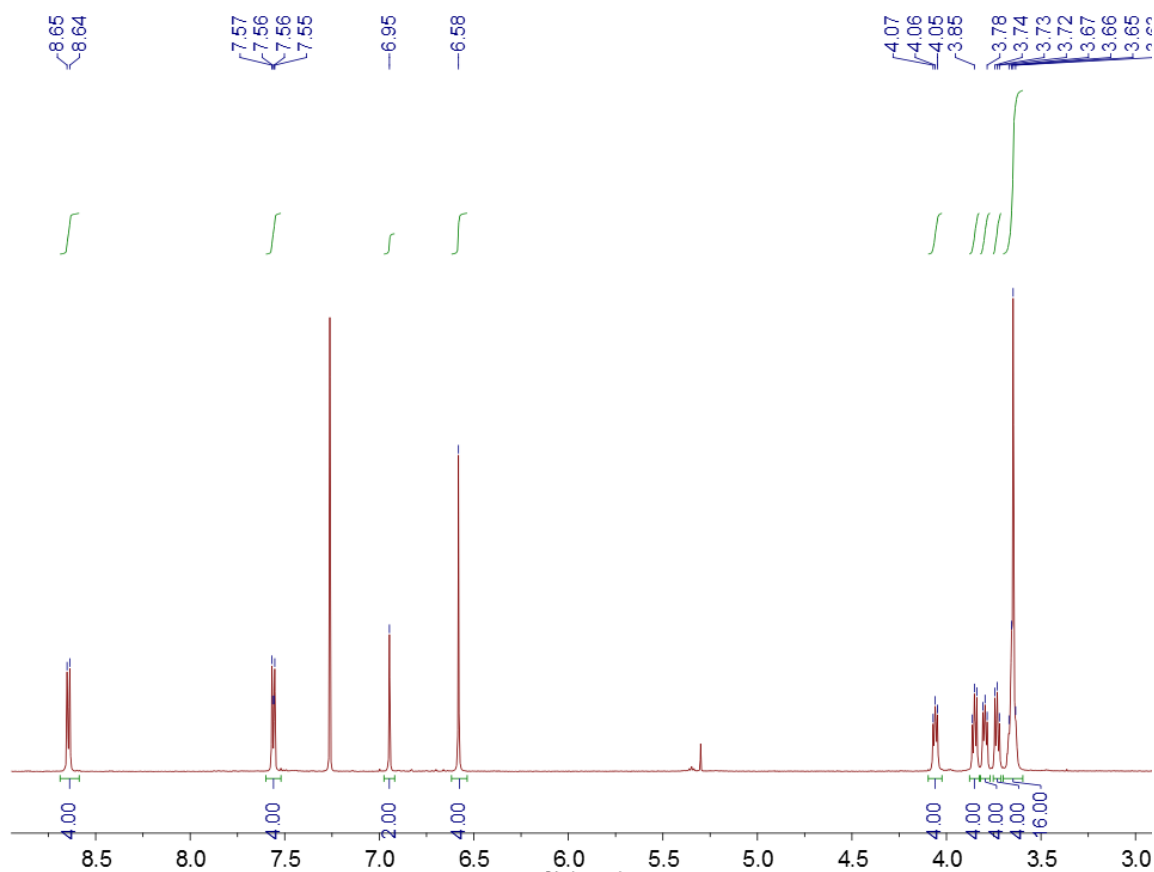


Figure S1. ^1H NMR spectrum (500 MHz, CDCl_3 , 293 K) of **1**.

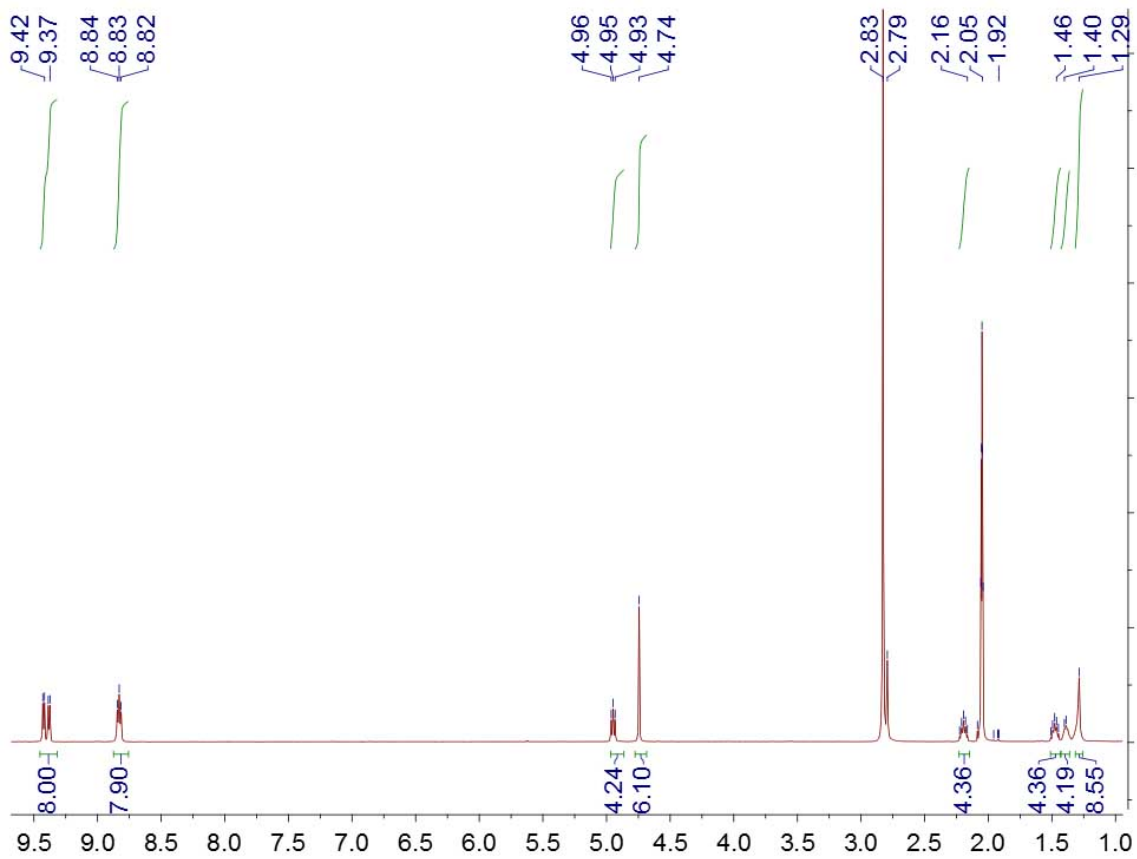


Figure S2. ^1H NMR spectrum (500 MHz, $\text{acetone-}d_6$, 293 K) of **2**.

3. Partial NOESY NMR spectrum of 1 \rightarrow 2 in acetone

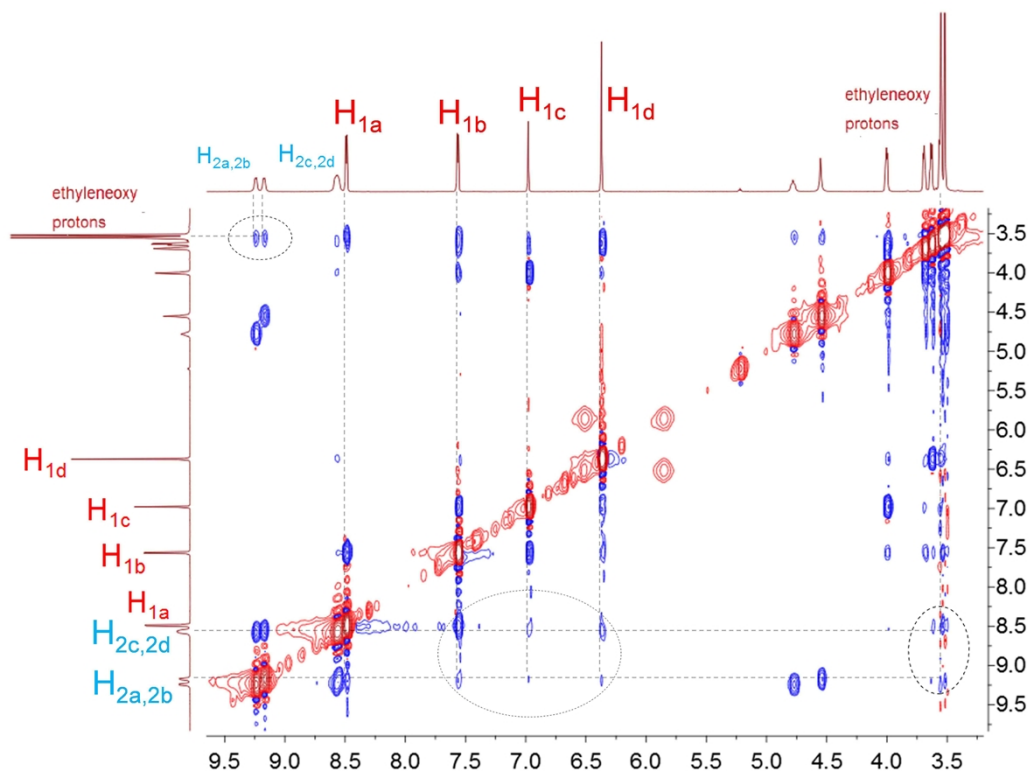


Figure S3. Partial NOESY NMR spectrum (500 MHz, acetone- d_6 , 293 K) of a mixture of **1** and **2** at 5.00 mM.

From this NOESY NMR spectrum, strong correlations are observed between the aromatic protons H_{1a-d} and the ethyleneoxy protons of the host and the pyridinium protons H_{2a-d} of the guest, confirming the occurrence of crown ether/paraquat complexation in acetone.

4. The absorption spectral changes of **1** upon addition of **2**

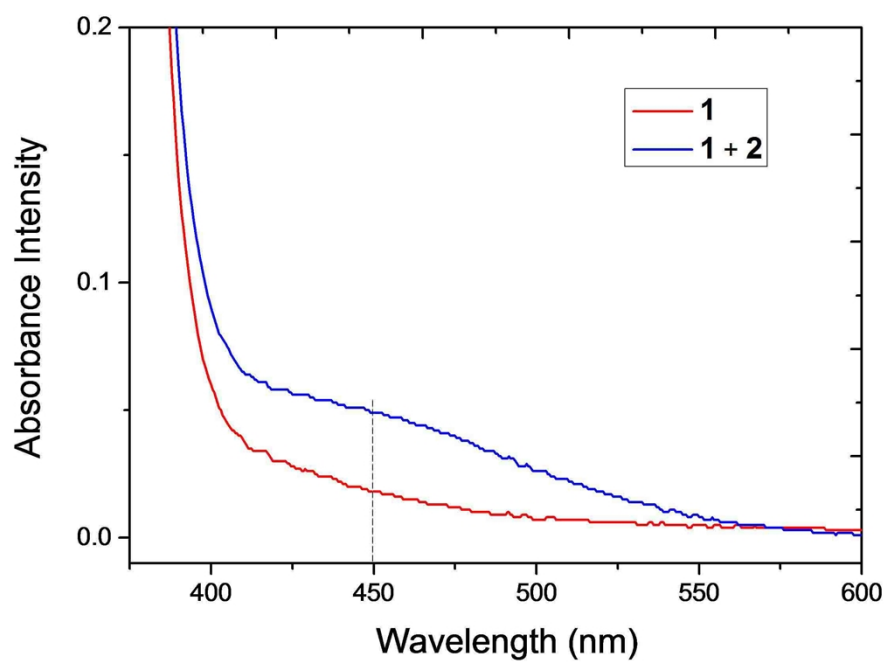


Fig. S4 The absorption spectral changes of **1** (5.00 mM) upon addition of **2** (5.00 mM) in acetone.

5. Partial DOSY NMR spectra of **1** + **2** and **1** + **2** + **3**

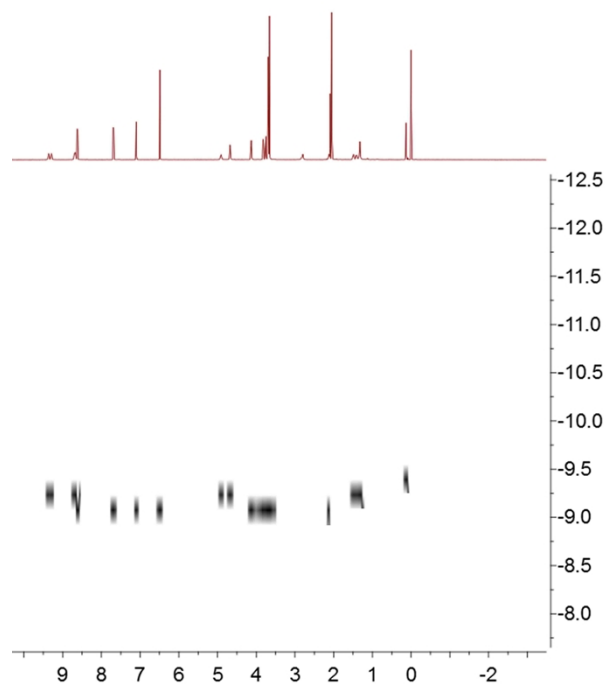


Fig. S5 Partial DOSY NMR spectrum (500 MHz, acetone- d_6 , 293 K) of a mixture of **1** and **2** at 5.00 mM.

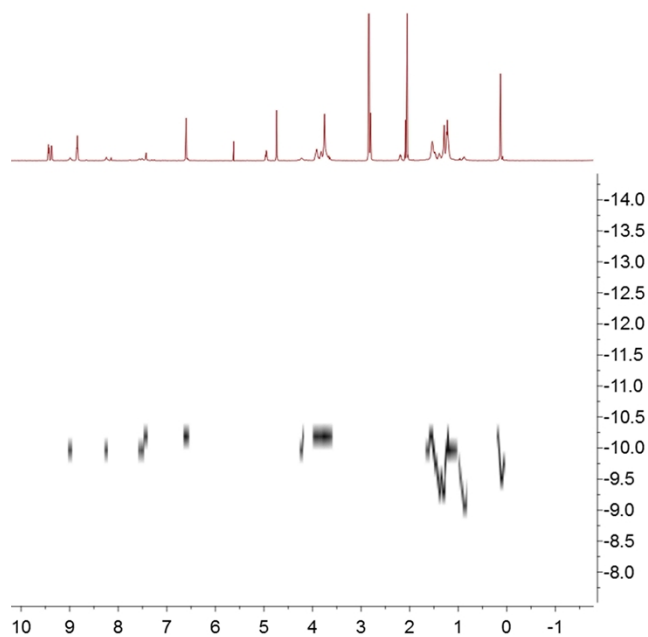


Fig. S6 Partial DOSY NMR spectrum (500 MHz, acetone- d_6 , 293 K) of a mixture of **1**, **2** and **3** at 5.00 mM.

According to the literature, we used the Stokes-Einstein relation to estimate the average degree of polymerization DP(DOSY) $\approx (D(\text{polymer}) / D(\text{monomer}))^3 = 8000$. We think this data is unreasonable so we do not plan to put this data in our manuscript.

6. Partial ^1H NMR spectra of the formation of the supramolecular gel upon addition of **3** and the destruction of the supramolecular gel upon addition of TBABr

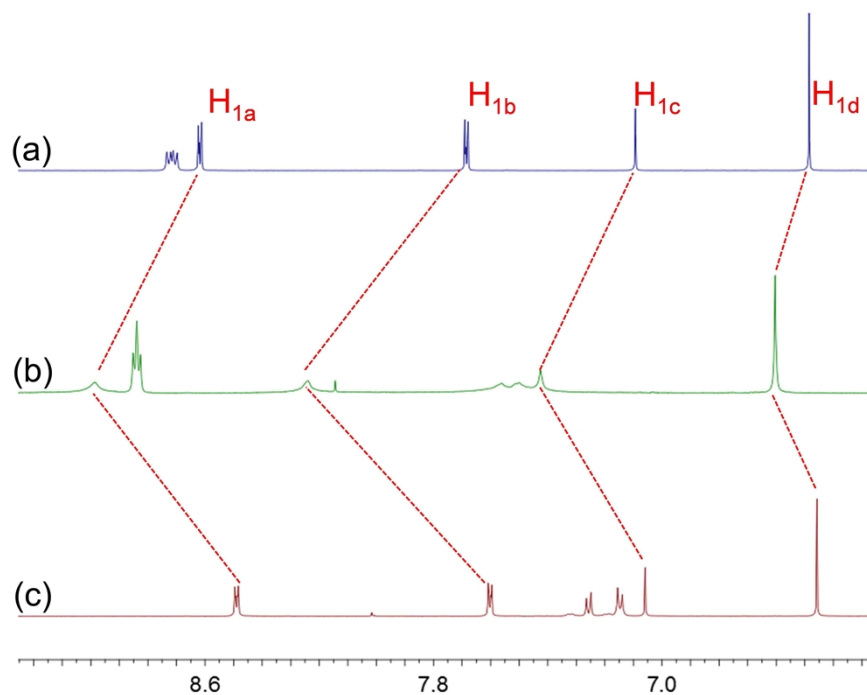


Fig. S7 Partial ^1H NMR spectra (500 MHz, acetone- d_6 , 293 K): (a) a mixture of **1** and **2** at 5.00 mM; (b) a mixture of **1**, **2** and **3** at 5.00 mM; (c) a mixture of **1**, **2**, **3**, and TBABr at 5.00 mM.

7. Partial ^1H NMR spectra of the formation of the coordination polymer and equimolar mixtures of **1** and **3** with successive addition of **2**

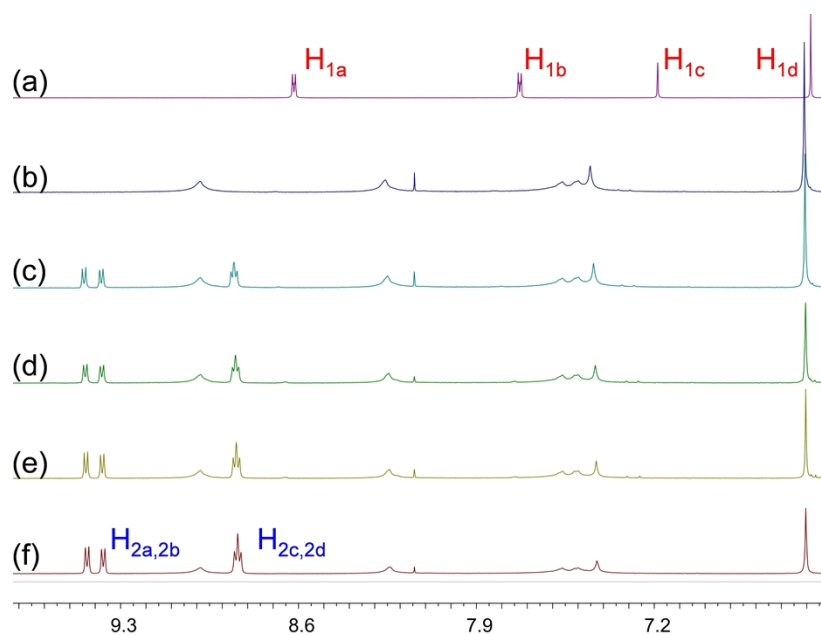


Fig. S8 Partial ^1H NMR spectra (500 MHz, acetone- d_6 , 293 K) of (a) **1** at 5.00 mM and equimolar mixtures of **1** and **3** at a concentration of 5 mM with successive addition of **2**: (b) 0 equiv.; (c) 0.2 equiv.; (d) 0.3 equiv.; (e) 0.4 equiv.; (f) 0.5 equiv.

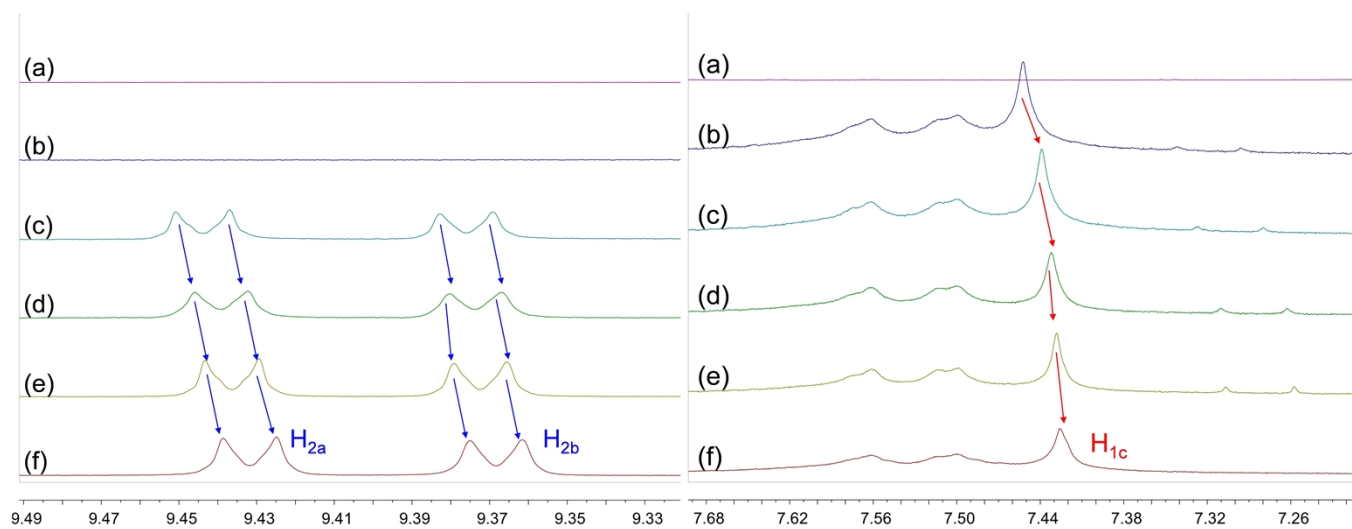


Fig. S9 Enlarged image of Figure S8 from 9.47 to 9.33 and from 7.62 to 7.26.

8. Variable temperature partial ^1H NMR spectra of **1** + **2** + **3**

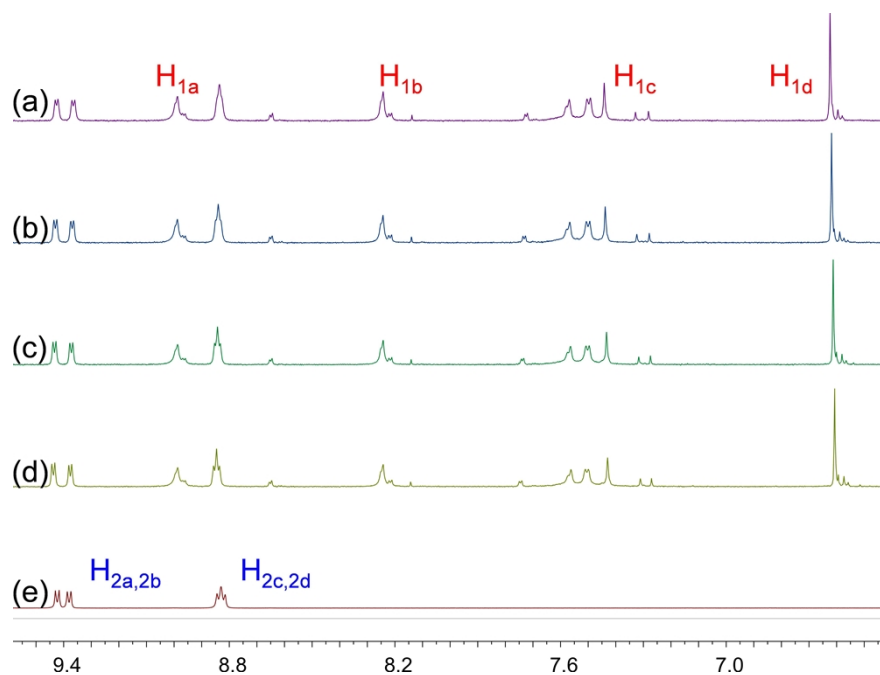


Fig. S10 Variable temperature partial ^1H NMR spectra of **1** + **2** + **3** (5.00 mM, acetone- d_6 , 600 MHz): (a) 313 K; (b) 308 K; (c) 303 K; (d) 298 K and (e) **2** at 5.00 mM at 298 K.

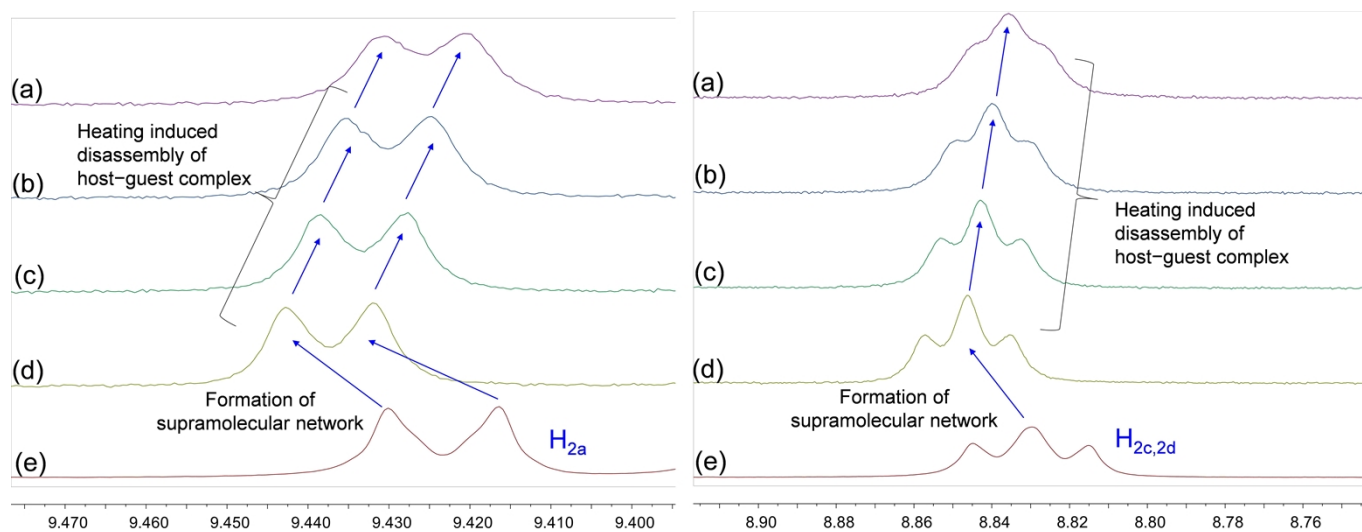


Fig. S11 Enlarged image of Figure S10 from 9.47 to 9.41 and from 8.88 to 8.80.

References:

- S1. H. Xing, P. Wei and X. Yan, *Org. Lett.* 2014, **16**, 2850–2853.
- S2. F. Wang, B. Zheng, K. Zhu, Q. Zhou, C. Zhai, S. Li, N. Li and F. Huang, *Chem. Commun.* 2009, 4375–4377.
- J. Manna, C. J. Kuehl, J. A. Whiteford, P. J. Stang, D. C. Muddiman, S. A. Hofstadler and R. D. Smith, *J. Am. Chem. Soc.* 1997, **119**, 11611–11619.