A supramolecular polymer network gel with stimuli-responsiveness constructed by orthogonal metal ion coordination and pillar[5]arene-based host–guest recognition

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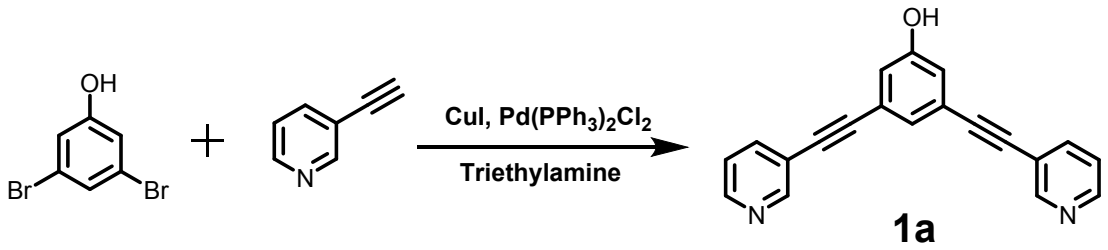
Electronic Supplementary Information (15 pages)

1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Compound **1a** and guest molecule **2** were prepared according to previously reported procedures[S1, S2]. ^{1}H NMR spectra, ^{13}C NMR spectra and NOESY and DOSY NMR were recorded with a Bruker Avance DMX 400 spectrophotometer or a Bruker Avance DMX 600 spectrophotometer with use of the 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. High-resolution mass spectrometric experiments were 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 by dissolving **1•Ag** and **1**$_2$**•Ag**$_2$**•2** in chloroform at 30.0 mM *via* the vacuum freeze-drying methodology for the supramolecular polymer.

2. Synthesis and characterizations of compounds



Compound **1a** was prepared according to previously reported procedures.[S1] The ^{1}H NMR spectrum of **1a** is shown in Fig. S1. ^{1}H NMR spectrum of **1a** (400 MHz, 298 K) in DMSO-d_6 δ (ppm): 10.19 (s, 1 H), 8.77 (s, 2 H), 8.60 (d, J = 4.8 Hz, 2 H), 7.99 (d, J = 8.0 Hz, 2 H), 7.48 (d, J = 8.0 Hz, 2 H), 7.24 (t, J = 1.5 Hz, 1 H), 7.02 (d, J = 1.2 Hz, 2 H). The ^{13}C NMR spectrum of **1a** is shown in Fig. S2. ^{13}C NMR spectrum of **1a** (100 MHz, 298 K) in DMSO-d_6 δ (ppm): 157.7, 151.7, 149.2, 138.7, 125.3, 123.6, 123.3, 119.1, 118.9, 91.2, 86.4. LRESIMS is shown in Figure S3: m/z 294.7.

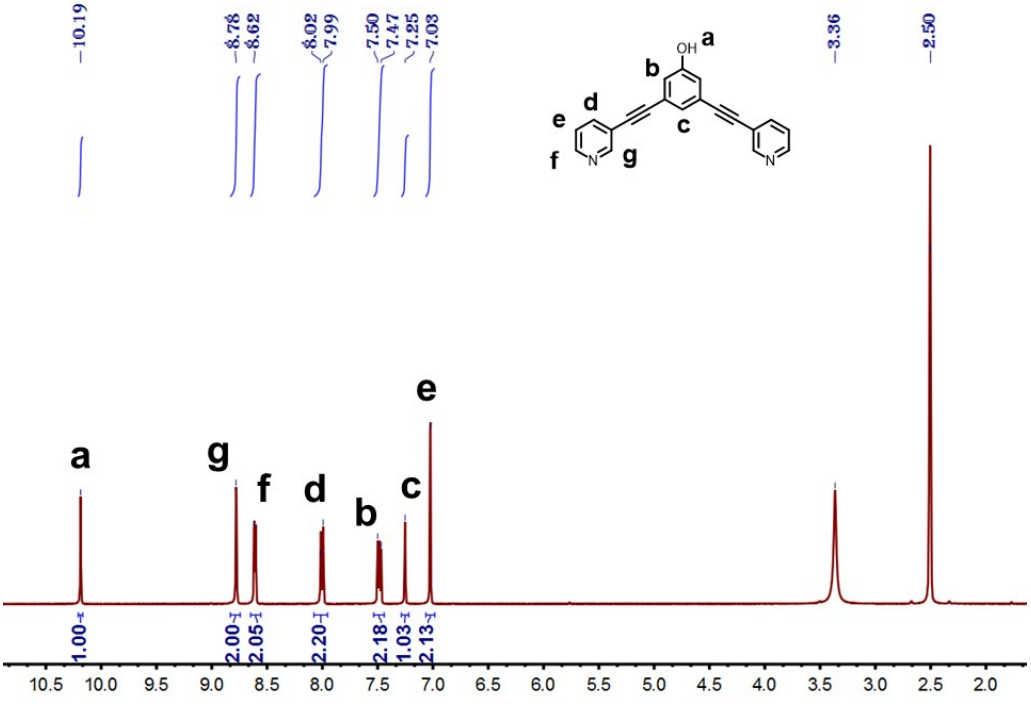


Fig. S1 ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298K) of **1a**.

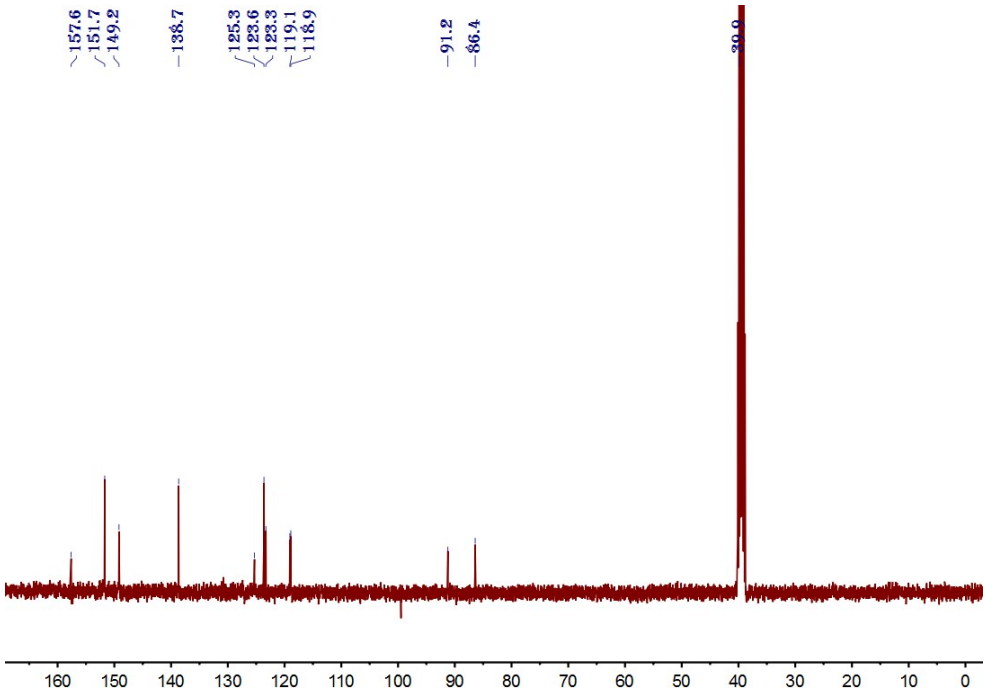


Fig. S2 ^{13}C NMR spectrum (100 MHz, DMSO-d_6, 298K) of **1a**.

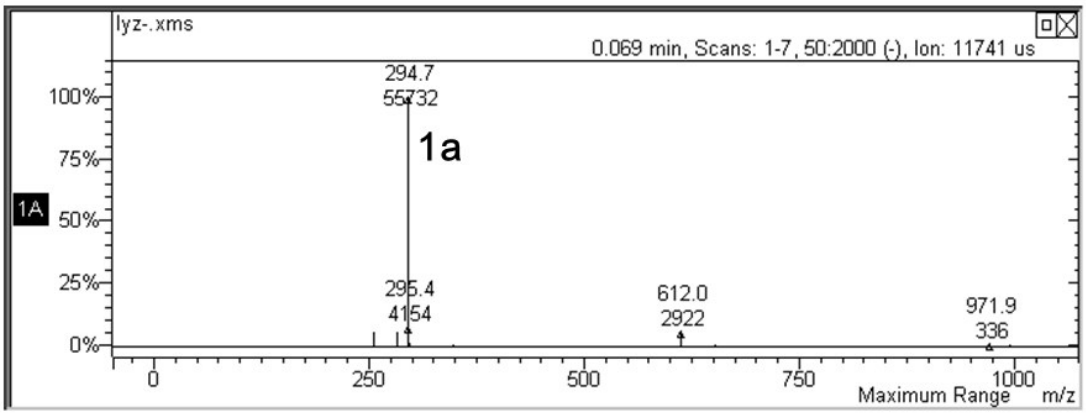
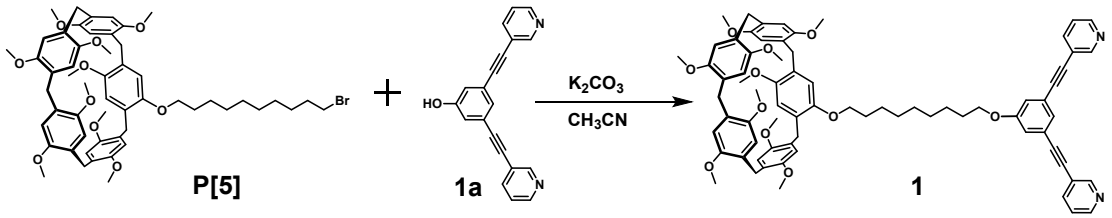


Fig. S3 LRESIMS spectrum of **1a** in DMSO-d_6.



A mixture of compound **1a** (1.48 g, 5.00 mmol), P[5] (5.73 g, 6.00 mmol), K_2CO_3 (2.76 g, 20.0 mmol) and KI (83.0 mg, 0.50 mmol) in CH_3CN (100 ml) was stirred at reflux for 48 hours. After the solid was filtered off, the solvent was concentrated by rotary evaporation. The crude product was dissolved in CH_2Cl_2 (150 mL) and washed three times with H_2O (150 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to afford a brown solid, which was further purified by column chromatography using dichloromethane/acetone (4:1). The fractions containing the product were concentrated to give **1** as a white solid. The ^{1}H NMR spectrum of **1** is shown in Fig. S4. ^{1}H NMR spectrum of **1** (400 MHz, 298 K) in $CDCl_3$ δ (ppm): 8.78 (s, 2 H), 8.58 (s, 2 H), 7.82 (s, 2 H), 7.35 (s, 1 H), 7.29–7.33 (s, 2 H), 6.77–6.91 (m, 10 H), 3.92 (t, 2 H), 3.78–3.67 (m, 37 H), 1.85–1.74 (m, 2 H), 1.60–1.47 (m, 2 H), 1.40–1.27 (m, 2 H), 1.14–0.35(m, 10 H). The ^{13}C NMR spectrum of **1** is shown in Fig. S5. ^{13}C NMR spectrum of **1** (100 MHz, 298 K) in $CDCl_3$ δ (ppm): 159.06, 152.19, 150.59, 149.79, 148.75, 138.60, 128.10, 127.14, 123.82, 127.14, 123.82, 123.18, 120.17, 118.15, 114.47, 113.94, 113.64, 91.81, 86.32, 68.56, 67.88, 55.99, 55.52, 53.15, 30.96, 29.67, 28.59, 25.43, 25.04. LRESIMS is shown in Figure S6: *m*/*z* 1172. HR ESI-MS: *m*/*z* found 1172.5734.

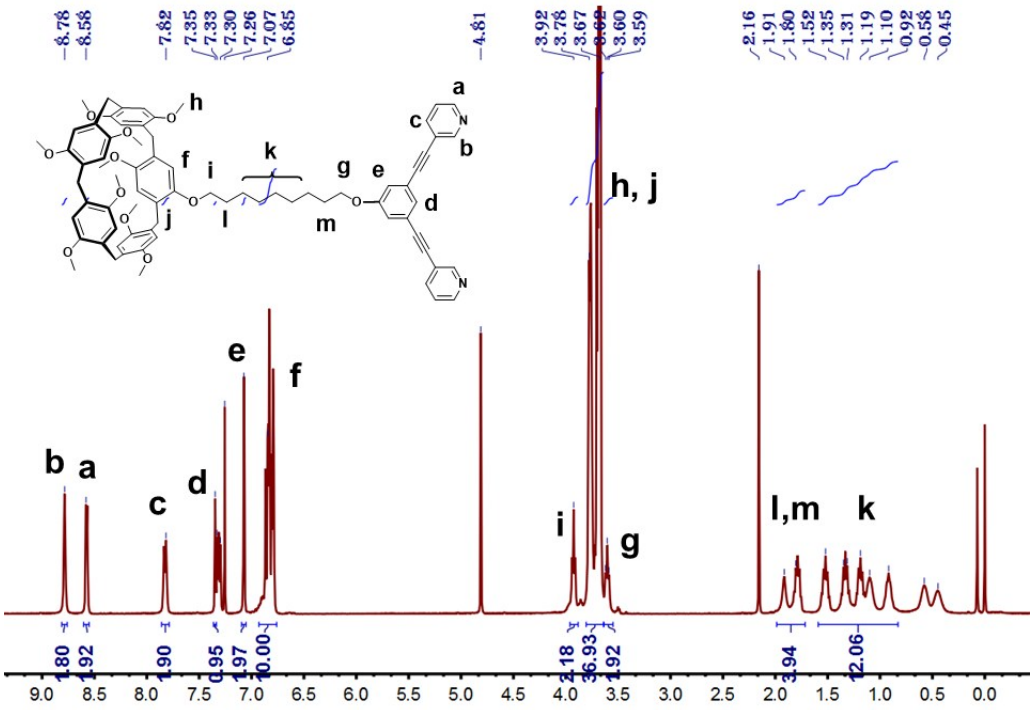


Fig. S4 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **1.**

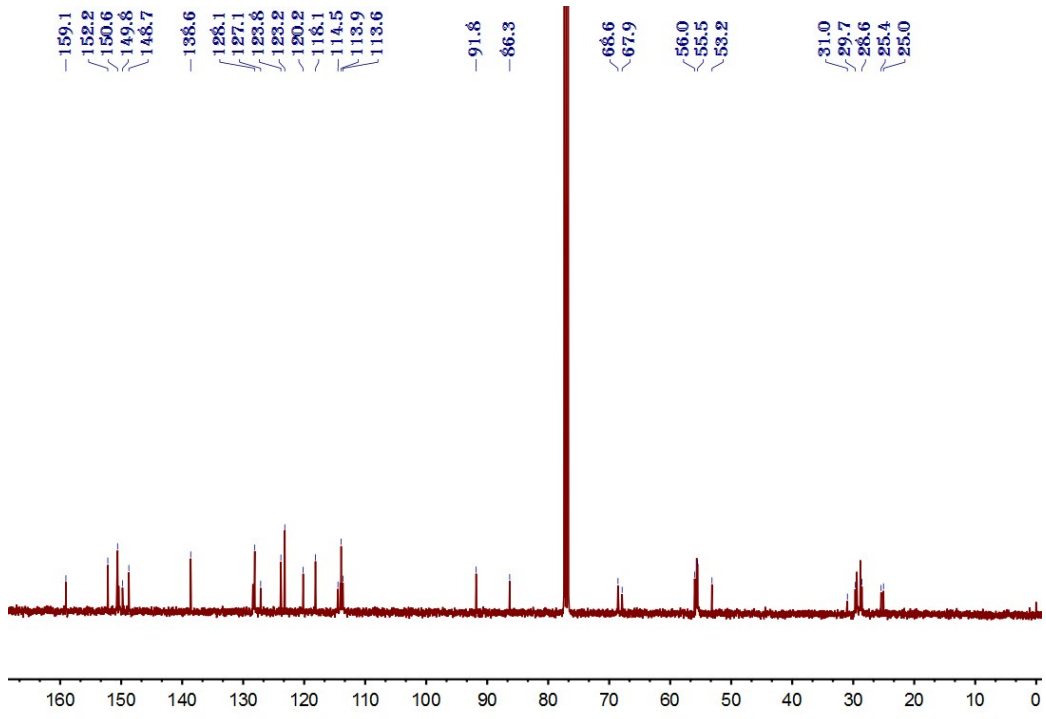


Fig. S5 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298K) of **1**.

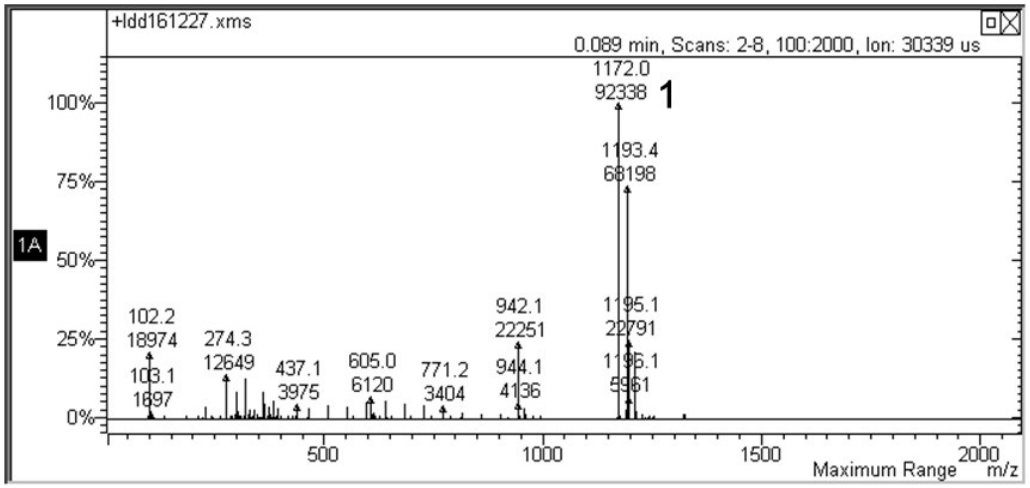


Fig. S6 LRESIMS spectrum of **1** in $CDCl_3$.

Compound **2** was prepared according to previously reported procedures.[2] The ^{1}H NMR spectrum of **2** is shown in Fig. S7. ^{1}H NMR spectrum of **2** (400 MHz, 298 K) in $CDCl_3$ δ (ppm): 7.61 (s, 2H), 6.89 (d, J = 8 Hz, 4H), 6.84 (d, J = 8 Hz, 4H), 5.16 (s, 4H), 4.43 (t, J = 12 Hz, 4H), 3.90 (t, J = 8 Hz, 4H), 2.41 (t, J = 8 Hz, 4H), 2.11–2.08 (m, 4H), 1.77–1.63 (m, 9H), 1.45–1.32 (m, 14H).

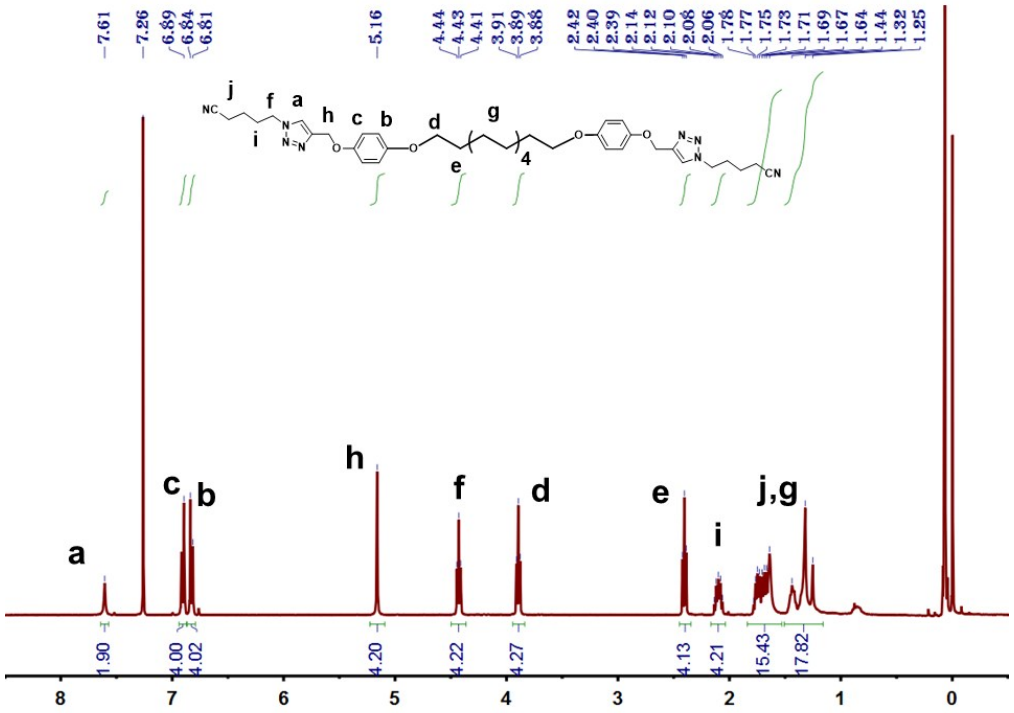


Fig. S7 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **2.**

*3. NOESY NMR spectra of **1** and **2** in $CDCl_3$*

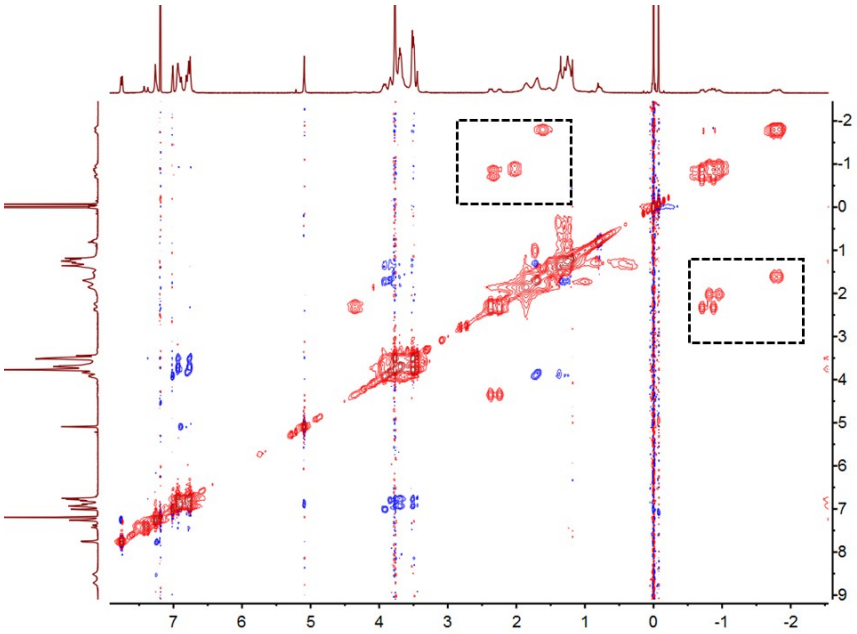


Fig. S8 2D NOESY NMR spectrum (400 MHz, 298 K) in $CDCl_3$ of 10.0 mM **1** and 5.00 mM **2**.

*4. The temperature-variant NMR experiments of **1** and **2** in $CDCl_3$*

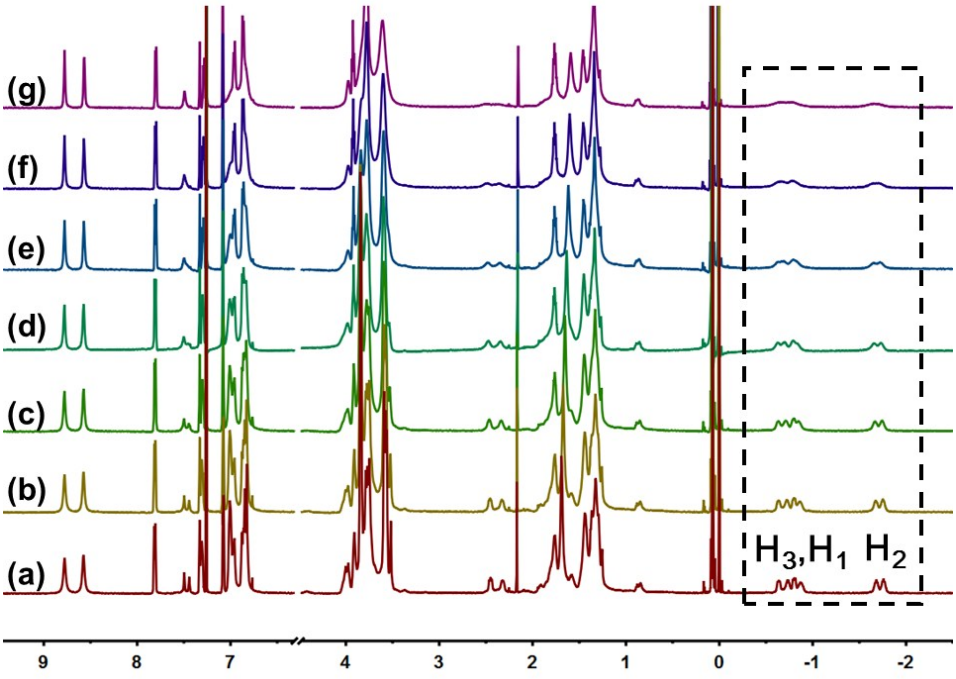


Fig. S9 ^{1}H NMR spectra (600 MHz) of **1•Ag** at 5.00 mM in $CDCl_3$ at various temperature: (a) 298 K; (b) 313 K; (c) 318 K; (d) 323 K; (e) 328 K; (f) 333 K; (g) 338 K.

*5. 2D DOSY NMR spectra of **1•Ag***

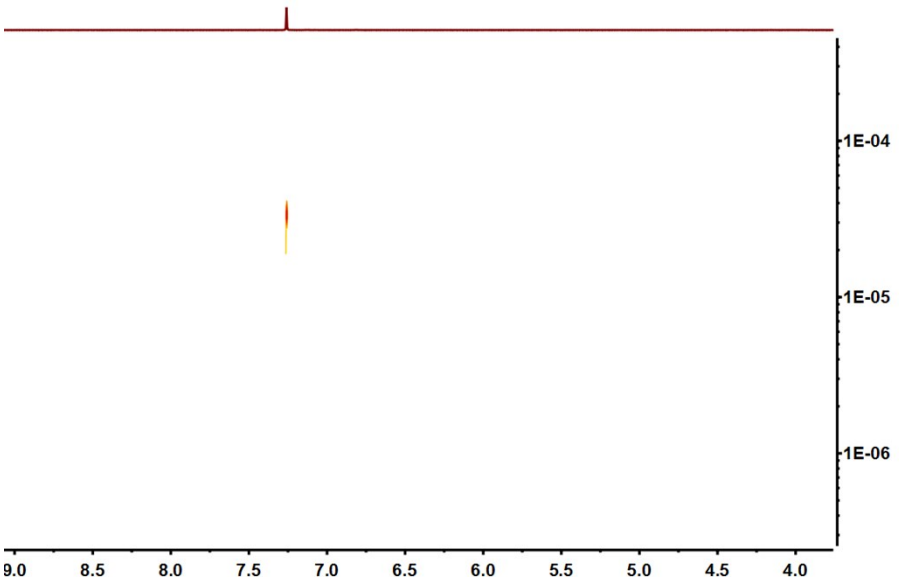


Fig. S10 2D DOSY NMR spectrum (600 MHz, $CDCl_3$, 298 K) of $CHCl_3$.

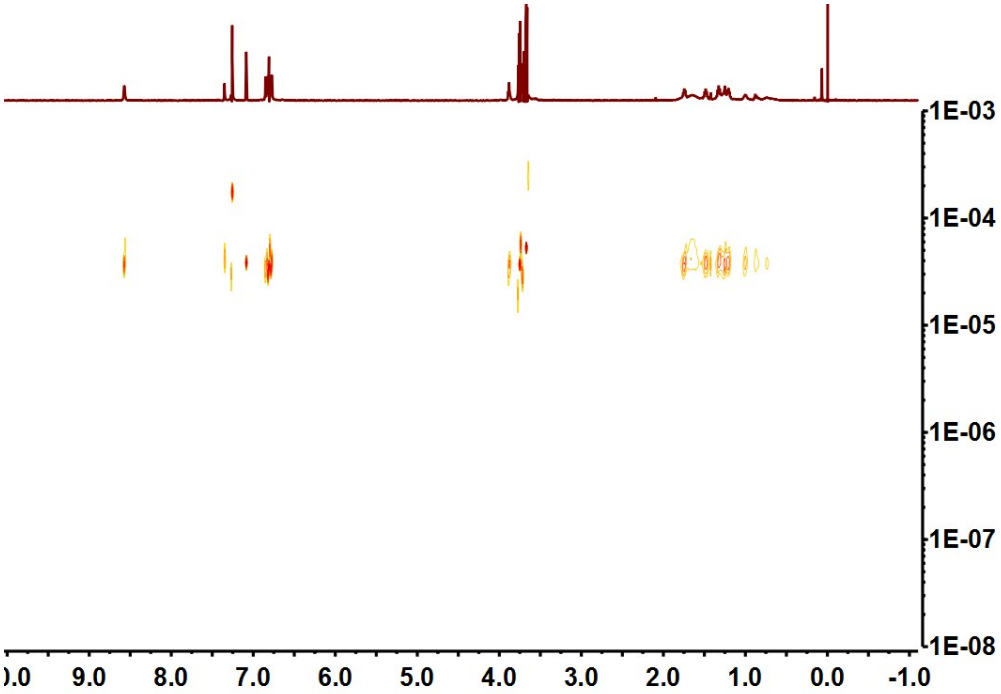


Fig. S11 2D DOSY NMR spectrum (600 MHz, $CDCl_3$, 298 K) of **1•Ag** at 2.00 mM.

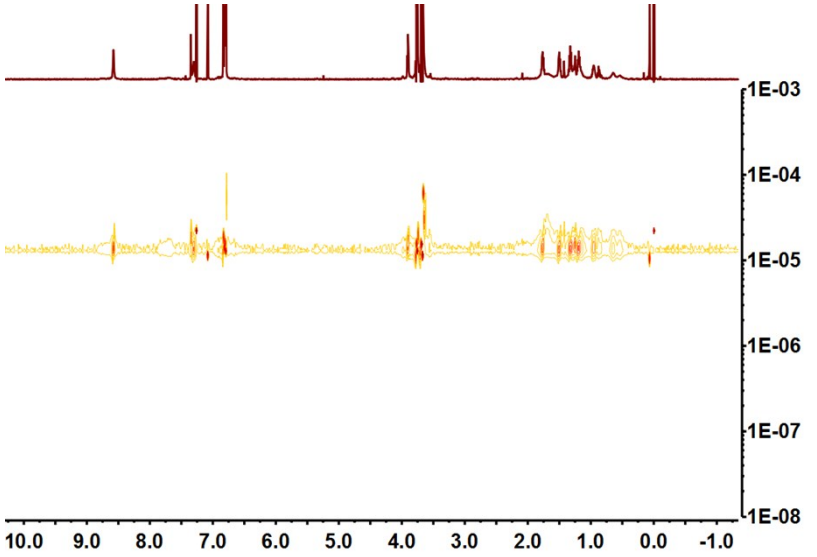


Fig. S12 2D DOSY NMR spectrum (600 MHz, $CDCl_3$, 298 K) of **1•Ag** at 3.00 mM.

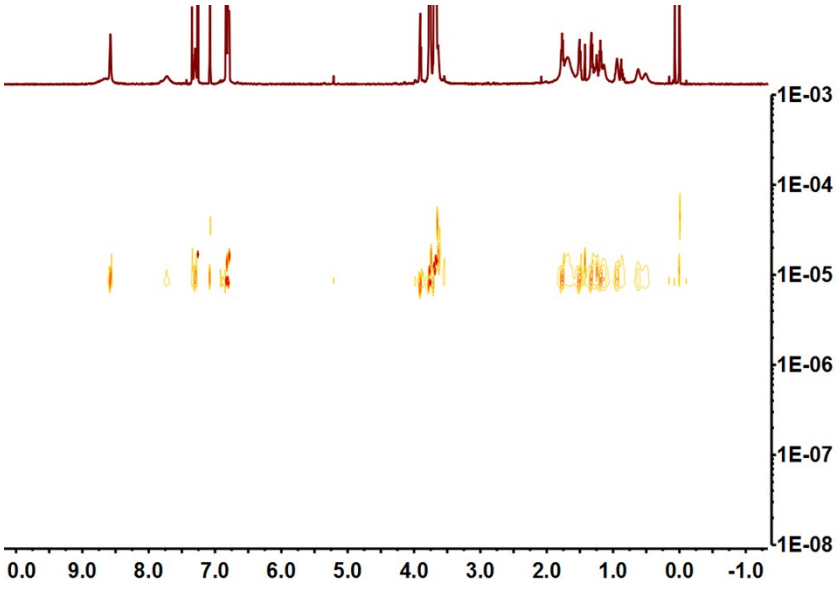


Fig. S13 2D DOSY NMR spectrum (600 MHz, $CDCl_3$, 298 K) of **1•Ag** at 4.00 mM.

We first measured the diffusion constant of $CHCl_3$ in $CDCl_3$ (99.8%) resulting in a value of 32.8 × 10^{-10} m^2/s at 298 K.[3] And then 2D DOSY measurements on **1•Ag** (2.00 mM, 3.00 mM, 4.00 mM) and **1_2•Ag_2•2** (1.00 mM, 3.00 mM, 5.00 mM) were carried out. The value for the diffusion constant of residual $CHCl_3$ in a solution of **1•Ag** or **1_2•Ag_2•2** in $CDCl_3$ deviates from the diffusion constant measured in $CDCl_3$ (99.8%). We therefore corrected the measured values according to the measured value

of the diffusion constant of $CHCl_3$ in $CDCl_3$ (99.8%).

*6. DLS experiments of **1•Ag** at different concentrations*

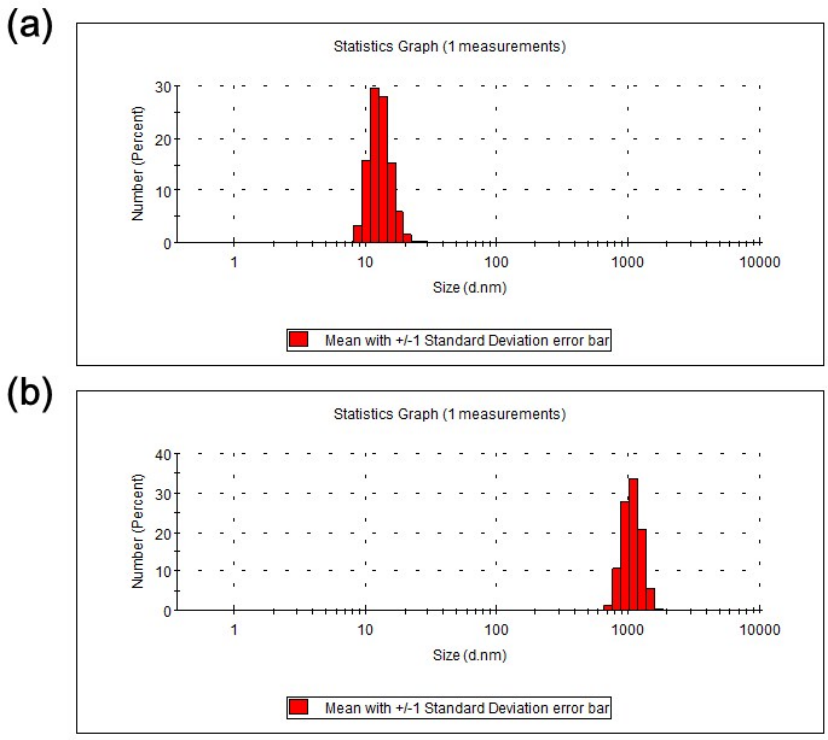


Fig. S14 DLS results of **1•Ag** at different concentrations: (a) 1.00 mM; (b) 10.0 mM.

*7. 2D DOSY NMR spectra of **1**$_2$**•Ag**$_2$**•2***

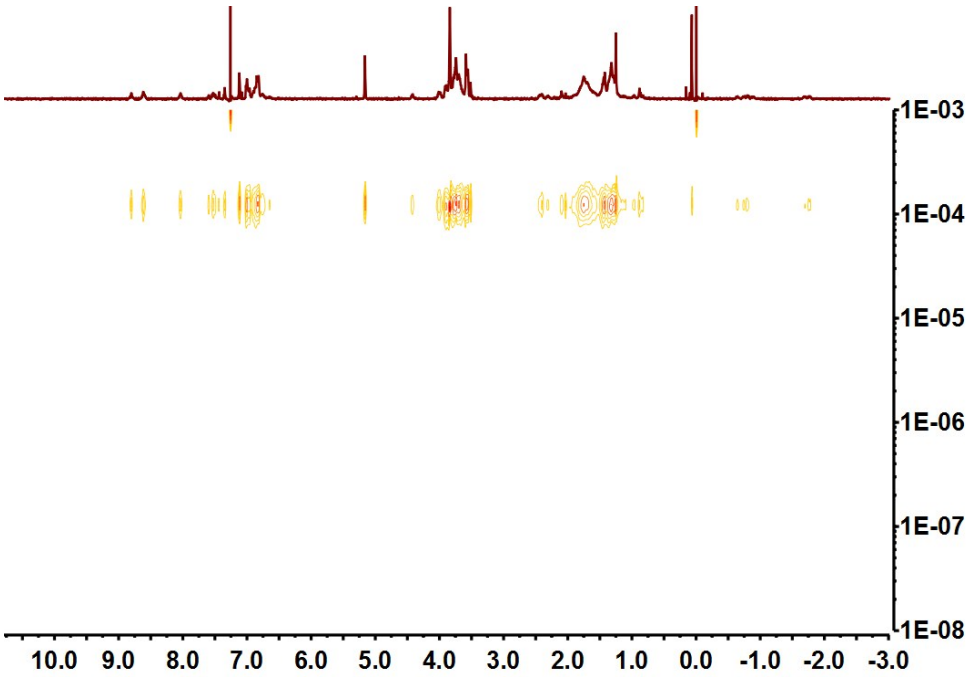


Fig. S15 2D DOSY NMR spectrum (600 MHz, $CDCl_3$, 298 K) of $\mathbf{1}_2$•$\mathbf{Ag}_2$•**2** at 1.00 mM.

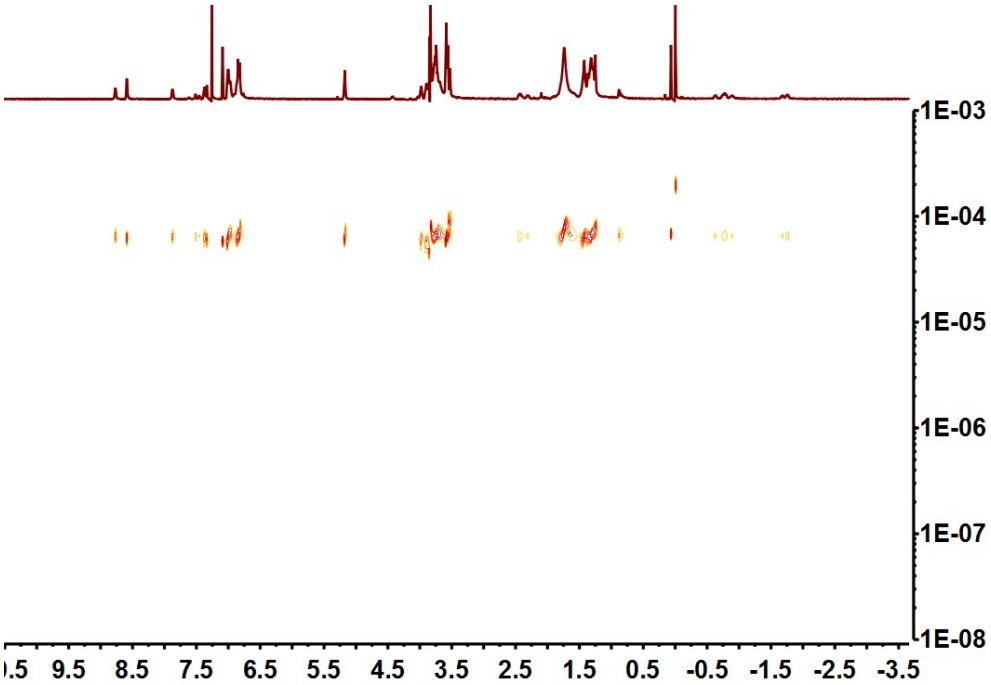


Fig. S16 2D DOSY NMR spectrum (600 MHz, $CDCl_3$, 298 K) of $\mathbf{1}_2$•$\mathbf{Ag}_2$•**2** at 3.00 mM.

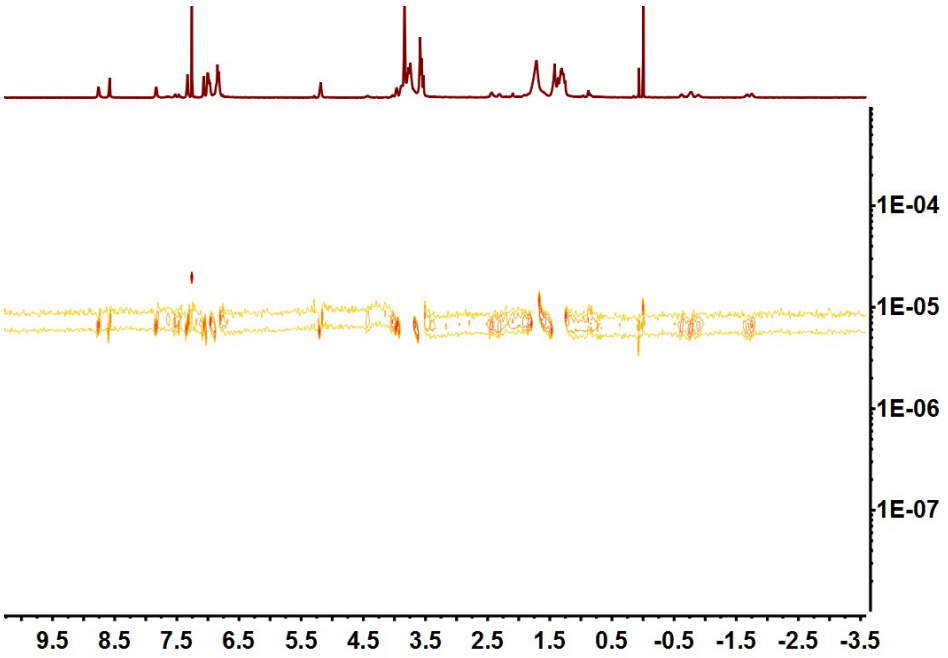


Fig. S17 2D DOSY NMR spectrum (600 MHz, $CDCl_3$, 298 K) of $\mathbf{1}_2$•$\mathbf{Ag}_2$•**2** at 5.00 mM.

The diffusion constant *D* of $\mathbf{1}_2$•$\mathbf{Ag}_2$•**2** at different concentrations was also calibrated.

*8. Partial ^1H NMR spectra of **1**, **1•Ag** and **1•Ag** + I^-*

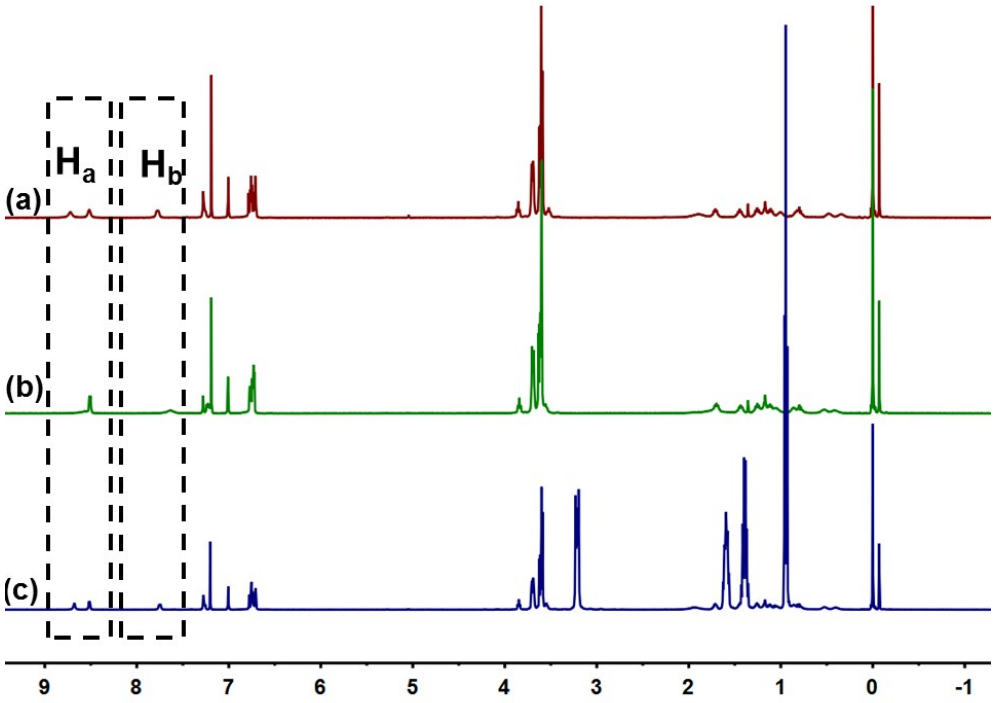


Fig. S18 Partial ^1H NMR spectra (400 MHz, 298K) in $CDCl_3$ (a) 5.00 mM **1**; (b) 5.00 mM **1•Ag**; (c) 5.00 mM **1•Ag** + I^-.

*9. Photos of adding different proportion of **2** into **1•Ag** at 30.0 mM*

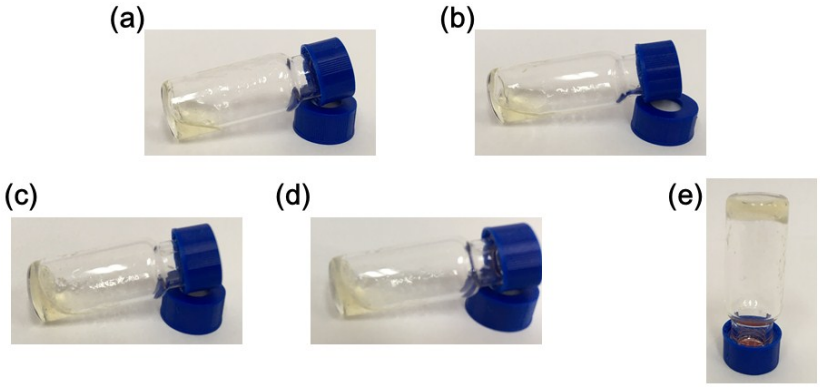


Fig. S19 Photos of **1•Ag** at a concentration of 30.0 mM with successive addition of **2**: (a) 0.1 equiv; (b) 0.2 equiv; (c) 0.3 equiv; (d) 0.4 equiv; (e) 0.5 equiv.

*10. Photos of different concentration of **1_2•Ag_2•2***

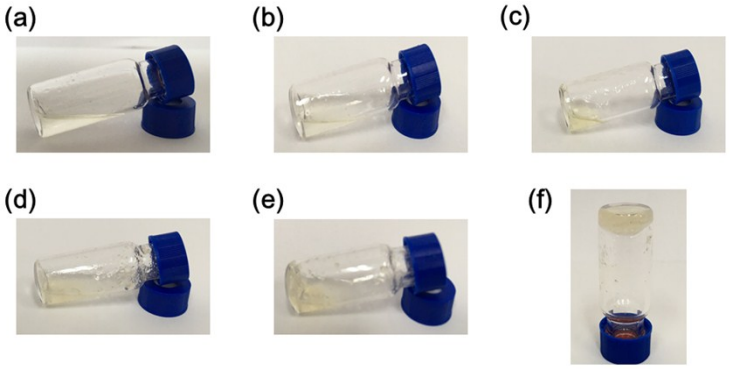


Fig. S20 Photos of $\mathbf{1}_2$•$\mathbf{Ag}_2$•**2** at different concentrations: (a) 5.00 mM; (b) 10.0 mM; (c) 15.0 mM; (d) 20.0 mM; (e) 25.0 mM; (f) 30.0 mM.

11. The rheological properties of the metallogel

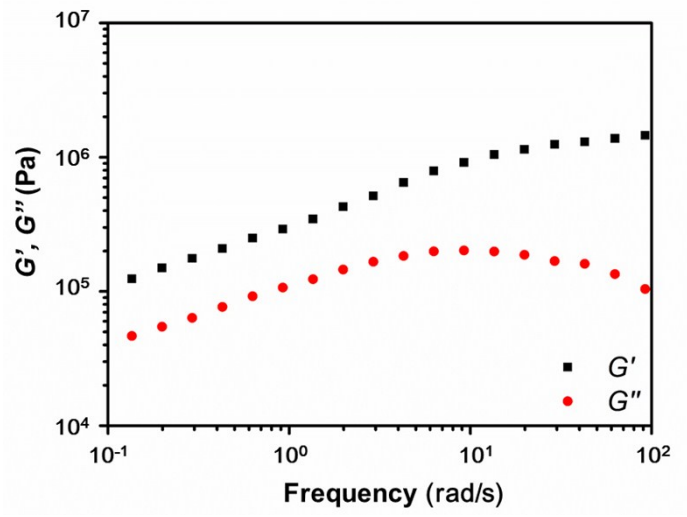


Fig. S21 Frequency dependency of the storage modulus *G'*, and loss modulus *G''* of the metallogel.

12. SEM images of a rod-like fiber

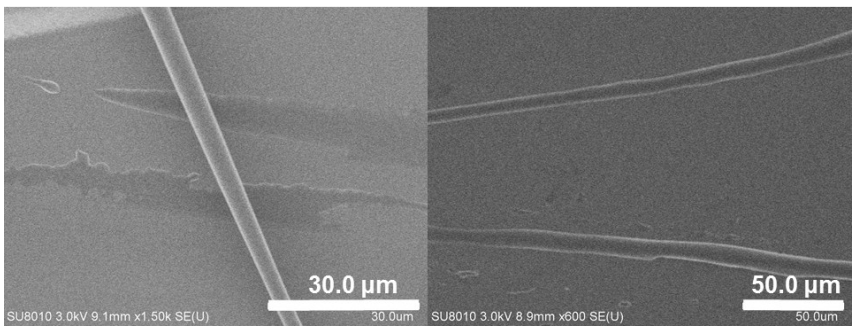


Fig. S22 SEM images of a rod-like fiber drawn from a solution of **1**•**Ag** at 10.0 mM in $CHCl_3$.

13. References:

S1. A. Schmidt, V. Molano, M. Hollering, A. Pçthig, A. Casini and F. Kühn, *Chem. Eur. J.*, 2016, **22**, 2253.

S2. B. Shi, K. Jie, Y. Zhou, D. Xia and Y. Yao, *Chem. Commun*., 2015, **51**, 4503.

S3. T. F. A. de Greef, M. M. L Nieuwenhuizen, P. J. M. Stals, C. F. C. Fitié, A. R. A. Palmans, R. P. Sijbesma, E. W. Meijer, *Chem. Commun*., 2008, 4306.