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# Supporting Information

# for

# Rapid and reversible thermochromic supramolecular polymer hydrogel and its application in protected quick response code

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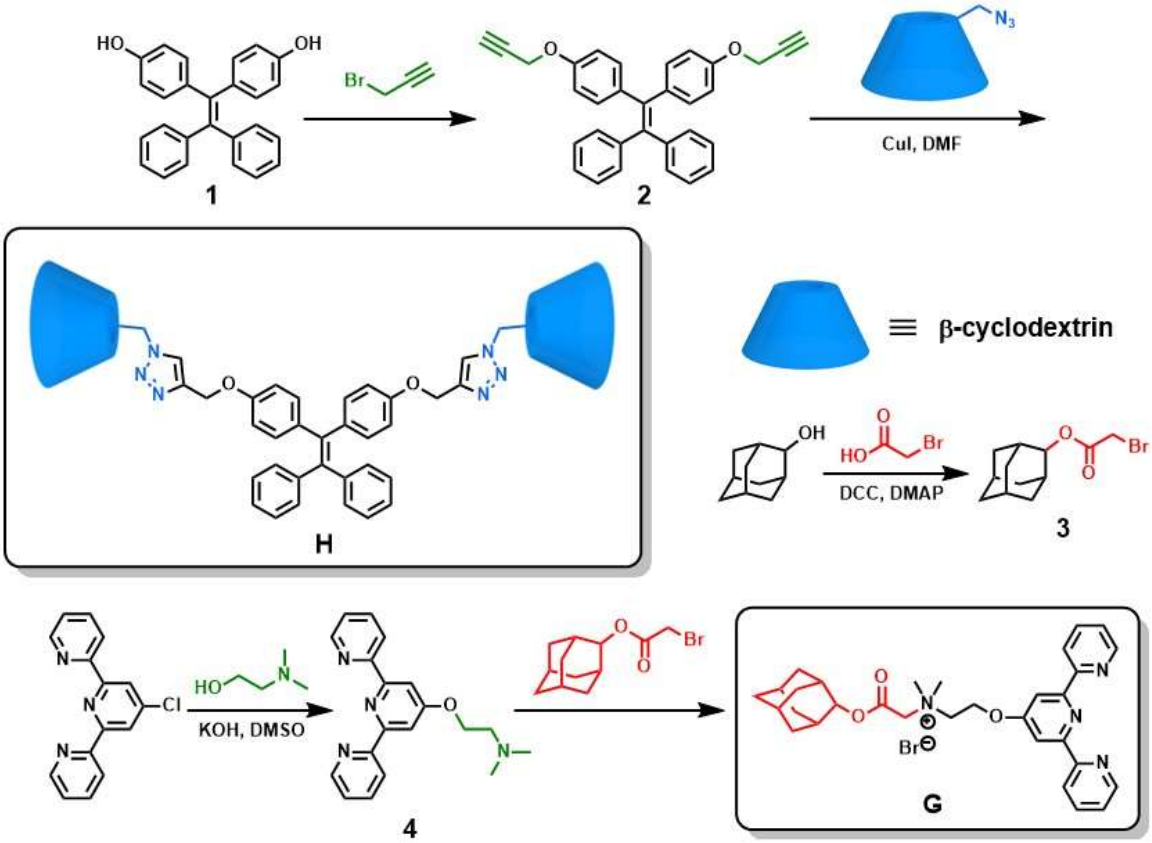
*1. Materials and methods*

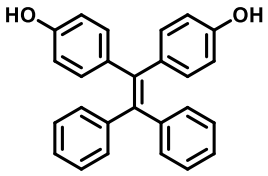
Reagents and deuterated solvents were commercially available and used without further purification except for *β*-cyclodextrin recrystallization three times. Compounds **1**[S1], **2**[S2], *β*-$N_3$-CD[S3] were synthesized according to the literature procedures. NMR spectra were recorded on a Bruker Avance 500 MHz pectrometer. $^1$H and $^{13}$C NMR chemical shifts are reported relative to residual solvent signals. High-resolution mass data were obtained with an Agilent Technologies 6530 Accurat-Mass Q-TOF LC/MC instrument. The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus. UV-Vis experiments were conducted on a Perkin Elmer Lambda 750 UV/Vis spectrophotometer. The fluorescent experiments were conducted on a Hitachi F-7000 fluorescence spectrophotometer. Scanning electron microscopy (SEM) was performed on a Carl Zeiss Jena supra55 sapphire instrument. Transmission electron microscope (TEM) was performed on a Hitachi HT-7700 instrument. Atomic force microscope (AFM) was performed on a E-Sweep instrument. Dynamic light scattering experiments were performed using a Mastersizer 2000 Malvern Zetasizer. Rheological data were obtained using an ARES-G2 rheometer (Waters) with plate-plate geometry (diameter of 25 mm, gap is 200 μm). Oscillatory frequency sweep experiments were performed from 0.1 rad/s to 100 rad/s with a strain in the linear region at 20 °C. The scanning frequency of self-healing experiments were performed was 10 rad/s at 20 °C. Tensile tests were performed on a universal materials testing machine (Instron, model 5966) with a tensile speed of 10 mm/min at room temperature. Cuboid gel samples (30 mm long × 3.5 mm wide × 2.24 mm deep) were constructed in molds at 60 °C and then cooled to room temperature for testing machine.

*2. Synthetic procedures and characterization data*




***Scheme S1***. Synthetic routes of host molecule **H** and guest molecule **G** and chemical structures of compounds used in this work.

*2.1 Synthesis of compound **1***

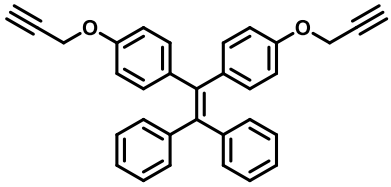



Compound **1** was synthesized according to literature procedure[S1]. $^{1}$H NMR (500 MHz, DMSO-$d_6$, 293K): 9.31 (s, 2H), 7.14 – 7.08 (m, 4H), 7.07 – 7.03 (m, 2H), 6.93 (d, $J$ = 7.6 Hz, 4H), 6.74 (d, $J$ = 8.6 Hz, 4H), 6.49 (d, $J$ = 8.6 Hz, 4H). $^{13}$C NMR (125 MHz, DMSO-$d_6$, 293K): 156.3, 144.6, 141.1, 138.2, 134.6, 132.5, 131.2, 128.2, 126.4, 115.0.

***Figure S1.*** $^{1}$H NMR spectrum (500 MHz, DMSO-$d_6$, 293K) recorded for **1**.

***Figure S2.*** $^{13}$C NMR spectrum (125 MHz, DMSO-$d_6$, 293K) recorded for **1**.

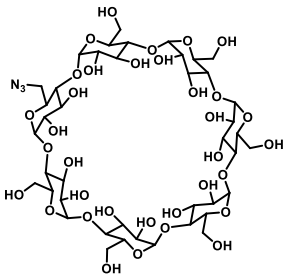
*2.2 Synthesis of compound **2***



Compound **2** was synthesized according to literature procedure[S2]. $^{1}$H NMR (500 MHz, $CDCl_3$, 293K): 7.13 – 7.05 (m, 6H), 7.01 (d, $J$ = 7.7 Hz, 4H), 6.94 (d, $J$ = 8.8 Hz, 4H), 6.70 (d, $J$ = 8.8 Hz, 4H), 4.61 (d, $J$ = 2.4 Hz, 4H). $^{13}$C NMR (125 MHz, $CDCl_3$, 293K): 156.2, 144.1, 139.8, 139.8, 137.2, 132.6, 131.4, 127.8, 126.2, 114.0, 78.6, 75.5, 55.7.

***Figure S3.*** $^{1}$H NMR spectrum (500 MHz, $CDCl_3$, 293K) recorded for **2**.

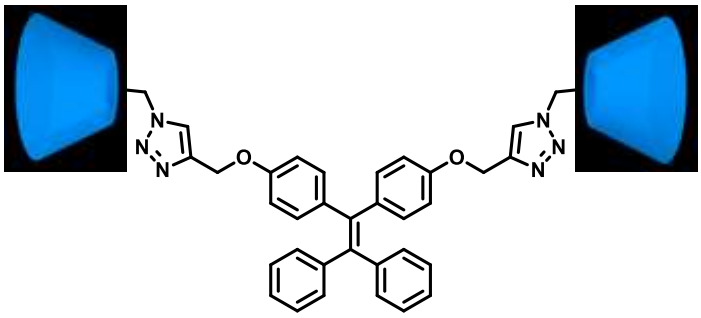
***Figure S4.*** $^{13}$C NMR spectrum (125 MHz, $CDCl_3$, 293K) recorded for **2**.



*2.3 Synthesis of compound β-$N_3$-CD*

Compound β-$N_3$-CD was synthesized according to literature procedure[S3]. $^1$H NMR (500 MHz, DMSO-$d_6$, 293K): 5.81 – 5.56 (m, 14H), 4.90 – 4.75 (m, 7H), 4.56 – 4.36 (m, 6H), 3.78 – 3.48 (m, 28H), 3.43 – 3.20 (m, overlapping with HDO, 14 H).

***Figure S5.*** $^1$H NMR spectrum (500 MHz, $CDCl_3$, 293K) recorded for β-$N_3$-CD.



*2.4 Synthesis of compound **H***

Compound **2** (260 mg, 0.58 mmol), β-$N_3$-CD (1460 mg, 1.46 mmol) were dissolved in DMF (30 mL) in a 50 mL flask and CuI (110 mg, 0.58mmol) was added as catalyst. The mixture solution was then stirred at 90℃ for 48 h. After cooling, the product was concentrated and purified by column chromatography on HP20 macroporous adsorbent resin with EtOH: $H_2O$ (1:1, v/v) as the eluent to afford compound **H** (1225 mg, 76%) as a yellow solid. $^1$H NMR (500 MHz, DMSO-$d_6$, 293K): 8.14 (s, 2H), 7.20 – 7.07 (m, 6H), 6.98 (d, $J$ = 7.1 Hz, 4H), 6.90 (d, $J$ = 8.6 Hz, 4H), 6.78 (d, $J$ = 8.8 Hz, 4H), 5.93 – 5.61 (m, 28H), 5.17 – 4.19 (m, 36H), 4.08 – 3.46 (m, 46H). ESI-MS: *m/z* 2760.9 [**H** + H]$^+$, calcd. for [C117H162N6O70]$^+$, 2760.8.

***Figure S6.*** $^{1}$H NMR spectrum (500 MHz, DMSO-$d_6$, 293K) recorded for **H**.

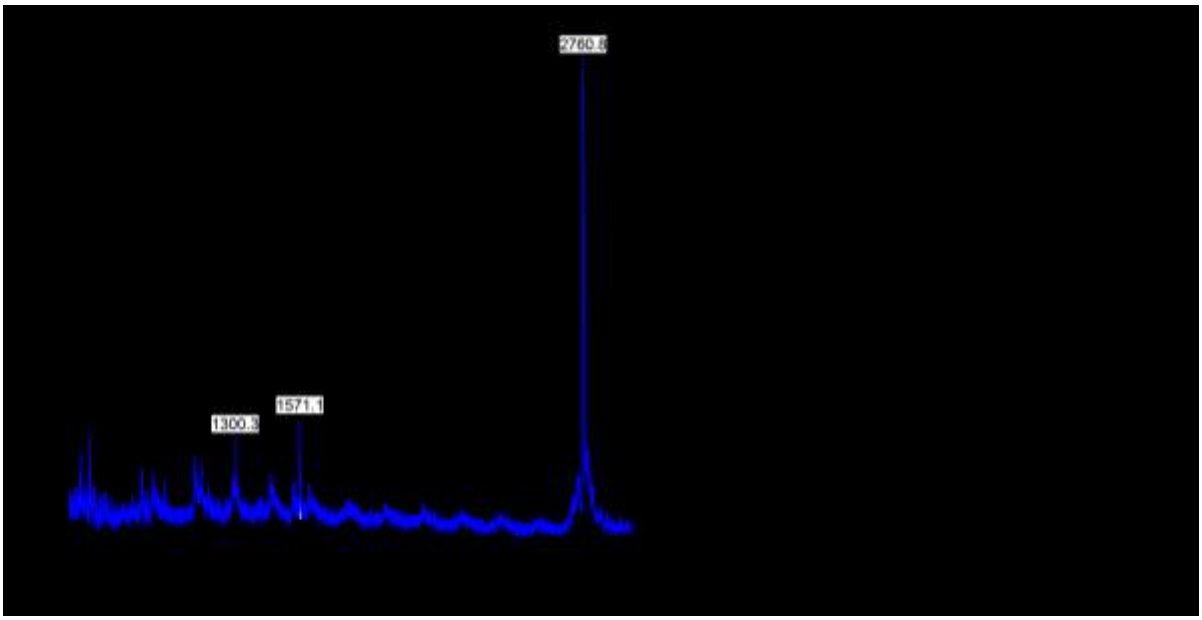



***Figure S7.*** ESI-HR-MS spectrum of **H**.

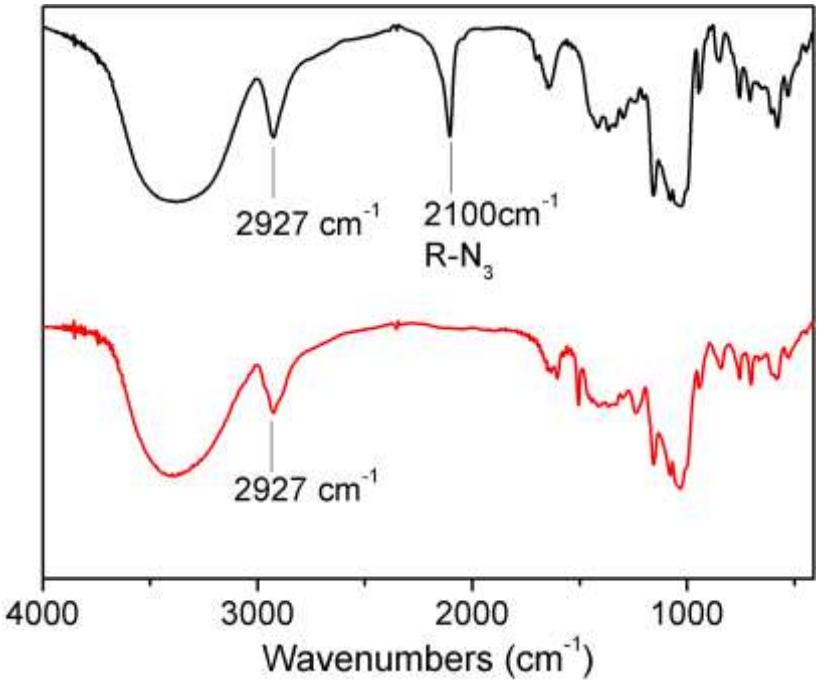
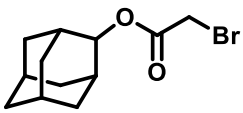



***Figure S8.*** FTIR spectrum of **H**.

*2.5 Synthesis of compound **3***

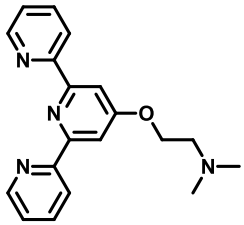



Adamantan-2-ol (1.0 g, 6.62 mmol) and bromoacetic acid (1.1 g, 7.95 mmol) were dissolved in anhydrous THF (30 mL) in a 100 mL flask. After the mixture solution was stirred at 0℃ under nitrogen, *N*, *N'*-dicyclohexylcarbodiimide (DCC) (1.36 g, 6.62 mmol) and 4-dimethylaminopyridine (DMAP) (0.08 g, 0.662 mmol) in anhydrous THF (30 mL) was added. The mixture was stirred at room temperature for 24 h, then the mixture was filtered, and the solvent was removed with a rotary evaporator. The residue was extracted with $CH_2Cl_2$ and washed. The crude product was purified by column chromatography with a mixture of $CH_2Cl_2$/petroleum ether (1:2, *v/v*) as eluent to afford compound **3** (815 mg, 45%) as a yellow oil. $^1$HNMR (500MHz, $CDCl_3$, 293K): 4.95 (s,1H), 3.83 (s, 2H), 2.02 (d, $J$ = 11.1 Hz, 4H), 1.84 (d, $J$ = 12.4 Hz, 4H), 1.74 (d, $J$ = 19.5 Hz, 4H), 1.55 (d, $J$ = 12.4 Hz, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$, 293 K): 166.5, 79.1, 37.25, 36.2, 31.7, 31.6, 27.1, 26.9, 26.5.

***Figure S9.*** $^{1}$H NMR spectrum (500 MHz, $CDCl_3$, 293K) recorded for **3**.

***Figure S10.*** $^{13}$C NMR spectrum (125 MHz, $CDCl_3$, 293K) recorded for **3**.

*2.6 Synthesis of compound **4***



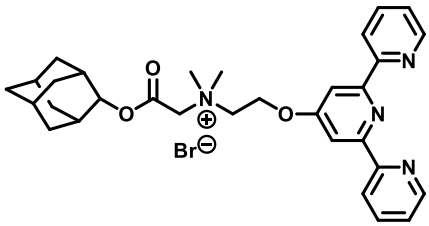
4-Chloro-2,2:6,2-terpyridine (250 mg, 0.93 mmol) and *N*, *N*-dimethylethanolamine (110 mg, 1.20 mmol) were slowly added to a stirred suspension of powdered KOH (280 mg, 5.00 mmol) in DMSO (5 mL) in a 25 mL flask. The mixture solution was then stirred at 80℃ for 12 h. After cooling, the product was concentrated and purified by column chromatography with ethyl acetate as eluent to afford compound **4** (238 mg, 80%) as a white solid. $^{1}$H NMR (500 MHz, $CDCl_3$, 293K): 8.69 (d, $J$ = 5.0 Hz, 2H), 8.61 (d, $J$ = 8.0 Hz, 2H), 8.05 (s, 2H), 7.84 (td, $J$ = 7.8 Hz, $J$ = 1.8 Hz, 2H), 7.33 (td, $J$ = 7.9 Hz, $J$ = 1.7 Hz, 2H), 4.35 (t, $J$ = 5.5 Hz, 2H), 2.84 (t, $J$ = 5.5 Hz, 2H), 2.39 (s, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$, 293K): 167.0, 157.1, 156.1, 149.0, 136.7, 123.8, 121.3, 107.4, 66.4, 58.0, 45.9. ESI-HRMS: *m/z* 321.1710 [**4** + H]$^{+}$, calcd. for [C19H21N4O]$^{+}$, 321.1708.

***Figure S11.*** $^{1}$H NMR spectrum (500 MHz, $CDCl_3$, 293K) recorded for **4**.

***Figure S12.*** $^{13}$C NMR spectrum (125 MHz, $CDCl_3$, 293K) recorded for **4**.

***Figure S13.*** ESI-HRMS spectrum of **4**.

*2.7 Synthesis of compound **G***




Compound **3** (384 mg, 1.41 mmol) and **4** (450 mg, 1.41 mmol) were dissolved in $CHCl_3$ (30 mL) in a 50 mL flask. The mixture solution was then stirred at room temperature for 24 h. After removing the solvent, the crude product was washed thoroughly with diethyl ether (50 mL × 3) to afford compound **G** (792 mg, 95%) as a white solid. $^1$H NMR (500 MHz, $CDCl_3$, 293K): 8.67 (d, $J$ = 4.1 Hz, 2H), 8.61 (d, $J$ = 7.9 Hz, 2H), 8.05 (s, 2H), 7.86 (td, $J$ = 7.8 Hz, $J$ = 1.6 Hz, 2H), 7.37 – 7.32 (m, 2H), 5.11 (s, 1H), 4.95 (s, 2H), 4.78 (d, $J$ = 4.2 Hz, 2H), 4.71 (d, $J$ = 4.2 Hz, 2H), 3.88 (s, 6H), 2.13 (s,

2H), 2.01 (d, $J$ = 12.7 Hz, 2H), 1.87 (d, $J$ = 13.3 Hz, 4H), 1.77 (d, $J$ = 11.8 Hz, 2H), 1.72 (s, 2H), 1.59 (d, $J$ = 12.6 Hz, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$, 293K): 164.0, 163.0, 156.5, 154.2, 148.0, 135.8, 123.1, 120.2, 105.9, 79.8, 61.7, 61.4, 61.2, 52.0, 36.1, 35.3, 30.7, 25.9. ESI-HRMS: m/z 513.2860 [**G** - Br]$^+$, calcd. for [C31H37N4O3]$^+$, 513.2875.

***Figure S14.*** $^1$H NMR spectrum (500 MHz, $CDCl_3$, 293K) recorded for **G**.

***Figure S15.*** $^{13}$C NMR spectrum (125 MHz, $CDCl_3$, 293K) recorded for **G**.

***Figure S16.*** ESI-HRMS spectrum of **G**.

2.8 *Synthesis of supramolecular hydrogel*

Compound **H** (220.8 mg, 80 umol), **G** (92.7 mg, 160 umol) and $Zn(NO_3)_2 \cdot 6H_2O$ (23.80 mg, 80 umol) were dissolved in 800 uL water. The mixture solution was then heated to 60 ºC for 2 h and cooled to room temperature to get the supramolecular hydrogel.

*2.9 Preparation of the quick response code*

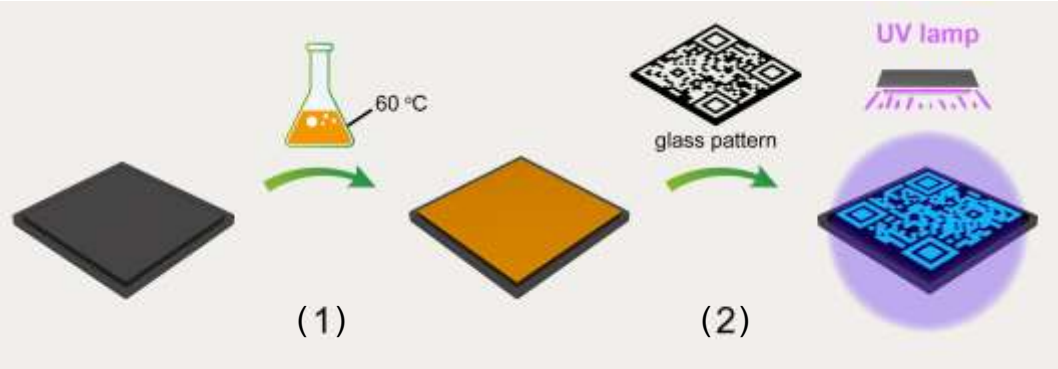



***Figure S17.*** Preparation of the quick response code

(1) Supramolecular hydrogels were heated to 60 ºC and then injected into molds;

(2) When the supramolecular hydrogels are cooled to room temperature, cover the glass mold.

*3. Stoichiometric ratio of **G** and **$Zn(NO_3)_2$***

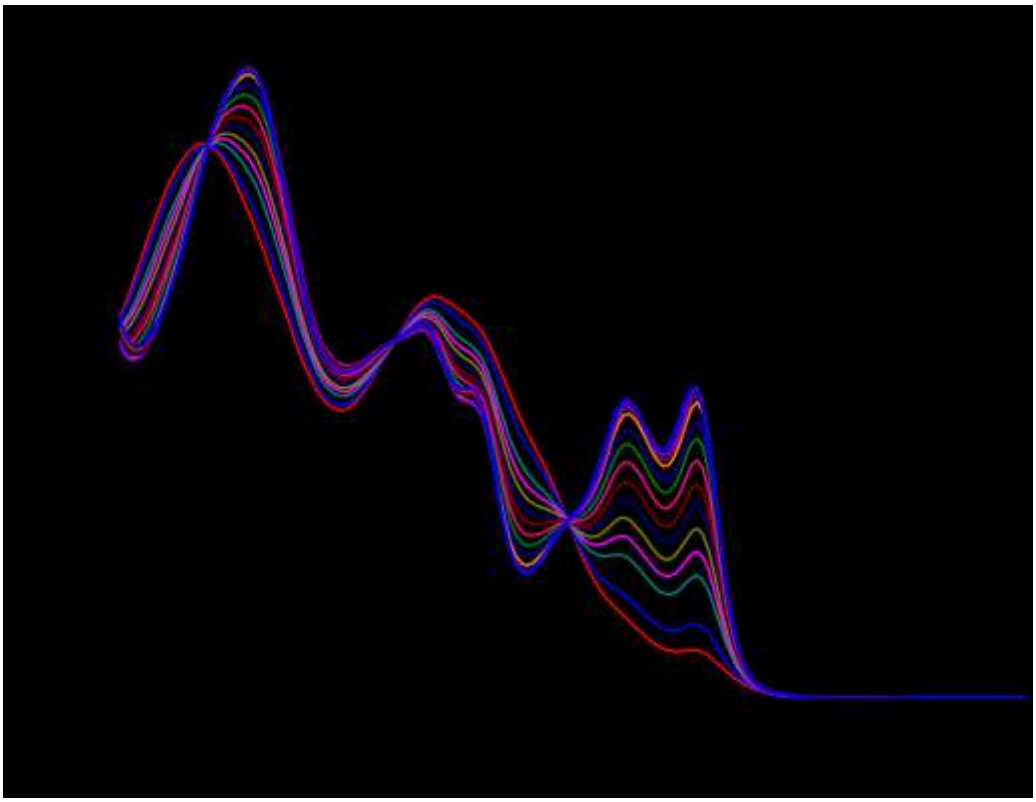


***Figure S18.*** Change in the UV/Vis absorbance intensity upon stepwise addition of $Zn(NO_3)_2$ to **G** in $H_2O$; Inset: Plot of the absorbance intensity at 305 nm versus the amount of $Zn(NO_3)_2$.

*4. Concentration-dependent $^1H$ NMR of **H**, **G** and $Zn(NO_3)_2$*

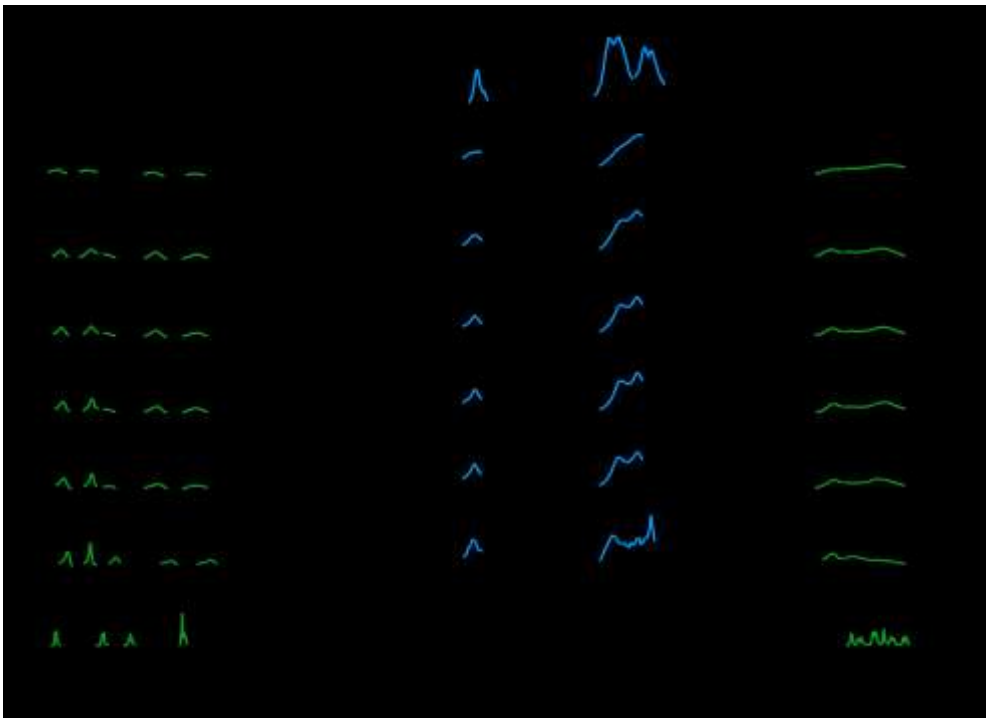


***Figure S19.*** Partial $^1H$ NMR spectra (500 MHz, $D_2O$, 293 K) of (a) **G**; and the mixture of **H**, **G**, and $Zn(NO_3)_2$ (1:2:1 molar ratio) at different concentrations: (b) 1.0 mM; (c) 5.0 mM; (d) 10.0 mM; (e) 20.0 mM; (f) 30.0 mM; (g) 40.0 mM; and (h) **H**.

*5. Concentration-dependent 2D DOSY test of **H**, **G** and $Zn(NO_3)_2$*

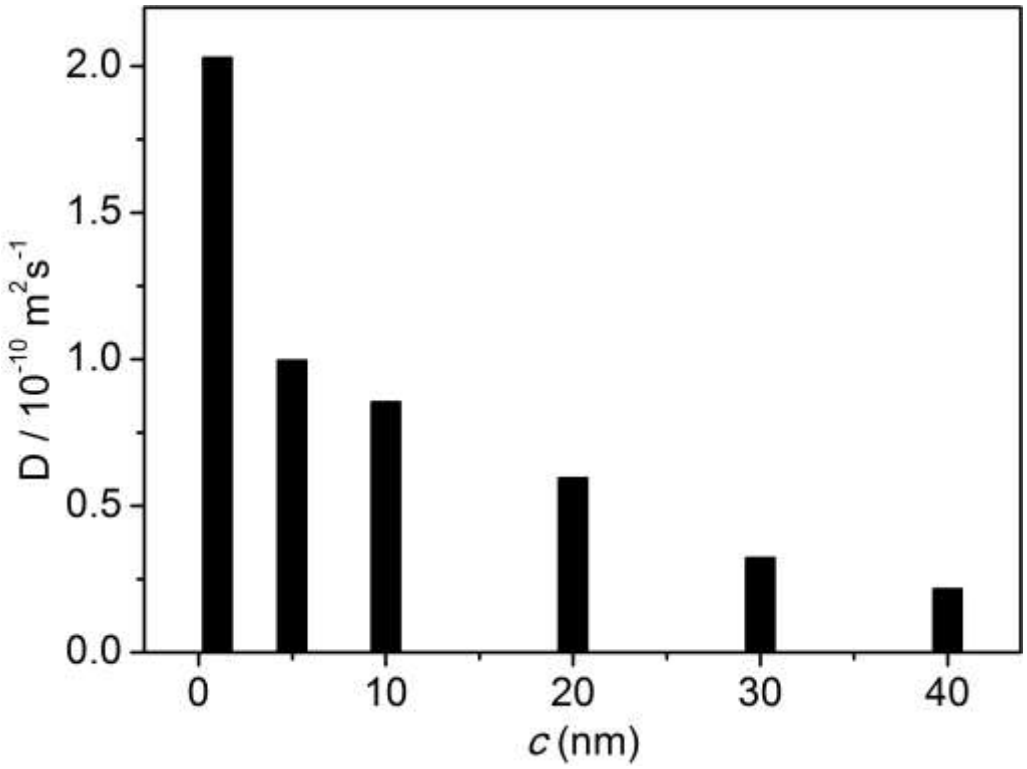



***Figure S20.*** Diffusion coefficient *D* ($D_2O$, 295K, 500 MHz) of the mixture of **H**, **G**, and $Zn(NO_3)_2$ (1:2:1 molar ratio) at different concentration: 1.0 mM; 5.0 mM; 10.0 mM; 20.0 mM; 30.0 mM; 40.0 mM.

*6. Concentration-dependent DLS test of **H**, **G** and $Zn(NO_3)_2$*

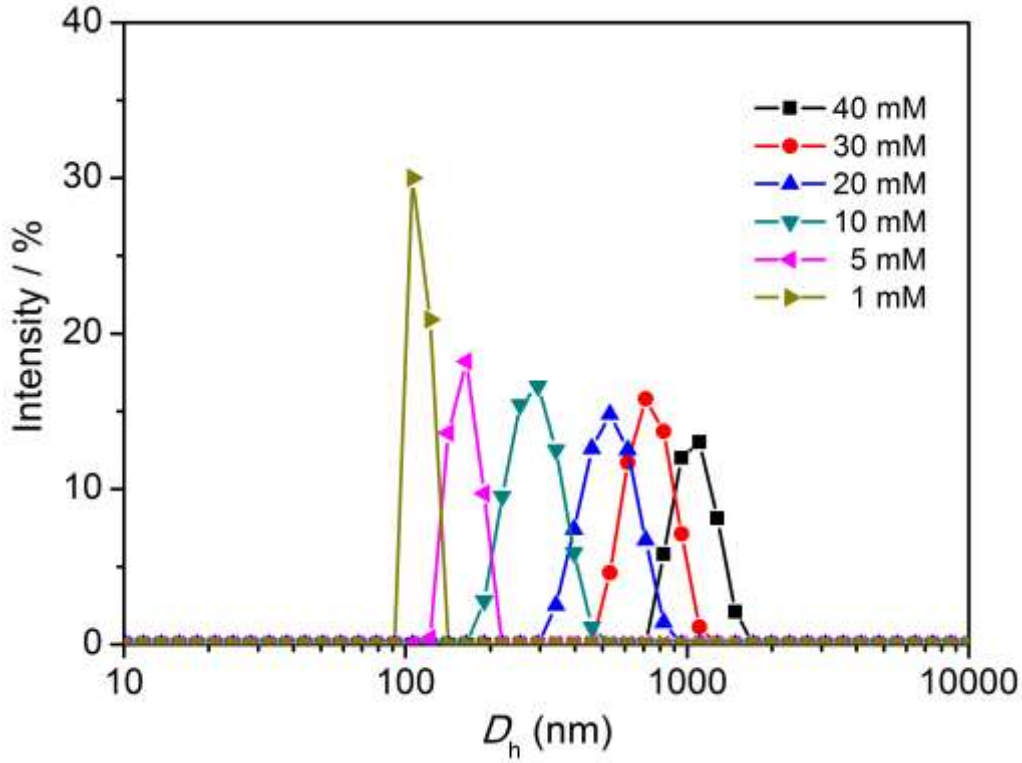



***Figure S21.*** Size distributions of the mixture of **H**, **G**, and $Zn(NO_3)_2$ (1:2:1 molar ratio) at different concentrations: 1.0 mM; 5.0 mM; 10.0 mM; 20.0 mM; 30.0 mM; 40.0 mM.

*7. TEM images of **H·G·Zn**$^{2+}$ hydrogel*

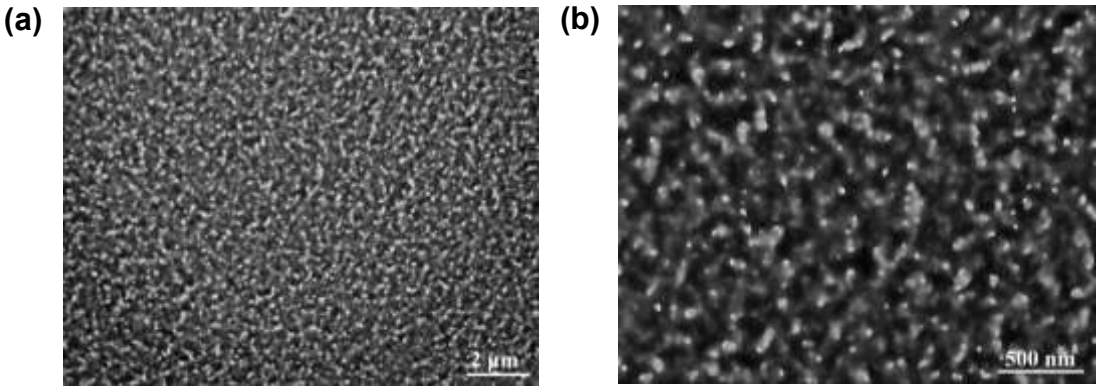



***Figure S22.*** TEM images of supramolecular polymer of **H**, **G** and $Zn^{2+}$ at 10.0 mM.

*8. AFM images of **H·G·Zn**$^{2+}$ hydrogel*

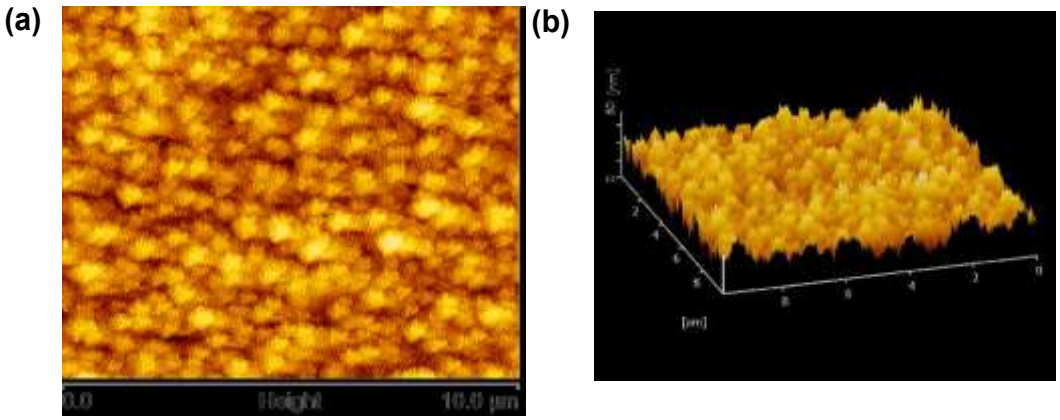



***Figure S23.*** (a) General view of AFM images of supramolecular polymer of **H**, **G** and $Zn^{2+}$ at 10.0 mM, (b) three-dimensional image.

*9. Stress–strain curves of original and self-healed supramolecular hydrogel*

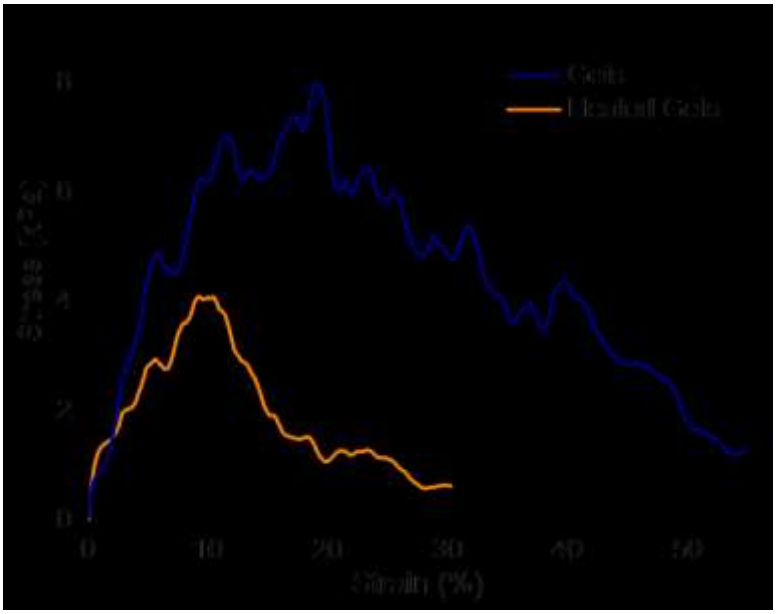


***Figure S24.*** Stress–strain curves of original and self-healed supramolecular hydrogels.

*10. Strain sweep test of supramolecular polymer hydrogel*

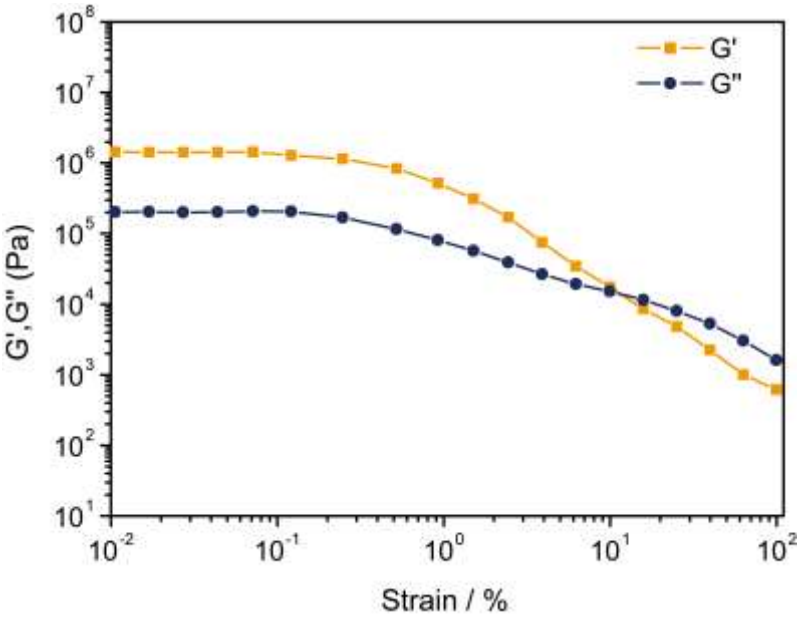



***Figure S25.*** Storage modulus (*G′*) and loss modulus (*G″*) values of supramolecular hydrogel on strain sweep.

*11. References*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