

A double supramolecular crosslinked polymer gel exhibiting macroscale expansion and contraction behavior and multistimuli responsiveness

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Electronic Supplementary Information (13 Pages)

1. <i>Materials and methods</i>	S2
2. <i>Synthesis and characterization of polymer 1 and polymer 2</i>	S3
3. <i>Stability of the double supramolecular crosslinked polymer gel in solution</i>	S10
4. <i>Control experiment for the expansion of the gel</i>	S11
5. <i>Control experiments for supporting the noninterference of the two types of noncovalent interactions and comparing the singly and doubly cross-linked gels</i>	S11
<i>References</i>	S13

1. *Materials and methods*

Monomer 1,^{S1} **monomer 2**,^{S2} **monomer 3**,^{S1} **monomer 4**,^{S3} **polymer 3**,^{S3} **polymer 4**,^{S3} **polymer 5**,^{S1} and **polymer 6**^{S1} were prepared according to literature procedures. Solvents were either employed as purchased or dried according to procedures described in the literature. ¹H NMR spectra were collected on a Bruker Advance DMX-500 spectrometer with internal standard TMS. Molecular weight distributions were measured on a conventional gel permeation chromatography (GPC) system equipped with a Waters 1525 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a set of Waters Styragel columns (HR1, HR2 and HR4, 7.8 mm × 300 mm). GPC measurements were carried out at 35 °C using a DMF solution as the eluent with a flow rate of 1.0 mL/min. The system was calibrated with linear polystyrene standards. Rheological data were obtained using a Physica MCR302 rheometer (Anton Paar) with cone-plate geometry (diameter of 25 mm, 2° cone, truncation height of 0.3 mm). Oscillatory frequency sweep experiments were performed from 0.1 rad/s to 100 rad/s with a strain in the linear region at 10 °C. SEM investigations were carried out on a JEOL 6390LV instrument. UV-vis spectra were taken on a Shimadzu UV-2550 UV-vis spectrophotometer.

2. Synthesis of **polymer 1** and **polymer 2**

Polymer 1 was prepared from **monomer 1**, **monomer 2**, and styrene by free radical polymerization. A mixture of 503 mg (1.00 mmol) of **monomer 1**, 335 mg (1.00 mmol) of **monomer 2**, and 4.60 mL (40.0 mmol) of styrene in 20 mL of benzene was stirred at room temperature. A stream of argon (Ar) was bubbled through for 30 min. In one portion was added 20.5 mg (0.125 mmol) of azobisisobutyronitrile (AIBN) and the mixture was stirred for 10 min, sealed with a rubber septum and heated at 60 °C for 24 h. The polymerization was quenched by rapid freezing in liquid nitrogen and the solvent was removed under vacuum. The crude product was dissolved in 2 mL of CHCl₃ and precipitated into 200 mL of methanol, a solvent in which **monomer 1** was soluble. The precipitated solid was collected by vacuum filtration. This process was repeated three times and the collected polymer was dried in vacuo (1.90 g, 38%). ¹H NMR (CDCl₃) δ 8.51–8.38 (m, naphthyridine-*H*), 8.18–8.05 (m, naphthyridine-*H*), 7.26–6.87 (br m, Ar-*H* in styrene unit), 6.80–6.18 (br m, Ar-*H* in styrene unit), 5.12–4.90 (br s, Ar-CH₂O), 4.28–4.00 (br s, CH₂-NH₂-CH₂), 2.46 (br s, CH₂), 2.35 (br s, CH₂), 2.22 (br s, CH₂), 2.13–1.13 (br s, Ar-*H* in styrene unit overlapped with CH₂), 1.24–1.11 (m, CH₂), 1.03–0.70 (m, CH₃) (Figure S2). *M*_n = 20.2 kDa, *M*_w = 35.6 kDa, PDI = 1.76 (Figure S4).

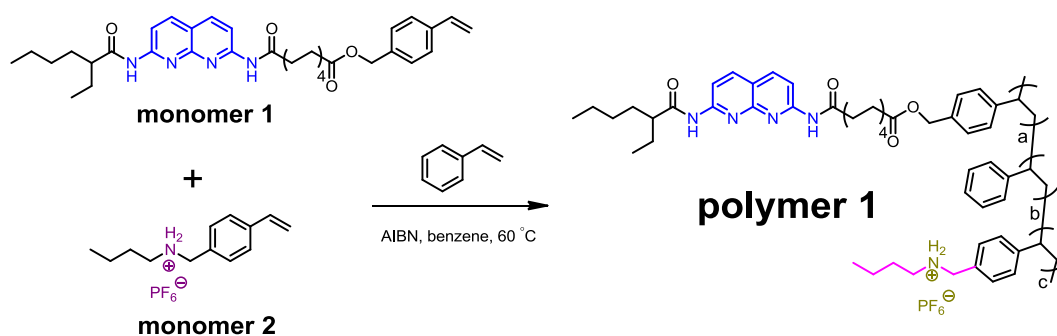


Figure S1. Synthetic route to **polymer 1**.

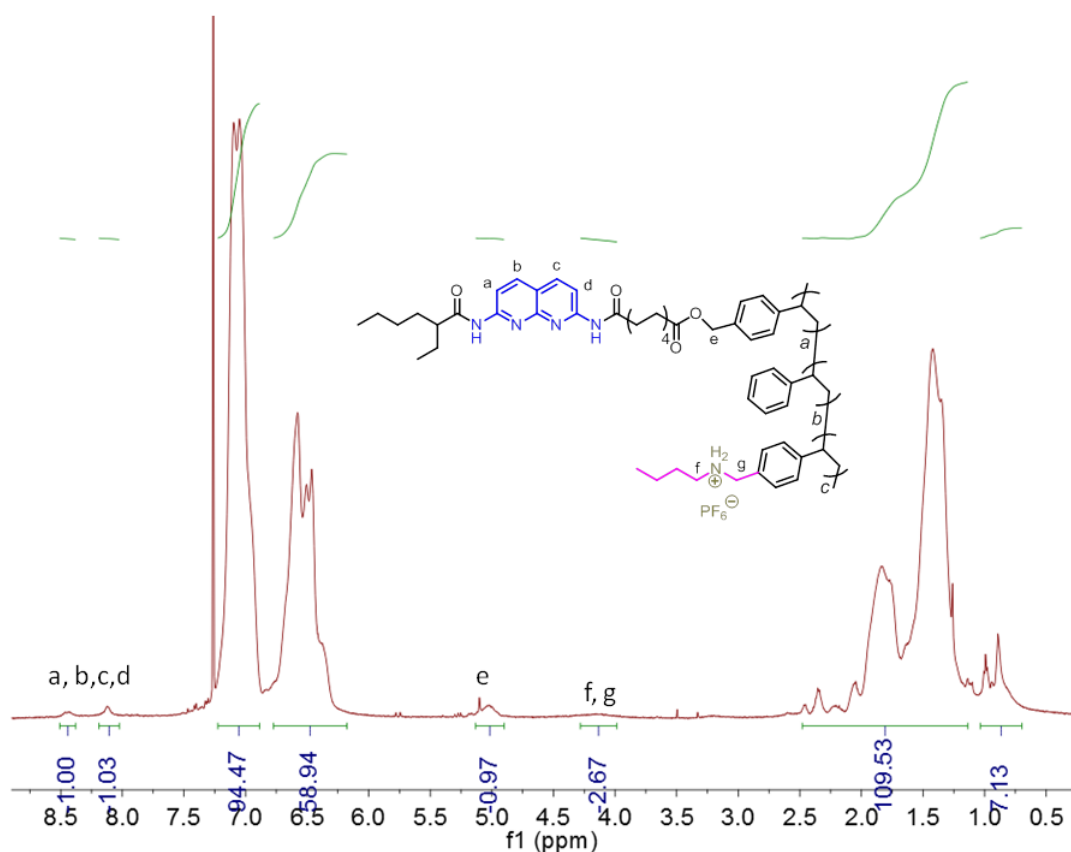


Figure S2. ¹H NMR spectrum (500 MHz, CDCl₃, 298 K) of **polymer 1**.

The ratio of a/c was 1/1.34 as calculated based on the integrations of peaks of DAN units (H_a , H_b , H_c , H_d) and dialkylammonium salt groups (H_f , H_g), and a/b was 1/58 as calculated based on the integrations of peaks of DAN units and benzene protons. Therefore, the ratio of $a/b/c$ was 1/58/1.34 for **polymer 1**, indicating that the incorporation degrees of DAN units and dialkylammonium salt groups were both 1.7 and 2.3 mol% for **polymer 1**.

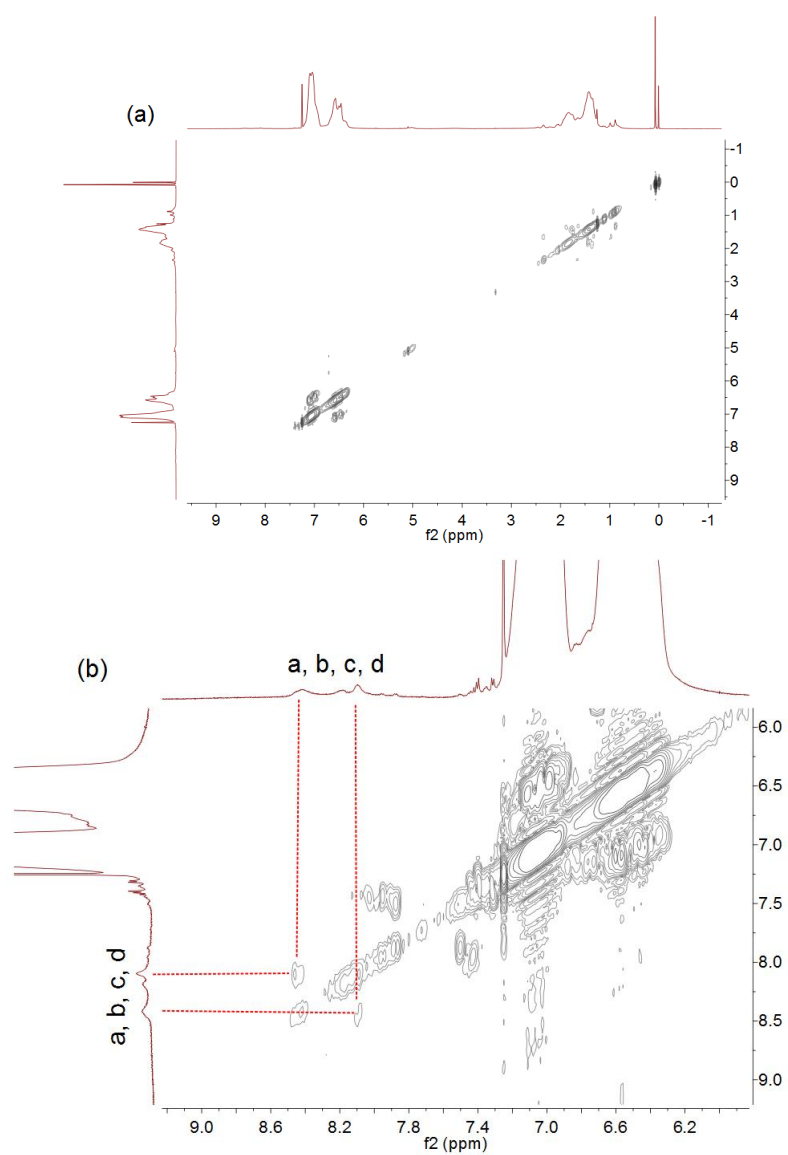
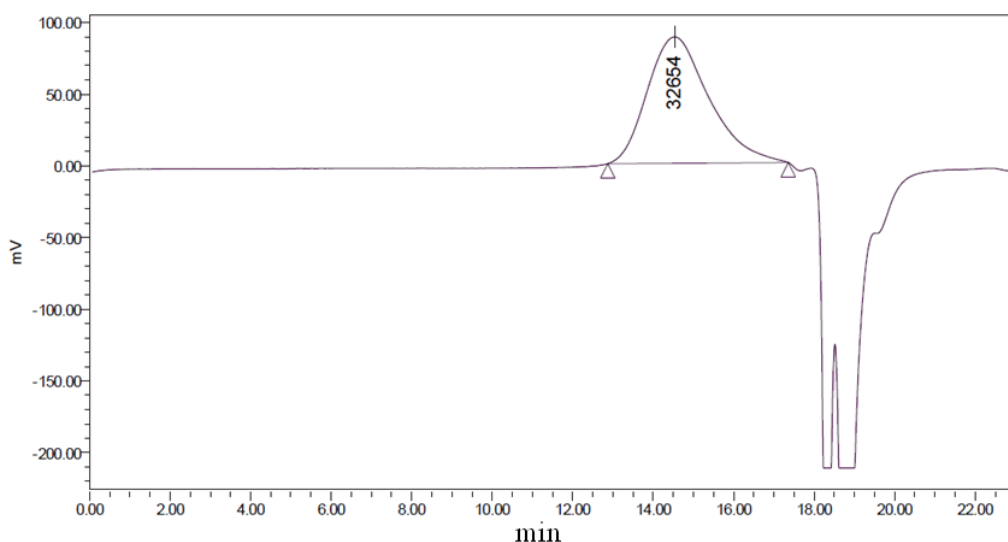


Figure S3. Full (a) and partial (b) COSY NMR spectrum (500 MHz, CDCl₃, 298 K) of **polymer 1**.



M_n	M_w	M_p	M_z	M_{z+1}	PDI
20167	35551	32654	54425	74782	1.762840

Figure S4. GPC analysis of **polymer 1** using conventional calculations, with polystyrene as the standard and DMF as the solvent.

Similarly, **polymer 2** was prepared from **monomer 3**, **monomer 4**, and butyl methacrylate (BMA) by free radical polymerization (Figure S5). A mixture of 660 mg (1.00 mmol) of **monomer 3**, 440 mg (1.00 mmol) of **monomer 4**, and 4.80 mL (30.0 mmol) of BMA in 100 mL of DMSO was stirred at room temperature. A stream of Ar was bubbled through for 30 min. In one portion was added 16.4 mg (0.100 mmol) of AIBN and Ar was bubbled for 10 min. The mixture was sealed with a rubber septum and heated at 60 °C for 18 h. The polymerization was quenched by rapid freezing in liquid nitrogen. The crude product was diluted with 100 mL of CHCl_3 and washed with 120 mL of water. The water layer was extracted twice with 80 mL of DCM. The organic layers were combined, washed with 150 mL of saturated brine, dried over sodium sulfate, gravity filtered and concentrated *in vacuo*. The crude product was dissolved in 3 mL of CHCl_3 and dispersed in 800 mL of methanol, a solvent in which **monomer 3** was soluble. The precipitate was collected by filtration. This process was repeated twice. The collected polymer was dried *in vacuo* at 40 °C (1.60 g, 30%). ^1H NMR (5% $\text{DMSO-}d_6$ in CDCl_3) δ 10.90 (s, NH), 8.88 (s, NH), 6.91–6.69 (br m, Ar-H in benzo-21-crown-7 group), 6.37 (s, CH), 4.23 (s, $\text{OCH}_2\text{CH}_2\text{O}$ in BMA-DeUG), 3.95–3.46 (br m, CH_2 in BMA and $\text{OCH}_2\text{CH}_2\text{O}$ in benzo-21-crown-7 group), 3.20 (s, CH_2), 2.00–0.66 (br m, CH_2 and CH_3) (Figure S6). $M_n = 25.8$ kDa, $M_w = 41.6$ kDa, PDI = 1.61 (Figure S8).

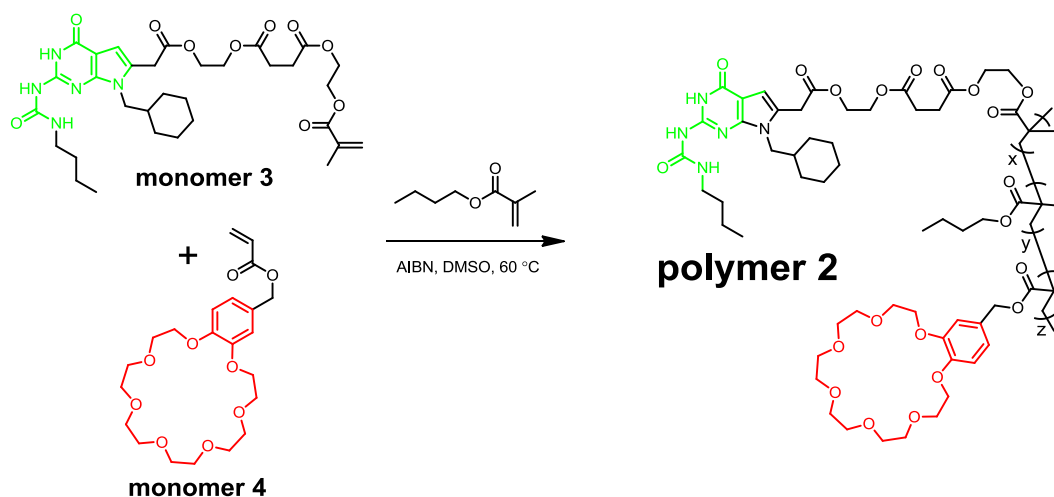


Figure S5. Synthetic route to **polymer 2**.

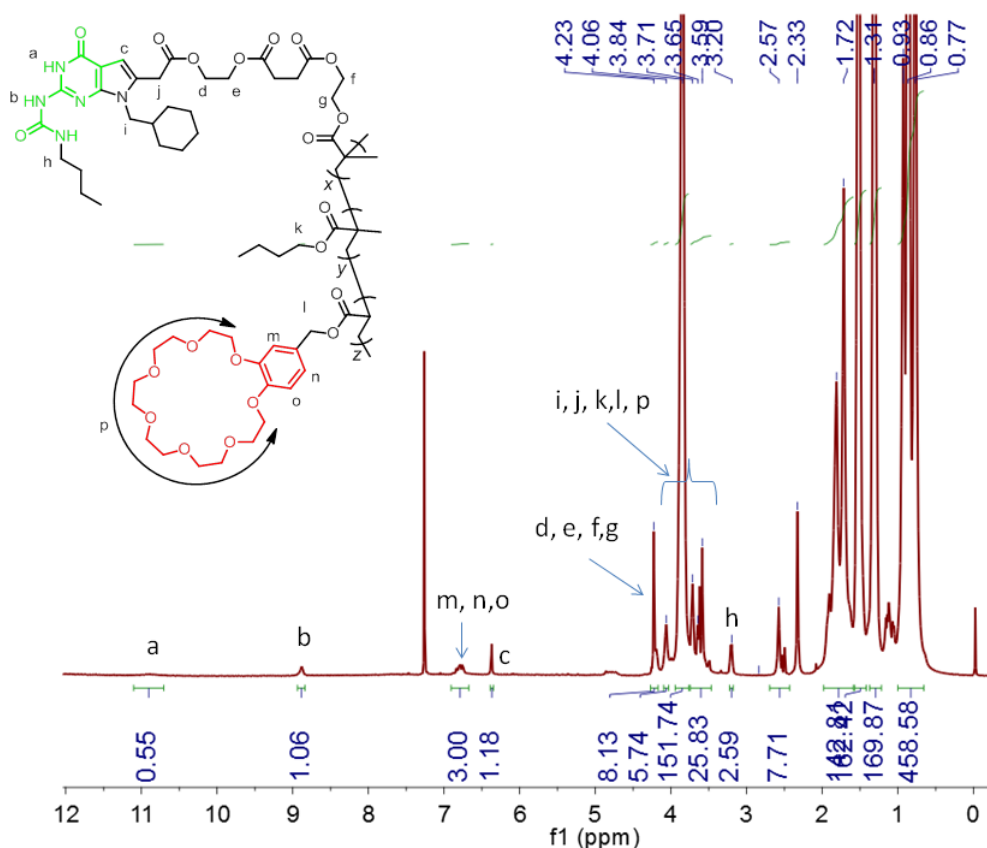


Figure S6. ^1H NMR spectrum (500 MHz, 5% DMSO- d_6 in CDCl_3 , 298 K) of **polymer 2**.

The ratio of x/z was 1/1 as calculated based on the integrations of peaks of DeUG units (H_c) and crown ether groups (H_m , H_n , H_o), and x/y was 1/70 as calculated based on the integrations of peaks of crown ether groups and benzene protons. Therefore, the ratio of $x/y/z$ was 1/70/1 for **polymer 2**, indicating that the incorporation degrees of DeUG units and crown ether groups were both 1.4 mol% for **polymer 2**. Here the unequal integrations of protons H_a and H_b was the result of the intermolecular interactions of DeUG units.

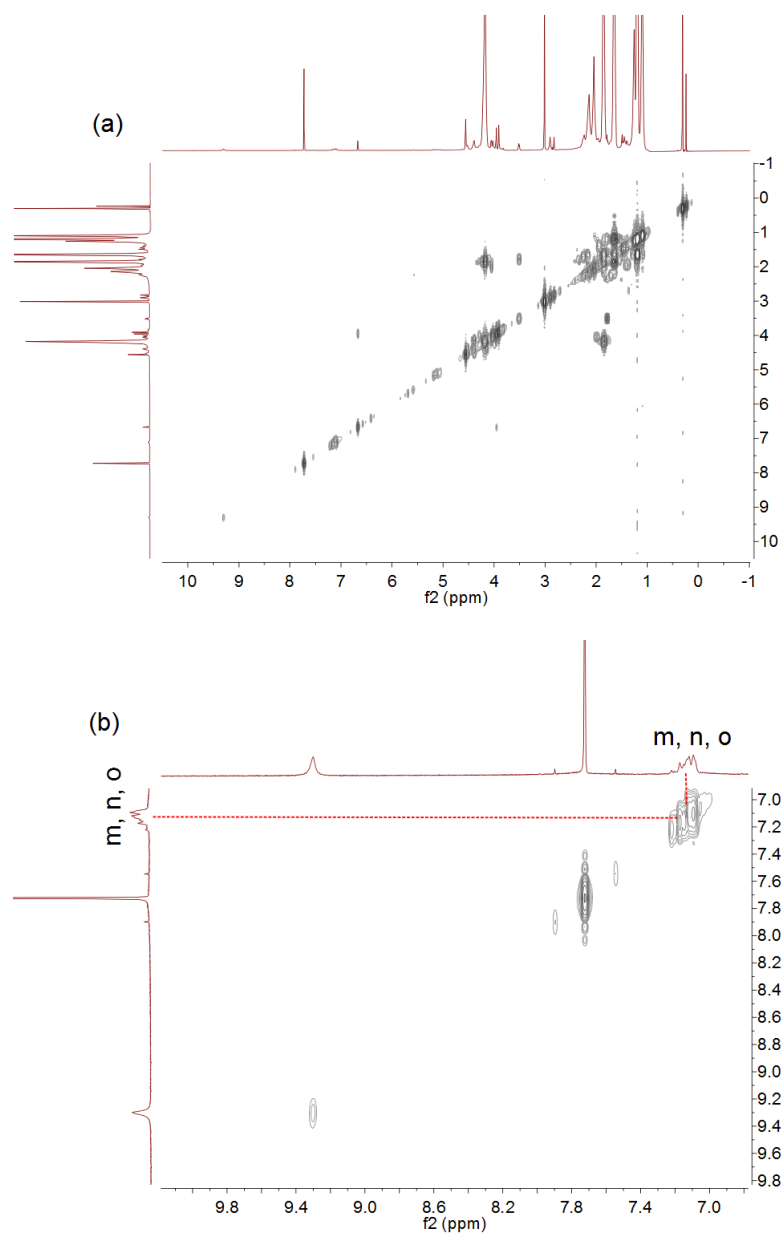
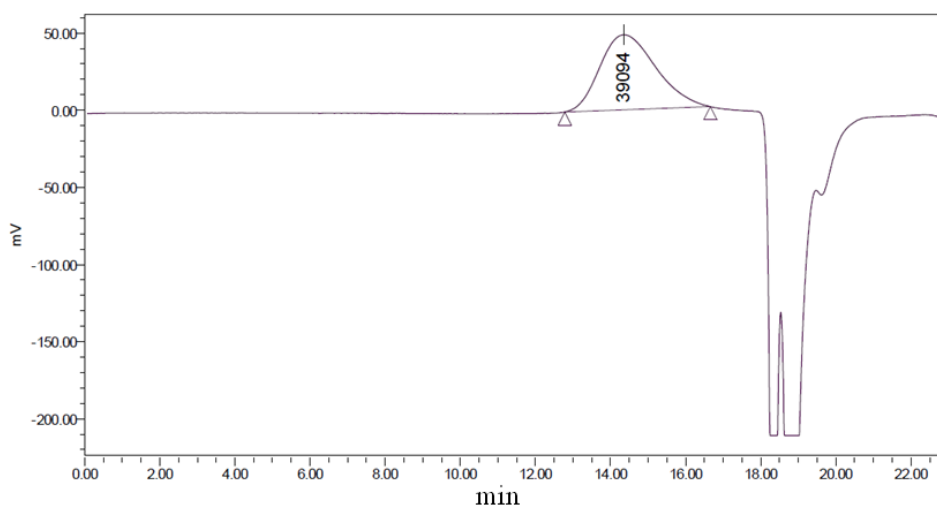


Figure S7. Full (a) and partial (b) COSY NMR spectrum (500 MHz, 5% DMSO- d_6 in $CDCl_3$, 298 K) of **polymer 2**.



M_n	M_w	M_p	M_z	M_{z+1}	PDI
25806	41583	39094	61604	83240	1.611390

Figure S8. GPC analysis of **polymer 1** using conventional calculations, with polystyrene as the standard and DMF as the solvent.

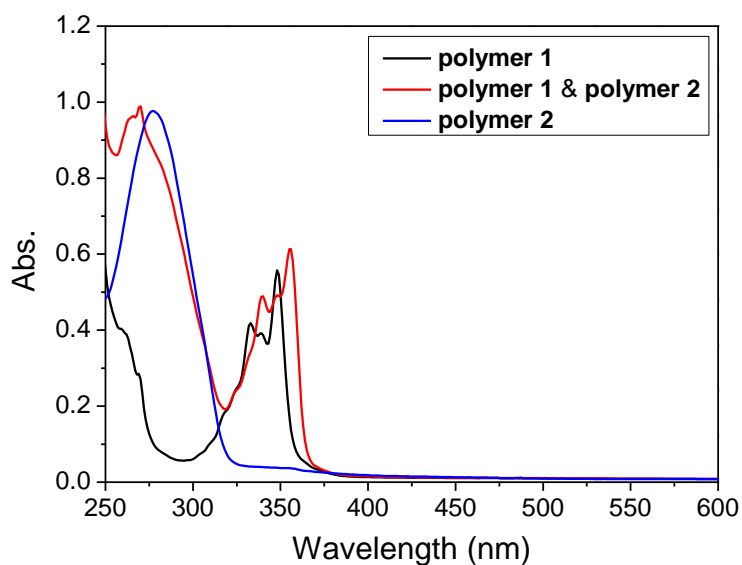


Figure S9. UV-Vis spectra (CHCl_3) of **polymer 1** (0.01 mM), **polymer 2** (0.01 mM), and the mixture of 0.01 mM **polymer 1** and **polymer 2**.

The UV-Vis spectra of **polymer 1** and **polymer 2** confirmed the attachment of DAN and DeUG, and that of their mixture confirmed the complexation of DAN and DeUG, namely the crosslinking of the two polymers.

3. Stability of the double supramolecular crosslinked polymer gel in solution

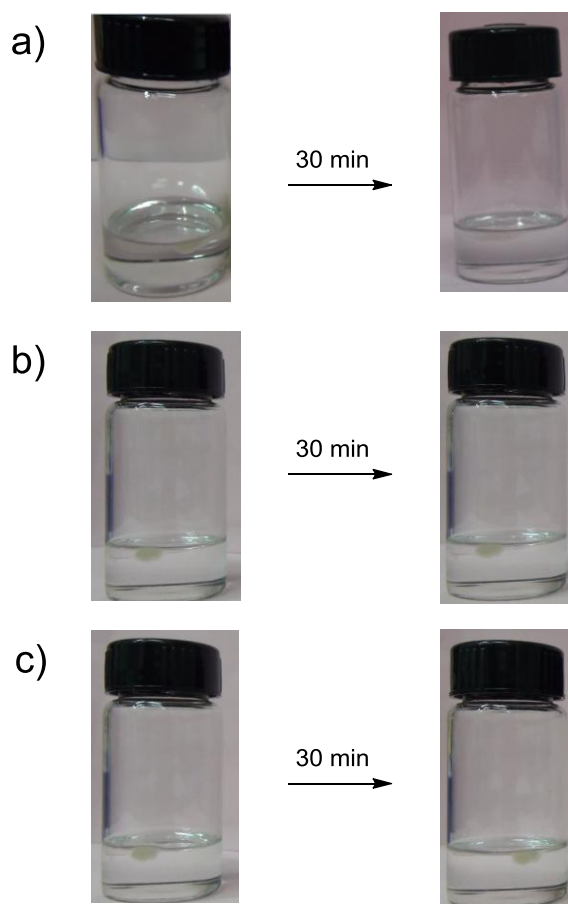


Figure S10. The changes of the 60 g/L (a), 100 g/L (b), and 150 (c) g/L samples after being immersed in chloroform for 30 min at room temperature.

When the 60 g/L sample was immersed in chloroform, it showed autodegradation within 30 min (Figure S10a), whereas the 100 and 150 g/L samples were stable (Figure S10, b and c), and their weights were 103% and 102% of the original weights, respectively.

4. Control experiment for the expansion of the gel

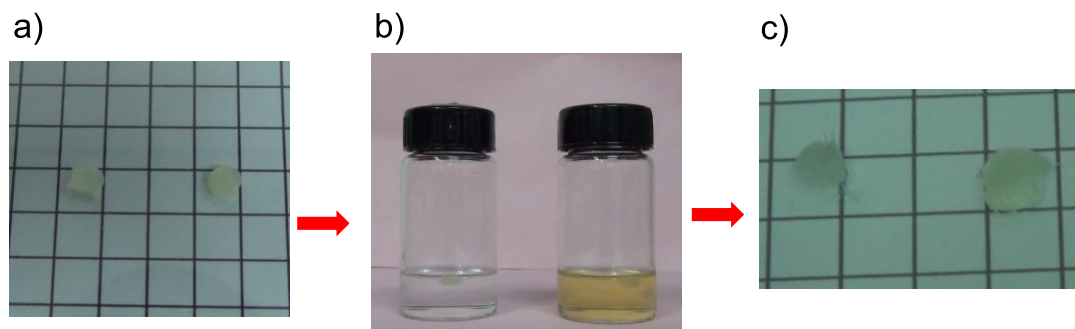


Figure S11. a) Two 150 g/L samples with the same weight. b) Left bottle: the gel was immersed in chloroform; right bottle: the gel was immersed in a chloroform solution of eDAN (100 mM). c) The two gels after being immersed in chloroform (left) and the chloroform solution of eDAN (right), respectively.

The above photos came from the supporting movie. We can see that the volume of the right gel was larger than that of the left one, indicating that the expansion of the gel was induced by the addition of eDAN.

5. Control experiments for supporting the noninterference of the two types of noncovalent interactions and comparing the singly and doubly cross-linked gels

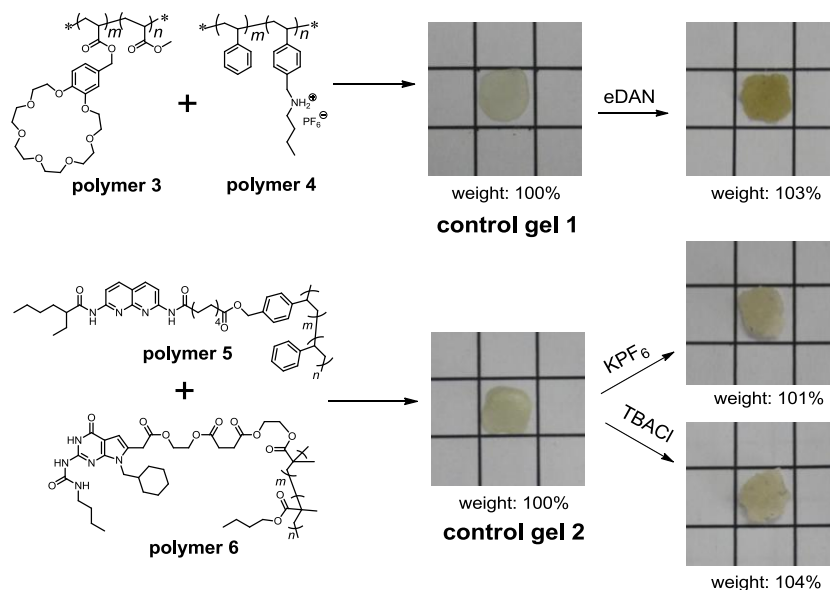


Figure S12. Chemical structures of the control polymers, and the visualized volume changes of the control supramolecular gels under different stimuli.

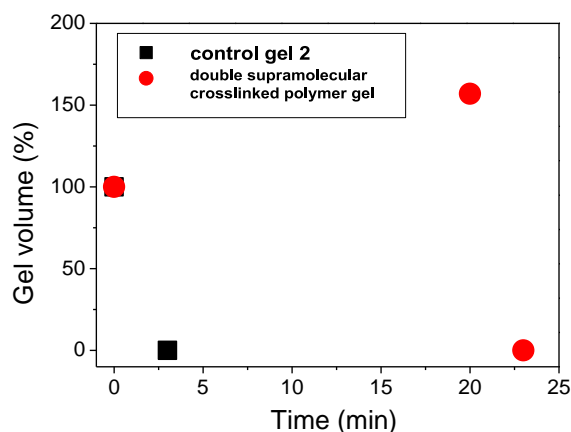


Figure S13. The gel volume of singly vs doubly cross-linked gels against immersion time: **control gel 2** was immersed in a chloroform solution of eDAN (100 mM); double supramolecular crosslinked polymer gel was immersed in a chloroform solution of eDAN (100 mM) and after 20 min, TBACl (100 mM) was added.

To support the noninterference (orthogonality) of the two types of noncovalent interactions and compare the singly and doubly cross-linked gels, control experiments were carried out using two additional supramolecular crosslinked gels.

Polymer 3,^{S3} **polymer 4**,^{S3} **polymer 5**,^{S1} and **polymer 6**^{S1} were prepared according to literature procedures with similar M_n to **polymer 1** and **polymer 2**, around 2.0 kDa. As shown in Figure S12, **control gel 1** and **control gel 2** contain only benzo-21-crown-7/dialkylammonium salt host-guest interactions and DAN·DeUG quadruply hydrogen-bonding interactions, respectively. No obvious change was observed in weight or volume for the two control gels after identical treatments with the different stimuli, confirming that the competitive hydrogen-bonding molecule (eDAN) does not affect the benzo-21-crown-7/dialkylammonium salt host-guest interactions, and also both K^+ and Cl^- show no influence on the hydrogen-bonding complexation.

As shown in Figure S13, **control gel 2** showed gel to sol transition after it was immersed in a chloroform solution of eDAN for only 3 min. However, the volume of the double supramolecular crosslinked polymer gel increased to 157% of the original volume after it was immersed in a chloroform solution of eDAN for 20 min, and 3 min after the subsequent addition of TBACl, the transition from gel to sol occurred. This confirmed that the consequence of using a single type of supramolecular crosslink is that above some level of external stimulation, sufficient cross-links are broken that a cooperative gel to sol transition usually occurs. However, for the double type of supramolecular crosslink, the employment of a second, noncovalent polymer network can maintain the polymer network's integrity; meanwhile, the gel to sol transition can also be achieved by breaking the second supramolecular crosslink.

References:

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