

A self-healing supramolecular polymer gel with stimuli-responsiveness constructed by crown ether based molecular recognition

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1. Synthesis of monomer **1**

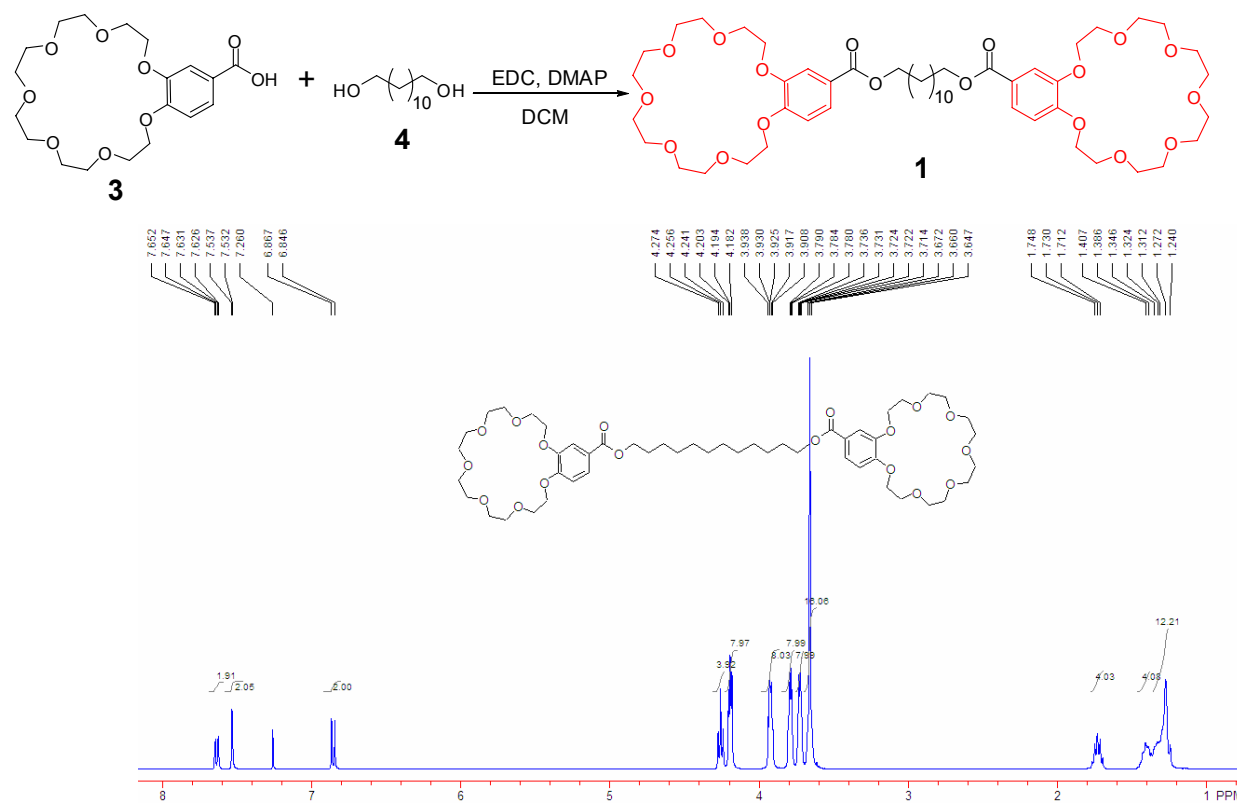


Figure S1. ¹H NMR spectrum (CDCl₃, 293 K, 400 MHz) of monomer **1**.

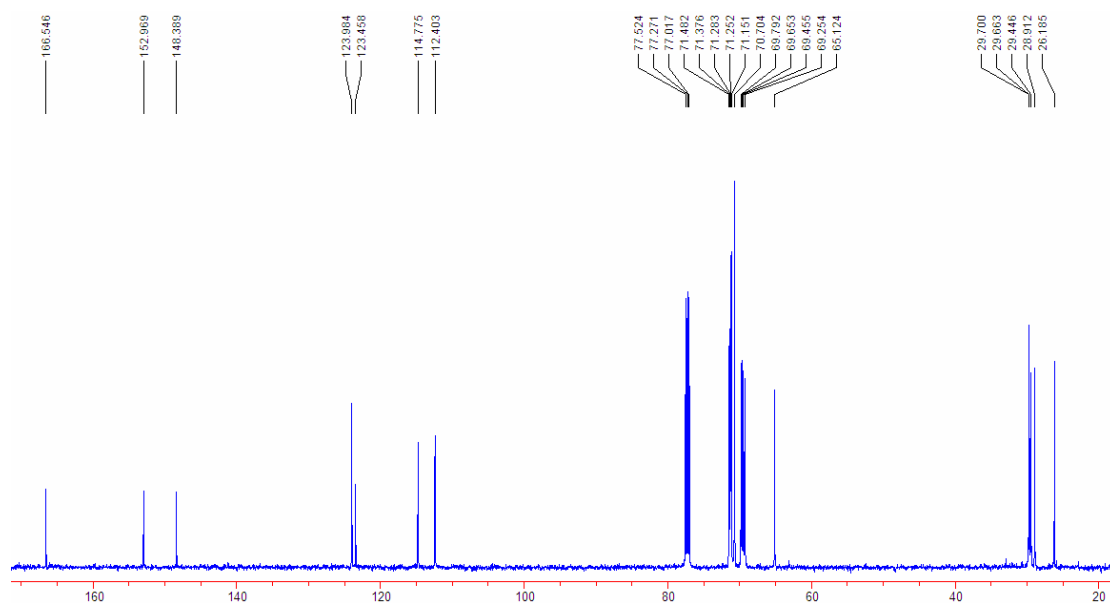


Figure S2. ¹³C NMR spectrum (CDCl₃, 293 K, 125 MHz) of monomer **1**.

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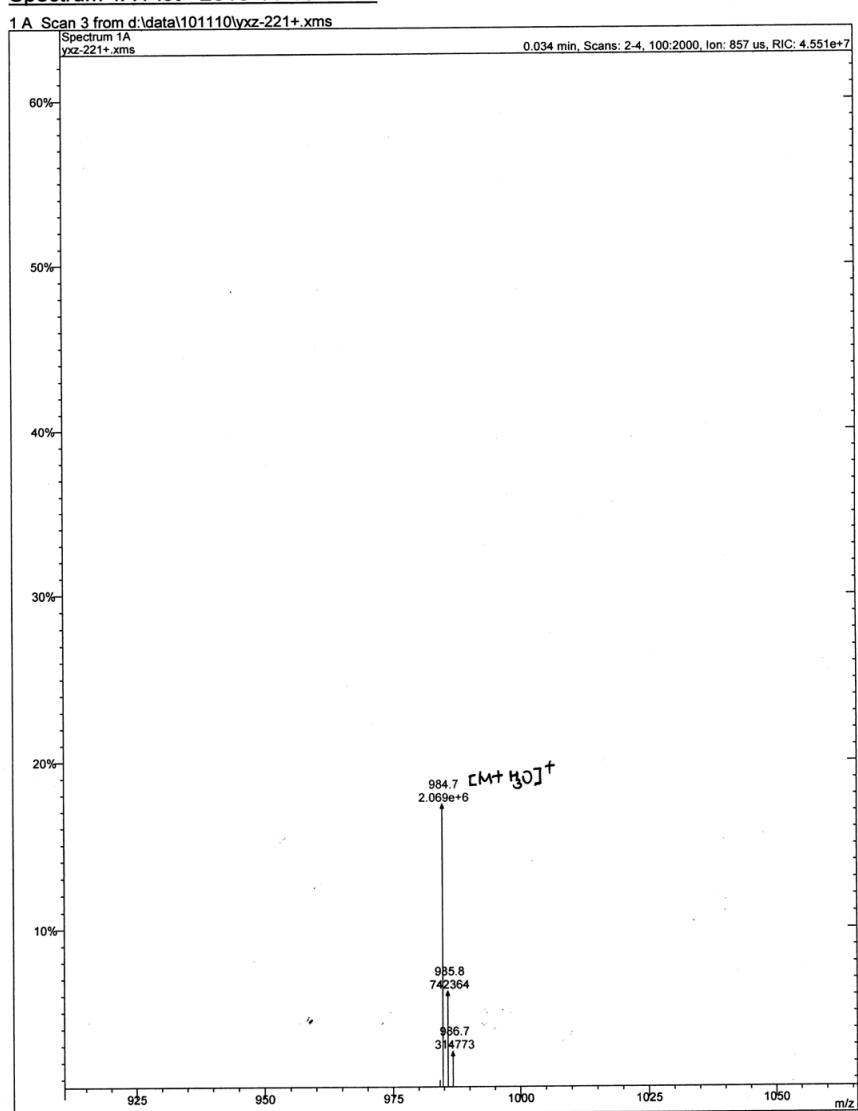


Figure S3. Electrospray ionization mass spectrum of **1**.

2. Synthesis of monomer 2

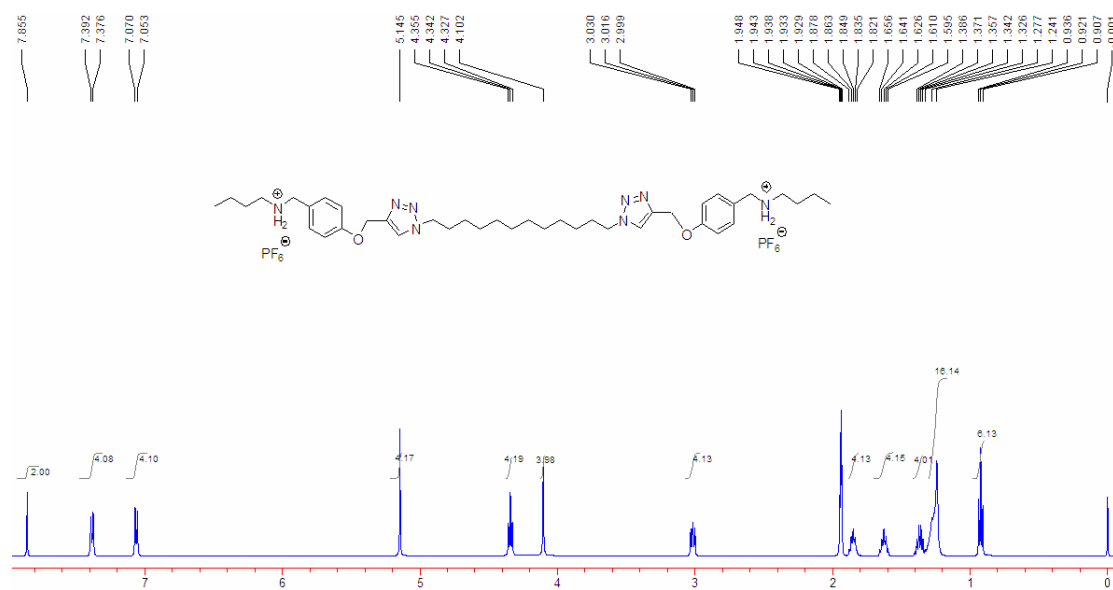
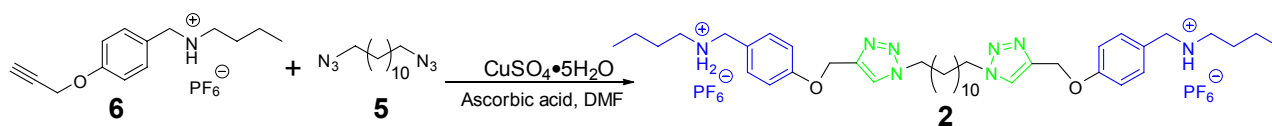


Figure S4. ^1H NMR spectrum (CD₃CN, 293 K, 400 MHz) of **2**.

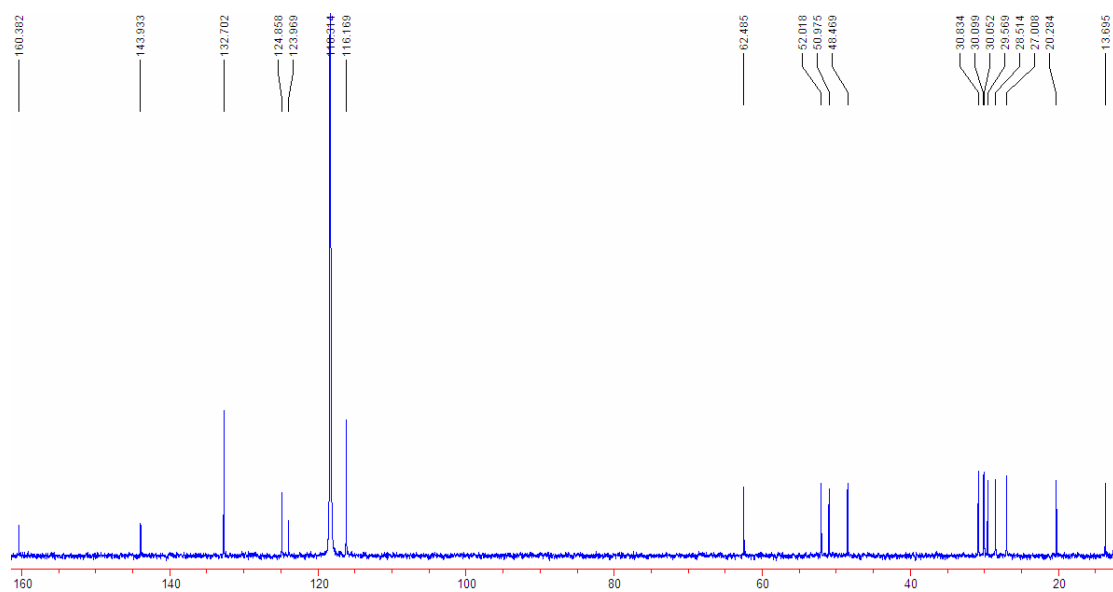


Figure S5. ^{13}C NMR spectrum (CD₃CN, 293 K, 125 MHz) of **2**.

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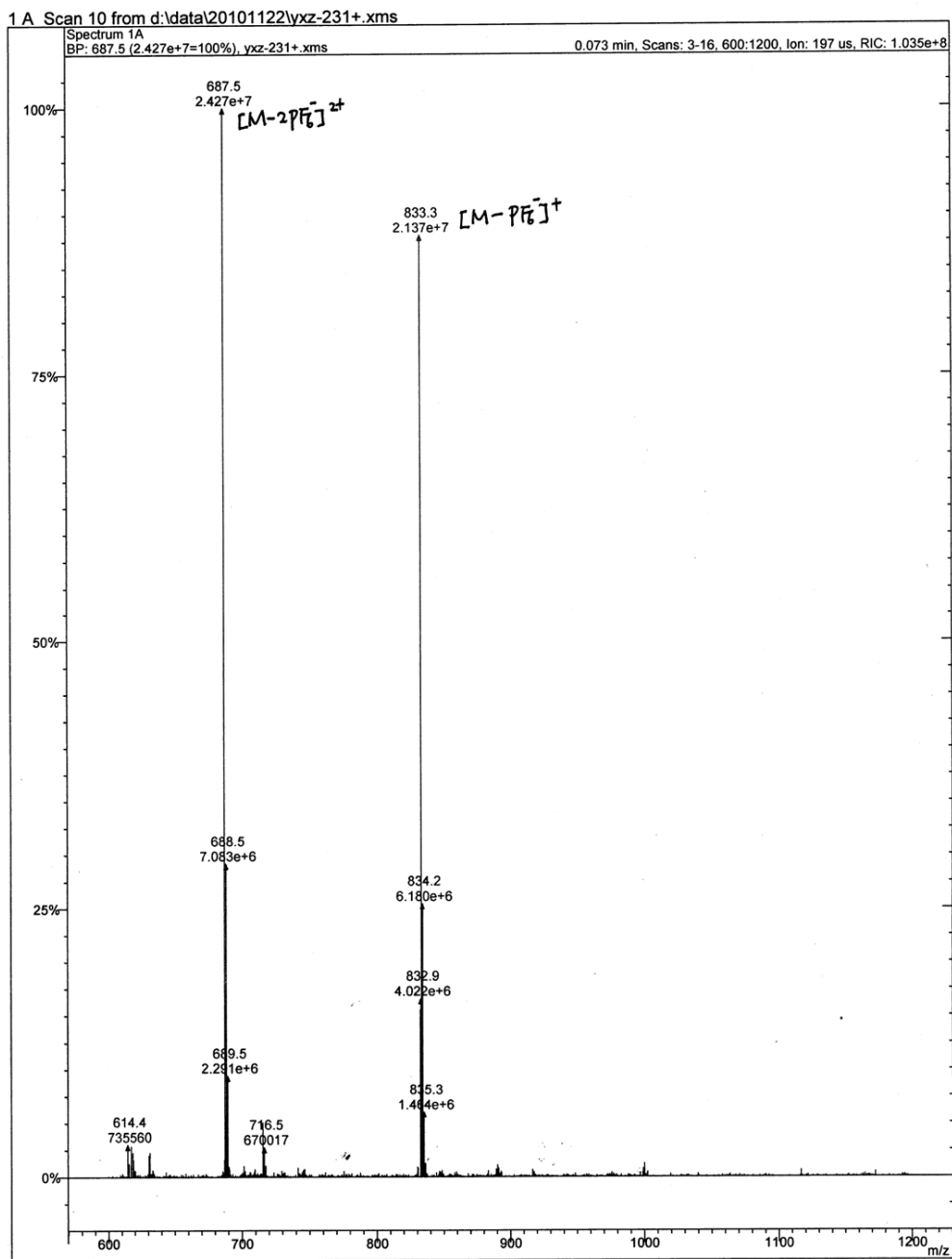


Figure S6. Electrospray ionization mass spectrum of **2**.

3. Partial COSY NMR spectrum of an equimolar solution of **1** and **2** in acetonitrile

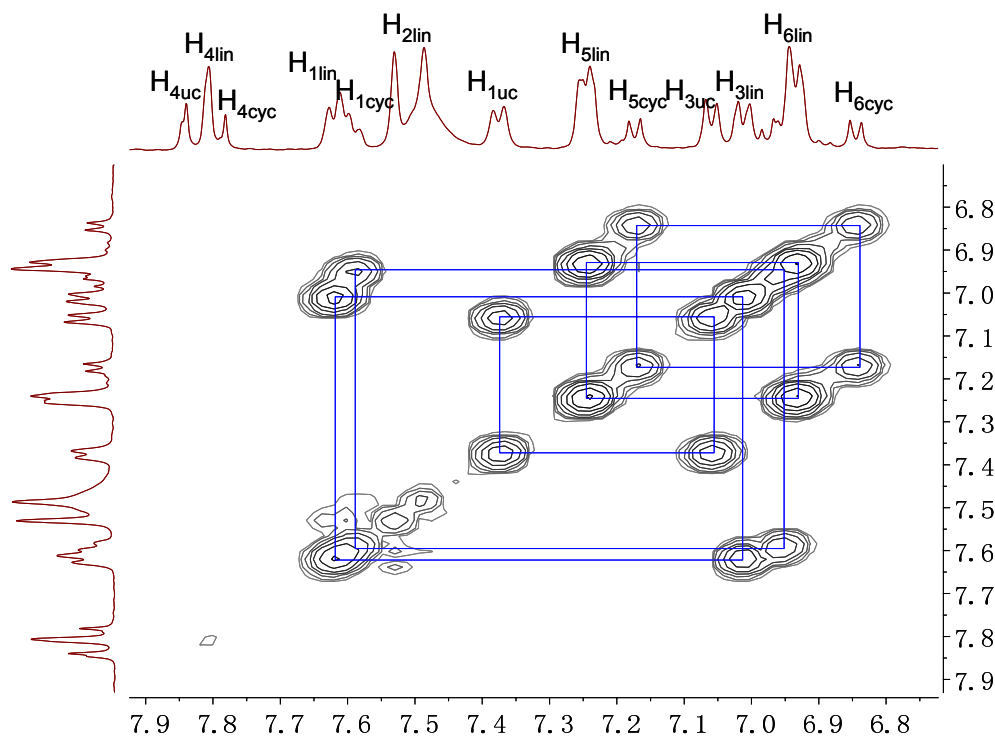


Figure S7. Partial COSY NMR (CD₃CN, 293 K, 500 MHz) spectrum of an equimolar solution of **1** and **2** at a concentration of 50.0 mM.

The COSY NMR experiment was carried out at a concentration of 50.0 mM because the linear, cyclic and uncomplexed peaks of the supramolecular polymer all appeared. From the 2D COSY NMR spectrum, strong correlations were observed between the aromatic protons H_{5cyc} and H_{6cyc}. Meanwhile, the uncomplexed correlative peaks between H_{1uc} and H_{3uc} and the linear correlative peaks between H_{1lin} and H_{3lin}, and H_{5lin} and H_{6lin} were also observed as shown in Figure S7. On the basis of the analysis mentioned above, clear assignments of the complicated concentration-dependent ¹H NMR spectra (Figure 1) and proof of the formation of the supramolecular polymer were achieved.

4. Linear oscillatory frequency sweep experiments of the gels with different cross-linking densities

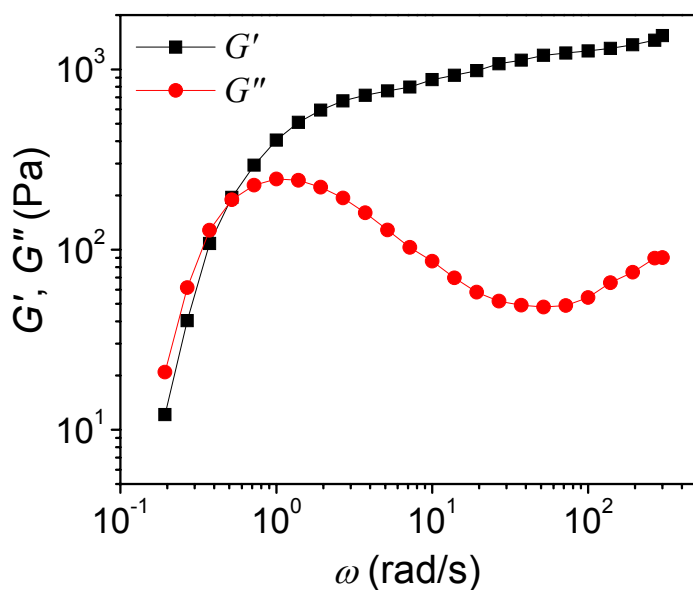


Figure S8a. Storage modulus (G') and loss modulus (G'') of the supramolecular polymer network versus scanning frequency (ω) for the samples made from equimolar monomers **1** and **2** (100 mM for the total concentration) with 20% cross-linking density in acetonitrile ($T = 20$ °C).

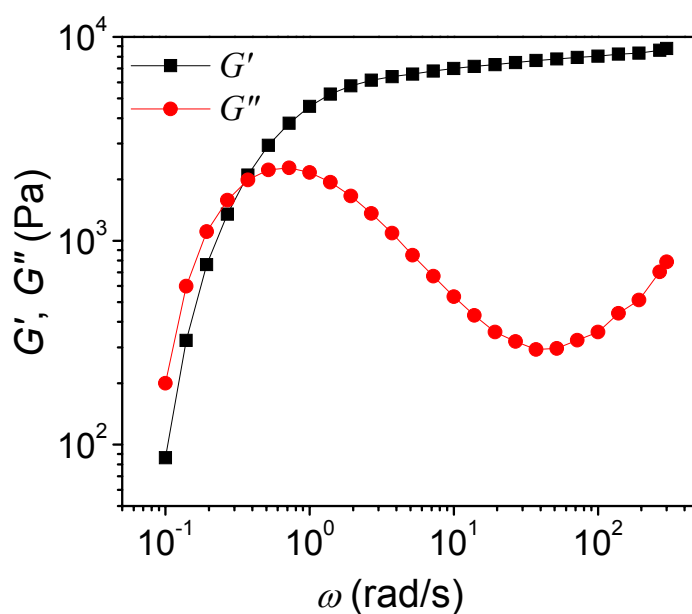


Figure S8b. Storage modulus (G') and loss modulus (G'') of the supramolecular polymer network versus scanning frequency (ω) for the samples made from equimolar monomers **1** and **2** (100 mM for the total concentration) with 40% cross-linking density in acetonitrile ($T = 20$ °C).

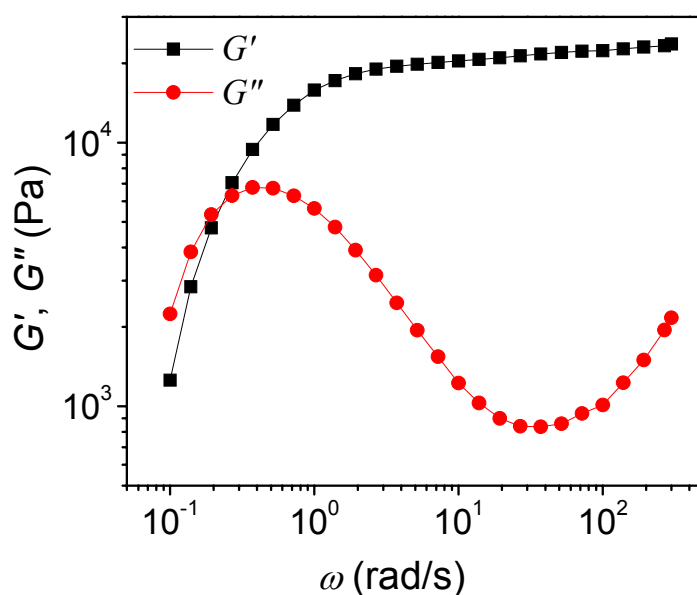


Figure S8c. Storage modulus (G') and loss modulus (G'') of the supramolecular polymer network versus scanning frequency (ω) for the samples made from equimolar monomers **1** and **2** (100 mM) with 60% cross-linking density in acetonitrile ($T = 20$ °C).

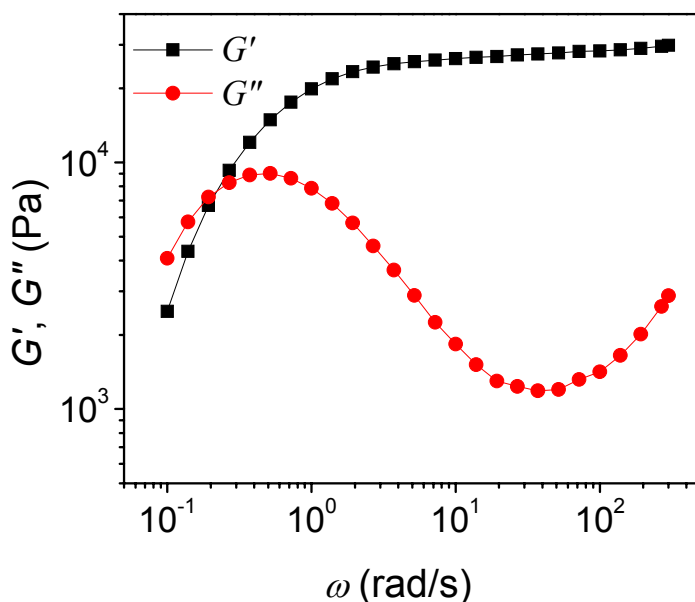


Figure S8d. Storage modulus (G') and loss modulus (G'') of the supramolecular polymer network versus scanning frequency (ω) for the samples made from equimolar monomers **1** and **2** (100 mM) with 80% cross-linking density in acetonitrile ($T = 20$ °C for the total concentration).

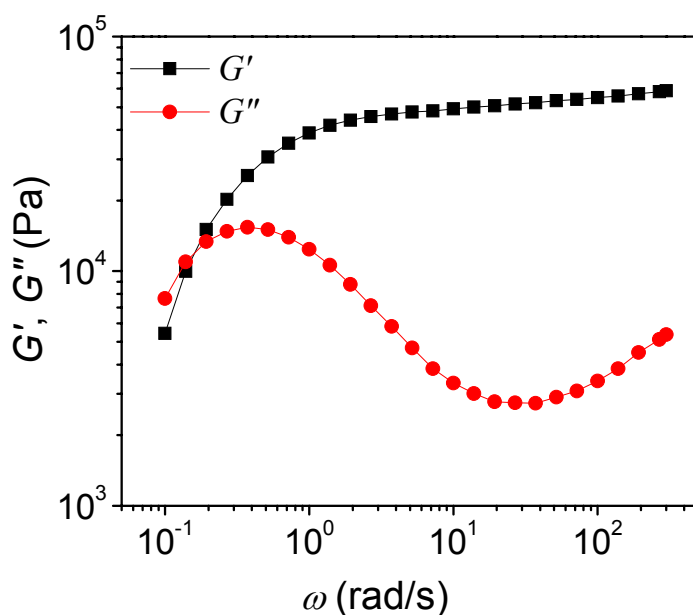


Figure S8e. Storage modulus (G') and loss modulus (G'') of the supramolecular polymer network versus scanning frequency (ω) for the samples made from equimolar monomers **1** and **2** (100 mM for the total concentration) with 100% cross-linking density in acetonitrile ($T = 20$ °C).

In Figures S8a–8e, the linear oscillatory frequency sweep experiments on samples made from equimolar monomers **1** and **2** with different cross-linking densities are shown. For the samples made from equimolar monomers **1** and **2** with cross-linking densities from 20 to 100%, there were crossover frequencies (ω_c) between G' and G'' . When the scanning frequency (ω) was lower than ω_c , G' was smaller than G'' , and the viscous property was predominant. When the scanning frequency (ω_c) was higher than ω_c , G' was larger than G'' , and the elastic property was dominant.

5. The elastic experiment of a healed supramolecular polymer gel

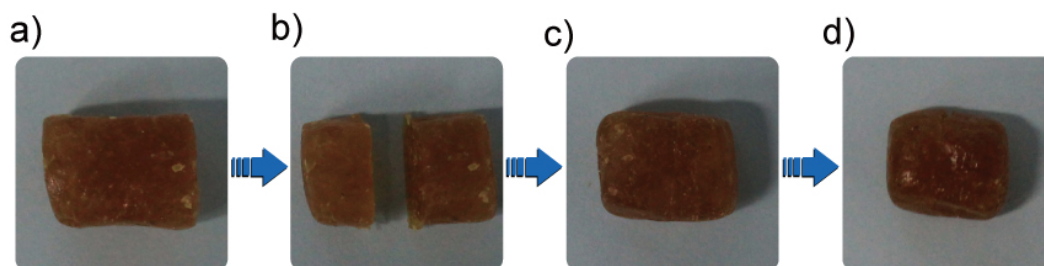


Figure S9. Photographs: a) the supramolecular polymer gel block; b) after being cut into two pieces; c) the healed gel block; d) the well-kept shape of the gel block after the elastic experiment.

Herein, we used a healed gel (Figure S9c) to do the elastic experiment. Excitingly, the healed gel did not break at the connection position and kept its shape well when it was subjected to elastic movements for many cycles (as shown in Movie 2). This phenomenon showed that the supramolecular polymer gel has good self-healing ability, although the gel was constructed by self-assembly of low molecular weight molecules. The gel block in Figure S9d was smaller than the one in Figure S9c possibly because of the solvent evaporation during the experiment.