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

Xuzhou Yan,[a] Donghua Xu,[b] Jianzhuang Chen,[a] Mingming Zhang,[a] Bingjie Hu,[c] Yihua Yu[c] and Feihe Huang*[a]

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A cross-linked supramolecular polymer network gel was prepared by orthogonal self-assembly of two homoditopic monomers and a metallic cross-linker. The gel is transparent and free-standing, which not only shows an interesting gel–sol transition in response to quadruple-stimuli, but also exhibits self-healing properties, as can be seen by the naked eye and as evidenced by rheological characterization. These unique features are all due to the dynamically reversible host–guest complexation and good mechanical properties of the cross-linked polymer network. Therefore, these fascinating properties make this supramolecular gel an unprecedentedly intelligent material.

Introduction

The ability of biological systems to spontaneously self-heal and regenerate their functions upon the infliction of environmentally-induced damage is amazing and enormously inspiring.[1] In nature, self-healing is ubiquitous and can occur either at the molecular level (*e.g.*, repair of DNA) or at the macroscopic level (*e.g.*, healing wounded skin). Inspired by this, scientists have been trying their utmost to design and impart intriguing self-healing properties to well-defined materials, thereby extending the lifetime of the materials, lowering production costs, and improving product safety.[2] In general, there are mainly two kinds of artificial polymeric self-healing materials: extrinsic self-healing materials and intrinsic self-healing materials. Extrinsic self-healing materials rely on the release of healing agents embedded in microcapsules or microvascular networks by crack propagation.[3] On the other hand, materials based on dynamic covalent bonds and/or noncovalent bonds, which can achieve a repeatable healing response as a result of the inherent reversibility of these chemical bonds, are known as intrinsic self-healing materials.[4] Nowadays, research on intrinsic self-healing materials has attracted much more attention from the scientific community compared to their counterpart, because they do not require the incorporation of healing agents and can achieve repeated repair.[4,5] However, such materials are generally less structurally stable and have poor mechanical properties. Therefore, the design and preparation of intrinsic self-healing materials, which possess good mechanical strength, structural stability, and stimuli-responsiveness, still remain a big challenge.

Supramolecular polymers,[6] an elegant combination of supramolecular chemistry and polymer science, which can be defined as polymeric arrays of low molecular weight monomeric units that are brought together by noncovalent interactions, have found a wide range of applications in materials science.[4b,d,6i,o,s] In consideration of the dynamic and reversible nature of noncovalent interactions, supramolecular polymers show promising characteristics for fabricating intrinsic self-healing materials. For example, Leibler and coworkers reported a supramolecular polymeric network consisting of fatty acid and diethylene diamine functionalized with urea, which not only has the properties of rubber, but also is self-healing at room temperature.[4b] Rowan *et al.* developed optically healable metallo-supramolecular polymers that display high efficiency and can be healed exclusively.[4d] Colquhoun and Hayes *et al.* explored interesting supramolecular polymeric networks based on electronically complementary π–π stacking interactions that exhibit thermo-triggered self-healing properties.[7] Recently, we reported a mechanically interlocked polymeric network gel with excellent self-healing properties.[8] Although much advancement has been achieved on self-healing supramolecular materials with polymeric backbones, self-healing supramolecular polymer materials assembled from low molecular weight monomers by crown ether-based molecular recognition have never been reported.

[a]*MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Chemistry, Zhejiang University, 310027 Hangzhou, P. R. China. E-mail: fhuang@zju.edu.cn; Fax: +86-571-8795-3189; Tel: +86-571-8795-3189*

[b]*State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 130022, Changchun, P. R. China*

[c]*Shanghai Key Laboratory of Magnetic Resonance, Department of Physics, East China Normal University, 200062 Shanghai, P. R. China*

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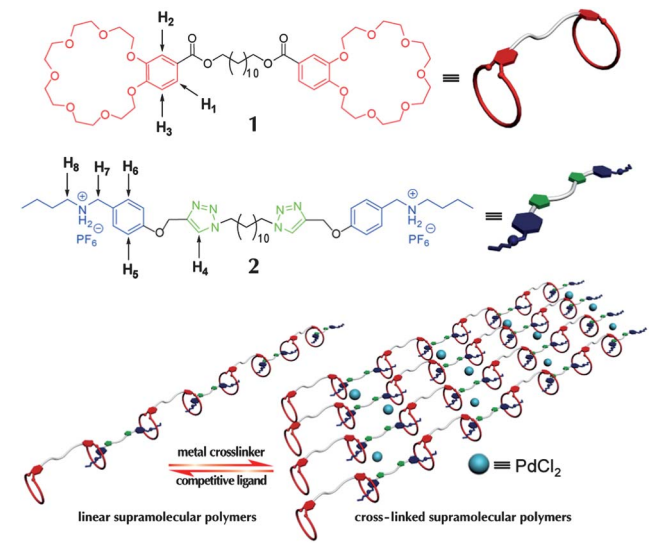
As an intriguing and unique subject of self-assembled supramolecular materials, supramolecular polymer gels (hydro- or organo-gels) have attracted intense attention on account of the stimuli-responsiveness and processability inherent to the noncovalent units and the mechanical properties gained from the formation of supramolecular polymer backbones.[9] However, the study of supramolecular polymer gels was mainly focused on their stimuli-responsiveness; self-healing properties have been rarely addressed, especially those based on host–guest interactions.[5c,8,9] Considering that a lot of interesting host–guest systems have been actively fabricated in the last decade,[10] it is surprising to see that only a few self-healing systems based on host–guest interactions have been reported.[5c,8] In order to prepare multiple stimuli-responsive self-healing supramolecular polymer gels with satisfactory mechanical properties from low molecular weight molecules, three stringent standards need to be fulfilled. First, the supramolecular polymer has to be an efficient gelator. Second, the host–guest molecular recognition must be highly efficient and environmentally sensitive. Third, the supramolecular polymer gels have to be free-standing and have good viscoelastic properties. It is therefore difficult to obtain supramolecular polymer gels with all these favorable features.

Herein, we report a stimuli-responsive self-healing supramolecular polymer gel, which is constructed by metal-coordination-cross-linking of a linear supramolecular polymer assembled from complementary homoditopic building blocks comprised of bis(benzo-21-crown-7 (**B21C7**))-based AA monomer **1** and bis(dialkylammonium salt)-based BB monomer **2**. The BB monomer **2** contains two 1,2,3-triazole groups which can act as ligands for coordination with the cross-linker, $[PdCl_2(PhCN)_2]$. A linear supramolecular polymer was first obtained in acetonitrile and then the cross-linker was added to construct a cross-linked supramolecular polymer network (Scheme 1), which is responsible for the gelation. The supramolecular polymer gel not only is transparent and free-standing and displays interesting gel–sol transitions in response to multiple stimuli (metallo-, thermo-, pH-, and cation-induced) and good mechanical properties (shape-persistent and elastic), but also exhibits self-healing properties.



Scheme 1 Cartoon representation of controlling the topology of supramolecular polymers from the self-assembly of AA monomer **1** and BB monomer **2**.

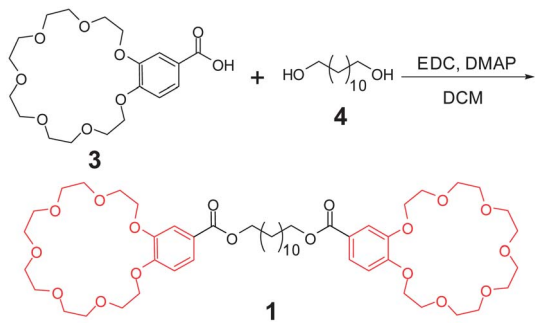
Experimental section

General methods

All reagents were commercially available and were used as supplied without further purification. Compounds **3**,[11] **5**,[12] and **6** (ref. 6*o*) were prepared according to the published procedures. 1,12-Dodecanediol **4** and $[PdCl_2(PhCN)_2]$ were purchased from Alfa Aesar. ^1H or ^{13}C NMR spectra were recorded with a Bruker Avance DMX 500 spectrophotometer or a Bruker Avance DMX 400 spectrophotometer with the use of deuterated solvent as the lock and residual solvent or TMS as the internal reference. The two-dimensional diffusion-ordered (2D DOSY) NMR spectra were recorded on a Bruker DRX500 spectrometer. Low-resolution electrospray ionization mass spectra were recorded with a Bruker Esquire 3000 Plus spectrometer. High-resolution mass spectrometry experiments were performed with a Bruker Daltonics Apex III spectrometer. The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus. Rheological data were obtained by using an ARES G2 rheometer (TA Instruments) with cone-plate geometry (diameter of 25 mm, 0.1 rad cone, truncation height 46 μm). Oscillatory frequency sweep experiments were performed from 0.1 rad s^{-1} to 300 rad s^{-1} with a strain in the linear region at 20 °C. Viscosity measurements were carried out with a Cannon-Ubbelohde semi-micro dilution viscometer at 25 °C in acetonitrile. Scanning electron microscopy investigations were carried out on a JEOL 6390LV instrument.

Synthesis of monomer 1

A solution of **3** (4.00 g, 10.0 mmol), 1,12-dodecanediol **4** (0.810 g, 4.00 mmol) and 4-dimethylaminopyridine (DMAP) (0.490 g, 4.00 mmol) in dichloromethane (150 mL) was stirred for 10 minutes at 0 °C (Scheme 2). To this solution was added EDC (3.07 g, 16.0 mmol). The reaction mixture was stirred for 24 h at room temperature, filtered, and concentrated to give a crude product, which was purified by flash column chromatography (methanol–dichloromethane, 1 : 100 v/v) to afford **1** as a pale



Scheme 2 Synthesis of monomer **1**.

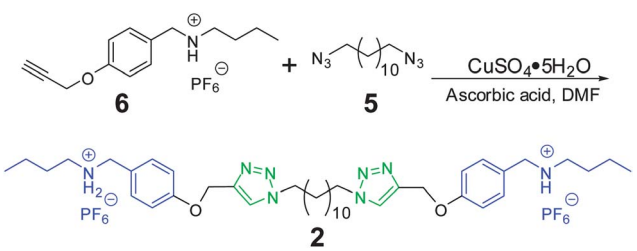
yellow solid (3.42 g, 88%). M.p. 57.4–58.2 °C. The ^{1}H NMR spectrum of **1** is shown in Fig. S1.† ^{1}H NMR ($CDCl_3$, 293 K, 400 MHz) δ (ppm): 7.63–7.65 (m, 2H), 7.53 (d, J = 2.0 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 4.26 (t, J = 6.6 Hz, 4H), 4.16–4.22 (m, 8H), 3.88–3.96 (m, 8H), 3.76–3.83 (m, 8H), 3.69–3.75 (m, 8H), 3.62–3.68 (m, 16H), 1.38–1.47 (m, 4H), 1.25–1.36 (m, 12H). The ^{13}C NMR spectrum of **1** is shown in Fig. S2.† ^{13}C NMR ($CDCl_3$, 293 K, 125 MHz) δ (ppm): 26.19, 28.91, 29.45, 29.66, 29.70, 65.12, 69.26, 69.46, 69.65, 69.79, 70.70, 71.15, 71.25, 71.28, 71.38, 71.48, 112.40, 114.78, 123.46, 123.98, 148.39, 152.97, and 166.55. LRESIMS is shown in Fig. S3:† m/z 984.7 $[M + H_3O]^+$ (100%). HRESIMS: m/z calcd for $[M]^+$ $C_{50}H_{78}O_{18}$, 966.5188; found 966.5186; error −0.2 ppm.

Synthesis of monomer 2

A mixture of **5** (1.26 g, 5.00 mmol) and **6** (3.63 g, 10.0 mmol) in a mixture of DMF and H_2O (8 : 1, 90.0 mL) in the presence of $CuSO_4 \cdot 5H_2O$ (0.250 g, 1.00 mmol) with sodium ascorbate (0.500 g, 2.50 mmol) was stirred at 50 °C for 24 h (Scheme 3). The reaction mixture was concentrated and purified by flash column chromatography (methanol–dichloromethane, 1 : 50 v/v) to afford compound **2** as a white solid (3.24 g, 66%). M.p. 156.9–157.9 °C. The ^{1}H NMR spectrum of **2** is shown in Fig. S4.† ^{1}H NMR (CD_3CN, 293 K, 400 MHz) δ (ppm): 7.86 (s, 2H), 7.38 (d, J = 6.6 Hz, 4H), 7.06 (d, J = 6.6 Hz, 4H), 5.15 (s, 4H), 4.34 (t, J = 5.9 Hz, 4H), 4.10 (s, 4H), 3.2 (t, J = 5.9 Hz, 4H), 1.88–1.90 (m, 4H), 1.58–1.67 (m, 4H), 1.33–1.41 (m, 4H), 1.19–1.32 (m, 16H), 0.92 (t, J = 5.8 Hz, 6H). The ^{13}C NMR spectrum of **2** is shown in Fig. S5.† ^{13}C NMR (CD_3CN, 293 K, 125 MHz) δ (ppm): 13.70, 20.28, 27.01, 28.51, 29.57, 30.05, 30.10, 30.83, 48.47, 50.98, 52.02, 62.49, 116.17, 123.97, 124.86, 132.70, 143.93, and 160.38. LRESIMS is shown in Fig. S6:† m/z 833.3 $[M - PF_6]^+$ (100%), m/z 687.5 $[M - 2PF_6]^{2+}$ (100%). HRESIMS: m/z calcd for $[M - H - 2HPF_6]^+$ $C_{40}H_{61}N_8O_2^+$, 685.4917; found 685.4926; error 1.3 ppm.

Sample preparation

In a typical procedure of gelation, equimolar monomers **1** and **2** were dissolved in acetonitrile (100 mM for the total concentration) in a vial, followed by the addition of 100% cross-linker, $[PdCl_2(PhCN)_2]$, and subsequent heating to 50 °C led to a transparent solution. Upon cooling in a refrigerator at 4 °C, gelation took place. The critical gel concentration, which showed the gelation ability of the gelators, was determined to be 50.0 mM for the total concentration at −4 °C by continuously diluting a gel with heating and cooling cycles until the gel did not regenerate. On the other hand, the gel can be obtained by dissolving equimolar monomers **1** and **2** in acetonitrile (100 mM for the total concentration) in a vial, followed by the addition of 60% cross-linker, $[PdCl_2(PhCN)_2]$ and then standing for one hour at room temperature. In Fig. 8a, the gel was prepared by mixing 100 mM monomers and 80% cross-linker in 0.500 mL of acetonitrile. In Fig. 11a, the transparent gel was prepared by evaporating the solvent slowly until the gel became transparent (150 mM monomers for the total concentration, 60% cross-linker). The thickness of the transparent gel was 0.400 cm. The gel block used in Fig. 11b and the gel for elasticity test (Movie 2†) was prepared by mixing 300 mM monomers and 60% cross-linker in acetonitrile. Meanwhile, the free-standing and shape-persistent gel block was molded by hand (Fig. 11b and Movie 1†). In Fig. 11c–f and Movie 1,† the gel was prepared by mixing 150 mM monomers and 80% cross-linker in 2.00 mL of acetonitrile. The reversible gel–sol transitions of the supramolecular polymer network gel triggered by four different stimuli, namely, pH (adding 1.50 equiv. of Et_3N and 1.80 equiv. of TFA), thermal (heating to 50 °C and then cooling at 4 °C for 2 min), cation (1.50 equiv. of KPF_6 and then 1.50 equiv. of DB18C6), and metallo (adding 2.00 equiv. of PPh_3 (after filtration) and then 1.00 equiv. of $[PdCl_2(PhCN)_2]$). In rheological experiments, the samples were prepared as follows: a linear supramolecular polymer was first constructed by dissolving equimolar monomers **1** and **2** in 0.600 mL of acetonitrile (100 mM for the total concentration), and then different amounts of $[PdCl_2(PhCN)_2]$ were added to make cross-linked supramolecular polymer network gels with different cross-linking densities, 0%, 20%, 40%, 60%, 80%, and 100%. SEM samples were prepared by dissolving equimolar monomers **1** and **2** in 0.500 mL of acetonitrile (50.0 mM for the total concentration), and then 100% $[PdCl_2(PhCN)_2]$ was added.



Scheme 3 Synthesis of monomer **2**.

Results and discussion

Self-assembly of AA/BB monomers and metallic cross-linker

First, host–guest complexation studies of the self-assembly of monomers **1** and **2** were carried out. It is well known that the **B21C7** unit forms a 1 : 1 threaded structure with the dialkylammonium salt moiety.[6o,s,13] Furthermore, the COSY NMR spectrum (Fig. S7, ESI†) of **1** and **2** in acetonitrile allowed the assignments of complicated concentration-dependent ^{1}H NMR spectra (Fig. 1), which are due to the slow-exchange nature of the complexation relative to the proton NMR timescale. At low concentration (0.500 mM), peaks for cyclic oligomers and uncomplexed monomers were obvious and only very weak signals for linear species were observed (Fig. 1, spectra g and h), representing a tendency towards the formation of cyclic oligomers. When the monomer concentration was up to 10.0 mM (Fig. 1, spectrum f), the signals of H_{3lin}, H_{4lin}, and H_{5lin} for the linear species became clear. With the increase of the initial monomer concentration, the cyclic species dominates at the beginning, and then its concentration decreases, whereas the concentration of the linear species increases constantly. At a high concentration of 300 mM (Fig. 1, spectrum a), the peak splitting of protons H_1, H_5, and H_6 disappeared, along with a

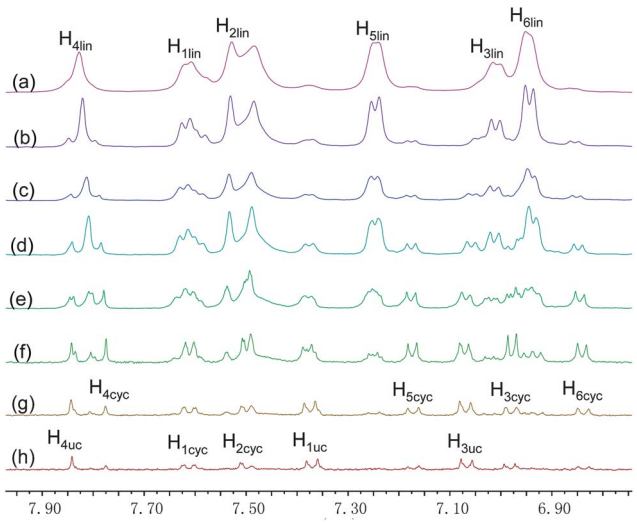


Fig. 1 Partial ^{1}H NMR spectra of equimolar mixtures of **1** and **2** (CD_3CN, 293 K, 500 MHz) at different concentrations: (a) 300 mM; (b) 200 mM; (c) 100 mM; (d) 60.0 mM; (e) 40.0 mM; (f) 10.0 mM; (g) 1.50 mM; (h) 0.500 mM. Peaks of linear polymers, cyclic oligomers, and uncomplexed monomer are designated by lin, cyc, and uc, respectively.

broadening of all signals, which demonstrated the formation of high molecular weight aggregates driven by host–guest interactions between the **B21C7** host units and the dialkylammonium salt guest moieties.

We then investigated the conversion from the linear to cross-linked supramolecular polymer; this was accomplished by forming a disubstituted palladium(II) complex between $[PdCl_2(PhCN)_2]$ and 1,2,3-triazole moieties, bringing about the sol to gel transition. Upon progressive addition of $[PdCl_2(PhCN)_2]$, the resonance for the triazole H_{4lin} proton was found to shift downfield (Fig. 2, spectra a–e), demonstrating preferential complexation between the triazole ligands and the palladium(II) atom. The gradual strengthening of newly formed H_{4lin} signals, as well as the gradual disappearance of uncomplexed species peaks (for example H_{1uc}), along with a broadening of all signals (for example $H_{3,5,6lin}$) with increasing amount of $[PdCl_2(PhCN)_2]$, indicated the formation of a cross-linked supramolecular polymer network (Fig. 2). Furthermore, deconstruction of the supramolecular polymer network can trigger the gel to sol transition (Fig. 8a), which was achieved by the addition of a competitive ligand, PPh_3, for palladium(II). The ^{1}H NMR experiment demonstrated the restoration of the linear structure when two equivalents of PPh_3 were added to the solution (Fig. 2, spectrum f). Therefore, the reversible transition between the linear and cross-linked supramolecular polymer provides a convenient way for the gel–sol transition induced by the successive addition of the metal cross-linker and the use of the competitive ligand.

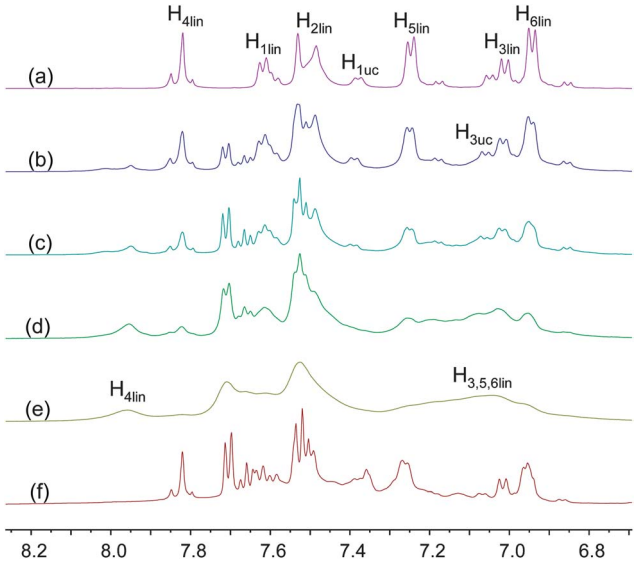


Fig. 2 Partial ^{1}H NMR spectra (CD_3CN, 293 K, 500 MHz) of equimolar mixtures of **1** and **2** at a concentration of 100 mM with successive addition of $[PdCl_2(PhCN)_2]$ and PPh_3: (a) 0 equiv.; (b) 0.20 equiv.; (c) 0.40 equiv.; (d) 0.70 equiv.; (e) 1.0 equiv. of $[PdCl_2(PhCN)_2]$; (f) 2.0 equiv. of PPh_3 was added to (e), after filtration.

To further study the self-assembled behaviors of the linear and cross-linked supramolecular polymers, viscosity measurements were carried out in acetonitrile using a Cannon-Ubbelohde semi-micro dilution viscometer. The linear supramolecular polymer assembled from the monomers **1** and **2** presented a viscosity transition, and was characterized by a change in slope in the double logarithmic plot of specific viscosity *versus* concentration (Fig. 3a). At low concentration, the slope of the curve is 1.05, demonstrating a linear relationship between specific viscosity and concentration, which is characteristic for non-interacting assemblies of constant size; these results indicate the presence of cyclic oligomers (mostly dimers) in dilute solution. With increasing concentration, a sharp increase in the viscosity was observed (slope = 2.77). This stronger concentration dependence indicates the formation of a linear supramolecular polymer of increasing size. The formation of cross-linked supramolecular polymer networks was also confirmed using viscosity studies (Fig. 3b). In the concentration range 1–120 mM, the reduced viscosity of the linear supramolecular polymer varied linearly. Conversely, the reduced viscosity of the cross-linked supramolecular polymer network varied exponentially, indicating growth of the cross-linked supramolecular polymer chain length with increasing concentration. A comparison of reduced viscosity obtained for the two types of supramolecular polymers tells us that the addition of the cross-linker dramatically changes the rheology of the supramolecular polymer.

In addition, two-dimensional diffusion-ordered ^{1}H NMR spectroscopy (DOSY), a convenient and reliable method to test the dimensions of polydisperse supramolecular aggregates, was also performed to investigate the self-aggregation of monomers **1** and **2** to form the linear or cross-linked supramolecular polymers. As the monomer concentration increased from 40.0 mM to 300 mM, the measured weight average diffusion coefficient decreased from 7.16×10^{-10} to 1.89×10^{-10} m^2 s^{-1} (Fig. 4), indicating the concentration dependence of the linear supramolecular polymerization between monomers **1** and **2**. When 0.5 equivalent of $[PdCl_2(PhCN)_2]$ was added to a 150 mM solution of monomers **1** and **2**, a decrease in the diffusion

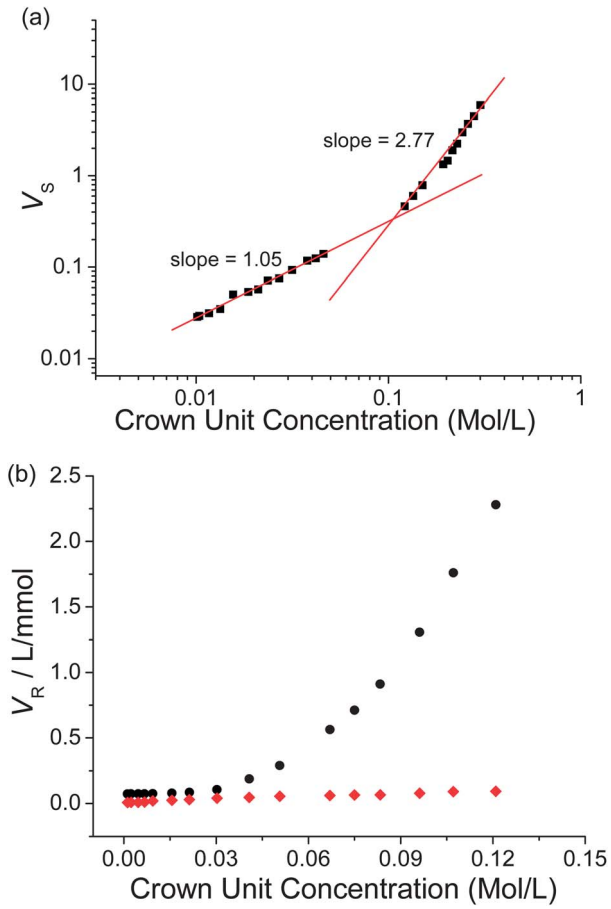


Fig. 3 (a) Specific viscosity V_S of equimolar monomers **1** and **2** in acetonitrile at 298 K *versus* the crown unit concentration, and (b) reduced viscosity V_R (acetonitrile, 298 K) of equimolar monomers **1** and **2** (■) or 1 equiv. of **1** and **2** plus 1 equiv. of $[PdCl_2(PhCN)_2]$ (●) *versus* the crown unit concentration.

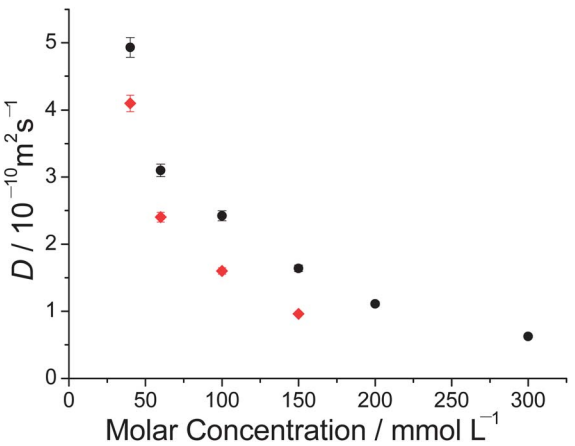


Fig. 4 Concentration dependence of diffusion coefficient D (CD_3CN, 293 K, 500 MHz): equimolar monomers **1** and **2** (●); 1 equiv. of **1** and **2** plus 1 equiv. of $[PdCl_2(PhCN)_2]$ (◆).

coefficient from 1.64×10^{-10} to 9.6×10^{-11} m^2 s^{-1} was observed. Furthermore, under the same conditions, the cross-linked supramolecular polymer exhibited a lower measured weight average diffusion coefficient than its linear counterpart, as shown in Fig. 4. These two observations simultaneously proved an increase in the average aggregation size owing to cross-linking of the linear supramolecular polymer. The stable supramolecular polymer gel was formed at room temperature at high concentration (>150 mM), so the DOSY NMR cannot be tested at a higher concentration.

Bulk rheological analyses of the cross-linked supramolecular polymer network gel

Rheological characterization can provide insight into the bulk material properties of dynamically cross-linked supramolecular materials.[9c,14] Therefore, we carried out linear oscillatory frequency sweep experiments to obtain the rheological properties of the supramolecular polymer network. The storage (G') and loss (G'') moduli for the gel made from equimolar monomers **1** and **2** (100 mM) with increasing cross-linking density in acetonitrile are shown as functions of frequency in Fig. 5 and S8a–e.† The moduli of the sample without cross-linker are small and close to the measurement error range of the rheometer. As the cross-linking density increases from 0 to 100%, both G' and G'' increase by more than four orders of magnitude. For

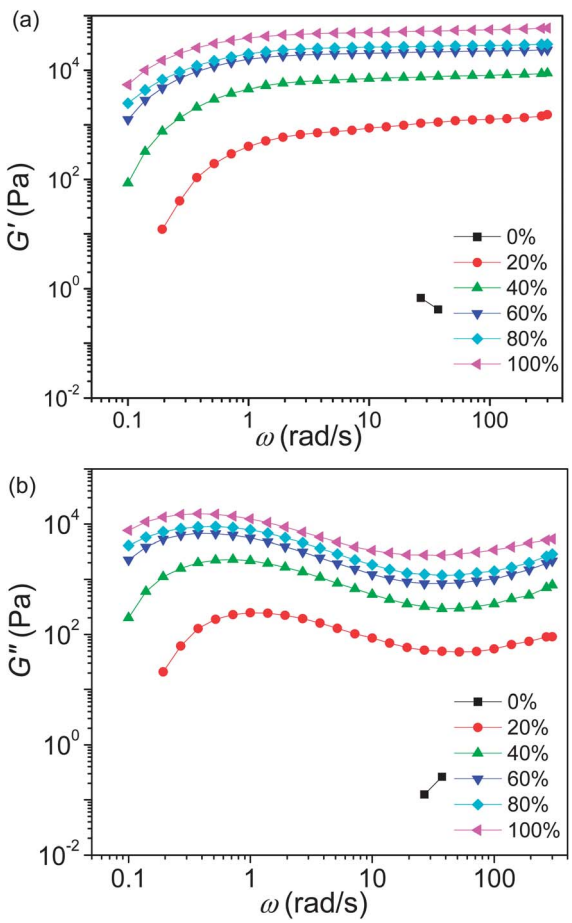


Fig. 5 (a) Storage modulus (G') and (b) loss modulus (G'') of the supramolecular polymer network *versus* scanning frequency (ω) for the samples made from equimolar monomers **1** and **2** (100 mM) with different cross-linking densities from 0 to 100% in acetonitrile.

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'' (Fig. S8a–e ESI†). When the scanning frequency (ω) was lower than ω_c, G' was smaller than G'', and the viscous properties were predominant. When the scanning frequency (ω) was higher than ω_c, G' was larger than G'', and the elastic properties were dominant. At high frequency, G' reaches a plateau value, defined as the plateau modulus (G_0). The G_0 value increases proportionally with the cross-linking density from $\sim 10^3$ to $\sim 10^5$ Pa. This material therefore showed intermediate mechanical properties (*i.e.*, plateau modulus $\approx 10^3$ to 10^5 Pa) and provides an excellent complement to Aida's dendritic polymer–clay hybrid hydrogel system (plateau modulus > 10^4 to 10^6 Pa).[4c]

To further obtain the value of the fraction of elastically active cross-links, the fraction of cross-linked triazole groups and the average number of elastic cross-linkers along the linear supramolecular polymer chain in the samples on the basis of the values of G_0 of the samples made from equimolar monomers **1** and **2** with cross-linking densities from 20 to 100%, we considered the extent of cross-linking. According to the phantom network model,[14,15] the number density of elastically active chains (ν) is given by[15]

$$\nu = \frac{G_0}{k_B T(1 - 2/f)} \quad (1)$$

In eqn (1), G_0 is the plateau modulus obtained from the constant value of G' at high frequency, k_B is Boltzmann's constant, and T is the temperature, f is the functionality of the cross-linker. As four supramolecular polymer strands join at one cross-linker, a functionality of four ($f = 4$) is used here. As one cross-linker can bind two triazole groups and form a cross-linking point, ν is treated as the number density of cross-linkers which have been bound with two triazole groups. The maximum theoretical number of elastically active cross-linkers per unit volume (ν_0) in the samples is simply calculated from the concentration of cross-linkers. We refer to the ratio of apparent to theoretical elastically active cross-linkers, ν/ν_0, as the fraction of bound cross-linker.[14] The fraction of bound triazole groups ($p_{triazole}$) in monomer **2** was also calculated according to the value of ν and the number density of monomer **2**. From the values of G_0 of the samples in Fig. 6, the fraction of elastically active cross-linker (ν/ν_0) and the fraction of cross-linked triazole groups ($p_{triazole}$) in the samples formed by equimolar monomers **1** and **2** (100 mM) with different cross-linking densities from 20 to 100% were calculated (eqn (1) and Fig. 7). As the cross-linking density increased from 20 to 60%, ν/ν_0 and $p_{triazole}$ increased. When the cross-linking density increased further from 60 to 100%, the values of ν/ν_0 and $p_{triazole}$ did not change much (Fig. 7). In the case of the sample formed by equimolar monomers **1** and **2** (100 mM) with 100% cross-linking, the cross-linker or triazole group in monomer **2** can be 100% bound theoretically. From Fig. 7, the fraction of elastically active cross-linkers or cross-linked triazole groups in monomer **2** in the sample formed by equimolar monomers **1** and **2** (100 mM) with 100% cross-linking was 0.96, which is close to the theoretical maximum value.

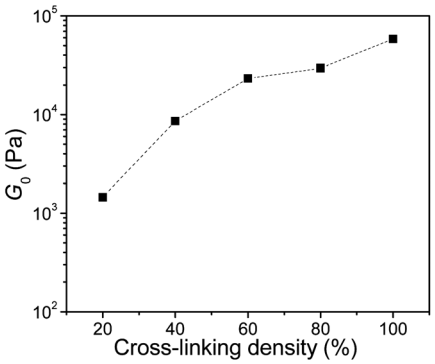


Fig. 6 Plateau modulus (G_0) *versus* cross-linking density for the samples made from 100 mM monomers **1** and **2** with different cross-linking densities in acetonitrile at 20 °C.

The criteria for the formation of the supramolecular polymer network are discussed below. For the supramolecular polymer formed by equimolar monomers **1** and **2**, there are cyclic supramolecular polymers and linear supramolecular polymers, as illustrated by the NMR results in Fig. 1. From the results in Fig. 1, we also know that the concentration of linear supramolecular polymer (C_c) is much higher than the concentration of ring supramolecular polymer (C_R) at high concentration.[6f] In this case ($C_c \gg C_R$), the number-average degree of polymerization of the linear supramolecular polymer (N_C) formed by equimolar monomers **1** and **2** has the following relationship with association constant, K_a and concentration of monomers **1** or **2** (C)[6a,b,m]

$$\langle N_C \rangle = \sqrt{K_a C} \quad (2)$$

For equimolar monomers **1** and **2** with a total concentration of 100 mM (the concentration of monomers **1** or **2** is 50.0 mM), as the association constant K_a between the **B21C7** host and secondary ammonium salt guest moieties is 250 M^{-1},[6s] N_C is estimated to be 3.5. For samples with cross-linkers, the average number of elastic cross-linkers along the linear supramolecular polymer chain (f^*) formed by monomers **1** and **2** is $f^* =$

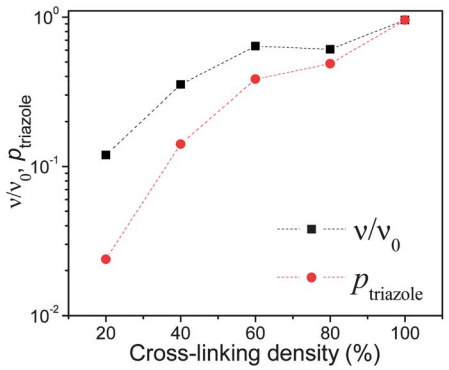


Fig. 7 Fraction of elastically active cross-linker (ν/ν_0) and fraction of cross-linked triazole groups ($p_{triazole}$) in the samples made from 100 mM monomers **1** and **2** with increasing cross-linking density from 20 to 100% in acetonitrile, respectively, at 20 °C.

$N_C p_{triazole}$. From the results in Fig. 6, for the samples formed by equimolar monomers **1** and **2** with 20%, 40%, 60%, 80%, and 100% of cross-linking, f^* are 0.08, 0.49, 1.3, 1.7, and 3.4, respectively. As described by Flory,[16] the criterion for the network formation is the mean number of elastically active cross-linkers per chain $f^* > 2$. From this criterion, it is apparent that the samples formed by equimolar monomers **1** and **2** with 100% of cross-linking formed a network structure. We note that the networks are necessarily heterogeneous, and, in all cases, there must be some fraction of cyclic, branched or linear supramolecular polymers in the network. Additionally, we point out that the heterogeneity means that the value of f^* as calculated above underestimates the true average number of active cross-linkers per polymer chain within the network. For the samples formed by equimolar monomers **1** and **2** with 20% and 80% of cross-linking, the samples were not well developed networks according to the above criteria. However, the samples formed by equimolar monomers **1** and **2** with 20% and 80% of cross-linking must have big clusters of network, which dominate the viscoelastic properties of the samples, as illustrated by the high G_0 and long relaxation time ($\tau > 2$ s, $\tau = 1/\omega_c$) of the samples formed by equimolar monomers **1** and **2** with 20% and 80% of cross-linking in Fig. S8a–d.† At the same time, the samples formed by equimolar monomers **1** and **2** with 20% and 80% of cross-linking are "gels" according to tube reverse experiments.[17] Therefore, the samples formed by equimolar monomers **1** and **2** with 20% to 100% are all called supramolecular polymer gels in this paper. Therefore, these results further confirmed the formation of the supramolecular polymer gels and the good mechanical properties of the metal-coordinated supramolecular polymer networks.

Stimuli-responsiveness and morphologies of the cross-linked supramolecular polymer network gel

Interestingly, except for the above-mentioned metallo-induced gel–sol transition, the cross-linked supramolecular polymer gel can also respond to thermo-, pH-, and cation-stimuli. It is well known that the host–guest interaction between the **B21C7** and dialkylammonium salt units could be reduced by heating. Therefore, heating and cooling can result in a reversible gel–sol transition (Fig. 8a), as shown by the variable temperature ^{1}H NMR spectra (Fig. 9). At a relatively low temperature, the ^{1}H NMR resonance signals for equimolar monomers **1** and **2** became broad and almost disappeared because of the formation of the stable gel, suggesting strong intermolecular aggregation. When the temperature rose gradually, the original weak signals became well-dispersed and could be easily identified. These results showed that the gel–sol transition is temperature-dependent.

Also, the complexation between the **B21C7** unit and the dialkylammonium salt moiety can be controlled by adjusting the solution pH because of the reversible deprotonation of the dialkylammonium salt. Hence, triethylamine (TEA) and trifluoroacetic acid (TFA) were used as the operating acid–base pair, which resulted in a reversible gel–sol transition (Fig. 8a and 10a–c). When TEA was added, H_{4lin} shifted upfield,

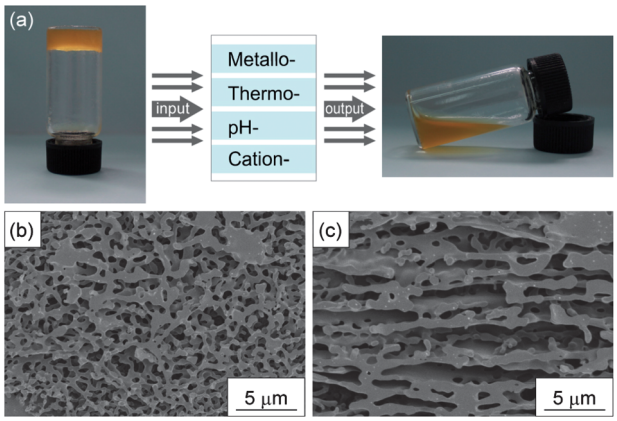


Fig. 8 (a) The reversible gel–sol transitions of the metallo-supramolecular polymer network triggered by different stimuli; (b and c) SEM images of the metallo-supramolecular polymer xerogels.

indicating that TEA coordinated with Pd. Therefore, the gel to sol transition was induced by deprotonation of the dialkylammonium salt and decoordination of the triazole to Pd in a cooperative manner. After TFA was added to this solution, the complexation between the **B21C7** and dialkylammonium salt moieties was nearly recovered and the complicated signals and coordination signals were observed again. However, the chemical shift changes of the protons on the host, guest, and ligand after complexation and coordination could not be fully recovered. Three possible reasons are: (i) the solution was diluted, (ii) the ionic strength of the solution increased, and (iii) different counterions are introduced, influencing ion pairing.[18] These factors change the chemical shifts and/or decrease the complexation percentage. Furthermore, it was found that triethylamine is a competitive ligand for palladium(II).[6s] Therefore, this gel–sol transition was achieved by decoordination of the triazole to palladium(II) and deprotonation of the dialkylammonium salt in a cooperative manner.

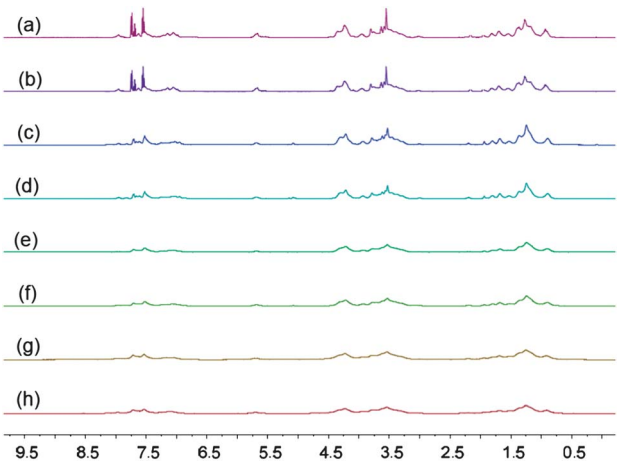


Fig. 9 Variable temperature ^{1}H NMR spectra of equimolar monomers **1** and **2** plus 1.0 equiv. of $[PdCl_2(PhCN)_2]$ (100 mM, CD_3CN, 500 MHz): (a) 313 K; (b) 308 K; (c) 298 K; (d) 293 K; (e) 288 K; (f) 283 K; (g) 278 K; (h) 273 K.

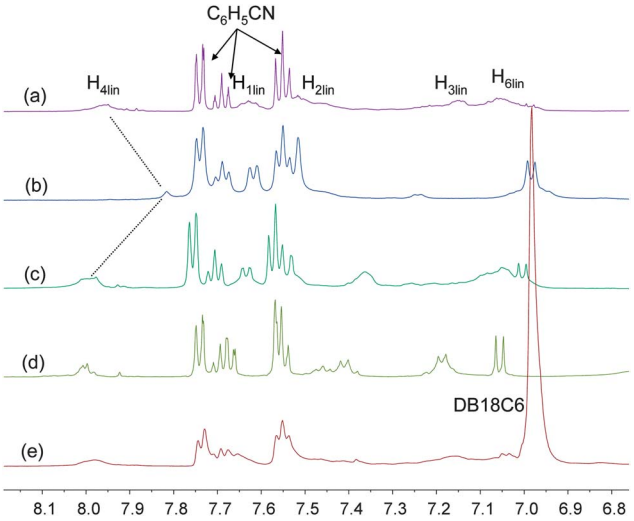


Fig. 10 Partial ^{1}H NMR spectra (CD_3CN, 293 K, 500 MHz): (a) monomers **1** and **2** and 1 equiv. of $[PdCl_2(PhCN)_2]$ (50.0 mM); (b) after addition of 1.5 equiv. of Et_3N to (a); (c) after addition of 1.8 equiv. of TFA to (b); (d) after addition 1.5 equiv. of KPF_6 to (a); (e) after addition of 1.5 equiv. of DB18C6 to (d).

Moreover, the **B21C7** host can form a more stable 1 : 1 complex with K^+,[6s] which results in the decomplexation between the **B21C7** unit and the dialkylammonium moiety. Therefore, the reversible gel–sol transition can also be triggered by adding and removing the K^+ (Fig. 8a), and the reversible process can be monitored by ^{1}H NMR experiments (Fig. 10d and e). The addition of KPF_6 to a solution of equimolar monomers **1** and **2** in acetonitrile caused remarkable changes of the proton chemical shifts, indicating that the complexation between **B21C7** and dialkylammonium salt was essentially quenched. After DB18C6 was added to this solution, the complexation between **B21C7** and dialkylammonium salt was recovered and the complicated signals were observed again. Thus, the above-mentioned quadruple-stimuli can be employed as effective inputs to control the self-healing properties of the gel (Fig. 8a), such as re-adhesion between two cut surfaces.

The morphologies of the supramolecular polymer xerogels prepared by freeze-drying methodology were examined by scanning electron microscopy (SEM), revealing extended and interconnected porous structures (Fig. 8b) responsible for the observed gelation.[9c,19] Also, a layered network with holes was also observed (Fig. 8c), showing the diversity of microstructures of the supramolecular polymer gel. The SEM images showed that the average pore diameter was about 3 μm (Fig. 8b). It should be noted that porous microstructures are currently of great scientific and technological interest due to their potential application in materials science, such as tissue engineering, water purification, *etc.*[20] Therefore, it is possible to make this gel potentially applicable in such fields.

Self-healing properties of the supramolecular polymer network gel

Our gel is transparent (Fig. 11a) and free-standing (Fig. 11b). Considering that the supramolecular polymer network gel was prepared by using orthogonal noncovalent recognition motifs, host–guest and metal–ligand interactions, we speculated that the gel would exhibit self-healing. Therefore, we performed a break test. When the gel was broken, it healed itself in a short time (Fig. 11c–f and Movie 1†). Meanwhile, the healing time was found to be related to the size of the damage, the concentration, and the cross-linking density of the samples. Generally, the gel self-healed *in situ* (Fig. 11f). Excitingly, it was found that 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 (Fig. S9 and Movie 2†).

Rheological experiments were also conducted to confirm the self-healing properties of the supramolecular polymer gel. According to the strain sweep results of the samples formed by equimolar monomers **1** and **2** with 60% cross-linkers (Fig. 12a), as the strain was less than 125%, G' was larger than G'' of the sample and the sample was predominantly elastic, while the sample was predominantly viscous when the network of the sample was partly broken under higher strain (>125%), as G'' is larger than G' of the sample under larger strain.[21] In Fig. 12b, during the strain sweep of the samples from 0.1% to 200% strain at 10 rad s^{-1}, the breakage of the network at higher strain was apparent since G'' was larger than G'. During the following time sweep experiments at 1% strain for 350 s at 10 rad s^{-1}, the rapid recovery of the network structure was also apparent as G' became larger than G'' in a short time. Two other cycles of strain sweep and subsequent time sweep experiments were performed for the same sample; a similar trend was observed. The results in Fig. 12b illustrated that the supramolecular polymer gel has self-healing properties. Therefore, for the supramolecular polymer network gel, the self-healing mechanism is inferred to be due to reversible host–guest interactions (Fig. 11g). When the gel is broken, the host–guest complexes disassemble. At rest, the complexes reform again, leading to self-healing behavior. It is worth noting that the self-healing process in the

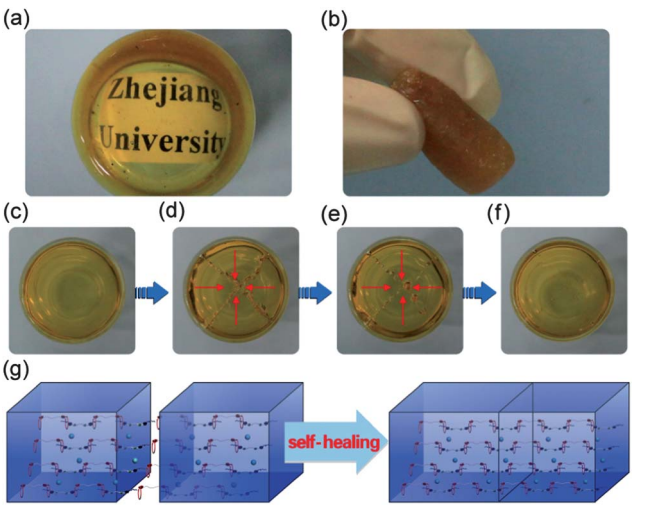


Fig. 11 (a) Transparent and (b) free-standing cross-linked supramolecular polymer gels. Photographs: (c) the supramolecular polymer gel; (d) after damage; (e) after free-standing for 1.5 min; (f) after free-standing for 3 min. (g) Cartoon illustration of the proposed mechanism of self-healing.

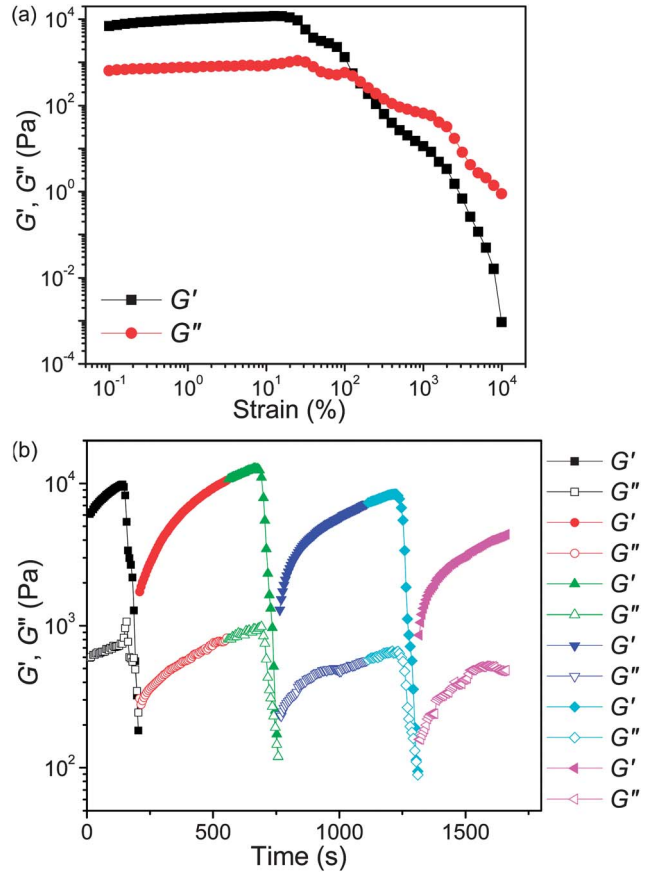


Fig. 12 (a) G' and G'' values of a sample made from equimolar monomers **1** and **2** (100 mM) with 60% cross-linkers during strain sweep, and (b) G' and G'' values of the above sample during the time sweep. Time-dependent strain sweep from 0.1% to 200% and then back to 1% strain for 350 s at a scan frequency of 10 rad s^{-1}. Furthermore, two other cycles were done (T = 20 °C).

supramolecular polymer gel occurs autonomously without any external intervention, which is superior to those that need external treatment.

Conclusions

In summary, we have prepared a supramolecular polymer network gel by orthogonal self-assembly of two homoditopic monomers and a metallic cross-linker. The gel is transparent and exhibits quadruple-stimuli induced reversible gel–sol transitions. Moreover, the supramolecular polymer gel has good viscoelastic properties and can be moulded into free-standing, shape-persistent objects, which are all due to the dynamically reversible complexation between the **B21C7** and dialkylammonium salt moieties and the good mechanical properties of the cross-linked network. Furthermore, the gel possesses self-healing capabilities. It self-heals *in situ*, as can be seen by the naked eye and characterized by rheological measurements. More excitingly, the healed gel retains its shape well, even after multiple mechanical movements. These interesting properties make this gel an unprecedented soft material. Therefore, this multi-functional supramolecular polymer gel is promising as an advanced material with potential applications in drug-delivery systems, biomedical fields, *etc.*

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