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A Multiresponsive, Shape-Persistent, and Elastic Supramolecular Polymer Network Gel Constructed by Orthogonal Self-Assembly

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Nature provides a huge range of examples of precise and efficient self-assembly processes, such as DNA with its functionalities of replication and transcription in biological systems. Inspired by this, scientists have been applying themselves to design and develop structurally defined materials with unprecedented properties and intriguing functions.[1] In view of the dynamic and reversible nature of noncovalent interactions, supramolecular polymers[2] not only show traditional polymeric properties, but also possess new structures and functions, such as degradability, stimuli-responsiveness, and self-healing, making them exceptional candidates for adaptive or smart materials.[1i,2e,3] Therefore, supramolecular polymers may be expected to have a strong impact on material science via the explicit manipulation of the noncovalent forces that hold the monomeric units together.[2–4] Constructed from low-molecular-weight molecules by reversible noncovalent interactions, supramolecular gels,[5] which undergo stimuli-responsive (including temperature, pH, solvent composition, electric/magnetic fields, etc.) gel–sol transitions, have increasingly attracted attention as a kind of adaptive material because of their potential applications, such as controlled release, drug carriers, and molecular sensing.[3g,6]

Of particular interest is the construction of externally addressable supramolecular assemblies, because responses to more stimuli would give rise to more flexibility for the creation of smart materials.[7] Generally, to design and achieve single- or even dual-responsive soft materials is facile. However, supramolecular gels integrated by independent multi-responsiveness (more than dual-responsive) are rare because it may require a
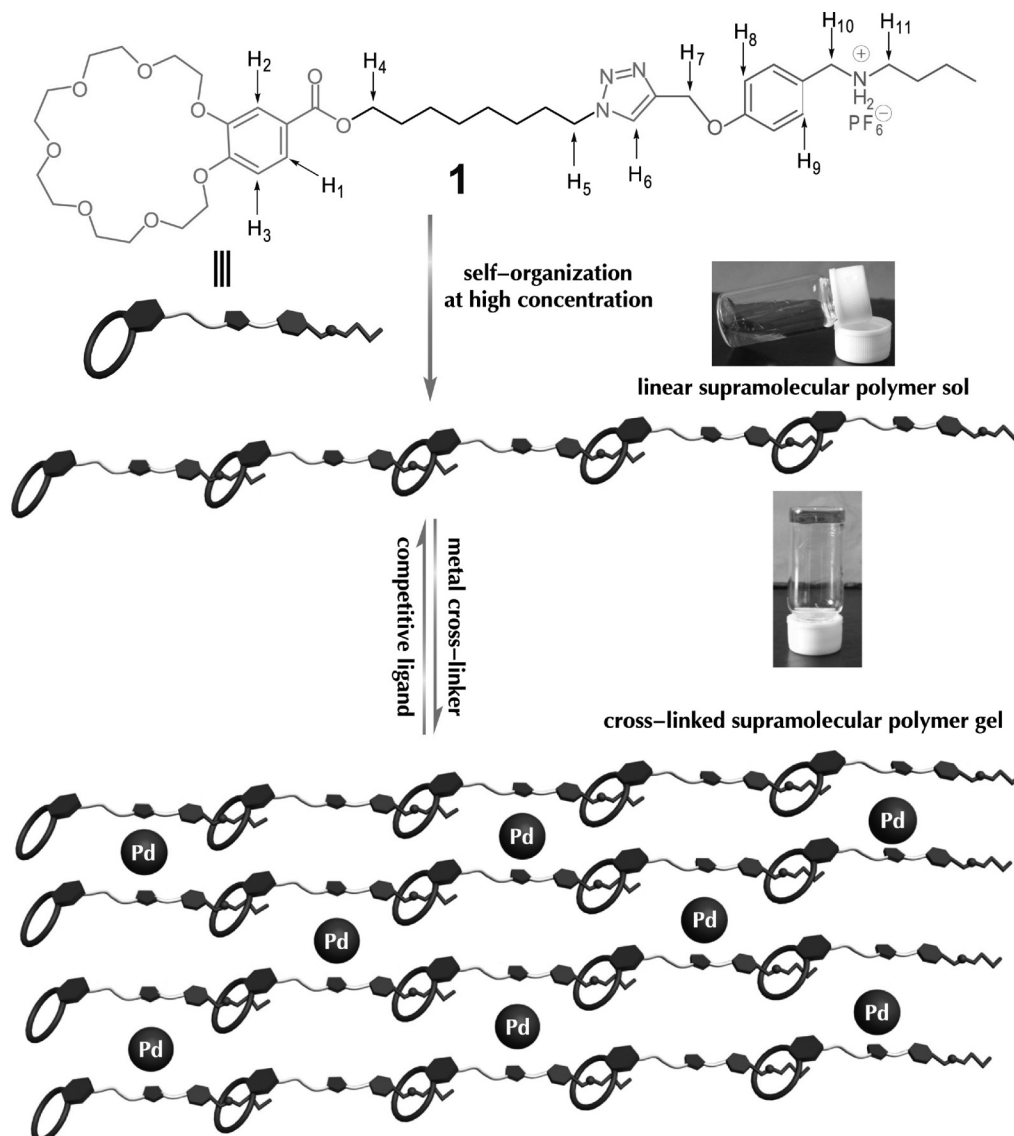
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consummate integration between the gelator's structures and the environment of the noncovalent interactions.[5c,8] As we know, physical (noncovalent) gels are generally less stable and have poor mechanical properties compared to covalent gels.[9] Therefore, integrating the stimuli responsiveness and processability inherent to the noncovalent units and the mechanical properties obtained from covalent building blocks into a single material is a real challenge.[9c,18b] Crown ethers, the first artificially synthesized macrocyclic hosts, have been widely used as building blocks to create a variety of molecularly assembled structures with complementary guest molecules.[10] Meanwhile, using metals as cross-linkers allows regulation of the aggregate properties, such as topological and morphological behaviors and mechanical properties.[11] Fortunately, we found that our cross-linked supramolecular polymer network gel has shape-persistent and elastic properties, which have rarely been reported in the field of supramolecular assemblies without polymeric backbones. Although crown ether-based organogels and supramolecular gels have drawn considerable attention in recent years,[3g,7d,12] metal-co-ordination-mediated supramolecular polymer gels assembled orthogonally from metal ions and low-molecular-weight monomers with bridging ligands by crown ether-based molecular recognition have never been reported. On account of the desired multiple-responsive, shape-persistent, and elastic properties in a single material, it is really a big challenge to design and achieve such supramolecular polymer network gels.

In our previous work, we assembled dynamic supramolecular polymers that have linear or cross-linked topologies using orthogonal noncovalent recognition motifs, host–guest and metal–ligand interactions.[11a] However, with the aim to introduce some smart properties into supramolecular polymers, we extended our studies towards a supramolecular polymer gel with palladium(II)-containing co-ordination cross-linked networks inside. Therefore, we report herein a novel quadruple-responsive, shape-persistent, and elastic supramolecular polymer network gel, which is formed by a combination of a heteroditopic monomer **1**[13c] with bridging ligand and the cross-linker, $[PdCl_2(PhCN)_2]$. Both the ligand and metallic cross-linker play complementary roles in the self-assembly of this supramolecular material. Heteroditopic monomer **1** contains a 1,2,3-triazole group between the benzo-21-crown-7 (**B21C7**) host and its complementary guest dialkylammonium salt and the 1,2,3-triazole acts as a ligand for co-ordination with palladium(II). A linear supramolecular polymer was first constructed in acetonitrile and then the cross-linker was added

Scheme 1. Schematic representation of controlling the topology and rheology of the supramolecular polymer prepared from heteroditopic monomer **1**.

to make a cross-linked supramolecular polymer (**Scheme 1**). At a critical gel concentration, a metal co-ordination-mediated supramolecular polymer network gel formed, exhibiting an interesting reversible gel–sol transition in response to quadruple distinct stimuli (pH-, thermo-, cation-, and metallo-induced) and good mechanical properties (shape-persistent and elastic). It was expected that using metal-co-ordinaiton as one of the supramolecular motifs would provide the self-assembled supramolecular polymer with peculiar properties.

Initially, host–guest complexation studies of the heteroditopic monomer **1** were carried out. It is well known that the **B21C7** unit forms 1:1 threaded structure with the dialkylammonium salt moiety.[13] In addition, the correlation spectroscopy (COSY) NMR spectrum (Supporting Information (SI), Figure S2) of **1** allowed the assignment of its complicated concentration-dependent ^{1}H NMR spectra (SI, Figure S3), which can be used as a convenient method to demonstrate the formation of high

molecular weight aggregates driven by host–guest interactions between the **B21C7** host and dialkylammonium salt guest moieties. Viscometry is another convenient method to probe the propensity of monomers to self-assemble into large aggregates. Therefore, viscosity measurements were carried out in acetonitrile using a Cannon-Ubbelohde semi-micro dilution viscometer to support the formation of large polymeric aggregates of **1** (SI, Figure S4).

2D diffusion-ordered ^{1}H NMR spectroscopy (DOSY), a convenient and reliable method to test the dimensions of polydiperse supromolecular aggregates,[3g,11a,13c] was performed to investigate the self-aggregation of monomer **1** to form the linear or cross-linked supramolecular polymer. As the monomer concentration increased from 40 to 300 mM, the measured weight average diffusion coefficient decreased from 7.16×10^{-10} to 1.89×10^{-10} m^2 s^{-1} (**Figure 1**), indicating the concentration dependence of the linear supramolecular polymerization of
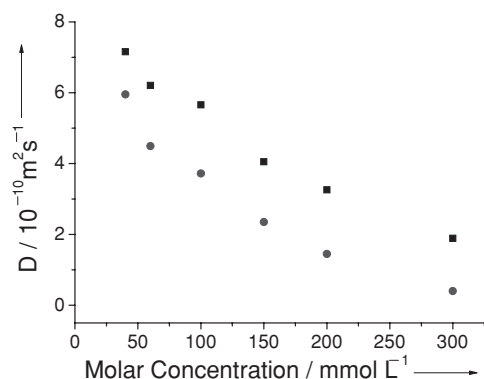
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Figure 1. Concentration dependence of diffusion coefficient D (500 MHz, [D$_3$]acetonitrile, 293 K) of **1** (■) and 1 equiv of **1** plus 0.5 equiv of [PdCl$_2$(PhCN)$_2$] (●).

Figure 2. Partial ^{1}H NMR spectra (400 MHz, [D$_3$]acetonitrile, 293 K) of **1** at a concentration of 200 mM with successive addition of [PdCl$_2$(PhCN)$_2$] and PPh$_3$: a) 0 equiv; b) 0.1 equiv; c) 0.2 equiv; d) 0.3 equiv; e) 0.4 equiv; f) 0.5 equiv. of [PdCl$_2$(PhCN)$_2$]; g) 1.0 equiv of PPh$_3$ was added to (f), after filtration.

monomer **1**. When 0.5 equivalent of [PdCl$_2$(PhCN)$_2$] was added to a 300 mM solution of monomer **1**, a decrease in the diffusion coefficient from 1.89×10^{-10} to 4.00×10^{-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 Figure 1. These two observations simultaneously proved an increase in the average aggregation size owing to cross-linking of the linear supramolecular polymer.

In addition, rodlike fibers with regular diameters (SI, Figure S5) were drawn from a high concentration solution using a pin and observed by scanning electron microscopy (SEM), providing direct evidence of the formation of the supramolecular polymer with high molecular weight and a high degree of linear chain extension.[2s,3g] Next, the gel was prepared by dissolving **1** in acetonitrile (60 mM) in a vial, followed by the addition of 0.5 equivalent of [PdCl$_2$(PhCN)$_2$], and subsequent heating to 50 °C led to a transparent solution. Upon cooling in a refrigerator at 4 °C, gelation takes place. The critical gel concentration, which shows the gelation ability of the gelators, was determined to be 30 mM by continuously diluting a gel with heating and cooling cycles until the gel didn't regenerate.[14]

The conversion from linear to cross-linked supramolecular polymer which was accomplished by forming a disubstituted palladium(II) complex between [PdCl$_2$(PhCN)$_2$] and 1,2,3-triazole moieties brings about the sol to gel transition (Scheme 1). Upon progressive addition of [PdCl$_2$(PhCN)$_2$], it was found that the resonance for the triazole H^{6lin} proton shifted downfield (**Figure 2**), indicating preferential complexation between the triazole ligands and the palladium atom. The gradual strengthening of newly formed H^{6lin} signals as well as the gradual disappearance of uncomplexed species peaks (for example H^{9uc}), along with broadening of all signals (for example H^{3,8,9lin}) with increasing amount of [PdCl$_2$(PhCN)$_2$], demonstrated the formation of a cross-linked supramolecular polymer (Figure 2). Interestingly, the supramolecular gel formed with the progressive addition of the cross-linker, which can be ascribed to the restricted flow of the solvent within the newly formed supramolecular polymer network. Deconstruction of the supramolecular polymer network can induce the gel to sol phase transition, which was achieved by addition of
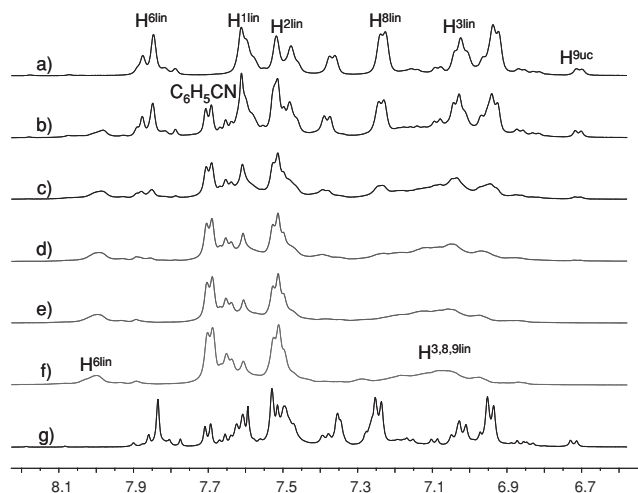
a competitive ligand, PPh$_3$, for Pd. As shown in further on, the competition reaction forms the [PdCl$_2$(PPh$_3$)$_2$] complex, which was visually confirmed by the precipitation of a white solid on the bottom of a vial. Meanwhile, the ^{1}H NMR experiment also demonstrated the restoration of the linear structure when one equivalent of PPh$_3$ was added to the solution (Figure 2, spectrum g). Therefore, the reversible transition between the linear and cross-linked supramolecular polymer provides a convenient way for the gel–sol transition induced by successive addition of the metal cross-linker and use of the competitive ligand.

Rheological characterization is important because it can provide insight to the bulk material properties of dynamically cross-linked supramolecular assemblies.[15,18b] To characterize the rheological properties of the supramolecular polymer network gel, the linear oscillatory frequency sweep experiments of the samples made from a certain concentration of monomer **1** with increasing cross-linking density were carried out. The storage (G') and loss (G'') moduli for the sample made from 200 mM monomer **1** with increasing cross-linking density from 0 to 100% in acetonitrile are shown as a function of frequency in **Figure 3**. The modulus of 200 mM monomer **1** without cross-linker is small and close to the measurement range of the rheometer. As the cross-linking density increases from 0 to 100%, both G' and G'' increases more than four orders of magnitude. For 200 mM monomer **1** with cross-linking densities from 20 to 100%, there were crossover frequencies (ω_c) between G' and G'' (SI, Figure S6–S10). When the scanning frequency (ω) is lower than ω_c, G' is smaller than G'', and the viscous property of samples is predominant. When the scanning frequency (ω) is higher than ω_c, G' is larger than G'', and the elastic property of samples is dominant. G' reaches a plateau value at high frequency, which is termed as plateau modulus (G_0). The value of G_0 (SI, Figure S11) increases proportionally with the cross-linking density from 10^1 to 10^4 Pa. Therefore, this supramolecular material exhibits intermediate mechanical properties (i.e., plateau modulus ≈ 10–1000 Pa) and provides an excellent
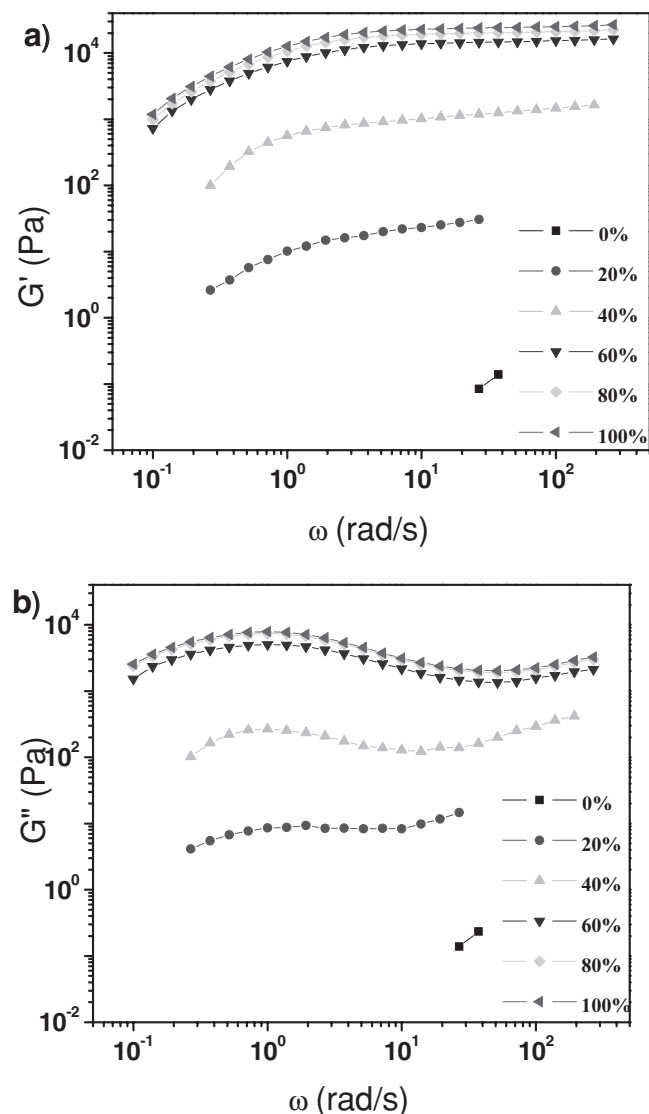
Figure 3. a) Storage modulus (G') and b) loss modulus (G'') of the supramolecular polymer network versus scanning frequency (ω) for the samples made from 200 mM monomer **1** with different cross-linking densities from 0 to 100% in acetonitrile. $T = 20\ °C$.

complement to the Aida and co-workers' polymer–clay hybrid hydrogel system,[5g] which exhibits a much higher mechanical strength (plateau modulus > 10^4–10^6 Pa). Furthermore, with the increase of the cross-linking density, a greater number of active cross-links present in the supramolecular polymer network (for a detailed discussion see SI, Figure S12). These observations further confirmed the formation of the supramolecular polymer network gel and the good mechanical properties of the resultant supramolecular network through orthogonal noncovalent interactions.

As expected, the gel is sensitive to temperature. Heating and cooling can result in a reversible gel–sol transition, as shown by the variable temperature ^{1}H NMR spectra (SI, Figure S13). At a relatively low temperature, the ^{1}H NMR resonance signals for monomer **1** almost disappeared, suggesting strong intermolecular aggregation. When the temperature rose gradually,

the original weak signals became well-dispersed and can be easily identified. These results showed that gel–sol transition is temperature-dependent.

The complexation between **B21C7** and the dialkylammonium salt can be controlled by changing the solution pH due to the reversible protonation of the dialkylammonium salt. Therefore, we used triethylamine (Et$_3$N) and trifluoroacetic acid (TFA) as the operating acid/base pair, which resulted in the reversible gel–sol transition (**Figure 4**). The ^{1}H NMR experiment demonstrated this reversible process (SI, Figure S14 and S15). When Et$_3$N was added to a solution of monomer **1** in acetonitrile, almost all complexed signals disappeared and the chemical shifts corresponding to aromatic protons returned to almost their uncomplexed values, indicating that the complexation between **B21C7** and dialkylammonium salt was essentially totally quenched (SI, Figure S14, spectrum b). Further studies showed that triethylamine can also be a competitive ligand for Pd (SI, Figure S16). Therefore, the gel-to-sol transition was induced by deprotonation of the dialkylammonium salt and de-co-ordination of the triazole to Pd in a co-operative manner (SI, Figure S15). After TFA was added to this solution, the complexation between **B21C7** and dialkylammonium salt was recovered and the complicated signals and co-ordination signals were observed again.[3g,16]

More interestingly, the reversible gel–sol transition could be induced by adding and removing the potassium cation (K$^+$) (Figure 4). When K$^+$ was added, the **B21C7** host should form a more stable 1:1 complex with K$^+$, which caused the complex between the **B21C7** unit and the dialkylammonium salt moiety to disassemble. Later, when enough dibenzo-18-crown-6 (**DB18C6**), which binds the metal ion more strongly than the **B21C7** unit, was added to trap K$^+$, the **B21C7**/dialkylammonium salt complex reformed. This was also confirmed by an ^{1}H NMR experiment (SI, Figure S14 and S15). The addition of KPF$_6$ to a solution of monomer **1** in acetonitrile caused remarkable changes of the proton chemical shifts. Almost all complexed signals disappeared and uncomplexed aromatic protons exhibited downfield shifts, indicating that the complexation between **B21C7** and dialkylammonium salt was essentially totally quenched. After **DB18C6** was added to this solution, the complexation between **B21C7** and dialkylammonium salt was recovered and the complicated signals were observed again.[17]

Thus, the four distinct stimuli (Figure 4) mentioned above can be used as effective inputs to adjust the reversible gel–sol transitions of the supramolecular gel obtained by orthogonal self-assembly based on two kinds of noncovalent interactions, host–guest and metal–ligand interactions, reflecting the dynamic and reversible nature of the supramolecular gel system.

The morphology of the xerogels which were prepared by freeze-drying methodology was examined by SEM, revealing an interconnected porous structure in which nanofibers create a 3D network responsible for the observed gelation.[14b,18] It is worth noting that porous structures are currently of great scientific as well as technological interest as a result of their potential application in many areas of advanced materials science.[19] More interestingly, with the increase of the cross-linking density, the pore size within the cross-linked supramolecular polymer network decreases from approximately 3 µm
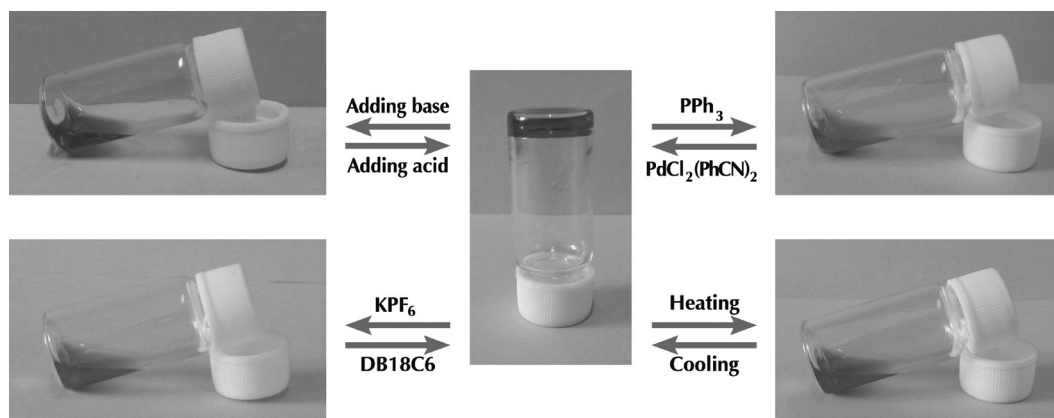
Figure 4. The reversible gel–sol transitions of the supramolecular polymer network gel (50 mM of monomer **1**) triggered by four different stimuli (pH-, thermo-, cation-, and metallo-induced).

to 300 nm, indicating the influence of the cross-linking density on the formation of the supramolecular gel (**Figure 5**). However, by comparison of the superstructures imaged by SEM between the linear and cross-linked supramolecular polymers, it was found that the linear supramolecular polymer did not form networks. These results showed that the introduction of cross-linker, [PdCl$_2$(PhCN)$_2$], not only achieved the reversible conversion between linear and cross-linked supramolecular polymer, but also made an impact on the microscopic nature of the resultant supramolecular polymer.

As shown in **Figure 6**, the cross-linked supramolecular polymer gel is shape-persistent and free-standing. Two gel blocks prepared freshly can adhere to each other (Figure 6a,b).

Furthermore, when we connected four gel blocks together, a bridge was constructed which is strong enough to hold when suspended horizontally between two posts (Figure 6c). However, if the gel blocks are not fresh, the fusion does not take place, showing the fresh surfaces of the gel blocks are essential for adhesion. These intriguing properties of our cross-linked supramolecular polymer gel contradict the preconception that physical gels are less stable and have poor mechanical properties compared to covalent gels and integrate the stimuli responsivity and processability inherent to the noncovalent units with the mechanical properties obtained usually from covalent building blocks into a single supramolecular material.

Elastomers consist of macromolecular chains that are bound together into a network by covalent or non-covalent cross-links.[20] Thus, we assume that our cross-linked supramolecular polymer network gel containing reversible binding unites is capable of storing elastic energy on multiple time-scales, especially the time scale shorter than the relaxation time (τ, $\tau = 1/\omega_c$) of the supramolecular polymer gel when the elastic property of the samples is dominant, giving rise to its elastic behavior. As shown in Figure 6d, a fresh gel block (1.5 g) at a height of 25 cm fell freely to the bottom of the beaker and then rebounded. Meanwhile, Figure 6d also shows the trajectory of the gel block after rebounding from the bottom of the beaker (for details see the movie in the SI). To our surprise, the gel block rebounded unexpectedly to a maximal height of 20 cm, indicating that our supramolecular polymer network gel has an excellent elastic property. We believe the elastic mechanism (for cartoon representations see SI, Figure S17) is mainly attributable to the dynamically reversible complexation between **B21C7** and dialkylammonium salt moieties and the good mechanical properties of the cross-linked supramolecular polymer network. In the
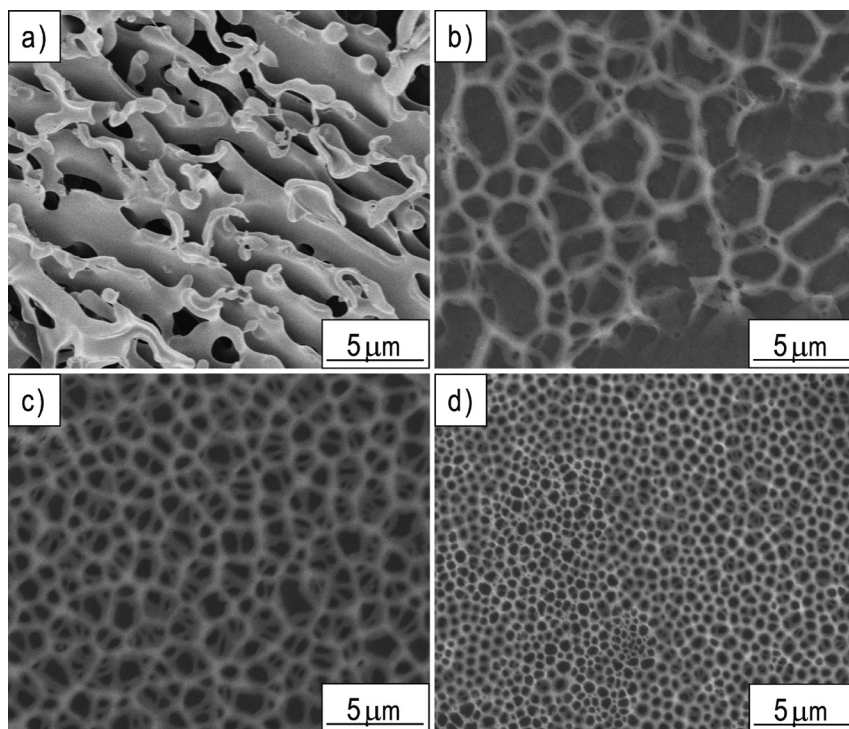

Figure 5. a) SEM image of linear supramolecular polymer; SEM images of the supramolecular polymer network gels with different cross-linking densities: b) 20%, c) 60%, and d) 100%.
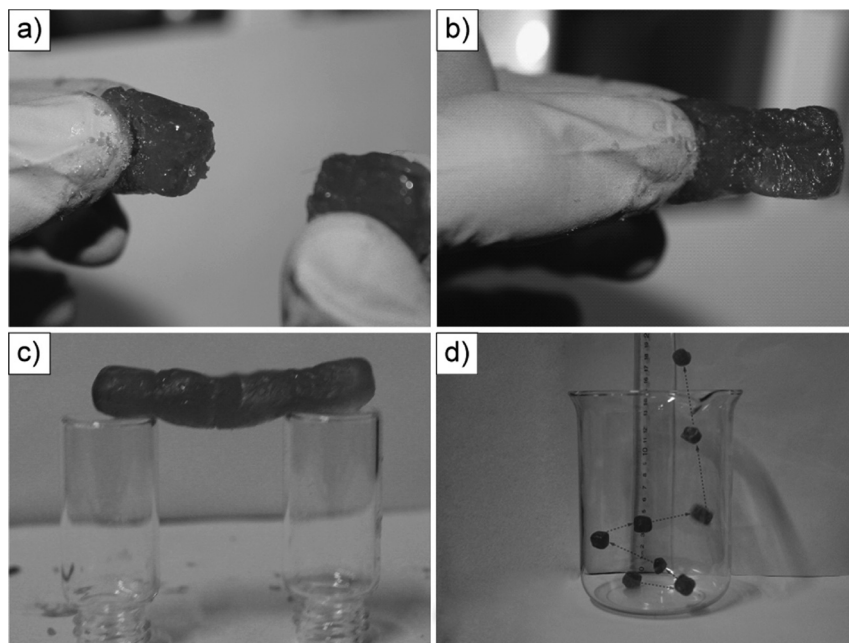
Figure 6. Shape-persistent, free-standing macroscopic objects molded from a supramolecular polymer gel with a concentration of monomer **1** at 300 mM (a–c) and the elastic response of the supramolecular polymer gel (d). a) two supramolecular polymer gel blocks; b) the two gel blocks in (a) adhere to each other and become a free-standing object; c) a bridge constructed by connecting together four gel blocks suspended horizontally; d) the moving trajectory of the gel block after rebounding from the bottom of the beaker (eight pictures overlaid together).

are all due to the dynamically reversible complexation between **B21C7** and dialkylammonium salt moieties and the good mechanical properties (plateau modulus = 10^1–10^4 Pa based on rheological analysis) of the cross-linked supramolecular polymer network. So far, no other supramolecular organogels have been reported to possess all these features, making this supramolecular polymer network gel an unprecedentedly intelligent soft material. Now, our current efforts are focused on exploring applications of supramolecular gels and realizing other functionalities of supramolecular polymers, such as shape-memory functions.

Experimental Section

General Methods: Model compound **4** was synthesized according to literature procedures.[13c] [PdCl$_2$(PhCN)$_2$] was obtained from Alfa Aesar and solvents were used as received. ^{1}H, ^{13}C and 2D COSY NMR spectra were recorded with a Bruker Advance DMX 500 spectrophotometer or a Bruker Advance DMX 400 spectrophotometer with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. The 2D diffusion-ordered NMR (2D DOSY NMR) spectra were recorded on a Bruker DRX 500 spectrometer. 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 is 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. SEM investigations were carried out on a JEOL 6390LV instrument.

Sample Preparation: In a typical example of gelation, we dissolved monomer **1** (550 mg) in 2 mL of acetonitrile (300 mM), followed by the addition of 0.5 equivalent of [PdCl$_2$(PhCN)$_2$] (115 mg), and subsequent heating and oscillating led to a solution. The mixture became completely stiff (gel state) within only 2 min at 20 °C, forming a shape-persistent, free-standing macroscopic material (Figure 5a–c) at 20 °C. The gel block used in the elastic show (Figure 5d) was prepared in the same way. In Figure 4, the gel formed by dissolving 22.9 mg of monomer **1** and 5.0 mg of cross-linker in 0.50 mL of acetonitrile (50 mM) and then cooling in a refrigerator at 4 °C for 2 min. The reversible gel–sol transitions of the supramolecular polymer network gel triggered by four different stimuli, namely, pH-induced (adding 13 μL, 1.5 equiv., of Et$_3$N and then 8.0 μL, 1.8 equiv., of TFA), thermo-induced (heating to 50 °C and then cooling at 4 °C for 2 min), cation-induced (adding 6.0 mg, 1.5 equiv., of KPF$_6$ and then 11.0 mg, 1.5 equiv., of **DB18C6**), and metallo-induced (adding 6.6 mg, 1.0 equiv., of PPh$_3$ and then 5.0 mg, 0.50 equiv., of [PdCl$_2$(PhCN)$_2$], after filtration). In rheological experiments, samples were prepared as follows: a linear supramolecular polymer was first constructed by dissolving 183 mg of monomer **1** in 1.0 mL of acetonitrile (200 mM), 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 36.7 mg of monomer **1** in 0.50 mL of acetonitrile (80 mM), and then different amounts of [PdCl$_2$(PhCN)$_2$] were added to make gels with different cross-linking densities, 0%, 20%, 60%, and 100%.

normal state, the cross-linked supramolecular polymer network is under thermodynamic equilibrium. During the free-falling process, the potential energy of the gel block transfers to kinetic energy. When the gel block hits the bottom of the beaker, the reverse force from the beaker bottom dissociates some of the host-guest complexes between the **B21C7** and dialkylammonium salt moieties. Subsequently, the host–guest interactions recover, which simultaneously drives the gel block to rebound. In sharp contrast, the linear supramolecular polymer prepared from monomer **1** in the same solvent did not show any elasticity. This indiciated that a 3D network structure is necessary for the elasticity. Furthermore, an appropriate amount of the acetonitrile solvent is also required, showing that the mobility of the host and guest units is also necessary for the supramolecular polymer system to demonstrate elasticity. It is worth noting that the elastomer we present here is made of small molecules instead of macromolecular chains used in the traditional elastomers.

In summary, we have used the combination of a heteroditopic monomer with bridging ligand and the metallic cross-linker to orthogonally self-assemble into an extended supramolecular polymer network, resulting in the gelation. The cross-linked supramolecular polymer network gel shows pH-, thermo-, cation-, and metallo-induced reversible gel–sol transitions. Characterization of the resultant gel demonstrates that the supramolecular gel pore size can be modulated by the amount of cross-linker added to the system, which facilitates its application as a smart material. More importantly, this supramolecular polymeric material can be molded into shape-persistent, free-standing objects and rebound after a free-falling process, which

Supporting Information

Supporting Information is avaiable from the Wiley Online Library or from the author.

Acknowledgements

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