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COMMUNICATION

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

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Supramolecular crosslinked polymer gels show special properties largely as a result of the combined mechanical properties contributed by the covalently linked polymer chains and the reversible, stimuli-responsive supramolecular crosslinks. Most supramolecular crosslinked polymer gels contain only one kind of physical cross-link. Herein we report a novel supramolecular polymer gel containing two types of physical crosslinks based on two kinds of non-covalent interactions that are orthogonal: DAN·DeUG quadruply hydrogen-bonding interactions and benzo-21-crown-7/dialkylammonium salt host–guest interactions. One of the crosslinked networks is used to maintain the gel state while the other modulates the crosslink density through an external stimuli, thereby causing a volume change of the gel. This double supramolecular crosslinked polymer gel shows macroscale expansion and contraction behavior and multistimuli responsiveness. Therefore, we successfully demonstrate that the macroscopic property changes of supramolecular systems can be induced by controlled self-assembly on the molecular scale.

Introduction

Polymer gels have tremendous potential as smart materials because they offer a special combination of the elastic behavior of solids and the microviscous properties of fluids.[1] They can be conventionally prepared by permanently cross-linking the polymer chains.[2] Such covalently bonded materials have the advantage that they can be both strong and stable over long periods. However, they usually lack the ability to self-heal or adapt to their environment. This stimuli responsive behavior is more frequently found in supramolecular polymer gels wherein the three-dimensional gel structure contains dynamic non-convalent crosslinks between traditional polymers.[3] These soft materials exhibit emergent properties originating both in the mechanical properties of the covalent polymer backbones and the reversibility and stimuli-responsiveness of the supramolecular network crosslinks. Supramolecular gels can show responsiveness to light,[4a] redox environment,[4b] temperature,[4c] ionic species,[4d] and other external stimuli depending on the specific nature of the noncovalent interaction.[4] This high level of versatility makes these gels ideal candidates for environmentally-adaptive materials.[3,4]

The non-convalent interactions used to form the crosslinks in supramolecular polymer gels mainly involve hydrogen bonds,[5] metal coordination,[6] and host-guest interactions based on macrocyclic hosts.[7-10] For example, Zimmerman and coworkers developed a redox-responsive, quadruple hydrogen bonding module and successfully applied it to construct a reversible supramolecular polymer gel.[5a] Schubert and co-workers reported the formation of a supramolecular polymer gel *via* metal-ligand interactions, which was used to produce a self-healing film.[6b] In another example, Huang and co-workers demonstrated a self-healing supramolecular polymer gel formed by crown ether-based host-guest interactions.[7a] Harada and coworkers reported a photoresponsive gel through the molecular recognition of a cyclodextrin host to an azobenzene guest.[8a] Scherman and co-workers developed extremely high water content hydrogels (up to 99.7% water by weight) driven by the strong host–guest complexation of cucurbit[8]uril in water.[9] Recently, Bielawski, Sessler, and coworkers utilized the host-guest interactions between calix[4]pyrrole and dianions to prepare supramolecular crosslinked polymer gels.[10b] Interestingly, the ability to form these gels allowed for the extraction and separation of dianions from aqueous media under conditions of liquid-liquid extraction.

From the few selected examples above and many other published reports, one can reach two general conclusions: 1) many kinds of non-convalent interactions can be used to crosslink polymeric chains to yield supramolecular gels and 2) usually these supramolecular gels contain only one kind of noncovalent crosslink. 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 gel to sol transition may occur. This transition often occurs across a narrow stimulus window and can limit applications in several ways. For example, full loss of the material integrity above a certain level of stimulation limits the sensing range of the material. One solution to this problem is to use a second polymer network to maintain the polymer network integrity. We were interested in supramolecular crosslinked polymer gels containing two types of physical crosslinks based on two orthogonal supramolecular interactions. In such a system, one supramolecular crosslink could be used to maintain the gel state, and the other to change the crosslinking density of the gel under external stimuli, thereby giving rise to the macroscale expansion-contraction behavior of the gel without a gel-sol transition.

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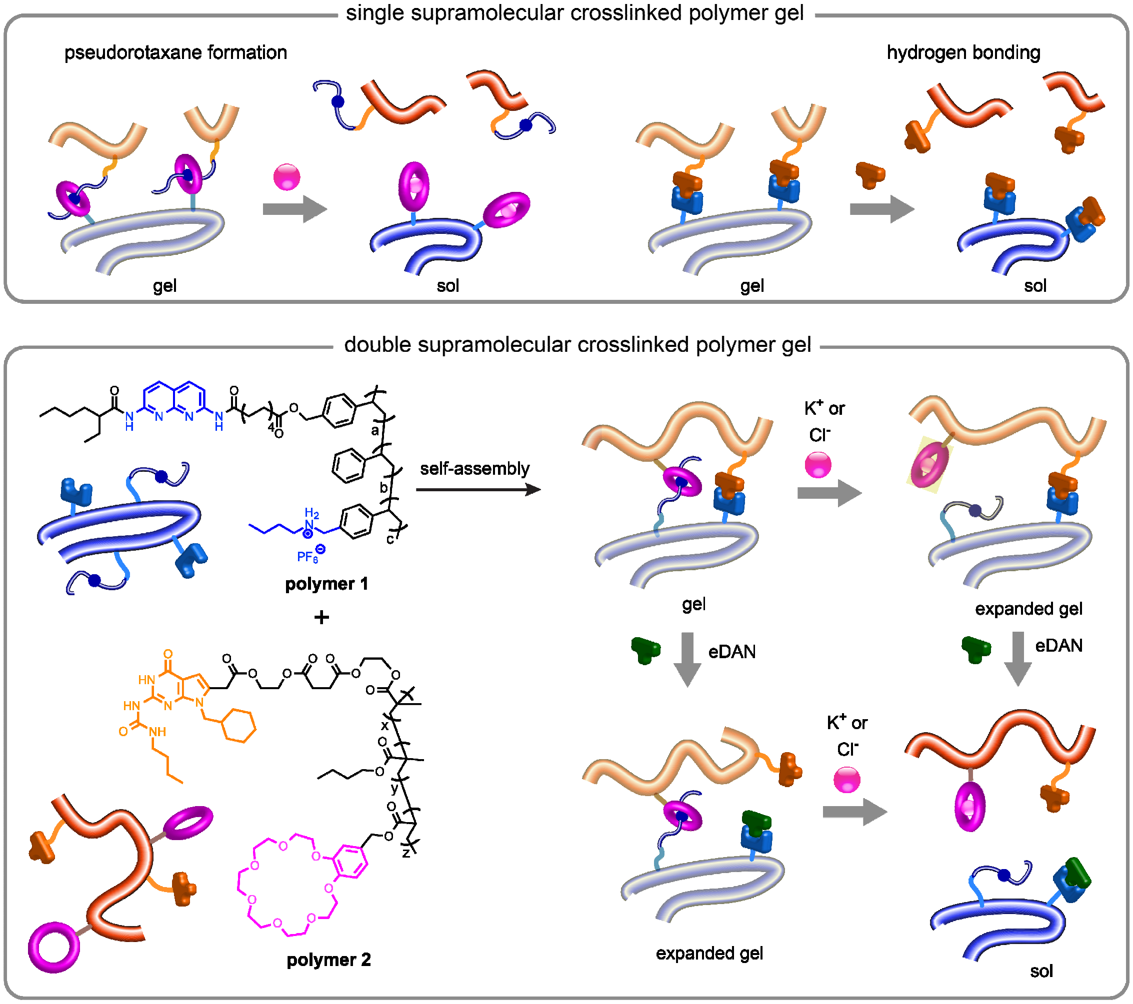

Scheme 1. Cartoon representations of **polymer 1** and **polymer 2** and the illustration of the advantage of doubly *vs* singly supramolecular crosslinked polymer gels.

Polymer gels with macroscale expansion-contraction behavior are of great importance because they can mimic the actions of muscles and potentially serve as an artificial version with a wider range of functions.[11] In spite of the fact that some previously reported polymer gels have shown such expansion and contraction behavior, many of them have covalent crosslinking.[12] The employment of two kinds of non-covalent interactions as crosslinks in this work will endow supramolecular gels with responsiveness to more stimuli, making them more adaptive to the environment. The roles of the two networks could be reversed, allowing for a multi-responsive, expansion-contraction system that would be more adaptive (Scheme 1). Finally, addition of both stimuli would allow breakdown of the gel. Herein we report that exactly such a double supramolecular crosslinked polymer gel based on hydrogen bonding and a macrocycle threading process.

Results and Discussion

The challenge in using two noncovalent interactions simultaneously to construct supramolecular polymer gels is that they must be orthogonal to one another.[13] Most of the reported related systems use metal coordination for one of the interactions.[5b,5c,14] We were particularly interested in combining a heterocomplementary quadruple hydrogen bonded pair and a threaded complex formed between an alkyl ammonium ion and a crown ether. These two supramolecular contacts respond to quite different stimuli and had excellent potential to be orthogonally and reversibly responsive.

As shown in Scheme 1, **polymer 1** (M_n = 20.2 kDa, the ratio of *a*/*b*/*c* was 1/58/1.3) is polystyrene (PS) with pendant 2,7-diamido-1,8-naphthyridine (DAN) units and dialkylammonium salt groups, and **polymer 2** (M_n = 25.8 kDa, the ratio of *x*/*y*/*z* was 1/70/1) is poly(butyl methacrylate) (PBMA) containing deazaguanosine (DeUG) units and benzo-21-crown-7 (B21C7) groups. The incorporation degrees of DAN units and dialkylammonium salt groups were 1.7 and 2.2 mol%, respectively, for **polymer 1**, and those of DeUG units and crown ether groups were both 1.4 mol% for **polymer 2**. As demonstrated in our previous studies, DAN can bind DeUG to form highly stable and highly orthogonal quadruply hydrogen-bonded complexes,[15] and the dialkylammonium salt unit is known to slip through the cavity of B21C7 to form a stable 1 : 1 threaded structure.[16] Therefore, **polymer 1** and **polymer 2** could be crosslinked by two kinds of non-covalent interactions when mixed together, inducing the formation of a supramolecular polymer gel. The employment of two types of supramolecular interactions produces a double supramolecular crosslinked polymer gel, which in this case is a blend of two normally immiscible polymer backbones (polystyrene and polybutylmethacrylate). Importantly, it was previously reported that either the quadruply hydrogen-bonding motif or crown ether-based host-guest interactions could be used to make stimuli-responsive gels.[4d,5a]

The DAN·DeUG quadruply hydrogen-bonding interactions are strong in cholroform and benzo-21-crown-7/dialkylammonium salt host–guest interactions are strong in cholroform too.[15,16] Moreover, DMSO is a strong competitive solvent for hydrogen-bonding, so DMSO will destroy the DAN·DeUG hydrogen-bonding interactions and benzo-21-crown-7/dialkylammonium salt host–guest interactions. Therefore, we selected cholroform as the solvent in our system studied here.

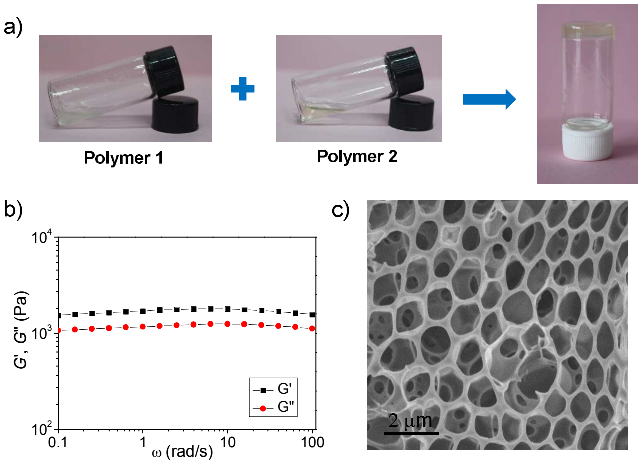

Fig. 1 (a) Formation of the double supramolecular crosslinked polymer gel; (b) Rheological characterization of the gel (T = 283 K, the concentrations of the two polymers were 60 g/L); (c) SEM image of the gel.

A viscous gel was obtained upon mixing the clear, free flowing chloroform solutions of **polymer 1** (3.00 mM) and **polymer 2** (2.33 mM) each at a concentration of 60 g/L (Figure 1a). To confirm the formation of a polymer gel, a rheological experiment was carried out. The results (Figure 1b) indicated that the storage modulus (G') is larger than the loss modulus (G''), and both properties (G' and G'') are independent of the angular frequency (ω), giving direct evidence for the formation of supramolecular gel.[7a] Furthermore, scanning electron microscopy (SEM) was used to examine the morphology of the polymer gel. As shown in Figure 1c, a three-dimensional porous network structure was observed, supporting the formation of crosslinks between polymer chains.

Gels composed of different concentrations of polymers (60, 100, and 150 g/L) were used to investigate their stability in solvent. As shown in Figure S10, when the 60 g/L sample was transferred into chloroform, it showed autodegradation within 30 min, whereas the 100 and 150 g/L samples were stable. Therefore, the 150 g/L (7.44 mM of **polymer 1**, and 5.81 mM of **polymer 2**) sample was utilized for expansion and contraction studies.

The expansion and contraction behavior of the supramolecular gel was investigated using eDAN as a competitive inhibitor of the hydrogen-bonding crosslinks (Figure 2a), thereby regulating the crosslinking density and potentially producing an expansion. A previous study reported the value of K_{assoc} for eDAN·DeUG to be 1.4×10^6 M^{-1},[5a] which was similar to that of the DAN·DeUG complex. The eDAN unit was electroactive, undergoing oxidative interconversion from a donor-acceptor-acceptor-donor (DAAD) to a DAAA hydrogen bonding array.[5a] That structural change was sufficient to produce a dramatic decrease in hydrogen-bonding complexation strength (i.e., from 1.4×10^6 to 6.7×10^2 M^{-1}) which in the current system might lead to a reformation of the DAN·DeUG supramolecular crosslinking and recovery of the gel volume. Moreover, the reduction of the oxidized eDAN could be achieved by the addition of a reductant. Therefore, the eDAN redox switch was applied to reversibly control the expansion and contraction of the supramolecular gel.

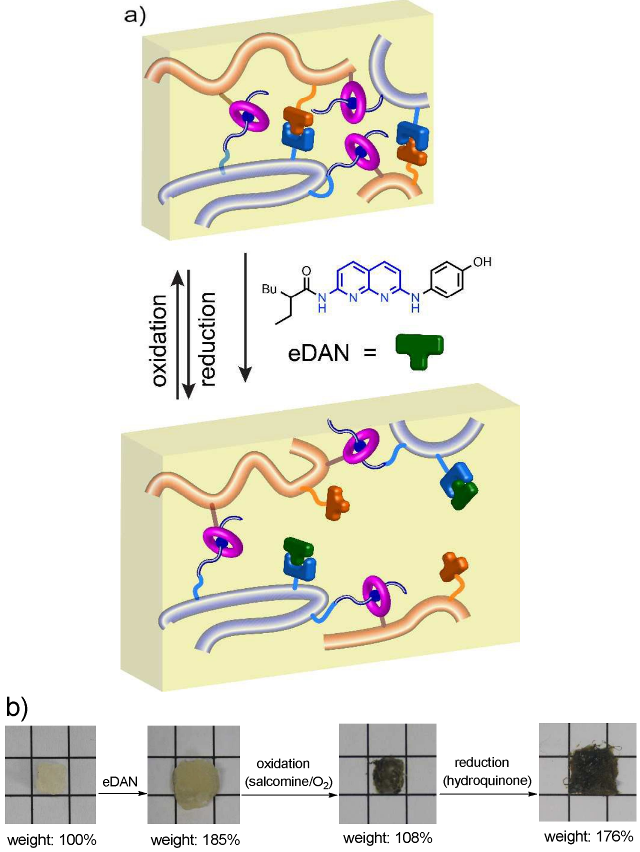

Fig. 2 (a) Schematic illustration of the redox-responsive expansion and contraction of the supramolecular gel; (b) Photographs of the visualized

volume changes of the supramolecular gel in response to a competitive hydrogen-bonding compound and its redox switch.

A starting gel with a volume of 0.500 mL and the concentrations of the two polymers set at 150 g/L was immersed into a chloroform solution of eDAN (5.00 mL, 100 mM) for 20 min. After immersion, the weight of the gel increased to 185% of the original weight (Figure 2b), indicating that the addition of a competitive hydrogen-bonding molecule broke down the DAN·DeUG supramolecular network, swelling the supramolecular gel. That the expansion of the gel was induced by the addition of eDAN was supported by a control experiment identical in all regards but lacking the addition of eDAN (see the movie in SI and photos in Figure S11).

To turn the eDAN inhibitor off, 0.5 equivalent of salcomine per eDAN was added to the solution followed by bubbling of oxygen gas for 5 min. The weight of the gel returned to 108% of the original weight, suggesting that the oxidized eDAN molecules indeed lost their competitiveness with the DAN units on **polymer 1**, reforming the DAN·DeUG supramolecular crosslinks with attendant shrinking of the gel. The overall cycle could be completed with the subsequent addition of reductant (hydroquinone, 1.20 equiv to eDAN) leading to the reduction of oxidized eDAN and a 76% increase in the weight. These results indicated that redox-responsive eDAN influences the crosslinking density of the supramolecular gel and induces the macroscale expansion and contraction of the supramolecular gel.

To estimate the percentage volume change of the gel, the mass and density of the polymers and solvent were considered.[12a,17] The volume of the gel (V) can be treated as the sum of the volumes of the polymer network (V_p) and the solvent in the gel (V_s). One can define the mass of polymer network and solvent as M_p and M_s and the densities as ρ_p and ρ_s, respectively, then $V = V_\mathrm{p} + V_\mathrm{s} = (M_\mathrm{p}/\rho_\mathrm{p}) + (M_\mathrm{s}/\rho_\mathrm{s})$. Because of the fact that the change of volume and mass of the gel is caused by absorption and release of the solvent, the change in the gel volume can be expressed by $\Delta V = \Delta M_\mathrm{s}/\rho_\mathrm{s} = \Delta M/\rho_\mathrm{s}$, where ΔM is the measured mass change. Therefore, the corresponding percentage volume changes in Figure 2b were 57%, 5.3%, and 51%, respectively.

Next, we investigated the effects of ion stimuli on the size of the supramolecular gel using the quadruply hydrogen-bonding interactions to maintain the gel state. It is well-known that the benzo-21-crown-7 (B21C7)/dialkylammonium salt host-guest recognition motif has been utilized for the construction of various stimuli-responsive materials owing to its abundant stimuli-responsiveness.[16] For example, K^+ forms a more stable 1:1 complex with B21C7,[16b] causing the disassembly of the B21C7/dialkylammonium salt complex. When 18-crown-6 (18C6) was added to trap K^+, the B21C7/dialkylammonium salt complexation reformed.[16b] Moreover, because the dialkylammonium salt moiety with chloride counteranion (Cl^-) is a contact ion pair, it can not form a threaded structure with the B21C7 unit. However, after the removal of Cl^- by the addition of Ag^+, the threaded structure was recovered. Accordingly, the competitive guest or counteranion can be applied to regulate the size of the supramolecular gel (Figure 3a).[16b]

Similarly, when the same starting gel with a volume of 0.5 mL and the concentrations of the two polymers set at 150 g/L was immersed into a chloroform solution of KPF_6 (5 mL, 100 mM) for 20 min, the weight of the gel was 156% of the original weight (Figure 3b), and the corresponding volume change was 37% of the original volume. Ten min after the addition of 18C6 (1.20 equiv to KPF_6), the weight of the gel reduced to 106% of the original weight. The swelling and shrinking behavior of the supramolecular gel was also observed upon sequential treatment with TBACl and $AgPF_6$, producing a change in weight from 100% to 152% and then to 103% of the original weight. Therefore, the physical crosslinking density in the polymer network is controlled by cation and anion stimuli, thereby causing the macroscale volume changes of the supramolecular gel.

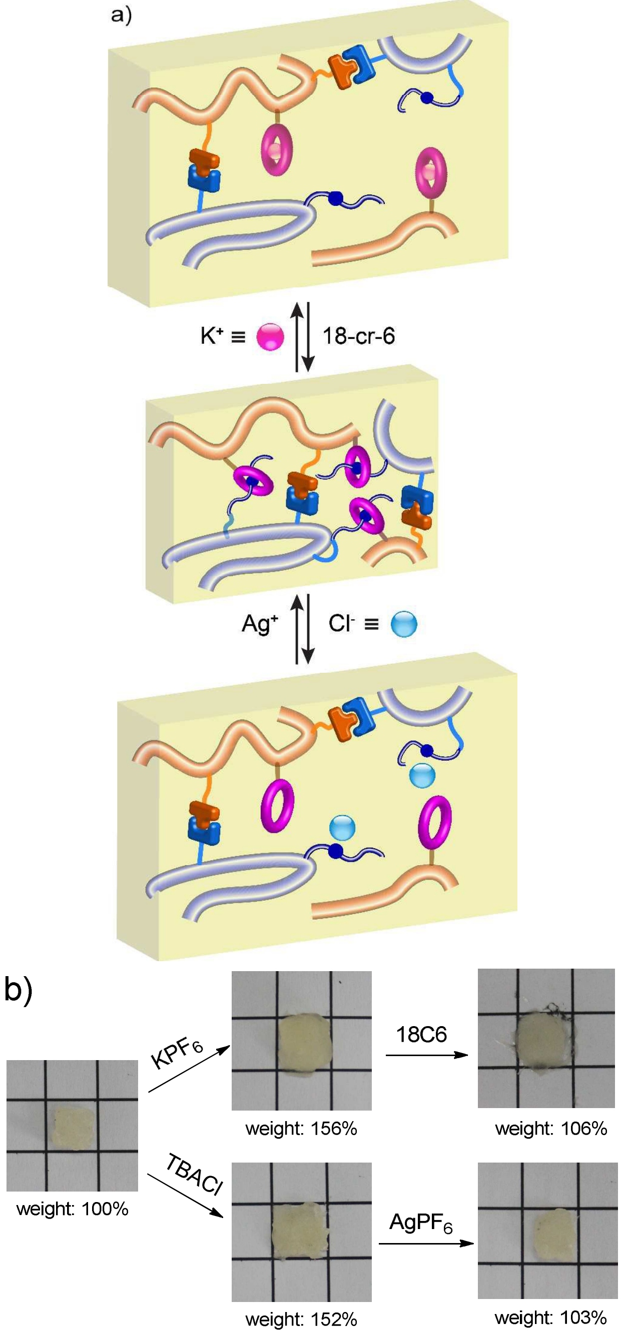

Fig. 3 (a) Schematic illustration of the ion-responsive expansion and contraction of the supramolecular gel; (b) Photographs of the visualized volume changes of the supramolecular gel in response to ion stimuli.

Conclusions

In conclusion, we have successfully prepared a double supramolecular crosslinked polymer gel exhibiting macroscale expansion and contraction behavior and multistimuli responsiveness. The supramolecular polymer gel is composed of traditional polymers connected by two types of supramolecular crosslinks. One type of supramolecular interaction was used to maintain the gel state, and the other to allow the crosslinking density of the gel to be altered by external stimuli, thereby causing the expansion-contraction behavior of the gel, but with no possibility of a gel-sol transition. The expansion and contraction behavior of this supramolecular gel is similar to the movement of muscles. Therefore, the concept in this study may aid in the design of medical devices, micromachines, and biomaterials. Our future research will focus on the macroscopic photoelectrical and other property changes of supramolecular systems induced by the control of the molecular scale self-assembly processes .

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† Electronic Supplementary Information (ESI) available: Characterizations, ^{1}H NMR data and other materials. See DOI: 10.1039/b000000x/

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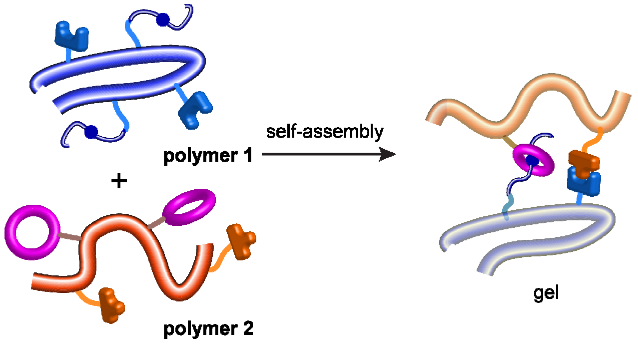
ToC Graphic



Here we report a novel supramolecular polymer gel containing two types of physical crosslinks that are orthogonal to one another. One physical crosslink is used to keep the gel state, and the other one is employed for changing the crosslinking density of the gel under external stimuli. This double supramolecular crosslinked polymer gel shows macroscale expansion and contraction behavior and multistimuli responsiveness.