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Paper

# A supramolecular polymer gel with dual-responsiveness constructed by crown ether based molecular recognition†

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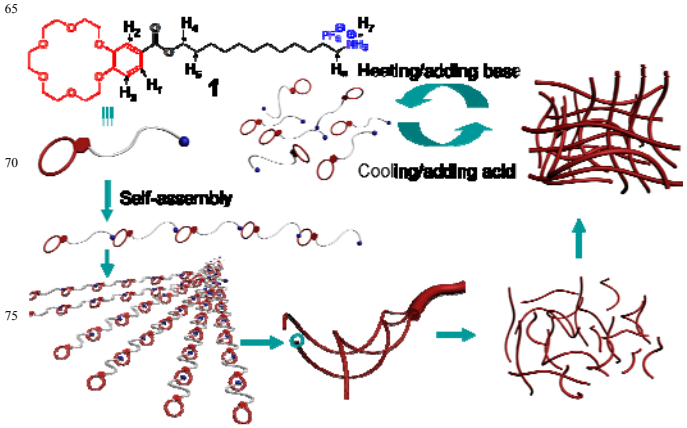
A supramolecular polymer gel was prepared by self-assembly of a heteroditopic A–B monomer based on benzo[18]crown-6. Such gel shows interesting gel-sol transition in response to dual-stimuli owing to the dynamically reversible complexation between the benzo[18]crown-6 and primary alkylammonium salt moieties. Therefore, these fascinating properties make this supramolecular gel a promising intelligent material.

## Introduction

Supramolecular materials,[1] whose components are connected via reversible noncovalent and/or dynamic covalent interactions thus to gain recyclability and stimuli-responsiveness, have attracted great attention in recent years because of their intrinsic scientific interests as well as technological applications. Supramolecular polymers,[2] an excellent combination of supramolecular chemistry and polymer science, not only show traditional polymeric properties, but also possess new structures and functions, making them valuable candidates for supramolecular materials. Furthermore, due to the dramatic growth of interest in the fabrication and functionalization of supramolecular polymers in recent years, supramolecular polymeric materials have had a strong impact on materials science.[3] Constructed by molecules with low-molecular-weight based on reversible noncovalent interactions, supramolecular polymer gels are a distinct and interesting subject of supramolecular materials due to their stimuli-responsiveness and mechanical properties obtained from the formation of supramolecular polymer backbones.[4] Noncovalent interactions, such as host–guest interactions, hydrogen bonding, metal-coordination, have been introduced to fabricate supramolecular polymer gels.[4,5] Being sensitive to the changes of pH value, temperature, solvent, chemical stimuli, and even the concentration of components, supramolecular polymer gels are expected to be remarkably advantageous over traditional polymer gels and armed with many unique properties that have been applied in various areas such as controlled release,[4c,6] novel membranes,[7] drug-delivery systems,[8] and molecular sensing.[9]

Crown ethers, as the first generation of artificial macrocyclic hosts, have been widely applied as building blocks to construct different supramolecular architectures with complementary guest molecules.[4h–k,10] Among them, supramolecular polymer gels play an important role. The study of supramolecular polymer gels based on crown ethers were mainly focused on their stimuli-responsiveness, especially those based on host–guest interactions.[4h–k,10o] The well-known host–guest motif in crown ether area, namely [18]crown-6 and protonated primary amino-group ($RNH_3^+$) was reported in 1967s by Pedersen and co-workers.[11] However, it has not been used to fabricate supramolecular polymer gels. Herein, we designed and synthesized a novel supramolecular polymer gel with dual-responsiveness based on a heteroditopic A–B monomer **1** (Scheme 1) *via* the reversible host–guest interactions between benzo[18]crown-6 (B18C6) and the primary alkylammonium salt (PAA). The complexation between B18C6 and PAA units can be responsive to pH change for the reversible deprotonation and protonation of the primary alkylammonium salt, and the host–guest interactions between B18C6 and PAA can be destroyed by heating. Moreover, the flexible long alkyl chain favors the formation of linear supramolecular polymers.[5f] As a result, monomer **1** can form a supramolecular polymer gel in acetonitrile which can go through reversible sol–gel transitions by alternating heating and cooling, or acidification and neutralization.




**Scheme 1** Cartoon representation of the formation supramolecular polymer gel from self-assembly of monomer **1**.

Driven by the host–guest interactions between B18C6 and PAA, linear supramolecular polymers in solution formed, laying a foundation for the formation of supramolecular fibrils. These linear supramolecular polymers self-assembled into bundles, namely one-dimensional fibrils. The van der Waals forces, increasing with the alkyl chain length, plays an important role in the formation of organogel.[5b,5c] Driven by the van der Waals forces between long alkyl chains, these bundles subsequently self-organized to form a cross-linked network which acted as the matrix for the supramolecular gel. Thus three-dimensional fiber networks were constructed via the entanglement of supramolecular fibrils and macroscopic organogels finally formed by combination with solvent molecules (Scheme 1).[4c,4j,12]

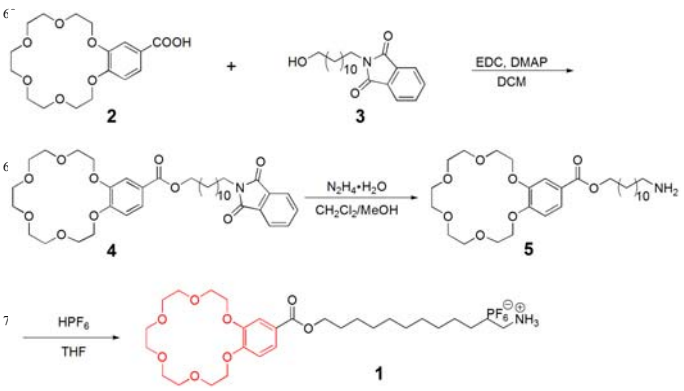
## Experimental section

### General methods

All reagents were commercially available and used as supplied without further purification. Compounds **2**[13] and **3**[14] were prepared according to the published procedures. $^1$H or $^{13}$C NMR spectra were recorded with a Bruker Avance DMX 500 spectrophotometer or a Bruker Avance DMX 400 spectrophotometer with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. 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). Viscosity measurements were carried out with a Cannon-Ubbelohde semi-micro dilution viscometer at 25 °C in chloroform. Scanning electron microscopy investigations were carried out on a JEOL 6390LV instrument or an Ultra-55 instrument .

### Synthesis of 4

A solution of **2** (8.90 g, 25.0 mmol), **3** (16.6 g, 50.0 mmol) and 4-dimethylaminopyridine (DMAP) (3.06 g, 25.0 mmol) in dichloromethane (500 mL) was stirred for 10 minutes at 0 °C. Then EDC (14.4 g, 75.0 mmol) was added. 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 **4** as a pale yellow oil (14.7 g, 88%). The $^1$H NMR spectrum of **4** is shown in Fig. S1. $^1$H NMR ($CDCl_3$, 293 K, 400 MHz) $\delta$ (ppm): 7.82−7.84 (dd, 2H), 7.70−7.71 (m, 2H), 7.65 (d, $J$ = 8.4 Hz, 1H), 7.54 (s, 1H), 6.86 (d, $J$ = 8.4 Hz, 1H), 4.26 (t, $J$ = 6.6 Hz, 2H), 4.19−4.24 (m, 4H), 3.94−3.96 (m, 4H), 3.77−3.78 (m, 4H), 3.65−3.73 (m, 8H), 1.70−1.75 (m, 2H), 1.64−1.67 (m, 2H), 1.25−1.40 (m, 18H). The $^{13}$C NMR spectrum of **1** is shown in Fig. S2. $^{13}$C NMR ($CDCl_3$, 293 K, 125 MHz) $\delta$ (ppm): 167.44, 165.40, 151.87, 147.27, 132.82, 131.16, 122.76, 122.21, 122.11, 113.48, 111.11, 76.31, 76.06, 75.80, 69.92, 69.90, 69.78, 69.72, 69.67, 69.63, 68.47, 68.35, 68.09, 67.85, 63.96, 37.04, 28.49, 28.47, 28.43, 28.27, 28.15, 27.74, 27.57, 25.83, 25.02. LRESIMS is shown in Fig. S3: *m*/*z* 705.8 $[M + Cl]^-$ (100%). HRESIMS: *m*/*z* calcd. for $[M]^-$ $C_{37}H_{51}NO_{10}$, 669.3513; found 669.3508; error –0.7 ppm.




**Scheme 2** Syntheses of compound **4, 5** and **1**.

### Synthesis of 5

To a solution of compound **4** (6.00 g, 8.96 mmol) in $CH_2Cl_2$ (120 mL) and $CH_3OH$ (150 mL) under $N_2$, hydrazine monohydrate was added and the mixture was stirred at 50 °C for 5 h. After evaporation, the mixture was dissolved in chloroform and washed with 3.00 M aqueous NaOH, water, brine and dried over anhydrous $Na_2SO_4$. After filtration, the solvent was removed under reduced pressure to afford **5** as a white solid (4.68 g, 97%). Mp 83.5–85.1 ºC. The $^1$H NMR spectrum of **5** is shown in Fig. S4. $^1$H NMR ($CDCl_3$, 293 K, 400 MHz) $\delta$ (ppm): 7.63−7.65 (dd, 1H), 7.53 (s, 1H), 6.85 (d, $J$ = 8.4 Hz, 1H), 4.26 (t, $J$ = 6.6 Hz, 2H), 4.18−4.20 (m, 4H), 3.91−3.95 (m, 4H), 3.75−3.76 (m, 4H), 3.71−3.72 (m, 4H), 3.68 (s, 4H), 1.70−1.75 (m, 2H), 1.38−1.41 (m, 4H), 1.28−1.32 (m, 16H). The $^{13}$C NMR spectrum of **5** is shown in Fig. S5. $^{13}$C NMR ($CDCl_3$, 293 K, 125 MHz) $\delta$ (ppm): 165.39, 151.77, 147.19, 122.78, 122.24, 113.37, 111.03, 76.30, 76.05, 75.80, 69.88, 69.86, 69.72, 69.66, 69.59, 69.55, 68.43, 68.31, 68.00, 67.77, 63.95, 28.60, 28.51, 28.48, 28.46, 28.45, 28.18, 27.70, 25.91, 24.99. LRESIMS is shown in Fig. S6: *m*/*z* 540.3 $[M + H]^+$ (100%). HRESIMS: *m*/*z* calcd for $[M]^+$ $C_{29}H_{49}NO_8$, 539.3458; found 539.3456; error –0.4 ppm.

### Synthesis of 1

A solution of compound **5** (4.00 g, 7.41 mmol) and excess $HPF_6$ (60%, 5.00 mL) was stirred in THF (50.0 mL) for 24 h to afford a white precipitate which was filtered off and washed with deionized water to afford monomer **1** as a pale yellow oil (4.32 g, 85%). The $^1$H NMR spectrum of **1** is shown in Fig. S7. $^1$H NMR (DMSO, 293 K, 400 MHz) $\delta$ (ppm): 7.56−7.58 (dd, 1H), 7.50 (s, 2H), 7.44 (s, 1H), 7.09 (d, $J$ = 8.4 Hz, 1H), 4.23 (t, $J$ = 8.4 Hz, 2H), 4.13−4.17 (m, 4H), 3.77 (s, 4H), 3.60−3.62 (m, 4H), 3.54−3.56 (m, 8H), 2.75 (t, $J$ = 7.4 Hz, 2H), 1.67−1.69 (m, 2H), 1.42−1.45 (m, 2H), 1.35−1.38 (m, 16H). The $^{13}$C NMR spectrum of **1** is shown in Fig. S8. $^{13}$C NMR (DMSO, 293 K, 125 MHz) $\delta$ (ppm): 165.41, 152.08, 147.50, 123.16, 122.12, 112.68, 111.98, 69.84, 69.67, 69.54, 68.51, 68.41, 68.14, 68.06, 66.98, 64.32, 39.98, 39.81, 39.74, 39.65, 39.48, 39.31, 39.14, 38.98, 38.88, 28.79, 28.74, 28.43, 28.38, 28.03, 26.92, 25.70, 25.30. LRESIMS is shown in Fig. S9: *m*/*z* 540.4 $[M - PF_6]^+$ (100%). HRESIMS: *m*/*z* calcd for $[M]^+$ $C_{29}H_{50}NO_8$, 540.3536; found 540.3536; error 0

ppm.

**Sample preparation**

First, **1** was dissolved in acetonitrile (120 mM) in a vial, followed by subsequently heating to 25 °C to form a transparent solution. Upon cooling in a refrigerator at 4 °C, gelation occured. The reversible gel-sol transitions of the supramolecular polymer gels were induced by two different stimuli: thermo- (heating to 25 °C and then cooling at 4 °C for 2 min) and pH-stimuli (adding 1.50 equiv of triethylamine (TEA) and 1.80 equiv of trifluoroacetic acid (TFA)). In rheological experiments, the samples were prepared as follows: a linear supramolecular polymer was first constructed by dissolving **1** in 0.600 mL of acetonitrile (100 mM). SEM samples were prepared by dissolving monomer **1** in chloroform at high concentration for the supramolecular polymer and in acetonitrile at 100 mM *via* freeze-drying methodology for the gel.

## Results and discussion

**Self-assembly of AB monomer to form supramolecular polymers**

First, host–guest complexation studies of the self-assembly of **1** were carried out. It is known that the complex of B18C6 and the primary ammonium salt has a perched geometry.[11,15] All of the characterizations for the formation of the supramolecular polymers were performed in chloroform owing to the relatively poor solubility of the monomer **1** in acetonitrile. At the beginning, the COSY NMR spectrum (Fig. 1) of **1** in chloroform-*d* confirmed the assignments of concentration-dependent $^1$H NMR spectra (Fig. 2). The complexation between B18C6 and PAA is fast-exchanging systems on the proton NMR time scale. With the increase of the initial monomer concentration, the peaks related to protons $H_1$, $H_2$ and $H_6$ shifted upfield. At high concentration, the peak splitting of all protons disappeared along with broadening, which confirmed the formation of high molecular weight aggregates driven by host–guest interactions between the B18C6 host units and the PAA guest moieties.

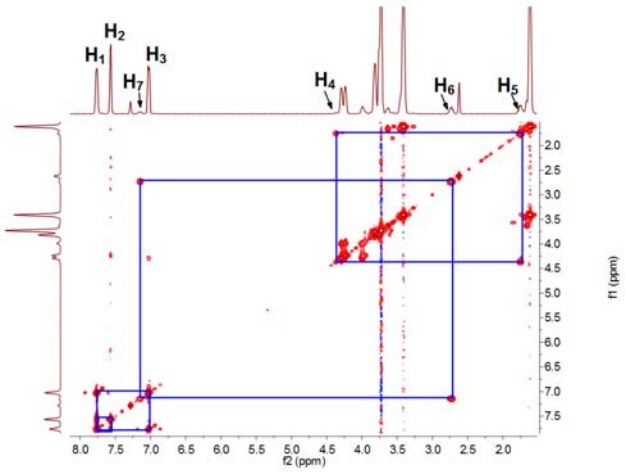



**Fig. 1** Partial COSY NMR ($CDCl_3$, 293 K, 500 MHz) spectrum of **1** at a concentration of 80.0 mM.

To further investigate the self-assembled behaviors of the supramolecular polymers, viscosity measurements were performed in chloroform using a Cannon-Ubbelohde semi-micro dilution viscometer. The linear supramolecular polymer assembled from the monomer **1** showed a viscosity transition and a double logarithmic plot of specific viscosity versus concentration was obtained, indicating a viscosity transition (Fig. 3). At low concentration, the slope of the curve is 1.00, a linear relationship between specific viscosity and concentration was confirmed, suggesting non-interacting assemblies of constant size. With increasing concentration, a remarkable increase in the viscosity was observed as the slope increased to 2.07. Thus the formation of linear supramolecular polymer of increasing size was observed by the stronger concentration dependence.

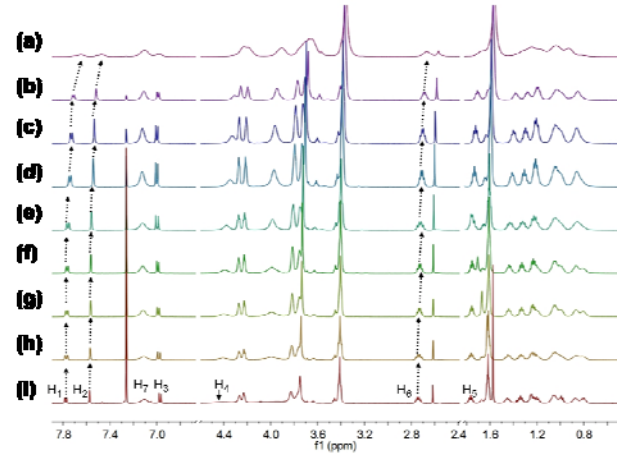



**Fig. 2** Partial $^1$H NMR spectra of **1** ($CDCl_3$, 293 K, 500 MHz) at different concentrations: (a) 400 mM; (b) 250 mM; (c) 182 mM; (d) 100 mM; (e) 50.0 mM; (f) 36.4 mM; (g) 20.0 mM; (h) 11.5 mM; (i) 5.00 mM.

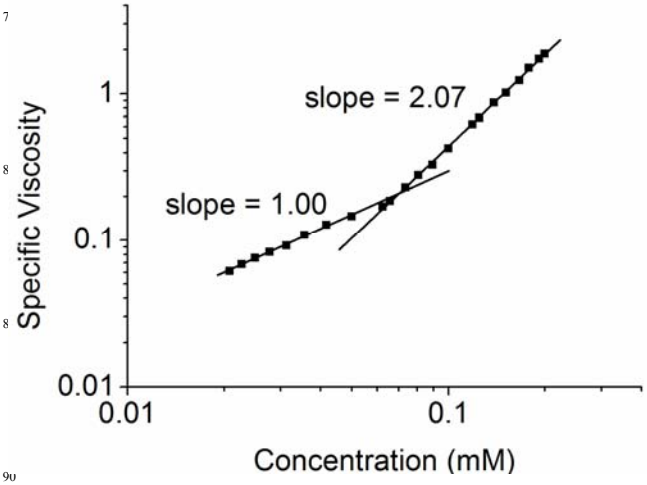



**Fig. 3** Specific viscosity $V_S$ of **1** in chloroform at 298 K versus the crown unit concentration.

Moreover, the formation of supramolecular polymers by monomer **1** in chloroform with high molecular weight and a high degree of linear chain extension can be confirmed by observing rodlike fibers with diameter of ~10.0 μm obtained from a high concentration solution by scanning electron microscopy (SEM) experiments (see Fig. 7a).

**Bulk rheological analyses of the supramolecular polymer gel**

Rheology is perhaps the most important defining feature of supramolecular gels.[16] Therefore, we performed linear oscillatory frequency sweep experiment to obtain the rheological properties of the supramolecular polymer gel constructed from monomer **1**. The storage ($G'$) and loss ($G''$) moduli for a gel made from monomer **1** (150 mM) in acetonitrile are shown as functions of frequency in Fig. 4. According to the frequency sweep curve, there were crossover frequency ($\omega_c$) between the storage modulus $G'$ and the loss modulus $G''$. When the scanning frequency ($\omega$) is lower than $\omega_c$, $G'$ is smaller than $G''$, and the viscous property of samples is predominant. When the scanning frequency ($\omega$) is higher than $\omega_c$, $G'$ is larger than $G''$, and the elastic property of samples is dominant, thus indicating the formation of an organogel.

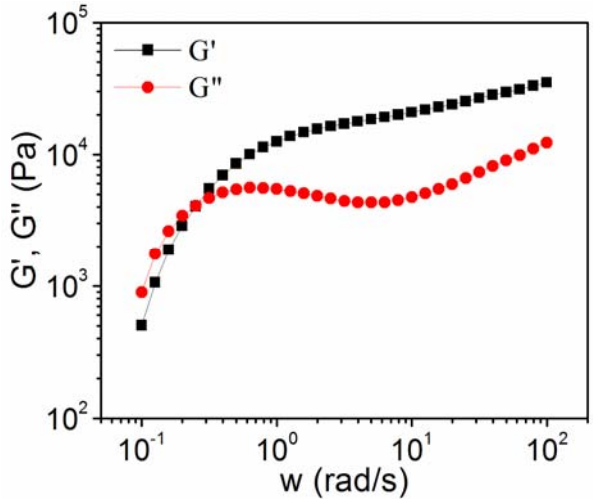



**Fig. 4** Storage modulus ($G'$) and loss modulus ($G''$) of the supramolecular polymer gel versus scanning frequency ($\omega$) for the samples made from monomer **1** (150 mM) in acetonitrile (T = 293 K).

**Stimuli-responsiveness and morphologies of the supramolecular polymer gel**

The A–B monomer **1** can form a supramolecular polymer gel in acetonitrile. Therefore, the gel was prepared by dissolving monomer **1** in $CH_3CN$ at 25 °C and then cooling to room temperature. With the increase of the concentration from 10.0 mM to 60.0 mM of monomer **1**, the solution eventually formed a gel at a temperature of about 25 °C and the critical gel concentration was calculated to be 5.00 wt%.

Interestingly, the supramolecular polymer gel was responsive to two stimuli: thermo and pH-change. As the host–guest interactions between the B18C6 and primary ammonium salt units could be reduced by heating, heating and cooling can result in a reversible gel-sol transition. As shown in Fig. 5, after heating to 25 °C, the gel dissociated into a transparent solution at soon. Re-formation of the gel was achieved by cooling to 4 °C for a while. Meanwhile, the reversible formation of noncovalent bonds between B18C6 and PAA can be controlled by changing the solution pH because of the reversible deprotonation and protonation of the primary alkylammonium salt. Thus, the reversible gel-sol transition can also be realized by alternately adding triethylamine (TEA) and trifluoroacetic acid (TFA) (Fig. 5). It can also be demonstrated by $^1$H NMR experiments for detection of this process. According to Fig. 6, when 40.0 μL of TEA was added, the peaks related to $H_1$, $H_2$, $H_3$ , and $H_4$ and protons on the crown ether ring shifted upfield and split obviously, indicating that TEA broke the host–guest interactions between B18C6 and PAA. On the contrary, after 30.0 μL of TFA was added, the signals of the protons mentioned above shifted downfield and exhibited broadening effect, suggesting the host–guest complexation between B18C6 and PAA was recovered. Moveover, this reversible decomplexation–complexation transition could be repeated (Fig. 6, spectra d and e).

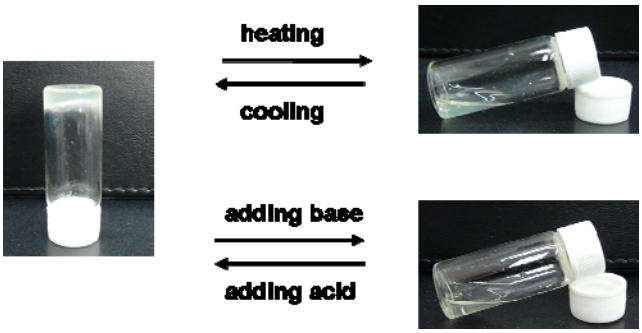



**Fig. 5** The reversible gel-sol transitions of the supramolecular polymer gel triggered by thermo- and pH-stimuli.

The morphologies of the supramolecular polymer xerogels prepared by freeze-drying methodology were examined by scanning electron microscopy (SEM) experiments, exhibiting an extended and interconnected three-dimensional fibrous structures, responsible for the observed gelation.[5a,17] These images provided evidence for that monomer **1** self-assembled at nanoscale through host–guest interactions to form one dimensional fibrils (Fig. 7a). Then a more dense, three-dimensional network was obtained by entangling and cross-linking of these long and fine self-assembled fibrils (Fig. 7b and c). The macroscopic organogel formed *via* entrapping solvent molecules. Moreover, when TEA was added, the organogel collapsed due to the breakage of the host–guest interactions between B18C6 and PAA (Fig. 7d), further confirming the pH-responsiveness of the supramolecular polymer gel.

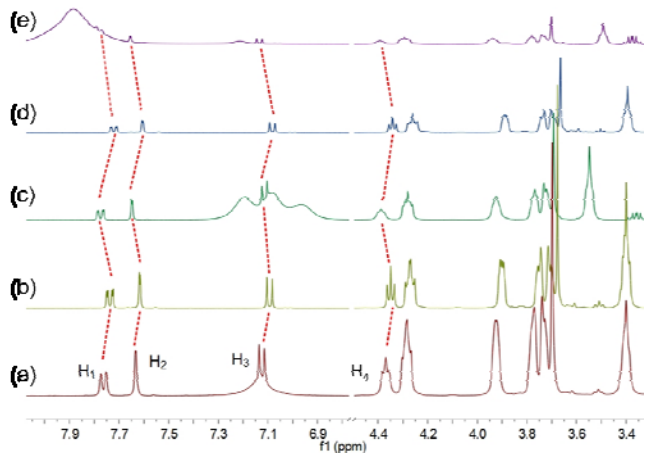


**Fig. 6** Partial $^1$H NMR spectra ($CD_3CN$, 293 K, 500 MHz) of: (a) monomer **1** (100 mM); (b) after addition of 40.0 μL of TEA to a; (c) after addition of 30.0 μL of TFA to b; (d) after addition 40.0 μL of TEA to c; (e) after addition of 30.0 μL of TFA to d.

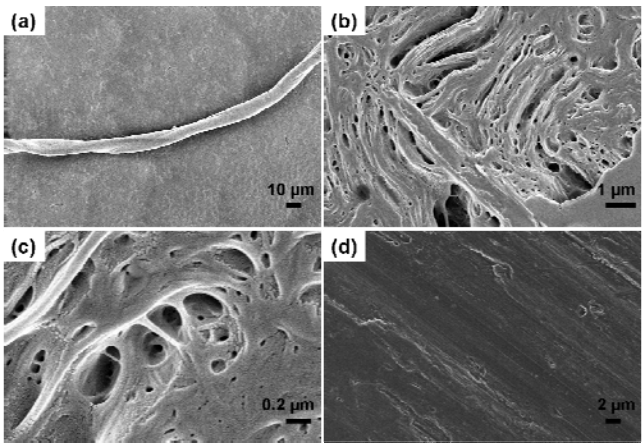



**Fig. 7** SEM images of the aggregates of **1**: (a) rod-like fiber, (b, c) structure of the supramolecular polymer gel, (d) collapsed gels.

## Conclusions

In summary, we have prepared a supramolecular polymer gel by self-assembly of a A–B monomer based on benzo[18]crown-6. The gel is transparent and displays thermo- and pH-stimuli induced reversible gel-sol transitions owing to the dynamically reversible complexation between B18C6 and primary alkylammonium salt moieties. It can be seen that the complex of B18C6 and PAA can be used as a building block to construct supramolecular aggregates, suggesting a promising candidate for advanced material with desired functionalities and potential applications, such as drug-delivery systems, smart actuators, adaptive coatings, biomedical fields and so on.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: compound characterization, full synthetic details, and other materials. See DOI: 10.1039/b000000x/

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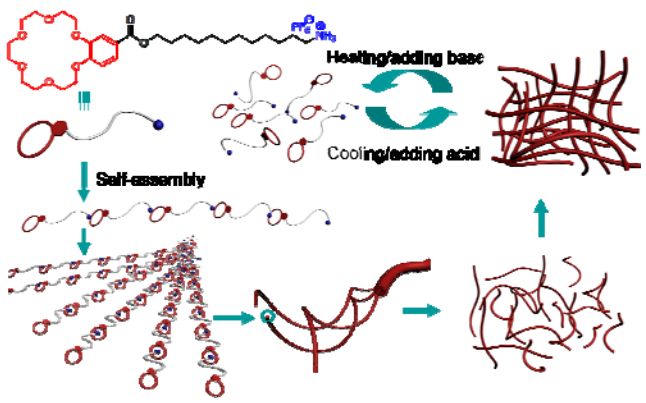
## ToC Graphic:




## Text

A supramolecular polymer gel was prepared from self-assembly of a heteroditopic A–B monomer based on benzo[18]crown-6. Such gel shows interesting gel-sol transitions in response to dual-stimuli owing to the dynamically reversible complexation between benzo[18]crown-6 and primary alkylammonium salt moieties.