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Responsive Gel-like Supramolecular Network Based on Pillar[6]arene−Ferrocenium Recognition Motifs in Polymeric Matrix

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Ⓢ *Supporting Information*
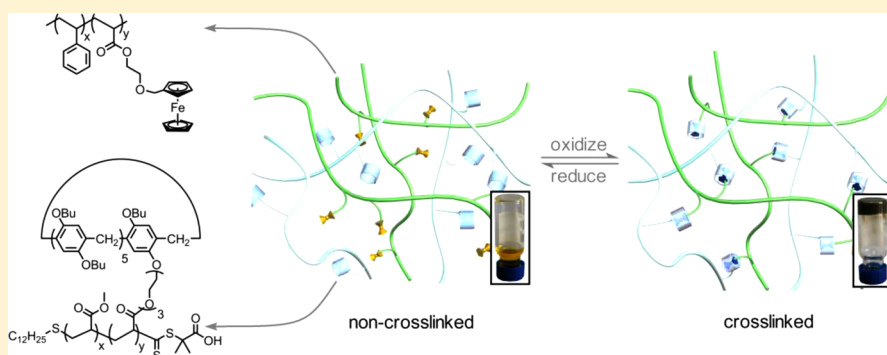
ABSTRACT: A dual-responsive supramolecular network based on pillar[6]arene−ferrocenium redox-controllable recognition motifs in polymeric backbones is constructed with a ferrocenium-functionalized copolymer and a pillar[6]arene copolymer, in which the first example of pillar[6]arene-functionalized copolymer was synthesized through the reversible addition/fragmentation chain-transfer copolymerization of an acrylate-functionalized pillar[6]arene and methyl acrylate. The resulting supramolecular network exhibits dramatically increased viscosity than the non-cross-linked mixtures and demonstrates a gel-like behavior on macroscale with a transient-network behavior revealed by rheology study. Furthermore, the viscoelastic properties of such supramolecular network can be easily controlled by different external stimuli including redox stimulus and competing host/guest reagents.

■ INTRODUCTION

Stimuli-responsive systems, which exhibit controllable properties upon external stimuli such as pH, light, redox, and temperature, have great potentials in the construction of functional materials.[1−4] Developing functional materials based on the responsive host−guest motifs, especially the one with redox-responsiveness, has received remarkable research interests for their wide applications.[1,5,6] Up to now, by applying various redox-active guests, for example tetrathiafulvalene,[7−9] viologen,[10−12] and ferrocene,[13−25] plenty of redox-responsive supramolecular materials have been fabricated with remarkable success. Among them, the redox couple ferrocene/ferrocenium is of particular significance with well-developed synthetic methods and facile redox control in host−guest interactions.[14−25] Numerous studies have already demonstrated the advantages of ferrocene in the construction of redox-controllable systems with its strong binding abilities to suitable hosts such as cyclodextrin and cucurbituril.[14−28] As a matter of fact, most of these reported supramolecular architectures exhibited their self-assembling behaviors only with ferrocene, which

would disassemble when ferrocene was oxidized into ferrocenium. However, few studies in the opposite way have been reported, in which host−guest systems could be constructed from ferrocenium moieties[29−32] but disassembled by the reduction of ferrocenium into ferrocene. The reasons might be the great difficulty in constructing and studying the ferrocenium-based host−guest architectures caused by the instability[33] and paramagnetism of ferrocenium and the usually weaker host−guest binding abilities of ferrocenium than that of ferrocene. Nevertheless, employing ferrocenium moiety to construct novel functional supramolecular materials is of particular significance since ferrocenium species could be used as ionic liquids[34,35] or synthetic reagents[36] and also showed some biochemical applications.[37] Recently, a dual-responsive supramolecular system was reported by Harada and co-workers, in which the ferrocenium species exhibited
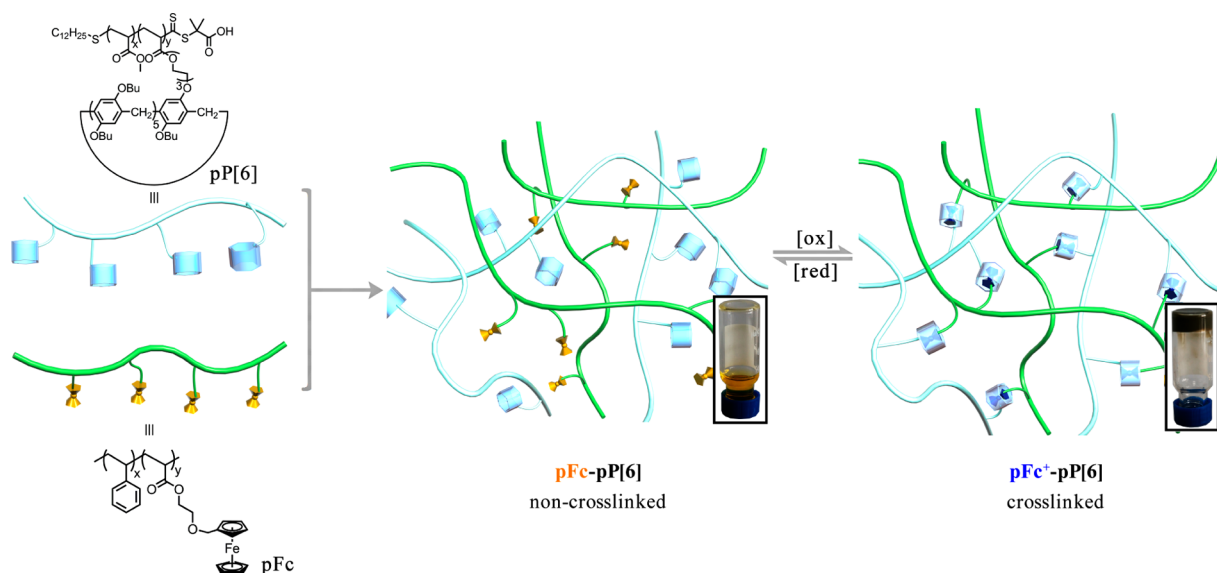
Scheme 1. Representation of the Redox-Controllable Supramolecular Network pFc⁺-pP[6] Based on the Functionalized Polymers

pFc-pP[6]
non-crosslinked

pFc⁺-pP[6]
crosslinked

Scheme 2. Synthesize of the Copolymer pP[6] and pFc

(a)

pP[6]
x/y = 20

(b)

pFc
x/y = 8
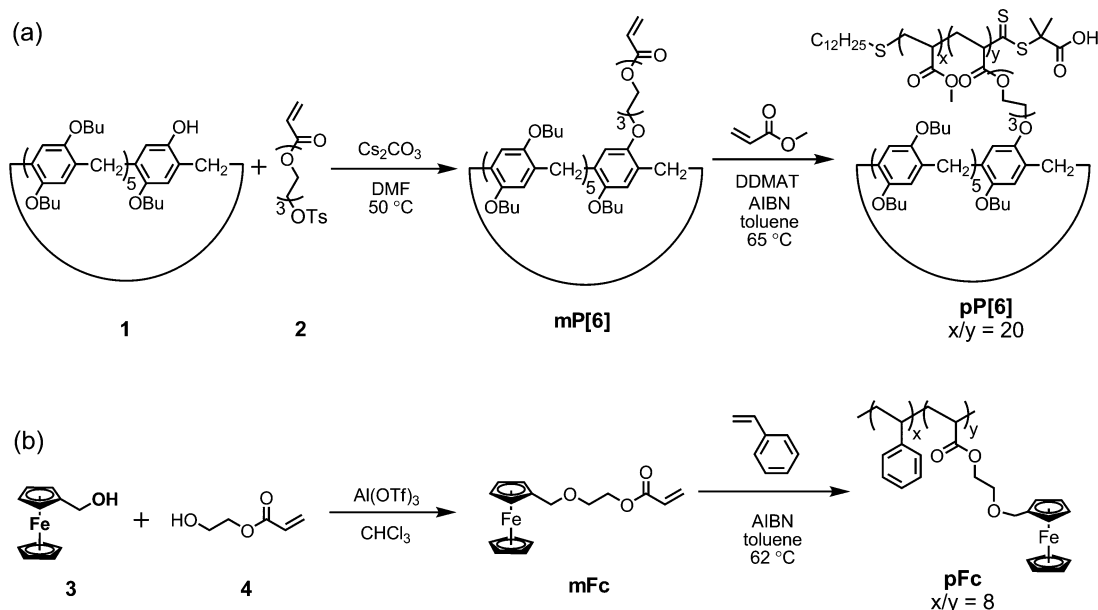
impressive macroscopic self-assembling properties based on electrostatic interactions.[38] However, the construction of responsive supramolecular self-assembled materials based on the host–guest interactions of ferrocenium moiety still remains a big challenge.

Pillar[6]arene, as a member of the macrocyclic host family, has a unique cylinder-like shape and a suitable cavity,[39−42] which endows pillar[6]arene quite attractive binding ability with various guests[43−51] and extensive applications in the construction of novel supramolecular architectures.[52−57] Our previous work demonstrated that ferrocenium (Fc⁺) cation exhibited strong binding affinity and considerably improved stability with per-butylated pillar[6]arene in organic solvent; in addition, their host–guest inclusion complex exhibited remarkable redox-responsive properties with reduction-induced disassemble behaviors due to the negligible binding affinity of

ferrocene with pillar[6]arene.[46] Accordingly, ferrocenium-based redox-controllable supramolecular dynamic materials could be constructed by using pillar[6]arene-functionalized polymeric materials. However, pillar[6]arene-functionalized "traditional" polymers still have not been synthesized until now, leaving a family of promising polymeric materials remains to be explored. Therefore, preparing pillar[6]arene-based polymeric materials and further use them to construct redox-controllable functional materials with ferrocenium derivatives is quite an attractive and challenging task.

Herein, we design and synthesize the first random copolymer with pendant pillar[6]arene groups, pP[6], by using the reversible addition/fragmentation chain-transfer (RAFT) method. It was found that pP[6] exhibited strong binding affinity with ferrocenium moieties. By mixing pP[6] and a ferrocenium-functionalized copolymer pFc⁺, a redox-controllable supra-

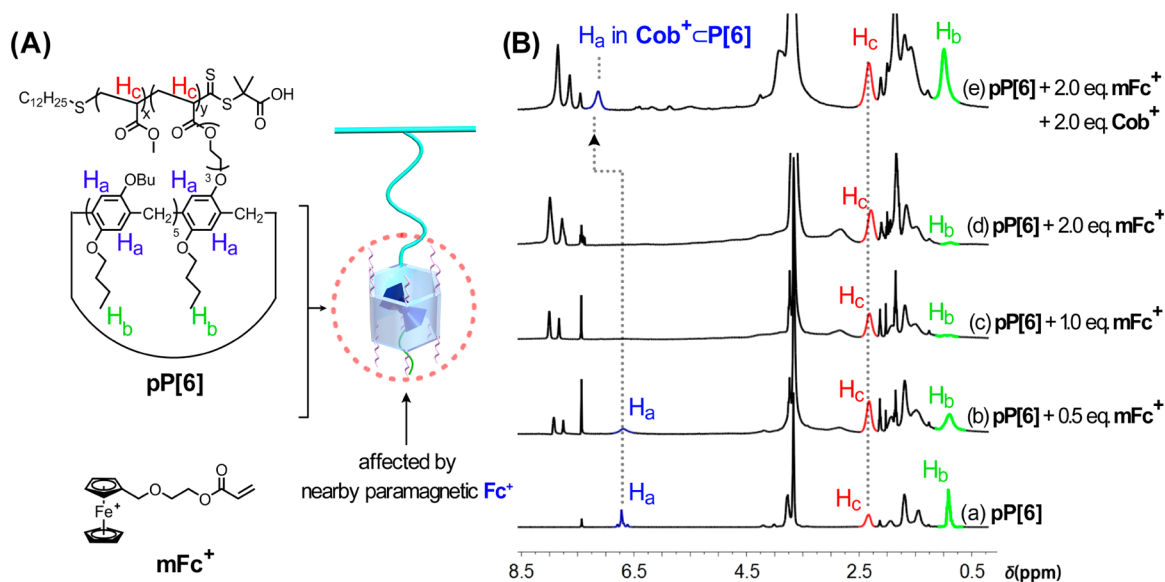**Figure 1.** (A) Cartoon representation of the binding between the pP[6] and mFc[+]. (B) ^{1}H NMR spectra (CDCl$_3$/CD$_3$COCD$_3$ = 5/1, v/v, 300 MHz, 298 K) of pP[6] in the presence of increasing equiv of guest: (a) 0.0 equiv, (b) 0.5 equiv of mFc[+], (c) 1.0 equiv of mFc[+], (d) 2.0 equiv of mFc[+], (e) both 2.0 equiv of mFc[+] and 2.0 equiv of Cob[+]PF$_6$[−] (blue: H$_a$; green: H$_b$; red: H$_c$).

molecular network could be formed based on the host−guest interaction between the ferrocenium−pillar[6]arene recognition motifs (Scheme 1). This redox-controllable supramolecular network exhibited a gel-like behavior on macroscale and a transient-network behavior revealed by rheology study. Moreover, such host−guest-based supramolecular cross-linking could be controlled by different external stimuli including redox and competing host/guest reagents, accompanied by an obvious change in the macroscopic behavior of the sample.

■ RESULTS AND DISCUSSION

Design and Synthesis of the Functionalized Copolymers. To prepare the pillar[6]arene copolymer pP[6], an acrylate functionalized pillar[6]arene monomer (mP[6]) was first synthesized in good yields via the etherification of monodeprotected per-butylated pillar[6]arene 1 and a tosylated acrylate derivatives 2 in DMF (Scheme 2a), in which the triethylene glycol was introduced as a spacer between the acrylate and the pillar[6]arene moieties in consideration of the bulky butyl groups on the pillar[6]arene moiety. Initially, attempts to achieve the homopolymer of mP[6] were found to be quite difficult since most of the monomer mP[6] remained unreacted even after heating at 80 °C for 48 h, which might be attributed by the strong steric hindrance of the bulky pillar[6]arene moiety. However, to our delight, the copolymerization of methyl acrylate and mP[6] could provide a facile approach to the target polymer with pendant pillar[6]arene groups. The RAFT polymerization process, where 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT) was employed as the chain transfer agent (CTA) under a feeding ratio of 95/5 (methyl acrylate/mP[6]), gave the random copolymer pP[6] with 4.8% pendant pillar[6]arene groups (Scheme 2a; M_n = 104 kDa, PDI = 1.34). To the best of our knowledge, this is the first synthesis of a random copolymer with pendant pillar[6]arene groups.

Next, the random copolymer with pendant ferrocene groups, pFc, was synthesized by a traditional "uncontrolled" free radical copolymerization of styrene and an acrylated ferrocene monomer (mFc), which was synthesized in moderate yield

through the direct etherification of hydroxymethylferrocene (3) and 2-hydroxyethyl acrylate (4) under the catalysis of aluminum triflate (Scheme 2b).[58] And the random copolymer pFc with 11.1% pendant ferrocene groups was successfully obtained (Scheme 2b; M_n = 174 kDa, PDI = 1.95). In our case, compared with the more commonly used ferrocenecarboxylic acid derivatives,[15−18,21,38] mFc provides both less steric hindrance and moderate oxidization conditions with the electron-donating methylene group. More importantly, it is much easier to be oxidized by Ag^{+} cation in organic solvents, which is practically important since the pillar[n]arenes has been reported to be easily oxidized by strong oxidant such as (NH$_4$)$_2$[Ce(NO$_3$)$_6$].[59]

Host−Guest Complexation Studies. Our previous work demonstrated that pillar[6]arenes have strong binding affinities with ferrocenium and its analogue cobaltocenium (K_a = (2.0 ± 0.1) × 10[4] and (3.1 ± 0.1) × 10[4] M^{−1}, respectively).[46] In the present work, we found that the steric hindrance of the copolymer backbone was not prohibitive, and the pendant pillar[6]arene groups remained its good host−guest recognition properties to ferrocenium and cobaltocenium. First, an attempt to investigate the interactions between the ferrocenium moiety mFc[+] and pP[6] was carried out by ^{1}H NMR titration experiment in the mixed solvent (CDCl$_3$/CD$_3$COCD$_3$ = 5/1, v/v). To our surprise, despite the paramagnetic nature of ferrocenium derivatives, the ^{1}H NMR titration study demonstrated distinct change during the titration, which provided critical evidence for the inclusion of ferrocenium moiety into the pendant pillar[6]arene groups of pP[6]. During the ^{1}H NMR titration, monomer mFc[+] was used as a template instead of the copolymer since the aromatic protons of the styrene from pFc[+] significantly overlap with the aromatic protons of pillar[6]arene. The ferrocene derivatives mFc, which stores in the more stable reduced state after the etherification, was oxidized to ferrocenium derivatives mFc[+] with Ag{B-[C$_6$H$_3$(CF$_3$)$_2$]$_4$} (AgBArF) before use. Upon addition of the mFc[+], the protons of the aromatic rings from the pendant pillar[6]arene groups (H$_a$) dramatically broadened, decreased, and further disappeared completely after adding 1.0 equiv of

mFc$^+$. Meanwhile, the protons from the methyl groups of the pillar[6]arene (H$_b$) exhibited a similar behavior, whereas the signal of the polymer backbone CH (H$_c$) did not exhibit any changes during the titration process (Figure 1a−d). Disappearance of the other protons from pillar[6]arene groups could hardly be distinguished because of their severe overlapping with the polymer backbone protons. It is clear that in the titration experiments the paramagnetic ferrocenium groups were acting as paramagnetic probes driven by the host−guest interactions. And the changes on the above NMR titration spectra have demonstrated that the paramagnetic mFc$^+$ was included in the pillar[6]arene cavity and far away from the polymer backbone (Figure 1A), since the paramagnetic probes normally affect the signals of nearby nucleus.[60] More importantly, cobaltocenium hexafluorophosphate (Cob$^+$PF$_6^-$) was further added as a competing guest since Cob$^+$PF$_6^-$ has a stronger binding affinity with mP[6] (K_a = (3.9 ± 0.9) × 10^4 M^{-1}; see Figure S11, Supporting Information). When the same equiv of Cob$^+$PF$_6^-$ was added, the reappearance of the pillar[6]arene protons was observed (Figure 1e) due to the fact that the added Cob$^+$PF$_6^-$ led to partial replacement of mFc$^+$⊂pP[6] inclusion complex with Cob$^+$⊂P[6], which resulted a broadened singlet peak very similar to that of the titration experiments of Cob$^+$PF$_6^-$ and pP[6] (Figure S9, Supporting Information). Additionally, by comparing the integrals of H$_a$ and H$_c$, we could conclude that about half of the pillar[6]arene was recovered after the competing experiments (Figure 1e), which further revealed the binding ability of the mFc$^+$ with the copolymer pP[6].

Furthermore, electrochemistry methods including cyclic voltammetry (CV) and square-wave voltammetry (SWV) studies were also used to investigate the binding properties of pFc$^+$-pP[6] complex. In CV experiments, the pFc exhibited a typical one-electron redox process of ferrocene group in the mixed solvent (CHCl$_3$/CH$_3$COCH$_3$ = 5/1, v/v). Compared with the normally reversible process of small molecular ferrocene derivatives, the CV of the copolymer pFc was irreversible with a ΔE_p larger than 130 mV, similar to some other ferrocene-based polymers.[61] Upon addition of pP[6], an obvious cathodic shift could be observed (Figure 2a and Figure S12, Supporting Information), indicating that the oxidized form pFc$^+$ exhibited much stronger binding affinities with pP[6] than pFc. Similar to the ^{1}H NMR titration experiments, further addition of competing guest Cob$^+$PF$_6^-$ into the pFc$^+$-pP[6] mixture led to the disassembly of pFc$^+$-pP[6] complex, resulting in a backward shift (anodic) in the CV tests (Figure 2a). Moreover, SWV tests were also carried out to give a detailed comparison of the E_p (Figure 2b and Figure S13, Supporting Information). Similar to the CV experiments, the SWV curves showed that the oxidizing potential of pFc first exhibited a cathodic shift of 57 mV upon addition of 4.0 equiv of pP[6], while a backward shift (anodic) of 34 mV was observed when another 4.0 equiv of the competing guest Cob$^+$PF$_6^-$ was continuously added into the mixture (Figure 2c). The SWV experiments also suggested the superior binding affinities of pFc$^+$ to pP[6] than that of pFc. Furthermore, an estimation about the binding constant of these ferrocenium and pillar[6]arene motifs was carried out by electrochemical methods, since their exact binding constant is rather difficult to be calculated by NMR or UV technique. By using the monomer as templates, an estimated binding constant between mFc$^+$ and mP[6] (K_{ox} = (3.8 ± 0.04) × 10^3 M^{-1}) was given based on the method reported by Godínez, Kaifer, and co-workers (Figures S20 and S21, Supporting Information).[62]
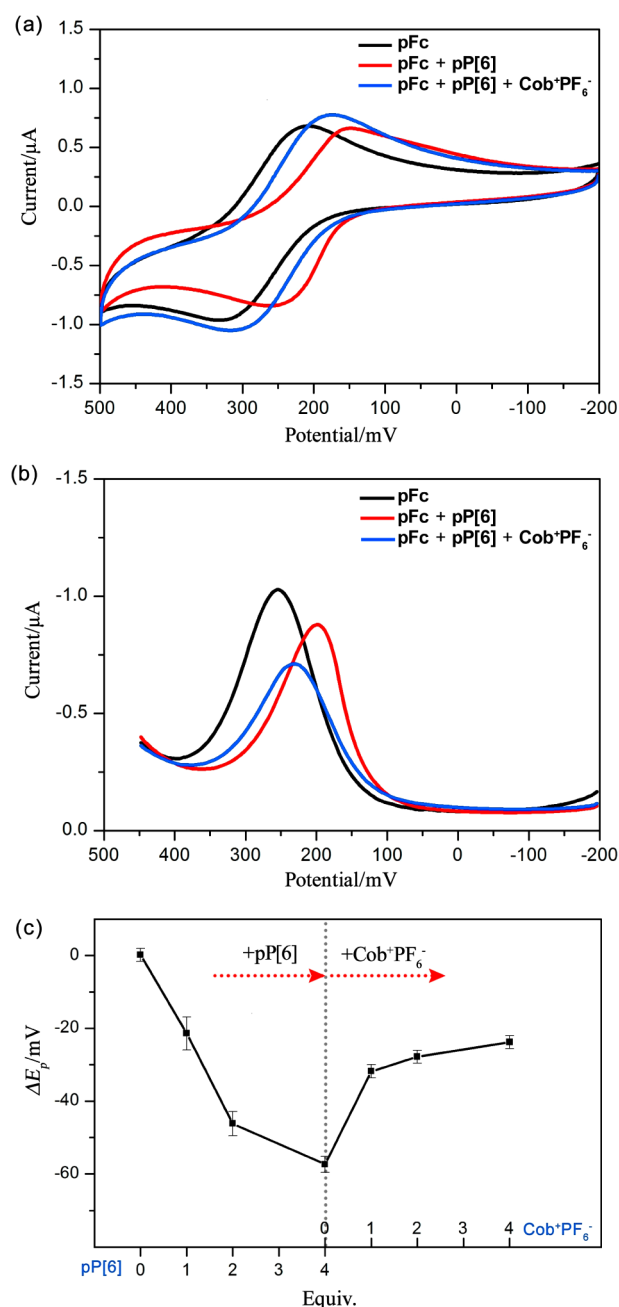

Figure 2. (a) Cyclic voltammograms (scan rate = 50 mV s^{-1}) and (b) square-wave voltammograms (pulse amplitude = 20 mV, step potential = 4 mV, frequency = 5 Hz) of the pFc in the absence or presence of pP[6] and Cob$^+$PF$_6^-$ (black: pFc; red: pFc with 4.0 equiv of pP[6]; blue: pFc with both 4.0 equiv of pP[6] and 4.0 equiv of Cob$^+$PF$_6^-$). (c) ΔE_p of the pFc in the SWV experiments upon the addition of pP[6] and Cob$^+$PF$_6^-$. The mixed solvent (CHCl$_3$/CH$_3$COCH$_3$ = 5/1, v/v) containing 0.1 M NaBArF was used in both CV and SWV experiments. See Experimental Section for detailed information.

Formation of the Gel-like Supramolecular Network.

As we have demonstrated that the pendant ferrocenium/pillar[6]arene groups on pFc$^+$ and pP[6] could bind with each other, a redox-trigged supramolecular network could thus be constructed by the two random copolymer pFc and pP[6]. Simply dissolve the pFc and pP[6] in equal equivalent with a mixed solvent (CHCl$_3$/CH$_3$COCH$_3$ = 5:1, v/v, 10 wt %), resulting in a free-flowing orange solution, demonstrated the negligible interactions between pFc and pP[6]. However,

further oxidizing the ferrocene groups with AgBArF immediately affords a pFc⁺-pP[6] supramolecular network cross-linked by the ferrocenium—pillar[6]arene host—guest interactions. Meanwhile, mixing a solution of pP[6] and a solution of preoxidized pFc⁺ could also give the same supramolecular polymeric network. This pFc⁺-pP[6] network exhibited a dramatically increased viscosity comparing to the corresponding non-cross-linked pFc⁺ and pP[6] solutions, which behaved as low-viscosity free-flowing solutions. This significant difference in the macroscopic properties between cross-linked pFc⁺-pP[6] and non-cross-linked solutions could be demonstrated by the invert-vial experiments (Figure 3a,b). Rheology results
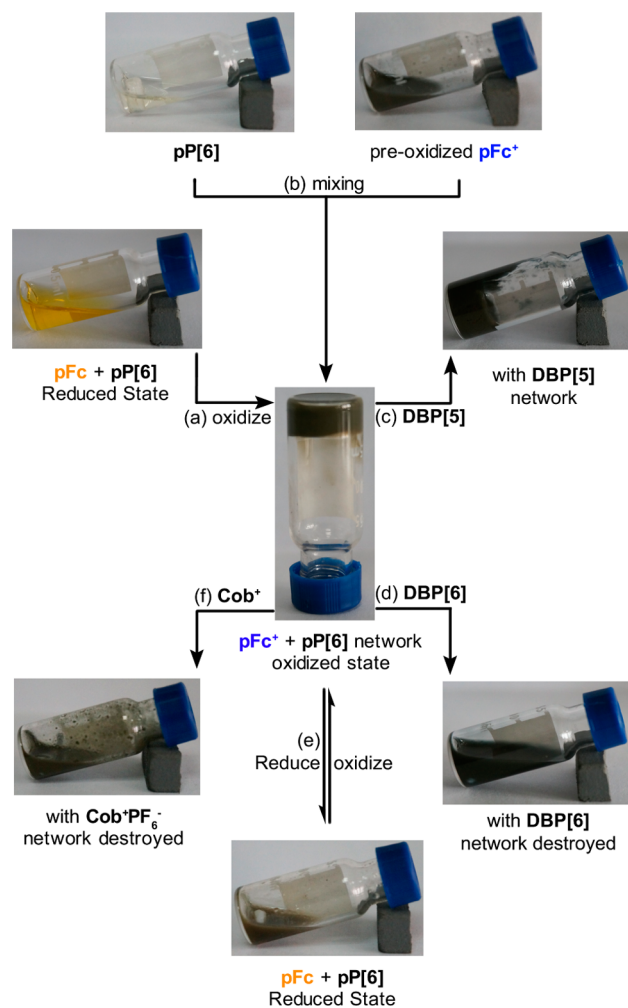

Figure 3. Formation of the pFc⁺-pP[6] network (a, b). Responses to external stimuli: (c) 5.0 equiv of DBP[5], (d) 5.0 equiv of DBP[6], (e) redox control (oxidant: AgBArF; reductant: hydrazine), (f) 5.0 equiv of Cob⁺PF₆⁻.

showed detailed information on the pFc⁺-pP[6] supramolecular network. An oscillatory experiment of the pFc⁺-pP[6] suggested a transient network behavior with the storage modulus G' larger than the loss modulus G'' at high oscillatory frequency, but less than the loss modulus G'' at low frequency at 0 °C (with a crossover point at $G' = G'' = 9945$ Pa, Figure 4a). Furthermore, the SEM images revealed the microstructure of the pFc⁺-pP[6] supramolecular network, and its freeze-dried sample exhibited a nonuniform, net-like structure (Figure 4b and S18, Supporting Information).
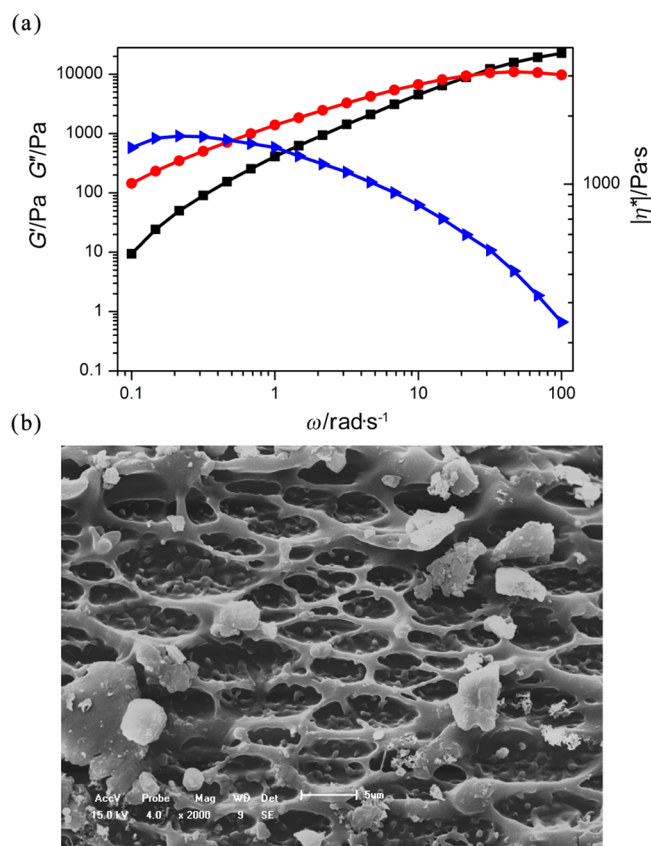

Figure 4. (a) Oscillation frequency sweep of pFc⁺-pP[6] network at 0 °C (storage modulus G' (black, ■), loss modulus G'' (red, ●), complex viscosity (blue, ▶)). (b) SEM images of the freeze-dried network sample.

Stimuli-Responsive Properties. The macroscopic properties of the pFc⁺-pP[6] supramolecular network could be controlled by different external stimuli. First, competing host/guest studies were performed to investigate the responsiveness of the pFc⁺-pP[6] network. As expected, the network exhibited obvious response to the competing host/guest with a significant decrease in viscosity. Excess amount of the competing host/guest (DBP[6] or Cob⁺PF₆⁻) could prevent the cross-linking and make it become a low-viscosity fluid (Figure 3d,f); in contrast, the presence of noncompeting host (per-butyl pillar[5]arene, DBP[5]) could not affect the cross-linking (Figure 3c), since the cavity of pillar[5]arene is too small for ferrocenium guests.[46] Furthermore, a comparison of the viscoelastic properties with increasing amount of the competing host was given (Figure S17, Supporting Information). Upon the addition of competing host DBP[6], a dramatic decrease of the viscosity could be observed (up to 7000-fold decrease in the presence of 5.0 equiv of DBP[6]), which clearly demonstrated the critical role of the ferrocenium-pillar[6]arene supramolecular interactions in the formation of the network (Figure 5).

Subsequently, the cross-linking of the network could also be switched by chemical redox reagent, by which the redox control of the supramolecular network was achieved. In our case, hydrazine was used as the reduce reagent to reduce the oxidized pFc⁺ to pFc (Figure 3e). It was found that adding a slightly excess amount of hydrazine to the pFc⁺-pP[6] network which was obtained by oxidizing the pFc-pP[6] mixture using AgBArF could lead to the de-cross-linking of such network, and the
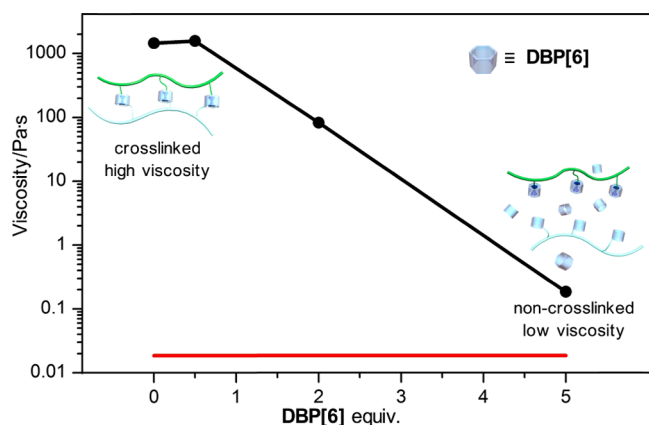
Figure 5. Viscosity of pFc⁺-pP[6] network in the presence of increasing equiv of DBP[6] (black point) and the viscosity of the pFc-pP[6] mixture (represent by the red line, without additional DBP[6]) before oxidize (ω = 1.0 rad s^{-1}).

resulting reduced pFc-pP[6] mixture behaved as a low-viscosity free-flowing fluid. Moreover, such redox cycles could be performed when the reduced sample was further oxidized with 2.0 equiv of AgBArF, and the reduced mixture could cross-link again, which could be monitored by an invert-vial experiment (Figure 3e).

EXPERIMENTAL SECTION

Materials. The synthetic details of acrylate derivatives **2**, pillar[6]arene monomer mP[6], ferrocene monomer mFc, copolymer pP[6], and copolymer pFc are shown in the Supporting Information. The mixed solvent (CHCl₃/CH₃COCH₃ = 5/1, v/v) was prepared just before use. All samples containing ferrocenium were prepared in a glovebox, sealed carefully, and tested as soon as possible to prevent the possible decomposition of ferrocenium. The mole ratios (equiv) described in this article were all calculated by comparing the mole number of the pendant functional groups (pillar[6]arene and ferrocenium), instead of the exact mole number of the copolymer.

Preparation of the mFc⁺. The monomer mFc⁺ used in the ¹H NMR titration experiments was preoxidized before titration. To perform the experiment, the monomer mFc was first dissolved in the mixed solvent (CDCl₃/CD₃COCD₃ = 5/1, v/v) to form an orange solution, which was then oxidized with 2.0 equiv of Ag{B[C₆H₃(CF₃)₂]₄} (AgBArF) and filtrated with a 0.45 μm filter membrane to afford a clear blue solution as the stock solution of mFc⁺ and used in the titration experiments.

Electrochemistry. The CV and SWV experiments were carried out on a CHI630D electrochemical analysis system in the mixed solvent (CHCl₃/CH₃COCH₃ = 5/1, v/v) containing 0.1 M Na{B[C₆H₃(CF₃)₂]₄} (NaBArF). A glassy carbon working electrode (disk, A = 0.07 cm²) and a platinum flag counter electrode (0.2 mm × 0.5 mm) were used. The reference electrode used in these experiments was an Ag/Ag⁺ reference electrode filled with 0.010 M AgNO₃ solution (in acetonitrile). All CV experiments were performed with a scan rate of 50 mV s^{-1}. SWV experiments were conducted with 4 mV step potential and 20 mV pulse amplitude at 5 Hz.

Rheology. The sample was prepared by mixing the solutions of pP[6] and oxidized pFc⁺ together under stirring (mixed solvent, CHCl₃/CH₃COCH₃ = 5/1, v/v). In brief, pFc (0.070 g) was dissolved in the mixed solvent (0.60 mL), and a

solution of AgBArF (0.117 g) in the mixed solvent (0.60 mL) was added to oxidize the ferrocene groups. The mixture was then passed through a 0.45 μm filter membrane and used as the stock solution. To a solution (0.09 mL) of pP[6] (0.0326 g) in the presence (or absence) of competing host DBP[6], the pFc⁺ stock solution (0.20 mL) was added under stirring to prepare the sample (10 wt % for the polymer blends). Rheology experiments were conducted on a HAAKE Rheo-Stress 600 instrument. All rheological experiments were carried out at 0 °C to reduce the evaporation of the solvent during measuring. All the steady shear measurements were conducted with a set of 35 mm diameter parallel plates to obtain the viscosity at the first Newtonian region. All the dynamic oscillatory shear measurements were conducted from 0.1 to 100 rad s^{-1} with a set of 20 mm diameter parallel plates under a strain of 1%.

CONCLUSIONS

In summary, we have developed an effective method to synthesize the first example of pillar[6]arene-functionalized copolymer pP[6] by using the RAFT polymerization method. Moreover, a ferrocene-functionalized copolymer pFc was prepared and then used to fabricate the pFc⁺-pP[6] supramolecular network, which showed a transient-network behavior revealed by rheology studies and exhibited a gel-like behavior on macroscale. Additionally, based on the redox-responsive ferrocenium-pillar[6]arene host−guest interactions, the supramolecular cross-linking of the network could be controlled by different external stimuli, including chemical redox reagent and competing host/guest. Various techniques including ¹H NMR, electrochemistry, and rheology were applied to prove the critical role of the ferrocenium−pillar[6]arene host−guest interactions in the formation of this supramolecular network. This present study has provided a novel and useful approach to construct redox-controllable supramolecular architectures based on ferrocenium motifs. Further exploring of functional materials and multiresponsive supramolecular systems with ferrocenium derivatives is now ongoing in our lab.

ASSOCIATED CONTENT

ⓈSupporting Information

Experimental procedures and characterization data for new compounds; analytical data including ¹H NMR titration spectra, electrochemical and rheology studies. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.5b00889.

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Notes

The authors declare no competing financial interest.

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