ACS Macro Letters

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Multistimuli Responsive and Electroactive Supramolecular Gels Based on Ionic Liquid Gemini Guest

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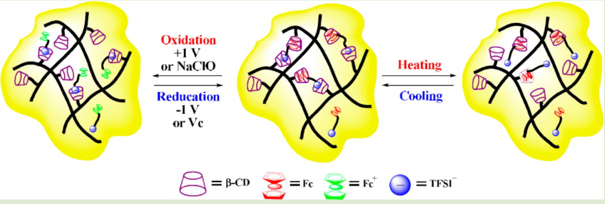
Supporting Information

ABSTRACT: Electroactive supramolecular gels with multistimuli responsiveness were fabricated through host–guest interactions between a host polymer containing β-cyclodextrin (CD) and an ionic liquid (IL) type asymmetric gemini guest, which contains both ferrocene (Fc) and bis(trifluoromethyl-sulfonyl)imide (TFSI$^-$) as the respective α- and ω-guest groups. Owing to the multiple stimuli-responsiveness of the host–guest interactions, reversible sol–gel phase transition could be triggered by various stimuli, including temperature, electrochemical/chemical redox and anion-exchange reactions. Due to the intrinsically conductive properties of the IL gemini guest, the sol–gel transition behavior could be electrochemically controlled by the applied voltage, without using additional supporting electrolyte.



Supramolecular gels with fascinating molecular structures and unique chemical/physical properties have attracted much attention in recent years.[1] Noncovalent interactions, such as hydrogen-bonding,[2] metal-coordination bonding,[3] $\pi-\pi$ stacking,[4] and hydrophobic effect[5] have been successively employed in this research field. Compared with traditional gels, supramolecular gels show not only traditional gel properties but also possess additional functions (such as stimulus-responsiveness[6] and self-healing[7]) arising from their dynamic behavior. During the past years, the development of stimulus-responsive gels has attracted much attention due to their potential applications in smart materials, and the fields of matrix chemistry, medicine, and biochemistry.[1a,8]

Macrocyclic hosts, including cyclodextrins (CDs),[9] crown ethers,[10] pillar[n]arenes,[11] and cucurbit[n]urils,[12] have been extensively studied to fabricate supramolecular gels. The resultant gels show designed stimulus-responsiveness upon temperature,[13] pH,[14] light,[15] or oxidizing/reducing agents.[16] However, most of these studies mainly focus on the stimuli responsive sol–gel phase transition behavior, other physical properties changes behind the sol–gel transition phenomena (more than dual-responsiveness) have been rarely reported because this may require complicated chemical synthesis and rational molecular design.

Ionic liquids (ILs) are organic salts which have gained a great deal of both academic and industrial attention because of their low volatility, high ion conductivity, and wide electrochemical window.[17] It has been recently shown that ILs containing bis(trifluoromethyl-sulfonyl)imide (TFSI$^-$) anions are able to form host–guest complexes with CD,[18] consequently, pseudo-LCST phase behavior in water is observed.[19] On the other hand, inclusion complexation between CD and ferrocene (Fc) derivatives has also been highly studied because the dissociation and reassembly of CD and Fc based on the redox state of Fc can be tuned by either redox reagents or electrochemical stimulus[6b,20] and, thus, may be applied for the design of electrically switchable materials.

In this work, we report the preparation of electroactive supramolecular gels with multiple stimuli-responsiveness. The supramolecular gels were fabricated by the host–guest interactions between a host polymer containing β-CD (pAOI-β-CD, see Figure 1 and Scheme S1), and a designed asymmetric IL gemini guest, a Fc-based imidazolium-type IL (Fc-[BIM]TFSI), which using Fc and TFSI$^-$ as the respective α- and ω-guest groups to act as a noncovalent cross-linker, as presented in Figure 1. The reversible sol–gel phase transition behavior could be easily triggered by multiple stimuli, including temperature, anion-exchange, electrochemical, and chemical redox reactions. It should be noted that electrochemical stimulus plays an important role in controlling the assembly/disassembly of supramolecular systems because it does not contaminate the system. Compared with the stimulus-responsive gels reported,[6b] of special note here is that the use of the present intrinsically electroactive asymmetric IL gemini guest leads to a novel electroactive supramolecular material without additional supporting electrolyte.

Herein, pAOI-β-CD was synthesized via traditional radical polymerization (Scheme S1 and Table S1). The asymmetric IL gemini guest, Fc-[BIM]TFSI, was readily accessible from the esterification and quaterisation reaction between Fc and imidazolium cations (Scheme S2). The 1:1 (molar ratio) mixture of pAOI-β-CD (15 wt %) and Fc-[BIM]TFSI (4 wt %)

Received: February 24, 2014
Accepted: February 27, 2014
Published: March 3, 2014

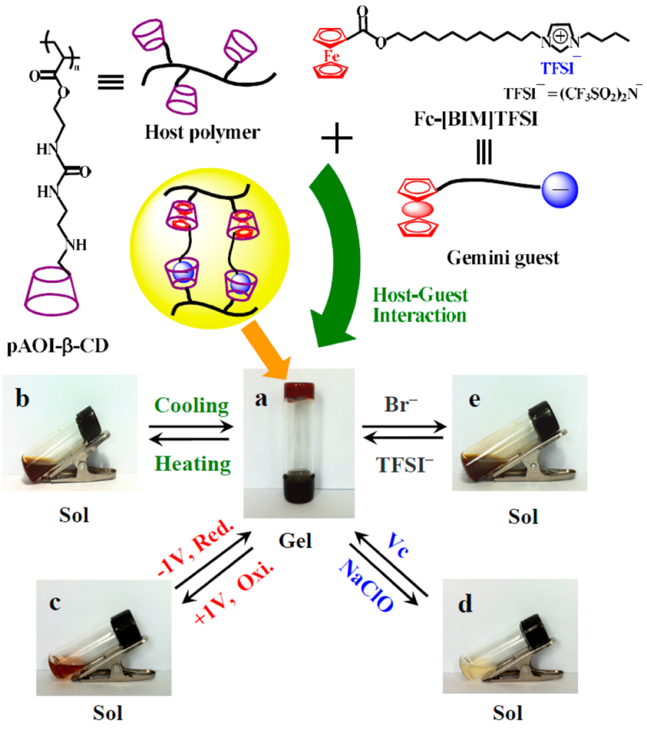


Figure 1. Preparation of ionic liquid gemini guest cross-linked electroactive supramolecular gels and their assembly and disassembly induced by multistimuli.

in DMSO/CHCl$_3$ (4:1, *v*/*v*) solution instantaneously produced a light-brown gel (Figure 1a).

In order to get detailed insights into the nature of the complex system, NMR spectrum analysis was first carried out. As shown in ^{1}H NMR spectra (Figure 2A) that the pure gemini guest Fc-[BIM]TFSI (before the interacted with pAOI-*β*-CD) shows three sets of peaks (H_{1-2}, H_{3-4}, H_{5-9}) with similar positions that were assigned to the protons of pure ferrocene.[6b,20] However, upfield shifts were observed for H_{1-2}, H_{3-4}, and H_{5-9} after the addition of pAOI-*β*-CD, indicating the inclusion complexation between *β*-CD and Fc group occurred. Nuclear Overhauser enhancement NMR spectroscopy (NOESY) also provided direct evidence for this inclusion complex (Figure S2). The inner protons of *β*-CD at the side chain of pAOI-*β*-CD were correlated to the protons of the Fc group of Fc-[BIM]TFSI, confirming that spatial proximity of the Fc group and *β*-CD. Moreover, a significant influence of pAOI-*β*-CD on the fluorine signals of the TFSI— anion was also observed in ^{19}F NMR spectra (Figure 2B). As the concentration of pAOI-*β*-CD was increased, clear downfield shifts were observed for the fluorine atoms TFSI$^-$ (from −78.75 to −78.68 ppm) due to the supramolecular interaction between pAOI-*β*-CD and TFSI$^-$. However, no sol−gel transition was obtained for pAOI-*β*-CD/Fc-[BIM]Br (Figure S3), because the hydrophobic cavity of *β*-CD could not form the complex with the hydrophilic Br$^-$. These results confirmed that both Fc and TFSI$^-$ groups were successfully encapsulated into the cavity of pAOI-*β*-CD through host−guest interactions, yielding the formation of a noncovalent cross-linked supramolecular gel.

Previous studies have demonstrated that the complex between TFSI$^-$ and *β*-CD would lead to a reversible thermoresponsive complexation-diassociation effect at relatively low temperature.[19a] The supramolecular gel with a gel-to-sol

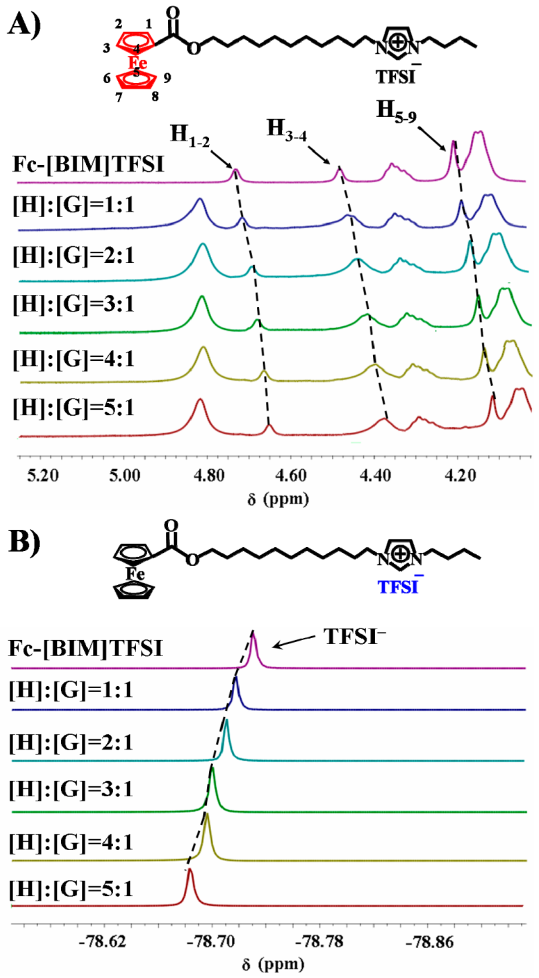


Figure 2. (A) Partial ^{1}H NMR spectra for pure Fc-[BIM]TFSI and various molar ratio of pAOI-*β*-CD ([H]) to Fc-[BIM]TFSI ([G]). Upfield shifts of H_{1-2}, H_{3-4}, and H_{5-9} indicating the interaction of pAOI-*β*-CD with Fc group. (B) ^{19}F NMR spectra (using NaF as an internal reference) for pure Fc-[BIM]TFSI and various molar ratio of pAOI-*β*-CD ([H]) to Fc-[BIM]TFSI ([G]). Clear downfield shifts from −78.75 to −78.68 ppm indicate the interaction of pAOI-*β*-CD with TFSI$^-$ anion. All the samples were dissolved in DMSO-d_6/CDCl$_3$ (4:1, *v*/*v*).

phase transition temperature ($T_{gel-sol}$) was determined by differential scanning calorimeter (DSC) measurements (Figure S4). It was found that $T_{gel-sol}$ increased gradually with the increase of molecular weight of pAOI-*β*-CD (Figure S5), as well as the increase molar ratio of pAOI-*β*-CD to Fc-[BIM]TFSI. For example, $T_{gel-sol}$ increased from 32.2 to 41.6 °C with the increase of pAOI-*β*-CD to Fc-[BIM]TFSI ratio from 0.6:1 to 1.2:1 (Figure S5). For simplicity, 1.2:1 molar ratio mixture of pAOI-*β*-CD (M_n = 0.93 × 10^4 g mol^{-1}) and Fc-[BIM]TFSI in DMSO/CHCl$_3$ (4:1, *v*/*v*) with a $T_{gel-sol}$ at 42 °C was chosen for the following gel−sol transition studies.

Temperature-dependent ^{19}F NMR spectra (Figure 3) were applied to reveal the mechanism of the thermo stimuli sol−gel transition. The fluorine signal of the pAOI-*β*-CD/Fc-[BIM]-TFSI complex is at about −78.73 ppm at 25 °C. A significant change of TFSI$^-$ anion signals shift from −78.73 ppm (at 25 °C) to −78.49 ppm (at 42 °C, $T_{gel-sol}$ of the gel) was observed. Upon cooling, the fluorine signal of the complex was observed again. As a control experiment, however, only a very small shift (less than 0.06 ppm) was observed in temperature-dependent

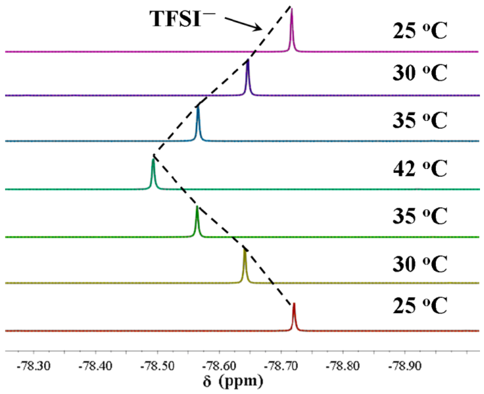


Figure 3. ^{19}F NMR spectra of pAOI-*β*-CD/Fc-[BIM]TFSI (1.2:1, molar ratio) in DMSO-d_6/$CDCl_3$ (4:1, *v*/*v*) using NaF as an internal reference. The sample was heated from 25 to 42 °C and then cooled down to 25 °C (from top to bottom).

^{19}F NMR for Fc-[BIM]TFSI (without the addition of *β*-CD; Figure S6). The results of ^{19}F NMR spectra further confirm the interactions between *β*-CD and TFSI$^-$.

At the same time, it has already been demonstrated that the Fc group can be included in the cavity of *β*-CD due to its hydrophobic nature and be excluded upon oxidation to Fc$^+$.[6b,20] Here, we attempted to employ this electrochemical behavior to control the gel−sol transition of the pAOI-*β*-CD/Fc-[BIM]TFSI supramolecular system. The gel was electrolyzed with a potentiostat using a conventional three-electrode system. It is noteworthy that no additional supporting electrolytes are needed for the electrolysis of pAOI-*β*-CD/Fc-[BIM]TFSI complex system because Fc-[BIM]TFSI itself is intrinsically electroconductive.

As shown in Figure 1a,c that at an oxidative potential of +1 V, an obvious transition from gel to sol was observed; while with the subsequent reduction potential at −1 V, the gel was gradually formed again. A chronoamperometry (CA) experiment was further used to investigate this electrochemical stimulus reversible phase changes. Applying an oxidative potential (+1 V) to the gel resulted in an observable decrease of oxidation current within the first 200 s (Figure 4A), indicating that the concentration of Fc groups on the electrode surface decreased and free Fc$^+$ species were released. The generated Fc$^+$ groups were then excluded from *β*-CD, leading to dissociation of Fc-[BIM]TFSI from the polymer side chains and thus the gel-to-sol phase transition occurred. Additionally, the recorded current was found to decay continuously in time, and a plot of current value versus $t^{-0.5}$ was linear (inset of Figure 4A), indicative of a reaction rate limited by semilinear diffusion. Simultaneously, the CA curve of the reduction experiment observed in Figure 4B clearly demonstrated that Fc-[BIM]TFSI could reassembly with the polymer side chains during the subsequent electrochemical reduction, resulting in a sol-to-gel transition.

More intriguingly, an obvious reversible conductivity switching was observed accompanying with the sol−gel transition without any additional supporting electrolytes. As shown in Figure 5A,B, it can be clearly seen that the switching of the conductivity could be repeated several times triggered by electrochemical redox reactions (Figure 5A), as well as by temperature-dependent sol−gel transition (Figure 5B). Such properties may greatly benefit its potential use as a highly temperature sensitive soft material.

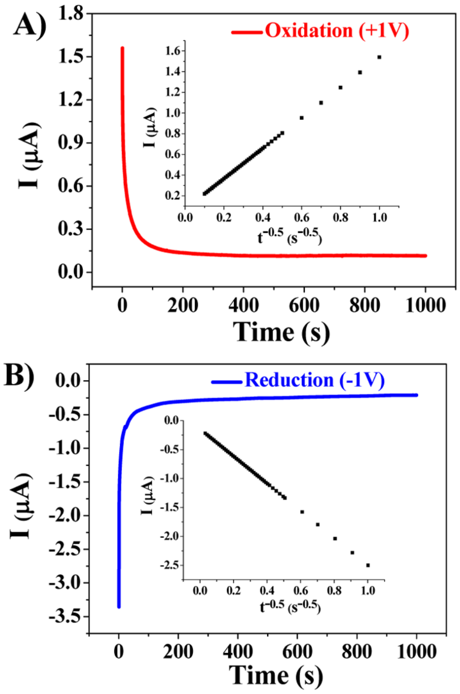


Figure 4. Chronoamperometry (CA) experiments for (A) oxidation (at +1 V, red curve) and (B) reduction (at −1 V, blue curve) of the supramolecular system.

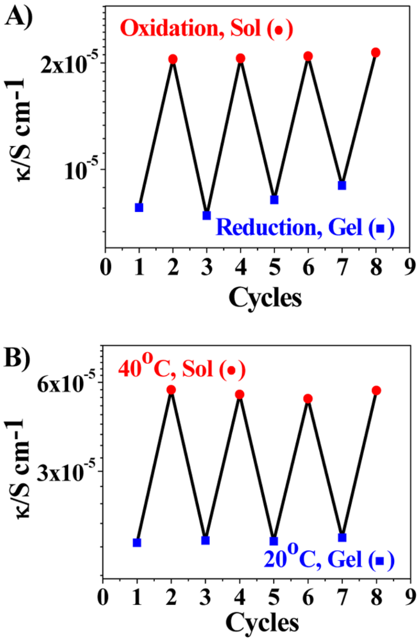


Figure 5. Conductivity of the supramolecular gel (blue square) and sol solution (red circle) induced by (A) the applied voltages at +1 V and −1 V, respectively (measured at 18 °C), and by (B) temperatures at 20 and 40 °C, respectively.

In addition, the effect of the chemical redox reagents on the sol−gel phase transition behavior was studied as well. Aqueous solution of NaClO and vitamin C (Vc) was used as the oxidizing and reducing reagents, respectively. A clear and transparent solution was obtained upon the addition of NaClO to the pAOI-*β*-CD/Fc-[BIM]TFSI supramolecular gel (Figure 1d). The yielded solution was gradually transformed to gel again with the continuous addition of Vc. This result can be explained by the corresponding UV experiments (Figure S7). Two peaks at 350 and 450 nm were ascribed to the absorptions of Fc/β-CD complexes. Both two peaks decreased gradually and finally disappeared with the increase of NaClO, indicating the disassembly of the Fc/β-CD complexes. The absorption peaks at 350 and 450 nm appeared again, and a gel was gradually formed simultaneously with the addition of Vc. Therefore, it can be concluded that chemical redox reactions can also lead to the reversible sol−gel phase transitions of the present supramolecular gel.

Excellent ion-exchange ability is one of the unique properties of ILs. Therefore, we wonder whether the sol−gel phase transitions of the present supramolecular gel could be controlled via anion-exchange of IL gemini guest. As shown in Figure 1e that the gel gradually collapsed and finally became a solution upon the addition of tetrabutylammonium bromide (TBABr, 0.04 mol L^{-1}). The suparmolecular gel could be reformed after the addition of LiTFSI (0.05 mol L^{-1}) to the solution. After the anion-exchange of TFSI$^-$ with Br$^-$, the hydrophobic cavity of the CD could not form complex with the hydrophilic Br$^-$. The host−guest interaction between pAOI-β-CD and Fc-[BIM]TFSI was destroyed, and thus, the gel changed to solution. With the addition of LiTFSI, the counterion of imidazolium cation was changed back to TFSI$^-$, and the host−guest solution gradually yielded the gel again.

In conclusion, we have developed electroactive supramolecular gels based on the host−guest interactions between pAOI-β-CD (the host polymer) and a newly designed IL type asymmetric gemini guest containing both Fc and TFSI$^-$ guest groups as a noncovalent cross-linker. This supramolecular gel not only exhibits multiple stimuli-responsive reversible sol−gel transitions upon temperature, electrochemical and chemical redox reactions, and anion-exchange, but also shows synchronously reversible conductivity switching behavior upon such stimuli. Taking the full advantage of these unique multiresponsiveness reversible macroscopic physical and electronic transitions, we believe that the supramolecular gels prepared in this work would have applications in advanced sensor and semisolid state electrolyte materials.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, 2D NOESY NMR spectrum, DSC thermograms, temperature-dependent ^{19}F NMR spectrum, and UV−vis spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by Natural Science Foundation of China (No. 21274101), National Basic Research Program of China (973 Program, No. 2012CB825800), and the Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions.

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