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An Organometallic Super-Gelator with Multiple-Stimulus Responsive Properties**

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Stimulus-responsive gels have recently attracted widespread attention as new functional materials for potential applications in sensors,[1] actuators,[2] shape memories,[3] drug delivery devices,[4] and displays.[5] One of the promising properties that organogels based on low molecular mass organic gelators (LMOGs) can offer is their reversible sol–gel phase transition as a result of external stimuli.[6] As far as we know, redox-responsive organogels from LMOGs, however, are limited. Shinkai and coworkers[7a] reported the first example of organogels of this kind, which contains a redox-active Cu^{I}/Cu^{II} center. Besides, they also synthesized a series of quater-, quinque-, and sexithiophene derivatives bearing two cholesteryl moieties at the α-position. It was found that a sol–gel phase transition can be implemented by addition of oxidizing and reducing reagents.[7b] Zhu and colleagues[7c] prepared an electro-active LMOG containing a tetrathiafulvalene (TTF) entity. The gel formation can be tuned by means of oxidation/reduction of the TTF group chemically or electrochemically. Although these gel systems are redox responsive, their properties, such as mechanical strength, flexibility, and sensitivity to external stimulus, are far from those required for practical uses. Therefore, creating instant, reversible, redox-responsive, and mechanically flexible organogels still remains a challenge.

As a remarkable organometallic compound, ferrocene (Fc) contains an oxidizable metal ion, Fe^{II}, and is a nonpolar compound in the neutral state, and thereby it dissolves readily in hydrocarbon solvents. This property, however, can be easily reversed by simple oxidation of the central ion. Our interest in stimulus-responsive supramolecular gel systems led us to consider the compound as a neutral–cation redox pair that may be employed to tune the gelling ability of a gelator containing it. Actually, the same idea has been adopted by a number of groups for studies of switchable complexation and molecular aggregation in micelles and vesicles.[8] However, all compounds containing the apolar ferrocenyl or charged ferrocenium moiety reported so far do not result in gelation, as documented for a number of solvents.[8b,8c] Introduction of metal ions is a practical way of giving organogels some smart properties.[9] For example, Sijbesma and coworkers[9a] designed and prepared two chloroform gels with Rh-^{I} or Ir^{I}-containing coordination networks inside. It was reported that the gels possess the property of reversible sol–gel phase transition initiated by ultrasound treatment. Similarly, Rowan and coworkers[9b] prepared three Zn^{II}-containing supramolecular gels. The gels exhibit dramatic reversible responses to a variety of stimuli, including thermal, mechanical, and chemical. Unlike organic LMOGs and those based on coordination compounds, ognanometallic LMOGs are rare,[10] but the performances of some of them are very exceptional. For example, recently Dötz and coworkers[10c] reported a palladium-based organometallic LMOG that is able to catalyze C–C bond formation even in the gel state.

We report here four novel cholesterol-appended ferrocene derivatives (Fig. 1a; see Supporting Information for preparation details), and present first evidence for the gelation ability of organometallic compounds of this kind, and particularly the unusual redox-, mechanical-, and ultrasonic-controllable sol–gel phase transition phenomena. These gelators contain one redox-active ferrocenyl moiety and one cholesteryl residue linked by different diamino units. This design was chosen on the basis of the analysis of the structures and association behavior of the cholesterol-appended ferrocene derivatives reported by Gokel and coworkers.[8b,8c] In the design, carbonyl amide groups were intentionally introduced into the linker structures in order to give the ferrocene derivatives some hydrogen-bond formation sites and to enhance their aggregation ability, and thereby lead to extended structures. It is expected that a change in the oxidation state of the central ion of the ferrocenyl residue would largely modulate the interaction of adjacent ferrocenyl moieties of the compounds, which would impair the intermolecular hydrogen bonding interaction and hence affect the supramolecular structures of the aggregates.

Gelation behavior studies demonstrated that compound **1** is more efficient than its analogues with longer spacers and represents an excellent gelator (see Supporting Information, Table S1). It gels cyclohexane and CCl_4 at room temperature, and the critical gelation concentration (CGC) for cyclohexane is only 0.09 wt %, which is much lower than 0.2 wt %, the lowest

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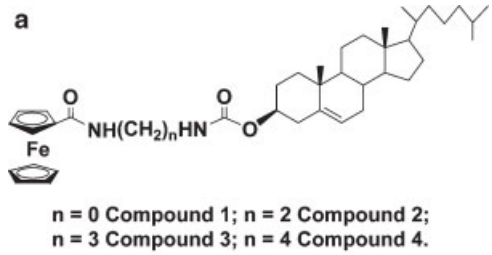

Figure 1. Cholesterol-appended ferrocene derivatives whose gelation abilities were studied (a), and a photograph of a gel film of the **1**/cyclohexane system (b).

value documented for organometallic gelators, and falls into the category of ''super-gelators''.[10a,10c,11,12]

Compound **2**, however, requires distinctly higher concentration (2.5%, w/v) and longer time to gelatinize cyclohexane. Increasing the length of the spacer as in compounds **3** and **4** results in a complete loss of the gelating ability (see Supporting Information, Table S1). Therefore, it turned out that the length and structure of the spacer connecting the cholesterol entity and ferrocene residue is crucial for the gelation abilities of these compounds. This might explain why the cholesterol-appended ferrocene derivatives reported in the literature could not gelatinize the solvents tested.

Slightly surprisingly, we found that a gel film can be prepared by injecting the hot cyclohexane solution of **1** into a film mold and then cooling the solution to room temperature. The film is stable in the wet state, and can be bent into a coil-like structure (Fig. 1b), representing the second example of a supramolecular gel film formed through aggregation of LMOGs.[13]

The ferrocenyl group is easy to oxidize both chemically and electrochemically.[8,14] Accordingly, an equal amount (in moles) of $(NH_4)_2Ce(NO_3)_6$ dissolved in a minimum amount of H_2O was carefully placed above the gel of **1**/cyclohexane, and it was found that the gel gradually turned into a dark green suspension. Afterwards, an equivalent amount (in moles) of hydrazine was added, and then the mixture was stirred or shaken at room temperature for a few seconds, producing an orange gel (Fig. 2). To our knowledge, this represents a second rare example of a heating-free sol–gel phase transition attained by combination with a chemical oxidation and reduction reaction,[7b] but the sol–gel phase transition in this system could be instant. The conclusion that the sol-gel phase transition was induced by chemical oxidation and reduction of the ferrocenyl moiety was confirmed by parallel experiments, in which NH_4NO_3 and $Ce(NO_3)_3$ were used instead of $(NH_4)_2Ce(NO_3)_6$ and no change was observed during the time scale of the experiment. Further evidence was obtained by measuring the UV-vis spectra of the **1**/cyclohexane gel system and its oxidized suspension sample (see Supporting Information, Fig. S1). It was found that the former is characterized by an absorption band around 438 nm, and the latter by one around 635 nm, characteristic absorptions of the ferroenyl residue and ferrocinum cation, respectively.[8c,15]

More interestingly, immediate sol–gel phase transition can be induced by shaking the gel vigorously, and, in contrast, resting the solution results in gelation again (Fig. 2). This shear-stress-triggered reversible sol–gel phase transition phenomenon was further studied by rheological techniques, and the details can be found in the Supporting Information.

Ultrasonic treatment is another effective way to trigger the phase transition of the gel. In this case, however, the liquid is a viscous suspension, rather than a clear solution (Fig. 2). As

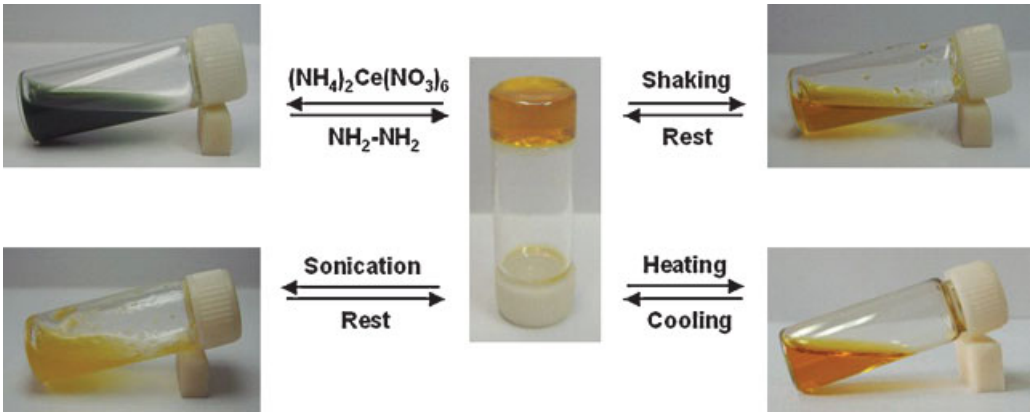

Figure 2. Reversible sol–gel phase transition of the gel of **1**/cyclohexane triggered by chemical redox reaction, shear stress, sonication, and temperature.

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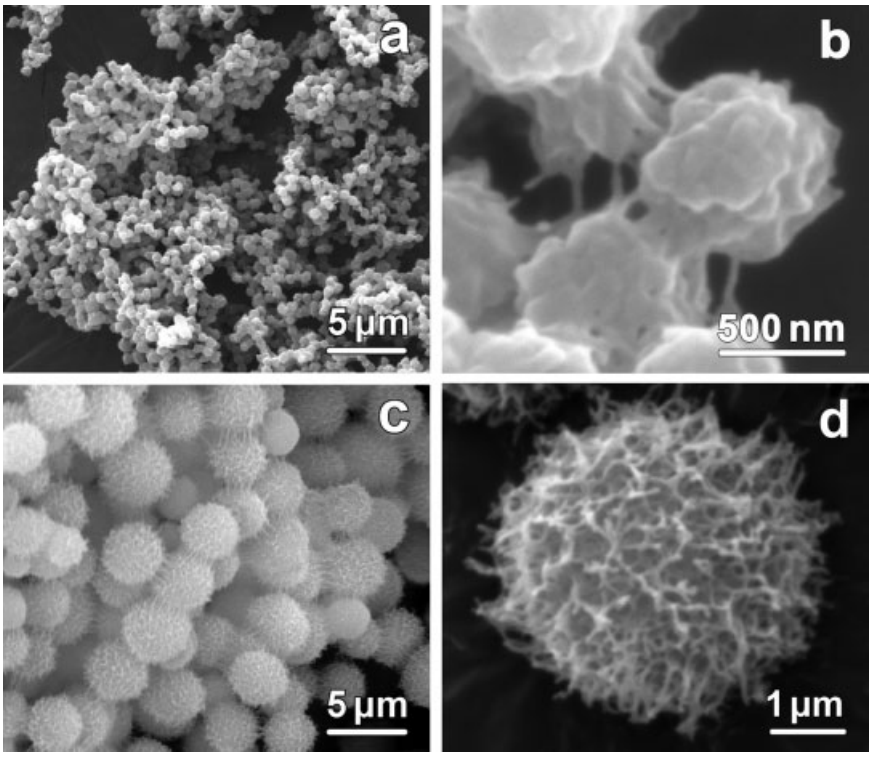

Figure 3. SEM images of the xerogels of **1**(a) and **2**(c) in cyclohexane (2.5%, w/v) and their enlarged cotton- and bur-like structures (b,d).

expected, the gel is also temperature sensitive. It dissolves when the temperature increases, and gels upon cooling (Fig. 2).

Scanning electron microscopy (SEM) studies revealed that **1** and **2** aggregated into microspheres of diameters of about 0.5 μm and 4 μm, respectively, in their cyclohexane gels (Fig. 3). The former adopts ''cotton-like'' structures, while the later adopts ''bur-like'' network structures with fibers as primary structures. As for the microspheres existing in **1**/cyclohexane, their primary structure is also nanofibers. Increasing the concentration of **1** in cyclohexane from 0.1% to 4.0% w/v made its aggregates changed from spider-web-like structures to fiber–microsphere mixed structures, and then to independent microsphere structures, indicating that the formation of the ''cotton-like'' structures is an evolutionary process (see Supporting Information, Fig. S4). The XRD pattern of **1**/cyclohexane gel exhibits a peak around 3.57°, corresponding to a *d*-spacing of 24.70 Å (see Supporting Information, Fig. S5), which is just the length of molecule **1**.

Fourier transform infrared (FTIR) studies demonstrated that upon gelation, the signals corresponding to the stretching vibrations of amide NH, the ester C=O, the amide C=O, and the bending vibration of amide NH significantly shifted (see Supporting Information, Fig. S6), indicating formation of intermolecular hydrogen bonds.[16] This conclusion is further supported by the results from concentration- and temperature-dependent ^{1}H NMR studies of the system of **1**/C_6D_6 (see Supporting Information, Figs. S7,S8) suggesting that not only the cholesteryl and ferrocenyl units, but also the hydrogen bonds between adjacent linkers of the gelators play important roles in the formation of the gel networks.

In summary, four cholesterol-appended ferrocene derivatives have been designed and prepared. It was demonstrated that in addition to general properties possessed by supramolecular gels formed by LMOGs, the gel system formed by compound **1** and cyclohexane has a number of unique properties, including: 1) **1** is a supergelator; 2) the gel forms at room temperature; 3) the gel can be molded into films of a certain flexibility; and 4) the gel is responsive to various stimuli. All these features make this gel an unprecedentedly intelligent soft material with promising potential applications, and motivate us to explore more ferrocene derivatives as LMOGs.

Experimental

Synthesis: Details of the synthesis and characterization of the cholesterol-appended ferrocene derivatives are explained in the Supporting Information.

Characterization: UV-vis spectra were measured at room temperature using a PerkinElmer Lambda 950 UV/vis spectrophotometer. Rheological experiments were performed on a stress-controlled rheometer (TA Instruments AR-G2) equipped with a parallel plate (40 mm diameter). The plate temperature was kept at 15 °C. A solvent-trapping device was placed above the plate to avoid evaporation. SEM pictures of the xerogel were taken on a Quanta 200 SEM spectrometer (Philips-FEI). The accelerating voltage was 15 kV, and the emission was 0.1 mA. The xerogel was prepared by freezing the gel in liquid nitrogen followed by freeze drying. XRD measurements were conducted on a Japan Rigaku D/max- diffractometer. Fresh gel samples were directly loaded onto a rectangular glass sample holder. The XRD patterns were obtained using Cu Kα radiation with an incident wavelength of 0.1541 nm. The scan rate was 3° min^{-1}. The FTIR spectra of the solution and gel samples were recorded in an attenuated total reflectance (ATR) mode using a Bruker Equinox 55 infrared spectrometer. The gel sample for measurement was prepared by coating it on a KBr slice as a smooth film and then freeze-drying it. ^{1}H NMR spectra were measured on Bruker AV 300 (300 MHz) and Bruker AV 500 (500 MHz) NMR spectrometers.

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