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Published on Web 02/16/2010

Multistimuli Responsive Organogels Based on a New Gelator Featuring Tetrathiafulvalene and Azobenzene Groups: Reversible Tuning of the Gel−Sol Transition by Redox Reactions and Light Irradiation

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Abstract: For the development of multistimuli responsive organogels, the new organic gelator LMWG **1**, featuring electroactive TTF and photoresponsive azobenzene groups, was designed and studied. By manipulating the redox state of the TTF group in LMWG **1**, the gel−sol transition for organogels with the LMWG **1** can be reversibly tuned by either chemical or electrochemical oxidation/reduction reactions. Alternatively, the photoisomerization of the azobenzene group in LMWG **1** can also trigger the gel−sol transition. Therefore, organogels with LMWG **1** respond not only to thermal stimuli but also to redox reactions and light irradiation.

Introduction

Organogels are formed by assembling low-molecular-weight gelators (LMWGs) into entangled three-dimensional networks with solvent molecules entrapped inside through weak intermolecular interactions such as H-bonding and $\pi-\pi$ stacking.[1−3] Accordingly, the gel−solution (gel−sol) transition for organogels is thermally reversible. It is appealing to obtain organogels whose gel−sol transitions can be further tuned by other physical and chemical stimuli,[4−6] since such external stimuli responsive gels are highly desirable for advanced applications of organogels such as the sol−gel process,[7,8] drug delivery,[9] sensors, and molecular logic gates. Development of such organogels may lead to novel smart materials.[10]

One way to generate responsive organogels is to develop LMWGs with photoresponsive/electroactive/chemically reactive groups. For instances, organogels which respond to light irradiation to effect the gel−sol transition have been achieved by incorporating photoresponsive moieties (e.g., azobenzene and stilbene)[11,12] into the corresponding LMWGs. By designing

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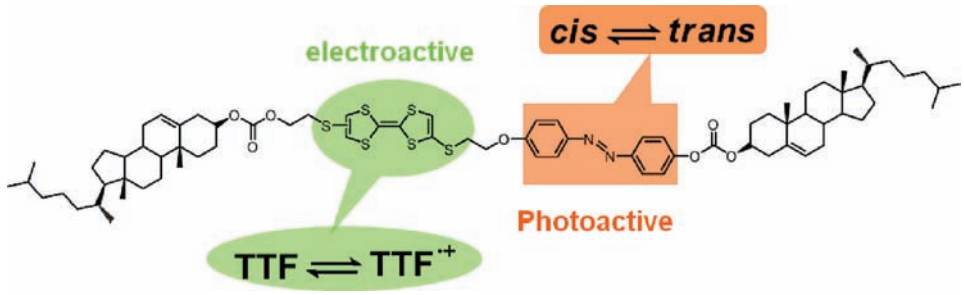
 10.1021/ja910721s

Scheme 1. Chemical Structure of the LMWG **1** and Schematic Representation of the Design Rationale for Reversible Multistimuli Responsive Organogels



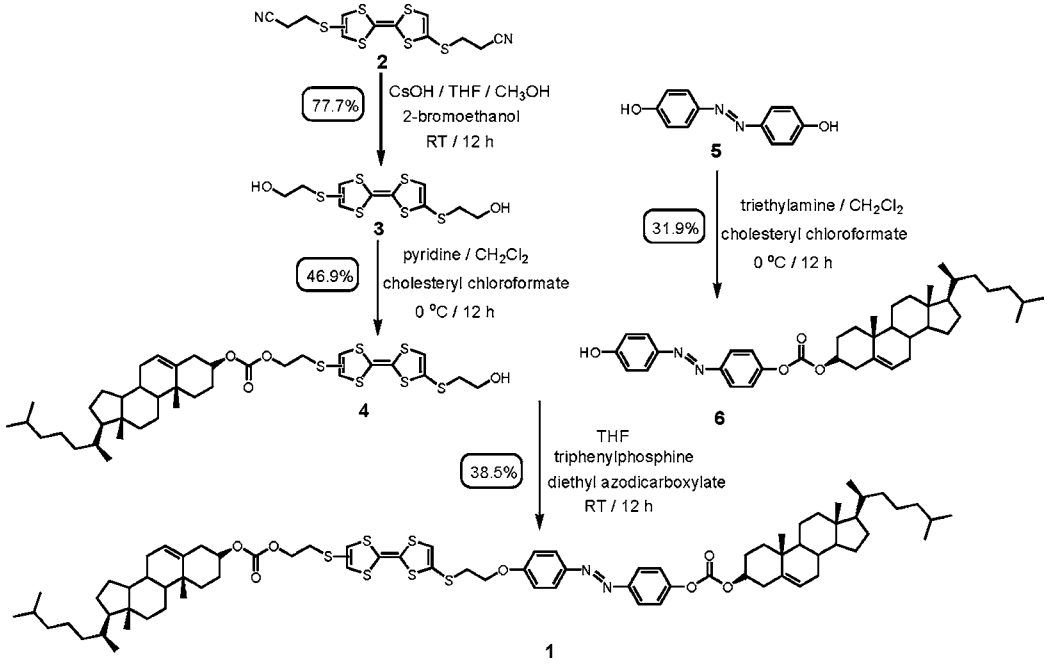
LMWGs with electroactive moieties, organogels showing responsiveness to redox reactions have been described.[13,14] We have recently reported a new LMWG with the tetrathiafulvalene moiety, and the corresponding gel−sol transition can be tuned by oxidation and reduction as well by reactions with electron acceptors.[15] Akutagawa et al.[16] and Shinkai et al.[17] separately described organogels derived from tetrathiafulvalene derivatives. Amabilino et al.[18] have also detailed another new LMWG containing the tetrathiafulvalene moiety.

However, multistimuli responsive organogels still remain rare.[19] In this paper, we report the new LMWG **1** (Scheme 1) with electroactive TTF and photoresponsive azobenzene groups. The resulting organogels respond to both redox reactions and light irradiation. The molecular design is based on the following considerations. (1) TTF and its derivatives can be reversibly transformed into the radical cations ($TTF^{\bullet+}$) and dications (TTF^{2+}) either chemically or electrochemically.[20−22] (2) Light irradiation can trigger the cis and trans isomerization of the azobenzene group, and as a result the conformation of the molecule will be changed. Accordingly, the intermolecular interactions will be altered. (3) Incorporation of cholesterol group into LMWG **1** will increase its gelation ability, according to previous studies.[23] It is expected that concatenation of these functional groups into one molecule would lead to a new gelator, which may generate thermally responsive gels also showing responses to redox reactions and light irradiations.

Results and Discussion

Redox and Photoisomerization Properties. The synthesis of the LMWG **1** started from compounds **2** and **5**, as shown in Scheme 2, and synthetic details and characterization data are provided in the Supporting Information. It should be mentioned that the TTF unit in LMWG **1** has two possible isomers, because of the structures of the precursor compounds **2** and **3**. It was not possible to separate these two isomers by column chromatography and HPLC. Also, pure isomers could not be obtained by crystallization. In fact, unsymmetric TTF compounds usually isomerize easily, according to previous reports,[24] and thus isolation of the two isomers of unsymmetric TTF compounds becomes difficult. However, this does not affect the gelation and relevant studies with LMWG **1** significantly. LMWG **1** shows two quasi-reversible redox potentials at +612 mV (vs Ag/AgCl) and +1062 mV (vs Ag/AgCl) (see Figure S1), corresponding to the TTF/$TTF^{\bullet+}$ and $TTF^{\bullet+}$/TTF^{2+} transformations, respectively, according to previous studies.[20−22] LMWG **1** shows a broad absorption around 360 nm mainly due to the trans form of the azobenzene group. Upon UV light (365 nm) irradiation, the absorption around 360 nm gradually became

Scheme 2. Synthetic Approach to the LMWG **1**



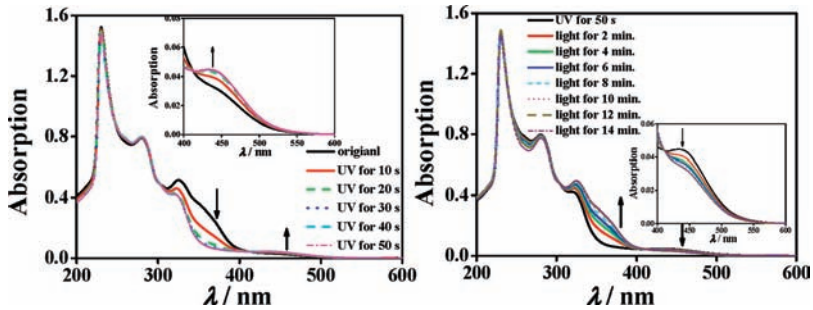


Figure 1. Absorption spectra of (left) the LMWG **1** (1.0×10^{-5} M in CH_2Cl_2/CH_3OH (3/1, v/v)) under UV light (365 nm) irradiation for different times and (right) the LMWG **1** (1.0×10^{-5} M in CH_2Cl_2/CH_3OH (3:1)) under UV light irradiation for 50 s and further visible light irradiation for different times. The insets show absorption spectral variation in the 400−600 nm range.

Table 1. Gelation Experimental Results with LMWG **1**[a]

solvent	gelation examination
CH_2Cl_2/CH_3OH (3/1, v/v)	G (4.0 mg/mL)
$CHCl_3/CH_3OH$ (3/1, v/v)	G (8.0 mg/mL)
CH_2Cl_2/*n*-hexane (1/1, v/v)	G (15.0 mg/mL)
$CHCl_3$/*n*-hexane (1/1, v/v)	G (25.0 mg/mL)
THF	G (40.0 mg/mL)
toluene	G (65.0 mg/mL)
CH_2Cl_2, $CHCl_3$	S
1,2-dichloroethane, CCl_4	P
n-hexane, cyclohexane, methanol, ethanol, DMF, DMSO, acetone, CH_3CN, ethyl acetate	I

[a] Legend: (G) gel (minimum gelation concentration presented in mg/mL); (S) solution; (P) precipitation; (I) insoluble.

weak, and simultaneously the absorption intensity around 450 nm (due to the cis form of the azobenzene group) gradually increased (Figure 1, left). This is simply due to the transformation of the trans form of the azobenzene group in LMWG **1** into the corresponding cis form. On the basis of the HPLC analysis data (Figure S2), the initial solution of **1** was composed of 18.4% cis form and 81.6% trans form; after UV light irradiation for 50 s the photostationary state, which contained 96.8% cis form and 3.2% trans form, was generated. Further visible light irradiation led to an increase in the absorption intensity around 360 nm and a decrease of that around 450 nm, and the original absorption spectrum can be recovered (Figure 1, right).

Gelation Studies. The gelation ability of LMWG **1** was tested in several solvents, and the results are given in Table 1. Among the solvents examined, LMWG **1** can gel THF, toluene, a CH_2Cl_2/methanol mixture (3/1, v/v), a CH_2Cl_2/hexane mixture (1/1, v/v), a $CHCl_3$/methanol mixture (3/1, v/v) and a $CHCl_3$/hexane mixture (1/1, v/v). As an example, Figure 2 illustrates the formation of a transparent orange gel from a mixture of the solvent CH_2Cl_2/CH_3OH (3/1, v/v) with LMWG **1** (8 mg/mL). The SEM and TEM (Figure 2) images of the xerogel of LMWG **1** indicate that molecules of LMWG **1** are self-assembled into an entangled network of thin fibers with lengths up to tens of micrometers. Interestingly, the organogel formed with LMWG **1** exhibited positive CD signals around 368 and 384 nm, as shown in Figure 3, although the solution of LMWG **1** was CD silent. The appearance of CD signals for the organogels based on LMWG **1** indicates the formation of chiral supramolecular structures induced by the cholesterol group in LMWG **1**.[11a] The CD signals became gradually weak and disappeared when the gel was transformed into the solution by heating or UV light irradiation, as will be discussed below.

Tuning the Gel−Sol Transition by Redox Reactions and Light Irradiation. In the following we will demonstrate that the sol−gel transition for the organogels formed with LMWG **1** can be reversibly tuned by either redox reactions or UV/visible light irradiations. It is known that the TTF group can be reversibly transformed to the corresponding radical cation ($TTF^{\bullet+}$) either chemically or electrochemically. It is expected that the transformation of TTF in LMWG **1** into the corresponding $TTF^{\bullet+}$ would alter the intermolecular actions (e.g., van der Waals and $\pi-\pi$ interactions due to the cholesterol and TTF groups); accordingly, the gel phase may become unstable and a gel−sol transition would occur upon oxidation of the TTF group in LMWG **1**. As shown in Figure 4a, when 1.0 equiv of $Fe(ClO_4)_3$ was carefully placed above the gel of LMWG **1** in CH_2Cl_2/CH_3OH (3/1, v/v), the gel was gradually destroyed within 10 min, leading to a dark green suspension. Interestingly, when excess ascorbic acid, which was able to reduce $TTF^{\bullet+}$ to the neutral TTF, was added to the oxidized solution, the dark green solution became an orange solution instantly; after further heating and cooling the gel phase was regenerated. Such a gel−sol transition can be repeated for at least three cycles. In fact, the gelation ability of the radical cation salt of **1** in which the TTF unit was oxidized to $TTF^{\bullet+}$ by $Fe(ClO_4)_3$ was examined in several solvents, including THF and the CH_2Cl_2/CH_3OH mixture. In all cases, no gels were formed by cooling the hot solution of the radical cation salt of **1** with concentrations as high as 30 mg/mL down to room temperature. Moreover, gelation did not occur by further cooling the solution to 2.0 °C and even to −22.0 °C.

Interestingly, the gel−sol transition can also be tuned by electrochemical oxidation and reduction. LMWG **1** can gel the CH_2Cl_2/CH_3OH mixture (3/1, v/v) containing Bu_4NPF_6 (0.1 M). Electrodes were carefully inserted into the gel. As shown in Figure 4b, the gel was converted to the dark green solution after application of an oxidation potential (0.75 V vs Ag/AgCl) for 90 s. When a reduction potential of −0.20 V (vs Ag/AgCl) was sequentially applied for 140 s, the solution changed to orange with a small amount of precipitate; after slight heating and further cooling, the gel phase was restored. The gel was transformed into the dark green solution again by applying an oxidation potential, and the gel phase can be recovered again by applying a reduction potential as discussed above. Such a gel−sol transition with electrochemical oxidation and reduction can be successfully carried out for three cycles. These results clearly indicate that the gel−sol transition for gels with LMWG **1** can be reversibly tuned by manipulating the redox state of the TTF group in LMWG **1**. Therefore, organogels showing response to redox reactions can be obtained with LMWG **1**.

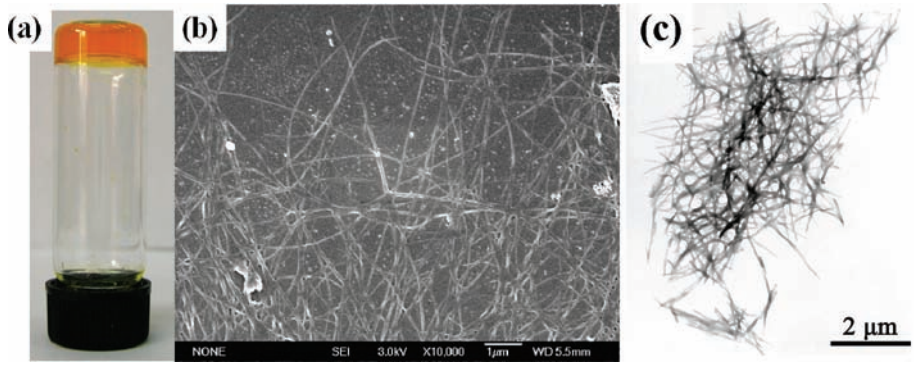


Figure 2. (a) Photograph of the organogel in CH_2Cl_2/CH_3OH (3/1, v/v), (b) SEM image of the xerogel **1** (the scale bar is 1.0 μm), and (c) TEM image of the xerogel **1**.

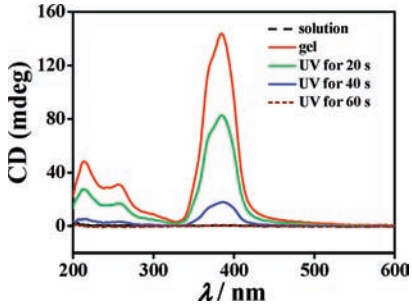


Figure 3. CD spectra of the solution of LMWG **1** (8.0 mg/mL) in CH_2Cl_2/CH_3OH (3/1, v/v) and the resulting organogel **1** in a 0.05 mm quartz cell and those after UV irradiation for different periods of time.

The organogels with LMWG **1** also exhibit responses to UV and visible light irradiation. As an example, the organogel of LMWG **1** in CH_2Cl_2/CH_3OH (3/1, v/v, 8.0 mg/mL) in an NMR tube was gradually collapsed and transformed into solution after UV (365 nm) light irradiation for 1.0 h at room temperature, as shown in Figure 5. It was found that the UV light irradiation time for the complete transformation of gel into solution was dependent on the amount of the gel under investigation. For instance, the gel from a 50 μL solution of LMWG **1** in CH_2Cl_2/CH_3OH (3/1, v/v, 6.0 mg/mL) was converted to solution after UV light irradiation for just 10.0 min. The solution generated from the gel after UV light irradiation was composed of 94.6% cis form and 5.4% trans form on the basis of the HPLC analysis (see Figure S5 in the Supporting Information). Accompanying the transition of gel into solution, the positive CD signals around 368 and 384 nm observed for the gel gradually reduced and disappeared, as is shown in Figure 3. It is probable that the photoisomerization of the azobenzene group in LMWG **1** may destabilize the chiral self-assembly structure.[11a] Conversely, it also becomes possible to monitor the gel−sol transition induced by UV light with CD spectroscopy.

As discussed above, this UV light triggered sol−gel transition should be due to the photoisomerization of the azobenzene group in LMWG **1**.[11a] The gelation ability of the photoisomerization compound in which the azobenzene unit in **1** was in the cis form was examined in the following way: a CH_2Cl_2 solution of LMWG **1** (6.2 mg/mL) was exposed to UV light (365 nm) until the photostationary state was achieved. After removal of solvents the sample was divided and dissolved in several solvents (up to 30.0 mg/mL in the CH_2Cl_2/CH_3OH mixture, the $CHCl_3/CH_3OH$ mixture, etc.) with heating.[25] In all cases no gels were generated by cooling the hot solution down to 2.0 °C. Gelation did not occur by cooling the hot solutions even to −22.0 °C and keeping at this temperature for 1 h. This is indeed in

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(25) However, it should be noted that heating facilitated the transformation of the cis form of azobenzene unit into the trans form, as indicated by the absorption spectral investigation (see Figure S6 in the Supporting Information).

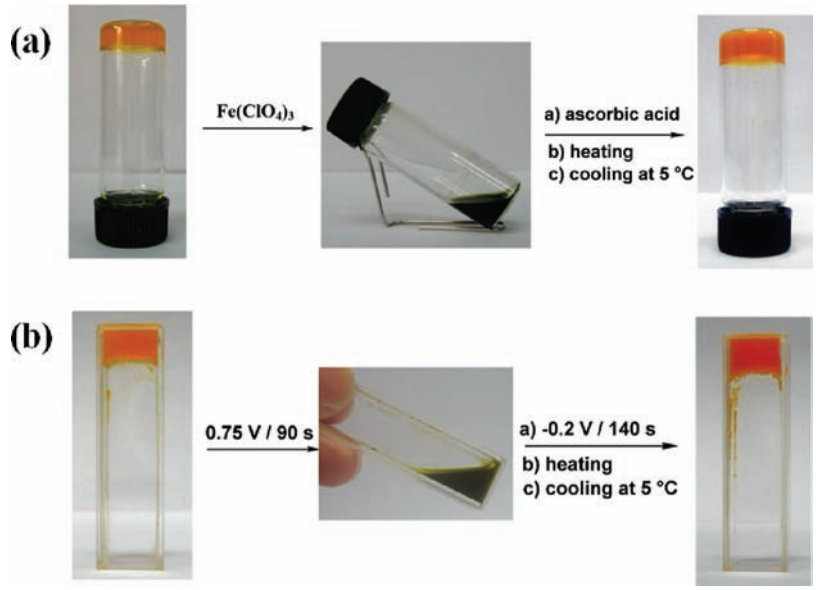

Figure 4. Reversible tuning of the gel formation of **1** (8.0 mg/mL) in CH_2Cl_2/CH_3OH (3/1, v/v) (a) by chemical oxidation and reduction and (b) by sequential electrochemical oxidation and reduction.

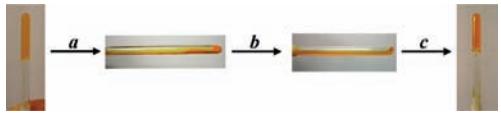

Figure 5. Reversible tuning of the gel formation of **1** (8.0 mg/mL) in CH_2Cl_2/CH_3OH (3/1, v/v) by UV light irradiation and further visible light irradiation: (a) UV light irradiation for 30 min; (b) UV light irradiation for 1.0 h; (c) further visible light irradiation for 2.0 h and then darkness at 5.0 °C for 18 h.

agreement with the previous finding that the cis forms of azobenzene derivatives are usually not favorable for gelation.[11a] However, when the above solution was further exposed to visible light (λ >460 nm) irradiation for 2 h and left in darkness at 5.0 °C for 18 h, the orange-yellow gel was regenerated (see Figure 5). In this way, the gel−sol transitions for the organogels with LMWG **1** can be reversibly tuned by alternating UV and visible light irradiation. Such a gel−sol transition triggered by UV and visible light irradiation can be successfully repeated for three cycles. Therefore, photoresponsive organogels can be obtained with LMWG **1**.

Conclusion

In summary, we report the new organic gelator LMWG **1**, featuring electroactive TTF and photoresponsive azobenzene groups. By manipulating the redox state of TTF group in LMWG **1**, the gel−sol transition for the organogels with LMWG **1** can be reversibly tuned by either chemical or electrochemical oxidation/reduction reactions. Alternatively, the photoisomerization of the azobenzene group of LMWG **1** can trigger the gel−sol transition. Therefore, organogels with LMWG **1** respond not only to thermal stimuli but also to redox reactions and light irradiation. Note that a number of dually responsive organogels have been described, but such multistimuli responsive organogels still remain rare.[19] These results also imply that incorporation of functional groups into LMWGs is one efficient way to produce stimuli-responsive organogels. A number of application possibilities can be imagined for these multistimuli responsive organogels as new smart materials. For instance, as the gel−sol transition for such stimuli-responsive gels can be tuned, the transportation of the corresponding solutions containing LMWG **1** may be controllable by making use of the tunable gel−sol transition; therefore, these stimuli-responsive gels may be potentially useful in microfluidic devices.

Acknowledgment. The present research was financially supported by the NSFC, the State Basic Research Program, the Chinese Academy of Sciences, and the Transregio Project (TRR61).

Supporting Information Available: Text and figures giving details of the synthesis, characterization, gelation and tuning, a cyclic voltammogram, HPLC analysis, and XRD and TEM characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

JA910721S