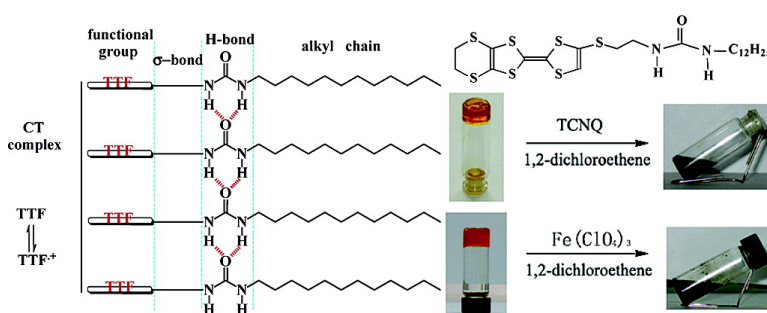


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A Low-Molecular-Mass Gelator with an Electroactive Tetrathiafulvalene Group: Tuning the Gel Formation by Charge-Transfer Interaction and Oxidation

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Gelation of organic solvents by low-molecular-mass compounds,¹ known as gelators, is the subject of increasing attention because of numerous potential applications as well as properties exhibited by these low-molecular-mass gelators (LMMG) with respect to the self-assembly phenomena. Different types of LMMGs have been developed, including steroid,² amino acid,³ bis-urea,⁴ and sugar compounds.⁵ Several functional groups⁶ (e.g., cyanostilbene and bithiophene) were successfully integrated into LMMGs, leading to gels showing high charge-carrier mobility and enhanced fluorescence. Moreover, LMMGs featuring stilbene and azo groups were described,⁷ and the corresponding gels were found to be photoreversible. It should be noted that development of “smart” or “responsive” gels is very appealing. It has been reported very recently that the sol–gel transition can be tuned by oxidation of the coordination Cu(I) complex gelator.⁸ Herein we describe a new LMMG, **1** (Scheme 1), containing an electroactive tetrathiafulvalene (TTF) group and the tuning of gel formation by charge-transfer (CT) interaction and oxidation.

The design rationale is shown in Scheme 1. LMMG **1** contains one TTF and one urea group. Neighboring urea groups tend to form intermolecular H-bonds leading to extended structures, and for this reason, urea compounds are good candidates for LMMGs.⁴ TTF and its derivatives act as good electron donors to form CT complexes with electron acceptors.⁹ Formation of CT complexes will cause the TTF unit to bear positive charge. As a result, the interaction of adjacent TTF units of **1** would be altered, which would influence the intermolecular H-bonding interactions arising from urea groups. TTF group can also easily be transformed to the corresponding radical cation (TTF^{•+}) and even dication (TTF²⁺) either chemically or electrochemically.¹⁰ Conversion of the TTF group to either TTF^{•+} or TTF²⁺ would largely modulate the interaction of adjacent TTF units of **1**, which would impair the intermolecular H-bonding interaction and hence affect the gel formation. Jorgensen et al.¹¹ reported the hydrogel induced by a TTF derivative, but tuning the gel formation by CT interaction and oxidation was not tried yet.

The synthesis and characterization of **1** are provided in Supporting Information (p S2). LMMG **1** gels five organic solvents among tens of solvents tested at room temperature (see Table S1 of Supporting Information). Figure 1A shows the SEM images of xerogel **1** in cyclohexane. As expected, an entangled network of thin solid fibers with diameters of ca. 40–80 nm and lengths up to tens of microns was formed as illustrated (also see Figure S9 of Supporting Information for TEM image). The gels of **1** in these solvents listed in Table S1 of Supporting Information show a similar XRD pattern exhibiting a peak around 1.6° corresponding to $d = 5.5$ nm (see Figure S7 of Supporting Information), which is about

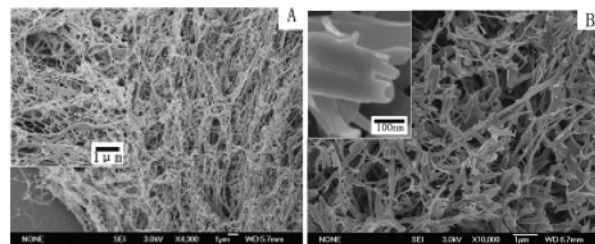
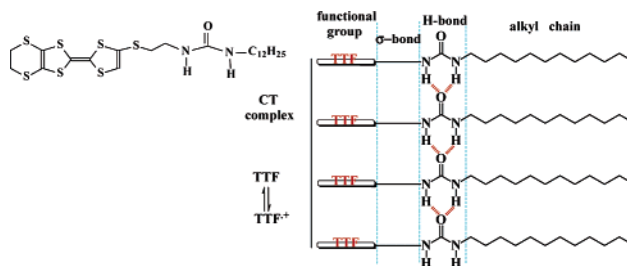


Figure 1. SEM image of the gel of **1** in cyclohexane (A) and that of the CT complex of **1** with TCNQ (B); the inset shows the tube-like structure.

Scheme 1. Chemical Structure of LMMG **1** and the Schematic Representation of the Design Rationale for Multi-Stimuli Responsive Organic Gel



2 times as long as that of the molecular length of **1**. It is interesting to note that direct cooling of the hot solution of **1** in 2-propanol led to precipitation and no gel was formed; however, if the solution was subjected to ultrasonic treatment for a few minutes before cooling, gelation occurred.¹²

The IR signals at 3339, 1641, and 1549 cm^{-1} observed for the diluted solution of **1** in CHCl_3 (1.0 mM) were due to the urea unit. By increasing the concentration of **1**, the signals at 3339 and 1641 cm^{-1} were shifted toward shorter wavenumbers, while that at 1549 cm^{-1} was shifted toward higher wavenumbers (see Table S2). According to previous studies,^{4a} such IR spectral variation is indicative of the formation of the intermolecular H-bonding of adjacent urea groups of **1**. The ^1H NMR data also supported the formation of H-bonding. The signals at 4.58 and 4.25 ppm detected for the CDCl_3 solution of **1** (3.4 mM) were due to the urea group of **1**. When the concentration of **1** was increased, the corresponding signals due to urea group were gradually shifted to downfield, as shown in Figure S5 of Supporting Information. Furthermore, the ^1H NMR spectra of **1** were also recorded in CDCl_3 at different temperatures (see Figure S6). A gel of **1** in CDCl_3 resulted at 300 K. In this case, broad ^1H NMR signals were observed, and the signals due to the urea group were found at 5.24 and 4.90 ppm. By increasing the temperature, the gel of **1** was transformed into solution. As a result, the signals due to urea group were shifted to 5.08 and 4.76 ppm, respectively. This result implies that the H-bonding due to

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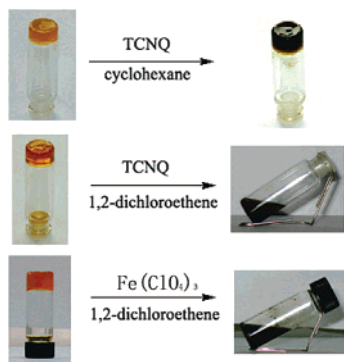


Figure 2. Tuning the gel formation by formation of CT complexes and oxidation.

urea groups is responsible for the gel formation of **1** in organic solvents.

Gelator **1** can form CT complexes with electron acceptors, such as TCNQ (7,7,8,8-tetracyanoquinodimethane). The CT complexes of **1** with TCNQ were formed in these solvents, listed in Table S1. The CT complex formed in cyclohexane can form a dark-green gel in cyclohexane. However, in other solvents, the reaction of **1** with TCNQ led to destruction of the gel state and generation of a dark-green suspension, as illustrated in Figure 2. When 1.1 equiv of TCNQ was directly added on top of a gel of **1** (10 mg in 1.0 mL of $\text{ClCH}_2\text{CH}_2\text{Cl}$), the gel was gradually destroyed after 10 h (see p S6 of Supporting Information), leading to a dark-green suspension.

It is generally accepted that the charge-transfer degree from a neutral electron donor to a neutral acceptor is comparably larger in polar solvents than in nonpolar solvents in that the corresponding radical cation and anion generated through CT process would be more stabilized in polar solvents. For the CT complex of **1** with TCNQ, the TTF group should bear more positive charge in polar solvents, such as 1,2-dichloroethane, than nonpolar solvents, such as cyclohexane.¹³ Therefore, on the basis of the gelation results of the CT complexes of **1** with TCNQ in solvents with various polarity, it may be concluded that the interaction of neighboring TTF groups would be modulated largely so as to impair the intermolecular H-bonding of urea groups and hence interfere with the gel formation, when the TTF group bears more positive charge.

TTF group can be easily oxidized to $\text{TTF}^{+\bullet}$ chemically or electrochemically. As shown in Figure 2, when an equivalent amount of $\text{Fe}(\text{ClO}_4)_3$ or NOPF_6 in $\text{ClCH}_2\text{CH}_2\text{Cl}$ was carefully placed above the gel of **1** in 1,2-dichloroethane, the gel was gradually destroyed within 30 min, and a dark-green suspension was afforded. Electrochemical oxidation led to similar phenomenon (see Figure S3). These results provide further support for the above conclusion that a positively charged TTF group would impair the H-bonding of adjacent urea groups, probably through intermolecular electrostatic repulsion due to positively charged TTF groups and, hence, cause the gel to be destroyed.

Moreover, it is interesting to mention that the structure of the gel of **1** was changed after formation the CT complex with TCNQ in cyclohexane. The entangled thin fiber structure of the gel of **1** in cyclohexane was transformed to a tube-like structure with diameters of ca. 20–60 nm after formation of a CT complex with TCNQ in cyclohexane, as shown clearly from SEM (Figure 1B and Figure S8) and TEM images (Figure S9). To our knowledge, such tubular structure of CT complexes of TTF derivatives was not reported previously. A relatively broad peak around 3.5° (Figure S7) (corresponding to $d = 2.5$ nm) was observed for the dark-green gel of the CT complex of **1** with TCNQ in addition to the

one around 1.6° , which is similar to the gel of **1** in cyclohexane. Further investigation with respect to the mechanism has yet to be carried out.

In summary, we report a new gelator of **1** containing one TTF and one urea group. The gelation ability of **1** was tested, and it was interesting to find that ultrasonic treatment can induce the gel formation for **1** in 2-propanol. The reaction of **1** with TCNQ in cyclohexane, a nonpolar solvent, led to a dark-green gel, for which tubular structure was observed. On the contrary, formation of CT complexes in polar solvents caused the disappearance of the gel state. Direct oxidation of the TTF group either chemically or electrochemically also resulted in destroying the gel state. These results clearly show that it is possible to tune the formation of the gel of **1** in organic solvents by either reaction with electron acceptors or oxidation of the TTF group. It is proposed that positively charged TTF group would impair the intermolecular H-bonding of urea groups of **1**. Therefore, the presence of a TTF group enables the corresponding organic gels to become multi-stimuli responsive, not only to thermal heating but also to CT interaction and oxidation.

Supporting Information Available: Synthesis of **1**, CV, IR, ^1H NMR, XRD, SEM, and TEM characterization of the gels, tuning the gel formation by electrochemical oxidation and reduction, and the absorption spectra of the CT complexes. This material is available free of charge via Internet at <http://pubs.acs.org>.

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