Self-Assembly of a Dendron-Attached Tetrathiafulvalene: Gel Formation and Modulation in the Presence of Chloranil and Metal Ions

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The self-assembly of a tetrathiafulvalene (TTF)-based molecular gelator with a dendron substituent into a gel is described. Scanning electron microscope and atomic force microscope studies show that the xerogels exhibit rope-like frameworks or interwoven nanofibers, depending on the polarity of solvent from which the gel is formed. Gels containing chloranil can also be successfully prepared. Interestingly, this two-component gel can be easily transformed into solution after the addition of either Sc^{3+} or Pb^{2+}. Both absorption and electron spin resonance (ESR) spectroscopic investigations reveal that the TTF unit is oxidized into TTF^{+} by chloranil in the presence of either Sc^{3+} or Pb^{2+}. Moreover, the gel phase can be restored by reduction of TTF^{+} into the neutral form using magnesium.

1. Introduction

Self-assembly of organic functional molecules into nanostructures has been intensively addressed for more than ten years.[1,2] A number of molecules, referred to as low-molecular-weight gelators (LMWGs), can be self-assembled into entangled 3D networks which entrap and immobilize solvent molecules by capillary forces leading to solvent gelation and formation of molecular gels.[3,4] Recent studies have demonstrated that molecular gels may have potential applications in a number of areas including nanomaterials and delivery or modification agents for paints, inks, cleaning agents, drugs, etc.[5] As a result, they have received increased attention in recent years. Apart from the studies about the gel formation and structures, extensive efforts have been made to investigate functional and stimuli responsive gels. These stimuli-responsive molecular gels offer us promising opportunities for designing and constructing new functional materials, such as sensors, actuators, etc.[6]

By incorporation of photoresponsive-/electroactive-/chemically active segments into the respective LMWGs, a number of stimuli-responsive gels are prepared. For instance, molecular gels which respond to metal ions and anions were obtained by using LMWGs containing specific moieties that can selectively bind the corresponding metal ions and anions.[5c,5d] Similarly, LMWGs with photoresponsive (e.g., azobenzene and stilbene)[7,8] and electroactive moieties[9–12] can lead to gels responding to light and redox reactions, respectively. We and others have reported redox reaction-responsive gels with LMWGs featuring tetrathiafulvalene (TTF) groups which can be reversibly transformed into radical cations and dications.[10–13] Moreover, we have also described gels for which the gel–sol transitions can be triggered by chemical reactions by designing LMWGs with chemically active segments.[14]

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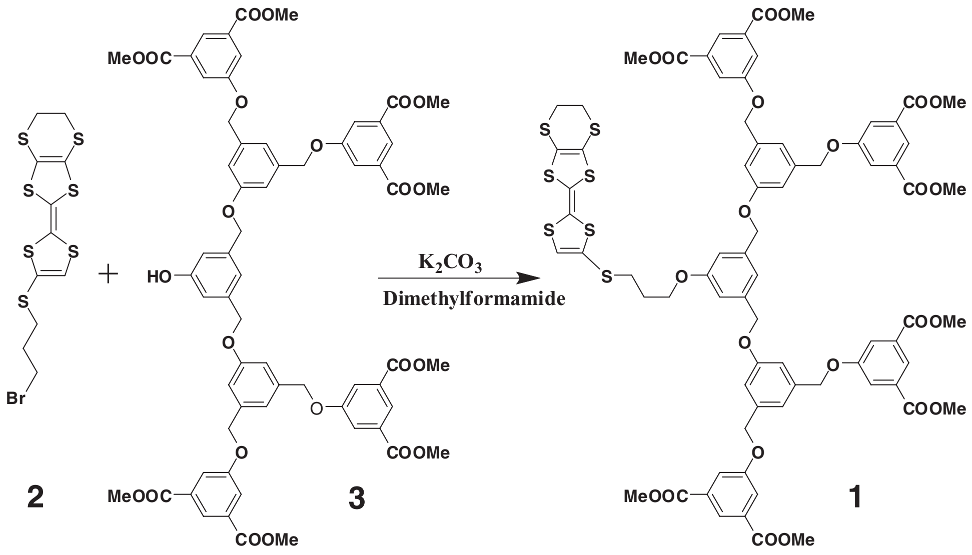

Scheme 1. The chemical structure of compound **1** and the synthetic approach.

In this paper, we report a new TTF-based gelator, **1** (**Scheme 1**), with a dendron substitutent. The molecular design is based on the following considerations: 1) the dendron moiety in **1** has been found to be favorable for the gelation of solvents because of the formation of 3D self-assembly structures due to the interactions of benzene rings.[8b,8c,15] As a result, guest molecules may be easily captured into the 3D self-assembly structures of the dendron; 2) the oxidation of **1** will lead to the transformation of TTF into $TTF^{\bullet+}$, which may affect the interactions of dendron moieties and, as a result, the gel–sol transition can be triggered. We have recently reported the oxidation of TTF by quinones such as chloranil in the presence of metal ions, if the TTF and quinone units are spatially close.[16] It is anticipated that the self-assembly structures of **1** can be modulated, and consequently the gel–sol transition can occur after the addition of chloranil and certain metal ions. As to be discussed below, molecules of **1** can self-assemble into interconnected nanofibers in solution leading to gel formation; moreover, the gel–sol transition occurs easily after the addition of chloranil and Pb^{2+}/Sc^{3+}.

2. Results and Discussion

2.1. Self-Assembly and Solution/Gel Formation

Compound **1** was synthesized by the reaction of compounds **2**[17] and **3**[15] in the presence of K_2CO_3, as shown in Scheme 1. Its chemical structure and purity were established and confirmed by spectroscopic and elemental analysis data (see Experimental Section). The gelation ability of **1** was examined in different solvents, and the results are listed in **Table 1**. Among the solvents tested, compound **1** can gel aromatic solvents including benzene, toluene, *p*-xylene, and a mixture of benzene and acetonitrile (1:1, v/v). As demonstrated in **Figure 1**, a transparent yellow gel was formed by cooling a hot solution of **1** (28 mg mL^{-1}) in a mixture of benzene and acetonitrile (1:1, v/v), and the gel was transformed into the respective solution after further heating. Interestingly, gels of **1** from either benzene or *p*-xylene were opaque, but they were thermally reversible. The corresponding critical gelation concentrations (CGC) at 25 °C were also measured and listed in Table 1.

The self-assembly structures of **1** after formation of gels were examined in the following way: the gels were firstly cooled and the solvents in gels were carefully removed under reduced pressure to yield the respective xerogels; the xerogels were further dispersed in poor solvents and the suspensions were subjected to scanning electron microscope (SEM) and atomic force microscope (AFM) analysis. **Figure 2**a–d show the SEM images of xerogels of **1** from benzene and *p*-xylene, respectively. Interconnected rope-like nanostructures, being typical of the organogels, were observed. These rope-like structures were ca. 500 nm in width and several micrometers in length. Moreover, magnified images revealed

Table 1. The gelation experimental results with compound **1** in different solvents.

Solvents tested	Gelation results[a)]
Benzene	G_o (26 mg mL^{-1})
p -Xylene	G_o (40 mg mL^{-1})
Toluene	G_t (44 mg mL^{-1})
Benzene/Acetonitrile = 1: 1	G_t (27 mg mL^{-1})
Ethyl acetate; 1,2-Dichloroethane; Tetrahydrofuran	S
CCl_4; Acetone	P
Methanol; Ethanol; Acetonitrile; Cyclohexane; n-Hexane; Methylcyclohexane	I

[a)] G_t: transparent gel; G_o: opaque gel; *I*: insoluble; *S*: solution; *P*: precipitate; each CGCs was measured at 25 °C; all gels listed in this table were found to be stable in closed tubes at room temperature for at least three months; the gel–sol transition temperatures of all gels listed in this table (T_g) were ca. 25 °C.

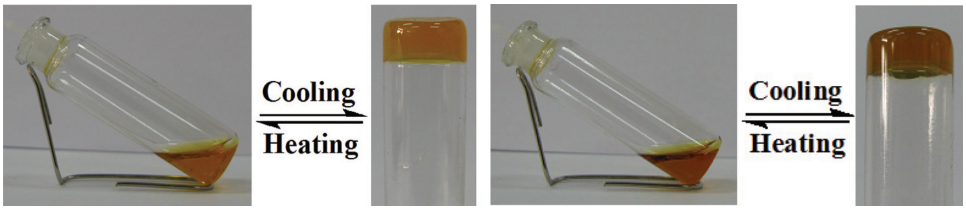

Figure 1. Left part: illustration of the gel formation with compound **1** (28 mg mL^{-1}) in the absence of *p* -chloranil in benzene/CH_3CN (1:1, v/v); Right part: illustration of the gel formation with compound **1** (28 mg mL^{-1}) in the presence of 1.0 eq. of *p* -chloranil in benzene/CH_3CN (1:1, v/v).

that the surfaces of these ropes were hierarchically structured with nanofibers of 50–100 nm in diameter. However, it is interesting to note that xerogels of **1** from the mixture of benzene and acetonitrile (1:1, v/v), contain bundles of long nanofibers which are randomly interconnected as depicted in Figure 2e,f. It can be seen from the magnified image that the nanofibers are smooth, being a few micrometers in length and ca. 50 nm in width. Thus, these results also manifest that the self-assembled structures of **1** in solution through gelation can be affected by the solvent properties: by increasing the solvent polarity, the rope-like self-assembly structures of **1** is changed into nanofibers.

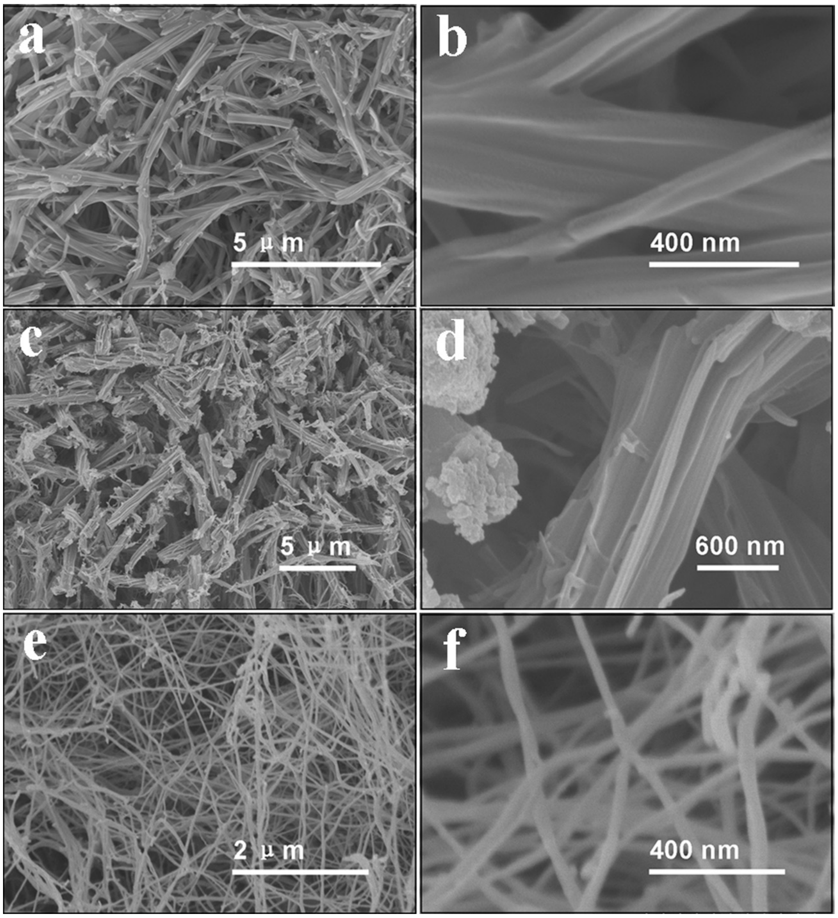

Figure 2. SEM image of the xerogel of **1** from benzene (a) and the corresponding high-magnification image (b); that from *p* -xylene (c) and the corresponding high-magnification image (d); that from the mixture of benzene and acetonitrile (e) and the corresponding high-magnification image (f).

The self-assembly structures of **1** in solutions were also investigated with AFM. As an example, **Figure 3** shows the topography and phase images (recorded in taping mode) of the xerogel from the mixture of benzene and acetonitrile. Again, molecules of **1** are assembled into nanofibers of ca. 50 nm in diameter which are further interconnected to form 3D nanostructures. This is consistent with the SEM observations as discussed above.

On the basis of previous studies[8b,8c,15] and the ^{1}H-NMR investigation, the intermolecular π–π and the hydrophobic interactions due to the dendron segment in **1** may be responsible for the self-assembly and gel formation. **Figure 4** displays the ^{1}H-NMR spectra for the gel of **1** from the mixture of d_6-benzene and d_3-acetonitrile (1:1, v/v) at different temperatures and the corresponding solution at 343 K. The signals around 8.1 ppm, 7.6 ppm, and 6.9 ppm due to the aromatic protons (marked as **a**, **b**, **c**, and **d**) of the benzene units in **1** were gradually shifted downfield when the temperature increased from 298 to 343 K. In addition, down-field shifts were also observed for the signals around 4.8 ppm due to the benzyl-CH_2 protons (marked as **e**). This result implies that π–π stacking owing to the dendron units in **1** exists in the gel phase and it becomes weak after heating as anticipated.

2.2. Tuning the Gel–Sol Transition

By taking advantage of the electroactive feature of TTF, molecular gels responding to redox reactions were reported early.[10–12] Gels of **1** can be easily converted into the respective solution after the addition of $Fe(ClO_4)_3$. Alternatively, TTF can also be oxidized into the radical cation ($TTF^{\bullet +}$) by quinone in the presence of certain metal ions.[16] Thus, it is interesting to study the responsiveness of gels of **1** toward the ensemble of quinone and metal ions.

Figure 5 shows the absorption spectrum of **1** and those of the ensemble of **1** and chloranil at different concentrations.

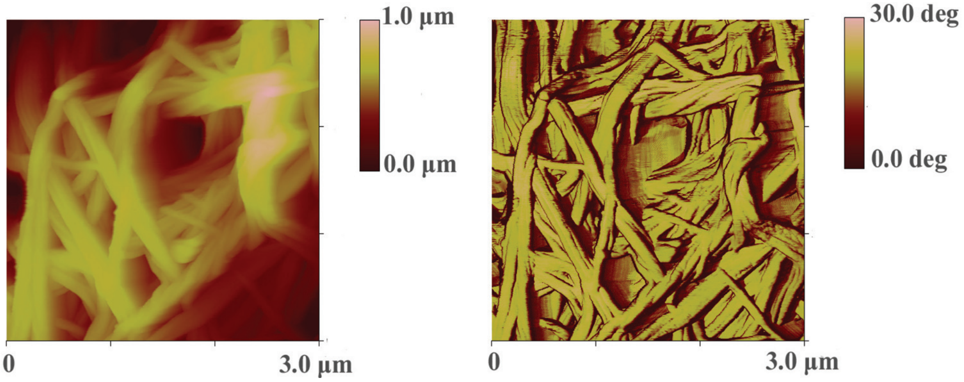

Figure 3. The topography (left) and phase (right) AFM images of the xerogel of **1** from the mixture of benzene and acetonitrile.

Obviously, no new absorptions were detected when the concentrations of **1** and chloranil were lower than 1.0 × 10^{-4} M. But, weak new absorption around 900 nm was observed when the concentrations of **1** and chloranil reached 8.0 mM (12.5 mg mL^{-1}). This new absorption should be owing to the intermolecular charge-transfer interaction between TTF unit in **1** and chloranil. It is interesting to note that such weak intermolecular charge-transfer interaction

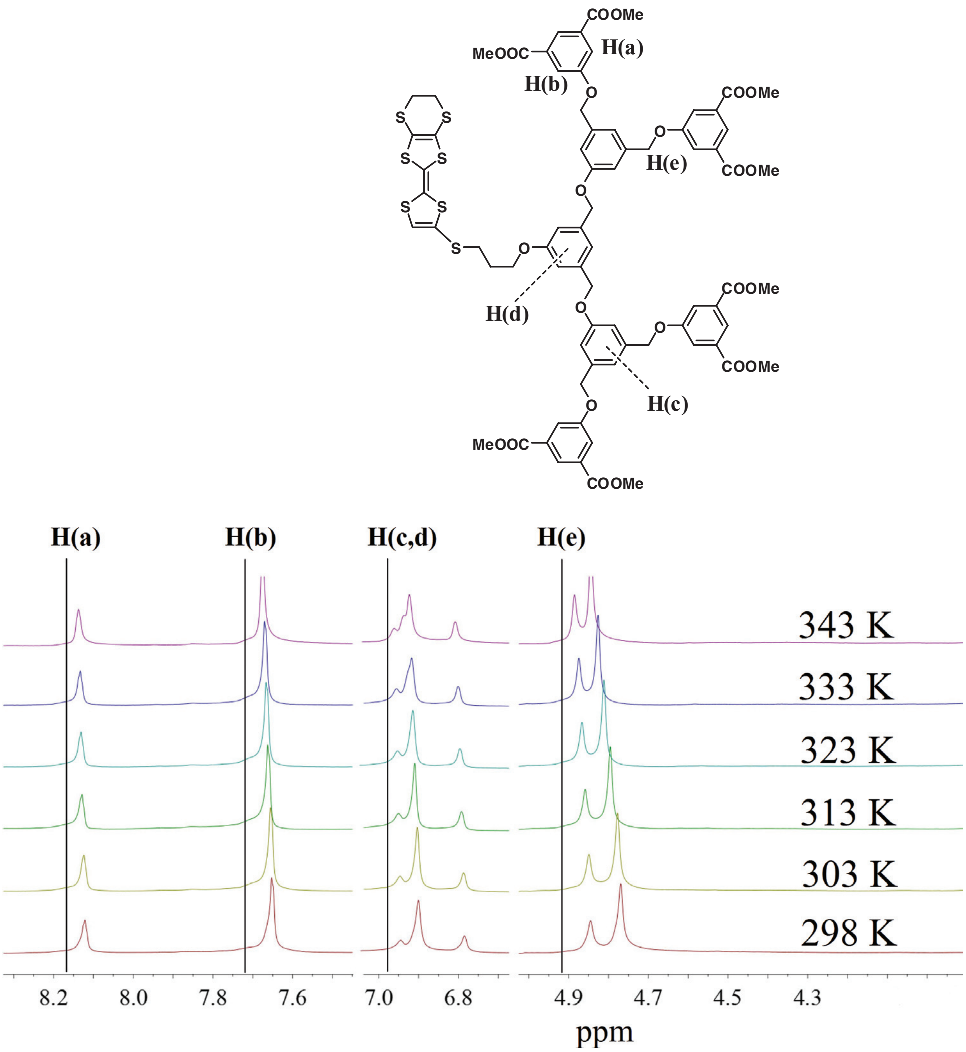

Figure 4. Partial ^{1}H-NMR spectra for the gel formed with **1** (28 mg mL^{-1}) in the mixture of d_6-benzene and d_3-acetonitrile (1:1, v/v) at different temperatures and that for the corresponding solution at 343 K.

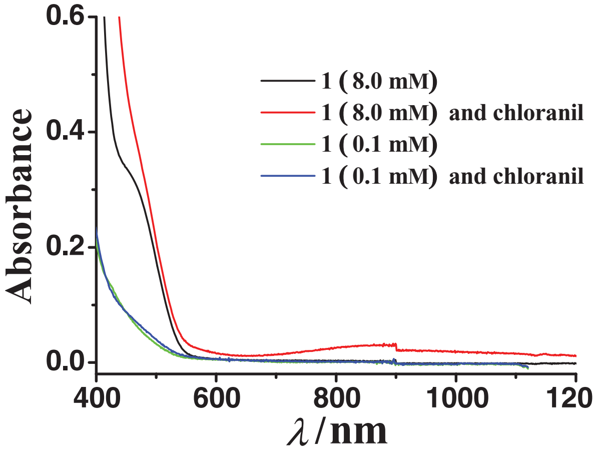

Figure 5. The absorption spectra of **1** in solution with concentrations of 0.1 mM (green) and 8.0 mM (black); that of the equivalent mixture of **1** (0.1 mM) and chloranil (blue); that of the equivalent mixture of **1** (8.0 mM) and chloranil (red); in each case the mixture of benzene and acetonitrile (1:1, v/v) was used as the solvent.

cannot trigger the gel–sol transition as depicted in Figure 1. The gels of **1** containing an equiv amount of chloranil can be formed by cooling the corresponding hot solutions and the gels can be tuned by alternating heating and cooling. As shown in **Figure 6**, the xerogel of **1** and chloranil also contains interwoven nanofibers of ca. 60 nm in width. Clearly, the self-assembly structure of **1** was not largely modulated by the presence of chloranil. This is indeed in agreement with the weak charge-transfer interaction between TTF unit in **1** and chloranil.

Interestingly, gels of **1** and chloranil can be transformed into the solutions after introducing metal ions such as Pb^{2+} and Sc^{3+} as shown in **Figure 7**. But, other ions including Na^+, K^+, Cd^{2+}, Mg^{2+}, Ca^{2+} and Ba^{2+} cannot induce the gel–sol transition. Both absorption and ESR spectroscopic studies indicate such gel–sol transition is induced by the oxidation of TTF unit in **1**.

Figure 8 shows the absorption spectra of **1** (0.1 mM) and chloranil (0.1 mM) in the absence and presence of Sc^{3+}. Before the addition of Sc^{3+} there is no strong absorption above 400 nm. However, new absorptions around 460 and 860 nm emerge after the addition of Sc^{3+}. The color of the solution changed from light-yellow to red-brown after introducing Sc^{3+}, as shown in Figure 8. According to previous reports,[12,13,18] the appearance of absorptions around 460 and 860 nm indicates the generation of $TTF^{\bullet+}$. In fact, direct oxidation of **1** by Fe^{3+} led to the same absorptions at around 460 and 860 nm. Moreover, a strong ESR signal due to $TTF^{\bullet+}$ ($g = 2.0097$, $a_H = 1.13$ G) was detected. The absorption spectra of **1** and chloranil in the gel phase before and after the addition of Sc^{3+} were also recorded (see SI, Figure S1). Again, new absorptions around 460 nm and in the range of 600–1200 nm were observed. Other metal ions were also allowed to react with the ensemble of **1** and chloranil. Among the ions tested, Pb^{2+} can induce similar absorption spectral changes for the ensemble of **1** and chloranil (see SI, Figure S2). Therefore, it can be concluded that $TTF^{\bullet+}$ is generated for the ensemble of **1** and chloranil in the presence of Sc^{3+}/Pb^{2+}. The formation of $TTF^{\bullet+}$ is assumed to be due to the intermolecular electron transfer between the TTF unit in **1** and chloranil, facilitated by Sc^{3+}/Pb^{2+}. Our recent studies indicated that metal ions promote smooth electron transfer between TTF and quinone when they are spatially close.[16] Briefly, the reduction potential of quinone (e.g., chloranil) is positively shifted in the presence of certain metal ions (see SI, Figure S3,S4) and, as a result, the electron transfer is thermodynamically more feasible; in addition, the $TTF^{\bullet+}$ and the radical anion of quinone (e.g., chloranil),[19] which are generated through electron transfer, can be stabilized by the electrostatic interaction.

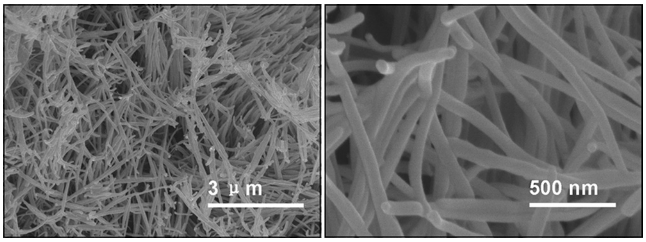

Figure 6. SEM images of the xerogel of **1** containing 1.0 eq. of chloranil from the mixtue of benzene and acetonitrile (1:1, v/v) (left) and the corresponding high-magnification image (right).

Figure 7. The transition of the gel formed with **1** (30 mg mL^{-1}) and 1.0 eq. of chloranil from the mixture of benzene and acetonitrile (1:1, v/v) into the solution after addition of $Sc(CF_3SO_3)_3$; the recovery of the gel phase after further stirring with magnesium strips, followed by heating and cooling.

The $TTF^{\bullet+}$ can be reduced to a neutral TTF unit. For instance, the absorptions around 460 and 860 nm due to $TTF^{\bullet+}$ for the ensemble of **1** and chloranil, to which an equivalent amount of either Sc^{3+} or Pb^{2+} was added, became gradually weaker after the solution was stirred with magnesium strips (see SI, Figure S5,S6). This is simply due to reduction of the $TTF^{\bullet+}$ into the neutral form by magnesium. Simultaneously, the solution was transformed into a gel after the excess magnesium strips were removed, followed by heating and cooling the solution, as indicated in Figure 7. These results clearly indicate that the self-assembled structures and the gel phase of **1** are influenced by the oxidation state of TTF; the transformation of TTF into $TTF^{\bullet+}$, which can be realized by either direct oxidation with Fe^{3+} or with the ensemble of chloranil and Sc^{3+}/Pb^{2+}, accompanies the gel–sol transition, and the gel phase can be restored after the reduction of $TTF^{\bullet+}$ into the neutral form by magnesium.

3. Conclusion

A new TTF-based molecular gelator (**1**) with a dendron substituent is reported. Compound **1** can gel several solvent

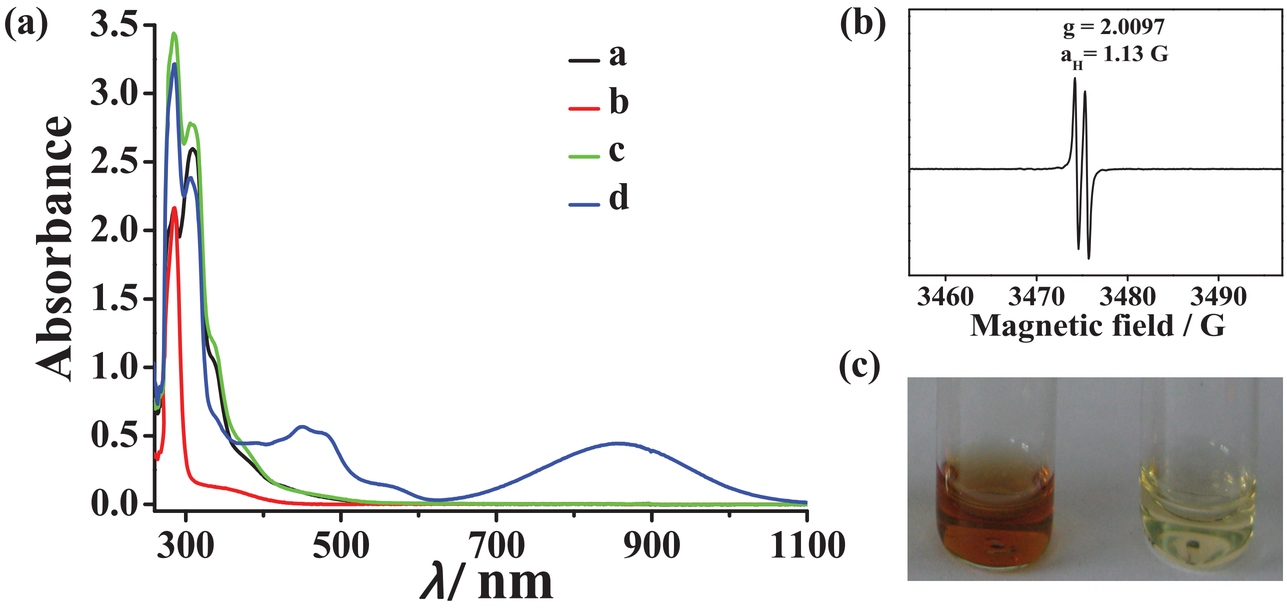

Figure 8. Left: the absorption spectra of **1** in solution (0.1 mM, black), chloranil (0.1 mM, red), the equivalent mixture of **1** (0.1 mM) and chloranil (green), and the equivalent mixture of **1** (0.1 mM) and chloranil in the presence of 1.0 eq. of Sc^{3+} (blue); Top Right: the ESR spectrum of **1** (0.1 mM) and 1.0 eq. of chloranil in the presence of Sc^{3+} (1.0 eq. vs. **1**) recorded at room temperature; Lower Right: illustration of the color change for the solution of **1** (0.1 mM) and 1.0 eq. of chloranil before and after addition of 1.0 eq. of Sc^{3+} (red-brown). For each measurement, a mixture of benzene and acetonitrile (1:1, v/v) was employed as the solvent.

systems, leading to transparent or opaque gels. SEM and AFM studies show that the self-assembled structures of **1** in the form of xerogels can be rope-like frameworks or interwoven nanofibers, depending on the solvent polarity. The gels of **1** containing chloranil can also be prepared. Interestingly, further addition of either Sc^{3+} or Pb^{2+} led to the gel–sol transition. Both absorption and ESR spectroscopic investigations reveal that the TTF unit in **1** is oxidized into $TTF^{\bullet +}$ by chloranil in the presence of either Sc^{3+} or Pb^{2+}. Moreover, the gel-phase can be restored by reduction of $TTF^{\bullet +}$ into the neutral form with magnesium. This responsive molecular gel is based on the modulation of the intermolecular interactions between gelator (i.e., compound **1**) and guest (i.e., chloranil) molecules by external stimuli (Sc^{3+}/Pb^{2+}). Therefore, the current studies may open a new venue for designing responsive molecular gels.

4. Experimental Section

General: All chemicals were from commercial sources and used as received, and solvents were purified and dried following standard procedures unless otherwise stated. Compounds **2** and **3** were prepared according to the reported procedures.[15,17] ^{1}H-NMR, ^{13}C-NMR, MS, elemental analysis, UV–vis absorption, cyclic voltammograms, and ESR spectra were measured with conventional spectrometers.

Scanning electron micrographs were taken with Hitachi S-4800 microscope equipped with a digital camera. Samples of suspension were dropped on silicon and the solvent was evaporated under ambient conditions. All the samples were sputtered with Pt. AFM measurements were taken on a commercial AFM instrument (DI Dimension 3000 with Nanoscope IIIa controller) in tapping mode.

Synthesis of Compound **1**: A solution of compound **2** (446 mg, 1.0 mmol), compound **3** (650 mg, 0.55 mmol), and K_2CO_3 (760 mg, 5.50 mmol) in dimethyl formamide (DMF, 10 mL) was stirred at room temperature for 3 days. The resulting reaction mixture was extracted with dichloromethane and washed with water. The organic layer was dried over anhydrous Na_2SO_4. The solvents were removed under vacuum, and the residue was purified by column chromatography on silica gel with CH_2Cl_2/EtOAc (30/1, v/v) to give compound **1** as a yellow solid powder (653 mg, 76%). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, δ): 8.29 (s, 4 H), 7.82 (s, 8 H), 7.13 (s, 2 H), 7.10 (s, 1 H), 7.05 (s, 4 H), 6.95 (s, 2 H), 5.13 (s, 8 H), 5.08 (s, 4 H), 4.08-4.10 (m, 2 H), 3.93 (s, 24 H), 3.25 (s, 4 H), 2.93-2.95 (m, 2 H), 2.09-2.11 (m, 2 H). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, δ): 166.03, 159.32, 158.64, 138.65, 138.19, 131.87, 123.35, 120.10, 118.79, 118.62, 113.60, 113.08, 70.08, 69.91, 65.54, 51.65, 30.18, 29.24. MALDI-TOF *m/z*:[M^+] 1560.2. Anal. calcd. for $C_{75}H_{68}O_{23}S_7 \cdot H_2O$: C, 57.02; H, 4.47; S, 14.21. Found: C, 57.09; H, 4.33; S, 14.50.

Gel Formation: In a typical gelation experiment, a weighed amount of gelator was mixed with a solvent (0.5 mL) in a test vial, which was sealed and than heated. If the compound was unable to dissolve, it was noted as insoluble (I). After cooling down to room temperature, if a stable and transparent gel was formed when inverting the vial, it was noted as gelation G_t; if a stable and opaque gel was formed, it was noted as gelation G_o; if the clear solution (>60 mg mL^{-1}) was retained, it was marked as soluble (*S*); if precipitate was formed, it was marked *P*. Repeated heating and cooling confirmed the thermoreversibility of the gelation process. The critical gelator concentration (CGC) was determined by measuring the minimum amount of gelator required for the formation of a stable gel at 25 °C.

Reduction with Magnesium: A few magnesium strips, which were treated with HCl (1.0 M), washed sequentially with water and ethanol and further dried, were added to the brown-dark solution of **1** and Sc^{3+}. After stirring for ca. 3.0 min. the brown-dark solution was transformed into the yellow one. Then, the magnesium strips were carefully removed by tweezers. The resulting solution was further heated to ca. 70 °C, and gel phase was re-formed again after the hot solution was further cooled down to room temperature.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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