FULL PAPER

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Multiple-Stimuli Responsive Luminescent Gels Based on Cholesterol Containing Benzothiadiazole Fluorophores

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Two new fluorescent organogelators based on cholesterol containing benzothiadiazole group have been designed and synthesized. Three methods for gels preparation have been presented, such as heating-cooling process, ultrasonic treatment and mixed solvents under room temperature. For both of the gels, their states and emission colors exhibit striking changes upon addition of Hg^{2+}. The gelation properties, structural characteristics and fluorescence of the gels were studied by FT-IR, UV-Vis absorption and PL spectra. The underlying mechanism of gelation property was studied by X-ray diffraction combined with theoretical calculation, and the important role of π-π interactions in forming the gels has been proved.

Keywords organogel, nanofibers, nanotubes, fluorescence, sensor

Introduction

Low-molecular-weight gelators (LMWGs) have been arousing great interest during the past few years due to their potential uses as soft material.[1-4] They can form stable three dimensional (3D) nanoscale superstructures by self-assembly stabilized through weak noncovalent forces, such as π-π stacking, van der Waals forces, hydrogen bonding and hydrophobic-hydrophobic interactions. Recently, organogels that consist of nanotubes by self-assembly have also been investigated.[5,6] As we know, nanotubes, which have hollow structure with less than 100 nm inner diameters, have highly potential applications in drug delivery and nanoobjects.[7] In addition, the helical nanostructures constructed from π-conjugated fluorescent LMWGs, such as twisted ribbons and fibers, are also a topic of increasing interest[8] due to their academic importance and promising applications in chiral recognition, optoelectronic devices and biomaterials.[9-12]

Stimuli-responsive organogels are a kind of fascinating LMWGs in which the morphology of molecules is regulated by external stimuli, including light,[13,14] pH,[15,16] ions,[17,18] sound,[19,20] and so on. A fascinating characteristic of stimuli-responsive organogels is their potential applications in sensor in view of the changes of morphology or other properties upon external stimuli. Particularly, ultrasound has been received much attention because of its value in gene therapy.[21] Since Sijbesma[22,23] and Naota[24,25] investigated organogel by sonication, some examples of sonication-induced morphology changes of gels have been reported.[26] However, their structure-property relationships and mechanisms are not clear and more extensive investigation is neccesary. Therefore, the design, synthesis, and investigation of novel sonication-responsive organogels are very important.

As a class of well-known organogel factor, cholesterol-based derivatives can form helical structure upon ultrasound through hydrogen bonding, π-π interactions, hydrophobic-hydrophobic interactions and chirality of the molecule. In order to further understand the role of hydrogen bonding and π-π interactions and study the changes of fluorescent properties in the process of gelation of cholesterol-based π-conjugated organolgels, we designed and synthesized two cholesterol-based mutiple-stimuli responsive luminescent LMWGs, **1a** and **1b** (Scheme 1). Both of them contain π-conjugated backbone based on benzothiadiazole, which is not only a good fluorophore, but also a recognition group for Hg^{2+} due to the specific interaction between Hg^{2+} and sulfur atom.[27] Interestingly, **1b** can form gels in dichloromethane and show slightly better gelation ability than **1a** even though there is no hydrogen bonding presented. It is also noteworthy that the morphology of **1a** gels

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consisted of left-handed helical nanostructures, while that of **1b** was composed of nanotubes with the uniform dimensions as shown in the photographs of SEM and TEM. The multiple-stimuli responsive properties of **1a** and **1b** gels were studied, and FT-IR, UV-Vis absorption spectra and PL spectra were carried out to investigate the driving force.

Experimental

Materials and instruments

The reaction of cholesteryl chloroformate with 4-iodoaniline or 4-iodophenol gave compounds **2** and **3**, respectively. Target compounds **1a** and **1b** were subsequently synthesized by Sonogashira coupling reaction of 4,7-diethynyl-2,1,3-benzothiadiazole with **2** and **3**, respectively. 4,7-Dibromo-2,1,3-benzothiadiazole and 4,7-diethynyl-2,1,3-benzothiadiazole were synthesized according to previous literatures.[28,29] The structures of the target compounds were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy.

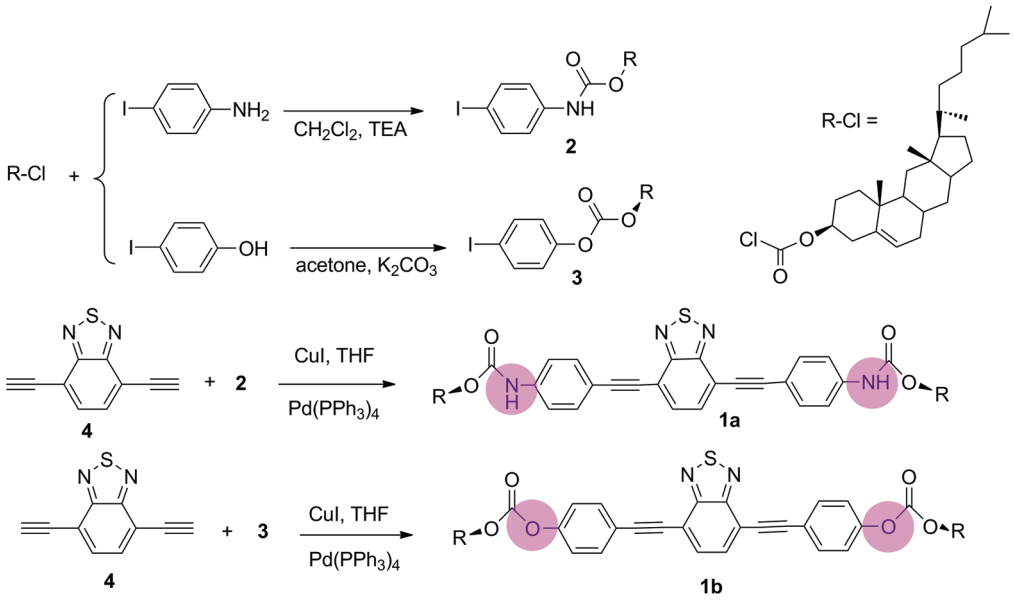
Synthesis and characterization

2: 4-Iodoaniline (0.219 g, 1.0 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 12 h, while cholesteryl chloroformate (0.539 g, 1.2 mmol) in CH_2Cl_2 (10 mL) and triethylamine (0.4 mL) were added dropwise. The reaction mixture was concentrated in vacuum, and the residue was purified by column chromatography (SiO_2, $CHCl_3$: MeOH=20 : 1) to yield white solid (0.33 g, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 (d, J=8.8 Hz, 2H), 7.21 (d, J=9.9 Hz, 2H), 6.46 (s, 1H), 5.33 (d, J=5.1 Hz, 1H), 4.61−4.46 (m, 1H), 2.41−2.21 (m, 2H), 2.03−1.69 (m, 6H), 1.63−0.87 (m, 23H), 0.85 (d, J=6.5 Hz, 3H), 0.82−0.77 (m, 6H), 0.61 (s, 3H).

3: 4-Iodophenol (2.2 g, 10.0 mmol), cholesteryl chloroformate (5.39 g, 12.0 mmol) and K_2CO_3 (5.6 g, 40.58 mmol) in 60 mL acetone were stirred at 59 ℃ for 24 h under nitrogen atmosphere. The reaction mixture was concentrated in vacuum, and then washed twice with CH_2Cl_2. The filtrate was collected and concentrated under reduced pressure. The resulting crude product was purified by column chromatography (SiO_2, CH_2Cl_2 : hexane=1 : 1) to yield **3** as a white solid (4.33 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (d, J=8.8 Hz, 2H), 6.89 (d, J=8.8 Hz, 2H), 5.35 (d, J=5.0 Hz, 1H), 4.58−4.43 (m, 1H), 2.49−2.31 (m, 2H), 2.04−1.58 (m, 6H), 1.58−0.87 (m, 23H), 0.85 (d, J=6.5 Hz, 3H), 0.82−0.77 (m, 6H), 0.61 (s, 3H).

1a: Compound **2** (0.332 g, 0.526 mmol), **4** (0.045 g, 0.24 mmol), and CuI (0.005 g, 0.026 mmol) were added to a 100 mL flask under a nitrogen atmosphere. In the glovebox, $Pd(PPh_3)_4$ (0.030 g, 0.026 mmol) was added to the flask. When a degassed mixed solution of anhydrous THF (20 mL) and anhydrous diisopropylamine (20 mL) were added to the flask, the mixture was stirred under reflux for 24 h. The reaction mixture was concentrated in vacuum, the residue was purified by column chromatography (SiO_2, CH_2Cl_2 : THF=20 : 1) to yield red solid (0.209 g, 75%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ: 7.68 (s, 2H), 7.43 (d, J=46.1 Hz, 8H), 6.66 (s, 2H), 5.34 (d, J=5.1 Hz, 2H), 4.50−4.42 (m, 2H), 2.45−2.10 (m, 4H), 2.05−1.68 (m, 12H), 1.65−0.89 (m, 46H), 0.85 (d, J=6.5 Hz, 6H), 0.82−0.72 (m, 12H), 0.62 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.53, 151.54, 151.02, 139.03, 138.48, 132.46, 123.31, 123.28, 120.18, 117.13, 89.88, 79.18, 79.13, 56.69, 56.14, 49.99, 42.33, 39.71, 39.52, 37.93, 36.83, 36.56, 36.19, 35.80, 31.92, 31.85, 28.23, 28.02, 27.64, 24.29, 23.84, 22.83, 22.57, 21.06, 19.29, 18.72, 11.87.

Scheme 1 Chemical structures and synthetic routes of **1a** and **1b**



1b: Compound **3** (0.332 g, 0.526 mmol), **4** (0.045 g, 0.24 mmol), and CuI (0.005 g, 0.026 mmol) were added to a 100 mL flask under a nitrogen atmosphere. In the glovebox, $Pd(PPh_3)_4$ (0.030 g, 0.026 mmol) was added to the flask. When a degassed mixed solution of anhydrous THF (20 mL) and anhydrous diisopropylamine (20 mL) were added to the flask, the mixture was stirred under reflux for 24 h. The reaction mixture was concentrated in vacuum, and the residue was purified by column chromatography (SiO_2, CH_2Cl_2 ∶ THF＝20 ∶ 1) to yield red solid (0.203 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (s, 2H), 7.61 (d, J＝8.7 Hz, 4H), 7.18 (d, J＝8.7 Hz, 4H), 5.36 (d, J＝5.1 Hz, 2H), 4.62－4.45 (m, 2H), 2.53－2.33 (m, 4H), 2.03－1.60 (m, 12H), 1.57－0.87 (m, 46H), 0.85 (d, J＝6.5 Hz, 6H), 0.82－0.77 (m, 12H), 0.62 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.35, 152.50, 151.54, 139.07, 133.23, 132.46, 123.31, 121.32, 120.18, 117.13, 96.60, 85.46, 79.18, 56.69, 56.14, 49.99, 42.33, 39.71, 39.52, 37.93, 36.83, 36.56, 36.19, 35.80, 31.92, 31.85, 28.23, 28.02, 27.64, 24.29, 23.84, 22.83, 22.57, 21.06, 19.29, 18.72, 11.87.

Preparation of gels

Thermodynamic gels were acquired after the hot solution (at about 75 ℃) has been cooled to room temperature (15 ℃). Ultrasonic gels were obtained when the hot solution was heated (at about 75 ℃) until the solid was completely dissolved to form transparent solutions and was treated immediately with ultrasound for 30 s (0.33 W•cm^2, 40 kHz, 15 ℃). Compounds that could form gels in mixed solvents were obtained by adding non-solvent dropwise to solution of compounds.

Results and Discussion

Gelation properties of 1a and 1b

The gelation properties of **1a** and **1b** were carried out with various solvents by inverting the test tube method. **1a** and **1b** can form stable organogels in several organic solvents, including mixed solvents, under room temperature (Table 1), and the gel state can be maintained for more than a month. Generally, in our system, thermodynamic gels were obtained by cooling the hot (about 75 ℃) and transparent solution to low temperature (about 15 ℃) and sonication gels were acquired through the process of exposing the transparent solution with ultrasound for about 30 s (0.33 W•cm^{-2}, 40 kHz). Interestingly, upon ultrasonic treatment or heating-cooling process, **1a** could form reversible gels not only in dichloromethane and *p*-xylene, but also in mixed solvents, such as THF/acetonitrile (5 ∶ 1) and THF/methanol (5 ∶ 1) (Figure S1 in the Supporting Information). The gels emitted bright yellow light upon 365 nm irradiation. It is surprising that **1b**, without hydrogen bonding, could form reversible gels in dichloromethane and tetrahydrofuran, as well as in the mixed solvents of chloroform/acetonitrile (5 ∶ 1) and chloroform/methanol (5 ∶ 1) upon ultrasonic treatment or heating–cooling process (Figure S2 in the Supporting Information). It can be seen that **1b** gels displayed green light upon 365 nm irradiation. As a further investigation, we took a group of photos illustrating the dynamic process of **1b** gel formation in chloroform/acetonitrile (5 ∶ 1) (Figure 1). The results showed that hydrogen bonding is non-essential in the gelation process in our system.

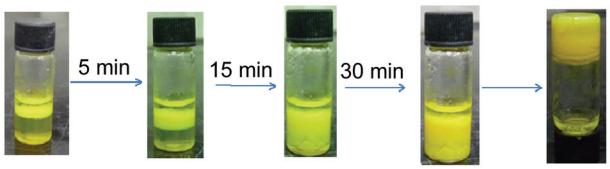


Figure 1 The formation process of gel of compound **1b** by adding 0.1 mL of acetonitrile dropwise to the solution of **1b** in 0.5 mL of chloroform.

Table 1 Gelation ability of **1a** and **1b** (20 mg•mL^{-1})

Solvent	**1a**^{a}	**1a**^{b}	**1b**^{c}	**1b**^{d}
Dichloromethane	OG	OG	OG	OG
Acetone	P	P	P	P
Methanol	P	P	P	P
Acetonitrile	P	P	P	P
p-Xylene	OG	OG	OG	P
Tetrahydrofuran	S	S	OG	OG
Chloroform	S	S	S	S
Tetrahydrofuran/acetonitrile (5 ∶ 1)	OG	OG	P	P
Tetrahydrofuran/methanol (5 ∶ 1)	OG	OG	P	P
Chloroform/methanol (5 ∶ 1)	S	S	OG	OG
Chloroform/acetonitrile (5 ∶ 1)	S	S	OG	OG

^{a,c} Thermodynamic gel (samples were heated to 75 ℃ to be dissolved and then cooled to 15 ℃). ^{b,d} Ultrasound for 30 s (0.33 W•cm^{-2}, 40 KHz); OG: opaque gel; P: heated to dissolve and precipitated; S: solution.

Response to Hg^{2+} of the gels

Interestingly, the gel state, solution and emission color exhibited striking changes upon addition of 6.6 equiv. Hg^{2+} (0.276 mol•L^{-1} in acetonitrile, 0.2 mL) into the gel. The addition of Hg^{2+} resulted in a transition from yellow gel to black solution after 30 min and 2 d for **1a** and **1b**, respectively, and the fluorescence was quenched simultaneously (Figure 2). The much longer time required for **1b** changing from yellow gel to black solution than that of **1a** showed that the gelation properties of **1b** are obviously better than **1a**. After adding appropriate amount of ethylene diamine tetraacetic acid (EDTA) to the broken gels, the gels could not be recovered, indicating that Hg^{2+} might destroy the molecule structures of **1a** and **1b** via the specific interaction between Hg^{2+} and sulfur atom.[31]

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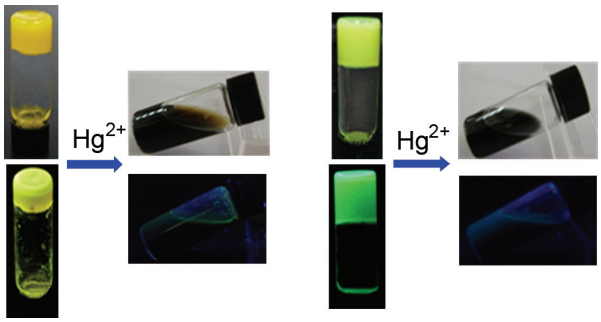

Figure 2 Photograph of gels of **1a** (left) and **1b** (right) in dichloromethane (10 mg/0.5 mL) under daylight (top) and UV light (bottom) before and after Hg^{2+} addition (0.276 mol•L^{-1} in acetonitrile, 0.2 mL).

Self-assembly process and mechanism study

The supramolecular structures formed by the xerogels (air-dried gels) of **1a** and **1b** were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Figure 3). The xerogels of **1a** formed in dichloromethane (20 mg•mL^{-1}) showed network structures consisting of nanofibers with a width of 30—100 nm (Figure 3a). From the TEM image as shown in Figure 3b, it can be found that the xerogels of **1a** showed left-handed helical fibers. The gels of **1a** that exhibit non-uniform nanofibers may be due to the accumulation among nanofibers in different dimensions. On the other hand, the morphologies of xerogels from **1b** in dichloromethane (20 mg•mL^{-1}) consisted of hollow nanotubes by entrapping the solvent molecules. The SEM images from sectional view and TEM images indicated that the nanotubes had the same dimensions, inner diameter with 16 nm and a wall thickness of 13 nm (Figure 3c and 3d). We found that the morphologies of xerogels from **1a** and **1b** formed by thermodynamic process were similar to those formed by ultrasonic treatment or in mixed solvents.

In order to investigate the driving force leading to the formation of the organogels, FT-IR, UV-Vis absorption and PL spectrum investigations were performed. As shown in FT-IR spectrum, the gel samples of **1a** in dichloromethane (20 mg•mL^{-1}) showed NH stretching band at 3324 cm^{-1}, corresponding to that in the solution state (3334 cm^{-1}), which means the obvious hydrogen bonding interaction in the gel formed from **1a** (Figure S3 in the Supporting Information). The UV-Vis absorption spectrum of **1a** solution (2×10^{-5} mol•L^{-1}) in dichloromethane showed the characteristic absorption peaks appearing at 248, 315, 325 and 434 nm, corresponding to those at 251, 322, 341 and 474 nm in gel state formed in dichloromethane (20 mg•mL^{-1}), displaying obvious redshift phenomena from solution to gel state (Figure S4 in the Supporting Information). The same redshift phenomena occurred between **1b** gels and solution (Figure S5 in the Supporting Information). The UV-Vis absorption spectra of **1a** and **1b** with an obvious redshift were attributed to the formation of a *J*-type aggregate of the

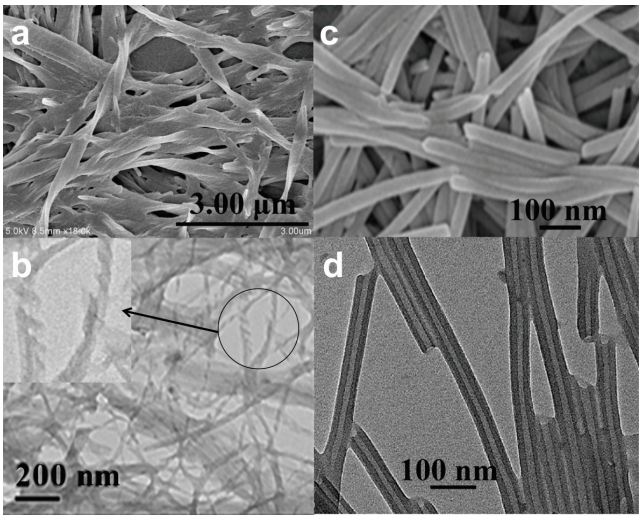

Figure 3 SEM images of xerogels of **1a** (a) and **1b** (c) from dichloromethane solution (20 mg•mL^{-1}), TEM images of xerogels of **1a** (b) and **1b** (d) from dichloromethane solution (20 mg•mL^{-1}).

gelators, and π-π interactions of benzothiadiazole cores may be one of the main driving force for the aggregation.[30] The PL spectrum of **1a** displayed a 21 nm redshift from the solution (2×10^{-5} mol•L^{-1}, λ=535 nm) to the gel (20 mg•mL^{-1}, λ=555 nm) (Figure S6 in the Supporting Information). The emissions of **1b** also showed a redshift of 20 nm from the solution (2×10^{-5} mol•L^{-1}, λ=518 nm) to the gel (20 mg•mL^{-1}, λ=538 nm) (Figure S7 in the Supporting Information). The redshift of UV-Vis absorption and PL spectra of the gelators implies the remarkable π-π interactions between benzothiadiazole cores in the gel state.

To gain a deeper insight into the assembly mechanism, **1a** and **1b** in the xerogels state from dichloromethane were further investigated by powder X-ray diffraction. We also used semiempirical AM1 based on RB3LYP/3-21G to carry out ground-state optimized molecular-geometry calculations (Figure S8 in the Supporting Information). Compound **1a** in gels state showed one sharp peak at 2θ of 1.84° (Figure 4), corresponding to *d* spacing of 4.81 nm, measured for the xerogels formed in dichloromethane. This distance of **1a** indicates the molecules aggregate by linear type,[31,32] which could be due to π-π interactions and hydrogen bonding interactions. Especially, hydrogen bonding interactions make molecule linear between benzothiadiazole group and cholesterol. However, **1b** (the xerogel formed in dichloromethane) displays a peak at 2.84°, corresponding to *d* value of 3.10 nm (Figure 4), which is shorter than the length of the bent molecular distance of **1b**. The *d* value suggests the molecules assembled by tight bilayers, in which π-π interactions play an important part and the molecule tends to be bent between benzothiadiazole group and cholesterol. As a result, We supposed possible accumulation modes of **1a** and **1b** in the gels state as shown in Figure 5.

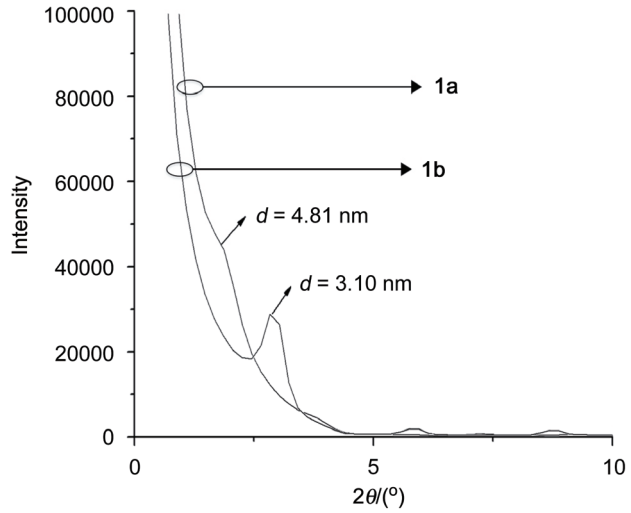

Figure 4 XRD of **1a** and **1b** xerogel from dichloromethane.

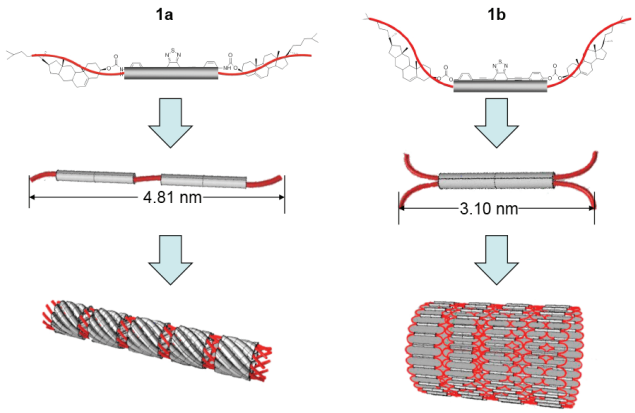

Figure 5 Possible self-assembly modes of **1a** and **1b** in the gel state.

Conclusions

In conclusion, we have designed and synthesized two multiple-stimuli responsive luminescent gels based on cholesterol containing benzothiadiazole fluorophores, which can be used as smart soft materials sensitive to temperature, solvent, ultrasound and Hg^{2+}. The underlying mechanisms of gels formation have been investigated. The results showed that π-π and hydrogen bonding interactions should be the key contributors in forming gels of **1a**, while π-π interactions played an important part in forming gels of **1b** without hydrogen bonding interactions. Hydrophobic–hydrophobic interactions and van der Waals forces also contributed to the process of gelation. We think that the results obtained in this work will be helpful to the further development of smart-responsive soft materials with interesting luminescent properties.

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