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Cholesteryl derivatives as phase-selective gelators at room temperature

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ABSTRACT

One cholesterol-based ALS and two dimeric cholesterol-based $A(LS)_2$ low-molecular-mass organic gelators (LMOGs) containing phthaloyl, isophthaloyl, and terephthaloyl moieties, respectively, were prepared. Gelation test revealed that **2** and **3** are more efficient gelators than **1**. Interestingly, **2** and **3** can gel several solvents spontaneously at room temperature and these gels posses thixotropic properties as revealed by rheological studies. More interestingly, **2** and **3** show selective gelation of the solvents from their mixtures with water. The network structures of some gels were investigated by SEM measurements, and the molecular packing mode of the LMOGs in the gel was studied by XRD analysis. Temperature- and concentration-dependent ^1H NMR measurements revealed that hydrogen bonding between the gelator molecules is an important driving force for the gel formation.

1. Introduction

Design, preparation, and performance studies of low-molecular-mass organic gelators (LMOGs) have attracted considerable interest during the last few decades. The molecules with structural diversity have been reported to gelatinize organic liquids efficiently.[1] The structures of such gelators vary from simplest alkanes [2] to giant phthalocyanine-bearing crown ether derivatives.[3] Molecules of LMOGs create entangled supramolecular networks with solvent molecules entrapped inside by self-assembly of the monomeric species to higher-order structures, such as fibrous, tubular, or helical, etc.[4] The driving forces of such self-assembling processes could be specific non-covalent intermolecular interactions, commonly electrostatic, dipole–dipole, van der Waals, π–π stacking, and/or hydrogen bonding, etc.[5] A great deal of research about LMOGs has been performed not only for probing the relationship of the structure of a gelator and the properties of the gels once formed,[6] but also for exploiting their potential applications in sensors,[7] shape memories,[8] drug delivery devices,[9] displays,[10] etc.

Of all the LMOGs reported, cholesterol-based compounds form a versatile and well-studied class.[11] For instance, George and Weiss[12] reported a series of cholesterol-based LMOGs, which were denoted as ALS gelators, and displayed effective and somewhat predictable gelation abilities. Dimeric cholesterol-based derivatives, which were denoted as $A(LS)_2$ gelators, were reported as another class of LMOGs containing a cholesteryl residue.[13] The diversity in the architectures of the $A(LS)_2$ compounds brought new potential to create some new potentialities for creating novel LMOGs with unusual properties. For example, ionic aromatic species and coordination moieties were successfully incorporated into gel superstructures, leading to stable organogels with unique functionalities.[14] Therefore, the variation in the structures and lengths or even the flexibility and hydrophobic/hydrophilic property may still be one of the most effective routes to create new LMOGs with unusual gelling properties.

Generally speaking, most of the LMOG gels have been prepared via a heating–cooling cycle, and this is, of course, a major disadvantage for the real-life applications of the gels. Therefore, exploring gel systems, which can be formed at room temperature and posses some unusual properties is still a challenge in this field. In fact, up to now, only a few examples of this kind of gels have been reported.[15]

Although large numbers of LMOGs have been developed, gelators to gelate one solvent in preference to another from a given mixture have been rarely reported. Phase-selective gelation of organic solvents could be used for the collection of oil spills, extraction of oil from its mixture with water, and purification of water. In addition to the first phase-selective gelation reported by Bhattacharya and Ghosh,[16] a few more examples for the selective gelation of oil from an oil/water mixture have also been reported.[17] However, for the systems reported, phase-selective gelation can be realized only after a heating–cooling cycle, which may limit their applications. Therefore, it is very important to develop new gelators, which are capable of achieving solvent-specific gelation from a two-phase mixture at room temperature.

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Very recently, we reported three novel dimeric cholesterol-based $A(LS)_2$ type LMOGs, and one of them could gel xylene spontaneously at room temperature.[15a] It is this work that gives us a clue that cholesterol-based $A(LS)_2$ type compounds may be good candidates to show unusual properties. Based upon this consideration, three cholesteryl derivatives (two of them posses a $A(LS)_2$ type structure) have been specially designed and prepared. The main alterations were made in the structure of the linker. As expected, selective gelation at room temperature was realized. The details of the findings are presented in this report.

2. Results and discussion

2.1. Gelation behaviors of the compounds

The gelation properties of the three compounds (Scheme 1) have been tested for 26 different solvents including protic/aprotic and polar/non-polar solvents in a concentration of 2.5% (w/v). The results are summarized in Table 1. Within the solvents tested, compound **1** formed a stable gel in 1-decanol, and a partial gel in 1-nonanol. For **2** and **3**, however, they gelled 8 and 12 solvents, respectively. Furthermore, the solvents gelled by **3** range from polar solvents like 1-hexanol to non-polar solvents like CCl_4. It is very clear that **2** and **3** are more efficient gelators than **1** if we only consider the number of solvents gelled by them.

Also shown in Table 1, **3** gelled some of the alcohols tested, but **2** did not. Instead, it dissolved in the solvents, resulting in viscous solutions. These findings demonstrate clearly that the difference in the relative positions of the two linkers attached to the benzene ring can produce a dramatic change in the gelation behavior of the compounds. The poor gelation ability of **1** might be a result of ALS type since there is only one cholesteryl moiety in one molecule of the compound.

Generally speaking, a LMOG gel is formed during the cooling of the gel system or at the end of the cooling process. In other words, a heating–cooling cycle is necessary for the formation of the gel. However, some of the gels listed in Table 1 can form spontaneously at room temperature. For example, upon dissolving **2** in $CHCl_3$, CCl_4, toluene or xylene at room temperature through sufficient shaking, and then keeping the solutions without agitation, transparent gels formed spontaneously (Fig. 1). Similar phenomenon was also found for **3**/CCl_4 system.

Table 1
Gelation properties of compounds **1**, **2**, and **3** and the critical gelation concentrations (%, w/v) of the five gel systems formed at room temperature

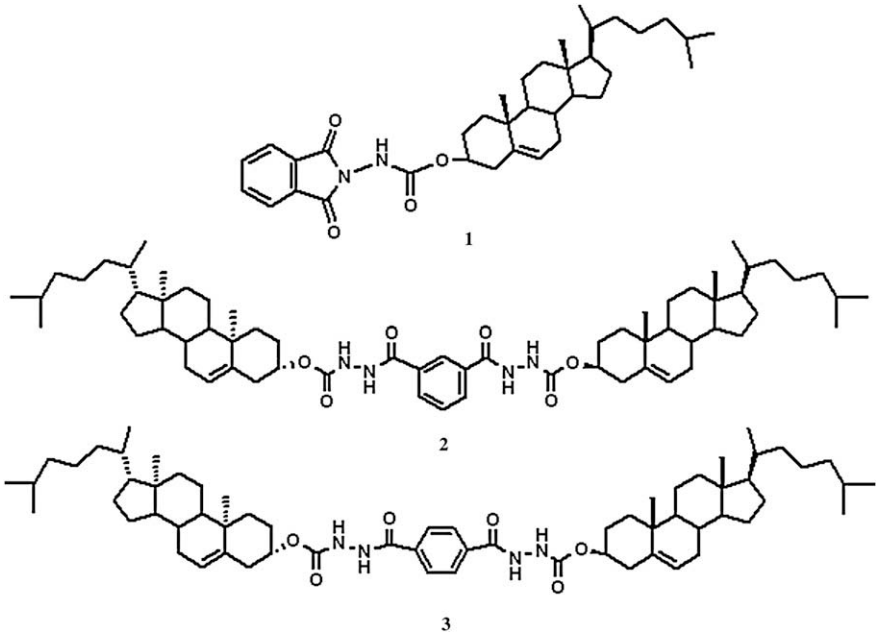
Solvent	1	2	3	Solvent	1	2	3
THF	S	S	S	Cyclohexane	I	G	G
CH_2Cl_2	I	G	I	1-Hexane	I	I	I
$CHCl_3$	S	TG(rt, 0.31)	I	Methanol	I	I	I
CCl_4	I	TG(rt, 0.39)	TG(rt, 0.25)	Ethanol	I	I	I
Toluene	P	TG(rt, 0.33)	G	1-Propanol	P	I	I
Xylene	P	TG(rt, 0.36)	G	1-Butanol	P	I	G
Benzene	P	PG	PG	1-Pentanol	P	P	P
DMSO	P	P	P	1-Hexanol	P	VS	G
DMF	S	P	P	1-Heptanol	R	VS	G
Acetone	I	I	I	1-Octanol	R	VS	G
TEA	I	PG	P	1-Nonanol	PG	VS	G
Ethyl acetate	I	I	I	1-Decanol	G	VS	G
Butyl acetate	I	I	G	Isopentyl alcohol	P	P	P

G=Turbid gel; PG=Partial gel; TG=Transparent gel; P=Precipitate; I=Insoluble; VS=Viscous solution; R=Recrystallization; G(rt)=gels formed at room temperature; the values denoted in the bracket are the critical gelation concentrations (%, w/v) of the gel systems.

For a given gelator, in addition to the number of solvents it gels, the minimum amount needed to gel a given volume of solvent (critical gelation concentration, CGC) is also an important factor to estimate its gelling ability. The CGC values of the gel systems specially mentioned above were determined (cf. Table 1). Examination of the data shown in the table reveals that the CGC values of the systems are less than 0.4% (w/v), quite low values if compared with those of other gelators containing cholesteryl unit, indicating again that the compounds prepared in the present study are efficient gelators. Furthermore, the gels formed at room temperature are very stable and no observable change occurs after several months' storage in a closed container.

2.2. Morphologies of the xerogels

To obtain a visual insight of the network structures of the gels containing different organic solvents, the morphologies of several



Scheme 1. Molecular structures of the three cholesteryl derivatives.

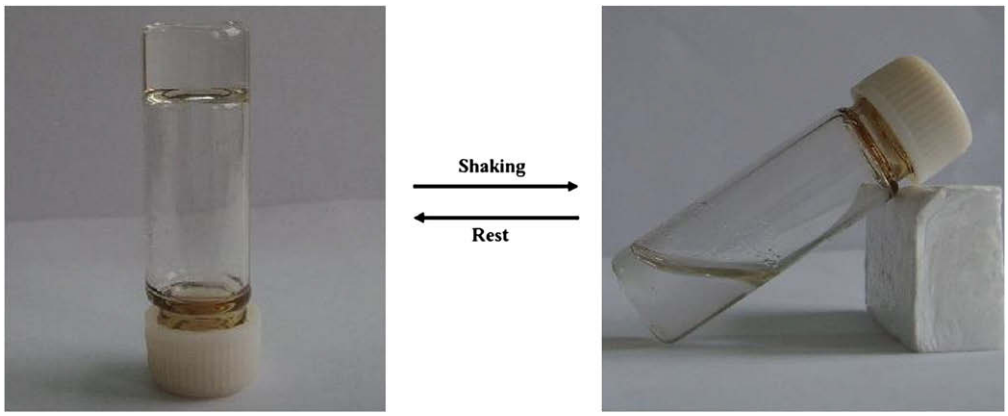


Figure 1. Reversible sol–gel phase transition of the gel of **2**/$CHCl_3$ triggered by shear stress.

xerogels containing **2** or **3** were examined by scanning electron microscopy (SEM). Representative SEM images of the xerogels are shown in Figure 2. Based on the images, all xerogels from the gels containing **2** have a clear fibrous network structures. However, the fine structures of the fibers are dependent upon the nature of the solvents. The xerogels of **2** in $CHCl_3$ and toluene exhibit network structures of very thin fibers (cf. Fig. 2a and c). However, the network structures of the xerogels of **2** in CCl_4 and xylene are composed of much thicker fibers (cf. Fig. 2b and d).

Further examining the images shown in Figure 2 reveals that the xerogels containing **3** posses very different microstructures from those containing **2**. For example, the xerogel of **3** in xylene shows prism-like rods with a diameter of about 1–2 μm (Fig. 2e). Moreover, as shown in Figure 2f, **3** aggregates into thin fibers in CCl_4 and then further assembles into flake-like structures. Based on the comparisons of the microstructures of xerogels of **2** and **3** in different solvents, and considering the structures of the two compounds, it is safe to conclude that the difference in the relative positions of two linkers attached to a benzene ring can produce a dramatic effect upon the aggregation behavior of the gelators.

2.3. Rheological studies

One of the promising properties of **2** and **3** is that they gel several organic solvents spontaneously at room temperature. More importantly, all these gels exhibit a very smart thixotropic property, which is a phase transition from a gel state to a solution state resulted from shaking, and the gel state recovers immediately once the shaking is stopped. To further investigate this thixotropic property, the rheological properties of some selected examples were studied.

In order to determine the linear regime, the gel of **2** in $CHCl_3$ (2.0%, w/v) was chosen as an example, and its storage modulus G', associated with the energy storage, and loss modulus G'', associated with the loss of energy, were measured as functions of shear stress at a constant frequency of 1 Hz at 15 °C. Figure 3 shows the result of this measurement. At low stress values, the G' parameter is more than 1 order of magnitude greater than G'', which shows the dominant elastic character of the sample.[18] Both moduli remain roughly constant below the critical shear stress value of around 6 Pa, known as the yield stress value of the gel, representing the upper limit of the linear regime. Above this value, sharp decreases of both G' and G'' are observed, which can be attributed to a partial breakup of the gel that begins to flow.

In rheological studies, frequency sweep is frequently used to detect the tolerance performance of a material to external forces.[19] The frequency sweep of the gel of **2** in $CHCl_3$ (2.0%, w/v) was conducted at a low shear stress, well within the linear regime. As shown in Figure 4, the sample is a true gel since G' is always greater than G'', and both moduli are fairly independent of frequency, a typical viscoelastic behavior, indicating that the gel has a good tolerance to external forces.

The thixotropic property of the sample was examined in a routing way, that is, the gel was sheared at a constant stress of 100 Pa for 2 min at a shearing frequency of 1 Hz. The evolution of the elastic modulus of the system was monitored as a function of time once the mechanical stress was released. The result is shown in Figure 5. It is noted that in order to perform the monitoring precisely, a very low shear stress of 0.1 Pa is applied at a frequency of 1 Hz to avoid destruction or perturbation of the gel reforming process.

As shown in Figure 5, at t equals zero, the start of the gel recovery, the sample was more like a viscous solution rather than an elastic solid ($G'<G''$), suggesting that the gel was destroyed by the initial shear stress. But the sample recovered its elastic property almost at once after the external stress was removed as that the value of G' is larger than that of G''. Clearly, the gel exhibits an unusual and very smart thixotropic property.[20]

It is known that the rheological property of a gel is also dependent upon the concentration of a gelator in it, and thereby it should be of values to investigate concentration effect upon the rheological property of a gel. Accordingly, the linear regimes of the gels of **2** in $CHCl_3$ at different concentrations were measured. As shown in Figure 6a, the values of G' increased from 2.4 Pa to 44.1 Pa with increase of the gelator concentration from 0.5 to 2.5% (w/v), and correspondingly, the yield stress increased from 1.7 Pa to 11.3 Pa, indicating that both the stability of the gel and the elastic property of the gel are well dependent upon the concentration of the gelator in the solvent.

To further elucidate the importance of different solvents to the rheological properties of a supramolecular gel, the G' values of the gels of **2** in different solvents (2.0%, w/v) were measured as functions of shear stress and the results are shown in Figure 6b. For $CHCl_3$, CCl_4, toluene, and xylene, the values of G' are about 30 Pa, 20 Pa, 23 Pa, and 21 Pa, respectively, and correspondingly, the yield stresses of them are 11 Pa, 22 Pa, 25 Pa, and 11 Pa, suggesting that the nature of a solvent could significantly influence the rheological property of a gel.

2.4. ^{1}H NMR spectroscopy studies

It is well known that, similar with other non-covalent interactions between molecules, hydrogen bonding is a commonly encountered driving force for the formation of supramolecular gels

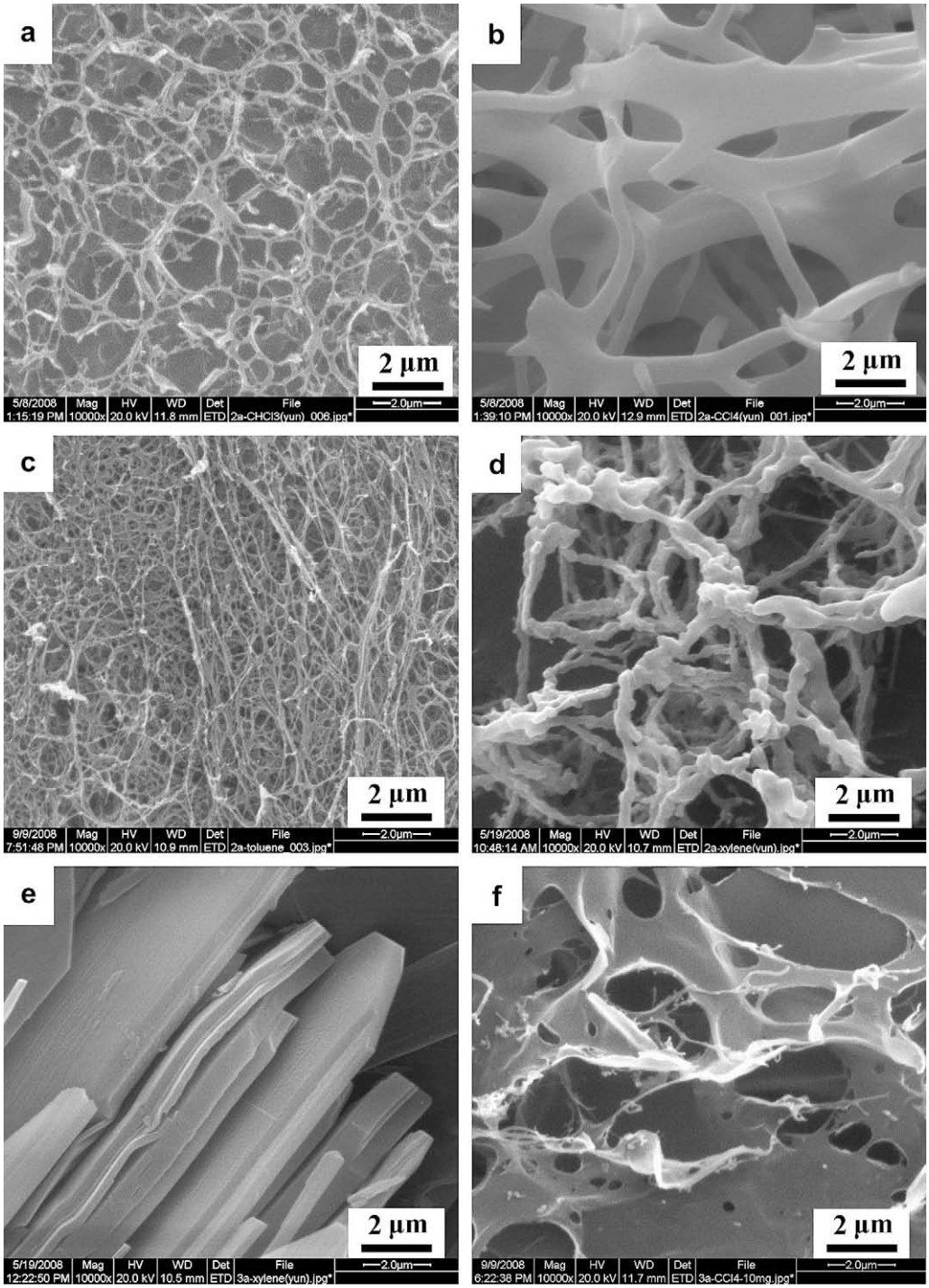


Figure 2. SEM images of the xerogels of **2** and **3** formed from different solvents. (a) **2**/$CHCl_3$; (b) **2**/CCl_4; (c) **2**/toluene; (d) **2**/xylene; (e) **3**/xylene; (f) **3**/CCl_4.

of LMOGs.[21] Considering the molecular structures of the gelators prepared in the present work, it is anticipated that hydrogen bonding might have played some roles for the formation of the gels listed in Table 1. To elucidate this hypothesis, temperature- and concentration-dependent ^{1}H NMR spectroscopy measurements of **2** in $CDCl_3$ (25 mg/mL) were conducted as these techniques can provide valuable information on the formation of hydrogen bonding between gelator molecules within a self-assembled supramolecular structure.[22] The results are shown in Figure S1. It is clear that at 308 K, the two amide protons exhibited weak and broad NMR peaks at δ=9.58 and 7.12 ppm, respectively. But the signals shifted to δ=9.41 and 7.06 ppm, respectively, at 323 K (Fig. S1a), indicating that the two amide protons had taken part in some interactions because other signals did not shift as much as the two amide proton signals did. These results supported the presence of intermolecular hydrogen bonds between neighboring gelator molecules in the gel state of **2**/$CHCl_3$ system. This tentative conclusion was further supported by the result from concentration-dependent ^{1}H NMR spectroscopy studies of the system of **2**/$CDCl_3$ at 318 K. As shown in Figure S1b, with increase of the concentration of **2**, the signals of the two amide protons gradually but significantly shifted to downfield. For instance, the chemical shifts of the two

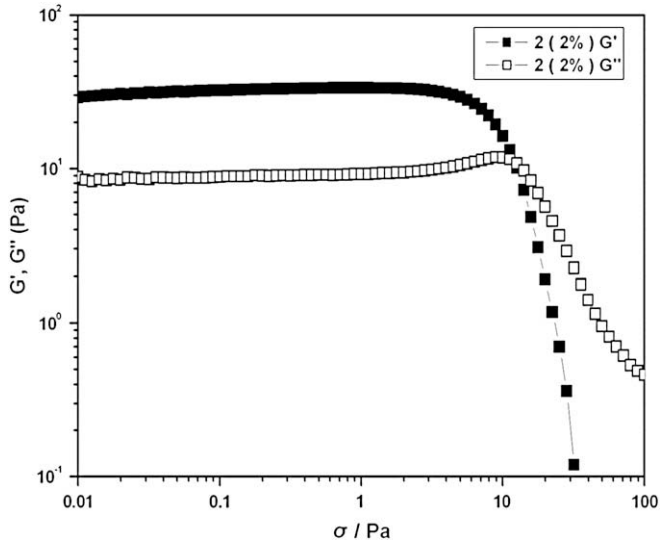


Figure 3. Determination of the linear regime. The evolution of G' and G'' as functions of the applied shear stress. The sample is a gel of **2**/$CHCl_3$ (2.0% (w/v)).

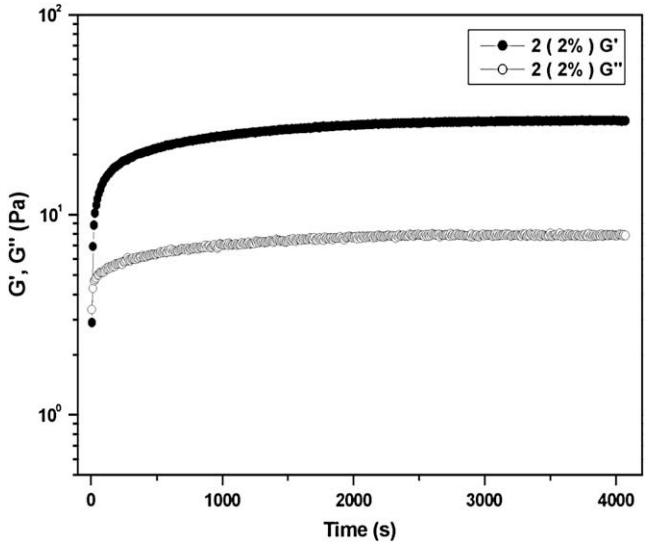


Figure 5. Evolution of G' and G'' as functions of the time after an initial shear stress of 100 Pa for 2 min stopped at t equals zero. The applied stress is 0.1 Pa and the frequency of the measurement is 1 Hz. The sample is a gel of **2**/$CHCl_3$ (2.0% (w/v)).

amide protons were 9.29 and 6.93 ppm, respectively, at 10 mg/mL, but the values change to 9.47 and 7.08 ppm, respectively, when the gelator concentration was increased to 25 mg/mL, another indication of intermolecular hydrogen bonding formation. Additional evidences can be also obtained from FTIR measurements. The results are shown in Supplementary data.

2.5. XRD studies

XRD analysis is a powerful technique to elucidate molecular packing in crystalline samples, and widely used to clarify gelation mechanism of LMOGs in gel phases.[23] To reveal the detailed molecular packing modes of the gelators in the gels as prepared, XRD analyses of the powdered samples of **2** and **3** and their xerogels in CCl_4 were conducted. The results are listed in Figures S3 and S4, respectively. As shown in Figure S3 the XRD trace of powdered **2** is characterized by three reflection peaks, and the corresponding spacings (d) are 4.28, 2.14, and 1.42 nm, respectively, almost exactly following the ratio of 1:1/2:1/3, indicating that the powered **2** posses a layered structure, and the interlayer distance is 4.28 nm, which is just the fully stretched length of **2** (cf. the inset of Fig. S3a). The xerogel of **2** in CCl_4, however, only shows one reflection peak in the low angle region (cf. Fig. S3b), and the obtained spacing (d) is 3.45 nm, which is just the calculated length of **2** as modeled by MD simulation (cf. the inset of Fig. S3b), the minimum repeat unit of the network structure of the gel of **2** in CCl_4.

For compound **3**, its xerogel from CCl_4 exhibits four reflection peaks corresponding to d spacings of 3.65, 1.82, 1.22, and 0.91 nm, respectively, following the ratio of 1:1/2:1/3:1/4 (cf. Fig. S4a), indicating that the xerogel maintains a layered structure with a interlayer distance of 3.65 nm, which is also the calculated length of **3** as modeled by MD simulation (cf. the inset of Fig. S4b). Very interestingly, the X-ray diffraction pattern of the powdered **3** is almost the same with that of the xerogel mentioned above (cf. Fig. S4b), suggesting that **3** packs in a similar way in CCl_4 as that in its solid state.

Based on the nature of the interactions between the gelator molecules and the packing mode of the gelator molecules revealed by ^{1}H NMR and XRD studies, a possible structure evolution process for the system of **3**/CCl_4 was proposed, and the result is schematically shown in Figure 7. The model is characterized by the presence of hydrogen bonding between the linkers and the aggregation of the cholesteryl units of the gelators. Furthermore, the molecules of **3** are arranged to form thin fibers, and it is these fibers that further aggregate into thick fibers and even lake-like structures. The proposed evolution process was further supported by the SEM images of the aggregates of **3** in CCl_4 at different concentrations (Fig. S5).

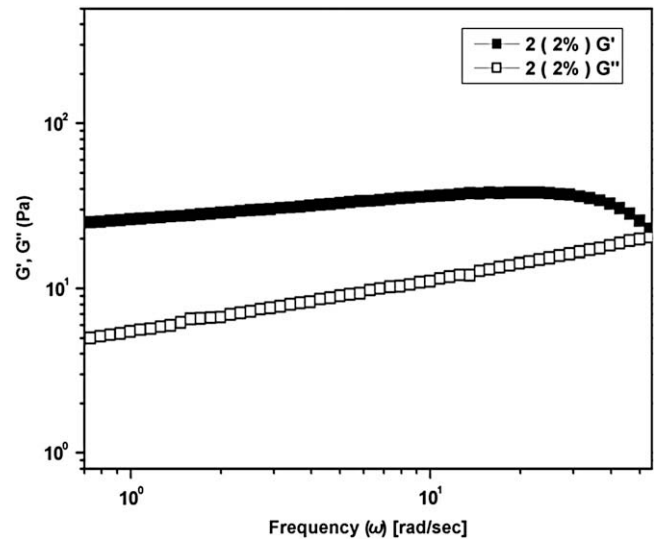


Figure 4. Evolution of G' and G'' as functions of the frequency. The applied shear stress is equal to 0.1 Pa. The sample is a gel of **2**/$CHCl_3$ (2.0% (w/v)).

2.6. Phase-selective gelation

Realization of phase-selective gelation from two-phase mixtures of solvents is valuable but challenging. This becomes an even more daunting task when one of the solvents in such a mixture is water. The reason might be that water competes for the hydrogen bonding sites in the gelator molecules, and thereby disrupting the self-association of the gelator and ruining gelation. Interestingly, gelator **2** and **3** presented in the present study display remarkable abilities to gelate selectively $CHCl_3$, CCl_4, toluene or xylene from their mixtures with water without the need of heating or addition of another solvent. To our knowledge, **2** and **3** are the first examples

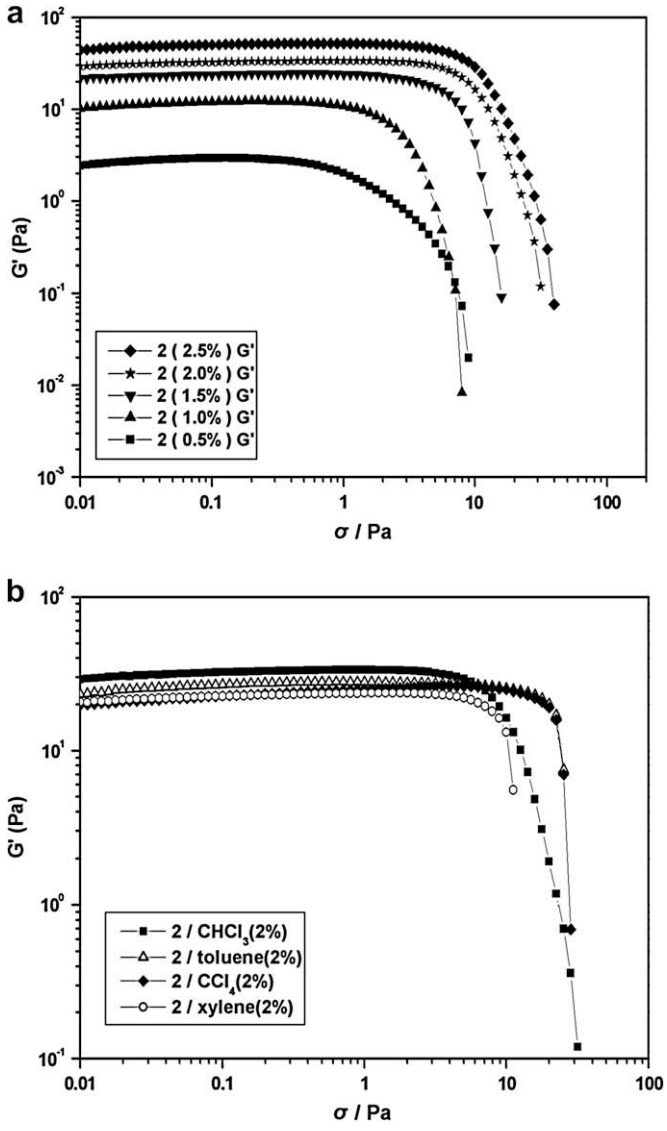


Figure 6. Determination of the linear regime. (a) The evolution of G' as functions of the applied shear stress at different concentrations of **2** in $CHCl_3$. (b) The evolution of G' as functions of the applied shear stress of **2** in different solvents.

of selective gelation of $CHCl_3$ and CCl_4 from their mixtures with water. In a typical procedure, 2 mL of water was mixed with 0.5 mL of toluene in a tube, then 0.015 g of **2** was added. The mixture was shaken sufficiently until **2** was dissolved. After a while, the toluene layer became a gel and the water layer was still in fluid state (Fig. 8a–c). For the mixture of $CHCl_3$ and water, a similar result was obtained as shown in Figure 8d–e. Heating or addition of a co-solvent is not necessary for the realization of the present phase-selective gelation process. The same observation was also found for other three room temperature gel systems.

2.7. Purification of water

Removal of water-soluble toxic dyes and other pollutants from water is a very prominent subject of research for obvious environmental reasons. Recently, there have been reports on removal of different toxic dyes and pollutants from water by suitable organogels.[24] In the present work, we tried to develop a new methodology to purify water via a phase-selective gelation process. As an example, Figure S6 shows the purification of water contaminated by rhodamine B. To the contaminated water (a), 0.5 mL of toluene was added, and the color of the water layer disappeared upon gentle shaking, indicating that the dye was extracted to the organic layer. And then, 0.015 g of **2** was added to the mixture, and the tube was shaken again until **2** was dissolved completely. Two hours later, the toluene layer became a gel. Presence of rhodamine B in the organic layer was confirmed by the light color. No doubt, as a gel, the organic layer was easily separated from the mixture, and thereby the contaminated water was purified. The efficiency of this purification process was also studied and the result is provided in Supplementary data.

3. Conclusion

In this study, a new cholesterol-based ALS type compound (**1**) and two novel dimeric cholesterol-based $A(LS)_2$ type compounds (**2** and **3**) have been designed and prepared. Gelation test in 26 solvents revealed that **2** and **3** are more efficient gelators than **1**. For **2** and **3**, the difference in the relative positions of the two linkers attached to benzene ring can produce a dramatic change in the gelation behavior and in the packing mode of the compounds. Within the solvents studied, **2** gels $CHCl_3$, CCl_4, toluene, and xylene, and **3** gels CCl_4 spontaneously at room temperature, resulting in thixotropic gels. More interestingly, **2** and **3** show phase-selective gelation of the solvents from their mixtures with water at room temperature. Purification of water contaminated with toxic dyes by selective gelation has been conceptually demonstrated. In addition to the well-known van der Waals interaction, temperature- and concentration-dependent ^1H NMR measurements revealed that hydrogen bonding is also an important driving force for the formation of the gels. XRD analysis demonstrated that the packing mode of **3** in its gel with CCl_4 is the same with that of it in solid state.

4. Experimental section

4.1. Materials

Cholesteryl chloroformate, phthaloyl chloride, isophthaloyl chloride, and terephthaloyl chloride were purchased from Across and used as received. Other reagents were obtained from Sinopharm Chemical Reagent Co., Ltd., and used without further purification. All solvents used in the syntheses were purified, dried, or freshly distilled as required.

*4.1.1. Preparation of compound **a***

Hydrazine hydrate (85%) (4.42 ml, 75 mmol) and triethylamine (695 μL, 5 mmol) were dissolved in dry dichloromethane (100 ml), and the mixture was stirred at 0 °C. To the system, 50 mL of dichloromethane solution of cholesteryl chloroformate (2.25 g, 5 mmol) was added slowly dropwise. After adding, the reaction mixture was stirred for 10 h at room temperature. After the reaction, the mixture was filtered, the filtrate was washed with water, dried over anhydrous magnesium sulfate, and evaporated in vacuum to dryness. The obtained solid was dried in vacuum to give a desired product in 65% yield as a white powder. Mp: 224–226 °C. ^1H NMR ($CDCl_3/Me_4Si$, 300 MHz): δ (ppm) 6.24 (s, 1H, COONH), 5.38 (s, 1H, alkenyl), 4.50–4.56 (m, 1H, oxycyclohexyl), 3.75 (s, 2H, $-NH_2$), 0.69–2.33 (m, 43H, cholesteryl protons). MS (MALDI-TOF): m/z calcd for $[(M-NH_2NHCOO)^+]$: 369.36, found: 369.52.

*4.1.2. Preparation of compound **1***

Compound **a** (1.56 g, 3.5 mmol) and triethylamine (1.0 ml, 7.0 mmol) were dissolved in 100 mL THF, and the mixture was stirred at 0 °C. To the system, 40 mL of THF solution of phthaloyl chloride (0.71 g, 3.5 mmol) was added slowly dropwise. After

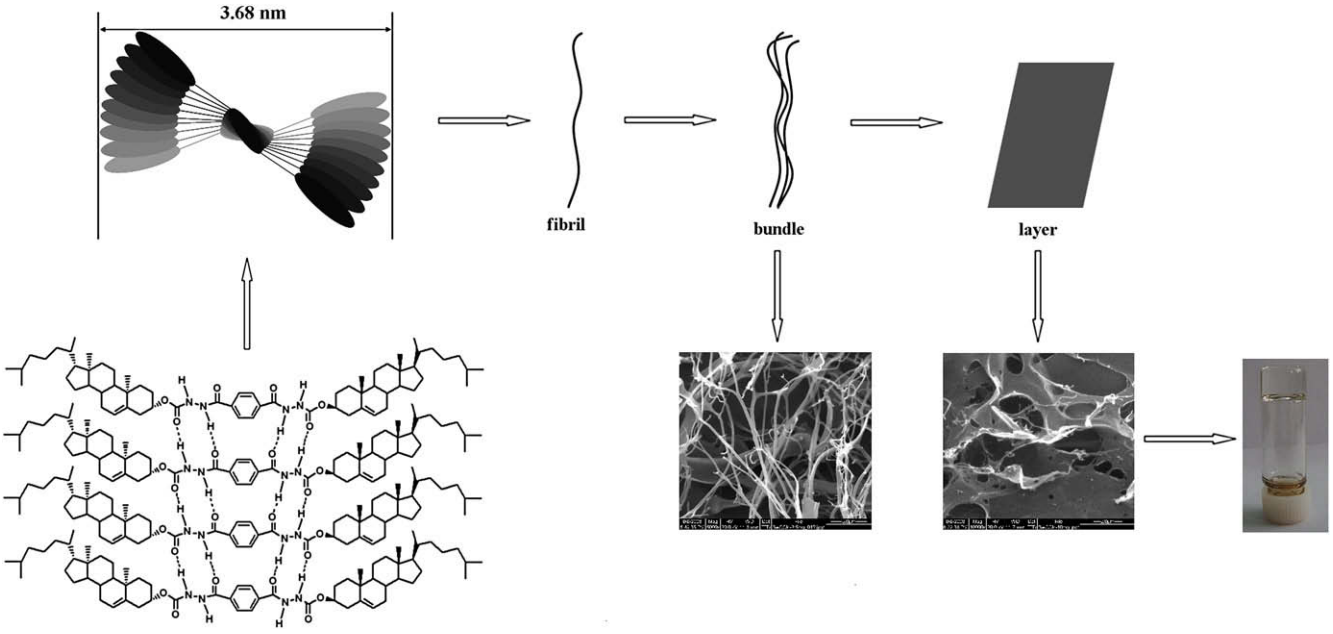


Figure 7. Schematic representation of the possible formation processes of the gel network of **3** in CCl_4.

adding, the reaction mixture was stirred for 10 h at room temperature. After the reaction, the mixture was filtered, the filtrate was evaporated to dryness, and the resulting solid was washed with hot methanol for four times, and dried in vacuum to give a desired product in 40% yield as a white powder. For **1**: mp: 269–271 °C. ^{1}H NMR ($CDCl_3$/Me_4Si, 300 MHz): δ (ppm) 7.91 (t, J=7.8 Hz, 2H, benzene), 7.80 (t, J=8.1 Hz, 2H, benzene), 6.70 (s, 1H, CONH), 5.38 (s, 1H, alkenyl), 4.57–4.62 (m, 1H, oxycyclohexyl), 0.69–2.41 (m, 43H, cholesteryl protons). FTIR, ν_{max}/cm^{-1}: 3433 (NH), 2945 (CH), 1740 (C═O, –O), 1651 (C═O, –NH), 1537 (NH, bending) and 1208 (–C–O). Anal. Calcd for $C_{36}H_{50}N_2O_4$: C, 75.22; H, 8.77; N, 4.87. Found: C, 75.32; H, 8.85; N, 4.78%. MS (MALDI-TOF): m/z calcd for [(M−$C_9H_5N_2O_4$)$^+$]: 371.36, found: 372.45.

*4.1.3. Preparation of compounds **2** and **3***

Compound **a** (3.11 g, 7.0 mmol) and triethylamine (1.0 ml, 7.0 mmol) were dissolved in 100 mL THF, and the mixture was stirred at 0 °C. To the system, 40 mL of THF solution of isophthaloyl chloride (0.71 g, 3.5 mmol) was added slowly dropwise. After adding, the reaction mixture was stirred for 10 h at room temperature. After the reaction, the mixture was filtered, the filtrate was evaporated to dryness, and the resulting solid was washed with hot methanol for four times, and the crude product was recrystallized from THF/CH_3OH mixture to give the desired product in 58% yield. The procedures used for the preparation of **3** are similar to that for **2**. For **2**: mp: 270–273 °C. ^{1}H NMR ($CDCl_3$/Me_4Si, 300 MHz): δ (ppm) 9.41 (s, 2H, COONH), 8.14 (s, 1H, benzene), 7.81 (d, J=6 Hz, 2H, benzene), 7.25 (s, 1H, benzene), 7.06 (s, 2H, CONH), 5.38 (s, 2H, alkenyl), 4.55–4.59 (m, 2H, oxycyclohexyl), 0.69–2.36 (m, 86H, cholesteryl protons). FTIR, ν_{max}/cm^{-1}: 3297 (NH), 2945 (CH), 1726 (C═O, –O), 1674 (C═O, –NH), 1518 (NH, bending), and 1243 (–C–O). Anal. Calcd for $C_{64}H_{98}N_4O_6$: C, 75.40; H, 9.69; N, 5.50. Found: C, 75.73; H, 9.70; N, 5.35%. MS (MALDI-TOF): m/z calcd for [(M+K)$^+$]: 1057.85, found: 1057.74. For **3**: mp: 282–284 °C. FTIR, ν_{max}/cm^{-1}: 3298 (NH), 2948 (CH), 1737 (C═O, –O), 1666 (C═O, –NH), 1534 (NH, bending), and 1248 (–C–O). Anal. Calcd for $C_{64}H_{98}N_4O_6$: C, 75.40; H, 9.69; N, 5.50. Found: C, 75.38; H, 9.86; N, 5.29%. MS (MALDI-TOF): m/z calcd for [(M+Na)$^+$]: 1041.74, found: 1041.76.

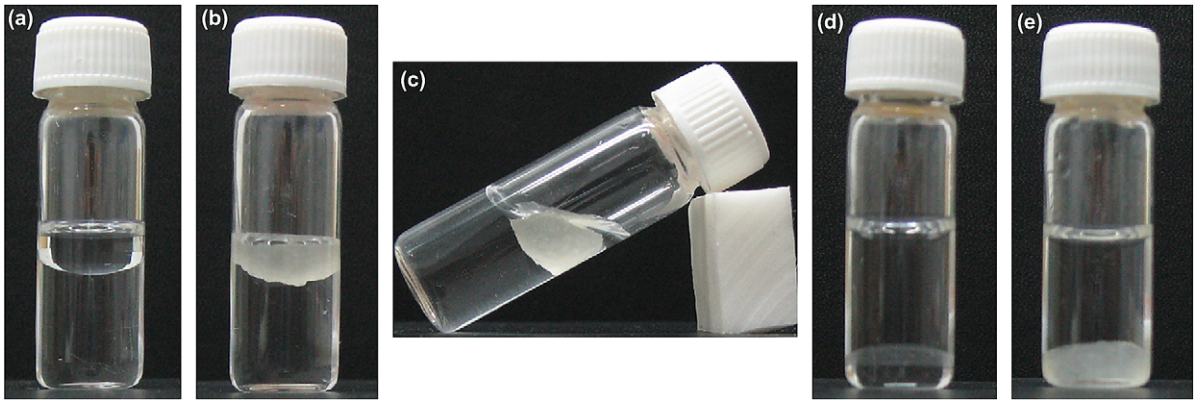


Figure 8. (a) 2 mL water and 0.5 ml toluene; (b) selective gelation of toluene layer by **2** at room temperature; (c) the inclined tube after selective gelation of toluene layer; (d) 2 mL water and 0.5 mL $CHCl_3$; (e) selective gelation of $CHCl_3$ layer by **2** at room temperature.

4.2. General methods

4.2.1. Preparation of gels

In a typical gelation experiment, a weighted amount of a potential gelator and a measured volume of selected pure solvent were placed in a sealed test tube, and then the mixture was heated until the solid was completely dissolved. The resulting solution was cooled slowly to room temperature in air, and finally the test tube was inversed to observe if the solution inside could still flow. Gelation was considered to have occurred when a homogenous substance was obtained and exhibited no gravitational flow. This was denoted by 'G'. In some cases, solution and solid-like gel may coexist within a system. This kind of system has been referred to as 'partial gels (PG)'. The systems in which only solution was remained until the end of the tests were referred as solution (S). Some systems are clear solutions when they are hot, but precipitation or crystallization occurs when they are cooled down to room temperature. These systems are denoted by 'P' (precipitation) and 'R' (recrystallization), respectively. The system in which the potential gelator was not dissolved even at the boiling point of the solvent was called an insoluble system (I).

4.3. SEM measurement

A Quanta 200 scanning electron microscopy spectrometer (Philips-FEI) was used for taking the SEM pictures. The accelerating voltage was 20 kV and the emission was 10 mA. The gel was prepared in a sample tube and frozen by liquid nitrogen. The frozen specimen was evaporated by a vacuum pump for 12–24 h. Prior to examination the xerogel was attached to a copper holder by using conductive adhesive tape, and then it was coated with a thin layer of gold.

4.4. Rheological measurement

Rheological measurements were carried out with a stress-controlled rheometer (TA instrument AR-G2) equipped with steel-coated parallel-plate geometry (40 mm diameter). The gap distance was fixed at 500 μm. A solvent-trapping device was placed above the plate to avoid evaporation. All measurements were made at 15 °C.

First, a stress sweep at fixed frequency (1 Hz) allowed determination of the linear regime of the sample. This was made by measuring the storage modulus G' and the loss modulus G'' as a function of the stress amplitude.

Second, the frequency sweep was obtained from 0.01 Hz to 100 Hz at a constant stress of 0.1 that results in small strains, well within the linear regime.

At the third step of the experiment, the time sweep was made to observe the recovery property of the gel. First, a constant oscillatory shear stress that is enough to destroy gel structure is applied to the sample for 2 min. And then, a very small constant shear stress (1 Hz, 0.1 Pa) in the linear regime is applied in the same procedure. The shear stress chosen was so low to prevent any major disturbance but remained adapted to deliver a satisfactory signal. The storage modulus G' and the loss modulus G'' are recorded as a function of time in this experiment.

4.5. FTIR measurement

All FTIR measurements were performed on a Brucher EQUINX55 spectrometer in an attenuated total reflection (ATR) way with ZnSe as sample slot. The KBr pellets mixed with samples were measured on the transparent mode.

4.6. ^{1}H NMR measurement

^{1}H NMR data of samples were collected on Bruker AVANCE 300 MHz spectrometer.

4.7. XRD measurement

Diffraction patterns were carried out on a Japan Rigaku D/max-III diffractometer with Cu Kα X-ray generated (λ=1.5418 Å) under a voltage of 40 kV and a current of 40 mA. The scan rate was 0.5°/min. The xerogel was prepared by freezing the gel in liquid nitrogen, and then evaporated by a vacuum pump for 12–24 h.

4.8. MS measurement

MALDI-TOF mass spectra were recorded in a Kratos' AXIMA-CFR plus instrument using 2,5-dihydroxybenzoic acid (DHB) as matrixes.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.02.056.

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