New dicholesteryl-based gelators: gelling ability and selective gelation of organic solvents from their mixtures with water at room temperature†

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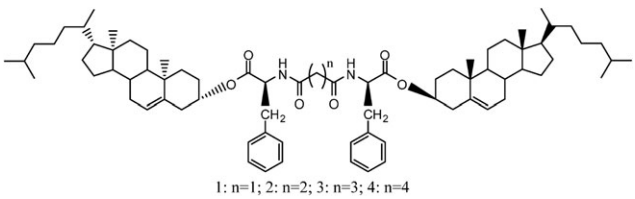
Four new diacid amides of dicholesteryl L-phenylalaninate were designed and prepared. The compounds with spacers containing three, four, five, or six carbon atoms are denoted as **1–4**, respectively. Gelation tests showed that the four compounds are versatile organogelators, and a subtle change in the length of the spacer can produce a dramatic change in the gelation behaviors of the compounds, as well as the micro-structures of the gel networks as revealed by SEM and XRD measurements. Within the 77 gel systems studied, at least seven of them, including **2**/kerosene, **2**/toluene, **2**/xylene, **3**/kerosene, **3**/1-pentanol, **3**/1-hexanol and **3**/1-heptanol, gel spontaneously at room temperature. Furthermore, **2** and **3** can be used for the selective gelation of xylene or kerosene from their mixtures with water. Importantly, heating and cooling cycle or addition of a co-solvent is not necessary for the selective gelation. Furthermore, the gels of **2**/xylene are mechanically strong enough for separation, and thereby it is believed that **2** is a strong candidate for the practical separation of xylene from its mixture with water. FT-IR and temperature-dependent ^{1}H NMR measurements demonstrated that inter-molecular hydrogen bonding plays an important role for the formation and maintenance of the gel networks.

Introduction

Recent years have witnessed an intense investigation on the design and preparation of new low molecular mass gelators (LMGs) for the purpose of creating functional nanostructured soft materials with properties that are tunable by external stimuli,[1] such as light, temperature, sonication and chemical additives. It is believed that these materials are important for forward-looking applications of them,[2] such as confined reaction media, templates for well-defined inorganic materials or polymers, light-harvesting systems, sensors, biomaterials and optoelectronic devices. However, structural requirements for LMGs are not well understood, and a rational correlation of molecular structure and gelation ability in a given solvent still remains a challenge.[3] Therefore, intensive effort has been expended to understand the structure–property relationships to tailor LMGs, and has resulted in the discovery of a variety of small molecules which are efficient gelators.[4]

Up to now, gelators, which can gelate one solvent in preference to another from a given mixture, particularly, if one of the solvents in such a mixture is water, have still been rarely reported. The reason might be that water competes for the hydrogen bonding sites in the gelator molecules, and thereby disrupts the self-association of the gelator and so hindering gelation. A few examples for the selective gelation of oil from an oil/water mixture have been reported,[5] but the phase selective gelation could only be achieved by heating and cooling the mixtures, or by addition of another co-solvent into the systems, which must limit the practical applications of the findings. In addition, LMGs for selective gelation of aromatic solvents such as toluene and xylene from their mixtures with water have not been reported. Separation of them from water is crucial because these solvents are widely used, are toxic, and very difficult to be decomposed naturally.[6]

In that connection, from both fundamental and practical standpoints, development of these LMGs is of great importance, particularly, when the structures of the LMGs are simple, and can be synthesized from naturally available, and cheap starting materials. L-Amino acid- and cholesterol-based gelators are some of the best gelators according to the following concepts: they are safe for the environment and living organisms, most L-amino acids and cholesterol are commercially available and relatively cheap, and the relevant synthetic methodologies have been already established.[7] Our group has developed some efficient LMGs through combination of the two components.[8] In this study, we describe the synthesis of new LMGs (Scheme 1) based on L-phenylalanine and



1: n=1; 2: n=2; 3: n=3; 4: n=4

Scheme 1 Molecular structures of the diacid amides of dicholesteryl L-phenylalaninate.

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† Electronic supplementary information (ESI) available: XRD patterns of powder samples **1–4** and of xerogels of compounds **1–4** from cyclohexane. SEM images of xerogels of **1**/cyclohexane. See DOI: 10.1039/b807576j

cholesterol, and their gelation properties. To our delight, we observed firstly the selective gelation of kerosene, toluene or xylene from their mixtures with water without the need of heating or addition of a co-solvent. More interestingly, the gels of the organic solvents possess salt resistant properties, adding value for the practical uses of the systems.

Results and discussion

Gelation behavior of the compounds

The gelation properties of compounds **1–4** were examined in various organic solvents at a concentration of 2.5% (w/v) by the "stable to inversion of a test tube" method and the results are listed in Table 1. With reference to the data shown in Table 1, it can be seen that **1**, **2**, **3** and **4** are versatile LMGs and can gelate 20, 20, 19 and 18 of the 29 solvents tested, respectively.

Although the numbers of solvents gelated by each of the four gelators are almost the same, differences between them still exist. For example, unlike others, **4** can gelate only a few of the alcohols tested in the experiment, and similarly **1** can gelate ethyl acetate, DMF and acetic acid, but others cannot. Another interesting comparison is among benzene, toluene, xylene and CCl_4, **2** and **4** show better gelation ability even though the systems of **2**/CCl_4, **4**/benzene, and **4**/CCl_4 are marked as "s", but they are viscous solutions. By contrast, dissolution of **1** and **3** in the solvents is a spontaneous process,

Table 1 Gelation performances of some diacid amides of dicholesteryl L-phenylalaninate in various organic solvents[a]

Solvents	1	2	3	4
Methanol	I	I	I	I
Ethanol	G	PG	PG	PG
1-Propanol	G	PG	S	P
1-Butanol	G	PG	PG	PG
1-Pentanol	G	G	G*	G
1-Hexanol	G	G	G*	P
1-Heptanol	G	G	G*	P
1-Octanol	G	G	G	P
1-Nonanol	G	G	G	P
1-Decanol	G	G	G	P
Cyclohexane	G	G	G	G
n-Hexane	I	I	G	PG
n-Heptane	G	G	G	G
n-Octane	G	G	G	G
n-Nonane	G	G	G	G
n-Decane	G	G	G	G
Kerosene	P	G*	G*	G
Benzene	S	TG	S	S
Toluene	S	TG*	S	TG
Xylene	S	TG*	S	G
CCl_4	S	S	S	S
Ethyl acetate	G	P	P	PG
Acetone	G	I	G	G
Ether	I	G	G	PG
Triethylamine	G	G	G	G
Pyridine	S	S	S	PG
DMSO	G	P	G	S
DMF	G	P	P	P
Acetic acid	G	P	P	PG

[a] Concentration of gelator: 2.5%, w/v; G: turbid gel; PG: partial gel; TG: transparent gel; P: precipitate; I: insoluble; S: solution; G*: gels forming at room temperature.

Table 2 The critical gelation concentrations (CGC) of the gels of different gelators in cyclohexane

Gelator	1	2	3	4
CGC (%, w/v)	2.00	1.17	1.11	0.28

and there is no appreciable viscosity difference between the solvents and the solutions.

Further investigation reveals that the critical gelation concentrations (CGC) are also spacer length dependent. As examples, Table 2 provides the CGC values of the gelators in cyclohexane. Clearly, CGC decreases gradually with increasing the spacer length of the gelators. For gelator **4**, the value is only 0.28% (w/v), which is quite low if compared with those of other cholesterol-based gelators.

It is somewhat surprising to find that seven of the gels listed in Table 1 could be formed at room temperature without sonication, or heating. For example, dissolving **2** in kerosene, toluene or xylene at room temperature, and then keeping the solution without agitation resulted in gelation spontaneously. A similar behavior was also observed for **3**/1-pentanol, **3**/1-hexanol, **3**/1-heptanol and **3**/kerosene. The kinetics of the gel formation processes differ from each other. At 25 °C, the gel of **3**/kerosene formed within 10 min. For other systems, however, the gels formed 1–12 h later after dissolution of the gelators in the solvents. It is of note that variation of temperature produces little effect upon the formation of the gels of **2** in toluene and xylene even down to 0 °C. In contrast, for other systems decreasing temperature prohibits gelation. Specifically, 12 h at 15 °C leads to no indication of gelation.

These findings demonstrate clearly that the length of the spacer connecting the two cholesteryl units has a pronounced effect upon the gelling performance of the compounds studied. This is not difficult to understand because the length of the spacer must affect the conformational and assembling behaviors of the gelators, and thereby result in different supramolecular structures in the solvents.

Scanning electron microscopy (SEM) studies

The gel systems of cyclohexane were adopted as examples and investigated in order to see how the network structures of the gels were influenced by the lengths of the spacers of the gelators. Xerogels were prepared by freeze-drying of each of the gels (3%, w/v). Fig. 1 shows the SEM images of the xerogels. With reference to the images, it can be seen that the network structures are very different from each other although they are all well developed, a distinct spacer length effect.

Further examination of the SEM images reveals: (1) the morphologies of the gel networks in this investigation varied from ribbons (Fig. 1(a)) to sheets (Fig. 1(b) and (c)) and fibers (Fig. 1(d)); (2) unlike **1** and **2** in the gels, the aggregate of **3** in the solvent adopted beautiful and nearly perfect feather-like structures, which is rarely reported in the literature; (3) the morphology of the xerogel of **4**/cyclohexane is characterized by routine fibrous networks; (4) a further difference among the aggregates is the flexibility of the aggregates. Clearly, the aggregates of **1** and **2** are more brittle than those of **3** and **4**,

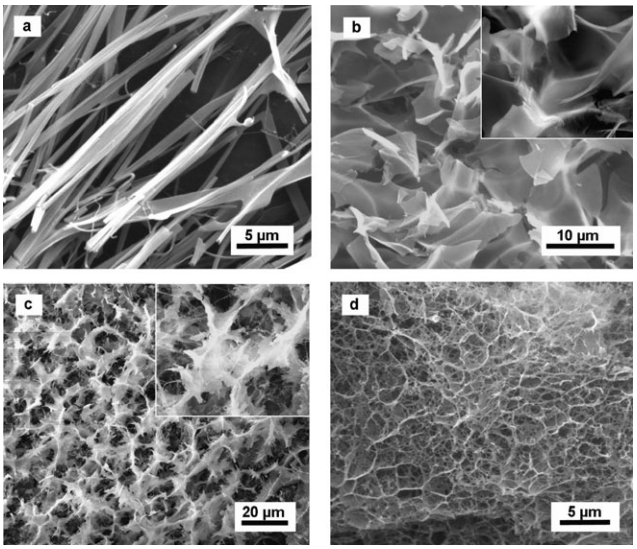

Fig. 1 SEM images of the gel networks of the gelators of different spacer length *n* in cyclohexane: (a) $n = 1$; (b) $n = 2$ (inset, high-magnification image); (c) $n = 3$ (inset, high-magnification image); (d) $n = 4$.

as revealed by the existence of the breakpoints in the xerogels of **1**/cyclohexane and **2**/cyclohexane (Fig. 1(a) and (b)). These observations demonstrate that only one CH_2 difference can result in a great difference in the structures of the gel networks.

FT-IR spectroscopy studies

Considering the structures of the LMGs prepared in this work, and the well-known fact that hydrogen bonding is one of the main driving forces for the self-assembly of cholesterol-based LMGs, it is expected that intermolecular hydrogen bonding should exist in the gel systems studied. Accordingly, FT-IR measurements were conducted due to their usefulness in revealing such intermolecular interaction. During the measurement, **4**/cyclohexane was adopted as a representative system, and the solution of **4** in $CDCl_3$ was chosen as a reference. The FTIR spectra of both systems are depicted in Fig. 2. With reference to the spectrum of the control, it can be observed that the two typical bands of **4** corresponding to the stretching vibrations of NH and C═O in the amide, appeared at 3321 and 1650 cm^{-1}, respectively. Upon gelation, the bands shifted to 3311 and 1644 cm^{-1}, respectively, suggesting the participation of the amide NH and C═O groups in hydrogen bonding.[9] Similar spectral shifts were also found for other gel systems (Table 3). It is somewhat surprising that the direction of the spectral shifts of the systems containing **2** is different from other gel systems (Table 3), indicating that a different aggregation mode might be adopted by this system.[10] It is to be noted that in contrast, the characteristic absorptions of the ester C═O groups did not change very much during the gelation processes (Fig. 2 and Table 3), an evidence of their non-participation in the aggregation processes.

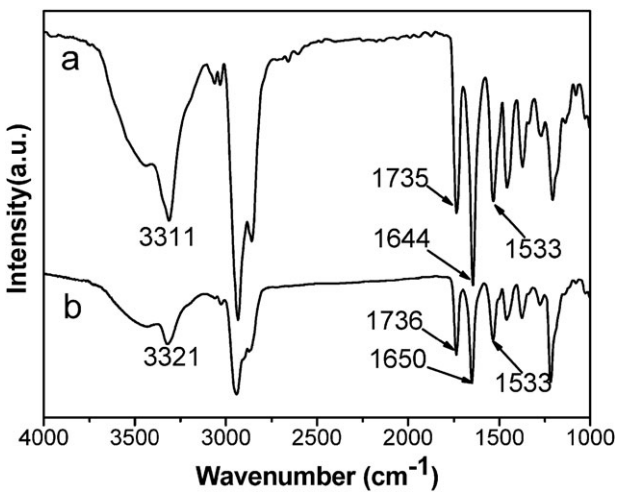

Fig. 2 FT-IR spectra of (a) a gel of **4** in cyclohexane and (b) a solution of **4** in $CDCl_3$.

^{1}H NMR spectroscopy studies

The aggregation behavior of the gelators in gel and solution state was studied in detail by conducting temperature- dependent ^{1}H NMR measurements of **2** and of **4** in benzene-d_6 in order to obtain further information on the formation mechanism of the gel networks. The results are shown in Fig. 3 and 4, respectively. It can be seen that change in temperature has a distinct effect upon the chemical shifts of the N–H protons of the gelators. For the system of **2** in benzene-d_6, the signal was a broad band and appeared at 6.55 ppm at 25 °C, but it gradually shifted to up-field (6.37–6.40 ppm) and separated into two peaks at 65 °C. As mentioned already, **4** can not gelate benzene under the experimental conditions, but dissolving it into the solvent can increase the viscosity of the solution significantly, an evidence of association of the gelator molecules in the system.[11] This association was confirmed by an obvious up-field shift of the ^{1}H NMR signal of N–H upon increasing the temperature of the solution (Fig. 4). Again, the NH group of **4** plays a role in the self-assembly of the gelator molecules, in support of the tentative conclusion from FTIR studies.

XRD studies

The packing structures of the gelator molecules in gels with cyclohexane as a solvent and in the solid state were investigated using XRD technique (see ESI†). The major peaks observed are listed in Table 4. It can be seen that the diffraction pattern of the powder sample of compounds **1** and **2** are characterized by four obvious reflection peaks, and the ratio of the *d* values is 1 : 1/2 : 1/3 : 1/4, suggesting a perfect lamellar organization.[12] Further examination of the XRD data of the xerogels reveals that compound **1** adopted a similar structure *via* the aggregation of the gelator **1** in the gel state, even though peak 3 did not appear in its XRD pattern. However the aggregated structure of gelator **2** in the gel state is different from that of **2** in the solid state. As for compounds **3** and **4**, it was impossible to deduce detailed structural information as a result of the limited data available in the XRD patterns.

The interlayer distance of the lamellar structure, the *d* spacing, just equals the molecular length (4.11 nm) of the gelator **1**, indicating that the advanced structures of the aggregates of **1** in the gel state might be based on this

Table 3 FT-IR data for gelators in $CDCl_3$ (solution) and in cyclohexane (gel)

		$\tilde{\nu}_{max}/cm^{-1}$			
		NH stretch	C═O ester	C═O amide	NH bend
1	Solution	3446	1738	1648	1540
	Gel	3320	1736	1652	1525
2	Solution	3296	1737	1646	1539
	Gel	3300	1737	1646	1533
3	Solution	3300	1736	1651	1539
	Gel	3284	1740	1648	1536

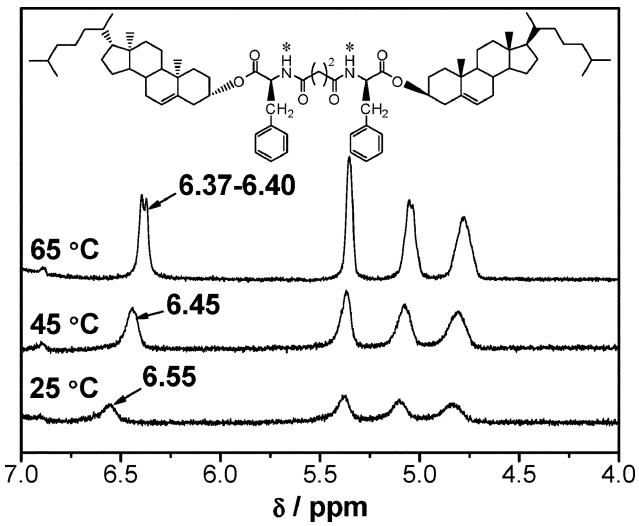

Fig. 3 Temperature-dependent ^1H NMR spectra of the gel of **2** in benzene-d_6 at a concentration of 3% (w/v).

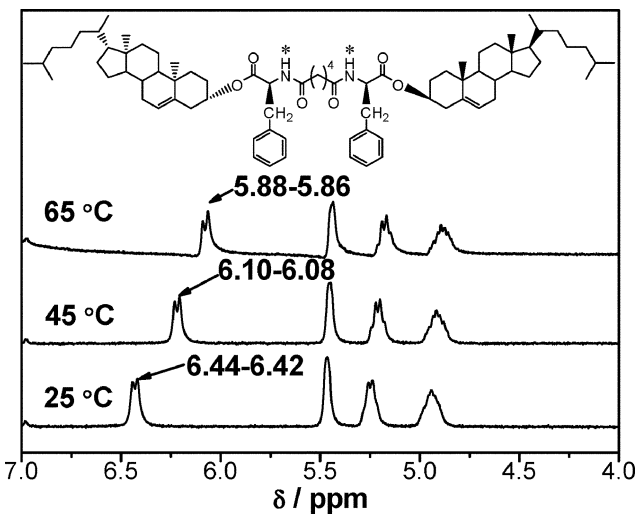

Fig. 4 Temperature-dependent ^1H NMR spectra of the solution of **4** in benzene-d_6 at a concentration of 3% (w/v).

Table 4 Major peaks in the XRD patterns for compounds **1–4**

	d-Spacing/nm
1	Solid: 4.21, 2.12, 1.43, 1.07; gel: 4.05, 2.10
2	Solid: 4.58, 2.29, 1.62, 1.09; gel: 2.79
3	Solid: 1.33, 0.99; gel: 2.61
4	Solid: 1.38, 1.02; gel: 4.14, 2.2

fundamental structure (Fig. 5). By reference to the model shown in Fig. 5, it can be seen that it is characterized by hydrogen bonds between the spacers, as already demonstrated by FTIR and ^1H NMR studies, and the aggregation of the cholesteryl units of the gelators. Furthermore, the molecules of the gelator are arranged in parallel to form spherical aggregates. The aggregates are further amalgamated into a 1D fibrous structure, and eventually these elemental fibers form ribbons *via* the above-mentioned interactions. These hypotheses have been proved by observing the SEM images of the aggregates of **1** in the solvent at different concentrations (see ESI†).

Selective gelation of xylene from its mixture with water

Selective gelation of organic solvents, such as commercial oil and aromatic solvents, from their mixtures with water is very important in view of its applications in oil extraction, collection of leaked oil, and purification of water contaminated by oil.[5] Interestingly, **2** displays a remarkable ability to gelate xylene selectively from its mixture with water without the need of heating or addition of another co-solvent. **3** gelates kerosene from its mixture with water in a similar way. To our knowledge, **2** and **3** are the first examples of this kind of gelators even though other selective gelators have been reported. Unlike **2** and **3**, the gelators as reported in the literature can only show selective gelation with the aid of heating or addition of a co-solvent.

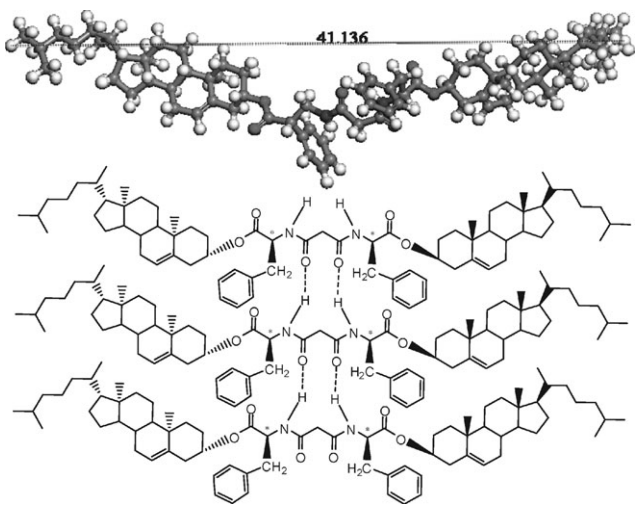

Fig. 5 Schematic representation of the possible aggregation mode of **1** in cyclohexane.

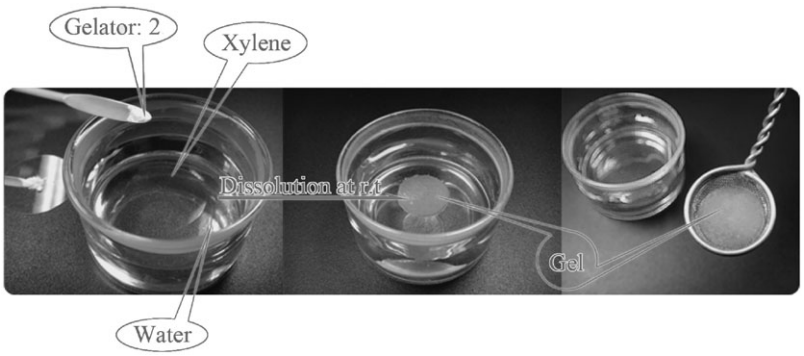

Fig. 6 Selective gelation of xylene from its mixture with water.

Fig. 6 shows a typical result of the selective gelation of xylene by **2** from a xylene/water mixture. In the experiment, 10 mL of water was mixed with 0.1 mL of xylene in a 25 mL weighing bottle, then a amount of **2** was added, and then the bottle was shaken gently until **2** was dissolved. After some time an organogel formed. Importantly, the selective gelation still works at temperatures as low as 0 °C, which is believed to be very crucial for practical uses. In contrast, selective gelation of kerosene by **3** from its mixture with water only works at a temperature range between 25 and 30 °C.

Rheological properties of the gels

The mechanical properties of the gels above are important for practical separation of them from water, and thereby their 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 room temperature by using **2**/xylene (3.0%, w/v) as an example. The results are shown in Fig. 7. By reference to Fig. 7(a), it is seen that at low stress values (below 10 Pa), G' is about one order of magnitude greater than its corresponding G'', indicating that the gel is dominated by elastic character.[13] Furthermore, both G' and G'' remain roughly constant below a critical stress value of around 50 Pa, known as the yield stress value. Frequency sweep is a method to detect the tolerance performance of a material to external forces. Accordingly, this test was also conducted for the sample gel, and the results are shown in Fig. 7(b). Clearly, both G' and G'' of the gel increased slightly with increasing the frequency, specifically, from 100 Pa for G' and 40 Pa for G'' at 0.628 rad s^{-1} to 600 Pa for G' and 200 Pa for G'' at 300 rad s^{-1}, a typical viscoelastic behavior, suggesting that the gel has a good tolerance to external forces. With further increasing the frequency, however, the G' and G'' of the gel of **2** in xylene become erratic (*e.g.* $f > 300$ rad s^{-1}), an indication of breaking of the gel. These results demonstrate that this system is a very competitive candidate for gentle separation of xylene from its mixture with water.

Conclusion

It has been demonstrated that the diacid amides of dicholesteryl L-phenylalaninate described in this article can act as versatile gelators. Both the aggregation mode, the morphologies of the gel networks, and the gelation abilities of the compounds are very dependent upon the length of the spacer connecting the two cholesteryl moieties. Within the gel systems studied, at least seven of them, including **2**/kerosene, **2**/toluene, **2**/xylene, **3**/kerosene, **3**/1-petanol, **3**/1-hexanol and **3**/1-heptanol, gel spontaneously at room temperature. Importantly, **2** can gel xylene and **3** can gel kerosene selectively from mixtures of the two solvents with water, respectively. More importantly, heating and cooling cycle or addition of a co-solvent, which is recognized as an essential procedure for selective gelation, is unnecessary for the systems discovered. Furthermore, rheological studies revealed that the gels of **2**/xylene are soft, but mechanically strong enough for collection,

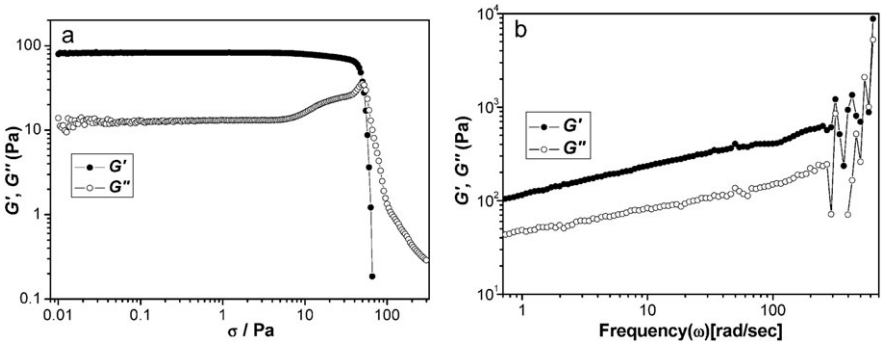

Fig. 7 (a) Determination of the linear regime. Measurement of the evolution of G' and G'' as a function of the applied shear stress, and the frequency of the measurement is $f = 1$ Hz. (b) Evolution of G' and G'' as a function of the frequency. The applied shear stress is equal to 0.5 Pa, and the experiment is performed in the linear regime. The sample is a gel of **2** ($c = 3.0\%$, w/v) in xylene, and the experiments were performed at 25 °C.

and thereby **2** is potentially applicable for the separation of the solvent from its mixture with water. FTIR and temperature-dependent ^{1}H NMR studies revealed that hydrogen bonding plays an important role for the formation and maintenance of the gel networks.

Experimental

Materials

Cholesteryl, L-phenylalaninate, dicyclohexylcarbodimide (DCC), *N*,*N*-dimethylaminopyridine (DMAP) and diacid were supplied from the Sinopharm Chemical Reagent Co., Ltd, and used without further purification. All solvents used in the syntheses were purified, dried, or freshly distilled as required.

General procedure for the synthesis of compound 1

Cholesteryl L-phenylalaninate primary amine was synthesised according to a previous report. malonic acid (0.208 g, 2 mmol) was dissolved in 20 mL tetrahydrofuran (THF), and then 40 mL of THF solution containing 1.83 g (4 mmol) of cholesteryl phenylalaninate primary amine and 0.824 g (4 mmol) of dicyclohexylcarbodimide (DCC) was added dropwise to the above solution with stirring. The reaction mixture was stirred at 50 °C for 10 h. After the reaction, the mixture was filtered, the filtrate was evaporated to dryness, and the resulting solid was washed with hot methanol three times, and dried in vacuum to give the desired product as a white or yellowish powder. Satisfactory results were obtained.

1: Yield: 30%. IR (KBr) ν/cm^{-1}: 3305 (νN–H, amide), 1739 (νC=O, ester), 1658 (νC=O, amide I), 1525 (δN–H, amide II); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25 °C) δ 7.14–7.25 (m, benzyl, CONH, 12H), 5.36 (s, alkenyl, 2H), 4.77–4.79 (d, C*H*(CH_3)COO, 2H), 4.58 (s, oxycyclohexyl, 2H), 3.14 (s, –C*H*$_2$(C_6H_5), 4H), 3.09 (s, $COCH_2CO$, 2H), 0.68–2.47 (m, cholesteryl protons, 86H); elemental analysis: calc. (%) for $C_{75}H_{110}N_2O_6$ (1134.84): C, 79.32; H, 9.76; N, 2.47; Found: C, 78.64; H, 9.85; N, 2.29.

General procedure for the synthesis of compounds 2, 3 and 4

Cholesteryl L-phenylalaninate primary amine (1.83 g, 4 mmol) and succinic acid (0.24 g, 2 mmol) were dissolved in 50 mL tetrahydrofuran, and the mixture was stirred at 0 °C. To the system, 0.824 g (4 mmol) of dicyclohexylcarbodimide (DCC) and 0.048 g (0.4 mmol) of *N*,*N*-dimethylaminopyridine (DMAP) were added, and the mixture stirred at 0 °C for 4 h. After the reaction, the mixture was filtered, the filtrate was evaporated to dryness, and the resulting solid was washed with hot methanol for three times, and dried in vacuum to give a desired product as a white powder. The procedures used for the preparation of **3** and **4** are similar to that for **2**. Satisfactory results were obtained.

2: Yield: 48%. IR (KBr) ν/cm^{-1}: 3255 (νN–H, amide), 1739 (νC=O, ester), 1640 (νC=O, amide I), 1540 (δN–H, amide II). ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25 °C): δ 7.15–7.26 (m, benzyl, 10H), 6.43 (s, CONH, 2H), 5.36 (s, alkenyl, 2H), 4.79 (s, C*H*(CH_3)COO, 2H), 4.59 (s, oxycyclohexyl, 2H), 3.08 (s, –C*H*$_2$(C_6H_5), 4H), 2.29–2.49 (d, $COCH_2$, $–CH_2CO$, 4H), 0.68–1.99 (m, cholesteryl protons, 86H); elemental analysis: calc. (%) for $C_{76}H_{112}O_6N_2$ (1148.85): C, 79.39; H, 9.82; N, 2.44; Found: C, 79.18; H, 10.02; N, 2.24.

3: Yield: 55%. IR (KBr) ν/cm^{-1}: 3306 (νN–H, amide), 1738 (νC=O, ester), 1649 (νC=O, amide I), 1539 (δN–H, amide II). ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25 °C): δ 7.71–7.74 (d, J = 8.2 Hz, CONH, 2H), 7.26 (m, benzyl, 10H), 5.38 (s, alkenyl, 2H), 4.80–4.82 (d, C*H*(CH_3)COO, 2H), 4.64 (s, oxycyclohexyl, 2H), 3.09–3.10 (d, –C*H*$_2$(C_6H_5), 4H), 2.91–2.87 (m, $COCH_2$, $–CH_2CO$, 4H), 2.00–2.28 (m, $–CH_2–$, 2H), 0.69–1.93 (m, cholesteryl protons, 86H); elemental analysis: calc. (%) for $C_{77}H_{114}O_6N_2$ (1162.87): C, 79.47; H, 9.87; N, 2.41; Found: C, 78.77; H, 10.05; N, 2.24.

4: Yield: 63%. IR (KBr) ν/cm^{-1}: 3315 (νN–H, amide), 1740 (νC=O, ester), 1651 (νC=O, amide I), 1537 (δN–H, amide II). ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25 °C): δ 7.15–7.29 (m, benzyl, 10H), 6.19 (s, CONH, 2H), 5.36 (s, alkenyl, 2H), 4.82–4.84 (d, C*H*(CH_3)COO, 2H), 4.60 (s, oxycyclohexyl, 2H), 3.10 (s, –CH_2(C_6H_5), 4H), 2.18–2.23 (m, $COCH_2$, $–CH_2CO$, 4H), 0.68–1.99 (m, $–CH_2CH_2–$, cholesteryl protons, 90H); elemental analysis: calc. (%) for $C_{78}H_{116}O_6N_2$ (1176.88): C, 79.54; H, 9.93; N, 2.38; Found: C, 78.93; H, 10.18; N, 2.28.

General methods

Measurements. The elemental analyses were performed using CHNS/O analyzer Vario EL III. Scanning electron micrograph (SEM) images of the xerogel were taken on a Quanta 200 scanning electron microscopy spectrometer (Philips-FEI). The accelerating voltage was 15 kV, and the emission was 10 mA. Rheological measurements were performed using a stress-controlled rheometer (TA instrument AR-G2) equipped with aluminum-coated parallel-plate geometry (40 mm diameter, 0.400 mm gap between the two plates). A solvent-trapping device was placed above the plate to avoid evaporation. The FT-IR spectra were recorded by a Brucher EQUINX55 spectrometer in an attenuated total reflection (ATR) way with ZnSe as sample slot. ^{1}H NMR data of samples were collected on Bruker AVANCE 300 MHz spectrometer. X-Ray diffraction (XRD) data of samples were collected on a D/Max-2550/PC with Cu-Kα X-ray radiation generated under a voltage of 40 kV and a current of 40 mA. The scan rate was 0.5° min^{-1}.

Gelation test. A weighed amount of potential gelator and a measured volume of selected pure organic solvent were placed into a sealed glass tube (10 mm i.d.), and the system was heated in an oil or water bath until all solid materials were dissolved. The solution was cooled to room temperature (~25 °C) in the air, and finally, the test tube was turned upside down to observe if the solution inside could still flow. A positive test is obtained if the flow test is negative. It is to be noted that some of the gels obtained are turbid (G), but some are transparent (TG). In some cases, solution and gel may coexist within a system and they are referred to as "partial gels" (PG). Systems in which only solution remained until the end of the tests are referred to as solution (S). Systems that are clear solutions when they are hot but in which precipitation or crystallization occurs when they are cooled down to room temperature are denoted by P (precipitation) and R

(recrystallization), respectively. Insoluble systems, in which the potential gelator could not be dissolved even at the boiling point of the solvent, were also found, and they are labeled as insoluble (I).

SEM. The xerogel was prepared by freezing the gel in liquid nitrogen, and then 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.

Rheology. The first step of an experiment consists of determining the so-called linear regime of the gel. This was done by measuring the storage modulus G', associated with the energy storage, and the loss modulus G'', associated with the loss of energy, as a function of the stress amplitude. The linear regime is such that both dynamic moduli are independent of the stress amplitude and reflect the properties of the unperturbed network. In that regime, G' and G'' are measured as functions of the oscillatory shear stress.

In the second step of the experiment, the modulus as a function of frequency was measured from 0.1 Hz to 100 Hz at a constant shear stress of 0.5 Pa in the linear regime.

FT-IR. The samples were placed on a glass or a mica slide as a gel film, then frozen in liquid nitrogen, and finally dried in vacuum condition for 12–24 h.

XRD. The xerogel was prepared by slow evaporation of the solvent in the atmosphere of cyclohexane.

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