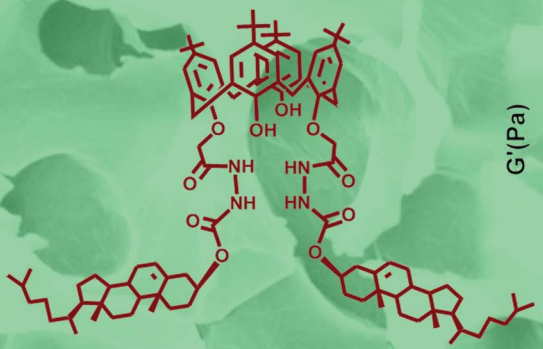
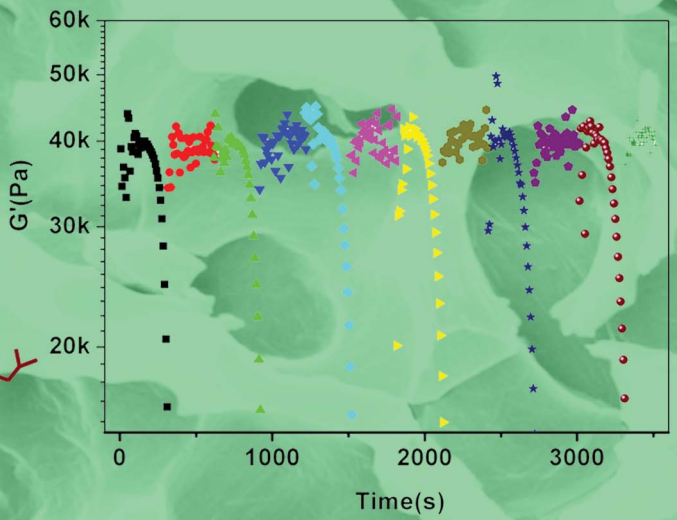
Rheologically Super-Smart Supramolecular Gels





Showcasing research from Fang lab, Shaanxi Normal University, China.

Title: Calix[4]arene-based supramolecular gels with unprecedented rheological properties

A mixture of *n*-decane and acetonitrile can be efficiently gelled by introduction of a small amount of a specific calix[4]arene-based dimeric-cholesteryl derivative as designed and synthesized in the present work. The gel exhibits super-smart thixotropic property and adopts an unusual O/O gel-emulsion structure.

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PAPER

Calix[4]arene-based supramolecular gels with unprecedented rheological properties†

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A novel calix[4]arene-based dimeric-cholesteryl derivative was synthesized, and its gelation behaviour in thirty organic solvents was investigated. It has been shown that the compound cannot gel any of the pure solvents tested. However, it gels a mixture of solvents n-decane and acetonitrile efficiently, provided the volume ratio of the two solvents in a mixture is within 9 : 1 and 3 : 2. AFM and SEM measurements revealed that the molecules of the compound aggregate into micro-/nano-rods first, then fine fibers, and then thick fibers, and finally networked structures in the mixture solvents. Interestingly, the gel with a composition of 1 to 1 ($V_{n\text{-Decane}}$:$V_{\text{Acetonitrile}}$) and 2.5% (*w*/*v*) of the compound exhibits super-smart and fully reversible thixotropic properties, a phenomenon never reported before. Furthermore, the mechanical strength of the gel could be easily adjusted by altering the concentration of the gelator and the composition of the mixture solvents. Further interrogation of the gel revealed that structurally the gel is a gel-emulsion with acetonitrile dispersed in n-decane, a rarely found O/O (oil in oil) gel-emulsion which may find uses in the templated preparation of low-density materials with complicated internal structures.

Introduction

Supramolecular gels based on low-molecular-mass gelators (LMMGs) have attracted great attention during the last two decades.[1–6] This is because, on one hand, it offers unique features to create various superstructures with respect to self-assembly phenomena,[7–12] and on the other hand it has potential for creating new soft materials, which may find use in oil recovery, controlled release, bioactivity maintenance, protein separation, regenerative medicine, tissue engineering, and template preparation of micro-/nano- materials *etc.*[13–19] To date, several classes of low-molecular mass compounds from simple alkanes to crown ethers, cyclodextrins and cholesteryl derivatives have been shown to be efficient LMMGs for water or/and organic solvents.[20–26] However, from the view point of practical uses of LMMGs-based supramolecular gels there haven't been many reported. In particular, LMMGs containing macrocyclic components, such as crown-ethers, cyclodextrins, calixarenes and cucurbiturils are very limited.[20–26] These components are important because they are rich in host–guest and supramolecular chemistry, and thereby it is anticipated that combining them into LMMGs may bring molecular gels new functionalities.

Among the macrocyclic compounds known till now, calixarenes are unique because of their ability to be modified, and their "unlimited possibilities".[27] It is these advantages that make them have a wide variety of applications in molecular recognition, sensing, selective binding and carrying, *etc.*[28] However, calixarenes have been rarely studied as a component of LMMGs. To the best of our knowledge, only 7 reports have been published till now, of which 5 were published recently.[27,29–35] In 1993, Shinkai and coworkers presented the first report on the gelation properties of calix[4]arene derivatives, which bear long alkyl groups at their lower rims. It was demonstrated that the calix[4]arene derivatives could serve as a gelator for some apolar solvents, including cyclohexane, hexane, and carbon disulfide.[29,30] To mimic the uptake of alkanes by bacteria from the aqueous phase, Xu and coworkers created a stable DMSO gel by reacting 3-pyridine-azo-calix[4] arene with $[Pd(en)(H_2O)_2](NO_3)_2$ (en = ethylenediamine) *in situ*. Model system studies demonstrated that the organogel "uptakes" toluene from an aqueous solution selectively and completely, and the absorbing process follows first order kinetics.[31,32] Ogden and coworkers designed and prepared a proline-functionalized calix[4]arene, which forms hydrogels when triggered by the presence of specific anions. The properties of the gels could be modified by the associated cations, and furthermore, the gels could be disassembled by increasing the pH above 7. It was believed that a new kind of LMMGs-based stimulus-responsive hydrogel was found.[33] Zheng and coworkers reported a series of calix[4]arene derivatives, which

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† Electronic supplementary information (ESI) available: Gelation behaviours of the compound 4; Microscopy images; Molecular structure of the fluorescent probe and rheological studies. See DOI: 10.1039/c2sm07251c

bear long tertiary alkyl groups at the upper rim and *S*-1-phenyl ethylamine groups at the lower rim.[34] Gelation and aggregation studies showed that in the presence of D-2,3-dibenzoyltartaric acid, the compounds gelate cyclohexane when heated or aggregate into egg-like vesicles, which is the first example of heat-set gels resulting from a difference in interactions between two component gelators. Recently, the same group prepared another calix[4]arene derivative, which bears L-2,3-dibenzoyltartaric acid groups at the lower rim.[35] This compound could *enantio*-selectively self-assemble and result in a gel or suspension only with one enantiomer of a number of chiral amines, as revealed by SEM. The results from Zheng and coworkers' research demonstrated clearly that molecular recognition could be utilized, *via* careful selection of two recognition units, for the construction of supramolecular gels, a strategy rarely employed and reported in the literature. Very recently, Liu and coworkers employed a similar strategy to create a series of supramolecular binary hydrogels.[27] This calix[4]arene derivative was prepared by binding four proline structures at the upper rim of the macrocyclic compound. A combination of this calix[4]arene derivative with arginine, histidine or lysine gels water efficiently. The structures of the gel networks are dependent upon the nature of amino acid employed.

As is well known, calixarenes bear multiple binding sites that promotes self-assembly into 3-D structures *via* specific weak interactions.[36–38] Furthermore, the cavity of calixarene could hold solvent molecules or other guest molecules.[39,40] Similarly, cholesterol is a well studied fragment for building up LMMGs during the last few decades. It has been shown that cholesterol self-assembles in a directional way *via* van der Waals interactions and forms aggregates with specific structures.[41–45] It should be of interest to see what the gelation behaviours of compounds, which contain the two components, are. Driving by the curiosity discussed above, calix[4]arene and cholesterol were chosen as key components for the first time to construct a novel LMMGs. In the effort, two cholesteryl residues were successfully attached to the lower rim of calix[4]arene *via* flexible linkers. Gelation tests revealed that the compound is an efficient gelator for mixed solvents of n-decane and acetonitrile provided the volume ratios of them are within the range 9 : 1 to 3 : 2 (V_{decane}: $V_{acetonitril}$). Interestingly, the gel of a mixed solvent (1 : 1) exhibits a very smart thixotropic property whereby the sol–gel phase transition could be reversibly controlled by imposing or removing a simple shake or shear stress.

Experimental section

Reagents and materials

p-Tertbutyphnol (Aladdin Chemistry Co. Ltd., 98%) used directly without further purification. THF was distilled over sodium in the presence of benzophenone under N_2 atmosphere before use. All other reagents were analytically pure.

General methods

Preparation of gels: in a typical gelation test, a weighed amount of the potential gelator and a measured volume of the solvent mixture were placed in a sealed test tube, followed by shaking or sonicating for a while. And then, the system was left to equilibrate for some time. Finally, the test tube was inverted to observe if the solution inside could still flow. The systems which lose fluidity are denoted as "G". Those that remained as solutions are denoted "S". However, systems with precipitates or crystals are denoted as "P".

SEM pictures of xerogels were taken on a Quanta 200 scanning electron microscopy spectrometer (Philops-FEI). The accelerating voltage was 20 kV, and the emission was 10 mA. The xerogel was prepared by freeze-drying a gel of the mixture solvent at a gelator concentration of 2.5% (*w*/*v*). 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.

AFM measurements were conducted on a SOLVER P47 PRO system. The sample was prepared by drop casting the dilute solution of the compound onto a freshly cleaved mica surface.

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

Rheological measurements were carried out with a stress-controlled rheometer (TA instrument AR-G2) equipped with steel-coated parallel-plate geometry (20 mm diameter). The gap distance was fixed at 1000 μm. A solvent trapping device was placed above the plate and measurement temperature was set at 15 °C in order to avoid solvent evaporation.

For rheological measurements, a stress sweep measurement at fixed frequency was firstly conducted, which provides information about the mechanical strength of the gel sample. And then, a time sweep was made to observe the recovery property of the gel. For this measurement, a constant oscillatory shear stress was applied to destroy the sample, and then, a small constant shear stress was applied, and the storage modulus G' and the loss modulus G'' of the sample were monitored as functions of time.

^{1}H NMR and MS measurements: ^{1}H NMR data of samples were collected on Bruker AVANCF 300 MHz spectrometer. MALDI-TOF mass spectra were recorded in a Kratos' AXIMA-CFR plus instrument by using 2,5-dihydroxybenzoic acid (DHB) as a matrix.

Synthetic procedure

Synthesis of the cholesteryl derivative of calix[4]arene is schematically shown in Scheme 1, and the details of the synthesis are described below.

Preparation of compound 1. Referencing to a work reported by Gutsche,[46] compound **1** was synthesized by the following method. 20.5 g (140 mmol) of *p*-tertbutyphnol, 14.5 mL of 37% formalin (200.2 mmol), and 0.5 mL of 12.5 mmol mL^{-1} NaOH solution were mixed together in a 500 mL four-neck flask. Then, the mixture was stirred, and heated under a nitrogen atmosphere for 2 h in an oil bath at 110–120 °C. The mixture became viscous and took an orange color. Furthermore, water in the system was almost distilled out completely at this temperature. The system was then cooled down to room temperature, resulting in a solid-like mixture. The mixture was suspended by stirring in 200 mL of diphenyl ether under nitrogen atmosphere. The suspension was refluxed again for 2 h, and its color became dark red eventually.

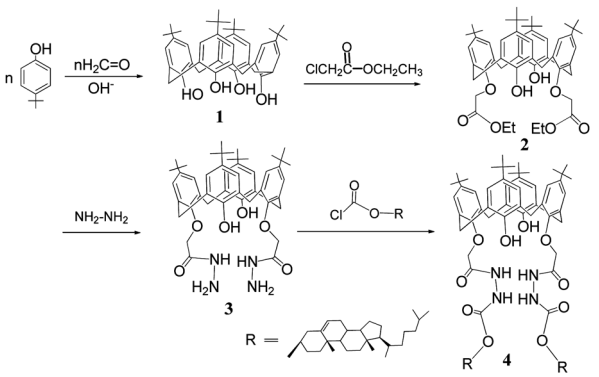
After cooling the system down to room temperature, 200 mL of ethyl acetate was added. Then the system was stirred for another 30 min, and then it was allowed to stand for at least 30 min. *Via* filtration, a precipitate that was formed in the mixture was collected and washed twice with ethyl acetate and acetic acid, separately. The crude product was purified by re-crystallization from toluene to give a white product (compound **1**) in 50% yield. For compound **1**: ^{1}H NMR ($CDCl_3$/Me_4Si, 300 MHz): δ = (ppm) 1.21(s, 36H, –C(CH_2)$_3$), 3.47 (d, J = 12.0, 4H, –ArCH_2Ar–), 4.23 (d, J = 12.0, 4H, –ArCH_2Ar–), 7.04 (s, 8H, –Ar*H*), 10.34 (s, 4H, –O*H*); MS: *m*/*z* calcd for [(M + Na)+]: 671.41, found: 671.41.

Preparation of compound 2.[47] Compound **1** (0.648 g, 1 mmol), potassium carbonate (0.166 g, 1.2 mmol) and potassium iodide (0.017 g, 0.1 mmol) were dissolved in 80 mL of acetone, and then ethyl chloroacetate (0.294 g, 2 mmol) was added slowly with stirring. The mixture was refluxed for 10 h under nitrogen atmosphere. The solvent was evaporated, and the residue obtained was dried. Then, it was dissolved or suspended in chloroform and then extracted (washed) with 10% hydrochloric acid for three times. The organic phase was collected and dried with anhydrous magnesium sulfate, and further evaporated to dryness. In this way, a crude product was prepared.

The crude product was firstly purified by column chromatography (silicone, 200–300 mesh; acetone/petroleum ether, *v*:*v* = 1 : 9), and then by re-crystallization from petroleum ether three times to give compound **2** as white crystals in a yield of 51%. For compound **2**: ^{1}H NMR ($CDCl_3$/Me_4Si, 300 MHz): δ (ppm) 1.04 (s, 18H, –C(CH_2)$_3$), 1.25 (s, 18H, –C(CH_2)$_3$), 1.31(t, 6H, –CH_3), 3.29 (d, J = 15.0, 4H, –ArCH_2Ar–), 4.26 (q, 4H,–CH_2CH$_3$), 4.10 (d, J = 15.0, 4H, –ArCH_2Ar–), 4.72 (s, 4H, –ArOCH_2), 6.81 (s, 4 H, –Ar*H*), 7.01 (s, 4H, –Ar*H*), 7.09 (s, 2H, –*OH*); MS: *m*/*z* calcd for [(M + Na)$^+$]: 844.08, found: 844.08.

Preparation of compound 3. Compound **2** (0.820 g, 1.0 mmol) and hydrazine hydrate (1.0 mL) were dissolved in a mixed solvent of toluene and methanol (20 mL, v:v = 1 : 1) under nitrogen atmosphere. The mixture was refluxed under stirring for 10 h. Then, the solvent was evaporated under vacuum, and then a precipitate was produced by addition of a small amount of water and collected by filtration. Finally, the crude product obtained was washed, respectively, with methanol and water twice, and dried under vacuum. In this way, a white powder (compound **3**) was obtained (yield: 91%) For **3**: ^{1}H NMR ($CDCl_3$/Me_4Si, 300 MHz): δ (ppm) 0.95 (bs, 4H, –NH_2), 1.04 (s, 18H, -C(CH_2)$_3$), 1.27 (s, 18 H, –C(CH_2)$_3$), 3.43 (d, J = 15.0, 4H, –ArCH_2Ar–), 4.10 (d, J = 15.0, 4 H, –ArCH_2Ar–), 4.64 (s, 4H, –ArOCH_2–), 6.92 (s, 4 H, –Ar*H*), 7.04 (s, 4H, –Ar*H*), 7.76 (bs, 2H, –N*H*CO–), 9.67 (s, 2H, –O*H*); MS: *m*/*z* calcd for [(M + Na)$^+$]: 814.02, found: 814.02. Anal. calcd for $C_{48}H_{64}N_4O_6$: C 72.70, H 8.14, N 7.06; found: C 72.61, H 8.17, N 7.13.

Preparation of compound 4. Compound 3 (0.790 g, 1 mmol) and cholesteryl choloformate (0.898 g, 2 mmol) were dissolved in 60 mL of tetrahydrofuran (THF), and the mixture was refluxed for 5 h. After the reaction, the mixture was evaporated to dryness. The precursor was re-crystallized with ethanol, and then dried in vacuum as a white powder (yield: 92%). For 4: ^{1}H NMR($CDCl_3$/Me_4Si, 300 MHz) δ(*ppm*): 0.68–1.84 (m, 132H, –CH_2CH_2–, –C(CH_3)$_3$, methyl, cholesteryl protons) 3.39 (d, J = 18.0, 4H, –ArCH_2Ar–), 4.10 (d, J = 18.0, 4 H, –ArCH_2Ar–), 4.58–4.67 (s, 6H, ArOCH_2, oxcyclohexyl), 5.39 (s, 2H, –O*H*), 5.40 (s, 2H, alkenyl), 6.87 (s, 4H, –Ar*H*), 7.08 (d, 4H,–Ar*H*), 7.41 (s, 2H, –N*H*CO–), 10.35 (s, 2H, –N*H*CO-); FTIR, ν_{max}/cm^{-1}: 3417 (NH), 2955 (CH), 1715 (C=O, –O), 1687 (C=O, NH), 1529 (NH, bending vibration), and 1327 (–C–O). MS: *m*/*z* calcd for [(M + Na)$^+$]: 1640.14, found: 1640.14. Anal. calcd for $C_{104}H_{152}N_4O_{10}$: C 77.18, H 9.47, N 3.46; found C 76.74, H 9.75, N 3.09.



Scheme 1 Synthesis of a dimeric-cholesteryl derivative bridged by a calix [4]arene unit.

Results and discussion

Gelation behaviours

The gelation behaviours of the compound were tested in 30 different organic solvents including protic/aprotic and polar/apolar solvents in a concentration of 2.5% (*w*/*v*) (*c.f.* Table S1, ESI†). It was found that the compound dissolves in most of the solvents tested excluding methanol, acetonitrile, and triethylamine (TEA). However, the compound aggregates slowly in n-decane and it was found, experimentally, that some flocculants appear 12 h later after the compound was dissolved in the solvent at room temperature. For this system, gelation occurs at room temperature when the concentration of the compound exceeds 7% (*w*/*v*), the critical gelation concentration (CGC) of the pure solvent. To decrease the CGC, a poor solvent, acetonitrile was introduced. It was believed that introduction of this poor solvent must promote the aggregation of the compound, which may enhance the establishment of gel networks, a necessity for gelation. In this way, the addition of 1.0% (*w*/*v*) of the compound at room temperature results in instant gelation ina 1 : 1 mixed solvent system of n-decane and acetonitrile (in volume) provided simple shaking or sonication was given, which must bring

Table 1 Gelation behaviours of the compound in n-decane and acetonitrile mixture (2.5%, *w*/*v*)

V_{Decane}:$V_{Acetonitrile}$	10 : 0	9 : 1	8 : 2	7 : 3	6 : 4	5 : 5
Result	S	G*	G*	G	G	G
V_{Decane}:$V_{Acetonitrile}$	4 : 6	3 : 7	2 : 8	1 : 9	0 : 10	
Result	G	P	P	P	P	

additional advantages for the system to find real-life applications.[48] It is to be noted that mixtures of other volume ratios of the two solvents can be also gelled in the same way provided their volume ratios are within the range of 9 : 1 to 2 : 3 (*cf.* Table 1). However, not all poor solvents, such as methanol, show the same effect of acetonitrile.

To further investigate the effect of the compound on the phase behaviour of the mixed solvent, a simple but illustrative experiment was conducted and the results are shown in Fig. 1. Reference to the figure reveals: (1) for the system without the compound, the mixture solvent separated into two layers at once after sufficient shaking (Fig. 1a); (2) for the systems with the compound, the phase behaviour of them changes along with increasing the concentration of the compound. It can be seen that the introduction of the compound results in some vacuoles at the interface of the two solvents, and the number and volume of them increase but they are always in the acetonitrile side (lower part of the mixture) along with increasing the compound concentration. Eventually, the system becomes a turbid gel when the gelator concentration reaches 1% (*w*/*v*).

Microscopy studies

Gelation of the mixed n-decane and acetonitrile system must be a result of a gelator network formation during the shaking process. These kind of networks or gelator aggregates should be measurable by atomic force microscopy (AFM) and scanning electron microscopy (SEM) provided the samples are properly prepared.

Fig. 2 shows a series of AFM images of the aggregates of the compound in pure n-decane and its mixture with acetonitrile. It is seen that the molecules of the compound start to aggregate at a very low concentration in its "good" solvent n-decane, and forms rod-like structure of different sizes. With increasing its concentration in the solvent, the rodlike structures further aggregated into network structures (*cf.* Fig. 2b). Introduction of a poor solvent, acetonitrile, promotes the aggregation as revealed by the AFM images shown in Fig. 2c and 2d. In fact, 1% (*w*/*v*) of the compound is not enough to gel pure n-decane, but introduction of acetonitrile changes the phase behaviour as shown in Table 1. Actually, the gels are two-phase systems, and acetonitrile was trapped within the n-decane gel. This is evidenced by the SEM images of the xerogels which were prepared from the gels of the mixed solvents (Fig. 3). It is clearly seen that there are a big number of holes of different sizes, which are believed to be the sites of acetonitrile. The characteristic structures were supported

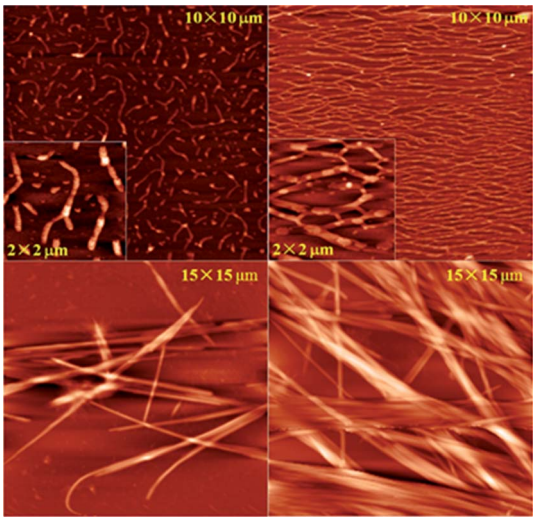


Fig. 2 AFM images of the aggregates of the compound in pure n-decane (a and b; 0.005% and 0.02%, *w*/*v*) and mixtures of n-decane and acetonitrile (c and d; 1 : 1, v/v; 0.01% and 0.05%, *w*/*v*).

by optical and fluorescence microscopy observations (*cf.* Fig. S2, ESI†). During the observation, an acetonitrile soluble but n-decane insoluble fluorescent compound was employed as a probe.

From further inspection of the AFM and SEM images, it can also be seen that the aggregation of the molecules of the compound starts from micro-/nano-rod like, then thin fibers, and then thick fibers, and finally networks. Both introduction of the poor solvent and increasing the concentration of the compound favors formation of the gel networks. It might be interesting to note that the immiscible two organic solvents, n-decane and acetonitrile, form O/O (oil in oil) type gel emulsions in the presence of the compound, a system rarely reported before.

Rheological studies

The mechanical performance of a material is extremely important for its practical uses. To explore this property of the gel in detail, rheological measurements were conducted on a series of gels, which had been prepared by using different concentrations of the compound and different volume ratios of the mixture solvents. The storage modulus, G' and the loss modulus, G'' of the gels were measured as functions of shear stress at a constant

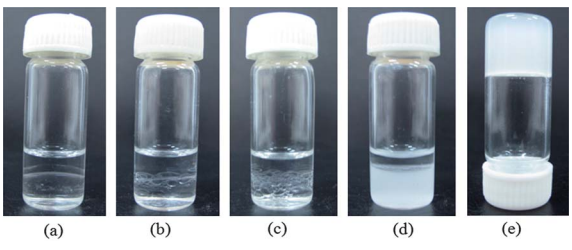


Fig. 1 Phase behaviour of the system of gelator/n-decane and acetonitrile (*v*:*v* = 1 : 1) with different gelator concentrations (*w*/*v*). (a) 0, (b) 0.05%, (c) 0.1%, (d) 0.5%, (e) 1%.

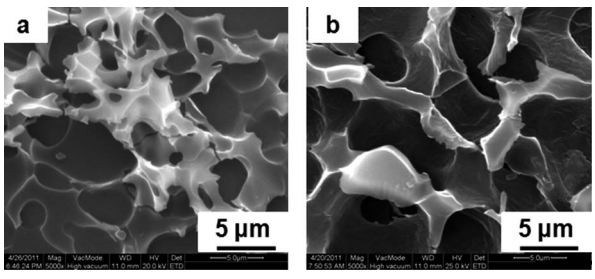


Fig. 3 SEM images of the gel networks from mixture solvent of n-decane and acetonitrile (1 : 1, *v*:*v*) in the presence of the gelator (1.0%, 2.5%, *w*/*v*; a, b).

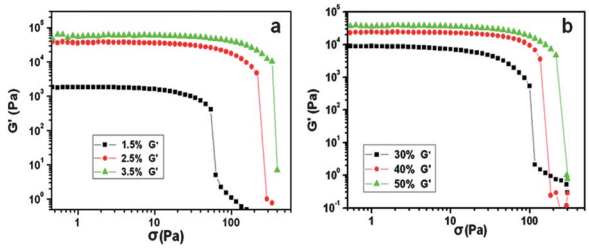


Fig. 4 Evolution of G' as a function of the applied shear stress at different concentrations of the compound (a) and at different contents of acetonitrile in the mixture solvents (volume ratio, b).

frequency of 1.0 Hz at 15 °C (Fig. 4). It can be seen that the value of G' increases from 1830 to 63460 Pa along with increasing the concentration of the compound from 1.5 to 3.5% (*w*/*v*), and correspondingly, the yield stress changes from 54 to 398 Pa, indicating that both the stability of the gel network and the elastic property of the gel are well dependent upon the concentration of the gelator in the mixture solvents.

Further reference to Fig. 4b reveals that G' increases from 9061 to 36 350 Pa along with increasing acetonitrile content from 30% to 50% (volume to volume), and at the same time, the yield stress increases from 116 to 215 Pa, suggesting that both the stability and the elastic property of the gels are also dependent upon the composition of the mixture solvent. These observations may be understood by considering the fact that either increase in the gelator concentration or in the volume ratio of acetonitrile must enhance the strength of the gel networks.

Interestingly, all these gels exhibit a clear thixotropic property. In order to learn more about the property, the gel of a mixed solvent of n-decane and acetonitrile (1 : 1 in volume) with the compound (2.5%, *w*/*v*) was chosen as an example and its thixotropic property was studied. The measurement was conducted at a constant frequency of 1.0 Hz and at 15 °C and the results are shown in Fig. 5(a). It is seen that at the beginning G' is about five times greater than G'', indicating the dominant elastic character of the gel.[48–53] The values of the two parameters remain almost unchanged before the shear stress reaches 100 Pa. However, a sudden decrease in the two values is observed above this shear stress, and furthermore the order of the values of the two parameters is reversed after a critical shear stress, 251 Pa, indicating the breakup of the gel networks, in other words an indication of dominated fluidity character.

To further examine the thixotropic property, the recovery of the destroyed gel system was studied. For this purpose, the same gel sample was re-examined by two continuous processes: (1) deformation: in this process, the gel was sheared at a continuous stress from 0.1 to 300.0 Pa at a frequency of 1.0 Hz; (2) recovery: a low shear stress of 1.0 Pa was applied on the destroyed gel at same frequency, and the recoveries of storage modulus, G' and the loss modulus, G'' of the system were monitored as a function of time. The results are shown in Fig. 5(b). Reference to the figure reveals that the gel recovers immediately after removing of the destroyed shear stress. This sol–gel phase transition process could be repeated for at least six times (*cf.* Fig. 6). These results demonstrate that this calix[4]arene-based gel possesses unprecedented, smart and fully reversible thixotropic property, an observation never reported before. No doubt, this property is valuable for some specific applications such as injection molding and drug delivery *etc.* To have further understanding of the sol–gel phase transition behaviour of the system, the same experiment was also conducted for the systems with gelator concentration of 1 and 1.5% (*w*/*v*), respectively, and the results are listed in Fig. S2 (ESI†). It can be seen that the reversibility of the two systems is not as good as the one shown in Fig. 6. For the system containing 1% (*w*/*v*) of the gelator, full recovery of the gel needs longer time, and for the other the reversibility of the system is much improved. It should not be difficult to understand that the full and instant recovery of the gel state is not only dependent upon the nature of the system, but also the concentration of the gelator. This may explain why recovery of the gel state of the system containing 1% (*w*/*v*), which is the CGC of the gel, needs a longer time and the one with higher concentration of the gelator is improved.

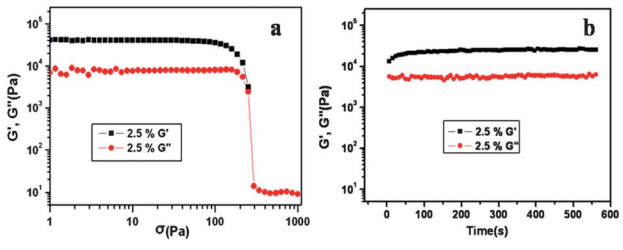


Fig. 5 Evolution of G' and G'' of the gel as functions of the applied shear stress (a), and evolution of G' and G'' of the system as functions of recovery time (b).

Conclusions

A calix[4]arene derivative of cholesterol was designed and synthesized. Gelation tests demonstrated that the compound is an effective gelator for the mixed solvents, n-decane and acetonitrile. The gels of the mixed solvents form at room temperature providing a simple shaking or sonication is given. The gels possess super-smart and fully reversible thixotropic property.

Furthermore, it has been revealed that structurally the gels are gel-emulsions, implying that acetonitrile is dispersed in the gel of n-decane. It is believed that both the smart thixotropic property and the gel-emulsion structure possessed by the mixed solvent gel guarantee its potential use in a wide variety of areas including

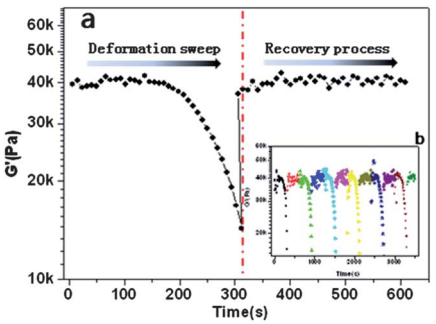


Fig. 6 Evolution of G' as functions of applied shear stress and recovery time (2.5%, *w*/*v*).

template preparation of low-density materials with complex internal structures.

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