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PAPER

Cholesterol-based low-molecular mass gelators towards smart ionogels†

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Ionic liquids are solvents of future. One of the promising methods to boost their uses is to solidify them in a physical way but with little interruption of their properties. It is therefore of interest to create gels of ionic liquids by using low-molecular mass compounds as gelators (LMMGs). Herein, we report a number of ionic liquid gels (ionogels) of which specially designed and synthesized cholesteryl derivatives were employed as gelators. The ionogels as obtained are thermo-reversible. In particular, the one with 1-butyl-3-methylimidazolium tetrafluoroborate (IL2) as solvent and a cholesteryl derivative containing a D-phenylalanine residue (**1D**) as a gelator is very stable both in neutral and acidic mediums as demonstrated by a yield stress of 76 Pa for a self-standing cylinder of the ionogel. Furthermore, the ionogel can be easily converted into a hydrogel *via* simple replacement of the solvent with water *in situ*. More interestingly, the conversion is reversible, a phenomenon never reported before. At the same time, the critical gelation concentration (CGC) of **1D** for IL2 is only 0.06%, w/w, which is almost the lowest value reported for ionogels till now, and falls into the category of "super-gelator". Magnetization of the ionogel has been realized by introduction of micro-/nano-Fe_3O_4 particles. As expected, the magnetic gel as obtained is responding to external magnetic field. Specifically, it changes into fluid with the presence of a magnetic field exceeding certain strength, and retains to gel upon removing the magnetic field and with a treatment of sonication and heating–cooling cycle. SEM and TEM observations revealed the continuous fibrous network structures of the molecules of the gelator in the ionogels. To the best of our knowledge, this is the first report on ionogels possessing stimulus-responsive properties, good mechanical strength, and super-gelation talent.

Introduction

Ionic liquids (ILs) are regarded as "solvents of future", "designed solvents" and "green solvents" due to their high ionic conductivity, wide electrochemical window, negligible vapor pressure, nonflammable character, great thermal, and chemical stability. These characteristics have endowed them with a broad range of applications in science, technology and industry.[1–7] Recently, ILs gels (ionogels), in particular supramolecular ionogels, of which the gelator networks are formed and maintained by non-covalent interactions, have attracted great interest due to their combination of both the advantage of ILs and those of the supramolecular gels.[8–14] It is believed that this combination must boost the practical applications of ILs.

Up to now, gelators employed for the gelation of ionic liquids consist of micro-/nano-particles, polymers, and low-molecular mass gelators (LMMGs).[13–18] Micro-/nano-particle based ionogels are versatile hosts for catalysts and luminescent materials.[19–22] In particular, ionogels with carbon nanotubes as gelators have been used as electrodes in double-layer capacitors or actuators due to their great electro-activity and ionic conductivity.[23] The primary interest for polymer-based ionogels is their potential applications in electrochemical devices.[24–31] In fact, the performances of perfluorinated polymer ionogels in actuators, gate dielectrics and thin-film transistors have been investigated recently.[32–34] Compared with the polymer or inorganic micro-/nano-particle based ionogels, LMMGs-based ionogels have attracted increasing attention during the past few years due to versatility of the gelators in design and synthesis. Kimizuka and co-workers reported the first LMMG-based ionogel of which a glycolipid derivative was employed as a gelator and an ether-containing ionic liquid as a solvent.[35] Shinkai *et al.* succeeded in physical gelation of both imidazolium and pyridinium types of ionic liquids by using some

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† Electronic supplementary information (ESI) available: Synthetic schemes of compounds, rheological properties and gel-to-sol transition temperature of **1D**/IL2 ionogel, FTIR spectra of **1D** and **1D**/IL2 ionogel, optical images of magnetic ionogel and ^{13}C NMR spectra of compounds. See DOI: 10.1039/c2sm26332g

cholesteryl derivatives as gelators and some non-ILs solvents as co-solvents.[36] Recently, a number of ionogels has been developed by taking amino acid derivatives,[15,37] sorbitol derivatives,[38] compounds containing urea structure,[39] organometallic compounds,[40] and ionic compounds as gelators.[41] Albeit these ionogels possess the characteristics of supramolecular gels, their mechanical strength, stimulus-responsive and acid/alkali resistance properties are far from that required for practical uses. Therefore, creating stimulus-responsive, super-stable ionogels sill remains a big challenge.

Cholesteryl derivatives are one kind of the most important and powerful LMMGs for organic solvents.[12,42] And in particular, supramolecular gels of unusual properties, including phase-selective gelation at room temperature, gel emulsion and gel film formation, and super-gelation *etc.*, have been successfully developed by employing the compounds as LMMGs during the last few years.[42–49] However, gelation of ILs with cholesteryl derivatives has been widely neglected, and in fact there has been only one report which is relevant to the gelation of ILs by cholesteryl derivatives till now.[36] It is of this reason that gelation of ILs by some simple but specially designed cholesteryl derivatives have been investigated. The gelators have been designed by considering the following points and are composed of one cholesteryl structure and two hydroxyl groups.

(1) ILs possess superior dissolving ability to commonly found low-molecular mass organic compounds, and this brings difficulties to the search of effective LMMGs for them. Considering the versatility of cholesterol-based LMMGs in the gelation of a variety of solvents, and the highly polar nature of ILs, it was decided to combine a cholesteryl structure, which possesses typical hydrophobic property, with hydrophilic structures.

(2) To improve the adaptiveness of the final cholesteryl derivatives in the formation of self-assembled network structures, the hydrophilic part of the compounds to be prepared should be flexible and possess a variety of hydrogen bonding formation sites. It was considered that only in this way the strength of the inter-molecular association of the cholesteryl derivatives could be strong enough to counter their dissolution when they are introduced into ILs, and a balance between the dissolution and precipitation, which is a necessity for formation of supramolecular gels, may be established. Accordingly, two hydroxyl groups were introduced at the end of the hydrophilic part of the cholesteryl derivatives.

(3) Different amino acid residues were chosen as a spacer to offer both hydrogen bond formation sites and variation in structures to check if a small difference in the side groups of the hydrophilic part could significantly affect the gelation behavior of the compounds in the selected ILs as found in the gelation of common organic solvents.[48]

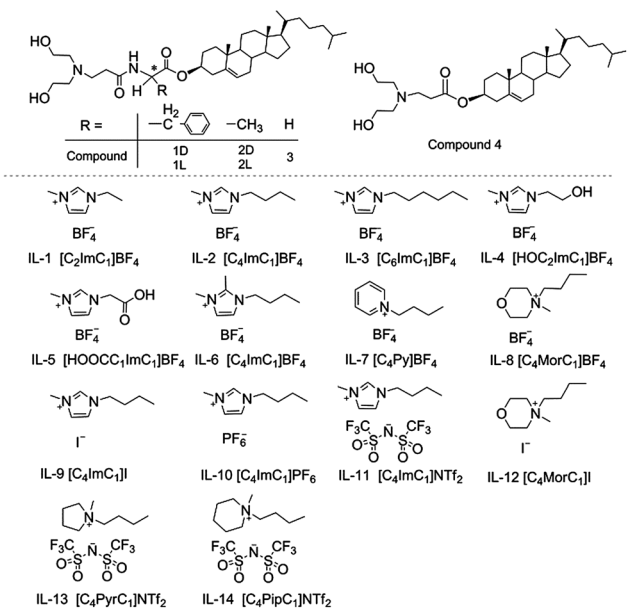
We are lucky to find that some of them are super-effective to gelate the selected ILs. More interestingly, the ionogels as developed possess a number of superior properties, for example, good mechanical strength, stimulus-responsive properties, and super gelation talent (CGC, 0.06%, w/w). To the best of our knowledge, this is the first report on an ionogel with multiple exceptional properties. This paper reports the details.

Results and discussion

Gelation behaviours and properties

The gelation behaviours of compounds **1–4** (Scheme 1) are summarized in Table 1. Reference to the table, it is seen that among the 84 combinations (ILs-cholesteryl derivatives), only 8 of them are gels. However, some of the cholesteryl derivatives gel some of the ILs efficiently. More exactly, the gelator containing D-phenylalanine residue (**1D**) is the most effective gelator, which can gel four imidazolium salts with different alkyls and anions (IL2, IL3, IL4 and IL11; Scheme 1), and one methylmorpholinium salt (IL12). While compound **1L**, which was obtained by simple replacing the D-phenylalanine residue in **1D** with L-phenylalanine, gels only one ionic liquid (IL12). Moreover, replacing the phenyl group in **1D** and **1L** with methyl group (**2D**, **2L**) eliminated their gelation property completely. However, compound **3**, which contains neither phenyl group nor methyl group, can gel two of the ILs under test (IL11 and IL14). Compound **4**, with no amino acid residue in the structure, could not gel any of the selected ILs.

From the above gelation results, it may be concluded that a subtle variation in the structures of the cholesteryl derivatives results in substantial change in the gelation properties of the compounds, a common phenomenon in supramolecular gels.[47] For example, the replacement of aromatic amino acids by a aliphatic residues clarified the importance of aromatic rings in ionogelation, a result similar to that reported by Das and coworkers.[15] In addition, the configurations of the amino acid residues are also important in the gelation. As revealed already, the compounds containing amino acid residues of D configuration is more effective in gelation than those containing amino acid residues of L configuration, in particular for the ones with phenylalanine as the amino acid residue. Upon further inspection of the results shown in the table, it is also seen that the gelation



Scheme 1 The chemical structures of cholesteryl-based gelators and ionic liquids tested.

Table 1 Gelation behaviors of compounds **1–4** in ILs[a]

Solvent	1D	1L	2D	2L	3	4
IL1	P	P	P	P	P	P
IL2	G(0.06)	P	P	P	P	I
IL3	G(2.0)	P	P	P	P	P
IL4	G(1.3)	P	P	P	P	P
IL5	I	I	I	I	I	P
IL6	P	P	P	P	P	P
IL7	P	P	P	P	P	P
IL8	P	P	I	I	I	I
IL9	P	S	P	P	P	P
IL10	P	P	P	P	I	P
IL11	G(1.5)	P	P	P	G(2.0)	P
IL12[b]	G(0.8)	G(1.0)	I	I	I	I
IL13	P	P	P	P	P	P
IL14	P	P	P	P	G(2.5)	P

[a] G = gel, S = soluble, P = precipitation, I = insoluble. [b] The gel was formed with water (10%, v/w), the number in bracket is the CGC of the system (%, w/w).

behaviours of the compounds are not only dependent upon their own structures, but also upon the fine structures of the ILs under study, a result entirely different from other amino acid-based gelators for ILs.[37] For example, **1D** gels either IL2 or IL3, but not IL1, of which the only difference is the length of alkyl side chain in the imidizolium cation. Beside the substitute alkyl, the anion can also tune the gelation behaviors. For instance, **1D** gels IL2, but not IL9 and IL11, which contain the same cation but different anions.

Gel stability studies

As shown in Table 1, among the cholesteryl derivatives, **1D** is the most effective gelator both according to the number of ILs gelled and the critical gelation concentration (CGC) values (*cf.* Table 1) if compared to those of the relevant compounds. Particularly, the CGC of **1D** in IL2 is only 0.06% (w/w), which is almost the lowest value reported for ionogels till now,[40] and falls into the category of "super-gelator" (CGC < 0.1%, w/w).[42] Furthermore, the **1D**/IL2 gel is transparent provided the gelator concentration is lower than 0.1% (w/w). More interestingly, a self-standing gel could be prepared by simple injecting a hot solution of **1D** in IL2 into a cylinder mold and then cooling to room temperature (inset (a) in Fig. 1). The critical pressure to break the self-standing gel (10 mg mL^{-1}) is 76 Pa (Fig. 1), a value determined by using a dynamic mechanical analyzer (DMA) on a compress model. This exceptional mechanical character was confirmed by the result from rheological property measurements. Firstly, the value of the yield stress of the **1D**/IL2 ionogel (10 mg mL^{-1}) is 630 Pa (left inset in Fig. 1), which is much greater than those of other cholesterol-based physical gels reported till now.[37] Secondly, the storage modulus (G') of **1D**/IL2 ionogel (10 mg mL^{-1}) exhibits week dependence on frequency sweep (Fig. S1, ESI†), indicating the good tolerance of the gel to external forces.

Another meaningful character of **1D**/IL2 ionogel is its stability both in neutral and acidic mediums. The ionogel looks like a fresh one after sealed in a vial for one year at room temperature (Fig. 2c). Additionally, it was found that **1D**/IL2 ionogel (0.5%, w/v) keeps its gel state for at least one week after addition of 100 μL of hydrochloric acid (36%, Fig. 2e). This is a rather surprising

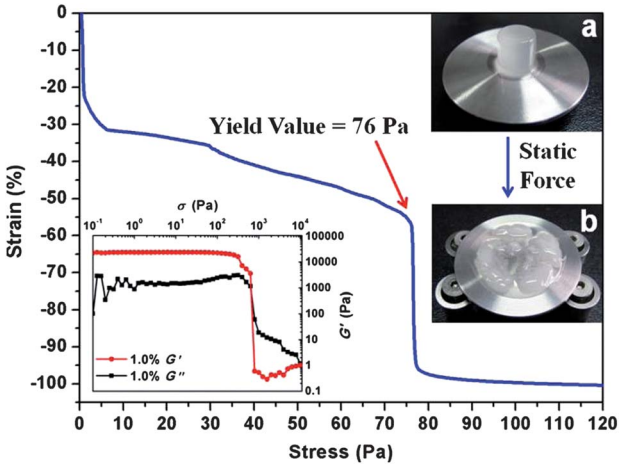


Fig. 1 Static compression strain *vs.* stress curve of a cylinder ionogel of **1D**/IL2 at 10 mg mL^{-1} and its rheological behaviors (left inset), the cylinder ionogel before (a) and after (b) compression (right inset).

result because of the expectation that the ionogel should be sensitive to the presence of protons due to existence of a tertiary amine structure in the gelator. More surprisingly, although the gelator, **1D**, cannot gel water directly through a regular heating–cooling cycle, a hydrogel of **1D** can be prepared by replacing IL2 in **1D**/IL2 ionogel with water (Fig. 2d). It is to be noted that the transformation can be reversed and the process can be repeated for several times, an observation never reported before.

Effect of external magnetic field upon the magnetic ionogel

Inspired by the reports that inorganic micro-/nano-particle based ionogels are versatile hosts for functional components, such as

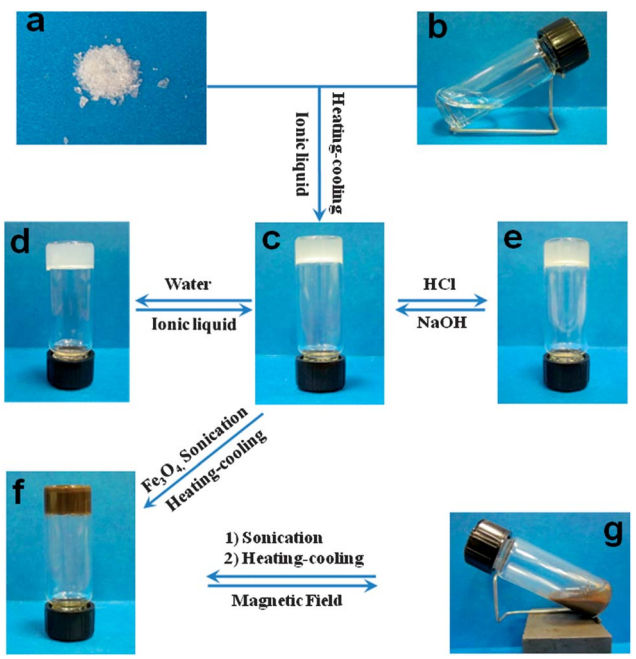


Fig. 2 The phase behavior of **1D**/IL2 (0.5%, w/v) at different conditions. (a) gelator **1D**; (b) IL2; (c) ionogel; (d) hydrogel; (e) gel under HCl atmosphere; (f) magnetic gel containing Fe_3O_4; and (g) magnetic gel under external magnetic field.

catalysts, luminescent compounds and conductive components, the inclusive property of **1D**/IL2 gel was specially studied. It was found gratifyingly that the ionogel under study is an ideal host for micro-/nano-particles (~50 nm or ~5 μm) of Fe_3O_4 (Fig. S3, ESI†), which possesses typical paramagnetic property. The loading of the particles (~50 nm) can be as high as 30% (w/w, Fig. 2f). Presence of an external magnetic field (Neodymium–Iron–Boron Magnet, maximum pull 18.3 kg, McMaster-Carr) shows little effect upon the macroscopic property of the ionogel provided the loading content of the magnetic particles is less than 12% (w/w). However, the gel changes into fluid instantly upon imposing it within the magnetic field when the loading density of the magnetic particles extends 20% (w/w, Fig. 2g), a result of breakage of the gel networks which must be caused by the magnetic field oriented movement of the particles doped in the gel (Fig. S3f, ESI†). As expected, the gel-state can be easily recovered by simple sonication of the system and then by a treatment of heating–cooling cycle. Furthermore, these processes can be repeated for many times, a typical and rarely found magnetorheological fluids (Fig. 2g).[46]

Morphology studies

Scanning electron microscopy observations were conducted to investigate the network morphologies of some of the ionogels. For this purpose, their xerogels were prepared by extracting the ILs from the ionogels with water, and then freezing–dried under vacuum. Reference to the images (Fig. 3a–d), it was revealed that the xerogels are characterized by continuous fibrous network structures no matter what nature of the solvent is. To reveal the formation process of the gel networks, concentration-dependent SEM images of the **1D**/IL2 xerogels were also taken (Fig. 3e–g). With reference to the figures, it is clearly seen that the fibrous structure becomes thinner with decreasing the gelator concentration in the ionogel. For example, the width of the continuous fiber decreases from 2 μm (1%, w/v) to less than 200 nm (0.2%, w/v). Moreover, the width decreases to 50 nm when the concentration of the gelator reaches to 0.1% (w/v) as examined by TEM measurement (Fig. 3h).

Mechanism of the gelation

It is well known that for a physical gel, the main reason for the existence of it is the formation of 3D networks, which are results of aggregation of the gelator molecules in the gel. The driving forces behind the aggregation can be various non-covalent interactions. In particular, for the present systems, intermolecular hydrogen bonding may play a crucial role considering the structures of the gelators. Accordingly, the FTIR spectra of **1D** in $CDCl_3$ and that of **1D**/IL2 xerogel were recorded and the results are shown in Fig. S4 (ESI†). It is shown that in solution state **1D** shows a broad band at 3400 cm^{-1} owing to the coupling of the stretching vibration of O–H with that of the N–H, and two sharp bands at 1646 cm^{-1} and 1541 cm^{-1} which can be assigned to the stretching vibration of C═O and the bending vibration of N–H, respectively. However, with the aggregation of **1D**, the band splits into 3536 cm^{-1} and 3321 cm^{-1}, and the stretching vibration of C═O and the bending vibration of N–H shift to 1667 cm^{-1} and 1569 cm^{-1}, respectively, direct evidences for the existence of hydrogen bonds in the xerogel. This tentative conclusion is further supported by the result from ^1H NMR measurements. Fig. 4 shows the temperature- and concentration-dependent ^1H NMR spectra of **1D** in $CDCl_3$. It is clearly seen that at 293 K, the amide proton exhibits a ^1H NMR signal at $\delta =$ 7.68 ppm. However, the signal shifts to $\delta = 7.61$ ppm and $\delta =$ 7.53 ppm at 303 K and 313 K, respectively (Fig. 4, up). With increase of the concentration of **1D**, the signal of the amide proton significantly shifts to downfield (Fig. 4, down), a definite evidence of intermolecular hydrogen bonding formation. Similar to that of amide proton, the signal of hydroxyl protons at about 3.5 ppm shifts to up field along with increasing temperature (Fig. 4, up). However, unlike amide proton, the hydroxyl proton is not sensitive to the variation in concentration (Fig. 4, down), suggesting that the hydroxyl protons may encounter

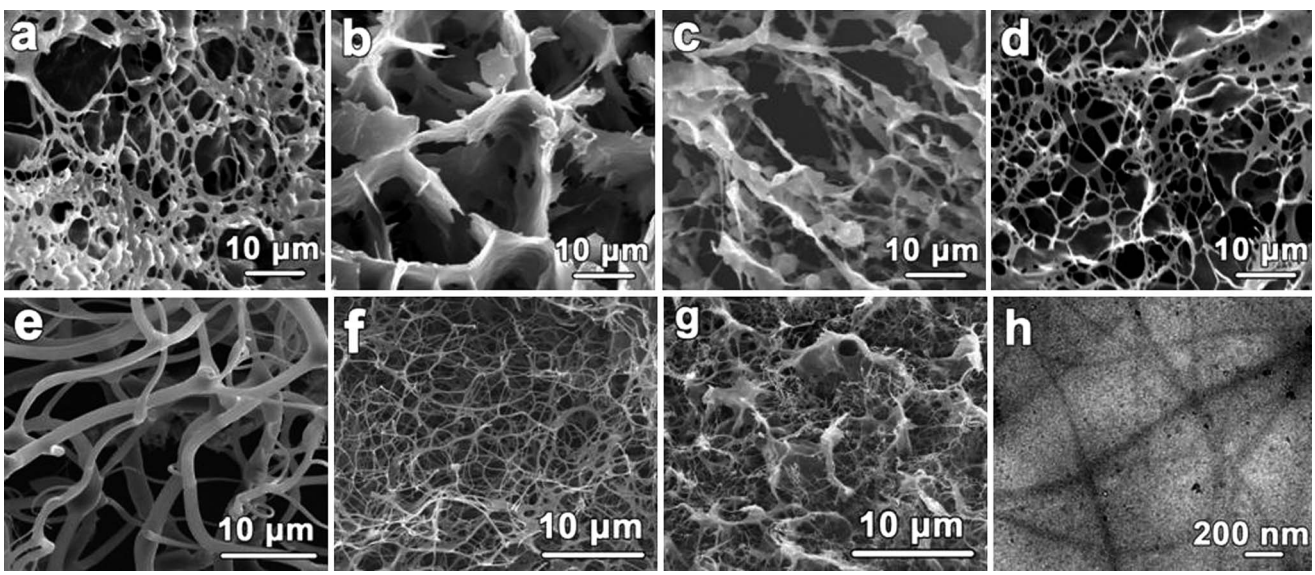


Fig. 3 SEM images of the xerogels of **1D**/IL2 (a), **1D**/IL4 (b), **1D**/IL12 (c), and 1 L/IL12 (d) (2.5%, w/v); concentration-dependent SEM images of **1D**/IL2 xerogels at 1%, w/v (e), 0.5%, w/v (f), and 0.2%, w/v (g), TEM image of **1D**/IL2 ionogel at 0.1%, w/v (h).

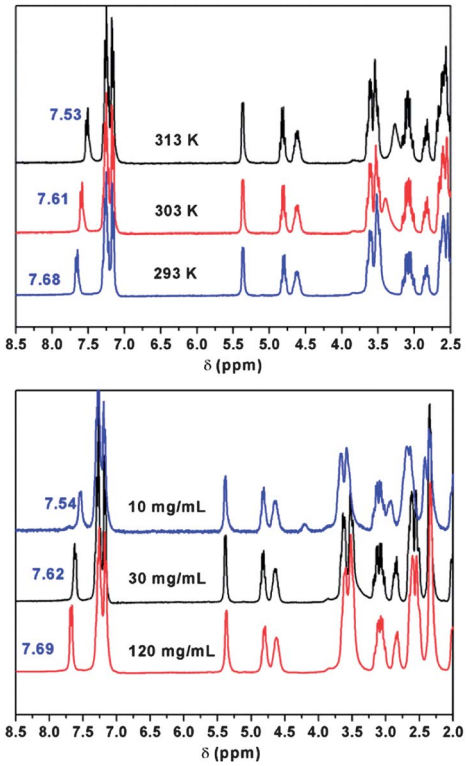


Fig. 4 Partial ^{1}H NMR spectra of **1D** in $CDCl_3$: up, temperature dependence at a concentration of 12% (w/v); down, concentration (w/v) dependence at 25 °C.

intra-molecular hydrogen bonding. Considering the main interactions between the gelator molecules, and the network structure of the assembly in ionogel as discussed above, the gelation process could be described as following. At the beginning, the molecules of the gelator aggregate into fibrils at a molecular level *via* intermolecular hydrogen bonding and van der Walls interaction, a widely recognized interaction among cholesteryl moieties, then the fibrils pile up to thicker fibers and networked structures, and finally, the solvent was confined due to interface tension and capillary force within the system.

Experimental section

Materials and methods

All chemicals were bought from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. The solvents were purified according to the standard methods. Fourteen ILs, which are 1-alkyl-3-methylimidazolium tetrafluoroborate ($[C_nImC_1]BF_4$, IL1 ($n = 2$), IL2 ($n = 4$), IL3 ($n = 6$)), 1-hydroxyethyl-3-methylimidazolium tetrafluoroborate (IL4), 1-carboxymethyl-3-methylimidazolium tetrafluoroborate (IL5), 1-butyl-2,3-methylimidazolium tetrafluoroborate (IL6), butylpyridinium tetrafluoroborate (IL7), 1-butyl-1-methylmorpholinium tetrafluoroborate (IL8), 1-butyl-3-methylimidazolium iodine (IL9), 1-butyl-3-methylimidazolium hexafluorophosphate (IL10), 1-butyl-3-methylimidazolium bis-(trifluoromethylsulfony)imide (IL11), 1-butyl-1-methylmorpholinium iodine (IL12), 1-butyl-1-methylpyrazolidinium bis(trifluoromethylsulfony)imide (IL13) and 1-butyl-1-methylpiperidinium bis(trifluoromethylsulfony)imide (IL14), respectively (Scheme 1), were purchased from Chengjie Chemical Co. Ltd. (Shanghai, China) and used without further purification.

Gelation test was conducted by adding a certain amount of gelator in 1 mL ILs under a heating–cooling cycle. IL12 is liquefied by adding 10% of water (H_2O/IL = 1 : 10, v/v) in it before the test as it is a solid at room temperature. The transformation of the ionogel into a hydrogel was performed by immersing the ionogel in water for four weeks, and during that period water was refreshed three times a day. The reverse process was conducted in an open vial, in which the hydrogel was covered by IL2 and the water was evaporated naturally. The mechanical strength test of the gel was performed by using a dynamic mechanical analyzer (Q800DMA, TA Instrument, USA) at a compression model on 25 °C. For mechanical strength test, a self-standing cylinder of an ionogel (1.2 cm in diameter and 0.6 cm in height) was prepared by injecting the hot solution of a gelator in IL2 into a stainless hollow cylinder mold, cooling slowly to room temperature and keeping overnight. Rheological experiments were performed on a stress-controlled rheometer (TA Instruments AR-G2) equipped with a parallel plate (20 mm diameter). SEM images of the xerogel were taken on a Quanta 200 SEM (Philips-FEI). The accelerating voltage was 20 kV, and the emission was 10 mA. The xerogel was prepared by freezing the obtained hydrogels in liquid nitrogen followed by frozen drying. For TEM measurement (JEOL JEM-2100), carbon-meshed copper grid was dipped twice into the above mentioned "hydrogel" and dried at room temperature. The FTIR spectra of the solution and gel samples were recorded in a transmission mode by a Bruker Equinox 55 infrared spectrometer. The gel sample for measurement was prepared by coating it on a KBr slice as a smooth gel film and then freeze-drying it. ^{1}H and ^{13}C NMR spectra were recorded with Bruker AV 600 (600 MHz) NMR spectrometer.

General procedures for preparation of the gelators

General procedures for synthesis of the cholesterol-based compounds are schematically shown in Scheme S1 (ESI†). Step (a): a mixture of the hydrochloride salt of an amino acid derivative of cholesterol (2.5 mmol), which was prepared and characterized according to the procedures reported before,[50] and triethylamine (5 mmol) in 50 mL dry benzene was refluxed for 4 h and cooled to room temperature. Then 10 mL dry benzene containing 2.5 mmol of acryloyl chloride was added dropwise to the solution at 0 °C under stirring. The system was left to react for another 2 h after finishing the dropping process. After filtration and evaporation of the solvent, the residue was re-crystallized from cyclohexane to give the desired intermediate as white crystals.

Step (b): the above intermediate (3.5 mmol) and diethanolamine (5.2 mmol) were dissolved in 10 mL $CHCl_3$ and the solution as prepared was stirred for 7 days at room temperature. The final mixture was washed with saturated sodium chloride solution for six times. The organic layer was collected, dried with anhydrous $MgSO_4$ and then evaporated to dryness. The final residue was purified by using a silica gel column to give the desired compound as a white powder. As a control, another compound **4** (Scheme S2, ESI†) of similar structure to those listed in Scheme S1† was also designed and prepared, but in this case, there is no amino acid residue in the structure.

For **1′**: mp = 117–118 °C (**1′D**), 153–154 °C (**1′L**); $[\alpha]_D^{25}$ −46.6 (**2′D**) (c = 0.003 $CHCl_3$), −53.6 (**2′L**) (c = 0.0019 $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ = 7.27 (m, 3H, C_6H_5), 7.12 (d, 2H, C_6H_5, J = 6.9 Hz), 6.30, 6.27 (dd, 1H, CH_2=CH, J = 1.1, 15.6 Hz), 6.10 (q, 1H, CH_2=CH, J = 10.3 Hz), 6.03 (d, 1H, NH, J = 7.4 Hz), 5.67 (d, 1H, CH_2=CH, J = 10.3 Hz), 5.38 (m, 1H, alkenyl), 4.93 (q, 1H, CH, J = 5.8 Hz), 4.63 (m, 1H, oxycyclohexyl), 3.17 (d, 2H, CH_2, J = 5.7 Hz), 2.33–2.21 (b, 2H, CH_2), 2.02–0.68 (m, 41H, cholesteryl protons). ^{13}C NMR (600 MHz, $CDCl_3$, TMS) 171.0, 164.9, 139.2, 135.9, 130.4, 129.5, 128.5, 127.1, 123.0, 75.6, 56.7, 56.2, 53.3, 50.0, 42.3, 39.5, 38.0, 37.9, 36.9, 36.6, 36.2, 35.8, 31.9, 31.8, 28.2, 28.0, 27.7, 24.3, 23.8, 22.8, 22.6, 21.1, 19.3, 18.7, 11.9. FTIR (KBr), $\nu_{max/cm}{}^{-1}$: 3300 (N–H), 3040 (C–H), 1740 (C=O). Elemental analysis (%): calcd for $C_{39}H_{57}NO_3$: C, 79.68; H, 9.77; N, 2.38. Found: C, 79.52; H, 9.46; N, 2.17%.

For **2′**: mp = 133–134 °C (**2′D**), 148–149 °C (**2′L**); $[\alpha]_D^{25}$ = −8.0 (**2′D**), −26.1 (**2′L**) (c = 0.003 $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ = 6.30 (d, 1H, CH_2=CH, J = 17.0 Hz), 6.21 (b, 1H, NH), 6.14 (q, 1H, CH_2=CH, J = 10.3 Hz), 5.67 (d, 1H, CH_2=CH, J = 10.3 Hz), 5.38 (d, 1H, alkenyl, J = 4.9 Hz), 4.66 (m, 2H, CH and oxycyclohexyl), 2.33 (m, 2H, CH_2), 2.02–0.68 (m, 44H, CH_3 and cholesteryl protons). ^{13}C NMR (600 MHz, $CDCl_3$, TMS) 172.6, 164.9, 139.3, 130.6, 126.9, 123.0, 75.4, 56.7, 56.2, 50.0, 48.3, 42.3, 39.5, 38.0, 36.9, 36.6, 36.2, 35.8, 31.9, 31.8, 28.2, 28.0, 27.6, 24.3, 23.9, 22.8, 22.6, 21.1, 19.3, 18.7, 11.9. FTIR (KBr), $\nu_{max/cm}{}^{-1}$: 3300 (N–H), 3040 (C–H), 1740 (C=O). Elemental analysis (%): calcd for $C_{33}H_{53}NO_3$: C, 77.45; H, 10.44; N, 2.74. Found: C, 77.08; H, 10.50; N, 3.01%.

For **3′**: mp = 167–168 °C; $[\alpha]_D^{25}$ = −40.9 (c = 0.003 $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ = 6.32 (d, 1H, CH_2=CH, J = 17.0 Hz), 6.16 (q, 1H, CH_2=CH, J = 10.3 Hz), 6.10 (b, 1H, NH), 5.70 (d, 1H, CH_2=CH, J = 10.3 Hz), 5.38 (d, 1H, alkenyl, J = 4.7 Hz), 4.70 (m, 1H, oxycyclohexyl), 4.10 (d, 2H, CH_2, J = 5.0 Hz), 2.34 (d, 2H, CH_2, J = 7.0 Hz), 2.03–0.68 (m, 41H, cholesteryl protons). ^{13}C NMR (300 MHz, $CDCl_3$, TMS) 169.4, 165.5, 139.3, 130.2, 127.2, 123.0, 75.6, 56.7, 56.2, 50.0, 42.3, 41.7, 39.5, 38.0, 36.9, 36.6, 36.2, 35.8, 31.9, 31.8, 28.2, 28.0, 27.7, 24.3, 23.9, 22.8, 22.6, 21.1, 19.3, 18.7, 11.9. FTIR (KBr), $\nu_{max/cm}{}^{-1}$: 3300 (N–H), 3080, 2950 (C–H), 1750 (C=O). Elemental analysis (%): calcd for $C_{32}H_{51}NO_3$: C, 77.22; H, 10.33; N, 2.81. Found: C 77.11; H, 10.33; N, 2.51%.

For **4′**: mp = 125–126 °C; $[\alpha]_D^{25}$ = −41.2 (c = 0.003 $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ = 6.40, 6.37 (dd, 1H, CH_2=CH, J = 1.4 Hz, 15.9 Hz), 6.10 (q, 1H, CH, J = 10.4 Hz), 5.80 (dd, 1H, CH_2=CH, J = 1.4, 10.4 Hz), 5.38 (d, 1H, alkenyl, J = 4.8 Hz), 4.70 (m, 1H, oxycyclohexyl), 2.36 (d, 2H, CH_2, J = 7.1 Hz), 2.02–0.68 (m, 41H, cholesteryl protons). ^{13}C NMR (600 MHz, $CDCl_3$, TMS) 165.6, 139.6, 130.2, 129.1, 122.7, 74.1, 56.7, 56.2, 50.1, 42.3, 39.8, 39.5, 38.1, 37.0, 36.6, 36.2, 35.8, 31.9, 31.8, 28.2, 28.0, 27.8, 24.3, 23.9, 22.8, 22.6, 21.1, 19.4, 18.7, 11.9. FTIR (KBr), $\nu_{max/cm}{}^{-1}$: 2940 (C–H), 1720 (C=O). Elemental analysis (%): calcd for $C_{30}H_{48}O_2$: C, 81.76; H, 10.98. Found: C, 81.91; H 11.06%.

For **1** (purified by a silica gel column eluting with tetrahydrohexane–hexane (3 : 1, v/v)): mp = 101–102 °C (**1D**), 90–91 °C (**1L**); $[\alpha]_D^{25}$ = −29.6 (**1D**), −13.0 (**1L**) (c = 0.003 $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ = 7.58 (b, 1H, NH), 7.29 (m, 3H, C_6H_5), 7.17 (d, 1H, J = 7.3 Hz), 5.38 (b, 1H, alkenyl), 4.82 (q, 1H, CH, J = 4.8 Hz), 4.64 (m, 1H, oxycyclohexyl), 3.64 (t, 2H, OH, J = 8.5 Hz), 3.52 (b, 4H, CH_2), 3.13, 3.10 (dq, 2H, CH_2, J = 6.6, 13.9 Hz), 2.64 (t, 4H, CH_2, J = 9.7 Hz), 2.54 (d, 2H, CH_2, J = 13.3 Hz), 2.35 (b, 4H, CH_2), 2.02–0.68 (m, 41H, cholesteryl protons). ^{13}C NMR (600 MHz, $CDCl_3$, TMS) 172.9, 172.4, 139.2, 136.3, 129.3, 128.5, 127.0, 123.0, 76.0, 60.0, 56.9, 56.7, 56.2, 53.5, 51.5, 50.1, 42.3, 39.5, 37.8, 37.0, 36.5, 36.2, 35.8, 34.0, 31.9, 30.4, 28.2, 28.0, 27.5, 24.3, 23.8, 22.8, 22.6, 21.1, 19.3, 18.7, 11.9. FTIR (KBr), $\nu_{max/cm}{}^{-1}$: 3360 (O–H), 2940 (C–H), 1740, 1640 (C=O). Elemental analysis (%): calcd for $C_{43}H_{68}N_2O_5$: C, 74.52; H, 9.89; N, 4.04. Found: C, 74.39; H, 9.80; N, 3.63%. MS (m/z): calcd for [(M + H)$^+$]: 693.5206, found: 693.5164.

For **2** (purified by a silica gel column eluting with tetrahydrohexane–hexane (3 : 1, v/v)): mp = 119–120 °C (**2D**), 116–117 °C (**2L**); $[\alpha]_D^{25}$ = −15.3 (**2D**), −49.4 (**2L**) (c = 0.003 $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ = 7.37 (b, 1H, NH), 5.36 (s, 1H, alkenyl), 4.66 (b, 1H, CH), 4.54 (m, 1H, oxycyclohexyl), 3.72 (t, 2H, OH, J = 6.0 Hz), 3.62 (b, 4H, CH_2), 2.72 (b, 4H, CH_2), 2.60 (b, 2H, CH_2), 2.45–2.30 (m, 4H, CH_2), 2.02–0.68 (m, 44H, CH_3 and cholesteryl protons). ^{13}C NMR (600 MHz, $CDCl_3$, TMS) 174.3, 172.4, 139.2, 123.0, 75.7, 59.9, 56.8, 56.7, 56.1, 51.2, 50.0, 48.3, 42.3, 39.5, 37.8, 36.9, 36.6, 36.2, 35.8, 34.1, 31.9, 28.2, 28.0, 27.6, 24.3, 23.8, 22.8, 22.6, 21.0, 19.3, 18.7, 18.0, 11.9. FTIR (KBr), $\nu_{max/cm}{}^{-1}$: 3390 (O–H), 2940 (C–H), 1740, 1660 (C=O). Elemental analysis (%): calcd for $C_{37}H_{64}N_2O_5$: C, 72.04; H, 10.46; N, 4.54. Found: C, 71.62; H, 10.45; N, 4.52%. MS (m/z): calcd for [(M + H)$^+$]: 617.4893, found: 617.4869.

For **3** (purified by a silica gel column eluting with tetrahydrohexane–cyclohexane, 8 : 1, v/v): mp = 81–82 °C; $[\alpha]_D^{25}$ = −31.7 (c = 0.003 $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, TMS): 8.13 (b, 1H, NH), 5.37 (s, 1H, alkenyl), 4.63 (m, 1H, oxycyclohexyl), 3.95 (d, 2H, CH_2, J = 4.5 Hz), 3.75 (m, 4H, CH_2OH), 3.60 (t, 2H, OH, J = 5.6 Hz), 3.14 (b, 2H, CH_2), 2.93 (q, 2H, CH_2, J = 6.7 Hz), 2.61 (s, 4H, CH_2), 2.50 (m, 4H, CH_2), 2.32 (m, 2H, CH_2), 2.02–0.68 (m, 41H, cholesteryl protons). ^{13}C NMR (600 MHz, $CDCl_3$, TMS) 172.4, 170.2, 139.3, 122.9, 75.5, 62.0, 58.1, 56.7, 56.3, 56.2, 50.7, 50.0, 42.3, 39.7, 39.5, 37.9, 36.9, 36.5, 36.2, 35.8, 31.9, 31.8, 28.2, 28.0, 27.6, 24.3, 23.9, 22.8, 22.6, 21.0, 19.3, 18.7, 11.9. FTIR (KBr), $\nu_{max/cm}{}^{-1}$: 3390 (O–H), 2940 (C–H), 1740, 1660 (C=O). Elemental analysis (%): calcd for $C_{35}H_{60}N_2O_5$: C, 71.49; H, 10.27; N, 4.76. Found: C, 71.72; H, 10.37; N, 4.65%. MS (m/z): calcd for [(M + H)$^+$]: 603.4737, found: 603.4697.

For **4** (purified by a silica gel column eluting with tetrahydrofuran–*n*-hexane, 2 : 1, v/v): mp = 58–59 °C; $[\alpha]_D^{25}$ −28.4 (c = 0.003 $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ = 5.36 (m, 1H, alkenyl), 4.65 (m, 1H, oxycyclohexyl), 3.62 (t, 2H, OH, J = 5.2 Hz), 3.52 (m, 2H, CH_2), 2.84 (q, 2H, CH_2, J = 6.0 Hz), 2.65 (t, 4H, CH_2, J = 5.2 Hz), 2.48 (t, 4H, CH_2, J = 6.2 Hz), 2.32 (m, 2H, CH_2), 2.02–0.68 (m, 41H, cholesteryl protons). ^{13}C NMR (600 MHz, $CDCl_3$, TMS) 172.3, 139.4, 122.7, 74.3, 59.3, 56.6, 56.1, 56.07, 50.0, 42.2, 39.7, 39.5, 38.0, 36.9, 36.5, 36.2, 35.8, 31.9, 31.8, 28.2, 28.0, 27.7, 24.2, 23.9, 22.8, 22.6, 21.0, 19.3, 18.7, 11.8. FTIR (KBr), $\nu_{max/cm}{}^{-1}$: 3410 (O–H), 2940 (C–H), 1730 (C=O); elemental analysis (%): calcd for $C_{34}H_{59}NO_4$: C, 74.81; H, 10.89; N, 2.57. Found: C, 74.98; H, 11.16; N, 2.34%. MS (m/z): calcd for [(M + H)$^+$]: 546.4522, found: 546.4490.

Conclusion

A number of stable and smart ionogels were successfully created by using specially designed and synthesized cholesteryl

derivatives as LMMGs. Interestingly; **1D** is a super-gelator to IL2 with a CGC of 0.06% (w/w). The ionogel is stable both in neutral and acidic mediums. Furthermore, the magnetic field responsive ionogel is attained by doped with magnetic particles. FTIR and ^{1}H NMR spectroscopy measurements revealed that hydrogen bonding is one of the main driving forces for formation and maintenance of the ionogel networks. This finding opens a rational way to design cholesterol-based LMMGs for ionic liquids and boosts both the potential uses of supramolecular gels and ionic liquids, such as in magnetorheological fluids and electrochemical devices.

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