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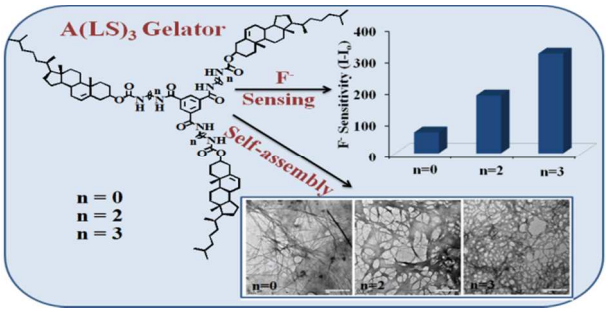

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ARTICLE

New triangular steroid-based $A(LS)_3$ type gelators for selective fluoride sensing application

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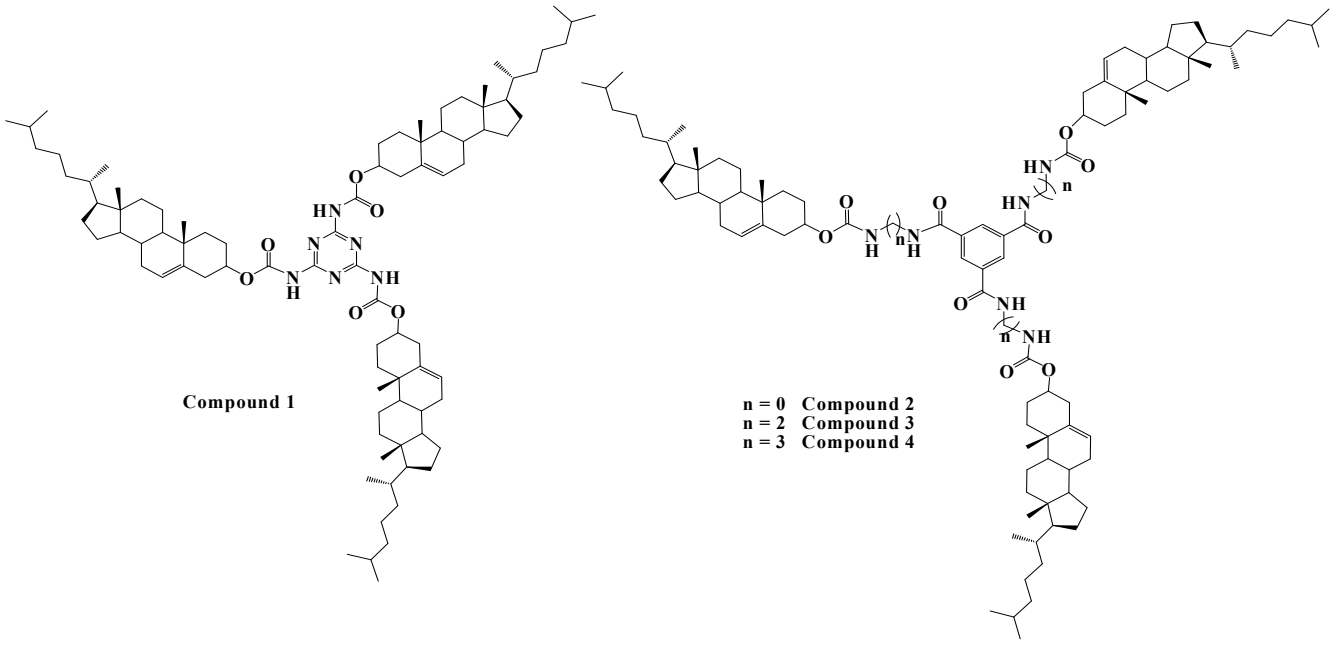
A new series of cholesteryl based triangular $A(LS)_3$ type molecules, compounds **1-4**, has been synthesized and tested for gelation and anion sensing applications. Melamine or benzene-1,3,5-tricarbonyl chloride (BTC) was used as aromatic platform precursor (A) in these compounds around which three cholesteryl derivatives (S) were arranged using linker units (L). In compounds **1-4**, the molecular structures were systematically altered by changing the aromatic platform, the chain lengths of the linker units as well as by introducing additional hydrogen bonding functionalities onto the linker units. It was found that the gelling as well as self-assembly properties of the compounds **1-4** can be controlled by systematically changing their structural components. STEM and TEM analyses on xerogels of **2-4** from triethylamine solvent revealed that the fundamentals of these xerogel networks are fibres which get assembled into more porous fibrous networks as a function of the chain length of the linker units. Moreover, these compounds were capable of sensing the hazardous F^- ions selectively out of the 11 anions tested by exhibiting fluorescence enhancement. The F^- sensing ability of these compounds could be controlled by changing the length of the linker unit. In some cases, visual changes such as change in color of the gel or gel to sol transformation were also observed on addition of F^- ions. A possible mechanism for the observed sensing of F^- ions is also proposed in this study.

Introduction

Low molecular mass gelators (LMGs) have attracted considerable interest in recent years because of their ability to generate smart supramolecular gels having potential applications in diverse fields.[1] Among various LMGs reported, steroid based LMGs, especially, cholesterol based systems are among the successful systems because of the inherent ability of cholesterol motifs to undergo self-assembly through van der Waals' interactions leading to remarkable gelators.[2] Generally, the molecular design of cholesterol based LMGs involves the rational assembly of various building units such as a steroid derivative (S), a linker unit (L) and often an aromatic platform (A) around which the steroid units can be positioned through linkers. This successful design strategy has led to the development of a series of steroid based gelators classified as ALS, $A(LS)_2$, LS, and LS_2 types[3], which may collectively be represented by the formula $(A)_x(L)_y(S)_z$.

Systematic studies on $(A)_x(L)_y(S)_z$ type gelators have shown that the nature of the molecular building units A, L and S can all play critical roles in determining the overall properties of the system.[3,4] By the rational tweaking of building units, cholesteryl based LMGs are made useful in the preparation of a variety of materials such as visible light harvesting organogels,[5] phase selective gelators,[6] antibacterial composites,[7] smart thixotropic gels,[8] ionogels[9] and so on. Stimuli responsive gels including photo-, thermo-, mechano- and chemo- responsive gels have also been accomplished from cholesteryl derivatives.[10] These examples therefore highlight the utility and versatility of cholesteryl based LMGs and hence point to the importance of further studies in this area. In this context, one potential avenue for further explorations could be the sensor applications of cholesteryl based LMGs. LMGs generally contain weak bonding sites on their structural backbone, which could help them in binding to other ions leading to their sensing applications. Although a large number of sensors for environmentally and biologically important cations and anions have been reported in the literature, those based on LMGs are rather limited in number.[11]



Scheme 1 Molecular structures of triangular $A(LS)_3$ type cholesteryl derivatives with different aromatic platforms and linkers.

Our research aims to develop new organic, inorganic and hybrid systems for materials and sensing applications.[12] In the present study, we have designed a rare class of cholesteryl based $A(LS)_3$ type LMGs, compounds **1-4** (Scheme 1), for exploring their gelation and anion sensing applications. Reports on cholesteryl based triangular LMGs are rare in the literature.[13] In compounds **1-4**, we have introduced systematic structural changes such as change in the aromatic platform (A) and changes in the flexibility as well as the hydrogen bonding ability of the linker unit (L). By introducing these structural changes in a systematic manner, we could successfully control the gelling abilities, self-assembly behaviours as well as anion sensing abilities of these gelators. These compounds were found to be capable of sensing the hazardous[14] F^- ions selectively from the 11 anions tested through fluorescence enhancement accompanied by visual changes in the system. Most importantly, the F^- sensing abilities of compounds **2-4** could be enhanced by increasing the chain length of their linker units. A probable mechanism for the sensing of F^- ions by these compounds is also proposed herewith which is supported by UV-vis, HR-MS and ^1H NMR spectrometric experiments.

Experimental

Material and methods

Materials

All reagents were purchased from Sigma Aldrich and were used without further purification. Acetonitrile, triethylamine and dichloromethane were used after purification. Absolute ethanol and HPLC grade tetrahydrofuran (THF) were used to perform analytical studies.

Synthesis of $A(LS)_3$ type cholesteryl based compounds 1-4

Synthesis of compound 1

Melamine (0.126 g, 1 mmol) and cholesteryl chloroformate (1.437 g, 3.2 mmol) were added to 50 ml of dry acetonitrile taken in a round bottom flask. Triethylamine (150 µl, 1.07 mmol) was added drop-wise into this solution and the resulting mixture was refluxed for 9 days. During this time, a gel like solid material was separated out from the solution which was collected by filtration and dried under vacuum. Yield: 40%, mp 152 ^oC. ^1H NMR (DMSO, 400 MHz, TMS): δ ppm 6.99 (s, CONH, 3H), 5.36 (s, alkenyl, 3H), 3.82-3.74 (m, oxycyclohexnyl, 3H), 0.66-2.55 (m, cholesteryl protons, 129H). ^{13}C NMR (DMSO, 400 MHz, TMS): δ ppm 170.59, 159.71, 145.36, 144.81, 136.46, 132.18, 127.26, 126.94, 78.70, 65.16, 61.36, 60.39, 59.60, 54.71, 54.67, 50.70, 48.17, 48.09, 47.22, 47.04, 45.48, 45.27, 45.07, 44.86, 44.65, 44.44, 44.23, 44.19, 43.70, 43.50, 41.81, 41.47, 41.31, 41.16, 41.02, 40.87, 40.43, 38.19, 38.19, 36.60, 36.48, 33.13, 33.04. FT-IR (KBr), υ_{max}/cm^{-1}: 3422 (NH), 2950.8 (CH), 1705.3 (C=O, -O), 1626 (C=O, -NH), 1548.2 (NH bending) and 1278 (C-O). MS-*m/z* calculated for [**1**+3K]: 1479.9583; found 1480.2623.

General procedure for the synthesis of compounds 2-4

Compounds **2-4** were synthesized using a two-step approach as given below:

Step 1

To 75 ml dry dichloromethane taken in a round bottom flask were added the diamine (hydrazine hydrate, ethylenediamine or 1,3-diaminopropane) (50 mmol) and triethylamine (348 µl, 2.5 mmol) at 0 ^oC. To this mixture, a solution of cholesteryl chloroformate (1.12 g, 2.5 mmol) in 50 ml dichloromethane was added slowly over a period of 1 h under stirring. The resulting mixture was stirred overnight. Filtered it and washed the filtrate thoroughly with water, dried over anhydrous sodium

sulphate and further dried in vacuum. This crude product was dissolved in 10 ml of dichloromethane and to this solution, methanol was added drop-wise resulting in precipitation. Filtered the precipitate off and dried under vacuum to give the corresponding cholesteryl-amine derivative as white solid.[3(c)]

Step 2
Product of the first step (cholesteryl-amine derivative) (3 mmol) and triethylamine (3 mmol) were dissolved in 75 ml of THF and stirred at 0 ^{o}C. To this, a solution of benzene-1,3,5-tricarbonyl chloride (1 mmol) in 25 ml of THF was added drop-wise. The resulting mixture was stirred overnight. Filtered and the filtrate was evaporated under vacuum to yield the crude product as a solid. This crude product was washed with hot methanol and acetone and dried under vacuum to give pure solid of the corresponding product **2**, **3** or **4**.

Compound 2. Yield: 34%, mp 196 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS): δ ppm 8.36 (s, ArH, 3H), 7.98 (s, COONH, 3H) 5.37 (s, alkenyl & CONH, 6H), 4.64 (s, CONH, 3H), 3.48 (m, oxycyclohexyl, 3H), 0.62–2.39 (m, cholesteryl protons, 129H). ^{13}C NMR ($CDCl_3$, 500 MHz, TMS): δ ppm 169.13, 154.35, 139.51, 135.72, 128.31, 123.15, 75.71, 56.64, 42.33, 39.90, 36.22, 36.16, 35.79, 31.87, 31.83, 28.23, 28.00, 24.27, 22.83, 22.56, 21.16, 19.33, 18.70, 11.85, 8.76. FT-IR (KBr), υ_{max}/cm^{-1}: 3492 (NH), 2949 (CH), 1727 (C=O, -O), 1609 (C=O, -NH), 1525.4 (NH bending) and 1244.3 (-C-O). MS-*m/z* calculated for [**2**+Na]: 1513.091973; found 1513.0949.

Compound 3. Yield: 37%, mp 198 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS): δ ppm 8.30 (s, ArH, 3H), 8.11 (t, COONH, 3H), 5.33 (s, alkenyl and CONH, 6H), 4.63 (m, oxycyclohexyl, 3H), 3.52 (s, $COONHCH_2$, 6H), 3.26 (s, $CONHCH_2$, 6H), 0.65–2.47 (m, cholesteryl protons, 129H). ^{13}C NMR ($CDCl_3$, 500 MHz, TMS): δ ppm 166.71, 156.92, 139.71, 135.27, 128.76, 122.55, 74.55, 56.64, 56.09, 49.96, 46.05, 42.28, 39.70, 39.50, 38.66, 36.93, 36.53, 36.16, 35.79, 31.87, 31.83, 28.23, 28.01, 24.27, 22.83, 22,56, 21.01, 19.33, 18.70, 11.85, 8.63. FT-IR (KBr), υ_{max}/cm^{-1}: 3340.1 (NH), 2943 (CH), 1708.7 (C=O, -O), 1653.7 (C=O, -NH), 1531.5 (NH bending) and 1256.5 (-C-O). MS-m/z calculated for [**3**-3H]: 1571.1882; found 1571.1812.

Compound 4. Yield: 28%, mp 201 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS): δ ppm 8.28 (s, ArH, 3H), 7.63 (s, COONH, 3H), 5.34 (s, alkenyl & CONH, 6H), 4.47 (m, oxycyclohexyl, 3H), 3.48 (s, $COONHCH_2$, 6H), 3.24 (s, $CONHCH_2$, 6H), 0.67–2.33 (m, cholesteryl protons and CH_2, 129H and 6H). ^{13}C NMR ($CDCl_3$, 500 MHz, TMS): δ ppm 166.68, 156.80, 139.95, 122.62, 74.50, 56.80, 56.23, 50.11, 45.97, 42.42, 39.84, 39.64, 38.68, 37.47, 37.11, 36.68, 36.30, 35.94, 32.02, 31.98, 30.44, 28.37, 28.15, 24.42, 23.96, 22.97, 22,71, 21.16, 19.47, 18.84, 11.99, 8.77. FT-IR (KBr), υ_{max}/cm^{-1}: 3340.1 (NH), 2943 (CH), 1708.7 (C=O, -O), 1653.7 (C=O, -NH), 1531.5 (NH bending) and 1256.5 (-C-O). MS-*m/z* calculated for [**4**-H]: 1615.2352; found 1615.1893

Methods

Gelation test. In a typical procedure, a known amount (2.5%, w/v) of the sample was mixed with the corresponding solvent (1 mL) in a sealed test tube. The mixture in the test tube was slowly heated in a water bath/oil bath until the solid was completely dissolved (if applicable). The resulting solution was allowed to cool to the room temperature spontaneously. Finally, the test tube was inversed to see if the solution inside could flow or not. When there is no flow in the system, this stage is denoted as G (gel). In some cases, a solution and gel coexist within the system, which is denoted as PG (partial gel). Cases in which gels are obtained by the simple shaking at room temperature are denoted as G* (gel formed at room temperature). When there is only solution up to the end of the tests, that stage is denoted as S (solution). Cases in which gelator could not be dissolved even at the boiling point of the solvent are denoted by I (insoluble). In some cases, gelator forms solution on heating and precipitate on cooling. Such systems are denoted by P (precipitates). G^{0} denotes that gel is formed at 0 ^{o}C.

Fluorescence quantum yield. Fluorescence quantum yield for **2**, **3** and **4** were calculated at room temperature in HPLC grade THF using optically matching solutions of pyrene (ϕ_r = 0.546) in ethanol as standard. The excitation wavelength used for this was 342 nm from xenon lamp. Quantum yields were calculated by using the equation given below,

$$\emptyset_s = \emptyset_r \times \frac{A_r}{A_s} \times \frac{D_s}{D_r} \times \left(\frac{n_s}{n_r}\right)^2$$

where ϕ_s and ϕ_r are radiative quantum yield of sample and reference respectively; A_s and A_r are the absorbances of the sample and reference respectively; D_s and D_r are the emission areas of sample and reference respectively; n_s and n_r are the refractive indices of sample and reference solutions (pure solvents) respectively. The solutions used for quantum yield analyses were degassed by purging nitrogen prior to the experiment.

TEM and STEM measurements. Transmission electron microscopy (TEM) and scanning transmission electron microscopy analyses of gels were conducted on SEI TECNAI F 20 HRTEM instrument operating at an accelerating voltage of 120 KV. Samples were prepared by drying the gel on the grid slowly at room temperature.

FT-IR measurement. FT-IR spectra were recorded on PerkinElmer FT-IR spectrometer (Spectrum Two, Serial No: 88689) using KBr pellets of the samples.

Powder XRD analyses. The powder X-ray diffraction (XRD) were performed on a Rigaku Smart Lab 9 KW rotating anode powder X-ray diffractometer using a Cu-Kα radiation source (λ= 0.15418 nm) at room temperature.

Fluorescence spectroscopy. All the fluorescence spectra were recorded on Agilent Technologies Cary Eclipse fluorescence spectrometer. Spectra were recorded by using 1 × 10^{-6} M solutions of compounds **1-4**.

NMR spectroscopy. ^{1}H NMR and ^{13}C NMR spectra of compound **1** were recorded on Bruker Avance II 400 NMR spectrometer. For compounds **2-4,** NMR spectra were recorded on Jeol JNM-ECX 500 NMR spectrometer in $CDCl_3$ or DMSO solvents using TMS as internal standard. Data are presented as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, br = broad singlet, m = multiplet).

Results and discussion

Design of gelators

Various $(A)_x(L)_y(S)_z$ type gelators have been reported in the literature, some of which show excellent gelling behaviours towards certain solvents.[3,4] It is reported that the gelation behaviour of these molecules can be tuned by changing their structural motifs like aromatic group A, the linker L or the steroid derivative S. Majority of the above mentioned molecules are linear or nearly linear in geometry.[3] To the best of our knowledge, there is only one triangular gelator reported so far based on cholesteryl derivatives, which contains an aromatic, non-flexible moiety as the linker unit.[13] Therefore, in the present study, we thought of designing a new series of triangular $A(LS)_3$ type molecules in which steroid units are arranged around an aromatic platform through flexible linker units. We chose such a system because of the fact that the triangular $A(LS)_3$ type LMGs is a less explored class of gelators and such a type allows more number of weak bonding cholesteryl derivatives and linker units on the gelator molecule compared to the existing $(A)_x(L)_y(S)_z$ type gelators. It was expected that the change in geometry, aromatic unit A and linker L can all confer different properties to these molecules and hence would be of interest to study their properties in the context of the known $(A)_x(L)_y(S)_z$ type compounds. The molecular structures of compounds **1-4** are shown in Scheme 1. Compound **1** contains melamine derivative as the aromatic platform around which cholesteryl units are coupled through –CO-NH– bonds. Meanwhile, compounds **2-4** contain BTC derivative as the aromatic platform. Unlike in compound **1**, each linker unit in compounds **2-4** contains two –CO-NH– units which could further alter the properties of these molecules as amide bond is a well-known H-bonding group capable of playing important roles in deciding the self-assembly behaviours of molecules. Again, the linker units in compounds **1-4** differ in their chain lengths. We expected that these changes in the molecular structures of compounds **1-4** could lead to considerable differences in their properties as well.

Synthesis of compounds 1-4

Compound **1** was prepared by refluxing melamine and cholesteryl chloroformate in acetonitrile in presence of trace amounts of triethylamine (TEA) as shown in ESI (S2). Product was separated out as a gel like material from the reaction mixture, which was collected and dried. Compound **1** was characterized by ^{1}H NMR, ^{13}C NMR, HR-MS and FT-IR spectroscopic techniques. ^{1}H NMR spectrum showed a singlet at 6.99 (3H, CONH) in addition to the cholesteryl peaks. One of the characteristic IR peak of this compound appeared at 3422 cm^{-1} corresponding to N−H stretch vibrations. Compounds **2-4** were synthesized using a two-step procedure. Here, cholesteryl chloroformate was first reacted with a diamine such as hydrazine hydrate/ethylenediamine/1,3-diaminopropane to form the corresponding amide derivative which on subsequent reaction with BTC in dichloromethane (DCM) in presence of TEA yielded the corresponding products **2**, **3** and **4** respectively as given in ESI (S4, S7, S10). Compounds **2**, **3** and **4** were characterized by FT-IR, ^{1}H NMR, ^{13}C NMR and HR-MS spectroscopic studies. ^{1}H NMR spectra of these compounds show peaks corresponding to the aromatic protons and NH protons in the range 8.36-8.28 ppm and 8.11-7.63 ppm respectively in addition to cholesteryl peaks.

Gel forming properties

The gelation behaviours of compounds **1-4** were examined in 35 different solvents at a concentration of 2.5 % (w/v) by using the "stable to inversion of test tube" approach. Here, 2.5 % (w/v) of the sample was mixed with the solvent in a sealed test tube and was slowly heated in a water or oil bath till the sample is dissolved (if applicable). The resulting solution was cooled to room temperature spontaneously and the test tube was inversed to see if the solution inside can flow or not. The results of these gelation experiments are presented in Table 1.

While analyzing the data given in Table 1, it can be seen that the compound **1** does not gel any solvents tested under the experimental conditions but the compounds **2-4** exhibit gelling properties towards certain organic solvents.

Table 1 Gelation properties of compounds **1-4** in various organic solvents[a].

S No	Solvent	1	2	3	4
1.	CH_2Cl_2	P	G^0	G^0	G^0
2.	$CHCl_3$	P	S	S	S
3.	CCl_4	P	S	S	S
4.	THF	I	S	S	S
5.	Toluene	I	S	PG	G
6.	Benzene	I	PG	PG	PG
7.	Xylene	I	S	S	S
8.	DMSO	S	I	I	I
9.	DMF	S	P	P	P
10.	Acetone	I	I	I	I
11.	Ethyl acetate	I	I	I	I
12.	Cyclohexane	I	S	S	S
13.	Hexane	I	G^0	G^0	G^0
14.	Heptane	I	I	I	I
15.	Decane	I	I	I	I
16.	Methanol	S	I	I	I
17.	Ethanol	S	I	I	I
18.	Cyclopentane	I	S	S	S
19.	1,4-dioxane	P	P	P	P
20.	Hydrazine	I	I	I	I
21.	Triethylamine	P	G	G	G
22.	Diethylamine	P	P	P	P
23.	N,N-Diisopropylethylamine	P	G	G	G^*
24.	Ethyl amine	P	P	P	P
25.	Ammonia solution	I	I	I	I
26.	Ethanol amine	I	I	I	I
27.	Ethylene glycol	I	P	P	P
28.	Tetraethylene glycol	I	P	P	P
29.	Hexanol	S	S	S	S
30.	Heptanol	S	S	S	S
31.	Octanol	S	S	S	S
32.	Acetonitrile	I	I	I	I
33.	H_2O	P	I	I	I
34.	Styrene: THF	P	G	G	G
35.	Tetraethyleneglycol	P	P	P	P

[a]Concentration of gelator: 2.5%, w/v; G: Gel, PG: Partial gel; P: Precipitate; I: Insoluble; S: Solution and G^*: Gels forming at room temperature; G^0: Gels forming at 0 ^{0}C.

Compounds **2-4** show gelation with triethylamine (TEA), N,N-diisopropylethylamine (DIPEA) and styrene:tetrahydrofuran (THF) (1:1 v/v) mixture under the experimental conditions. The photographs of some of these

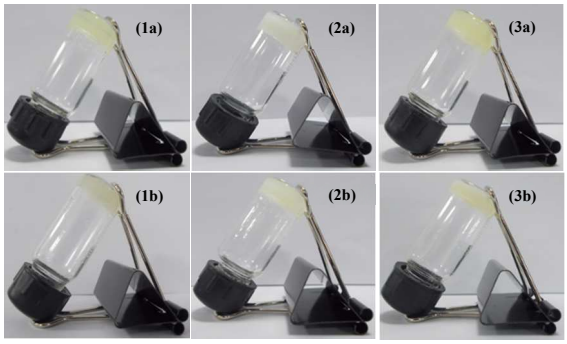


Fig. 1 Photographs of gels obtained from **2**, **3** and **4** after gelation with N,N-diisopropylethylamine (DIPEA) and triethylamine (TEA): (1a) **2**/DIPEA; (1b) **2**/TEA; (2a) **3**/DIPEA; (2b) **3**/TEA; (3a) **4**/DIPEA; (3b) **4**/TEA.

organogels are given in Fig. 1 and ESI (S6, S9, S12). The gels formed from compounds **2-4** are found to be reversible in nature; they form sol on heating and become gel on cooling. Additionally, compounds **2-4** are also capable of forming partial gels with benzene. With solvents like dichloromethane and hexane compounds **2-4** form gels at 0 ^{o}C. Between the solvents TEA and DIPEA, compounds **2-4** exhibit faster gelation with DIPEA. Also it was observed that the gels formed from DIPEA are stable upto one month at normal conditions while the gels formed from TEA are found to degrade after 3-4 days.

The above studies clearly demonstrate the differences in the gelation properties exhibited by compounds **1-4**. Compounds **2-4** exhibit better gelation properties compared to compound **1** as they form gels with a number of solvents while compound **1** does not show any gelation with the solvents tested. One possible reason for the enhanced gelation properties of compounds **2-4** compared to compound **1** could be the differences in the chain lengths of their linker units, which are higher in compounds **2-4** compared to compound **1**. Another reason could be the fact that the compounds **2-4** contain two –CO-NH– moieties in their linker units which could enhance their hydrogen bonding abilities as compared to compound **1**, which has only one –CO-NH– unit per linker unit.

Morphology of xerogels

Gelator molecules are known to form different microstructures such as fibres, ribbons, sheets and so on in a gel.[15] In order to see how the network structures of the gels are influenced by the molecular structures of the gelators **1-4**, their TEA gels were adopted as examples and analysed using STEM and TEM techniques.

TEM analysis showed that compound **1** is a crystalline material and does not form any fibrous or layered networks, see ESI (S17a). This explains the poor gelling ability of this compound as observed earlier. The xerogels of compounds **2-4** for microstructure analyses were prepared by drying their gels (2.5%, w/v) from TEA. Their STEM and TEM images given in Fig. 2 show that the fundamentals of the xerogel network of **2-4** in TEA are fibres. On analysing the STEM and TEM images, one can visualize a gradual transition in the morphological features from long fibres for **2**/TEA to entangled porous fibrous network structure for **4**/TEA. Closer look at the fibre morphology (See ESI (S17b)) revealed that the fibres of **2**/TEA and **3**/TEA are relatively straight, while fibres of **4**/TEA shows some spiral nature, which could be due to the structural flexibility of gelator **4** compared to gelators **2** and **3**, see ESI (S17(c & f)) for details. The observed morphological features of the gelators may be correlated with the length and flexibility of their linker units. As the linker flexibility increases, the gelator adopts a more porous fibrous network structure in the xerogel increasing its gel forming capabilities. The linker length and flexibility therefore play important roles in defining the morphology of these xerogels.

The xerogels of triangular A(LS)$_3$ type gelators **2-4** thus exhibit routine fibrous networks as reported earlier for majority of the cholesteryl based A(LS) or A(LS)$_2$ type gelators.[3] This observation can be rationalized by considering the fact that the gelators **2-4** contain two H-bonding –CO-NH– moieties in each of their linker units and such highly directional H-bonding functional groups are known to favour the formation of fibres.[13]

Powder XRD analysis

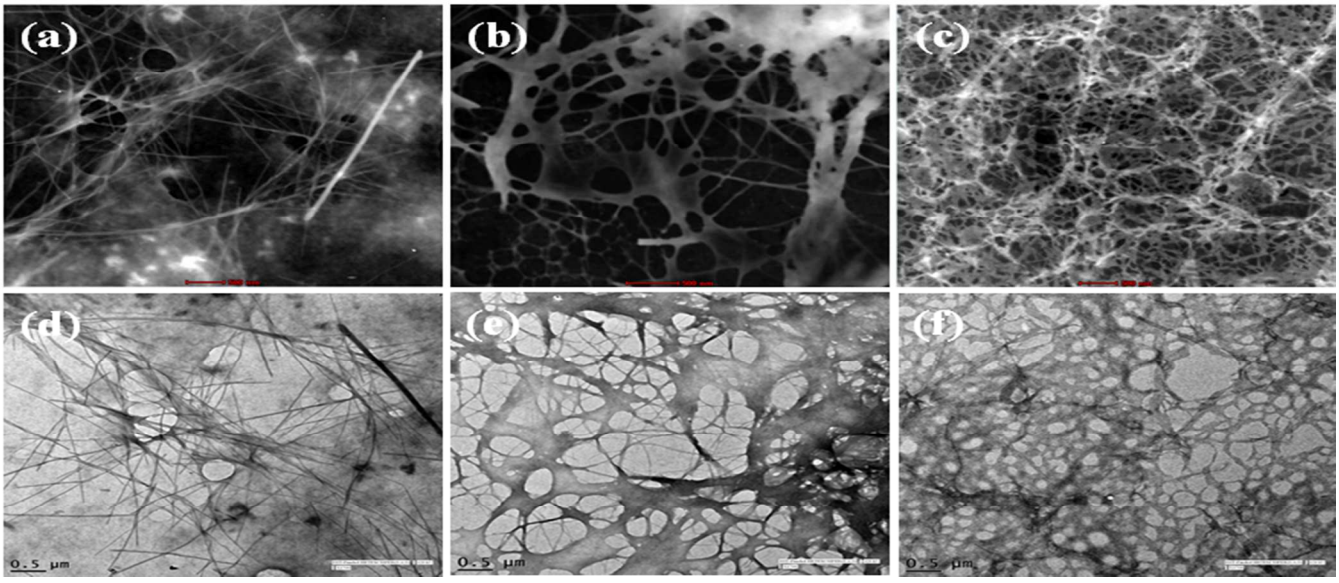


Fig. 2 STEM images of the xerogels: (a) **2**/TEA; (b) **3**/TEA; (c) **4**/TEA.; and TEM images of xerogels: (d) **2**/TEA; (e) **3**/TEA; (f) **4**/TEA. The scale bar is 500 nm for all the images.

Powder X-ray diffraction is a widely used technique for getting information on the molecular packing of gelators in the gel network and hence to get a better understanding of the gelation mechanism.[16] Powder XRD measurements on compound **1** and xerogels **2-4**/TEA were performed. The results are shown in Fig. 3 and 4. As shown in the Fig. 3, the powder XRD of compound **1** showed sharp peaks which indicates its crystalline nature as already shown by its TEM analysis. Reflections observed in the 2θ range 10–30° correspond to d-spacing values of 0.85 nm–0.32 nm.

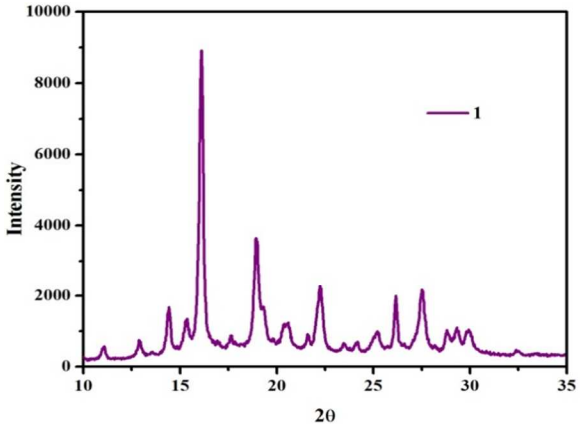


Fig. 3 X-ray diffraction pattern of compound **1**.

In the case of gelators **2-4**, XRD analyses were conducted on their TEA xerogels as model samples and the resulting patterns are given in Fig. 4. Clearly, all these patterns are characterized by four reflection peaks. For xerogel **2**/TEA, peaks were observed at 2θ values of 3.86°, 5.41°, 15.32° and 23.32° corresponding to the d-spacing values of 2.28 nm, 1.63 nm, 0.57 nm and 0.38 nm respectively. Similarly, xerogl **3**/TEA exhibited peaks at 2.98°, 5.86°, 15.68° and 26.34° corresponding to the d-spacings of 2.96 nm, 1.50 nm, 0.56 nm and 0.33 nm respectively; while **4**/TEA exhibited XRD peaks at 3.48°, 5.32°, 15.62° and 26.34° corresponding to the d-spacing values of 2.53 nm, 1.66 nm, 0.56 nm and 0.33 nm respectively. According to previous studies, many of the cholesteryl based xerogels are found to exhibit layered or lamellar structures in which the d-spacings follow 1:1/2:1/3:1/4 ratio.[3(h),8(a)] But for **2-4**/TEA, such a clear relation does not exist ruling out the possibility of perfect lamellar or layered morphologies.

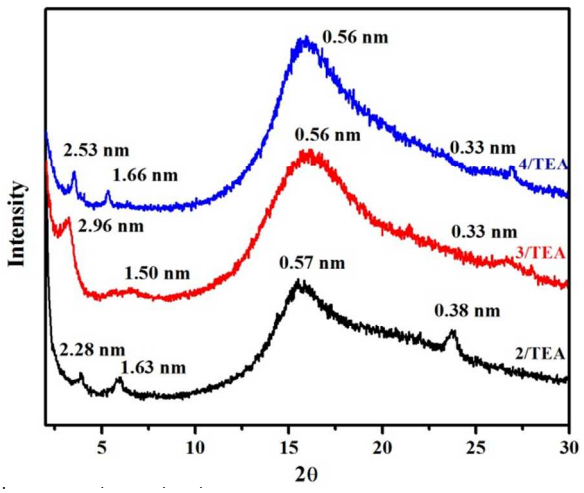


Fig. 4 X-ray diffraction patterns of xerogels **2**, **3** and **4** obtained from triethylamine (TEA).

From Fig. 4, it can be noted that the overall XRD profiles of **2-4**/TEA are similar, but with differences in individual d-spacing values. Xerogels **2-4**/TEA display the first d-spacing values of 2.28 nm, 2.96 nm and 2.53 nm respectively, which roughly correspond to their molecular lengths 2.23 nm, 2.75 nm and 2.47 nm as modelled by MD simulations, see ESI (S16). The other diffraction signals observed in each case may correspond to the intermolecular separations in different directions. Due to the limited data available in the XRD patterns, it is difficult to deduce detailed structural information of these xerogels. The previously reported cholesteryl based $A(LS)_3$ type gelator exhibited complexed signals in its XRD pattern indicating that it aggregated in polycrystalline structure.[13]

FT-IR spectroscopic studies

Hydrogen bonding and van der Waals' interactions are among the main driving forces for the self-assembly of cholestrol based LMGs.[3] To study the inter-molecular hydrogen bonding interaction among the gelator molecules, FT-IR measurments were conducted on pure compounds **2-4** as well as on their xerogels. As shown in Table S2 of ESI (S18), there are shifts in the streching vibrations of amide N-H and C=O groups upon gelation for the compounds **2-4**. These observations suggest that the extend of the intermolecular H-bonding interactions occuring in pure solids **2-4** are different from that of their xerogels. Also these values suggest differences in H-bonding interactions in xerogels of the same gelator from different solvents possibly due to the differences in solvent polarities.[17]

Anion binding studies

Some of the cholesteryl based LMGs are known to exhibit sensing abilities towards certain anions.[11] This prompted us to explore the anion sensing abilities of compounds **1-4** using fluorescence spectroscopy. Fluorescence titration experiments were conducted on compounds **1-4** (1×10^{-6} M) with 11 different anions as their tetrabutylammonium salts (F^-, Cl^-, Br^-, HSO_3^-, SCN^-, CN^-, NO_3^-, CH_3COO^-, PO_4^-, ClO_4^- and SO_4^{2-}) in THF:H_2O (9.5:0.5 *v/v*) solvent buffered with HEPES (pH=7) solutions. Among all the anions tested, F^- ion was found to have biggest effect on the fluorescence properties of compounds **1-4**. The fluorescence spectrum of compound **1** (λ_{ex}= 251 nm) showed very weak emission at 305 nm, see ESI (S3). The fluorescence spectra of compounds **2** (λ_{ex}= 271 nm), **3** (λ_{ex}= 266 nm) and **4** (λ_{ex}= 271 nm) showed emission bands at 307 nm, 301 nm and 288 nm respectively. It was found that these compounds show considerable changes in their florescence intensities on addition of 1 mM of F^- ions. The fluorescence quantum yield[18] (ϕ_s) of compounds **2-4** in absence and presence of F^- ions were found to be 0.035 and 0.044, 0.002 and 0.056, 0.001 and 0.130 respectively. Color changes were also observed on addition of F^- ions to the solutions of compounds **2-4,** as shown in ESI (S5(a), S8(a) and S11(a)). Addition of other anions did not cause considerable changes in their fluorescence intensity, see ESI (S5(b), S8(b) and S11(b)).

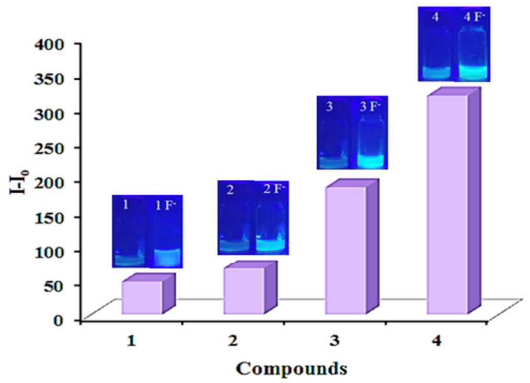


Fig. 5 Compounds **1**, **2**, **3** and **4** showing I-I_o; I is final fluorescence intensity after addition of 1 mmol of F^- ions and I_o is initial fluorescence intensity of compounds. Insets show the changes in respective compounds on addition of F^- ions under 365 nm illumination.

To have an insight in to the mechanism of F^- recognition by these cholesteryl based compounds, we carried out mass spectroscopic studies on one of the compounds (compound **4**) in presence of F^- ions. We chose compound **4** for this studies because it showed maximum fluorescence intensity with F^- ions compared to other compounds. A mass spectrum peak at 1878.6277 corresponding to the species [**4**+F(TBA)] was observed indicating the complex formation between **4** and F^- ions, see ESI (S14). The complex between **4** and F^- ions is possible only through hydrogen bonding between F^- and amide NH protons.[19] To rule out any de-protonation phenomenon between host and the guest, we carried out UV-vis studies between host/F^- and host/OH^- under similar conditions as, OH^- being a very strong base is known for its deprotonating abilities. We observed that the UV-vis behaviours with both the analytes were different, ESI (S13), revealing that a different mechanism exists with F^- ions which could only be hydrogen bonding as proved by the mass spectroscopic studies. To further confirm this, we carried out ^{1}H NMR titrations experiments in which spectra were recorded by adding varying equivalents of F^- ions (0.0, 0.2, 0.4, 0.6. 0.8 & 1 equivalents) to the solution of **4** in $CDCl_3$. It was observed that the peaks due to –COO-NH– proton (δ 7.63 ppm) and –CO-NH– proton (δ 5.34 ppm) undergo downfield shift accompanied by broadening of the signals, see ESI (S15) for details. The occurrence of peak shifts and peak broadening rather than peak disappearance confirm that the observed F^- sensing involves H-boding rather than de-protonation. The binding constants for the formation of hydrogen bonded fluoride complexes of compounds **2**-**4** were calculated as 2.05×10^6, 2.72×10^7 and 6.45×10^6 respectively using a Benesi-Hildebrand plot of fluorescence titration data.[20] In contrast, the binding constant values reported in literature for similar fluoride sensing systems are in the range 2.07×10^3 – 5.46×10^4 [11(e,f,i)] thus highlighting the superior fluoride binding ability of the gelators **2**-**4** compared to the existing systems. The detection limit[21] of compounds **2**-**4** as a fluorescence sensor for F^- was determined from a plot of fluorescence intensity as a function of the concentration of added F^- anions. Detection limits for compounds **2**-**4** were found to be 4×10^6 mol/L, 5×10^6 mol/L and 7×10^6 mol/L respectively.

The extent of fluorescence intensity changes exhibited by compounds **2**-**4** on addition of F^- ions is shown in Fig. 5. It can be seen that the fluorescence intensity change increases with increase in the number of $–CH_2$ groups on the linker units (Fig. 5). Though, there is relatively less difference between change in fluorescence intensities of compounds **3** & **4**, the changes are higher between compounds **1** & **3**-**4** and compounds **1**-**2** & **4**. Therefore, the spacer length is playing a crucial role in detection and sensitivity of these compounds towards F^- ions.

Further we explored the effect of F^- ions on gels. We found that on addition of F^- into the gels, degradation of gels occurred which may be due to disruption of the intermolecular hydrogen bonding interactions among the amide groups on adjacent molecules, which was one of the main driving force for the gel formation[11(b)]

Anions play crucial roles in wide range of chemical and biological processes. Among various anions, F^- is of special importance because of their adverse effects. Although fluoride is useful in dental care and in the treatment of osteoporosis, excess of F^- can cause fluorosis.[14] Therefore, sensors capable of detecting F^- ions are highly important and the chemosensing ability of compound **1**-**4** towards these ions is highly relevant in this context.

Conclusions

A new series of $A(LS)_3$ type triangular compounds containing cholesteryl derivatives have been designed and synthesized. Gelation and self-assembly properties of this new class of compounds were studied in the context of the existing cholesteryl based LMGs. This study revealed that by controlling the structural features of the $A(LS)_3$ type gelator molecules one can control their gelation and self-assembly properties. In addition, these triangular compounds were found to act as selective sensors for F^- ions exhibiting fluorescence enhancement. The F^- sensitivity of these compounds could be enhanced by increasing the chain length of their linker units. A possible mechanism for the observed sensing of F^- ions is also proposed in this study.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Synthetic schemes, fluorescence and UV-vis data, MS data, photographs of gels, table of IR data, NMR titration data, MD simulation data, TEM images]. See DOI: 10.1039/b000000x/

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