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Sulfonyl Hydrazone Cholesterol Conjugate: Gelation, Anion Interaction with Application in Dye Adsorption

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Abstract: Cholesterol appended sulfonyl hydrazone derivative **1** has been designed and synthesized as supramolecular gelator for anionic sensing and dye adsorption. Gelator **1** forms a stable gel from DMSO-H_2O. Intermolecular H-bonding involving the sulfonamide moieties and hydrophobic interaction between the cholesterol units encourage gelation. SEM images of the xerogels show tiny rod-like fibrous structures. Rheological studies of the gel reveal the viscoelastic nature of the material . The gels of **1** exhibit a sharp and selective response toward CN^- and F^- ions causing gel-to-sol transformation. The gels of **1** are also potent in adsorption and removal of anionic dyes, such as erythrosine B and uranine, from water. Preparation of a gel column with the gel of **1** shows reasonably high one time erythrosine B removal efficiency and establishes its potential and promising real-life applicability in water purification.

Introduction

Development of new low molecular weight supramolecular gelators (LMWGs) of simple architectures has become pertinent over the years owing to their wide potential applications from medical science to material chemistry.[1-7] Supramolecular gels are obtained through self assembly of small molecules involving several weak forces such as hydrogen bonding, π-π stacking, van der Waals interactions etc.[2] Non-covalent weak interactions can easily be tuned by external physical and chemical stimuli (heat, light, redox, pH, ions etc.) resulting in either weakening (gel-to-sol transition) or restoring (sol-to-gel transition) the self-assembled architectures.[3] Such phase transformation in the presence of chemical analytes is a familiar approach to developing new sensor devices for naked-eye detection of biologically relevant metal ions and anionic substrates.[2-6]

Beside sensing, the use of supramolecular gels as water cleaning agents is interesting.[7,8] Supramolecular gels are often used in adsorption and removal of heavy metal salts, nitroaromatic explosives and dyes form water. Removal of water soluble toxic dyes draws attention as its consumption in human body leads to serious health damages. Organic dyes are widely used in various industries like food, textile, lather etc. However, they are difficult to degrade owing to their inertness toward photochemical decomposition and oxidation. Direct discharge of dyes into the environment can be a potent threat to human and aquatic organisms. Thus there is always a need of efficient dye adsorbent system. Supramolecular gelators having the suitable hydrophilic/hydrophobic sites are usually found to be promising in this event.[4c,4f,7a]

As part of our ongoing research programme in designing stimuli responsive LMWGs,[4] herein, we report a new LMWG **1** of simple architecture that finds applications in anion sensing and dye adsorption. Different functional segments of compound **1** are highlighted in .Figure 1. Sulfonamide moiety is introduced as anion binding site[9] and also to encourage the formation of molecular-assembly *via* H-bonding interaction. Cholesterol motif has been incorporated to assist molecular aggregation through hydrophobic interaction.[1f] The large hydrophobic surface of cholesterol has significant impact in dye adsorption also.[4c,4d,4f]

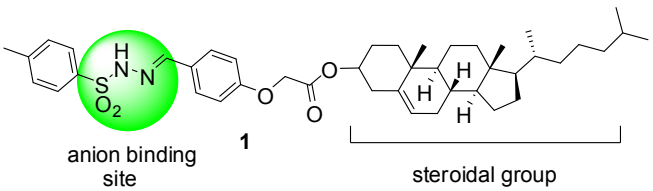

Figure 1. Structure of compound **1**.

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†Electronic Supplementary Information (ESI) available: Gelation tests, gel pics, binding curves, detection limit, comparative tables, ^1H, ^{13}C NMR and HRMS are available. See http://dx.doi.org/10.1039/b000000x/

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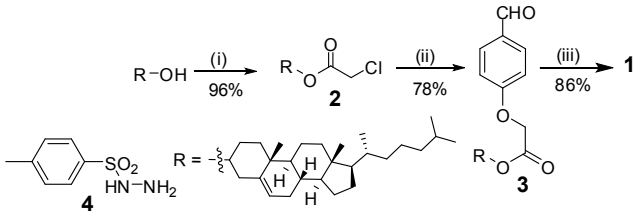
As anticipated, gelator **1** acts as a good anion sensor as well as an efficient dye adsorbing agent. It forms a stable thermoreversible gel from DMSO-H_2O and the gel exhibits visual detection of CN^- and F^- ions involving gel-to-sol phase transition. In addition, DMSO-H_2O gel of **1** was used as a good adsorbent of anionic dyes such as erythrosine B and uranine from water.

Results and discussion

Synthesis

Synthesis of compound **1** was achieved according to the Scheme 1. Initially, cholesteryl-aldehyde **3** was prepared from the reaction of 4-hydroxy benzaldehyde with compound **2** according to our reported procedure.[4a-d] *p*-Toluene sulphonyl hydrazide **4** was next coupled with compound **3** to have the Schiff base **1** in reasonable yield. All the compounds were fully characterized by ^1H, ^{13}C NMR and mass spectral analysis.



Scheme 1. (i) Chloroacetyl chloride, pyridine, dry $CHCl_3$, rt, 10h; (ii) 4-hydroxy benzaldehyde, K_2CO_3, dry CH_3CN, reflux, 5h; (iii) **4**, dry benzene, reflux, 24.

Gelation study

Gelation study of compound **1** was performed in a wide range of solvents by means of typical inversion of vial method (Table S1). While compound **1** was soluble in most of the organic solvents (toluene, DMF and DMSO etc.), it was insoluble in water or MeOH due to the presence of cholesterol motif that provides large hydrophobic surface. So, a better gelation could be anticipated from solvent mixtures having MeOH or water as co-solvent. In practice, tosylhydrazone **1** exhibitted excellent self-aggregation in DMSO-H_2O (1:1, v/v) mixture solvent (mgc = 20 mg/mL and T_{gel} = 44°C). The gel was thermoreversible as shown in Figure S1.

However, gelation was unsucessful from other solvent mixtures including semi-aqueous compositions (Table S1). Even the presence of anions, such as F^- and AcO^-, in toluene-MeOH solvent did not bring gelation of compound **1** (Table S1).

Probable mode of aggregation

The gel formation of **1** in DMSO-H_2O (1:1 v/v) occurs due to functioning of several weak forces. The hydrogen bonding characteristics of sulfonamide –NH, hydrophobic interactions exerted by cholesterol surface are the possible responsible forces to induce gelation. In order to understand the hydrogen bonding behaviour, FTIR analysis was done. The imine signal appeared at 1608 cm^{-1} in the amorphous state suffered a large shift to 1645 cm^{-1} in gel state (Figure S2). This is attributed to the rigidification of imine bond that arises from the engagement of the sulfonamide –NH in hydrogen bonding. A small change in stretching frequency of the ester carbonyl which could not be ruled out, was possibly due to intermolecular hydrogen bonding with water of the gelling solvent (Figure S2).

Morphology of the gel

The aggregated morphology of the gel was examined by using scanning electron microscopy (SEM). SEM image of the xerogel revealed the fibrous structure (Figure 2). Large numbers of tiny rod-like fibers were in chaotic order to establish a 3D network.

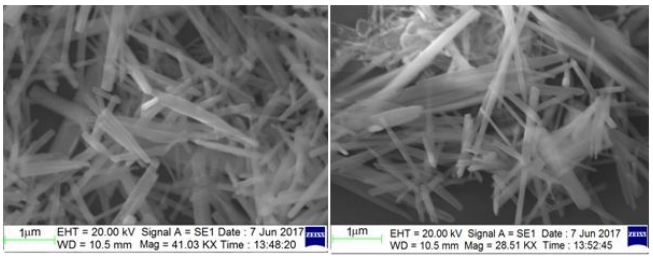


Figure 2. SEM images of the DMSO-H_2O (1:1 v/v) gel of **1**.

Rheological study

To evaluate the mechanical behaviour of DMSO-H_2O (1:1 v/v) gel of **1**, oscilatory rheology experiment (dynamic amplitude sweep and frequency sweep) was carried out (Figure 3 and Table 1). For this, gel was prepared at a concentration of 1.2 wt% of its mgc and the experiment was carried out at 25 °C. Amplitude sweep experiment (at constant frequency of 1 Hz) determined the linerar viscolelastic region of the gel, which

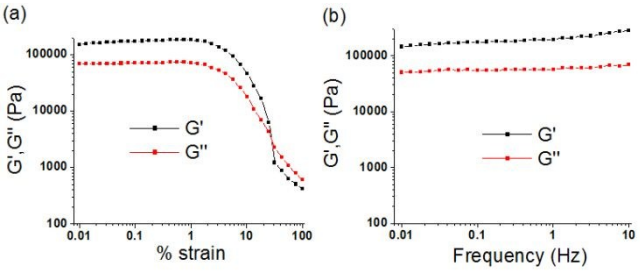


Figure 3. Rheology study of the DMSO-H_2O (1:1 v/v) gel of **1**; (a) amplitude sweep and (b) frequency sweep experiments.

Table 1. Summary of rheological properties of the gel of **1**.

Solvent	Crossover (% of strain)	G'_{av} (Pa)	G''_{av} (Pa)	tan δ (G''_{av}/G'_{av})
DMSO-H_2O (1:1 v/v)	27	175572	54918	0.31

was upto ~2% of strain where both the storage modulus (G′) and the loss modulus (G′′) were independent of strain (Figure 3a). With further increase in strain, both G′ and G′′ were decreased. At 27% of strain a crossover between G′ and G′′ was noticed indicating demolition of the gel. In frequency sweep measurement (at constant strain of 0.1%), both G′ and

G'' were almost independent of strain in the entire range studied (Figure 3b). Higher values of G' over G'' suggested the true gel nature of the gel material.

Anion responsive nature of the gel

To evaluate the stimuli responsive behaviour of the gel, the effect of different anions on gel phase of **1** was investigated. Since intermolecular H-bonding between the sulfonamide groups is one controlling factor in gelation of **1**, anions with their basicities and hydrogen bonding capabilities are expected to influence the gel state *via* the perturbation of this weak interaction. Accordingly, in the experiment, 2 equiv. amounts of different anions (CN^-, F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, and NO_3^- as their tetrabutylammonium salts, c = 0.2 M in water) were added to the gel of **1**. Both CN^- and F^- ions caused a complete destruction of the gels, whereas other anions were practically non interfering (Figure 4).

Both CN^- and F^- ions interact with the sulfonamide –NH- and disrupt the hydrogen bonds to give sol as evident from the ^1H NMR study discussed latter. In the event, the gel state of **1** was transformed into sol within 30 min in the presence of CN^-. By contrast, F^- ion took almost 2h to bring a similar change. As optimization, minimum 2 equiv. amounts of F^- ion was necessary to cause such gel to sol conversion. The gel was virtually stable in the presence of 1.5 equiv. amounts of F^- ion even after 2h. We observed the instant gelation when the gel was prepared in the presence of 1 equiv. amount of F^- ion. On the other hand, under similar conditions, CN^- ion-induced gel to sol phase transition was noticed in presence of its 1 equiv. amount. As reason, F^- ion being smaller in size is more hydrated in water compared to CN^- ion and remains less free to interact with gelator **1**.[10] On contrary, CN^- ion being less hydrated could display its basic nature and thereby caused deprotonation of sulfonamide –NH- for which gel structure was destroyed.

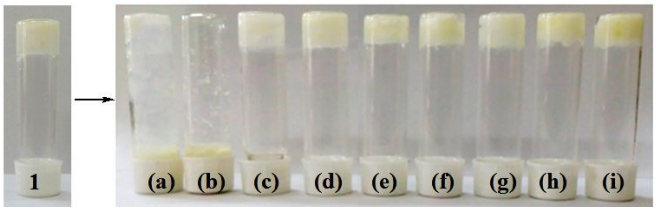


Figure 4. Pictorial representation of the phase changes of **1** (c = 20 mg/ml) in DMSO-H_2O (1:1 v/v) upon treatment with 2 equiv. amounts of the different anions (as tetrabutyl ammonium salt, c = 0.2 M) after 2h. [from left to right: (a) CN^-, (b) F^-, (c) AcO^-, (d) $H_2PO_4^-$, (e) Cl^-, (f) Br^-, (g) I^-, (h) HSO_4^- and (i) NO_3^-].

To discriminate CN^- and F^- ions, we prepared the gel of **1** in DMSO-H_2O (1:1 v/v) separately in presence of these anions and different chelating agents. Under this circumstance, while the content of the vial containing Ca^{2+} and CN^- ions did not gelate, gelation was successfully observed in the vial that contains Ca^{2+} and F^- ions (Figure 5A). This was due to scavenging of F^- ions by Ca^{2+} ions from the medium. Importantly, it was very difficult to distinguish between CN^- and F^- ions by using Fe^{3+} ions as chelating agent. Preparation of the gels in the presence of both anions and Fe^{3+} ions was successful (Figure 5A). Thus apart from the gel-to-sol conversion of **1** in different time frames, use of Ca^{2+} ions was important in discriminating CN^- from F^- ions.

To be familiar with the case of deprotonation, responsible for gel destruction, the effect of tetrabutylammonium hydroxide (TBAOH) on gelation of **1** was investigated. When aqueous solution of TBAOH was added to a DMSO solution of **1**, no gel formation was observed even after 1h, instead it produced a clear solution (Figure 5B). These findings suggested the H-bonding and deprotonation of sulfonamide –NH- in presence of CN^- and F^- ions for which rupturing of the gels occurred. In this context, it is also mentionable that DMSO-H_2O (1:1 v/v) gel of **1** was stable in a wide range of pH (from pH 2-11). Precipitation was noted at pH 11 (Figure 5B).

In order to be acquainted with the reason of anion-induced gel breaking, pHs of the broken gels were determined. In the study, DMSO-H_2O (1:1 v/v) gel of **1** (prepared with or without using tris HCl buffer, 10 mM) was destroyed in the presence of 2 equiv. amounts of anions (e.g., F^-, CN^- and OH^-) and pHs of the sols were found to increase above 11 (Figure 5C). This

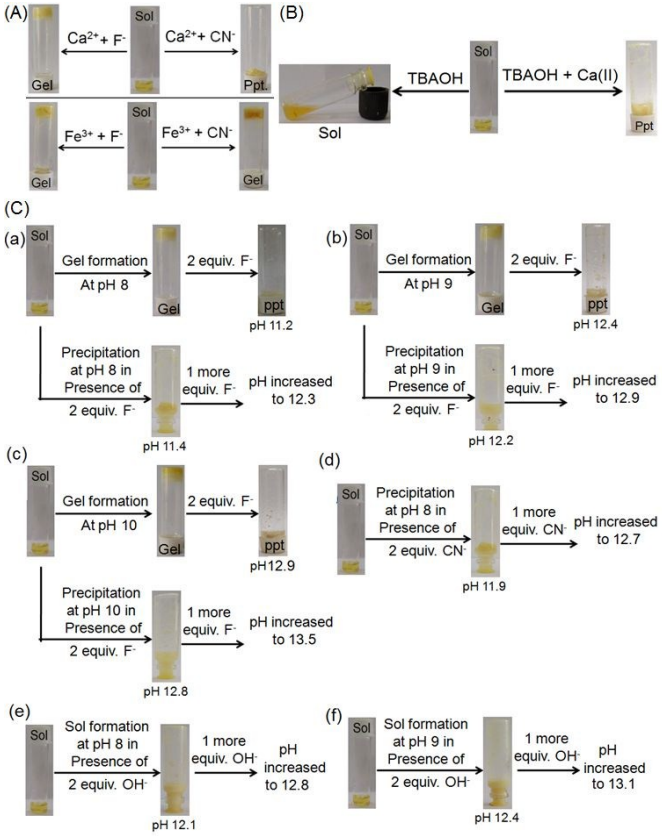


Figure 5. (A) and (B) are the photographs to show the effects of different chemical analytes on sol-to-gel conversion of **1** in DMSO-H_2O (1:1, v/v) (2 equiv. amounts of each analytes were used in the experiment and the photographs were taken after ~15 min of sample preparation, Ca^{2+} and Fe^{3+} ions were taken as perchlorate and nitrate salts, respectively); (C) Effects of different stimulus on the gel formation of **1** in DMSO: H_2O (1:1, v/v) and measurement of pH of the resulting systems (CN^-, F^- and OH^- were taken as TBA-salts, pH of the final systems (solutions/'precipitations) were measured after solubilising them in 10 mL of DMSO).

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results indicated that the increasing basicity of the medium due to H-bonding followed by deprotonation of sulfonamide –NH- was reponsible for gel breaking (Figure 5C). Inspite of having almost identical pH of the sols, externally added chelating agents successfully distinguished F^-, CN^- from OH^- ions (Figure 5).

^{1}H NMR study

To support the mechanism of interaction, ^{1}H NMR of **1** in the presence of anions were recorded in $CDCl_3$ (Figure 6). In presence of equiv. amount of CN^- ions, while the signal for sulfonamide $–NH_a$- at 7.67 ppm underwent downfield chemical shift by 0.1 ppm, the signal for imine proton (H_b) remained unchanged in position. However, in the presence of excess of CN^- ions (2 equiv.), the signal for sulfonamide $–NH_a$- was vanished and a small upfield chemical shift of other aromatic protons was observed. This demonstrated the H-bonding followed by deprotonation of sulfonamide $–NH_a$- with CN^-. Deprotonation induces extensive delocalization of electron density towards the aromatic rings and results in upfield chemical shift of the aromatic protons.

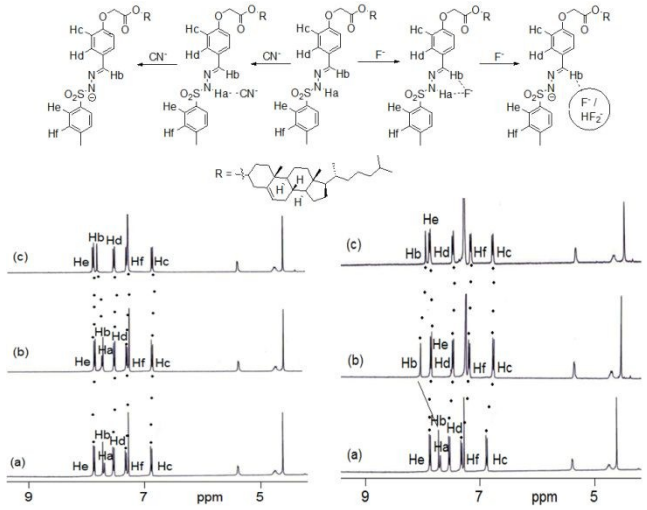

Figure 6. Partial ^{1}H NMR spectra of **1** (c = 0.01 M) (a) in the absence and presence of (b) 1 equiv. and (c) 2 equiv. amounts of CN^- (c = 0. 3 M) (left) and F^- (c = 0.5 M) (right) ions in $CDCl_3$.

Similarly, in the presence of 1 equiv. amount of F^- ions, the signal of sulfonamide $–NH_a$- was vanished and the imine proton (H_b) underwent a downfield chemical shift by ~0.2 ppm. Addition of excess F^- ions (2 equiv.) caused upfield chemical shift of all the aromatic protons including the imine proton. Possibly, HF_2^- ion, resulting from the deprotonation of sulfonamide –NH-, is involved in H-bonding with the imine proton (H_b) and induces downfield chemical shift.[11] However, the signal for HF_2^- was difficult to trace possibly due to broadening.

Anion binding in solution

To understand the host-guest interactions in solution, we recorded UV-vis spectral changes of **1** [$c = 2.50 \times 10^{-5}$ M, taken in DMSO-H_2O (1:1 v/v)] upon addition of the different anions (as tetrabutylammonium salts; $c = 1.0 \times 10^{-3}$ M, taken in DMSO) (Figure 7). Titration with CN^- ions caused ratiometric changes in absorption spectra of **1** (Figure 7a). Successive addition of CN^- ions resulted in gradual decrease in initial absorption band at 282 nm with the simultaneous increase of a new absorption band at 330 nm. This new absorption band at 330 nm progressively reached the plateau region with the addition of 40 equiv. of CN^- ions where a clear isosbestic point at 312 nm was observed, which clearly indicated the existence of a new species in the medium. Further addition of CN^- ions did not change the absorption of **1** significantly.

A similar spectral change but to the small extent was observed with F^- ions (Figure 7b). Other anions did not induce any considerable change in the absorption spectrum of **1** (Figure 7c). Such weak interaction was attributed to their poor basicities. By contrast, measurable interactions for CN^- and F^- ions were due to their marked basicities that caused deprotonation of sulfonamide –NH-. Importantly, CN^- ion is easily distinguished from F^- ion from the strong ratiometric nature of the absorption spectra (Figure 7).

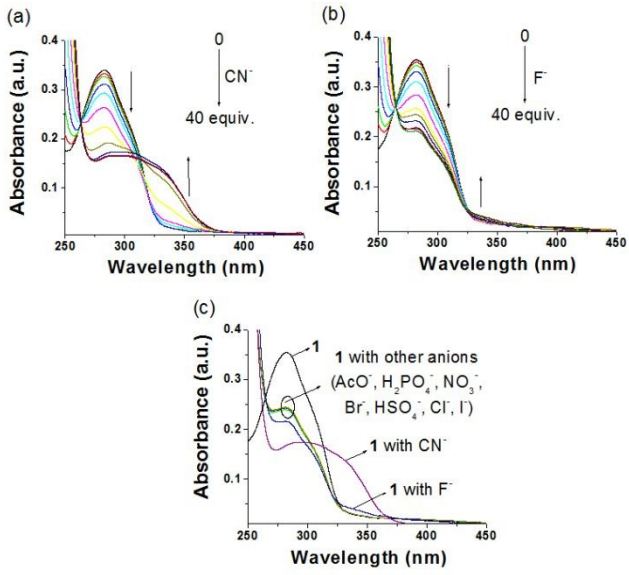

Figure 7. Change in absorbance of **1** [c = 2.50 x 10^{-5} M, taken in DMSO-H_2O (1:1 v/v)] upon addition of 40 equiv. amounts of (a) CN^-, (b) F^- and (c) different anions (c = 1.0 x 10^{-3} M, taken in DMSO).

Benesi–Hilderband plot of **1** with the respective anions reflected linear binding stoichiometry (Figures S3 and S4).[12] In this process, detection limits for different anions were also calculated (Figures S3 and S4)[13]. As can be seen from Table S2, CN^- ions display marginally stronger binding than F^- ions. Thus compound **1** is established as a visual sensor of CN^- and F^- ions in sol-gel medium.

Among the different anions, sensing and detection of CN^- and F^- ions demand merit because of their biological relevance. CN^- is extremely toxic to human body. Accumulation of CN^- causes serious damages to health, even can lead to death within few minutes.[14] However, it is extensively used in many industries, especially in gold and silver extraction processes.[15] On the other hand, F^- is essential in preventing dental cavities and osteoporosis whereas presence of excess amount of F^- leads to fluorosis.[16] In regard to the detection of these two ions,

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although there are various reports on their fluorogenic and chromogenic sensing,[5i,17] the use of supramolecular gels in this capacity is limited,[5,6] especially LMWGs for CN^- ion.[6] In this capacity, a comparative view is represented in Table S3.

Dye adsorption experiment

Apart from the exploring of gelator **1** as sensor for CN^- and F^- ions, DMSO-H_2O gel of **1** was further subjected to the adsorption and removal of dyes from aqueous solution. Supramolecular gelators having the appropriate hydrophilic/hydrophobic sites find potential application toward this event.[4c,4d,4f,7a] In the present state of art, sulfonamide moiety of our designed molecule as hydrophilic unit is expected to initiate the adsorbtion of dyes efficiently on the hydrophobic cholesteryl surface.

To execute the experiment, a series of aqueous dye solutions (dianionic dye erythrosine B, monoanionic dye uranine and monocationic dyes crystal violet and malachite green, 3 mL each) was separately placed on the top of the gel of **1**. Adsorption of dyes was monitored by UV-vis spectroscopy. The efficiency of the gel in uptaking dye molecules was determined by comparing the UV-vis spectral change of respective dye solutions, recorded before and after the experiment.[4f] The outcomes are summarised in Figures 8-9 and in Table 2.

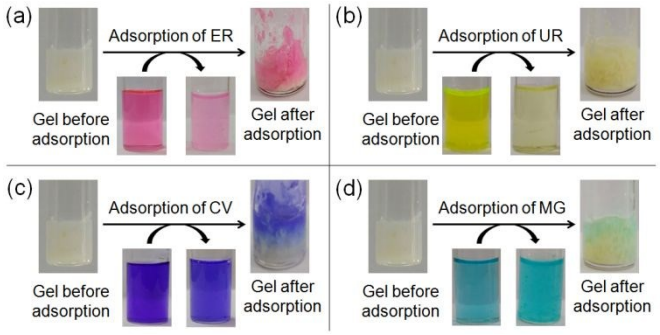

Figure 8. Photograph showing the adsorption of (a) Erythrosine B (ER), (b) Uranine (UR), (c) Crystal Violet (CV) and (d) Malachite Green (MG) by the DMSO-H_2O (1:1 v/v) gel of **1** (25 mg/mL). In all cases, [dye] = 3.5 x 10^{-5} M.

It was found that the gel of **1** could remove the anionic dyes more efficiently than the cationic dyes. About 83% of erythrosine B (ER), a dianionic dye, was adsorbed by the gel within 2h (Figures 8-9 and Table 2). A similar situation was observed with the other monoanionic dye uranine (UR). In this case, ~82% adsorption of UR was observed within 2h (Figures 8-9 and Table 2). Importantly, adsorption of both these dyes was very rapid in first few minutes. After 5 min, ~57% and ~70% adsorptions were noted for ER and UR, respectively. On contrary, adsorption of crystal violet (CV) was moderate (~28%) and very small adsorption of malachite green (MG, ~4%) was noticed after 2h (Figures 8-9 and Table 2).

The selective removal of anionic dyes over cationic dyes was attributed due to H-bonding interaction between the anionic dyes and sulfonamide moiety. Again, relatively better adsorption of CV over MG was possibly due to extra $-NMe_2$ group in CV that may participate in additional H-bonding with the sulfonamide moiety. However, an increase in anionic site in dye structure had negligible effect during adsorption.

Comparison of normalized UV-vis and FTIR spectra of the dye adsorbed gels (erythrosine B was taken as representative sample) with the pristine gel of **1** undeniably established the adsorption event. A prominent absorption band at 545 nm in the adsorbed gel supported the successful adsorption of ER (Figure 10). This peak was absent in UV-vis spectrum of the pristine gel. The FTIR spectrum of the ER-adsorbed gel showed the presence of characteristic stretching signals of both ER and gelator **1** (Figure S5).

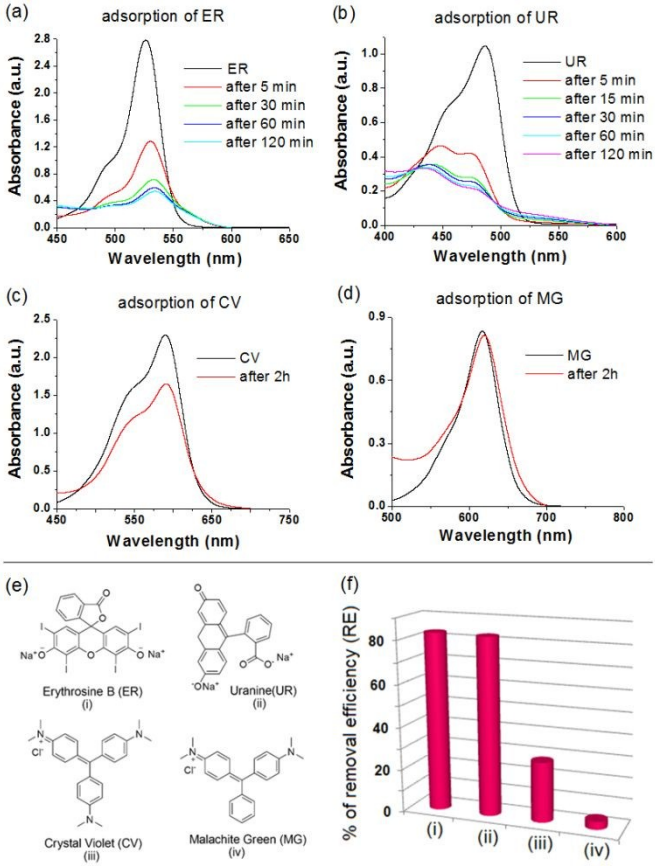

Figure 9. Change in absorbance of (a) Erythrosine B (ER), (b) Uranine (UR), (c) Crystal Violet (CV) and (d) Malachite Green (MG) solutions by the DMSO-H_2O (1:1 v/v) gel of **1 (**25 mg/mL). In all cases, [dye] = 3.5 x 10^{-5} M.

Table 2. Summary of adsorption data of the gel **1** using various dyes.

Dye (λ_{max} in nm)	Initial conc. of the dye (C_i) [mM] (mgL^{-1})	Equilibrium conc. of the dye (C_f) [mM] (mgL^{-1})	Quantity of the adsorbed dye (mg per gram of the gelator)
Crystal Violet (CV) (590)	3.5 x 10^{-2} (14.3)	2.5 x 10^{-4} (10.3)	480
Malachite Green (MG) (615)	3.5 x 10^{-2} (12.8)	3.4 x 10^{-4} (12.3)	60
Uranine (UR) (485)	3.5 x 10^{-2} (12.4)	0.6 x 10^{-4} (2.2)	1224
Erythrosine B (ER) (525)	3.5 x 10^{-2} (29.3)	0.6 x 10^{-4} (4.9)	2928

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Finally, to facilitate the practical utility of gel **1** in dye removal and water purification, a gel column was set up by filling a plastic syringe with the gel, shown in Figure 11. Aqueous solution of ER was then passed through it. Interestingly, one time removal efficiency of the **1**-gel column showed ~87% adsorption of ER and the resulting solution appeared to be light in color. The efficiency of the gelator in adsorption was significantly increased with gelator concentration. When a similar experiment was conducted by preapring the gel column with a higher amount of gelator, one-time dye removal efficiency reached upto ~95% (Figure S6).

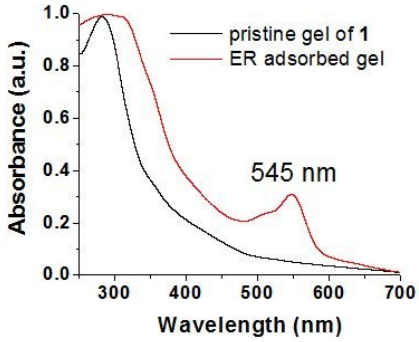

Figure 10. Comparision of normalized UV-vis spectra of DMSO-H_2O (1:1, v/v) gel of **1** before and after adsorption of Erythrosine B (ER).

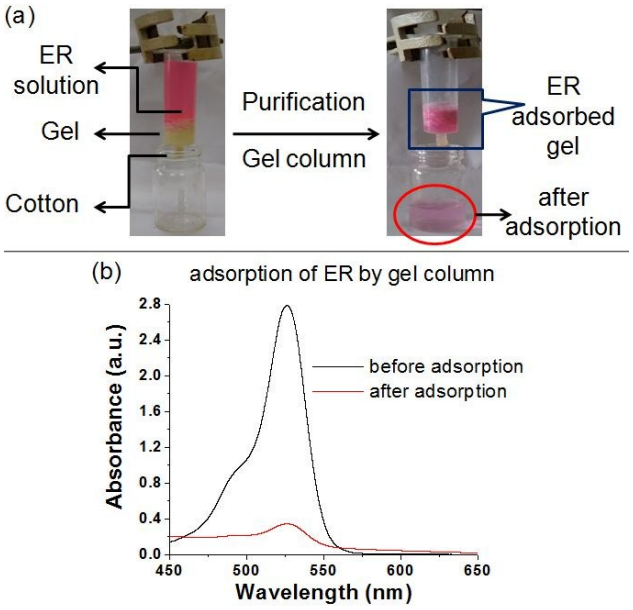

Figure 11. (a) Removal of Erythrosine B (ER) from its aqueous solution using gel column and (b) change in absorbance of Erythrosine B (ER) solution during purification using the gel column [for the gel column [**1**] = 25 mg/mL and [ER] = 3.5 x 10^{-5} M].

These observations established the gelator **1** as an excellent water purifing agent for toxic anionic dyes. Specific removal of anionic dyes with high efficiency in short response time makes it unique in comparision to other reported supramolecular gels which usually take several hours even a day to achieve a reasonable dye removal efficiency.[4f,7a,8] A comparative view, in this regard, is highlighted in Table S4.

Conclusions

In conclusion, we have designed and synthesized a simple cholesterol coupled sulfonyl hydrazone funtionalised LMWG **1** that acts as a sensor both in solution and gel states for detection of the basic anions, such as CN^- and F^-. DMSO-H_2O gel of **1** displays sharp and selective interaction toward CN^- and F^- ions causing gel-to-sol phase transition. In the presence of CN^- the gel state of **1** undergoes fast conversion to sol compared to F^-. Moreover, in solution, a high ratiometric change in absorption was another distinctive feature for selective detection of CN^- over F^-.

Gelator **1** forms a stable and thermoreversible gel from DMSO-H_2O as confirmed by rheological studies. Intermolecular H-bonding involving the sulfonamide moieties and the hydrophobic interaction exerted by the cholesterol units are the possible driving forces, responsible for gelation. The morphology of the gel reveals tiny rod-like fibrillar structure. The DMSO-H_2O gel of **1** has been explored in dye adsorption. The gel exhibits excellent efficiency towards adsorption and removal of the anionic dyes, such as erythrosine B and uranine, from water. Finally, demonstration of adsorption of erythrosine B by a gel column corroborates its high one-time removal efficiency. This establishes the potential and promising real-life application of gelator **1** in water purification.

Experimental

Materials and methods

All the chemicals and reagents were purchased from Spectrochem, India. Tetrabutylammonium salts of the anions were purchased from Sigma-Aldrich. Solvents used in the synthesis were purified, dried and distilled before use. Solvents used in NMR experiments were obtained from Aldrich. ^1H and ^{13}C NMR spectra were recorded using Bruker 400 MHz instrument using TMS as internal standard. FTIR measurements of the compounds were carried out using Perkin-Elmer L120-00A spectrometer (ν_{max} in cm^{-1}) using KBr pellet. UV-vis studies were performed using Shimadzu UV-2450 spectrophotometer.

Synthesis

Compound 1:

Compounds **3** (1.0 g, 1.82 mmol) and **4** (0.68 g, 3.64 mmol) were taken in 20 ml of dry benzene and refluxed for 24h. Progression of the reaction was monitored by checking TLC. After completion of the reaction, benzene was evaporated and the reaction mixture was repeatedly washed with MeOH to have the pure compound **1** in appreciable yield (1.12 g, yield 86%, mp 134 ^oC). ^1H NMR (400 MHz, $CDCl_3$): δ 8.59 (s, 1H), 7.77 (d, J = 8 Hz, 2H), 7.63 (s, 1H), 7.44 (d, J = 8 Hz, 2H), 7.23 (d, J = 8 Hz, 2H), 6.79 (d, J = 8 Hz, 2H), 5.31 (s, 1H), 4.72-4.68 (m, 1H), 4.53 (s, 2H), 2.33 (s, 3H), 2.27–0.68 (43H, cholesteryl protons); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 159.5, 147.7, 144.1, 139.1, 135.3, 129.6, 128.9, 127.9, 126.9, 123.1, 114.7, 75.4, 65.3, 56.6, 56.1, 49.9, 42.3, 39.6, 39.5, 37.9, 36.8, 36.5, 36.1,

35.8, 31.89, 31.82, 28.2, 28.0, 27.6, 24.2, 23.8, 22.8, 22.5, 21.6, 21.0, 19.3, 18.7, 11.8; FTIR (KBr, cm^{-1}): 3445, 3214, 2949, 1766, 1608, 1440, 1363, 1213, 1163; HRMS (TOF MS ES+): calcd. 717.4301 $(M+H)^+$, found 717.4385 $(M+H)^+$; calcd. 739.4121 $(M+Na)^+$, found 739.4122 $(M+Na)^+$.

General procedure for gelation test

The required amount of compound **1** was dissolved in desired solvent (1 mL) by slight warming and then cooled to room temperature to form a gel. For solvent mixtures, compound **1** was first dissolved in a solvent and then the co-solvent was added as per requirement. The gel was tested *via* the usual inversion of vial method. The gel-to-sol transition temperature (T_{gel}) was measured by dropping ball method. Sample of gel for SEM imaging was dried under vacuum and then coated with a thin layer of gold metal.

General procedures for UV-vis titrations

Stock solution of the compound **1** ($c = 2.50 \times 10^{-5}$ M) was prepared in DMSO-H_2O (1:1 v/v). Stock solutions of anions ($c = 1.0 \times 10^{-3}$ M) were prepared in DMSO. Then 2 mL solution of the compound was taken in the cuvette and different amounts of various anions were sequentially added to it. Upon addition of anions, change in absorbance of the compound was recorded.

Binding constant determination[12]

Benesi-Hildebrand plot was adopted to determine the binding constant value using the expression: $A_0/(A\text{-}A_0) = [\varepsilon_M/(\varepsilon_M - \varepsilon_C)](K_a^{-1}C_g^{-1} + 1)$, where ε_M and ε_C represent molar extinction coefficients for the compound **1** and the complex, respectively, at a selected wavelength, A_0 denotes the absorbance of free compound **1** at that specific wavelength and C_g is the concentration of the anion. The measured absorbance $A_0/(A\text{-}A_0)$ as a function of the inverse of the anion concentration fits a linear relationship, indicating 1:1 stoichiometry of the compound **1**-anion complex. The ratio of the intercept to slope was used to determine the binding constant K_a.

Calculation of detection limit[13]

Detection limit was calculated by using the UV-vis titration data. The absorbance of **1** was measured 5 times, and the standard deviation of blank measurement was achieved. To have the slope, absorbance values were plotted against the concentrations of anion. The detection limits were calculated using the equation: Detection limit = 3σ/k, where σ is the standard deviation of blank measurement, and k is the slope.

Dye adsorption experiment[4f]

For this experiment, gel of **1** [25 mg/ml] was prepared in DMSO-H_2O (1:1 v/v). Dye solutions were prepared in the concentration of c = 3.5 x 10^{-5} M in pure water. Then an amount of 3 ml of different dye solutions was separately added to the gel. Adsorption of dyes was monitored by UV-vis spectroscopy. The dye adosrption efficiency of the gel was determined by comparing the absorption spectral changes of respective dye solutions, recorded before and after the experiment. The final concentration of the dye in solution was calculated according to the Beer-Lambert law (A = εcl, A is the absorbance of the dye at a certain absorption wavelength in solution, ε is the molar extinction coefficient and l is the path length of the incident light) which ultimately determined the removal efficiency of the dye *via* the equation as: $RE = (C_i - C_f)/C_i$, in which C_i represents the initial concentration of the dye in solution, C_f is the final concentration of dye in the presence of adsorbing gel.

For the gel column, gel of **1** (50 mg) was prepared in 2 mL DMSO-H_2O (1:2, v/v) in the syringe. Then aqueous solution of ER solution (5 mL, c = 3.5 x 10^{-5} M) was passed through it. The removal efficiency (RE) of ER from its aqueous solution (2 mL) was estimated according to the procedure as described above.

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GRAPHICAL ABSTRACT

Sulfonyl Hydrazone Cholesterol Conjugate: Gelation, Anion Interaction with Application in Dye Adsorption

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- Cholesterol appended sulfonyl-hydrazone derivative **1** has been designed and synthesized as supramolecular gelator for anionic sensing and dye adsorption. Gelator **1** forms strong gel from DMSO-H_2O and the morphology of xerogel shows tiny rod-like fibrous network. The gel of **1** shows selective response toward CN^- and F^- ions causing gel-to-sol transformation. The gel of **1** acts as efficient matrix for adsorption and removal of anionic dyes such as erythrosine B and uranine from water.