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PAPER

Cholesterol appended pyridinium ureas: a case of gel making and breaking for selective visual readout of F^-†

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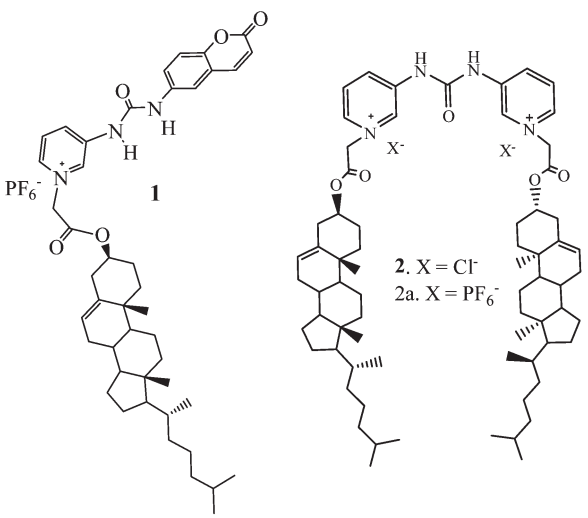
Cholesterol appended pyridinium ureas **1** and **2** have been designed and synthesized. The unsymmetrical urea-based chemosensor **1** fluorimetrically distinguishes F^- from the other anions examined in both CH_3CN and DMSO with appreciable binding constant values. The pyridinium – based symmetrical compound **2** acts as a low molecular weight gelator (LMWG) in $CHCl_3$ and is capable of detecting F^- visually by breaking the gel. On the contrary, the chemosensor **1** in DMSO in the presence of tetrabutylammonium fluoride undergoes a change from sol to gel state that produces an unambiguous visual readout of F^-.

Introduction

Supramolecular structures, composed of low molecular weight organic compounds, are of much interest due to their unique features and wide range of potential applications.[1] In this context, low molecular weight organic compounds which are capable of forming supramolecular gels with various organic solvents draw attention in the visual detection of some ionic species.[2] It is well documented that supramolecular gels are dimensionally controlled assemblies comprising low-molecular-weight molecules held together by noncovalent interactions, such as hydrogen bonding, metal coordination, van der Waals interaction, and π–π stacking.[2,3] Stimuli responsive gels that are highly desirable for the development of sensor devices are of considerable attention in recent time. Many research groups in this domain have shown interest in the construction of anion-responsive supramolecular gels.[4,3a] Among these, fluoride-sensing gels have received a great deal of attention[4c,5] because fluoride is involved in preventing dental caries and in medical treatment for osteoporosis.[6] Fluoride and proton are reported to elicit gel to sol transition and fluorescence emission after interaction with bisurea-functionalized naphthalene organogelators.[5f] In addition, organogelators based on urea,[5k] oxalamide,[5m] or hydrazide[5n] motifs are found to induce gel to sol transitions and optical changes[5o] after the addition of fluoride anions. This happens due to the interaction of fluoride with the amide NHs of these amide-containing organogelators for which the effective hydrogen-bonding interactions between the gelators are disturbed. However, because amidic NHs in the organogelators could also interact with other anions, the initiation of gel to sol transitions and optical changes would not necessarily be selective to fluoride. Under these circumstances, the design of receptor that is capable of detecting and sensing fluoride selectively through gel making and breaking processes is of immense interest. In regard to this, during our on-going research on anion recognition,[7] we report here two supramolecular structures **1** and **2** that are cholesterol appended pyridinium ureas. Both of them recognize F^- selectively either by forming or breaking gels in organic solvents.



Interestingly, while the structure **1** forms gel in DMSO in the presence of tetrabutylammonium fluoride, chloroform gel of symmetric structure **2** shows a sharp conversion to the sol state

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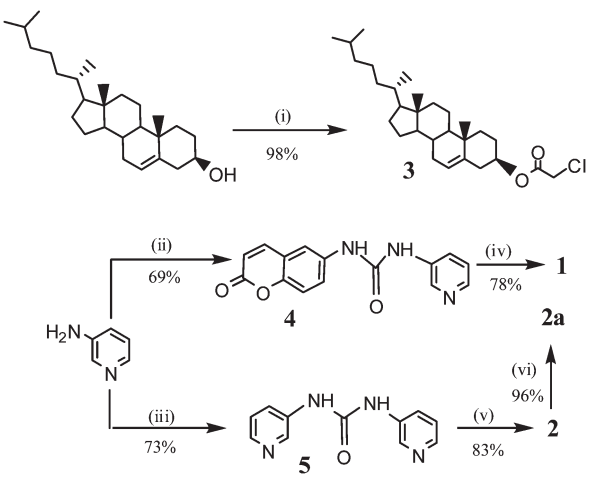
†Electronic supplementary information (ESI) available: Figures showing the change in fluorescence and UV-vis titrations of receptor **1** with various anions in different solvents, binding constant curves, Job plot, photograph of gel of **1**, IR spectra, ^1H, ^{13}C NMR and mass spectra and other selected spectra. See DOI: 10.1039/c2ob26631h

in the presence of the same and thus produces an unambiguous visual readout of F^- over a series of other anions studied.

Results and discussion

Compounds **1** and **2** were synthesized according to Scheme 1. Initially, cholesterol was converted to the chloride **3** which on treatment with the pyridine-based unsymmetrical urea **4** and symmetrical urea **5** gave the chloride salts. The unsymmetrical urea **4** of 3-aminopyridine was obtained from its reaction with triphosgene followed by the addition of 6-aminocoumarin in CH_2Cl_2. The symmetrical urea **5** was accomplished from the reaction of 3-aminopyridine in the presence of triphosgene in CH_2Cl_2. However, the compounds **4** and **5** were refluxed individually with the cholesterol-based chloride **3** in dry CH_3CN to afford their respective mono and dichloride salts. Anion exchange reaction of the chloride salt of **1** using NH_4PF_6 gave the desired compound **1** in appreciable yield. A similar anion exchange in **2** produced the salt **2a**. All the compounds were characterized by ^1H NMR, ^{13}C NMR, FTIR and mass analysis.



Scheme 1 (i) Chloroacetyl chloride, pyridine, dry CH_2Cl_2, rt, 10 h; (ii) 6-aminocoumarin, triphosgene, Et_3N, dry CH_2Cl_2, rt, 24 h; (iii) triphosgene, Et_3N, dry CH_2Cl_2, rt, 24 h; (iv) a. **3**, dry CH_3CN, reflux, 3 days, b. aq. NH_4PF_6, DMF–CH_3OH, rt, $\frac{1}{2}$ h; (v) **3**, dry CH_3CN, reflux, 3 days; (vi) aq. NH_4PF_6, DMF–CH_3OH, rt, $\frac{1}{2}$ h.

Complexation studies

The underlying theme for the design of molecules **1** and **2** in the gelation study is as follows: (1) cholesterol unit can aggregate in solution through van der Waals and hydrophobic interaction; (2) the pyridinium urea motif has the propensity to complex anions involving hydrogen bonds and charge–charge interactions. To investigate the relevance of the design in anion recognition through gelation, complexation properties of **1** and **2** towards a series of anions were evaluated.

Due to the presence of coumarin probe in **1**, UV-vis and fluorescence titration experiments were performed in addition to its gel study to determine its sensing behavior in solution. Compound **1** ($c = 6.32 \times 10^{-5}$ M) showed emission at 430 nm when excited at 340 nm in CH_3CN. Upon titration with F^-, the emission intensity at 450 nm decreased with a blue shift of ~20 nm (Fig. 1). Such spectral change was also seen while the titration of **1** was performed with $H_2PO_4^-$, AcO^-. In the case of $H_2PO_4^-$, fluorescence intensity of **1** decreased upon the addition of 2 equiv. amounts of guest. Further addition of $H_2PO_4^-$ caused an increase in emission which was assumed to be due to decomplexation (See ESI†).[8] Fig. 2 represents the change in fluorescence ratio of **1** at 430 nm, upon addition of 10 equiv. amounts of individual anion. As can be seen from Fig. 2, the receptor shows less selectivity in the identification of F^-. In the profile, the other anions such as AcO^- and $H_2PO_4^-$ also exhibit a similar perturbation in emission of **1** as noticed with F^- ions.

In the interaction, the 1 : 1 stoichiometry of **1** with F^- was confirmed by Job plot[9] (Fig. 3) and the binding constant (K_a)[10] was determined to be 2.07×10^3 M^{-1}. This moderate interaction of F^- with the binding site was also realized in the ground state.

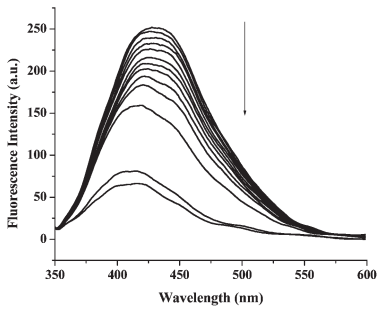


Fig. 1 Change in emission of **1** ($c = 6.32 \times 10^{-5}$ M) with an increase in concentration of F^- ($\lambda_{exc} = 330$ nm) in CH_3CN.

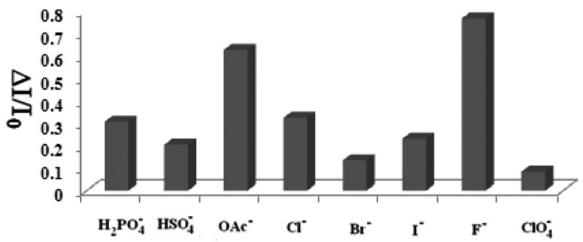


Fig. 2 Change in fluorescence ratio ($I_0 - I/I_0$) of **1** ($c = 6.32 \times 10^{-5}$ M) upon addition of 10 equiv. amounts of a particular anion in CH_3CN.

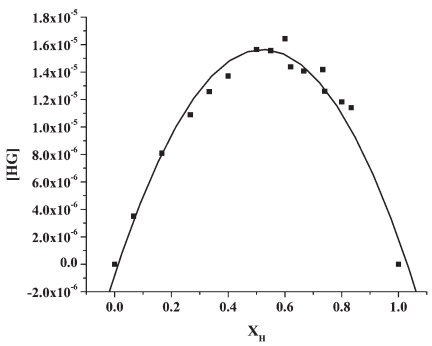


Fig. 3 Fluorescence Job plot for **1** with TBAF in CH_3CN ([H] = [G] = 5.56×10^{-5} M).

In the UV-vis titration of **1** with F^- (Fig. 4) while the absorbance at 271 nm decreased, the absorbance at 331 nm increased upon gradual addition of F^- to the solution of **1** in CH_3CN and a well defined ratiometric behavior was noticed. This indicated the formation of a new species in solution which may remain in equilibrium with the free receptor **1**.

However, in order to ascertain the selectivity in the recognition process, the polarity of the solvent was changed. Interestingly, in DMSO, chemosensor **1** showed greater change in emission upon addition of F^- ions (ESI†). In this regard, Fig. 5 corroborates this feature at the emission 430 nm in the presence

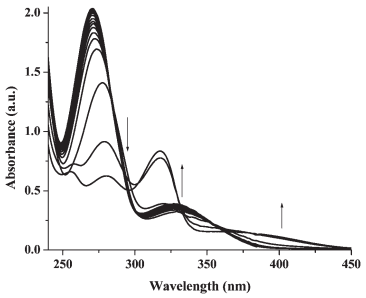


Fig. 4 Change in absorption of **1** ($c = 6.32 \times 10^{-5}$ M) in CH_3CN with increase in concentration of F^-.

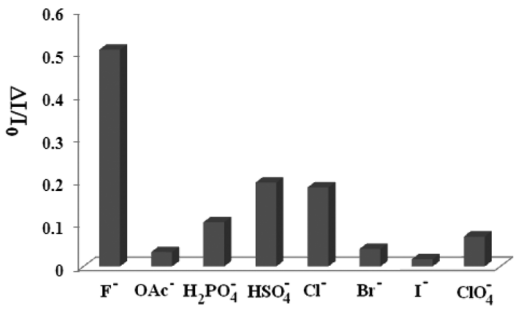


Fig. 5 Change in fluorescence ratio ($I_0 - I/I_0$) of receptor **1** ($c = 3.75 \times 10^{-5}$ M) upon addition of 10 equiv. amounts of a particular anion in DMSO.

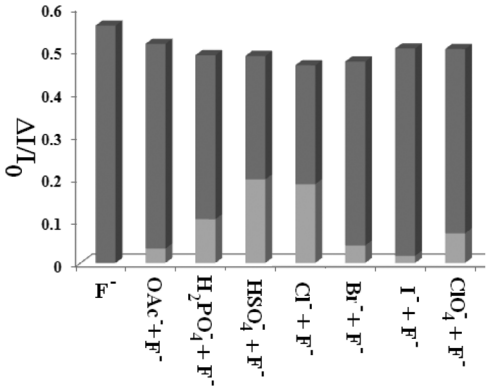


Fig. 6 Change in fluorescence ratio of **1** ($c = 6.35 \times 10^{-5}$ M) upon addition of 15 equiv. amounts of F^- in the presence of other anions in DMSO.

of 10 equiv. amounts of each anion in DMSO. Similar to the case in CH_3CN, the receptor **1** binds F^- with the binding constant value[10] of 3.21×10^3 M^{-1} involving a 1 : 1 stoichiometry[9] (ESI†).

The selectivity in the binding of F^- in DMSO was ascertained by observing the change in fluorescence in the presence and absence of other anions. Fig. 6 shows the profile where it is observed that the other anions negligibly interfered in the binding of the F^- anion.

In addition to this fluorometric behavior in solution, the receptor **1** exhibited some new findings in DMSO. While the receptor **1** was taken in $\sim 10^{-3}$ M concentration range in DMSO, the addition of tetrabutylammonium fluoride ($c = 5.0 \times 10^{-3}$ M) brought about a marked color change. The almost colorless solution of **1** turned into intense yellow color. In the presence of AcO^- and $H_2PO_4^-$ a faint yellow color was noticed (Fig. 7).

We believe that F^- being more basic initially interacts with the pyridinium urea site of **1** through hydrogen bonding and then deprotonates the more acidic urea protons in the presence of its excess concentration in solution (Fig. 8). In the deprotonated species the delocalization of charge resulted in color change in solution. This is evident from the observation noted when tetrabutylammonium hydroxide was added to the solution of **1** (Fig. 7). The hydrogen bonding and the deprotonation phenomena were established by ^1H NMR study. Fig. 9, in this context, describes the change in ^1H NMR of **1** in the presence and absence of equiv. amount of tetrabutylammonium fluoride (TBAF) in d_6-DMSO. Due to the deprotonation of urea protons (a and b), the signals of both the pyridinium and coumarin motifs underwent little upfield shift.

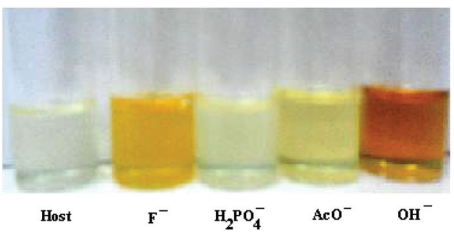


Fig. 7 Photographs of colour changes of **1** ($c = 1.0 \times 10^{-3}$ M) upon addition of F^-, $H_2PO_4^-$, AcO^- and OH^- ($c = 5.0 \times 10^{-3}$ M) as their tetrabutylammonium salts in DMSO.

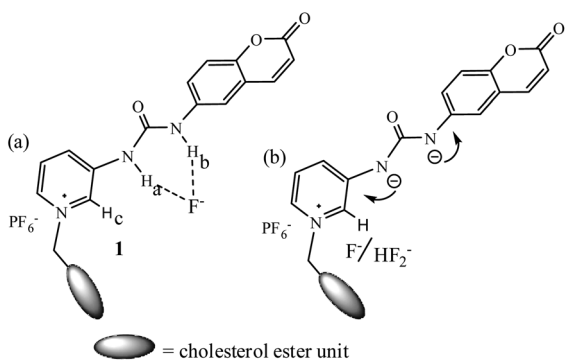


Fig. 8 Suggested scheme for (a) hydrogen bonding and (b) deprotonation in **1** in the presence of F^- ions.

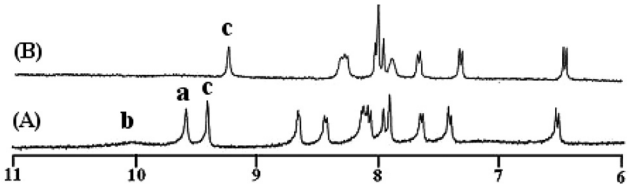


Fig. 9 Partial ^{1}H NMR (400 MHz, d_6-DMSO) of (A) **1** (c = 4.8 × 10^{-3} M) and (B) in the presence of equiv. amount of TBAF (see Fig. 8 for labelling of protons).

Table 1 Results of gelation test for **1**

Solvent	Result[a]
DMSO	G (3.0)
DMF	S
Methanol	S
Chloroform	S
Ethanol	S
Acetonitrile	S
n-Hexane	I
Diethyl ether	I
Propanol	S

[a] S = solution; G = transparent gel (mgc = minimum gelatination concentration in mg mL^{-1}); I = insoluble.

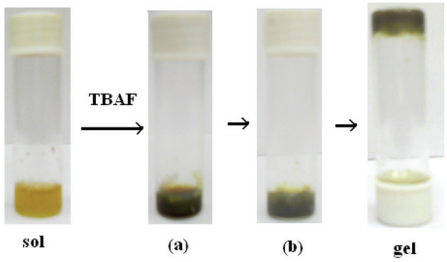


Fig. 10 The changes in the DMSO solution of **1** (10 mg/0.5 mL) after addition of TBAF (2 equiv). Brownish solution slowly gelates after (a) 5 min and (b) 10 min.

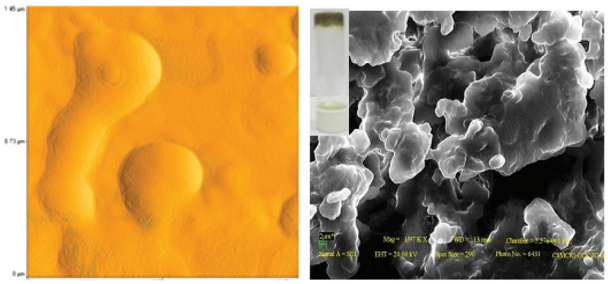


Fig. 11 (a) AFM image of xerogel obtained from **1** and TBAF (scale bar: = 1.45 μm); (b) SEM image of xerogel from DMSO gel of **1** with fluoride (scale bar: = 2 μm).

Beside the colorimetric response, compound **1** in ~10^{-3} M concentration formed gel in the presence of 5 equiv. amounts of TBAF. Other anions taken in the study were non-responding in this new findings. The gelation propensity of **1** was examined in a wide range of solvents and solvent mixtures (Table 1). Only the 'instant metastable gel' from the DMSO in the NMR tube was observed when 5 equiv. amounts of fluoride was added (ESI†). The gelation property of the compound **1** was checked in various solvents as well as solvent mixtures, and the results are given in Table 1.

In regard to this gelation study, it is mentionable that compound **1** in high concentration in DMSO (10 mg/0.5 mL) showed impressive gelation behavior upon addition of TBAF. Addition of 2 equiv. amounts of F^- to the brownish solution of **1** in DMSO induced gelation within 5 min. After 10 min, a complete gel was noticed with a change in color (brown to greenish brown; see Fig. 10). It is important to note that anions usually disrupt the supramolecular gels although there are few examples known where the presence of anions stimulates gel formation and allows their naked eye detection.[4b,7h,11] In our opinion, in the present study, the sol-to-gel transition induced by F^- occurs as a result of the effective aggregation of gelators. The hydrogen bonding properties of urea as well as pyridinium motifs set a complex network in DMSO in the presence of F^-. Excess concentration of F^- carries deprotonation of the urea protons and the resulting dianionic species as shown in Fig. 8 possibly forms intermolecular contacts with the pyridinium part and entrapped HF_2^- ion *via* hydrogen bond formation and charge–charge interaction and leads to the formation of a network in solution. Formation of this network is further encouraged by large hydrophobic surface of the cholesterol part. During interaction the formation of bifluoride (HF_2^-) was supported by the appearance of broad signal at 16 ppm[12] in ^{1}H NMR (ESI†). The morphology of the gel was investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM) as shown in Fig. 11. The SEM image reveals a microstructure of the xerogel of **1** with F^- in DMSO. Three-dimensional network is found to contain globules with some imprecise cavities. At 68 °C, gel was converted to the sol state with deep green color. It is important to be mentioned here that the chloride salt of **1** did not form any gel with the addition of TBAF in DMSO. Instead, a viscous and yellow colored solution containing some precipitates was obtained. This is thought to be due to the interference of Cl^- ion in hydrogen bonding.

As we move from compound **1** to **2**, a different behavior towards gelation is noted. Interestingly, when compound **2** is dissolved in $CHCl_3$ on warming and then kept at room temperature, a nice thick yellow colored gel is formed. However, this gelation property was not at all observed while the chloride anions in **2** are exchanged with PF_6^- ions to have the compound **2a**. It is believed that Cl^- ions in **2** plays a key role in establishing a hydrogen bonded network in solution, especially in $CHCl_3$. The *syn* and *anti* orientations of the urea motif may assemble the molecules through hydrogen bonding (see Fig. 12). The pyridinium ring protons such as H_o, H_o' and H_p also can take part in hydrogen bonding with the interstitial Cl^- ions, urea and ester carbonyl oxygens. Thus this arrangement may establish a complex network in less polar $CHCl_3$ which is substantially stabilized by the cholesterol units with large hydrophobic surfaces. We further believe that replacement of Cl^- by the larger PF_6^- ion disrupts the assemblies as shown in Fig. 12 by

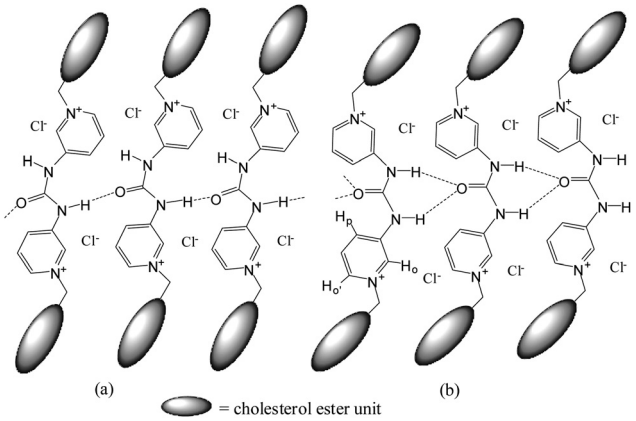


Fig. 12 Suggested arrangements of molecules of **2** in establishing the hydrogen bonded network involving (a) the *anti* and (b) *syn*-orientations of urea motif.

Table 2 Results of gelation test for **2**

Solvent	Result[a]
DMSO	S
DMF	S
Methanol	S
Chloroform	G (7.5)
Ethanol	S
Acetonitrile	S
n-Hexane	I
Diethyl ether	I
Propanol	S

[a] S = solution; G = transparent gel (mgc = minimum gelatination concentration in mg mL^{-1}); I = insoluble.

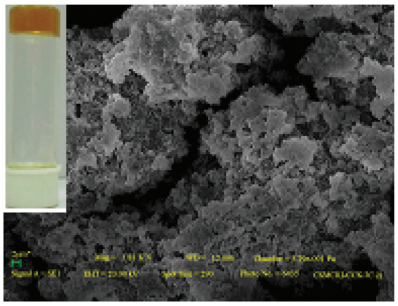


Fig. 13 SEM image of xerogel from $CHCl_3$ gel of **2** (scale bar = 2 μm).

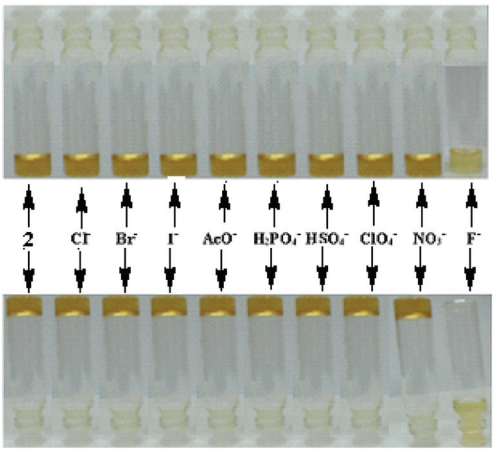


Fig. 14 Photographs of chloroform gels of **2** (c = 6.58 × 10^{-3} M) upon addition of 10 equiv. amounts of each anion.

destroying a number of intermolecular hydrogen bonds. This was realized from FTIR studies of compounds **2** and **2a**. While NH stretching in **2** appeared at 3418 cm^{-1} as a broad signal due to hydrogen bonding effects, compound **2a** showed stretching at 3637 cm^{-1} for free NH (ESI†). In ^{1}H NMR the signals for urea and pyridinium ring protons in **2** appeared in the more downfield region compared to **2a** (ESI†). A similar observation was noted in **1** (ESI†). Thus both FTIR and ^{1}H NMR studies reveal that compound **2** and chloride salt of **1** are different from their hexafluorophosphate analogues with respect to the hydrogen bonding characteristics. Such different hydrogen bonding behavior of Cl^- and PF_6^- is well established.[13] However, the gelation propensity of **2** in other dielectric media was also examined. The results are summarized in Table 2.

The T_{gel} at which the gel state of **2** was transformed into the sol state was recorded as 67 °C and the morphology of the gel was realized from SEM image. As can be seen from Fig. 13, compound **2** is self-assembled with a three-dimensional network composed of some aggregates. FTIR study of the amorphous **2** and its gel from $CHCl_3$ reveals that there is a shift of the urea carbonyl stretching to a lower wave number ($\nu_{amorphous} - \nu_{gel}$ = 48 cm^{-1}). This shift provides evidence for the existence of intermolecular hydrogen bonds of **2** involving the urea part in the Gel (ESI†). A chloroform gel of **2** formed a homogeneous solution on addition of F^- (TBAF) in excess (10 equiv) (Fig. 14). Addition of less than 10 equiv. of F^- caused partial disintegration of the gel. However, completion of gel to sol transition occurred within 10 min. at room temperature. The disruption of the gel structure took place only in the presence of fluoride anions, rapid gel-to-sol transition were not observed in the presence of other anions examined (Fig. 14). This is attributed to the more basic character of F^- due to which deprotonation of urea protons led to the disruption of the hydrogen bonded network in solution. The F^- induced broken gel reappeared in the presence of $BF_3{\cdot}OEt_2$ (Fig. 15). Due to the reaction of BF_3 with F^-, the influence of F^- on the gel is nullified. However, further addition of F^- transformed the gel into the sol state. This cycle could be repeated at least three times.

The interaction of F^- with **2** was understood by investigating the UV-vis titration in $CHCl_3$ in the concentration range of ~10^{-5} M.

It is evident from Fig. 16 that the compound **2** (c = 6.07 × 10^{-5} M) typically shows two absorption peaks at 273 nm and 313 nm which undergo ratiometric change with the formation of three isosbestic points at 326 nm, 297 nm and 277 nm upon titration with F^- in $CHCl_3$. Interaction of **2** with other anions considered in the study was also followed through UV-vis titration. Change in absorbance was minor and irregular in some cases except F^- and Cl^-. The binding constant values for F^- and Cl^-

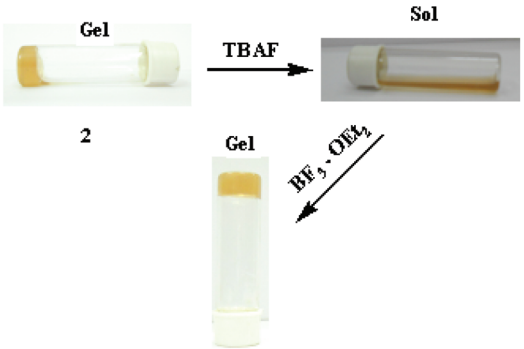


Fig. 15 Photographs for gel–sol and *vice-versa* phase transitions of chloroform gel of **2** in the presence of F^- and $BF_3 \cdot OEt_2$.

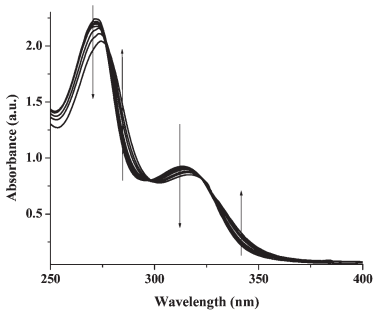


Fig. 16 UV-vis titration spectra of **2** (c = 6.07 × 10^{-5} M) upon addition of 10 equiv. amounts of F^- (c = 1 × 10^{-3} M) in $CHCl_3$.

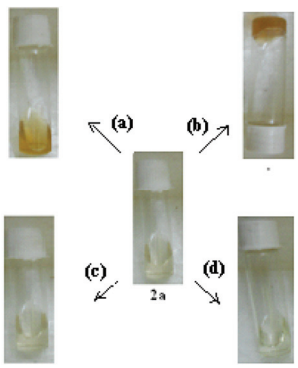


Fig. 17 Photographs showing the phase changes of **2a** (c = 8.76 × 10^{-3} M) in $CHCl_3$ upon addition of 2 equiv. amounts of (a) TBAF, (b) TBACl, (c) TBABr and (d) TBAI (concentration of all halides was 1.6 × 10^{-2} M).

were determined to be 3.14 × 10^3 M^{-1} and 4.20 × 10^4 M^{-1}, respectively. On the other hand, in ^1H NMR either broadening or deprotonation of urea protons was the main hindrance to conduct the titration experiment smoothly for determining the binding constant values for **2** with the anions accurately.

An additional feature was observed while the compound **2** was converted into **2a**. Compound **2a** did not form any gel under the condition as maintained for **2**. But addition of TBACl to the solution of **2a** in $CHCl_3$ induced gel formation. Under this condition, addition of TBAF and TBAI did not induce any gel in the medium. Only TBABr made the solution viscous. Fig. 17 corroborates these features. To our opinion, Cl^- ions enter in the gelation process due to the formation of **2** in solution on exchange of PF_6^- ions and sets up a hydrogen bonded network as shown in Fig. 12. To gain more information about the possibility of gel formation of **2a** with F^- like the case of **1** with F^-, a similar experiment in DMSO was performed. But we failed. Although it is believed that similar phenomena (Fig. 8) may happen, the non appearance of gel of **2a** with F^- in DMSO is presumably due to the structural aspect of **2a**. The presence of two pyridinium sites in **2a** will follow a different hydrogen bonded assembly from that of **1** in solution.

Conclusion

In conclusion, we have shown that the cholesterol appended pyridinium ureas (symmetrical as well as unsymmetrical) exhibit excellent property towards gelation in organic solvent. The sol or gel state of the compounds is the reliable media in selective sensing of F^- in organic solvents. While the compound **1** forms gel in DMSO in the presence of F^-, compound **2** undergoes a change from gel to sol state in $CHCl_3$ in the presence of the same anion. This produces an unambiguous visual readout towards the selective recognition of F^- in organic solvent through the making and breaking of gels. Moreover, in such process the change in colour of the solutions of the compounds shows a convenient way to the selective detection of F^- anion. Compound **2a** in the study is also capable of detecting Cl^- ions in $CHCl_3$ by forming yellowish brown gel. It is further mentionable that unsymmetrical urea-based chemosensor **1** fluorimetrically distinguishes F^- from the other anions examined in both CH_3CN and DMSO with appreciable binding constant values. The extent of selectivity towards F^- ion has been noted to be admirable in DMSO.

Experimental Section

Chloro-acetic acid 17-(1,5-dimethyl-hexyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl ester (3)

To a stirred solution of cholesterol (1 g, 2.59 mmol) in 30 mL dry CH_2Cl_2 was added chloroacetyl chloride (0.31 mL, 3.88 mmol) and pyridine (0.1 mL, 1.3 mmol) under nitrogenous atmosphere. The mixture was allowed to stir for 10 h at room temperature. After completion of reaction, the solvent was evaporated and the crude was extracted with $CHCl_3$ (3 × 50 mL). The organic layer was washed several times with water and separated and dried over Na_2SO_4. Evaporation of the solvent gave white solid compound. Recrystallization from petroleum ether afforded pure product **3** (1.18 g, yield 98%), mp 148 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 5.37 (m, 1H), 4.72 (m, 1H), 4.03 (s, 2H), 2.36 (m, 2H), 2.02–0.85 (m, 38H), 0.67 (s, 3H); FTIR (KBr, cm^{-1}): 2939, 2907, 2821, 1753, 1620, 1195.

1-(2-Oxo-2*H*-chromen-6-yl)-3-pyridin-3-yl-urea (4)

To a stirred solution of triphosgene (0.920 g, 3.10 mmol) in 10 mL dry CH_2Cl_2, 3-aminopyridine (0.292 g, 3.10 mmol)

dissolved in 10 mL CH_2Cl_2 was added dropwise along with Et_3N (0.45 mL, 3.10 mmol). The reaction mixture was allowed to stir for 1 h. Then 6-aminocoumarin (0.5 g, 3.10 mmol), dissolved in 10 mL CH_2Cl_2, was added dropwise from a dropping funnel. The reaction mixture was allowed to stir for further 24 h. After completion of reaction, solvent was evaporated off. The crude mass was extracted with $CHCl_3$ (3 × 30 mL). The organic layer was washed with water and dried over Na_2SO_4. Evaporation of the solvent *in vacuo* gave crude mixture which was chromatographed on a silica gel column using 80% ethyl acetate in petroleum ether as eluent. The desired product **4** was obtained in 68% yield (0.6 g), mp 130 °C. ^{1}H NMR (400 MHz, $CDCl_3$ containing two drops of d_6-DMSO) δ 8.47 (m, 3H), 8.24 (d, 1H, J = 4 Hz), 8.13 (m, 1H), 7.96 (d, 1H, J = 2.40 Hz), 7.73 (d, 1H, J = 8 Hz), 7.37 (s, 1H), 7.33 (dd, 1H, J_1 = 8 Hz, J_2 = 4 Hz), 7.24 (m, 1H), 6.42 (d, 1H, J = 8 Hz); ^{13}C NMR (100 MHz, d_6-DMSO) δ 160.0, 152.6, 148.7, 144.2, 142.8, 139.9, 136.3, 135.8, 125.5, 123.6, 122.7, 118.7, 116.7, 116.5, 116.4; FTIR (KBr, cm^{-1}): 3466, 1720, 1695, 1567, 1552.

1,3-Di-pyridin-3-yl-urea (5)[14]

To a stirred solution of triphosgene (0.92 g, 3.10 mmol) in 5 mL dry CH_2Cl_2, 3-aminopyridine (0.5 g, 5.37 mmol) in 10 mL CH_2Cl_2 along with Et_3N (0.38 mL, 2.68 mmol) was added dropwise from a dropping funnel. The reaction mixture was stirred for 24 h. After completion of reaction, solvent was evaporated off. The crude mass was extracted with $CHCl_3$ (3 × 30 mL). The organic layer was washed with water and dried over Na_2SO_4. Evaporation of the solvent gave crude mass which was purified by column chromatography using silica gel and 80% ethyl acetate in petroleum ether. Compound **5** was isolated in 73% yield (0.42 g), mp 209 °C.

Receptor 1

Compounds **3** (0.49 g, 1.07 mmol) and **4** (0.3 g, 1.07 mmol) were taken in dry CH_3CN (30 mL) and the mixture was refluxed for 3 days. The precipitate appeared was filtered off and washed with hot CH_3CN to have pure chloride salt of **1**. Next the chloride salt of **1** (0.6 g, 0.8 mmol) was dissolved in DMF–MeOH (1 : 1 v/v; 10 mL) and an aqueous solution of NH_4PF_6 (0.262 g, 1.61 mmol) was added under hot condition. After stirring the mixture for 30 min, the precipitate was filtered. Repeated crystallization of the precipitate from diethyl ether afforded pure compound **1** (0.66 g) in 78% yield, mp 186 °C. ^{1}H NMR (400 MHz, d_6-DMSO) δ 10.0 (brs, 1H), 9.57 (s, 1H), 9.39 (s, 1H), 8.65 (d, 1H, J = 8 Hz), 8.42 (d, 1H, J = 8 Hz), 8.07 (m, 2H), 7.89 (s, 1H), 7.63 (d, 1H, J = 8 Hz), 7.40 (d, 1H, J = 8 Hz), 6.51 (d, 1H, J = 8 Hz), 5.66 (s, 2H), 5.37 (s, 1H), 4.62 (m, 1H), 2.37 (m, 2H), 1.95–0.99 (m, 38H), 0.67 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 166.3, 162.5, 152.5, 144.4, 141.2, 140.2, 139.9, 139.5, 135.8 (two carbons unresolved), 134.8, 128.1 (two carbons unresolved), 126.6, 124.1, 122.9 (two carbons unresolved), 76.4, 61.3, 56.5, 56.0, 49.8, 42.3, 39.7, 39.4, 37.9, 36.8, 36.5, 36.1, 35.6, 31.7, 31.1, 28.2, 27.8, 27.6, 24.3, 23.6 (two carbons unresolved), 23.0, 22.8, 21.0, 19.3, 18.9 (one carbon in the aromatic region is missed); FTIR (KBr, cm^{-1}): 3400, 2950, 2868, 1737, 1719, 1543, 1182; HRMS (TOF MS ES$^+$): $C_{44}H_{58}N_3O_5PF_6^+$, (M − PF_6 + 1) requires 708.4371 found 709.3343.

Receptor 2

Compounds **3** (0.454 g, 0.98 mmol) and **5** (0.1 g, 0.45 mmol) were taken in dry CH_3CN (30 mL) and the mixture was refluxed for 3 days. Precipitate appeared was filtered off and washed with hot CH_3CN to afford the pure compound **2** (0.66 g) in 83% yield.

^{1}H NMR (400 MHz, d_6-DMSO) δ 10.9 (brs, 2H), 9.37 (s, 2H), 8.72 (d, 2H, J = 8 Hz), 8.51 (d, 2H, J = 8 Hz), 8.17 (t, 2H, J = 8 Hz), 5.75–5.69 (m, 4H), 5.63 (m, 2H), 4.63 (m, 2H), 2.35 (m, 4H), 1.98–0.81 (m, 76H), 0.83 (s, 6H); FTIR (KBr, cm^{-1}): 3435, 1745, 1640, 1594; Mass (ES$^+$): 1067.4 (M − 2Cl$^-$ − 1)$^+$.

Receptor 2a

The dichloride salt **2** (0.5 g, 0.438 mmol) was dissolved in DMF–MeOH (1 : 1 v/v; 10 mL) and an aqueous solution of NH_4PF_6 (0.187 g, 1.08 mmol) was added under hot condition. After stirring the mixture for 30 min, the precipitate was filtered. Repeated crystallization of the precipitate from diethyl ether afforded pure compound **2a** (0.57 g) in 96% yield, mp 232 °C. ^{1}H NMR (400 MHz, d_6-DMSO) δ 11.04 (brs, 2H), 9.37 (s, 2H), 8.71 (d, 2H, J = 8 Hz), 8.51 (d, 2H, J = 8 Hz), 8.16 (t, 2H, J = 8 Hz), 5.68 (m, 4H), 5.36 (brs, 2H), 4.61 (m, 2H), 2.35 (m, 4H), 1.95–0.85 (m, 76H), 0.83 (s, 6H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 166.2, 162.7, 141.2, 139.4, 135.8, 128.3, 126.5, 124.1, 122.9, 76.4, 61.3, 56.5, 56.1, 49.8, 42.3, 39.7, 39.3, 37.9, 36.8, 36.5, 36.2, 35.7, 31.7, 31.2, 28.2, 27.8, 27.6, 24.3, 23.8 (two carbons unresolved), 23.0, 22.8, 21.0, 19.3, 18.9; FTIR (KBr, cm^{-1}): 3395, 1747, 1653, 1595, 1563; Mass (TOF MS ES$^+$): 1214.32 (M − PF_6^- + 1)$^+$, 1068.29 (M − 2PF_6^-)$^+$.

General procedure of fluorescence titration. Stock solutions of the hosts and guests were prepared in CH_3CN or DMSO and 2 ml of the host solution was taken in the cuvette. The solution was irradiated at the excitation wavelength maintaining the excitation and emission slits. Upon addition of guest anions, the change in fluorescence emission of the host was noticed. The corresponding emission values during titration were noted and used for the determination of binding constant values.

General procedure of UV-vis titration. The receptors were dissolved in dry UV grade CH_3CN or DMSO and taken in the cuvette. Then anions dissolved in dry CH_3CN or DMSO, were individually added in different amounts to the receptor solution. The corresponding absorbance values during titration were noted.

Method for job plot. The stoichiometry was determined by the continuous variation method. In this method, solutions of host and guests of equal concentrations were prepared in dry CH_3CN or DMSO. Then host and guest solutions were mixed in different proportions maintaining a total volume of 3 mL of the mixture. The related compositions for host–guest (v/v) were 3 : 0, 2.8 : 0.2, 2.5 : 0.5, 2.2 : 0.8, 2 : 1, 1.8 : 1.2, 1.5 : 1.5, 1 : 2,

0.8 : 2.2, 0.5 : 2.5, 0.2 : 2.8. All the prepared solutions were kept for 1 h with occasional shaking at room temperature. Then emission and absorbance of the solutions of different compositions was recorded. The concentration of the complex *i.e.*, [HG] was calculated using the equation [HG] = $\Delta I/I_0$ × [H] where $\Delta I/I_0$ indicates the relative emission intensity and [H] corresponds the concentration of pure host. Mole fraction of the host (X_H) was plotted against concentration of the complex [HG]. In the plot, the mole fraction of the host at which the concentration of the host-guest complex concentration [HG] is maximum, gives the stoichiometry of the complex.

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