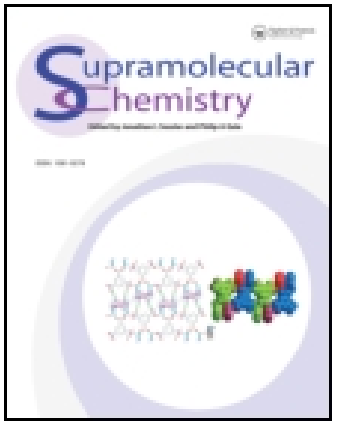

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Fluoride-responsive hydrogel of cholesterol appended pyridinium urea and its metal detecting ability and semi-conducting behaviour

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Fluoride-responsive hydrogel of cholesterol appended pyridinium urea and its metal detecting ability and semi-conducting behaviour

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Cholesterol appended pyridinium urea **1** acts as low molecular weight gelator in DMSO:H_2O (1:1, v/v) showing distinct colour change in the presence of aqueous solution of KF as well as tetrabutylammonium fluoride and recognises F^- specifically. In addition, this hydrogel is noted to detect aqueous solution of Cu^{2+} and Pb^{2+} ions over a series of other metal ions and exhibits good semi-conducting property.

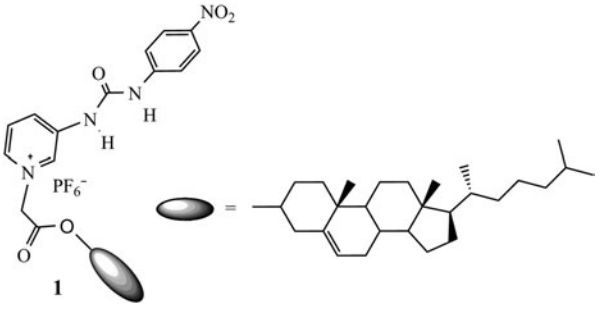
Keywords: fluoride detection; cholesterol-based gel; pyridinium motif; semi-conducting gel; metal ion detector

Introduction

The design and synthesis of small organic molecules capable of forming gel in aqueous organic solvent is a rapidly expanding area of research, in particular due to their possible practical applications in tissue engineering (*1*), controlled drug release (*2*), medical implants (*2*, *3*) and environmental science (*4*). Responsive hydrogels based on different stimuli, such as temperature, light, magnetic field and chemical entities are widely explored by various research groups (*5*). Among the different stimuli, anion response is of increasing attention because anion is linked to vital processes in biology, chemistry and environment (*6*). Therefore, searching of simple and easy-to-make designed molecules that undergo gel-to-sol or sol-to-gel transition in the presence of selective anion due to the creditable role of weak forces, such as hydrogen bonding, π-stacking, hydrophobic–hydrophobic interactions and so on, has been a major focus in supramolecular chemistry (*7*).

Of the different anions, fluoride recognition receives great significance because of its important roles in environmental monitoring and biomedicine, which is associated with organism health including dental, skeleton, gastric and kidneys (*8*). Fluoride is reported to elicit gel-to-sol transition after interaction. There are various reports (*9*) in this regard. In contrast, gelation of small organic molecules in the presence of fluoride is less explored in the literature (*10*). Moreover, although there are reports, many of fluoride-responsive gels operate in organic solvents rather than in aqueous environment (*9a, 11*), which severely limits their potential application. Due to strong salvation of anions in water, the development of anion-responsive systems in water is thus challenging.

In continuation of our earlier observation (*10a*), we report in this full account a cholesterol appended pyridinium urea **1** that selectively forms gel from DMSO/water in the presence of either tetrabutylammonium fluoride (TBAF) or other fluoride salts such as KF, NaF and CsF. Furthermore, this fluoride-induced gel is disintegrated only in the presence of aqueous solution of Pb^{2+} and Cu^{2+} ions over a series of other cations and thus serves as metal ion sensor too.



Results and discussion

Compound **1** was accomplished according to Scheme 1. Initially, cholesterol was converted to chloride **2** which upon reaction with pyridine-based urea **3**, obtained from 4-nitroaniline on reaction with triphosgene followed by addition of 3-aminopyridine in CH_2Cl_2, gave the chloride salt of **1**. Anion exchange reaction of the chloride salt of **1** using NH_4PF_6 furnished the desired compound **1** in appreciable yield.

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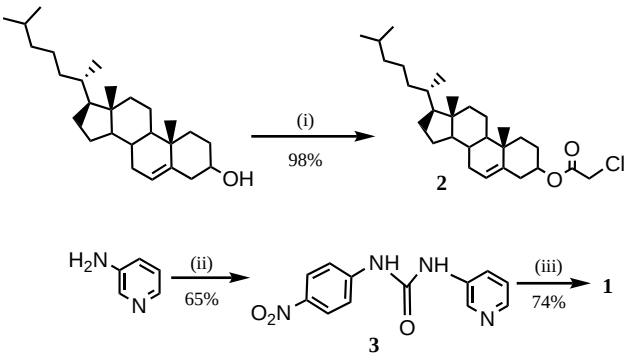

Scheme 1. (i) Chloroacetyl chloride, pyridine, dry CH_2Cl_2, room temperature (r.t.), 10 h; (ii) 4-nitroaniline, triphosgene, Et_3N, dry CH_2Cl_2, r.t., 24 h; (iii) a. **2**, dry CH_3CN, reflux, 3 days, b. NH_4PF_6, DMF–water, r.t., $\frac{1}{2}$ h.

The high selectivity of fluoride to form gel with **1** was demonstrated by turning the sample bottles upside down, as shown in Figure 1. All of the samples flowed downwards indicating their solution state except for the sample treated with aqueous solution of KF. This indicates a distinct state transformation from aqueous organic solution to gel. Compound **1** formed a bright yellow coloured gel upon addition of KF only. Hydroxide ion changes the colour of the solution from light yellow to orange but the other anions failed to do so (Figure 1).

The gelation propensity of **1** was examined in a wide range of solvents and solvent mixtures (Table 1). Only the 'instant gel' from DMSO:H_2O (1:1, v/v) was observed when 10 equiv. amounts of KF with concentration of 10^{-3} M was added. Indeed, addition of fluoride salts with concentration of 10^{-4} M and onwards did not induce gelation.

The gel state was transformed into sol upon heating ($T_{gel} = 83$°C), and the resultant solution changed to the gel upon cooling to room temperature, showing that the gel formation and collapsing are thermo reversible.

It is important to note that anions usually disrupt the supramolecular gels, although there are only few examples including our recent observation (*10a*) where

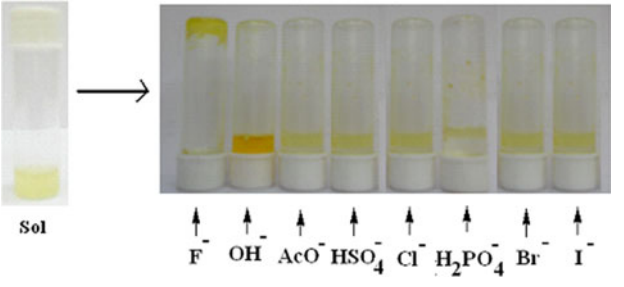

Figure 1. (Colour online) Photographs showing the phase changes of **1** in DMSO:H_2O (1:1, v/v; 10 mg/ml) upon addition of 10 equiv. amounts of each anion of potassium salt ($c = 1.0 \times 10^{-3}$ M).

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

Solvent	
DMSO	S
DMF	S
Methanol	I
Chloroform	I
Ethanol	S
Acetonitrile	I
n-Hexane	I
Diethyl ether	I
DMSO:H_2O (1:1, v/v)	G[a]

S, solution; G, transparent gel; I, insoluble.
[a] mgc, Minimum gelatinisation concentration = 10 mg/ml.

presence of anions stimulates gel formation and allows their naked eye detection (*12*). In the present example, we believe that the sol-to-gel transition induced by F^- occurs on account of effective aggregation of gelators. The hydrogen bonding properties of urea and pyridinium motifs set a complex network in DMSO:H_2O (1:1, v/v) in the presence of F^-. Excess concentration of F^- carries deprotonation of the urea protons, and the resulting dianionic species as shown in Figure 2 possibly forms intermolecular contacts with the pyridinium part and entrapped HF_2^- ion via hydrogen bond formation and charge–charge interaction. This leads to the formation of a network in solution. Formation of this network is further assisted by large hydrophobic surface of the cholesterol part.

The morphology of the gel was investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM) as shown in Figure 3. The SEM image (Figure 3(a)) reveals a microstructure of the xerogel of **1** with F^- in DMSO:H_2O (1:1, v/v). Three-dimensional network is found to contain some rods with cavities. The AFM study confirms the uneven surface of the gel (Figure 3(b)).

The storage modulus (G') and loss modulus (G'') with respect to applied stress and applied frequency were

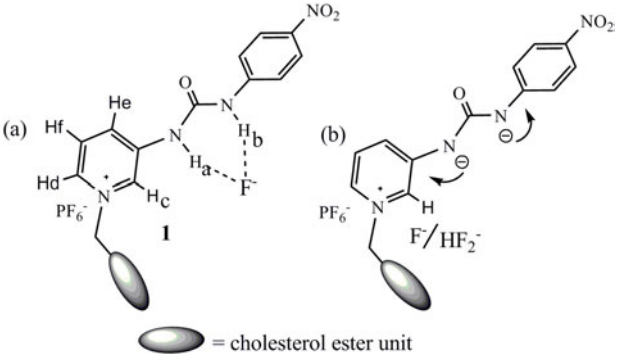

Figure 2. (Colour online) Suggested scheme for (a) hydrogen bonding and (b) deprotonation in **1** in the presence of F^-.

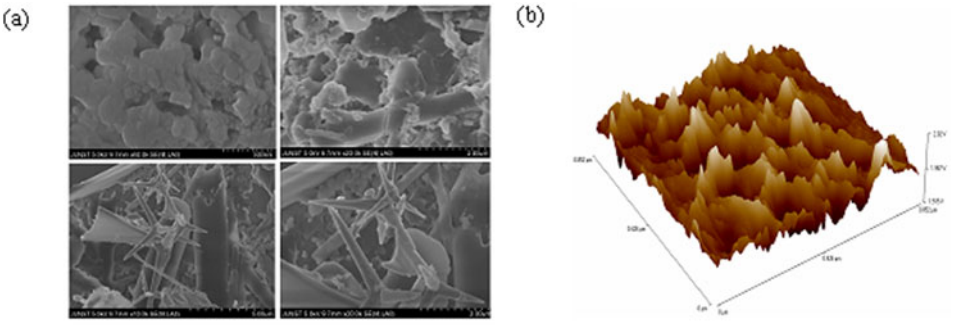

Figure 3. (Colour online) (a) SEM image of xerogel (at different scale bars) and (b) three-dimensional view of AFM image of xerogel from **1** and KF in DMSO:H_2O (1:1, v/v).

measured (Figure 4) to understand the mechanical property of the gel. As can be seen from Figure 4, both G' and G'' are almost independent of frequency. The value of G' was about seven times larger than that of G'' over a long range of frequency, suggesting that the gel is fairly tolerant to external force.

To enquire any role of K^+ ion in the gel formation of **1** with KF in DMSO:H_2O (1:1, v/v), a similar experiment under identical condition with TBAF, NaF and CsF was conducted. Indeed, all of them induced gelation (Supplementary data, available online). For example, Figure 5 represents the faint yellow coloured gel appeared in the presence of TBAF. This observation pointed out the key role of F^- ion in the gelation process rather than the counter cation.

Interestingly, in pure DMSO, compound **1** ($c = 1.5 \times 10^{-3}$ M) exhibited a sharp colour change in the presence of TBAF that enabled to read out F^- visually. Tetrabutylammonium hydroxide turned the colour of the solution of **1** to deep red. Other basic ions such as AcO^- and $H_2PO_4^-$ did not bring any marked change in colour as observed for F^- and OH^- ions (Figure 6(a)). Colour change of **1** in the presence of F^- and OH^- is attributed to the delocalisation of negative charge (see Figure 2), produced via deprotonation of urea protons, to the 4-nitropheyl motif. UV–vis titration of **1** ($c = 4.25 \times 10^{-5}$ M) in DMSO with TBAF revealed distinct change in absorbance with clear isosbestic point at 361 nm (Figure 6(b)) and gave association constant (*13*) of $8.93 \times 10^3\ M^{-1}$ following a 1:1 stoichiometry (Supplementary data, available online) (*14*). In the process, other anions did not show much change in absorbance and, therefore, binding constant values for them were not ascertained.

The deprotonation phenomenon in the interaction of **1** with F^- was established by ^{1}H NMR in DMSO-d_6. In the presence of 1 equiv. amount of TBAF, the urea (H_a and H_b) and pyridinium (H_c) protons became broad and finally vanished in the presence of 2 equiv. amounts of TBAF. The signals for the ring protons of pyridinium and 4-nitrophenyl moieties moved to the upfield directions, indicating the increase in electron density in the corresponding nucleuses (Figure 7).

In FTIR (Figure 8(a)), the sharp signal at 1753 cm^{-1} is assigned to the carbonyl stretching of the ester group in **1**. The signal for urea carbonyl stretching at ~1700 cm^{-1} is overlapped with the ester carbonyl stretching. Upon gelation in the presence of F^-, the ester carbonly stretching was noticed to be almost positionally unpurturbed (1752 cm^{-1}). The urea carbonyl stretching appeared at 1634 cm^{-1}. This significant reduction in stretching

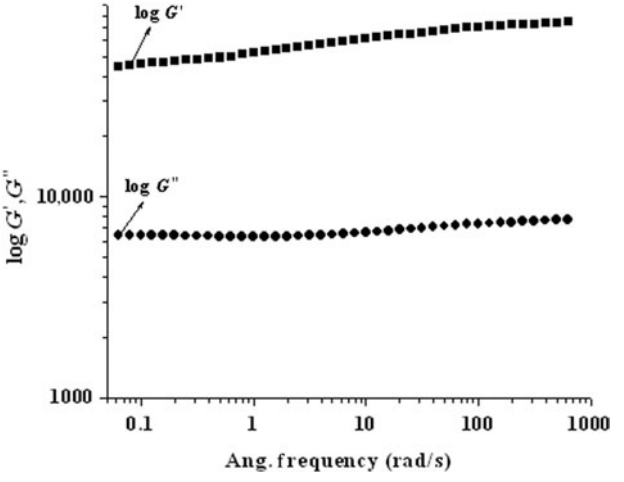

Figure 4. Variation of storage modulus (G') and loss modulus (G'') with frequency.

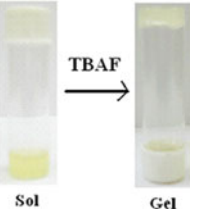

Figure 5. (Colour online) Photographs showing the phase changes of **1** in DMSO:H_2O (1:1, v/v; 10 mg/ml) upon addition of 10 equiv. amounts of TBAF ($c = 1.0 \times 10^{-3}$ M).

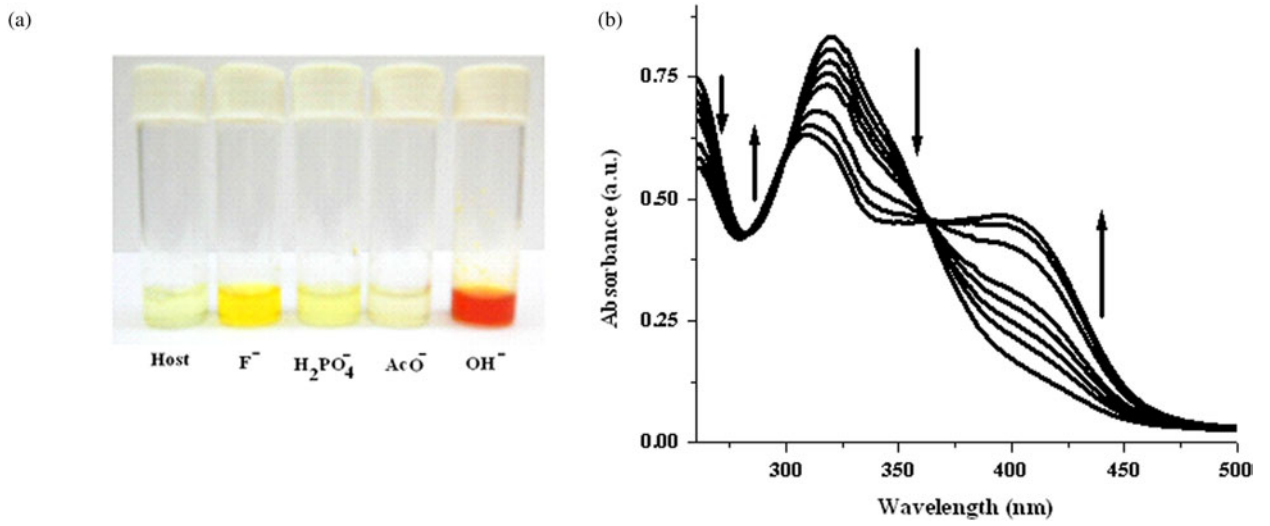

Figure 6. (Colour online) (a) Photographs of colour change of **1** ($c = 1.5 \times 10^{-3}$ M) upon addition of TBAF, dihydrogenphosphate, acetate and hydroxide ($c = 3.0 \times 10^{-3}$ M) in DMSO and (b) UV–vis titration spectra of **1** ($c = 4.25 \times 10^{-5}$ M) with TBAF in DMSO.

frequency of the urea cabonyl is ascribed to the F^--induced deprotonation of the urea protons of **1** (see Figure 2).

Fluorescence of **1** and its fluoride-induced gel was recorded in the solid state upon excitation at 340 nm. As can be seen from Figure 8(b), a significant decrease in emission at 445 nm is observed in the gel state. This decrease in emission is due to the interaction of F^- with the pyridinium urea motif in the gel network.

The F^- sensing ability of **1** was also monitored by electrochemical technique. Representative cyclic voltammograms of **1** in the presence and absence of F^- are represented in the supplementary data. The quasi-reversible reduction potential wave of **1** in the presence of F^- in cyclic voltammogram corroborates the formation of radical anion involving electron transfer with $E_0 = -0.6121$ V. In comparison, compound **1** in the absence of F^- did not show any characteristic response in the cyclic voltammogram (Supplementary data, available online).

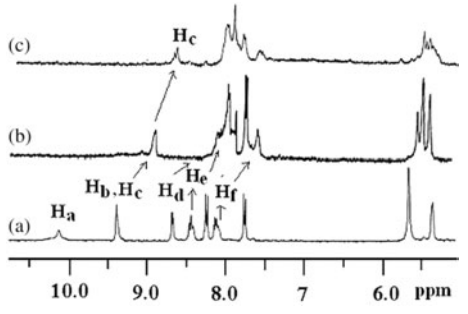

Figure 7. Partial ^{1}H NMR (400 MHz, DMSO-d_6) of (a) **1** ($c = 3.28 \times 10^{-3}$ M); (b) in the presence of 1 equiv. amount of TBAF and (c) in the presence of 2 equiv. amounts of TBAF (for labelling, see Figure 2).

In order to shed light on the application of the fluoride-based hydrogel of **1**, we carried out experiments on some useful specific metal ions. When aqueous solutions of different metal ions ($c = 1.0 \times 10^{-3}$ M) were added to the gel derived from **1** with 10 equiv. amounts of KF in DMSO:H_2O (1:1, v/v), only Cu^{2+} and Pb^{2+} ions among the other cations in the study disrupted the gel to the sol (Figure 9(a)) state. In the transition, 10 equiv. amounts of the metal salts of copper and lead were necessary. A closer look intimated that Cu^{2+} ion disintrigated the gel at a much faster rate than Pb^{2+}. Such a finding is explained presumably from strong interaction of Cu^{2+} with aqueous fluoride due to which the gelation role of F^- is nullified. Similar is the case with Pb^{2+} ion. The complex formation of both Cu^{2+} and Pb^{2+} ions with F^- is known in the literature (*15*). In the report, it is stated that Pb^{2+}, Cu^{2+} and Zn^{2+} ions form fluoride complexes in moderate rate. Although Zn^{2+} ion like $Pb^{2+}$and Cu^{2+} ions was expected to destroy the gel by withdrawing F^- from the medium, its non-interference in the present case is unclear to us at this moment. We believe that it may be due to the nature of the medium of the gel where the reaction of Zn^{2+} ion with F^- is not favourable.

Further exploration intimated the semi-conducting nature of the gel. Figure 9(b) demonstrates the variation of current within the voltage range from -5 to $+5$ V at room temperature (303 K) for the dried gel. The gel was drop cast on separate copper electrodes of a cell having gap of 50 μm between them and then was allowed to dry in air overnight. The I–V measurement of the cell containing the

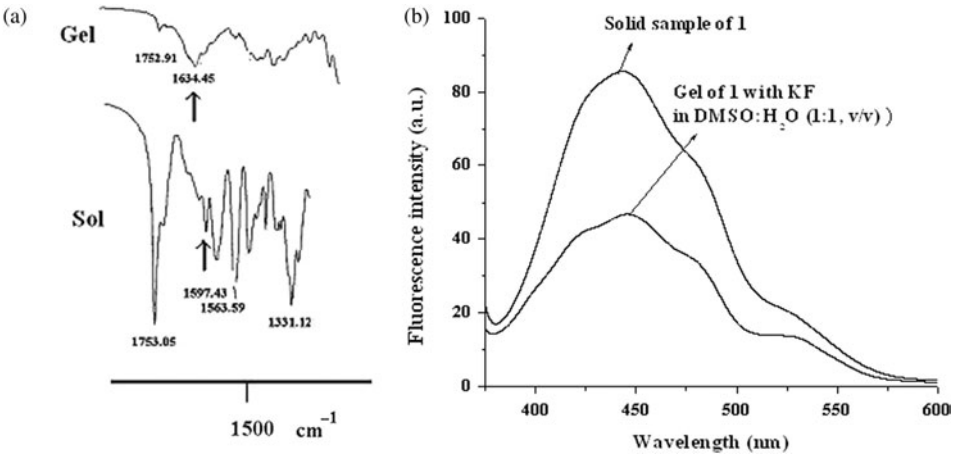

Figure 8. (a) Partial IR spectra of **1** in solution and gel (on addition of KF) states and (b) fluorescence change of **1** and its fluoride-induced gel in the solid state.

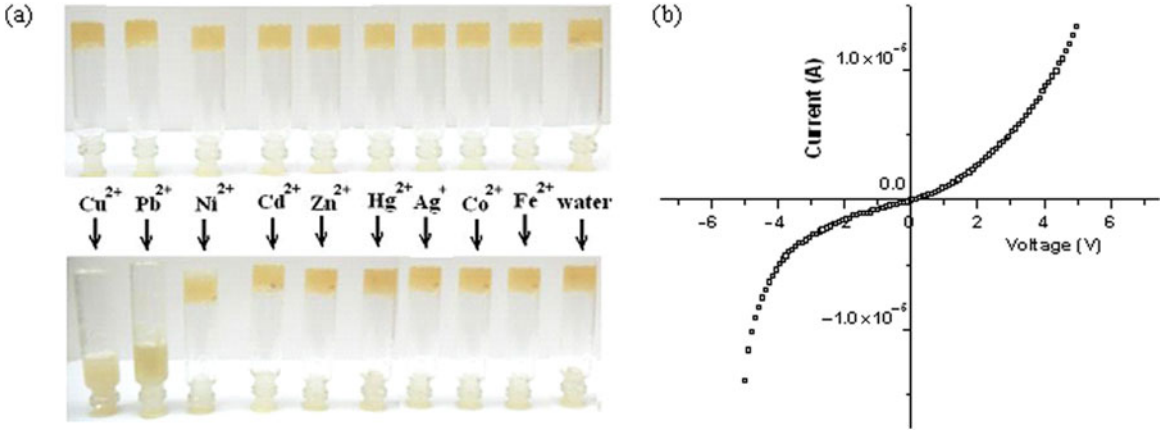

Figure 9. (Colour online) (a) Photographs showing the phase changes of receptor **1** in DMSO:H_2O (1:1, v/v) (10 mg/ml) upon addition of 10 equiv. amounts of potassium fluoride salt and addition of aqueous solution of different metal ions and water in the gel. (b) *I–V* characteristics of the dried gel by two-probe 4-wire measurement.

dried gel was carried out under dynamic vacuum by adopting the two-probe 4-wire measurement (Supplementary data, available online) using a Keithely 2400 source meter. It is noteworthy that the gel showed ideal semiconducting nature with nonlinear increase of current with the increase in voltage. The possible reason for the above electronic conductivity can be approved by fluoride-assisted deprotonation of urea protons followed by electron transfer in the gel matrix.

In order to be acquainted with the electron transfer, a model structure **4** was undertaken for DFT calculation where the cholesterol-linked ester part has been replaced by $-CH_3$ group. DFT optimisation (*16*) was carried out using B3LYP functional and 6-31(g) basis set. The hydrogen bonded complex of **4** with F^- (**4a**) and fluoride-induced deprotonated species **4b** were also separately optimised and the disposition of the HOMO and LUMOs for each case is represented in Figure 10. As can be seen from Figure 10, the HOMO and LUMO are separately spread over two domains in **4**. While HOMO is mostly centred on the 4-nitrophenyl moiety, LUMO is mostly centred on the pyridinium nucleus. In contrast, the disposition of HOMO and LUMOs in the fluoride complexed structure **4a** is observed to be different. The HOMO is spread over the entire region consisting of pyridinium, urea and 4-nitrophenyl moieties. LUMO is greatly populated on the pyridinium nucleus. Thus, there is an overlapping region of the MOs on the pyridinium motif. In case of deprotonated species **4b**, the HOMO and LUMOs are spread over a common region and corresponds a small gap (−0.0744 eV). This small energy gap and overlapping HOMO/LUMOs in **4b** are presumably the possible reasons of semi-conducting behaviour of the fluoride-induced gel of **1**.

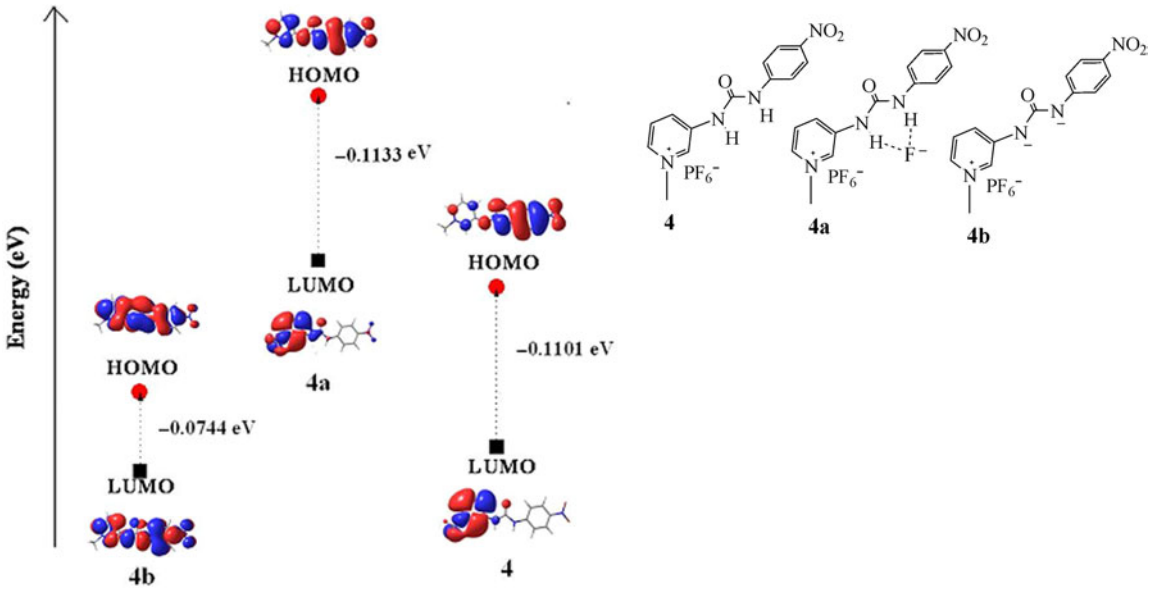

Figure 10. (Colour online) HOMO and LUMOs of the model structures **4**, **4**.F^- and dianionic form of **4**.

Conclusion

In conclusion, we have shown that the cholesterol appended pyridinium urea **1** form hydrogel in the presence of F^- in DMSO/H_2O. Furthermore, the colour change in the sol-to-gel transition is convenient to detect F^- in the aqueous phase. The gel state is established to be a good semiconductor and also a medium to detect some specific transition metal ions such as Cu^{2+} and Pb^{2+} by showing a transition from gel to sol. To the best of our knowledge, such cholesterol appended pyridinium derivative which shows multi-features (F^--induced hydrogel formation, detection of Cu^{2+} and Pb^{2+} ions and acts as semiconductor) in the recognition of F^- is a first time report from our laboratory in continuation of our earlier work (*10a*).

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-1H-cyclopenta[a]phenanthren-3-yl ester (3): (10a)

To a stirred solution of cholesterol (1 g, 2.59 mmol) in 30 ml dry CH_2Cl_2, chloroacetyl chloride (0.31 ml, 3.88 mmol) and pyridine (0.1 ml, 1.3 mmol) were added in the 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 a white solid compound. Recrystallisation from petroleum ether afforded pure product **3** (1.18 g, yield 98%), melting point (m.p.) 148°C. ^{1}H 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-(4-Nitro-phenyl)-3-pyridin-3-yl-urea (4)

To a stirred solution of triphosgene (1.07 g, 3.62 mmol) in 10 ml dry CH_2Cl_2, 3-aminopyridine (0.375 g, 3.98 mmol) dissolved in 10 ml CH_2Cl_2 was added dropwise along with Et_3N (0.56 ml, 3.98 mmol). The reaction mixture was allowed to stir for 1 h. Then, 4-nitroaniline (0.5 g, 3.62 mmol), dissolved in 10 ml CH_2Cl_2, was added dropwise from a dropping funnel. The reaction mixture was allowed to stir for a further 24 h. After completion of reaction, the 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 90% ethyl acetate in petroleum ether as eluent. The desired product **4** was obtained in 65% yield (0.61 g), m.p. 226°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.21 (s, 1H), 10.04 (s, 1H), 8.91 (s, 1H), 8.42 (br s, 1H), 8.23–8.19 (m, 3H), 7.73–7.68 (m, 3H).

Compound 1

Compounds **3** (0.8 g, 1.74 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**. The chloride salt of **1** (0.6 g, 0.8 mmol) was next dissolved in MeOH (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 crystallisation of the precipitate from petroleum ether afforded pure compound **1** in 74% yield (0.51 g, m.p. 163°C). ^{1}H NMR (400 MHz, $CDCl_3$ containing few drops of DMSO-d_6) δ 9.88 (s, 1H), 9.38 (s, 1H), 9.20 (s, 1H), 8.30 (d, 1H, $J = 4$ Hz), 8.19 (d, 1H, $J = 8$ Hz), 7.91 (d, 2H, $J = 8$ Hz), 7.69 (t, 1H, $J = 8$ Hz), 7.43 (d, 2H, $J = 8$ Hz), 5.29 (s, 2H), 5.11 (s, 1H), 4.40 (m, 1H), 2.11 (m, 2H), 1.75–0.58 (m, 38H), 0.41 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.8, 162.3, 151.6, 145.2, 141.7, 139.8, 139.4, 139.0, 135.5, 127.7, 125.0, 122.5, 118.2, 75.9, 60.8, 56.0, 55.5, 49.3, 41,8, 37.4, 36.3, 36.0, 35.7, 35.6, 35.1, 31.2, 30.7, 27.7, 27.3, 27.1, 23.8, 23.1, 22.6, 22.3, 20.5, 18.8, 10.2 (one carbon in the aliphatic region unresolved); FTIR (KBr, cm^{-1}): 3401, 2938, 2868, 1753, 1597, 1563, 1504; HR-MS (TOF MS ES$^+$): $C_{41}H_{57}N_4O_5PF_6^+$, (M-PF_6) requires 685.4323 found 685.4378.

Supplementary data

Experimental procedures for spectroscopic studies, Figures showing the change in UV–vis titrations of receptor **1** with various anions, Job plot, binding constant curve and electrical measurement method, and characterisation spectra of **1** can be found online.

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