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Ion conducting cholesterol appended pyridinium bisamide-based gel for the selective detection of Ag^+ and Cl^- ions†

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Cholesterol appended bispyridinium isophthalamide dichloride (**1**) has been designed and synthesized. While compound **1** forms a gel in $CHCl_3$, the cholesterol appended bispyridinium isophthalamide dihexafluorophosphate (**1a**) analogue that results from **1** on anion exchange does not form a gel in any solvent combination. The chloroform gel of **1** is pH responsive and shows thermally activated ionic conductivity. It serves as a medium for the specific detection of Ag^+ ions over a series of examined cations. Compound **1a**, on the other hand, acts as a selective Cl^- ion detector by forming a gel in chloroform in the presence of tetrabutylammonium chloride.

Introduction

In recent past, considerable efforts have been focused on the design and synthesis of low-molecular-weight organogelators (LMOGs) that exhibit responsive properties in the presence of certain external stimuli (*e.g.*, temperature, light, pH, solvents, chemicals and so on).[1] Organogels are formed by assembling LMOGs into entangled three-dimensional networks containing solvent molecules trapped *via* weak interactions such as hydrogen bonding, π–π stacking, coordination, electrostatic and van der Waals interactions.[2] Various low-molecular-weight based organogels that are associated with chemical, photo, proton, metal, mechanical and redox responsiveness have been recognized in the last few years.[3] In relation to this, the development of stimuli responsive gels, whose properties can be tuned by an external anion or cation is of increasing interest as both anion and cation are linked to many vital processes in biology, chemistry and the environment.[4] With this in mind, pyridinium-based compounds are of potential interest as they are easily synthesizable and show good electrophilic character.[5] They moderately bind to anions through hydrogen bonding and charge–charge interaction. Exploitation of this motif with suitable structural modification in gel chemistry is hardly reported.[6]

In this full account, we herein report the synthesis of simple cholesterol appended bispyridinium isophthalamide dichloride (**1**) that forms a gel in $CHCl_3$ (Fig. 1). The gel shows thermally activated ionic conductivity. Furthermore, it is pH responsive and shifts to the sol state selectively in the presence of Ag^+ ion due to its strong affinity for Cl^- ions. A review of the literature reveals that the majority of Ag^+-selective gels concern the involvement of the Ag^+ ion in gelation through coordination between the Ag^+ ion and a donor atom such as nitrogen or sulfur.[7] Similarly, examples of organogelators that undergo a gel to sol transition in the presence of Ag^+ ions are reported in the literature, where Ag^+–alkene or Ag^+–aromatic ring nitrogen interactions have been exploited in this study.[8]

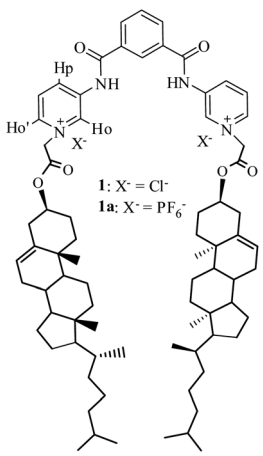

Fig. 1 Chemical structures of **1** and **1a**.

Furthermore, it is to be noted that the cholesterol appended bispyridinium isophthalamide dihexafluorophosphate (**1a**) (Fig. 1), obtained from anion exchange of **1**, forms a gel in

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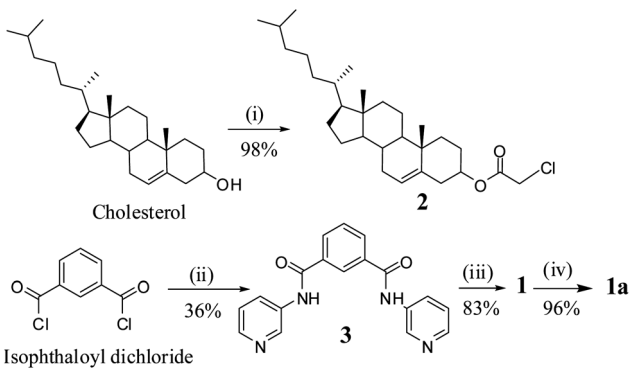
† Electronic supplementary information (ESI) available: Figures showing the change in fluorescence and UV-vis titrations of receptor **1a** with the halides and OH^- ions, Job plots, binding constant curves, comparison of ^1H NMR of **1** in the presence and absence of F^- and OH^- ions, FTIR spectral comparison, AFM image, Arrhenius plot, experimental procedures, ^1H, ^{13}C NMR spectra and mass spectra of the final compounds are available. See DOI: 10.1039/c3ra44718a

$CHCl_3$ selectively in the presence of tetrabutylammonium chloride (TBACl) in preference to other halides, thereby facilitating the recognition of Cl^- ions by the naked eye. Chloride is one of the most essential anions of biological significance,[9] and it is related with cystic fibrosis.[10] Therefore, the recognition of this ion is essentially important.

Results and discussion

The synthesis of compound **1** was accomplished according to Scheme 1. Initially, cholesterol was converted to the chloride **2**, which on refluxing with isophthaloyl diamide **3** in dry CH_3CN gave the chloride salt **1**. The isophthaloyl diamide **3** was obtained from the reaction of 3-aminopyridine with isophthaloyl dichloride in the presence of Et_3N in dry CH_2Cl_2. Anion exchange of the dichloride salt **1** using NH_4PF_6 gave the desired compound **1a** in good yield. All of the compounds were fully characterized by spectroscopic methods.

Compound **1** contains different segments that play a critical role in gelation. The cholesterol unit in **1** is hydrophobic in nature and can interact through van der Waals interaction. This increases the gelation ability of **1**.[11a] The pyridinium diamide as an anion binding site may trigger the arrangement of the molecules involved in hydrogen bonding and charge–charge interaction with the anions. Keeping these features in mind, the gelation propensity of **1** was examined in a wide range of solvents and solvent mixtures (Table 1). As can be seen from Table 1, the only 'instant gel' of **1** was obtained from $CHCl_3$. The gel was thermo reversible and upon heating ($T_{gel} = 66$ °C), was transformed into sol and the resultant solution changed back into the gel upon cooling to room temperature. In contrast, compound **1a** which is devoid of Cl^- ions, did not form a gel under similar conditions. It is assumed that the Cl^- ions in **1** play a key role in establishing a hydrogen bonded network in solution, especially in $CHCl_3$. It is mentionable that the isophthaloyl diamide moiety can attain different equilibrium conformations[11b] (In–In, In–Out and Out–Out; see Fig. 2) in solution. The population of the individual form is dependant upon the nature of the substituent present in the amide part. To our belief, in the present case, any one of the conformers in solution may form a Cl^--templated hydrogen bonded network into which the solvent molecules are entrapped to form a gel.



Scheme 1 (i) Chloroacetyl chloride, pyridine, dry CH_2Cl_2, rt, 10 h; (ii) 3-amino pyridine, Et_3N, dry CH_2Cl_2, rt, 24 h; (iii) **2**, dry CH_3CN, reflux, 3 days; (iv) NH_4PF_6, DMF : CH_3OH (1 : 5, v/v), H_2O.

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

Solvent	Result[a] (**1**)	Result[a] (**1a**)
$CHCl_3$	G*	I
1% CH_3OH in $CHCl_3$	S	S
3% DMSO in $CHCl_3$	S	S
CH_3CN	I	S
DMSO	S	S
DCM	S	I
CH_3OH	I	S
DMF	S	S
DMF : H_2O (1 : 1, v/v)	P	P
1,2-Dichlorobenzene	I	I
CH_3CN : H_2O (1 : 1, v/v)	I	P
DMSO : H_2O (1 : 1, v/v)	P	P

[a] S, solution; G, transparent gel; I, insoluble; P, Precipitation, *mgc = minimum gelatination concentration = 10 mg mL^{-1}.

The amide and pyridinium ring protons such as H_o, H_o' and H_p, are the possible hydrogen bond donors that complex with the Cl^- ions to establish a network in solution. Fig. 3 represents a suggested mode of hydrogen-bonding in this network. A similar network of a pyridinium system is reported by Das *et al.*[6b] The cholesterol motif with a large hydrophobic surface stabilizes the network in the less polar solvent, $CHCl_3$. Fig. 3 highlights a probable mode of arrangement of the molecules of **1** considering the 'Out–Out' conformation as shown in Fig 2. It is believed that the replacement of Cl^- by the larger PF_6^- ion disrupts the suggested network shown in Fig. 3, by destroying a number of intermolecular hydrogen bond contacts.

In the FTIR spectrum of **1**, while a broad signal appeared at 3402 cm^{-1}, attributable to NH stretching due to hydrogen bonding effect, the FTIR spectrum of compound **1a** exhibited NH stretching at 3448 cm^{-1} attributable to free NH (Fig. 4). Even the amide carbonyl stretching in **1** observed at 1689 cm^{-1} was shifted to 1703 cm^{-1} in the spectrum of **1a**. This lower stretching of the amide carbonyl in **1** demonstrates its involvement in hydrogen bonding. In ^1H NMR, the signals for the amide NH and the pyridinium ring protons of **1** appeared further downfield compared to those of **1a** (Fig. 5). Thus both FTIR and ^1H NMR studies indicate that the dichloride salt **1** is different from its dihexafluorophosphate analogue **1a** with respect to their hydrogen bonding characteristics. Such different hydrogen bonding behaviours of Cl^- and PF_6^- ions are well established by us and other groups.[6a,12]

The morphology of the chloroform gel of **1** was characterized by AFM (ESI, Fig. S11†) and SEM studies. The SEM image in Fig. 6 shows the aggregation of three dimensional networks with

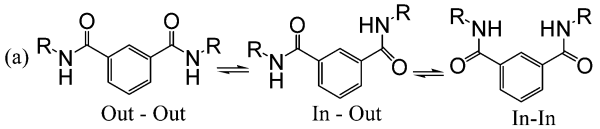


Fig. 2 The different conformations of isophthaloyl diamide.

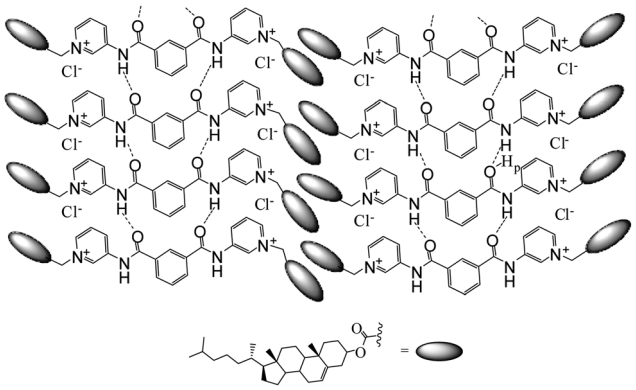


Fig. 3 Schematic representation of the possible arrangement of molecules during the gelation of **1**.

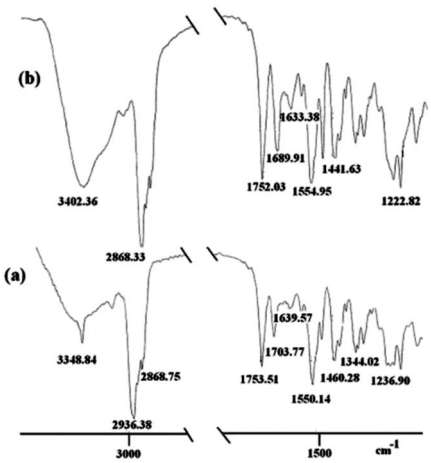


Fig. 4 Partial FTIR spectra of (a) **1a** and (b) **1**.

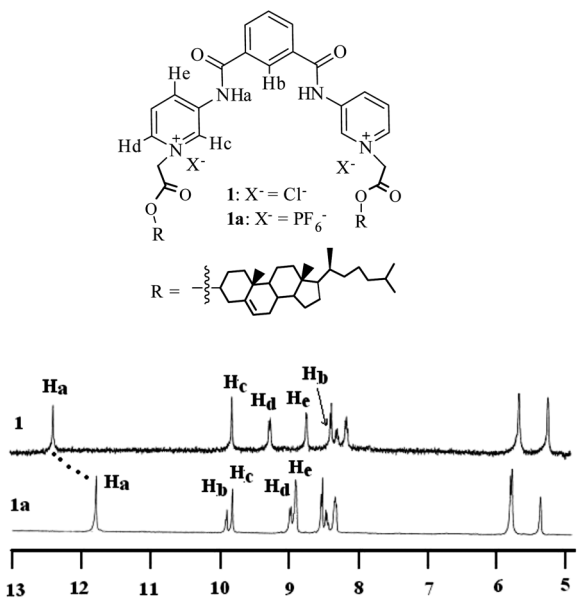


Fig. 5 Partial ^{1}H NMR spectra (400 MHz, d_6-DMSO) of **1** and **1a**.

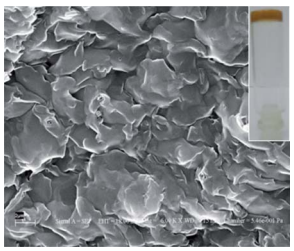


Fig. 6 SEM image of the xerogel from the $CHCl_3$ gel of **1** (scale bar: = 2 μm).

an uneven surface. Studying the FTIR spectra of the amorphous **1** and its chloroform gel reveals that there is a small increase in amide carbonyl stretching ($\upsilon_{gel} - \upsilon_{amorphous} = 6\ cm^{-1}$) in the gel state (ESI, Fig. S10†). This shift provides the evidence of the breaking of some intramolecular hydrogen bonds in the amorphous state to establish some new intermolecular hydrogen bonds in the gel state. On the other hand, a small decrease in ester carbonyl stretching ($\upsilon_{amorphous} - \upsilon_{gel} = 7\ cm^{-1}$) is also an indication of its involvement in intermolecular contact in the gel state.

It was noted that the gelator **1** composed of the pyridinium-based cations and chloride anions in the gel state gave a response in electrical conductivity. It is usual that the dielectric properties of a medium containing charges are usually measured by means of the impedance spectroscopy technique.[13] In this technique, the sample is subjected to an external voltage of the type $V_t(\omega) = V_0 \exp i\omega t$, where V_0 is the amplitude, $\omega = 2\pi f$ is the circular frequency, and f is the frequency. Since dielectric spectroscopy in the frequency domain covers a broad frequency range, in the present case from 42 Hz to 5 MHz, this technique allowed the measurement of ionic conductivity of the chloroform gel of **1**. In analogy with dielectric models that consider the electric polarization of counter ions induced by an external electric field, the observed ionic conductivity can be ascribed to the diffusion processes of ions, bound to the Columbic potential up to the typical size of different regions that may characterize the whole system. In this regard, for a particular temperature the real and imaginary parts of the complex impedance $Z^*(\omega) = Z' - iZ''$ at frequency ω were determined from the measured capacitance $C(\omega)$ and conductance $G(\omega)$ data using the following relations:

$$Z' = \frac{G(\omega)}{G^2(\omega) + \omega^2(C(\omega) - C_0)^2} \quad (1)$$

$$-Z'' = \frac{G(\omega)(C(\omega) - C_0)}{G^2(\omega) + \omega^2(C(\omega) - C_0)^2} \quad (2)$$

where $C_0 = \varepsilon_0 A/t$ is the capacity with a free space between the electrodes, ε_0 is the permittivity of the free space, and A is the surface area. Fig. 7a shows the variation of the real (Z') and imaginary (Z'') parts of impedance with frequency at two different temperatures for the cell containing the gel. Indeed, the magnitude of Z' increases with decrease in both frequency and temperature, indicating the corresponding decrease in

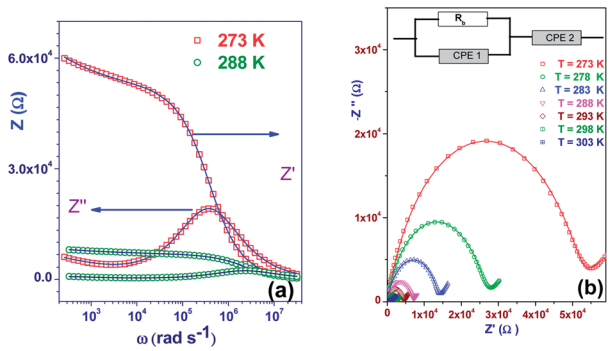


Fig. 7 (a) The real and imaginary parts of the complex impedance spectra of the chloroform gel of **1** at two different temperatures; (b) the Argand diagram of the gel at different measured temperatures. Solid lines in both of the figures are the best fits of the data to eqn (3) and (4) considering the equivalent circuit shown in the inset of (b).

ionic conductivity of the gelatinous system. Fig. 7b shows the resultant Argand diagram [imaginary part of complex impedance (Z'') *versus* its real part (Z')] at different measured temperatures. As temperature increases, the radius of the arc that corresponds to the bulk resistance of the gel decreases. This demonstrates a thermally activated conduction mechanism. The small tail observed for each semicircle is due to the double layer capacity of an in-homogeneous electrode surface.

The impedance data was analyzed by considering an equivalent circuit describing the gel–electrode interface as shown in the inset of Fig. 7b. In this circuit, the parallel combination of polarization resistance R_b (bulk resistance) and a constant phase element (CPE1) accounts for the depression of the semicircles observed in Fig. 7b. The constant phase element (CPE2) in series resembles the effect due to non-ideal electrode geometry. The CPE impedance is $Z_{CPE} = Q(j\omega)^{\lambda}$ where $0 \leq \lambda \leq 1$ is the measure of the capacitive nature of the element. If $\lambda = 1$, the element is an ideal capacitor and if $\lambda = 0$, it behaves as a frequency independent Ohmic resistor.

The expressions of the real and imaginary components of the impedance related to the equivalent circuit were calculated according to the following equations,

$$Z' = \frac{R_b^2 Q_1 \omega^{\lambda} \cos\left(\frac{\lambda\pi}{2}\right) + R_b}{\left(1 + R_b Q_1 \omega^{\lambda} \cos\left(\frac{\lambda\pi}{2}\right)\right)^2 + \left(R_b Q_1 \omega^{\lambda} \sin\left(\frac{\lambda\pi}{2}\right)\right)^2} + \cos\left(\frac{\alpha\pi/2}{Q_2 \omega^{\alpha}}\right) \quad (3)$$

$$-Z'' = \frac{R_b^2 Q_1 \omega^{\lambda} \sin\left(\frac{\lambda\pi}{2}\right)}{\left(1 + R_b Q_1 \omega^{\lambda} \cos\left(\frac{\lambda\pi}{2}\right)\right)^2 + \left(R_b Q_1 \omega^{\lambda} \sin\left(\frac{\lambda\pi}{2}\right)\right)^2} + \sin\left(\frac{\alpha\pi/2}{Q_2 \omega^{\alpha}}\right) \quad (4)$$

The resistance R_b, Q_1, Q_2, λ and α have been simulated using a mean square method which consists of minimizing the difference between the experimental and calculated data. The simulated curves are shown in Fig. 7a and b using the solid lines, showing good conformity of the calculated lines with experimental data. This indicates that the suggested equivalent circuit describes the gel–electrode interface reasonably well.

Considering the R_b values obtained from the above simulation as the bulk resistance of the system, the dc conductivity was evaluated using the relation $\sigma_{dc} = t/R_b A$ (where 't' and 'A' are the thickness and area of the sample respectively) and is shown in Fig. S12 (ESI†). The linear plot in Fig. S12 (ESI†) indicates the thermally activated ionic conductivity (activation energy E_a = ~0.89 eV) that presumably arises from the migration of loosely bound Cl^- ions within the gel network. With a decrease in temperature, the movement of such ions within the gel framework is considered to be slowly restricted, resulting in a significant reduction in the conductivity of the system. Thus the experimental observation reveals that the chloroform gel of **1** is effectively a good ionic conductor at room temperature.

Apart from ionic conductivity, the gel was also established to be responsive towards both cationic and anionic substrates. To study the effect of anions, a concentrated solution of anions was added on the top of the chloroform gel of **1** and was kept at room temperature. Among the different anions tested (taken as their tetrabutylammonium salt), only OH^- ions disrupted the gel immediately (Fig. 8). It is interesting to note that fluoride being a basic ion was unable to affect any change in the gel, even when added in excessive amounts. This is in contrast to our previous observation on the urea analogue of this pyridinium system.[6a] Such difference of the amide compound from its urea analogue is attributed to the greater acidic character of the urea protons.

However, the OH^- ion induced broken gel reappeared only upon the addition of HCl (Fig. 9). Thus the gel in the present study is pH responsive. It is worth mentioning that the chloroform gel of **1** started to disintegrate when the pH of the medium was raised above 7.0 and it became a clear solution at pH 8.0. The gel started to appear again when the pH of the medium was reduced to 7.0 and it became thick at pH 6.0. In our opinion, OH^- abstracts the acidic pyridinium protons in **1** and destroys the intermolecular hydrogen bond contacts. Protonation arising from the addition of HCl results in the resetting of the original structure due to hydrogen bond contacts reforming and gelation taking place. The deprotonation of amide protons in **1** in the presence of tetrabutylammonium hydroxide was proved by ^{1}H NMR (see ESI†).

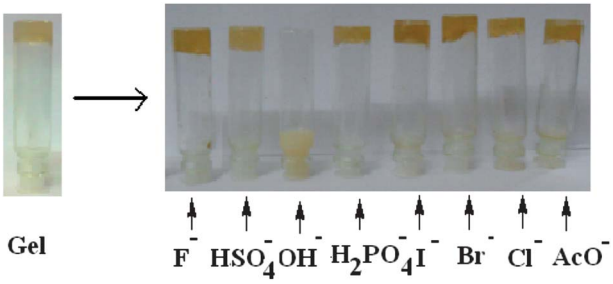


Fig. 8 Photograph showing the changes in the $CHCl_3$ gel of **1** (10 mg mL^{-1}) after the addition of 2 equiv. amounts of various anions ($c = 2.0 \times 10^{-2}$ M).

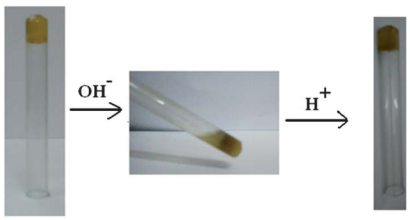


Fig. 9 The changes of the $CHCl_3$ gel of **1** (10 mg mL^{-1}) on successive addition of TBAOH ($c = 2.0 \times 10^{-2}$ M) and HCl.

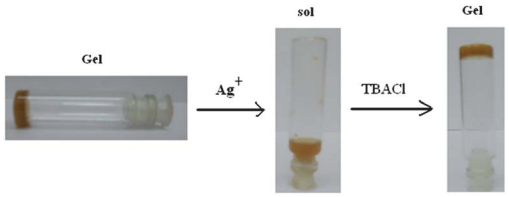


Fig. 11 The phase changes of the $CHCl_3$ gel of **1** (10 mg mL^{-1}) on successive addition of $AgClO_4$ (2 equiv.) and TBACl (2.5 equiv.). The gel to sol conversion was completed within 20 min and reappeared upon the addition of TBACl after 30 min.

In addition to the effects of anions, the effects of cations on the chloroform gel of **1** were also studied. For this, a series of metal ions (taken as their perchlorate salts) were employed. Among the different metal ions tested, only the Ag^+ ion destroyed the gel (Fig. 10), which reappeared in the presence of TBACl (Fig. 11).

Upon the breaking of the gel, the stretching frequencies of the amide and ester carbonyls in the FTIR spectrum reached the values of the amorphous state of **1** (ESI†). This can be explained by the silver ions scavenging the chloride ions form the network, and due to the template effect of Cl^- ion as proposed in Fig. 3, the removal of Cl^- leads to the breaking down of the gel structure. However, externally added Cl^- ions further resulted in the slow formation of gel (Fig. 11) by establishing the network as shown in Fig. 3. This process was successfully repeated three times. So, this study is worthwhile in that this gel is capable of detecting the Ag^+ ion visually.

It is worth mentioning that although the dihexafluorophosphate analogue **1a** was not responsive in gelation, it produced a transparent gel from $CHCl_3$ in the presence of TBACl (ESI†). Other halides (taken as their tetrabutylammonium salt) did not form a gel under similar conditions. In the presence of Cl^- ions, compound **1a** is supposed to attain the hydrogen bonding attributes of **1** due to which gelation takes place. In contrast, other halide ions did not permit a suitable interaction between pyridinium bisamides, thus preventing gel formation. Therefore, the dihexafluorophosphate analogue **1a** is usable in the visual detection of Cl^- ions with respect to the other halides.

In our earlier publication, we have reported that different fluorophore-labeled pyridinium bisamides, built on the isophthaloyl motif, are prone to bind different anions such as F^-, $H_2PO_4^-$, carboxylates *etc.*[14] Thus, in solution the hydrogen bonding interaction of the pyridinium-based isophthaloyl diamide is established and well explored. In spite of that we performed UV-vis and fluorescence titrations of **1a** ($c = 2.25 \times 10^{-5}$ M) in $CHCl_3$ containing 0.2% DMSO to understand its affinity for the halides in solution. Halides showed measurable interaction (see ESI†). Fig. 12a represents the emission profile where the selective increase in emission in presence of Cl^- ions is the distinguishing feature from the other halides for its selective detection in the solution phase. Compound **1a** binds[15] Cl^- ions with K_a of 1.31×10^4 M^{-1} in a 1 : 1 stoichiometric[16] fashion. Fluoride initially takes part in hydrogen bonding in the cavity and then deprotonates in the presence of its excess concentration.[14b] This brought about a greater change in emission. In contrast, Br^- and I^- ions quenched the emission significantly due to the heavy atom effect (see ESI†). The F^- induced a greater change in the absorption (Fig. 12b) and emission of **1a** due to hydrogen bonding, and deprotonation was confirmed by recording the same spectra of **1a** in the presence of tetrabutylammonium hydroxide which also brought about a marked change (Fig. 12c).

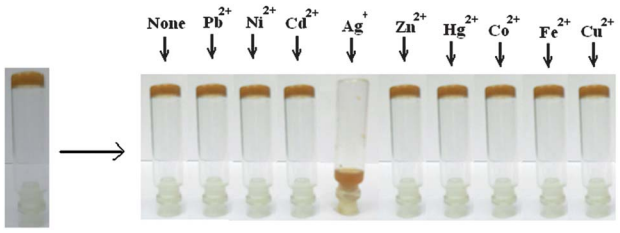


Fig. 10 Photograph showing the phase changes of **1** in $CHCl_3$ (10 mg mL^{-1}) upon the addition of 2 equiv. amounts of different metal ions ($c = 2.0 \times 10^{-2}$ M).

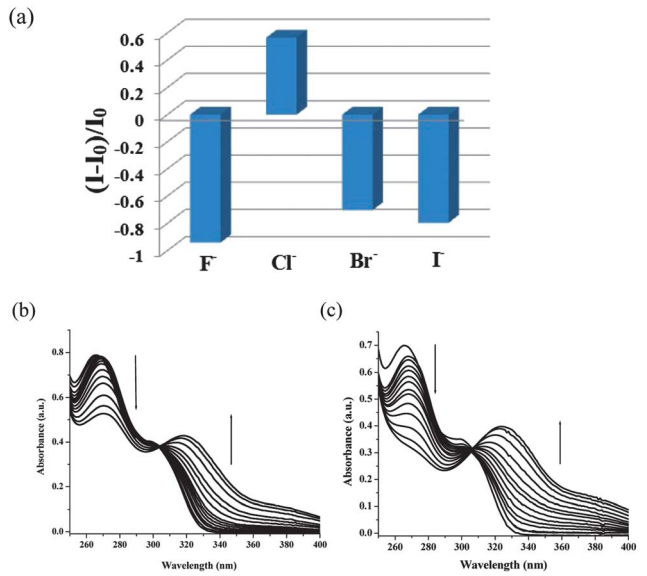


Fig. 12 (a) Fluorescence ratio [$I - I_0/I_0$] of **1a** ($c = 2.25 \times 10^{-5}$ M) at 360 nm upon addition of 6 equiv. of a particular anion ($c = 9.0 \times 10^{-4}$ M) in $CHCl_3$ containing 0.2% DMSO, (b) change in absorbance of **1a** ($c = 2.25 \times 10^{-5}$ M) upon addition of F^- and (c) OH^- ions.

Conclusion

In conclusion, we have demonstrated that cholesterol appended bispyridinium isophthalamide dichloride **1** instantly forms a gel in chloroform. The gel is stable at room temperature and exhibits ionic conductivity due to the movement of unrestricted Cl^- ions within the network. Furthermore, the gel is pH responsive and acts as a medium for the recognition of Ag^+ ions over a series of other cations by exhibiting a gel to sol transformation. Furthermore, the reappearance of the gel in the selective presence of the chloride salt underlines the reversibility in the process. Notably, we found that the dihexafluorophosphate analogue **1a** which is obtained from **1** by anion exchange could allow the selective recognition of Cl^- over the other halides by forming a transparent yellow colored gel in $CHCl_3$. In solution, an opposite mode of emission of **1a** upon addition of Cl^- ions further demonstrated this compound's ability to distinguish Cl^- from the other halides examined. Thus, cholesterol appended pyridinium-based isophthaloyl diamide exhibits versatile gel chemistry facilitating the visual detection of both cations and anions. Further exploration in this direction is underway in our laboratory.

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