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# Cholesterol linked benzothiazole: A versatile gelator for detection of picric acid and metal ions such as Ag<sup>+</sup>, Hg<sup>2+</sup>, Fe<sup>3+</sup> and Al<sup>3+</sup> under different conditions

Subhendu Mondal, Rameez Raza and Kumaresh Ghosh\*

**Abstract:** Cholesterol-appended benzothiazole **1** has been designed and synthesized. Compound **1** exhibits gelation in different solvents. The benzothiazole and cholesteryl motifs plays pivotal role in making aggregation in organic solvents involving  $\pi$ -stacking and hydrophobic interaction, respectively. As application, the nitrobenzene gel with good rheological property has been noted to be useful in molecular recognition studies of multiple analytes ranging from neutral to ionic in nature. It selectively recognizes picric acid (PA) over a series of nitroaromatics by exhibiting gel-to-sol phase transition with distinguishable color change from pale yellow to deep yellow. On the other hand, the nitrobenzene gel shows the selective recognition potential for Ag<sup>+</sup> and Hg<sup>2+</sup> ions through gel-to-sol phase transition and the cations are distinguished by F<sup>-</sup>. The gelator **1** also reveals measurable selective interaction with picric acid over a series of nitroaromatics in CH<sub>3</sub>CN containing 1% CHCl<sub>3</sub>, compound **1** further, shows affinity towards Fe<sup>3+</sup>, Al<sup>3+</sup> and Hg<sup>2+</sup> with distinctive features.

#### Introduction

Design and synthesis of low molecular weight gelators that find applications in detecting toxic ions, chemicals and hazardous is of paramount interest in the research area of supramolecular chemistry.<sup>1</sup> The effect of toxic and hazardous pollutants on the environment is a major concern in environment pollution especially in third world countries. It is thus more important to protect the environment from toxic and hazardous pollutants.<sup>2-3</sup> Toxic materials cover a wide range of substrates ranging from neutral to charge in nature. Out of such substrates, different nitroaromatics as well as different metal mentionable.4-6 ions are Among nitroaromatics, trinitrotoluene (TNT) and picric acid (PA) are used as powerful explosives. Thus there is a need for detection of these species for homeland security and public safty.7-8 Importantly, PA causes several skin diseases, allergy, eye irritation, liver malfunction which lead to chronic diseases like cancer.9 Moreover, due to greater water solubility, it contaminates ground water and causes water and soil pollutions.<sup>10</sup> Therefore, detection and sensing of PA in an

easiest way is considered to be important from environment, social and security issues. Till now, detection of PA either in solution or vapour phase, involves the use of different spectroscopic techniques (especially fluorescence),<sup>11</sup> nanoparticles/nanofibers<sup>12</sup> and polymers<sup>13</sup> etc. By contrast, the detection of PA using supramolecular gel matrix is merely explored. Gel phase sensing of PA in naked-eye attracts attention as it does not require any sophisticated instrument. The literature study reveals that there are few examples of gel phase detection of PA (Table S2).<sup>14</sup>

Beside picric acid, the detection of metal ions of biological relevance is also of prime importance. For example, mercury,<sup>15</sup> one of the most hazardous pollutants, is released in the environment through several natural and industrial processes. The exposure of this ion even at low concentration leads to various health problems, especially neurological disorders. Similarly, Ag<sup>+</sup> ion<sup>16</sup> is biologically relevant mainly due to its antibacterial activity. It has great applications in organic synthesis, electronics, photography, and imaging industry.<sup>17</sup> Aluminum and iron are the third most abundant elements in the earth crust. While excess Al<sup>3+</sup> may cause damage to certain human tissues and cells which may lead to Parkinson's disease and Alzheimer's diease,<sup>18</sup> deficiency of Fe<sup>3+</sup> leads to liver damage, anaemia, Alzheimer's disease, Parkinson's disease and cancer.<sup>19</sup> To sense these metal ions, most of the probes, found in the literature, work in solution phase; there are very

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<sup>&</sup>lt;sup>†</sup>Electronic Supplementary Information (ESI) available: Figures showing the gelation profile change in fluorescence and UV-vis titrations of **1** and **2** with various metal ions, ion conducting plots, spectral data. See http://dx.doi.org/10.1039/b000000x/

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few reports on the probes that detect such ions in the gel phase (Tables S3 and S4).

Recognition and detection of these multiple analytes by using a simple design-based probe is challenging and interesting. In this full account, we wish to report the design and synthesis of a simple, new cholesterol-linked benzothiazole supramolecular gelator **1** (Fig. 1) that selectively recognizes picric acid (PA) from a series of other nitroaromatics and some bio relevant metal ions such as  $Ag^+$ ,  $Hg^{2+}$ ,  $Fe^{3+}$  and  $Al^{3+}$  under different conditions. Gelator **1** forms gel from nitrobenzene, benzene, toluene and DMF etc.



Fig. 1. Structure of compound 1.

In the presence of PA, the nitrobenzene-gel of **1** is broken to the sol and validates its visual sensing. In addition, the nitrobenzene gel of **1** is selectively broken to the sol in the presence of  $Ag^+$  and  $Hg^{2+}$  ions. Alongside, the sensing of  $Fe^{3+}$ and  $Al^{3+}$  ions is further ascribed through ratiometric spectral change in both emission and absorption spectra of **1** in CH<sub>3</sub>CN.

#### **Results and discussion**

#### Synthesis

Compound **1** was achieved according to the Scheme **1**. Initially, cholesterol was converted to the chloride **2** according to our reported procedure.<sup>20</sup> Oxidative condensation<sup>21</sup> of 2-aminothiophenol with 4-hydroxybenzaldehyde in EtOH containing few drops of trifluoroacetic acid (TFA) at 90 °C afforded compound **3** which on coupling with compound **2** in the presence of K<sub>2</sub>CO<sub>3</sub> in CH<sub>3</sub>CN under refluxing condition introduced the desired compound **1** in appreciable yield. All the compounds were characterized by usual spectroscopic techniques.



**Scheme 1.** (i) Chloroacetyl chloride, pyridine, dry CHCl<sub>3</sub>, rt, 10h; (ii) 4-hydroxybenzaldehyde, trifluoroacetic acid, C<sub>2</sub>H<sub>5</sub>OH, reflux 12h; (iii) **2**,. K<sub>2</sub>CO<sub>3</sub>, CH<sub>3</sub>CN, reflux, 10h.

#### Gelation study

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Gel formation of **1** was primarily investigated from various solvents using the conventional heating-cooling method. Gelation of **1** was observed in pure organic solvents such as nitrobenzene, benzene, toluene and DMF (Table S1 Art Elgo S1) while in semi-aqueous compositions DPI: Perhamed Jetter insoluble or gave precipitate. Analysis of the results reveals that gelation of 1 occurs from DMF with lowest mgc in the series (10 mg/mL). The benzene gel of 1 displays poor thermal stability in the series inspite of showing maximum mgc. In this context, the minimum gelation concentration (mgc) and the gel melting temperature ( $T_{gel}$ ) of the gels in different solvents are summarised in Table S1.

Structural analysis of compound **1** indicates that the cholesterol as hydrophobic surface is connected to the benzothiazole moiety *via* a rigid aromatic spacer (Fig. 1). It is presumed that  $\pi$ - $\pi$  stacking between the benzothiazole moiety and van der Waals interaction between the cholesteryl surface tune the self-aggregation of molecules.

In solution, compound **1** exhibited two closely spaced absorption peaks at 305 nm and 316 nm for the benzothiazole moiety. In gel state (nitrobenzene), a broad red shifted absorption at 340 nm was observed (Fig. 2a). Similarly, in fluorescence, the emission at 365 nm of the sol was shifted to 412 nm in the gel state with increase in intensity (Fig. 2b). Such spectral appearances were attributed to the aromatic stacking which encouraged the formation of *J*-aggregate.<sup>22</sup> Due to aggregation, the emission of **1** in the gel state was enhanced significantly (Fig. 2b).<sup>23</sup>



**Fig. 2.** Comparison of (a) normalised UV-vis and (b) fluorescence spectra ( $\lambda_{ex}$  = 310 nm) of **1** in sol and gel states; (c) X-Ray diffractogram of the nitrobenzene gel of **1**; (d) Probable mode of interaction of **1** in gel state.

Powder X-ray diffraction (XRD) study of the nitrobenzene gel of **1** was further done to understand the influence of  $\pi$ -stacking in the aggregation (Fig. 2c). Although the XDR diffraction did not show any sharp peak, a broad peak at  $2\theta = 23.7^{\circ}$  of significant intensity along with a shouldering at  $2\theta = 42.3^{\circ}$  was noted. The strong diffraction at  $2\theta = 23.7^{\circ}$  (d = 3.7 Å) is likely to be due to the occurence of two types of interactions within the gel matrix simultaneously *viz*. the van der Waals interactions between the cholesterol units and the  $\pi$ - $\pi$  stacking interaction of the aromatic units in **1**, suggested in

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Fig. 2d.<sup>14e,24</sup> The broad shouldering in the X-ray diffractogram at  $2\theta = 42.3^{\circ}$  corresponding to the d-spacing of 2.15 Å describes the crystalline nature of the gel fibers.

#### Morphology of the gels

Journal Name

The surface morphologies of the nitrobenzene and DMF gels of **1** were understood from SEM images. Both the nitrobenzene and DMF gels revealed the formation of highly cross-linked fibrous network (Fig. 3). The gels were thermoreversible in nature and exhibited temperature-induced reversible gel-sol phase transition.



Fig. 3. SEM images of xerogel of 1 prepared from (a), (b) nitrobenzene and (c), (d) DMF.

#### **Rheological study**

To evaluate the mechanical properties of the nitrobenzene (NB) and DMF gels of **1**, rheological studies were carried out (Fig. 4 and Table 1). In amplitude sweep (at lower strain) and frequency sweep (over the entire range studied) experiments of both the gels, the storage modulus (G') was significantly higher than the corresponding loss modulus (G'') indicating their true gelling behaviour. However, the gels displayed considerable differences in G' and G'' values, critical strength, crossover and gel strength.

The DMF-gel of **1** exhibited ~1.7 times higher storage modulus (*G'*) than the nitrobenzene gel establishing to be more stiffer than the later one. Furthermore, the DMF gel showed higher critical strength (measurement of gel strength) as well as higher crossover (measurement of maximum strain bearing capability before complete demolition of the gel) than the nitrobenzene-gel, suggesting greater strain-bearing capability of the gel. Again, lower value of tan  $\delta$  of the DMF-gel, in comparison to the nitrobenzene gel, demonstrated its higher mechanical strength. However, both the gels were completely destroyed (gel-to-sol transition) at very low strain (crossover at < 10% strain) and thereby suggested their brittle natures. In short, higher magnitude of *G'*, critical strain and crossover and lower tan  $\delta$  values of DMF gel established DMF as the good solvent of choice than nitrobenzene for gelation of **1**.



**Figure 4**. Rheology study of the gels of **1**; (a and c) amplitude sweep (at constant frequency of 1Hz) and (b and d) frequency sweep (at constant 0.05% strain) experiments [gels were prepared at a concentration 1.2 wt% of respective mgc and the experiments were carried out at 25 °C].

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

Solvent	Critical strain (%)	Crossover (% strain)	G′ <sub>av</sub> * (Pa)	G″ <sub>av</sub> * (Pa)	tan δ ( G″ <sub>av</sub> /G′ <sub>av</sub> )
NB	0.08	0.6	34447	8788	0.25
DMF	0.41	1.6	59829	2855	0.04

\*  $G'_{av}$  and  $G''_{av}$  values were calculated from frequency sweep data

#### Sensing and detection of Picric Acid (PA) Gel phase interaction

In order to understand the sensing behavior of the gel towards nitroaromatics (especially nitrophenols), nitrobenzene gel was chosen. Importantly, DMF gel was not considered due to its nonresponsive behavior towards inertness or the nitroaromatics studied. However, in the experiment, the gel formation ability of 1 in nitrobenzene at room temperature was examined in the presence of nitrophenols and phenols (Fig. 5). It was observed that only picric acid (PA) resisted gelation. On the other way, when the solution of PA (1 equiv.) in nitrobenzene was added on the top of the nitrobenzene gel of 1, the gel was slowly destroyed into yellow colored sol. Under identical conditions, other nitrophenols in the study did not disturb the gel. Hence, we believe that PA being strongly acidic than other phenolic analytes protonates benzothiazole nitrogen and is involved in developing charge transfer complex with the protonated benzothiazole for which the gel is ruptured.<sup>14</sup> Under the same conditions, survival of the gel in the presence of other phenolic analytes of lower acidic character than PA ruled out the possibility proton transfer from phenolic oxygen to the benzothiazole nitrogen. Interestingly, the gel state remained unaffected in the presence of organic acids like benzoic and acetic acids. However, protonation of the benzothiazole nitrogen using strong acid like trifluoroacetic acid (TFA) ruptured the gel immediately and gave pale yellow colored sol (Fig. 5). Both

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sols, obtained from the treatment of PA and TFA were converted to yellow colored gels upon adding triethylamine (Fig. S2). Thus the gel state of **1** not only recognized PA but also distinguished acetic/benzoic acid from TFA visually.



**Fig. 5.** Photograph showing the phase changes of **1** (20 mg/mL) in nitrobezene in the presence of 1 equiv. amount of (a) picric acid, (b) onitrophenol, (c) p-nitrophenol, (d) 2,4-dinitrotoluene, (e) m-dinitrobenzene, (f) p-cresol, (g) o-chlorophenol, , (h) benzoic acid, (i) acetic acid and (j) trifluroacetic acid after 2h.

#### Solution phase interaction

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To understand the solution phase interaction, UV-vis and fluorescence titrations of **1** were performed with the said analytes in CH<sub>3</sub>CN containing 1% CHCl<sub>3</sub>. Here, nitrobenzene solvent was replaced by CH<sub>3</sub>CN to avoid its interference in the spectroscopic study. In UV-vis, compound **1** exhibited absorptions at 305 nm and 316 nm with equal intensities. Addition of the nitrophenols except PA did not produce any change in the UV-vis spectrum. In fluorescence, on excitation at 310 nm, compound **1** displayed emission at 365 nm. The intensity of this emission was gradually decreased upon titration with PA (Fig. 6). Under similar conditions, other nitrophenols showed moderate or weak change in emission. In particular, simple phenols and aromatic acids did not produce any noticeable change in the emission spectrum of **1** (Fig. S3).



**Fig. 6.** (a) Probable mechanism of interaction of **1** with picric acid; (b) Change in emission of **1** ( $c = 2.50 \times 10^{-5}$  M) upon addition of 12 equiv. amounts of picric acid ( $c = 1.0 \times 10^{-3}$  M) in CH<sub>3</sub>CN containing 1% CHCl<sub>3</sub>; (c) Stern-Volmer plot for **1** ( $c = 2.50 \times 10^{-5}$  M) with different analytes ( $c = 1.0 \times 10^{-3}$  M) in CH<sub>3</sub>CN containing 1% CHCl<sub>3</sub>.

The Stern-Volmer plot as shown in Fig. 6c clearly reveals the strong quenching of fluorescence of **1** by PA. In this

connection, it is to note that although both  $\sqrt{12}$  Arrandon Predestroyed the gel of **1**, the solution of phase of the gel of **1** and the solution of phase of the gel of **1** (Fig. S3). Thus this result substantiates that not only the protonation of benzothiazole as depicted in Fig. 6a is responsible for introducing the change in emission but also the charge transfer complex formation between picrate and benzothiazolium units has the discrete role in quenching of emission. This is in accordance with the observations noted by us and others.<sup>11,14</sup>

To understand the interaction of picric acid with **1**, <sup>1</sup>H NMR was recorded. In presence of picric acid, the aromatic signals, especially of the benzothiazole motif, exhibited small downfield chemical shift (Fig. S4). The picric acid signal at 9.137 ppm underwent upfield chemical shift by 0.021 ppm on complexation. To our belief, this was attributed to the proton transfer from picric acid to benzothiazole nitrogen.

The emission titration data of **1** with picric acid were fitted in Benesi-Hildebrand equation to calculate the strength of interaction. The linear plot indicated 1:1 complexation (Fig. S5) and the association constant<sup>25</sup> was evaluated to be 4.59 x 10<sup>4</sup> M<sup>-1</sup>. The detection limit<sup>26</sup> of compound **1** for picric acid was calculated to be 9.55 x 10<sup>-7</sup> M (Fig. S5).

#### Metal ion sensing Gel phase interaction

Due to presence of benzothiazole unit that has the ability to bind metal ions,<sup>27</sup> we were keen to note the metal ion interaction features of **1** both in the sol and gel states. In this regard, the nitrobenzene gel of **1** was treated with several



**Fig.7.** (A) Photograph showing the phase changes of 1 (20 mg/mL) in nitrobezene in the presence of 1 equiv. amounts of (a) Hg<sup>2+</sup>, (b) Al<sup>3+</sup>, (c) Fe<sup>3+</sup>, (d) Ag<sup>+</sup>, (e) Cu<sup>2+</sup>, (f) Fe<sup>2+</sup>, (g) Zn<sup>2+</sup>, (h) Co<sup>2+</sup>, (i) Ni<sup>2+</sup>, (j) Cd<sup>2+</sup> and (k) Cu<sup>+</sup> after 2h; (B) Photograph representing the phase change of the nitrobenzene gel of 1 (20 mg/mL) upon successive addition of 1 equiv. amount of AgClO<sub>4</sub>, Hg(ClO<sub>4</sub>)<sub>2</sub> and excess TBACI.

metal ions such as  $AI^{3+}$ ,  $Fe^{3+}$ ,  $Hg^{2+}$ ,  $Cu^{2+}$ ,  $Cu^+$ ,  $Fe^{2+}$ ,  $Zn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cd^{2+}$  and  $Ag^+$  (used as their perchlorate salts). Importantly, DMF gel of **1** did not show any phase transformation or color change in presence of these metal ions. However, upon individual addition of 1 equiv. amount of

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these metal ions to the nitrobenzene gel, there was only gelto-sol phase transformation in the presence of  $Hg^{2+}$  and  $Ag^+$ ions (Fig. 7A). We presume that binding interaction of sulfur of benzothiazole unit with the thiophilic ions  $Hg^{2+}$  and  $Ag^+$ destroys the gel network to give the sol.

Comparison of <sup>1</sup>H NMR of **1** in the absence and presence of  $Ag^+$  and  $Hg^{2+}$  ions showed the downfield chemical shift of the benzothiazole ring protons and thereby confirmed the interaction although it was difficult to predict the binding mode (Fig. S6).

To distinguish between Hg<sup>2+</sup> and Ag<sup>+</sup>, tetrabutylammonium chloride was added to the broken gels. While Ag<sup>+</sup>-induced broken gel was retrieved in the presence of tetrabutylammonium chloride, Hg<sup>2+</sup>-induced broken gel remained undisturbed (Fig. 7B).

#### Solution phase interaction

To understand the binding interaction in solution, UV-vis and fluorescence titrations were performed with the metal ions in CH<sub>3</sub>CN containing 1% CHCl<sub>3</sub>. In UV-vis, compound **1** showed strong absorptions at 305 nm and 316 nm. On titration with Fe<sup>3+</sup> ion, the absorption bands at 305 nm and 316 nm were gradually decreased in intensity with simultaneous growth of a new peak at 350 nm. This resulted in the formation of a clear isosbestic point at 325 nm which confirmed the formation of a new species in solution (Fig. 8a). A similar drastic change in absorption spectrum of **1** was found in the presence of Al<sup>3+</sup> ion (Fig. 8b). Under the identical conditions, small change in absorption of **1** in the presence of Hg<sup>2+</sup> (Fig. 8c) and other metal ions expressed significantly weak interaction (Fig. S7). Figure 8d, in this regard, shows the change in relative intensity of absorbance at 350 nm with the metal ions.



**Fig.8.** UV-vis titration spectra of **1** ( $c = 2.50 \times 10^{-5}$  M) upon successive addition of 3 equiv. amounts of (a) Fe<sup>3+</sup>, (b) Al<sup>3+</sup>, (c) Hg<sup>2+</sup> ( $c = 1.0 \times 10^{-3}$  M) in CH<sub>3</sub>CN containing 1% CHCl<sub>3</sub> and the relative change in absorbance of **1** ( $c = 2.50 \times 10^{-5}$  M) at 350 nm in the presence of 3 equiv. amounts of different metal ions.

In fluorescence, compound 1 on excitation at 310 nm gave sharp emission at 365 nm. Upon gradual addition of  $Fe^{3+}$  and

#### ARTICLE

Al<sup>3+</sup> ions to the solution of **1**, the emission at  $365_{\text{A},\text{PM}}$  was gradually decreased with the formation  $361_{\text{A},\text{PM}}$  was 405 nm. The newly appeared peak at 405 nm was gradually intensified during progression of the titration and gave an isoemissive point at 373 nm. Figure 9 indicates the change in emission of **1** with Fe<sup>3+</sup> and Al<sup>3+</sup> ions. In the event, Hg<sup>2+</sup> ion showed a similar spectral change but to the smaller extent as compared to that of Al<sup>3+</sup> and Fe<sup>3+</sup> ions (Fig. S8). Other metal ions were non-interacting (Fig. S8).



Fig. 9. Change in emission of 1 ( $c = 2.50 \times 10^{-5}$  M) in presence of 3 equiv. amount of (a) Fe<sup>3+</sup> and (b) Al<sup>3+</sup> ( $c = 1.0 \times 10^{-3}$  M) in CH<sub>3</sub>CN containing 1% CHCl<sub>3</sub>.

The binding interaction of Fe<sup>3+</sup> and Al<sup>3+</sup> ions with **1** was realized from <sup>1</sup>H NMR. Significant downfield chemical shift of benzothiazole protons in **1** occurred in the presence of Fe<sup>3+</sup> ions in CDCl<sub>3</sub>. Spectral shits were small in the presence of Al<sup>3+</sup> ion compared to the case of Fe<sup>3+</sup> ion (Fig. 10).

To understand the interference of other metal ions in the sensing of Fe<sup>3+</sup> and Al<sup>3+</sup> ion, competitive experiment was carried out by adding Fe<sup>3+</sup> and Al<sup>3+</sup> to the solutions of **1** in CH<sub>3</sub>CN containing other metal ions (Fig S9). As can be seen from Fig S9, no metal ion interfered in the binding of Fe<sup>3+</sup> and Al<sup>3+</sup> ions.



**Fig.10.** Partial <sup>1</sup>H NMR (400 MHz) of **1** ( $c = 3.07 \times 10^{-3}$ ) in the absence and presence of 1 equiv. amount of (a) Fe<sup>3+</sup> and (b) Al<sup>3+</sup> in CDCl<sub>3</sub>.

To distinguish  $Fe^{3+}$  from  $Al^{3+}$  ion, anion-induced decomplexation study was performed. In the event, upon addition of tetrabutylammoniumfluoride (TBAF), the ensemble of **1**-Fe<sup>3+</sup> lost its absorption and returned to the initial spectrum of **1** due to the formation of stable  $FeF_6^-$  complex. Under identical conditions, no significant spectral change was

Journal Name

#### ARTICLE

followed upon addition of TBAF to the ensemble of  $1\mbox{-}Al^{3\mbox{+}}$  (Fig. 11).



Fig. 11. Change in absorbance of (a)  $1-Fe^{3+}$  and (b)  $1-Al^{3+}$  complexes upon successive addition of TBAF ( $c = 1 \times 10^{-3}$  M) in CH<sub>3</sub>CN containing 1% CHCl<sub>3</sub>.

The stoichiometry of both the complexes were found to be 1:1 as determined from the Benesi-Hildebrand plot.<sup>25</sup> The association constants for Fe<sup>3+</sup> and Al<sup>3+</sup> ions were determined to be 1.42 x 10<sup>4</sup> M<sup>-1</sup> and 1.04 x 10<sup>4</sup> M<sup>-1</sup>, respectively. Analysis of the results gave the detection limits<sup>26</sup> of 4.07 x 10<sup>-8</sup> M and 1.65 x 10<sup>-8</sup> M for Fe<sup>3+</sup> and Al<sup>3+</sup> ions, respectively (Fig. S10).

#### Conclusions

In conclusion, cholesterol appended simple benzothiazole derivative 1 has been designed and synthesized. Hydrophobichydrophobic interaction between cholesterol units and the  $\pi\text{-}\pi$ stacking interaction of the benzothiazole moieties led to the gelation of 1 in various solvents such as nitrobenzene, benzene, toluene and DMF. Morphology of the nitrobenzene and DMF gels, as established from SEM study, revealed the formation of densely packed highly cross-linked fibrous network. The nitrobenzene gel was impressive in visual sensing of nitro aromatics and metal ions. The nitrobenzene gel selectively recognizes picric acid, Ag<sup>+</sup> and Hg<sup>2+</sup> by exhibiting gel-to-sol phase transition. Differential gel phase detection of Ag<sup>+</sup> from Hg<sup>2+</sup> has been possible with the aid of tetrabutylammonium chloride. While in fluorescence compound 1 in CH<sub>3</sub>CN exhibits selective sensing of PA over other nitro aromatics through quenching of emission, it effectively senses Fe<sup>3+</sup> and Al<sup>3+</sup> ions by showing ratiometric change in emissions. Further, differential sensing of Fe<sup>3+</sup> from Al<sup>3+</sup> has been possible through the addition of tetrabutylammonium fluoride to the ensembles of 1.Fe<sup>3+</sup> and **1**.Al<sup>3+</sup>. Thus, the present report dealing with a structurally simple and easily synthesizable gelator 1 for effective sensing of PA and a number of metal ions such as Ag<sup>+</sup>, Hg<sup>2+</sup>, Fe<sup>3+</sup> and  $Al^{3+}$  ions under different conditions is praiseworthy and it deserves attention in material chemistry. Further work along this direction is underway in the laboratory.

#### Experimental

#### Materials

Cholesterol, chloroacetyl chloride, pyridine, 2-aminothiophenol and trifluoroacetic acid were purchased from Spectrochem.

Tetrabutylammonium salts of anions and metal perchlorates used in the study were purchased from Sigma-Aldrich and were karefully handled. All solvents used in the synthesis were dried and distilled before use. Solvents used in NMR experiments were obtained from Aldrich. Thin layer chromatography was performed on Merck precoated silica gel 60- F254 plates. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker 400 MHz instrument. High resolution mass data were acquired by the electron spray ionization (ESI) technique on QTOf Micro YA 263 mass spectrometer. FTIR measurements of all the compounds and dried gels (xerogels) were carried out using a PerkinElmer L120-00A spectrometer (v<sub>max</sub> in cm<sup>-1</sup>) using KBr cell and KBr pellets, respectively. Scanning electron microscopy (SEM) images were obtained on EVO LS-10 ZEISS instrument. Fluorescence and UV-Vis studies were performed using ParkinElmer spectrofluorimeter and Shimadzu UV-2450 spectrophotometer, respectively. The X-ray diffraction study was carried out in a Bruker D8 Advance X-ray diffractometer operating at 40 kV and 20 mA with a Cu-target ( $\lambda = 1.54$  Å).

#### Synthesis

#### 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-1Hcyclopenta[a]phenanthren-3-yl ester (2):<sup>20</sup>

To a stirred solution of cholesterol (0.5 g, 1.29 mmol) in 20 mL dry CHCl<sub>3</sub> was added chloroacetyl chloride (0.16 mL, 1.93 mmol) and pyridine (0.05 mL, 0.65 mmol) under nitrogen atmosphere. The mixture was allowed to stir for 10 h at room temperature. After completion of reaction, the reaction mixture was neutralized with NaHCO<sub>3</sub> solution, and then was extracted with CHCl<sub>3</sub> (3 × 30 mL). The organic layer was washed several times with water and separated and dried over Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent gave white solid compound. Recrystallization from CH<sub>3</sub>OH afforded pure product **2** (0.58 g, yield 96%, mp 148 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  5.37 (m, 1H), 4.72 (m, 1H), 4.03 (s, 2H), 2.36 (m, 2H), 2.02–0.85 (m, 38H, cholesteryl protons), 0.67 (s, 3H); FTIR (KBr, cm–1): 2939, 2907, 2821, 1753, 1620, 1195.

#### 4-Benzothiazol-2-yl-phenol (3):

2-Amonobenzothiol (1 g, 8.0 mmol) and 4-hydroxybenzaldehyde (0.95 g, 7.78 mmol) were taken in 50 mL of EtOH containing few drops of trifluoroacetic acid (TFA) and the reaction mixture was refluxed at 90 °C for 8h. The progress of the reaction was monitored by TLC. After completion of reaction, the organic solvent was evaporated under reduced pressure and water was added to the crude mass. The reaction mixture was extracted with CHCl<sub>3</sub>. Evaporation of the solvent gave the product which was purified by column chromatography using 30% ethyl acetate in petroleum ether as eluent to afford the pure compound 1 in 70 % yield (1.23 g), mp 212 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub> containing two drops of  $d_{6}$ -DMSO, 400 MHz): δ 9.45 (s, 1H), 7.93 (d, 1H, J = 8 Hz), 7.87 (d, 2H, J = 8 Hz), 7.80 (d, 1H, J = 8 Hz), 7.39 (t, 1H, J = 8 Hz), 7.27 (t, 1H, J = 8 Hz), 6.89 (d, 2H, J = 8 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub> containing two drops of  $d_{6}$ -DMSO, 100 MHz): 168.3, 160.2, 154.0, 134.5, 129.1, 126.0, 124.8, 124.5, 122.4, 121.4, 116.0 ; FTIR (KBr) v cm<sup>-1</sup>: 3443, 2919, 2667, 2587, 1605, 1522, 1482, 1454, 1430, 1381, 1285; HRMS (TOF MS ES+): calcd. for  $C_{13}H_{10}NOS \ [M+H]^+: 228.0478 \ and \ found \ 228.0484 \ (M+H)^+.$ 

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#### Compound 1:

Journal Name

A mixture of compound 3 (1g, 4.44 mmol) and  $K_2CO_3$  (1.24 g, 9.0 mmol) was refluxed in dry CH<sub>3</sub>CN for 2h and then compound 2 (2.46 g, 5.32 mmol) was added to it. The reaction mixture was further refluxed for 12h. After completion of reaction, the organic solvent was evaporated under reduced pressure and water was added to the crude mass. The reaction mixture was extracted with 2% CH<sub>3</sub>OH in CHCl<sub>3</sub>. Evaporation of the solvent gave the product which was purified by column chromatography using 20% ethyl acetate in petroleum ether as eluent to afford the pure compound 4 in 82 % yield (2.38 g), mp 182 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.98-7.95 (m, 3H), 7.81 (d, 2H, J = 8 Hz), 7.40 (t, 1H, J = 8 Hz), 7.29 (d, 1H, J = 8 Hz), 6.94 (d, 2H, J = 8 Hz), 5.32 (d, 1H, J = 4 Hz), 4.70-4.68 (m, 1H), 4.60 (s, 2H), 2.30-0.67 (m, 43H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 167.9, 167.5, 160.0, 154.1, 139.1, 134.9, 129.1, 127.3, 126.2, 124.9, 123.1, 122.9, 121.5, 115.0, 75.4, 65.5, 56.6, 56.1, 49.9, 42.3, 39.6, 39.5, 37.9, 36.8, 36.5, 36.1, 35.8, 31.89, 31.81, 28.2, 28.0, 27.6, 24.2, 23.8, 22.8, 22.5, 21.0, 19.3, 18.7, 11.8; FTIR (KBr) v cm<sup>-1</sup>: 3416, 2933, 2867, 1760, 1606, 1483, 1433, 1206. HRMS (TOF MS ES+): calcd. for  $C_{42}H_{56}NO_3S$  [M+H]<sup>+</sup>: 654.3975 and found 654.3979 (M+H)+.

#### Gelation test and SEM imaging

Required amount of compound **1** was dissolved in desired solvents (nitrobenzene and DMF, shown in Table 1S) (1 mL) forming a homogeneous solution, slightly warmed and then allowed to cool slowly to room temperature to form a gel. To study the effect of nitrophenols and metal ions, required amounts of analytes were added to the nitrobenzene gel of compound **1**. All the gels were tested by an inversion of vial method. Samples of gels for SEM imaging were dried under vacuum and then coated with a thin layer of gold metal.

#### Determination of gel melting temperature (T<sub>gel</sub>)

The gel-to-sol transition temperature  $(T_{gel})$  was measured by the dropping ball method. In this test, a small glass ball was carefully placed on the top of the gel to be tested, which was present in a test tube. The tube was slowly heated in a thermostated oil bath until the ball fell to the bottom of the test tube. The temperature at which the ball reaches the bottom of the test tube is taken as  $T_{gel}$  of that system.

#### General procedures for fluorescence and UV-vis titrations

Stock solutions of compound **1** were prepared in CH<sub>3</sub>CN in the concentration range of ~  $10^{-5}$  M. An amount of 2 mL of the solution of **1** was taken in the cuvette. Stock solutions of guests/analytes were prepared in the same solvents in the concentration range of ~  $10^{-3}$  M and were individually added in different amounts to the solution of **1**. Upon addition of analytes, the change in emission of **1** was noted. Same stock solutions for **1** and guests/analytes were used to perform the UV-vis titration experiment. Solution of the analyte was successively added in different amounts to the solution of **1** (2 mL) taken in the cuvette and the absorption spectra were recorded. Both fluorescence and UV-vis titration experiments were carried out at 25 °C.

Binding constant determination from fluorescence<sup>25</sup>

Benesi-Hildebrand plot was adopted to determine interibinding constant value using the expression:  $I_0/(I-I_0) \oplus [e_M^{-1}f(e_M^{-3}G)/e_G)](K_0^{-12}C_g^{-F}$ +1), where  $\epsilon_M$  and  $\epsilon_C$  represent molar extinction coefficients for compound **1** and the complex, respectively, at a selected wavelength,  $I_0$  denotes the emission intensity of free compound **1** at that specific wavelength and  $C_g$  is the concentration of the guest/analyte. The measured emission  $I_0/(I-I_0)$  as a function of the inverse of the guest concentration fits a linear relationship, indicating 1:1 stoichiometry of the compound **1**- guest complex. The ratio of the intercept to the slope was used to determine the binding constant K<sub>a</sub>.

#### Calculation of detection limit<sup>26</sup>

Detection limit was calculated by using fluorescence titration data. The emission of compound **1** was measured 6 times, and the standard deviation of blank measurement was achieved. To have the slope, emission intensities were plotted against concentrations of guests. The detection limits were calculated using the equation: detection limit = 3s/k, where s is the standard deviation of the blank measurement, and k is the slope.

#### **Conflicts of Interest**

There are no conflicts to declare.

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#### **GRAPHICAL ABSTRACT**

## Cholesterol linked benzothiazole: A versatile gelator for detection of picric acid and metal ions such as Ag<sup>+</sup>, Hg<sup>2+</sup>, Fe<sup>3+</sup> and Al<sup>3+</sup> under different conditions

#### Subhendu Mondal, Rameez Raza and Kumaresh Ghosh\*

Cholesterol appended benzothiazole **1** has been designed, synthesized and studied interaction with nitrophenols and bio relevant metal ions in solgel medium. Compound **1** exhibits gelation in different solvents. As application, the nitrobenzene gel selectively recognizes picric acid (PA) over a series of nitroaromatics by exhibiting gel-to-sol phase transition with distinguishable color change from pale yellow to deep yellow. On the other hand, the nitrobenzene gel shows selective recognition potential for  $Ag^+$  and  $Hg^{2+}$  ions through gel-to-sol phase transition and the cations are distinguished by F<sup>+</sup>. The gelator **1** also reveals measurable selective interaction with picric acid over a series of nitroaromatics in CH<sub>3</sub>CN containing 1% CHCl<sub>3</sub>, compound **1** further, shows affinity towards Fe<sup>3+</sup>, Al<sup>3+</sup> and Hg<sup>2+</sup> with distinguishing features.

