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"*Switch on*" fluorescent sensor for the detection of fluoride ions in solution and commercial tooth paste

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Abstract: A simple and novel uracil based chemosensor (**1)** has been developed by one step reaction, which selectively detected F^- ions via "*switch on*" fluorescence mode. Upon the addition of F^- ion to CH_3CN solution of **1**, the non-fluorescent probe became highly fluorescent, showing a color change from colorless to fluorescent blue, when irradiated with 280 nm light. ^1H NMR studies revealed the binding sites of chemosensor **1,** where C-5 hydrogen and amine hydrogens formed hydrogen bonding with F^- ion. This binding mode was further confirmed using DFT calculations. Significantly, the detection limit of chemosensor **1** towards F^- has been evaluated to be 47.6 nM, which is lower than the maximum values of F^- (1.5 mg/L) ions permitted by WHO. The *in-situ* generated **1**-F^- complex has been used for secondary sensing of $Ca(NO_3)_2$, one of the component of the fertilizer. Moreover, the sensor has been successfully applied for detection of fluoride ion in commercial tooth paste.

Keywords: Uracil; F^- sensor; fluorescence on; Secondary sensor

1. Introduction

Recently, the field of anion sensing and recognition is in continuous growth as this area of supramolecular chemistry have a great relevance and applications, such as in organocatalysis where metal-free molecules can catalyze reactions via hydrogen-bonding interactions, and in separation of mixtures including anions at industrial scale [1]. Anions play a vital role in a number of biological and environmental processes and they can be either fundamental to sustain growth or work as harmful pollutants [2]. So, the development of sensors for anions that can be used under real-world to sense trace quantities of anions is the main concern of today's world. It is therefore not of any surprise that their synthesis have become a target of research in the last decade [3-4].

Amongst all the biologically essential anions, the fluoride (F^-) ion is attracting scientist's interest due to its small size, high charge density and hard Lewis basic nature. The F^- ion is known to play important roles in various biological, medical and environmental processes and is very

important for dental health and treatment of osteoporosis[5,6]. However, its overexposure may have a severe effect on human health and can cause gastric and bone diseases as fluorosis, urolithiasis, and even cancer [7,8]. The variance in its utility, equally valuable and otherwise, makes its recognition considerable. Further, calcium nitrate (a calcium salt), perform an essential role in agricultural industry as it is a very useful part of fertilizer and also employed for disease control and wastewater treatment [9]. It is the only water soluble source of calcium available for plants. Diseases like blossom end rot are easily controlled with calcium nitrate. Consequently, effective and investigative methods have to be applied for development of a sensing system for recognition of F^- ion and calcium nitrate ($Ca(NO_3)_2$).

Now-a-days, in the midst of all the constantly used techniques, the research on constructing sensors with good sensitivity and selectivity has been of great concern [10]. Among them, the fluorescent sensors have attracted a considerable interest which has led to the development of highly specific probes with a wide range of applications in environmental chemistry, biochemistry, and cell biology [11]. The fluorescent methods present the advantages of simplicity, rapid response, sensitivity, low cost, non-destructive methodology, real-time monitoring and high spatial resolution via microscopic imaging [12-14]. Also, the analyses based on fluorescent sensors are easy to handle and more economical.

In the present study, we have designed and synthesized simple uracil appended chemosensor **1,** possessing uracil backbone, which is known to display a wide range of pharmacological activities and free-NH_2 group that can be used for detection of anions. This chemosensor **1** has been used for the selective recognition of F^- in CH_3CN using fluorogenic "*switch-on*" modes. This can be attributed to the perturbation of excimer band of uracil due to F^- binding with **1**, resulting in released fluorescence of individual molecule of **1**. Furthermore, the complexed **1**-F^- species generated in situ has been used as a platform for recognition of $Ca(NO_3)_2$ via fluorescence quenching. Thus, chemosensor **1** behaves like a fluorescence sensor for both anionic and cationic species, based on a different approach to that of a chemosensing ensemble. The analytical applications of **1** were also tested for the detection of F^- in commercial tooth paste powder.

2. Experimental

2.1 Materials and methods

6-Amino-1, 3-dimethyluracil, 2-hydroxybenzaldehyde, trifluoroacetic acid, calcium nitrate, tetrabutylammonium salts of various anions and perchlorate salts of various metal ions were purchased from Aldrich. All other chemicals were used as received without further purification. Acetonitrile (CH_3CN) was of HPLC grade. Melting points were determined in capillary and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a BRUKER AVANCE 400 and 100 MHz instrument using tetramethylsilane as an internal standard. Various anions such as F^-, Cl^-, Br^-, I^-, OH^-, AcO^-, HSO_4^-, $H_2PO_4^-$, SO_4^- were added as their tetrabutylammonium salts, whereas all the metal ions such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Hg^{2+} were added as their perchlorate salts for UV-vis and fluorescence experiments. Aliquots of analytes (anions or metal ions) under investigation were then injected into the sample solution and the solutions were kept for some time to get stabilized after each addition and then they were scanned.

2.2 General procedure for UV-vis and fluorescence experiments

The UV-vis and fluorescence titrations were performed using 20 μM and 2 μM solution of **1,** respectively, in acetonitrile solution. All the UV-vis experiments were conducted on Shimadzu UV-240 spectrometer; while fluorescence spectra were carried out using HITACHI-7000 spectrophotometer equipped with 220-240 V Xe lamp with quartz cell of 1 cm width and 3.5 cm height. The excitation wavelength was taken as 350 nm for sensor **1** with 5 nm excitation as well as emission slit widths for fluorescence studies. Stock solutions of the sensor **1** (0.01 M) were prepared in DMSO and were diluted with CH_3CN solution for further different spectroscopic analyses. All absorption scans were saved as ACS II files and further processed in Excel(tm) to produce all graphs shown.

2.3 General procedure for ^1H NMR experiments

Two stock solutions were prepared in $CDCl_3$, one of them containing host (**1** of 3.59 x10^{-2} M conc.) only and other containing an appropriate concentration of guest (F^-). Aliquots of these two solutions were mixed directly in NMR tube, which then was diluted to 0.5 mL with $CDCl_3$ if required.

*2.4 Synthesis of 10-(6-Amino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydro-pyrimidin-5-yl)-1,3-dimethyl-1,10-dihydro-9-oxa-1,3-diaza-anthracene-2,4-dione **(1)***

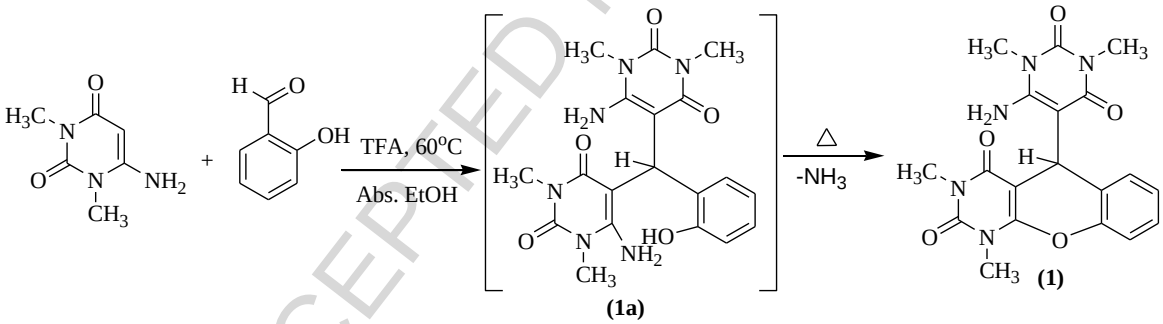
2-Hydroxybenzaldehyde (0.343 ml, 3.22 mmol) was dissolved in 40 ml absolute ethanol in a round bottom flask. To this mixture, 6-amino-1, 3-dimethyluracil (0.5 g, 3.22 mmol) and few drops of trifluoroacetic acid were added. The reaction mixture was heated at 60^{o}C for 5 h (as indicated by

TLC). The reaction mixture was then cooled to room temperature. The solid formed was filtered and recrystallized from chloroform/methanol mixture to get the desired product **(1).** Off-white soild; 86% yield; m.p. (^{o}C) 245-248; FT-IR (neat, ν cm^{-1}): 3381 ($\upsilon_{O\text{-}Hstr.}$), 1694 ($\upsilon_{C=Ostr.}$), 1581 ($\upsilon_{Ar\text{-}C=Cstr.}$); ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 7.22 (s, 1H, Ar-H), 7.13 (s, 1H, Ar-H), 7.11-7.08 (m, 2H, Ar-H), 5.81 (s, 2H, NH_2, exchanges with D_2O), 4.84 (s, IH, C-H), 3.53 (s, 3H, CH_3), 3.48 (s, 3H, CH_3), 3.33 (s, 3H, CH_3), 3.10 (s, 3H, CH_3); ^{13}C NMR (100MHz, $CDCl_3$, ppm): δ 164.1, 161.3, 154.3, 151.5, 128.3, 127.9, 125.2, 123.4, 115.6, 93.2, 87.8, 30.3, 29.3, 28.2, 27.7; HRMS : *m/z* (relative abundance (%), assignment) = 817.23 [100, $(2xM + 23)^{+}$]. ^{1}H NMR (in $CDCl_3$), ^{1}H NMR (in $CDCl_3$+D_2O), ^{13}C NMR and HRMS spectra of **1** have been shown in Figs. S1-S4.

3. Results and discussion

*3.1 Synthesis of chemosensor **1***

Chemosensor **1** has been synthesized by refluxing 6-amino-1,3-dimethyluracil and salicyladehyde in ethanol containing few drops of TF. Here, initially open di(uracilyl) derivative, **1a,** was formed, which finally underwent cyclocondensation to form chemosensor **1.** Earlier, Dabiri et al. also reported that 6-amino-1,3-dimethyluracil upon reaction with aromatic aldehydes catalysed by HOAc in ionic liquid as solvent, resulted to the formation of such closed ring structure [15].



Scheme 1. Synthesis of the target chemosensor **1**.

3.2 Absorption spectral studies towards anions

The recognition behaviour towards various anions such as CN^{-}, F^{-}, Cl^{-}, Br^{-}, I^{-}, AcO^{-}, HSO_4^{-}, $H_2PO_4^{-}$, SO_4^{2-} was examined by observing the changes in the UV-vis absorption spectra of the chemosensor **1** (20 μM) in CH_3CN (Fig. S5). The UV-vis spectrum of sensor **1** displayed a peak at 280 nm, which decreased in intensity along with appearance of new band around 370 nm with the addition of F^{-} ions. The addition of other ions did not show any changes in absorption spectra. To quantitatively sense F^{-} ions, UV-vis titrations were carried out by adding different

concentrations of F^- ions to the CH_3CN solution of **1** (20 μM) (Fig 1). Upon subsequent addition of F^- ions, a new absorption band starts forming at 372 nm, whose intensity increased with increase in concentration of F^- ions and attained plateau after addition of 120 μM of F^- ion. The appearance of new band at longer wavelength has been attributed to increased ICT within whole molecule arising due to F^- ion binding [16]. The binding constant of **1** with F^- was evaluated to be 1.1 x 10^4 M^{-1} based on UV-vis titration using Benesi-Hildebrand equation given as below [17];

$$\frac{1}{A-A_o} = \frac{1}{A_{max}-A_o} + \frac{1}{[A_{max}-A_o]\,K\,[C]}$$

Here, A_o, A, and A_{max} is the absorbance of free **1**, measured with F^- and measured with excess amount of F^- at 372 nm, respectively. K is the association constant and [C] is the concentration of F^- ions added. A linear plot of $1/(A-A_0)$ versus $1/[F^-]$ indicated 1:1 stoichiometry of **1** with F^- ions . The limits of detection (LOD) value has been reasonably estimated to be 75 μM for F^- using the relation [18]:

$$LOD = 3\sigma s^{-1}$$

where σ = standard deviation of response and s = slope of the calibration curve.

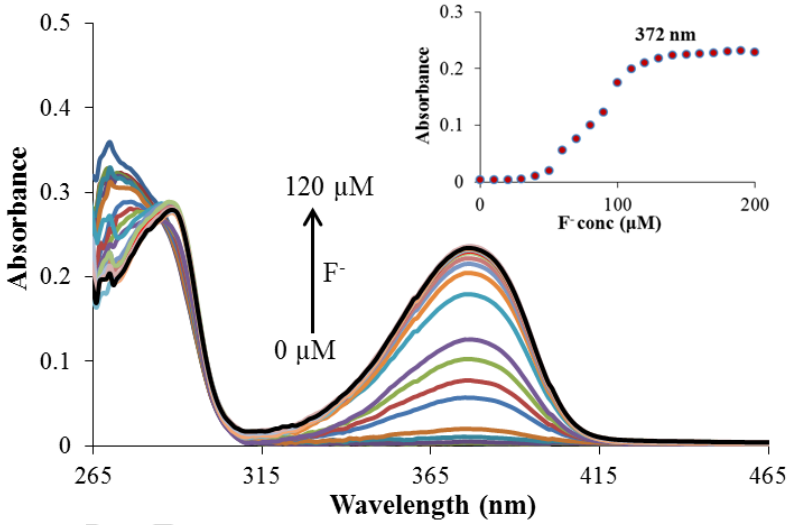


Fig. 1. UV-vis titration spectrum of **1** (20 μM) in CH_3CN in the presence of various concentrations of F^- ion; Inset: Plot of absorption intensity at 372 nm versus the concentration of added F^- ions.

3.3 Fluorescence emission spectral studies towards anions

The sensor **1** exhibits a non-fluorescent nature when excited at 280 nm. However, upon addition of various anions such as CN^-, F^-, Cl^-, Br^-, I^-, AcO^-, HSO_4^-, $H_2PO_4^-$, SO_4^{2-}, only addition of F^- ions to solution of **1** (2 μM; CH_3CN) enhanced its fluorescence intensity (Fig. S6). All other tested ions displayed negligible fluorescence response under the same spectroscopic environment. This

fluorescence enhancement was also accompanied by color change from colorless to dark fluorescent blue, when irradiated with light of wavelength 280 nm (Fig. 2 inset).

To study the interaction between **1** and F^- ion quantitatively, fluorescence titration experiment was performed by the addition of different concentrations of F^- ions to solution of sensor molecule **1** (2 μM). The chemosensor **1** (2 μM) exhibited a weak excimer emission band at 419 nm with a stoke's shift of 139 nm, when excited at 280 nm (Fig. 2). The dimer peak corresponding to $[2x\ M+23]^+$ in mass spectra (Fig. S3) also supported to the excimer formation in chemosensor **1**.With the gradual addition of F^-, the fluorescence intensity increased progressively with negligible spectral shift. This has been attributed to the perturbation of excimer band and fluorescence emission of individual molecules of chemosensor **1** due to formation of **1**-F^- structure [19]. The Job's plot, ^{1}H NMR titrations and DFT calculations further supported this assumption.

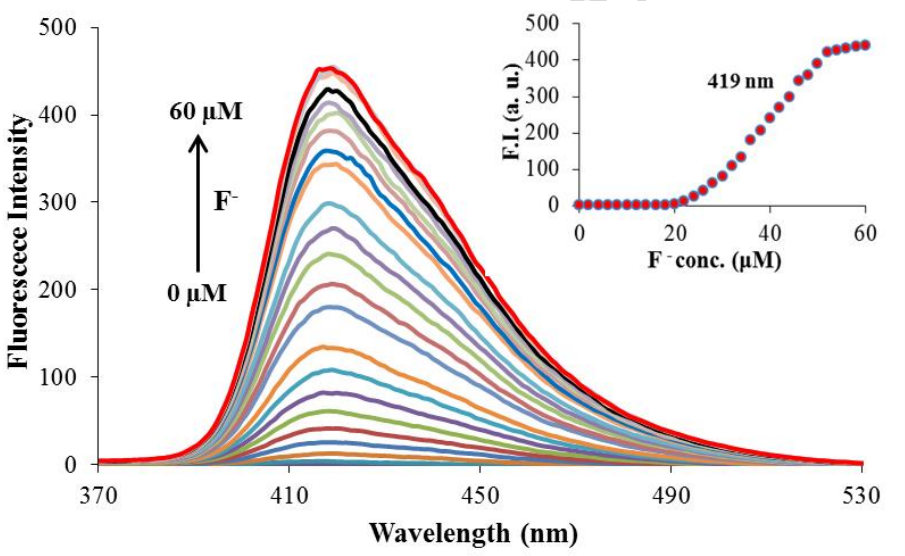


Fig. 2. Fluorescence titration spectrum of **1** (2 μM; λ_{ex} 280 nm) in CH_3CN in the presence of various concentrations of F^- ions; Inset: Plot of fluorescence intensity at 419 nm versus the concentration of added F^- ions.

The job's plot revealed the 1:1 binding stoichiometric ratio of chemosensor **1** with F^- ion (Fig. S7). The binding constant between sensor **1** and F^- and the limit of detection was calculated to be 3.15 x 10^4 M^{-1} and 47.6 nM, respectively. Importantly, the calculated LOD values is lower than WHO limits of detection for F^- (1.5 mg/l) [20].

3.3 ^{1}H NMR titration

To examine the binding sites responsible for the optical (absorption and fluorescence) changes observed in the sensor **1** upon the addition of F^- ion, ^1H NMR titration experiment was performed (Fig. 3). With the addition of 0.05 equiv. of F^- ions, the signal due to $–NH_2$ of free sensor **1** at δ 5.7 ppm was initially broadened. However, clear downfield shifting along-with further broadening of $–NH_2$ signal with the addition of 1.5 equiv. of F^- ion pointed to formation of hydrogen bonding between $–NH_2$ of sensor **1** and F^- ion. Also the peak due to C-5H broadened upon the addition of 1.5 equiv. of F^- ion, indicating its involvement in F^- binding.

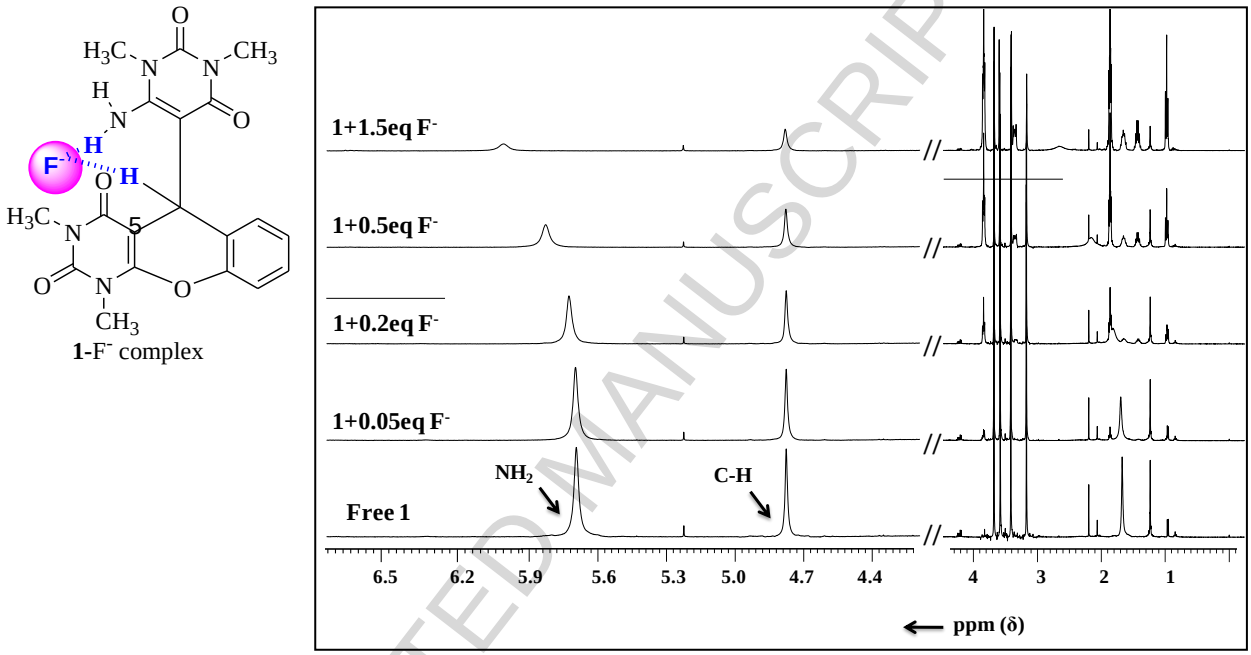


Fig. 3. ^1H–NMR titration of **1** (3.59 x10^{-2} M) with incremental addition of F^- in $CDCl_3$.

3.4 DFT Computational studies

To evaluate the structural properties and binding nature of the chemosensor **1**, computational calculations were carried out with and without F^- ion. The optimization of the structures of chemosensor **1** and the **1**-F^- complex (1:1) were performed by Density Functional Theory (DFT) method. The DFT calculations were done using the Gaussian 09 package using the exchange correlation function B3LYP and the basis set 6–31G (d, p) for C, H, N, O and F atoms. The energy evaluation diagram (Fig. 4) showed that on complexation of **1** with one F^- ion, the energy gap of HOMO and LUMO decreased with respect to free chemosensor indicating the formation of a stable complex and validating the 1:1 binding stoichiometry. Also, the bond length of one N-H got increased from 1.007 Å (in **1)** to 1.503 Å (in the **1**-F^- complex); whereas the bond distance of the

other N-H remained the same, i.e., 1.009 Å. Moreover, there was a slight increase in the C-5H bond distance from 1.0953 Å (in **1)** to 1.1455 Å (in **1**-F^- complex). This clearly indicated the interaction of F^- ion with only one N-H of free $–NH_2$ group and the hydrogen of C-5H in **1**- F^- complex. Furthermore, the electron density of the LUMO of **1** lied on the electron donating part of the respective ligands and for the HOMO, the electron density was spread over both the electron donating and electron withdrawing parts. The contour plots of the LUMO after the addition of F^- ions illustrated that the electron density was over the electron donating part of chemosensor **1**, however the electron density of the HOMO was only on the electron withdrawing part (Fig. 4).

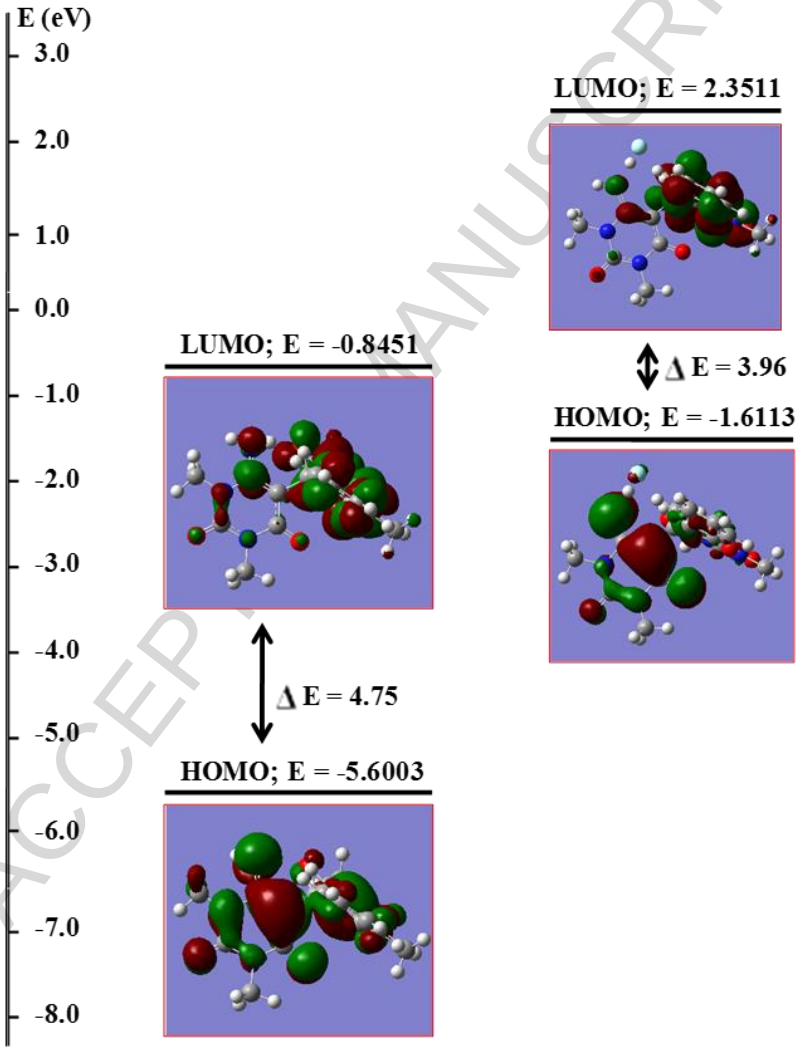


Fig. 4. DFT computed LUMO and HOMO diagrams of sensor **1** and **1 +** F^- complex.

3.5 Selectivity in the presence of competitive anions

The selectivity of chemosensor **1** was endorsed towards F^- ions in the presence of various interfering ions (Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4 and SO_4^{2-}) by using fluorescence spectroscopy. 100 equiv. of aforementioned ions were added to 1-F^- (2 μM of **1** with 10 added equiv. of F^-) acetonitrile solution. The bar graphs (Fig. 5) clearly represent the non-interference of various anions in the recognition process.

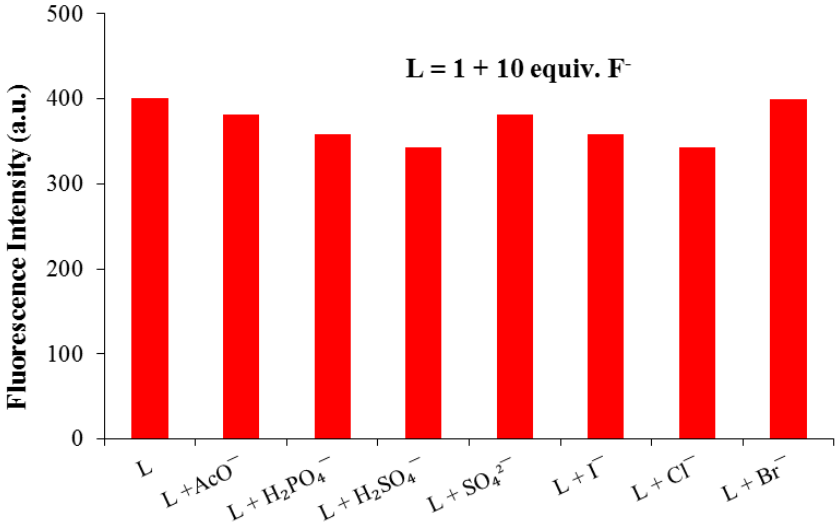


Fig. 5. Anion selectivity graph of **1** (2 μM) via changes observed in fluorescence emission spectra with addition of 10 equiv. of F^- and 100 equiv. of other interfering cations in CH_3CN.

3.6 Fluorescence switch off sensing of Ca^{2+}

As sensor **1** possessed various heteroatoms, so, its interaction with different metal ions such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Hg^{2+} (perchlorate was used as a counter ion) along with $Ca(NO_3)_2$ was investigated through UV–vis and Fluorescence spectra by adding their 100 equivalents to CH_3CN solution of **1** (20 μM for UV–vis spectra / 2 μM for fluorescence spectra). The absorption band of **1** lying in range of 275–290 nm was negligibly perturbed with addition of 100 equiv. of mentioned metal ions (Fig. S8a). The increased absorbance due to Hg^{2+} and Cu^{2+} ions at 270 nm was due to their own absorbance below 300 nm and for the same reason, any actual changes observed with Hg^{2+} and Cu^{2+} ions cannot be identified. Also, the chemosensor **1** remained non-fluorescence in the absence or presence of any of the said metal ions (Fig. S8b).

Recently, various F^- ion possessing moieties have been utilized for the recognition of calcium compounds, which are one of the components of fertilizers as calcium salts are known to have excellent affinity for fluoride [21-23]. For checking the viability of this approach, **1**-F^- complex was utilized as a platform for detection of above mentioned metal ions by fluorescence

spectroscopy in CH_3CN (Fig. 6a). Thus, the probe **1**-F^- was prepared *in situ* by addition of 30 equiv. of Ca^{2+} to **1** solution (2 µM). As shown in fig. 6b, **1**-F^- has strong emission peak at 419 nm (λ_{ex} 280 nm). The addition of $Ca(NO_3)_2$ ions to the solution of *in situ* generated **1**-F^- complex i.e. "*on state*" resulted in the quenching of fluorescence emission i.e. "*off state*". It is important to mention that addition of calcium perchlorate to solution of 1-F- complex also quenched fluorescence, but, even then $Ca(NO_3)_2$ is selected to study the sensing properties as $Ca(NO_3)_2$ is a very useful part of fertilizer and is the only water soluble source of calcium available for plants.

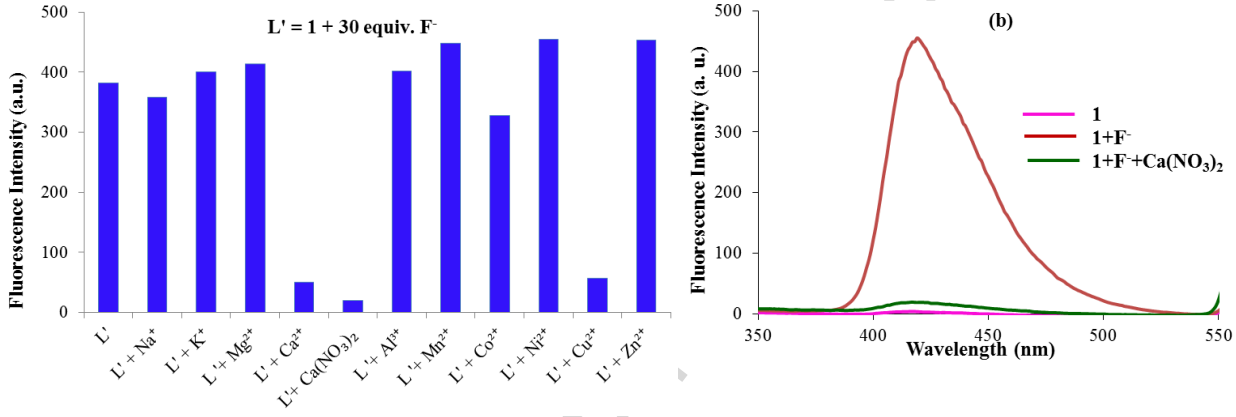


Fig. 6. Fluorescence spectra of **L' (1**-F^- complex) in CH_3CN in the presence of 50 equiv. of different metal ions.

The fluorescence spectra of **1**-F^- complex in acetonitrile solution in the presence of various amounts of Ca^{2+} is shown in figure 8. Upon addition of incremental amounts of Ca^{2+} ions (0-30 equiv.) to solution of **1**-F^- complex, a significant fluorescence quenching has been observed at 419 nm along with change in the color of the fluorescence back to colorless (Fig. 7). The binding constant between 1-F^- complex and Ca^{2+} has been determined as 4.13 x 10^4 M^{-1} with LOD to be 0.80 µM.

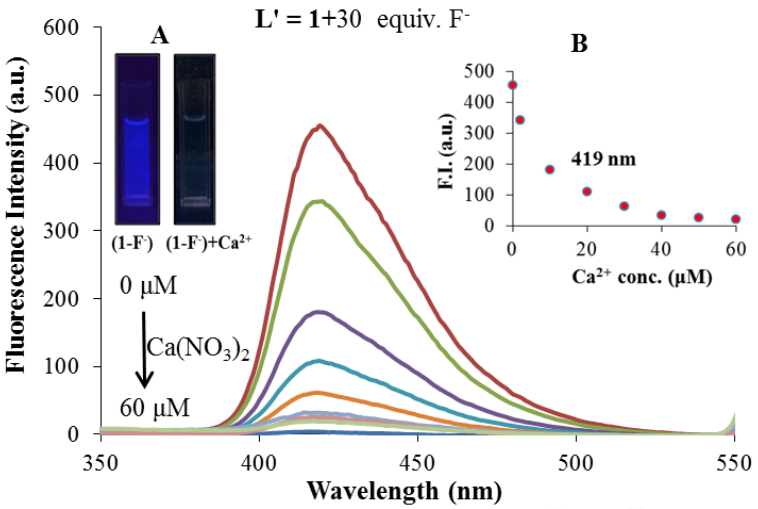
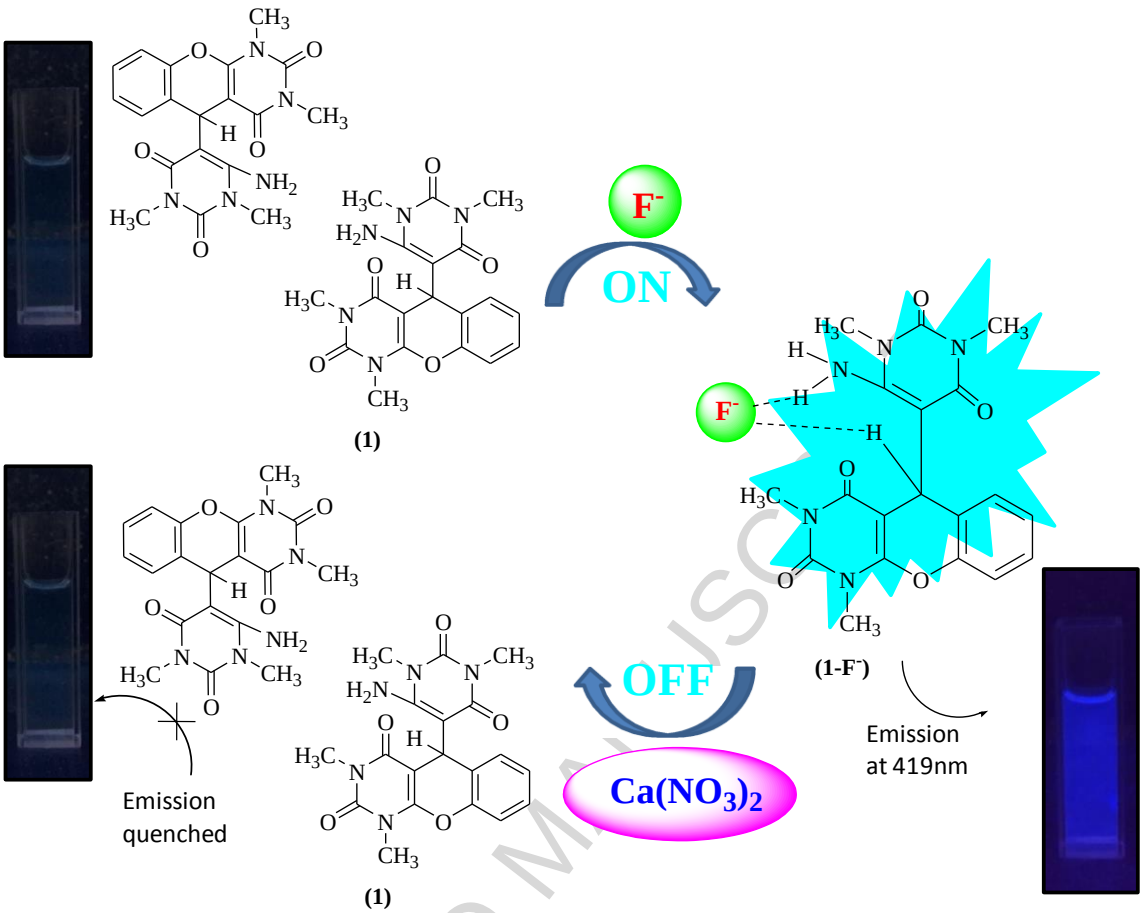


Fig. 7. Fluorescence titration spectrum of **1**-F^- complex in the presence of various concentrations of Ca^{2+} excited at 280 nm in CH_3CN; Inset A: Fluorescence color change in **1**-F^- complex before and after addition of Ca^{2+} ions; Inset B: Plot of fluorescence intensity at 419 nm versus the concentration of added Ca^{2+}.

To check the reversible nature of the chemosensor **1**, the F^- ion and $Ca(NO_3)_2$ were alternatively added to the solution of **1** and the fluorescence spectrum was recorded (Fig. S9). It was observed that the F^- ion enhanced the emission intensity remarkably, hence, showing "*switch on*" behavior. Furthermore, the addition of $Ca(NO_3)_2$ to the 1-F^- complex provoked a noticeable fluorescence change by showing "*switch off*" behaviour. Therefore, the repeated exhibition of "*switch on-off*" behaviour of the complex in fluorescence clearly implies that **1** is a reversible sensor.

*3.7 Plausible sensing model for chemosensor **1***

The plausible sensing mechanism of chemosensor **1** towards F^- and then $Ca(NO_3)_2$ has been proposed on the basis of fluorescence titration studies, job's plot, DFT computational calculations and ^1H NMR titration studies. Here, the free amino group of uracil along with C-5H takes part in hydrogen bonding with F^- ion in 1:1 stoichiometric manner (Scheme 2). The known strong binding of calcium salts towards F^- has been utilized to reverse the fluorescence as well as color changes.



Scheme 2: Proposed sensing mechanism for chemosensor **1** with F^- and $Ca(NO_3)_2$ in solution.

3.9 Real-life applications

To check the applicability of the proposed chemosensor **1** in real-life, it was tested for the determination of F^- ions in the toothpaste samples. For this analysis, 20 mg of toothpaste was taken and it was dispersed in 2 mL of acetonitrile. The obtained mixture was first sonicated, centrifuged and then filtered to separate the precipitates. The filtrate was used for the qualitative investigation of F^- ion. The addition of 100 µL of toothpaste solution into the 20 µM solution of the sensor **1** in acetonitrile solution resulted in fluorescent color changes from colorless to light fluorescent blue (Fig. 8), which clearly indicates the presence of F^- ion in the sample. Also, fluorescence emission spectrum was recorded for this sample which also showed the presence of F^- ion in the mixture. Hereafter, it can be said that the chemosensor **1** can be effectively applied for detection of F^- in real-life samples.

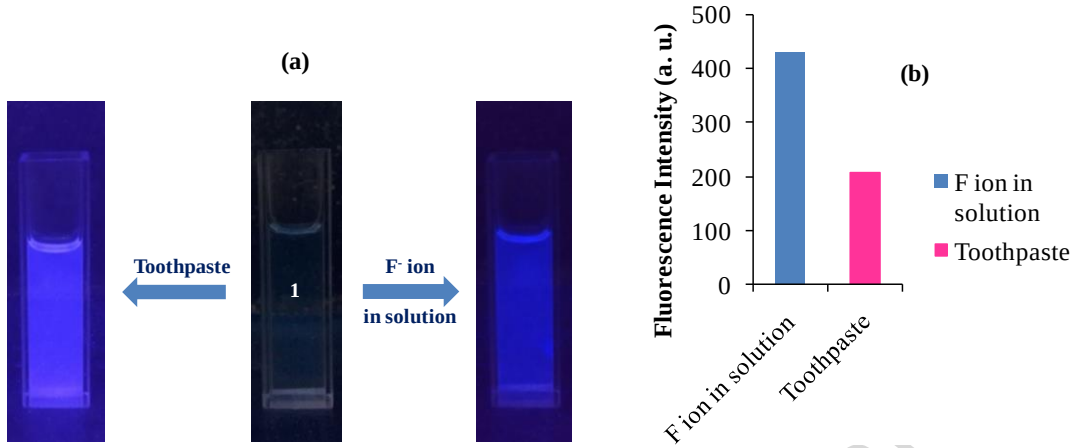
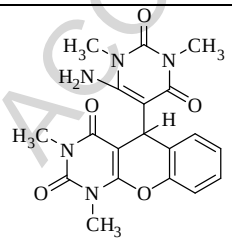
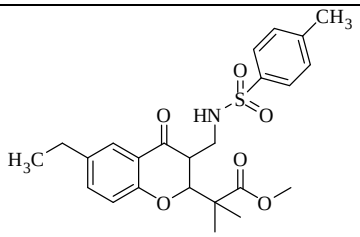
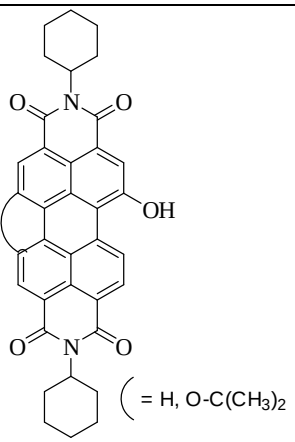
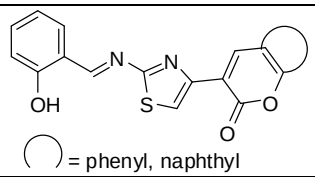
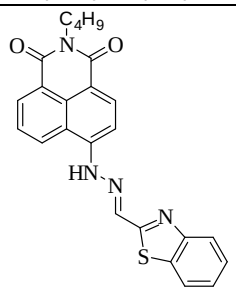


Fig. 8. (a) Fluorescence color changes and (b) fluorescence spectra in the presence of F^- ion and toothpaste.

3.10. Comparison with literature sensors for F^-

The comparison of the present chemosensor **1** with some previously reported receptors for F^- has been given in Table 1. From this table, it is clearly observed that the most of the reported sensors involve F- induced deprotonation of acidic OH or NH. In contrast, in the present work the free amino group of uracil along with C-5H in chemosensor **1** takes part in hydrogen bonding with F^- ion and detected F^- ions with lowest LOD value as compared to other reported sensors. Moreover, chemosensor **1** has the real life application in terms of detection of F^- ion in toothpaste. The **1.F**$^-$ complex has also been used for secondary sensing of $Ca(NO_3)_2$. Thus, the simple, one-step methodology of synthesis of chemosensor **1** makes it superior in terms of its easy synthesis, low LOD values and real life applications.

S. No.	Chemosensor	Binding sites	Fluorescence changes with F^- ions	LOD (in μM)	Ref.
1		-NH_2 and -CH	Fluorescence enhancement	0.0476	Present work
2		amidic NH	Fluorescence quenching	26	24

3		-OH	Fluorescence quenching	1.37, 1.24	25
4		-OH	Fluorescence enhancement	0.72, 0.46	26
5		=N-NH	Fluorescence quenching	0.41	27

Conclusions: To conclude, a simple and novel uracil based chemosensor **(1)** has been synthesized for fluorescent detection of F^- ion in acetonitrile. The addition of F^- ion to solution of **1** made it highly fluorescent along with color change from colorless to fluorescent blue. The sensing mechanism and the binding stoichiometry were confirmed by Job's plot, DFT computational calculations and ^{1}H NMR studies. The *in-situ* generated **1**-F^- complex has been used for secondary sensing of $Ca(NO_3)_2$, one of the component of the fertilizer. Moreover, the sensor can be applied in daily-life for the detection of fluoride ions. So, the work described in this paper strongly supports the excellent prospects of design envision of a simple multichannel chemosensor **1** and afforded a propitious outcome which is paramount for the advancement of research on chemosensing formats.

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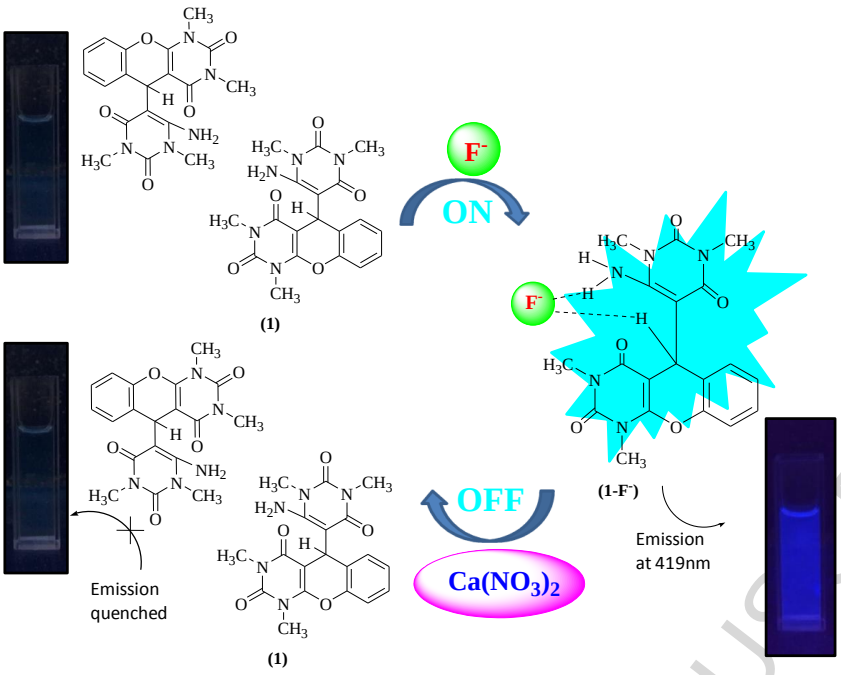

Graphical abstract

Research Highlights

- A simple, novel, tailor-made chemosensor synthesized by one-step reaction.
- Selective detection of F^- ions via "*switch on*" fluorescence mode.
- Binding mode was confirmed using fluorescence studies, ^1H NMR studies and DFT calculations
- LOD value for F- detection was 47.6 nM, which is lower than the maximum values of F^-.
- Secondary sensing of $Ca(NO_3)_2$, one of the component of the fertilizer.
- Detection of fluoride ion in commercial tooth paste