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Selective detection of fluoride and hydrogen sulfate anions by pyrimidine-based fluorescence chemosensor

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The binding and sensing abilities of pyrimidine based fluorescence chemosensor **L** towards different anions such as F^-, Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, $H_2PO_4^-$ and HSO_4^- have been examined by fluorescence spectroscopy in DMSO-H_2O (7: 3, v/v). Upon successive addition of various anions to DMSO-H_2O solutions of **L**; quenching in emission fluorescence is observed at 480 nm. Analysis of fluorescence emission changes suggested the formation of 1:1 complex of **L** with the anions. From the fluorescence binding constant data, it is found that **L** form strong complexes with F^- and HSO_4^- ions through H-bonding interactions. The selective response of F^- over other halides and HSO_4^- amongst other oxo-anions towards **L** may be explained on the basis of photo-induced electron transfer process.

Keywords: Fluorescence sensor, Pyrimidine-based probe, Binding constant, Colour change, Photo-induced electron transfer

Design of biologically active molecular probes for selective and sensitive detection of biological anions has fascinated significant interest[1-8]. Selective and specific recognition of biological anions play vital role in environmental, clinical and biological systems[9-14]. Apart from that, it is well documented that high doses of anionic species cause adverse health effects in humans[15-21].

Fluoride plays important role in biological, medical and other technological processes than other halides due to its unique properties such as small ionic radius, high charge density and basic character. Fluoride plays vital role in dental health and has found potential application in the treatment of osteoporosis. As a result, excess of F^- causes the dental or skeletal fluorosis, acute gastric and kidney problems[22-29]. On the other hand, hydrogen sulfate anions play most vital role in biological and industrial areas[30,31]. Recently, much attention has been given on developed of techniques for monitoring and detection of hydrogen sulfate anions. Amongst various methods used, optical sensing, colorimetric and fluorimetric titrations are most widely methods. Fluorescence spectroscopy is the most promising methods for sensing and recognizing because of its simplicity, high degree of specificity and low detection limit. Pyrimidine scaffold ascribed excellent fluorescence sensing due to its amazing photo physical properties. Here in, we wish to choose Rilpivirine drug, a pyrimidine based molecular probe (**L**) for selective and sensitive recognition of anions[32]. From fluorescence emission, it was found that receptor **L** showed significant fluorescence responses towards fluoride and hydrogen sulfate ions.

Materials and Methods

Materials

All chemicals are obtained from commercial sources and used without further purification. Dimethyl sulfoxide (DMSO) (HPLC grade) and all anions purchased were purchased from Merck and were used as received. Rilpivirine was purchased from Sigma-Aldrich (USA) and used as received.

Physical measurement

The FTIR spectra were recorded on Perkin-Elmer spectrum one spectrometer using KBr pellets. ^1H NMR (400 MHz), and ^{13}C NMR (100 MHz) spectra were recorded in DMSO-d6 with tetramethylsilane as the internal standard. UV-visible spectra were obtained by usuing Perkin-Elmer Lambda 750 UV-vis spectrophotometer.Fluorescence measurements were carried out with a Carry eclipse spectrofluorometer. The fluorescence titrations were carried out by taking 3 mL solution of **L** (10^{-5} M) and adding definite aliquot of various anions (10^{-5} M).

Calculation of binding constants

Binding constants of **L** with various anions were determined using the Benesi-Hildebrand equation by the fluorescence method.

$$\frac{1}{[I\text{-}I_0]} = \frac{1}{[I_1\text{-}I_0]} + \frac{1}{[I_1\text{-}I_0]k[Compound]} \quad \ldots(1)$$

Where I_0, I and I_1 are the emission intensities in absence of compounds, in presence of compounds and when the molecule is completely solubilized in compounds, respectively.

Results and Discussion

NMR and FTIR and mass spectra of **L** are given in Supplementary Data, Figs S1-S4 and S11. The anion binding properties of **L** were studied in DMSO-H_2O using absorption and fluorescence emission spectroscopy. From the absorption spectra; **L** was found to show absorption maxima at 330 nm. The absorption band at 330 nm appears due to π-π* charge transfer. In presence of F^- ions, a clear visual change from light greenish to colour less was observed by naked eye under UV-lamp at 365 nm (Supplementary Data, Fig. S10). However, in presence of other anions such as NO_3^-, $H_2PO_4^-$, ClO_4^-, Br^-, Cl^-, I^-, **L** failed to yield any significant colorimetric responses. Upon excitation at 340 nm, the fluorescence emission peak appeared at 480 nm. It was interesting to note that the presence of F^- and HSO_4^- ions altered the fluorescence emission behaviours; on the other hand, only slight change in fluorescence emission occurred on successive addition of other anions (Supplementary Data, Figs S5-S9). Upon addition of F^- to **L** turn off fluorescence was observed as show in Fig. 1. On the other hand, under similar condition, addition of HSO_4^- to **L**, resulted in quenching of fluorescence. The light greenish colour solution of **L** turned colourless in presence of F^- and HSO_4^- visible by naked eye under UV-lamp at 365 nm, (Supplementary Data, Fig. S10). To obtain a quantitative insight of the relation between **L** with F^- and HSO_4^- ions, a fluorescence titration was carried out with varying the concentration of F^- and HSO_4^- ions. Successive addition of F^- (10 µL each aliquots) to **L**, quenching in emission was observed. Similar observations were reported previously for Pyrrole-substituted Salicylimine Zn^{2+} complex[33,34]. From the fluorescence titrations, it is assumed that anion-H-bonding with the receptor changes the photo physical properties of fluorophores. In literature, receptors having -NH functional groups are found to be better, as chemosensor of F^- ions as shown in Scheme 1[35,36].

A small change in fluorescence emission was observed upon addition of Cl^- and Br^- to **L**, whereas no significant change was observed in case of I^-. By using Bensi-Hildebrand equation[37], it was found that **L** led a 1:1 complex with F^- with binding constant 6.32×10^6 M^{-1}. From the binding constant data, it showed that **L** formed strong complex with F^- over other halide and the binding trend follows the order $F^- > Cl^- > Br^-$. From the fluorescence experiment, it displays that the detection limit is lower than the permitted limit set by World Health Organization and Environment Protection Agency[38]. The lowest detection limit was found to be 2.21×10^{-7} M. In case of HSO_4^-, a quenched fluorescence emission was observed like F^- ions. From the binding constant it was found that HSO_4^- forms a 1:1 complex with **L** with binding constant 9.88×10^5 M^{-1}. The calculation shows that the detection limit (8.81×10^{-5} M) is much lower than the previous reported probes[39].

From the binding constant analysis, it was found that the ligand **L** formed complexes with different anions as following the binding trend $F^- > HSO_4^- > Cl^- > Br^- > ClO_4^- > H_2PO_4^- > NO_3^-$ as shown in Table 1. The quenched fluorescence emission occurred due to PET (photo-induced electron transfer) process as shown in Scheme 1. Strong complex formation of **L** with F^- as compared to HSO_4^- may be due to small ionic radius, high charge density and Lewis basic character of F^-.

In the field of supramolecular anion recognition, it is found that the behaviour of receptors is really quite different in dilute or in very dilute solution from their behaviour in the solid state. Hence, investigation of the binding mode in solution is very essential. Herein, ^1H NMR titration was carried out between **L** and F^- in DMSO-d6 at room temperature to support the sensing behaviour. Significant changes were observed for both-NH protons of **L**, suggesting that the -NH groups provide suitable sites of interaction between the receptor and anion in solution as shown in Fig. 2. From the ^1H NMR spectrum, the downfield shift of the -NH protons indicates strong interaction between F^- and **L** in solution state.

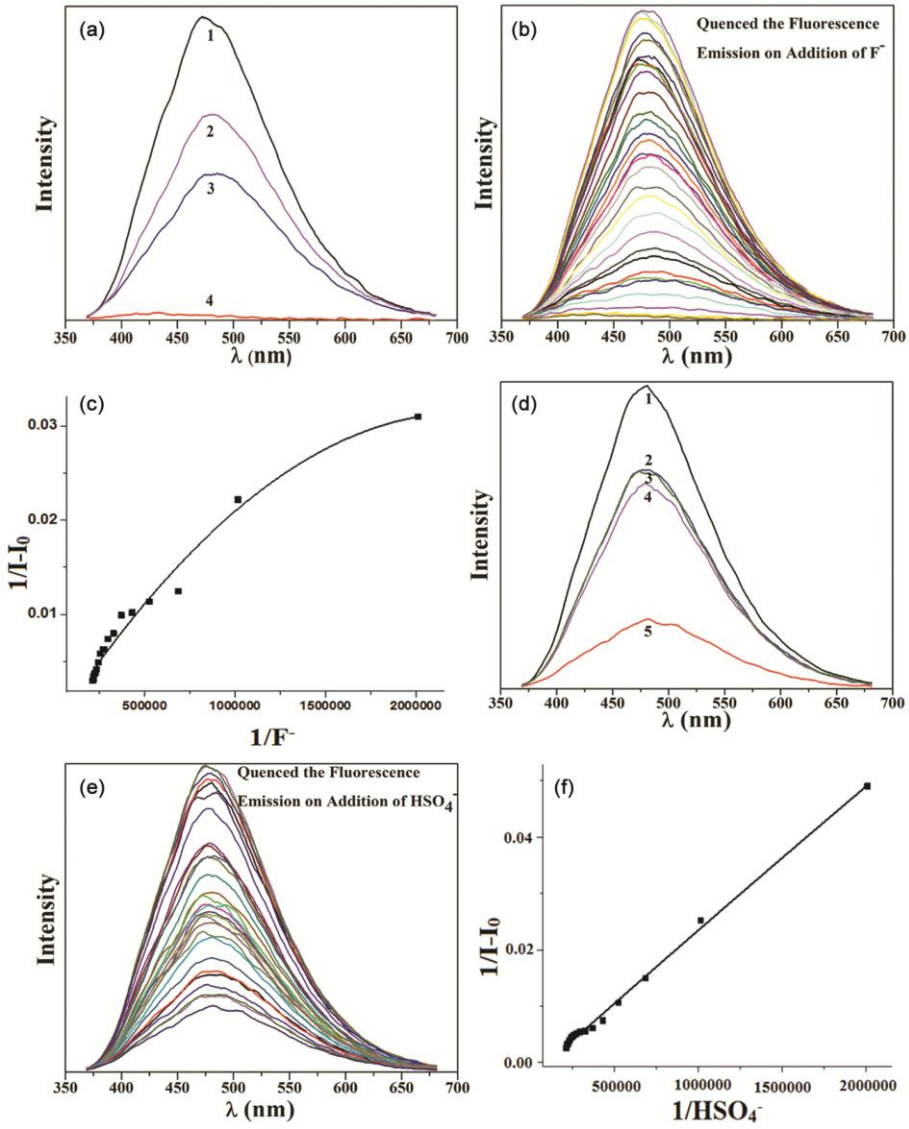
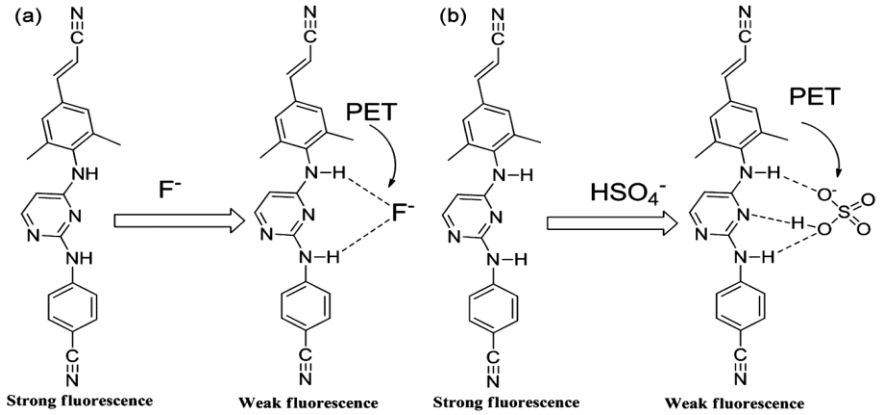


Fig. 1 — (a) Fluorescence spectra of (1) L (10^{-5} M), (2) L with Br^-, (3) L with Cl^-, (4) L with F^-, respectively; (b) Quenching in the fluorescence emission of L upon addition of F^-; (c) Binding constant plot for F^- ions; (d) Fluorescence spectra of (1) L (10^{-5} M), (2) L with NO_3^-, (3) L with $H_2PO_4^-$, (4) L with ClO_4^-, (5) L with HSO_4^-, (in the presence of 10^{-5}), respectively; (e) Quenching in the fluorescence emission of L on addition of HSO_4^-



Scheme 1 — Plausible mechanism of (a) L with F^- and (b) L with HSO_4^-

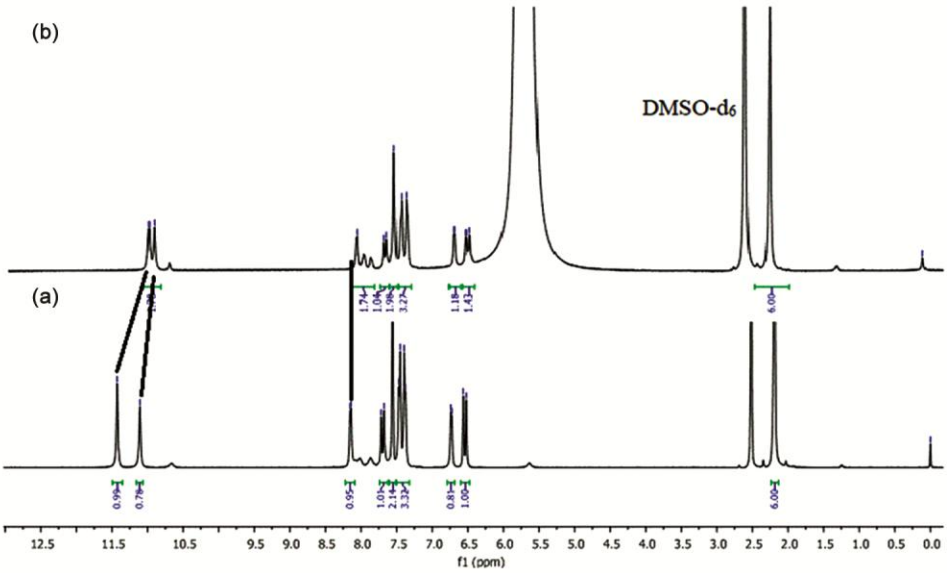


Fig. 2 — ^{1}H NMR spectra of (a) receptor (L) and (b) receptor L (in DMSO-d_6) + F^- (in D_2O)

Table 1 — Apparent binding constant (M^{-1}) for **L**

Receptor (L)	Anions	K (M^{-1})
L	F^-	6.32×10^6
	Cl^-	2.21×10^5
	Br^-	3.4×10^5
	NO_3^-	8.33×10^3
	$H_2PO_4^-$	2.64×10^4
	ClO_4^-	2.24×10^5
	HSO_4^-	9.88×10^5

Conclusions

In this study, we reported a pyrimidine based fluorescence molecular probe for selective recognition of anions by fluorescence titrations. The receptor **L** displayed strong binding affinity towards F^- compared to other halides and HSO_4^- (amongst other oxoanions). The receptor showed sensitive and selective recognition ofF^- and HSO_4^- ions, respectively. Due to the lower detection limit than the permitted limit set by World Health Organization and Environment Protection Agency, the receptor will be helpful to detect the F^- ions. It would help supramolecular researchers to understand the host-guest interactions.

Supplementary Data

Supplementary Data associated with this article are available in the electronic form at http://nopr.niscair.res.in/jinfo/ijca/IJCA_59A(12)1809-1813_SupplData.pdf.

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