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ARTICLE TYPE

Colorimetric and Ratiometric Fluorescent Chemosensor for Fluoride Ion Based on Phenanthroimidazole (PI): Spectroscopic, NMR and Density Functional Studies

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The anion chemosensor based on Phenanthroimidazole conjugate of biscarbanohyrazone, probe **PI** was designed, synthesized and characterized. Probe **PI** detected fluoride ion selectively with unique absorption as well as fluorescence changes which were not observable for other halides & anions. ^{1}HNMR and density functional studies on the system have been carried out to determine the nature of the interaction between probe **PI** and F^- responsible for the significant fluoride-induced changes in the absorption and emission properties of probe **PI**. The experimental results reveal that hydrogen-bonding followed by abstraction of acidic protons of imidazole –NH and urea –NH of probe **PI** by the fluoride ion, leading to the formation of anionic species, is responsible for the spectral changes. Finally, the use of test strip of the probe **PI** to detect fluoride was also reported.

Introduction

Anions are ubiquitous and play important roles in many chemical, environmental, and biological systems.[1-7] Anions like fluoride, acetate and phosphate play major roles in a wide range of chemical and biological systems and sometime they are of environmental concern.[8] For example, Fluoride is commonly used in dental care applications and exhibits inhibition of certain enzyme functions;[9] however, dental and skeletal fluorosis associated with high levels of fluoride in drinking water have been reported in various countries.[10] Recently, fluoride has been associated with osteosarcoma,[11] and exerting some effects on the brain, such as lower IQ (Intelligence Quotient) values in humans, in the presence of high fluoride concentrations in water.[12] High levels of fluoride have also been correlated with the inhibition of neurotransmitter biosynthesis in fetuses.[13] The recognition and detection of the fluoride ion are of growing interest because it is associated with nerve gases, the analysis of drinking water, and the refinement of uranium used in nuclear weapons manufacture. As a consequence, fluoride-indicating methodologies, which are developed to provide critical information for fluoride hazard assessment and fluoride pollution management, are in high demand. Among these techniques, fluorescent molecular sensing, which translates molecular recognition into tangible fluorescence signals, has received much attention.[14]

In recent years, considerable interest has focused on designing receptors for the highly sensitive and selective detection and monitoring of fluoride ions.[15] A fluorescent anion receptor may, upon addition of anions, give rise to a change in the absorption spectra, the associated color changes of which are visible to the naked eye.[16-18] As several factors contribute to the modulation of the fluorescence intensity of a system, considerable research has been devoted to the development of ratiometric fluorescent receptors, since they permit signal rationing and provide a built-in correction for environmental effects as well as increasing the dynamic range of emission measurements.[19] In light of the aforementioned, much more attention has been given to the design of artificial receptors with both colorimetric and ratiometric capabilities, because of their simple and fast implementation as well as their high selectivity of anion detection. Up to now, several ratiometric fluorescent receptors for F^- have been reported,[20] however, the realization of both colorimetric and ratiometric measurements for F^- is still a challenge. Colorimetric anion chemosensors are generally based on a receptor–chromophore format, where urea or thiourea units, among others (amides, pyrroles etc.), are usually used as the binding sites. For this kind of sensor, hydrogen-bond-induced π-electron delocalization, or NH deprotonation, are believed to be responsible for signalling the binding event.[21,22] Several investigations have been conducted to create ratiometric fluorescent receptors based on indole, carbazole and Bodipy[23,24] whereas Phenanthroimidazole based receptors as fluorescence ratiometric receptors for F^- have rarely been reported.

In this paper, our research group prepared a new and simple colorimetric anion receptor based on Phenanthroimidazole **(PI)** derivative, which showed efficient colorimetric and fluorometric selective sensor for F^- *via* naked eye detection. This receptor contains the hydrogen-bond-donor groups (biscarbonohydrazone and imidazole), fluorophore and the colorimetric groups (phenanthracyl and imidazole). The receptor exhibit remarkable fluorescence color changes visible to the naked eye in the presence of the fluoride anion, furthermore the receptor **PI** shows the expected change in fluorescence characteristics in a ratiometric manner. The experimental results show that receptor **PI** is highly selective and effective to recognize F^- in dry DMSO. More importantly, the recognition system is tolerant to protic solvents such as H_2O and MeOH in mixed DMSO/H_2O (95:5, v/v) solution.

The imidazole group has often been used as the binding group for anion chemosensors.[25] It is known that imidazole proton is stronger hydrogen bond donors than the protons in the amide bonds.[26] The acidity of the imidazole-NH proton with a pKa value of 11– 13, is much higher than an (C=O)NH amide with a pKa of 17. Considering that the imidazole and amide groups offers an ideal binding and signal transduction unit,[27] we envisage utilizing this property with a receptor (**PI**), which contains two types of acidic protons, imidazole –NH and carbonohydrazone –NH (C=O)NH– that can bind anion and based on the basicity and equivalence of the anion, multiple acidic protons could also be deprotonated. Our results show that the class of biscarbonohydrazone compounds are easily prepared, and are sensitive, selective, ratiometric, and colorimetric chemosensors for F^- anion.

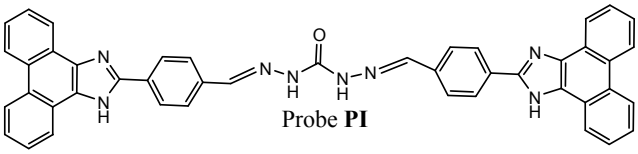
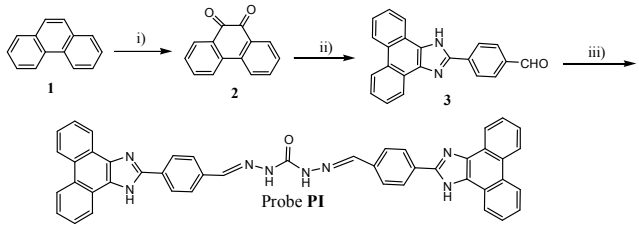


Fig.1. Structure of the new probe (**PI**).

Results and discussion

Phenanthroimidazole conjugate of biscarbanohyrazone, **PI** was synthesized in three consecutive steps starting from phenanthrene followed by the preparation of its imidazole derivatives **3,** as shown in scheme 1.



Scheme 1 Synthesis of probe PI**:** (i) $K_2Cr_2O_7$, H_2SO_4/Δ (ii) 1, 4-terephthalaldehyde,NH_4Ac/AcOH,reflux,3hrs.(iii)Carbohydrazide , EtOH/H_2O, reflux, 24hrs.

The receptor molecules **PI** has been synthesized by the condensation of aldehyde **3** with 1,3-diaminourea in refluxed ethanol–water (1:1) mixture. Probe **PI** has been characterized by various spectral techniques such as ^1H, ^{13}C NMR and high resolution ESI-MS (Experimental section and Fig. S1-S3,ESI†).

The free probe **PI** displayed an intense absorption band at 375 nm and a 392 nm. In the presence of 0–20 equivalents of F^-, the peak at 375 nm and 392 nm, the π- π^* transition of the chromophore, disappeared gradually, and there was simultaneous growth of a new strong absorption band centered at 435 nm, which is the charge transfer (CT) band.

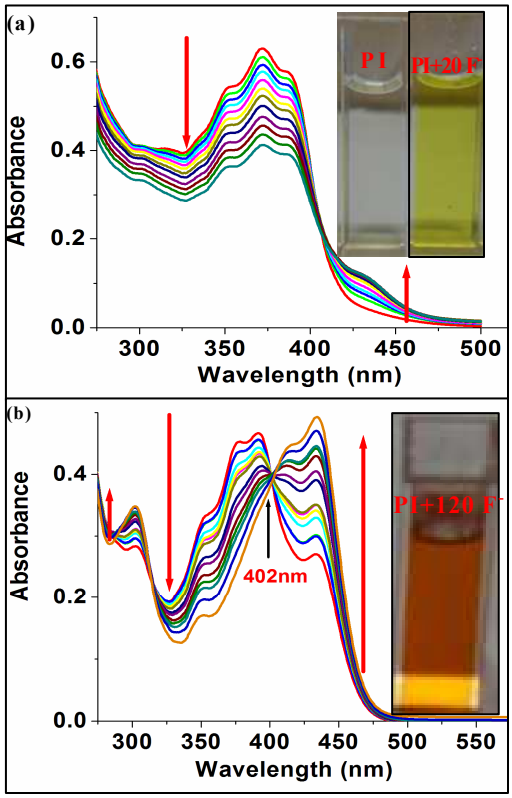


Fig. 2 The changes in UV/Vis spectra of probe **PI** in DMSO (10^{-5}M) after addition of a) 0-20 equiv of F^- and b) 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85,90, 100,110 and 120 equiv of F^-.

The interaction of probe **PI** with anions was investigated through spectrophotometric titrations by adding a standard solution of the tetrabutylammonium salt of anions in DMSO solution of the probe. The absorption band at 375nm and at 392 nm decreased and a new red shifted band at 435 nm appeared and developed due to the hydrogen binding interaction between imidazole -NH and urea -NH of probe **PI** and fluoride anions. Consequently colorless solution of the probe turned light yellow (Fig.2a). To our surprise, distinct changes in the spectra following color changes from light yellow to brownish red were observed after the addition of about 30-120 equivalents of F^- (Fig.2b). Correspondingly, the intensity of the band at 372 nm and 392 nm dropped gradually and this was accompanied by a blue shift of the absorption peak. We propose that these spectral changes are due to the deprotonation of imidazole -NH and urea -NH with

formation of the FHF^- ion, similar to the previously reported phenomena.[28] Analogous investigations were carried out on a variety of anions such as Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-}, AcO^-, HSO_4^- and $H_2PO_4^-$. Other anions such did not induce any spectral response. The binding constant for F^- at 392nm was determined to be 3.93 $\times 10^4$ M^{-1} (Fig. 4, ESI†).

The anion-binding properties of probe **PI** were then studied in DMSO solution by emission spectroscopy. The results obtained were in good agreement with those of UV/vis absorption spectroscopy. The ability of probe **PI** to detect F^- was shown by ratiometric fluorescence measurements (Fig. 3).

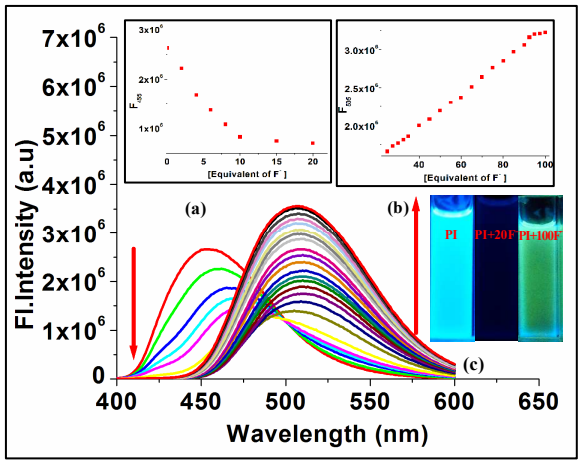


Fig.3 Fluorescence (Excitation=392 nm) titration of probe **PI** with F^- (as a TBAF salt from 0 to 100 equiv) in DMSO. [**PI**]= 10^{-5}(M). Inset: a) change in fluorescence intensity monitored at 455 nm, b) change in fluorescence intensity monitored at505 nm, c) fluorescence emission color changes of the probe **PI** solution on the addition of F^-.

With the addition of F^- from 0 to 20 equivalents, the color changed from blue to light blue, and strong fluorescence quenching at 455 nm(Excitation=392 nm) without any spectral shift was observed. Hence, the fluorescence quenching by PET can be attributed to the hydrogen bonding formed between probe **PI** and F^-. When the F^- concentration was further increased, the blue fluorescence of probe **PI** turned green and the emission red-shift was observed. The intensity of the new emission peak at 505nm increased remarkably and finally stopped increasing after the addition of 100 equivalents of F^-. Furthermore, the intensity of the peak at 505 nm exceeded the original intensity at 455 nm. These phenomena indicate that the N-H bond of the imidazole and urea moiety is deprotonated by F^- in DMSO, thereby increasing the negative charge density at the imidazole and urea nitrogen atom. Thus, the extent of intramolecular charge transfer (ICT) from the imidazole anion to the phenyl rings was enhanced. This enhancement in ICT affords a shift in the wavelength of the fluorescence as a function of fluoride concentration. Hence for probe **PI**, the emission intensity at 455nm is gradually 'switched off' upon incremental addition of F^- and simultaneously, the emission intensity at 505 nm is 'switched on'. This situation provides the opportunity for elaborating a ratiometric probe which permits signal rationing and allows the estimation of analyte independent of the concentration of the receptor. Figure 3 inset shows a correlation between intensity ratios of emission intensity at 505 nm with those at 455 nm (FI_{505}/FI_{455}) versus fluoride ion concentration.

As expected from the three potential anion-binding pockets within the structure of probe **PI**, the anion-binding modes fitted to 1:3 (receptor/anion). The proposed 1:3 binding stoichiometry was supported by the Job plots for the complexes of the probe **PI** with F^- in DMSO solution (Fig. S5, ESI†).The fluoride sensing process was also clearly seen not only by color change but also by bright fluorescence under a UV lamp. During the fluorometric titration of probe **PI** with F^- ions the blue color solution of the receptor became deep green.

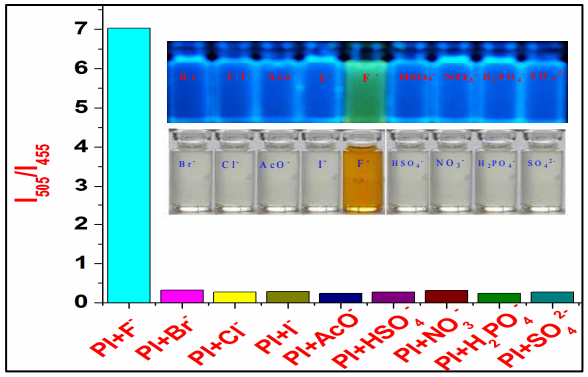


Fig.4 Relative fluorescence changes of probe **PI** after treatment with various relevant analytes (100 equiv. for F^-, 200 equiv. for other anions) in DMSO solution. The inset show the photograph of visible color (bottom) under ambient light and visual fluorescence color (top) under a hand–held UV lamp.

Thus, the sensor provided a significant ratiometric fluorescent response (**I_{505}/I_{455}**) to F^- anions as seen in Fig. 4. When the deprotonation reaction probe **PI** was carried out in a mixture of anions containing Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-}, HSO_4^- and $H_2PO_4^-$, no fluorescence appeared, but a strong fluorescence emission appeared only when fluoride anion was added to this mixture (Fig. 4). These observations suggest that compound is highly selective toward F^- even in the presence of a complex mixture of other anions. The binding constant for F^- at 455nm was determined to be 5.23 $\times 10^3$ M^{-1}(Fig. S6, ESI†). The detection limit of fluoride was about 5.2 μM (Fig.S7, ESI†). The experimental results suggest that probe **PI** shows high selectivity in colorimetric and fluorescent sensors for the fluoride anion.

The UV/Vis absorption and fluorescent spectra present a clue that formation of NH···F^- hydrogen bond and subsequent deprotonation is responsible for the behaviour of probe **PI**. Therefore, the ^1H NMR titration studies of **PI** with progressive addition of F^- were carried out in [d_6] DMSO (see Fig. 5). As shown in Fig 5, It was found that the imidazole -NH proton signal (δ =13.57ppm) and urea -NH proton signal(δ =10.958ppm) in the drastic downfield shift (Δδ = 1.5 ppm and 1.4 ppm) of the

spectrum broadened and then finally disappeared with an increase in the concentration of F^-. In Fig. 5, the majority of signals on the aryl rings shift up field distinctly after the addition of 6.0 equiv. of fluoride ions owing to the through-bond effects, and complete disappearance of the signals for the -NH proton of imidazole (δ =13.57 ppm) and -NH proton of urea (δ =10.958 ppm) was also observed at the same time.

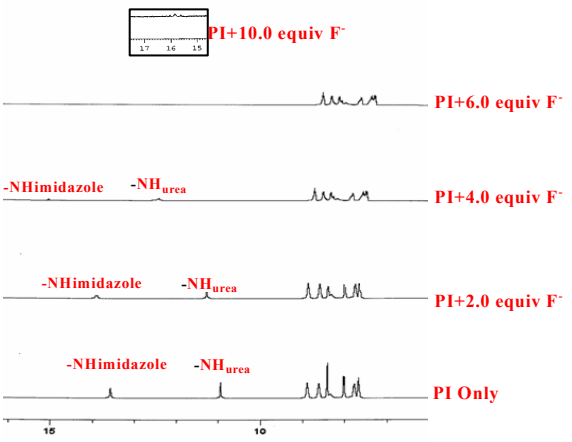
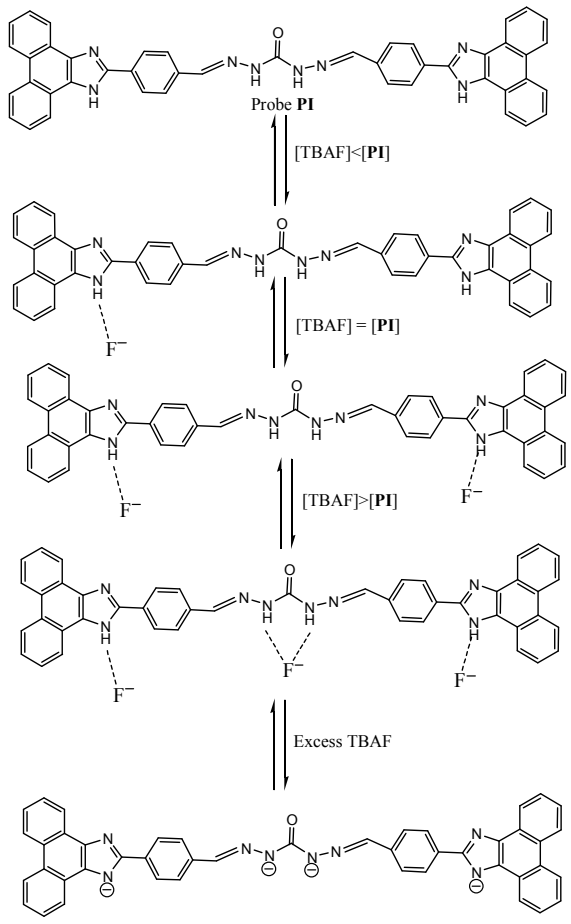


Fig.5. ^{1}H NMR (400 MHz) spectra of probe **PI** in [d_6] DMSO with addition of TBAF.

These observations clearly support the theory that the proton transfer interaction between Probe **PI** and F^- involves the imidazole NH proton and urea NH proton. Fluoride has a high affinity towards hydrogen and could easily induce N–H bond cleavage. Interestingly, after the addition of 10.0 equiv. of fluoride ions, anew 1: 2: 1 triplet signal at 15.8 ppm appeared, which is ascribed to the FHF^-dimer.[29] The existence of this new species indicates the deprotonation of the NH groups.

The absorbance, emission and ^{1}H titration data show that the first changes at low amounts of F^- added are due to a hydrogen-bonded complex. As the amount of F^- increases, the sensor interacts with two fluoride ions to form a **PIF_2** complex and is deprotonated to the conjugate base with formation of the FHF^- ion. At even higher F^- concentration a second deprotonation occurs to produce a second FHF^- ion and the tetra anionic of **PI** through the formation of **PIF_3** complex. Such differences in complexation behaviour of **PI** are in agreement with changes in the chemical shifts of the protons in their ^{1}H NMR spectra, on addition of fluoride. These results suggest that probe **PI**-fluoride interaction is indeed a two-step process shown in Scheme 2 at low fluoride concentration, probe **PI** -fluoride interaction is the authentic hydrogen binding, and with the increase of the fluoride ions, excess fluoride interact with the probe **PI**-fluoride complex and induce the deprotonation of the probe **PI**.

The deprotonation of the Probe **PI** was confirmed by the Bronsted acid–base reaction between probe **PI** and $[Bu_4N]^+OH^-$. This deprotonation process was also confirmed by the identical UV-vis spectral changes observed in the titration experiment with tetrabutylammoniumhydroxide (TBAOH) to that observed for fluoride ions (Fig. S8, ESI†). A stepwise increase in the concentration of TBAOH produced results analogous to those found in the case of F^- ion and other ions less basic than OH^- .



Scheme 2 Proposed binding mode of probe **PI** with F^- anions.

For the hydrogen-bonding-based F^- chemosensors, except for a few successful cases,[21d] only aprotic solvents are usually permitted. In protic solvents such as H_2O or MeOH, the binding of the sensor with anions would be completely quenched due to the effective competition of the solvent molecules. As the pKa of imidazole-NH proton is in the range of 11–13 and an carbonohydrazone (C=O)NH amide with a pKa of 17 as well as pKa values of H_2O and MeOH are 15.7 and 15.5, respectively, we speculated that an imidazole-carbonohydrazone hybrid F^- sensor would be tolerant to H_2O and MeOH, at least to some extent. In view of the high selectivity of probe **PI** in the dry DMSO, we also design the experiments in DMSO–water (95:5, v/v) solution, to further investigate their performance. The results showed no coloration and the fluorescence quenching upon addition of 1000 equivalents of fluoride to probe **PI** (Fig. S9, ESI†).

We speculated that fluoride could be sensed by deprotonation of imidazole proton followed by urea protons,[30] and that the resultant change in the electronics of the receptor would be readily transmitted through the conjugated circuit. The geometry optimizations for probe **PI** and its anionic species were done in a

cascade fashion starting from semiempirical PM2 followed by *ab initio* HF to DFT B3LYP by using various basis sets, *viz*., PM2 → HF/STO-3G → HF/3-21G → HF/ 6-31G → B3LYP/ 6-31G(*d,p*). The optimized geometries of probe **PI** and its anion complex and deprotonated struucture are shown in (Fig.6).

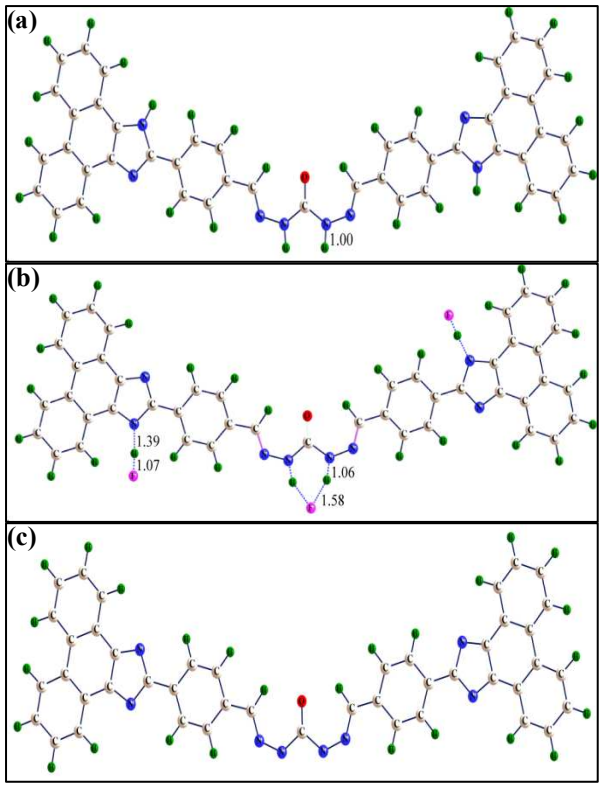


Fig.6. Optimized geometries of the (a)Probe **PI,** (b) Probe **PI**-fluoride complex,(c) deprotonated structure of Probe **PI** at the B3LYP/6-31G* level of theory.

The spatial distributions of frontier orbitals and orbital energies of HOMO and LUMO of Probe **PI** was also determined (Fig.7).

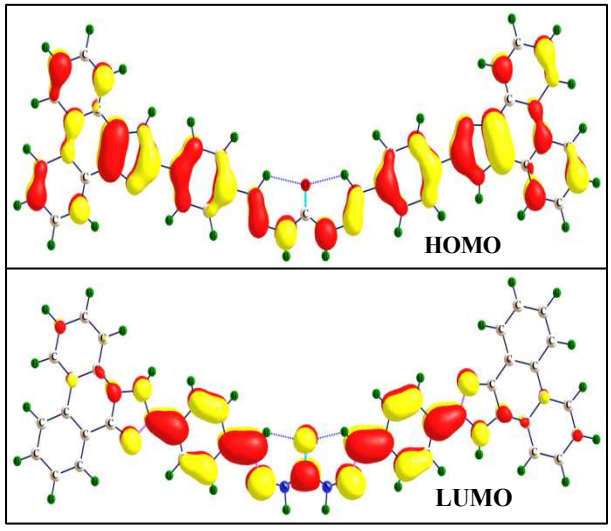


Fig.7. HOMO and LUMO distributions of the probe **PI.**

In addition, we also performed time-dependent density function theory (TD-DFT) calculations for both the Probe **PI** and the deprotonated product. The lowest energy excitation of probe **PI** is predicted to lie at 431 nm (f = 2.35) and to arise primarily from the HOMO→LUMO one electron transition (Table. S1, ESI†). In the case of the deprotonated product, TD-DFT calculations provide a calculated absorption band at 459 nm (f = 2.518) and 366 nm (f = 0.315) belonging to the $S_0 \rightarrow S_1$ (HOMO→LUMO) and $S_0 \rightarrow S_6$ (HOMO-1→LUMO+1) energy state, respectively (Table S1, ESI†). This is consistent with the experimentally obtained absorbance band at 435 nm and 375 nm respectively. The HOMO-LUMO transition contributed 92% and 93% to the excitation of PI and its anion energy state, respectively.

Finally, analytical application and the use of test strip of the probe **PI** to detect fluoride were also reported. Generally, for anions based solely on hydrogen bonding interactions cannot serve as efficient sensors in aqueous media, due to the strong solvent competition. To avoid the competing solvation effect of water, we prepared a test strips of probe **PI** for inspecting F^- in DMSO environments by putting a filter paper (2.0× 0.5 cm^2) into the DMSO solution of probe **PI** (2.0×10^{-3}M) and then drying it by two way (i) exposure to air and (ii) in vacuum (oven temperature 90–100 ^{0}C, 70 mmHg).

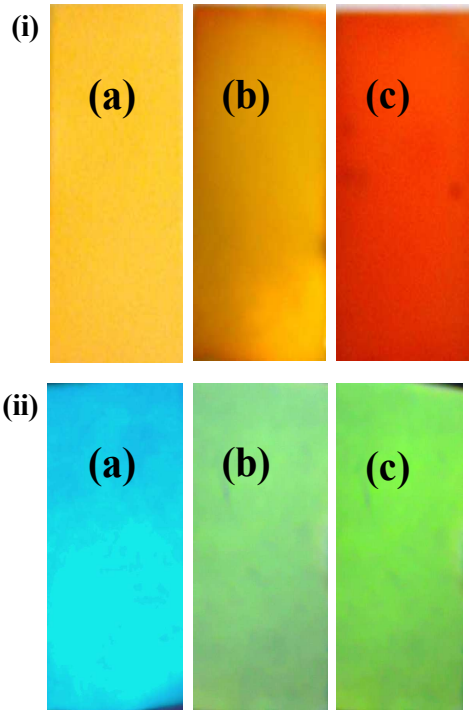


Fig.8. Photographs of the test kits with probe **PI** for detecting fluoride ion in DMSO solution with different F^- concentrations. (i)(a) Probe **PI** only (b) Probe **PI** +10mg/L fluoride ion , (c) Probe **PI** +0.1g/L fluoride ion under ambient light conditions on TLC plate strips and (ii))(a) Probe **PI** only (b) Probe **PI** +10mg/L fluoride ion , (c) Probe **PI** +0.1g/L fluoride ion fluorescence color changes visualized on TLC plate strips .

The test strips containing probe **PI** were utilized to sense different anions. For detecting the fluoride anion a test strips was immersed in the test fluoride solution for several seconds and

then exposed to air or in vacuum to remove water. An immediate obvious color change was observed only with fluoride solution visible color under ambient light and visual fluorescence color under a hand–held UV lamp. Fig. 8 exhibits the color changes of the test papers with different fluoride concentrations.

Conclusion

In conclusion, we successfully designed and prepared carbonohydrazone brigged Schiff base of phenanthroline-imidazole (**PI**). It display an excellent selectivity toward the detection of F^- in DMSO, with clear color changes from colorless to light yellow to brownish red and remarkable fluorescent changes. The results show that the deprotonation rather than the H-bonding is the key factor triggering the chromogenic effect. This deprotonation is being facilitated by the high intrinsic acidity of imidazole-NH, highly basic F^- ion, and a polar solvent like DMSO. In particular, probe **PI** displays a 50 nm red-shift of fluorescence emission as well as colormetric and ratiometric features upon addition of F^-. A stepwise deprotonation of an imidazole-carbonohydrazone hybrid framework of **PI** was observed. Density function theory and time-dependent density function theory calculations were conducted to rationalize the optical response of the probe **PI.** Further work will concentrate on the development of F^-sensors that are effective in aqueous solution.

Experimental Section

General Information and Materials

The ^1H and ^{13}C NMR spectra were measured on Bruker–400 MHz spectrometer. Mass spectra were carried out using a Water's QTOF Micro YA 263 mass spectrometer. UV–visible and fluorescence spectra measurements were performed on a SHIMADZU UV-1800 and a Perkin Elmer LS55 spectrofluorimeter respectively.

All reagents for synthesis obtained commercially were used without further purification. In the titration experiments, all the anions were added in the form of tetrabutylammonium (TBA) salts, which were purchased from Sigma–Aldrich. All solvents used in the present experiments were spectroscopic grade from Spectrochem, India. d_6 - DMSO was used for the ^1H NMR experiment procured from Sigma-Aldrich.

Preparation of Test solution for UV-vis and fluorescence study. UV-vis spectra were recorded on a JASCOV-530 spectrophotometer using a dissolution cell of 10mmpath and the fluorescence spectra were recorded on a Perkin Elmer Model LS 55 spectrophotometer using a fluorescence cell (10 mm). For UV-vis and fluorescence titrations, stock solution of receptor was prepared (C= 10^{-5} (M)) in DMSO solution. The solution of the guest anions using their TBAX salts in the order of 10^{-4} (M) was also prepared in DMSO solution. The test solution of Probe **PI** was prepared by the proper dilution method. The spectra of these solutions were recorded by means of UV-vis and fluorescence methods. The substrate binding interaction was calculated according to the Benesi–Hildebrand equation.

$$\frac{A_0}{A-A_0}=\left(\frac{\varepsilon_0}{\varepsilon_0-\varepsilon}\right)^2\left(\frac{1}{K_B[Substrate]^2}+1\right)$$

Here Ao is the absorbance of receptor in the absence of guest, A is the absorbance recorded in the presence of added guest, ε_0 and ε are the corresponding molar absorption co-efficient and K_B represents the substrate binding interaction with guest.

Computational Studies. The ground-state geometry optimization of **Probe PI** and its receptor-additive form (PI-$3X^-$) and deprotonated form were performed at the B3LYP/6-31G(d) level of theory in vacuo using GAUSSIAN 03.

Synthesis of Probe PI : A solution of **3** (161mg, 0.5mmol) in 30% ethanol (10 ml) was added slowly to a solution of carbohydrazide (22.5mg, 0.25mmol) in water (10 ml). Initially the solution turned turbid and after complete addition, the solution became clear. A solution of **3** (161mg, 0.5mmol) in 30% ethanol (10 ml) was added slowly to a solution of carbohydrazide (22.5mg, 0.25mmol) in water (10 ml). Initially the solution turned turbid and after complete addition, the solution became clear. The reaction mixture was refluxed with stirring for 24 hrs. A precipitate formed which was cooled and filtered. The precipitate was washed with ethanol and dried under reduced pressure to obtain Probe **PI**. (yield: 286mg, 82 %); M.P>300^0C. ^{1}HNMR Data for Probe **PI**: ^{1}H NMR (400MHz, [d_6]DMSO,TMS):δ(ppm)=13.55(s,2H,$NH_{imidazole}$),10.93(s,2H,NH_{urea}),10.53(s,2H,CH_{imine}),8.91(m,4H),8.63(m,4H),8.44(m,4H),8.01(m,4H),7.787.65(m,8H).^{13}CNMR([d_6]DMSO,100MHz)δ(ppm):183.90,179.21,177.41,172.98,169.06,165.75,164.46,163.56,162.68,152.2,149.86,147.2.142.80,138.95,131.40,128.64,127.50,126.35,124.92,122.84,118.75,114.54,112.60. ESI-MS: m/z[M−2]$^+$: 423.1; calculated, 425.3. Anal. cald for $C_{45}H_{30}N_8O$ (425.3); C: 56.47; H: 5.40; N: 23.04; Found: C: 56.52; H: 5.31; N: 23.07; S: 15.01%.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/.

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