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Anion induced azo-hydrazone tautomerism for the selective colorimetric sensing of fluoride ion

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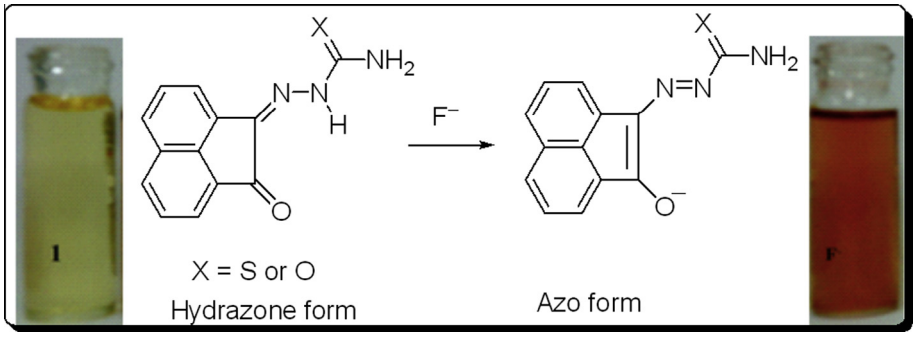
HIGHLIGHTS

- Anion sensing through azo-hydrazone type tautomerism.
- Mechanism of sensing involves anion induced change of chromophore from C=N to N=N.
- The receptors are highly selective towards fluoride ion over other anions.

GRAPHICAL ABSTRACT



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ABSTRACT

The design, synthesis, characterization and their anion sensing properties of two receptors capable of exhibiting azo-hydrazone tautomerism are reported. The anion sensing properties have been investigated using electronic, fluorescence and nuclear magnetic spectral studies in addition to electrochemical and visual detection experiments. Both the receptors selectively bind fluoride ion with >100 nm red-shift in the electronic spectrum and the color changes from yellow to red. The results of the spectral studies revealed that the sensing mechanism involves fluoride ion induced change of chromophore from C=N (hydrazone form) to N=N (azo form) in these receptors leading to the visible color change. Density Functional Theory calculations were conducted to rationalize the optical response of the receptors.

Introduction

Recently the studies on chemosensors for anions have received continuous attention as anions play important role in many fields. Fluoride ion is of particular interest due to its importance in dental care, treatment of Osteoporosis and its toxicity due to excess intake (>1.5 mg/L) [1]. Review of literature revealed that the fluoride ion sensors fall on either one of the following types namely N—H based H-bonding, Lewis acid, metal ion template, metal complexes, guest displacement and chemoreactants [2]. However, only very few anion sensors based on tautomerism has been reported so far [3].

Azo dyes are the largest group of colorants with respect to number and production volume, with applications in many fields for coloring variety of substrates [4]. Azo-hydrazone tautomerism is

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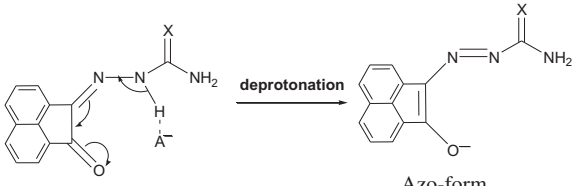
a phenomenon that occurs in azo dyes possessing substituent conjugated to the azo linkage which has labile proton that can be exchanged intramolecularly. A typical example of such tautomerism exist in 2-phenylazo-1-naphthol is shown below [5].

Azo form Hydrazone form

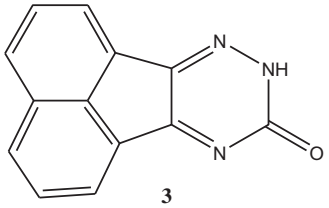
This over 100 year's old tautomerism has been extensively studied because the azo and hydrazone tautomers show different optical and physical properties. The color and properties of one tautomer may be completely different from the other [6]. Hence, it is presumed that a chemosensor with similar structural features would exhibit the anion sensing behavior. This is because when the added anions abstract the proton, from one tautomeric form, that will be converted to other tautomer and consequently exhibit striking color change for visual detection. With this idea in mind the following sensors have been synthesized and screened for their anion sensing behavior. The selection of urea moiety as the receptor unit is based on the fact that it out numbered all other types and in many cases they exhibit high selectivity for fluoride ion over the other anions [7–12]. As a result of anion sensing we expect the following azo-hydrazone type tautomerism in these compounds which would lead to observable color change.



hydrazone-form Azo-form

Where
X=O; Receptor **1**
X=S; Receptor **2**
A⁻= Anion

Also, with an aim to shed some light on the mechanism of this proposed anion sensing the following compound (**3**) was also prepared and applied as sensor in the present study. The selection of the compound is based on the fact that it may possess different H-bonding property and also the azo-hydrazone type tautomerism may not occur in this compound.



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The main objective of the present endeavor, therefore, is the synthesis, characterization and anion sensing properties of these three compounds (**1–3**). The anion sensing behavior has been investigated using UV–Vis, fluorescence and ^{1}H NMR spectral techniques in addition to electrochemical and visual detection experiments. Theoretical computations, based on the Density Functional Theory, have also been carried out to get a better insight into the mechanism (tautomerism) of sensing. The survey of literature revealed that only very few works has been published with similar type of compounds. But either they are less studied or not selective towards fluoride ions [13–16].

Experimental section

Chemical and apparatus

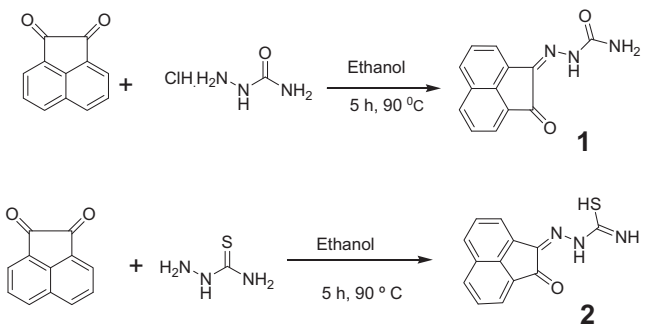
All reagents for synthesis of the receptors were obtained commercially (Sigma Aldrich, India) and were used without further purification. All anions, in the form of tetrabutylammonium salts, and spectroscopic grade solvents (Merck, India) were used as received. UV–Vis spectral studies were carried out in DMSO on a (Jasco V-630) double beam spectrophotometer. Steady state fluorescence spectra were obtained on a spectrofluorometer (Jasco-FP-6200). The excitation and emission slit width (5 nm) and the scan rate (250 nm) was kept constant for all of the experiments. FT-IR spectra were obtained as KBr pellets on FT-IR spectrometer (Jasco 460 plus). Nuclear magnetic resonance spectra were recorded in DMSO-d_6 (Bruker, ^{1}H NMR 300 MHz, ^{13}C NMR 75 MHz). The ^{1}H NMR spectral data is expressed in the form: Chemical shift in units of ppm (normalized integration, multiplicity, the value of *J* in Hz). Differential pulse voltammetry was performed with a conventional three electrode system consisting of a glassy-carbon-disk working electrode which was polished using 0.05 μm (alumina/water slurry) and rinsed thoroughly with double distilled water and DMSO. Solutions for DPV were typically 1.0 mM in the redox-active species and were deoxygenated by purging with nitrogen.

Synthesis of the receptors

The method of synthesis of the receptors is shown in Scheme 1.

(Z)-1-(1-oxoacenaphthylen-2(1H)-ylidene)semicarbazide (1)

To a stirred solution of acenaphthenequinone (1 g, 0.0054 mol) in ethanol semicarbazide hydrochloride (0.6122 g, 0.0054 mol) was added at RT under N_2 atmosphere and then few droops of Con.H_2SO_4 was added to the reaction mixture. The reaction mixture was refluxed under N_2 atmosphere for 5 h. The reaction was monitored by TLC, after completion of the reaction; the reaction mixture was cooled to RT and then filtered through the filter paper. The settled residue was washed with cold ethanol (20 mL) to get the pure product as a yellow solid. FT-IR (KBr) ν/cm^{-1}: 3407, 3241(—NH_2), 3145 (—NH—), 1687 (C=O), 1610 (NH—C=O), 1571 (C=N). ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.25 (s, 2H), 7.90 (m, 2H),



Scheme 1. Preparation receptors **1** and **2**.

7.95 (d, 1H, J = 6.9 Hz), 8.11 (t, 2H, J = 7.2 Hz & 6.3 Hz), 8.38 (d, 1H, J = 8.4 Hz), 11.84 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 189.02, 155.69, 138.71, 137.06, 133.13, 130.96, 130.33, 129.31, 128.90, 126.91, 122.63, 118.10. LCMS (ESI-APCI) m/z: Cal. for $C_{13}H_9N_3O_2$, 239.0, Found, 240.0 $[M+H]^+$.

Elemental analysis: Anal. Calcd. for $C_{13}H_9N_3O_2$: C, 65.27; H, 3.79; N, 17.56. Found: C, 65.39; H, 3.62; N, 17.44. M.P: 209–211 °C

1-(1-Oxoacenaphthylen-2(1H)-ylideneamino)isothiourea (2)

To a stirred solution of acenaphthenequinone (1 g, 0.0054 mol) in ethanol thiosemicarbazide (0.4921 g, 0.0054 mol) was added at RT under N_2 atmosphere and then few drops of Con.H_2SO_4 was added to the reaction mixture. The reaction mixture was refluxed under N_2 atmosphere for 5 h. The reaction was monitored by TLC, after completion of the reaction; the reaction mixture was cooled to RT and then filter through the filter paper. The settled residue was washed with cold ethanol (20 mL) to get the pure product as a yellow solid. FT-IR (KBr) ν/cm^{-1}: 3477 (—NH—), 3280 (NH=C), 2638 (S—H), 1743 (C=O), 1689 (N=C—S), 1589 (C=N). ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.90 (m, 2H), 8.01 (d, 1H, J = 6.6 Hz), 8.15 (m, 2H), 8.39 (d, 1H, J = 8.4 Hz), 8.84 (s, 1H), 9.13 (s, 1H) 12.52 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 189.00, 179.46, 139.65, 137.83, 133.22, 130.86, 130.46, 130.32, 129.36, 129.00, 127.54, 122.87, 118.83. LCMS (ESI-APCI) m/z: Cal. for $C_{13}H_9N_3OS$, 255.0, Found, 256.0 $[M+H]^+$.

Elemental analysis: Anal. Calcd. for $C_{13}H_9N_3OS$: C, 61.16; H, 3.55; N, 16.46, S, 12.56. Found: C, 61.21; H, 3.58; N, 16.39, S, 12.47. M.P: 220–224° C.

Acenaphtho[1,2-e][1,2,4]triazin-9(8H)-one (3)

The compound **1** was dissolved in 10 mL of acetic acid and refluxed for 12 h, the reaction mixture was monitored by TLC and then acetic acid was concentrated under reduced pressure. The crude material was basified with saturated $NaHCO_3$ solution and extracted with ethyl acetate. The extracted organic layer was washed with water and brine solution. The separated organic layer was evaporated under vaccum to get the yellow colored powder. The crude material was purified by (60–120 mesh) silica gel column chromatography by using 15% ethyl acetate-pet ether mixture to get the pure.

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.28 (m, 2H), 8.13 (t, 2H, J = 6 Hz), 7.90 (m, 2H), 6.16 (s, 1H). LCMS (ESI-APCI) m/z: Cal. for $C_{13}H_7N_3O$, 221.0, Found, 222.0 $[M+H]^+$.

Elemental analysis: Anal. Calcd. for $C_{13}H_7N_3O$: C, 70.58; H, 3.19; N, 19.00. Found: C, 70.63; H, 3.17; N, 19.07. M.P: 190–193° C.

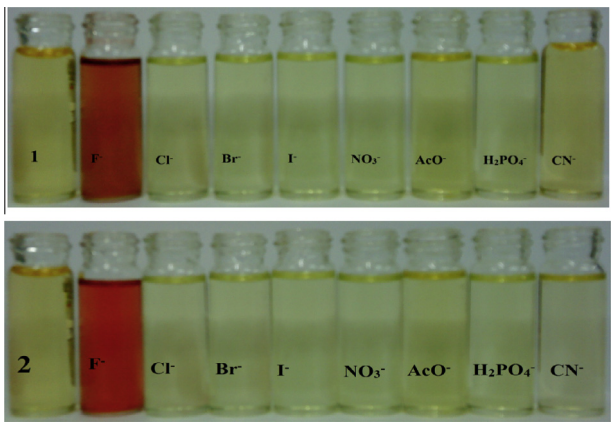
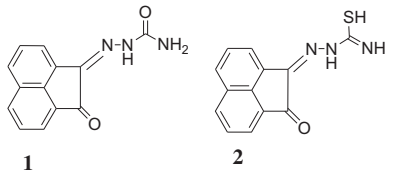


Fig. 1. Color change of receptors 1 and 2 with anions.

Results and discussion

Facile condensation of acenaphthoquinone with semicarbazide and thiosemicarbazide in ethanol gave receptors **1** and **2**, respectively in good yields. The receptors **1** and **2** were characterized using UV–Vis, FT-IR, ^{1}H and ^{13}C NMR and LCMS spectral techniques. Based on the results the following structures were proposed for **1** and **2**.



Visual detection

Visual inspection of solutions of the compounds **1** and **2** (1.25×10^{-4} M) in DMSO before and after addition of 1 eqv. of tetrabutylammonium salt of various anions such as F^-, Cl^-, Br^-, I^-, NO_3^-, $H_2PO_4^-$, CN^- and AcO^- was carried out. As depicted in Fig. 1 solution of **1** and **2** turned yellow to[1] intense red color after the addition of fluoride ions. However, the color remained unchanged after the addition of the other chosen anions. This observation indicated the selectivity of **1** and **2** towards fluoride ion.

UV–Vis spectral studies

The anion sensing ability of **1** and **2** with all the chosen anions such as F^-, Cl^-, Br^-, I^-, AcO^-, NO_3^-, $H_2PO_4^-$ and CN^- were examined by using UV–Vis spectral technique. The UV–Vis spectral changes of **1** and **2** upon addition of these anions are shown in Fig. 2. Likewise, the intensity of absorbance of the **1**-F^- and **2**-F^- complex showed no appreciable change in the presence of other anions (Fig. S1). The electronic spectrum of the receptor **1** exhibited maximum absorbance at 408 nm (ε = 3768 M^{-1} cm^{-1}) in DMSO corresponds to the electronic transition in the imine (C=N) chromophore [17]. This observation also indicated that the receptor **1** exist in hydrazone form in DMSO solutions [17]. As evidenced from the Fig. 2A, addition of fluoride ions to **1**, bathochromically shifted the λ_{max} to 517 nm with an instantaneous formation of red color with a $\Delta\lambda_{max}$ of 109 nm. The new peak appeared at 517 nm may corresponds to the azo (N=N) chromophore [17]. However, addition of other anions produced no significant shifts in λ_{max}. Likewise, the receptor **2** also selectively senses F^- ions with a formation of red color and a concurrent shift in the λ_{max} from 375 (ε = 3898 M^{-1} cm^{-1}) to 500 nm in DMSO with a $\Delta\lambda_{max}$ of 125 nm (Fig. 2B).

With the addition of incremental amounts of fluoride ions to the solution of both **1** and **2**, the absorbance of the higher energy peak (due to C=N chromophore) diminished gradually and that of the lower energy peak (due to N=N chromophore) increased gradually (Fig. 3). This observation suggested that addition of fluoride ion might have converted the hydrazone form (with C=N chromophore) of the receptors to the azo form (with N=N chromophore). The stoichiometry of the interaction between the receptors **1** and **2** and fluoride ions was determined using the electronic spectral data. The Job's plot for **1** and **2** is shown in Fig. 4. In both the cases curve with a maximum at 0.5 mol fraction indicated the

[1] For interpretation of color in Figs. 1 and 2, the reader is referred to the web version of this article.

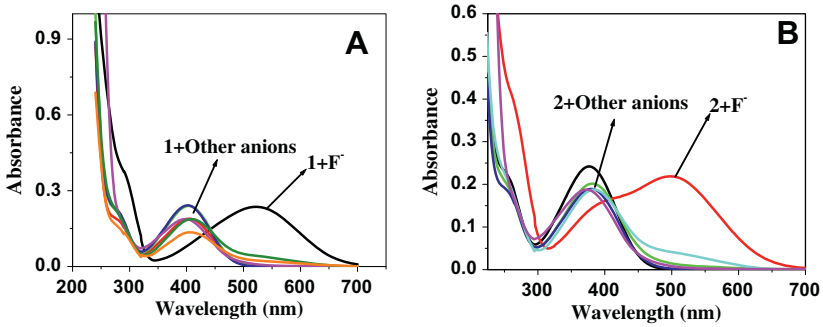


Fig. 2. UV–Vis absorption changes of compound **1** and **2** (6.25×10^{-5} M) upon addition of [$(Bu)_4N$] salts of F^-, CN^-, Cl^-, Br^-, I^-, AcO^-, NO_3^-, $H_2PO_4^-$ in DMSO.

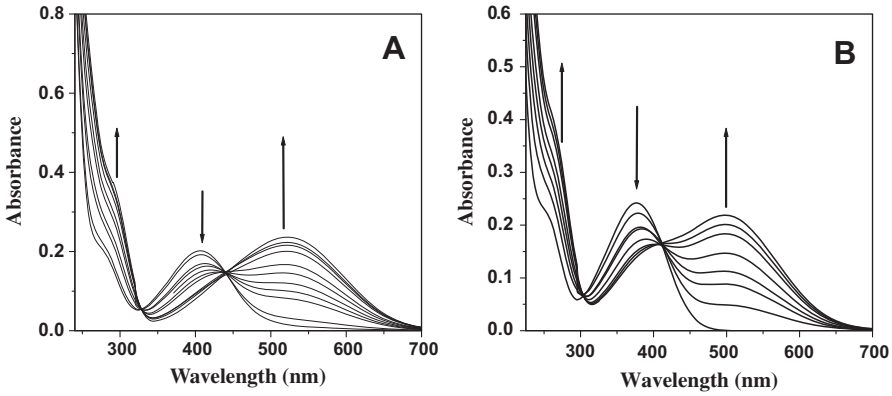


Fig. 3. UV–Vis absorption spectra of **1** and **2** (6.25×10^{-5} M) with F^- ion (0–8.50×10^{-6} M).

formation of a 1:1 (receptor:F^-) complex [18]. The formation constant for these complexes was determined using the Scott equation [19]. The values thus obtained for **1**.F^- and **2**.F^- complexes (Fig. S2) were found to be 7.7×10^3 and 24×10^3 L mol^{-1}, respectively. The relatively higher value obtained for **2**.F^- indicated that the interaction between the receptor **2** with F^- ions is stronger than that in receptor **1**. This is well supported by the observation made in $\Delta\lambda_{max}$ with the addition of fluoride ions to the receptors.

Fluorescence study

The fluoride ion binding ability of the receptors **1** and **2** was also evaluated using fluorescence titration studies. The fluorescence spectra of the receptors **1** and **2** (6.25×10^{-5} M) in DMSO were recorded with an excitation at 388 and 398 nm, respectively. The fluorescence emission spectra of the receptors **1** and **2** showed a broad peak at 420 nm and 430 nm respectively (Fig. 5). In both the cases, upon gradual addition of fluoride ions to the receptor solution, quenching of fluorescence of **1** and **2** was observed indicating the complex formation between the receptors and fluoride ions [20]. From the decrease in fluorescence intensity the binding constant of the receptor-F^- complex was calculated using the following equation [21].

$$\log(F_0 - F/F) = \log K_A + n \log[Q] \quad (1)$$

where F_0 is emission intensity in the absence of quencher (Q), F is that at quencher concentration [Q] and K_A is the binding constant. In both the cases, a plot of $\log(F_0 - F/F)$ versus $\log[Q]$ is linear (Fig. S3). The K_A values computed for the receptors **1** and **2** were found to be 1.4×10^3 and 4.5×10^3 L mol^{-1}, respectively. In line with the observation made in the electronic spectral studies, the fluorescence spectral studies also indicated that the **2**.F^- complex is relatively stronger than **1**.F^- complex.

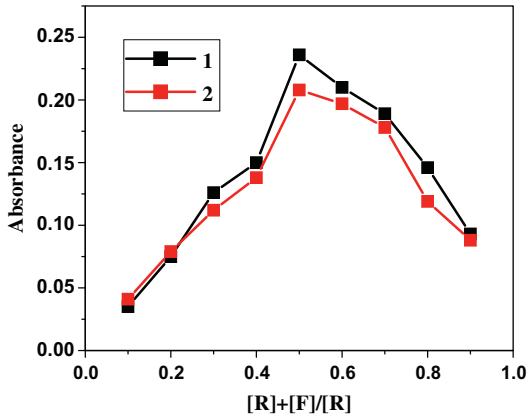


Fig. 4. Job's plot for **1** and **2**.

^{1}H NMR titration

The results of electronic and fluorescence spectral studies indicated that both the receptors **1** and **2** sense fluoride ions by interacting with it. To investigate the nature of the interaction between them, ^{1}H NMR titration experiments were carried out in DMSO-d_6. The results obtained are depicted in Fig. 6. It is evident from the Fig. 6 that, in the receptor **1**, the signal for N—H proton (hydrazone proton) appeared at $\delta = 11.84$ ppm (Fig. 6A) while that in the receptor **2**, it appeared at $\delta = 12.52$ ppm (Fig. 6B). This indicated that the H-atom in **2** is relatively more acidic than that in **1** and thus can act as a better H-bond donor towards fluoride ion. Upon addition of 0.25 eqv. of fluoride ions to **1**, the signal due to this proton exhibited a downfield shift. This may be due to the H-bond

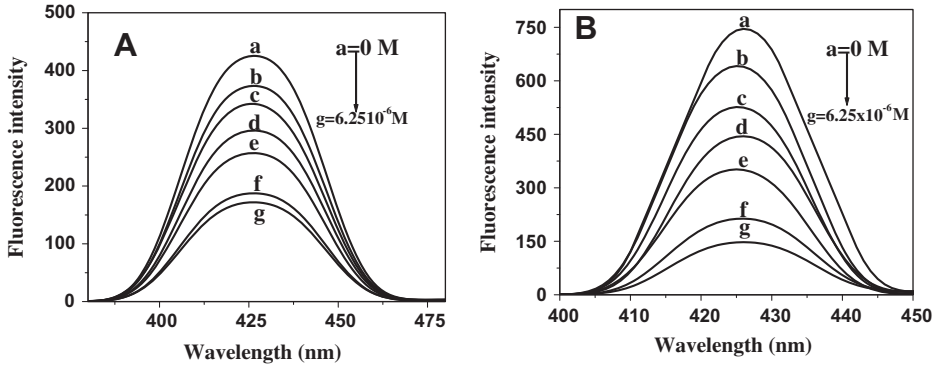


Fig. 5. Change in fluorescence emission spectra for (A) receptor **1** (6.25×10^5 M), (B) receptor **2** (6.25×10^5 M) in DMSO upon the addition of TBAF in DMSO from (0–6.25×10^6 M).

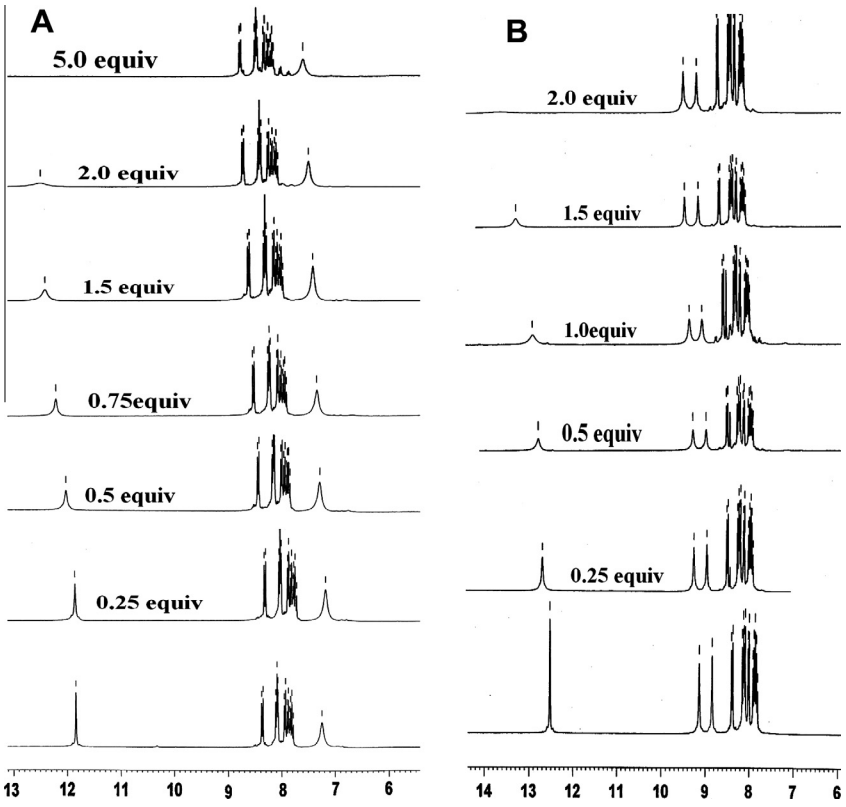


Fig. 6. Change in partial ^{1}H NMR (300 MHz) spectra of (A) receptor **1** in DMSO-d_6 with various concentration of F^-; (B) receptor **2** with various concentration of F^-.

formation between the N—H proton and fluoride ions. The results depicted in the Fig. 6A indicated that with the incremental addition of fluoride ions to **1**, the N—H proton signal experienced progressive downfield shift, simultaneously broadness and disappeared at a fluoride ion concentration of 5 equivalent i.e. deprotonation has occurred. In the case of **2** also, similar H-bond formation followed by deprotonation of the N—H proton has occurred with the addition of incremental amounts of fluoride ions to the receptor solution. However, we did not observe any signal for HF_2^- ion. This may be due to its instability in highly polar solvent like DMSO [22]. It is interesting to note that the $\Delta\delta$ observed in **1** and **2** on adding 0.25 equivalents of fluoride ions were found to 0.04 and 0.1 ppm, respectively. This indicated that the receptor **2** binds relatively stronger with fluoride ion than the receptor **1** does. This is because in the receptor **2**, the N—H proton is relatively more acidic than that in **1**. This is well supported by the observation that in **2**, complete deprotonation occurred on adding two equivalents of fluoride ions while in **1**, it happened at five equivalents of fluoride ions.

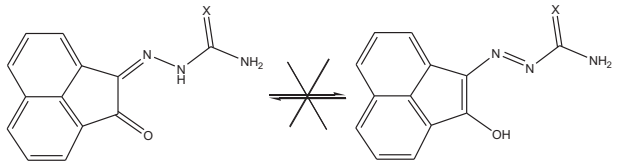
Electrochemical studies

In order to substantiate the nature of the interaction between the receptors and fluoride ions, the electrochemical properties of **1** and **2** in the absence and presence of variable concentrations of fluoride ions were investigated using differential pulse voltammetry (DPV) technique. The DP voltammograms obtained for the reduction of the ring carbonyl moiety in **1** and **2** are shown in Fig. 7. It is evident from the figure that the reduction peak for **1** and **2** appeared at −1.45 and −1.25 V, respectively [23]. In both the cases, on the addition of incremental amounts of fluoride ions, the current intensity of the peak decreased with a concomitant shift of the peak to a more negative potential. That is addition of fluoride ions to these receptors made the electro-reduction of the

keto group relatively more difficult [24]. This may be due to the fact that deprotonation of the hydrazone N—H proton by fluoride ions, render the O-atom (C=O) relatively more electron rich by delocalization of electrons through the conjugated system. Such a conversion of C=O to C—O$^-$ (hydrazone form to azo form) render the electro-reduction of the keto group progressively more difficult.

Theoretical study

DFT calculations [25] have been performed for the two receptors and their complexes with fluoride ions. The optimized geometries of **1** and **2** and their complexes **1**.F$^-$ and **2**.F$^-$ obtained at the B3LYP/6-311G level are shown in Fig. S4. The optimized geometries of the hydrazone and azo forms of **1** and **2** are given in Fig. S5. As spelt in the introduction section, these receptors may exhibit azo-hydrazone tautomerism. The calculated energies, in the case of **1**, for the hydrazone and azo forms are found to be −511701.67 and −511721.90 hartree, respectively. Their relative energies indicated that the hydrazone form is more stable than azo form by 20.23 kcal mol^{-1}. In the case of the receptor **2**, the energies of the hydrazone and azo tautomers are −714342.67 and −714356.08 hartree, respectively. The calculated results showed that the hydrazone tautomer of **2** is 13.09 kcal mol^{-1} more stable in energy than the azo tautomer. These results ruled out the existence of the following tautomerism in **1** and **2** [26].



Hydrazone form Azo form

Thus, these two receptors exist exclusively in the hydrazone form. This is well supported by the results of UV–Vis and ^{1}H NMR spectral studies. The calculated spatial representations of the frontier molecular orbitals (HOMO and LUMO) for these receptors and their complexes with fluoride ions are depicted in Fig. 8. The evenly distribution of HOMO and LUMO in **1** and **2** showed that the intramolecular charge transfer character is only modest [27,28]. Therefore, the electronic transition observed (Fig. 2) in these receptors may be due to the C=N chromophore as discussed in the UV–Vis spectral studies. Same is the case with the receptor–fluoride complex also. The energies of the MOs and the energy corresponds to the electronic transition ΔE (= $E_{HOMO}-E_{LUMO}$) are collected in Table 1. The results indicated that, in both the cases, the magnitude of ΔE in receptor–fluoride complex is less than that in free receptor. Thus, in the receptor–fluoride complexes, the electronic transition occurred at a higher wavelength than in the free receptor as observed in the UV–Vis spectra. In the complexes, the resultant N=N chromophore absorbs at a higher wavelength (Fig. 3.)

The calculated bond lengths of some important bonds are also given in Table 1. In the free receptors the N—N bond length is close to the standard single bond length (1.40 Å) [29]. This suggested that these two receptors exist predominantly in hydrazone form. One can see that, in the receptor–fluoride complexes, the N—N distance is shortened significantly. This is due to the fact that deprotonation of the N—H proton by fluoride ion converts the hydrazone form to azo form wherein the N—N is a double bond. This is well supported by the observation that, after the addition of fluoride

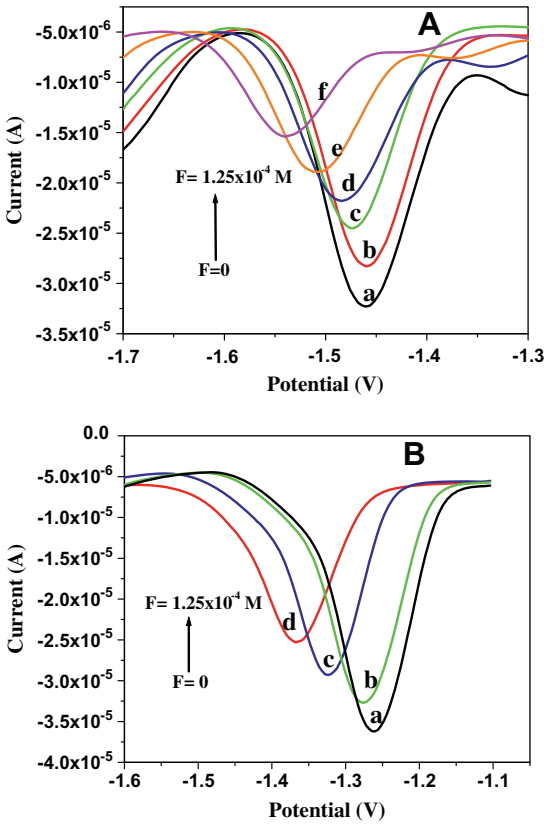


Fig. 7. The electrochemical sensing property of receptor **1** (A) and **2** (B) in the presence of various concentration of $[(Bu)_4N]F$ in DMSO from 0–1.25 × 10^{-4} M.

ions to these receptors, the formed N=N chromophore absorbs at a higher wavelength in the electronic spectrum. The distance between H and F in the receptor–fluoride complexes is 0.97 Å which is close to the bond length in hydrogen fluoride molecule (0.92 Å) [28], suggesting a very strong interaction between the H-atom and fluoride ion.

Mechanism of fluoride ion sensing

Based on the foregoing results and discussion the following plausible mechanism has been proposed for the fluoride ion sensing by these two receptors (Scheme 2). The UV–Vis and ^{1}H NMR spectral studies indicated that the receptors exist exclusively in the hydrazone form. In the free receptors, the electronic transition corresponds to the λ_{max} is due to the C=N chromophore. The various spectral and electrochemical investigations indicated that the fluoride ion sensing by **1** and **2** is through the anion induced formation of azo form. Such an azo form formation involves the following step: deprotonation of N—H proton by fluoride ion, delocalization of electrons through the conjugated system and which lead to the formation of N=N chromophore. This newly formed chromophore absorbs at a different wavelength and thus imparts a noticeable color change which can be seen visually. The results of the spectral studies corroborate well with that of the DFT calculations.

With an aim to substantiate the proposed mechanism for the sensing behavior of these two receptors, the effect of addition of hydroxide ion has also been carried out as hydroxide ion is well known for its deprotonation capacity. The electronic spectra of the receptors **1** and **2** recorded in the presence of hydroxide ion (as its tetrabutylammonium salt) are shown in Fig. S6. As seen from the Figures, addition of one equivalent of fluoride and hydroxide ions exhibited identical shifts in the absorption maximum of both the receptors. Such a similar electronic spectral

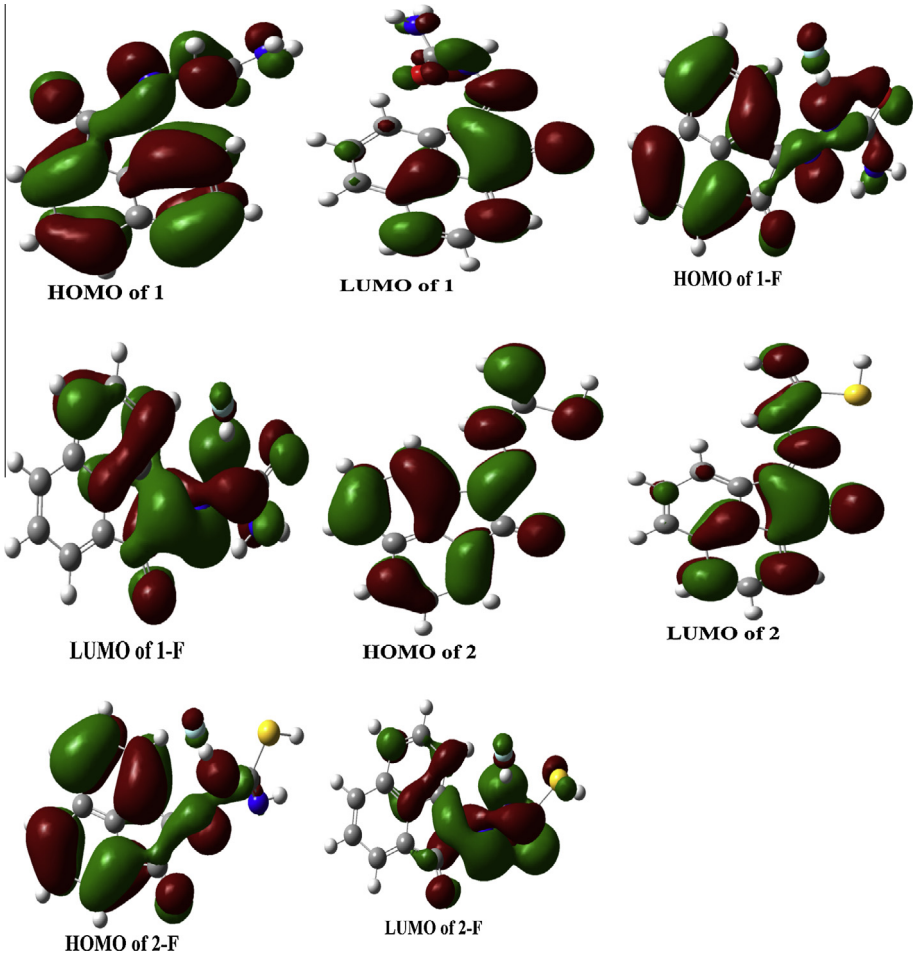
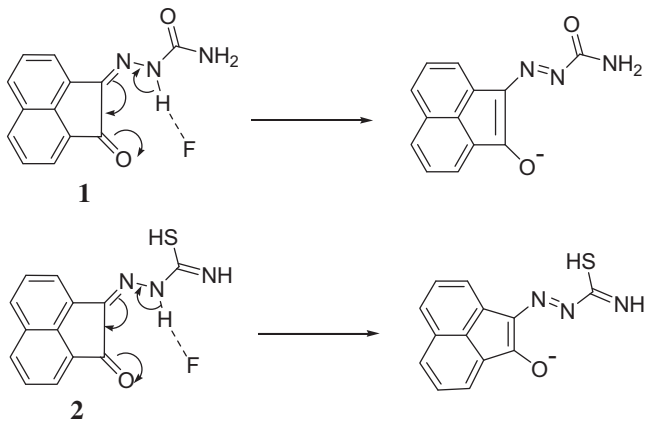


Fig. 8. Forntier MOs of free receptor and their complexes with fluoride ion.

Table 1
Energies of selected MOs and lengths of selected bonds.

System	HOMO (eV)	LUMO (eV)	ΔE (eV)	N—N (Å)	N—H (Å)	H—F (Å)
1	−6.2518	−2.3453	3.9065	1.3910	1.0087	–
1.F	−6.8377	−4.8461	1.9916	1.3083	1.6779	0.9759
2	−6.5272	−2.6150	3.9122	1.3528	1.0126	–
2.F	−6.7688	−4.3671	2.4017	1.3125	1.6456	0.9790



Scheme 2. Mechanism of fluoride ion sensing. .

behavior exhibited by **1** and **2** on the addition of hydroxide and fluoride anions indicated that fluoride ion also results deprotonation through initial H-bond formation. It is interesting to note that, the electronic spectrum of **3** in the presence of either fluoride or hydroxide ions exhibited no change in the absorption maximum (Fig. S6). This is due to the absence of an anion induced azo-hydrazone tautomerism i.e. there is no generation of N=N chromophore. And thus this compound failed to sense fluoride ions with noticeable color change.

Conclusion

For the first time, selective fluoride ion sensing via anion induced change of chromophore from C=N to N=N (azo) in two receptors has been investigated and reported. The mechanism of 'azo-hydrazone' tautomeric signaling has been supported by UV–Vis, fluorescence and ^{1}H NMR spectral studies in addition to electrochemical and theoretical investigations.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2014.02.200.

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