

Coumarin based azo dyes as anion sensors: A spectrophotometric study

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Two 4-hydroxy coumarin based dyes (**1** and **2**) have been synthesized and their anion detection ability has been studied, for detection of fluoride and acetate ions selectively through the naked eye. On addition of 4 equivalents of fluoride and acetate to the CH₃CN solution of the receptors **1** and **2**, colour changes from light yellow to light red while the similar addition of other anions like dihydrogen phosphate, chloride, bromide and iodide does not show any significant change in colour under identical experimental conditions. The corresponding UV-vis data show a blue shift of the band of receptor **1** and a red shift of the band of receptor **2** for both fluoride and acetate ions. In fluorescence studies, both the receptors show quenching in the presence of fluoride and acetate ions. Stoichiometry of anionic interaction has been determined from ¹H-NMR titrations and Job's plot. Theoretical studies using density functional theory and time dependent density functional theory have been explored. Detection of fluoride in aqueous medium by paper strips is also reported.

Keywords: Sensors, Anion sensors, Colorimetric sensors, Fluoride ions, Acetate ions, Azo dyes, 4-Hydroxycoumarins, Coumarins NMR titrations

Development of effect chemosensors for environmentally and biologically significant species has become an important topic of today's scientific research.¹⁻⁸ Beside cations, anions also play an essential role in biological systems and synthetic world and the recognition of anions is a focus point in today's detection studies.⁹⁻¹⁵ However, developing practical strategies for anion detection are more challenging than that for metal cations as anions are larger in size and highly solvated. This implies less effective electrostatic interactions which impair the anion binding strength and selectivity.¹⁶ Fluoride ion is one of the most toxic anions and harmful to the environment and human health, though its beneficial

effects are also known for tooth and bone health particularly in dental caries and osteoporosis.^{17, 20} However, acute exposure to fluoride ions can weaken bones and ligaments, can cause problems in the nervous system, changes in thyroid hormone status, hypocalcemia, dental fluorosis (discoloration of teeth) and infertility.¹⁸⁻²⁰ Another important and common anion in biology is the acetate ion. It is utilized by organisms in the form of acetylcoenzyme. Acetate[(11) C-Acetate] ion acts as a sensitive and specific radiotracer in PET imaging of HCC and evaluation of other liver masses.²¹ It also acts as radioactive tracers in protein-ion binding measurements.²² Thus, there is a need of rapid and convenient analytical techniques for both qualitative and quantitative detection of biologically important anions such as F⁻ and AcO⁻. Techniques based on colorimetric/chromogenic and UV-vis determination are especially attractive due to the naked eye guest determination, simple instrumentation, not so extensive sampling and less expensive equipment. Colorimetric receptors that are easy and safe to handle have received significant attention due to their ability to achieve high selectivity and sensitivity.

The synthesis of azo dyes on 4-hydroxy coumarin has been reported earlier²³ but it has not been utilized as chromogenic sensor till 2014. In the recent past, anion recognition ability of an azo dye derived from 4-hydroxycoumarin has been investigated by Chandel *et al.*²⁴ We have selectively chosen two different aniline derivatives (one having a -Cl group (**1**) and the other having an electron withdrawing -NO₂ group (**2**)) for diazotization of 4-hydroxy coumarin and compared the results of their sensitivity towards anions. The behavior of these synthesized azo dyes towards different anions (F⁻, AcO⁻, H₂PO₄⁻, Cl⁻, Br⁻ and I⁻) was investigated through naked-eye detection, UV-vis spectroscopy, fluorescence method, DFT and TD-DFT methods. Solvatochromism of the dyes in presence of other solvents of different polarities was also investigated. Practical application of the sensor **1** was investigated by paper strip test.

Experimental

All the reagents were purchased and used without further purification. 2-Chloroaniline and 4-nitroaniline

reagents were purchased from SRL. 4-Hydroxy coumarin was purchased from Spectrochem, India. Solvents used were obtained from E. Merck. The anions, F^- , AcO^- , $H_2PO_4^-$, Cl^- , Br^- and I^- were purchased from Spectrochem, India as their tetrabutylammonium salts.

1H NMR spectra were recorded on a Bruker 300 MHz (Bruker AVANCE 300) spectrometer at an ambient temperature. UV-vis spectra of the receptors were recorded in HPLC grade acetonitrile on a Perkin-Elmer UV/vis spectrometer (model Lambda 25). The melting points were determined on a LabX, India Digital Melting point apparatus and are uncorrected.

(*E*)-3-((2-chlorophenyl)diazenyl)-4-hydroxy-2*H*-chromen-2-one (**1**) was synthesized as follows: 2-Chloroaniline (2 mmol) was mixed with 2.5 mL conc. HCl and 2.5 mL cold aqueous solution of 4*M* $NaNO_2$ was added to the prepared mixture with frequent stirring. The temperature of the reaction was maintained at 0-5 °C during diazotization process. Diazonium salt solution prepared above was added drop wise to the alkaline solution of 4-hydroxy coumarin, prepared earlier by dissolving 4-hydroxy coumarin (2 mmol) in 10% NaOH (2 mL). The reaction mixture was stirred for 10-20 min, maintaining the temperature at 0-5 °C. The orange colored product obtained was filtered, washed with water and finally dried. The product was crystallized from 50% ethanol. M. pt.: 244 °C. 1H NMR (DMSO- d_6 , 300 MHz) δ : 7.43 (d, $J = 6.06$ Hz, 3H), 7.61 (d, $J = 7.44$ Hz, 1H), 7.72 (d, $J = 7.2$ Hz, 1H), 7.84 (t, $J = 7.68$, 1H), 7.98 (d, $J = 8.64$ Hz, 1H), 8.09 (d, $J = 7.86$ Hz, 1H), 16.03 (s, 1H) (Fig. S1). ^{13}C NMR (DMSO- d_6 , 300 MHz) δ : 117.59, 118.41, 120.21, 123.66, 123.76, 124.79, 127.12, 128.51, 128.61, 129.97, 136.56, 137.58, 154.51, 158.81, 178.48 (Fig. S2). ESI-MS: 300.98 $[1+H]^+$, Calc.: 301.04 $[1+H]^+$ (Fig. S3). (*E*)-4-hydroxy-3-((4-nitrophenyl)diazenyl)-

2*H*-chromen-2-one (**2**) was synthesized similarly, with 4-nitroaniline instead of 2-chloroaniline. The yellow coloured product was crystallized from acetonitrile. M. pt.: 260-262 °C. 1H NMR (DMSO- d_6 , 300 MHz) δ : 7.44-7.48 (m, 2H), 7.84 (d, $J = 6.80$ Hz, 1H), 7.99-8.07 (m, 3H), 8.41 (d, $J = 8.89$ Hz, 2H), 15.22 (s, 1H) (Fig. S4). ESI-MS: 312.01 $[2+H]^+$, Calc.: 312.06 $[2+H]^+$ (Fig. S5).

To ascertain the molecular mechanism involved in the experimentally observed photophysical properties of the synthesized (**1** and **2**) compounds upon interaction with anions, we investigated the structural, electronic and optical properties using density functional theory (DFT) combined with time dependent density functional theory (TD-DFT) calculations using the Gaussian 09 package.²⁵⁻²⁷ Here we performed the calculations in two sections: (i) Optimization of the ground-state geometry of both compounds using the B3LYP/6-311G (d, p) level of theory, and, (ii) After the minimization process, the optimized geometry in the ground state was used to obtain framework of TD-DFT and to determine the electronic excitation energies using the TD-DFT framework.

Results and discussion

Compound **1** and **2** were synthesized by known procedures of diazotization of 4-hydroxy coumarin with diazonium salts of substituted anilines.²³ However, herein (1:10) sulfuric acid-water medium was used during diazotization unlike the referred procedure where conc. hydrochloric acid medium was used. The main theme of our work is to exploit the deprotonation of hydrogen bonded -NH moiety (Scheme S1) of the isomers of the synthesized compounds (**1** and **2**) by the anions. This phenomenon would enable it to determine the involvement of anions which would make it an efficient sensor for anion detection.

In the naked-eye experiment (Fig. 1), the light yellow colored (5.0×10^{-5} M) solution of **1** in

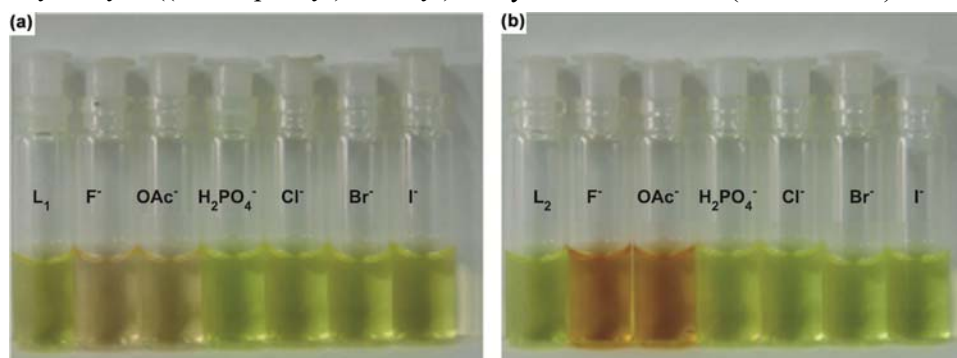


Fig. 1 — Naked eye responses of (a) **1** (L_1), and, (b) **2** (L_2) with anions.

acetonitrile became reddish in colour in the presence of 4 equivalents of F^- or AcO^- as their tetrabutylammonium salts. Similarly, the light yellow coloured **2** ($5.0 \times 10^{-5} M$) became reddish in the presence of 4 equivalents F^- or AcO^- . However, no obvious color change was detected in the case of $H_2PO_4^-$, Cl^- , Br^- and I^- of similar concentration. This may be due to their weaker and insignificant interactions with the receptors.

The sensing behaviour of the receptors **1** and **2** towards various anions (F^- , AcO^- , $H_2PO_4^-$, Cl^- , Br^- and I^-) was investigated by the UV-vis studies (Fig. 2). Both the receptors **1** and **2** responded more favourably towards F^- and AcO^- than other anions. UV-vis titrations of **1** and **2** with F^- and AcO^- were performed by successive incremental addition of tetrabutylammonium salts of the corresponding anions. (Figs 3 & 4). The free receptor **1** showed a strong absorption band at 422 nm. When increasing

concentrations of F^- and AcO^- were added to receptor **1**, a new blue-shifted absorption band at 380 nm, was gradually developed, while the intensity of absorption at 422 nm was diminished (Fig. 3). Figure 3 shows isosbestic points at 472 nm and 393 nm for the titration of both F^- and AcO^- , which implies the formation of host-guest complex. The appearance of the blue shifted band is possibly due to internal charge transfer (ICT) between the 4-hydroxy coumarin and 2-chloroaniline units for deprotonation of $-NH$ moiety and/or due to H-bonding interaction (Scheme S2). Similarly, receptor **2** showed a strong absorption band at 416 nm. When it was titrated with increasing concentration of F^- and AcO^- , it was red shifted to 434 nm and 423 nm respectively. Isosbestic points were observed at 434 nm and 438 nm. There was a decrease in the absorption intensity of the ligand **2** after gradual addition of F^- and AcO^- (Fig. 4). The negative charge brought about by the anion-induced deprotonation increases the dipole

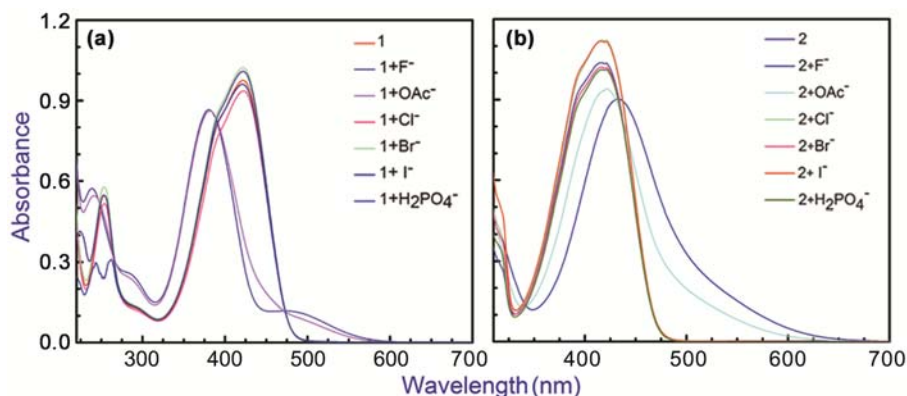


Fig. 2 — Changes in absorption spectra of (a) **1** ($5.0 \times 10^{-5} M$) and (b) **2** ($5.0 \times 10^{-5} M$) upon addition of 4 equiv. of anions in CH_3CN .

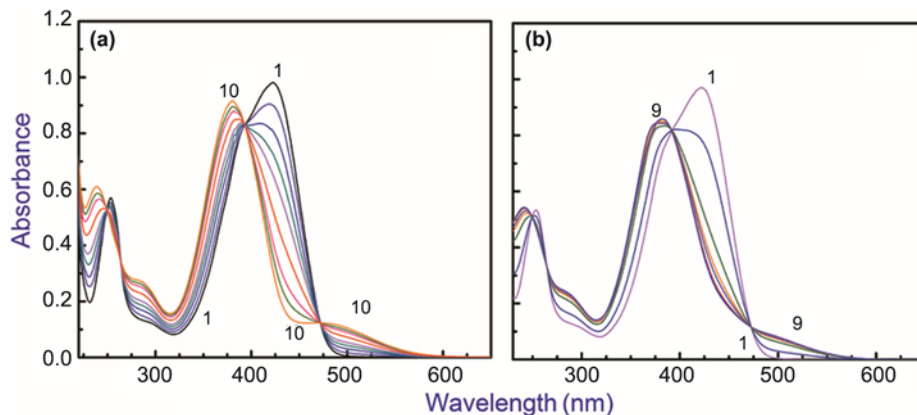


Fig. 3 — (a) Spectral titration of **1** ($5.0 \times 10^{-5} M$) in CH_3CN (2 mL) (curve 1) with the addition of incremental amounts of F^- up to 10 equiv. (curve 16). (b) Spectral titration of **1** ($5.0 \times 10^{-5} M$) in CH_3CN (2 mL) (curve 1) with the addition of incremental amounts of AcO^- up to 10 equiv. (curve 9).

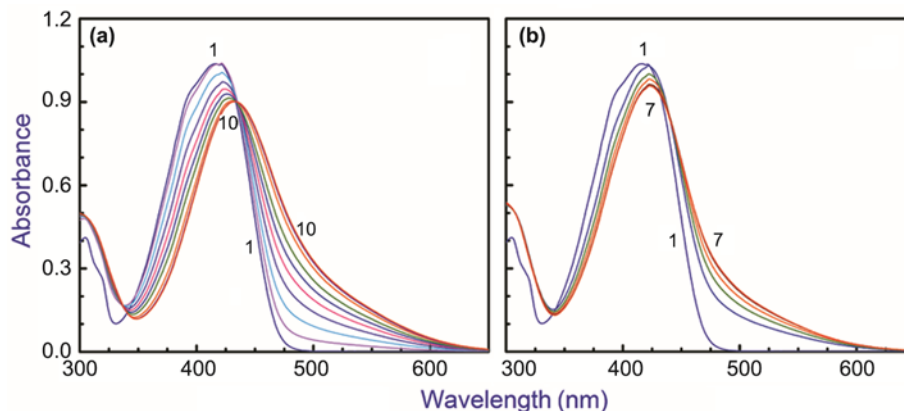


Fig. 4 — (a) Spectral titration of **2** ($5.0 \times 10^{-5} M$) in CH_3CN (2 mL) (curve 1) with the addition of incremental amounts of F^- up to 10 equiv. (curve 10). (b) Spectral titration of **2** ($5.0 \times 10^{-5} M$) in CH_3CN (2 mL) (curve 1) with the addition of incremental amounts of AcO^- up to 10 equiv. (curve 7).

moment and stabilizes the excited state causing a red shift of host **2**. These results demonstrate that a complex formation of **1** and **2** with F^- and AcO^- anion is taking place via electrostatic interactions of hydrogen bonding. However, no change was observed with H_2PO_4^- , Cl^- , Br^- and I^- in CH_3CN . From the UV-vis titrations, the detection limits ($3\sigma/S$) of **1** were $3.9 \times 10^{-6} M$ and $6.9 \times 10^{-7} M$ determined for F^- and AcO^- respectively, and for **2** these were $8.8 \times 10^{-6} M$ and $5.6 \times 10^{-6} M$ determined for F^- and AcO^- respectively.

Anion recognition was investigated by $^1\text{H-NMR}$ spectral titrations. The ^1H spectra of azodyes **1** and **2** were recorded in the presence and absence of varying equivalents of F^- ion in $\text{DMSO-}d_6$ (Figs S6 & S7). In the case of compound **1**, the two proton signals at 16.03 ppm and 14.2 ppm due to the $-\text{NH}$ proton indicate the existence of two intermolecular H-bonded hydrazones isomers, i.e., *E* and the *Z* form in solution. Upon incremental addition of F^- ion, the signal intensity due the proton at 16.03 ppm diminished and vanished after addition of 1 equivalent of F^- ion. The peaks due to the aromatic protons showed a slight upfield shift, initially which ceased with further addition of F^- ion. Probably the increasing electron density in the aromatic system enhanced the shielding effect due to the through-bond effects but beyond 1 equivalent, there was no further shifting of the aromatic proton peaks, indicating the deprotonation process. A similar type of observation was noted for compound **2** also where the intensity of the proton signal due to $-\text{NH}$ proton of the intermolecular H-bonded isomers at 15.22 ppm and 13.8 ppm was

decreased with incremental addition of F^- ion and disappeared at 0.75 equivalent of F^- ion.

To complement the deprotonation process indicated by the $^1\text{H-NMR}$ titration, the compounds **1** and **2** were titrated with tetrabutylammonium hydroxide and the binding nature observed from UV-vis studies were compared with those obtained from UV-vis spectra on interaction with F^- and AcO^- ions. Under conditions similar to UV-vis titration with other anions, $5.0 \times 10^{-5} M$ of **1** and **2** in acetonitrile were titrated with tetrabutylammonium hydroxide. The nature of the spectra obtained for **1** and **2** with OH^- (Fig. S8) ion was similar to that with F^- ion and AcO^- ion. The results indicate that interaction with OH^- created similar species in solution as was in the case of F^- and AcO^- ions. This further confirms the deprotonation mechanism.

Fluorescence titration was carried out for anion recognition with **1** and **2**. Both the compounds, **1** and **2**, were excited at their absorption maxima at 422 nm and 416 nm respectively in acetonitrile. The compound **1** exhibited a weak emission maximum at 495.5 nm with a shoulder peak at 523 nm (Fig. S9(a)). With addition of 4 equivalents of the anions to $2.5 \times 10^{-5} M$ of **1** in acetonitrile, there was quenching in the emission spectra with F^- and AcO^- ions whereas insignificant change was observed with other anions (Fig. S9(a)). The quenching of emission intensity at 495.5 nm was less prominent for AcO^- than for F^- . The fluorescence titration was carried out from 0–150 μM F^- (Fig. 5(a)) i.e., till saturation, and, from 0–140 μM AcO^- (Fig. S10 (a)). Receptor **2** ($2.5 \times 10^{-5} M$) also exhibited a weak emission maximum at 487 nm

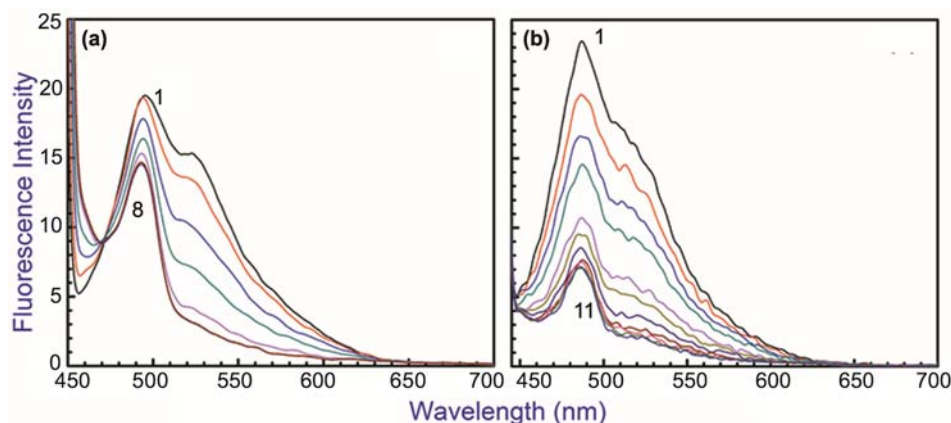


Fig. 5 — (a) Fluorescence titration of **1** ($2.5 \times 10^{-5} M$) in CH_3CN (2 mL) (curve 1) with the addition of incremental amounts of F^- up to $150 \mu\text{M}$ (curve 8). (b) Spectral titration of **2** ($2.5 \times 10^{-5} M$) in CH_3CN (2 mL) (curve 1) with the addition of incremental amounts of F^- up to $50 \mu\text{M}$ (curve 11).

with a shoulder peak at 512 nm when 2 equivalents of anions were added (Fig. S9(b)). Prominent quenching of emission intensity at 487 nm for both F^- and AcO^- ion was noticed, while there was no noticeable change in emission spectra with other anions. In the case of **2**, during titration the F^- and AcO^- ion concentration was varied from 0– $50 \mu\text{M}$ to obtain saturation (Fig. 5(b) and S10(b)). Even in emission studies the selectivity of the sensors **1** and **2** for F^- and AcO^- were very much noticeable.

To study the selectivity of the receptors towards the anions, competitive experiments were done by fluorescence methods in presence of other interfering ions. For both the compounds **1** and **2**, other anions were added to the receptor solutions containing either F^- or AcO^- . In a reverse way, the F^- and AcO^- were also added to receptor solutions containing other anions. In all the cases, quenching due to the F^- and AcO^- for the compound **1** and **2** was barely effected in presence of the interfering anions, indicating the specific and selective anion recognition ability of the sensors **1** and **2** (Supplementary data, Figs S11 & S12).

Job's method of continuous variation was employed to verify the stoichiometry of complexation of anions (F^- and AcO^-) with compounds **1** and **2** using absorbance spectroscopy (Supplementary data, Figs S13 & S14). Sum of the concentration of ligand and anion was maintained as $50 \mu\text{M}$ and varying their mole fraction from 0–1. The inflection points were found to be at $\chi_{\text{F}^-} = 0.524$ and $\chi_{\text{AcO}^-} = 0.489$ for **1** from which the stoichiometries of the F^- :**1** and AcO^- :**1** complex were calculated to be $\sim 1:1$ and $1:1$

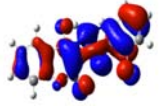
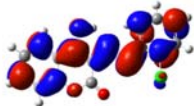
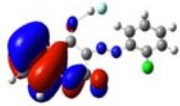
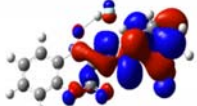
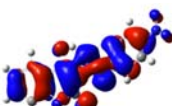
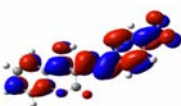

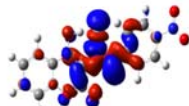
respectively. For compound **2**, the inflection point was found to be at $\chi_{\text{F}^-} = 0.484$ and $\chi_{\text{AcO}^-} = 0.506$, and stoichiometries of the F^- :**2** and AcO^- :**2** complexes were calculated to be $\sim 1:1$ and $1:1$ respectively.

To test the reversibility of the anion recognition ability and aqueous tolerance, the solutions of **1** and **2** with F^- in CH_3CN were titrated by successive addition of $5 \mu\text{L}$ of water. The anion recognition ability of **1** and **2** diminished drastically and reversibly on addition of small amount H_2O ($65 \mu\text{L}$) (Supplementary data, Fig. S15). The addition of H_2O is expected to compete with the anions to form complexes with the ligands. It forms a strong hydrogen bond interaction with the $-\text{NH}$ moiety hampering the process of deprotonation. The results obtained here indicate the possible application of these systems as a sensor for the quantitative detection of water present in organic solvents like CH_3CN .

The effects of medium and solvents on the UV-vis absorption spectra of **1** and **2** were investigated for four organic solvents of different polarities viz., N, N-dimethylformamide, dimethylsulfoxide, toluene and tetrahydrofuran (Supplementary data, Fig. S16). The band at 422 nm for the receptor **1** shows blue shift (negative solvatochromism) upon increasing solvent polarity. On the other hand, absorption band at 416 nm for the receptor **2** shows red shift (positive solvatochromism) as the polarity of solvent was increased.

The DFT optimized structures of compound **1** and **2** are shown in Fig. S17 (Supplementary data). The relevant frontier molecular orbitals (HOMO and LUMO) of the compounds and their complexes with

Table 1 — DFT computed HOMO and LUMO diagrams and corresponding HOMO and LUMO energy of ligands (**1** and **2**) and their fluoride complexes (**1** + F⁻ and **2** + F⁻)

Ligand	HOMO (H)	LUMO (L)	H-L (eV)
1	 -6.313 eV	 -2.884 eV	3.469
1 +F ⁻	 -10.585 eV	 -8.082 eV	2.503
2	 -6.721 eV	 -3.374 eV	3.347
2 +F ⁻	 -11.129 eV	 -9.225 eV	1.904

F⁻ ions along with their energies are summarized in Table 1. As shown in Table 1, the HOMO distribution of **1** is concentrated primarily on the chlorobenzene ring and N=N (azo group) moiety, while LUMO, distribution is concentrated on the 4-hydroxy coumarin moiety. The HOMO-to-LUMO excitation is responsible for the maximum observed at 422 nm in the UV-vis spectrum of **1** (Fig. 2). In the case of **1**-F⁻ complex, the HOMO is delocalized over the aromatic ring of the coumarin moiety opposite to that of free **1** and LUMO is distributed over N=N and chlorobenzene ring. After the formation of H-bond with F⁻ ions, the HOMO-LUMO energy gap decreases ($\Delta E = 2.503$ eV) as compared to that in the free receptor **1** ($\Delta E = 3.469$ eV). In the case of receptor **2**, the HOMO is concentrated on the N=N moiety moiety and the LUMO is concentrated on the nitrobenzene ring. The maximum observed (at 416 nm) in the electronic spectrum is due to the HOMO to LUMO excitation. The energy gap between these two frontier molecular orbital is 3.347 eV, which is slightly less than that in **1**. On interaction with F⁻ ion the energy gap decreases to 1.904 eV. In both **1** and **2**, the energy gap between HOMO and LUMO is much greater than that in their

corresponding fluoride complexes. Thus, **1** and **2** are comparatively more stable in their free states than in their corresponding fluoride complexes. Hence, both **1** and **2** prefer to exist in the hydrogen-bond form rather than in deprotonation state.

The experimental and theoretical UV-vis. spectra of compounds **1** and **2** were compared. The theoretical absorption bands were computed at 378 and 404 nm from TD-DFT for compound **1** and **2** respectively. Experimentally, the maxima appeared at 422 and 416 nm for **1** and **2** respectively. TD-DFT calculations predicted the electronic spectra as a quite logical and in agreement with experimental one. In case of ligand **1**, the largest contribution to charge transition in 378 nm (theoret.) was from the HOMO (H)→LUMO (L) (95%). For ligand **2**, the major contribution for 404 nm belongs to H→L transition (87%) and H→L+2 (9%).

Generally anionic sensors involving hydrogen bonding or deprotonation process do not respond to anions in water medium due to strong solvent competition as also the case herein. To make the sensors effective for practical applications paper strip test for compound **1** was carried out. The paper strips of compound **1** were prepared by dipping the paper strips in 5 mM solution of compound **1** in CH₃CN and oven dried. The strips were dipped in neutral anionic solutions in water (1 mg/ mL) and again made vacuum dried. In the strip test, receptor **1** appeared to be most selective for F⁻ (Supplementary data, Fig. S18).

In the present study the anion recognition abilities through deprotonation mechanism of azo dyes **1** and **2** were studied via naked eye detection, and spectrophotometric and fluorescence studies. The studies showed binding of the ligands to fluoride and acetate ions selectivity and specifically among other anions. ¹H-NMR titration studies indicated 1:1 complex formation for both the associations. The ability of the receptors to detect presence of water quantitatively in solvents like acetonitrile was also studied from reversible titration studies where reversibility of binding with fluoride was seen with trace amount of water. **1** showed negative solvatochromism and **2** showed positive solvatochromism with increase in solvent polarity. DFT study showed that both **1** and **2** preferred to exist in the intra-molecular hydrogen bonded form rather than in the deprotonation state. The practical applicability of the sensor **1** towards F⁻ has been demonstrated via strip tests.

Supplementary data

Supplementary data associated with this article are available in the electronic form at [http://www.niscair.res.in/jinfo/ijca/IJCA_57A\(01\)59-65_SupplData.pdf](http://www.niscair.res.in/jinfo/ijca/IJCA_57A(01)59-65_SupplData.pdf).

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