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SHORT COMMUNICATION

Spectroscopic and Computational Study of a Naphthalene Derivative as Colorimetric and Fluorescent Sensor for Bioactive Anions

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Abstract The anion recognition property of a naphthalene based receptor (**L**) was investigated by naked-eye, UV-Vis, fluorescence, ^{1}H NMR and computational methods. The receptor **L** showed fluoride selective naked-eye detectable colorimetric and UV-Vis spectral changes over other tested anions due to the formation of hydrogen bonding complex in 1:1 stoichiometry and/or deprotonation between fluoride and the receptor. Interestingly, the fluorescence of **L** was quenched by fluoride but enhanced by acetate.

Keywords Anion recognition · Colorimetric and fluorescent sensor · Fluoride · Acetate · DFT

Introduction

Anion recognition continues to be a major research goal for many supramolecular chemistry groups around the world. This is because anions play crucial role in a wide range of biological phenomena, chemical and environmental processes [1–6]. Anions are roughly present in 70 % of all enzymatic sites, which play essentials roles in many proteins and are critical for the manipulation and storage of genetic information [7]. It is also essential in the formation of majority of enzyme-substrate and enzyme-cofactor complexes as well as in the interactions of proteins with DNA or RNA. Among the different bio-active anions, fluoride and acetate are of prime importance. Acetate acts as a critical component in numerous metabolic processes [8, 9]. On the other hand, interest in the detection and recognition of fluoride ion is because of its significant role in dental caries, clinical treatment for osteoporosis, toxicity resulting from it's over accumulation in the bone, and association with hydrolysis of the nerve gas sarin [10–12]. Because of the advancement in the supramolecular concepts on host-guest chemistry, numbers of suitable receptors have been developed for the selective encapsulation and sensing the biologically important anions for the qualitative and quantitative determination [13–16]. Particularly, the sensing of anion through the naked-eye (colorimetric), fluorescent and/or electrochemistry responses have attracted considerable attention.

In this communication, we have introduced a simple and easy to prepare anion sensor **L** by combining 2-hydroxy-1-naphthaldehyde with 2-aminophenol. Addition of one equivalent of F^-, AcO^- and $H_2PO_4^-$ anions to **L** solution in acetonitrile, naked-eye detectable color changes was observed from yellow to orange. Importantly, spectroscopic results reveal that the sensor **L** showed fluoride selective behavior in the presence of other competitive anions. The experimental evidences were well supported by theoretically estimated anion recognition ability of **L**.

Materials and Methods

Unless otherwise specified, all reagents for synthesis were obtained commercially and used without further

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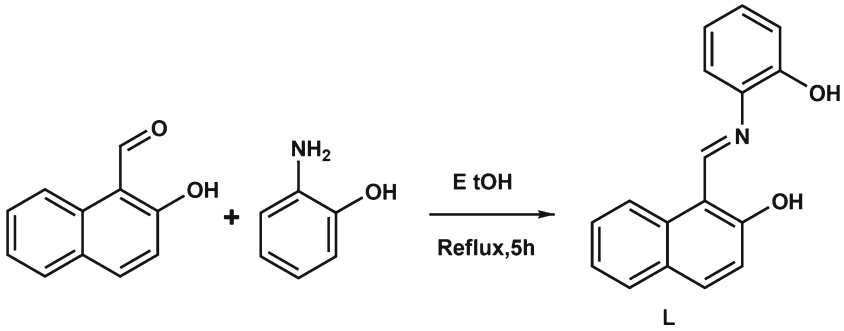
Scheme 1 Synthesis of the receptor **L**



purification. In the titration experiments all the anions were added in the form of tetra-n-butyl ammonium (TBA) salts, which were purchased from Spectrochem Pvt. Ltd., India or Acros Organic, and stored in a vacuum desiccator containing self-indicating silica and dried fully before using. Analytical grade acetonitrile and absolute ethanol were used after distillation. ^{1}H NMR and ^{13}C NMR spectra were determined in DMSO-d_6 on BRUKER AVANCE II 400 MHz NMR using TMS as an internal standard. Melting point were measured on digital melting point apparatus VMP-DS "VEEGO" which was uncorrected. UV-Vis spectra were recorded on VARIAN CARY 50 Spectrophotometer with a quartz cuvette (path length=1 cm). The fluorescence spectra were recorded on a Perkin-Elmer LS55 luminescence spectrometer.

Stock solution of the receptor (1.0×10^{-3}M) and anions (1.0×10^{-3}M) were prepared in acetonitrile. These solutions were used for all spectroscopic studies after appropriate dilution. For spectroscopic titrations, required amount of the receptor ($C_L=1.0\times10^{-5}$M) was taken directly into cuvette and spectra were recorded after successive addition of anion by using micropipette. The sample for ^{1}H NMR study was prepared by mixing both anion and receptor in an appropriate ratio. Then, the mixture was made soluble in DMSO-d_6 and the spectrum was recorded.

All theoretical calculations were carried out with the Gaussian 09W computer program [17] using the density functional theory (DFT) method. Optimizations of the receptor and `anions have been carried out without symmetry constraints by applying B3LYP/6-31G(d,p) method in gas phase. The harmonic vibrational frequency calculations using the same methods as for the geometry optimizations were used to ascertain the presence of a local minimum.

Synthesis of **L**

2-hydroxy-1-naphthaldehyde (0.5 g, 0.0029 mol) in 20 ml absolute ethanol was added drop wise into a solution of 2-aminophenol (0.31 g, 0.0029 mol) in 30 ml absolute ethanol with magnetic stirring. After the addition, the mixture was heated at reflux for 5 h, and then the solvent was concentrated under reduced pressure. The solid obtained was recrystallized from ethanol to give orange-yellow crystals. Yield: 85 %., M.P: 210 °C. IR (KBr pellet, 400–4,000 cm^{-1}): 3,433, 1,632; ^{1}H NMR (DMSO-d_6, δ, ppm): 15.65 (s, 1H), 10.11 (s, 1H), 9.41 (s, 1H), 8.24 (d, 1H), 7.73 (d, 1H), 7.72 (d, 1H), 7.61 (d, 1H), 7.45 (d, 1H), 7.24 (d, 1H), 7.08-7.00 (m, 2H), 6.92 (t, 1H), 6.81 (d, 1H); ^{13}C NMR (DMSO-d_6, δ, ppm): 177.08, 149.22, 148.53, 137.47, 133.69, 128.75, 128.68, 127.81, 126.41, 125.81, 124.73, 122.75, 119.57, 118.99, 117.23, 115.96, 107.60; LC-MS for $C_{17}H_{13}NO_2$: calculated 263.30, found 264.10.

Results and Discussion

Receptor **L** was synthesized by simple condensation method according to Scheme 1 and the molecular structure was established from different spectroscopic studies. The

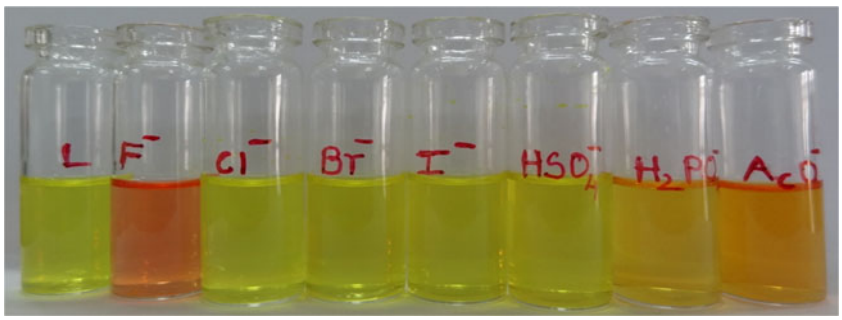


Fig. 1 Color change of the sensor **L** (5.0×10^{-5}M) upon addition of equivalent amount of different anions in acetonitrile

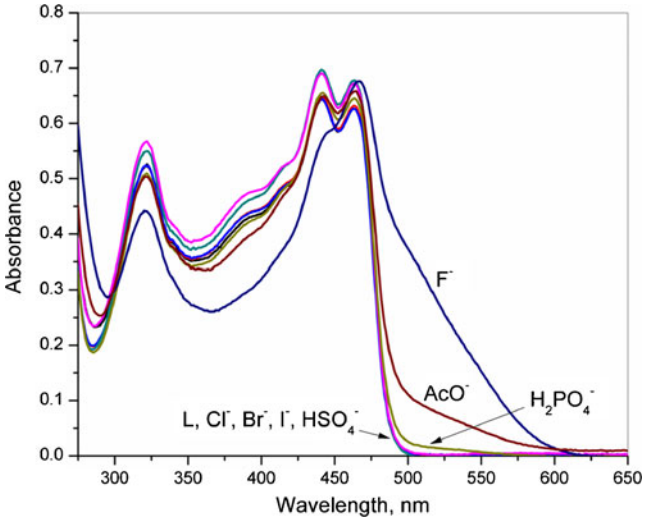


Fig. 2 UV-Vis spectra changes of sensor **L** (5.0×10^{-5}M) upon addition of one equivalent of different anions in acetonitrile

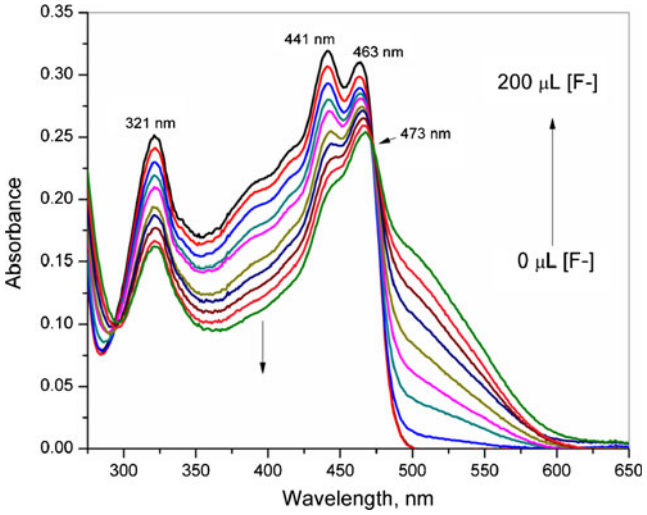


Fig. 4 UV-Vis absorbance spectra of **L** (1.0×10^{-5}M) upon successive addition of fluoride (1.0×10^{-4}M) in acetonitrile

recognition property of the receptor **L** towards different anions was studied by naked-eye experiment, UV-Vis and fluorescence titrations.

In naked-eye experiment, the yellow of the receptor **L** becomes orange upon addition of equivalent amount of F^- due to the formation of H-bond interactions between electron-rich F^- and the receptor **L** (Fig. 1). Similarly, a detectable color change from yellow to light orange was observed with receptor **L** in presence of AcO^- and $H_2PO_4^-$. However, no obvious color changes was observed in presence of HSO_4^-, Cl^-, Br^- and I^-, even the anions were excessive presumably due to weaker interactions with the receptor that failed to alter any structural changes. Spectrophotometrically, the UV-Vis absorption spectra of **L** (5.0×10^{-5}M) were recorded in absence and presence of equivalent amount of different anions in acetonitrile. As shown in Fig. 2, the free receptor showed a broad absorption between 300 nm and 500 nm with λ_{max} at 321 nm, 441 nm and 463 nm presumably due to π-π^* transitions. On addition of F^- to **L** solution, the receptor peaks at 321 nm and 441 nm decreases with the appearance of new broad peak between 500 nm and 600 nm due to the Internal Charge Transfer (ICT). Similarly, the new broad peak was also detected due to AcO^- and $H_2PO_4^-$ but the intensity was appreciably lower than the F^- which indicate the fluoride selective recognition ability of **L**. The addition of other anions Cl^-, Br^-, I^- and HSO_4^- did

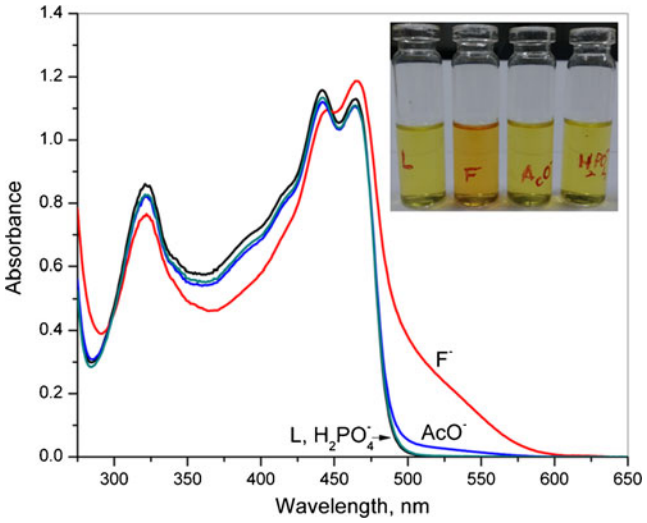


Fig. 3 UV-Vis spectra and color changes of sensor **L** (1.0×10^{-4}M) upon addition of one equivalent of different anions in 1%water:acetonitrile solution. Insert showing Color change of the sensor **L** upon addition of equivalent amount of different F^-, AcO^- and $H_2PO_4^-$

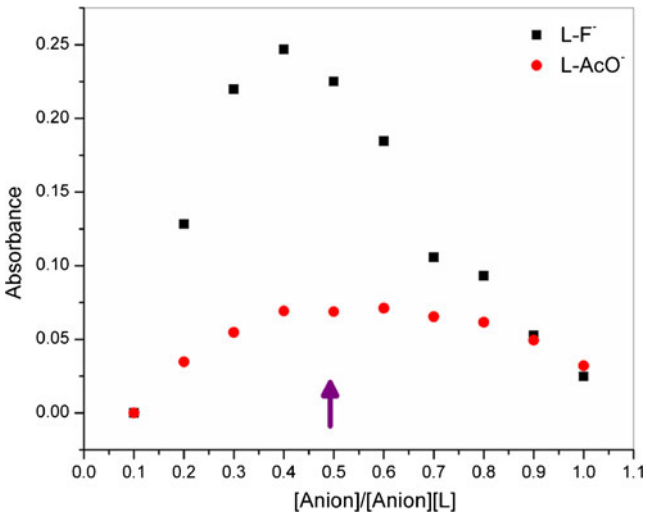


Fig. 5 Job's plots for the complexation of **L** with F^- and AcO^- in acetonitrile

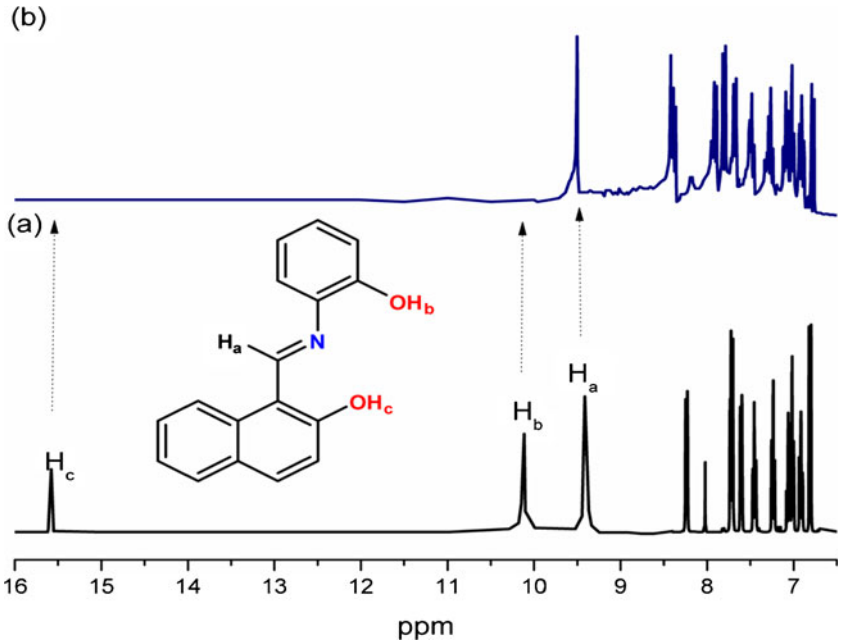


Fig. 6 ^{1}H NMR spectra of **L** in absence (**a**) and presence (**b**) of one equivalent of fluoride anion in DMSO-d_6

not result in obvious spectral responses even in abundance.

Further, it was observed that the intensity of color decreases reversibly on addition of small amount of water. The presence of protic solvents such as water can compete with anions for binding sites and disturb the H-bond interactions between the host and the anionic guest that lead to a reversal of the visual color [18]. However, at 1 % water:acetonitrile solution, the receptor **L** showed fluoride selective naked-eye detectable color and spectral changes (Fig. 3). Also, the color and spectral changes induced by the fluoride ion can still be observed when the aqueous content was as high as 4 % in acetonitrile, which makes the receptor **L** suitable for different biochemical applications. In addition, the fluoride-induced color change remains the same even in the presence of other anions including AcO^- and $H_2PO_4^-$.

Spectrophotometric titrations were carried out in acetonitrile at 1.0×10^{-5}M concentration of receptor **L** upon the addition of incremental amounts of F^- or AcO^-. These results are shown for the most selective anion, fluoride (Fig. 4). The spectral changes with the formation of isosbectic point at 473 nm indicate the formation of single

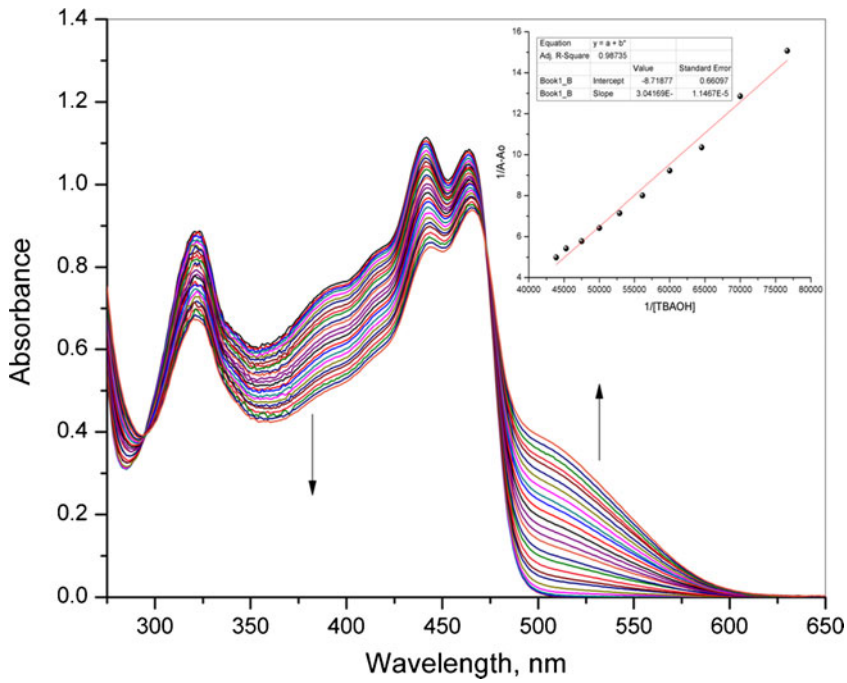


Fig. 7 UV-Vis absorbance spectra of **L** (1.0×10^{-4}M) upon successive addition of TBAOH (1.0×10^{-3}M) in acetonitrile. Insert showing the B-H plot

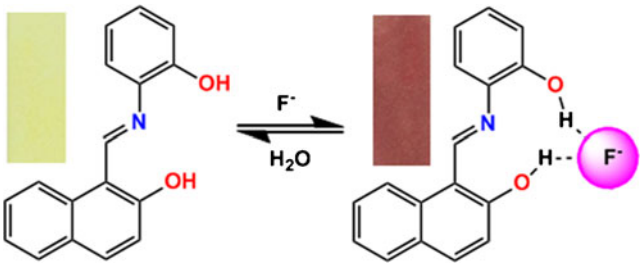


Fig. 8 Binding modes of **L** with F^- and the color change observed with test paper kit

complex species between the receptor **L** and the anion added. The calculated binding constant (K) by applying Benesi-Hildebrand equation for F^- ($7.76\times10^4 M^{-1}$) is higher than AcO^- ($6.24\times10^3 M^{-1}$), which supported the fact that the F^- binds strongly with the receptor as compared to AcO^-. The reason was probably that the higher electronegativity and smaller size of the F^- favors stronger binding with the receptor **L** by forming hydrogen bonding interactions and/or deprotonating the OH groups.

The Job's plot suggested that there was only one type of 1:1 binding interaction between the receptor **L** and anions (F^- or AcO^-) added (Fig. 5). Further, to gain an insight into the host-guest interaction between **L** and anions, ^1H NMR of **L** was measured in absence and presence of one equivalent of the fluoride anion as TBA salt in DMSO-d_6 solution (Fig. 6). The free receptor showed signals at 15.65 ppm and 10.11 ppm due to OH groups attached to the naphthalene and phenolic units, respectively. Addition of just one equivalent of F^- resulted complete disappearance of receptor peaks due to OH protons. No remarkable variations were observed with other signals due to imine proton at 9.41 ppm and aromatic protons between 8.25 ppm and 6.80 ppm. In addition, no peaks around ~16 ppm observed due to the formation of F-H-F^- complex [19]. These observations inferred that the receptor is recognizing fluoride anion through O-H…F hydrogen bonds without any apparent conformational changes and deprotonation. Further to confirm the anion binding modes of the receptor **L**, the absorption titration of **L** with tetrabutylammonium hydroxide (TBAOH) was performed in acetonitrile. As shown in Fig. 7, the absorption band induced by TBAOH matched well with the band formed in the presence of fluoride ion (Fig. 4). The results clearly demonstrate that both anions are

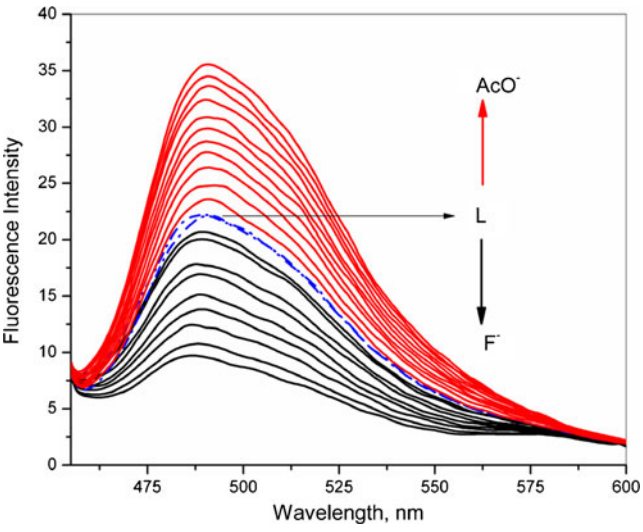


Fig. 9 Fluorescence titration spectra of receptor **L** (1.0×10^{-5}M, λ_{ex}=430 nm) upon the gradual addition of fluoride (8.0×10^{-8}M to 1.0×10^{-5}M) and acetate (6.0×10^{-8}M to 1.0×10^{-5}M) in acetonitrile

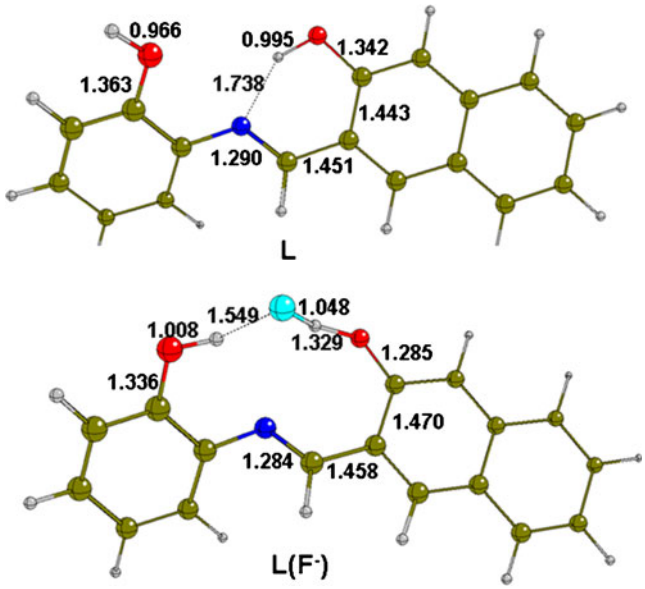


Fig. 10 Optimized structure of **L** and **L**-F^- in gas phase at B3LYP/6-31G(d,p)

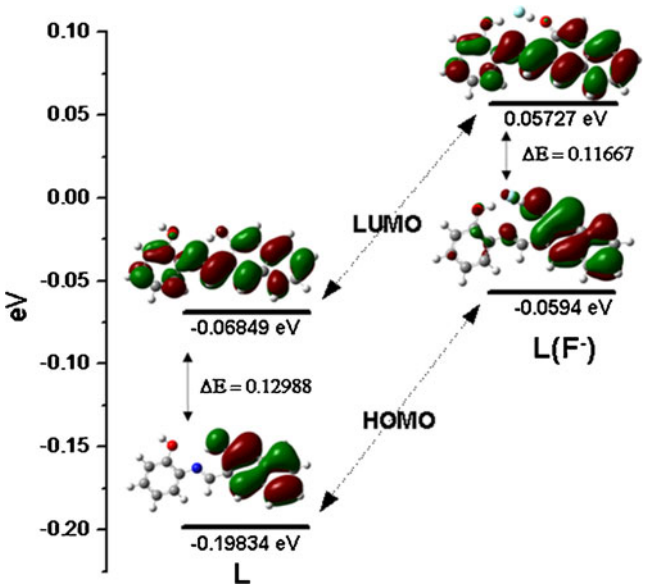


Fig. 11 HOMO and LUMO diagrams for **L** and **L**(F^-) obtained at B3LYP/6-31G(d,p) method

functioning here as a base, giving rise to the deprotonation upon interaction with the receptor **L** [20]. Based on the above experimental evidences, the possible complexation modes of the receptor **L** was shown in Fig. 8.

The anion binding behavior of the receptor **L** (1.0×10^{-5}M) was also investigated by fluorescence titrations in acetonitrile (Fig. 9). The sensor **L** showed an emission band centered at 490 nm (λ_{ex}=430 nm). Upon addition of fluoride, there was a significant quenching in the emission intensity of **L**. The fluorescence quenching may be due to the intermolecular hydrogen bonding interactions between fluoride and **L**, where the hydrogen bond acts as an efficient accepting mode for radiationless deactivation processes from the excited state via internal conversion (IC) [21]. Interestingly, under similar condition the fluorescence of receptor **L** was enhanced upon incremental addition of acetate presumably because of the formation of rigid acetate-**L** complex through multiple hydrogen bonding that restricts tautomeric transformation at the excited state and therefore, ceases non-radiative decay and consequently the emission intensity was increased [22]. Further study under competitive environment inferred that the receptor **L** with equivalent amount of both acetate and fluoride ions showed fluorescence enhancement as observed only with acetate.

In order to complement our experimental findings, structural optimization of receptor **L** and its host-guest complexes were performed at B3LYP/6-31G(d,p) level by focusing on the proposed 1:1 binding modes between **L** and anions (F^-, AcO^- and $H_2PO_4^-$). The interaction (or binding) energies [$\Delta E=E_{elec}$(complex)-E_{elec}(anion)-E_{elec}(**L**)] were computed for the complexes formed between receptor **L** and anions to provide a useful scale to assess the relative strengths of these interactions. The calculated results [ΔE(**L**-AcO^-)=−151.18 kJmol^{-1}, ΔE(**L**-F^-)=−409.89 kJmol^{-1},) ΔE(**L**-$H_2PO_4^-$)=−105.52 kJmol^{-1}] verify that F^- forms the strongest complex with the receptor **L**. The optimized global minimum structure of **L** and its **L**-F^- complex (Fig. 10) indicates that the receptor **L** preferred enolimine form and the two OH moieties of **L** interacts with the anion through hydrogen bonding to form the anion-receptor complex. Further analysis of HOMO and LUMO diagrams (Fig. 11) of **L** and **L**-F^- indicate the $\pi\rightarrow\pi^*$ electronic transition and the internal charge transfer occurred during the anion recognition process. The HOMO electron density distributed mainly over naphthalene unit of **L** can also be observed over imine-N and phenolic unit on interaction with fluoride ion because of the charge delocalization occurred by deprotonation process. In addition, the HOMO-LUMO band gap of **L** decreases on interaction with anion, which supports the absorbance at longer wavelength and orange coloration.

Conclusions

We have introduced a simple chemosensor **L** for bioactive anions. Sensor **L** portrayed a colorimetric change from yellow to orange on interaction with F^-, AcO^- and $H_2PO_4^-$ in 1:1 stoichiometry in pure CH_3CN. In mixed solvent 1%H_2O:CH_3CN, sensor **L** exhibited selective recognition towards fluoride anion. In addition, receptor **L** can be implemented to develop test paper kit for analytical application (Fig. 8). More importantly, the fluorescence of **L** was quenched by fluoride but enhanced by acetate. The enhancement and quenching of **L** fluorescence can be helpful to discriminate the two bioactive anions AcO^- and F^-.

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