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# Naked-eye detection of $F^-$ and $AcO^-$ ions by Schiff base receptor

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ABSTRACT

A Schiff base **2**, composed with *o*-phenylenediamine and 5-nitro-salicylaldehyde have been synthesized as an anion receptor. It consists with conjugated imine, phenolic –OH and electron withdrawing substituent nitro ($-NO_2$) group. Receptor **2** can recognize selectively biologically important $F^-$ and $AcO^-$ ions. The recognition properties have been investigated by naked-eye color change (colorless to yellow), followed by UV–vis spectral changes. Predicted stoichiometries of the complexes between receptor **2** and anions based on density functional theory (DFT) level calculations, corroborates well with experimental findings.



## 1. Introduction

For decades, Schiff bases were prepared mainly for complex formation with several metal ions [1,2], for their potential applications in catalysis [3], asymmetric synthesis [4], epoxidation [5], electrochemistry [6], magnetochemistry [7], molecular separation and biomedical applications [8]. On the other hand, Schiff bases as anion receptors are almost unexplored because interaction between metal and Schiff base are in general stronger than the hydrogen bond interactions between anion and Schiff base. Recently, only few examples are in the literature, where Schiff bases can also be used as anions receptor [9–12]. The reason behind utilizing Schiff bases includes (a) Schiff bases are easily obtained through one-step procedure *via* condensation of aldehydes with amines and (b) in particular, Schiff bases derived from salicylaldehyde derivatives having 2-hydroxy group are of interest mainly due to the existence of O–H···N and O···H–N type hydrogen bonds and tautomerization exist between phenol-imine and keto-amine forms. In contrast, many excellent chemosensors for anion detection have been reported. However, they need very complicated synthetic routes or troublesome purification procedures [13,14].

The recognition and sensing of anions by proper design of anion receptors is currently an expanding research area within the field of supramolecular chemistry [15–17]. Various kind of anions such as $F^-$, $Cl^-$, $I^-$, $PO_4^{3-}$, $CH_3COO^-$, etc. play a major role both in environmental and biological systems [18–20]. Among the above anions, fluoride ion received the most attention from chemists because of its unique properties. It is well known that a small quantity of fluoride ion is present in biological fluids, tissues and especially in bone and tooth. However, excess fluoride anions cause several serious diseases such as fluorosis, thyroid activity depression, bone disorders and immune system disruption [21,22]. Because of these significant importances, detection of anions with the help of easily synthesized receptor and minimal instrumental assistance is desirable towards practical applications.

Here, we report a Schiff-base receptor **2**, obtained by condensation of 5-nitro-salicylaldehyde with *o*-phenylenedianine, can recognize biologically important $F^-$ and $AcO^-$ anions exclusively, by visual observation without need of any spectroscopic instruments. Furthermore, the density functional theory (DFT) level calculations for the determination of stoichiometries of the complexes between receptor **2** and anions corroborates well with experimental results.

## 2. Results and discussion

Schiff base **1** (reference compound) was synthesized according to the literature procedure by mixing salicylaldehyde and *o*-phenylenediamine in methanol (Scheme 1) [23]. Schiff base **2** has been synthesized according to the literature method by heating 5-nitro salicylaldehyde and *o*-phenylenediamine in methanol

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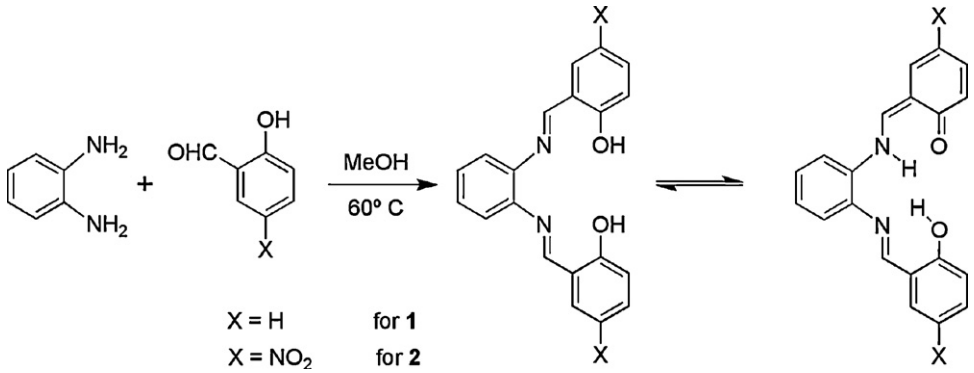



**Scheme 1.** Syntheses of reference compound **1** and receptor **2**.

(Scheme 1) [24–26]. We have chosen nitro substituted Schiff-base receptor **2** mainly for two reasons: (a) the presence of *para* substituted $-NO_2$ group, having electron withdrawing effect is expected to enhance the acidity of the phenolic –OH and as a consequence, the hydrogen donor properties of the receptor **2** is also increase. (b) The UV–vis absorption properties of the chromogenic nitrophenyl moiety may be altered by receptor–anions interaction, thus providing colorimetric and spectral sensing recognition event [27,28]. Due to poor solubility of receptor **2** in $CH_3CN$, we used a mixture of DMSO and $CH_3CN$ solvent (5:95, v/v ratio) for spectroscopic titration.

### 2.1. Visual sensing of anions

Visual color change of receptor **2** ($1.0 \times 10^{-5}$ M) was investigated in mixed solvent ($CH_3CN$ and DMSO 95:5, v/v). Upon addition of $F^-$ and $CH_3COO^-$ ion to the solution of **2**, a detectable naked-eye color change was observed from colorless to intense yellow color (Fig. 1). Other ions such as $Cl^-$, $Br^-$, $I^-$ and $HSO_3^-$ did not exhibit any detectable color change. Under similar experimental condition, $H_2PO_4^-$ ion did not exhibit considerable color change, but at higher concentration of $H_2PO_4^-$ ion a faint yellow color was observed by naked-eye (Fig. 1).

Schiff-bases having 2-hydroxy group are generally undergoes phenol-imine and keto-amine tautomerization equilibrium. The keto-amine tautomerism in receptor **2** is facilitated by the electron withdrawing nitro ($-NO_2$) group, situated at the *para* position with respect to the phenolic –OH group, resulting in an increase in acidity of the phenolic –OH group and thereby enhance the hydrogen bonding interaction with the anions, as a result the increasing electron density on the "O" atom can resonate with $-NO_2$ group through the conjugated benzene ring (Scheme 2), resulting appearance of the yellow color [10]. It is noteworthy that the yellow color was disappeared and the original colorless solution came back on addition of protic solvent such as $H_2O$ or $CH_3OH$, since the anions are no more bound with the receptor **2**, as they are highly solvated with the protic solvent.

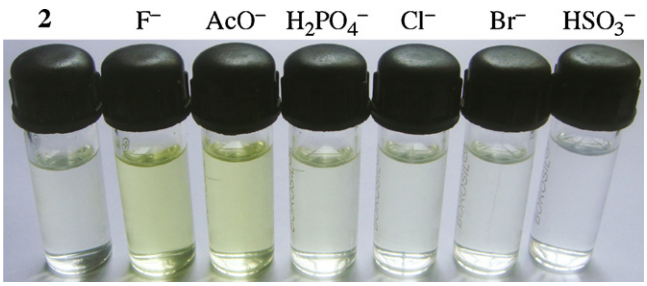


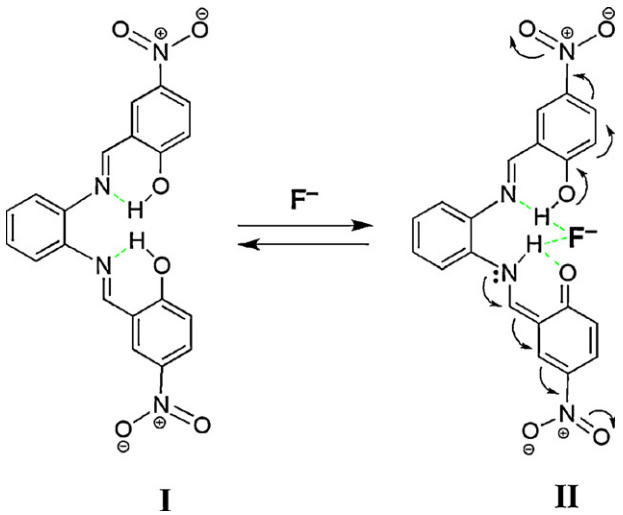

**Fig. 1.** Naked-eye color changes of receptor **2** ($1.0 \times 10^{-5}$ M) after addition of 2 equivalent of various anions in DMSO and $CH_3CN$ solvent mixture (5:95, v/v).

### 2.2. UV–vis spectroscopic titration spectra

The anion recognition properties of receptor **2** have been investigated by monitoring UV–vis spectral change upon addition of different anions in a mixed solvent ($CH_3CN$ and DMSO 95:5, v/v). Receptor **2** exhibited a strong and broad absorption band from 298 to 329 nm, peaked at 312 nm (Fig. 2). Fig. 2 shows the absorption spectral changes of **2** ($1.0 \times 10^{-5}$ M in $CH_3CN$ and DMSO) in presence of $F^-$ ion. Upon adding increasing amount of $F^-$ ion to receptor **2** in $CH_3CN$ solution, the peak at 312 nm gradually decreased its intensity and new absorption peaks at 360 nm and 422 nm gradually appeared. A distinct isosbestic point at 336 nm was observed during the titration process between the receptor **2** and $F^-$ ion, which clearly indicated the formation of complex between **2** and $F^-$ ion. During this titration the initial colorless solution gradually changed to yellow color. Similar type of UV–vis spectral changes were observed upon addition of acetate ($AcO^-$) ion into the solution of **2** (Fig. 3).

In contrast, under the similar experimental condition, $H_2PO_4^-$ ion exhibits only a tiny spectral change of **2**, which is difficult to detect by naked-eye. On addition of other anions such as $Cl^-$, $Br^-$, $I^-$, and $HSO_3^-$ ions did not show any notable spectral or color change, indicating no interaction or complexation of these anions with receptor **2**. As shown in Fig. 4, compound **2** can selectively detect fluoride and acetate ion compared to the rest of the anions tested.

The selectivity and sensitivity of receptor **2** towards the $F^-$, $AcO^-$, $H_2PO_4^-$, $Cl^-$, $Br^-$, $I^-$, and $HSO_3^-$ ions can be rationalized on




**Scheme 2.** The plausible mechanism for keto-amine tautomerization and cause of color change upon complexation between **2** and anions.

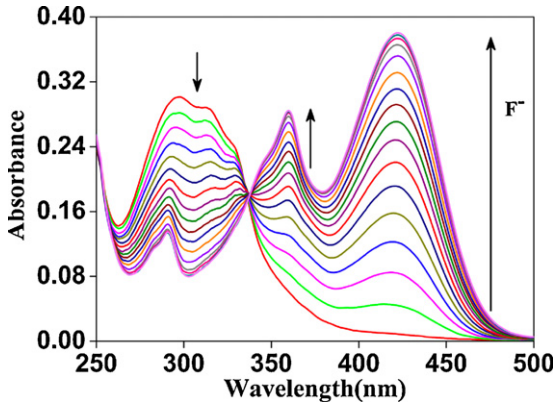



**Fig. 2.** UV–vis titration spectra of receptor **2** ($1.0 \times 10^{-5}$ M) upon addition of $F^-$ ion (0–5 equiv.) in DMSO and $CH_3CN$ solvent mixture (5:95, v/v).

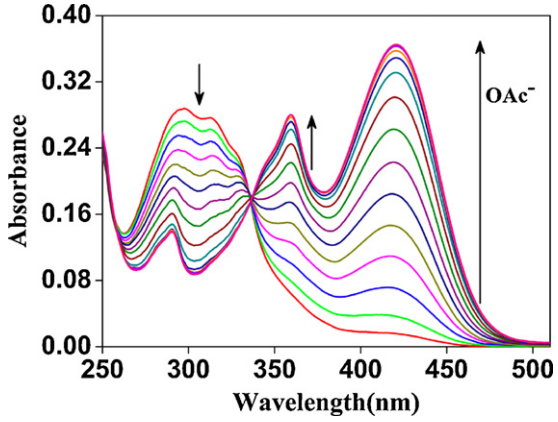



**Fig. 3.** UV–vis spectral changes of receptor **2** ($1.0 \times 10^{-5}$ M) upon addition of $OAc^-$ ion (0–5 equiv.) in DMSO and $CH_3CN$ solvent mixture (5:95, v/v).

the basis of their basicity. As the basicity of $F^-$ and $AcO^-$ ion are higher than the rest of the tested anions, $F^-$ and $AcO^-$ ions are bound to form stronger complexes with the receptor **2** and show noticeable color changes. However, the color discrimination for $F^-$ and $AcO^-$ ions were not observed. In contrast, dihydrogen phosphate ($H_2PO_4^-$) with lower basicity and inability to bind in similar fashion as that of $F^-$ and $AcO^-$ ions, form weaker complex with the receptor **2** and exhibit faint naked-eye color change and tiny spectral change were observed during UV–vis titration experiment.

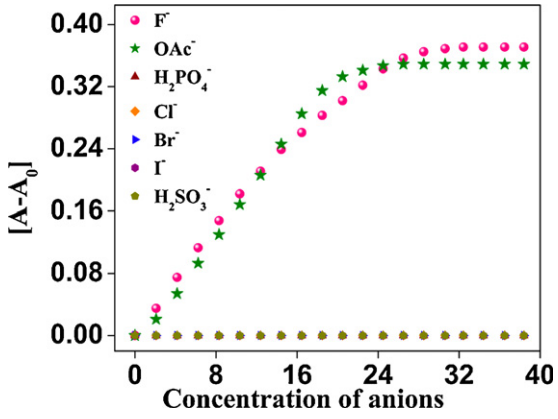



**Fig. 4.** Plot of relative absorbance of receptor **2** ($1.0 \times 10^{-5}$ M) as a function of different anions concentration.

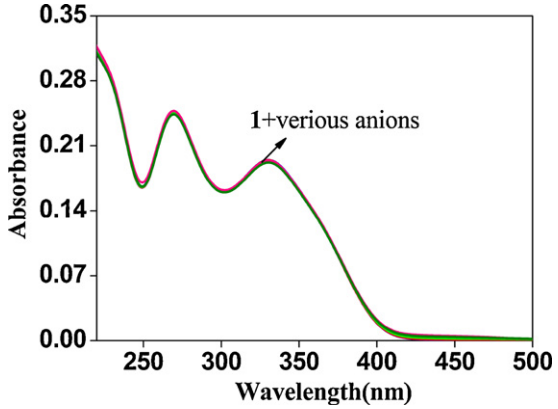



**Fig. 5.** UV–vis spectra of compound **1** ($1.0 \times 10^{-5}$ M) and after addition of 10 equiv. of various anions in DMSO and $CH_3CN$ solvent mixture (5:95, v/v).

In order to investigate the role of nitro group within the receptor **2** on recognition behaviors, compound **1** has been synthesized as a reference compound. Interestingly, under similar experimental condition, compound **1** neither exhibits any UV–vis absorption spectral change nor naked-eye detection of color upon addition of all the anions (Fig. 5) including $F^-$ and $AcO^-$ ions. The above facts fully proved the indispensable roles of the nitro group within receptor **2** for realizing efficient anion recognition.

### *2.3. UV–vis titration for determination of stoichiometries and association constants*

For the determination of stoichiometry and the association constants between receptor **2** and anions, we used UV–vis titration data. The binding constants ($K$) for the complex formed between receptor **2** and anion have been determined by using Benesi–Hildebrand (B–H) relation [29,30]. The association constant of the complex have been determined from the following complexation equilibrium

$$L + mX^{n-} \leftrightarrow (X_mL)^{mn-}$$

$$K = \frac{(X_mL)^{mn-}}{[L][X^{n-}]^m}$$

Benesi–Hildebrand relation with $m = 1$ for 1:1 complex can be expressed in terms of optical density ($A$) as follows:

$$A = \frac{A_0 + A_1K[X^{n-}]}{1 + K[X^{n-}]}$$

Or,

$$\frac{1}{A - A_0} = \frac{1}{A_1 - A_0} + \frac{1}{(A_1 - A_0)K[X^{n-}]}$$

where $[X^{n-}]$, $[L]$, and $[(X_mL)^{mn-}]$ are the concentrations of anions added, receptor **2** and the complex formed between anion and receptor **2**, respectively. $A_0$, $A$ and $A_1$ indicate the optical density or absorbance at a particular wavelength of receptor **2** without anion, absorbance after adding an anion at every successive steps and excess amounts of anion added, respectively. The terms $K$, $m$ and $n$ are binding constants or association constants of the complex, moles of anion, and charge of the anion, respectively. The binding

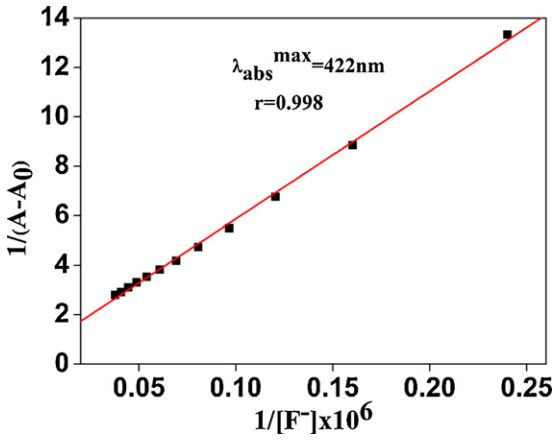



**Fig. 6.** Benesi–Hildebrand plot for 1:1 complex formed between **2** and $F^-$ ion.

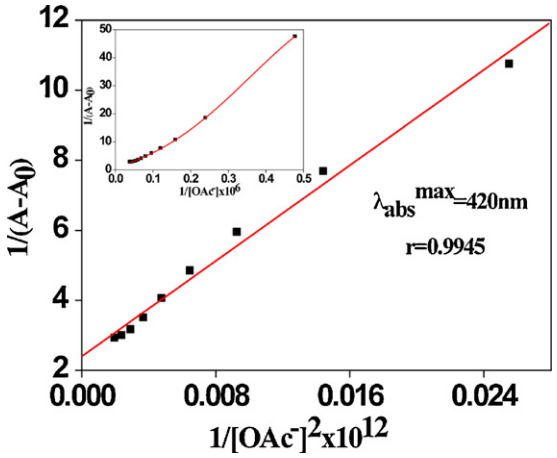



**Fig. 7.** Benesi–Hildebrand plot for 1:2 complexation between **2** and $OAc^-$ ion, inset shows B–H plot by considering 1:1 complexation.

constant or association constant, $K$ ($M^{-1}$ or $M^{-2}$) was determined from the ratio of intercept and slope of Benesi–Hildebrand plot of the optical density.

As shown in Fig. 6, the Benesi–Hildebrand (B–H) plot of $1/[A-A_0]$ vs $1/[F^-]$ for the titration of **2** and $F^-$ ion provides a straight line, indicating 1:1 complex formation with association constant ($K$) $1.36 \times 10^4\ M^{-1}$. On the other hand the (B–H) plot (Fig. 7) of $1/[A-A_0]$ vs $1/[AcO^-]^2$ exhibit a straight line, which indicates 1:2 complexation between **2** and acetate ion ($OAc^-$) with association constant $7.05 \times 10^9\ M^{-2}$. Different stiochiometry of complexes between receptor **2** with fluoride and acetate ion predicts that the binding pattern are of different kinds.

### 2.4. Molecular simulation

To understand the most stable conformers of **2** and the nature of bonding interaction with the anions, the ground state optimization was carried out in vacuum using Gaussian 03 software with B3LYP-hybride functional and 6-31++G(dp) basis set at density functional theory (DFT) level. The optimized global minima of receptor **2** shows that the two nitro-salicylidine moieties are not in the same plane (Fig. 8). Similar kind of twisted structure was reported for compound **1** [24]. The optimized structure of **2** shows that each phenolic –OH is intramolecularly H– bonded with imine nitrogen (distances H1···N1 and H2···N2 are 1.707 Å and 1.707 Å, respectively, Table 1). Importantly, on the basis of the above optimization method, in presence of acetate ion the receptor **2** rearrange itself from its stable conformer (Fig. 8) to a twisted

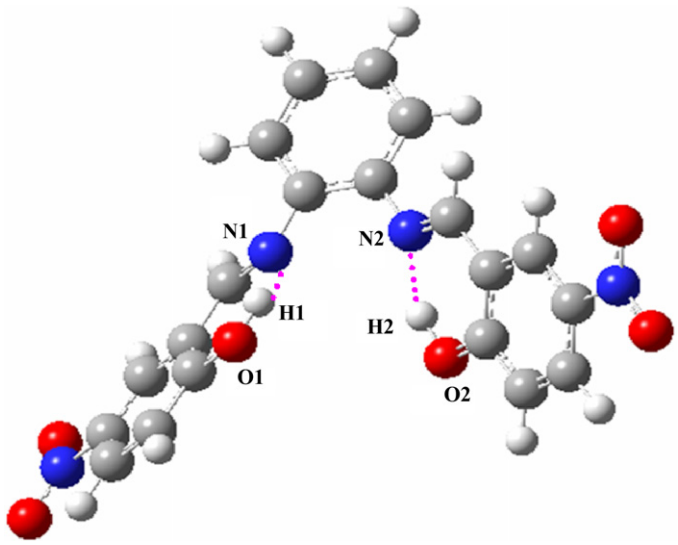



**Fig. 8.** Optimized geometry of **2**.

**Table 1**
Some useful theoretical parameters of receptor **2** and after complexation with anions ($A^-$ is $F^-$ and $AcO^-$ anions).

| Substrates | H1···N1 | H1–O1 | H2···N2 | H2–O2 | O1·$A^-$ | O2·$A^-$ |
|---|---|---|---|---|---|---|
| Receptor **2** | 1.707 | 1.003 | 1.707 | 1.003 | – | – |
| **2**·$AcO^-$ | 2.703 | 1.566 | 3.004 | 1.625 | 2.569 | 2.616 |
| **2**·$F^-$ | 2.576 | 1.377 | 2.425 | 0.998 | 2.384 | 2.568 |

conformer where the two nitro-phenol containing units are pointing in opposite direction (Fig. 9) and form 1:2 complexes with acetate ion. The structure of **2**·$AcO^-$ complex shows that two acetate units are hydrogen bonded within donor–acceptor distances O1···$A^-$ = 2.569 Å and O2···$A^-$ = 2.616 Å ($A^-$ is $AcO^-$, Table 1, Fig. 9). On the other hand, the smaller size fluoride ion can fit in between the twisted structure of **2**, and thus form 1:1 stable complex (Fig. 10), where donor–acceptor distances are O1···$A^-$ = 2.384 Å and O2···$A^-$ = 2.568 Å ($A^-$ is $F^-$, Table 1). The optimized structure shows that in both complexes (**2**·$F^-$ and **2**·$AcO^-$) the O1–H1 and O2–H2 distances are changed compare to the bare receptor **2** (Table 1). Finally, the prediction of stoichiometry from theoretical structural optimization corroborate with the outcome of UV–vis titration experiment and B–H plot.

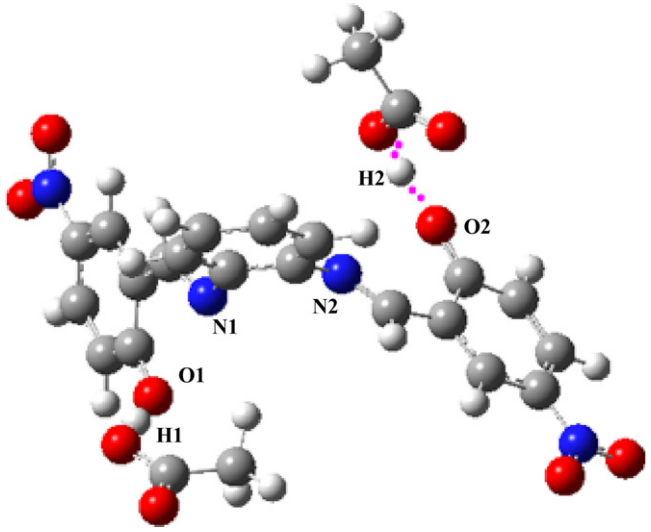



**Fig. 9.** Optimized geometry of **2**·$OAc^-$ complex.

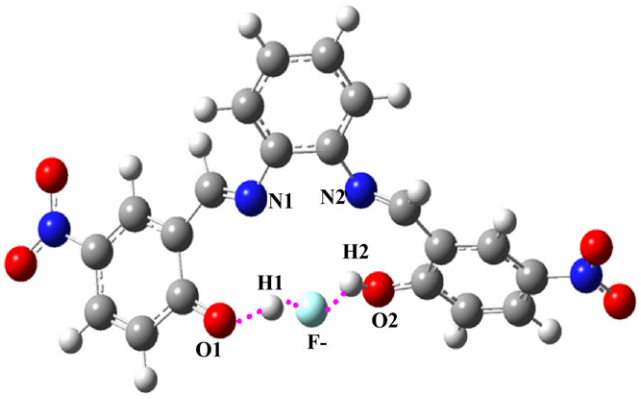



**Fig. 10.** Optimized geometry of **2**·$F^-$ complex.

## 3. Conclusions

In summary, we have demonstrated that the Schiff-base **2** having electron deficient group can selectively detect $F^-$ and $AcO^-$ ion by naked-eye color change (colorless to yellow) as well as UV–vis spectral changes. Thus Schiff-base **2** can be called as colorimetric receptor, selective detection for fluoride and acetate ions. Other anions were found to hardly induce any variation either in the absorption spectra or in visible color change. The effect of anion was diminished by adding protic solvent. Spectroscopic measurements well agree with the theoretical results, receptor **2** and $AcO^-$ ion form 1:2 complex but $F^-$ ion form 1:1 complex.

## 4. Experimental

### 4.1. Materials and methods

All reagents and solvents were used as received from commercial sources without further purification. The anions, tetrabutylammonium fluoride hydrate (98%), tetrabutylammonium chloride hydrate (98%), tetrabutylammonium bromide (98%), tetrabutylammonium iodide (98%), and tetrabutylammonium dihydrogenphosphate (97%), tetrabutylammonium acetate (97%), were purchased from Sigma–Aldrich Chemical Company. Tetrabutylammonium hydrogensulphite (97%) was purchased from Spectrochem Pvt. Ltd., India. All solvents used for the spectroscopic studies are with spectroscopic grade. Electronic absorption spectra were recorded by a Hitachi UV–vis (Model U-3501) spectrophotometer. Gaussian 03 software was used for all theoretical calculations [31].

### 4.2. Syntheses of Schiff bases

Compound **1** and receptor **2** have been synthesized according to the literature procedure and were used without further characterization [23–26].

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