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Selective anion recognition by inhibition of excited state intramolecular proton transfer process via hydrogen bonding interaction and efficient deprotonation: Spectroscopic and theoretical investigation

Anuva Samanta, Sasanka Dalapati, Nikhil Guchhait*

Department of Chemistry, University of Calcutta, 92 A.P.C. Road, Calcutta 700009, India

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ABSTRACT

Anion (X) recognition fluorescent chemosensor 5-(4-Fluoro-phenyl)-2-hydroxy-nicotinonitrile (FP2HN) having both –NH and –OH groups in its two tautomeric forms has been synthesized and its excited state intramolecular proton transfer (ESIPT) reaction has been investigated by UV–vis, fluorescence, ^{1}H NMR spectroscopy in combination with computational calculations. The experimental findings show that FP2HN selectively recognizes F^-, AcO^- and $H_2PO_4^-$ ions through the formation of –N(O)H···X hydrogen bonding (HB) complex. The binding constant obtained by non-linear fit predicts the binding order of $F^- > AcO^- > H_2PO_4^- > Cl^-$. The ESIPT process of FP2HN is inhibited either by the fluoride induced deprotonation of acidic proton of FP2HN or by the formation of a strong –N(O)H···X intermolecular hydrogen bonding complex. Further insights into the recognition mechanism of the receptor–anion complexes using ab initio calculations have been performed which support the experimental binding affinity order of $F^- > AcO^- > H_2PO_4^- > Cl^-$.

1. Introduction

A great deal of attention has recently been focused to design chemosensors for anions, since they play crucial roles in environmental, chemical and biological systems in the forms of food additives, drugs, agricultural fertilizers, biologic metabolites, etc. [1–5]. Among halide ions, the fluoride ion is vital for prevention of dental caries and treatment of osteoporesis [6,7], while detection of chloride ion is essential to monitor intrusion of salt water into drinking water supply [8]. On the other hand, oxoanions such as phosphate ions play important roles in signal transduction and energy storage in biological systems [9], the acetate anion exhibits specific biochemical behaviors towards enzymes and antibodies [10]. In general, the phenomenon of anion binding can be transduced into noticeable indications by color changes, UV–vis spectral changes, redox potential and so on [11]. Among them, colorimetric sensing processes have huge advantages over any other sensing modes. While the fluorescence response is also preferred as it can improve the sensitivity of detection method. Neutral anion sensors are generally made up of two parts. One part is the binding unit containing some groups like ammonium, amide, urea, thiourea, sulfonamide, pyrrole, etc. which can have the ability of coordination with anion via hydrogen bonding (HB) and electrostatic interaction. The second part is the signaling unit which is capable of translating the binding event into the outside world through color changes, UV–vis and fluorescence signals, etc. [12]. Since the anion recognition based on fluorescence technique is highly sensitive, many fluorescent sensors for anions have been developed on the basis of a variety of signaling mechanisms such as photoinduced electron transfer [13,14], metal to ligand charge transfer [15], competitive binding [16], intramolecular charge transfer [17], excimer/exciplex formation [18], and intermolecular proton transfer [19]. In the field of anion recognition process, the binding ability of receptor with anion is primarily related to hydrogen bonding. According to the literature reports, the HB interaction has been defined as an incipient of proton transfer process from the receptor to the anion. Intermolecular proton transfer (IPT) is a commonly recognized method in designing new anion chemosensors because of its mechanistic simplicity [20,21]. Recently, Boiocchi et al. [22] established that the trend of deprotonation has been enhanced by the increase of the acidity of the hydrogen bond donors through the insertion of electron withdrawing substituents such as $–NO_2$, $–CF_3$, –CN, etc. in the molecular framework. The phenomenon of excited state intra- or intermolecular proton transfer has been well documented for anion sensing [19], but the inhibition of excited

* Corresponding author. Tel.: +91 33 2350 8386; fax: +91 33 2351 9755.
E-mail addresses: nikhil.guchhait@rediffmail.com, nguchhait@yahoo.com (N. Guchhait).

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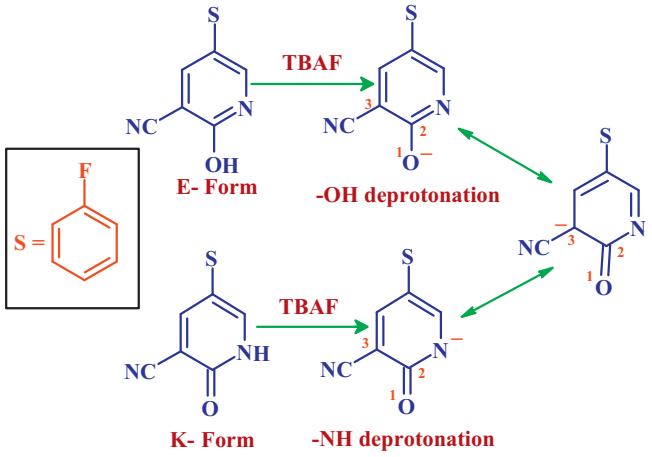


Scheme 1. The proposed receptor–anion interaction mode in acetonitrile solvent.

state intramolecular proton transfer (ESIPT) was poorly applied for anion recognition [21,23,24]. In the ESIPT molecules, the five or six member intramolecular hydrogen bonded ring formed between the H-bond acceptors (=N–, =C=O) and donors (—OH, —NH_2, etc.) in close proximity are vital to the ESIPT process [25,26]. By controlling the acidity and H-bond donor ability of the protons that are crucial to the ESIPT process, the above mentioned biologically and chemically fascinating anions can be distinguished from the different spectral outputs for anion–sensors interactions.

In order to get such anion receptors, we have designed and synthesized a novel anion receptor with flexible structure: 5-(4-fluoro-phenyl)-2-hydroxy-nicotinonitrile (FP2HN). This molecule is quite similar to the previously discussed ESIPT probe 5-(4-fluoro-phenyl)-2-hydroxypyridine (FP2HP) [27]. The –CN group is incorporated in FP2HP in order to increase the acidity of –OH and –NH groups. A resonating structure of the deprotonated form of FP2HN (Scheme 1) reflects that the electron density at the three position is enhanced upon deprotonation. So the acidity of the protons can be increased by the introduction of electron withdrawing group at three position. Thus FP2HN becomes a new candidate to investigate the anion–receptor interaction process. This molecule is also very important since it undergoes keto-enol tautomerism and the existing –OH and amide –NH groups are well-known to be involved in natural anion binding sites of peptides [28,29]. Besides this, upon photoexcitation the acidities of –OH and –NH protons are drastically enhanced [30,31] thereby opening up the excited state intermolecular proton transfer channel for anion binding. So the anion–receptor binding inhibits the expected ESIPT but unlocks the intermolecular proton transfer channel. Therefore, the anion binding ability of FP2HN in acetonitrile has been investigated using UV–vis, steady state as well as time resolved emission technique and quantum chemical calculations.

2. Experimental

2.1. Materials

To a solution of Vilsmeier reagent at 10 °C, 4-fluorophenyl acetic acid was added and the mixture was stirred and heated at 70 °C for 7 h. After cooling to room temperature, the mixture was added slowly to a mixture of ice and water and then a solution of Na_2CO_3 was added slowly until pH 11 was achieved. Toluene was added to the alkaline mixture and the resulting mixture was refluxed for 1.5 h. After cooling to room temperature the separated aqueous layer was extracted with toluene. The combined organic extracts were washed with water and dried Na_2SO_4 and toluene was evaporated in vacuum. The solid residue was recrystallized from the mixture of dichloromethane and n-heptanes to yield yellow crystals of 3-dimethylamino-2-(4-fluorophenyl)-proplactim. To a solution of sodium methoxide in methanol cyanoacetamide, the above product was added. The mixture was stirred at room temperature for 1.5 h and then refluxed for 10 h. During this time, a yellow solid precipitate was formed. The reaction mixture was diluted with water and acidified with 10% HCl. The yellow solid was filtered off, washed with water, ethanol and diethyl ether and then with n-hexane. This afforded 5-(4-fluoro-phenyl)-2-hydroxy-nicotinonitrile as a yellow solid. The solid was filtered off and washed with n-heptanes and then recrystallized from a mixture of dichloromethane and n-heptanes to get pure 5-(4-fluoro-phenyl)-2-hydroxy-nicotinonitrile.

The tetra-*n*-butylammonium (TBA) salts of different anions were purchased from Spectrochem, India and used without further purification. Acetonitrile (ACN) was obtained from Spectrochem, India and the purity of solvent has been checked in the wavelength range used. Triple distilled water and HCl from Merck were used as obtained.

2.2. Apparatus

The absorption and emission spectra of FP2HN have been taken by Hitachi UV-Vis (Model U-3501) spectrophotometer and Perkin Elmer (Model LS-55) fluorimeter, respectively. In all measurements, the sample concentration has been maintained within the range of 10^{-5}–10^{-6} mol/dm^3. ^{1}H nuclear magnetic resonance (NMR) spectra were taken in d_6–DMSO using tetramethylsilane as an internal standard on a Bruker AV 3000 supercon spectrometer (300 MHz).

The fluorescence quantum yields of FP2HN in its enol as well as keto forms in ACN solvent were measured relative to α-napthol (Φ_F = 0.173) in cyclohexane and quinine sulphate in 0.1 M H_2SO_4 (Φ_F = 0.577 at 293 K) as secondary standard [32].

All the fluorescence decays were obtained with a Time Correlated Single Photon Counting (TCSPC) set up employing a picosecond diode laser (IBH, UK, nanoLED-07) operating at λ_{ex} = 290 nm as the light source [33]. Instrument response function is ~90 ps. The fluorescence decay was collected with an emission polarizer kept at the magic angle (~54.7°) using Hamamatsu MCP PMT (3809U). The decays were analyzed using IBH DAS-6 decay analysis software. The fluorescence decay curves were analyzed by biexponential fitting program of IBH in order to obtain best residuals and acceptable χ^2 values. Intensity decay curves were obtained as a sum of exponential terms

$$F(t) = \sum_i a_i \exp\left(\frac{-t}{\tau_i}\right) \quad (1)$$

where $F(t)$ is the fluorescence intensity at time t, a_i the pre-exponential factor representing the fractional contribution to the time resolved decay of the ith component with a lifetime τ_i. Average lifetimes (τ_{avg}) of fluorescence were calculated from the decay times and pre-exponential factors using the following equation:

$$\tau_{avg} = \sum_i a_i \tau_i \quad (2)$$

2.3. Computational details

Quantum chemical calculations were performed using Gaussian 03 program [34]. The optimized structure of the ligand (FP2HN) and its complexes with halide ions (F^-, Cl^-) and oxoanions (AcO^-, $H_2PO_4^-$) were carried out by Hartree Fock (HF) level using 6-31G** basis set. The binding energy or interaction energy of the

receptor–anion complex was calculated using the following equation

$$\Delta E_{int} = -(E_R + E_{X^-} - E_{[R\cdots X]}) \quad (3)$$

where ΔE_{int} is the difference between the energy of the complex ($E_{[R\cdots X]}$) and the total energy of the two free monomers i.e. the receptor (E_R) and anions (E_{X^-}).

Additionally, the binding energy was corrected (ΔE_{int}^{corr}) by subtracting the basis set superposition error (BSSE):

$$\Delta E_{int}^{corr} = -[(E_R + E_{X^-} - E_{[R\cdots X]}) + BSSE] \quad (4)$$

BSSE corrections were done by using the full counterpoise method of Boys and Bernardi [35].

3. Results and discussion

3.1. UV–vis spectral responses of FP2HN

In order to establish the sensing properties of FP2HN towards various anions, spectrophotometric titration experiments have been carried out by adding a standard solution of tetrabutylammonium (TBA) salt of anions to acetonitrile solution of the sensor at 298 K. The study of anion sensing is preferably carried out in aprotic media (e.g. $CHCl_3$, DMSO, ACN) to avoid the competitive interaction of anion with the molecules and with the H-bond donating solvents. In the absence of TBA salts, FP2HN displays two absorption bands at ~254 nm and ~356 nm. Comparing with the absorption spectra of previously reported analogous molecule FP2HP [27] having similar absorption bands at ~266 nm and at ~325 nm, the higher energy band of FP2HN at ~254 nm and the lower energy band at ~356 nm are ascribed to the absorption band of the enol and keto form of FP2HN, respectively (Scheme 1). All spectral parameters have been summarized in Table 1. As shown in Fig. 1a, upon addition of increasing amounts of F^- ion a dramatic change in the absorption spectra is observed. Addition of Y-shaped oxoanions (AcO^-, $H_2PO_4^-$) produces a family of spectra (Fig. 1b and c) very similar to that obtained on titration with F^- but the spectral responses with $H_2PO_4^-$ are not as sensitive as F^- and AcO^- ions. However, the peak at ~254 nm for the π–π^* transition of the enol tautomer vanishes gradually with the formation of a new band at ~290 nm. Similarly, addition of TBA salts induces the formation of a new red shifted absorption band at ~370 nm with the disappearance of the π–π^* transition of the keto tautomer. As these newly generated absorption bands match well with the absorption band originated in presence of TBAOH (Fig. 2a), these absorption bands have been assigned to the corresponding deprotonated form. The noticeable bathochromic shift of the absorption maxima (~35 nm and ~15 nm for E- and K-form respectively) originates on complexation of the receptor with F^-, AcO^- and $H_2PO_4^-$ ions due to charge transfer process by interaction between the proton of –OH or –NH group of donor (receptor) and the acceptor (anion). The distinct isosbestic points at ~273 nm and ~358 nm indicate that the stoichiometry of the complex between anion with enol and keto forms are 1:1. This is also confirmed by the Job's plot (Fig. 2b). Binding constants (K_a) of the receptor for anions, shown in Table 1, are determined by the nonlinear curve fitting analysis of the titration curves (inset of Fig. 1) utilizing the following equation considering 1:1 host guest complexation [36].

$$A = A_0 + \frac{A_{lim} - A_0}{2C_H}\left[C_H + C_G + \frac{1}{K_a} - \left[\left(C_H + C_G + \frac{1}{K_a}\right)^2 - 4C_H C_G\right]^{1/2}\right] \quad (5)$$

where A is the absorption intensity of the whole system, A_0 is the absorbance of the receptor in absence of anions, A_{lim} is the maximum absorbance of host when guest is added, and C_H and C_G are the concentration of host and guest respectively. Obviously from Table 1, the K_a value showing the selectivity of FP2HN and its tautomer to the anions have the order of $F^- > AcO^- > H_2PO_4^- > Cl^-$. With the addition of TBA salts of other inorganic ions such as Cl^-, Br^-, HSO_4^-, NO_3^- to the acetonitrile solution of the receptor do not trigger noticeable spectral changes of FP2HN (Fig. 2c) indicating no or very weak interactions between these ions and the receptor. Fig. 3a clearly predicts that the sensor can detect selectively with

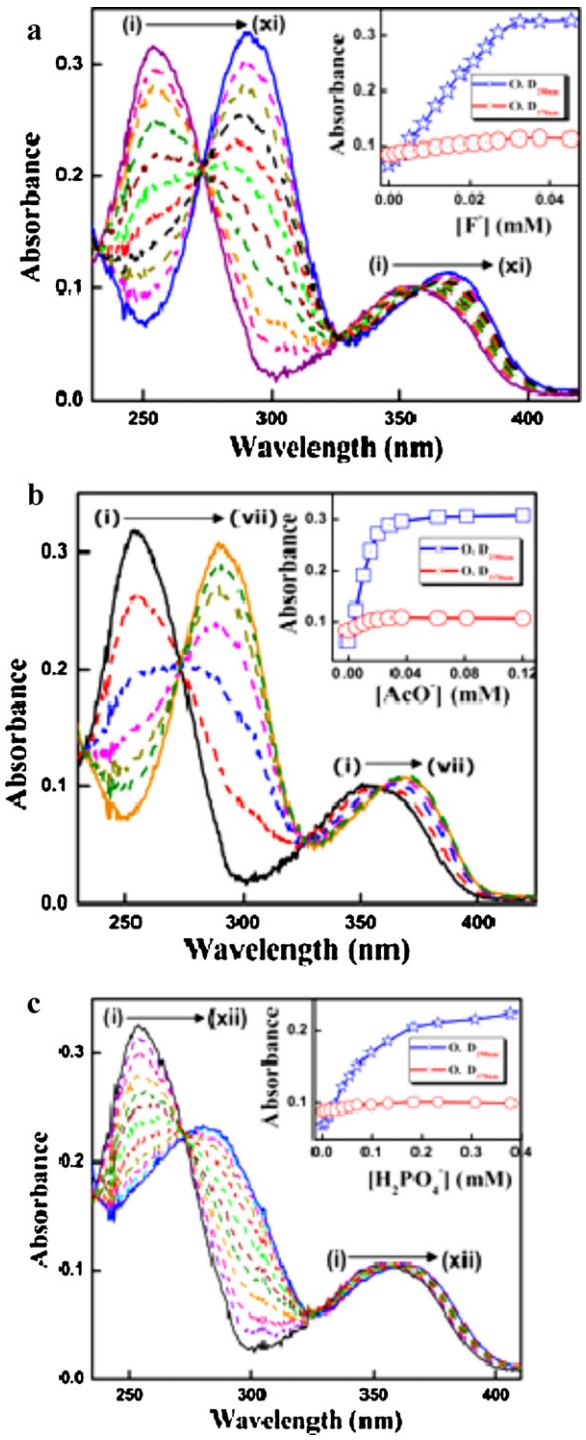


Fig. 1. Changes in the UV–vis absorption spectra for FP2HN (21.7 μM) in ACN with the addition of (a) F^- ((i)–(xi) corresponds to 0–44.78 μM of F^-), (b) AcO^- ((i)–(vii) corresponds to 0–120 μM of AcO^-), and (c) $H_2PO_4^-$ ((i)–(xii) corresponds to 0–380 μM of $H_2PO_4^-$) ions. The corresponding inset shows the plots of absorbance at 290 nm and 370 nm of FP2HN as a function of anion concentration.

Table 1
UV–vis and fluorescence spectral data for FP2HN in presence of different anions.

Anion	λ_{abs} (nm)		λ_{em} (nm)	Φ_F		log K_a	
	E-form	K-form		λ_{ex} = 273 nm	λ_{ex} = 358 nm	E-form	K-form
None	254	355	424	0.3612	0.3926	–	–
F^-	292	370	417	0.0872	0.2826	5.86 ± 0.60	5.95 ± 0.53
AcO^-	291	371	417	0.0867	0.2470	5.52 ± 0.95	5.60 ± 0.81
$H_2PO_4^-$	282	363	420	0.1158	0.2586	4.33 ± 0.86	4.67 ± 0.46
Cl^-	289	368	–	–	–	3.53 ± 0.68	3.65 ± 0.72

Table 2
Time resolved decay parameters of FP2HN in presence of different anions (λ_{ext} = 290 nm).

Anion	a_1	T_1	a_2	T_2	τ_{avg}	χ^2	k^r ($\times 10^9$ s^{-1})	k^{nr} ($\times 10^9$ s^{-1})
None	1	4.99	–	–	4.99	1.17	0.072	0.128
0.25 equiv. F^-	0.71	5.11	0.29	2.01	4.66	1.08	–	–
0.6 equiv. F^-	0.28	4.97	0.72	2.07	5.11	1.07	–	–
1.0 equiv. F^-	0.12	4.38	0.88	2.05	4.97	1.01	–	–
1.5 equiv. F^-	–	–	1	2.29	2.29	1.20	0.038	0.399
+H_2O	0.93	5.21	0.07	2.38	5.0	0.92	–	–
2 equiv. AcO^-	0.26	1.48	0.74	2.47	2.22	0.82	0.039	0.411
2 equiv. $H_2PO_4^-$	0.71	1.93	0.29	4.07	2.55	0.83	0.045	0.346

high sensitivity towards F^-, AcO^- and $H_2PO_4^-$ ions compared to rest of anions. This anion selectivity is thought to be dictated by the anion basicity: F^-, AcO^-, and $H_2PO_4^-$ are stronger hydrogen acceptors than other tested anions. This result is further supported by the schematic plot of relative change (Fig. 3b) in the absorbance of FP2HN at 290 nm upon titrating with different ions.

3.2. Inhibition of ESIPT

The binding properties of FP2HN towards various anions were subsequently investigated by fluorescence spectra (Fig. 4). The free receptor exhibits an emission maximum at ~426 nm irrespective of the excitation wavelength at 255 nm or 355 nm. We have already studied FP2HP exhibiting proton transfer emission at ~410 nm and local emission of enol form at ~340 nm [27]. Due to the presence of electron withdrawing –CN group, proton transfer ability of FP2HN increases thereby showing only PT emission at ~426 nm on 255 nm excitation. Local emission of the keto tautomer, on 355 nm excitation, occurs at ~426 nm. Absorption study shows that strong bases such as F^-, AcO^- may remove the –OH and –NH proton of enol and keto tautomer respectively to form the corresponding anion in the ground state (Scheme 1). So the anion titration fluorescence spectra are expected to experience dramatic changes in the tautomer emission, since the ligand shows only keto emission. Fig. 4a displays the fluorescence responses of the interaction of FP2HN with F^- ions with excitation at 273 nm and 358 nm (Figure not shown), corresponding to isosbestic points of the 1:1 equilibrium between FP2HN and F^- (Fig. 1a). With increase of F^- ion concentration, the emission intensity progressively decreases with slight blue shifting of the band from ~426 nm to ~416 nm. Among the anions investigated, only AcO^- and $H_2PO_4^-$ induce similar spectral changes (Fig. 4b and c), but the ratiometric responses of $H_2PO_4^-$ is not as sensitive as F^- and AcO^- ions. No significant changes are observed for the tautomer emission when weak bases such as Cl^-, Br^-, HSO_4^-, NO_3^- were added to the system. We proposed that addition of fluoride/acetate ions results in the deprotonation of the receptor site thereby inhibiting the intramolecular proton transfer ability of the target molecule. In case of other anions, $H_2PO_4^-$, Cl^- the fluorescence quenching of the keto emission occurs because ESIPT process of FP2HN is inhibited by the hydrogen bond formation between anions and the aimed molecule. Here the intermolecular HB between –OH/–NH and anions can compete with the intramolecular HB to inhibit the ESIPT process. Significant fluorescence quenching of the keto tautomer emission is observed in these cases. In case of ~358 nm excitation, due to the newly formed intermolecular HB between receptor and anions being another source of internal conversion, the local emission of the keto form also quenches. As shown in Table 1, Φ_F value of FP2HN decreases due to the deprotonation or formation of hydrogen bonding complex with anions.

3.3. Fluorescence time-resolved studies

The complexation between anions and FP2HN has also been investigated by the time resolved fluorescence technique. Fig. 5 displays the fluorescence decay profiles of FP2HN with different concentration of F^- ion. FP2HN undergoes single exponential decay for the keto emission (Table 2) in acetonitrile solvent. In presence of F^- ion, the bi-exponential decay profiles indicate the coexistence of two distinct species in solution which are the free and anion bound forms. The contribution of the longer component (free receptor) decreases while that of the newly generated shorter

Table 3
Calculated (HF/6-31G** level) interaction energies and structural parameters of the various receptor–anion complexes.

Anion	ΔE_{int}^{corr} (E^a) (kcal/mol)	ΔE_{int}^{corr} (K^b) (kcal/mol)	O–H (E^a) (Å)	N–H (K^B) (Å)	OH···X^c (E^a) (Å)	NH···X^c (K^B) (Å)
None	0.0	0.0	0.947	0.997	–	–
F^-	−97.05	−98.42	1.651	1.715	0.929	0.934
AcO^-	−43.91	−47.48	1.665	1.021	0.982	1.811
$H_2PO_4^-$	−35.58	−39.28	1.049	1.013	1.378	1.883
Cl^-	−22.33	−32.93	0.989	1.013	2.019	2.357

[a] Enol.
[b] Keto.
[c] Anion.

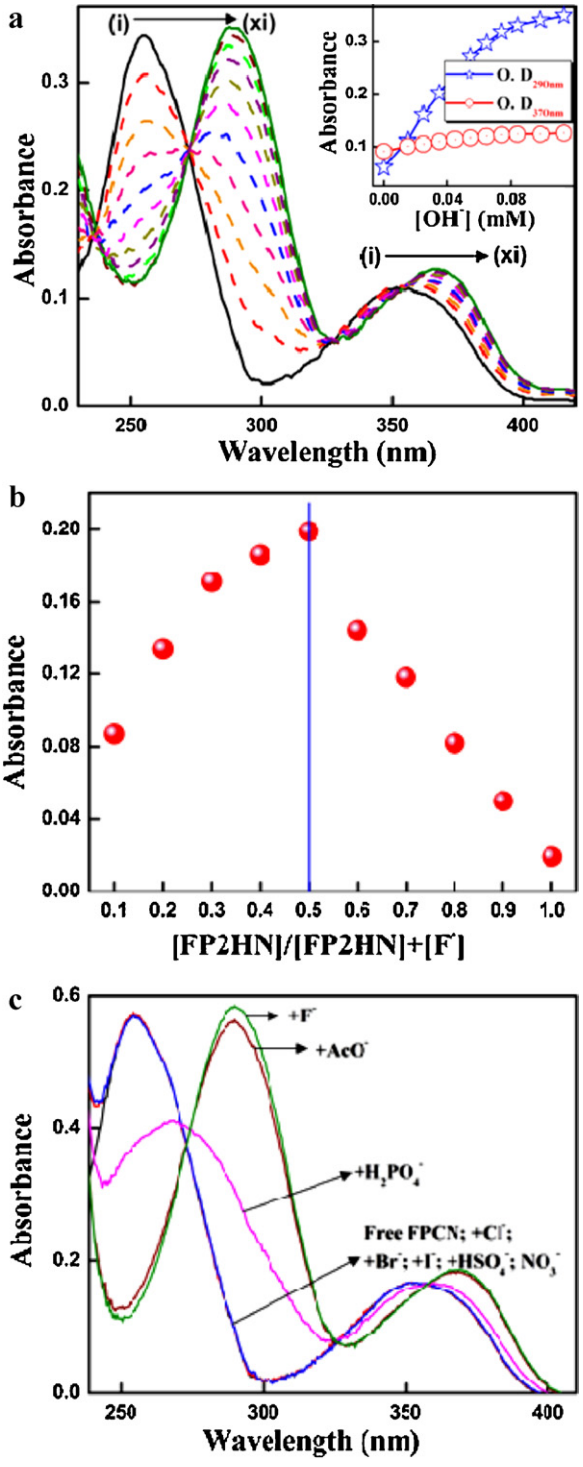


Fig. 2. (a) Changes in the UV–vis absorption spectra for FP2HN (22 μM) in ACN with the addition of OH^- ions ((i)–(xi) corresponds to 0–113 μM of OH^-). (b) The stoichiometry analysis for F^-–FP2HN interaction by Job's plot ($[FP2HN]+[F^-]=5\times10^{-5}$ mol/l). (c) Absorption spectra of FP2HN (21.7 μM) after addition of 10 equiv. of representative anions (F^-, AcO^-, $H_2PO_4^-$, Cl^-, HSO_4^-, Br^-, I^-, and NO_3^- as TBA salts).

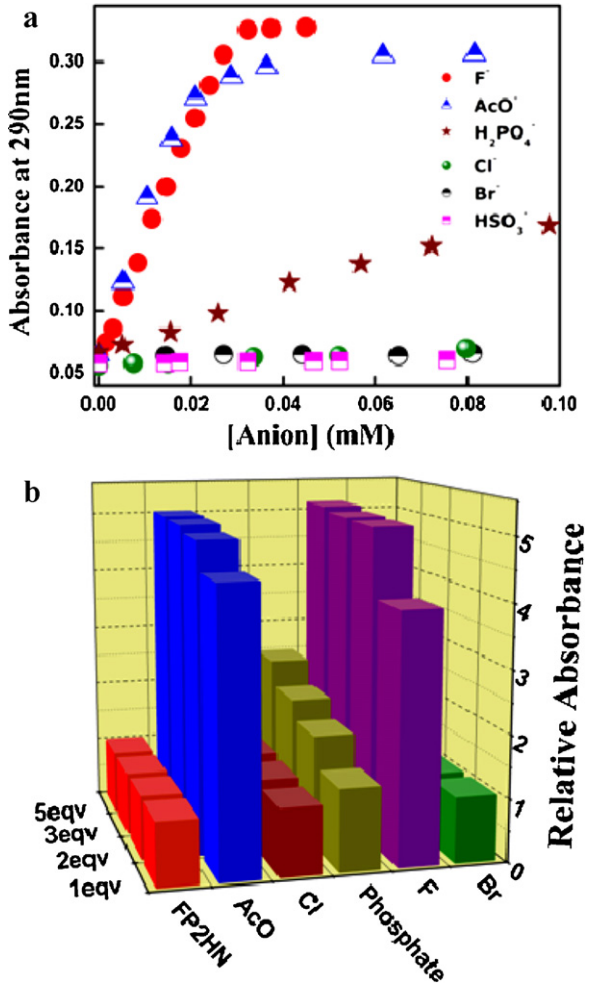


Fig. 3. (a) The changes in the absorbance of FP2HN (21.7 μM) at 290 nm upon titration with different anions in acetonitrile. (b) Relative changes in the absorbance of FP2HN (21.7 μM) at 290 nm with addition of 0–5 equiv. of different anion in ACN.

component (bound) increases (Table 2). When more than 1 equiv. F^- ion is added which would deprotonate the receptor completely, the decay is turned to single exponential (Table 2). As depicted in Table 2, average lifetime of receptor–anion binding complex decreases from that of the receptor itself because of the non-radiative deactivation assisted by the intermolecular hydrogen bonding between the receptor and anions. The radiative (k^r) and non-radiative (k^{nr}) decay rate constants are calculated using the following relations and these values are enlisted in Table 2:

$$k^r = \frac{\Phi_F}{\tau_{avg}}, \qquad k^{nr} = \frac{1-\Phi_F}{\tau_{avg}} \tag{6}$$

The decrease of Φ_F and decay times promotes substantial increase of k^{nr} due to intermolecular HB formation. Fig. 6 portrays the fluorescence decay profiles of the receptor with other anions in acetonitrile. Same results obtained here as obtained for F^-, but the decrease of average decay times and increase of k^{nr} with respect to the receptor is less for other anions than F^- because of the stronger basicity of F^-.

3.4. ^1H NMR spectra study

On the basis of the spectrophotometric investigation on receptor–anion binding, it is difficult to clarify whether the prominent changes occur due to the formation of complex between receptor and anion through hydrogen bonding or deprotonation of receptor by sufficient strong basic anions. ^1H nuclear magnetic resonance (NMR) spectroscopy is a versatile tool to probe such issues more accurately and hence we have carried out ^1H NMR titration experiment with receptor in d_6–DMSO solvent by stepwise addition of equivalents of F^- and AcO^- as their TBA salts. The corresponding ^1H NMR spectra are displayed

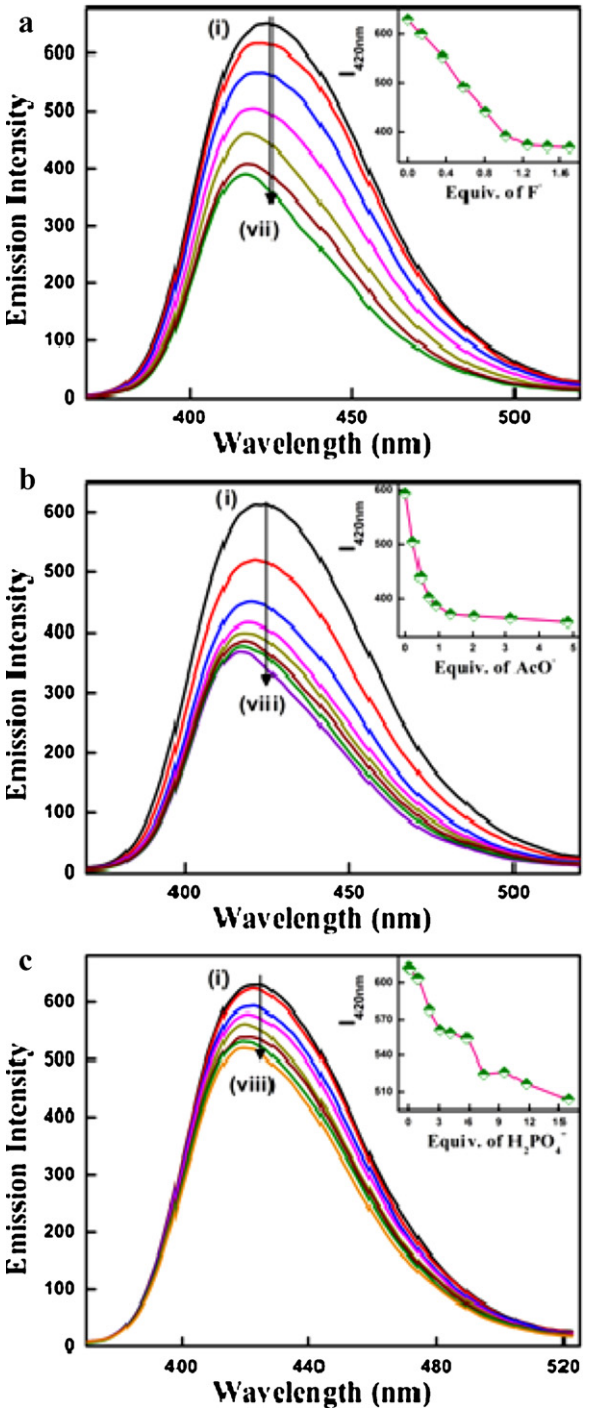


Fig. 4. Changes in the fluorescence spectra (λ_{ext} = 273 nm) of FP2HN (21.7 μM) upon addition of (a) F^- ((i) to (vii) corresponds to 0–39 μM of F^-), (b) AcO^- ((i) to (viii) corresponds to 0–120 μM of AcO^-), and (c) $H_2PO_4^-$ ((i) to (viii) corresponds to 0–368 μM of $H_2PO_4^-$) ions. Inset: fluorescence intensity change of 420 nm band of FP2HN versus equivalents of the corresponding anions.

in Figs. 7 and 8. From these spectra, the characteristic peaks namely H_1, H_2, H_3, H_4/H_5 and H_6/H_7 were observed at 12.816, 8.065, 8.5185, 7.633 and 7.218 ppm respectively. Upon addition of minor amount of acetate or fluoride ions, the signal of H_1 disappears completely which signifies the deprotonation of the H_1 by anions. H_4/H_5 and H_6/H_7 proton shift towards upfield which illustrate the increase of electron density on the aromatic rings owing to through bond effect. The results obtained from ^{1}H NMR titration are consistent with the breaking of hydrogen

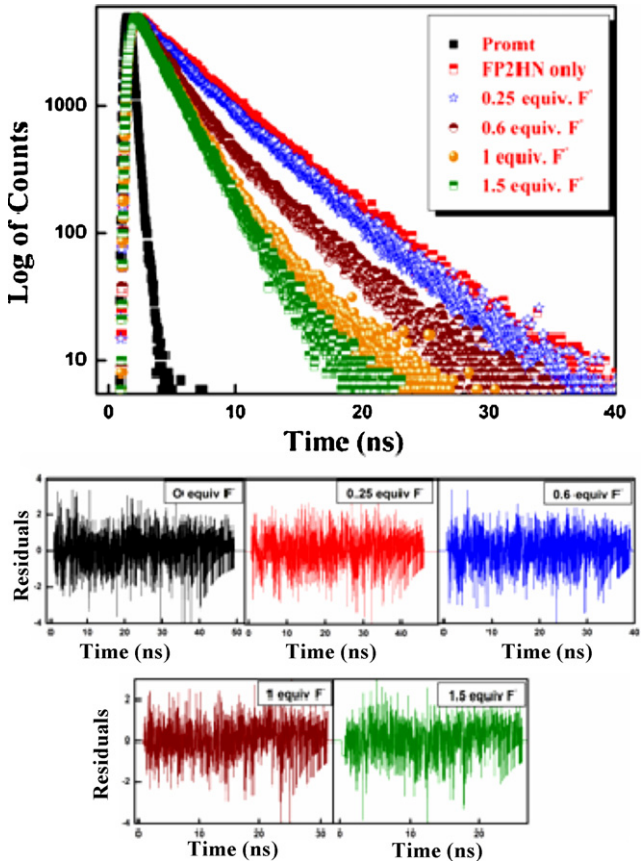


Fig. 5. Fluorescence decay profiles (λ_{ext} = 290 nm) of FP2HN (21.7 μM) at different equivalents of F^- in ACN with their corresponding best fitted residuals.

bonding where F^- or AcO^- ions are added. Addition of 1 equiv. of other anions (Cl^-, Br^-, I^-, etc.) to d_6–DMSO solution of FP2HN, no detectable chemical shift changes are seen (not shown).

3.5. Reversibility studies

Deprotonation mechanism of the sensor FP2HN with F^- can well be understood in presence of protic solvents as protic solvents like

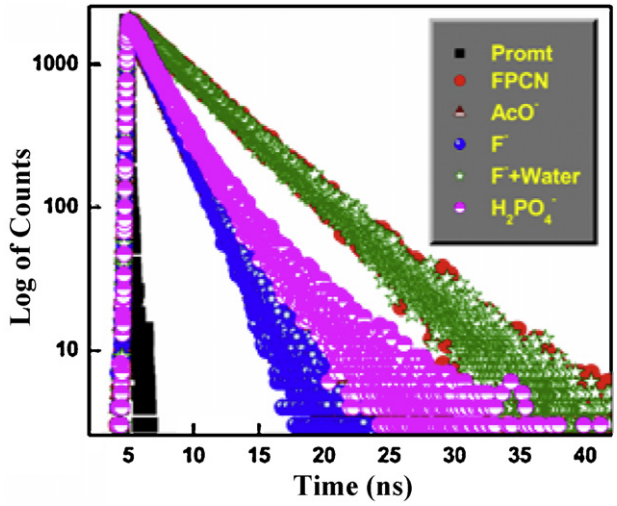


Fig. 6. Fluorescence decay profiles (λ_{ext} = 290 nm) of FP2HN (21.7 μM) with the addition of 2 equiv. of F^-, AcO^-, $H_2PO_4^-$ and addition of water in presence of F^- with their best fitted residuals.

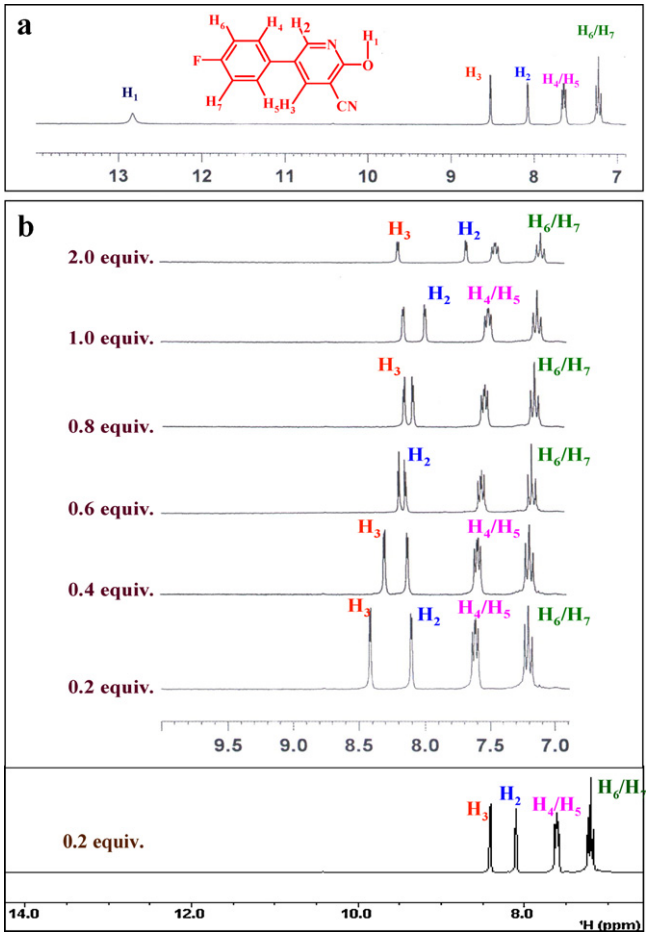


Fig. 7. (a) ^{1}H NMR (300 MHz) spectra of 46.7 mM solution of FP2HN in d_6–DMSO. (b) ^{1}H NMR titration spectra of FP2HN (46.7 mM) in the presence of 0.2 to 2 equiv. of F^- in d_6–DMSO.

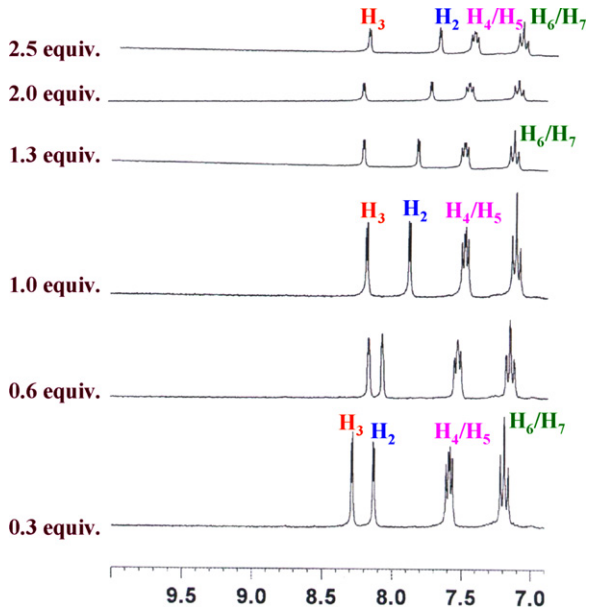


Fig. 8. ^{1}H NMR (300 MHz) titration spectra of FP2HN (46.7 mM) with addition of acetate anion (TBA salt) in d_6–DMSO (0.3–2.5 equiv.).

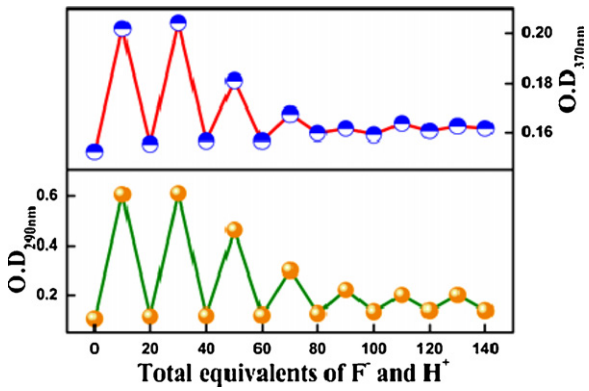


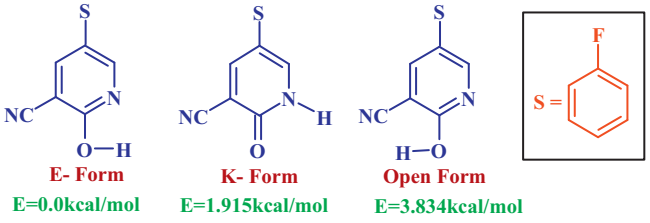
Fig. 9. Reversible turned "ON" and "OFF" anion sensing ability of FP2HN (21.7 μM) in presence of 10 equiv. of TBAF in ACN and 10 equiv. of H^+ in form of HCl in ACN–0.5% H_2O as recovering agent.

water can reverse the deprotonation induced spectra by protonation of the corresponding anions. We have preferred 0.01 M HCl in ACN–0.5% H_2O as recovering agent over protic solvents because the deprotonation process can be hardly proceed again if much water was brought in the system. From Fig. 9 it is lucid to us that the absorption band can be reversibly turned "ON" and "OFF" for at least three times by adding 10 equiv. of F^- and 10 equiv. of H^+. After three reversible steps, there occurs decay of the reversibility phenomenon because of the presence of slight amount of water in HCl solution. So this molecule can be successfully utilized in designing new molecular logic gates.

3.6. Quantum chemical calculations

Hartree Fock calculations have been carried out for the receptor anion complexes between the both forms of the receptor FP2HN and oxoanions, halides, etc. to cast further light on their relative stabilities and binding mechanism. First of all, we examine the structures and relative stabilities of the various possible conformers of FP2HN (Scheme 2). Considering all possible structures of FP2HN (Scheme 2), the enol form is found to be the most stable one than any of the other forms in the gas phase. Intramolecular hydrogen bonded keto form of FP2HN is also more stable than the open form (3.834 kcal/mol). As the energy difference between the enol and keto form is sufficiently small (~1.915 kcal/mol), these two forms may exist in the ground state. These two conformers are preferable because of the favorable –OH···N (2.268 Å) and –NH···O (2.415 Å) hydrogen bond interaction which are significantly less than the sum of their van der Waals atomic radii (2.75 Å for H···N and 2.70 Å for H···O).

In order to investigate either the recognition process is mediated through the hydrogen bonding interaction (N–H···X) or deprotonation process (N···HX), the structure of complex systems consist of FP2HN with anions are optimized at HF/6-31G** level of theory (Fig. 10). Comparing the N—H and O—H bond length of FP2HN.F



Scheme 2. Structures of various conformations of receptor (FP2HN) optimized at HF/6-31G** level.

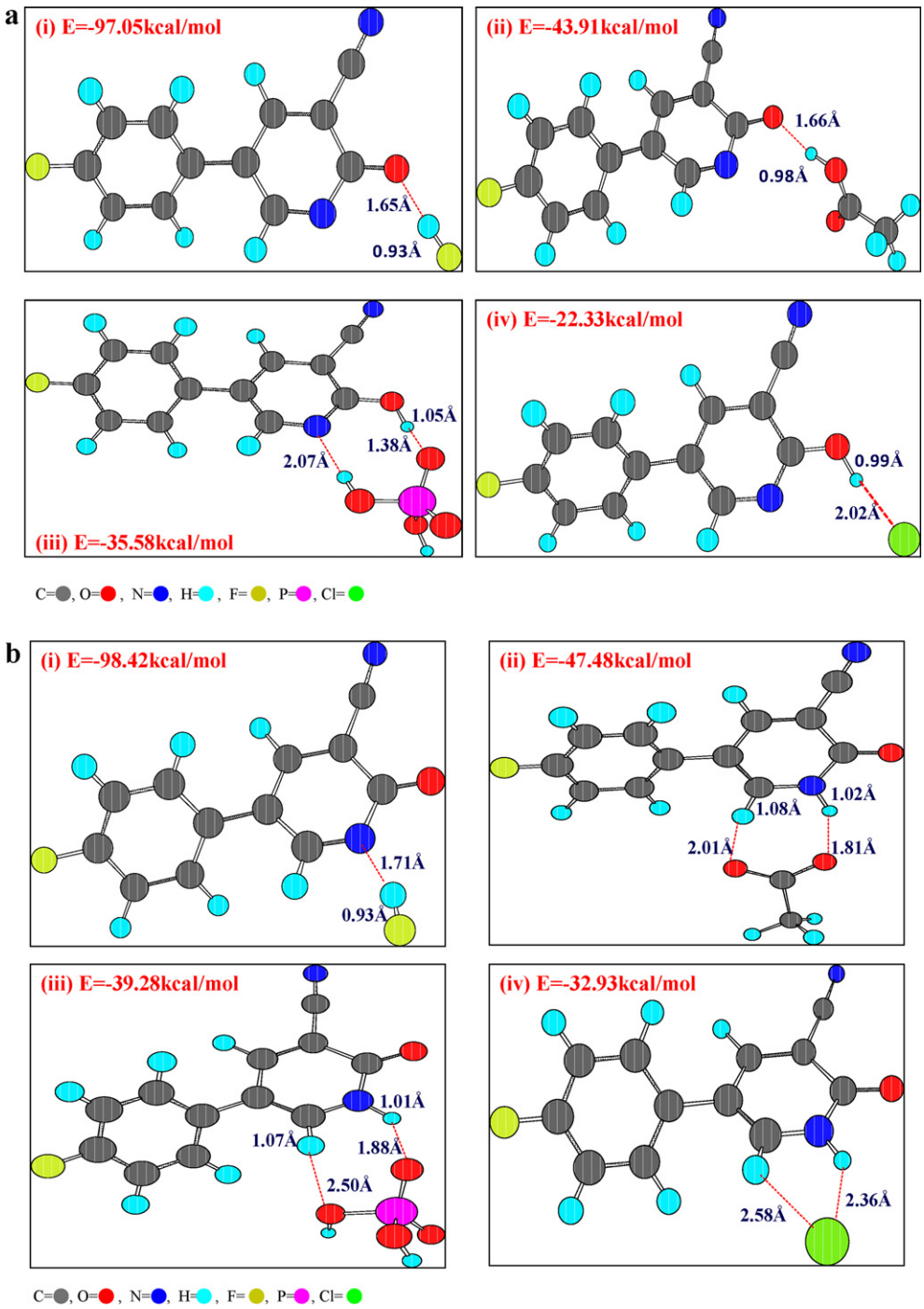


Fig. 10. HF/6-31G** optimized geometries for the complexes of FP2HN with (i) F^-, (ii) AcO^-, (iii) $H_2PO_4^-$, and (iv) Cl^- in its (a) enol form and (b) keto form.

complex with both of the tautomeric form of FP2HN molecule, it is clear that N—H/O—H bond disrupts in the optimized complex wherein N—H distance is 1.715 Å (instead of normal N–H distance of 0.997 Å) for keto tautomer and O–H distance is 1.651 Å (instead of 0.947 Å) for the enol tautomer. From the changes of N–H/O–H distances (greater than 0.7 Å) it is obvious that the N—H/O—H bond breaks and H^+ moves closer to F^- ion with H···F distance 0.934 Å and 0.929 Å for keto and enol tautomer, respectively. In case of other anions, as shown in Table 3 and Fig. 10, N–H/O–H distances with anions decreases in the order of $AcO^- > H_2PO_4^- > Cl^- > Br^-$ because of their lower basicity. On the other hand, the distance of hydrogen bond between O—H/N—H with anions increases in the order of $F^- < AcO^- < H_2PO_4^- < Cl^- < Br^-$ thereby supporting the greater binding efficiency of F^- than the others. To check the selectivity of the molecule towards anions as is observed experimentally, we have calculated BSSE corrected interaction energy (ΔE_{int}^{corr}) of the two tautomers of FP2HN with anions according to Eq. (4) and has been listed in Table 3. From this table, it is clear to say that the binding affinity of F^- with the receptor is greater than any other anions. In addition to the basicity of the anions, the geometrical

complementarity between receptor and anions may also play a significant role in governing the binding affinity. As fluoride ion has high electronegativity and smaller size; it reacts more vigorously to the acidic proton of the receptor as compared with other anions. So our theoretical findings confirm that the receptor–F^- binding is the ground state deprotonation mediated hydrogen bonding interaction. The calculated binding energy and geometrical parameters demonstrate the stronger affinity of F^- than other anions and this selectivity trend is in accordance with experiment.

4. Conclusion

In conclusion, we present the photophysical properties of a new synthetic receptor 5-(4-fluoro-phenyl)-2-hydroxy-nicotinonitrile (FP2HN) and its fluorosensitivity towards selective anions by UV–vis, steady state and time resolved emission and ^{1}H NMR experiments. Here, we present a new kind of fluorescent anion sensor based on inhibition of ESIPT process. Summing up all the data, we can claim that the sensing property of FP2HN is based on an acid–base reaction, while deprotonation process occurs in the presence of a stronger base. This molecule demonstrates selective but different binding ability for F^-, AcO^-, $H_2PO_4^-$, Cl^- ions. Almost no binding effect is observed for Br^-, HSO_4^-, NO_3^-, etc. Measured binding constant as well as fluorescence lifetime indicate the sensitivity of anions toward the receptor in the order of $F^- > AcO^- > H_2PO_4^- > Cl^-$. Theoretical calculations lend further support on stronger binding affinity of fluoride ion towards FP2HN compared to AcO^- and $H_2PO_4^-$ ions. The inhibition abilities of anions towards ESIPT reaction of the title molecule will be a useful clue to design more delicate ESIPT-based chemosensors.

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