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Graphical abstract

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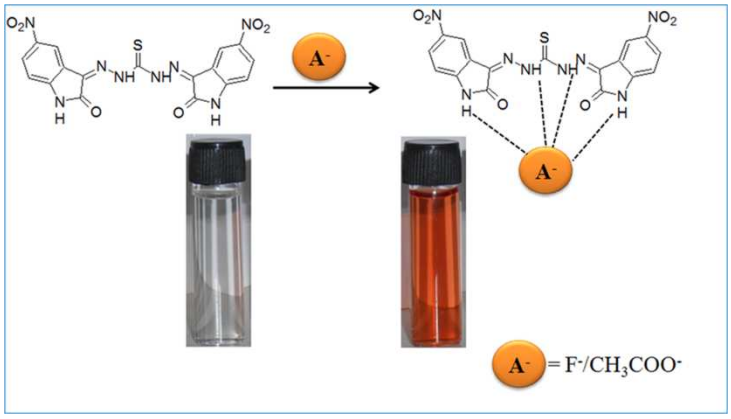

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ARTICLE TYPE

Colorimetric anion sensor based on receptor having indole and thiourea binding sites

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A new colorimetric sensor **L** containing nitro substituted indole and bisthiocarbonohydrazone units for selective fluoride and acetate ions is designed and synthesized. The receptor **L** shows well defined color change in visible region of the spectrum with an absorption band at ~ 515 nm and 506 nm, respectively for F^- and CH_3COO^- ion in acetonitrile solution. Job plots indicated the formation of 1:1 (**L** with CH_3COO^-) and 1:2 (**L** with F^-) complexes. The interaction of **L** with F^- ion undergoes a deprotonation process and release of $[HX_2]^-$,whereas with CH_3COO^- ion forms stable $[LH_2\cdots X]^-$complex. The relative affinities of the anions with **L** are rationalized using computational studies.

Introduction

In recent years, the design and synthesis of new receptors capable of sensing neutral and charged species have attracted considerable interest.[1,2,3] In particular, the development of colorimetric sensors has been attracted for their "naked eye" detection of target species and offer qualitative and quantitative information without the help of any spectroscopic instruments.[4,5,6,7] New chemosensor for the colorimetric sensing of fluoride and acetate ions have been paid much attention due to their requirement in the environmental, security and health sciences.[8,9,10] Moreover, selective recognition of these anions is of realistic significance. Therefore, several synthetic receptors with high affinity and selectivity for fluoride and acetate ion sensing have been reported along with the reports which show selective visible color changes in the presence of these ions.[11,12,4,13] However, examples for the sensitive and simple-to-use colorimetric anion sensors are rather limited compared to the fluorescence based sensors.[14,15]

In overall, development of new receptors that show controllable anion selectivity and sensitivity still remains as a challenging task for a chemist. Common colorimetric anion chemosensor moieties for anion sensors are based on amide, urea, thiourea, phenol, pyrrole, imidazolium and indole moieties.[16,17,18,19,20,21] In all these subunits, O–H···X^- and N–H···X^- hydrogen bonding sites play an important role in selective sensing of anions . It is believed that, the hydrogen-bond-induced π-electron delocalization or NH deprotonation are responsible for signaling the binding event in such classes of sensor activity.[22,23,24]

Among the various functional groups available, the thiourea group is often chosen as the anion binding site because it is a good hydrogen-bond donor resulting in stable and strongly hydrogen-bonded complexes with various anions.[25,26,27] Hence, large number of thiourea based anion receptors have been designed, synthesized and tested for anion recognition and sensing during the past decades.[14,24,28] On the other hand, several indole and related heterocyclic compounds having acidic hydrogen atoms exhibited strong anion recognition ability.[29,30,21,31] However, in order to enhance the acidity of the anion binding unit, the electron withdrawing nitro group is often introduced into the receptor which further improves the binding affinity of the anions towards receptor.[32,11]

In this context, a simple indole conjugated thiourea as efficient colorimetric anion sensor, *N″,N‴*-bis[5-nitro-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene]thiocarbono hydrazide (**L**), that can selectively detect F^- and CH_3COO^- ions by naked eye has been reported. The receptor **L** is expected to show the improved binding affinity with anions due to the enhanced acidity of the thiourea protons and the stabilization effect of the negative deprotonated species induced by the electron withdrawing $-NO_2$ group. The interaction of the receptor with anions has been evaluated through UV-Visible titrations. In addition, the anion recognition via hydrogen bonding interactions were monitored using ^{1}H NMR experiments and a feature of the binding mode was predicted on the basis of ab initio calculations.

Experimental section

Materials and methods

5-nitroindoline-2,3-dione and anions of tetrabutylammonium salts were purchased from Sigma Aldrich Ltd (St. Louis, MO). All other reagents were purchased from locally available commercial suppliers and were used without further purification. A. R grade solvents were purchased from Merck Inc. ^{1}H NMR spectra were recorded with BRUKER 400 MHz NMR spectrometer using trimethylsilane as internal reference. Elemental analyses were performed using Thermo Scientific Flash 2000 organic elemental analyzer. UV-Vis absorption spectra were measured using Perkin Elmer spectrophotometer.

Synthesis of *N'',N'''*-bis[5-nitro-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene]thiocarbono hydrazide (L)

To a stirred solution of 5-nitroindoline-2,3-dione **1** (0.5 g, 2.6 mmol) in 10 ml of ethanol: water (1:1) mixture, 1,3-diaminothiourea **2** (0.135g, 1.3 mmol) were added under nitrogen atmosphere. The reaction mixture was then refluxed for 12 h. Subsequent to completion of the reaction (monitored by thin layer chromatography), the solvent of the resultant mixture was removed under reduced pressure. The obtained crude product **L** was purified by recrystallization using ethanol to obtain pure product as yellow solid with 75 % yield. M.P: 208–210 ^{o}C. ^{1}H NMR (400MHz,DMSO-d_6, ppm): 14.84 (s, 2H), 12.91 (s, 2H), 8.34 (d, 2H, *J*=8 Hz), 7.93 (s, 2H, *J*=8 Hz), 7.17 (d, 2H, *J*=8 Hz). ^{13}C NMR (400MHz,DMSO-d_6, ppm): 186, 168.5, 147.3, 143.6, 134.5, 126.4, 123, 122.6, 118.6. Element. Anal. Calcd. For ($C_{17}H_{10}N_8O_6S$): C, 44.94; H, 2.22; N, 24.66; S, 7.06. Found: C, 44.98; H, 2.26; N, 24.72; S, 7.14.

Results and discussion

A highly selective fluoride and acetate ion sensing indole conjugated thiourea receptor **L**, which was synthesized by condensation of 5-niotroindoline-2,3-dione and 1,3-diaminothiourea in ethanol–water (1:1) mixture under reflux condition is reported (Scheme 1). The receptor **L** consists of two types of acidic protons, –NH (thiourea) and –NH (indole), which can bind with anions. In addition, multiple acidic protons in the receptor could be deprotonated that depends on the basicity of the anion and their equivalence.[24] Initially, the colorimetric detection ability of the receptor **L** (1.0×10^{-5} M) was studied by treating it with various tetrabutylammonium salts (2 equivalent) such as fluoride, acetate, chloride, bromide, iodide and dihydrogen phosphate in acetonitrile. It was observed that the color of the receptor changes from colorless to red only in the case of fluoride and acetate anion salts. The color change could be detected by the naked eye (Fig. 1).

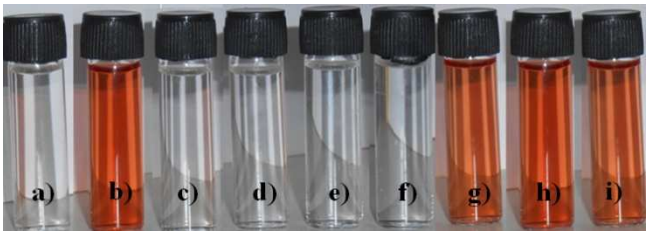
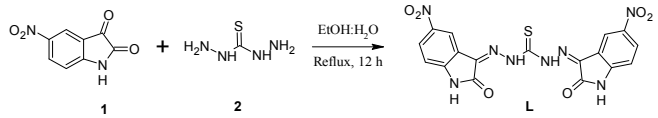


Fig. 1 Visual color change of **L** (1 x 10^{-5} M) in dry CH_3CN after the addition of 2 equivalents of TBA salts. a) Free receptor L, b) F^-, c) Cl^-, d) Br^-, e) I^-, f) $H_2PO_4^-$, g) CH_3COO^-, h) mixture + $F^-$and i) mixture + CH_3COO^-.

However, the addition of other anions did not result in detectable color changes. In addition, the receptor **L** shows selective color changes from colorless to red specifically for fluorides and acetates even in the presence of other anions. Overall the dramatic color change signifies that hydrogen bonding interaction between anion and the receptor which affects the electronic properties of the chromophore, which induces a new charge-transfer interaction and resulting in visible color change.[33,23]



Scheme 1

Therefore, selectivity of the receptor **L** with various anions was further evaluated by UV-Vis absorption spectroscopy. As shown in Fig. 2, it was found that the receptor could selectively detect fluoride and acetate anions with visible signature, whereas the receptor did not show any spectral change with other anions.

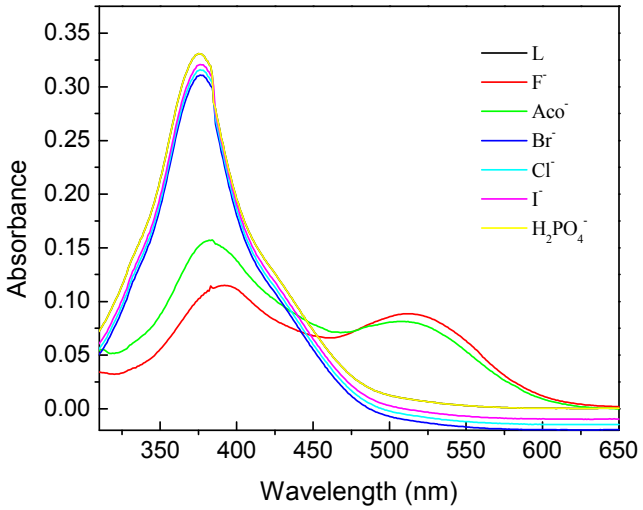


Fig. 2 UV-Vis absorption spectrum of **L** (1 x 10^{-5} M) in CH_3CN solution after addition of 4 equiv. of anions in the form of TBA salts

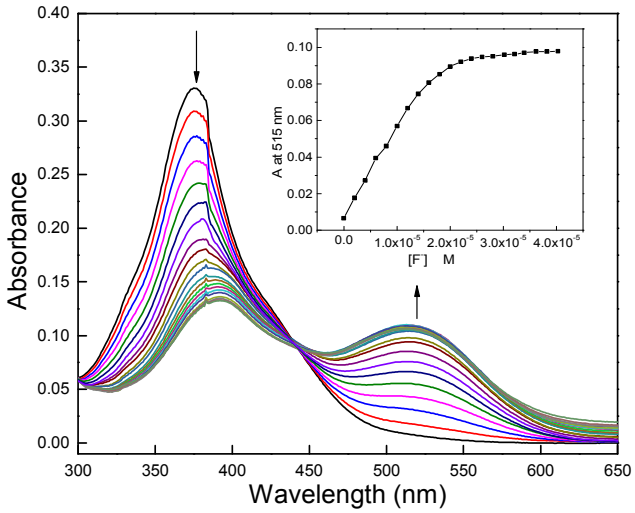


Fig. 3. UV-Vis absorption titration of **L** (1 x 10^{-5} M) in CH_3CN solution on addition of $\mathbf{F^-}$ ions (0 to 4 x 10^{-5} M) Inset: absorbance at 515 nm versus F^- concentration

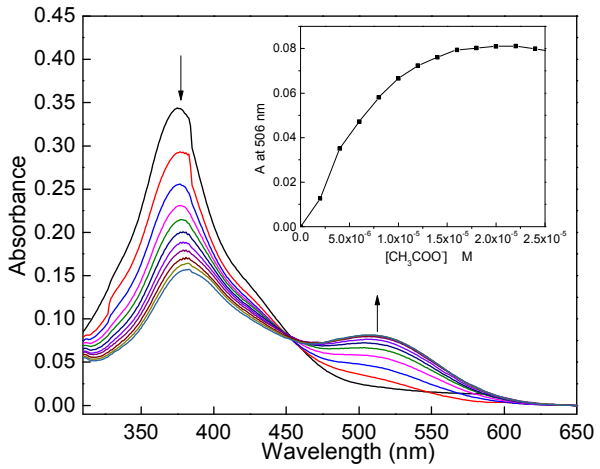


Fig. 4. UV-Vis absorption titration of **L** (1 x 10^{-5} M) in CH_3CN solution on addition of $\mathbf{CH_3COO^-}$ ions (0 to 2 x 10^{-5} M) Inset: absorbance at 506 nm versus CH_3COO^- concentration

UV-Vis studies

The selectivity and sensitivity of binding affinity of anion with the receptor **L** was further investigated through UV-Vis spectrophotometric titrations. The absorption spectrum of receptor **L** (1 x 10^{-5} M) with various concentrations of standard tetrabutylammonium salts of fluoride and acetate ions were recorded (Fig. 3 and 4). The absorption spectrum of receptor **L** in acetonitrile solution showed a characteristic band at 376 nm due to the π–π^* electronic transition of the receptor.[34,35] On addition of fluoride (0 to 4 x 10^{-5} M) and acetate anion (0 to 2 x 10^{-5} M), the intensity of characteristic absorption spectra of **L** decreased significantly. On the other hand, a new band was observed at 515 and 506 nm with a significant color change from colorless to red for fluoride and acetate ion, respectively.

Further, no obvious changes were observed in the absorption spectrum with the increase in concentration of these anions. As shown in Fig. 3 and 4, the observed bathochromic (red) shift in the absorption spectra of receptor **L** indicates the formation of the receptor-anion complex (L-F^-/CH_3COO^-) and is more stabilized by the anion binding.[36] This could be attributed to the charge transfer interaction between electron rich thiourea bound anion and the electron deficient 5-nitro indoline-2,3-dione moieties present in **L**.[37] Here the presence of electron withdrawing $-NO_2$ group in indoline-2,3-dione ring governs the acidity of the –NH (thiourea) proton and thereby influencing the deprotonation phenomena and affinity towards anions.[38] However, the detailed information on the nature of the receptor-anion complex could be obtained from ^{1}H NMR titrations. Furthermore, well defined isosbestic points were observed at 445 and 455 nm, respectively for fluoride and acetate ions. This further signifies that the new component was formed in response to the interaction with receptor and the anion.[13] Jobs plots for the receptor with F^- and CH_3COO^- ions (1 x 10^{-4} M) in acetonitrile solution is given in Fig. 5. The maxima at a mole fraction of 0.625 with F^- and 0.5 with CH_3COO^- ion, signifies the binding of receptor anion in 1:2 and 1:1 stoichiometric ratio, respectively.

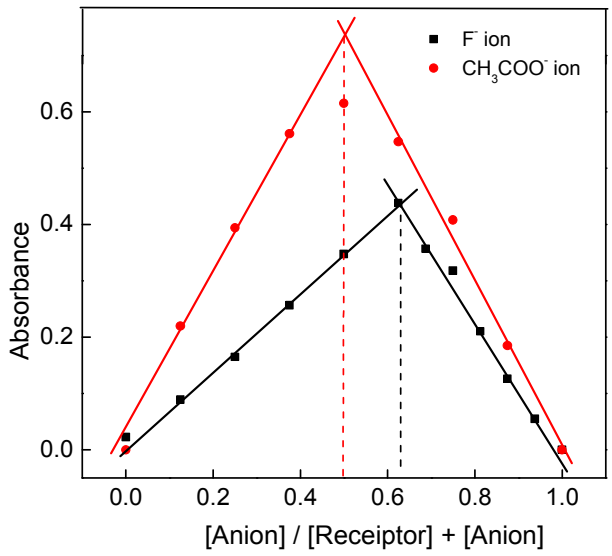


Fig. 5 Job's plot for receptor **L** with $\mathbf{F^-}$, $\mathbf{CH_3COO^-}$ anions, with a total concentration of 1.0 × 10^{-4} M

The binding constant values for anion complexation with receptor **L** in acetonitrile were determined from the absorption spectra by the following modified Benesi–Hildebrand method.[39]

$$\frac{1}{\Delta A} = \frac{1}{\Delta \varepsilon l[F^{-sat}]} + \frac{1}{\Delta \varepsilon l K[L][F^{-sat}]^n} \qquad (1)$$

Where $\Delta A = A - A_{min}$ and A_{min}, A, are the absorption of **L** considered in the absence of anion and at an intermediate. K is binding constant, $[F^{-sat}]$ is concentration of anion at saturation and n is the stoichiometric ratio. In the case of fluoride and acetate ion, the values of n were found to be 2 and 1 respectively from the linear fits with respect to $1/[F^-]^n$. This shows the formation of a stable 1:2 stoichiometric complex between receptor **L** and F^- ion and a 1:1 complex between **L** and CH_3COO^- ion (Fig. 6 and 7).

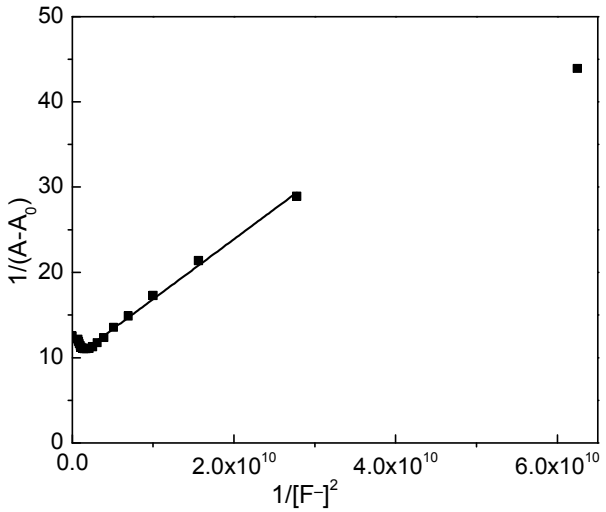


Fig. 6.Benesi–Hildebrand plot of receptor **L** binding with $\mathbf{F^-}$ ion associated with absorbance change at 515 nm in CH_3CN solvent

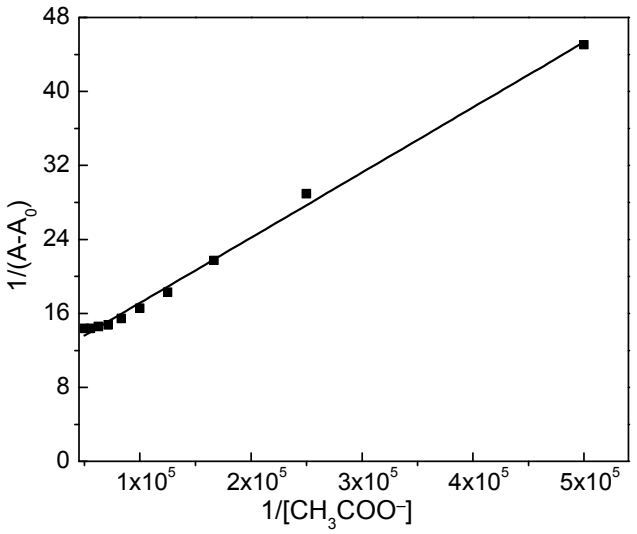


Fig. 7.Benesi–Hildebrand plot of receptor **L** binding with **CH_3COO^-** ion associated with absorbance change at 506 nm in CH_3CN solvent

The binding constants (K) values for the receptor **L** with F^- and CH_3COO^- ions were found to be 4.89 x 10^4 M^{-2} and 2.63 × 10^5 M^{-1}, respectively. The observed strong binding response of receptor **L** towards CH_3COO^- ion could be explained on the basis of their basicity and structure of the complex.[40] It is known that receptor containing thiourea functional group is a good hydrogen bond donor and have tendency to form multiple hydrogen bonds with the anions having tetrahedral and Y-shaped structure.[23,41] Therefore, here CH_3COO^- ion having triangular planar structure, fit within the hydrogen atoms on binding sites of the receptor **L** through multiple hydrogen bonding interaction. In addition, the preferential binding of CH_3COO^- ion with receptor **L** was also rationalized using computational studies.

Computational studies

The observed selectivity of receptor **L** towards CH_3COO^- anion can be explained on the basis of density functional theory (DFT) calculations. All the geometries were optimized following gradient corrected functional, GGA-BLYP using TS scheme for DFT-D correction with double nuclear polarization and 3.5 atomic orbital basis set.[42,43,44,45,46,47] The optimization methods were used from DMol3 module of Materials Studio 6.0, Accelrys Inc. The optimized structures of receptor **L** and with F^- and CH_3COO^- ions are represented in Fig. 8. The intermolecular hydrogen bond distance between F^-ion and one of the –NH (thiourea) proton was found to be ~1 Å, after geometry optimization. On the other hand, the two oxygen atoms of acetate ion are participated in hydrogen bond formation with both the –NH (thiourea) protons of the each receptor L and were observed at 2.68 and 2.92 Å. The observed shorter hydrogen bond distance for fluoride anion with the receptor can be attributed to its smaller size as compared to the acetate ion.[14] Single point interaction energies were calculated using optimized geometries are found to be –103.28 Kcal mol^{-1} and –474.0 kcal mol^{-1} for F^- and CH_3COO^- ions, respectively with receptor **L**. This result indicates that the binding affinity for acetate ion with receptor **L** is much higher than that of fluoride ion which is in accordance with the experimental results.

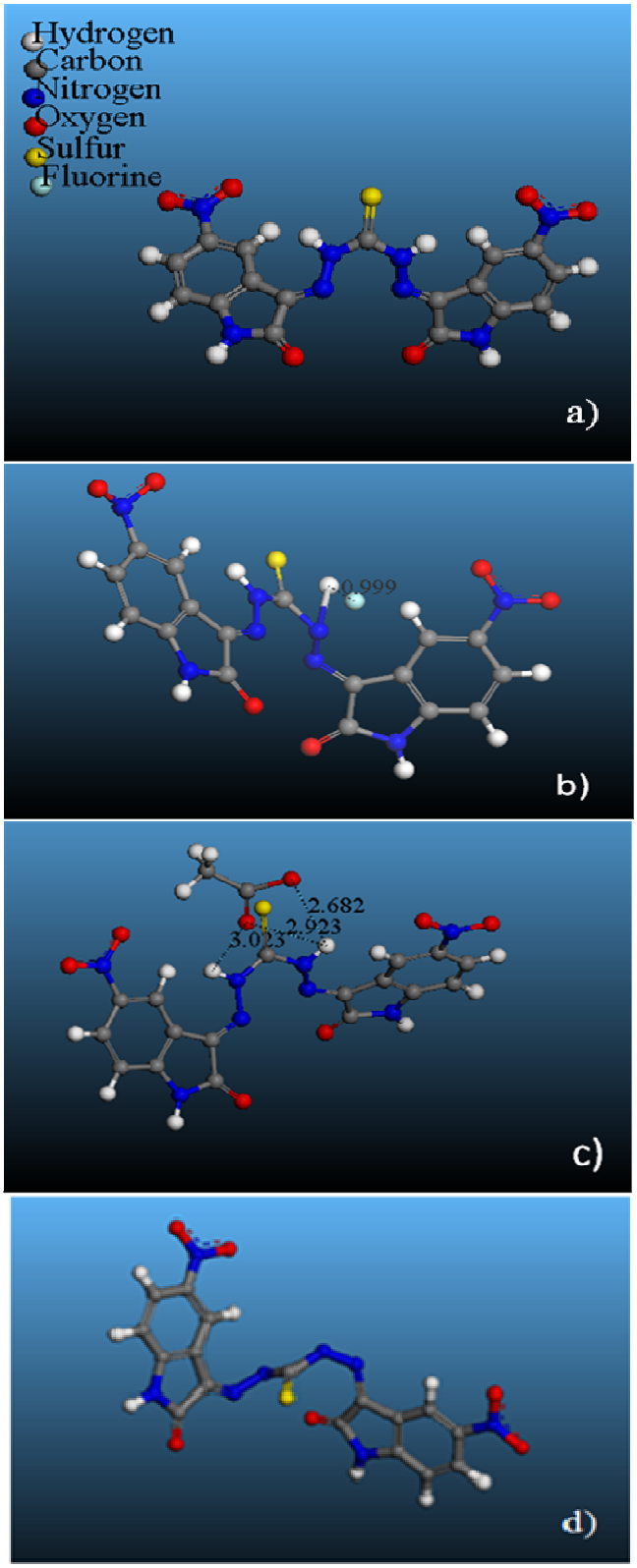


Fig. 8 BLYP/DNP optimized geometries for receptor **L** (a), its complexes with the **F^-** (b), **CH_3COO^- (c)** and structure of **L** after deprotonation (d)

^{1}H NMR studies

To get insight into the binding ability of receptor **L** with anions, ^{1}H NMR titration experiments were carried out in DMSO-d_6 solution. As shown in Fig. 9, the proton $-NH_a$ of thiourea group of receptor appeared at 14.84 due to the formation of intramolecular hydrogen bonding,[48] whereas the $-NH_b$ proton of indole unit appeared at 12.91 ppm. After the addition of lower concentration of fluoride ion (0.5 equivalents), the signal for $-NH_b$ proton of indole subunit exhibited a downfield shift (13.25 ppm) and was broadened. In addition, signal of $-NH_a$ proton of thiourea subunit disappeared completely. It is known that the receptor containing more acidic thiourea protons undergo deprotonation selectively in the presence of fluoride and acetate ions.[25] Here, the deprotonation of thiourea proton occurred at low concentration of fluoride ions can be attributed to the electron withdrawing effect of nitro group which further served to enhance the -NH acidity. These results indicate that two sets of $-NH$ protons ($-NH_a$ and $-NH_b$) of receptor were involved in the hydrogen bond interaction with the fluoride ion. Further, subtle shifts in the aromatic protons of **L** (Ar-H_d from 8.34 ppm to 8.22 ppm, Ar-H_e from 7.93 ppm to 7.90 ppm and Ar-H_c 7.17 ppm to 7.10 ppm) were observed.

Here, the two different effects on the aromatic ring of the receptor could be considered as a result of the formation of hydrogen bonding between anions and the receptor. Firstly, through-bond propagation which increases the electron density on the aromatic ring and produces a shielding effect. Thus, generates an upfield shift in the C-H protons of the phenyl ring. Secondly, through-space effect which increases the polarization of the C-H bonds, where partial positive charge is formed on the proton causes a deshielding effect and hence downfield shift in the aromatic protons.[25]

After addition of 1→2 equivalent of fluoride ion, significant downfield shift in the resonance signal of NH_b and upfield shift in the aromatic protons (H_c, H_d and H_e) were observed. The observed trend in the aromatic region of **L** could be due to the increase in electron density of the receptor's framework through-bond propagation mechanism. Nevertheless, signals of NH_b (indole) proton neither shifted nor disappeared after the addition of excess of fluoride ion (5 equivalents) during the titration. On the other hand, the broad triplet signal was appeared at 16.1 ppm attributed to the formation of the HF_2^-

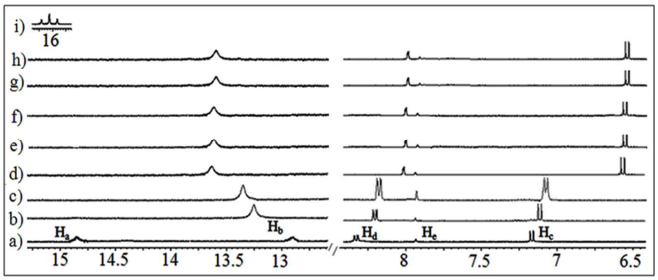


Fig. 9.^{1}H NMR (400 MHz) spectra of **L** in DMSO-d_6 after the addition of F^-a) 0 equivalent, b) 0.5 equivalent, c) 1 equivalent, d) 2 equivalent, e) 2.5 equivalent, f) 3 equivalent, g) 4 equivalent, h) 5 equivalent, i) HF_2^- peak

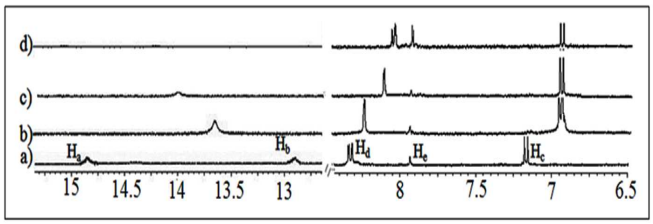


Fig. 10.^{1}H NMR (400 MHz) spectra of **L** in DMSO-d_6 after the addition of CH_3COO^-a) 0 equivalent, b) 0.5 equivalent, c) 2 equivalent, d) 5 equivalent

species (Fig. 9), which further supports the proposed deprotonation mechanism.[11] Herein, it should be noted that the deprotonation is likely to occur at much lower concentration of F^- ion as supported by the UV-Vis spectral changes. At higher concentrations of F^- ion, HF_2^- species is sufficiently, kinetically stable and is available in abundance, high enough to be detected by ^{1}H NMR. These results indicate that, the following two equilibria exist in receptor-anion complex formation.[28]

$$LH_2 + X^- \rightleftharpoons [LH_2\cdots X]^- \quad (2)$$

$$[LH_2\cdots X]^- + X^- \rightleftharpoons [LH]^- + HX_2^- \quad (3)$$

The formation of hydrogen bond complex between receptor and F^- ion is described by eqn. (2). Whereas, second anion (X^-) abstracts a fragment of HX from the complex to form HX_2^- and to leave the deprotonated [LH^-] derivative as described in eqn. (3).

In the case of CH_3COO^- ion, after the addition of 0.5 equivalents, the signal for $-NH_a$ proton disappeared rapidly while the $-NH_b$ proton exhibited a downfield shift and was broadened. Further, aromatic protons of **L** were shifted to upfield region (Fig. 10). Here also similar trend was observed as in the case of fluoride ion was titrated with receptor **L**. At higher concentrations of acetate ions (5 equivalents), signal of NH_b proton disappeared completely and on contrary, a characteristic peak of HF_2^-did not appears. The disappearance of self complex HF_2^-species could be due to its less stability in presence of acetate ion.[11] Here, the receptor and acetate ion forms complex $[LH_2\cdots X]^-$through hydrogen bond interaction and is described by eqn. (2). Overall, the negative charge of the deprotonated receptor **L** is delocalized over the molecule which leads to the enhancement in the push-pull effect of the internal charge transfer. Thus, the resulted effect could be responsible for the visible signal at greater than 500 nm along with a diagnosable visible color change in the presence of fluoride and acetate ions.

Conclusions

In summary, here a new colorimetric sensor **L** having nitro substituted indole and bisthiocarbonohydrazone units for the selective detection of fluoride and acetate ions have been developed. The receptor displayed naked eye detection in the presence of respective anions at room temperature. Further, their selectivity towards fluoride and acetate ions was investigated experimentally and theoretically. The ab initio calculations were in good agreement with the experimental results. Finally, the interaction mode of the receptor with the anions was investigated using ^{1}H NMR titrations.

Acknowledgments

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Notes and references

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