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Spectral and DFT studies on simple and selective colorimetric sensing of fluoride ions via enhanced charge transfer using a novel signaling unit

Angupillai Satheshkumar, Kuppanagounder P. Elango*

Department of Chemistry, Gandhigram Rural Institute (Deemed University), Gandhigram 624 302, India

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ABSTRACT

Two new colorimetric sensors for fluoride ions [N,N′-(anthracene-9,10-dione-1,2-diyldicarbamothioyl) dibenzamide] and [N,N′-(naphthalene-1,4-dione-2,3-diyldicarbamothioyl) dibenzamide] have been prepared and characterized using various spectral techniques. The quinonoid receptors exhibited high selectivity for fluoride ion detection over other anions. The association constant of the receptor-F complexes were found to be 6.3×10^8 and 7.7×10^{15} M^{-1} for the anthroquinone and naphthoquionone receptors, respectively. ^1H NMR studies indicated that the fluoride ion sensing by the receptors is due to the formation of H-bonds between F-ions and the –NH moiety of the receptors which has been enhanced by directly attaching signaling unit to the receptor unit in the naphthoquinone derivative. The naphthoquinone receptor also exhibited colorimetric sensing of fluoride ions present in commercially available toothpaste samples in aqueous medium. The structural and electronics properties of the sensors and their fluoride complexes were also investigated using *ab initio* DFT calculations.

1. Introduction

Recently considerable effort has been made to design chemosensors for anions. The reason for this intensive interest is the importance of the detection of anions in disciplines such as biology, and environmental science [1]. Among the interest in biologically functional anions, fluoride is one of particular importance owing to its established role in dental care [2] and treatment of osteoporosis [3]. Fluoride is also present in toothpaste in the form of NaF or sodium monoflurophosphate which are used to prevent cavities in teeth. However, excessive use may create fluorosis resulting in the discoloration of teeth [4,5]. As the smallest and the most electronegative atom, fluorine has unique chemical properties and can form the strongest hydrogen bond interaction with hydrogen bond donors. Consequently, selective detection of this anion becomes essential either visually or spectroscopically. The visual detection of analytes has shown huge advantage over sensing methods due to its quick response and simplicity as it does not require any equipment for analyte detection [6–11].

A chemical sensor is generally composed of two units, a receptor and a signaling unit [12,13]. When signaling unit contains chromophores, the receptor is known as chromogenic (or) colorimetric sensor. Various authors have developed chromogenic sensors containing urea/thioureas [14–18], calyx – [4] – pyrrole [19–22], imidazole [23], and calixarenes [16,24,25] as the binding functionalities due to their hydrogen bond donor properties. Moieties such as nitrophenyl [26–28], anthroquinone [10,23], and azo-dye [11,13,29] were used as signaling units in these sensors. A survey of literature revealed that, many attempts have been made to increase the H-bond donor property of the receptor moiety in the urea/thiourea based sensors. Amilan Jose et al. [10] have studied the fluoride ion sensing property of anthroquinone based urea/thiourea systems. The results indicated that the thiourea system was found to posses relatively higher binding ability with fluoride ion in DMSO (the formation constant in the order of 10^5 M^{-1}). Mei-Zhen Sun et al. [30] have reported that Hg (II)-thiourea based complexes promoted intramolecular charge transfer (ICT) between receptor and signaling units which selectively sense fluoride ion in acetonitrile. Cho and co-workers [31] investigated the fluoride ion sensing property of anthroquinone based urea system. Vinod kumar et al. [27] have reported the fluoride ion and CN^- sensing behavior of urea/thiourea based sensor with p-nitrophenyl as the signaling unit. Likewise, Duke and Gunnlaugsson [32] have investigated the fluoride ion sensing property of a urea based sensor with p-trifluoromethylphenyl as the signaling unit. The literature suggests that the fluoride ion sensing ability of a sensor is based on the ease with which the occurrence of the ICT between receptor and signaling units in the sensor occurs. The main objective,

* Corresponding author. Tel.: +91 451 245 2371; fax: +91 451 2454466.
E-mail address: drkpelango@rediffmail.com (K.P. Elango).

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therefore, of the present endeavor is to tune the electron accepting property of the signaling unit of thiourea based receptors to selectively sense fluoride ion in an aqueous–organic medium. Hence two new thiourea based receptors were prepared, characterized and employed as colorimetric fluoride ion sensors. Various spectral techniques such as UV–Vis, spectrofluorometer, and ^{1}H NMR have been used to investigate the interaction between the receptor and F^- ions.

2. Experimental

2.1. Chemical and apparatus

All reagents for synthesis of the receptors were obtained commercially and were used without further purification. Spectroscopic grade solvents were used as received. UV–Vis spectral studies were carried out in ACN (or) ACN/water (9:1 v/v) on a (JASCO V-630-double beam spectrophotometer). Steady state fluorescence spectra were obtained on a spectrofluorometer (JASCO-FP-6200). The excitation and emission slit width (5 nm) and the scan rate (250 mV s^{-1}) was kept constant for all of the experiments. FT-IR spectra were obtained as KBr pellets on an FT-IR spectrometer (JASCO 460 Plus, Japan). Nuclear magnetic resonance spectra were recorded in DMSO-d_6 in Madurai Kamaraj University (Bruker, ^{1}H NMR 300 MHz, ^{13}C NMR 75 MHz). The ^{1}H NMR spectra data is expressed in the form: chemical shift in units of ppm (normalized integration, multiplicity, and the value of *J* in Hz).

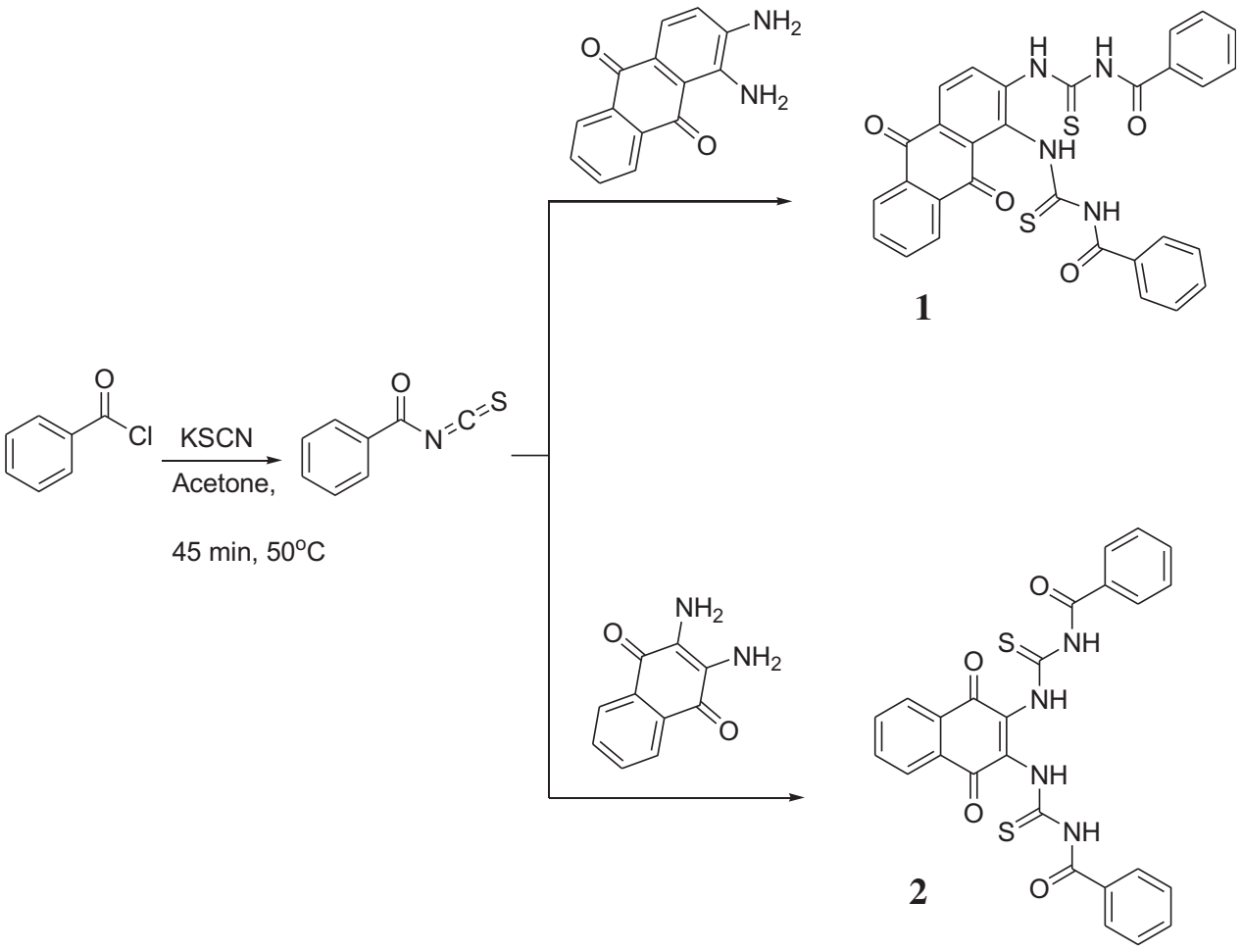
2.2. Synthesis of thiourea compounds (**1**-**2**)

2.2.1. N,N′-(antharacene-9,10-dione-1,2-diyldicarbamothioyl) dibenzamide (**1**)

A solution of benzoyl chloride (1.4058 g, 0.01 mol) in acetone (50 mL) was added drop wise to a suspension of potassium thiocyanate (0.9718 g, 0.01 mol) in anhydrous acetone (50 mL). The reaction mixture was heated under reflux for 45 min and then cooled to room temperature. A solution of 1,2-diaminoanthracene-9,10-dione (1.0826 g, 0.005 mol) in acetone was added and the resulting mixture was stirred for 2 h. 0.1 N HCl (300 mL) was added to the reaction mixture and resulting solid was filtered, washed with water and dried in vacuum. The crude material was purified by 100–200 mesh flash column by using 30% of ethylacetate in petroleum ether to get the pure product as a dark orange solid (yield 72%). The schematic equation was mentioned in Scheme 1. UV–Vis (λ_{max} = 428 nm), ^{1}H NMR (DMSO-D_6, 300 MHz): δ (ppm) 7.49–7.59 (m, 3H), 7.66–7.75 (m, 3H), 7.84–7.95 (m, 3H), 8.04 (d, *J* = 6 Hz, 4H), 8.17 (d, *J* = 6 Hz, 1H), 8.24 (d, *J* = 6 Hz, 2H), 11.79 (s, 2H), 12.06 (s, 2H). FT-IR (KBr) (cm^{-1}) 3398 (NH–C=S), 3244 (NH–C=O), 1708, 1601 (C=O), 1345 (C=S–). Elemental analysis : Anal.Calcd. for $C_{30}H_{20}N_4O_4S_2$: C, 63.81; H, 3.57; N, 9.92. Found: C, 63.31; H, 3.20; N, 9.78.

2.2.2. N,N′-(naphthalene-1,4-dione-2,3-diyldicarbamothioyl) dibenzamide (**2**)

A solution of benzoyl chloride (1.4058 g, 0.01 mol) in acetone (50 mL) was added drop wise to a suspension of potassium thiocyanate (0.9718 g, 0.01 mol) in anhydrous acetone (50 mL). The



Scheme 1. Preparation of thiourea compounds **1** and **2**.

reaction mixture was heated under reflux for 45 min and then cooled to room temperature. A solution of 2,3-diaminonaphthoquinone (1.0 g, 0.005 mol) in acetone was added and the resulting mixture was stirred for 2 h. 0.1 N HCl (300 mL) was added to the reaction mixture and resulting solid was filtered, washed with water and dried in vacuum. The crude material was purified by (100–200) mesh flash column by using 40% of ethylacetate in petroleum ether to get the pure product as a dark orange solid (yield 62%). The schematic equation mentioned in Scheme 1. UV–Vis ($\lambda_{max} = 459$ nm), ^{1}H NMR (DMSO-D_6, 300 MHz): δ (ppm) 7.08 (t, $J = 6$ Hz, 2H), 7.31 (t, $J = 9$ Hz, 4H), 7.45 (t, $J = 9$ Hz, 4H), 7.76–7.89 (m, 2H), 7.99–8.09 (m, 2H), 12.01 (s, 2H), 13.31 (s, 2H). ^{13}C NMR (DMSO-D_6, 75 MHz): δ (ppm) 121.9, 125.2, 125.8, 128.2, 130.0.130.9, 132.3, 132.5, 132.6, 134.7, 155.3, 168.1, 177.1, 180.4. FT-IR (KBr, cm^{-1}) 3414 (NH–C=S), 3218 (NH–C=O), 1663, 1549 (C=O), 1277 (C=S). Elemental analysis: Anal.Calcd. for $C_{26}H_{18}N_4O_4S_2$: C, 60.69; H, 3.53; N, 10.89. Found: C, 60.50; H, 3.61; N, 10.60.

3. Results and discussion

Two new thiourea based receptors (**1**-**2**) with varying signaling units were efficiently prepared (Scheme 1) and characterized. The F^- ion sensing behavior of these receptors has been investigated using various spectral techniques (UV–Vis, Fluorescence and ^{1}H NMR). The colorimetric sensing of F^- ions can effectively been done either by increasing the H-bond donor ability of the receptor unit or by increasing the electron accepting ability of the signaling unit of a sensor. The systems so for reported in the literature contains a phenyl ring with an electron withdrawing substituent as the signaling unit [27]. The receptor **1**, employed in the present study, possesses an anthroquinone moiety and the carbonyl group as signaling units. In receptor **2**, the electron acceptor naphthoquinone is selected as the signaling unit. Further, in this system, electron deficient quinone unit is directly attached to the thiourea nitrogen so as to have easy and maximum ICT transition. To the best of our knowledge this is the first attempt to prepare such a novel moiety to sense F^- ions colorimetrically. The results and discussion of the colorimetric sensing of F^- ions by these receptors are presented below.

3.1. Visual detection

The colorimetric sensitivity of **1** and **2** toward various anions such as F^-, Cl^-, Br^-, I^-, NO_3^-, $H_2PO_4^-$, AcO^-, and CN^- in their tetrabutylammonium form were monitored visually. As depicted in Fig. 1 solutions of compound **1** (in ACN) and **2** (in ACN/water) turn yellow to intense red color after the addition of fluoride. However, their color remained unchanged after the addition of other chosen anions. This indicated the selectivity of **1** and **2** toward fluoride ion.

3.2. UV–Vis titration

The molecular interaction of **1** and **2** with all the anions under investigation were studied using UV–Vis spectral changes and the results are depicted in (Fig. 2). The electronic spectrum of receptor

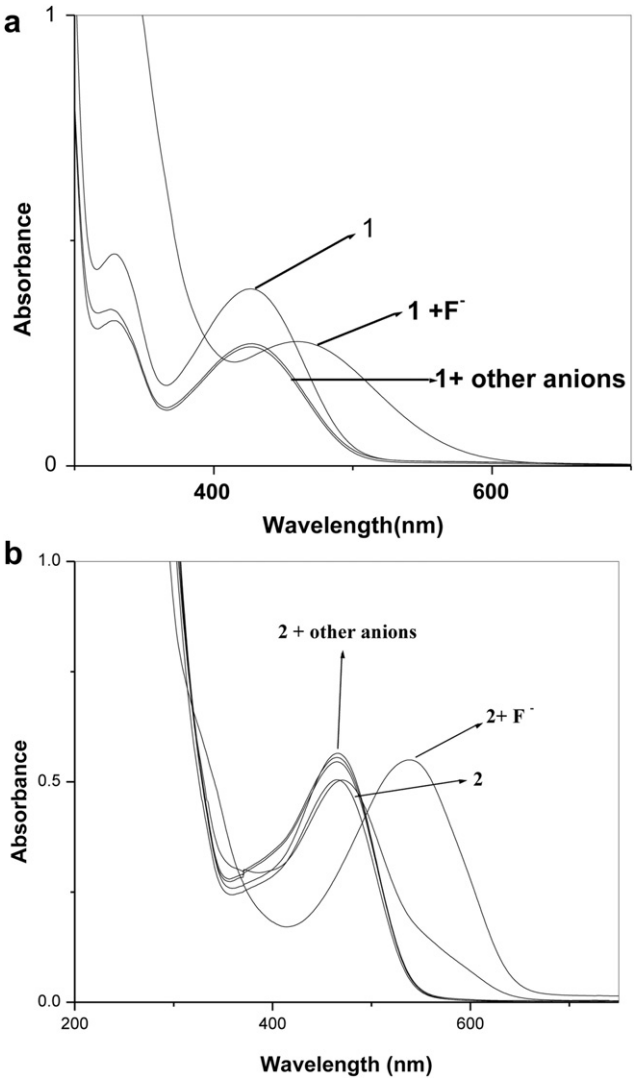


Fig. 2. Changes of UV–Vis spectra of receptor **1** (a) and **2** (b) upon the addition of 1 equiv. of F^- and other anions.

1 (Fig. 2a) exhibited maximum absorbance at 428 nm (log $\varepsilon = 4.39$) in ACN. As evidenced from Fig. 3a, addition of anions such as Cl^-, Br^-, I^-, $H_2PO_4^-$, AcO^-, NO_3^- and CN^- did not produce any significant change in λ_{max}. However, addition of F^- ions bathochromically shifts the λ_{max} to 476 nm with an instantaneous formation of red color. Likewise receptor **2** also selectively senses F^- ions with a formation of red color and a concurrent shift it λ_{max} from 468 nm (log $\varepsilon = 4.48$) to 540 nm in ACN/water (Fig. 2b). With the addition of incremental amounts of F^- ions to the solution of **1**, the absorption peak at 428 nm diminished gradually accompanying the formation of a new band at 476 nm (Fig. 3a.). This new band is due to ICT between the receptor (>NH···F^-) and signaling (quinone) units

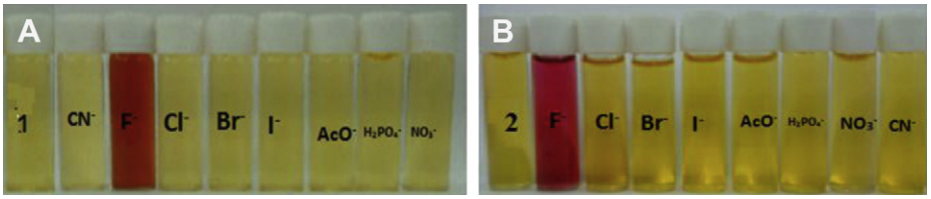


Fig. 1. Color changes upon addition of (1.875×10^{-3} M) of various anions in (1.25×10^{-5} M) ACN solution of receptor **1** (A) and **2** (B).

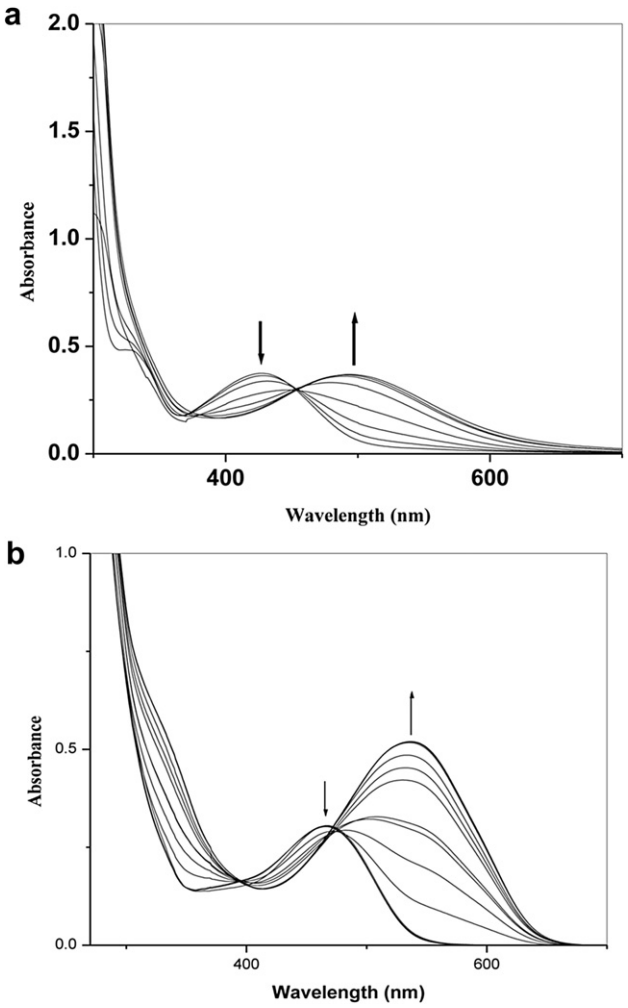


Fig. 3. Change in UV–Vis spectra for (a) receptor **1** (1.25×10^{-5} M) in ACN upon the addition of (0.187×10^{-4} M–1.875×10^{-4} M) of fluoride ion, (b) receptor **2** (1.25×10^{-5}) in ACN/water (9:1) upon the addition of (7.5×10^{-7} M–2.25×10^{-5} M) of fluoride ion. No further change was observed on addition of even higher concentration of fluoride ion.

[27]. The isobetic point (at 455 nm) indicated that there exists only one type of receptor–fluoride complex formation [27]. Parallel to this observation, with the addition of incremental amount of F^- ions to the ACN/water solution of **2**, the absorption of the band at 468 nm (λ_{max}) diminished gradually and that of the new band at 540 nm increased gradually (Fig. 3b) with a clear isobetic point at 477 nm. The association constant of receptor-F^- ion complex, in both the cases, has been estimated using the Scott equation [33]. In both the cases the Scott plot is linear (Fig. 2S) and the association constants were found to be 1.14×10^5 and 4.09×10^6 M^{-1} for the receptors **1** and **2**, respectively. The relatively higher values for the receptor **2** may be due to the fact that in this case the signaling unit (electron deficient quinone) is directly attached to the receptor unit. The observed magnitude of the association constant is higher than that reported for similar thiourea based receptor [10].

3.3. Fluorescence study

The association constants for the receptor-F^- ion complex formation were also determined by a fluorescence study. The fluorescence responses of the interaction of **1** and **2** with F^- ions were recorded with an excitation at 428 and 468 nm, respectively. The emission maximum for the receptors **1** and **2** is 560 and 580 nm, respectively (Fig. 4a and b). It is evident from the figures that, in both the cases, with the addition of incremental amount of F^- ions to the receptors, the emission intensity decreased gradually. From the decrease in the emission intensity the association constant of the receptor-F^- ion complex was calculated using the following equation [34].

$$\log_{10}(F_o - F)/F = \log K_A + n \log_{10}[Q]$$

where, F_o is emission intensity in the absence of quencher (Fluoride ion) (Q), F is the emission intensity at quencher concentration [Q], K_A is the binding constant for the receptors (**1** and **2**) with the F^- ion complex. In the present study, a plot of $\log_{10}$ (F_o–F)/F versus $\log_{10}$ [Q] is linear in both cases (Fig. 3S). The association constants thus computed were 6.3×10^8 and 7.7×10^{15} mol^{-1} L for the receptor **1** and **2**, respectively. The results of fluorescence study also indicated that the association of receptor **2** with F^- ion is relatively stronger than that in the case of receptor **1**.

3.4. Job's plot

The Job's continuous variation method [27] has been used to determine the stoichiometry of the interaction between the receptors (**1** and **2**) and F^- ions. The results are depicted in (Fig. 5a

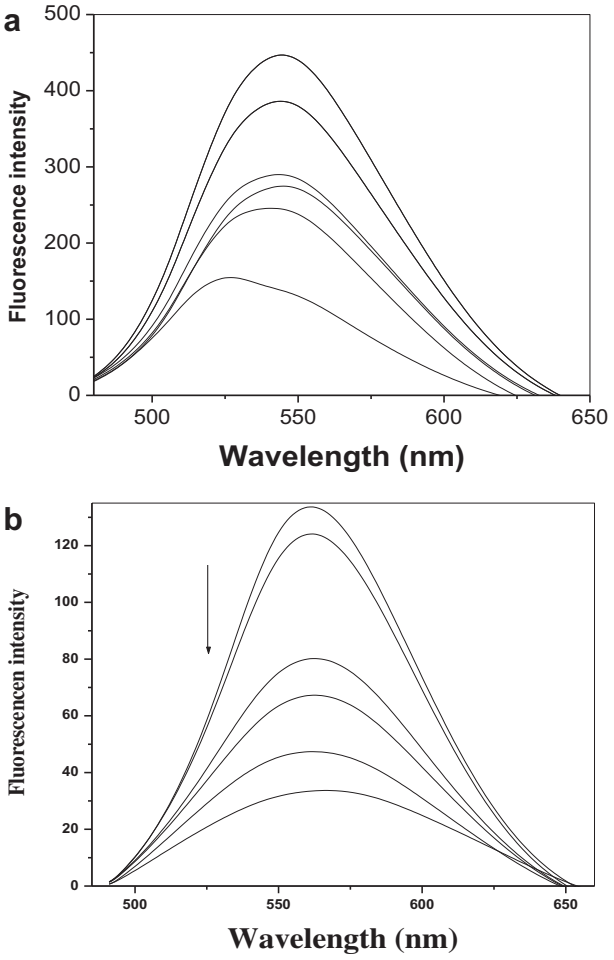


Fig. 4. Change in fluorescence emission spectra for (a) receptor **1** (1.25×10^{-5} M), (b) receptor **2** (1.25×10^{-5} M) in ACN upon the addition of TBAF in ACN from 0 to 0.875×10^{-6} M.

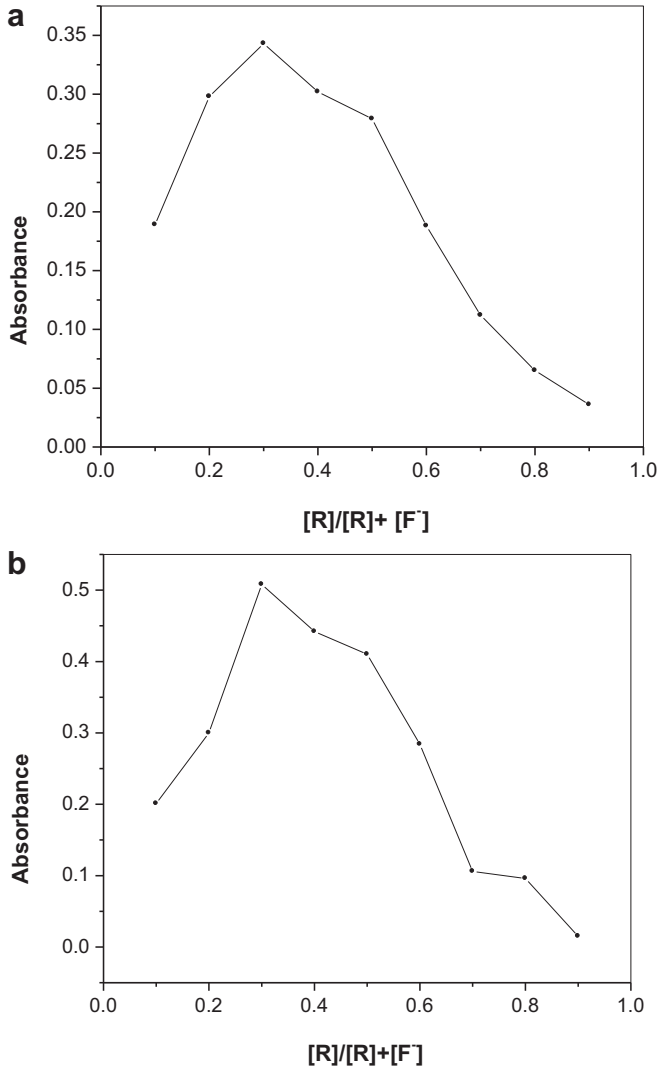


Fig. 5. The stoichiometry analysis of **1** (a) and **2** (b) with F^-.

and b). In both the cases, the curve with a maximum at 0.3 mol fraction, indicated the formation of 1:2 (receptor:F^-) complex.

3.5. ^1H NMR titration

The mechanism of binding of F^- ions with the receptor **1** and **2** has been studied using the ^1H NMR titration experiment in DMSO-d_6. The results of this study are shown in (Figs. 6 and 7), respectively, for the receptors **1** and **2**. In the case of pure receptors, ^1H-NMR chemical shift, for NH protons were observed at δ 11.7 and 12.0 ppm (For **1**) and at δ 12.0 and 13.3 ppm (For **2**). In both the cases, after the addition of 0.1 equivalents of F^- ions to the receptor, the characteristic NH signal becomes broad. In the case of receptor **1**, fluoride ion causes shielding of NH protons while in the case of **2** deshielding of NH protons occurs. This is due to the fact that complexation of F^- ions with the receptors through the H-bonding [27]. It is also interesting to note that, in the case of receptor **2**, the NH protons which are directly attached to the signaling unit (quinone) are relatively more acidic (δ 13.3 ppm). When compared to that in the other receptor. Such an N–H moiety would behave as a better receptor unit and consequently binds relatively stronger with F^- ions leading to a higher association constant for the

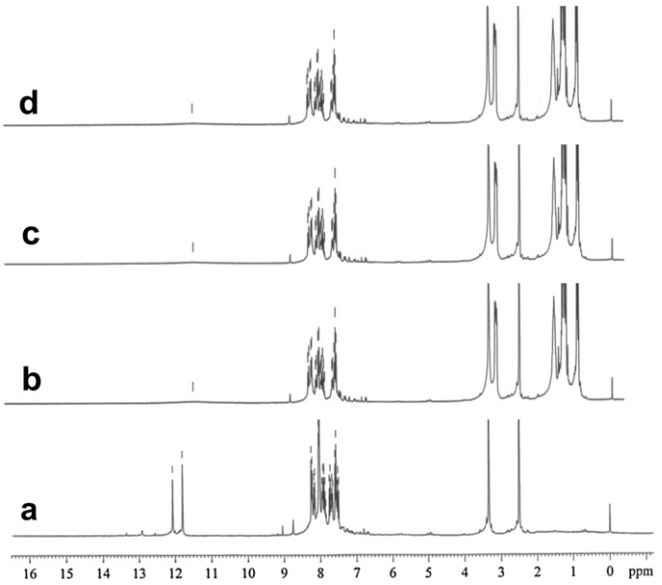


Fig. 6. Change in partial ^1H NMR (300 MHz) spectra of (a) receptor **1** in DMSO-D_6; (b) receptor **1** + 0.1 equiv. F^-; (c) receptor **1** + 0.2 equiv. F^-; (d) receptor **1** + 0.3 equiv. F^-.

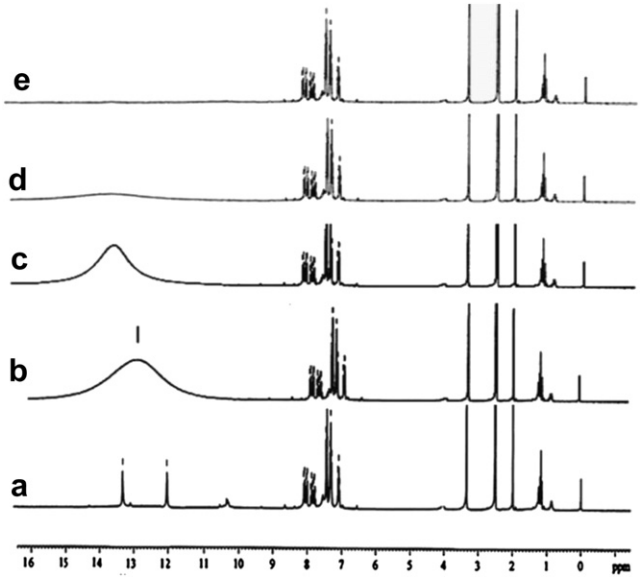


Fig. 7. Change in partial ^1H NMR (300 MHz) spectra of (a) receptor **2** in DMSO-D_6; (b) receptor **2** + 0.1 equiv. F^-; (c) receptor **2** + 0.2 equiv. F^-; (d) receptor **2** + 0.3 equiv. F^-; (e) receptor **2** + 0.4 equiv. F^-.

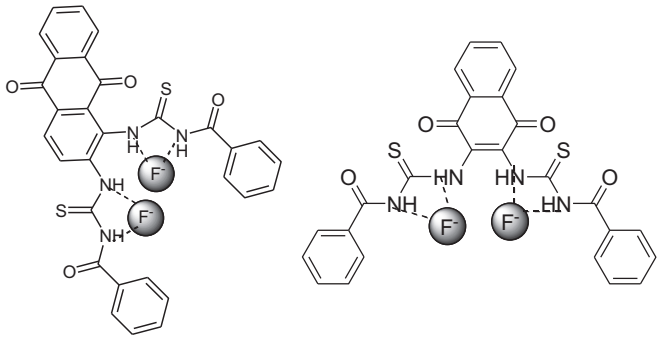


Fig. 8. The possible structure of the complex formed between sensors **1** and **2** with F^- ion.

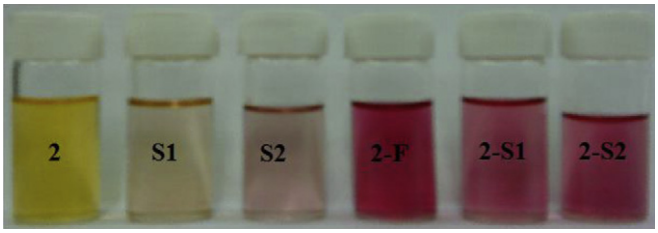


Fig. 9. From left to right: receptor **2**, S1 and S2 are toothpaste solution in water, 2 + S1, 2 + S2.

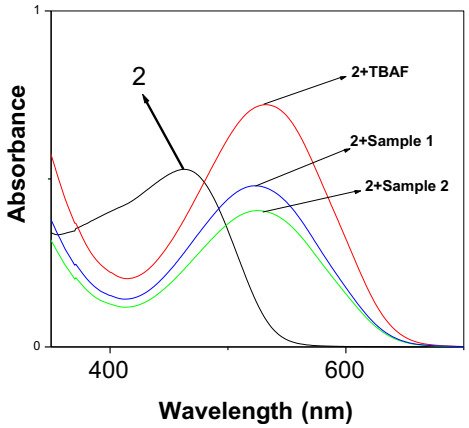


Fig. 10. UV–Vis spectrum of receptor **2** (2.50×10^{-5} M), **2** + TBAF, **2** + Sample 1 (**S1**), **2** + sample 2 (**S2**).

receptor-F^- ion complex and corroborates the trend observed from UV–Vis and fluorescence studies.

Based on the foregoing results and discussion it is evident that the receptors **1** and **2** form 1:2 (receptor:F^-) complex via H-bonding as shown in (Fig. 8).

4. Practical application

With an aim to investigate the real time application of these receptors, an attempt was made to qualitatively detect F^- ions in toothpaste. For this, 200 mg each of two commercially available toothpastes (sample **S1** and **S2** belonging to different companies) were dissolved in water and filtered. Then 0.1 mL of the filtrate was added separately to ACN solution of both **1** and **2** (1.25×10^{-5} M). The results are shown in (Fig. 9). The results indicated that addition of the toothpaste samples instantaneously produced a red color with receptor **2**. However, receptor **1** failed to impart any color change which may be due to the addition of water [35]. Qualitative analysis of the toothpaste samples was also studied using UV–Vis spectroscopy (Fig. 10). The results are in line with that discussed earlier (with F^- ion solution).

5. Theoretical study

The foregoing discussion indicated that the receptors **1** and **2** selectively sense fluoride ions through H-bond formation between the thiourea N–H and F^- ion. To elaborate upon the mechanism of recognition abilities of **1** and **2** toward F^- ions are have investigated the structural and electronic properties, of the receptors and their complexes with F^- ions were investigated using *ab initio* Density Functional Theory (DFT) calculations as implemented in the

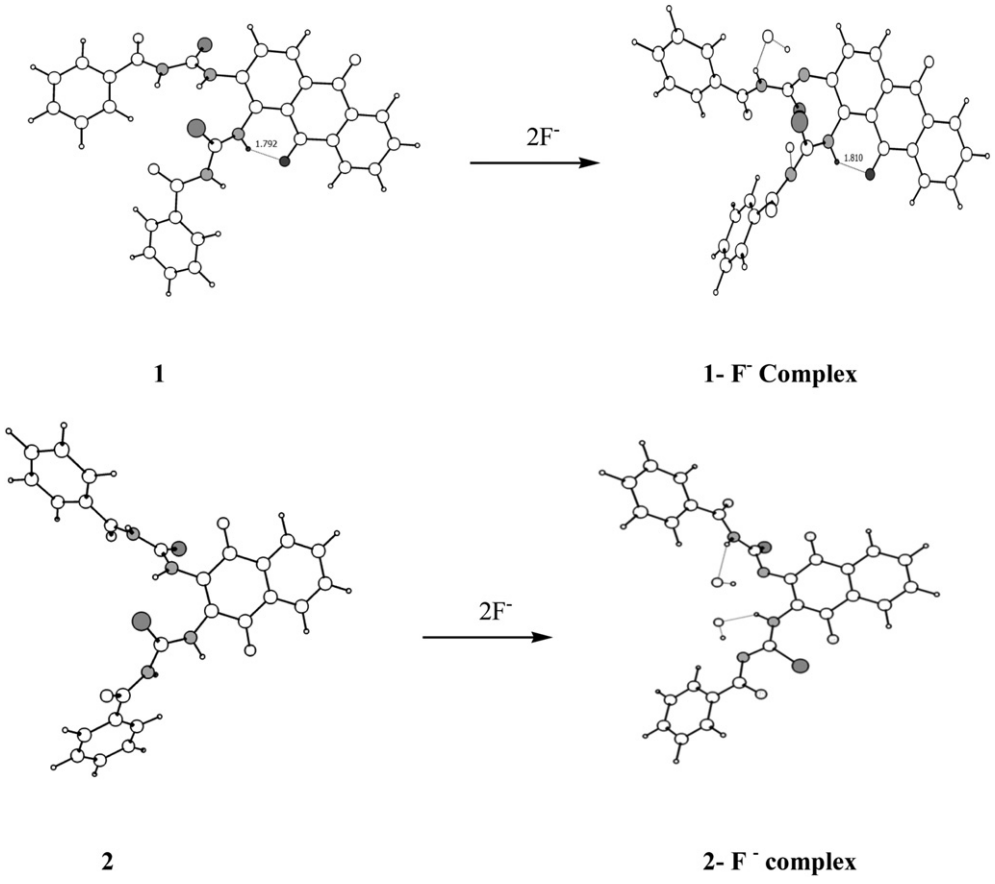


Fig. 11. Optimized structure of receptor **1**, **2** and receptor-F^- complex.

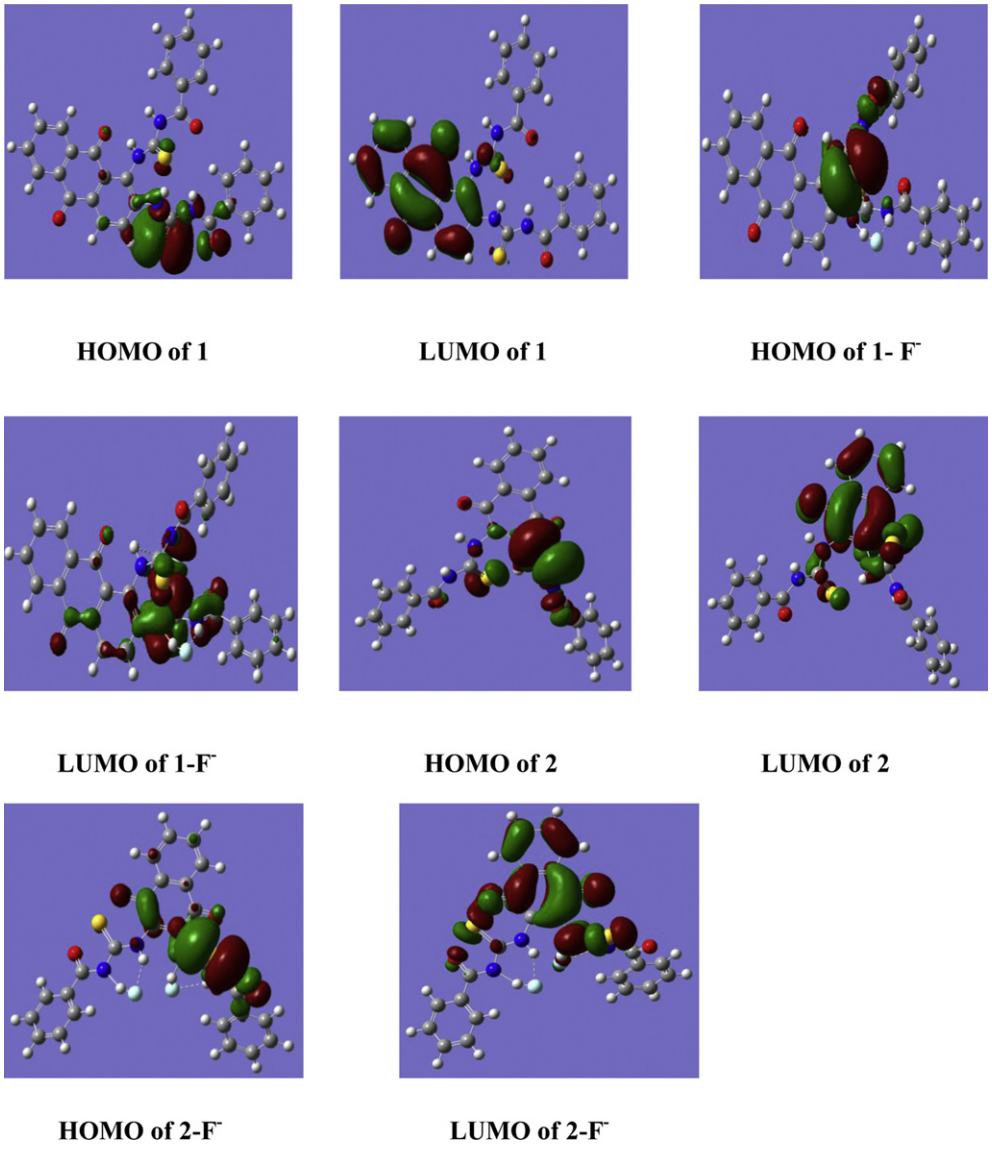


Fig. 12. HOMO-LUMO orbitals of the receptor and receptor-F^- complex.

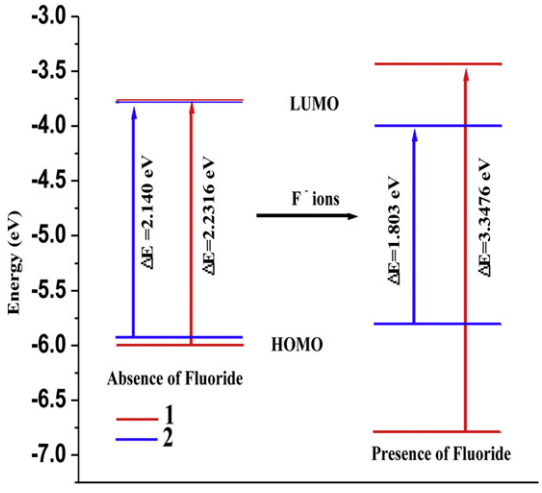


Fig. 13. Energy level diagram of HOMO and LUMO orbitals of receptor **1** and **2** and receptors-F^- complex.

Gaussian 03 package [36]. DFT calculations with Becker's three parameterized Lee-Yang-Par (B3LYP) exchange functional with 6311G basis sets were carried out for the geometry optimizations. All of the DFT optimized geometries are shown in Fig. 11. The relevant frontier molecular orbitals of the receptor and their complexes with F^- ions are shown in Fig. 12. The bond lengths and the Mulliken charges on selected atoms of **1** and **2** and their complexes with F^- ions are collected in Tables S1 and S2 (Supplementary data).

As shown in Fig. 12, the HOMO distribution of **1** is concentrated on the N–H moiety of one of the thiourea arms. The LUMO, as expected, is concentrated on the quinone ring. The HOMO to LUMO excitation is responsible for ICT observed at 428 nm in the electronic spectrum of **1**. In the case of **1**-F^- complex the LUMO is delocalized over the thiourea moiety but not on the quinone as in free **1**. Hence, after the formation of H-bond with F^- ions, the HOMO-LUMO energy gap is increased ($\Delta E = 3.3476$ eV, Fig. 13) and when compared to that in the free receptor **2** ($\Delta E = 2.2316$ eV). The delocalization of both HOMO and LUMO over the N–H moiety in the **1**-F^- complex might have caused the up field shift of N–H protons in the ^{1}H NMR spectrum. Also, the existence of a strong

H-bond (1.792 Å) between H_7 of the thiourea N–H and O_1 of the quinone carbonyl group (Fig. 11) might also have contributed to the increase in ΔE value after the addition of F^- ions to **1**. This may be due to the fact that F^- ions have to expend energy to overcome the $H_7\cdots O_1$ H-bonding to form $H_7\cdots F^-$ H-bond in other words this is the energy required for the structural reorganization to form the **1**-F^- complex. This is supported by the weakening of $H_7\cdots O_1$ H-bond (1.810 Å) in the **1**-F^- complex.

In the case of receptor **2**, the HOMO is concentrated on the N–H moiety and the LUMO is concentrated on the quinone ring. The ICT transition exhibited on free **2** (at 468 nm) in the electronic spectrum is due to the HOMO to LUMO excitation. The energy gap (ΔE) between these two frontier molecular orbital is 2.140 eV which is slightly less than that in **1** and hence the ICT transition occurs at a relatively higher wavelength in **2** than in **1**. This difference in wavelength (40 nm) may be due to the fact that, in the case of **2**, the receptor unit (N–H) is directly attached to the signaling unit (quinone) thus favoring relatively easy ICT. In contrast to receptor **1**, in the case of the **2**-F^- complex the LUMO is concentrated on the quinone ring and of course the HOMO resides dominantly on the N–H moiety. This in the case of receptor **2**, addition of F^- ions to the N–H moiety through H-bonding decreased the HOMO–LUMO energy gap (ΔE = 1.803 eV, Fig. 13) (makes $N-H\cdots F^-$ moiety a better donor) and red shifted the ICT to 540 nm ($\Delta\lambda_{ICT} = 72$ nm) and consequently makes the colorimetric recognition of F^- ions energetically easier. Such an observed large red shift in λ_{ICT}, after complexation with F^- ions renders the compound **2**, a novel receptor wherein the receptor unit is directly attached to the signaling unit.

Furthermore, in both the receptor **1** and **2**, the Mulliken charge on the four NHs increased significantly after complexation with fluoride ions indicating formation of $N-H\cdots F^-$ H-bond. This is because F^- ions will abstract the H-atom of the N–H moiety as H^+ to form the H-bond. This fact is well supported by the results of ^1H NMR titration experiments. Interestingly it is observed that the results of the theoretical study corroborate well with the experimental findings.

6. Conclusion

We have designed, synthesized and characterized two new thiourea based sensors for fluoride ions with different signaling units. The results of UV–Vis, fluorescence and ^1H NMR studies indicated that the receptors **1** and **2** showed high selectivity for fluoride ion detection over other anions such as Cl^-, Br^-, I^-, OAc^-, NO_3^-, $H_2PO_4^-$, and CN^-. As the receptor **2** possesses a highly electron deficient signaling unit directly attached to the receptor unit with enhanced F^- ion sensing, it works well for the selective sensing of F^- ions in an aqueous medium. Hence it is no doubt that the receptor **2** is novel. The results obtained from the *ab initio* DFT calculations agree well with the experimental observations. At the same time, the practical application of this receptor was demonstrated by the visual selective detection of fluoride ion in toothpaste samples.

Appendix A. Supplementary material

Supplementary data (characterization data and ^1H and ^{13}C NMR, spectra of all the products) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.dyepig.2012.08.014.

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