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A coumarin based ICT probe for fluoride in aqueous medium with its real application

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ABSTRACT

A new coumarin based hydrazone (receptor 1) synthesized by modifying one of our earlier reported receptor detected fluoride ion selectively through naked eye in aq. DMSO (5:95, v/v). It was also able to detect fluoride through naked eye in a toothpaste sample. The addition of 1 equiv. of fluoride as its tetrabutylammonium salt to the 5×10^{-5} M aq. DMSO solution of the receptor 1 produced red color while the similar addition of acetate produced faint pink color. The dihydrogenphosphate and a variety of other anions were not able to produce any significant color change with receptor 1 under similar experimental conditions. The corresponding UV–vis measurements showed a bathochromic shifting of 455 nm band of receptor 1 to 514 and 484 nm for fluoride and acetate, respectively. The non-linear fittings of corresponding UV–vis titration data in 1:1 binding equation yielded association constants in 10^5:1 ratio for fluoride and acetate, respectively. The ^{1}H NMR titrations studies shade further light on their mode of binding with receptor 1. The quantum mechanical calculations through time dependant density functional theory (TD-DFT) using basis set b3lyp/6-311g** supported our experimental findings nicely.

1. Introduction

Anions play a variety of roles in living systems in the form of various chemical transformations [1–5]. At the same time, they are also relevant for many industrial processes and are often found as harmful pollutants [6]. The recognition and sensing of anionic analytes have emerged as a key research theme within the generalized area of supramolecular chemistry for last few decades [7–11]. Among the chemosensors the naked eye ones have an edge over others in view of their cost effectiveness and easy handling [9,12]. Among the entire range of biologically important anions fluoride and acetate are useful in many biochemical reactions with particular role of fluoride in preventing dental caries [13] as well as treatment for osteoporosis [14,15]. However, excess of fluoride can lead to fluorosis [16–18] also, which is a type of fluoride toxicity that generally manifests itself clinically in terms of increase in bone density. Besides its biological role, fluoride is also known as a very strong Lewis base and is a good potential catalyst for a number of inorganic and organic synthesis [19–23]. This diversity of its function, both beneficial and otherwise, makes its detection important. The biggest bottleneck in developing the naked eye receptor for the fluoride is interference by acetate and other anions of comparative basicity. The present chemoreceptor being reported through this communication is a simple structural modification of one of our earlier report [24]. This modification was beneficial in two ways: first of all this was able to introduce selectivity in to the receptor 1 towards the fluoride over acetate through naked eye, at the same time this lead further tolerance of 5–10% water in the experimental medium during naked eye sensing while it was nil in our earlier report.

Barring a few [25] most of the hydrazone based receptors reported in literature showed their sensitivity towards anions through acid–base reaction and act as an indicator rather than sensor [24,26] hence lacking specificity. Furthermore, on binding with anions they do not show shifting of ICT in terms of λ_{max}, i.e. bathochromic or hypsochromic shift. They involve only hyper or hypochromic shifts which are due to completion of the acid–base equillibria to different extent for different anion. Hence, such types of receptors undergo modulation of their ICT by anionic analyte in terms of only intensity (ε_{max}) of the ICT. Hence, they are not considered to be a good receptor until and unless the intensity change is very high. The hydrazone based anion colorimetric receptors where hydrogen bonding plays the key role towards sensing are the rare ones. The previous version of receptor 1 lacked specificity and was not able to differentiate among the anions of higher basicity. Hence, we thought it worthwhile to modify our earlier report by introducing a pendant arm of N,N-diethylamino group over the coumarin moiety, so that the new receptor may be able to

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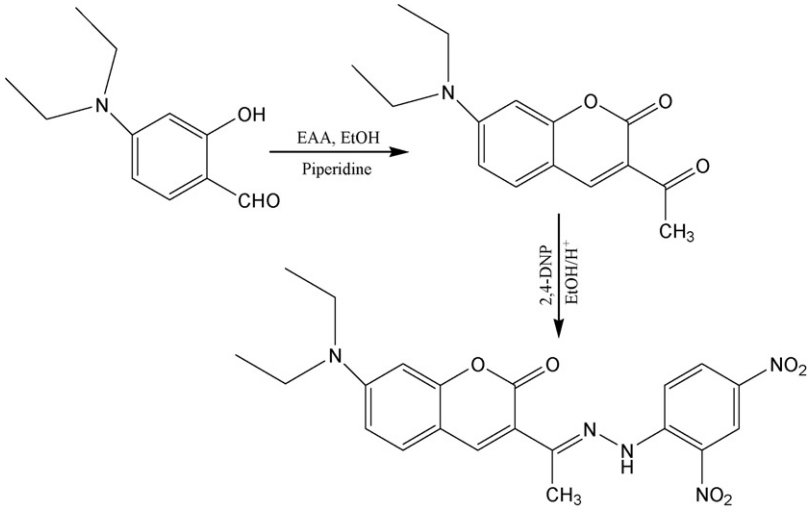


Scheme 1. Synthesis of receptor 1.

discriminate between anions of high and comparable basicity like fluoride and acetate. Our strategy really worked because receptor 1 produced not only naked eye discrimination between fluoride and acetate but it was able to differentiate them in terms of λ_{max} also by a margin of 30 nm, which is a kind of rare observation. The hydrogen donor ability of the receptor 1 towards fluoride and acetate has been well established through corresponding ^{1}H NMR titrations. The details of anion binding characteristics of the receptor 1 have been investigated by UV–vis, and ^{1}H NMR titrations along with quantum mechanical calculations at the level of density functional theory (DFT).

2. Experimental

2.1. Apparatus

^{1}H and ^{13}C NMR studies were performed on a JEOL AL 300 FT NMR and Bruker-400 Avance NMR Spectrometer using TMS as internal reference standard. ESI-MS was carried out on a MDS Sciex API 2000 LCMS spectrometer. C, H and N elemental analysis were done on Model CE-440 CHN analyzer. UV–vis spectra were recorded on a UV-1700 Pharmaspec spectrophotometer with quartz cuvette (path length = 1 cm) at 298 K.

2.2. Materials

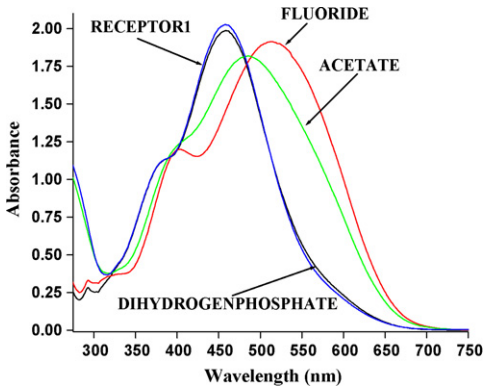
All reagents for synthesis were purchased from Sigma–Aldrich Pvt. Ltd. and were used without further purification. The DMSO of spectroscopic grade was purchased from Spectrochem Pvt. Ltd., Mumbai, India and was used for the preparation of solutions in the UV–vis titrations. The anions as their tetrabutylammonium salts were purchased from Sigma–Aldrich Pvt. Ltd.

2.3. General method

All UV–vis titration experiments were carried out at room temperature. To the 5×10^{-5} M aq. DMSO solution of the receptor, the varying equivalents of the anions were added separately and spectra were recorded. Similar studies were performed in dry DMSO also. Titration plots were generated by using Origin (Microcal software). The ^{1}H NMR titrations were carried out in DMSO-d_6 using TMS as an internal reference standard. To the 5×10^{-3} M solution of the receptor in DMSO-d_6 the varying equivalents of acetate as its tetrabutylammonium salt were added and the ^{1}H NMR spectra recorded after each addition.

2.4. Synthesis of receptor 1

N,N-diethyl-7-aminocoumarin-3-yl methyl ketone-2,4-dinitrophenylhydrazone, i.e. receptor 1 was synthesized by adding 2.0 m molar ethanolic solution of 2,4-dinitrophenylhydrazine to the equimolar ethanolic solution of N,N-diethyl-7-amino-3-acetylcoumarin having one drop of HCl followed by constant stirring (Scheme 1). The stirring of the reaction mixture was further continued for ~2 h with mild heating (~60 °C). A dark



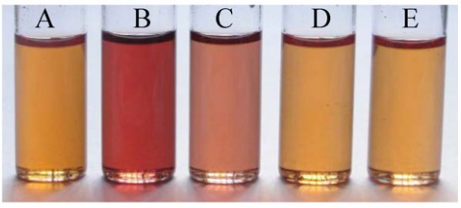


Fig. 1. Absorption spectra of receptor 1 (5×10^{-5} M) upon addition of 1 equiv. of tetrabutylammonium fluoride, acetate, dihydrogenphosphate in aqueous DMSO (water:DMSO, 5:95, v/v) and corresponding color changes (A) free receptor, (B) fluoride, (C) acetate, (D) dihydrogenphosphate and (E) all other anions.

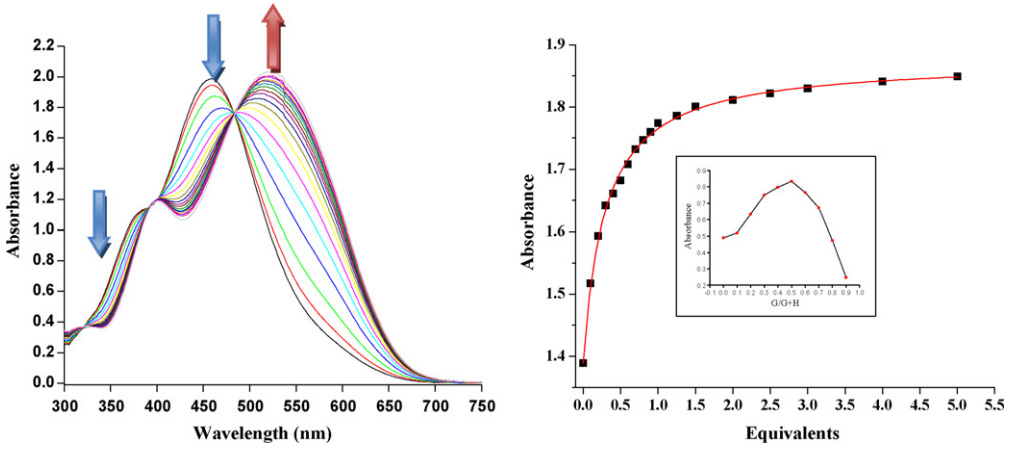


Fig. 2. UV–vis titration pattern of receptor 1 (5×10^{-5}) in aq. DMSO on addition of varying equivalent of fluoride ion as tetrabutylammonium salt. The corresponding binding curve and Job's plot (inset).

red colored solid was precipitated which was filtered followed by its washing with ethanol–water mixture (50%, v/v) and finally dried under vacuum over anhydrous $CaCl_2$. The crude product was recrystallized by methanol–water mixture (50:50, v/v). N,N-diethyl-7-amino-3-acetylcoumarin was synthesized by reported method [27]. Receptor 1 was characterized through IR, ^{1}H and ^{13}C NMR spectral studies along with mass determination through ESI-MS as well as CHN analysis (ESI, Figs. S1–S4). Yield ~90%. IR/cm^{-1}: 3422, 3289, 3110, 2980, 2928, 1713, 1614, 1513, 1421, 1334, 1268, 1222 1190, 1137, 839; ^{1}H NMR (300 MZH, $CDCl_3$, 298 K, TMS): δ 11.36 (s, 1H, HN-), 9.17 (d, 1H, H-Ar), 8.36 (m, 1H, H-Ar), 8.07 (m, 1H, H-Ar), 7.40 (d, 1H, H-Ar), 6.64 (d, 1H, H-Ar), 6.52 (s, 1H, H-Ar), 3.49 (q, 4H, CH_2), 2.93 (s, 3H, CH_3), 1.27 (t, 6H, CH_3), ^{13}C NMR (75 MZH, $CDCl_3$, 298 K, TMS): 12.46, 15.44, 44.99, 96.94, 108.36, 109.48, 116.68, 117.73, 123.55, 129.64, 130.00, 130.09, 138.16, 142.50, 144.73, 151.64, 152.19, 157.22. ESI Mass: *m/z* Calculated for $C_{21}H_{21}N_5O_6$ [M]: 439.5, found [M+H] – 440.6, CHN (%): Calculated: C = 57.40, H = 4.82, N = 15.94, O = 21.25. Found C = 57.71, H = 4.79, N = 15.49, O = 22.00.

3. Results and discussion

The anion binding abilities of the receptor 1 with F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-, BF_4^-, PF_6^-, in aq. DMSO were studied through naked eye color changes, UV–vis and ^{1}H NMR titrations. The anions tested were used as their tetrabutylammonium salts while receptor 1 was taken as its 5.0×10^{-5}M aq. DMSO solution.

3.1. UV–vis studies

The corresponding naked eye and spectral changes are presented in Fig. 1. The separate additions of 1 equiv. each of fluoride and acetate to the 5×10^{-5} M aq. DMSO solution of the receptor 1 produced red and faint pink color, respectively, while similar additions of dihydrogenphosphate, chloride, bromide, iodide, hydrogensulfate, perchlorate, tetrafluoroborate and hexafluorophosphate did not produce any significant visible change. The red color produced by fluoride was sufficiently dark enough to be discriminated from acetate through naked eye itself. The corresponding UV–vis and naked eye changes have been shown in Fig. 1.

In order to have the further details of the binding characteristics of the receptor 1 with above chosen anions we performed UV–vis titrations by adding various equivalents (0–5.0) of a particular anion to the 5×10^{-5} M in DMSO–H_2O mixture (95:5, v/v) of the receptor 1 concomitantly. The receptor 1 absorbs itself at 386 and 455 nm due to π–π^* and n–π^* transitions, respectively [28]. The separate additions of 1 equiv. of fluoride to the aq. DMSO solution of the receptor 1 modulated its absorption bands in terms of λ_{max} and ε_{max} both. The 386 and 455 nm absorption bands underwent bathochromic shifting to 411 and 514 nm, respectively. This observation was ascribed to the modulation of intramolecular charge transfer (ICT) by extension of pi-conjugation as the consequence of fluoride binding through –NH of the receptor 1. On the other hand, similar addition of acetate produced comparatively less extent of bathochromic shifting (386 → 411 and 455 → 484 nm) and only a faint pink color visibly. The four isosbestic points at 485, 392, 400 and 316 nm were observed for both the ions indicating formation of their respective common intermediates species with the receptor 1. The rest of the ions did not produce any significant observable changes. The UV–vis titrimetric analysis between receptor 1 and fluoride has been presented in Fig. 2 while that with acetate has been given in ESI (Fig. S5a). The corresponding titration data confirmed 1:1 stoichiometry with binding constants $3.60(\pm0.47) \times 10^5$ M^{-1} and 3.42653 M^{-1} for fluoride and acetate, respectively. The stoichiometry was further confirmed by Job's plot (Fig. 2, inset and ESI Fig. S7b). The above sensing studies were also done in 10:90 aq. DMSO and similar naked eye changes were observed with lesser intensity (ESI Fig. S5c).

Table 1
Association constants for the various anions towards receptor 1 in aqueous and dry DMSO.

Anions[a]	F^-	CH_3COO^-	$H_2PO_4^-$	Cl^-, Br^-, I^-, HSO_4, ClO_4^-, PF_6^-, BF_4^-
K (M^{-1})	[b]$3.60\ (\pm0.47) \times 10^5$	[b]3.42653		nd[d]
	[c]$6.41\ (\pm2.02) \times 10^6$	[c]$4.11\ (\pm0.28) \times 10^5$	[c]$1.22(\pm0.10) \times 10^4$	
R^2	[b]0.9968	[b]0.9977	0.9964	
	[c]0.9996	[c]0.9995		

[a] All the anions have been used as tetrabutylammonium salts.
[b] Binding constant determined in aqueous DMSO.
[c] Binding constant determined in DMSO.
[d] Not determined due to small spectral changes.

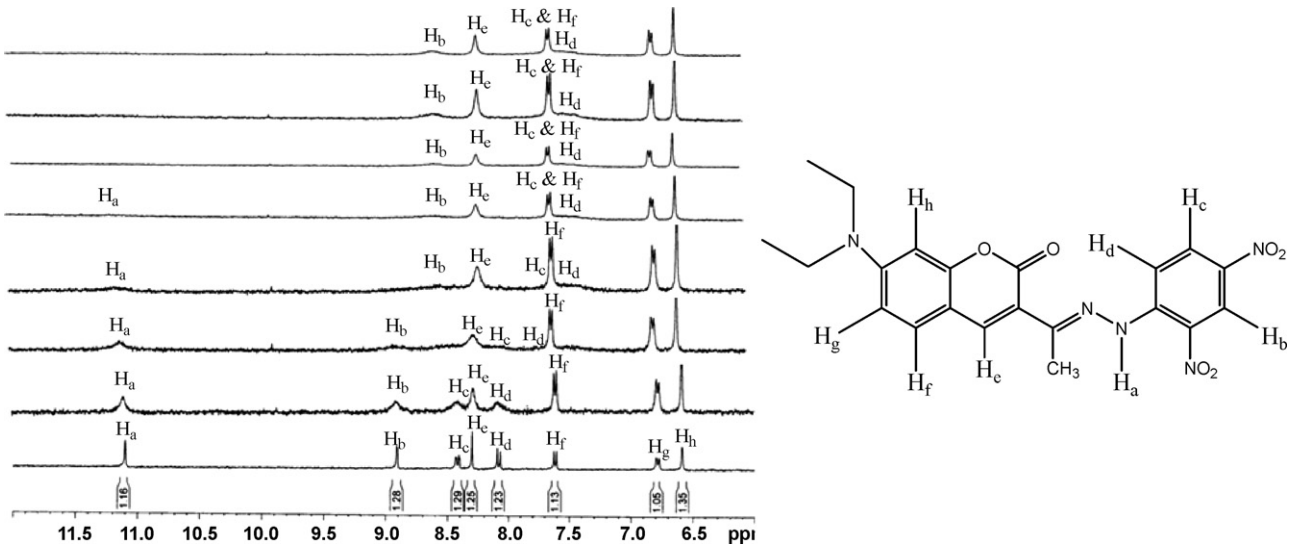


Fig. 3. Partial ^{1}H NMR spectra showing changes in receptor 1 on concomitant addition of tetrabutylammonium fluoride (from bottom to up); receptor 1; 1 + 0.20 equiv. $TBAF^-$, 1 + 0.40 equiv. $TBAF^-$, 1 + 0.60 equiv. $TBAF^-$, 1 + 0.80 equiv. $TBAF^-$, 1 + 1.00 equiv. $TBAF^-$, 1 + 1.50 equiv. $TBAF^-$, 1 + 2.00 equiv. $TBAF^-$ and corresponding numbering scheme of protons.

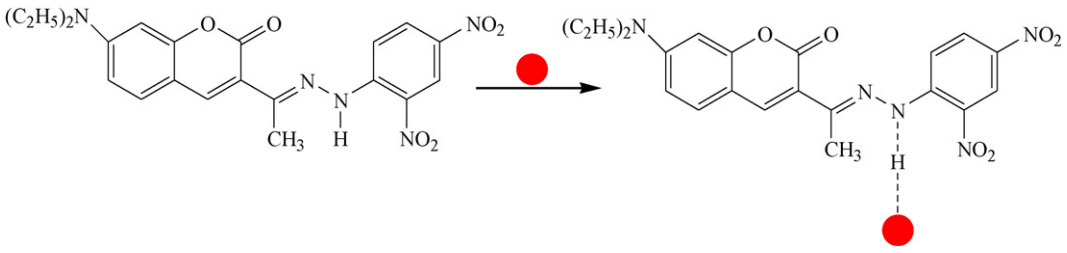


Fig. 4. A general chemical structure images for possible binding mode of receptor 1 with anions.

The corresponding studies were also performed in dry DMSO and have been given in ESI (Figs. S6 and S7). The naked eye changes were able to discriminate between fluoride and acetate but to a lesser extent than the same in aqueous DMSO. However, the binding constants for both fluoride and acetate were much higher than the same in aqueous DMSO. It is worth to mention that the corresponding difference in bathochromic shifting of the ICT for the receptor 1 between the fluoride and acetate was 18 nm as compared to 30 nm in the aq. DMSO. Hence, it may be concluded at this stage that the aq. DMSO is a better medium than dry DMSO for the naked eye discrimination between the fluoride and acetate by the receptor 1.

The corresponding binding constants for aqueous and dry DMSO (Table 1) were determined by the non-linear fitting of the respective UV–vis titration data in 1:1 binding equation as follows [29].

$$A = A_o + \frac{A_{lim} - A_o}{2C_o}\left[C_o + C_m + \frac{1}{K} - \left\{\left(C_o + C_m + \frac{1}{K}\right)^2 - (4C_oC_m)\right\}^{1/2}\right] \quad (1)$$

where A: absorbance of the solution during the titration, A_0: absorbance of the ligand, A_{lim}: absorbance of the ML complex, C_0: concentration of the ligand, C_m: concentration of the metal cation during the titration, and K: equilibrium constant of the complex formation. In this way, the equilibrium constant K can be determined by means of a non-linear least square fitting of the measured absorbance A as a function of C_m.

The large decrease (1×10^5) in the binding constant of receptor 1 with acetate on going from dry DMSO to aq. DMSO may be understood in terms of better hydrogen bonding ability of acetate with water in comparison to fluoride in the light of higher basicity of the previous over the later one (pKa, HOAc = 4.76; pKa, HF = 3.17) [30]. Water competes with receptor 1 for anions in aqueous DMSO and it prefers the acetate ions leading to less availability of the same for the receptor 1 ultimately leading to a large decrease in the binding constant value. Literature reports also indicated the higher solubility of acetate in water [31]. Hence, in aqueous DMSO the amount of acetate available to receptor 1 is less than the pure DMSO. This also may be contributing towards the

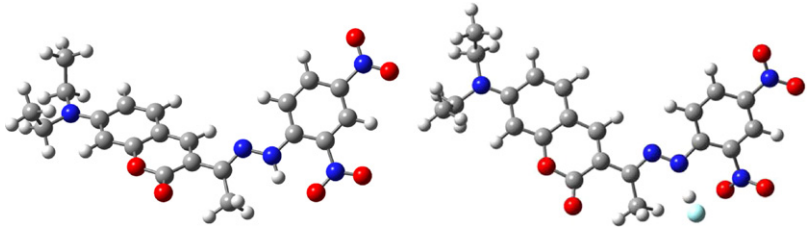


Fig. 5. Optimized structure of receptor 1 and [receptor-F^-] complex.

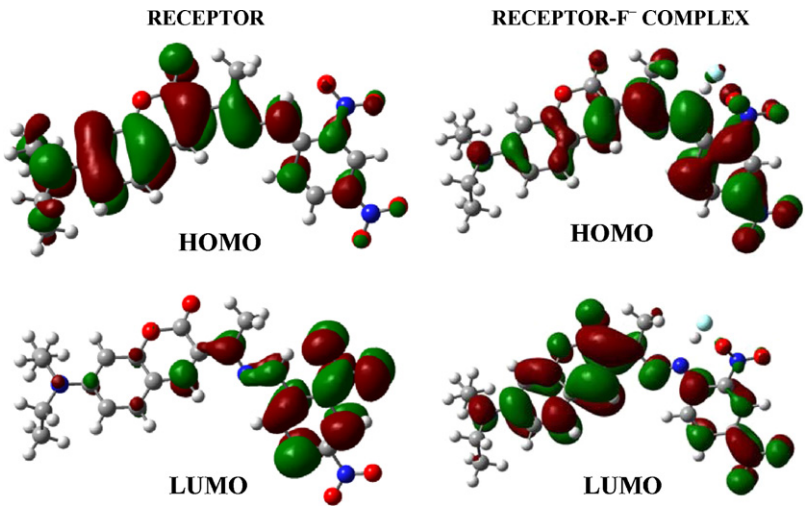


Fig. 6. HOMO–LUMO orbitals of the receptor and receptor-F^- complex.

large decrease of binding constant value for the acetate in aqueous DMSO.

3.2. ^1H NMR studies

As the visible changes were observed with only fluoride and acetate hence, ^1H NMR titrations of receptor 1 were performed with only these anions by their concomitant additions as their tetrabutylammonium salts to the 5×10^{-3} M solution of the receptor 1 in DMSO-d_6. The partial ^1H NMR spectra of the same have been given in Fig. 3 (for acetate see ESI Fig. S8). Almost similar types of changes were observed in the ^1H NMR signals of the receptor 1 with both the anions. The –NH proton showed broadening and downfield shifting with progressive additions of anions and ultimately got vanished while all the other protons of phenyl rings were upfield shifted as the result of through-bond propagation effect. This vanishing of –NH took place at 1.0 and 0.5 equiv. for fluoride and acetate, respectively, which may be understood in terms of following equilibria:

$$LH + X^- \leftrightarrow [L{\cdot}H{\cdot}X]^- \quad (1')$$

$$[L{\cdot}H{\cdot}X]^- \leftrightarrow L^- + HX \quad (2)$$

$$[L{\cdot}H{\cdot}X]^- + X^- \leftrightarrow L^- + [HX_2]^- \quad (3)$$

The ^1H NMR titration pattern for acetate indicated involvement of equilibria 1 and 2 during its recognition process by the receptor 1 while same with fluoride involved all the three equilibria. Hence, consuming twice equivalents of fluoride in comparison to acetate. Although we did not observe any signal for $[HF_2]^-$ in its ^1H NMR spectral titrations even up to δ 20 ppm probably due to its instability in highly polar solvents like DMSO [32].

Based on above observation following chemical structure images may be given for possible binding mode of receptor 1 with anions (Fig. 4).

3.3. Density functional theory (DFT) studies

The mechanism of the recognition process by receptor 1 and corresponding changes in its UV–vis absorption spectra were correlated with electronic ground and exited states of the same through time dependent density functional theory (TD-DFT) calculations using b3lyp/6-311g** basis set within the Gaussian 03 programs [33]. The optimized geometry of the receptor 1 and its F^- complex have been given in Fig. 5.

The receptor itself absorbed in the form of a broad band centered at 455 nm with its full width at half maximum (fwhm) ~114 nm leading to the range of the same band 397–512 nm. The computed electronic transitions of two lowest energies for the receptor 1 were 489 nm and 433 nm due (HOMO-LUMO) and (HOMO-LUMO + 1), respectively. Hence, the UV–vis absorption at 455 nm may be taken as the envelop band incorporating these two transitions. The receptor-F^- complex absorbs at 514 nm with its full width at half maximum (fwhm) ~154 nm hence ranging in 430–600 nm. The corresponding computed electronic transitions were obtained at 556, 478 and 414 nm, respectively, involving a full range of transitions like HOMO–LUMO, HOMO–LUMO+1 and HOMO–LUMO+2 transitions, etc. (ESI, Table S9).

As it can be seen, the HOMO and LUMO of the receptor 1 are highly polarized since they are prominently localized on the coumarin and dinitrophenyl (DNP) moieties, respectively (Fig. 6). The binding of fluoride with receptor 1 makes them apolar due to homogenization of electron density through extended pi-conjugation. In other words the binding of fluoride introduces a high extent of planarity into the receptor 1 which leads to the homogeneous distribution of electron density throughout. This phenomenon has been well documented in the literature as planar intramolecular charge transfer (PICT). The ^1H NMR studies also indicate similar type of electron density changes across the receptor 1 in form of up field shifting of the signals and merging of a few of them.

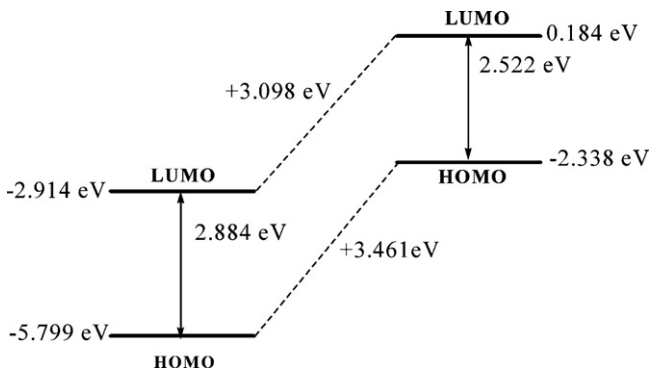


Fig. 7. Energy level diagrams of HOMO and LUMO orbitals of receptor 1 and receptor-F complex calculated on the DFT level using a b3lyp/6-311g** basis set.

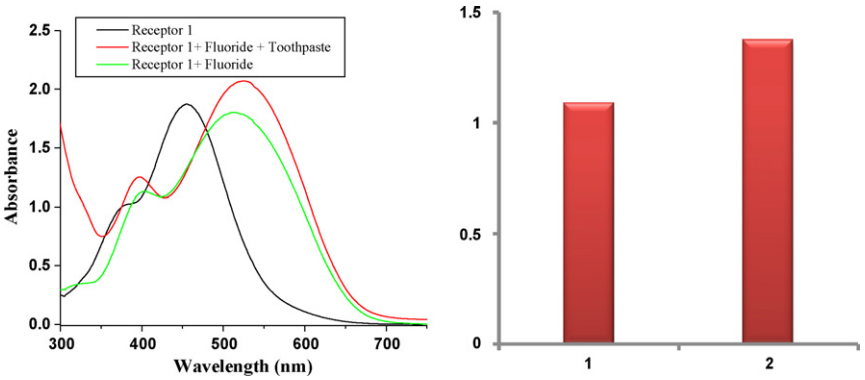


Fig. 8. (a) UV–vis spectra of receptor 1and in the presence $1 + F^-$; $1 + F^-$ + toothpaste. (b) The proof of concept for fluoride detection in toothpaste. (1) $1 + F^-$; (2) $1 + F^-$ + toothpaste ($\Delta A = A_{host} + A_{guest} - A_{host\ only}$).

The bathochromic shifting in the 455 nm band of the receptor 1 on its binding with fluoride may further be understood in terms of raising of the potential energy of its HOMO and LUMO. As it can be seen in Fig. 7 that energy gap between HOMO and LUMO of receptor 1 decreases on its binding with fluoride. As we have pointed out above that out of HOMO and LUMO the later one is the electron deficient hence, fluoride will prefer it more rather than the coumarin moiety. Hence, on binding with fluoride the potential energy of the LUMO is raised to comparatively lesser extent than that of the HOMO, which is less preferred by fluoride. This ultimately leads to narrowing of the energy gap between HOMO and LUMO, which is ultimately responsible for the bathochromic shifting of the 455 nm band on its binding with fluoride.

4. Practical application

As all the commercial toothpastes contain fluoride as an essential constituent for dental hygiene, hence it was thought worthwhile to apply the receptor 1 for the determination of same in a toothpaste sample. For this purpose, a small amount of the toothpaste was mixed with 5×10^{-5} M aq. DMSO solution of the receptor 1, which lead to similar color change and almost same UV–vis spectral changes as we observed for the fluoride as its tetrabutylammonium salt. The outcome of UV–vis spectral scanning for the $1 + F^-$ + toothpaste have been given in Fig. 8(a) and (b). The Fig. 8(b) clearly showed a rise in the intensity of 515 nm band for receptor $1 + F^-$ on addition of toothpaste sample. Thus the receptor 1 did not discriminate between the source of fluoride be it tetrabutylammonium fluoride or a toothpaste having fluoride.

5. Conclusion

Thus, we were able to synthesize receptor 1 by a simple modification of our earlier report. At the same time, we were also successful in demonstrating the practical application of this receptor in the naked eye selective recognition of fluoride as its tetrabutylammonium salt as well as in a toothpaste sample with lowest naked eye detection limit of 5×10^{-6} M. Although the receptor 1 also recognizes the acetate ion but this will not interfere in its recognition process towards fluoride because there is a much difference of naked eye appearance between them as well as a margin of 30 nm in their UV–vis spectrophotometric recognition. The tolerance of 5–10% water in the experimental medium along with DMSO is a good sign towards the biological applications of such type of systems in future. The further substitution studies over receptor 1 towards increasing its water tolerance limit is in progress in our laboratory.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2010.04.041.

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