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Rationally designed tri-armed imidazole-indole hybrids as naked eye receptors for fluoride ion sensing

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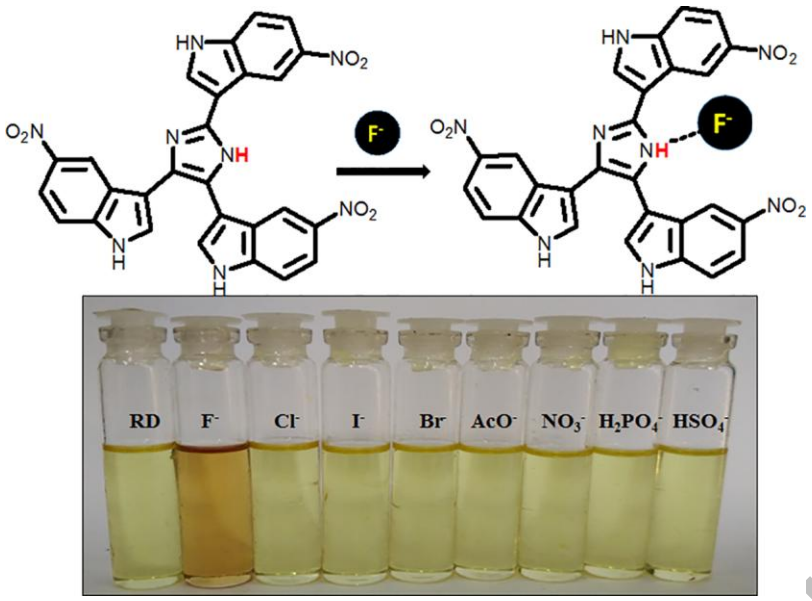
Abstract

The present communication describes the design, synthesis and characterization of unique tri-armed imidazole-indole hybrids **RA**-**RE** for naked eye detection of fluoride ion in 9:1 DMSO-water at concentration level of 1.5 ppm, which is recommended permissible limit of fluoride ion. Molecular structures of the receptors are so fabricated that both heterocyclic units, *viz.*, indole and imidazole have been rationally employed as chromophore and binding unit, respectively. Strategical introduction of nitro group(s) at the 5th position of indole ring remarkably enhances the binding ability of receptor **RD** making it highly selective towards fluoride ion (tetrabutylammonium salt) over other typical anionic species. The sensing event can be visualized by naked eyes swiftly with colour change. This observation is well corroborated by a red shift of 80 nm in UV-visible spectroscopic studies. A peak at 16.1 ppm due to HF_2^- in ^1H NMR titration validates the deprotonation of imidazolium N-H by fluoride ion.

GRAPHICAL ABSTRACT



KEYWORDS: colorimetric sensing, fluoride receptor, imidazole, indole, naked eye sensing

INTRODUCTION

Anion complexation chemistry has evolved as a stimulating multidisciplinary research area across chemistry, environment and biology, considering the importance of anion-molecule interactions in the areas of medicine, materials development, physiology, synthetic chemistry and analyte sensing [1]. From spherical fluoride ion to tetrahedral sulphate and phosphate ions, anions find their importance everywhere in nature, with involvement in vital functions and thus demand continuous research [2]. Drawing inspiration from nature, together with acquired knowledge of chemistry, researchers are artistically manipulating the chemical moieties to craft the diverse array of receptors for the selective recognition of desired anion [3]. Till date, multitude of approaches have been attempted with various functionalities to achieve selective binding with anions, most

commonly being preorganization of N-H and O-H moieties for effective hydrogen bonding [4], tailoring the acidity of N-H group for deprotonation to occur [5], anion-π interactions [6] and hydrophobic effects [7], etc.

Amongst the ubiquitous anions, fluoride anion recognition has captured a substantial attention of scientific community because it is one of the trace element required in the formation of teeth and bones in humans [8]. However, it is well documented that excessive intake of fluoride ion through drinking water causes dental fluorosis, bone diseases and lesions of thyroid and liver [9]. This proves that beneficial and injurious effects of fluoride ion intake is concentration dependant, which has been set as 1.5 ppm in drinking water by World Health Organization (WHO) [10]. Available conventional method to quantitatively ascertain the concentration of fluoride in drinking water by lanthanum fluoride based membrane electrode is time consuming and requires skilful handling, since the electrode is quite fragile and expensive [11]. To overcome these obstacles, development of a simple and robust procedure for the fabrication of anion receptor is essential, which can detect analyte *via* naked eye and give semi quantitative information about safe/ unsafe fluoride levels. In view of this requirement, colorimetric receptors provide easy detection of analyte *via* naked eye under visible light [12].

A review of literature reveals the employment of molecules containing functional groups, urea/thiourea [13], secondary amide [14] and thiosemicarbazide [15] to effectively and selectively bind fluoride ion through the formation of hydrogen bond with N-H units of these groups. Covalent attachment of these molecules with appropriate signalling unit,

such as, nitrophenyl, azo dye etc. yields the complete receptor, which can convert anion-receptor binding event into either colour or fluorescence change as an output [16]. Heterocycles, which have recently been introduced as anion receptors, can act as both chromophore and binding units [17]. Interesting photophysical properties of heterocycles make them strong contenders for chromophoric unit and further, inbuilt acidic hydrogen bond donor groups (N-H) in several heterocyclic moieties can serve as binding sites for anions [18]. Amongst these heterocycles, imidazole N-H is acidic enough to act as an excellent hydrogen bond donor [19]. Moreover, acidity can be tailored by proper insertion of electron withdrawing substituents in the ring at critical positions and it can be annulated with another imidazole, benzene, anthraquinone, naphthalene and naphthalimide units for enhancing its NH acidity, rendering it fit to effectively bind fluoride ion by several research groups [20]. Recently, quinone-ferrocene systems bridged by imidazole moiety and quinone-imidazole system have been reported by Elango *et. al*., which exhibited naked eye response towards fluoride and cyanide ions in aqueous media at neutral pH [21]. Although an appreciable number of receptors are known for fluoride ion detection, their applicability to real life applications is restricted to very few since most of them are urea/thiourea based, which exhibit multi-anion sensitivity and lack selectivity [22]. Further, there exists a challenge to develop receptor for detecting fluoride ion in competitive media, owing to its high hydration enthalpy (-505 KJ/mol) [23].

Taking into perpective all this scenario [24], it was envisaged that the introduction of electron withdrawing nitro group at 5^{th} position of indole ring could fine-tune the binding

property of imidazole moiety and serve as selective naked eye receptor for fluoride ion sensing. To the best of our knowledge, this system has not been documented earlier.

RESULTS AND DISCUSSION

Compounds **RA-RE** have been synthesized by environment friendly protocol (**Scheme 1**). 1,2-bis(indolyl)-ethane-1,2-dione derivatives **(3a-c)** were prepared in stepwise reaction of appropriately substituted indole **(1a-c)** and oxalyl chloride in dichloroethane to give compound **2a-c**, which on further treatment with indole derivatives in presence of aluminium chloride afforded compounds **3a-c**. Compounds **3a-c** are irradiated with formyl indole derivatives **(4a-c)** and ammonium acetate in polyethylene glycol (PEG 400) at 300 W and 180^{o} C in microwave to yield desired final product **RA-RE** in good yields. Compared with the traditional method, this protocol offers several advantages like excellent yields, shorter reaction times, minimal environmental effects and clean reaction. Reaction proceeds without the addition of acid or base catalyst.

All the compounds were characterized by ^{1}H NMR, ^{13}C NMR, FTIR and mass spectroscopy. FTIR of receptors **RA-RD** show characteristic broad absorption band due to N-H stretching of imidazolium N-H and indolic N-H in the region 3417-3313 cm^{-1} and 3185-3055 cm^{-1} respectively. Receptor **RE** shows absorption band at 3375 cm^{-1} due to N-H stretching of only imidazole N-H. A broad peak from 2978-2914 cm^{-1} is assigned to aromatic C-H vibration. Absorption band from 1644-1618 cm^{-1} and 1328-1208 cm^{-1} have been assigned to C=C and C-N streching vibrations. Two bands in the region 1550-1515 cm^{-1} and 1390-1350 cm^{-1} are observed due to N-O stretching in nitro group(s)

present in receptors **RB-RE**. ^{1}H NMR spectra of receptors, **RA-RD** exhibit characteristic sharp singlets due to imidazolium N-H and indole N-H in the region δ 12.10-12.55 and δ 9.7-9.81 ppm, respectively. Receptor **RE** displays a sharp singlet at δ 12.15 ppm due to imidazolium N-H. A multiplet from δ 7.11-8.28 ppm is observed for aromatic protons. Peaks at m/z 414, 549, 459, 504 and 849 $[M+H]^+$ in the mass spectra of **RA-RE**, also confirm the formation of products.

Colorimetric Sensing, Interference Studies And UV-Visible Titration Experiment

The anion recognition proficiencies of receptors **RA-RE** (10^{-4} M in DMSO) were vigilantly probed by naked eye, UV-visible and NMR spectroscopic techniques using different anions as their tetrabutylammonium salts (TBA) *viz.*, fluoride, acetate, chloride, bromide, iodide, dihydrogen phosphate, hydrogen sulphate and nitrate in competitive media, 9:1 DMSO-water. Receptors **RA-RC** were found insensitive to the addition of anions and no change in colour was noticed in their solutions, even at high concentration (10^{-3} M) of anions (TBA salts). On the other hand, an instant and distinctive colour change from yellow to orange was observed on addition of TBA salt of fluoride ion into receptor **RD** (10^{-4} M in DMSO) (**Fig 1(a)).** It is worthy to mention that detection limit for fluoride ion detection is found to be 1.5 ppm, which is regarded as the maximum permissible limit for fluoride in drinking water. Other anions, when were added to receptor individually, they did not show any colour change **(Fig. 1(a))**. However, when 1 equivalent of fluoride ion (TBA salt) was added to these solutions, an instantaneous change in colour was noticed in receptor **RD** (10^{-4} M in DMSO) **(Fig. 1(b))**, similar to colour change induced by fluoride ion alone. It establishes that receptor **RD** can

selectively bind fluoride ion irrespective of the presence of other anions. Another receptor **RE** was found to give similar qualitative colour change with fluoride ion as receptor **RD**. In order to enhance the binding affinity and selectivity, electron withdrawing nitro group(s) was introduced at 5^{th} position of indole rings in molecular framework of receptors and it was observed that receptors **RD** and **RE** gave promising results in terms of naked eye change in presence of fluoride ion (TBA salt).

Further investigation on anion affinity studies of receptor **RD** is performed using UV-visible spectrophotometer to corroborate the initial qualitative studies. Receptor **RD** reveals a maxima at 330 nm in UV-visible spectra. Different anions, acetate, chloride, bromide, iodide, dihydrogen phosphate, hydrogen sulphate and nitrate (TBA salts), when added into the solution of receptor **RD** in DMSO, produces no change in spectrum of receptor **(Fig. 2)**. On the other hand, when fluoride is added, peak at 330 nm disappears and a new peak at 410 nm appears. The red shift of 80 nm establishes that the binding event takes place between fluoride ion and receptor. The results obtained establishes the selective and sensitive nature of receptor for fluoride spectroscopically. To ascertain the receptor-fluoride ion interaction, UV-visible titration experiment was carried out with incremental addition of fluoride to receptor solution. On titration with fluoride from 10^{-5} M to 10^{-3} M, peak at 330 nm decreases and absorbance of new peak at 410 nm increases **(Fig. 3)**. From the results obtained, the formation of hydrogen bonding interaction between fluoride ion and receptor is expected to be responsible for the large bathochromic shift in the maxima of receptor [25]. However, more information on the binding process can be obtained by ^{1}H NMR titration only.

Determination of binding constant

Continuous variation method is employed for the determination of stoichiometric ratio of the complex formed between fluoride ion and receptor **RD**, where the concentration of both receptor and fluoride ion salt are kept constant (10^{-4} M in DMSO). The molar fraction of fluoride/ (receptor + fluoride) is continuously varied. At the molar fraction of 0.50, the absorbance reaches its maxima, revealing that receptor forms 1:1 complex with fluoride ion **(Fig. 4)**. 1:1 Stoichiometry was also proved by mass spectra of receptor **RD** with fluoride ion (TBA salt), which exhibited a peak at m/z 568.0351 [Receptor **RD** + F^- +H^+] **(Fig. 5). Figure 6** depicts the change in absorbance at wavelength 410 nm upon gradual addition of fluoride ion (10^{-5} to 10^{-3} M) into receptor RD solution (10^{-4} M in DMSO).

The binding constant of receptor **RD** with fluoride is evaluated by Benesi Hildbrand equation [26]

$1/A\text{-}Amin = 1/(\Delta Amax + (1/K[F^-])(1/\Delta Amax)$.

Here, $\Delta Amax = Amax - Amin$, where, Amin, A, Amax are the absorptions of receptor **RD** considered in the absence of F^-, at an intermediate, and at a concentration of complete concentration. K is binding constant, $[F^-]$ is concentration of F^-. From the plot of $1/ (A-Amin)$ against $[F^-]$ for receptor **RD**, the value of K (+10%) was calculated from the ratio of intercept/slope. Binding constant K, calculated from the graph **(Fig. 7)** is found to be $0.15 \times 10^4\ M^{-1}$.

^{1}H NMR Titration Experiment

The foregoing result of UV-visible spectroscopic titration indicates towards the formation of binding interaction between receptor **RD** and fluoride ion. In order to affirm the mechanism of sensing event, ^{1}H NMR titration is carried out. Receptor **RD** solution is prepared in DMSO-d_6 (10^{-2} M) and fluoride ion in the form of its TBA salt of varying concentrations (2.5, 5, 7.5 and 10 equivalents) has been added sequentially **(Fig. 8)**. It is observed in the ^{1}H NMR spectra of receptor **RD**, the sharp singlet at δ 12.2 ppm, corresponding to imidazole N-H, shows a downfield shift upon addition of fluoride ion and intensity of peak decreases as the concentration of fluoride ion increases, which disappears altogether, when fluoride concentration reaches 10 equivalents. Indole N-H at δ 9.8 ppm remains unchanged during titration. It is evident that interaction between receptor and fluoride ion initiates by hydrogen bonding, as depicted by downfield shift of imidazolium N-H proton in initial stage. Later, excess addition of fluoride ion triggers the deprotonation process, witnessed by the disappearance of N-H peak and appearance of peak corresponding to HF_2^- ion at 16.1 ppm [27]

Further evidence is provided by the synthesis of compound **RE**, where three indole NH are protected by di-tert-butyl dicarbonate (Boc). It exhibits naked eye colour change from yellow to orange in presence of fluoride ion similar to receptor **RD**, which proves that three indole NH are not involved in binding process.

On the basis of above studies, the plausible mechanism of binding between **RD** and fluoride ion is depicted in **Scheme 2.**

The plethora of anion binding studies conducted has shown that the introduction of nitro group at the 5th position of the indole ring enhances the binding ability of receptor **RD** (10^{-4} M in DMSO) towards fluoride ion (1.5 ppm)**.** Further, it gave a visible colour change from yellow to orange upon addition of fluoride ion into the solution of receptor **RD** in DMSO. This phenomenon may be explained by the fact that nitro groups are electron withdrawing in nature and their insertion onto the molecular framework of receptor **RD** increased the acidity of imidazole N-H, which can establish hydrogen binding interactions with highly basic fluoride ion. This event was followed by deprotonation of N-H, which was evident in ^{1}H NMR titration, where a new peak at 16.1 ppm appeared due to HF_2^- ion. Deprotonation triggers an extended conjugation or π-delocalisation and alters the dipole associated to the charge-transfer transition or in other words, stabilizes the excited state of chromophoric group [28]. This ultimately is observed as a vivid colour change as output. Similar findings have been documented by other research groups too [6, 29].

Ph Effect On RD-F$^-$ Interaction

To investigate the effect of pH on receptor RD-F$^-$ binding affinity, changes in the intensity of the absorbance band at 410 nm were observed over a pH range 2-12 **(Fig. 9).** The working pH range was found to be 6.5-8.0, where the intensity of absorbance remains constant. Below pH 6.5, intensity of absorbance band at 410 nm decreased rapidly. This is probably due to protonation of fluoride ion, to form weakly ionized hydrofluoric acid, which decreases the affinity of fluoride ion to bind receptor binding site, N-H. Above pH 8.0, intensity of this absorption band increased, which can be

attributed to increased availability of deprotonated fluoride ion to establish stronger hydrogen binding interactions with receptor's binding site, N-H.

CONCLUSIONS

Structurally simple and easy to synthesize imidazole-indole based receptor **RD** has been synthesized for easy and robust detection of inorganic fluoride in 9:1 DMSO-water. It senses fluoride at 1.5 ppm with colour change from yellow to orange, perceivable by naked eye. Detection of fluoride in aqueous media makes the receptor suitable for practical applications.

EXPERIMENTAL

All chemicals were purchased from Sigma Aldrich, TCI and Spectrochem Chemicals, India and were used without further purification. Starting substrates, 3-formylindoles were prepared by following literature [30].

Melting points were determined in open glass capillaries and are reported uncorrected. ^{1}H NMR and ^{13}C NMR were recorded on a Jeol ECS 400 MHz spectrophotometer using DMSO-d_6 as solvent. TMS was taken as an internal standard and the chemical shifts are reported in δ ppm. Resonance multiplicities are described as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). FTIR spectra were recorded on a Perkin Elmer Spectrum Two spectrophotometer using pressed KBr discs in the region of 400 – 4000 cm^{-1}. Mass spectra were recorded on a Xevo G2-S Q-Tof spectrometer (Waters, USA), capable of recording high-resolution mass spectrum (HRMS) in the ESI (Electrospray

Ionization) modes. CEM discover mono mode microwave reactor with magnetron frequency of 2455 MHz was used for microwave reaction. Ultrasonication synthesis was performed using Elma S 70 H Ultrasonicator with 37 KHz output frequency. UV-visible spectra was recorded on a Perkin Elmer Lambda 750 UV-Vis NIR spectrophotometer in standard 3.5 mL quartz cells with 10 mm path length. The purity of all compounds was checked by TLC using silica gel as adsorbent and solvents of increasing polarity as mobile phase.

Synthesis Of Receptors 3-[2,5-{(Un)Substituted-1H-Indol-3-Yl}-1H-Imidazol-4-Yl]-(Un)Substituted-1H-Indole (RA-RE)

A mixture of 1,2-bis(substituted-indolyl)-ethane-1,2-dione (3a-c) (1mmol), indole aldehyde (4a-c) (1mmol) and ammonium acetate (4 mmol) in polyethylene glycol (2 ml) was irradiated at 180 $^{\circ}$C and 350 W power for 8-10 minutes. The progress of reaction was monitored by thin film chromatography 4:1 (ethyl acetate: methanol). The reaction mixture was cooled to room temperature and poured on 100 ml ice water. The separated solid was filtered and washed with water to yield brown solid as desired title product.

3-[2,5-(1H-indol-3-yl)-1H-imidazol-4-yl]-1H-indole (**RA**): Brown solid, yield: 89.10 %, m.p.: 164 ^{o}C. FTIR (KBr, υ cm^{-1}): 3406 (Imidazole N-H), 3170 (Indole N-H), 2924 (=C-H), 1644 (C=C), 1234 (C-N). ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): δ (ppm) 7.38-7.94 (m, 15H, Ar-H), 9.23 (s, 3H, indole N-H), 12.10 (s, 1H, imidazole N-H). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm) 104.48, 105.55, 112.35, 117.811, 129.80, 133.46, 142.06, 147.98. MS (ESI) m/z: 414.1884 $[M+H]^{+}$ Calculated for $C_{27}H_{19}N_5$: 413.1840.

SUPPLEMENTARY MATERIAL

Experimental details and ^{1}H NMR, ^{13}C NMR and mass spectral data for this article can be accessed on the publisher's website.

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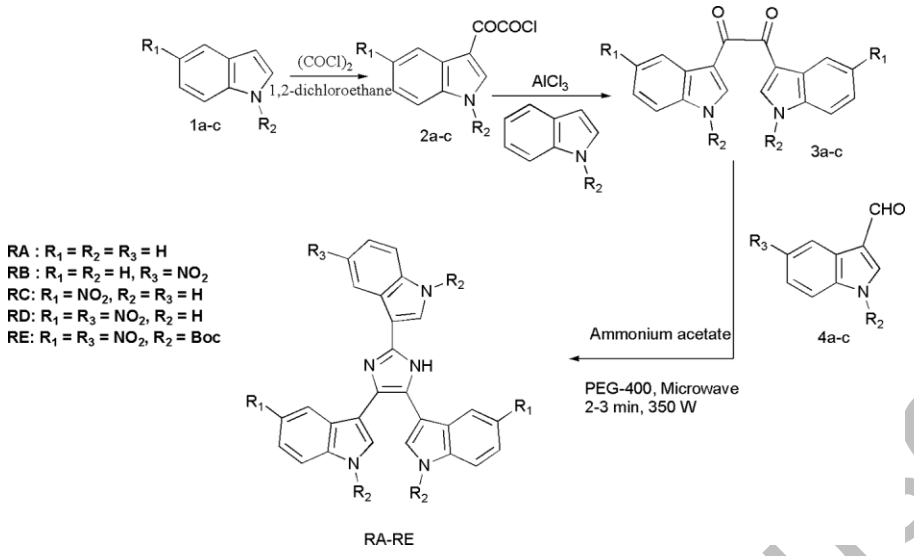
Scheme 1.



Scheme 2.

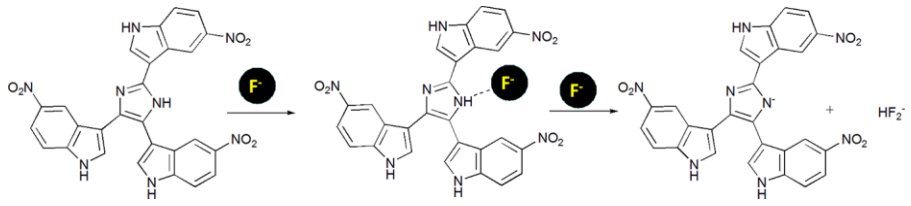


Figure 1. (a) Colour changes in the receptor RD (10-4 M in DMSO), in presence of 1equivalent of different anions (TBA salts) in 9:1 DMSO-water, where A, B, C, D, E, F and G represent F-, Cl-, Br-, I-, CH3COO-, H2PO4-, HSO4- and NO3- ions, respectively. (b) Colour changes in the receptor RD (10-4 M in DMSO), in presence of 1equivalent each of fluoride and different anions (TBA salts) in 9:1 DMSO-water, where A, B, C, D, E, F, G and H are receptor and, F- + Cl-, F- + Br-, F- + I-, F- + CH3COO-, F- + H2PO4-, F- + HSO4- and F- + NO3-, respectively

Figure 2. UV-visible spectra of receptor RD (10-4 M in DMSO) upon addition of different anions (TBA salts, 10-4 M) in 9:1 DMSO-water

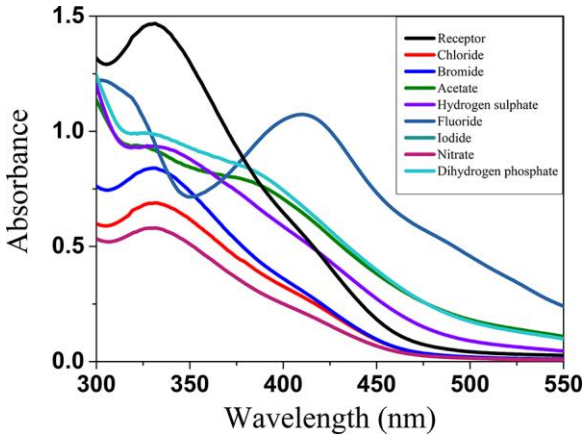


Figure 3. UV-visible spectra of receptor RD (10-4 M in DMSO) upon addition from 0.1 to 10 equivalents of fluoride ion (TBA salt) in 9:1 DMSO-water

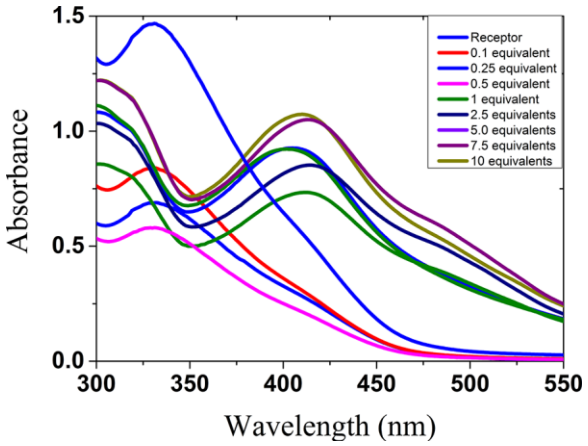


Figure 4. Jobs Plot with receptor RD (10-4 M in DMSO) and fluoride ion (TBA salt) 10-4 in 9:1 DMSO-water

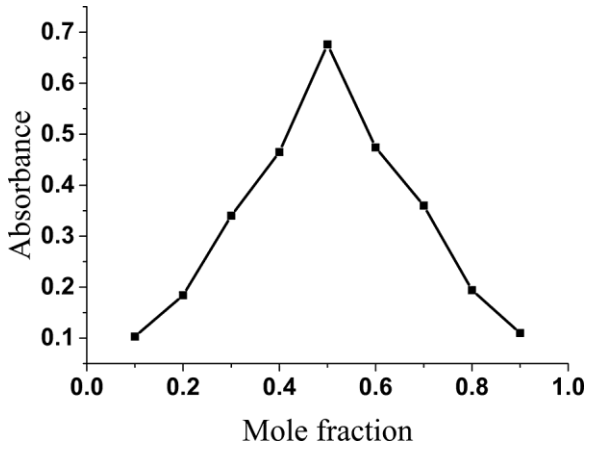


Figure 5. ESI-mass spectrum of complex of fluoride ion and receptor RD

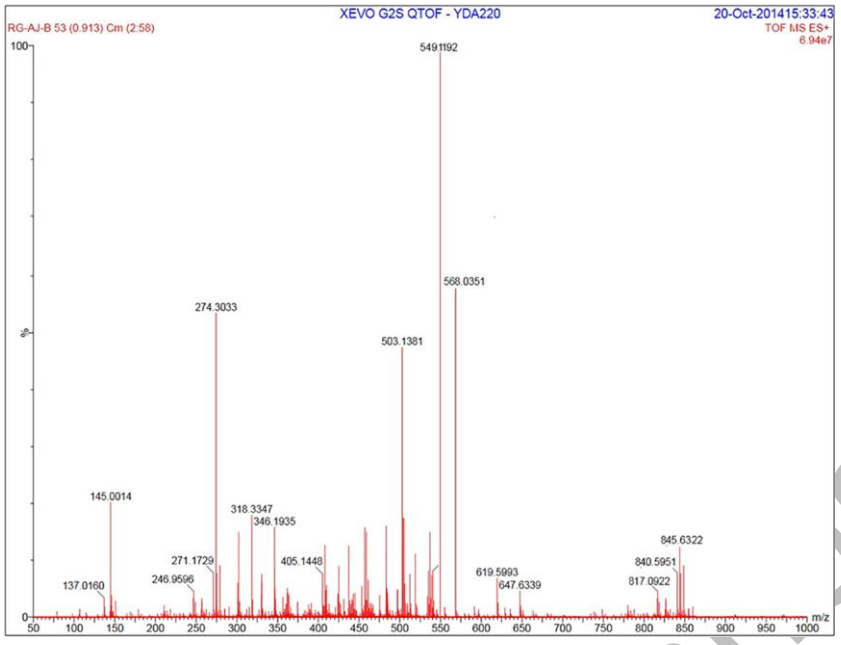


Figure 6. Changes in absorbance at 410 nm of receptor RD (10-4 M in DMSO) with increase in fluoride ion concentration (10-5 to 10-3 M in 9:1 DMSO-water)

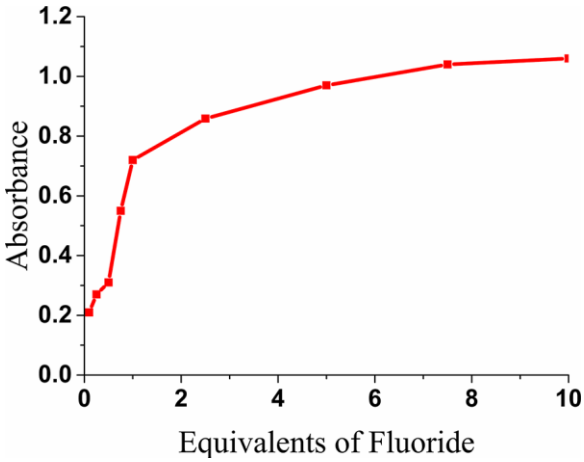


Figure 7. Fitting curve of Benesi Hildbrand equation

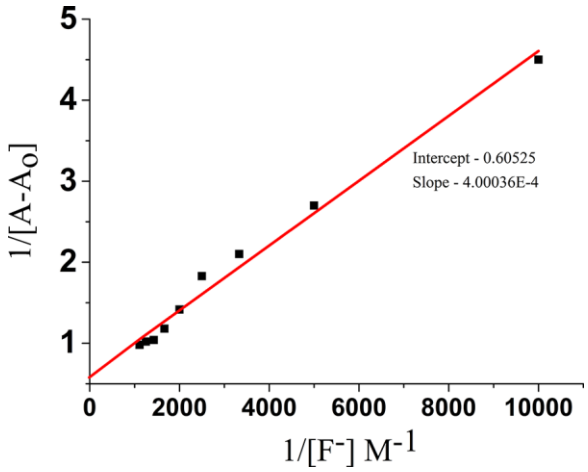


Figure 8. Partial 1H NMR (400 MHz) spectra of receptor RD in DMSO-d6 (10-2 M) in the presence of (a) 2.5, (b) 5, (c) 7.5 and (d) 10 equivalents of TBAF in DMSO-d6

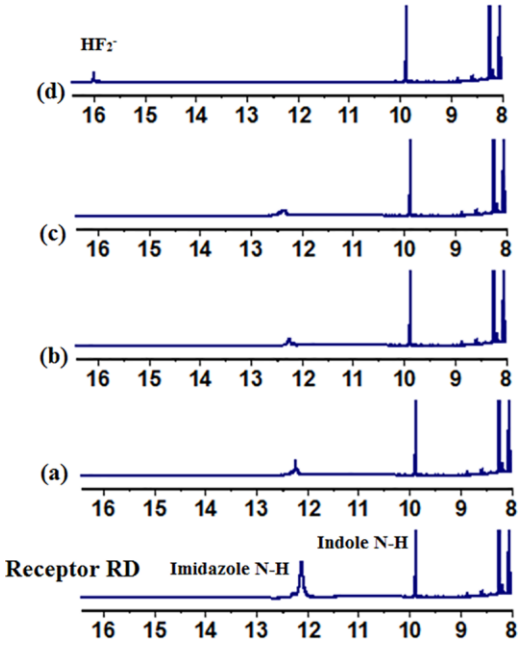


Figure 9. Changes in absorbance of receptor RD (10-4 M in DMSO) and fluoride ion (10-4 M in 9:1 DMSO-water) with varying pH (2-12)