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An imidazole based colorimetric sensor for fluoride anion

Shyamaprosad Goswami* and Rinku Chakrabarty

Department of Chemistry, Bengal Engineering and Science University, Shibpur, Howrah-711103, India

**Corresponding author at: Department of Chemistry, Bengal Engineering and Science University, Shibpur, Howrah-711103, India. Tel.: +91.33.26684561-3/498; fax: +91.33.26682916. E-mail address: spgoswamical@yahoo.com (S. Goswami).*

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ABSTRACT

Nine 2,3,5-triphenylimidazole derivatives having nitro and/or OH groups at their phenyl groups as receptors have been designed and synthesized for the colorimetric detection of F- ion, among which receptor (1) having a nitro group at the para position of the 2-phenyl group with respect to the imidazole moiety shows colorimetric responses (yellow to red) in acetonitrile-water (9:1, v:v) mixture towards F- anion selectively among other anions studied. Here nitro group acts as a signaling unit and OH and NH of imidazole moieties act as binding sites respectively.

1. Introduction

In recent years the design of synthetic receptors that can selectively recognize anions through visible, electrochemical and optical responses has got considerable attention because anions play an important role in many biological, industrial and environmental processes [1-4]. Molecules containing functional groups such as amides, ureas/thioureas, guanidinium and ammonium derivatives can effectively bind anions using directional hydrogen bonding interactions and these types of compounds have widely been used for the binding of anions [5-13]. In most of the synthetic chemosensors the optical signaling chromophore fragment is covalently linked to a neutral anion receptor containing urea, thiourea, amide, phenol or pyrrole subunits. They can provide one or more H-bond donor sites for selective binding and sensing of anions, e.g. F^-, OAc^-, $H_2PO_4^-$ etc. The H-bond complex and the basicity of the anions effect their selectivity.

Many works have been reported for the recognition of negatively charged species [1-4]. But still the search of structurally simple receptor which can be easily synthesized and efficiently used has been of keen interest in the area of molecular recognition.

Among the biologically important anions, F^- is the most basic and most electronegative anion and it can form strongest H-bond with H-bond donor groups like NH or OH. The presence of excess F^- can cause deprotonation following classical Bronsted acid-base type reaction.

Fluoride has well established role in preventing dental caries [2]. It has also been used extensively for the treatment of osteoporesis. Fluoride can lead to fluorosis [14-17], a type of fluoride toxicity that generally manifests itself clinically in terms of increasing bone density if it is used on a less salubrious level. It has applications in the analysis of drinking water and in the detection of chemical warfare agents [18]. Fluoride is also associated with diseases like Alzeimer's disease [19]. Thus fluoride has both beneficial as well as toxic effects. Therefore detection of F^- anion has been one of the most interested current topics of research [20-50] via an easy-to-detect optical method, due to its simplicity. Again the colorimetric chemosensors offer naked-eye detection without having any spectroscopic instrumentation technique.

2. Experimental

2.1. Instrumentation

^1H NMR spectra were recorded either with a Bruker AM 300 MHz or a Bruker 400 MHz spectrometer. For NMR, DMSO-d_6 and $CDCl_3$ were used as solvents, unless otherwise mentioned, TMS as internal standard. Chemical shifts are expressed in d units and ^1H-^1H coupling constants in Hz. IR spectra were recorded with a JASCO FT/IR-460 plus spectrometer, using KBr discs. Melting points are deterdmined in hot coil Adair-Dutt Instrument and are uncorrected. UV-vis spectra were recorded using spectroscopic grade acetonitrile, chloroform and double distilled water was used as solvents with a JASCO V-530 spectrometer. Fluorescence spectra were recorded in PTI spectrophotometer.

2.1. Synthesis

All commercially available chemical reagents were used without further purification. All the reactions were carried out in glacial acetic acid. Receptor **1** has been designed in such a way that larger anions like Cl^-, Br^- and I^- may face some steric hindrance with the phenyl rings of the substituted imidazole moiety when they come close to the vicinity of the NH proton of imidazole moiety for binding purpose.

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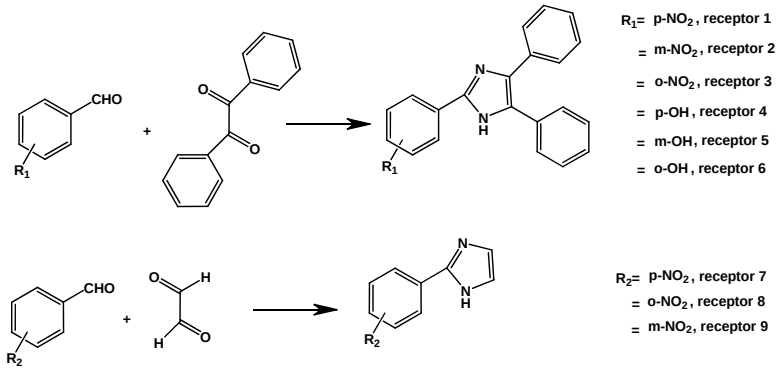


Reagents and conditions: NH_4OAc, glacial AcOH, 90 °C, 9 h.

Scheme 1

Receptor **1** is structurally simple and easy to synthesize in single step condensation of 4-nitrobenzaldehyde with benzil [51] in presence of ammonium acetate and acetic acid at 90 °C for 8 h (Scheme 1). Washing with sufficient water followed by chromatographic purification gives orange colored receptor **1**. The receptors **2**, **3**, **4**, **5**, **6**, **7**, **8** and **9** have been synthesized by the similar procedure as was applied in case of receptor **1**.

Representative reaction procedure: 4-Nitrobenzaldehyde (1 g, 6.62 mmol), benzil (1.39 g, 6.62 mmol) and ammonium acetate (5.1 g, 66.2 mmol) were taken in a round bottomed and glacial acetic acid (1 mL) was added to it. The whole mixture was heated to 80-90 °C with stirring for 9 hours. The reaction mixture was cooled, neutralized with saturated sodium bicarbonate solution, and the precipitated orange solid was collected by filtration, washed with plenty of distilled water and then dried to give receptor **1** (720 mg, 31.8%).

2-(4-Nitro-phenyl)-4,5-diphenyl-1H-imidazole (Receptor **1**): M.p.: 141-142 °C. IR [KBr, ν_{max} (cm^{-1})]: 3390, 3057, 2360, 1598, 1514, 1338, 855. ^{1}H NMR (300 MHz, DMSO-d_6): 13.17 (s, 1H), 8.35 (bs, 4H), 7.66 (bs, 1H), 7.57-7.45 (m, 7H), 7.33-7.28 (m, 2H). Mass (HRMS): Calcd. for $C_{21}H_{16}N_3O_2$ $[M+H]^+$ is 342.1250. Found: 342.1230. ^{1}H NMR of receptor 1 + TBAF (300 MHz, DMSO-d_6): 8.35 (bs, 4H), 7.66 (bs, 1H), 7.57-7.45 (m, 7H), 7.33-7.28 (m, 2H). IR [KBr, ν_{max} (cm^{-1})]: 3435, 2961, 1598, 1517, 1337, 883, 765, 480.

2-(3-Nitro-phenyl)-4,5-diphenyl-1H-imidazole (Receptor **2**): Yield: 33%. M.p.: 210 °C. ^{1}H NMR (300 MHz, DMSO-d_6): 13.11 (s, 1H), 8.96 (s, 1H), 8.52 (d, 1H, *J*= 7.5 Hz), 8.22 (d, 1H, *J*= 7.8 Hz), 7.79 (t, 1H, *J*= 7.6 Hz), 7.58-7.45 (m, 6H), 7.53-7.26 (m, 4H). Mass (HRMS): Calcd. for $C_{21}H_{16}N_3O_2$ $[M+H]^+$ is 342.1250. Found: 342.1230.

2-(2-Nitro-phenyl)-4,5-diphenyl-1H-imidazole (Receptor **3**): Yield: 24%. M.p.: 150 °C. ^{1}H NMR (300 MHz, DMSO-d_6): 12.98 (bs, 1H), 8.26 (s, 1H), 7.96 (d, 1H, *J*= 7.5 Hz), 7.92 (d, 1H, *J*= 7.9 Hz), 7.79 (t, 1H, *J*= 7.7 Hz), 7.64 (t, 1H, *J*= 7.9 Hz), 7.47-7.46 (m, 8H), 7.36 (bs, 1H). Mass (HRMS): Calcd. for $C_{21}H_{16}N_3O_2$ $[M+H]^+$ is 342.1250. Found: 342.1230.

4-(4,5-Diphenyl-1H-imidazol-2-yl)-phenol (Receptor **4**): Yield: 41%. M.p.: 135-136 °C. ^{1}H NMR (500 MHz, DMSO-d_6): 12.42 (bs, 1H), 9.83 (s, 1H), 7.89 (d, 2H, *J*= 7.97 Hz), 7.49 (d, 4H, *J*= 7.1 Hz), 7.35-7.28 (m, 6H), 6.86 (d, 2H, *J*= 7.9 Hz). Mass (HRMS): Calcd. for $C_{21}H_{16}N_2O$ $[M+H]^+$ is 313.1335. Found 313.1339.

3-(4,5-Diphenyl-1H-imidazol-2-yl)-phenol (Receptor **5**): Yield: 34%. M.p.: 115 °C. ^{1}H NMR (300 MHz, DMSO-d_6): 12.59 (s, 1H), 9.78 (s, 1H), 9.54 (s, 1H), 7.54-7.48 (m, 6H), 7.44 (t, 2H, *J*= 7.4 Hz), 7.38 (d, 1H, *J*=7.5 Hz), 7.30 (t, 2H, *J*= 7.5 Hz), 7.23 (t, 1H *J*=7.5 Hz), 6.78 (d, 1H, *J*= 7.8 Hz). Mass (HRMS): Calcd. for $C_{21}H_{16}N_2O$ $[M+H]^+$ is 313.1335i Found: 313.1339.

2-(4,5-Diphenyl-1H-imidazol-2-yl)-phenol (Receptor **6**): Yield: 45%. M.p.: 150 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 12.59 (s, 1H), 11.63 (s, 1H), 8.47 (d, 1H, *J*= 7.6 Hz), 7.62 (bs, 4H), 7.31-7.27 (m, 6H), 7.11 (t, 2H, *J*= 7.6 Hz), 6.86 (d, 1H, *J*= 8.2 Hz). Mass (HRMS): Calcd. for $C_{21}H_{16}N_2O$ $[M+H]^+$ is 313.1335. Found: 313.1339.

2-(4'-Nitro-phenyl)-1H-imidazole (Receptor **7**): Yield: 11%. M.p.: 160-162 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 7.99 (d, 1H, *J*= 7.9 Hz), 7.82 (d, 1H, *J*= 8.2 Hz), 7.60 (t, 2H, *J*= 7.7 Hz), 7.45 (t, 1H, *J*= 3.9 Hz), 7.18 (s, 1H). Mass (HRMS): Calcd. for $C_9H_8N_3O_2$ $[M+H]^+$ is 190.0611. Found 190.0614.

2-(2'-Nitro-phenyl)-1H-imidazole (Receptor **8**): Yield: 14%. M.p.: 180 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 8.80 (bs, 1H), 8.32 (d, 2H, *J*= 6.9 Hz), 7.12 (s, 2H), 5.68 (bs, 1H). Mass (HRMS): Calcd. for $C_9H_8N_3O_2$ $[M+H]^+$ is 190.0611. Found: 190.0614.

2-(3-Nitro-phenyl)-1H-imidazole (Receptor **9**): Yield: 10%. M.p.: 98-100 °C. Mass (HRMS): Calcd. for $C_9H_8N_3O_2$ $[M+H]^+$ is 190.0611. Found: 190.0614.

The colorimetric sensing ability of **1**-**8** with halides, OAc^-, HSO_4^-, $H_2PO_4^-$ and N_3^- were monitored by visual (naked eye) and UV-vis spectroscopic technique in acetonitrile-water medium. Solutions of $3.06x10^{-4}$ M anions were added as tetrabutylammonium salts to $4.18x10^{-5}$ M solutions of the receptors.

3. Results and discussion

In spite of the popularity of the anion recognition, the design of synthetic receptors still remains a great challenge due to their larger size than cations, and the effects of other variables like their chemical environments and the pH of the medium on the behavior of anions. Due to larger size and higher charge density they remain highly solvated in polar protic solvent e.g. H_2O. Therefore recognition of anions in water is really a challenging work. Herein we report simple imidazole based colorimetric receptors for the selective recognition of F^- in CH_3CN-H_2O (9:1, v/v) (Scheme 1) medium. Receptor **1** selectively binds F^- and the yellow solution of **1** turned red in acetonitrile-water medium. However red color is also observed for OAc^- anion when added in very higher concentration.

3.1. Color change

The color change i.e. naked-eye experiment was carried out using 1.47 x 10^{-5} M solutions of four receptors in CH_3CN-H_2O (9:1, v/v) medium among which only receptor **1** showed red

color from yellow (Figure 1) in the presence of TBAF ($3.06x10^{-4}$ M). Other receptors except **7** were found to be insensitive after the addition of anions (even up to 100 equivalents). Only the acetate anion influences color change from yellow to red at larger concentration when it is compared to F^- ion. The change in the electronic property of the chromophore gets affected resulting intense red color because of the charge transfer interaction between fluoride bound NH of imidazole and the electron deficient nitro group at *para* position. Among the other receptors color change is observed in the case of receptor **7** after addition of comparatively larger amounts of fluoride ion. In case of receptor **3** color change is observed after addition of very large amounts of fluoride anion.

Figure 1. Color changes of receptor **1** due to addition of F- ion.

For the receptors **1**-**3**, the 4 and 5 sites of imidazole moiety have two phenyl ring and 2 site of imidazole has nitro-phenyl ring, two phenyl ring and nitro are electron withdrawing groups. Therefore the acidic property of H of NH of imidazole moiety remarkably increased and binding ability of the receptors **1**-**3** for anions remarkably increased accordingly, but for the receptors **2** and **3** the nitro group of m-site or o-site blocked binding of receptors **2** and **3** to bind with F^-. For the receptor **7**-**9**, the 4 and 5 sites of imidazole moiety have no phenyl ring and the acidic property of H of HN of imidazole moiety remarkably decreased, therefore they can't bind anions.

For the receptors **4**-**6**, 2-site of imidazole moiety has phenol group, the electron donating OH group decreased the acidic property of H of NH of imidazole moiety, therefore the receptors 4-6 can't bind anions in effective way.

Color changes are also observed in $CHCl_3$, CH_3CN and in DMSO solvents in case of **1** on addition of F^-. Other receptors still remain unaffected in these solvents also. It corroborates with the fact that the sensor **1** is selective for F^- ion based on deprotonation and is not very much related to the polarity of solvent (as color change has been observed in mixed aqueous solvent as well as in DMSO or CH_3CN or $CHCl_3$), but is dependent on the basicity of the anion.

3.2. Binding studies

3.2.1. UV-vis experiments

The deprotonation of the receptor was confirmed by Bronsted acid-base reaction between the receptor **1** and tetrabutylammonium hydroxide. Due to addition of OH^- as its tetrabutylammonium salt the spectrum (UV-vis) is similar to that of F^- anion and the solution becomes red.

The anion binding ability of the eight receptors (**1**, **2**, **3**, **4**, **5**, **6**, **7**, **8** and **9**) with anions were investigated using UV-vis titration method. The titrations were carried out in acetonitrile-water medium at $1.47x10^{-5}$ M concentrations of host and increasing concentrations of $3.06x10^{-4}$ M solutions of the guest anions as their tetrabutylammonium salts. The UV-vis spectrum of **1** upon addition of F^- is shown in Figure 2a. The UV-vis spectra of receptor **1** showed 3 bands, one at around 241 nm, the other at 298 nm (due to the π electrons of the aromatic system) and another one at 386 nm (due to the substituted imidazole moiety). After the addition of F^- anion the intensity of peaks gradually decreases and a new peak arises at 484 nm with the appearance of isosbestic point at ~422 nm. But this isosbestic point does not include the original spectra of receptor **1**. This phenomenon will be explained in future research. Due to the addition of F^- anion the yellow color of the solution becomes red. The appearance of color may be due to Internal Charge Transfer (ICT). This ICT process becomes facilitated in case of receptor **1** compared to the other eight receptors and for this reason sensor **1** shows color change in presence of fluoride anion prominently. The change in absorbance spectra is more prominent in case of fluoride but other anions affect very small changes after addition of same equivalents (Figure 3a, 3b). The equilibrium constant or proton dissociation constant *Ka* determined by UV-vis method using the Benesi-Hildebrand equation [53-55] is 1.42×10^4 M^{-1} for the binding of receptor **1** and fluoride (see supporting information). Receptor **7** influences color change after addition of comparatively larger amounts of fluoride anion (supporting information). Equilibrium constants and the proton dissociation constants have been determined at 295±0.5 K. OAc^- anion also influences the spectrum of receptor **1** but less effectively. In this case, the change of the peak at 386 nm is quite irregular. Although a new peak is generated at around 400 nm after addition of about 10-12 equivalents of acetate anion, its increase is also not regular.

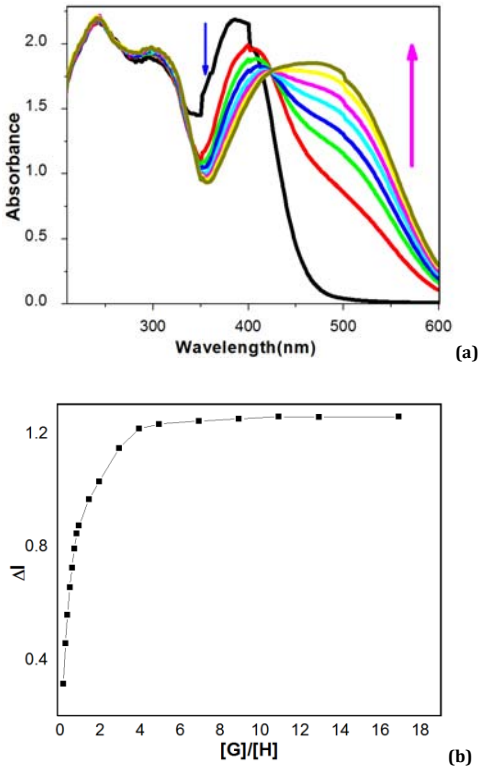
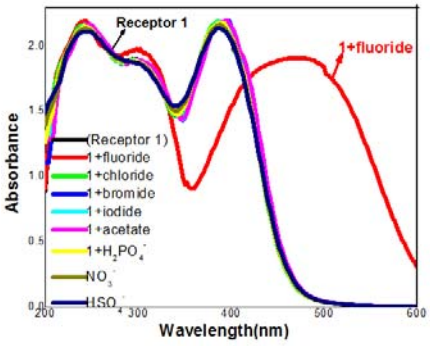
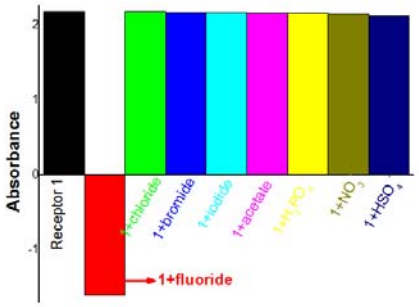


Figure 2. (a) The changes of absorption spectra of receptor **1** after addition of TBAF (0, 0.2, 0.4, 0.5, 1.0, 1.5, 2.0 equivalents); (b) the graph of concentration of guest/host with the change of absorbance at 386 nm.

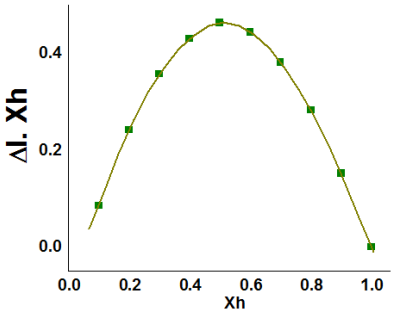
To understand the stoichiometry of complexation between **1** and F^-, we have plotted [H]/[H]+[G] against changes of absorbance values at 386 nm (Figure 3b). The break at around 1 at *x*-axis reveals the 1:1 binding of **1** with F^-. To confirm the stoichiometry we have again done the Job plot (Figure 3c) experiment by preparing the solutions of **1** and F^- in different concentrations and the UV-vis spectra were recorded. The maxima of mol fraction of host at 0.5 strongly demonstrated the 1:1 binding mode of **1** with F^-.



(a)



(b)



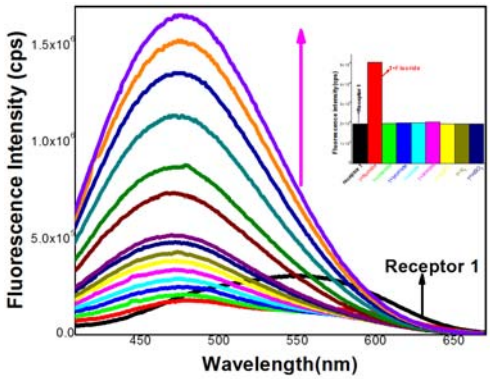
(c)

Figure 3 (a) Changes of absorption spectra of receptor **1** after addition of 1 equivalent of anions as their tetrabutylammonium salts; (b) plot of absorbance *vs* guest concentrations at 386 nm; (c) Job plot of receptor **1** with F^- in acetonitrile-water solvent determined by the continuous variation method.

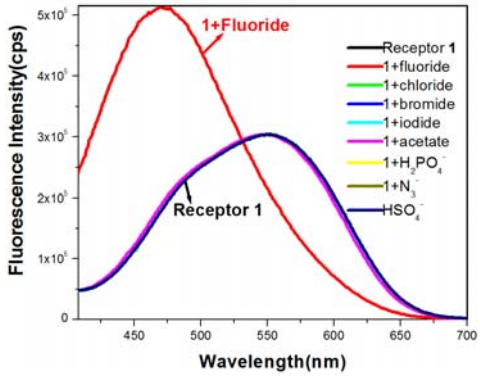
3.2.2. Fluorescence experiments

The emission spectrum of receptor **1** is also interesting. **1** possesses emission maxima at 550 nm. But upon addition of tetrabutylammonium fluoride emission maxima shifted to shorter wavelength i.e. emission maximum appears at 477 nm (Figure 4a). The peak at 477 nm gradually increases as the concentration of fluoride is increased. The fluorescence spectra remained almost unchanged on addition of other anions stated earlier (Figure 4). Again the emission spectra of the other receptors remain unaffected on addition of anions as their tetrabutylammonium salts.

The equilibrium constant *Ka* of receptor **1** and fluoride by fluorescence method was calculated and it was found to be $1.48 \times 10^4\ M^{-1}$. To determine the stoichiometric ratio of receptor **1** and fluoride, continuous variation methods in Job plot (Figure 5) were used. The results illustrate that in this case the concentration of receptor-guest complex approaches a maximum when the mole fraction of receptor is about 0.5, indicating the formation of 1:1 complex between receptor **1** and fluoride.



(a)



(b)

Figure 4. (a) Changes of fluorescence spectra of receptor **1** upon addition of tetrabutylammonium fluoride in CH_3CN-H_2O (9:1 v/v) (inset shows the plot of fluorescence intensity vs concentration of anions (2 equivalents) as their tetrabutylammonium salts at a wavelength of 477 nm; (b) Emission spectra of receptor **1** after addition of different anions (1 equivalent) 477 nm.

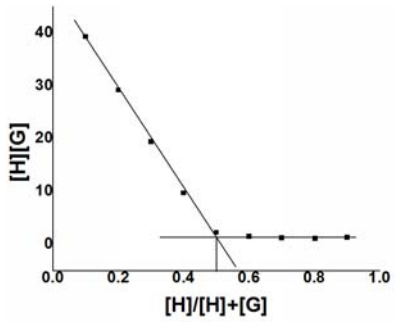


Figure 5. Job plot between receptor **1** and TBAF. The concentration of [H][G] was calculated by the equation [H][G]= ΔI/IoX[H]; where [H], [G] are concentrations of host, receptor **1** and TBAF respectively, X[H] is the mol-fraction of receptor **1**, ΔI is the change of fluorescence intensity at 477 nm.

3.2.3. IR study

To investigate the hydrogen bonding ability of receptor **1**, FT-IR study (Figure 6) was carried out. The N-H stretching appears at 3390 cm^{-1} in case of receptor **1** whereas after complex formation with fluoride it becomes broad and gets shifted to higher frequency at 3435 cm^{-1}.

3.2.4. NMR study

The binding of receptor **1** with TBAF is also clear from the NMR spectra of receptor **1** with fluoride ion. The NH [δ (in ppm) 13.17] proton of imidazole moiety of receptor **1** gets shifted to 15.32 ppm and becomes broad after addition of fluoride anion (Figure 7) and disappeared completely much before the complete addition of TBAF, indicating that the interaction with the fluoride ions through hydrogen bond formation followed by deprotonation [24,38,51,52].

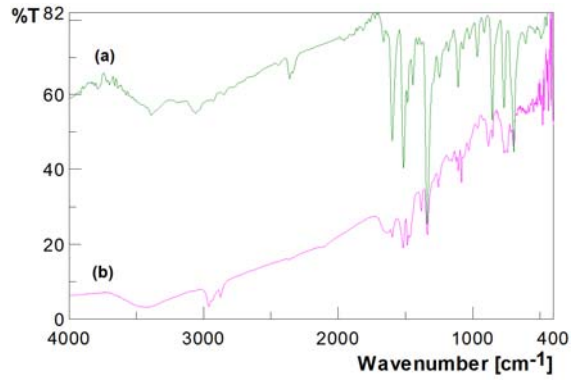


Figure 6. IR spectra of receptor **1** (a) and receptor **1**+TBAF (1:0.2 equivalent) (b) using KBr discs.

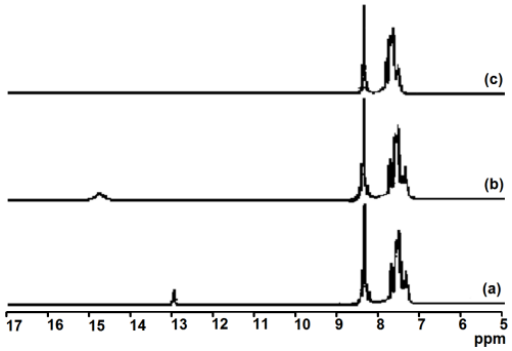


Figure 7. ^{1}H nmr of receptor **1**(a), receptor **1** with 0.1 equivalent of fluoride anion (b) and 0.2 equivalent fluoride (c).

4. Conclusion

In conclusion, we have synthesized nine (substituted) imidazole based fluorescent receptors **1**, **2**, **3**, **4**, **5**, **6**, **7**, **8** and **9**. In receptors **1**, **2**, **3**, **7** and **8** each contains one NO_2 group but **4**, **5** and **6** each has one OH group. Among all the receptors, receptor **1** has been found to be the suitable one for fulfilling the purpose of chromogenic sensor for fluoride ion. Receptor **1** shows color change from yellow to red after addition of fluoride anion. The binding of receptor **1** has been studied by naked-eye experiment as well as the UV-vis and fluorescence methods.

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Supplementary material

UV-Vis spectra of receptors **2**, **3**, **4** and **7**, ^{1}H and ^{13}C NMR, HRMS spectra, general procedures and preparation of the receptors.

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