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ORIGINAL PAPER

Pyrrole Based Schiff Bases as Colorimetric and Fluorescent Chemosensors for Fluoride and Hydroxide Anions

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Abstract An efficient colorimetric sensor with pyrrole-NH moiety as binding site and nitro group as a signaling unit has been synthesized by a one step procedure and characterized by spectroscopic techniques, which displays excellent selectivity and sensitivity for fluoride and hydroxide ions. The hydrogen bonding with these anions provides remarkable colorimetric responses. ^{1}H NMR and FT IR studies has been carried out to confirm the hydrogen bonding. UV–vis and fluorescence spectral changes can be exploited for real time and on site application.

Keywords Schiff base · Pyrrole · Fluoride and hydroxide ions · Sensors · UV–vis spectroscopy · Fluorescence

Introduction

Significant interest has been laid on the development of synthetic anion sensors capable of converting the binding event into readable signal output through optical, electrochemical and magnetic resonance responses because of their importance in many biological, industrial and environmental processes [1–5]. In particular, the selective sensing of fluoride has gained attention due to its significance in clinical treatment for osteoporosis and detection of fluoride as a result of its over accumulation in bones [6–13], also fluoride is a common ingredient in anesthetics, hypnotics, psychiatric drugs, rat and cockroach poisons and military nerve gases and is a contaminant in drinking water. Excess fluoride exposure may cause collagen breakdown, bone disorders, thyroid activity depression and immune system disruption. In this context a colorimetric chemo sensor is of particular interest. 'Colorimetric chemo sensors' are molecules that allow naked-eye detection of anions without resort to any spectroscopic instrumentation. Such sensor systems are generally composed of two parts: the first one is anion binding part (receptor) which is typically based on various combinations of (CH=N) [14, 15], hydroxyl (−OH) [16–18], amide (−CONH) [19–21], urea ($(NH_2)_2C$=O) [22–25], thiourea ($(NH_2)_2C$=S) [26–30], pyrrole (−NH) [31, 32], coumarin [33, 34] moieties and the another one is a chromophore which converts binding induced changes into an optical signal such as an appearance of color. These two parts are either linked directly or intra molecularly associated [35]. Many reports have appeared describing the synthesis and study of very sophisticated anion sensors [36–40]. This is because, anions seem to interact with a hydrogen bond donors of a receptor (NH_2, −OH,−C(O)NHR) more strongly.

The pyrrole based anion probes show excellent stability over a wide range of pH 3–10. To raise the detection sensitivity the pyrrole units can be incorporated into a conjugated system for colorimetric responses. The pyrrole Schiff bases, discussed in this paper, are easily synthesizable from pyrrole-2-carboxaldehyde and corresponding amines. These are also isolated in good yields in the lab. Though similar type of

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pyrrole based Schiff bases are reported in the literature [41, 42] and studied extensively, Receptors **1** and **2** are reported for the first time and tested for their anion sensing property. In this paper we demonstrate for the first time the synthesis, characterization and anion sensing property of pyrrole based chromogenic receptors.

Experimental

All reagents used for synthesis were obtained commercially and were used without further purification. In the titration experiments, all the anions were added in the form of Tetra butyl ammonium salts, which were purchased from Sigma Aldrich chemical and analytical grade solvents such as acetonitrile (CH_3CN), dimethyl sulfoxide (DMSO) and chloroform ($CHCl_3$) used were all dry. Proton NMR was obtained on a Bruker 400 MHz spectrometer using Tetramethylsilane (TMS) as an internal standard, LCMS was taken on Agilent trap control LCMS, IR spectra was recorded by KBr pellet method on a Perkin-Elmer Spectrum One FTIR spectrometer. UV-visible spectra was recorded in 1 cm path length quartz cell using a T90+ model (PG instruments, UK) UV–vis spectrophotometer. Fluorescence emission spectra were recorded in a Shimadzu RF-5301 PC spectrofluorophotometer at a scan rate of 500 nm/min. Excitation wavelength chosen was 300 nm. All reactions were carried out in the atmosphere of purified nitrogen.

Receptor **1** *N*-[(1*E*)-1*H*-pyrrol-2-ylmethylene] benzene-1, 4-diamine (**1**)

1, 4- Phenylene diamine (0.5 g, 1 mmol) was stirred with pyrrole 2- carboxaldehyde (0.435 g, 1 mmol) in dry dichloromethane (DCM) at 25 °C for 20 h. The reaction mass was concentrated under vacuum. The residue was triturated with n-hexane and filtered. This solid was again triturated with DCM, filtered and dried to yield pure (**1**). (60% yield). ^{1}H NMR (δ ppm, 400 MHz, DMSO-d_6): 11.4 (1H, s), 8.3 (1H, s), 6.9–7.1 (3H, m), 6.3 (3H, m), 6.1 (1H, m), 5.0 (d, 2H) ^{13}C NMR (δ ppm, 100 MHz, DMSO-d_6): 149.5, 149.1, 130.7, 123.7, 121.5, 116.2, 109.6 IR (KBr, cm^{-1}): 3658, 3232, 3108, 2972, 3043, 2897, 2558, 2742, 2562, 2403, 1689, 1625, 1550, 1490, 1452, 1419, 1334, 1311, 1246, 1203, 1164, 1012 LCMS: m/z 262.9, 185.8.

Receptor **2**: (4-amino-3-nitrophenyl) [(1*E*)-1*H*-pyrrol-2-ylmethylene] Amine (**2**)

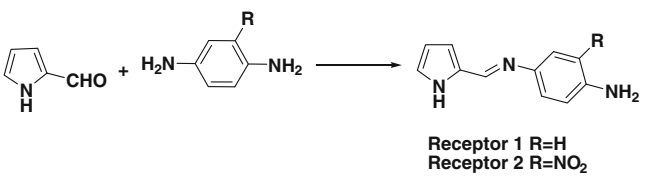
2- Nitro- 1, 4 -phenylene diamine (0.6 g, 1 mmol) was refluxed with pyrrole 2- carboxaldehyde (0.435 g, 1 mmol) in ethanol (10 ml) for 16 h. Reaction mixture was concentrated under vacuum and the residue was triturated with n-hexane. The residue was filtered and dried to yield pure (**2**) (73% yield) ^{1}H NMR (δ ppm, 400 MHz, DMSO-d_6): 11.6 (1H, s), 8.3 (1H, s), 7.7 (1H, d), 7.4 (3H, m) 7.0 (1H, d), 6.9 (1H, d), 6.6 (1H, d), 6.1 (1H, d). ^{13}C NMR (δ ppm, 100 MHz, DMSO-d_6): 148.6, 144.3, 140.0, 130.5, 130.1, 129.9, 123.6, 120.0, 116.0, 115.7, 109.6. IR (KBr, cm^{-1}): 3480, 3429, 3395, 3254, 3119, 2892, 1772, 1634, 1596, 1557, 1503, 1451, 1369, 1339, 1249, 1095 LCMS: m/z 231.0.

Results and Discussion

The receptors **1** and **2** were synthesized by Schiff base condensation of pyrrole −2- carboxaldehyde with 1, 4-phenylene diamine (receptor **1**) and 2-nitro-1, 4-phenylene diamine (receptor **2**) (Scheme 1). They were well characterized by IR, NMR spectroscopic methods before using them in sensor studies. In IR spectroscopy, the presence of C=N in the molecule is confirmed by the vibrations between 1690 and 1640 cm^{-1} and aromatic C=C stretching frequency between 1600 and 1473 cm^{-1}. NH stretching for receptor **1** and **2** was observed at 3541 $cm^{-1.}$ In ^{1}H NMR both the receptors showed a singlet at around δ 8.3–8.4 ppm corresponding to the CH=N proton indicating the formation of imine and the protons of pyrrole ring resonate in the δ 6.0–7.0 region. Aromatic (phenyl ring) protons were observed in the δ 7.0–7.7 ppm region including the NH_2 protons this confirms the formation of mono imine without any ambiguity, in addition the N-H proton of pyrrole ring is shown as a singlet at around δ 11.6–11.7 ppm. In the case of ^{13}C NMR spectroscopy CH=N carbon came as a sharp peak at δ 148–149 ppm. Mass spectral analysis confirms the molecular structure of the compounds synthesized without any ambiguity. M+1 (protonated molecular ion peak) clearly proved the complete formation of the Schiff bases. The complete data of all the compounds is given in the Experimental section.

Colorimetric Sensing Studies

The colorimetric sensing ability of receptors **1** and **2** with anions (F^-, Cl^-, Br^-, I^-, OH^-) was monitored by visual (naked eye), ^{1}H NMR, FT IR, UV–vis and fluorescence spectroscopic methods. Initially, 5.0×10^{-5} M solution of



Scheme 1 Synthesis of receptors **1** and **2**

the receptors **1** and **2** and 1.5×10^{-3} M solution of the tetrabutylammonium (TBA) salts of the respective anions were prepared in CH_3CN. In naked eye experiments, 200 μL (2 equivalent) of anion solution was added to the solutions of the receptors. Receptor **1** turned from colorless to yellow on the addition of F^- and OH^- ions and receptor **2** showed dramatic color change from yellow to permanganate color in presence of F^- and OH^- ions (Fig. 1a and b). Both receptors were found to be insensitive to the addition of large excess of Cl^-, Br^-, I^- ions. The color change is most probably due to formation of hydrogen bonds or deprotonation of receptor on the addition of fluoride and hydroxide ions. These hydrogen bonds or deprotonation affects the electronic properties of the chromophore, resulting in color change along with a new charge-transfer interaction between the anion bound NH and electron deficient nitro group [43, 44].

The presence of nitro group in the receptor **2** acts as an excellent signaling unit compared to the other receptor. In aprotic solvents, solutions of receptors **1** and **2** underwent a color change with fluoride and hydroxide ions; upon addition of few drops of a protic co-solvent (water, methanol etc.) the color disappeared. This is because protic solvents compete for fluoride ions with NH group. In most cases, fluoride ion is bound to the receptor through F^-…H-N (pyrrole) hydrogen bonding interactions (Fig. 2). The presence of excess of fluoride ion even causes deprotonation resulting in classical Bronsted acid base type reaction.

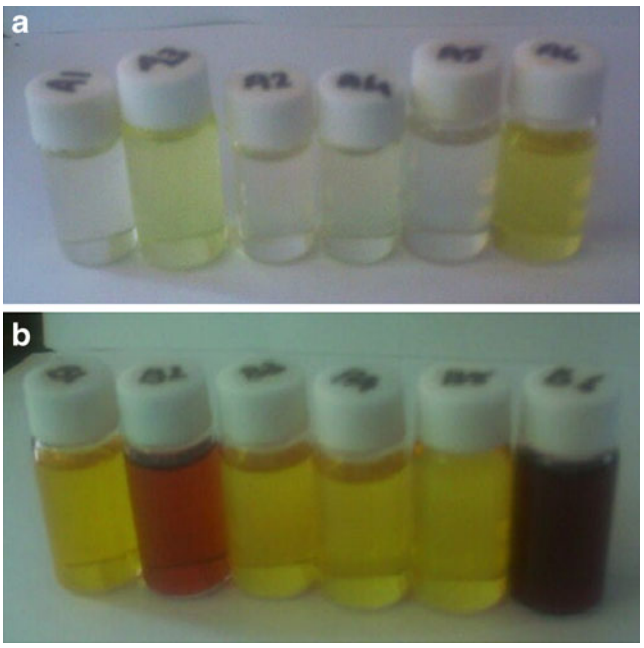


Fig. 1 **a** Colour changes of receptor **1** in acetonitrile before and after the addition of representative anions (from left to right R, R+F^-, R+Cl^-, R+Br^-, R+I^-, R+OH^-). **b** Colour changes of receptor **2** in acetonitrile before and after the addition of representative anions (from left to right R, R+F^-, R+Cl^-, R+Br^-, R+I^-, R+OH^-)

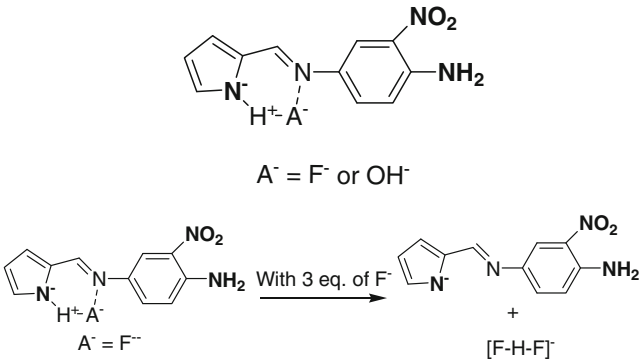


Fig. 2 The possible structure of the complex formed between receptor **2** and F^-/OH^- ion

NMR and IR Spectroscopic Studies

The binding ability of receptor **2** for fluoride and hydroxide ions was also evident in proton NMR titration experiments in DMSO-d_6 (Fig. 3). Before the addition of fluoride or hydroxide ions, proton NMR chemical shift of NH proton of receptor **2** was at 11.6 δ and imine proton was at 8.3 δ as sharp singlets. After addition of 100 μL (1 equivalent) of fluoride ions, the peak at 11.6 δ disappeared immediately, indicating the formation of hydrogen bonding interaction between the F^- ion and pyrrole NH group of the receptor. On further addition of more than 3 equivalents of fluoride ions, additional sharp triplet peak at δ 16 ppm appeared, which is due to the formation of HF^{2-} species (Fig. 2). Similar shifts were observed in the case of receptor **1** also (See Supporting information). In the case of hydroxide anion, due to the increased size and basicity of OH^- ion, charge was delocalized on the nearby CH=N moiety, which is evident from the drastic upfield shift of the CH=N proton and the disappearance of pyrrole NH proton. In the case of receptor **1** shifting to the greater extent was not observed and this may be due to the absence of the NO_2 substituent, which acts as an excellent signaling unit. There are two possible effects responsible for chemical shift changes in proton NMR upon the NH-F^- hydrogen complexation; (a) through bond effects, which would increase the electron density to cause upfield shifts and (b) through space effects, which would polarize the C-H bond proximal to the NH-fluoride moiety to induce a downfield shift due to partial positive charge developed on the N-proton. When more F^- ions are added, complete deprotonation might occur subsequently to form the anion, so that the through bond effect would predominate over the through-space effect.

To investigate hydrogen bonding ability of receptors **1** and **2**, FTIR spectral studies were carried out. The FTIR spectra of receptors **1** and **2** were recorded in the absence and presence of fluoride and hydroxide ions. The expected

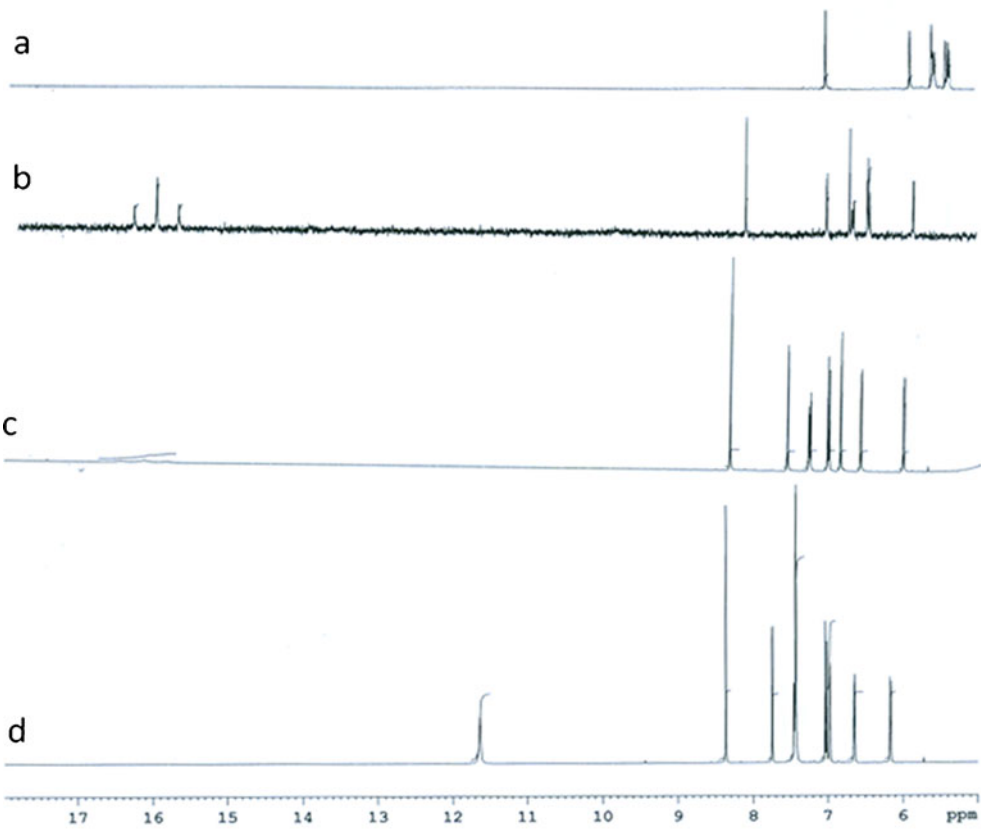


Fig. 3 ^{1}H NMR (DMSO-d6) spectra of the receptor **2** in presence of (**a**) 1 equiv., of tetramethyl ammonium hydroxide (**b**) 3 equiv., of TBAF (**c**) 1 equiv., of TBAF and (**d**) in the absence of anions

band for NH stretching for receptor **1** and **2** was observed at 3541 cm^{-1} in the absence of fluoride and hydroxide anions. A shift to around 3616 cm^{-1} in the spectrum was observed in the presence of nearly 1 equivalent of fluoride and hydroxide anion with receptor **2**. The shift might be due to the participation of the NH groups of the receptors in hydrogen bonding with fluoride ions [45, 46]. Only marginal shift was observed in the case of receptor **1**.

UV–vis Spectroscopic Studies

UV–vis spectroscopy was used to measure the absorption changes for the receptors **1** and **2** in the presence of F^- and OH^- ion. The spectroscopic titrations were carried out in acetonitrile medium at 5.0×10^{-5} M concentrations of receptors **1** and **2** upon incremental addition of 20μL (0.2 equiv) of 1.5×10^{-3} M solution of F^- ion and OH^- ions. 3 ml of 5.0×10^{-5} M receptor **1** was taken in the quartz cuvette and the increased amount of anions (20μL) tested was added to the solution. The electronic absorption spectra of the receptors **1** and **2** in the absence of anions show that π–π* transitions (maximum wavelength) for the compounds **1** and **2** are almost within 230–345 nm. Also there is an absorption band at 470 nm for receptor **2** in the visible region due to the coloured nature of the receptor **2**. However there is no band for receptor **1** in visible region due to its colorless nature. The absorption band at 230 nm is most probably due to the excitation of the π electrons of the aromatic system. The absorption band at 290–300 nm for receptor **1** and receptor **2** is mainly due to the transition between the π orbital localized on the azomethine group (C=N). The band in the region around 350 nm and 380 nm is due to existence of n- π* transition of azomethine group (C=N) for receptors **1** and **2** respectively.

After the addition of the F^- ion to the receptor **2** (Fig. 4), intensity of band at 450 nm and 380 nm decreased which is due to the hydrogen bonding interaction between the pyrrole NH and F^- ion. Intensity of band was gradually decreasing with increasing F^- concentration (Fig. 4 inset). Linearity of the sensing action was evident from the inset graph which is plotted against the changes of absorbance at 445 nm upon the addition of anion. Two isosbestic points were observed at 230 nm and 400 nm confirming the equilibrium existing between the receptor **2** and receptor **2**+F^- complex. Similarly, upon incremental addition of the OH^- ion to the receptor **2** (Fig. 5), a new band appears at 530 nm which is due to the formation hydrogen bonding between the receptor **2** and OH^- ion. For addition of 0-60μL (0–0.6 equivalents) of OH^- ion, intensity of the band at 300 nm was decreasing which can be attributed to

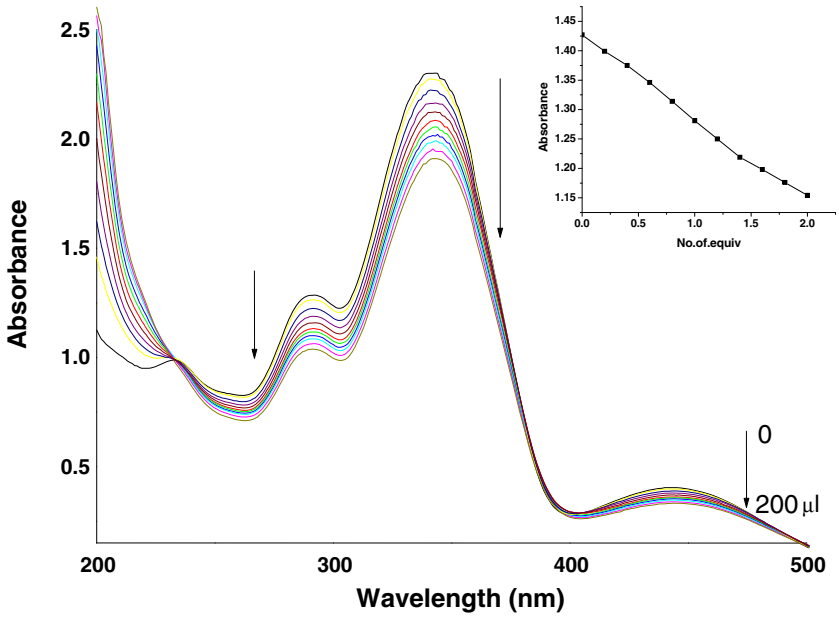


Fig. 4 Absorption spectrum of receptor **2** recorded in acetonitrile (5.0×10^{-5} M) after addition of 0–200 µl of tetrabutylammonium fluoride. (Inset: Changes of absorbance upon addition of F^- ion at 445 nm)

the [N-H——$^-$OH] interaction and further increased addition of (80–200 µL) of OH^- ion resulted in the complete deprotonation of the pyrrole NH which is evident from the reduced intensity (Fig. 5 inset) and red shift (upto 20 nm) of the 340 nm band. As a function of OH^- ion, a new red shifted absorption band centered at 530 nm increased with a concomitant decrease of the band at 450 nm. This can be attributed to the internal charge transfer (ICT) developed by the deprotonation of -NH in receptor **2**. From the UV–vis absorption measurements, the binding constant (K_{ass}) of the F^-, OH^- ion complexes of the receptor **2** was calculated. Benesi-Hildebrand (B-H) plot was used for the binding constant calculation. Plot can be made with $1/\Delta A$ as a function of $1/[H]_0$. $\Delta\varepsilon$ can be derived from the intercept while K_{app} can be calculated from the slope based on the linear least square fitting line. K_{app} was found to be 2.08×10^4 and 3.47×10^4 for receptor **2** with F^- and OH^- ion respectively**.** All the analysis were repeated many times and the results obtained are consistent in all the trials.

Similar titration studies were carried out for receptor **1**. After the addition of (0–200 µL) of F^- ions intensity of the peaks at 230 nm, 300 nm and 360 nm were decreasing and no new peaks were formed as in the case of receptor **2**

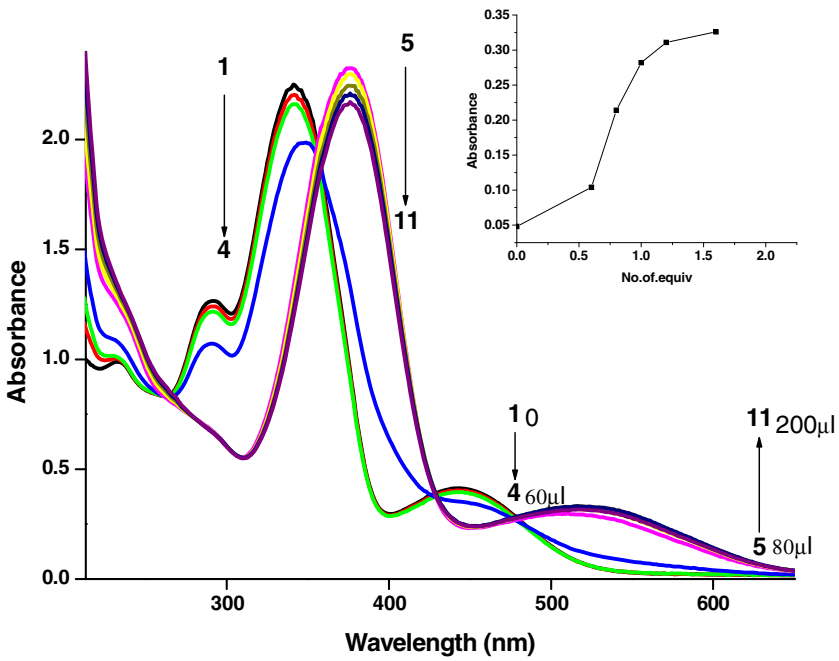


Fig. 5 Absorption spectrum of receptor **2** recorded in acetonitrile (5.0×10^{-5} M) after addition of 0–200 µl of tetrabutylammonium hydroxide. (Inset: Changes of absorbance upon addition of OH^- ion at 525 nm)

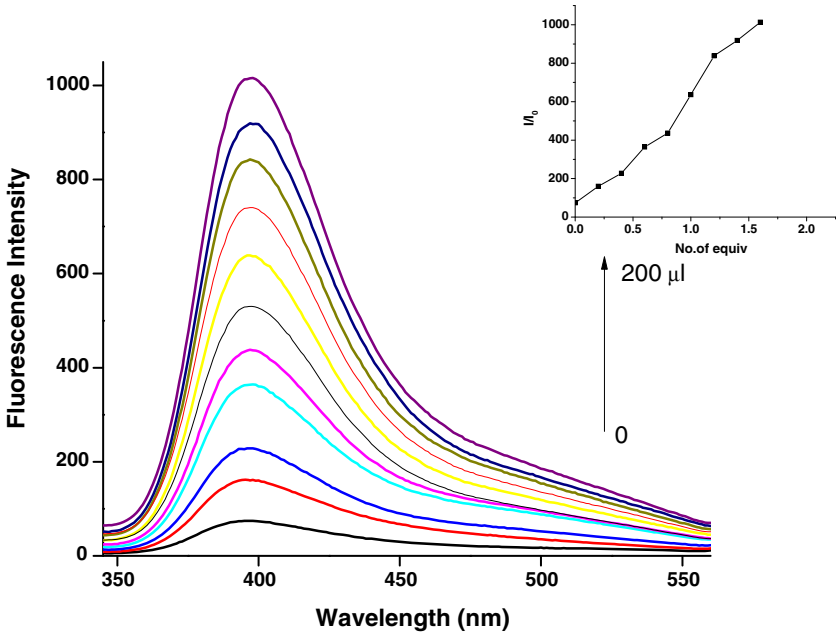


Fig. 6 Emission spectrum of receptor **2** (5.0×10^{-5} M) recorded in acetonitrile after addition of 0–200 µl of tetrabutylammonium fluoride. (Inset: Changes of fluorescence emission upon addition of F^- ion at 398 nm)

which can be attributed to the lesser acidity of the receptor **1** due to the absence of the NO_2 group in it. Similarly after the addition of OH^- ions, there was no band in the region of 530 nm and the extent of red shift was also marginal. This may be due to the absence of NO_2 group which reduces the acidity of pyrrole NH and the subsequent deprotonation in the presence of 2 equivalents of OH^- ion. Absence of new bands in the visible region could be the reason for the slight color change in the colorimetric analysis. K_{ass} was found to be 5.28×10^3 and 2.62×10^3 for receptor **1** with F^- and OH^- ion respectively. This confirms that the presence of nitro group in the receptor **2** acts as an excellent signaling unit compared to receptor **1** and exhibit stronger binding towards F^- and OH^- ions. (UV–vis absorption spectra for receptor **1** in presence of F^- and OH^- ions are given in Supporting information)

Fluorescence Spectroscopic Studies

In order to learn more about the sensing ability of the receptors, fluorescence measurements were carried out similar to UV-visible measurements. Both receptors were excited at 300 nm. At 5×10^{-5} M, the emission maximum of the receptor **2** was around 400 nm with diminished

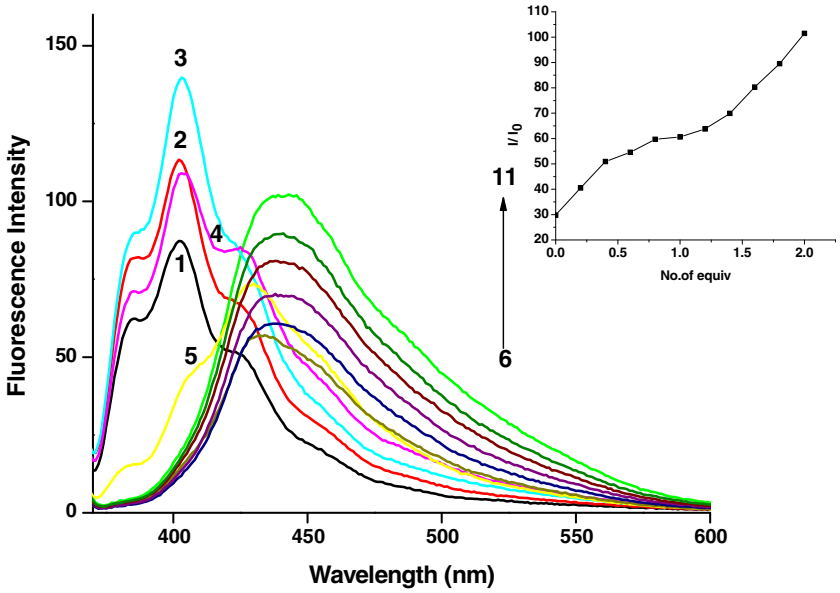


Fig. 7 Emission spectrum of receptor **2** (5.0×10^{-5} M) recorded in acetonitrile after addition of 0–200 µl of tetrabutylammonium hydroxide. (Inset: Changes of fluorescence emission upon addition of OH^- ion at 445 nm)

fluorescence intensity. However, the addition of fluoride anion to the receptor **2** markedly enhances the emission intensity as shown in Fig. 6. Upon addition of 20μL of fluoride anion to the receptor **2**, shows emission maximum at 390 nm in acetonitrile solution, whereas no emission was observed with other anions like chloride, bromide and iodide. Further, the emission intensity at 398 nm band was gradually increasing with the increasing F^- concentration with marginal changes in their emission maxima (Fig. 6 inset). This observed enhancement in the fluorescent intensity upon addition of fluoride ion may be due to the formation of intermolecular hydrogen bond (−NH—F), which promotes the delocalization of π electrons through CH=N functionality and makes the radiative decay from the excited state more probable. Whereas in the case of hydroxide ion after the incremental addition of OH^- ions the initial broad emission around 400 nm with lesser intensity tends to increase (Fig. 7). With increased concentration of OH^- ions red shift takes place and a new emission maxima centered at around 450 nm appears which can be attributed to the anionic form of the pyrrole confirming the deprotonation taking place with increased concentration of OH^- ion this observation is also supported from the literature [37].

Similar studies were also carried out with receptor **1** (for fluorescence spectra see Supporting information). Receptor **1** showed broad emission around 430 nm with less fluorescence intensity. Upon addition of 0–2 equivalents of F^- ion the emission intensity increases without any substantial changes in their emission maxima. In the case of OH^- ion addition to the receptor **1** the initial emission maxima at 430 nm was quenched when 0–0.6 equivalents was added. Upon the subsequent addition of OH^- ion (0.8–2.0 eq) a new emission maximum was observed at 490 nm with a red shift. The quenching effect after the formation of the anion bound receptor can be attributed to the anion to the receptor electron transfer. The enhanced red shift occurred in the case of OH^- ion can be ascribed to the increased basicity of the OH^- compared to F^- ion.

Among the two receptors, receptor **2** showed maximum sensitivity to the anion which may due to the presence of strong electron withdrawing substituent (−NO_2). The reason for fluorescence enhancement in presence of nitro group may be explained on the basis of electron transfer mechanism as follows: It has generally been recognized that emission was usually accompanied by the delocalization of the electrons within the molecules. In the case of pyrrole based Schiff base receptors the excited state of the fluorophore was primarily quenched by reduced electron transfer from receptor (pyrrole -NH) to the fluorophore (−C=N) unit. However, upon interaction with anions, the electron transfer from the electron rich –NH moiety bonded with anion to the electron deficient –NO_2 became more feasible and hence fluorescence enhancement was observed. Upon further addition of anion it appeared that the deprotonated species being more electron rich compared to the hydrogen bonded complex with anion, undergo very fast electron transfer and showed up greater fluorescence enhancement. There is a red shift and an enhancement in the fluorescence intensity upon the addition of guest anions F^- and OH^-. It is worth mentioning that for a strong hydrogen bonding configuration in polar solvent like CH_3CN intermolecular excited state proton transfer takes place for indole type chromophores [47]. Thus similar mechanism can operate in the present case of pyrrole based receptor **2** leading to ion pair formation. Thus, it is logical to expect for an increase in acidity of receptor **2** upon electronic excitation in the anion bound complex, such that proton transfer might take place from 2 to OH^- to account for the anion emission at 450 nm.

Conclusion

In conclusion, highly anion sensitive chemosensors **1** and **2** were designed and used for the F^- and OH^- ions detection. Chromogenic receptors **1** and **2** were synthesized in good yields via Schiff base condensation. Receptors **1** and **2** became yellow and permanganate colored upon addition of F^- and OH^- ions respectively. Receptor **2** shows predominant color change than receptor **1** due to the presence of NO_2 group, which acts as a chromogenic signaling unit. Both the receptors are excellent colorimetric and fluorescent sensors for F^- and OH^-ions. This is further supported by the binding constant values.

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