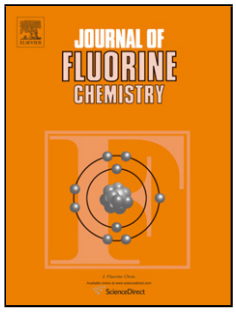

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Synthesis and anion binding studies of azo-schiff bases: selective colorimetric fluoride and acetate ion sensors

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Highlights

Receptor 1 and 2 has been synthesized by a two step procedure and characterized.

Receptors has Azo as signaling unit and hydroxyl group as the binding unit.

Selectively senses fluoride and acetate over other halide ions in stoichiometry of 1:1.

Abstract

Two artificial colorimetric sensors 4-[(*E*)-phenyldiazenyl]-2-[(*E*)-(phenylimino)methyl]phenol and 2-{(*E*)-[(4-nitrophenyl)imino]methyl}-4-[(*E*)-phenyldiazenyl]phenol has been synthesized

by a two step procedure and characterized. The interactions of these receptors with halide ions are determined by colorimetric, UV-vis and NMR studies. Due to the presence of hydroxyl moiety as binding site in receptors **1, 2** and nitro group as a signaling unit in receptor **2**, both system displays excellent selectivity and sensitivity for fluoride and acetate ions with intense yellow and red color changes. The sensors changes its color obviously on addition of the fluoride and acetate ion and that makes the naked-eye recognition in CH_3CN solution come true.

Key words: Azo-schiff Bases, naked eye sensing, F^- and AcO^- sensors, UV-vis spectroscopy, binding constant study.

1. Introduction

Because of anion's crucial role in the biological fields, medical systems and environmental science a great deal of work has been focused on the design and synthesis of the selective receptors for anions in the past two decades. As a result, anion recognition has been developed into a fastest growing branch of supramolecular chemistry [1-2]. Among all the anions, fluoride ion [3-5] is the biologically active ion and acts as a frequent constituent in most of the drug molecules and used for the treatment of hypnotics, anesthetics, psychiatric drugs and cockroach poisons. When the fluoride ion exceeds from its normal level it may cause diseases like flourosis, thyroid activity depression, bone disorders and also contamination can occur in

drinking water [6-8]. Similarly acetate ions [9-11] also play an important role and it is present in living system as acetyl coenzyme A. Sodium acetate is used as main ingredient in some medicines and involves in biological process like enzyme metabolism. Also the production of acetic acid from fermentation process is the main component present in vinegar used in foods. Accordingly, how to effectively recognize and sense anions through the naked eye, electrochemistry and/or optical responses have attracted considerable attention [12-14]. Generally speaking, colorimetric chemosensor are made up of two main fragments, which involve the binding sites that interact with anions either electrostatically or through hydrogen bonding, etc., and the signal parts that connect to the binding sites either directly or intramolecularly linked which show the color changes [15-18] in the anion recognition procession. With regard to the binding sites, the functional groups such as imine [19], urea [20], thiourea [21], amide [22], pyrrole (NH) [23], imidazolium [24], hydrazones [25] and hydroxyl groups [26] are numerously used owing to their capacity to perform as hydrogen donors. Otherwise, if taking advantage of the electrostatic interaction, the quartenized nitrogen [27] and positively charged pyridine [28] may be firstly chosen as binding sites. However, among the colorimetric and optical parts of the receptors for the anion sensing, simplicity and high selectivity [29-30] are still challenges for investigators and they attract much interests. In particular, to develop the naked-eye detection technique for the analytes without using any expensive equipment is of great interest in recent years. Azophenyl as the optical group has been less explored as the functional group of the sensor molecules in the literature [31-32].

In this paper, we designed and synthesized new and simple anion receptors **1, 2** contains both hydrogen-bond-donor group (phenolic –OH and imine) as well as chromogenic unit (azophenyl) and studied its anion recognition behaviors towards biologically important fluoride

and acetate ions over other anions with high selectivity. The recognition is found by forming the hydrogen bonding at charge-neutral sites. In addition, the sensing processes can be realized by the 'naked-eye' determination as it has a remarkable color response.

2. Results and discussion

Both the receptors **1** and **2** were synthesized by simple condensation reactions between aldehyde and amine. The structure of the receptors **1** and **2** were proved by FTIR, ^{1}H and ^{13}C NMR spectroscopic methods. In the FT-IR spectroscopy we get information about the presence of functional groups in the compound such as C=C, CH=N etc by the position of absorption peaks which arise due to stretching vibration of the bonds in the groups. The presence of CH=N in the molecule is confirmed by the vibrations between 1690-1640 cm^{-1} and aromatic C=C between 1600-1473 cm^{-1}in the FT-IR spectrum. In ^{1}H NMR (Fig 2a, 3a) both the receptors showed a singlet at around δ 9.2 ppm corresponding to the CH=N proton indicating the formation of imine and the aromatic protons resonate in the δ 7-8.3 ppm region. The peak around δ 13-14 ppm indicates OH proton. It was found that In the case of ^{13}C NMR spectroscopy CH=N carbon came as a sharp peak at δ 145-147ppm. Mass spectral analysis confirms the molecular structure of the compounds synthesized without any ambiguity. M+1 (protonated molecular ion peak) clearly proves the complete formation of the azo-Schiff bases. We investigated the interactions of fluoride ion towards receptors 1 and 2 in the ground state by running proton NMR titrations both in absence and presence of fluoride ion. Generally, the interaction between the receptor and anions could be explained on the basis of up field shift in aromatic, imine protons and downfield shift in OH protons. Two main effects occurred in OH proton of receptor in the presence of anions are hydrogen bonding and deprotonation effects.

2.1. ^{1}H NMR spectroscopic studies

We investigated the interactions of fluoride ion towards receptors **1** and **2** in the ground state by running ^{1}H NMR titrations both in absence and presence of fluoride ion. Generally, the interaction between the receptor and anions could be explained on the basis of up field shift in aromatic, imine protons and downfield shift in OH protons. Two main effects occurred in OH proton of receptor in the presence of anions are hydrogen bonding and deprotonation effects.

In ^{1}H NMR spectral titration curves of the receptor **1**, the peak at 13.85 ppm, assigned to OH group, disappears with the addition of 0-2 equiv. of fluoride ion (Fig. 1). The hydroxyl group was completely deprotonated even with 0.5 equiv. of fluoride ion and a new triplet signal appeared at 15.7-16.4 ppm indicating the formation of HF_2^- complex. Unlike receptors containing electron withdrawing group, in azo linked receptor systems the acidity will be enhanced by azophenyl unit. Y.Li et.al [33] reported azo based phenyl hydrazone as anion receptor and the proton of OH group is getting deprotonated with the addition of 0.4 equiv. of acetate ion. Similarly J. Shao et.al [34] reported the deprotonation of OH by fluoride ion with 0.5 equiv. and form a HF_2^- complex in azo based thiosemicarbazone. Hence the presence of azophenyl unit in receptor **1** will enhance the acidity of OH proton and the deprotonation is mainly occurred at 0.5 equiv. of F^- ion. Consequently up field shift was observed for imine and phenyl rings protons due to the increase in the electron density around aromatic system. In case of receptor **2** also, the similar shifts were observed in presence of 0-2 equiv. of fluoride ion (Fig. 2). Because, the presence of NO_2 group in receptor **2** is just acting as signaling unit which is not responsible for the increasing the acidity of OH group in receptor **2**. These observations clearly support that anion recognition by both receptor **1, 2** underwent through the deprotonation of the hydroxyl group proton induced by the fluoride anion. In addition OH^- also involves in the

deprotonation of OH group in receptor **1, 2** due to the similar basicity as F^- ion in ^1H NMR (Fig. 3, 4). But the distinct color and UV-vis changes were not observed with OH^- ion due to the size of OH^- ion is not adoptable to bind with receptors.

2.2 Colorimetric and UV-vis studies

The anion binding properties of the synthesized receptor **1** and **2** were investigated by naked eye analysis and UV–vis titrations at room temperature in CH_3CN solution. The color change was visualized by naked eye observation and optical response was studied by UV-vis spectroscopy. In the naked eye experiments, visual inspection of receptor **1** and **2** ($5x10^{-5}$ M in CH_3CN) showed dramatic color change from light yellow to intense yellow for receptor **1** and dark red for receptor **2** with the addition of 2 equiv. of F^- and AcO^- ions ($1.5x10^{-3}$ M) (Fig. 5, 6).

In order to have a deeper understanding of the binding action, UV-vis spectral studies were carried out. As we gradually added the F^- ion into the solution of receptors **1** and **2** ($1.5x10^{-3}$ M), the absorbance bond centered at 353 nm, ascribed to the charge- transfer in the molecule [35], diminished little by little accompanied with a new band generated at 450 nm, suggesting the formation of the complex between receptor **1** and fluoride ion. The color change from light yellow to intense yellow and red could be easily detected by the naked eye. Similar changes in the colorimetric from light yellow to intense yellow for receptor **1** and red color for receptor **2** were observed with the addition of 2 equiv. of AcO^- ion. Consequently, the formation of a new band at 450 nm in the UV-vis spectrum was also observed with the addition of 2 equiv. of AcO^- ion. On the contrary, the addition of excess amount of other anions like Cl^-, Br^-, OH^-, and $H_2PO_4^-$ into the solution of receptors **1** and **2** did not show considerable result in any visible spectrum

responses. There was a well-defined isosbestic point at 390 nm in all cases, which indicated the presence of only one type of host–F^-/AcO^- ion complexes (Fig. 7, 8).

From the UV-vis absorption measurements, the binding constant of the anion complexes of two receptors were calculated using Benesi- Hildebrand (B-H) plot. F^-/AcO^- complexes of receptor **1** were (4.996±0.36) $x10^3$, (2.793±0.25) $x10^3$ and F^-/AcO^- complexes of receptor **2** were (3.206±0.05) $x10^4$ and (2.538±0.34) $x10^4$ respectively. The Job's plot (Fig. 9a, 9b) gives a stoichiometry of 1:1 for both F^-/ AcO^- ion complexes of receptor **1** and **2**.

A full understanding of the principles that govern anion recognition has not yet been achieved, it already becomes clear early on that the selectivity for special anions can be rationalized on the basis of guest basicity and shape complementarities between host and anionic guests. Actually, it is necessary that the sensor possesses the multiple hydrogen-bonding interaction offering the high-affinity anion binding sites. In particular, the best selective recognition for F^- and AcO^- ions was most likely due to its best complementarily between the anions and receptors among the anions tested.

3. Conclusion

In summary, simple azo based colorimetric receptors **1** and **2** were successfully synthesized in high yields. Azophenyl unit was treated as a signaling unit and hydroxyl group acted as the binding sites of framework related to receptor **1** and **2** that could detect F^- and AcO^- ions selectively over other anions confirmed by colorimetric and UV-vis spectroscopic methods. The binding affinity of the receptors **1, 2** and 1:1 stoichiometry of the host-guest complex was calculated from B-H plot and Job's plot. The yield of the reactions is good which is an important aspect of commercial scale along with the simplicity of the synthesis scheme.

4. Experimental Section

4.1 Materials and Methods

All reagents for synthesis obtained commercially were used without further purification. In the titration experiments, all anions were added in the form of tetrabutylammonium (TBA) salts, which were purchased from Sigma-Aldrich Chemical, stored in a vacuum desiccator containing self-indicating silica. The cations were added in the form of bivalent salts. 1H NMR spectra were recorded on a Bruker 400 MHz spectrometer in DMSO-d_6. FT-IR spectra were measured on a Perkin-Elmer Spectrum One FT-IR spectrometer using KBr plates. UV- vis and Fluorescence spectra were recorded in 1 cm path length quartz cell on a Shimadzu UV-2600 spectrophotometer and Shimadzu RF-5301 PC spectrofluorophotometer respectively.

A $5x10^{-5}$ M solution of receptors was made up with HPLC grade acetonitrile (CH_3CN) solvent. UV-vis absorption titrations were carried out by adding 0.2 equiv. aliquots of the titrant as tetrabutyl ammonium (TBA) halides ($1.5x10^{-3}$ M) in CH_3CN. The UV-vis spectra were recorded after each addition. All reactions were carried out in the atmosphere of purified nitrogen. They were well characterized by LCMS, NMR spectroscopic methods before using them in sensor studies.

4.2 General experimental procedure for the synthesis of the receptors

The intermediate for the receptors **1** and **2** were synthesized according to a reported method [36] To a solution of aniline (5ml; 0.05 mol) in 5ml of water, was slowly added, 6 ml of 37 % aq. HCl solution at 0-5 °C with stirring. 20 ml of 20 % aq. $NaNO_2$ solution was added to the mixture and resulting solution was stirred for 1h, affording a bright yellow solution. Salicylaldehyde (5 ml; 0.05 mol) was dissolved in a solution comprising 18 g Na_2CO_3 and 150 ml water and the

resulting solution of salicylaldehyde was added dropwise to the bright yellow colored solution over 1h. After stirring for 4h, the reaction mixture was neutralized with HCl, the brown crude solid was filtered and recrystallized from ethanol to afford pure yellow product. Mp.120°C. The solid isolated was used to synthesize two sensors by stirring with Aniline (1 mol, Receptor **1**) and nitro aniline (1 mol. Receptor 2) respectively in ethanol for 24 h. The solids are filtered and then recrystallised from n-hexane (Fig. 10).

Receptor **1:** (4-((E)-phenyldiazenyl)-2-((E)-(phenylimino)methyl)phenol)

Yield: 76%. IR (KBr pellets, (cm^{-1}): 3445, 3052, 1620, 1594, 1572, 1495, 1485, 1430, 1348, 1286,1184. ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.8 (s, 1H, OH), 9.2 (s, 1H, CH=N), 8.3 (s, 1H, Ar), 8.0 (d, 1H, Ar), 7.8 (d, 2H, Ar), 7.4-7.6 (m, 7H, Ar), 7.3 (m, 1H, Ar), 7.1(d, 1H, Ar). ^{13}C NMR (100 MHz, DMSO-d_6): δ 164.5, 163, 152, 148, 145,132, 130, 130, 129, 128, 128, 123, 122, 120, 118. LCMS: Calcd: 301.3, Found: 301.5.

Receptor **2:** (2-((E)-(4-nitrophenylimino)methyl)-4-((E)-phenyldiazenyl)phenol)

Yield: 67%. IR (KBr pellets, (cm^{-1}): 3465, 3074, 1617, 1603, 1590, 1518, 1486,1343. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.8 (s, 1H, OH), 9.1 (s, 1H, CH=N), 8.4 (s, 1H, Ar), 8.3 (d, 2H, Ar), 8.1 (d, 1H, Ar), 7.8 (d, 2H, Ar), 7.5-7.6 (m, 5H, Ar), 7.2 (d, 1H, Ar). ^{13}C NMR (100 MHz, DMSO-d_6): δ 165, 163, 154, 152, 145, 131, 130, 129, 128, 127, 125, 120, 118, 117, 112. LCMS: Calcd: 346.3, Found: 347.2.

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List of Figure Captions.

Fig. 1. ^{1}H NMR spectra of receptor **1** in the recorded on a Bruker 400 MHz spectrometer in DMSO-d_6. (a) Free receptor **1**, (b) 0.5 equiv, (c) 1 equiv, (d) 1.5 equiv, (e) 2 equiv of F^- ion.

Fig. 2. ^{1}H NMR spectra of receptor **2** in the recorded on a Bruker 400 MHz spectrometer in DMSO-d_6. (a) Free receptor **2**, (b) 0.5 equiv, (c) 1 equiv, (d) 1.5 equiv, (e) 2 equiv of F^- ion.

Fig. 3. ^{1}H NMR spectra of receptor **1** in the (a) absence and (b) presence of 2 equiv. OH^- ion recorded on a Bruker 400 MHz spectrometer in DMSO-d_6.

Fig. 4. ^{1}H NMR spectra of receptor **2** in the (a) absence and (b) presence of 2 equiv. OH^- ion recorded on a Bruker 400 MHz spectrometer in DMSO-d_6.

Fig. 5. Color changes of receptor **1** ($5x10^{-5}$ M in CH_3CN) on addition of 2 equiv. of various anions ($1.5x10^{-3}$ M in CH_3CN): R1, R1+F^-, R1+Cl^-, R1+Br^-, R1+AcO^-, R1+$H_2PO_4^-$ and R1+OH^-.

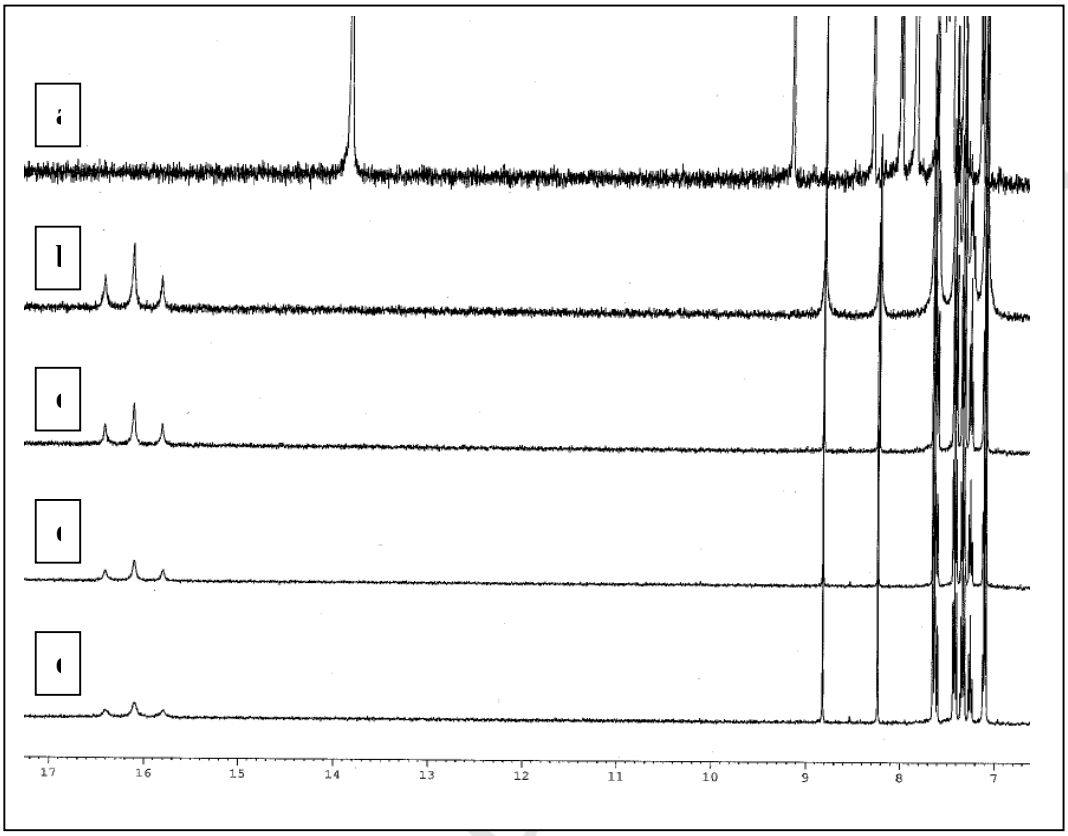
Fig. 6. Color changes of receptor **2** ($5x10^{-5}$ M in CH_3CN) on addition of 2 equiv. of various anions ($1.5x10^{-3}$ M in CH_3CN): R1, R1+F^-, R1+Cl^-, R1+Br^-, R1+AcO^-, R1+$H_2PO_4^-$ and R1+OH^-.

Fig. 7. UV-vis titration spectra of receptor **1** ($5x10^{-5}$ M in CH_3CN) on gradual addition of 2 equiv. of (a) fluoride and (b) acetate ions ($1.5x10^{-3}$ M in CH_3CN).

Fig. 8. UV-vis titration spectra of receptor **2** ($5x10^{-5}$ M in CH_3CN) on gradual addition of 2 equiv. of (a) fluoride and (b) acetate ions ($1.5x10^{-3}$ M in CH_3CN).

Fig. 9. Job's plot for receptor (a) **1**and (b) **2**.

Fig. 10. Synthesis of receptors **1** and **2.**



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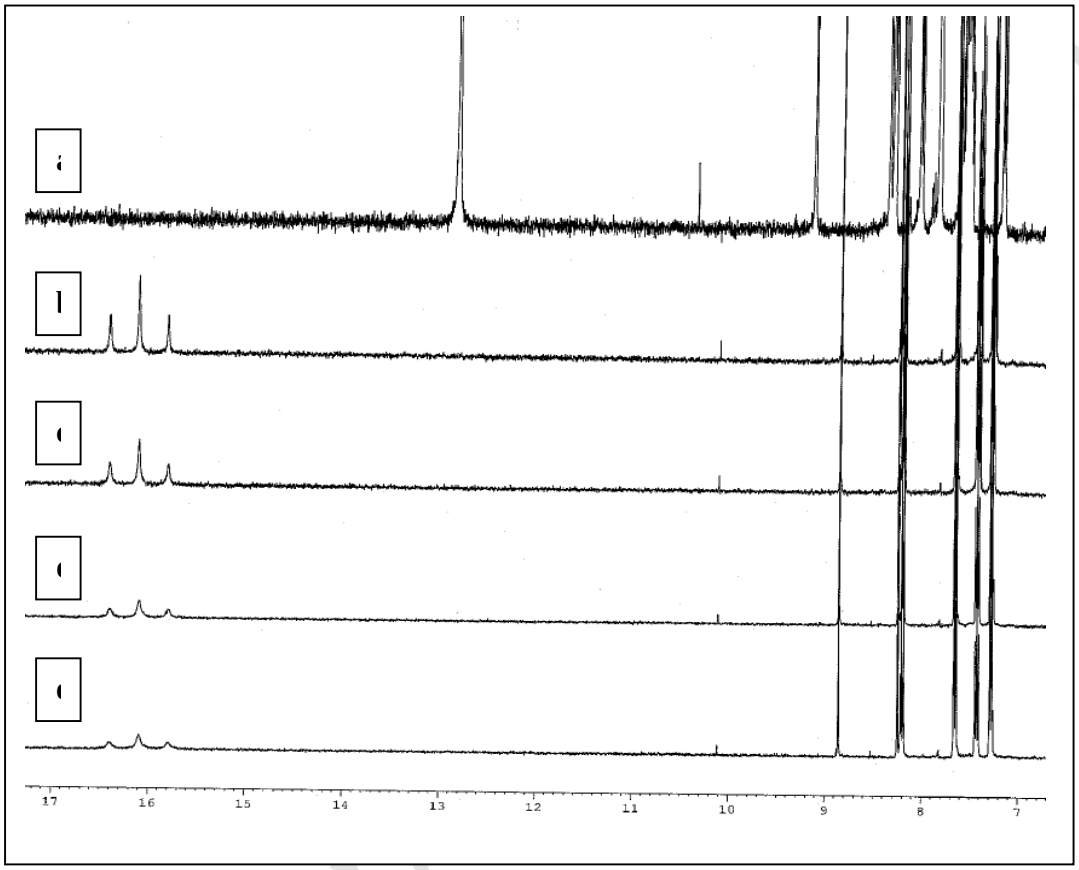


Fig. 2. ^{1}H NMR spectra of receptor **2** in the recorded on a Bruker 400 MHz spectrometer in DMSO-d_6. (a) Free receptor **2**, (b) 0.5 equiv, (c) 1 equiv, (d) 1.5 equiv, (e) 2 equiv of F^- ion.

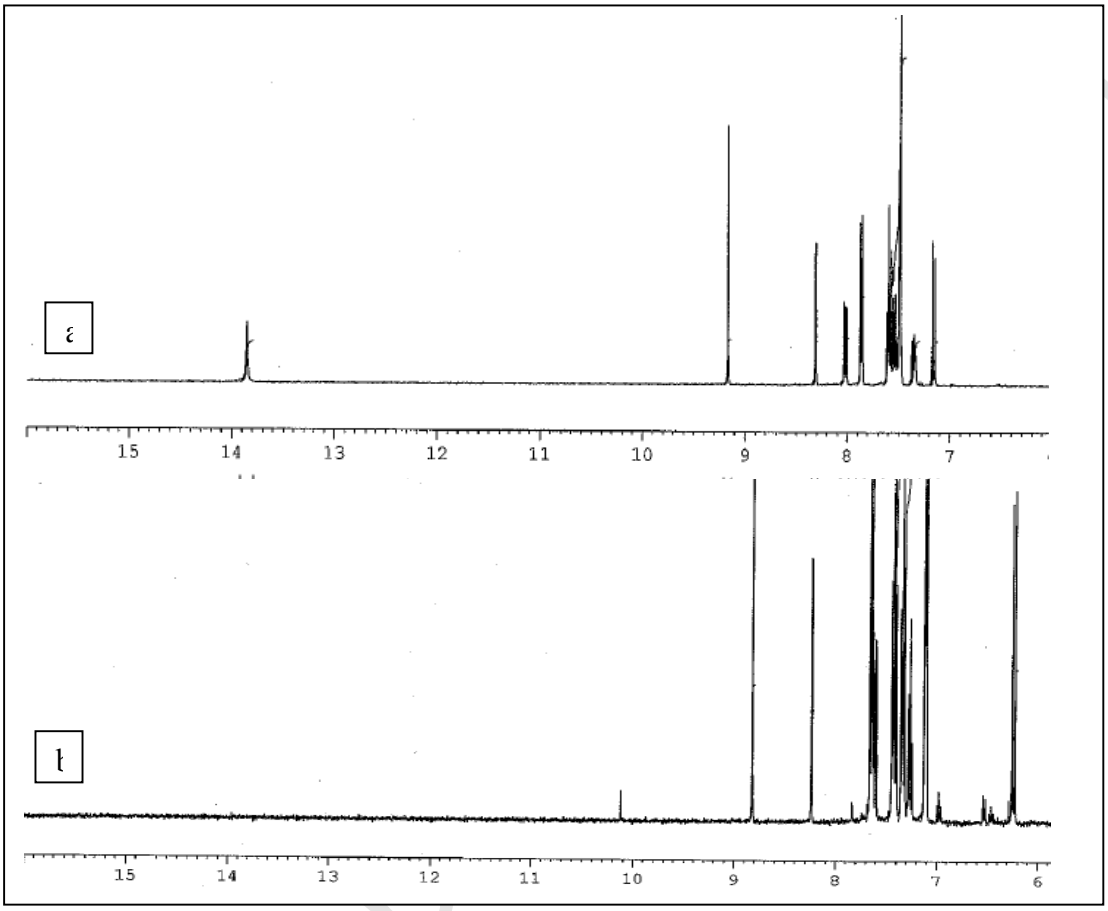
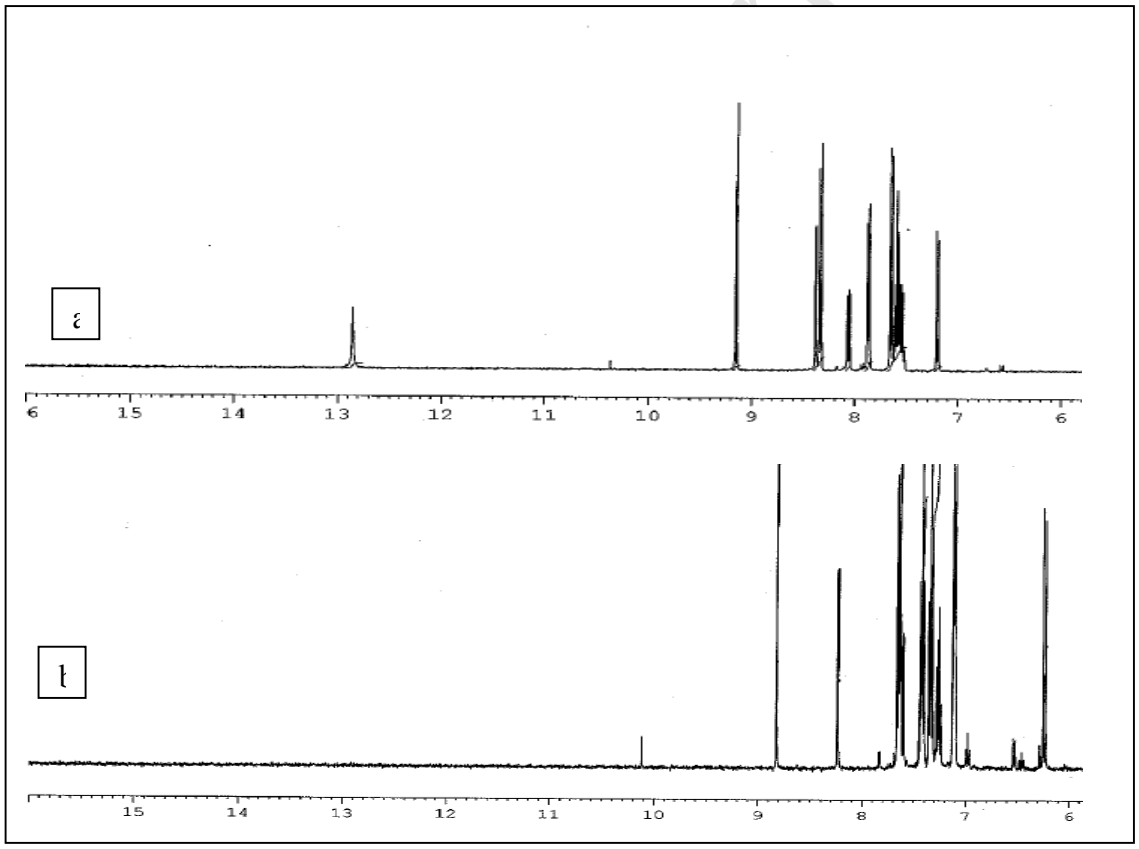


Fig. 3. ^{1}H NMR spectra of receptor **1** in the (a) absence and (b) presence of 2 equiv. OH^- ion recorded on a Bruker 400 MHz spectrometer in DMSO-d_6.



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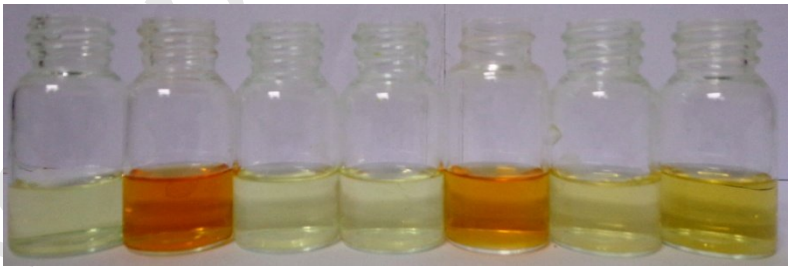

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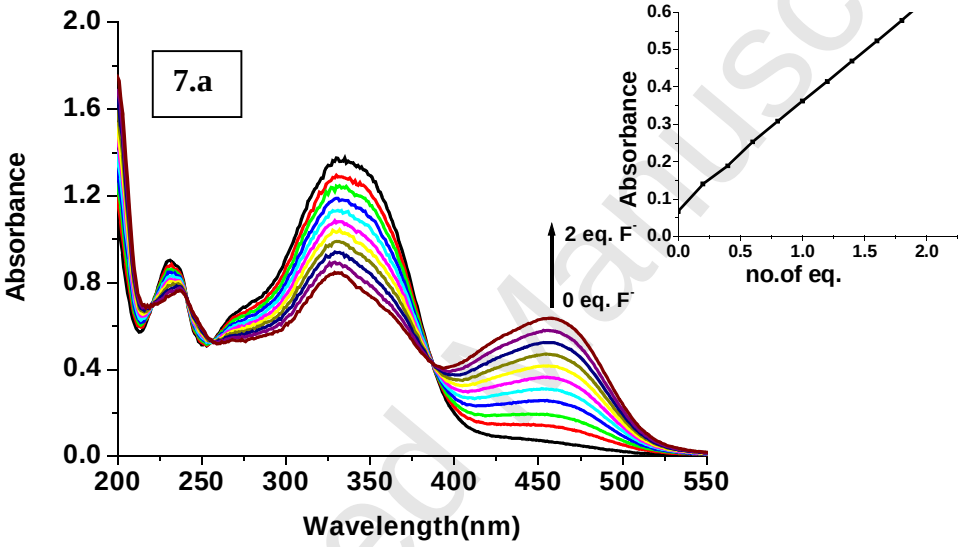


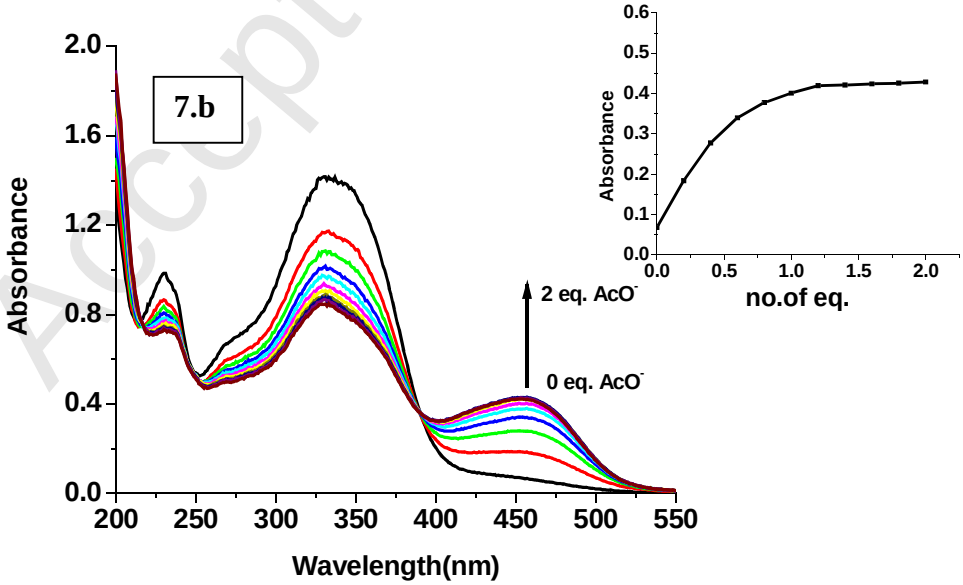


Fig. 7. UV-vis titration spectra of receptor **1** ($5x10^{-5}$ M in CH_3CN) on gradual addition of 2 equiv. of (a) fluoride and (b) acetate ions ($1.5x10^{-3}$ M in CH_3CN)

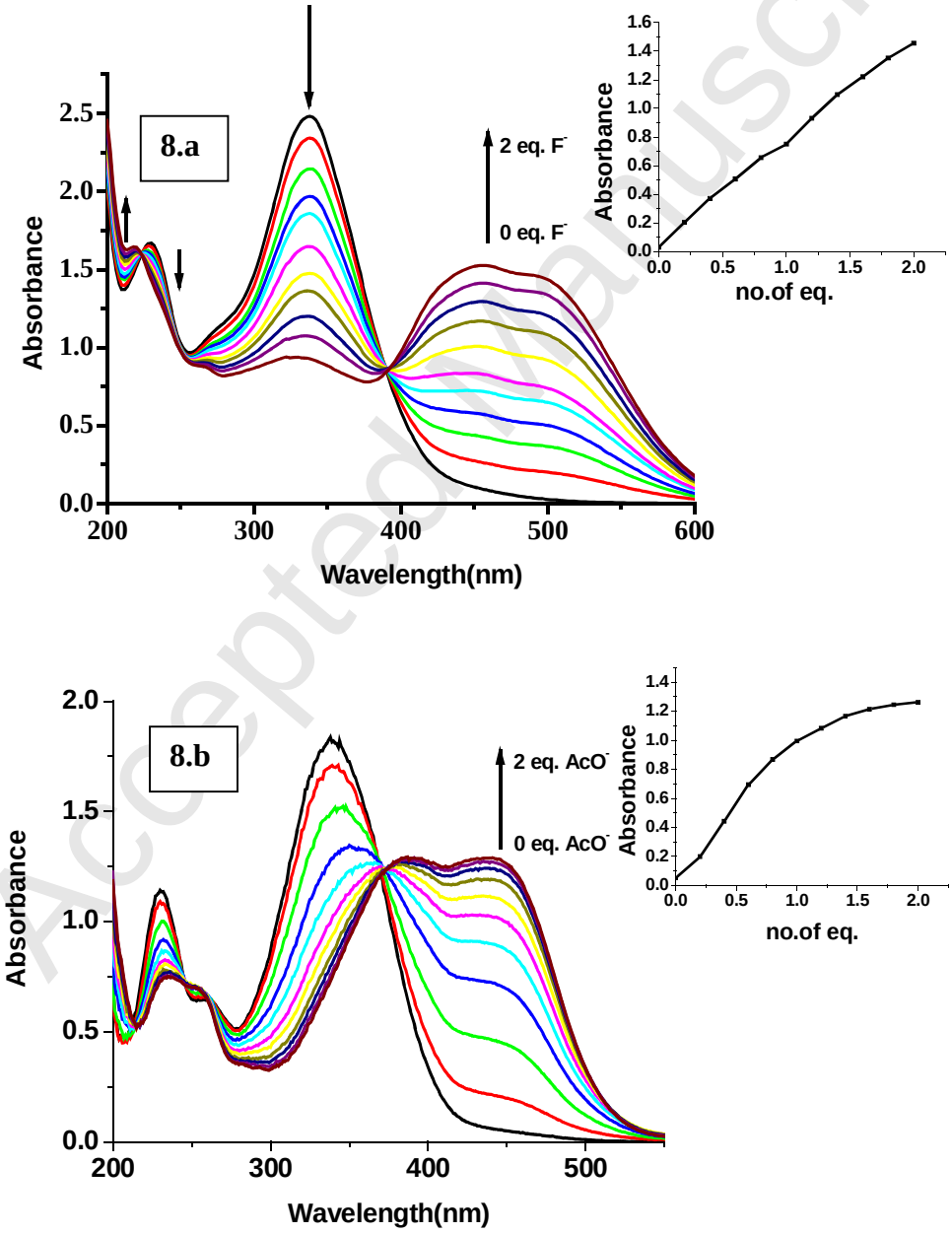


Fig. 8. UV-vis titration spectra of receptor **2** ($5x10^{-5}$ M in CH_3CN) on gradual addition of 2 equiv. of (a) fluoride and (b) acetate ions ($1.5x10^{-3}$ M in CH_3CN)

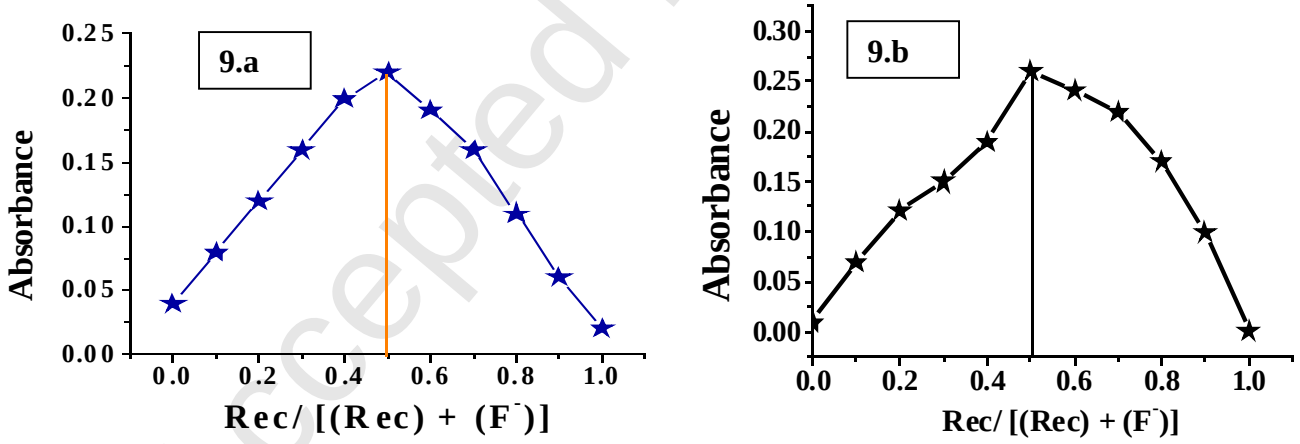
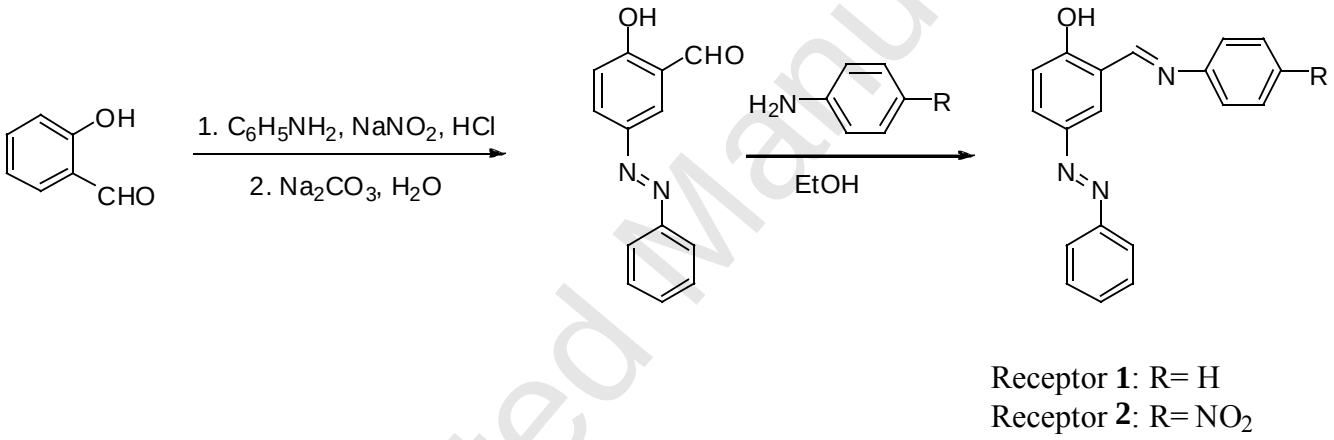


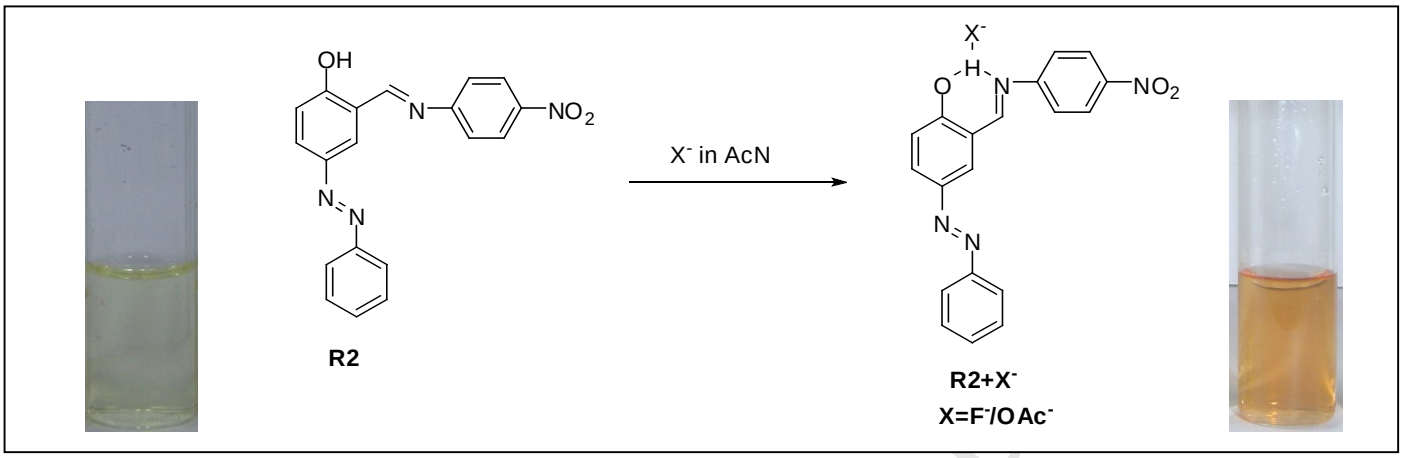
Fig. 9. Job's plot for F^- complex of receptor (a) **1** and (b) **2**



Receptor **1**: R= H
Receptor **2**: R= NO_2

Fig. 10. Synthesis of receptors **1** and **2**

Graphical Abstract



Graphical abstract

Two artificial colorimetric sensors 4-[(E)-phenyldiazenyl]-2-[(E)-(phenylimino)methyl]phenol and 2-{(E)-[(4-nitrophenyl)imino]methyl}-4-[(E)-phenyldiazenyl]phenol has been synthesized by a two step procedure and characterized. The interactions of these receptors with anions are determined by colorimetric, UV-vis and NMR studies. Due to the presence of hydroxyl moiety as binding site in receptor 1, 2 and nitro group as a signaling unit in receptor 2, both system displays excellent selectivity and sensitivity for fluoride and acetate ions with intense yellow and red color changes. The sensors changes its color obviously on addition of the fluoride and acetate ion and that makes the naked-eye recognition in CH_3CN solution come true.