

'Naked-eye' detection of fluoride and acetate anions by using simple and efficient urea and thiourea based colorimetric sensors



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HIGHLIGHTS

- Novel urea and thiourea-based on colorimetric sensors were synthesized.
- These sensors were characterized with ^1H , ^{13}C , APT, COSY NMR, FTIR, elemental, UV–vis data.
- It was found that the receptors are highly selective toward fluoride and acetate anions.

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ABSTRACT

Simple and efficient sensors 1 and 2 possessing azo and nitrophenyl as signaling units and urea and thiourea moieties as binding sites were designed and synthesized. These sensors were characterized by combination of ^1H , ^{13}C , APT, COSY NMR, FTIR, elemental analysis, and UV–vis spectral data. The interaction and colorimetric sensing properties of receptor 1 and 2 with different anions were investigated by the naked eye, as well as UV–visible and ^1H NMR experiments. It was found that the receptor 1 and 2 are highly selective toward fluoride and acetate anions in CHCl_3 .

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1. Introduction

The selective recognition and sensing of anions via artificial organic chemosensor molecule/probe, containing a suitable receptor site, have attracted considerable attention for chemists in past decades [1]. Anions play significant roles in chemical, environmental and biochemical processes [2–8], hence their recognition is important. The development of simple receptors capable of recognizing biologically relevant anions such as fluoride, chloride, phosphate, and carboxylate has attracted considerable interest [9]. The design of these receptors has focused on the ability to recognize and sense selectively biologically important anions through naked eye, electrochemical and optical responses [10]. The incorporation of fluorescent chromophores into receptors has gained considerable attention owing to their high sensitivities and easy detection [11]. The investigation of anion-selective receptors based on colored chromophores is also studied [12]. In particular, the development of colorimetric anion sensing is important and useful since it allows so-called 'naked-eye' detection of anions without the use

of any spectroscopic instrumentation. Such receptors would be more valuable if they could be obtained by a simple synthetic method [13].

One successful approach for preparing chromogenic sensors involves the formation of molecular architectures, which contain one or more optical-signaling chromophoric groups that are covalently or noncovalently linked to the receptor moiety, and thus colorimetric sensing of anions with both temporal and spatial resolution would be achieved. Hydrogen-bonding sites used in chromogenic or fluorogenic chemosensors are urea [14,15], thiourea [16], amide [17], phenol [18], or pyrrole subunits [19]. The large numbers of anion receptors containing these subunits have been designed, synthesized and tested for anion recognition and sensing during the past decades. For example, Liu and coworkers reported synthesis of a simple and efficient chemosensor containing naphthalene signal moiety and thiourea recognition and that this sensor has proven to be highly selective for fluoride and show a remarkable color change and fluorescence quenching [20]. A novel colorimetric and fluorescent sensor possessing fluorenone and naphthalene moieties as signaling groups for fluoride and pyrophosphate anions was prepared by Thangadurai and coworkers [21].

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Herein, we have designed a new class of urea and thiourea-based receptors **1** and **2** containing azophenol–imine platform and investigated their anion sensing properties towards F^- , Br^- , Cl^- , I^- , AcO^- , ClO_4^- , NO_3^- , HSO_4^- , and $H_2PO_4^-$ anions. The spectroscopic data showed that receptor **1** and **2** are selective colorimetric sensor for fluoride and acetate anions in $CHCl_3$.

2. Experimental

2.1. General

NMR spectra were recorded at room temperature on a Varian 400 MHz spectrometer in d_6 -DMSO and $CDCl_3$. FT-IR spectra were obtained on a Perkin Elmer Spectrum 100 FTIR spectrometer. UV/Vis spectra were measured with a Perkin Elmer Lambda 25 spectrometer. Elemental analyses were performed using a Leco CHNS-932 analyzer. Melting points were determined on an Electrothermal 9100 apparatus in a sealed capillary and are uncorrected. Analytical TLC was performed using Merck prepared plates (silica gel 60 F254 on aluminum). Flash chromatography separations were performed on a Merck Silica Gel 60 (230–400 Mesh). All reactions, unless otherwise noted, were conducted under nitrogen atmosphere. All starting materials and reagents were of standard analytical grade from Fluka, Merck, and Aldrich and used without further purification.

2.2. Synthesis

2.2.1. Synthesis of 5-(4-nitro-phenylazo)-salicylaldehyde (S1)

Synthesis of S1 was carried out according to known procedure [22] For this, to a solution of 4-nitroaniline (3.5 g, 0.025 mol) in water (2 mL) was slowly added 3 ml of 37% aq HCl solution at 0–5 °C. 10 ml of 20% aq $NaNO_2$ solution was added to this mixture and the resulting solution was stirred for 1 h, affording a yellow solution. Salicylaldehyde (2.5 ml, 0.025 mmol) was dissolved in a solution comprising 9 g Na_2CO_3 and 75 ml H_2O and the resulting solution of salicylaldehyde was added dropwise to the bright yellow colored solution over 1 h. After stirring for 4 h, the reaction mixture was neutralized with HCl, the brown crude solid was filtered and recrystallized from ethanol to afford a pure yellow product. Yield: 90%. 1H NMR (400 MHz, $CDCl_3$): δ 7.16 (d, 1H, $J = 8.8$ Hz, ArH), 8.02 (d, 2H, $J = 8.9$ Hz, ArH), 8.11 and 8.14 (dd, 1H, $J = 2.3$ Hz, $J = 8.8$ Hz, ArH), 8.34 (d, 1H, $J = 2.3$ Hz, ArH), 8.37 (d, 2H, $J = 8.9$ Hz, ArH), 10.30 (s, 1H, CHO).

2.2.2. Synthesis of the receptors **1** and **2**

To a solution of S1 (0.2 g, 0.74 mmol) in EtOH (20 mL) was added a solution of 4-phenylsemicarbazide or 4-phenylthiosemicarbazide (0.74 mmol) and a catalytic amount of *p*-toluenesulfonic acid in dry EtOH (10 mL). The mixture was refluxed for 24 h under nitrogen. The product, which was precipitated during stirring, was filtered off, washed with ethanol and dried in vacuo.

Receptor 1; Orange solid, Yield: 85%; Mp = 252–254 °C; 1H NMR (400 MHz, d_6 -DMSO): δ 7.00 (t, 1H, $J = 7.4$ Hz, ArH), 7.08 (d, 1H, $J = 8.8$ Hz, ArH), 7.28 (t, 2H, $J = 7.4$ Hz, ArH), 7.62 (d, 2H, $J = 7.6$ Hz, ArH), 7.83 and 7.85 (dd, 1H, $J = 2.5$ Hz, $J = 8.8$ Hz, ArH), 8.02 (d, 2H, $J = 8.9$ Hz, ArH), 8.32 (s, 1H, ArH), 8.40 (d, 2H, $J = 8.9$ Hz, ArH), 8.66 (d, 1H, $J = 2.5$ Hz, CHN), 9.01 (s, 1H, NH), 10.74 (s, 1H, NH), 11.25 (br s, 1H, OH). ^{13}C NMR (100 MHz, d_6 -DMSO): δ 160.68, 155.85, 153.42, 148.34, 145.90, 139.52, 137.36, 128.87, 125.65, 125.55, 123.71, 123.56, 122.97, 121.90, 120.55, 117.46; Anal. Calcd. for $C_{20}H_{16}N_6O_4$ (404.38): C, 59.40; H, 3.99; N, 20.78. Found: C, 59.67; H, 4.05; N, 20.82.

Receptor 2; Orange solid, Yield: 86%; Mp = 235–237 °C; 1H NMR (400 MHz, d_6 -DMSO): δ 7.07 (d, 1H, $J = 8.8$ Hz, ArH), 7.19 (t, 1H, $J = 7.4$ Hz, ArH), 7.36 (t, 2H, $J = 7.4$ Hz, ArH), 7.52 (d, 2H, $J = 7.6$ Hz, ArH), 7.82 and 7.84 (dd, 1H, $J = 2.5$ Hz, $J = 8.8$ Hz, ArH), 7.98 (d, 2H, $J = 9.1$ Hz, ArH), 8.37 (d, 2H, $J = 9.1$ Hz, ArH), 8.54 (s, 1H, ArH), 8.81 (d, 1H, $J = 2.2$ Hz, CHN), 10.22 (s, 1H, NH), 11.19 (br s, 1H, OH), 11.86 (s, 1H, NH). ^{13}C NMR (100 MHz, d_6 -DMSO): δ 176.53, 161.17, 155.82, 148.29, 145.96, 139.60, 138.90, 128.49, 126.81, 126.77, 125.88, 125.49, 123.52, 123.33, 121.71, 117.52; Anal. Calcd. for $C_{20}H_{16}N_6O_3S$ (420.44): C, 57.13; H, 3.84; N, 19.99. Found: C, 57.25; H, 3.91; N, 20.02.

2.3. UV–vis experiments

The solutions of the receptor **1** and **2** (4.0×10^{-5} M) and the guest anions (2.0×10^{-3} M) were prepared in $CHCl_3$. The volume of the receptor **1** and **2** solutions used in the UV–vis measurements was 3 mL. Absorption spectra were recorded by adding different amounts of anion solution to the receptor **1** and **2** solutions. The colorimetric studies of **1** and **2** towards various anions can be easily observed by the naked eye in $CHCl_3$ at concentration of 4.0×10^{-5} M.

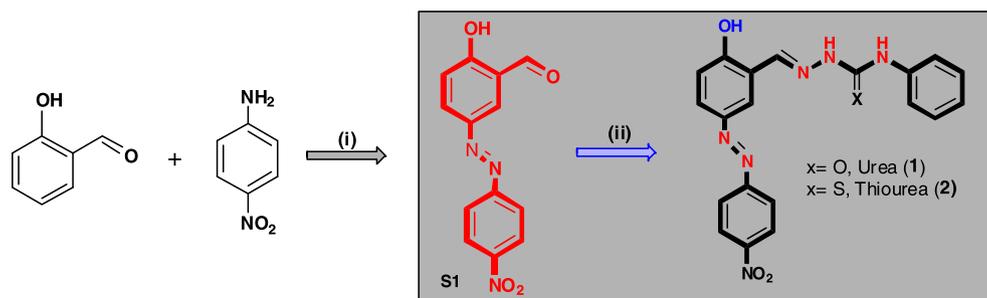
2.4. 1H NMR experiments

1H NMR titrations were performed on a Varian 400 MHz spectrometer at 298 K. The solution of the receptors **1** and **2** (0.0255 M in d_6 -DMSO) was titrated by adding known quantities of concentrated solution of tetrabutylammonium fluoride and acetate (0.02 M). The chemical shift changes of the receptors **1** and **2** were monitored. All titrations were repeated at least twice to get the consistent values.

3. Result and discussion

3.1. Synthesis of novel receptors

As can be seen in Scheme 1, the receptors **1** and **2** were obtained in 85% and 86% yields, respectively by reacting 5-(4-nitro-phenylazo)-salicylaldehyde S1 with 4-phenylsemicarbazide or 4-phenylthiosemicarbazide in dry EtOH. Their molecular structures and purities were established from spectroscopic studies including 1H



Scheme 1. Synthesis of the receptors **1** and **2**; Reagents and conditions: (i) Na_2CO_3 , $NaNO_2/HCl$, H_2O , 0–5 °C; 90%; (ii) 4-phenylsemicarbazide or 4-phenylthiosemicarbazide, EtOH.

NMR, ^{13}C NMR, APT, COSY NMR, elemental analysis, and FT-IR analysis (Supplementary data). The formation of receptors 1 and 2 was confirmed by the disappearance of aldehyde protons (CHO) belong to S1 at δ 10.30, and the appearance of Schiff base (CH=N), urea and thiourea protons (NH) at δ 8.66, δ 9.01 and δ 10.74 ppm for 1 and δ 8.81, δ 10.22 and δ 11.86 ppm for 2 in ^1H NMR spectra, respectively. The synthesis of receptors 1 and 2 was also confirmed by the disappearance of the characteristic aldehyde carbonyl band belong to S1 at about 1656 cm^{-1} and by the appearance of the urea carbonyl bands at about 1690 cm^{-1} for 1 and 1631 cm^{-1} for 2 (Supplementary data).

3.2. Naked eye detection

The colorimetric sensitivity of 1 and 2 ($4.0 \times 10^{-5}\text{ M}$) towards various anions such as F^- , Br^- , Cl^- , I^- , AcO^- , ClO_4^- , NO_3^- , HSO_4^- , and H_2PO_4^- in their tetrabutylammonium form, were monitored visually concomitantly. As depicted in Figs. 1 and 2, the color of the receptor 1 solution changed from yellow to blue and pale purple upon addition of F^- and AcO^- anions (5 equiv.), respectively, which could be easily observed by the naked eye. Under similar conditions, the color of the receptor 2 changed from yellow to purple upon addition of F^- and AcO^- anions. At the same time, their

color remained unchanged after the addition of Br^- , Cl^- , I^- , ClO_4^- , NO_3^- , HSO_4^- , and H_2PO_4^- . This is probably due to high negative charge density on F^- and AcO^- which bring about the strong hydrogen bonding with NH and OH in 1 and 2. The formation of these hydrogen bonds affects the electronic properties of the chromophore, concluding a color change with a subsequent new intraligand or internal charge transfer (ICT) band including between the F^- or AcO^- -bound hydroxyl group and electron deficient azo moiety [22].

3.3. UV studies

The anion binding affinities of receptors 1 and 2 were investigated using UV-vis spectroscopy in CHCl_3 solution at $4.0 \times 10^{-5}\text{ M}$ concentration. The receptors 1 and 2 were titrated by successive increment of number of equivalents for acetate and fluoride ion separately and monitored by UV-vis absorption spectra. The titrations were carried out with all anion and UV-vis spectral changes are depicted in Figs. 3 and 4. The UV-vis absorption spectra of the receptors 1 and 2 in CHCl_3 are dominated by strong absorption bands at 325 and 390 nm for 1 and 348 nm for 2. Upon the addition of F^- to 1 and 2, prominent changes was observed in UV-vis absorption spectra due to complexation between host-guest



Fig. 1. Colorimetric response upon addition of 5.0 equiv. of TBA salt of anions into CHCl_3 solutions of 1.

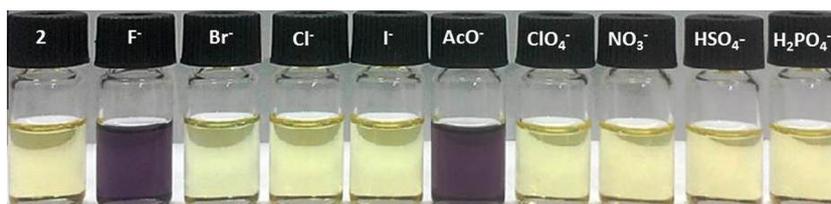


Fig. 2. Colorimetric response upon addition of 5.0 equiv. of TBA salt of anions into CHCl_3 solutions of 2.

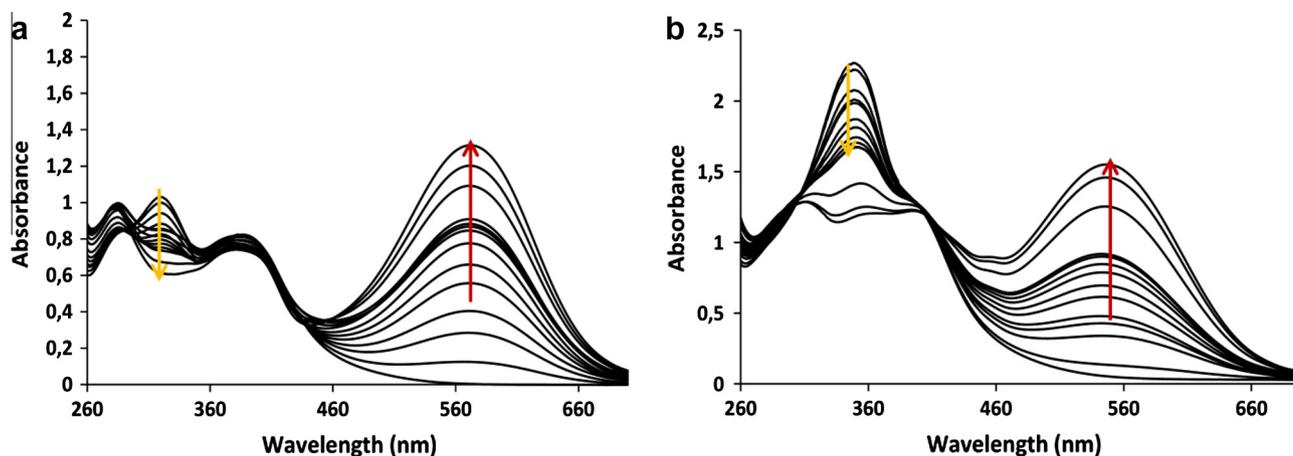


Fig. 3. UV-vis titration spectra for receptors 1 (a) and 2 (b) ($4.0 \times 10^{-5}\text{ M}$) at room temperature on increasing the concentration of tetrabutylammonium fluoride in CHCl_3 .

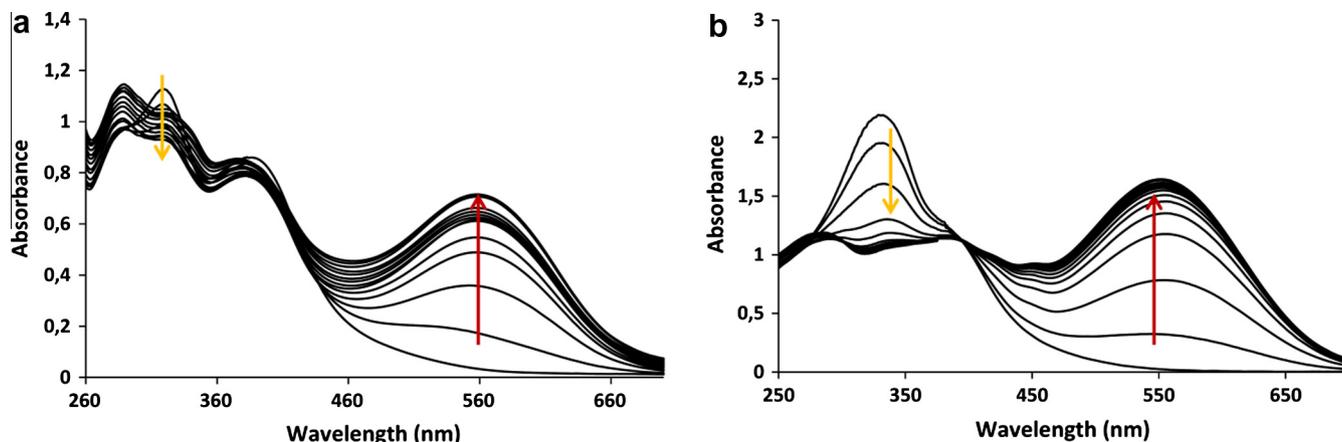


Fig. 4. UV-vis titration spectra for receptors 1 (a) and 2 (b) (4.0×10^{-5} M) at room temperature on increasing the concentration of tetrabutylammonium acetate in CHCl_3 .

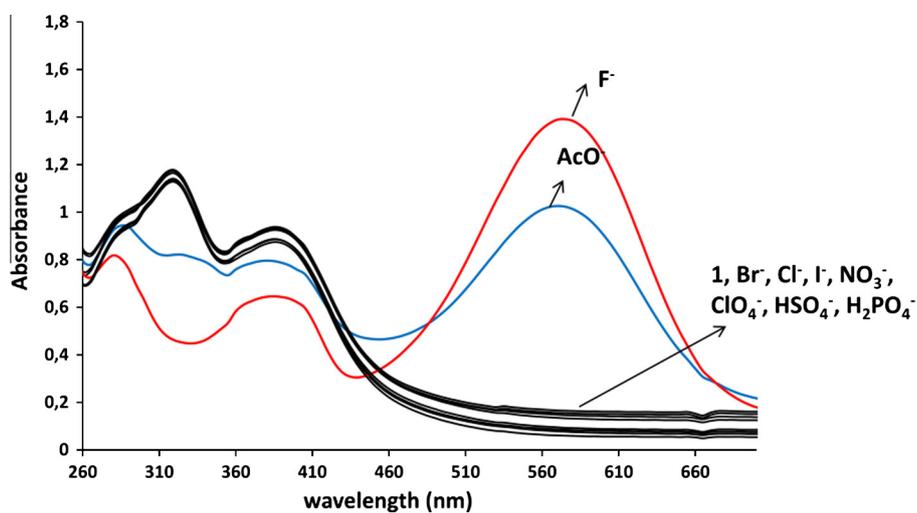


Fig. 5. UV-vis absorption spectra of 1 (4.0×10^{-5} M) in CHCl_3 after the addition of 5 equiv of each of the different guest anions.

molecules. The ICT bands at 325 nm for 1 and 348 nm for 2 as shown in Fig. 3, disappear gradually with the formation of new peaks centered at 577 and 555 nm (bathochromic shift). A clear isosbestic points were observed at 295 and 410 for 1 and 440 nm for 2. On the other hand, it can be seen in Fig. 4 that as the number of equivalents of AcO^- increases, the absorption bands, appeared at

325 and 348 nm wavelengths gradually reduced and new bands appeared at 555 and 551 nm. On addition of other anionic species as their tetrabutylammonium salts no significant modulation in the UV-vis absorption spectra was observed thus, showing the specificity of the chemosensor for selective binding interaction with AcO^- and F^- anions (Fig. 5). The data showed that receptors

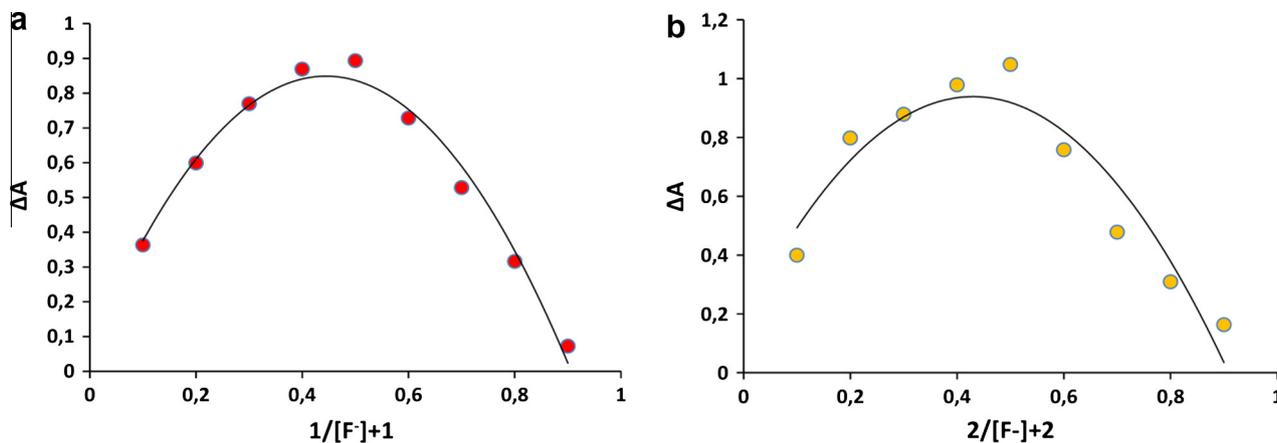


Fig. 6. The Job plots of receptors 1 (a) and 2 (b) with tetrabutylammonium fluoride using UV-vis.

Table 1
Association constants (K_{ass} , M^{-1}) of 1 and 2 with F^- and AcO^- anions in CHCl_3 .

Receptor	Anion	K_{ass} (M^{-1})
1	F^-	$1.27 (\pm 0.20) \times 10^4$
	AcO^-	$7.04 (\pm 0.35) \times 10^4$
2	F^-	$1.08 (\pm 0.12) \times 10^4$
	AcO^-	$6.13 (\pm 0.25) \times 10^4$

1 and 2 have higher selectivity for fluoride and acetate than other anions. In addition, the fluorescence behavior of the receptors to anions was examined, but any fluorometric change could not be observed.

In order to determine the stoichiometric ratio between receptors and anionic guests, the method of continuous variation (Job's plot) was used. The total concentration of 1 or 2 and anionic guest was constant ($1.0 \times 10^{-4} \text{ M}$) with continuous variation of mole fraction of 1 and 2 ($[\text{host}]/([\text{host}] + [\text{guest}])$). Fig. 6 shows the Job's plots of 1 and 2 with F^- . The receptors 1 and 2–anions complex concentration approaches a maximum when the mole fraction of 1 and 2 is 0.5, which means 1 or 2 and anions form 1:1 complexes. We found similar stoichiometric ratio also in case of 1 and 2 with AcO^- (Supplementary data). On the basis of 1:1 stoichiometry, the corresponding binding constants (K_{ass}) of 1 and 2 for F^- and

AcO^- anions were calculated in CHCl_3 based on the UV–vis titration experiments by Benesi–Hildebrand plots [23] and the results were presented in Table 1. Benesi–Hildebrand plots of 1 and 2 for F^- were depicted in Fig. 7 (see also supplementary data). Also, the detection limits of receptors 1 and 2 towards F^- and AcO^- anions were calculated by using UV titration data and found to be $1.05 \times 10^{-6} \text{ M}$ and $9.43 \times 10^{-6} \text{ M}$ for receptor 1 and $1.37 \times 10^{-5} \text{ M}$ and $1.35 \times 10^{-6} \text{ M}$ for receptor 2, respectively.

3.4. ^1H NMR titration

On the basis of spectrophotometric experiments it is difficult to predict whether the noticeable changes include formation of complex between host and guest through hydrogen bonding or deprotonation of host by sufficient basic strength of guest molecules. To affirm the real phenomenon we performed ^1H NMR titration experiments with receptors 1 and 2 in $\text{DMSO}-d_6$ ($c = 2.55 \times 10^{-2} \text{ M}$) by stepwise addition of equivalents of F^- and AcO^- as their tetrabutylammonium salts and displayed in Figs. 8 and 9. Before the addition of F^- and AcO^- , the ^1H NMR chemical shifts of the OH protons of receptors 1 and 2 were δ 11.25 and δ 11.19 ppm, respectively. The phenolic OH protons in 1 and 2 disappeared after the addition of 0.5 equiv of tetrabutylammonium fluoride and acetate to the receptor solutions. On the other hand,

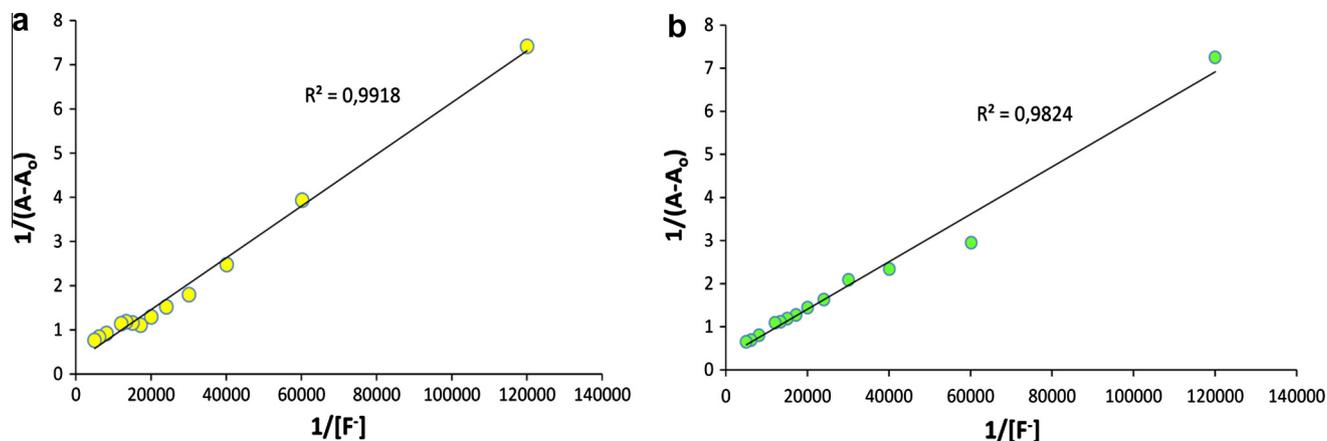


Fig. 7. Benesi–Hildebrand plots from UV–vis titration data of receptor 1 (a) and 2 (b) ($4.0 \times 10^{-5} \text{ M}$) with F^- .

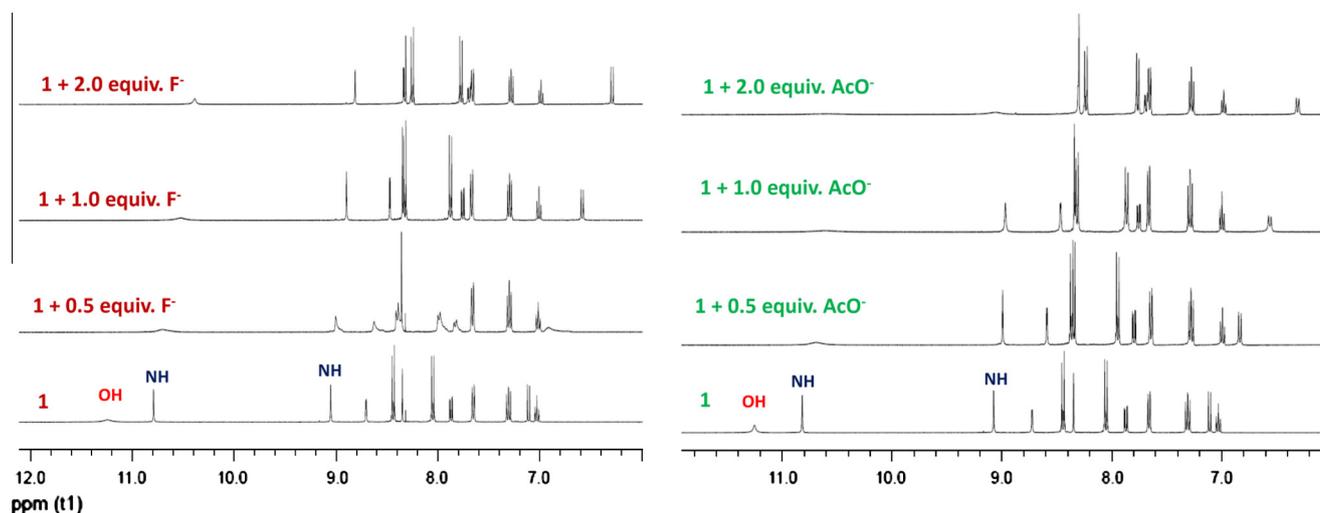


Fig. 8. Changes in ^1H NMR titration spectra for receptor 1 ($2.55 \times 10^{-2} \text{ M}$) in $\text{DMSO}-d_6$ solution with gradual addition of equiv. of tetrabutylammonium fluoride and acetate.

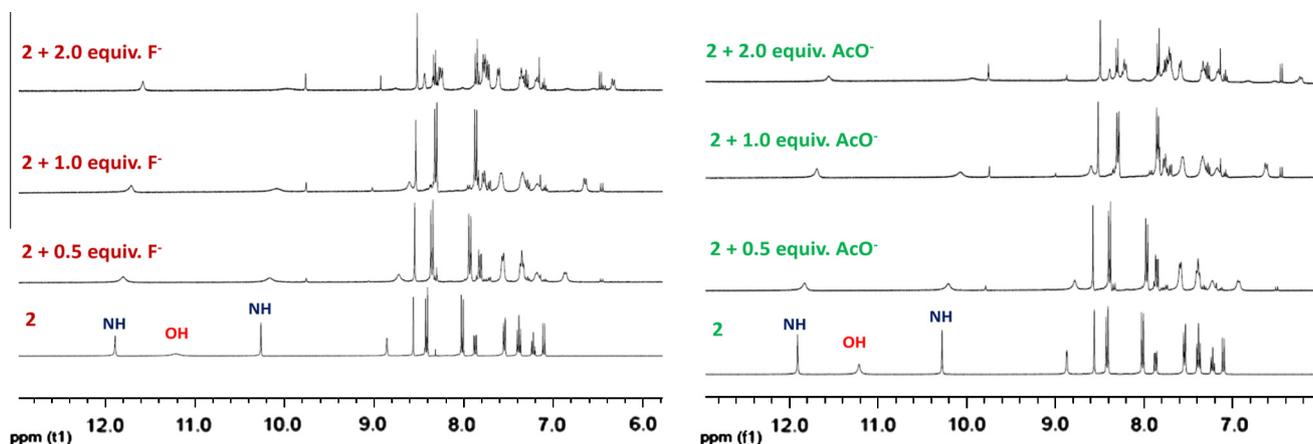


Fig. 9. Changes in ^1H NMR titration spectra for receptor 2 (2.55×10^{-2} M) in $\text{DMSO}-d_6$ solution with gradual addition of equiv. of tetrabutylammonium fluoride and acetate.

additions of F^- and AcO^- (2.0 equiv.) upon the receptor 1 and 2 induce shifts upfield of the Schiff base protons from 8.66 and 8.81 ppm to 8.34 and 8.43 ppm for F^- and to 8.32 and 8.38 ppm for AcO^- , respectively. At the same time, while the some signals of the aromatic protons in receptors 1 and 2 after the addition of tetrabutylammonium fluoride and acetate shifted upfield, the other signals shifted downfield. The deprotonation of the phenolic OH subunits in receptors 1 and 2 can induce two distinct effects on the aromatic substituents: (i) it increases the electron density on the phenyl rings with through bond propagation which generates a shielding effect, and should produce an upfield shift of the C–H protons; (ii) it induces polarization of the C–H bonds via a through-space effect, where the partial positive charge causes a deshielding effect and produces a downfield shift. On the other hands, the characteristic urea (NH) proton signals in receptors 1 appeared at δ 9.01 and δ 10.74 (Fig. 8) and the thiourea (NH) signals in receptor 2 appeared at δ 10.22 and δ 11.86 (Fig. 9). On addition of 0.5–2.0 equiv. of F^- and AcO^- to a solution of 1, the signal of urea NH at δ 10.74 shifted towards upfield with broadening in signal (Fig. 8). On addition of 0.5–2.0 equiv. of F^- and AcO^- to a solution of 2, both singlet signals for NH protons shifted towards upfield with broadening and weakening in signals and also observed new signals at \sim 9.8 and \sim 8.9 ppm (Fig. 9). We think that the new signals at \sim 9.8 and \sim 8.9 ppm belong to four identifiable

NH resonances, which integrate for two protons. These resonances were clearly indicative of the formation of new species, which was structurally different from that seen for receptor 2 and the formation of a host–guest hydrogen-bonding complex and an overall change of the electron distribution [24,25].

The possible complexes with the anion are depicted in Fig. 10. The binding between host and guest may be attributed to possible double hydrogen bonding of receptors with anions causing strong binding due to high basicity of F^- and AcO^- .

4. Conclusion

In summary, we have synthesized two novel colorimetric anion sensors which selectively recognize fluoride and acetate over other anions (Cl^- , Br^- , I^- , NO_3^- , ClO_4^- , HSO_4^- , and H_2PO_4^-) in chloroform. More importantly, these sensors show naked-eye detection for fluoride and acetate anions at room temperature. The nature of the anion receptor interaction has been defined by UV–vis and NMR spectroscopy, and we concluded that in the case of 1 and 2, hydrogen bonding interactions are most likely involved in the recognition process.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.molstruc.2013.04.077>.

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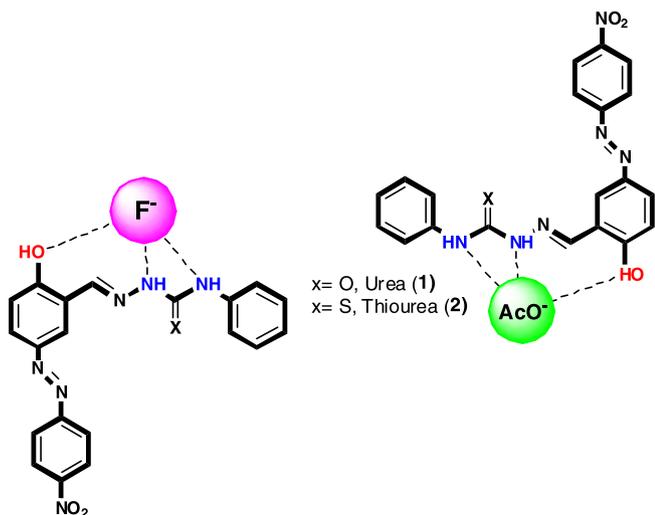


Fig. 10. The possible structure of the complex formed between receptors with F^- and AcO^- .

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