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'Naked-eye' detection of F⁻ ions by two novel colorimetric receptors

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ABSTRACT

Two novel colorimetric receptors, **S1** and **S2**, linked to one or two nitrophenylurea groups were synthesized in good yields, characterized and their chromogenic properties investigated towards various anions (F^- , Cl^- , Br^- , I^- , NO_3^- , AcO^- , ClO_4^- , HSO_4^- , and $H_2PO_4^-$) by UV–vis and ¹H NMR techniques. The receptors, effectively and selectively, recognized and distinguished the biologically important F^- from other anions such as Cl^- , Br^- , I^- etc. in CH₃CN. This selectivity could be easily observed by the naked eye, indicating that receptors **S1** and **S2** are potential colorimetric sensors for fluoride ion.

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Sensing of anions in both organic and aqueous solutions has become an active field of research within supramolecular chemistry. Anions are mainly recognized through hydrogen-bonding interactions,¹ electrostatic interactions² and coordination with metal ions.³ Among various non-covalent interactions, hydrogen-bonding is particularly useful and effective in this respect. Receptors bearing functional groups such as amides,⁴ ureas,⁵ thioureas,⁶ and imidazolium⁷ have been widely used to recognize anions via hydrogen-bonding interactions.

The development of simple receptors capable of recognizing biologically relevant anions such as fluoride, chloride, phosphate, and carboxylate has attracted considerable interest.⁸ 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.⁹ While the incorporation of fluorescent chromophores into receptors has gained considerable attention owing to their high sensitivities and easy detection,¹⁰ the investigation of anion-selective receptors based on colored chromophores is less studied.¹¹ 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.¹²

Herein, we report the synthesis of two new receptors, **S1** and **S2** containing one or two nitrophenyl groups as the chromogenic signalling subunits and urea/phenolic-OH groups as binding sites. Their anion binding properties were investigated by means of UV–vis and ¹H NMR spectroscopy, as well as by the 'naked-eye'.

The synhthesis of receptors **S1** and **S2** is depicted in Scheme 1. The Schiff bases **1** and **2** were synthesized in one step by condensation of 2-hydroxy-1-naphthaldehyde and diethylenetriamine or triethylenetetramine in ethanol.

Receptors **S1** and **S2** were obtained in 71% and 75% yields, respectively by reacting 4-nitrophenylisocyanate with **1** or **2**. Their molecular structures and purities were established from spectroscopic studies including ¹H NMR, ¹³C NMR, HRMS, and FT-IR analysis (Supplementary data). For example, the ¹H NMR (400 MHz, DMSO-*d*₆) spectra of **S1** and **S2** showed two singlets at δ 9.09 and δ 9.20 characteristic of urea protons, whilst the ¹³C NMR (100 MHz, DMSO-*d*₆) spectra showed the expected number of resonances.

The binding behaviour of receptors **S1** and **S2** with different anions was studied in acetonitrile. The titrations were carried out in CH₃CN at a 1.0×10^{-5} M concentration of receptors **S1** and **S2**, by the addition of incremental amounts from (0–500 µL) of tetrabutylammonium fluoride (1.0×10^{-3} M); the spectra of the receptors are shown in Figure 1.

The electronic spectra of receptors **S1** and **S2** showed four transitions. As shown in Figure 1, upon a gradual increase of the fluoride ion concentration, the bands at 300–350 nm gradually decreased and the bands at 400–440 nm increased, and new bands appeared at 470 and 455 nm with isosbestic points at 376 and 346 nm, indicating the formation of new complexes between the receptors **S1** and **S2** and fluoride anions (Fig. 1). The receptors **S1** and **S2** (1.0×10^{-5} M) in CH₃CN showed dramatic colour changes from colourless to yellow in the presence of TBAF, respectively. The colour changes are most probably due to the formation of hydrogen bonds or deprotonation of receptors **S1** and **S2** on addition of the fluoride ions. These H-bonds or deprotonations affect





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Scheme 1. Synthesis of the receptors S1 and S2: (i) diethylenetriamine, EtOH, rt; (ii) triethylenetetramine, EtOH, rt; (iii) 4-nitrophenylisocyanate, dry CH₂Cl₂, reflux.



Figure 1. UV-vis titration spectra for receptors S1 (a) and S2 (b) (1.0×10^{-5}) at room temperature on increasing the concentration of TBAF in CH₃CN.

the electronic properties of the chromophore, resulting in a colour change along with a new charge-transfer interaction between the fluoride-bound OH and NH and the electron-deficient nitro group.^{13,14}

Titrations were also carried out with various anions such as AcO^- , Cl^- , Br^- , I^- , NO_3^- , ClO_4^- , HSO_4^- , and $H_2PO_4^-$ as their tetrabutyl ammonium salts. Interestingly, there was no obvious change observed in the UV spectra, except with acetate, which gave slight interference (Supplementary data). However new, albeit minor peaks appeared at 480 and 465 nm which indicated that the receptors **S1** and **S2** showed a slight response to acetate ions.

The deprotonation occurred at a higher concentration of acetate than fluoride; this is due to the higher electronegativity, smaller size and higher basicity of F^- ions, which makes them bind more strongly with the receptors **S1** and **S2**. That is why F^- could be recognized selectively from the other anions (Figs. 2a and 3a). Figures 2b and 3b reflect the selectivity for F^- over the other anions which are shown by the blue bars for **S1** and **S2**. The slight interference of acetate is shown by the pink bars, but it cannot be detected by the naked eye as shown in Figure 4. This Figure shows the color change of the solutions of the receptors **S1** and **S2** in the presence of various anions in CH₃CN. It can be seen with the naked eye that



Figure 2. (a) UV-vis absorption spectra and (b) the absorption ratios at 470 nm of **S1** (1.0×10^{-5} M) in CH₃CN after the addition of 10 equiv of each of the different guest ions.



Figure 3. (a) UV-vis absorption spectra and (b) the absorption ratios at 455 nm of **S2** (1.0×10^{-5} M) in CH₃CN after the addition of 10 equiv of each of the different guest ions.



Figure 4. The visible color changes observed for **S1** and **S2** in CH₃CN solution $(1.0 \times 10^{-5} \text{ M})$ upon addition of 10 equiv of anions as TBA salts: from left to right: free **S1** and **S2**, F⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, HSO₄⁻, ClO₄⁻, H₂PO₄⁻ and AcO⁻.

the colors of the **S1** and **S2** solutions change from colourless to yellow after the addition of fluoride. Other anions did not induce any color changes even in excess amounts. From these experimental data, it can be concluded that the receptors **S1** and **S2** have high selectivity and sensitivity toward F^- ions in acetonitrile. The other anions examined, except acetate, had no significant influence.

Judging from the titrations, the strong binding of fluoride allowed a Job's plot¹⁵ to be used in the determination of the binding stoichiometry. The stoichiometries between the receptors **S1** or **S2** and fluoride were determined from the Job plots using the UV-vis spectra, which showed evident 1:2 and 1:3 stoichiometries, respectively (Fig. 5a and b).



Figure 5. The Job plots of S1 (a) and S2 (b) with tetrabutylammonium fluoride using UV-vis.



Figure 6. Partial ¹H NMR spectra of **S1** (7.24×10^{-2} M) in DMSO- d_6 at 25 °C and the corresponding changes after the addition of various equivalents of tetrabutylammonium fluoride (2.0×10^{-2} M).

Benesi–Hildebrand plots¹⁶ derived from the changes at 470 and 455 nm in the UV–vis spectra of **S1** and **S2** gave the association constants. The association constants of F⁻ with **S1** and **S2** were calculated as 6.38×10^3 and 1.11×10^3 M⁻¹ from the UV–vis titrations (Supplementary data).

In order to understand the effect of fluoride anions on the NH and OH protons of the receptors **S1** and **S2**, the ¹H NMR spectra were recorded in DMSO-*d*₆. The urea NH and OH signals in receptor **S1** appeared at δ 9.09 and δ 13.95 (Fig. 6) and at δ 9.20 and δ 13.98 in receptor **S2** (Fig. 7). The urea NH protons in **S1** and **S2** disappeared after the addition of 1.0 equiv of tetrabutylammonium fluoride to the receptor solutions. The deprotonation of the urea subunits in receptors **S1** and **S2** 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 polarisation of the C–H bonds via a through-space effect, where the partial positive charge causes a deshielding effect and produces a downfield shift.

At the same time, the –OH protons of **S1** and **S2** appeared at δ 13.95 and δ 13.98, downfield from their expected value (δ 10 ppm), owing to intramolecular H-bonding between the imine



Figure 7. Partial ¹H NMR spectra of **S2** (7.24×10^{-2} M) in DMSO- d_6 at 25 °C and the corresponding changes after the addition of various equivalents of tetrabutylammonium fluoride (2.0×10^{-2} M).

nitrogens and the naphthol –OH groups.¹⁷ However, the titration experiments on the receptors **S1** and **S2** and tetrabutylammonium fluoride in DMSO- d_6 showed that the proton signals of the naphthol hydroxyl disappeared after the addition of 1.0 equiv of fluoride and there was no appearance of proton signals due to this group even after the addition of 2, 3, 4 and 5 equiv of fluoride. This demonstrates formation of a new complex between the naphthol hydroxyl and fluoride.

In summary, we have developed two novel colorimetric anion sensors which selectively recognize fluoride over other anions $(AcO^-, Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, HSO_4^-, and H_2PO_4^-)$ in acetonitrile. More importantly, these chemosensors display naked-eye detection at room temperature. The nature of the anion receptor interaction has been defined by absorption and NMR spectroscopy, and we have demonstrated that in the case of **S1** and **S2**, deprotonation interactions are most likely involved in the recognition process.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012. 11.138.

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