

Simple and efficient colourimetric F⁻ sensors and a test paper for fluorine

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A series of colourimetric fluoride ion sensors bearing azo-phenolic hydroxyl and Schiff base groups were synthesised. In CH₃CN solutions, these sensors showed colourimetric single selectivity for F⁻. An easy-to-prepare test paper based on the sensor was developed, which could colourimetrically conveniently detect fluoride ion.

Keywords: Schiff base, anion recognition, deprotonation

The development of selective optical signalling systems for anions has received considerable attention in recent decades due to their important roles in biological and environmental processes.¹⁻³ Fluoride anion recognition is attracting a mounting interest due to its duplicitous nature. It is a useful chemical for many industrial applications, and it has been used in human diet⁴ and health sciences.⁵ There are many receptor species that contain a number of different types of anion binding group.^{6,7} For the sensors based on hydrogen bonds, urea or thiourea units, among others, are usually used as the binding sites.⁸ Few receptors bearing a phenolic O–H have been reported in the literature. With an interest in developing novel colourimetric anion sensors,⁹ we have synthesised a series of anion sensors bearing phenol O–H.

Result and discussion

1 was synthesised according to literature methods.¹⁰ Sensors **3a–c** were synthesised by the condensation of azo-salicylaldehyde with a corresponding aminophenol. The results are listed below.

2-(2-hydroxyphenylaminomethyl)-4-(4-nitrophenylazo)phenol (3a): Yield: 74%, m.p. 294–296 °C; ¹H NMR (DMSO-*d*₆, 400 MHz) δ 15.34 (s, 1H, O–H), 10.24 (s, 1H, O–H), 9.27 (s, 1H, N=C–H); IR (cm⁻¹) ν: 3436 (O–H), 1616 (C=N), 1332 (N=N); Anal. Calcd for C₁₉H₁₄N₄O₄: C, 62.98; H, 3.89; N, 15.46. Found: C, 63.04; H, 4.01; N, 15.63%.

2-(3-hydroxyphenylaminomethyl)-4-(4-nitrophenylazo)phenol (3b): Yield: 61%, m.p. 297–299 °C; ¹H NMR (DMSO-*d*₆, 400 MHz) δ 14.64 (s, 1H, O–H), 9.81 (s, 1H, O–H), 9.14 (s, 1H, N=C–H); IR (cm⁻¹) ν: 3444 (O–H), 1612 (C=N), 1342 (N=N); Anal. Calcd for C₁₉H₁₄N₄O₄·1/2H₂O: C, 61.45; H, 4.07; N, 15.09. Found: C, 61.54; H, 3.84; N, 15.22%.

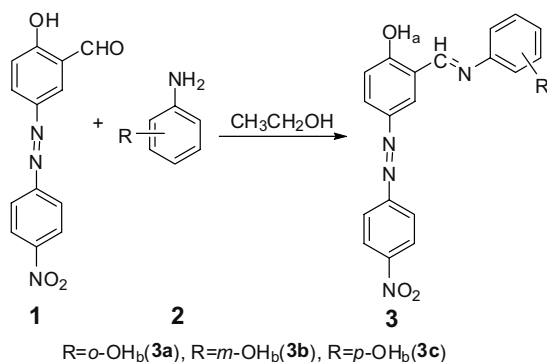
2-(4-hydroxyphenylaminomethyl)-4-(4-nitrophenylazo)phenol (3c): Yield: 54%, m.p. 300 °C; ¹H NMR (DMSO-*d*₆, 400 MHz) δ 14.27 (s, 1H, O–H), 9.76 (s, 1H, O–H), 9.14 (s, 1H, N=C–H); IR (cm⁻¹) ν: 3445 (O–H), 1615 (C=N), 1332 (N=N); Anal. Calcd for C₁₉H₁₄N₄O₄: C, 62.98; H, 3.89; N, 15.46. Found: C, 62.89; H, 3.96; N, 15.67%.

Receptor (**3a–c**) had a better selectivity for F⁻. When adding 50 equiv. of F⁻ to the CH₃CN solution of (**3a–c**), visual colour changes from light yellow to dark purple were observed. In the corresponding UV-vis spectrum, a new strong absorption peak appeared at 550 nm (Fig. 1). Based on the colourimetric recognition abilities of these

sensors, we developed a F⁻ detect test paper by absorbing the **3a** on treated filter paper, that could colourimetrically detect F⁻ conveniently.

Neither did all the anions lead to any significant absorption in the visible region changes, **3a**, **3b** and **3c** showed high sensitivity and selectivity toward F⁻, competing anions + F⁻ gave absorption changes similar to those of single F⁻ experiment (Fig. 2).¹⁵ These facts were indicative of a high selectivity of **3a**, **3b** and **3c** toward F⁻ ion over other competitive anions.

The interaction properties of receptor **3a** and fluoride anion were further investigated by using ¹H NMR titration experiment in



Scheme 1 Synthesis of receptors.

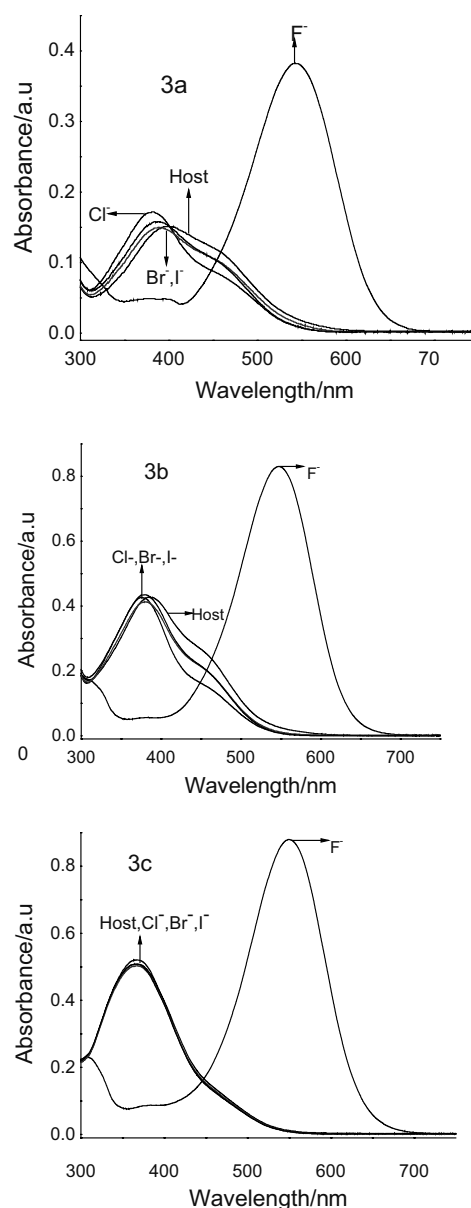


Fig. 1 The UV-Vis spectra of receptor **3a**, **3b**, **3c** (2×10^{-5} M) with anions in CH₃CN (298K).

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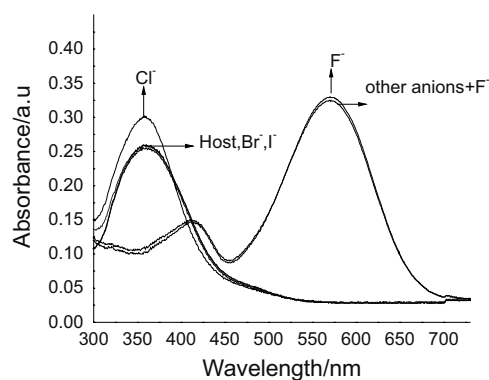


Fig. 2 The UV-Vis spectra of receptor **3a** (2×10^{-5} M) in CH_3CN solution in the presence of various anions.

DMSO- d_6 . A partial ^1H NMR spectrum of sensor **3a** is shown in Fig. 3. Before the addition of anions, the ^1H NMR chemical shifts of the O-H_a protons on sensor **3a** were at δ 15.31, 10.31 ppm. After addition of 0.1 equiv. of tetrabutylammonium fluoride to receptor **3a**, it was found that the O-H_a, O-H_b group proton signal disappeared, after the addition of 5 equiv. of F⁻, a new broad signal appeared at 14.88 ppm, with the continuous addition of F⁻, the signal shifted to 16.03 ppm, which indicated the formation of HF_2^- .^{11,12} These results suggested that the O-H groups possibly underwent a deprotonation process.¹³ The deprotonation of O-H groups led to an increase in electronic density of the phenyl group, which induced the colour of sensor change and the signal of the -HC=N- proton and phenyl protons shifted to upfield.

In summary, three novel sensors based on Schiff base and two phenolic hydroxy groups have been synthesised and characterised. The Schiff base group and two phenolic hydroxy groups act as the binding sites for sense anion. These sensors showed high sensitivity and selectivity toward F⁻ in CH_3CN solution. Furthermore, an easy-to-prepare test paper¹⁴ was developed to detect F⁻ in CH_3CN solution. We believe that the anion responsive test paper reported here may provide the basis for the development of a useful anion detection kit.

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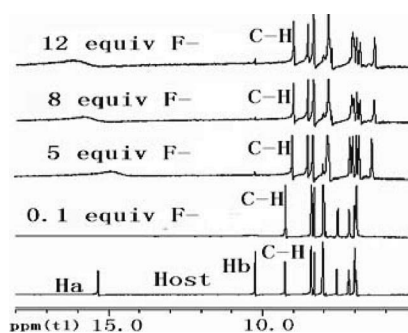


Fig. 3 ^1H NMR spectra of receptor **3a** in $\text{DMSO-}d_6$ upon the addition of various quantities of Bu_4NF .

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