Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron Letters
Tetrahedron Letters 49 (2008) 127–132

Schiff's base phenol–hydrazone derivatives as colorimetric chemosensors for fluoride ions

Duraisamy Saravanakumar,[a] Soosai Devaraj,[a] Subramaniyan Iyyampillai,[b] Kanakaraj Mohandoss[b] and Muthusamy Kandaswamy[a,*]

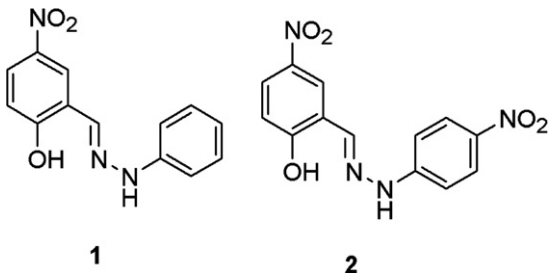
[a]*Department of Inorganic Chemistry, School of Chemical Sciences, University of Madras, Guindy Campus, Chennai 600 025, India*
[b]*Department of Chemistry, Madras Christian College Tambaram, Chennai 600 059, India*

Received 4 May 2007; revised 23 October 2007; accepted 1 November 2007
Available online 6 November 2007

Abstract—Two new chromogenic receptors 4-nitro-2-[(phenylhydrazoimino)methyl]phenol (**1**) and 4-nitro-2-[(4-nitrophenylhydrazoimino)methyl]phenol (**2**) containing a nitro group as a signalling unit and OH and NH groups as binding sites have been synthesized and characterized by spectroscopic techniques and XRD. Both receptors show colorimetric responses and UV–vis spectral changes in the presence of fluoride ions in organic solvents.

The recognition and the sensing of anions have received considerable attention because of their important roles in many biological, industrial and environmental processes.[1] In particular, the selective sensing of fluoride has gained attention due to its significance in clinical treatment for osteoporosis and the detection of fluoride as a result of its over-accumulation in bones.[2] In this context, a colorimetric chemosensor is of particular interest due to its simplicity. 'Colorimetric chemosensors' are molecules that allow 'naked-eye' detection of anions without resort to any spectroscopic instrumentation.[3] Such sensor systems are generally composed of two parts: one is the anion binding part (receptor), which is typically based on various combinations of pyrrole,[4] urea/thiourea,[5] amine[6] or phenol[7] moieties, and the other is a chromophore, which converts binding induced changes into an optical signal such as the appearance of colour. These two parts are either linked directly[8] or intramolecularly associated.[9] With reference to binding groups, only a limited number of reports are available using OH as a binding site.[10] In most cases, F^- is bound to the receptor through $F^-\cdots H$–O hydrogen-bonding interactions. The presence of excess F^- may even cause deprotonation, resulting in a classical Bronsted acid–base type reaction.[11–14] Hence, we report chromogenic receptors possessing a phenolic OH and hydrazine NH groups, which are able to bind fluoride via H-bond interactions or deprotonation with an electron withdrawing nitro group which acts as a chromogenic signalling unit. The nature of these simple Schiff's base phenol–hydrazone receptors is altered by incorporation of an additional nitro group in the receptor, which is able to tune the anion recognition selectivity.

The chromogenic receptors **1** and **2** were synthesized by Schiff's base condensation between 5-nitrosalicylaldehyde and phenylhydrazine (**1**) or 4-nitrophenylhydrazine (**2**). Crystals of receptor **1** suitable for single crystal X-ray diffraction analysis were obtained from acetonitrile. An ORTEP plot of **1** along with the atom labelling is shown in Figure 1. The receptor **1** crystallized as monoclinic with the space group $P2_1/c$ and cell parameters $a = 12.8167$ Å (13), $b = 8.2176$ Å (8), $c = 12.5848$ (12) Å and $Z = 4$ and the final R-value was found to be 0.048.[15] The elemental and spectroscopic analysis results were consistent with the proposed structures of the receptors.[16]



1 **2**

Keywords: Chemosensors; Colorimetric; Hydrazones and fluoride sensors.
* Corresponding author. Tel./fax: +91 44 22300488; e-mail: mkands@yahoo.com

0040-4039/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2007.11.006

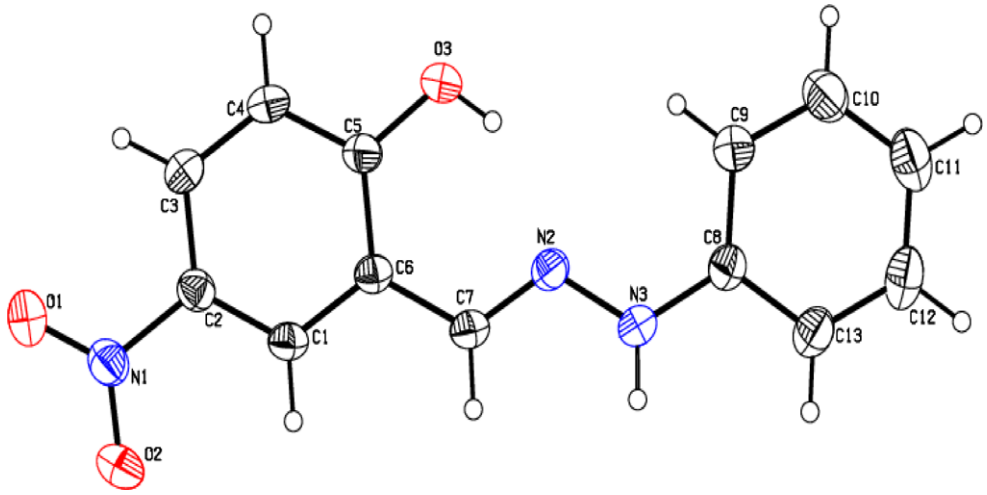


Figure 1. ORTEP plot of the crystal structure of **1**.

To investigate the 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 acetonitrile in the absence and the presence of fluoride ions (see Figs. S1–S4, Supplementary data). The expected bands for receptor **1**, OH and NH stretching were observed at 3624 and 3541 cm^{-1}, respectively, in the absence of fluoride. The stretching frequency of the OH group shifted to 3615 cm^{-1} and that of the NH group shifted to 3535 cm^{-1} when the spectra were recorded in the presence of nearly 1 equiv of F^- (Fig. S2). The same trend was observed for receptor **2**, in the presence of nearly 1 equiv of F^-, the OH stretching frequency shifted from 3630 to 3616 cm^{-1} and the NH shifted from 3542 to 3535 cm^{-1} (Fig. S4). These shifts might be due to the participation of the OH and NH groups of the receptors in hydrogen bonding with fluoride ions. Similar observations on the shifting of OH and NH functionalities on H-bonding have been reported earlier.[17,18]

The binding ability of receptor **1** for F^- was also evident from ^1H NMR titration experiments in DMSO-d_6. A partial ^1H NMR spectrum of receptor **1** is shown in Figure 2. Before the addition of F^-, the ^1H NMR chemical shifts of the OH and NH protons of receptor **1** were δ 11.65 and 10.64 ppm, respectively. After the addition of 1 equiv of F^-, the resonances were shifted upfield to δ 10.65 ppm for OH and δ 10.21 ppm for NH. This might be due to the formation of hydrogen bonds between the fluoride ions and the OH and NH groups of receptor **1**.[19,20] On further addition of more than 2 equiv of F^-, deprotonation of the receptor can possibly occur, and indeed, we observed such deprotonation and the formation of HF_2^- in the ^1H NMR spectra of 1 (DMSO-d_6) as a new signal at ca. 16 ppm[21] (Fig. 2).

The colorimetric sensing ability of receptors **1** and **2** with halide anions (F^-, Cl^-, Br^- and I^-) in CH_3CN was monitored by visual (naked-eye) and UV–vis spectroscopic methods. Solutions of 5×10^{-4} M halide anions (F^-, Cl^-, Br^- and I^-) were added as tetrabutylammonium salts to 5×10^{-5} M solutions of the receptors.

In the naked-eye experiments, receptors **1** and **2** (5×10^{-5} M in CH_3CN) showed dramatic colour changes from colourless to orange and fluorescent yellow, respectively, in the presence of TBAF (2.5×10^{-4} M) (Figs. 3 and 4). Both the receptors were found to be insensitive to the addition of large excess of Cl^-, Br^- and I^- (even up to 100 equiv). The colour changes are most probably due to the formation of hydrogen bonds or deprotonation of receptors **1** and **2** on the addition of fluoride ions. These H bonds or deprotonations affect 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.[22,23]

Observable colour changes also took place in $CHCl_3$ and DMSO. Upon the addition of fluoride ions, the colourless solutions of **1** and **2** became yellow and fluorescent yellow coloured solutions, respectively, in $CHCl_3$, and orange in DMSO. The colours of the receptors in $CHCl_3$ and DMSO remained the same in the presence of chloride, bromide and iodide.

The anion binding ability of receptors **1** and **2** with F^- were investigated using UV–vis titration experiments. The titrations were carried out in CH_3CN at 5.0×10^{-5} M concentrations of receptors **1** and **2** upon the addition of incremental amounts of 0.02 ml (5×10^{-4} M) of tetrabutylammonium fluoride, the spectra of the receptors are shown in Figures 5 and 6. The electronic spectra of receptors **1** and **2** showed four transitions. The first two bands (190–230 nm) could be assigned to excitation of the π electrons of the aromatic system. The third band (around 300 nm) is due to the transition between the π orbital localized on the azomethine group (C=N). The band in the region of 350 nm may occur due to intramolecular charge-transfer transitions within the whole structure of the Schiff's base.[23] In the case of receptor **1**, the intensity of the peaks at 232, 300 and 348 nm progressively decreased on the addition of F^- ions. However, beyond 0.12 ml

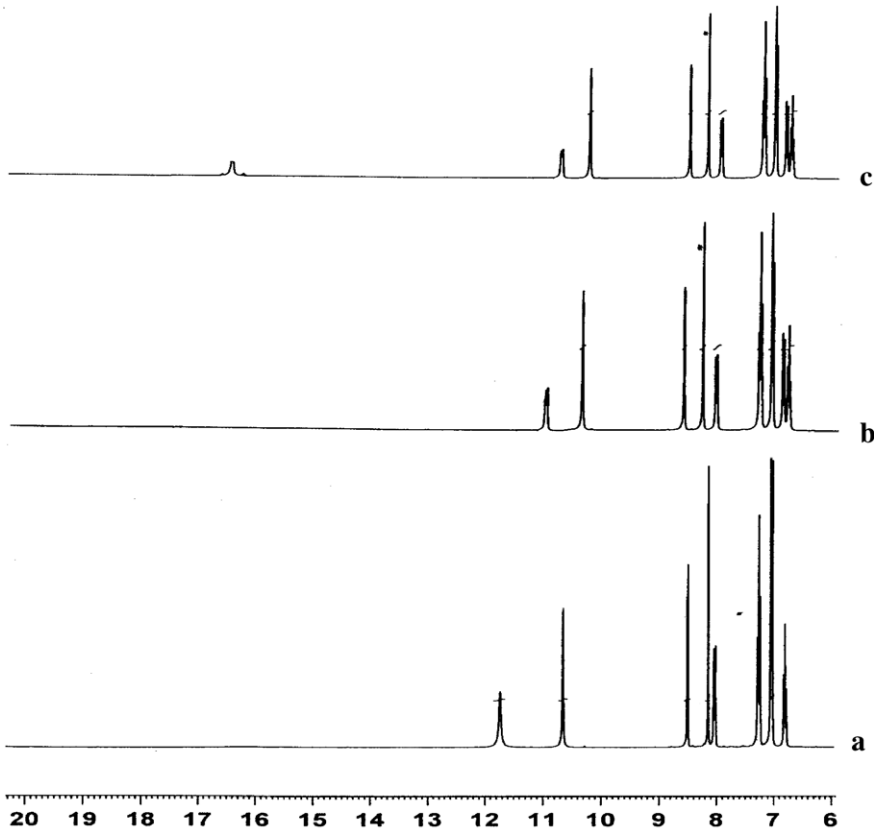


Figure 2. Partial ^{1}H NMR (400 MHz) spectra of receptor **1** in DMSO-d_6, (a) in the absence, (b) presence of 1 equiv and (c) 3 equiv of [*n*Bu4N]F.

Figure 3. Colour changes of receptor (R) **1** in CH_3CN (5.0×10^{-5} M) before and after the addition of 2 equiv of representative anions (from left to right: R, R + F^-, R + Cl^-, R + Br^-, R + I^-).

Figure 4. Colour changes of receptor (R) **2** in CH_3CN (5.0×10^{-5} M) before and after the addition of 2 equiv of representative anions (from left to right: R, R + F^-, R + Cl^-, R + Br^-, R + I^-).

(slightly higher than 1 equiv) addition of F^-, the colour of the solution gradually turned to light orange and new peaks at 369 and 457 nm were formed (Fig. 5). On further addition of F^-, the orange colour became more intense and the intensity of the peaks at 369 and 457 nm increased stepwise. The intensities of these peaks reached their maxima after the addition of 4 equiv of F^-. With receptor **2**, the intensity of the peaks at 233, 301 and 362 nm decreased on the addition of F^- ions. However, beyond 0.1 ml addition of F^-, the colour turned to fluorescent yellow and a new peak at 417 nm was observed. Also an increase in the intensity of the peak at 362 nm occurred (Fig. 6). On further addition of F^-, the fluorescent yellow colour became more intense and the intensity of the peaks at 362 and 417 nm increased in a stepwise manner reaching a limit after the addition of 4 equiv of F^-. To confirm that deprotonation had occured, receptors **1** and **2** (5×10^{-5} M) were titrated with a standard solution of [*n*Bu_4N]OH (0.01–0.1 ml; 5×10^{-4} M). In the case of receptor **1**, the intensity of the peaks at 232, 301 and 348 nm decreased following the addition of OH^- ions (Fig. 7). Beyond 0.5 equiv of OH^-, new peaks at 371 and 459 nm appeared along with a colour change from colourless to orange and with further successive

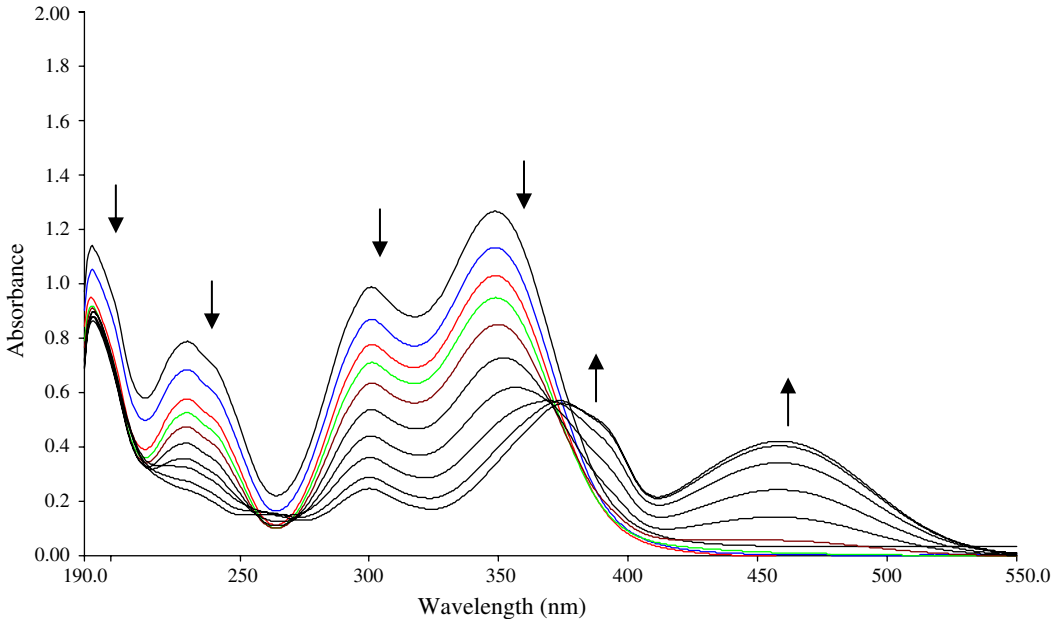


Figure 5. Changes in the electronic spectra for acetonitrile solutions of receptor **1** (5.0×10^{-5} M) at different fluoride [F^-] ($0.02–0.2 \times 10^{-4}$ M).

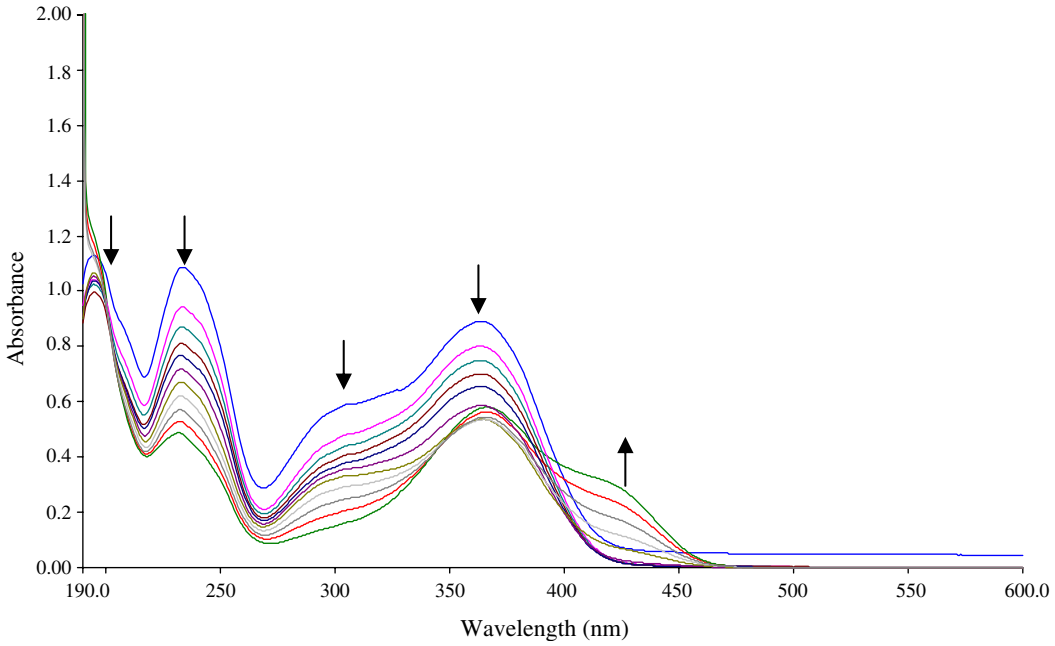


Figure 6. Changes in the electronic spectra for acetonitrile solutions of receptor **2** (5.0×10^{-5} M) at different fluoride [F^-] ($0.02–0.2 \times 10^{-4}$ M).

additions of OH^- ions, these peaks increased intensity stepwise. These peaks reached their limiting values after the addition of 2 equiv of OH^-. Similarly, for receptor **2**, the intensity of the peaks at 234, 303 and 362 nm decreased upon the addition of OH^-. Beyond 0.5 equiv of OH^-, a new peak at 417 nm appeared and the intensity of the peak at 362 nm increased with a colour change from colourless to fluorescent yellow. On further addition of OH^-, the peaks at 363 and 418 nm increased in intensity stepwise (Fig. S5). The new peaks at 363 and 418 nm reached their limiting value after the addition of 2 equiv of OH^-. From these results, the decrease in peak intensities at 348 and 362 nm up to 0.5 equiv may be due to H-bond complex formation [R–OH--OH].[12] However, when approaching 0.5 equiv of OH^- (Fig. 7 and S5) for the receptors **1** and **2**, new peaks appeared and this might be due to deprotonation of the receptors.[13] The same spectral behaviour was observed for receptors **1** and **2** on titration with F^-, however, new peaks were observed after the addition of 1 equiv. From this study, we infer that the receptors **1** and **2** formed hydrogen bonds with F^- ions up to the addition of 1 equiv and that deprotonation took place after the addition of 1 equiv, which was evidenced by the appearance

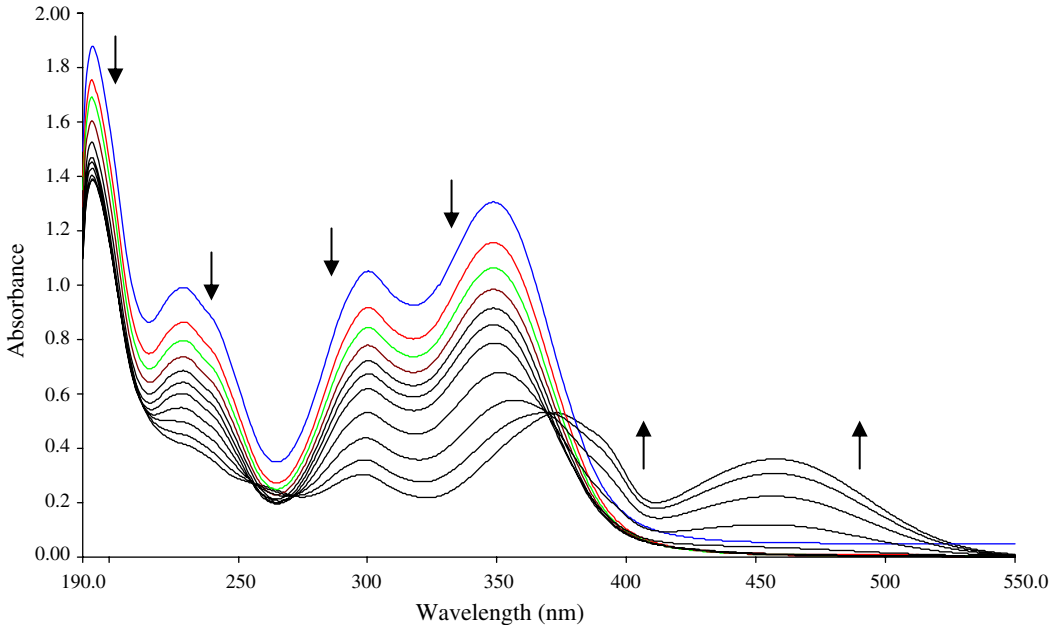


Figure 7. Changes in the electronic spectra for acetonitrile solutions of receptor **1** (5.0×10^{-5} M) at different [OH^-] ($0.01–0.1 \times 10^{-4}$ M).

of new peaks at 369 and 457 nm for receptor **1** and at 417 nm for receptor **2**. These observations suggest that the addition of more than 1 equiv of F^- resulted in the formation of the stable H-bond complex $[HF_2]^-$ inducing deprotonation and hence the Bronsted acid–base[11–14] reaction prevails, whereas, up to 1 equiv of F^-, hydrogen-bonding [F^-–H–O–R] interactions are operative.

Similarly, the binding properties of receptors **1** and **2** with AcO^- were investigated using UV–vis titration experiments. The titrations were carried out in CH_3CN at 5.0×10^{-5} M concentrations of receptors **1** and **2** upon the addition of incremental amounts of 0.02 ml (5×10^{-4} M) of tetrabutylammonium acetate. The spectra of the receptors showed similar behaviour for AcO^- upon the addition of 1 equiv (0.1 ml) as in the case of F^-. In the case of acetate, the deprotonation took place after the addition of 1.4 equiv (0.14 ml) for the receptors **1** and **2** and the solutions turned yellowish brown. But in the case of F^-, the deprotonation was observed upon the addition of 1.2 equiv (0.12 ml). The deprotonation occurred at slightly higher concentration of AcO^- than F^-, which may be attributed to the higher electronegativity and smaller size of the fluoride ions that makes them to bind strongly with the receptors.[8c,d]

On the other hand, exposure to chloride, bromide and iodide did not result in any spectral changes in the receptors. Moreover, the fluoride-induced colour changes remain the same even in the presence of other halide anions. Upon the addition of less than 1 equiv of fluoride (1×10^{-6} M), the colour of the solution changed from colourless to orange and fluorescent yellow for the receptors **1** and **2**, respectively. Hence, fluoride anions could be detected even at low concentrations (10^{-6} M).

The binding constant for the fluoride complexes of receptors **1** and **2** were obtained from the variation in the absorbance at 458 and 422 nm, respectively. The binding constants (K_a) for **1** and **2** with fluoride were determined to be 2.52×10^3 M^{-1} and 6.20×10^3 M^{-1}, respectively. Receptor **2** showed a higher binding constant than receptor **1** due to the introduction of another nitro group in **2**, which increased the acidity of the OH and NH protons and enhanced the hydrogen bonding ability, resulting in a strong binding with fluoride.[24]

In aprotic solvents, solutions of receptors **1** and **2** underwent a colour change with fluoride ions; upon the addition of a few drops of a protic solvent (water, methanol, etc.) the colour disappeared. This is because protic solvents compete for fluoride ions with OH and NH groups. This observation also indicated that hydrogen bonding was involved between the receptors and fluoride ions.[11]

In conclusion, chromogenic receptors **1** and **2** were synthesized in good yields via Schiff's base condensation. Solutions of **1** and **2** became orange and fluorescent yellow in colour, respectively, upon the addition of fluoride, which could be detected by the naked-eye at ppm level concentrations of fluoride ions. Hence, receptors **1** and **2** can be used as selective colorimetric sensors for fluoride ions.

Acknowledgements

The authors gratefully acknowledge DST (FIST) and URF, University of Madras for financial assistance. M.K. also acknowledges the Department of Science and Technology (Government of India) for the project grant.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.11.006.

References and notes

1. (a) Amendola, V.; Esteban-Gomez, D.; Fabbrizzi, L.; Licchelli, M. *Acc. Chem. Res.* **2006**, *39*, 343–353; (b) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486–516.
2. (a) Geddes, C. D. *Meas. Sci. Technol.* **2001**, *12*, R53; (b) Kleerekoper, M. *Endocrinol. Metab. Clin. North Am.* **1998**, *27*, 441–452; (c) Kirk, K. L. *Biochemistry of Halogens and Inorganic Halides*; Plenum Press: New York, 1991.
3. (a) Xu, J.; Liu, K.; Di, D.; Shao, S.; Guo, Y. *Inorg. Chem. Commun.* **2007**, *10*, 681–684; (b) Suksai, C.; Tuntulani, T. *Chem. Soc. Rev.* **2003**, *32*, 192–202; (c) Wiskur, S. L.; Ait-Haddou, H.; Lavigne, J. J. V.; Anslyn, E. *Acc. Chem. Res.* **2001**, *34*, 963–972; (d) Inouye, M. *Color. Non-Text. Appl.* **2000**, 238–274; (e) Lohr, H. G.; Vogtle, F. *Acc. Chem. Res.* **1985**, *18*, 65–72.
4. Ghosh, T.; Maiya, B. G. *J. Chem. Sci.* **2004**, *116*, 17–20.
5. (a) Duke, R. M.; Gunnlaugsson, T. *Tetrahedron Lett.* **2007**, *48*, 8043–8047; (b) Jose, D. A.; Kumar, D. K.; Ganguly, B.; Das, A. *Org. Lett.* **2004**, *6*, 3445–3448.
6. Kim, H. J.; Lee, J. H.; Kim, T. H.; Lyoo, W. S.; Kim, D. W.; Lee, C.; Lee, T. S. *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 1456–1546.
7. (a) Yu, M.; Lin, H.; Zhao, G.; Lin, H. *J. Mol. Recognit.* **2007**, *20*, 69–73; (b) Luxami, V.; Kumar, S. *Tetrahedron Lett.* **2007**, *48*, 3083–3087; (c) Fabbrizzi, L.; Marcotte, N.; Stomeo, F.; Taglietti, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 3809–3811.
8. (a) Lee, C.; Lee, D. H.; Hong, J.-I. *Tetrahedron Lett.* **2001**, *42*, 8665–8668; (b) Lee, K. H.; Lee, H.-Y.; Lee, D. H.; Hong, J.-I. *Tetrahedron Lett.* **2001**, *42*, 5447–5449; (c) Lee, D. H.; Lee, K. H.; Hong, J.-I. *Org. Lett.* **2001**, *3*, 5–8; (d) Lee, D. H.; Lee, H. Y.; Lee, K. H.; Hong, J.-I. *Chem. Commun.* **2001**, 1188–1189; (e) Anzenbacher, P., Jr.; Try, A. C.; Miyaji, H.; Jursikova, K.; Lynch, V. M.; Marquez, M.; Sessler, J. L. *J. Am. Chem. Soc.* **2000**, *122*, 10232–10268.
9. (a) Gale, P. A.; Twyman, L. J.; Handlin, C. I.; Sessler, J. L. *Chem. Commun.* **1999**, 1851–1852; (b) Niikura, K.; Bisson, A. P.; Anslyn, E. V. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1111–1114.
10. (a) Chen, C. F.; Chen, Q. Y. *New J. Chem.* **2006**, *30*, 143–147; (b) Libra, E. R.; Scott, M. J. *Chem. Commun.* **2006**, 1485–1487; (c) Channa, A.; Steed, A. W. *Dalton Trans.* **2005**, 2455–2461; (d) Ghosh, S.; Choudhury, A. R.; Row, T. N. G.; Maitra, U. *Org. Lett.* **2005**, *7*, 1441–1444; (e) Lee, K. H.; Lee, H. Y.; Lee, D. H.; Hong, J.-I. *Tetrahedron Lett.* **2001**, *42*, 5447–5449; (f) Lee, C.; Lee, D. H.; Hong, J.-I. *Tetrahedron Lett.* **2001**, *42*, 8665–8668.
11. Ghosh, T.; Maiya, B. G.; Wong, M. W. *J. Phys. Chem. A.* **2004**, *108*, 11249–11259.
12. (a) Boiocchi, M.; Del Boca, L.; Gomez, D. E.; Fabbrizzi, L.; Licchelli, M.; Monazani, E. *J. Am. Chem. Soc.* **2004**, *126*, 16507–16514; (b) Gomez, D. E.; Fabbrizzi, L.; Lichelli, M.; Monazani, E. *Org. Biomol. Chem.* **2005**, *3*, 1495–1507.
13. (a) Peng, X.; Wu, Y.; Fan, J.; Tian, M.; Han, K. *J. Org. Chem.* **2005**, *70*, 10524–10531; (b) Gomez, D. E.; Fabbrizzi, L.; Licchelli, M. *J. Org. Chem.* **2005**, *70*, 5717–5720; (c) Gronert, S. *J. Am. Chem. Soc.* **1993**, *115*, 10258–10266.
14. (a) Amendola, V.; Boiocchi, D.; Colasson, B.; Fabbrizzi, L. *Inorg. Chem.* **2006**, *45*, 6138–6147; (b) Boiocche, M.; Boca, L. D.; Gomez, D. E.; Fabbrizzi, L.; Liccheli, M.; Monzanic, E. *Chem. Eur. J.* **2005**, *11*, 3097–3104; (c) Amendola, V.; Boiocchi, M.; Fabbrizzi, L.; Palchetti, A. *Chem. Eur. J.* **2005**, *11*, 5648–5660; (d) Peng, X.; Wu, Y.; Fan, J.; Tian, M.; Han, K. . *J. Org. Chem.* **2005**, *70*, 10524–10531; (e) Gunnlaugasson, T.; Kruger, P. E.; Jensen, P.; Tierney, J.; Ali, H. D. P.; Hussey, G. M. *J. Org. Chem.* **2005**, *70*, 10875–10878.
15. Gayathri, D.; Velmurugan, D.; Ravikumar, K.; Saravanakumar, D.; Kandaswamy, M. *Acta Crystallogr. E* **2007**, *63*, o2224–o2225.
16. (a) *Selected data for receptor* **1**: $C_{13}H_{11}N_3O_3$: Yield: 1.09 g (89%); mp: 180 °C. Elemental Anal. Calcd: C, 60.70; H, 4.31; N, 16.33. Found: C, 60.69; H, 4.29; N, 16.32. EI mass (*m*/*z*): 257 $(M)^+$; IR (KBr, ν cm^{-1}): 3434 (OH), 3333 (NH), 1600 (C=N), 1496 (NO_2). ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 11.65 (s, 1H), 10.64 (s, 1H), 8.50 (s, 1H), 8.14 (s, 1H), 8.03 (d, 2H, $J = 8$ Hz) 7.22 (t, 2H, $J = 7.8$ Hz), 7.01 (d, 2H, $J = 8.8$ Hz), 6.76 (t, 1H, $J = 7$ Hz); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 112.0, 116.3, 119.4, 121.2, 122.2, 124.4, 129.3, 132.4, 140.1, 144.5, 160.8. λ_{max} (nm) in CH_3CN: 348, 300, 232, 194; (b) *Selected data for receptor* **2**: $C_{13}H_{10}N_4O_5$: Yield: 1.23 g (89%); mp: 254 °C. Elemental Anal. Calcd: C, 51.66; H, 3.33; N, 18.54. Found: C, 51.66; H, 3.32; N, 18.54. EI mass (*m*/*z*): 302 $(M)^+$; IR (KBr, ν cm^{-1}): 3445 (OH), 3361 (NH), 1613 (C=N), 1471 (NO_2). ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 11.78 (1H, s), 10.27 (s, 1H), 9.06 (1H, s), 8.38 (1H, s), 8.16 (1H, d, $J = 9.2$ Hz), 8.03 (1H, d, $J = 8$ Hz), 8.16–8.28 (m, 4H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 112.1, 116.0, 119.3, 122.4, 123.2, 124.1, 129.3, 139.2, 145.4, 152.2, 161.1, 163.2. λ_{max} (nm) in CH_3CN: 348, 301, 233, 192.
17. (a) Ahmed, I. T. *Spectrochim. Acta Part A* **2006**, *65*, 5–10; (b) Lee, D. H.; Lee, H. Y.; Hong, J.-I. *Tetrahedron Lett.* **2002**, *43*, 7273–7276; (c) Fujii, A.; Ebata, T.; Mikami, N. J. *Phys. Chem. A* **2002**, *106*, 8554–8560; (d) Gerhards, M.; Unterberg, C.; Kleinermanns, K. *Phys. Chem. Phys.* **2000**, *2*, 5538–5544.
18. Varquez, M.; Fabbirizzi, L.; Taglietti, A.; Pedrido, R. M.; Gonzalez-Noya, A. M.; Bermejo, M. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 1962–1965.
19. Shao, S.; Guo, Y.; He, L.; Jiang, S.; Yu, X. *Tetrahedron Lett.* **2003**, *44*, 2175–2178.
20. (a) Descalzo, A. B.; Jimenez, D.; Marcos, M. D.; Martinez-Manez, R.; Soto, J.; El Haskouri, J.; Guillem, C.; Beltran, D.; Amoros, P.; Borrachero, M. V. *Adv. Mater.* **2002**, *14*, 966–969; (b) Bargossi, C.; Fiorini, M. C.; Montalti, M.; Prodi, L.; Zaccheroni, N. *Coord. Chem. Rev.* **2000**, *208*, 17–32.
21. (a) Gunnlaugsson, T.; Kruger, P. E.; Jensen, P.; Pfefer, F. M.; Hussey, G. M. *Tetrahedron Lett.* **2003**, *44*, 8909–8913; (b) Carmiolo, S.; Gale, P. A.; Hursthouse, M. B.; Light, M. E. *Org. Biomol. Chem.* **2003**, *1*, 741–744; (c) Shenderovich, I. G.; Tolstoy, P. M.; Golubev, N. S.; Smirnov, S. N.; Denisov, G. S.; Limbach, H.-H. *J. Am. Chem. Soc.* **2003**, 11710.
22. (a) Miyaji, H.; Sato, W.; Sessler, J. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 154–157; (b) Black, C. B.; Andrioletti, B.; Try, A. C.; Ruiperez, C.; Sessler, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 10438–10439.
23. Hammud, H. H.; Ghannoum, A.; Masoud, M. S. *Spectrochim. Acta Part A* **2006**, *63*, 255–265.
24. Kato, R.; Nishizawa, S.; Hayashita, T.; Teramae, N. *Tetrahedron Lett.* **2001**, *42*, 5053–5056.