Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Devaraj, Soosai , Saravanakumar, Duraisamy and Kandaswamy, Muthusamy(2009) 'Simple colorimetric fluoride sensors based on nitrophenyl derivatives', Supramolecular Chemistry, 21: 8, 717 — 723
To link to this Article: DOI: 10.1080/10610270902795376
URL: http://dx.doi.org/10.1080/10610270902795376

Supramolecular Chemistry
Vol. 21, No. 8, December 2009, 717–723

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Simple colorimetric fluoride sensors based on nitrophenyl derivatives

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(*Received 17 September 2008; final version received 21 January 2009*)

Easy to prepare fluoride ion sensors bearing OH and NH groups as binding sites and nitrophenyl group as a chromophore [2-[(4-nitrophenylimino)methyl]-4-methylphenol (**1**), 2-[(4-nitrophenylamino)methyl]-4-methylphenol (**2**), 2-[(2,4-dinitrophenylimino)methyl]-4-methylphenol (**3**) and 2-[(2,4-dinitrophenylamino)methyl]-4-methylphenol (**4**)] were synthesised and characterised. The visible colour changes, the UV–vis and ^{1}H NMR spectral changes towards anions were studied. The sensing ability of the receptor depends on the presence of electron-withdrawing group attached to the receptors and extended conjugation in the receptor framework and the order of the sensing ability is found to be **3** > **1** > **4** > **2** based on binding constant.

Keywords: colorimetric sensors; chemosensors; NMR studies; fluoride sensors

Introduction

Colorimetric molecular sensors are attractive because they can be implemented into simple low-cost devices and can often be monitored by the naked eye (*1*). The general strategy to produce a colorimetric anion sensor is based on an anion-binding group with a chromogenic moiety capable of signalling the binding event through intramolecular charge-transfer (ICT) process that leads to a change invisible to the naked eye (*2*). Anions play an important role in numerous kinds of chemical and biological processes, and considerable efforts have been devoted to design the receptors or sensors that have the ability to selectively bind and sense anions (*3*). In particular, the selective sensing of fluoride ions has gained attention because of their importance in the clinical treatment of osteoporosis and the fluoride produced as a result of over-accumulation of fluoride in the bone. While a number of receptors that are able to bind fluoride ions with high affinity and selectivity have been reported (*4–6*), the sensing and detection of fluoride ion to produce a measurable output still remains challenging. Moreover, all of the attention has been focused on receptors incorporating amides (*7*), ureas/thioureas (*8*, *9*) and pyrroles (*10*, *11*), with only limited number of reports available using OH as a binding site so far (*12–19*). Hence, in this present study, we report chromogenic and selective fluoride chemosensors possessing a phenolic OH group in **1** and **3**, and OH and NH groups in **2** and **4** able to bind fluoride via H-bond interactions or deprotonation, and π-conjugating nitrophenyl group that acts as a chromogenic signalling unit in continuation of our previous work (*20–23*). The nature of these simple phenol-based sensors can be altered by introducing one or two nitro groups on phenyl ring, which are able to tune the anion recognition selectivity (*24*).

Results and discussion

Receptors **1** and **3** were synthesised in good yield (Scheme 1) by using Schiff's base condensation of equivalent molar 5-methylsalicylaldehyde with 4-nitroaniline (**1**) and 2,4-dinitroaniline (**3**), respectively. Furthermore, reduction of receptors **1** and **3** with sodium borohydride yielded the receptors **2** and **4**. The microcrystalline of receptor **1** was recrystallised from ethanol and the crystals suitable for XRD were obtained on slow evaporation. Receptor **1** was characterised by XRD (*25*) and the ORTEP plot is shown in Figure 1.

FT-IR studies

FT-IR spectra for **1**–**4** were recorded in acetonitrile solution in the absence and presence of fluoride ions (see Figures S1–S8 of Supplementary data). The band at around 1620 cm^{-1} in the spectra (Figures S1 and S5) of receptors **1** and **3** is due to $\nu_{(C=N)}$, which does not occur in the case of **2** and **4**, but showed a new band around 3100 cm^{-1} for the presence of $\nu_{(NH)}$ (Figures S3 and S7). As expected, the spectra of receptors **1**–**4** display $\nu_{(OH)}$ band at around 3400 or 3300 cm^{-1}. When spectra were recorded in the presence of 1 equiv. of F^-, the stretching frequency of the —OH group for **1** and **3** is found to be shifted from 3449 to 3409 cm^{-1} and from 3421 to 3396 cm^{-1}, respectively (Figures S2 and S6). Both the stretching frequency of —OH and —NH groups for

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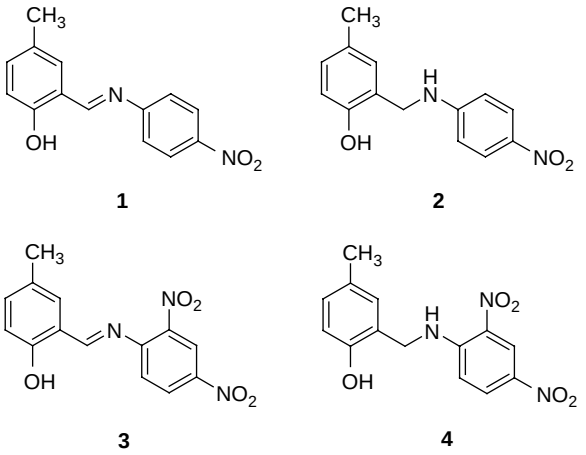
ISSN 1061-0278 print/ISSN 1029-0478 online

DOI: 10.1080/10610270902795376
http://www.informaworld.com



Scheme 1. Structures of receptors **1**–**4**.

receptor **2** shifted from 3398 to 3378 cm^{-1} and from 3092 to 3081 cm^{-1}, respectively (Figure S4). The same trend was observed for receptor **4**, with a shift from 3447 to 3417 cm^{-1} (—OH) and from 3135 to 3122 cm^{-1} (—NH) (Figure S8). 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 (*26*–*30*).

^{1}H NMR studies

The ^{1}H NMR (400 MHz) spectroscopy has been widely used to investigate the receptor–substrate interactions as it provides details of interactions between the host and the guest. To evaluate the intermolecular interactions between the receptors **1**–**4** with fluoride anion, we carried out ^{1}H NMR studies in DMSO-d_6. A partial ^{1}H NMR spectra of the receptors **1**–**4** are shown in Figures 2, S9–S11 (Supplementary data), respectively. The ^{1}H NMR spectrum in DMSO-d_6 of **1** showed (Figure 2) changes on the addition of fluoride ions: the —OH proton signal (s, 1H) shifted from δ 12.01 to 10.05 ppm when 1 equiv. of F^- ions was added. The ^{1}H NMR spectrum of receptor **3** showed the signal at δ 12.8 (Figure S10) for —OH proton. The —OH proton signal (s, 1H) of receptor **3** was shifted from δ 12.5 to 9.8 ppm during the titration with 1 equiv. of tetrabutylammonium fluoride (TBAF). The ^{1}H NMR spectrum of receptor **4** is shown in Figure S11, which shows the shifting of peaks from δ 9.82 to 9.39 ppm for —OH and from δ 5.3 to 5.2 ppm for —NH, respectively, upon addition of 1 equiv. of F^- ion. With higher equivalents of F^-, deprotonation of the receptors **1**, **3** and **4** is possible to occur, and, indeed, we observed such deprotonation and formation of HF_2^- in the ^{1}H NMR spectra of **1**, **3** and **4** (DMSO-d_6) as a new signal at 16 ppm (*36*–*38*) (Figure 2). The ^{1}H NMR spectrum of receptor **2** showed the presence of —OH and —NH protons at δ 9.32 and 5.15 ppm, respectively (Figure S9). After the addition of 1 equiv. of F^-, the peaks were shifted from δ 9.32 to 9.02 ppm for —OH and from δ 5.15 to 5.10 ppm for —NH, respectively. This result indicates that a hydrogen bond complex between **2** and fluoride ion is formed (*44*). The increase of electron density in the phenyl ring causes a shielding effect and should promote an upfield shift that is expected to come from the formed hydrogen bond (*45*). The absence of signal at 16 ppm might be due to the strong formation of hydrogen bonds between the fluoride ions and the —OH and —NH groups of receptor **2**.

Colorimetric studies

The colorimetric sensing ability of receptors **1**–**4** with halide anions (F^-, Cl^-, Br^- and I^-) in CH_3CN was monitored by visual (naked eye) and UV–vis absorption

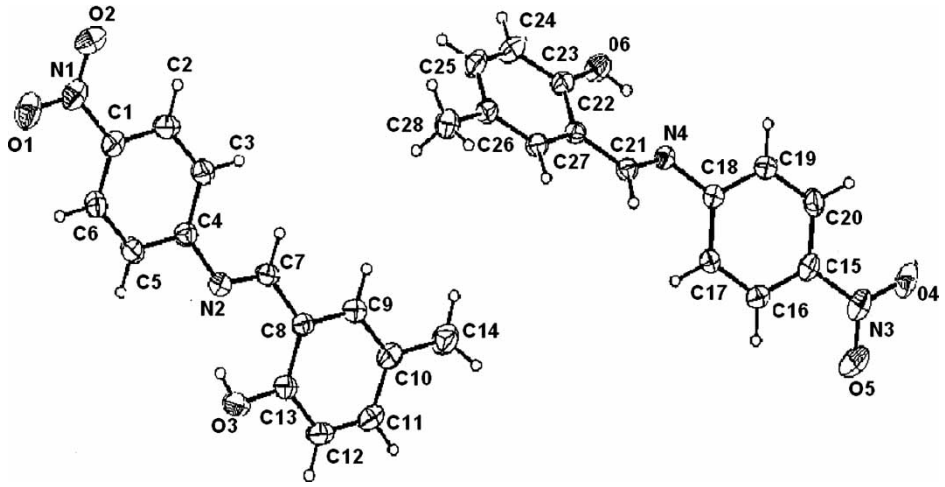


Figure 1. ORTEP plot of the crystal structure of **1**.

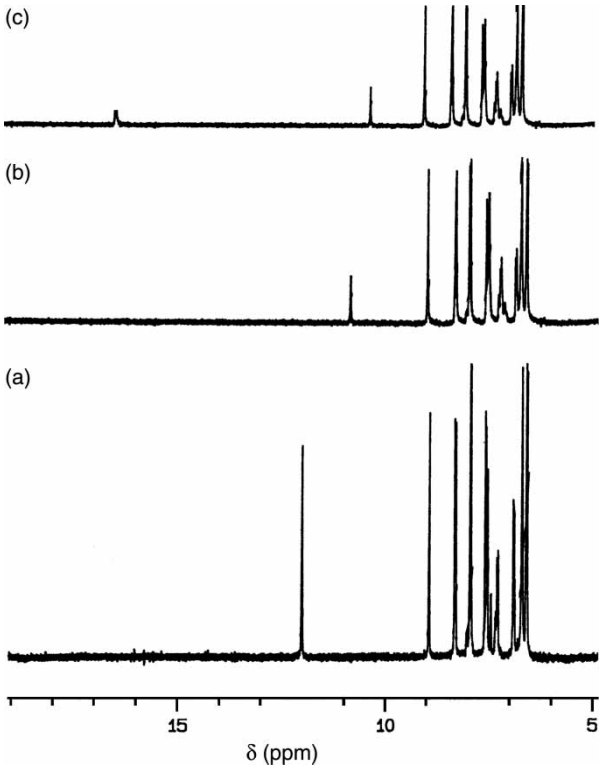


Figure 2. Partial ^{1}H NMR (400 MHz) spectra of receptor **1** in DMSO-d_6 in the (a) absence, (b) presence of 1 equiv. and (c) 3 equiv. of [n-Bu_4N]F.

methods. Microlitres of 1×10^{-2} M halide anions (F^-, Cl^-, Br^- and I^-) were added as tetrabutylammonium salts to 5×10^{-5} M solutions of the receptors in CH_3CN. In the naked-eye experiments, receptors **1**–**4** (5×10^{-5} M in CH_3CN) showed dramatic changes from colourless to yellowish brown (**1** and **2**), yellow (**3**) and red (**4**), respectively, in the presence of 5×10^{-3} M TBAF (Figures S12–S15). All the four receptors were found to be insensitive to the addition of a large excess of Cl^-, Br^- and I^- (up to 100 equiv.). Colour changes are most probably due to the formation of hydrogen bond or deprotonation between the —OH groups (**1** and **3**) and —OH and —NH (**2** and **4**), and fluoride ions. These H-bond interactions or deprotonation affects the electronic properties of the chromophore, resulting in a colour change along with a new charge-transfer interaction between the fluoride-bound —OH (**1** and **3**) and —OH and —NH (**2** and **4**), and the electron-deficient nitrophenyl group (*42*, *43*). Fluoride ions interact with the receptors more strongly due to their higher electronegativity and their smaller size compared with the other halides (*44*).

Observable changes also took place in $CHCl_3$ and DMSO solutions. Upon the addition of fluoride ions, the colourless solutions became light yellow (**1** and **3**), yellowish brown (**3**), red (**4**) in $CHCl_3$ and, turned red (**1**, **3** and **4**) and yellowish brown (**2**) in DMSO. The colours of the receptors in $CHCl_3$ and DMSO remained the same in the presence of chloride, bromide and iodide.

UV–vis studies

The recognition behaviour of receptors **1**–**4** towards halide anions was also investigated by UV–vis absorption methods. Electronic spectra of the receptors showed different transitions in $CHCl_3$, CH_3CN and DMSO and the data are given in Table 1. UV–vis titrations were carried out in CH_3CN at a concentration level of 5.0×10^{-5} M upon addition of 0.01 ml (0.33 equiv.; 5×10^{-3} M) of TBAF and the spectra recorded are shown in Figure 3(a)–(d). The band at around 220 nm is assigned to the excitation of the π electrons of the aromatic system. The band around 320 nm is due to the transition between the π orbital localised on the azomethine group (C═N) (*45*).

When fluoride anion was added to the solution of **1**, the intensity of bands at 323 and 366 nm decreased, while a new peak at 503 nm appeared with a change of the solution from colourless to yellowish brown as the fluoride concentration increased, which indicated that a strong binding interaction or deprotonation took place between the anions and receptor **1** with an isosbestic point at 405 nm. However, addition of fluoride ions produced a shift around 18 nm in the absorption for receptor **2** at 378 nm and also an increase in the intensity of the absorption spectra with an isosbestic point at 388 nm was observed with a colour change from colourless to yellowish brown.

For receptor **3**, the intensity of the peak at 300 nm decreased with the addition of fluoride, whereas two new peaks at 374 and 455 nm increased with an isosbestic point at 363 nm was observed with a colour change of the solution from colourless to yellow. Due to hydrogen bond

Table 1. UV–vis data for **1**–**4** in different solvents.

	λ_{max} (nm)			
Solvent	1	2	3	4
$CHCl_3$	334, 275, 241	372, 271, 210	349, 299, 243	385, 331, 220
CH_3CN	366, 323, 215, 192	378, 286, 224, 197	347, 300, 299, 192	389, 336, 225, 210
DMSO	375, 328, 256	385, 292, 242	384, 317, 261	401, 342, 231

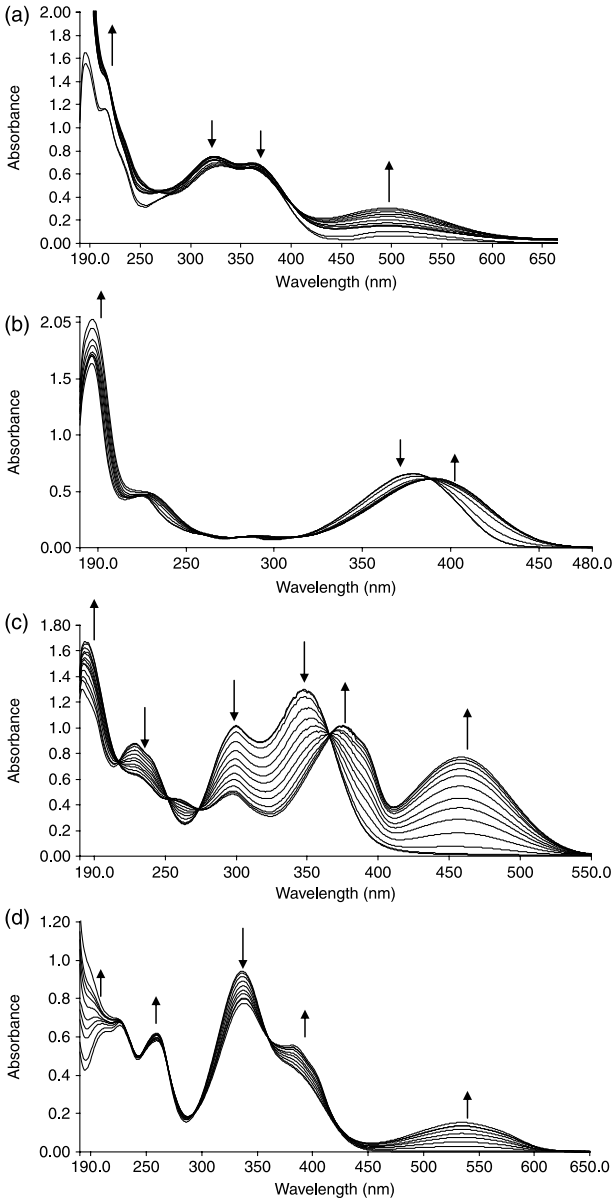


Figure 3. (a) UV–vis spectral changes observed for **1** upon addition of fluoride anions in CH_3CN. $[1] = 5 \times 10^{-5}$ M; $[F^-] = 0$–2 equiv. (b) UV–vis spectral changes observed for **2** upon addition of fluoride anions in CH_3CN. $[1] = 5 \times 10^{-5}$ M; $[F^-] = 0$–2 equiv. (c) UV–vis spectral changes observed for **3** upon addition of fluoride anions in CH_3CN. $[1] = 5 \times 10^{-5}$ M; $[F^-] = 0$–2 equiv. (d) UV–vis spectral changes observed for **4** upon addition of fluoride anions in CH_3CN. $[1] = 5 \times 10^{-5}$ M; $[F^-] = 0$–2 equiv.

formation of —OH (*8*) with F^- in organic medium, the UV–vis absorption band was shifted to a longer wavelength. It can be observed for receptor **4** that the band at 336 nm decreased with two new peaks at 389, 535 nm and an increase with an isosbestic point at 361 nm was observed with a colour change of the solution colourless to red. Under the same conditions, there were no significant changes with spectrum upon the addition of tetrabutylammonium chloride, bromide and iodide ions even in the presence of high concentration of anions (> 100 equiv.).

UV–vis titrations were carried out in CH_3CN at a concentration level of 5.0×10^{-5} M for the receptors **1**–**4** with a standard solution of *n*-Bu_4OH [(0.01–0.06 ml) 5×10^{-3} M] and the spectra are shown in Supplementary data (Figures S12–S15). In case of **1**, **3** and **4**, the receptors absorbed at 366, 300 and 336 nm, respectively. Upon titration with more than 1 equiv. of —OH^-, these bands were decreased in intensity along with the appearance of new absorption bands at 534, 533 and 529 nm, respectively. With further successive addition of —OH^- ions, these peaks increased in intensity stepwise. These peaks reached their limiting value after the addition of 2 equiv. of OH^-. This observation indicates that the addition of more than 1 equiv. of —OH^- deprotonates the receptors indicated by the appearance of new absorbance peaks (*31*–*33*).

On comparing the receptors **1**–**4**, receptor **3** gave rise to major changes in the ICT band at long wavelength in the presence of 0–2 equiv. of F^-. No such large variations at longer wavelength absorption were observed for **1**, **2** and **4** up to 2 equiv. of F^-. Deprotonation of receptor **3** is more favourable than other receptors because of the presence of two nitro groups with extended π-conjugation. But deprotonation of receptors **1** and **4** is favoured upon an addition of more than 2 equiv. of F^-. These observations suggest that addition of more than 1 (**3**) or 2 (**1** and **4**) equiv. of F^- resulted in the formation of the stable H-bond complex $[HF_2]^-$ inducing deprotonation prevails the Bronsted acid–base reaction (*34*, *35*, *37*–*41*). For receptor **2**, no such absorption changes were observed. Hence, we do not think that such deprotonation occurs in **2**. Consequently, we propose that the F^- recognition occurs by the initial hydrogen bonding up to 1 (for receptor **3**) or 2 (for receptors **1** and **4**) equiv. of F^- to the receptor, followed by deprotonation.

Similarly, the binding properties of receptors **1**–**4** 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**–**4** upon addition of incremental amounts of 0.01 ml (5×10^{-3} M) of tetrabutylammonium acetate. No significant change was observed with these receptors even after the addition of 3 equiv. of acetate ion, which may be attributed to their lower basicity.

The binding constant for the fluoride complex for receptors **1**–**4** was obtained from the variation in the absorbance at the appropriate wavelength (503, 378, 455 and 336 nm, respectively). The binding constants (K_a) for **1**–**4** with fluoride were determined to be 5.2×10^4, 1.6×10^3, 1.7×10^5 and 8.6×10^3 M^{-1}. The higher binding constant was achieved for receptor **3**, which might

be due to the introduction of another nitro group in **3**, which increases the acidity of phenolic —OH group and enhances the hydrogen bond-donating character of this receptor (*46*). However, the decrease in the binding constant values for **2** and **4** may be due to the absence of extended π-conjugation.

Solvent effect can play a role in governing anion binding and selectivity. Hence, the sensing ability of the compound in the presence of halide anions has been studied in different solvents, such as $CHCl_3$ and DMSO. The dipole and dielectric constant of DMSO are much larger than that of $CHCl_3$ and CH_3CN is the reason for the different behaviour observed for receptors **1**–**4** in the presence of fluoride ions.

In aprotic solvents, the receptors **1**–**4** induced a colour change with fluoride ions and upon addition of a few drops of protic solvents (water, methanol, etc.), the colour disappeared. This is because protic solvents compete for fluoride ions with amide or amino groups. This observation indicated that hydrogen bonding is involved between the receptors and fluoride ions (*47*).

Experimental

Materials and methods

All the solvents $CHCl_3$, CH_3CN and DMSO were used as HPLC grade and purchased from Qualigens (Mumbai, India). Tetrabutylammonium salts of halides were purchased from Aldrich Chemicals (Milwaukee, WI, USA).

The ^1H and ^{13}C NMR spectra were recorded on a JEOL 400 MHz spectrometer in DMSO-d_6. The IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer. UV–vis experiments were performed on a Perkin-Elmer FT UV–vis spectrometer. Elemental analysis of the receptors was obtained in Heraeus CHN rapid analyser. The EI-MS was recorded using JEOL Gcmate. The crystal data were collected on a Bruker Smart Apex CCD Diffractomer equipped with a fine-focus sealed tube employing graphite monochromatised Mo Kα radiation using ω scan mode. The structures were solved using SHELXS-97 and the model was refined using SHELXL-97.

Synthesis of receptors

*Synthesis of 4-methyl-2-[(4-nitrophenylimino)methyl]-phenol (**1**)*

Receptor **1** was synthesised by Schiff's base condensation between 2-hydroxy-5-methylbenzaldehyde and *p*-nitroaniline. To a solution of 2-hydroxy-5-methylbenzaldehyde (0.5 g, 3.67 mmol) in methanol (25 ml), *p*-nitroaniline (0.506 g, 3.67 mmol) in methanol (25 ml) was added under stirring. The resulting mixture was refluxed for 3 h and cooled to room temperature. The solid product was collected by filtration and washed with cold methanol. The microcrystalline compound was recrystallised from hot ethanol; yellow coloured crystals suitable for XRD were obtained on slow evaporation. Yield: 90%; mp: 148°C. Elemental analysis: calcd: C, 65.62; H, 4.72; N, 10.93%. Found: C, 65.60; H, 4.73; N, 4.70%. EI mass (*m*/*z*): 257 $(M+1)^+$; IR [KBr, ν (cm^{-1})]: 3449, 1628, 1497. ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 12.3 (s, 1H), 8.57 (s, 1H), 8.30–8.28 (d, 2H, $J = 8$ Hz), 8.35–8.21 (m, 4H), 6.96–6.94 (d, 1H, $J = 7.76$ Hz), 3.52 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 20, 117, 119, 122, 125, 129, 133, 136, 145, 147, 166.

*Synthesis of 4-methyl-2-[(3-methyl-5-nitrophenylimino)methyl]-phenol (**2**)*

Receptor **2** was synthesised by the method as described above from 2-hydroxy-5-methylbenzaldehyde (0.5 g, 3.67 mmol) and 2,4-dinitroaniline (0.672 g, 3.6 mmol) in methanol (25 ml). Yield: 80%; mp: 110°C. Elemental analysis: calcd: C, 65.11; H, 5.46; N, 10.85%. Found: C, 65.09; H, 5.47; N, 10.83%. EI mass (*m*/*z*): 259 $(M+1)^+$; IR [KBr, ν (cm^{-1})]: 3398, 3092, 1497; ^1H NMR (400 MHz, $CDCl_3$): δ 9.25 (s, 1H), 8.06–8.04 (d, 2H, $J = 7.6$ Hz), 8.03–8.01 (d, 2H, $J = 7.2$ Hz), 7.01 (s, 1H), 6.97–6.95 (d, 1H, $J = 7.1$ Hz), 6.78–6.76 (d, 1H, $J = 7.2$ Hz), 5.15 (s, 1H), 4.38 (s, 2H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 20.4, 43.7, 111.7, 113.3, 115.7, 123.7, 138.2, 158.3, 153.5.

*Synthesis of 2-{(2,4-dinitrophenylimino)methyl}-4-methylphenol (**3**)*

To receptor **1** in methanol (25 ml), excess $NaBH_4$ was added in small portions and the mixture was stirred for 2 h at 25°C. The solvent was removed in vacuum and the product was suspended in water (60 ml) and extracted with $CHCl_3$ (3 × 50 ml). The organic phase was dried with anhydrous $MgSO_4$, filtered and evaporated to dryness. The product was recrystallised using chloroform to yield receptor **2**. Yield: 85%; mp: 154°C. Elemental analysis: calcd: C, 55.82; H, 3.68; N, 13.95%. Found: C, 55.79; H, 3.70; N, 13.97%. EI mass (*m*/*z*): 303.1 $(M+2)^+$; IR [KBr, ν (cm^{-1})]: 3421, 1624, 1484. ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 12.5 (s, 1H), 8.75 (s, 1H), 8.70–8.68 (d, 2H, $J = 7.9$ Hz), 8.35 (s, 1H), 8.13–8.11 (d, 1H, $J = 8.2$ Hz), 8.10–8.08 (d, 1H, $J = 7.2$ Hz), 7.09 (s, 1H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 25.1, 119, 123, 128, 129, 131, 135, 142, 149, 152, 155, 169.

*Synthesis of 2-{(2,4-dinitrophenylamino)methyl}-4-methylphenol (**4**)*

Receptor **4** was synthesised by the method as described above.

Yield: 78%; mp: 178°C. Elemental analysis: calcd: C, 55.45; H, 4.32; N, 13.86%. Found: C, 55.46; H, 4.31; N, 13.84%. EI mass (*m/z*): 305 $(M+1)^+$; IR [KBr, ν (cm^{-1})]: 3417, 3322, 1469; ^1H NMR (400 MHz, $CDCl_3$): δ 9.82 (s, 1H), 8.33–8.31 (d, 2H, $J = 7.2$ Hz), 8.29 (s, 1H), 6.92 (s, 1H), 6.84–6.82 (d, 1H, $J = 7.4$ Hz), 6.81–6.79 (d, 1H, $J = 7.7$ Hz), 5.30 (s, 1H), 4.48 (s, 2H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 24.6, 45.1, 112.1, 113.1, 114.2, 129.1, 130.1, 132.2, 133.4, 149.2, 151.1, 152.3.

UV–vis spectroscopic methods

All solutions of receptors **1**–**4** (5×10^{-5} M) were made up with HPLC grade CH_3CN solvent. UV–vis absorption titrations were carried by the addition of microlitres of anions as tetrabutylammonium salts (5×10^{-3} M) and cations as its perchlorate salts (5×10^{-3} M). The UV–vis spectra were recorded after each addition.

Conclusion

In summary, we have designed and synthesised new chromogenic receptors **1**–**4** containing phenolic moiety. These receptors exhibit very high selectivity for fluoride in the presence of large excess of Cl^-, Br^- and I^-. The chromogenic receptors **1**–**4** developed yellowish brown (**1** and **2**), yellow and red colours upon addition of fluoride ions, respectively. Fluoride ions can be detected at ppm level concentrations by the naked eye. Hence, the receptors **1**–**4** can be used as a selective and simple colorimetric sensor 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.

References

(1) Nguyen, B.T.; Anslyn, E.V. *Coord. Chem. Rev.* **2006**, *250*, 3118–3127.
(2) Suksai, C.; Tuntulani, T. *Chem. Soc. Rev.* **2003**, *32*, 192–202.
(3) Ren, J.; Zhao, X.L.; Wang, Q.-C.; Ku, C.F.; Qu, D.H.; Chang, C.P.; Tian, H. *Dyes Pigments* **2005**, *64*, 193–200.
(4) Esteban-Gomez, D.; Fabbrizzi, L.; Licchelli, M. *J. Org. Chem.* **2005**, *70*, 5717–5720.
(5) Miao, R.; Zheng, Q.Y.; Chen, C.F.; Huang, Z.T. *Tetrahedron Lett.* **2004**, *45*, 4959–4962.
(6) Day, J.K.; Bresner, C.; Coombs, N.D.; Fallis, I.A.; Ooi, L.-L.; Aldridge, S. *Inorg. Chem.* **2008**, *47*, 793–804.
(7) Kim, H.J.; Lee, J.H.; Kim, T.H.; Lyoo, W.S.; Kim, D.W.; Lee, C.; Lee, T.S. *J. Polym. Sci. A: Polym. Chem.* **2007**, *45*, 1546–1556.
(8) Duke, R.M.; Gunnlaugsson, T. *Tetrahedron Lett.* **2007**, *48*, 9039–9043.
(9) Jose, D.A.; Kumar, D.K.; Ganguly, B.; Das, A. *Org. Lett.* **2004**, *6*, 3445–3448.
(10) Ghosh, T.; Maiya, B.G. *J. Chem. Sci.* **2004**, *116*, 17–27.
(11) Piatek, P.; Jurczak, J. *Chem. Commun.* **2002**, 2450–2451.
(12) Yu, M.; Lin, H.; Zhao, G.; Lin, H. *J. Mol. Recognit.* **2007**, *20*, 69–73.
(13) Luxami, V.; Kumar, S. *Tetrahedron Lett.* **2007**, *48*, 3083–3087.
(14) Chen, C.F.; Chen, Q.Y. *New J. Chem.* **2006**, *30*, 143–147.
(15) Libra, E.R.; Scott, M.J. *Chem. Commun.* **2006**, 1485–1491.
(16) Channa, A.; Steed, A.W. *Dalton Trans.* **2005**, 2455–2461.
(17) Ghosh, S.; Choudhury, A.R.; Row, T.N.G.; Maitra, U. *Org. Lett.* **2005**, *7*, 1441–1445.
(18) Lee, K.H.; Lee, H.Y.; Lee, D.H.; Hong, J.I. *Tetrahedron Lett.* **2001**, *42*, 5447–5449.
(19) Lee, C.; Lee, D.H.; Hong, J.I. *Tetrahedron Lett.* **2001**, *42*, 8665–8668.
(20) Saravanakumar, D.; Sengottuvelan, N.; Kandaswamy, M.; Aravindan, P.G.; Velmurugan, D. *Tetrahedron Lett.* **2005**, *46*, 7255–7258.
(21) Saravanakumar, D.; Sengottuvelan, N.; Kandaswamy, M. *Inorg. Chem. Commun.* **2005**, *8*, 386–389.
(22) Devaraj, S.; Saravanakumar, D.; Kandaswamy, M. *Tetrahedron Lett.* **2007**, *48*, 3077–3081.
(23) Saravanakumar, D.; Devaraj, S.; Iyyampillai, S.; Mohandoss, K.; Kandaswamy, M. *Tetrahedron Lett.* **2008**, *49*, 127–132.
(24) Gunnlaugsson, T.; Davis, A.P.; O' Brien, J.E.; Glynn, M. *Org. Biomol. Chem.* **2005**, *3*, 48–56.
(25) Gayathri, D.; Velmurugan, D.; Ravikumar, K.; Saravanakumar, D.; Kandaswamy, M. *Acta Cryst.* **2007**, *E63*, o2324–o2326.
(26) Ahmed, I.T. *Spectrochim. Acta A* **2006**, *65*, 5–10.
(27) Lee, D.H.; Lee, H.Y.; Hong, J.-I. *Tetrahedron Lett.* **2002**, *43*, 7273–7276.
(28) Fujii, A.; Ebata, T.; Mikami, N. *J. Phys. Chem. A* **2002**, *106*, 8547–8554.
(29) Gerhards, M.; Unterberg, C.; Kleinermanns, K. *Phys. Chem. Phys.* **2000**, *2*, 5538–5544.
(30) Varquez, M.; Fabbirizzi, L.; Taglietti, A.; Pedrido, R.M.; Gonzalez-Noya, A.M.; Bermejo, M.R. *Angew. Chem., Int. Ed.* **2004**, *43*, 1962–1965.
(31) Gunnlaugsson, T.; Kruger, P.E.; Jensen, P.; Pfefer, F.M.; Hussey, G.M. *Tetrahedron Lett.* **2003**, *44*, 8909–8913.
(32) Carmiolo, S.; Gale, P.A.; Hursthouse, M.B.; Light, M.E. *Org. Biomol. Chem.* **2003**, *1*, 741–744.
(33) Shenderovich, I.G.; Tolstoy, P.M.; Golubev, N.S.; Smirnov, S.N.; Denisov, G.S.; Limbach, H.-H. *J. Am. Chem. Soc.* **2003**, 11709–11717.
(34) Camiolo, S.; Gale, P.A.; Hursthouse, M.B.; Light, M.E.; Shi, A.J. *Chem. Commun.* **2002**, 758–759.
(35) Gale, P.A.; Navakhun, K.; Camiolo, S.; Light, M.E.; Hursthouse, M.B. *J. Am. Chem. Soc.* **2002**, *124*, 11228–11229.
(36) Evans, L.S.; Gale, P.A.; Light, M.E.; Quesada, R. *Chem. Commun.* **2006**, 965–967.
(37) Evans, L.S.; Gale, P.A.; Light, M.E.; Quesada, R. *New J. Chem.* **2006**, *30*, 1019–1025.
(38) Caltagirone, C.; Bates, G.W.; Gale, P.A.; Light, M.E. *Chem. Commun.* **2008**, 61–63.
(39) Peng, S.; Wu, Y.; Fan, J.; Tian, M.; Han, K. *J. Org. Chem.* **2005**, 10524–10525.

(40) Boiocchi, M.; Baca, L.D.; Gomez, D.E.; Fabbrizzi, L.; Licchelli, M.; Monzani, E. *J. Am. Chem. Soc.* **2004**, *126*, 16507–16514.
(41) Kim, Y.-J.; Kwak, H.; Lee, S.J.; Lee, J.S.; Kwon, H.J.; Nam, S.H.; Lee, K.; Kim, C. *Tetrahedron* **2006**, *62*, 9635–9640.
(42) Miyaji, H.; Sato, W.; Sessler, J.L. *Angew. Chem., Int. Ed.* **2001**, *40*, 154–157.
(43) Black, C.B.; Andrioletti, B.; Try, A.C.; Ruiperez, C.; Sessler, J.L. *J. Am. Chem. Soc.* **1999**, *121*, 10438–10439.
(44) Hammud, H.H.; Ghannoum, A.; Masoud, M.S. *Spectrochim. Acta A* **2006**, *63*, 255–265.
(45) Tuntulani, T.; Poompradub, S.; Thavornyutikarn, P.; Jaiboon, N.; Ruangpornvisuti, V.; Chachit, N.; Asfari, Z.; Vicens, J. *Tetrahedron Lett.* **2001**, *42*, 5541–5544.
(46) EI-Haty, M.T.; Adam, F.A.; Mohammed, A.E.; Gabr, A.A. *J. Indian Chem. Soc.* **1990**, *67*, 743–747.
(47) Ghosh, T.; Maiya, B.G.; Wong, M.W. *J. Phys. Chem. A* **2004**, *108*, 11249–11259.