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RSC Advances

Cite this: *RSC Advances*, 2012, **2**, 10499–10504

www.rsc.org/advances

PAPER

Colorimetric receptors for naked eye detection of inorganic fluoride ion in aqueous media using ICT mechanism†

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Received 18th July 2012, Accepted 5th September 2012
DOI: 10.1039/c2ra21478d

A new series of receptors were designed and synthesized based on benzohydrazide for the colorimetric detection of fluoride ion. The receptors **L1** and **L2** are highly selective towards fluoride ion over other anions. These receptors are able to detect inorganic fluoride such as NaF in aqueous solutions. The presence of two carbonyl groups in the receptor molecule makes the –NH proton highly acidic and hence these receptors are capable of competing with water molecules to bind fluoride ion. The receptors **L1** and **L2** showed a significant colour change from colourless to yellow in aqueous solutions of NaF with a $\Delta\lambda_{max}$ of 149 nm and 147 nm respectively. The mechanism involved in the colour change was deprotonation, formation of imidic acid intermediate followed by stabilization of complex through Intramolecular Charge Transfer (ICT). This was further confirmed by ^{1}H NMR titrations where the formation of imidic acid was observed. The receptor **L1** proved itself to be potentially useful for real-life applications by detecting fluoride ion quantitatively in sea water and commercially available mouth wash.

Introduction

The design and synthesis of artificial organic receptors for selective detection of anions is an attractive area of research in supramolecular chemistry[1] due to their wide applications in chemical, agricultural, industrial and biological processes.[2] However, among the wide range of anions the detection of fluoride ion has gained greater attention because of its dual functionality.[3,4]

Colorimetric receptors with high selectivity and sensitivity, which are easy and safe to handle, have received significant attention. A number of colorimetric receptors which are capable of detecting fluoride ions have been reported.[5] However, the majority of these receptors could be operated only in non-competitive organic solvents for the detection of tetrabutylammonium fluoride (TBAF) and in absolute non-aqueous conditions. This drawback is due to the higher acidity of water than that of protons which are involved in binding process and hence the F^- ion readily gets solvated even with a trace amount of water. On the other hand, the design and synthesis of receptor molecules capable of detecting inorganic fluoride such as sodium fluoride in aqueous conditions for real-life applications is a daunting task and has yet to be explored by chemists.

The detection ability of receptors with urea, thiourea, amide and pyrrole/imidazole/indole functional groups[5] where –NH acts as the binding site, depends on the acidity of –NH proton.[6] However, this acidity can be tuned by inserting different electron withdrawing groups to the molecular backbone. As the acidity of –NH increases, the hydrogen bond donor tendency of –NH also increases, which at extreme acidity leads to deprotonation of the receptor. This deprotonation establishes the charge transfer complexes which results in significant colour change of the solution with a large red shift and hence the detection of anions by the naked eye becomes feasible. Thus the stability of charge transfer complexes directly depends on the acidic nature of –NH proton.[7]

Few receptors have been reported that are capable of detecting fluoride ion in aqueous solutions (organic–water mixture). However, the majority of these detection processes are restricted either to TBAF[8] or only to test papers which require several minutes for the detection process.[9] These drawbacks restrict the use of reported receptors for real-life applications such as detection of inorganic fluoride in ground water. However, Kruger *et al.* designed and synthesized 1,8-naphthalimide derivatives for the detection of NaF in aqueous solutions.[10] Recently Das *et al.* designed and synthesized a receptor to show practical applicability by detecting inorganic fluoride ions in organic media and extracting them from ground water to organic solvent.[11] Nevertheless, the challenges of designing and synthesizing receptors with real-life applications, such as detection of inorganic fluoride in aqueous media, still remain.

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† Electronic Supplementary Information (ESI) available: ^{1}H NMR spectrum of **L1**–**L4**., Photographs of **L1**, **L2**, **L3** and **L4** with different ions. UV–vis spectroscopic titration studies of receptors **L1** and **L2** with TBAF. UV–vis spectroscopic titration studies of receptors **L1** and **L2** with NaF in 9 : 1; DMSO–H_2O system. Selectivity investigations of **L1** and **L2** with different anions using UV–vis spectroscopy. Stoichiometric determination of all complex by Benesi–Hildebrand method. See DOI: 10.1039/c2ra21478d

Herein, we report new receptors **L1**–**L4** (Scheme 1) based on benzohydrazide for the detection of inorganic fluoride ion in DMSO–H_2O (9 : 1 v/v) solution. Notably we have incorporated two carbonyl (–C=O) groups adjacent to –NH and a nitro group (–NO_2) at the *p*-position of the phenyl ring in case of **L1** and **L2** to increase the acidity of –NH proton. Hence these receptors would compete with water to bind with inorganic fluoride for detection by the naked eye.

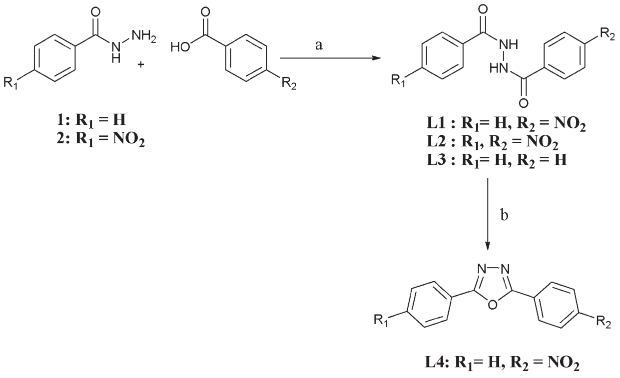
The receptors **L1**–**L3** were designed to demonstrate the effect of nitro substitution at the *p*-position of the phenyl ring on Intramolecular Charge Transfer (ICT). Receptor **L4** was synthesized to study the role of –NH in the fluoride ion binding process. Receptors **L1**–**L4** were synthesized as depicted in Scheme 1 and characterized using standard spectroscopic techniques (ESI†).

Results and discussion

Initially the receptors **L1** and **L2** were investigated for colorimetric detection application in the presence of different anions in dry DMSO solvent. Both the receptor solutions (2.5×10^{-5} M) were treated with different anions (1 equiv.) such as fluoride, chloride, bromide, iodide, nitrate, hydrogensulphate, dihydrogenphosphate and acetate in the form of tetrabutylammonium (TBA) salts. These receptors showed a remarkable colour change from colourless to red instantaneously with F^- ion whereas that associated with AcO^- ion was less intense. This confirms the selective binding of F^- ion to the receptors. However, no colour change was observed on addition of other anions. Fig. 1 shows the change in the colour of receptor **L1** on addition of 1 equiv. of different anion solutions as TBA salts.

As a justification for selectivity, the changes in UV–vis absorption of receptor **L1** were recorded in dry DMSO (2.5×10^{-5} M), after adding 10 equiv. of different anions. As shown in Fig. 2 only F^- ion and AcO^- ion induced instantaneous red shift in the absorption maxima and all other anions did not cause any change in the absorption. Hence only the presence of AcO^- ion can interfere with the detection of F^- ion, whereas other anions did not show any interference with detection process (Fig. S9 and Fig. S10 ESI†).

The sensing ability of receptor **L1** in dry DMSO solution (2.5×10^{-5} M) was investigated using UV–vis spectrophotometric titration experiments by gradually adding a standard solution of TBAF.



Scheme 1 Synthesis of **L1**–**L4**. (a) EDC·HCl, HOBt, DCM, 12 hours, (b) $POCl_3$, 80 °C, 6 h.

Fig. 1 Change in colour of **L1** (2.5×10^{-5} M) in dry DMSO after the addition of 1 equiv. of tetrabutylammonium salt of anions. (a) Free Receptor **L1**, (b) F^-, (c) Cl^-, (d) Br^- (e) I^-, (f) NO_3^-, (g) HSO_4^-, (h) $H_2PO_4^-$ and (i) AcO^-.

Fig. 3 shows the UV–vis spectral changes of **L1** on titrating with F^- ions. With the constant increase in the concentration of F^- ion, the peak at 268 nm was slightly increased due to a change in the $\pi \rightarrow \pi^*$ transition. A new band at 446 nm formed and developed with a red shift of 178 nm, which was ascribed to the formation of Intramolecular Charge Transfer (ICT) complex. The receptor reached saturation (Fig. 3, inset) at 3 equiv. of TBAF. The same trend was observed in the case of the receptor **L2** where a red shift of 177 nm was observed (Fig. S18, ESI†).

To explore the applicability of receptor **L1**, UV–vis titration was carried out in aqueous DMSO (9 : 1 v/v) using a solution of sodium fluoride (NaF) as the fluoride source.

Upon increasing addition of NaF to receptor **L1**, the intensity of the peak at 268 nm slightly increased and a new peak at 417 nm with a $\Delta\lambda_{max}$ of 149 was observed (Fig. 4). The saturation point was reached after the addition of 15 equiv. of NaF solution in water. The receptor **L2** showed a new peak at 431 nm with a red shift of 147 nm. These results revealed that the titration spectra did not show much difference on addition of inorganic fluoride to aqueous receptor solution (DMSO–H_2O, 9 : 1 v/v) when compared to TBAF with dry DMSO solution of **L1**. The 10% aqueous solution of receptor **L1** was further titrated with TBAF which showed similar spectral changes (Fig. S21, ESI†). This indicates that the same ICT mechanism was followed in the case of organic and aqueous media for detection of F^- ion. The presence of two carbonyl groups adjacent to –NH and the nitro substitution at the *p*-position of the phenyl ring made the –NH protons highly acidic[12] and hence the receptors **L1** and **L2**

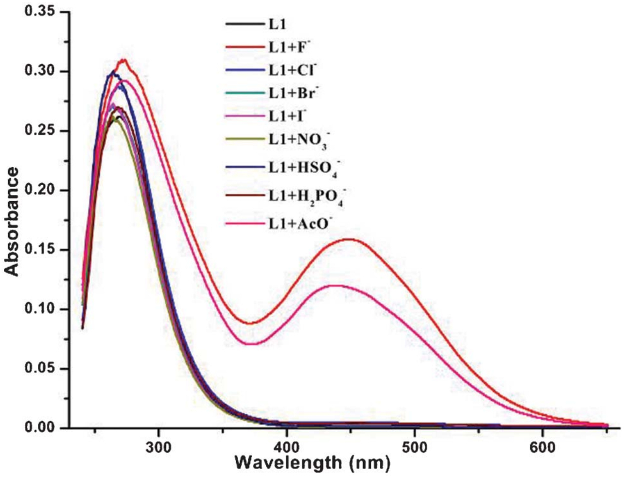


Fig. 2 UV–Vis absorption spectra of **L1** in dry DMSO (2.5×10^{-5} M) after addition of 10 equiv. of different anions in the form of TBA salts.

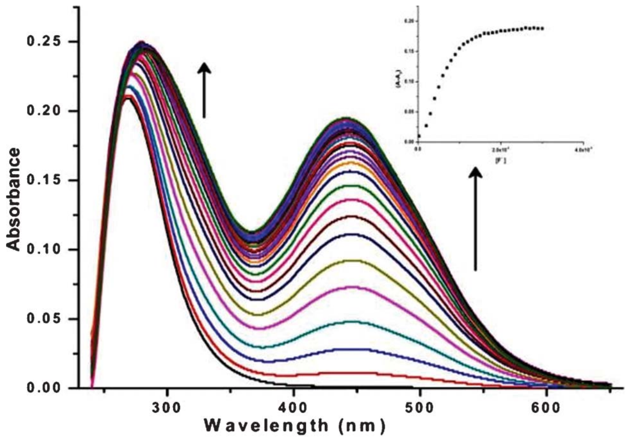


Fig. 3 UV–vis titration of **L1** (2.5×10^{-5} M) with increasing concentrations of TBAF (0–10 equiv.) in dry DMSO. Inset: corresponding titration plot of **L1** at 446 nm ($A\text{-}A_0$) *vs.* [F⁻].

readily get deprotonated in the presence of basic F⁻ ion. Thus, these receptors can detect both organic as well as inorganic fluorides. However, slightly less red shift in the case of aqueous DMSO when compared to dry DMSO was observed, perhaps due to the solvation of F⁻ ions in water which decreased its binding with receptors.[13]

A colour change from colourless to yellow was observed on addition of inorganic fluoride to 10% aqueous solution of receptors (Fig. S11, ESI†). Experimental studies showed that the receptors **L1** and **L2** could colorimetrically detect the presence of inorganic fluoride even at the 0.5 ppm level, which is much lower than the WHO permissible level of F⁻ ions (maximum of 1 ppm) in drinking water.[14] Furthermore, the receptor **L1** was tested for the detection of F⁻ ions in sea water, collected from the Arabian Sea (latitude13°0′33.99′′, longitude 74°47′17.23′′), and commercial mouthwash. When a drop of sea water/mouthwash was added to a DMSO solution of receptor **L1**, a permanent change in colour from colourless to yellow was observed (Fig. S12 and Fig. S13, ESI†). Thus, F⁻ ion in sample water can be detected with the naked eye by adding a drop of water sample containing F⁻ ion to the receptor solution. The amount of F⁻ ions present in sea water/mouthwash was determined using a calibration curve which was established by plotting absorbance *vs.* concentration of F⁻ ions (Fig. 5). The curve showed 1.54 ppm of F⁻ ions in sea water (215.5 ppm in mouthwash), which is comparable with standard values.[14b]

The $\Delta\lambda_{max}$ for organic and aqueous solutions of receptors **L1**–**L4** upon addition of TBAF and NaF are summarized in Table 1. In the case of **L1** and **L2**, extended conjugation was observed upon binding of F⁻ ion due to the presence of the $-NO_2$ group at the *p*-position of the phenyl ring and as a result ICT was achieved with maximum red shifts of 178 nm and 177 nm (149 nm and 147 nm in the case of 10% aqueous solution) respectively. However, in the case of **L2**, the presence of two $-NO_2$ groups at the *p*-positions of the phenyl rings did not make much difference in the sensitivity. For the receptor **L3**, being deficient in a $-NO_2$ group, ICT was not feasible and hence only the broad band centred at 313 nm with a red shift of 39 nm was observed due to hydrogen bonding on addition of F⁻ ion. The receptor **L4** did not showed any shift in absorbance on addition of F⁻ ion. This further confirms that the –NH protons are responsible for the binding process of F⁻ ion.

The stoichiometry of the F⁻ ion complexation with receptor **L1** in DMSO–H_2O (9 : 1 v/v) was determined by the Benesi–Hildebrand method[15] (Fig. 6) using NaF. This clearly confirmed the formation of a stable 1 : 2 stoichiometric complex between receptor **L1** and F⁻ ions. The binding constants for the receptor **L1** in organic medium and aqueous solution were found to be $4.26 \pm 0.66 \times 10^8$ and $8.64 \pm 0.23 \times 10^7$ respectively. Thus, the receptor **L1** strongly binds to the F⁻ ions even in aqueous solutions.

From stoichiometric studies it is clear that F⁻ ion detection using receptor **L1** is a two-step process. First, a F⁻ ion binds to the receptor through hydrogen bonding and thus a 1 : 1 adduct is generated to form a **L1**···F⁻ complex.[16] The second F⁻ ion causes deprotonation of –NH proton in receptor **L1** which results in increased electron density over the complex system. This induces a charge separation in the molecule (Scheme 2) and hence Intramolecular Charge Transfer (ICT) interaction is

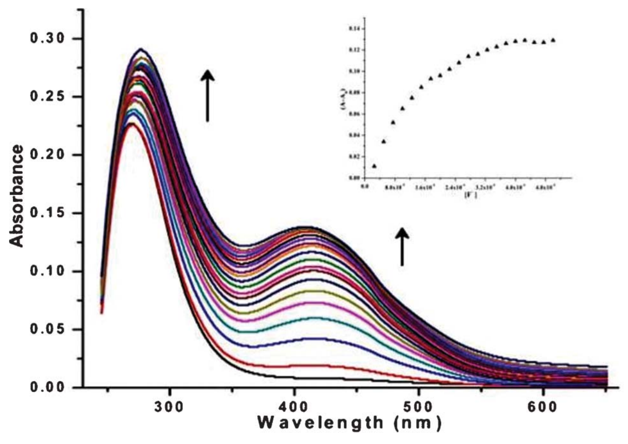


Fig. 4 UV–vis spectra of **L1** (2.5×10^{-5} M) with increasing concentrations of NaF (0–20 equiv.) in DMSO–H_2O (9 : 1 v/v). Inset: corresponding titration plot of **L1** at 417 nm ($A\text{-}A_0$) *vs.* [F⁻].

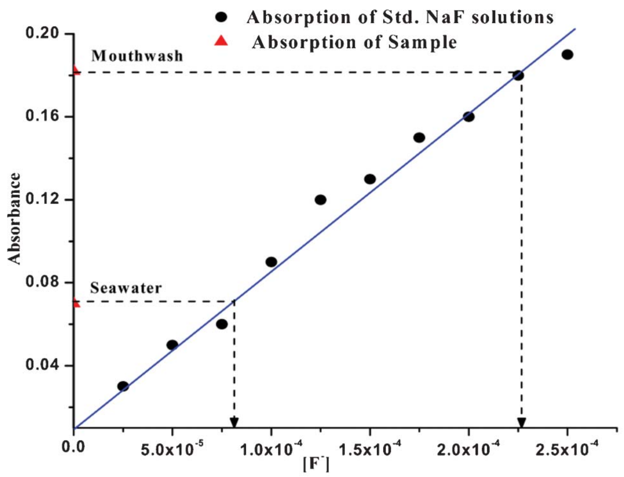


Fig. 5 Calibration curve to determine the amount of F⁻ ions in seawater/mouthwash sample.

Table 1 Change in absorption ($\Delta\lambda_{max}$) of receptors **L1–L4** (2.5×10^{-5} M) in the presence of F^- ion (10 equiv.)

Receptor (R)[a]	λ_{max} (R + TBAF)[b]	λ_{max} (R + NaF)[c]	$\Delta\lambda_{max}$ (Organic)	$\Delta\lambda_{max}$ (Aqueous)
L1	446 nm	417 nm	178 nm	149 nm
L2	452 nm	431 nm	177 nm	147 nm
L3	313 nm	274 nm	39 nm	0 nm
L4	311 nm	311 nm	0 nm	0 nm

[a] Absorption spectra were taken for receptors at a concentration of 2.5×10^{-5} M in DMSO. [b] TBAF solution (10 equiv. in dry DMSO) was added to receptor solution (dry DMSO). [c] NaF solution (10 equiv. in H_2O) was added to receptor solution (DMSO–H_2O, 9 : 1 v/v)

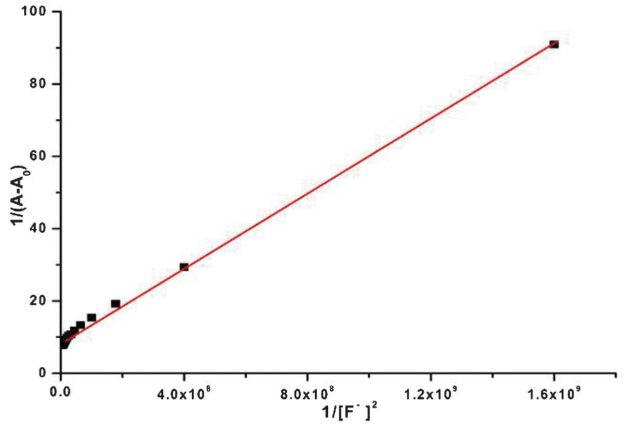
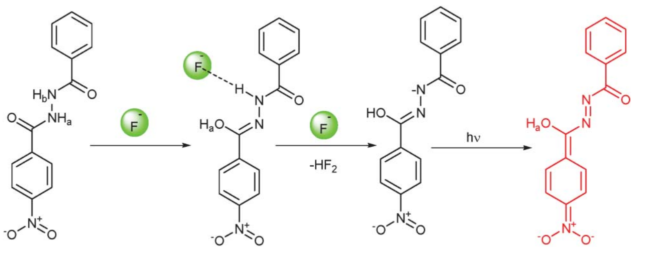


Fig. 6 Benesi–Hildebrand plot of receptor **L1** binding with F^- ion (NaF) associated with absorbance change at 417 nm in DMSO–H_2O (9 : 1 v/v) solvent.

increased between the electron deficient nitro group and the electron rich –N$^-$ which results in the optical colour change.[17] However, the formation of ICT complex was not observed in the case of receptor **L3** as it has no electron withdrawing group attached. This resulted in the low sensitivity of receptor **L3** while detecting the F^- ion.

The –NH proton H_a tautomerizes to imidic acid from the amide form under basic conditions. However, at lower concentrations (0–2 equiv.) of TBAF the fast exchange of this proton between the two tautomers could be observed and at a higher concentration (5 equiv.) of TBAF, the imidic acid tautomer was stabilized.

As evidence, the process of tautomerism can be clearly observed in ^{1}H NMR titration experiments of **L1** carried out in DMSO-d_6 solution (Fig. 7) using TBAF. Due to the fast exchange between the two tautomers, the proton H_a was unavailable for resonance. As a result, the signal at δ 10.9 has completely disappeared. At higher concentration (5 equiv.) the reappearance of the signal at δ 10.4 confirmed the formation of the stable imidic acid tautomer. Up to 2 equiv. of F^- ion the resonance signal corresponding to H_b (δ 10.65) showed broadening and splitting patterns in the aromatic region were retained. On the other hand, at higher concentration of F^- ion (5 equiv.) the peak corresponding to H_b as well as the splitting pattern in the aromatic region completely disappeared. This indicates the formation of NH···F^- hydrogen bonding followed by deprotonation[17] of receptor **L1**. Due to the formation of ICT, the electron density of the phenyl rings increased and this resulted in upfield shifts in the signals[18] of all aromatic protons. Furthermore, splitting in the signals of the aromatic protons completely disappeared (Fig. 7). This observation was due to the fast proton exchange within the molecule.



Scheme 2 Predicted mechanism for the fluoride ion binding to receptor **L1**.

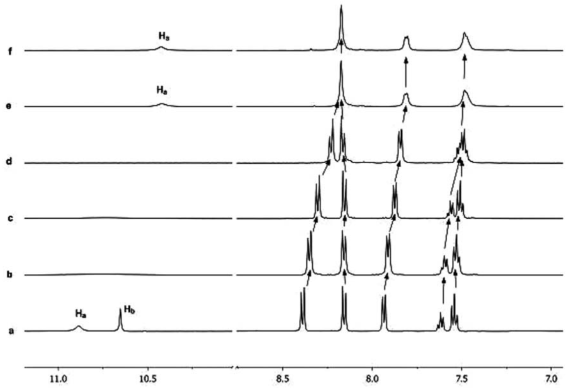


Fig. 7 Partial ^{1}H NMR spectra of receptor **L1** in DMSO-d_6 after the addition of (a) 0 equiv., (b) 0.5 equiv., (c) 1 equiv., (d) 2 equiv., (e) 5 equiv. and (f) 10 equiv. of TBAF.

Experimental

General information

All chemicals were purchased from Sigma-Aldrich, Alfa aesar or from Spectrochem and used without further purification. All the solvents were procured from SD Fine, India of HPLC grade and used without further distillation.

The ^{1}H NMR spectra were recorded on a Bruker, Avance II (500 MHz) instrument using TMS as internal reference and DMSO-d_6 as solvent. Resonance multiplicities are described as s (singlet), br s (broad singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Melting points were measured on a Stuart-SMP3 melting-point apparatus in open capillaries. Infrared spectra were recorded on a Thermo Nicolet Avatar-330 FT-IR spectrometer; signal designations: s (strong), m (medium), w (weak), br.m (broad medium) and br.w (broad weak). UV–vis spectroscopy was carried out with Ocean Optics SD2000-Fibre Optics Spectrometer in standard 3.5 mL quartz cells (2 optical windows) with 10 mm path length. Elemental analyses were done using Flash EA1112 CHNS analyzer (Thermo Electron Corporation).

Synthetic procedure

Intermediates **1** and **2** were synthesized according to the reported procedure.[19]

General procedure for the synthesis of receptors L1, L2 and L3

To a solution of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl) (2.94 mmol) in 3 mL of dichloromethane, 1-hydroxybenzotriazole (HOBt) (0.147 mmol), benzoic acid derivative (1.47 mmol), and triethylamine (2.94 mmol) were added and stirred for 30 min. The starting material 1 or 2 (1.47 mmol) was added and stirred at room temperature for overnight. The reaction mixture was diluted with 2 mL of dichloromethane, washed with 2N HCl (3 mL × 2) followed by 10% sodium bicarbonate solution (3 mL × 2). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to yield the product.

Synthetic procedure for L4

A mixture of compound **L1** (0.35 mmol) and 2 mL of phosphorus oxychloride was heated at 80 °C for 6 h. The reaction mixture was cooled to room temperature and poured into 20 mL ice cold water. The resulting precipitate was filtered, washed with water and dried to yield the compound **L4**.

Spectroscopic data for benzohydrazide, 1

Yield: 92%. m.p. 114.6 °C.

Elemental analysis; Calculated for $C_7H_8N_2O$: C 71.75, H 5.92, N 20.58. Experimental: C 71.65, H 5.98, N 20.38 IR (FT-IR), $\tilde{\nu}$ (cm^{-1}): 3292.9 (m), 3190.4 (s), 3010.4 (s), 1607.9 (s), 1559.5 (s), 1335.5 (s), 671.9 (s).

Spectroscopic data for 4-nitrobenzohydrazide, 2

Yield: 89%. m.p. 216.4 °C.

Elemental analysis; Calculated for $C_7H_7N_3O_3$: C 46.41, H 3.89, N 23.20. Experimental: C 46.25, H 3.62, N 23.38

IR (FT-IR), $\tilde{\nu}$ (cm^{-1}): 3316.8 (m), 3037.6 (w), 1608.6 (m), 1511.6 (s), 1313.8 (m), 926.2 (m), 857.1 (m), 589.7 (m).

Spectroscopic data for 4-nitro-*N′*-(phenylcarbonyl)benzohydrazide, L1

Yield: 89%. m.p. 234.9 °C.

Elemental analysis; Calculated for $C_{14}H_{11}N_3O_4$: C 58.95, H 3.89, N 14.73. Experimental: C 58.65, H 3.95, N 14.78.

^{1}H NMR (DMSO-d_6) δ 10.88 (s, 1H, NH), δ 10.65 (s, 1H, NH), δ 8.40 (d, 2H, ArH, J = 8.5 Hz), δ 8.17 (d, 2H, ArH, J = 9 Hz), δ 7.94 (d, 2H, ArH, J = 7.5 Hz), δ 7.62 (t, 1H, ArH, J = 7.25 Hz), δ 7.54 (t, 2H, ArH, J = 7.5 Hz),

IR (FT-IR), $\tilde{\nu}$ (cm^{-1}): 3341.5 (br.m), 3201.7 (br.m), 3060.5 (m), 1679.8 (w), 1641.2 (s), 1598.7 (m), 1516.9 (s), 1337.5 (s), 1270.0 (s), 690.2 (m).

MS (ESI): *m*/*z*: Calculated: 285.2548 $[M]^+$ Experimental: 284.0241$[M - H]^+$

Spectroscopic data for 4-nitro-*N′*-[(4-nitrophenyl)carbonyl]benzohydrazide, L2

Yield: 86% m.p. 234.8 °C.

Elemental analysis; Calculated for $C_{14}H_{10}N_4O_6$: C 50.92, H 3.05, N 16.96. Experimental: C 51.03, H 2.98, N 16.89.

^{1}H NMR (DMSO-d_6) δ 11.00 (s, 2H, NH), δ 8.41 (d, 4H, ArH, = 8.5 Hz), δ 8.18 (d, 4H, ArH, J = 9.0 Hz).

IR (FT-IR), $\tilde{\nu}$ (cm^{-1}): 3381.2 (br.m), 3211.8 (s), 3108.8 (m), 1578.9 (s), 1519.0 (s), 1455.7 (s), 1345.9 (s), 860.9 (m), 704.3 (m).

MS (ESI): *m*/*z*: Calculated: 330.2523 $[M]^+$ Experimental: 331.2208 $[M + H]^+$

Spectroscopic data for *N′*-(phenylcarbonyl)benzohydrazide, L3

Yield: 89%. m.p. 139.4 °C.

Elemental analysis; Calculated for $C_{14}H_{12}N_2O_2$: C 69.99, H 5.03, N 11.66. Experimental: C 69.74, H 5.10, N 11.68

^{1}H NMR (DMSO-d_6) δ 11.56 (s, 2H, NH), δ 7.80–7.75 (m, 5H, ArH), δ 7.58 (t, 2H, ArH, J = 7.75 Hz), δ 7.49 (t, 3H, ArH, J = 7.75 Hz).

IR (FT-IR), $\tilde{\nu}$ (cm^{-1}): 3382.7 (br.m), 3265.5 (s), 3058.6 (m), 1696.6 (s), 1651.7 (s), 1246.8 (s), 688.9 (m).

MS (ESI): *m*/*z*: Calculated: 240.2573 $[M]^+$ Experimental: 241.1732 $[M + H]^+$

Spectroscopic data for 2-(4-nitrophenyl)-5-phenyl-1,3,4-oxadiazole, L4

Yield: 92%. m.p. 212.4 °C.

Elemental analysis; Calculated for $C_{14}H_9N_3O_3$: C 62.92, H 3.39, N 15.72. Experimental: C 63.01, H 3.36, N 15.68

^{1}H NMR (DMSO-d_6) δ 8.48 (d, 2H, ArH, J = 9 Hz), δ 8.42 (d, 2H, ArH, J = 9 Hz), δ 8.20 (d, 2H, ArH, J = 7.75 Hz), δ 7.65–7.70 (m, 3H, ArH).

IR (FT-IR), $\tilde{\nu}$ (cm^{-1}): 3382.7 (br.m), 3265.5 (s), 3058.6 (m), 1696.6 (s), 1651.7 (s), 1246.8 (s), 688.9 (m).

Conclusion

To summarize, we have designed and synthesized benzohydrazide derivatives **L1** and **L2** for the instantaneous and selective detection of inorganic fluoride (NaF) in aqueous media. The receptors possess high sensitivity towards F^- ion with a detection limit of 0.5 ppm in aqueous media which is much less than the WHO permissible level (1 ppm) in drinking water. The mechanism followed for the detection process is ICT and formation of a stable imidic acid tautomer which was evidenced by ^{1}H NMR titrations. Hence on interaction with F^- ion the receptors **L1** and **L2** showed a brilliant colour change from colourless to yellow with large red shifts of 149 nm and 147 nm respectively. These derivatives proved themselves as potent colorimetric fluoride ion receptors by detecting the presence of fluoride in sea water and commercial mouthwash.

Acknowledgements

Authors acknowledge The Director and The HOD (Department of chemistry), NITK, for providing the research infrastructure. MP is thankful to NITK for the research fellowship. MP and DRT thank Dr D. Amilan Jose, Post-Doctoral Research

Associate, Friedrich-Schiller-Universität Jena, IAAC, Germany, for valuable scientific advice, and Optoelectronics Laboratory, Department of Physics, NITK and CSMCRI, Bhavnagar for the spectral analysis. The authors thank both the reviewers for their insightful suggestions and comments to improve the manuscript scientifically.

References

1 (*a*) R. M. Duke, E. Veale, F. M. Pfeffer, P. E. Kruger and T. Gunnlaugsson, *Chem. Soc. Rev.*, 2010, **39**, 3936–3953; (*b*) P. A. Gale, *Chem. Soc. Rev.*, 2010, **39**, 3746–3771; (*c*) P. A. Gale, *Chem. Commun.*, 2011, **47**, 82–86.

2 (*a*) J. L. Sessler, P. A. Gale and W.-S. Cho, *Anion Receptor Chemistry*, Royal Society of Chemistry, Cambridge, 2006; (*b*) I. Stibor, *Anion sensing. Top. Curr. Chem*, Springer, Heidelberg, Berlin, 2005, **255**; (*c*) P. A. Gale, *Coord. Chem. Rev.*, 2003, **240**, 1–226.

3 (*a*) K. L. Kirk, *Biochemistry of the Halogens and Inorganic Halides*, Plenum Press, New York, 1991, **13**; (*b*) B. L. Riggs, *Bone and Mineral Research*, Annual 2, Elsevier, Amsterdam, 1984, 366-393; (*c*) M. Kleerekoper, *Endocrinol. Metab. Clin. North Am.*, 1998, **27**, 441.

4 (*a*) A. Wiseman, *Handbook of Experimental Pharmacology XX/2*, Part 2, Springer-Verlag, Berlin, **970**, 48–97; (*b*) J. A. Weatherall, *Pharmacology of Fluorides. In Handbook of Experimental Pharmacology XX/1*, Part 1, Springer-Verlag, Berlin, 1969, 141–172; (*c*) R. H. Dreisbuch, *Handbook of Poisoning*, Lange Medical Publishers, Los Altos, CA, 1980; (*d*) Y. M. Shivarajashankara, A. R. Shivashankara, S. H. Rao and P. G. Bhat, *Fluoride*, 2001, **34**, 103–107; (*e*) D. L. Ozsvath, *Rev. Environ. Sci. Biotechnol.*, 2009, **8**, 59–79.

5 (*a*) P. Dydio, D. Lichosyt and J. Jurczak, *Chem. Soc. Rev.*, 2011, **40**, 2971–2985; (*b*) A.-F. Li, J.-H. Wang, F. Wang and Y. B. Jiang, *Chem. Soc. Rev.*, 2010, **39**, 3729–3745; (*c*) V. Kumar, M. P. Kaushik, A. K. Srivastava, A. Pratap, V. Thiruvenkatam and T. N. Guru Row, *Anal. Chim. Acta*, 2010, **663**, 77–84; (*d*) J. V. Ros-Lis, R. Martinez-Manez, F. Sancenon, J. Soto, K. Rurack and H. Weißhoff, *Eur. J. Org. Chem.*, 2007, 2449–2458; (*e*) D. A. Jose, D. K. Kumar, B. Ganguly and A. Das, *Org. Lett.*, 2004, **6**, 3445–3448; (*f*) E. B. Veale, G. M. Tocci, F. M. Pfeffer, P. E. Kruger and T. Gunnlaugsson, *Org. Biomol. Chem.*, 2009, **7**, 3447–3354; (*g*) P. Bose and P. Ghosh, *Chem. Commun.*, 2010, **46**, 2962–2964; (*h*) P. Piatek and J. Jurczak, *Chem. Commun.*, 2002, 2450–2451; (*i*) W.-t. Gong, K. Hiratani and S. S. Lee, *Tetrahedron*, 2008, **64**, 11007–11011; (*j*) J. J. Park, Y.-H. Kim and C. Kim, *Tetrahedron Lett.*, 2011, **52**, 2759–2763; (*k*) P. A. Gale, S. E. Garcia-Garrido and J. Garric, *Chem. Soc. Rev.*, 2008, **37**, 151–190.

6 V. Amendola, D. Esteban-Goä Mez, L. Fabbrizzi and M. Licchelli, *Acc. Chem. Res.*, 2006, **39**, 343–353.

7 J. J. Park, Y.-H. Kim and C. Kim, *Tetrahedron Lett.*, 2011, **52**, 3361–3366.

8 (*a*) P. Sokkalingam and C.-H. Lee, *J. Org. Chem.*, 2011, **76**, 3820–3828; (*b*) Y.-M. Zhang, Q. Lin, T.-B. Wei, D.-D. Wang, H. Yao and Y.-L. Wang, *Sens. Actuators, B*, 2009, **137**, 447–455; (*c*) A. K. Mahapatra, G. Hazra and P. Sahoo, *Beilstein J. Org. Chem.*, 2010, **6**, 1–8.

9 (*a*) Z-h. Lin, S-j. Ou, C-y. Duan, B-g. Zhang and Z-p. Bai, *Chem. Commun.*, 2006, 624–626; (*b*) Z-h. Lin, Y-g. Zhao, C-y. Duan, B-g. Zhang and Z-p. Bai, *Dalton Trans.*, 2006, 3678–3684.

10 T. Gunnlaugsson, P. E. Kruger, P. Jensen, J. Tierney, H. D. P. Ali and G. M. Hussey, *J. Org. Chem.*, 2005, **70**, 10875–10878.

11 P. Das, A. K. Mandal, M. K. Kesharwani, E. Suresh, B. Ganguly and A. Das, *Chem. Commun.*, 2011, **47**, 7398–7400.

12 J. Clayden, N. Geeves, S. Warren and P. Wothers, *Organic Chemistry*, Oxford University Press, New York, 2001, Chapter 8, 197.

13 S. Kumar, V. Luxami and A. Kumar, *Org. Lett.*, 2008, **10**, 5549–5552.

14 (*a*) J. Fawell, K. Bailey, J. Chilton, E. Dahi, L. Fewtrell and Y. Magara, *Fluoride in Drinking-water*, IWA Publishing, London, 2001, 32; (*b*) WHO Technical Report Series-846, Fluoride and Oral Health, Geneva, 1994.

15 H. Benesi and H. Hildebrand, *J. Am. Chem. Soc.*, 1948, **71**, 2703–2707.

16 A. Ghosh, S. Verma, B. Ganguly, H. N. Ghosh and A. Das, *Eur. J. Inorg. Chem.*, 2009, 2496–2507.

17 E. J. Cho, B. J. Ryu, Y. J. Lee and K. C. Nam, *Org. Lett.*, 2005, **7**, 2607–2609.

18 M. Boiocchi, L. D. Boca, D. E. Gomez, L. Fabbrizzi, M. Licchelli and E. Monzani, *J. Am. Chem. Soc.*, 2004, **126**, 16507–16514.

19 Z. N. Cui, J. Huang, Y. Li, Y. Ling, X. L. Yang and F. H. Chen, *Chin. J. Chem.*, 2008, **26**, 916.