Influence of aromatic nitro-substituents on auto-reusability of oxime-based fluoride receptors

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Abstract. The interaction of fluoride ion with three oxime based receptors containing additional aromatic nitro-substituents was studied by using colorimetric and NMR spectroscopy. Colorimetric responses of the receptors towards fluoride ion were found to be highly dependent on the position of the nitro substituent in the aromatic backbone. While the ortho and para nitro-substituted receptors showed intense colour change and associated colorimetric response upon addition of fluoride, the meta derivative did not provide any visible deviation in colour as well as colorimetric behaviour. Further, due to the presence of H-bond acceptor motif, the receptor–fluoride complexes formed by both ortho and para nitro-substituted derivatives are reasonably labile and dissociate to automatically result in the free receptor species within a short time span. This allowed reuse of the receptor solution for selective and successive recognition of fluoride by colorimetric technique without any external trigger.

Keywords. Oxime receptors; fluoride recognition.

1. Introduction

The well-recognized benefit of fluoride in preventing dental decay is far eclipsed by its adverse effects on human health when consumed beyond a threshold limit. This concern has catapulted an outburst of activities in developing receptors, which can efficiently and selectively recognize fluoride ion in an aqueous medium. Consequently, a plethora of fluoride ion sensors have been developed and the binding mechanism in these receptors primarily rely on non-covalent interactions *e.g.*, electrostatic, H-bonding, hydrophobicity, coordination to a metal ion, etc.^{1–5} Among these, H-bonding interaction mediated fluoride recognition remains one of the most preferred choices due to the high selectivity for fluoride ion as well as efficiency. Due to large charge/size ratio, fluoride ion is an efficient hydrogen bond acceptor and therefore can trigger partial charge transfer in a fascinating assortment of H-bond donor motifs *e.g.*, amide, sulphonamide, urea, thiourea, pyrrole, indole, oxime, Schiff base, etc.^{6–17} Thus, most of

these H-bond donor motifs can strongly and irreversibly bind fluoride ion leading to the formation of stable receptor–fluoride complexes. The associated changes of the electronic structure of the receptors on binding with fluoride are generally monitored as a permanent bathochromic shift in electronic spectra or quenching/enhancement of photoluminescence. However, irreversible binding of fluoride by receptors prevent reuse of the receptors and this severely limits their application. Nevertheless, a handful of receptors showing reversible fluoride binding have been reported recently.^{18–22} In these cases, the release of the free receptor from the receptor–fluoride complex is triggered by the addition of a mineral acid and subsequent addition of fluoride regenerate the receptor–fluoride complex.

It is pertinent to note here that a series of oxime-based receptors for colorimetric detection of fluoride in the semi-aqueous medium has been reported recently.^{23,24} The oxime $>C=N-OH$ proton is moderately acidic and therefore H-bond interactions between the oxime group and fluoride ions are reasonably strong. Consequently,

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receptor–fluoride complexes formed upon addition of fluoride to oxime-based receptors are considerably stable and the accompanying colorimetric changes are irreversible. In this regard, we have recently shown that the incorporation of an H-bond acceptor site within the oxime-based receptor molecule enhances the liability of the receptor–fluoride complex. In such cases, the free receptor species is automatically regenerated from the receptor–fluoride complex after a certain time interval.²⁵ Indeed, the regenerated free receptor species thus obtained can be further employed for colorimetric detection of fluoride up to three cycles. Herein, we have investigated structure–property relationship to impart auto-reusability in oxime-based fluoride receptors by varying the position of the nitro substituent on the aromatic ring present in the receptor. Three new oxime based receptors containing nitrobenzene substituents are prepared and their fluoride recognition abilities are studied by using spectroscopic studies.

2. Experimental

2.1 Materials and methods

Starting materials were procured from commercial sources and used without any further purification. Solvents were freshly distilled before use by standard purification techniques. 3-Hydrazono-butan-2-one oxime was synthesized according to the reported procedure.²⁶ Melting points were recorded on a BUCHI (B-540) melting point apparatus and reported uncorrected. Elemental analysis was performed by using Perkin Elmer 2400 series analyzer. Infrared spectra were recorded with a Perkin Elmer Frontier MIR-FIR FT-IR spectrophotometer as KBr diluted discs. The ¹H NMR spectra (400 MHz) and ¹³C NMR spectra (100 MHz) were recorded on a 'JEOL' NMR spectrophotometer in DMSO-*d*₆, CD₃COCD₃ and CD₃CN. In NMR spectra, chemical shifts are reported in parts per million downfield to Me₄Si (TMS) as an internal standard. The UV-visible data were recorded with a Shimadzu UV 2550 spectrophotometer. Suitable single crystal of compound **1** and **3** were obtained from acetonitrile solutions of respective compounds and used for diffraction measurements. The compounds were dissolved in dimethylsulfoxide (DMSO) for UV-visible diffraction studies. The TBA anion solutions used in anion binding studies were also prepared in DMSO medium. The diffraction data for the compound was collected on a Bruker APEX-II CCD diffractometer using MoK α radiation (λ = 0.71073 Å) using φ and ω scans of narrow (0.5°) frames at 90–100K. The crystal structure was solved by direct methods using SHELXL-97 as implemented in the WinGX program system.²⁷ Anisotropic refinement was executed on all non-hydrogen atoms. Positions of N-H and O-H hydrogen atoms were located on a difference Fourier map and allowed to ride on their parent atoms

during subsequent cycles of refinements. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC 1586405–1586406 (**1** & **3**) (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>).

2.2 Synthesis of compound **1**

3-Hydrazono-butan-2-one oxime (0.889 g, 7.72 mmol) was dissolved in 20 mL methanol taken in a 50 mL round bottom flask. To the above solution, 4-nitrobenzaldehyde (1.167 g, 7.72 mmol) was added and then refluxed for 1 h with continuous stirring. A yellow mass precipitated out within 10 min of reflux. After that, the reaction mixture was allowed to cool down at room temperature. The precipitate obtained was filtered and washed several times with distilled methanol, followed by diethyl ether, dried in air and collected. The yield of the product obtained is 1.4307g. Yield: 60%; M_r: 248.24 g; M.p.: 197–198 °C. FT-IR (KBr, cm^{−1}): $\tilde{\nu}$ = 3228 (br), 2926 (w), 1658 (w), 1595 (s), 1555 (w), 1519 (s), 1418 (w), 1357 (w), 1343 (s), 1295 (w), 217 (m), 937 (s), 936 (m), 844 (m), 749 (m), 627 (m), 705 (m); ¹H NMR (DMSO-*d*₆ 400 MHz, δ ppm): 11.89 (s, 1H), 8.40 (s, 1H), 8.30–8.27 (d, ³*J* = 8.7 Hz, 2H), 8.06–8.04 (d, ³*J* = 8.7 Hz, 2H), 2.14(s, 3H), 2.00(s, 3H); ¹³C NMR (DMSO-*d*₆, 100 MHz, δ ppm): 162.97, 155.10, 154.89, 149.05, 140.57, 129.61, 124.58, 13.01, 9.28; Elemental analysis % calculated for C₁₁H₁₂N₄O₃: C = 53.22, H = 4.87, N = 22.57; Found: C = 52.39, H = 4.49, N = 23.68; UV-visible (λ_{max}): 254, 323 nm.

2.3 Synthesis of compound **2**

3-Hydrazono-butan-2-one oxime (0.962 g, 8.35 mmol) was dissolved in 20 mL methanol taken in a 50 mL round bottom flask. To the above solution 3-nitrobenzaldehyde was added (1.26 g, 8.35 mmol) and refluxed overnight with continuous stirring. A yellow mass precipitated out from the reaction mixture. The reaction mixture was allowed to cool down for one hour at room temperature. The precipitate obtained was filtered and washed several times with distilled methanol, followed by diethyl ether, dried in air and collected. Yield: 77%; M_r: 248.24 g; M.p.: 165.1–166.7 °C. FT-IR (KBR, cm^{−1}): $\tilde{\nu}$ = 3239.62 (br), 2925 (w), 1614(s), 1523 (s), 1359 (s), 1136(s), 979(s), 475 (s); ¹H NMR (DMSO-*d*₆ 400 MHz, δ ppm): 11.90 (s, 1H), 8.47 (s, 1H), 8.06–8.03 (m, 2H), 7.82–7.78 (t, *J* = 15.6, 1H), 7.72–7.68 (t, *J* = 16.4, 1H), 2.46 (s, 3H), 2.45 (s, 3H); ¹³C NMR (CD₃CN, 100 MHz, δ ppm): 162.57, 156.11, 151.87, 148.99, 133.61, 131.36, 129.60, 128.82, 124.66, 12, 7.6; Elemental analysis % calculated for C₁₁H₁₂N₄O₃: C = 53.22, H = 4.87, N = 22.57; Found: C = 51.98, H = 5.01, N = 22.37; UV-visible (λ_{max}): 268 nm.

2.4 Synthesis of compound 3

3-Hydrazono-butan-2-one oxime (0.501 g, 4.35 mmol) was dissolved in 20 mL methanol taken in a 50 mL round bottom flask. To the above solution 3-nitrobenzaldehyde was added (0.657 g, 4.35 mmol) and refluxed overnight with continuous stirring. A yellow mass precipitated out from the reaction mixture. The reaction mixture was allowed to cool down for one hour at room temperature. The precipitate obtained was filtered and washed several times with distilled methanol, followed by diethyl ether, dried in air and collected. The yield of the product obtained is (0.579 g). Yield: 53.7%; M_r : 248.24 g, M.p.: 181.4–181.8 °C. FT-IR (KBR, cm^{-1}): $\bar{\nu}$ = 3436 (br), 3235 (w), 2925 (m), 1619 (s), 1583 (m), 1529 (s), 1475 (w), 1435 (w), 1417 (w), 1339 (s), 1369 (w), 1137 (m), 1077 (m), 1041 (m), 979 (s), 953 (w), 918 (m), 736 (s), 675 (s), 480 (s); ^1H NMR (DMSO- d_6 400 MHz, ppm): 11.87 (s, 1H), 8.60 (s, 1H), 8.44 (s, 1H), 8.30–8.24 (m, 2H), 7.77–7.73 (t, ^3J = 8Hz, 1H), 2.15(s, 3H), 2.01 (s, 3H); ^{13}C NMR (DMSO- d_6 , 100 MHz, ppm): 163.09, 155.13, 155.02, 148.73, 136.34, 134.53, 131.07, 125.81, 122.86, 13.55, 9.87; Elemental analysis % calculated for $\text{C}_{11}\text{H}_{12}\text{N}_4\text{O}_3$: C = 53.22, H = 4.87, N = 22.57; Found: C = 52.18, H = 4.97, N = 22.08; UV-visible (λ_{max} , 262 nm).

3. Results and Discussion

3.1 Synthesis and characterization of 1–3

All the three receptors **1–3** were easily synthesized by a simple Schiff base condensation reaction of 3-hydrazono-butan-2-one oxime and appropriate $-\text{NO}_2$ substituted benzaldehydes (Scheme 1). The synthesized compounds were characterized by using different spectroscopic techniques such as FT-IR, UV-visible, ^1H -NMR, ^{13}C -NMR, etc. Single crystal X-ray structure of compound **1** and **3** were also determined to unambiguously establish their solid-state structures. The FT-IR spectrum of **1**, **2** and **3** showed sharp peaks at 1343, 1359 and 1339 cm^{-1} respectively and these can be attributed to N–O stretching vibration of oxime group. Intense peaks observed at $\sim 1525 \text{ cm}^{-1}$ for all three compounds are characteristic of $\text{C}=\text{N}$ stretching vibrations (Figures S1–S3). ^1H NMR and ^{13}C NMR (Figures S4–S9) studies unambiguously established the identity of all the

three compounds and peaks for all nuclei present in **1–3** are observed at expected chemical shifts. ^1H NMR spectrum of **1–3** shows that the protons associated with the oxime $=\text{N}-\text{OH}$ groups resonate as singlets at 11.94, 11.93 and 11.91 ppm respectively. The downfield shift of the oxime proton in case of the para- and ortho-isomer as compared to the meta isomer can be attributed to high acidic nature of oxime group in these **1** and **2**. The pKa of oxime protons in DMSO- d_6 can be estimated from the chemical shifts of the associated protons by using an established empirical relationship, $\text{pKa}: 29.10 - 1.63\delta_{\text{OH}}$.²⁸ pKa values estimated for **1–3** by using the above expression are 9.63, 9.65 and 9.68 respectively.

Single crystals of compound **1** and **3** suitable for X-ray diffraction analysis are obtained by slow evaporation of acetonitrile solutions of respective compounds. However, repeated efforts to grow suitable single crystals of **2** failed and this prevented structural characterization by single crystal X-ray diffraction analysis. Both compound **1** and **3** crystallize in monoclinic $\text{P}2_1/\text{n}$ space group. Perspective views of their molecular structures are depicted in Figure 1 and important structural parameters are listed in Table S1. Due to the presence of conjugated double bonds across the molecule, both the compounds have a planer shape. Moreover, the oxime double bond has a trans- orientation with respect to N–N single bond in both compound **1** and **3**. The oxime oxygen atom O(3) is hydrogen bonded to the N(4) atom of the adjacent molecule resulting in the formation of an $\text{O}(3)-\text{H}(3\text{A}) \cdots \text{N}(4)$ bonded dimer, as shown in Figure S10.

3.2 Anion binding studies on 1–3

The interactions of **1**, **2** and **3** with different anions were initially studied in DMSO medium with the help of UV-visible spectroscopy. The UV-visible spectrum of 40 μM DMSO solution of compound **1–3** recorded in the absence and presence of 40 equivalents of different anions (F^- , Cl^- , Br^- , I^- , CN^- , CH_3COO^- , HSO_4^- , H_2PO_4^- , ClO_4^-) as their tetrabutylammonium (TBA)

Scheme 1. Synthesis of **1**, **2** and **3**.

salts are depicted in Figure 2 and Figure S11. The UV-visible spectrum of compound **1**, **2** and **3** shows maximum absorption centred at 323, 268 and 262 nm respectively. Apart from TBAF, the addition of TBA salts of all other anions under investigation did not produce any significant changes in the initial colour as well as the UV-visible spectrum of the compound **1**

Figure 1. Thermal ellipsoid plot (50% probability) of the molecular structures of (a) compound **1** and (b) compound **3**.

& **2**. However, upon addition of TBAF, distinct colour changes from colourless to dark brown and golden yellow was observed in case of **1** and **2** respectively (Figure 2). UV-visible measurements show that the addition of TBAF generates new absorption peaks centred at 498 nm for compound **1** and at 379 & 437 nm for compound **2**, while the intensity of the parent peaks significantly decreased. Further, the intensity of the newly emerged peak is maximum in case of TBAF and all other anions apart from cyanide produce no appreciable absorbance in that wavelength (Figures S12–S13). Moreover, fluoride-binding studies carried out in presence of other anions show that the presence of other anions diminishes the colorimetric response expected upon addition of fluoride to the receptors (S14–S15). To determine the minimum limit of fluoride detection, UV-visible spectra of the receptors with the gradually decreasing amount of TBAF were recorded and the absorbance at 498 nm and 437 nm were monitored for **1–2** respectively (Figures S16–S17). The colorimetric fluoride detection limits were found to be 20 and 40 equivalents of fluoride for each equivalent of **1** and **2** respectively. However, unlike **1** and **2**, no change in colour was observed upon addition of TBAF or TBA salt solution of any other anion under investigation to a solution of **3**.

Figure 2. The naked eye view of the colour change after addition of 40 equivalent different anions as their tetrabutylammonium salts to a 40 μ M solution of **1** (a) and **2** (b) in DMSO medium. UV-Visible absorbance spectra of the receptors **1** (c) and **2** (d) (40 μ M, DMSO solution), instantly after addition of 40 equiv. of different anions as their tetrabutylammonium salts.

Figure 3. Evolution of UV-visible spectra of **1** & **2** with time in DMSO upon addition of TBAF for 1st cycle (a) & (b); Plot of $\ln(A_t/A_0)$ against time for two consecutive cycles of TBAF addition to receptor **1** (c); Plot of $\ln(A_t/A_0)$ against time for first cycle of TBAF addition to receptor **2** (d).

Careful observation after one hour of TBAF addition revealed that the distinct brown colour change of the solutions of **1** and **2** associated with F^- addition is completely diminished. UV-visible spectra of compound **1** and **2** recorded every 2 min after addition of 40 equivalents of TBAF reveal that the intensity of the newly generated peak decreases uniformly with time, while the peak associated with the free receptor species increases with time (Figure 3, Figures S18–S19). The UV-visible spectrum of both the receptors recorded after ~30 min of TBAF addition is identical to the spectra of the free receptors. Thus, UV-visible analyses establish that the free receptor is regenerated from the receptor–fluoride complex after a certain duration and this clearly indicates that the receptor–fluoride complex formed by **1** and **2** are significantly labile. The above behaviour is typical of oxime-based receptors containing hydrogen bond acceptor functionality.²⁵ The rate constant of

decomposition of the receptor–fluoride complexes were determined from the decrease in absorbance with time at wavelength 498 and 437 nm for **1** and **2** respectively. A straight line is obtained when $\ln(A_t/A_0)$ is plotted against time where A_t represents absorbance at the above-specified wavelengths after time t and A_0 is the initial absorbance instantly after addition of anion (Figure 3). Thus, the dissociation of the receptor–fluoride complex follows a first order kinetics and the rate constants obtained for **1** and **2** are 0.13822 and 0.08477 min^{-1} respectively.

The receptor–fluoride complexes formed by **1** and **2** are reasonably labile and therefore undergo dissociation to regenerate the free receptors species. Thus, in principle, it should be possible to further use the same receptor solution for fluoride recognition. Indeed, the addition of TBAF to decolorized solutions of **1** or **2** leads to the reappearance of the distinct colour

Figure 4. Evolution of UV-visible spectrum immediately after each cycle of TBAF addition: **1** (a), **2** (b); Appearance and disappearance of colour upon addition of 40 equivalents of TBAF to solutions of receptors in DMSO (30 μ M): **1** (c), **2** (d).

change associated with the addition of TBAF to a blank receptor solution. Moreover, the UV-visible spectra of both the solutions also reveal the appearance of peaks associated with TBAF addition while the absorbance of the peaks for the free receptors species decreases (Figure 4).

However, the absorbance of the new peaks observed for both **1** and **2** are considerably less as compared to the absorbance of peaks observed during TBAF addition for the first cycle. Moreover, the de-colorization, as well as a concomitant decrease in the absorbance of peaks observed upon TBAF addition, also happens rather quickly as compared to the initial cycle. Further, the addition of TBAF to a decolorized solution obtained after the second cycle produces neither any significant change in the colour and nor any new peak is observed in the UV-visible spectrum. Thus, the receptors **1** and **2** can be used for the naked eye detection of fluoride ion up to two consecutive cycles without application of any external trigger.

In order to get a more detailed insight into the fluoride binding event of compound **1** and **2**, ¹H NMR titration of both of the compounds with the gradual addition of fluoride was carried out in DMSO-*d*₆ and acetone-*d*₆ medium respectively. ¹H NMR titration of both **1** and **2** show that the signal for the oxime O-H proton which resonates at about 11.9 ppm in the free receptor (Figure 5) completely diminishes upon addition of only 0.2 equivalent of TBAF.

However, the addition of TBAF did not change the position of the signals for the four aromatic C-H protons and the imine C-H protons in both **1** and **2**. Addition of two successive aliquots of TBAF leads to a slight broadening of the signals for aromatic protons and a downfield shift of the imine proton signal is also observed in case of receptor **1**. Addition of further aliquots of TBAF to receptor **1** broadens the aromatic C-H peaks to a larger extent and a new broad peak characteristic of HF₂⁻ emerges at ~16 ppm. However, in the case of receptor **2**, neither the broadening of the aromatic proton signal nor

Figure 5. Selected portions of ^1H -NMR indicating changes in ^1H -NMR of **R** upon gradual addition of TBAF in $\text{DMSO}-d_6$; (i) **R** (ii) **R** + 0.2 equiv. TBAF (iii) **R** + 0.4 equiv. TBAF (iv) **R** + 0.6 equiv. TBAF (v) **R** + 0.8 equiv. TBAF (vi) **R** + 1.0 equiv. TBAF; **R** = **1** (a), **R** = **2** (b).

the signal for HF_2^- is observed even when 1 equivalent of TBAF is added in acetone medium. Thus, the ^1H NMR titration of the receptors with TBAF establish that the receptor–fluoride complex formed by compound **2** is significantly more labile than the corresponding receptor–fluoride complex formed by **1**. Moreover, due to the labile nature of the receptor–fluoride complexes formed by both the receptors, the proton exchange rates between the fluoride ion and the receptors are faster as compared to the NMR timescale. This could be attributed to the complete disappearance of the oxime proton signal even when only 0.2 equivalent of TBAF is added to the receptor solutions.

3.3 Mechanism of reversible fluoride binding

Anion binding studies of the receptors **1–3** clearly show that **1–2** selectively bind fluoride ion and the associated changes in the electronic environment can be visualized by the naked eye. The lack of any colorimetric response to fluoride in case of **3** can be primarily attributed to the meta-directing nature of the nitro-substituent. The electron withdrawing nature of the nitro substituent decreases electron density at the ortho and para position and therefore the oxime protons in **1–2** are reasonably acidic. The moderately strong acidic nature of the oxime protons can be accounted for the strong nature of the interaction between the receptors and fluoride. However, both UV-visible and ^1H NMR spectroscopic studies corroborate that the receptor–fluoride complexes formed by **1–2** are considerably labile as compared to those formed by earlier reported oxime based fluoride receptors.^{24,25} It has been observed that the presence of phenolic $-\text{OH}$, an

additional H-bond donor moiety within the oxime-based receptor facilitates fluoride binding and this leads to the formation of relatively inert receptor–fluoride complexes.²⁴ However, the presence of H-bond acceptor functionality within the receptor facilitates dissociation of the fluoride-receptor species.²⁵ A probable mechanism for automatic regeneration of fluoride-free receptor was proposed earlier and we anticipate interplay of a similar mechanism (Figure 6) in case of **1** and **2** as well.²⁵ Even though the acidity of oxime protons present in the receptors reported herein are comparable to earlier reported oxime receptors, the receptor–fluoride complexes formed by **1–2** are considerably labile. In order to form H-bonded host–guest complex in solution, fluoride ion has to compete with H-bond acceptor moiety present within the receptors. The lability of the host–guest interaction is further augmented by hydration of fluoride ion by water present within the medium, which can be attributed to the hydrophilic nature of the solvent used. Further, the water tolerance limit of **1–2** was determined colorimetrically by addition of a calculated amount of H_2O to a receptor–TBAF mixture and monitoring the absorbance of the peak associated with fluoride addition (Figures S21–S22, Supplementary Information). The water tolerance limit for receptor **1–2** was found to be 400 and 80 equivalent of water respectively against every equivalent of fluoride. The binding between the receptors and fluoride is not strong enough to show appreciable colorimetric change when water is present above this limit. Thus, the interplay of two simultaneous competitions facilitating dissociation of the receptor–fluoride complex can be attributed to the automatic regeneration of the fluoride free species. This

Figure 6. Probable mechanism for auto-regeneration of active receptor species from receptor–fluoride complexes in case of receptor **1** and **2**.

eventually allows repetitive fluoride detection by using **1–2**. Lack of any colorimetric response after three cycles can be attributed to the variation of the polarity of the medium varies after each successive addition of TBAF.

4. Conclusions

The correlation between auto-reusability and position of H-bond acceptor substituent in the aromatic backbone of a class of oxime-based receptors is studied. Three new oxime based receptors **1–3**, containing nitrobenzene substituents have been synthesized and their fluoride recognition abilities were investigated. The para- and ortho- nitro derivatives, **1** and **2** show the naked eye discernible color change and associated colorimetric response upon addition of fluoride ion solution in DMSO. However, the meta- derivative **3** did not show any color change or colorimetric response upon addition of fluoride ion. Evaluation of pKa of the oxime protons in **1–3** from ^1H NMR studies revealed that the oxime protons in these compounds are reasonably acidic in nature and comparable to those reported for earlier oxime based fluoride receptors. Therefore, the receptor–fluoride complexes formed by **1–2** are expected to be reasonably stable to trigger an irreversible colorimetric response. However, the presence of H-bond

acceptor aromatic nitro substituents in both the receptors augment the dissociation of receptor–fluoride complexes and this leads to automatic regeneration of the free receptor species within a short time span. Consequently, the regenerated receptor species can be employed for visual as well as colorimetric recognition of fluoride. While, the para-substituted derivative, **1** can be used up to three cycles for recognition of fluoride ion, no appreciable response was observed after the second cycle for the ortho-substituted derivative, **2**. The oxime proton in **2** is slightly less acidic as compared to the oxime proton in **1** and therefore the receptor fluoride complex formed by **2** is more labile than the corresponding receptor–fluoride complex formed by **1**. Thus proper tuning the acidity of the oxime proton and inclusion of suitable H-bond acceptor motif will allow us to enhance the auto-reusability of these receptors in colorimetric recognition of fluoride ion.

Supplementary Information (SI)

Supplementary Information is available at www.ias.ac.in/chemsci.

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