Journal of Fluorine Chemistry 160 (2014) 1–7

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

"Naked-eye" detection of inorganic fluoride ion in aqueous media using base labile proton: A different approach

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ARTICLE INFO

Article history:
Received 8 October 2013
Received in revised form 6 January 2014
Accepted 12 January 2014
Available online 23 January 2014

Keywords:
Anion receptor
Aqueous detection
Acidic proton
Fluoride
Hydrogen bonding
Deprotonation

ABSTRACT

Two new receptors R1 and R2 were designed and synthesized based on 1-naphthohydrazide Schiff's bases for the colorimetric detection of fluoride ion. The receptor R1 was selective toward fluoride ion over other anions in organic media. The presence of carbonyl group in 1-naphthohydrazide makes –NH proton acidic and therefore it could deprotonate with addition of basic anion such as fluoride. However, the acidic –NH proton easily gets solvated even with the trace amount of water. Alternatively, the receptor R2, encompasses highly base labile, hydroxyl (–OH) functionality which detects basic fluoride ions via deprotonation mechanism not only in organic solutions but also in aqueous media. The mechanism involved in the color change of receptor R1 is deprotonation of acidic –NH followed by stabilization of complex through intramolecular charge transfer (ICT) transition which was evidenced by the formation of HF_2^- peak in ^1H NMR titration. The color change of receptor R2 involves initial hydrogen bond formation of F^- ion with –NH group and deprotonation at higher concentration of F^- ions which leads to intramolecular charge transfer transition in organic media. On the other hand, in aqueous solution of receptor R2, addition of the basic fluoride ion leads to the deprotonation of base labile hydroxyl (–OH) proton, which is responsible for colorimetric detection.

1. Introduction

The anion sensing via synthetic organic receptor is a field of interest in supramolecular chemistry because of their importance in chemical and biological systems [1–8]. Among the range of anions, fluoride ion has attained significance because of its role in preventing dental decay [9,10] and in the treatment of osteoporosis [11,12]. However, in excess, fluoride can lead to fluorosis [13–17] and other bone related diseases [18,19]. This dual functionality of fluoride, with respect to beneficial as well as non-beneficial has acquired interest of the supramolecular chemists.

Conventional fluoride ion detection using electrode is costly, time consuming and requires complicated instrumentation with confusing handling procedures [20]. On the other hand, colorimetric receptors appear to be attractive because of their simplicity, high sensitivity, high selectivity and real-time 'naked eye' detection. This colorimetric detection of fluoride could be achieved by designing a host molecule where the binding of anion can change the color of host molecule. Based on this strategy, a number of receptors have been reported for the selective binding of fluoride [21–25]. Many well-known functional groups such as urea/thiourea, amides, pyrrole and imidazolium are proved themselves as effective binding sites for the fluoride ion through the formation of a hydrogen bond with N–H unit of these functional groups [26–38]. Silyl group deprotection based colorimetric receptors were also verified in various literatures [39–42]. The affinity of a boron atom toward fluoride ions were well utilized for the detection of fluoride ions [43–50]. Unfortunately, majority of them are capable of detecting fluoride ions only in absolute non-aqueous conditions and for the detection of organic fluoride sources such as tetrabutylammonium fluoride (TBAF) and therefore cannot be used for the real-life applications. Alternatively, if the receptor could detect inorganic fluorides such as sodium fluoride in aqueous media then it could be useful for the real-life application.

The detection ability, selectivity and sensitivity of a receptor depends on the acidity of protons where the F^- ions bind [51]. If the acidity of these protons is lesser than that of water then the F^- ions get solvated. Hence, contamination of receptor even with trace amount of water could result in the failure of colorimetric detection process. However, this drawback can be resolved to some extent by designing a receptor where the F^- ion binding protons are more acidic than water or by incorporating a base labile group such as hydroxyl (–OH) functionality, which can readily deprotonate with the basic ions such as F^- ion [52,53].

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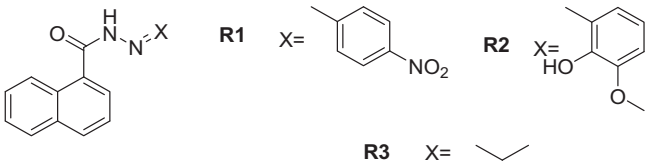
http://dx.doi.org/10.1016/j.jfluchem.2014.01.009



Scheme 1. Molecular structures of R1, R2 and R3.

Few receptors which are capable of detecting fluoride ions in organo–aqueous solvent mixture were reported recently. Unfortunately, majority of them are limited to organic fluoride source such as TBAF [54–56] or to make test papers, which is not instantaneous toward detection process [57,58]. On the other hand, there are few reports which showed admirable results such as detection of inorganic fluoride ions in aqueous media [59] and removal of inorganic fluoride ions by extracting them to organic media [60]. Nevertheless, the synthesis of receptors for the practical or real-life applications still persist as the detection of fluoride ions in 'water-only' conditions are hard to achieve.

Herein, we report the design and synthesis of new colorimetric receptors R1, R2 and R3 (Scheme 1), based on 1-naphthohydrazide Schiff's base for F^- ion detection. The receptor R1 was synthesized for the detection of F^- ion in organic media. The receptor R2 comprises hydroxyl (–OH) functional group and therefore it was able to detect the F^- ion in the form of NaF in organo–aqueous mixture (9:1 ratio) with this receptor. The receptor R3 was synthesized to depict the role of aromatic substitution to 1-naphthohydrazide backbone.

2. Results and discussion

The single crystal of the receptors R2 suitable for X-ray diffraction analysis was obtained by slow evaporation of methanol–chloroform (1:1) solution at room temperature. The ORTEP diagrams (50% probability) of the receptor R2 is given in Fig. 1. Detailed crystallographic data of receptor R2 is given in Table 1.

The receptor R2 was crystallized in orthorhombic lattice with space group Pbca. The naphthalene ring of the molecule is distorted from the plane by an angle of 44.4 (2)°. The carbonyl (–C=O) group of the receptor is linked by intermolecular H-bond via N–H···O=C interactions. The hydroxyl group of the receptor is connected by intramolecular H-bond to the imine N via O–H···N=C interactions. The details of H-bonding parameters (bond lengths and angles) have been mentioned in Table 2.

The receptors R1 and R2 were initially investigated for selective colorimetric detection of F^- ion over other anions in DMSO solvent. The receptors (2.5×10^{-5} M) were treated with 1 equiv. of various anions such as fluoride, chloride, bromide, iodide, acetate, hydrogensulphate and dihydrogenphosphate in the form of tetrabutylammonium (TBA) salts. A color change from colorless to red and colorless to bright yellow was observed instantaneously upon adding F^- ions and AcO^- ions to the receptors R1 (Fig. 2) and R2 (Fig. S7, see Supporting information) respectively. The color intensity was more in case of F^- ion for both the receptors which indicates strong binding of F^- ion to the receptors whereas, a much weaker interaction between receptors and AcO^- ion was resulted in decreased intensity in colorimetric detection.

The colorimetric detecting ability of receptors R1 and R2 were studied in ACN solvent. Unfortunately, the receptor R1 was partially soluble in ACN and therefore, it was not able to study for colorimetric applications. The receptor R2 displayed similar color change from colorless to bright yellow on addition of F^- ions and AcO^- ions (Fig. 3).

However, the color intensity for AcO^- ion was less when compared to F^- ion because of the weaker interaction of AcO^- ion with receptor.

The selectivity of receptor R1 was further confirmed with UV–vis spectroscopy where it showed significant shift in the absorption band upon addition of F^- ions and AcO^- ions. The intensity of this newly generated absorption band after addition of AcO^- ions was much less than that of F^- ions (Fig. 4). However, all other anions did not show any color change as well as did not show

Table 1
Crystallographic data of receptor R2.

Parameters	Receptor R2
CCDC No.	938645
Chemical formula	$C_{19}H_{16}N_2O_3$
Formula weight	320.34
Crystal system	Orthorhombic
Space group	Pbca
a (Å)	13.8637(14)
b (Å)	8.5605(9)
c (Å)	27.679(3)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
V (Å)^3	3284.9(6)
Z	8
Crystal size	$0.49 \times 0.45 \times 0.39$
F (000)	1344
R-Factor (%)	4.3

Table 2
H-bonding parameters for receptor R2.

S. no.	Type of interactions	Distance (Å)	Angle (°)
1	N–H···O	2.810 (2)	166 (2)
2	O–H···N	2.681 (2)	145.66

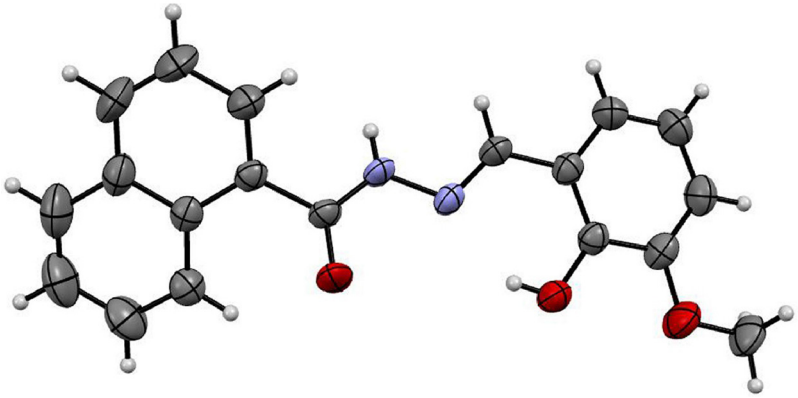


Fig. 1. The ORTEP diagrams (50% probability) of receptor R2.

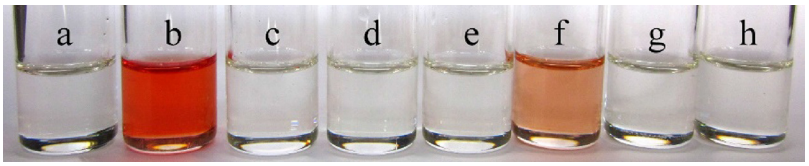


Fig. 2. Change in color of R1 (2.5×10^{-5} M) in DMSO solution on adding 1 equiv. of tetrabutylammonium anions: (a) free receptor R1, (b) F^-, (c) Cl^-, (d) Br^-, (e) I^-, (f) AcO^-, (g) HSO_4^- and (h) $H_2PO_4^-$ ions.

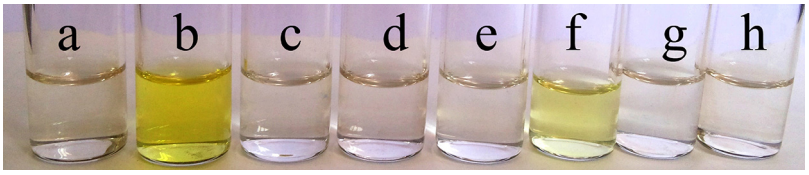


Fig. 3. Change in color of R2 (2.5×10^{-5} M) in ACN solution on adding 1 equiv. of tetrabutylammonium anions: (a) free receptor R2, (b) F^-, (c) Cl^-, (d) Br^-, (e) I^-, (f) AcO^-, (g) HSO_4^- and (h) $H_2PO_4^-$ ions.

any change in UV–vis absorption band, which indicated either these anions are not interacted with receptor R1 or the interaction was much weaker to create any changes in colorimetric detection and in UV–vis absorption. The same selectivity confirmation was extended to the receptor R2 in DMSO as well as in ACN solvents (Fig. S12 and Fig. S13, see Supporting information). In both the solvents the receptor R2 showed substantial shift in the absorption band only upon adding F^- ions and AcO^- ions. However, the intensity of absorption band was much lesser upon adding AcO^- ions, which clearly indicates that the interaction between receptor R2 and AcO^- ion is much weaker.

In order to examine the selectivity toward F^- ion over other anions, receptor R1 was treated with 1 equiv. of F^- ion in presence of Cl^-, Br^-, I^-, HSO_4^- and $H_2PO_4^-$ ions (1 equiv.). As shown in Fig. S10 (see Supporting Information), presence of other ions virtually made no difference on the colorimetric detection of F^- ion. Thus receptor R1 could selectively detect the fluoride ion even in presence of other competing anions.

To understand the nature of the receptor–anion interactions, a UV–vis titration was performed by increasing addition of TBAF to R1 (2.5×10^{-5} M) in absolute dry DMSO. The constant increase in the concentration of TBAF resulted in steady decrease in the intensity of absorbance band at 328 nm. Meanwhile, a new absorption band at 476 nm with the formation of a clear isosbestic point at 362 nm (Fig. 5) appeared. This bathochromic shift of 148 nm was attributed to the intramolecular charge transfer transition in the receptor R1.

The UV–vis titration of receptor R2 was carried out in both DMSO as well as ACN solutions. The DMSO solution showed constant decrease in the absorption band at 301 nm with gradual increasing addition of F^- ions. Meanwhile a new band centered at 413 nm appeared and intensity of this absorption band was increased continuously with increasing concentration of F^- ions (Fig. S15, see Supporting information). A gradual addition of F^- ions to receptor R2 in ACN, a new absorption peak at 440 nm corresponding to intramolecular charge transfer, was established. Concurrently, the absorption maxima corresponding to –OH functional group at 296 nm gradually shifted to a new absorption maxima at 344 nm creating an isosbestic point at 315 nm (Fig. 6). This 48 nm bathochromic shift in the absorption maxima was due to the stabilization of *keto* tautomer of hydroxyl functional group. However, this *enol* to *keto* tautomeric shift was not observed in case of DMSO solution as the *keto* tautomer itself is more stable in more polar solvents like DMSO [61,62] The DMSO solvent forms hydrogen bond with the –C=O of *keto* tautomer and therefore, *keto* tautomer becomes stable in receptor R2. As a result, *keto* tautomer

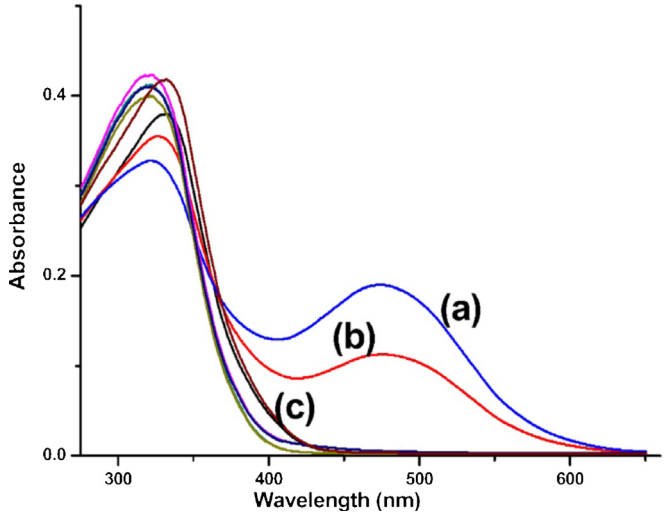


Fig. 4. UV–vis spectral changes of R1 (2.5×10^{-5} M) in DMSO after addition of 10 equiv. of (a) F^-, (b) AcO^- and (c) Cl^-, Br^-, I^-, HSO_4^- and $H_2PO_4^-$ ions in the form of TBA salts.

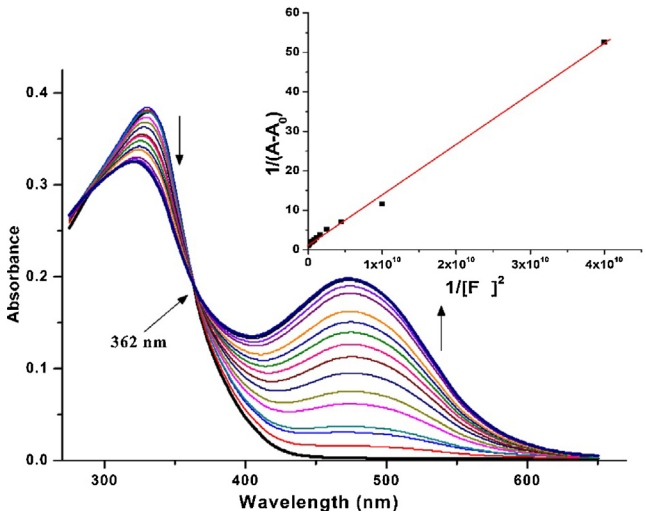


Fig. 5. UV–vis titration of R1 (2.5×10^{-5} M) with TBAF (0–15 equiv.) in DMSO. Inset: Benesi–Hildebrand plot of receptor R1 binding with F^- ion associated with absorbance change at 476 nm in DMSO.

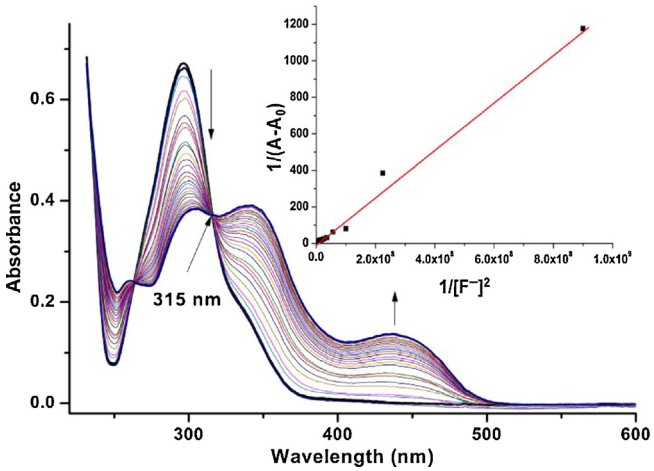


Fig. 6. UV–vis titration of R2 (2.5×10^{-5} M) with TBAF (0–15 equiv.) in ACN. Inset: Benesi–Hildebrand plot of receptor R2 binding with F^- ion associated with absorbance change at 440 nm in ACN.

predominates over *enol* tautomer in DMSO solvent and the –C=O functional group of *keto* tautomer has no binding site to participate in the detection process.

The stoichiometry of the anion complexation for both receptors R1 and R2 was determined by Benesi–Hildebrand method [63] using UV spectrometric titration data at 476 nm and 440 nm respectively (Fig. 5, inset and Fig. 6, inset). The linearity in graph confirms formation of a stable 1:2 stoichiometric complex for both receptors with F^- ions. The binding constant was calculated using Benesi–Hildebrand equation (Eq. (1)) and was found to be $2.36 \pm 0.33 \times 10^6\ M^{-2}$ for receptor R1 and $0.973 \pm 0.09 \times 10^6\ M^{-2}$ for Receptor R2.

$$\frac{1}{(A - A_0)} = \frac{1}{(A_{max} - A_0)} + \frac{1}{K[F^-]^n (A_{max} - A_0)} \quad (1)$$

where A_0, A, A_{max} are the absorption considered in the absence of F^-, at an intermediate, and at a concentration of saturation. K is binding constant, $[F^-]$ is concentration of F^- ion and n is the stoichiometric ratio.

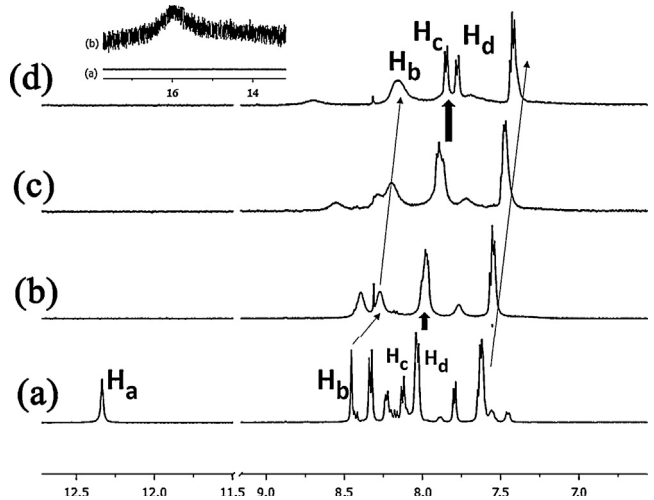
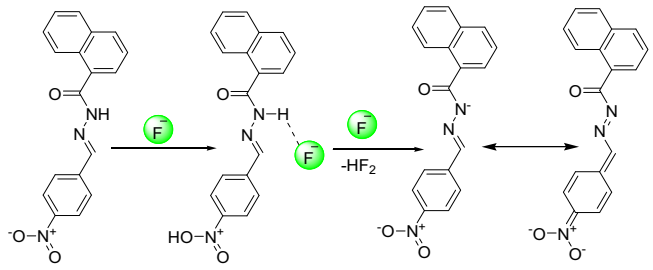


Fig. 7. Partial ^1H NMR spectra of receptor R1 in DMSO-d_6 after the addition of (a) 0 equiv., (b) 1 equiv., (c) 2 equiv. and (d) 5 equiv. of F^- ions. Inset: (a) no peak at 16.1 at 0 equiv. F^- ions and (b) peak corresponding to HF_2 on adding 5 equiv. of F^- ions.



Scheme 2. Proposed mechanism for binding of fluoride ions with receptor R1.

^1H NMR titration experiments of R1 and R2 with F^- ion (as TBA salt) were carried out in DMSO-d_6 to understand the mechanism of receptor–anion interactions.

The proton H_a at δ 12.34 corresponding to –NH of receptor R1 was initially disappeared on adding TBAF (1 equiv.) as a result of fast proton exchange. The signals at δ 8.15 (H_c) and δ 8.05 (H_d) corresponding to nitro phenyl group were merged together till 2 equiv. of F^- ions due to the fast proton exchange through the receptor R1. At 5 equiv. of F^- ions the –NH of receptor deprotonates and a conjugated quinonoid form of receptor R1 was stabilized. As a result, splitting of the signals corresponding to nitro phenyl group reappeared (Fig. 7). As the concentration of F^- ion increased from 1 equiv. to 5 equiv., signal at δ 8.45 corresponding to imine proton (H_b) was slowly upfielded owing to the formation of exocyclic double bond during detection process. The deprotonation lead to increase in electron density over receptor R1 which resulted in upfielded aromatic protons.

The most important result observed in ^1H NMR titration was appearance of a new peak at δ 16.1 (Fig. 7, inset) at higher concentration (5 equiv.) of F^- ion. This corresponds to HF_2 (hydrogen difluoride) [64] which further confirm deprotonation of –NH proton in receptor R1.

The binding mechanism of receptor R1 to F^- ions was proposed by evaluating the results obtained from UV–vis titration and ^1H NMR titration (Scheme 2). The F^- ion detection using receptor R1 is two-step process. At first, a F^- ion binds through hydrogen bonding to the –NH proton of the receptor R1 which results in 1:1 adduct and a R1···F^- complex is formed [65]. The second F^- ion induces deprotonation of –NH proton in the receptor R1 and as a result, the electron density increases over the deprotonated receptor R1. Thus, the charge separation in the receptor is introduced which

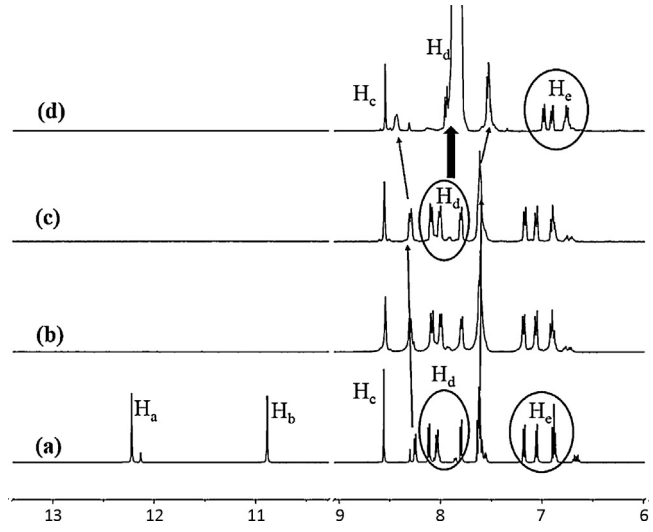
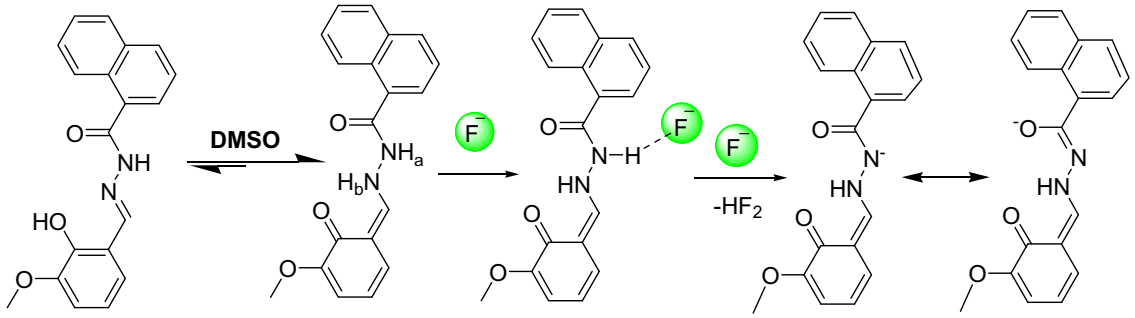


Fig. 8. Partial ^1H NMR spectra of receptor R2 in DMSO-d_6 after the addition of (a) 0 equiv., (b) 1 equiv., (c) 2 equiv. and (d) 5 equiv. of F^- ions.



Scheme 3. Proposed mechanism for binding of fluoride ions with receptor R2.

results in ICT transition between the electron deficient $-NO_2$ group at *p*-position and electron rich $-N^-$ which lead to intense colorimetric change [66].

As stated previously, the *keto* tautomer of receptor R2 will be predominated over the *enol* tautomer in polar solvents such as DMSO. This tautomerism is confirmed by ^{1}H NMR spectrum where the proton at δ 12.25 (H_a) corresponds to –CONH and proton at δ 10.9 (H_b) corresponds to –NH of *keto* tautomer. In ^{1}H NMR titration of receptor R2, both the protons corresponding to –NH at δ 12.25 and at δ 10.9, were disappeared upon adding 1 equiv. of F^- ions (Fig. 8), which is owing to the formation of hydrogen bond between F^- ion and –NH proton of –CONH followed by fast proton exchange. Surprisingly, no other major changes were observed in ^{1}H NMR signals corresponding to the aromatic protons while adding F^- ions up to 2 equiv. However, at higher concentration of F^- ions (5 equiv.) the proton H_a deprotonates which resulted in the charge transfer transition in receptor R2 arises. Consequently, the aromatic signals corresponding to naphthyl protons (H_d) were merged together. This deprotonation, leads to increased electronic density over the phenyl group and signals corresponding to these protons (H_e) were slightly upfielded. The imine –CH in receptor R2 was not participated in the detection process. This was confirmed by ^{1}H NMR titration spectra where the signals at δ 8.6 was not shifted either upfield or downfield even after adding 5 equiv. of F^- ions.

Thus, the results of UV–vis titration and ^{1}H NMR titration were compiled to determine the binding mechanism of receptor R2 with F^- ions (Scheme 3). Being a keto tautomer in DMSO, the –NH proton of receptor R2 initially forms hydrogen bond with F^- ion to stabilize a R2···F^- adduct. Further addition of F^- ion persuades deprotonation of the –NH proton in receptor R2 and thus establishes charge on the receptor. This leads charge transfer transition within the receptor R2 and thus the receptor show a significant color change.

The receptor R3 was evaluated for colorimetric detection of F^- ions over other anions in DMSO. The color of receptor was not changed even after adding 20 equiv. of anions. The absorbance in UV–vis spectroscopy was also not changed with the addition of any anions. Therefore, it is clear that the presence of aromatic unit

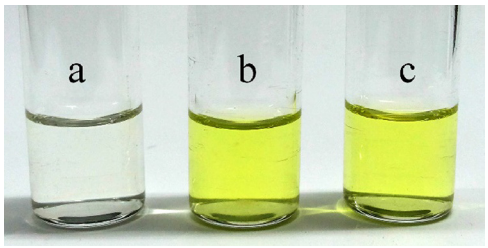
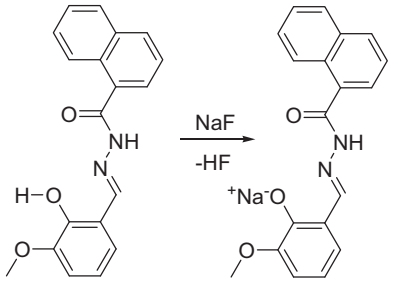


Fig. 9. Color change of the receptor R2 after adding the F^- ions in 9:1 ACN:H_2O solvent mixture: (a) R2 (1×10^{-3} M), (b) R2 + 3 equiv. NaF and (c) R2 + 3 equiv. TBAF.



Scheme 4. Proposed mechanism for detection of inorganic fluoride ions in aqueous media.

attached to naphthohydrazide unit is indispensable for the F^- ion detection process.

To evaluate real-life applicability of any receptor, it should detect the inorganic fluoride ions such as sodium fluoride particularly in aqueous media. Therefore, to ensure the real-life significance, the receptors R1 and R2 were evaluated for the colorimetric detection of sodium fluoride in 9:1 (1×10^{-3} M solution in DMSO:H_2O for R1 and ACN:H_2O for R2) organo–aqueous mixture. Though the receptor R1 showed remarkable color change in organic solvents for the detection of TBAF, it failed to detect inorganic fluoride ions in aqueous media. However, the receptor R2 showed a significant color change from colorless to pale yellow on adding 5 equiv. of sodium fluoride in aqueous media (Fig. 9). The receptor R2 showed same color change even with the addition of 5 equiv. TBAF as F^- ion source in aqueous media. Unfortunately, UV–vis studies were unable to determine as the receptor concentration exceeded absorption limit.

The receptor R1 failed to detect inorganic fluoride ions as the binding site (–NH) readily gets solvated in presence of water even in trace amounts. On the other hand, receptor R2 has a phenolic –OH which is highly base labile and immediately binds with basic inorganic fluoride ions to form respective salt. As a result, upon adding sodium fluoride to the receptor R2, phenolic –OH readily gets deprotonated to form corresponding sodium salt (Scheme 4) and this deprotonation leads to the color change of receptor R2 from colorless to pale yellow.

The receptor R2 was able to colorimetrically detect the F^- ions with a minimum concentration of 1×10^{-6} M in organic media and 1×10^{-4} M in organo–aqueous mixture. The amount of F^- ions required for detection in organo–aqueous mixture is high as the binding site of receptor gets solvated in the presence of water.

3. Conclusion

To summarize, the receptors R1 and R2 were designed and synthesized based on 1-naphthohydrazide Schiff's base for the selective colorimetric detection of F^- ions over other anions. The detection process involves initial 1:1 receptor–F^- ion adduct formation followed by deprotonation at higher concentration of

F^- ions. This resulted in charge transfer transition through the receptors and thus remarkable color change from colorless to red in case of receptor R1 and colorless to bright yellow for receptor R2 was observed. Though the receptor R1 displayed prominent color change in organic media, it failed to show the same result for the detection of inorganic fluoride ions in aqueous media as the binding site easily gets solvated with trace amount of water. Alternatively, the receptor R2 was able to detect inorganic fluoride in aqueous media. This observation was owing to the presence of base labile –OH functionality in receptor R2 which will be deprotonated with basic F^- ions, even in aqueous media. Thus, present study could be further explored for the development of new colorimetric anion receptors in aqueous media with a new approach.

4. Experimental

4.1. 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.

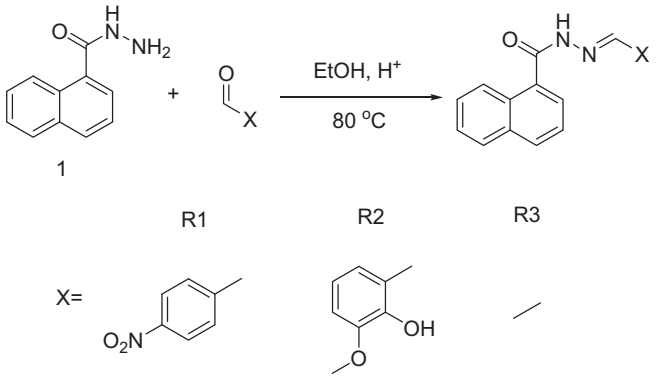
The ^{1}H NMR spectra were recorded on a Bruker, Avance II (500 MHz) instrument using TMS as internal reference and DMSO-d_6 as solvent. Resonance multiplicities are described as s (singlet), br s (broad singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Melting points were measured on 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 and Analytikjena Specord S600 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).

4.2. Synthesis of target receptors R1, R2 and R3 and characterization

The synthesis of receptors R1, R2 and R3 were achieved by a straightforward process (Scheme 5). The structures were characterized by standard spectroscopic methods.

Intermediate 1 was synthesized according to the reported procedure in literature [67].

A mixture of aldehyde (2.69 mmol) and 1-naphthohydrazide 1 (2.69 mmol) reacted in ethanol under reflux for 5 h. The reaction was catalyzed by a drop of acetic acid. After cooling, the formed solid was filtered and washed with ethanol to obtain the target compounds (R1, R2 and R3). All the synthesized compounds were solid. Their structures were confirmed by ^{1}H NMR, FT-IR, elemental analysis and mass spectra.



Scheme 5. Synthesis of the receptors R1, R2 and R3.

4.3. (E)-N′-(4-nitrobenzylidene)-1-naphthohydrazide (R1)

Yield: 92%; m.p. 313–314 °C.

Elemental analysis; Calculated for $C_{18}H_{13}N_3O_3$: C 67.71, H 4.10, N 13.16, Found: C 67.53, H 4.23, N 13.24.

^{1}H NMR (DMSO-d_6) δ 12.34 (s, 1H, NH), δ 8.45 (s, 1H, –CH), δ 8.34 (d, 3H, ArH, J = 8.5 Hz), δ 8.24 (d, 1H, ArH, J = 7.5 Hz), δ 8.14 (d, 1H, ArH, J = 8.0 Hz), δ 8.04 (d, 2H, ArH, J = 8.0 Hz), δ 7.80 (d, 1H, ArH, J = 7.0 Hz), δ 7.63 (d, 3H, ArH, J = 6.0 Hz).

FT-IR in cm^{-1}: 3163.5 (br.w), 3005.7 (br.m), 2842.0 (br.w), 1640.7 (s), 1556.6 (m), 1509.9 (s), 1334.6 (s), 1293.0 (s), 1254.1 (m), 1201.1 (m), 1143.8 (w), 1075.1 (w), 1027.5 (w), 779.9 (m).

MS (ESI): m/z: Calculated: 318.3062 $[M-H]^+$, Experimental: 318.0919 $[M-H]^+$.

4.4. (E)-N′-(2-hydroxy-3-methoxybenzylidene)-1-naphthohydrazide (R2)

Yield: 90%; m.p. 169–170 °C.

Elemental analysis; Calculated for $C_{19}H_{16}N_2O_3$: C 71.24, H 5.03, N 8.74, Experimental: C 71.28, H 5.09, N 8.76.

^{1}H NMR (DMSO-d_6) δ 12.22 (s, 1H, –NH), δ 10.89 (s, 1H, –OH), δ 8.56 (s, 1H, –CH), δ 8.26 (d, 1H, ArH, J = 9.0 Hz), δ 8.13 (d, 1H, ArH, J = 8.5 Hz), δ 8.04–8.03 (m, 1H, ArH), δ 7.81 (d, 1H, ArH, J = 8.5 Hz), 7.64–7.60 (m, 3H, ArH), 7.19 (d, 1H, ArH, J = 8.5 Hz), δ 7.07 (d, 1, ArH, J = 8.0 Hz), δ 6.87 (t, 1H, ArH J = 8.25 Hz), δ 3.83 (s, 3H, –CH_3).

FT-IR in cm^{-1}: 3170.3 (w), 3041.1 (w), 2856.2 (w), 1640.0 (s), 1564.5 (m), 1468.5 (m), 1245.8 (s), 722.8 (w), 659.5 (w).

4.5. (E)-N′-propylidene-1-naphthohydrazide (R3)

Yield: 88%; m.p. 191–192 °C.

Elemental analysis: Calculated for $C_{14}H_{14}N_2O$: C 74.31, H 6.24, N 12.32, Experimental: C 74.23, H 6.21, N 12.41.

^{1}H NMR (DMSO-d_6) δ 11.58 (s, 1H, NH), δ 8.16–8.12 (m, 1H, ArH), δ 8.07 (d, 1H, –CH, J = 8.5 Hz), δ 8.01–8.7.98 (m, 1H, ArH), δ 7.67–7.64 (m, 2H, ArH), δ 7.60–7.57 (m, 3H, ArH), δ 2.33–2.28 (m, 2H, –CH_2), δ 1.08 (t, 3H, –CH_3, J = 7.5 Hz).

FT-IR in cm^{-1}: 3181.1 (br.m), 3034.6 (m), 2068.0 (m), 1870.3 (br.w), 1633.6 (s), 1549.1 (s), 1352.8 (m), 1295.6 (m), 1252.7 (m), 1147.4 (w), 777.6 (s).

MS (ESI): m/z: Calculated: 249.2635 $[M+Na]^+$, Experimental: 249.1578 $[M+Na]^+$.

Acknowledgements

The 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. DRT acknowledges Department of Science and Technology (DST, Government of India, New Delhi) for the financial support. MP and DRT thank Optoelectronics Laboratory, Department of Physics, NITK and CSMCRI, Bhavnagar for the spectral analysis.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2014.01.009.

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