

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



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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 HF₂ 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.

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1. Introduction

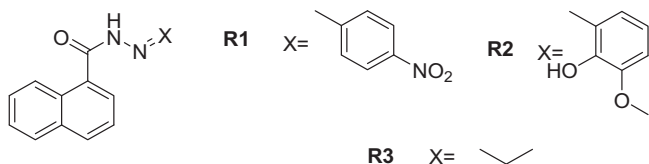
The anion sensing via synthetic organic receptor is a field of interest in supramolecular chemistry because of their importance in chemical and biological systems [1–8]. Among the range of anions, fluoride ion has attained significance because of its role in preventing dental decay [9,10] and in the 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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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 Pbc_a. 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,

Table 1
Crystallographic data of receptor R2.

Parameters	Receptor R2
CCDC No.	938645
Chemical formula	C ₁₉ H ₁₆ N ₂ O ₃
Formula weight	320.34
Crystal system	Orthorhombic
Space group	Pbc _a
<i>a</i> (Å)	13.8637(14)
<i>b</i> (Å)	8.5605(9)
<i>c</i> (Å)	27.679(3)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
<i>V</i> (Å ³)	3284.9(6)
<i>Z</i>	8
Crystal size	0.49 × 0.45 × 0.39
<i>F</i> (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

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

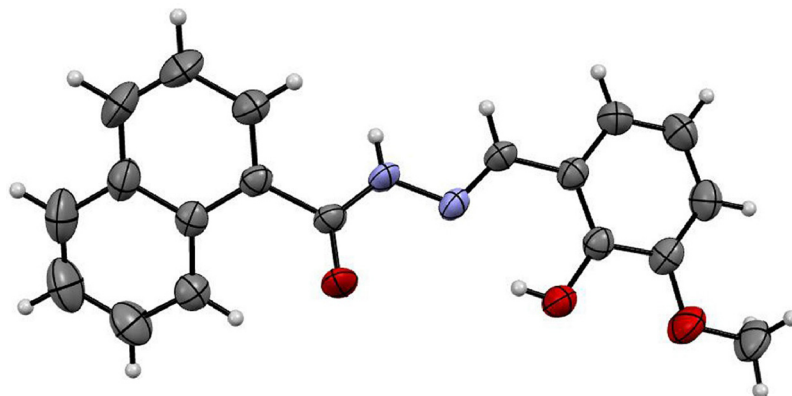


Fig. 1. The ORTEP diagrams (50% probability) of receptor R2.

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