



Contents lists available at ScienceDirect

Tetrahedron Letters

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

A reaction based chromofluorogenic turn-on probe for specific detection of fluoride over sulfide/thiols

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ARTICLE INFO

Article history:

Received 11 July 2014

Revised 9 September 2014

Accepted 10 September 2014

Available online xxxxx

Keywords:

Fluorescein

Chemodosimeter

Fluoride ion

Nucleophilicity/basicity

Optical sensors

ABSTRACT

A new reaction based probe fluorescein nosylate (**R1**) has been designed and synthesized for selective recognition of F^- in acetonitrile (CH_3CN) by exploiting both its nucleophilic and basic character. Probe **R1** consists of fluorescein dye as a signalling unit while 4-nitrobenzenesulfonyl chloride as the masking unit. The F^- plays the role of de-masking agent to set free the fluorescein moiety in its open form from **R1** leading to significant changes in its absorption/emission profile. The detection of F^- amidst of sulfide/thiols through receptors undergoing nucleophilic scission is a tedious job due to similarity in their extent of basicity/nucleophilicity. Here, we present a convenient solution for the same in the form of **R1** which detects F^- selectively over sulfide/thiols in CH_3CN with a high detection limit of 4.6×10^{-7} M and 2.75×10^{-8} M determined through UV–visible and fluorescence titration data, respectively.

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The recognition and sensing of anions have attracted a great deal of attention because of their biological and environmental importance.¹ Being very small in size and having high charge density the fluoride ion (F^-) contributes towards diverse health and environmental issues.² The pivotal role of F^- in dental care as preventing cavities and strengthening teeth is well known.³ However, a high intake of F^- may cause most widespread side effects like fluorosis, urolithiasis, osteoporosis etc. in human beings.⁴ Fluorides also enter the environment from various anthropogenic activities besides the fluoridation of drinking water.⁵ For these reasons, considerable efforts have been devoted towards the development of novel receptors for the selective detection of F^- . The optical probes for the analysis of different analytes have been in the process of development for the last few decades owing to their simplicity, high selectivity and sensitivity.⁶

Till now, a number of diverse sensing mechanisms have been employed for optical detection of F^- ,^{4a,7} including hydrogen bonding interactions, Lewis acid/base coordination, F^- induced leaving of the trialkylsilyl group,⁸ F^- substitution for p-dimethylaminopyridine,⁹ F^- induced B–N bond cleavage¹⁰ and de-protection of dinitro/nitrobenzenesulfonyl (DNBS/NBS)-protected fluorophores.¹¹ Out of the above the hydrogen bonding interaction based receptors are generally non-selective and face interferences from a number of anions of comparable basicity, for example, OH^- , AcO^- , $H_2PO_4^-$ etc.¹² To overcome the same, researchers have synthesized

reaction based probes, that is, chemodosimeters^{7,13} which utilize chemical affinity between F^- and silicon/boron involving facile cleavage of the C–Si, O–Si or B–N/O bond by F^- .^{8–10} Moreover fluoride is most electronegative, and has a strong nucleophilic character which may lead to F^- induced nucleophilic cleavage of C–S bond also.¹¹

The basic synthetic approach of these kinds of probes mainly involves F^- directed cleavage of the protecting group and release of fluorophore in the solution which leads to appropriate optical changes. For this purpose a variety of fluorophores viz., resorufin, BODIPY, fluorescein, coumarin etc. were used by various workers.¹³ Fluorescein is an inexpensive, practical and reliable molecular tool for the construction of optical probes due to its large visible-range extinction coefficients and high fluorescence quantum yields.¹⁴ Although a few F^- responsive probes incorporating the fluorescein moiety have been explored previously^{11,15–19} (Fig. 1), a few common drawbacks are associated with these probes viz., moderate detection limit, selectivity, poor off-on response, tedious synthetic approach etc.

In order to tackle the above limitations of the current F^- probes, herein we devised a highly selective reaction based chromofluorogenic turn-on probe (**R1**) for F^- which incorporates fluorescein as the fluorophore and 4-nitrobenzenesulfonyl (NBS) as the masking agent (Fig. 1). Previously reported fluorescein based probes/chemodosimeters are associated with some limitations. For example, Shiraishi and co-workers¹⁵ reported an unmodified fluorescein (**R2**) as fluorescent sensor for F^- but it experiences interferences from AcO^- and $H_2PO_4^-$ due to their comparable

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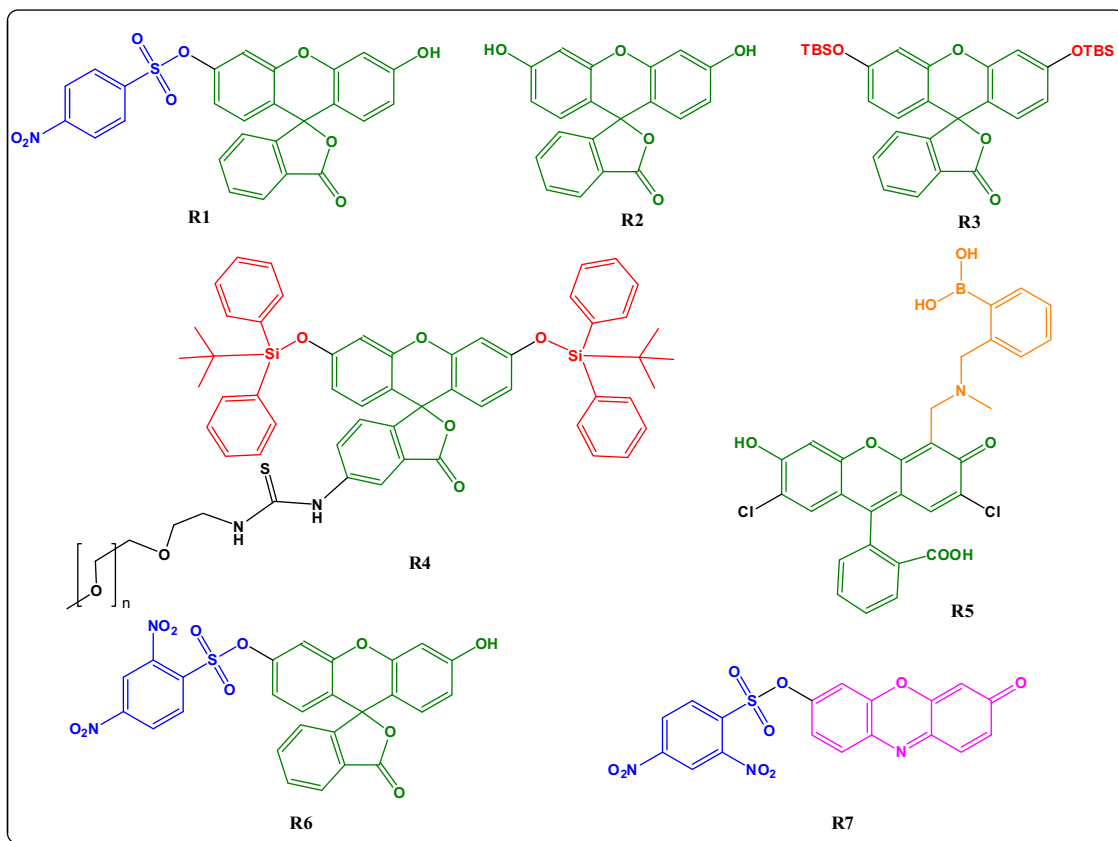


Figure 1. Chemical structure of probe **R1** (present study) along with probes **R2–R7** for F^- reported by other workers.

basicity to F^- . The probe reported by Yang et al. **R3**,¹⁶ showed interference only by a less common anion BF_4^- . A biocompatible probe reported by Zheng et al. (**R4**)¹⁷ could detect the F^- selectively with a detection limit of 19 ppb in the aqueous medium but the synthetic strategy of the same is a tedious one. Swamy et al. reported yet another fluorescein derivative bearing a boronic acid group (**R5**)¹⁸ but with a less intense fluorescent response with the interference of Cl^- .

The probe **R1** which we report in the present Letter is synthesized through slight structural modification of the chemodosimeter (**R6**)¹⁹ of Yang et al. by utilizing NBS instead of the DNBS group as the masking agent. Yang's chemodosimeter (**R6**) selectively detects sulfide in aqueous acetone solution. We also tried the same solvent system for sulfide detection but to our surprise **R1** did not respond. However, when we checked ion sensing property of **R6** in CH_3CN , it gave optical responses for sulfide along with F^- also. Chang and co-workers developed a resorufin sulfonate (**R7**) recently¹¹ which exhibited significant signalling towards F^- with remarkable interferences from sulfide ions. Hence, probes based on de-protection of dinitro/nitrobenzenesulfonyl (DNBS/NBS)-protected fluorophores responded mainly for thiols²⁰ and only a few of them could detect F^- with significant interferences from sulfide.^{11,19}

Thus, compared to the previously reported reaction based F^- probes **R2–R7**^{11,15–19} (Fig. 1), our results demonstrate that **R1** is more potent towards F^- in terms of selectivity as it does not respond to the most commonly interfering analytes like sulfide/thiols. The **R1** detected F^- ion with lowest limits of 4.6×10^{-7} M and 2.75×10^{-8} M, determined through UV-visible and fluorescence titration data, respectively, which is either comparable/better than a number of reaction based fluorescent probes reported recently by various workers.

R1 was prepared following the known synthetic procedure (Scheme 1).²¹ The probe **R1** was fully characterized by 1H NMR, ^{13}C NMR, IR and ESI-MS spectrometries (ESI; Figs. S1–S4).

The absorption and emission properties of probe **R1** towards F^- as its tetrabutylammonium (TBA) salt were firstly evaluated in CH_3CN . The UV-visible studies were carried out in 20 μM CH_3CN solution of **R1**. The UV-visible absorption spectrum of **R1** exhibited two bands at 457 and 490 nm with poor intensity hence giving a colourless appearance to the same. However, with the addition of F^- , a new strong absorption band centred at 517 nm appeared which can be ascribed to the deprotection of NBS group from **R1** hence liberating the parent fluorescein dye in its open form (Fig. 2). At this stage the colour of the solution became yellow from colourless instantaneously, indicating that **R1** can be used as a 'naked-eye' indicator for F^- (Fig. 2). A considerable number of other anions viz., S^{2-} , Cl^- , Br^- , I^- , CH_3COO^- , $C_6H_5COO^-$, ClO_4^- , SO_3^{2-} , N_3^- , HSO_4^- , HSO_3^- , BF_4^- , $H_2PO_4^-$, PF_6^- and HPO_4^{2-} did not show any significant absorption/colour response towards **R1** (ESI; Fig. S5).

Since receptor **R1** showed the specificity towards F^- in colorimetric measurement as described above, the fluorescence emission of the same was further investigated to explore the possibility of dual mode sensing of F^- by **R1**. At the same time the fluorescent methods possess even lower detection limits as compared to the colorimetric ones. The 5 μM CH_3CN solution of **R1** was colourless and non-fluorescent upon excitation at 490 nm, indicating the predominant existence of the closed spirocycle form of fluorescein. As expected, after esterification with NBS the fluorescein dye lost its original fluorescence property and turned colourless. However upon gradual additions of F^- as its TBA salt to the CH_3CN solution of **R1**, the same experienced fluorescence switching and exhibited a single emission band at 530 nm with ~ 60 -fold emission enhancement (Fig. 3). Thus addition of F^- restored the original

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