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SEARCH FOR CHEMOSENSORS FOR FLUORIDE IONS: A HIGHLY PROMISING AREA OF RESEARCH

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Abstract

In recent times, chemosensors for fluoride ions have attracted a great deal of attention. Fluoride ions play an important role in many biological, industrial and environmental processes and are associated with diseases like Alzeimer's disease. This paper covers imidazole, indole, azo-phenol and benzohydrazide based chemosensors for F^- ion with synthesis and detection methods.

Key words

Receptors; naked-eye detection; optical responses; chemical shifts; chromophor

Introduction

In recent years the design of synthetic receptors that can selectively recognize anions through visible, electrochemical and optical responses has got considerable attention because anions play an important role in many biological, industrial and environmental processes (Sohn et al., 2000). Many works have been reported for the recognition of negatively charged species (Martinez-Manez et al., 2003). But still the search of structurally simple receptor which can be easily synthesized and efficiently used has been of keen interest in the area of molecular recognition.

Among the biologically important anions, F^- is the most basic and most electronegative anion and it can form strongest H-bond with H-bond donor groups like NH or OH. The presence of excess F^- can cause deprotonation following classical Bronsted acid-base type reaction.

Fluoride has well established role in preventing dental caries (Kirk, 1991). It has also been used extensively for the treatment of osteoporesis. Fluoride can lead to fluorosis, a type of fluoride toxicity that generally manifests itself clinically in terms of increasing bone density if it is used on a less salubrious level (Jessell et al., 1993). It has applications in the analysis of drinking water and in the detection of chemical warfare agents (Sohn et al., 2000). Fluoride is also associated with diseases like Alzeimer's disease (Varner et al., 1998).

In recent years, benzohydrazide, imidazole,

indole and azo-phenol derivatives have been shown to be excellent receptors for fluoride ions.

Strategy

A general strategy for synthesis of benzohydrazide derivative (Madhuprasad et al., 2012) is depicted in Fig. 1.

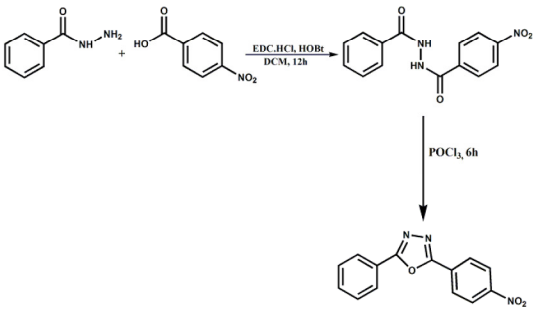

Fig 1: Synthesis of benzohydrazide derivative.

Detection methods

The binding of fluoride ions generally causes change in colour of the solution of chemosensor, red shift in Uv-vis spectra, increase in fluorescence intensity and chemical shifts or disappearance of NH or OH proton signals of chemosensors.

Colour change

The color change i.e. naked-eye experiment was carried out using 2.5 x 10^{-5} M solution of benzohydrazide based receptor in dry DMSO and addition of 1 eq. of tetrabutylammonium salt of anions. In the presence of TBAF, the receptor shows change of colour from colourless to red. The acetate anion influences color change from colourless to yellow at larger concentration when it is compared to F^- ion. The change in the electronic property of the chromophore gets affected resulting intense red color because of the charge transfer interaction between fluoride bound NH and the electron deficient nitro group at para position. The change in colour of receptor after addition of anions is shown in Fig. 2 (Madhuprasad et al., 2012).

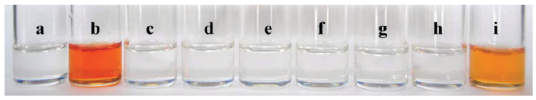

Fig 2: Change in colour of a benzohydrazide based receptor after addition of anions (a) Free receptor, (b) F^-, (c) Cl^-, (d) Br^-, (e) I^-, (f) NO_3^-, (g) HSO_4^-, (h) $H_2PO_4^-$ and (i) ACO^-.

UV-vis experiment

The UV–vis spectra of an azo-based receptor after addition of 1 equivalent of each anion are presented in Fig. 3. The addition of fluoride ions causes red shift and the absorption maxima at 615 nm is due to formation of salt complex (Lee et al., 2001).

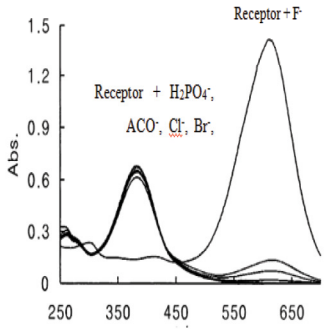

Fig 3: UV-vis spectrum of an azo-phenol based chemosensor after addition of anions.

Fluorescence experiment

The emission spectrum of receptor (Fig. 4) possesses emission maxima at 550 nm. But upon addition of tetrabutylammonium fluoride emission maxima shifted to shorter wavelength i.e. emission maximum appears at 477 nm. The peak at 477 nm gradually increases as the concentration of fluoride is increased. The fluorescence spectra remained almost unchanged on addition of other anions stated earlier. Again the emission spectra of the other receptors remain unaffected on addition of anions as their tetrabutylammonium salts (Goswami et al., 2011).

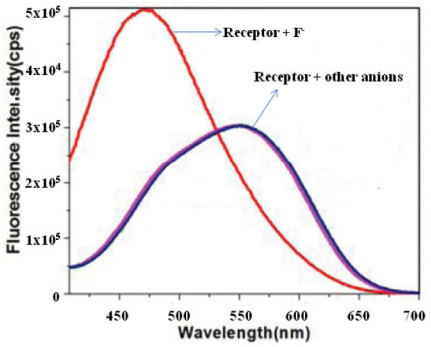

Fig. 4: Change of fluorescence spectra of an imidazole based receptor on addition of various anions.

NMR titration

The chromogenic indole NH proton signal appears at 11.67 ppm in DMSO-d_6. As depicted in Fig. 5, the signal of indole NH proton at 11.67 ppm disappeared after the addition of 0.4 equiv of F^- anion. With the gradual addition of F^- a new singlet signal developed at 16.10 ppm and then split into a 1:2:1 triplet signal. The appearance of new signals can be ascribed to the FHF^- dimer, which demonstrated the occurrence of the deprotonation of the NH group of the indole ring (Lv et al., 2011).

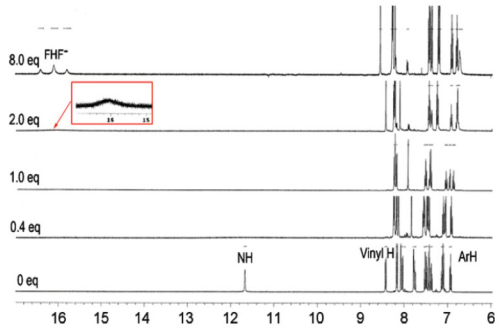

Fig. 5: NMR spectra of an indol based chemosensor in the presence of 0, 0.4, 1.0, 2.0 and 8.0 eq. of F^-.

Conclusion

In conclusion, detection of fluoride ions has been a matter of prime importance because of its biological, industrial and environmental concerns. The benzohydrazide, azo-phenol, imidazole and indol derivatives have been found to be excellent receptors for fluoride ions because of easy synthetic and detection monitoring methods.

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