

Methodological Development for Sensing of Fluoride ion in Aqueous Medium Using Organic Probe Molecules

**A thesis submitted in partial fulfillment of the requirements for the degree of
Doctor of Philosophy**

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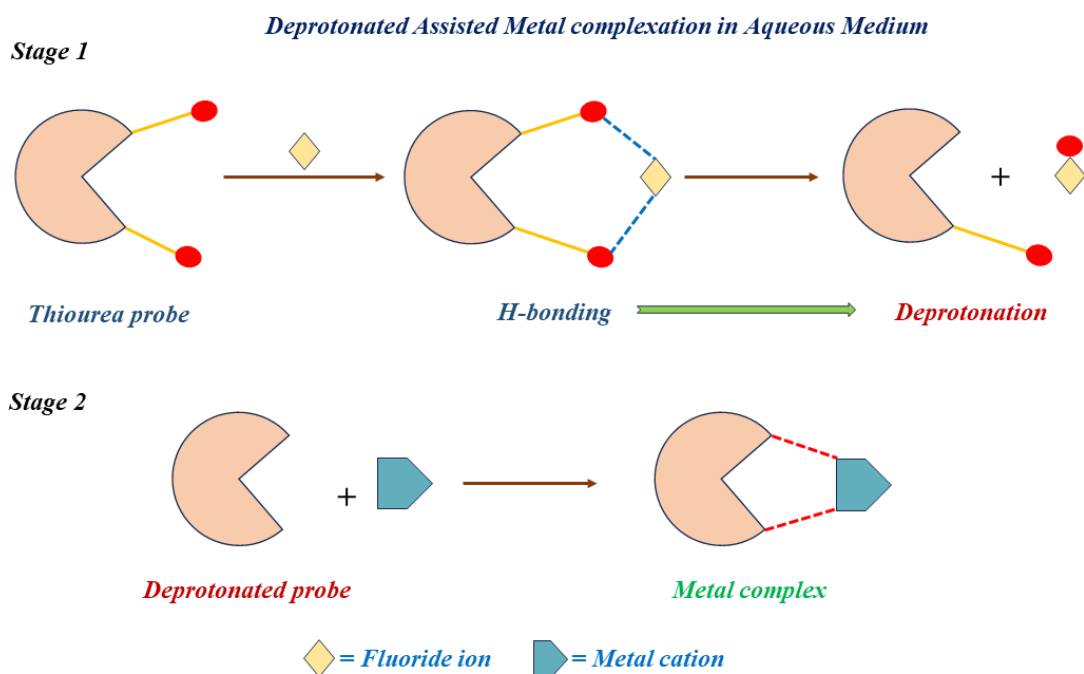
Chapter 7

Conclusion and Future Scopes

7.1: Summary and Conclusions

The thesis, entitled "*Methodological Development for Sensing of Fluoride Ion in Aqueous Medium Using Organic Probe Molecules*," successfully addresses the detection of fluoride in both aqueous and pure water mediums. The research primarily explores two hypotheses for designing methodologies to detect fluoride ions. One hypothesis was successfully applied to sense fluoride ions in aqueous conditions, while the other was effective in 100% pure water.

The first hypothesis involves the strategic deprotonation of acidic protons in the selected probe molecules in the presence of fluoride ion, followed by complexation of the resulting Bronsted conjugate base with a metal ion. This subsidiary method enables to detect fluoride anion in aqueous medium in the presence of a suitable transition metal ion (Scheme 7.1). The formation of in situ metal complexes is found to improve the reporting signals that can be studied using various spectroscopic and electrochemical techniques. This method was successfully validated for amine, amide, and thiourea-based receptor molecules in detecting aqueous fluoride upon introduction of Ni(II) or Cu(II) ion in the sensing medium. This hypothesis is comprehensively addressed across three chapters (chapter 2,3 and 4).



Scheme 7.1: Schematic representation for the deprotonation assisted metal complexation strategy (hypothesis 1) for sensing of fluoride ion in aqueous conditions.

Chapter-7: Conclusion

Chapter 2 demonstrated the recognition of fluoride in aqueous medium with benzothiazole-based probe molecules with secondary N-H and amide groups as F⁻ recognition units. The probe molecule **P** with amide binding site successfully recognized fluoride ions in DMSO-water medium with the limit of detection of 0.57 ppm in the presence of Ni(II) ions. The sensing is validated through colorimetric changes visible to the naked eye and electrochemical methods.

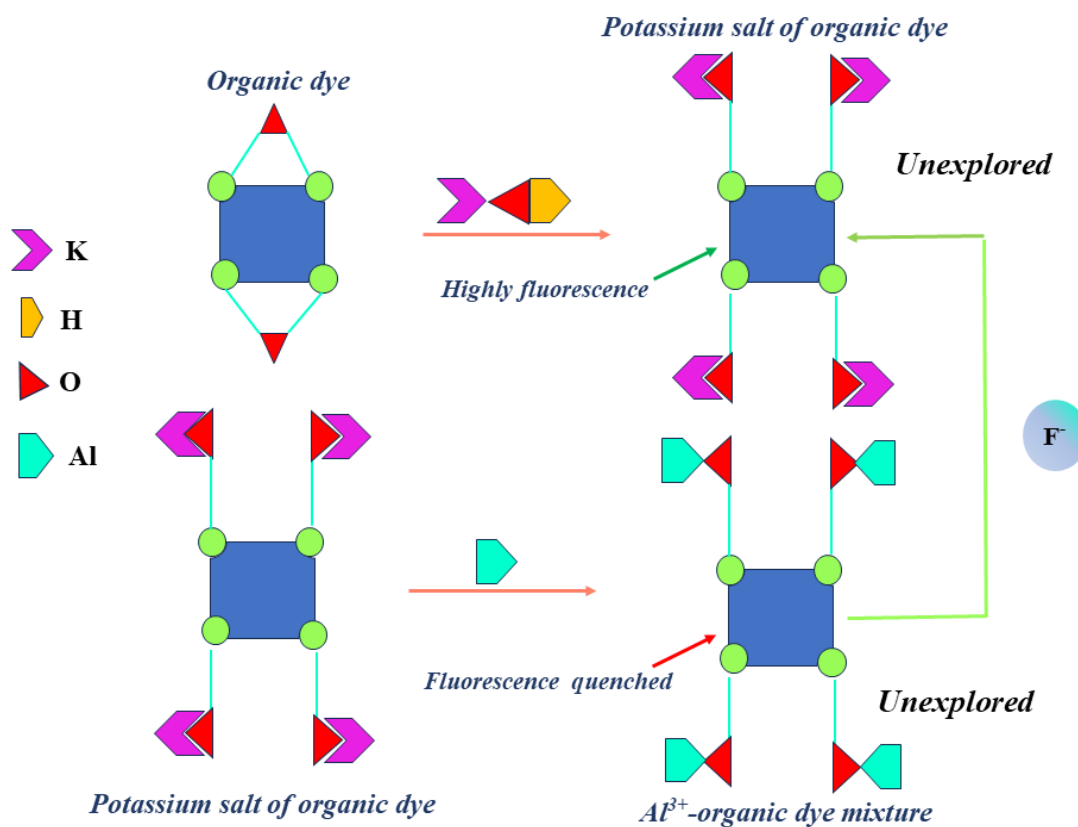
Chapter 3 explored the metal-mediated strategy with thiourea-based probes. The findings revealed that thiourea-based probe molecules could effectively sense fluoride ions in water when Ni(II) ions are present. Additionally, it was shown that increasing the acidity of the N-H group reduces selectivity, leading to interference from anions like acetate ion.

The chapter 4 focused on *bis*-thiourea-based tweezer probe molecules, which selectively sensed fluoride ions in an aqueous medium in the presence of Ni(II) ion. The sensing performance of the *bis*-thiourea was validated using UV-Vis spectroscopy and electrochemical methods, with LOD values of 0.2 ppm and 0.3 ppm for UV-Vis spectroscopy and DPV techniques, respectively.

The mechanistic investigation in all the above mentioned systems revealed the in-situ Ni(II) complexation of the deprotonated probe molecules, facilitating the deprotonation equilibrium in DMSO-water medium. In conclusion, the work presented in Chapters 2, 3, and 4 illustrates that the in situ Ni(II) complexation strategy is a highly effective method for sensing fluoride ions in water using organic probe molecules with acidic hydrogen prone to deprotonation. This approach allows for fluoride detection in water, which is otherwise limited to binding as tetra-butyl ammonium salt in organic mediums. Furthermore, the introduction of Ni(II) ions into the sensing strategy significantly enhances the probe's selectivity for fluoride ions over acetate ions. This is achieved through the facile formation of Ni(acetate)₂, which effectively removes acetate ions from the medium, ensuring more accurate fluoride detection.

In the second part of the thesis, the work on hypothesis 2 is focussed in the attempt to develop a low-cost fluoride chemosensor which performs in 100% water medium. Hypothesis 2 is primarily based on Pearson's hard and soft acid-base (HSAB) concept, where the hard base F⁻ ion is presumed to displace the hard acid Al³⁺ ion from a relatively labile Al³⁺-complex (Scheme 7.2). This hypothesis is explored in Chapters 5 and 6 where

we investigated the possible use of common dyes, such as fluorescein and 3,4,9,10-perylenetetracarboxylic acid, as chemosensor probe molecules for fluoride ions without any structural modification.



Scheme 7.2: Schematic representation for sensing of fluoride ion by F⁻ triggered dye displacement strategy of Al³⁺-dye complexes (hypothesis 2).

The methodology for sensing fluoride in 100% water using these dyes was successfully standardized and shown to be free from interference by common ions like Al³⁺, Cl⁻, Fe³⁺, SO₄²⁻, and PO₄³⁻. The mechanism of sensing was found to involve F⁻ triggered displacement of the organic dye from the Al³⁺-dye complex, resulting a distinctive dual (colorimetric and fluorometric) signal.

In Chapter 5, we examined the potassium salt of perylene tetracarboxylic acid, a highly water-soluble and stable compound that exhibits dual optical phenomena (colorimetric and fluorometric). Our findings confirmed that this compound aligns well with the hypothesis

2, demonstrating high selectivity in sensing fluoride ions in a pure water medium, with detection levels reaching up to 1 ppb.

Chapter 6 focused on fluorescein dye, which, when converted into its potassium salt form, showed significantly improved sensing efficiency for fluoride ions, with detection capabilities up to 2 ppb. This modification also reduced interference from cations such as Ca^{2+} and Fe^{3+} , providing a highly contrasting optical response.

Finally, the key findings of this thesis, highlighting the contributions to the development of fluoride sensors for water media are illustrated in figure 7.1

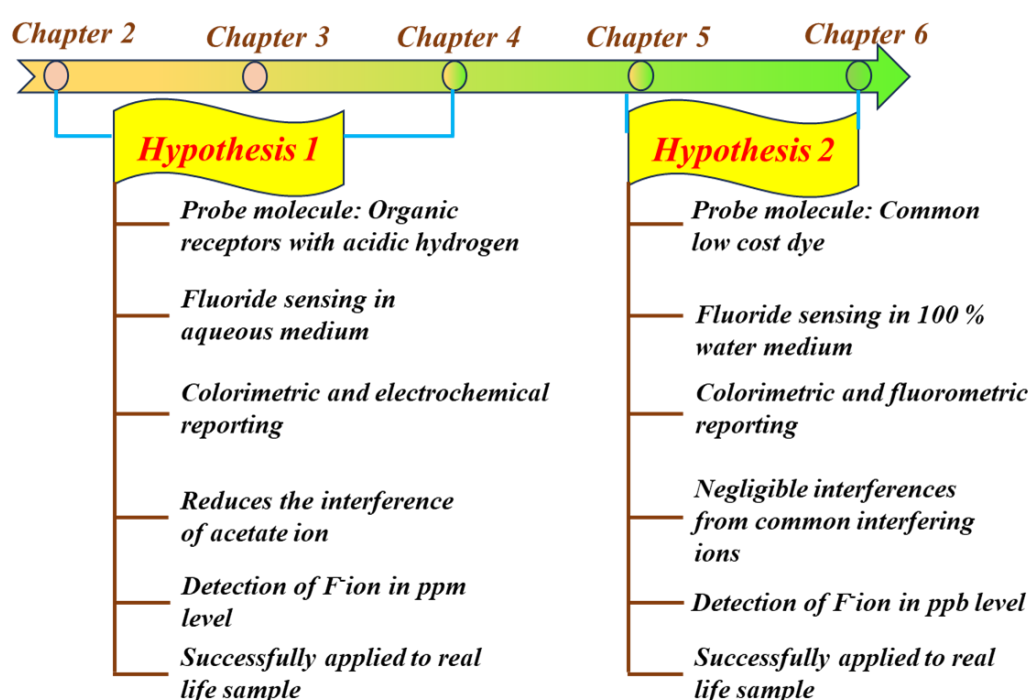


Figure 7.1: Schematic flowchart of the probe molecules towards F^- ion detection based on two hypotheses.

In conclusion, the work discussed in the thesis successfully provides new insight in the design of new chemical sensors towards sensing of fluoride ion drinking water. Moreover, the designed sensing strategy have been effectively applied to real-life samples, demonstrating their practical utility and reliability in environmental monitoring and public health contexts. This comprehensive approach highlights the accuracy and reliability of the methods discussed in practical applications, such as analysing water samples from regions

with known fluoride contamination for environmental monitoring and public health applications.

7.2: Future Prospects

The findings of this thesis open several promising avenues for advancing fluoride sensing technologies, particularly for routine monitoring in remote areas. These scope for future research in the fluoride sensor development are outlined below:

Expansion of Ni (II) Mediated Strategies: Further exploration of Ni(II) mediated approaches with additional probe molecules is needed to enhance sensitivity and precision in fluoride estimation.

Testing Additional Organic Dyes: Evaluating a broader range of common organic dyes could improve fluoride sensing efficiency and effectiveness.

Development of Colour Indicator Testing Kits: Creating a colour indicator testing kit could facilitate routine monitoring of fluoride levels in drinking water.

Mobile Phone-Based Detection Devices: Advancing mobile phone-based devices for on-site quantification of fluoride in drinking water could offer convenient and accessible solutions for real-time analysis.