

Chapter-1

INTRODUCTION

1.1. Introduction

The unprecedented growth of the global population has led to the augmentation of industries, resulting in various environmental issues. This industrial expansion has released numerous toxic ionic species, causing significant ecological disruptions. Groundwater quality has been compromised by both inorganic and organic pollutants, which arise from industrial activities and geological processes, impacting human health and marine ecosystems. (Figure 1.1) [1-7]. The detection and identification of biologically and environmentally crucial ions are still a major research focus in supramolecular chemistry research especially in the field of chemical sensors development [8-15]. Fluoride, in particular, stands out among the various anions studied for sensor design and development due to its unique chemical characteristics, such as its smallest ionic radius, high charge density, and hard Lewis basic nature [16,17]. Fluorine, a naturally occurring element present in soil, water, and various minerals like fluorapatite and cryolite, is found in the environment as fluoride compounds due to its high reactivity (figure 1.1). Industrial activities, food, water sources, and natural geological processes contribute to fluoride exposure, impacting the health of millions worldwide [18-20]. The main source of intake of fluoride to human health is through drinking water. Fluoride plays two-faced role in human health. Continuous overexposure to fluoride leads to diseases like teeth mottling, thyroid inflammation, dental and skeletal fluorosis, kidney and organ lesions osteosarcoma, neurotoxicity affecting child development, and increased risks of ADHD and gastrointestinal issues [21-25]. Controlling fluoride intake through drinking water is crucial to mitigate these impacts, driving significant research into sensitive fluoride detection methods in water. Conversely, when used within the limits recommended by the WHO, fluoride is known to improve dental health and prevent osteoporosis by stimulating osteoblast activity and inhibiting osteoclast activity. WHO recommends a maximum fluoride limit of 1.5 mg/L in drinking water, permitting fluoride additions to toothpaste, pharmaceuticals, and water in regions where fluoride levels are below this standard [26]. As mentioned above, fluoride contamination in soil and groundwater is primarily geogenic leading to widespread fluorosis in over 25 countries across Asia, Africa, Europe, and the America [27-29]. Thus, treating water before consumption is crucial in these regions for public health benefits, necessitating routine monitoring and quantification of fluoride levels. Effective water treatment decisions, including fluoride addition or installation of de-

fluoridation units, demand reliable and cost-effective fluoride detection and estimation methods for real-time monitoring and maintenance.

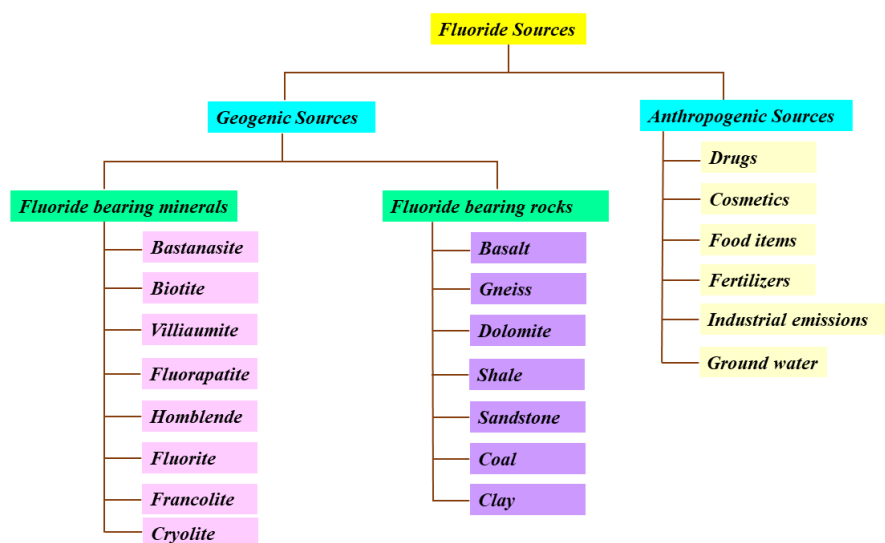


Figure 1.1: Natural and anthropogenic sources of fluoride in surface and groundwater systems [30-31].

Groundwater, typically a safe drinking water source for billions, can sometimes be contaminated to unacceptable levels, necessitating treatment before use. Fluoride contamination poses a significant environmental concern affecting large populations globally, particularly in countries like India, Bangladesh, China, Pakistan, Ghana, and Tanzania, where high fluoride concentrations lead to widespread health issues [32-34]. Effective fluoride removal is challenging because fluoride ions are smaller in size and highly hydrophilic, which hampers its efficient adsorption by traditional drinking water treatment materials. Inadequate infrastructure and technological expertise further complicate the issue. Despite these challenges, efforts in countries such as India [35] and China [36] are steadily improving the situation. As a result, fluoride removal technologies have attracted considerable interest, with various approaches including ion exchange, membrane processes, coagulation, adsorption, chemical precipitation, and bio-remediation being explored and implemented in both laboratory and field environments. [37-40]. Due to significant health impact of fluoride, a number of techniques were developed and marketed to get fluoride free drinking water (Figure 1.2). Despite the variety of available methods for treating fluoride contaminated water, each comes with significant drawbacks. Ion-exchange, for instance, is impeded by the high cost of resin, the complexities of

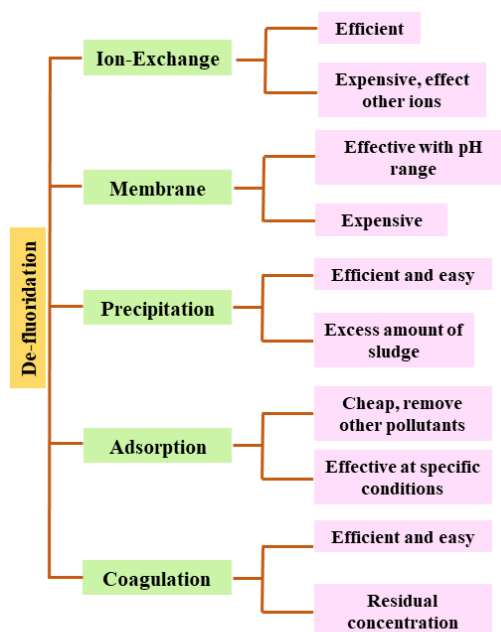


Figure 1.2: Methods for removing fluoride from drinking water and their pros and cons [41-42].

regeneration, waste disposal challenges, and inadequate selectivity, making it neither efficient nor cost-effective [43]. Similarly, membrane technology faces high acquisition and operational costs, along with the need for post-treatment of water due to concentrate disposal, making the process uneconomical [44]. Coagulation is a cost-effective de-fluoridation technique, but it needs large quantities of chemicals, which can create high residual levels of harmful sludge. Precipitation methods using calcium, aluminium, and iron salts are well-documented; however, lime-based processes struggle due to the lower solubility of calcium hydroxide, which hampers effective fluoride removal from water [42,43]. Among these, adsorption emerged as a promising technique as it is simple, cost-effective, enhanced selectivity, and the accessibility of adsorbents. However, the adsorbent loses efficiency over time and necessitates the development of novel adsorbent materials. Furthermore, the use of de-fluoridation treatment of drinking water is associated with the analytical techniques for the estimation of fluoride as to know when to start the de-fluoridation and to monitor the efficiency of the de-fluoridation method time to time.

1.2. Analytical techniques for fluoride detection

Due to fluoride's significant impact on teeth and bones, the sensitive and accurate analytical methods to measure fluoride concentration in water has become essential for maintaining public health. The growing use of fluoride-containing compounds in industries also further

highlights the necessity of fluoride sensing methods. Over the last few decades, various techniques have been emerged to estimate fluoride levels in drinking water such as chromatographic, electrochemical, spectroscopic, microfluidic analysis, optical sensors etc. [44]. Among chromatographic methods, Ion chromatography (IC), High Performance Liquid Chromatography (HPLC) and Gas Chromatography (GC) are widely explored in determining and estimating fluoride in water. Electrochemical techniques comprise potentiometry, ion-selective potentiometry, polarography, and voltammetry. Spectroscopic methods typically encompass UV-Visible spectroscopy, fluorescence spectroscopy, ^{19}F -NMR spectroscopy, and atomic absorption spectroscopy (AAS). Flow injection analysis (FIA) and sequential injection analysis (SIA) are the main techniques involved in microfluidic approaches [45]. Chemical sensors involve interacting with chemical substances to produce observable optical signals. Consequently, developing novel, cost-effective fluoride monitoring systems to assess drinking water quality remains a key research focus [44, 46].

1.2.1: Electrochemical methods

Various analytical techniques exist for determining fluoride in water samples. Electroanalytical methods like potentiometry [47-49], voltammetry [50], and polarography [51] are among the earliest techniques used to measure fluoride concentration in drinking water, tracing back to the introduction of fluoride ion-selective electrode by Frant and Ross in 1966 [52]. To enhance fluoride pre-concentration, several materials have been studied, such as zirconia, an inorganic ion exchanger known for its selective adsorption of fluoride from acidic solutions, and Zr(IV) complex in combination with hydrophilic resin that contains iminodiacetic acid [53]. Mao *et al.* developed dicalcium phosphate dihydrate and hydroxyapatite based solid-phase microextraction (SPME) coatings via electrodeposition on glassy carbon electrodes which displayed good adsorptivity of fluoride ion [50]. Ion-selective electrodes (ISEs) offer precise estimation of ionic substances with the help of ionophore acting as the recognition unit for specific ion detection. ISEs have several advantages, such as ease of handling, rapid, non-destructive measurements and lower costs relative to chromatographic and atomic absorption methods. However, ISE measurements are greatly affected by temperature changes, potential shifts, ion activity, and sample interferences like colour and other ions. Despite these limitations, ISEs are simpler and faster compared to spectrophotometric methods, which are more complex and time-consuming when dealing with interfering ions.

1.2.2. Chromatographic Methods

Numerous chromatographic methods have been documented for determining fluoride levels. Ion Chromatography is effective for detecting trace amounts of fluoride in water samples due to its stability, reproducibility, and simplicity. However, it faces challenges like weak retention of fluoride ions, and interference from magnesium ion, monocarboxylic acids etc. [54]. To address these issues, Jones *et al.* developed a method for IC utilizing chromatographically stable AlF_2^+ species in the presence of excess aluminium and reduces the magnesium interference by modifying the post-column reaction pH [55]. Bayon *et al.* created an IC method for indirectly determining trace fluoride levels in natural waters using aluminium monofluoride complexes by ICP-MS and online post column fluorimetry [56]. Despite its benefits, the high cost, time, and complexity of ICP-MS limit its use in developing countries.

High-performance liquid chromatography is also been utilized for determination of fluoride content in water. As a commonly used equipment in many laboratories, HPLC provides a convenient method for fluoride analysis and can address some of the challenges associated with ion chromatography (IC), such as overlapping fluoride peaks and void volume issues. Musijowski *et al.* proposed using reversed-phase HPLC with ultraviolet (UV) detection to analyse fluoride as a fluorosilane derivative for total organic fluorine analysis [57]. They employed triphenylhydroxysilane as the derivatizing agent followed by product extraction with n-heptane. Xu *et al.* recommended the use of the La^{3+} -alizarin-fluoride complexes for fluoride estimation in water in the reverse phase HPLC using photodiode array detector to achieve high sensitivity for analysing water in natural resources. Additionally, Gas Chromatography-Mass Spectroscopy has also been used for determination of fluoride in water [58]. Pagliano *et al.* demonstrated an ethyl derivatization method for fluoride to create fluoroethane gas using triethyloxonium tetrachloroferrate(III) [59] which was then analysed by GC-MS. This method avoided the use of organic solvents, and the derivatizing agent was both non-volatile and safe. These methods although give quantitatively accurate amount of fluoride but not useful for regular monitoring of fluoride in drinking water as they are time consuming, high cost and requires sophisticated laboratory space.

1.2.3. Spectroscopic Methods

Atomic absorption spectrometry (AAS) is extensively utilized for analysis of fluoride ion in inorganic and organic samples, owing to its excellent selectivity and sensitivity. It

involves monitoring the absorption of radiation by the atoms generated from the digestion of analyte species. Quantification in AAS entails measuring the overall absorbing atomic species at a specific wavelength, utilizing high-resolution spectroscopic techniques. However, AAS differs in its use of a line source radiation, such as a hollow cathode lamp, which produces atomic lines narrow enough to mitigate drawbacks related to the apparatus's finite band pass. In contrast, molecular absorption spectrometry (MAS) is employed for determining non-metals in flames and graphite furnaces, challenging to analyse using AAS due to difficulties in atomizing these elements and their absorbance in the UV range [60]. MAS offers superior detection limits compared to AAS. Despite numerous studies on non-metals using MAS, low-resolution MAS is inadequate for field analysis due to inadequate excitation wavelength, lower spectral resolution, and different interferences. Fluorine is particularly well-characterized using MAS, given its high electronegativity, high ionization potential, and absorption below 100 nm. ICP-MS is unsuitable for fluoride sensing due to argon's insufficient ionization potential for fluorine, except with electrothermal vaporization for dry sample introduction. Thus, MAS in flames and furnaces serves as an alternative for fluoride determination. Various studies have employed molecular absorption spectroscopy in graphite tube furnaces for quantifying fluorine using gallium, indium, and aluminium mono-fluoride. High-resolution continuum source MAS (HR-CS-MAS) has been utilized for fluoride sensing in flames, employing techniques like double monochromators and echelle gratings mitigate spectral interferences and to improve resolution [61-63]. Gleisner *et al.* further optimized fluoride detection methods using additives and modifiers but faced challenges in its application due to the procedure's complexity and high reagent consumption. Subsequent studies applied these methods to detect fluoride in toothpaste, demonstrating automation and faster analysis compared to modified headspace gas chromatographic methods [60]. In another method, Mores *et al.* streamlined fluoride detection in tea by employing MAS with high-resolution continuum source AAS with electrothermal vaporization, utilizing the CaF_2 absorption at 606.4 nm. This approach uses the calcium as the molecule-forming reagent and chemical modifier, eliminating the need for additional reagents and decreased the high blank values typically associated with GaF methods [64].

1.2.4. Microfluidic Methods

Flow Injection Analysis (FIA), introduced by Ruzicka and Hansen [65], involves injecting the analyte into a moving solution of carrier that transports the sample to the flow-through

detector. FIA is recognized for its simplicity, cost-effectiveness, precision, and versatility [66]. It has been combined with different detector systems, such as ISE [67], spectrophotometry [68-71], and ICP-OES [72] etc. to determine fluoride levels in water samples. Ruzicka and Marshall further developed Sequential Injection Analysis (SIA), a sample handling and manipulation process, to minimize the limitations of FIA [73]. It uses a multi-position selection valve, typically connected to a holding coil at its common port, and can be linked to various flow-through modules through its selection ports. After sample aspiration, the sample is stored in the coil for subsequent processing [74]. Alpizar *et al.* applied SIA for the instantaneous estimation of fluoride and chloride in water by using ISEs [75].

1.3. Chemical sensors

Although the abovementioned analytical techniques are commonly employed to determine fluoride in drinking water, they have notable drawbacks like high cost, requirement of highly skilled operators, and are unsuitable for on-site detection. Consequently, there has been significant research effort devoted in the development of chemical sensors for fluoride ion with an objective of low cost and on-site detection purpose. Chemical sensors are indispensable tools in various domains, offering the ability to detect and measure specific chemical substances with high sensitivity and selectivity. Advances in materials science, nanotechnology, and biochemistry continue to enhance the performance and versatility of these sensors, expanding their applications and improving their effectiveness in diverse fields. Chemical sensors are devices that detect and measure chemical substances, and convert this information into a readable signal. They are essential tools in various fields such as environmental monitoring, medical diagnostics, industrial processes, and food safety. Chemical sensors typically consist of a recognition element that interacts with the target analyte and a transducer that converts this interaction into a measurable signal.

1.3.1. Classification based on the signalling element

Based on the nature of signals, chemical sensors can be classified into electrochemical, optical, mass-sensitive, calorimetric, mechanical, and thermal sensors [76]. Among the chemical sensors, optical sensing methods like chromogenic (or colorimetric) and fluorogenic (or fluorometric) sensing methods are frequently employed for fluoride detection. Chromogenic sensing involves a sensor's signalling unit with chromophores, while fluorogenic sensing relies on fluorophores within the sensor's signalling unit.

1.3.1.1. Chromogenic/Colorimetric sensors

A chromogenic chemosensor is characterized by the colour change that happens when the receptor binds to a specific analyte [77]. After the binding of the receptor and analyte, the chemosensor's signalling unit shows a change in colour and a corresponding change in the UV-Vis absorption spectra (figure 1.3, 1.4) [78]. The chromogenic sensor relies on the direct proportionality between the absorbance of light and the analyte concentration for the estimation of analyte. Colorimetric chemosensors have attracted considerable attention because they enable both qualitative and quantitative data to be obtained visually, thereby removing the need for complex analytical techniques [79,80].

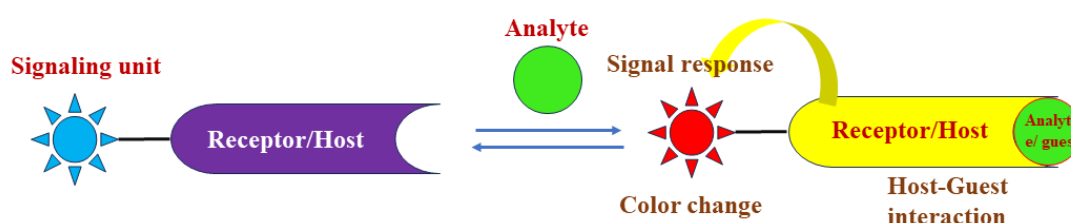


Figure 1.3: General sensing mechanism of colorimetric chemosensor.

1.3.1.2. Fluorogenic/Fluorometric sensors

A fluorescent sensor is a device that links a receptor (ionophore) with a fluorophore to translate a recognition event into a photophysical signal, such as changes in fluorescence spectra, fluorescence quantum yield, or fluorescence lifetime. Fluorogenic sensor allows detection at the picomolar scale of the analyte, whereas colorimetric sensors can only detect concentrations at micromolar levels. The primary advantage of fluorescent chemosensors is the direct proportionality between the emitted fluorescence and the analyte concentration. Fluorescent chemo sensors have become increasingly popular for detecting specific anions

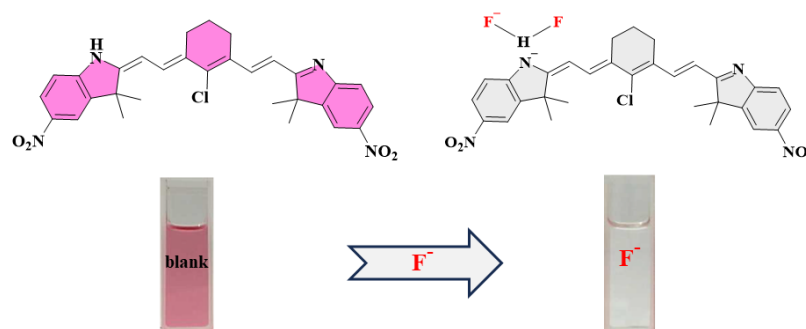


Figure 1.4: Colorimetric change upon interaction of fluoride with the probe molecule [81].

or cations due to their high sensitivity (capable of single molecule detection), high selectivity, rapid response time, high spatial and temporal resolution, low cost, and ease of instrumentation [82-85]. The fluorometric sensor generally responds to the binding of the analyte either by fluorescent turn off response where the analyte acts as a quencher or by fluorescence turn on response (Figure 1.5, 1.6). The On/Off switching behaviour of fluorescence of the probe molecules upon interaction with analyte is due to the triggering of the photophysical processes like Photo induced electron transfer (PCET), Fluorescence Resonance Energy Transfer (FRET) etc.

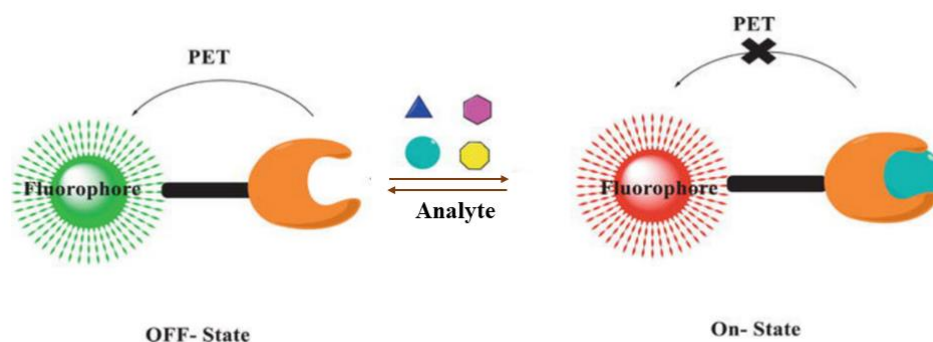


Figure 1.5: Diagram illustrating the operation of a fluorescent chemosensor during the sensing process.

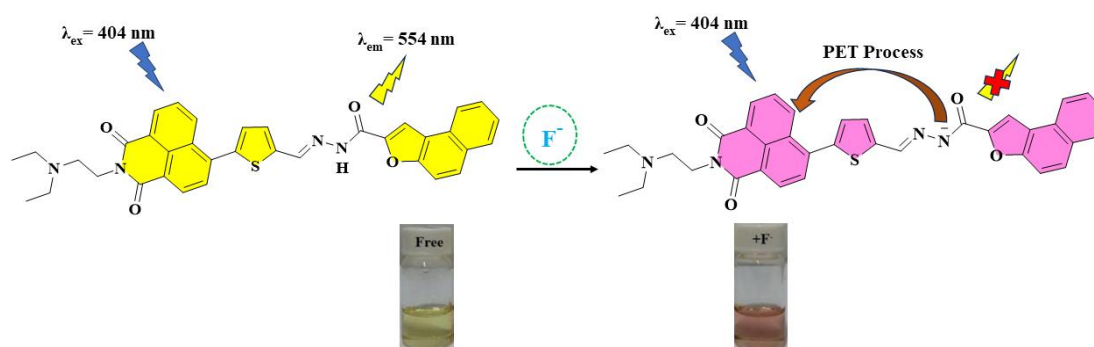


Figure 1.6: Fluorometric change upon interaction of fluoride with the probe molecule [86].

1.3.1.3. Electrochemical sensor

In electrochemical sensor, the sensor receptor contains the recognition unit which are mostly H-bond donor along with a redox active reporter group. The interaction of the probe molecules with the F^- ion led to the change in the redox behaviour of the probe molecule which is monitored by techniques like cyclic voltammetry, differential pulse voltammetry, chronoamperometry etc. (Figure 1.7, 1.8) [87].

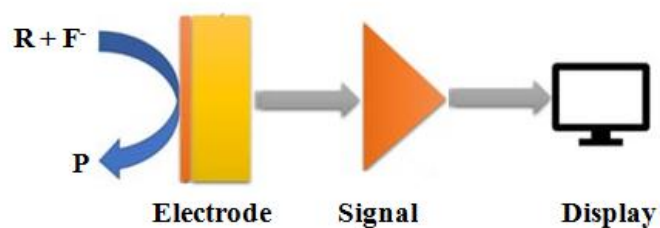


Figure 1.7: Diagram illustrating the process of electrochemical chemosensor.

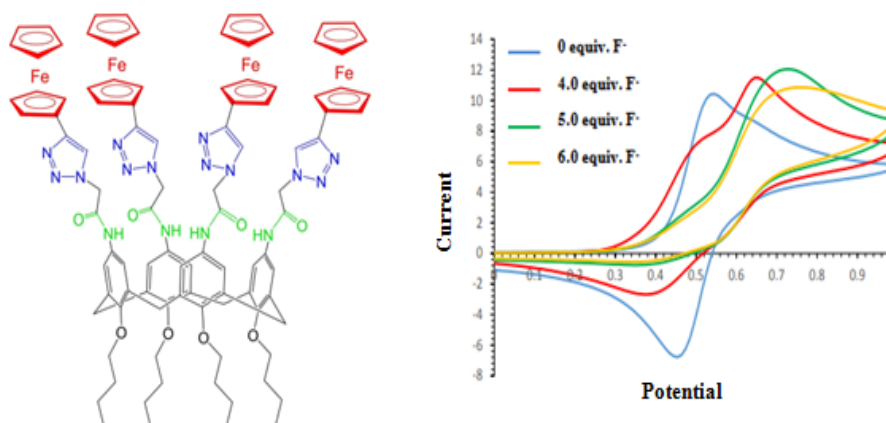


Figure 1.8: Tetra ferrocene-triazole-amide functionalized calix[4]arene, 5,11,17,23-tetra(ferrocenyl-1H-triazolo-acetamido)-25,26,27,28-tetrabutylloxycalix[4]arene as an effective electrochemical fluoride sensor in acetotrile-dichloromethane mixture[88].

1.3.2. Classification based on the recognition process

Based on the nature of interaction between the recognition unit and the fluoride ion, fluoride sensors can be categorised into two classes: chemosensors, where the interaction is reversible and chemodosimeters which provide irreversible responses due to a permanent chemical change [88, 89].

1.3.2.1. Chemosensor

Czarnick defines the term chemosensor as a "molecule of abiotic origin that indicates the presence of matter or energy." [91]. Essentially, chemosensors are molecular receptors capable of detecting and interacting specifically with an analyte, producing a response readable to a specific instrument. The structure of chemosensor involves a binding moiety responsible for recognition of the specific analyte and a signalling moiety to translate the interaction event to a detectable signal [92].

The detection mechanism of chemosensors for fluoride ions mostly involves non-covalent interactions like H-Bonding, F- π interactions, Lewis's acid-base interactions etc. [92-94] Fluoride ions are small, highly electronegative, and have high tendency to form strong hydrogen bonds with suitable hydrogen bond donors like -NH, -OH, or -CH groups. The sensor's receptor part typically contains functional groups that can effectively form hydrogen bonds with fluoride ions and the interaction leads to a change in the electronic properties of the sensor molecule, resulting in readable signal [95-96]. The common choices of H-bond donating motif in the design of receptors for anion recognition includes amide and amine derivatives, Urea and thiourea derivatives, hydroxyl groups etc. (Figure 1.9) [95]. Furthermore, heterocycles involving acidic hydrogens are also proved as an efficient H-bond donor motif for recognition of anions [98-100].

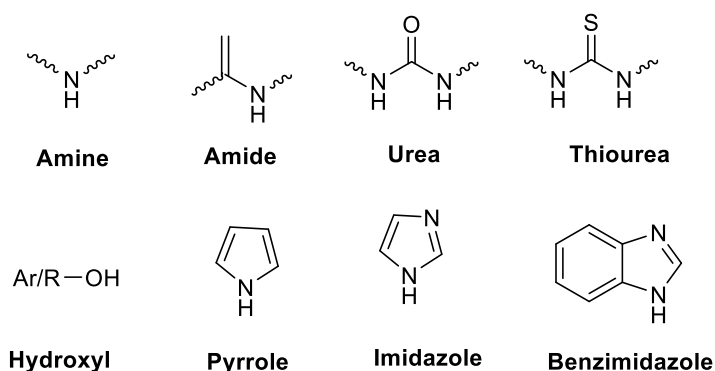


Figure 1.9: Structure of some H-bonding motif used in the design of chemosensors for fluoride ion.

In some of the H-bonding based chemosensors, the sensor receptor initially interacts through H-bonding accompanied by abstraction of the acidic proton. Ureas, with their -NH groups, provide a rigid strong H-bonding motif for anions which is prone to deprotonate in favourable conditions. Thiourea form weaker hydrogen bonds than urea but have higher N-H acidities, making them more prone to deprotonation by the fluoride ion [94]. Because of the comparatively larger basicity of fluoride in organic medium, the fluoride recognition through H-bonding interaction is more favourable in organic medium and in most of the cases the H-bonding interaction is accompanied by deprotonation of the sensor probe molecule. Over the past decade, a plethora of fluorescent or colorimetric receptors incorporating H-bond donating functionality like amine and urea have been reported for selective recognition of fluoride ion with an aim to develop a fluoride chemosensor (Figure 1.10, 1.11) [92].

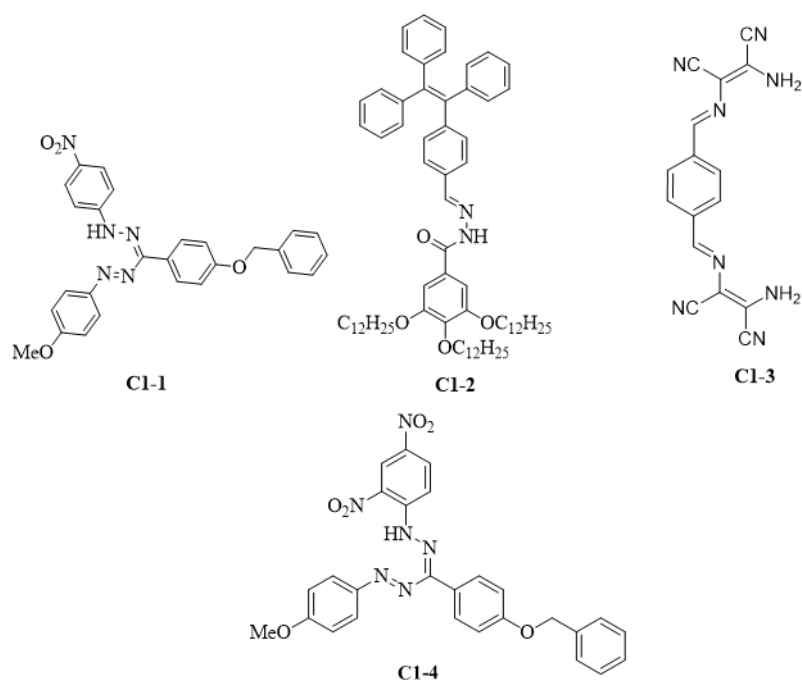


Figure 1.10: Some of the literature reported amine -NH recognition unit based probe molecule.

1.3.2.2. Chemodosimeter

Chemodosimeters are a subclass of chemosensors designed for the irreversible detection of specific analytes. Unlike chemosensors, which can often be used repeatedly, chemodosimeters undergo a chemical reaction with the target analyte, resulting in a permanent change that provides a measurable signal. Chae and Czarnik were the first to use the term "chemodosimeter" to describe an abiotic molecule designed for analyte recognition that also provides an irreversible, observable signal [99]. This chemodosimetric method relies on irreversible reactions triggered by the specific analyte resulting a cumulative response that is directly proportional to the analyte's concentration [100-101]. There are two strategies adopted by researchers in the development of chemodosimeters. In the first strategy, the analyte reacts directly with the chemodosimeter, leading to the formation of a new product. In the second strategy, the analyte acts as a catalyst for a chemical reaction, altering the chemodosimeter and changing its optical properties.

The field of chemodosimeter development for fluoride recognition has become a vibrant research area due to their high sensitivity and rapid response. The key reactions in designing

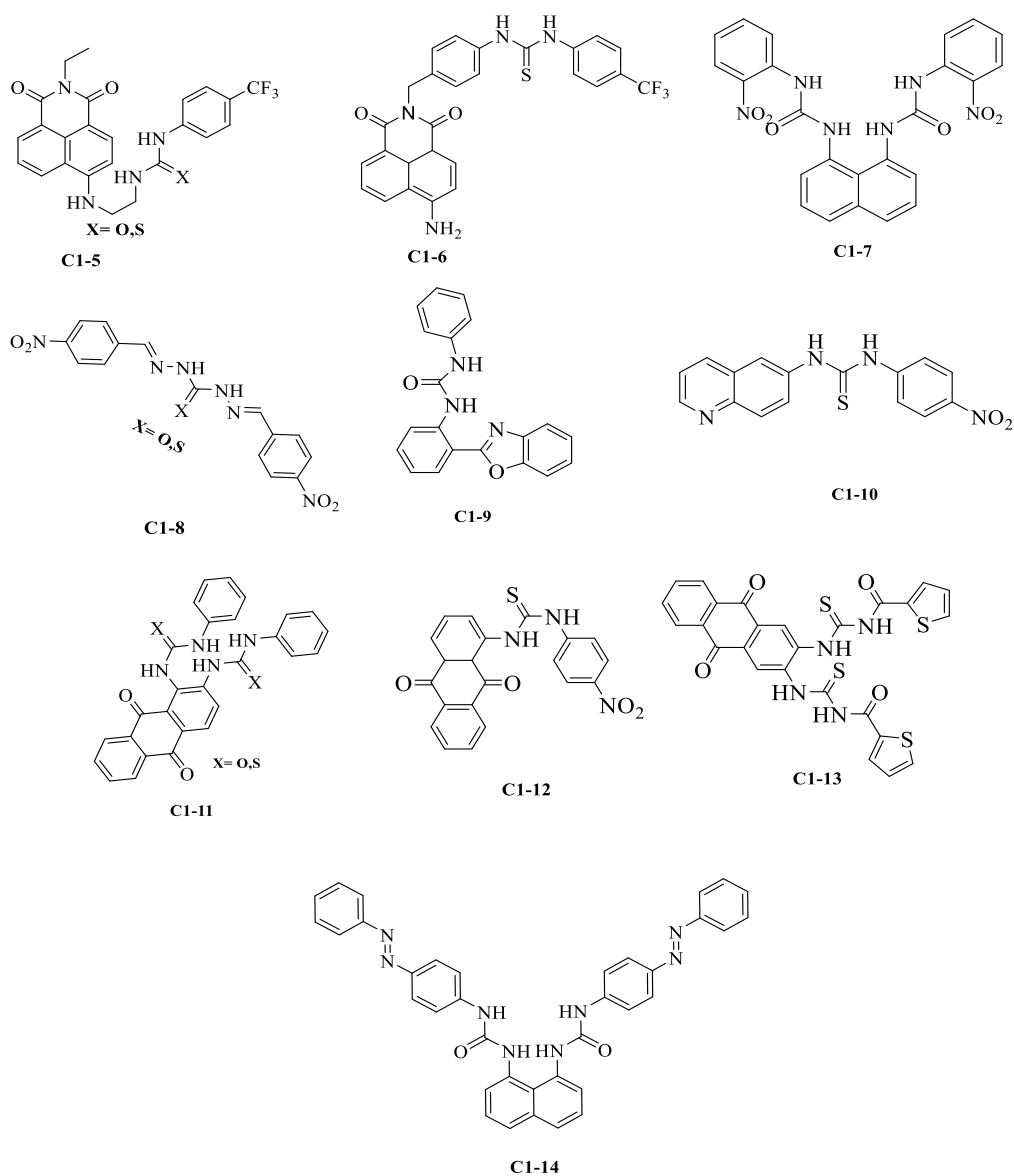


Figure 1.11: Some of the literature reported urea/thiourea based probe molecule as fluoride sensor.

fluoride-selective optical chemodosimeters involves utilizing the unique interactions between fluoride ions and Lewis's acids. Over time, three primary pathways have been popularized in the development of fluoride sensors such as (i) the Si–O and Si–C bond cleavage of the sensor probe molecule by fluoride; (ii) the interaction of boron and the fluoride (Lewis acid–base) ion; (iii) the interaction of fluorides with metal complexes. These sensors facilitate the qualitative or quantitative detection of fluoride ions mostly via optical methods.

1.3.2.2.1. Chemodosimeters based on F⁻ promoted cleavage of Si-O Bonds

These sensors exploit the strong affinity between fluoride ions and silicon, which leads to the cleavage of Si-O bonds within the sensor molecule. When fluoride ions are present, they attack the silicon centre, breaking the Si-O bond and triggering a detectable change depending on the reporter group present. This mechanism is highly sensitive and specific to fluoride ions owing to the strength of the Si-F bond that forms [89, 102-106]. This approach offers simplicity, high selectivity, and the ability to function without the need for complex instrumentation or conditions. Some of the recently reported fluoride chemodosimeters based on this strategy are shown in figure 1.12. Due to the low solubility of the probe molecules in water and the less reactivity of fluoride in water medium, the efficiency of this methodology is found to be decreased in water medium.

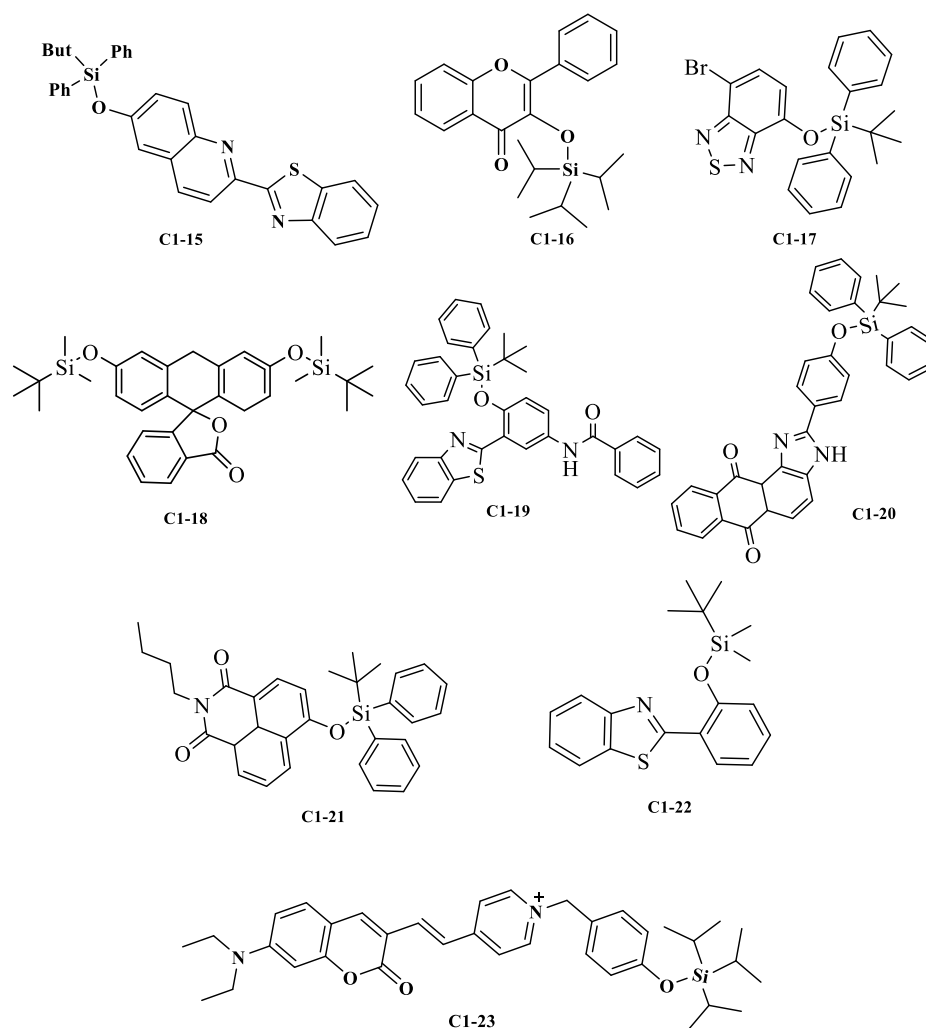


Figure 1.12: Chemodosimeters based on F⁻ ion promoted cleavage of Si-O bonds.

1.3.2.2.2. Chemodosimeters based on F⁻ promoted cleavage of Si-C Bonds

Anionic fluoride is known to selectively react with compounds that contain the $\text{-C}\equiv\text{C-}$ SiMe_3 group, resulting in the formation of terminal acetylenes. These terminal silyl acetylenes are linked to suitable chromophores or fluorophores to produce a detectable response when reacting with fluoride [89, 107-108]. The Si-C bond cleavage is more sensitive to F⁻ than Si-O, making it a promising approach for developing fluoride chemodosimeter. A large number of chemodosimeter probe molecules have been documented in the literature, showcasing excellent sensitivity and selectivity for fluoride (figure 1.13). However, most of this probe molecule has solubility issues in water which limits their application in water medium.

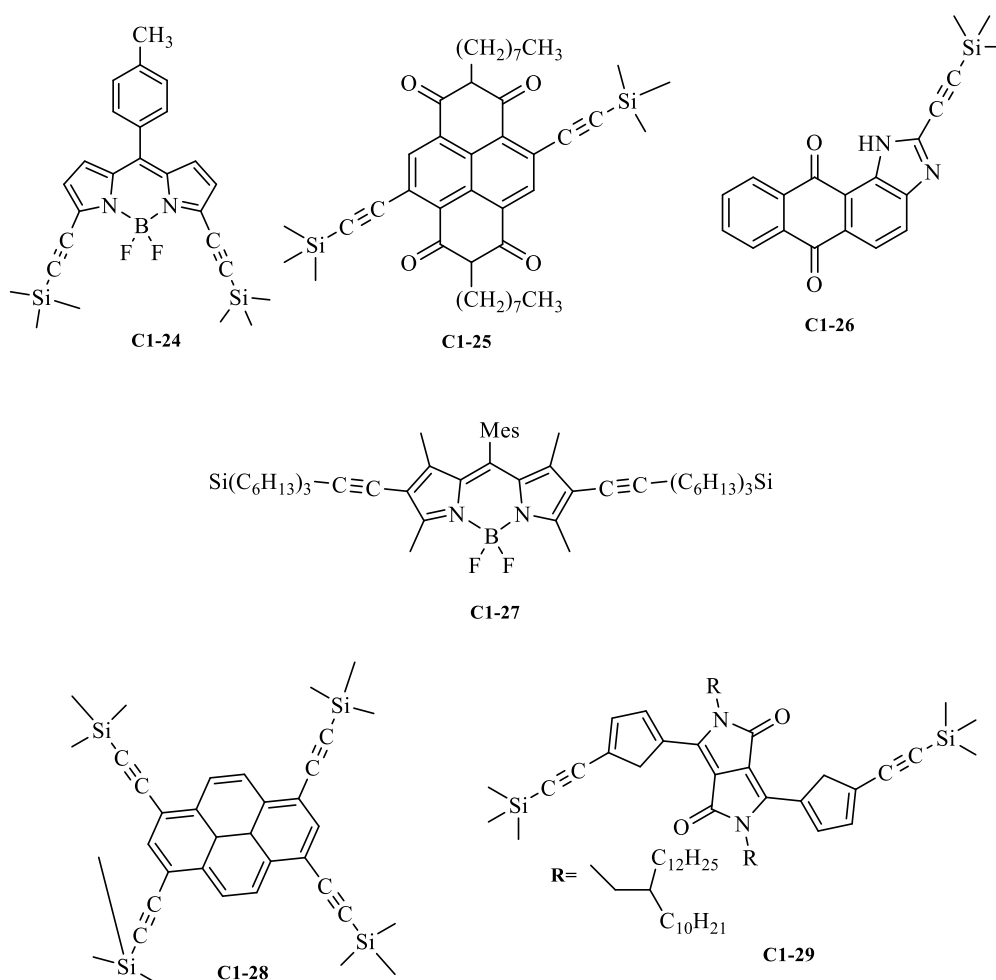


Figure 1.13: Chemodosimeters based on F⁻ ion promoted cleavage of silicon-Carbon bonds.

1.3.2.2.3. Chemodosimeters based on Boron-fluoride interaction

Fluoride readily binds with aryl boronic acids with high selectivity and sensitivity (Figure 1.14) [109]. This unique reactions between fluoride ions and boron moieties, along with the resultant changes in the spectroscopic properties of the receptor, is explored by various research groups to design sensors for detecting F^- ions.

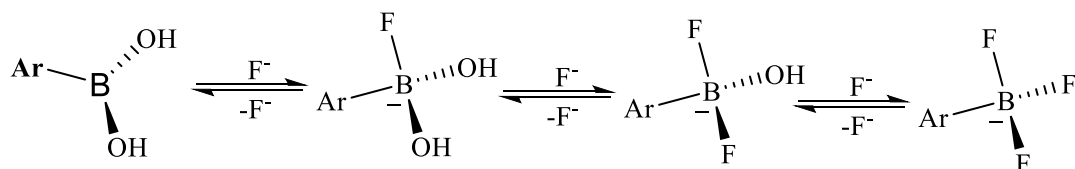


Figure 1.14: Interaction of fluoride with boronic acid moiety.

Building on this concept, a large number of boronic acid-based receptors functionalized with suitable chromophore and fluorophore are reported and studied their fluoride sensing ability (figure 1.15) [89, 110]. The high cost and complicated synthetic strategy limits their applicability of this method.

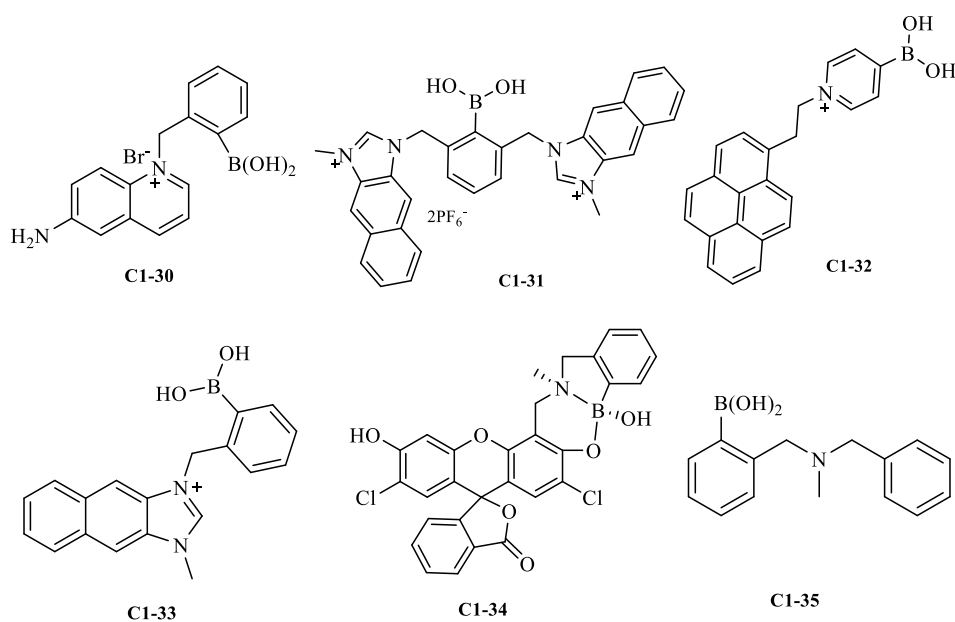


Figure 1.15: Chemodosimeters based on F^- ion and Boron interaction.

1.3.3. Chemosensors based interaction of fluorides with metal complexes

Generally, most of the probe molecules reported as fluoride sensor are organic and hence their solubility is low in aqueous medium. Due to their solubility issue, their fluoride sensing performance in aqueous medium is not upto the mark. To address this issue,

researcher has also attempted metal complexes as chemosensor and studied their fluoride sensing ability in water medium. Another method involving metal complexes uses the displacement approach, where fluoride ions replace the ligands or components of the metal complex, leading to notable changes in the sensor's optical response. Sensors utilizing displacement ensembles with metal complexes offer an advanced technique for fluoride detection, capitalizing on the distinctive properties of metal-ligand interactions to achieve high sensitivity and selectivity. Furthermore, the reactions are highly favourable in water, due to which these reactions are imperative in the development of fluoride sensor for water medium. A notable example of this strategy for detecting fluoride ions is the SPADNS-Zr method where SPADNS (2-para-sulphophenylazo)-1,8-dihydroxy-3,6-naphthalene-disulfonate) dye, sensitive to environmental changes, is mixed with a zirconium in water medium to form a stable complex with a distinct colour (figure 1.16). When fluoride ions are added, they displaced the SPADNS dye from the zirconium, resulting in a noticeable colour change. As fluoride ions bind to the zirconium, the concentration of the complex decreases in proportion to the fluoride concentration in the water. The resulting decrease in the colour intensity can be precisely correlated with the concentration of fluoride. Despite its satisfactory performance, this method is prone to interference from Al^{3+} , Cl^- , Fe^{3+} , SO_4^{2-} and PO_4^{3-} ions, necessitating the removal of these interfering ions prior to estimation [110]. Similarly, Elango *et al.* studied a quinone-imidazole fluoride binding receptor and its metal chelates (Cu(II), Co(II), Ni(II), and Zn(II)), and their anion affinity were investigated using UV-Vis, fluorescence, and ^1H NMR spectroscopy (figure 1.16). The receptor selectively detects fluoride ions in pure DMF, while its metal chelates shows recognition in 80% aqueous DMF. The fluoride recognition occurs through hydrogen bonding between the imidazole N-H and the fluoride with large binding constants (107 M^{-1}). Metal ion coordination further enhances the hydrogen bond donating ability of the N-H group toward fluoride ions [111].

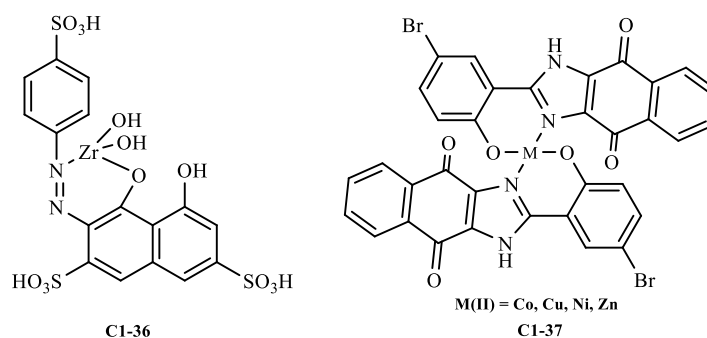


Figure 1.16: Metal complex-based fluoride sensing probes.

In the quest for better colorimetric chemosensors for fluoride ions, many probe molecules with acidic hydrogen have been reported as optical chemosensors for the selective detection of F^- , interacting via hydrogen bonding and subsequent Brønsted acid-base deprotonation reactions. However, the presence of water disfavours the deprotonation owing to fluoride's low basicity as well as low stability of the deprotonated probe molecules in aqueous environment which limits their applicability in real conditions. To achieve favourable deprotonation in aqueous medium, Das *et al.* introduced metal mediated strategy to stabilize the deprotonated species by forming a stable in-situ metal complex in aqueous medium which eventually facilitates the deprotonation equilibrium. Das *et al.* validated the methodology with dipyrrolylquinoxaline (**C1-38**), a well establish highly selective fluoride sensor in organic medium, and demonstrated its colorimetric fluoride sensing affinity in water medium when Cu(II) are present in the medium (figure 1.17) [112]. Later, Mahanta and coworkers demonstrated the metal mediated strategy with a thiourea-based compound **C1-39** with an anchoring hydroxyl group. The study revealed that receptor **C1-39** showed selective fluoride ion affinity in DMSO, but loses the affinity in water medium. They introduced a method that stabilizes deprotonated thiourea by coordinating with Ni^{2+} ion, which facilitates colorimetric sensing of fluoride in water. The study showed that in-situ Ni^{2+} complex offers greater stability of the deprotonated thiourea in water and makes the probe molecule effective for detecting fluoride in groundwater samples [113]. Although this strategy has shown promising potential in development of sensor for recognition of fluoride ion in aqueous media with the organic probe molecules having acidic hydrogen, a lot of work still need to be done to achieve chemosensor for real sample analysis.

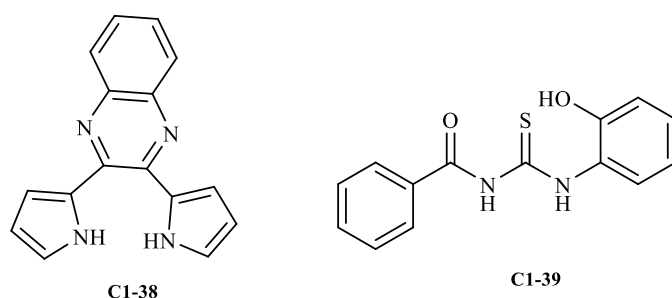


Figure 1.17: Probe molecules used in the demonstration of metal mediated strategy.

1.3.4: Importance of the development of Fluoride sensing methodology in the context of current status

The high cost, delicate instrumentation, time-consuming manipulations, and transportation limitations hinder the utility of most popular fluoride detection methodologies for routine monitoring in remote areas. Chemosensors, in this context, offer a promising strategy as their signal processing can be performed using low-cost portable devices. One such standard chemodosimetric colorimetric method for fluoride estimation in water, used in public health laboratories, is the SPADNS-Zirconium method. While effective, this method is prone to interference from ions like Al^{3+} , Cl^- , Fe^{3+} , SO_4^{2-} , and PO_4^{3-} , necessitating the removal of these interfering ions from samples before estimation [110]. Efforts to develop a better optical sensing method for fluoride ion sensing in water have led to the creation of numerous organic chemosensors, but a review of Web of Science data indicates that most studies were conducted in organic media (Figure 1.18)

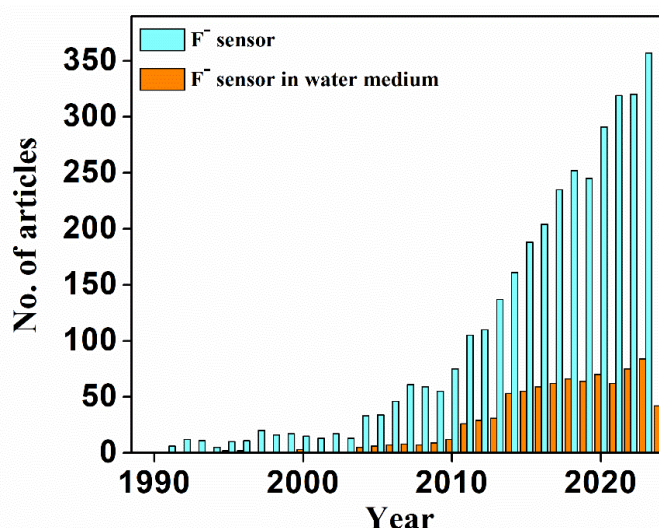


Figure 1.18: Comparison of the reported article on F^- sensing (over-all) vs F^- sensing in water medium (Source: Web of Science, Clarivate).

Many reported chemosensor receptors use H-bonding functionality with acidic hydrogen as the recognition unit, interacting with fluoride through H-bonding followed by Brönsted acid-base deprotonation at higher fluoride concentrations. These chemosensors generally show excellent selectivity and sensitivity towards organic fluoride ions (such as tetraalkyl fluoride salts) in organic media. However, the presence of even a small amount of water in the sensing medium drops their sensitivity significantly, making it challenging to detect

fluoride in aqueous media using those receptors. This inefficiency is primarily due to the fluoride's high hydration enthalpy and low basicity in water, which disrupt the deprotonation equilibrium, rendering the receptors ineffective in recognizing fluoride in water. These factors limit their application in aqueous environments.

Therefore, it is essential to develop a novel methodology for detecting fluoride ions in water using chemosensors previously reported as to be effective in organic media. This would simplify the process by avoiding the need to synthesize new chemosensor molecules, which often involves complex synthetic protocols. The main objective of this thesis is to create a method for sensing fluoride ions in aqueous media with organic probe molecules already proven as fluoride ion receptors in organic media. Additionally, the thesis also investigates the potential use of some common dyes as chemosensor probe molecules for fluoride ion detection in water.

1.4.: Objective of the thesis

The prime objective of this proposal was to develop a low-cost fluoride detection methodology which is easy to learn and applicable for onsite detection. It was envisaged that fluoride sensing methodology for aqueous medium which provide the information through a naked eye detectable optical change is a valuable strategy for this purpose.

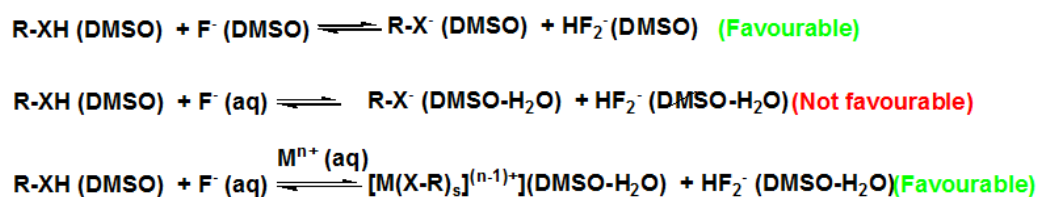
The objective of the thesis are

- Development of a strategy for sensing of fluoride ion in water medium. The objective will be achieved by two approaches
 - ❖ Development of a protocol for detection of fluoride ion in aqueous medium using some reported organic probe molecule that are known to bind fluoride ion in organic medium
 - ❖ Development of a protocol for sensing of fluoride ion in water medium by using some low-cost common dyes to achieve high contrast optical response
- Study the sensing process with analytical techniques such as UV-Visible spectroscopy, Fluorescence spectroscopy and Electrochemical methods like Cyclic Voltammetry, Differential Pulse voltammetry etc.
- Investigation of the mechanism and performance evaluation of the methodologies
- Validation of the methodology with real life samples collected from fluoride affected areas.

1.5.: Hypothesis adopted to meet the objectives

The thesis aimed to achieve the objectives by exploring two hypotheses mentioned below:

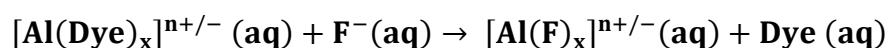
1.5.1: Hypothesis 1: This hypothesis focuses on developing a protocol for detecting fluoride ion in aqueous media using organic probe molecules known to bind fluoride ions in organic media. Typically, organic chemosensors with sufficiently acidic hydrogen detect fluoride ions in organic media through H-bonding followed by deprotonation. However, in the presence of water, the deprotonation equilibrium shifts towards the protonated probe molecule and hence decreases the sensitivity. It is hypothesized that stabilizing the deprotonated species of the organic probe molecule through in-situ metal complexation might favour the equilibrium towards deprotonation (Scheme 1.1), thus facilitating the recognition of fluoride ions in water. Incorporating a metal centre is expected to enhance the hydrophilicity, further reinforcing the sensing process in aqueous media. Additionally, potential charge transfer transitions between the metal and the probe molecule could make this methodology promising for colorimetric sensor development.



Scheme 1.1: The Brosted acid-base reaction of probe molecule at under different conditions

1.5.2: Hypothesis 2:

According to Pearson's hard and soft acids and bases (HSAB) theory, fluoride ions, with their high electronegativity and small ionic size, are classified as hard Lewis bases and are expected to have a strong attraction to Al(III) ions, which are hard Lewis acids. As a result, aluminium-containing materials have been thoroughly researched for their effectiveness in fluoride removal from water [114].



Scheme 1.2: Schematic representation of the proposed dye replacement reaction

In aqueous solutions, aluminium ions (Al^{3+}) react with fluoride ions (F^-) to form various aluminium-fluoride complexes, such as $[\text{AlF}_x]^{n+/-}$ (where x ranges from 1 to 6) and

Al(OH)F₂ [115-116]. This interaction endorsed that fluoride ions could displace Al³⁺ from a labile aluminium complex. Thus, it is hypothesized that the labile [Al(Dye)_x]ⁿ⁺ complex can be utilized as a chemosensor probe to detect fluoride-induced displacement reactions of the dye, thereby providing a means to monitor fluoride ion concentrations.

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