DIFFERENT TYPES OF CHEMOSENSORS USED TO DETECT FLUORIDE ION IN WATER MEDIUM

Abstract

Fluoride is one of the fascinating anions that is abundantly prevalent in the natural world, industry, and organisms. It has the smallest dimension, biggest density of charge, hard Lewis basic property, and most electronegative atom. The human body can easily absorb fluoride, but it is difficult to eliminate it. An excessive intake of fluoride can cause kidney problems, skeletal fluorosis, gastrointestinal issues, and tooth mottling. The The actionable and non-enforceable drinking water limits for fluoride anion were set by the Environmental Protection Agency (EPA, USA) at 4 mg L-1 and 2 mg L-1, respectively. Therefore, it is crucial to develop quick and accurate analytical methods for fluoride identification in real samples. In this study LOD value of different type of chemosensors are compaired, which are reported in different research paper.

Keywords: Chemosensor, fluoride ion, fluorosis, water medium.

Author

Chandana Pramanik
Assistant Professor
Department of Chemistry
Dinabandhu Andrews College
Garia, Kol, India.
chandanapramanik83@gmail.com.

I. INTRODUCTION

Anions play crucial roles in biological processes and chemical processes, hence it is crucial to design and produce molecular detectors that can do so with a certain level of selectivity [1]. Because fluoride ions have a long history of being connected to several biological, medicinal, and industrial processes, there is rising interest in developing colorimetric neutral chemosensors for them [2].

One of the fascinating anions that is abundantly prevalent in the environment as a whole, industry, and living things is fluoride. It has the smallest dimension, highest density of charge, hard Lewis basic property, and highest electronegative atom [3]. Because it helps to prevent dental decay [4], the fluoride ion has become significant among the many anions and also it used in osteoporosis treatment [5]. Thus, fluoride must be added to drinking water and toothpaste [6]. Fluoride also plays a significant part in several military applications, such as the nuclear industry's uranium separation process and the detection of nerve agents like sarin and soman [3,7].

Fluoride is quickly absorbed by the human body but difficult to eliminate [8]. An excessive consumption of fluoride can cause renal difficulties, skeletal fluorosis, gastrointestinal issues, and tooth mottling [9]. The ideal concentrations for drinking water are 1.0–1.5 mg/L (ppm) and 2–4 mg/L [11], according to the World Health Organisation (WHO) and Environmental Protection Agency (USEPA) respectively [1,10].

Over the course of the year, several F^- detection methods have been developed, including potentiometry [11], F NMR analysis[14,12], mass spectrometry[13], ion chromatography [14] electrochemical approaches [15], colorimetric process[16], and fluorescence-based sensing systems.

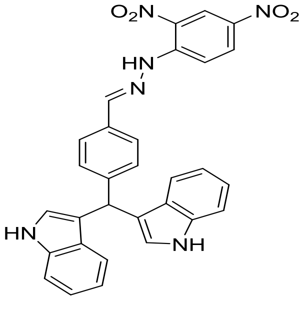
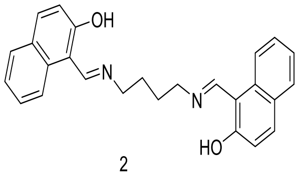
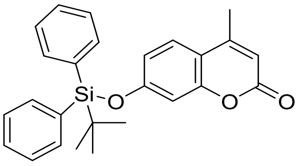
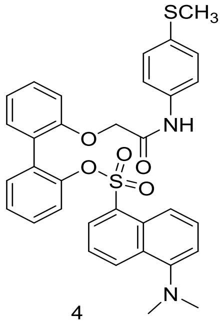
II. HARMFUL EFFECTS OF FLUORIDE ION IN HUMAN BEINGS

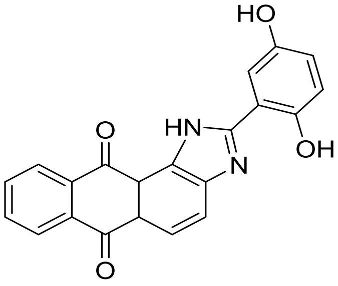
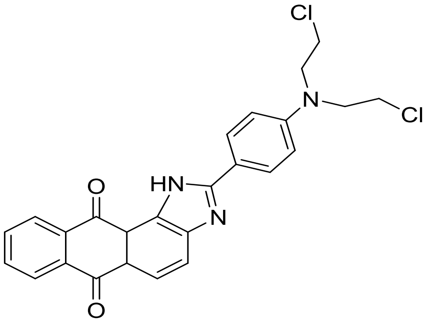
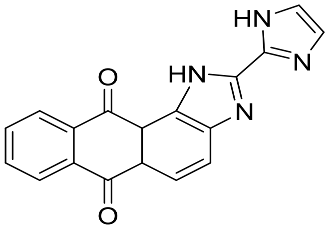
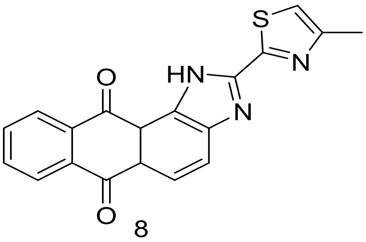
Fluoride ions are fundamentally created by fluorine atoms. Fluorine atoms are found in several minerals as fluorides, which include fluorspar, cryolite, and fluorapatite, and they constitute about 0.3 g/kg of the crust of the Earth because of their high degree of reactivity. [5, 20,22].

The WHO established the 1.5 mg/litre (or 1.5 ppm) acceptable limit of fluoride in water in 1994 and reiterated this policy in 1993. If the fluorides ions are present at concentrations of 1.5 ppm or below, they are not hazardous. Fluoride's deadly consequences are experienced by millions of individuals worldwide.

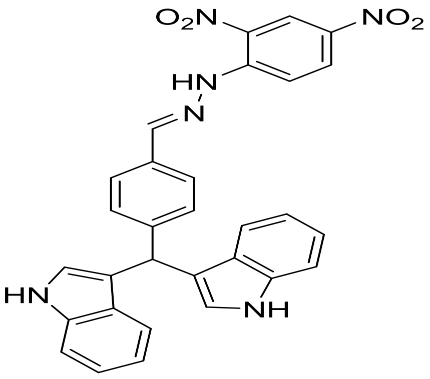
A high amount of fluoride ingestion throughout childhood reduces IQ, according to a systematic review of 27 epidemiological investigations. In contrast to high fluoride, which has been related to bone thinning and a rise in wrist cracks, water that is fluoridated has been connected with reduced rates of breaks in a community. Damage were shown to be linked to fluoride levels of 1-4 mg/L, according to data from the U. S. National Research Council, demonstrating a dose-response relationship. Skeletal fluorosis is a result of long-term overconsumption of fluoride. Skeletal fluorosis is prevalent in some regions, such as the Asian subcontinent. High hazardous amounts of serum fluoride cause nephrotoxicity other kidney damage. It frequently occurs as a consequence of the expulsion of fluoride from different drugs, like the fluorine-containing drug methoxyflurane. When we take the right dosage, no adverse consequences occur. Chronic use of more over 12 mg per day has negative consequences. Inorganic fluoride prevents the effects of antidiuretic hormone on the convoluted tubule in the distal part in the kidney by lowering the level of activity of the enzyme known as adenylate cyclase. Fluoride also stimulates internal vasodilation, which improves medullary blood flow and interferes with the kidney's countercurrent system, which is necessary for urine concentration. The failure to concentrate urine is what has caused the kidney damage [21].

Table 1: Different chemosensors for fluoride ion recognition and their LOD value

Probe	**Sensing response**	**Solvent system**	**LOD**	**Ref.**
 1	F^- turn on three peaks- at 266, 322, and 445nm	DMSO	2 µM	[17]
 2	F^-turn-on	DMSO	1.4×10-8 M	[18]
 3	F^- turn on	THF	0.2 mg/L	[19]
 4	F^-turn-on	(DMSO).	18 µM	[24]

 5	F^- and CN^- Turn on	Acetonitrile and DMSO mixture (40:1)	25 μM	[25]
 6	Weak sensitive towards F,CN-	-	-	[25]
 7	Weak sensitive towards F,CN-	Acetotonitrile and DMSO mixture (40:1)	-259mM	[25]
 8	F^- and CN^-	Acetonitrile and DMSO mixture (40:1)	25 μM	[25]

III. APPLICATION OF FLUORIDE ION SENSING PROBES (1-8)



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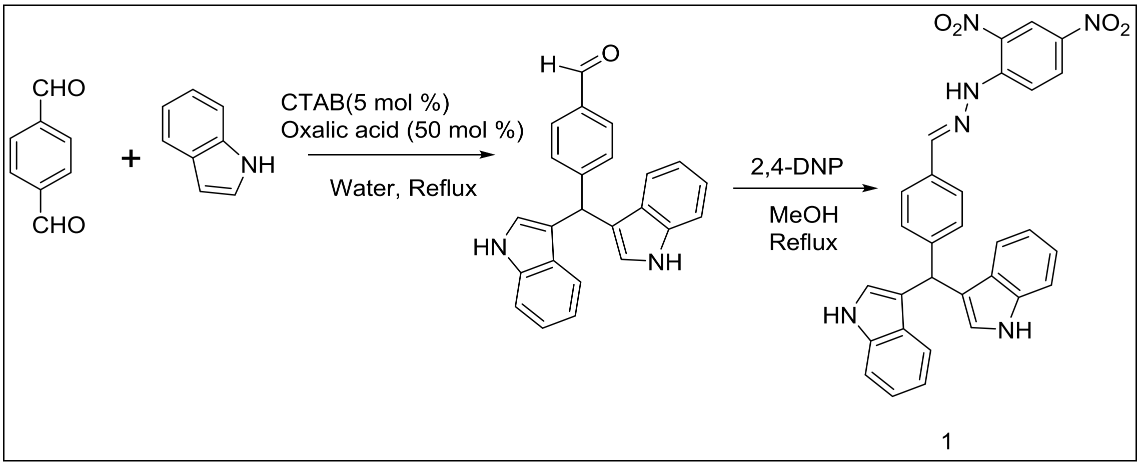
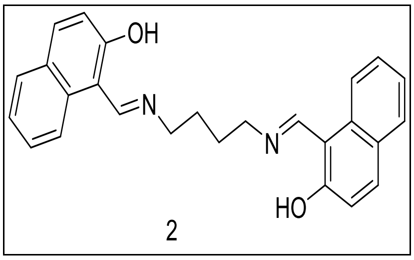
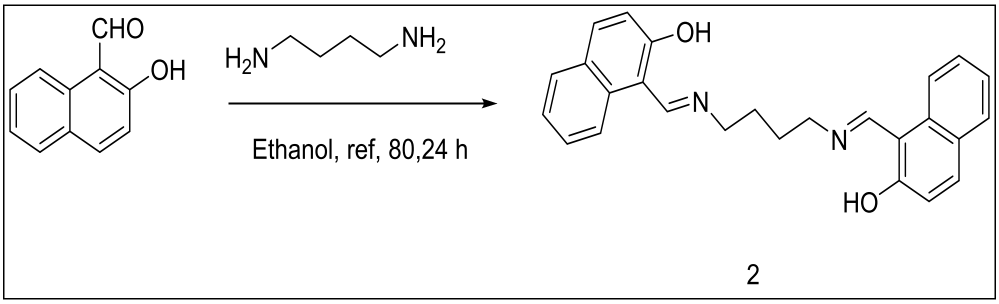


Scheme 1: Synthetic rout of compound 1 [17]

Using a pattern of color changes and changes in absorption signals, the 2,4-dintrophenylhydrazine (DNP) derivative of 4-(di(1H-indol-3-yl)methyl)benzaldehyde (hereinafter 2a) was designed, synthesized, and used as a selective optical chemosensor for fluoride by R Pegu et al. in 2012. According to evidence from 1 H NMR, UV-Vis, and density functional studies, fluoride-induced interaction subsequent to reducing the protons to its matching tri-anion is assumed to be the reason for the pronounced alterations to color and spectrum in the absorption characteristics of 1. Up to 2 M, the ion of fluoride content may be accurately detected and estimated using Probe 1 [17]. Compound 1 showed three peaks in DMSO at 266, 322, and 445 nm, with extinction coefficients (€, mol-1Lcm-1) of 5103, 2.64103, and 2.2102, respectively. To determine the binding stoichiometry, the Job's plot experiment was employed with a fixed fluoride amount of 1000 M and the first compound concentration. This revealed a 1:2 binding of compound 1 and fluoride. Compound 1 is created when 2,4-Dinitrophenyl)hydrazine (DNP) condenses, increasing the molecules ability to accept electrons

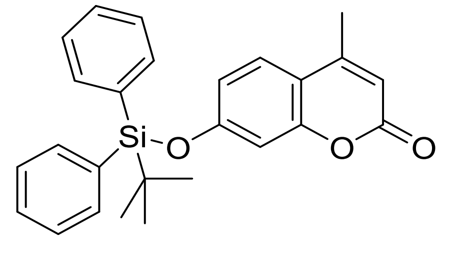




Scheme 2: Synthetic rout of compound 2 [18]

Testing strips constructed around sensor 2 were developed that could quickly identify F^- in an aqueous solution. Sensor 2 in DMSO demonstrated great sensitivity as well as excellent selectivity for the identification of ions of fluoride in aqueous solution. The identification limit was 2.66×10^{-4} ppm (1.4×10^{-8} M), which is substantially less than the 0.1×10^{-4} ppm WHO recommendation. The sensor can therefore be used to detect ions of fluoride in water. The sensor in DMSO is based on 2-hydroxy-1-naphthalene formaldehyde bis-Schiff base and is a colorimetric and turn-on fluorescence sensor for fluoride ions. It exhibits high sensitivity and strong selectivity for fluoride ions that come from aqueous medium.

The F- response mechanism is based on the bonding of hydrogen and deprotonation activities in the sensor, which led to color changes from light yellow to an intense yellow and observable fluorescence intensification. [18]. Sensor 2 in DMSO was not luminous in due to the lack of fluoride ions. A striking fluorescence was produced when 50 equivalents of fluoride ions were added to an aqueous solution.A maximum (30-fold) emission amplification was seen at 467 nm.



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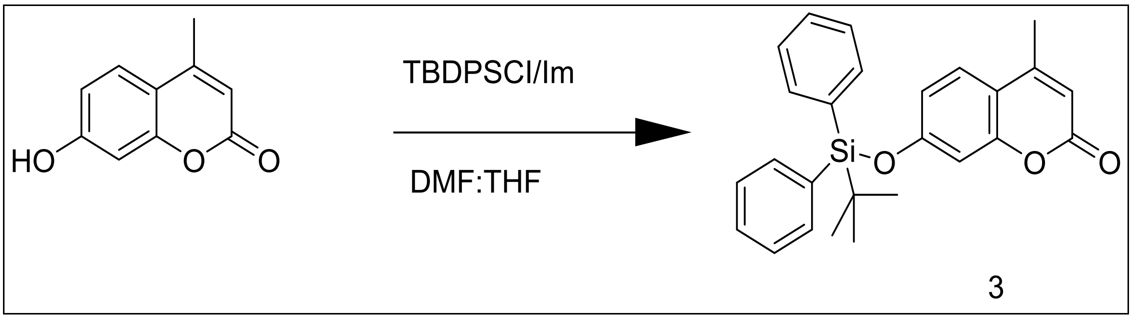
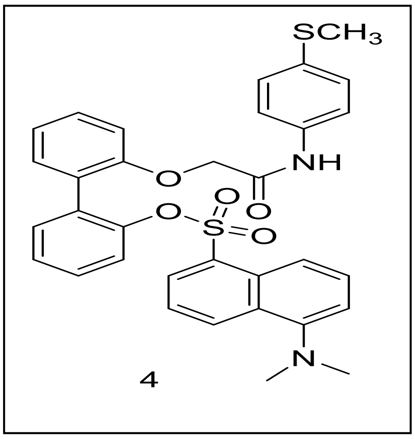
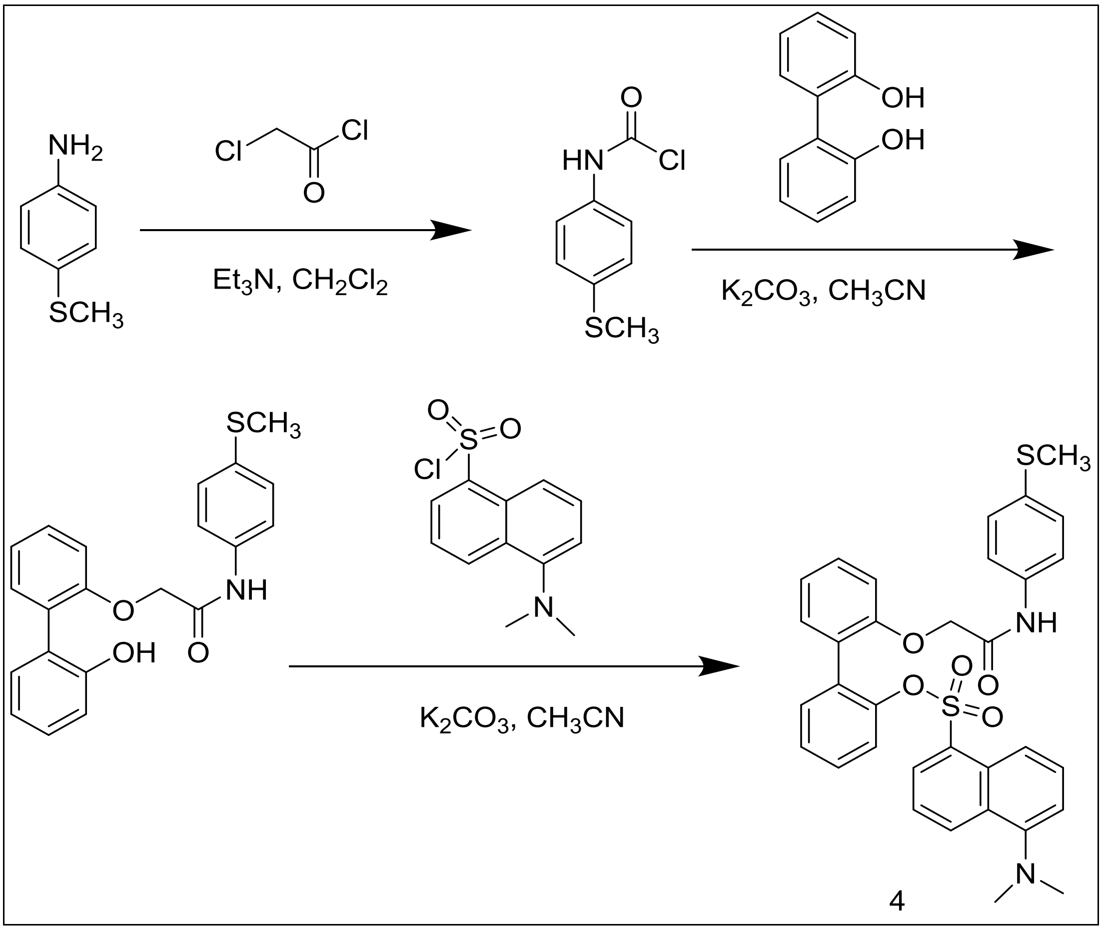


Scheme 3: Synthetic rout of compound 3 [19]

R . Chavali et al. created a novel, colourless chemical compound called 7-O-tertbutyldiphenylsilyl-4-methylcoumarin (TBDPSC), which, when it interacts with fluoride ions in water, produces fluorescent molecules that give the solution a blue glow. The blue fluorescence may be seen with inexpensive, portable UV lights. They assert that the TBDPSC has outstanding sensitivity as well as selectivity towards fluoride, allowing for the rapid and reliable detection of levels of fluoride as low as 0.2 mg/L. When compared to conventional methods, TBDPSC's fluoride analysis is rapid, simple, and requires no expert personnel. As a result, the current fluoride detection technology may be quickly deployed in the field and is especially helpful for monitoring water quality in areas with low resources. 450 nm and 360 nm, respectively, are the excitation and emission wavelengths for the fluorescence of TBDPSC [19].





Scheme 4: Synthetic rout of compound 4 [24]

In 2021, S. Mongkholkaew et al. reported 2′-(2-((4-(methylthio)phenyl)amino)-2-oxoethoxy)-[1,1′-biphenyl] a F^- ion sensor known as -2-yl 5(dimethyl amino)naphthalene-1-sulphonate (4). Four anthraimidazoledione compounds each of which contains 2,5-dihydroxybenzene, imidazole, 4-(bis(2-chloroethyl) amino) benzene, and 4-methylthiazole moieties (5-8) reported. By using UV-visible, 1 HNMR, and fluorescence studies, the selectivity of sensor 4 with several ions such as F^-, Cl^-, Br^-, CH_3COO^-, $C_6H_5COO^-$ and$H_2PO_4^-$ using DMSO as a solvent was assessed. When the F^- ion was added to the 1 H NMR experiment, a sensor 4's amide proton vanished as a result of the deprotonation process.

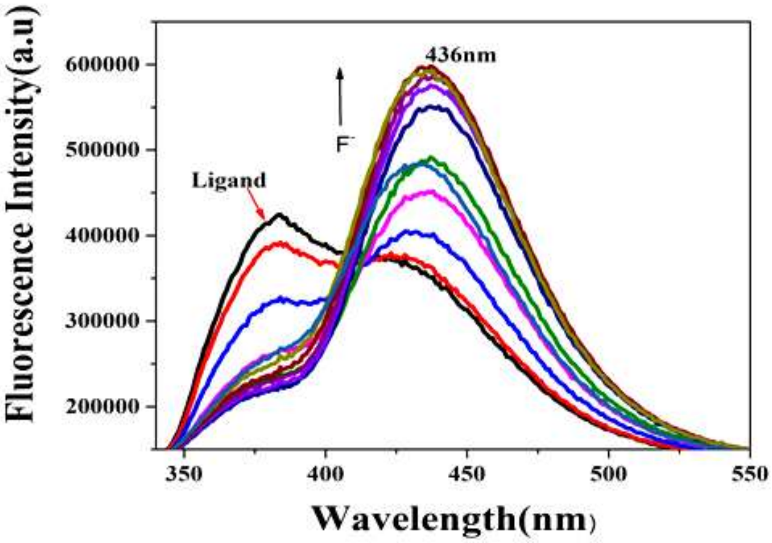
On the other hand, the proton signal of HF_2 started to show at 16.11 ppm. Whenever the F- ion was incorporated, Sensor 4 revealed a new absorption band at 300 nm, and the mixture turned colorless. If fluorescence response was titrated with F^-ion, sensor 4 displayed an increase in intensity of emission at 434 nm with a slight blue shift. These results suggest that the sensor 4 offers excellent selectivity and sensibility for F_-ion detection. Furthermore, it was demonstrated that a sensor 4 test strips covered on plates made of TLC and filter papers has the ability of a certain form of ion identification.

This incident once more provided evidence that a deprotonated form exists. Between detector 4 and F-ion, the limit of recognition and association constant were calculated to be 6.86 10^5 M^{-1} and 18 M, respectively. The detector 4-based experiment on the plate with TLC and filtering paper was also employed as a fundamental method for F-ion identification by the human sight [24]. A Sarkar et al. proposed an anthraimidazoledione -based detector for colorimetric ion of fluoride detection in an environment of Cu(II) ions in 2015[25].

Anthraquinone-based ions receptors have gained importance because of the colorimetric response that occurs upon detecting a certain anion and the possibility to modify this quality by altering the attached moiety that donates it to the diamine.. This study synthesized and characterized four anthraimidazoledione compounds having 2,5-dihydroxybenzene, 4-(bis(2- chloroethyl)amino)benzene, 4-methylthiazole moiety , imidazole and (5-8)..

In the presence of additional anions H_2PO_4, I, Cl, OAC, Br, ClO_4 and NO_3, both F and CN could be detected by the anthraimidazolediones coupled to p-hydroquinone and thioimidazole, respectively. However, 5 and 8 offered similar responses to both F and CN because they were unable to tell them apart.

The results demonstrate how a hetero atom change in the donor moiety of an anthraimidazoledione can cause a substantial variance in sensitivity. In Example 8, the specific identification of F-, which showed a distinct green color and an increase of around 50 nm, as compared to CN-, which showed orange coloring with a change of only 15 nm, was made possible by the use of 0.5 equivalents of Cu2+. At a receptor concentration of 25 M, the WHO-specified F-detection limit in a solution of Cu2+ was 0.038(5) ppm. The two different forms of imidazole molecules ring compound 7-, as previously mentioned, did not exhibit the anion identification at precisely the same target concentration of 5 and 8. The charge transferring band around 500 nm scarcely turns crimson upon adding 7 up to 6 similar ions. (F- equivalent of OH-). Due to the ineffectiveness of the bis(2-chloroethylamine) moiety's ability to remove electrons from the imidazole proton, which makes 6 inappropriate to be used as a probed anion sensor that exists, the F- or CN- adduct is more weak and brittle..



The importance of anthraquinone-based the anion receptors has increased due to the colorimetric sensitivity upon detection of a specific anion and the potential to modify this property by switching the connected moieties (known as the donor) to the diamine. Each of them was put to the test to see if it could function as an anion sensor in order to analyze the effects of variations in the hydrogen bond donor-acceptor.

Both ions CN^- and $^-$ F^- could be detected in case of there are additional anions present by the anthraimidazolediones attached to p-hydroquinone and thioimidazole, respectively. Cl, H_2PO_4, Br, OAc, I, NO_3, and ClO_4 are some examples. Neither 5 nor 8 could tell F^- from CN^- apart, and both gave similar answers. Studies of 5 and 8 with F^- using 1 H NMR revealed the production of $[HF_2]$ at 16.3 ppm, and both cases' 19F NMR results displayed a strong peak at -145 ppm. However, if the CT band remains almost intact, as was the case for 7, the F^- may not be identified colorimetrically even though there may be NMR evidence of $[HF_2]$ production [1]. The findings highlight the possibility of a significant variation in sensitivity when a hetero atom in an anthraimidazoledione's donor moiety is changed.

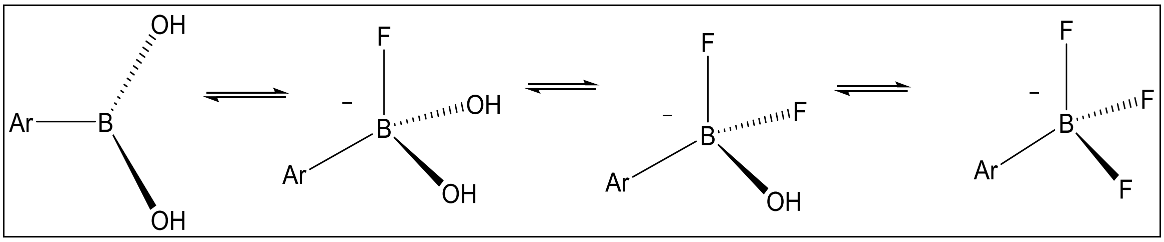
In case 8, selective recognition of F- was made possible in by the presence of 0.5 corresponding of Cu2+, displaying a unique green color with a shift of about 50 nm, in contrast to CN-, which exhibited orange coloring with a variation of just 15 nm. The F-detection limit in detecting the presence of Cu2+ was 0.038(5) ppm at a receptor concentration of 25 M, which is less than the WHO-specified norm. The findings emphasise that the deprotonation of the benzimidazole-NH in the presence of the anion renders the recognition owing to the shift of the CT band in the detection of F^- and CN^- employing anthraimidazolediones. We have observed that the donor arm's variation controls deprotonation, and consequently, the capacity for recognition. However, due to Cu2+'s capacity to coordinate with the receptor and its impact on the deprotonation of the benzimidazole -NH, selectivity for F^- increased in the presence of Cu^{2+} [1]. The selectivity for F^- in case of 8 and the detection limit of 0.038 ppm are promising. The findings show that even while HF_2 is formed in cases 1, 3, and 4, 3 is unable to recognise F^- at concentrations equivalent to those of 5 and 8.

In order to test the acidity of the benzimidazole -NH, UV-vis spectral investigations with OH were conducted. The findings show the compound benzimidazole -NH is the most acidic in both compounds 8 and 5, and significantly less acidic in the compounds 6 and 7. It should be emphasised that while the creation of HF_2 may be a useful indicator of the process, it does not necessarily provide insight into the sensitivity of recognition. Sulfur on the heterocyclic ring has a beneficial impact on the anion identification characteristic at lower concentrations. In fact, when we contrast the activity of 8 with the other members of the series, we can also observe that the heterocycle's S helps distinguish F^- from CN^- when Cu^{2+} is present [1].

IV. NANO PARTICLE BASE FLUORIDE SENSOR

In 2015, H. Wu et al. created a colorimetric sensor for the quick and accurate detection of fluoride anion using gold nanoparticles modified with 4-mercaptophenylboronic acid [9].

A basic one-pot technique was applied to create the gold nanoparticles modified with 4-mercaptophenylboronic, and the interaction between the fluoride anion and 4-mercaptophenylboronic on the surface of the gold nanoparticles caused them to aggregate. In order to monitor fluoride anion, a highly sensitive and specific colorimetric sensor based on aggregation-induced color shift of gold nanoparticles was created. High fluoride anion selectivity and sensitivity are displayed by the sensor. Fluoride has a linear range of 10.0-30.0 M and a detection limit of 3.45 10-7 M, both of which are determined using the IUPAC criterion (3' rule). The sensor has also been used to detect fluoride anion in samples of tap water, ground water, and human blood, with recovery ranging from 94.0% to 103.3%, 94.7% to 101.0%, and 89.8 to 100.9%, respectively [1,2,3]. The outstanding fluoride anion detection performance of the colorimetric sensor revealed the device's potential use in fluoride anion detection in challenging environmental and biological materials [26].



Scheme 5: Fluoride detection utilizing AuNPs modified with 4-mercaptophenylboronic acid is shown schematically [26].

V. CONCLUSION

The sensors in DMSO demonstrated high sensitivity along with excellent selectivity for the detection of ions of fluoride in aqueous solution. These sensors allow for the detection of ions of fluoride in water that is consumed. Different group of compounds such imidazole base compound, coumarine base probe, goldnanano particle containing acidic proton show sensitivity towards fluoride ion in water medium. In this review discussed about limit of detection and binding mode towards fluoride and how colour change in nacked eye when probe form aggregate with fluoride ion.

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