Chemosensors Used to Detect Fluoride ion in Water Medium

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ABSTRACT:

With the smallest dimension, largest charge density, hard Lewis basic character, and most electronegative atom, fluoride is one of the intriguing anions that is widely present in the natural environment, industry, and creatures. 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 Environmental Protection Agency (EPA, USA) set the enforceable and non-enforceable drinking water standards for fluoride anion at 4 mg L^{-1} and 2 mg L^{-1}, respectively. As a consequence, developing rapid and sensitive analytical approaches for fluoride detection in real sample are of great importance. In this study LOD value of different type of chemosensors are compaired, which are reported in different research paper.

Key words; chemosensor, fluoride, Environmental Protection Agency, fluorosis, water medium.

INTRODUCTION:

Anions play important roles in biological systems and chemical reactions, hence the design and production of molecular sensors that can detect the anions with particular selectivity are necessarily always of great importance [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].

With the smallest dimension, largest charge density, hard Lewis basic character, and most electronegative atom, fluoride is one of the intriguing anions that is widely present in the natural environment, industry, and creatures [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 [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, according to the World Health Organisation (WHO) and Environmental Protection Agency (USEPA) respectively [10].

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

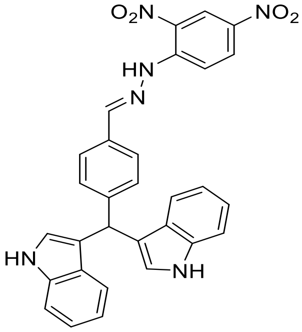
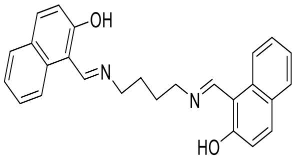
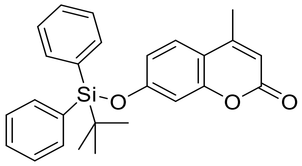
Harmful effects of fluoride ion in human beings.

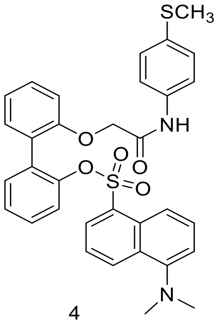
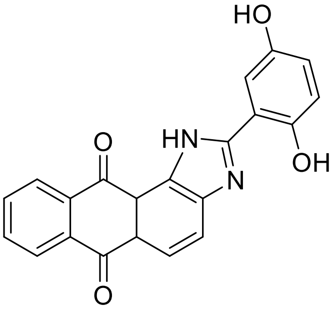
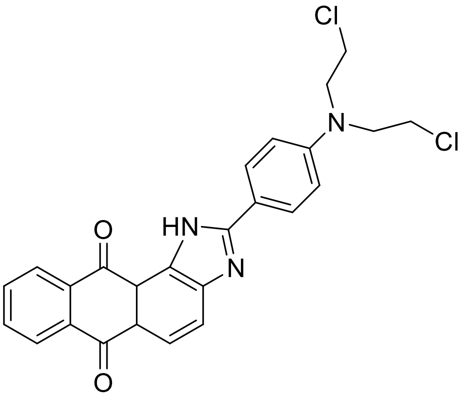
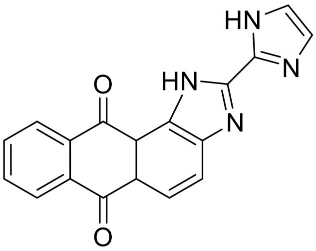
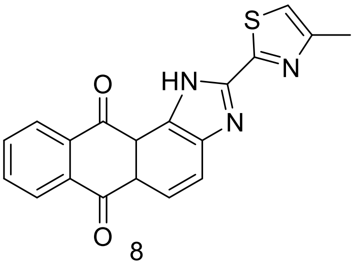
Fundamentally, fluorine atoms produce fluoride ions. Due to their strong reactivity, fluorine atoms are found in numerous minerals as fluorides, such as cryolite, fluorspar, and fluorapatite, and they make up around 0.3 g/kg of the Earth's crust [20,22].

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.

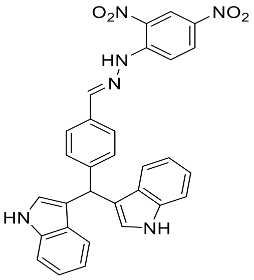
In a meta-analysis of 27 epidemiological studies, it was discovered that excessive fluoride intake during childhood lowers IQ. Fluoridated water has been linked to lower rates of fractures in a community, while excessive fluoride has been linked to weakening of bones and an increase in wrist fractures.The U.S. National Research Council came to the conclusion that fractures were associated with fluoride levels of 1-4 mg/L, indicating a dose-response connection.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 and other kidney damage. It frequently happens as a result of the release of fluoride from various medications, such as methoxyflurane, which contains fluorine. If we take the right dosage, no adverse consequences occur. Chronic use of more over 12 mg per day has negative consequences. The impact of antidiuretic hormone on the distal convoluted tubule of the kidney is inhibited by inorganic fluoride because it reduces the activity of the enzyme 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:- Different chemosensor 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-	acetonitrile and DMSO mixture (40:1	-259mM	[25]
 8	F^- and CN^-	acetonitrile and DMSO mixture (40:1	25 µM	[25]

Application of fluoride ion sensing probes (1-8)



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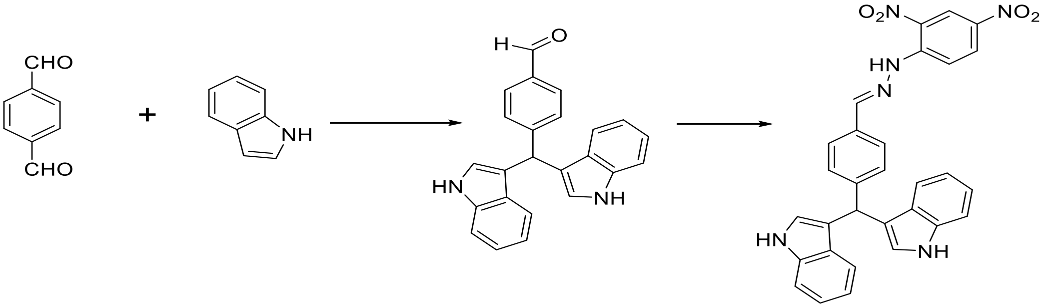
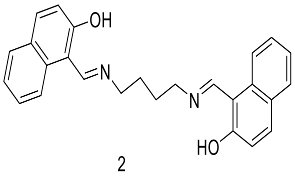
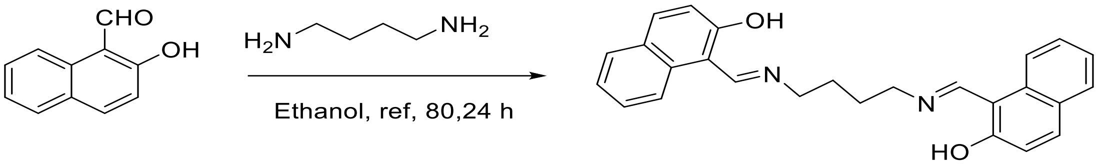


Scheme-1 Synthetic rout of compound 1 [17]

The 2,4-dintrophenylhydrazine (DNP) derivative of 4-(di(1H-indol-3-yl)methyl)benzaldehyde (hereinafter 2a) was designed, synthesized by R Pegu et al. in 2012, and used as a selective optical chemosensor for fluoride through naked eye detection via pattern of colour changes as well as change in absorption signals. Fluoride-induced contact followed by deprotonation to its matching tri-anion is thought to be the cause of the dramatic colour and spectrum changes in the absorption characteristics of 1, according to data from 1 H NMR, UV-Vis, and density functional investigations. Probe 1 can correctly detect and estimate the fluoride ion concentration up to 2 µM [17]. In DMSO, compound 1 had three peaks with extinction coefficients (€, mol^{-1}Lcm^{-1}) of 5×10^{3}, 2.64×10^{3}, and 2.2×10^{2}, at 266, 322, and 445 nm respectively. The Job's plot experiment with a fixed fluoride concentration of 1000 M and compound 1 concentration was used to estimate the binding stoichiometry, which reveals a 1:2 binding between 1 and fluoride. 2,4-Dinitrophenyl)hydrazine (DNP) condenses to form compound 1, which increases the molecule's capacity to receive electrons.



2

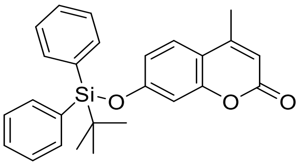


Scheme-2 Synthetic rout of compound 2 [18]

The sensor 2 in DMSO displayed high sensitivity and good selectivity for the detection of fluoride ions in aqueous solution, and test strips based on 2 were created, which could easily detect F^- in aqueous solution. The detection limit was 1.4 $\times 10^{-8}$ M (2.66$\times$ 10^{-4} ppm), which is much lower than the WHO guideline of 0.1$\times$ 10^{-4} ppm. Consequently, the sensor may be utilised to find fluoride ions in water.

The sensor in DMSO demonstrates great sensitivity and strong selectivity for fluoride ions from aqueous medium and is a colorimetric and turn-on fluorescence sensor for fluoride ions based on 2-hydroxy -1-naphthalene formaldehyde bis-Schiff base.

The hydrogen bonding and deprotonation processes in the sensor, which caused colour shifts from light yellow to deep yellow and noticeable fluorescence intensification, are the basis for the F^- response mechanism. [18]. In the absence of fluoride ions, sensor 2 in DMSO was non-fluorescent. 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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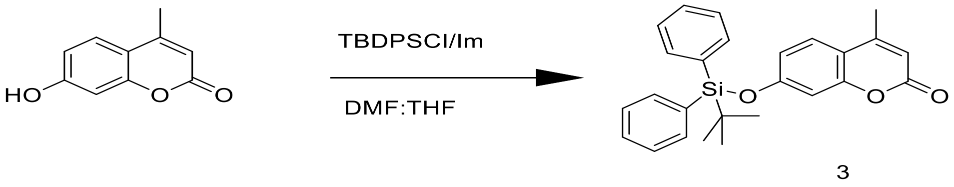
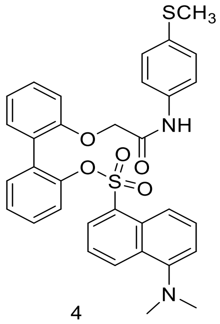


Scheme-3 Synthetic rout of compound 3 [19]

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 suggest that fluoride concentrations as low as 0.2 mg/L can be accurately detected within a few seconds because TBDPSC possesses exceptional sensitivity and selectivity towards fluoride. Compared to traditional approaches, fluoride testing with TBDPSC is quick and easy and doesn't require skilled staff. 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].



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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, 4-(bis(2-chloroethyl)amino)benzene, imidazole, and 4-methylthiazole moieties (5-8) reported. By using 1 H NMR, UV-visible, and fluorescence studies, the selectivity of sensor 4 with several anions (F, Cl, Br, CH3COO, C6H5COO, and H2PO4) in DMSO 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.

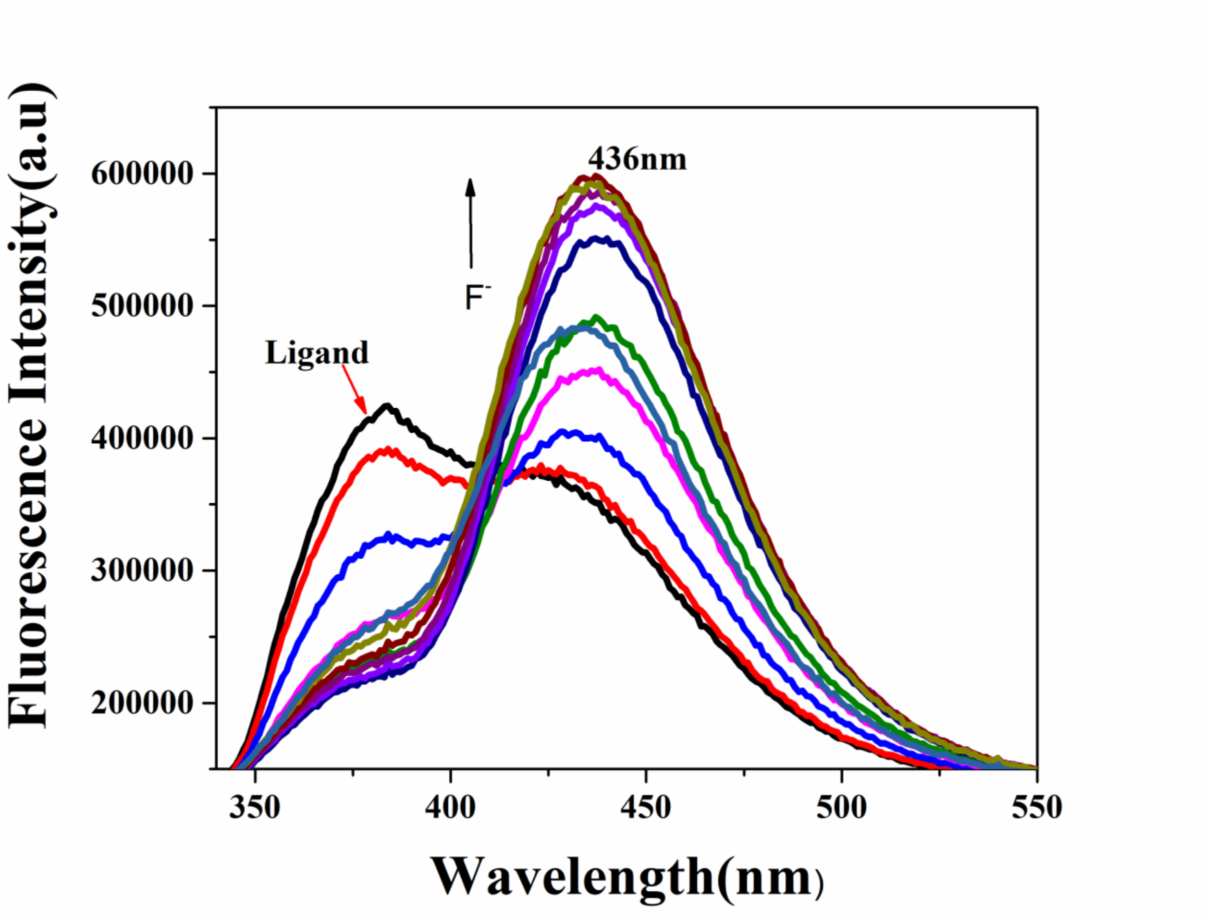
HF$_2$'s proton signal, on the other hand, first appeared at 16.11 ppm. Sensor 4 displayed a new absorption band at 300 nm when the F$^-$ ion was added, and the mixture became colourless. When titrated with F$^-$ ion for the fluorescence response, sensor 4 showed an improvement in emission intensity at 434 nm with a minor blue shift. These findings imply that sensor 4 has good F$^-$ ion detection sensitivity and selectivity. Additionally, the sensor 4 test strip coated on TLC plates and filter papers was shown to be capable of a certain type of ion detection.

This incident once more provided evidence that a deprotonated form exists. The limit of detection and association constant between sensor 4 and F$^-$ ion were calculated to be 6.86×10^5 M^{-1} and 18µ M, respectively. Also used as a basic technique for F$^-$ ion detection by the naked eye was the sensor 4-based test on the TLC plate and filter paper [24].

Anthraimidazoledione-based sensor for colorimetric fluoride ion detection in the presence of Cu(II) ions reported by A. Sarkar et al in 2015 [25]. Due to the colorimetric response upon detecting a particular anion and the potential to tune this attribute by changing the conjugated moiety (the donor) to the diamine, anthraquinone-based anion receptors have become more significant. In this study, four anthraimidazoledione compounds with 2,5-dihydroxybenzene, 4-(bis(2- chloroethyl)amino)benzene, imidazole, and 4-methylthiazole moieties have been synthesised and characterised (5-8).

The p-hydroquinone bound anthraimidazoledione (5) and the thioimidazole bound anthraimidazoledione (8) were able to detect both F and CN in the presence of other anions Cl, Br, I, H2PO4, OAc, NO3 and ClO4. However, both 5 and 8 were unable to distinguish between F and CN and gave a similar response to both.

The findings highlight how a hetero atom shift in an anthraimidazoledione's donor moiety can result in a significant variation in sensitivity. In example 8, 0.5 equivalents of Cu2+ allowed for the selective detection of F$^-$, which displayed a distinct green colour with a shift of around 50 nm, as opposed to CN$^-$, which displayed orange coloration with a shift of just 15 nm. The WHO-specified F$^-$ detection limit in the presence of Cu2+ was 0.038(5) ppm at a receptor concentration of 25µ M. As previously indicated, 7- which contains two imidazole rings did not demonstrate anion recognition at the same receptor concentration as 5 and 8. Addition of 7 up to 6 comparable anions (F equivalent of OH-) hardly causes the charge transfer band at 500 nm to turn red. Because the imidazole proton is less acidic in case of 6 due to the weak electron withdrawing bis(2-chloroethylamine) moiety, the F- or CN- adduct is weaker and more unstable, making 6 unsuitable as a probed anion sensor.



The colorimetric response upon detecting a particular anion and the potential for tweaking this attribute by changing the conjugated moiety (the donor) to the diamine have led to the increased relevance of anthraquinone-based anion receptors.For the purpose of analysing the impact of changes in hydrogen bond donor-acceptor, each one of them was tested for its potential as an anion sensor.

Both F^- and CN^- could be detected in the presence of other anions by the anthraimidazolediones attached to p-hydroquinone and thioimidazole, respectively. Cl, Br, I, H2PO4, OAc, NO3, and ClO4 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. The findings highlight the possibility of a significant variation in sensitivity when a hetero atom in an anthraimidazoledione's donor moiety is changed.

In the instance of 8, selective detection of F^- was made feasible in the presence of 0.5 equivalents of Cu^{2+}, exhibiting a distinct green colour with a shift of around 50 nm, as opposed to CN^-, which displayed orange coloration with a shift of just 15 nm. At a receptor concentration of 25µ M, the F^- detection limit in the presence of Cu^{2+} was 0.038(5) ppm, which is below the WHO-specified standard.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+}.

The selectivity for F^- in case of 8 and the detection limit of 0.038 ppm are promising. The findings show that even while HF2 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 results demonstrate that the benzimidazole -NH is most acidic in the compounds 8 and 5, and comparably considerably less acidic in 6 and 7.

It should be emphasised that while the creation of HF2 may be a useful indicator of the process, it does not necessarily provide insight into the sensitivity of recognition. At lesser concentrations, the presence of sulphur in the heterocyclic ring positively affects the anion recognition characteristic.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 Cu2+ is present.

NANO PARTICLE BASE FLUORIDE SENSOR

Rapid and precise fluoride anion detection using a colorimetric sensor based on gold nanoparticles modified with 4-mercaptophenylboronic acid was synthesized by H. Wu et al. in 2015.

The 4-mercaptophenylboronic modified gold nanoparticles were produced by a straightforward one-pot reaction, and the aggregation process occurred when interaction between fluoride anion and 4-mercaptophenylboronic on the surface of gold nanoparticles. As a result, a highly sensitive and selective colorimetric sensor based on aggregation-induced colour change of gold nanoparticles was developed to measure fluoride anion. The sensor exhibits high fluoride anion selectivity and sensitivity. According to IUPAC criteria (3' rule), the linear range for fluoride is 10.0-30.0 M, while the detection limit is 3.45×10^{-7} M. The sensor has also been utilised 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. 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].

CONCLUSION

High sensitivity and good selectivity were exhibited by the sensors in DMSO for the detection of fluoride ions in aqueous solution. Using these sensor, fluoride ions in drinking water can be found. 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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