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A REVIEW ON RECENTLY DEVELOPED SCHIFF BASES AS CHROMO-FLUOROGENIC CHEMOSENSORS FOR ALUMINUM (III) ION DETECTION: MECHANISTIC INSIGHTS AND APPLICATIONS

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ABSTRACT

The consumption of non-essential aluminum ions (Al^{3+}) at higher concentrations from biotic and abiotic sources can cause serious adverse effects on the human body. Therefore, there is a bourgeoning need to develop facile analytical methods for the on-site and real-time monitoring of Al^{3+} concentration in various environmental and biological samples. The chromo-fluorogenic based sensors have been widely developed in recent years to detect and monitor Al^{3+} ions. Among the various types of developed chemical sensors, the Schiff bases proved to have several advantages due to their facile synthesis with high yield, fascinating coordination behavior and easy structural modification. The presented review article starts with a general introduction to the beneficiary and harmful effects of Al^{3+} ion and to the Schiff base as a promising candidate for detecting the said ion and the rest of the review article consists of two main sections. The first section illustrates different mechanistic insights into metal ion detection using Schiff base sensors. The second section includes a review of the recently reported Schiff base-based chemosensors for Al^{3+} ion detection along with various applications of Al^{3+} sensing. Additionally, a summary of the reviewed recent Schiff base sensors is presented in a table format. Finally, the conclusion and future scope of Schiff base sensors for Al^{3+} ion detections are discussed.

KEYWORDS

Chromo-fluorogenic, Schiff bases and Aluminum ions (Al^{3+}).

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INTRODUCTION

In recent decades, researchers have focused on metal ion recognition, recognizing its significance in pharmacology, biology, environmental studies, catalysis, green chemistry and analytical fields[1-2]. Certain cations, despite their numerous day-to-day utilities, pose significant hazardous effects as a result of the overuse of chemicals in both industrial and agricultural applications, thus emphasizing the importance of their role in various biological processes[3]. Particularly in health and environmental applications, there is a high demand for specific and sensitive identification of pollutant species, such as toxins and metal ions[4-6].

Among all these metal ions, Al^{3+} is the most abundant metal ion after oxygen and silicon and due to its cheap availability, aluminum metal is extensively used in household appliances, transport, and machinery. Additionally, owing to its good conductor behavior of electricity, aluminum is utilized in the manufacture of electric wires, as well as various electronic and electrical appliances[7,8.]

While aluminum (Al^{3+}) finds extensive application in our daily lives, it is deemed non-essential for biological systems[8]. As per a report by the World Health Organization (WHO), the average daily consumption of Al^{3+} for humans ranges from approximately 3-10mg per day, while the permissible threshold for Al^{3+} in drinking water is 7.41μM[9-11]. It is solely responsible for various kinds of environmental degradations and human health issues when accumulated in excess amounts in both the aquatic-terrestrial ecosystems and the human body such as osmoregulatory failure in invertebrates and fish while Alzheimer's, Parkinson's disease in the human body[12].

Therefore, there exists an immense demand to prioritize the advancement of rapid detection devices for monitoring the concentration of these hazardous ions[13,14]. Several promising processes exist to detect these ions, though they tend to be quite time-consuming and cost-effective[15-17]. To address these limitations, various optical chemosensors have been developed for the detection of heavy metal ions. In the realm of detecting biologically and environmentally significant ions, fluorescence-based tools are recognized for their heightened capacity to sense specific target analytes[18,19]. Fluorescent or colorimetric multi-ion chemosensors are increasingly prominent due to their myriad advantages, such as effortless operation, enhanced and broader detection capacity, as well as the potential to reduce analytical time, costs, and synthetic endeavors[20].

Schiff base receptors stand out among various known binding motifs as highly efficient for chemosensing[21]. Their ease of synthesis and purification makes them particularly noteworthy in this regard. Additionally, Schiff bases exhibit a broad spectrum of biological applications, attributed to their anti-inflammatory, antimalarial, antitumor, antimicrobial, and antibacterial properties. The inherent attributes of anthracene, such as notable stability, luminescent qualities, and elevated π-electron density, motivated our exploration of its recognition properties through the integration of a Schiff base moiety. Recent developments in the realm of sensing have illuminated the efficacy of Schiff base host molecules harboring an 'imine moiety' as superior binding sites for guest ions[22,23]. Structural attributes, encompassing the cavity dimensions orchestrated by the molecule, the oxidation state of the metal ion, its electronic configuration, and steric considerations, alongside the hard and soft acid-base properties of ligand donors, coupled with the metal ion engaged in the binding mechanism of the Schiff base, provide avenues for discerning specific metal ions amidst a plethora of co-existing counterparts[24]. Detection of analytes utilizing Schiff bases primarily involves the modulation of optical properties through interactions with acidic hydrogen atoms within the C=N bonded moiety or the influence of fluoride ions on functional units within C=N bonded compounds. The pivotal function of the C=N bond lies in its control over geometry and conjugation, while also furnishing binding sites essential for detection[25]. The fundamental mechanism guiding the detection of aluminum ions by a supramolecular receptor primarily involves sophisticated processes such as intramolecular charge transfer (ICT), excited-state intramolecular proton transfer (ESIPT), chelation-enhanced fluorescence (CHEF), photoinduced electron transfer (PET) and related phenomena[26].

Chemistry of Schiff base

Schiff bases are compounds with an imine or azomethine (–C=N–) functional group where an N atom is bonded to an aliphatic/aromatic group, not a H atom. They were originally reported by the pioneer Hugo Schiff in 1864 and are the condensation products of aldehydes or ketones with primary amines[27].

The Schiff bases have drawn a lot of attention due to their intriguing physical and chemical characteristics[28], involvement in biologically significant reactions[29], chemical catalysis[30,31] medicine, and pharmacy[32] and the widespread use of their metal complexes in modern technologies[33-35]. The formation of a Schiff base (imine) involves the simple condensation of an aldehyde or ketone with primary amines (Scheme No.1) and generally takes place under acid catalysis[36-40].

Mechanistic insights into metal ions detection

The general approach for detecting metal ions involves interactions between the chemosensor and the metal ions through coordination. A Schiff base chemosensor contains two parts, a signaling unit, and a binding unit, sometimes they are connected with a spacer. The latter part coordinates with the metal ions, causing changes in the visible as well as fluorescence color of the solution, enhancement/quenching of emission intensity, and ratiometric fluorescence change, leading to intra/intermolecular charge transfer (ICT) and chelation-enhanced fluorescence (CHEF) or chelation-enhanced quenching (CHEQ) effect. The commonly used mechanisms for metal ions detection by the Schiff bases are photo-induced electron transfer (PET), intra/intermolecular charge transfer (ICT), metal-to-ligand charge transfer (MLCT), ligand-to-metal charge transfer (LMCT), fluorescence resonance energy transfer (FRET), excited state intramolecular proton transfer (ESIPT), and C=N isomerization.

Photoinduced Electron Transfer (PET)

Among the mechanisms being followed in the sensing of fluorescent chemosensors, the photoinduced electron transfer (PET) mechanism is the most important one. Most of the fluorescent chemosensors that follow the PET mechanism during the sensing process are ‘fluorophore-spacer-acceptor’ type chemosensors where the covalently bonded non-conjugated spacer reduces the ground state interactions ($n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$) between the fluorophore and the receptor. Chelation-enhanced fluorescence (CHEF), also known as fluorescence ‘turn-on’, and chelation-quenched fluorescence (CHQF), also known as ‘turn-off’ fluorescence are the two types of sensing mechanisms based on PET that are categorized according to the kind of receptor present in the fluorescent chemosensor.

Chelation-enhanced fluorescence (CHEF)

In this instance, the receptor of the fluorescent chemosensor has non-bonding electron pairs (lone pairs) that are localized on the donating atom such as O, N, S, etc. in the receptor site. Therefore, the receptor possesses the highest occupied molecular orbital (HOMO) with a higher energy than that of HOMO of the fluorophore. The fluorophore promotes an electron from the highest occupied molecular orbital (HOMO) to its lowest unoccupied molecular orbital (LUMO) after it has absorbed a photon. When there are not any analytes present, the receptor’s electron pair of HOMO prevents the relaxation process of the fluorophore by rapid transfer of one of the electrons to the half-filled HOMO of the fluorophore and quench the emission (PET-ON) as shown in Scheme 1. But, when suitable analytes (metal cations) are present, the receptor’s electron pair of HOMO is engaged to make a bond to the analyte, and the energy of HOMO of the receptor decreases than that of HOMO of the fluorophore. As a result, the transfer of electrons from the HOMO of the receptor to the initial HOMO of the fluorophore is no longer favorable and consequently, the PET process is also no longer operated (PET-OFF). This PET-OFF state allows the excited electron of the fluorophore to relax to its ground state (initial HOMO) by releasing the absorbed energy through emission. Therefore, upon binding with the targeted analyte (chelate), the fluorescence emission of the fluorophore becomes enhanced due to the off-state of the PET process. This phenomenon of chemosensors is called chelation-enhanced fluorescence (CHEF).

R. Kumar *et al*. reported a bis-rhodanine-derived ‘turn-on’ fluorescent chemosensor for selective recognition of Hg^{2+} in DMSO/H_2O mixed solvent medium[41]. The ‘turn-on’ fluorescence response of the reported probe is due to the constraint of the

PET process which is responsible for the 'turn-off' fluorescence response of the probe upon chelation or complexation with the Hg^{2+} ion i.e., the CHEF mechanism is operated after the formation of a complex of the probe to the Hg^{2+} ion (Figure No.1). They also showed that the stoichiometric ratio of complexing is 1:1 to the probe and the Hg^{2+} ion.

Chelation-Quenched Fluorescence (CHQF)

In distinction to the above case, if the initial energy of the receptor's HOMO is lower compared to the fluorophore's HOMO, then the scope of the relocation of an electron from the former to the latter no longer exists in the excited state. Therefore, the relaxation of the excited electron of the fluorophore is not interrupted by the PET process (PET-OFF), and the chemosensor shows a strong emission (Scheme No.2). Now, the energy of the receptor's HOMO and LUMO is further lower than that of the fluorophore's HOMO and LUMO, respectively, when the chemosensor interacts with a particular analyte (metal cations) by gaining some stabilization. The excited electron of the fluorophore relaxed through a non-radiative pathway if the energy of the receptor's LUMO is greater or lower than the energy of the fluorophore's HOMO or LUMO, respectively. This means that the excited electron first transferred from the fluorophore's LUMO to the receptor's LUMO, and then returned to the fluorophore's ground state (initial HOMO). As a result, the fluorescence emission of the chemosensor becomes quenched (Scheme No.2). Therefore, in the presence of a specific analyte, the PET process becomes 'ON', and the quenching of fluorescence emission results. This type of phenomenon is called chelation-quenched fluorescence (CHQF).

Zhao *et al*, reported a thiophene-substituted naphthyl hydrazone derivative, which has been utilized as a chemosensor for the selective detection of trivalent chromium (Cr^{3+}) ion[42]. By studying various spectroscopic experiments and doing theoretical calculations, they revealed that the response of sensing is a 'turn-off' due to the chelation-enhanced fluorescence quenching (CHEQ) or chelation-quenched fluorescence (CHQF) effect upon exposure of the probe to the Cr^{3+} ion at a 1: 1 binding stoichiometry [Figure No.2].

Photoinduced Intramolecular Charge Transfer (ICT)

A signaling process called intramolecular charge transfer (ICT) is typically observed in ratiometric fluorescent chemosensors. Where a change of color of the chemosensor is predominant in either ground or excited state and as a result, a red or blue shift of absorption or emission of the chemosensor was observed. Chemosensors showing the ICT phenomenon do not have a spacer between the fluorophore and the receptor, they are connected directly or through conjugation unlike the chemosensors showing the PET process. The conjugation of the fluorophore to the receptor unit makes the whole chemosensor a dipole i.e., one part of the chemosensor is electron-rich, acts as an electron-donor and the other part becomes electron-deficient, acts as an electron-acceptor. When photons stimulate such chemosensors there will be a transfer of charge (electrons) occurs from the electron-donor site to the electron-acceptor site of the chemosensor i.e., intramolecular charge transfer (ICT) observed in the chemosensor resulting in the change of dipole moment of the chemosensor. Here, we simply take into the situation that the excited state's dipole moment is greater in comparison to the ground state. As a result, the target analyte interacts with the excited state dipole to modify the fluorophore's photophysical properties and the efficiency of the ICT process, which significantly changes the chemosensor's absorption and emission[43]. The electron pair of an electron-donating group present in the receptor site such as the amino group participates in conjugation with the fluorophore. Now, if the incoming analyte interacts with the electron-donating group, the likelihood of electron donation declines to the fluorophore resulting in a drop in conjugation which causes the absorption shift to the blue of the chemosensor. However, when the analyte interacts with the receptor that has an electron-withdrawing group, such as the carbonyl group, it amplifies the electron-withdrawing property which causes conjugation to increase and results in a red-shifted absorption of the chemosensor[44]. The emission of chemosensors is shifted similarly to the absorption.

Charge dipole interaction can explain the photophysical alterations in the fluorophore upon binding of the chemosensor to the analyte[45]. The electron-donating group in the receptor unit becomes positively charged in the excited state, and because of its energetically unfavorable interactions with the positively charged cation, it becomes more unstable than the ground state. Consequently, the chemosensor's ground and excited states have a wider energy difference, which causes the absorption and emission to shift toward blue (Scheme No.3). On the other hand, the electron density in the electron-withdrawing group increases in the excited state if the receptor site has that group conjugated to the fluorophore of the chemosensor. It therefore interacts with the positively charged cation in an energetically favorable manner and the cation stabilizes the excited state more in comparison to the ground state. Because of this, the energy difference between the states (ground and excited) will close which causes the absorption and the emission of the chemosensor to shift to the red (Scheme No.3).

Ghosh *et al*, designed a carboxylic acid functionalized chemosensor (L2). They reported that their synthesized chemosensor is a promising candidate for the selective sensing of Hg^{2+} by turning ‘on’ the fluorescence emission of the chemosensor over the other heavy metal ions[46]. The bidentate chemosensor is initially a fluorescent compound because of the ICT process happening between the $-NH_2$ group (donor) and the -COOH group (acceptor). But, upon complexation with Hg^{2+}, the ICT process becomes ‘off’ and the emission of the chemosensor is quenched in a neutral medium. In the slightly basic medium (pH = 7.45) deprotonation of two acidic protons occurs and the Hg^{2+}-complex of the chemosensor shows a ‘turn-on’ fluorescence with a blue-shifted emission because of the ICT process as the conjugation becomes increased by deprotonation (Figure No.3).

Excited-State Intramolecular Proton Transfer (ESIPT)

If a probe's structure allows for the generation of hydrogen bonding intramolecularly, it will frequently exhibit fluorescence as a result of excited state intramolecular proton transfer (ESIPT) i.e., the structure must have a hydrogen bond donor (-OH, -SH, or $-NH_2$) and acceptor (>C=O or imine nitrogen) group. The most popular fluorophores for the fabrication of ESIPT-based probes are derivatives of 2-(2`-hydroxyphenyl) benzimidazole (HBI), 2-(2`-hydroxyphenyl) benzthiozole (HBT), and 2-(2`-hydroxyphenyl) benzoxazole (HBO). ESIPT-based probes frequently have the enol form (E) in their ground state. The respective acidity and basicity of the hydrogen donor and acceptor groups are both increased in the excited enol form (E*) as a result of the redistribution of electron density that takes place inside the molecule during excitation. The relaxation of the stimulated enol via the fluorescence emission is substantially slower than the ESIPT process. As a result, an incredibly quick proton transfer takes place from donor to acceptor which causes the excited enol form (E*) to quickly phototautomerize into the excited keto form (K*). Now, that excited keto form (K*) has come to its ground state keto form (K) by decaying radiatively. Eventually, a fast reverse proton transfer (RPT) takes place to return the system to its initial enol form (E) (Scheme No.4). Therefore, the emission seen with the ESIPT-based probe is caused by the relaxation of the excited keto form (K*) to its ground state keto form (K)[9]. The ESIPT-based probe exhibits an atypically large shift (~ 200nm) in comparison to the ICT or PET-based probes, preventing the effects of self-reabsorption and inner filtering. Therefore, the majority of ESIPT-based probes exhibit ratiometric sensing. As the primary driving force behind the ESIPT process is intramolecular hydrogen bonding, the solvent’s polarity and the medium’s pH are impacted greatly in the ESIPT process[47]. The target analytes may interact with the enol or keto form of the ESIPT-based chemosensor and show respective signals and also the analyte can interrupt or stop the ESIPT process upon binding with the ESIPT-based probes.

Ansori *et al*, reported a 2-hydroxynaphthaldehyde-based fluorescent chemosensor that displays high selectivity and reversible off-on behavior against Al^{3+}[48]. The chemosensor forms a stable 1: 1 complex with Al^{3+} at physiological pH conditions in a DMSO/H_2O mixture solvent system. Upon binding with Al^{3+}, the reported chemosensor shows a 'turn-on' emission due to the inhibition of excited-state intramolecular proton transfer (ESIPT) (Figure No.4).

Fluorescence Resonance Energy Transfer (FRET)

The intramolecular charge transfer (ICT) process can produce ratiometric changes in a single fluorophore-based chemosensor, however, in this instance, only a little Stokes shift is seen. If a probe with two or more fluorophores can be constructed, it will allow for the monitoring of two emission intensities simultaneously at different wavelengths as well as the generation of significant pseudo-Stokes shift both of which are extremely helpful for the resolution of emission wavelength and fluorescence detection. Because distinct fluorophores have varied absorption and emission characteristics as well as variable energy levels, one of them functions as an energy donor (D) and another as an energy acceptor (A). Thus, intramolecular energy transfer across the fluorophores may be taking place. The excited donor fluorophore (D*) transferred its absorbed energy of a comparatively shorter wavelength to the ground state acceptor fluorophore (A) and the latter became excited, which emits energy of a longer wavelength. In other words, energy transfer takes place to excite the acceptor fluorophore (A) using the energy of the excited donor fluorophore (A*). Fluorescence resonance energy transfer, or FRET, is an electrodynamic process that transfers energy from the excited state donor (D*) to the ground state acceptor (A) fluorophore through a non-radiative dipole-dipole coupling[49]. To put it another way, absorption of the relaxation energy of the excited state donor (D*) occurs by the ground state acceptor (A) which is spatially close as a result electron is promoted to the excited state acceptor (A*) and eventually, an emission is experiential from the excited state of the acceptor fluorophore (Scheme No.5). Therefore, there needs to be a spectrum overlap between the acceptor fluorophore's absorption and the donor fluorophore's emission i.e., the resonance of emission and absorption energy (wavelength) of the donor and acceptor fluorophore respectively.

A novel spirolactum derivative with fluorescein-appended ratiometric fluorescent chemosensor for Zn^{2+} is reported by Zhang's group[50]. Well-resolved emission peaks are shown for two fluorophores and an intramolecular fluorescence resonance energy transfer (FRET) mechanism is operated during the ratiometric fluorescent signal change by Zn^{2+} induced ring opening process of the rhodamine spirolactum (Figure No.5). The reported probe shows selective sensing over a wide range of concentrations of Zn^{2+} and the probe is conducive for the ratiometric cellular imaging investigations.

Recent developments of Al^{3+} chemosensors and their applications

Aydin *et al*, synthesized and analyzed a compound based on phenolphthalein (A1) and investigated its potential as a fluorescent chemosensor that illuminates when Al^{3+} is present in aqueous CH_3CN medium[51]. Their probe A1 itself is non-fluorescent but depicted a strong fluorescence in a complex form with Al^{3+} at 468 nm over other competitive cations and the - C =N isomerization as well as blocking the PET process are the mechanisms that enhanced the emission of A1 upon complexation with a significant change of color to blue from colorless. They found the limit of detection of probe A1 to Al^{3+} to be 51.5 nM i.e., at the nanomolar level, demonstrating a high degree of sensitivity of A1 for Al^{3+}. They have approved the authenticity of the 1:2 stoichiometry between probe A1 and Al^{3+} by investigating Job's plot, 1H NMR titration, and Mass analysis as well as by the theoretical study. Additionally, they have demonstrated the usefulness of the fluorescence detecting capabilities of probe A1 towards Al^{3+} in simple test kits, food samples and drinking water.

The Alam group has reported a two-armed chemosensor (A2) synthesized from biphenyl that features hard donor centers that facilitate the chelation with the hard metal centers[52]. Their chemosensor A2 itself formed a monoclinic crystal structure with the space group *I*2/a and exhibited a variety of stability provided H-bonded interactions acting intra- or intermolecularly. They have used several analytical approaches to demonstrate the sensing property of A2 towards different metal ions and have shown strong fluorescence selectivity and sensitivity towards Al^{3+} in an aqueous DMF medium. Interestingly, they are the first group to report the complex of six-coordinate dinuclear Al^{3+}, $[Na(Al_2L_2)\cdot 2H_2O\cdot 4DMF]$ characterized structurally (where L = A2). The complex under discussion crystallizes in the space group P1 and the diffraction of single crystal X-ray analyses of that complex show that two nitrogen and four oxygen atoms from each arm of the two probes hexa-coordinate each Al^{3+} ion. They have not observed any spectral or naked-eye color change upon the addition of Na_2EDTA to the Al^{3+} complex of A2 indicating the formed complex is very much stable. Furthermore, the application of sensor A2-coated “test kits” for the selective detection of Al^{3+} was successful under UV light.

Hu *et al*, developed a fluorescent probe (A3) that can detect small levels of Al^{3+} in DMSO and EtOH mediums with selectivity. They did this by employing phenolphthalein and thiophene hydrazide as raw materials[53]. As per their statement, the inhibition of the PET process of probe AZ3 takes place upon binding with Al^{3+}, and a strong blue fluorescence at 453 nm resulted, demonstrating the specific detection of A3 towards Al^{3+}. They have determined the binding constant and stoichiometry between the probe A3 and Al^{3+} by B–H and Job’s method, found to be $5.6 \times 10^{5}\ M^{-1}$ and 1: 2 respectively. The latter is further confirmed by the ^{1}H NMR titration experiment. The minimal limits of detection of A3 were 2.75×10^{-8} M and 1.8×10^{-8} M in DMSO and ethanol respectively, as demonstrated by their fluorescence gradient concentration measurement. These values were also less than the WHO norm for Al^{3+} in drinking water (7.41μM). Their reported fluorescent probe A3 can act as a detection solvent and be utilized in the test strips for the detection of Al^{3+}.

Two novel fluorescent Schiff bases (A4 and A4') were designed and synthesized by Liu et al. to enable the selective detection of Al^{3+} in aqueous media[54]. They used IR, ^{1}H NMR and ^{13}C NMR spectroscopic analysis to establish the proper structures of synthesized compounds A4 and A4'. Furthermore, using UV–vis absorption and fluorescence spectra in an aqueous media, researchers have methodically examined the photochromic and fluorescent behaviors of their probes toward solely Al^{3+}. They postulated a potential recognition mechanism in which the abundance of the species best suited for complex formation would cause the metal ions to complex with Schiff base probes, blocking the structural -C=N isomerization and ESIPT process, which altered the color and the fluorescence behavior of both probes. Additionally, they demonstrated the capacity of both probes to identify Al^{3+} in the environment with excellent precision and selectivity, offering a fresh approach to the synthesis and design of multifunctional sensors.

The Ye group devised and synthesized a new isophorone-based fluorescent probe A5, which has the potential to function as an extremely selective Al^{3+} detector in an aqueous DMSO solvent[55]. They suggested the 1:1 stoichiometry of probe A5 with Al^{3+}, based on the outcome of Job's plot and HRMS analysis of the formed complex between A5 and Al^{3+}. They observed a red-shifted fluorescence enhancement of probe A5 upon allowing it to interact with Al^{3+} and alteration of color to bright orange-red from lavender under UV-light irradiation. They have stated the attribution for the observation could be the complexation occurring between A5 and Al^{3+}, and that could inhibit -C=N isomerization as well as strengthen the ICT effect. Their reported probe A5 can be utilized in environmental water sample analysis as well as in biological fluorescence imaging for the detection of Al^{3+}.

Chaskar *et al*, designed function-oriented water-soluble sulfonated scaffolds of salicylaldehyde (A6 and A6’) to selectively detect Al^{3+} in an aqueous solution[56]. They have examined the photophysical characteristics of A6 and its π-conjugated sulfanilinic acid counterpart, A6', and discussed their sensitivity towards metal ions as well as applications in various aspects. Both A6 and A6' probes were highly selective towards Al^{3+} with a 3:1 stoichiometry demonstrated by B-H and quantitation plots, validated by ESI-MS. They observed a proportionate enhancement in emissions of both probes in the presence of Al^{3+} attributing to the inhibition of the ESIPT process and the subsequent CHEF process. The binding modes, stoichiometry and complexes of sensors were confirmed by DFT studies using B3LYP hybrid functional, correlating well with experimental findings. Excellent solubility in water and the consequent biomembrane permeability enabled both reported probes to be used in DNA bioimaging. They have shown that onion root tip cells incubated with Al^{3+} and probe A6 may be imaged under a fluorescent microscope throughout various stages of mitosis. Additionally, the sensors (A6 and A6') have been used for qualitative visual detection of Al^{3+} in aqueous solution through a paper strip test.

Through a simple condensation between benzoyl hydrazine and salicylaldehyde, a Schiff base chemosensor (A7) has been prepared by the Yan group and discussed its reversible photochromic features relying on isomerization and ESIPT processes[57]. Following a two-minute exposure to 365 nm UV light in organic solvents, the absorption of A7 at 367 nm significantly decreased, and a double absorption peak at 418 nm and 438 nm arose along with a notable shift in the hue of the solution from colorless to yellow. In contrast, they observed that the fluorescence spectral nature of A7 did not alter noticeably in the presence of Al^{3+} upon exposure to 365nm UV light. As per their observation, probe A7 forms a complex with Al^{3+} selectively and enhances the fluorescence of A7 at 475 nm upon excitation at 385nm in aqueous solution. As per their observation, probe A7 forms a complex with Al^{3+} selectively and enhances the fluorescence of A7 at 475nm upon excitation at 385 nm in an aqueous solution attributed to the Al^{3+} coordination with A7 blocked -C=N isomerization and the ESIPT process. By investigating Job's plot analysis and measuring the mass of the complex of A7 to Al^{3+}, they confirmed the 2: 1 complexation molar ratio. Additionally, their probe A7 was able to detect Al^{3+} fluorescence in aqueous samples and live cells.

The Xu group systematically devised and synthesized a straightforward Schiff-base fluorescence probe A8, which is generated from naphthalimide and picolinohydrazide, for the effective detection of Al^{3+}[58]. Through the enhancement of emission and color shifting (doder blue to spring green) observation, they reached a decision that probe A8 is a selective sensor towards Al^{3+}. The complexation of A8 with Al^{3+} and the consequences of -C=N isomerization and inhibition of the PET process are likely the causes of this unique "signal-on" response characteristic of A8 toward Al^{3+}. Job's plot analysis revealed that the binding ratio of the A8-Al^{3+} complex was 1:1, and the LOD calculation indicated the nanomolar level of detection. In addition, they have proposed and substantiated the chelation mechanism of A8 with Al^{3+} by the FT-IR and ^1H NMR spectroscopic experiments as well as by DFT and TD-DFT. Moreover, this "signal-on" probe A8 was effectively employed as a potential indication for biological and environmental sample Al^{3+} detection.

A 'turn-on' fluorogenic chemosensor (A9) has been developed by Aydin et al. to detect Al^{3+} in an ethanolic HEPES buffer solution at λem = 475nm[59]. Their fluorescent probe A9 detects Al^{3+} at the micromolar level obtained from the LOD calculation and binds to Al^{3+} in 1:2 stoichiometry verified by Job's plot and ^1H NMR titration as well as ESI-MS analysis. They have investigated that pH 6 to pH 8 is the range where the fluorescence "turn-on" response of chemosensor A9 to Al^{3+} functioned effectively and developed a blue color emission. Probe A9 showed a very high binding constant (K_b) and quantum yields (Φ) upon complexation with Al^{3+}. The methods of preventing the PET process and -C=N isomerization mechanisms were shown to be responsible for the enhancement of the emission response of chemosensor A9 to Al^{3+}. Finally, they used the sensing property of the chemosensor A9 to find Al^{3+} in drinking water, food samples and herbal teas.

A novel phenolphthalein-scaffolded Schiff base appended 2-furoic hydrazide fluorescence probe (A10) has been synthesized by the Alici group and applied to be a fluorescence 'turn-on' sensor for Al^{3+} in acetonitrile HEPES buffer solution[60]. They explained the 'turn-on' emission response of probe A10 toward Al^{3+} that chelation resulted from the interaction between the probe and Al^{3+} enhances the fluorescence i.e., CHEF which prevents PET and ESIPT processes as well as -C=N isomerization of A10. They revealed 1:2 stoichiometric complexation between the sensor A10 and Al^{3+}, confirmed by Job's plot analysis and ^{1}H–NMR titration. They have mentioned the optimized pH range for the formation of a stable complex between probe A10 and Al^{3+} to be 6.0 to 8.0, favorable for biological experiments. They estimated the limit of detection to be 7.0 nM of probe A10 for Al^{3+}, indicating that the chemosensor A10 may be used as a 'turn-on' fluorescent chemosensor for the efficient and selective detection of Al^{3+}. In addition, they demonstrated the sensing phenomenon of probe A10 towards Al^{3+} in the TLC plate and also checked the sensing ability for detecting Al^{3+} in environmental water.

Zhang *et al*, developed a new salamo-scaffolded probe A11, characterized by ^{1}H and ^{13}C NMR spectrometry, mass spectrometry, and FT-IR spectrometry[61]. As per their report, probe A11 shows fluorescent selectivity towards Al^{3+} through enhancement of emission at 492 nm upon 365nm excitation in aqueous ethanol solution and also induced green color under UV light irradiation which could be used as a naked eye detection tool. They observed that the enhancement of fluorescence reaches its plateau at the 1: 1 molar ratio of sensor A11 and Al^{3+} indicating the stoichiometric ratio of interaction and the Job's plot also confirmed the same. Their reported probe A11 shows a very fast fluorescent response to Al^{3+} and also the best recognition capability within the 5-11 pH range. They ascribed the chelation-enhanced emission (CHEF) effect to the recognition mechanism of A11 towards Al^{3+}. Finally, they studied the cytotoxicity of the probe in HeLa cells and extrinsic determination of Al^{3+} in Zebrafish which showed good cell membrane permeability of the probe A11.

The Singh group has developed a novel silatrane-scaffolded Schiff base (A12) as a promising chemosensor for the identification of Al^{3+} with excellent selectivity and characterized thoroughly by a variety of spectroscopic methods, including mass, TGA, ^{1}H NMR, and ^{13}C NMR[62]. They have explored the chemosensing properties by investigating the ultraviolet-visible and emission spectra of the reported chemosensor A12 and both are altered only by the addition of Al^{3+}, while the alteration of others is negligible. Their chemosensor A12 detects Al^{3+} in a 1: 1 stoichiometric manner confirmed by Job's plot at micromolar and nanomolar levels in UV-vis and fluorescence spectroscopic techniques. They observed a shift of the absorption band at 302 nm to red and a quench of emission at 354nm of probe A12 upon interaction with Al^{3+}. The establishment of the complexation of probe A12 to Al^{3+} was also done by the group through the theoretical DFT analysis.

The Ramu group demonstrated AZ13, a newly developed and manufactured probe, to be an effective chemosensor by using a variety of spectroscopic methods, including ^{1}H NMR, ^{13}C NMR, and ESI-MS[63]. Comparing their probe A13 to the other competing cationic metal ions, they find that it is far more sensitive and selective to Al3+ ions. The "turn-on" fluorescence and chromogenic behavior of this developed probe towards Al3+ may be observed separately under UV light and with the naked eye. From the Job's plot analysis, they showed a 1:1 stoichiometric interaction of A13 with Al^{3+} ions and the determined LOD value was $13x\ 10^{-7}$ M, which is far below the allowed threshold. The suggested mechanism as CHEF and ICT has also been supported by their DFT figures and calculations based on the obtained spectroscopic results.

By condensing 2-(benzo [b] thiophen-2-yl) benzenamine and salicylaldehyde in an ethanolic solution, Sahoo *et al*. synthesized a tridentate Schiff base receptor A14 and identified using a variety of spectrum data, including mass, ^{1}H NMR, ^{13}C NMR, and FT-IR[64]. For the fluorescence detection of metal ions dissolved in an aqueous media, they used the methanolic solution of A14. They carried out a selectivity experiment, and the results demonstrated that the chelation-induced fluorescence (CHEF) enhancement mechanism was responsible for the notable fluorescence amplification of the receptor A14 at 430nm when Al^{3+} was present. As shown by their Job's figure, receptor A14 and Al^{3+} formed a complex with a 2:1 binding ratio, and receptor A14 is capable of detecting Al^{3+} concentrations as low as 256nM. With the use of confocal imaging, the receptor BPB, which exhibited good cell permeability, was utilized for the qualitative and quantitative detection of intracellular Al^{3+} in the A549 cell line, which represents adenocarcinomic human alveolar basal epithelial cells.

For the first time, a Schiff base receptor scaffold of phenyl thiadiazole (A15) has been reported by Patra et al. to enable fluorescent ‘turn-on’ and colorimetric detection of Al^{3+}[65]. Their chemosensor A15 demonstrated exceptional sensitivity, selectivity and very fast response to Al3+ in the MeOH–Tris–HCl buffer medium with 1.15×10^{-7} M and 1.43×10^{-7} M limit of detection in fluorometric and colorimetric methods, respectively. By using the ESI-MS and Job plot analyses, they were able to determine the binding stoichiometry between A15 and Al^{3+}, which came out to be 2:1. They have stated that probe A15 exhibits strong ICT, PET and -C=N isomerization but upon complexation with Al^{3+} all these processes are restricted, resulting change of color from yellow to colorless as well as ‘turn-on’ fluorescence. Through comprehensive DFT and TD-DFT analysis, they have further confirmed the experimental results. The development of binary logical devices, the retrieval of tainted water samples, and smartphone-based chemical analysis can all benefit from the chemosensing response of A15 to Al^{3+}.

The Zhao group designed and developed an effective triazole-based fluorescent Schiff base (A16) under microwave irradiation for detecting Al^{3+} selectively[66]. They conducted spectral measurements and elemental analysis and determined the structure of fluorescent probe A16. The probe A16 exhibits excellent chemo-selectivity for Al3+ ions, which can be easily detected with the naked eye under UV light, distinguishing it from other metal ions. Al^{3+} makes the fluorescence high of their probe A16 through complex formation in a 1: 1 stoichiometric ratio and they confirmed the latter by Job’s plot, ^{1}H NMR titration and ESI-MS. Their mechanistic approaches behind the fluorescence enhancement of probe A16 upon complexation with Al^{3+} are structural rigidification, restriction of the photo-induced electron transfer (PET-OFF), and inhibition of the -C=N isomerization process. Furthermore, they have ensured the suitability of probe A16 for detecting Al^{3+} in different environments and also in biological samples through the investigation of the optimal pH of the medium which is pH 6-9.

Amirnasr *et al*, synthesized and reported a new colorimetric and fluorescence chemosensor, A17, which is based on a 2-hydroxynaphthalen-scaffolded Schiff base and is selective for sensing Al^{3+} ions. The sensor was characterized by various physicochemical and spectroscopic methods[67]. The A17 probe exhibited enhanced fluorescence and a prominent color change to colorless from bright yellow in the presence of Al^{3+} ions in an aqueous methanol solution. This occurred without interference from other metal ions. Through the use of UV-vis, fluorescence titration, jobs plot analysis and ESIMS, they investigated the binding mechanism of A17 with Al^{3+} and the last two techniques identified the 1:1 stoichiometric ratio. The probe functions as a bidentate ligand binds Al^{3+} with a high binding constant (K_a) and detects Al^{3+} at the micromolar level as well. Using the MTT test, they assessed the cytotoxicity of the probe on the MCF-7 cell line, finding that there was no significant cytotoxicity and over 92% cell viability in the 1.25-50μM concentration range. According to their live cell imaging investigation, A17 can identify Al^{3+} in living cells.

A novel water-soluble fluorescence sensor with salicylaldehyde azine scaffolding for Al^{3+} detection in aqueous solutions has been proposed by Leray *et al*[68]. The addition of sulfonate functional groups makes their probe A18 water-soluble, an essential characteristic for the direct examination of contaminated specimens. They demonstrated how the complexation of Al^{3+} with A18 in water causes an aggregation-induced emission enhancement (AIEE) process that results in the formation of distinct dendritic structures that have been identified using several analytical methods (DLS, FLIM, and SEM). They found that the limit of detection for aluminum (III) was 153nM, which is significantly less than the ~3.7µM World Health Organization (WHO) recommendation. Furthermore, their reported compound A18 has been shown to have good selectivity towards Al^{3+} over a wide range of metal cations. In the end, they included A18 into a digital microfluidic sensor chip, resulting in a portable sub-micromolar detection tool for water samples tainted with Al^{3+}.

To selectively detect Al^{3+} ions in a completely aqueous solution, Lv *et al*, created a porphyrin dimer (A19)[69]. After Al^{3+} complexation, A19 emits a near-infrared (NIR) emission spectrum that is ratiometric. According to their paper, the sensing mechanism is based on the involvement of intramolecular charge transfer (ICT) and photoinduced electron transfer (PET) processes. Using spectroscopic titration, TCSPC study, nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry (MS) and infrared studies, they have thoroughly investigated the binding mechanism of A19 to Al^{3+}. A19 exhibits great selectivity and a low detection limit of 2.65×10^{-8} M in aqueous environments due to the strong interaction between nitrogen atoms and Lewis acid Al^{3+}, which allows A19 to overcome the solvent's high energy barriers for just Al^{3+}. With positive findings, they have looked at the beneficial applications of BPD for Al^{3+} assessment in actual samples and fluorescent prints. Finally, their reported A19 probe is suitable for ratiometric imaging of Al^{3+} in live cells due to its high biocompatibility, lack of organic solvent in its sensing medium, and NIR ratiometric emission capabilities.

The Zhang group developed and characterized a new fluorescent chemosensor (A20) scaffold of crown ether-acylhydrazone[70]. The sensor A20 demonstrated a notable fluorescence "turn-on" response at 444nm in MeOH, indicating strong selectivity and sensitivity identification towards Al^{3+} in preference to other competitive ions. By using fluorescence titration, ESI-MS spectrometry, ^{1}H NMR titration and IR analysis, they were able to establish the suggested binding mechanism of A20-Al^{3+}. The accompanying spectrum modification of probe A20 may be ascribed to the creation of a 2:1 A20-Al^{3+} complex which they have ensured by Job's plot and also reported a micromolar level detection ability of probe A20 by the LOD calculation. Based on several experimental findings, they have been proposed that probe A20 obeyed a mechanism of turn-on fluorescence that involves the inhibition of -C=N isomerization, the ESIPT process and the stimulation of chelation-enhanced fluorescence (CHEF) process. They also used the DFT/B3LYP method for theoretical calculations to get insight into the mechanism of sensing for the Al^{3+} detection and electronic structure of probe A20. Therefore, according to their suggestion, one may see sensor A20 as a useful and efficient fluorescent chemosensor for measuring Al^{3+}.

A new and straightforward Schiff base receptor (A21) that was scaffolded by a chromone was studied by Yang et al. as a sensitive and selective probe for Al^{3+} that exhibited colorimetric and fluorescence responses when exposed to visible light at 423nm[71]. The interaction of their receptor A21 to Al^{3+} in the ethanolic solution produced an excellent selective colorimetric signal that was visible to the unaided eye, transitioning from colorless to yellowish green. They observed a remarkable fluorescence enhancement of A21 to Al^{3+} with a triggered “OFF-ON” signal in contrast to other metal ions. They claim that this increase in fluorescence can be linked to the chelation of receptor A21 with Al^{3+}, which triggers the chelation-enhanced fluorescence (CHEF) process that ends the PET process and restores the fluorescence of the chromone moiety. Their investigated continuous method (Job’s plot) suggests a 2: 1 complexation ratio between the receptor A21 and Al^{3+}, further confirmed by ESI-MS analysis. In addition, they evaluated the limit of detection of receptor A21 for the recognition of Al^{3+}

to be 1 × 10^{-7} M, which is sufficiently low for the detection of Al^{3+} in environmental and biological samples.

A new 'off-on' fluorescent Al^{3+} sensor (A22) has been synthesized and reported by Yang et al. which is a chromone-scaffolded Schiff-base[72]. Al^{3+} in aqueous ethanol could be consistently detected by sensor A22 in the pH range of 5 - 8. They observed a remarkable enhancement in fluorescence at 508nm upon 420nm excitation with the addition of 1equivalent Al^{3+}, showing good selectivity and high sensitivity towards Al^{3+} of sensor A22. They ascribed that the attribution of the emission enhancement is the cancel out of the PET and the -C=N isomerization process of sensor A22 upon complexation with Al^{3+}. Based on the results of the ESI-MS spectrum and the fluorescence titration, they have concluded that the binding ratio of A22 to Al^{3+} is 2:1. Besides, 9.24 x 10^3 M^{-1} is the binding constant (K_a) of A22 to Al^{3+}, they have calculated the limit of A22 for Al^{3+} detection to be 1.82 x 10^{-7} M. Finally, they have demonstrated the sensing property of sensor A22 in the solid state by performing paper strips study using filter paper.

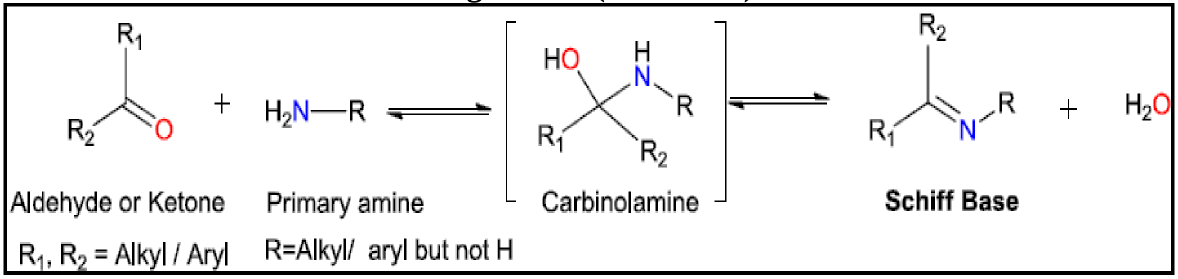
The John group has synthesized and analyzed A23, a Schiff-base molecule, using several spectroscopic techniques[73]. In the presence of Al^{3+}, the chemosensor A23 selectively and against a wide range of other competing metal ions exhibits a cyan color fluorescence ‘turn-on’ response at 462nm. In addition, they saw comparable fluorescence behavior when Al^{3+} was present in a range of solvents and solvent combinations. They have evaluated the stoichiometry and the limit of detection of A23 towards Al^{3+} from UV-vis and fluorescence titration experiments respectively and found them to be 2: 1 and 4.32µM. Forming a complex with Al^{3+} chemosensor A23 enhanced its fluorescence emission and this complex formation is facile in the acidic medium (pH 2-5) rather than the basic medium as their observation in the pH variation study of the solvent containing A23 and Al^{3+}. They reported that the chelation-enhancement fluorescence (CHEF) effect, which is caused by the prevention of -C=N isomerization, may be the cause of the fluorescent enhancement of A23 upon complexation with Al^{3+}. Their calculations on A23, its anionic part and its aluminum complex using DFT and TD–DFT provide information on the electronic, geometric, thermodynamic, and optical characteristics of the chemosensor A23 and the interactions with Al^{3+}.

Sahoo *et al,* have developed and reported a novel Al3+ selective fluorescence turn-on sensor (A24) scaffold of hydrazidenaphthalic anhydride conjugate[74]. Their probe A24 exhibited a clear color shift from light brown to colorless in an aqueous DMSO solution due to its selective and specific character towards Al^{3+}, which was achieved by quenching and a blue shift in the absorption of A24 at 465nm. Under the same conditions, they observed that the receptor A24, which has weak fluorescence, exhibited a significant increase in fluorescence at 555nm when exposed to Al^{3+} in comparison to other metal ions and anions that were tested. The researchers evaluated the selective complexation of A24 to Al^{3+} using ^{1}H NMR and DFT methods. They demonstrated the reversible complex formation of A24 with Al^{3+} by the addition of EDTA, a strong chelating agent and Al^{3+} can be detected with their receptor A24 down to 2.9µM with the 1: 1 stoichiometric binding ratio. The turn-on fluorescence at 555nm is the consequence of the complex formation of A24 with Al^{3+}, which has altered the PET and ICT efficiency of the fluorophore. They saw a sharp increase in fluorescence following complexation formation with Al^{3+}, which they attributed to the suppression of PET and the chelation-enhanced fluorescence (CHEF) mechanism. Finally, they have successfully applied the Al^{3+} detection of receptor A24 in live HeLa cells.

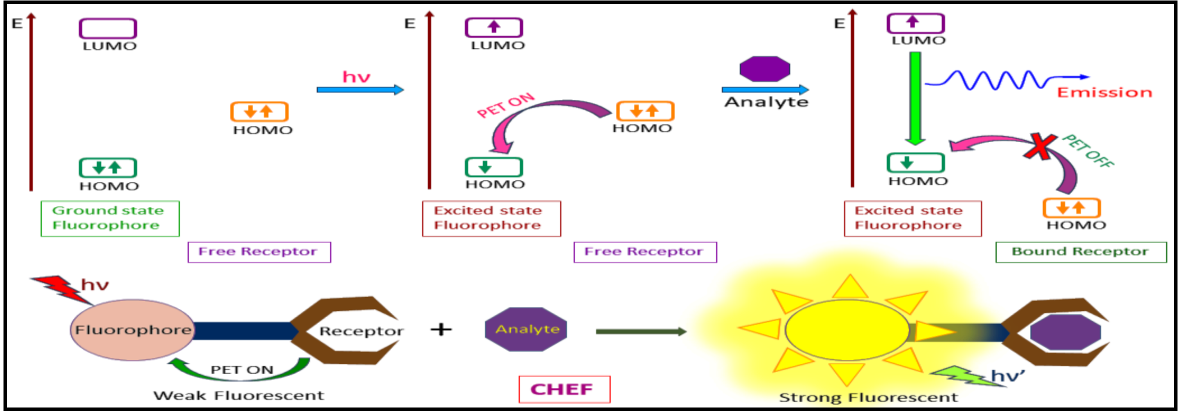
Table No.1: Summary of recently reported Schiff base Al^{3+} chemosensors and their selective analytical parameters

Chemo sensors	Solvents	Sensing methods	Binding ratio (L: Al^{3+})	Binding constant (M^{-1})	LOD	Applications	Ref.
A1	aqueous CH_3CN	C=N isomerization; Inhibition of PET	1: 2	1.58×10^{7}	51.5nM	Test kits, food samples, drinking water	52
A2	aqueous DMF	ESIPT; C=N isomerization; CHEF	1: 1	3.48×10^{3}	119nM	Test kits	53
A3	DMSO and EtOH	Inhibition of PET	1: 2	5.6×10^{5}	7.41μM	Test strips	54
A4 and A4’	DMSO/H_2O	C=N isomerization; ESIPT	1: 2 1: 2	-----	19.8nM 47.9nM	Test strips	55
A5	DMSO/H_2O	C=N isomerization; ICT	1:1	3.07×10^{4}	82.5nM	water samples, Cell imaging	56
A6 & A6’	H_2O	ESIPT; CHEF	3:1 3:1	1.1×10^{4} 5.7×10^{3}	1.67μM 7.1μM	DNA bioimaging, Paper strip	57
A7	MeCN/H_2O	C=N isomerization; ESIPT	2: 1	5.62x 10^{4}	11.9nM	Water samples, Cell imaging	58
A8	DMSO/H_2O	C=N isomerization; Inhibition of PET	1: 1	4.02x 10^{4}	39nM	Paper strip, Cell imaging	59
A9	C_2H_5OH-HEPES	C=N isomerization; Inhibition of PET	1: 2	1.21×10^{8}	0.113μM	food samples, drinking waters, and herbal teas	60
A10	MeCN-HEPES	ESIPT; CHEF; PET; C=N isomerization	1:2	2.9×10^{9}	7.0nM	Paper strip	61
A11	EtOH/H_2O	CHEF	1: 1	1.51×10^{4}	5.98nM	Cell imaging	62
A12	MeOH	ICT	1: 1	0.23x 10^{6}	9.8nM	-----	63
A13	DMSO	ICT; CHEF	1: 1	3.2×10^{3}	1.3μM	-----	64
A14	MeOH/H_2O	Inhibition of PET; CHEF	2: 1	3.02×10^{8}	256nM	Cell imaging	65
A15	methanol–Tris–HCl buffer	ICT; PET; C=N isomerization	2: 1	1.76x 10^{2}	0.12μM	INHIBIT logic gate, color image	66
A16	EtOH/H_2O	PET; C=N isomerization	1: 1	9.3×10^{4}	29.9nM	------	67
A17	MeOH/H_2O	ICT; CHEF	1: 1	1.6×10^{5}	0.64μM	Cytotoxicity; Cell imaging	68
A18	H_2O	AIEE	---	---	153nM	digital microfluidic sensor chip	69
A19	H_2O	ICT; PET	1: 1	3.1×10^{7}	0.27nM	Cell imaging	70
A20	MeOH	CHEF; C=N isomerization	2:1	8.19×10^{7}	0.24μM	------	71
A21	EtOH	PET; CHEF	2:1	2.5×10^{3}	0.1μM	-----	72
A22	EtOH/H_2O	PET; C=N isomerization	2:1	9.24x 10^{3}	0.18μM	Paper strip	73
A23	MeOH/H_2O	CHEF	2:1	2.1×10^{4}	4.32μM	------	74
A24	DMSO/H_2O	PET; CHEF	1: 1	1.5×10^{3}	2.9μM	Cell imaging	75

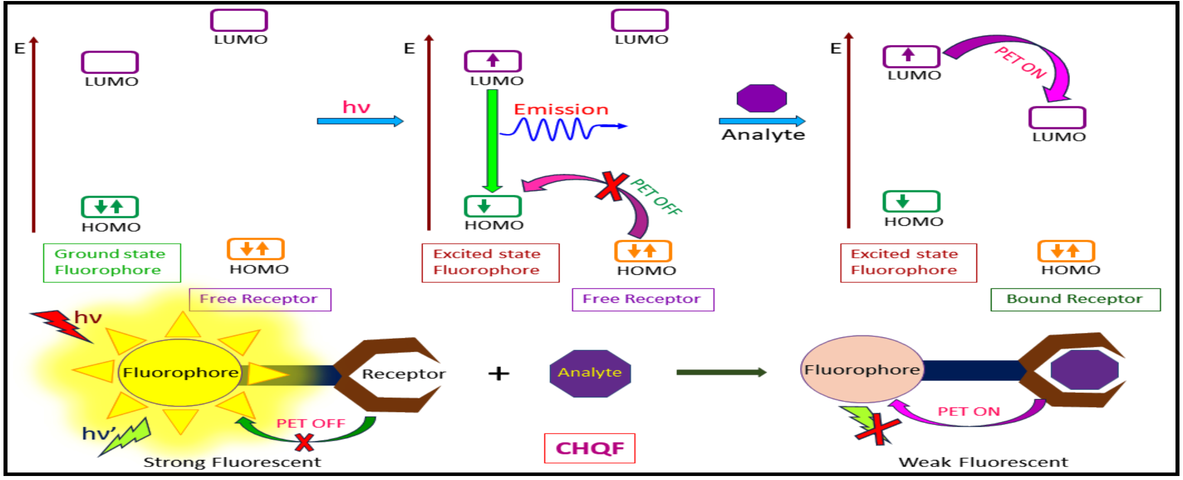
Hugo Schiff (1834-1915)



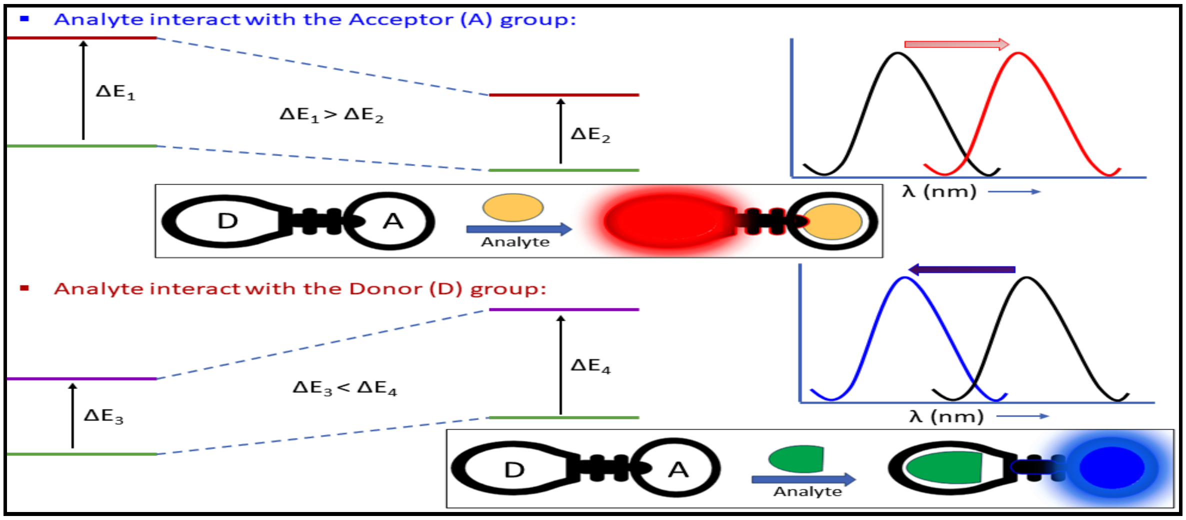
Scheme No.1: General schematic route of Schiff base synthesis



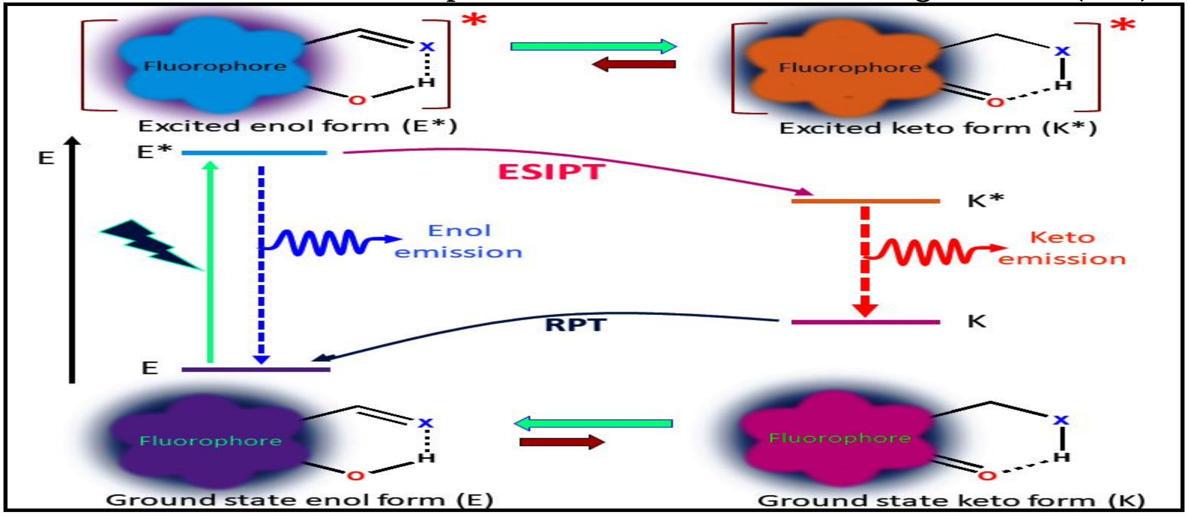
Scheme No.2: Mechanism for chelation-enhanced fluorescence (CHEF)



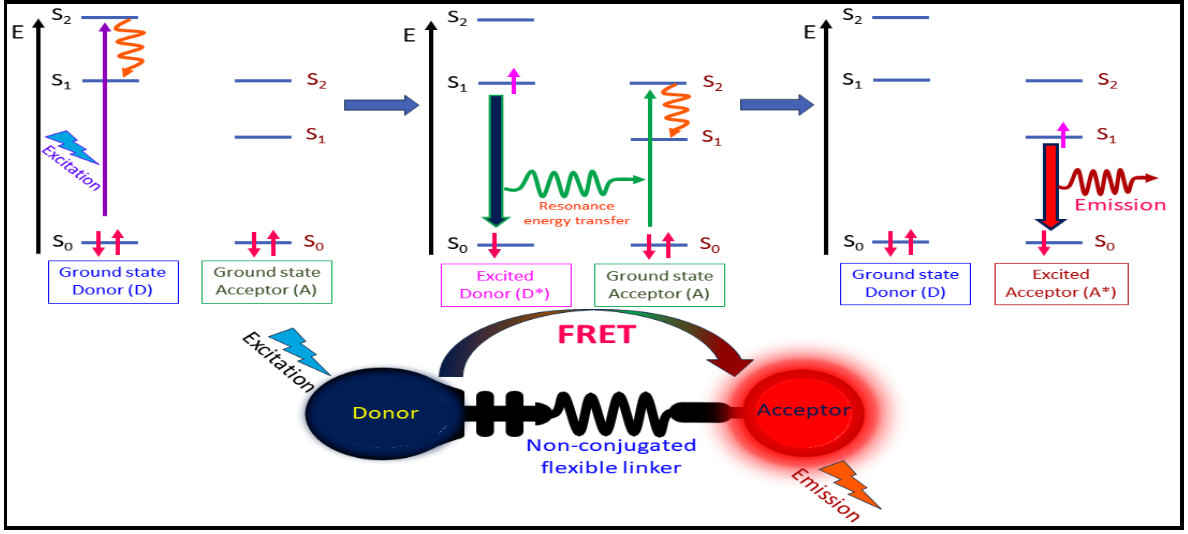
Scheme No.2: Mechanism for chelation-quenched fluorescence (CHQF)



Scheme No.3: Mechanism for photoinduced intramolecular charge transfer (ICT)

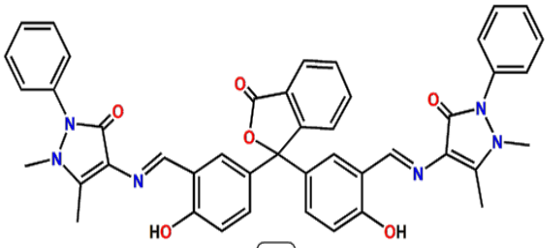


Scheme No.4: Mechanism for excited-state intramolecular proton transfer (ESIPT)



Scheme No.5: Mechanism for intramolecular fluorescence resonance energy transfer (FRET)

Recent developments of Al^{3+} chemosensors and their applications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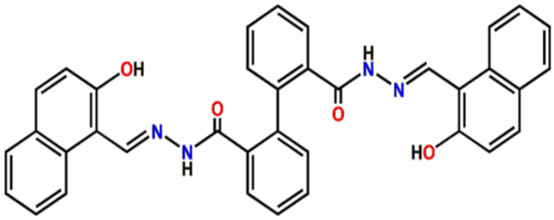
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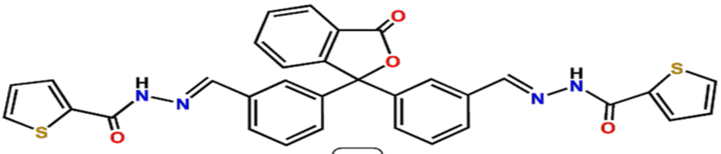
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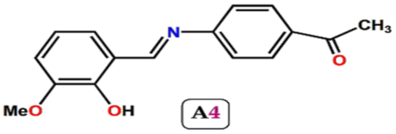
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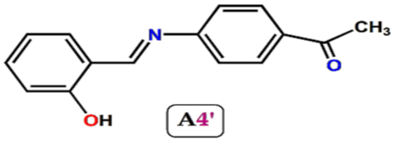
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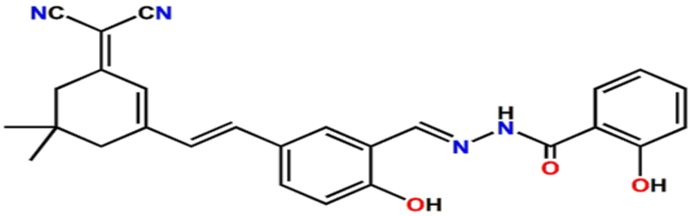
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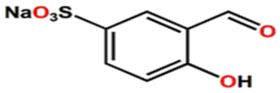
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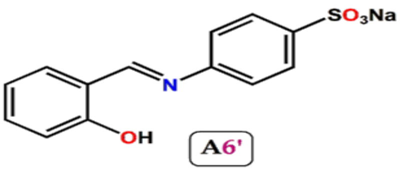
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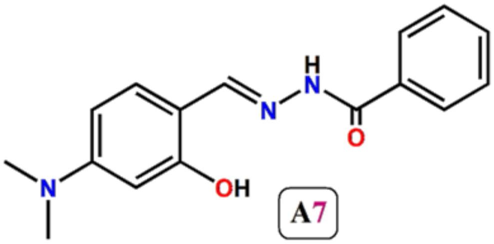
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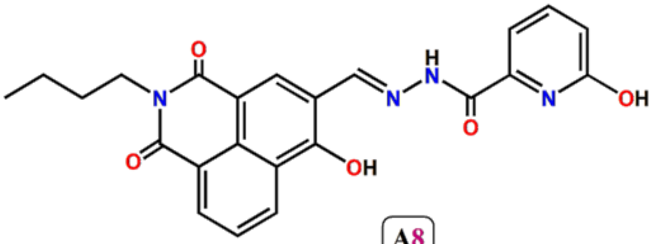
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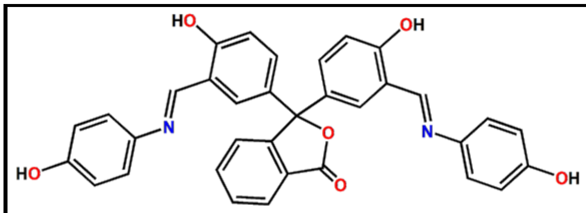
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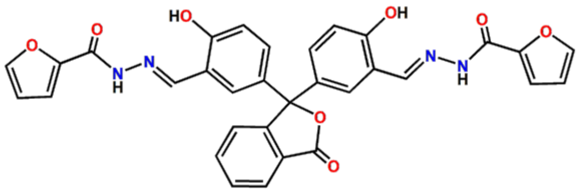
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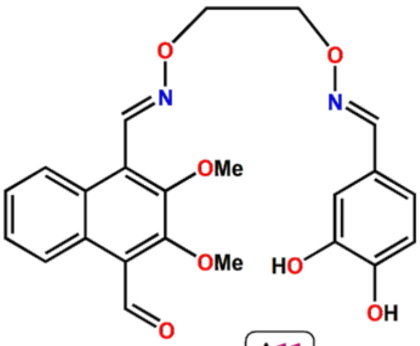

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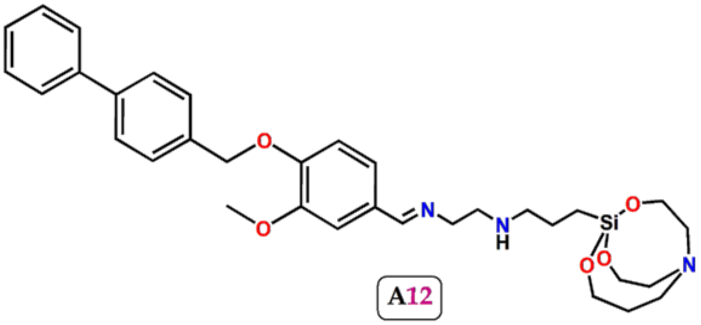

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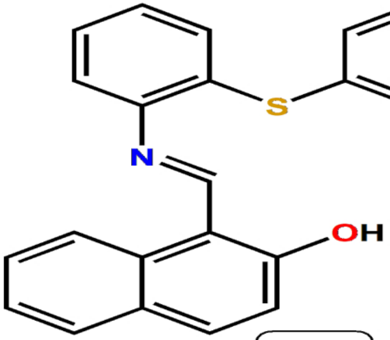

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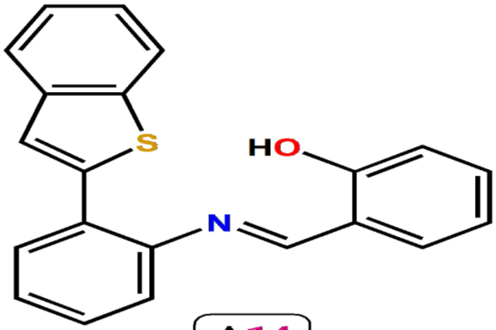

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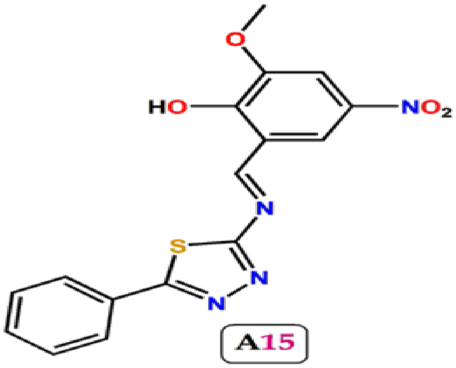

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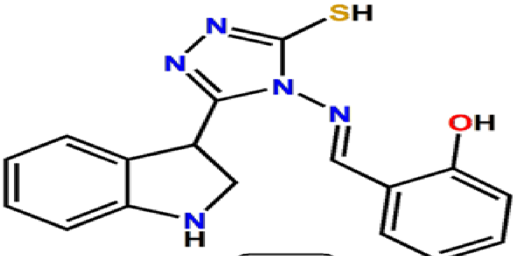

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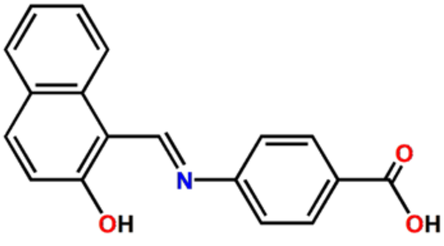

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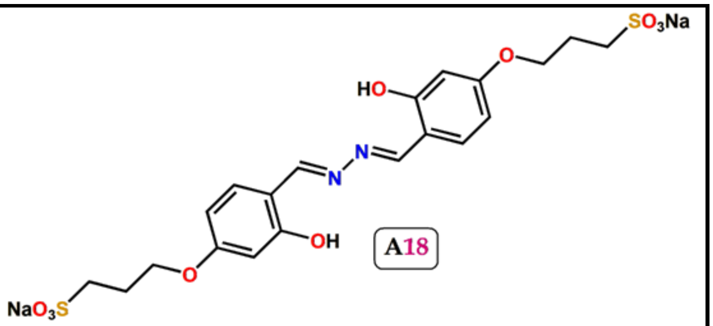

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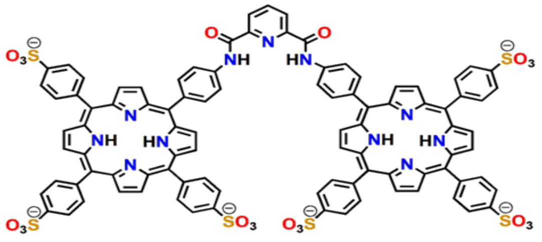

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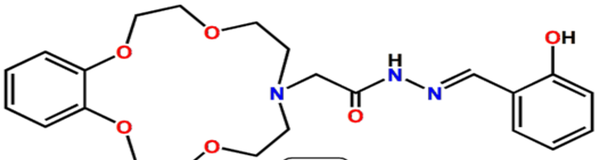

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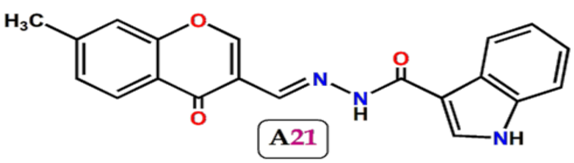

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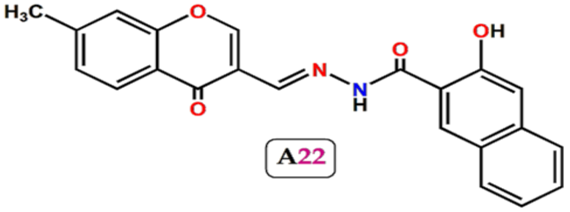

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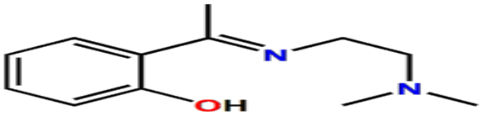
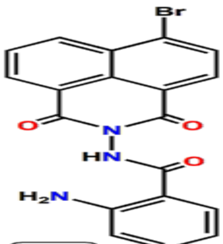


A23



A24

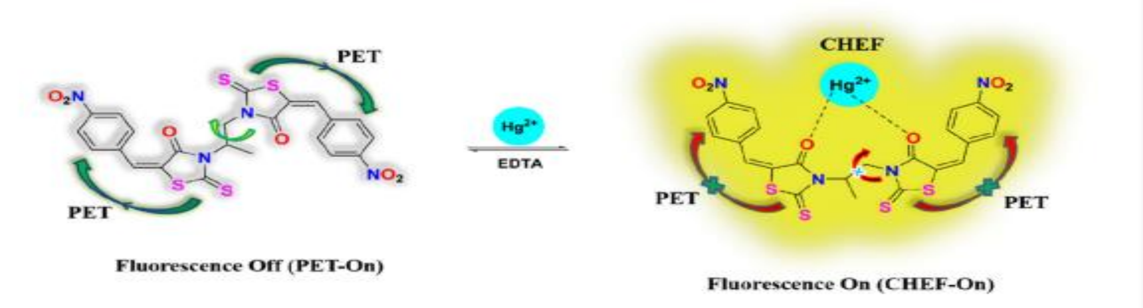


Figure No.1: Example of a chemosensor following CHEF mechanism for sensing of analyte

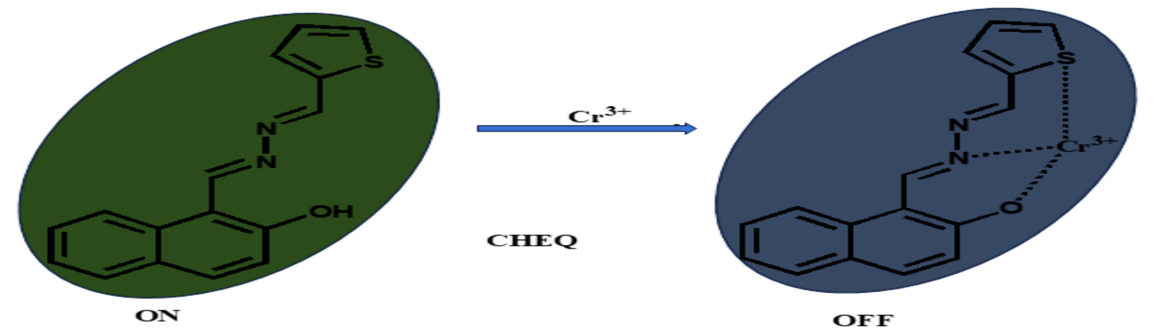


Figure No.2: Example of a chemosensor following CHQF mechanism for sensing of analyte

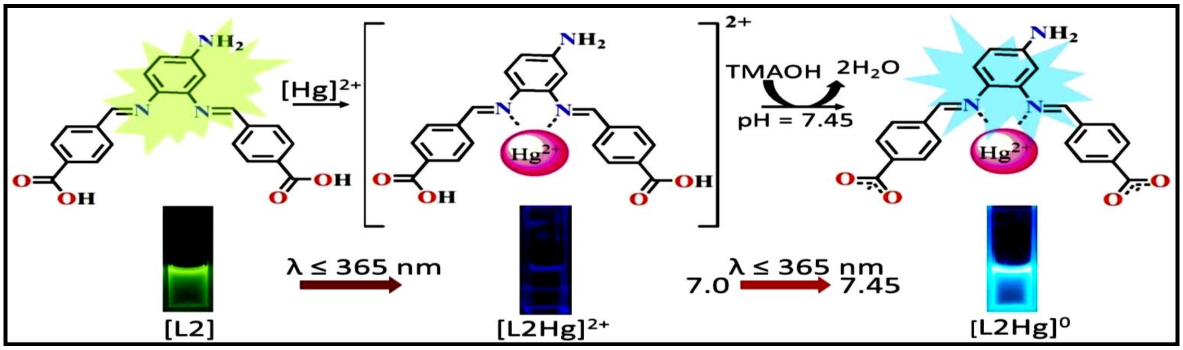


Figure No.3: Example of a chemosensor following ICT mechanism for sensing of analyte

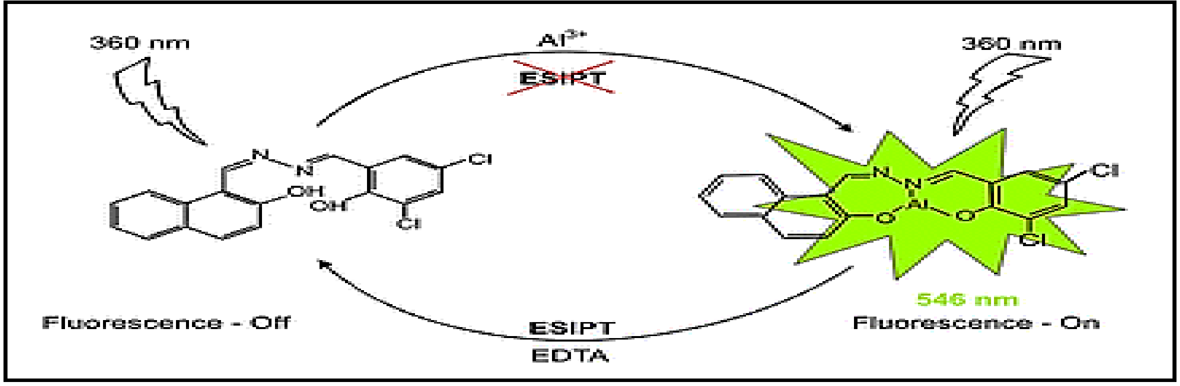


Figure No.4: Example of a chemosensor following ESIPT mechanism for sensing an analyte

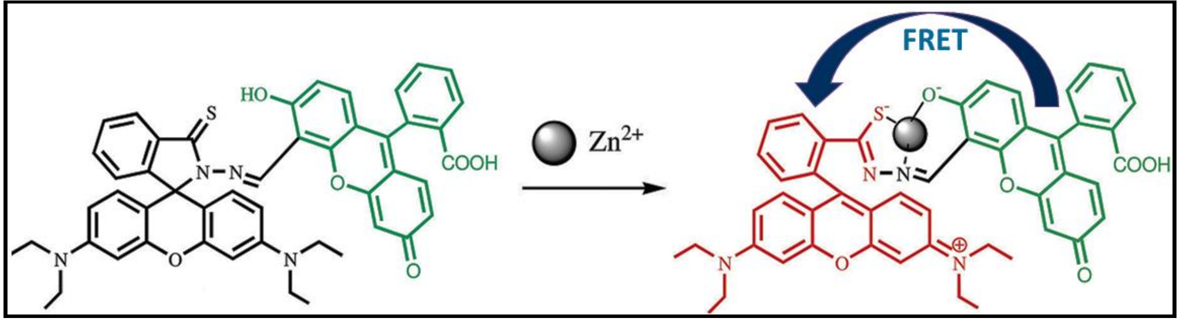


Figure No.5: Example of a chemosensor following the FRET mechanism for sensing an analyte

CONCLUSION

This review summarizes the recent applications of Schiff bases for the chromo-fluorogenic sensing of Al^{3+} and takes a detailed discussion about the major mechanisms being followed by Schiff bases during the sensing of metal ions. Schiff bases are well-known for their various biological activities (like anti-inflammatory, antibacterial, antifungal, anticancer, antimalarial, antioxidant, anti-ulcerogenic, antiviral, antiglycation, etc.). Schiff bases are also widely applied for the chromo-fluorogenic sensing of metal ions including Al^{3+} due to their fascinating coordination behavior. The presence of an azomethine-N donor atom makes the Schiff base a good chelator to complex metal ions. The Schiff bases can be easily synthesized in one or a few steps and can be structurally modified to design a variety of sensors with multi-donor sites to coordinate metal ions more effectively. The commonly used mechanisms for metal ions detection include self-assembly/disassembly, aggregation/disaggregation, photo-induced electron transfer (PET), intra/intermolecular charge transfer (ICT), metal-to-ligand charge transfer (MLCT), ligand-to-metal charge transfer (LMCT), fluorescence resonance energy transfer (FRET), excited state intramolecular proton transfer (ESIPT), and C=N isomerization. Metal ions upon coordination with Schiff base sensors generally show fluorescence enhancement or quenching leading to the CHEF or CHEQ effect, respectively. Among all these mechanisms, widely followed mechanisms by Schiff base chemosensors like PET, CHEF or CHEQ, ICT, FRET and ESIPT are discussed here elaborately.

This review summarizes 24 Schiff base sensors and their chromo-fluorogenic sensing ability of Al^{3+} was discussed. Most of the sensors are highly selective and sensitive towards Al^{3+}. The spectral changes of the Schiff bases have occurred mainly after complexation. Therefore, the CHEF mechanism was dominant in explaining the change in the fluorescence behavior. Mechanisms like C=N isomerization, ESIPT, ICT and PET were utilized to explain the sensing mechanism of the sensors. Interestingly, most of the summarized sensors showed fluorescent turn-on response upon complexation with Al^{3+}, which makes them ideal for various bioimaging applications. Most of the developed sensors are applied for the quantification of Al^{3+} in real environmental samples and to detect Al^{3+} in live cells through fluorescence bioimaging. We believe this review will be useful in learning the recent advancement in the Al^{3+} sensing using Schiff bases and also the researchers will get future ideas to design new Schiff bases with improved analytical parameters for the sensing of Al^{3+} and other biologically and environmentally important metal ions.

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CONFLICT OF INTEREST

There are no conflicts to declare.

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