



Review article

# Chalcogenated Schiff base ligands utilized for metal ion detection

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## ABSTRACT

Metal poisoning has recently arisen as a global concern, which imposes a significant threat to both the environment and human health. Schiff bases and related metal ion complexes are being researched due to their remarkable applications in metal ion detection. Here in this review, we present many chalcogenated sensors for metal ion detection for both biological and heavy metals and a comparison based on detection limit and sensor techniques is discussed. This review also describes the performance of the Schiff base with a multi-donor set for metal ion detection. Aside from prospects, this evaluation offers a general guide to using such environmentally beneficial Schiff bases to identify dangerous chemicals. This review discusses recent advancements in the detection system of metal, including their synthesis methods and sensing applications for the detection of heavy metal ions such as Iron (III), Mercury (II), Copper (II), Chromium (VI), Lead (II), Cobalt (II), Aluminum (III), Zinc (II), Silver (I), and Gold (III), all of which are major environmental pollutants. Different mechanisms of detection such as ICT, IFE, CHEF, CHEQ, etc are also discussed here in detail with examples.

## 1. Introduction

Metal ions are hazardous to both human health and the environment so metal detection systems are becoming more important as metal concentrations rise due to industrialization and urbanization [1–5]. Metals are essential in medicine to keep serum lithium and potassium levels under control in patients being treated for manic depression or high blood pressure [6]. Although various approaches are accessible, and despite previous successes, new work in these areas is necessary. The Schiff base is capable of detecting various metal ions as it contains an azomethine unit [7]. Although Schiff bases are well known for their different biological and catalytic applications [8–10]. Schiff bases are a kind of ligand that has a wide range of applications in coordination chemistry. Their donor–acceptor ease with different metal ions provides

efficient use in metal ion detection. They may act as multidentate ligands for transition and typical metals and anions [11–20]. As a result, significant effort is being put into building viable sensors capable of detecting and evaluating heavy, transition metal ions, and anions in biological systems to detect serious human illnesses include cancer, diabetes, neurological disorders, and cardiovascular disease [21–24]. In agriculture, it is useful for the detection of organophosphate, nitrite, and carbamate insecticides. [25,26]. Two broad metal detection approaches that are being explored are “recognition” and “reactivity” by Aron et al. 2015. For example, a recognition-based approach is used to construct transition metal probes for copper and nickel, whereas the approach provided here is employed to study cobalt and iron in Fig. 1 [27].

Metal ions also play an important role in donor selection, depending on donor groups and the type of ligands. Several studies have reported

*Abbreviations:* DAP, N0-((1E,2E)-3-(4-(dimethylamino)phenyl)allylidene)-3-nitrobenzohydrazide; ROS, Reactive oxygen species; GSH, Glutathione; AIE, Aggregation-induced emission; ESIP, Excited-state intramolecular proton transfer; FRET, Forster resonance energy transfer; LMCT, Ligand to metal charge transfer; ICT, Intra/intermolecular charge transfer; TICT, Twisted intramolecular charge transfer; CHEF, Chelation enhancement fluorescence; IFE, Inner filter Effect; NBSPD, N,N'-bis(salicylidene)-2,6-pyridine-diamine; MPMNP, (2-[(4-methoxy-phenylamino)-methyl]-4-nitro phenol); DSAB, (2-((E)-1,2-diphenyl-2-[(2-2-sulfanylphenyl)imino]ethylideneamino)-1-benzenethiol); MCPH, methoxy chromone-3-carbaldehyde-(30,40-dimethyl)pyrrole hydrazone; MTT, 3-(4,5-dimethyl thiazole-2-yl)-2,5-diphenyl tetrazolium bromide; 4-DHBB, (E)-N'-(4-(diethylamino)-2-hydroxybenzylidene)-2-(benzamido)benzo hydrazide; NDBHC, N'-(4-diphenylamino) benzylidene) hydrazinecarbothiohydrazide; CHEQ, chelation-enhanced fluorescence quenching; SNN, N-(1-thien-2-ylethylidene)benzene-1,2-diamine; NHT, thiophene-substituted naphthyl hydrazone derivative; QT, 8-aminoquinoline thiophene-2-carboxaldehyde; MTT, 3-(4,5-dimethyl thiazole-2-yl)-2,5-diphenyl tetrazolium bromide; HMBT, 2-((5-(2-hydroxy-3-methoxybenzylideneamino)-2H-1,2,4-triazole-3-ylimino)methyl)-6-methoxyphenol; MCAH, 7-methoxy chromone-3-carbaldehyde-((2'-Benzothiazolylthio)-acetyl) hydrazone; HNAT, 2-hydroxy-1-naphthaldehyde-2-amino thiazole; NIMN, 1-[(2-naphthalenylimino)methyl]-2-naphthalenol; MTMBT, 2-((3-methylthiophen-2-yl) methylene-amino)benzenethiol; AR, Aminated rhodamine; AA, Antraldehyde; LOD, Limit of detection; LOQ, Limit of quantification; TPA-Py, triphenylamine-functionalized salicylaldehyde-pyridine.

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that the complexes of more versatile containing both hard and soft donor groups [28–30]. Although a broad variety of donors are available only a few atoms are commonly used which include S, P, N, O [248], and whereas As, Se, and Te to a lesser extent [31–33]. X. Zhang, Wu, et al. in 2021 studied various metal–ligand interactions and through various mechanisms, metal ions can be detected which depends on various factors such as time, temperature, pH, and concentration via multimetallic ion sensing, cumulative or stepwise sensing. Here is an example of a cumulative sensor that depends on the concentration of  $\text{Cu}^{2+}$  ion as shown in Fig. 2. The ligand triphenylamine-functionalized salicylaldehyde-pyridine first reacts with  $\text{Cu}^{2+}$  ([ligand]: $[\text{Cu}^{2+}] = 1:1$ ), which further reacts with an extra  $\text{Cu}^{2+}$  ion to afford 2TPA-Py-4  $\text{Cu}^{2+}$  with the following stepwise with excellent sensitivity and specificity toward  $\text{Cu}^{2+}$  ions in THF/water media with a low limit of detection of 26.87  $\mu\text{M}$  [34].

The existence of additional functional groups in the initial carbonyl and/or amine used to synthesize the Schiff base gives the imine with two or more distinct donor atoms to chelate metals and ions, primarily nitrogen, oxygen, and sulphur, but also phosphorus, selenium, and tellurium [35–37]. The chalcogen bond has evolved as an unusual sort of non-covalent contact that provides a helpful synthetic tool for catalysis, and metal or anion sensing has become one of chemistry's frontiers [38–44]. Certain redox catalysts containing selenium and tellurium atoms have shown great promise since they are non-toxic on their own but produce an effective, frequently selective cytotoxicity when the 'proper' intracellular redox partners are present [45]. Furthermore, the presence of donors with opposing features, such as an N-donor and an O/S/Se/Te-donor, changes the selection of metal ions as well as the stability, spectroscopic, and redox properties of their complexes [27,34,46–55]. A pictorial presentation of electronic transition and different mechanisms of colorimetric and fluorometric detection is shown in Fig. 3.

## 2. Metal ions toxicity

Metal ions are necessary for all kinds of life to survive because they allow all cells inside living organisms to operate appropriately. There are two sorts of significant biologically relevant metals in the living system. The first is Group I and II metals, which comprise  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  and are abundant in most living things. Second, the most dangerous metal ions are  $\text{Pb}^{2+}$ ,  $\text{As}^{3+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Cu}^{2+}$ , which are classified as heavy metal ions and have a significant impact on a variety of environmental contamination problems [56,57]. Metal poisoning is now recognized as one of the most serious threats to agricultural productivity, with the possibility to become significantly more common in the coming decades. Among the 52 metals that have a

concentration-dependent impact on plant performance are Pb, Mn, Cu, Ni, Co, Cd, Hg, and As [58,59]. Micronutrients and macronutrients, when present at sufficient levels, support the operation of essential enzymes and regulate metabolic processes such as photosynthesis, DNA synthesis, protein modifications, sugar metabolism, and redox equilibrium. Chemicals, in greater concentrations, are hazardous and can kill all lifeforms, including plants and animals [60–62]. In contrast, the presence of metal ions at levels greater than or less than the permitted limit (Table 1) may be harmful to both the environment and people. ICP, AAS, ICPMS, electrochemical detection, and ion chromatography were formerly employed in metal ion detection technologies [63–66].

Schiff bases are molecular devices that modify one or more system attributes, such as electrical, electronic, magnetic, or optical signals, to transfer chemical information into electronic transition [71]. These features prove Schiff base sensors useful in metal ion detection, biological imaging, environmental monitoring, and optoelectronic systems. The most difficult and crucial area of investigation is just recognizing or identifying them [72–81]. Among known sensors, Schiff bases are well-known chemosensors for sensing cations as well as anions [82–86]. Sensors with molecular architectures made of a crown ether, naphthalene, coumarin, pyridines, pyrene, and quinolones have been created to bond with metal ions for selective and sensitive detection of various metal ions has received remarkable attention since exposure to metal ions could lead to several diseases in human beings [87–90]. So research is going on for this purpose to identify different metal ions via various mechanisms such as PET, ESIPT, FRET, CHEF, CHEQ, and Excimer formation which is generally based on electron/proton transfer or electronic interactions [91–97].

## 3. Chalcogenated Schiff base sensors

Schiff bases may coordinate with almost any metal ion by N-atom of the azomethine group with extra donating atoms of nitrogen, oxygen, or sulphur atoms close to the azomethine group [98]. Hemilabile hybrid ligands are chalcogenated Schiff bases with both soft and 'hard' donor sites. Because of their metal chelation, such ligands have been frequently employed as catalysts and chemosensors [99]. They have an interesting catalyst and sensor design. The invention and use of new ligands for the manufacture of efficient sensors and long-lasting catalysts is an intriguing subject to investigate, and sensors are plentiful [100,101]. Mostly Schiff bases used as metal ion detection of  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Pb}^{2+}$  [102–107]. Oxygen Sulphur, selenium, and tellurium-containing ligands are environmentally friendly and less hazardous compared to phosphorus, arsenic, and mercury complexes which are widely carefully

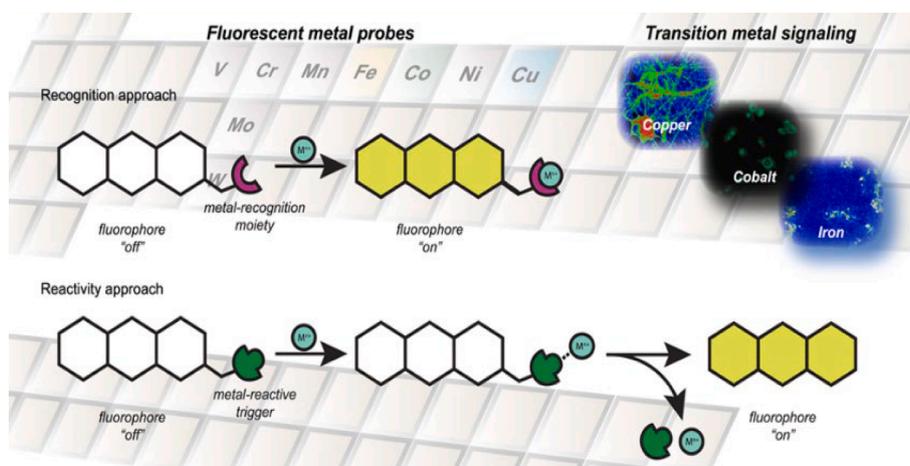


Fig. 1. Representation for detection strategies recognition and reactivity (Figure is reproduced by the permission taken from ACS, copyright).

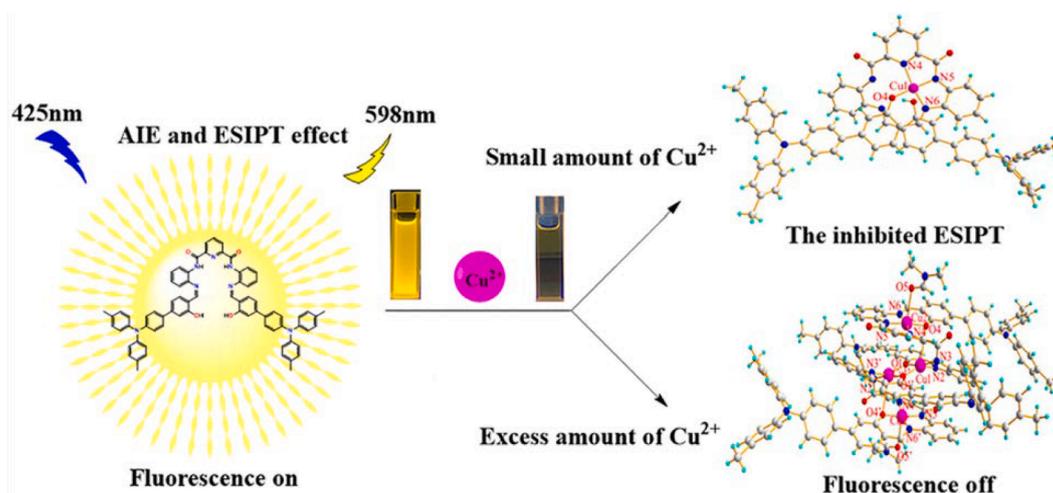


Fig. 2. AIE and ESIPT effect with cumulative sensing effect by the ligand TPA-Py (Figure is reproduced by the permission taken from ACS, Copyright).

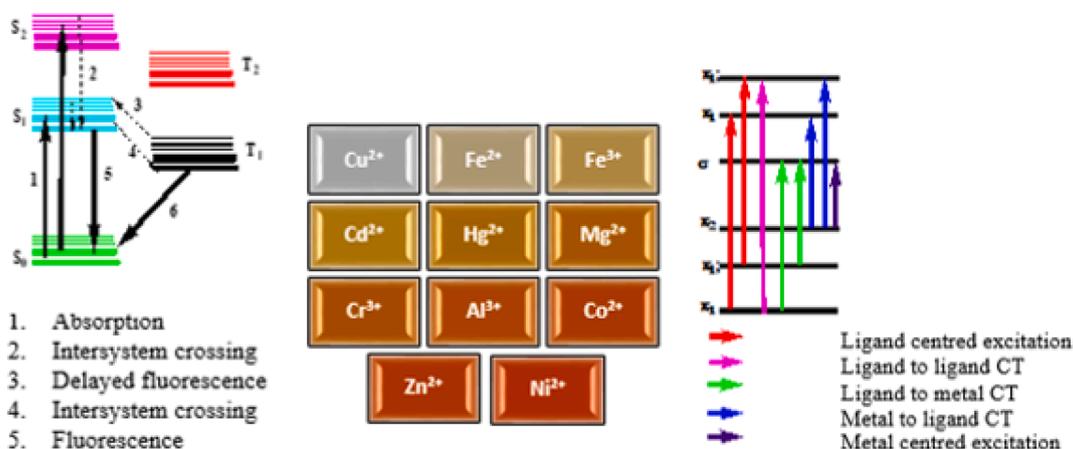


Fig. 3. Electronic transition and different mechanisms of colorimetric and fluorometric detection.

studied but they harm the environment. However, there has been increasing interest in S/Se/Te ligands in recent years which are suitable replacements [108–110]. Detty et al. developed a series of organic-selenium/-tellurium dye fluorescent compounds sensitive to redox processes [111]. Since then, innovative chalcogen-based fluorescent compounds have been employed in biomedical imaging and as chemosensors to detect endogenous oxidants, thiols, and specific metals. However, very few reports of tellurium-based chemosensors have been published due to the various obstacles of tellurium-based molecular systems [111–120]. One of the examples is discussed here, Tellurium-Rhodamine-based fluorescence probes (1) were developed (Scheme 1) which is based on the oxidation of tellurium by  $\text{Hg}^{2+}$ , a technique for detecting  $\text{Hg}^{2+}$  was seen and well understood (2). TR, a new monomer chemosensor, exhibits a high fluorescence quantum yield of 0.41, excellent selectivity, and exceptional sensitivity to  $\text{Hg}^{2+}$ , with a detection limit of 2.95 mol/L [121].

It was developed that a near-IR reversible fluorescent probe with an organoselenium (3) may be used to monitor peroxynitrite oxidation and reduction events under physiological conditions sensitively and selectively (4) as shown in Scheme 2. When tested in both aqueous solution and living cells, the probe successfully avoided the effects of autofluorescence in biological systems and generated favorable results [116].

Among chalcogenated Schiff bases with thioether, donor sites have attracted more attention [122–124]. For example, Schiff bases 5

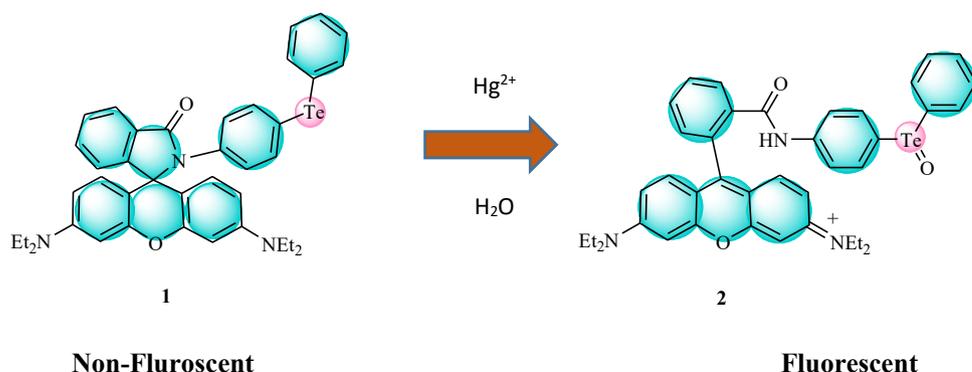
containing nitrogen, sulphur, and oxygen donor atoms, were designed and synthesized in a multi-step reaction sequence (Chart 1). The Schiff base 5 was used in solvent extraction of metal chlorides such as Cu(II) from the aqueous phase to the organic phase and the concentration of the extractant was investigated to shed light on their chemical extracting properties upon the extractability of metal ions [125].

Tellurium is the most common non-radioactive element in the chalcogen family, which also contains oxygen, sulphur, and selenium. Tellurium's primary industrial application has traditionally been metallurgy [126,127]. Organotellurium chemistry has advanced rapidly in the recent two decades or more, embracing a wide range of applications [127–132]. The simplest organotellurium ligands were thought to be difficult to synthesize because of their sensitivity to oxygen. Mostly only monodentate tellurium ligands are well-known [133]. Telluroxides are structurally similar to sulfoxides and selenoxides. organotellurium compounds are being studied to fully understand metal–ligand dynamics and their potential use in the synthesis of catalysts [134–141]. Due to the volatility of selenols and tellurools, creating arylselenolato and telluroloato ligands is often more difficult than making phenolato and thiophenolato ligands. However, there is scant data on the use of metal complexes containing organotellurium ligands in medicine and catalysis [142,143]. Typically, selenium is part of the probe's reactive, or active site; in other circumstances, it is the analyte, either as a reduced or oxidized form of selenium. In addition, the link between reduced and oxidized selenium is explored [144]. It is discussed the chemistry of a

**Table 1**

WHO (World Health Organization) permissible metal concentration levels in drinking water and metal ion RDA (recommended daily allowance) in the human body.

Metal ion	In human body	In drinking water	Author name	Ref.
Fe <sup>2+</sup> / Fe <sup>3+</sup>	8 mg day <sup>-1</sup>	0.3	M. Kumar (2012) et al., F. S. Al-fartusie (2017) et al., A. L. Berhanu (1962) et al.	[67–69]
Ni <sup>2+</sup>	80–130 µg day <sup>-1</sup>	0.0008	M. Kumar (2012) et al., F. S. Al-fartusie (2017) et al., A. L. Berhanu (1962) et al.	[67–69]
Cu <sup>2+</sup>	2 mg day <sup>-1</sup>	1.0	M. Kumar (2012) et al., F. S. Al-fartusie (2017) et al., A. L. Berhanu (1962) et al.	[67–69]
Cr <sup>3+</sup>	50–200 mg day <sup>-1</sup>	0.05	A. L. Berhanu (1962) et al.	[69]
Mg <sup>2+</sup>	~300–400 mg day <sup>-1</sup>	50	M. Kumar (2012) et al., F. S. Al-fartusie (2017) et al.	[67,68]
Ca <sup>2+</sup> Mn <sup>2+</sup>	– 2.3 mg day <sup>-1</sup>	75 0.1 mg/l	M. Kumar (2012) et al. M. Kumar (2012) et al., F. S. Al-fartusie (2017) et al., A. L. Berhanu (1962) et al., J. K. Fawell (2004) et al.	[67] [67–70]
Hg <sup>2+</sup>	–	0.001–65	M. Kumar (2012) et al., A. L. Berhanu (1962) et al.	[67,69]
Zn <sup>2+</sup>	8 mg day <sup>-1</sup>	5.0	F. S. Al-fartusie (2017) et al., A. L. Berhanu (1962) et al.	[68,69]
Cd <sup>2+</sup>	–	0.005	M. Kumar (2012) et al., A. L. Berhanu (1962) et al.	[67,69]
Al <sup>3+</sup>	3–10 mg day <sup>-1</sup>	0.03 mg l <sup>-1</sup>	F. S. Al-fartusie (2017) et al., A. L. Berhanu (1962) et al.	[68,69]
Co <sup>2+</sup>	5–40 µg day <sup>-1</sup>	0.001	M. Kumar (2012) et al., F. S. Al-fartusie (2017) et al., A. L. Berhanu (1962) et al.,	[67–69]
Sn <sup>2+</sup> Pb <sup>2+</sup>	– 93.5 µg day <sup>-1</sup>	1–2 µg l <sup>-1</sup> 0.05	J. K. Fawell (2004) et al. M. Kumar (2012) et al.	[70] [67]

**Scheme 1.** Tellurium-Rhodamine (TR)-based fluorescence probes.

series of azomethine macrocycles with selenium/tellurium atoms in *o*-positions concerning the C=N bond. The macrocyclic polyamine ligands, which are formed by reducing the appropriate Schiff bases, readily form complexes with a variety of metal ions, with the same denticity but differing flexibility. Other Seleno- and telluric-macrocycles (**6–8**) are also given for comparison (Chart 2) [145,146].

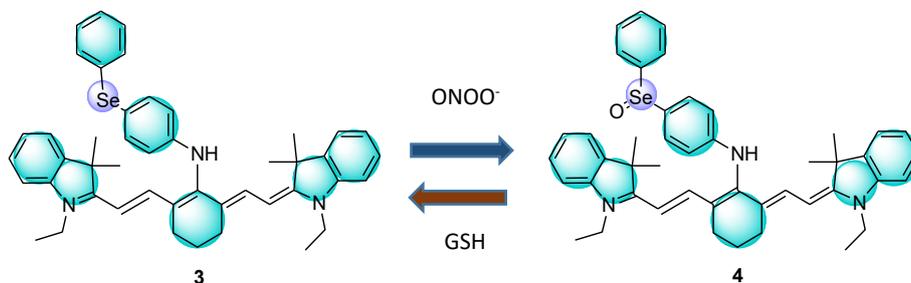
Secondary interactions with heavier chalcogens (Se, Te) are more common than secondary interactions with sulphur. Tellurium chemistry, in particular, demonstrates “intramolecular coordination” in the form of diazenes, pyridines, amines, and carbonylic compounds because (Se, Te) in azamacrocycles would boost anion binding selectivity over plain aza monocycles [144,145,147] resulting in a puckered structure rather than a flat structure for the monocycle. Chalcogens (Se, Te) azamacrocycles (**9–16**) are shown in Chart 3 [145].

**1**, 8-anthraquinone-18-crown-5 sulphur (**17**), selenium (**18**), and tellurium (**19**) derivatives were produced by reacting Na<sub>2</sub>S, Na<sub>2</sub>Se, Na<sub>2</sub>Te (Chart 4). The optical properties of the new compounds are investigated, and the sulphur and selenium analogs exhibit a significant increase in green emission when combined with Pb(II) in acetonitrile. Titrations with UV–Visible and luminescence reveal that **17** and **18** form 1:1 complexes with Pb<sup>2+</sup> [148].

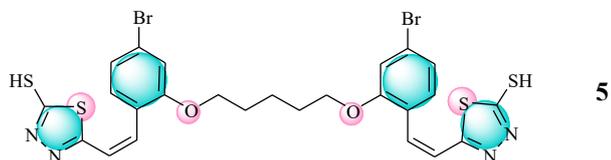
Supramolecular chemistry is involved too for sensing material in the construction of potentiometric ion selective electrodes (**20–23**) for different metal ion sensing (Chart 5) [149].

A. Abbaspour, et al. in 2002 study on the electrode for aluminum ions using the ion carrier bis(5-phenyl azo salicylaldehyde) 2,3-naphthalene diimine **20**. This membrane sensor demonstrated high selectivity for Al<sup>3+</sup> across a wide range of other metal ions. The detection limit is 2.5 × 10<sup>-6</sup> M. It has a quick reaction time of roughly 10 s and may be used for at least 10 weeks without causing any problems [150]. B. Khan et al., 2016 synthesized a new luminous bis-calix[4]arene macrocycle **30** with metal-binding pockets (Chart 6). The Cu<sup>2+</sup> detection limit was discovered to be 40 nM, which is substantially lower than the US Environmental Protection Agency’s threshold level in drinking water. The findings demonstrated excellent agreement with the fluorescence quenching phenomena of macrocycle observed in deionized water. Importantly, chemosensor **30** can detect Cu<sup>2+</sup> in live cells [151].

D. Çakmak et al., 2017 study on 2-amino benzylamine, an unsymmetrical salen-type Schiff base **31**, and its metal complexes which were investigated in the detection of compounds such as dopamine, catechol, cysteine, and uric acid. The salen-type Schiff base-Ni(II)(**32**)-modified graphite electrode generated the best results for catechol and dopamine determination in these trials with LOD values of 0.03 M and 0.06 M for catechol and dopamine respectively [152] (See Scheme 3)



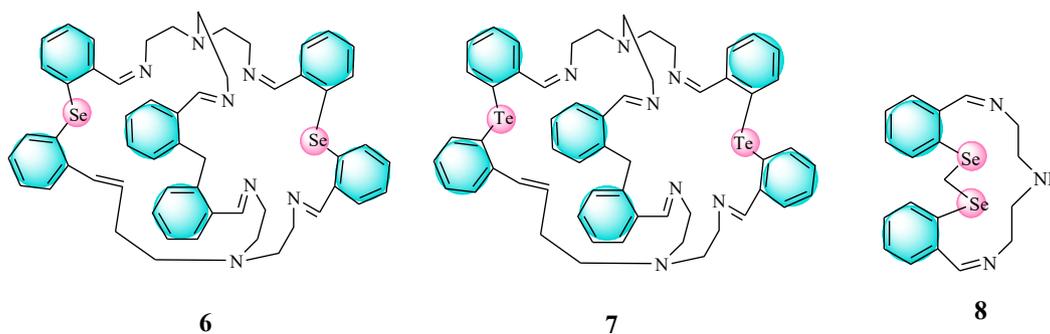
**Scheme 2.** Near-IR reversible fluorescent probe with an organoselenium functional group.



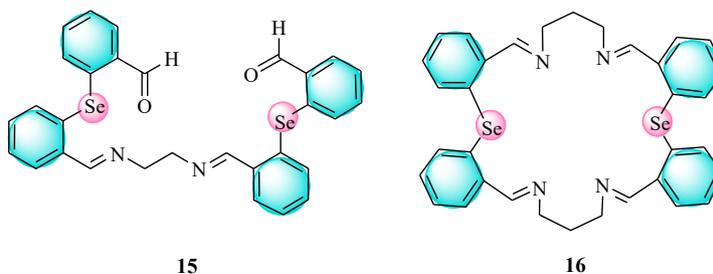
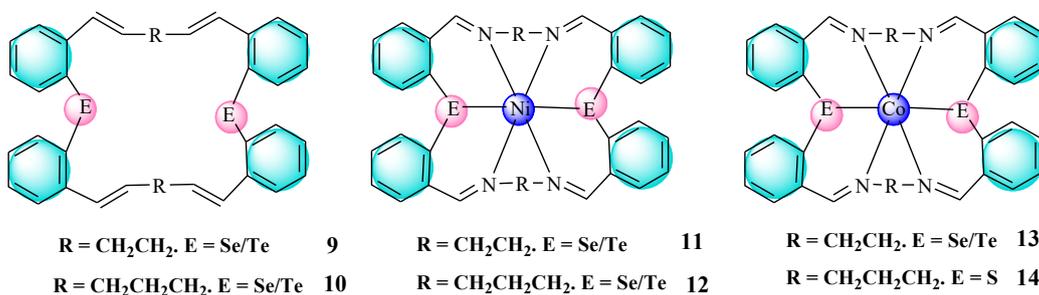
**Chart 1.** Schiff bases containing nitrogen, sulphur, and oxygen donor atoms.

#### 4. Mechanistic strategies based on colorimetric and fluorometric analysis

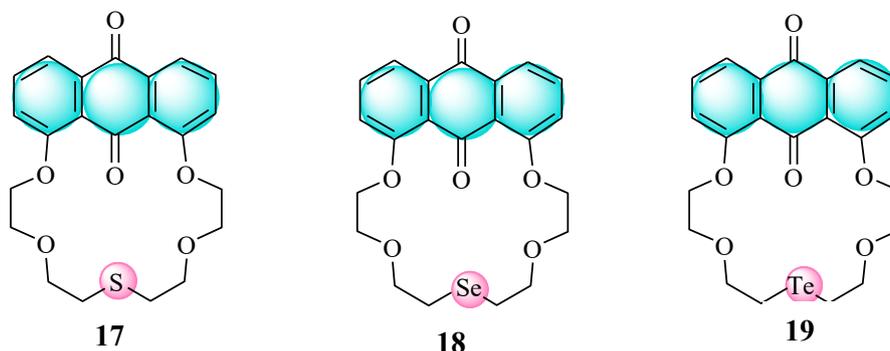
In general, a sensor with metal ion coordinates which involves in a metal detecting system. A binding functional unit in a Schiff base sensor can coordinate with a metal ion, resulting in CHEF or CHEQ activity. Bimodal methods (colorimetric and fluorometric) (Fig. 4) are nowadays used for metal detection. Here, is an example of it, G. Tamil Selvan et al. (2018) proposed a naphthalene diamine-based  $\beta$ -diketone derivative which was successfully used as a dual signaling probe for divalent cations,  $\text{Fe}^{2+}$ , and  $\text{Cu}^{2+}$  ions. It showed fluorescent enhancement for  $\text{Fe}^{2+}$



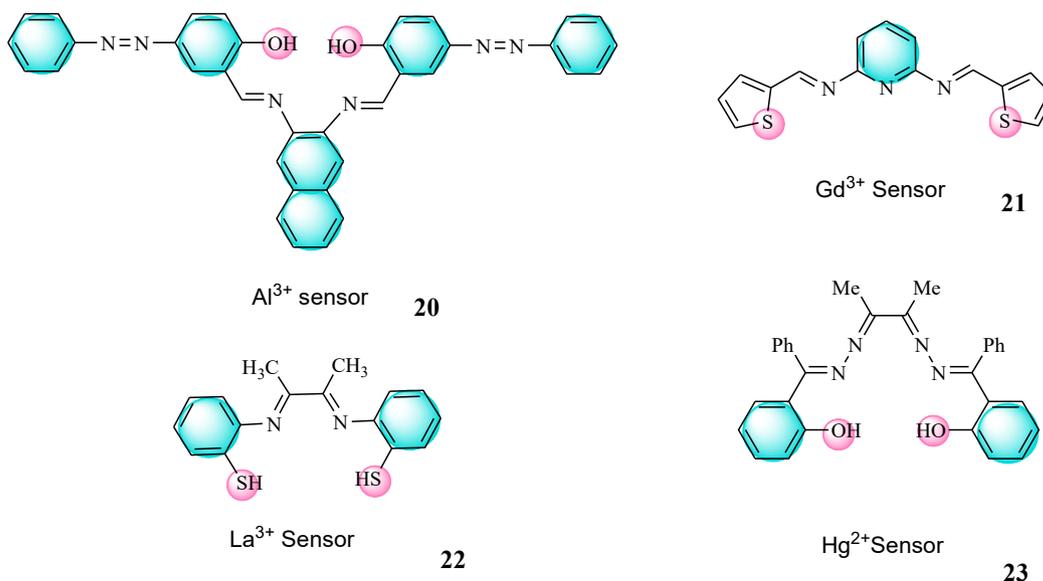
**Chart 2.** Selenium and tellurium macrocycles.



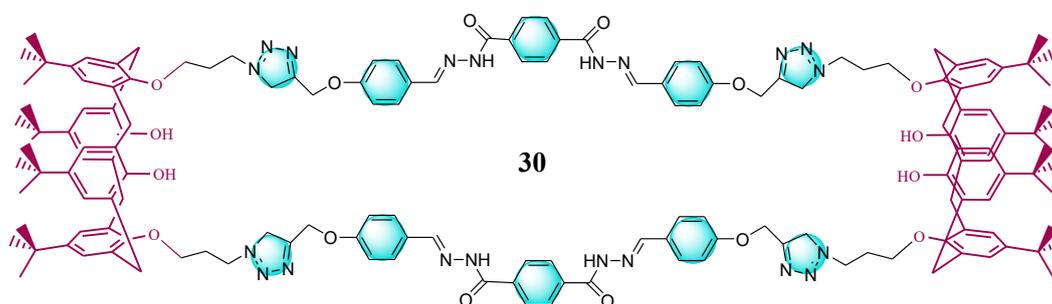
**Chart 3.** Schiff bases containing heavier chalcogens (Se, Te) into macrocycles.



**Chart 4.** 1,8-antraquinone-18-crown-5 sulphur, selenium, and tellurium derivatives.



**Chart 5.** Different chalcogenated Schiff base sensors (20–23) for different metal cations.



**Chart 6.** Luminous bis-calix[4]arene macrocycle 30 with metal-binding pockets.

ion by photoinduced electron transfer mechanism and fluorescence quenching for  $\text{Cu}^{2+}$  ion by charge-transfer process by both colorimetric and fluorometric experiments [53].

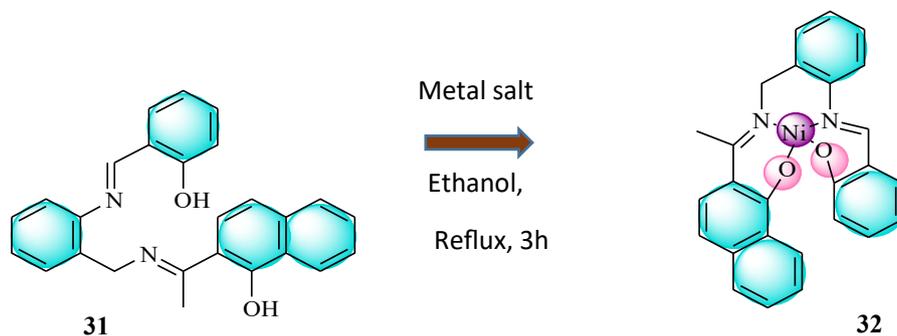
The following are the most often utilized metal ion detection mechanisms for chalcogenated Schiff bases.

#### 4.1. Photoinduced electron transfer

PET is a technique where the transport of electrons between the donor and acceptor is stimulated. Metal ion coordination with the Schiff

base sensor can either help or inhibit the PET process, resulting in an emission shift (Fig. 5) [153].

J. Xue *et al.* (2018) studied a simple condensation process between chromone and rhodamine B hydrazide occurs to form a dual probe 33, due to the restriction of the PET mechanism and the CHEF impact, it showed obvious responses to  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$  in various solutions. At multiple excitations and emission wavelengths, this probe displayed remarkable selectivity towards  $\text{Fe}^{3+}$  via the ring-opening mechanism of the rhodamine Spirolactam, accompanied by a color shift that could be visualized by the naked eye. Furthermore, the detection limits of the



Scheme 3. Synthesis of nickel metal salt as sensor.

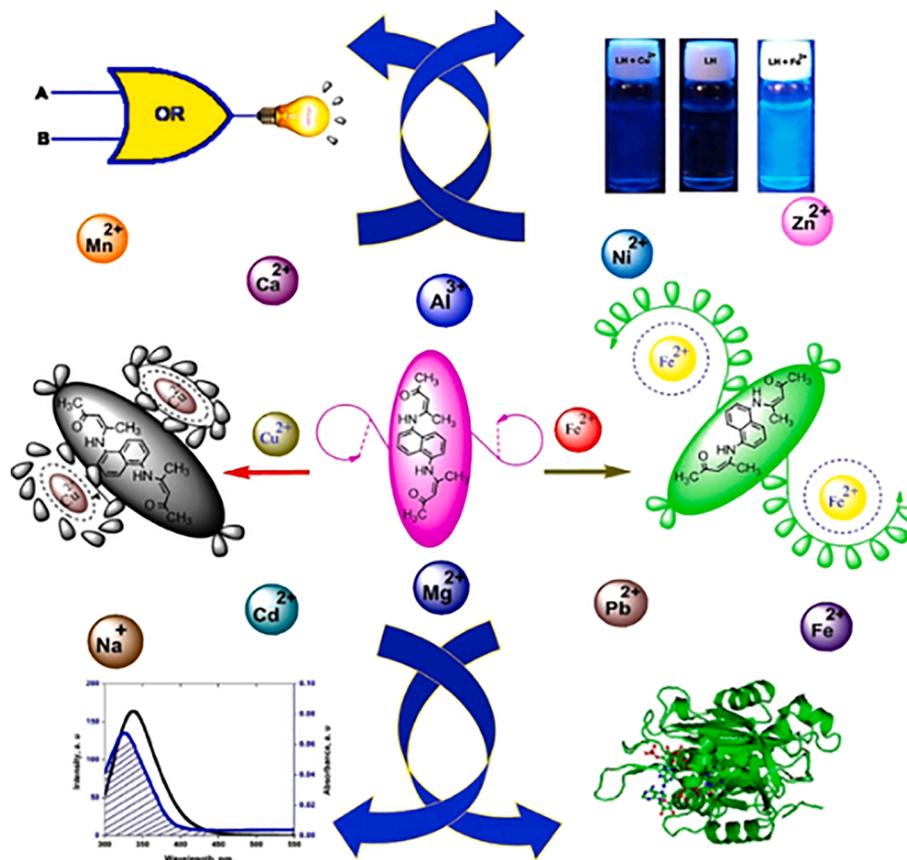


Fig. 4. Bimodal methods (colorimetric and fluorometric) are used for metal detection (Figure is reproduced by the permission taken from ACS, copyright).

probe for detecting  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$  were low (Scheme 4) [154].

C. Liu et al. (2012) study of a Schiff-based fluorescent sensor, MCPH, **92** showed high selectivity for  $\text{Al}^{3+}$  over other metal ions examined in acetonitrile (Chart 7). Upon binding  $\text{Al}^{3+}$ , a significant fluorescence enhancement with a turn-on ratio over 101-fold was triggered. The detection limit of MCPH for  $\text{Al}^{3+}$  was  $0.25 \mu\text{M}$ . PET and CHEF mechanisms demonstrated good selectivity for  $\text{Al}^{3+}$  over other metal ions with a 101-fold fluorescence increase and high sensitivity with the detection limit MCPH might serve as an ideal chemosensor for the very hazardous aluminum ion [155].

Y. Li et al. (2017) develop a highly selective and sensitive probe **93** for  $\text{Hg}^{2+}$  detection in aqueous environments, and a new mono-thiosemicarbazone Schiff base chemosensor NDBHC was developed and produced. In the presence of  $\text{Hg}^{2+}$ , there was a dramatic quenching of fluorescence at 487 nm, which was followed by a red shift in the

absorption spectra. The detection limit was  $31.1 \text{ nM}$  and the association constant was  $7.485 \times 10^7 \text{ M}^{-1}$  respectively. The charge density of the mono-thiosemicarbazones- $\text{Hg}^{2+}$  moiety rose following coordination resulting in a CHEQ effect caused by PET (Scheme 5) [156].

#### 4.2. Intra/intermolecular charge transfer (ICT)

The excited molecule's energy is relaxed throughout the ICT process by a charge transfer event, which can be intramolecular or intermolecular and comprises charge transport by the donor molecule in an excited state to the surrounding acceptor [157–159]. G. Yin et al. (2020) develop a coumarin-based probe **39** which exhibits a significant increase in fluorescence owing to ICT, as illustrated in Scheme 6. It is a colorimetric and ratiometric fluorescence detector with great selectivity for  $\text{Fe}^{3+}$  that has been devised and produced, with the capacity to exclude other

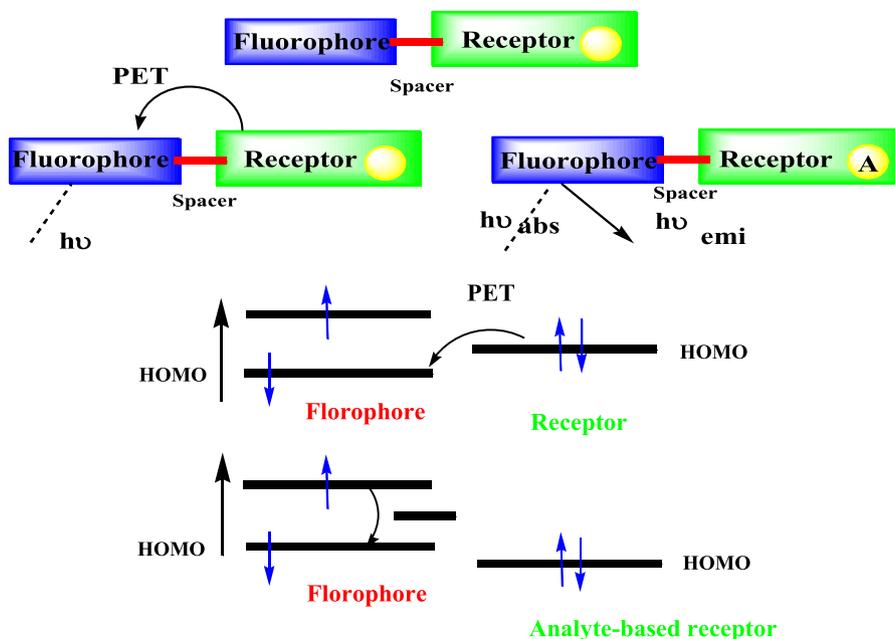
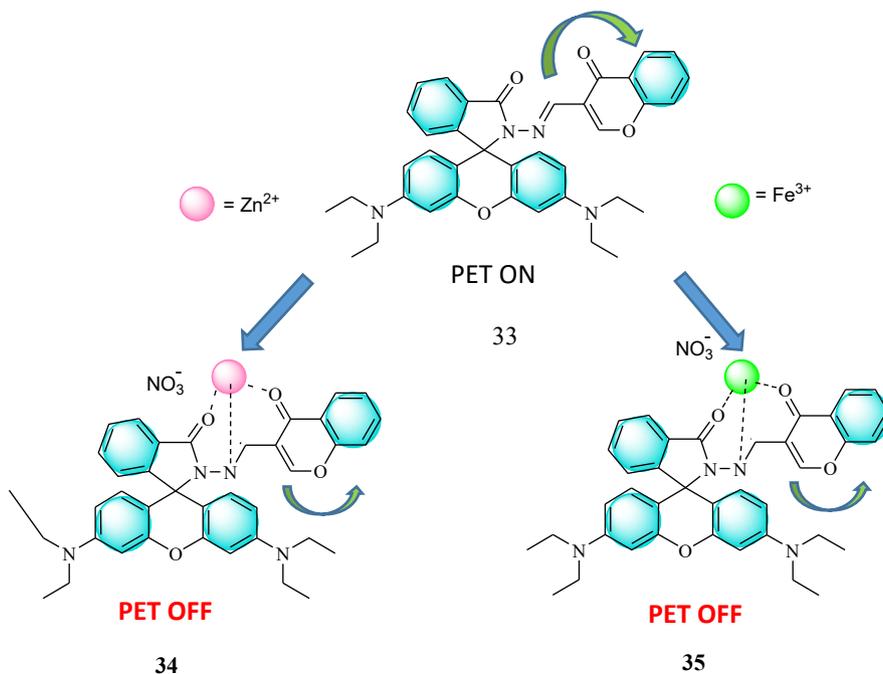


Fig. 5. Fluorescence quenching by the PET process is depicted using orbital energy graphs.



Scheme 4. Binding mechanism of  $Zn^{2+}$  (34) and  $Fe^{3+}$  (35) by PET process.

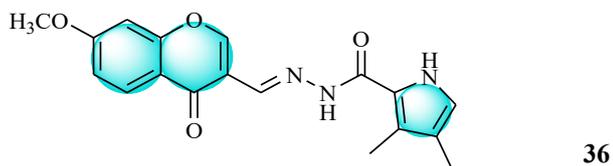
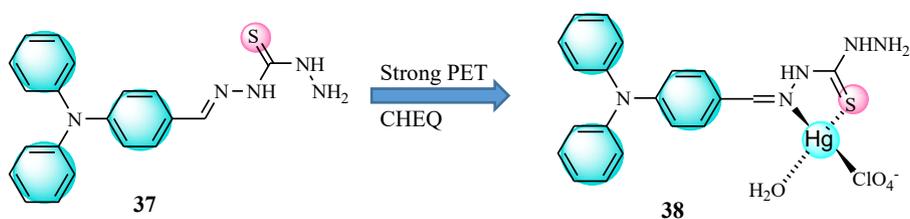


Chart 7. Schiff-base fluorescent sensor, MCPH.

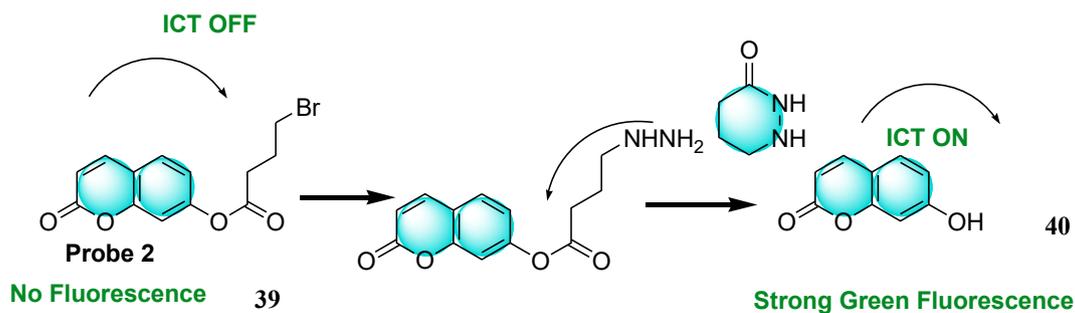
heavy as well as transition metal ions (40) [158].

The colorimetric and fluorometric dual-channel sensing of  $Hg^{2+}$  ions via the twisted intramolecular charge transfer (TICT) mechanism is described by Y. Zhang et al. (2013) for a non-sulphur chemosensor based on a simple-to-produce double naphthalene Schiff base. The complex 41- $Hg^{2+}$  may therefore be employed as a fluorescent sensor for iodine anions (42) (Scheme 7). Notably, the color changes are dramatic, and all of the identification and recycling processes can be seen with the naked eye [160].

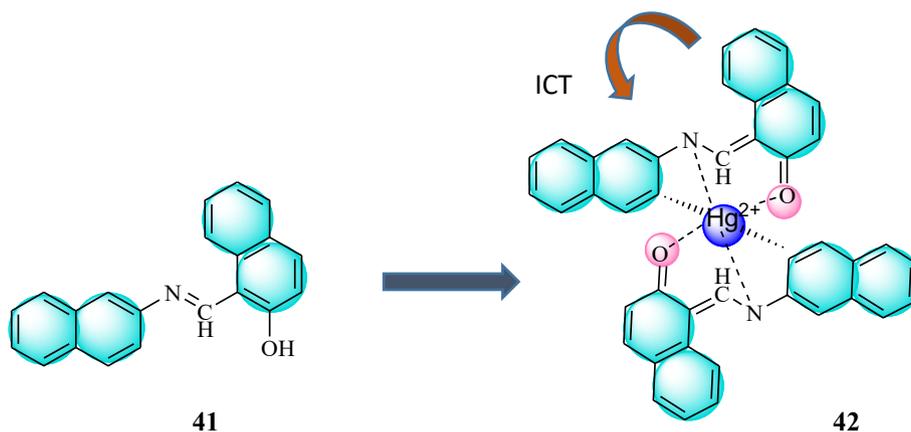
A. K. Manna et al. (2018) develop a reversible Schiff base chemosensor 4-DHBB 43 and used to detect  $Cu^{2+}$  ions. The detection limits for  $Cu^{2+}$  went up to  $0.93 \mu M$ , which was significantly below the WHO drinking



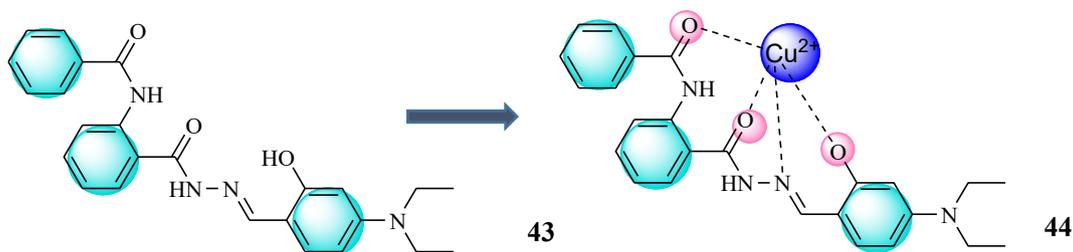
Scheme 5. Thiosemicarbazones-Hg<sup>2+</sup> moiety (38) coordination resulting in a CHEQ effect.



Scheme 6. Intra/intermolecular charge transfer (ICT) by coumarin molecules.



Scheme 7. The colorimetric and fluorometric dual-channel sensing of Hg<sup>2+</sup> ions via TICT.



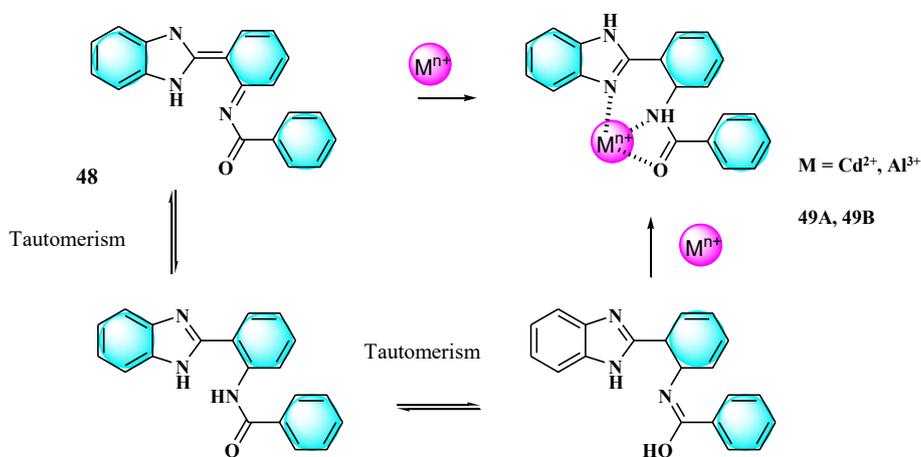
Scheme 8. Reversible Schiff base chemosensor 4-DHBB is created and used to detect Cu<sup>2+</sup> ions.

water standards. Using Job's plot analysis, the binding mode of probe **99** with Cu<sup>2+</sup> ion is determined to have a 1:1 complexation stoichiometry (**44**) (Scheme 8). The synthesized chemosensor **43** is used in real-time sample analysis and the construction of INHIBIT and IMPLICATION logical devices [161].

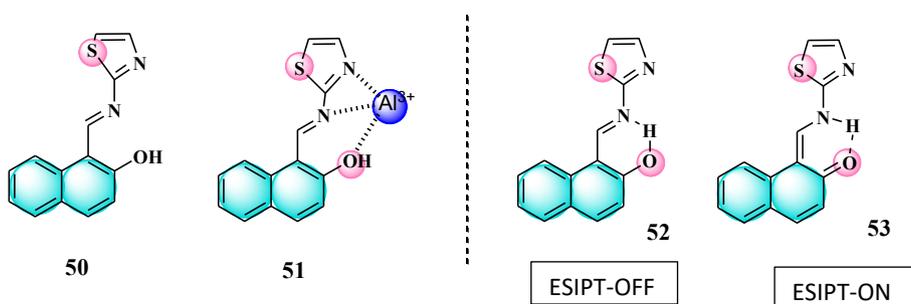
#### 4.3. Ligand to metal charge transfer (LMCT)

P. G. Sutariya et al.(2020) develop a Naphthalene moiety as a fluorophore with calix[4]arene, **45** (Chart 8) for the construction of the C<sub>4</sub>N fluorescence sensor showing ON-OFF-ON behavior for Zr<sup>4+</sup> and Fe<sup>2+</sup>. This type of transfer occurs more frequently in complexes containing metals with low-lying empty orbitals or ligands with relatively high-energy lone pairs (such as O, S, or Se). LMCT complexes are created





Scheme 9. ESIPT phenomenon of 48 via keto-enol tautomerization.



Scheme 10. Thiazole based Schiff base HNAT.

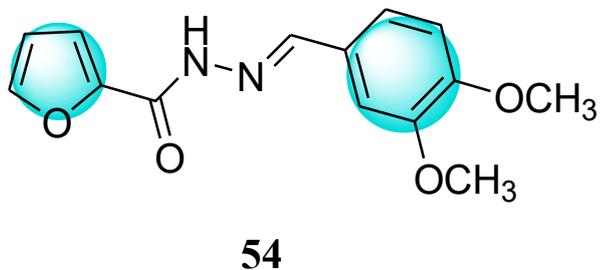


Chart 9. Chemical structure of IFE sensor 54.

titration was found 20  $\mu\text{M}$  [169].

#### 4.9. Fluorescence quenching mechanism

Quenching refers to any procedure that diminishes the intensity of fluorescence in a sample. Excited-state processes, molecular rearrangements, energy transfer, the formation of ground-state complexes, and collision quenching are examples of molecular interactions that result in quenching which generally occur with paramagnetic metal ions ( $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cu}^{2+}$ ) [170–172]. Bhaskar and Sarveswari in 2020 study on an efficient thiocarbonylhydrazide-based fluorescence sensor **60** for the selective detection of  $\text{Hg}^{2+}$  in a semi-aqueous medium have been successfully designed and synthesized. The interaction of **60** with  $\text{Hg}^{2+}$  leads to a color change from colorless to yellow (Scheme 14). The observed quenching in fluorescence intensity may be due to chelation-enhanced fluorescence quenching (CHEQ) (**61**). The limit of detection was found to be 1.26 nM with a wide pH range of 4–10. Its performance,

as a test strip and in the analysis of various water samples conferred its superior selectivity [173].

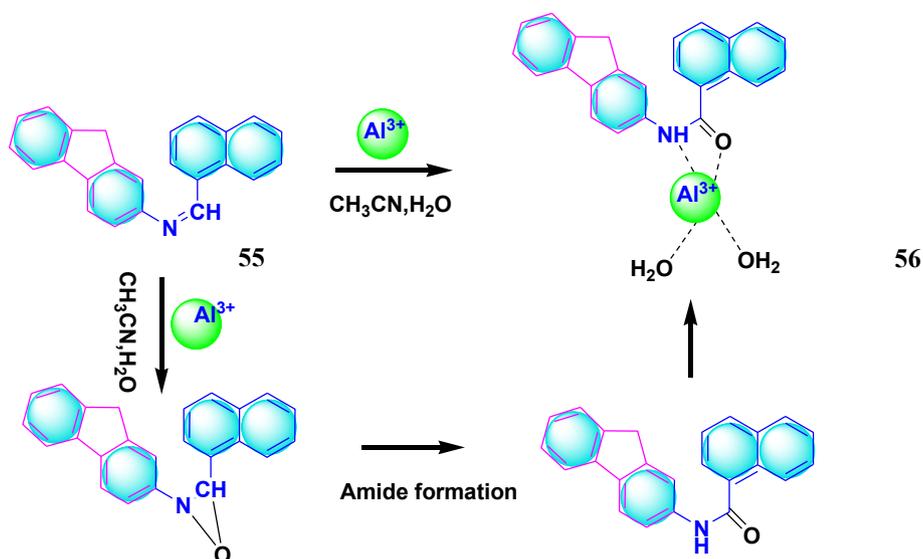
#### 4.10. Excimer/excplex formation

Excimer or exciplex is a dimeric or heterodimeric species with a small lifetime that can be generated in the excited state but dissociates in the ground state. In general, the excimer is the excited homodimeric species, whereas the exciplex is the heterodimeric species. Excimers and exciplexes can be synthesized in a variety of ways. An electrical connection to one aromatic ring encourages interaction with its neighbouring ring, resulting in either an excited dimer formed by the collision of two similar fluorophore species or two different fluorophore species [174]. Rani and John (2018) develop a Probe **62**, a pyrene-based Schiff base, and shows sensing for  $\text{Hg}^{2+}$  by excimer formation **63** for detection (Scheme 15)[175].

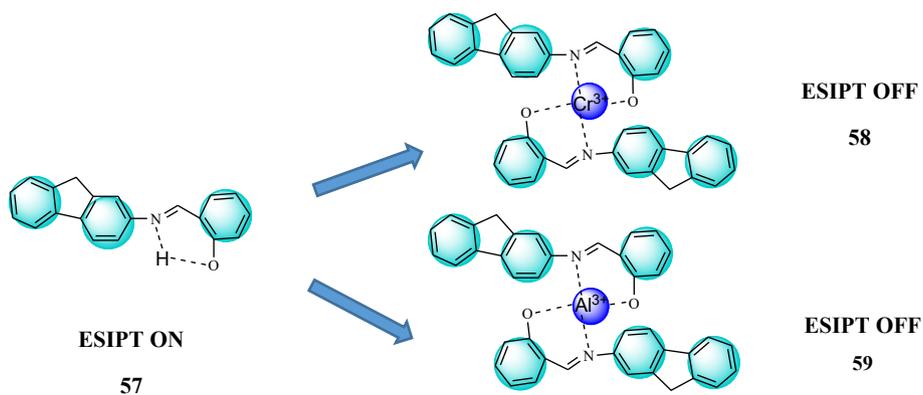
#### 4.11. Aggregation/Disaggregation

Aggregate is the creation of clusters of particles from single particles as a result of their hydrophobicity and intermolecular van der Waals-like attraction interactions, for the simple understanding shown by Fig. 7 [176]. The concept of “aggregation-caused signal change” is already well known and frequently utilized as a foundation for optical probe and sensor development. Disaggregation reverses aggregation, Self-assembly is the process of assembling individual units of a substance into highly arranged/ordered structures/patterns [177,178]. Here is an example of aggregation and disaggregation by **64** in Fig. 7.

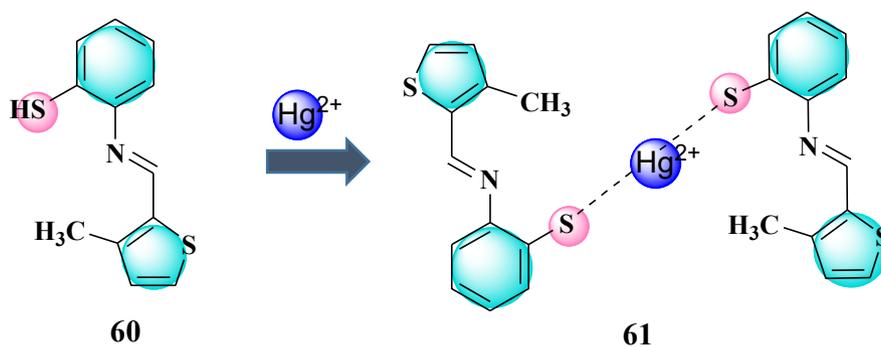
X. Zhang, Shen, et al. (2021) investigate AIEE fluorescence sensor **65** for  $\text{Cu}^{2+}$  ion detection due to risen of LMCT. Probe **65** exhibited emission peaks at 565 nm ( $\text{ex} = 428 \text{ nm}$ ) in THF- $\text{H}_2\text{O}$  solution (Scheme 16),



Scheme 11. The sensing mechanism of the sensor 55 with  $\text{Al}^{3+}$ .



Scheme 12. The sensing mechanism of the sensor 57 with  $\text{Cr}^{3+}$  58,  $\text{Al}^{3+}$ , 59 By CHEF mechanism.



Scheme 13. Fluorescence turn-on sensor for  $\text{Hg}^{2+}$  ion detection via chelation enhanced fluorescence.

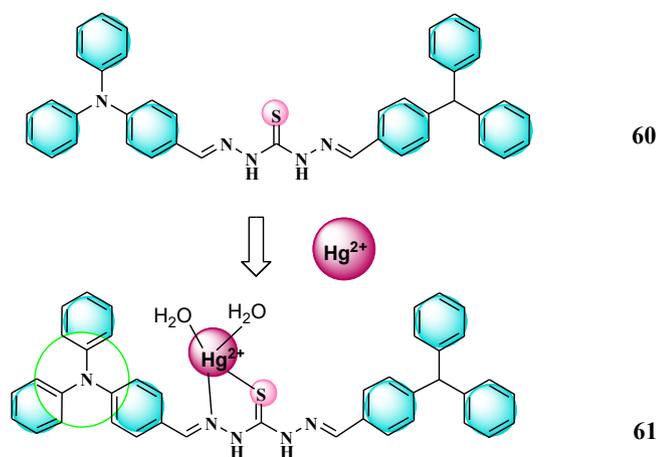
16.4 nM is the detection limit for  $\text{Cu}^{2+}$  and stoichiometry of the binding was 1: 2 and the binding constant was  $1.22 \times 10^3 \text{ M}^{-1}$  (66) [179].

Wen and Fan in 2016 studied how to prevent the quenching effect caused by chemical aggregation. For molecular-based AIE characteristics, active molecular rotation reduces fluorescence intensity in a diluted solution by lowering intramolecular mobility, and the probe's AIE activity in the aggregate state increases fluorescence intensity. Fluorescence probes made of AIE materials, such as metal ion detectors, biomolecule detectors, and pH and gas sensors, have been employed

successfully in a variety of applications [180].

## 5. Various transition metal and heavy metal ion sensing

The following several sections describe the sensors for different heavy metals and transition metals. There is detailed information on the solvent used and the LOD is given in Table 2 (125–158).

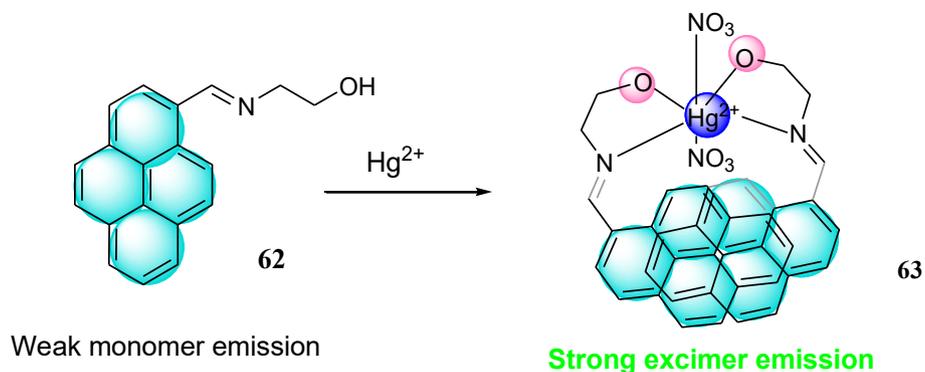


**Scheme 14.** Thiocarbonylhydrazone-based fluorescence sensor **60** for the selective detection of Mercury ion.

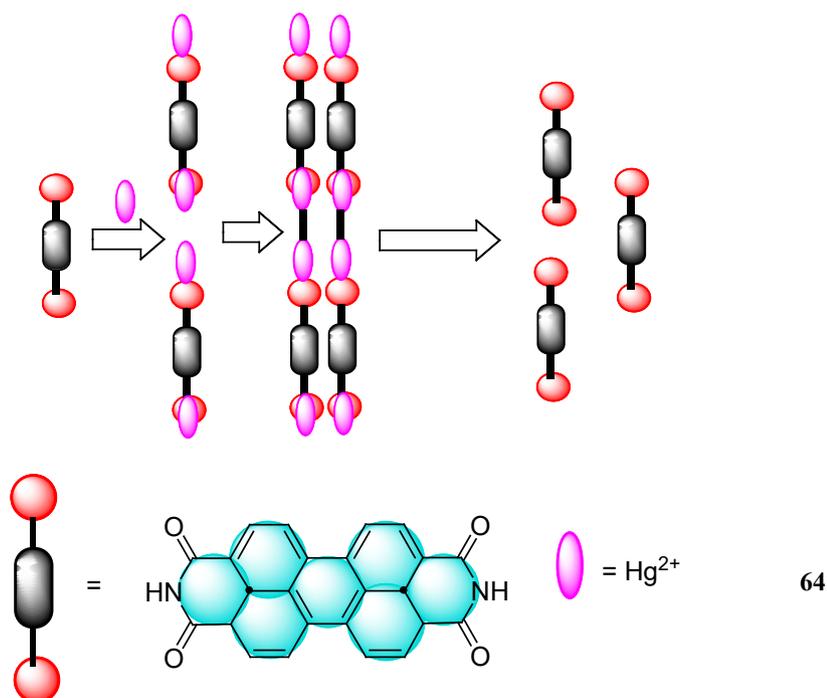
### 5.1. $\text{Hg}^{2+}$ detection

Mercury ions ( $\text{Hg}^{2+}$ ), a serious poisonous hazard, have toxic effects on humans and other living organisms. Various methods have been reported to detect  $\text{Hg}^{2+}$  ions but suffer from limitations like the requirement of bulky and expensive equipment [181–183]. Several guidelines for the molecular design of excellent  $\text{Hg}^{2+}$  receptors, as well as the optimal fluorophore/receptor pair settings for the building of high-performance off/on  $\text{Hg}^{2+}$  fluorescence sensors, were proposed [184,185]. A. Kim *et al.* (2020) developed DAP, a newly designed conjugated Schiff base-based chemosensor that displayed remarkable selectivity for mercury ions by changing its colour from pale yellow (**67**) to orange (**68**) (Scheme 17). The detection limit was  $0.11 \mu\text{M}$ , which was the second lowest recorded previously employing colorimetric mercury sensors in a near-perfect aqueous medium. DAP measurement and mercury ion detection in actual water samples were also performed [186].

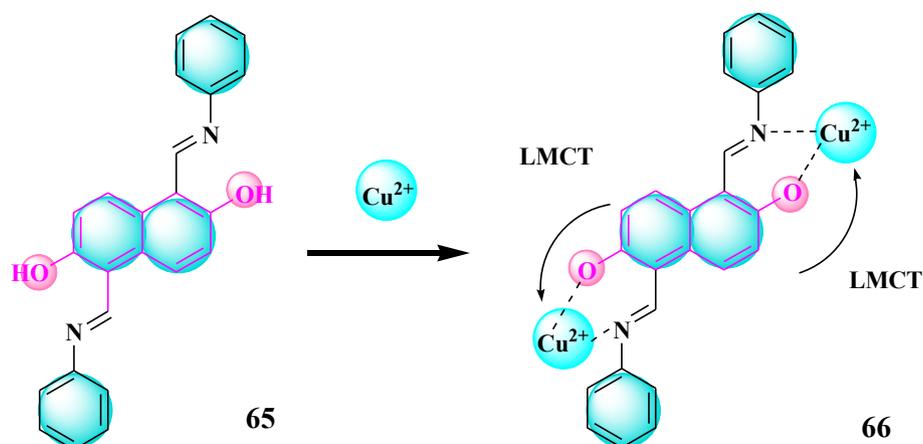
M. Muthusamy, *et al.* (2022) studied the new Schiff base probe-QT **69**, which was created by combining 8-aminoquinoline and thiophene-2-carboxaldehyde moieties (Scheme 18). When exposed to



**Scheme 15.** Illustration of excimer formation (**63**) by **62**.



**Fig. 7.** Illustration of assembly/disassembly by **64**.



Scheme 16. Sensing mechanism for  $\text{Cu}^{2+}$  detection **66** by AIE, turn-off fluorescence.

$\text{Hg}^{2+}$ , QT experiences CHEQ due to coordination by the sulphur and nitrogen atoms of QT, providing a simple “turn-off” sensor (**69**). The detection limit was set at 23.4 nM, and a Job plot confirmed a 2:1 stoichiometry between QT and  $\text{Hg}^{2+}$  (**70**), and its appropriateness for usage in the field with environmental samples was examined using Whatman filter paper strips [187].

Another cellulose–lysine Schiff-base-based sensor **71** adsorbent from biowaste was designed by King 2008 to be an effective sensor and adsorbent for the adsorption of  $\text{Hg}^{2+}$  from its aqueous solutions (Chart 10).  $\text{Hg}^{2+}$  sensing was studied from the lower limit of 10 ppm, and adsorption was found to be effective at pH 5.0 and 50 °C with 150 ppm  $\text{Hg}^{2+}$  ion solution for 1 h. The sensor demonstrated a very high maximum removal capacity and acceptable reusability up to 8 cycles, indicating that these Schiff base materials are suitable choices. For  $\text{Hg}^{2+}$  ion detection and removal in water purification technologies [188].

Alzahrani et al. (2022) determine the concentration of  $\text{Hg}^{2+}$  ions in the presence of the Schiff base ligand named HMBT(**72**), at pH 10 using Briton Robinson Buffer. The method Obey Beer’s law in concentration range 0.1–6  $\mu\text{g mL}^{-1}$  of Hg with a limit of detection (LOD) 0.016  $\mu\text{g L}^{-1}$  and limit of quantification (LOQ) 0.051  $\mu\text{g/L}$ . The molar ratio ensured the formation of a metal complex between HMBT and Hg ions was in the molar ratio 2:1 (HMBT:  $\text{Hg}^{2+}$ ) [189]. Tumay and Yeşilotin 2021 develop novel pyrene and anthracene-based Schiff base derivatives (**73**, **74**) that were designed and prepared for selective “turn-on” fluorescence determination of  $\text{Hg}^{2+}$  ions in food and environmental samples. The paper-based test kit was prepared with pyrene appended Schiff base which could be applied successfully for monitoring  $\text{Hg}^{2+}$  ions. The detection limits of the presented methods were determined as 12.22 nM and 8.32 nM. **73** and **74** can sensitively and selectively detect  $\text{Hg}^{2+}$  ions in real samples via inhibition of PET processes after 1:1 complex formation [190].

## 5.2. $\text{Al}^{3+}$ metal detection

$\text{Al}^{3+}$  is a metal that is unsafe for living things as well as the environment. It has been linked to several serious conditions, including osteoporosis and Alzheimer’s disease. [6]. Hence the development of sensors to detect  $\text{Al}^{3+}$  ions is highly important, therefore Karak et al. in 2012 develop a novel pyrimidine-based  $\text{Al}^{3+}$  selective fluorescent probe **75**. It has been synthesized by a facile one-step coupling of 4, 5-diamino pyrimidine with 2-hydroxy naphthaldehyde. Upon binding  $\text{Al}^{3+}$ , the single emission band of **75** undergoes a red shift from 470 nm to 505 nm and 538 nm. **75** could detect as low as  $2.9 \times 10^{-7}$  M [191]. Wen and Fan 2016 studied simple Schiff-base derivative with salicylaldehyde moieties as fluorescent probe **76** (**76**, Chart 11) by AIE characterization for the detection of metal ions. The detection limit of  $\text{Al}^{3+}$  was 0.4 mM,

which is considerably lower than the WHO standard (7.41 mM), and the acceptable level of  $\text{Al}^{3+}$  (1.85 mM) in drinking water. The job plot indicated that the binding stoichiometry ratio of probe 1 to  $\text{Al}^{3+}$  was 1:2 [180]. Another Schiff-base MCAH (**77**, Chart 11) was synthesized by C. J. Liu et al. (2015) which possesses dual PET processes, simultaneously introduced by both nitrogen and sulphur donors. Upon binding  $\text{Al}^{3+}$  a significant fluorescence enhancement with a turn-on ratio over 500-fold was triggered. The detection limit of MCAH for  $\text{Al}^{3+}$  was  $3.19 \times 10^{-8}$  M [192].

Immanuel David et al. (2020) investigated and observe a simple S—S (disulfide)-bridged dimeric Schiff base probe for the specific recognition of  $\text{Al}^{3+}$  and  $\text{Fe}^{2+}$  ions as fluorometric and colorimetric “turn-on” responses in a DMF- $\text{H}_2\text{O}$  solvent mixture, respectively. By fluorescence and UV–Vis spectroscopy techniques up to nanomolar detection limits,  $38.26 \times 10^{-9}$  and  $17.54 \times 10^{-9}$  M (Fig. 8), respectively. The practical utility of the chemosensor was further demonstrated in electrochemical sensing, antimicrobial activity, molecular logic gate function, and quantification of the trace amount of  $\text{Al}^{3+}$  and  $\text{Fe}^{2+}$  ions in real water samples [193] (See Chart 12)

## 5.3. $\text{Pb}^{2+}$ detection

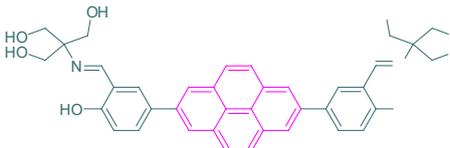
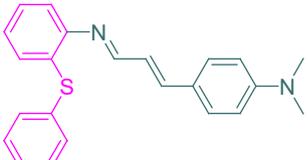
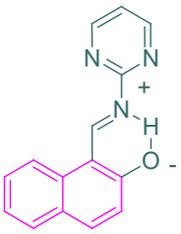
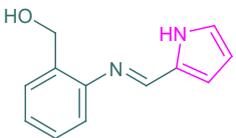
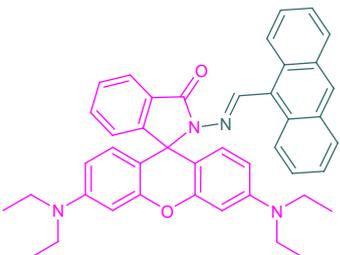
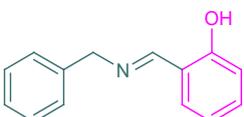
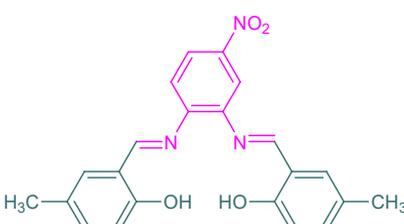
$\text{Pb}^{2+}$  has significant physicochemical characteristics which have been traced back to ancient times. Its significance cannot be overlooked, although the neurotoxicity of lead and its adverse effects on almost every organ in the body have long been known.  $\text{Pb}^{2+}$  is non-biodegradable and therefore persists in the environment [194,195]. Rout et al. 2019 develop fluorescence spectra of probe **78** revealing  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  increment in the intensity of emission as a result of the PET process being blocked along with the ICT process being strengthened. fluorometric detection limits for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  were observed at  $12 \times 10^{-7}$  M and  $9 \times 10^{-7}$  M in a pH span of 4.0–12.0 (Scheme 19) [196].

Jeong et al. (2005) generated PVC membrane electrodes for lead ions using **81**, and **82** as the membrane carrier. This electrode demonstrated high selectivity and responsiveness for  $\text{Pb}^{2+}$  in  $\text{Pb}(\text{NO}_3)_2$  solutions at room temperature, with a response (29.4 mV/decade) and a limit of detection of  $\log_{10}(\text{M}) = 6.04$ . It has a speedy broad range of other metal ions in pH 5.0 buffer solutions, as well as high repeatability of the baseline in repeated measurements (Chart 13) [197].

## 5.4. $\text{Cr}^{3+}$ ion detection

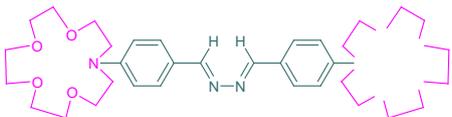
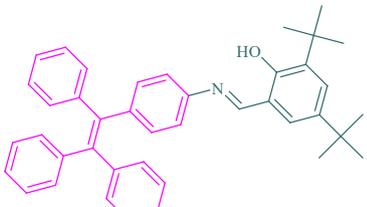
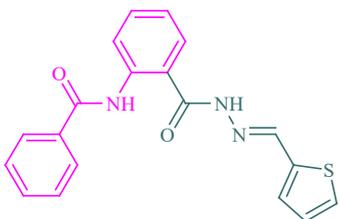
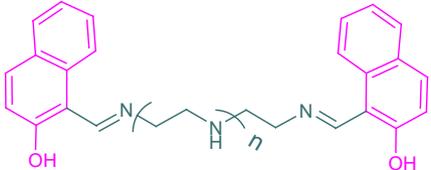
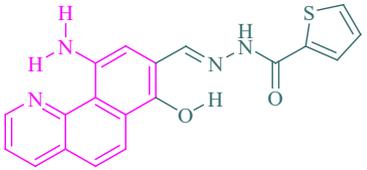
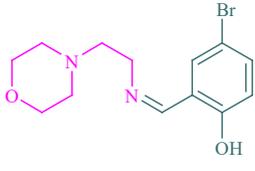
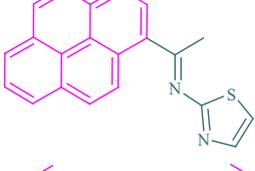
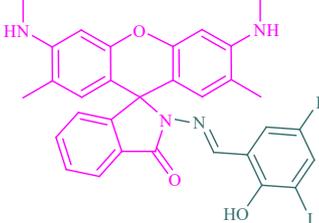
Krishnan et al.(2022) develop a new diphenyl imidazole-based fluorescent probe (**83,84**) bearing the 2-aminothiophenol moiety, which is showing dual-sensing behavior for  $\text{Hg}^{2+}$  and  $\text{Cr}^{3+}$  ions in  $\text{CH}_3\text{CN-H}_2\text{O}$  solution(Chart 14). The addition of  $\text{Hg}^{2+}$  and  $\text{Cr}^{3+}$  ions

**Table 2**  
Another example of chalcogenated Schiff bases.

S. No.	Sensor	Solvent	Mechanism	Metal ions	LOD	Author name	Ref
1.		Ethanol and DMSO	PET	Zn <sup>2+</sup> Al <sup>3+</sup>	23.9 nM-	Hsu and Chen 2018	[221]
2		ACN)/water (v/v 2: 1)	LMCT	Cu <sup>2+</sup>	2.85 μM	Aydin and Keles 2020	[222]
3		Acetonitrile solution	CHEF	Ce <sup>3+</sup>	34 nM.	Sadia et al. 2020	[223]
4		Aqueous solution	NIRLuminescent Sensing	PO <sub>4</sub> <sup>2-</sup> and 2,4,6-trinitrophenol	–	Xia Liu et al. 2020	[224]
5		Aqueous solution	ESIPT	Cu <sup>2+</sup>	4.9 μM	Garcias-Morales et al. 2021	[225]
6		AA-AR/ DMF	Intra-ligand π-π* charge transfer	Hg <sup>2+</sup>	0.87 μM	Cicekbilek et al. 2019	[73]
7		Ethanol-water	LMCT	Zn <sup>2+</sup> Cd <sup>2+</sup> Hg <sup>2+</sup>	27 μM, 75 μM 60 μM	İnal 2020	[14]
8		Ethanol	CHEF	Al <sup>3+</sup> Fe <sup>3+</sup>	0.33 μM 0.36 μM	G. Dong, et al., 2018	[226]

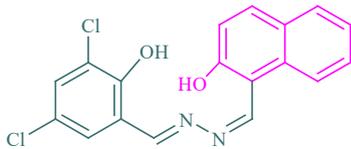
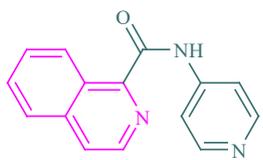
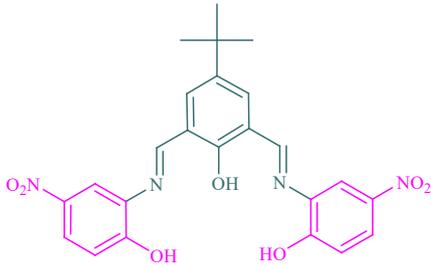
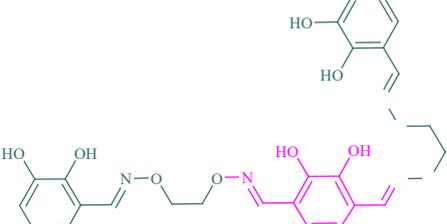
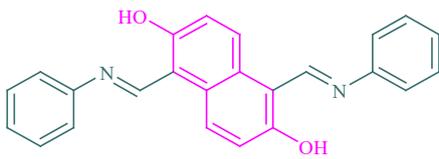
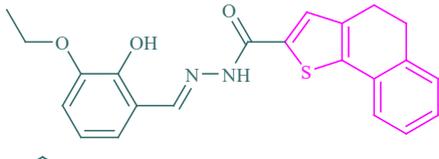
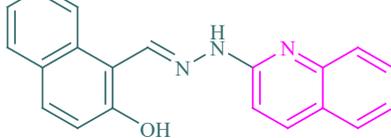
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Table 2 (continued)

S. No.	Sensor	Solvent	Mechanism	Metal ions	LOD	Author name	Ref
9		DMF/Water	CH=N Isomerization	Cu <sup>2+</sup> Co <sup>2+</sup>	– –	(Özdemir 2016	[227]
10		Aqueous solution	Inhibition of PET and the ESIP/AIE-active	CO <sub>3</sub> <sup>2-</sup> Zn <sup>2+</sup>	71.2 nM 80 nM	Jia and Zhao 2019	[228]
11		CH <sub>3</sub> OH/H <sub>2</sub> O (1:1 v/v, pH = 7.2)	Selective colorimetric detection	Cu <sup>2+</sup>	1.8 μM	Manna et al. 2020	[229]
12		Aqueous Solution	AIE	Pb <sup>2+</sup>	2.23 μM	Rahimi, Amini, and Behmadi 2020	[230]
13		Wastewater	Synergistic effect of hydrophobic, π-π stacking, and electrostatic noncovalent interactions	Cu <sup>2+</sup>	–	Y. Liu et al. 2019	[231]
14		Aqueous solution	NIR Fluorescence	Al <sup>3+</sup>	–	Pan et al. 2019	[48]
15		Aqueous solution	CHEQ	Hg <sup>2+</sup>	–	Sarkar et al. 2020	[49]
16		Aqueous medium	Colorimetric and fluorogenic chemodosimeter	Hg <sup>2+</sup>	0.270 μM	Tekuri, Sahoo, and Trivedi 2019	[83]
17		Aqueous medium	Para-magnetic metal couple	Cu <sup>2+</sup> Fe <sup>3+</sup>	263 pM 2 nM	A. Senthil Murugan et al., 2020	[232]

(continued on next page)

Table 2 (continued)

S. No.	Sensor	Solvent	Mechanism	Metal ions	LOD	Author name	Ref
18		DMSO: H <sub>2</sub> O (99:1, v/v) (pH 7–8)	Inhibition of ESIPT	Al <sup>3+</sup>	0.04 μM	Al Anshori et al. 2018	[233]
19		CH <sub>3</sub> CN/HEPES (3: 2, v/v) buffer	AIEE	Cu <sup>2+</sup>	3 μM	He et al. 2019	[234]
20		Aqueous solution	PET	Al <sup>3+</sup> Fe <sup>3+</sup>	0.24 μM	B. K. Kundu et al. 2019	[235]
21		H <sub>2</sub> O-DMSO (1:1, v/v) medium	Nucleophilic addition of CN <sup>-</sup> onto imine C-atom.	CN <sup>-</sup> Al <sup>3+</sup>		Poongodi et al. 2021	[236]
22		EDTA solution	ICT process	Cu <sup>2+</sup>	7.7 nM	Goel et al. 2021	[237].
23		Living cell	CHEF/CHEQ	B <sub>4</sub> O <sub>7</sub> <sup>2-</sup>	0.69 nM	Pu et al. 2021	[238].
24		Aqueous solution	AIEE	Cu <sup>2+</sup>	16.4 nM	X. Zhang, Shen, et al. 2021	[179].
25		DMF-H <sub>2</sub> O (9: 1, v/v)	CHEF	In <sup>3+</sup> Fe <sup>3+</sup>	8.05 nM 25.9 nM	Bing Li et al. 2021	[17]
26		ACN:H <sub>2</sub> O (8:2, v/v)	LMCT	Cd <sup>2+</sup>	14.8 nM	Mohanasundaram et al. 2021	[239]

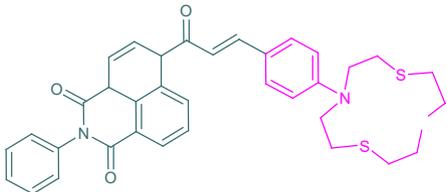
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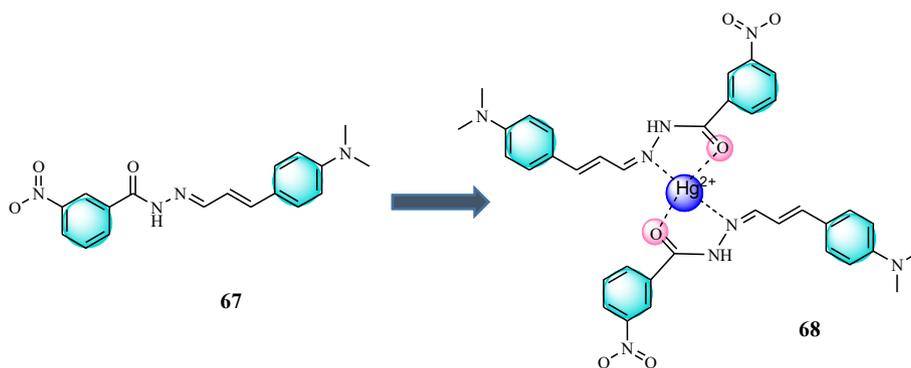
Table 2 (continued)

S. No.	Sensor	Solvent	Mechanism	Metal ions	LOD	Author name	Ref
27		MeOH:H <sub>2</sub> O (v/v = 1:1, HEPES buffer, pH = 7.2)	CHEF and ICT	Co <sup>2+</sup>	91 nM	Bartwal, Aggarwal, and Khurana 2020	[240]
28		MeOH:H <sub>2</sub> O (v/v = 1:1, HEPES buffer, pH = 7.2)	CHEF and ICT	Al <sup>3+</sup>	10 nM	Bartwal, Aggarwal, and Khurana 2020	[240]
29		Aqueous solution	IC	Hg <sup>2+</sup>	0.11 μM	A. Kim, Kim, and Kim 2020	[186]
30		Ethanol-water solution (8:2, v/v, 20 mM HEPES, pH 7.0)	FRET	Hg <sup>2+</sup>		W. Zhang et al. 2021	[241]
31		MeCN-Tris (v/v, 2:1, 10 mM)	CHEF	Fe <sup>3+</sup> and F <sup>-</sup>		Bai Li et al. 2021	[242]
32		Methanol/H <sub>2</sub> O (19:1)	LMCT	Fe <sup>2+</sup>		S. Q. Makki, 2020	[243]
33		Aqueous media	CHEF	Fe <sup>3+</sup>	0.8 ppb	N. H. Kim et al. 2019	[244]

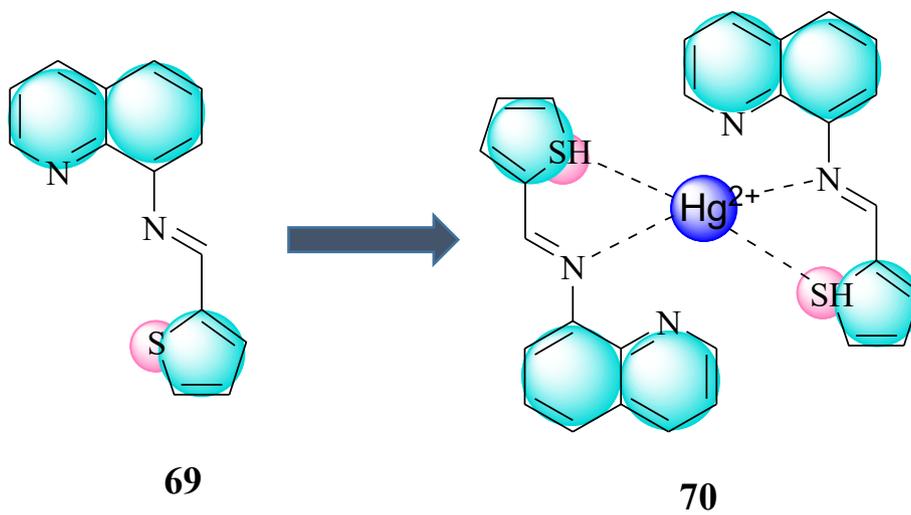
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Table 2 (continued)

S. No.	Sensor	Solvent	Mechanism	Metal ions	LOD	Author name	Ref
34		Buffered aqueous solutions	IC/ET	Fe <sup>3+</sup>		Bricks et al. 2005	[245]



Scheme 17. DAP showed strong selectivity for mercury ions.



Scheme 18. . Binding mechanism of 8-aminoquinoline thiophene-2-carboxaldehyde.

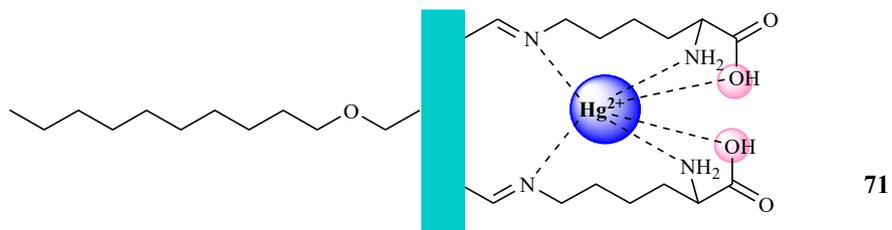


Chart 10. Cellulose lysine Schiff-base-based sensor.

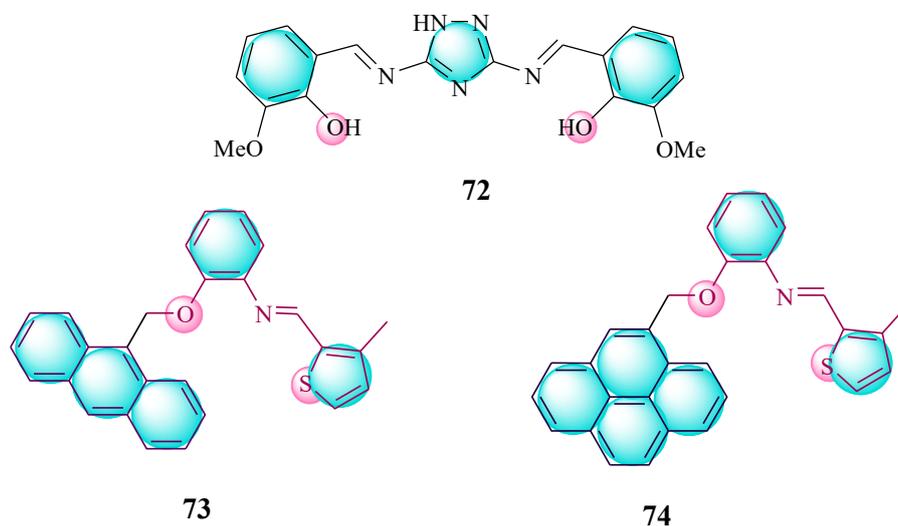
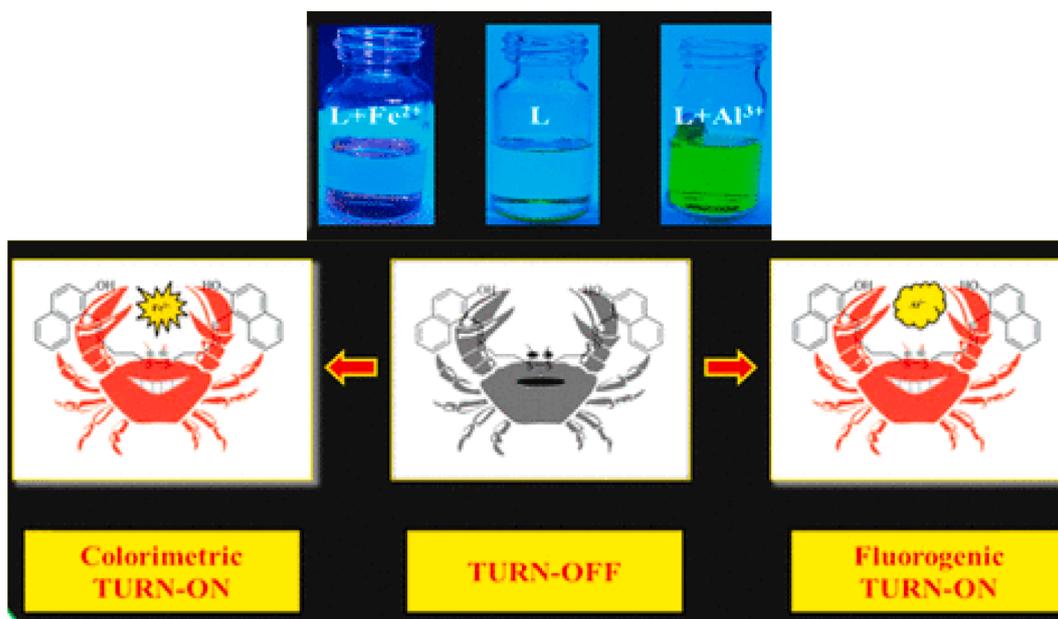


Chart 11. Sensor for mercury detection.

Fig. 8. Specific recognition of  $\text{Al}^{3+}$  and  $\text{Fe}^{2+}$  ions as fluorometric and colorimetric “turn-on” responses (Figure is reproduced by the permission taken from ACS, copyright).

showed a 59 nm blue shift in fluorescence emission (from 494 to 435 nm). The analytical limit of detection was estimated to be 6 nM for  $\text{Hg}^{2+}$  and 1.96 nM for  $\text{Cr}^{3+}$ , respectively. The detection of  $\text{Hg}^{2+}$  and  $\text{Cr}^{3+}$  due to ion-induced complex formation with imine nitrogen ( $-\text{CH}=\text{N}$ ). formation and the binding mode was proposed as 1:1 stoichiometric between  $\text{Hg}^{2+}/\text{Cr}^{3+}$  ions [11].

Ganjali et al. (2006) get a view of the tendency of **SNN-85**, toward chromium and some other metal ions, theoretical calculations and conductance studies were carried out. Sensor **85** shows a linear dynamic range of  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-1}$  M with high selectivities for the vast majority of the key metal ions. It was also successful in identifying  $\text{Cr}^{3+}$  in chrome electroplating and leather effluent. The sensor was also used to count the chromium ions in the effluent of chromate production [198]. Another sensor **86** also shows sensing for  $\text{Cr}^{3+}$  as shown in Chart 15.

Musikavanhu, Zhang, et al.(2022) observed a Schiff base **NHT**, **87** containing SNO donor set confirmed that the probe underwent a turn-off response via the CHEF quenching effect upon exposure to  $\text{Cr}^{3+}$  and the **NHT- $\text{Cr}^{3+}$**  complex **88** was formed at a 1:1 binding stoichiometry (Scheme 20). **NHT** exhibited a fast response rate of 2.3 min in buffer solution and a relatively low limit of detection of 41 nM. In addition, the Schiff base chemosensor exhibited excellent selectivity with high affinity towards  $\text{Cr}^{3+}$  in the presence of other competing cations. Bioimaging of the probe in PC3 cells further demonstrated the potential real-life application of the probe in detecting  $\text{Cr}^{3+}$  [199].

Reimann et al. (2019) studied that when the metal ion coordinates with the ligand in a 1:1 ratio, the fluorescence is quenched. The selectivity of metal ions  $\text{Cu}^{2+}$  (**89**),  $\text{Ni}^{2+}$  (**90**),  $\text{Cr}^{3+}$  (**91**), and  $\text{Co}^{2+}$  (**92**) is exhibited via fluorescence quenching accompanied by colorimetric changes, whereas that of  $\text{Ag}^{+}$  and  $\text{Co}^{2+}$  is observed through colorimetric

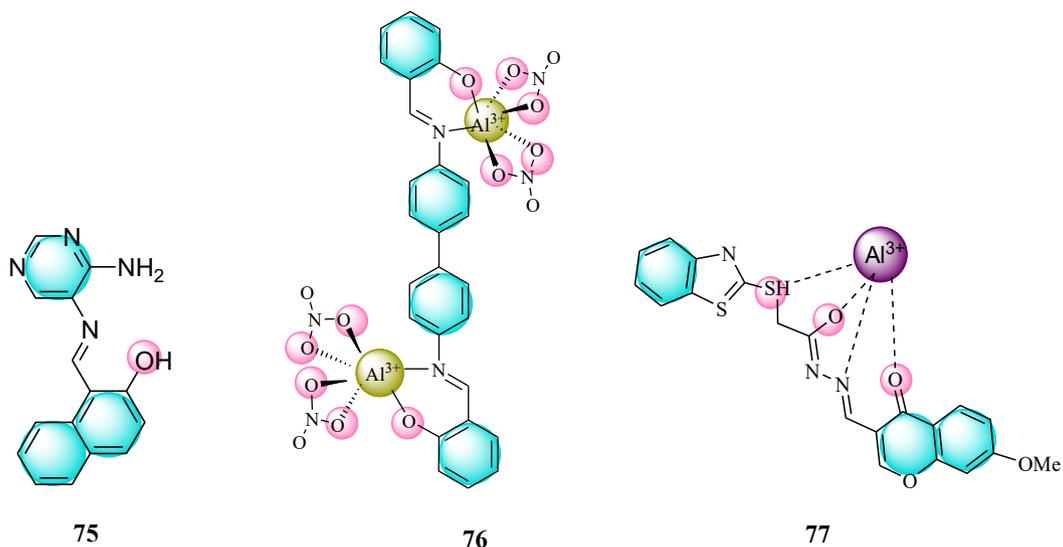
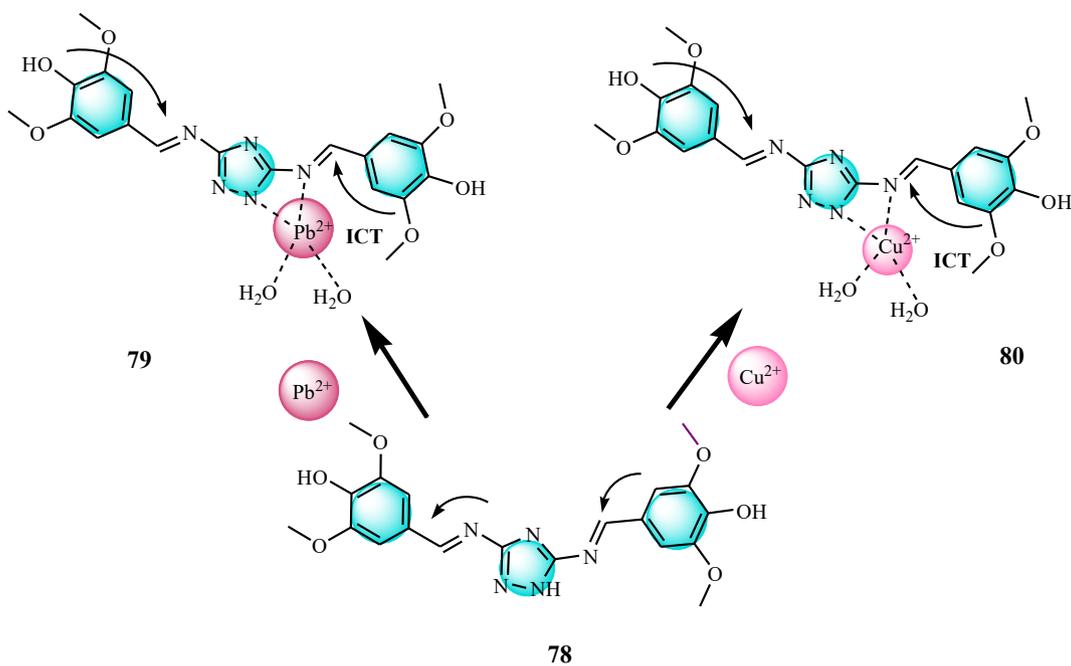


Chart 12. Selected examples of Al<sup>3+</sup> sensors with binding sites.



Scheme 19. Pb<sup>2+</sup> (79) and Cu<sup>2+</sup> (80) detection via ICT and PET process.

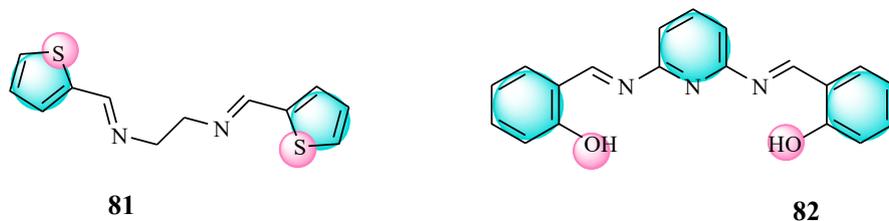
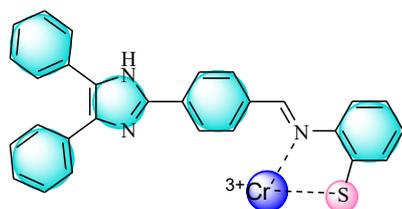


Chart 13. Schiff base sensor of lead.

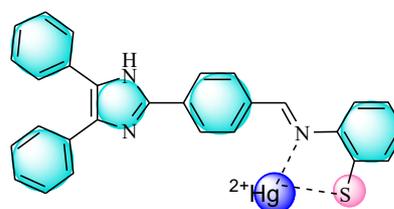
changes alone. Additionally, pH sensing studies were performed for the potential use of these ligands in biological applications (Chart 16) [51].

### 5.5. Cadmium ion detection

Cadmium is a deadly non-essential heavy metal that is detrimental to human beings as well as animals. It comes from industrial and

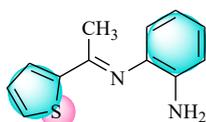


83



84

Chart 14. Diphenyl imidazole-based fluorescent probe bearing the 2-aminothiophenol moiety.



85



86

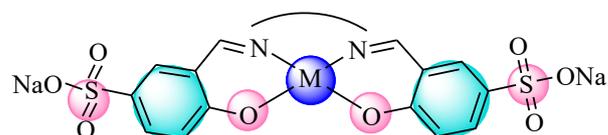
Chart 15. Cr<sup>3+</sup> sensors.M = Cu<sup>2+</sup> (89), Ni<sup>2+</sup> (90), Cr<sup>3+</sup> (91), and Co<sup>2+</sup> (92)

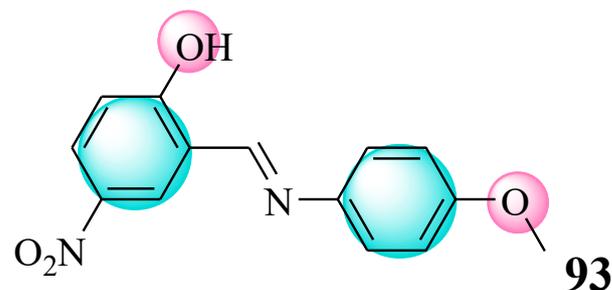
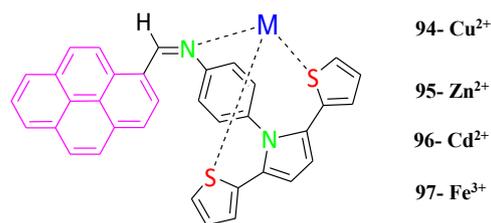
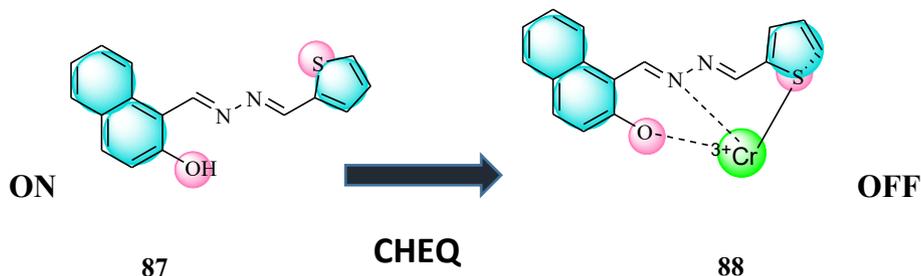
Chart 16. Multimetallic ion sensor.

agricultural sources and is a naturally occurring contaminant in nature. The most typical way to receive cadmium is via ingesting contaminated food and drink, however, it can also be absorbed by inhalation and cigarette smoking. Both plants and animals over time collect cadmium [200–203]. Schiff base, MPMNP 93 (Chart 17) as a capping agent used as N, O-donor ligand with ZnS NPs act as selective probe detection of Fe<sup>3+</sup>, Cr<sup>2+</sup>, and Cd<sup>2+</sup> ions fluorometrically, and the emission band disappears in the presence of increasing concentrations of Fe<sup>3+</sup>, Cr<sup>2+</sup>, and Cd<sup>2+</sup> ions. A simple co-precipitation method to fabricate and stabilize ZnS NPs. The ZnS NPs exhibited good fluorescence quenching selectivity to Fe<sup>3+</sup>, Cr<sup>2+</sup>, and Cd<sup>2+</sup> ions in the range of 10–500 μM. The LOD was estimated to be 10.24 μM, 31.48 μM, and 64.56 μM for Fe<sup>3+</sup>, Cr<sup>2+</sup>, and Cd<sup>2+</sup>, respectively [204,205].

The Schiff base of the pyrene-SNS system (94–97), a multimetallic sensor has been investigated as a fluorescence probe for the detection of metal ions (Chart 18). It has been found that this probe is suitable for the sensing of metal ions such as Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, and Fe<sup>3+</sup>.

### 5.6. Fe<sup>2+</sup> and Fe<sup>3+</sup> ions

G. Chen *et al.* in 2019 studied the effective design and synthesis of two stable crystalline 2,5-dihydroxyterephthalaldehyde, 2,5-dimethoxyterephthalaldehyde, or benzene-1,3,5-tricarbohydrazone-linked covalent organic frameworks with functional O, N, O. It's noteworthy to note that the Fe(III) ion in an aqueous solution may be detected by the Bth-

Chart 17. Sensor for Fe<sup>3+</sup>, Cr<sup>2+</sup>, and Cd<sup>2+</sup> ions.94- Cu<sup>2+</sup>95- Zn<sup>2+</sup>96- Cd<sup>2+</sup>97- Fe<sup>3+</sup>Chart 18. Sensing of metal ions such as Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, and Fe<sup>3+</sup>.

87

CHEQ

88

Scheme 20. Schiff base NHT containing SNO donor set.

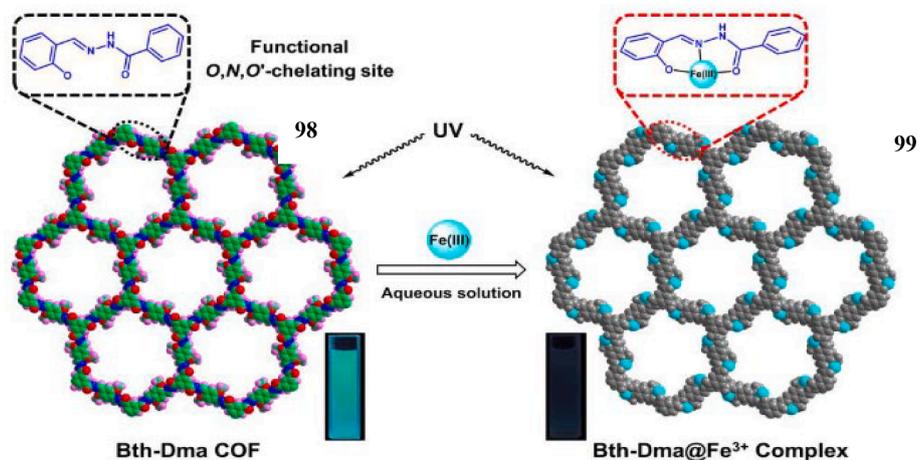


Fig. 9. Bth-Dma as a turn-off fluorescence sensor for the Fe(III) ion in aqueous solution (Figure is reproduced by the permission taken from ACS, copyright).

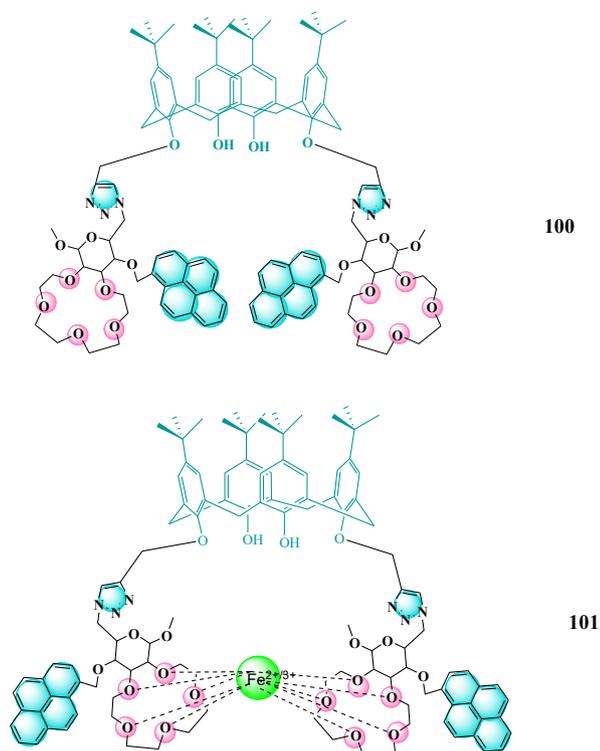


Chart 19. Detection of iron and its binding mechanism.

Dma molecule **98** with exceptional selectivity and sensitivity as a turn-off fluorescence sensor (**99**) as presented in Fig. 9 [46].

Santhosh Kumar et al. synthesized a naphthalene pyridine Schiff base chemosensor **100** for the detection of Fe<sup>2+</sup> ions in a CH<sub>3</sub>CN-H<sub>2</sub>O solution (Chart 19). The sensor showed high selectivity and sensitivity towards Fe<sup>2+</sup> ions in aqueous media (**101**) with a lower detection limit of  $1.5 \times 10^{-7}$  M. Fluorescence “turn-on” recognition follows the ICT process and C=N isomerization. Moreover, the determination of Fe<sup>2+</sup> in a variety of samples was analyzed including commercially available tablets, tomato juice, dark chocolate, and tap water [206].

Zhu et al. (2019) investigated a new and tri-responsive fluorescent Schiff base probe (DBAB) **102** that has been designed and developed for the recognition of Fe<sup>3+</sup>, Fe<sup>2+</sup>, and Cu<sup>2+</sup> simultaneously (**103–105**). This sensor displays a favorable selectivity for Fe<sup>3+</sup>, Fe<sup>2+</sup>, and Cu<sup>2+</sup> ions over a range of other common metal cations in DMF solution, leading to

prominent fluorescence on-off. The detection limits were  $2.17 \times 10^{-6}$  M for Fe<sup>3+</sup>,  $2.06 \times 10^{-6}$  M for Fe<sup>2+</sup>, and  $2.48 \times 10^{-6}$  M for Cu<sup>2+</sup> respectively. The recognition mechanism of DBAB toward Fe<sup>3+</sup>, Fe<sup>2+</sup>, and Cu<sup>2+</sup> has been investigated in detail by Job plot measurements (Scheme 21) [71].

### 5.7. Cobalt ion detection

Gurusamy, S et al. found that NNO **70** had a preferential colorimetric reaction toward Co<sup>2+</sup> (**108**) and Cu<sup>2+</sup> (**107**) cations that could be seen with the naked eye. Their binding mechanism is shown in Scheme 22. Furthermore, at a detection limit of 1.92 M, the NNP demonstrated selectivity for F<sup>-</sup> over other anions in the THF solution. The NNP ligand was also shown to be related to DNA from the calf thymus (CT-DNA) [207].

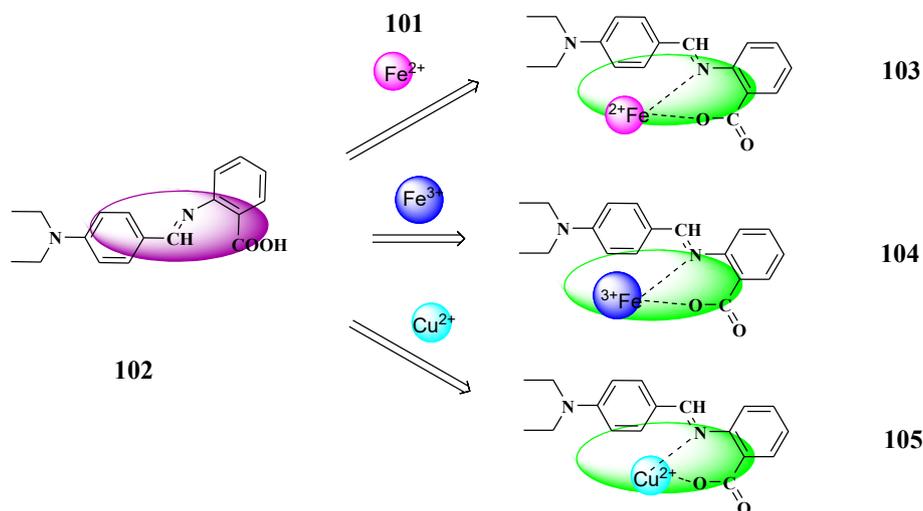
### 5.8. Zinc detection

P. Saluja et al. created an imine-based benzimidazole chemosensor capable of chromogenic detection of Mg<sup>2+</sup> and fluorescence recognition of Cr<sup>3+</sup>. It may also be used to detect Mg<sup>2+</sup> via UV-vis absorption spectroscopy and DFT calculations. The sensor may be used to stretch microbe cells without breaking them [208]. Anbu, S. et al. build a novel benzimidazole-based Schiff base type fluorogenic chemosensor (DFB) **73** that detects Cu<sup>2+</sup> (LOD = 24.4 0.5 nM) (**75**) and Zn<sup>2+</sup> (LOD = 2.18 0.1 nM) (**74**) in a fluorescence “off-on” way which given by Scheme 23 [209].

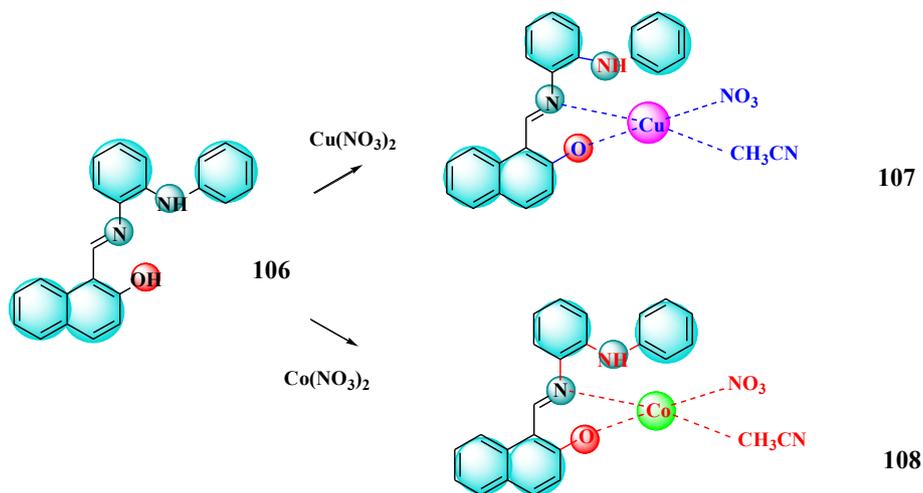
A new photochromic diarylethene was produced by C. Zhang et al. (2015) by combining thiocarbamide as a functional group and perfluorodiarylethene as a photoswitching trigger through a salicylidene Schiff base linkage. When triggered by base/acid, light, and metal ions, diarylethene might be used as a multi-controllable fluorescence switch. Furthermore, the diarylethene’s obvious fluorescence change in acetonitrile from light blue to bright yellow indicated its strong Zn<sup>2+</sup> ion selectivity [55].

### 5.9. Cu ion sensing

Transition metal ions, such as Cu<sup>2+</sup>, are harmful to living organisms even in tiny concentrations. Sidana, Devi, and Kaur et al. (2022) found a Sensor **113** is remarkably selective for the sensing of Cu<sup>2+</sup> and Hg<sup>2+</sup> ions and shows colorimetric changes with a stoichiometric ratio of the probe with Cu<sup>2+</sup> and Hg<sup>2+</sup> ions was found to be 2:1. The limit of detection for Cu<sup>2+</sup> was observed to be 50 nM. Solid substrates such as test strips were developed for field usefulness to provide rapid, reliable, user-friendly, and real-time sensing of both Cu<sup>2+</sup> and Hg<sup>2+</sup> ions (Chart 20) [210].



**Scheme 21.** Example of sensing of  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Fe}^{3+}$  by NO donor Schiff base ligand 102 and their way of binding (103–105).



**Scheme 22.** Colorimetric reaction toward  $\text{Co}^{2+}$  (108) and  $\text{Cu}^{2+}$  (107) cations by 106.

Shakir and Abbasi 2017 develop an isatin-based Schiff base sensor, 114 exhibited a fluorescence turn-off response to  $\text{Cu}^{2+}$  in DMSO: methanol solvent mixture which was further used to detect  $\text{S}^{2-}$  with fluorescence turn-on response (Chart 21). On changing the solvent mixture from DMSO + methanol to DMSO + water reversal of fluorescence behavior was observed for  $\text{Cu}^{2+}$  and  $\text{S}^{2-}$ . Also, the in-situ formed L- $\text{Cu}^{2+}$  ensemble showed a colorimetric response to  $\text{S}^{2-}$  at a high concentration of sulphide ions in both solvent mixtures. Sensor, 114 was successfully applied to recognize  $\text{Cu}^{2+}$  and  $\text{S}^{2-}$  in human blood serum with micro molar detection limits [211].

$\text{Cu}^{2+}$  detection turn-off sensors which are AIE-active sensors 79, 80 as shown in Chart 22. They emitted strongly at 484 nm in a solvent THF- $\text{H}_2\text{O}$  combination. When  $\text{Cu}^{2+}$  was added to the solution, the fluorescence intensity decreased significantly, which was ascribed to MLCT between  $\text{Cu}^{2+}$  and Probe 115 and 116, which may be the result of the CHEQ effect [212,213].

Another few examples of copper ion sensors 117–120 are shown below in Chart 23 [214].

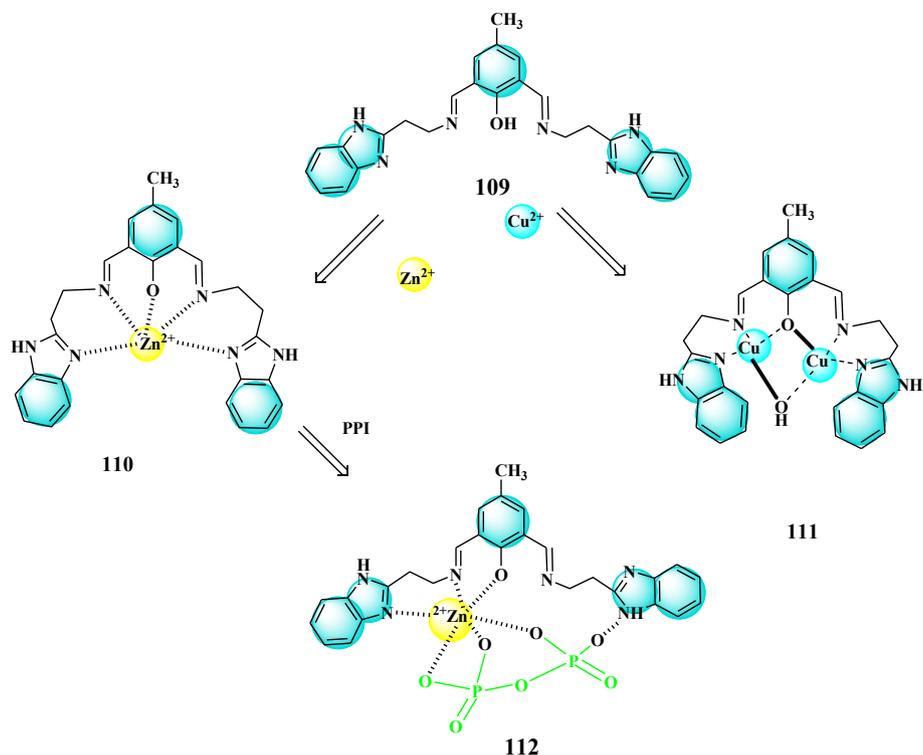
### 5.10. $\text{Au}^{3+}$ probe

Gold is used in pharmaceutical formulations to treat disorders including cancer, TB, and arthritis. Gold ions have the potential to cause

cell toxicity in living things due to their strong affinity for biomolecules like DNA and enzymes. Furthermore, the liver, kidneys, and peripheral nervous system can also be impacted by gold ions [215,216]. S. Mondal et al. designed and synthesized a chromogenic and “off-on” fluorogenic chemodosimeter based on a naphthalene-rhodamine B derivative 121 that demonstrated a 696-fold “turn-on” fluorescence signal amplification toward  $\text{Au}^{3+}$  ions, with an  $\text{Au}^{3+}$  detection limit of approximately 1.51  $\mu\text{M}$  and a color shift from colorless to pink visible with the naked eye due to the  $\text{Au}^{3+}$  ions (Chart 24) [217].

### 5.11. Silver ion detection

Silver ion is one of the most poisonous heavy metals, after mercury in terms of toxicity, and has thus been assigned the highest toxicity rating, with cadmium, chromium, copper, and mercury [218,219]. Bhasin et al. (2017) develop a colorimetric and fluorometric dual-channel non-sulphur chemosensor based on an easy-to-prepare double naphthalene Schiff base is described (122), and its synthesis procedure is shown in Scheme 24. The twisted intramolecular charge transfer (TICT) technique was used to detect  $\text{Hg}^{2+}$  ions. Furthermore, because the complex 122- $\text{Hg}^{2+}$  is a potentially recyclable component in sensing materials, it might be employed as a bright sensor for iodine anions. Notably, there are considerable color shifts, and all of the identification and recycling



Scheme 23.  $Zn^{2+}$  (**110**, **112**) and  $Cu^{2+}$  sensing (**111**) by **109** with their binding mechanism.

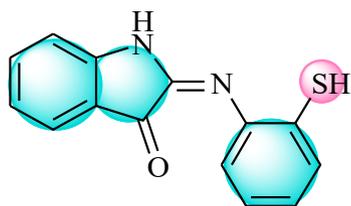


Chart 20. Sensor for  $Cu^{2+}$  ion.

processes are apparent to the naked eye [220]. Another sulphur-containing macrocycle **122** for silver sensing is observed (Chart 25) [214].

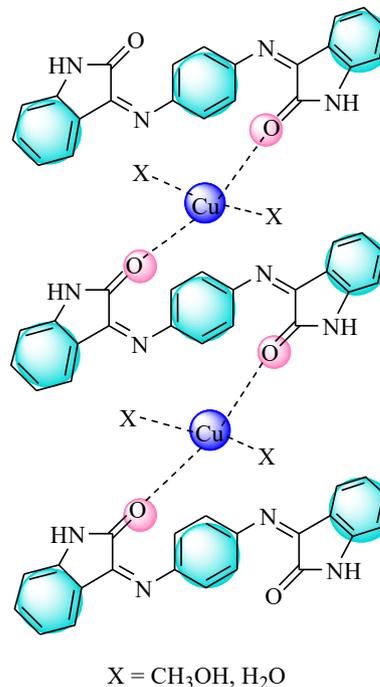
#### 5.12. Another metal-Yttrium

As a membrane-active component, a novel Schiff's base containing sulphur and nitrogen donor atoms DSAB, **124** was employed to construct a  $Y^{3+}$  selective polymeric membrane microelectrode (Chart 26). The electrode displays a Nernstian response to  $Y^{3+}$  ions, with a detection limit of  $7.0 \times 10^{-8}$  M (6.2 g/mL) with a quick reaction time of 5 s. The suggested microsensor was also utilized to determine yttrium in a sample of yttrium-aluminum alloy [214].

## 6. Advantages

Chalcogen-based sensors are capable of a wide range of functions, particularly in biological systems, since they possess many important characteristics. One of the most prominent properties of compounds containing selenium and tellurium is their ease of oxidation, which results in the production of chalcogenides and chalcogenoxide, which is helpful for metal ion detection.

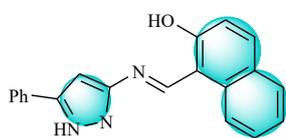
**113**



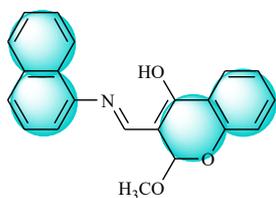
**114**

Chart 21. An isatin-based Schiff base sensor a fluorescence turn-off response to  $Cu^{2+}$ .

1. Tellurium has the unusual ability to quickly insert into and withdraw from organic molecular scaffolds. Metal/oxidant selectivity is closely related to several structural factors, such as preferred donor atoms, ligand field geometries, hard-soft acid-base ratios, and chemical redox properties.



115



116

**Chart 22.** Chemical structure of triazole-based Schiff base sensors 115 and 116.

2. Due to their stability, simplicity in preparation, structural flexibility, and wide range of coordinating abilities, chalcogenated Schiff bases play a significant role in coordination chemistry, and their coordination complexes have a wide range of applications.
3. The detection technique used offers many benefits, including convenience of use, quick detection, minimal ligand consumption, and high sensitivity.
4. Donor ligand-containing Se/Te electrode-based sensor for diverse metals. These are used for producing electrical signals for various metals and identification.

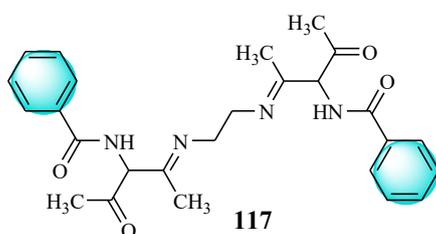
#### 7. Disadvantages

The major issue is their low stability, especially probes containing organo-tellurium residues.

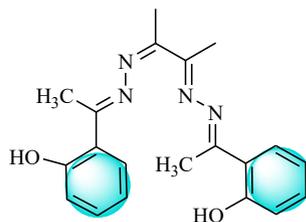
1. In an aqueous medium, the fundamental constraints of as-developed Schiff base sensors are instability and poor water solubility.
2. A strong odour of tellurium/selenium/sulphur compounds.
3. The harmful impact on the health of these chalcogen-containing donor ligands has been demonstrated in several instances.
4. Because most Schiff bases are yellow-colored ligands, they are difficult to identify.
5. It is required special and complicated conditions to manufacture Se/Te-containing ligands.

#### 8. Future prospective

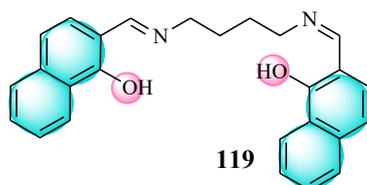
The addition of Se/Te to the various ring diameters of the Schiff base macrocycle has resulted in novel coordination chemistry as well as rich



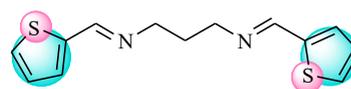
117



118

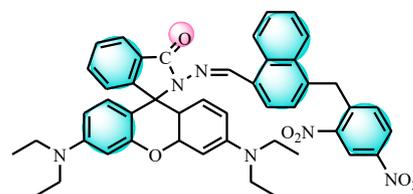


119



120

**Chart 23.** Examples of Cu<sup>2+</sup> sensor.



121

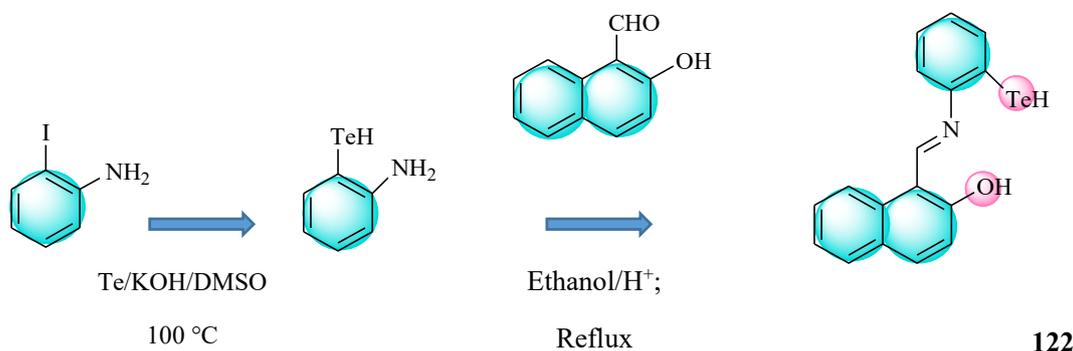
**Chart 24.** Rhodamine-based Schiff base sensor 85.

structural chemistry. By varying the kind, number, and arrangement of ligand donors, as well as ligand conjugation, substitution, and flexibility, novel macrocycles can be created. Many fresh and intriguing avenues must yet be explored. Larger ring-size macrocycles, for example, may be very helpful for the coordination of big cations such as lanthanides and actinides and may be good for the removal of these ions from radioactive and non-radioactive wastes, which is quite intriguing in terms of protection.

1. The donor ligand oxygen and sulphur is frequently explored, but relatively few ligands of selenium and tellurium donor atoms are investigated. A unique donor set with selenium and tellurium may be created and used for metal ion sensing.
2. Chelation efficiently binds bidentate and tridentate ligands to other metal ions. Many phenolphthalein, anthracene, and pyrene-based ligands have been investigated and can be yielded interesting results.
3. Schiff bases' distinctive complexing ability makes them very selective and sensitive in detecting numerous targets in nature itself along with various metals [246,247]
4. There is still a pressing need to examine the optical sensing qualities of previously manufactured Schiff base metal complexes, as well as to develop new ones with superior sensing properties.
5. Online detection is a challenging topic that requires attention among the many detection options. To do this, chemosensor-equipped electronic probes might be created, and the signals would then be connected to the internet to allow for real-time online mapping of various environmental samples.

#### 9. Conclusions

Schiff-based chemosensors are used in multi-metal ion sensors, sequential ion sensors, optoelectronic systems, etc. Schiff bases utilized as chelating agents can be used to detect and sense various ions utilizing several analytical procedures. Through the use of fluorescence turn-on or turn-off procedures visible to the naked eye or under UV light, toxic



Scheme 24. Sequential NOTe sensor.

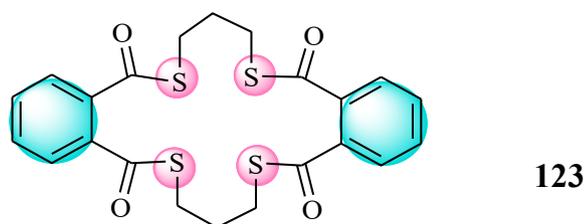


Chart 25. Sulphur containing macrocycle for silver sensing.

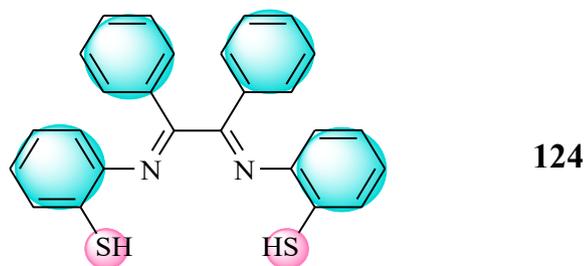


Chart 26. Schiff's base containing sulphur and nitrogen donor atoms DSAB.

metals, and ions may be quickly recognized after complexation with Schiff base ligands. Nevertheless, it is becoming more and more important to research the optical sensing properties of already discovered Schiff base metal complexes and to create new ones with improved sensing capabilities. As a result, rapid deployment of efficient control measures would be possible. This will help in the early detection of pollution and related issues. Metal ions and the Schiff base ligand formed a connection on their own. Despite the numerous difficulties in experimental investigation and practical application, Schiff bases and their metal ion complexes are exploited by researchers for synthetic applications due to their outstanding performance in metal ion detection. It is anticipated that Schiff base detectors will soon be utilised as needed and be commercially available in strip and tablet form by combining the aforementioned elements into sensor design and application-focused research.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

No data was used for the research described in the article.

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