

Recent Developments in the Detection of Zn²⁺ Ions Using Schiff Base Probes

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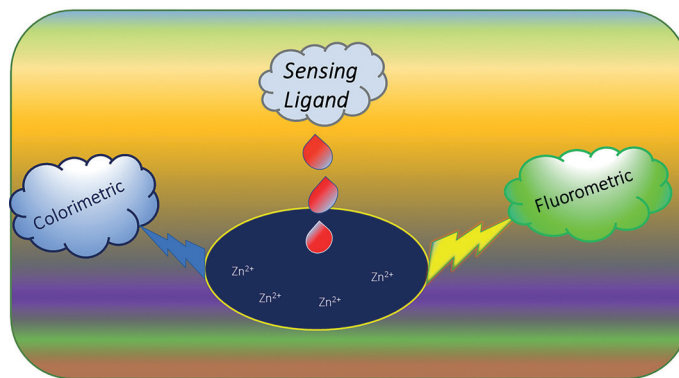
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Abstract In the past few decades, zinc has attracted great attention from the scientific community due to its supreme importance in living organisms. Zinc is a trace element that is vitally important to all living organisms and it plays an important role in the immune system, wound healing, growth, and division. Therefore, the development and advancement of simple, efficient, selective, and inexpensive chemosensors for the determination of Zn²⁺ is a paramount prerequisite. Chemosensors have unique properties that are used for the specific and selective determination of several metal ions. This review summarizes the Schiff base chemosensors designed and synthesized by several research groups from the year 2018. The interaction of these probes with zinc metal ions has also been discussed briefly in this review. Furthermore, the comparison of detection limits of these probes demonstrated that the Schiff base probe possessing two benzothiazole moieties exhibits the lowest detection limit (0.00028 μM), indicating it to be the lead compound in the determination of Zn²⁺ ions in the near future.

Keywords chemosensors, detection, probes, zinc, Schiff base

Introduction

Zinc is a crucial trace element for human health; it is essential for maintaining our physical and mental well-being as well as for the growth of our immunity.^{1–4} Intake of either an excess or deficiency of Zn²⁺ ions can cause several diseases.^{5–12} Deficiency of Zn²⁺ ions in the human body is known to be associated with the onset of Alzheimer's disease.^{13–15} While, its excess can hamper the bacteriostatic

power of scavenger cells, which reduces the immune functions of the body, resulting in decreased capability to fight diseases.^{16–18} In addition, Zn²⁺ is crucial to plant metabolism because it influences the growth and development of plants.¹⁹ However, an excess of zinc in the environment can cause serious harm. Given these difficulties, it is essential to discover and develop sensitive and specific ways to identify Zn²⁺ ions that are simple to use and provide a swift response.^{20–22} Currently, several techniques are available for metal ion recognition, such as electrochemical,²³ neutron activation analysis,²⁴ high-performance liquid chromatography (HPLC),²⁵ atomic absorption and emission spectroscopy,^{26,27} mass spectrometry,²⁸ anodic stripping voltammetry,²⁹ electrothermal atomic absorption spectrometry,³⁰ capillary electrophoresis,³¹ and inductively coupled plasma mass spectrometry.³² Although these techniques have good selectivity, sensitivity, and rapid response, they also have some limitations or drawbacks because these techniques can be expensive, require complex instrumentation handling, and require significant sample pre-treatment.^{33,34} Therefore, highly sensitive, selective, and efficient methods are still needed for the detection of Zn²⁺ ions at trace levels. Two types of promising chemosensors have been attracting significant attention; namely, colorimetric and fluorometric chemosensors. Both approaches are targets of vigorous research for the detection of Zn²⁺ ions, the majority of which are based on Schiff bases.

Schiff bases have a spectacular coordinating affinity with zinc ions and are recognized as exceptional chelating ligands.^{35,36} Given their extraordinary properties, Schiff bases are currently employed as efficient chemosensors for the identification of various cations and anions and electron-deficient substances such as nitro-aromatics.^{37,38}

Colorimetric sensors are a type of chemical sensor that detects analytes by producing visible color change. Colorimetric sensing³⁹ offers selective and sensitive detection of various kinds of species such as metal cations, anions, drugs, toxic waste, biomolecules, and organic dyes. Without the use of sophisticated devices, the colorimetric chemosensors provide reproducible, low-cost, effective, fast, and appropriate detection of environmental and biological toxicities through indicators that are visible to the unaided eye.⁴⁰ Internal charge transfer (ICT), which is brought on by interactions between the chromophore and the hydrogen atoms of the analyte, leads to a considerable shift in the

ability of the chromophore unit to absorb light,⁴¹ which means that such systems have great potential for analyte detection methods.

The fluorometric chemosensors are a chemical family that can be used to easily determine various types of analytes. When interacting with different species of analytes,⁴² such as biological scaffolds, neutral molecules, anions, and cations, fluorometric chemosensors can detect a specific substance based on its ability to emit fluorescence because its fluorescent characteristics can undergo photophysical changes. Fluorescent sensors are frequently utilized as analyte-determining probes for an extensive variety of biologi-

Biographical Sketches



Ram Kumar completed his M.Sc. in 2019 from the Indian Institute of Technology Indore (IIT Indore), and his B.Sc. (H) in Chemistry

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Dr. Bholey Singh received his Ph.D. in supramolecular chemistry from the leading branch of Inorganic Chemistry from the Department of Chemistry, University of Delhi in 2021 under the supervision of Prof. Balaram Pani and an M.Sc. from the same institution in 2015. He graduated with a B.Sc from the Faculty of Natural Sciences, Jamia Millia Islamia University, New Delhi with the highest

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tive rhenium-based metal complexes and for studies of energetics and DNA-ligand interactions. More recently, he has focused on the design and synthesis of chemosensors that may be used as molecular probes to study biological function by application of an exciting and fundamentally new approach.



Dr. Shwetank Shashi Pandey completed his Ph.D. at the University of Delhi (specialization in environmental chemistry). He obtained his MTech in Environ-

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Prof. Balaram Pani (Dean of Colleges at the University of Delhi) received his Ph.D. in environmental sciences from Jawaharlal Nehru University (J.N.U) Delhi, M.Phil. in environmental sciences from the same institution, and M.Sc. in chemistry

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strumental methods of analysis, and polymer science are some of his areas of expertise. He was awarded with the prestigious Soul of India Award in a monumental ceremony honoring their remarkable contributions to nation-building.

cal applications because they exhibit a change in emission spectra, wavelength, and lifetime decay during molecule recognition.⁴³ While increasing the wavelength, a probe is deactivated from the excited singlet state to the ground state, to produce fluorescence with a typical lifespan decay of 10–9 seconds.⁴⁴ There are two types of phenomena involved in fluorescence: quenching and enhancement. Fluorescence enhancement is the process of increasing the intensity of fluorescence emitted by the fluorescent molecules. Whereas, fluorescence quenching is the process that decreases the emission intensity of the fluorescent probes.⁴⁵ Most of the reported fluorometric and colorimetric probes are based on organic skeletons that include Schiff

base moieties, because of their simple synthetic accessibility and because of the extraordinary coordination of the binding sites with the ions.⁴⁶

In this article, Schiff base chemosensors that have been synthesized by different research groups since 2018 to encapsulate zinc metal ions selectively and specifically using various spectrophotometric techniques are summarized.

It is believed that these Schiff base probes will provide crucial information for the further development of chemosensors that are more efficient. Table 1 compares the ability of Schiff base probes to recognize Zn²⁺ ions and summarizes the current lowest detection limits.

Table 1 Schiff Base Probes for the Recognition of Zn²⁺ Ions with the Lowest Detection Limit

Entry	Chemical structure	Ions detected	Detection limit (μM)	Ref.
5		Zn ²⁺	0.00223	51
9		Zn ²⁺	0.00421	55
14		Zn ²⁺	0.00343	60
16		Zn ²⁺	0.00272	62
18		Zn ²⁺	0.00129	64
30		Zn ²⁺	0.00560	76
34		Zn ²⁺	0.00028	80
44		Zn ²⁺	0.0012	90
49		Zn ²⁺	0.00675	95

Schiff Base Probes for Zn²⁺ Recognition

For the determination of Zn²⁺ ions, a fluorescent Schiff base sensor **1** (Figure 1) was synthesized by Gau Xu and his research group.⁴⁷ Xu *et al.* reported a hydrazone Schiff base based chemosensor that was further characterized by various spectroscopic techniques. The sensor showed weak fluorescence alone, but with the incorporation of Zn²⁺ ions, the intensity of fluorescence enhanced rapidly and exhibited an intense yellow-green emission. The binding stoichiometry ratio of sensor **1** was observed to be 1:1, as confirmed by the Job plot, and the binding constant was found to be 184 M⁻¹. The limit of determination was found to be 112 μM and the authors also designed a test paper strip for rapid detection of Zn²⁺ ions.

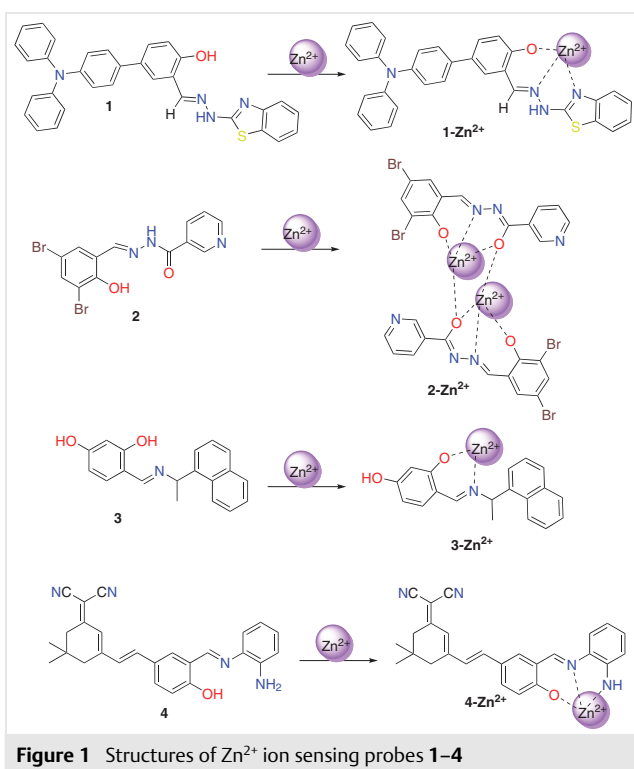


Figure 1 Structures of Zn²⁺ ion sensing probes 1–4

A responsive multi-stimulated organic fluorescent compound **2** (Figure 1) was synthesized by Francis Joy and her research group⁴⁸ for the detection of Zn²⁺ ions in a water-based solution. This hydrazone-based Schiff base turn-on chemosensor was highly sensitive and selective in nature towards the Zn²⁺ ion. The chemosensor was investigated and showed a remarkable increase in emission intensity towards the Zn²⁺ cation in a water-based solution, whereas the intensity drastically decreased for other metal cations. The stability constant was found to be 4.587 × 10³ and the detection limit was 9.315 μM. The researchers also made a film composite of the synthetic compound to sense Zn²⁺

ions in the solid state. In addition, the determination of Zn²⁺ ions from images of nervous cells of rats using this fluorescent sensor **2** was demonstrated.

Li *et al.*⁴⁹ reported, a novel naphthalene-based Schiff base probe **3** (Figure 1) for the detection of Zn²⁺ ions. This synthesized probe showed a turn-on fluorescent nature towards Zn²⁺ ions. The probe shows good sensitivity and selectivity towards Zn²⁺ ions in DMF/H₂O solution. The sensing was ascribed to a chelation-enhanced fluorescence mechanism (CHEF) and the probe showed absorbance bands at 280 and 380 nm after adding Zn²⁺ ions into the solution. When Zn²⁺ was introduced, the absorption peak of **3** shifted towards the blue spectrum, shifting from 312 nm to 308 nm. At 357 nm, a new absorption band was identified. This finding supports the theory that Zn²⁺ coordination increased conjugation within the L-Zn²⁺ system, resulting in the formation of a unique absorption peak. The emission intensity shown by the probe - Zn²⁺ ions at 425 nm. The coordination ratio was observed to be 3:1 between the probe and Zn²⁺ ion, which was determined with a Job's plot. The lower limit of detection was 8.94 × 10⁻⁸ M and the response time was just a few seconds.

Yang and co-workers⁵⁰ synthesized a dicyanisophorone-based fluorescent probe **4** (Figure 1) for the detection of Zn²⁺ ions. This synthesized probe was rapidly combined with Zn²⁺ ions and shows an absorbance band at 500 nm. During the combination of the probe and Zn²⁺ ions, color changes were observed from light-yellow to orange. Meanwhile, the intensity of fluorescence shows a large Stokes shift of 179 nm. The response time was found to be less than 30 seconds. The limit of detection was calculated to be 4.8 nM, which was suitable for the detection of Zn²⁺ ions in real water samples. In addition, a sharp and clear image was obtained in A549 cells.

To detect the Zn²⁺ ions, a Schiff base scaffold chemosensor **5** (Figure 2) was developed by Malini Nelson and her research group.⁵¹ This synthesized chemosensor was characterized with the help of different spectroscopic techniques and showed high selectivity and responsiveness toward Zn²⁺ ions in DMSO/H₂O solution. The sensor showed a fluorogenic response with Zn²⁺ ions and weak emission of bluish-green fluorescence accompanied by turn-on and -off processes. The limit of detection and binding constant for the Zn²⁺ ions were calculated to be 2.23 nM and 2.3115 × 10³ M⁻¹, respectively. In addition, the quantum yield calculated for the sensor and complex was determined to be 0.008 and 0.8, respectively. Water samples, swab tests, and test strips were also used to demonstrate the determination of Zn²⁺ ions. This sensor was also compatible with the detection of Zn²⁺ ions in A549 cell imaging.

Fluorescent probe **6** (Figure 2) was designed by Yu and his group⁵² for the determination of Zn²⁺ ions in an aqueous solution. A rapid increase in the fluorescent emission intensity was observed with Zn²⁺ ions in the solution that was very specific towards the Zn²⁺ ions. The molar binding ratio

was 2:1 between the probe **6** and the Zn^{2+} ion. The limit of detection was calculated to be 2.43×10^{-5} M. No cytotoxicity towards HeLa cells was observed.

A benzothiazole-based fluorescent chemosensor **7** (Figure 2) was reported by Li *et al.*⁵³ The sensing capacity was identified using fluorescence spectroscopy and there was a high degree of selectivity of the probe towards Zn^{2+} ions. This sensor works well within a wide pH range of 7–10. The sensor had a stoichiometry ratio of 1:1, with a detection limit of $0.68 \mu\text{M}$. The response time for the detection of Zn^{2+} ions was just 30 seconds.

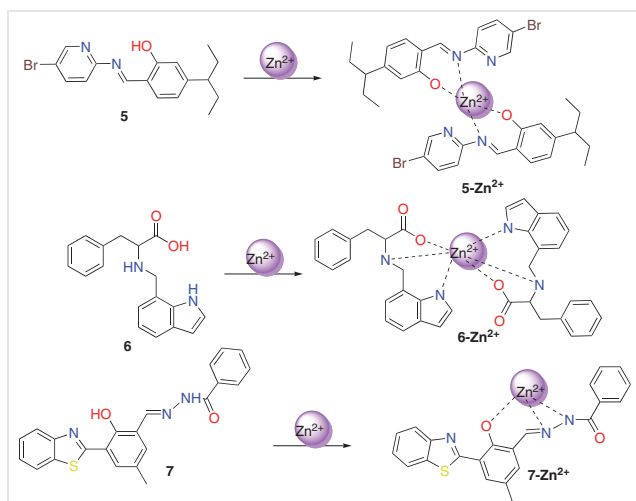


Figure 2 Structures of Zn^{2+} ion sensing probes 5–7

A bidentate Schiff base ligand **8** (Figure 3) was synthesized for the determination of Zn^{2+} ion in water by Viviana *et al.*⁵⁴ The structure of the synthesized ligand **8** was characterized with the help of FTIR and NMR analyses, and its optical characteristics were established by UV/Vis absorbance spectroscopy and photoluminescence measurements. In the UV/Vis spectra, the synthesized probe shows two intense absorption bands that were observed at 318 nm and 380 nm due to the $\pi-\pi^*$ electronic transition of the conjugated aromatic ring and $n-\pi^*$ electronic transition of the amine group, respectively. Fluorescence studies revealed that luminescent quenching of the ligand occurred upon the addition of Zn^{2+} ions to the ligand. Furthermore, a simple modified screen-print carbon electrode (SPCE) was used to determine the micro detection limit of the synthesized ligand with Zn^{2+} ion. For the detection of Zn^{2+} ion, good linearity, high sensitivity, and selectivity of 50.1 mV/dec were established. The response time was calculated to be 10 seconds.

The successful synthesis of a phenolphthalein derivative chemosensor **9** (Figure 3) for the detection of Zn^{2+} ions was reported by Aydin and Alici.⁵⁵ This sensor **9** could be used to selectively monitor Zn^{2+} ions easily and impart color change in EtOH/HEPES buffer solution. On the addition of Zn^{2+} ions

into the solution, sensor **9** showed a high enhancement in the fluorescence intensity. The stoichiometry ratio was found to be 1:2 between the sensor **9** and Zn^{2+} ions. The detection limit was calculated to be 4.21 nM, determined from a Job's plot. This chemosensor also detects Al^{3+} ions.

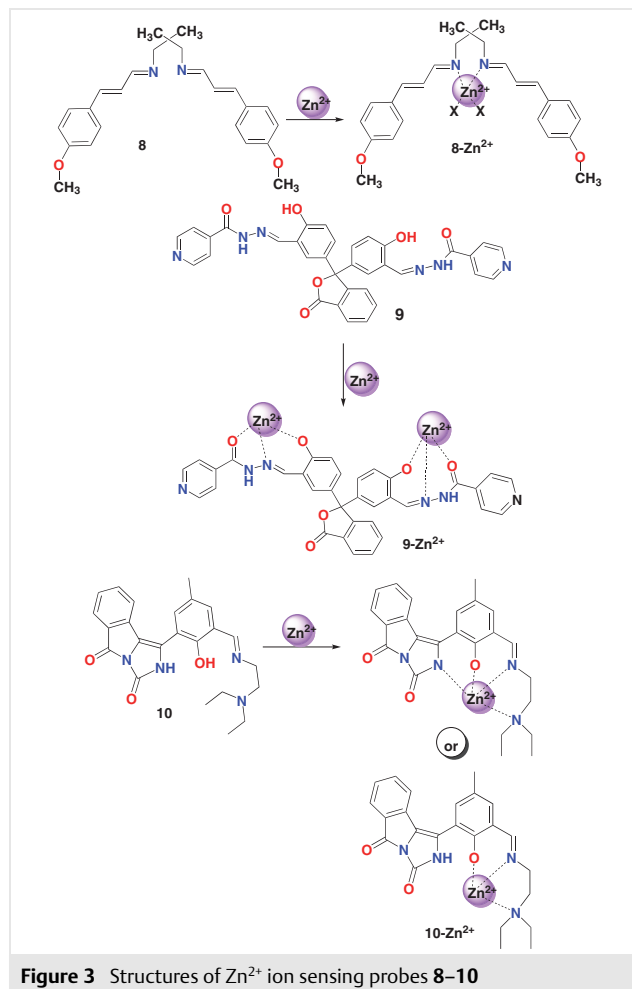


Figure 3 Structures of Zn^{2+} ion sensing probes 8–10

Sahu *et al.*⁵⁶ synthesized a turn-on fluorescence moiety **10** (Figure 3) based on the isoindole-imidazole scaffold for the detection of Zn^{2+} ions. This Schiff base chemosensor was synthesized and characterized with the help of various spectroscopic techniques such as HRMS, HMR, and FTIR spectroscopy. The optical properties were investigated using UV/Vis and fluorescence spectroscopic techniques. From the UV/Vis studies, the absorption peaks of the moiety were identified at 405 nm and 480 nm. This moiety changed color from colorless to pale yellow in the presence of Zn^{2+} ions. Gradual increase in the concentration of Zn^{2+} ions in the solution increased the absorbance peak at 419 nm, which showed the interaction of Zn^{2+} ions with probe **10**. The moiety shows weak fluorescence intensity with a quantum yield of 0.036, while the addition of Zn^{2+} ions to the solution resulted in a 19-fold fluorescence intensity en-

hancement with a quantum yield of 0.69. The detection limit was found to be $0.073 \mu\text{M}$. The titration and Job's plot indicate the formation of 1:1 of moiety/ Zn^{2+} bindings. The binding constant was found to be $3 \times 10^4 \text{ M}^{-1}$.

Han and his research group⁵⁷ developed a quinoline-based supramolecular gel **11** (Figure 4) for the selective detection of Zn^{2+} ions. This Schiff base probe **11** forms organogels with organic solvents such as acetone, DMSO, DMF, ACN, EtOH, and 1,4-dioxane. This assembly was analyzed by field emission scanning electron microscopy (FESEM), UV/Vis, fluorescence, and FTIR spectroscopy, and by XRD and water content angles. Under noncovalent interactions, self-assembly takes place to form nanofiber structures. Weak fluorescence intensity was shown by the gelator group on the addition of Zn^{2+} ions into the solution. The sensitivity and selectivity were also relatively high towards Zn^{2+} ions. This shows an enhancement in the fluorescence intensity. The emission intensity increased from 423 nm to 545 nm, and the limit of detection was found to be $5.5 \mu\text{M}$.

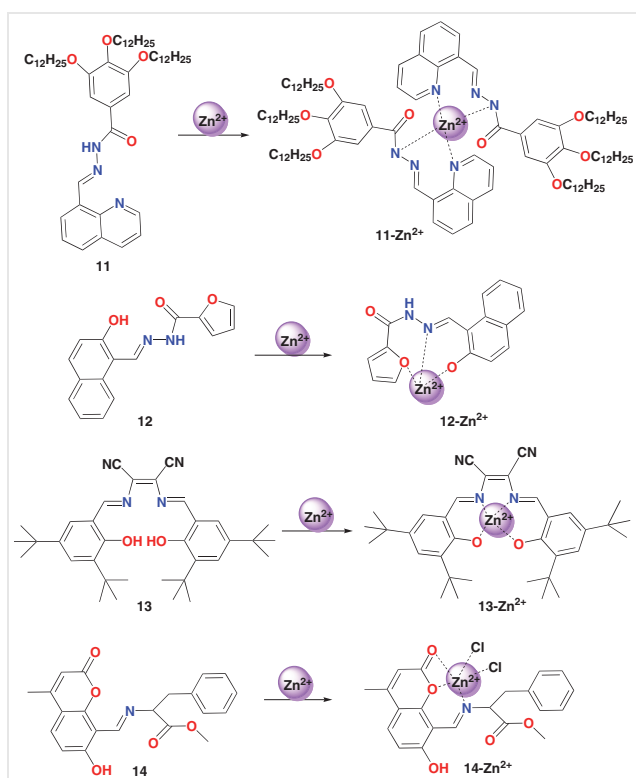


Figure 4 Structures of Zn^{2+} ion sensing probes **11–14**

A turn-on fluorescence Schiff base probe **12** (Figure 4) based on 2-hydroxy-1-naphthylaldehyde was developed for the recognition of Zn^{2+} ions in real water samples by Mu *et al.*⁵⁸ The probe was analyzed by absorption spectroscopy and showed three absorption bands at 262, 325, and 362 nm. A gradual decrease in the absorbance band was observed with the addition of Zn^{2+} in the solution. New bands

appeared at 337 nm and 428 nm, and a color change was observed from colorless to yellow. Four isosbestic points were observed at 284, 333, 339, and 387 nm, which indicate the formation of a new complex between the probe and the Zn^{2+} ion. The emission intensity was enhanced by the addition of Zn^{2+} ions to the solution. The complexation constant was found to be $1.13 \times 10^5 \text{ M}^{-1}$. The HOMO-LUMO energy gap between the probe and Zn^{2+} was 1.49 eV. The stoichiometry ratio was 1:1 between the probe and Zn^{2+} . Moreover, cell imaging fluorescence experiments demonstrated that trace Zn^{2+} could be observed in living cells with low cytotoxicity.

A visible colorimetric probe **13** (Figure 4) was designed and synthesized by Venkatesen *et al.*⁵⁹ Schiff base condensation reaction was performed using this diaminomaleonitrile derivative to sense Zn^{2+} ions selectively. The sensing ability of this probe was successfully investigated with the help of visual and UV/Vis techniques. The absorption band appeared at 595 nm with molar absorptivity $14578 \text{ LM}^{-1}\text{cm}^{-1}$. This arises due to the metal-to-ligand charge-transfer phenomenon (MLCT). The response of the ligand was dependent on the pH of the solution; complex formation easily takes place within the range of pH 8–11. The stoichiometry and binding constant calculated with the help of B-H plots were 1:1 and $2.63 \times 10^3 \text{ M}^{-1}$. The HOMO-LUMO energy gap between the probe and complex was found to be 2.23 and 2.63 eV, respectively. The points of reference for coordination were (N,N,O,O). The detection level was found to be $5.8 \times 10^{-7} \text{ M}$. The employment of **13** in logic gates is one of its additional beneficial applications.

A new innovative coumarin-based fluorescent probe **14** (Figure 4) was synthesized and characterized. The fluorescent probe was shown by Arvas *et al.*⁶⁰ to exhibit significant fluorescent quenching in the presence of Zn^{2+} ions. The limit of detection was found to be $3.43 \times 10^{-9} \text{ M}$ for the detection of Zn^{2+} ion. The stoichiometry ratio of the probe and Zn^{2+} ion, as determined by the Job's plot linear function was 1:1, and the association constant was calculated to be $2.39 \times 10^4 \text{ M}^{-1}$. No toxic effect was observed on L929 cells by the MMT method.

He, Cheng, and Zheng⁶¹ synthesized two fluorescent probes **15** (Figure 5) for the detection of Zn^{2+} ions in real water. These two probes were synthesized from salicylaldehyde benzoyl hydrazine using the Schiff base condensation reaction pathway and were characterized by various spectroscopic techniques. Probe **15** showed weak fluorescence intensity but, on the addition of Zn^{2+} ion in solution, a very high enhancement in the intensity of fluorescence was observed even in the presence of many other metal ions. This shows the selectivity and sensitivity of the designed probe **15** towards Zn^{2+} metal ions. The calculated molar binding ratio of the probe and Zn^{2+} ion was 1:1, and the coordinating sites were O and N of the fluorophore. The probe was also used for bio-imaging after incubation of ECV304 with

the probe for 30 min at 37 °C. A red color was emitted from the intracellular area, which indicates that **15** could be used for dynamic imaging and for tracing Zn²⁺ ions in living cells.

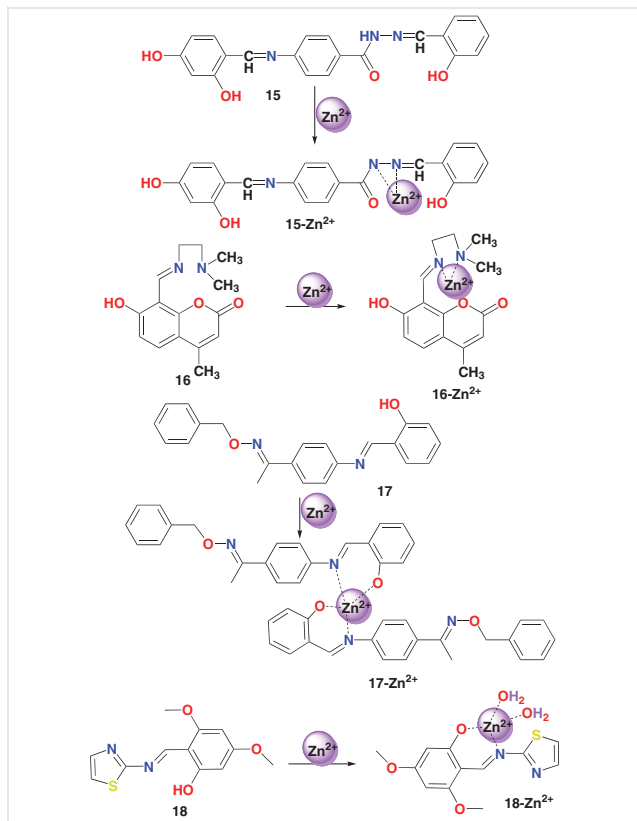


Figure 5 Structures of Zn²⁺ ion sensing probes **15–18**

A coumarin-tagged diprotic scaffold fluorophore **16** (Figure 5) was derived by Bhasin and co-workers⁶² for the detection of Zn²⁺ ions in semi-aqueous medium. This multidentate ligand works well with Zn²⁺ ion, with which it can easily bind, and shows turn-on fluorescence with 0.272 nM concentration in a semi-aqueous medium. The multidentate ligand has a triclinic crystal system and P-1 space group with a three-coordinating site. The molar ratio of the probe and Zn²⁺ ion binding was 1:1, and the detection limit was calculated to be 0.272 nM. Another potential application of **16** is in the field of medicine, as Zn²⁺ ion-binding moieties play vital roles as pharmacophores in certain drugs.

To sense metal ions such as Zn²⁺ ions, Juan Li and his group⁶³ synthesized probe **17** (Figure 5) based on oxime and salicylaldehyde. This chemosensor performed well in the case of an aqueous medium (DMSO/H₂O, 9:1 v/v). The selectivity and sensitivity of probe **17** towards Zn²⁺ ions were determined using fluorescence and UV/Vis spectroscopic techniques. A weak absorption band was shown by the ligand at 425 nm, but after the addition of Zn²⁺ ions to the solution, the absorbance band shifted towards a higher

range around 458 nm; i.e., a redshift was observed with a color change of the solution from colorless to yellow. The UV/Vis characteristics show that the molar ratio of metal and ligand was 1:2, and the association constant was $5.6 \times 10^4 \text{ M}^{-1}$. For the fluorescence recognition of Zn²⁺ ions using probe **17**, the emission peak of the probe was observed at 437 nm, and, after the addition of Zn²⁺ ions, the emission peak moved to higher wavelength at 502 nm. When Zn²⁺ ions were introduced to the solution the intensity increased by 16 times. It was determined that the detection threshold was $2.53 \times 10^{-8} \text{ M}$. The HOMO-LUMO energy gap between the probe and complex, based on DFT calculations, was found to be 3.44 eV. This was utilized in various water samples, including drinking water, tap water, and water from the Yellow River.

For the detection of Zn²⁺ ions in water, food supplements, and bio-imaging applications, Aydin *et al.*⁶⁴ designed a new ultra-sensitive sensor using a thiazole derivative. This novel fluorescent probe **18** (Figure 5) was excited at 420 nm, and its emission peak was observed at 503 nm in HEPES/MeCN buffer (5:95 v/v, pH 7.4). The quantum yield of the probe increased from 0.073 to 0.78 with Zn²⁺ ions. The detection limit and binding constant were calculated to be 1.29 nM and $1.102 \times 10^6 \text{ M}^{-1}$, respectively. The stoichiometric ratio between the probe and Zn²⁺ ion was 1:1 as determined by a Job plot. The mechanism of fluorogenic response was explained by photoelectron transfer, and further theoretical DFT studies were also performed.

A solvent-dependent fluorescent probe **19** (Figure 6) for the detection of Zn²⁺ ions was developed by Qin *et al.*⁶⁵ by using the Schiff base condensation reaction pathway. This chemosensor was synthesized with the help of the 8-hydroxyquinoline group and used to determine the Zn²⁺ ions in an EtOH solvent with high sensitivity and selectivity. The stoichiometric molar ratio of this sensor was determined to be 1:1. It was found to inhibit the PET process due to the presence of lone pairs on the nitrogen atom of the C=N group, resulting in an enhancement of fluorescence intensity. The limit of detection was calculated to be $2.36 \times 10^{-7} \text{ M}$ for Zn²⁺ ion. DFT calculations were performed that verified the binding ratio and HOMO-LUMO energy gap between the sensor and complex.

Zhang *et al.*⁶⁶ designed a fluorescent organic nano-material having well-defined AIE characteristics for a colorimetric chemosensor. This organic fluorescent coumarin-based material has been synthesized for the determination of Zn²⁺ ions. Probe **20** (Figure 6) shows AIE aggregation-induced luminescence enhancement properties under various aqueous conditions. The determination of Zn²⁺ ion concentration was carried out using UV/Vis and fluorescent multi-mode analysis of the given probe and showed high sensitivity and selectivity or specificity. The response time of the probe was significantly reduced because of the high instability of the complex. The limit of detection was observed to be 0.026 μM in an aqueous solution. The probe

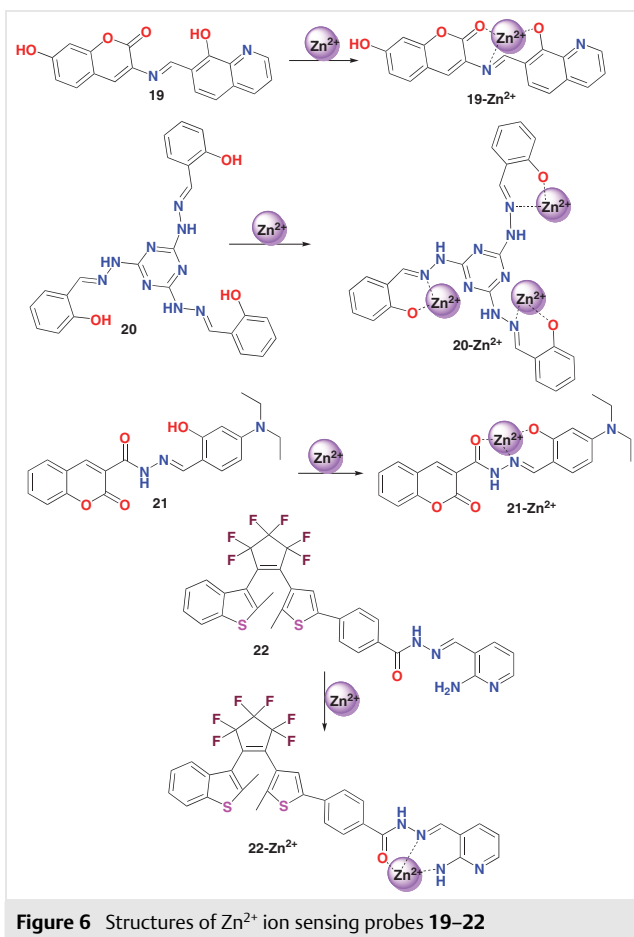


Figure 6 Structures of Zn^{2+} ion sensing probes **19–22**

displayed green fluorescence in the solid powder phase, which can be used to sense ZnCl_2 powder. The material was also combined with a paper strip and polymer thin-film to indicate Zn^{2+} ions with a color change. The probe was also used to detect Zn^{2+} ions *in vivo* in zebrafish cell imaging.

Mondal and her research group⁶⁷ developed a colorimetric and fluorometric triazine-based sensor **21** (Figure 6) for the recognition of Zn^{2+} ions. This new probe has three different binding sites for three metal ions. It is selective for detecting Zn^{2+} ions at all the sites of the molecule; i.e., all the three cavities of the probe **21**. The probe was present in two forms, one was the enol-form, and the second was the keto-form. The selectivity of this probe was observed with the help of UV/Vis and emission spectroscopy. The absorbance of this probe was observed at 330 nm and 338 nm, and after the addition of Zn^{2+} ions, a new peak appeared at 385 nm with a sharp isosbestic point at 355 nm that indicates the formation of a new complex. The emission peak was observed at 430 nm. After the addition of Zn^{2+} ions, a new peak was observed in the emission spectra also at 468 nm with fluorescence intensity enhancement of up to five

times. The coordination ratio of the probe and Zn^{2+} ion was 3:1. The limit of detection was calculated to be 1.22×10^{-7} and 1.13×10^{-7} M for R1 and R2, respectively.

Liu *et al.*⁶⁸ synthesized and designed a novel diaryl-ethene derivative for the detection of Zn^{2+} ions. The structure of the synthesized probe **22** (Figure 6) was characterized with various spectroscopic techniques. The emission spectra displayed excellent sensitivity and selectivity towards Zn^{2+} ions, with emission intensity enhancement of 154-fold with bright-blue fluorescence. The stoichiometric ratio of the probe and Zn^{2+} ion was 1:1, as confirmed by a Job's plot. The probe can also detect phosphate and sulfate via the quenching effect, and another application is that it could also be used as a logic gate.

A new fluorescent moiety was synthesized by Mathew and Sreekanth.^[69] The thiophene-dicarbohydrazone based moiety works well as a colorimetric sensor for the detection of Zn^{2+} ions. The chemosensor **23** (Figure 7) was observed to be highly emissive in nature when it binds with the Zn^{2+} ions and forms the complex in DMSO/water (6:4, v/v) medium. The binding constant was calculated to be $1.15 \times 10^4 \text{ M}^{-1}$. The detection limit was found to be 1.51×10^{-7} M, which is well below the permissible level of Zn^{2+} ion (70 μM) in drinking water listed by the WHO. The binding molar ratio was 1:1 between Zn^{2+} ions and probe **23**. The reversibility and INHIBIT/IMPLICATION logic gate behavior were also shown for this chemosensor.

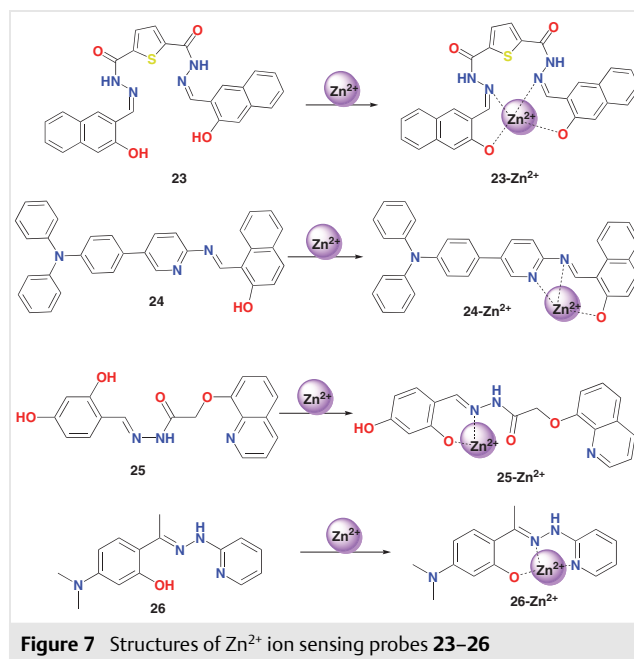


Figure 7 Structures of Zn^{2+} ion sensing probes **23–26**

An important fluorescent probe **24** (Figure 7) was designed by Wang and his research group⁷⁰ for the detection of Zn^{2+} ions in a real water sample. This synthesized probe was shown to have very high selectivity and sensitivity towards Zn^{2+} ions. Emission spectroscopy techniques were

used to show a large Stokes shift of 110 nm with a change in the concentration of solution of Zn^{2+} ions from 0 to 20 μM . The limit of detection was 19.1349 nM and the binding constant was calculated to be $3.24 \times 10^4 M^{-1}$ and the stoichiometric binding ratio was 1:1. This probe was sensitive to a wide pH range. All the interactions of ligand and Zn^{2+} ions were verified by density function theory studies.

Two similar kinds of Zn^{2+} ion sensors **25** (Figure 7) were developed based on a quinoline derivative by Fan *et al.*⁷¹ This fluorescent probe was synthesized with the help of a Schiff base condensation pathway. These two sensors were investigated using UV/Vis and fluorescence spectroscopy. In the UV/Vis spectrum, these sensors showed peaks at 321 nm and 295 nm, respectively. The intensity of these bands decreased gradually upon the addition of Zn^{2+} ions to the probe solution, with the appearance of a new band at 306 nm. Two isosbestic points were also observed at 341 nm and 267 nm, which indicates that the stable complex was formed between the sensor and the Zn^{2+} ion. The emission band appeared at 450 nm in an ethanolic solution. Significant enhancement in emission intensity was observed with the addition of Zn^{2+} ions. The molar stoichiometric ratio was 1:1 for the sensor and Zn^{2+} ions. The lower value of detection was found to be $3.5 \times 10^{-7} M$.

A simple synthesis of probe **26** (Figure 7) for the detection of Zn^{2+} ion was developed by Jiao *et al.*⁷² This synthesized fluorescent probe was highly sensitive and selective towards Zn^{2+} ions and was successfully investigated by emission spectroscopy. The Job's plot and HRMS experiments showed that the probe **26** and Zn^{2+} ion binding ratio was 1:1, and that the binding constant was $7.998 \times 10^4 M^{-1}$. The detection limit was observed to be 46 μM . The probe could also be applied for the determination of Zn^{2+} ions in living C6 cells.

A fluorometric-based chemosensor **27** (Figure 8) that can easily sense Zn^{2+} ions in an aqueous medium was established by Kim *et al.*⁷³ This sensor was designed with the help of salicylaldehyde and benzyl carbonate in the ethanol solvent using Schiff base condensation methods. Emission spectroscopy was used to investigate its sensitivity and selectivity. The fluorescence emission of the sensor was observed at around 452 nm, but after the addition of Zn^{2+} ions into the solution, a significant enhancement of fluorescence intensity was observed. The binding molar ratio of the sensor and Zn^{2+} ion was 1:1, as determined by analyzing B-H and the Job's plot. The association constant was calculated to be $2.1 \times 10^3 M^{-1}$. The LOD was found to be 1.12 μM , which is lower than the permissible value given by the WHO. The binding interaction was also explained with the help of DFT calculations. The probe was also used for zebrafish cell imaging.

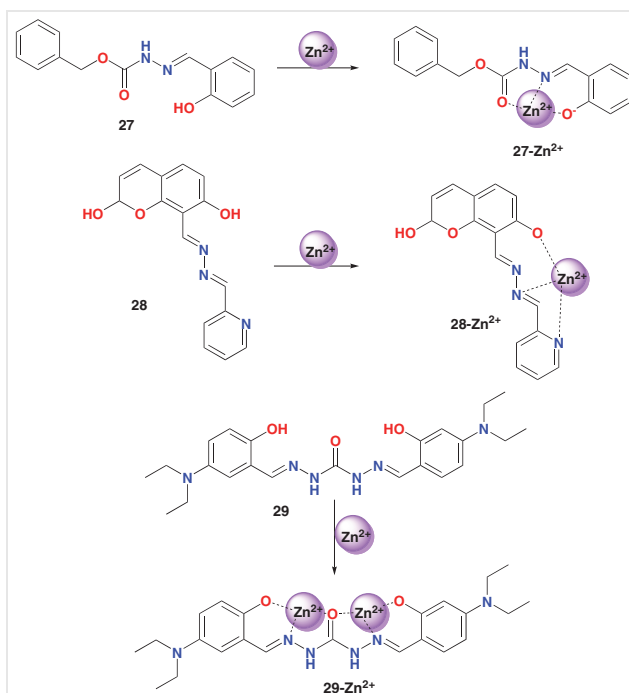


Figure 8 Structures of Zn^{2+} ion sensing probes **27–29**

Coumarin-based Schiff base fluorescent chemosensor **28** (Figure 8) was designed for the detection of Zn^{2+} ions by Fu *et al.*⁷⁴ The probe displayed high selectivity and sensitivity for Zn^{2+} ions in a buffered medium (DMF/HEPES) solution. The sensor showed a good fluorescent response on the addition of Zn^{2+} ions into the solution, resulting in an enhancement of fluorescence intensity that can be seen in the visible range by the naked eye. The detection limit of probe **28A** and **28B** towards Zn^{2+} ion was separately calculated as $1.03 \times 10^{-7} M$ and $1.87 \times 10^{-7} M$, respectively. These two probes can also be used to detect phosphate anions. Furthermore, the cell imaging demonstrated that these probes could detect Zn^{2+} ions in cells *in vitro*.

A Schiff base probe **29** (Figure 8) was designed for the determination of Zn^{2+} ions in acetonitrile/HEPES solution at pH 7.0 by Chang *et al.*⁷⁵ The probe showed high enhancement in fluorescence intensity towards Zn^{2+} ions, with a color change from faint yellow to blue. The molar stoichiometric ratio between the probe and Zn^{2+} ion was 1:2, which resulted in the inhibition of intramolecular charge transfer and chelation-enhanced fluorescence process. The mechanism of bonding was also confirmed by using UV/Vis, fluorescence, HRMS, and NMR techniques, and theoretical calculations were performed using DFT computational studies. The probe can be used efficiently to detect Zn^{2+} ions in living cells. The limit of detection was calculated to be $8.19 \times 10^{-8} M$, and the binding constant was found to be $1.75 \times 10^4 M^{-2}$.

Lu and his research group⁷⁶ successfully designed and synthesized a novel kind of fluorescent moiety **30** (Figure 9), based on the diarylethene and benzohydrazide unit, to detect Zn^{2+} ions. The fluorescent and photochromic switching properties have been studied in detail by UV/Vis spectroscopy. The moiety shows very high sensitivity and selectivity towards the Zn^{2+} ion in tetrahydrofuran solvent. The fluorescence intensity was enhanced by 84 times on the addition of Zn^{2+} ions in solution and a 44 nm blueshift was also observed after the addition of Zn^{2+} ions. The molar ratio of sensor **30** and Zn^{2+} ion was 1:1 and the limit of detection was found to be 5.60×10^{-9} M.

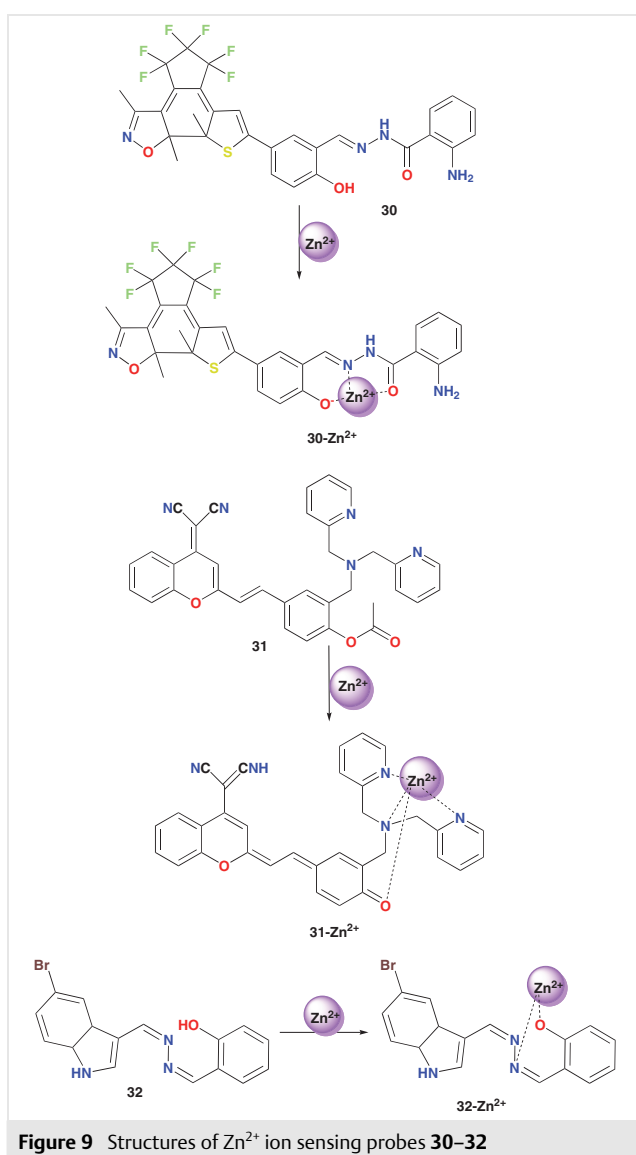


Figure 9 Structures of Zn^{2+} ion sensing probes **30–32**

Ahmed and his research group⁷⁷ developed probe **31** (Figure 9) with the help of malonitrile for the detection of Zn^{2+} ions. To investigate the sensitivity and selectivity of this probe, UV/Vis spectroscopic analysis was used, which

showed an absorbance band at 487 nm. Further, with the addition of Zn^{2+} ions, a light-brown color was observed in the solution, even in the presence of other metal ions and amino acids. In the case of fluorescence emission, the enhancement of fluorescence intensity was observed after the addition of Zn^{2+} ions into the solution. The response time was just a few minutes. This probe works well with a wide range of pH 3–13. Cytotoxicity and cell imaging of living cells were also studied with this probe.

For the detection of Zn^{2+} ions, Karuppan and her group⁷⁸ synthesized an indole-derived colorimetric and fluorometric chemosensor **32** (Figure 9). This probe underwent a tremendous fluorescent enhancement towards Zn^{2+} ions in DMSO/ H_2O (9:1 v/v) medium. This shows metal-to-ligand charge transfer operated with the synthesized probe, which was clearly visible to the naked eye. The binding ratio of the probe **32** and Zn^{2+} was 1:1, which was confirmed by Job's plot analysis. DFT computational calculations were also done successfully for this probe and its complex with Zn^{2+} ions. This probe could also sense F^- ions. One of the probe's essential applications is in cell bio-imaging to monitor Zn^{2+} ions in HeLa cells and living cell imaging in zebrafish embryos.

Acridine-based chemosensor **33** (Figure 10) was developed to sense Zn^{2+} ions in aqueous medium by Nunes.⁷⁹ It has been found that this sensor is extremely selective for Zn^{2+} ions when used as a chemosensor for metal ions. With a concentration range of 17.8–600 M, a linear fluorescence enhancement of approximately 230% was attained. Understanding how the stable complex was formed was made easier by B-H and Job's plots, and the stoichiometry ratio of the sensor **33** and Zn^{2+} ion was found to be 1:2. The lowest level of detection was 5.36 μM . The association constant was found to be $2.43 \times 10^{14} \text{L}^2 \text{mol}^{-2}$.

A turn-on fluorescent-based chemosensor **34** (Figure 10) was synthesized by Rajasekaran and his research group⁸⁰ for the determination of Zn^{2+} ions. The chemosensing behavior of this probe was established with the help of absorption, fluorescence, NMR, HRMS, and FTIR spectroscopic methods. This probe selectively detects Zn^{2+} ions even in the presence of other metal ions. The probe shows absorbance peaks at 335 and 370 nm, but upon the addition of Zn^{2+} ions into the solution, a slight redshift appeared to 338 and 385 nm. The probe shows weak emission at 515 nm but enhanced fluorescence intensity was observed on the addition of Zn^{2+} ions. The binding constant was calculated to be $9.3 \times 10^7 \text{M}^{-1}$. The quantum yield was 0.016 and 0.173 for the probe **34** and complex, respectively. The limit of detection was found to be 0.28 nM. This probe could also detect phosphate anions.

For the detection of Zn^{2+} ions in real water samples, Aziz and his research group⁸¹ synthesized a fluorometric probe **35** and characterized it with the help of different spectroscopic techniques (Figure 10). Weak emission intensity was shown by the probe at 586 nm (quantum yield was 0.026)

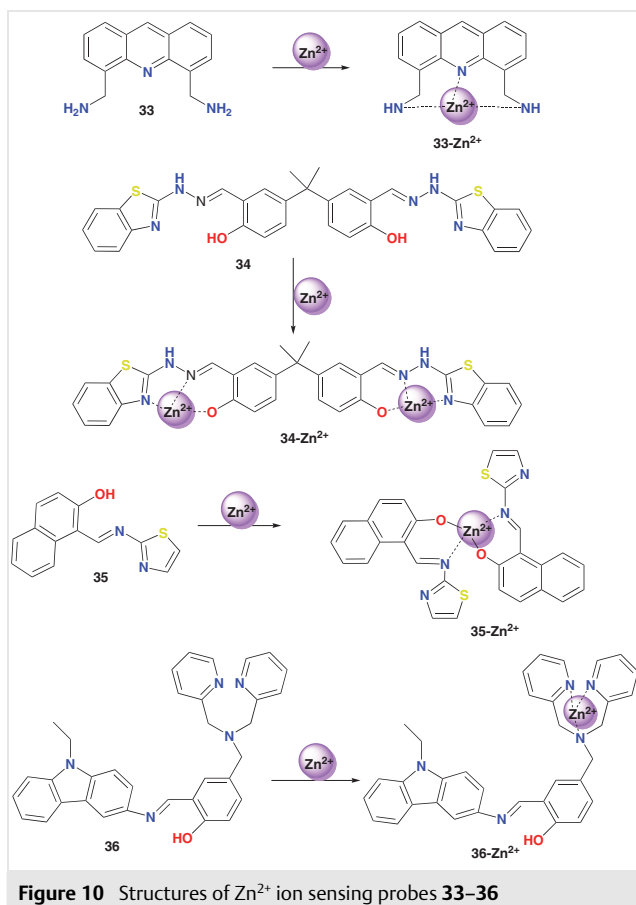


Figure 10 Structures of Zn^{2+} ion sensing probes **33–36**

and further excitation upon the wavelength 360 nm showed enhancement of emission intensity. A 1:2 stoichiometric ratio was found between the probe **35** and the Zn^{2+} ion. The probe has a rapid response time, and its limit of detection was found to be $0.0311 \mu\text{M}$. The fluorescence cell imaging demonstration reveals that the probe has good cell-membrane permeability and can be used for Zn^{2+} ion detection in living cells.

Yan *et al.*⁸² synthesized a fluorescent probe **36** to detect Zn^{2+} ions based on aggregation-induced emission using picolyl-amine (Figure 10). This probe showed very high selectivity towards Zn^{2+} ions and displayed good Stokes shift (100 nm) after the addition of Zn^{2+} ions to the probe solution. The color change was visible to the naked eye. The detection limit was observed to be $1.3 \times 10^{-7} \text{ M}$. Low toxicity and excellent permeability of this probe were beneficial for its use in living cell imaging.

The development of a Schiff base probe **37** for the determination of Zn^{2+} ions based on the naphthyl group was established by Li *et al.* (Figure 11).⁸³ This probe displayed absorbance bands at 353 nm and 367 nm in ethanol. Upon the addition of Zn^{2+} ion to the solution, its absorbance decreased; i.e., a blueshift was observed with an isosbestic point at 376 nm that tells us about the formation of new in-

teracted species. In emission intensity, almost no fluorescence emission was observed, whereas adding Zn^{2+} ions to the solution resulted in a sharp and clear enhancement in fluorescence intensity (63-fold). The stoichiometric ratio of the given complex was 2:1, as determined by a Job's plot. The limit of detection was found to be 7.52 M .

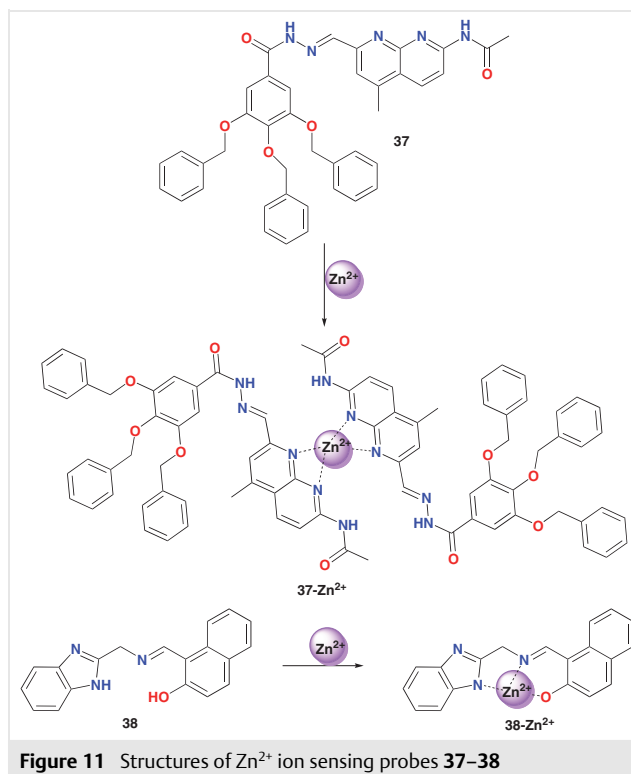


Figure 11 Structures of Zn^{2+} ion sensing probes **37–38**

Yun *et al.*⁸⁴ reported a novel benzimidazole-based fluorescence moiety **38** for the recognition of Zn^{2+} ions in aqueous medium (Figure 11). This moiety shows a turn-on fluorescence effect for the detection of Zn^{2+} ions. The sensor showed weak fluorescence, but upon the addition of Zn^{2+} ions into the solution, a remarkable emission intensity shift was observed. The quantum yield was calculated to be 0.0012 and 0.0122 for the moiety and the complex, respectively. The limit of detection was calculated to be $2.26 \mu\text{M}$, which was below the WHO permissible limits. This probe could be recycled with EDTA. This moiety was also used in the case of cell imaging to detect Zn^{2+} ions in zebrafish embryos.

A fluorescent chemosensor **39** for the detection of Zn^{2+} ions was designed by Yang Li and his research group⁸⁵ based on diarylethene hybrids (Figure 12). The probe acts as a turn-on fluorescence chemosensor to detect Zn^{2+} ions in MeOH. The chemosensor is highly selective and sensitive in nature over the other metal ions. This chemosensor shows weak fluorescence emission alone, but after the addition of Zn^{2+} ions into the solution, a new strong fluorescence peak was observed with high intensity (105-fold) and showed a

color change in solution from dark- to bright-yellow. The detection limit was 13.4 nM. This sensor was used to design a logic gate and could also be used in the case of real water analysis to detect Zn^{2+} ions.

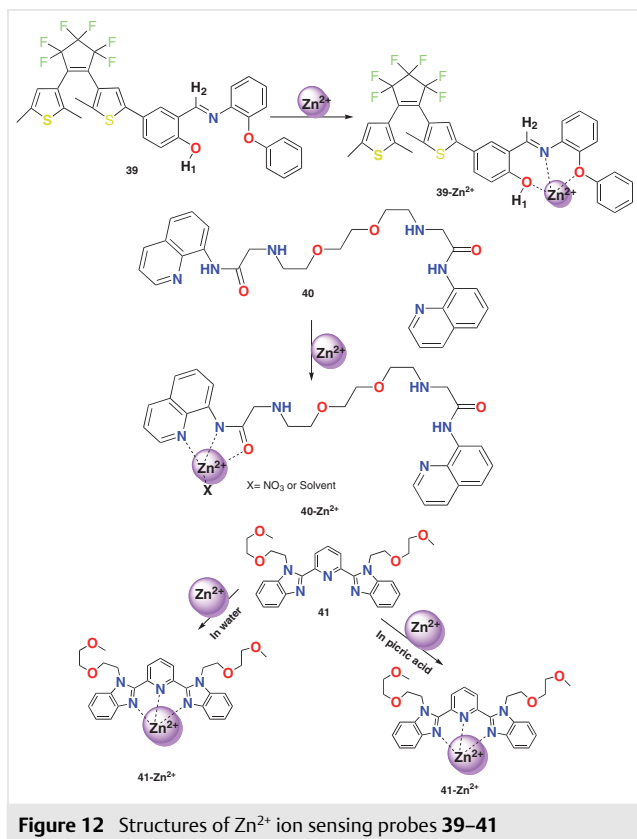


Figure 12 Structures of Zn^{2+} ion sensing probes 39–41

Chae *et al.*⁸⁶ developed a fluorometric sensor **40** for the determination of Zn^{2+} ions in aqueous solutions (Figure 12). Fluorescent titration was done to investigate the sensitivity and selectivity of the sensor. On the addition of Zn^{2+} ions into the solution, there was a rapid increase in the fluorescence intensity. The quantum yield was calculated to be 0.0083 and 0.0387 for the Sensor and complex, respectively. The interaction behavior between the sensor and Zn^{2+} ion was established with the help of UV/Vis titration, which showed absorbance bands at 300 nm and 350 nm with two isosbestic points at 277 and 330 nm, respectively. The limit of detection was calculated to be 0.27 μ M. The probe could also apply to live-cell imaging for HeLa cell imaging in zebrafish.

A water-soluble fluorescence sensor **41** was synthesized based on the benzoimidazolyl-pyridine by Jiang and research group⁸⁷ for the detection of Zn^{2+} ions and picric acid using a cascade mechanism (Figure 12). To investigate the sensing ability of sensor **41**, UV/Vis and fluorometric analyses were performed. When Zn^{2+} ions were added to the solution, the fluorescence intensity increased rapidly to 415

nm and the color changed from colorless to blue. The emission band of the sensor alone had a wavelength of 383 nm. A 1.83×10^{-7} M limit of detection was discovered.

Wyss and his group⁸⁸ developed a pyridine-containing Schiff base probe **42** for the detection of Zn^{2+} ions (Figure 13). This multidentate ligand was examined with the help of absorbance and emission spectroscopy, and was found to be highly sensitive and selective in nature with a rapid response time. The quantum yield was calculated to be 1.60% for the complex. The stoichiometric ratio of the ligand **42** and complex was 1:1, and the lower limit of detection value was 7.2 μ M.

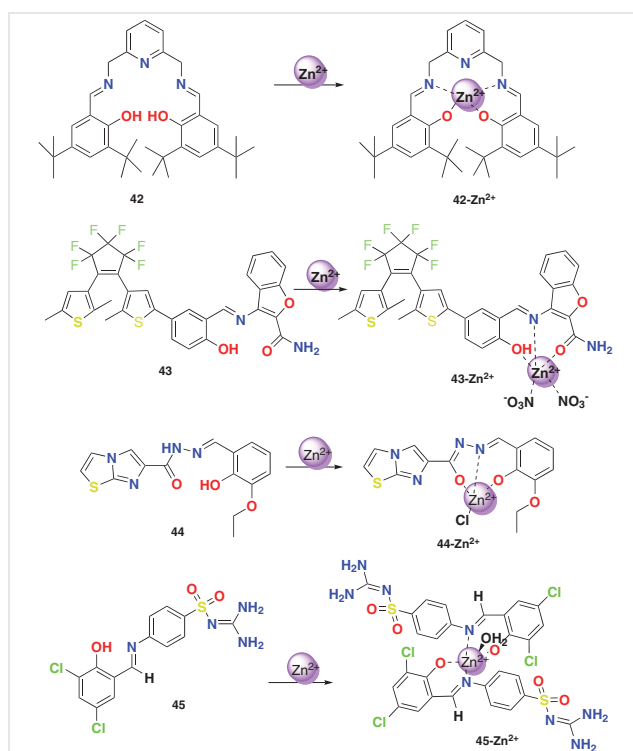


Figure 13 Structures of Zn^{2+} ion sensing probes 42–45

A chemosensor **43** was synthesized by Gao *et al.* based on a 3-aminobenzofuran carboxamide Schiff base reaction pathway (Figure 13).⁸⁹ The chemosensor has good sensing ability towards Zn^{2+} ions, which was established by using several spectroscopic tools. This chemosensor binds with the Zn^{2+} ion selectively and shows enhancement in fluorescence emission intensity. A color change was observed from dark- to bright-orange and could be seen by the naked eye. The binding stoichiometry was observed as 1:1, and the association constant was calculated to be 1.77×10^5 ML^{-1} . The limit of detection was calculated to be 3.2×10^{-8} M. A logic gate circuit was also developed with the help of fluorescence intensity optical signals.

With the help of a simple process, a Schiff base probe **44** was developed by Xu and his research group⁹⁰ to detect Zn^{2+} ions based on imidazo[2,1-*b*]thiazole-6-carboxylic acid and ethoxy hydroxybenzaldehyde (Figure 13). This probe showed binding capability towards Zn^{2+} ions and was investigated by using various spectroscopic techniques. This probe shows excellent fluorescence enhancement with Zn^{2+} ions in the presence of other metal ions, and shows an enrichment in sensitivity and selectivity towards Zn^{2+} ions. The binding stoichiometry was observed to be 1:1 between the probe **44** and Zn^{2+} ion, and was confirmed by a Job's plot. The association constant was calculated to be $2.22 \times 10^5 \text{ ML}^{-1}$. The detection limit was $1.2 \times 10^{-9} \text{ M}$ and the fluorescent signals were utilized in the formation of logic gates.

A turn-on fluorescent probe **45** was synthesized for the detection of Zn^{2+} ions by Mondal and her group (Figure 13).⁹¹ The fluorescent probe was based on the sulfaguadine Schiff base. This probe has high selectivity and sensitivity, which was investigated with various photo-optical tools and several spectroscopic techniques. The limit of detection was observed to be 37.2 nM, which is much lower than the WHO guidelines. The stoichiometry ratio was 2:1 for the probe and Zn^{2+} ions in the complex. The complex shows antibacterial activity against gram-positive and gram-negative bacteria.

Based on acylpyrazolones and benzhydrazide, the novel ligand **46** was found to work well for the detection of Zn^{2+} ions by Shaikh *et al.* (Figure 14).⁹² The working of the ligands was investigated with various spectroscopic techniques. This ligand also showed anti-malarial activity.

A new Schiff base probe **47** (Figure 14) was developed by using a condensation reaction path by Chen and research group.⁹³ This probe shows a rapid response towards the Zn^{2+} ion. The probe shows an enhancement of fluorescence intensity while detecting Zn^{2+} ion in an aqueous media; a color change was also observed from yellow-green to intense-green. The limit of detection of the probe was $1.9 \times 10^{-8} \text{ M}$. Furthermore, a filter paper-based strip-indicator with a response that could be observed with the naked eye also demonstrated good ability to bind Zn^{2+} ion. The binding ratio was 1:1.

A simple naphthylamide-based fluorescent sensor **48** was developed for the determination of Zn^{2+} ion via a Schiff base condensation reaction pathway by Xiang *et al.* (Figure 14).⁹⁴ This probe shows a very rapid response time (30 s) and high selectivity towards the Zn^{2+} ions. The probe also showed a remarkable enhancement in fluorescence intensity. The binding ratio of the probe and Zn^{2+} ion was found to be 1:1 based on a Job's plot, and the association constant was calculated to be $1.18 \times 10^5 \text{ M}$. The limit of detection was found to be 39 μM , which is lower than the permissible limit set by the WHO. A plausible mode of binding of the complex was verified by DFT computational studies.

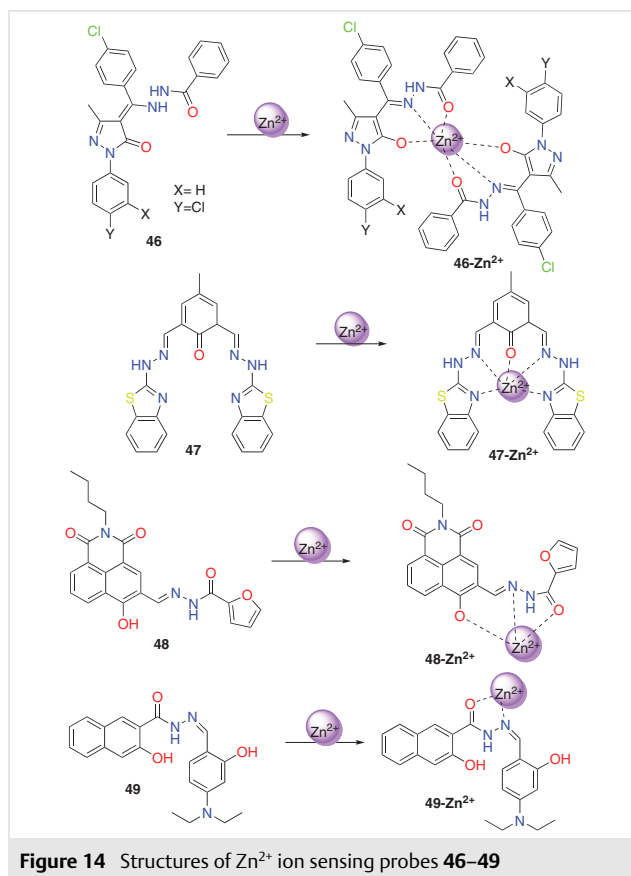


Figure 14 Structures of Zn^{2+} ion sensing probes **46–49**

To remove Zn^{2+} ions from water, Wang and his research group⁹⁵ reported a turn-on fluorescent ligand **49** for the recognition of Zn^{2+} ions (Figure 14). The synthesized ligand was investigated using several spectroscopic techniques. The sensitivity and selectivity of the ligand towards the Zn^{2+} ion were analyzed by emission spectroscopy. The intensity of fluorescence increased with the addition of Zn^{2+} ions to the solution. The stoichiometric ratio was found to be 1:1 and the detection limit was $6.75 \times 10^{-9} \text{ M}$. This probe was also utilized to detect Zn^{2+} ions in living tumor cells.

Conclusion

Zinc's significance for human growth and industrial development has recently attracted a lot of attention, necessitating the development of effective techniques for the rapid detection of Zn^{2+} ions. This review paper emphasizes how effective colorimetric and fluorometric Schiff base chemosensors could potentially be. Due to their superior ability to detect metal ions, Schiff bases are a crucial family of organic probes. These colorimetric and fluorometric probes are extremely efficient for the detection of Zn^{2+} ions with low response time, economical cost, and quick color change. In addition, most of the Schiff base ligands are biocompatible

and were used in the cell imaging of various living organisms to detect Zn²⁺ ions. Schiff base probe **34**, bearing the two benzothiazole moieties, was found to exhibit the lowest detection limit of 0.00028 μM, and it is anticipated that this could become the best lead for the recognition of Zn²⁺ ions. Further research will continue in the near future to uncover further colorimetric and fluorometric probes to determine Zn²⁺ ions.

Conflict of Interest

The authors declare no conflict of interest.

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