



Synthesis and Applications of Fluorescent Chemosensors: A Review

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Abstract

Fluorescent sensors have emerged as powerful tools in analytical chemistry for the detection and quantification of heavy and transition metal ions in aqueous samples. These metal ions pollute the environment and cause a number of diseases, such as irritability, anaemia, muscle paralysis, neurological damage, and memory loss. Moreover, we explore the wide spectrum of applications in environmental monitoring, where these sensors enable precise detection of contaminants, as well as in biomedical fields, facilitating diagnostic and therapeutic advancements. While highlighting the exceptional progress achieved in this field, I also address the challenges and future prospects for the continued development of fluorescent sensors, emphasizing their potential to shape the future of water quality assessment and analytical chemistry. Heavy and transition metals are of great concern because of their extreme toxicity even at very low concentration and tendency to be accumulated in bodies of living organisms. During the recent years, the design and synthesis of fluorescent chemosensors for sensing environmentally and biologically relevant important metals, particularly for heavy and transition metals, is of great interest. Upon complexation with heavy and transition metals, the fluorescence intensity of these fluorescent chemosensors either quenched or enhanced. The current review paper explains various fluorescent chemosensors for determination of toxic heavy and transition metals in environmental water samples.

Keywords Fluorescent sensors · Water analysis · Fluorescence · Schiff base · Heavy and transition metals

Introduction

A chemosensor is a molecule that interacts with an analyte to produce a detectable change. Chemosensors consist of receptor and reporter, and after the receptor binds with metal, the signal observed by the reporter will change. Fluorescent chemosensor is an important class of chemosensors which uses fluorescence as the output signal, and also a powerful tool to monitor toxic heavy and transition metals in environmental water samples. Fluorescent chemosensors for determination of toxic heavy and transition metals have been a subject of numerous research publications and review articles over the last decades. Recently a new fluorescent signaling mechanism, binding induced conformational restriction, was discovered. Determination of toxic heavy and transition metals is of great interest to chemists. Several methods for the determination of these toxic metals have

been reported. They include atomic absorption spectrometry, inductively coupled plasma mass spectroscopy, neutron activation analysis, anodic stripping voltammetry, X-ray fluorescence spectrometry, electrothermal atomic absorption spectrometry, cold vapor atomic absorption spectrometry and potentiometric ion-selective electrodes for these metals determination. Though these methods are sensitive, selective and accurate, but they require expensive instruments, well-controlled experimental conditions, time consuming and complicated sample pretreatment procedures. Among the numerous analytical methods that are available, those based on fluorescence offer several distinct advantages in terms of sensitivity, selectivity, simplicity, response time, non-destructive methodology, high sampling frequency, low cost of equipment, direct visual perception and easy signal detection. Therefore considerable efforts are made to develop selective fluorescence chemosensors for toxic heavy and transition metals determination. The current review paper is based on the mode of action of a number of fluorescent chemosensor for determination of toxic heavy and transition metals in environmental water samples.

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Permissible Concentration of Some Heavy and Transition Metals in Environmental Samples

Permissible concentration of heavy and transition metals in various environmental samples, such as air, water, soil, and food, are typically regulated by government agencies and international organizations to protect human health and the environment. These permissible levels, often referred to as regulatory or safety limits, can vary depending on the specific metal, the type of sample, and the intended use of the environment or product. Here are some common examples of permissible levels for selected heavy and transition metals: It's important to note that permissible levels may change over time as new research on the health and environmental impacts of these metals becomes available. Additionally, local regulations and guidelines may differ from international standards, so it's essential to refer to the relevant regulatory authorities and agencies for the most up-to-date and region-specific information on permissible levels of heavy and transition metals in environmental samples. Table 1 summarizes the permissible levels of some heavy and transition metals in aqueous samples as recommended by the World Health Organization (WHO).

Various Reported Optical Probes

Enamullah and co-workers, developed Schiff bases, (R)-N-(Ar)ethyl-2-hydroxy-1-naphthalimine (Ar=C₆H₅, 3-/4-MeOC₆H₄, 4-BrC₆H₄) by condensation of 2-hydroxy-1-naphthaldehyde with (R)-(Ar)ethylamine. These Schiff bases readily react with the dinuclear complex [Rh(g4-cod)(l-O 2CMe)] to afford the mononuclear complexes [Rh(g4-cod){(R)-N-(Ar)ethyl-2-oxo-1 naphthaliminato- N, O}] (Ar = C₆ H₅ (I); 3-MeOC 6H₄ (II); 4-BrC₆ H₄(III)), respectively in C₆H₆/MeOH (5:1, v/v). The Schiff bases and

complexes are characterized by IR, UV-Vis, ¹H/¹³CNMR and mass spectrometry, polarimetry and HPLC. The polarimetric measurements show the enantiopurity of the Schiff bases as well as the complexes. The X-ray structure determination for sensor demonstrates that the deprotonated Schiff bases, (R)-N (Ar)ethyl-2-oxo-1-naphthalimine, co-ordinate to the [Rh(g4 -cod)]-fragment as a six membered N ,O -chelate chemosensors with distorted square planar geometry at the rhodium metal. Reaction of III with O₂ leads to the formation of the oxidative adduct [Rh(g4 -cod)(l -O)] 2 (III). [Rh(g4-cod){(S or R)-N -(phenyl)ethyl-salicylal diminato}] were used for reduction of acetophenone with diphenylsilane into (±)-1-phenyl-ethanol, and conversions up to 93–97 % have been achieved [1]. Jayaraman Dessingiu et-al, developed 2-Hydroxynaphthylidene derivatives of hydrazine by via two-step reactions and the products were characterized. The ion recognition properties of these receptors were studied using fluorescence and absorption spectroscopy. The receptors were found to be sensitive and selective towards Cu²⁺ in methanol solution among the 13 metals studied, namely Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Hg²⁺, Pb²⁺, Na⁺, K⁺, Ca²⁺ and Mg²⁺, by exhibiting switch off fluorescence. The stoichiometry of the complexed species was found to be 2:1. These conjugates were also found to act as colorimetric chemosensors for Cu²⁺ in solution by exhibiting visual colour change. The 2:1 complex shows a centrosymmetric structure based on DFT computations [2].

Hoe-Jin Yoon et-al, 2-Hydroxy-6-(1-(3-phenyluryl-phenyl)ethoxy)-benzaldehyde (2) has been synthesized in racemic form from 1,3-Dihydroxybenzene via formylation and reaction with 3-phenyluryl-methylbenzylbromide. The optically pure form of 2 was separated by normal silica column chromatography from the imine diastereomer which was obtained by the reaction of racemic mixture of 2 with optically pure leucinol. The absolute configuration of the separated enantiomer of 2 was decided from the energy calculation of the corresponding imine diastereomers. The activity of 2 as a chirality conversion reagent for amino acids was determined by ¹H NMR analysis. The efficiency of 2 is not better than the previous CCRs based on binaththol. Compound 2, however, has lower molecular weight compared to other chirality conversion reagents. This work demonstrates that asymmetric carbon can control the selectivity of amino acids [3].

Ruslan Guliyev et-al, reported a highly selective and sensitive reversible cyanide chemosensor operating in the 'turn-off- on' mode via decomplexation of Cu(II) from a brightly fluorescent boradiazaindacene derivative. The chemosensor is reversible as the emission signal originates from the dynamic equilibration of dipicolylamine Cu(II) and tetracyanocuprate complex [4]. Jian-Fa Zhu et-al (2010), synthesized a water soluble colorimetric and fluorescent turn-on

Table 1 Permissible level of some heavy and transition metals in aqueous samples by WHO

| Metal | Permissible concentration (mg/L) | Metal | Permissible concentration (mg/L) |
|-----------|----------------------------------|------------|----------------------------------|
| Arsenic | 0.01 | Cadmium | 0.003 |
| Chromium | 0.05 | Copper | 2.0 |
| Iron | 0.3 | Lead | 0.01 |
| Zinc | 3.0 | Manganese | 0.4 |
| Cobalt | 0.01 | Vanadium | 0.05 |
| Silver | 0.1 | Thallium | 0.001 |
| Beryllium | 0.001 | Antimony | 0.006 |
| Strontium | 0.05 | Molybdenum | 0.07 |

chemosensor by conjugating piropyrin chloride with 2-amino-N-(quinolin-8-yl)acetamide, multi functionalized spirobenzopyran derivative for Zn^{2+} . In 50% aqueous ethanol buffer solution, SPQN displayed a selective chelation fluorescence enhancement (16-fold) at 650 nm and visible color change (from colorless to red) with Zn^{2+} among the metal examined. In addition, as the third channel to display the metal binding characteristics of SPQN, operating on an efficient FRET process between the quinoline and the merocyanine moiety of the chemosensor, ratiometric determination of Zn^{2+} can be realized [5].

Da-Yu Wu et-al, designed selective Zn^{2+} fluorescent chemosensors, di(2-quinoline-carbaldehyde)-2,2-bibenzoyl-hydrazone and di(2-quinolinecarbaldehyde)-6,6-dicarboxylic acid hydrazone-2,2-bipyridine. Both chemosensors exhibit an emission band centered at 405 nm with low quantum yield. Zinc binding not only red-shifts the emission band to 500 nm, but also enhances the fluorescence intensity by an order of magnitude based on the deprotonization strategy via self-assembly. These chemosensors are highly selective for Zn^{2+} over biologically relevant alkali metals, alkaline earth metals and the first row transition metals such as Mn^{2+} , Fe^{2+} , Co^{2+} and Ni^{2+} in buffered aqueous DMSO solution [6]. Shi-Rong Liu et-al, developed a new rhodamine-based chemosensor exhibits excellent selectivity for Fe^{3+} over a wide range of tested metals Ag^+ , Al^{3+} , Ca^{2+} , Cd^{2+} , Co^{2+} , Cr^{3+} , Cu^{2+} , Fe^{2+} , Hg^{2+} , Mg^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , and Zn^{2+} in an aqueous solution. The binding of Fe^{3+} to chemosensors produces an absorption band at 564 nm and an emission band at 588 nm because Fe^{3+} -binding induces ring-opening of the spirolactam. The binding ratio of the 1- Fe^{3+} complexes was determined to be 1:1 according to a Job plot. The association constant of Fe^{3+} binding in chemosensors was $6.9 \times 10^3 M^{-1}$. The maximum fluorescence enhancement caused by Fe^{3+} binding in chemosensors occurred at a pH range of 6–7.5. Thus chemosensor used as an efficient fluorescent probe for determination Fe^{3+} in living cells [7].

Min Wang et-al, synthesized a fluorescent chemosensor N-n-butyl-3,4-diamino-1,8-naphthalimide for determination of NO on the basis of 1,8-naphthalimide with a similar structure of o-phenylenediamine as a NO reaction site. Due to the interaction between the photoinduced electron transfer and the intra-molecular charge transfer, the chemosensor exhibits a remarkable enhancement in the emission intensity. It showed 160-fold increase and a blue shift in the emission wavelength after the addition of NO. Meanwhile, it displayed a colorimetric response accompanied with a color change from yellow to colorless. The chemosensor showed a high selectivity for NO in the presence of various reactive nitrogen and oxygen species. Also, chemosensor was used for bio imaging of NO in living cells [8]. Yan Li-Wei et-al, developed new perylenediimide chemosensor functionalized with a dipicolylethylenediamine moiety and first used

as a colorimetric and fluorometric dual channel chemosensor to specifically detect the presence of Cu^{2+} over a wide range of other metals. The solution of chemosensor upon addition of Cu^{2+} displayed distinguishing pink color compared with other metals including K^+ , Ni^{2+} , Ca^{2+} , Mn^{2+} , Na^+ , Sr^{2+} , Zn^{2+} , Co^{2+} , Cd^{2+} , Mg^{2+} , Cr^{3+} , Ag^+ , and Ba^{2+} , indicating the sensitivity and selectivity of chemosensor to Cu^{2+} . Thus, the advantage of this assay is that naked-eye detection of Cu^{2+} becomes possible. Moreover, among these metals analyzed, only Cu^{2+} quenched more than half fluorescent intensity of chemosensor. The ESI-TOF spectrum of a mixture of chemosensor and $CuCl_2$ in combination of the fluorescence titration spectra of chemosensor upon addition of various amounts of Cu^{2+} revealed the formation of a 2:1 metal-chemosensor complex through the metal coordination interaction [9].

Hongda Li et-al, designed a new fluorescent chemosensor based on diaza-18-crown-6 ether, which was appended with dual coumarins, exhibited high selectivity and anti-disturbance for Fe^{3+} among iron mentally and biologically relevant metals. Fe^{3+} sensing was performed via the complexation of Fe^{3+} with the chemosensor. In addition, the detection limit of the fluorescence response of the chemosensor to Fe^{3+} was $0.31 \mu M$ with a rapid response of less than 10 s [10]. S. Suresh et-al, synthesized a new pyrene based chalcone receptor and was used for Pb^{2+} in waste water. Receptor showed a highly selective and sensitive recognition of Pb^{2+} over other heavy and transition metals. The turn “off-on” fluorescent detection of Pb^{2+} by chemosensor is free from the interference of other metals. A possible PET mechanism is proposed for the “off-on” fluorescent enhancement [11]. Heba A et-al, Based on chelation-enhanced fluorescence, a new fluorescent coumarin derivative chemosensor 3-(1-(7-hydroxy-4-methylcoumarin)ethylidene)hydrazinocarbothioate for Hg^{2+} , Ag^+ , and Ag^+ , nanoparticles is reported. Chemosensor acts as a rapid and highly selective “off-on” fluorescent chemosensor and fluorescence enhancement by factors 5 to 12 times was observed upon selective complexation with Hg^{2+} , Ag^+ nanoparticles. The molar ratio plots indicated the formation of 1:1 complexes between Hg^{2+} and Ag^+ with the probe. The linear response range covers a concentration range 0.1×10^{-5} – 1.9×10^{-5} mol/L, 0.1×10^{-5} – 2.3×10^{-5} mol/L and 0.146×10^{-12} – 2.63×10^{-12} mol/L for Hg^{2+} , Ag^+ and Ag^+ nanoparticles, respectively [12].

Yu-Hui Zhang et-al, synthesized a water-soluble fluorescent Zn^{2+} chemosensor, 1,10-phenanthroline bridged bis(β -cyclodextrin), was synthesized by “click chemistry” and its fluorescence sensing behavior toward Zn^{2+} against various toxic heavy and transition metals was investigated under physiological conditions. Significantly, chemosensor showed high selectivity and sensitivity toward Zn^{2+} with a limit of detection down to 10^{-7} M. Moreover, the

spectrophotometric studies demonstrated that after complexation with chemosensor- carboxylic acid sodium salt, the chemosensor complex gave much stronger binding affinity and lower limit of detection value toward Zn^{2+} through a cyclodextrin/ substrate/ Zn^{2+} triple recognition mode. The fluorescence stopped-flow experiments also indicated that the association rate of complex to Zn^{2+} was much faster than chemosensor to the same metal. Furthermore, the fluorescence intensity of chemosensor and was greatly enhanced after binding Zn^{2+} in living cells, and thus chemosensor and complex was used as a chemosensor for Zn^{2+} at the cellular level [13]. X. Chen et-al, developed a new bis(rhodamine)-based fluorescent chemosensor, and it exhibited high selectivity for Fe^{3+} over other commonly coexistent metals in both 50% ethanol and Tris- HCl buffer. Upon the addit ion of Fe^{3+} the spirocyclic ring of chemosensor was opened and a significant enhancement of visible color and fluorescence in the range of 500–600 nm was observed [14]. L. Jun et-al, synthesized fluorescent chemosensor-based on benzimidazole for recognition of Fe^{3+} and H_2PO_4 . Chemosensor displays rapid, highly selective, and sensitive recognition to Fe^{3+} in $H_2O/DMSO$ (1:1, v/v) solutions. The in situ-generated L- Fe^{3+} complex solution exhibits a fast response and high selectivity toward dihydrogen phosphate via the Fe^{3+} displacement approach. The detection limits of chemosensor to Fe^{3+} and chemosensor- Fe^{3+} complex to H_2PO_4 were estimated to be 1.0×10^9 mol/L. Notably, the chemosensor was retrievable to indicate dihydrogen phosphate with Fe^{3+} and H_2PO_4 in turn increased. This successive recognition feature of chemosensor makes it a potential utility for Fe^{3+} and H_2PO_4 detection in waste water samples [15].

Xiang Yong Zheng et-al, developed a novel fluorescent chemosensor, comprised of two rhodamine B lactams as fluorophores that are 1,3-alternately linked to a thiacalix[4] arene, behaves as a highly sensitive ion-induced fluorescent chemosensor for Fe^{3+} and Cr^{3+} . The compound was synthesized, and its recognition of metal ions was evaluated by fluorescence and absorption spectroscopy. The possible mechanism of Fe^{3+} and Cr^{3+} -induced spirocycle opening of chemosensor leads to fluorescent enhancement, and these properties were investigated by spectroscopy, 1H -NMR and IR. The stoichiometric ratios and association constants of the complexes between 1 and these ions have been measured and calculated, and showed that the presence of Fe^{3+} or Cr^{3+} induced chemosensor to form a stable 1:1 complex [16]. O. Sahin et al, synthesized new anthracene derivative of calix[4]arene as a highly fluorescent chemosensor. The developed chemosensor was examined for its fluorescent properties towards different metals (Li^+ , Na^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+}) by UV and fluorescence spectroscopy. On complexation by alkaline earth and transition metals, the fluorescence spectrum was quenched. In

particular, Ca^{2+} caused greater than 98% quenching of the anthracene derivative of calix[4]arene [17].

I. Grabchev et al, designed and studied the basic characteristics of a novel green fluorescent polyvinylcarbazole polymer containing 4-N, N-dimethylaminoethyleneamino-1,8-naphthalimide side chains has been described. The ability to sense metals has been monitored by fluorescence spectroscopy. It is shown that the fluorescent intensity is very sensitive to the Fe^{2+} cations and the copolymer was used as a homogeneous and heterogeneous fluorescent chemosensor for Fe^{2+} [18]. M. R. Pourjavid et al., synthesized a simple and selective metal hold using a column packed with graphene oxide (GO) as a solid phase extract for the multi element preconcentration of $Fe(III)$, $Ni(II)$, $Cu(II)$ and $Zn(II)$ ions prior to flame atomic absorption spectrometric determinations. The current method is based on the sorption of mentioned ions on synthesized GO using 2-(tert-butoxy)-N-(3-carbamothioylphenyl)acetamide as a chelating agent. Several parameters on the extraction and complex formation were optimized. Under the optimized conditions (pH 6, flow rate 9 mL/min), metal ions were retained on the column, then quantitatively eluted by HNO_3 solution (5 mL, 3.0 mol/L). The preconcentration factor was calculated as 250. The detection limits for the analyte ions of interest were found in the range of 0.11 ng/mL (Ni^{2+}) to 0.63 ng/mL (Cu^{2+}). The column packed with GO was adequate for metal ions separation in matrixes containing alkali, alkaline earth, transition and heavy metal ions [19]. J. K. Choi et al, designed a photoinduced charge transfer-based 1,3-alternate calix[4]crown fluoroionophore containing two cation recognition sites, a crown ether ring and two facing pyreneamide groups. Upon addition of K^+ , Pb^{2+} wavelength changes was observed in both the fluorescence and absorption spectra, but with different binding modes. With K^+ , fluorescence emissions of the chemosensor narrowly change, while addition of Pb^{2+} produces a remarkable change in both the excimer and monomer emissions. The observed data indicate that the metal cation is encapsulated in the crown-5 ring for K^+ and by the two facing amide groups in the latter case, which is verified by a metal ion exchange experiment. The wavelength shifts in both fluorescence and absorption spectra upon addition of Cu^{2+} showed that Pb^{2+} interacts with the nitrogen atoms of the amide groups, resulting in a PCT mechanism [20]. I. E. Tolpygina et al, presented N, N'-Bis(9-anthryl)-substituted diamines, imidazolidines, and hexahydropyrimidines. The luminescence and complexing ability of the developed compounds were studied. In the presence of a number of metal ions the PET based compounds were found to effectively and selectively detect Zn^{2+} and H^+ ions [21].

H. Chen et al, developed chemosensor/[N, N 0-di(quinoline-2-methylene)-1,2-phenylenediimine]. It was found that the synthesized compound exhibited high selectivity toward Zn^{2+} over other metal ions. In acetonitrile, the

red shift of fluorescent emission from 396 nm to 426 nm upon zinc binding was due to the formation of a 1:1 metal/chemosensor complex [22]. M. Milewska et al, synthesized chelate chemosensors, benzoxazol-5-yl-alanine derivatives substituted in position 2 by heteroaromatic substituent, to form complexes with selected metal ions in acetonitrile are studied by means of absorption and steady-state and time-resolved fluorescence spectroscopy. Among the chemosensors studied, only azaaromatic derivatives form stable complexes with transition metal ions in the ground state. Their absorption bands are bathochromically shifted enabling to use those chemosensors as ratiometric chemosensors. The fluorescence of each chemosensor was quenched by metal ions, however, in the presence of Cd(II) and Zn(II) ions a new red shifted emission band was observed [23]. I. C. Esteves et al, developed highly emissive heterocyclic asparagine derivatives bearing a 1,3,4-thiadiazolyl unit at the side chain, functionalized with electron donor or acceptor groups. The synthesized compounds were evaluated as amino acid-based fluorimetric chemosensor for metal cations, including Cu^{2+} , Zn^{2+} , Co^{2+} and Ni^{2+} . The obtained results suggested that there was a strong interaction through the donor heteroatoms at the side chain of the various asparagine derivatives, with high sensitivity towards Cu^{2+} in a chemosensor–metal complex with 1:2 binding ratio. Association constants and detection limits for Cu^{2+} were also calculated. The photophysical and metal ion sensing properties of these asparagine derivatives confirmed their potential as fluorimetric chemosensor and suggested that they are appropriate for incorporation into chemosensor peptidic frameworks [24].

Y.J. Chang et al., synthesized a simple Schiff- base receptor. The developed sensor exhibits an “off–on-type” mode with high sensitivity in the presence of Al^{3+} and showed a high association constant ($5.89 \times 10^6 \text{ M}^{-2}$) toward Al^{3+} in DMSO– H_2O (4:6 v/v) solution. The addition of EDTA to receptor Al^{3+} complex quenches the fluorescent intensity, indicating good reversibility of these sensors [25]. V.M.V. Enoch et-al., Inclusion complexation of 2,6-dipsfzenylphenol with β -cyclodextrin and its photoprototropic behavior was studied with absorption and fluorescence spectra. The synthesized compound forms 1:1 inclusion complex with a binding constant of 272.12 M^{-1} . It was found to show more acidic characteristics in β -cyclodextrin. Dissimilar to the observation of stretched sigmoidal fluorimetric titration curves in aqueous solution, the fluorimetric titration curves for the neutral–monoanion equilibrium of 2,6-diphenylphenol in β -cyclodextrin are sharp and they meet at the middle of inflection showing that the prototropic equilibrium is attained in the S1 state [26]. Rather et al, designed a new 7-nitrobenz-2-oxa-1,3-diazole based colorimetric and fluorescence chemosensor for Zn^{2+} , an ion involved in many biological processes. The NBD-probe displays a red-to-yellow color change and an enhancement of fluorescent intensity in

the presence of an aqueous solution of Zn^{2+} ions (pH 7.2). Internal charge transfer and photo induced electron transfer mechanisms are responsible for these changes. The practical use of this probe was demonstrated by its application to the biologically relevant detection of Zn^{2+} ions in pancreatic β -cells [27]. Z. Yang et al, reported a receptor/3-amino-5-(4, 5, 6, 7-tetrahydro-1H-indol-2-yl)isoxazole-4-carboxamide, contains pyrrole, amide and amino subunits. The developed receptor showed both changes in its UV–Vis absorption and fluorescence emission spectra upon the addition of fluoride ion, resulting in highly selective response for fluoride ion detection over similar anions, like chloride, bromide, iodide, hydrogen sulphide, hydrogen bi phosphate and AcO^- in CH_3CN . $^1\text{HNMR}$ titration, time-dependent density, functional theory (DFT) simulation and all experiments data confirm that the sensing mechanism is based on deprotonation of pyrrole-NH moiety [28].

S. Sumathi et al, Synthesized complexes with transition metals of various acetylacetonate-based ligands of the type ML (where M=Cu(II), Ni(II), Co(II); L = 3-(aryl)-pentane-2,4-dione). The structures were derived from their elemental analysis, magnetic susceptibility, molar conductance and $^1\text{HNMR}$ spectral studies. Conductivity study showed that all developed complexes are nonelectrolytic. Spectroscopic studies proposed square planar geometries for studied metal complexes. The free ligands and their metal complexes have been screened for their in vitro biological activities against bacteria and fungus. These complexes are found to possess increased activities compared to those of the free ligands. All synthesized compounds may serve as potential photoactive materials as indicated from their characteristic fluorescence properties [29]. Y.H. Zhao et-al., synthesized quinoline-vinyl-dihydroxylphenyl linkage comprising a donor–bridge-acceptor structural motif, in which the quinoline serves as an electron-withdrawing core. The developed compound was used as a fluorescent sensor for Al^{3+} and F^- recognition via fluorescence. The ligand showed minimum fluorescence as a result of excited-state intra-molecular proton transfer from the hydroxyl oxygen to the nitrogen of the quinoline unit. Oppositely, on coordination of Al^{3+} or F^- , compound showed high fluorescence. A reversible “off–on” mode was demonstrated by sequential inputs from Al^{3+} and F^- ions to the sensor by varying wavelengths of excitation and emission. $^1\text{HNMR}$ and IR spectroscopic analysis results coordinatedination of aluminium ion to oxygen of quinoline and phenolic oxygen atom, whereas the F^- center is only coordinated by two phenolic oxygen atoms [30]. H. Chen et al, Spectroscopic studies revealed that the compound [N, N 0-di(quinoline-2-m ethylene) -1,2-phenylenediimine] exhibited a rather high selectivity toward Zn^{2+} over other metal, even Cd^{2+} . In acetonitrile, the red shift of fluorescent emission from 396 nm to 426 nm upon zinc binding is due to the formation of a 1:1 metal/ligand complex [31].

He, X et-al., reported that zinc as an essential trace element for humans, playing a crucial role in maintaining normal growth, development, and metabolism in the body. However, both excess and deficiency of Zn(II) can lead to metabolic abnormalities and various diseases. Hydroxide ions (OH^-) are also essential for biosystem, particularly in the context of harsh pH environments. Currently the need for practical and convenient fluorescence imaging tools to trace Zn(II) and OH^- in biosystems. This is because the homeostasis of these ions is crucial, and their levels can have significant biological implications. DACH-fhba is introduced as a dual-channel fluorescent chemosensor designed for selective sensing of Zn(II) and OH^- . It is designed to emit blue fluorescence (at 455 nm) in the presence of Zn(II) and green fluorescence (at 530 nm) upon the addition of OH^- . This dual-channel response allows for the simultaneous detection of both ions. The chemosensor is noted for its high stability and reversibility, indicating that it can be used reliably for repeated measurements. DACH-fhba is applied in live cells, larval zebrafish, and plants for bioimaging purposes. It successfully tracks the levels of Zn(II) and OH^- in these organisms, suggesting its potential as a visual detection tool for these ions in living systems. The passage concludes by highlighting the importance of this work in monitoring Zn(II) and OH^- in organisms, which can contribute to a better understanding of the roles these ions play in biosystems [32]. Figure 1 indicate the graphical representation of DACH-fhba dual-channel fluorescent chemosensor for selective Zn(II) and OH^- detection.

He et-al, designed and synthesized Schiff base sensor CMTAH containing coumarin fluorophores by the coupling of coumarin aldehyde and thiophene-2-carbohydrazide and acts as differentially selective chemosensor via colorimetric responses to Cu(II)/Zn(II) ions with fluorescence in aqueous media. Variation in absorption and emission

spectra of CMTAH with different metal cations in aqueous media reveal high-affinity binding to Cu(II)/Zn(II) ions over other coexisting cations. Moreover, the spectrometric titrations and Job's plot curves substantiated the stoichiometric ratio of 1:1 for Cu(II)/Zn(II) complexes formation with low detection limits of 141 nM and 72 nM, respectively. Particularly, the responding mechanism of CMTAH toward Cu(II)/Zn(II) ions was investigated by density functional theory calculations. Notably, the molecular logic gates were established with the combination of CMTAH for the intelligent recognition of Cu(II)/Zn(II) ions. Additionally, the compatibility and permeability of CMTAH were attributed to Schiff base group, which exhibited remarkable responding and bioimaging in living cells and zebrafish. Schiff base sensor for sensing Cu(II)/Zn(II) ions is presented in Fig. 2. Notably, CMTAH could be used to image in *Drosophila* larvae with a clearly visible profile of internal organs and effectively capture Cu(II) and Zn(II) ions in living *Drosophila* larvae, which lay the foundation of sensors in the field of *Drosophila* biological imaging research [33].

Zheng et-al. stated that Aluminum (Al), gallium (Ga), indium (In) are three essential elements in group IIIA of the periodic table, which all share similar chemical properties and are also vital in many aspects of bio and environmental systems. Proper control of their levels is thus necessary as overexposure to them has been linked to onsets of many diseases. Fluorescence based molecular probes have always been the driving horse for detecting vital ions including group IIIA ions. However, only a few such probes have been reported so far and all of them are faced with one or more shortcomings such as not very high sensitivity, incapability to detect multiple ions simultaneously, and poor cell penetration abilities due to emitted fluorescence at shorter wavelengths. To meet those challenges, we herein presented the successful development and application of a

Fig. 1 Graphical representation of dual-channel fluorescent signal response chemosensor for Zn(II) detection

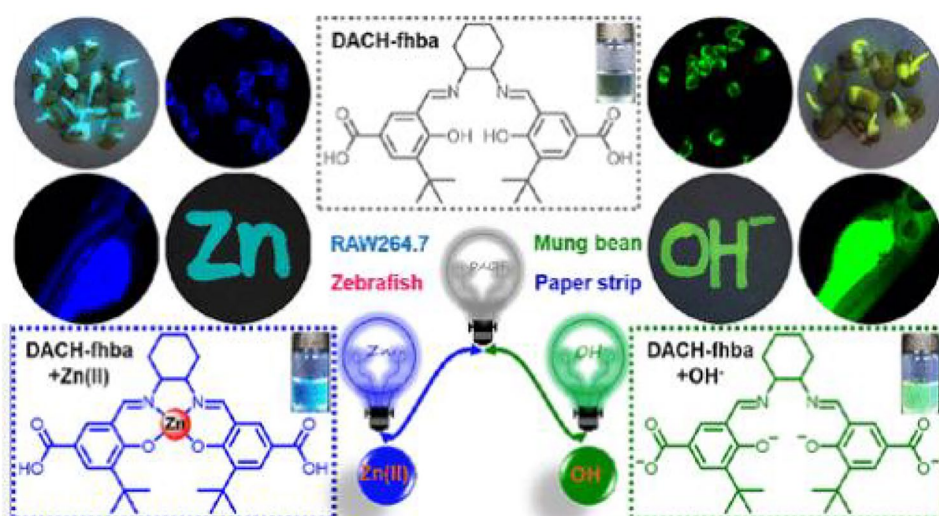


Fig. 2 Graphical representation of Schiff base sensor containing coumarin fluorophores for sensing of Cu(II)/Zn(II) ions

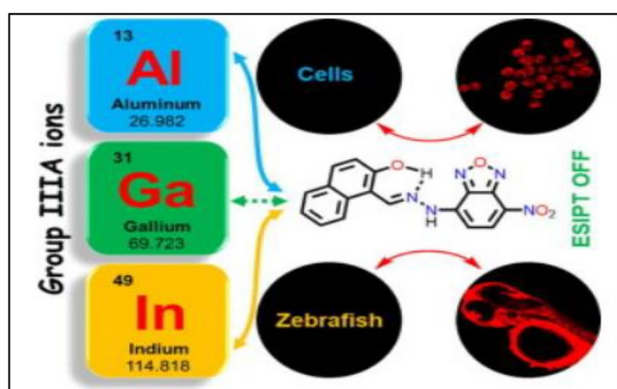
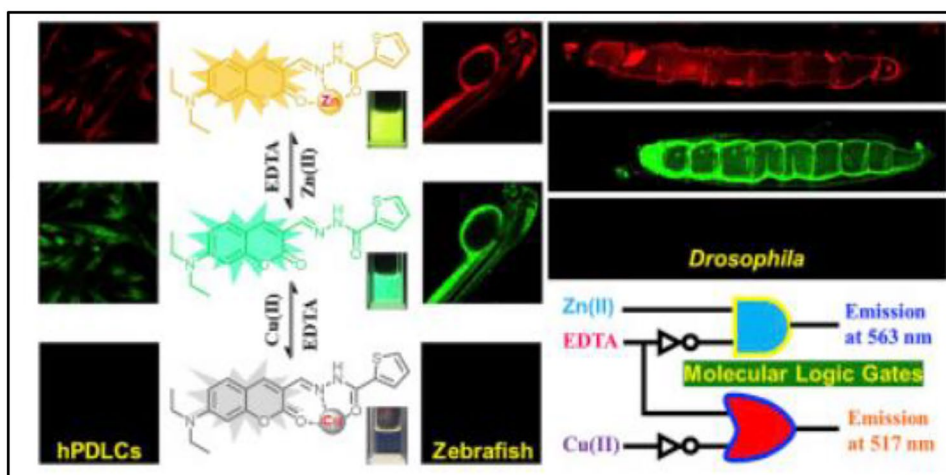
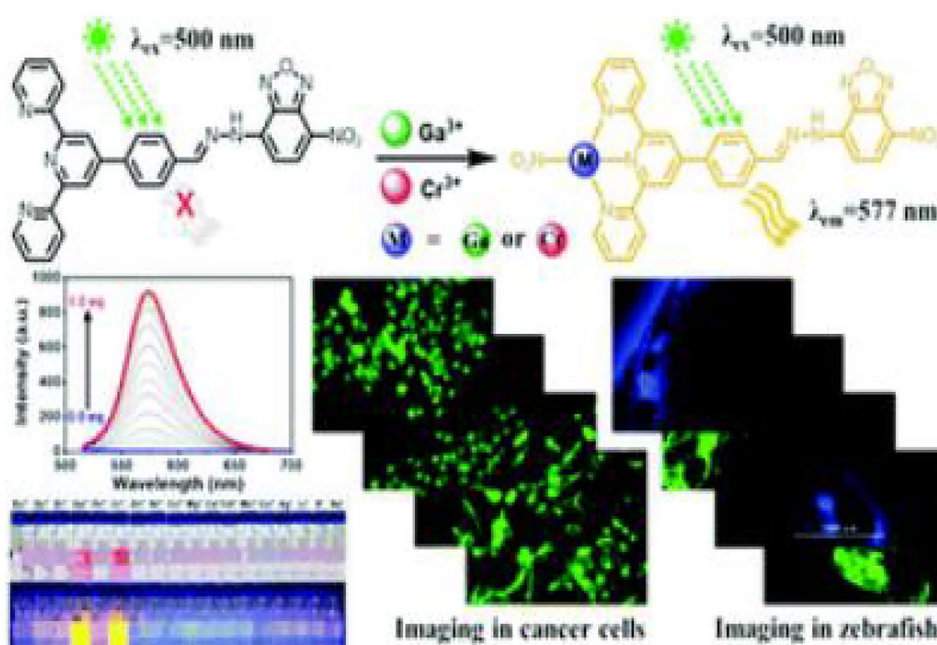


Fig. 3 Fluorescent based sensor for selected group IIIA ions detection

novel group IIIA ions fluorescent probe, NBD-hnap, in live RAW264.7 cell and zebrafish models, especially the imaging of ocular tumor cell OCM-1 (human choroid melanoma cells). NBD-hnap was synthesized by a simple conjugation of NBD and hnap molecules under suitable conditions. Subsequent experimental analysis and theoretical calculations confirmed that NBD-hnap forms a 1:1 chelate with each of three selected group IIIA ions. Further evaluation proved that NBD-hnap can realize highly sensitive [LODs of 113, 82 and 150 nM for Al(III), Ga(III), and In(III) respectively in aqueous solutions] and highly selective (over a dozen of interfering cations) through an ESIPT-based fluorescent sensing mechanism with strong far-red emission around 640 nm. Those value merits make NBD-hnap superior to other group IIIA ion probes reported before and NBD-hnap is thus expected to find wider and greater applications in the near future [34]. The applications of developed Schiff base sensor for selected group III ion is diagrammatically presented in Fig. 3.

He et-al. explained that gallium (Ga) compounds have gained importance in the field of cancer treatment. Gallium acts as an iron mimic and disturbs iron-dependent propagation and other processes in tumor cells. However, the toxicity of gallium was also well documented in vitro and in vivo in animals. Though the oral administration of gallium in humans is less toxic, it has also been shown that a long period of administration could induce tumor fibrosis. Chromium (Cr), a naturally occurring heavy metal, is commonly used in industrial processes and can cause severe health problems in humans. It has been found to be closely involved in the metabolism of nucleic acids, proteins and fats in humans. Cr(III) salts can be used as micronutrients and dietary supplements. However, similar to gallium (Ga^{3+}), chromium (Cr^{3+}) can build up to an excessive degree that is harmful to the human body. Therefore, it would be of great interest to develop chemosensing for the selective and sensitive detection of gallium and chromium ions in vitro and in vivo. Herein, we reported that an NBD-based (4-chloro-7-nitrobenzo-2-oxa-1,3-diazole) fluorescent probe (NBDT) was fabricated with demonstrated extraordinary specificity and sensitivity. A swift response toward Ga^{3+} and Cr^{3+} ions was discovered using fluorescence enhancement over a wide pH range and with cycle stability. Furthermore, lighted up by Ga^{3+} and Cr^{3+} ions in vitro, this NBDT sensor was successfully applied to detect exogenous Ga^{3+} and Cr^{3+} ions in MDA-MB-231 and HepG2 cells. Additionally, using zebrafish as the in vivo model, we demonstrated the capability of this NBDT for detecting and imaging Ga^{3+} and Cr^{3+} ions in zebrafish. Taken together, this NBDT has indicated great potential for detecting and monitoring Ga^{3+} and Cr^{3+} ions in vitro and in vivo [35]. Figure 4 graphically shows gallium and chromium ion detection using NBD based optical probe.

Fig. 4 Selective gallium and chromium ions in vitro and in vivo assay by employing NBD-based optical sensor



Limit of Detection and Quantification At Optimized Parameters of Some Fluorescent Chemosensors

The limit of detection (LOD) and quantification (LOQ) are essential parameters for evaluating the performance of fluorescent sensors. They provide information about the lowest concentration of an analyte that can be reliably detected and quantified using the sensor. Here's a brief explanation of these terms in the context of fluorescent sensors. LOD represents the lowest concentration of the analyte that can be reliably distinguished from background noise but may not necessarily be quantified with high precision. It is typically defined as the concentration at which the sensor's response is significantly different from the blank or background signal and is statistically significant. In the context of fluorescent sensors, LOD is determined by measuring the sensor's fluorescence signal in the presence of varying concentrations of the target analyte. The LOD is often calculated as a multiple of the standard deviation of the blank signal divided by the slope of the calibration curve.

LOQ is a step beyond the LOD and represents the lowest concentration of the analyte that can be both reliably detected and quantified with a defined level of precision and accuracy. It is typically defined as a concentration at which the coefficient of variation (CV) or relative standard deviation (RSD) is below a specified threshold (e.g., 10 %). LOQ takes into account the precision of the sensor's measurements at low concentrations, ensuring that the detected concentration can be reported with confidence. Achieving low LOD and LOQ values is crucial for the practical utility of fluorescent sensors, especially in applications where trace

amounts of analytes need to be detected and quantified accurately, such as environmental monitoring, clinical diagnostics, and food safety testing. Optimizing the sensor's design, sensitivity, and selectivity is essential for achieving lower LOD and LOQ values. The Optical properties at optimized parameters of some chemosensors are given in Table 2.

Conclusion

In conclusion, this review article has provided a comprehensive overview of the diverse and ever-expanding landscape of applications for fluorescent chemosensors. These remarkable molecular tools have revolutionized the field of analytical chemistry and beyond, offering innovative solutions for a wide range of real-world challenges. Through a meticulous examination of the literature, I have explored the versatility of fluorescent chemosensors in various domains, including environmental monitoring, clinical diagnostics, food safety, and drug discovery. Further the current articles explain those sensors evolved to detect an extensive array of analytes, particularly heavy and transition metal ions and biomolecules to pH changes and gas molecules. Their adaptability, high sensitivity, and selectivity have made them indispensable in providing rapid, cost-effective, and non-invasive solutions to complex problems. Moreover, the development of novel sensor materials, advanced instrumentation, and sophisticated data analysis techniques has opened up new frontiers in the field. As we move forward, it is evident that the journey of fluorescent chemosensors is far from over. Emerging technologies, such as fluorescent-based sensors promise to enhance their capabilities even further.

Table 2 Optical properties along with optimized parameters of some reported chemosensors for heavy and transition metal ions

| Sensors | LOD (nM) | LOQ (nM) | Optical response | Analyte | Optimal pH | Testing media | Ref. |
|------------------------|----------------------|-----------------------|------------------|--|------------|-----------------------|------|
| CdTe quantum dots | 7×10^{-7} | 21×10^{-7} | turn-off | Cr^{3+} , Ni^{2+} | 8 | Environmental samples | [36] |
| Curcumin based sensor | 5.9×10^{-9} | 17.7×10^{-9} | turn-off | Cu^{2+} , Zn^{2+} | 9 | Aqueous samples | [37] |
| Au nanoclusters | 8.4×10^{-7} | 25.2×10^{-7} | turn-off | Co^{2+} , Pb^{2+} , Hg^{2+} | 7 | Aqueous samples | [38] |
| Curcumin based probe | 6.7×10^{-6} | 20.1×10^{-6} | turn-off | Pb^{2+} | 9 | aqueous media | [39] |
| Carbazole based sensor | 7.5×10^{-7} | 22.5×10^{-7} | turn-off | Ni^{2+} , Pb^{2+} | 9 | Aqueous samples | [40] |
| trityl-picolinamide | 5.7×10^{-5} | 17.1×10^{-5} | Turn-on | Hg^{2+} , Zn^{2+} , Pb^{2+} | 8 | Food Samples | [41] |
| Gold based sensor | 5.9×10^{-4} | 17.7×10^{-4} | Turn-off | Ni^{2+} , Pb^{2+} | 10 | Aqueous | [42] |
| Anthracene based probe | 6.3×10^{-6} | 18.9×10^{-6} | fluorescence off | Pb^{2+} , Co^{2+} | 11 | Aqueous | [43] |
| Optical probes | 8.6×10^{-5} | 25.8×10^{-5} | turn-on | Ni^{2+} , Pb^{2+} , Zn^{2+} | 8 | Aqueous | [44] |
| carbon based sensor | 8.3×10^{-5} | 24.9×10^{-5} | turn-off | Pb^{2+} | 12 | Aqueous | [45] |
| Ag based sensor | 5.7×10^{-8} | 17.1×10^{-8} | turn-on | Pb^{2+} | 9 | Aqueous | [46] |

Additionally, the integration of these sensors into portable and wearable devices is revolutionizing point-of-care testing and personalized healthcare. The present review article explored potential future directions and emerging technologies in the field of environmental monitoring for heavy and transition metal ions. This has added depth and relevance to the review, making it more valuable to readers interested in the broader context of environmental monitoring.

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Declarations

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