STM JOURNALS

International Journal of
Cheminformatics

Volume 2, Issue 2, 2024
July–December
DOI (Journal): 10.37591/IJCI

https://journals.stmjournals.com/ijci/

Research IJCI

Synthesis and Characterization of a Naphthalene-Derived Schiff Base for Fe^{3+} Sensing Applications

Kalyani Praksh Arote[1,*]

Abstract

The development of chemosensors for metal ions has gained significant attention due to their crucial role in industrial, environmental, and biological applications. Metal ion detection is essential for monitoring environmental pollution, industrial processes, and biological systems in which metal homeostasis plays a vital role. In this study, we focus on the synthesis, characterization, and application of a novel naphthalene-based Schiff base ligand derived from the condensation reaction between 1,8-diaminonaphthalene and 3-nitrobenzaldehyde. The ligand was synthesized using a simple and efficient approach and subsequently characterized using spectroscopic techniques, including UV–Vis spectroscopy, Fourier-transform infrared (FTIR) spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy. A key finding of this study is the ligand's high selectivity and sensitivity toward Fe^{3+} ions, which were confirmed through UV–Vis spectroscopic analysis. Job's plot analysis revealed a 1:1 binding stoichiometry between the ligand and Fe^{3+} ions, indicating strong coordination and potential applications in metal ion sensing. The Schiff base ligand exhibits a distinct colorimetric response upon interaction with Fe^{3+}, making it a promising candidate for visual detection. This work underscores the significance of Schiff base ligands in environmental and metallurgical applications, particularly in the selective detection of metal ions. The findings contribute to the advancement of chemosensor development for analytical and industrial purposes, highlighting their potential for detecting and monitoring biologically and industrially relevant metal ions with high precision and efficiency.

Keywords: Schiff base ligand, Fe^{3+} ion sensing, 1,8-diaminonaphthalene, UV–vis spectroscopy, metal ion chemosensor

INTRODUCTION

The study of coordination compounds has been central to inorganic chemistry since Alfred Werner introduced the concept in 1893. Coordination complexes, where a central metal atom binds to electron-rich species (ligands), exhibit a wide array of magnetic, optical, and electronic properties. These properties can be harnessed for applications in sensing, catalysis, and material science. Schiff bases, characterized by their imine (-C=N-) functional group, have garnered significant attention for their ability to form stable coordination complexes with transition metal ions, making them ideal candidates for chemosensor development.

***Author for Correspondence**
Kalyani Praksh Arote
E-mail: kalyaniarote2020@gmail.com

[1]Student, Savitribai Phule Pune University, Pune, Maharashtra, India

Received Date: January 27, 2025
Accepted Date: January 31, 2025
Published Date: February 14, 2025

Citation: Kalyani Praksh Arote. Synthesis and Characterization of a Naphthalene-Derived Schiff Base for Fe^{3+} Sensing Applications. International Journal of Cheminformatics. 2024; 2(2): 1–8p.

Iron (Fe^{3+}) ions play a crucial role in biological and industrial processes, including oxygen transport, enzymatic catalysis, and metallurgical operations. However, their excess or deficiency can lead to disorders such as hemochromatosis, Alzheimer's, and Parkinson's disease. Furthermore, Fe^{3+} ions are of immense importance in the field of metallurgy, where their precise detection and quantification can enhance process efficiencies. Hence, there is a pressing need for simple, efficient, and cost-effective methods for Fe^{3+} detection. This study presents the synthesis and characterization of a naphthalene-based Schiff base as a selective Fe^{3+} sensor, shedding light on its potential applications in both industrial and environmental domains [1].

REVIEW LITERATURE

Schiff bases are easy to synthesize, show structural variability, and can be used for the recognition of metal ions with a range of applications. This fact attracted the researchers to synthesize and study Schiff base as a ligand.

Wu et al. [1] reported an easily synthesized colorimetric and fluorescent chemosensor by coupling 1-hydroxynaphthalene-2-carbaldehyde and 1-amino-2-naphthol hydrochloride with 78% yield in ethanol in one step. The chemosensor significantly showed a red shift by color change from yellow to orange and enhanced fluorescence after binding to $A1^{3+}$ in acetonitrile. Further, it has also shown a color change from yellow to dark blue in aqueous acetonitrile for Cu^{2+} with a highly selective fluorescence quenching effect. This naphthol-based Schiff base showed colorimetric and fluorescence selectivity for Cu^{2+} in aqueous acetonitrile solution.

Researchers [2] have synthesized a new Salicylaldehyde bis-Schiff base. This sensor exhibits a naked eye colour change from colorless to yellow for Cu^{2+} with high selectivity and sensitivity at the microlevel in aqueous solution and for $A1^{3+}$ by a significant fluorescent enhancement in ethanol over a wide range of tested metal ions including Ag^{+}, $A1^{3+}$, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Hg^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2}. This was first reported Salicylaldehyde Schiff - based sensor capable of detecting both Cu^{2+} and $A1^{3+}$ using two different modes [3].

Reports in literature showed that scientist Jinli Zhu and his co-workers [4] synthesized a simple Schiff base derived from 2-hydroxy-naphthalene-1-carbaldehyde and benzene-1, 2- diamine, which can detect $A1^{3+}$ in living cells by emitting visible fluorescence and in environmental water samples. The sensor thus acts as a fluorescent probe with a turn-on response for the detection of $A1^{3+}$, based on a photoinduced electron transfer (PET) mechanism. It showed a high selectivity for $A1^{3+}$ over other tested metal ions like Hg^{2+}, Ag^{+}, Pb^{2+}, Cu^{2+}, Ba^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Li^{+}, Cr^{3+}, Ca^{2+}, Mg^{2+}, K^{+}, Na^{+} in EtOH buffer.

95:5 v/v at pH=7.2. The detection limit of the sensor is also low, that is, 1.08×10^{-7}. Thus, the sensor can be easily used as a promising probe for recognition of Al^{+3} [5].

Literature review reveals that the Schiff base derived from the coumarin ring can act as a good fluorophore due to a large Stokes shift and visible excitation and emission wavelengths. Researchers have reported a Schiff base based on coumarin. It acts as a dual sensor, like a colorimetric sensor for Fe^{+3} ion and a fluorescent sensor for Mg^{+2} ion [6].

The addition of Fe^{+3} changes the color of the ligand from colorless to brown in CH_3CN solution, thus exhibiting naked eye detection. The fluorescence intensity was enhanced by 70- fold towards Mg^{+2} in CH_3CN/H_2O solution. The selectivity of Fe^{+3} and Mg^{+2} was not interfered by the other metal ions like Cr^{+3}, Mn^{+2}, Co^{+3}, Ni^{+2}, Cu^{+2}, Ag^{+}, Cd^{+2}, Pb^{+2}, Ca^{+2}, K^{+} ions [7–12].

Reports in the literature reveal that the Schiff base can also act as a secondary sensor. In this complex, formed by a metal ion and Schiff base, i.e., Schiff base metal complex, can act as a ligand. Thus, the resultant complex can be used to detect other ions. Kamalpreet Kaur et al. [13] reported such a secondary sensor based on 4-(diethyl amino)-2-hydroxybenzaldehyde Schiff base. It acts as a fluorescent sensor by showing a change in fluorescence intensity for Zn^{+2} ion. The cation displacement approach was exhibited by the Zn^{+2} complex of the chemosensor for the detection of phosphate and phosphorylated biomolecules. Thus, Schiff base behaves as a primary sensor for Zn^{+2} ion and a secondary sensor for phosphate ion [4, 14–17].

One more secondary chemosensor was reported by Kamalpreet Kaur and co- workers [13] for Al^{+3} and its complex for detecting C1O4. HEPES-buffered THF/H_2O (7:3, v/v) was used as a solvent for detecting the metal binding affinity of the chemosensor. After the addition of Al^{+3} at 355 nm, fluorescence intensity was quenched, while at 480 nm, an enhancement in emission intensity was observed in HEPES-buffered THF/H_2O (7:3 v/v). This change was observed only for Al^{+3} ions, not for other metal ions. The aluminium complex of the same receptor was then tested for different anions such as F^-, Cl^-, Br^-, I, NO^{3-}, CN^-, ClO^4, AcO^-, HSO_4, H_2PO_4, and some other phosphate anions such as TBA phosphate, ATP, ADP, NADH, and NADP in THF/H_2O (7:3 v/v) solvent system. A new peak at 428 nm after addition of ClO^{4-} indicates the capability of Al^{+3} complex to detect ClO^{-4} ion selectivity [18].

Schiff base ligands not only detect the metal ions but are also able to detect the anions. Here are some reviews that suggest the applications of Schiff bases to detect the anions. Shyamaprosad Goswami and co-workers [19] derived a simple naphthalene-based colorimetric sensor that is selective for the acetate anion. Naphthalene-based receptor shows a change in color from colourless to pink by the naked eye during the UV-vis titration experiment over the other anions. This selectivity is based on charge-charge interactions along with the involvement of both N-H-O and O-H-O hydrogen bonds.

EXPERIMENTAL SECTION

Materials and Methods

1,8-Diaminonaphthalene, 3-nitrobenzaldehyde, ethanol, and glacial acetic acid were procured from standard chemical suppliers and used without further purification. Analytical grade reagents ensured the accuracy and reliability of the results.

Synthesis of Schiff Base Ligand

- *Step 1:* Dissolve 6.04 g of 3-nitrobenzaldehyde in 15 mL of ethanol.
- *Step 2:* Dissolve 3.16 g of 1,8-diaminonaphthalene in 10 mL of ethanol.
- *Step 3:* Add the 1,8-diaminonaphthalene solution dropwise to the aldehyde solution under constant stirring to facilitate homogeneous mixing.
- *Step 4:* Adjust the pH to 5 using 4-5 drops of glacial acetic acid.
- *Step 5:* Reflux the reaction mixture for 20 minutes to promote the condensation reaction.
- *Step 6:* Stir the mixture at room temperature for 5-6 hours, ensuring complete reaction.
- *Step 7:* Pour the reaction mixture into ice-cold water to precipitate the product.
- *Step 8:* Filter, wash the product with distilled water, dry, and recrystallize it using ethanol.

The resulting Schiff base ligand was characterized by its reddish-brown color and melting point of 140°C (Figure 1).

Preparation of Stock Solutions

A 1.0 mM Fe^{3+} solution was prepared using $FeCl_3$. Stock solutions of other metal ions (Al^{3+}, Ba^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Ag^+, Mg^{2+}, Co^{2+}, Cd^{2+}, Cu^{2+}, Fe^{2+}) were similarly prepared using their respective salts. These solutions were utilized for all spectroscopic measurements to evaluate the ligand's selectivity and sensitivity (Figure 2).

Figure 1. Synthesized Schiff base ligand.

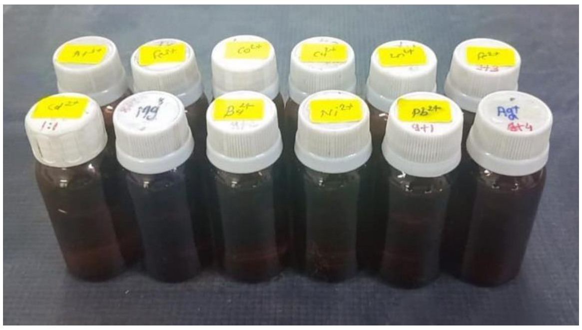

Figure 2. Preparation of stock solutions.

RESULTS AND DISCUSSION

UV-Visible Spectroscopy

To measure UV readings, a Schiff base ligand complex was first prepared and dissolved in ethanol, followed by dilution to a concentration of 10^{-3} M. Stock solutions of metal ions were prepared using their chloride and nitrate salts. A 1:1 ratio of the metal ion solution and the Schiff base ligand solution was then mixed, and the resulting metal-ligand solution was transferred into the cuvette of a UV-Visible spectrophotometer for analysis [20–22].

The UV-Visible spectra of the Schiff base ligand were recorded both before and after the addition of various metal ions. The ligand exhibited a characteristic absorption peak at 420 nm upon interaction with Fe^{3+} ions, indicating the formation of a highly stable complex. This pronounced increase in absorbance was not observed with other metal ions, demonstrating the ligand's specificity for Fe^{3+}. Such remarkable selectivity highlights its potential for applications in selective metal ion detection (Figure 3).

Job's Plot Analysis

Job's variant method was employed to determine the binding stoichiometry of the Schiff base ligand-Fe^{3+} complex. In this method, the total concentration of Fe^{3+} and the Schiff base ligand was kept constant, while the mole fraction of Fe^{3+} was varied from 0.0 to 1.0. A Job's plot was then constructed to analyze the interaction [2, 23–25].

The plot exhibited maximum absorbance at a mole fraction of 0.5, indicating a 1:1 binding stoichiometry between the Schiff base ligand and Fe^{3+} ions. This straightforward the stoichiometric relationship underscores the ligand's potential as a reliable sensor for Fe^{3+} ion detection (Figure 4).

Spectroscopic Characterization

UV and visible electromagnetic radiation are more energetic than others. When electromagnetic radiation continuously passes through a transparent material, a part of the radiation will be absorbed, and the residual radiation then passes through a prism, then it produces a spectrum, called an absorption spectrum. Absorption of these radiations by any sample brings about electronic excitation known as electronic transitions. These excitations are conducted by changes in vibrational and rotational energy levels, resulting in a spectrum. Four types of transitions are shown by organic molecules, which are listed below.

IR Spectroscopy

Infrared spectroscopy, or Vibrational spectroscopy, is concerned with the study of absorption of infrared radiation, which results in vibrational transitions. IR radiation refers broadly to that part of the electromagnetic spectrum between the visible and microwave regions.

The IR spectrum showed a strong absorption band at ~1600 cm^{-1}, confirming the presence of the imine (-C=N-) group (Figure 5).

- *NMR Spectroscopy:* The 1H and 13C NMR spectra corroborated the ligand structure. Key chemical shifts associated with the aromatic and imine functionalities were observed, confirming the successful synthesis of the Schiff base ligand (Figure 6).

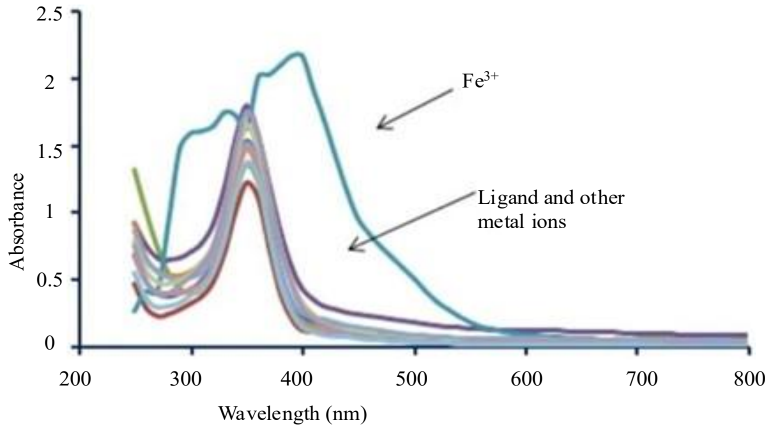

Figure 3. UV-Vis spectra of the synthesized Schiff base ligand.

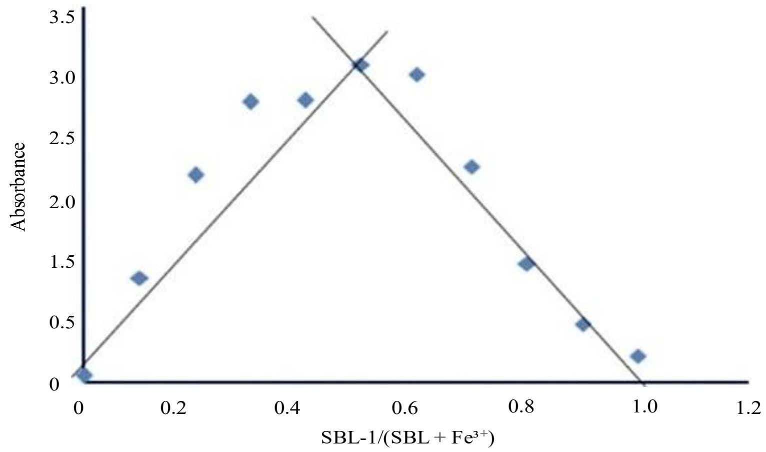

Figure 4. Job's plot analysis.

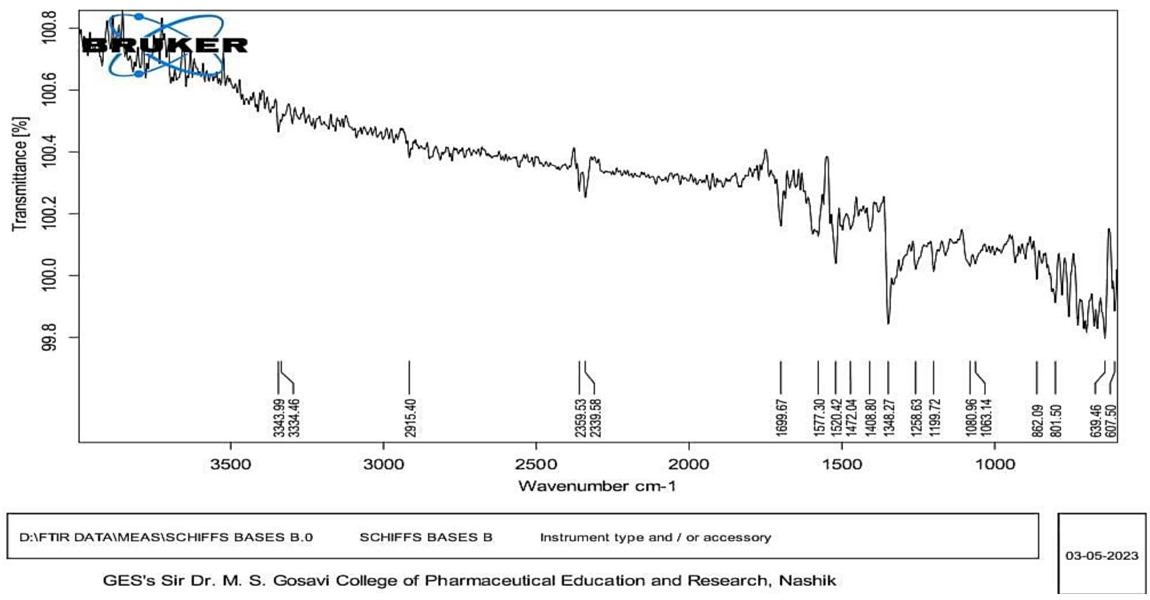

Figure 5. IR spectrum confirming the presence of the imine (-C=N-) group.

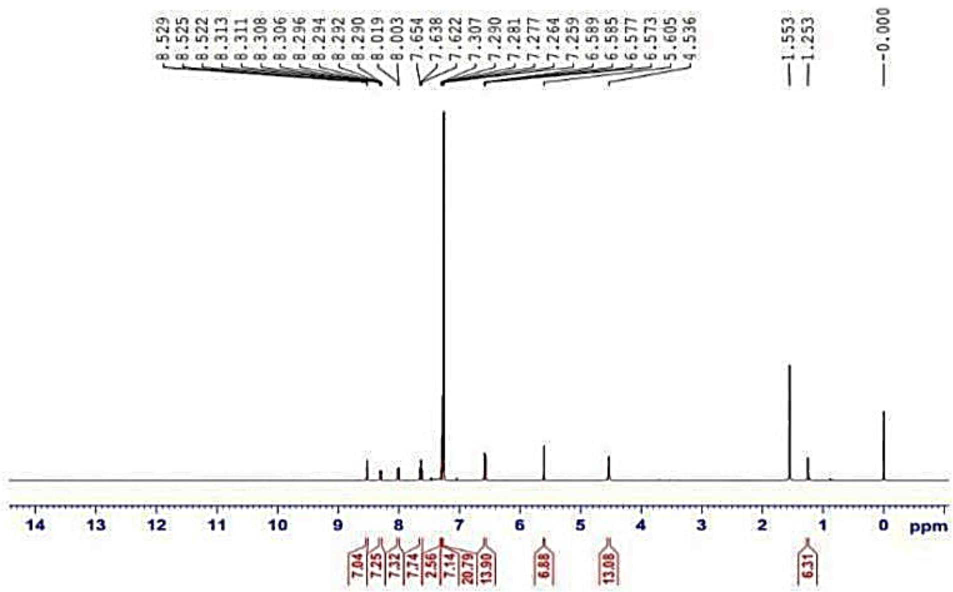

Figure 6. ^{1}H NMR spectrum.

CONCLUSION

In this study, a novel naphthalene-based Schiff base ligand was synthesized and systematically characterized to evaluate its efficacy in selectively detecting Fe^{3+} ions. The ligand demonstrated exceptional sensitivity and specificity, which were thoroughly validated through UV-Vis spectroscopy and Job's plot analysis. These properties underscore the ligand's robustness and reliability in detecting Fe^{3+} ions even at low concentrations, making it a promising candidate for diverse applications.

The high selectivity of the ligand towards Fe^{3+} ions is particularly noteworthy in the context of metallurgical processes where precise monitoring of iron content is critical for quality assurance and process optimization. Furthermore, the ligand's potential extends to environmental monitoring by facilitating accurate detection of iron ions in water and soil samples, thereby contributing to the mitigation of pollution. Additionally, its industrial applications in quality control processes emphasize its utility in ensuring compliance with stringent regulatory standards.

Future studies will aim to expand this work by evaluating the ligand's performance in real-world sample analysis, such as in complex matrices like industrial effluents and natural waters. Moreover, the scope of research will be broadened to investigate the ligand's binding affinity and selectivity for other transition metal ions, potentially leading to the development of a versatile detection platform. This work lays the foundation for advanced sensor development and opens avenues for interdisciplinary applications spanning materials science, environmental science, and analytical chemistry.

REFERENCES

1. Wu P, Yan XP. Ni2+-modulated homocysteine-capped CdTe quantum dots as a turn-on photoluminescent sensor for detecting histidine in biological fluids. Biosens Bioelectron. 2010;26(2):485–490.
2. Shelar DP, Birari DR, Rote RV, Patil SR, Toche RB, Jachak MN. Novel synthesis of 2-aminoquinoline-3-carbaldehyde, benzo[b][1,8]naphthyridines and study of their fluorescence behavior. J Phys Org Chem. 2011;24(3):203–211.
3. Kim GJ, Kim HJ. Highly selective and sensitive fluorescence turn-on probe for proline. Tetrahedron Lett. 2010;51(35):4670–4672.
4. Li M, Sun Y, Dong L, Feng QC, Xu H, Zang SQ, et al. Colorimetric recognition of Cu2+ and fluorescent detection of Hg2+ in aqueous media by a dual chemosensor derived from rhodamine B dye with an NS2 receptor. Sens Actuators B Chem. 2016;226:332–341.

5. Xu NZ, Liu MM, Ye MA, Yao YW, Zhou Y, Wu GZ, et al. A rhodamine-naphthalimide conjugated chemosensor for ratiometric detection of Hg2+ in actual aqueous samples. J Lumin. 2017;188:135–140.
6. Kara DA, Donmez A, Kara H, Coban MB. Structural and spectroscopic characterization of a new luminescent Ni(II) complex: Bis{2,4-dichloro-6-[(2-hydroxypropyl)iminomethyl]phenolato-κ3O,N,O′}nickel(II). Acta Crystallogr C Struct Chem. 2018;74(8):901–906.
7. Kumar B, Prasad KK, Srivastava SK. Synthesis of oxygen bridged complexes of Cu(II) or Ni(II)-salicylaldoxime with alkali metal salts of some organic acids and studies on their antimicrobial activities. Orient J Chem. 2010;26(4):1413–1420.
8. Ramachandran E, Thomas SP, Poornima P, Kalaivani P, Prabhakaran R, Padma VV, et al. Evaluation of DNA binding, antioxidant and cytotoxic activity of mononuclear Co(III) complexes of 2-oxo-1,2-dihydrobenzo[h]quinoline-3-carbaldehyde thiosemicarbazones. Eur J Med Chem. 2012;50:405–415.
9. Eshkourfu R, Čobeljić B, Vujčić M, Turel I, Pevec A, Sepčić K, et al. Synthesis, characterization, cytotoxic activity and DNA binding properties of the novel dinuclear cobalt(III) complex with the condensation product of 2-acetylpyridine and malonic acid dihydrazide. J Inorg Biochem. 2011;105(9):1196–1203.
10. Raja DS, Bhuvanesh NS, Natarajan K. Synthesis, crystal structure and pharmacological evaluation of two new Cu(II) complexes of 2-oxo-1,2-dihydroquinoline-3-carbaldehyde (benzoyl) hydrazone: A comparative investigation. Eur J Med Chem. 2012;47:73–85.
11. Nasomphan W, Tangboriboonrat P, Smanmoo S. Dansyl-based "turn-on" fluorescent sensor for Cu2+ ion detection and application to living cell imaging. J Fluoresc. 2017;27:2201–2212.
12. Das DK, Goswami P, Sarma S. Salicylaldehyde phenylhydrazone: A new highly selective fluorescent lead(II) probe. J Fluoresc. 2013;23:503–508.
13. Kaur K, Bhardwaj VK, Kaur N, Singh N. Fluorescent chemosensor for Al3+ and resultant complex as a chemosensor for perchlorate anion: First molecular security keypad lock based on Al3+ and ClO4− inputs. Inorg Chem Commun. 2012;26:31–36.
14. Fan Z, Ye JH, Bai Y, Bian S, Wang X, Zhang W, et al. A new dual-channel ratiometric fluorescent chemodosimeter for Cu2+ and its imaging in living cells. Tetrahedron Lett. 2016;57(47):5281–5285.
15. Wang W, Wei J, Liu H, Liu Q, Gao Y. A novel colorimetric chemosensor based on quinoline for sequential detection of Fe3+ and PPi in aqueous solution. Tetrahedron Lett. 2017;58(11):1025–1029.
16. Muwal PK, Nayal A, Jaiswal MK, Pandey PS. A dipyrromethane-based receptor as a dual colorimetric sensor for F− and Cu2+ ions. Tetrahedron Lett. 2018;59(1):29–32.
17. Jang YK, Nam UC, Kwon HL, Hwang IH, Kim C. A selective colorimetric and fluorescent chemosensor based on naphthol for detection of Al3+ and Cu2+. Dyes Pigments. 2013;99(1):6–13.
18. Mitra A, Mittal AK, Rao CP. Carbohydrate-assisted fluorescence turn-on gluco–imino–anthracenyl conjugate as a Hg(II) sensor in milk and blood serum milieu. Chem Commun (Camb). 2011;47(9):2565–2567.
19. Goswami S, Das AK, Sen D, Aich K, Fun HK, Quah CK. A simple naphthalene-based colorimetric sensor selective for acetate. Tetrahedron Lett. 2012;53(36):4819–4823.
20. Huang CY, Wan CF, Chir JL, Wu AT. A Schiff-based colorimetric fluorescent sensor with potential for detection of fluoride ions. J Fluoresc. 2013;23:1107–1111.
21. Sıdır YG, Aslan C, Berber H, Sıdır İ. Electronic structure, solvatochromism and electric dipole moments of new Schiff base derivatives using absorbance and fluorescence spectra. Struct Chem. 2019;30:835–851.
22. Raja DS, Bhuvanesh NS, Natarajan K. DNA binding, protein interaction, radical scavenging and cytotoxic activity of 2-oxo-1,2-dihydroquinoline-3-carbaldehyde (2′-hydroxybenzoyl) hydrazone and its Cu(II) complexes: A structure–activity relationship study. Inorg Chim Acta. 2012;385:81–93.

23. Wu P, Yan XP. Ni2+-modulated homocysteine-capped CdTe quantum dots as a turn-on photoluminescent sensor for detecting histidine in biological fluids. Biosens Bioelectron. 2010;26(2):485–490.
24. Lu W, Jiang H, Hu F, Jiang L, Shen Z. A novel chemosensor based on Fe(III)-complexation for selective recognition and rapid detection of fluoride anions in aqueous media. Tetrahedron. 2011;67(41):7909–7912.
25. Zhou L, Cai P, Feng Y, Cheng J, Xiang H, Liu J, et al. Synthesis and photophysical properties of water-soluble sulfonato-Salen-type Schiff bases and their applications as fluorescence sensors for Cu2+ in water and living cells. Anal Chim Acta. 2012;735:96–106.

