The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM)
ISSN: 2602-3199

The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM), 2024

Volume 29, Pages 55-60

ICRETS 2024: International Conference on Research in Engineering, Technology and Science

Synthesis and Fluorimetric Application of Novel Schiff Base Compound Containing 8-Hydroxyquinoline

Meliha Kutluca-Alici
Nigde Omer Halisdemir University

Abstract: Firstly, in this study, aldehyde derivative compound containing 5-chloro-8-hydroxyquinoline was obtained as literature information. Then, for the target compound, which is Schiff base derivative, was obtained from the condensation reaction of the aldehyde derivative compound containing chinolin with salicylaldehyde hydrazone. Chemical structure of synthesized Schiff base compound was confirmed as using various spectroscopic techniques (^{1}H-NMR and ^{13}C-NMR). Then, the interactions of the synthesized Schiff base compound with metals (Li^{+}, Ni^{2+} Co^{2+}, Ag^{+}, Al^{3+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cu^{2+}, Hg^{2+}, Fe^{2+}, Pb^{2+}, Fe^{3+}, Cr^{3+} and Zn^{2+}) under convenient conditions were investigated using fluorescence spectrophotometry. In the fluorimetric investigations, primarily, the selectivity study was carried out. The free sensor target compound at 538 nm did not produce any significant emission intensity with excitation at 405 nm. The each of the cations (10.0 equiv) were separately added to target compound, only Zn^{2+} caused to a single band at 538 nm with a notable emission enhancement. As a result of the measurements, it was determined that the target compound had fluorimetric selectivity against only Zn^{2+} metal within all metals (Li^{+}, Ni^{2+}, Co^{2+}, Ag^{+}, Al^{3+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cu^{2+}, Hg^{2+}, Fe^{2+}, Pb^{2+}, Fe^{3+}, Cr^{3+}).

Keywords: 8-Hydroxyquinoline, Fluorescence, Zn^{2+}, Schiff base.

Introduction

The development of high-performance fluorogenic chemosensors for sensitive and selective detection of cations, including Zn^{2+} recognition, holds great importance. In the human body, zinc is the second essential and most abundant transition element after iron, and zinc ions play a crucial role in neural signal transmission, regulation of the immune system, nucleic acid and protein synthesis, and numerous molecular mechanisms. Zinc, found in the cell membrane, plays a vital role in protecting the cell from damage caused by oxidative reactions. On the other hand, numerous studies have shown that an excessive amount of Zn^{2+} in the human body can lead to various diseases including epilepsy, osteoporosis, prostate and breast cancers, and neurodegenerative disorders such as Alzheimer's disease (Sethupathi, et al., 2020; Erdemir & Malkondu, 2020; Ghaedi et al., 2009). Therefore, it is crucial to regulate and monitor the levels of Zn^{2+} in order to prevent potential adverse effects on the human body.

In recent years, various traditional analytical methods such as differential pulse stripping anodic voltammetry, electrochemical analysis, atomic absorption spectroscopy, flame atomic absorption spectrometry, isotope chromatography, and chromatography have been commonly used for the detection of Zn^{2+} ions. On the other hand, these conventional detection methods have drawbacks including time-consuming analysis, complicated sample preparation, reliance on expensive and specialized equipment, and cumbersome procedures, which limit their suitability for real-time and large-scale monitoring of samples. In comparison to traditional analytical methods for detecting Zn^{2+} ions, fluorescence-based recognition techniques offer high sensitivity and selectivity. Moreover, this recognition technology offers several benefits, such as quick response times and straightforward sample preparation (Sethupathi, et al., 2020; Erdemir & Malkondu, 2020; Ghaedi, et al., 2009). Furthermore, fluorescence-based techniques are highly sensitive and selective, and they are easy to operate. As a result,

fluorescence-based recognition techniques for cation detection have been widely used in fields such as medicine, chemistry, life sciences, environmental science, and many other research areas. Numerous synthesized fluorescence-based molecules for the detection of Zn^{2+} ions have been reported in the literature. These molecules are typically based on coumarin, fluorescein, calixarene, and thiazole structures (Erdemir & Malkondu, 2020) (Aydin, et al., 2021). Many of these molecules exhibit high detection limits or low selectivity in the recognition of Zn^{2+} ions. Therefore, it is highly significant to develop novel fluorogenic chemosensors for efficient and rapid fluorescence analysis of Zn^{2+} detection in environmental waste.

In this study, aldehyde derivative compound containing 5-chloro-8-hydroxyquinoline was obtained as literature information (Wantulok, et al., 2008). Then, for the target compound (5-chloro-7-(((-2-hydroxybenzylidene) hydrazineylidene) methyl)quinolin-8-ol) (**8HQ-SA**) which is Schiff base derivative, was obtained from the condensation reaction of the aldehyde derivative compound containing chinolin with salicylaldehyde hydrazone. Chemical structure of synthesized **8HQ-SA** was confirmed as using various spectroscopic techniques (^{1}H-NMR and ^{13}C-NMR). Then, the interactions of the synthesized **8HQ-SA** compound with some metals (Li^{+}, Ni^{2+} Co^{2+}, Ag^{+}, Al^{3+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cu^{2+}, Hg^{2+}, Fe^{2+}, Pb^{2+}, Fe^{3+}, Cr^{3+} and Zn^{2+}) under convenient conditions were investigated using fluorescence spectrophotometry. In the fluorimetric investigations, primarily, the selectivity study was carried out. The free sensor target compound at 546 nm did not produce any significant emission intensity with excitation at 405 nm. The each of the cations (6.0 equiv) were separately added to target compound, only Zn^{2+} caused to a single band at 546 nm with a notable emission enhancement. As a result of the measurements, it was determined that the target compound had fluorimetric selectivity against only Zn^{2+} metal within all metals (Li^{+}, Ni^{2+}, Co^{2+}, Ag^{+}, Al^{3+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cu^{2+}, Hg^{2+}, Fe^{2+}, Pb^{2+}, Fe^{3+}, Cr^{3+}).

Method

Chemicals and Instruments

All necessitated chemicals are analytical grade and were obtained from Sigma-Aldrich Chemicals (Zwijndrecht, The Netherlands) and utilized with no further processing. The perchlorate salts of the cations were utilized in this study. ^{1}H and ^{13}C-NMR spectral studies were measured by a Spinsol and Magritek NMR spectrometer and emission spectra of the chemosensor **8HQ-SA** were recorded in a Varian Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies Inc, Santa Clara, CA, USA).

Synthesis of 5-chloro-8-hydroxyquinoline-7-carbaldehyde (1)

Compound (1) was prepared according in the literature (Wantulok, et al., 2008).

Synthesis of the chemosensor 5-chloro-7-(((-2-hydroxybenzylidene)hydrazineylidene)methyl)quinolin-8-ol (8HQ-SA)

Absolute ethanolic solutions (10 mL) of compound (1) (0.05 g, 0.240 mmol) was added to 2-(hydrazineylidenemethyl)phenol (0.036 g, 0.264 mmol) in absolute EtOH and stirred under reflux for 24 hours. After completion of the reaction, the precipitate formed was filtered off. The precipitate was washed three times with water and ethanol, dried in a vacuum oven. Finally, the Schiff base compound (**8HQ-SA**) was recrystallized with hot ethanol to obtain yellow crystals.

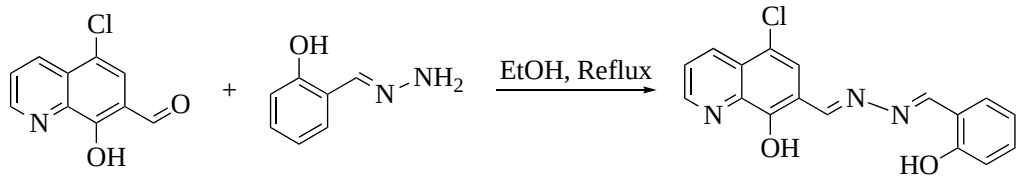
Yield: 59 %, Melting Point: 273.6 ^{0}C, ^{1}H NMR (400 MHz, DMSO) δ 11.19 (s, 1H), 9.14 (s, 1H), 9.03 (d, *J* = 4.4 Hz, 2H), 8.54 (d, *J* = 8.2 Hz, 1H), 8.11 (s, 1H), 7.82 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (100 MHz, DMSO) δ 163.65, 159.20, 157.97, 155.08, 150.27, 140.12, 133.70, 133.32, 131.49, 128.13, 124.97, 124.42, 120.06, 120.06, 118.71, 116.99, 116.46.

Results and Discussion

Preparation of the Chemosensor 8HQ-SA

The synthesis routes of TC include three steps: the preparation of compound 2-(hydrazineylidenemethyl)phenol was prepared by the reaction of 2-hydroxybenzaldehyde with %80 hydrazine hydrate, and 5-chloro-8-hydroxyquinoline-7-carbaldehyde by the Duff reaction with HMTA in trifluoroacetic acid. The chemosensor

8HQ-SA was easily prepared by the condensation reaction of 5-chloro-8-hydroxyquinoline-7-carbaldehyde (1) and 2-(hydrazineylidenemethyl) phenol (2) in ethanol with 59 % yield as illustrated in Schema 1.



(1) **(2)** **(8HQ-SA)**

Schema 1. The Synthesis Procedure for the **8HQ-SA**

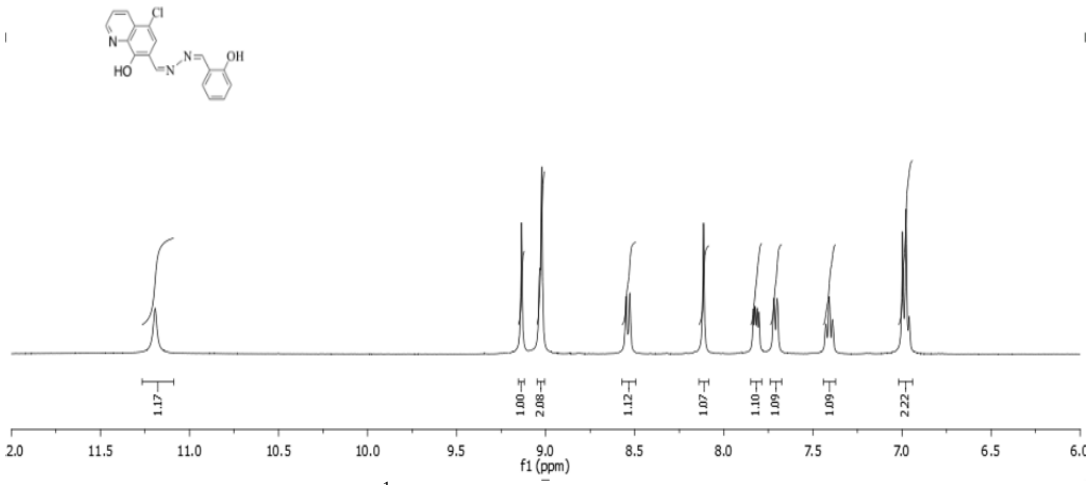


Figure 1. ^{1}H-NMR spectrum of compound **8HQ-SA**

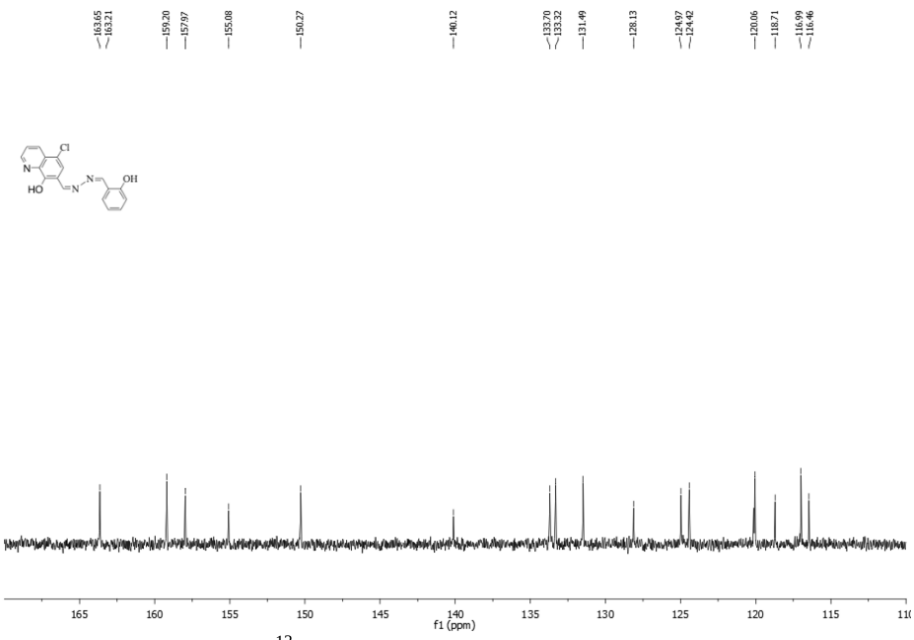


Figure 2. ^{13}C-NMR spectrum of compound **8HQ-SA**

Emission Study

The stock solution of 8HQ-SA (10 mM) was prepared in DMSO and then diluted 10 μM in EtOH/H_2O (9/1, v/v). The tested metal perchlorate salts were utilized as (10^{-2} M).

Fluorescence Studies of 8HQ-SA versus Zn^{2+}

The fluorescent study of **8HQ-SA** was conducted in EtOH−H_2O (9:1, v/v) with Li^+, Ni^{2+}, Co^{2+}, Ag^+, Al^{3+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cu^{2+}, Hg^{2+}, Fe^{2+}, Pb^{2+}, Fe^{3+}, Cr^{3+}, and Zn^{2+}. At first, **8HQ-SA** showed no emission at 546 nm; however, the addition of Zn^{2+} to 8HQ-SA resulted in a significant increase in intensity at 546 nm. Addition of the other mentioned cations to the 8HQ-SA solution did not cause a significant increase at 546 nm (Figure 3). This significant increase in fluorescence intensity indicates a strong interaction between 8HQ-SA and Zn^{2+}.

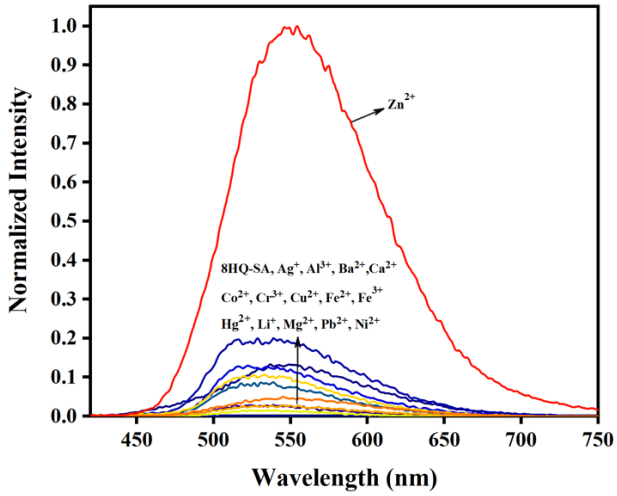


Figure 3. Changes in emission intensity of 8HQ-SA (10 μM) in the presence of various tested cations.

To assess the sensitivity and quantify the response of 8HQ-SA toward Zn^{2+}, a standard titration analysis was performed, as shown in Fig. 4a. The fluorescence intensity of 8HQ-SA at 546 nm increased due to the concentration of Zn^{2+} ions increased. As can be seen from the Fig 4a., no change in fluorescence intensity was observed after a certain point. This is an indication that the 8HQ-SA-Zn^{2+} complex has reached saturation. Additionally, a Job's plot experiment was conducted using a fluorescence spectrometer to confirm the final complexation between 8HQ-SA and Zn^{2+}. As shown in Fig 4b, the Job's plot analysis indicates a 1:1 complexation ratio between 8HQ-SA and Zn^{2+}, as the highest ordinate value is observed at a molar fraction of Zn^{2+} with 8HQ-SA close to 0.5, confirming the 1:1 stoichiometric binding ratio.

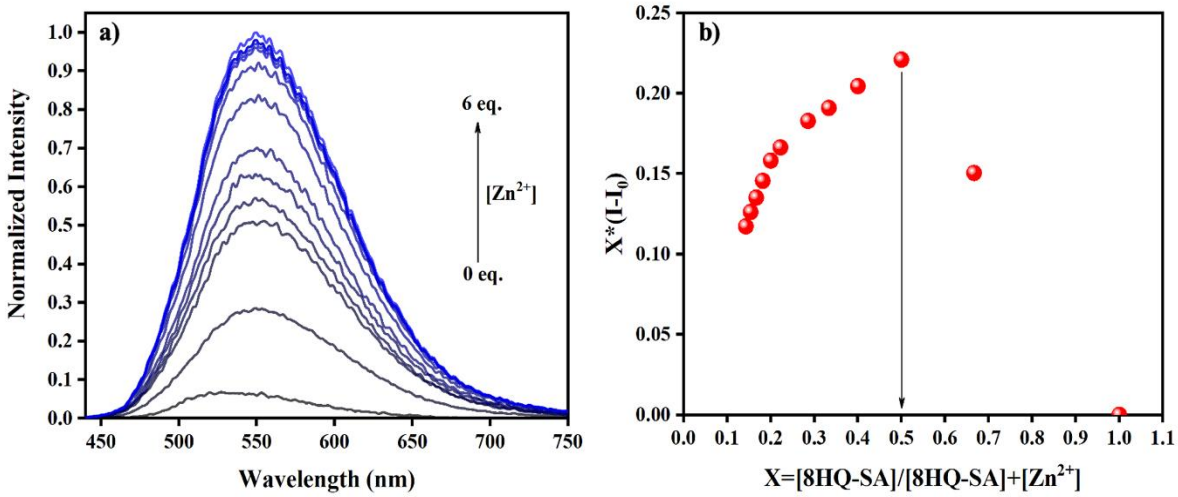


Figure 4. a) The emission spectra of 8HQ-SA were measured at various concentrations of Zn^{2+}. b) Job's plot demonstrating the 1:1 stoichiometry

The emission values were plotted as a function of the concentrations of Zn^{2+} Fig 5a to investigate the limit of detection (LOD) value of **8HQ-SA** for Zn^{2+} determination the LOD value of compound **8HQ-SA** was determined as 1.22 mM according to the equation: LOD = 3σ/k (σ: symbolizes the root-mean-square of blank measurements, k: the slope of the linear calibration curve). Furthermore, the log(Ka) value for the **8HQ-SA**-Zn^{2+} system was 2,93 M^{-1} in accordance with the Benesi–Hildebrand plot of the alterations in the titration of the **8HQ-SA** toward Zn^{2+} (Fig 5b).

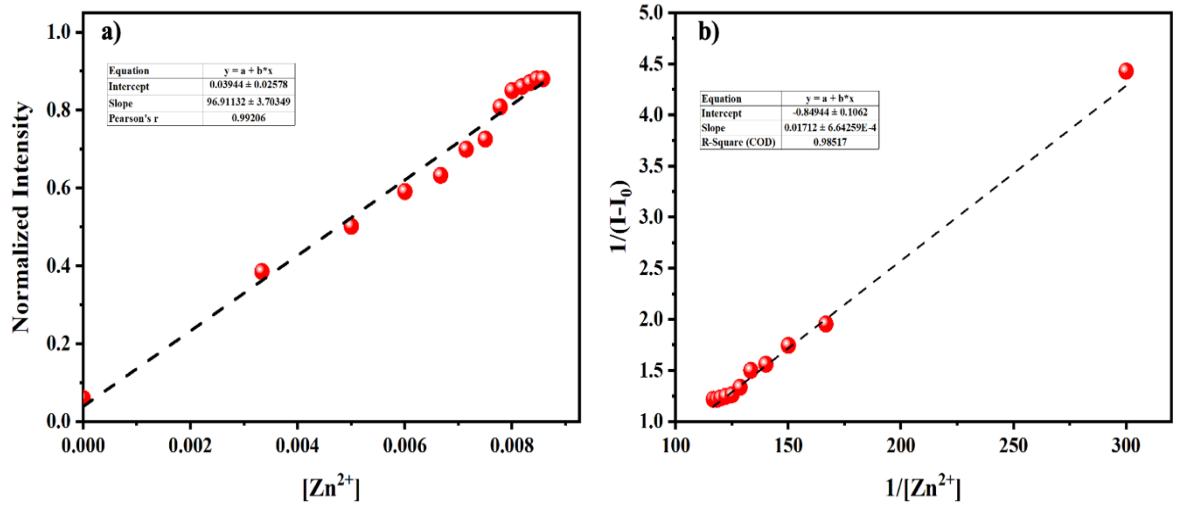


Figure 5. a) The plot of emission intensity of 8HQ-SA at 546 nm versus Zn^{2+} cation concentration, b) Benesi–Hildebrand plot assuming 1:1 stoichiometry from fluorometric titration data of receptor **8HQ-SA** (10 μM) with Zn^{2+}

Conclusion

In summary, a new quinoline-based fluorogenic chemosensor for Zn^{2+} detection has been successfully created. The change in intensity of the 8HQ-SA solution is a result of its interaction and coordination with Zn^{2+}, indicating the strong affinity between 8HQ-SA and Zn^{2+}. The proposed fluorogenic chemosensor 8HQ-SA has the potential to serve as a simple and effective tool for detecting Zn^{2+} in solutions, and it can inspire the design of different fluorogenic probes for Zn^{2+} recognition.

Scientific Ethics Declaration

The author declares that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the author.

Acknowledgements or Notes

* This article was presented as an oral presentation at the International Conference on Research in Engineering, Technology and Science (www.icrets.net) held in Tashkent/Uzbekistan on August 22-25, 2024.

References

Aydin, D., Elmas, S. N. K., Savran, T., Arslan, F. N., Sadi, G., & Yilmaz, I. (2021). An ultrasensitive ″OFF–ON ″fluorogenic sensor based on thiazole derivative for Zn2+: Food supplement, water and bio–imaging applications. *Journal of Photochemistry and Photobiology A: Chemistry*, *419*, 113459.

Erdemir, S., & Malkondu, S. (2020). Calix [4] arene based a NIR-fluorescent sensor with an enhanced stokes shift for the real-time visualization of Zn (II) in living cells. *Sensors and Actuators B: Chemical*, *306*, 127574.

Ghaedi, M., Shokrollahi, A., Niknam, K., & Soylak, M. (2009). Cloud point extraction of copper, zinc, iron and nickel in biological and environmental samples by flame atomic absorption spectrometry. *Separation Science and Technology*, *44*(3), 773-786.

Kutluca Alici, M. (2020). Phentroimidazole based fluorescence “turn on” sensor for highly sensitive detection of Zn2+ ions. *Journal of Fluorescence*, *30*(2), 269-273.

Sethupathi, M., Jayamani, A., Muthusankar, G., Sakthivel, P., Sekar, K., Gandhi, S., ... & Selvaraju, C. (2020). Colorimetric and fluorescence sensing of Zn2+ ion and its bio-imaging applications based on macrocyclic “tet a” derivative. *Journal of Photochemistry and Photobiology B: Biology*, *207*, 111854.

Voloshin, N. A., Chernyshev, A. V., Bezuglyi, S. O., Metelitsa, A. V., Voloshina, E. N., & Minkin, V. I. (2008). Spiropyrans and spirooxazines: 4. Synthesis and spectral properties of 6′-halo-substituted spiro [indoline-2, 2′-2 H-pyrano [3, 2-h] quinolines]. *Russian Chemical Bulletin*, *57*, 151-158.

Author Information

Meliha Kutluca-Alici
Nigde Omer Halisdemir University
Laboratory Assistant and Veterinary Health
Bor Vocational School , Nigde, Türkiye
Contact e-mail: *melihakutlucaalici@gmail.com*

To cite this article:

Kutluca-Alici, M. (2024). Synthesis and fluorimetric application of novel schiff base compound containing 8-hydroxyquinoline. *The Eurasia Proceedings of Science, Technology, Engineering and Mathematics (EPSTEM), 29,* 55-60.