

## Synthesis, Characterization and Selective Fluorimetric Detection of $\text{Al}^{3+}$ by A Schiff Base Derived From 5-Chloro-8-Hydroxyquinoline

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**Abstract:** In this study, an aldehyde derivative compound containing 5-chloro-8-hydroxyquinoline was synthesized based on literature procedures. Subsequently, the target compound, a Schiff base derivative (**HQ-BH**), was obtained via a condensation reaction between the quinoline-based aldehyde and benzaldehyde hydrazone. The chemical structure of the synthesized HQ-BH compound was confirmed using various spectroscopic techniques, including FT-IR, TOF-MS,  $^1\text{H}$ -NMR, and  $^{13}\text{C}$ -NMR. Next, the interactions of the **HQ-BH** compound with various metal ions ( $\text{Li}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Rb}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cs}^+$ ,  $\text{Cd}^{2+}$ ) were investigated under suitable conditions using fluorescence spectrophotometry. Initially, a selectivity study was performed. The sensor **HQ-BH** did not exhibit any significant fluorescence emission at 499 nm upon excitation at 360 nm. However, upon the individual addition of each cation (20.0 equivalents), only  $\text{Al}^{3+}$  induced a distinct emission band at 499 nm with a notable enhancement in intensity. As a result of these measurements, it was concluded that the **HQ-BH** compound displays selective fluorimetric response exclusively toward  $\text{Al}^{3+}$  among all tested metal ions.

**Keywords:**  $\text{Al}^{3+}$ , Quinoline, Fluorescence, Schiff base

### Introduction

Aluminium (Al) is one of the most abundant elements in nature and is extensively used in various industrial applications. It plays a critical role in sectors such as water treatment, food additives, pharmaceuticals, and household appliances (Aydin, 2021; Alici, 2021; Heena et al., 2023). Due to its widespread use, there is a significant risk of unintentional excessive exposure to aluminium in daily life. According to the World Health Organization (WHO), the human body can only absorb up to 7 mg/kg of  $\text{Al}^{3+}$  ions. Exposure beyond this threshold has been associated with serious health issues, including Alzheimer's disease, osteoporosis, and kidney dysfunction (Deibel et al., 1996). As a result, the reliable detection of  $\text{Al}^{3+}$  ions in environmental and biological systems have become an increasingly important research focus. In recent years, UV-visible (UV-vis) spectroscopy and fluorescence spectroscopy have emerged as leading analytical techniques for the detection of  $\text{Al}^{3+}$  ions. Fluorescent sensors have garnered significant attention due to their advantages, such as low cost, high sensitivity, rapid response, and operational simplicity (Fu et al., 2019; Yan et al., 2023). A wide range of fluorescent chemosensors with selective recognition capabilities for  $\text{Al}^{3+}$  have been developed and reported in the literature (Sen et al., 2012; Mahalakshmi et al., 2020; Ali et al., 2021; Erdemir & Malkondu, 2021). In this context, Schiff base compounds have attracted considerable interest due to their ability to form strong and stable complexes with metal ions. These compounds, which contain various donor atoms, serve as key structural motifs in macrocyclic chemistry and offer broad application potential in environmental and biomedical fields (Keypour et al., 2019; Nemati et al., 2021; Zeynali et al., 2021; Hajari et al., 2022). Moreover, the favourable electronic and structural features of Schiff bases enable the selective and efficient detection of specific metal ions, including  $\text{Al}^{3+}$  (Alici & Erdemir, 2015; Golbedaghi et al., 2022).

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In this study, an aldehyde derivative compound containing 5-chloro-8-hydroxyquinoline was synthesized based on literature procedures (Wantulok et al., 2020). Subsequently, the target compound, a Schiff base derivative (**HQ-BH**), was obtained via a condensation reaction between the quinoline-based aldehyde and benzohydrazide. The chemical structure of the synthesized HQ-BH compound was confirmed using various spectroscopic techniques, including FT-IR, TOF-MS,  $^1\text{H}$ -NMR, and  $^{13}\text{C}$ -NMR. Next, the interactions of the **HQ-BH** compound with various metal ions ( $\text{Li}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Rb}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cs}^+$ ,  $\text{Cd}^{2+}$ ) were investigated under suitable conditions using fluorescence spectrophotometry. Initially, a selectivity study was performed. The sensor **HQ-BH** did not exhibit any significant fluorescence emission at 499 nm upon excitation at 360 nm. However, upon the individual addition of each cation (20.0 equivalents), only  $\text{Al}^{3+}$  induced a distinct emission band at 499 nm with a notable enhancement in intensity. As a result of these measurements, it was concluded that the **HQ-BH** compound displays selective fluorimetric response exclusively toward  $\text{Al}^{3+}$  among all tested metal ions.

## 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. FT-IR, TOF-MS,  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectral studies were measured by Bruker Vertex 70, Bruker Microflex LT MALDI-TOF MS, Bruker, 400 MHz, Avance NEO (Broadband) and emission spectra of the chemosensor **TDH-CB** were recorded in a Edinburgh Instruments FS5 Fluorescence Spectrophotometer.

### Synthesis of 5-Chloro-8-Hydroxyquinoline-7-Carbaldehyde (HQA)

Compound (**HQA**) was prepared according to the literature (Wantulok et al., 2020).

### Synthesis of the Receptor *N'*-((5-Chloro-8-Hydroxyquinolin-7-yl) Methylene) Benzohydrazide (**HQ-BH**)

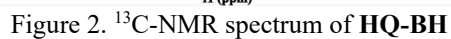
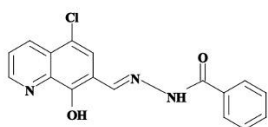
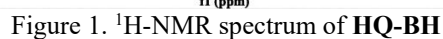
Absolute ethanolic solutions (25 mL) of 5-chloro-8-hydroxyquinoline-7-carbaldehyde (100.00 mg, 0.481 mmol) were added to benzohydrazide (78.70 mg, 0.578 mmol) in absolute EtOH and stirred under reflux for 12 hours. After completion of the reaction, the precipitation formed was filtered off. The precipitate was washed three times with water and ethanol and dried in a vacuum oven. Finally, the Schiff base compound (**HQ-BH**) was recrystallized with hot ethanol to obtain yellow crystals.

Yield: 84 %, Melting Point: 260  $^{\circ}\text{C}$ ,  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  12.14 (s, 1H), 9.06 (dd,  $J = 4.2, 1.5$  Hz, 1H), 9.03 (s, 1H), 8.58 (dd,  $J = 8.5, 1.6$  Hz, 1H), 8.14 (s, 1H), 8.07 – 7.96 (m, 2H), 7.84 (dd,  $J = 8.5, 4.2$  Hz, 1H), 7.70 – 7.64 (m, 1H), 7.61 (dd,  $J = 8.2, 6.5$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ )  $\delta$  163.52, 152.94, 150.10, 143.50, 140.07, 133.60, 133.25, 132.38, 129.01, 128.14, 127.16, 124.32, 123.78, 120.10, 117.63.

## Results and Discussion

### Preparation for the Receptor **HQ-BH**

The synthesis of the **HQ-BH** compound was carried out through a two-step reaction process. In the first step, 5-chloro-8-hydroxyquinoline was used as the starting material and subjected to a Duff reaction. Hexamethylenetetramine (HMTA) was employed as the formylating agent, and trifluoroacetic acid (TFA) served as the reaction medium. Under these conditions, a formyl group was selectively introduced at the 7-position of the aromatic ring, yielding 5-chloro-8-hydroxyquinoline-7-carbaldehyde (**HQA**). In the second step, the obtained **HQA** was reacted with benzohydrazide via a condensation reaction. This transformation, which involves the formation of a Schiff base, occurs through the reaction of the aldehyde group with the hydrazide, forming an aryl-hydrazone structure. The reaction synthesized the target compound **HQ-BH** in high yield (84%), as shown in Schema 1. In addition, the chemical structure of the **HQ-BH** compound was elucidated using various spectroscopic methods (Fig.1-3).

O=C1C=CC=C(C=C1)NC(=O)N=Cc2c(O)c(Cl)c3ccncc23

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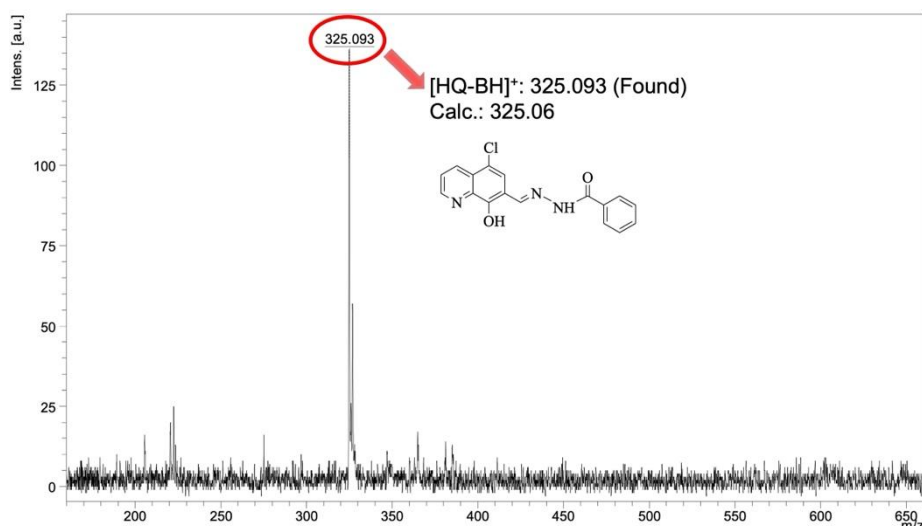


Figure 3. TOF-MS spectrum of **HQ-BH**

### Fluorescence Studies of **HQ-BH** versus $\text{Al}^{3+}$

Firstly, selectivity determination was made within metals ( $\text{Hg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Li}^+$ ,  $\text{Ag}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Rb}^{2+}$ ,  $\text{Cs}^{2+}$ ). For this study, the interaction between the solution of **HQ-BH** compound prepared in DMSO/HEPES (8:2) solvent medium and metal ions was investigated by fluorescence spectroscopy, and for this investigation, various metal ions (20 equiv.) were added to 10  $\mu\text{M}$  **HQ-BH** solution. As shown in the graph in Figure 4, among all the metals tested, the **HQ-BH** compound exhibits a significant emission at 486 nm in the presence of  $\text{Al}^{3+}$  ions, indicating that **HQ-BH** is selective toward  $\text{Al}^{3+}$  metal ions.

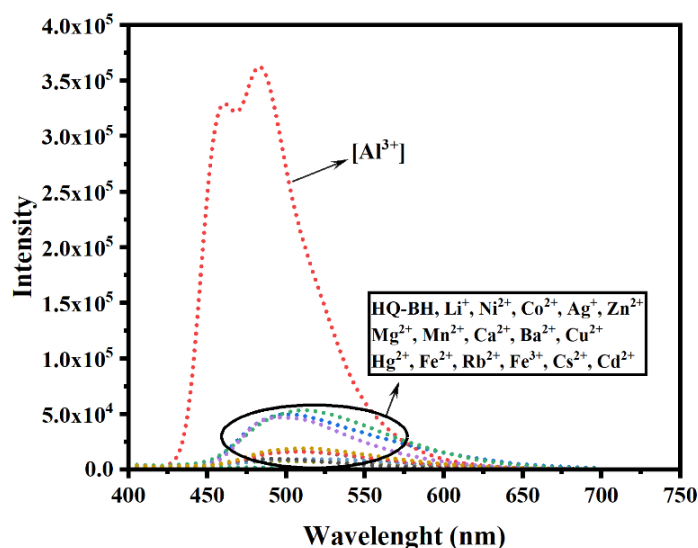


Figure 4. Fluorescence spectrum of **HQ-BH** compound in the presence of different metals ( $\lambda_{\text{ex}}$ : 360 nm; Ex-Slit: 1, Em-Slit: 1;  $\lambda_{\text{em}}$ : 486 nm)

Following the determination that the **HQ-BH** receptor exhibits fluorometric selectivity toward  $\text{Al}^{3+}$  ions, fluorescence titration experiments were conducted to investigate its interaction with this ion in more detail. For these experiments, a solution of **HQ-BH** (10  $\mu\text{M}$ ) in DMSO/HEPES (v/v, 8:2) was excited at 360 nm, and increasing concentrations of  $\text{Al}^{3+}$  solution was added. As shown in Figure 5, a gradual increase in the emission intensity at 486 nm was observed with increasing  $\text{Al}^{3+}$  concentrations. This enhancement in emission intensity reached a plateau after the addition of approximately 20 equivalents of  $\text{Al}^{3+}$ , indicating no significant further change beyond this point.

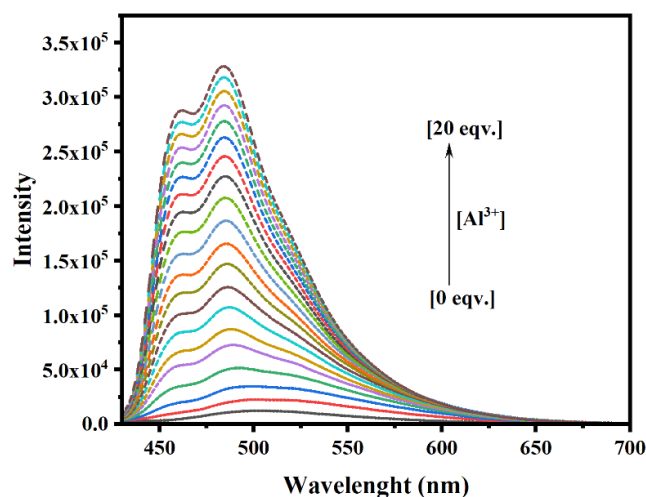


Figure 5. FL response of **HQ-BH** with increasing amount of  $\text{Al}^{3+}$  (0–20 eqv) ( $\lambda_{\text{ex}}$ : 360 nm,  $\lambda_{\text{em}}$ : 486 nm; Ex-Slit: 1, Em-Slit: 1).

To investigate the complexation between the HQ-BH receptor and  $\text{Al}^{3+}$  ions, the Job Plot method was employed. The resulting Job Plot graph is presented in Figure 6. Upon examination of the graph, it is clearly observed that the maximum point occurs at a molar fraction of 0.5. This indicates that the complexation between HQ-BH and  $\text{Al}^{3+}$  follows a 1:1 stoichiometry (Figure 6). In other words, one molecule of HQ-BH forms a complex with one  $\text{Al}^{3+}$  ion.

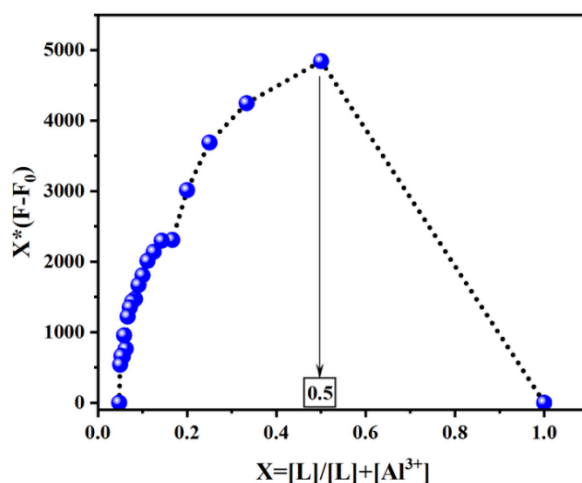


Figure 6. Job's plot showing the 1:1 stoichiometry

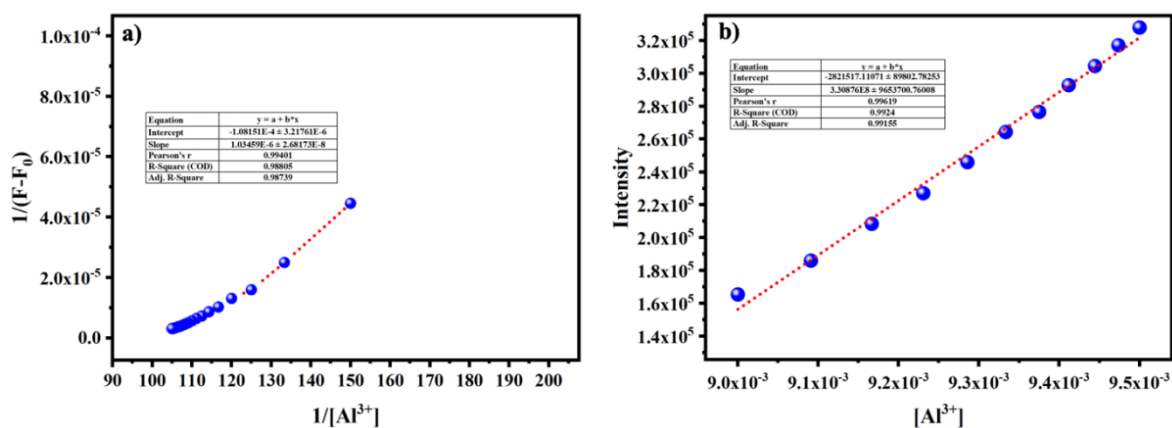


Figure 7. a) Benesi–Hildebrand plot assuming 1:1 stoichiometry from fluorometric titration data of receptor HQ-BH (10  $\mu\text{M}$ ) with  $\text{Al}^{3+}$  b) The plot of emission intensity of **HQ-BH** at 486 nm versus  $\text{Al}^{3+}$  cation concentration

The binding constant ( $\log K_a$ ) for the HQ-BH- $\text{Al}^{3+}$  complex was determined to be 7.5 using the Benesi–Hildebrand equation and fluorescence titration studies (Figure 7a). Additionally, a calibration plot of fluorescence intensity vs  $\text{Al}^{3+}$  concentration was created using fluorescence titration data obtained at 486 nm (Figure 7b). The limit of detection (LOD) for  $\text{Al}^{3+}$  ions using the **HQ-BH** probe was found to be 0.408  $\mu\text{M}$  based on the slope of this curve.

## Conclusion

In this study, a novel fluorogenic chemosensor based on 5-chloro-8-hydroxyquinoline (**HQ-BH**) was successfully synthesized for the selective detection of  $\text{Al}^{3+}$  ions. The observed enhancement in fluorescence intensity upon the addition of  $\text{Al}^{3+}$  indicates a strong coordination interaction between **HQ-BH** and  $\text{Al}^{3+}$ , confirming the high affinity of the sensor towards the target ion. These findings demonstrate that **HQ-BH** is a promising candidate for the sensitive and straightforward detection of  $\text{Al}^{3+}$  in solution. Furthermore, the structural and photophysical features of **HQ-BH** may provide a valuable framework for the future development of a broad range of fluorogenic probes targeting aluminium ions.

## Scientific Ethics Declaration

\*The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

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## Conflict of Interest

\*The authors declare that they have no conflicts of interest

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\*This work is part of Maghan I CAMARA's Master thesis.

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