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# 8-Hydroxyquinoline-5-carbaldehyde Schiff-base as a highly selective and sensitive Al<sup>3+</sup> sensor in weak acid aqueous medium

Xin-hui Jiang <sup>a</sup>, Bao-dui Wang <sup>a</sup>, Zheng-yin Yang <sup>a,\*</sup>, Yong-chun Liu <sup>b</sup>, Tian-rong Li <sup>a</sup>, Zeng-chen Liu <sup>a</sup>

<sup>a</sup> College of Chemistry and Chemical Engineering, Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, Lanzhou University, Lanzhou 730000, PR China <sup>b</sup> College of Chemistry and Chemical Engineering, Key Laboratory of Longdong Biological Resources in Gansu Province, Longdong University, Qingyang 745000, PR China

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## ABSTRACT

In the paper, a novel fluorescent sensor (1) based on 8-hydroxyquinoline carbaldehyde Schiff-base was synthesized and characterized. This fluorescent sensor exhibited high selectivity for  $Al^{3+}$  over other metal ions with the detection limit reaching below  $10^{-7}$  M under weak acid aqueous conditions. These suggested that 1 could be served as a highly selective and sensitive fluorescence sensor for aluminum ion in acid medium. © 2011 Elsevier B.V. All rights reserved.

Aluminum is the third most prevalent element and the most abundant metal in the earth's crust. But mounting evidences suggest that aluminum has severe toxicity in the central nervous system, which can cause idiopathic Parkinson's disease, impairment of memory and Alzheimer's Disease [1–3]. In addition, the toxicity endangers freshwater fish species and influences agricultural production in acidic soils (pH  $\leq$  5.5) [4,5]. In acid condition, solubility of aluminum minerals raises the amount of available Al<sup>3+</sup>, and it was found to be more toxic in weak acid aqueous environment [6]. Toxicity of aluminum is often highly concerned due to its wide distribution in acid environment. Consequently, it is a challenging work to design and synthesize a highly selective and sensitive chemosensor for Al<sup>3+</sup> in acid aqueous medium.

Recently, fluorescent sensors for various metal ions have attracted much interest because of the advantages such as high sensitivity, selectivity, rapid response time and versatility [7]. Up to now, several fluorescent sensors for  $AI^{3+}$  have been designed [8], but most of them were operated in organic solvent, which limited their applications. Furthermore, very few fluorescent chemosensors for  $AI^{3+}$  in acid aqueous medium have been found in literature [8]]. 8-Hydroxyquinoline (HQ) as a desirable fluorophore and binding moiety was employed widely in designing chemsensors for detection transition metal ions [9]. But few  $AI^{3+}$  fluorescence sensors derived from HQ were synthesized up to now [8c].

Herein, a novel fluorescent Al<sup>3+</sup> chemosensor, 4-(8'-hydroxyquinolin-5'-yl)methyleneimino-1-phenyl-2,3-dimethyl-5-pyzole (1), was synthesized by Schiff-base condensation of 8-hydroxyquinoline-5carbaldehyde (HQ5A) and 4-aminoantipryrine as shown in Scheme 1. HQ5A was obtained conveniently from HQ by the Reimer–Tiemann Reaction [10]. The single crystal of **1** was obtained by evaporated method in ethanol (Fig. 1). The receptor could be dissolved in water when 10% (v/v) of methanol was added. To obtain a selective Al<sup>3+</sup> chemsensor operated under acid aqueous solution, the value of pH was adjusted to 4.5 by acetate buffer and all the following studies were carried out in aqueous solution containing 10% methanol (acetate buffer, pH 4.5) at room temperature.

The binding properties of **1** with  $Al^{3+}$  were measured by UV-vis titration study in the first place in the acid aqueous solution (Fig. 2). Upon addition of  $Al^{3+}$ , the absorbance bands at 251 nm, 283 nm and 362 nm enhanced and at 225 nm and 325 nm decreased in the UV-vis spectra. These findings are characteristic of the HQ derivatives when a complexation process is accompanied by the deprotonation of the hydroxyl group [11]. Moreover, there are clear six isosbestic points at 242, 258, 271,298, 334 and 411 nm, which clearly indicated the presence of a single complex in equilibrium with the free receptor [12]. Such spectral changes of **1** in the presence of 0-2 equiv of  $Al^{3+}$  were ascribed to a 1:2 complex formation.

The fluorescence intensity changes of **1** in the presence of  $Al^{3+}$  was investigated in the acid aqueous medium. The lone pair electrons from the Schiff-base and quinoline nitrogen atoms contributed to the photoinduced electron-transfer (PET) phenomenon, which quenched fluorescence emission of **1**. Then the quenched fluorescence could increase dramatically upon chelating metal ion by occurring highly efficient chelation-enhanced fluorescence (CHEF) effect [13]. As shown in Fig. 3, the free **1** (10 µM,  $\lambda_{ex}$  = 378 nm) emitted weak fluorescence at 480 nm. Upon titration of 2 equiv of Al<sup>3+</sup>, as much as 30-fold fluorescence enhancement was detected. This demonstrated

<sup>\*</sup> Corresponding author.

E-mail address: yangzy@lzu.edu.cn (Z. Yang).

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Scheme 1. Synthesis of fluorescence sensor 1.

that the 8-hydroxyquinoline-5-carbaldehyde Schiff-base, which could be used as off-on type chemsensor, had potential application in sensing  $Al^{3+}$ . And the stoichiometry of  $1-Al^{3+}$  complex was determined by changes in the fluorogenic response in the presence of varying  $Al^{3+}$  concentrations, and the results indicated the formation of a 1:2 complex (Fig. 3(b)).

The selectivities of 1 to various metal ions were examined in acid aqueous. As shown in Fig. 4, upon addition of 2 equiv Al<sup>3+</sup>, Ag<sup>+</sup>, Ca<sup>2+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Cr<sup>3+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Hg<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup>, Na<sup>+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup>, sensor **1** (10  $\mu$ M,  $\lambda_{ex}$ =378 nm) showed large fluorescence enhancement with Al<sup>3+</sup>. And the other metal cations could not enhance the fluorescence intensity efficiently. The large difference of the fluorescence spectra of **1** in the presence of different metal ions might be explained as follows. On the one hand, transition metal ions (except  $Zn^{2+}$  and  $Cd^{2+}$ ) often guenched fluorescence via energy or electron transfer [14] or the heavy atom effect [15]. On the other hand, Zn<sup>2+</sup> and Cd<sup>2+</sup> could increase fluorescence intensity of some 8-hydroxylquinoline derivatives in organic or weak base aqueous medium have been reported in many paper, but the enhanced fluorescence was quenched significantly in acid aqueous [16]. In this paper, weak fluorescence enhancements of the sensor induced by Zn<sup>2+</sup> and Cd<sup>2+</sup> were also observed in acid aqueous environment. The HQ derivative chelating aluminum ions with high affinity displayed strong CHEF effect. Therefore, large fluorescence enhancement was observed.

To validate the high selectivity of **1** in practice, the systems of other metal ions and  $Al^{3+}$  coexisted were examined in 10% (v/v) methanol aqueous medium (acetate buffer, pH 4.5). As shown in Fig. 5, the

![](_page_1_Figure_6.jpeg)

Fig. 1. X-ray single crystal structure of sensor 1.

![](_page_1_Figure_8.jpeg)

**Fig. 2.** UV–vis spectra of **1** (10  $\mu$ M) with addition of increasing amount of Al<sup>3+</sup> (0, 2.5, 5, 7.5, 10, 12.5, 15, 17.5 and 20  $\mu$ M) in 10% (v/v) methanol aqueous medium (acetate buffer, pH 4.5). Inset: the absorption of **1** at 361 nm as a function of Al<sup>3+</sup> concentration in 10% (v/v) methanol aqueous medium (acetate buffer, pH 4.5).

fluorescence intensity of **1** only slightly changes in the presence of 2 equiv other metal ions, respectively. Then 2 equiv  $Al^{3+}$  was added to the above solutions, the fluorescence intensities were instantly and remarkably enhanced. Despite  $Fe^{3+}$  and  $Cu^{2+}$  could quench fluorescence of the ligand via energy or electron transfer [14], the quenched fluorescence emissions could be enhanced 8.6-fold and 11.5-fold upon addition 2 equiv of  $Al^{3+}$ , respectively. Therefore, **1** showed a high selective chemosensor for  $Al^{3+}$  in the presence of these coexistent metal ions in acid aqueous medium.

The detection limit of **1** in recognizing  $Al^{3+}$  was also evaluated using fluorescence spectra (Fig. S1). Upon addition of 0.5  $\mu$ M  $Al^{3+}$  to the sensor **1** (1  $\mu$ M, with an excitation of 378 nm), 3.2-fold emission enhancement demonstrated that the chemsensor could detect  $Al^{3+}$  at  $10^{-7}$  M level. So **1** illustrated highly sensitive for  $Al^{3+}$  under the weak acid aqueous medium.

![](_page_1_Figure_12.jpeg)

**Fig. 3.** Fluorescence spectra of **1** (10 µM) with addition of increasing amount of Al<sup>3+</sup> (0, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, and 22 µM) in 10% (v/v) methanol aqueous medium (acetate buffer, pH 4.5), ( $\lambda_{ex}$ =378 nm,  $\lambda_{em}$ =470 nm, slit: 3 nm/3 nm). Inset: (a), Fluorescence emission intensity of **1** at 488 nm as a function of Al<sup>3+</sup> concentration. (b), Fluorescence changes of **1** (10 µM) upon addition of Al<sup>3+</sup> (20 µM) in acid aqueous solution containing 10% methanol (acetate buffer, pH 4.5).

![](_page_2_Figure_2.jpeg)

Fig. 4. Fluorescence spectra of 1 (10  $\mu$ M,  $\lambda_{ex}\!=\!378$  nm) with addition of various general metal ions (2 equiv, respectively) in 10% (v/v) methanol aqueous medium (acetate buffer, pH 4.5).

![](_page_2_Figure_4.jpeg)

**Fig. 5.** Fluorescence responses of **1** (10  $\mu$ M,  $\lambda_{ex} = 378$  nm) to various metal ions (20  $\mu$ M) in methanol/water (1:9, v/v, acetate buffer, pH 4.5). Light gray bars represent the addition of metal ions to a 10  $\mu$ M solution of **1**, respectively. Black bars represent emission intensity of a mixture of **1** (10  $\mu$ M) with other metal ions (20  $\mu$ M) followed by addition of 20  $\mu$ M Al<sup>3+</sup> to the solutions, respectively.

To check the pH effecting on the fluoresence response, the fluorescence spectra of **1** with  $Al^{3+}$  under different pH conditions were examined. It was found that the fluorescence intensity of **1**- $Al^{3+}$  could almost remain constant under weak acid system (Fig. S2). From the data

of Fig. S2, the pH dependence of fluorescence intensities has been analyzed, and it was plotted according to the following equations:

$$pK_{a} = pH - \log \frac{F_{max} - F}{F - F_{min}}$$

where  $F_{max}$ ,  $F_{min}$  and F are the maximum, the minimum and the measured fluorescence intensities at 370 nm, respectively. The average pKa value calculated of **1** is 6.8.

At last, determination of binding constant and stoichiometry was determined from the fluorescence titration spectra of **1** with  $AI^{3+}$  in the acid solution. As shown in Fig. S3, the total binding constant B (log  $\beta$ ) is deduced to be 8.012 and the fluorescence response fits to a Hill coefficient of 2 (2.0171). The formation of a 1:2 stoichiometry complex is illustrated [17]. Then the stoichiometry of the complex was also determined by the Job's method from the fluorescence intensity (Fig. S4), indicating a 1:2 stoichiometry complex that was formed in the presence of 2 equiv  $AI^{3+}$ . The result was consistent with data from UV-vis and fluorescence spectra titration experiments for **1**- $AI^{3+}$  complex in solutions. The calculation formula of total binding constant and Hill coefficient was given as follows,

$$\log \frac{F - F_{\min}}{F_{\max} - F} = n \log[M] + B$$

where  $F_{max}$ ,  $F_{min}$  and F are the same as that in above equation, respectively.

According to the above discussion, the coordination formation of the complex 1-Al<sup>3+</sup> and the mechanism of electron or energy transfer for the sensor 1 in sensing Al<sup>3+</sup> were put forward in this paper, as shown in Scheme 2. Upon binding with Al<sup>3+</sup>, the PET phenomenon of Schiff-base and quinoline nitrogen atoms was inhibited efficiently, so the fluorescence intensity was increased dramatically.

In conclusion, a highly selective and sensitive fluorescence sensor for  $Al^{3+}$  was synthesized. And the Schiff-base receptor exhibited high selectivity for  $Al^{3+}$  over other metal ions with 30-fold fluorescence enhancement and high sensitivity with the detection limit reaching at  $10^{-7}$  M level under weak acid aqueous conditions (acetate buffer, pH 4.5). These suggested that **1** could be served as an excellent chemsensor for highly toxical aluminum ion in weak acid aqueous medium.

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### Appendix A. Supplementary data

Synthetic procedure, spectroscopic data and figures (SEI3); crystallographic data of **1** (SEI2) and Check CIF data report (SEI1).

![](_page_2_Figure_19.jpeg)

Scheme 2. The possible coordination formation of the complex 1-Al<sup>3+</sup> and the mechanism of significant fluorescence enhancement for the sensor 1 chelating with Al<sup>3+</sup>.

Supplementary materials related to this article can be found online at doi:10.1016/j.inoche.2011.04.027.

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