

# Development of a simple pyrazine-derived “turn on” Al<sup>3+</sup> fluorescent sensor with high selectivity and sensitivity



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## ABSTRACT

In this article, a novel pyrazine-derived hydrazone Schiff-base ligand bearing the quinoline unit (**1**) has been designed, synthesized and evaluated as a “turn on” fluorescent chemosensor for Al<sup>3+</sup> based on the photoinduced electron-transfer (PET) mechanism and the chelation-enhanced fluorescence (CHEF) phenomenon. The sensor **1** showed remarkably enhanced fluorescence intensity at 488 nm in the presence of Al<sup>3+</sup> ion and it also showed high selectivity and sensitivity towards Al<sup>3+</sup> ion over a wide range of metal ions in ethanol, for the detection limit of **1** for Al<sup>3+</sup> could reach at 10<sup>-7</sup> mol/L.

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## 1. Introduction

The development of methods for the detection and recognition of biologically related metallic ions has attracted much interest due to their importance in the human body [1,2]. In recent years, many techniques, such as atomic absorption spectrometry (AAS) [3], atomic emission spectrometry (AES) [4], and electron paramagnetic resonance (EPR) [5], have been developed to detect metal ions. However, these techniques suffer from complicated operational sequence, sophisticated synthetic procedure and expensive operational cost in medicinal and environmental research [6]. Owing to the features of high sensitivity, facile operation, real time detection and instantaneous response, the fluorescence technique has received considerable attention in the field of detecting and recognizing metallic ions [7]. Consequently, fluorescent sensors have been recognized as powerful tools for monitoring biologically related metal ions [8–13].

The detection of Al<sup>3+</sup> is of great importance because Al<sup>3+</sup> is an essential metal ion in the biological and physical systems [14]. It is well known that aluminum is the most abundant metallic element in the earth's crust and has widespread applications in modern life [15,16]. However, Al<sup>3+</sup> can cause harm to human beings when it is exposed to high concentration levels [17]. Aluminum is regarded as a toxic element, because Al<sup>3+</sup> can cause damage to central nervous system and immune system in human bodies [18], affecting the absorb and use of other trace elements [19],

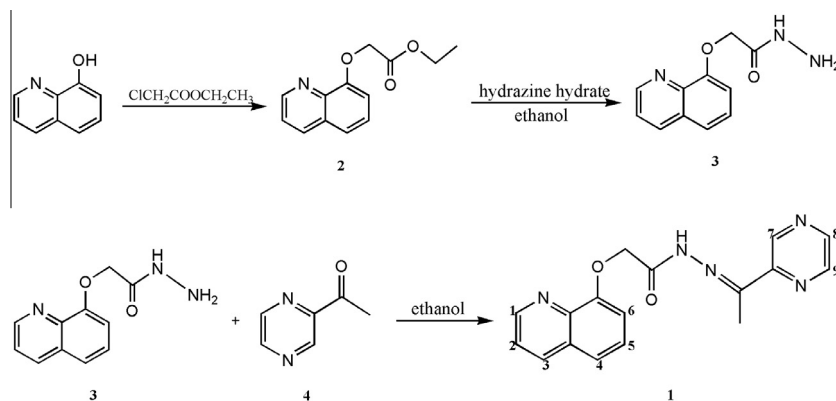
and induce many health problems, such as Alzheimer's disease and Parkinson's disease [20]. Nevertheless, there have been only a few reports about the development of fluorescent chemosensors for Al<sup>3+</sup> because of its poor coordination ability [21]. Therefore, it is a great demand to design and synthesize Al<sup>3+</sup> selective and sensitive fluorescent chemosensors [22–26].

For a sensor which is based on the photoinduced electron-transfer (PET) mechanism and the chelation-enhanced fluorescence (CHEF) phenomenon, it is evident that the PET from the amine group to the excited singlet state of fluorophore makes the fluorescence of the sensor quenched. However, when a suitable metal ion is added to the sensor solution, the inhibition of PET process will occur with the complexation of the sensor and this specific metal ion, which will cause a large chelation-enhanced fluorescence (CHEF) effect [27–30]. Thus, the enhancement of the fluorescence emission intensity of the sensor can be observed. However, some of the fluorescent sensors reported are lack of selectivity and sensitivity over other common biologically related metal ions, which restrains these sensors for practical application [31].

Herein, a novel pyrazine-derived hydrazone Schiff-base ligand called 2-Acetylpyrazine (8'-hydroxyquinolineyl-2'-acetyl) hydrazone (**1**) was designed and synthesized through a three-step reaction (Scheme 1). For this compound had so simple structure, it could be used as a fluorescent chemosensor to detect and recognize Al<sup>3+</sup> ion. From the experimental process, we can observe that the ethanol solution of **1** was nearly nonfluorescent. However, when Al<sup>3+</sup> was added to the solution of **1**, the fluorescence emission intensity at 488 nm would enhance remarkably. Furthermore, this fluorescent sensor **1** had high selectivity and

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Scheme 1. The synthetic route of compound 1.

sensitivity over a wide range of other common biologically related metallic ions tested, and could respond  $\text{Al}^{3+}$  in a reversible manner, which developed **1** for practical application.

## 2. Experimental

### 2.1. Materials

8-Hydroxyquinoline, ethyl chloroacetate, hydrazine hydrate, acetyl pyrazine, absolute ethanol and salts of  $\text{Al}^{3+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  were obtained from commercial suppliers and used without further purification.

### 2.2. Methods

Distilled water was used throughout all experiments.  $^1\text{H}$  NMR spectra were measured on the JNM-ECS 400 MHz instruments using TMS as an internal standard in  $\text{CDCl}_3$ . The ESI-MS data were obtained in ethanol from a Bruker Esquire 6000 spectrometer. FT-IR spectra were recorded with a VERTEX-70 spectrometer. Elemental analyses were performed using a VarioEL Cube V1.2.1 analyzer. UV-Vis absorption spectra were recorded on a Perkin Elmer Lambda 35 UV-Vis spectrophotometer in ethanol medium at 298 K. Fluorescence spectra were generated on a Hitachi RF-4500 spectrophotometer equipped with quartz cuvettes of 1 cm path length. Melting points were determined on a Beijing X-4 microscopic melting point apparatus.

### 2.3. Synthesize

#### 2.3.1. Synthesize of compound 1 (2-(quinolin-8-yloxy)-N-(2-acetylpyrazin-5-yl)acetohydrazide)

Ethyl 2-(quinolin-8-yloxy)acetate (**2**) and 2-(quinolin-8-yloxy)acetohydrazide (**3**) were prepared by the reported method [32]. A solution of the 2-(quinolin-8-yloxy)acetohydrazide (0.199 g, 0.968 mmol) in ethanol was added to a solution containing acetylpyrazine (0.118 g, 0.968 mmol) in ethanol. The mixture was refluxed for 26 h, and the obtained light yellow solution was then cooled to room temperature. Then the light yellow product was filtered, washing three times with distilled water and absolute ethanol, respectively. Finally, the solid was dried under drying oven overnight to give the desired product **1** as a white powder (0.24 g, 77.24%) (Scheme 1). m.p. 213–215 °C,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) (Fig. S1): 11.26 (s, 1H, -NH-), 9.49 (d, 1H,  $J = 1.6$  Hz,  $\text{H}_1$ ), 8.94 (dd, 1H,  $J = 4.0$  Hz, 1.6 Hz,  $\text{H}_3$ ), 8.55–8.50 (m, 2H,  $\text{H}_2$ ,  $\text{H}_4$ ), 8.28 (d, 1H,  $J = 8.0$  Hz,  $\text{H}_5$ ), 7.59–7.51 (m, 3H,  $\text{H}_7$ ,  $\text{H}_8$ ,  $\text{H}_9$ ), 7.29 (dd, 1H,

$J = 7.2$  Hz, 1.6 Hz,  $\text{H}_6$ ), 5.03 (s, 2H,  $-\text{CH}_2-$ ), 2.63 (s, 3H,  $-\text{CH}_3$ ). MS (ESI) (Fig. S2):  $m/z$  322.1219 [ $\text{M}+\text{H}^+$ ] $^+$ , 344.1037 [ $\text{M}+\text{Na}^+$ ] $^+$ , 665.2140 [ $2\text{M}+\text{H}^+$ ] $^+$ . FT-IR (KBr pellet,  $\text{cm}^{-1}$ ) (Fig. S3): 3441 (N-H), 1695 (C=O), 1622 (C=N), 1275 (C-O), 1119 (C-N). UV-Vis (nm) (Fig. 1): 295, 350. Anal. Calcd. for  $\text{C}_{17}\text{H}_{15}\text{N}_5\text{O}_2$  (%): C, 63.54; H, 4.71; N, 21.79; O, 9.96. Found: C, 63.04; H, 4.57; N, 21.40; O, 10.99.

### 2.4. Analysis

Stock solutions (10 mM) of the salts of  $\text{Al}^{3+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  in ethanol were prepared. Stock solution of the compound **1** (10 mM) in dimethyl sulfoxide (DMSO) was also prepared. Test solutions were prepared by placing 10  $\mu\text{L}$  of the probe stock solution into cuvettes, adding an appropriate aliquot of each metal ion stock, and diluting the solution to 2 mL with ethanol. For all measurements, excitation wavelength was at 350 nm; the excitation slit width was 5.0 nm, and the emission slit width was 3.0 nm.

The binding constant values were determined from the emission intensity data following the modified Benesi-Hildebrand Eq. (1) [33]:

$$\frac{1}{F - F_{\min}} = \frac{1}{K(F_{\max} - F_{\min})[\text{AL}^{3+}]} + \frac{1}{F_{\max} - F_{\min}} \quad (1)$$

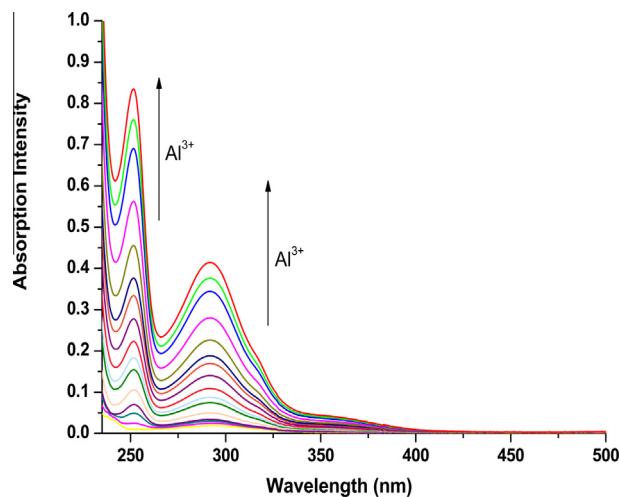


Fig. 1. UV-Vis absorption of compound **1** (100  $\mu\text{M}$ ) measured in ethanol upon addition of various concentration of  $\text{Al}^{3+}$  (0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.4, 2.8, 3.2, 3.6, 4.0 equiv., respectively).

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