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# Bis-Schiff base as a donor-acceptor fluorescent probe : Recognition of Al<sup>3+</sup> ions in near 100% aqueous solution

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Graphical abstract

Upon addition of  $Al^{3+}$ , compared with the free receptor, the fluorescence intensity of HL shows significant fluorescence enhancement accompany with about 40 nm blue shift in the presence of  $Al^{3+}$ , the reasons for this phenomenon are attributed to forms 1:1 complex which inhibit internal charge transfer process.

### Highlights

- A novel bis-Schiff base fluorescent probe for Al<sup>3+</sup> has been designed and synthesized
- The probe for Al<sup>3+</sup> shows significant fluorescence enhancement accompany with about 40 nm blue shift on the basis of the mechanism of ICT.
- The detection limit for  $Al^{3+}$  reached at  $10^{-7}$  M level in 100% aqueous solution.

#### Abstract

In this paper, a novel bis-Schiff base fluorescent probe (HL) for  $Al^{3+}$  has been designed and synthesized on the basis of the mechanism of internal charge transfer (ICT). Compared with the free receptor, the fluorescence intensity of HL shows significant fluorescence enhancement accompany with about 40 nm blue shift in the presence of  $Al^{3+}$ . More importantly, the lowest detection limit for  $Al^{3+}$  can reach at  $10^{-7}$  M level in near 100% aqueous solution.

Keywords: Bis-Schiff base; Fluorescent probe; Al<sup>3+</sup>; Internal charge transfer

### 1. Introduction

The development of fluorescent chemosensors with high selectivity, sensitivity and realtime detection for metal ions such as aluminum ion remains an important endeavor in chemistry due to their significant importance roles in environmental research and analytical fields [1-6]. Aluminum is the third most abundant of all elements (after oxygen and silicon) and is the most widely existing metal ion in the environment because of acidic rain and human activities [7-8]. Nevertheless, aluminum has severe toxicity and is a non-essential element for biological systems, high concentration of aluminum ion not only hampers plant growth but also has been implicated in various neurodegenerative and neurological disorders, such as Alzheimer's disease, dialysis encephalopathy, and problems in bone, muscles etc [9-14]. Additionally, According to a WHO report, the average daily human intake of aluminum is around 3–10 mg. Tolerable weekly aluminum dietary intake in the human body is estimated to be 7mg / kg body weight [15-16]. In order to protect the environment and human

health, it is crucial to develop an effective fluorescent probe for detection of the concentration levels of aluminum in the environment [17-20].

Compared with other metal ions, the development of fluorescent probe for  $Al^{3^+}$  has always been problematic because of its poor coordination ability, strong hydration ability and the lack of spectroscopic characteristics [21-23]. Even if there are some of reported  $Al^{3^+}$ sensors, the majority of them worked well only in organic or a mixture of organic solvent and water which are difficult to detect the submicromolar concentration of the  $Al^{3^+}$  in environment [24-29]. The design and synthesis of fluorescent sensors in water or in near 100% aqueous solution is still a challenge [30].

2, 6-diformyl-4-substituent phenol with strong binding ability and excellent optical properties has attracted considerable attention [31-33]. A growing number of fluorescent probes have been designed and synthesized based on its bis-Schiff base [34-36]. The structure of bis-Schiff base contains nitrogen–oxygen-rich coordination environments which provide enough binding sites for metal ions. However, most of the sensors are synthesized by 2, 6-diformyl-4-methyl phenol, which was performed in non-aqueous solvents, and that the sensing mechanisms are attributed to a single and simple photo-induced electron transfer (PET) process [37-39]. So, it is not only limited in range of application but also their sensitivity and the built-in correction was apt to be affected by environmental condition.

Out of consideration of these circumstances, we response to these problems through a possible strategy that if the methyl group is displaced by the ester group at the 4-position of benzene ring, the bis-Schiff base will probably provide a donor-acceptor system

which is a prerequisite for intramolecular charge transfer (ICT) process [40-42]. And, in short, herein, we have designed a bis-Schiff base which derives from Methyl 3, 5-diformyl-4-hydroxybenzoate and Nicotinohydrazide as shown Scheme 1. Upon binding of Al<sup>3+</sup>, the fluorescence intensity of HL exhibits a large fluorescence enhancement accompany with about 40 nm blue-shift in water. All of these are attributed to forms 1:1 complex effect on inhibition of intramolecular charge transfer (ICT) process.

### 2. Experimental

### 2.1. Apparatus and reagents

All chemicals were obtained from commercial suppliers and used without further purification. <sup>1</sup>H NMR spectra were measured on the JNM-ECS 400MHz instruments using TMS as an internal standard. Bruker esquire 6000 spectrometer, Perkin Elmer Lambda 35 UV-Vis spectrophotometer, Hitachi RF-5301 spectrophotometer equipped with quartz cuvettes of 1 cm path length, Beijing XT4-100x microscopic melting point apparatus. 2.2 Analysis

Stock solutions of various metal ions (5 mM) were prepared using nitrate salts in twodistilled water. A stock solution of HL (1 mM) was prepared in DMSO, the solution of HL was then diluted to 10  $\mu$ M in water. In titration experiments, each time a 2 mL solution of HL (10  $\mu$ M) was filled in quartz optical cell of 1 cm optical path length, and then the ions stock solution were added into the quartz optical cell. In selectivity experiments, the test samples were prepared by placing appropriate amounts of ions stock into 2 mL solution of HL (10

 $\mu$ M). For fluorescence measurements, the excitation slit width was 5 nm, the emission slit width was 3 nm.

2.3. Synthesis

2.3.1. Synthesis of Methyl 3, 5-diformyl- 4-hydroxybenzoate [43-44]

Methyl 4-hydroxybenzoate (2.5g, 16.25mmol) and Hexamethylenetetramine (9.39g, 66.91 mmol) were dissolved in trifluoroacetic acid (20 mL) and the yellow solution was heated at reflux for 4 d. Water (100 mL) was added to the viscous dark-orange solution and the mixture was heated up to give a homogeneous solution. After cooling, the product was precipitated slowly from solution. Yield: 65%, M.p.120-122°C.

2.3.2 Synthesis of HL

An ethanol solution of Nicotinohydrazide (0.27 g, 2 mmol) was added to a solution containing methyl 3, 5-diformyl 4-hydroxybenzoate (0.21g, 1mmol) in ethanol. The mixture was refluxed for 12 h. The solution was then cooled to room temperature, and the solvent was evaporated. The final product was recrystallized from ethanol and DMF. The yield of HL was 65%, M. p. 274–276°C. <sup>1</sup>H NMR (400 MHz; DMSO-d<sub>6</sub>), (Fig. S1):  $\delta$ =3.85 (s, 3H), 7.54~7.57 (m, 2H), 8.24~8.26 (m, 2H), 8.33 (s, 2H), 8.73 (s, 2H), 8.75 (s, 2H), 9.06 (s, 2H), 12.46 (s, 2H), 13.16 (s, H) ESI-MS (Fig. S2): [M+H]<sup>+</sup>: 447.05. (Calcd: 447.14).

### 3. Results and discussion

3.1 General information

The detection limit was evaluated based on the fluorescence titration. And then it was calculated with the following equation: detection limit  $3\sigma/K$ . where  $\sigma$  is the standard deviation of blank measurements, and K is the slope between intensity versus sample concentration [45].

The binding constant values were determined from the emission intensity data following the modified Benesi–Hildebrand equations [46].

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

Where  $F_{min}$ , F, and  $F_{max}$  are the emission intensities of the organic moiety considered in the absence of aluminum ion, at an intermediate aluminum concentration, and at a concentration of complete interaction, respectively, and where  $K_a$  is the binding constant concentration were also used for the characterization of novel compound.

### 3.2 UV-vis analysis

The interaction of HL and  $Al^{3^+}$  was initially evaluated by UV-visible analysis in near 100% aqueous solution. The changes in the spectra of HL as a function of the concentration of  $Al^{3^+}$  were shown in Fig. 1( $\varepsilon_{max}$ =3.9×10<sup>4</sup>). The absorption spectrum of the free receptor showed three absorption bands at 298 nm, 350nm and 422 nm. Upon addition of  $Al^{3^+}$  to a solution of HL, the former two bands significantly decreased while the third band gradually disappeared ( $\varepsilon_{max}$ =5.8×10<sup>3</sup>), more importantly, a new band appeared at 389 nm with increasing intensity and a clear isosbestic points at 360 nm was observed which clearly indicated the presence of new complex in equilibrium with the receptor. In addition, the third band of HL (at 422 nm) exhibited a blue shift compared to the new band in the spectrum of

[HL +Al] (at 389nm), perhaps the reasons for this phenomenon was that the aluminium ion bonding with the donor moiety (-C=N,-OH) changed the photophysical properties of ICT fluorophore (the acceptor-COOCH<sub>3</sub>) and further influences the efficiency of charge transfer [47-49]. Of course, all of these were further confirmed by ESI-MS, <sup>1</sup>HNMR titration. 3.3 Fluorescence response of HL to Al<sup>3+</sup>

The selectivity of HL was investigated upon addition of several metal ions such as Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Ba<sup>2+</sup>, Fe<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, Pb<sup>2+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup>, and  $Al^{3+}$  in near 100% aqueous solution. As shown in Fig. 2, the free sensor showed only a weak fluorescence emission at 506 nm, when it is excited at 389 nm (quantum yield = 5.13%). On addition of various metal ions to aqueous solution of HL, there is no remarkably change in its fluorescence spectrum except in the case of  $Zn^{2+}$ ,  $Al^{3+}$ . But the fluorescence enhancement which  $Zn^{2+}$  generates is significantly lower than with  $Al^{3+}$ . Thus, the fluorescence intensity of HL showed a large fluorescence enhancement along with a blue shift of 40 nm in the present of  $Al^{3+}$  (quantum yield =15.53%), which was enough to selectivity detection of Al<sup>3+</sup>. To understand the recognition abilities of HL toward Al<sup>3+</sup>, the fluorescence titration of HL toward  $Al^{3+}$  was further carried out. As shown in Fig. 3, upon the addition of increasing amount of Al<sup>3+</sup> into the solution of HL, the emission peak of HL at 460 nm was significantly enhanced. The spectral blue shift should be attributed to a donoracceptor system which is a prerequisite for ICT process. More specifically, before addition of  $Al^{3+}$ , the receptor displayed an emission band at 506 nm which arose from the ICT involved electron-donor group (-C=N, -OH) electron-withdrawing group (-COOCH<sub>3</sub>). Up addition of

 $Al^{3+}$ , the interaction of  $Al^{3+}$  and the electron-donor group of the receptor would be sufficient to reduce the electron density in electron-donor group, as a result, the efficiency of charge transfer be weaken from the donor to the acceptor and further occurred a blue shift as shown in Scheme 2.

To check the practical applicability of HL as a selective fluorescent sensor for  $Al^{3^+}$ , the systems of other metal ions and  $Al^{3^+}$  coexisted were examined in near 100% aqueous solution. As shown in Fig. 4, the receptor HL was treated with 1.0 equiv of  $Al^{3^+}$  in the presence of other metal ions. Relatively low interference was observed for the detection of  $Al^{3^+}$  in the presence of other metal ions except for  $Cu^{2^+}$ ,  $Fe^{3^+}$ ,  $Ni^{2^+}$ ,  $Co^{2^+}$ , which be attributed to their inherent to the magnetic property. However,  $Ni^{2^+}$ ,  $Co^{2^+}$ , somewhat inhibited the interaction between HL and  $Al^{3^+}$ , and  $Cu^{2^+}$  did so strongly. In addition, from fluorescence titration, the detection limit of HL for  $Al^{3^+}$  was found to be  $6.9 \times 10^{-7}$  M based on  $3\sigma/K$  ( $\sigma$ =2.76) which was is below the WHO acceptable limit (7.4 $\mu$ M) in drinking water [50-51] (Fig. S3). Therefore, it means that the receptor HL can be used as a selective fluorescent sensor for detection and recognition of  $Al^{3^+}$  in environmental analysis and analytical chemistry.

#### 3.3. Job plot measurements

In order to validate the stoichiometry of HL and  $Al^{3+}$ , we carried out Job's plot in near 100% aqueous solution.. The total concentration of HL and  $Al^{3+}$  was 50  $\mu$ M.  $X_{Al} = ([Al^{3+}]/([Al^{3+}] + [HL]))$ . As shown in Fig. 5, the maximum point appeared at a mole fraction of 0.5. The result has indicated that it was a 1:1 stoichiometry of the binding mode of HL and  $Al^{3+}$ 

which is further confirmed by the appearance of a peak at m/z 471.02 assignable to  $[HL+Al^{3+}-2H]^+$  and a peak at m/z 517.05 assignable to  $[HL+CH_3CH_2OH+Al^{3+}-2H]^+$  in the ESI/MS (Fig. S4). In addition, a main peak at m/z 447.06 was assigned to  $[HL+H]^+$ . More importantly, from titration profile, the binding constant of HL for Al<sup>3+</sup> have been estimated as  $1.67 \times 10^4$  (R<sup>2</sup>=0.991) (Fig.S5) based on the modified Benesi–Hildebrand equation.

### 3.4 <sup>1</sup>H NMR titration

In order to further validate the conjugation of HL and  $Al^{3+}$ , <sup>1</sup>HNMR titration was desperately needed besides the above experiments. Al<sup>3+</sup> (as its nitrate salt) was added to the DMSO-d<sub>6</sub> solution of HL (Fig. S6), significant spectral changes were observed as shown in Fig. 6. In the <sup>1</sup>H NMR of the neutral HL, the broad peaks at 12.46 ppm and 13.19 ppm should be corresponding to the labile protons of -C-NH and –OH, respectively. Upon addition of  $Al^{3+}$ , the proton peak of the phenolic hydroxyl at 13.19 ppm weaken significantly, this could be because addition of  $Al^{3+}$  to HL caused the loss of the –OH proton with subsequent binding to electron deficient  $Al^{3+}$ . The broad peak also became weak at 12.46 ppm while the new signal was observed at 12.26 ppm which be attributed to the binding mode of  $Al^{3+}$  and the oxygen of -CO-NH. the signal for the -CH=N proton at 8.73 ppm was shifted to low-field compared to that in the <sup>1</sup>HNMR spectrum of the parent ligand in the presence of Al<sup>3+</sup> Furthermore, the new signals for the aryl protons also appeared compared to those in the spectrum of the free receptor. Therefore, the large differences of the <sup>1</sup>H NMR spectra of HL in the absence and presence of  $Al^{3+}$ , couple with ESI-MS and Job's plot

analysis, suggested that HL could chelate Al<sup>3+</sup> through interactions with carboxylate oxygen, imine nitrogen and oxygen of phenolic hydroxyl group and forms 1:1 complex[52-53].

### 4. Conclusion

In summary, we have successfully designed a novel bis-Schiff base chemosensor based on a donor-acceptor system by introducing ester group. The receptor exhibited high selectivity for  $Al^{3+}$  over other metal ions in near 100% aqueous solution (Fig.S7). More importantly, because of lower detection limit in aqueous solution, the chemosensor may find potential applications to detect micromolar concentrations of  $Al^{3+}$  in both biological systems and the environment.

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Figure captions

Scheme1. Reagents and conditions: (a) HMTA, TFA, reflux, 4d; (b) EtOH, reflux, 10-12 h.
Scheme2. Proposed mechanism for detection of Al<sup>3+</sup> by HL.

**Fig.1.** Absorption spectra of HL (10.0  $\mu$ M) in near 100% aqueous solution. at room temperature as a function of added Al(NO<sub>3</sub>)<sub>3</sub> (0, 0.5, 1.0, 1.5, 2.0, 2.5, 3, 3.5, 4.0, 4.5, 5.0 equiv.).

**Fig.2**. Fluorescence spectra of HL (10  $\mu$ M) upon the addition of metal salts (5.0 equiv.) of Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Ba<sup>2+</sup>, Fe<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, Pb<sup>2+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup>, and Al<sup>3+</sup> in near 100% aqueous solution. Excitation wavelength was 389 nm.

**Fig.3.** Fluorescence spectra of HL (10  $\mu$ M) in near 100% aqueous solution. upon the addition of Al(NO<sub>3</sub>)<sub>3</sub> (0, 0.5, 1.0, 1.5, 2.0, 2.5, 3, 3.5, 4.0, 4.5, 5.0 equiv.) with an excitation of 389 nm. Inset: color of HL and HL+Al<sup>3+</sup> system under UV lamp.

**Fig.4.** Fluorescence intensity of HL and its complexation with  $Al^{3+}$  in the presence of various metal ions in near 100% aqueous solution. Black bar: HL (10.0  $\mu$ M) and HL with 1.0 equiv. of Li<sup>+</sup> Mg<sup>2+</sup>, Mn<sup>2+</sup>, Ca<sup>2+</sup>, Ni<sup>2+</sup>, K<sup>+</sup>, Co<sup>2+</sup>, Cr<sup>3+</sup>, Ba<sup>2+</sup>, Pb<sup>2+</sup>, Na<sup>+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Zn<sup>2+</sup>, stated. Red bar: 10.0  $\mu$ M of HL and 1.0 equiv. of Al<sup>3+</sup> with 1.0 equiv. of metal ions stated ( $\lambda_{ex}$ =389 nm,  $\lambda_{em}$ =460 nm).

**Fig.5.** Job's plot for determining the stoichiometry of HL and  $AI^{3+}$  in near 100% aqueous solution,  $(X_{AI}=[AI^{3+}]/([AI^{3+}] + [HL]))$ , the total concentration of HL and  $AI^{3+}$  was 50  $\mu$ M). **Fig.6.** <sup>1</sup>H NMR spectra of HL with  $AI(NO_3)_3$ ·9H<sub>2</sub>O in DMSO-d<sub>6</sub>: (I) HL; (II) HL and  $AI^{3+}$ Inset: the expansion of chemical shift at11~14ppm



Fig.1









Fig. 4



Fig. 5





Fig. 6



Scheme 1



Scheme 2