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# A fluorescent and colorimetric chemosensor for selective detection of aluminum in aqueous solution

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ABSTRACT

We have synthesized a new Schiff base **1**, which detects $Al^{3+}$ through fluorescence and naked eye in aqueous solution. The sensor **1** exhibited selective and sensitive recognition toward $Al^{3+}$ via significant fluorescence enhancement (31-fold). Moreover, it showed a significant color change from colorless to yellow. The complex formation was proposed to be 1:1 ratio, based on the Job plot, ESI-mass spectrometry analysis, $^1H$ NMR titration, and IR analysis. The detection limit was 1.00 μM, which is below the WHO acceptable limit (1.85 μM) in drinking water. In addition, the sensor **1** could be recyclable simply through treatment with a proper reagent such as EDTA.



The development of selective and sensitive chemosensors for the detection of metal ions has received considerable attention because of their important roles in medicine, living systems and the environment.[1,2] Among the various types of sensors, fluorescent chemosensors are widely used as powerful tools to spy on neutral and ionic species owing to their high sensitivity, selectivity, versatility, and relatively simple handling.[3–27] Moreover, chromogenic receptors are especially attractive because the recognition process is accomplished with an easy-to-detect perceptible color evolution.[28–44] Therefore, significant efforts have been carried out in the last years for developing the fluorescent and colorimetric chemosensors for metal ions.

Aluminum is the third most prevalent metallic element in the Earth. People are widely exposed to aluminum because of its widespread use in food additives, aluminum-based pharmaceuticals, and storage/cooking utensils. However, unregulated amounts of aluminum in the human body may lead to central nervous system malfunction, Parkinson's disease, and Alzheimer's disease.[45] The iron binding protein is the main carrier for $Al^{3+}$ in plasma and $Al^{3+}$ can enter the brain and reach the placenta and fetus. Aluminum concentrations in the brain should be maintained at <2 mg/g.[46] Moreover, the World Health Organization (WHO) recommends the average daily human intake of aluminum to be about 3–10 mg. Tolerable weekly aluminum dietary intake in the human body is estimated to be 7 mg/kg of the body weight.[2,47,48]

For these reasons, it is important to control the concentration of $Al^{3+}$ at a constant level, and therefore, much effort has been devoted to the design of various chemosensors specific for $Al^{3+}$ detection.[49–58] While several $Al^{3+}$ chemosensors have been reported to date, dual colorimetric and fluorescent chemosensors for $Al^{3+}$ were still rare and some of them were not efficient enough to be selective toward $Al^{3+}$ or sensed it in organic solvents.[59–66] Therefore, developing sensors which are able to detect $Al^{3+}$ by both fluorescence and naked eye in aqueous solution are very valuable.

Herein, we report a new fluorescent and colorimetric Schiff base chemosensor which exhibited selective and sensitive detection toward $Al^{3+}$ via significant fluorescence enhancement in aqueous solution, and, at the same time, showed a significant color change from colorless to yellow.

As shown in Scheme 1, receptor **1** was simply synthesized by the coupling reaction of ethanolamine and 8-hydroxyjulolidine-9-carboxaldehyde, and characterized by $^1H$ NMR and $^{13}C$ NMR spectroscopy, ESI-mass spectrometry, and elemental analysis.

The effect of common metal ions on the fluorescence spectra of **1** was studied in a mixture of DMF/HEPES buffer (v/v = 9:1, pH 7.4) (Fig. 1a). $Al^{3+}$ enhanced remarkably the emission intensity (31-fold) of **1** with the quantum yield of 0.17 upon excitation at 370 nm while the cations such as $Na^+$, $K^+$, $Mn^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Fe^{3+}$, $Cd^{2+}$, $Mg^{2+}$, $Ca^{2+}$, $Pb^{2+}$, $Cr^{3+}$, $Ga^{3+}$, and $In^{3+}$ did not show any significant effect except $Zn^{2+}$. $Zn^{2+}$ also enhanced somewhat the

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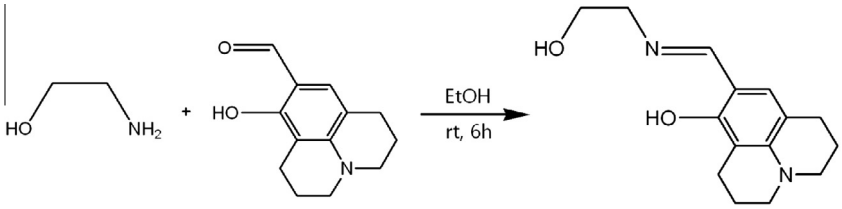


**Scheme 1.** Synthesis of receptor **1**.

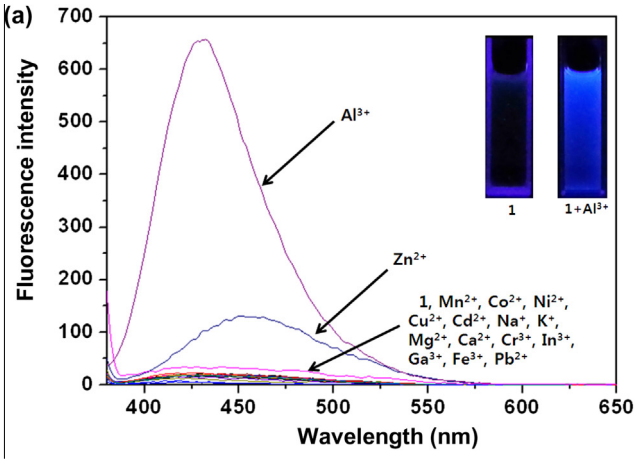


**Figure 1.** (a) Fluorescence spectra of **1** (10 μM) in the presence of various metal ions (220 μM) such as $Mn^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Na^{+}$, $K^{+}$, $Mg^{2+}$, $Ca^{2+}$, $Al^{3+}$, $Cr^{3+}$, $In^{3+}$, $Ga^{3+}$, and $Pb^{2+}$ in a mixture of DMF/HEPES buffer (10 mM, pH 7.4) (9:1). (b) Bar graph shows the relative emission intensity of **1** at 430 nm upon treatment with various metal ions.

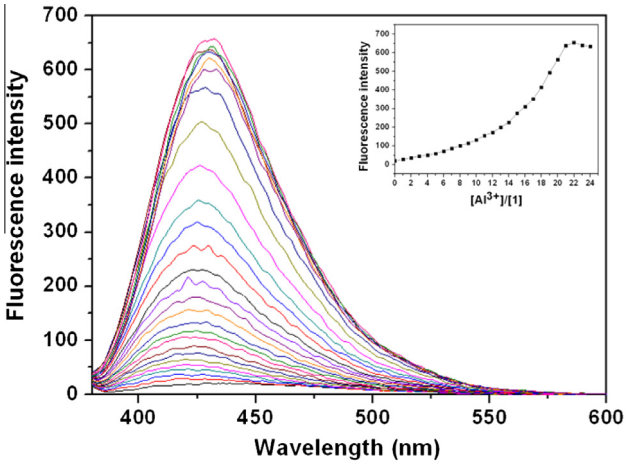


**Figure 2.** Fluorescence spectra of **1** (10 μM, $\lambda_{ex}$ = 370 nm) after addition of increasing amounts of $Al^{3+}$ ion (1–22 equiv) in a mixture of DMF/HEPES buffer (10 mM, pH 7.4) (9:1) at room temperature. Inset: intensity at 430 nm versus the number of equiv of $Al^{3+}$ added.

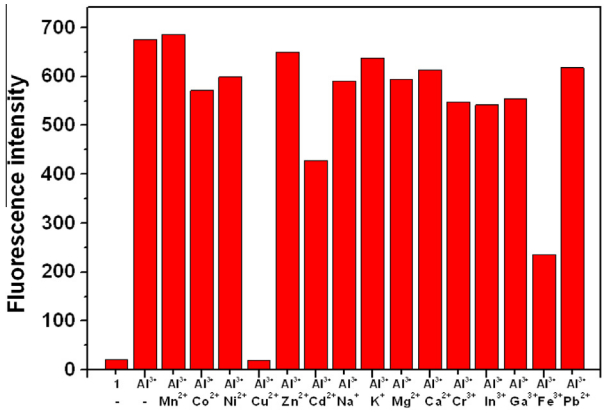


**Figure 3.** Competitive selectivity of **1** toward $Al^{3+}$ in the presence of other metal ions. Response of **1** was included as controls. **1** alone, **1** + $Al^{3+}$, **1** + $Al^{3+}$ + $Mn^{2+}$, **1** + $Al^{3+}$ + $Co^{2+}$, etc. (Left to right). Conditions: **1**, 10 μM; $Al^{3+}$, 22 equiv; other metal ions, 22 equiv ($\lambda_{ex}$ = 370 nm).

emission intensity, but it is not significantly enough to affect the detection of $Al^{3+}$ (Fig. 1b). The observed fluorescence enhancement may be attributed to the formation of a rigid complex after binding of **1** with $Al^{3+}$, causing the chelation-enhanced fluorescence effect and inhibiting the C=N isomerization.[67–69]

The fluorescence titration experiments were performed by gradually increasing aluminum ion concentration into a DMF/buffer solution of **1** (10 μM) (Fig. 2). The fluorescence intensity increased up to 22 equiv and then no change was observed. To examine the selectivity for $Al^{3+}$ in a complex background of potentially competing species, the fluorescence enhancement of **1** with $Al^{3+}$ was investigated in the presence of other metal ions (Fig. 3). A background of most competing metal ions did not interfere with the detection of $Al^{3+}$ by **1** in the mixture of DMF/HEPES buffer solution, except for $Fe^{3+}$ and $Cu^{2+}$, which, respectively, quenched about 65% and 97% of the fluorescence obtained with $Al^{3+}$ alone. Nevertheless, **1** still had a sufficient 'turn-on' ratio for the detection of $Al^{3+}$ in the presence of $Fe^{3+}$. These results indicate that **1** exhibits good selectivity for $Al^{3+}$ over competing relevant metal ions.

To further explore the utility of **1** as an ion-selective colorimetric chemosensor for $Al^{3+}$ ion, the absorption behaviors of **1** were investigated in DMF/buffer solution. Upon addition of $Al^{3+}$ into **1**, the absorption spectra were changed accompanied by a red shift of 46 nm from 351 to 397 nm (Fig. 4), demonstrating that the color of **1** changes from colorless to yellow. In the presence of other metal ions ($Na^{+}$, $K^{+}$, $Mn^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Mg^{2+}$, $Ca^{2+}$, $Pb^{2+}$, $Cr^{3+}$, $Ga^{3+}$, and $In^{3+}$), **1** showed either no change or a slight change in the absorption intensity relative to the free receptor **1**.