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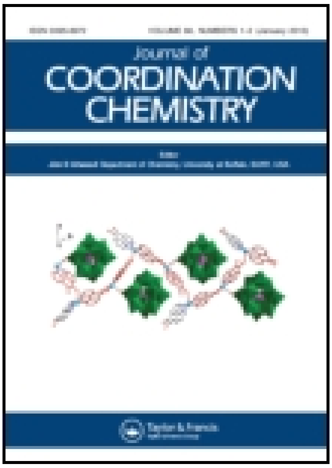

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Xiao-Ying Cheng[a], Ran Fang[a], Zheng-Yin Yang[a], Ming-Fang Wang[a], Qiao-Xia Zhou[a], Tian-Rong Li[a] & Yong Li[b]

[a] State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, PR China

[b] Faculty of Material Science and Chemistry, China University of Geosciences, Wuhan, PR China

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# Interaction of a Schiff-base fluorescent sensor with $Al^{3+}$: experimental and computational studies

XIAO-YING CHENG†, RAN FANG†, ZHENG-YIN YANG*†, MING-FANG WANG†, QIAO-XIA ZHOU†, TIAN-RONG LI† and YONG LI‡

†State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, PR China
‡Faculty of Material Science and Chemistry, China University of Geosciences, Wuhan, PR China

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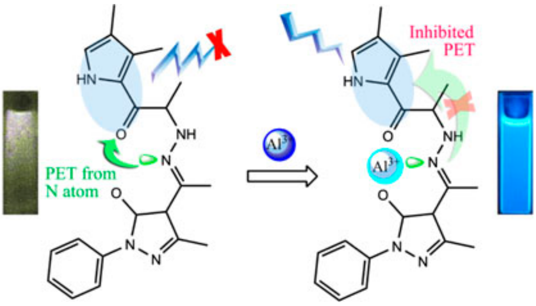

A fluorescent $Al^{3+}$ chemo-sensor, 1-phenyl-3-methyl-5-hydroxypyrazole-4-acetone-(3′,4′-dimethyl-pyrrole-2′-formyl) hydrazone (**L**), has been synthesized and characterized. **L** can detect $Al^{3+}$ in ethanol solution with a significant fluorescence enhancement of a turn-on ratio over 155-fold due to the formation of a 1 : 1 complex which is based on the molar ratio between **L** and $Al^{3+}$ ions, and the 1 : 1 stoichiometric complexation can be obtained from density functional theory calculations. No significant interference of other metal ions such as $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Co^{2+}$, $Cu^{2+}$, $Fe^{3+}$, $Cr^{3+}$, $Pb^{2+}$, and $Ag^+$ was found. The detection limit for $Al^{3+}$ was $5 \times 10^{-9}$ M in ethanol.

*Keywords*: Aluminum; Chemo-sensor; Schiff base; Density functional theory

## 1. Introduction

Aluminum is widely used in food additives, cookware, drinking water supplies, antiperspirants, deodorants, bleached flour, and antacids [1–3]. Exposure to aluminum can cause damage to the environment and human health; aluminum not only hampers plant growth but also damages the human nervous system. It has been reported that aluminum can induce Alzheimer's disease, Parkinson's disease, amyotrophic lateral sclerosis, etc. [4–10]. As high

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*Corresponding author. Email: yangzy@lzu.edu.cn levels of aluminum can cause such serious damage, detection of $Al^{3+}$ is crucial to control its concentration levels in the biosphere, which has a direct impact on human health and environmental safety.

Some conventional methods with high sensitivity for $Al^{3+}$ detection based on atomic absorption or emission spectroscopy have been developed [11–13], but they are generally expensive, complicated, and time consuming. Considerable attention has focused on fluorescent chemo-sensors because of their potential application in medicinal and environmental research. A number of experiments indicated that fluorescent probes for $Al^{3+}$ can solve the barriers [14–16]. However, among these chemo-sensors, there still exist problems, such as tedious synthetic routes of probes, high detection limit, etc. Therefore, design of selective and sensitive chemo-sensors for $Al^{3+}$ remains desirable.

Due to the presence of two electron donor nitrogens and two hydroxyl sites, hydrazones derived from 1-phenyl-3-methyl-4-acetyl-pyrazolone-5 (PMAP) are important for metal ion complexation, resulting in stable complexes [17]. Previous reports validated that structures of the most fluorescent sensors for $Al^{3+}$ contain nitrogen–oxygen-rich coordination environments providing a hard-base environment for the hard-acid $Al^{3+}$ [16]. 1-phenyl-3-methyl-5-hydroxypyrazole-4-acetone-(3′,4′-dimethylpyrrole-2′-formyl) hydrazone (**L**) is a sensitive and selective sensor for $Al^{3+}$ with the detection limit of $5 \times 10^{-9}$ M. The detection limit of most fluorescent sensors for $Al^{3+}$ is in the range of $1.0 \times 10^{-7}$–$1.0 \times 10^{-8}$ M [18–21], higher than that of the sensor we have synthesized. In addition, it is prepared through a simple synthetic route. Model calculations at the density functional theory (DFT) level further suggest the possible interaction mode of 1 : 1 stoichiometry, and the relative steric position between the host and guest influences the fluorescent response.

## 2. Experimental setup

### 2.1. *Materials and instrumentation*

Unless otherwise stated, all solvents and reagents were obtained from commercial suppliers and used without purification. Solutions of metal ions were prepared from the corresponding metal nitrate salts. Stock solutions of metal ions were prepared by dissolving the desired amount of material in ethanol. $^1$H NMR spectra were measured on a Bruker Avance Drx 300-MHz spectrometer with TMS as an internal standard. ESI-MS were determined on a Bruker Esquire 6000 spectrometer. UV–Vis absorption spectra were recorded on a Perkin Elmer Lambda 35 UV–Vis spectrophotometer. Fluorescence spectra were generated on a Hitachi RF-5301 spectrophotometer equipped with quartz cuvettes of 1 cm path length. The melting point of the Schiff base was determined on a Beijing XT4-100x microscopic melting point apparatus.

### 2.2. *Synthesis of L*

The synthetic route of **L** is shown in scheme 1. The Schiff base was synthesized by simple Schiff-base condensation of (PMAP) and 3,4-dimethyl-1H-pyrrole-2-carbohydrazide. PMAP was prepared according to the previous literature [22]. A solution of 3,4-dimethylpyrrole hydrazone (1.53 g, 0.01 M) in ethanol was added to a solution containing PMAP (2.17 g, 0.01 M) in ethanol. With refluxing at 80–85 °C for 12 h, beige precipitates were collected, and then washed twice with ethanol, m.p. 243–244 °C, yield: 89.4%. $^1$H NMR (300 MHz, DMSO-d$_6$) [figure S1, Supplemental data for this article can be accessed http://dx.doi.10.1080/00958972.2014.901506] 12.912 (s, 1H, H8), 11.408 (s, 1H, H9), 10.470 (s, 1H, H10), 8.279 (d, 2H, $J = 7.5$ Hz, H1, H5), 7.667 (m, 2H, $J = 7.2$ Hz,H2, H4), 7.401 (t, 1H, $J = 7.1$ Hz, H3), 7.070 (s, 1H, H11), 2.736 (s, 3H, H6), 2.639 (s, 3H, H7), 2.500 (s, 3H, H12), 2.234 (s, 3H, H13). ESI-MS *m/z* ([M + H]$^+$): Calcd 352.17; found: 352.3.

## 3. Results and discussion

### 3.1. *Spectral studies*

The spectrofluorimeter titration of **L** upon addition of Al$^{3+}$ is shown in figure 1. A 155-fold increase of fluorescence intensity of the [**L**-Al$^{3+}$] complex was observed and the quantum yield reached 0.3202. When the sensor was titrated with Al$^{3+}$, the fluorescence intensity increased up to 3 equivalents and then remained almost the same when additional Al$^{3+}$ was added. When compared to other Al$^{3+}$ fluorescent sensors which met their fluorescence peaks when the concentration of Al(III) was about 10 equivalents or more, **L** exhibited a very efficient fluorescence response [23–26]. The fluorescence band of **L** at 428 nm with low intensity is due to the quenching mechanism by the carbonyl group receptor through a photo-induced electron transfer (PET), and it is induced by lone pair electrons from the Schiff-base nitrogen (scheme 2) [27]. After addition of Al$^{3+}$, the fluorescence intensity increased significantly which can be attributed to the decrease of PET effect and the chelation-enhanced fluorescence (CHEF) effect [28, 29]. The sensor property is due to emission

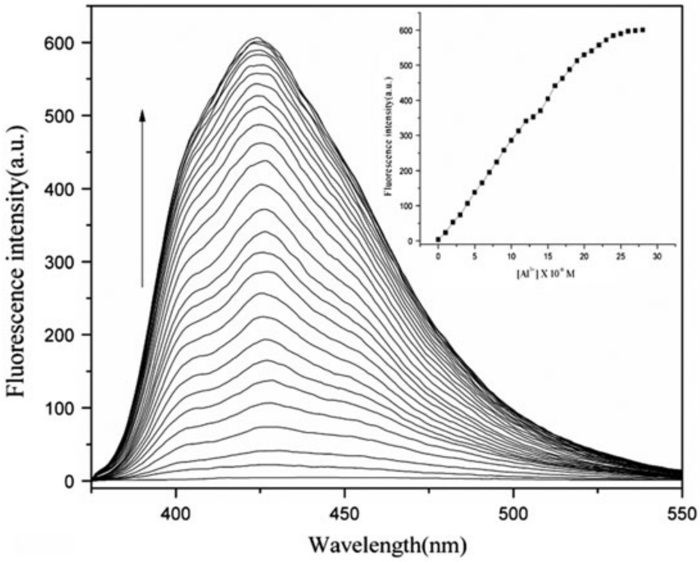


Figure 1. Changes of the fluorescence intensity of **L** (10 μM, $\lambda_{ex}$: 370 nm, $\lambda_{em}$: 428 nm, slit: 3 nm/3 nm) in ethanol with addition of increasing amounts of Al$^{3+}$. Inset: Graph of the fluorescence intensity at 428 nm as a function of Al$^{3+}$ concentration.

of the exciplex formed between excited acetylpyrrole and the lone pair electrons on N of the –C=N– group [30]. From the fluorescence titration data (figure 1), the binding constant ($\log K_a$) for **L**-$Al^{3+}$ in ethanol was 8.09 according to a reported method (figure S2) [31]. According to the method, the binding constant $K_a$ was obtained from the plot of linear regression of $\log[(F - F_{min})/(F_{max} - F)]$ *versus* $\log[M]$ in equation (1), where the intercept was $\log K_a$. In the equation, $F_{min}$, $F_{max}$, and $F$ are the fluorescence intensity in the absence of $Al^{3+}$, presence of saturated $Al^{3+}$, and the fluorescence intensity of the [**L**-$Al^{3+}$] complex at time intervals. [M] is the concentration of free metal ions which can be assumed equal to its total concentration [28].

$$\log \frac{F - F_{min}}{F_{max} - F} = \log K + n \log [M] \tag{1}$$

The addition of $Pb^{2+}$, $Ni^{2+}$, $Na^{+}$, $Mn^{2+}$, $Zn^{2+}$, $K^{+}$, $Fe^{3+}$, $Cu^{2+}$, $Cd^{2+}$, $Cr^{3+}$, $Co^{2+}$, $Ca^{2+}$, $Ba^{2+}$, $Ag^{+}$, $Ga^{3+}$, $In^{3+}$, and $Mg^{2+}$ caused little enhancement in the fluorescent intensity (figure 2). Only $Mg^{2+}$ can enhance the fluorescent intensity, yet the intensity was far less than that of $Al^{3+}$. Moreover, $Ga^{3+}$ and $In^{3+}$, which belong to the same group as $Al^{3+}$, cannot increase fluorescence intensity. The results indicate the high selectivity of **L** for $Al^{3+}$. Competition experiments of $Al^{3+}$ and other metal ions were also performed to investigate the binding affinity of **L** with metal ions (figure 2). Each metal ion (30 µM) was added separately into the stock solution of **L** (10 µM) and $Al^{3+}$ (30 µM), and the corresponding fluorescence spectra were obtained by exciting **L** at 370 nm. As a result, only $Fe^{3+}$ can decrease the fluorescence intensity slightly and few of the other ions had a distinct impact on the value of the $Al^{3+}$ complex. We conclude that the sensor can detect $Al^{3+}$ in ethanol solution without inference of other metal ions. Due to the low fluorescence of the **L**-$Mg^{2+}$ complex, the binding constant ($\log K_a$) for **L**-$Mg^{2+}$ in ethanol was 4.66 via the same method (figure S3), indicating its combination ability is much lower than that of **L**-$Al^{3+}$. The

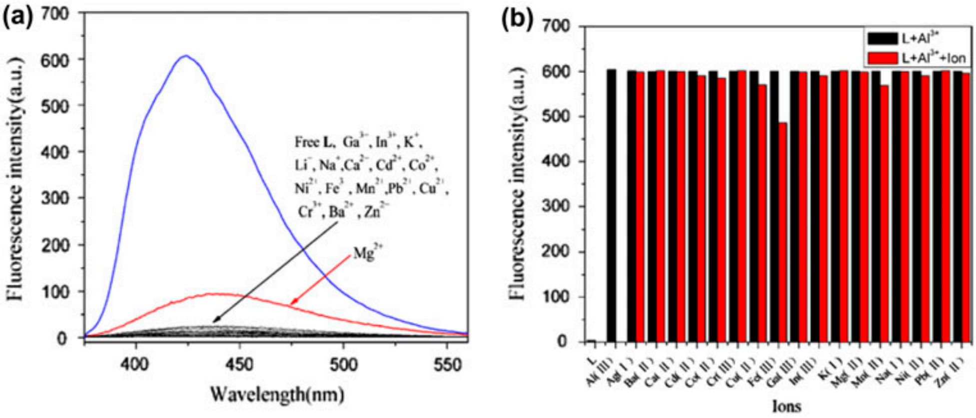


Figure 2. (a) Studies on the interference of common ions (30 µM) on the emission intensity of [**L**-$Al^{3+}$] complex ([**L**] = 10 µM and [$Al^{3+}$] = 30 µM). (b) Fluorescence responses of **L** (10 µM) to various metal ions (30 µM) in ethanol solution. Black bars represent fluorescence intensity of [**L**-$Al^{3+}$] ([**L**] = 10 µM and [$Al^{3+}$] = 30 µM). Red bars represent emission intensity of a mixture of **L** (10 µM) with the metal ions written below the bars (30 µM) followed by addition of 30 µM $Al^{3+}$ to the mixed solutions (see http://dx.doi.10.1080/00958972.2014.901506 for color version).

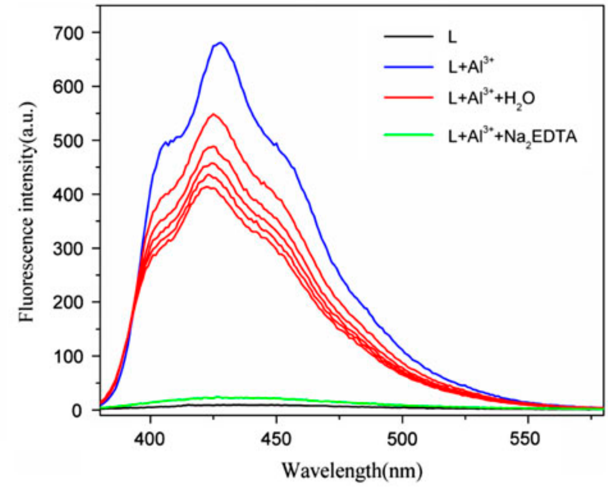


Figure 3. Fluorescence emission spectra of **L**-$Al^{3+}$ in the presence of 10–50 µM $H_2O$ or 50 µM $Na_2EDTA$ in ethanol.

experimental results reveal that $Al^{3+}$-induced fluorescence response was unaffected by the interfering metal ions.

To examine the reversibility of the sensor **L**, we conducted reversibility experiments using $Na_2EDTA$. When 50 µM $Na_2EDTA$ was added into a mixed solution of **L** (10 µM) and $Al^{3+}$ (30 µM), the fluorescence signal at 428 nm was completely quenched, as shown in figure 3. Water is a usual fluorescence quencher which exists in EDTA solution, we therefore investigated its influence on **L**-$Al^{3+}$. We found that when 10 µM water was added to the mixed solution of **L** (10 µM) and $Al^{3+}$ (30 µM), the fluorescence intensity decreased gradually. As seen from figure 3, when the amount of water reached 50 µM, the fluorescence intensity decreased by one-third, and the fluorescence intensity would not decrease further. From the above analysis, we know that $Na_2EDTA$ can quench the fluorescence of **L**-$Al^{3+}$, and the combination of **L** and $Al^{3+}$ is reversed.

As $Al^{3+}$ can be detected by changes in the fluorescence intensity, it is reasonable to estimate its detection limit [32]. The detection limit of the fluorescent sensor was determined from fluorescence titration data at 428 nm with lower concentration. When 1 µL ($1 \times 10^{-5}$ M) $Al^{3+}$ ions was added to the solution of 10 µM **L**, the fluorescence intensity increased 2.35-fold, which showed that the sensor can detect $Al^{3+}$ below $5 \times 10^{-9}$ M. The detection limit was considered to be $5 \times 10^{-9}$ M, indicating that the Schiff base is a promising, sensitive chemo-sensor. The Job plot showed that the chemo-sensor **L** forms a 1 : 1 complex with $Al^{3+}$ (figure S4), consistent with the ESI mass spectral results. The peak at *m/z* 486.2 corresponds to $[\mathbf{L} + Al^{3+} + NO_3 + C_2H_5OH]^+$. To further confirm the coordination of Al and **L**, ultraviolet-visible (UV–Vis) titration experiments were performed. The UV–Vis titration of $Al^{3+}$ was carried out using a solution of 10 µM of **L** in ethanol. The UV–Vis absorption spectrum of **L** at 410 nm decreased with addition of $Al^{3+}$, and finally disappeared. Meanwhile, a new peak at 350 nm appeared, indicating that a new compound was formed. The results of the absorption titration studies were in agreement with the fluorescence turn-on response. Arabahmadi *et al.* synthesized three new chromogenic receptors containing electron-withdrawing groups, and found these sensors showed visual changes toward some common ions

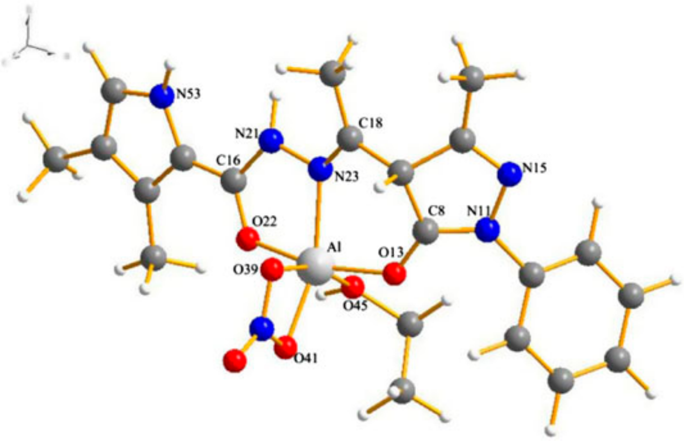
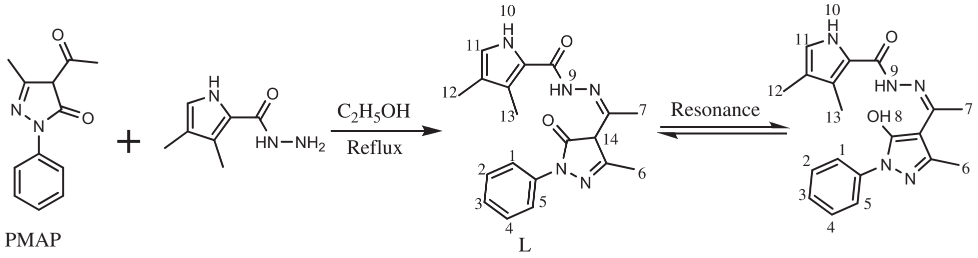


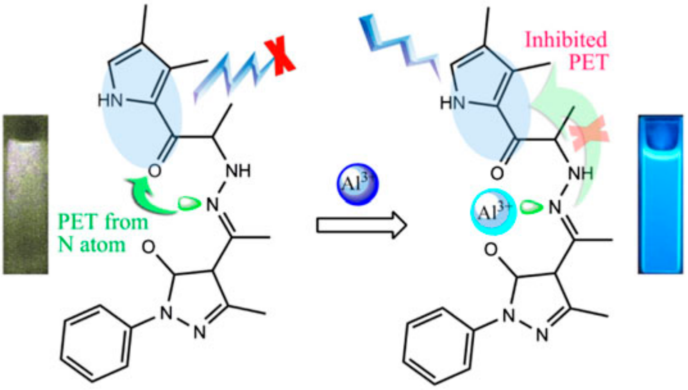
Figure 4. Optimized structure of [Al(**L**)($C_2H_5OH$)($NO_3$)]$^+$.



Scheme 1. Synthetic route of **L**.

[33]. However, the sensors had no selectivity and sensitivity toward toxic ions, such as $Al^{3+}$. Jin *et al.* prepared a new sensor via a very tedious route, and found that the sensor can detect $Mg^{2+}$ ions in acetonitrile media and the detection limit is $9 \times 10^{-8}$ M [34]. A sensor toward $Al^{3+}$ was prepared by Cheng *et al.* and its detection limit and fluorescence enhancement are $2.5 \times 10^{-8}$ M and about 56-fold in ethanol, respectively [35]. Liu *et al.* reported the synthesis and characterization of a new compound which shows a high sensitivity and selectivity toward $Al^{3+}$ with detection limit of $2.5 \times 10^{-7}$ M in acetonitrile [36]. In our article, the sensor was prepared by the simple route and showed greater sensitivity and selectivity toward $Al^{3+}$ in benign ethanol. In addition, its detection limit is $5 \times 10^{-9}$ M, which is lower than that of other sensors. All the above analysis indicated that our sensor is more useful than the sensors reported.

To get insight into the proposed binding mode, DFT calculations were conducted. Geometries, energies, and first- and second-energy derivatives of all of the stationary points found here were fully optimized by hybrid DFT using the GAUSSIAN 09 program suite [37]. For our DFT calculations, M06-2X [38] density functionals were used. A standardized 6-31G basis set [39, 40] was used together with polarization (d and p) functions. As depicted in figure 4, **L** formed a 1 : 1 complex with $Al^{3+}$. The two oxygens and nitrogen from –C=N–



Scheme 2. Possible PET process of **L**.

can coordinate with $Al^{3+}$, while the nitrogen in –C–N– cannot coordinate with $Al^{3+}$ due to the influence of energy and space. The optimized geometry indicated that the bond length between Al and O of **L** was 1.8553 or 1.8437, shorter than that of Al–N. However, they were all in the common range for coordination bonds. The donors of the sensor are almost on the same plane with Al, further corroborating the proposed sensing mechanism.

## 4. Conclusion

We have developed a simple fluorescent chemo-sensor with higher sensitivity based on PET and CHEF mechanisms. **L** exhibited high selectivity for $Al^{3+}$ over interfering metal ions with more than 155-fold fluorescence enhancement and high sensitivity with the LOD at $5 \times 10^{-9}$ M in ethanol. It is suggested that **L** could serve as an excellent fluorescent chemo-sensor for $Al^{3+}$ and might accelerate the development of new efficient chemo-sensors.

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