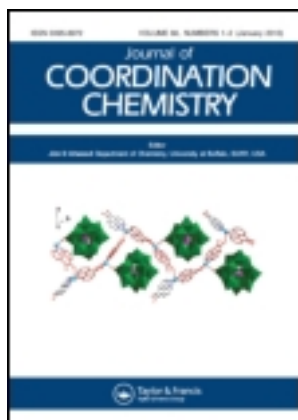


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A highly sensitive and selective Schiff base fluorescent chemodosimeter for aluminum(III)

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A highly sensitive and selective Schiff base fluorescent chemodosimeter for aluminum(III)

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A fluorescent probe for Al^{3+} , 4-(1'-phenyl-3'-methyl-5'-hydroxypyrazole)-1-acetone-(2'-hydroxybenzoyl) hydrazone (**L**), was prepared through a simple synthetic route. The fluorescent probe can detect Al^{3+} ions sensitively, in ethanol solution with the detection limit of 2.5×10^{-8} M via photoinduced electron transfer progress. The presence of interfering metal ions and chelators had little influence on the selectivity of Al^{3+} . The probe could serve as an excellent chemodosimeter for Al^{3+} in ethanol.

Keywords: Schiff base; Chemodosimeter; Al^{3+} Ions; PET Progress

1. Introduction

Concern for human health with metal cations has stimulated active research on chemodosimeters for toxic ions. Among cations, investigations on designing probes for aluminum cations (Al^{3+}) are attracting attention due to its toxicity and its effect on human health [1]. Neurotoxicity of Al^{3+} can damage the human nervous system and lead to Alzheimer's disease [2]. The accumulating evidence suggests that Al^{3+} can cause damage to certain human tissues and cells, because Al^{3+} plays an important role in potentiating oxidative and ammatory events, resulting in diseases such as dialysis dementia, osteomalacia, microcytic anemia [3], lung cancer, bladder cancers, etc. [4, 5]. In the ecosystem, toxicity of Al^{3+} is a grave concern. Almost 40% of the world's acidic soils are caused by phytotoxic Al^{3+} [6, 7]. Al^{3+} ions become more soluble in acidic media, and hence, Al^{3+} ions are potentially more toxic to aquatic biota [8].

The adverse health effects caused by Al^{3+} have stirred considerable attention on detection of Al^{3+} . Among all the Al^{3+} ion detection techniques, graphite furnace atomic absorption spectrometry [9] and inductively coupled plasma-atomic emission spectrometry [10] are developed, but expensive, complicated, and time consuming [11]. A number of experiments indicate that fluorescent probes for Al^{3+} can solve such problems. Thus the design and preparation of fluorescent probes with high selectivity and sensitivity are

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needed. However, many probes still have disadvantages, such as tedious synthetic routes [12], poor coordination ability with Al^{3+} [13], high detection limit [14, 15], etc. Thus, we pursue new Al^{3+} probes with easier synthetic procedure, higher stability, and lower detection limits.

Previous reports indicate that structures of most fluorescent probes for Al^{3+} contain nitrogen and oxygen-rich coordination environments providing a hard base environment for the hard acid Al^{3+} [16]. Previously, our group developed a series of acylhydrazone compounds as fluorescent sensors. Chunjiao Liu *et al.* have done experiments with 7-methoxychromone-3-carbaldehyde-(3',4'-dimethyl) pyrrole hydrazone (MCPH) as fluorescent sensor for Al^{3+} in acetonitrile, and the detection limit of MCPH for Al^{3+} was 2.5×10^{-7} M [17]. Xiulong Jin *et al.* synthesized 8-hydroxyquinoline-5-carbaldehyde-(benzotriazol-1'-acetyl) hydrazone as Mg^{2+} sensor with the detection limit of 9×10^{-8} M in acetonitrile [18]. In order to improve on these systems, we have synthesized a Schiff base ligand, 4-(1'-phenyl-3'-methyl-5'-hydroxypyrazole)-1-acetone-(2'-hydroxybenzoyl) hydrazone (**L**) to detect Al^{3+} through fluorescence spectra; ions such as Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , Ba^{2+} , Mg^{2+} , Pb^{2+} , Cr^{3+} , and Ca^{2+} have little influence on the detection of Al^{3+} . Moreover, the probe can detect Al^{3+} in ethanol without sodium tartrate dibasic dehydrate (STDD), sodium citrate (SC), or ethylenediamine tetraacetate (EDTA) altering the fluorescence intensity. The detection limit of the probe was considered to be 2.5×10^{-8} M, indicating that the Schiff base ligand is a promising sensitive chemodosimeter.

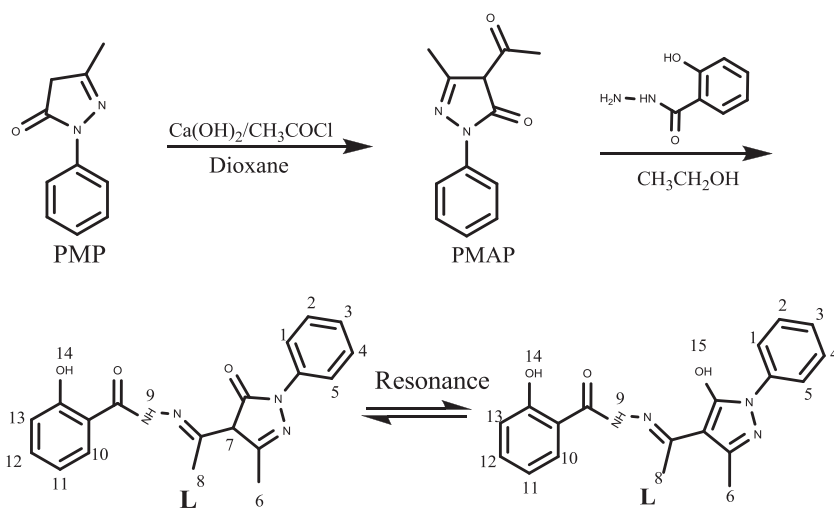
2. Experimental

2.1. Materials and instrumentation

All chemicals were obtained from commercial suppliers and used without purification. ^1H -NMR spectra were measured on Bruker 400 MHz instruments using TMS as an internal standard. ESI-MS were determined on a Bruker esquire 6000 spectrometer. UV-vis absorption spectra were determined on a Shimadzu UV-240 spectrophotometer. Fluorescence spectra were recorded on a Hitachi RF-4500 spectrophotometer equipped with quartz cuvettes of 1 cm path length.

2.2. Synthesis of the probe

The synthetic route of **L** is shown in figure 1. 1-Phenyl-3-methyl-4-acetyl-pyrazolone-5 (PMAP) was prepared according to the literature [19]. The Schiff base was synthesized by simple Schiff base condensation of PMAP and 2-hydroxybenzene-1-carbohydrazide. The mixed solution of PMAP and 2-hydroxybenzohydrazide was refluxed for eight hours at 85°C , giving bright yellow powder, m.p. $226\text{--}227^\circ\text{C}$. The Schiff base was confirmed by ^1H NMR spectra (figure S1) and IR spectra (figure S2). ^1H NMR of **L** (400 MHz in $\text{DMSO-}d_6$): δ : 12.543 (s, 1H, H^{15}), 11.193 (s, 1H, H^9), 7.996 (d, $J=8.0$ Hz, 2H, $\text{H}^{1,5}$), 7.822 (d, $J=9.2$ Hz, 1H, H^{10}), 7.455 (t, $J=7.6, 4.8$ Hz, H^{13}), 7.399 (m, 2H, $\text{H}^{11,12}$), 7.135 (t, $J=6.8$ Hz, 1H, H^3), 6.968 (dd, $J=8.0, 6.8$ Hz, 2H, $\text{H}^{3,4}$), 2.446 (s, 3H, CH_3 , H^8), and 2.372 (s, 3H, CH_3 , H^6).

Figure 1. Synthetic route of **L**.

3. Results and discussion

The binding of **L** and Al^{3+} was investigated by UV-vis titration in ethanol at room temperature (figure S3). Upon addition of Al^{3+} (0–2 equiv.) the absorbance at 365 nm for **L** decreased gradually, while the absorbance at 381 nm increased with an isosbestic point at 373 nm, indicating a balance between **L** and Al^{3+} -**L**. Therefore, we conclude that complexation of **L** and Al^{3+} occurred [20]. IR spectra (figure S4) also proved formation of a complex between **L** and Al^{3+} . The $\nu(\text{O-H})$ for **L** is at 3261 cm^{-1} and shifts to 3309 cm^{-1} in the complex. The $\nu(\text{C=O})$ of **L** is at 1627 cm^{-1} and the complex is shifted to 1597 cm^{-1} ; $\Delta\nu$ (**L**-complex) is 30 cm^{-1} . In the complex, the band at 542 cm^{-1} was assigned to $\nu(\text{M-O})$. These demonstrate that oxygen of carbonyl forms a bond with aluminum ions. A weak-band at 413 cm^{-1} was assigned to $\nu(\text{M-N})$ in the complex, confirming that nitrogen of the imino-group bonds to aluminum. The δ_{NNH} of the free **L** (1496 cm^{-1}) and that of the complex (1498 cm^{-1}) shows that the active hydrogen of the $-\text{NHN}-$ still exists in the complex.

Fluorescence titration experiments were also performed in ethanol solution (figure 2). The fluorescence spectra of **L** have a weak peak at 452 nm, but with addition of increasing concentration of Al^{3+} , a significant increase in fluorescence intensity at about 452 nm occurs. Upon addition of Al^{3+} , there was a dramatic fluorescence enhancement at 396 nm and 419 nm, due to promotion of an emissive excimer channel formation, and the fluorescence enhancement factors at 396 and 419 nm were determined as 53- and 56-fold, respectively. Excitation spectra of the Al^{3+} -bound probe (figure S5) suggest that the three emission bands at 396, 419, and 452 nm originate from the same ground state [21]. The fluorometric titration reaction curve showed two different peaks close to each other, attributed to the $-\text{NH-N}=\text{}$ structure. We also found that water can quench one peak and make it become more intense due to coordination. When the amount of Al^{3+} reached two equiv., the fluorescence intensity remains constant, indicating that the probe and Al^{3+} are coordinated with 1:2 stoichiometry. This is also in agreement with Job's plot (figure S6). Job's plot for the emission changes was applied by keeping the total concentration of **L** and Al^{3+} at $10\text{ }\mu\text{M}$, varying the molar fraction of Al^{3+} ions. From Job's

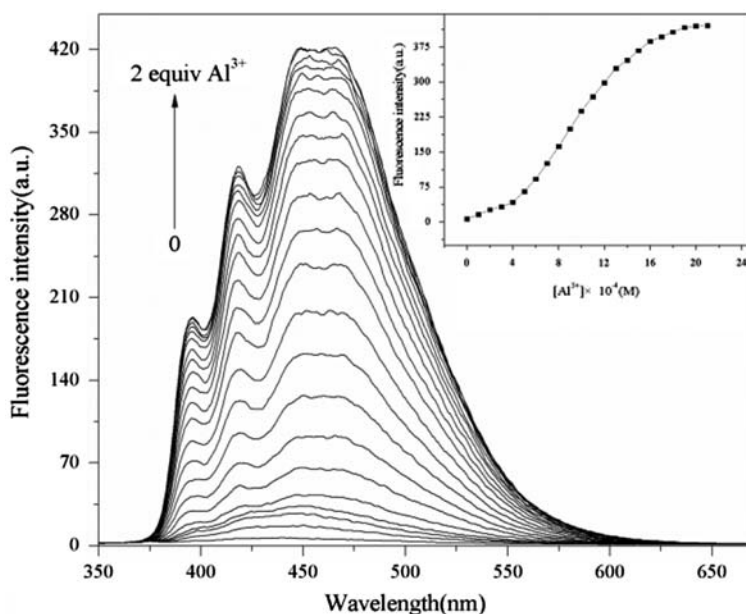


Figure 2. Changes in fluorescence emission spectra of **L** ($10\ \mu\text{M}$) upon titration by $\text{Al}(\text{NO}_3)_3$ in ethanol. Inset: fluorescence intensity as a function of $\text{Al}(\text{NO}_3)_3$ concentration.

plot, when the molar fraction reached 0.67, the fluorescence intensity was maximum. From the plot of the fluorescence intensity changes at 452 nm, the association constant was determined from the intercept $\log K$, which was 6.39, and the slope was $n=2.0783$, indicating that **L** and Al^{3+} coordinated with the stoichiometry of 1:2 [22]. Literature reported on coordination of Al^{3+} in similar complexes helped us to conclude the present **Al-L** complex [23]. The ESI-mass (figure S7) peaks at 453 and 466 were also proof of the 1:2 stoichiometry.

The detection limit of the fluorescent probe was determined from fluorescence titration data at 452 nm with lower concentration (figure S8). When $0.5\ \mu\text{L}$ ($1 \times 10^{-4}\ \text{M}$) Al^{3+} ions were added to solution of $10\ \mu\text{M}$ **L**, the fluorescence intensity increased 2.35-fold, showing that the probe can detect Al^{3+} below $2.5 \times 10^{-8}\ \text{M}$. The detection limit was considered to be $2.5 \times 10^{-8}\ \text{M}$, indicating that the Schiff base is a promising sensitive chemodosimeter. Figure S9 shows that in ethanol or water-ethanol, the ligand can detect Al^{3+} ions with high sensitivity. In other organic solvents or mixed solvents, the Schiff base cannot detect Al^{3+} ions efficiently. STDD, sodium citrate SC, and EDTA are good chelators. However, when STDD, SC, and EDTA (10 equiv.) were added into solution of Al^{3+} -**L** (figure 3), its fluorescence intensity remains almost constant, indicating that the complex Al^{3+} -**L** was very stable and difficult to be damaged by other chelators.

To investigate the selectivity of the Schiff base, fluorescence titration experiments were performed (figure 4a). In the experiment, two equiv. of nitrate salts of Hg^{2+} , Na^+ , K^+ , Li^+ , Ca^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} , Fe^{3+} , Mn^{2+} , Mg^{2+} , Pb^{2+} , Cu^{2+} , Cr^{3+} , Ba^{2+} , and Zn^{2+} ions were added to **L** in ethanol solution, and we found that the fluorescence intensities change subtly, showing that the ligand exhibited excellent fluorescence selectivity towards Al^{3+} over other alkali and alkaline earth metal ions, transition, and heavy metal ions. Competition experiments of Al^{3+} with other metal ions were also performed. As shown in figure 4b,

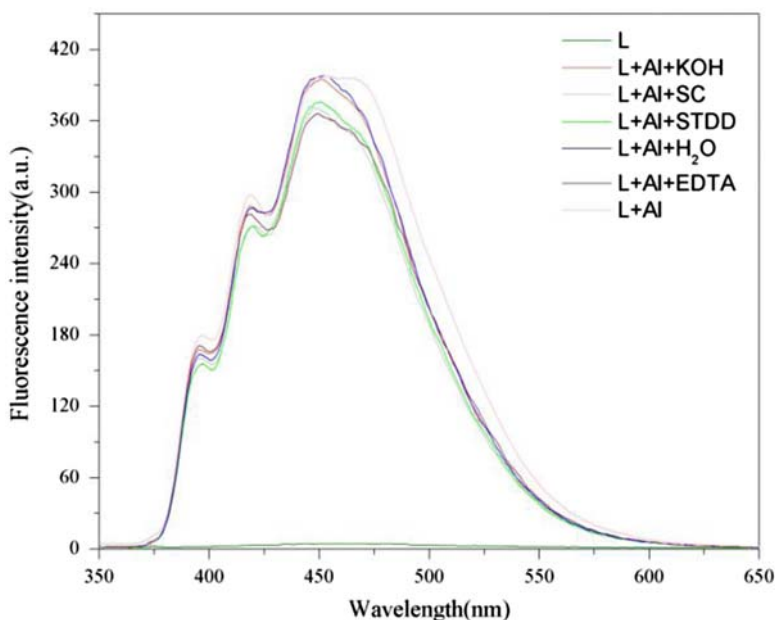


Figure 3. Fluorescence responses of **L** ($10\ \mu\text{M}$) upon addition of 20 equiv ($200\ \mu\text{M}$) of $\text{Al}(\text{NO}_3)_3$ in ethanol. Chelators (STDD, SC, and tetrasodium EDTA) were added to the Al^{3+} -**L** mixture to investigate reversible binding of Al^{3+} with **L**.

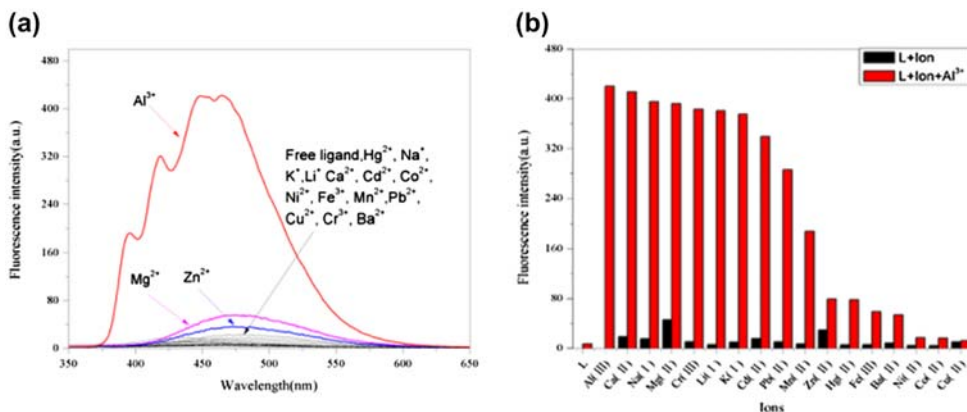


Figure 4. (a) Fluorescence spectra of **L** ($10\ \mu\text{M}$) with addition of interfering metal ions ($20\ \mu\text{M}$) in ethanol; (b) Fluorescence responses of **L** ($10\ \mu\text{M}$) to various metal ions ($20\ \mu\text{M}$) in ethanol. Black bars represent the addition of metal ions written below the bars to a $10\ \mu\text{M}$ solution of **L**. Red bars represent emission intensity of a mixture of **L** ($10\ \mu\text{M}$) with the metal ions written below the bars ($20\ \mu\text{M}$) following addition of $20\ \mu\text{M}$ Al^{3+} to the solutions.

when Al^{3+} ions were added into solution of the interfering ion (Hg^{2+} , Na^+ , K^+ , Li^+ , Ca^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} , Fe^{3+} , Mn^{2+} , Mg^{2+} , Pb^{2+} , Cu^{2+} , Cr^{3+} , Ba^{2+} , or Zn^{2+}) and **L**, the fluorescence intensity increased greatly, indicating that Al^{3+} can bind to **L** strongly and the Schiff base ligand can detect Al^{3+} ions in the presence of other interfering ions.

According to the above discussion, **L** possess efficient probe properties due to the emission of the exciplex formed between excited acetophenone and lone pair electrons on

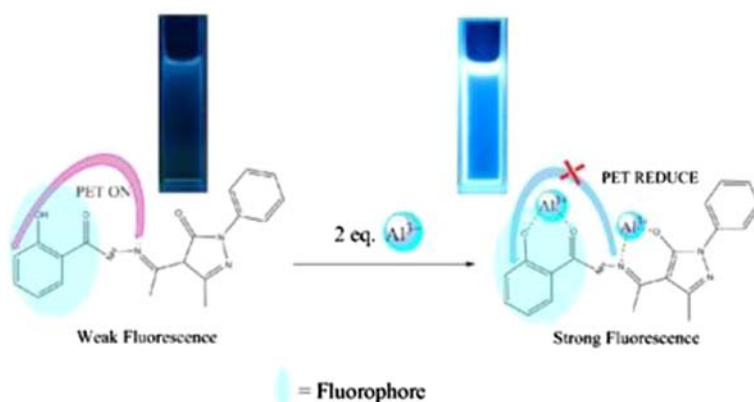


Figure 5. Possible coordination of Al^{3+} -L and the mechanism of fluorescence enhancement for L chelating with Al^{3+} .

N from $-\text{C}=\text{N}$ group [24]. The fluorescence band at 452 nm with low intensity is due to quenching by the $-\text{OH}$ receptor through a photoinduced electron transfer (PET), induced by a lone pair electrons from the Schiff base and quinoline nitrogens [25]. After addition of Al^{3+} , the fluorescence intensity increased dramatically, attributed to decrease of the PET effect and the highly efficient chelation-enhanced fluorescence effect [26, 27]. The conceptual architecture and mechanism for fluorescence enhancement of L upon the addition of Al^{3+} are shown in figure 5.

4. Conclusion

We have synthesized and characterized a Schiff base ligand. The Schiff base showed high selectivity for Al^{3+} over other metal ions with 60-, 53-, and 56-fold enhancement at 452, 396, and 419 nm in ethanol. The presence of interfering metal ions had little influence on the binding of Al^{3+} . These properties suggest that L could be an excellent chemodosimeter for Al^{3+} ions in ethanol solution.

Supplementary data

Supplementary material (some supporting figures) associated with this article can be found in the online version.

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