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Synthesis and Characterization of a New Al^{3+}-Selective Probe Based on Benzoyl Hydrazine Derivative

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Abstract. A new 'off-on' type Al^{3+}-selective fluorescent probe derived from benzoyl hydrazine has been synthesized and characterized. This probe shows high selectivity towards Al^{3+} compared to other common metal ions, and complexing with Al^{3+} triggers a new bond at 450 nm. With optimized conditions, the probe gives a linear response of 8.9×10^{-7}–9.0×10^{-6}M with a detection limit of 2.9×10^{-7} M Al^{3+} in ethanol.

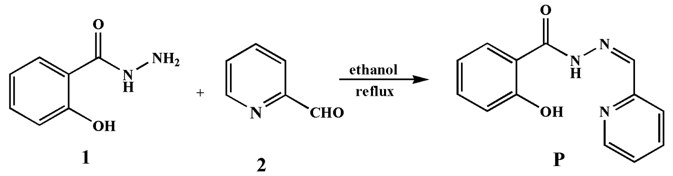
Key-Words:*Benzoyl hydrazine derivative, Al^{3+}, Fluorescent probe, Schiff base.*

1. Introduction

Compounds ofaluminum are widely dispersed in the environment in various ways, i.e. aluminum cookware, cans, paper industry, food additives, water treatment plants,textile industry, bleached flour,production of light alloys, etc, which caused the increase of the amount of free Al^{3+} in surface water due to the leaching from the waster matters. Although, aluminum is a non-essential element for living systems, the ionic radius (0.051nm) and charge of Al^{3+} makes it a competitive inhibitor ofseveral essential elements of similar characteristics like Mg^{2+} (0.066 nm), Ca^{2+} (0.099 nm) and Fe^{3+} (0.064 nm) [1,2]. It causesdialysis dementia in patients who are unable to eliminate Al^{3+}because of renal dysfunction and also affects the central nervous system to cause different diseases like amyotrophiclateral sclerosis [3]. Besides, aluminum toxicity causes microcytichypochromic anaemia, Al-related bone disease (ARBD),encephalopathy and has the potential to produce some neurobehavioraland neuro-pathologic changes that are similar tothose found in Alzheimer's disease and breast cancer [4].

Therefore, themethods to detect chelatable aluminum (Al^{3+}) have attracted much attention in recent times [5]. Due to the high sensitivity, fast analysis with spatial resolution for providing in situ and real-time information, and nondestructive sample preparation, fluorescent chemosensors have proved to be useful tools for sensing important species such as metal ions, anions and amino acids [6-11].However, the detection of Al^{3+} has always been problematic due to the lack ofspectroscopic characteristics and poor coordination abilitycompared to transition metals [5].For this reason, the developmentof Al^{3+} sensors are comparatively more difficult than thoseof other metal ions. In general, Al^{3+} being a hard acid, prefershard donor sites like N and O in its coordination sphere.

With above-mentioned in mind, in this work a new Schiff base compound containing N and O donor sites was synthesized and successfully characterized as Al^{3+}-selective probe (**Scheme 1**).



Scheme 1. The synthesis route of probe P

2. Experimental

2.1. Reagents and instruments

All reagents and solvents are of analytical grade and used without further purification.

Fluorescence emission spectra were conducted on a Hitachi 4600 spectro fluo meter. UV-Vis spectra were obtained on a Hitachi U-2910 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were measured with a Brucker AV 400 instrument and chemical shift were given in ppm from tetramethylsilane (TMS). Mass

(MS) spectra were recorded on a Thermo TSQ Quantum Access Agillent 1100.

2.2. Synthesis of compoundP

Compound **1**160.8mg (0.4 mmol) and 121.2 μL**2** (1.1 mmol) were mixed in ethanol (20 mL). The reaction mixture was stirred at 80 °C for 4 h, and then cooled to room temperature, the white percipitate so obtained was filtered and dried under vacuum and used directly. Yields: 82.6 %. MS (ES+) m/z: 242.25 $[M+H]^+$, 264.20 $[M+Na]^+$.^1H NMR (δ ppm, d_6-DMSO): 12.04 (s, 1H), 11.70 (s, 1H), 8.65 (d, 1H, J = 4.24), 8.50 (s, 1H), 8.01 (d, 1H, J = 7.84), 7.92 (d, 1H, J = 7.44), 7.88 (d, 1H, J = 7.36), 7.47 (d, 1H, J = 7.80), 7.44 (d, 1H, J = 5.48), 7.00 (d, 1H, J = 8.00), 6.97 (d, 1H, J = 7.56).^{13}C NMR (δ ppm, d_6-DMSO): 165.92, 159.81, 154.01, 150.48, 149.65, 137.82, 134.82, 129.59, 125.46, 120.99, 119.91, 118.17, 117.08.

2.3. General spectroscopic methods

Metal ions and chemo sensor **P** were dissolved in deionized water and DMSO to obtain 1.0 mm stock solutions, respectively. Before spectroscopic measurements, the solution was freshly prepared by diluting the high concentration stock solution to the corresponding solution.For all measurements, excitation and emission slit widths were 10 nm, excitation wavelength was 280 nm.

3. Results and discussion

3.1. Uv-vis spectral response of P

The UV/vis affinity of **P** to Al^{3+} was illustrated in **Figure1**. Upon the addition of Al^{3+}, electronic spectra of **P** (10 μM) in ethanol exhibited a new absorption band at 365 nm. This result in absorbance clearly suggested the binding of **P** with Al^{3+}.

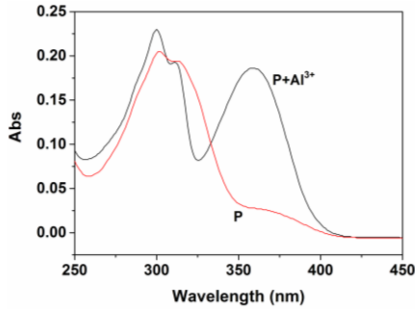


Figure 1. UV-vis spectra of **P** (5 μM) with Al^{3+} (50 μM) in ethanol.

3.2. Fluorescence spectral response of P

To further evaluate the selectivity of chemo sensor **P**, the fluorescent spectra (ex=280 nm) of **P** (10 μM) in ethanol with the addition of respective metal ions (10 equiv.) was investigated (**Figure2**). In the fluorescent tests, compared to other examined ions, only Al^{3+}generated a significant ‘turn-on’ fluorescent response at 457 nm with a fluorescence enhancement up to 45-fold. These results suggest that **P** has a higher selectivity toward Al^{3+}than other metal ions.

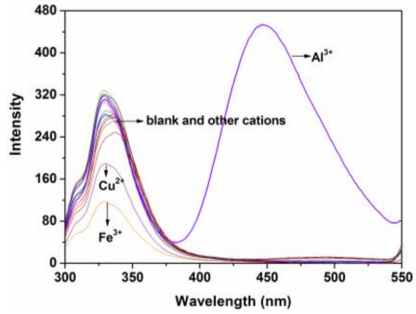


Figure 2. Fluorescence response of **P** (5 µM) with different metal ions (50 µM) in ethanol.

To further investigate the interaction of $Al^{3+}$with **P**, the fluorescent titration experiment was carried out. Upon titration with Al^{3+}, the fluorescence of the monomer peak at 457 nm increased gradually (**Figure3)**, and the fluorescent intensity of **P** was proportional to the concentration of Al^{3+} in the range of 8.9×10^{-7} to 9.0×10^{-6}M with a detection limit of 2.9×10^{-7} M Al^{3+}in ethanol. This clearly demonstrated that chemo sensor **P** could sensitively detect environmentally relevant levels of Al^{3+}.

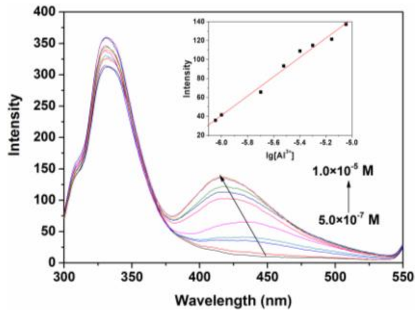


Figure 3. Fluorescence response of **P** (5 µM) with various concentrations of Al^{3+} in ethanol. Inset: the fluorescence of **P** (10 µM) as a function of Al^{3+} concentrations (8.9×10^{-7} to 9.0×10^{-6}M).

3.3. The proposed reaction mechanism

The linear dependence of the intensity at 457 nm within the equivalent range of the Al^{3+}showed that **P** forms a 1:1 complex with Al^{3+}.Moreover, the Job's plot experiment confirmed 1:1 stoichiometry for the **P-**Al^{3+} complex, which strongly supported the above conclusion (**Figure4)**.Thus, according to the obtained results, the coordination mode between **P** and Al^{3+} was proposed as shown in **Scheme 2**.

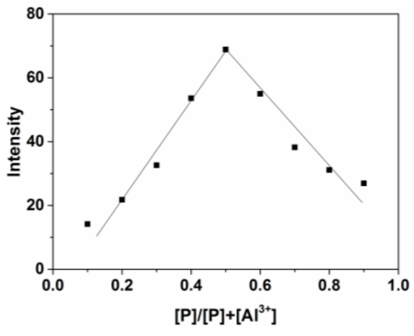
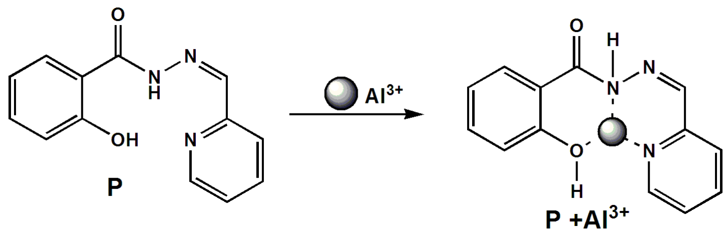


Figure 4. Job's plot of **P** with Al^{3+}. Total concentration of **P** and $Al^{3+}$was kept at a fixed 50 µM.



Scheme 2. Proposed reaction mechanism of **P** with Al^{3+}

4. Conclusions

A new probe derived from benzoyl hydrazine containing pyridine as subunit was designed and characterized. This proposed chemo sensor has good selectivity to Al^{3+} compared to other tested metal ions and exhibited a dynamic response range for Al^{3+} from 8.9×10^{-7} to 9.0×10^{-6}M with a detection limit of 2.9×10^{-7} M Al^{3+}in ethanol.

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