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RESEARCH ARTICLE **OPEN ACCESS**

AN Al^{3+}-SELECTIVE FLUORESCENT PROBEBASED ON BENZOYL HYDRAZINE DERIVATIVE

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ABSTRACT

A new Schiff base compound P was synthesized and characterized as an Al^{3+}-selective fluorescent probe. Study indicated that this proposed probe P has good selectivity and sensitivity to Al^{3+} compared to other tested metal ions in ethanol. A linear relationship was found between the fluorescence intensity at 445 nm from 3.0×10^{-6} to 7.0×10^{-6} M of Al^{3+} concentration with a detection limit of 1.0×10^{-6} M of Al^{3+}. The possible binding mode of P with Al^{3+} was also suggested.

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INTRODUCTION

Fluorescence techniques offer significant advantages over other methods for species monitoring inside living cells because of the non-destructive character, instantaneous response, and the availability of a wide range of indicator dyes, and many biologically important species such as metal ions, anions and amino acids have been successfully detected by this method in vitro and in vivo (Singh *et al.*, 2021; Ritter *et al.*, 2020; Roy *et al.*, 2021). Many research groups in the world contributed to the development of design and synthesis of new probes with perfect fluorescent response (Sedgwick *et al.*, 2018; Alamiry *et al.*, 2012; Yu *et al.*, 2020). Among the targets detected, coordination property of Al^{3+} was poor, and compared to the success of characterization of Cu^{2+} and Hg^{2+} probes (Roy *et al.*, 2021; Guo *et al.*, 2014; Zhang *et al.*, 2012), only a few Al^{3+} probes were reported (Yu *et al.*, 2018; Zhang *et al.*, 2020; Lin *et al.*, 2019, Dai *et al.*, 2014). More importantly, increasing exposure to free aluminum ions (Al^{3+}) poses a severe threat to biospheres and human health because of human activities in the environment.

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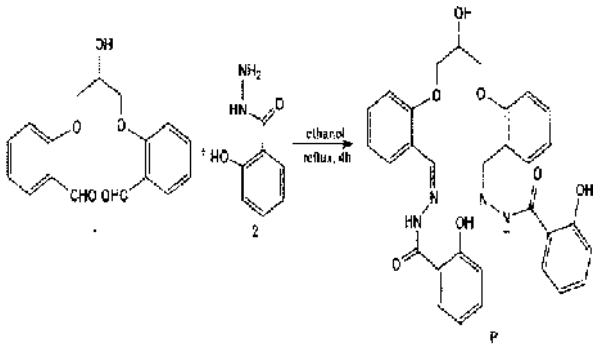
The average daily human intake of aluminium is approx. 3–10 mg/d, and the tolerable weekly aluminium intake in the human body is estimated to be 7 mg/kg body weight (Singh *et al.*, 2021). Thus, the detection of Al^{3+} is of great important (Yu *et al.*, 2020; Yu *et al.*, 2018), and the detection of Al^{3+} with fluorescence method attracted the interests of researchers. Based on the reasons mentioned above, a new Al^{3+}-selective fluorescent probe P derived from benzoyl hydrazine was synthesized and characterized in this work.

The synthesis route of P was shown in Scheme 1.



Scheme 1. Synthesis route of P

Experimental Section

Reagents and Instruments: All reagents are commercially available and used directly. MS were recorded on a Thermo TSQ Quantum Access Agillent 1100 system. Fluorescence emission spectra were conducted on a Hitachi 4600 spectrofluorimeter. UV-Vis spectra were obtained on a Hitachi U-2910 spectrophotometric. Nuclear magnetic resonance (NMR) spectra were measured with a Bruker AV 400 instrument and chemical shifts are given in ppm from tetramethylsilane (TMS).

Synthesis of P: Compound **1** was synthesized according to the reported method (Zhao *et al.*, 1996). Compound **1** (0.15 mmol) and **2** (0.31 mmol) were mixed in ethanol (40 mL) and stirred under reflux for 4 h. After the reaction was completed, the solution was cooled to room temperature, the white precipitate so obtained was filtered and dried in vaccum. The product was used directly. Yields: 83.4. MS m/z: 569.14 $(M+H^+)^+$, 591.27 $(M+Na^+)^+$. ^1H NMR (DMSO-d_6): 11.88 (s, 2H), 8.81 (s, 2H), 7.88 (d, 2H), 7.87 (t, 2H), 7.85 (t, 2H), 7.44 (d, 2H), 7.39 (t, 2H), 7.16 (d, 2H), 7.01 (t, 2H), 6.96 (d, 2H), 6.34 (d, 2H), 5.46 (m, 1H), 4.28 (d, 4H) , 4.22 (t, 1H).

General Spectroscopic Methods: 1.0 mM stock solutions were obtained by dissolving cations and P in deionized water and DMSO, respectively. The solution was freshly prepared before spectroscopic measurements and the desired concentration was obtained by diluting the high concentration stock solution. For all the fluorescent measurements, slit widths of excitation and emission were both 10/10 nm, and the excitation wavelength was fixed as 340 nm.

RESULTS AND DISCUSSION

Selectivity Measurement: The selectivity of probe P was firstly studied by using fluorescence method. The spectra of P (10 μM) were investigated in ethanol with the addition of respective metal ions (100 μM) (Figure 1). The tested metal ions were K^+, Na^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, Pb^{2+}, Co^{2+}, Cd^{2+}, Cu^{2+}, Fe^{2+}, Cr^{3+}, Ni^{2+}, Hg^{2+}, Cu^{2+}, Fe^{3+}, Al^{3+} and Ag^+. From the result we can know that P has better selectivity towards Al^{3+} than other tested metal ions, and so the proposed P was characterized as an Al^{3+}-selective probe in ethanol.

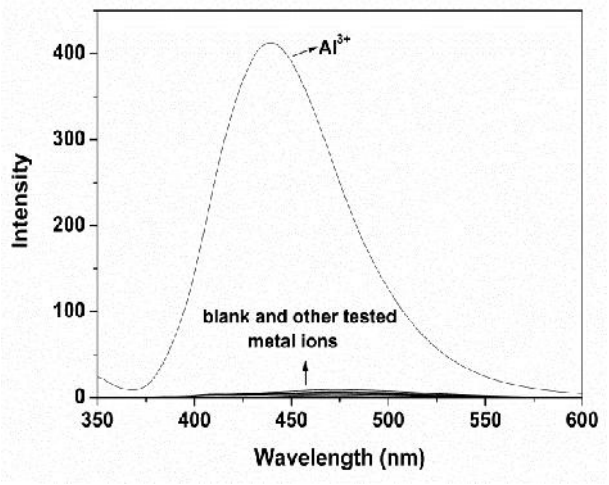


Figure 1. Selectivity measurement of P with tested metal ions in ethanol

Fluorescent Titration of P with Al^{3+}: In order to study the reaction between P and Al^{3+} furtherly, fluorescent titration experiment was carried out (Figure 2). The results indicated that with the increase of content of Al^{3+} the fluorescent intensity at 445 nm enhanced accordingly, and a linear relationship was found between the fluorescence intensity at 445 nm from 3.0×10^{-6} to 7.0×10^{-6} M of Al^{3+} concentration with a detection limit of 1.0×10^{-6} M of Al^{3+}.

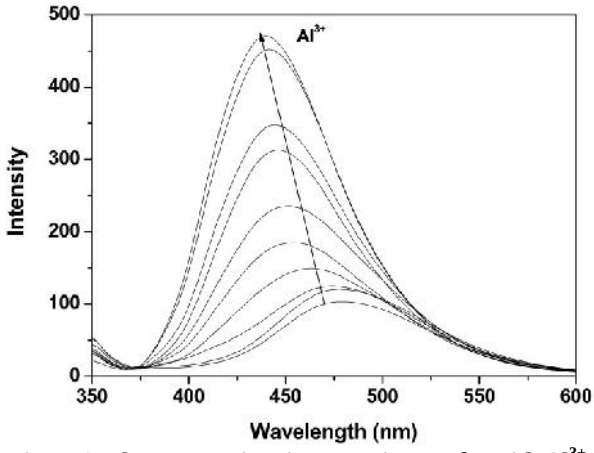
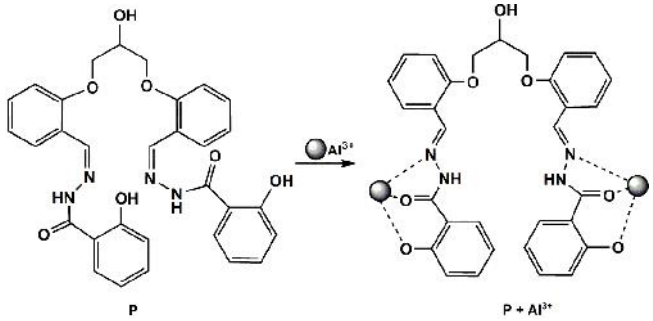


Figure 2. Fluorescent titration experiment of P with Al^{3+}

Proposed Binding Mode of P with Al^{3+}: According to the Soft-hard Acid-base theory, Al^{3+} showed affinity to compounds containing O and N atoms, which could explain why this probe has good selectivity to Al^{3+}. Based on the experiment results, the binding mode of P with Al^{3+} was proposed as shown in Scheme 2. The N (-C=N) and O (-C=O and –OH) participated in the formation of P-Al^{3+} complex.



Scheme2. Binding mode of P with Al^{3+}

Conclusion

In summary, a new probe **P** derived from benzoyl hydrazine was characterized as Al^{3+}-selective probe. The proposed probe **P** showed an "off-on" response in the presence of Al^{3+} in ethanol. We believe that this study will significantly promote the development of effective Al^{3+}-selective probes.

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