SSRG International Journal of Applied Chemistry
ISSN: 2393 – 9133 /doi:10.14445/23939133/IJAC-V8I2P101
Volume 8 Issue 2, 1-3, May-Aug 2021

A New Al^{3+}-Selective Fluorescent Probe Based on a Schiff-base Compound

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Received Date: 11April 2021
Revised Date: 21 May 2021
Accepted Date: 26 May 2021

***Abstract** - A new Al^{3+}-specific fluorescent probe P based on a Schiff-base compound was designed and synthesized, and its property was determined by fluorescent and UV-vis spectrometry. The results showed that the fluorescence intensity of probe P was significantly enhanced after the addition of Al^{3+} in ethanol. The binding ratio of probe P to Al^{3+} was 1:2 determined by the equimolar continuous method. The linear response range of probe P to Al^{3+} was 1.0×10^{-5}-5.5×10^{-5}M, and the detection limit of P for Al^{3+} was 3.3×10^{-6} M.*

Keywords — *Al^{3+}, Binding sites, Benzoyl hydrazide, Fluorescent probe, Schiff-base*

I. INTRODUCTION

Among the reported host compounds [1-3], Schiff-base compounds were easy to prepare and made used in many fields [4-8]. Fluorescent probes derived from benzoyl hydrazide had many advantages, such as good coordination sites, big stock shift, et al., which had been widely used for the detection of environmentally relative targets [9-11]. The design and synthesis of Al^{3+}-selective fluorescent probes had caused the interest of researchers because of their toxicity to the nervous system [12-16]. However, the study of Al^{3+} fluorescent probes was somewhat behind other metal ions because of the poor coordination property of Al^{3+} [15-20]. According to the reported works, Al^{3+} showed affinity to compounds containing O and N binding sites [21-24], and salicylhydrazide just meets this demand because of the O and N sites it was born. Based on these reasons, an Al^{3+}-selective fluorescent probe P derived from salicylhydrazide was synthesized and characterized in this work.

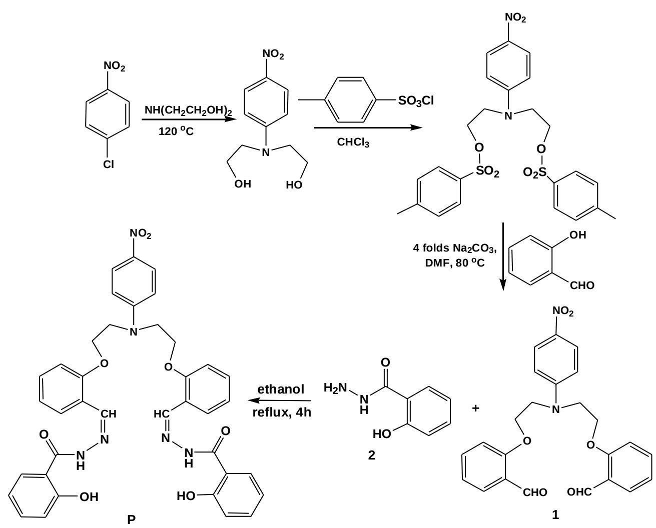
II. EXPERIMENTAL SECTION

A. Reagents and Instruments

All reagents are commercially analytical grade reagents and used without further treatment. Fluorescent spectra were obtained with Hitachi 4600 spectrofluorimeter. UV-Vis spectra were conducted on Hitachi U-2910 spectrophotometric. ^{1}H-NMR spectra were carried out with Bruker AV 400 instrument, and chemical shifts are given in ppm from tetramethylsilane (TMS).

B. Synthesis of P

The synthesis route of probe P was shown in Scheme 1.



Scheme 1. Synthesis route of P

Compound 1 was synthesized according to the reported method [25].

Compound 1 (1.0 mmol) and salicylhydrazide (2.2 mmol) were added in a flask and then refluxed in ethanol (40 mL) for 4 h. The mixture was cooled to room temperature, and the white precipitate so obtained was filtered and used directly. Yields: 80.7%. ^{1}H-NMR (δ ppm, DMSO-d_6): 11.84 (s, 2H), 8.76 (s, 2H), 8.07 (d, 2H, J=9.20), 7.83 (d, 4H, J=8.40), 7.42 (t, 2H, J=7.80), 7.36 (d, 2H, J=7.40), 7.08 (d, 2H, J=8.00), 7.02 (t, 2H, J=6.00), 6.99 (d, 2H, J=8.40), 6.95 (d, 4H, J=8.40), 6.93 (t, 2H, J=6.40), 4.33 (t, 4H, J=7.80), 4.09 (t, 4H, J=8.00).

C. General Spectroscopic Methods

1.0 mM stock solutions of cations and P were obtained by dissolving the salts and P in deionized water and DMSO, respectively. The testing solution was freshly prepared before measurements. 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.

III. RESULTS AND DISCUSSION

A. Selective Study of P

An excellent probe must have good selectivity. So the selectivity of this proposed probe P (10 μM) was firstly studied in ethanol (Fig. 1), and the tested metal ions were Na^+, K^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Fe^{3+}, Ag^+, Hg^{2+}, $Al^{3+,}$ and Cr^{3+}. From the results, we can see that only the addition of Al^{3+} caused an obvious fluorescent enhancement at 430 nm. The Uv-vis spectra also supported the fluorescent results (Fig. 2). Thus, this compound was characterized as an Al^{3+}-selective fluorescent probe in ethanol.

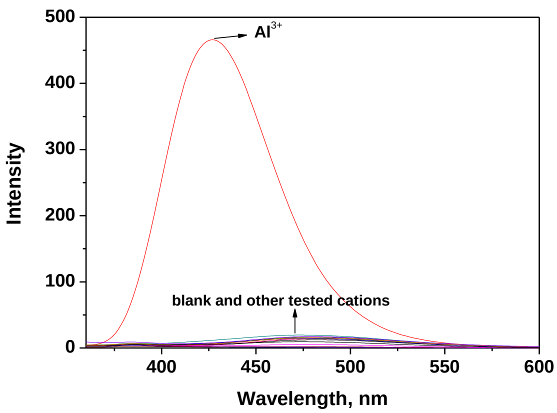


Fig. 1 Fluorescence spectra of probe P (10 μM) with different metal ions (100 μM) in ethanol.

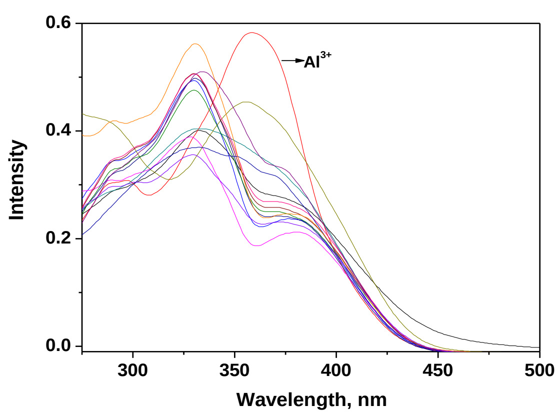


Fig. 2 UV-vis spectra of different metal ion (100 μM) to probe P (10 μM) in ethanol.

B. Fluorescent Titration Experiment

In order to study the reaction of P with Al^{3+} further, a fluorescent titration experiment was carried out (Fig. 3). The fluorescent intensity of P regularly increased with the addition of Al^{3+}, and a linear range was found in the concentration range of 1.0×10^{-5}-6.0×10^{-5} M with a detection limit of 3.3×10^{-6} M.

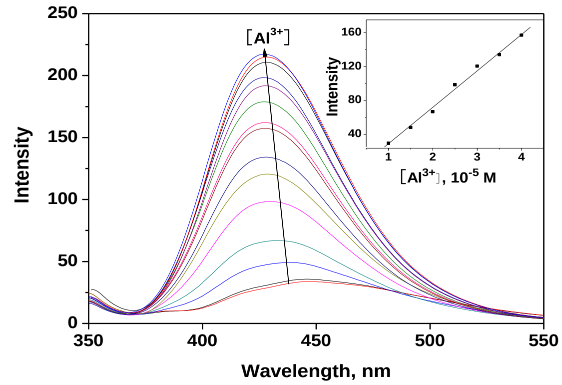


Fig. 3 Fluorescence titration of probe P (10 μM) with different concentrations of Al^{3+} in ethanol

C. Binding Mode Study of P with Al^{3+}

Job' plot method was used for the study of the binding mode of P with Al^{3+}, and the total concentration of P and Al^{3+} was kept as 50 μM (Fig. 4). When the ratio of P to Al^{3+} was 0.33, the fluorescent intensity reached the maximum value. These results indicated that P coordinated with Al^{3+} in a mode of 1:2. The proposed reaction mechanism was showed in Scheme 2. The N (-C=N) and O (-C=O and –OH) participated in the coordination process [26].

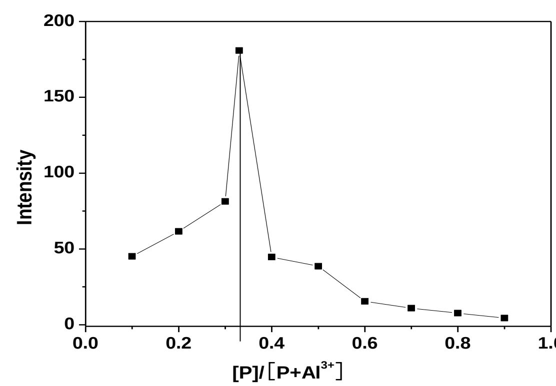
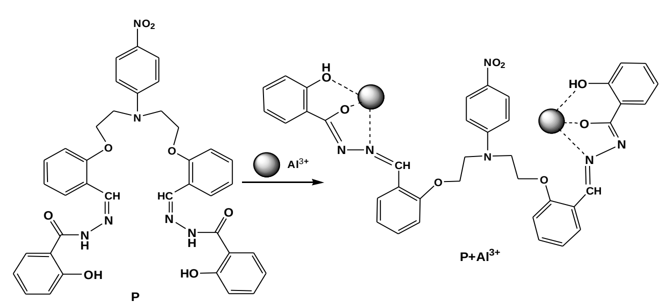


Fig. 4 Job's plot of P with Al^{3+}. The total concentration of P and Al^{3+} was kept at a fixed 50 μM



Scheme 2 Binding mode of probe P with Al^{3+}

IV. CONCLUSIONS

A benzoyl hydrazide-based Schiff base was synthesized and characterized as an Al^{3+}-selective fluorescent probe. The study showed that this probe had good selectivity and sensitivity to Al^{3+} compared to other tested metal ions, and a detection limit of 3.3×10^{-6} M was obtained.

ACKNOWLEDGMENT

This work was financially supported by the Natural Science Foundation of Hainan Province (No. 820RC626), the Research and Training Foundation of Hainan Medical University (No. HYYS2020-16), and the National Natural Science Foundation of China (No. 81760387, 81860381).

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