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RESEARCH ARTICLE

AN Al³⁺⁻SELECTIVE FLUORESCENT PROBE DERIVED FROM OF NAPHTHALENE

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A novel Al³⁺selective probe was rationally constructed based on naphthalene derivative. Compared to

other tested metal ions, the probe displayed the selective recognition for Al³⁺which could be detected

by a significant turnon fluorescent response at 442 nm with a detection limit of 1.33 μ M Al³⁺.

Besides, a 1:1 metal-ligand complex was confirmed by Job's plot experiment.

ARTICLE INFO

ABSTRACT

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INTRODUCTION

Due to the large number of aluminum ions used in daily life, aluminum ions will enter the human body through the food chain, which can increase people's risk of aluminum poisoning, resulting in calcium metabolism disorders, interference with iron concentration in the blood^[1-4]. Under overload conditions, Al³⁺ may be involved in the production of reactive oxygen species, contributing to neurodegenerative diseases such as Alzheimer's disease, Wilson's disease and Parkinson's disease ^[5-7]. The World Health Organization has reported that humans can consume the maximum amount of aluminum per day is about 3 mg, and the highest concentration of aluminum in drinking water is 7.41 µ M. Therefore, it is particularly important to establish an efficient and accurate method for detecting Al^{3+} in the environment. As a method to overcome alumina defects, fluorescent probe technology has been widely used in the study of sensitive and rapid detection of alumina^[8-10]. This technique allows real-time detection of target ions at very low ion concentrations without any special treatment of the sample. They are highly selective, sensitive and suitable for biological imaging and medical diagnosis^[11-22].Naphthalene derivatives are excellent fluorophores because of their large two-photon absorption cross section. Naphthalene derivatives are combined with compounds or materials to construct a novel efficient fluorescence probe which may selectively respond to small molecules. It is of great significance for the analysis and detection of small molecules. Based on the above considerations, naphthalene was selected as fluorescent group and ethylenediamine functional unit was introduced in this study.

The probe showed excellent selectivity for aluminum ions in ethanol, and the interference of other ions was very small. It was preliminarily proved that the binding ratio between the probe and aluminum ions was 1:1 by equimolar continuous change method. When Al^{3+} was present, the fluorescence intensity of the system at 442 nm was positively correlated with the concentration of Al^{3+} .



Scheme 1 Synthetic route of P

EXPERIMENTAL SECTION

Reagents and Instruments: The metal ions used in the experiment are mainly chloride. They were from NaCl, MgCl₂·6H₂O, CdCl₂, HgCl₂, CaCl₂·2H₂O, FeCl₃·6H₂O, CrCl₃·6H₂O, Zn(NO₃)₂·6H₂O, AgNO₃,

 $AlCl_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$, $CuCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 6H_2O$, and $PbCl_2$, respectively. Fluorescence emission spectra were conducted on a Hitachi4600 spectrofluorometer.

Synthesis of P: 2-hydroxy-1-naphthalene formaldehyde (0.01017 g) was added in ethanol (30 mL), and then 100 μ L ethylenediamine was added drop by drop in the stirring state. Yellow solids were precipitated at the beginning of the reaction. After reflux reaction for 6 h, the mixture was cooled to room temperature, then filtered and washed with ethanol to get dark brown solid P.

General spectroscopic methods: Metal ions were dissolved in deionized water to obtain stock solution (10 mM); the probe was dissolved in DMSO to obtain stock solution (1 mM). All of the fluorescence spectra were recorded at room temperature (25 °C). Test solutions were prepared by placing 50 μ L of the probe stock solution (1 mM) and an appropriate aliquot of individual ion stock solution into a test tube, and then diluting the solution with ethanol to 5 mL, the resulting solution was shaken well before recording the spectra. Excitation and emission slit widths were 10/10 nm, respectively. The excitation wavelength was 350 nm.

RESULTS AND DISCUSSION

Selectivity Measurement of P: Selectivity was the most important property of probes, which decided the further use of probe. Thus, the selectivity of P (10µM) to different metal ions (100 µM) (Ag⁺, Ca²⁺, Mg²⁺, Zn²⁺, Pb²⁺, Cu²⁺, Hg²⁺, Cd²⁺, Cr³⁺, Fe³⁺ and Al³⁺) was detected in ethanol firstly (Figure 1). Among the tested ions, only the addition of Al³⁺ caused an obvious enhancement of fluorescence of P at 442 nm, which proved that P was a good Al³⁺-selective probe.



Figure 1. Fluorescence emission spectra of different metal ionson P in ethanol

Fluorescent titration experiment of P with $AI^{3+:}$ In order to study the sensitivity of P on the detection of AI^{3+} , fluorescent titration experiment was carried out (Figure 2). The experiment results showed that P had a good linear relationship with AI^{3+} with wide concentration range of 4-10 µM, and the detection limit was 1.33μ M (based on LOD= $3\sigma/s$, σ was the standard deviation of blank solution, S was the slope of calibration curve).



Figure 2. Fluorescent titration experiment of P with Al³⁺.Inset: linear plot of P with Al³⁺ concentration

Combination mode of P with AI^{3+} : It was determined by equimolar continuous change method to evaluate the combination ratio of Pwith AI^{3+} . Judging from the results in the Figure 3, when [P]/ [AI³⁺] was close to 0.5, the intensity at 442 nm was maximum and the possible combination patterns were shown in the Figure 4, the carbonyl oxygen on the naphthalene ring and the nitrogen atom on ethylenediamine may participate in the coordination.



Figure 3. Job's-plot of $P-Al^{3+}$, and the total concentrations of P and Al^{3+} was kept as 50 μ M.



Figure 4. Proposed combination of P and Al³⁺

CONCLUSION

An Al^{3+} -selective fluorescent probe was successfully characterized, compared other tested metal ions, this probe showed good selectivity and sensitivity to Al^{3+} . This study will promote the development of the design of ligands for the detection of Al^{3+} .

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