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CHARACTERIZATION OF Mg^{2+}-SELECTIVE FLUORESCENT PROBE BASED ON BENZOYLHYDRAZINE

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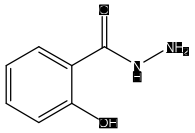
Abstract - A Mg^{2+}-selective probe based on commercial available benzoylhydrazine was characterized. Study show that this probe has good selectivity to Mg^{2+} compared to other tested ions.

Keywords -Mg^{2+}, Benzoylhydrazine, Fluorescent probe, Fluorescence, Synthesis

I. INTRODUCTION

Mg^{2+} is the most abundant divalent cation in living cells, and participates in many important cellular processes,[1] and dietary deficiency of Mg^{2+} appears to play an etiological role in many diseases.[2] Thus, the detection of Mg^{2+} is extensively required.[3]

In recent years, different methods for the detection of Mg^{2+} have been developed. Among them, fluorescent probe method has many advantages compared to other methods, such as high selectivity, good sensitivity.[4] But compared to the success of Ca^{2+}-selective probes,[5] the design and synthesis of highly selective Mg^{2+} fluorescence probes is still an intriguing challenge. In this paper, a commercially available compound benzoylhydrazine **P** was characterized as Mg^{2+}-selective probe, the structure of the probe as show in **Scheme 1**.



Scheme 1 Structure of probe **P**

II. EXPERIMENTAL SECTION

A. Reagents and Instruments

All reagents and solvents are of analytical grade and used without further purification. The metal ions employed are NaCl, KCl, $CaCl_2 \cdot 2H_2O$, $MgCl_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $PbCl_2$, $CdCl_2$, $CrCl_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $HgCl_2$, $CuCl_2 \cdot 2H_2O$, $FeCl_3 \cdot 6H_2O$ and $AgNO_3$, respectively.

Fluorescence emission spectra were conducted on a Hitachi 4600 spectrofluometer. 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.

B. General Spectroscopic Methods

Metal ions and probe **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 10/5 nm, excitation wavelength was 340 nm.

III. RESULTS AND DISCUSSION

*a. Fluorescence Spectral Response of **P***

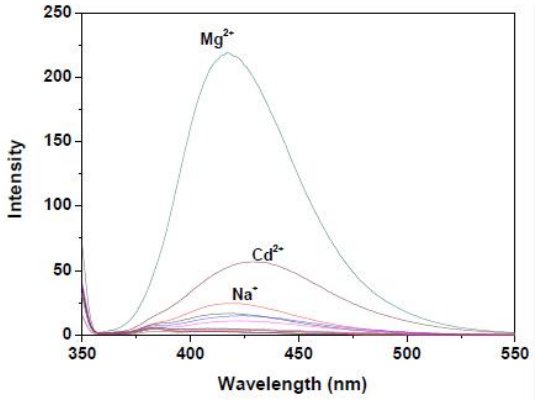


Fig.1 Fluorescence spectra of **P** (10 μM) with different metal ions (10 equiv.) in ethanol.

Firstly, the selectivity of probe **P** was evaluated. The fluorescence spectra (ex=340 nm) of **P** (10 μM) were investigated with the addition of respective metal ions (10 equiv.) in ethanol (**Fig. 1**). Study shows that compared to other ions examined, only Mg^{2+} generated a significant "turn-on" fluorescence response of the monomeric peak at 410 nm with a fluorescence enhancement. This result suggested that **P** had a higher selectivity toward Mg^{2+} than the other metal ions.

To further investigate the interaction of Mg^{2+} and **P**, the fluorescent titration experiment was carried out. The result shows that the fluorescence intensity of **P** was enhanced upon addition of various amounts of Mg^{2+} in ethanol as depicted in **Fig. 2**. Under the present conditions, when **P** was employed at 10 μM level, the fluorescent intensity of **P** was

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proportional to the concentration of Mg^{2+} in the range of 1.0×10^{-6} to 7.0×10^{-6} M with a detection limit of 3.3×10^{-7} M Mg^{2+}. This clearly demonstrated that probe **P** could sensitively detect environmentally relevant levels of Mg^{2+}.

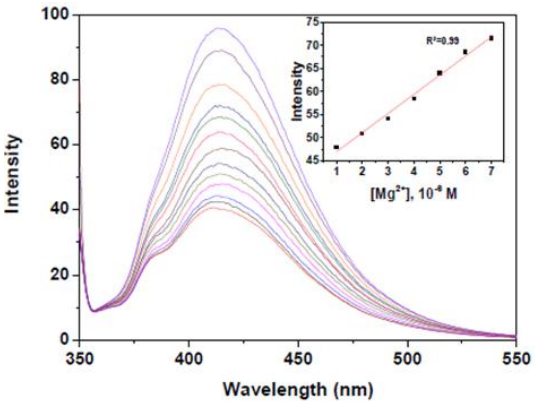


Fig. 2 Fluorescence response of **P** (10 μM) with various concentrations of Mg^{2+} in ethanol. Inset: the fluorescence of **P** (10 μM) as a function of Mg^{2+} concentrations (1.0–7.0 μM).

b. Proposed Reaction Mechanism

To study the reaction mechanism of **P** with Mg^{2+}, the Job's plot experiment was carried out, and the result indicated that a **P**-Mg^{2+} complex was formed in 1:1 stoichiometry (**Fig. 3**).

Thus, according to the obtained results, the coordination mechanism of **P** with Mg^{2+} was proposed. Probe **P** was most likely to chelate with Mg^{2+} as shown in **Scheme 2**, which blocked the photo induced electron transfer (PET) mechanism and greatly enhanced the fluorescence of **P**.

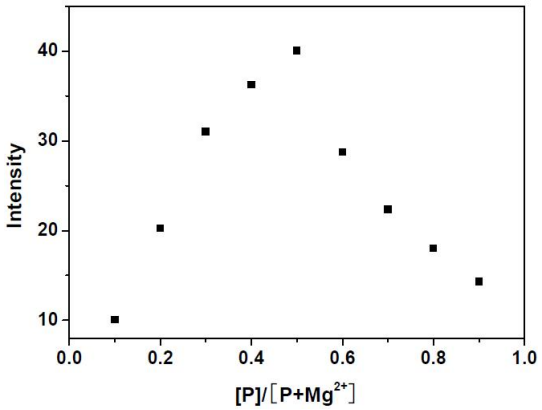
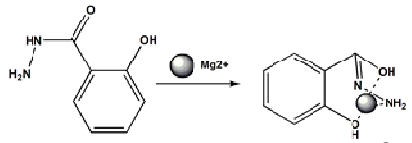


Fig. 3 Job's plot for determining the stoichiometry of **P** and Mg^{2+}. Total concentration of **P** and Mg^{2+} was kept 10 μM.



Scheme 2 Proposed binding mode of **P** with Mg^{2+}

IV. CONCLUSIONS

In summary, a commercial available compound was characterized as Mg^{2+}-selective fluorescent probe. This fluorescent probe showed significant fluorescence enhancement in presence of Mg^{2+} in ethanol. We believe that these observations should serve as the platform to develop new probes for other metal ions.

ACKNOWLEDGMENT

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