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CHARACTERIZATION OF A NEW Al^{3+}-SELECTIVE FLUORESCENT PROBE BASED ON NAPHTHALENE DERIVATIVE

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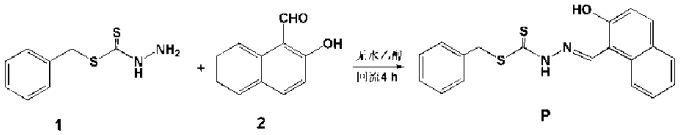
ABSTRACT

A new compound derived from naphthalene was successfully characterized as Al^{3+}-selective fluorescent probe. The proposed probe has better selectivity and sensitivity compared to other tested metal ions. A prominent fluorescence enhancement was observed in the presence of Al^{3+}, accompanied by the change in the absorption spectrum.

INTRODUCTION

Compared to conventional methods, such as inductively coupled plasma-atomic emission spectrometry (ICP-OES), inductively coupled plasma-mass spectroscopy (ICP-MS) and atomic absorption spectrometry (AAS), fluorescence spectroscopy displayed high selectivity and sensitivity, and easy to operate with low limits of detection. In addition, the equipment of detection was simple and without a complex multistage sample preparation (Elizabeth and Stephen, 2008; Quang and Kim, 2010; Yu *et al.*, 2014; Yu *et al.*, 2014). Fluorescent spectroscopy has been proved to be useful tools for sensing important species, many fluorescent probes for the detection of metal ions, anions and small moleculars have been proposed and characterized (Zhang *et al.*, 2014; Sun *et al.*, 2009; Li *et al.*, 2005). Aluminum is a non-essential element for living system and can cause severe diseases to human, and severe environmental pollution was caused along with the use of aluminum products (Campbell and Bondy 2000). Thus, the detection of Al^{3+} had attracted spread interests of researchers in recent years (Dai *et al.*, 2014; Das *et al.*, 2013; Banerjee *et al.*, 2012). Due to the poor coordination ability, the detection of Al^{3+} has always been problematic, and the development of Al^{3+} probes is comparatively more difficult than those of other metal ions. Keep this in mind, in this work a new Schiff-base compound was synthesized and successfully characterized as Al^{3+}-selective probe (Scheme 1).



Scheme 1. Synthesis route of probe P

Experimental Section

Reagents and Instruments

All reagents and solvents are of analytical grade and used without further purification. The metal ions and anions salts employed are NaCl, KCl, $CaCl_2 \cdot 2H_2O$, $MgCl_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $PbCl_2$, $CdCl_2$, $CrCl_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $HgCl_2$, $CuCl_2 \cdot 2H_2O$, $FeCl_3 \cdot 6H_2O$, $AlCl_3 \cdot 6H_2O$

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and $AgNO_3$, respectively. Nuclear magnetic resonance (NMR) spectra were measured with a Brucker WM-500 instrument and chemical shift were given in ppm from tetramethylsilane (TMS). Mass (MS) spectra were recorded on a Thermo TSQ Quantum Access Agillent 1100. UV-Vis spectra were obtained on a Hitachi U-2910 spectrophotometer. Fluorescence emission spectra were conducted on a Hitachi 4600 spectrofluometer.

Synthesis of compound P

Compound **1** was synthesized as described before (Zheng *et al.*, 2007). Compound **P**: Compound **1** 0.198 g (1.0 mmol) and 0.172 g **2** (1.0 mmol) were mixed in ethanol (30 mL). The reaction mixture was stirred under reflux for 4 h. After the reaction was finished, the mixture was cooled to room temperature. The precipitate so obtained was filtered and used directly. Yields: 85.2 %. MS m/z: 375.2 $[M + Na]^+$, 351.4 $[M - 1]^-$. ^1H NMR: 13.48 (s, 1H), 11.09 (s, 1H), 9.22 (s, 1H), 8.71 (d, 1H, J = 8.5), 7.93 (d, 1H, J = 9.0), 7.86 (s, 1H, J = 7.5), 7.54 (t, 1H, J = 8.0), 7.43 (d, 2H, J = 9.0), 7.37 (d, 1H, J = 8.0), 7.35 (t, 2H, J = 7.7), 7.26 (t, 1H, J = 8.0), 7.21 (d, 1H, J = 9.0), 4.60 (s, 2H). ^{13}C NMR: 194.90, 158.76, 146.60, 137.43, 134.31, 131.74, 129.64, 129.38, 128.98, 128.72, 128.59, 127.73, 124.19, 123.51, 118.71, 109.68, 38.00.

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/ emission slit widths were 10/10 nm, excitation wavelength was 415 nm.

RESULTS AND DISCUSSION

Uv-vis spectral response of P

In the UV-vis spectrum of **P**, there is an obvious absorption change between **P** and **P** plus Al^{3+}, which shows the reaction of **P** with Al^{3+} (Figure 1).

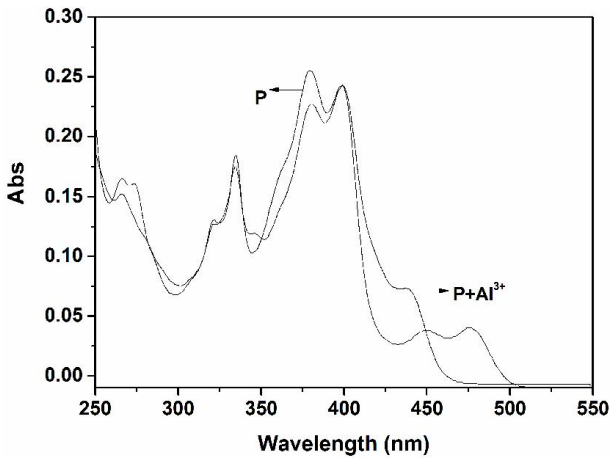


Figure 1. UV-vis spectra of P (10 μM) with Al^{3+} (100 μM) in ethanol

Notably, upon sequential addition of Al^{3+} to the **P** solution induced a regular change of the absorption of **P** (Figure 2).

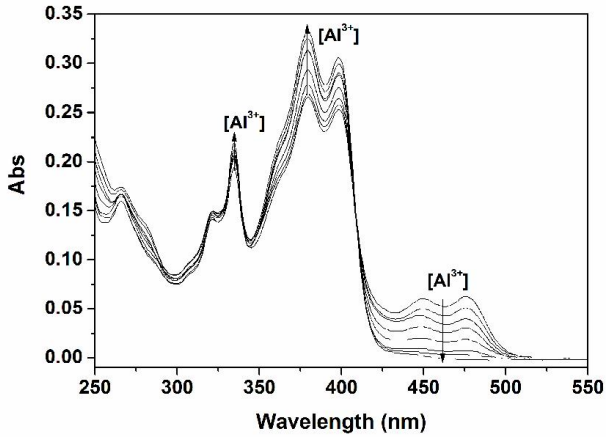


Figure 2. Changes in UV-vis spectra of P (10 μM) in ethanol with various amounts of Al^{3+} (0-10 μM)

Fluorescence spectral response of P

The fluorescence spectra of **P** were measured to investigate the probe's ability to indentify different metal ions in ethanol (Figure 3).

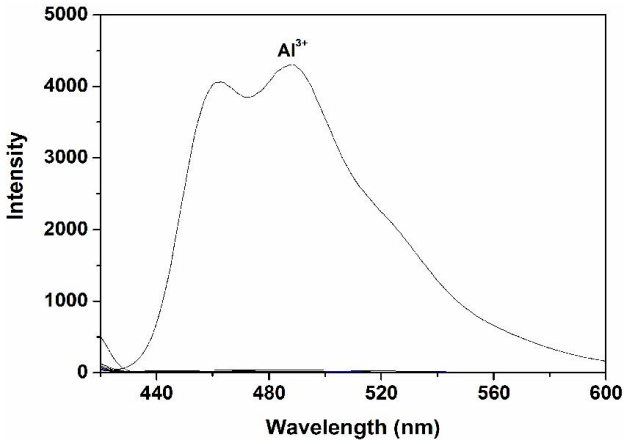


Figure 3. Fluorescence response of P (10 μM) with different metal ions (100 μM) in ethanol

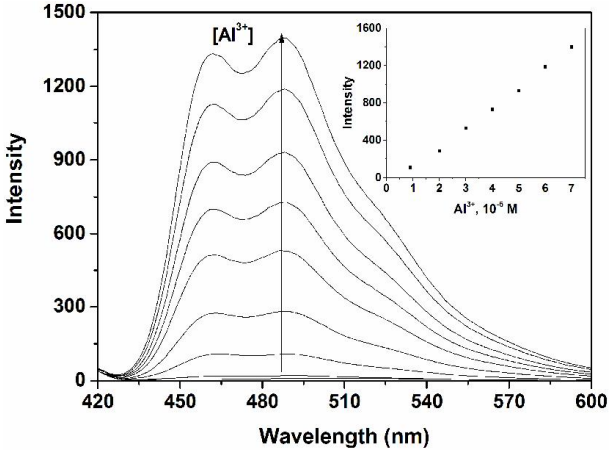


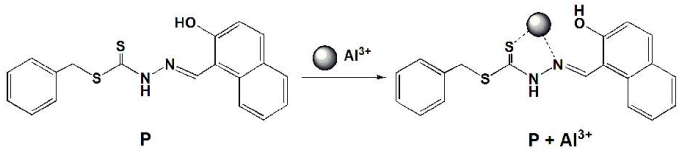
Figure 4. Fluorescence response of P (10 μM) with various concentrations of Al^{3+} (0-7 μM) in ethanol. Inset: the fluorescence of P (10 μM) as a function of Al^{3+} concentrations

The fluorescence spectra of **P** in the presence of Al^{3+} showed the enhancement of fluorescent intensity. Under the same conditions, other metal ions such as Na^{+}, K^{+}, Ag^{+}, Ca^{2+}, Mg^{2+}, Zn^{2+}, Pb^{2+}, Hg^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+} and Fe^{3+} did not cause any discernible changes.

It indicated that **P** could selectively recognize Al^{3+} in ethanol and the interference of other metal ions on detecting Al^{3+} could be negligible. In the emission spectra (Figure 4), the fluorescence peak increased upon the gradual addition of Al^{3+}, the linear portion of the plot of fluorescence intensity *vs.* Al^{3+} could be used to detect the unknown concentration of Al^{3+} over the range of 1.5×10^{-6} to 7.0×10^{-6} M with a detection limit of 5.0×10^{-7} M.

Proposed reaction mechanism

The Job's plot was carried out to prove the complex ratio of **P** with Al^{3+}. Total concentration of **P** and Al^{3+} was kept at a fixed 50 μM. The results showed that the fluorescent emission intensity leak of **P**-Al^{3+} complex appeared at 0.5, which firstly indicated the 1:1 mole ratio of **P**-Al^{3+} complex, and the reaction mechanism was given in Scheme 2.



Scheme 2. Proposed binding mode of P with Al^{3+}

Conclusions

A novel Al^{3+}-selective fluorescent probe derived from naphthalene was constructed. Al^{3+} could induce an obvious enhancement of the fluorescent property of **P** and achieved "off-on" effect.

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