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SYNTHESIS AND CHARACTERIZATION OF A NEW Al3+-SELECTIVE PROBE BASED ON NAPHTHALIMIDE DERIVATIVE

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ABSTRACT

A naphthalimide derivative was successfully synthesized and characterized as an Al3+-selective fluorescent probe. An obvious red-shift of the signal was observed in the presence of Al3+ in ethanol solution. This proposed probe exhibited a dynamic response range for Al3+ from 1.3 × 10^{-6} to 7.0 × 10^{-6} M with a detection limit of 8.2 × 10^{-7} M.

INTRODUCTION

Among the metal ions, aluminum is a non-essential element for living systems, but the ionic radius and charge of Al^{3+} makes it a competitive inhibitor of several essential elements like Mg^{2+}, Ca^{2+} and Fe^{3+}. (Das *et al*., 2013) Therefore, the methods to detect chelatable aluminum (Al^{3+}) in biological studies have attracted much attention recently. (Karak *et al*., 2012; Karak *et al*., 2012; Sen *et al*., 2012) However, the lack of spectroscopic characteristics and poor coordination ability compared to transition metals makes the detection of Al^{3+} has always been problematic. (Das *et al*., 2013) For this reason the development of Al^{3+} probes are comparatively more difficult than those of other metal ions. In general, Al^{3+} being a hard acid, prefers hard donor sites like N and O in its coordination sphere. As a result, most of the reported Al^{3+} probes contain mixed N and O donor sites. (Das *et al*., 2013; Sen *et al*., 2012; Zhao *et al*., 2011; Jiang *et al*., 2011; Xie *et al*., 2012; Zhang *et al*., 2015) With above-mentioned in mind, in this work a new Schiff base compound containing N and O donor sites was synthesized and successfully characterized as Al^{3+}-selective probe (Scheme 1).

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Experimental Section

Reagents and Instruments

All of the materials were analytical reagent grade and used without further purification. NMR spectra were measured with TMS as an internal standard. MS spectra were recorded on a Thermo TSQ Quantum Access Agillent 1100. Fluorescence emission spectra were conducted on a Hitachi 4600 spectrofluometer.

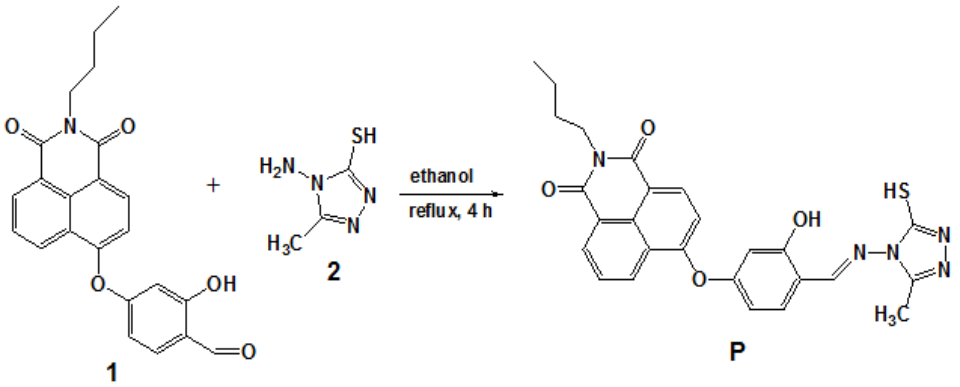
Synthesis

Compound 1 (Zhang *et al*., 2012) 69.6 mg (0.5 mmol) and 120.23 μL 2 (Li *et al*., 2015) (1.1 mmol) were mixed in ethanol (20 mL). The reaction mixture was stirred at 80 °C for 4 h, and then cooled to room temperature. The yellow precipitate so obtained was filtered and used directly. Yields: 85.6 %. MS (ES+) m/z: 502.43 $[M+H]^+$. ^{1}H NMR (δ ppm, DMSO-d_6): 11.41 (s, 1H), 9.24 (s, 1H), 7.80 (d, 1H, J = 7.72), 7.48 (s, 1H), 7.39 (d, 1H, J = 7.40), 7.30 (d, 1H, J = 7.12), 7.27 (d, 1H, J = 7.20), 7.13 (t, 1H, J = 7.38), 6.97 (d, 1H, J = 7.60), 6.89 (s, 1H), 6.83 (d, 1H, J = 7.56), 6.76 (d, 1H,

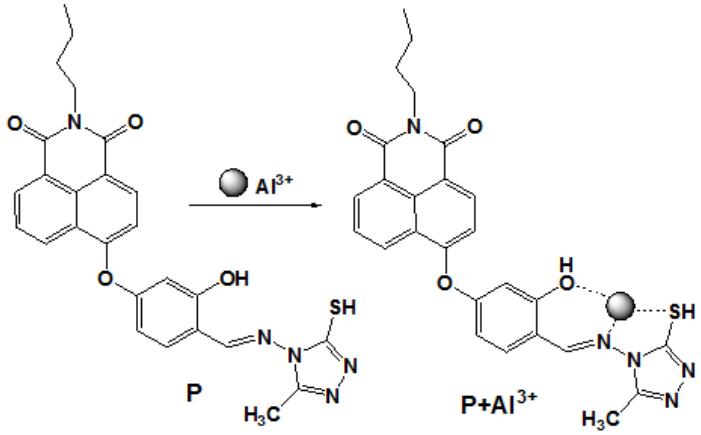
J = 7.36), 4.04 (t, 2H, J = 7.32), 2.23 (s, 3H), 1.62 (m, 2H, J = 7.41), 1.36 (m, 2H, J = 7.37), 0.93 (t, 3H, J = 7.35). ^{13}C NMR (δ ppm, DMSO-d_6): 163.83, 163.25 (C=O); 161.23, 159.41, 155.63, 150.64, 147.28, 135.14, 132.50, 131.38, 130.78, 129.00, 126.90, 125.08, 120.12, 119.93, 119.24, 118.54, 117.48, 116.75, 115.79, 36.25, 30.14, 20.27, 14.19, 13.29.

General spectroscopic methods

All of the fluorescence titration data were recorded at 25 °C. Test solutions were prepared by placing 50 μL of the P stock solution (1 mM) and an appropriate aliquot of individual ions stock solution into a test tube, and then diluting the solution to 5 mL with ethanol. For all fluorescent measurements, excitation and emission slit widths were 10 nm, respectively. Excitation wavelength was 380 nm.



Scheme 1. The synthesis route of the proposed probe P



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

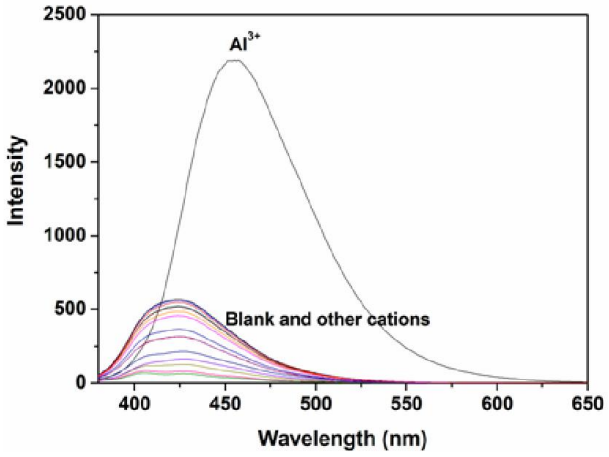


Figure 1. Fluorescence response of P (10 μM) with different metal ions (100 μM) in ethanol

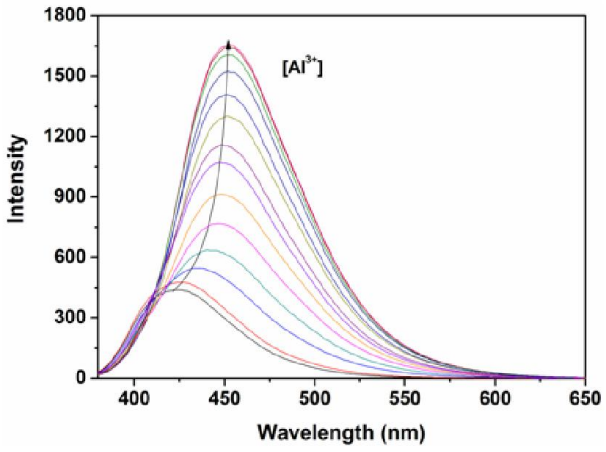


Figure 2. Fluorescence response of P (10 μM) with different concentrations of Al^{3+} in ethanol

RESULTS AND DISCUSSION

Selectivity of P

The fluorescent spectra (ex=380 nm) of P (10 μM) in ethanol with the addition of respective metal ions (K^+, Na^+, Ca^{2+}, Mg^{2+}, Pb^{2+}, Co^{2+}, Cd^{2+}, Ag^+, Zn^{2+}, Ni^{2+}, Hg^{2+}, Cr^{3+} and Fe^{3+}, 10 equiv.) was investigated to evaluate the selectivity of probe P (Figure 1). Compared to other tested ions, only Al^{3+} generated a significant "turn-on" fluorescent response at 460 nm with a red-shift signal. It suggested that P has a higher selectivity toward Al^{3+} than other metal ions.

Fluorescent titration experiment of P

The fluorescent titration experiment was carried out for further investigation of the interaction of Al^{3+} with the proposed probe P. Upon the titration with Al^{3+}, the fluorescence intensity of the monomer peak at 460 nm increased gradually (Figure 2), and the fluorescent intensity of P was proportional to the concentration of Al^{3+} in the range of 1.3×10^{-6} M to 7.0×10^{-6} M with a detection limit of 8.2×10^{-7} M Al^{3+}. This clearly demonstrated that probe P could sensitively detect environmentally relevant levels of Al^{3+}.

The proposed binding mode of P with Al^{3+}

The linear dependence of the intensity at 460 nm within the equivalent range of the Al^{3+} showed that a 1:1 complex was formed between P and Al^{3+}. Moreover, binding analysis using the method of continuous variations (Job's plot) was measured, and a maximum fluorescent intensity at 460 nm was observed when the molecular fraction of P was close to 0.5, which established the 1:1 complex formation between P and Al^{3+}. Thus, according to the obtained results and reported work, the binding mode of P and Al^{3+} was proposed as shown in Scheme 2.

Conclusions

In summary, an "off-on" type probe P for Al^{3+} was presented. The conception may expand a promising approach to develop new fluorescent probes for Al^{3+} and lead to the development "off-on" type probes for other metal ions.

Acknowledgments

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