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RESEARCH ARTICLE

PHOTOCHEMICAL RESPONSES OF THREE SCHIFF BASES DERIVED FROM BENZOYL HYDRAZINE: A COMPARATIVE STUDY

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ABSTRACT

Three Schiff bases P_{1-3} derived from benzoyl hydrazine was synthesized and characterized. Study revealed that P_1 with –OH as substitute had good selectivity to Al^{3+}, other two compounds P_{2-3} did not show any selective property. These results indicated that different active groups in the probe system had great effect on the selectivity and sensitivity. P_1 was characterized as an Al^{3+}-selective fluorescent probe in detail.

INTRODUCTION

Since the fluorescent probes have the advantages, such as good selectivity and high sensitivity in the detection of environmental and biological relative targets, there is a fast develop in this fields (1-3), and many researchers in the world focused on the development of design and synthesis of new probes (4-6). The fluorescent properties of probe was affected by the active groups in the probe system (7-10), so the comparative study of compounds derived from same chromophore bearing different substitutes is helpful to find suitable coordination group for certain targets. According to the reported works, increasing exposure to Al^{3+} poses a severe threat to biospheres and human health because of human activities in the environment. The average daily human intake of aluminium is 3–10 mg/d, and the tolerable weekly aluminium intake in the human body is estimated to be 7 mg/kg body weight (1). Thus, the detection of Al^{3+} is of great important (1,4,5). Based on the above-mentioned reasons, three different compound bearing –OH (P_1), -NH_2 (P_2) and -H (P_3) as substitutes were synthesized. Study showed that only P_1 has selectivity to Al^{3+} among the tested ions. So P_1 was characterized as Al^{3+}-selective fluorescent probe in detail. The synthesis route of P_{1-3} was shown in Scheme 1.

Experimental Section

Reagents and Instruments: All reagents and solvents are commercially available and used without further treatment. Mass (MS) spectra were recorded on a Thermo TSQ Quantum Access Agillent 1100 system. Fluorescence emission spectra were conducted on a Hitachi 4600 spectrofluorimeter. UV-Vis spectra were obtained on a Hitachi U-2910 spectrophotometric. Nuclear magnetic resonance (NMR) spectra were measured with a Bruker AV 400 instrument and chemical shifts are given in ppm from tetramethylsilane (TMS).

Synthesis of Probe P_{1-3}: Under N_2 gas, 20 mL ethanol solution of compound **1** (0.15 mmol) was added drop by drop to 30 mL ethanol containing compound **2** (0.31 mmol). Then, the mixture was stirred under reflux for 4 h and cooled to room temperature. The precipitate so obtained was filtered and dried in vaccum. The product was used directly without further purification.

P_1. Yields: 83.2%. MS m/z: 291.32 $(M+H^+)^+$. ^1H NMR (DMSO-d_6): 11.94 (s, 1H), 11.88 (s, 1H), 9.12 (s, 1H), 8.91 (d, 1H), 8.02 (t, 1H), 7.94 (d, 1H), 7.66 (t, 1H), 7.62 (t, 1H), 7.59 (t, 1H), 4.78 (d, 1H), 7.46 (s, 1H), 7.44 (d, 1H), 7.00 (t, 1H), 6.99 (d, 1H).

P_2. Yields: 81.8%. MS m/z: 290.24 $(M+H^+)^+$. ^1H NMR (DMSO-d_6): 11.69 (s, 1H), 9.04 (s, 1H), 8.88 (d, 1H), 8.01 (d, 2H), 7.89 (d, 1H), 7.65 (t, 1H), 7.61 (t, 2H), 7.58 (d, 1H), 7.22 (t, 1H), 6.77 (d, 1H), 6.60 (t, 1H), 6.45 (b, 2H).

P_3. 86.3%. MS m/z: 275.37 $(M+H^+)^+$. ^1H NMR (DMSO-d_6): 11.94 (s, 1H), 9.11 (s, 1H), 8.87 (d, 1H), 8.02 (t, 2H), 7.97 (d, 2H), 7.93 (d, 1H), 7.67 (t, 1H), 7.62 (d, 1H), 7.60 (d, 2H), 7.55 (t, 2H).

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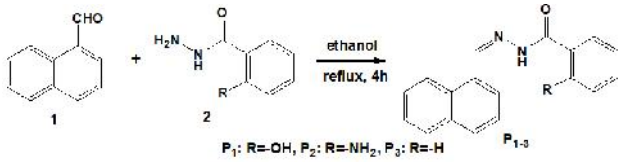


Scheme 1 Synthesis route of P_{1-3}

General Spectroscopic Methods: Metal ions and P_{1-3} were dissolved in deionized water and DMSO to obtain 1.0 mM stock solutions, respectively. The solution was freshly prepared by diluting the high concentration stock solution. 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.

RESULTS AND DISCUSSION

Selectivity measurements: Good selectivity is a necessary characteristic for probes. So the selectivity of probes P_{1-3} (10 μM) were investigated in ethanol with the addition of respective metal ions (100 μM). The testing metal ions were Na^+, K^+, Ag^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, Pb^{2+}, Co^{2+}, Cd^{2+}, Cu^{2+}, Fe^{2+}, Ni^{2+}, Hg^{2+}, Cu^{2+}, Fe^{3+}, Al^{3+} and Cr^{3+}.The results showed only the addition of Al^{3+} caused the enhancement of fluorescent intensity of P_1 at 435 nm (Figure 1a), P_{2-3} had no selectivity to tested metal ions (Figure 1b-c). So P_1 was characterized as an Al^{3+}-selective probe in detail.

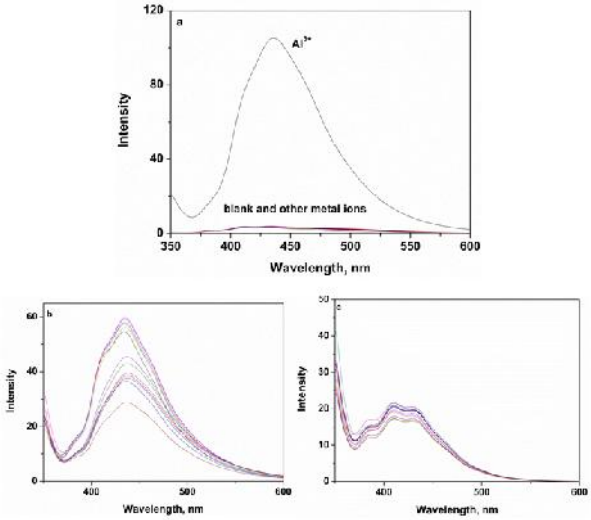


Figure 1. Selectivity measurements of P_{1-3} (10 μM) with tested metal ions (100μM) in ethanol

Fluorescent titration of P_1 with Al^{3+}: In order to study the reaction between P_1 and Al^{3+}, fluorescent titration experiment was carried out (Figure 2). From the results we could include that with the increase of content of Al^{3+} the fluorescent intensity enhanced accordingly.

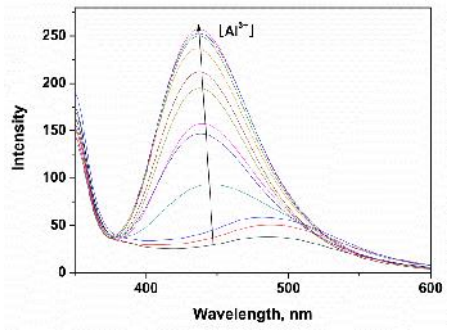


Figure 2. Fluorescent titration experiment of P_1 (10 μM) with Al^{3+} (0-10 μM) in ethanol

Binding mode study of P_1 with Al^{3+}: Job' plot experiment was conducted to study the binding mode of P_1 with Al^{3+} (Figure 3). When concentration ratio of $(Al^{3+})/(P)$ was 1:1, the fluorescent intensity reached maximum, which indicated that the stoichiometry ratio of P_1 and Al^{3+} was 1:1. According to the results obtained as above-mentioned, the binding mode of P_1 with Al^{3+} was proposed as shown in Scheme 2, and the N (-C=N) and O (-C=O and –OH) participate in the coordination process of P_1-Al^{3+}.

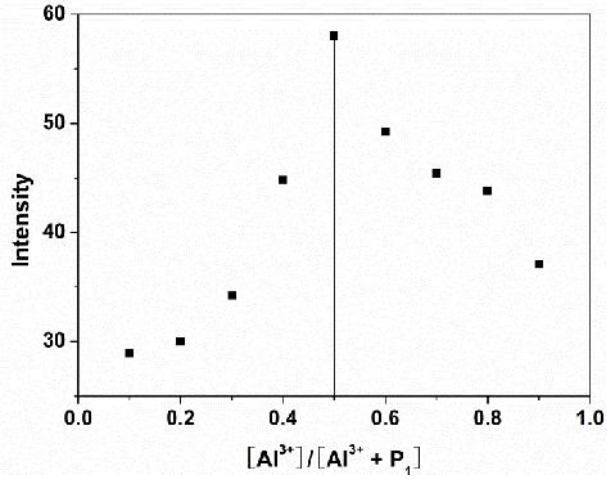
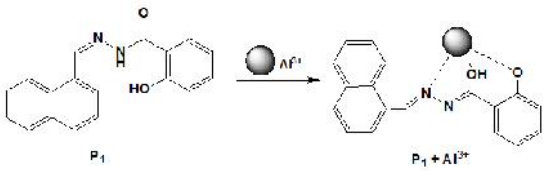


Figure 3. Job's plot of P_1-Al^{3+}. Total concentration of P_1 and Al^{3+} was kept as 10 μM



Scheme 2. Proposed binding mode of P_1 with Al^{3+}

Conclusion

Three benzohydrazide derivatives were synthesized and characterized, study showed that active groups had great effect on the fluorescent properties of the proposed compounds. We believe that this study will significantly promote the development of effective Al3+-selective probes.

Acknowledgements

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