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A Comparative Study of Three Fluorescent Probes Derived from Benzoyl Hydrazine

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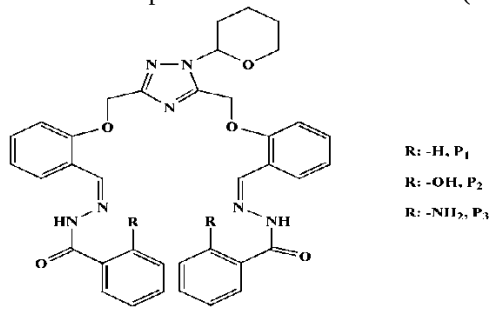
Abstract *- Functional groups have a big effect on the selectivity and sensitivity of fluorescent probes, and many new fluorescent probes with different active groups were proposed every year. However, the most focused on the characterization of a single probe, system study of probes with similar structure and different active groups were rarely reported. In this work, three fluorescent probes derived from benzoyl hydrazine with different functional groups (-H, -OH, and -NH_2) were comparatively studied. Results showed that the probes' selectivity was mainly decided by the active group's property bearing with the probes.*

Keywords — *Fluorescent probes; Active groups; Benzoyl hydrazine derivative; Heavey metals; Synthesis*

I. INTRODUCTION

Because of the advantages such as good selectivity and high sensitivity, fluorescent probes have been widely used to detect environmentally relative targets [1-4]. The design and synthesis of new probes with excellent performance are still interesting in this research area.[5-7] Since the probes' selectivity and sensitivity are affected by the active groups in the probe system,[6-9] so the comparative study of probes derived from the same chromophore with different active groups can provide a useful message for the construction of new probes. In this work, three probes derived from benzoyl hydrazine with -H, -OH, and -NH_2 as functional groups were studied, and the influence of the active groups on the performance of the probes were studied in detail (**Scheme 1**).



Scheme 1 Structure of probes

II. EXPERIMENTAL SECTION

A. Reagents and Instruments

The reagents were commercially available and used without further treatment. NMR spectra were measured with TMS as an internal standard. MS spectra were recorded on a Thermo TSQ Quantum Access Agilent 1100. Fluorescence emission spectra were conducted on a Hitachi 4600 spectrofluorometer. The pH values were measured with a pH-meter PBS-3C.

B. Synthesis of P_{1-3}

P_{1-3} was synthesized as a reported method.[10,11]

C. General spectroscopic methods

All of the fluorescence spectra were recorded at room temperature (25 ºC). Test solutions were prepared by placing 50 μL of the probe stock solution (1 mM), an appropriate aliquot of individual ions stock solution into a test tube, and then diluting the solution to 5 mL. For **P_{1-2}** fluorescent measurements, excitation and emission slit widths were 10/10 nm, and the excitation wavelength was 360 nm. The testing media was ethanol. For **P_3** fluorescent measurements, excitation and emission slit widths were 5/10 nm, and the excitation wavelength was 335 nm; the testing media was the ethanol-water solution (8:2, v:v, pH6.3, 50 mM HEPES).

III. RESULTS AND DISCUSSION

A. Selectivity of P_{1-3}

The selectivity of the proposed probes **P_{1-3}** was firstly studied in ethanol. Compared to other tested metal ions (K^+, Na^+, Ca^{2+}, Mg^{2+}, Pb^{2+}, Co^{2+}, Cu^{2+}, Cd^{2+}, Ag^+, Zn^{2+}, Ni^{2+} and Hg^{2+}), the proposed probes **P_{2-3}** have good selective property to Al^{3+} and Fe^{3+}, respectively. However, **P_1** has no obvious selectivity. The addition of Al^{3+} to the **P_2** system and Fe^{3+} to the **P_3** system generated a significant "turn-on" fluorescent response at 440 nm and 420 nm, respectively (**Figure 1**, **Figure 2**[11]). It suggested that **P_2** and **P_3** have a better selectivity and sensitivity toward Al^{3+} and Fe^{3+} than other tested metal ions.

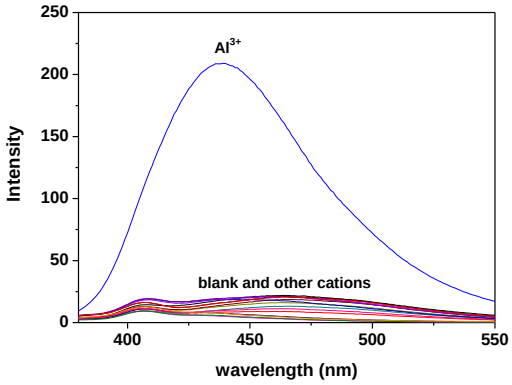


Fig. 1 Fluorescence response of P_2 (10 μM) with different metal ions (100 μM) in ethanol

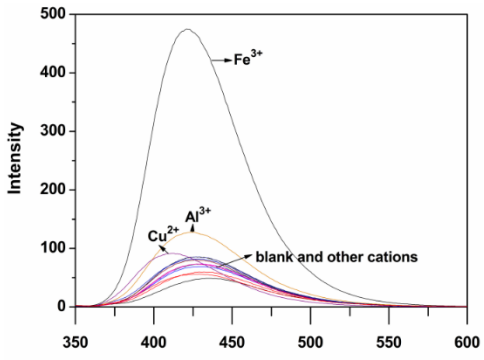


Fig. 2 Fluorescence response of P_3 (10 μM) with different metal ions (100 μM) in ethanol-water solution (8:2, v:v, pH 6.3, 50 mM HEPES)

B. Water effect on the fluorescent response of P_{2-3}

The effect of water on the response of **P_{2-3}** was also studied. The results showed that water has a big influence on the fluorescent response of P2, and fluorescence quenching was observed with water in the testing system. Hence, it limited the use of **P_2** in environmental samples. Water effect on **P_3** was slightly observed, and it can be used in the ethanol-water solution (8:2, v:v, pH6.3, 50 mM HEPES)[11], which greatly expands the scope of use.

C. Effect of functional groups on the response of P_{1-3}

From the selectivity study, we can see that different functional groups greatly influenced probes' responses to targets. **P_1** did not have any selectivity to the testing ions because there are not enough active groups to coordinate with metal ions. According to the soft-hard acid-base theory, Al^{3+} shows good affinity to groups with O atom, so **P_2** shows good selectivity to Al^{3+},[12-14] and the lone pair electrons of N in the $-NH_2$ groups of **P_3** are easy to transfer and coordinate with Fe^{3+}.[15] All results are following this theory.

IV. CONCLUSIONS

In summary, three benzoyl hydrazine derivatives bearing different groups were synthesized and characterized. The results showed that active groups in the probe system significantly affect the probe's selectivity and sensitivity. The conception may expand a promising approach to developing selective detection methods for targets and lead to the development of "off-on" type probes for other metal ions.

V. ACKNOWLEDGMENT

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