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RESEARCH ARTICLE

DESIGN, SYNTHESIS AND APPLICATION OF FLUORESCENT PROBES BASED ON PYRENE FLUORESCENT GROUPS

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ABSTRACT

Fluorescence probe method is widely used for the detection of environmental target substances due to the advantages of high selectivity and stability. This paper used pyrene as the fluorescent group, introduced excellent coordination groups, and constructed a new type of highly selective fluorescent probe. Probe P was highly selective for Cu^{2+}over other metal ions. With the increase of Cu^{2+} concentration, the fluorescence intensityat463nm increased with a linear correlation from 1.0 to 9.0 μ M, and a minimum detection limit of 0.33μM.

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INTRODUCTION

Due to the environmental problems brought about by industrial development, some heavy metal ions remain in the environment, causing serious harm to the environment and endangering life forms in nature. As the food chain enters the human body, it poses a serious threat to human life and health. Metal ions are widely present in nature and play a crucial role and impact on organisms and the surrounding environment (Yang, 2018 and Jarczewska, 2022). The content balance of various metal ions is also closely related to human health and ecological balance, (Săcărescu, 2022 and Wang, 2022). However, due to the rapid development of industry and technology, a large amount of metal ions were discharged into the environment (Du, 2022; Xv, 2022; Dong et al., 2023). Therefore, efficient and sensitive fluorescent probes have received widespread attention (Gao, 2022 and Li, 2019); The detection of heavy metal ions has been a research hotspot in recent years (Ding, 2022 and Liu, 2020). Generally speaking, fluorescent probes typically include two parts: a recognition unit (receptor) and a signal unit (Chen, 2018 and Zhang, 2023). The former is used for selective binding with the tested species (guest), while the latter displays this binding effect through specific signal forms. The recognition unit and signal unit can be covalently bound or non covalently bound (Liu, 2022; Kakimoto, 2023 and Gálico, 2022). Pyrene luminescent groups, as polycyclic aromatic hydrocarbons, have excellent fluorescence properties, and their derivatives have abundant π electron, which also makes pyrene derivatives have excellent optical transmittance in the visible light region (Lv, 2023; Xiong, 2022; Gümüş, 2022; Chen, 2019; Yu, 2018 and Li, 2019).

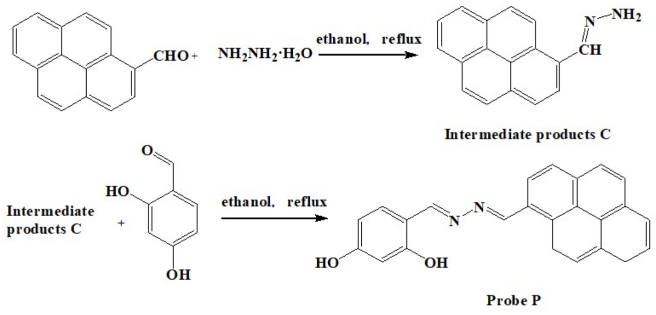
Based on this, pyrene as the fluorescent group and oxygen-containing functional fragments as the excellent coordination groups were be combined to construct a new type of Cu^{2+} selective fluorescent probe. Meanwhile, testing conditions, sensitivity and selectivity were also studied.

EXPERIMENTAL SECTION

Reagents and Instruments: All reagents were commercially available and used directly. The reagents used in the experiment were pyrene-1-formaldehyde, 2,4-dihydroxybenzaldehyde,hydrazine hydrate, N-2-hydroxyethylpiperazine-N-2-ethylene sulfonic acid (HEPES), dimethyl sulfoxide, and anhydrous ethanol. The metal ions used in experiments were chlorides and anions were potassium or sodium salts. The reagents used were all analytical pure, purchased from Aladdin Chemical Reagents Co., Ltd., and no other treatment reactions were performed before use. UV-vis spectra were carried on a Hitachi U-2910 spectrophotometric. Fluorescent spectra were recorded using a Hitachi F-4600spectrofluometer.

Synthesis of Probe P: Synthesis route of P was shown in Scheme 1. Synthesis of intermediate product C: 0.4 g of pyrene-1-formaldehyde was added into a round bottom beaker. Then 16 mL (6 times excess) of 85% hydrazine hydrateandappropriate amount of 50 mL ethanol were also added. The reaction was heated and refluxed in an oil bath for 4 h, After that, it was cooled to room temperature. The solid C was obtained by filtration (263.0 mg, yield 61.98%).

Synthesis route of P was shown in Scheme 1.



Scheme 1. Synthesis route of P

Synthesis of probe P: 150 mg C and 85 mg 2,4-dihydroxybenzaldehyde were added into a round bottom beaker. Then appropriate amount of 50 mL ethanol was also added until the solid was completely dissolved. The reaction was heated and refluxed in an oil bath for 6 h. After that, it was cooled to room temperature. Probe P (167.8 mg, 74.99% yield) was obtained by filtration.

General Spectroscopic Methods: The stock solutions of P and metal ions (1.0 mM) were obtained by dissolving in deionized water and dimethylsulfoxide, respectively, and the testing solutions was freshly prepared before measurements by diluting the stock solutions.

RESULTS AND DISCUSSION

Selectivity Measurement: The selectivity of probe P was firstly studied using fluorescent method. The tested metal ions were K^+, Na^+, Mg^{2+}, Ca^{2+}, Cd^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Pb^{2+},Fe^{2+},Ni^{2+}, Hg^{2+},Al^{3+} andCr^{3+}. Among the tested ions, only the addition of Cu^{2+} (100μM) caused an obvious fluorescent enhancement at 463 nm, other metal ions caused a negligible spectra change, which didn't affect the detection of Cu^{2+} (Fig. 1). All these results showed that the probe P had a good selectivity to Cu^{2+} compared to other tested metal ions.

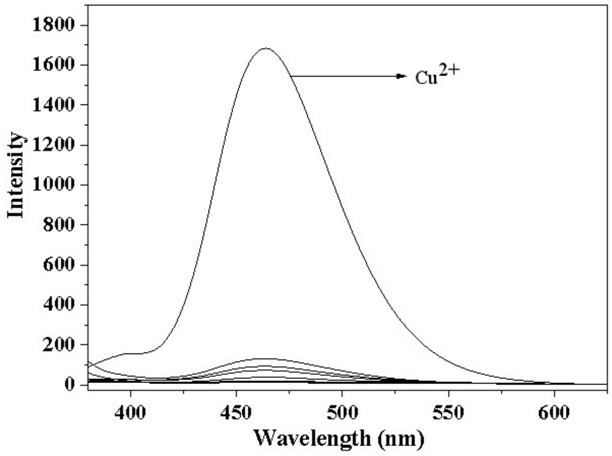


Fig. 1. Selectivity of probe P(10 μM) for different metal ions(100μM)in water-ethanol solution (3:7, V/V, pH 6, 20 mM HEPES)

Effect of water content and pH on Cu^{2+} recognition: The water content and pH had great influence on fluorescence properties. As the water content decreased, the fluorescence intensity gradually increased at 463 nm. By calculating the ratio of the control group to the blank group, the maximum ratio of 3:7(V/V) in the water-ethanol system was selected as the medium for subsequent testing (Fig. 2a). The effect of pH on the fluorescence performance was also examined. In the range of pH 4-6, the fluorescence intensity fluctuated less up and down, but the intensity at 463 nm began to decrease significantly after pH 6.5. pH 6 was selected for subsequent experimental studies (Fig. 2b).

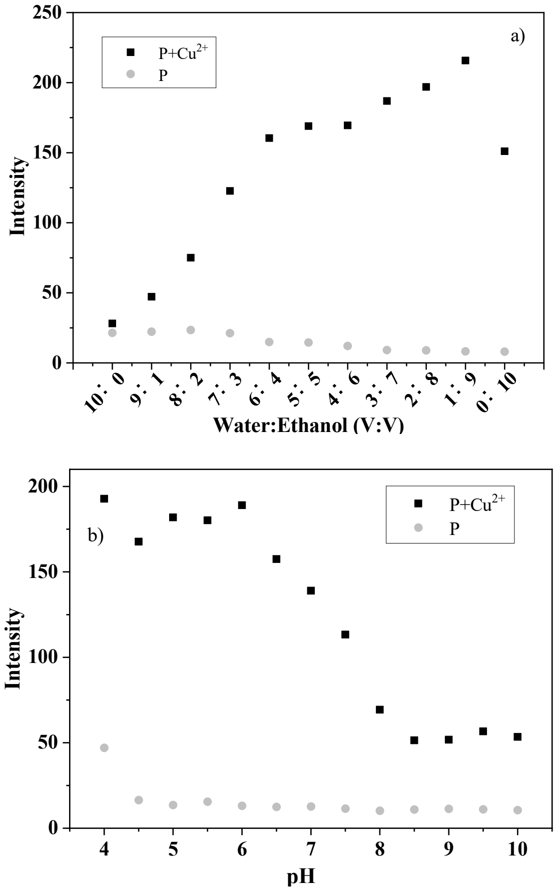


Fig. 2(a) Effect of water content on the recognition of Cu^{2+} (100 μM) by probe P (10 μM); (b) Effect of pH on Cu^{2+} (100 μM) recognition by probe P (10 μM)

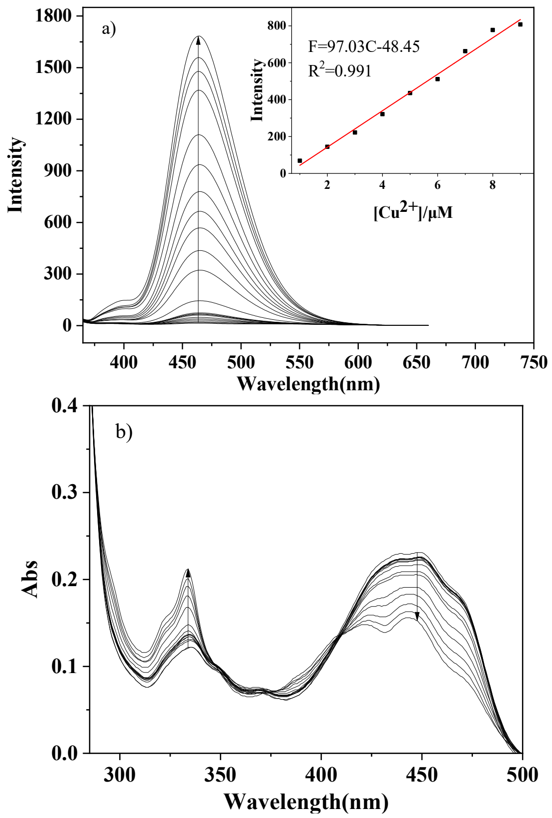


Fig. 3(a) Fluorescence titration spectra of probe P (10 μM) at different concentrations of Cu^{2+} (0.1-10 μM); (b) UV absorption spectra of probe P (10 μM) with different concentrations of Cu^{2+} (0.1-10 μM) in water-ethanol solution (3:7, V/V, pH 6, 20 mM HEPES)

Titration experiment of P with Cu^{2+}: Fluorescent titration experiment was carried out for the further study of P withCu^{2+}. It could be seen that the fluorescent intensity at 463nm enhanced with the increase of Cu^{2+}, and a linear relationship was found in the range of 1.0-9.0 μM with a detection limit of 0.33 μM (Fig.3a). The influence of Cu^{2+}concentration change on absorbance was further investigated. It was found that with the increase of Cu^{2+}, absorbance at 330 nm also increased regularly, which was accompanied by a decrease in absorbance at 440 nm. These results indicated that the probe can be used for quantitative analysis of Cu^{2+}, which laid a foundation for future sample detection.

CONCLUSIONS

In summary, a Cu^{2+} selective fluorescent probe was successfully characterized, compared other tested metal ions, this probe showed good selectivity and sensitivity to Cu^{2+}. This study could facilitate the development of the Cu^{2+} fluorescent probes

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