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ISSN : 2350-0743

International Journal of Recent Advances in Multidisciplinary Research
Vol. 08, Issue 05, pp. 6837-6839, May, 2021

RESEARCH ARTICLE

Hg^{2+}-FLUORESCENT PROBE BASED ON NAPHTHALIMIDE DERIVATIVE

Yu Lin, Mao Haiqing, Liu Ang and Yu Chunwei*

Laboratory of Environmental Monitoring, School of Tropical and Laboratory Medicine, Hainan Medical University, Haikou, 571199

ARTICLE INFO

Article History:
Received 20th February, 2021
Received in revised form
15th March, 2021
Accepted 18th April, 2021
Published online 30th May, 2021

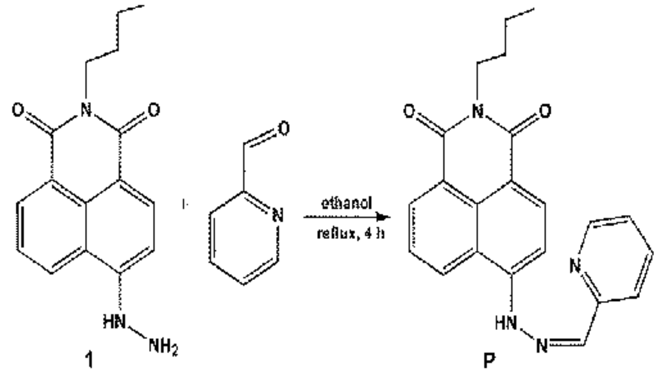
Keywords:
Naphthalimide,
Fluorescent probe, Hg^{2+}

ABSTRACT

Naphthalimide has been widely used in probe research because of its unique structure. Therefore, using naphthalimide as matrix, a compound P was obtained by the reaction of pyridine-2-formaldehyde with naphthalimide derivative. Among the tested metal ions, the addition of Hg^{2+} to the solution of P in ethanol quenched the fluorescence of P at 525 nm, and a linear relationship between fluorescent intensity tothe concentration of Hg^{2+} in the range of 2.0×10^{-6}-1.6×10^{-5} M was observed.

INTRODUCTION

Mercury is a highly toxic environmental pollutant that exists widely in the world. Various forms of mercury are widely found in nature, posing a threat to wildlife, human safety and ecological environment health [1]. Mercury in nature can accumulate in humans through the food chain, leading to widespread exposure risks[2]. Mercury is a chemical substance with serious physiological toxicity, which can be ingested by human body through breathing, food, drinking water, etc. After mercury is ingested, it is difficult to be excreted, and excessive mercury inhalation will cause mercury poisoning [3]. At present, commonly used metal detection methods include inductively coupled plasma-atomic emission spectrometry [4], inductively coupled plasma-mass spectrometry [5], electrochemical method [6], atomic fluorescence analysis [7] and other methods. Although these methods have the advantages of automation and intelligence, they are costly, cumbersome and can be applied in organisms. Fluorescent probe imaging technology is widely used in intracellular analytical sensing and optical imaging due to its advantages of simplicity, directness, good selectivity, high sensitivity and in situ visualization [8-11]. Therefore, it has been widely studied by scholars. In recent years, several excellent metal ion fluorescent probes have been developed and reported[12,13]. Naphthalimide has been widely studied for a long time, and has been widely used in the fields of fluorescent brighteners [14-18], organic photoelectric materials [19], DNA immobilizers and anti-tumor drugs [20,21]. Naphthalimide fluorescent probes have excellent biocompatibility and can be used for confocal imaging in biological cells, and the structure of these probes is simple and easy to modify. Zhang [22], such as synthesis and reported a new type of 1, 8-naphthalene imide type ratio fluorescent probes, use isocyano group modified. It showed good selectivity to Hg^{2+} in the solvent of tetrahydrofuran-water (THF-H_2O) (v/v=3/7, pH 7.4). The probe can be used to detect Hg^{2+} in aqueous media with relatively high water content. Wang et al. designed, synthesized and reported a fluorescent probe for detection of Fe^{2+} based on naphthimide fluorophore [23]. The probe produces a strong green fluorescence with Fe^{2+}. Moreover, the probe has a fast response (15 min), high selectivity and a detection limit of 0.5 μM. Based on this, a fluorescent probe based on naphthalimide was designed and synthesized in this paper for the detection of Hg^{2+}. The probe synthesis route is shown in Scheme 1.



Scheme 1. Synthesis route of probe P

Corresponding author:** ***Yu Chunwei,
Laboratory of Environmental Monitoring, School of Tropical and Laboratory Medicine, Hainan Medical University, Haikou, 571199.

METHODS AND MATERIALS

Reagents and Instruments: All reagents and solvents are commercially available and used directly. Fluorescence emission spectra were measured on a Hitachi F-4600 spectrofluometer. UV-Vis spectra were obtained on a Hitachi U-2910 spectrophotometer. Mass (MS) spectra were recorded on a Thermo TSQ Quantum Access Agillent 1100. pH values were conducted on a pH-meter PBS-3C.

Synthesis of P: Compound 1 was synthesized as reported method [24]. Under N_2 atmosphere, compound 1 (98.8 mg, 0.35 mmol) and pyridine (33 μL, 0.36 mmol) were mixed in 20 mL ethanol, and then stirred under reflux for 4 h. After the reaction was finished, the precipitate was filtered off and recrystallized by ethanol to get pure P. Yields: 78.5%. ^{1}H NMR (DMSO-d_6): 11.66 (s, 1H), 7.79 (d, 1H, J=7.60), 8.61 (d, 1H, J=4.80), 8.49 (d, 1H, J=7.20), 8.47 (s, 1H), 8.39 (d, 1H, J=8.00), 8.10 (d, 1H, J=8.00), 7.88 (t, 1H, J=8.60), 7.81 (t, 1H, J=8.60), 7.38 (t, 1H, J=6.80), 7.80 (d, 1H, J=8.00), 4.02 (t, 2H, J=7.60), 1.59 (m, 2H, J=7.40), 1.34 (m, 2H, J=7.44), 0.91 (t, 3H, J=7.20).

General Spectroscopic Methods: The stock solutions (1.0 mM) of metal ions and P were obtained by dissolving the relative salts and P in deionized water and DMSO, respectively. For all measurements, excitation wavelength was 430 nm, and the excitation and emission slit widths were all 10 nm.

RESULTS AND DISCUSSION

Selectivity Measurement of P: Selectivity of probe P (10 μM) was firstly measured and the testing ions used in this work were Hg^{2+}, Na^+, K^+, Ag^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Co^{2+}, Zn^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, Cr^{3+} and Al^{3+} (10 μM), respectively (Figure 1). The results showed that the addition of Hg^{2+} caused an obvious of fluorescent quenching of P in ethanol compared to other tested metal ions. So, the proposed probe P was characterized a Hg^{2+}-selective fluorescent probe in ethanol.

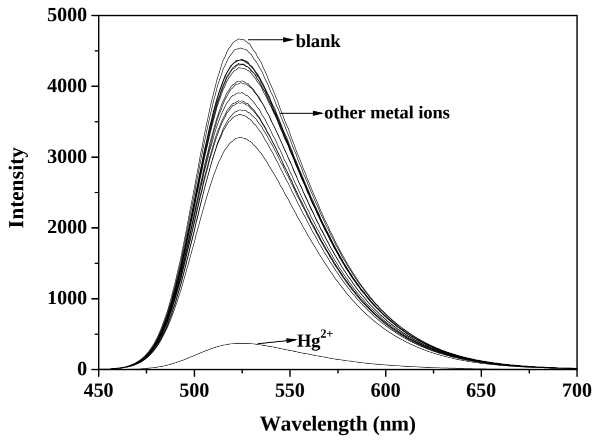


Figure 1. Fluorescence selectivity of P (10 μM) with tested metal ions (10 μM)

Sensitivity behaviour of P for Hg^{2+}: Sensitivity of P to Hg^{2+} was examined by titrating different concentration of Hg^{2+} to the P solution in ethanol (Figure 2). With the increase of the concentration of Hg^{2+}, the fluorescent intensity decrease at 525 nm gradually, and showed a linear response in the range of 2.0×10^{-6}-1.6×10^{-5} M Hg^{2+} with a detection limit of 8.5×10^{-7} M.

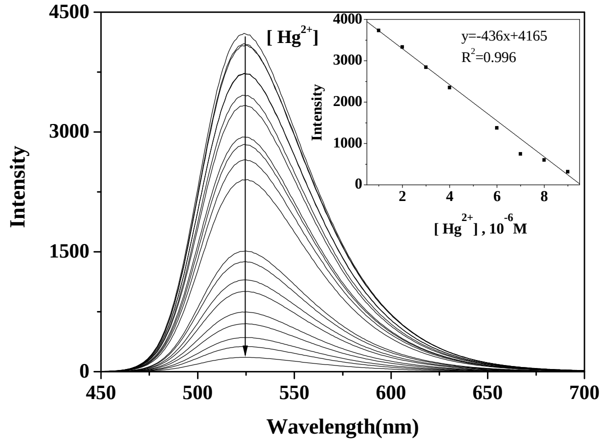


Figure 2. Fluorescence diagram of increasing Hg^{2+} (0-1.0×10^{-5} M) in P (1.0×10^{-5} M)

The proposed reaction mechanism: According to the results above mentioned, the coordination mode of P-Hg^{2+} was proposed as shown in Scheme 2. The N atoms of pyridine rings and C=N groups participated inthe formation of P-Hg^{2+} complex.

Conclusion

In summary, the coordination property of a new compound was studied in detail. The results indicated that this compound had good selectivity to Hg^{2+} compared to other tested metalions. We believe that this study will significantly promote the development of effective ligands for the selective detection of metal ions.

Acknowledgment

This work was financially supported by the Natural Science Foundation of Hainan Province (No. 820RC626), the Research and Training Foundation of China (No. X201911810134) and the National Natural Science Foundation of China (No. 81760387, 81860381).

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