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Research Paper

A pyridinyl-organoboron complex as dual functional chemosensor for mercury ions and gaseous acid/base



Yuyang Zhang^a, Gaobin Zhang^a, Ruilong Zhang^a, Longmei Yang^{a,*}, Xianyun Xu^a, Lin Kong^a, Yupeng Tian^a, Jiaxiang Yang^{a,b,**}

- a College of Chemistry & Chemical Engineering, Anhui University and Key Laboratory of Functional Inorganic Materials of Chemistry of Anhui Province, Hefei 230601, PR China
- ^b State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, PR China

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ABSTRACT

Recently, most of fluorescent sensors have been focused on in diluted solutions because $\pi^-\pi$ stacking of traditional fluorescent materials would quench their emissions in solid state, and meanwhile some fluorescent materials in aggregation were reported as chemosensors to detect target analytes although they always were involved in photonic and electronic devices. Fluorescent probes in both the diluted solutions and aggregation have scarcely been developed in reported works. In this study, we report a novel pyridinyl-organoboron complex as a probe to detect mercury ions (Hg^{2+}) in diluted solution and gaseous acid/base in aggregation. The as-synthesized probe with strong fluorescence contained a pyridine unit, as the reactive site of both Hg^{2+} and gaseous acid in the environmental monitoring. Upon the addition of Hg^{2+} , the fluorescence ratio of I_{480}/I_{515} was changed immediately accompanying with the color variation from cyan to green under a UV lamp. On the other hand, the complex probe was prepared as a film on a glass pallet for the detection of gaseous acid with the emissive color evolution from yellow to orange-red. Interestingly, the film sensor for acid/base gas had a reversible property with 10 cycles at least due to its much higher photostability.

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1. Introduction

Fluorescent materials have been drawn more and more attention due to their wide applications in the fields of sensors, bio-imaging, light emitting diodes, and so on [1–10]. The traditional fluorescent dyes such as fluorescein and Rhodamine B display excellent fluorescent properties with strong emissions in diluted solutions, but they cannot emit strong fluorescence in aggregation resulting from the strong π - π stacking between adjacent molecules [11–13]. To overcome these disadvantages of traditional dyes, considerable efforts have been devoted to the development of aggregation-induced emission (AIE) materials, which can emit strong fluorescence in solid state by the inhibition of σ -bond rotations in molecules [14–18]. However, most of AIE materials cannot give strong emission with their optimal excitation wavelengths in

E-mail addresses: ylm@ahu.edu.cn (L. Yang), jxyang@ahu.edu.cn (J. Yang).

diluted solution. Namely, the common fluorescent materials can be used as the precursors to synthesize chemosensors which produce fluorescent signals change in either solutions or solid state rather than in both two states, largely compressing the application ranges of fluorescent dyes. Therefore, there is an urgent demand to develop the materials with strong fluorescence in both monomer and aggregation states. Moreover, the fluorescent dyes still have to face with other serious disadvantages, such as very weak photostability [19–22].

To obtain an excellent material with strong fluorescence in both monomer and aggregation, it is important to select an appropriate fluorophore and then modify its structure. As a candidate, organoboron complexes having high fluorescence quantum yields and good photostability can satisfy with these demands [23–27]. In the present work, we reported a pyridinyl-organoboron complex (**POB**), achieving to detect mercury ions (Hg^{2+}) in diluted solution and acid gas in atmosphere. In molecular structure of **POB**, the introduced *N*,*N*-diethylamino group could effectively decrease the π - π interactions, and pyridine moiety played a key role to sense Hg^{2+} and acid gas in different states. In the environmental monitoring, Hg^{2+} and gaseous acid are important to evaluate the pollutions of water and air, respectively. As we known, Hg^{2+} is a highly toxic

^{*} Corresponding author.

^{**} Corresponding author at: College of Chemistry & Chemical Engineering, Anhui University and Key Laboratory of Functional Inorganic Materials of Chemistry of Anhui Province, Hefei 230601, PR China.

Scheme 1. Synthetic route of probe **POB**.

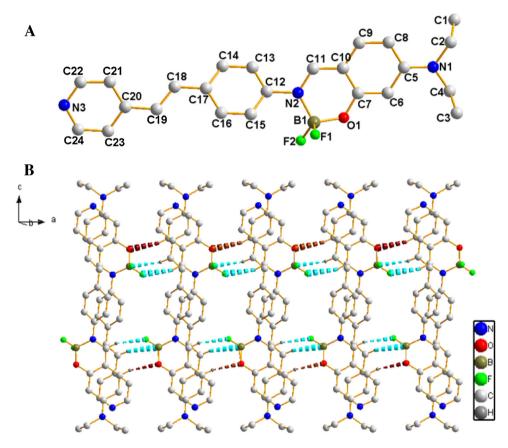


Fig. 1. (A) The crystal structure of POB. (B) Two-dimensional layer structure of POB viewed along b-axis. Hydrogen atoms except H9, H19 and H11 are omitted for clarity.

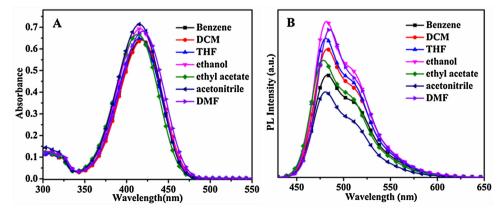


Fig. 2. (A) The UV-vis spectra and (B) fluorescence spectra of **POB** in different solvents (1×10^{-5} M).

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