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A functional applied material on recognition of metal ion zinc based on the double azine compound

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ABSTRACT

A colorimetric and fluorescent probe **L** has been designed and synthesized, which bearing the double azine moiety and showing a detection limit of 2.725×10^{-7} M towards Zn^{2+}. Based on the basic recognition mechanism of ESIPT and CHEF effect, the **L** has high selectivity and sensitivity to only Zn^{2+} (not Fe^{3+}, Hg^{2+}, Ag^{+}, Ca^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Cr^{3+}, and Mg^{2+}) within the physiological pH range (pH = 7.0–8.4) and showed a fluorescence switch. Moreover, this detection progress occured in the DMSO/H_2O ~ HEPES buffer (80/20, v/v; pH 7.23) solution which can conveniently used on test strip.

1. Introduction

Due to the effects of metal ions in the environment and human health, there are many selective chemo probes for these metal ions have been developed.[1] Living system and natural human health need quantitative intakes of most of the metal ions including heavy metal ions.[2–4] Zinc is one of the essential trace metal elements in the human body like ferrum[5] and copper,[6] which occupies an important position in various chemical, environmental and physiological systems. Although the majority of the biological zinc ions are tightly sequestered by proteins, free Zn^{2+} pools containing large amounts of Zn^{2+} exist in certain tissues, for example, high concentrations up to 0.1–0.5 mM of Zn^{2+} have been reported in brain tissues.[7] Moreover, the unregulated zinc level in the body may lead to a number of severe neurological diseases (e.g. Alzheimer's disease and epilepsy).[8–11] Thus, the detection and recognition for the metal ion zinc are necessary, and we need various convenient methods or chemical molecules to realize it. For example, Yang Wei and his coworkers[12] synthesized a Europium-based luminescent chemo probes for Zn^{2+} with quinoxaline; and Ajay Misra's group constructed a hydrazine to detect Zn^{2+}[13]. And it is imperative to search for more practical fluorescent probes for selective detection of zinc.

Field application requires the techniques which process wonderful selectivity, speedy sensitivity, consistency, and exclusively easy operation. Various methods have been reported to detect both the metal ions and anions such as atomic absorption spectroscopy,[14] inductively coupled plasma atomic emission spectrometry[15] and electrochemical methods.[16] This techniques employ convenient approaches to realize more accurate detection. And several methods require tedious sample preparation procedures, sophisticated instrumentation and trained operators. Fluorescence technology provides a convenient and ordinary method in the context of sensing of environmentally and biologically pertinent metal ions.[17] The literature reported one kind of fluorescent probes is composed of azine compounds.

Azine is a special kind of conjugate schiff base, which is a general term for unsaturated six membered heterocyclic or heteroatom compounds containing one or more nitrogen atoms. There are many kinds of compounds which process some structural similarity to the Azine compounds, such as pyridine, pyrimidine, triazine and thiophene, have being attached attentions in recent years.[18]

The structures of nitrogen atoms which contain lone pair

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electrons, can lead to the formation of coordination effect with many metals owing their outer space orbits. Supplemented by the ortho-oxygen and sulfur atoms on this kind of compounds, the research on it complied in the field of fluorescence detection becomes more and more active.[19] Azine, as a kind of fluorescence probe, contains great opportunity of sensitivity, selectivity, real-time and in situ detection effect.[20] On the other hand, Azine compounds as a kind of organic molecules, process great advantages in the fields of molecular design and structural characterization. And can employ its own distinctive chemical bonds, coordination bonds and unique spatial molecular conformation to selectively bind with specific metal ions, which shows high recognition ability and have attracted great interest of researchers.[21] According to these researches have been made, we synthesized a dialdehyde azine compound (**L**), which showed great opportunity of sensitivity and selectivity in the progress of detecting the metal ion Zn^{2+}.

2. Results and discussion

The synthesis course of chemical probe **L** was depicted in Scheme S1 and operation details were described in experimental section in the Supporting information. It was fully characterized by spectroscopic analysis and mass-spectrography. The ^{1}H NMR and ^{13}C NMR (Figs. S1–S6) spectra were used to confirm the structure and the purity of the probe. The ESI–MS (Fig. S7) spectrum showed the major peak at *m*/*z* 385.1021 [M–H]$^-$, which perfectly matched the estimated molecular weight of $[C_{22}H_{17}N_4O_3\text{- } H]^-$. IR (Fig. S8) spectrum for the molecule **L** showed a vibration band at 1654 cm^{-1} assigned to stretching vibrational mode of imine (-CH=N-) groups and a broad peak at 3469 cm^{-1} assigned to stretching vibrational mode of hydroxyl (-OH) groups.

In the fluorescence experiments of the probe **L** responsing to Zn^{2+}, we selected the DMSO/H_2O ~ HEPES buffer (80/20, v/v; pH 7.23) as solution for the target of excluding the possibility in fluence of pH fluctuation. As shown in Fig. 1, the **L** had no fluorescent nature with the excitation wavelength was at 425 nm, but an unique and new emission peak appeared at 520 nm when added 20 equiv. of Zn^{2+} into the solution of **L,** and the color of this complex shew fluorescently green.

To find the response property of the probe **L** to other various cations, such as Fe^{3+}, Hg^{2+}, Ag^{+}, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Cr^{3+} and Mg^{2+}, we added these cations according to the priority to DMSO/H_2O ~ HEPES buffer (80/20, v/v; pH 7.23) solutions of probe **L** no significant color or spectrum changes were observed (Fig. 2). Which Suggested that the probe **L** was a special recognition subject for Zn^{2+}.

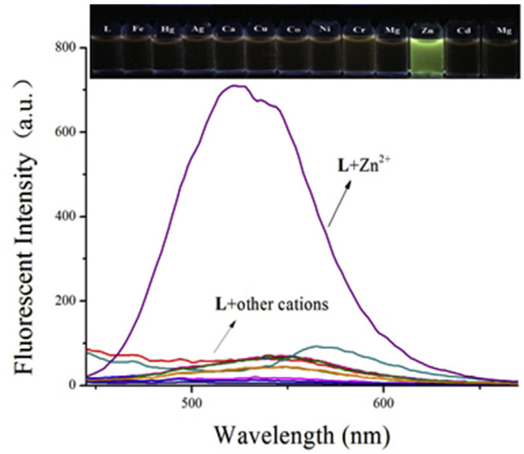

Fig. 2. Fluorescence spectra of probe **L** (2×10^{-5} mol L^{-1}) with various cations (Fe^{3+}, Hg^{2+}, Ag^{+}, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+} and Mg^{2+}) in DMSO/H_2O ~ HEPES buffer (80/20, v/v; pH = 7.23) solutions. Inset: color changes of **L** with various anions.

The probe **L** could act as a functional material for the detection of Zn^{2+} in DMSO/H_2O ~ HEPES buffer (80/20, v/v; pH = 7.23) solutions. For instance, only Zn^{2+} (4.0×10^{-4} mol L^{-1}) could open the fluorescence emission of **L,** not other various ions when adding them into 2×10^{-5} mol L^{-1} solutions of **L**. Moreover, as shown in Fig. 3, the fluorescence emission at 520 nm increased when gradually added the Zn^{2+} into this solution of probe. The detection limit of **L** to Zn^{2+} is estimated to be 2.725×10^{-7} M. Meanwhile, the fluorimetric detection limit of Zn^{2+} by the naked eye for probe **L** was also tested. As shown in Fig. 4, under an UV lamp at 360 nm the minimum concentration of Zn^{2+} for the fluorescence color change, observed by the naked eye was 2.0×10^{-5} M.

Although the probe **L** exhibited the single colorimetric and fluorescent recognition ability for Zn^{2+}, the ability of detecting metal cations selectively over other competing metal cations was an essential aspect for many prospective chemical probes. In order to utilize compound **L** as a Zn^{2+} ion-selective fluorescence probe, competition experiments were made at the presence of Zn^{2+} (10 μM) mixed with 10 μM of another cations. As shown in Fig. 5, there was no significant interference when we used the probe **L** to detect Zn^{2+} at the presence of many competitive metal cations and all of the solutions containing Zn^{2+} shew green under an UV lamp at 360 nm. The results showed that the complex state of the probe **L** with Zn^{2+} was almost unaffected by the exists of other cations.

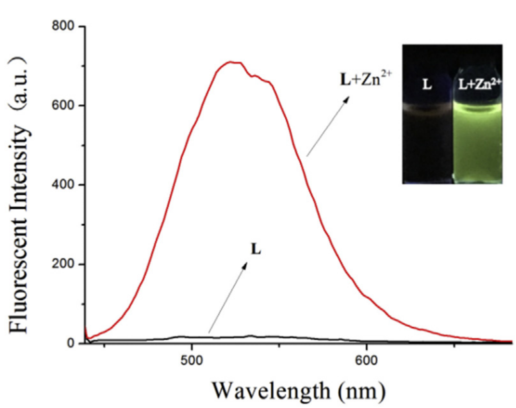

Fig. 1. Fluorescence spectra of the probe **L** (2×10^{-5} mol L^{-1}) with adding Zn^{2+} in DMSO/H_2O ~ HEPES buffer (8/2, v/v; pH = 7.23) solution. Inset: color changes of **L** and with Zn^{2+}.

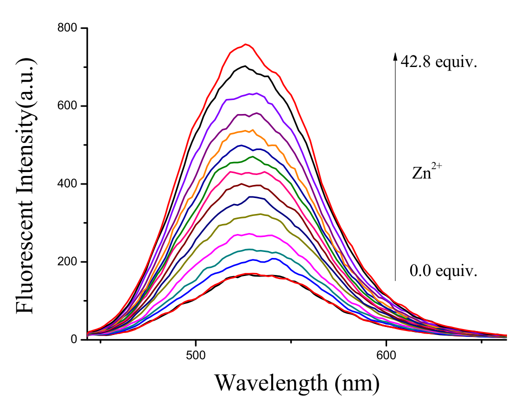

Fig. 3. Fluorescence spectral changes of **L** (c = 2×10^{-5} M) in the presence of different concentrations of Zn^{2+} ions in DMSO/H_2O ~ HEPES buffer (80/20, v/v; pH = 7.23) solutions.