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Design, properties and application of a facile fluorescence switch for Cu(II)

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ABSTRACT

A facile fluorescence switch based on Schiff base 2,2′-[1,3-phenylenbis- (methylidynenitrilo)]bis[benzenethiol] (PMBB) has been developed and used to sensing metal ions. UV–vis absorption and fluorescence emission spectra show that the PMBB receptor has high selectivity and sensitivity for Cu(II) ions. Based on the photoinduced electron transfer (PET) and chelation enhanced fluorescence (CHEF) mechanisms, the receptor exhibits an fluorescence "turn-on" switch signal for Cu(II). The 1:1 binding mode of PMBB and Cu (II) ions can be obtained by the Job-plot and ESI-Mass spectra data. Noticeably, the color changes (from colorless to yellow) of PMBB solutions for Cu(II) sensing can be observed by naked eyes in the sunlight. The detection limit of the receptor for Cu(II) may reach 10^{-7} mol/L with a good linear relation in the lower concentrations of Cu(II). To develop the practical application, the Cu(II) ions in swimming pool water samples were detected. Results show that PMBB receptor as a fluorescent probe can use to detect the trace level of Cu(II) in the environmental samples. This work contributes to providing a facile strategy for designing efficient probes and developing their practical application value.

1. Introduction

Copper as one of the constituent elements of hemocyanin has a significant impact on the development and function for the blood, central nervous and immune systems, hair, skin and bone tissue as well as brain and liver, heart and other organs [1–4]. Copper ion is the second largest essential trace element of body, and has a strong anti-cancer function [5]. Meanwhile, the lack of copper ions in human body may cause anemia, bone changes, coronary heart disease, vitiligo, female infertility and neurasthenia. But excess copper ions can destroy the activity of the protein, resulting in tissue necrosis [6]. Additionally, extensive use of copper also results in the environmental pollution. Hence, it is always a concerned topic on how to detect Cu(II) ions by various analytic techniques, especially, the facile spectrum techniques.

The field of photochemistry technology demands simple synthesis, high sensitivity and selectivity, low cost and specific recognition of a broad range of metal ions [7]. With the rapid development of Cu(II) chemosensors, various types of sensing systems for copper ions have been reported in recent years [8–24]. In this aspect, Lin and his coworkers developed a fluorescent probe based on rhodamine-B derivatives for Cu(II) ions [25]. Wang and his coworkers successfully synthesized some anthracene derivatives to detect Cu(II) ions [26]. Additionally, an isoflavone Cu(II) probe based on intramolecular charge transfer (ICT) mechanism was also developed by Pitchumani [27]. The common drawback of these probes lied in the higher detection limit (μM) for Cu(II) ions. With further in-depth research, more and more fluorescence probes have been developed and applied in biological field. Chan and his coworkers successfully developed a new type probe as the photoacoustic tomography, which played a crucial role in chronic neurological disorders such as Alzheimer's disease [28]. Tunable fluorescent silica-coated carbon dots probe for Cu(II) was reported by Lin and coworkers, which could sense extracellular Cu(II) in rat brain [29]. Beside these small molecule probes, some polymers were also applied to detect Cu(II) ions by the fluorescence spectrum technique [30]. Among all types of fluorescence probes, the probes based on Schiff bases were widely used because of their flexible design and low cost.

Recently, our group reported a Schiff base HMBSB probe, which was a facile regulation function by Al(III) and Cu(II) ions. Regretfully, the probe also had a higher detection limit for metal ions [31]. In view of practicality and efficiency of fluorescent probes, we tried to develop easy and facile fluorescence receptors to sense Cu(II) ions. In the contribution, we adopted a low-cost Schiff base derivate (PMBB, scheme 1) for fluorescence probe to sensing Cu(II). In PMBB, the lone electron pair of N and S atoms can be used as bonding sites to combine metal ions. The experimental results indicate that the PMBB probe high sensitivity and selectivity to Cu(II) ions. Through Job-plot and ESI-SM spectra,

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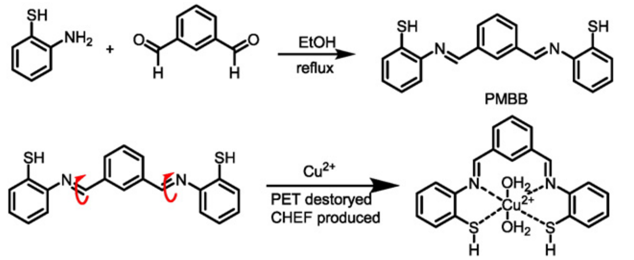

Scheme 1. The synthesis route of PMBB and the binding mode of PMBB with Cu^{2+}.

the bonding mode of PMBB with Cu(II) also was studied. Importantly, PMSB probe can be used to detect the trace level of Cu(II) ions in the swimming pool of water.

2. Experimental

2.1. Materials and instruments

Unless otherwise stated, all chemical reagents were obtained from commercial suppliers and used without further purification. Solvents used were purified and dried by standard method prior to use. Isophthalaldehyde and 2-aminobenzenethiol were purchased from Aldrich (Steinheim, Germany). Metal ions both were nitrates and were provided from Alfa Aesar (Tianjin, China). ^{1}H NMR and ^{13}C NMR were measured on a Bruker ARX400 spectrometer with chemical shifts reported as ppm (TMS as an internal standard). High-resolution mass spectra (HRMS) were measured on an Agilent 6510 Q-TOF LC/MS instrument (Agilent Technologies, Palo Alto, CA) equipped with an electrospray ionization (ESI) source. UV–vis absorption spectra were taken on a Hitachi UH5300 spectrophotometer. Fluorescence spectra were investigated by Hitachi F-4600 fluorescence spectrophotometer, the excitation and emission slit widths both were 5.0 nm.

2.2. Fluorescence and UV–vis spectra measurements

All experiments were performed in mixed media ($MeCN/H_2O = 2/3$, v/v). The stock solution (1.0×10^{-2} mol/L) of PMSB in MeCN were diluted in 1.0 L measuring flask with $MeCN/H_2O$ to obtain the working solution (1.0×10^{-5} mol/L). The stock solutions of metal ions were both 1.0×10^{-2} mol/L in water. The standard stock solutions of lower concentrations were prepared by suitable dilution of the stock solutions. All spectra analysis studies were carried out in a quartz cuvette with 1 cm path. The total volume of working solutions was 2.0 mL. The excitation wavelength was set in 295 nm according to experimental requirements. Both excitation and emission slit were 5 nm. All of the experiments were performed at room temperature.

2.3. Synthesis of the compound

The receptor 2,2′-[1,3-phenylenbis-(methylidynenitrilo)]bis[benzenethiol] (PMBB) was prepared by 2-aminothiophenol and isophthalaldehyde according to the previous reported work [32].

3. Results and discussion

3.1. Photophysical properties and UV–vis absorption spectra of PMBB with Cu(II)

The UV–vis absorption and fluorescence emission spectra of PMBB in $MeCN/H_2O$ (2:3, v/v) media firstly were investigated and showed in Fig. 1. The absorption spectrum of PMBB receptor exhibits two main absorption peaks, and the maximum absorption peak is around 305 nm. Accordingly, the emission peak of PMBB locates at 365 nm and has a weak fluorescence because of photoinduced electron transfer (PET)

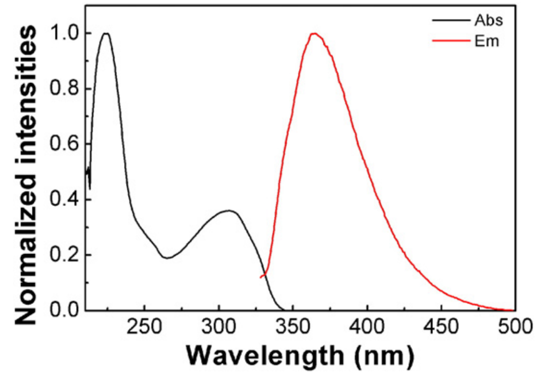

Fig. 1. Fluorescence emission and UV–vis absorption spectra of PMBB. The concentration of PMBB was 1.0×10^{-5} mol/L.

action from rich electron group (—SH) to lack electron body (—C═N). In order to investigate the sensing capacity of PMBB to metal ions, the interactions of PMBB with metal ions were studied by the UV–vis absorption technique (Fig. 2). As can be seen from Fig. 2, the UV–vis absorption spectra of PMBB have no obvious changes in the present of other metal ions, except that Fe(II), Fe(III) and Cu(II), respectively. An apparent blue-shifted of PMBB absorption weak can be observed in the present of Cu(II) ions. While, the absorption intensity of PMBB happens obvious increase in the present of Fe(II) and Fe(III), respectively. Due to the change of absorption wavelength, the solution color of PMBB display an gradual variation from colorless to yellow by introducing Cu(II) ions in the sunlight. Additionally, the relative intensity changes of PMBB with the increase of Cu(II) concentrations have a good linear relation, and the linear independent constant (R^2) is 0.9979 (Fig. S1). The result displays that PMBB receptor is a potential probe for Cu(II) ions sensing.

3.2. Fluorescence spectra of PMBB with metal ions

To further study the recognition effect of PMBB to Cu(II) ions, the fluorescence quenching technique was used to investigate the interactions of PMBB with metal ions (Fig. 3). As shown in Fig. 3, the weak fluorescence of PMBB takes place an obvious enhancement in the present of Cu(II) ions. When the concentration of Cu(II) ions reaches 1.0×10^{-5} mol/L (1.0 eq.), a 3.5-fold enhancement of PMBB intensity is observed. For other metal ions, there are no apparent changes in PMBB fluorescence. So that, PMBB receptor has high selectivity for Cu(II) with the fluorescence “off-on” response. The interference experiments further verify that the probe has good selectivity for Cu(II) ions

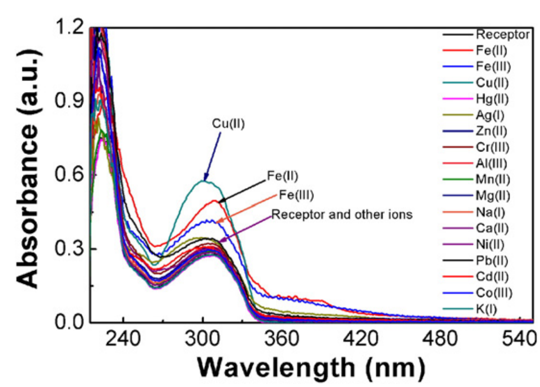

Fig. 2. The UV–vis absorption spectra of PMBB with the addition of metal ions in mixted media ($MeCN/H_2O = 2/3$), respectively. The effect of physiologically active metal ions investigated on UV–vis spectrophotometer. The concentrations of PMBB and metal ions were 2.0×10^{-5} mol/L and 1.0×10^{-5} mol/L, respectively.