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A small molecular fluorescent sensor functionalized silica microsphere for detection and removal of mercury, cadmium, and lead ions in aqueous solutions

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ABSTRACT

In this paper, we report a sensitive fluorescent sensor (FSCHP) for detection and removal of toxic metal ions (Cd^{2+}, Hg^{2+} and Pb^{2+}) in aqueous samples. FSCHP is a 2,2-dipicolylamine (DPA) modified naphthalimide fluorophore followed by immobilization to the surface of silica microsphere and support high affinity for Cd^{2+}, Hg^{2+} and Pb^{2+}. Metal adsorption by FSCHP was featured by an enhancement in its fluorescence intensity. The limit of detection of 36 nM for Cd^{2+}, 48 nM for Hg^{2+}, and 39 nM for Pb^{2+}, was measured respectively. Moreover, FSCHP can also be used as adsorbent for the separation of toxic metal ions in the contaminated aqueous solution with high adsorptivity, and can be regenerated by acid treatment. The metal ion removal capacity of FSCHP was retained after five removal/regeneration cycles.

1. Introduction

Cadmium, mercury, and lead are naturally occurring toxic heavy metals in air, water and soil [1,2], they are not biodegradable, and accumulate in the environment. These toxic metals enter human body through contaminated food or water, and cause damages to the cardiovascular system, the nervous system, the immune system and organs including kidney, lungs, liver, etc. [3–7]. Therefore, the heavy metal pollution has attracted intensive attention since last century [3]. The Food and Agriculture Organization (FAO), Environmental Protection Agency (EPA) and World Health Organization (WHO) have regulated the concentration limits of these metals in food and drinking water [2,4].

Sensitive detection of heavy metals plays a key role in the control of heavy metal pollution, atomic absorption spectrometry [5] and inductively coupled plasma mass spectrometry [6] are the most common methods used to detect toxic metals (cadmium, lead and mercury). On the other hand, removal of toxic metals from contaminated water is necessary to remedy the heavy metal pollutions. Nowadays, some techniques have been developed to separate toxic metals from various samples, such as, redox co-precipitation, chemical deposition, ion displacement, membrane filtering, absorption technique and solid-phase extraction [7–14].

Fluorometry is a convenient method for simply, accurately and rapidly tracking metal ions in biological and environmental samples [2,15–17]. In recent years, small molecule fluorescent probes for heavy metal ions have flourished in detection of metal ions. However, they are incapable of removing of heavy metal ions upon recognition due to their diffusive nature. Therefore, immobilization of a small molecule probe to a solid surface to prepare heterogeneous fluorescent sensors has been an ongoing interest of the field [18–25]. Previously, we reported a bifunctional fluorescent sensor for sensing and separating Hg^{2+} [26], it can detect trace mercury ions in aqueous sample, and can be used as an adsorbent to remove mercuric ions from contaminated aqueous sample. Herein, we report our recent progress in improvement of the detection sensitivity, adsorptivity and regeneration capability of new bifunctional fluorescent sensor.

With good affinity to Zn^{2+}, 2,2-dipicolylamine (DPA) unit and its derivatives have been the most widely used receptors for zinc ions since 1996 [27]. DPA and its derivatives can also chelate with various heavy metal ions and have been harnessed by some fluorescent sensors to detect Cd^{2+}, Pb^{2+} or Cu^{2+} [28–34]. We envisage that DPA derivatives might be a versatile receptor for heavy metal ions, which can be used to develop a fluorescent sensor for detect and remove these ions. In this work, we have prepared a novel heterogeneous reusable assembly (FSCHP) for

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detection/removal of toxic metal ions, i.e. mercury, cadmium, and lead ions, by conjugate ion, *N*,*N*′-bis(pyridin-2-ylmethyl)ethane-1,2-diamine modified naphthalimide fluorophore onto the surface of silica microsphere (Scheme 1).

2. Experimental

2.1. Materials and instruments

Dimethylformamide were purified by reduced pressure distillation; other solvents were purchased from TCI Co or J&K Co. Tetraethoxysilane (TEOS); aminopropyltriethoxysilane was purchased from TCI Co. ^{1}H NMR spectra; ^{13}C NMR spectra were recorded in $CDCl_3$ at 25 °C on a Bruker AV-400 spectrometer. All pH titration were carried out by using a pH-Meter PB-10. Elemental analysis was done with a Germany Elementar Vario EL III. Concentrations of metal ions were determined by a Varian 710ES Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

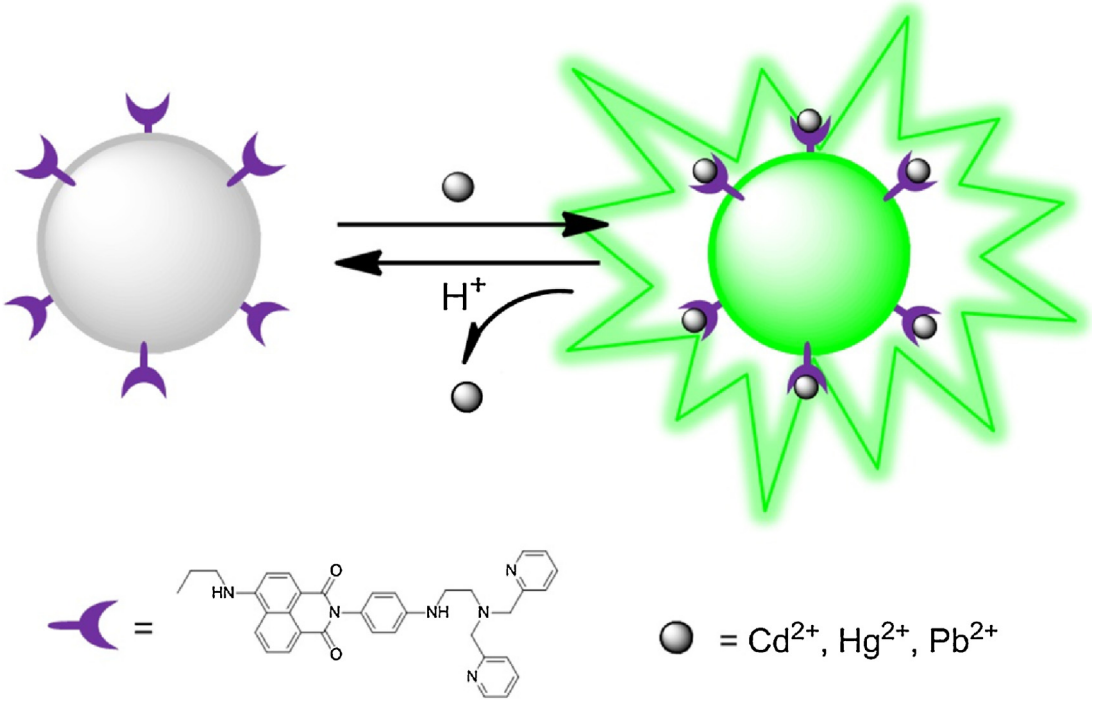
SEM images of the microsphere were taken by Hitachi S-520 scanning electron microscopy to assess the size and shape of the microsphere samples. Dynamic light scattering (DLS) was measured by an ALV/CGS-5022F from ALV Ltd. (German).

2.2. Preparation

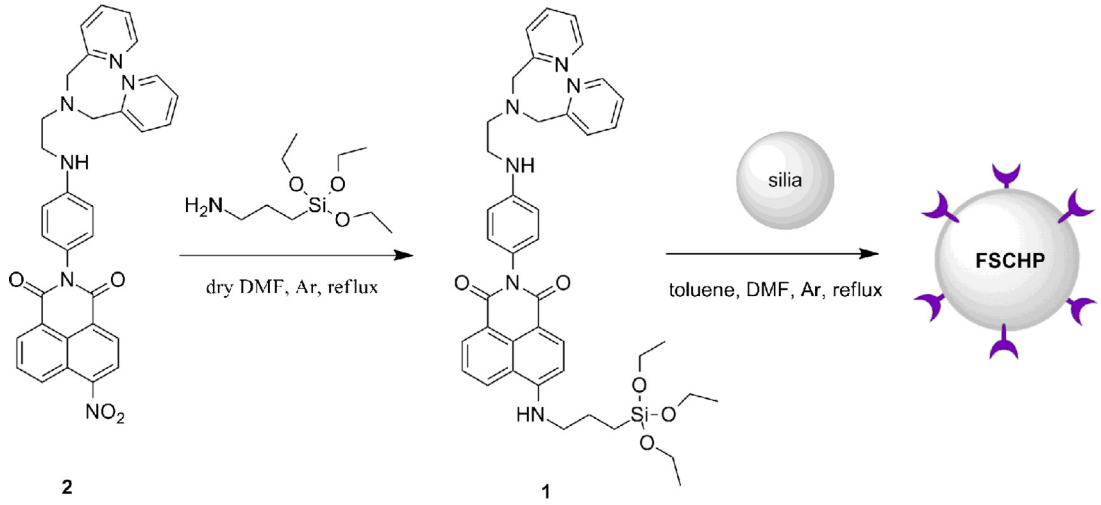
The synthetic route of bifunctional fluorescent sensor FSCHP is depicted in Scheme 2.

2.2.1. Synthesis of compound *1*

Compound **2** (100 mg, 0.179 mmol) and aminopropyltriethoxysilane (38 mg, 0.172 mmol) were dissolved in 5 mL of anhydrous DMF and heated to 60 °C for 1 h under nitrogen



Scheme 1. Plausible mechanism of bifunctional fluorescent sensor FSCHP for the detection and removal of toxic metal ions.



Scheme 2. Preparation of bifunctional fluorescent sensor FSCHP.