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A hybrid mesoporous material functionalized by 1,8-naphthalimide-base receptor and the application as chemosensor and absorbent for Hg^{2+} in water

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ABSTRACT

A novel hybrid material (SBA-**P1**) is prepared through the functionalization of mesoporous silica (SBA-15) with a 1,8-naphthalimide-based dye by sol–gel reaction. The characterization results of elemental analysis (EA), X-ray powder diffractometer (XRD) and spectroscopic methods demonstrate the fluorescence dye **P1** is successfully grafted onto the inner surface of SBA-15 and the organized structure is preserved. SBA-**P1** can detect Hg^{2+} with high selectivity to Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Ag^{+}, Cr^{3+}, and Mg^{2+}, Ca^{2+}, Li^{+}, Na^{+}, K^{+} in water and sensitivity to environmentally relevant mercury in complex natural samples. The quenching fluorescence detection is also reversible by treating with EDTA/base. Furthermore, its fluorescence intensity keeps stable in the physiologically relevant pH range. The extraction ability of SBA-**P1** is also estimated by inductively coupled plasma source mass spectrometer (ICP), showing that approximately 90% of the Hg^{2+} ion is extracted. These results imply that the hybrid material has potential application for sensing and removing of Hg^{2+} ions in waste water and working as toxicide for acute mercury poisoning.

1. Introduction

Mercury is one of the most dangerous and ubiquitous of pollutants, and its contamination is widespread and arises from a variety of natural and anthropogenic sources [1,2]. Once mercury is introduced into the food chains as a result of bioaccumulation, this environmental cycle causes serious threat to the human health and ecology [3–5]. Accordingly, the development of new or improved analytical methods for sensing and removing of Hg^{2+}, applicable in a wide range of different sites and environments, is highly desirable [6–11]. Up to now, several types of small organic molecules [12–19], oligonucleotides [20], proteins [21], DNA and DNAzyme [22] platforms have been examined as Hg^{2+}-responsive groups in fluorescent chemosensors. However, their use in related analytical techniques in the homogeneous phase has not been appropriate for the separation, removal, and enrichment of target species.

Recently, organic–inorganic hybrid materials have received much attention due to their potential use in catalysis [23], optical devices [24–28] and drug delivery [29,30]. Receptors immobilized on inorganic nanomaterials have important advantages when used in the heterogeneous solid–liquid phase [31]. In particular, mesoporous silica (e.g., SBA-15 or MCM-41) appears to be more attractive as a promising inorganic support material due to its excellent properties [32]. Firstly, mesoporous silica materials themselves are nonfluorescent, but they possess high surface area with abundant hydroxyl groups on the pore walls that can act as binding sites for the covalent grafting of fluorophores on the silicon wall. Furthermore, the mesoporous silica materials are optical transparency in the visible region, which also makes such silica-based material particularly suitable for promising chemosensor substrates. Secondly, the ordered channel and larger pore size of mesoporous silica facilitate the lowering of diffusion resistance and enhancement of accessibility. Thirdly, the ordered porous structure of mesoporous silica provides a sheltered environment that enhance the stability of immobilized organic molecules to heat, extreme pH values, denaturants, and enzymatic digestion and thus beneficial for long-term remaining in force [33]. Lastly, mesoporous silica materials have good thermal stability, high mechanical robustness and favorable biocompatibility. Recently, a lot of such hybrid materials have been used for optical detection and separation of toxic metal ions [34–37]. However, most of them are operated in organic or in mixed aqueous-organic solvents [38–40]. Thus, the development of solid chemosensors with high selectivity and sensitivity for monitoring and absorbing Hg^{2+} in complex natural water samples remains a significant challenge.

Bearing this in mind, we synthesized a 1,8-naphthalimide-based receptor **P1** (Scheme 1) and immobilized it onto the channel surface of mesoporous silica (SBA-15) to develop new multifunctional nanomaterial SBA-**P1** used as chemosensor, adsorbent and toxicide

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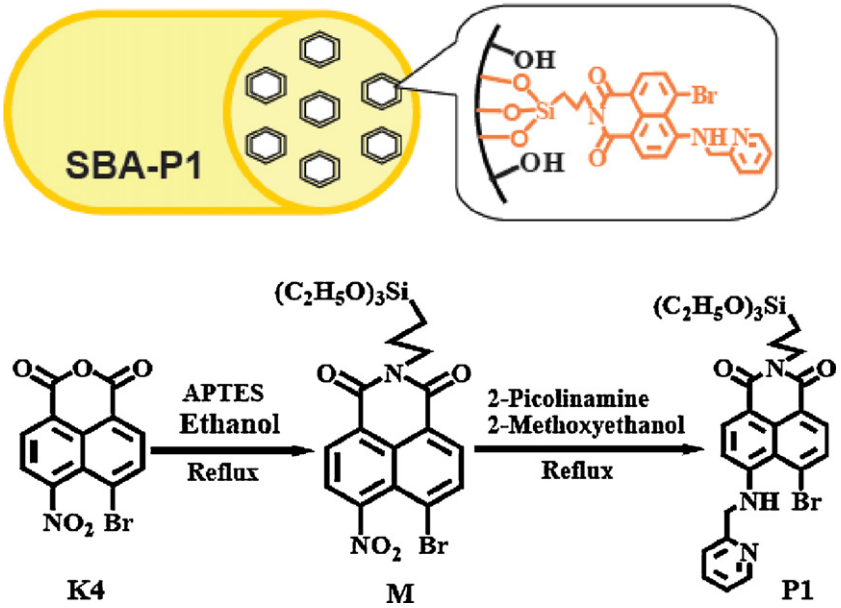
Scheme 1 Synthesis procedure of SBA-P1



Scheme 1. Synthesis procedure of the SBA-**P1**.

responsible for Hg^{2+} with highly selective fluorescence changes and excellent adsorption.

2. Experimental

2.1. Reagents and instruments

All reagents and solvents were of analytical reagent (AR) grade and used without further purification unless otherwise noted. SBA-15 was procured from Jilin University High Technology Co. Ltd. (3-Aminopropyl)triethoxysilane, 2-(aminomethyl)pyridine were purchased from Aldrich. The metal salts employed were $LiClO_4$, $NaClO_4$, $KClO_4$, $Mg(ClO_4)_2$, $Cd(ClO_4)_2{\cdot}6H_2O$, $Mg(ClO_4)_2$, $Hg(ClO_4)_2{\cdot}3H_2O$, $Cr(ClO_4)_3{\cdot}6H_2O$, $Zn(ClO_4)_2{\cdot}6H_2O$, $AgClO_4{\cdot}H_2O$, $Co(ClO_4)_2{\cdot}6H_2O$, $Cu(ClO_4)_2{\cdot}6H_2O$ $Mn(ClO_4)_2{\cdot}6H_2O$, $Ni(ClO_4)_2{\cdot}6H_2O$, and $Pb(ClO_4)_2{\cdot}3H_2O$, respectively.

^1H NMR and ^{13}C NMR spectra were measured on a Varian INOVA 400M spectrometer with chemical shifts reported as ppm ($CDCl_3$, TMS as internal standard). ESI mass spectra were carried out on a HPLC-Q-TOF MS spectrometer using methanol as the mobile phase. X-ray powder diffraction (XRD) patterns of the SBA-15 and SBA-**P1** were recorded on a Rigaku D/max- 2000 X-ray powder diffractometer (Japan) using Cu Kα (l = 1.5405 Å) radiation. Transmission electron microscope (TEM) images were taken on a Hitachi H-9000 NAR transmission electron microscope under a working voltage of 300 kV. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Nicolet Magna-IR 750 spectrometer equipped with a Nic-Plan Microscope. UV–vis diffuses reflectance spectra were taken on a Shimadzu UV-2401PC spectrophotometer using $BaSO_4$ as the reference. Elemental analyses (C, H, N) were performed on an Elementar Vario EL analyzer. The nitrogen adsorption and desorption isotherms were measured at 77 K using an ASAP 2010 analyzer (Micromeritics Co. Ltd.). Surface areas were calculated by the Brunauer–Emmett–Teller (BET) method, and the pore volume and pore size distributions were calculated using the Barret–Joyner–Halenda (BJH) model. Fluorescence spectra of the solution were obtained using the FS920 spectrometer (Edinburgh Instruments). Both excitation and emission slit widths were 5 nm. The adsorption abilities of SBA-**P1** and SBA-15 for Hg^{2+} in water were measured by inductively coupled plasma spectrometer (Perkin Elmer). Fluorescence measurements were carried out in a 1 cm quartz cuvette with stirring the suspension of SBA-**P1**.

2.2. General procedures of spectra detection

Stock solution (2×10^{-2} M) of the aqueous perchlorate salts of Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+},Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag^+, Pb^{2+}, Cu^{2+} and Hg^{2+} were prepared. The suspension solutions of SBA-**P1** were prepared in pure water. Each time a 2 mL suspension of SBA-**P1** was filled in a quartz cell of 1 cm optical path length, and different stock solutions of cations were added into the quartz cell gradually by using a micro-pipette. The volume of cationic stock solution added was less than 100 μL with the purpose of keeping the total volume of testing solution without obvious change. All the spectroscopic measurements were performed at least in triplicate and averaged.

2.3. Synthesis of K4

Compound **K4** was synthesized according to the published procedures [41].

To a solution of acenaphthene (3.1 g, 20 mmol) in anhydrous DMF (10 mL) solution, n-bromosuccinimide (NBS) (3.6 g, 20.2 mmol) in anhydrous DMF (10 mL) was added dropwise in half an hour, the mixture was stirred for 4 h at room temperature. After the reaction was completed, the solvent was poured into water, yellow precipitates obtained were filtered off, washed with water and dried under vacuum. The crude product was then purified by chromatography on a silica gel column with petroleum ether to give 4-bromo-acenaphthene as a colorless crystal in 83% yield.

To a 100 mL flask, 4-bromo-acenaphthene (4.48 g, 19.3 mmol) was dissolved in glacial acetic acid (40 mL). The mixture solution of fuming nitric acid (4 mL) and glacial acetic acid (8 mL) was added dropwise in half an hour at 10–15 °C. The mixture was stirred for 10 h at room temperature, yellow precipitates obtained were filtered off. Crude product was purified by recrystallization from glacial acetic acid to give 1.9 g of 4-bromo-5-nitro-acenaphthene (yellow solid) in 36% yield.