

# Reversible solid optical sensor based on acyclic-type receptor immobilized SBA-15 for the highly selective detection and separation of Hg(II) ion in aqueous media†

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**An acyclic receptor immobilized mesoporous silica (ARMS) was prepared by sol-gel reaction and its optical sensing ability was studied upon the addition of heavy metal ions in aqueous solution.**

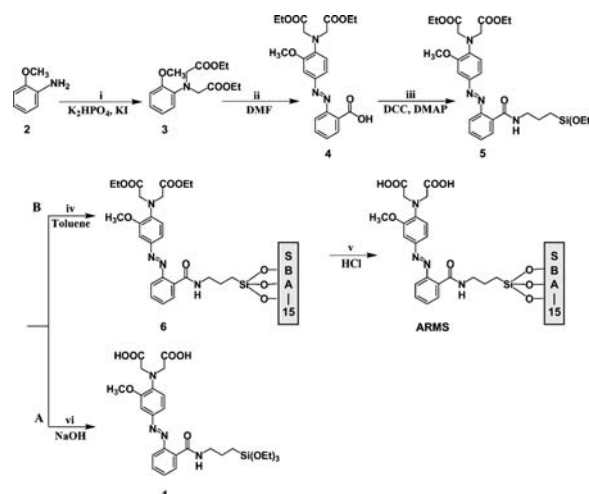
Chemical sensors are molecular receptors that transform their chemical information into analytically useful signals upon binding to specific guests. These sensors are attracting attention owing to their potential for easy detection and quantification of pollutant species in fields such as waste management, environmental chemistry, clinical toxicology and bioremediation of radionuclides.<sup>1–9</sup> Among these, the selective detection of metal ions such as mercury and lead is critical for environmental monitoring, as these are highly toxic and common environmental pollutants.

Very recently, organic–inorganic hybrid materials have been investigated in the search for new methodologies for ion recognition and sensing. As solid chemosensors, receptors immobilized on inorganic nanomaterials such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> have important advantages when used in the heterogeneous solid–liquid phase.<sup>10–17</sup> First, immobilized receptors on an inorganic support can remove the guest molecules (toxic metal ions or anions) from the pollutant solution. Second, these oxides can be fabricated as functionalized porous-type nanomaterials. When combined with chemophores, this allows for extremely highly selective, sensitive absorption or fluorescence changes compared with macro-sized spherical structures because of the larger surface areas and well-defined pores of nanomaterials.

In particular, the homogeneous porosity and large surface area of mesoporous silica (SBA-15 and MCM-41) make it a promising inorganic support. However, only limited examples of such heterogeneous sensors have been reported,<sup>10–17</sup> despite the fact that they take advantage of the independent solubility properties of the receptor in water and organic solvents. Based on this idea, we synthesized an azobenzene-coupled acyclic receptor **5** (Scheme 1) and immobilized **5** onto the surface of mesoporous silica as a new approach to the development of nanomaterial chemosensors and adsorbent. We then transformed the ester of receptor **5** into the acid of the receptor **1** attached onto mesoporous silica by hydrolysis (receptor **1** refers

to the acid type receptor attached onto mesoporous silica after hydrolysis). We herein report the fabrication and coloration of acyclic receptor **1** immobilized mesoporous silica (ARMS), which selectively changes color upon the addition of Hg<sup>2+</sup>.

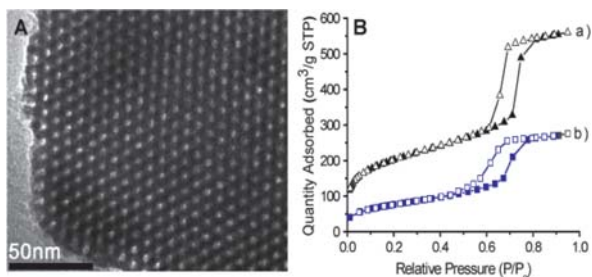
The synthesis of the target compound **1** is difficult due to the polymerization of the triethoxyl group during hydrolysis, which removes the ethyl groups of **5** by pathway A in Scheme 1. Thus, we tried to obtain **1** by hydrolysis of **5** in acidic conditions after immobilization of receptor **5** onto the surface of mesoporous silica by pathway B. To prepare a selective chromogenic receptor for Hg<sup>2+</sup>, we began with **2**, then formed *o*-anisidine (**3**) by alkylation using two equivalents of ethyl bromoacetate in the presence of potassium dihydrogen phosphate and potassium iodide in CH<sub>3</sub>CN. The azobenzene ester **4** was made by the reaction of the diazonium salt of *o*-aminobenzoic acid with **3**. Subsequently, treatment with **4** and aminopropyltriethoxysilane as precursor for the sol-gel reaction afforded compound **5** as a yellow powder. Then, immobilization of the chromogenic receptor **5** to mesoporous silica was conducted under reflux for 24 h in toluene. In this process, the triethoxysilyl group of **5** attached onto mesoporous silica undergoes hydrolysis and attaches covalently to the



**Scheme 1** Synthetic method. Reagents and conditions: (i) BrCH<sub>2</sub>CO<sub>2</sub>Et, 60 °C; (ii) diazonium salt, DMF, 0 °C; (iii) 3-aminopropyltriethoxysilane, DCC, DMAP, EA, RT; (iv) mesoporous silica, reflux; (v) Na<sub>2</sub>CO<sub>3</sub>, NaNO<sub>3</sub>, 90 °C; (vi) H<sub>2</sub>O; DMF = *N,N'*-dimethylformamide, DCC = 1,3-dicyclohexyl carbodiimide, DMAP = *N,N'*-dimethyl-4-pyridinamine, EA = ethyl acetate.

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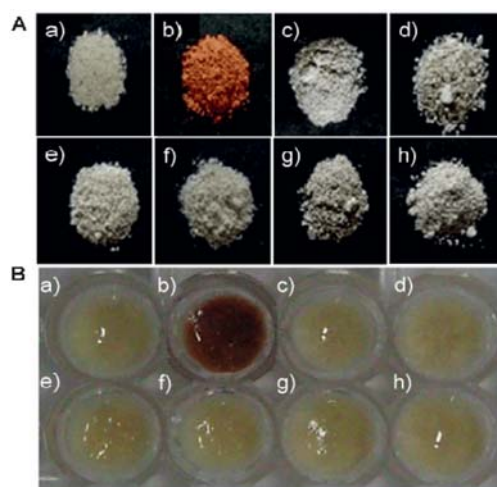
**Fig. 1** (A) TEM image of ARMS. (B) The nitrogen adsorption-desorption isotherms of (a) mesoporous silica and (b) ARMS.

surface of the mesoporous silica.<sup>17</sup> After cooling to room temperature, the yellow solid product was filtered off, washed with THF and dried. Finally, a chemosensing material was obtained as a light yellow solid by hydrolysis of **5** attached onto mesoporous silica under acidic conditions. The acyclic receptor **1** immobilized mesoporous silica (ARMS) was characterized by transmission electron microscopy (TEM), UV-Vis spectroscopy, thermogravimetric analysis (TGA) and FT-IR.

In Fig. 1 and S1 (ESI<sup>†</sup>), TEM images of ARMS and mesoporous silica clearly show the formation of a well-ordered hexagonal arrangement of mesoporous channels before and after attaching the receptor **1**. To investigate the porosity changes of the mesoporous silica induced by introduction of the azo-coupled derivative **1**, we measured the surface area, pore volumes and pore diameters of both mesoporous silica and ARMS using nitrogen adsorption-desorption isotherms (Fig. 1(B)). The mesoporous silica has a BET (Brunauer-Emmett-Teller) surface area of 1119.72 m<sup>2</sup> g<sup>-1</sup> and a pore volume of 0.49 cm<sup>3</sup> g<sup>-1</sup>. On the other hand, we observed that the ARMS has a BET surface area of 673.21 m<sup>2</sup> g<sup>-1</sup> and a pore volume of 0.26 cm<sup>3</sup> g<sup>-1</sup>. The mesoporous silica and the ARMS have BJH (Barrett-Joyner-Halenda) pore diameters of 2.24 and 2.15 nm, respectively (Fig. S2, ESI<sup>†</sup>). The decreased surface area and pore diameter in ARMS are attributable to the attachment of the acyclic azo-coupled derivative to the mesoporous silica. Furthermore, from the results of the TGA measurement (Fig. S3, ESI<sup>†</sup>), we determined that the ARMS consists of only 18.0 wt% of **1**.

For further structural proof of the ARMS, we carried out IR spectroscopy of both mesoporous silica and ARMS. For the mesoporous silica, IR peaks appear at 3450, 1658 and 1084 cm<sup>-1</sup>. For ARMS (Fig. S4, ESI<sup>†</sup>), peaks appear at 3382, 2976, 2933, 2884, 1626, 1615, 1570, 1471, 1446, 1428 and 1382 cm<sup>-1</sup>. These new peaks originate from the acyclic azo-coupled receptor **1**, providing solid evidence that **1** is indeed attached to the surface of the mesoporous silica.

Next, we investigated spectroscopic properties of the ARMS towards the metal ions K<sup>+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Co<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Fe<sup>3+</sup>, Cu<sup>2+</sup> and Hg<sup>2+</sup> in aqueous solution (pH = 7.4, all as chlorides, 5.0 equiv. with respect to **1** anchored to the mesoporous silica). Interestingly, upon the addition of Hg<sup>2+</sup> in H<sub>2</sub>O suspension, ARMS resulted in a color change from light yellow to red within 10 s (Fig. 2(A)(b) and (B)(b)). In this category of chromophore, photoexcitation causes a net electronic charge transfer from the donor end (bridgehead nitrogen) to the acceptor end within the chromophore. Thus, the observed color change is ascribed to the formation of a



**Fig. 2** The colorimetric response of (A) dried and (B) H<sub>2</sub>O suspension samples of ARMS (5.0 mg) in the (a) absence and the presence of (b) HgCl<sub>2</sub>, (c) CoCl<sub>2</sub>, (d) CdCl<sub>2</sub>, (e) PbCl<sub>2</sub>, (f) ZnCl<sub>2</sub>, (g) FeCl<sub>3</sub> and (h) CuCl<sub>2</sub>.

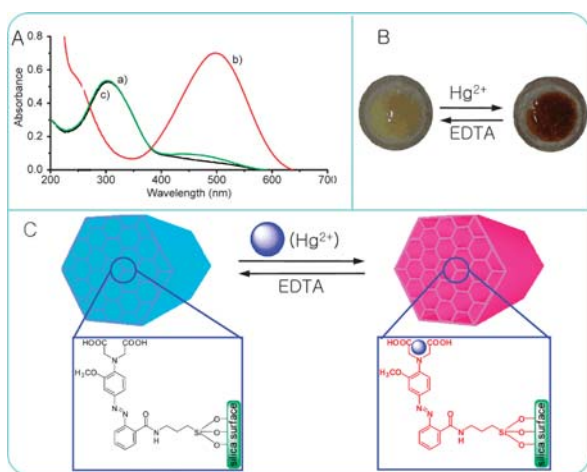
complex with strong coordination bonding between the bridgehead nitrogen atom of aniline group of **1** and Hg<sup>2+</sup>.<sup>10,18</sup> Except for Hg<sup>2+</sup>, no significant color changes were observed in the experiments using other metal ions (Fig. 2(A)(c-i) and Fig. S5, ESI<sup>†</sup>). These findings confirm that ARMS can be useful as a colorimetric sensing material for selective detection of Hg<sup>2+</sup> in the presence of other metal ions. This is a rare example of chromogenic sensing for a specific metal ion by functional inorganic nanomaterials.

To develop the ARMS as a general mercury cation sensor which is independent of the anion present, we investigated the anion effect by addition of other anions such as NO<sub>3</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup> (Fig. S6, ESI<sup>†</sup>). As observed for HgCl<sub>2</sub> solution, the color of the ARMS also changed from yellow to red. This finding indicates that the ARMS can be employed for the detection of Hg<sup>2+</sup> independently of the other anion(s) present.

The Hg<sup>2+</sup>-loaded ARMS was isolated to confirm the binding efficiency of Hg<sup>2+</sup> by ARMS. Then, the solid UV-Vis spectrum for the Hg<sup>2+</sup>-loaded ARMS was compared with that for ARMS alone (Fig. 3A). The Hg<sup>2+</sup>-loaded spectrum of ARMS exhibits an absorption maximum at 495 nm, whereas the absorption peak appears at 310 nm for the Hg<sup>2+</sup>-free ARMS, indicating that the Hg<sup>2+</sup> is efficiently bound to **1** attached in the ARMS by covalent bonds.<sup>10</sup>

In addition, we confirmed the reversibility of the color change of ARMS by removing the Hg<sup>2+</sup> ion bound to ARMS by treatment with EDTA. As expected, the red color of ARMS in the presence of Hg<sup>2+</sup> ion was changed into light yellow upon the EDTA treatment (Fig. 3(B)). Once again, the color change was fully reversible by the addition of EDTA. Because Hg<sup>2+</sup> ion bound to ARMS is dissociated by EDTA, the ARMS can be repeatedly used by renewing with EDTA (Fig. 3(C)).

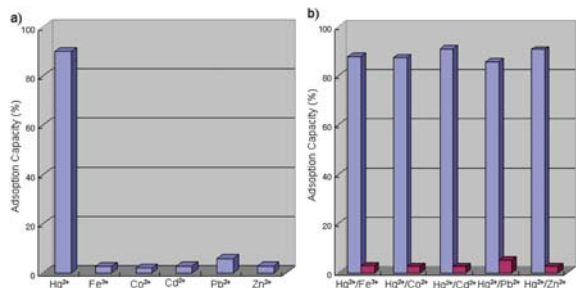
In order to understand the coordination behavior between receptor **1** attached to ARMS and Hg<sup>2+</sup>, we made repeated attempts to obtain the crystal structure of complex **1** with Hg<sup>2+</sup>, but were not successful. As an alternative, we measured



**Fig. 3** (A) Solid UV-Vis spectra of ARMS (5.0 mg) in the (a) absence and (b) the presence of  $\text{HgCl}_2$  (5.0 equiv.), and (c) after addition of EDTA (10 mmol, 2 mL). (B) Picture and (C) proposed structure of ARMS- $\text{Hg}^{2+}$  before and after treatment of EDTA.

the UV-Vis spectra of ARMS with the addition of  $\text{Hg}^{2+}$  to confirm the stoichiometry between **1** attached onto ARMS and  $\text{Hg}^{2+}$  ion. The spectral variation of ARMS in  $\text{H}_2\text{O}$  was observed upon the gradual addition of  $\text{HgCl}_2$ . As a function of the  $\text{Hg}^{2+}$  concentration, a new absorption band centered at 495 nm leading to obvious color change from light yellow to red was observed. The red-shift from 310 to 495 nm of the absorption of ARMS is attributed to a strong binding affinity between the nitrogen atom of **1** attached to ARMS and  $\text{Hg}^{2+}$  (Fig. S7, ESI†).<sup>10</sup> The stoichiometry for the complex of **1** with  $\text{Hg}^{2+}$  was examined by a Job plot. As shown in Fig. S8, ESI†, it was found that the **1**- $\text{Hg}^{2+}$  complex concentration approaches a maximum when the molar fraction of  $[\mathbf{1}]/([\mathbf{1}] + [\text{Hg}^{2+}])$  is about 0.5, indicating that  $\text{Hg}^{2+}$  forms a 1 : 1 complex with **1** attached to ARMS as shown in Fig. 3(C).

Fig. S9, ESI† shows standard calibration data (Abs. vs.  $[\text{Hg}^{2+}]$ ) for ARMS. A linear response is observed (between 1.0–10  $\mu\text{M}$ ) with a sensitivity of  $\sim 1.0 \mu\text{M}$ . This sensitivity is equivalent to those previously reported for spectrophotometric sensors anchored to mesoporous aluminosilicates.<sup>19</sup> Furthermore, we examined the pH effect on  $\text{Hg}(\text{II})$  uptake by measuring absorbance of ARMS treated with  $\text{Hg}(\text{II})$  solutions (pH 1.0–12.0). As shown in Fig. S10, ESI†, no significant absorbance or color changes were observed between pH 2–9, suggesting the proposed ARMS sensor can be used in this pH range.



**Fig. 4** Adsorption capacities of ARMS for (a) single and (b) binary metal ions in  $\text{H}_2\text{O}$ .

The extraction ability of the ARMS was also estimated by measuring the amount of  $\text{Hg}^{2+}$  adsorbed on the ARMS by ICP, resulting in 90% of  $\text{Hg}^{2+}$  ion being extracted by ARMS. This result suggests that the ARMS is potentially useful as a stationary phase for separation of  $\text{Hg}^{2+}$  in liquid chromatography. Also, the adsorption capacity of the ARMS was measured through solid extraction using solutions of binary metal ions ( $\text{Hg}^{2+}/\text{Fe}^{3+}$ ,  $\text{Hg}^{2+}/\text{Co}^{2+}$ ,  $\text{Hg}^{2+}/\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}/\text{Pb}^{2+}$  and  $\text{Hg}^{2+}/\text{Zn}^{2+}$ ) resulting in 85.7–90.5% of  $\text{Hg}^{2+}$  being adsorbed by ARMS (Fig. 4). In contrast, other metal ions such as  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  were extracted into the solid phase at percentages of only 2.5–5.2% in the competition system. These results suggest that ARMS is a useful adsorbent for the selective separation of  $\text{Hg}^{2+}$  over a range of transition and heavy metal ions.

In conclusion, we have fabricated ARMS using a functional azobenzene-coupled acyclic receptor. The ARMS recognized and separated  $\text{Hg}^{2+}$  with a high degree of selectivity among heavy metal ions in aqueous solution. Beyond its immediate applications in environmental cleanup, ARMS provides a unique opportunity to introduce molecular binding sites and to rationally design the surface properties of inorganic nanomaterials. We believe the combination of well-defined inorganic nanomaterials and functionalized organic receptors can play a pivotal role in the development of a new generation of hierarchical structures and functionalized composites.

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