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Pillar[5]arenes bearing phosphine oxide pendants as Hg²⁺ selective receptors

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ABSTRACT

Pillar[5]arenes bearing ten phosphine oxide groups (**1a–e**), as analogs of their corresponding calix[4]arene-based phosphine oxide, have demonstrated intriguing recognition performance for some representative heavy metal cations including Co²⁺, Cu²⁺, Ni²⁺, Zn²⁺, Cd²⁺, Pb²⁺, Ag²⁺ and Hg²⁺ compared to their acyclic species (**2a–e**). Their extraction abilities toward these cations were evaluated by the solvent extraction method. The extraction results revealed that **1a–e** were efficient and selective cation receptors for Hg²⁺ over other selected cations. In addition, the complexation behavior of **1a–e** for Hg²⁺ was also investigated by using NMR and UV–vis techniques. The pillararene receptors have been first used in the determination of inorganic mercury in natural water by inductively coupled plasma atomic emission spectrometry (ICP–AES), after back-extracting into aqueous phase with 3 mol L^{−1} HCl and 1% CS(NH₂)₂ solution.

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1. Introduction

Pursuit for efficient and selective removal of heavy metal ions from water or various industrial effluents has long been a subject in environmental science due to concerns of their growing discharge, toxicity and inimical effects on human health [1]. Particularly, removal of mercury, a representative environmental contaminant, aroused considerable research efforts to resolve issues of its efficient detection and separation [2,3]. The motivation of these studies associated with mercury hazards stems from the concerns of easy volatility of mercury when exposed to human environment [4]. To this end, organic receptors of various types that are capable of forming such heavy metal complexes or selectively extracting these cations have been created. Macrocyclic molecules, such as crown ethers, cryptands, spherands, cyclophanes, cyclodextrins and calixarenes, are among the most widely used hosts [5–9]. It has been well established that preorganizing multiple chelating groups onto a framework with a limited conformation freedom enhance the extraction efficiency [10–12] as revealed in calixarenes [13,14], resorcarenes [15,16], tripodants [17–19] and trityls [20,21], as well as in other scaffold systems [22]. Organophosphorus species have been anchored to the calixarene platform, which exhibited differentiation of the actinide from

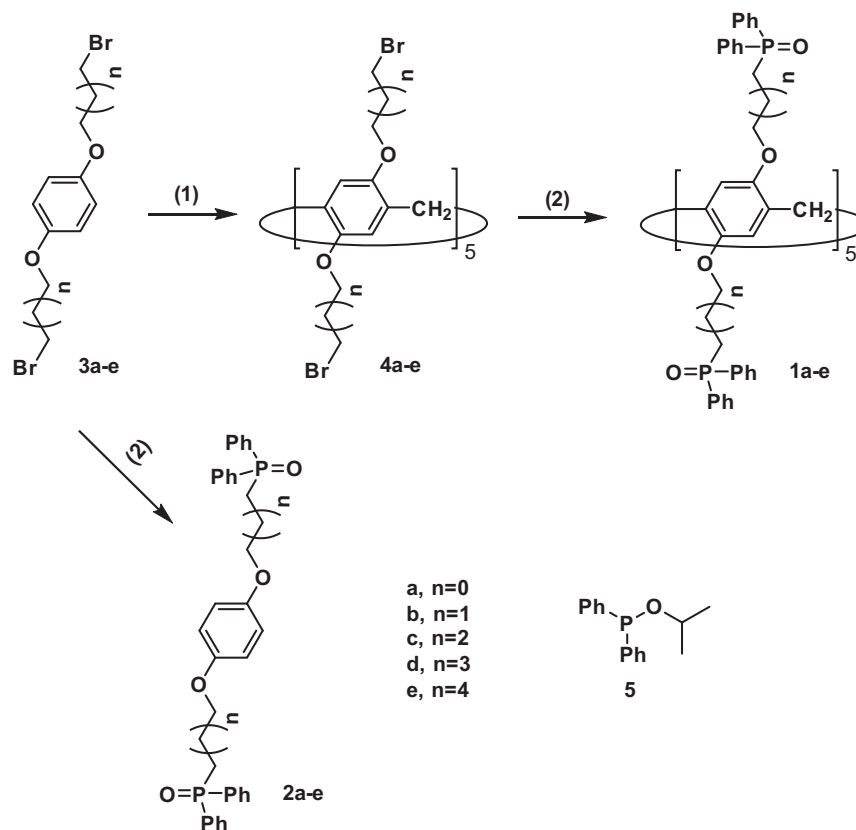
lanthanide elements and other radioactive pollutants in the environment. For example, placement of four carbamoyl phosphine oxide groups at the calix [4]arene platform gives a remarkable cooperative effect in extraction of actinides and lanthanides [23,24]. The attachment of several of these single molecules to a macrocyclic platform or rigid scaffold results in the multivalency effect that increases complexation constants, separation efficiency and selectivity.

Recently, pillararenes have appeared as a new intriguing class of calixarene analogs [25]. They are made up of hydroquinone units linked by methylene (–CH₂–) bridges at the 2 and 5 positions with pillar-shaped conformation. With highly symmetrical pillar architecture that differs from the typical calix [4]arenes in basket conformation, these macrocyclic compounds have been found to bind both neutral and ionic guests such as viologen and pyridinium derivatives, amino acid, imidazolium cations, (bis)imidazolium dication, quaternary ammonium salts, secondary ammonium salts and alkyl chain derivatives such as *n*-hexane, alkanediamines [26–34] via the hydrophobic cavity. Since their first discovery by Ogoshi et al., pillar[*n*]arenes (*n* = 5–10) have received increasing attention due to the ease in the synthesis of the basic platform and ready functionalization at both ends of molecules. As the smallest member of this family, pillar[5]arenes are readily available by the macrocyclic reaction under Friedel–Crafts conditions [35]. Given the similarity in rigid framework like calixarenes, these macrocycles are envisioned to be good candidates as a platform for preorganizing chelating groups for metal ion separation.

In the continuity of the work searching for organic ligands that are useful for separation of actinides and lanthanides as well as transition

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Scheme 1. Synthesis of pillar[5]arene-based phosphine oxides **1a–e** and their acyclic monomeric analogs **2a–e**. Reagents: (1) $(\text{CH}_2\text{O})_n$, $\text{BF}_3 \cdot \text{OEt}_2$, CH_2Cl_2 , r.t.; (2) iso-propoxydiphenylphosphine **5**, N_2 , 160°C .

metal ions [36–41], we have recently reported the synthesis of a new class of pillar[5]arene-based ligands **1a–c** functionalized with phosphine oxide groups and demonstrate their extraction capability in selective separation of some representative lanthanides and actinides. In the course of the research, we happened to find that these ligands also show complexation towards some heavy metal ions. To the best of our knowledge, pillar[5]arene-based phosphine oxides have never been used for heavy metal extraction and complexation. We report herein on investigation of recognition properties of pillar[5]arenes **1a–e** (Scheme 1) modified with ten phosphine oxide moieties for heavy transition metal cations by liquid-liquid solvent extraction method. Compounds **1b** and **1d** were newly synthesized in this study. Acyclic derivatives **2a–e** have also been used for comparison (Scheme 1).

2. Experimental

2.1. Instruments and apparatus

UV–vis spectra were measured on a SHIMADZU UV-2450. An IRIS Advantage ER/S inductively coupled plasma emission spectrometer (TJA, USA) was employed for metal ion determination. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE AV II-400 MHz (^1H : 400 MHz; ^{13}C : 100 MHz; ^{31}P : 162 MHz). Chemical shifts are reported with δ values in ppm and coupling constants (J) are denoted in Hz. Multiplicities are denoted as follows: s=singlet, d=doublet, t=triplet, and m=multiplet. High resolution mass data were obtained on a WATERS Q-TOF Premier. CDCl_3 and CD_3CN were from Cambridge Isotope Laboratories (CIL).

2.2. Chemicals and reagents

Compounds **1a**, **1c**, **1e**, **2a**, **2c**, **2e**, **4a**, **4b**, **4c** and **4e** were synthesized following the similar reported procedures [42]. Dichloromethane, picric acid, anhydrous Na_2SO_4 , $\text{Hg}(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}$, AgNO_3 , $\text{Pb}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were the analytical grade reagents and were purchased from Chengdu Kelong Chemical Factory. All other solvents and chemicals used for the synthesis were of reagent grade and used as received.

The standard stock solution of $\text{Hg}(\text{II})$ (1.0 mg mL^{-1}) was prepared by dissolving a proper amount of mercury nitrate in milli-Q water with the addition of nitric acid, which was subsequently diluted with water to reach a secondary mixed stock solution with a concentration of 1.0 mg L^{-1} . All working standard solutions were freshly prepared by diluting standard solution with water to the required concentration.

2.3. Sample preparation

River water was collected from Jinjiang River, Chengdu, China. The water samples were filtered through a $0.45 \mu\text{m}$ pore size membrane to remove the suspended particles and acidified to a pH of about 3 with HNO_3 prior to storage for use. Tap water samples were taken from our laboratory without pretreatment before determination, the pH value was adjusted to 3 with 0.1 mol L^{-1} HNO_3 prior to use. The water samples were analyzed within 2 weeks after collection.

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