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Pillar[5]arenes bearing phosphine oxide pendents as Hg^{2+} selective receptors

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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 Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Ag^{2+} and Hg^{2+} 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 Hg^{2+} over other selected cations. In addition, the complexation behavior of **1a–e** for Hg^{2+} was also investigated by using NMR and UV–vis techniques. The pillarareen 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% $CS(NH_2)_2$ solution.

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, cryptants, 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 ($-CH_2-$) 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 dications, 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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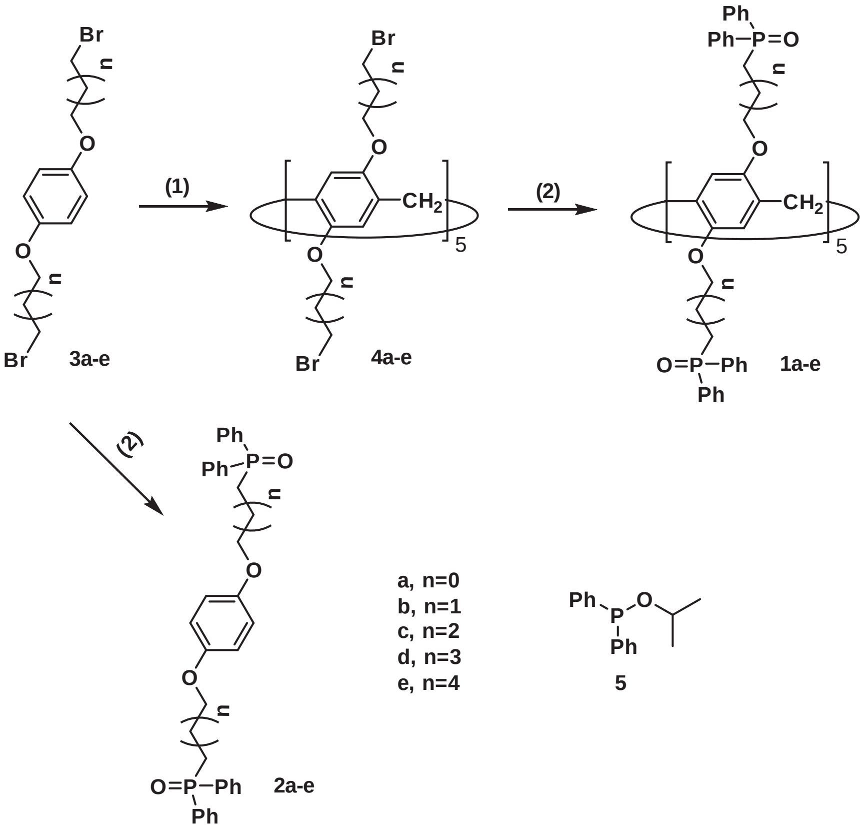

Scheme 1. Synthesis of pillar[5]arene-based phosphine oxides **1a**–**e** and their acyclic monomeric analogs **2a**–**e**. Reagents: (1) $(CH_2O)_n$, $BF_3 \cdot OEt_2$, CH_2Cl_2, r.t.; (2) *iso*-propoxydiphenylphosphine **5**, N_2, 160 °C.

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 phoshpine 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 phoshpine oxides 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, $Hg(NO_3)_2 \cdot 1/2H_2O$, $AgNO_3$, $Pb(NO_3)_2$, $Ni(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ 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 Hg(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 μm 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.

2.4. *Synthesis of compounds **4d**, **1b**, **1d**, **2b** and **2d***

2.4.1. *Synthesis of **4d***

To a mixture of **3d** (10 mmol), paraformaldehyde (10 mmol) in dry dichloromethane (80 mL) was added boron trifluoride diethyl etherate (12 mmol). The mixture was stirred at room temperature for 2 h. A green solution was obtained. After the solvent was removed, the resulting residue was dissolved in CH_2Cl_2 (100 mL) and washed with water repeatedly. The organic layer was dried over anhydrous Na_2SO_4 and evaporated to afford the crude product. The obtained solid was purified by column chromatography on silica gel with petroleum ether/ dichloromethane (1:1, v/v) as the eluent to afford a white powder. Yield 31%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (s, 10H), 3.88 (t, 20H), 3.75 (s, 10H), 3.30 (t, 20H), 1.81 (m, 40H), 1.59 (m, 20H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.03, 29.02, 29.62, 32.50, 33.67, 68.12, 114.90, 128.29, 149.75.

2.4.2. *Synthesis of **1b** and **1d***

The preparation of **1b** and **1d** follows the procedure as described below.

A mixture of **4b** or **4d** (0.2 mmol) and iso-propoxydiphenylphosphine **5** (8.0 mmol) was stirred at 160 °C for 60 min. The reaction mixture was then cooled to room temperature and washed three times with petroleum ether. The obtained solid was finally purified by fast chromatography on silica gel with dichloromethane/methanol (20:1, v/v) as the eluent to afford the product as a white solid.

1b. Yield 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, 40H), 7.39 (dd, 60H), 6.52 (s, 10H), 3.63 (s, 10H), 3.58 (s, 10H), 3.44 (s, 10H), 2.49 (s, 10H), 2.26 (s, 10H), 1.94 (s, 20H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.08, 25.59, 26.46, 29.54, 68.15, 114.74, 128.09, 128.69, 130.59, 131.80, 132.32, 149.30. ESI-HRMS (*m*/*z*) calcd. for $C_{185}H_{180}O_{20}P_{10}$ $[M+H]^+$ 3033.0556; found $[M+H]^+$ 3033.0596.

1d. Yield 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, 40H), 7.39 (dd, 60H), 6.64 (s, 10H), 3.74 (s, 10H), 3.59 (s, 10H), 3.52 (s, 10H), 2.27 (s, 20H), 1.64 (s, 60H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.50, 27.80, 29.34, 30.00, 68.01, 114.77, 128.62, 130.65, 131.73, 132.59, 133.39, 149.45. ESI-HRMS (m/z) calcd. for $C_{205}H_{220}O_{20}P_{10}$ $[M+H]^+$ 3313.3686; found $[M+H]^+$ 3313.3708.

2.4.3. *Synthesis of **2b** and **2d***

The preparation of **2b** and **2d** was under the same condition as that of **1b** and **1d**.

2b. Yield 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (m, 8H), 7.46 (m, 12H), 6.74 (s, 4H), 3.94 (m, 4H), 2.46 (m, 4H), 2.08 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.85, 26.05, 26.77, 68.13, 115.41, 128.75, 130.73, 131.76, 132.39, 133.73. ESI-HRMS (m/z) calcd. for $C_{36}H_{36}O_4P_2$ $[M+H]^+$ 595.2167, $[M+Na]^+$ 617.1987; found $[M+H]^+$ 595.2167, $[M+Na]^+$ 617.1993.

2d. Yield 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (m, 8H), 7.49 (m, 12H), 6.77 (s, 4H), 3.87 (m, 4H), 2.30 (m, 4H), 1.76 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.30, 27.45, 28.90, 29.36, 30.08, 68.16, 115.38, 128.71, 130.72, 131.67, 132.62, 133.59, 153.08. ESI-HRMS (m/z) calcd. for $C_{40}H_{44}O_4P_2$ $[M+H]^+$ 651.2793, $[M+Na]^+$ 673.2613; found $[M+H]^+$ 591.2785, $[M+Na]^+$ 673.2616.

2.5. *Solvent extraction studies*

Picrate extraction experiments were performed following Pedersen's procedure [43]. 10 mL of a 2.0×10^{-5} M aqueous picrate solution and 10 mL of a 2×10^{-4} M solution of receptors in CH_2Cl_2 were put in a thermostated water bath at 25 °C and vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 h, then it was left standing for an additional 2 h to render two phases fully separate from each other. The concentration of the picrate anion remaining in the aqueous phase was determined by UV spectrophotometry at λ_{max} 355 nm. Blank experiments showed that no picrate extraction occurred in the absence of ligands. The extractability of each metal by the ligands (*E*%) was calculated based on the equation: $E\%=100(A_0-A)/A_0$, where A_0 is the absorbance of the aqueous solution in the absence of ligand, A is the absorbance of the aqueous phase after extraction. Three independent experiments were carried out and the average value of percent picrate extracted was calculated.

2.6. *Procedure for determination of natural water*

The extraction was performed according to the following procedure. The aqueous phase containing mercury nitrate (0.1 mM) was acidified to pH=3 by concentrated HNO_3; the organic phase was a solution of ligand **1c** in dichloromethane at 1.5×10^{-3} M. A 10 mL aliquot of each phase was thoroughly mixed by stirring in a stoppered glass tube at 25 °C for 2 h. After full separation of the two phases, the metal ions were stripped off from the organic phase with 1% (w/w) $CS(NH_2)_2$ and 3 mol L^{-1} HCl solution. The concentration of the metal ion was determined by ICP-AES.

3. Results and discussion

3.1. *Synthesis*

The pillar[5]arenes (**1a**, **1c** and **1e**) and their corresponding monomeric analogs (**2a**, **2c** and **2e**) were prepared according to the previously described methods [42], whereas **1b**, **1d**, **2b**, **2d** and **4d** were first synthesized in this work. All the target molecules and intermediates were characterized using ^{1}H NMR, ^{13}C NMR and high resolution mass spectroscopy (HRMS). The characteristic NMR signals for **1b** and **1d** exhibited characteristic signals for the aromatic hydrogens at 6.52–6.64 ppm, the aromatic hydrogens from $Ph_2P=O$ moieties at 7.39–7.74 ppm, and the singlets for the methylene bridge hydrogens at 3.44–3.59 ppm. The methylene hydrogens of **1b** and **1d** adjacent to the O atoms were split into two groups of signals in a 1:1 ratio due to the bulky $Ph_2P=O$ substituents that reduce the conformation freedom of the pillar[5]arenes as excepted. Besides, all the characteristic signals for the aromatic hydrogens and methylene bridge hydrogens shifted significantly to high field as a result of the shielding effect of the electron-rich $Ph_2P=O$ groups (e.g. Figs. S2 and S5). ^{13}C NMR spectra also revealed an upfield shift of the methylene carbons of **1b** and **1d** adjacent to the $Ph_2P=O$ groups. For example, for **1b**, the signal of methylene carbons adjacent to the $Ph_2P=O$ shifted upfield by +2.98 ppm. ESI-MS spectra revealed highly intense peaks at *m*/*z* 3033.0596 ($[\mathbf{1b}+H]^+$, calculated: 3033.0556), 3313.3708 ($[\mathbf{1d}+Na]^+$, calculated: 3313.3686), corroborating the designed structures.

3.2. *Solvent extraction*

The metal ion recognition abilities of pillar[5]arenes **1a**–**e** were evaluated by liquid–liquid solvent extraction method from aqueous solution into dichloromethane. Eight metal cations were employed in the study including Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Ag^{2+} and Hg^{2+} (Fig. 1). Compounds **2a–e** were also tested as reference for comparison.

All five **1a**–**e** apart from **1d** present excellent extractability towards Hg^{2+} ranging from 75.2% to 90.9% at a ligand concentration of 2×10^{-4} M, indicating a slight increase of extraction efficiency from **1a** to **1e**. A remarkable selective affinity was

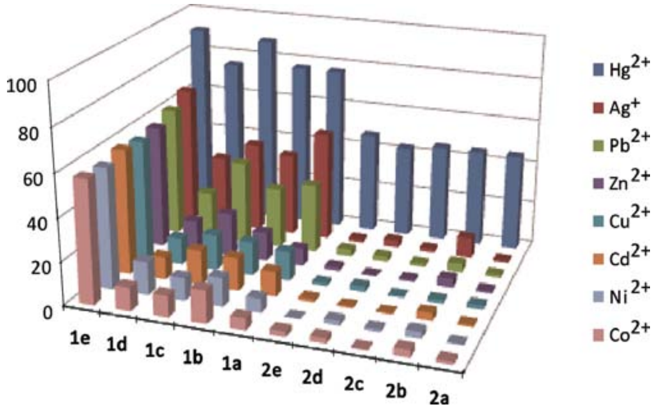

Fig. 1. Extraction of selected aqueous heavy metal picrates (2×10^{-5} M, 10 mL) by pillar[5]arenes **1a**–**e** (2×10^{-4} M, 10 mL) and **2a**–**e** (1×10^{-3} M, 10 mL) into dichloromethane at 298 K.

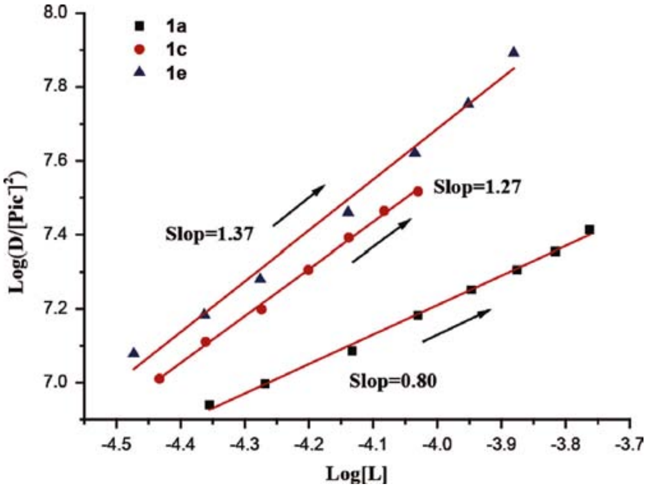

Fig. 2. Log{[D/[Pic$^-$]^2} versus log[L] for the extraction of Hg-picrate with ligands **1a**, **1c** and **1e**.

observed towards Hg^{2+} over other selected metal cations. However, they still exhibited a moderate to larger extractability for Ag^+ and Pb^{2+}. It is noticeable that **1a**, **1b**, **1c** and **1d** bearing shorter chain length extracted Zn^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+} and Co^{2+} only to a considerable low extent (< 20.1%), whereas **1e** having the longest chain length showed a higher extractability (> 56%). So, when the chain length increases to a certain extent, decreased selective affinity towards Hg^{2+} was observed over other metal cations. Unexpectedly, compound **1d** has the lower extraction percentage than **1c** towards Hg^{2+}. The reason for the observation is still unknown. The extraction preference of **1a**–**e** for Hg^{2+} over other metal ions may be explained by both the size selectivity and cooperative participation of ten ligating PPh_2O groups on both ends of the molecule to favorably accommodate Hg^{2+} instead of other cations.

Acyclic phosphine oxides **2a–e** were also employed for comparison at the same condition except for the use of an increased ligand concentration, 1×10^{-3} M, to have a comparable number of available donors. Except for Hg^{2+}, all other cations were extracted only in a trace amount by **2a**–**e**. It was observed that all five **1a**–**e** are more efficient extractants than acyclic derivatives **2a**–**e** (Table S1). For example, the extraction percentage for Hg^{2+} with **1a** is 76.4%, but it is only 45.0% with **2a**. The difference is much more pronounced in extraction of other metal cations, particularly Ag^+ and Pb^{2+}. Therefore, these results indicate that the phosphine oxide groups, when anchored on the pillararene platform, indeed show the preorganization effect just like calixarene derivatives bearing functional groups [23,24], which leads to the enhanced efficiency for extracting metal cations.

To retrieve further information on the nature of the extracted species of Hg^{2+}, such as stoichiometry and binding mode of the complexation, log–log plot analysis was investigated with pillar[5] arenes **1a**, **1c**, and **1e**, and NMR and UV–vis experiments were performed with **1c** as a model compound.

First, mercury (II) picrate was measured at different ligand concentration using log–log plot analysis. The dependence of the extraction of the cation represented as log {D/[Pic$^-$]^2} on the concentration of the ligand in log [*L*] offers the linear plots, from the slope of which the stoichiometry of the extracted complexes was obtained. Thus, the slope of the line was found to be 1.27 for ligand **1c**, suggesting the presence of the extracted species in approximately 1:1 (*L*:*M*) between **1c** and Hg^{2+}. The extraction constant log K_{ex} value was determined to be 12.65. Following the same method, the slope of the line was found to be 0.8 for ligand **1a** and 1.37 for ligand **1e** (Fig. 2) and the corresponding extraction

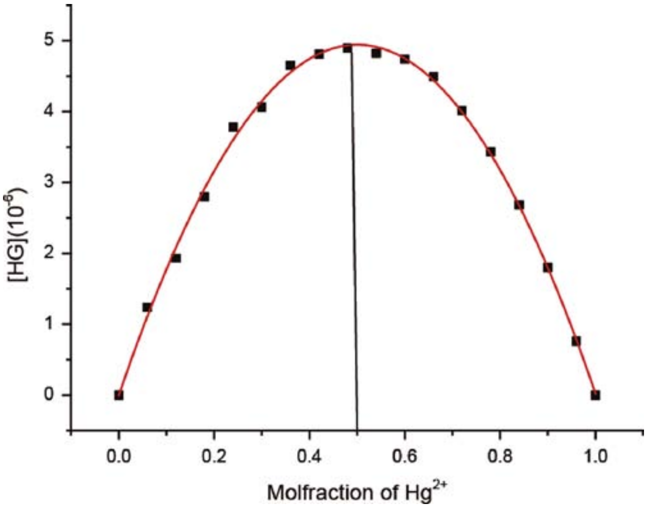

Fig. 3. Job's plot for the determination of the stoichiometry of **1c** and Hg^{2+} in the complex.

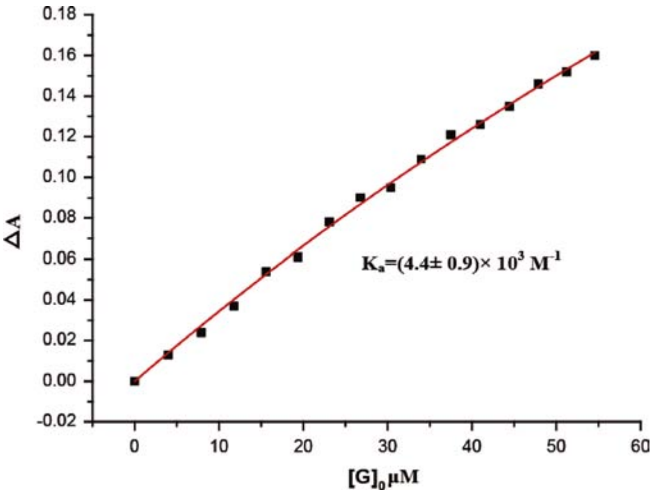

Fig. 4. Curve-fitting analysis for the complexation of **1c** with Hg^{2+} in C_2H_5OH/H_2O (v/v, 3/2).

constant log K_{ex} value was determined to be 10.40 for ligand **1a** and 13.18 for ligand **1e**.

3.3. Complexation studies

To obtain further information on the Hg^{2+} binding stoichiometry of pillar[5]arenes, the method of Job's plot was used to analyze **1a–e** and Hg^{2+}. Fig. 3 shows the resulting Job's plot of **1c**–Hg^{2+} complexation at 294 nm. The maximum point of the mole fractions was found to be about 0.5, suggesting a ligand-metal ratio of 1:1 in the extracted complex. On the basis of 1:1 stoichiometry and UV–vis titration data (Fig. S21), the binding constant (K_a) of **1c**–Hg^{2+} in C_2H_5OH/H_2O (v/v, 3/2) was estimated to be $(4.4 \pm 0.9) \times 10^3\ M^{-1}$ ($r^2 = 0.998$) (Fig. 4) using nonlinear curve fitting method [44]. From the titration results, the detection limit (DL) for receptor **1c** was calculated to be 2.4×10^{-6} M towards Hg^{2+}. The calibration curve [5,45] shows a good linearity with a correlation coefficient of 0.998 (Fig. 5), which allowed for the detection of micromolar concentration range of Hg^{2+}. Using the same method, the binding stoichiometry of **1a**–Hg^{2+}, **1b**–Hg^{2+}, **1d**–Hg^{2+} and **1e**–Hg^{2+} were also obtained as a ligand-metal ratio of 1:1 in the complex (Fig. S15-18) and the binding constants of **1a**–Hg^{2+}, **1b**–Hg^{2+}, **1d**–Hg^{2+} and **1e**–Hg^{2+} were found to be $(2.2 \pm 1.0) \times 10^3\ M^{-1}$, $(2.7 \pm 0.9) \times 10^3\ M^{-1}$, $(1.7 \pm 0.8) \times 10^3\ M^{-1}$ and $(4.3 \pm 1.1) \times 10^3\ M^{-1}$, respectively. For **1b**, the detection limit towards Hg^{2+} was calculated to be 2.8×10^{-6} M (Figs. S24–28).

Additionally, the complexation behaviors of receptors **1a**, **1c** and **1e** with Hg^{2+} were also examined by ^1H NMR and ^{31}P NMR technique. In mixed solvents of $CDCl_3/CD_3CN$ (v/v, 10/1) (Fig. 6), the signal changes in ^1H NMR of aromatic hydrogens (a, b, c and d) are insignificant. In ^{31}P NMR, the signal of phosphorus shows a downfield shift of 2.20 ppm. The results of ^1H NMR and ^{31}P NMR suggest that the receptor **1c** interacted with Hg^{2+} via coordination of its O=P group. Similar results were obtained by receptors **1a** and **1e** (Figs. S29 and S30).

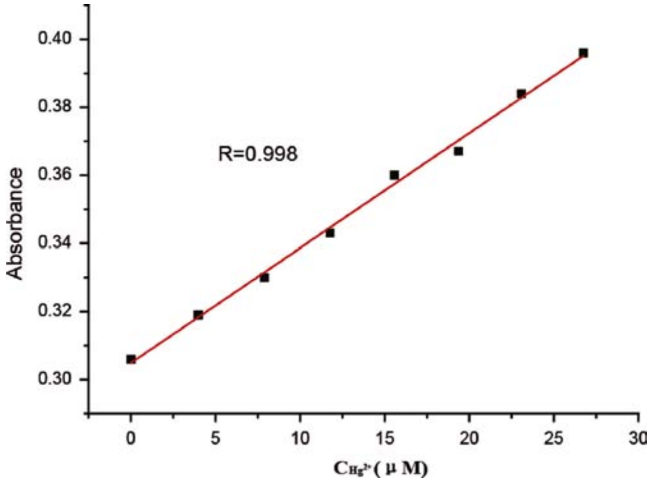

Fig. 5. UV–vis absorbance of receptor **1c** at 244 nm versus Hg^{2+} concentration.

Table 1
Interferences study for the determination of 1.0 μg mL^{-1} Hg(II) under the optimized conditions.

Species	Tolerance limit
Na^+, K^+, Zn^{2+}, Ca^{2+}	2000
Cu^{2+}, Mg^{2+}, SO_4^{2-}	1000
Ni^{2+}, NH_4^+	500
Cl^-, CH_3COO^-	100
Co^{2+}, Fe^{3+}	50

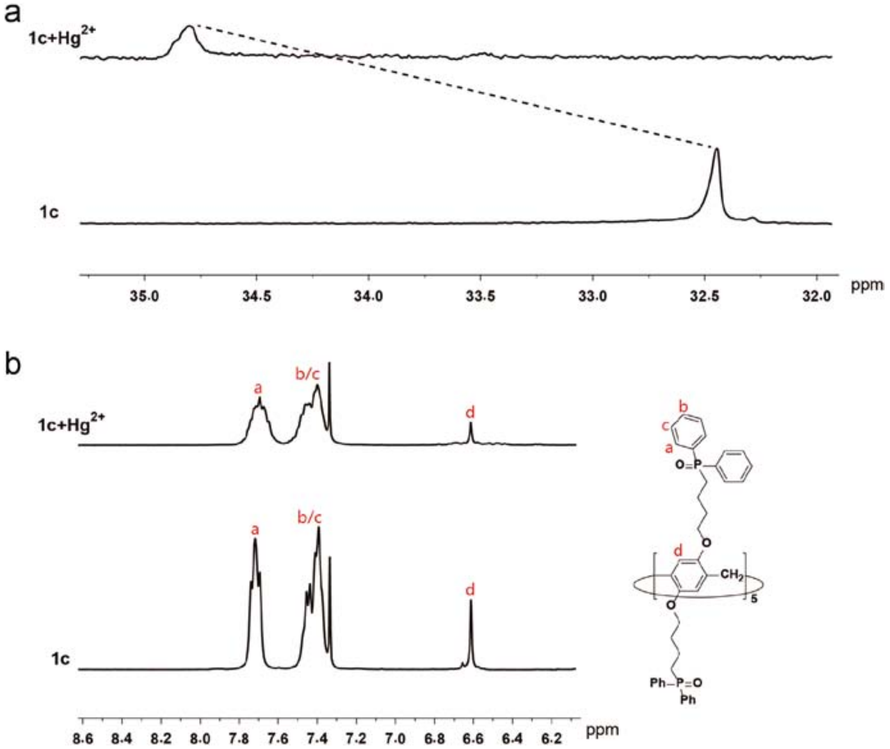

Fig. 6. Stacked ^{31}P NMR and partial ^1H NMR spectra in $CDCl_3/CD_3CN$ (v/v, 10/1). (a) ^{31}P NMR with **1c** and **1c**+Hg^{2+} (1:1) at 2 mM and (b) ^1H NMR with **1c** and **1c**+Hg^{2+} at 2 mM.

Table 2
Analysis of inorganic mercury in natural waters.

Water sample	Inorganic mercury ($\mu g\ mL^{-1}$)		Recovery (%)
	Added	Found[a]	
Deionized water	5	4.68($\pm$0.09)	93.7
	10	9.30($\pm$0.08)	93.0
Tap water	0	nd[b]	–
	5	4.52($\pm$0.07)	90.4
	10	8.98($\pm$0.10)	89.8
River water	0	nd	–
	5	4.41($\pm$0.08)	88.2
	10	8.76($\pm$0.11)	87.6

[a] The value following "±" is based on three replicate analyses.
[b] Not detected.

3.4. Interference study

The effect of diverse cations and anions on the determination of 1 $\mu g\ mL^{-1}$ Hg(II) by the proposed method was studied. For this study, various amounts of different ions were added by firstly testing a 2000-fold interference with mercury (w/w). If interference occurred, the ratio was gradually reduced until the interference ceased. Each ion substance was considered to be an interferent when it caused an error greater than ±5% in the determination of mercury [46]. The results represented in Table 1 showed that 2000-fold Na^+, K^+, Zn^{2+}, Ga^{2+}, 1000-fold Cu^{2+}, Mg^{2+}, SO_4^{2-}, 500-fold Ni^{2+}, NH_4^+, 100-fold Cl^-, CH_3COO^- and 50-fold Co^{2+}, Fe^{3+} did not interfere with the determination of the mercury. The high selectivity for Hg(II) in the presence of interfering substances revealed that the present extractant (**1c**) allowed the interference-free extraction of Hg(II) in the environmental samples.

3.5. Real sample analysis

The stripping condition was studied by using various concentrations of thiourea and HCl solution. The results showed that 3 mol L^{-1} HCl and 1% (w/w) $CS(NH_2)_2$ solution was proper to strip off the Hg(II) from organic phase with 100% recovery (Table S2).

For the analysis of deionized water, tap water and river water samples, all of them were spiked with Hg(II) at different concentration levels and then analyzed with the proposed method. The results were listed in Table 2 shows that the recoveries of Hg(II) were in range of 87.6–93.7%. The results indicated that **1c** was with high extraction efficiency for detecting Hg(II).

4. Conclusions

The pillar[5]arene receptors **1a–e**, which are closely related to calixarene family in terms of backbone structure, have shown a pronounced metal selectivity and a high extractability by attaching phosphine oxide groups to the pillararene platform. Their recognition abilities towards different cations (Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Ag^{2+} and Hg^{2+}) has been investigated by liquid–liquid solvent extraction and compared with their acyclic derivatives. The extraction results show that the pillararene-based phosphine oxides were more effective than their corresponding acyclic derivatives, especially in selective extraction of Hg^{2+} as extractants over other cations. In general, increase of the length of alkyl groups led to the increment of extractability for Hg^{2+} in the order: **1a**~**1b**<**1c**<**1e** with the exception of **1d**. The results from Job's plot experiments revealed that the binding stoichiometry between pillar[5]arene phosphine oxides and Hg^{2+} was 1:1. Additionally, these receptors exhibited high binding constants with micromolar detection for Hg^{2+} in C_2H_5OH/H_2O (v/v, 3/2) solution. More importantly, the good extraction efficiency for divalent mercury allowed their use in analyzing real water samples and enhanced the interference-free ability for quantitative analysis. Thus the pillar[5]arene receptors could be successfully applied for separation and detection of Hg(II) from environmental samples. Further modification of the molecular structures of these macrocyclic receptors may provide chances for developing novel sensors with higher sensitivity and wider range of applicable conditions.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.03.006.

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