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# Synthesis of macrocyclic polyphenol resin by methylene crosslinked calix[4]arene (MC-[4]H) for the adsorption of palladium and platinum ions†

Yoga Priastomo, 🕒 <sup>a</sup> Shintaro Morisada, <sup>a</sup> Hidetaka Kawakita, <sup>a</sup> Keisuke Ohto 🕩 \*<sup>a</sup> and Jumina<sup>b</sup>

A novel macrocyclic polyphenol resin, a calix[4]arene derivative, namely, a methylene crosslinked calix[4]arene (MC-[4]H), was successfully synthesised by demethylation of MC-[4]CH<sub>3</sub>. MC-[4]CH<sub>3</sub> was prepared by crosslinking [4]CH<sub>3</sub> with *s*-trioxane under acidic conditions. Methylation of calix[4]arene ([4]H) is strongly required to protect the oxygen atoms on the phenolic groups. It was found that the adsorption of palladium and platinum optimally occurred at low pH. The maximum loading capacity of palladium on the resin was found to be 0.41 mol kg<sup>-1</sup> while that of platinum was 0.23 mol kg<sup>-1</sup>. The stoichiometries of metal ions were found to be 5:1 of the calix[4]arene unit in MC-[4]H to Pd(II) and 3:1 of that in MC-[4]H to Pt(IV), respectively.

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## Introduction

Recently, the recovery process of precious metals, for example, platinum and palladium, has attracted attention due to the combination of their high economic value, relatively small concentration in the earth's crust and making the recovery process economically feasible.<sup>1,2</sup> Several methods for metal recovery have already been proposed, for example, adsorption,<sup>3</sup> liquid–liquid extraction,<sup>4</sup> chemical precipitation,<sup>5</sup> membrane filtration,<sup>6</sup> hydrometallurgy<sup>7</sup> and ion exchange.<sup>8</sup> The adsorption method has been regarded as one of the most efficient methods due to its high analyte recovery, higher treatment volume capacity, and highly regenerative and facile cleaning up procedure.<sup>9</sup>

Polyphenolic compounds are abundantly available in nature from biomass in a generally acyclic structure.<sup>10–13</sup> Previously, they have also been used as ligands or adsorbents to promote efficient recovery of platinum, palladium, and other precious metals *via* solid liquid extraction, due to their high ionexchange abilities.<sup>14–16</sup> The mechanism for their high ion exchange abilities is attributed to the ability of the hydroxyl groups of the phenolic functional groups to dissociate and form anionic groups that can interact and capture metal cations *via* ionic interactions.<sup>17</sup> There are two types of polyphenolic compounds based on their structure, acyclic and cyclic polyphenols. Acyclic polyphenols are different from the cyclic polyphenols in their low coordination ability, due to their dehydration degree toward metal cations.<sup>18</sup> Since adsorption ability directly correlates with the number of active sites, cyclic polyphenols can be considered as an attractive/promising material for metal recovery adsorbents.

However, studies of cyclic polyphenolic compounds/ligands for the recovery of precious metals are still limited. In this paper, we report the synthesis of a cyclic polyphenolic compound and its application as an adsorbent for precious metal recovery.

Calix[4]arene, a macrocyclic compound with four phenolic units on the lower rim, is used in our study. It has been widely studied for its discriminative uptake of molecules or ions in host–guest chemistry. In order to take advantage of the specific nature of the calix[4]arene framework, we prepare a new cyclic polyphenol from this compound by a resinification process. The resinification process typically employs methylene crosslinking using *s*-trioxane under acidic conditions.<sup>19</sup> This is a way to modify the upper rim of calix[4]arene to make the calix[4]arene molecules more rigid and water-insoluble and to improve the adsorption properties compared with a corresponding monomer of calix[4]arene. The resinification of calix[4]arenes to methylene crosslinked calix[4]arene resins is an attractive method for the development of new macrocyclic polyphenolic adsorbents.

In this work, a macrocyclic phenolic resin, shown in Fig. 1, was prepared by crosslinking calix[4]arene with *s*-trioxane to investigate Pd(n) and Pt(n) adsorption. Various operation parameters including pH values and salt concentration were optimized. The possible distribution of metal ions onto resins and



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<sup>&</sup>lt;sup>a</sup> Department of Chemistry and Applied Chemistry, Faculty of Science and Engineering, Saga University, 1-Honjo 840-8502, Saga, Japan.

E-mail: ohtok@cc.sag-u.ac.jp

<sup>&</sup>lt;sup>b</sup> Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Sekip Utara 55281, Yogyakarta, Indonesia

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Fig. 1 The structure of methylene crosslinked calix[4]arene (MC-[4]H).

the adsorption mechanism of Pt(rv) and Pd(ri) on the resins are also discussed.

## Materials and methods

The <sup>1</sup>H and <sup>13</sup>C-NMR spectra of the obtained compounds were recorded using NMR spectroscopy (JEOL-JNM-AL 300 MHz and Varian Premium Shielded 400 MHz (<sup>1</sup>H) and 100 MHz (<sup>13</sup>C) spectrometers) in CDCl<sub>3</sub> and (CD<sub>3</sub>)<sub>2</sub>CO with TMS as an internal standard. IR spectra were recorded using an IR spectrophotometer (JASCO FT-IR 410) in KBr pellets. Thermal analysis was carried out by using a simultaneous DTA-TG apparatus (Shimadzu, DTG-60H). Elemental analysis was carried out using SEM-EDX (JSM-6010PLUS/LA, JEOL). Morphological images were taken using scanning electron microscopy (SEM) (Hitachi SU-1500). The metal concentrations of aqueous solutions were measured by inductively coupled plasma atomic emission spectrophotometry (ICP-AES, Shimadzu ICPS-8100) and the pH values of aqueous solutions were measured by using a pH meter (TOA-DKK HM-30R). All starting materials and solvents were commercially available and used without further purification except otherwise noted. Dry acetone and dry chloroform were obtained by drying over anhydrous MgSO<sub>4</sub>.

#### Synthesis of intermediates

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene (<sup>*t*</sup>Bu[4]H) (2), 25,26,27,28-tetrahydroxylcalix[4]arene ([4]H) (3) and 25,26,27,28-tetramethoxycalix[4]arene ([4]CH<sub>3</sub>) (4) were synthesized by similar procedures to those reported by Gutsche *et al.*<sup>20,21</sup>

# Synthesis of methylene crosslinked 25,26,27,28-tetramethoxy calix[4]arene resin (MC-[4]CH<sub>3</sub>) (5)

Acetic acid (10.7 cm<sup>3</sup>, d = 1.05 g cm<sup>-3</sup>, 187 mmol) was added to a mixture of 4 (0.500 g, 1.04 mmol) and *s*-trioxane (0.47 g, 5.20 mmol, 5 eq.) and heated at 80 °C for 30 min. A mixed solution of acetic acid (10.74 cm<sup>3</sup>, d = 1.05 g cm<sup>-3</sup>, 187 mmol) and sulfuric acid (1.65 cm<sup>3</sup>, 30.9 mmol) was added dropwise to the reaction for 30 min; the mixture was heated at 110 °C for 8 h. The mixture was poured into a small portion of 5 wt% sodium hydrogen carbonate solution. The crude product was filtered off, and washed with hot distilled water, 1 M (M = mol dm<sup>-3</sup>) hydrochloric acid and normal distilled water, sequentially. The crude product was dried at 80 °C for 24 h and stirred with 0.05 M sodium hydroxide solution for several hours. After washing with hot distilled water, 1 M hydrochloric acid and distilled water, the pure product was dried at 110 °C for 48 h. The resin MC-[4]CH<sup>3</sup>, 5, was obtained as a brownish powder, in 0.71 g yield. IR:  $\nu_{max}$  (KBr)/cm<sup>-1</sup>: 2931 (C–H sp<sup>3</sup>), 1634 and 1464 (C–C), 1383 (stretching of O–CH<sub>3</sub>), 1236 (methylene bridge –CH<sub>2</sub>–), 1049 (bending of O–CH<sub>3</sub>). The peak at 772 cm<sup>-1</sup> for 1,2,3-trisubstituted benzene disappeared.

#### Synthesis of methylene crosslinked calix[4]arene (MC-[4]H) (6)

A mixture of compound 5 (1.00 g, 8.32 mmol) and sodium iodide (24.9 g, 166 mmol, 20 eq.) was added to dry CHCl<sub>3</sub> (200 cm<sup>3</sup>). After adding chloromethylsilane (TMSCl, 21.2 cm<sup>3</sup>, d = 0.85 g cm<sup>-3</sup>, 166 mmol, 20 eq.), the mixture was heated at 80–85 °C for 72 h. 0.1 M sodium thiosulfate solution (30 cm<sup>3</sup>) was added and the mixture was stirred for 1 h at room temperature. The mixture was stirred in 1 M HCl (50 cm<sup>3</sup>) for 1 h and filtered with distilled water. The product was washed with 1 M HCl and distilled water, and dried at 80 °C for 48 h. The resin MC-[4]H, **6**, was obtained as a black powder, in 1.04 g yield. The obtained compound was insoluble in any organic diluents and solution state characterization by <sup>1</sup>H-NMR spectroscopy could not be accomplished. IR:  $\nu_{max}$  (KBr)/cm<sup>-1</sup>: 3262 (O–H), 2931 (C–H), 1647 (crosslinked methylene), 1475 (C–C), 1230 (bridged methylene).

Spectral data for starting material **1**, together with un-crosslinked **3** and **4** are given in Fig. S1–S8 and Tables S1–S8 (ESI<sup>†</sup>).

# The solubility test of the resins 5 and 6 and the un-crosslinked compounds 3 and 4

 $5 \text{ cm}^3$  of acidic or alkaline solution, water or organic solvent was added to 5 mg of resin or the un-crosslinked compounds. The solubility test was simply carried out by a visual check.

#### The adsorption experiments

pH dependency. The percentage adsorption of metal ions as a function of pH was evaluated by the conventional batch method. The tested solutions of metal ions were prepared by dissolving metal salts of palladium nitrate hydrate and hydrogen hexachloro platinate(IV) hydrate in 0.1 M HNO3 and 0.1 M HEPES buffer and they were arbitrarily mixed to adjust to the desired pH value. 10 cm<sup>3</sup> of the solutions tested was added to 0.01 g of resin having a mesh size less than 150 µm. The heterogeneous mixture was shaken at a shaking speed of 150 rpm for 72 h at 30 °C. After equilibrium, the employed resin was separated by filtration (Advantec 5C filter having  $\emptyset$  0.5 mm retention characteristics). The metal ion concentrations before and after equilibrium in the filtrate were determined by ICP-AES. Using the initial and equilibrium concentrations of the metal ions, each metal percentage extracted in the solid phase extractant was calculated by the eqn (1)

% 
$$A = (C_i - C_e)/C_i \times 100,$$
 (1)

where  $C_i$  and  $C_e$  (M) are the initial and equilibrium concentrations of metal ions in aqueous solution, respectively.

**Loading metal capacity on the resin.** The loading adsorption capacity on the resin was also investigated by the conventional batch method. A heterogeneous mixture of 0.01 g of resin in 10 cm<sup>3</sup> of tested solution (metal concentration ranging from 0.1 to 10.0 mM) was shaken for 72 h at 303 K. After equilibrium, the employed resin was separated by filtration. The filtrate was

diluted and the metal concentration in the diluted sample was measured using ICP-AES. Using the initial and equilibrium concentrations of metal ions, the amount of metals taken up by the resin, q (mol kg<sup>-1</sup> dry resin), was estimated by eqn (2),

$$q = ((C_{\rm i} - C_{\rm e}) \times V)/W, \qquad (2)$$

where  $V(dm^3)$  is the volume of aqueous solution and W(kg) is the weight of the resin, respectively.

#### The distribution of metal ions on the resin structure

It was estimated that 10 mg of the methylene crosslinked resin contained approximately 0.021 mmol of monomer (calix[4]arene itself). By dividing the amounts of monomeric species of calixarene (mmol) by the loaded metal amount (mmol), the stoichiometry can be estimated by eqn (3),

Stoichiometry = (amount of calixarene monomer in the

resin (mmol))/(loaded metal amount (mmol)). (3)

### Results and discussion

#### Syntheses of intermediates and adsorbent

The synthesis of MC-[4]H, **6**, was accomplished in five steps starting from 5,11,17,23-tetra-*tert*-butyl-25,26,27,28 tetrahydroxy-calix[4]arene, **2**, as shown in Scheme S1 (ESI†). The protection of the phenolic groups of **3** was carried out using methyl iodide and sodium hydride in dry DMF to give 25,26,27,28-35 tetramethoxycalix[4]arene, 4, in 63.2% in Scheme 1. Methylene crosslinking, using *s*-trioxane and sulfuric acid in acetic acid, produced the resin MC-[4]CH<sub>3</sub>, **5**. Demethylation of **5**, using chloro trimethylsilane and sodium iodide in dry CHCl<sub>3</sub>, gave the desired resin MC-[4]H, **6**. Direct crosslinking from **3** to **6** seemed to be more appropriate and was tried, however, it failed, because the hydroxyl groups also partially reacted with *s*-trioxane. Methylation of **3** is strongly required to protect the oxygen atoms on the phenolic groups. The oxygen atoms can also react with *s*-trioxane during the crosslinking reaction.

The synthesised compounds were characterized by FT-IR,  $^{1}$ H and  $^{13}$ C-NMR spectra. The  $^{1}$ H-NMR spectrum of 4 showed two

broad singlet peaks at 3.59 and 4.79 ppm, which are methylene bridges in axial and equatorial positions. The aromatic protons resonated at 7.41 and 7.12 ppm. Methylation of 3 led to the disappearance of a singlet peak at 10.8 ppm and the appearance of new peaks at 4.24 and 4.05 ppm as the methoxy groups. In addition, all peaks of 4 in the <sup>1</sup>H-NMR spectrum were broad due to the unfixed and not-cone conformation.

Upon methylation of the phenolic oxygen atoms, the band at  $3200 \text{ cm}^{-1}$  disappeared and a sharp band at  $2932 \text{ cm}^{-1}$  for the stretching vibration of C–H alkyl derived from methoxy groups appeared for compound 4. New bands appeared at 1022 and 1085 cm<sup>-1</sup> for C–O bending of ether groups. In addition, compound 4 exhibited a band around 1201 cm<sup>-1</sup> caused by the bending vibration of the methylene bridge and a sharp band at around 770 cm<sup>-1</sup> for the 1,2,3-trisubstituted benzene of the calixarene backbone.

FT-IR spectra before and after the crosslinking are shown in Fig. 2. Methylene crosslinking was strongly indicated by the disappearance of the band at around 770 cm<sup>-1</sup> of compound 4. The absence of the sharp band at 770 cm<sup>-1</sup> and disappearance in the 855–800 cm<sup>-1</sup> region of the hydrogen atom of the aryl group support the fact that crosslinking successfully occurred at the 4-position of the aryl group and all the C-H bonds of the 4-position disappeared after the crosslinking.

Demethylation of 5 resulted in the phenol resin MC-[4]H (6), as shown in Fig. 3. The cleavage of methoxy ethers of calixarene derivatives successfully took place by TMSI, which was generated *in situ* from TMSCl and NaI following the direction of an established procedure.<sup>22,23</sup> The demethylation of 5 led to the disappearance of C–O bending and stretching of methoxy groups at 1001, 1064 and 1130 cm<sup>-1</sup> and the appearance of a broad peak at 3400 cm<sup>-1</sup> corresponding to the O–H of phenolic groups, as shown in Fig. 3. It was found that the demethylation of MC-CH<sub>3</sub> successfully occurred to give the desired resin MC-[4]H.

The result of thermal analysis using DTA-TG apparatus is shown in Fig. 4. The peak of the un-crosslinked compound 4 in Fig. 4(A) showed only a downward trend while those of crosslinked compounds 5 and 6 were upward. The profile of the DTA spectra revealed that the monomer compound decomposed,





Fig. 2 FT-IR spectra of compound 4 and resin 5



while the polymer compounds burned. This indicated that the un-crosslinked compound has low thermal stability. After crosslinking, the monomer converted to a thermally stable polymer. The thermal analysis also strongly supports the cross-

The elemental analysis of **6** was undertaken by using SEM-EDX (see Fig. S9 in ESI<sup>†</sup>). The result showed that the

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primary atom in resin **6** is carbon (74.20% as % mass). This almost corresponds to the theoretical % mass when all of the hydrogen atoms at the *p*-position are crosslinked (80.99% as % mass). The oxygen atoms were obtained as 13.48% as % mass. This value almost corresponds to the theoretical % mass when all of the methoxy groups at the phenolic groups were de-protected (14.69% as % mass). This also means that cross-linking and the following deprotection reactions were successfully achieved.

The adsorption profile measured by SEM-EDX also proved that resin **6** was successfully synthesized. The result is shown in Fig. S10 in the ESI.† After the Pd adsorption, Pd content increased with the increase of the loaded amounts of Pd on **6**, **as** shown in Fig. S11 and S12 (ESI†). The theoretical structure of MC-[4]H is proposed in Fig. 5.

The results of the solubility tests of the resins **5** and **6** and the un-crosslinked compounds **3** and **4** in various media are listed in Table 1. The un-crosslinked compounds **3** and **4** were soluble in any organic solvent, while the resins **5** and **6** were



Fig. 5 The theoretical structure of MC-[4]H.



Fig. 4 DTA-TG spectra of compound 4 (A), resins 5 (B) and 6 (C).

linking of 4.

Table 1 The solubility test of the resins 5 and 6 and the un-crosslinked compounds 3 and 4 in various media

Solvent	[4]H	$[4]CH_3$	$MC-[4]CH_3$	MC-[4]H
Methanol	×	×	×	×
Ethanol	×	×	×	×
Chloroform	0	0	×	×
DMSO	0	0	×	×
Acetone	0	0	×	×
$H_2O$	×	×	×	×
NaOH 1 M	×	×	×	×
NaOH 0.1 M	×	×	×	×
NaOH 0.05 M	×	×	×	×
HCl 1 M	×	×	×	×
HCl 0.1 M	×	×	×	×
HNO <sub>3</sub> 1 M	×	×	×	×
HNO3 0.1 M	×	×	×	×

insoluble. This is good evidence that un-crosslinked compound 4 was successfully crosslinked to 5.

The insolubility behavior of resins 5 and 6 in organic diluents in which 3 and 4 were soluble also supported the successful formation of a resin. This was caused by interconnections of the various calixarene units in a random fashion. In addition, the resin was insoluble in moderately acidic as well as mildly basic solutions. Since resin dissolution requires the cleavage of carbon-carbon bonds of the irregular threedimensional network, it was found to be insoluble in any solvents examined in which the carbon-carbon bonds were not disrupted. This property is particularly useful for adsorptive systems used in solid phase extraction.

Because resins 5 and 6 are insoluble in the diluents, the molecular weight of the unit structure in the resins cannot be determined by common methods. However, the surface morphologies of resins 5 and 6 can be confirmed by SEM, as shown in Fig. 6(A) and (B). The surfaces of resins 5 and 6 exhibit spherical particles with a regular shape.

#### Palladium and platinum adsorption

The results of the pH dependency of the Pd(II) and Pt(IV)adsorptions using MC-[4]CH<sub>3</sub> (5) or MC-[4]H (6) are shown in Fig. 7(A) and (B). The maximum percentage adsorption of palladium on MC-[4]CH<sub>3</sub> (5) and MC-[4]H (6) occurred at pH 6.99 and 2.02, respectively. Meanwhile, the maximum percentage adsorption of platinum on the compounds was reached at pH 7.88 and 0.97, respectively. In contrast, the corresponding monomers 3 and 4 (Fig. 8(A) and (B)) for the desired resins showed poor ability to adsorb these metal ions. It should be noted that resinification of calix[4]arene strongly enhanced the ability of the calix [4] arenes to adsorb palladium  $(\pi)$ and platinum(w) ions.

The structure and species of palladium and platinum in nitric acid medium were studied. Tarapcik reported that there are five palladium complexes that form depending on the nitrate concentration, *i.e.*  $Pd^{2+}$ ,  $Pd(NO_3)^+$ ,  $Pd(NO_3)_2$ ,  $Pd(NO_3)_3^-$ , and  $Pd(NO_3)_4^{2-}$  (log  $K_1 = 3.280$ , log  $K_2 = 0.649$ , log  $K_3 = 0.105$ , and  $\log K_4 = 0.018$ ). The predominant species of palladium is obtained as the free cationic species Pd<sup>2+</sup> at a lower nitrate concentration up to 0.3 M and cationic Pd(NO<sub>3</sub>)<sup>+</sup> at nitrate concentrations ranging from 0.3 up to 1.6 M.<sup>24,25</sup> The predominant platinum( $_{\rm IV}$ ) species is obtained as the complex  $[PtL^{6-x} (NO_3)_r]$ at a high concentration of nitric acid while at a low nitrate concentration, the platinum(IV) species obtained is the complex  $[PtCl_{6-r}(H_2O)_r].^{26,27}$ 

The highest palladium adsorption on MC-[4]H (Fig. 7) was obtained at a pH of 2.02 in nitric acid medium. The number of nitric ions in the solution was high enough to favour formation of cationic Pd<sup>2+</sup> or Pd(OH)<sup>+</sup> species. Dung, Ludwig<sup>28</sup> and Kubota<sup>18</sup> proposed that the multiple ionizable protons of a cyclic ligand highly converge and show chelating effects toward hydrated metal cations. Therefore, the MC-[4]H resin adsorbed cationic Pd<sup>2+</sup> species (6) by convergence of plural phenolic hydroxyl groups and chelating effects on phenolic sites. However, palladium was also easily hydrolyzed to Pd(OH)<sub>2</sub> and anionic  $Pd(OH)_4^{2-}$  species<sup>29</sup> at higher pH values. The presence of trace amounts of soluble  $Pd(OH)_2$  and  $Pd(OH)_4^{2-}$  caused the decrease of adsorption percentages.

In the platinum adsorption profile, the highest platinum adsorption on MC-[4]H took place at a pH of 0.97. Under this condition, platinum was adsorbed on 6 as PtCl<sub>4</sub> because platinum contained chloride ions. It can be adsorbed by migration to the surface of the adsorbent following a diffusion process. The adsorption took place by interaction with the



Fig. 6 SEM images of resins 5 (A) and 6 (B).

в



**Fig. 7** Effect of pH on the percentage adsorption of palladium (A) and platinum (B) ions on **5** and **6**.  $[Pd^{2+}]$  and  $[Pt^{4+}] = 0.1$  mM, weight of the methylene crosslinked resin = 0.01 g, volume of aqueous solution = 5 cm<sup>3</sup>, shaking time = 72 h, and adjustment of pH = 0.1 M HNO<sub>3</sub>, 0.1 M HEPES buffer and NH<sub>4</sub>OH solution.



**Fig. 8** Effect of pH on the percentage extraction of palladium (A) and platinum (B) ions on **3** and **4**.  $[Pd^{2+}]$  and  $[Pt^{4+}] = 0.1$  mM, concentration of calix[4]arenes in CHCl<sub>3</sub> = 5 mM in chloroform, volume of aqueous and organic solutions = 5 cm<sup>3</sup>, shaking time = 72 h, and adjustment of pH = 0.1 M HNO<sub>3</sub>, 0.1 M HEPES buffer and NH<sub>4</sub>OH solution.

phenolic site through ion exchange. However, at higher pH values, the adsorption percentage decreased; this behavior may be attributed to the presence of anionic  $PtCl_5^-$  and  $PtCl_6^{2-}$ . These anionic species show a larger size and higher electron densities than  $PtCl_4$ . Repulsion occurred between these anionic platinum species and the anionic hydroxyl group on MC-[4]H. Therefore, the adsorption percentage decreased at high pH values.

The highest palladium adsorption on 5 was obtained at pH 6.99 while that of platinum adsorption was observed at pH 7.89. Compared with MC-[4]H resin, 5 showed a poor ability to adsorb these metal ions due to the neutrality and non-ion-exchangeability. Since both metals are well-known as typical soft acids, and the oxygen atom of the methoxy group on 5 is classified as a hard base, neutral 5 providing only coordinating oxygen atoms is not suitable to adsorb palladium and platinum ions. In addition, demethylation of 5 to polyphenolic resin 6 significantly enhanced the adsorption abilities.

#### Loading capacity

Since 5 showed a low adsorption ability for palladium and platinum ions, the maximum palladium and platinum adsorption

capacities were only investigated on **6** by analyzing the isotherms shown in Fig. 9. The loaded amount of palladium and platinum ions on the resin (*q*) increased with increasing metal concentration and reached a constant value at high concentrations. The maximum loading amounts of metal adsorption on the resin were 0.41 and 0.23 mol kg<sup>-1</sup> for palladium and platinum, respectively. Due to monolayer adsorption on the active sites of the resin, the adsorption of these metal ions on **6** was governed by the Langmuir model.

Different metal species are the main factor suppressing the capacity of palladium and platinum adsorption on MC-[4]H resin. Palladium was adsorbed as cationic  $Pd^{2+}$  while platinum existed as PtCl4,  $PtCl_5^-$  and  $PtCl_6^{2-}$  that can still be ion-exchanged with hydroxyl groups because of the trace chloride concentration. Cationic  $Pd^{2+}$  was easily ion-exchanged with protons of hydroxyl groups as the active sites of **6**. However, anionic platinum was barely captured by the active site of **6** due to electric repulsion occurring between anionic platinum and the anionic hydroxyl group on MC-[4]H. Therefore, the capacity of palladium loading on MC-[4]H is greater than that of platinum.

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**Fig. 9** Maximum loading capacity of Pd(II) and of Pt(IV) on **6**. Weight of the resin = 0.01 g, volume of solution =  $5 \text{ cm}^3$ , shaking time = 72 h, and initial pH = 2.00 for Pd(II) and pH = 1.00 for Pt(IV). Adjustment of pH = 0.1 M HNO<sub>3</sub> and 0.1 M HEPES buffer.

Table 2 The maximum loading capacities for Pd(11) and Pt(1v) on MC-[4]H and their stoichiometries

Metal ion	Maximum loading capacity (mol kg $^{-1}$ )	Loading distribution ratio of metal ions (molecules of calixarenes:metal ions)
Pd Pt	0.41 0.23	5:1 3:1

Table 2 lists the maximum loading capacities for Pd(II) and Pt(IV) on MC-[4]H and their stoichiometries. Five unit molecules of calixarene are required to adsorb palladium while platinum adsorption needs three molecules of calixarene. These metal ions were adsorbed by surrounding calixarene molecules through interaction with hydroxyl groups on the calixarene molecules. Palladium was adsorbed as cationic  $Pd^{2+}$  while platinum was absorbed as  $PtCl_4$ . Cationic palladium has a small size and high affinity. Due to the small size, the five calixarenes struggle to surround  $Pd^{2+}$  due to the convergence effect of ionizable protons on the phenolic site. The affinity of  $Pd^{2+}$  enables it to easily interact with the hydroxyl groups of calixarene molecules by ion exchange and the loading capacity was observed to be high.

Platinum as  $PtCl_4$  has a large size and low affinity. The molecules of calixarenes struggled to surround this species because of the large size of the platinum species. Only three molecules of calixarene surrounded this species. The low affinity of this species caused poor interaction with the hydroxyl groups on the calixarene molecules by ion exchange; therefore, the loading capacity was observed to be low. The structure of the metal complexes could be determined as surrounding the metal ion species with molecules of calixarenes through an ion exchange interaction.

Table 3 lists a comparison of loading capacities on various polyphenolic adsorbents reported in some recent works (Bayberry tannin;<sup>13</sup> ligophenol derivatives (PA-CLP);<sup>10</sup> dimethyl-aminated paper (DMA-Paper),<sup>11</sup> waste paper cellulose (PAB-Paper);<sup>12</sup>

Table 3 Comparison of loading capacities of various polyphenolic adsorbents for  $Pd(\mu)$  and  $Pt(\nu)$ 

	Loading capacity $(mol kg^{-1})$			
Adsorbent	Pd(II)	Pt(IV)	Condition	Ref.
Bayberry tannin	0.41	0.90	pH 2	13
PA-CLP	0.38	0.22	1 M HCl	10
DMA-paper	2.1	0.90	1 M HCl	11
PAB-paper	1.5	0.5	1 M HCl	12
DMA CLP	0.62	0.62	0.5 M HCl	14
MC-[4]H	0.41	0.23	0.1 M HNO <sub>3</sub>	Present work

dimethylaminated crosslinked paper (DMA CLP)<sup>14</sup>). The loading capacities of these metals are slightly smaller or comparable compared to those of polyphenolic biomass sorbents. It was found that the maximum loading capacities for palladium and platinum adsorption on MC-[4]H are higher than those on PA-CLP. A lower functional group density causes a decrease in the capacity of palladium and platinum adsorption on such polyphenolic adsorbents.

Various polyphenolic adsorbents reported in some recent works were isolated and modified from biomass. They have a high phenolic group density facilitating adsorption by ion exchange. On the other hand, MC-[4]H still has a methoxy group on its structure because the demethylation process was not achieved perfectly. The methoxy group may still partially remain in low density, consequently it affects the conformation of calixarene and interferes with capturing metals due to its neutrality and non-ion-exchange ability.

Based on the structure, MC-[4]H and polyphenolic biomass are cyclic and acyclic ligands that have multiple functional groups on their structures. They also provide a high convergence effect due to a large number of proton ionizable functional groups.<sup>28</sup> However, the cyclic ligand has a larger coordination ability due to the chelating effect of multiple functional groups compared to the acyclic ligand because the dehydration ability of the cyclic ligand is larger than that of the acyclic ligand.<sup>30</sup> Due to the higher degree of convergence of multifunctional groups and the coordination effect, MC-[4]H showed a stronger dehydration ability towards metal cations than the polyphenolic biomass adsorbents.

#### Interaction

Fig. 10(A) illustrates the FT-IR spectra of **6** before and after Pd(II) loading (10 mM). The O–H stretching vibration at 3444 cm<sup>-1</sup> shifted to a lower wave number. Ion–exchange interaction between hydroxyl groups and cationic palladium occurred. This phenomenon may be attributed to the fact that a cationic species of Pd<sup>2+</sup> has a high affinity toward the active sites of resin **6** (anionic OH). Fig. 10(B) shows the FT-IR spectra of **6** before and after Pt(vI) adsorption showing good similarity with that of palladium. There is only one band shift from 3426 cm<sup>-1</sup> to 3219 cm<sup>-1</sup>. It is due to the ion–exchange interaction together with ionic interaction of coordinating phenol oxygen atoms to metal ions between hydroxyl groups



and platinum species. In addition, the interaction between the active site of MC-[4]H and both metal ions was facilitated by ion exchange.

Adsorbed palladium was also observed by EDX analysis, as shown in Fig. S11 and S12 (ESI<sup>†</sup>). The palladium content increased with the increase of the loaded amount of palladium ion on **6** evaluated by ICP-AES.

# Conclusions

A macrocyclic polyphenol synthetic adsorbent as a methylene crosslinked type of calix[4]arene resin (MC-[4]H) was successfully prepared. This resin exhibited high ability for palladium and platinum adsorption at low pH due to an ion exchange mechanism. It was found that the interaction between metal ions and the active sites of the resin is followed by chemisorption. The stoichiometries of the metal ions were found to be 5:1 for the MC-[4]H–Pd(II) complex and 3:1 for the MC-[4]H–Pt(IV) complex. Since the adsorption of palladium and platinum easily occurs under low pH conditions, the resin is useful in operations for the capture and recovery of these metals.

# Conflicts of interest

There are no conflicts to declare.

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