

Supporting Information

Extraction of Pd(II) and Pt(II) from aqueous hydrochloric acid with
1,3-diaminocalix[4]arene: Switching of the extraction selectivity by using
different extraction modes

Naoya Morohashi,* Yu Kurusu, Kosuke Akasaka and Tetsutaro Hattori*

*Department of Biomolecular Engineering, Graduate School of Engineering,
Tohoku University, 6-6-11 Aramaki-Aoba, Aoba-ku, Sendai 980-8579, Japan*

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I. Solvent extraction

Table S1 Dependence of $E\%$ on $[\text{HCl}]$ for the extraction of Pt(IV), Rh(III) and Ir(IV) with compound **2**.

$[\text{HCl}] / \text{M}$	$E\%$ [Pt(IV)]	$E\%$ [Rh(III)]	$E\%$ [Ir(IV)]
0.001	8	6	37
0.01	44	14	30
1	57	23	30
4	10	33	19
7	5	14	21

Aq. phase: $[\text{Metal}]_{\text{aq,init}} = 1.0 \times 10^{-4}$ M. Org. phase: CHCl_3 , $[\mathbf{2}]_{\text{org,init}} = 1.0 \times 10^{-3}$ M.

Table S2 Dependence of $E\%$ on $[\text{HCl}]$ for the extraction of Pd(II), Pt(II), Pt(IV), Rh(III) and Ir(IV) with compound **3**.

$[\text{HCl}] / \text{M}$	$E\%$ [Pd(II)]	$E\%$ [Pt(II)]	$E\%$ [Pt(IV)]	$E\%$ [Rh(III)]	$E\%$ [Ir(IV)]
0.001	19	0	3	8	15
0.01	23	15	18	12	8
1	17	16	14	15	12
4	12	10	8	12	14
7	9	8	13	10	20

Aq. phase: $[\text{Metal}]_{\text{aq,init}} = 1.0 \times 10^{-4}$ M. Org. phase: CHCl_3 , $[\mathbf{3}]_{\text{org,init}} = 1.0 \times 10^{-3}$ M.

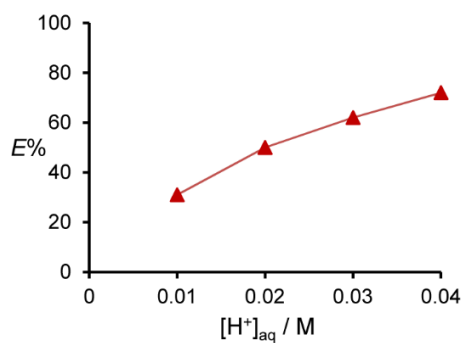


Fig. S1 Dependence of $E\%$ on $[H^+]$ for the extraction of Pt(II) with compound **2**. Aq. phase: $[Metal]_{aq,init} = 1.0 \times 10^{-4}$ M, $[Cl^-] = 0.04$ M. $[H^+]$ and $[Cl^-]$ was adjusted by the addition of HCl and LiCl. Org. phase: $CHCl_3$, $[2]_{org,init} = 1.0 \times 10^{-3}$ M.

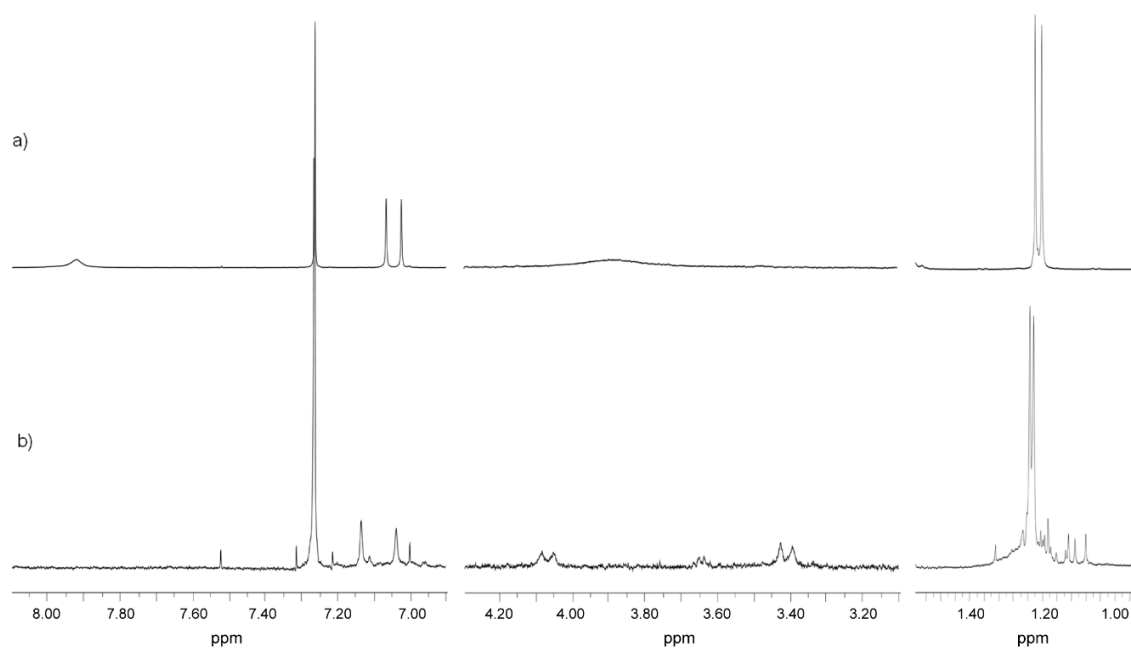


Fig. S2 Partial 1H NMR spectra of $CDCl_3$ solution of compound **2** before (a) and after (b) extraction of Pd(II). Condition for solvent extraction: Aq. phase: $[Pd(II)]_{aq,init} = 1.0 \times 10^{-3}$ M, $[HCl] = 0.001$ M. Org. phase: $CDCl_3$, $[2]_{org,init} = 1.0 \times 10^{-3}$ M.

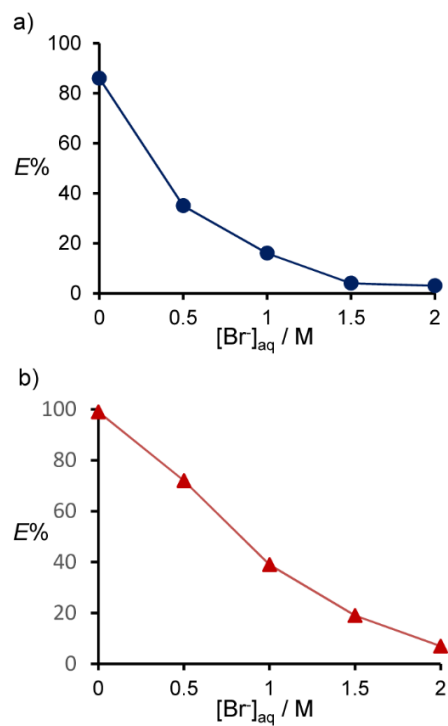


Fig. S3 Dependence of $E\%$ on $[\text{Br}^-]$ for the extraction of Pd(II) (a) and Pt(II) (b) with compound **2**. Aq. phase: $[\text{Metal}]_{\text{aq,init}} = 1.0 \times 10^{-4} \text{ M}$, $[\text{HCl}] = 0.5 \text{ M}$. $[\text{Br}^-]$ was adjusted by the addition of KBr. Org. phase: CHCl_3 , $[\mathbf{2}]_{\text{org,init}} = 1.0 \times 10^{-3} \text{ M}$.

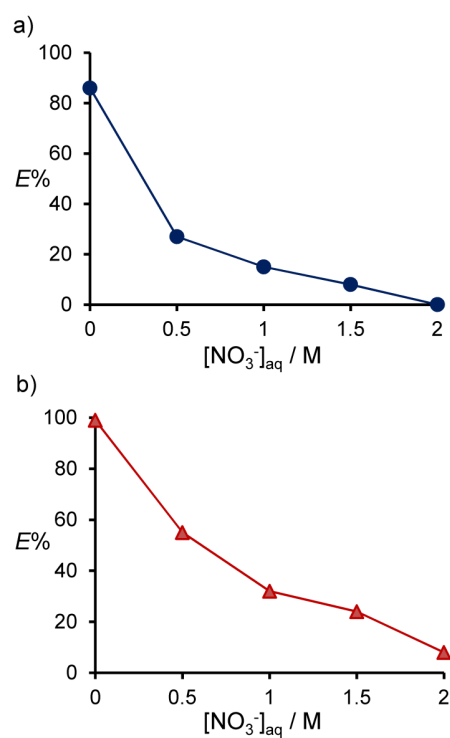


Fig. S4 Dependence of $E\%$ on $[\text{NO}_3^-]$ for the extraction of Pd(II) (a) and Pt(II) (b) with compound **2**. Aq. phase: $[\text{Metal}]_{\text{aq,init}} = 1.0 \times 10^{-4} \text{ M}$, $[\text{HCl}] = 0.5 \text{ M}$. $[\text{NO}_3^-]$ was adjusted by the addition of LiNO_3 . Org. phase: CHCl_3 , $[\mathbf{2}]_{\text{org,init}} = 1.0 \times 10^{-3} \text{ M}$.

II. ^1H and ^{13}C NMR of synthesized metal complexes

1. [PdL]

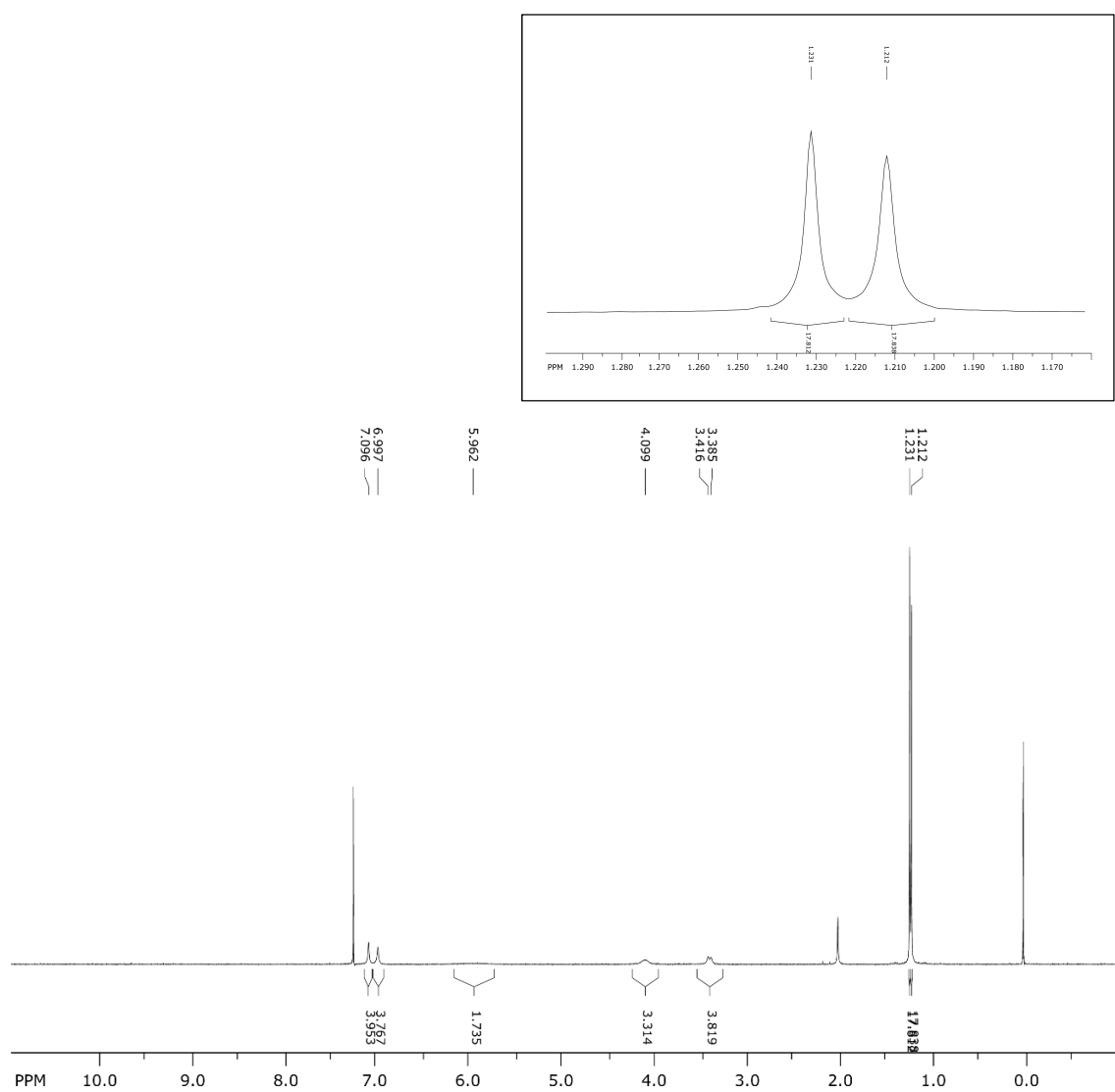


Fig. S5 ^1H NMR spectrum of [PdL] (CDCl_3 , 400 MHz).

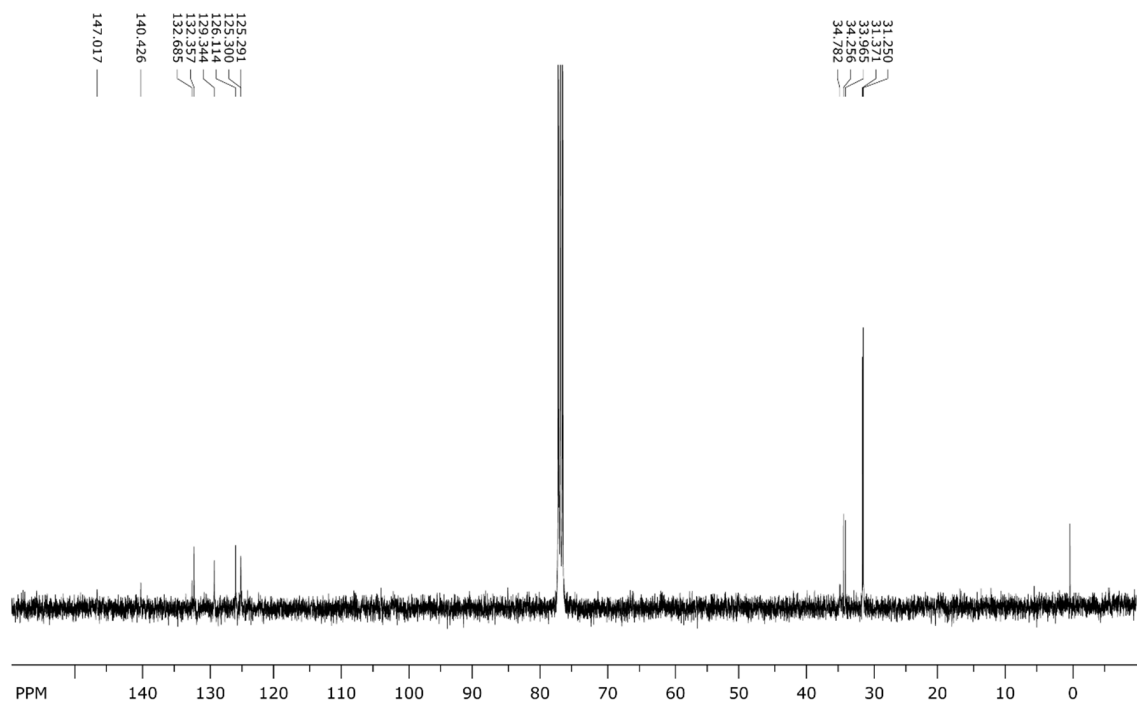


Fig. S6 ^{13}C NMR spectrum of [PdL] (CDCl_3 , 100 MHz).

2. $[\text{Pt}_2\text{Cl}_6(\text{H}_3\text{L})_2]$

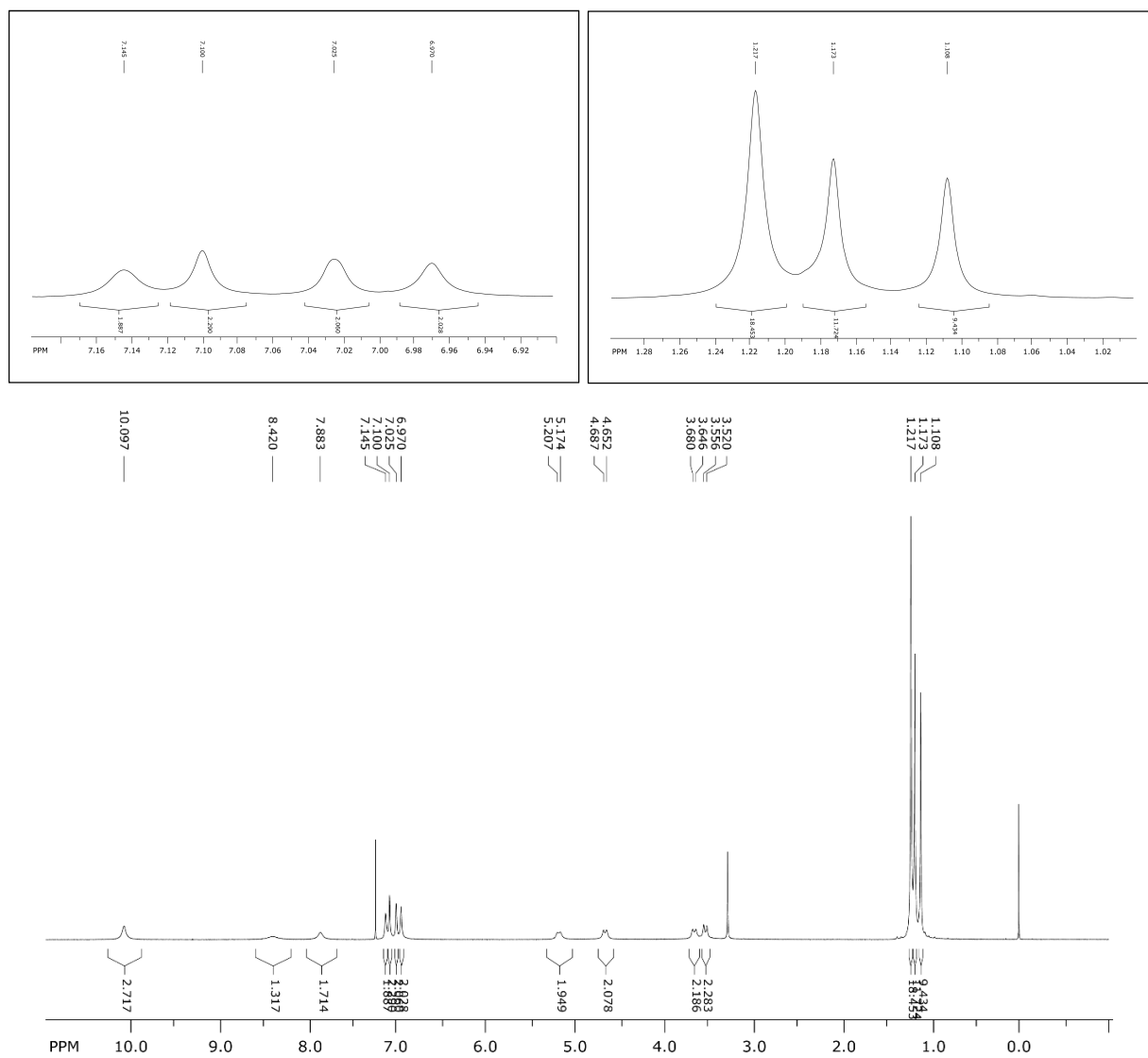


Fig. S7 ^1H NMR spectrum of $[\text{Pt}_2\text{Cl}_6(\text{H}_3\text{L})_2]$ (CDCl_3 , 400 MHz).

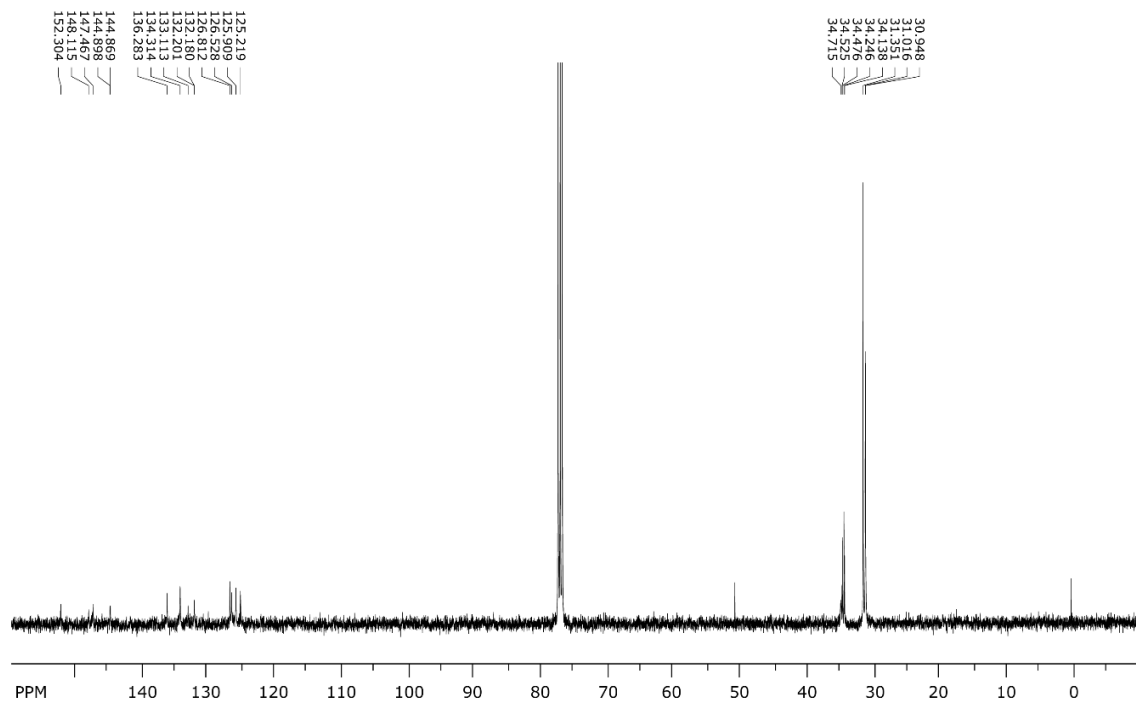


Fig. S8 ¹³C NMR spectrum of [Pt₂Cl₆(H₃L)₂] (CDCl₃, 100 MHz).