

Supplementary Information

Two chiral multinuclear palladium (II) complexes comprising alternatively arranged isomeric hexanuclear clusters

Zhengguo Lin^{a,b}, Baokuan Chen^{a,b}, Xiao Feng^a, Bo Wang^{*a}, Yingnan Chi^a, Yanxuan Fan^a, Xinhang Yang^a, Xianqiang Huang^a, and Changwen Hu^{*a}

^a Key Laboratory of Cluster Science, Ministry of Education of China, School of Chemistry, Beijing Institute of Technology, Beijing 100081, P. R. China

^b These authors contributed equally to this work.

General experimental section and synthesis methods

Materials and physical methods

In this work, all materials were reagent grade obtained from commercial sources and used without further purification. Crystal data for compounds **1** and **2** were collected at 297 (2) K on Bruker APEX-II CCD detector with graphite monochromatic Mo K α radiation ($\lambda=0.71073\text{\AA}$). The detail crystallographic data are summarized in **Table S1** and **Table S2**. IR spectra were recorded on a Nicolet 170SX-FT/IR spectrometer using KBr pellets in the range of 4000-400 cm^{-1} . The UV-Vis spectra were obtained on a TU-1901 spectrophotometer in the range 200-600 nm. The TGA was performed on a DTG-60AH instrument under N₂ atmosphere with a heating rate of 10°C/min. The CD spectra measurements were obtained on MOS-450 circular dichroism chiroptical spectrometer and JASCO J-810 dichroism chiroptical spectropolarimeter. Elemental (C, H, and N) analyses were performed on a Perkin-Elmer 2400 II analyzer. Mass spectra measurements were made in the negative ion mode on an Agilent 6520 Q-TOF LC/MS mass spectrometer. The X-ray powder diffraction (XPRD) of samples was collected on a Japan Rigaku X-ray diffractometer equipped with graphite-monochromatized Cu K α radiation ($\lambda=0.15418\text{\AA}$).

(1) Synthesis and discussion

Complexes 1: [Pd₆(Cys)₄(CysH)₄][Pd₆(CysH)₈]Cl₄·24H₂O

0.177g (1mmol) PdCl₂ dissolved in 10 ml of H₂O, which was stirred and heated to 90 °C for 20 min. Then 0.182g (1.5 mmol) L-cys was added to the solution, stirred and heated for 30 min, the deep red solution cooled to room temperature followed by removal of a small amount of precipitate through filtration. The pH value of the resulting solution is about 0.9, and the solution was left to evaporate at room temperature. After several weeks deep red needle crystals were obtained that were of suitable quality for single-crystal X-ray diffraction (yield based on Pd: 73%). Selected IR (KBr, cm^{-1}): 1717.1 (s), 1594.1 (m), 1417.1 (m), 1396.0 (s), 1283.0 (s), 1246.6 (s), 1216.6 (s), 1076.3 (s) Elemental analysis (%) found (calcd) for **2**: C, 15.30 (15.87); H, 3.74 (3.56); N, 5.95 (6.08).

Complexes 2: Pd₆(HCys)₁₀](NO₃)₂·11H₂O

0.0484g (0.4 mmol) L-cys and 0.088g (0.2 mmol) Er(NO₃)₃·5H₂O dissolved in 5 ml of H₂O. This solution was stirred and heated to 60°C for 20 minutes, a solution of 1 mol/L NaOH was added dropwise until the local precipitate not dissolved. After 5 minutes stirred and heated, 0.0354g (0.2 mmol) PdCl₂ was added to the above solution, and a yellow precipitate forms quickly, then a solution of 1 mol/L HNO₃ was added dropwise until the yellow precipitate dissolved, stirred and heated the solution for 3 hours, cooled to room temperature and filtrated, the pH value of resulting orange red solution is about 1.2. Then the resulting orange red solution was left to

evaporate at room temperature. After several days, salmon pink block-shaped crystals were obtained that were of suitable quality for single-crystal X-ray diffraction (yield based on Pd: 47%). Selected IR (KBr, cm⁻¹): 1719.1 (s), 1617.5 (s), 1498.5 (m), 1384.4 (s), 1353.2 (w), 1244.4 (m) Elemental analysis (%) found (calcd) for 2: C, 16.67 (17.91); H, 3.82 (3.64); N, 7.77 (7.89).

Complexes **1** and **2** were synthesized under controlled reaction conditions, the ratio of L-Cys ligands and Pd(II) ions and pH play a crucial role during the self-assembly of hexanuclear clusters. For complex **1**, the ratio of Pd(II) ions and L-Cys ligands should be controlled in 2:3 and the pH value of the resulting solution is about 0.9, if the reaction conditions are changed, there are no crystals of **1** obtained. For complex **2**, the ratio of Pd(II) ions and L-Cys ligands should be controlled in 1:2 and the pH value of the resulting solution is about 1.2, in addition, the Er(NO₃)₃·5H₂O play a significant part in the synthetic process which can provide the NO₃⁻ as the counterions. If the Er(NO₃)₃·5H₂O is absent during the reaction, there are no crystals of **2** obtained.

Notably, according to the reaction condition and the structure of complex **1**, we have tried to synthesize new chiral 3d-4f bimetallic complexes in this synthetic system in which the Er(NO₃)₃·5H₂O was selected as source of 4f ions under many different conditions. To our surprise, when the ratio of Pd(II) ions and L-Cys ligands was controlled in 1:2, a new chiral hexanuclear palladium(II) complex **2** was obtained under the special condition and the Er³⁺ is absent in the structure. However, the Er(NO₃)₃·5H₂O play a significant part in the synthetic process which can provide the NO₃⁻ as the counterions to synthesize **2**. If the Er(NO₃)₃·5H₂O is absent during the reaction, there are no crystals of **2** obtained. What's more, the KNO₃ was chosen as the source of NO₃⁻ instead of Er(NO₃)₃·5H₂O, but the complex **2** cannot be prepared, which means both the NO₃⁻ and Er³⁺ are important in this synthetic system, though the detail reason is still unclear. We think the two chiral clusters should synthesize under controlled reaction condition and the ratio of L-Cys ligands and Pd(II) ions and pH play a crucial role during the self-assembly of the two different hexanuclear clusters.

(2) Crystal data and structure refinements for Complexes **1** and **2**

Crystal data for complexes **1** and **2** were collected at 296(2) K on Bruker APEX-II CCD detector with graphite monochromatic Mo K α radiation ($\lambda=0.71073\text{\AA}$). Crystals were mounted on a glass fiber and fixed with glue. All absorption corrections were applied using multi-scan technique. The structures were solved by the direct method and refined through full-matrix least-squares techniques method on F2 using by the SHELXTL program package (Bruker).^[1-3] All non-hydrogen atoms were located by direct methods and were refined anisotropically. The hydrogen atoms were located by geometrical calculations, and their positions and thermal parameters were fixed during structure refinement, and in complex **2**, one of the nitrate anions is disordered. The crystal data and structure refinement for the two compounds were summarized in Table S1 and Table S2. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as entries. CCDC: 935798 and 935799.

Table S1. Crystallographic Data for Complexes **1** and **2**

<i>Compounds</i>	1	2
Formula	C ₄₈ H ₁₄₀ N ₁₆ S ₁₆ Cl ₄ Pd ₁₂ O ₅₆	C ₃₀ H ₈₂ N ₁₂ S ₁₀ Pd ₆ O ₃₇
<i>M_r</i>	3769.59	2162.20
Crystal system	Tetragonal	Orthorhombic
Space group	<i>P4</i> ₂ <i>1</i> ₂	<i>P2</i> ₁ <i>2</i> ₁ <i>2</i>
Temperature(K)	296(2)	296(2)
<i>a</i> (Å)	18.044(6)	16.252(3)
<i>b</i> (Å)	18.044(6)	19.150(3)
<i>c</i> (Å)	19.407(8)	22.751(4)
α (deg)	90	90
β (deg)	90	90

γ (deg)	90	90
V (Å ³)	6319(4)	7081(2)
Z	2	4
$D_{\text{calc.}}$ (g cm ⁻³)	1.98	2.01
Flack parameter	-0.09(7)	-0.01(6)
$F(000)$	3632	4224
$R_1[I > 2\sigma(I)]$	0.0664	0.0693
$wR_2[I > 2\sigma(I)]$	0.1717	0.1759
R_1 (all data)	0.1065	0.0914
wR_2 (all data)	0.2022	0.2020
GOOF	1.040	1.079

Table S2. Selected bond distances (Å) of Complexes **1** and **2**

<i>Compound 1</i>		<i>Compound 2</i>	
Pd(1)-S(1)	2.334(3)	Pd(1)-S(5)	2.246(2)
Pd(1)-S(1)#4	2.334(3)	Pd(1)-S(4)	2.291(2)
Pd(1)-S(1)#5	2.334(3)	Pd(1)-N(4)	2.081(9)
Pd(1)-S(1)#6	2.334(3)	Pd(1)-N(5)	2.102(8)
Pd(2)-S(2)	2.344(3)	Pd(2)-S(4)	2.316(2)
Pd(2)-S(2)#5	2.344(3)	Pd(2)-S(3)	2.320(2)
Pd(2)-S(2)#6	2.344(3)	Pd(2)-S(2)#1	2.325(2)
Pd(2)-S(2)#4	2.344(3)	Pd(2)-S(1)#1	2.334(2)
Pd(3)-S(1)	2.264(3)	Pd(3)-S(2)	2.326(2)
Pd(3)-S(2)	2.276(3)	Pd(3)-S(5)	2.327(2)
Pd(3)-N(1)	2.090(10)	Pd(3)-S(3)	2.337(2)
Pd(3)-N(2)	2.072(10)	Pd(3)-S(1)	2.348(2)
Pd(4)-S(4)#3	2.338(3)	Pd(4)-S(6)	2.252(2)
Pd(4)-S(4)#2	2.338(3)	Pd(4)-N(6)	2.080(7)
Pd(4)-S(4)	2.338(3)	Pd(4)-N(10)#1	2.062(7)
Pd(4)-S(4)#1	2.338(3)	Pd(4)-S(10)#1	2.252(2)
Pd(5)-S(3)#1	2.354(3)	Pd(5)-S(10)	2.3176(19)
Pd(5)-S(3)	2.354(3)	Pd(5)-S(8)	2.3269(18)
Pd(5)-S(3)#2	2.354(3)	Pd(5)-S(9)	2.329(2)
Pd(5)-S(3)#3	2.354(3)	Pd(5)-S(7)#1	2.3331(19)
Pd(6)-S(3)	2.273(3)	Pd(6)-S(6)	2.3107(19)
Pd(6)-S(4)	2.268(3)	Pd(6)-S(7)	2.318(2)
Pd(6)-N(3)	2.091(10)	Pd(6)-S(8)	2.3350(18)
Pd(6)-N(4)	2.111(9)	Pd(6)-S(9)	2.348(2)

Compound 1: Symmetry transformations used to generate equivalent atoms:

#1 $-x+1, -y+2, z$ #2 $y-1/2, -x+3/2, z$
 #3 $-y+3/2, x+1/2, z$ #4 $-y+3/2, x-1/2, z$
 #5 $y+1/2, -x+3/2, z$ #6 $-x+2, -y+1, z$

Compound 2: Symmetry transformations used to generate equivalent atoms:

#1 $-x, -y, z$ #2 $-x, -y+2, z$ #3 $-x+2, -y, z$

(3) Crystal structure of complex 1 and 2

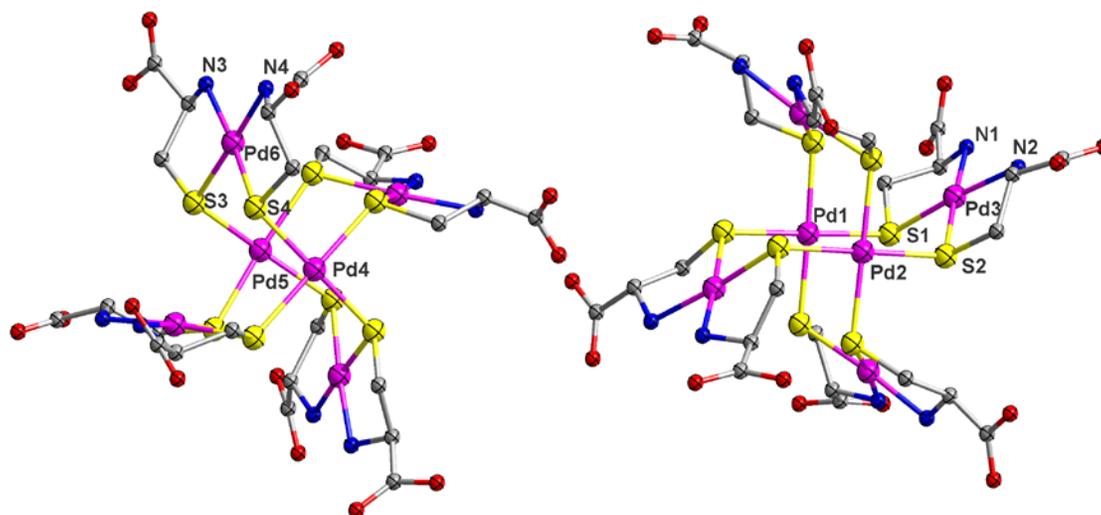


Fig. S1. The thermal ellipsoid picture of two isomeric hexanuclear Pd(II) clusters in Complex 1. (50 % probability ellipsoids). The hydrogen atoms are omitted for clarity.

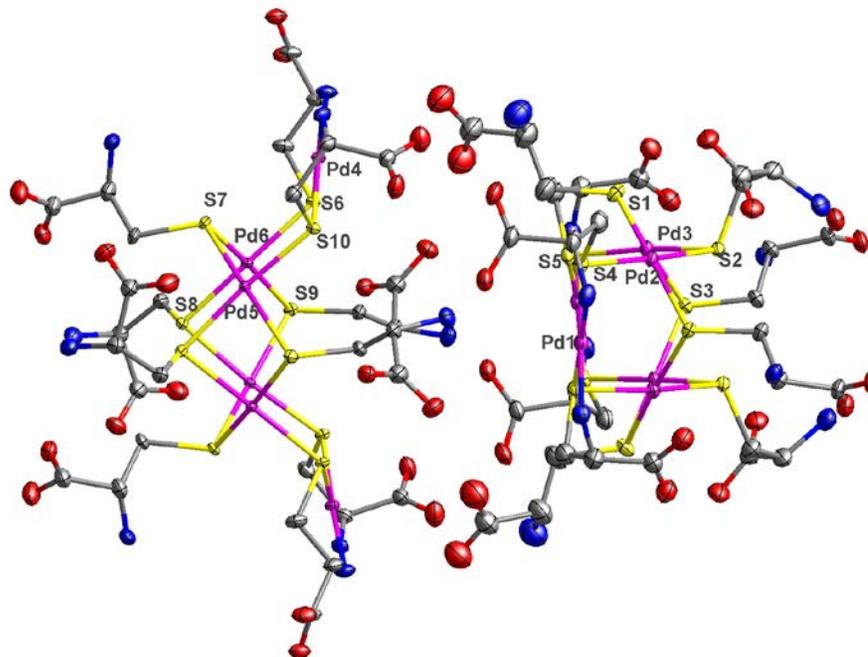


Fig. S2. The thermal ellipsoid picture of two isomeric hexanuclear Pd(II) clusters Complex 2. (50 % probability ellipsoids). The hydrogen atoms are omitted for clarity.

(4) IR Spectra of Complexes **1** and **2**

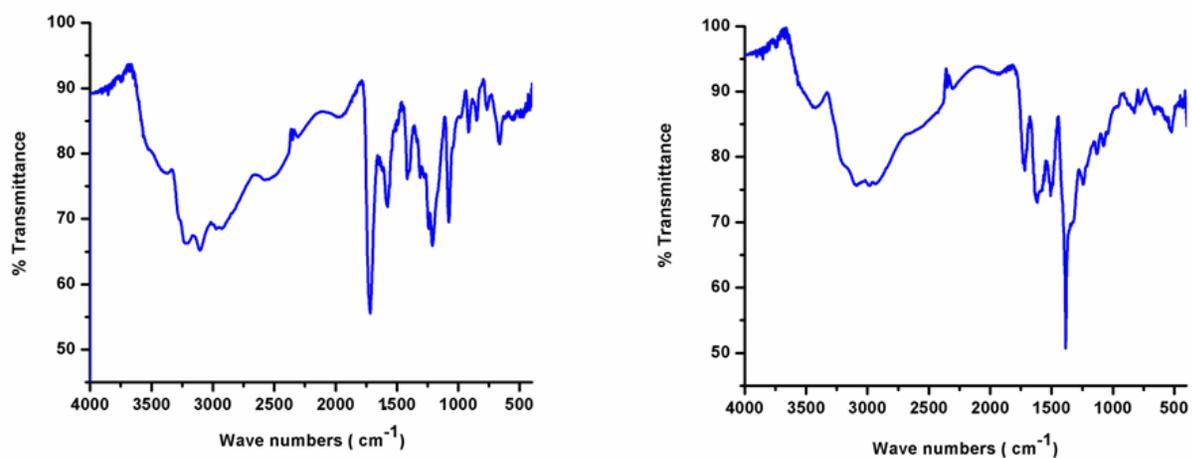


Fig. S3 IR spectra of compounds **1**(left) and **2** (right) single crystals

(5) Solid CD Spectra of Complexes **1** and **2**

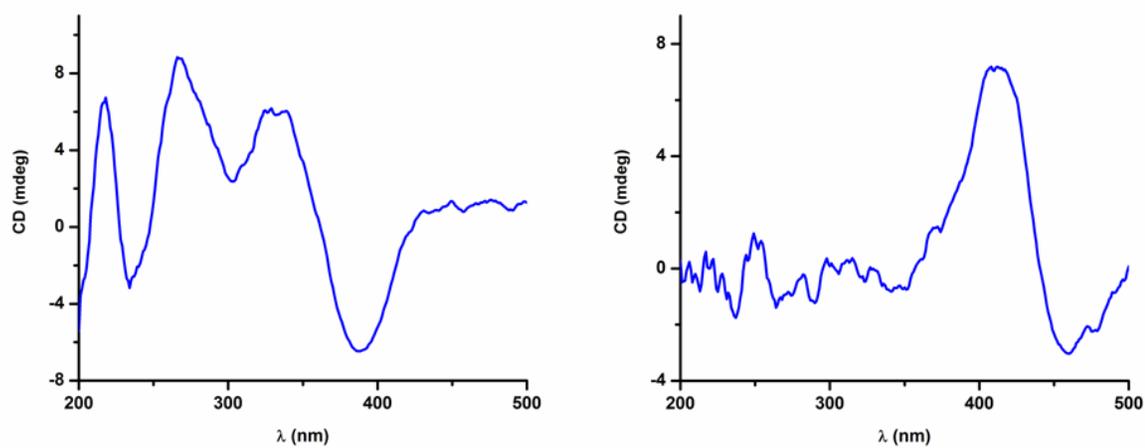


Fig. S4 Solid CD Spectra of compounds **1**(left) and **2** (right) single crystals

(6) Thermal gravimetric analyses for Complexes **1** and **2**

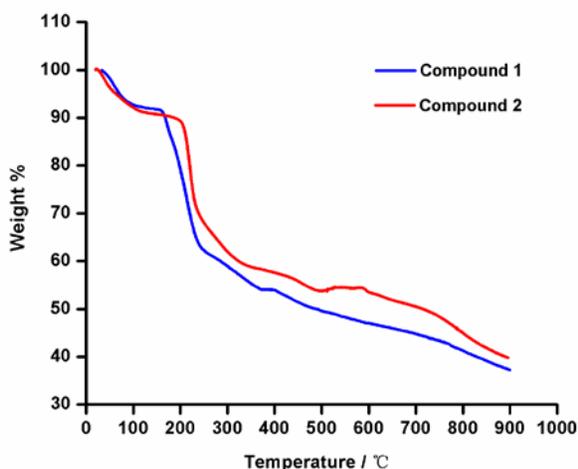


Fig. S5 Thermal gravimetric analyses for Complexes **1** and **2** from room temperature to 900 °C under N₂ atmosphere

TGA studies of **1** and **2** were performed under N₂ at a 10 °C/min rate (Fig S5). Three continuous weight losses steps were observed on the TGA curve of Complex **1**. The first weight loss of 9.7 % (calcd. 11.4%) in the range 25–210 °C is attributed to the removal of remaining water molecules in the compound and the continuous weight losses steps after 210 °C means the decomposition of the cluster **1**. TGA curve of Complex **2** is similar to that of Complex **1**. The first weight loss of 9.8% (calcd. 9.2 %) in the range of 25–230 °C is attributed to the removal of 11 water molecules and the continuous weight losses steps after 230 °C means the decomposition of the cluster **2**.

(7) XRD pattern of Complexes **1** and **2**

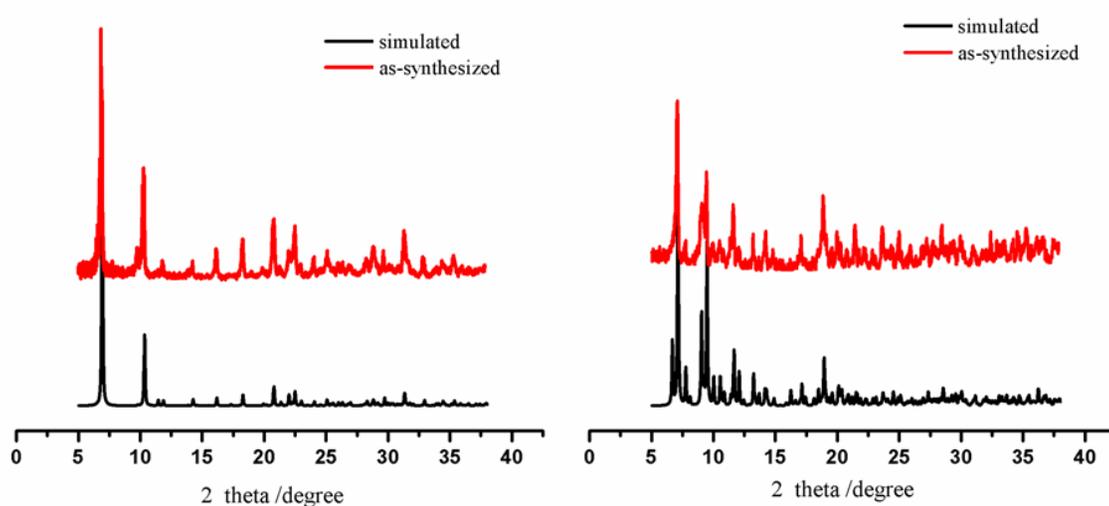


Fig. S6 The simulated and experimental powder XRD pattern of crystals of **1** (left) and **2** (right). Simulation based on the single crystal X-ray diffraction data.

(8) Selected ESI-MS spectra of complex **1** and **2**

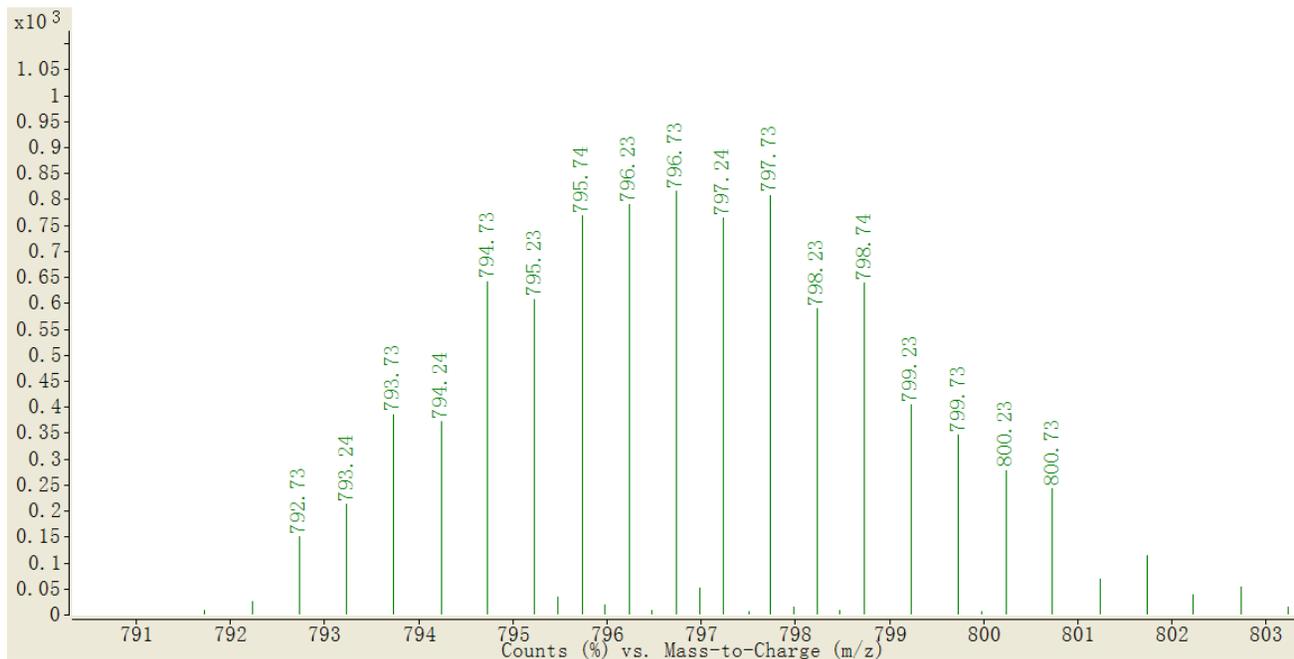


Fig. S7 Selected ESI-MS spectra of $[\text{H}_2\text{Pd}_6(\text{C}_3\text{H}_5\text{NO}_2\text{S})_8]^{2-}$ cluster in complex **1**.

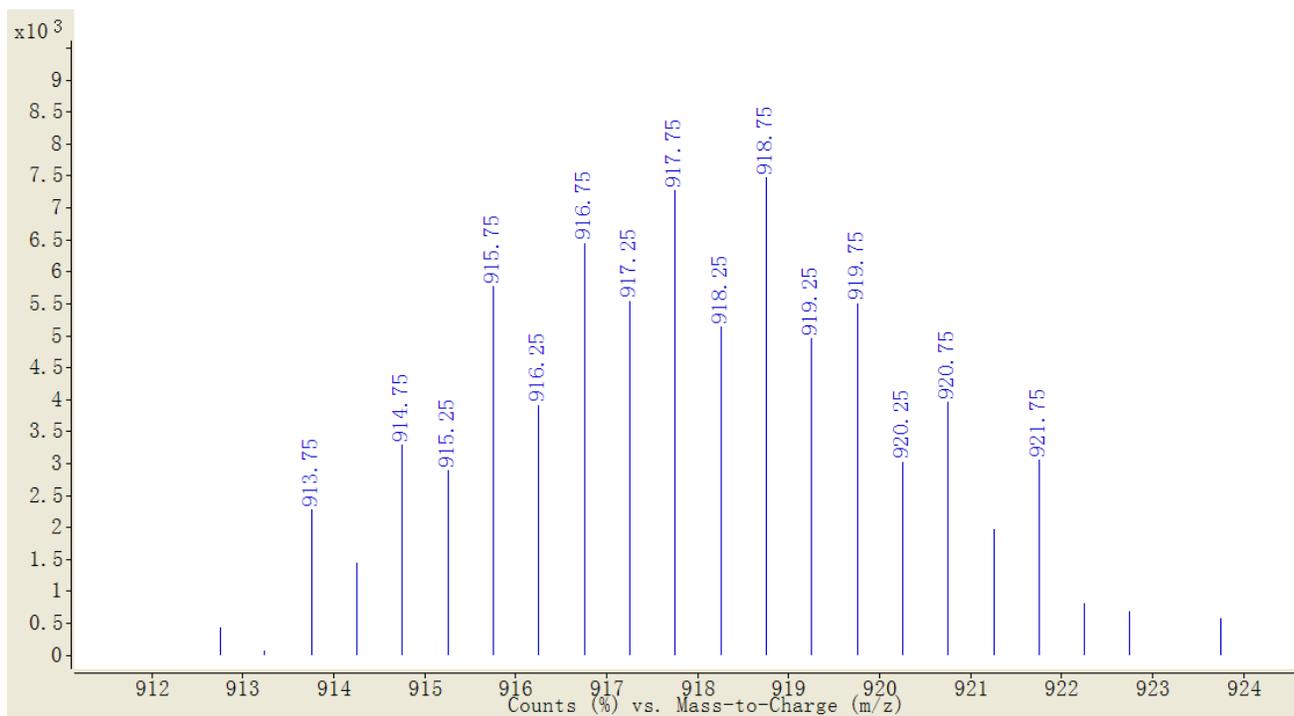


Fig. S8 Selected ESI-MS spectra of cluster $[\text{H}_6\text{Pd}_6(\text{C}_3\text{H}_5\text{NO}_2\text{S})_{10}]^{2-}$ in complex **2**.

References

- [1] Sheldrick, G. M. *SHELXL 97, Program for the Refinement of Crystal Structure*, University of Göttingen, Germany, 1997.
- [2] Sheldrick, G. M. *SHELXL 97, Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, 1997.
- [3] Sheldrick, G. M. *SHELXTL NT/2000*, v6.12; Bruker Analytical X-ray Systems.