

ELECTRONIC SUPPORTING INFORMATION (ESI)

for

Interconversion between square-planar palladium(II) and
octahedral palladium(IV) centres in a sulfur-bridged trinuclear
structure

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Materials

All chemicals were of commercial grade and were used without further purification. *fac*-[Rh(*apt*)₃] was prepared according to a previously reported method.^[S1]

General methods.

IR spectra were recorded on a JASCO FT/IR-4100 infrared spectrophotometer using KBr disks at room temperature. Elemental analysis (C, H, N) was performed at Osaka University using YANACO CHN coda MT-6. ¹H and ¹³C{¹H} NMR spectra were recorded in D₂O using 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS) as an internal standard with a JEOL ECA-500 instrument. Absorption spectra were recorded on a JASCO V-670 UV/VIS spectrometer at room temperature. Powder X-ray diffractions were recorded on a BRUKER D2 PHASER at room temperature. The powder simulation patterns were generated from the single-crystal X-ray structures using Mercury 3.0. The electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) data were recorded on BRUKER micrOTOF II-OS in H₂O/CH₃OH. X-ray fluorescence spectrometry was performed on a Shimadzu EDX-7000 spectrometer.

X-ray crystallography. Diffraction data for [2](NO₃)₂ were recorded on a Rigaku Mercury 2 CCD detector using synchrotron radiation ($\lambda = 0.700 \text{ \AA}$) at the BL02B1 beamline in SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI). The single-crystal X-ray diffraction measurement for [3](NO₃)₂ was performed at 100 K with synchrotron radiation ($\lambda = 0.6300 \text{ \AA}$) at a 2D beamline in the Pohang Accelerator Laboratory (PAL); a Rayonix MX225HS CCD area detector was used as a detector. Absorption correction for [3](NO₃)₂ was performed empirically with the program HKL3000sm. The single-crystal X-ray diffraction measurements for [4](NO₃)₃ and [1](NO₃)₄ were performed at 200 K with a Rigaku FR-E Superbright rotating-anode X-ray source with a Mo-target ($\lambda = 0.71075 \text{ \AA}$); a Rigaku RAXIS VII imaging plate was used as the detector. Intensity data were collected using the ω -scan technique and processed with a Rapid Auto software program. The structures were solved by direct methods using SHELXS-2014.^[S2] Structure refinements were carried out using full-matrix least squares (SHELXL-2014) analysis.^[S2] All calculations were performed using the Yadokari-XG software package.^[S3] Hydrogen atoms were included in the calculated positions except for those from water molecules. For [1](NO₃)₄, all non-hydrogen atoms were refined anisotropically. For [1](NO₃)₄, all non-hydrogen atoms were refined anisotropically. For [2](NO₃)₂, all non-hydrogen atoms were refined anisotropically. Each two nitrate anions (N16, O10, O11, O12, N17, O13, O14, O15) was disordered in each two positions. A part of the disordered *apt* ligand and nitrate anions were refined using DFIX, DFLU, FLAT and ISOR restraints and SIMU constraints. For [3](NO₃)₂ and [4](NO₃)₃, all non-hydrogen atoms were refined anisotropically.

The X-ray crystallographic coordinates for the structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers CCDC 20444288-

2044291. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Electrochemical experiments. Cyclic voltammetry (CV) measurements were performed at room temperature using an ALS/CHI-720ES voltammetric analyser. The working, reference, and counter electrodes were a glassy carbon disk electrode (ϕ 1.8 mm), a reference Ag/AgCl electrode (3.0 M NaCl aq.), and a platinum wire, respectively. Sample solutions were prepared at a concentration of 1.0 mM and contained 0.01 M HNO₃. Spectroelectrochemical experiments were performed using a thin-layer quartz cell (0.5 mm light path length) with a Pt-mesh (100 mesh) working electrode, an aqueous Ag/AgCl/NaCl (3 M) reference electrode, and a Pt-wire auxiliary electrode.

Preparation of [Pd{Rh(apt)₃}₂](NO₃)₄ ([1](NO₃)₄). Na₂[PdCl₄] (20 mg, 67 μ mol) was added to a yellow suspension of *fac*-[Rh(apt)₃] (50 mg, 0.13 mmol) in 25 mL of water. After stirring at room temperature for 3 h, the resulting orange suspension was filtered. A saturated aqueous solution of sodium nitrate (15 mL) and 0.1 M nitric acid (2.5 mL) were added to the clear orange filtrate, followed by stirring at room temperature for 20 min. The resulting dark red solution was incubated at room temperature. The black crystals that appeared were collected by filtration. Yield: 21.4 mg (26%). Anal. Calcd for [Pd{Rh(apt)₃}₂](NO₃)₄·6H₂O = C₁₈H₆₀N₁₀O₁₈Pd₁Rh₂S₆: C, 17.88; H, 5.00; N, 11.58%. Found: C, 17.76; H, 4.74; N, 11.87%. One of the crystals was used for single-crystal X-ray analysis. IR spectrum (cm⁻¹, KBr disk): 3157 (ν_{NH_2}), 3087 (ν_{NH_2}), 2953 (ν_{CH_2}), 1598 (δ_{NH_2}), 1385 (ν_{NO_3}). ¹H NMR spectrum (ppm from DSS, D₂O): 4.99 (1H, d, J = 10.9 Hz), 4.04 (1H, t, J = 9.5 Hz), 3.20-3.10 (2H, m), 3.05 (1H, d, J = 13.0 Hz), 2.83 (1H, t, J = 12.0 Hz), 2.39-2.30 (1H, m), 1.96 (1H, dd, J_1 =26.7 Hz, J_2 =11.4 Hz). ¹³C{¹H} NMR spectrum (ppm from DSS, D₂O): δ 44.24, 33.07, 30.16. UV-Vis absorption in water (λ_{max} / nm (ϵ / mol⁻¹dm³cm⁻¹): 500^{sh} (7020), 436 (19100), 336 (15600), 280 (23700). (sh denotes the shoulder band.) MS (ESI-pos): m/z = 434.0 (2+, {[Pd^{II}{Rh(apt)₃}₂]²⁺ + O}²⁺), 476.5 (2+, {[Pd^{II}{Rh(apt)₃}₂]²⁺ + O + NaNO₃}²⁺), 929.9 (1+, {[Pd^{II}{Rh(apt)₃}₂]²⁺ + O + NO₃}⁺).

Preparation of [Pd{Rh(apt)₃}₂](NO₃)₂ ([2](NO₃)₂). Na₂[PdCl₄] (20 mg, 67 μ mol) was added to a yellow suspension of *fac*-[Rh(apt)₃] (50 mg, 0.13 mmol) in 10 mL of water. After stirring at room temperature for 30 min, the resulting orange suspension was filtered. A saturated aqueous solution of sodium nitrate (10 mL) was added to the clear orange filtrate, followed by standing at room temperature. The orange crystals that appeared were collected by filtration. Yield: 28.5 mg (27%). Anal. Calcd for [Pd{Rh(apt)₃}₂](NO₃)₂·2H₂O·0.5NaNO₃ = C₁₈H₅₂N_{8.5}Na_{0.5}O_{9.5}Pd₁Rh₂S₆: C, 20.48; H, 4.96; N, 11.28%. Found: C, 20.33; H, 4.96; N, 11.26%. One of the crystals was used for single-crystal X-ray analysis. IR spectrum (cm⁻¹, KBr disk): 3216 (ν_{NH_2}), 3125 (ν_{NH_2}), 2921 (ν_{CH_2}), 1593 (δ_{NH_2}), 1385 (ν_{NO_3}). ¹H NMR spectrum (ppm from DSS, D₂O): 3.88-3.36 (4H, m), 3.32-3.13 (1H, m), 2.99 (2H, m), 2.90 (2H, m), 2.72 (1H, m), 2.63-2.36 (3H, m), 2.36-1.54 (7H, m). UV-Vis absorption in water (λ_{max} / nm (ϵ / mol⁻¹

$^1\text{dm}^3\text{cm}^{-1}$): 347 (12500). MS (ESI-pos): $m/z = 334.9$ ($2+$, $\{[\text{Pd}^{\text{II}}\{\text{Rh}(\text{apt})_3\}_2]^{2+} - 2\text{Hapt}\}^{2+}$), 380.4 ($2+$, $\{[\text{Pd}^{\text{II}}\{\text{Rh}(\text{apt})_3\}_2]^{2+} - \text{Hapt}\}^{2+}$), 427.0 ($2+$, $[\text{Pd}^{\text{II}}\{\text{Rh}(\text{atp})_3\}_2]^{2+}$).

Preparation of $[\text{Pd}\{\text{Rh}(\text{apt})_2(\text{apsi})\}_2](\text{NO}_3)_2$ ([3]** $(\text{NO}_3)_2$).** $\text{Na}_2[\text{PdCl}_4]$ (20 mg, 0.067 mmol) was added to a yellow suspension of *fac*- $[\text{Rh}(\text{apt})_3]$ (50 mg, 0.13 mmol) in 10 mL of water. After stirring at room temperature for 10 min, 3 mL of 3% H_2O_2 was added. The resulting yellow solution was filtrated. A saturated aqueous solution of sodium nitrate (10 mL) was added to the clear yellow, followed by standing at room temperature. The yellow crystals that appeared were collected by filtration. Yield: 27.1 mg (36%). Anal. Calcd for $[\text{Pd}\{\text{Rh}(\text{apsi})_3\}_2](\text{NO}_3)_2 \cdot 5\text{H}_2\text{O} = \text{C}_{18}\text{H}_{58}\text{N}_8\text{O}_{15}\text{Pd}_1\text{Rh}_2\text{S}_6$: C, 19.11; H, 5.17; N, 9.90%. Found: C, 19.06; H, 4.94; N, 10.07%. One of the crystals was used for single-crystal X-ray analysis. IR spectrum (cm^{-1} , KBr disk): 3234 (ν_{NH_2}), 3133 (ν_{NH_2}), 2923 (ν_{CH_2}), 1577 (δ_{NH_2}), 1385 (ν_{NO_3}), 1158 (ν_{SO_2}), 1030 (ν_{SO_2}). ^1H NMR spectrum (ppm from DSS, D_2O): 4.89 (1H, d, $J = 10.6$ Hz), 4.62 (1H, t, $J = 11.5$ Hz), 4.14 (1H, d, $J = 9.7$ Hz), 4.08 (1H, t, $J = 11.4$ Hz), 3.83 (1H, d, $J = 10.9$ Hz), 3.62 (1H, t, $J = 12.0$ Hz), 3.51 (2H, d, $J = 12.7$ Hz), 3.17 (1H, q, $J = 13.3$ Hz), 3.07-2.96 (3H, m), 2.88 (1H, q, $J = 13.1$ Hz), 2.68-2.43 (4H, m), 2.30 (1H, d, $J = 14.4$ Hz), 2.23-1.92 (5H, m), 1.74 (1H, q, $J = 12.0$ Hz). UV-Vis absorption in water ($\lambda_{\text{max}} / \text{nm}$ ($\epsilon / \text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$): 339 (20200), 265 (31500). MS (ESI-pos): $m/z = 397.4$ ($2+$, $\{[\text{Pd}\{\text{Rh}(\text{apt})_2(\text{apsi})\}_2]^{2+} - \text{apt} - 2\text{O}\}^{2+}$), 427.0 ($2+$, $\{[\text{Pd}\{\text{Rh}(\text{apt})_2(\text{apsi})\}_2]^{2+} - 4\text{O}\}^{2+}$), 459.0 ($2+$, $[\text{Pd}\{\text{Rh}(\text{apt})_2(\text{apsi})\}_2]^{2+}$).

Preparation of $[\text{AgPd}\{\text{Rh}(\text{apt})_3\}_2](\text{NO}_3)_3$ ([4]** $(\text{NO}_3)_3$).** $\text{Na}_2[\text{PdCl}_4]$ (40 mg, 0.14 mmol) and AgNO_3 (24 mg, 0.14 mmol) were added to a yellow suspension of *fac*- $[\text{Rh}(\text{apt})_3]$ (100 mg, 0.27 mmol) in 50 mL of water. After stirring at room temperature for 3 h, the resulting yellow solution was filtered. A saturated aqueous solution of sodium nitrate (1 mL) was added to the clear yellow filtrate, followed by standing at room temperature. The yellow crystals that appeared were collected by filtration. Yield: 80.0 mg (48%). Anal. Calcd for $[\text{AgPd}\{\text{Rh}(\text{apt})_3\}_2](\text{NO}_3)_3 \cdot 5\text{H}_2\text{O} = \text{C}_{18}\text{H}_{58}\text{Ag}_1\text{N}_9\text{O}_{14}\text{Pd}_1\text{Rh}_2\text{S}_6$: C, 17.47; H, 4.73; N, 10.19%. Found: C, 17.46; H, 4.65; N, 10.06%. One of the crystals was used for single-crystal X-ray analysis. IR spectrum (cm^{-1} , KBr disk): 3196 (ν_{NH_2}), 3108 (ν_{NH_2}), 2922 (ν_{CH_2}), 1592 (δ_{NH_2}), 1385 (ν_{NO_3}). ^1H NMR spectrum (ppm from DSS, D_2O): 4.47 (1H, t, $J = 10.2$ Hz), 4.23 (1H, d, $J = 10.5$ Hz), 3.67 (1H, d, $J = 10.8$ Hz), 3.49 (1H, t, $J = 11.7$ Hz), 3.29-3.19 (1H, m), 3.17-3.05 (2H, m), 2.96-2.88 (2H, m), 2.82-2.64 (4H, m), 2.55 (1H, q, $J = 11.8$ Hz), 2.46-2.38 (1H, m), 2.33-2.04 (6H, m), 1.80-1.57 (2H, m). UV-Vis absorption in water ($\lambda_{\text{max}} / \text{nm}$ ($\epsilon / \text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$): 381 (8800), 328^{sh} (8890), 292^{sh} (13800). (sh denotes the shoulder band.). MS (ESI-pos): $m/z = 320.3$ ($3+$, $[\text{AgPd}^{\text{II}}\{\text{Rh}(\text{apt})_3\}_2]^{3+}$), 434.4 ($2+$, $\{[\text{AgPd}^{\text{II}}\{\text{Rh}(\text{apt})_3\}_2]^{3+} - \text{Hapt} - \text{H}\}^{2+}$), 479.9 ($2+$, $\{[\text{AgPd}^{\text{II}}\{\text{Rh}(\text{atp})_3\}_2]^{3+} - \text{H}\}^{2+}$).

References.

- [S1] M. Kouno, N. Kuwamura, N. Yoshinari and T. Konno, *Chem. Lett.* 2017, **46**, 1542.
[S2] G. M. Sheldrick, *Acta Crystallogr.* 2008, **A64**, 112.

- [S3] C. Kabuto, S. Akine, T. Nemoto and E. Kwon, *Nihon Kessho Gakkaishi* 2009, **51**, 218.
- [S4] M. Kouno, N. Yoshinari, N. Kuwamura, K. Yamagami, A. Sekiyama, M. Okumura and T. Konno, *Angew. Chem. Int. Ed.* 2017, **56**, 13762.

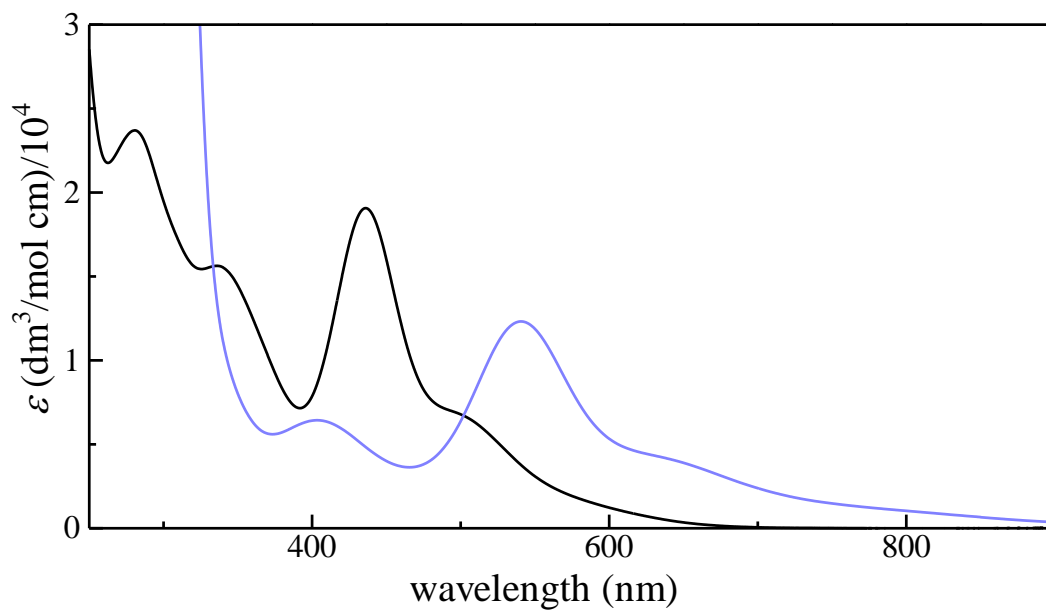


Fig. S1. Absorption spectra of [1](NO₃)₄ (black) and [Ni{Rh(apt)₃}₂](NO₃)₄ [S⁴] (blue) in water.

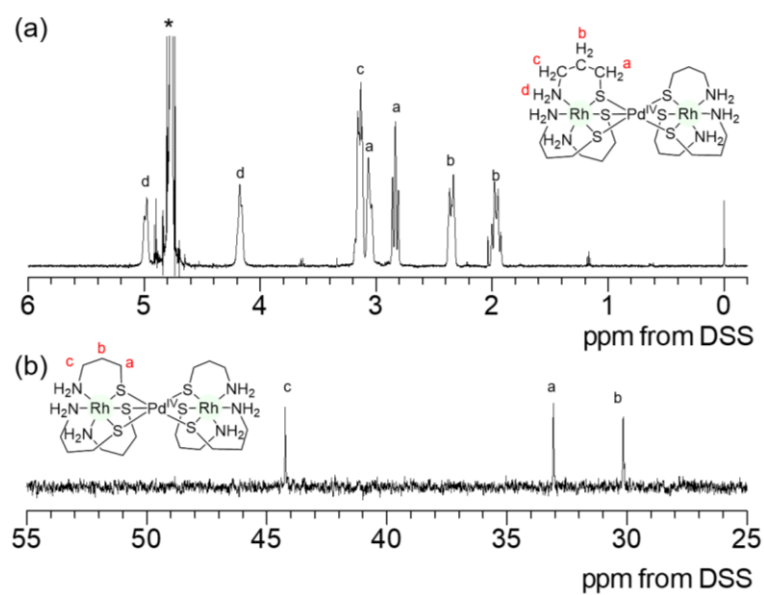


Fig. S2. (a) ^1H NMR and (b) $^{13}\text{C}\{^1\text{H}\}$ spectra of $[\mathbf{1}](\text{NO}_3)_4$ in D_2O . (*) denotes the signal from solvent.

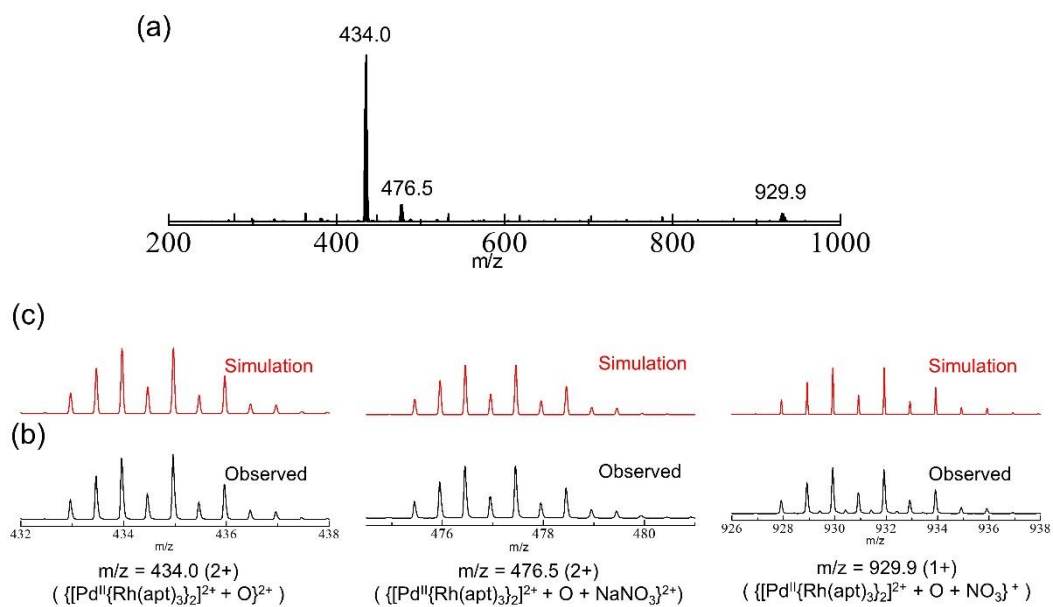


Fig. S3. (a) ESI mass spectrum of [1](NO₃)₄ in water/methanol (1:1). (b) Observed spectrum and (c) calculated isotope pattern of the dominant signals ($m/z = 434.0, 476.5, 929.9$).

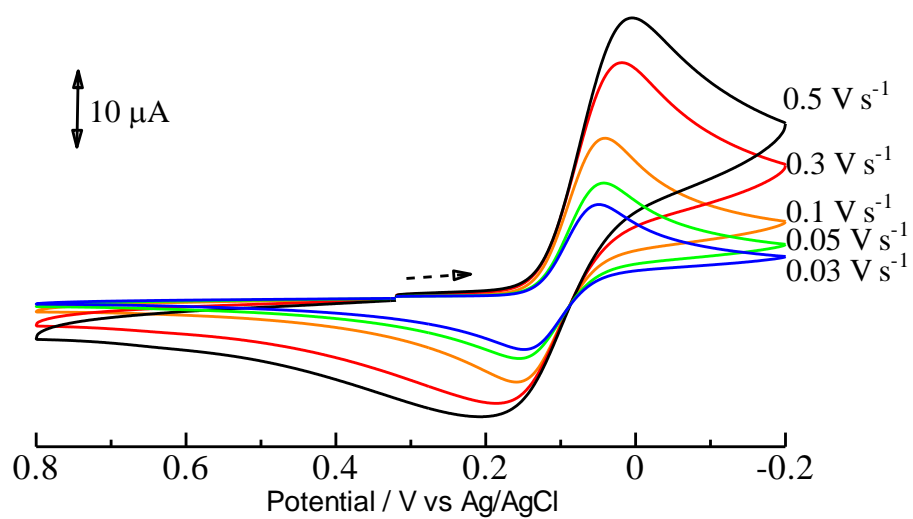


Fig. S4. Cyclic voltammograms of [1](NO₃)₄ in 0.01 M nitric acid with different scan rates within 0.03–0.5 V s⁻¹.

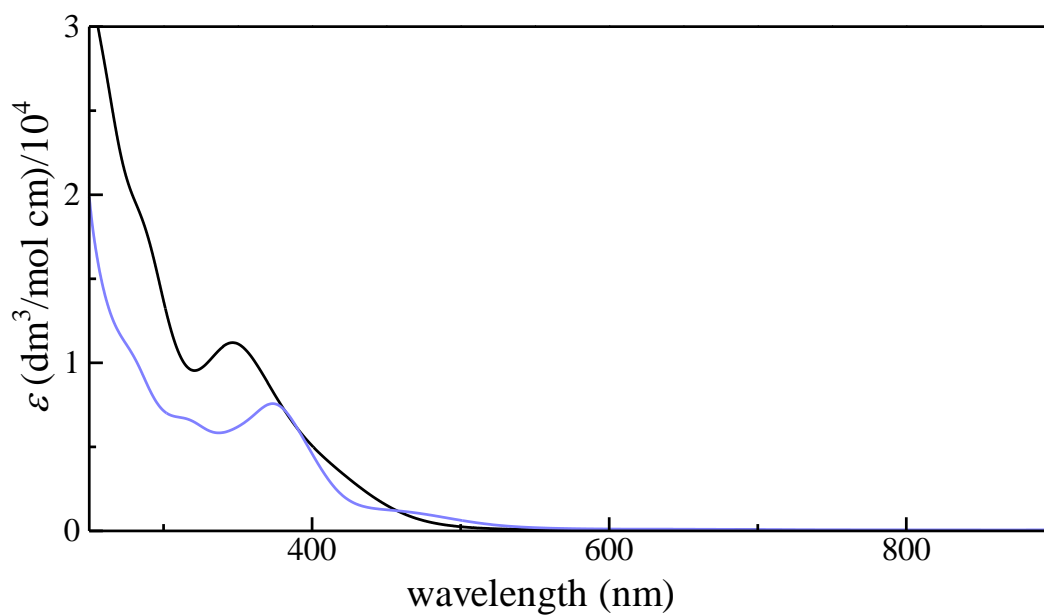


Fig. S5. Absorption spectra of $[\mathbf{2}](\text{NO}_3)_2$ (black) and $[\text{Ni}\{\text{Rh}(\text{apt})_3\}_2](\text{NO}_3)_2$ ^[S4] (blue) in water.

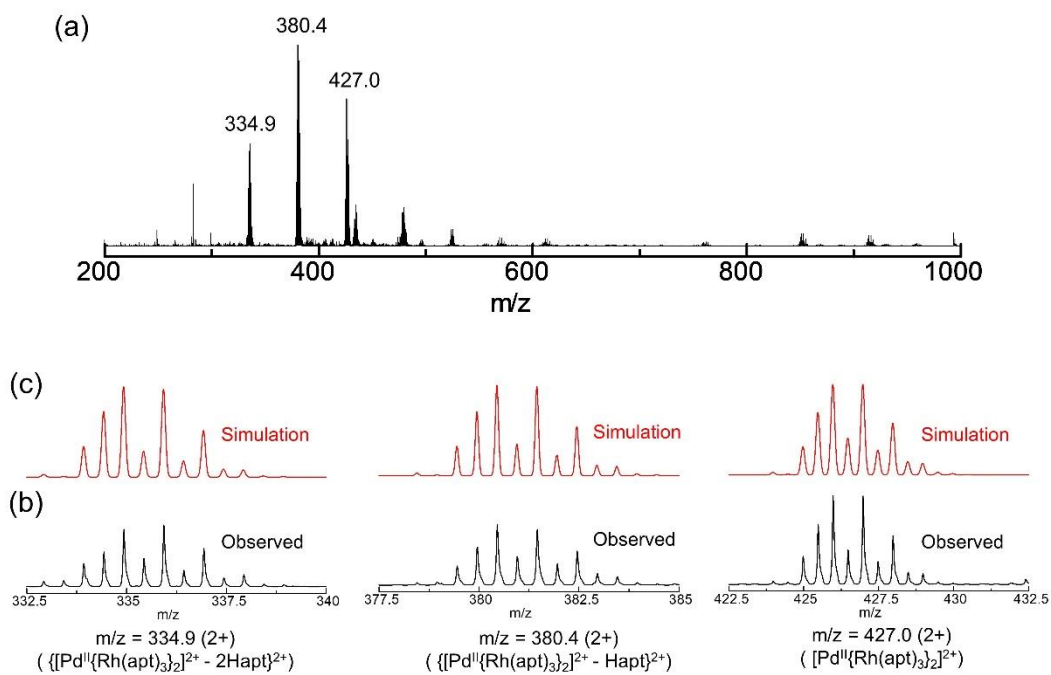


Fig. S6. (a) ESI mass spectrum of $[2](NO_3)_2$ in water/methanol (1:1). (b) Observed spectrum and (c) calculated isotopic pattern of the dominant signals ($m/z = 427.0, 380.4, 334.9$).

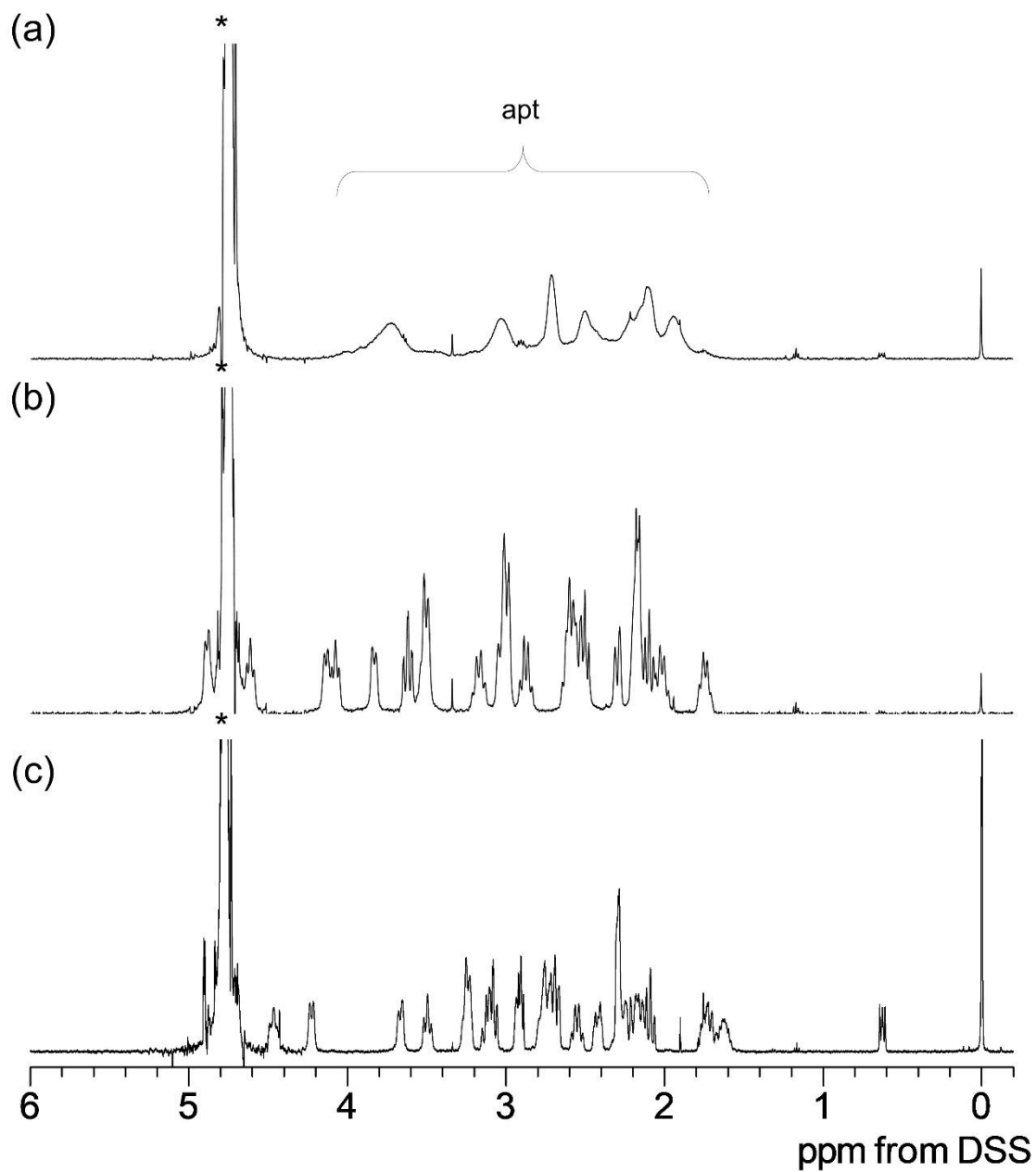


Fig. S7. ^1H NMR spectra of (a) $[\mathbf{2}](\text{NO}_3)_2$ (b) $[\mathbf{3}](\text{NO}_3)_2$, and $[\mathbf{4}](\text{NO}_3)_3$ (c) in D_2O . (*) denotes the signal from solvent.

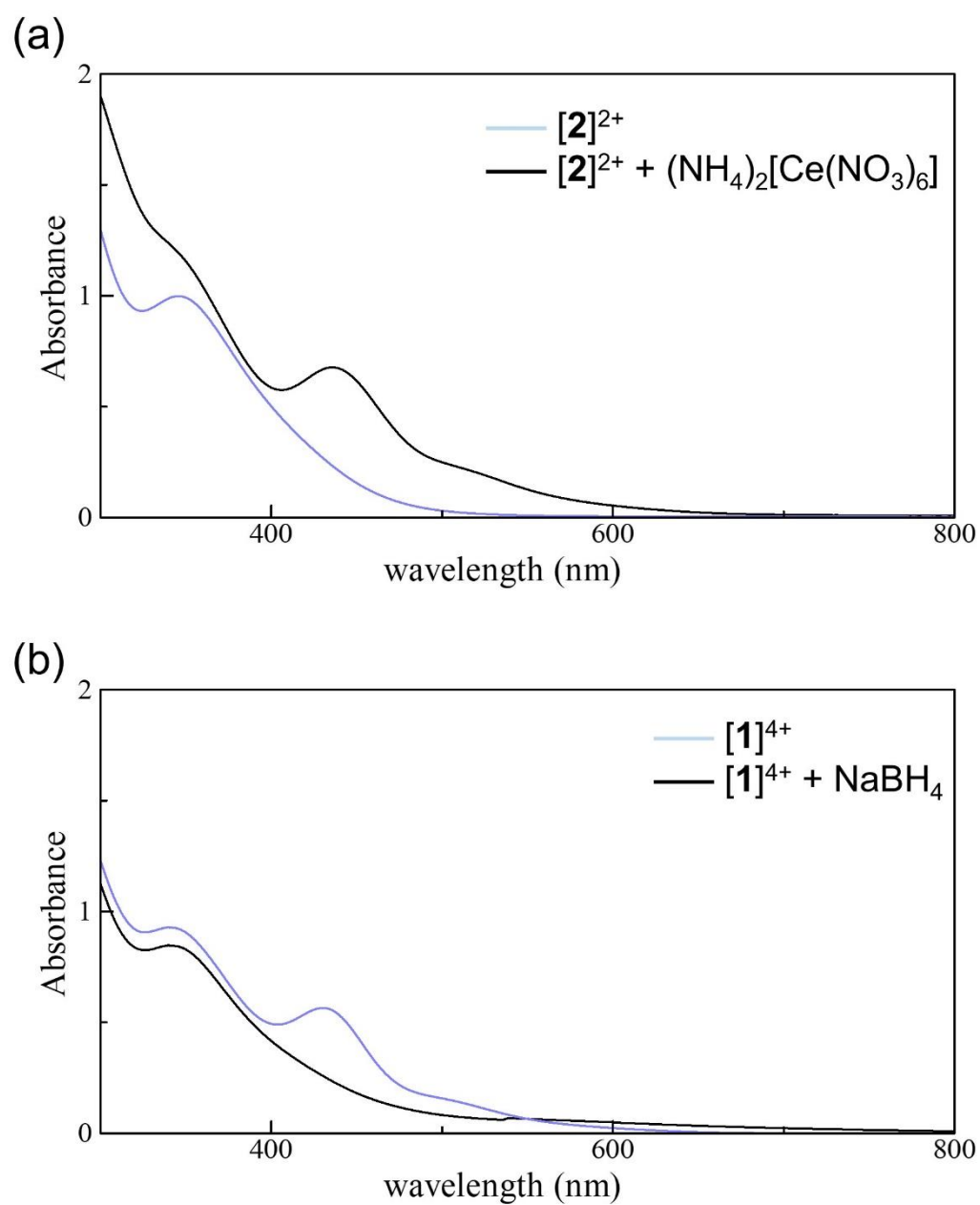


Fig. S8. Absorption spectra of (a) the reaction solution of $[2](\text{NO}_3)_2$ with $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ in water and (b) the reaction solution of $[1](\text{NO}_3)_4$ with NaBH_4 in water.

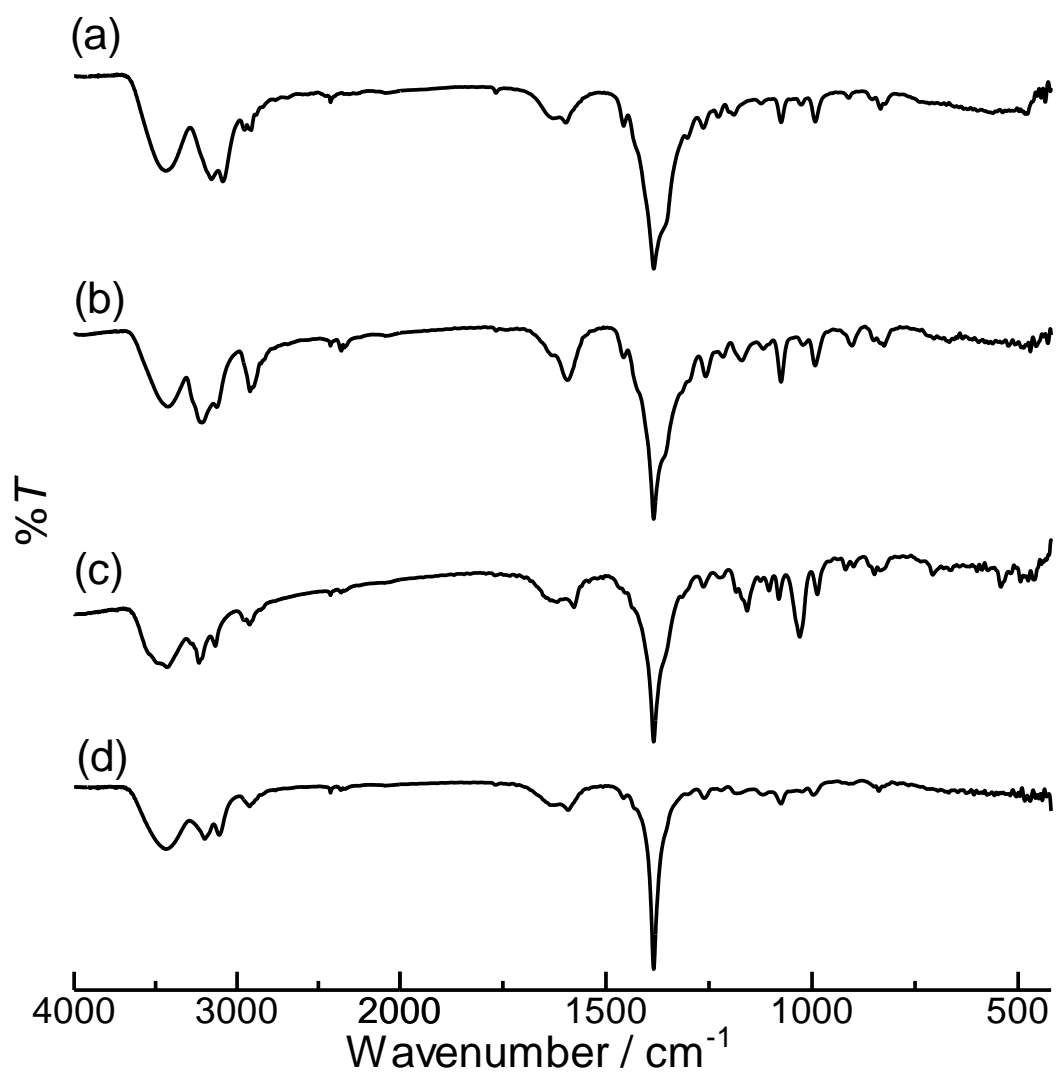


Fig. S9. IR spectra of (a) $[1](\text{NO}_3)_4$, (b) $[2](\text{NO}_3)_2$, (c) $[3](\text{NO}_3)_2$, and (d) $[4](\text{NO}_3)_3$ (KBr method).

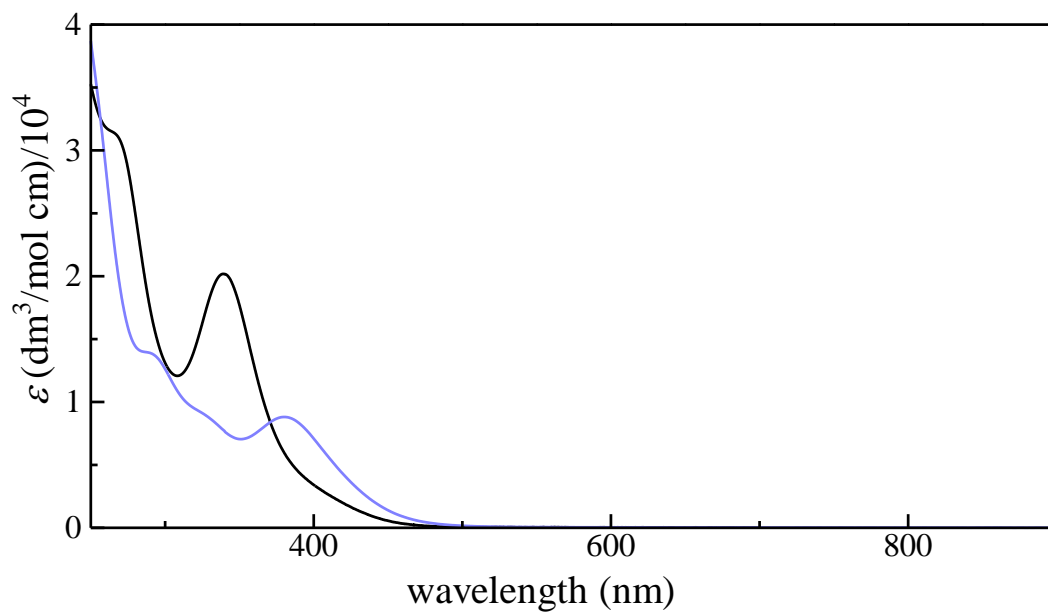


Fig. S10. Absorption spectra of $[\mathbf{3}](\text{NO}_3)_2$ (black) and $[\mathbf{4}](\text{NO}_3)_3$ (blue) in water.

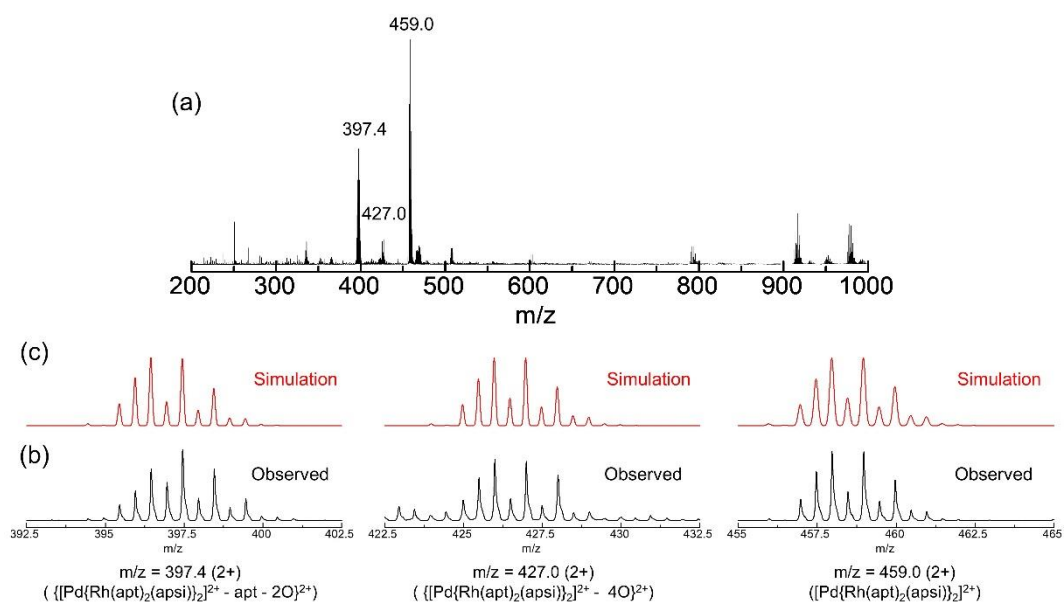


Fig. S11. (a) ESI mass spectrum of $[3](NO_3)_2$ in water/methanol (1:1). (b) Observed spectrum and (c) calculated isotope pattern of the dominant signals ($m/z = 459.0, 427.0, 397.4$).

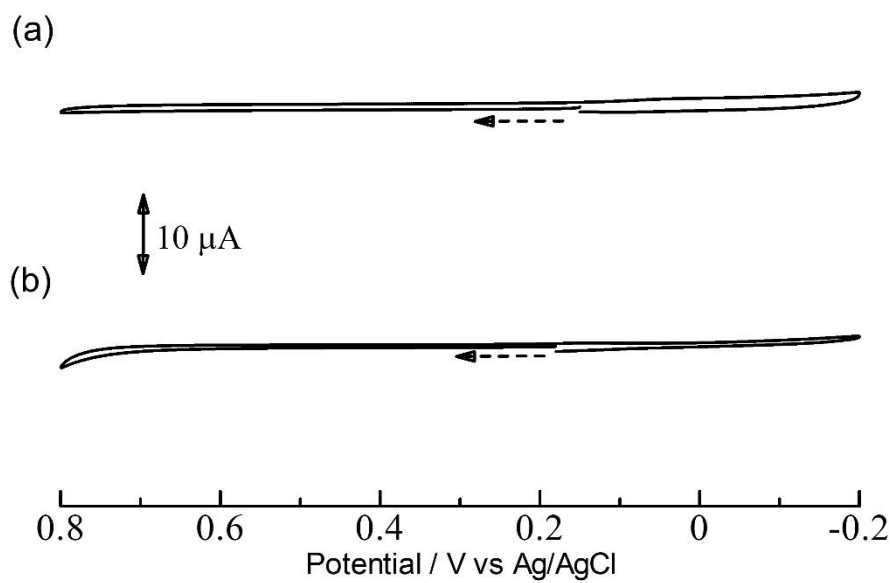


Fig. S12. Cyclic voltammograms of (a) $[\mathbf{3}](\text{NO}_3)_2$ and (b) $[\mathbf{4}](\text{NO}_3)_3$ in 0.01 M nitric acid with a scan rate of 0.1 V s^{-1} .

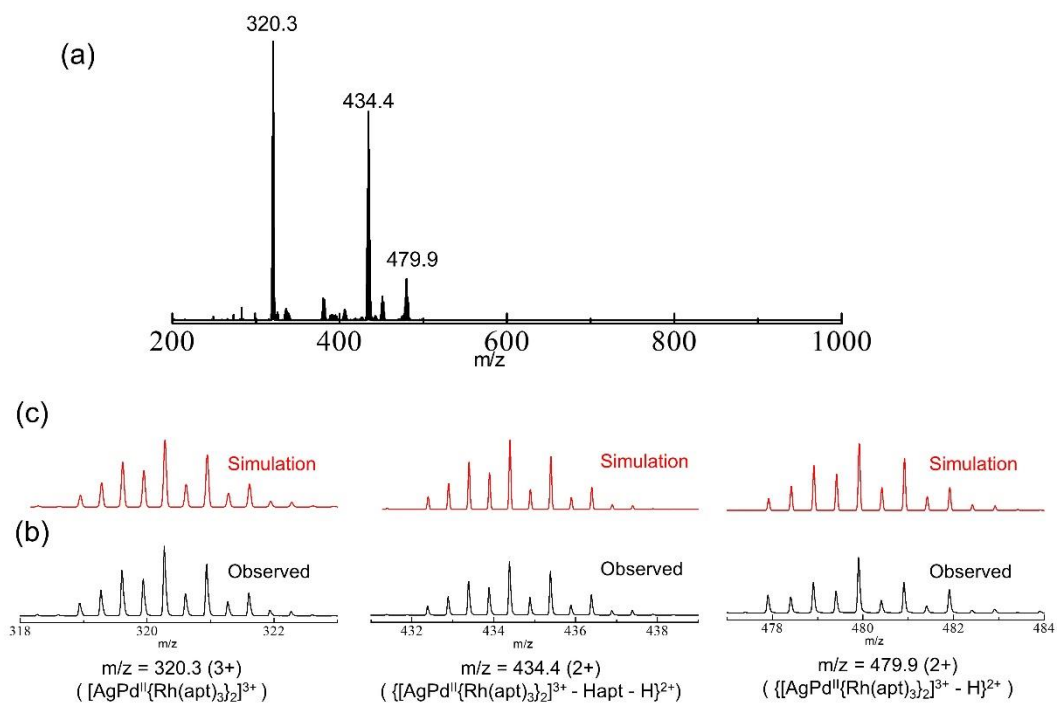


Fig. S13. (a) ESI mass spectrum of $[\mathbf{4}](\text{NO}_3)_3$ in water/methanol (1:1). (b) Observed spectrum and (c) calculated isotope pattern of the dominant signals ($m/z = 320.3, 434.4, 479.9$).

Table S1. Crystallographic data for [1](NO₃)₄, [2](NO₃)₂, [3](NO₃)₂, and [4](NO₃)₃.

| | [1](NO ₃) ₄ | [2](NO ₃) ₂ | [3](NO ₃) ₂ | [4](NO ₃) ₃ |
|--|--|---|---|---|
| Formula | C ₁₈ H ₄₈ N ₁₀ O ₁₆ Pd Rh ₂ S ₆ | C ₁₈ H ₄₅ N ₈ O _{8.50} Pd Rh ₂ S ₆ | C ₁₈ H ₄₈ N ₈ O ₁₄ Pd Rh ₂ S ₆ | C ₁₈ H ₄₈ AgN ₉ O ₁₂ Pd Rh ₂ S ₆ |
| <i>M</i> | 1165.24 | 1014.20 | 1105.22 | 1195.10 |
| Colour, form | Black, block | Orange, plate | Yellow, block | Yellow, block |
| Size/mm ³ | 0.33×0.16×0.13 | 0.14×0.08×0.02 | 0.29×0.16×0.11 | 0.12×0.09×0.04 |
| Crystal system | monoclinic | triclinic | monoclinic | monoclinic |
| Space group | <i>Cc</i> | <i>P</i> -1 | <i>P</i> 2 ₁ / <i>c</i> | <i>C</i> 2/ <i>c</i> |
| <i>a</i> /Å | 13.8176(3) | 9.5252(12) | 9.0560(18) | 21.241(3) |
| <i>b</i> /Å | 12.4115(2) | 13.778(4) | 12.029(2) | 20.717(3) |
| <i>c</i> /Å | 23.4669(4) | 27.631(4) | 17.767(4) | 20.087(3) |
| <i>α</i> /° | 90 | 102.207(7) | 90 | 90 |
| <i>β</i> /° | 97.207(7) | 96.462(7) | 104.27(3) | 120.014(8) |
| <i>γ</i> /° | 90 | 98.213(7) | 90 | 90 |
| <i>V</i> /Å ³ | 3992.71(14) | 3469.5(8) | 1875.7(7) | 7654(2) |
| <i>Z</i> | 4 | 4 | 2 | 8 |
| <i>T</i> /K | 200(2) | 100(2) | 100(2) | 100(2) |
| <i>R</i> (int) | 0.0220 | 0.1167 | 0.0395 | 0.0770 |
| $\rho_{\text{calcd}}/\text{g cm}^{-3}$ | 1.938 | 1.947 | 1.957 | 2.074 |
| μ (Mo K α), mm ⁻¹ | 1.652 | 1.707 | 1.242 | 2.089 |
| $\theta_{\text{Max}}/^\circ$ | 35.844 | 30.019 | 29.834 | 30.017 |
| Total no. of data | 15431 | 19918 | 7267 | 10521 |
| No. of unique data | 14852 | 9485 | 6687 | 5758 |
| No. of parameters | 479 | 820 | 223 | 442 |
| <i>R</i> (<i>I</i> >2 σ (<i>I</i>)) ^a | 0.0258 | 0.1011 | 0.0391 | 0.0841 |
| <i>R</i> w ^b | 0.0632 | 0.2287 | 0.1126 | 0.2686 |

^a $R_1 = \Sigma(|F_o| - |F_c|) / \Sigma(|F_o|)$.

^b $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$.