Supporting Information

Interconversions of Structural Isomers of $[PdAu_8(PPh_3)_8]^{2+}$ and $[Au_9(PPh_3)_8]^{3+}$ Revealed by Ion Mobility Mass Spectrometry

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Synthesis and characterization

$[Au_9(PPh_3)_8](NO_3)_3$ was synthesized by a method similar to that reported elsewhere.[1] First, ethanolic solution (13 mL) of $NaBH_4$ (9.4 mg, 0.25 mmol) was added to that (13 mL) of $Au(NO_3)(PPh_3)$ (521 mg, 1.0 mmol). The mixture was filtrated after stirring for 15 min at room temperature and the filtrate was evaporated. The residue was poured into tetrahydrofurane (THF) (35 mL) and made to standstill overnight. The precipitate was collected by filtration and washed with THF and hexane. The green solid (95 mg) was obtained by evaporating the residual solvent.

$[PdAu_8(PPh_3)_8](NO_3)_2$ was synthesized by a method similar to that reported elsewhere.[1] Dichloromethane solution (20 mL) of $Pd(PPh_3)_4$ (115 mg, 0.10 mmol) was quickly added to that (20 mL) of $Au(NO_3)(PPh_3)$ (421 mg, 0.81 mmol). After stirring for 1 min, ethanolic solution (15 mL) of $NaBH_4$ (20 mg, 0.53 mmol) was quickly added into the mixture. The mixture was evaporated after stirring for 1 min. The residue was poured into methanol (10 mL). The precipitate was filtrated and mixed with acetone (5 mL). The precipitate was filtrated and poured into methanol (50 mL). Diethylether (70 mL) was slowly added into the solution to precipitate $[PdAu_8(PPh_3)_8](NO_3)_2$. The brownish solid (193 mg) was obtained by filtration followed by washing with diethylether and hexane. Both samples were characterized by UV-vis absorption spectroscopy.

Table S1. Apparatus parameters

	Calibration[a)]	Figure 3	Figure 4	Figure 5
Capillary bias (kV)	3.5	3.0	3.5	2.0
Source temp. (°C)	100	100	100	100
Sampling core (V)	40	20	0	0
Source offset (V)	60	20	0	0
Desolvation temp. (°C)	150	150	150	150
Cone gas flow (L hr^{-1})	0	0	0	0
Desolvation gas flow (L hr^{-1})	400	400	400	400
Nebulizer gas (bar)	2.5	2.5	2.5	2.5
Trap gas flow (mL min^{-1})	0	0	0	0
Helium cell flow rate F_{He} (mL min^{-1})	43.2	0–150	35–80	43.2
TWIM cell flow rate F_{N2} (mL min^{-1})	55	45	55	47.3
Sample infusion flow rate (μL min^{-1})	10	10	10	20
Trap DC entrance (V)	0	0	0	0
Trap DC bias (V)	25.6	27.2	25.6	24.1
Trap DC exit (V)	0	3.0	0	0
Transfer voltage (V)	0	0	0	2
IMS wave velocity (m s^{-1})	650	700	650	658
IMS wave height (m s^{-1})	40	40	25	38.2

[a)]Acetonitrile/water mixed solution (1:1, v/v) containing myoglobin and 0.1% of formic acid was electrosprayed.

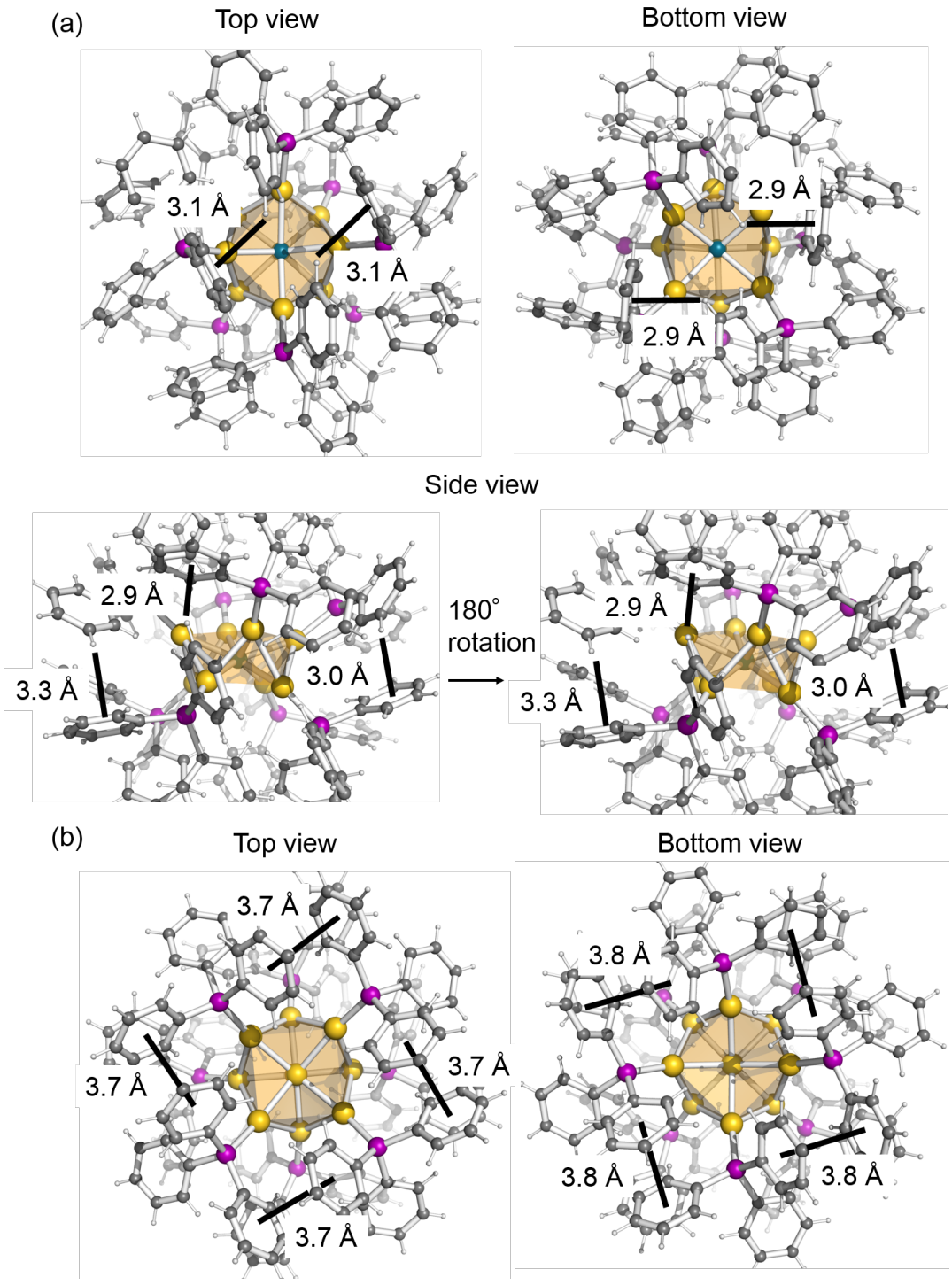

Figure S1. Ligand packing in the crown-shaped crystals of (a) $[PdAu_8(PPh_3)_8](NO_3)_2$ and (b) $[Au_9(PPh_3)_8](PW_{12}O_{40})$.[2,3]

References:

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2. Matsuo, S.; Takano, S.; Yamazoe, S.; Koyasu, K.; Tsukuda, T. Selective and High-Yield Synthesis of Oblate Superatom $[PdAu_8(PPh_3)_8]^{2+}$ *ChemElectroChem* **2016**, *3*, 1206–1211.
3. Jansen, M.; Schulz-Dobrick, M. Supramolecular Intercluster Compounds Consisting of Gold Clusters and Keggin Anions *Eur. J. Inorg. Chem.* **2006**, *2006*, 4498–4502.