Supporting Information

Interconversion between Superatomic 6-Electron and 8-Electron Configurations of $M@Au_{24}(SR)_{18}$ Clusters (M = Pd, Pt)

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1. Syntheses of $Au_{25}(SR)_{18}$, $PtAu_{24}(SR)_{18}$ and $PdAu_{24}(SR)_{18}$ clusters (SR = 1-hexanethiolate).

Chemicals. Hydrogen tetrachloroaurate trihydrate ($HAuCl_4 \cdot 3H_2O$, reagent grade), dihydrogen hexachloroplatinate(IV) hydrate ($H_2PtCl_6 \cdot xH_2O$, >99%), sodium tetrachloropalladate(II) trihydrate ($Na_2PdCl_4 \cdot 3H_2O$, >99%), 1-hexanethiol (98%), tetraoctylammonium bromide (Oct_4NBr, 98%), sodium borohydride ($NaBH_4$, 99%), hydrogen peroxide solution (H_2O_2, 34 wt%), *tert*-butylamine borane (TBAB) and tetrabutylammonim hexafluorophosphate (Bu_4NPF_6, >99%) were purchased from Aldrich. Extrapure grade toluene, acetone, absolute ethanol, methanol, acetonitrile, dichloromethane, tetrachloroethylene and tetrahydrofuran (THF) were used. Water was purified using a Millipore Milli-Q system (18.2 MΩ·cm). All the chemicals were used as received without further purification.

Synthesis of $[Au_{25}(SR)_{18}]^-$ and $[Au_{25}(SR)_{18}]^+$. $HAuCl_4 \cdot 3H_2O$ (0.196 g, 0.50 mmol) and Oct_4NBr (0.317 g, 0.58 mmol) were dissolved in 15 mL of THF in a 100 mL vial. After being vigorously stirred for 15 min, the solution color changed from yellow to red. Then, 1-hexanethiol (0.320 mL, 2.5 mmol) was slowly added to the above solution and stirring was continued for ~60 min until the red solution turned colorless. To the above solution, $NaBH_4$ (0.190 g, 5.0 mmol) dissolved in 5 mL of cold water was added all at once. The reaction generated some bubbles and the solution turned black, indicating the formation of gold clusters. After being stirred for additional 5 h, the aqueous phase was decanted and the remaining organic phase was washes with fresh water. The product solution was transferred to a 250 mL round-bottom flask and

rotary evaporated. The resulting oil-like product was washed with methanol and then collected by centrifugation. This process was repeated at least 10 times to completely remove reaction impurities. $Au_{25}(SR)_{18}$ clusters were then extracted from the cluster product with 1:1 (v/v) acetone/acetonitrile mixture repeatedly, providing a total yield of ~100 mg. The $Au_{25}(SR)_{18}$ clusters were isolated as anionic form, i.e., $[Au_{25}(SC_6H_{13})_{18}]^-$, along with a tetraoctylammonium cation.

Oxidation of $[Au_{25}(SR)_{18}]^-$ was performed in a two-phase system. In a typical procedure, 10 mg $[Au_{25}(SR)_{18}]^-$ was dissolved in 5 mL of CH_2Cl_2 in a 30 mL scintillation vial. 15 mL of 1:9 (v/v) ethanol/water mixture was added to make an immiscible layer above the CH_2Cl_2 phase. The two-phase solution was stirred vigorously for 60 h in an aerobic atmosphere. The progress of the cluster oxidation was monitored every 12 h by absorption spectra and open-circuit potential measurements. The resulting cluster solution was then rotary evaporated to near dryness and washed thoroughly with methanol and water. Highly oxidized $[Au_{25}(SR)_{18}]^+$ clusters were obtained after 60 h oxidation.

Synthesis of $PdAu_{24}(SR)_{18}$ and $PtAu_{24}(SR)_{18}$. Both $PdAu_{24}(SR)_{18}$ and $PtAu_{24}(SR)_{18}$ clusters were synthesized according to the one-phase procedure reported by Jin and et al. (*J. Am. Chem. Soc.* **2012**, *134*, 16159) with some modifications. Typically, $Na_2PdCl_4 \cdot 3H_2O$ (0.0294 g, 0.10 mmol), $HAuCl_4 \cdot 3H_2O$ (0.157 g, 0.40 mmol) and Oct_4NBr (0.317 g, 0.58 mmol) were dissolved in 15 mL of THF in a 100 mL vial. After being vigorously stirred for 60 min, the solution color changed from orange to dark red. Then, 1-hexanethiol (0.320 mL, 2.5 mmol) was added to the vial at room temperature without changing the stirring speed. Stirring was continued for 10 min until the solution color changed from dark red to orange. To the above solution, $NaBH_4$ (0.190 g, 5.0 mmol) dissolved in 5 mL of cold water was added all at once. After being stirred for additional 5 h, the aqueous phase was decanted and the remaining organic phase was washes with copious amounts of water to remove water soluble impurities. The product solution was subsequently rotary evaporated. The resulting product was thoroughly washed with methanol and then collected by centrifugation. A mixture of $Au_{25}(SR)_{18}$ and $PdAu_{24}(SR)_{18}$ was typically obtained from repeating extractions with 1:1 (v/v) acetone/acetonitrile mixture because of their similar solubility. Separation of $PdAu_{24}(SR)_{18}$ was achieved by selectively decomposing $Au_{25}(SR)_{18}$ using concentrated H_2O_2. Typically, to the cluster mixture dissolved in 10 mL of CH_2Cl_2, 5 mL of H_2O_2 (34 wt%) solution was added to react with clusters for 120 min. After decanting the aqueous phase, the CH_2Cl_2 solution was rotary evaporated at room temperature. The dried product was washed with ethanol and collected by centrifugation. $PdAu_{24}(SR)_{18}$ clusters were then extracted with 1:2 (v/v) dichloromethane/acetonitrile mixture repeatedly, providing a total yield of ~30 mg. $PtAu_{24}(SR)_{18}$ clusters were synthesized similarly except using $H_2PtCl_6 \cdot xH_2O$ (0.0410 g, 0.10 mmol)).

Measurements. Matrix-assisted laser desorption ionization (MALDI) mass spectra were acquired using an AB Sciex MALDI-TOF mass spectrometer (4800 plus) equipped with a standard UV nitrogen laser (337 nm). The accelerating voltage was held at 15 kV and the spectrum was collected in a refractron positive ion mode. Sample solution in CH_2Cl_2 (0.7 mM) was mixed with trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) as a matrix (saturated in CH_2Cl_2) and then applied to the sample plate and air-dried. UV-Visible spectra were obtained from the Shimadzu UV-Vis-NIR spectrophotometer (UV-3600) using freshly prepared cluster solutions in tetrachloroethylene. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an XPS system (K-alpha, Thermo UK) using a monochromatic Al Kα X-ray source (1486.6 eV). Samples were loaded onto glass for analysis, and binding energies were calibrated to the C 1s peak at 285.14 eV. The peak position and integrated intensities were obtained by curve fitting using surface chemical analysis software (Thermo Avantage version 5.35). Transmission electron microscopy (TEM) images were recorded with a JEOL transmission electron microscope (JEOL 2100F). Samples for TEM were prepared by drop-casting CH_2Cl_2 solution of clusters (0.5 mg/mL) on a 400 mesh Formvar/carbon-coated copper grid (01814-F, Ted Pella) and drying for 1 h at room temperature before imaging. ^{1}H-NMR were recorded on a 250 MHz FT-NMR spectrometer (DPX 250, Bruker Biospin) with chemical shifts reported relative to residual deuterated solvent peaks ($CDCl_3$ at 7.24 ppm). The ^{1}H-NMR samples were prepared using excess I_2 to decompose clusters and liberate the protecting ligands.

2. Supporting Figures and Tables

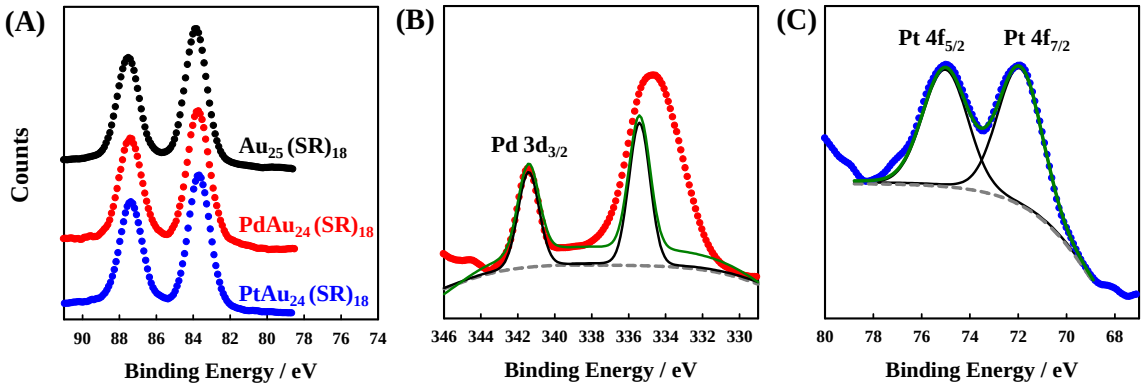

Figure S1. (A) Au 4f XPS spectra of $Au_{25}(SR)_{18}$ (black dots), $PdAu_{24}(SR)_{18}$ (red dots), and $PtAu_{24}(SR)_{18}$ (blue dots), (B) Pd 3d XPS spectra of $PdAu_{24}(SR)_{18}$, and (C) Pt 4f XPS spectra of $PtAu_{24}(SR)_{18}$. In (B) and (C), experimental data (dots) are shown with envelope (green line) and component fitting (black line). In (B), the Pd $3d_{5/2}$ XPS peak at 335.9 eV overlaps with Au 4d XPS peak at 335.4 eV.

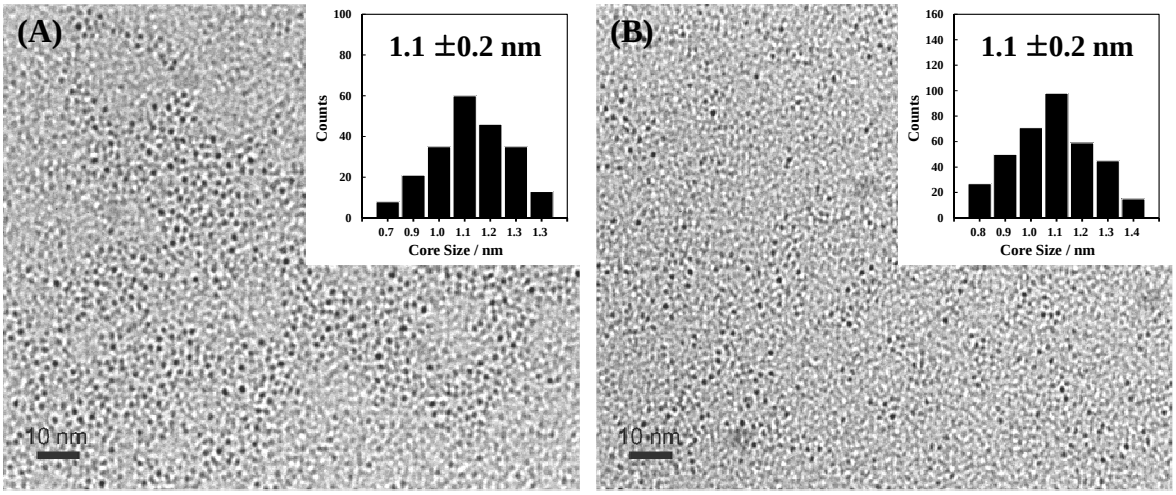

Figure S2. TEM images of the isolated (A) $PdAu_{24}(SR)_{18}$ and (B) $PtAu_{24}(SR)_{18}$ (scale bar = 10 nm) The insets show the histograms illustrating the core size distribution.

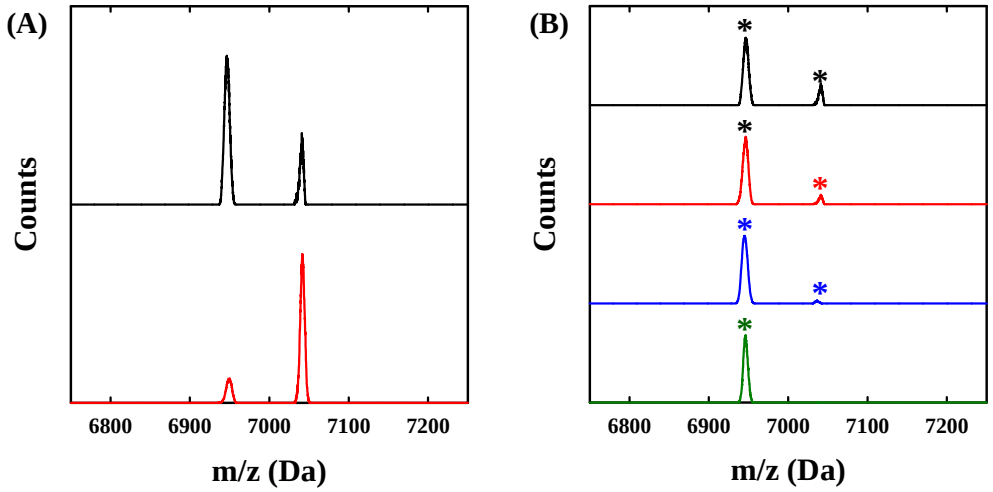

Figure S3. (A) MALDI mass spectra of a cluster product extracted with a 1:1 (v/v) acetone/ acetonitrile mixture. The cluster product was produced following Au-thiol aggregation for 10 min (black) and 60 min (red). (B) MALDI mass spectra of the cluster product containing $Au_{25}(SR)_{18}$ and $PdAu_{24}(SR)_{18}$ after being treated with H_2O_2 for 10 (black), 30 (red), 60 (blue), and 120 min (green).

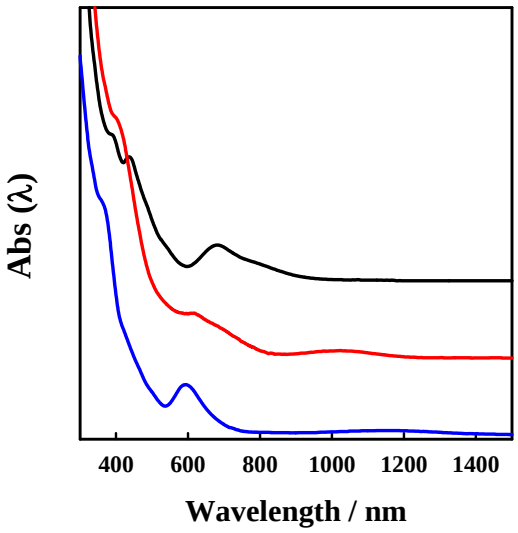

Figure S4. UV-Vis-NIR absorption spectra of $Au_{25}(SR)_{18}$ (black), $PdAu_{24}(SR)_{18}$ (red), and $PtAu_{24}(SR)_{18}$ (blue) clusters in trichloroethylene. The absorption spectra were offset for clarity.

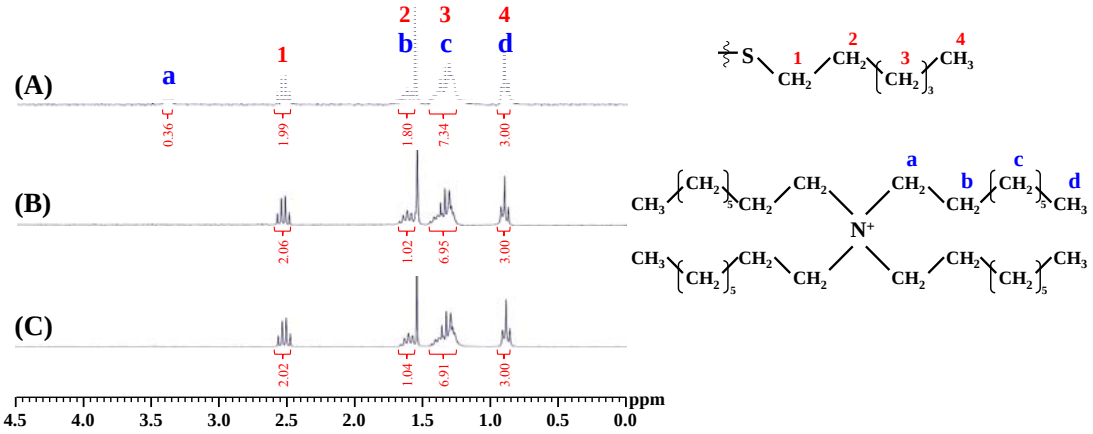

Figure S5. ^{1}H-NMR spectra of the isolated (A) $Au_{25}(SR)_{18}$, (B) $PdAu_{24}(SR)_{18}$, and (C) $PtAu_{24}(SR)_{18}$. For $Au_{25}(SR)_{18}$, the number of Oct_4N^+ cation bound to $Au_{25}(SR)_{18}$ was determined to be ~1 by comparing the intensity of the ^{1}H-NMR resonance for **a** (3.3-3.4 ppm) and **4+d** (0.8-0.9 ppm).

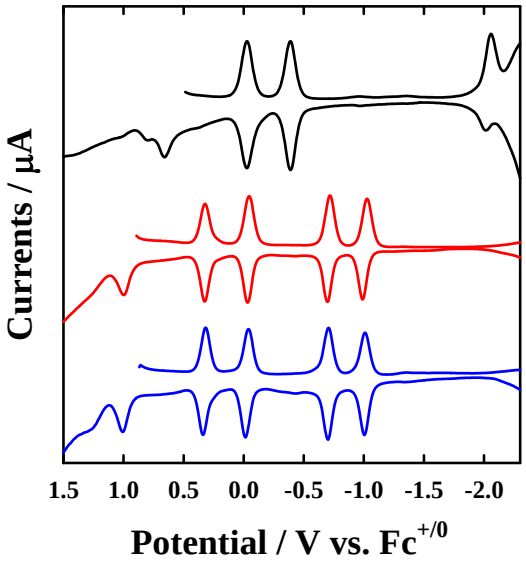

Figure S6. Square-wave voltammograms of $Au_{25}(SR)_{18}$ (black), $PdAu_{24}(SR)_{18}$ (red) and $PtAu_{24}(SR)_{18}$ (blue) under 195 K in CH_2Cl_2 containing 0.1 M Bu_4NPF_6.

Table S1. Formal Potentials (V vs $Fc^{+/0}$) and Potential Gaps (V) Observed in Figure S6.

	O4	O3	O2	O1	R1	R2	O1-R1	HOMO-LUMO
$Au_{25}(SR)_{18}$	0.80	0.66	-0.04	-0.39	-2.03		1.64	1.29
$PdAu_{24}(SR)_{18}$		1.00	0.32	-0.04	-0.71	-1.00	0.67	0.31
$PtAu_{24}(SR)_{18}$		1.00	0.33	-0.04	-0.70	-1.00	0.66	0.29

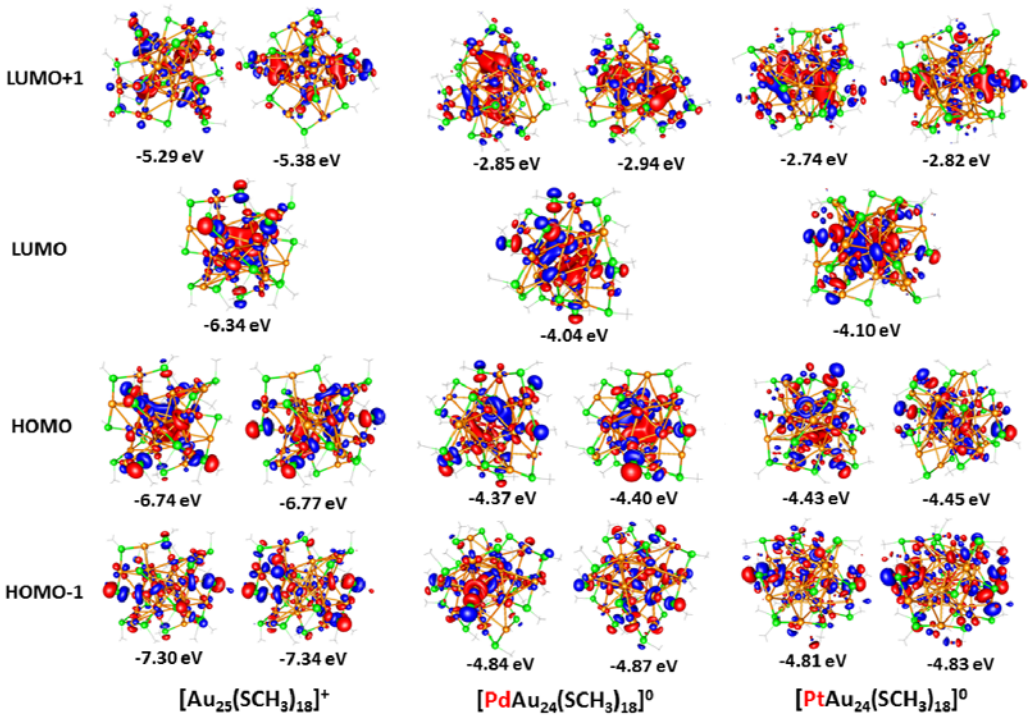

Figure S7. Frontier orbitals of the 6e systems: $[Au_{25}(SCH_3)_{18}]^+$, $[PdAu_{24}(SCH_3)_{18}]^0$ and $[PtAu_{24}(SCH_3)_{18}]^0$.

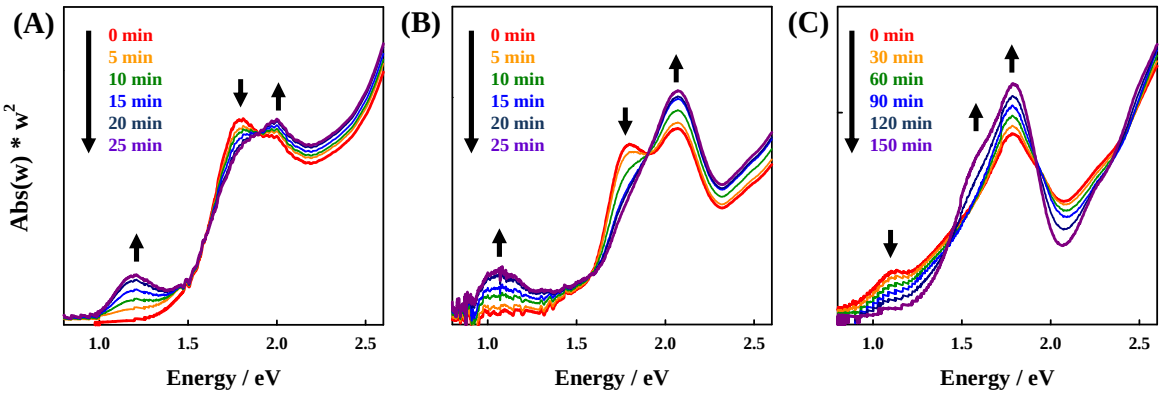

Figure S8. Absorption spectral changes during potentiostatic oxidation of the reduced (A) $[PdAu_{24}(SR)_{18}]^{2-}$ (0.5 mM) and (B) $[PtAu_{24}(SR)_{18}]^{2-}$ (0.5 mM) at -0.49 V (vs. $Fc^{+/0}$) in CH_2Cl_2. Prior to the oxidation experiment, both clusters were potentiostatically reduced at -1.04V for 25 min in CH_2Cl_2 containing Bu_4NPF_6 (0.1 M), TBAB (10mM), and Oct_4NBr (1.0 mM). (C) Absorption spectral changes of the oxidized $[Au_{25}(SR)_{18}]^+$ (0.5 mM) upon being treated with $NaBH_4$ (5.0 mM) for the indicated time.