

Supporting Information

Electron Microscopic Observation of an Icosahedral Au₁₃ Core in Au₂₅(SePh)₁₈ and Reversible Isomerization between Icosahedral and Face-Centered Cubic Cores in Au₁₄₄(SC₂H₄Ph)₆₀

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Chemicals The reagents and solvents were commercially available and used without further purification. Hydrogen tetrachloroaurate tetrahydrate (HAuCl₄·4H₂O) was purchased from Tanaka Precious Metals. The other reagents were purchased from Wako Pure Chemical Industries. Deionized water with a resistivity above 18.2 MΩ cm was used.

Synthesis and characterization of Au₂₅(SC₂H₄Ph)₁₈. The Au₂₅(SC₂H₄Ph)₁₈ clusters were synthesized following the previously reported methods.^{1,2} HAuCl₄·4H₂O (0.75 mmol) was dissolved in 25 mL of tetrahydrofuran (THF) solution containing tetraoctylammonium bromide (TOABr) (0.76 mmol) at room temperature. After stirring for 15 min, phenylethanethiol (4.7 mmol) was added to the solution and the solution was stirred for 15 min in an ice bath. A cold aqueous solution (5.8 mL) containing NaBH₄ (8.7 mmol) was then rapidly added to the solution and then the solution was stirred at room temperature. After 12 h, the THF solvent was evaporated and the remaining red brown oil was washed with methanol to remove the excess thiol and other byproducts. The obtained black precipitates were filtered by membrane filter. The black powder was dissolved in dichloromethane (DCM) and crystallized by the addition of ethanol.

Synthesis and characterization of Au₂₅(SePh)₁₈. The Au₂₅(SePh)₁₈ clusters were synthesized via ligand exchange of Au₂₅(SC₂H₄Ph)₁₈, following by a previous report.³ Au₂₅(SC₂H₄Ph)₁₈ (1.145 μmol) and selenophenol (0.225 mmol) were dissolved in 5 mL of toluene. The solution was stirred vigorously in an ice bath overnight. The resulting solvent was evaporated and black powder was precipitated by the addition of ethanol. The black precipitates were filtered by membrane filter and washed with ethanol to remove the excess selenophenols and byproducts. The purity was confirmed by UV-Vis spectroscopy and electrospray ionization mass spectrometry (ESI-MS) as shown below.

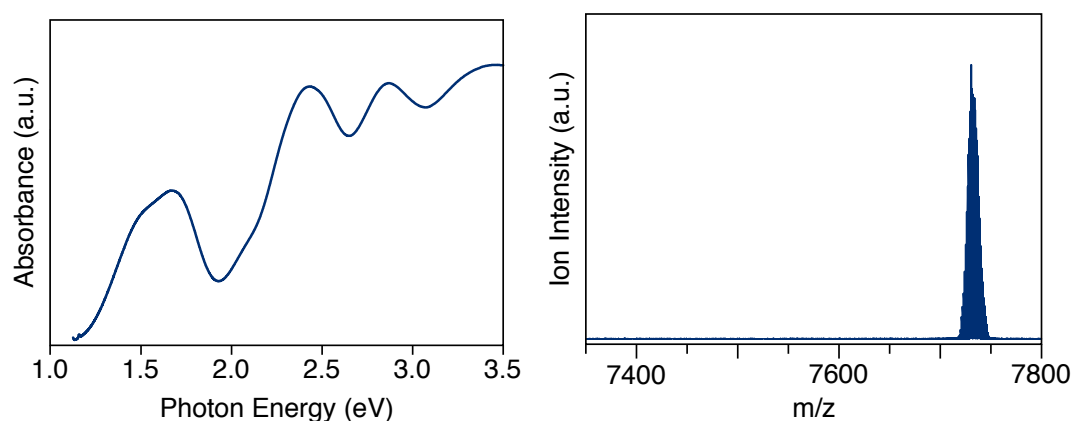


Figure S1. UV-Vis spectrum and ESI mass spectrum of $\text{Au}_{25}(\text{SePh})_{18}$.

Synthesis and characterization of $\text{Au}_{144}(\text{SC}_2\text{H}_4\text{Ph})_{60}$. The $\text{Au}_{144}(\text{SC}_2\text{H}_4\text{Ph})_{60}$ clusters were synthesized using a method similar to that in the literature.⁴ To a methanolic solution of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (0.60 mmol) was added TOABr (0.69 mmol) under stirring. After stirring for 5 min, phenylethanethiol (0.37 mmol) was added to this solution. A cold aqueous solution (10 mL) of NaBH_4 (6.0 mmol) was added to the solution to yield a black sticky oil. The mixture was stirred overnight and the black residue was collected by centrifugation. The residue was washed with excess methanol and the clusters were extracted using DCM. The extract was evaporated to dryness and acetonitrile was added to the dried sample to extract the Au_{25} clusters. The remaining residue was extracted using a minimum amount of toluene and then was further purified by gel permeation chromatography to guarantee the monodispersity of the sample. The purity was confirmed by UV-Vis spectroscopy and thermogravimetric analysis as shown below.

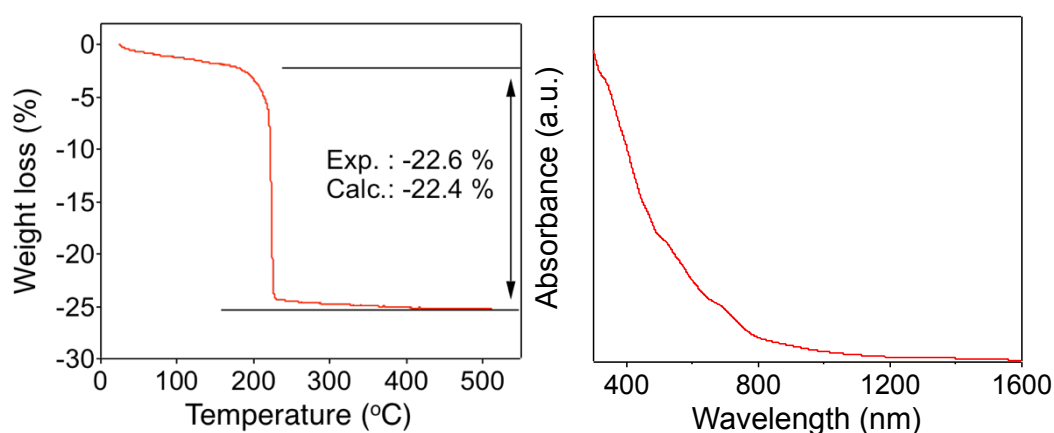


Figure S2. TG results and UV-Vis spectrum of $\text{Au}_{144}(\text{SC}_2\text{H}_4\text{Ph})_{60}$.

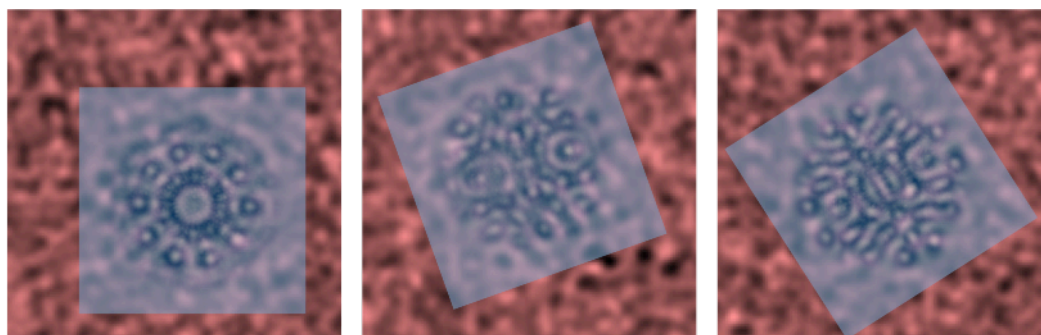


Figure S3. Overlays of TEM images and simulated patterns of $\text{Au}_{144}(\text{SC}_2\text{H}_4\text{Ph})_{60}$.

References

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