

SUPPORTING INFORMATION

Continuous modulation of electronic structure of stable thiolate-protected Au₂₅ cluster by Ag doping

Yuichi Negishi,*^a Takeyuki Iwai^a and Mao Ide^a

Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo, 162-8601, Japan.
Fax: +81-3-5261-4631; Tel: +81-3-5228-9145; E-mail: negishi@rs.kagu.tus.ac.jp

I. Experimental Procedure

A. Chemicals

All of the chemicals were commercially obtained and used without further purification. Hydrogen tetrachloroaurate tetrahydrate (HAuCl₄ · 4H₂O) was obtained from Tanaka Kikinzoku. Silver nitrate (AgNO₃), tetraoctylammonium bromide ((C₈H₁₇)₄NBr), sodium tetrahydroborate (NaBH₄), 1-dodecanethiol (1-C₁₂H₂₅SH), methanol, toluene, acetone, acetonitrile, and dichloromethane (CH₂Cl₂) were obtained from Wako Pure Chemical Industries. Phenylethanethiol (PhC₂H₄SH) and Tetrabutylammonium perchlorate ((C₄H₉)₄NClO₄) were purchased from Tokyo Kasei. Q-SWICH 5 was purchased from Indeco. *Trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) was purchased from Fluka. Deionized water with a resistivity of > 18 MΩ cm was used in the present study.

B. Synthesis of Au_{25-n}Ag_n(SC₁₂H₂₅)₁₈ (n = 0–11)

Au_{25-n}Ag_n(SC₁₂H₂₅)₁₈ (n = 0–11) were synthesized in the same manner as Au₂₄Pd₁(SC₁₂H₂₅)₁₈¹ except that a mixture of Au and Ag ions was used as the starting materials. First, a toluene solution (100 mL) of tetraoctylammonium bromide ((C₈H₁₇)₄NBr) (0.55 mmol) was added to the mixed aqueous solution (100 mL) of HAuCl₄ and AgNO₃ with a total metal concentration of 5 mM. The initial molar ratio of [HAuCl₄]:[AgNO₃] was set to 22:3, 19:6, 15:10, 10:15, 8:17, and 5:20. After stirring for 30 min, the organic phase was separated by removing the aqueous layer, and C₁₂H₂₅SH (6 mmol) was added to this separated toluene solution and the resulting solution was stirred for 30 min. The mixture was then cooled at ~0 °C in a ice bath for 30 min. An aqueous solution of NaBH₄ (5 mmol, 100 mL), cooled to ~0 °C, was then injected rapidly into this mixture under vigorous stirring. After 3 hours of reduction time, the organic phase was evaporated to dryness and the product was washed with methanol to remove excess C₁₂H₂₅SH, (C₈H₁₇)₄NBr, and byproducts. Clusters **1–6** were obtained by extraction from dried products with pure acetone (22:3 (**1**), 19:6 (**2**), 15:10 (**3**), 10:15 (**4**), 8:17 (**5**), 5:20 (**6**)).

C. Synthesis of Au_{25-n}Ag_n(SC₂H₄Ph)₁₈ (n = 0–13)

Au_{25-n}Ag_n(SC₂H₄Ph)₁₈ (n = 0–13) were also synthesized in a similar manner. First, a toluene solution (30 mL) of tetraoctylammonium bromide ((C₈H₁₇)₄NBr) (1.1 mmol) was added to the mixed aqueous solution (30 mL) of HAuCl₄ and AgNO₃ with a total metal concentration of 30 mM. The initial molar ratio of [HAuCl₄]:[AgNO₃] was set to 24.8:0.2, 24:1, 22:3, 18:7, 15:10, 12:13, and 10:15. After stirring for 30 min, the organic phase was separated by removing the

aqueous layer, and $\text{PhC}_2\text{H}_4\text{SH}$ (10 mmol) was added to this separated toluene solution and the resulting solution was stirred for 30 min. The mixture was then cooled at $\sim 0^\circ\text{C}$ in a ice bath for 30 min. An aqueous solution of NaBH_4 (1 M, 20 mL), cooled to $\sim 0^\circ\text{C}$, was then injected rapidly into this mixture under vigorous stirring. After 3 hours of reduction time, the organic phase was evaporated to dryness and the product was washed with methanol to remove excess $\text{PhC}_2\text{H}_4\text{SH}$, $(\text{C}_8\text{H}_{17})_4\text{NBr}$, and byproducts. Clusters **7-13** were obtained by extraction from dried products with pure acetonitrile (24.8:0.2 (**7**), 24:1 (**8**), 22:3 (**9**), 18:7 (**10**), 15:10 (**11**), 12:13 (**12**), 10:15 (**13**)).

D. Characterization

Transmission electron microscope (TEM) images were recorded with an electron microscope operated at 100 kV (Hitachi, H-7650). Typical magnification of the image was 1,000,000.

Matrix-assisted laser desorption ionization (MALDI) mass spectra and laser desorption ionization (LDI) mass spectra were collected on the linear-mode TOF mass spectrometer (Applied Biosystem, Voyager Linear RD VDA 500) using a nitrogen laser (337 nm). MALDI mass spectrometry was conducted to obtain the non-destructive mass spectra of clusters to precisely determine the chemical composition of the clusters. DCTB was used as the MALDI matrix. To minimize dissociation of the clusters caused by laser irradiation, we used a cluster-to-matrix ratio of 1:1000. The laser fluence was decreased to the lowest value that enables us to detect the ions. LDI mass spectrometry was conducted to obtain the dissociation pattern of the $\text{Au}_{25-n}\text{Ag}_n(\text{SC}_{12}\text{H}_{25})_{18}$ clusters generated by laser irradiation. The cluster on the stainless substrate was dissociated using a laser irradiation with a fluence slightly higher than that used for MALDI mass spectrometry.

Reverse-phase high-performance liquid chromatography (HPLC) was used to determine charge states of **1-6**.¹ HPLC experiments were carried out with an instrument that included a Waters controller (Waters, Waters 600), a pump (Waters, Waters 626), and a UV-Vis detector (Waters, Waters 486), using two stainless steel reverse-phase columns (Hypersil BDS C8 stationary phase 250 x 4.6 mm i.d. and Hypersil BDS Phenyl 150 x 4.6 mm, with both 5 μm particles) connected in series (C8 column first). The mobile phase was 10 mM $(\text{C}_4\text{H}_9)_4\text{NClO}_4/\text{CH}_2\text{Cl}_2$ with a flow rate of 0.4 mL/min.

X-ray photoelectron spectra were collected using an electron spectrometer (JEOL, JPS-9010MC) equipped with a chamber at a base pressure of $\sim 2 \times 10^{-8}$ Torr. X-rays from the Mg-K α line at 1253.6 eV were used for excitation.

UV-Vis absorption spectra and photoluminescence (PL) spectra of the clusters were recorded in toluene at ambient temperature by using a double-beam spectrometer (JASCO, V-630) and a spectrofluorometer (Shimadzu, NIR-PL system), respectively. The measurements were performed at room temperature without prior degassing of the sample solutions. The cluster concentrations for the PL measurement were typically $< 10\ \mu\text{M}$, where the PL intensities increase linearly with the cluster concentrations. The PL quantum yield, Φ , was determined by comparison with the known yields of laser dyes, Q-SWITCH 5 ($\Phi = 5 \times 10^{-4}$)². The raw spectral data, $I(w)$, which are functions of wavelength, were converted to energy-dependent data, $I(E)$, according to the following relation, such that the integrated spectral areas were conserved:

$$I(E) = I(w)/(\partial E/\partial w) \propto I(w) \times w^2$$

II. Results

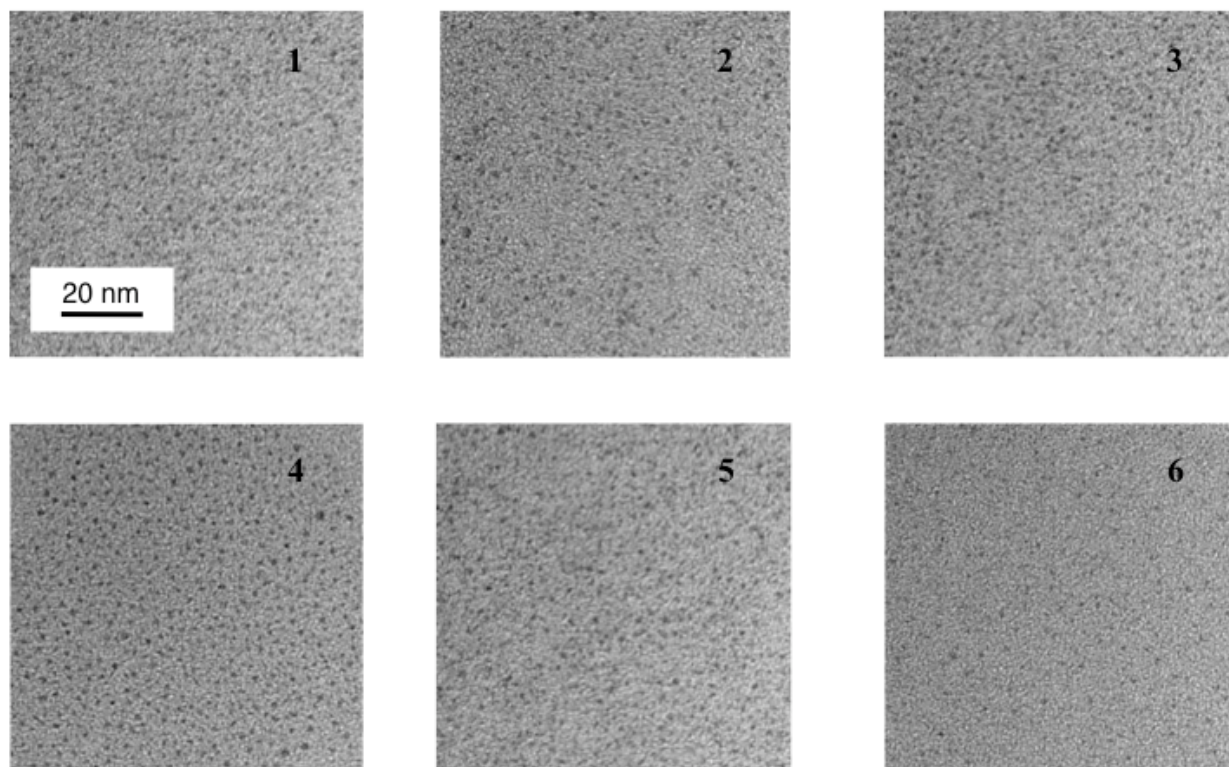


Fig. S1. TEM images of 1-6.

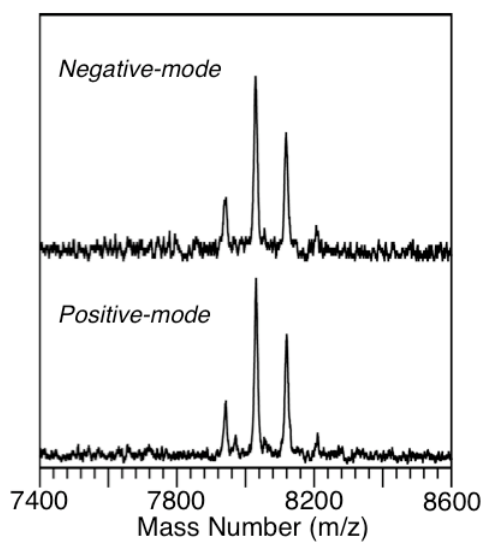


Fig. S2. Negative-mode and positive-mode MALDI mass spectra of 4. Similar results were also obtained for 1-3, 5, and 6.

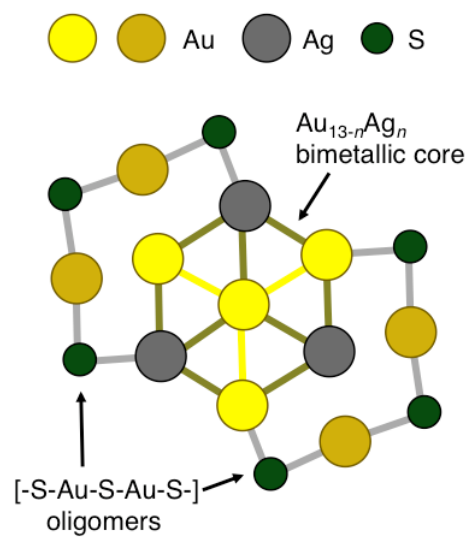


Fig. S3. Proposed structure for $\text{Au}_{25-n}\text{Ag}_n(\text{SC}_{12}\text{H}_{25})_{18}$ ($n = 0-11$).

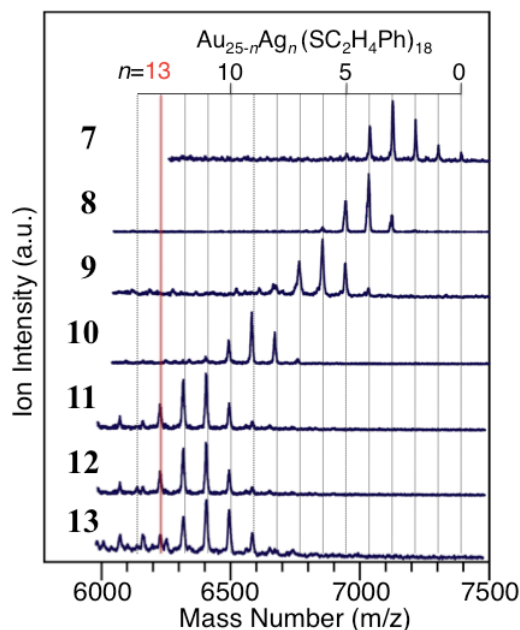


Fig. S4. Negative-ion MALDI mass spectra of 7-13.

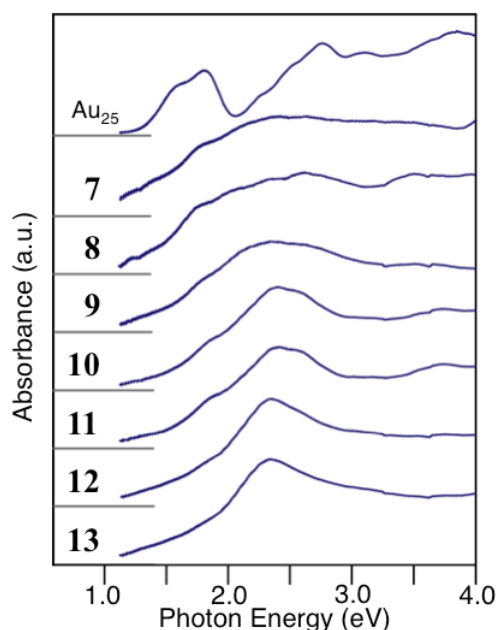


Fig. S5. Optical absorption spectra of the toluene solutions of $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}$ and 7-13.

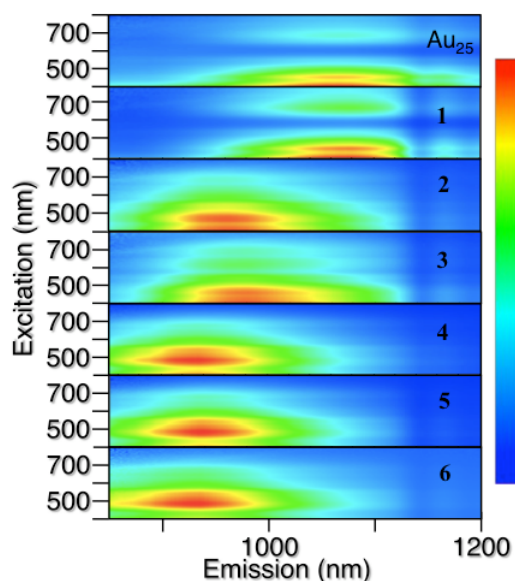


Fig. S6. Three-Dimensional (3D) PL spectra of $\text{Au}_{25}(\text{SC}_{12}\text{H}_{25})_{18}$ and 1-6. The 3D PL spectra were composed of the bundles of the emission spectra obtained by scanning the excitation wavelengths in the range of 400-1000 nm.

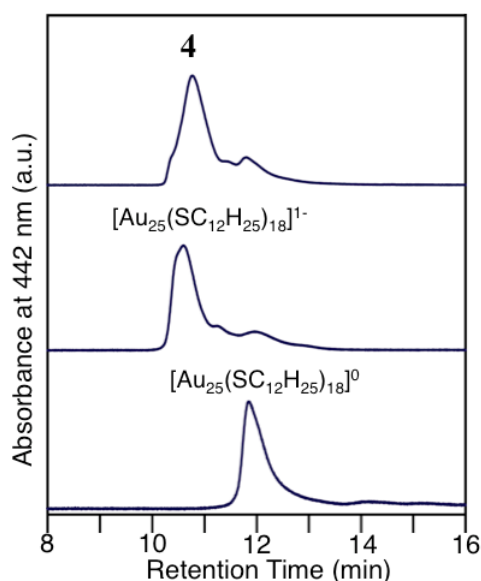


Fig. S7. Reverse-phase HPLC chromatograms of 4, $[\text{Au}_{25}(\text{SC}_{12}\text{H}_{25})_{18}]^{1-}$, and $[\text{Au}_{25}(\text{SC}_{12}\text{H}_{25})_{18}]^0$. The charge states of $[\text{Au}_{25}(\text{SC}_{12}\text{H}_{25})_{18}]^{1-}$ and $[\text{Au}_{25}(\text{SC}_{12}\text{H}_{25})_{18}]^0$ were confirmed by absorption spectra.^{3,4} The retention time of 4 is consistent with that of $[\text{Au}_{25}(\text{SC}_{12}\text{H}_{25})_{18}]^{1-}$, indicating that 4 is the anionic species $[\text{Au}_{21}\text{Ag}_4(\text{SC}_{12}\text{H}_{25})_{18}]^{1-}$.¹ Similar results were also obtained for 1-3, and 5, 6.

References

1. Y. Negishi, W. Kurashige, Y. Niihori, T. Iwasa and K. Nobusada, *Phys. Chem. Chem. Phys.*, 2010, DOI:10.1039/b927175a.
2. A. Seilmeier, B. Kopainsky, and W. Kaiser, *Appl. Phys.*, 1980, **22**, 355-359.
3. Y. Negishi, N. K. Chaki, Y. Shichibu, R. L. Whetten and T. Tsukuda, *J. Am. Chem. Soc.*, 2007, **129**, 11322-11323.
4. M. Zhu, W. T. Eckenhoff, T. Pintauer and R. Jin, *J. Phys. Chem. C*, 2008, **112**, 14221-14224.