SUPPORTING INFORMATION

Chromatographic Isolation of "Missing" Au_{55} Clusters Protected by Alkanethiolates

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1. Characterization

Laser desorption ionization (LDI) mass spectrometry

The details of the LDI mass spectrometer have been described elsewhere.[1] The ions formed by the irradiation of 355-nm laser light (fluence < 3 mJ $pulse^{-1}$) from a Nd:YAG laser were accelerated to 13 kV and detected by a linear time-of-flight mass spectrometer. Typical time duration between the laser irradiation and pulsed extraction was 6 μs. The ionic species of $Au_nS_m^+$ were mainly observed. Figure S1a shows the positive-ion LDI mass spectra of the 8-kDa Au:SC_{18} clusters obtained under different laser fluence. The distribution dose not change appreciably whereas the intensity increases with the fluence. The comparison between the positive and negative ion modes is shown in Figure S1b. The distribution is almost the same in both modes, whereas the positive-ion mode gives higher intensity. Thus, we probed the cluster size distributions by the LDI mass spectrometry in the positive-ion mode.

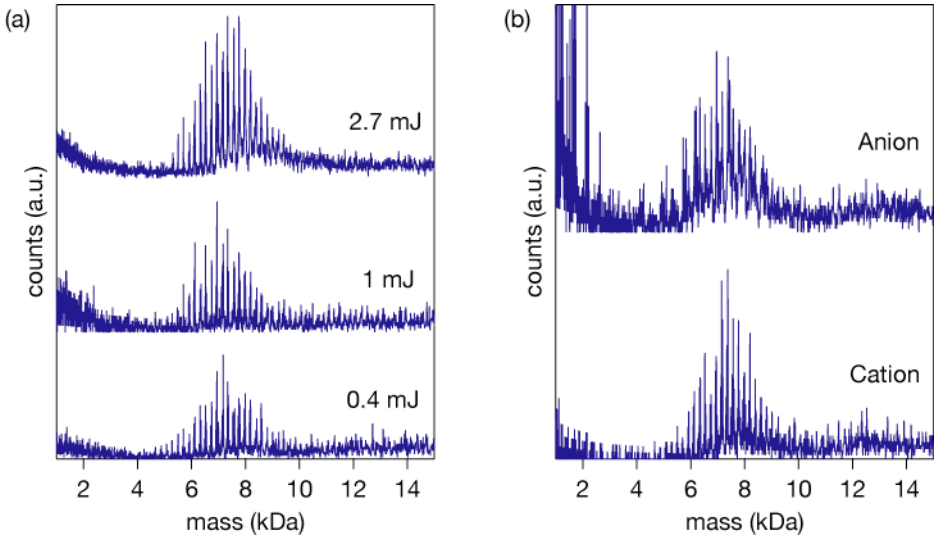

Figure S1. (a) Positive-ion LDI mass spectra of the 8-kDa Au:SC_{18} clusters obtained under different laser fluence. (b) LDI mass spectra of the 8-kDa clusters operated in positive and negative ion modes.

Figure S2 shows high-resolution LDI mass spectra of the 8-kDa and 11-kDa Au:SC_{18} clusters whose low-resolution mass spectra are shown in Figure 2. The chemical compositions of $Au_nS_m^+$ observed here are similar to those reported by Arnold and Reily.[2]

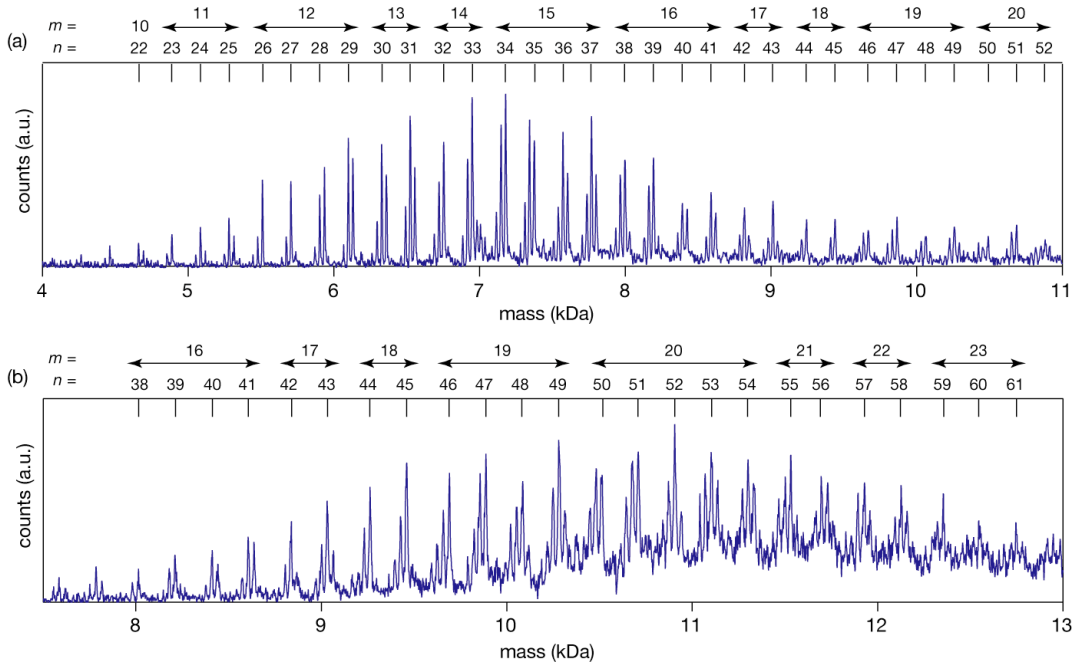

Figure S2. High-resolution LDI mass spectra of the (a) 8-kDa and (b) 11-kDa Au:SC_{18} clusters in the positive ion mode. The assignments for the $Au_nS_m^+$ ions are also denoted. Stick bars indicate the most intense peaks within each envelope.

Optical spectroscopy

UV-vis absorption spectra of the Au:SC_x clusters in $CHCl_3$ were recorded with a spectrophotometer (HITACHI, U-2010). The sample solutions were not deaerated prior to the measurement. All the measurements were performed at room temperature.

Infrared absorption spectroscopy

Infrared absorption spectra were recorded with an FT-IR spectrometer (JASCO, FT/IR-4200). Typical thickness of the liquid cell was 0.025 mm. The IR spectrum of Au_{55}:SC_{18} in chloroform is shown in Figure S3. The symmetric (d^+) and antisymmetric (d^-) CH_2 stretching modes were observed at 2853 and 2924 cm^{-1}, respectively. These frequencies are similar to those of a liquid-like CH_2 chain.[3,4] This result indicates that the alkyl chain of the monolayer contains gauche defects and as a result is highly disordered.

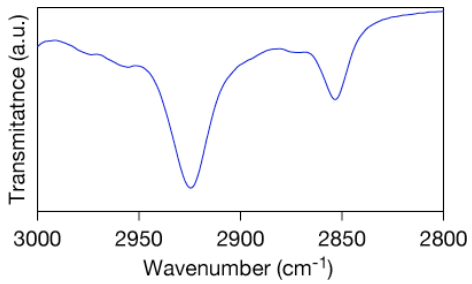

Figure S3. FT-IR spectrum of the11-kDa Au:SC_{18} clusters.

Thermogravimetric (TG) analysis

Thermogravimertic and differential thermoanalysis (TG/DTA) were performed on a TG/DTA analyzer (Brucker, TG-DTA2000SA) at a heating rate of 10 °C/min in the temperature range from 24 to 500°C under N_2 flow. Typically, 3-7 mg of the Au:SC_{18} cluster sample was used in the measurement. Figure S4 shows a typical result for the 11-kDa Au:SC_{18} clusters. From the weight loss at ~500 °C, the contents of organic compound and gold were determined to 45.6 and 54.4 wt%, respectively. This result indicates that the composition of the 11-kDa Au:SC_{18} is expressed as $Au_{55}(SC_{18}H_{37})_{32}$.

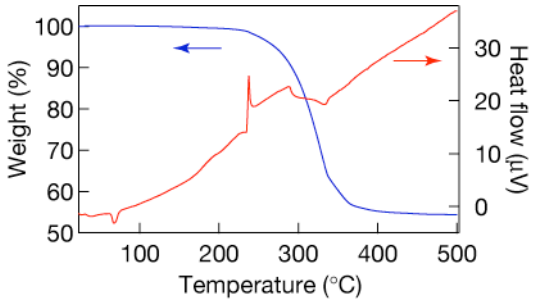

Figure S4. TG/DTA curves of the 11-kDa Au:SC_{18} clusters.

Gel permeation chromatography (GPC)

We used in the present study a recycling HPLC system (LC-908, Japan Analytical Industry Co., Ltd) equipped with two preparative columns (JAIGEL-W253) in series.[5] Toluene was used as eluent and was flowed at 3.5 mL/min. The UV-vis absorbance detector was operated at 290 nm.

The amount of the clusters eluted from the columns was estimated by comparing the optical absorbance with that of the original sample. Figure S5 shows that the transmittance of the Au:SC_{18} clusters is essentially ~100 %.

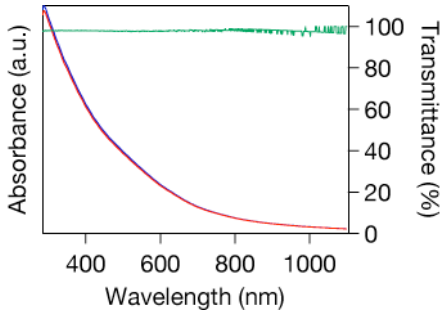

Figure S5. UV-vis absorption spectra of the Au:SC_{18} clusters. Blue and Red curves were recorded before and after GPC analysis, respectively. Green curve indicates the transmittance estimated from the two spectra.

The universal standard curve, shown in Figure S6, for the present system was obtained by using polystyrene (PS) standards: PS of a GPC grade (Mw 29,300, 18,700, and 13,700) were from Aldrich and those with Mw 50,000, 25,000, and 5,780 were from Chemco Scientific. Least-squares fit to the data gave the following conversion equation for the W253 × 2 system:

$$d\,/\,\mathrm{nm} = 265.2 \times \exp(-0.1064 \times (t\,/\mathrm{min})) \quad (1)$$

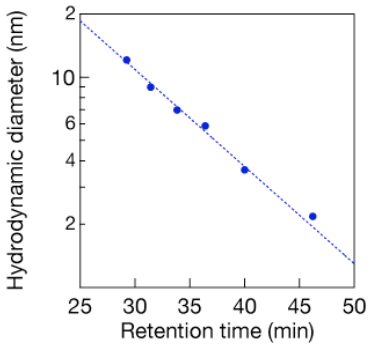

Figure S6. Universal standard curve for the W-253×2 setup. Blue points represent the retention times for the PS standards.

The retention times of the 8-kDa and 11-kDa Au:SC_{18} clusters (Figure S7) were 37.8 and 36.7 min, respectively. From eq. (1), the hydrodynamic diameters of the 8-kDa and 11-kDa clusters are estimated to be 4.8 and 5.4 nm, respectively.

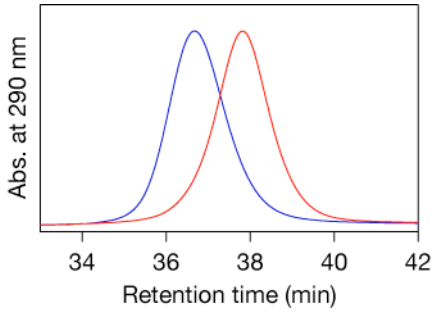

Figure S7. Chromatograms of 8-kDa (red) and 11-kDa (blue) Au:SC_{18} clusters.

Transmission electron microscopy (TEM)

TEM images were recorded with an electron microscope operated at 100 kV (Hitachi, H-7500). Typical magnification of the images was 100,000.

2. Etching Treatment

The Au:SC_x clusters obtained by thiolation of the Au:PVP clusters were further incubated at 80°C for more than 24 h in neat C_xSH liquid in air. Typical concentration of the clusters was 20-40 mg/mL. After the incubation, the clusters in C_nSH were put into warm ethanol (~50°C, 200 mL) and the supernatant was discarded to remove excess amount of C_xSH. This purification procedure was repeated more than three times. The Au:SC_x solid thus obtained was stored in a freezer (-18°C). Figure S8 shows the LDI mass spectra of the Au:SC_{18} clusters before and after etching treatment. The distribution of the Au:SC_{18} clusters shifts toward lower masses and becomes narrower after the etching treatment.

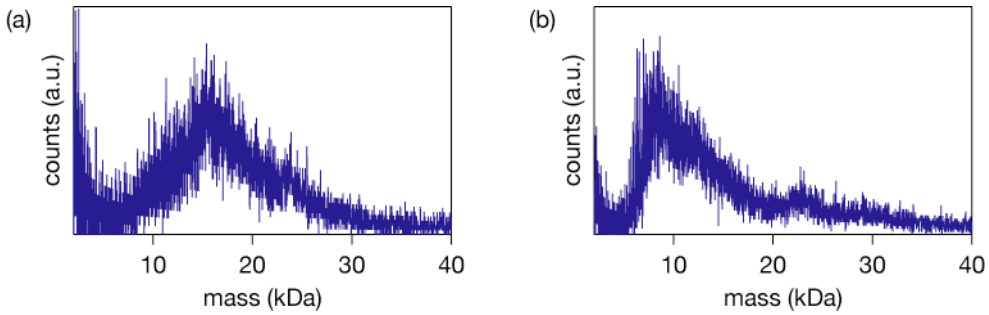

Figure S8. Positive-ion LDI mass spectra of (a) the as-prepared Au:SC_{18} clusters and (b) those after the etching treatment.

3. Isolation of Au_{55}:SC_{12} Clusters

The chromatographic isolation of the Au_{55}:SC_{12} clusters was also performed. Figure S9 shows the chromatogram of the Au:SC_{12} clusters prepared by the same procedure with Au:SC_{18}. Then, we collected fractions **a** and **b** at the 11th recycle (Figure S9). The LDI mass spectra (Figure S10) show that fractions **a** and **b** are dominated by the 11-kDa and 8-kDa clusters. Indeed, the UV-vis absorption spectrum (Figure S11) of fraction **a** was quite similar to that for the 11-kDa Au:SC_{18} clusters.

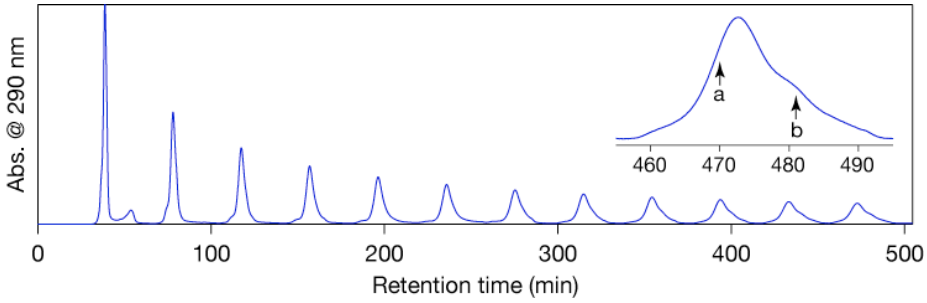

Figure S9. Typical chromatogram of the Au:SC_{12} clusters.

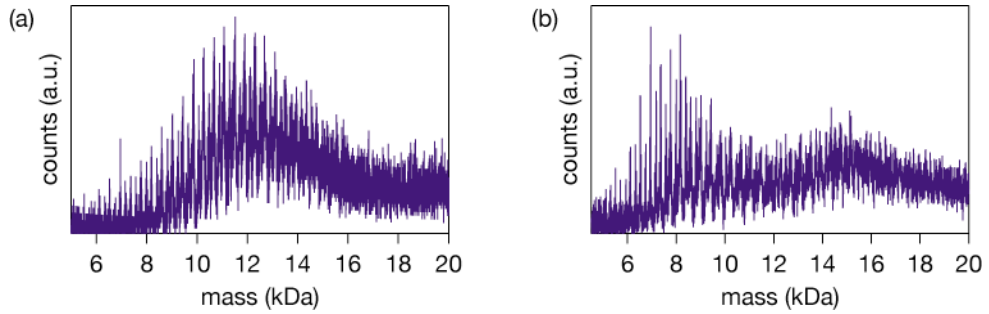

Figure S10. Positive-ion LDI mass spectra of (a) fraction **a** and (b) fraction **b**.

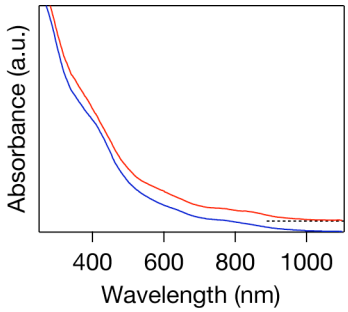

Figure S11. UV-vis absorption spectra of fraction **a** (blue) and the 11-kDa Au:SC_{18} (red).

References

[1] Negishi, Y.; Tsukuda, T. *J. Am. Chem. Soc*. **2003**, *125*, 4046.

[2] Arnold, R. J.; Reilly, J. P. *J. Am. Chem. Soc*. **1998**, *120*, 1528.

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[4] Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc*. **1987**, *109*, 3559.

[5] Murayama, H.; Narushima, T.; Negishi, Y.; Tsukuda, T. *J. Phys. Chem. B* **2003**, *108*, 3496.