SUPPORTING INFORMATION

Isolation and structural characterization of magic silver clusters protected by 4-(*tert*-butyl)benzyl mercaptans

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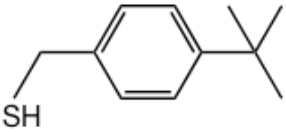
I. Experimental Procedure

A. Chemicals

All of the chemicals were commercially obtained and used without further purification. Silver nitrate ($AgNO_3$), sodium tetrahydroborate ($NaBH_4$), methanol, toluene, tetrahydrofuran (THF), and dichloromethane (CH_2Cl_2) were obtained from Wako Pure Chemical Industries. 4-(*tert*-butyl)benzyl mercaptan (BBSH, Scheme S1) were purchased from Aldrich. Deionized water with a resistivity of > 18 MΩ cm was used in the present study.



Scheme S1 Molecular structure of 4-(*tert*-butyl)benzyl mercaptan (BBSH)

B. Synthesis of Ag:SBB clusters (1)

All operations were performed under pure Ar atmosphere. First, $AgNO_3$ (1.6 mmol, 273 mg) was dissolved in 44 mL THF and the resulting solution was cooled to 0 °C in an ice bath. Then, BBSH (8 mmol) was added to the solution under slow stirring (~ 30 rpm). The colorless solution gradually became cloudy white, indicating the formation of Ag-SBB oligomers. After 15 h, the stirring speed was increased (~ 1300 rpm) and an aqueous solution of $NaBH_4$ (16 mmol, 2 mL) at 0 °C was rapidly added at once. The solution's color immediately changed to deep purple, indicating the formation of Ag:SBB clusters. The solution was stirred for 2 h. After the removal of the precipitates (by-products), the solution was concentrated and methanol (20 mL) was added. The collected precipitates (**1**) were thoroughly washed with methanol. 230 mg of cluster **1** was obtained.

C. Ripening of cluster 1 with BBSH

Cluster **1** (230 mg) was incubated in neat BBSH (15 mL) at 40, 60, or 80 °C with vigorous stirring under Ar atmosphere. The incubated samples were washed with methanol and then centrifuged with dichloromethane to remove by-products (materials insoluble in organic solvents). Typically, 60-70 mg of cluster **2** was obtained. Cluster **2** could be dispersed in THF, toluene, benzene, hexane, and chloroform, but could not in acetone, acetonitrile, and methanol.

D. Characterization

Transmission electron microscopy (TEM) images were recorded using an electron microscope operated at 100 kV (Hitachi, H-7650); typical magnification of the images was 100,000x. High-resolution TEM (HR-TEM) images were recorded using an electron microscope operated at 300 kV (JEOL, JEM-3200); typical magnification of the images was 300,000x. Electrospray ionization (ESI) mass spectra were recorded using a custom-designed time-of-flight (TOF) system.[1)] For the ESI mass analysis, dichloromethane solutions of the clusters with concentrations of 1 mg/mL were electrosprayed into the ambient atmosphere through the stainless steel needle of a syringe biased at ca. +3 kV. The charged liquid droplets were fed into a capillary and heated resistively to ca. 180 ºC to form intact cluster ions via desolvation. Laser desorption ionization (LDI) mass spectra were collected on a linear-mode TOF mass spectrometer (Applied Biosystem, Voyager Linear RD VDA 500) using a nitrogen laser (337 nm). Gel permeation chromatography (GPC) experiments were performed 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 a stainless steel column (Waters, Stragel HR2). The mobile phase was toluene having a flow rate of 2.0 mL/min. UV-Vis absorption spectra of the clusters were recorded in dichloromethane at the ambient temperature by using a double-beam spectrometer (JASCO, V-630). X-ray photoelectron spectra were collected using an electron spectrometer (JEOL, JPS-9010MC) equipped with a chamber at a base pressure of ~ 2×10^{-8} Torr. X-rays from the Mg-Kα line at 1253.6 eV were used for the excitation. X-ray diffraction measurements were performed on a Rigaku Rint2500, using CuKα radiation (λ = 1.54 A°). Thermogravimetric analysis (TGA) was performed on a TG analyzer (Bruker, TGA2000SA) at a heating rate of 5 °C/min in the temperature range 25–500 °C. $Ag_{\sim 280}(SBB)_{\sim 120}$ (8.8 mg) was used in the measurement.

II. Results

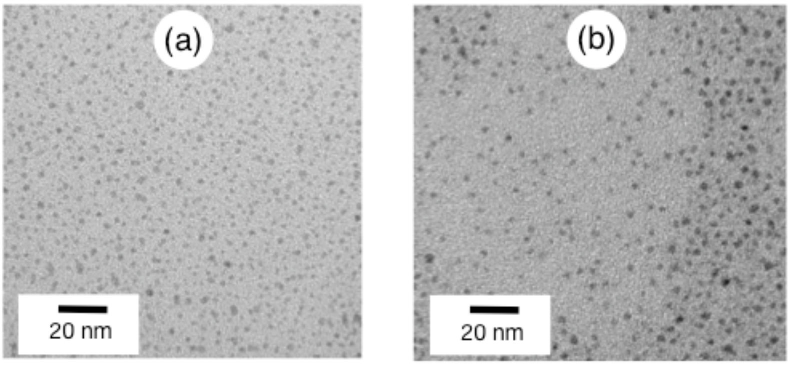


Fig. S1 TEM photographs of (a) **1** and (b) **2**.

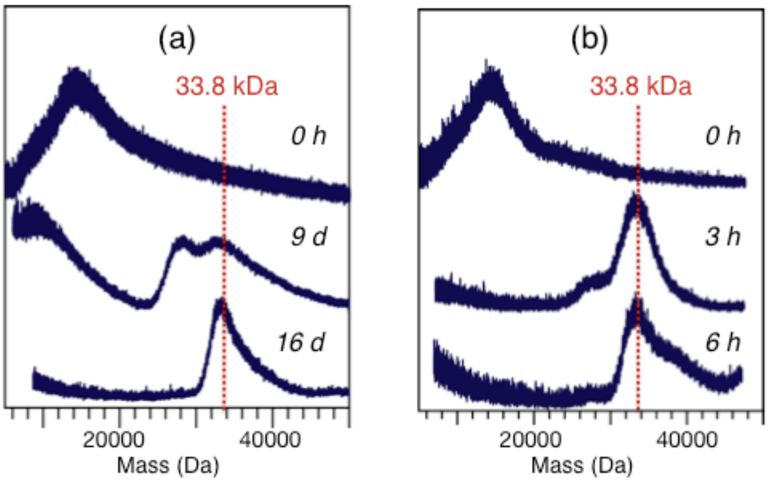


Fig. S2 Positive-ion LDI mass spectra of Ag:SBB clusters produced by the reaction of **1** with BBSH with respect to incubation time; (a) reaction temperature is 40°C and (b) that is 80°C. In the mass spectra, 33.8 kDa peaks are attributed to laser fragment ions of 51.8 kDa clusters (see Fig. 2(d)).

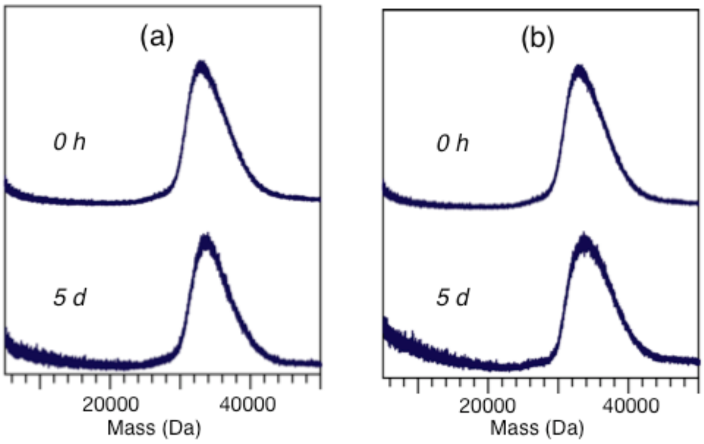


Fig. S3 Positive-ion LDI mass spectra of cluster **2** stored in air as (a) solid form and (b) dispersed in toluene.

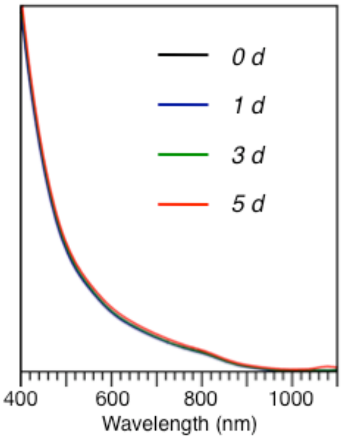


Fig. S4 Time dependence of optical absorption spectrum of a toluene solution of cluster **2** at ambient temperature.

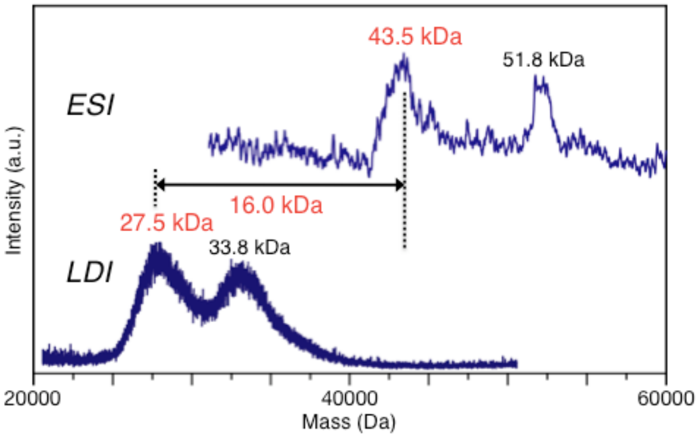


Fig. S5 Positive-ion LDI mass spectrum of a mixture of 43.5 kDa cluster and 51.8 kDa cluster. The ESI mass spectrum of a mixture is also shown for comparison. In the LDI mass spectrum, 27.5 kDa peak is assigned to laser fragment ions of 43.5 kDa clusters. A decrease in the mass of 16 kDa corresponds to dissociation of ~108 BBS aryl group. Thus, the chemical composition of 43.5 kDa cluster can be approximated as $Ag_{\sim 223}(SBB)_{\sim 108}$.

References

1. Y. Negishi, K. Nobusada and T. Tsukuda, *J. Am. Chem. Soc.*, 2005, **127**, 5261-5270