Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Anion Photoelectron Spectroscopy of Free $[Au_{25}(SC_{12}H_{25})_{18}]^-$

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Experimental

Chemicals

Hydrogen tetrachloroaurate tetrahydrate ($HAuCl_4 \cdot 4H_2O$) was purchased from Tanaka Precious Metals. Sodium tetrahydroborate ($NaBH_4$) and all organic solvents except for tetrahydrofuran were purchased from Wako Pure Chemical Industry. Phenylethanethiol (PET) was purchased from Tokyo Kasei Industry. Dodecanethiol (HSC12) and tetraoctylammonium bromide (TOABr) were purchased from Sigma-Aldrich. Stabilizer-free dehydrated tetrahydrofuran (THF) was purchased from Kanto Chemical Company. The water used was Milli-Q grade (>18 MΩ). All commercially available reagents were used without further purification.

Synthesis of $[Au_{25}(SC12)_{18}]^- \cdot TOA^+$

A 300 mL Erlenmeyer flask was charged with 523 mg of $HAuCl_4 \cdot 4H_2O$ (1.27 mmol), 779 mg of TOABr (1.43 mmol), and aTeflon-coated magnetic stir bar. 70 mL of THF was added to the flask and stirring was started at room temperature yielding a dark-red homogeneous solution. Then, 3.04 mL of HSC12 (12.7 mmol) was added dropwise to the solution under constant stirring and the stirring was continued for 1.5 h. At this stage, the color of the solution slowly turned to faint yellow. The stirring was set to vigorous (~750 rpm) and a freshly prepared $NaBH_4$ solution (480 mg; 12.7 mmol in 10 mL of cold water) was added to the solution all at once. Violent gas evolution occurred and the black colored solution was stirred at the same speed for 16 h. The THF layer was filtered through a paper filter and the volatiles were evaporated giving a black oil covered with water. The oil was precipitated by methanol and the precipitate was collected by centrifugation. This methanol washing procedure was repeated five times and the precipitate was dried *in vacuo*. The dried product was extracted by a minimum amount of dichloromethane and the solution was precipitated by methanol containing TOABr (2 mg/mL). The precipitates were washed by methanol two more times. Acetone (~50 mL) was added to the precipitate and the solution was centrifuged. The supernatant was evaporated to dryness and to the sticky black solid was added acetone (~50 mL). The solution was centrifuged and the supernatant was evaporated to dryness. The black residue was dissolved in a minimum amount of dichloromethane and the solution was concentrated by Ar flow. Finally, the solid was dried *in vacuo* at room temperature, giving 118.9 mg (26% yield based on Au) of the title compound as a brown powder.

Determination of adiabatic electron affinity (AEA) and vertical detachment energy (VDE)

AEA can be estimated from the onset of a peak. By fitting a tangential line to the inflection point of peak A, the intersection between the line and the baseline is determined as the AEA. A Gaussian function was fitted to peak A and the top is determined as the VDE.

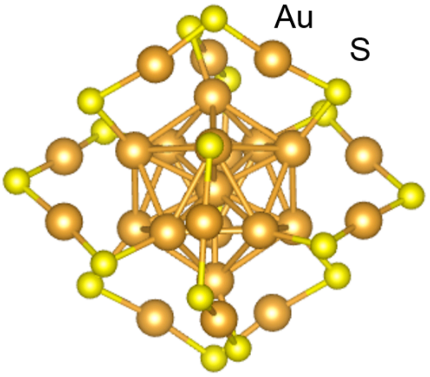

Figure S1. Crystal structure of $[Au_{25}(PET)_{18}]^-$ (PET = phenylethanethiolate). C and H are omitted for clarity.

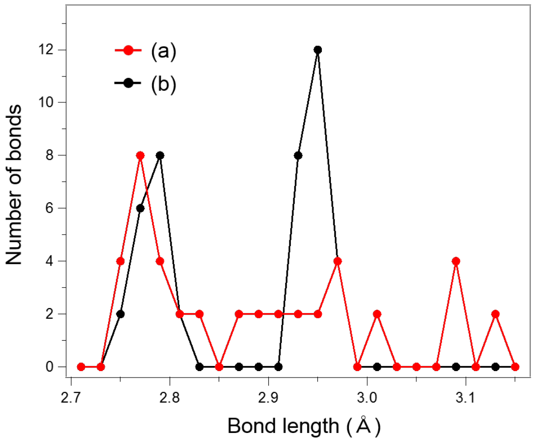

Figure S2. Distribution of Au–Au bond lengths within (a) $[Au_{25}(PET)_{18}]^0$ (Ref. 1) and (b) $[Au_{25}(PET)_{18}]^-$ (Ref. 2).

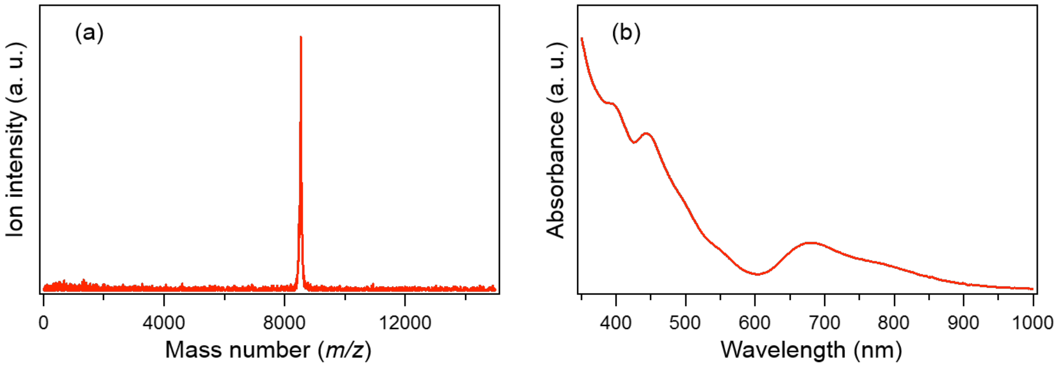

Figure S3. (a) ESI mass spectrum and (b) UV-Vis-NIR spectrum of $[Au_{25}(SC12)_{18}]^-$.

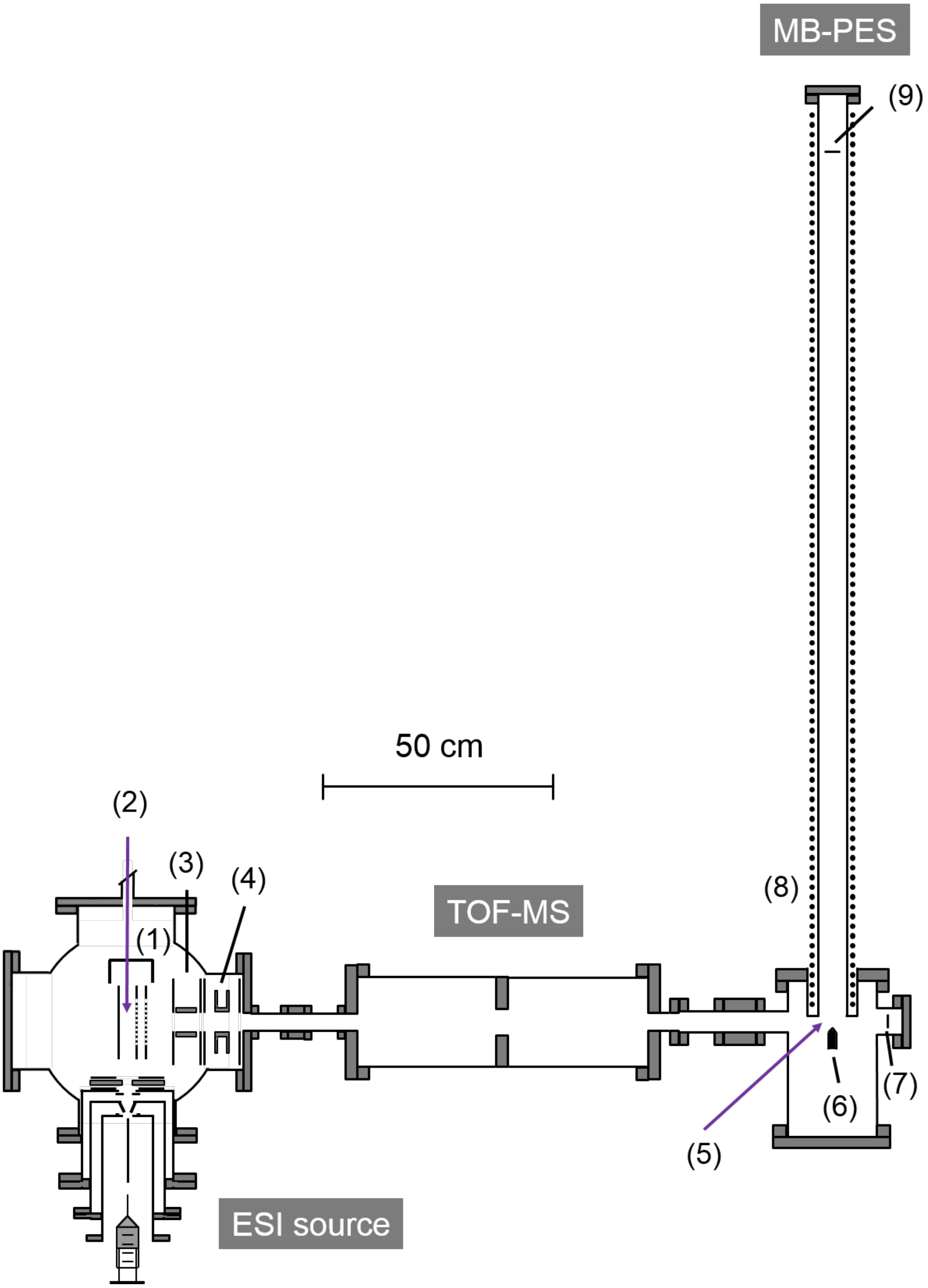

Figure S4. Schematic illustration of the apparatus used for photoelectron spectroscopy. (1) Wiley-McLaren type acceleration grids, (2) photodissociation laser, (3) deflectors, (4) einzel lens, (5) photodetachment laser, (6) permanent magnet, (7) microsphere plate, (8) coil, and (9) microchannel plate.

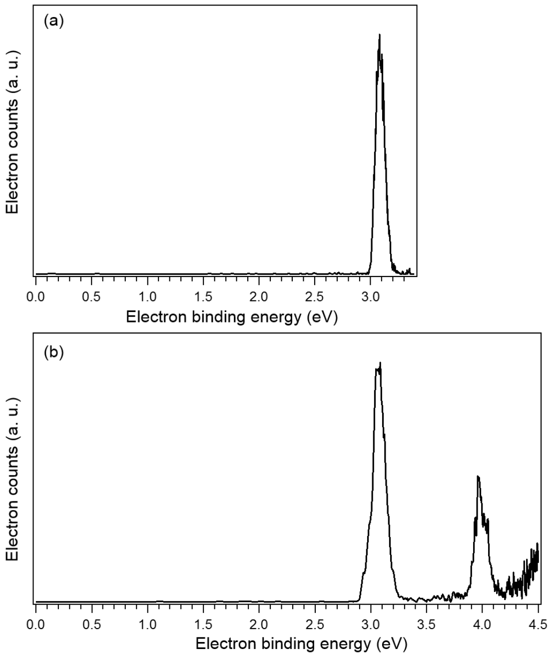

Figure S5. PE spectrum of I^- measured at (a) 355 nm and (b) 266 nm.

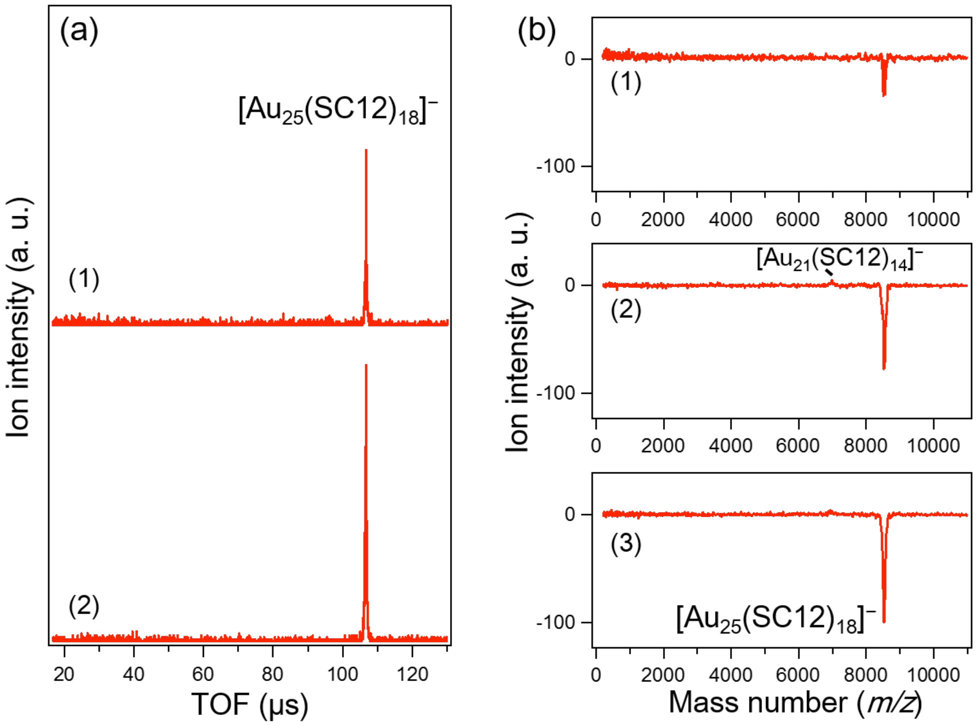

Figure S6. (a) TOF mass spectra of $[Au_{25}(SC12)_{18}]^-$ (1) with and (2) without the photodissociation laser (355 nm, <67 mJ/pulse/cm^2). (b) Photodissociation mass spectra of $[Au_{25}(SC12)_{18}]^-$ at 355 nm with laser fluences of (1) <14, (2) <42, and (3) <67 mJ/pulse/cm^2.

References

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