Supporting Information

Selective synthesis of organogold magic clusters $Au_{54}(C{\equiv}CPh)_{26}$

Prasenjit Maity,[a] Tomonari Wakabayashi,[b] Nobuyuki Ichikuni,[c] Hironori Tsunoyama,[a] Songhai Xie,[a] Miho Yamauchi,[a] and Tatsuya Tsukuda*[a,d]

[a] *Catalysis Research Center, Hokkaido University, Nishi 10, Kita 21, Sapporo 001–0021, Japan*

[b] *Department of Chemistry, School of Science and Engineering, Kinki University, Higashiosaka, 577-8502 Osaka, Japan*

[c] *Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University, Inage-Ku, Chiba 263-8522, Japan*

[d] *Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*

1. Experimental

A. Chemicals

All the reagents were commercially available and were used without further purification. Hydrogentetrachloroaurate tetrahydrate, sodium tetrahydroborate, methanol, toluene, chloroform, and polyvinylpyrollidine (PVP; K30, average molecular weight: 40 kDa), were obtained from Wako Pure Chemical Industries. Phenylacetylene, 4-ethynyl toluene, *trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB), cytochrome c and sinapinic acid were purchased from Sigma-Aldrich. Milli-Q grade water was used in the present study.

B. Preparation of phenylacetylene-protected Au clusters (Au:C_2Ph)

Au:PVP clusters with different diameters (1.2±0.2 nm (**1a**), 1.4±0.2 nm (**1b**), and 1.8±0.3 nm (**1c**)) were prepared according to the method given in Refs. 1 and 2. Details of the synthesis conditions for **1a**–**1c** are described in Ref. 3. The Au:C_2Ph clusters were then prepared by ligand exchange from Au:PVP by mixing water–organic biphasic systems. First, 50 mg of an Au:PVP sample (0.01 mmol of Au) was dissolved in water (10 mL) and 1 g of PhC_2H (10 mmol) was dissolved in toluene or chloroform (5 mL). These two solutions were then mixed at 333 K and stirred for 3 h (1350 rpm). After 3 h, the organic phase had turned deep brown and the water phase had become colourless, indicating complete ligand exchange had occurred. The Au:C_2Ph clusters in the organic

phase were collected by evaporating the solvents and repeatedly washing with methanol followed by centrifugation. This washing is crucial to remove some yellow by-products, possibly small gold clusters. Excess PhC_2H was collected by vacuum distillation and reused in later synthesis. The Au:C_2Ph clusters are soluble in apolar organic solvents (toluene, chloroform, and hexane), but insoluble in polar organic solvents (methanol and acetone). For large-scale synthesis, 150 mg of Au:PVP samples (0.03 mmol of Au) was dissolved in water (30 mL) and 3 g of PhC_2H (30 mmol) was dissolved in chloroform (20 mL) to produce ~5mg of $Au_{54}(C_2Ph)_{26}$.

C. Characterization

i) Optical absorption spectroscopy

UV–visible spectra of Au:C_2Ph were obtained in chloroform using a JASCO V-670 spectrophotometer.

ii) Transmission electron microscopy (TEM)

TEM images of Au:C_2Ph were recorded using a Philips JEM 2000FX microscope operated at 200 kV. A toluene solution of Au:C_2Ph was drop-casted onto hydrophobic carbon-coated copper grids and it was dried in open air for 2 h.

iii) Fourier-transform infrared (FT-IR) spectroscopy

FT-IR spectra of Au:C_2Ph were obtained using a JASCO FT/IR-4200 spectrophotometer with samples prepared as KBr pellets.

iv) Matrix-assisted laser desorption ionization mass spectrometry (MALDI MS)

Au:C_2Ph clusters (0.5 mg) were dissolved in toluene/chloroform (500 μL) and DCTB (1 mg) was dissolved in methanol (50 μL) in two different tubes. These two solutions were then mixed in a volume ratio of 1:1 and the mixture was drop-casted onto a sample plate and dried in air for over 1 h. MALDI mass spectra of thus prepared Au:C_2Ph were recorded using a time-of-flight mass spectrometer (Applied Biosystems, Voyager-DE STR-H) with a N_2 laser (337 nm; 3 Hz; <100 mJ). Mass spectra were recorded using an acceleration voltage of 25 kV with delayed extraction mode (delay time 300 ns) in the linear configuration and in both positive and negative detection modes. The mass spectra were calibrated by that of cytochrome c recorded under similar conditions using sinapinic acid as a matrix.

v) X-ray photoelectron spectroscopy (XPS)

XPS measurements were performed using a JEOL, JPS-9010MC spectrometer with a Mg Kα source. $Au_{54}(C_2Ph)_{26}$ clusters were pressed to form a pellet, which was vacuum dried before performing XPS measurements. The spectrum was calibrated relative to the C_{1s} peak, which was adjusted to an energy of 284.5 eV.

vi) Powder X-ray diffraction (PXRD)

A PXRD pattern of $Au_{54}(C_2Ph)_{26}$ was measured using a Bruker D8-advance diffractometer with a Cu Kα source. A powdered sample of $Au_{54}(C_2Ph)_{26}$ dried in vacuum was placed on a quartz plate with appropriate height adjustment.

vii) X-ray absorption spectroscopy (XAS)

XAS experiments were conducted using the BL-7C beam line at the Photon Factory of the Institute for Material Structure Science (PF-IMSS, KEK, Proposal No. 2008G638). Extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) spectra were recorded at the Au L_3 edge (11,562 eV). The synchrotron radiation emitted from the 2.5-GeV storage ring was monochromatized using a Si (111) double-crystal monochromator calibrated by the L_3 edge of metallic Au. The powder samples were pressed into self-supporting disks and sealed in polyethylene bags. All the spectra were recorded at room temperature in transmission mode using ion chambers for detection. EXAFS data were analyzed using the REX2000 program (Rigaku Co.). The EXAFS oscillations, $\chi(k)$, were obtained from the data by spline smoothing and normalized by the edge height. The k^3-weighted $\chi(k)$ in the range 35–145 nm^{-1} was Fourier transformed into r space and the peak region (0.221–0.313 nm) was filtered and inversely Fourier transformed into k space. The Fourier-filtered data were then analyzed by curve fitting; model parameters (back scattering amplitude and phase shift) were determined from an EXAFS oscillation observed for bulk Au.

viii) Raman spectroscopy

Raman spectra of PhC_2H and $Au_{54}(C_2Ph)_{26}$ were recorded on a polychromater at a resolution of 12 cm^{-1} (Acton SP300i 600 G/mm and 1200 G/mm with SPEC10-CCD at RT) using a CW laser system that generated 532 nm excitation (Coherent DPSS/Nd:YAG Compass 315 M; ~ 90 mW).

ix) Proton nuclear magnetic resonance (NMR)

NMR spectra were recorded using a 600-MHz OXFORD NMR AS600 instrument (EUR0041) using $CDCl_3$ as solvent at 295 K.

2. Results

A. PXRD pattern

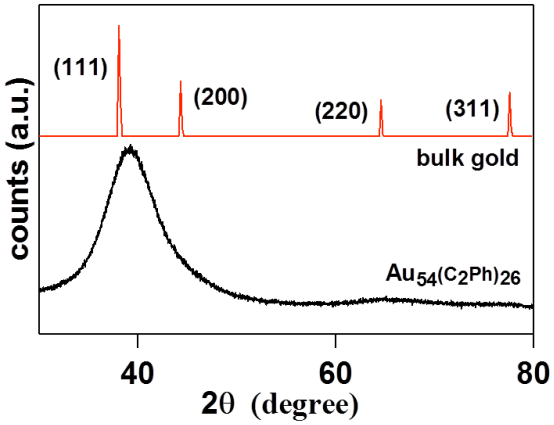

Figure S1. PXRD pattern of bulk gold (red) and $Au_{54}(C_2Ph)_{26}$ (black).

B. XANES and EXAFS spectra

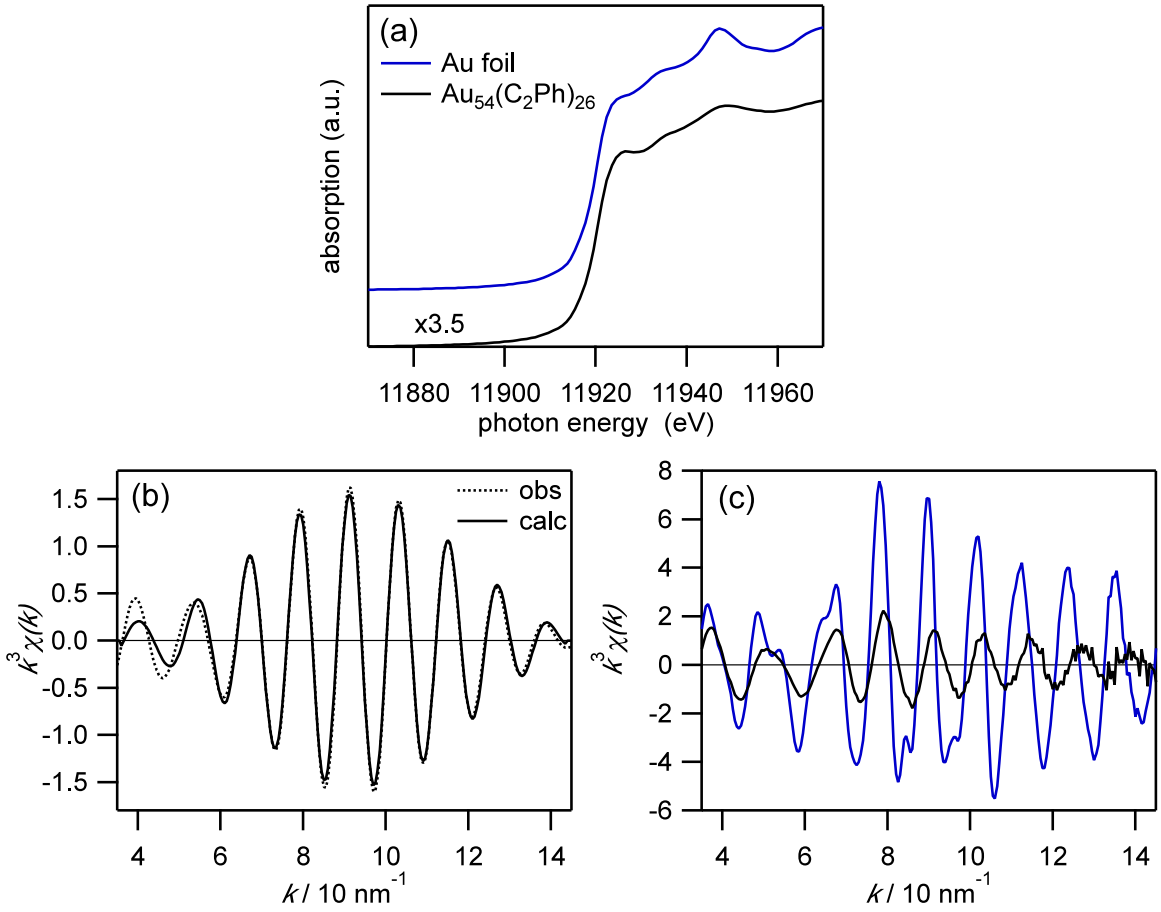

Figure S2. (a) Au L_3-edge XANES spectra for $Au_{54}(C_2Ph)_{26}$ (black) and bulk gold (blue), (b) curve fitting results of Au-Au coordination for $Au_{54}(C_2Ph)_{26}$, and (c) Au L_3-edge EXAFS functions (k^3-weighted) for $Au_{54}(C_2Ph)_{26}$ (black) and bulk gold (blue). The corresponding fourier transformed spectrum is given in main paper (Figure 4d).

Table S1. EXAFS analysis results for $Au_{54}(C_2Ph)_{26}$

samples	BFT range (nm)[a]	*CN*[b]	*r* (nm)[c]	*dE* (eV)[d]	*DW* (nm)[e]
Au foil	0.233–0.325	12	0.2885	0.0	0.006
$Au_{54}(C_2Ph)_{26}$	0.221–0.313	7.3±1.6[f]	0.2790 ±0.0011	-9.8±2.7	0.0079 ±0.0011

[a]Back Fourier Transformed range. [b]Coordination number. [c]Coordination distance. [d]The difference between theoretical and experimental threshold energies. [e]Debye-Waller factor. [f]The electron mean free path was assumed to be 0.5 nm.

C. FTIR spectra

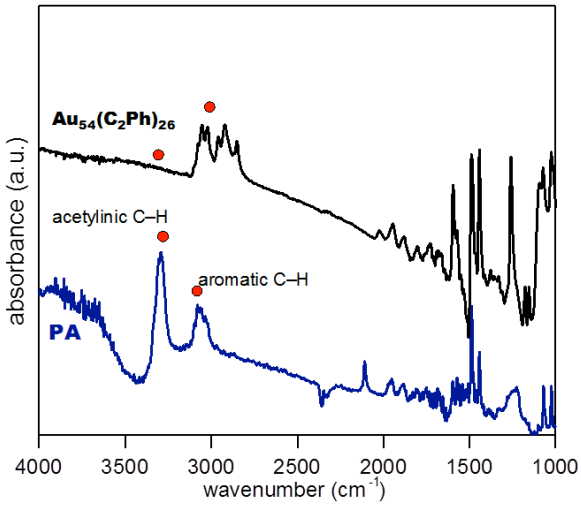

Figure S3. FTIR spectrum of PhC_2H (blue) and $Au_{54}(C_2Ph)_{26}$ (black).

D. Proton NMR spectra

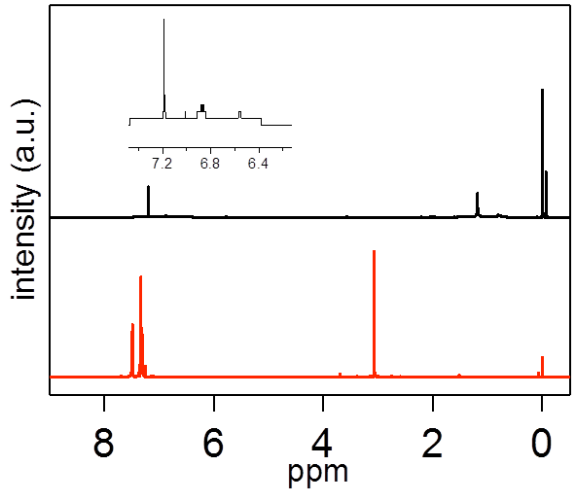

Figure S4. ^1H NMR spectra of PhC_2H (red) and $Au_{54}(C_2Ph)_{26}$ (black) in $CDCl_3$. Inset shows the magnified spectrum in the range of 6.1-7.5 ppm.

E. Mass spectra

i) Mass spectra recorded in the positive and negative-ion mode

The negative ion with the mass of 13267 Da was detected as a major species (Figure S5b). This species can be assigned to $Au_{54}(-C{\equiv}C-Ph)_{26}^-$ (calculated mass = 13265) rather than $Au_{54}(=C=CH-Ph)_{26}^-$ (calculated mass = 13291). $Au_{54}(C_2Ph)_{26}^+$ was also detected as a major species in MALDI mass spectra in the positive detector mode (Figure S5a).

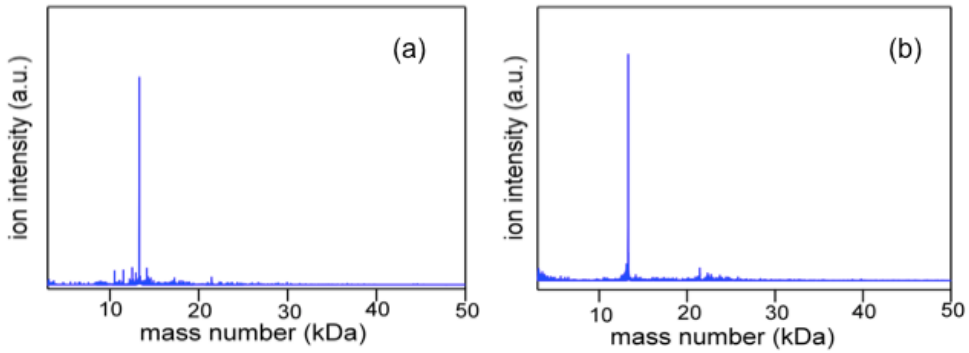

Figure S5. (a) Positive-ion and (b) negative-ion MALDI mass spectra of $Au_{54}(C_2Ph)_{26}$.

ii) Laser power dependence

Only a single peak associated with $Au_{54}(C_2Ph)_{26}$ was detected in the laser power range used in the present study.

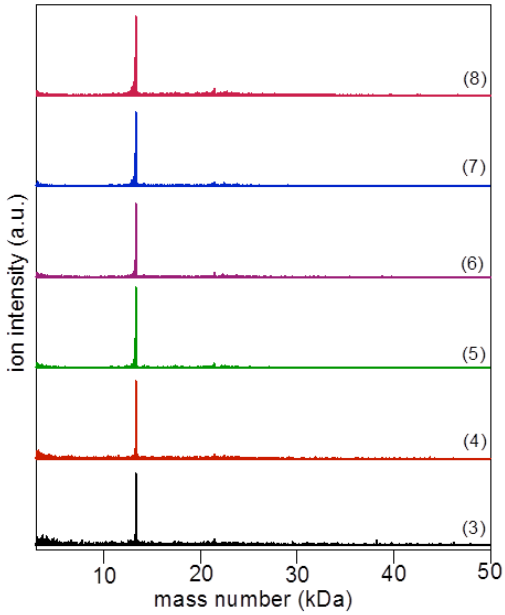

Figure S6. Negative-ion MALDI mass spectra of $Au_{54}(C_2Ph)_{26}$ recorded at various laser fluences. Values in parentheses represent the laser power in arbitrary units.

References

1. H. Tsunoyama, H. Sakurai, N. Ichikuni, Y. Negishi and T. Tsukuda, *Langmuir,* 2004, **20**, 11293.

2. H. Tsunoyama, N. Ichikuni and T. Tsukuda, *Langmuir,* 2008, **24**, 11327.

3. P. Maity, H. Tsunoyama, M. Yamauchi, S. Xie and T. Tsukuda, *J. Am. Chem. Soc.*, 2011, **133**, 20123.