



Supporting Information

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Alkynyl-Protected Au₂₃ Nanocluster: A 12-Electron System**

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I. Physical measurements

UV-VIS-NIR absorption spectrum was recorded on Cary 5000. Mass spectrum was recorded on an Agilent Technologies ESI-TOF-MS. NMR data were recorded on a Bruker Avance II spectrometer (500 MHz). Thermogravimetric analysis (TGA) was recorded on STDQ600. X-ray photoelectron spectroscopy (XPS) of $[\text{Au}_{23}(\text{PhC}\equiv\text{C})_9(\text{Ph}_3\text{P})_6](\text{SbF}_6)_2$ was recorded on PHI Quantum-2000 XPS. The sample was put under UHV to reach the 10^{-8} Pa range. The nonmonochromatized Al K α source was used at 10 kV and 10 mA. All binding energies were calibrated using the C(1s) carbon peak (284.6 eV), which was applied as an internal standard. High resolution narrow-scan spectra were recorded with the electron pass energy of 50 eV and takeoff angle of 55° to achieve the maximum spectral resolution.

X-ray Crystallography. Intensity data of compounds **1** in $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ were collected on an Agilent SuperNova Dual system (Mo K α). Absorption corrections were applied by using the program CrysAlis (multi-scan). The structure was solved by direct methods. Rigid group refinements were performed for many phenyl rings. Au, P, and Sb atoms were refined anisotropically by least-squares on F^2 using the SHELXTL program. However, carbon atoms were refined isotropically due to the poor behavior of carbon atoms, this led to an A class alert in CheckCIF. High and unusual atomic displacement parameters and low bond precision are mainly because of the poor high angle data and high absorption.

II. Synthesis

Materials and reagents. Ethynylbenzene ($\text{PhC}\equiv\text{CH}$, 98%), triphenylphosphine (Ph_3P , 99.5%) and Silver hexafluoroantimonate (AgSbF_6 , 98.0%) were purchased from J&K; sodium borohydride (NaBH_4 , 98%) and other reagents employed were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All reagents were used as received without further purification. $\text{Me}_2\text{SAuCl}^1$ and $\text{Ph}_3\text{PAuCl}^2$ were prepared according to literature methods.

$\text{PhC}\equiv\text{CAu}^3$

To 10.0 mL of acetone solution containing Me_2SAuCl (100.0 mg, 0.34 mmol) and ethynylbenzene 47.8 μL (44.5 mg, 0.44 mmol), 60.3 μL of NEt_3 (44.0 mg, 0.44 mmol) was added under stirring. The mixture was stirred for 2 h at room temperature in air in the dark. Then the solution was evaporated to dryness to give a pale yellow solid, which was washed with water (2×5 mL), ethanol (2×5 mL) and ether (5 mL) to give 89.7 mg (88.5% yield based on Au) of $\text{PhC}\equiv\text{CAu}$.

$[\text{Au}_{23}(\text{PhC}\equiv\text{C})_9(\text{Ph}_3\text{P})_6](\text{SbF}_6)_2$ (1)

To 2.0 mL CH_2Cl_2 solution containing Ph_3PAuCl (24.7 mg, 0.05 mmol), 0.1 mL of methanol solution of AgSbF_6 (17.2 mg) was added under vigorous stirring, and the solution turned into a suspension immediately. The reaction continued for 15 min at room temperature in air in the dark. The resulting solution was centrifuged for 4 min at 10000 r/min, and the AgCl precipitate was filtered off. The filtrate was evaporated to give $\text{Ph}_3\text{PAuSbF}_6$, which was dissolved in 4.0 mL CH_2Cl_2 . To this solution $\text{PhC}\equiv\text{CAu}$ (29.8 mg, 0.1 mmol) was added, then a freshly prepared solution of NaBH_4 (0.71 mg in 1.0 mL of ethanol) was added dropwise under vigorous stirring. The

solution color changed from orange to pale brown and finally to dark brown. Then the reaction continued for 20 h at room temperature in air in the dark. The mixture was evaporated to dryness to give a dark solid, which was washed with n-hexane (2×5 mL), then dissolved in CH_2Cl_2 (2.2 ml) and centrifuged for 4 min at 10000 r/min. The supernatant solution was subject to the diffusion of ether : n-hexane (v : v = 1 : 1) to afford 6.2 mg of black crystals after two weeks (12.7% yield based on Au).

Anal. UV-Vis-NIR (λ , nm): 273 nm; 380 nm; 525 nm; 600 nm ($E_g = 2.02$ eV). ^{31}P NMR (δ , ppm): 49.17 ppm (external reference 85% H_3PO_4). ESI-MS: m/z: 3506.57, $[\text{Au}_{23}(\text{PhC}\equiv\text{C})_9(\text{Ph}_3\text{P})_6]^{2+}$. TGA: found 67.7% (Calcd 66.8%). XPS (binding energy, eV): Au 4f_{7/2}, 84.4; Au 4f_{5/2}, 88.1.

III. Computational details

Density functional theory (DFT) calculations were performed with the quantum chemistry program Turbomole V6.5.⁴ To save computational time, we replaced Ph on Ph-CC and $(\text{Ph})_3\text{P}$ ligands with H. The def2-SV(P) basis sets were used for C, N, P, H, and Au.⁵ Geometry optimization was done with the functional of Perdew, Burke and Ernzerhof.⁶ Time-dependent DFT calculation of the UV-vis absorption spectra was done at the B3LYP level. All transitions together with their oscillator strengths were then convoluted with a Lorentzian line shape of 0.15 eV broadening to make the whole optical-absorption spectrum.

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IV. Supporting figures

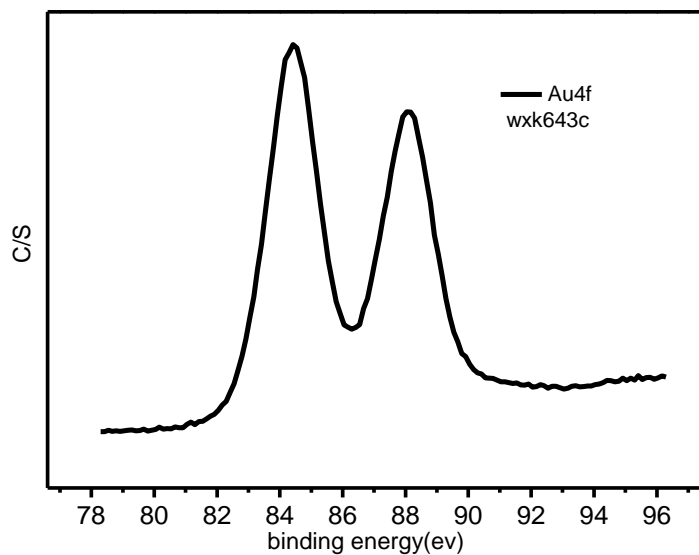


Figure S1. XPS spectrum of $[\text{Au}_{23}(\text{PhC}\equiv\text{C})_9(\text{Ph}_3\text{P})_6] (\text{SbF}_6)_2$. The bonding energy of Au $4f_{7/2}$ was determined to be 84.4 eV.

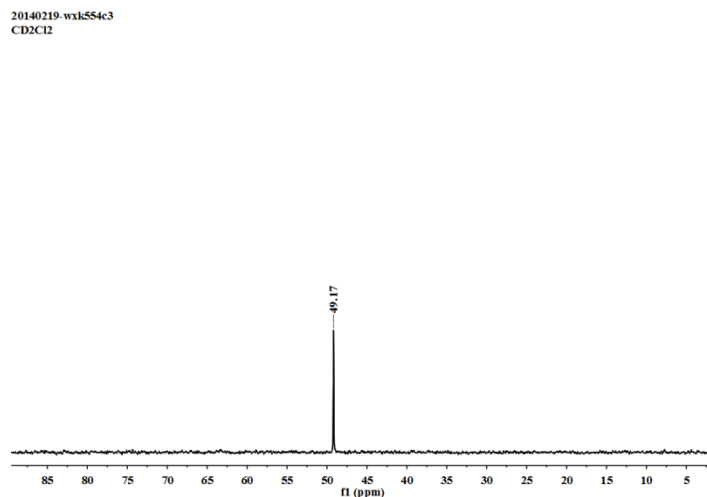


Figure S2. ^{31}P NMR spectrum of $[\text{Au}_{23}(\text{PhC}\equiv\text{C})_9(\text{Ph}_3\text{P})_6] (\text{SbF}_6)_2$ in CD_2Cl_2

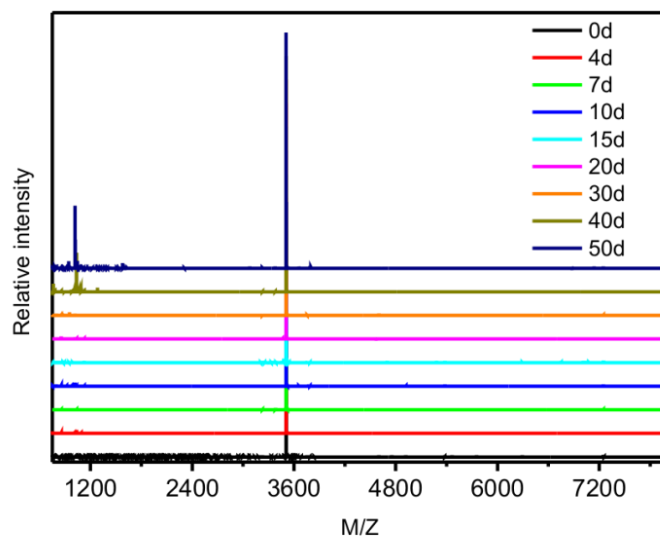


Figure S3. ESI-TOF mass spectra of $[\text{Au}_{23}(\text{PhC}\equiv\text{C})_9(\text{Ph}_3\text{P})_6] (\text{SbF}_6)_2$ measured at different time for stability check (CH_2Cl_2 solution in the absence of light). After about 40 days' storage, simple complex $[\text{PhC}\equiv\text{CAu}_2(\text{PPh}_3)_2]^+$ started to appear as decomposition occurred, indicated by the new peak at $m/z = 1019.15$.

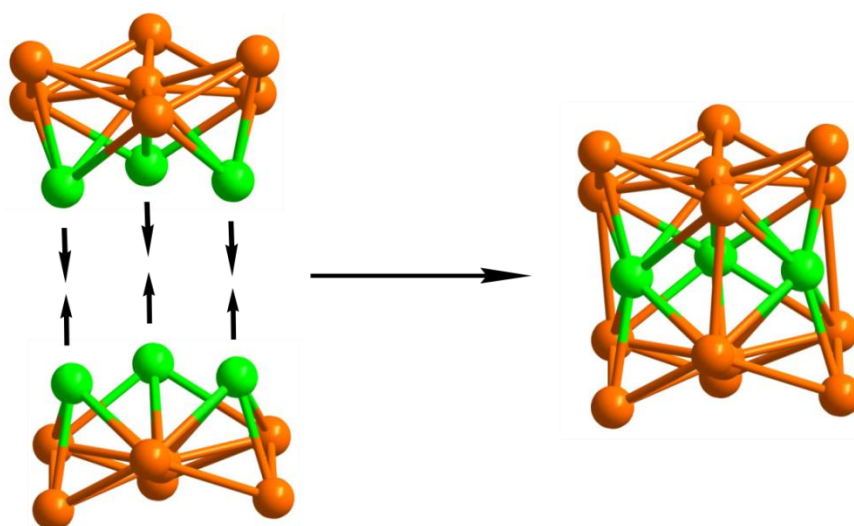


Figure S4. Anatomy of the Au_{17} core structure in Au_{23} (three green atoms denote the shared vertices), showing the fusion of two Au_{10} units.