

Supporting Information for

Unravelling the Formation Mechanism of Alkynyl Protected Gold Clusters: A Case Study of Phenylacetylene Stabilized Au₁₄₄ Molecules

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Experimental section

Physical measurements and instrumentation. The surface chemical compositions and valence states were examined by X-ray photoelectron spectroscopy (XPS, Phi X-tool instrument). Scanning electronic microscopic (SEM) images were collected with a field-emission scanning electron microscope (FESEM, Merlin). UV-visible absorption spectra of clusters, dimer and tetramer were recorded on a Shimadzu 2600/2700 spectrophotometer. The metal-to-organic ratio of the Au clusters was determined by thermogravimetry analysis (TGA) with a METTLER instrument under a N₂ atmosphere. Fourier-transform infrared (FTIR) spectrum was collected from KBr pellets in the range of 4000 - 400 cm⁻¹ with a Nicolet FTIR spectrometer. GC-MS was conducted with an instrument from EWI GC-MS 3200. GC test condition: The GC used manual injection style, with inlet temperature of 280 °C. The ion source temperature was also set at 280 °C. Argon (purity 99.9995%) was used as carrier gas. The gas flow rate through the column was 1 mL·min⁻¹ and the column temperature was held at 280 °C for 30 minutes. The GSV valve was opened for 2 mins. MS test condition: Solvent delay was 4 mins, and scan range was 35-300 amu (atomic mass unit) from 4 to 30 mins.

Electrospray ionization mass spectrometry (ESI-MS). The ESI mass spectra were recorded using a Waters Q-TOF mass spectrometer equipped with a Z-spray source.^{1, 2} The source temperature was kept at 70°C. The cluster sample was directly infused into the chamber at 5 µL/min. The spray voltage and the cone voltage were kept at 2.20 V and 60 V, respectively. The ESI sample was dissolved in dichloromethane (~1 mg/mL). All the mass spectra were obtained with positive ion mode. Calibration was performed using CsI clusters.

X-ray Crystallography. Data collection for (PA)₄ was carried on an Agilent Technologies SuperNova Single Crystal Diffractometer using Cu Kα radiation ($\lambda = 1.54178 \text{ \AA}$) at 100 K. Absorption corrections were applied by using the program CrysAlis (multi-scan).³ The structure was solved by direct methods, and non-hydrogen atoms were refined anisotropically by least-squares on F^2 using the SHELXTL program. C atoms and solvent molecules were refined isotropically due to weak diffraction. The structure was solved and refined using Full-matrix least-squares based on F^2 with program SHELXS-97 and SHELXL-97 within OLEX2.⁴

Materials and reagents. Acetone, ethanol, dichloromethane, Et₃N and n-hexane were purchased from Caiyunfei Chemical Reagents (Tianjin, China). Hydrogen tetrachloroaurate (III) trihydrate (HAuCl₄·3H₂O), 2-thiapropane (Me₂S) and phenylacetylene (PhC≡CH) were acquired from Energy Chemicals (Shanghai, China). Sodium borohydride (NaBH₄) was obtained from Aladdin Industrial Corporation (Shanghai, China). The water was supplied by using a Barnstead Nanopure water system and had a resistivity of 18.3 MΩ cm⁻¹. All chemicals were used as received without further purification.

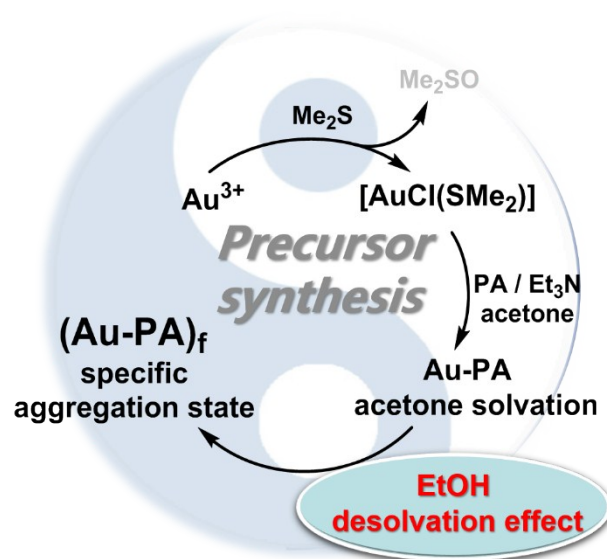
Synthesis of Me₂SAuCl. Me₂SAuCl was synthesized by stirring the mixture of HAuCl₄·3H₂O and SMe₂ in ethanol according to the procedure described by Russell et al.⁵ Briefly, Under Ar, a solution of Me₂S (0.65 mL, 8.82 mmol) in anhydrous ethanol (30 mL) was added directly to HAuCl₄·3H₂O (1.00 g, 2.94 mmol) dissolved in anhydrous ethanol (20 mL) under vigorous stirring (1000 rpm), a white precipitate began to form. Reaction mixture was stirred at room temperature for 2 h until aqueous phase was in colorless. The solution was cooled to 0 °C for 10

min, white precipitate isolated by filtration, washing with cold ethanol (3×10 mL) and dry diethyl ether (3×10 mL). The product was a white solid without drying (yield: 95%).

Caution! Me_2SAuCl was decomposed under the room temperature. However, it could be stored for a long time only in the low temperature ($< 8^\circ\text{C}$) and dry.

Synthesis of the $(\text{Au-PA})_f$ precursor. Low polymeric degree of precursor $(\text{Au-PA})_f$ was prepared according to a reported protocol with some minor modifications.⁶ In a typical synthesis, Me_2SAuCl (120.0 mg, 0.41 mmol) and $\text{PhC}\equiv\text{CH}$ (66.3 μL , 0.61 mmol) was dissolved in acetone (15 mL) under the ultrasound condition at room temperature (160 W, 40 kHz). After 10 min, Et_3N (83.6 μL , 0.61 mmol) was added with vigorous stirring (1000 rpm). Reaction mixture was stirred at room temperature for 1 h in absence of light. After reaction, the volume of the mixture was evaporated to 5 mL and 50 times excess (250 mL) ethanol was added dropwise (at intervals of 30 minutes, divided into four times, proportional 1: 2: 2: 4) with slight stirring (200 rpm) give light-yellow solid (~ 80 mg), which was successively washed with ethanol (2×10 mL), water (2×10 mL) dry diethyl ether (3×10 mL) to remove $\text{PhC}\equiv\text{CH}$ and dimethyl sulfoxide.

Synthesis of $\text{Au}_{144}(\text{PA})_{60}$ clusters. In a typical synthesis, precursor was directly reduced with NaBH_4 . Briefly, $(\text{Au-PA})_f$ (50.00 mg, 0.17 mmol) was dispersed in dichloromethane (20 mL) under the ultrasound condition at room temperature (160 W, 40 kHz). After 10min, a freshly NaBH_4 (0.03 mmol in 1.0 mL of ethanol) was added dropwise (in 10 min) with vigorous stirring (800 rpm). The color changed from yellow to pale brown and finally to dark brown. Reaction mixture was stirred at room temperature overnight in absence of light. After 12 h, excess $\text{PhC}\equiv\text{CH}$ (200 μL) and Et_3N (200 μL) were added to the mixture and the reaction aged for one day under the same ambient conditions. After reaction, the volume of the mixture was evaporated to 4 mL and 50 times excess (200 mL) n-hexane was added to give black solid, which was washed with excess n-hexane and collected by centrifugation. The crude products dissolved in 1 mL of CH_2Cl_2 were pipetted onto ten pieces of a PTLC plate (10 cm by 20 cm), and the separation was conducted in a developing tank (solvent: $\text{CH}_2\text{Cl}_2/\text{n-hexane}/\text{Et}_3\text{N} = 100: 20: 0.72$, volume ratio) for ~ 10 min. Then, the band of $\text{Au}_{144}(\text{PA})_{60}$ in the PTLC plate was cut, and the nanoparticles were extracted with pure CH_2Cl_2 and then dried by rotary evaporation.



Scheme S1. The synthetic route for the (Au-PA)_f precursor from Au³⁺ salt.

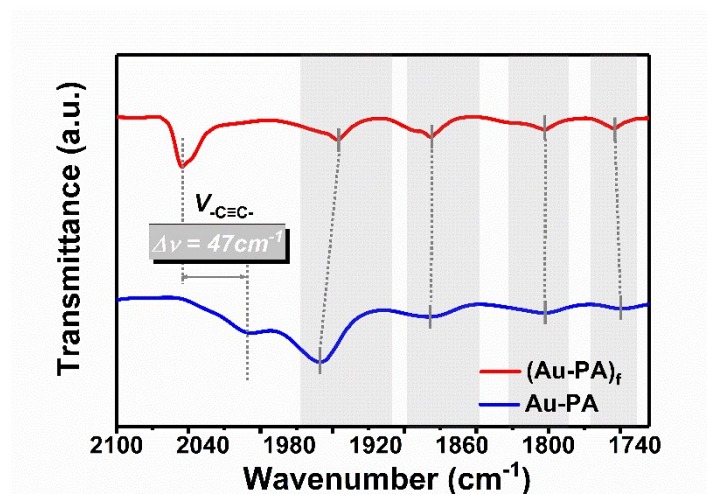


Figure S1. FTIR analyses of two different precursors $(\text{Au-PA})_f$ (this work) and Au-PA (prepared according to the reported method).⁶

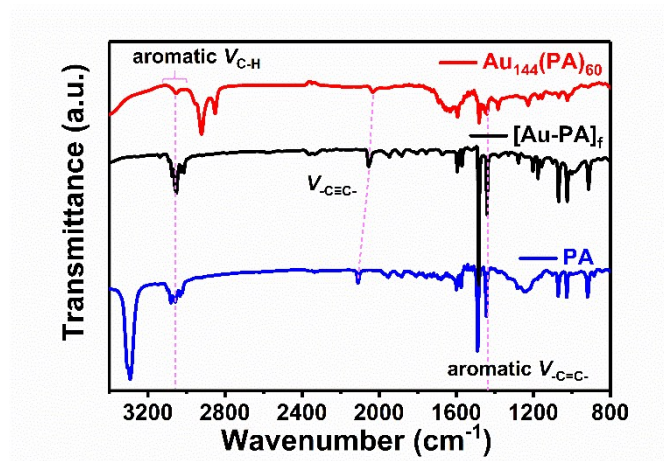


Figure S2. FTIR spectrum, from bottom to top: PA ligand only, the $(\text{Au-PA})_f$ precursor and $\text{Au}_{144}(\text{PA})_{60}$. $V_{\text{C-H}}$ stretching peak ($\sim 3300 \text{ cm}^{-1}$) signal disappears upon the formation of the bonding between carbon and gold in precursor and clusters.

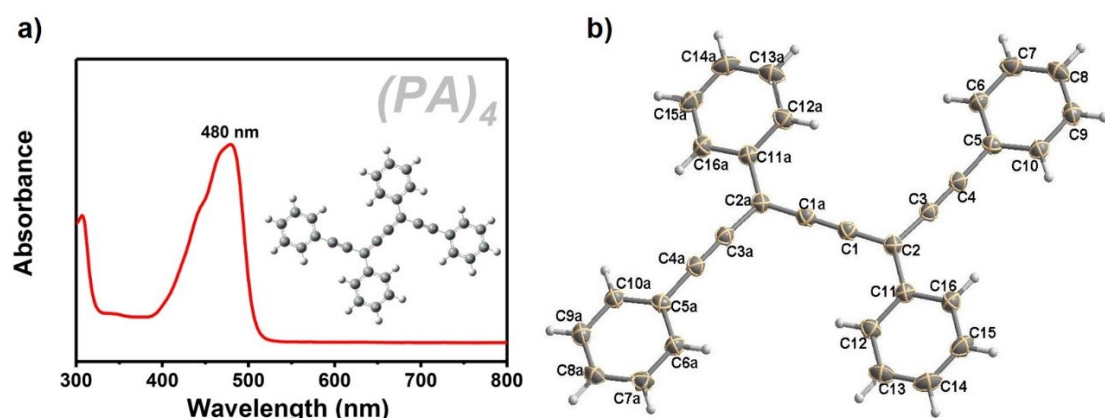


Figure S3. a) Absorbance spectrum of (PA)₄ in CH₂Cl₂. b) Molecular structure of the (PA)₄ tetramer determined by X-ray crystallography.

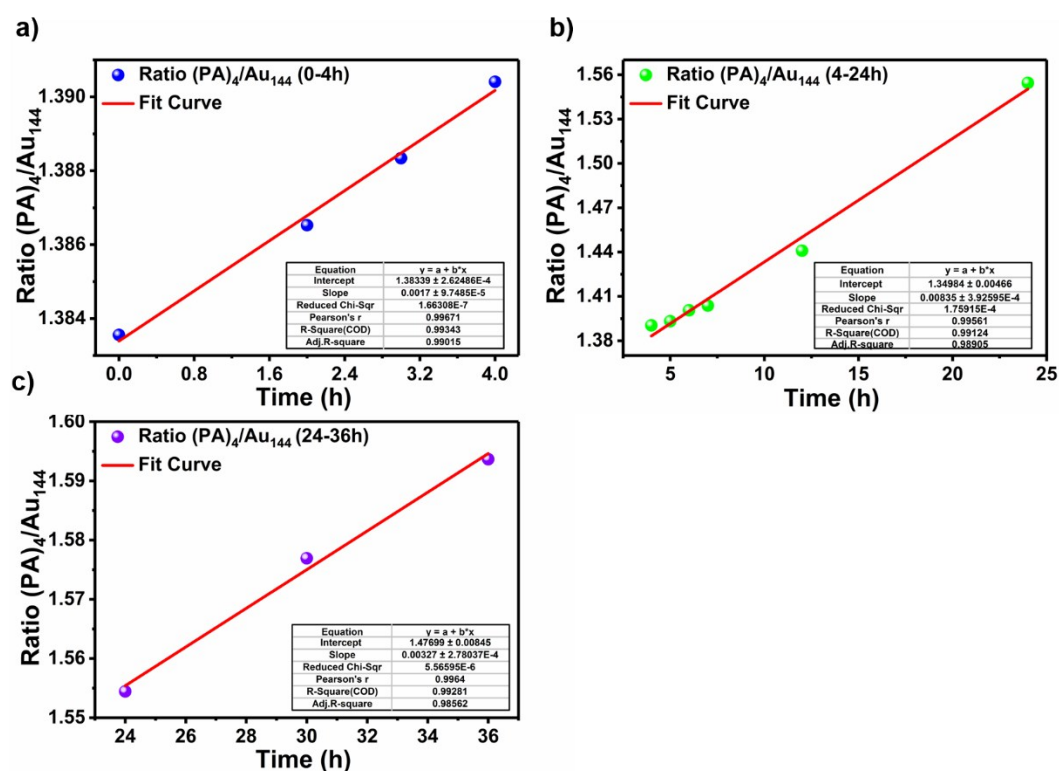


Figure S4. By using the absorbance value (480 nm for (PA)₄, 542 nm for Au₁₄₄) as the metric, the molecular ratio change of (PA)₄-to-Au₁₄₄(PA)₆₀ was qualitatively observed: a) In the first 4 h and its fitting curve; b) In the 4-24 h and its fitting curve and c) In the last 12 h and its fitting curve.

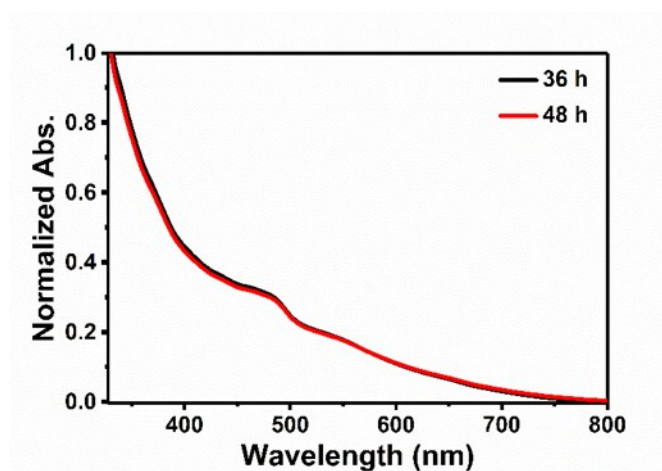


Figure S5. The absorbance of the reaction mixture at 36 h and 48 h. An aliquot of the reaction mixture in methylene chloride phase was diluted to the proper absorbance range for each measurement.

Table S1. The Au/C molar ratio in Au₁₄₄(PA)₆₀ evaluated by XPS analysis.

Samples	Au content by XPS (<i>at. %</i>)	C content by XPS (<i>at. %</i>)	Au: C ratio
Au ₁₄₄ (PA) ₆₀ (Au: C = 1: 3.3)	19.65	65.21	1: 3.3

Table S2. The fitting area of 4f_{7/2} and 4f_{5/2} in Au(I)/Au(0) by XPS analysis.

Samples	Fitting area ratio of Au(I): Au(0)	Atomic ratio of Au(I): Au(0)
Au ₁₄₄ (PA) ₆₀	13125.32: 52320.83	1: 3.9
Au ₁₄₄ (C≡CAr) ₆₀ (Ar= 2-F-C ₆ H ₄ -) ⁷	-	1: 3.8

Table S3. The crystal structure parameter for (PA)₄.

Identification code	(PA) ₄		
Empirical formula	C ₃₂ H ₂₀		
Formula weight	404.48		
Temperature/K	149.99(10)		
Crystal system	monoclinic		
Space group	P2 ₁ /c		
Unit cell dimensions	a = 6.13910(10) Å	α = 90°	
	b = 15.1547(2) Å	β = 94.6300(10)°	
	c = 11.9272(2) Å	γ = 90°	
Volume	1106.04(3) Å ³		
Z	2		
Density (calculated)	1.215 g/cm ³		
Absorption coefficient	0.523mm ⁻¹		
F(000)	424.0		
Crystal size	0.25 × 0.15 × 0.12 mm ³		
Radiation	CuK _α (λ = 1.54184)		
2θ range for data collection	9.456 to 146.176		
Index range	-6 ≤ h ≤ 7, -18 ≤ k ≤ 13, -12 ≤ l ≤ 14		
Reflections collected	4204		
Independent reflections	2164 [R _{int} = 0.0335, R _{sigma} = 0.0377]		
Data / restraints / parameters	2164/0/145		
Goodness-of-fit on F ²	1.040		
Final R indexes [I>=2σ (I)]	R ₁ = 0.0558, wR ₂ = 0.1413		
R indices (all data)	R ₁ = 0.0594, wR ₂ = 0.1479		
Largest diff. peak/hole	0.29/-0.41 e Å ⁻³		

References

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