**Supplementary Information**

# Transition-sized $Au_{92}$ nanoparticle bridging non-fcc-structured gold nanoclusters and fcc-structured gold nanocrystals

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## 1. Experiment section

### 1.1 Materials.

Tetrachloroauric(III) acid ($HAuCl_4 \cdot 4H_2O$, > 99.9 % metals basis,), Tetraoctylammonium bromide (TOAB, ≥ 98.0 %,), 4-tert-Butylbenzenethiol (TBBTH, 99 %, Sigma-Aldrich), Sodium borohydride ($NaBH_4$, 99.8 %, shanghai chemical reagent co., Itd.). Solvents: dichloromethane (DCM), toluene, acetonitrile, petroleum ether and methanol were purchased from Shanghai chemical reagent co., Itd. All chemicals were used as received. The water used in all experiments was ultrapure (resistivity 18.2 MΩ cm), produced by a Milli-Q NANO pure water system.

### 1.2 Synthesis of $Au_{92}(TBBT)_{44}$.

$HAuCl_4 \cdot 4H_2O$ (500 mg, 1.214 mmol) dissolved in 10 mL of water was added to 60 mL of dichloromethane solution containing TOAB (770 mg, 1.408 mmol). The mixture solution was vigorously stirred for ~ 30 min until the phase transfer was completed. The water layer was discarded by using a separatory funnel, and three equivalents of TBBTH (3.642 mmol) was added into the organic layer. 5 mL of aqueous solution containing 230 mg $NaBH_4$ was quickly added to the cooled reaction mixture (0 $^oC$) at once, after continuously stirring for ~ 3 h. The reduction was allowed to proceed overnight. A rotary evaporator was employed to remove the solvent in reduced pressure, and then a large amount of methanol was used to clean the product to remove the excess TBBTH and TOAB. 500 μL of TBBTH was added to the precursor under 65 $^oC$ for subsequent etching. The crude products dissolved in 5 mL of DCM were pipetted onto 20 pieces of PTLC plate (10 × 20 cm), and the separation was conducted in a developing tank (solvent: DCM / petroleum ether = 10 / 35 v / v) for ~ 30 min. A knife was used to cut the band of $Au_{92}(TBBT)_{44}$ in

the PTLC plate, which was extracted by pure DCM. The single crystal of $Au_{92}(TBBT)_{44}$ were formed by vapour diffusion of acetonitrile into the toluene solution of $Au_{92}(TBBT)_{44}$ after approximately 1- 2 day (s).

1.3 Characterizations.

Electrospray ionization (ESI) mass spectra were recorded on a Waters Q-TOF mass spectrometer using a Z-spray source. The sample was firstly dissolved in toluene (~ 0.5 g/L) and then diluted (2 / 1 v / v) with ethanol solution which contains 50 mmol of CsOAc. All UV/vis/NIR adsorption spectra were acquired in the range of 190-900 nm using a UV2550 spectrophotometer. The sample was directly infused into the chamber at 5 μL/min. The source temperature was kept at 70 $^{o}$C, the spray voltage was 2.20 kV and the cone voltage was adjusted at 60 V. Thermal gravimetric analysis (TGA) (~ 3 mg sample used) was conducted in a $N_2$ atmosphere (flow rate ~ 50 mL/min) on a TG/DTA 6300 analyzer (Seiko Instruments, Inc), and the heating rate was 10 $^{o}$C /min. X-ray Photoelectron Spectroscopy (XPS) measurements were conducted on an ESCALAB 250Xi XPS spectrometer (Thermo Scientific, America), using a monochromatized Al Kα source and equipped with an $Ar^+$ ion sputtering gun. All binding energies were calibrated using the C (1s) carbon peak (284.8 eV). The single-crystal X-ray diffraction data were collected on a Bruker D8 VENTURE CMOS photon 100 diffractometer with helios mx multilayer monochromator Cu Kα radiation (λ = 1.54178 Å).

1.4 Electrochemistry.

A conventional three-electrode system was applied for the experiments. Working electrode (WE) was a Pt disk electrode (1 mm diameter). Before the use, WE was firstly polished on emery paper of decreasing grades then with $Al_2O_3$ powders with size down to 50 nm and cleaned electrochemically by potential-cycling in 0.5 M $H_2SO_4$ solution, the electrode was then rinsed thoroughly with ultrapure water (18.2 M). Carbon rods and an SCE (with saturated KCl solution) electrode are employed as a counter electrode (CE) and reference (RE), respectively. The potentials of electrode were controlled by a potentiostat (Zahner, Germany). All of the experiments are carried out at room temperature.

**2. Supporting figures.**

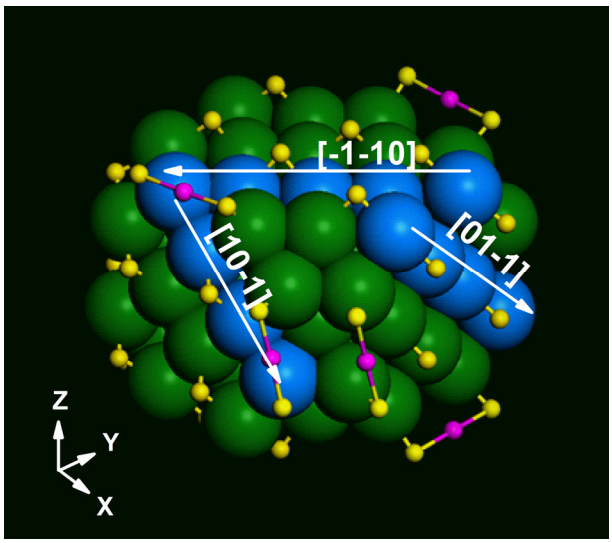


Figure S1. The surface structure of $Au_{92}(TBBT)_{44}$. For clarity, C and H atoms are omitted. Color labels: yellow = S; others = Au.

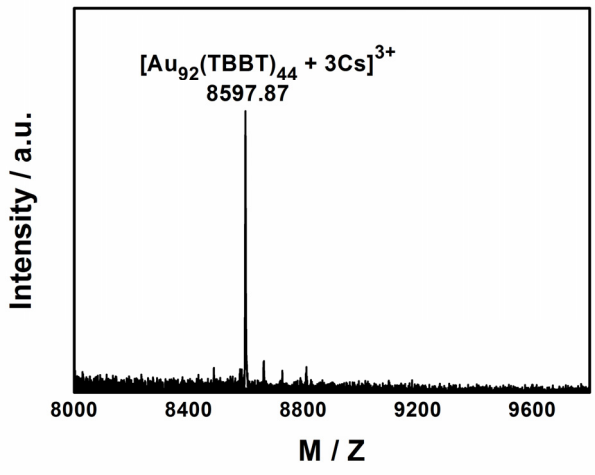


Figure S2. ESI-MS spectrum of $Au_{92}(TBBT)_{44}$.

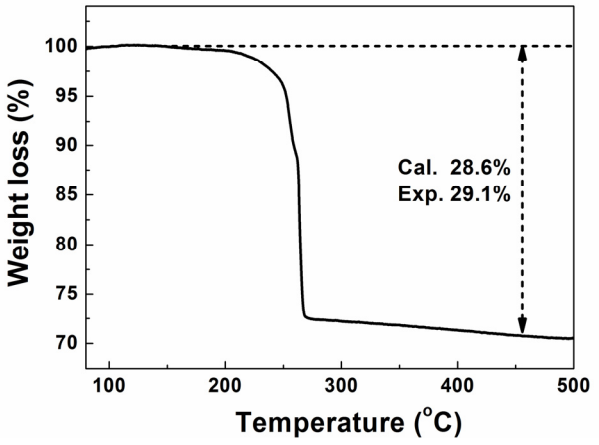


Figure S3. TGA analysis of $Au_{92}(TBBT)_{44}$.

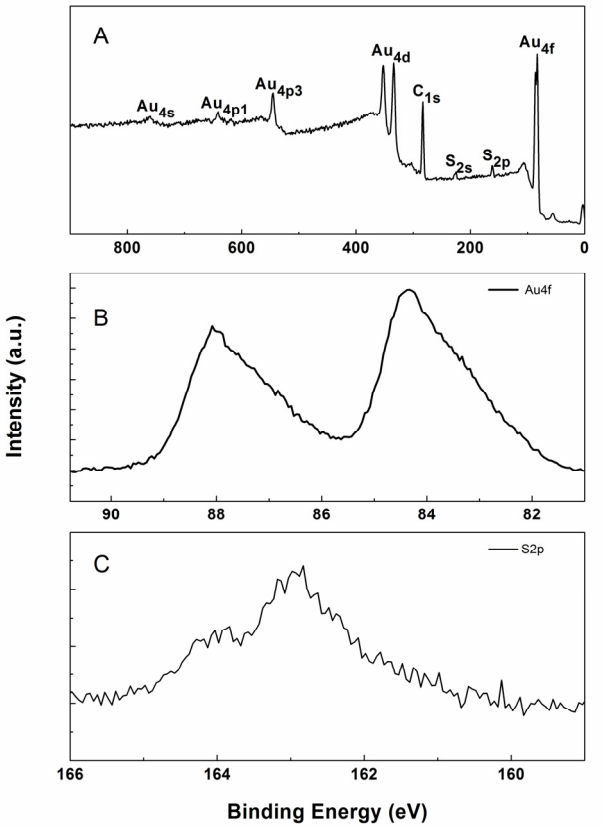


Figure S4. XPS spectra: (A) $Au_{92}(TBBT)_{44}$; (B) Au4f and (C) S2p.

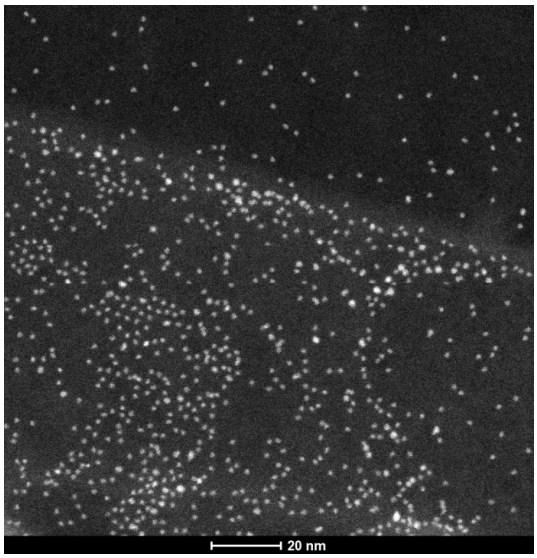


Figure S5. STEM images of $Au_{92}(TBBT)_{44}$ at low magnification (dark field).

### 3. Single crystal data of $Au_{92}(TBBT)_{44}$

Table S1. Crystal data and structure refinement for $Au_{92}(TBBT)_{44}$.

| | | |
|---|---|---|
| Identification code | 4_0m | |
| Empirical formula | C440 H572 Au92 S44 | |
| Formula weight | 25392.50 | |
| Temperature | 173.02 K | |
| Wavelength | 1.54178 Å | |
| Crystal system | Monoclinic | |
| Space group | C 1 2/c 1 | |
| Unit cell dimensions | a = 45.325(2) Å | α= 90°. |
| | b = 28.1243(14) Å | β= 91.544(2)°. |
| | c = 88.076(4) Å | γ = 90°. |
| Volume | 112231(10) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 3.006 $Mg/m^3$ | |
| Absorption coefficient | 45.716 $mm^{-1}$ | |
| F(000) | 89472 | |
| Crystal size | 0.25 x 0.14 x 0.30 $mm^3$ | |
| Theta range for data collection | 2.217 to 63.686°. | |
| Index ranges | -52<=h<=35, -32<=k<=25, -102<=l<=91 | |
| Reflections collected | 315258 | |
| Independent reflections | 89696 [R(int) = 0.0924] | |
| Completeness to theta = 63.686° | 97.1 % | |
| Refinement method | Full-matrix-block least-squares on $F^2$ | |
| Data / restraints / parameters | 89696 / 5433 / 4603 | |
| Goodness-of-fit on $F^2$ | 1.492 | |
| Final R indices [I>2sigma(I)] | R1 = 0.1859, wR2 = 0.4516 | |
| R indices (all data) | R1 = 0.2566, wR2 = 0.4904 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 8.086 and -7.947 $e.Å^{-3}$ | |