Supplementary information

STEM Electron Diffraction and High Resolution Images Used in the Determination of the Crystal Structure of $Au_{144}(SR)_{60}$ Cluster

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1. Experimental section

1.1 Nanocluster synthesis

The nanoclusters were synthesized by using modified Brust method[1] that was reported by Qian *et al.*[2] The pure Au_{144} nanocluster was obtained in two steps. In the first step, polydispersed nanoclusters were obtained. After further etching with excess thiol at 80 ºC purely monodispersed Au_{144} nanoclusters were obtained.

In the first step, tetractylammonium bromide (TOAB, 0.052 M, 10 mL toluene) was mixed with $HAuCl_4.3H_2O$ (0.09 M, 5mL H_2O) in 25 mL RB flask and vigorously stirred for 1 hour until the phase transfer of Au(III) from aqueous phase changed to Au(III) toluene phase. The clear two phase between toluene (deep red) and aqueous (colorless) indicated the complete phase transfer. The aqueous part was removed and the deep red toluene solution was cooled at 0 ºC for 30 minutes. Then 186 μL of $PhCH_2CH_2SH$ was added to the stirred solution of Au(III) and continued stirring for 1 hour. The color changed from deep red to yellow and finally colorless. The $PhCH_2CH_2SH$ capped Au(III) particles were reduced by adding $NaBH_4$ (0.171 gm, 5 mL in water) at once. The quick addition of $NaBH_4$ to the Au(III) solution changed the color to black indicating the formation of the nanoclusters. The reaction was allowed to proceed for 24 hours so that all the excess $NaBH_4$ will be decomposed. The aqueous phase was removed and the black residue with toluene was dried using rotary evaporator. The sample obtained after rotovapping was washed with ethanol and allowed to precipitate in a refrigerator. The washed precipitate was dried in atmosphere and ready for characterization and for etching in the next second step.

In the second step, 0.03 g of the sample obtained from the first step was dissolved in 1.5 mL toluene using a 5 mL vial. 1 mL of $PhCH_2CH_2SH$ was added and the solution continuously stirred for 24 hours at 80 ºC. Then the solution was transferred to the new 25 mL vial, excess methanol was added into it and the particles allowed to precipitate in a refrigerator during 15 hours. The methanol was removed and the precipitate was dissolved in CH_2Cl_2 (DCM). Only the Au_{144} will be soluble in CH_2Cl_2 (brown color) thus separating it from the insoluble byproduct. It was further purified for electron microscopy characterization.

References

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1.2 Sample Characterization

The UV-visible spectra were recorded using a Varian-Cary 5000 spectrophotometer in the double beam mode. Scans were run from 200 to 800 nm at a scan rate of 600 nm/min, a data interval of 1 nm and using a full slit height. All the mass spectra were acquired on a Bruker Ultraflextreme (Bruker Daltonics, Billerica, MA) matrix assisted laser desorption ionization (MALDI) time-of-flight (TOF) mass spectrometer using the linear positive-ion mode. The following instrument source parameters were used: ion source 1 voltage set to 25 KV, ion source 2 voltage set to 23.05 KV, lens voltage set to 6.5 KV and pulsed ion extraction (PIE) set to 300 ns. The matrix suppression cutoff mass was set at 8000 Da. The laser beam focus was set at 35 and 6000 shots were averaged for each spectrum. Mass calibration was done using the Protein 2 Calibration Standard (Bruker Daltonics part no. 207234). We used trans-2-[3-(4-*tert*-

butylphenyl)-2-methly-2-propenylidene malononitrile (DCTB, [300364-84-5], catalog no. 727881, ≥ 98%) as the matrix. MALDI samples were prepared using the mixed drop method using a stainless steel MALDI plate. The matrix was prepared in chloroform at a concentration of 20 mM. 10 µL of the $Au_{144}(SR)_{60}$ cluster solution (either DCM or toluene) was add to 10 µL of the DCTB matrix solution in a small spin tube and mixed thoroughly to generate a 2000:1 ratio between matrix and analyte. The spot was allowed to dry in a vacuum desiccator before loading into the MALDI TOF.

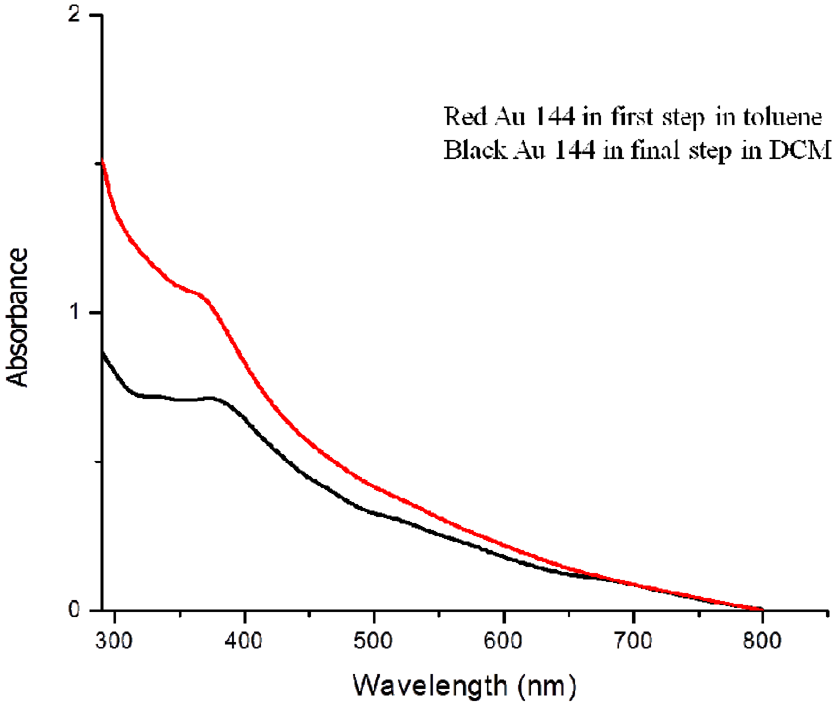

Figure S1. UV/Vis spectrum of Au_{144} nanocluster recorded prior to spotting in MALDI-MS. The red curve in the spectrum corresponds to polydispersed Au_{144} obtained in first step and the black curve represents the pure Au_{144} nanocluster obtained in second step.

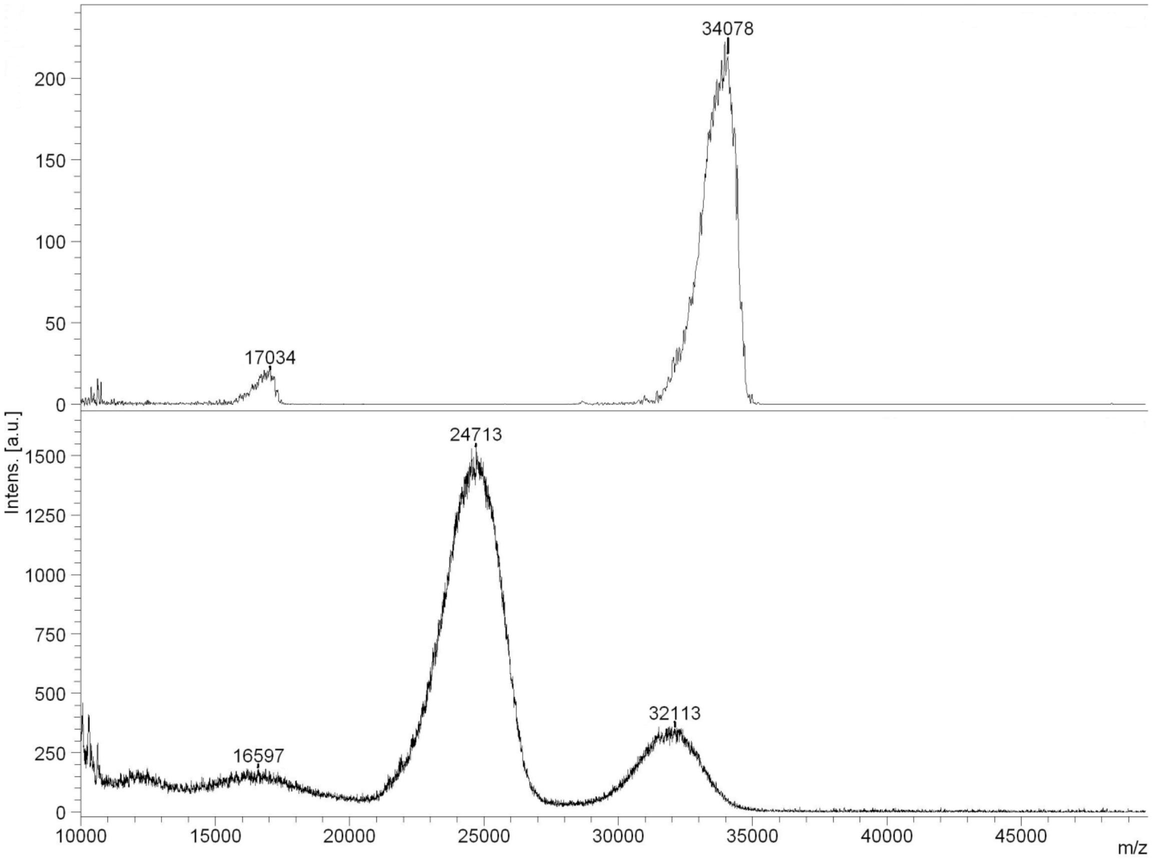

Figure S2. MALDI TOF generated mass spectra of the reaction mixture from the final step which was the clean-up in dichloromethane (top), and from the first step where the reaction mixture was polydispersed in toluene (bottom).

2. Theoretical First-Principle Computational Methods

The construction and optimization of the structure model described above has been achieved through large-scale electronic structure theoretical calculations (based on density-functional theory, DFT), with structural relaxations performed without any constraints. In these calculations we have employed two first-principles DFT-based methods: (1) the ab-initio Born-Oppenheimer molecular dynamics (AIBOMD) method[1], and (2) the VASP, DFT code.[2-4]

(1) The AIBOMD method has been originally formulated[1] for treating finite systems, and it is especially advantageous for treating charged systems, or systems that may develop multipolr moments, since it does not employ a supercell; that is, the ionic system is not periodically replicated and consequently no spurious contributions from image multipole interactions are encountered. In this method the Kohn-Sham equations are solved in conjunction with non-local

norm-conserving soft pseudopotentials[5] (using scalar relativistic ones for the Au atoms), with the valence $5d^{10}$ and $6s^1$ electronic states of the Au atoms, as well as the valence electrons of the S ($3s^2$, $3p^4$), C ($2s^2$,$2p^2$) and hydrogen atoms of the protecting layer, expanded in a plane-wave basis with a 62 Ry kinetic energy cutoff. The Perdew-Burke-Ernzerhof (PBE) functional is employed in the generalized gradient approximation (GGA) to the exchange-correlation corrections.[6] Because of the large number of electrons in the $Au_{144}(SR)_{60}$ Cluster (i.e. 2364) the spin degree of freedom was not explicitly considered. In structural relaxations convergence was achieved when the forces on the ions became smaller than 0.001 eV/Å.

(2) Initial structural relaxations were done with the VASP, DFT code [2-4] in the PW91generalized gradient approximation (GGA)[7]with electron core interactions represented by the projector augmented wave approximation.[4,8] The plane-wave cutoff was set to 400 eV.

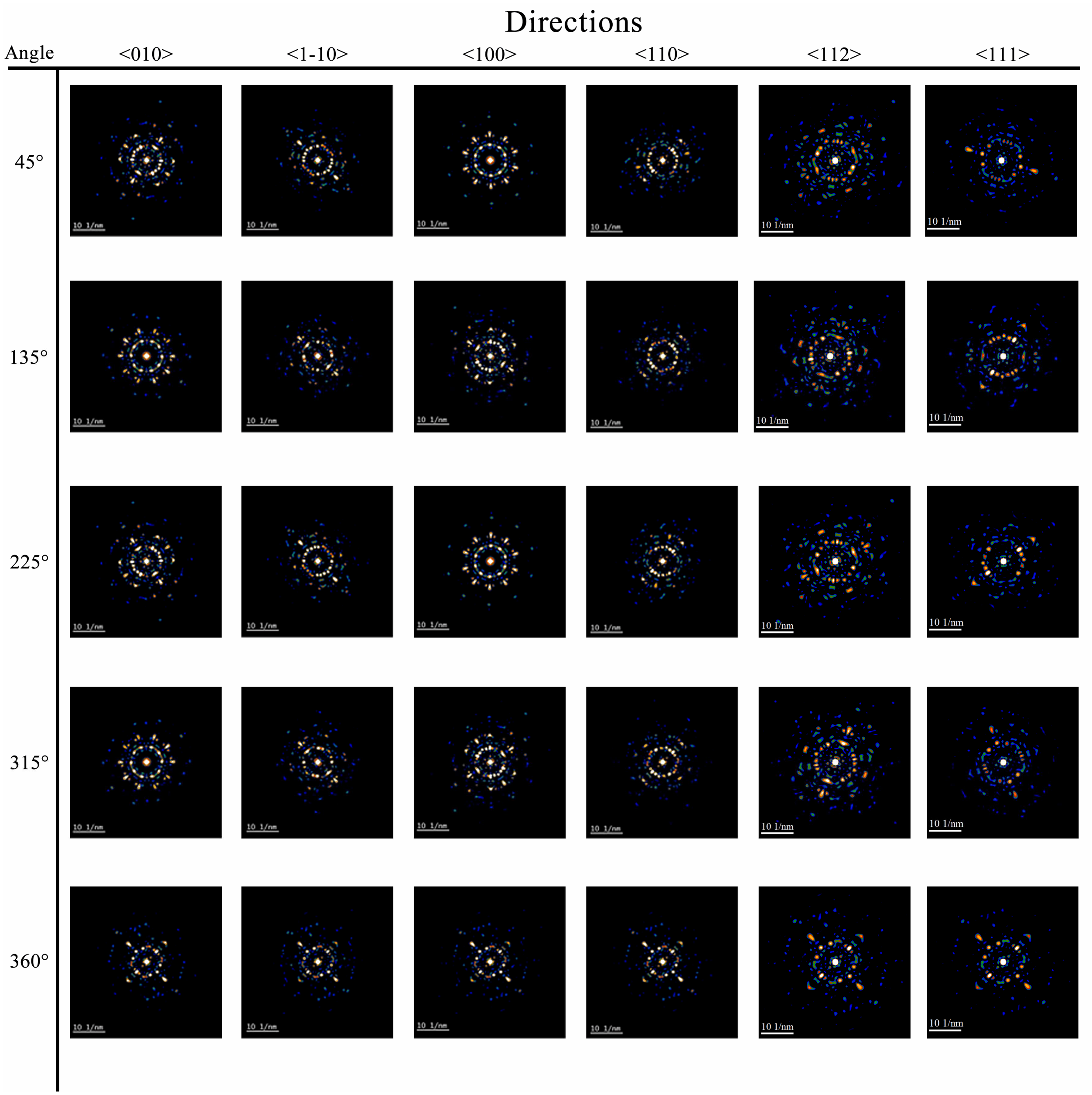

Figure S3. Map of rotations of the simulated electron diffraction patterns obtained from the calculated $Au_{144}(SR)_{60}$ model. Simulated electron diffraction patterns were used to compare with the experimental ones.

Supplementary Movie 1. Experimental NBD pattern. The comparison between experimental and theoretical NBD patterns is shown in Fig. 5 of the main text.

Supplementary Movie 2. Simulated electron diffraction pattern, direction <1-10>.

Supplementary Movie 3. Simulated electron diffraction pattern, direction <100>.

Supplementary Movie 4. Simulated electron diffraction pattern, direction <110>.

Supplementary Movie 5. Simulated electron diffraction pattern, direction <010>.

References

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3. Values of Interatomic Distances (Figure 3(a) in the main text) (distances are given in Å)

The $Au_{144}(SR)_{60}$ cluster can be described in terms of the following regions (see Fig, 1 of the main text, and caption to Fig. 3):
12 Au_{C1}, 42 Au_{C2}, 60 Au_{C3} ǀ 30 Au_{ad}, 60 S
←grand core ǀ protective shell →

In the following we give the (min, average, max) distances for each of the categories of interatomic distances (see Fig. 3a in the main text)
a: Au_{ad}-S_1 bond lengths (60 bonds) (min, average, max) = (2.327, 2.336, 2.344)
b: Au_{C3}-S_1 bond lengths (60 bonds) (min, average, max) = (2.458, 2.468, 2.481)
c_1: Au_{C2}-Au_{C3} bond lengths (shorter 60 bonds) (min, average, max) = (2.817, 2.830, 2.849)
c_2: Au_{C2}-Au_{C3} bond lengths (longer 120 bonds) (min, average, max) = (2.919, 2.940, 2.967)
d: Au_{C1}-Au_{C1} bond lengths (30 bonds) (min, average, max) = (2.829, 2.837, 2.843)
e: Au_{C1}-Au_{C2} bond lengths (12+30×2=72 bonds) (min, average, max) = (2.932, 2.953, 2.990)
f: Au_{C3}-Au_{C3} bond lengths (triangles) (60 bonds) (min, average, max) = (2.944, 2.959, 2.977)
g: Au_{C2}-Au_{C2} bond lengths (120 bonds) (min, average, max) = (2.968, 3.000, 3.037)
h_1: Au_{C3}-Au_{ad} bond lengths (60 shorter bonds) (min, average, max) = (3.043, 3.068, 3.092)
h_2: Au_{C3}-Au_{ad} bond lengths (60 longer bonds) (min, average, max) = (3.213, 3.260, 3.297)
i: Au_{C3}-Au_{C3} bond lengths (pentagons) (60 bonds) (min, average, max) = (3.278, 3.314, 3.377)