1. Experimental Section

1.1 Chemicals

Tetrachloroauroic(III) acid (HAuCl₄·3H₂O, 99.99%, Aldrich), 2-Phenylethanethiol (PhC₂H₄SH, 99%, Aldrich), Glutathione (G-SH, 98%, Acros Organics), Sodium borohydride (NaBH₄, 99.99%, Aldrich), Acetone (HPLC grade, 99.9%, Aldrich), Toluene (HPLC grade, 99.9%, Aldrich), Ethanol (HPLC grade, Aldrich), Methanol (HPLC grade, 99%, Aldrich), and Dichloromethane (HPLC grade, 99.9%, Aldrich) were used as received.

1.2 Synthesis of crude Auₙ(SC₂H₄Ph)ₘ clusters

Crude Auₙ(SC₂H₄Ph)ₘ clusters containing Au₃₈(SC₂H₄Ph)₂₄, Au₄₀(SC₂H₄Ph)₂₄ and core mass ~12 kDa Au clusters were prepared by a modified earlier procedure (see Qian et al, ACS Nano, 2009, 3, 3795-3803). In the first step, Auₙ(SC₂H₄Ph)ₘ mixture with ᶡ ranging from ~38 to ~102 were synthesize by reducing Au(I)-SG in acetone solution. In a typical reaction, HAuCl₄·3H₂O (0.199 g, 0.5 mmol) and GSH (0.614g, 2.0 mmol) were dissolved in 20 mL acetone at room temperature; the solution was vigorously stirred for ~20 min. The yellow cloudy suspension was then cooled to ~0 °C in an ice bath over ~20 min. A solution of NaBH₄ (0.19 g, 5 mmol, dissolved in 6 mL cold Nanopure water) was rapidly added to the suspension under vigorous stirring. The color of the solution immediately turned black, indicating the formation of Au nanoclusters. The reaction was allowed to continue for ~20 min. The black Auₙ(SG)ₘ nanoclusters precipitated out of acetone solution and deposited onto the inner wall of the flask. The clear acetone solution was decanted, and 6 mL water was added to dissolve the Auₙ(SG)ₘ clusters.

In the second step, Auₙ(SG)ₘ clusters were reacted with excess PhC₂H₄SH at 80 °C, during which ligand exchange and core etching occurred. Crude Auₙ(SC₂H₄Ph)ₘ clusters containing Au₃₈(SC₂H₄Ph)₂₄, Au₄₀(SC₂H₄Ph)₂₄ and core mass ~12 kDa Au clusters were obtained after ~12 hrs of reaction. In a typical experiment, the Auₙ(SG)ₘ clusters obtained from step 1 were dissolved in 6 mL Nanopure water and then mixed with 0.3 mL ethanol, 2 mL toluene and 2 mL PhC₂H₄SH (note: ethanol was added to facilitate the phase transfer of Auₙ(SG)ₘ from water to organic phase). Under air atmosphere, the diphase solution was heated to 80 °C. The Auₙ(SG)ₘ clusters were transferred from the water phase to the organic phase in less than 10 min. The thermal process was continued for ~12 hrs at 80 °C. Due to the particular stability of Au₃₈(SC₂H₄Ph)₂₄, Au₄₀(SC₂H₄Ph)₂₄ and the ~12 kDa clusters, these clusters were enriched in the final sample. Then, the organic phase was thoroughly washed with ethanol (or methanol) to remove excess thiol. The mixture of Au₃₈(SC₂H₄Ph)₂₄, Au₄₀(SC₂H₄Ph)₂₄ and the ~12 kDa clusters were separated from Au(I)-SR side product by extraction with CH₂Cl₂ (or toluene) (note: Au(I)SR is poorly soluble...
in almost all solvents). The black CH$_2$Cl$_2$ (or toluene) solution was dried by rotary evaporation, which contains mixed clusters of Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$, Au$_{40}$SC$_2$H$_4$Ph)$_{24}$ and the ~12 kDa clusters.

1.3 Isolation of Au$_{55}$(SC$_2$H$_4$Ph)$_{31}$ through size exclusion chromatography

The Au$_{55}$(SC$_2$H$_4$Ph)$_{31}$ clusters were isolated by size exclusion chromatography (SEC) using a PLgel column (particle size: 3 μm, pore diameter: 100 Å). SEC was conducted on a HP Agilent 1100 HPLC system equipped with a diode array detector (DAD). The UV-vis spectra (190 to 950 nm range) of the eluate were online recorded by a diode array detector (DAD). The mobile phase was CH$_2$Cl$_2$ at a flow rate of 0.5 mL/min. The collection time for Au$_{55}$(SC$_2$H$_4$Ph)$_{31}$ clusters was 13.7-14.0 min.

1.4 Characterization

Matrix-assisted laser desorption ionization (MALDI) mass spectrometry was performed with a PerSeptiveBiosystems Voyager DE super-STR time-of-flight (TOF) mass spectrometer. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenyldidene] malononitrile (DCTB) was used as the matrix for MALDI. 1 mg matrix and 0.1 mg analyte stock solution were mixed in 100 μL CH$_2$Cl$_2$. 10 μL solution was applied to the steel plate and then air-dried. All MALDI-MS data were collected under negative ion mode. UV-vis spectra of the Au clusters (CH$_2$Cl$_2$ as solvent) were recorded on a Hewlett-Packard (HP) Agilent 8453 diode array spectrophotometer. Electrospray ionization (ESI) mass spectra were recorded using a Waters Q-TOF mass spectrometer equipped with Z-spray source. The source temperature was kept at 70 °C. The sample was directly infused into the chamber at 5 μL/min. The spray voltage was kept at 2.20 kV and the cone voltage at 60 V. The ESI sample was dissolved in toluene (1 mg/mL) and diluted (1:2 v) by a dry methanol solution containing 50 mM CsOAc (to enhance cluster ionization in ESI).

2. Supporting Figures:

![Figure S1. MALDI-MS of the 12 hrs etched crude product. Note that the ~40 hr product will be pure Au$_{38}$(SR)$_{24}$.](image-url)
Figure S2. UV-Vis spectra of the eluted clusters for (A) 13.7-14.0 min, (B) 14.0-14.3 min, and (C) 14.3-15.0 min.

Figure S3. The fragmentation patterns of $\text{Au}_{55}(\text{SC}_2\text{H}_4\text{Ph})_{31}$ (top) and $\text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24}$ (bottom) in MALDI-MS.
Figure S4. (A) The core mass of the SEC isolated clusters determined by MALDI-MS at high laser intensity. (B) Powder XRD pattern of the clusters.