Electronic Supplementary Information

Synthesis of Au₄₄(SR)₂₈ nanocluster, structure prediction and evolution from Au₂₈(SR)₂₀, Au₃₆(SR)₂₄ to Au₄₄(SR)₂₈

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1. Experimental

Chemicals. Tetrachloroauric(III) acid (HAuCl₄·3H₂O, >99.99% metals basis, Aldrich), Tetraoctylammonium bromide (TOAB, \geq 98%, Fluka), 4-*tert*-butylbenzenethiol (TBBT, 97%, Alfa Aesar), thiophenol (HSPh, 97%, Aldrich), Sodium borohydride (NaBH₄, Aldrich). Solvents: Ethyl acetate (HPLC grade, \geq 99.9%, Aldrich), Toluene (HPLC grade, \geq 99.9%, Aldrich), Methanol (HPLC grade, \geq 99.9%, Aldrich), Ethanol (absolute, 200 proof, Pharmco), Dichloromethane (DCM, HPLC grade, \geq 99.9%, Aldrich). All chemicals were used as received.

Synthesis of Au₄₄(SR)₂₈

Au₄₄(SPh-*t*-Bu)₂₈: HAuCl₄ (0.034g, 0.09 mmol) and TOAB (0.0535g, 0.10 mmol) were dissolved in 5ml ethyl acetate and stirred for 4 hr. 70 μ l (4.2 mmol) of TBBT was added to the solution, and the solution was further stirred overnight, over which the originally reddish solution turned colorless. Then, NaBH₄ (0.033g, 0.9 mmol) was dissolved in 2 ml cold Nanopure water (18.2 MΩ·cm) and the NaBH₄ solution was rapidly poured *all at once* to the colorless gold salt solution. The solution color turned black immediately. The reaction was further continued for 24hr under stirring. After that, the solvent was dried by rotary evaporation, and the residual solid was washed with methanol for three times, and further extracted with DCM. The asobtained gold nanoclusters were then subjected to solvent fractionation by diffusion of methanol into the toluene solution of the clusters. After one month, dark precipitate was obtained (yield: ~5%, Au atom basis). The solid was separated from the supernatant and subjected to further characterization.

Au₄₄(SPh)₂₈: HAuCl₄ (0.18 mmol, dissolved in 10 mL water) and TOAB (0.21 mmol, dissolved in 10 mL toluene) were combined in a tri-neck round bottom flask. The solution was vigorously stirred to facilitate phase transfer. After 10 min, phase transfer was completed, the aqueous layer was then removed, and the organic layer was washed with 10 mL water. The toluene solution of Au(III) was cooled to 0 °C in an ice bath for about 15 min. After that, stirring was reduced to a very low speed (50 rpm), thiophenol (PhSH, 5 equivalents per mole of gold) was added, with the solution color slowly changed from deep red to clear. The solution was kept still overnight. 1 ml of aqueous solution of NaBH₄ (2 equivalents per gold) was slowly added to the solution in a dropwise fashion within 15 min with the reaction mixture under stirring at 600 rpm. After NaBH₄ addition, and the reaction was allowed to proceed for one day. The organic phase was removed and methanol was used to separate the Au nanoclusters from TOAB and other side products, and then extracted with acetone.

Characterization

Electrospray ionization (ESI) mass spectrometry was performed on a Waters Q-TOF mass spectrometer equipped with Z-spray source. The sample was dissolved in toluene (~0.5 mg/ml) and diluted (2:1v) by dry ethanol (containing 50 mM CsOAc to impart charge to the nanoclusters through the formation of Cs⁺ adducts). The sample was directly infused into the chamber at 5 μ L/min. The source temperature was kept at 70 °C. The spray voltage was kept at 2.20kV and the cone voltage at 60 V. Matrix-assisted laser desorption ionization (MALDI) mass spectrometry was performed with a PerSeptive-Biosystems Voyager DE super-STR time-of-flight (TOF) mass spectrometer. Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenyldidene] malononitrile (DCTB, ref: A. C. Dharmaratne, T. Krick and A. Dass, *J. Am. Chem. Soc.*, 2009, **131**, 13604–13605) was used as the matrix. Typically, 0.5 mg of matrix and 0.05 mg of sample stock solution were mixed in 50 μ L of CH₂Cl₂. A 10 μ L portion of solution was applied to the steel plate and air-dried. UVvis absorption spectrum of the sample (dissolved in CH₂Cl₂) was measured on a Hewlett-Packard (HP) Agilent 8453 diode array spectrophotometer at room temperature.

2. Supporting Figures



Figure S1. Crystal structures of $Au_{28}(SR)_{20}$ (left) and $Au_{36}(SR)_{24}$ (right). The carbon tail (-R) in the thiolate was omitted for clarity.

n (Au)	m (SR)	Mw cal.	Deviation	n (Au)	m (SR)	Mw cal.	Deviation
31	43	13212.37	-81.33	31	44	13377.64	83.94
32	42	13244.06	-49.64	32	43	13409.33	115.63
33	41	13275.75	-17.95	33	42	13441.02	147.32
34	39	13142.17	-151.53	34	40	13307.44	13.74
35	38	13173.86	-119.84	35	39	13339.13	45.43
36	37	13205.55	-88.15	36	38	13370.82	77.12
37	36	13237.24	-56.46	37	37	13402.51	108.81
38	35	13268.93	-24.77	38	36	13434.20	140.50
39	33	13135.35	-158.35	39	34	13300.62	6.92
40	32	13167.04	-126.66	40	33	13332.31	38.61
41	31	13198.73	-94.97	41	32	13364.00	70.30
42	30	13230.42	-63.28	42	31	13395.69	101.99
43	29	13262.11	-31.59	43	30	13427.38	133.68
44	28	13293.80	0.10	44	29	13459.07	165.37
45	26	13160.22	-133.48	45	27	13325.49	31.79
46	25	13191.91	-101.79	46	26	13357.18	63.48
47	24	13223.60	-70.10	47	25	13388.87	95.17
48	23	13255.29	-38.41	48	24	13420.56	126.86
49	22	13286.98	-6.72	49	23	13452.25	158.55
50	20	13153.40	-140.30	50	21	13318.67	24.97

Table S1. Mass calculation of $Au_n(TBBT)_m$ with candidate *n* and *m* values (exp. MW=13293.7 based on ESI-MS).



Figure S2. MALDI-MS spectrum of $Au_{44}(TBBT)_{28}$ nanocluster. No intact molecular ion peak was observed in MALDI; instead, many fragmentation peaks were observed. The two most distinct fragmentation peaks correspond to $Au_{40}(TBBT)_{23}$ and $Au_{44}(TBBT)_{25}$ and the highest-mass fragmentation peak (weak) is $Au_{44}(TBBT)_{27}$. Inset is the zoom-in spectrum. Losing one TBBT thiolate ligand is similar to the case of $Au_{36}(TBBT)_{24}$ and $Au_{28}(TBBT)_{20}$. Small amounts of $Au_{36}(TBBT)_{24}$ and $Au_{28}(TBBT)_{20}$ were found to coexist with $Au_{44}(TBBT)_{28}$.

Assignment	Experimental Mass	Calculated Mass	Derivation
Au ₄₄ (SPh-t-Bu) ₂₇	13126	13123	3
Au ₄₄ (SPh-t-Bu) ₂₅	12811	12793	18
Au ₄₄ (SPh-t-Bu) ₂₄	12645	12628	17
Au ₄₀ (SPh-t-Bu) ₂₃	11688	11675	13
Au ₄₀ (SPh-t-Bu) ₂₂	11519	11510	9
Au ₃₆ (SPh-t-Bu) ₂₃	10888	10887	1
Au ₃₆ (SPh-t-Bu) ₂₁	10569	10557	12
Au ₃₂ (SPh-t-Bu) ₁₉	9450	9439	11
$Au_{28}(SPh-t-Bu)_{19}$	8653	8651	2

Table S2. Assignments of peaks in MALDI-MS spectrum.



Figure S3. Observation of Au₄₄(SPh)₂₈ nanoclusters in the ESI-MS spectrum.



Figure S4. Crystal structures (left) and model illustrations (right) of the position of the dimeric staples (-SR-Au-SR-Au-SR-, green color) on the kernel: (A) $Au_{28}(SR)_{20}$; (B) $Au_{36}(SR)_{24}$. On the top of each blue diamond on the surface of the kernel is a dimeric staple. The carbon tail (-R) in the thiolate was omitted for clarity.



Figure S5. Crystal structures and model illustrations of the position of plain bridging thiolates (-SR-, yellow) in (A) Au₂₈(SR)₂₀ and (B) Au₃₆(SR)₂₄. On the top of each green line in the model kernel is a bridging thiolate. The carbon tail (-R) in the thiolate was omitted for clarity.