Supporting Information

Energy Gap Law for Exciton Dynamics in Gold Cluster Molecules

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1. Syntheses and Characterizations of Gold Clusters

Chemicals. Hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O, reagent grade), 1hexanethiol (HSC₆H₁₃, 98%), L-glutathione reduced (GS, >99%), tetraoctylammonium bromide (Oct₄NBr, 98%), sodium borohydride (NaBH₄, 99%), and tetrabutylammonim hexafluorophosphate (Bu₄NPF₆, >99%) were purchased from Aldrich. Extrapure grade toluene, acetone, absolute ethanol, methanol, acetonitrile, dichloromethane, and tetrahydrofuran (THF) were used. Water was purified using a Millipore Milli-Q system (18.2 M Ω ·cm). All the chemicals were used as received without further purification.

Synthesis of Au₂₅(SC₆H₁₃)₁₈. Au₂₅(SC₆H₁₃)₁₈ was synthesized according to the method reported elsewhere.^{S1} HAuCl₄·3H₂O (0.196 g, 0.50 mmol) and Oct₄NBr (0.317 g, 0.58 mmol) were dissolved in 15 mL of THF in a 100 mL vial. After being vigorously stirred for 15 min, the solution color changed from orange to red. Then, 1-hexanethiol (0.320 mL, 2.5 mmol) was slowly added to the above solution and stirring was continued for 60 min until the red solution turned colorless. To the above solution, NaBH₄ (0.190 g, 5.0 mmol) dissolved in 5 mL of cold water was added all at once. The reaction generated some bubbles and the solution turned black, indicating the formation of gold clusters. After being stirred for additional 5 h, the aqueous phase was decanted and the remaining organic phase was washed

with fresh water. The product solution was transferred to a 250 mL round-bottom flask and rotary evaporated. The resulting oil-like product was washed with ethanol and then collected by centrifugation. This process was repeated at least 10 times to completely remove reaction impurities. Au₂₅(SC₆H₁₃)₁₈ clusters were then extracted from the cluster product with 1:1 (v/v) acetone/acetonitrile mixture repeatedly, providing a total yield of ~100 mg.

Synthesis of Au₃₈(SC₆H₁₃)₂₄. Au₃₈(SC₆H₁₃)₂₄ was synthesized following a literature method^{S2} with some modifications. L-Glutathione (0.615 g, 2 mmol) was dissolved and stirred in 16 mL of water. HAuCl₄·3H₂O (0.197 g, 0.5 mmol) in 20 mL of methanol was added to the above solution and stirring was continued for 20 min until the solution turned white. The mixture was then cooled to 0 °C in an ice bath. After additional 20 min, NaBH₄ (0.1892 g, 5 mmol) dissolved in 10 mL of cold water was rapidly added to the suspension at 0 °C under vigorous stirring. The color of the solution immediately turned dark brown after addition of NaBH₄, indicating the formation of glutathione-stabilized gold clusters (Au_n(GS)_m). After additional stirring of 30 min, the product solution was transferred to a 250 mL round-bottom flask and rotary evaporated. The dark brown product was washed with methanol and then collected by centrifugation. This process was repeated at least 10 times to completely remove reaction impurities. The product was then dissolved in 6 mL of water and transferred to a 50 mL round-bottom flask. The solution of Au_n(GS)_m was mixed with 0.3 mL of ethanol, 2 mL of toluene, and 2 mL of 1-hexanethiol. Ethanol was added to prompt the phase transfer of Au_n(GS)_m from water to organic phase. The two-phase solution was heated and maintained at 80 °C under air atmosphere. The Au_n(GS)_m clusters were found to transfer from the water phase to the organic phase in less than 10 min. The thermal process was allowed to continue for 45 h at 80 °C. Over the long period of the etching process, the initial Au_n(GS)_m clusters were converted to hexanethiol-stabilized gold clusters. After being stirred for additional 3 h at room temperature, the aqueous phase was decanted and the remaining organic phase was thoroughly washed with ethanol and acetonitrile to remove excess thiol. The product solution was transferred to a 250 mL round-bottom flask and rotary evaporated. Then Au₃₈(SC₆H₁₃)₁₈ clusters were first separated from larger gold clusters by extraction with acetone, and collected by rotary evaporation. Highly pure Au₃₈(SC₆H₁₃)₂₄ clusters were then extracted from the cluster product with 2:1 (v/v) acetonitrile/dichloromethane mixture repeatedly, providing a total yield of ~30 mg.

Synthesis of $Au_{67}(SC_6H_{13})_{35}$. $Au_{67}(SC_6H_{13})_{35}$ was synthesized according to the reported procedure^{S3} with some modifications. In a 100 mL vial, HAuCl₄·3H₂O (0.512 g, 1.3 mmol) was dissolved in 50 ml THF and cooled to 0 °C in an ice bath for 30 min. After being vigorously stirred for 10 min, 1-hexanethiol (0.832 mL, 6.5 mmol) was slowly added to the vial at 0 °C without changing the stirring speed. Stirring was continued for 36 h at 0 °C until the yellow solution turned colorless. To the above solution, NaBH₄ (0.568 g, 15 mmol) dissolved in 10 mL of cold water was added all at once. The reaction generated some bubbles

and the solution turned black, indicating the formation of gold clusters. After being stirred for additional 30 min, the aqueous phase was decanted and the remaining organic phase was washed with copious amounts of fresh water. The product solution was subsequently rotary evaporated. The resulting oil-like product was thoroughly washed with ethanol and then collected by centrifugation. This process was repeated at least 10 times to completely remove reaction impurities. A mixture of Au₂₅(SC₆H₁₃)₁₈ and Au₆₇(SC₆H₁₃)₃₅ clusters were then obtained from repeating extractions with acetone, and collected by rotary evaporation. The subsequently washed with copious amounts of 10:5 mixture was (v/v)acetonitrile/dichloromethane mixture to remove Au₂₅(SC₆H₁₃)₁₈ clusters. Au₆₇(SC₆H₁₃)₃₅ clusters were then extracted with 10.7 (v/v) acetonitrile/dichloromethane mixture repeatedly, providing a total yield of ~30 mg.

Synthesis of $Au_{102}(SC_6H_{13})_{44}$ and $Au_{144}(SC_6H_{13})_{60}$. $Au_{144}(SC_6H_{13})_{60}$ was synthesized according to the one-phase procedure^{S4} with some modifications. Typically, HAuCl₄·3H₂O (0.24 g, 0.60 mmol) and Oct₄NBr (0.38 g, 0.70 mmol) were dissolved in 30 mL of methanol in a 100 mL vial. After being vigorously stirred for 15 min, the solution color changed from yellow to dark red. 1-hexanethiol (0.320 mL, 2.5 mmol) was then slowly added to the solution at room temperature and stirring was continued until the solution turned white. After 60 min, NaBH₄ (0.23 g, 6.0 mmol) dissolved in 12 mL of cold water was rapidly added to the solution under vigorous stirring. The color of solution immediately turned dark brown and produced gold clusters, which were subsequently precipitated out of the methanol solution. The reaction was stopped after 5 h, and the black brown precipitates were collected by centrifugation. The precipitates were washed with excess ethanol and collected by centrifugation again. This step was repeated at least 10 times to completely remove the free thiol residue. Small-sized clusters were then extracted using acetone, and collected by rotary evaporation. The extracted clusters contained $Au_{25}(SC_6H_{13})_{18}$, $Au_{38}(SC_6H_{13})_{24}$ and $Au_{67}(SC_6H_{13})_{35}$ clusters, which were removed by washing with copious amounts of 10:8 (v/v) acetonitrile/dichloromethane mixture. Au₁₄₄(SC₆H₁₃)₆₀ clusters were then extracted from the remaining clusters with 10:13 (v/v) acetonitrile/dichloromethane mixture repeatedly, providing a total yield of ~50 mg. Au₁₀₂(SC₆H₁₃)₄₄ was synthesized similarly except for conducting synthesis under the inert atmosphere.⁸⁵

Synthesis of Au₃₃₃(SC₆H₁₃)₇₉. Au₃₃₃(SC₆H₁₃)₇₉ was synthesized according to the reported method^{S6} with some modifications. Typically, HAuCl₄·3H₂O (0.138 g, 0.35 mmol) was dissolved in 5 mL of water, and Oct₄NBr (0.222 g, 0.41 mmol) was dissolved in 10 mL of toluene. The two solutions were combined in a 100 mL vial and the mixture was vigorously stirred until the aqueous phase turned colorless and the toluene solution became dark red. The clear aqueous phase was decanted and the remaining organic phase was washed with fresh water. Then, 1-hexanethiol (0.095 mL, 0.7 mmol) was added while the reaction mixture was under vigorous stirring at room temperature. The dark red solution gradually turned yellow

and finally nearly clear in about 15 min. NaBH₄ (0.133 g, 3.5 mmol) dissolved in 6 mL of cold water was then rapidly added to the solution all at once. The solution turned black immediately, indicating the formation of gold clusters. The solution was stirred for 8 h at room temperature. After decanting the aqueous phase, the organic phase was washed with water and rotary evaporated to obtain a black product. The cluster product was dissolved in 2 mL of toluene and 2 mL 1-hexanethiol, and the solution was heated at 90 °C for around 14 h. The solution was then transferred to a 250 mL round-bottom flask and rotary evaporated. The resulting oil-like product was washed with ethanol and collected by centrifugation. This process was repeated at least 10 times to completely remove reaction impurities. The resulting gold clusters were thoroughly washed with 1:1 (v/v) toluene/acetonitrile mixture to remove small gold clusters. Au₃₃₃(SC₆H₁₃)₇₉ clusters were then extracted with 2:1 (v/v) toluene/acetonitrile mixture repeatedly, providing a total yield of ~80 mg.

Characterization of gold clusters. Matrix-assisted laser desorption ionization (MALDI) mass spectra were acquired using a Bruker Daltonics MALDI-TOF mass spectrometer (Microflex) equipped with a standard UV nitrogen laser (337 nm). The accelerating voltage was held at 15 kV and the spectrum was collected in a refractron positive ion mode. Cluster solution in CH_2Cl_2 (0.7 mM) was mixed with trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB, Aldrich) as a matrix (saturated in CH_2Cl_2) and then applied to the sample plate and air-dried.

Electrochemical measurements. Square wave voltammetry (SWV) was performed at room temperature with a CH Instruments electrochemical workstation (Model 660B) using a Pt working electrode (diameter 0.4 mm), a Pt wire counter electrode, and Ag wire quasi-reference electrode (AgQRE) in CH_2Cl_2 containing 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆, Aldrich). SWV scan was conducted at 100 mV/s with a pulse height and a width of 20 mV and 20 ms, respectively. Cluster solutions (1 mM) were degassed and blanketed with high-purity Ar atmosphere during measurements.

Optical measurements. Ground state electronic absorption spectra were obtained from a Shimadzu UV 2101 PC absorption spectrometer or a Shimadzu UV-3600 spectrophotometer using freshly prepared cluster solutions in tetrachloroethylene. Femtosecond transient absorption measurements were carried out at the Center for Nanoscale Materials, Argonne National Laboratory.^{S7} Briefly, a Spectra Physics Tsunami Ti:Sapphire, 75 MHz oscillator was used to seed a 5 KHz Spectra-physics Spit-Fire Pro regenerative amplifier. 95% of the output from the amplifier is used to pump a TOPAS optical parametric amplifier, which is used to provide the pump beam in a Helios transient absorption setup (Ultrafast Systems Inc.). A pump beam of 370 nm was used for the measurements. The remaining 5% of the

amplified output is focused onto a sapphire crystal to create a white light continuum that serves as the probe beam in our measurements (440 to 780 nm). The pump beam was depolarized and chopped at 2.5 kHz and both pump and probe beams were overlapped in the sample. Optical absorption spectra were taken before and after the measurements and the clusters have shown little degradation. Nanosecond transient absorption measurements were carried out in an EOS transient absorption spectrometer with 370 nm as the excitation and a picosecond fiber optic continuum laser as the probe. All the data analysis was carried out using Surface Xplorer Pro from Ultrafast Systems.

References

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2. Supporting Tables and Figures

| Gold Clusters | 01-R1 (V) | Electrochemical HOMO-LUMO Gap (V) | Optical Gap (eV) | Reported HOMO-LUMO Gap (eV) |
|-------------------|-----------|--------------------------------------|------------------|-----------------------------------|
| Au ₂₅ | 1.66 | 1.32 | 1.3 | 1.3 ^a |
| Au ₃₈ | 1.21 | 0.99 | 0.9 | 1.01 ^b |
| Au ₆₇ | 0.75 | 0.61 | 0.7 | 0.75 ^c |
| Au ₁₀₂ | 0.49 | 0.18 | < 0.5 | 0.44^{d} |
| Au ₁₄₄ | 0.39 | 0.15 | < 0.5 | 0.2^{e} |
| Au ₃₃₃ | 0.22 | 0.04 | < 0.5 | |

Table S1. Energy gaps of gold clusters determined from SWVs in Figure 2 and absorption spectra in Figure 1B.

a. Jin, R. Nanoscale 2010, 2, 343–362.

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Table S2. Lifetimes obtained from fitting the femtosecond and nanosecond transient absorption decay traces.

| Clusters | Core-state relaxation | Exciton decay times |
|-------------------|-----------------------|--|
| Au ₂₅ | 790 fs | 24±3 ns (35.5%), 150±12 ns (64.5%) Avg = 109 ns |
| Au ₃₈ | 1.5 ps | 3.0 ± 0.1 ns (72.6%), 32 ± 3 ns (20.3%), 290 ±30 ns (7.1%) Avg = 29 ns |
| Au ₆₇ | | 1.8±0.1 ps (68.0%), 90±5 ps (21.6%), 3.4±0.5 ns (4.0%), 60±10 ns (6.4%) Avg = 4.0 ns |
| Au ₁₀₂ | | 1.9±0.2 ps (75.7%), 270±70 ps (24.3%) Avg = 67.0 ps |
| Au ₁₄₄ | 650 fs, 1.5 ps | 3.2±0.2 ps |



Figure S1. z-plots of formal potentials ($E_{z,z-1}^{o}$) of charging events versus cluster charge states (z) for (A) Au₁₀₂(SC₆H₁₃)₄₄, (B) Au₁₄₄(SC₆H₁₃)₆₀ and (C) Au₃₃₃(SC₆H₁₃)₇₉. Formal potentials were obtained from SWVs in Figure 2B.



Figure S2. Power dependence of the kinetic decay trace of (A) Au_{144} monitored at 620 nm and (B) Au_{333} monitored at 530 nm. Power-dependent decay traces for (C) Au_{144} at 620 nm and (B) Au_{333} at 530 nm. Negligible power dependence is observed for Au_{144} while appreciable power dependence is observed for Au_{333} clusters.



Figure S3. Transient absorption spectra (A) from 110 fs to 750 fs and (B) from 750 fs to 30 ps for Au_{333} after excitation at 370 nm. The data resemble the transient absorption spectra obtained for plasmonic gold nanoparticles.



Figure S4. Transient absorption spectra at (A) picoseconds time delays and (B) nanosecond time delay for Au_{38} after excitation at 370 nm monitored with femtosecond and nanosecond transient absorption, respectively. Insets show the kinetic decay traces at 520 nm.



Figure S5. Transient absorption spectra at (A) picoseconds time delays and (B) nanosecond time delay for Au_{67} after excitation at 370 nm monitored with femtosecond and nanosecond transient absorption, respectively. Insets show the kinetic decay traces at 680 nm.



Figure S6. (A) Transient absorption spectra at different time delays for Au_{102} after excitation at 370 nm. (B) Corresponding species associated spectra obtained from global fit analysis.



Figure S7. Transient absorption spectra (A) from 200 fs to 1 ps and (B) from 1 ps to 5 ps for Au_{144} after excitation at 370 nm. (C) Corresponding species associated spectra obtained from global fit analysis.