Electron localization in rod-shaped triicosahedral gold nanocluster

Meng Zhou,a,1 Renxi Jin,a,b, Matthew Y. Sfeir,b Yu Xiang Chen,a, Yongbo Song,a and Rongchao Jin,a,2

aDepartment of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213; bBeijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China; and ‘Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973

Edited by Richard Eisenberg, University of Rochester, Rochester, NY, and approved May 5, 2017 (received for review March 23, 2017)

Atomically precise gold nanocluster based on linear assembly of repeating icosahedrons (clusters of clusters) is a unique type of linear nanostructure, which exhibits strong near-infrared absorption as their free electrons are confined in a one-dimensional quantum box. Little is known about the carrier dynamics in these nanoclusters, which limit their energy-related applications. Here, we reported the observation of exciton localization in triicosahedral Au37 nanoclusters (0.5 nm in diameter and 1.6 nm in length) by measuring femtosecond and nanosecond carrier dynamics. Upon photoexcitation to S1 electronic state, electrons in Au32S undergo ~100-ps localization from the two vertexes of three icosahedrons to one vertex, forming a long-lived S* state. Such phenomenon is not observed in Au25 (dimer) and Au13 (monomer) consisting of two and one icosahedrons, respectively. We have further observed temperature dependence on the localization process, which proves it is thermally driven. Two excited-state vibration modes with frequencies of 20 and 70 cm−1 observed in the kinetic traces are assigned to the axial and radial breathing modes, respectively. The electron localization is ascribed to the structural distortion of Au37 in the excited state induced by the strong core vibrations. The observed electron localization phenomenon provides unique physical insight into one-dimensional gold nanoclusters and other nanostructures, which will advance their applications in solar-energy storage and conversion.

Significance

Understanding the carrier dynamics in ultrasmall (<2-nm) gold nanoclusters is fundamentally important for their applications in solar energy storage and conversion. This work tackles how the electrons of gold nanoclusters flow after photoexcitation. The electron localization/delocalization is commonly observed in polymers and other molecular aggregates, but little is known about this phenomenon in gold nanoclusters. Here, we observed ~100-ps excited-state electron localization in atomically precise rod-shaped Au32S nanoclusters made up of three icosahedrons. The electron transition was further obtained by temperature-dependent experiments. The excitation localization observed in rod-shaped clusters of clusters will advance their applications in nonlinear optics and energy harvesting.

Author contributions: M.Z. and Rongchao Jin designed research; M.Z., Renxi Jin, M.Y.S., Y.C., and Y.S. performed research; M.Z. and M.Y.S. analyzed data; and M.Z. and Rongchao Jin wrote the paper.

The authors declare no conflict of interest.

1M.Z. and Renxi Jin contributed equally to this work.

2To whom correspondence should be addressed. Email: rongchao@andrew.cmu.edu.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1704699114/-/DCSupplemental.
can be either semiconducting or metallic by tuning the charge state, whereas the long chain of Au13 icosahedra via face sharing is always metallic (35). Understanding the interaction between the individual building blocks is thus beneficial to future development of larger cluster-assembled materials and their applications (36–38). On the other hand, electron and phonon dynamics provides important information of how electrons flow in and out of the nanostructures, which has greatly improved the understanding of energy flow in gold nanoclusters (31, 39–43). It is therefore of paramount importance to investigate the ultrafast electron dynamics of these clusters of clusters and compare them with the individual Au13 unit.

Here, we report the ultrafast electron dynamics of Au13 (monomer) and Au25 (trimer) by femtosecond-transient absorption (TA) spectroscopy. Unlike simple molecular-like electron dynamics observed in Au13 and rod-shaped Au25, an additional electron localization (~100-ps) process was observed in the tricapped trigonal prism Au37, which is a unique observation in metal nanoclusters. Temperature-dependent analysis further confirmed that the observed excitation localization process is thermally driven and two activation energy values (Ea) were obtained. Furthermore, two phonon frequencies (20 and 70 cm−1) were observed from the TA kinetic traces, which can be assigned to the axial and radial breathing modes, respectively. These results provide fundamental insight into energy flow in the gold nanoclusters and will stimulate future work on other types of nanostructures composed of repeating building blocks.

Results and Discussion

Optical Absorption Features. Gold nanoclusters made up of linear combinations of Au13 building blocks (Au13, Au25, and Au37) exhibit an interesting trend in the optical spectra (9, 15, 32). In the short-wavelength range, the absorption spectra of the Au25 and Au37 resemble that of the Au13 building block (Fig. 1), whereas in the long-wavelength range, the absorption peaks are red-shifted due to the interaction between Au13 building blocks. The absorption spectrum of the rod-shaped [Au25(C2H5)30(SC2H5)2]2+ (X = Cl/Br) (Au13 for short) (44) nanoclusters was also shown for comparison. Compared with Au25, Au24 has a similar crystal structure but lacks the absorption around 670 nm due to the absence of the gold atom on the vertex position. Theoretical calculations revealed that the absorption peak around 670 nm in Au24 and 800 nm in Au13 originate from the dimeric interactions between Au13 units, whereas the additional peak around 1,230 nm in Au37 originates from trimeric interaction (10). The absorption peaks at shorter wavelengths originate from the individual Au13 icosahedrons. The highest occupied molecular orbital (HOMO)—lowest unoccupied molecular orbital (LUMO) gap was determined by extrapolating optical absorption to zero, that is, 1.96 eV for Au13, 1.73 eV for Au25, and 0.83 eV for Au37. The general trend—that is, the longer the aspect ratio, the more red-shifted the longer wavelength peak—resembles that of plasmonic gold nanorods (45), but the nature of the observed trend in Au13, Au25, and Au37 is due to quantum confinement in a one-dimensional box. Based on the previous theoretical calculation results, the distributions of LUMO of Au25 and Au37 are localized on the one and two vertexes of Au13 icosahedrons (10), respectively (Fig. 1).

Electron Dynamics of Au13 Monomer. Before looking into the interactions between Au13 building blocks in Au37, we first probed the photophysics of the monomer, [Au13(dppe)Cl]1+ nano-cluster (Au13 for short). Femtosecond TA with excitation of 360 nm (3.4 eV) and 560 nm (2.2 eV; HOMO–LUMO transition (46)) were carried out and compared (Fig. 2). Upon excitation at 360 nm, one can observe prominent excited-state absorption (ESA) centered at 630 nm and ground-state bleaching (GSB) at 500 nm (Fig. 2A). In about 1 ps, the 630-nm ESA decays to give rise to an additional ESA centered at 450 nm. In the case of excitation at 560 nm, the ESA around 450 nm can be directly excited and the 630-nm ESA is absent (Fig. 2B). The ESA at 630 nm can thus be assigned to S0→S2, whereas ESA at 450 nm should be assigned to S1→S2. The kinetic traces of femtosecond TA with excitation at 360 nm exhibit an ultrafast decay plus a nondecay plateau, whereas the TA decay traces with excitation at 560 nm lack the ultrafast component (Fig. 2 C and D). Nano-second TA and time-correlated single-photon counting (TCSPC) measurements suggest that the long-lived relaxation has only one decaying component (SI Appendix, Fig. S1). Global analysis on TA excited at 360 nm gives rise to two decay components (0.4 ps and 1.72 μs), which can be assigned to LUMO+n→LUMO internal conversion and relaxation back to the ground state, respectively (SI Appendix, Fig. S2). The monocahedral Au13 exhibits similar carrier dynamics to that of the dimer Au25, which also exhibits two decay components (0.8 ps and 2.3 μs), as previously reported (31). The relatively simple relaxation pathway in both the monomer and dimer suggests that there is no excited-state interaction between the icosahedron units in these two structures (Au13 and Au25).

Electron Dynamics of Au25 Trimer. Femtosecond TA spectroscopy was then performed on the Au25 mononanoclar (trimer). Excitation at 1,200 nm (1.03 eV) was chosen because it lies close to the band gap of Au25 (0.83 eV), which excluded the excess excited-state energy. Upon photoexcitation, ESAs at 515, 760, and 830 nm, and GSB at 480 nm were observed in the TA spectra (Fig. 3A and B). Between 1 and 500 ps, the ESA around 830 nm decays prominently to zero, and notably the ESA around 760 nm experiences a significant growth at the same time. Population evolution based on a two-state model (solid line, Fig. 3C) closely
resembles the femtosecond-TA kinetic traces (dots) at selected wavelengths, which indicates that the excited state follows a sequential $A \rightarrow B$ relaxation model. Nanosecond-TA experiments revealed that the lifetime of $\text{Au}_{37}$ is 28 ns (SI Appendix, Fig. S3). Global analysis can thus extract two species-associated spectra (SAS) with time constants of 115 ps and 28 ns. As the 1,200-nm excitation (1.03 eV) is only slightly above the band gap of $\text{Au}_{37}$, it can directly pump the electrons to the lowest excited state ($S_1$) so that the last long-lived state (defined as $S_1^*$) lies between $S_1$ and ground state. The 115-ps component, which was not observed in

![Figure 2](image)

Fig. 2. Electron dynamics of $\text{Au}_{13}$ nanoclusters. (A and B) Femtosecond-TA spectra at all time delays of $\text{Au}_{13}$ with excitation of 360 and 560 nm, scattering around 560 nm because the pump laser was cut off. (C and D) Selected decay traces and corresponding fit of $\text{Au}_{13}$ with excitation at 360 and 560 nm. The slow decay of 1.72 μs was fixed based on nanosecond-TA measurement in SI Appendix.

![Figure 3](image)

Fig. 3. TA spectra of $\text{Au}_{37}$ nanoclusters probed in the visible region. (A) Femtosecond-TA data of $\text{Au}_{37}$ with excitation of 1,200 nm. (B) TA spectra as a function of time delay between 1 and 300 ps. (C) Population evolution (solid line) based on a sequential model versus kinetic traces (dots) where decay (518 nm) and growth (710 nm) dominates, respectively. (D) Species-associated spectra (SAS) obtained from global fitting on the TA data. The second lifetime was fixed to 28 ns based on the nanosecond measurement.
the rod-shaped Au$_{25}$ (dimer) and Au$_{13}$ (monomer), can be tentatively ascribed to the coupling between three Au$_{13}$ units in the Au$_{37}$ nanocluster. Compared with the rod-shaped Au$_{25}$ nanocluster (2.3 μs) (31), the last long-lived state has a nearly 100 times shorter lifetime in Au$_{37}$ (28 ns). After repeating the experiment by bubbling argon into the solution and dissolving samples in solvents of different polarities, respectively, we further confirmed that the last long-lived state is neither a triplet state nor a charge transfer state (SI Appendix, Fig. S3).

The ∼100-ps process in Au$_{37}$ suggests the existence of additional electronic state between S$_1$ and S$_0$ states, which was not observed in both spherical Au$_{13}$ (Fig. 2) and rod-shaped Au$_{25}$ nanoclusters. By comparing the TA spectra between rod-shaped Au$_{25}$ (dimer) and Au$_{37}$ (trimer), it is found that the TA spectra of dimer and trimer at 1 ns have similar spectral features (Fig. 4); the ESA around 610 nm and GSB around 677 nm in the dimer were red-shifted to 760 and 800 nm in the trimer, respectively. Previous DFT calculations (9) indicated that the LUMO of the dimer is localized on the shared vertex of two icosahedra, whereas the LUMO of the trimer is distributed over the two vertexes of three icosahedra. By directly exciting the trimer to S$_1$ state, the additional S$_1^*$ state (similar to the S$_1$ state of dimer) is formed, indicating that the final excited states of dimer and trimer have similar electron distributions, that is, the electrons are finally localized at one vertex in the trimer. Therefore, the ∼100-ps process observed in Au$_{37}$ can be assigned to the excitation localization, in contrast with the simple relaxation pathways in the monomer and dimer cases. This assignment is reasonable considering that the electrons are less confined in the axial direction with increasing aspect ratio from Au$_{13}$ to Au$_{37}$.

To further probe the origin of the ∼100-ps process in Au$_{37}$, excitation wavelength-dependent TA experiments on Au$_{37}$ were performed. Carrier dynamics of Au$_{37}$ with different excitation energies were compared. Fig. 5 A–D shows the TA data after excitation with pump pulse at 380 nm (3.2 eV), 490 nm (2.5 eV), 820 nm (1.51 eV), and 1,200 nm (1.03 eV), respectively. With excitation energy higher than 1,200 nm (1.03 eV), one can observe additional ESA signals at 520 and 680 nm in the initial few picoseconds (Fig. 5 A–C). The negative signal (deep blue color around 800 nm) with excitation at 360 and 490 nm should be ascribed to the stimulated emission from higher excited states. To look into the ∼100-ps process, we monitor the kinetic traces

![Fig. 4. Comparison between TA spectra of rod-shaped Au$_{25}$ and Au$_{37}$ nanoclusters. (A) Transient spectra at 1 ns of Au$_{25}$ rod. (B) Transient spectra at 1 ns of Au$_{37}$ rod. (Inset) The distribution of electrons in Au$_{25}$ and Au$_{37}$ rod based on the electron localization model.](www.pnas.org/cgi/doi/10.1073/pnas.1704699114)
around 820 and 760 nm (Fig. 5 E and F) as a function of excitation wavelength. As shown in Fig. 5E, the decays of the kinetic traces probed at 820 nm (ESA) are independent of the excitation energy; all of the traces decay to zero within 600 ps. The ESA around 820 nm with 1,200-nm excitation grows immediately within the instrument response (∼100 fs), whereas at higher excitation energies the 820-nm ESA experiences slow growth in the first 5 ps. It suggests that the 820-nm ESA originates from S₁ to higher excited states. In the kinetics of ESA around 760 nm (Fig. 5F), one can observe prominent excitation-dependent growth: kinetics with near-band gap excitation exhibit single-exponential rise (115 ps), whereas at higher excitation energies, additional fast growth can be observed. Excited decaying time constants based on target global fitting are listed in Table 1 (for details of target global fitting, see SI Appendix, Figs. S4–S6).

The TA spectra probed in visible region are complicated due to strong overlap between ESA and GSB. To further elucidate the excited-state species, UV pump/near-infrared (NIR) probe TA was carried out to monitor the net bleaching dynamics around 1,200 nm. After excitation at 490 nm, strong and neat GSB centered at 1,230 nm can be observed (Fig. 6A), which corresponds to the absorption peak due to the trimeric interaction in Au₁₃₋₁₅. During the first few picoseconds, the GSB grows slowly and broad ESA at other wavelength decays at the same time (Fig. 6B and C). After global analysis, three decaying components (1.5 ps, 105 ps, >1 ns) are required for best fitting, and the time constants match well with those of TA probed at visible region. In Fig. 6D, one can observe that strong ESA spanning between 1,100 and 1,600 nm dominates the first decay-associated spectra (DAS) component, which explains the initial growth in the GSB around 1,230 nm. The 105-ps component, which has contribution all over the detection range, can be well explained by electron localization.

Based on the excitation-dependent ultrafast TA experiments, the energy diagram of Au₁₃₋₁₅ can be constructed (Fig. 7). As discussed above, the 820-nm ESA arises from S₁ state, whereas the 760-nm ESA originates from S₁* state between S₁ and S₃. With 1,200-nm excitation, Au₁₃₋₁₅ is directly excited to the S₁ state, and relaxation from S₁ to S₁* occurs in 115 ps. With higher excitation energies, the relaxations from S₁ to S₃ and from S₃ to S₁* occurs in a similar timescale, which leads to the fast growth in ESAs around both 820 and 760 nm. Subsequently, relaxation occurs from S₁ to S₁* at a similar time constant to that at near-band gap excitation (Table 1). As proposed above, the relaxation from S₁ to S₁* can be ascribed to an electron localization process. The relatively slow excited-state process (≈100 ps) suggests that there is a significant energy barrier between the initial and final electronic states. It is therefore of great interest to probe the activation energy of this process by carrying out temperature-dependent TA measurements.

**Temperature-Dependent Electron Dynamics of Au₁₃₋₁₅.** As shown in Fig. 8 A and B, TA spectra of Au₁₃₋₁₅ film [clusters in poly(methyl methacrylate) (PMMA)] at 5 ps and 1 ns measured at different temperatures are compared. At room temperature, the transient spectra exhibit the same features to those measured in solution. With temperature decreasing from 330 K down to 77 K, three features were observed: (i) both ESA and GSB peaks became sharper and additional peaks emerged; (ii) both the maxima of ESA and GSB evolve to higher energies, and (iii) the intensities of both ESA and GSB increased significantly. The steady-state absorption spectra of Au₂₅(SR)₁₅, Au₄₅(SR)₂₅, and rod-shaped Au₃₅ were reported to exhibit similar behaviors as the temperature decreases.
decreased (47, 48), which was explained by electron–phonon (e–p) coupling and lattice expansion interactions. Here, the blue shift and enhancement of ESA at low temperatures suggest that the ESA is also strongly affected by the e–p coupling effect. To look into the thermal effect on the electron dynamics, we compared the normalized kinetic traces measured at 290 and 77 K and the corresponding fits in Fig. 8 C and D. As the positions of ESAs around 760 and 820 nm shifted to 740 and 780 nm when the temperature decreased from 290 to 77 K, the maximum positions of ESAs were compared. It is found that the electron dynamics measured at 77 K is significantly slowed down compared with that measured at 290 K, which suggests that the

Fig. 7. Energy levels (Left), relaxation pathway (Middle), and diagram of electron localization (Right) of Au37 nanocluster.

Fig. 8. Temperature-dependent electron dynamics of Au37. (A and B) Temperature-dependent TA of Au37 film at time delay of 5 ps and 1 ns with 100-fs, 1,200-nm (1.03-eV) excitation. (C and D) Normalized kinetic traces at selected wavelengths measured at 290 and 77 K. (E) Normalized kinetics of concentration of the first component as a function of temperature obtained from global fitting. (F) ln k versus 1/T.
electron localization slows down as the temperature drops. The temperature dependence of the electron localization indicates that it is a thermally driven process.

To resolve the activation energy of this process, we performed the global fitting on the data of a series of temperatures and plotted the concentration dynamics of the first decaying component (Fig. 8E and SI Appendix, Fig. S7). According to the Arrhenius relationship:

\[
k = A \exp \left( -\frac{E_a}{k_B T} \right),
\]

where \( k \) is the reaction rate, \( A \) is the constant, \( E_a \) is the activation energy, \( k_B \) is the Boltzmann constant, and \( T \) is the absolute temperature, we plot \( \ln k \) as a function of \( 1/T \) (Fig. 8F) to extract the activation energy (\( E_a \)). It is interesting to see that the linear fitting gives rise to two slopes (–464 and –41), which indicates two activation energies (\( E_a \)), that is, 3.85 and 0.34 kJ mol\(^{-1}\). The emergence of two activation energies suggests that there might be two deactivation pathways, the origin of which has not been fully resolved yet. TA anisotropy measurements (SI Appendix, Figs. S8 and S9) were further performed to help identify the origin of the 115-ps process. Meanwhile, it is found that the rod-shaped Au\(_{25}\) nanocluster, which lacks the central gold atom, does not show e-localization process after photoexcitation (SI Appendix, Fig. S10).

Coherent Phonons of Au\(_{37}\). Besides the electron dynamics, phonon dynamics can also reflect the excited-state energy deactivation. Upon photoexcitation, the distinct different equilibrium between the configurations of ground state and excited state will give rise to coherent vibration of the nanoclusters along the potential energy surface (49). As long as the laser pulse is shorter than the vibration period, the coherent motion will be reflected as temporal oscillations in the early time of TA kinetic traces, which has been observed in a series of atomically precise gold nanoclusters (30, 31, 50). A closer look at TA spectra of Au\(_{37}\) pumped at 1.03 eV in the first 10 ps gives prominent oscillations at almost all wavelengths (SI Appendix, Fig. S11A). When probed around 750 and 820 nm, a 20 cm\(^{-1}\) (0.6 THz) oscillation can be observed, whereas at shorter probe wavelength, we observed a second mode with frequency of 70 cm\(^{-1}\) (2.1 THz). The relatively low vibration frequencies suggest that both modes arise from acoustic vibrations. The change in the phase in oscillations of different wavelengths (Fig. 9A) suggests that the vibration arise from the excited state rather than the ground state. We use the following equation to fit the oscillation superimposed on the kinetic decay:

\[
\Delta A = Ae^{-t^2/2\sigma^2} \left[ Be^{-t/\tau_1} + Ce^{-t/\tau_2} \cos(\omega t + \varphi) \right],
\]

where \( \sigma \) is the SD of Gaussian impulsive function, \( \tau_1 \) is the relaxation time (fixed to 100 ps), \( \tau_2 \) is the damping time of the oscillation, \( \omega \) is the frequency, and \( \varphi \) is the phase.

Compared with the rod Au\(_{25}\) dimer, which shows oscillations at 26 cm\(^{-1}\) (31), Au\(_{37}\) has a similar frequency mode (20 cm\(^{-1}\)) plus an additional higher frequency mode (70 cm\(^{-1}\)). Considering the anisotropic effect in their atomic structures, the low-frequency vibration in both Au\(_{25}\) (dimer) and Au\(_{37}\) (trimer) should be ascribed to the axial vibration mode (Fig. 9A, Inset). On the other hand, the higher frequency mode (70 cm\(^{-1}\)) observed in Au\(_{37}\) is quite similar to that (80 cm\(^{-1}\)) observed in spherical Au\(_{25}\)(SR)\(_{18}\) nanocluster (30). Therefore, the 70 cm\(^{-1}\) mode in Au\(_{37}\) should be assigned to the radial breathing mode (Fig. 9B, Inset). Moreover, at 77 K, one can observe enhanced oscillation as well as longer dephasing time compared with that at room temperature (SI Appendix, Fig. S11B). After comparing the data of solution and film at different temperatures, we found that the longer lifetime of oscillations occurs in film at both 290 and 77 K. Therefore, it is the surrounding matrix (PMMA) rather than low temperature that gives rise to the slower damping in the rod-shaped Au\(_{37}\) nanocluster. It is worth noting that one of the two activation energies (0.34 kJ mol\(^{-1}\), equal to 28 cm\(^{-1}\)) which we obtained from low-temperature TA, is very close to the energy of the axial vibration mode (20 cm\(^{-1}\)). Thus, it is very likely that the axial coherent vibration (20 cm\(^{-1}\)) gives rise to the structural distortion and thus the e-localization process.

Conclusion

In summary, we have observed the excited-state exciton localization in the Au\(_{37}\) nanocluster that is made up of three Au\(_{13}\) building blocks. In contrast with the monomer (Au\(_{13}\)) and dimer (Au\(_{25}\)), the trimer (Au\(_{37}\)) exhibits strong coupling between Au\(_{13}\) units after photoexcitation. The temperature-dependent dynamics suggests that the electron localization process is thermally driven. Two vibration modes are observed in the kinetic traces, and they are assigned to the radial and axial vibrations, respectively. The electron localization in rod-shaped Au\(_{37}\) is attributed to the structural distortion induced by the strong excited-state coherent vibrations. Gold clusters with longer linear chains of Au\(_{13}\) units are expected to exhibit similar coupling between units. Our work reports the observation of electron localization as well as coupling between building blocks in gold nanoclusters. These results are of fundamental importance for understanding the electronic properties of not only gold nanoclusters but also other.

![Fig. 9. Coherent phonons of Au\(_{37}\). (A) Selected kinetic traces which show coherent oscillations of 70 cm\(^{-1}\). (B) Selected kinetic traces that show coherent oscillations of 20 cm\(^{-1}\). (Insets) Schematic diagram of vibration modes.](image-url)
one-dimensional nanostructures composed of repeating building blocks. The obtained insight will help to advance the application of metal nanoclusters in solar-energy conversion.

Experimental Procedures

Sample Preparation. The syntheses of [Au12(dppe)Cl]3+ (dppe: 1,2-bis(diphenylphosphino)ethane), [Au12(dppe)2(SC6H4Ph)3]2+ (X = Cl), [Au12(S2C6H4Ph)3]2+ (X = Br) and [Au12(dppe)2(SC6H4Ph)2X2]2+ (X = Cl) follow the protocols reported previously (15, 32, 44, 51).

Steady-State Absorption and Fluorescence Measurements. The UV-Vis-NIR absorption spectra were measured on a Shimadzu UV-3600 plus spectrometer. The steady-state fluorescence was measured on a HORIBA Jobin Yvon SPEX Fluorolog-3 spectrometer. Fluorescence lifetimes were measured with a TCSPC technique; a pulsed LED source (376 nm, 1.1 ns) was used as the excitation source.

Femtosecond and Nanosecond TA. Femtosecond-TA spectroscopy were carried out using a commercial Ti:sapphire laser system (SpectraPhysics; 800 nm, 100 fs, 3.5 mJ, 1 kHz). Pump pulse was generated using a commercial optical parametric amplifier (Light Conversion). A small portion of the laser fundamental was focused into a sapphire plate to produce supercontinuum in the visible region, which overlapped in time and space with the pump. The diameter of the pump beam was 0.75 mm, and the pump power was adjusted to 0.5 mW using neutral density filter. Multivavelength transient spectra were recorded using dual spectrometers (signal and reference) equipped with array detectors whose data rates exceed the repetition rate of the laser (1 kHz). Solutions of clusters in 1-mm path length cuvettes were excited by the tunable output of the OPA (pump). Nanosecond-TA measurements were conducted using the same ultrafast pump pulses along with an electronically delayed custom continuum light source with a subnanosecond pulse duration (EOS; Ultrafast Systems). The polarization between pump and probe pulse was set to magic angle (54.7°) for all experiments. The Au12 and Au12 clusters were dissolved in methanol and dichloromethane, respectively, for time-resolved experiments in solution. For matrix measurements, Au12 was dissolved in dichloromethane along with commercial PMMA, followed by drop-casting of the solution onto a sapphire window and then solvent evaporation. We carefully checked the UV-Vis-NIR absorption spectra of Au12 before and after each femtosecond experiment, and the spectra always remained the same (SI Appendix, Fig. 512).

Data Analysis. Chirp correction was made before the global analysis. Before global fitting, singular value decomposition was performed to evaluate the number of time constants needed. Subsequently, graphical interface Giot- taran and TIMP (52) were applied to analyze the population dynamics based on the method reviewed by van Stokkum et al. (53).

ACKNOWLEDGMENTS. Rongchao Jin is grateful for financial support by the Academic Staff Office of Science Foundation of China (AFOSR) under AFOSR Award FA9550–15–1–9999 (FA9550–15–1–0154) and the Camille and Dreyfus Teacher–Scholar Awards Program. Transient optical measurements were carried out at the Center for Functional Nanomaterials, Brookhaven National Laboratory, which is supported by the US Department of Energy, Office of Basic Energy Sciences, under Contract DE-AC02-98CH10886.


