Electronic Supplementary Information

Effect of Single Electron on the Excited State Dynamics of Rod-Shaped Au_{25} Nanoclusters

Jie Kong,[1] Dayujia Huo,[2] Jialong Jie,[2] Yanzhen Wu,[1] Yan Wan,[2] Yongbo Song,[3] Meng Zhou[1*]

[1]*Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, Anhui 230026, China*

[2]*College of Chemistry, Beijing Normal University, Beijing 100875, China*

[3]*School of Biomedical Engineering, Research and Engineering Center of Biomedical Materials, Anhui Medical University, Hefei, Anhui 230032, China*

*To whom correspondence should be addressed. Email: mzhou88@ustc.edu.cn

Experimental Section

Synthesis of Au Nanoclusters The synthesis of two rod-shaped Au_{25} nanoclusters followed the procedures reported previously.[1]

Steady State Absorption Measurements The UV-vis absorption of two rod-shaped Au_{25} nanoclusters were collected with an Agilent HP8453 diode array spectrometer. The two nanoclusters were dissolved in CH_2Cl_2 for steady state absorption measurements.

Transient Absorption Spectroscopy The nanosecond transient absorption measurements were performed using nanosecond flash photolysis setup Edinburgh LP920 spectrometer (Edinburgh Instruments Ltd.), combined with a Nd:YAG laser at 355 nm (Surelite II, Continuum Inc.).

The femtosecond transient absorption measurements were performed on a commercial spectrometer (Harpia-TA, Light Conversion) as described previously.[2] In the isotropy TA measurements, the pump and probe pulse were set to magic angle (54.7). In the anisotropy TA measurements, the signal was calculated by：

$$r(t) = \frac{I_{VV} - I_{VH}}{I_{VV} + 2I_{VH}} \quad (1)$$

where I_{VV} and I_{VH} represent the TA signals with probe parallel and vertical to the pump, respectively. Global analysis on the TA data was performed using Glotaran followed the procedure reported previously. The UV-vis absorption spectra remain the same before and after the transient absorption measurements, indicating little decomposition of the nanocluster. All the transient absorption data was collected in CH_2Cl_2.

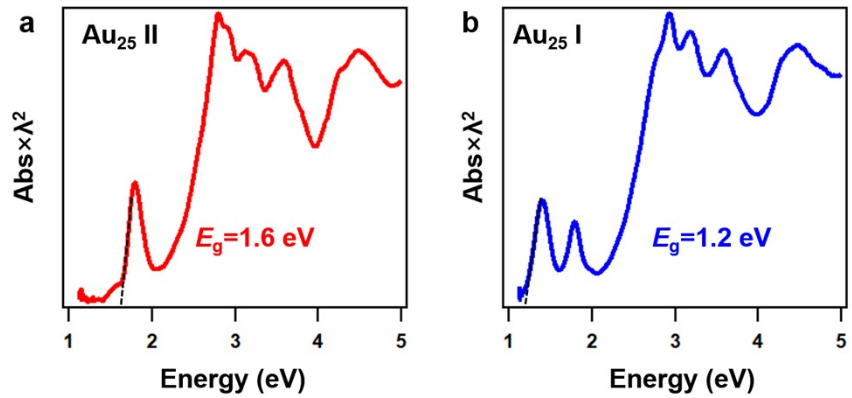

Figure S1. Steady state absorption spectra of (a) **Au_{25} II** and (b) **Au_{25} I** nanoclusters in energy scale. The band gaps of two nanoclusters are determined by extrapolating the absorbance to zero (black dashed lines).

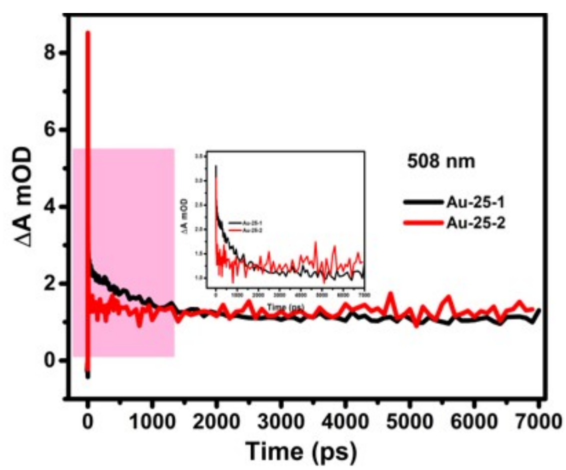

Figure S2. Comparison of transient absorption (TA) kinetics probed at 508 nm of two rod-shaped Au_{25} nanoclusters. The inset shows the zoom in of TA kinetics of two nanoclusters.

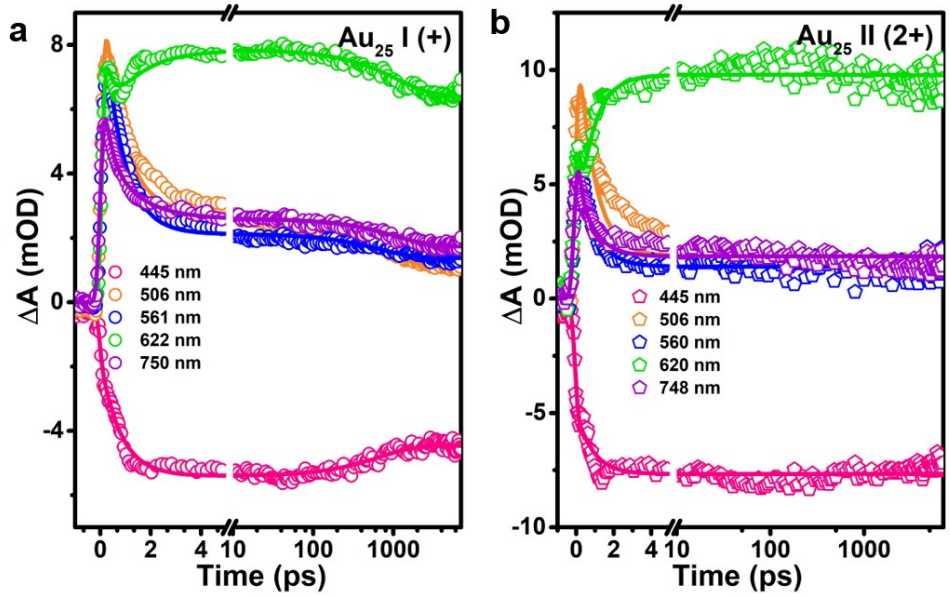

Figure S3. TA kinetic traces at selected probe wavelengths and corresponding fits from global analysis of (a) **Au_{25} I** and (b) **Au_{25} II**.

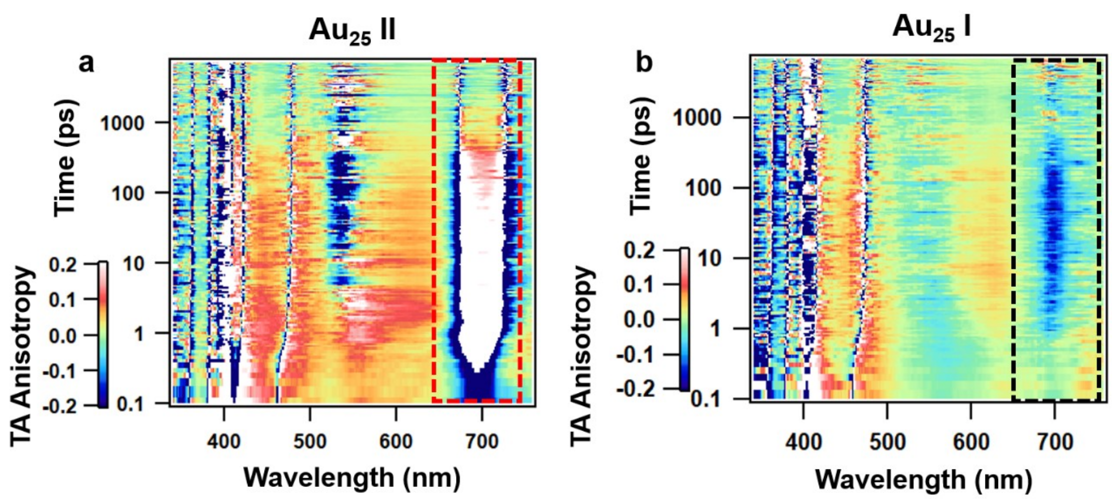

Figure S4. Transient absorption anisotropy (TAA) data map of **Au_{25} II** (a) and **Au_{25} I** (b) NCs with excitation. Dashed lines indicate the GSB positions around 700 nm of two NCs.

References.

(1) Song, Y.; Jin, S.; Kang, X.; Xiang, J.; Deng, H.; Yu, H.; Zhu, M., How a Single Electron Affects the Properties of the "Non-Superatom" Au25 Nanoclusters. *Chem. Mater.* **2016**, *28*, 2609-2617.

(2) Huo, D.; Peng, Q.; Xu, T.; Wang, X.; Wang, X.; Xia, A.; Lu, R.; Cui, G.; Wan, Y., Intramolecular Energy Transfer in a Series of Star-Shaped Molecules with a Central Porphyrin Core and Four Oligocarbazole Arms. *J. Phys. Chem. C* **2020**, *124*, 27356-27365.