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Electronic Supplementary Information

Coherent Vibrational Dynamics of $Au_{144}(SR)_{60}$ Nanoclusters

Wei Zhang,[a] Jie Kong,[a] Yingwei Li,[b] Zhuoran Kuang,[c] He Wang,[d] Meng Zhou[a,d,*]

[a]Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui 230026, China

[b]Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138, United States

[c]School of Science, Beijing University of Posts and Telecommunications (BUPT), Beijing 100876, P. R. China

[d]Department of Physics, University of Miami, Coral Gables, Florida 33146, United States

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

S1. Materials and Methods

Synthesis and Chemicals

The synthesis of $Au_{144}PET_{60}$ followed a previous method.[1] All chemicals used in this work were purchased from Sigma-Aldrich and used without further purification.

Steady-State Optical Absorption and Cryogenic Optical Measurements

The steady-state absorption spectra were measured using an Agilent Cary 60 absorption spectrometer. The cryogenic optical measurements were performed in a cryostat (Janis Research Company). For the temperature dependent measurements, Au NCs were dispersed in polymethyl methacrylate (PMMA) thin films. First, 80 mg of PMMA was dissolved in 1 mL of toluene to form a colorless solution. Then, 20 μL of toluene solution of $Au_{144}PET_{60}$ NCs (ca. 2mg/mL) was added into 10 μL of the PMMA solution. Finally, the mixture of $Au_{144}PET_{60}$ NCs and PMMA matrix was drop-cast onto a clean quartz plate, and the solvent was evaporated slowly at room temperature. The steady-state absorption spectra of $Au_{144}PET_{60}$ NCs dissolved in toluene and dispersed in PMMA were found to be identical.

Mass Spectrometry

MALDI-MS was performed with a PerSeptive-Biosystems Voyager DE super-STR time-of-flight (TOF) mass spectrometer.

Ultrafast Transient Absorption

The pump beam was generated in a collinear optical parametric amplifier (Light Conversion) pumped by the 800nm output of an amplified Ti:sapphire laser (Coherent Astrella, 5 kHz). The TA measurements were performed on a Helios Fire commercial spectrometer (Ultrafast System), which was described in a previous report in detail.[2] There is no photo degradation after the TA measurements checked by the steady-state absorption spectra.

S2. Temperature-Dependent TA

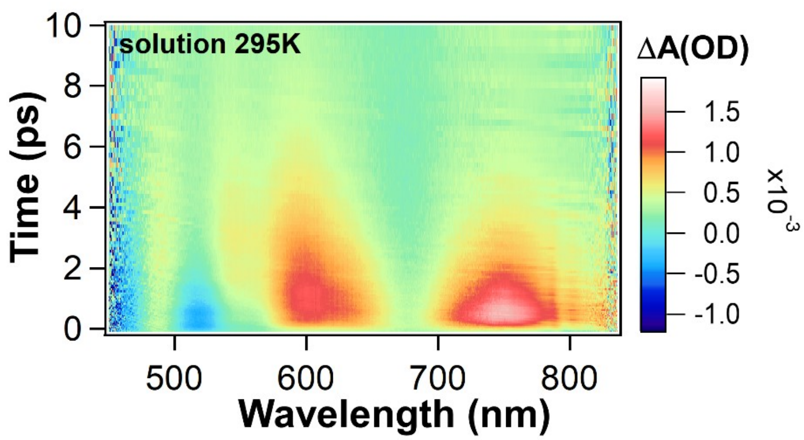

Fig. S1 The TA spectral data map of $Au_{144}PET_{60}$ solution (solvent is toluene) under excitation of 400 nm at 295 K.

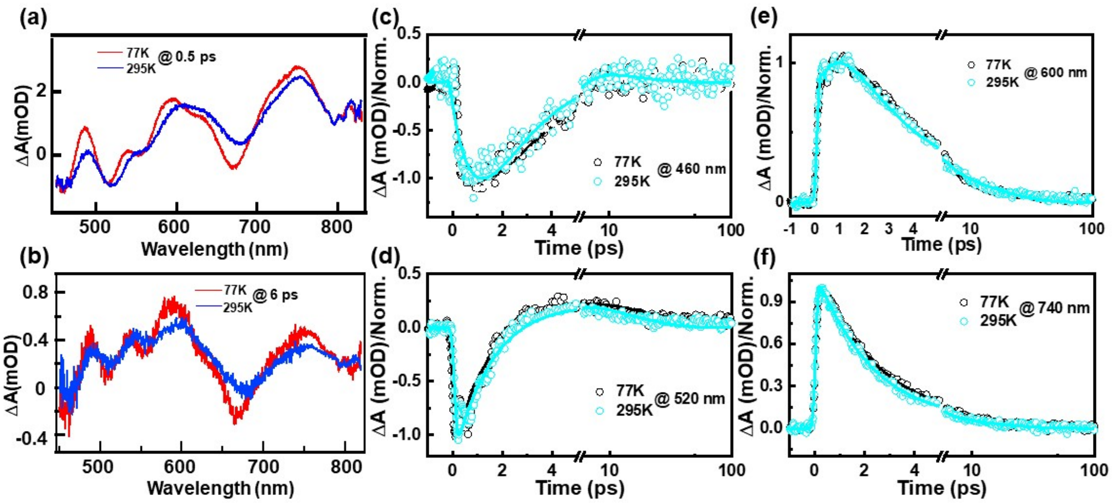

Fig. S2 The temperature-dependent TA spectra of $Au_{144}PET_{60}$ dispersed in PMMA thin film. The TA spectra displayed at time delay of (a) 0.5 ps and (b) 6 ps. (c)-(f) The kinetic traces of TA spectra obtained at different temperatures.

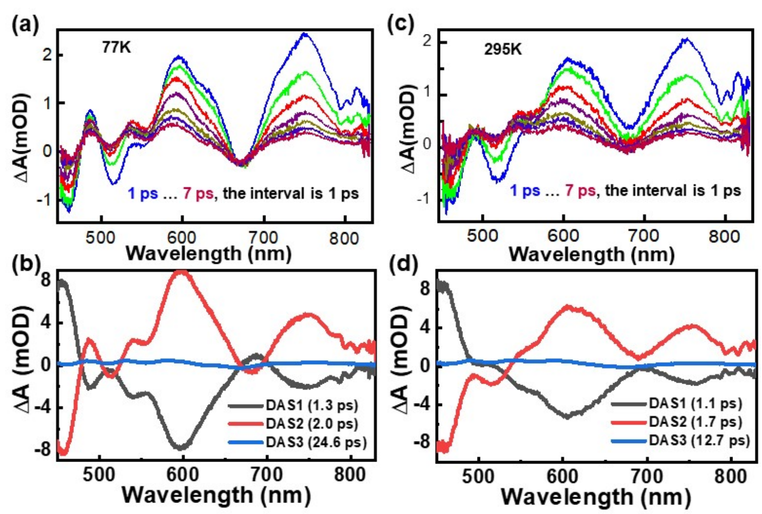

Fig. S3 The TA spectra of $Au_{144}PET_{60}$ dispersed in PMMA thin film and DAS results obtained at (a and b) 77 K, (c and d) 295 K. The data obtained at 77 K are shown as comparisons.

Table S1. The global analysis results obtained at different temperatures.

	Components	Time Constants/ ps
77K	DAS 1	1.3
	DAS 2	2.0
	DAS 3	24.6
295K	DAS 1	1.1
	DAS 2	1.7
	DAS 3	12.7

S3. Coherent Vibrations

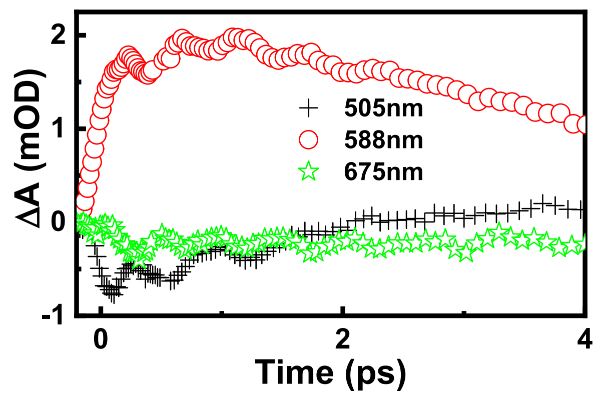

Fig. S4 The extracted kinetic traces of $Au_{144}PET_{60}$ at 505 nm, 588 nm and 675 nm which are monitored at 77K in film phase.

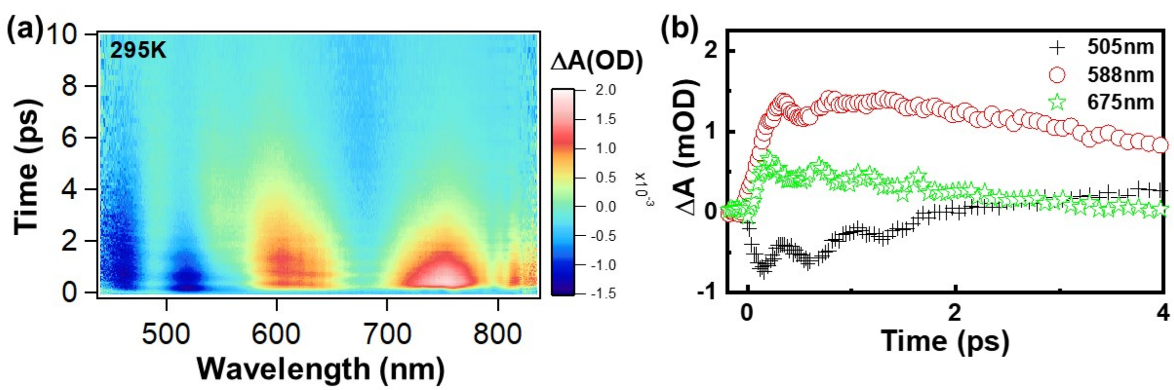

Fig. S5 (a) The pseudo-color TA map of $Au_{144}PET_{60}$ dispersed in PMMA thin film obtained at 295 K. (b) The extracted kinetic traces of $Au_{144}PET_{60}$ at 505 nm, 588 nm and 675 nm which are monitored at 295K in film phase.

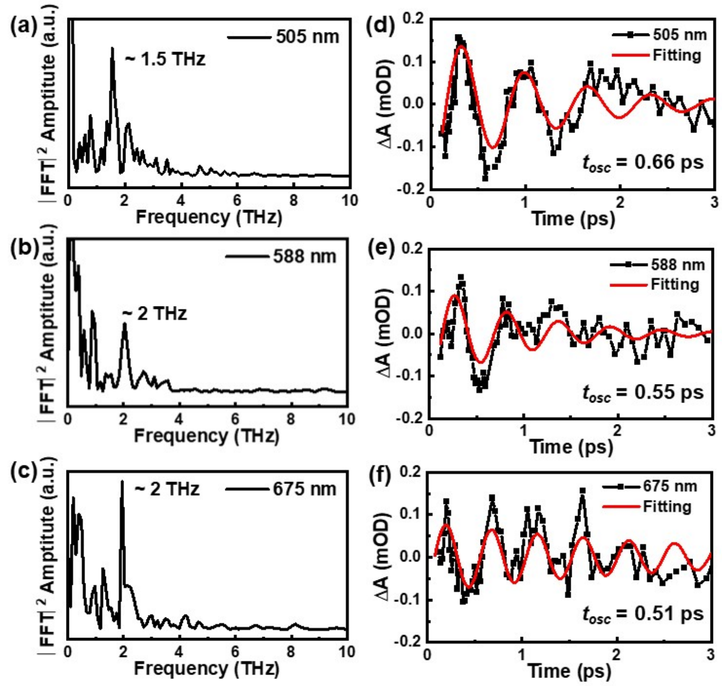

Fig. S6 The FFT results (a, b, c) and analysis of oscillatory components (d, e, f) on the coherent vibrational dynamics of $Au_{144}PET_{60}$ (295 K) probed at 505 nm, 588 nm, 675 nm.

S4. The TA profile of Au_{144} and Au_{25}

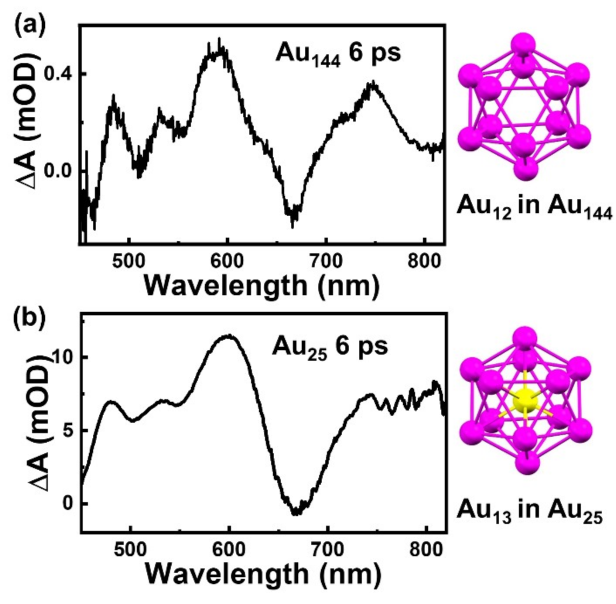

Fig. S7 The TA spectra of (a) $Au_{144}PET_{60}$ and (b) $[Au_{25}PET_{18}]^-$ probed at time delay of 6 ps, the data in (b) was reproduced from ref. 3. The structures of icosahedral Au_{12} core in Au_{144} and Au_{13} core in Au_{25} are shown for comparison.

S5. References

1. H. Qian and R. Jin, *Chem. Mater.*, 2011, **23**, 2209-2217.
2. M. Zhou, J. S. Sarmiento, C. Fei and H. Wang, *J. Phys. Chem. C*, 2019, **123**, 22095-22103.
3. M. Zhou, C. Yao, M. Y. Sfeir, T. Higaki, Z. Wu and R. Jin, *J. Phys. Chem. C*, 2018, **122**, 13435-13442.