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Supporting Information

Effects of Single Atom Doping on the Ultrafast Electron Dynamics of $M_1Au_{24}(SR)_{18}$ (M=Pd, Pt) Nanoclusters

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1. Transient absorption spectra of Pd_1Au_{24} with excitation of 785 nm.

With excitation of 785 nm, the femtosecond transient absorption of Pd_1Au_{24} cluster only exhibit two components after global analysis. Using 390 nm pump, both the metal core and surface ligands can be excited and excess energy will be dissipated via ultrafast relaxation within the metal core. With excitation of 785 nm, only the metal core can be excited to relatively low energy excited states so that the ultrafast relaxation is absent. From kinetic traces pumped at 785 nm, the ESA around 620 nm rises slowly during the first 20 ps accompanied by decay of ESA around 500 nm at the same time. It indicates that a new transient state is formed even at 785 nm excitation. Therefore, the few-picosecond component which can be seen under excitation at both 780 nm and 390 nm should be attributed to the core to shell relaxation.

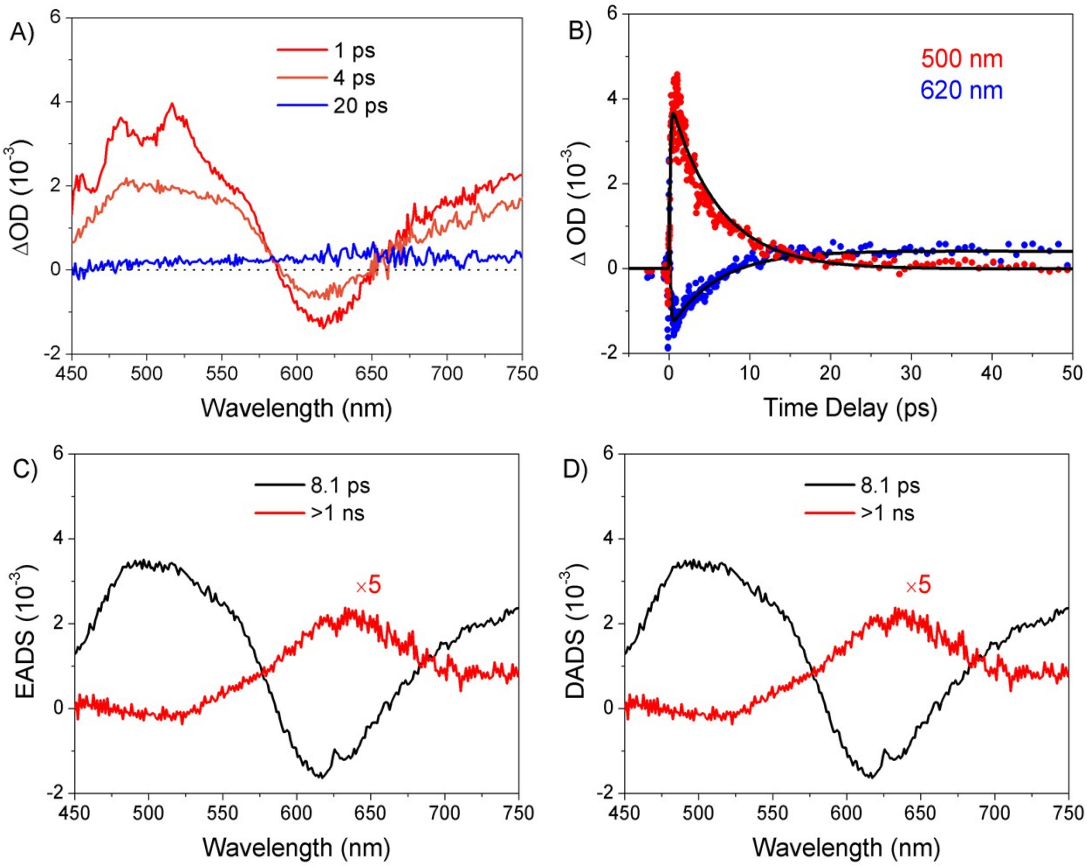

Figure S1. (A) Transient absorption spectra of Pd_1Au_{24} excited at 785 nm as a function of time delay. (B) Kinetic traces at selected wavelength and the fitting. (C) EADS and (D) DADS obtained from global analysis.

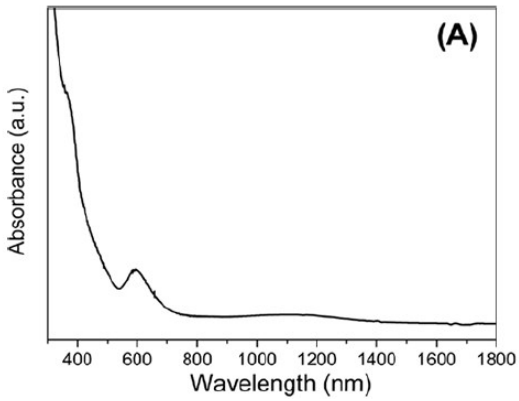

Figure S2. Steady state absorption of $Pt_1Au_{24}(SR)_{18}$ cluster from ref 1. Copyright American Chemical Society 2012.

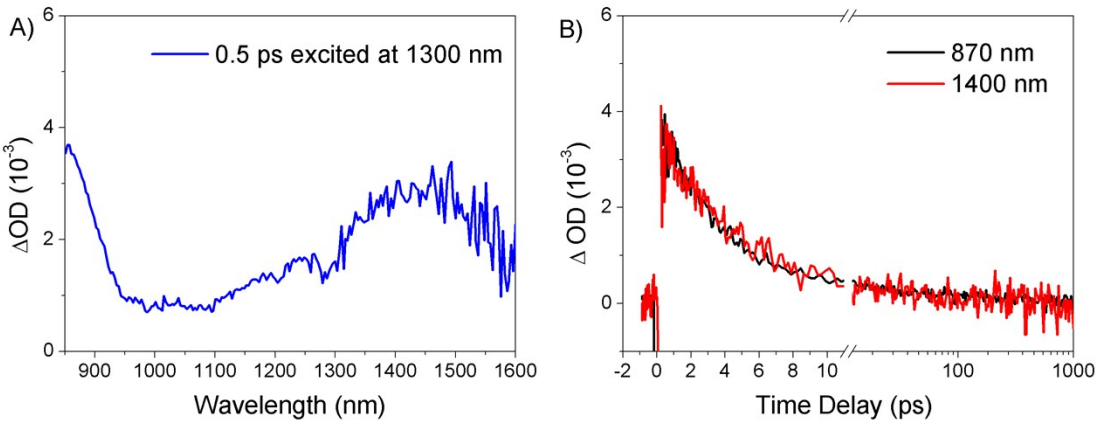

Figure S3. (A) Near infrared femtosecond TA spectra of Pt_1Au_{24} excited at 1300 nm. (B) Kinetic traces around 870 nm and 1400 nm.

Table S1. Atomic energy levels of orbitals in Au, Pd and Pt obtained from ref. 2.

		Ionization Energy (eV)
Au	6s	9.23
	5d	20.20
Pt	6s	8.96
	5d	18.56
Pd	4d	8.34

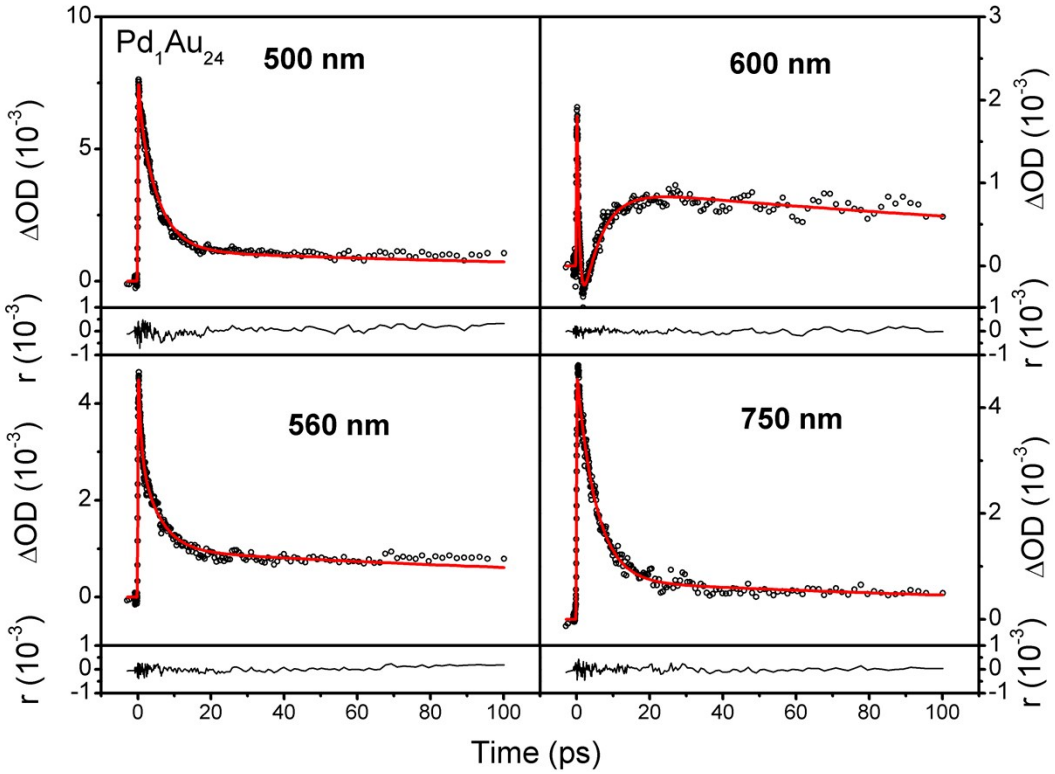

Figure S4. Selected kinetic traces, the corresponding fitting and residuals obtained from the global analysis of Pd_1Au_{24} cluster excited at 390 nm.

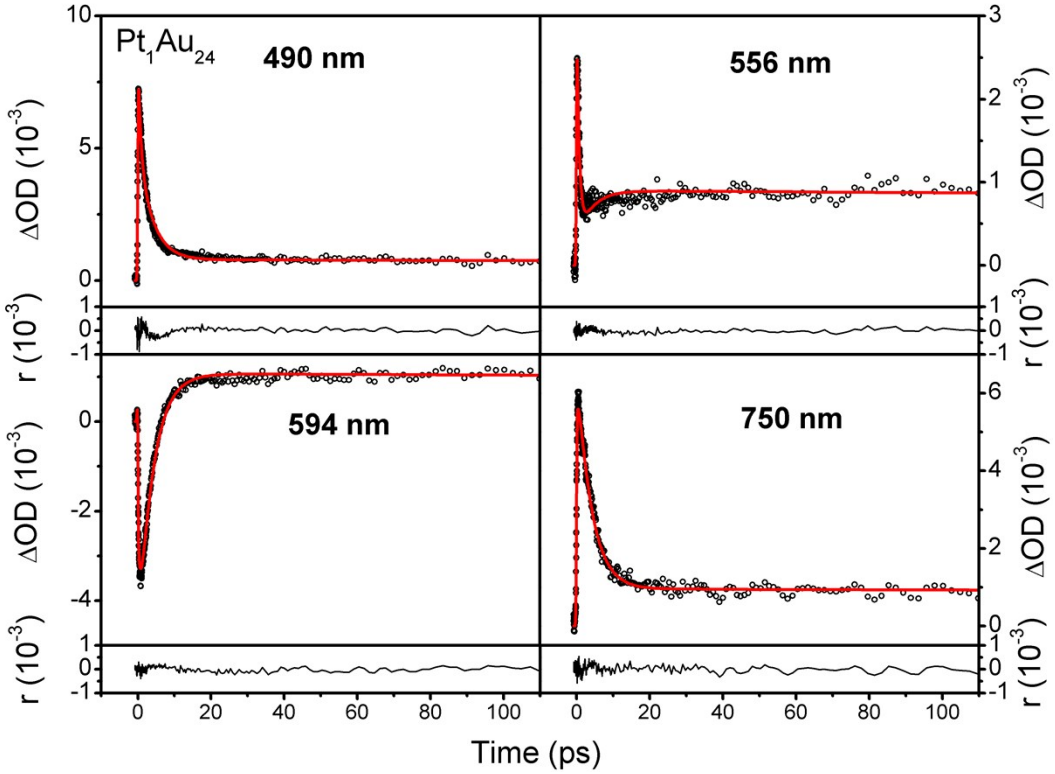

Figure S5. Selected kinetic traces, the corresponding fitting and residuals obtained from the

global analysis of Pt_1Au_{24} cluster excited at 390 nm.

References

(1) Qian, H.; Jiang, D..; Li, G.; Gayathri, C.; Das, A.; Gil, R. R.; Jin, R. Monoplatinum Doping of Gold Nanoclusters and Catalytic Application *J. Am. Chem. Soc.* 2012, *134*, 16159.

(2) Kramida, A., Ralchenko, Yu., Reader, J., and NIST ASD Team (2014). *NIST Atomic Spectra Database* (ver. 5.2), Available:http://physics.nist.gov/asd