## Supplementary Information

# Ultrafast Relaxation Dynamics of Phosphine-Protected, Rod-Shaped Au<sub>20</sub> Cluster: Interplay Between Solvation and Surface Trapping

Meng Zhou,<sup>*a*</sup> Saran Long,<sup>*a*</sup> Xiankai Wan,<sup>*b*</sup> Yang Li,<sup>*a*</sup> Yingli Niu,<sup>*a*</sup> Qianjin Guo, <sup>*a*\*</sup> Quan-Ming Wang<sup>*b*\*</sup> and Andong Xia<sup>*a*\*</sup>

<sup>a</sup>The State Key Laboratory of Molecular Reaction Dynamics, and Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, Beijing-100190, People's Republic of China

<sup>b</sup>State Key Laboratory of Physical Chemistry of Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, Fujian 361005, People's Republic of China

Corresponding authors: andong@iccas.ac.cn; guoqj@iccas.ac.cn; and qmwang@xmu.edu.cn

### **Table of Contents**

S1. The structure of the rod shaped Au <sub>20</sub> cluster	.3
S2. Details about the quantum chemical calculation	.4
S3. Quantum chemical calculation results	.5
S4. Transient absorption spectra fitted by multi Gaussian peaks	.7
S5. Oscillatory features	.9

#### S1. The structure of the rod shaped Au<sub>20</sub> cluster

The structure of  $[Au_{20}(PPhpy_2)_{10}Cl_4]^{2+}$  and the structure of  $[Au_{20}(PH_3)_6(PH_2py)_4Cl_4]^{2+}$  are shown in Fig. S1. It is seen that the cluster has a rod-shaped  $Au_{20}$  core protected by ten phosphine and four chloride ligands.



Fig. S1. Left: Structure of dicationic  $[Au_{20}(PPhpy_2)_{10}Cl_4]^{2+}$  (A1) cluster in  $[Au_{20}(PPhpy_2)_{10}Cl_4]Cl_2$  (1). Au atoms are colored yellow, P atoms orange, N atoms blue, Cl atoms green, C atoms dark grey, H atoms light grey. Right: Structure of  $[Au_{20}(PH_3)_6(PH_2py)_4Cl_4]^{2+}$  (A2).

#### S2. Details about the quantum chemical calculation

The stable ground state geometry was optimized using the PBE function with the LANL2DZ basis set for Au and the 6-31G(d,p) basis set for other atoms.<sup>1</sup> The vibrational frequency calculations and the single-point calculations were performed on the optimal geometry. The single-point calculations of the excited states of **A2** were computed by the time-dependent DFT (TD-DFT) at the same level and basis set. All the calculation were performed using Gaussian 03 package.<sup>2</sup>

The CDDs ( $\Delta \rho_{\mu\mu}$ ) and TDs ( $\rho_{\mu0}$ ) are given by:

$$\Delta \rho_{\mu\mu}(\mathbf{r}) = \sum_{a,i,j} C_{\mu\alpha i} C_{\mu\alpha j} \varphi_i(\mathbf{r}) \varphi_j(\mathbf{r}) - \sum_{a,b,i} C_{\mu\alpha i} C_{\mu b i} \varphi_a(\mathbf{r}) \varphi_b(\mathbf{r})$$
$$\rho_{\mu 0}(\mathbf{r}) = \sum_{a,i} C_{\mu\alpha i} \varphi_a(\mathbf{r}) \varphi_i(\mathbf{r})$$

where  $C_{\mu\alpha i}$  represents the  $\mu$ th eigenvector of the Hamiltonian in the basis of the occupied Hartree-Fock molecular orbital  $\varphi_i(\mathbf{r})$  and the unoccupied orbitals  $\varphi_a(\mathbf{r})$ . The CDD visualizes the difference in electron density upon electronic excitation between two electronic states (in this work between the ground state and the singlet excited state) while TD represents the distribution of transition dipole moment which indicates the region being excited during electronic transition. <sup>3-6</sup> The CDD spectra, TD spectra and the ground state frequency calculation were computed by the time-dependent DFT (TD-DFT) method using the PBE function,<sup>1</sup> with the LANL3DZ basis set for Au and the 6-31G(d,p) basis set for all other atoms.

#### S3. Quantum chemical calculation results

Fig. S2 shows the frontier molecular orbital of **A2**. From the molecular orbital, it is seen that the density of HOMO is mainly localized on the core while the density of LUMO is distributed over the cluster including the surface ligand shell. The results indicate the charge transfer from the Au core to the surface ligands. Table S1 shows the Transition Density (TD) and Charge Difference Density (CDD) results.



**Fig. S2.** The shape of HOMO and LUMO orbitals of **A2**. Green and red correspond to the different phases of the molecular wave functions for the HOMO and LUMO.

**Table S1. Transiton Density (TD) and Charge Difference Density (CDD) results.** Left: Red color represents positive while green negative. Right: Red color represents electron density while green color represents hole density.

	Transition Density	Charge Difference Density
absorption S1 (1.2 eV)		
absorption S16 (1.9 eV)		
absorption S112 (2.58 eV)		

#### S4. Transient absorption spectra fitted by multi Gaussian peaks

Broad band transient absorption peaks were fitted using Gaussian peaks (Fig. S3). The position of GSB around 480 nm (blue) was fixed during the fitting procedure. Solvent-dependent peak shift from ICT (ICT') around 550 nm (green) can be seen clearly. The position of ESA from surface trapping state around 440 nm (black) was not shifted during the measurement. The fitting results show that the transient absorption spectra exhibit prominent solvent-dependent ESA peak shift.





**Fig. S3.** Selected transient spectra (black dots) and fits (red line) of 1 in methanol (a), ethanol (b), *n*-propanol (c) at three exampled decay time, 0.3 ps, 5 ps, 80 ps. Dashed lines are guides to the eye for identifying the spectral shift.



**Fig. S4.** Kinetic traces and fits around 440 nm and 550 nm at initial time delay in methanol. The sharp peak in the 440 nm kinetics is due to coherent raman signal around time zero.

#### **S5. Oscillatory features**

Coherent oscillations were observed only in methanol. Fig. S5 shows the 2D plot of the transient absorption of **1** in methanol. The red to yellow part represents the ESA while the blue part stands for GSB. Modulation can clearly be seen around these peaks, where strong wavy features dominate down to about 20 ps after excitation. There is a 180 degree phase shift of oscillations on two sides of the GSB. Fig. S6 shows the calculated ground state raman spectra of **1** in the gas phase. The radial breathing mode, which mainly contributes to the coherent oscillation, is located at 104.4 cm<sup>-1</sup>, much higher than the observed vibrational frequency (21cm<sup>-1</sup>). It is suggested that he lower frequency observed in the experiments is due to the mass increase of methanol molecules adsorbed around the Au<sub>20</sub> cluster surface.



Fig. S5. Chirp corrected contour plot of transient absorption of 1 in methanol from -2 ps to 25 ps.



**Fig. S6.** Calculated Raman spectra of  $[Au_{20}(PH_3)_6(PH_2py)_4Cl_4]^{2+}$ . Symmetric modes are indicated with arrows, the radial breathing mode is located at 104.44 cm<sup>-1</sup>.

#### **References:**

- 1. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865-3868.
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci and G. A. Petersson, *Gaussian 03, Revision E.01;*, Gaussian, Inc.: Wallingford, CT, 2004.
- 3. M. T. Sun, J. Chem. Phys., 2006, **124**, 054903.
- 4. M. T. Sun, P. Kjellberg, F. C. Ma and T. Pullerits, *Chem. Phys. Lett.*, 2005, 401, 558-564.
- 5. N. K. Persson, M. T. Sun, P. Kjellberg, T. Pullerits and O. Inganas, *J. Chem. Phys.*, 2005, **123**, 204718.
- 6. X. N. Ma, L. Y. Yan, X. F. Wang, Q. J. Guo and A. D. Xia, *Phys. Chem. Chem. Phys.*, 2011, **13**, 17273-17283.