Supporting Information

How a Single Electron Affects the Properties of the "Non-Superatom" Au_{25} Nanoclusters

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1. The crystal structures of the Au_{25}-II and Au_{25}-I nanoclusters.

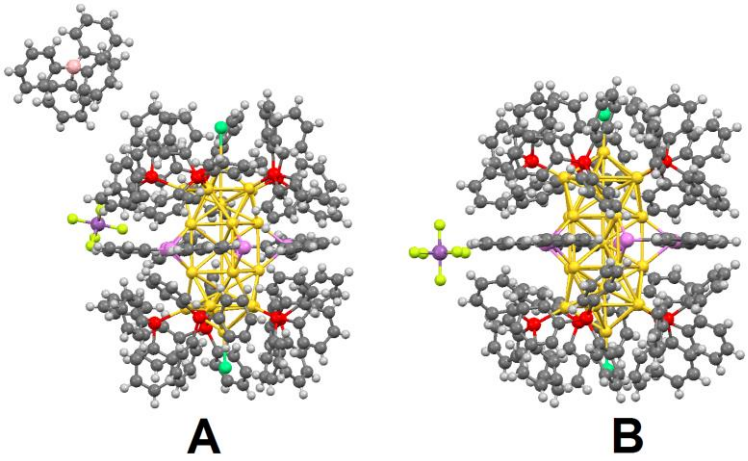

Figure S1. The total crystal structures of the **Au_{25}-II** and **Au_{25}-I** nanoclusters (color lables: Au = yellow; P = red; Cl = green; Se = violet; C = gray; H = white; F = kelly; Sb = purple; B = pink.)

2. The Time-dependent UV-vis absorption spectra.

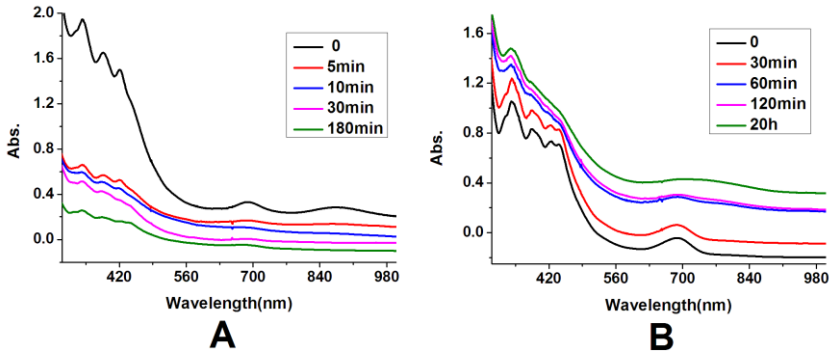

Figure S2. Time-dependent UV-vis absorption spectra of **Au_{25}-I** nanoclusters reacting with H_2O_2 (A) and **Au_{25}-II** nanoclusters reacting with $NaBH_4$ (B).

3. The assemble packing of Au_{25}-II and Au_{25}-I nanoclusters.

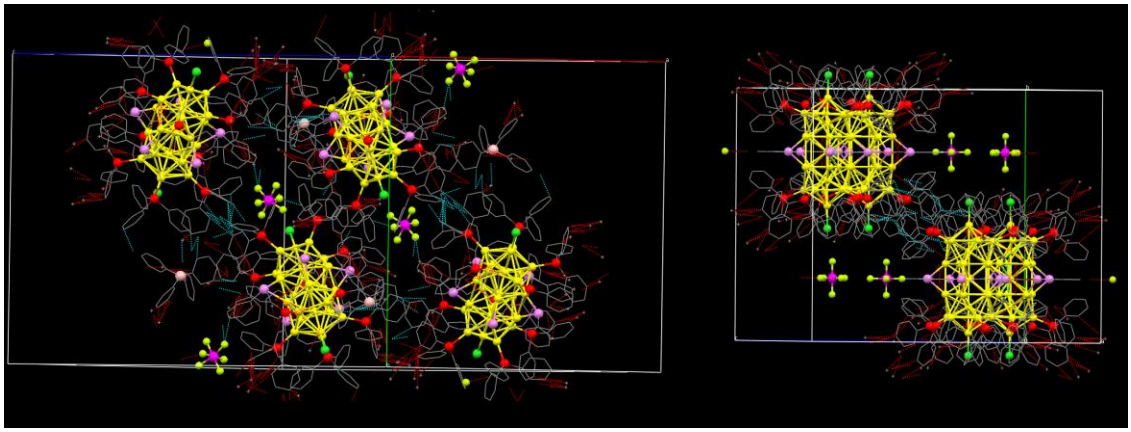

Figure S3. The assemble packing of **Au_{25}-II** (left) and **Au_{25}-I** (right) nanoclusters: The weak interactions between Ph_4B^- ions and rod-like **Au_{25}-II** nanoclusters (left) has been marked by the dot line. By constrast, the weak forces between SbF_6^- ions and rod-like **Au_{25}-I** nanoclusters are hardly achieved (right).

4. The optical gaps.

According to the mass-energy equation, we found the optical gap of the **Au_{25}-II** and **Au_{25}-I** nanoclusters is 1.62 eV and 1.21 eV, respectively.

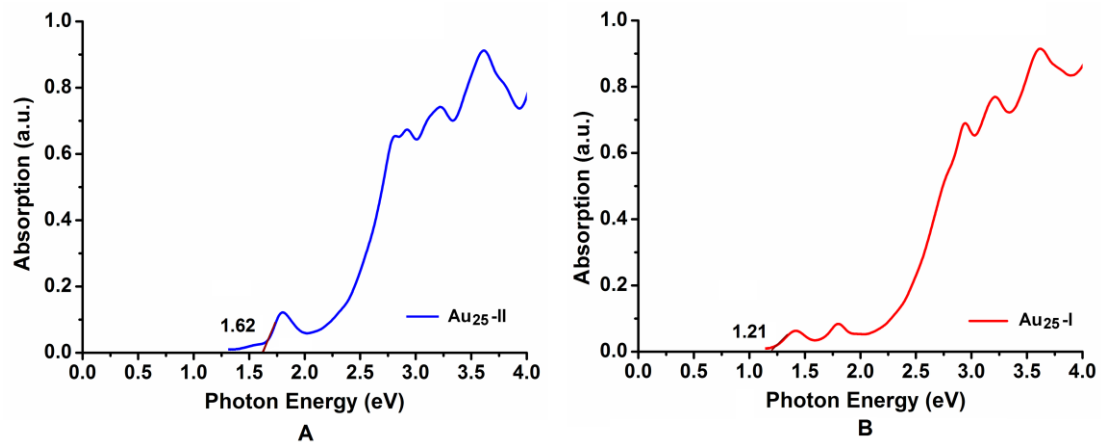

Figure S4. The optical gaps of the **Au_{25}-II** (A) and **Au_{25}-I** (B) nanoclusters.

5. TD-DFT analysis.

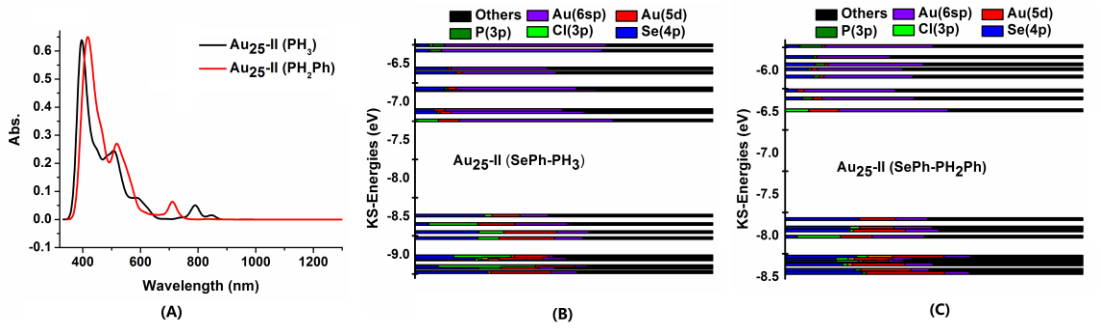

Figure S5. (A) Comparison of theoretical optical curves of **Au_{25}-II** (PH_3) and **Au_{25}-II** (PH_2Ph) nanoclusters. Comparison of the component of KS orbitals of **Au_{25}-II** (PH_3) (B) and **Au_{25}-II** (PH_2Ph) (C) nanoclusters.

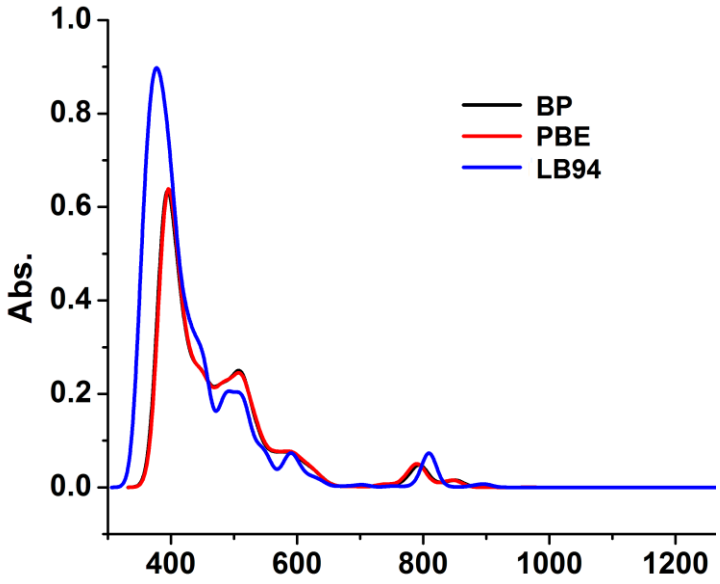

Figure S6. The theoretical optical curves with the different theoretical methods such as BP (black line), PBE (red line), LB94 (blue line).

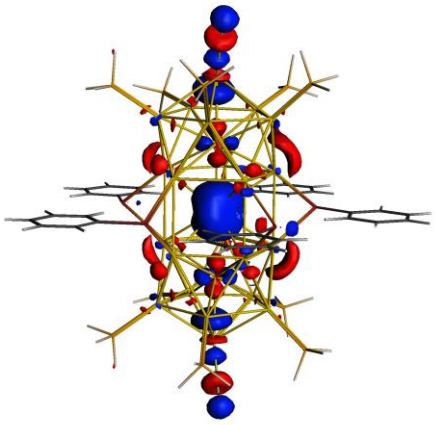

Figure S7. The distribution of electron density of SMO in the **Au_{25}-I** nanocluster.

6. X-ray Crystallographic Determination

Table S1. Crystal Data and Structure Refinement for the $[Au_{25}(PPh_3)_{10}(SePh)_5Cl_2](SbF_6)$ Nanocluster.

Identification code	$[Au_{25}(PPh_3)_{10}(SePh)_5Cl_2](SbF_6)$
Empirical formula	$C_{210}H_{175}Au_{25}Cl_2F_6P_{10}SbSe_5$
Formula weight	8633.81 g/mol
Temperature	291(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic P n m a
Unit cell dimensions	a = 30.927(4) Å α= 90°
	b = 26.416(3) Å β = 90°
	c = 31.341(4) Å γ =90°
Volume	25604(5) $Å^3$
Z, Calculated density	4, 2.240 Mg/mm^3
Absorption coefficient	15.200 mm^{-1}
F(000)	15476
Crystal size	0.24 x 0.22 x 0.20 mm^3
Theta range for data collection	0.92 to 27.45°
index ranges	0<=h<=39, 0<=k<=33, 0<=l<=40
Reflections collected	221040
Completeness to theta = 27.45	98.5%
Absorption correction	15.20
Refinement method	SHELXTL
Max. and min. transmission	0.15 and 0.12
Data / restraints / parameters	29451 / 0 / 1228
Goodness-of-fit on F^2	1.065
Final R indices [I>2sigma(I)]	R1 = 0.0503, wR2 = 0.1211
R indices (all data)	R1 = 0.0501, wR2 = 0.1215
Largest diff. peak and hole	1.713 and -2.305 e.$Å^{-3}$

Table S2. Crystal Data and Structure Refinement for the $[Au_{25}(PPh_3)_{10}(SePh)_5Cl_2](SbF_6)(BPh_4)$ Nanocluster.

Identification code	$[Au_{25}(PPh_3)_{10}(SePh)_5Cl_2](SbF_6)(BPh_4)$
Empirical formula	$C_{234}H_{195}Au_{25}Cl_2F_6P_{10}SbSe_5B$
Formula weight	8953.02 g/mol
Temperature	291(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic P2(1)/c
Unit cell dimensions	a = 27.378(2) Å α= 90.00°
	b = 29.361(2) Å β = 133.273(2)°
	c = 40.7368(16) Å γ =90.00°
Volume	23843(3) $Å^3$
Z, Calculated density	4, 2.494 Mg/mm^3
Absorption coefficient	16.328 mm^{-1}
F(000)	16152
Crystal size	0.31 x 0.26 x 0.17 mm^3
Theta range for data collection	0.98 to 27.45°
index ranges	-35<=h<=25, 0<=k<=38, 0<=l<=52
Reflections collected	233703
Completeness to theta = 27.45	100%
Absorption correction	16.328
Refinement method	SHELXTL
Max. and min. transmission	0.03 and 0.02
Data / restraints / parameters	54493 / 0 / 2557
Goodness-of-fit on F^2	1.009
Final R indices [I>2sigma(I)]	R1 = 0.0549, wR2 = 0.1375
R indices (all data)	R1 = 0.0564, wR2 = 0.1379
Largest diff. peak and hole	1.779 and -1.585 e.$Å^{-3}$