Electronic Supplementary Information

Modulating Photo-Luminescence of Au_2Cu_6 Nanocluster via Ligand-Engineering

Xi Kang, Xiaowu Li,* Haizhu Yu, Ying Lv, Guodong Sun, Yangfeng Li, Shuxin Wang, and Manzhou Zhu*
Department of Chemistry and Center for Atomic Engineering of Advanced Materials, Anhui Province Key Laboratory of Chemistry for Inorganic/Organic Hybrid Functionalized Materials, Anhui University, Hefei, Anhui 230601, China.

Chemicals

All reagents were purchased from Acros Organics or Sigma-Aldrichand used without further purification. Tetrachloroauric (III) acid ($HAuCl_4 \bullet 3H_2O$, 99.99% metals basis), copper(I) chloride (CuCl, 99.99%, metals basis), adamantane-1-thiol ($C_{10}H_{15}SH$, 95%), triphenylphosphine (PPh_3, 98%), tris(4-methoxyphenyl)phosphine ($P(Ph\text{-}OMe)_3$, 98%), tris(4-fluorophenyl)phosphine ($P(Ph\text{-}F)_3$, 98%), sodium borohydride ($NaBH_4$, 98%). Toluene (Tol, HPLC grade, Aldrich), methanol (CH_3OH, HPLC, Aldrich), acetonitrile (CH_3CN, HPLC grade, Aldrich), methylene chloride (CH_2Cl_2, HPLC grade, Aldrich), aether ($(CH_3CH_2)_2O$, A.R., Sinopharm Chemical Reagent Co. Ltd.). Pure water was purchased from Wahaha Co. Ltd. All reagents were used as received without further purification. All glassware was thoroughly cleaned with aqua regia ($HCl:HNO_3$ = 3:1 vol%), rinsed with copious pure water, and then dried in an oven prior to use.

Characterization

All UV-vis absorption spectra of nanoclusters dissolved in CH_2Cl_2 were recorded using an Agilent 8453 diode array spectrometer, whose background correction was made using a CH_2Cl_2 blank. Solid samples were dissolved in CH_2Cl_2 to make a dilute solution firstly with a subsequent transformation to a 1 cm path length quartz cuvette, followed by spectral measurements. Thermogravimetric analysis (TGA) was carried out on a thermogravimetric analyzer (DTG-60H, Shimadzu Instruments, Inc.) with 5 mg of nanocluster in a SiO_2 pan at a heating rate of 10 K min^{-1} from room temperature (about 298 K) to 1073 K. X-ray photoelectron spectroscopy (XPS) measurement was performed on a Thermo ESCALAB 250, configured with a monochromated AlKα (1486.8 eV) 150W X-ray source, 0.5 mm circular spot size, a flood gun to counter charging effects, and the analysis chamber base pressure lower than $1x10^{-9}$ mbar, data were collected with FAT=20 eV. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) measurements were performed on an Atomscan Advantage instrument made by Thormo Jarrell Ash Corporation (USA). The nanoclusters were digested by concentrated nitric acid and the concentration of the nanoclusters were set to 0.5 mg L^{-1} approximately. Photoluminescence spectra were measured on a FL-4500 spectrofluorometer with the same optical density (OD) ~0.05. In these experiments, the nanoclusters solution were prepared in CH_2Cl_2 at a concentration of less than 1 mg mL^{-1}. Absolute quantum yields (QY) were measured with dilute solutions of nanoclusters (0.05 OD absorption at 480 nm) on HORIBA FluoroMax-4P. The data collection for single crystal X-ray diffraction was carried out on a Bruker Smart APEX II CCD diffractometer under liquid nitrogen flow at 173 K, using graphite-monochromatized Cu Kα radiation (λ = 1.54178 Å). Data reductions and absorption corrections were performed using the SAINT and SADABS programs, respectively. The structure was solved by direct methods and

refined with full-matrix least squares on F^2 using the SHELXTL software package. All non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were set in geometrically calculated positions and refined isotropically using a riding model.

Syntheses

Synthesis of $Au_2Cu_6(S\text{-}Adm)_6(P(Ph\text{-}OMe)_3)_2$ nanocluster

Briefly, CuCl (0.0198 g, 0.2 mmol) was dissolved in 5mL CH_3CN and 5 mL CH_3OH, and AdmSH (0.1346 g, 0.8 mmol) was dissolved in 5 mL toluene. These two solutions were blended in a 100 mL tri-neck round bottom flask. The solution was vigorously stirred (~1200 rpm) with a magnetic stirring for 15 min. Then, $[AuP(Ph\text{-}OMe)_3Cl]$ (0.24 g, 0.4 mmol) was dissolved in 1 mL ice-cold toluene, and $NaBH_4$ (80 mg, ~5 equivalent per mole of gold) was dissolved in 1 mL ice-cold water. Both solvents were added drop-wise to the solution at the same time under vigorous stirring. The reaction was allowed to proceed for 60 hours under N_2 atmosphere. After that, the resulting solution mixture was centrifuged to obtain the solids, which was then washed several times with toluene. Then the final product was dissolved in CH_2Cl_2, and used to crystallize directly. The as-prepared nanocluster was crystallized in CH_2Cl_2/CH_3OH at room temperature (~3 days); dark red crystals were collected and subjected to X-ray diffraction analysis to determine the structure.

Syntheses of $Au_2Cu_6(S\text{-}Adm)_6(PPh_3)_2$ and $Au_2Cu_6(S\text{-}Adm)_6(P(Ph\text{-}F)_3)_2$ nanoclusters

The $Au_2Cu_6(S\text{-}Adm)_6(PPh_3)_2$ and $Au_2Cu_6(S\text{-}Adm)_6(P(Ph\text{-}F)_3)_2$ nanoclusters were prepared by the same method as that of the $Au_2Cu_6(S\text{-}Adm)_6(P(Ph\text{-}OMe)_3)_2$ nanocluster. The mole ratio of PPh_3 or $P(Ph\text{-}F)_3$ was the same as that of $P(Ph\text{-}OMe)_3$ ligand.

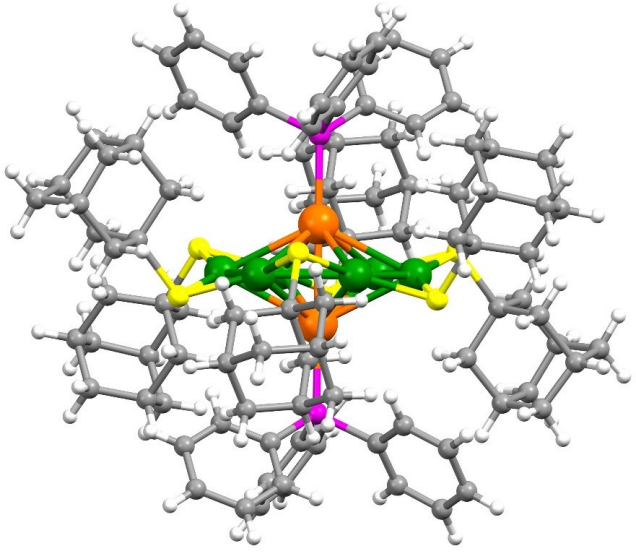

Fig. S1 The total structure of $Au_2Cu_6(S\text{-}Adm)_6(PPh_3)_2$. Color legends: orange, Au; green, Cu; yellow, s; purple, P; gray, C and light gray, H.

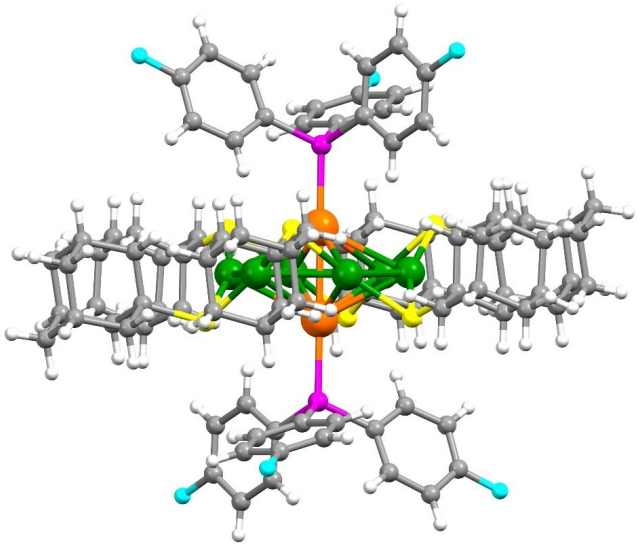

Fig. S2 The total structure of $Au_2Cu_6(S\text{-}Adm)_6(P(Ph\text{-}F)_3)_2$. Color legends: orange, Au; green, Cu; yellow, s; purple, P; cyan, F; gray, C and light gray, H.

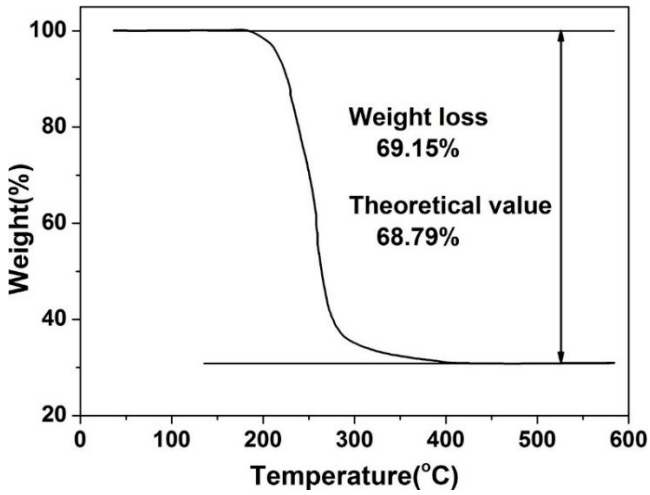

Fig. S3 TGA result of the $Au_2Cu_6(S\text{-}Adm)_6(P(Ph\text{-}OMe)_3)_2$ nanocluster.

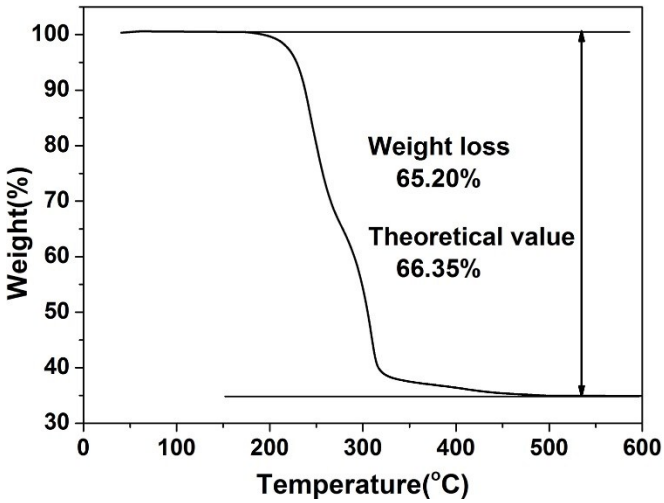

Fig. S4 TGA result of the $Au_2Cu_6(S\text{-}Adm)_6(PPh_3)_2$ nanocluster.

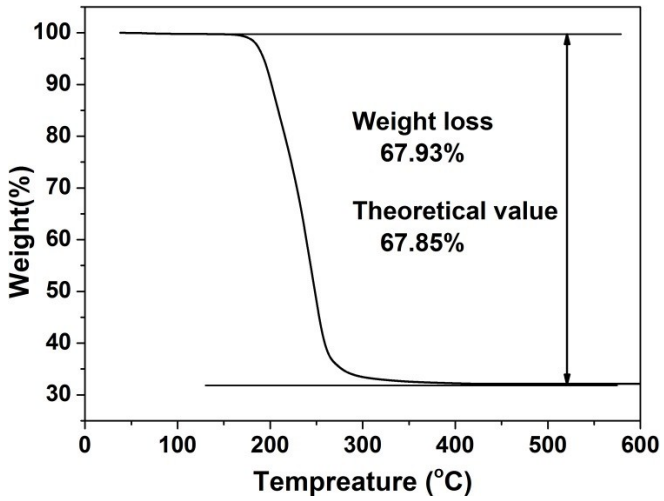

Fig. S5 TGA result of the $Au_2Cu_6(S\text{-}Adm)_6(P(Ph\text{-}F)_3)_2$ nanocluster.

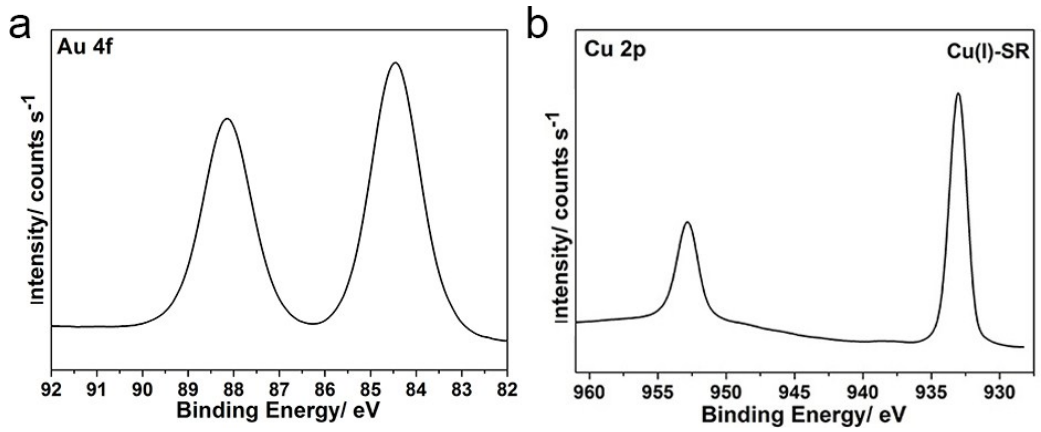

Fig. S6 X-ray photoelectron spectroscopy (XPS) of a) Au 4f, b) Cu 2p in $Au_2Cu_6(S\text{-}Adm)_6(P(Ph\text{-}OMe)_3)_2$ nanocluster.

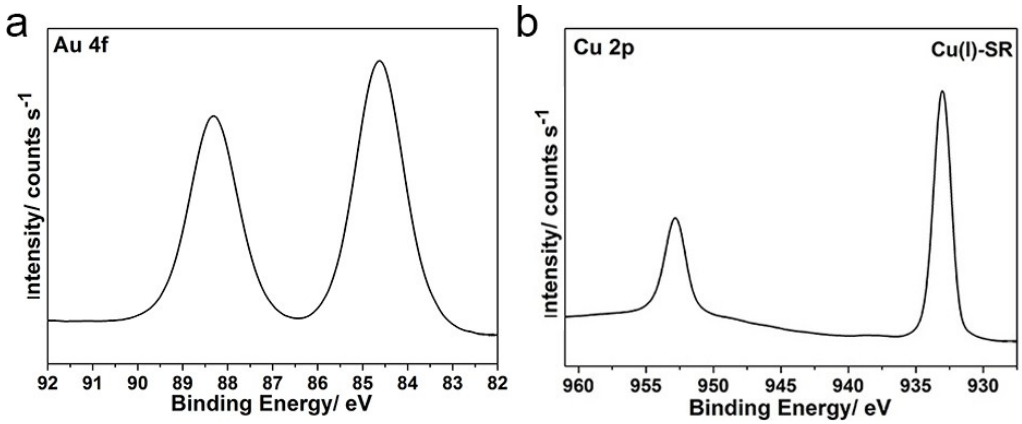

Fig. S7 X-ray photoelectron spectroscopy (XPS) of a) Au 4f, b) Cu 2p in $Au_2Cu_6(S\text{-}Adm)_6(PPh_3)_2$ nanocluster.

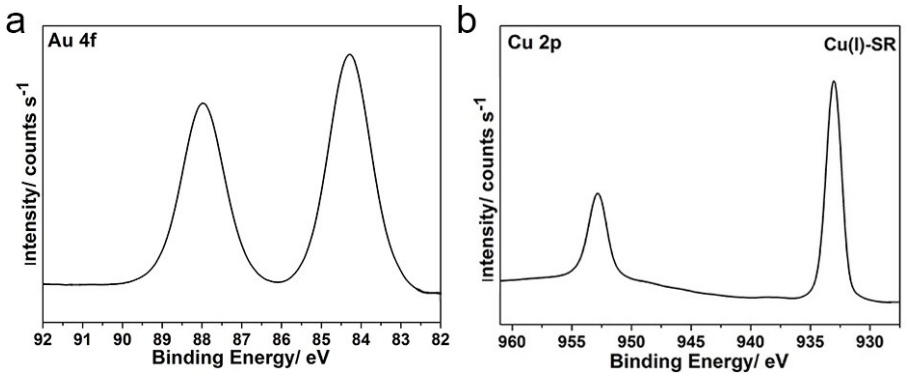

Fig. S8 X-ray photoelectron spectroscopy (XPS) of a) Au 4f, b) Cu 2p in Au_2Cu_6(S-Adm)$_6$(P(Ph-F)$_3$)$_2$ nanocluster.

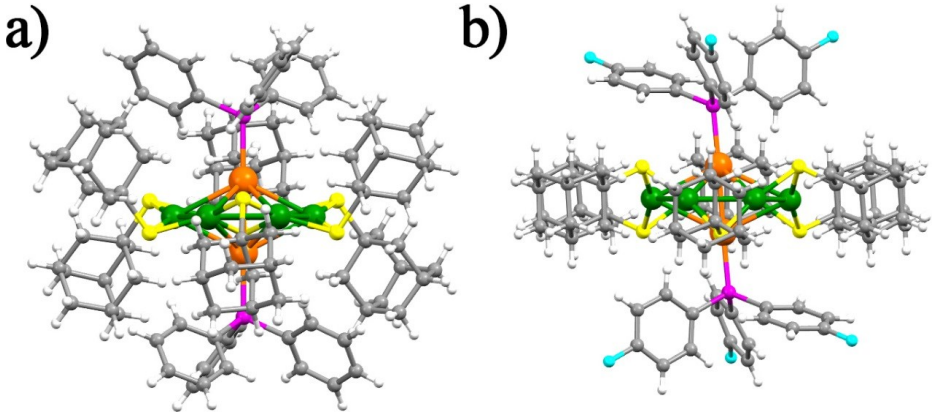

Fig. S9 Structure comparison of a) Au_2Cu_6(S-Adm)$_6$(PPh_3)$_2$ and b) Au_2Cu_6(S-Adm)$_6$(P(Ph-F)$_3$)$_2$. Color legends: orange, Au; green, Cu; yellow, s; purple, P; cyan, F; gray, C and light gray, H.

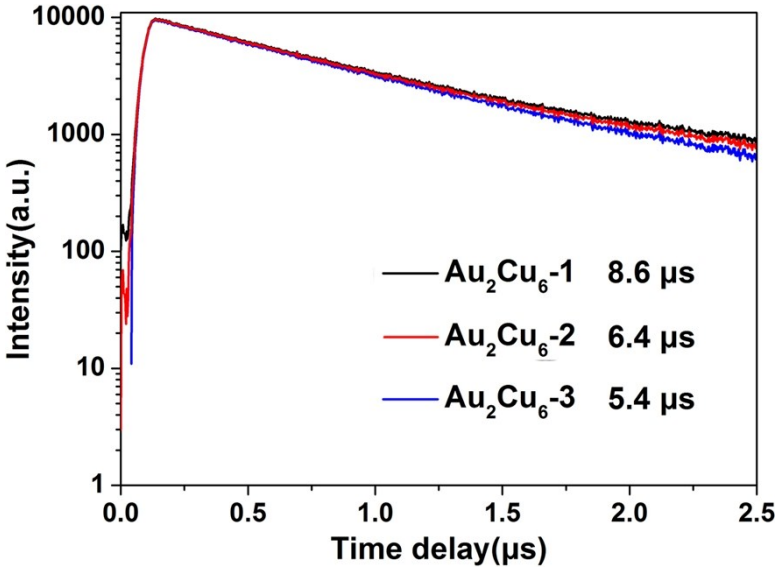

Fig. S10 The analyses on fluorescence lifetime of three Au_2Cu_6(S-Adm)$_6$(PR_3)$_2$ nanoclusters (Black line: R=Ph-OMe; Red line: R=Ph; Blue line: R=Ph-F).

Table S1: Crystal data and structure refinement for the $Au_2Cu_6(S\text{-}Adm)_6(PPh_3)_2$ nanocluster.

Compound reference	$Au_2Cu_6(S\text{-}Adm)_6(PPh_3)_2$
Empirical formula	C96H120Au2Cu6P2S6
Formula weight	2303.39
Temperature	173 K
Wavelength	1.54178 Å
Crystal system	Trigonal
Space group	R -3
Unit cell dimensions	A=20.9938(7) Å α=90°
	B=20.9938(7) Å β=120°
	C= 18.1449(7) Å γ=90°
Volume	6925.8(5) $Å^3$
Z	3
Density (calculated)	1.657 Mg m^{-3}
Absorption coefficient	9.222 mm^{-1}
F(000)	3462
Crystal size	0.03 × 0.03 × 0.02 mm^3
Theta range for data collection	3.44 to 66.78°
Index ranges	-24<=h<=24, -22<=k<=24, -21<=l<=21
Reflections collected	13540
Independent reflections	2592
Absorption correction	Multi scan
Refinement method	SHELXL-2013 (Sheldrick 2013)
Data / restraints / parameters	2592 / 360 / 169
Goodness-of-fit on F2	0.916
Final R indices [I>2sigma(I)]	R1=0.0473, wR2=0.1464
R indices (all data)	R1=0.0560, wR2=0.1550

Table S2: Crystal data and structure refinement for the $Au_2Cu_6(S\text{-}Adm)_6(P(Ph\text{-}F)_3)_2$ nanocluster.

Compound reference	$Au_2Cu_6(S\text{-}Adm)_6(P(Ph\text{-}F)_3)_2$	
Empirical formula	C96H114Au2Cu6F6P2S6	
Formula weight	2673.52	
Temperature	173 K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	A=13.5650(5) Å	α=111.329(2)°
	B=15.6970(6) Å	β=98.629(2)°
	C=15.8108(6) Å	γ=114.913(2)°
Volume	2654.64(18) $Å^3$	
Z	1	
Density (calculated)	1.672 Mg m^{-3}	
Absorption coefficient	9.878 mm^{-1}	
F(000)	1327	
Crystal size	0.03 × 0.02 × 0.01 mm^3	
Theta range for data collection	5.06 to 72.65°	
Index ranges	-16<=h<=15, -18<=k<=18, -17<=l<=16	
Reflections collected	11016	
Independent reflections	7655	
Absorption correction	Multi scan	
Refinement method	SHELXL-2013 (Sheldrick 2013)	
Data / restraints / parameters	7655 / 1194 / 560	
Goodness-of-fit on F2	1.057	
Final R indices [I>2sigma(I)]	R1=0.0670, wR2=0.1805	
R indices (all data)	R1=0.0800, wR2=0.1928	

Table S3: The atomically ratio of Au and Cu in Au_2Cu_6 NCs calculated from inductively coupled plasma (ICP) and X-ray photoelectric spectroscopy (XPS) measurements.

Measurement	Au (%)	Cu (%)
ICP result on**Au_2Cu_6-1**	24.5%	75.5%
XPS result on **Au_2Cu_6-1**	24.8%	75.2%
ICP result on **Au_2Cu_6-2**	21.7%	78.3%
XPS result on **Au_2Cu_6-2**	22.2%	77.8%
ICP result on **Au_2Cu_6-3**	24.2%	75.8%
XPS result on **Au_2Cu_6-3**	24.9%	75.1%