Supporting Information

## Single Ligand Exchange on an Au-Cu Bimetallic Nanocluster and Mechanism

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## 1. Experimental

**Chemicals.** All reagents and solvents were commercially available and used as received without further purification, including selenophenol (PhSeH,  $\geq$ 99.9%), tetrachloroauric(III) acid (HAuCl<sub>4</sub>·3H<sub>2</sub>O,  $\geq$ 99.99% metals basis), tetraoctylammonium bromide (TOAB,  $\geq$ 98%), sodium borohydride (NaBH<sub>4</sub>,  $\geq$ 98%), dichloromethane ( $\geq$ 99.9%), methanol ( $\geq$ 99.9%), 2-(diphenylphosphino) pyridine (PPh<sub>2</sub>Py,  $\geq$ 98.8%), acetylacetonate copper (II) (Cu(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub>,  $\geq$ 98.8%) and pure water.

Synthesis of the Au<sub>13</sub>Cu<sub>4</sub> nanocluster. Briefly, HAuCl<sub>4</sub>·3H<sub>2</sub>O (0.1576 g, 0.4 mmol) was dissolved in 5 mL nanopure water, and TOAB (0.2558 g, 0.47 mmol) was dissolved in 10 mL dichloromethane. These two solutions were combined in a 25 mL tri-neck round bottom flask. The solution was vigorously stirred (~1100 rpm) with a magnetic stir bar to facilitate phase transfer of Au(III) salt into the organic phase. After ~15 min, phase transfer was completed, leaving a clear aqueous phase at the bottom of the flask; the aqueous was then removed. After that, PPh<sub>2</sub>Py (0.31g, 1.2 mmol) was added into the dichloromethane solution of Au(III). Then Cu(II) (0.027g, 1.2 mmol) was added to the dichloromethane solution of the Au(PPh<sub>2</sub>Py) complex, and at the same time, 10 mL CH<sub>3</sub>OH was added into the solution; the solution color changed to light blue. After ~10min, 5 mL aqueous solution of NaBH<sub>4</sub> (0.08 g, 2.11 mmol) was rapidly added. After ~30 min, PhSeH (50 µL, 4.76 mmol) was directly added to the organic solution without any treatment. Then, the reaction was allowed to proceed for ~48 h. The product was washed several times with CH<sub>3</sub>OH to remove the redundant PhSeH, PPh<sub>2</sub>Py and by-products until the optical absorption spectrum showed two stepwise peaks at 375 and 500 nm, which gave rise to pure Au<sub>13</sub>Cu<sub>4</sub> nanoclusters.

**Characterization.** The crystal of  $[Au_{13}Cu_4(PPh_2Py)_3(SePh)_9]$  nanoclusters were dissolved in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) for spectral measurements. UV-vis spectroscopic studies were carried out with an Agilent HP8453 diode array spectrometer. Thermogravimetric analysis (TGA) was carried out on a thermogravimetric analyzer (DTG-60H, Shimadzu Instruments, Inc.) with 4.613 mg of clusters in a SiO<sub>2</sub> pan at a heating rate of 10 °C min<sup>-1</sup>. Electrospray ionization (ESI) mass spectra were acquired using a Bruker Q-TOF mass spectrometer equipped with ESI source. The sample was dissolved in methylbenzene (~1 mg  $\cdot$  ml<sup>-1</sup>). The sample was infused at 180 µL  $\cdot$  h<sup>-1</sup> directly. The source

temperature was kept at 50 °C with the spray voltage keeping at 4 kV.

**Crystal structure determination and refinement.** A suitable crystal was selected and performed on a Bruker X8 Prospector Ultra diffractometer. The crystal was kept at 230.0 K during data collection. Using Olex2<sup>[1]</sup>, the structure was solved with the ShelXT<sup>[2]</sup> structure solution program using Direct Methods and refined with the ShelXL<sup>[3]</sup> refinement package using Least Squares minimisation.

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**Cryogenic absorption and photoluminescence measurements.** Steady state absorption and temperature-dependent absorption measurements were performed using a Shimadzu UV-3600 plus absorption spectrometer. PL and temperature dependent PL were performed on a Fluorolog- 3 spectrofluorometer (Horiba Jobin Yvon). An OptistatCF2 cryostat (Oxford Instruments), temperature controller, and a pressure pump were used to perform the temperature dependent experiments from 80 to 300 K. 2-Methyltetrahydrofuran (99%, Alfa Aesar) were used as the solvents for temperature-dependence measurements.

**Femtosecond pump-probe experiments.** Femtosecond transient absorption spectroscopy were carried out using a commercial Ti:Sapphire laser system (SpectraPhysics, 800 nm, 100 fs, 3.5 mJ, 1 kHz). Pump pulse was generated using a commercial optical parametric amplifier (LightConversion). A small portion of the laser fundamental was focused into a sapphire plate to produce supercontinuum in the visible region, which overlapped in time and space with the pump. The diameter of the pump beam was 0.75 mm and the pump power was varied between 0.2 mw to 4.0 mw using a neutral density filter (NDF). Multiwavelength transient spectra were recorded using dual spectrometers (signal and reference) equipped with array detectors whose data rates exceed the repetition rate of the laser (1 kHz). Solutions of clusters in 1 mm path length cuvettes were excited by the tunable output of the OPA (pump). All data shown in this manuscript were performed in dilute solutions using dichloromethane as solvent.

## 2. Computational details.

Density function theory (DFT) calculations were implemented by ADF software.<sup>1</sup> GGA: PBE functional with scalar relativistic and TZP basis was used in optimizations of  $[Au_{13}Cu_4(PPh_2Py)_4(SePh)_8]^+$  and  $[Au_{13}Cu_4(PPh_2Py)_3(SePh)_9]$  nanoclusters.<sup>2-3</sup> The Mulliken charge was calculated at the same level of method with the geometry optimization. Based on the optimized structure of  $[Au_{13}Cu_4(PPh_2Py)_4(SePh)_8]^+$  nanocluster,<sup>4</sup> the bond dissociation energies ware gained from the energy gaps between the single point energy calculations on the separated moieties and that of  $[Au_{13}Cu_4(PPh_2Py)_4(SePh)_8]^+$  nanocluster.

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## **3. Supporting Figures**



Fig. S1 The side length of the equilateral triangle constructed by the Cu, N and P atoms, respectively.



Fig. S2 The side length of the equilateral triangle constructed by the Se atoms.



**Fig. S3** ESI-MS analysis of the  $[Au_{13}Cu_4(PPyPh_2)_4(SePh)_8]^+$  without adding Cs<sup>+</sup> under positive mode (inset: comparison of the experimental (blue) and simulated (green) isotope patterns of the nanocluster).



Fig. S4 Illustrative diagram for the calculation on the Au<sup>n</sup>- $P^n$  bond dissociation energy (BDE). Au<sup>4</sup>- $P^4$  bond dissociation was given as an example.

Table S1. Comparison of the key calculation results in gas and solution phase.

n	1	2	3	4	
Charge on $P^n$ (gas)	0.462	0.454	0.451	0.423	
Charge on $P^n$ (CH <sub>2</sub> Cl <sub>2</sub> )	0.493	0.488	0.509	0.483	
$BDE(Au^{n}-P^{n}) (gas/eV)$	2.73	2.64	2.60	2.43	
$BDE(Au^{n}-\boldsymbol{P^{n}}) (CH_{2}Cl_{2}/eV)$	2.40	2.34	2.38	2.25	



Fig. S5. The energy change for the single-ligand-exchange process between PPh<sub>2</sub>Py and -SePh.

Table S2.	<b>Crystal Data</b>	and Structure	<b>Refinement for</b>	[Au <sub>13</sub> Cu <sub>4</sub>	(PPh <sub>2</sub> Py) <sub>3</sub> (SeR) <sub>9</sub> ].
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Identification code	$[Au_{13}Cu_4(PPh_2Py)_3(SeR)_9]$
Empirical formula	C105H87Au13Cu4N3P3Se9F6P10Sb
	Se17
Formula weight	5009.05g/mol
Temperature	230 (2) K
Wavelength	1.54178 Å
Crystal system, space group	Trigonal R3c
Unit cell dimensions	a=24.2592(6)Å α=90°
	b=24.2592(6)Å β=90°
	c=74.473(2)Å γ=120°
Volume	37956(2) Å <sup>3</sup>
Z, Calculated density	12
Absorption coefficient	31.860 mm <sup>-1</sup>
F(000)	26784
Crystal size	0.18x0.06x0.04 mm <sup>3</sup>
Theta range for data collection	4.83° to 136.902°
index ranges	$-29 \le h \le 28, -29 \le k \le \!\!28, -88 \!\!\le \! l \le$
	89
Reflections collected	86209
Absorption correction	Multi scan
Data / restraints / parameters	7764/129/412
Goodness-of-fit on F <sup>2</sup>	1.063
Final R indexes [I≥2σ (I)]	$R_1 = 0.0564, wR_2 = 0.1777$
Final R indexes [all data]	$R_1 = 0.0779, wR_2 = 0.2014$
Largest diff. peak/hole	3.05/-3.79 e.Å <sup>-3</sup>
Independent reflections	7764 [ $R_{int} = 0.0898$ , $R_{sigma} = 0.0482$ ]