Supporting information

Insights into the Effect of Surface Coordination on the Structure and Properties of $Au_{13}Cu_2$ Nanocluster

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1. Experimental

1.1 Materials.

Unless specified, reagents were purchased from ACROS Organics or Sigma-Aldrich and used without further purification. Tetrachloroauric(III) acid ($HAuCl_4 \cdot 3H_2O$, ≥ 99.99% metals basis), copper(II) chloride (≥ 98%), sodium borohydride (> 98%), methylene chloride (HPLC, ≥ 99.9%), hexane (HPLC, ≥ 99.9%), ethanol (HPLC, ≥ 99.9%), triphenylphosphine (≥ 98.8%), sodium hexafluoroantimonate (≥ 98%), and phenylethylthiol (≥ 97%). Pure water was purchased from Wahaha Co. Ltd. All glassware was thoroughly cleaned with aqua regia (HCl: HNO_3 = 3:1, v:v), rinsed with copious pure water, and then dried in an oven prior to use.

1.2 Synthesis of Cu(Ⅰ)-thiolate

15 mg $CuCl_2$ was firstly dissolved in 10 ml ethanol under ultra-sounding; the blue solution became yellow turbid immediately after 100 μl phenylethanethiol was added under stirring. After centrifugation, the crude product was washed with ethanol for several times.

1.3 Synthesis of phosphine-protected Au nanoparticles

$HAuCl_4 \cdot 3H_2O$ (0.2 ml, 0.2 g/mL) dissolved in 5 ml of ethanol, and then triphenylphosphine (0.082 g) was added. After 5 minutes, an aqueous solution of $NaBH_4$ (0.020 g, dissolved in 5 mL water) was added. After one hour, the reaction mixture was rotavaporated and centrifugation to remove the by-product.

1.4 Synthesis of $[Au_{13}Cu_2(Ph_3P)_6(PhC_2H_4S)_6]^+$ nanocluster.

The NC was synthesized by the reaction of phosphine-protected Au nanoparticles with PhC_2H_4SCu(Ⅰ) complex. 40mg Au nanoparticles added into 5 ml ethanol which contains 30mg PhC_2H_4SCu(Ⅰ) complex under vigorous stirring. After 12 hours, the product was dried in vacuum and redissolved in a minimum amount of methanol. Then, excess $NaSbF_6$ added into the methanol solution. After centrifugation, the precipitate was washed with hexane at least 3 times and collected by centrifugation. Dark green rhombic crystals were crystallized from CH_2Cl_2/hexane at 4 °C after 5 days.

2. Characterization

2.1 X-ray crystallographic determination of the $[Au_{13}Cu_2(Ph_3P)_6(PhC_2H_4S)_6]^+$ nanocluster.

A suitable crystal was selected and performed on a 'Bruker APEX-II CCD' diffractometer. The crystal was kept at 296 (2) K during data collection. Using Olex2[1], the structure was solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

2.2 UV-vis absorption spectra were recorded on Agilent 8453 spectrophotometer. Single crystals were dissolved in CH_2Cl_2 for spectral measurements.

2.3 Electrospray ionization mass spectrometry (ESI-MS) measurement is performed by MicroTOF-QIII high-resolution mass spectrometer. The samples are directly infused into the chamber at 5 μL/min.

Table S1 The summary of bond lengths/angles of $[Au_{13}Cu_2(Ph_3P)_6(PhC_2H_4S)_6]^+$.

	Cu-Au	Cu-S	S-Au	Au-Au	Au-P	Cu-Au-S
bond length (Å) / angle (°)	2.826	2.287	2.315	2.857	2.309	51.26
	2.826	2.287	2.315	2.857	2.309	51.26
	2.832	2.300	2.324	2.880	2.305	51.74
	2.832	2.300	2.324	2.880	2.305	51.74
	2.853	2.291	2.305	2.881	2.310	51.95
	2.853	2.291	2.305	2.881	2.310	51.95
average	2.837	2.293	2.315	2.873	2.308	51.65

Note：Since the cluster is symmetric in the center, the two groups of data are consistent, and the same data is highlighted by shading.

Table S2 The summary of bond lengths/angles of $[Au_{13}Cu_2(Ph_3P)_6(SPy)_6]^+$.

□	Cu-Au	Cu-N	S-Au	Au-Au	Au-P	Cu-Au-S
bond length (Å)/ angle (°)	2.801	1.991	2.329	2.857	2.313	83.35
	2.833	2.105	2.324	2.920	2.300	83.22
	2.886	2.101	2.319	2.955	2.299	79.37
	2.775	2.088	2.356	2.882	2.305	80.43
	2.816	2.051	2.317	2.872	2.322	79.97
	2.834	2.061	2.333	2.911	2.305	82.40
average	2.824	2.066	2.330	2.900	2.307	81.46

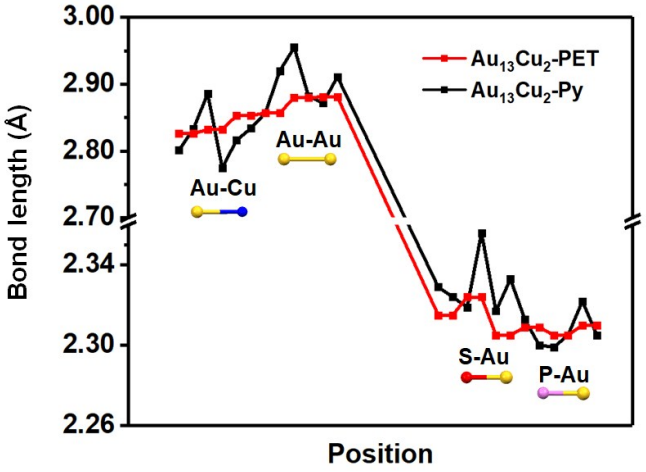

Fig. S1 The comparison of Au-Cu, Au-Au, S-Au and P-Au bond lengths in **$Au_{13}Cu_2$-PET** (the red line) and **$Au_{13}Cu_2$-Py** (the black line). (Color labels: yellow=Au; blue= Cu; red= S; violet=P).

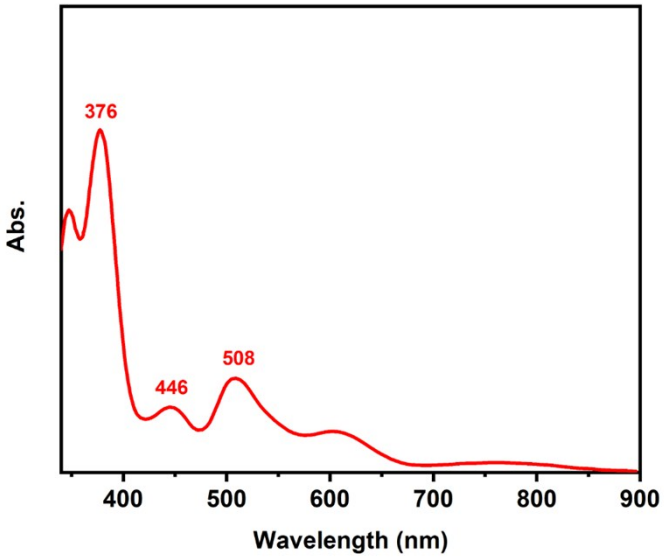

Fig. S2 Theoretical optical curves of $[Au_{13}Cu_2(PPh_3)_6(SPy)_6]^+$.

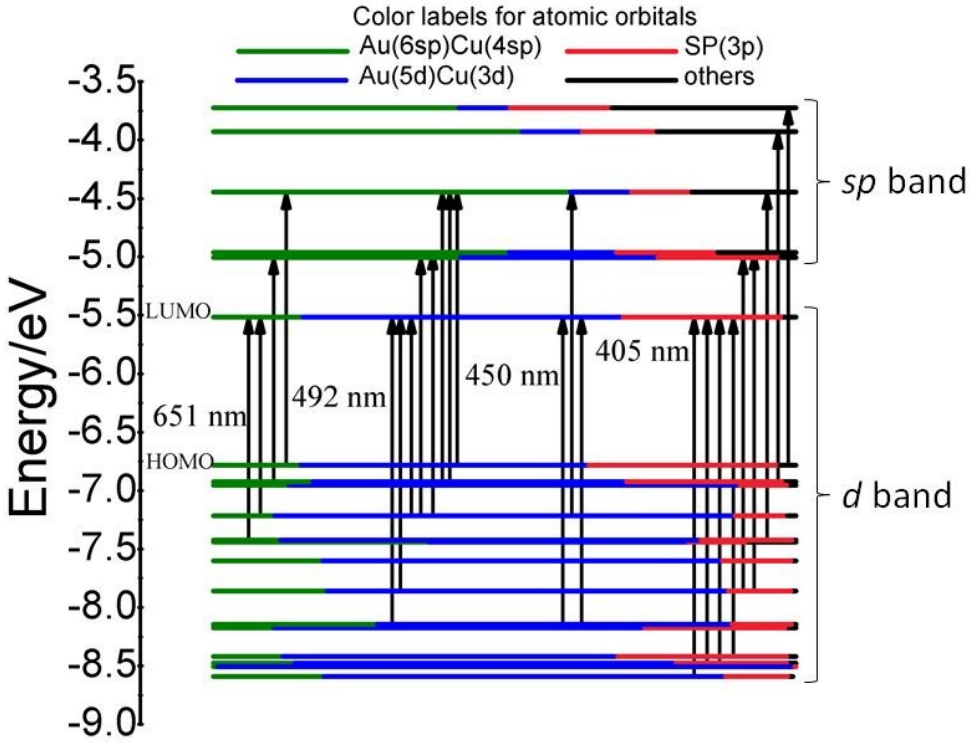

Fig. S3 The Kohn-Sham orbital energy of **$Au_{13}Cu_2$-PET'.**

Table S3 Crystal data and structure refinement for $[Au_{13}Cu_2(Ph_3P)_6(PhC_2H_4S)_6]^+$.

Identification code	$Au_{13}Cu_2$
Empirical formula	$C_{156}H_{144}Au_{13}Cu_2F_6P_6S_6Sb$
Formula weight	5320.28
Temperature/K	296 (2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.2565(18)
b/Å	26.289(3)
c/Å	19.280(2)
α/°	90
β/°	95.1080(10)
γ/°	90
Volume/Å^3	8711.5(16)
Z	2
ρ_{calc}g/cm^3	2.028
μ/mm^{-1}	11.464
F(000)	4912.0
Crystal size/mm^3	0.1 × 0.09 × 0.08
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	2.626 to 54.5
Index ranges	$-20 \le h \le 20$, $-32 \le k \le 32$, $-24 \le l \le 24$
Reflections collected	66374
Independent reflections	17904 [R_{int} = 0.0878, R_{sigma} = 0.0969]
Data/restraints/parameters	17904/513/889
Goodness-of-fit on F^2	1.070
Final R indexes [I>=2σ (I)]	R_1 = 0.0574, wR_2 = 0.1415
Final R indexes [all data]	R_1 = 0.1032, wR_2 = 0.1600
Largest diff. peak/hole / e Å^{-3}	2.54/-3.47