

Electronic Supplementary Information

An Insight, at the Atomic Level, into the Intramolecular Metallophilic Interaction in Nanoclusters

Hao Li,^a Chuanjun Zhou,^a Endong Wang,^b Xi Kang,^{a,*} Wen Wu Xu,^{c,*} Manzhou Zhu^{a,*}

^aDepartment of Chemistry and Centre for Atomic Engineering of Advanced Materials, Key Laboratory of Structure and Functional Regulation of Hybrid Materials of Ministry of Education, Institutes of Physical Science and Information Technology and Anhui Province Key Laboratory of Chemistry for Inorganic/Organic Hybrid Functionalized Materials, Anhui University, Hefei, Anhui 230601, China.

^bSchool of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian 116029, China.

^cDepartment of Physics, School of Physical Science and Technology, Ningbo University, Ningbo, 315211, China.

Materials and Methods

Chemicals

All reagents are commercially available and used directly without further purification: tetrachloroauric(III) acid ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, 99.9%, metal basis), copper(II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 99.9%, metal basis), tris(4-chlorophenyl)phosphine ($\text{C}_{18}\text{H}_{12}\text{Cl}_3\text{P}$, $\text{T}^{\text{P}}\text{CPP}$, 99.5%), 4-*tert*-butylthiophenol ($\text{C}_{10}\text{H}_{14}\text{S}$, TBBT, 98%), sodium borohydride (NaBH_4 , 99.9%), sodium hexafluoroantimonate (NaSbF_6 , 99%), dichloromethane (CH_2Cl_2 , HPLC grade), methanol (CH_3OH , HPLC grade), acetone ($\text{C}_3\text{H}_6\text{O}$, HPLC grade), acetonitrile (CH_3CN , HPLC grade), chloroform (CH_3Cl , HPLC grade), and *n*-hexane (C_6H_{14} , HPLC grade).

Syntheses

Synthesis of the $[\text{AuCu}_{14}(\text{TBBT})_{12}(\text{TPP})_6](\text{SbF}_6)$ nanocluster

The whole reaction process was carried out at room temperature. $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (0.2 mmol, 0.2 g/mL, 400 μL) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.23 mmol, 40 mg) were mixed in 20 mL of $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ mixed solution and stirred at 1200 rpm. After 10 minutes, tris(4-chlorophenyl)phosphine (0.82 mmol, 300 mg) was added. After 30 minutes, the solution color changed from orange to green. Then, 4-*tert*-butylthiophenol (0.6 mmol, 100 μL) was added to the flask. After 30 minutes, the solution turned white muddy. Finally, NaBH_4 (2.1 mmol, 80 mg, dissolved in 5 mL of H_2O) was injected into the reaction. After 12 hours, the aqueous solution was removed and NaSbF_6 (0.2 mmol, 50 mg, dissolved in 1 mL of CH_3OH) was added to the organic phase. The organic solution was dried by the rotary evaporation, and then washed several times by methanol and acetonitrile to remove the redundant ligands and by-products. The crude product was extracted with acetone. Black crystals of $[\text{Au}_{13}\text{Cu}_2(\text{TBBT})_6(\text{T}^{\text{P}}\text{CPP})_8](\text{SbF}_6)$ were obtained by the liquid-diffusion of *n*-hexane into the chloroform solution of the nanocluster for three days.

The CCDC number of $[\text{Au}_{13}\text{Cu}_2(\text{TBBT})_6(\text{T}^{\text{P}}\text{CPP})_8](\text{SbF}_6)$ is 2101796.

Syntheses of other $\text{Au}_{13}\text{Cu}_2$ nanoclusters

The syntheses of Au₁₃Cu₂-SPy and Au₁₃Cu₂-PET nanoclusters were based on previously reported methods.^{1,2}

Characterizations

Single crystal X-ray diffractometer. The data collection for single-crystal X-ray diffraction was carried out on a Stoe Stadivari diffractometer under nitrogen flow using graphite-monochromatized Cu K α radiation ($\lambda = 1.54186 \text{ \AA}$). Using Olex2,³ the structure was solved with the ShelXT⁴ structure solution program using Intrinsic Phasing and refined with the ShelXL⁵ refinement package using Least Squares minimization. All the non-hydrogen atoms were found directly. All the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were set in geometrically calculated positions and refined isotropically using a riding model. The diffuse electron densities resulting from the residual solvent molecules were removed from the data set using the SQUEEZE routine of PLATON and refined further using the data generated.

Electrospray ionization (ESI) mass spectrum was performed on Waters XEVO G2-XS QToF mass spectrometer. The samples are dissolved in a mixture solution of CH₂Cl₂/CH₃OH ($v:v = 1:1$), which is directly infused into the chamber at 10 $\mu\text{L}/\text{min}$ with positive mode.

UV-vis absorption spectra were recorded on the Metash UV-6000PC UV-vis spectrophotometer. Of note, all tests were performed by using the crystals of these Au₁₃Cu₂ nanocluster samples. The time-dependent optical absorptions were measured by using their crystals dissolved in CH₂Cl₂.

Thermal stability. The thermal stability of Au₁₃Cu₂ nanoclusters (CH₂Cl₂ solution) was measured in air at room temperature. The time-dependent UV-vis absorptions were then tested.

The NIR emission spectrum recorded on a FS5 spectrofluorometer (Edinburgh Instruments Ltd.) with an InGaAs detector.

Calculation details. Density functional theory (DFT) calculations are performed to obtain electronic structure of the three clusters with the PBE functional and pseudopotential basis set LANL2DZ for Au and Cu, the all-electron basis set 6-31G(d) for the other elements. The three clusters are optimized first to get stable geometries. The outer organic ligands are replaced by the -CH₃. All the calculations were performed using the Orca package.⁶ Super-fast approximate TD-DFT implemented in the Orca package by Grimme and co-workers was used to get the UV-abs spectrum.⁷

Reference:

- (1) H. Yang, Y. Wang, J. Lei, L. Shi, X. Wu, V. Makinen, S. Lin, Z. Tang, J. He, H. Hakkinen, L. Zheng and N. Zheng, *J. Am. Chem. Soc.*, 2013, **135**, 9568-9571.
- (2) C. Zhou, H. Li, Y. Song, F. Ke, W. W. Xu and M. Zhu, *Nanoscale*, 2019, **11**, 19393-19397.
- (3) Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K. & Puschmann, H. *J. Appl. Cryst.*, 2009, **42**, 339-341.
- (4) Sheldrick, G.M. *Acta Cryst.*, 2015, **A71**, 3-8.
- (5) Sheldrick, G.M. *Acta Cryst.*, 2015, **C71**, 3-8.

(6) F. Neese, F. Wennmohs, U. Becker and C. Riplinger, *J. Chem. Phys.*, 2020, **152**, 224108.

(7) M. de Wergifosse and S. Grimme, *J. Chem. Phys.*, 2018, **149**, 024108.

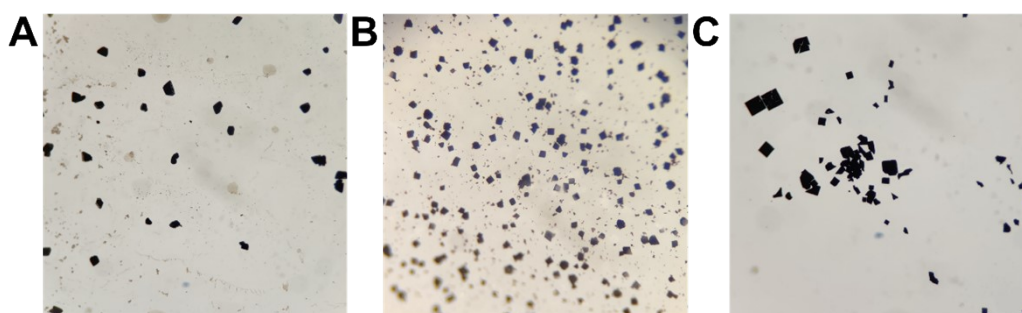


Fig. S1 Digital photograph of (A) $\text{Au}_{13}\text{Cu}_2\text{-TBBT}$, (B) $\text{Au}_{13}\text{Cu}_2\text{-Spy}$, and (C) $\text{Au}_{13}\text{Cu}_2\text{-PET}$ nanocluster crystals.

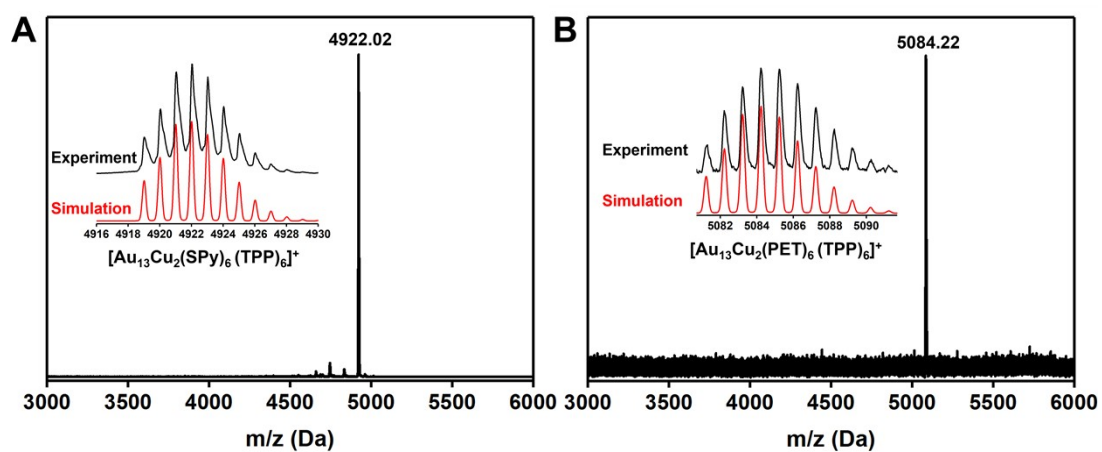


Fig. S2 The ESI-MS of (A) $\text{Au}_{13}\text{Cu}_2\text{-Spy}$ and (B) $\text{Au}_{13}\text{Cu}_2\text{-PET}$ nanoclusters.

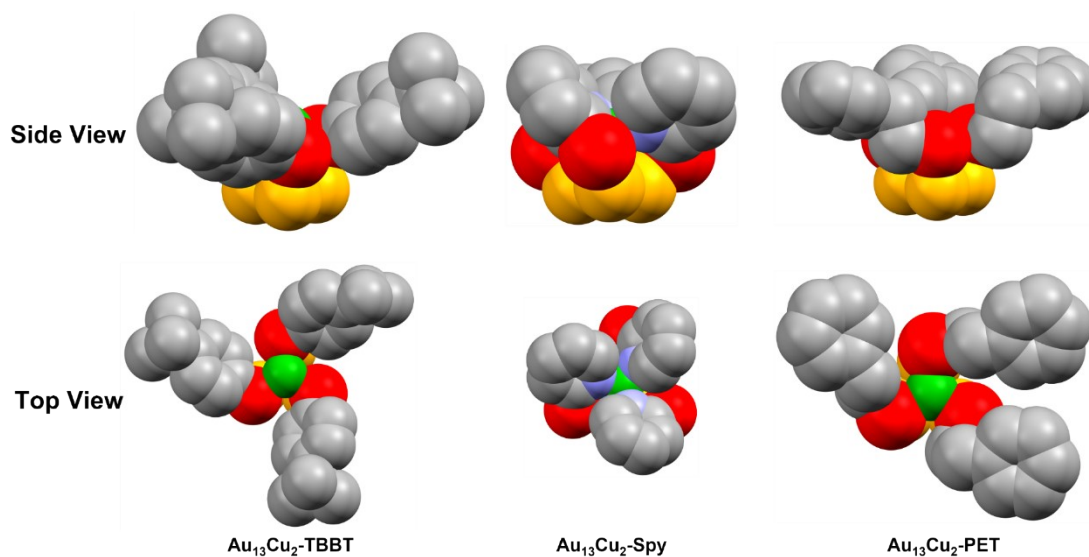


Fig. S3 The side and top views of the space-filling mode of $\text{Cu}(\text{SR})_3$ unit in $\text{Au}_{13}\text{Cu}_2$ nanoclusters.

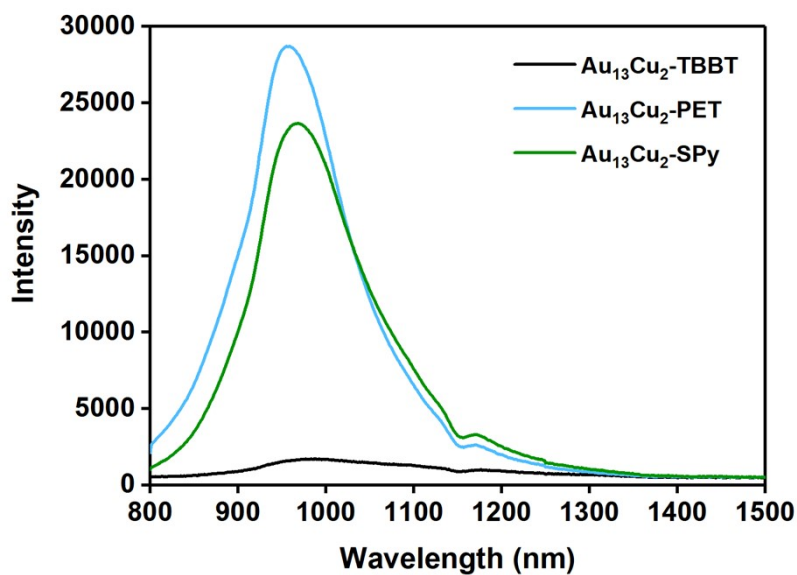


Fig. S4 The NIR emission spectra of these $\text{Au}_{13}\text{Cu}_2$ nanoclusters.

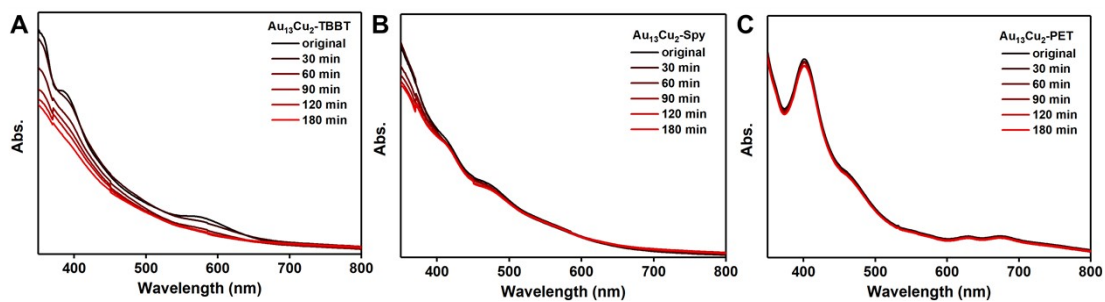


Fig. S5 The thermal stability of (A) $\text{Au}_{13}\text{Cu}_2$ -TBBT, (B) $\text{Au}_{13}\text{Cu}_2$ -Spy, and (C) $\text{Au}_{13}\text{Cu}_2$ -PET nanoclusters.

Table S1. Crystal data and structure refinement for Au₁₃Cu₂-TBBT nanocluster.

Identification code	Au ₁₃ Cu ₂ -TBBT	
Empirical formula	C ₂₀₄ H ₁₇₄ Au ₁₃ Cl ₂₄ Cu ₂ P ₈ S ₆ F ₆ Sb ₁	
Formula weight	6839.74	
Temperature	120 K	
Radiation	CuK α (λ = 1.54186)	
Crystal system	monoclinic	
Space group	<i>P</i> 2 ₁ / <i>c</i>	
Unit cell dimensions	a = 20.1117 (7) Å	α = 90°
	b = 35.1137 (10) Å	β = 97.253 (3)°
	c = 36.6942 (13) Å	γ = 90°
Volume	25706.0 (15) Å ³	
Z	4	
Density (calculated)	1.767 g/cm ³	
Absorption coefficient	18.131 mm ⁻¹	
F(000)	12848	
2 θ range for data collection/°	7.71 to 124.998	
Index ranges	-22 ≤ h ≤ 23,	
	-40 ≤ k ≤ 40,	
	-42 ≤ l ≤ 15	
Final R indices [<i>I</i> > 2 σ (<i>I</i>)]	R ₁ = 0.0438, wR ₂ = 0.1073	
R indices (all data)	R ₁ = 0.0713, wR ₂ = 0.1169	

Table S2. Detailed orbital component for the HOMO and LUMO orbital of Au₁₃Cu₂-PET, Au₁₃Cu₂-Spy, and Au₁₃Cu₂-TBBT nanoclusters.

Clusters	Orbitals	Au_sp	Au_d	Cu_sp	Cu_d	others
Au ₁₃ Cu ₂ -PET	HOMO	32.91%	25.33%	1.95%	5.52%	34.29%
	LUMO	43.21%	18.41%	0.65%	1.06%	36.67%
Au ₁₃ Cu ₂ -Spy	HOMO	9.02%	15.73%	1.54%	46.82%	26.89%
	LUMO	42.02%	18.46%	4.47%	0.95%	34.09%
Au ₁₃ Cu ₂ -TBBT	HOMO	11.69%	7.38%	5.35%	38.61%	36.98%
	LUMO	52.91%	14.69%	0.65%	0.74%	31.02%