

# Supporting Information

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## Experimental Procedures

**1.1. Materials.** All reagents are commercially available and used directly without further purification, including CuCl (98%), 4-methylbenzenethiolate (98%), 4-isopropylbenzenethiol (95%), 4-tert-butylbenzenethiol (98%), tetraoctylammonium bromide (TOAB, 98%), triphenylphosphine (TPP, 98%), sodium borohydride (99.99%), chloroform (HPLC grade,  $\geq 99.9\%$ ), methanol (HPLC grade,  $\geq 99.9\%$ ), *n*-hexane (HPLC grade,  $\geq 99.9\%$ ).  $\text{Me}_2\text{SAuCl}$ ,  $\text{Au}(\text{TPP})\text{Cl}$  and  $[\text{Cu}_{23}(\text{SC}_6\text{H}_4\text{-R})_{18}(\text{TPP})_6](\text{SbF}_6)$  were prepared according to literature methods.<sup>[1-3]</sup>

### 1.2. Synthesis of the $[\text{AuCu}_{14}(\text{SC}_6\text{H}_4\text{-CH}_3)_{12}(\text{TPP})_6](\text{SbF}_6)$ cluster.

The whole reaction process was carried out at room temperature. 5 mg of the  $[\text{Cu}_{23}(\text{SC}_6\text{H}_4\text{-CH}_3)_{18}(\text{TPP})_6](\text{SbF}_6)$  nanocluster was firstly dissolved in 2 mL of  $\text{CH}_2\text{Cl}_2$  under stirring. Then,  $\text{Au}(\text{TPP})\text{Cl}$  (0.5 mg) was added to the above solution. After irradiated at 365 nm for 30 seconds, the solution gradually changed from light yellow to red, accompanied by a bright red light. The organic solution was evaporated and washed several times with methanol. Finally, red crystals were obtained by liquid diffusion of *n*-hexane into a  $\text{CH}_2\text{Cl}_2$  solution of the nanocluster for three days with a  $\sim 60\%$  yield (Cu atom basis). ESI-MS ( $[\text{AuCu}_{14}(\text{SC}_6\text{H}_4\text{-CH}_3)_{12}(\text{TPP})_5]^+$ ):  $m/z = 3876.75$  (calcd. 3876.75).

### 1.3. Synthesis of the $[\text{AuCu}_{14}(\text{SC}_6\text{H}_4\text{-CH}(\text{CH}_3)_2)_{12}(\text{TPP})_6](\text{SbF}_6)$ cluster.

The whole reaction process was carried out at room temperature. 5 mg of the  $[\text{Cu}_{23}(\text{SC}_6\text{H}_4\text{-CH}(\text{CH}_3)_2)_{18}(\text{TPP})_6](\text{SbF}_6)$  nanocluster was firstly dissolved in 2 mL of  $\text{CH}_2\text{Cl}_2$  under stirring. Then,  $\text{Au}(\text{TPP})\text{Cl}$  (0.5 mg) was added to the above solution. After irradiated at 365 nm for 30 seconds, the solution gradually changed from light yellow to red, accompanied by a bright red light. The organic solution was evaporated and washed several times with methanol. Finally, red crystals were obtained by liquid diffusion of *n*-hexane into a  $\text{CH}_2\text{Cl}_2$  solution of the nanocluster for three days with a  $\sim 25\%$  yield (Cu atom basis). ESI-MS ( $[\text{AuCu}_{14}(\text{SC}_6\text{H}_4\text{-CH}(\text{CH}_3)_2)_{12}(\text{TPP})_5]^+$ ):  $m/z = 4213.15$  (calcd. 4212.75).

### 1.4. Synthesis of the $[\text{AuCu}_{14}(\text{SC}_6\text{H}_4\text{-C}(\text{CH}_3)_3)_{12}(\text{TPP})_6](\text{SbF}_6)$ cluster.

The whole reaction process was carried out at room temperature. 5 mg of the  $[\text{Cu}_{23}(\text{SC}_6\text{H}_4\text{-C}(\text{CH}_3)_3)_{18}(\text{TPP})_6](\text{SbF}_6)$  nanocluster was firstly dissolved in 2 mL of  $\text{CH}_2\text{Cl}_2$  under stirring. Then,  $\text{Au}(\text{TPP})\text{Cl}$  (0.5 mg) was added to the above solution. After irradiated at 365 nm for 30 seconds, the solution gradually changed from light yellow to red, accompanied by a bright red light. The organic solution was evaporated and washed several times with methanol. Finally, red crystals were obtained by liquid diffusion of *n*-hexane into a  $\text{CH}_2\text{Cl}_2$  solution of the nanocluster for three days with a  $\sim 38\%$  yield (Cu atom basis). ESI-MS ( $[\text{AuCu}_{14}(\text{SC}_6\text{H}_4\text{-C}(\text{CH}_3)_3)_{12}(\text{TPP})_4]^+$ ):  $m/z = 4119.19$  (calcd. 4118.46).

### 1.5. Titration experiments.

1.7 mg of  $\text{AgNO}_3$  was dissolved in 5 mL of methanol under stirring to obtain a homogeneous  $\text{AgNO}_3$  solution with a concentration of 0.34 mg/mL ( $\sim 2.0$  mM). Then, 3 mL of  $\text{AuCu}_{14}\text{-CH}(\text{CH}_3)_2$  (0.2 mg/mL) solution in  $\text{CH}_2\text{Cl}_2$  was placed in a cuvette to record its initial fluorescence spectrum. After the addition of  $\text{AgNO}_3$  solution (15  $\mu\text{L}$ ,  $\sim 10$   $\mu\text{M}$ ) to the above  $\text{CH}_2\text{Cl}_2$  solution, the cuvette was gently shaken to ensure thorough mixing and record its fluorescence spectrum. This process was repeated several times to obtain fluorescence titration spectra covering the  $\text{Ag}^+$  concentration range of 0-100  $\mu\text{M}$ . The titration experiments of other metal ions were similar to  $\text{Ag}^+$  ion.

## Characterization

**2.1. Photoluminescence spectra.** Photoluminescence spectra were measured using an FL-7000 spectrofluorometer with the same optical density (OD) of  $\sim 0.2$ . Absolute quantum yield (QY) and emission lifetime were measured on the HORIBA FluoroMax-4P.

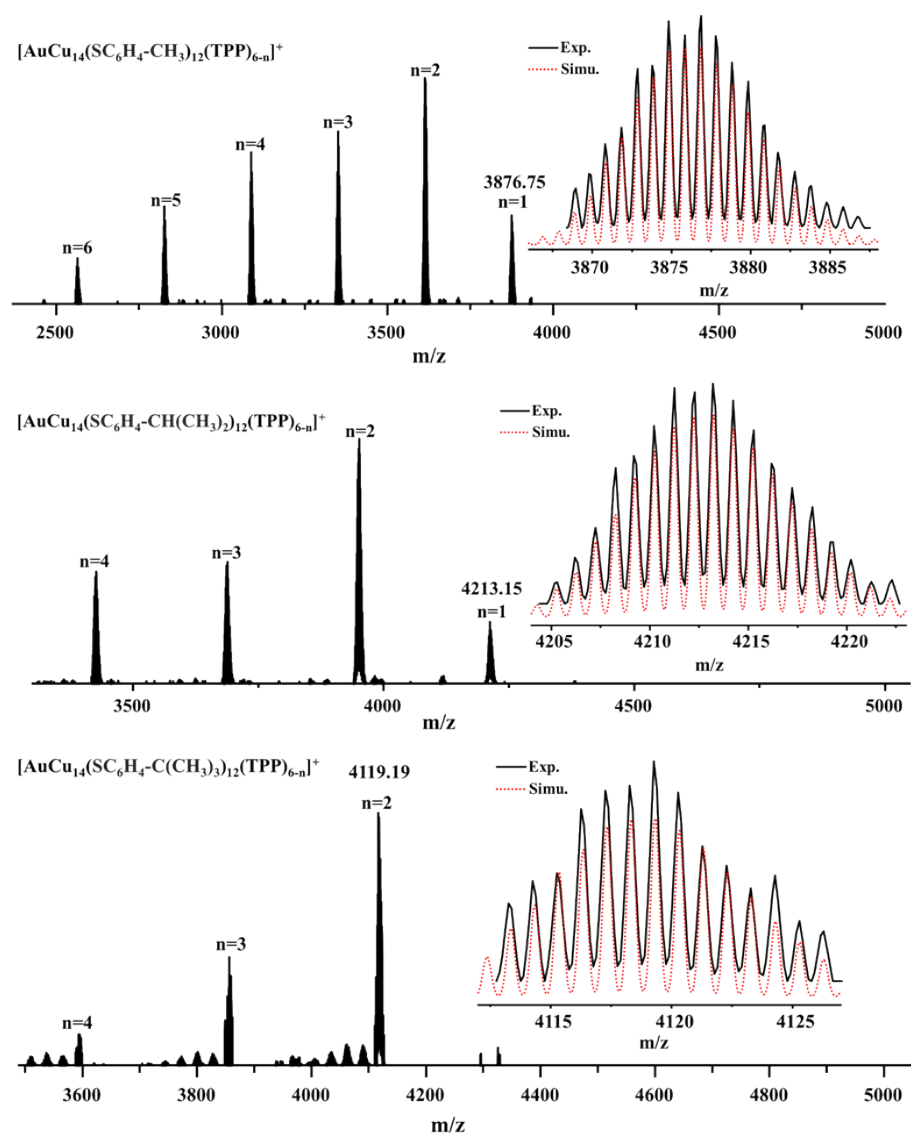
**2.2. UV-vis absorption spectra.** UV-visible absorption spectra were recorded on M4 spectrophotometer. Crystals are dissolved in solution.

**2.3. Single Crystal X-ray Diffraction.** Single crystal X-ray diffraction data were recorded on a Rigaku XtaLAB Synergy-R Diffraction equipped with a digital camera diffractometer comprising a microfocus rotating anode X-ray source (Cu  $K\alpha$ ,  $\lambda = 1.54178$  Å) and an HPC detector [HyPix-6000C] radiation for the crystal structures. The diffraction data were processed during data collection using CrysAlis<sup>Pro</sup>. The structures were solved and refined during data collection with AutoChem. Final structure refinements were performed using SHELXL implemented in Olex2.<sup>[4-6]</sup> Data collection, structure refinement parameters and crystallographic data for the crystals are given in Table S1.

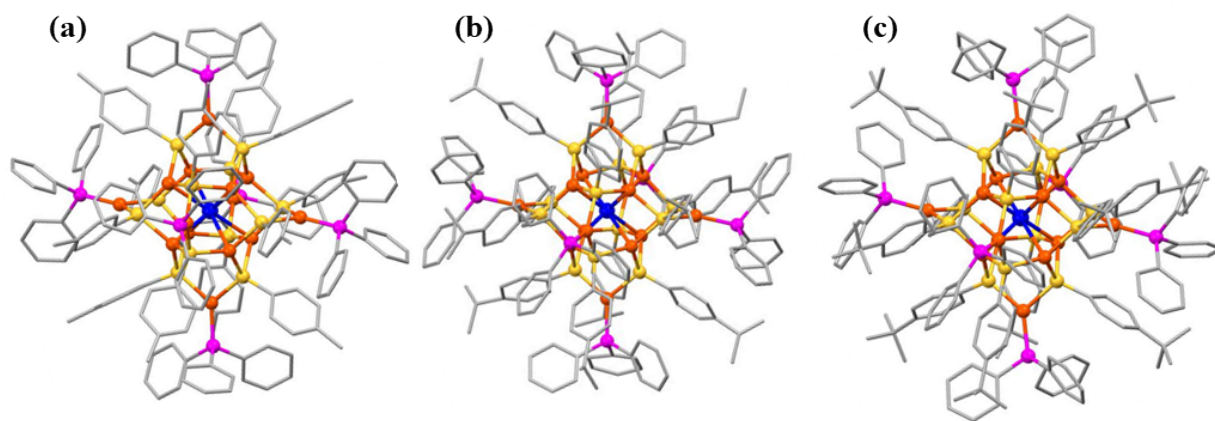
**2.4. Electrospray ionization (ESI) mass spectrum.** Electrospray ionization mass spectra (ESI-MS) were acquired on a Waters Q-TOF mass spectrometer equipped with a Z-spray source. The samples are dissolved in a mixture solution of  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  ( $v:v = 1:1$ ), which is directly infused into the chamber at 20  $\mu\text{L}/\text{min}$  with positive mode.

**2.5. X-ray photoelectron spectroscopy (XPS).** X-ray photoelectron spectroscopy measurements were performed on Thermo ESCALAB 250 equipped with a monochromated Al  $K\alpha$  (1486.8 eV) 150 W X-ray source, 0.5 mm circular spot size, a flood

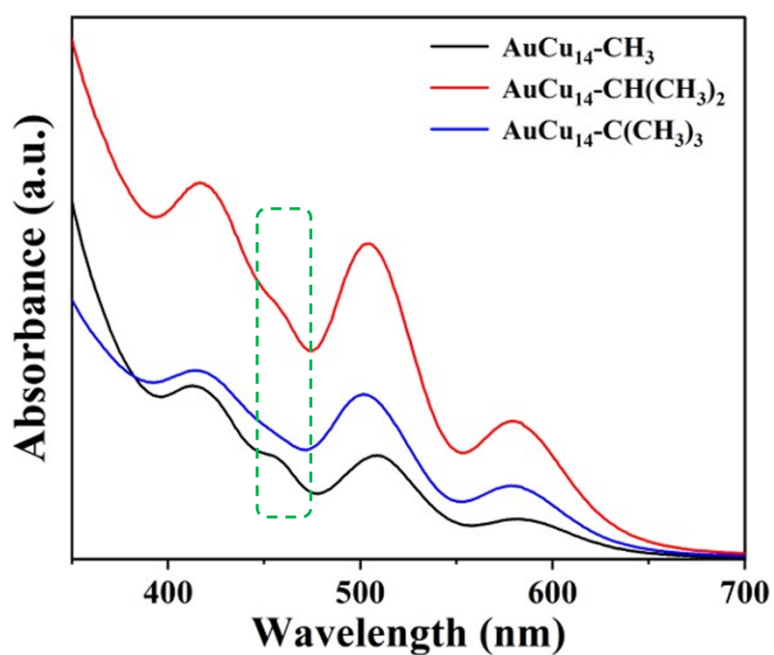
gun to counter charging effects, and the S3 analysis chamber base pressure lower than  $1 \times 10^{-9}$  mbar; data were collected with  $FAT = 20$  eV. The sample holder was aluminum plate used during the X-ray Photoelectron Spectroscopy (XPS) analysis.



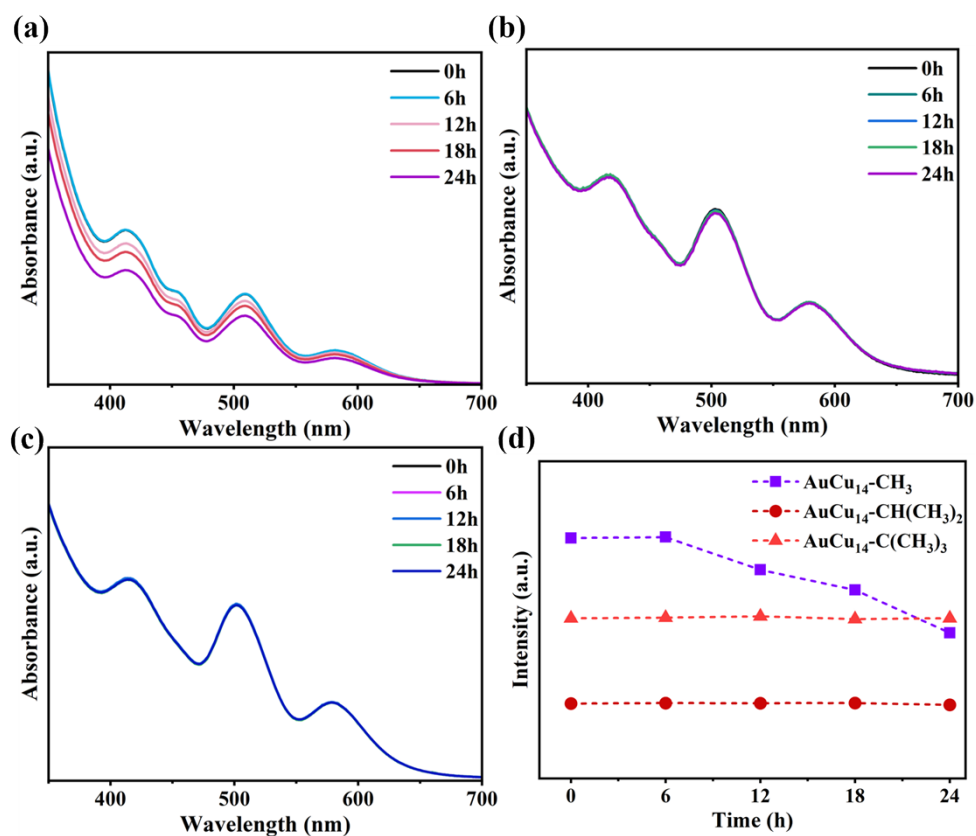
**Figure S1.** Positive-mode ESI mass spectra of  $\text{AuCu}_{14}\text{-CH}_3$ ,  $\text{AuCu}_{14}\text{-CH}(\text{CH}_3)_2$  and  $\text{AuCu}_{14}\text{-C}(\text{CH}_3)_3$ .



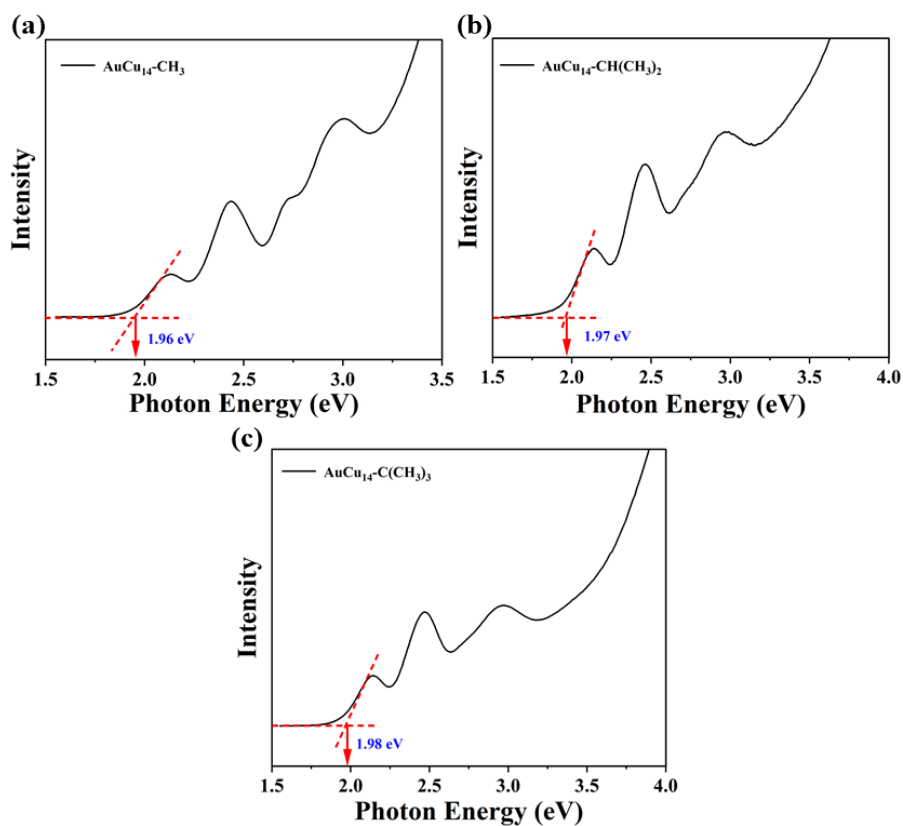
**Figure S2.** The overall structure of the  $\text{AuCu}_{14}$  cluster shown in ball-and-stick mode: (a)  $\text{AuCu}_{14}\text{-CH}_3$ , (b)  $\text{AuCu}_{14}\text{-CH(CH}_3)_2$  and (c)  $\text{AuCu}_{14}\text{-C(CH}_3)_3$ . Cu orange, Au blue, S yellow, P pink, C gray. H atoms are omitted for clarity.



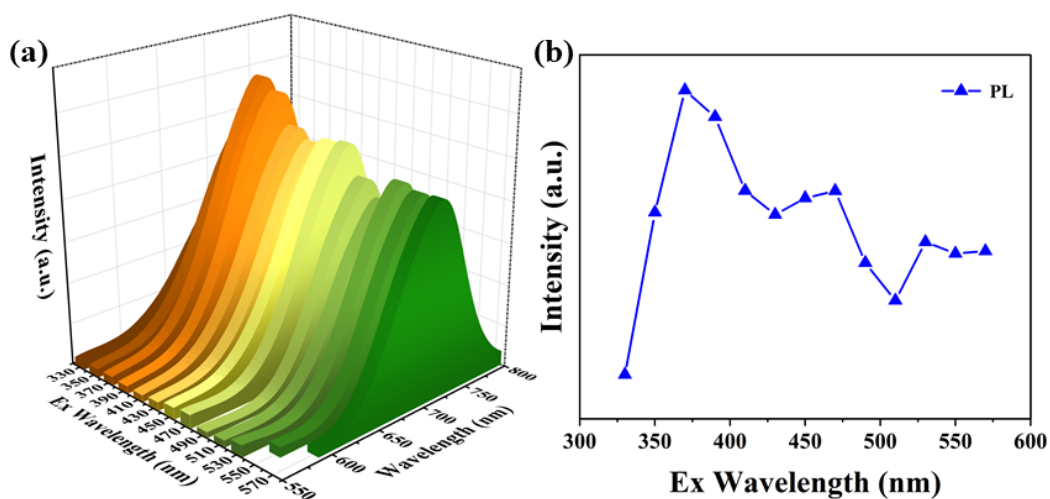
**Figure S3.** UV-vis absorption spectra of  $\text{AuCu}_{14}\text{-CH}_3$ ,  $\text{AuCu}_{14}\text{-CH(CH}_3)_2$  and  $\text{AuCu}_{14}\text{-C(CH}_3)_3$  in  $\text{CH}_2\text{Cl}_2$  solution at room temperature.



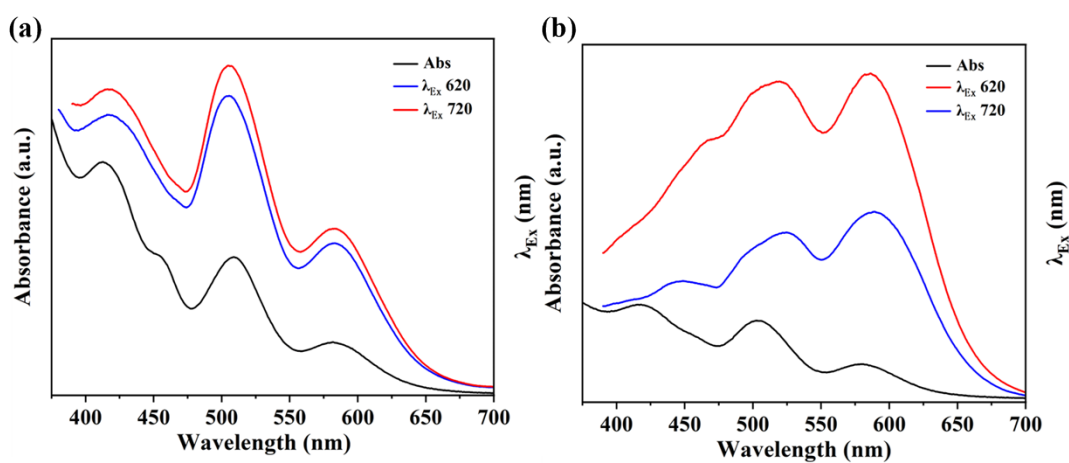
**Figure S4.** The time-dependent UV-vis absorption spectra of (a)  $\text{AuCu}_{14}\text{-CH}_3$ , (b)  $\text{AuCu}_{14}\text{-CH(CH}_3)_2$  and (c)  $\text{AuCu}_{14}\text{-C(CH}_3)_3$  in  $\text{CH}_2\text{Cl}_2$  solution at room temperature. (d) The change of absorption intensity located at 415 nm along with time.



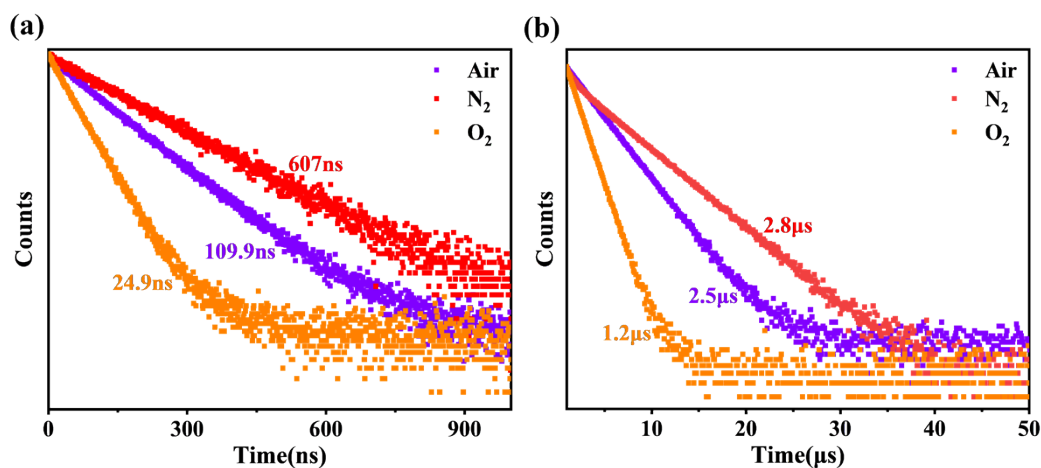
**Figure S5.** Optical gap determination of  $\text{AuCu}_{14}\text{-CH}_3$ ,  $\text{AuCu}_{14}\text{-C(CH}_3)_2$  and  $\text{AuCu}_{14}\text{-C(CH}_3)_3$  in  $\text{CH}_2\text{Cl}_2$  solution.



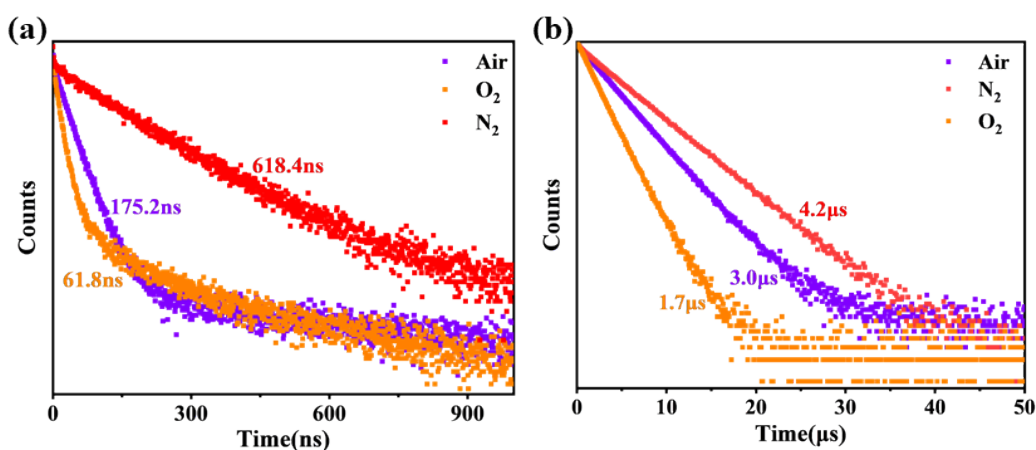
**Figure S6.** The change trends of PL centered at 720 nm of  $\text{AuCu}_{14}\text{-C}(\text{CH}_3)_3$  under different excitations in  $\text{CH}_2\text{Cl}_2$ .



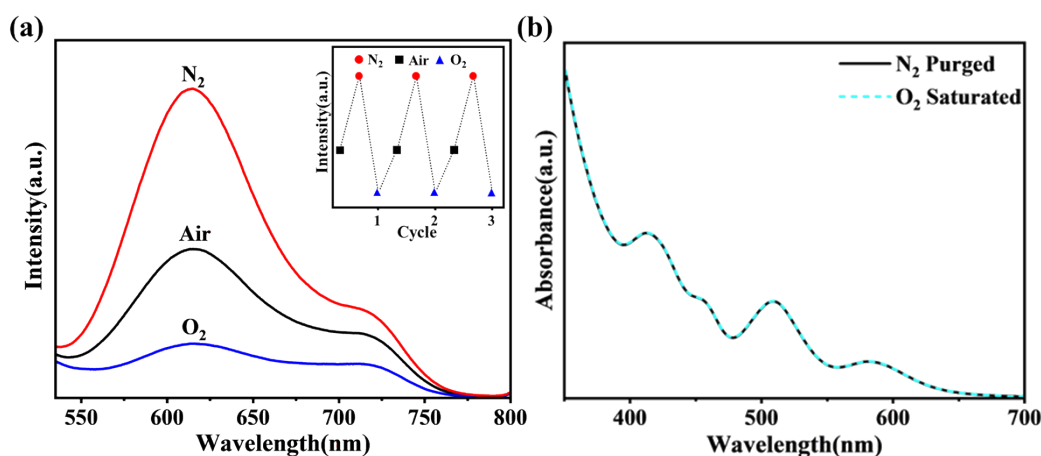
**Figure S7.** The PL excitation spectra and UV-vis absorption spectra of (a)  $\text{AuCu}_{14}\text{-CH}_3$  and (b)  $\text{AuCu}_{14}\text{-CH}(\text{CH}_3)_2$  in  $\text{CH}_2\text{Cl}_2$  solution at room temperature.



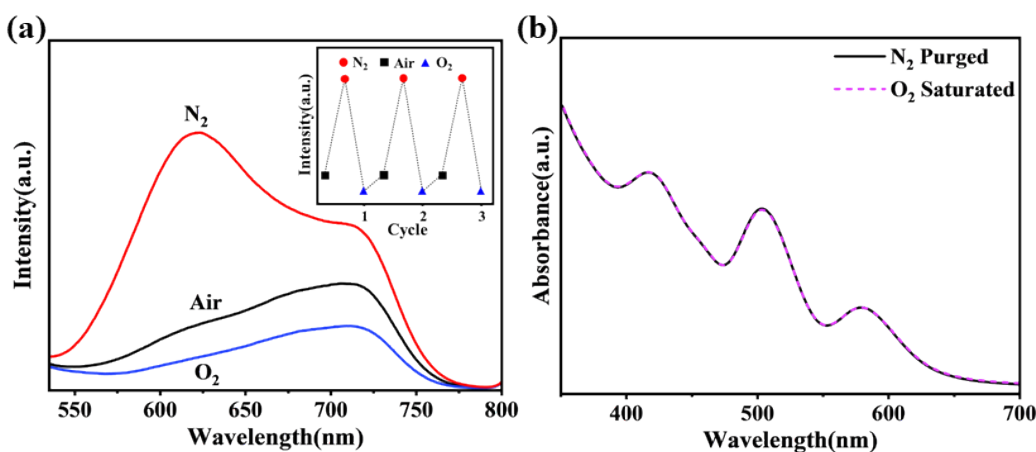
**Figure S8.** (a) The PL I and (b) PL II emission lifetime of  $\text{AuCu}_{14}\text{-CH}_3$  in  $\text{CH}_2\text{Cl}_2$  solution under air,  $\text{O}_2$  and  $\text{N}_2$  atmospheres, respectively.



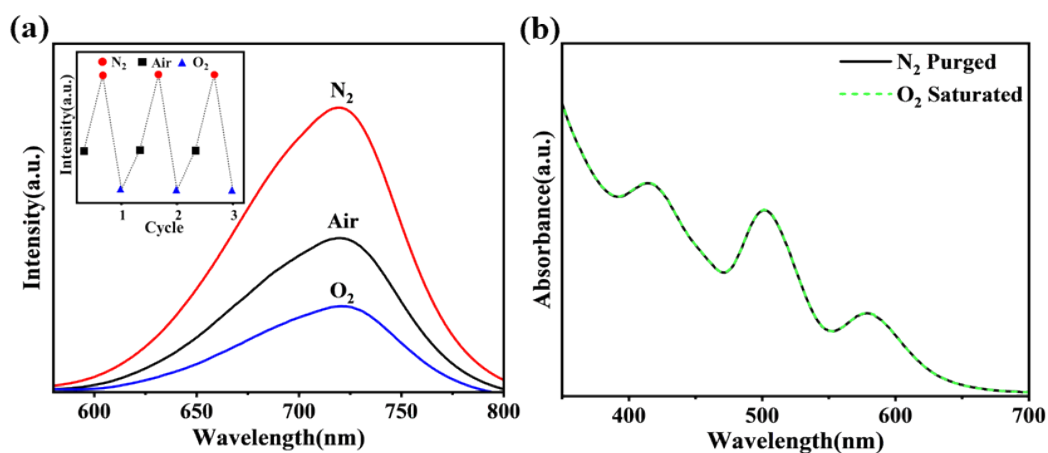
**Figure S9.** (a) The PL I and (b) PL II emission lifetime of  $\text{AuCu}_{14}\text{-CH}(\text{CH}_3)_2$  in  $\text{CH}_2\text{Cl}_2$  solution under air,  $\text{O}_2$  and  $\text{N}_2$  atmospheres, respectively.



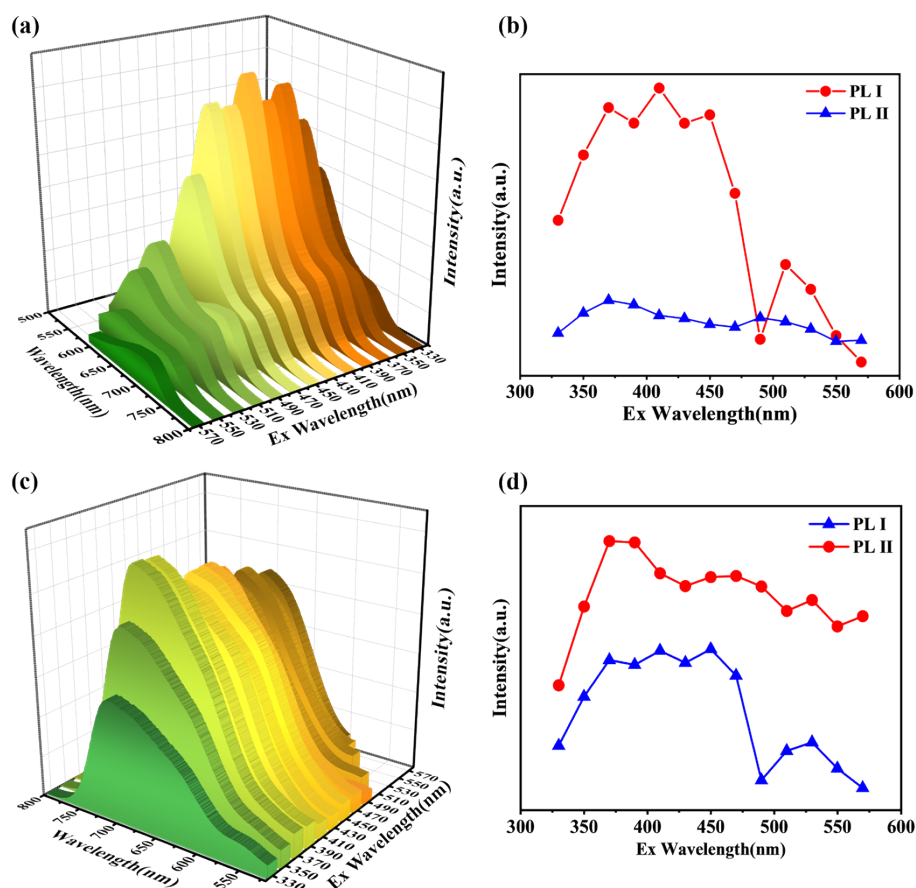
**Figure S10.** (a) Emission spectra of  $\text{AuCu}_{14}\text{-CH}_3$  in  $\text{CH}_2\text{Cl}_2$  solution under air,  $\text{O}_2$  and  $\text{N}_2$  atmospheres (inset: the intensity at 620 nm with 3 cycles under different atmospheres). (b) UV-vis spectra of  $\text{AuCu}_{14}\text{-CH}_3$  in  $\text{CH}_2\text{Cl}_2$  solution protected by  $\text{N}_2$  and  $\text{O}_2$ .



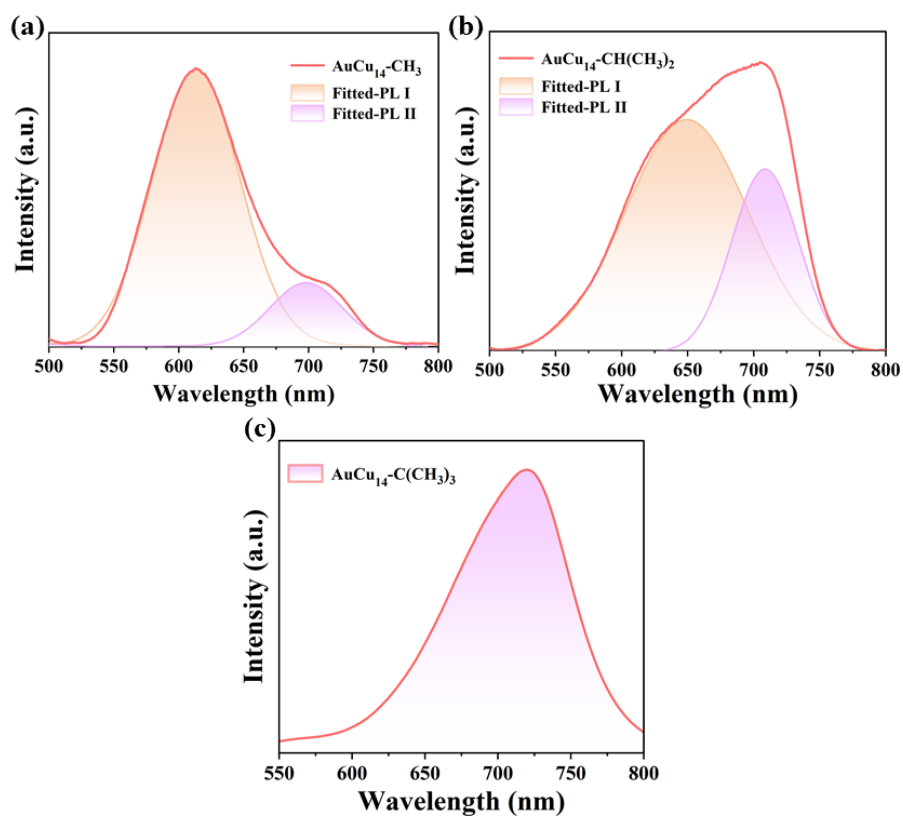
**Figure S11.** (a) Emission spectra of  $\text{AuCu}_{14}\text{-CH}(\text{CH}_3)_2$  in  $\text{CH}_2\text{Cl}_2$  solution under air,  $\text{O}_2$  and  $\text{N}_2$  atmospheres (inset: the intensity at 620 nm with 3 cycles under different atmospheres). (b) UV-vis spectra of  $\text{AuCu}_{14}\text{-CH}(\text{CH}_3)_2$  in  $\text{CH}_2\text{Cl}_2$  solution protected by  $\text{N}_2$  and  $\text{O}_2$ .



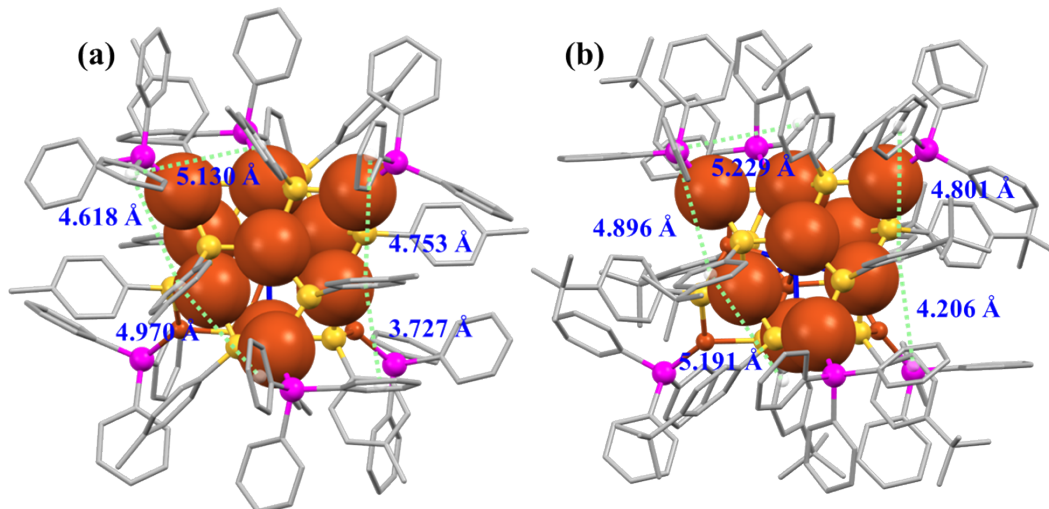
**Figure S12.** (a) Emission spectra of  $\text{AuCu}_{14}\text{-C}(\text{CH}_3)_3$  in  $\text{CH}_2\text{Cl}_2$  solution under air,  $\text{O}_2$  and  $\text{N}_2$  atmospheres (inset: the intensity at 720 nm with 3 cycles under different atmospheres); (b) UV-vis spectra of  $\text{AuCu}_{14}\text{-C}(\text{CH}_3)_3$  in  $\text{CH}_2\text{Cl}_2$  solution protected by  $\text{N}_2$  and  $\text{O}_2$ .



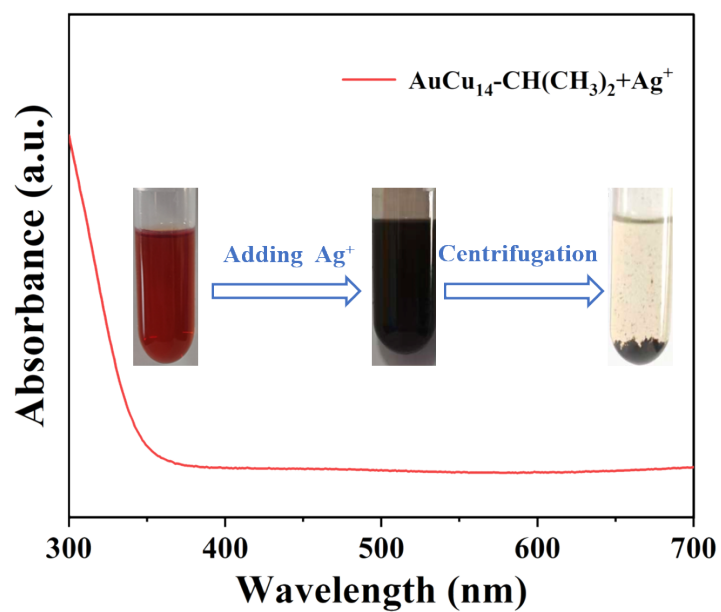
**Figure S13.** (a-b) The change trends of PL I and PL II of  $\text{AuCu}_{14}\text{-CH}_3$  under different excitations in  $\text{CH}_2\text{Cl}_2$ . (c-d) The change trends of PL I and PL II of  $\text{AuCu}_{14}\text{-CH}(\text{CH}_3)_2$  under different excitations in  $\text{CH}_2\text{Cl}_2$ .



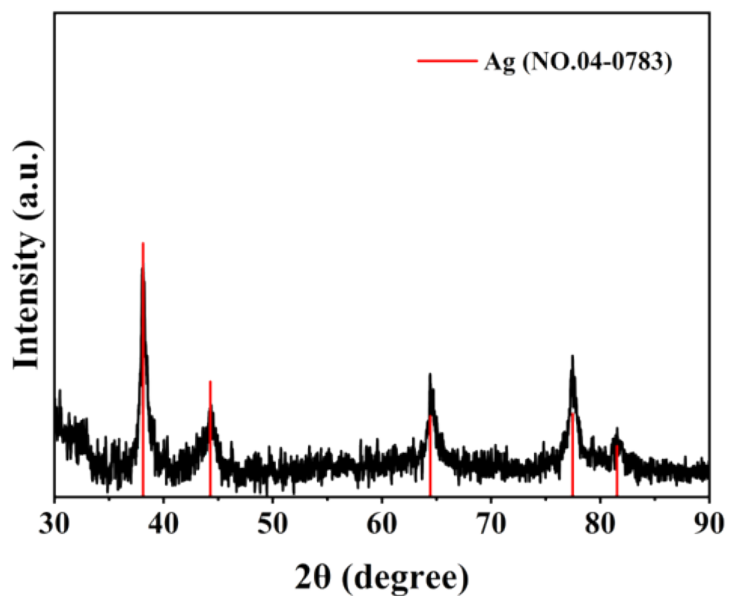
**Figure S14.** PL spectra of **AuCu<sub>14</sub>-CH<sub>3</sub>**, **AuCu<sub>14</sub>-CH(CH<sub>3</sub>)<sub>2</sub>** and **AuCu<sub>14</sub>-C(CH<sub>3</sub>)<sub>3</sub>** in DCM. Orange and purple areas represent the fitted PL I and PL II, respectively.



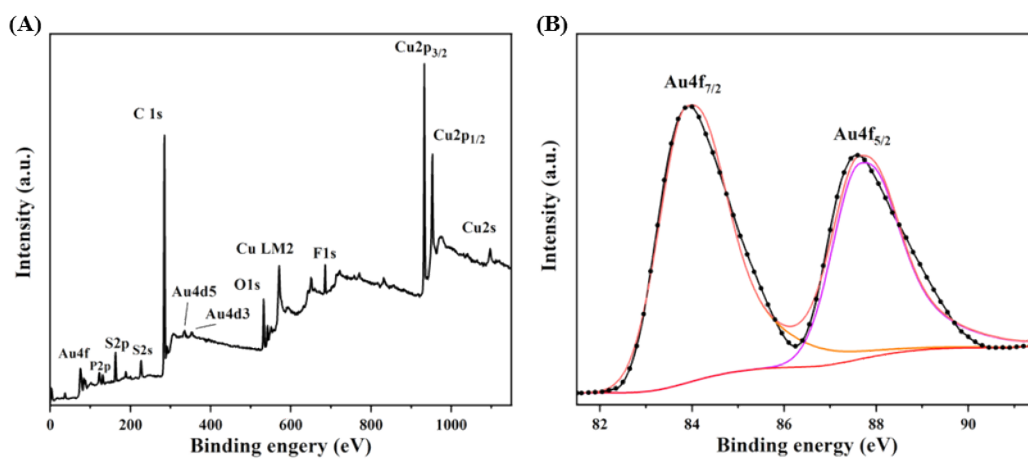
**Figure S15.** Overlay of (a) **AuCu<sub>14</sub>-CH<sub>3</sub>** and (b) **AuCu<sub>14</sub>-C(CH<sub>3</sub>)<sub>3</sub>** SCXRD structures capturing the orientation differences of carbon tails.



**Figure S16.** UV-vis absorption spectra of the supernatant after the addition of  $\text{Ag}^+$  ion into  $\text{AuCu}_{14}\text{-CH}(\text{CH}_3)_2$  solution (inset: photographs of the reaction system).



**Figure S17.** XRD spectrum of the precipitation after the addition of  $\text{Ag}^+$  ion into  $\text{AuCu}_{14}\text{-CH}(\text{CH}_3)_2$  solution.



**Figure S18.** (A) The X-ray photoelectron spectroscopy (XPS) spectrum of crystalline **AuCu<sub>14</sub>**; (B) the high-resolution of Au 4f part.

**Table S1.** Experimental single crystal X-ray data.

Identification code	<b>AuCu<sub>14</sub>-CH<sub>3</sub></b>	<b>AuCu<sub>14</sub>-CH(CH<sub>3</sub>)<sub>2</sub></b>	<b>AuCu<sub>14</sub>-C(CH<sub>3</sub>)<sub>3</sub></b>
Empirical formula	C <sub>192</sub> H <sub>174</sub> Au <sub>0.6</sub> Cu <sub>14</sub> F <sub>5.4</sub> P <sub>6</sub> S <sub>12</sub> Sb <sub>0.9</sub> <sup>a</sup>	C <sub>216</sub> H <sub>216</sub> AuCu <sub>14</sub> P <sub>6</sub> S <sub>12</sub>	C <sub>228</sub> H <sub>246</sub> AuCu <sub>14</sub> F <sub>6</sub> P <sub>6</sub> S <sub>12</sub> Sb
Formula weight	4271.76	4251.23	4879.05
Temperature /K	120	120.15	120
Crystal system	Triclinic	monoclinic	Triclinic
Space group	P-1	P2 <sub>1</sub> /n	P-1
a /Å	16.5353(2)	19.4553(2)	18.9192(3)
b /Å	16.7733(2)	27.6070(2)	20.0872(3)
c /Å	19.1444(3)	21.0119(3)	21.2779(2)
α /°	110.9310(10)	90	65.5700(10)
β /°	109.6290(10)	95.8050(10)	76.1360(10)
γ /°	98.0240(10)	90	62.742(2)
Volume /Å <sup>3</sup>	4463.14(11)	11227.7(3)	6532.17(19)
Z	1	2	1
ρ <sub>calc</sub> g/cm <sup>3</sup>	1.589	1.257	1.240
μ /mm <sup>-1</sup>	5.981	4.379	4.632
F(000)	2156.0	4126.0	2486.0
Radiation	CuKα (λ = 1.54186 Å)	CuKα (λ = 1.54184 Å)	CuKα (λ = 1.54184 Å)
2 θ range for data collection/°	5.438 to 132	5.576 to 129.996	5.264 to 140
Index ranges	-19 ≤ h ≤ 15, -19 ≤ k ≤ 19, -22 ≤ l ≤ 22	-22 ≤ h ≤ 17, -32 ≤ k ≤ 28, -24 ≤ l ≤ 23	-22 ≤ h ≤ 23, -24 ≤ k ≤ 24, -25 ≤ l ≤ 25
Reflections collected	55053	70984	93303
Independent reflections	15529 [R <sub>int</sub> = 0.0662, R <sub>sigma</sub> = 0.0475]	18938 [R <sub>int</sub> = 0.0631, R <sub>sigma</sub> = 0.0468]	24657 [R <sub>int</sub> = 0.0748, R <sub>sigma</sub> = 0.0505]
Data/restraints/parameters	15529/30/874	18938/4655/1099	24657/124/1298
Goodness-of-fit on F <sup>2</sup>	1.077	1.025	1.008
Final R indexes [I ≥ 2σ (I)] <sup>b</sup>	R <sub>1</sub> = 0.0748, wR <sub>2</sub> = 0.1997	R <sub>1</sub> = 0.0952, wR <sub>2</sub> = 0.2644	R <sub>1</sub> = 0.0544, wR <sub>2</sub> = 0.1484
Final R indexes [all data] <sup>b</sup>	R <sub>1</sub> = 0.0786, wR <sub>2</sub> = 0.2015	R <sub>1</sub> = 0.0992, wR <sub>2</sub> = 0.2690	R <sub>1</sub> = 0.0573, wR <sub>2</sub> = 0.1507
CCDC	2366812	2496270	1940446

<sup>a</sup> Formula is given based on single-crystal X-ray data.

<sup>b</sup>  $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ ,  $wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$

**Table S2.** Average bond length (Å) in **AuCu<sub>14</sub>-C(CH<sub>3</sub>)<sub>3</sub>**, **AuCu<sub>14</sub>-CH(CH<sub>3</sub>)<sub>2</sub>** and **AuCu<sub>14</sub>-CH<sub>3</sub>**.

	Au-Cu	Cu-Cu	Cu-S
<b>AuCu<sub>14</sub>-C(CH<sub>3</sub>)<sub>3</sub></b>	2.669	3.084	2.270
<b>AuCu<sub>14</sub>-CH(CH<sub>3</sub>)<sub>2</sub></b>	2.679	3.096	2.272
<b>AuCu<sub>14</sub>-CH<sub>3</sub></b>	2.706	3.127	2.278

**Table S3.** The primary bond length of **AuCu<sub>14</sub>-CH<sub>3</sub>**.

Bond	Length(Å)	Bond	Length(Å)
Au1-Cu2	2.778	Au1-Cu4	2.791
Au1-Cu5	2.594	Au1-Cu6	2.661
Au1-Cu8	2.778	Au1-Cu10	2.791
Au1-Cu12	2.594	Au1-Cu14	2.661
Cu2-Cu4	3.229	Cu2-Cu5	3.008
Cu2-Cu6	3.132	Cu4-Cu12	3.085

Cu4-Cu13	3.295	Cu5-Cu11	3.085
Cu5-Cu13	3.017	Cu6-Cu11	3.295
Cu6-Cu12	3.017	Cu9-Cu11	3.229
Cu9-Cu12	3.008	Cu9-Cu13	3.132
Cu2-S1	2.293	Cu2-S5	2.274
Cu2-S6	2.279	Cu4-S2	2.284
Cu4-S4	2.273	Cu4-S6	2.293
Cu5-S2	2.307	Cu5-S3	2.287
Cu5-S5	2.295	Cu6-S1	2.264
Cu6-S3	2.290	Cu6-S4	2.306
Cu9-S7	2.293	Cu9-S11	2.274
Cu9-S12	2.279	Cu11-S8	2.284
Cu11-S10	2.273	Cu11-S12	2.293
Cu12-S8	2.307	Cu12-S9	2.287
Cu12-S11	2.295	Cu13-S7	2.264
Cu13-S9	2.290	Cu13-S10	2.306
S3-Cu1	2.257	S6-Cu1	2.286
S4-Cu3	2.250	S5-Cu3	2.263
S1-Cu7	2.266	S2-Cu7	2.250
S9-Cu8	2.257	S12-Cu8	2.286
S10-Cu10	2.250	S11-Cu10	2.263
S7-Cu14	2.266	S8-Cu14	2.250

**Table S4.** The primary bond length of  $\text{AuCu}_{14}\text{-CH}(\text{CH}_3)_2$ .

Bond	Length(Å)	Bond	Length(Å)
Au1-Cu1	2.729	Au1-Cu3	2.721
Au1-Cu5	2.706	Au1-Cu7	2.561
Au1-Cu8	2.729	Au1-Cu10	2.721
Au1-Cu12	2.706	Au1-Cu14	2.561
Cu1-Cu7	3.012	Cu3-Cu7	2.974
Cu5-Cu7	2.949	Cu5-Cu10	3.217
Cu5-Cu8	3.217	Cu3-Cu12	3.203
Cu3-Cu8	3.225	Cu1-Cu12	3.225
Cu1-Cu10	3.203	Cu12-Cu14	2.949
Cu10-Cu14	2.973	Cu8-Cu14	3.013
Cu1-S2	2.289	Cu1-S4	2.289
Cu1-S5	2.266	Cu3-S1	2.292
Cu3-S3	2.275	Cu3-S4	2.292
Cu5-S1	2.295	Cu5-S2	2.285
Cu5-S6	2.270	Cu7-S3	2.276
Cu7-S5	2.279	Cu7-S6	2.286
Cu8-S8	2.289	Cu8-S10	2.289

Cu8-S11	2.266	Cu10-S7	2.292
Cu10-S9	2.275	Cu10-S10	2.292
Cu12-S7	2.295	Cu12-S8	2.285
Cu12-S12	2.270	Cu14-S9	2.276
Cu14-S11	2.279	Cu14-S12	2.286
S1-Cu2	2.256	S5-Cu2	2.238
S2-Cu4	2.261	S3-Cu4	2.255
S4-Cu6	2.263	S6-Cu6	2.246
S7-Cu9	2.256	S11-Cu9	2.238
S8-Cu11	2.261	S9-Cu11	2.255
S10-Cu13	2.263	S12-Cu13	2.246

**Table S5.** The primary bond length of  $\text{AuCu}_{14}\text{-C}(\text{CH}_3)_3$ .

Bond	Length(Å)	Bond	Length(Å)
Au1-Cu2	2.555	Au1-Cu3	2.743
Au1-Cu5	2.707	Au1-Cu7	2.670
Au1-Cu9	2.555	Au1-Cu10	2.743
Au1-Cu12	2.707	Au1-Cu14	2.670
Cu2-Cu3	3.005	Cu2-Cu5	2.914
Cu2-Cu7	3.033	Cu3-Cu12	3.337
Cu3-Cu14	3.122	Cu5-Cu10	3.337
Cu5-Cu14	3.092	Cu7-Cu10	3.122
Cu7-Cu12	3.092	Cu9-Cu10	3.005
Cu9-Cu12	2.914	Cu9-Cu14	3.033
Cu2-S2	2.281	Cu2-S3	2.281
Cu2-S5	2.281	Cu3-S1	2.275
Cu3-S2	2.273	Cu3-S6	2.273
Cu5-S4	2.299	Cu5-S5	2.258
Cu5-S6	2.281	Cu7-S1	2.302
Cu7-S3	2.285	Cu7-S4	2.275
Cu9-S8	2.281	Cu9-S9	2.281
Cu9-S11	2.281	Cu10-S7	2.275
Cu10-S8	2.273	Cu10-S12	2.273
Cu12-S10	2.299	Cu12-S11	2.258
Cu12-S12	2.281	Cu14-S7	2.302
Cu14-S9	2.285	Cu14-S10	2.275
S2-Cu1	2.247	S4-Cu1	2.240
S1-Cu4	2.267	S5-Cu4	2.246
S3-Cu6	2.247	S6-Cu6	2.247
S8-Cu8	2.247	S10-Cu8	2.240
S7-Cu11	2.267	S11-Cu11	2.246
S9-Cu13	2.247	S12-Cu13	2.247

**Table S6.** Photophysical data of three AuCu<sub>14</sub> nanoclusters in CH<sub>2</sub>Cl<sub>2</sub> under ambient conditions.°

Solution phase	AuCu <sub>14</sub> -C(CH <sub>3</sub> ) <sub>3</sub>	Solution phase	AuCu <sub>14</sub> -CH(CH <sub>3</sub> ) <sub>2</sub>	AuCu <sub>14</sub> -CH <sub>3</sub>
$\Phi_{\text{PL}}(\%)$	4.13	$\Phi_{\text{PL}}(\%)$	5.37	5.76
$\text{PL } \tau_{\text{ave}} (\mu\text{s})$	3.3	$\text{PL I } \tau_{\text{ave}} (\text{ns})$	175.2	109.9
		$\text{PL II } \tau_{\text{ave}} (\mu\text{s})$	3.0	2.5
$\text{PL } k_{\text{r}} (\text{s}^{-1})$	$1.4 \times 10^4$	$\text{PL I } k_{\text{r}} (\text{s}^{-1})$	$2.1 \times 10^5$	$4.2 \times 10^5$
		$\text{PL I } k_{\text{nr}} (\text{s}^{-1})$	$5.5 \times 10^6$	$8.7 \times 10^6$
$\text{PL } k_{\text{nr}} (\text{s}^{-1})$	$2.9 \times 10^5$	$\text{PL II } k_{\text{r}} (\text{s}^{-1})$	$5.4 \times 10^3$	$4.4 \times 10^3$
		$\text{PL II } k_{\text{nr}} (\text{s}^{-1})$	$3.3 \times 10^5$	$4.0 \times 10^5$

## Reference

- [1] T. N. Hooper, C. P. Butts, M. Green, M. F. Haddow, J. E. McGrady, C. A. Russell, *Chem. Eur. J.* **2009**, 15, 12196-12200.
- [2] K. J. Kilpin, R. Horvath, G. B. Jameson, S. G. Telfer, K. C. Gordon, J. D. Crowley, *Organometallics* **2010**, 29, 6186-6195.
- [3] P. Gao, J. Du, W. J. Hong, M. Z. Wu, Y. Feng, Y. J. Ding and M. Z. Zhu, *Small Struct.* **2024**, 6, 2400397.
- [4] O.V. Dolomanov, L.J. Bourhis, R.J Gildea, J.A.K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, 42, 339-341.
- [5] G.M. Sheldrick, *Acta Cryst.* **2015**, A71, 3-8.
- [6] G. M. Sheldrick, *Acta Cryst.* **2008**, A64, 112-122.