# The geometric and electronic structures of $Ag_{13}Cu_{10}(SAdm)_{12}X_3$ nanocluster

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## 1. Materials

Silver nitrate ($AgNO_3$, 98%), copper acetate ($Cu(CH_3COO)_2$), tetraoctylammonium bromide (TOAB, 98%), sodium borohydride ($NaBH_4$, 99.99%), bis-(diphenylphosphino)methane (Dppm, 98%), bis(diphenylphosphino)ethane (Dppe, 98%) to 1,6-bis(diphenylphosphino)hexane (Dpph, 98%), 1-Adamantanethiol (HSAdm, $C_{10}H_{16}S$, 99%), Sodium Hexafluoroantimonate ($NaSbF_6$), toluene (Tol, HPLC grade, Aldrich), methanol ($CH_3OH$, HPLC, Aldrich), n-hexane (Hex, HPLC grade, Aldrich), dichloromethane ($CH_2Cl_2$, HPLC grade, Aldrich), Pure water (Wahaha Co. Ltd). All reagents were used as received without further purification.

## 2. Synthesis of $Ag_{13}Cu_{10}(C_{10}H_{15}S)_{12}X_3$

The $Ag_{13}Cu_{10}(C_{10}H_{15}S)_{12}$ clusters were synthesized by phosphorus ligands auxiliary induction method. First, 100 mg TOAB was dissolved in 30 mL dichloromethane. Second, 60 mg silver nitrate (dissolved in mixture solution of 2 ml methanol and 2 ml $H_2O$) and 60 mg copper acetate (dissolved in mixture solution of 2 ml methanol and 2 ml $H_2O$) were added the dichloromethane solution and mixed. Third, 50 mg bis-(diphenylphosphino)methane (Dppm) and 60 mg adamantane mercaptan (HSAdm) were added together to the dichloromethane solution, stirred for 30 min. Forth, 2 mL of an aqueous solution containing 20 mg sodium borohydride was added quickly to the reactor. Finally, after 8 h, the crude product was obtained. The crude product was washed with hexane and collected by centrifugation again. Subsequently, $CH_3OH$ was used to separate the alloy nanoclusters, and the excess $NaSbF_6$ dissolved in $CH_3OH$ was added into the supernatant solution. This solution was centrifuged for 3 min at 8000 rpm and the target product was collected. The yield is about 20% based on the Ag element for $[Ag_{13}Cu_{10}(SAdm)_{12}]X_3$.

Single-crystal growth was performed via vapor diffusion of pentane into a $CH_2Cl_2$ solution of nanoclusters. Red single crystals of the $Ag_{13}Cu_{10}(C_{10}H_{15}S)_{12}\mathbf{X_3}$ nanoclusters are found to adapt the space group of *Fd***Error!**c. The highly symmetrical structure prevented us from finding free $SbF_6^-$, but the $SbF_6^-$ could be observed in the ESI spectra.

It is worth noting that the synthesis of the $Ag_{13}Cu_{10}(SAdm)_{12}X_3$ nanoclusters are not achievable if phosphorus ligands are absent. As shown in Figure S1, the nanoparticle, not the

target product $Ag_{13}Cu_{10}(SAdm)_{12}X_3$ was obtained when without adding Dppm ligand in the synthesis. In addition, phosphine ligands with different chain lengths 1,2-bis(diphenylphosphino)ethane (Dppe) to 1,6-bis(diphenylphosphino)hexane (Dpph) were also tried. Shown in Figure S2, although 1,3-bis(diphenylphosphino)propane, 1,5-bis(diphenylphosphino)pentane and 1,6-bis(diphenylphosphino)hexane can assist the synthesis of $Ag_{13}Cu_{10}(SAdm)_{12}X_3$, the product is unstable and decomposes during post processing. Even though the phosphorus ligands are not found in the final product, they act as promoters for the formation of the final product.

**3. Characterization**

UV/Vis absorption spectrum of $Ag_{13}Cu_{10}(C_{10}H_{15}S)_{12}X_3$ nanoparticle dissolved in $CH_3OH$ were recorded using an Agilent 8453. Electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) measurement was performed by Waters UPLC H-class/XEVO G2-XS Qtof mass spectrometer. The sample was directly infused into the chamber at 5μL/min. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on Bruker Autoflex III TOF. Trans-2-[3(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was used as the MALDI matrix. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250 configured with a mono chromated 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 1 x $10^{-9}$ mbar, data were collected with FAT = 20 eV. Photoluminescence spectra were measured on a FL-7000 spectrofluorometer with the same optical density (OD) ~0.2.

**4. X-ray Crystallographic Determination of $Ag_{13}Cu_{10}(C_{10}H_{15}S)_{12}X_3$**

The data collection for single crystal X-ray diffraction of $Ag_{13}Cu_{10}(C_{10}H_{15}S)_{12}$ was carried out on a Bruker Smart APEX II CCD diffractometer at 123 K. Using graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å). Data reductions and absorption corrections were performed using the SAINT and SADABS programs, respectively.[S1] The structure was resolved by direct methods and refined with full-matrix least squares on $F^2$ using the SHELXTL software package.[S2] All non-hydrogen atoms were refined anisotropically, and all of the hydrogen atoms were set in geometrically calculated positions and refined isotropically using a riding model.

S1. APEX II software suite, Bruker-AXS, 2006.

S2. SHELXTL, G. M. Sheldrick, *Acta Crystallogr., A* 2008, **64**, 112.

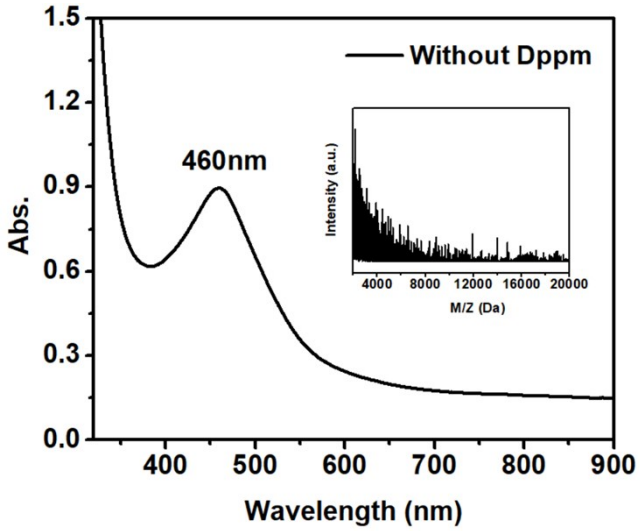


Figure S1. The UV-vis spectrum and MALDI spectrum of product synthesized without Dppm ligand during the synthesis process.

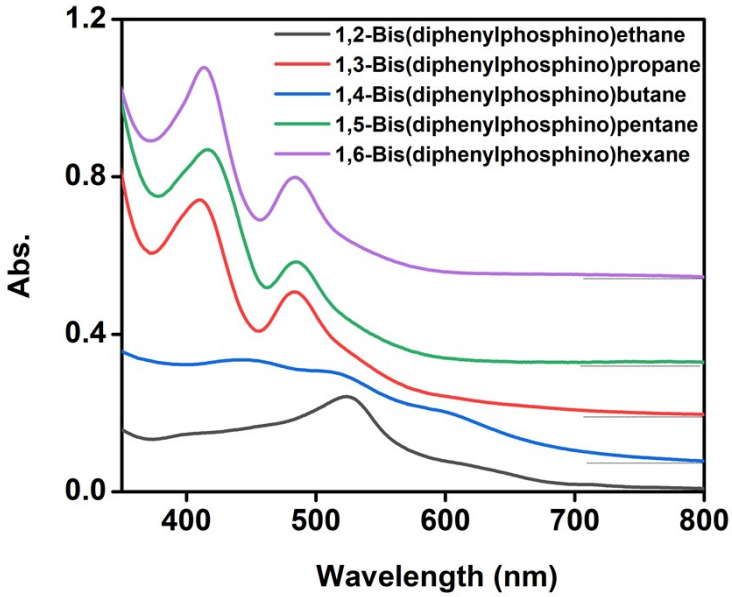


Figure S2. The UV-Vis spectra of crude product synthesized via adding phosphine ligands with different chain lengths

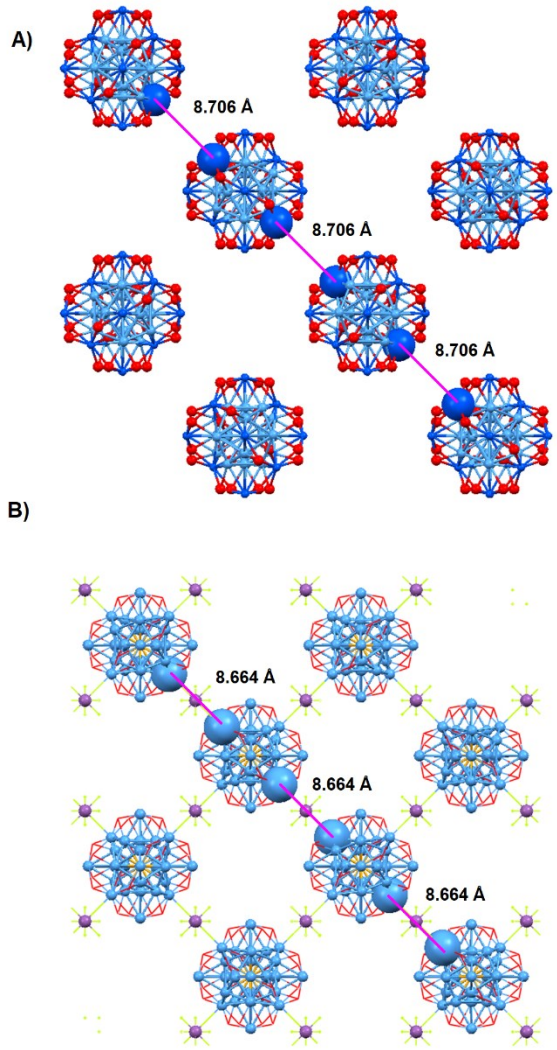


Figure S3. the packing model of $[Ag_{13}Cu_{10}(C_{10}H_{15}S)_{12}]X_3$ and $[Au_1Ag_{12}@Ag_{10}(S\text{-}Adm)_{12}](SbF_6)_2X$.

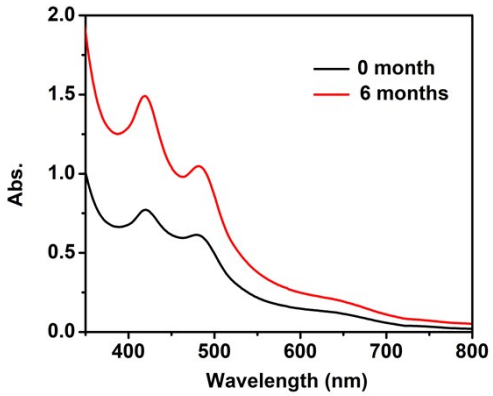


Figure S4. UV-vis spectra of $[Ag_{13}Cu_{10}(C_{10}H_{15}S)_{12}]X_3$ which stored in solid state for more than 6 months.

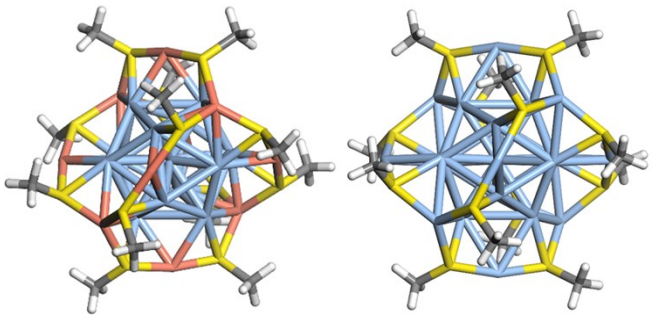

Figure S5. The optimized geometries of $\mathbf{Ag_{13}Cu_{10}}^{\mathbf{T}}$ and $\mathbf{Ag_{23}}^{\mathbf{T}}$in theoretical calculations. Color codes: blue, Ag; red, Cu; yellow, S; grey, C; white, H.

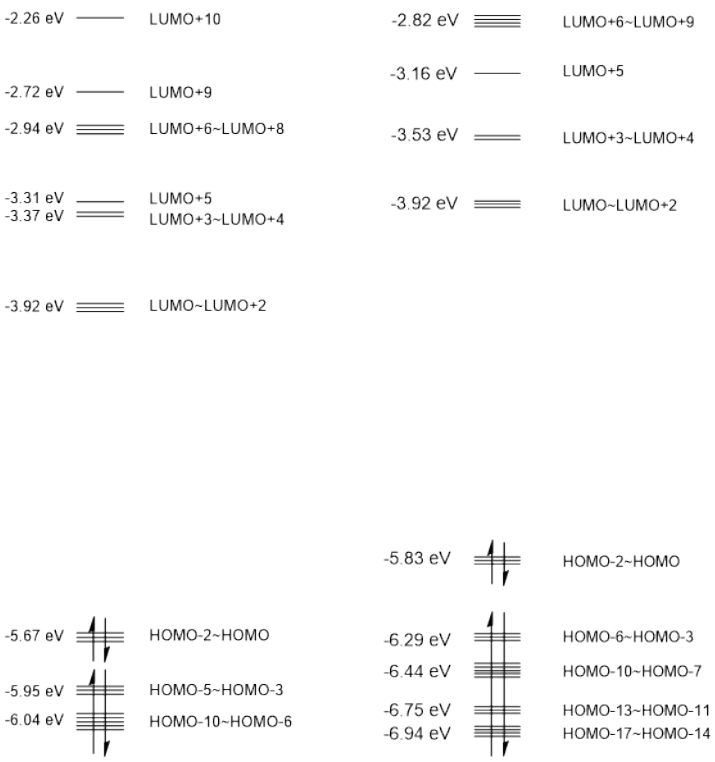


Figure S6. Energy level diagram of $\mathbf{Ag_{13}Cu_{10}}^{\mathbf{T}}$(left) and $\mathbf{Ag_{23}}^{\mathbf{T}}$(right).

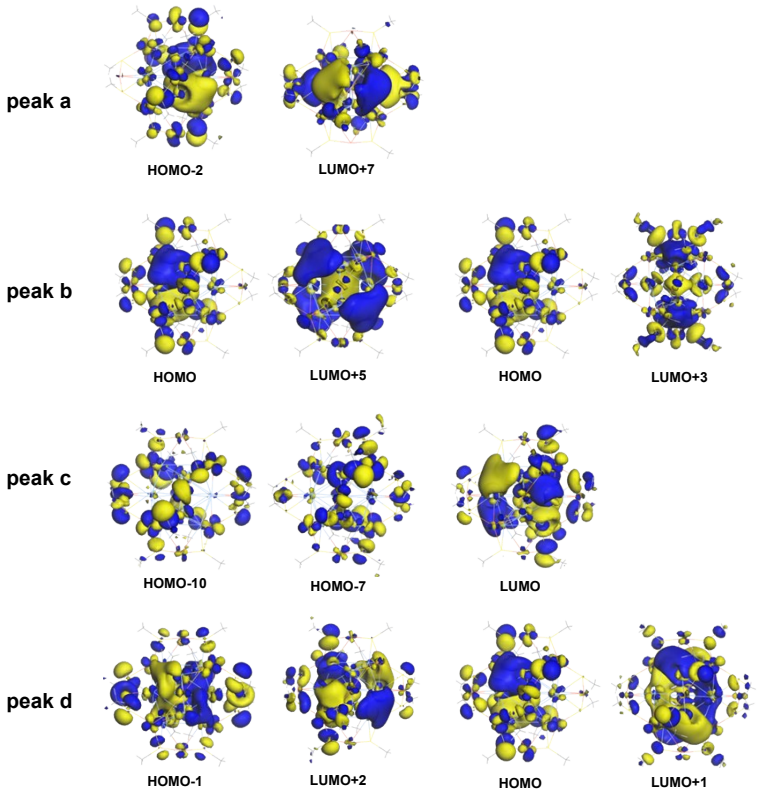


Figure S7. Transition involved frontier molecular orbitals of $\mathbf{Ag_{13}Cu_{10}}^{\mathbf{T}}$.

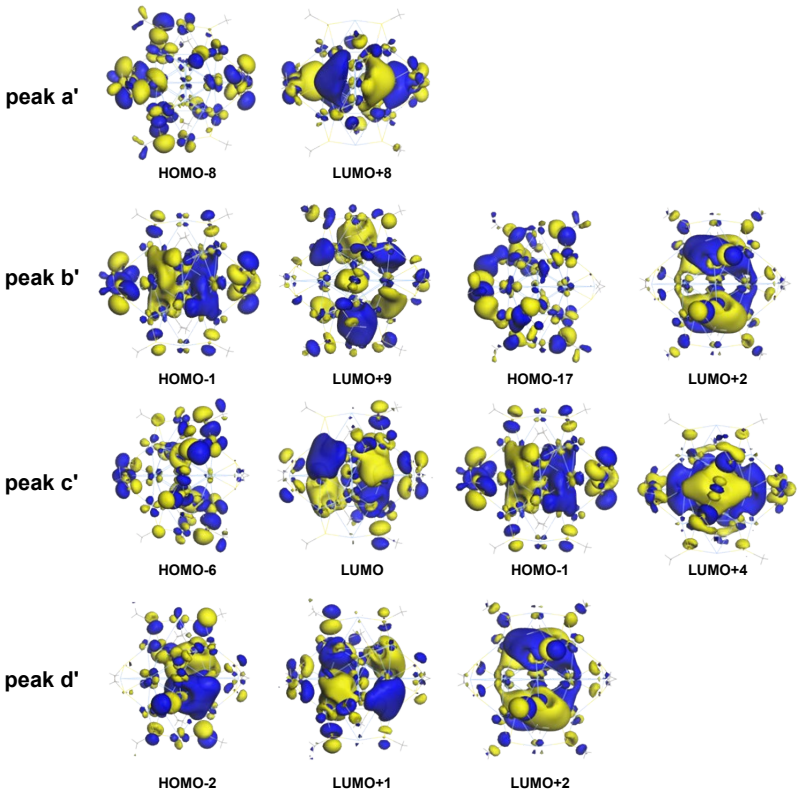


Figure S8. Transition involved frontier molecular orbitals of $\mathbf{Ag_{23}}^{\mathbf{T}}$.

**Table S1.** Crystal Date and Structure Refinement of the $[Ag_{13}Cu_{10}(C_{10}H_{15}S)_{12}]$ $\mathbf{X_3}$ nanocluster.

| | |
|---|---|
| Chemical formula | $C_{120}H_{180}Ag_{13}Cu_{10}S_{12}$ |
| Formula Mass | 4045.06 |
| Crystal system | cubic |
| *a*/Å | 41.4111(11) |
| *b*/Å | 41.4111(11) |
| *c*/Å | 41.4111(11) |
| *α*/° | 90 |
| *β*/° | 90 |
| *γ*/° | 90 |
| Unit cell volume/Å$^3$ | 71015(6) |
| Temperature/K | 123(2) |
| Space group | *Fd***Error!***c* |
| No. of formula units per unit cell, *Z* | 16 |
| No. of reflections measured | 227561 |
| No. of independent reflections | 3703 |
| $R_{int}$ | 0.0285 |
| Final $R_1$ values ($I > 2\sigma(I)$) | 0.0307 |
| Final $wR(F^2)$ values ($I > 2\sigma(I)$) | 0.1050 |
| Final $R_1$ values (all data) | 0.0475 |
| Final $wR(F^2)$ values (all data) | 0.1078 |

Table S2. The comparison of the bond length of the icosahedral metal core via surface doping or nuclear doping in reported nanoclusters.

| Cluster | Doping method | Kernel | Average bond length |
|---|---|---|---|
| $Ag_{29}(BDT)_{12}(TPP)_4$[S3] | none | $Ag_{13}$ | 2.889 Å |
| $Ag_{28}Au(BDT)_{12}(TPP)_4$[S4] | nuclear | $Au_1Ag_{12}$ | 2.890 Å |
| $[Ag_{25}(SR)_{18}]^-$[S5] | none | $Ag_{13}$ | 2.866 Å |

| | | | |
|---|---|---|---|
| $[Ag_{24}Au(SR)_{18}]^{-}$ (S6) | nuclear | $Au_1Ag_{12}$ | 2.862 Å |
| $[PtAg_{24}(SR)_{18}]^{2-}$(S7) | nuclear | $Pt_1Ag_{12}$ | 2.849 Å |
| $[PdAg_{24}(SR)_{18}]^{2-}$(S7) | nuclear | $Pd_1Ag_{12}$ | 2.882 Å |
| $Ag_{13}Cu_{10}(SAdm)_{12}X_3$ | surface | $Ag_{13}$ | 2.902 Å |

(S3) L. G. AbdulHalim, M. S. Bootharaju, Q. Tang, S. Del Gobbo, R. G. AbdulHalim, M. Eddaoudi, D.-E. Jiang and O. M. Bakr, *J. Am. Chem. Soc.* 2015, **137**, 11970-11975.

(S4) G. Soldan, M. A. Aljuhani, M. S. Bootharaju, L.G. AbdulHalim, M.R. Parida, A.-H. Emwas, O. F. Mohammed, and O. M. Bakr, *Angew. Chem. Int. Ed.* 2016, **55**, 5749-5753.

(S5) C. P. Joshi, M. S. Bootharaju, M. J. Alhilaly, and O. M. Bakr, *J. Am. Chem. Soc.* 2015, **137**, 11578-11581.

(S6) M. S. Bootharaju, C. P. Joshi, M. R. Parida, O.F. Mohammed, and O.M. Bakr, *Angew. Chem. Int. Ed.* 2016, **55**, 922-926.

(S7) J. Z. Yan, H. F. Su, H. Y. Yang, S. Malola, S. C. Lin, H. Hakkinen, and N. F. Zheng, *J. Am. Chem. Soc.* 2015, **137**, 11880-11883.

Table S3. The coordinate of the optimized geometry of **$Ag_{13}Cu_{10}$**.

| | | | |
|---|---|---|---|
| Ag | 5.165661 | 5.176509 | 5.176557 |
| Ag | 3.602486 | 7.577806 | 5.310839 |
| C | 1.932091 | 10.593519 | 4.454020 |
| Cu | 7.692574 | 2.665328 | 2.689666 |
| S | 9.645973 | 3.818330 | 3.402303 |
| Ag | 6.734190 | 2.784822 | 5.324153 |
| C | 8.408398 | -0.257040 | 4.499537 |
| Ag | 2.778742 | 5.026918 | 3.607834 |
| C | -0.216301 | 5.854170 | 1.914024 |
| S | 9.646029 | 6.534518 | 6.950610 |
| Ag | 6.734152 | 7.568091 | 5.028777 |
| C | 8.408335 | 10.609932 | 5.853011 |
| Cu | 5.182991 | 5.216676 | 9.821447 |
| Cu | 2.693483 | 2.677036 | 7.695547 |
| S | 3.823471 | 3.443100 | 9.660125 |
| Ag | 7.565125 | 5.306305 | 3.613185 |

| | | | |
|---|---|---|---|
| C | 10.609908 | 4.475448 | 1.955985 |
| Cu | 0.524618 | 5.176337 | 5.176401 |
| S | 0.722298 | 6.505482 | 3.378967 |
| Ag | 3.602747 | 2.775150 | 5.042261 |
| C | 1.931939 | -0.239983 | 5.897548 |
| Ag | 2.778684 | 5.325951 | 6.745305 |
| C | -0.216687 | 4.497497 | 8.438721 |
| S | 0.722466 | 3.847094 | 6.973742 |
| Cu | 5.182952 | 5.136102 | 0.531538 |
| S | 3.823456 | 6.909675 | 0.692849 |
| Ag | 7.565135 | 5.046645 | 6.739782 |
| Cu | 5.184353 | 9.826306 | 5.142187 |
| Cu | 2.693300 | 7.675655 | 2.657375 |
| S | 3.387928 | 9.631551 | 3.815857 |
| Ag | 5.315505 | 3.621373 | 7.583377 |
| C | 4.463807 | 2.019954 | 10.667346 |
| C | 10.609778 | 5.877284 | 8.397000 |
| S | 3.387831 | 0.721136 | 6.536859 |
| Ag | 5.315364 | 6.731472 | 2.769629 |
| C | 4.463859 | 8.332844 | -0.314281 |
| S | 6.955447 | 9.652470 | 6.504411 |
| Ag | 5.033193 | 3.593449 | 2.790100 |
| C | 5.858921 | 1.883907 | -0.206535 |
| S | 6.517605 | 3.347395 | 0.730090 |
| Cu | 7.692650 | 7.687610 | 7.663176 |
| Cu | 5.184369 | 0.526587 | 5.210661 |

| | | | |
|---|---|---|---|
| S | 6.955428 | 0.700491 | 3.848445 |
| Ag | 5.033115 | 6.759622 | 7.562958 |
| C | 5.859989 | 8.468824 | 10.559943 |
| S | 6.517774 | 7.005288 | 9.622762 |
| Cu | 9.812593 | 5.176413 | 5.176462 |
| H | 2.076467 | 10.859825 | 5.506472 |
| H | 1.029258 | 9.985149 | 4.333119 |
| H | 1.855232 | 11.502750 | 3.844656 |
| H | 9.118815 | -0.367943 | 3.671222 |
| H | 8.053153 | -1.244276 | 4.816639 |
| H | 8.882877 | 0.263961 | 5.336403 |
| H | 0.398508 | 5.990181 | 1.017620 |
| H | -1.140325 | 6.439929 | 1.831277 |
| H | -0.456143 | 4.795107 | 2.052361 |
| H | 9.118878 | 10.720909 | 6.681210 |
| H | 8.052995 | 11.597125 | 5.535876 |
| H | 8.882676 | 10.088860 | 5.016105 |
| H | 11.588798 | 4.808508 | 2.319825 |
| H | 10.082018 | 5.299124 | 1.466227 |
| H | 10.745276 | 3.643433 | 1.254298 |
| H | 2.076724 | -0.505740 | 4.845019 |
| H | 1.029271 | 0.368646 | 6.018356 |
| H | 1.854432 | -1.149540 | 6.506333 |
| H | 0.397954 | 4.361236 | 9.335198 |
| H | -1.140550 | 3.911417 | 8.520990 |
| H | -0.456817 | 5.556557 | 8.300861 |

| | | | |
|---|---|---|---|
| H | 5.459210 | 1.711976 | 10.334017 |
| H | 3.752706 | 1.192949 | 10.556267 |
| H | 4.493948 | 2.339161 | 11.716256 |
| H | 11.588602 | 5.543960 | 8.033226 |
| H | 10.081673 | 5.053771 | 8.886801 |
| H | 10.745314 | 6.709322 | 9.098627 |
| H | 5.459316 | 8.640689 | 0.018998 |
| H | 3.752859 | 9.159913 | -0.203073 |
| H | 4.493902 | 8.013769 | -1.363234 |
| H | 6.602473 | 1.633617 | -0.973577 |
| H | 4.905195 | 2.139641 | -0.680277 |
| H | 5.728567 | 1.041130 | 0.480923 |
| H | 6.603892 | 8.718540 | 11.326835 |
| H | 4.906253 | 8.213475 | 11.033878 |
| H | 5.729867 | 9.311823 | 9.872714 |

Table S4. The coordinate of the optimized geometry of **$Ag_{23}$**.

| | | | |
|---|---|---|---|
| Ag | 5.159818 | 5.176253 | 5.176400 |
| Ag | 3.618128 | 7.594244 | 5.259899 |
| C | 1.600988 | 10.548350 | 4.881118 |
| Ag | 7.884003 | 2.486440 | 2.517746 |
| S | 9.820527 | 4.051468 | 3.057646 |
| Ag | 6.690166 | 2.760295 | 5.268620 |
| C | 8.702718 | -0.165425 | 5.054761 |
| Ag | 2.752943 | 5.076443 | 3.633874 |
| C | -0.202995 | 5.408775 | 1.626070 |

| | | | |
|---|---|---|---|
| S | 9.820157 | 6.300370 | 7.296286 |
| Ag | 6.690455 | 7.591943 | 5.084721 |
| C | 8.702735 | 10.518266 | 5.299648 |
| Ag | 5.189966 | 5.209068 | 10.114323 |
| Ag | 2.510967 | 2.494790 | 7.898642 |
| S | 4.072288 | 3.083931 | 9.834375 |
| Ag | 7.587685 | 5.255269 | 3.649883 |
| C | 10.522252 | 4.996173 | 1.630314 |
| Ag | 0.227779 | 5.175491 | 5.176052 |
| S | 0.565580 | 6.294961 | 3.054054 |
| Ag | 3.618127 | 2.757873 | 5.092620 |
| C | 1.601038 | -0.196577 | 5.471319 |
| Ag | 2.752693 | 5.275321 | 6.718085 |
| C | -0.202134 | 4.947083 | 8.725045 |
| S | 0.565193 | 4.057158 | 7.298640 |
| Ag | 5.191524 | 5.142732 | 0.238430 |
| S | 4.072520 | 7.267165 | 0.518561 |
| Ag | 7.587457 | 5.096673 | 6.703970 |
| Ag | 5.174351 | 10.115084 | 5.155977 |
| Ag | 2.511395 | 7.857207 | 2.454186 |
| S | 3.055642 | 9.787244 | 4.035695 |
| Ag | 5.256216 | 3.663833 | 7.598962 |
| C | 5.046629 | 1.681555 | 10.547251 |
| C | 10.522824 | 5.357047 | 8.724068 |
| S | 3.055346 | 0.564914 | 6.316981 |
| Ag | 5.257219 | 6.688851 | 2.753696 |

| | | | |
|---|---|---|---|
| C | 5.043054 | 8.670447 | -0.197487 |
| S | 7.296479 | 9.816859 | 6.278710 |
| Ag | 5.077427 | 3.621418 | 2.771266 |
| C | 5.393743 | 1.569575 | -0.135995 |
| S | 6.291602 | 3.015379 | 0.585232 |
| Ag | 7.883509 | 7.865401 | 7.836029 |
| Ag | 5.174293 | 0.237003 | 5.197213 |
| S | 7.296617 | 0.535140 | 4.074890 |
| Ag | 5.076591 | 6.730962 | 7.581765 |
| C | 5.394672 | 8.783343 | 10.489795 |
| S | 6.290260 | 7.336527 | 9.767839 |
| Ag | 10.102214 | 5.175799 | 5.177023 |
| H | 1.801275 | 10.692171 | 5.946904 |
| H | 0.734812 | 9.893819 | 4.742237 |
| H | 1.414547 | 11.517046 | 4.401764 |
| H | 9.553442 | -0.280642 | 4.372855 |
| H | 8.401069 | -1.149543 | 5.430200 |
| H | 8.971035 | 0.493251 | 5.885599 |
| H | 0.437929 | 5.531842 | 0.747134 |
| H | -1.180303 | 5.871498 | 1.440843 |
| H | -0.330699 | 4.347204 | 1.857211 |
| H | 9.553222 | 10.633247 | 5.981879 |
| H | 8.400967 | 11.502541 | 4.924723 |
| H | 8.971475 | 9.860176 | 4.468460 |
| H | 11.497373 | 5.397490 | 1.928341 |
| H | 9.854107 | 5.805966 | 1.323992 |

| | | | |
|---|---|---|---|
| H | 10.657166 | 4.286258 | 0.805787 |
| H | 1.801722 | -0.340690 | 4.405646 |
| H | 0.734750 | 0.457891 | 5.609705 |
| H | 1.414526 | -1.165153 | 5.950876 |
| H | 0.438766 | 4.825223 | 9.604161 |
| H | -1.180033 | 4.486021 | 8.911372 |
| H | -0.328545 | 6.008289 | 8.491476 |
| H | 6.021540 | 1.590455 | 10.059902 |
| H | 4.465511 | 0.763939 | 10.403400 |
| H | 5.173150 | 1.871419 | 11.619542 |
| H | 11.498082 | 4.956040 | 8.426079 |
| H | 9.855229 | 4.547130 | 9.031264 |
| H | 10.657624 | 6.067642 | 9.548039 |
| H | 6.018307 | 8.764500 | 0.288598 |
| H | 4.460101 | 9.587011 | -0.054345 |
| H | 5.168742 | 8.479347 | -1.269651 |
| H | 5.994272 | 1.199309 | -0.976094 |
| H | 4.407296 | 1.877608 | -0.494507 |
| H | 5.296015 | 0.789292 | 0.624644 |
| H | 5.996392 | 9.152835 | 11.329380 |
| H | 4.408096 | 8.476692 | 10.849140 |
| H | 5.297383 | 9.563754 | 9.729247 |