Electronic Supplementary Material (ESI) for Nanoscale.

An Atomically Precise $Ag_{18}Cu_8$ Nanocluster with Rich Alkynyl-Metal Coordination Structures and Unique SbF_6^- Assembling Modes

Xueli Sun[1, +], Xiongkai Tang[2, +], Yan-Li Gao[3], Yujuan Zhao[1], Qingyuan Wu[2], Dongxu Cao[2] and Hui Shen[1, *]

[1] College of Energy Materials and Chemistry, Inner Mongolia University, Hohhot 010021, China

[2] College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

[3] School of Chemistry and Chemical Engineering, Yulin University, Yulin 719000, China

+These authors contributed equally to this work

E-mail: shen@imu.edu.cn

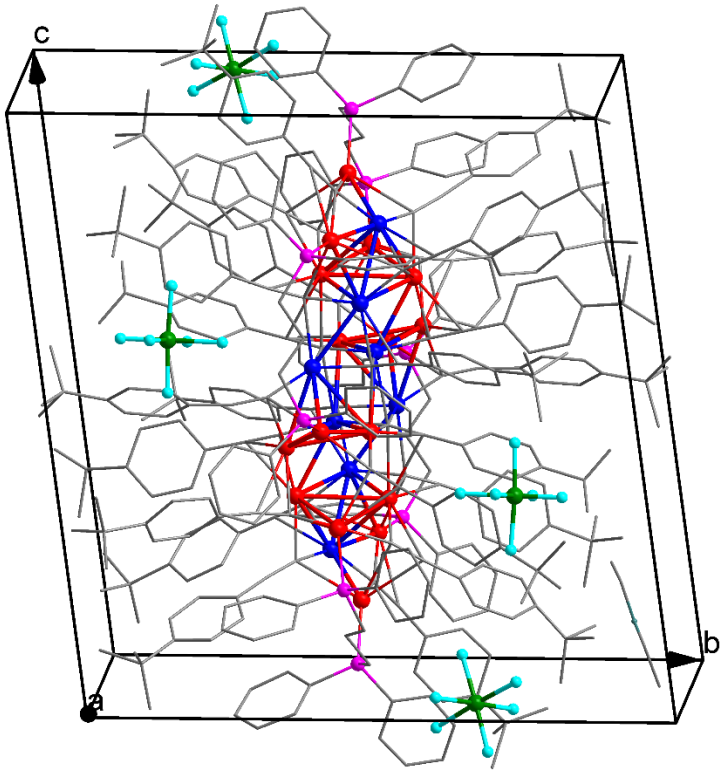

Figure S1. The packing structure of $[Ag_{18}Cu_8(dppp)_4(^tBu\text{-}C_6H_4C{\equiv}C)_{22}](SbF_6)_4$ in the unit cell. Color codes for atoms: red spheres, Ag; blue spheres, Cu; pink spheres, P; grey spheres, C; green spheres, Sb; turquoise spheres, F; teal spheres, O. All hydrogen atoms are omitted for clarity.

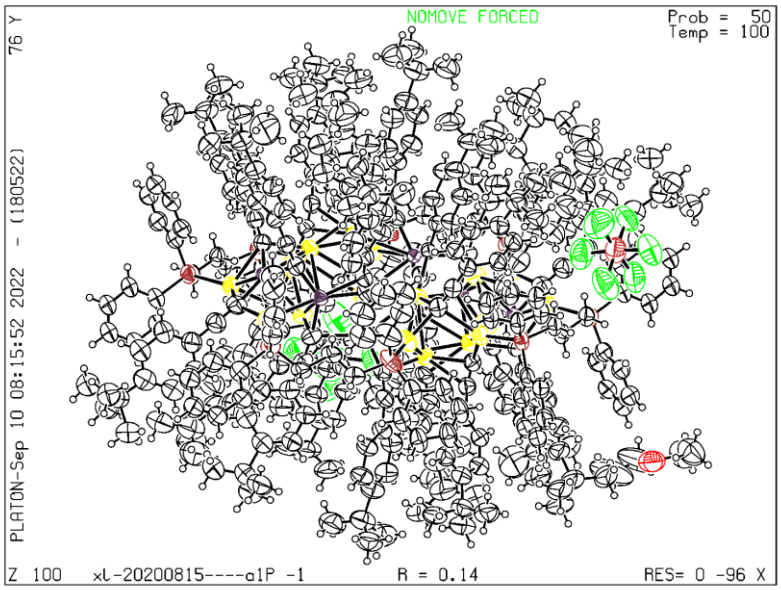

Figure S2. The thermal ellipsoids of the ORTEP diagram of $[Ag_{18}Cu_8(dppp)_4(^tBu\text{-}C_6H_4C{\equiv}C)_{22}](SbF_6)_4$.

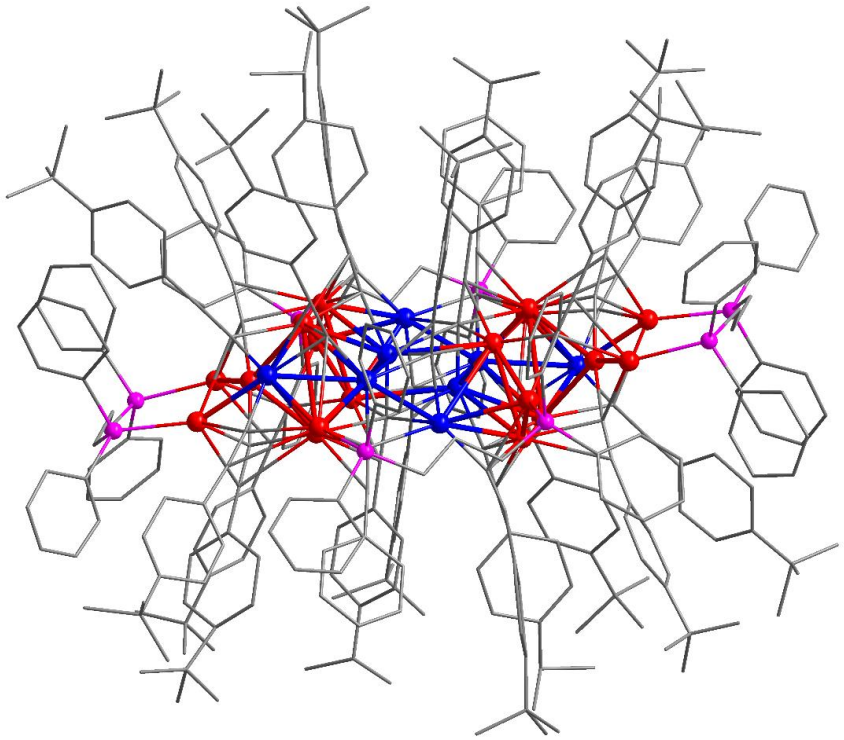

Figure S3. Total structure of $[Ag_{18}Cu_8(dppp)_4(^tBu\text{-}C_6H_4C{\equiv}C)_{22}]^{4+}$ in the side view. Color codes for atoms: red spheres, Ag; blue spheres, Cu; pink spheres, P; grey spheres, C. All hydrogen atoms are omitted for clarity.

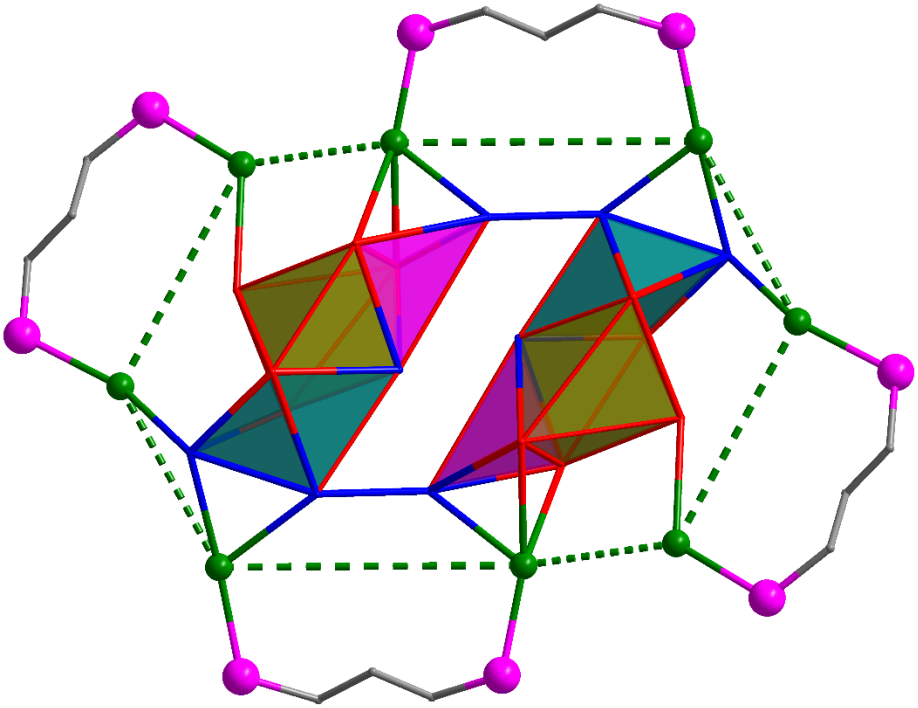

Figure S4. $Ag_{10}Cu_8$ core and an 8-silver-atom-shell in $[Ag_{18}Cu_8(dppp)_4(^tBu\text{-}C_6H_4C{\equiv}C)_{22}]^{4+}$ cluster. Color codes for atoms: red spheres, Ag in the $Ag_{10}Cu_8$ core; green spheres, Ag in the Ag_8 shell; blue spheres, Cu; pink spheres, P; grey spheres, C. All hydrogen atoms are omitted for clarity.

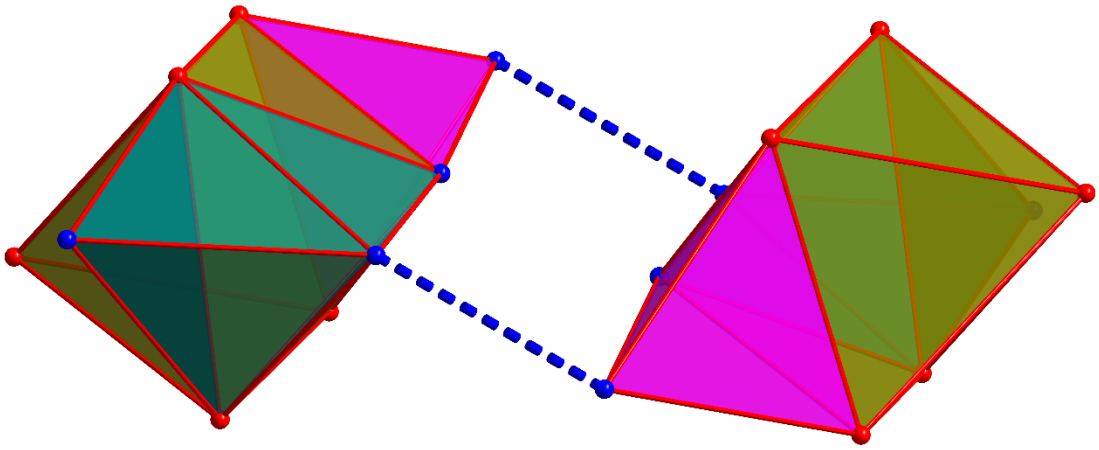

Figure S5. Combination of two mixed polyhedrons in $Ag_{18}Cu_8$ metal core in the side view.

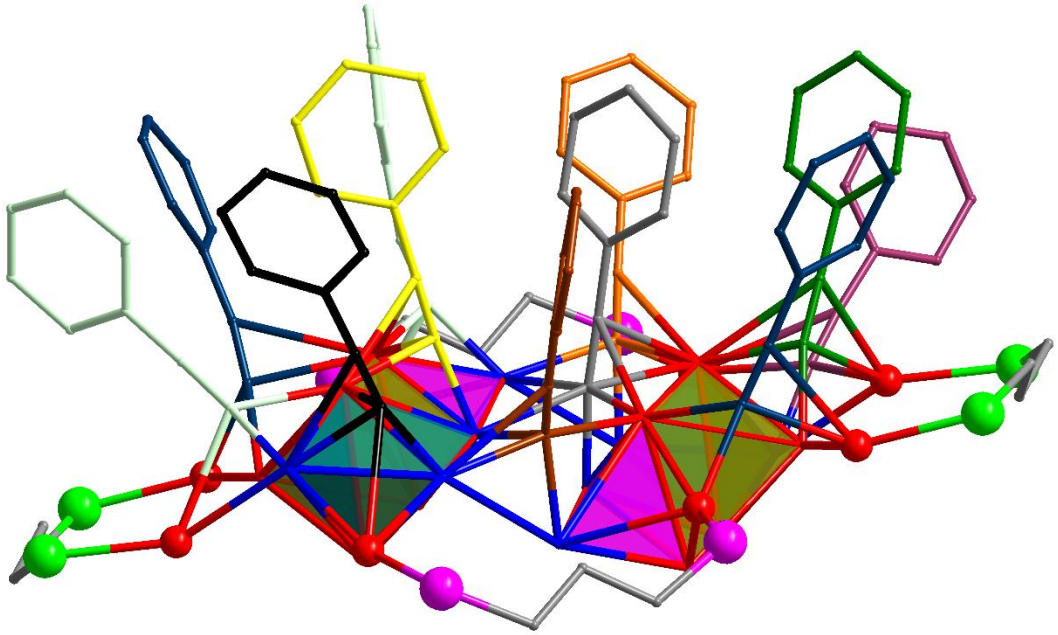

Figure S6. Rich coordination structure of alkynyl ligands and different coordination environment of dppp in $[Ag_{18}Cu_8(dppp)_4(^tBu\text{-}C_6H_4C{\equiv}C)_{22}]^{4+}$ cluster. Color codes for atoms: red spheres, Ag; blue spheres, Cu; pink and bright green spheres, P. The alkynyl ligands with different coordination modes are marked with different colors. All hydrogen atoms are omitted for clarity.

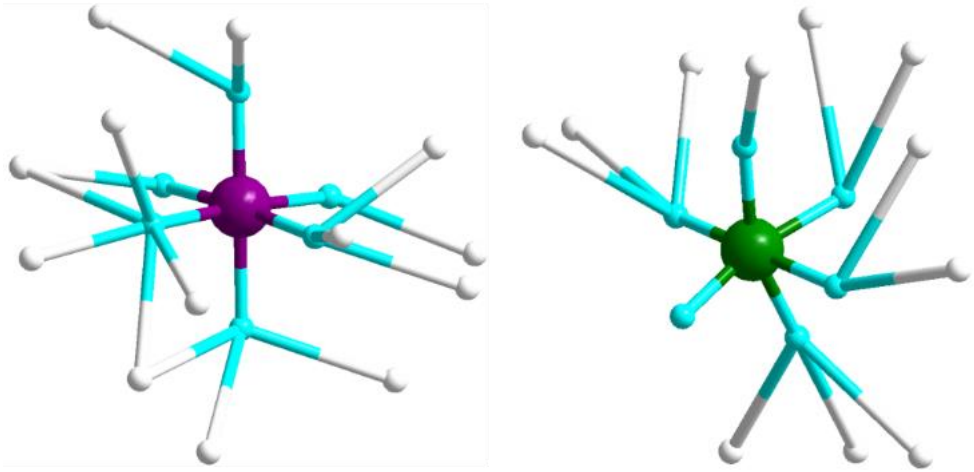

Figure S7. The SbF_6 anions interact with the cluster moieties in two kinds of modes: one (two for each cluster, marked with green) is sandwiching the cluster, and another (two for each cluster, marked with violet) is connecting two clusters. Color codes for atoms: violet and green spheres, Sb; white spheres, H. All other atoms are omitted for clarity.

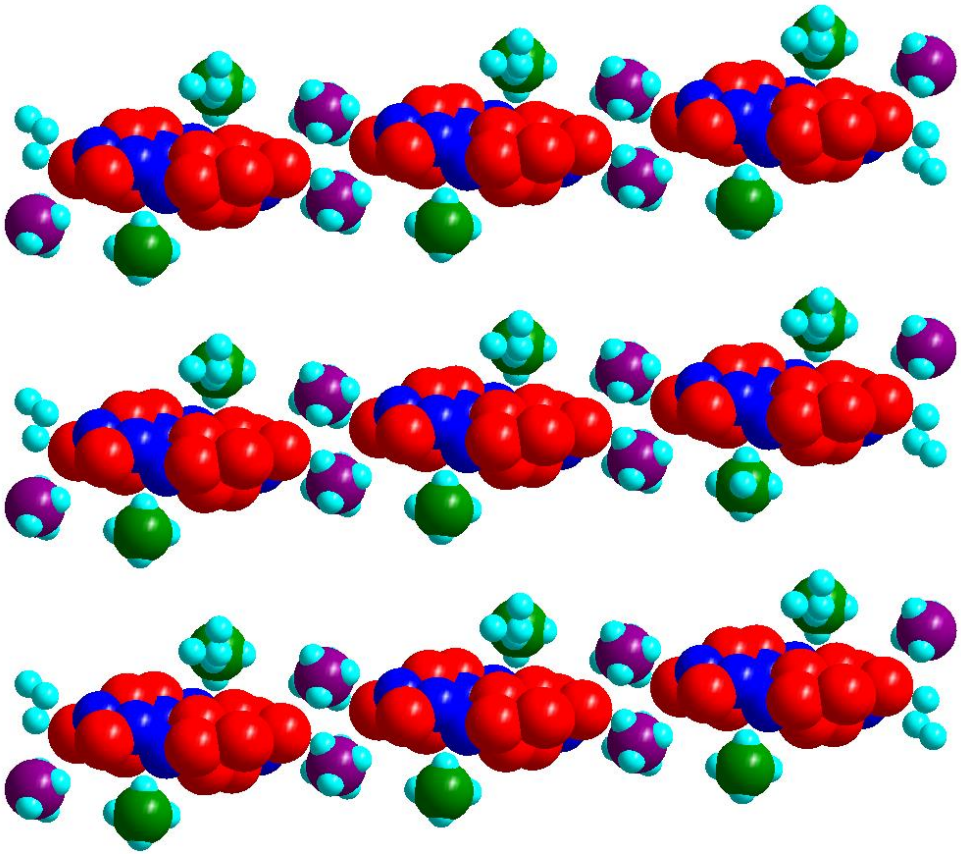

Figure S8. The packing structure of $[Ag_{18}Cu_8(dppp)_4(^tBu\text{-}C_6H_4C{\equiv}C)_{22}](SbF_6)_4$ highlighting the arrangement of cluster moieties and SbF_6 anions. The cluster moieties are arranged layer-by-layer along X-axis through SbF_6 anions of violet. Color codes for atoms: red spheres, Ag; blue spheres, Cu; orange spheres, P; grey spheres, C; green and violet spheres, Sb; turquoise spheres, F.

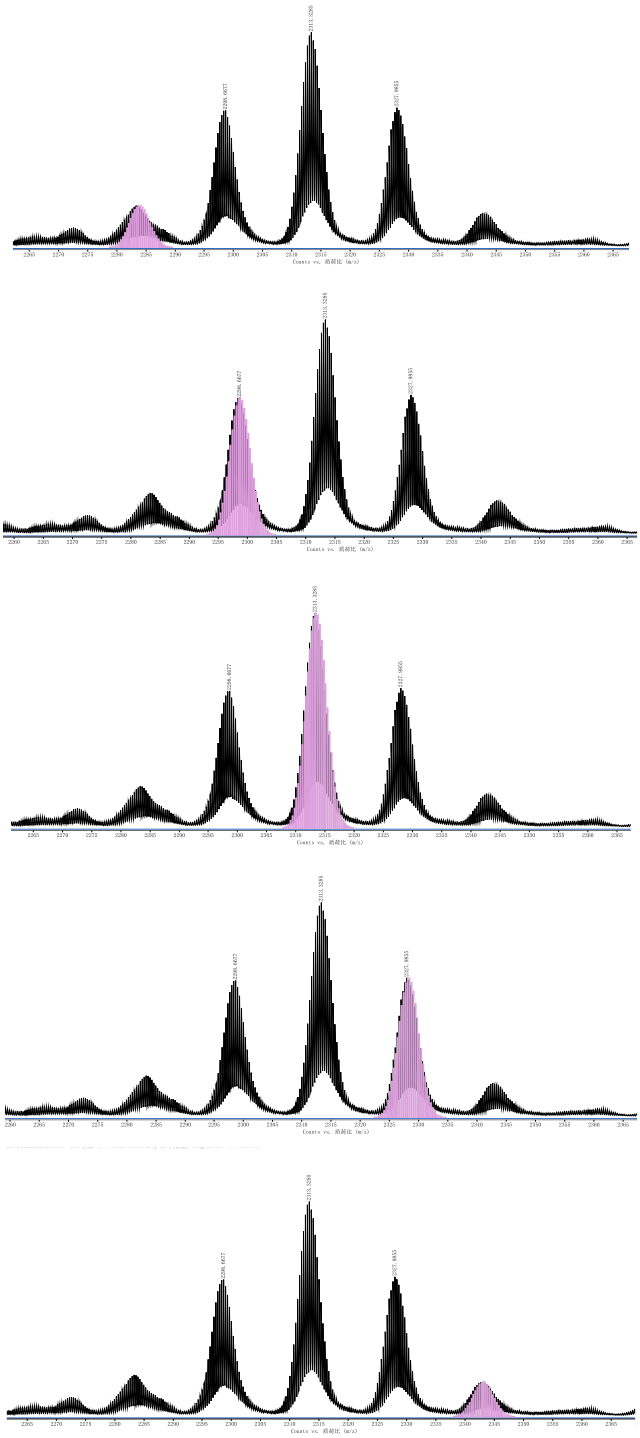

Figure S9. The presence of Ag-Cu exchange in ESI-MS spectra of $[Ag_{18}Cu_8(dppp)_4(^tBu\text{-}C_6H_4C{\equiv}C)_{22}]^{4+}$. From top to bottom is the experimental and simulated isotopic patterns of the molecular ion peak $[Ag_{16+x}Cu_{8-x}(dppp)_3(^tBu\text{-}C_6H_4C{\equiv}C)_{20}(SbF_6)]^{3+}$ (x=0-5), respectively.

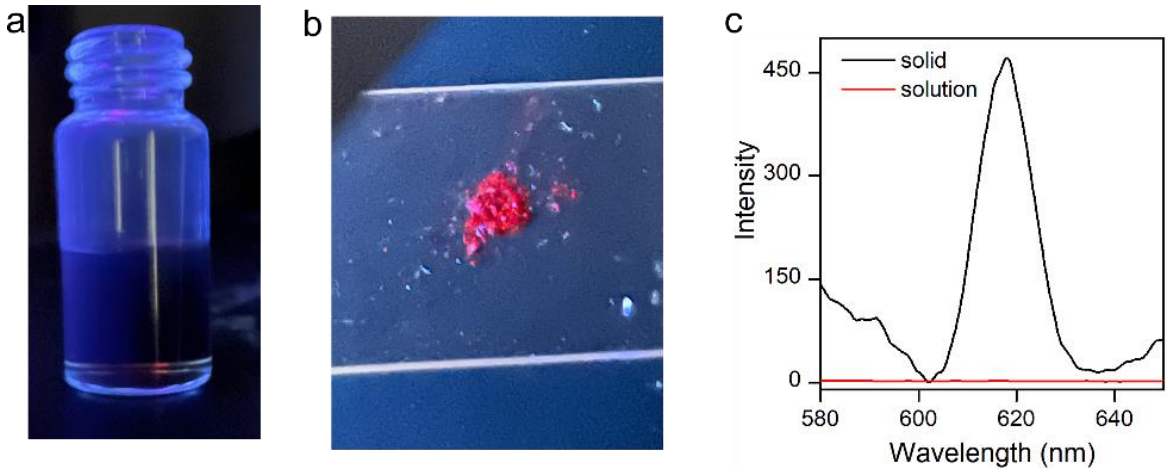

Figure S10. (a, b) Photographs of the solution and crystals of $Ag_{18}Cu_8$ clusters under UV light. (c) Emission spectra of $Ag_{18}Cu_8$ in crystalline and solution forms.

Table S1. Crystallographic data of $[Ag_{18}Cu_8(dppp)_4(^tBu\text{-}C_6H_4C\equiv C)_{22}](SbF_6)_4\bullet 2(C_4H_{10}O)$.

Identification code	$[Ag_{18}Cu_8(dppp)_4(^tBu\text{-}C_6H_4C\equiv C)_{22}](SbF_6)_4\bullet 2(C_4H_{10}O)$
Formula	$C_{380}H_{410}Ag_{18}Cu_8F_{24}O_2P_8Sb_4$
Formula wight	8649.79
Temperature/K	100.01(10)
Crystal system	triclinic
Space group	P -1
a (Å)	20.8417(11)
b (Å)	21.4892(12)
c (Å)	23.9061(12)
α (˚)	86.621(4)
β (˚)	66.127(5
γ (˚)	71.885(5)
V ($Å^3$)	9277.9(9)
Z	1
D_c / ($g\ cm^{-3}$)	1.548
Radiation	Cu Kα (λ= 1.54184 Å)
Theta (˚) range	3.7330 to 61.1100
Index ranges	$-23 \le h \le 23, -21 \le k \le 24, -27 \le l \le 24$
Refls. Total	28489
Restraints	13393
Parameters	1960
R_{int}	0.1458
R_1/wR_2 [I>2σ(I)]	0.1391 0.3293
R_1/wR_2 (all data)	0.2057 0.4267
Completeness	0.9986
GoF	1.127

Table S2. Selected bond lengths (Å) for compound $[Ag_{18}Cu_8(dppp)_4(^tBu\text{-}C_6H_4C{\equiv}C)_{22}](SbF_6)_4{\bullet}2(C_4H_{10}O)$.

Parameter	value	Parameter	value
Ag1-Ag2	2.935(2)	Ag5-Cu4	3.070(3)
Ag1-Ag3	2.941(2)	Ag6-Ag7	3.269(3)
Ag1-Ag6	3.318(2)	Ag6-Ag9	2.923(3)
Ag1-Ag9	3.304(2)	Ag7-Cu4	2.677(3)
Ag1-Cu1	2.969(3)	Ag7-P2	2.414(5)
Ag1-Cu2	3.009(3)	Ag8-Cu3	2.740(3)
Ag2-Ag3	2.808(2)	Ag8-Cu4	2.686(3)
Ag2-Cu2	2.988(3)	Ag8-P3	2.390(6)
Ag2-Cu1	3.102(3)	Ag9-Cu1	2.937(3)
Ag3-Cu2	2.784(3)	Ag9-Cu3	2.953(3)
Ag3-P4	2.404(6)	Ag9-Cu4	2.642(3)
Ag4-Ag6	2.805(3)	Cu1-Cu1′	2.973(4)
Ag4-P1	2.427(5)	Cu1-Cu2′	2.990(4)
Ag5-Ag6	2.916(3)	Cu2-Cu3	2.813(4)
Ag5-Ag9	3.187(2)	Cu3-Cu4	2.865(4)
Ag5-Cu3	2.812(3)		