A bimetallic $Ag_{15}Cu_{12}(S\text{-}c\text{-}C_6H_{11})_{18}(CH_3COO)_3$ nanocluster featuring an irregular Ag_{12} kernel

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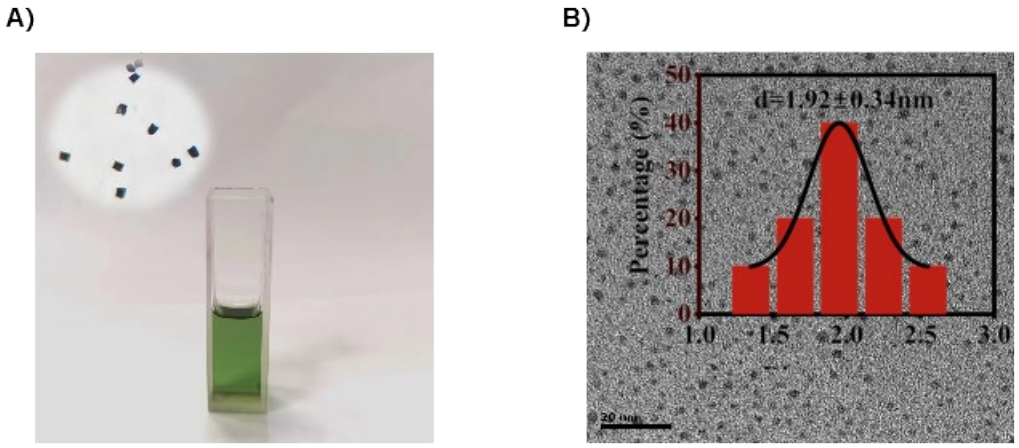


Fig. S1 The photos of (A) $\mathbf{Ag_{15}Cu_{12}}$ cluster dissolved in dichloromethane and crystals (insert of A). (B) Representative TEM images of $\mathbf{Ag_{15}Cu_{12}}$. Insert of (B) the corresponding histogram of $\mathbf{Ag_{15}Cu_{12}}$ nanocluster.

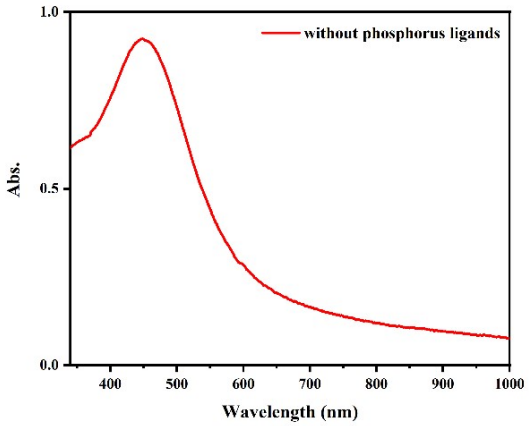


Fig. S2 The UV-vis spectrum of product synthesized without phosphorus ligands during the synthesis process.

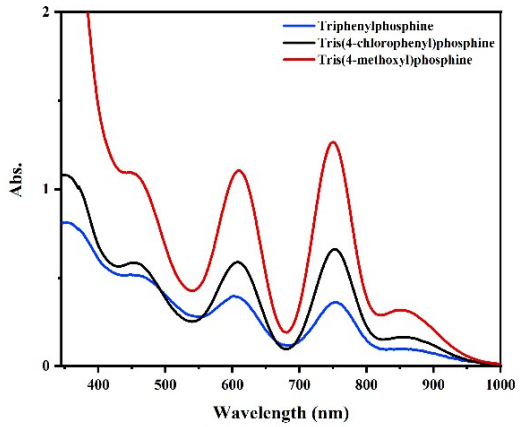


Fig. S3 The UV-Vis spectra of crude product synthesized via adding phosphine ligands with different substituting group.

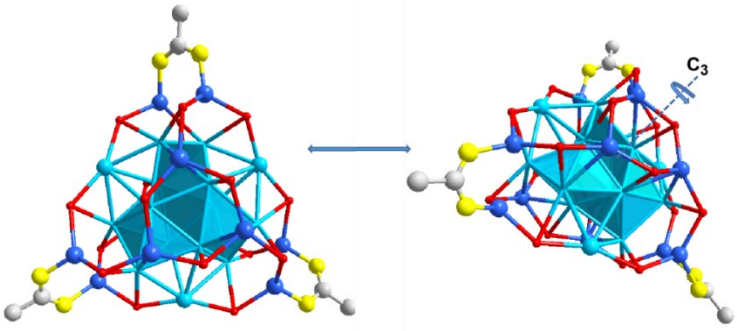


Fig. S4 Illustration of the C_3 axial symmetry in $\mathbf{Ag_{15}Cu_{12}}$. For clarity, hydrogen atoms and a part of carbon atoms are omitted. Color labels: sky blue = Ag; blue= Cu; red = S; yellow = O; and gray = C. All hydrogen atoms are omitted for clarity.

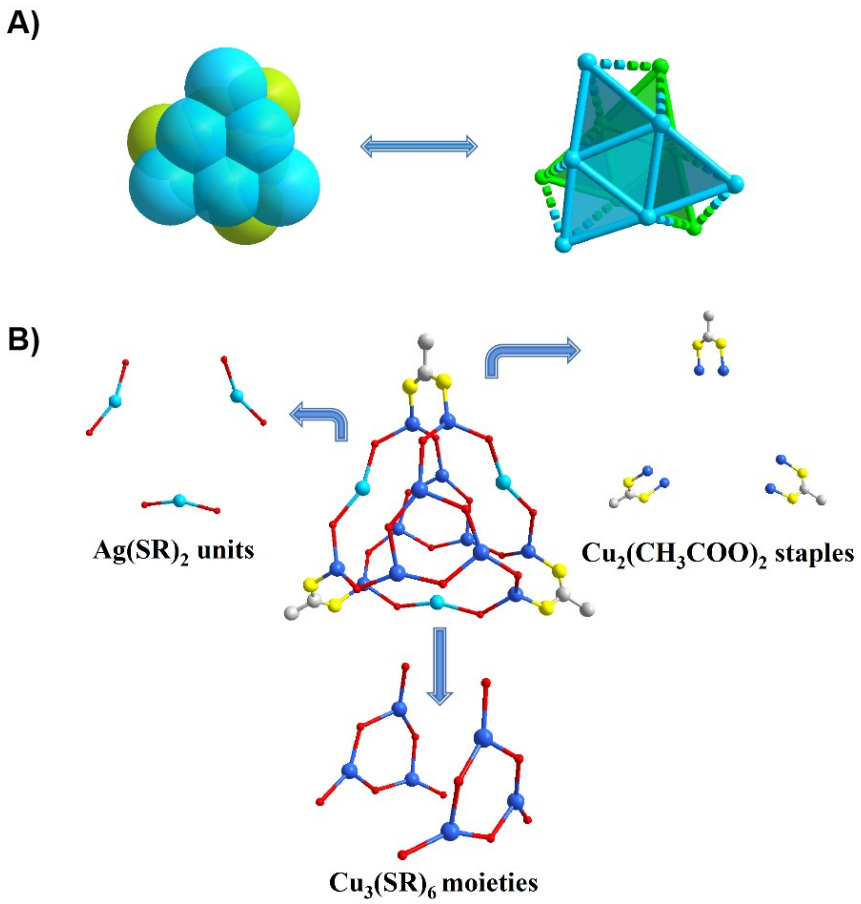


Fig. S5 Detailed structure analysis of (A) Ag_{12} core, two Ag_6 facets are cross interconnected in a slightly angular twist. (B) $Ag_3Cu_{12}(SR)_{18}(CH_3COO)_3$ shell, two $Cu_3(SR)_6$ moieties, three monomeric [−SR−Ag−SR−] units and three $Cu_2(CH_3COO)$ staples. Color labels: sky blue and light green = Ag, blue= Cu; red = S; yellow = O; and gray = C. All hydrogen atoms are omitted for clarity.

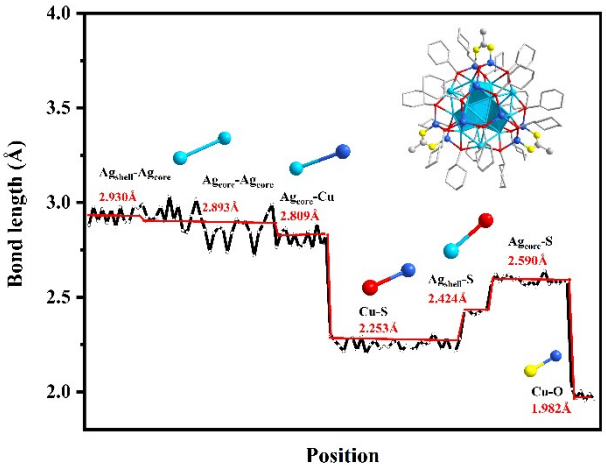


Fig. S6 Bond lengths of the $\mathbf{Ag_{15}Cu_{12}}$ nanocluster. Color label: sky blue = Ag; blue= Cu; red = S; yellow = O; and gray = C.

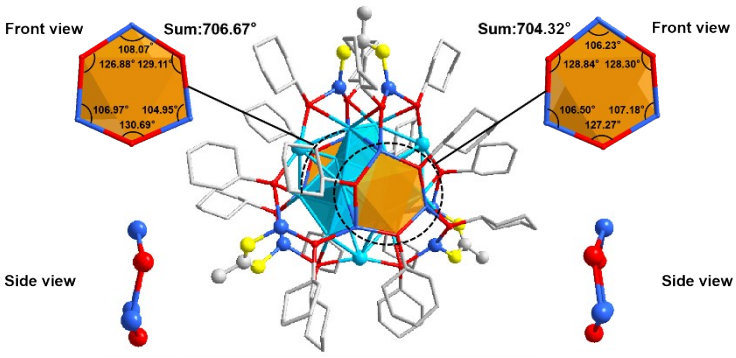


Fig. S7 The detailed angles in the $Cu_3(SR)_3$ structures of $\mathbf{Ag_{15}Cu_{12}}$ nanocluster. Color labels: sky blue = Ag; blue= Cu; red = S; yellow = O; and gray = C.

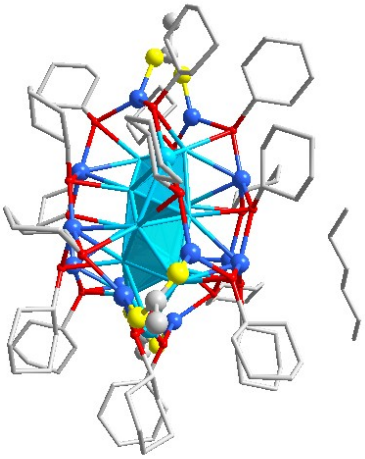


Fig. S8 The entire structure of $\mathbf{Ag_{15}Cu_{12}}$ nanocluster with one hexane solvent molecule around. Color labels: sky blue = Ag; blue= Cu; red = S; yellow = O; and gray = C.

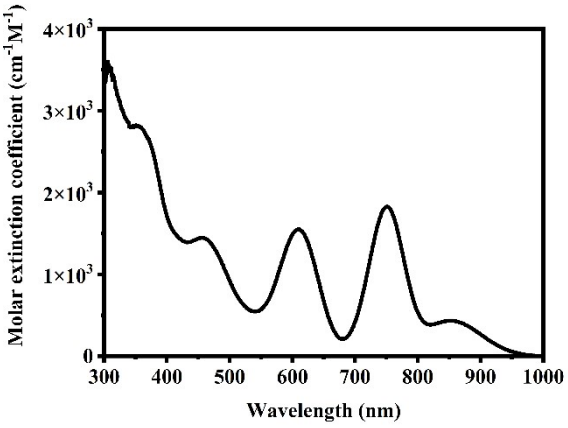


Fig. S9 Molar extinction coefficients of $\mathbf{Ag_{15}Cu_{12}}$.

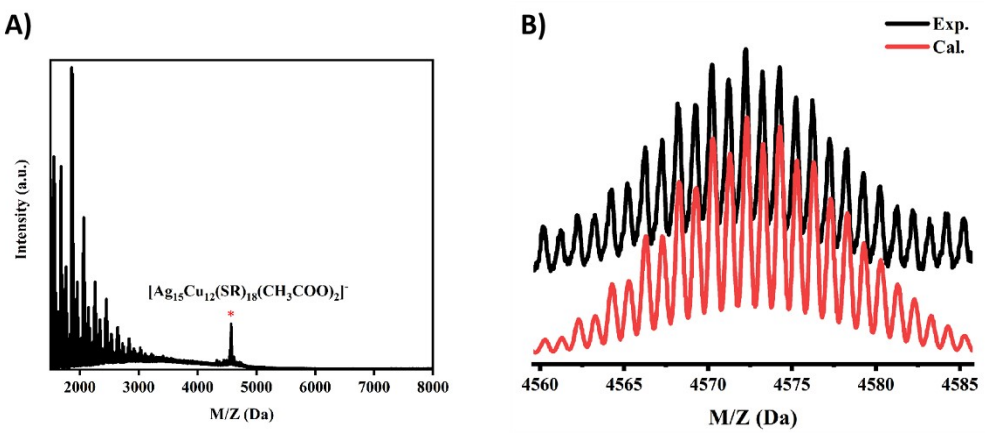


Fig.S10 (A) ESI mass spectrum in full width and (B) matching of isotope patterns between the experimental and simulated spectra of **$Ag_{15}Cu_{12}$**.

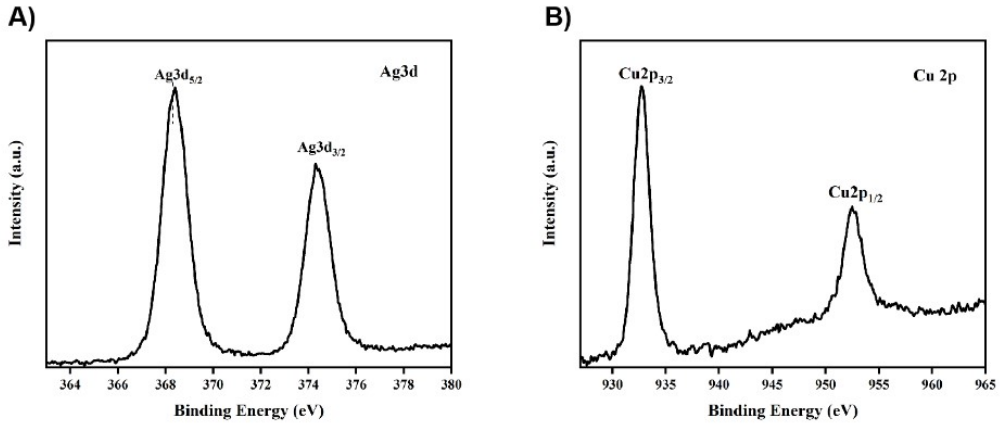


Fig.S11 (A) The High-resolution XPS spectra of Ag 3d of **$Ag_{15}Cu_{12}$**. (B) The High-res olution XPS spectra of Cu 2p of **$Ag_{15}Cu_{12}$**.

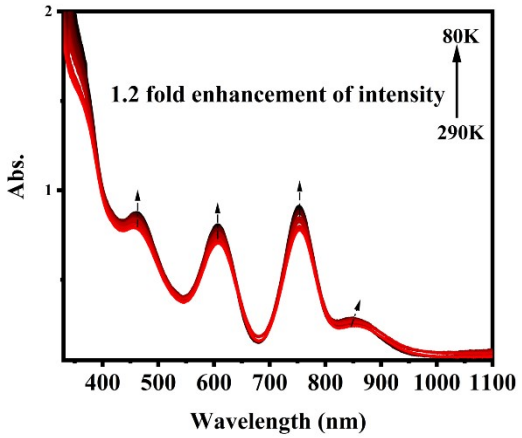


Fig.S12 Temperature-dependent UV-vis absorption of **$Ag_{15}Cu_{12}$** in CH_2Cl_2.

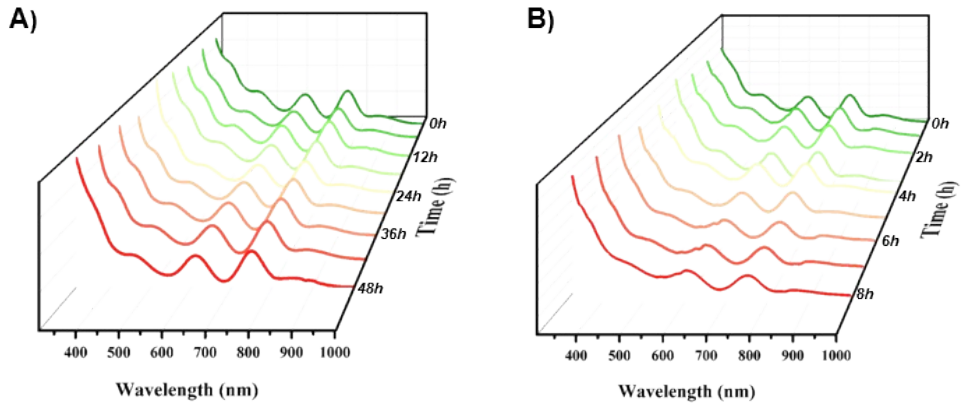


Fig.S13 Time-dependent UV-vis spectra (A) UV-vis spectra at room temperature (dissolved in CH_2Cl_2), and (B) at 45℃ (dissolved in $CHCl_3$).

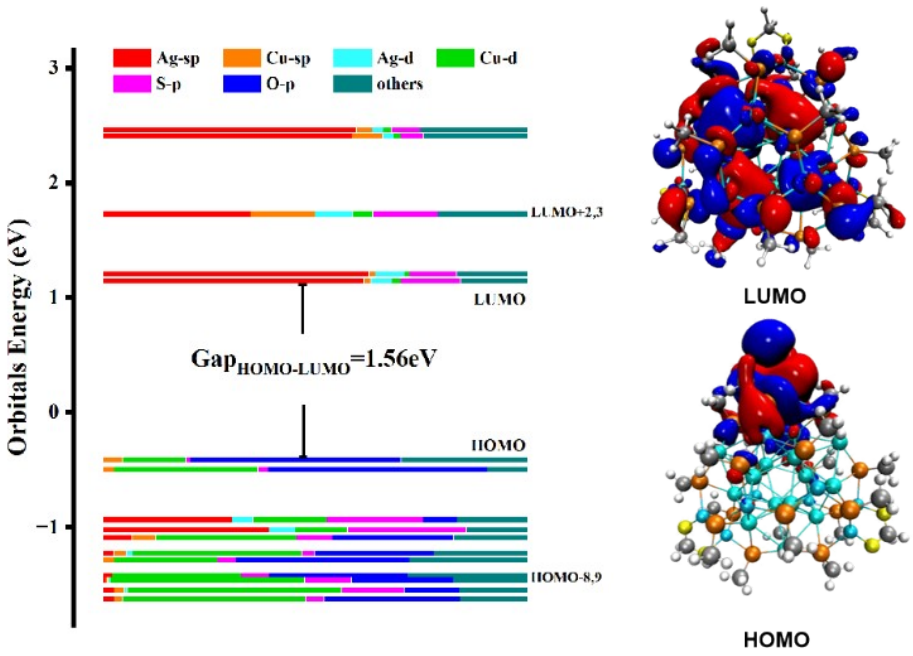


Fig.S14 Kohn–Sham (KS) orbital energy levels and the electron density profile of the HOMO and LUMO of $\mathbf{Ag_{15}Cu_{12}}$. Color labels: sky blue = Ag; lake blue= Cu; orange = S; yellow = O; and gray = C.

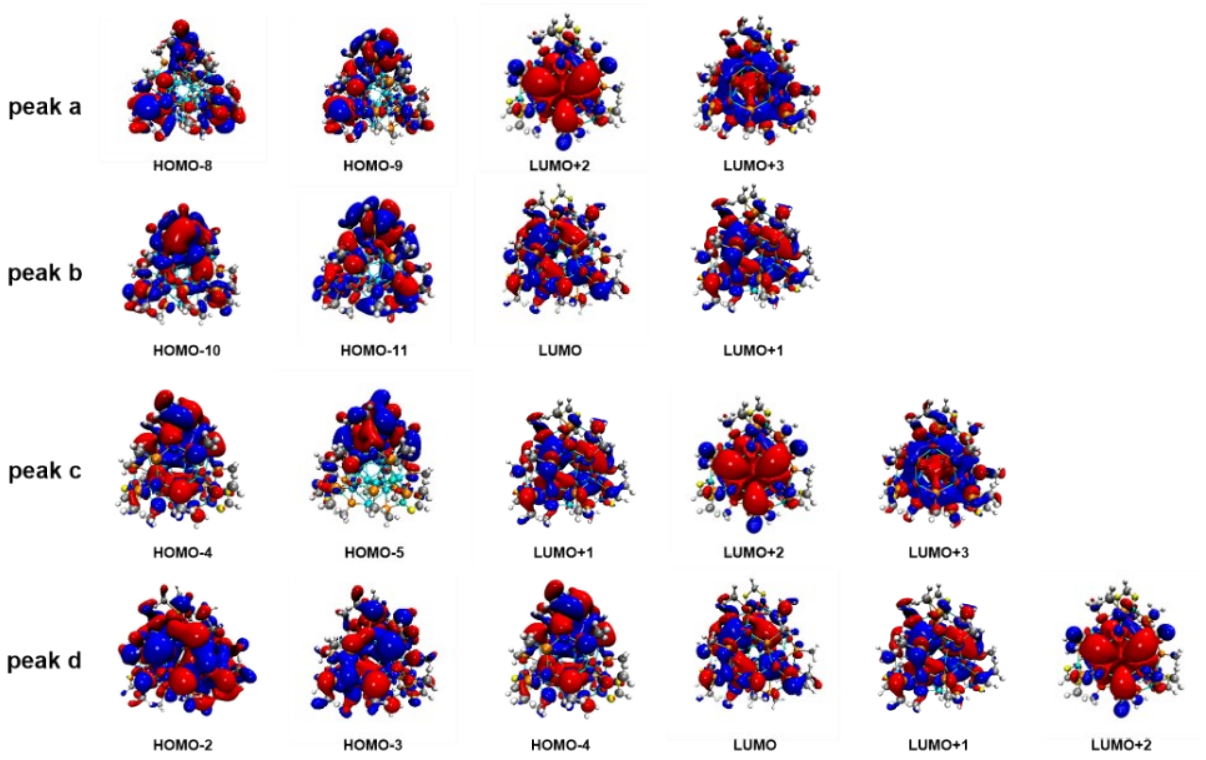


Fig.S15 Transition involved frontier molecular orbitals of $\mathbf{Ag_{15}Cu_{12}}^{\mathbf{T}}$.

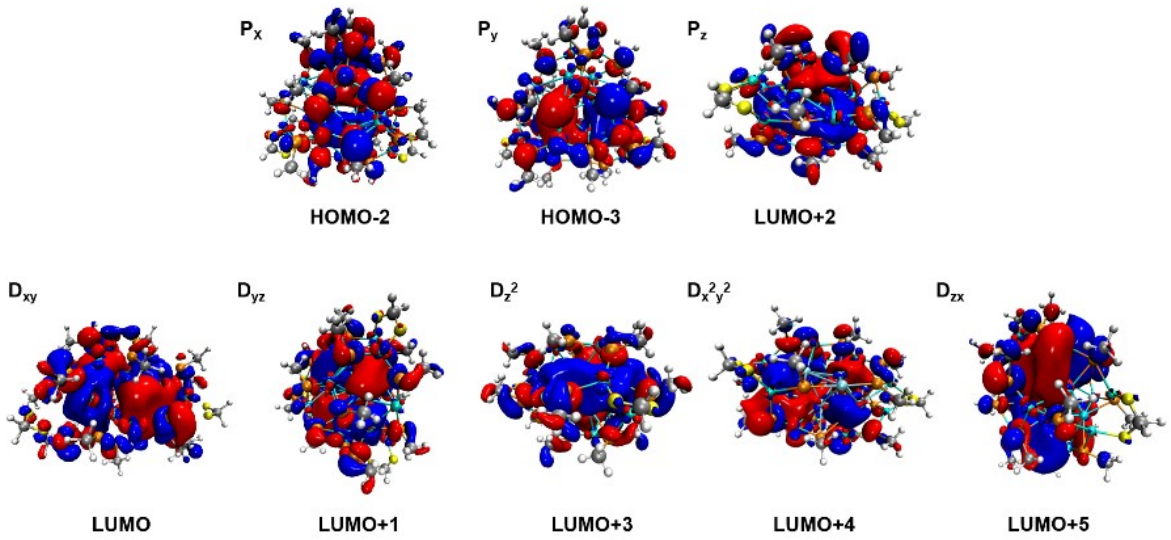
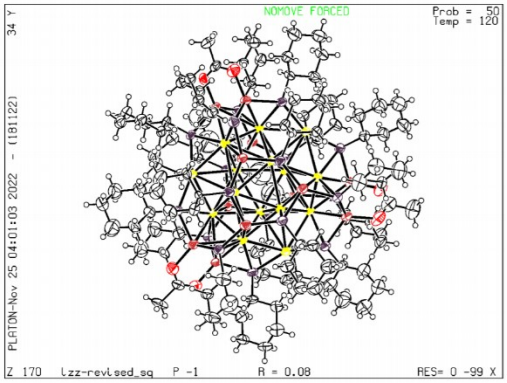
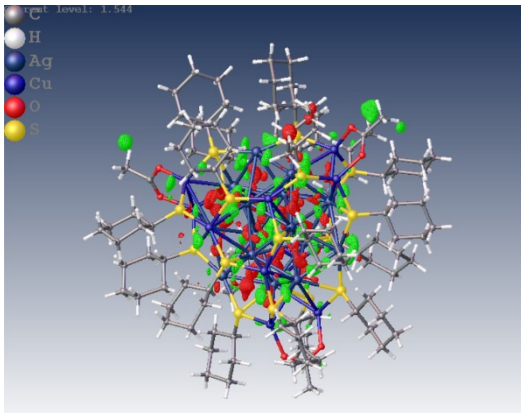


Fig.S16 Superatomic orbitals of $\mathbf{Ag_{15}Cu_{12}}^{\mathbf{T}}$.

Table S1. The comparison of the bond length of the icosahedral Ag_{13} metal core and Ag_{12} core of **$Ag_{15}Cu_{12}$**.

Cluster	Core	Average bond length
$[Ag_{25}(SR)_{18}]^-$	icosahedral Ag_{13}	2.866 Å
$Ag_{29}(SR)_{12}(PPh_3)_4$	icosahedral Ag_{13}	2.868 Å
$Ag_{15}Cu_{12}(SR)_{18}(CH_3COO)_3$	irregular Ag_{12}	2.893Å
$Ag_{27}H_{11}(SR)_{12}(DPPM)_6$	twisted Ag_{13}	2.993 Å

Table S2. Crystal Date and Structure Refinement of the $Ag_{15}Cu_{12}(SR)_{18}(CH_3COO)_3$ (C_6H_{14}) nanocluster.

Ellipsoid plot	ADPs
	
Identification code	lzz-revised_sq
Empirical formula	$C_{120}H_{221}Ag_{15}Cu_{12}O_6S_{18}$
Formula weight	4717.57
Temperature/K	120
Crystal system	triclinic
Space group	P-1
a/Å	17.4880(12)
b/Å	17.6703(12)
c/Å	30.473(2)
α/°	90.275(5)
β/°	96.680(5)
γ/°	93.511(5)
Volume/Å^3	9334.6(11)
Z	2
ρ_{calc}g/cm^3	1.678
μ/mm^{-1}	15.873
F(000)	4656.0
Crystal size/mm^3	0.02 × 0.01 × 0.01
Radiation	CuKα (λ = 1.54186)
2Θ range for data collection/°	6.924 to 124.996
Index ranges	$-19 \le h \le 20$, $-20 \le k \le 7$, $-35 \le l \le 33$
Reflections collected	56338
Independent reflections	28534 [R_{int} = 0.0693, R_{sigma} = 0.0818]

Data/restraints/parameters	28534/913/1543
Goodness-of-fit on F^2	0.993
Final R indexes [I>=2σ (I)]	R_1 = 0.0772, wR_2 = 0.1997
Final R indexes [all data]	R_1 = 0.1055, wR_2 = 0.2341
Largest diff. peak/hole / e $Å^{-3}$	2.67/-2.47