Supporting Information:

Multi-Ligand-Directed Synthesis of Chiral Silver Nanoclusters

Xuejuan Zou, ‡ Shan Jin, ‡ Wenjun Du, Yangfeng Li, Peng Li*, Shuxin Wang*, Manzhou Zhu*

Department of Chemistry and Center for Atomic Engineering of Advanced Materials, Anhui Province Key Laboratory of Chemistry for Inorganic/Organic Hybrid Functionalized Materials, Anhui University, Hefei, Anhui 230601, P. R. China.

Characterization

UV-Vis absorption spectra of the $[Ag_{32}(Dppm)_5(SAdm)_{13}Cl_8]^{3+}$ and $[Ag_{45}(Dppm)_4(S\text{-}Bu^t)_{16}Br_{12}]^{3+}$ NCs dissolved in CH_2Cl_2 were recorded using an Agilent 8453. X-ray photoelectron spectroscopy (XPS) measurements were performed on Thermo ESCALAB 250. Configured with a mono-chromated Al Kα (1486.8 eV) 150 W X-ray source, 0.5 mm circular spot size, a flood gun to counter charging effects, and the analysis chamber base pressure lower than 1×10^{-9} mbar; data were collected with FAT = 20 eV.

X-ray Crystallographic Determination of $[Ag_{32}(Dppm)_5(SAdm)_{13}Cl_8]^{3+}$ and $[Ag_{45}(Dppm)_4(S\text{-}Bu^t)_{16}Br_{12}]^{3+}$

The data collections of $[Ag_{32}(Dppm)_5(SAdm)_{13}Cl_8]^{3+}$ and $[Ag_{45}(Dppm)_4(S\text{-}Bu^t)_{16}Br_{12}]^{3+}$ were carried out on a Bruker Smart APEX II CCD diffractometer at 173 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 solved 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.

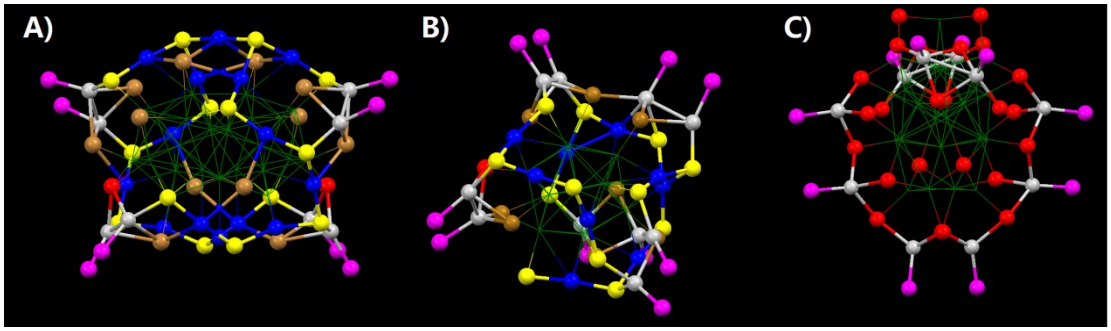

Figure S1. The total structure of A) $[Ag_{45}(Dppm)_4(S\text{-}Bu^t)_{16}Br_{12}]^{3+}$; B) $[Ag_{32}(Dppm)_5(SAdm)_{13}Cl_8]^{3+}$ report in this work, and C) $[Ag_{32}(Dppe)_5(SC_6H_4CF_3)_{24}]^{2-}$ nanocluster[S3]. Color labels: green, silver, blue = Ag; purple = P; red, yellow = S; brown =Br or Cl. All C and H atoms are omitted for clarity.

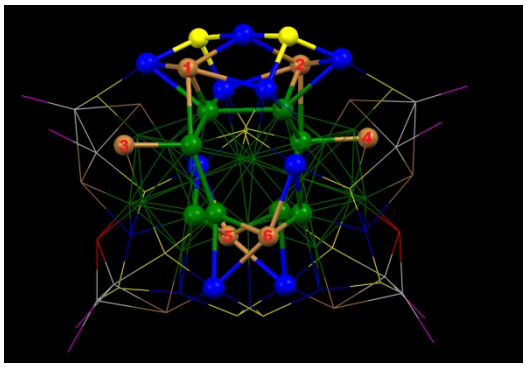

Figure S2. The bonding model of six independent Br atoms with different silver atoms in $[Ag_{45}(Dppm)_4(S\text{-}Bu^t)_{16}Br_{12}]^{3+}$ nanocluster. Color label: brown = Br; yellow = S; green and blue = Ag, other atoms are shown in line mode.

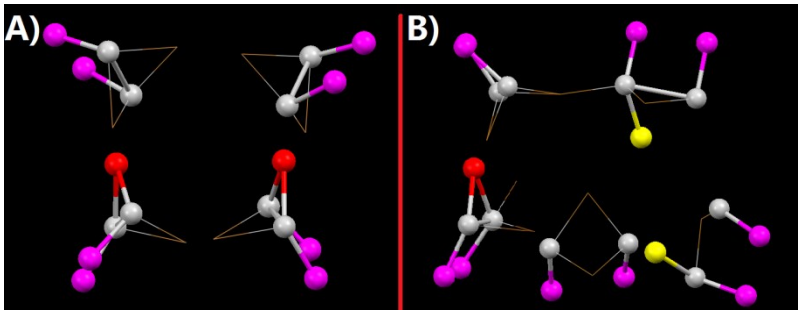

Figure S3. The comparison of staples in A) Ag_{45} and B) Ag_{32} nanoclusters based on the $\{Ag_2(Dppm)\}$ units.

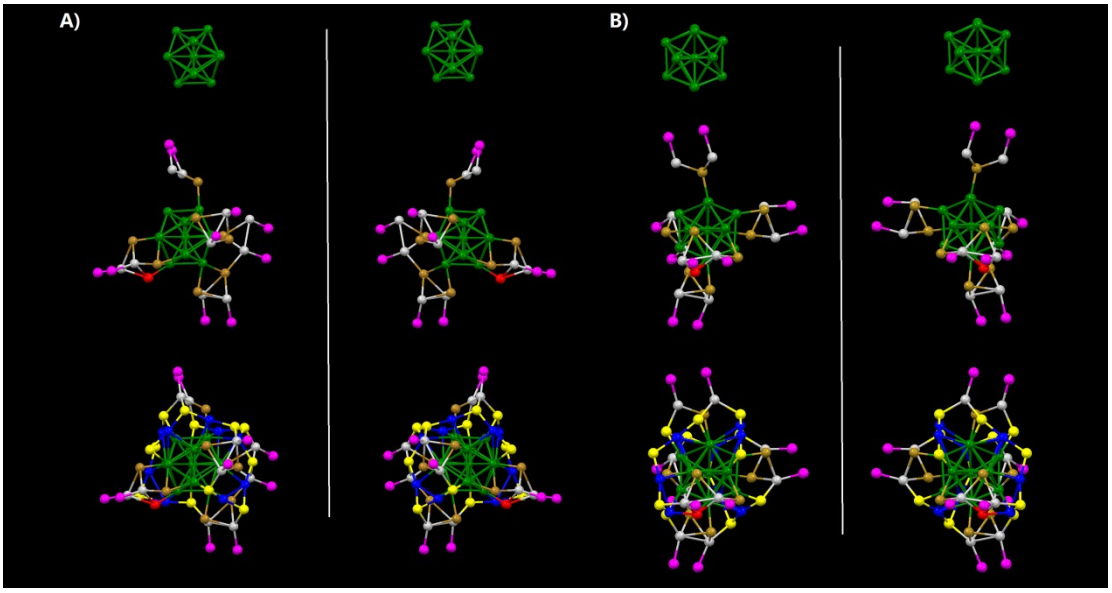

Figure S4. Two enantiomers found in $[Ag_{32}(Dppm)_5(SAdm)_{13}Cl_8]^{3+}$ nanocluster. For clarity, C and H atoms are omitted. Color labels: silver, green and blue = Ag; red, yellow = S; purple = P; brown = Cl.

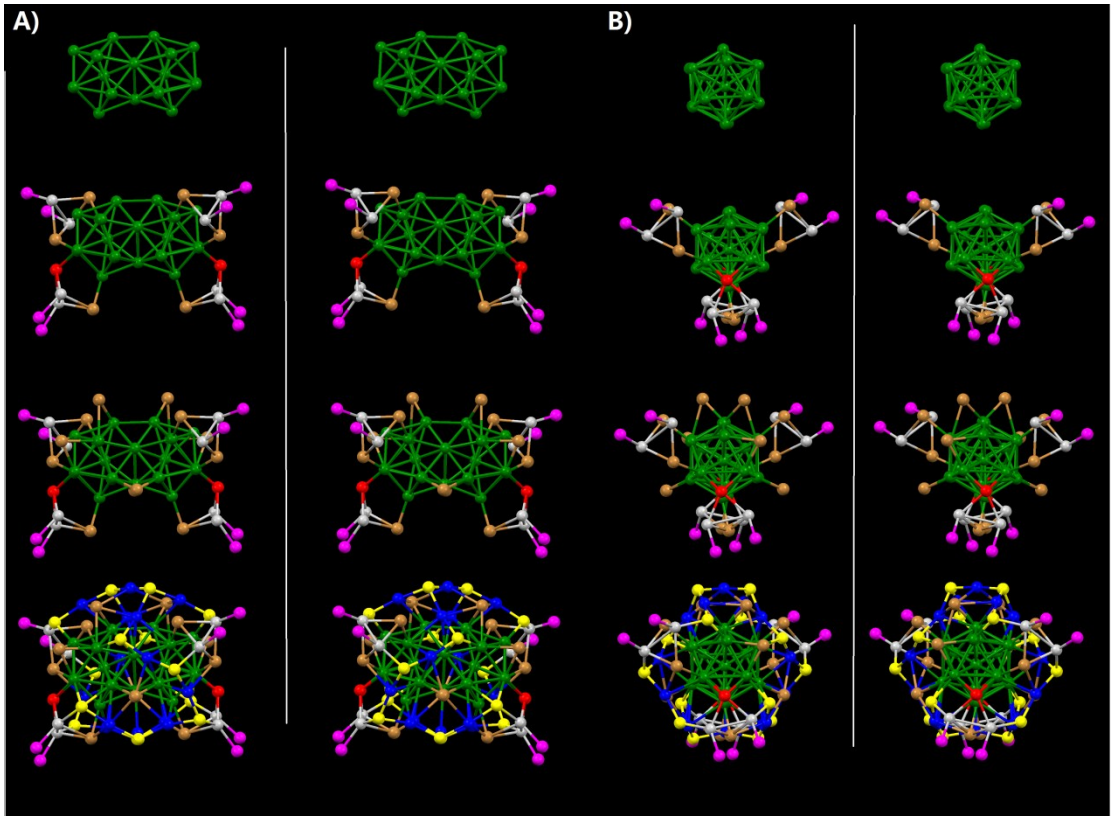

Figure S5. Two enantiomers found in $[Ag_{45}(Dppm)_4(S\text{-}Bu^t)_{16}Br_{12}]^{3+}$ nanocluster. For clarity, C and H atoms are omitted. Color labels: silver, green and blue = Ag; red, yellow = S; purple = P; brown = Br.

Table S1. Atom Ratio of (Ag / P / S / X) (X = Br / Cl) Measured by XPS and SCXRD Based on Silver atoms

	XPS experiment ratio $[Ag_{45}(Dppm)_4(S\text{-}Bu^t)_{16}Br_{12}]^{3+}$	SCXRD ratio $[Ag_{45}(Dppm)_4(S\text{-}Bu^t)_{16}Br_{12}]^{3+}$	XPS experiment ratio $[Ag_{32}(Dppm)_5(SAdm)_{13}Cl_8]^{3+}$	SCXRD ratio $[Ag_{32}(Dppm)_5(SAdm)_{13}Cl_8]^{3+}$
Ag atom	55.33%	55.56%	50.68%	50.79%
P atom	10.07%	9.88%	15.59	15.87%
S atom	19.62%	19.75%	20.79%	20.64%
X atom	14.98%	14.81%	12.94%	12.70%

Table S2. Crystal Date and Structure Refinement for the $[Ag_{32}(Dppm)_5(SAdm)_{13}Cl_8](SbF_6)_3$

Chemical formula	$C_{255}H_{300}Ag_{32}Cl_8P_{10}S_{13}\bullet 2.99(F_6Sb)\bullet CH_2Cl_2$
Formula Mass	8619.28
Crystal system	triclinic
a/Å	24.4964(3)
b/Å	36.3669(5)
c/Å	38.1702(5)
α/°	102.6310(10)
β/°	98.3050(10)
γ/°	100.3720(10)
Unit cell volume/Å^3	32035.0(7)
Temperature/K	150(2)
Space group	*P-1*
No. of formula units per unit cell, *Z*	4
No. of reflections measured	340624
No. of independent reflections	116936
R_{int}	0.1011
Final R_1 values ($I > 2\sigma(I)$)	0.1140
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.3027
Final R_1 values (all data)	0.1980
Final $wR(F^2)$ values (all data)	0.3656

Table S3. Crystal Date and Structure Refinement for the **$[Ag_{45}(Dppm)_4(S\text{-}Bu^t)_{16}Br_{12}](SbF_6)_3$**

Chemical formula	$C_{164}H_{232}Ag_{45}Br_6P_8S_{16}\bullet 3(F_6Sb)$
Formula Mass	9652.28
Crystal system	monoclinic
a/Å	34.3699(8)
b/Å	36.2763(9)
c/Å	26.3392(6)
α/°	90
β/°	95.223(2)
γ/°	90
Unit cell volume/Å^3	32703.5(13)
Temperature/K	150(2)
Space group	*C*12/*c*1
No. of formula units per unit cell, *Z*	4
No. of reflections measured	190096
No. of independent reflections	37525
R_{int}	0.0761
Final R_1 values ($I > 2\sigma(I)$)	0.0657
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1951
Final R_1 values (all data)	0.0996
Final $wR(F^2)$ values (all data)	0.2216

Reference

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

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

S3. Yang, H.; Wang, Y.; Zheng, N. *Nanoscale*., **2013**, 5, 2674-2677.