## Supporting Information

## Horizontal Expansion of Biicosahedral M<sub>13</sub>-Based Nanoclusters: Resolving Decades-Long Questions

Chuanjun Zhou,<sup>a,b,#</sup> Peiyao Pan,<sup>a,b,#</sup> Xiao Wei,<sup>a,b</sup> Zidong Lin,<sup>c</sup> Cheng Chen,<sup>c</sup> Xi Kang,<sup>a,b,\*</sup> Manzhou Zhu<sup>a,b,\*</sup>

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

<sup>b</sup>Key Laboratory of Structure and Functional Regulation of Hybrid Materials, Anhui University, Ministry of Education, Hefei 230601, P. R. China.

<sup>c</sup>Institutes of Physical Science and Information Technology, Anhui University, Hefei, Anhui 230601, P. R. China.

# C.Z. and P.P. contributed equally to this work.

\*E-mail: kangxi\_chem@ahu.edu.cn (X.K.); zmz@ahu.edu.cn (M.Z.)

Notes: The authors declare no competing financial interest.

This Supporting Information includes: Experimental Section Figures S1-S9 Tables S1-S7

## **Experimental Methods**

**Chemicals.** All following reagents were purchased from Sigma-Aldrich and used without further purification, including tetrachloroauric(III) acid (HAuCl<sub>4</sub>·4H<sub>2</sub>O, 99.99%), silver nitrate (AgNO<sub>3</sub>, 98%), bis(diphenylphosphino)methane (DPPM, 98%), triphenylphosphine (PPh<sub>3</sub>, 98.8%), phenylethylthiol (HSC<sub>2</sub>H<sub>5</sub>Ph, 97%), 1-adamantanethiol (AdmSH, 98%), sodium borohydride (NaBH<sub>4</sub>, 98%), ethanol (C<sub>2</sub>H<sub>5</sub>OH, HPLC grade), *n*-hexane (C<sub>6</sub>H<sub>12</sub>, HPLC grade), dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>, HPLC grade).

**Preparation of**  $[Au_{13}Ag_{12}(SC_2H_4Ph)_5(PPh_3)_{10}Cl_2]^{2+}$  ( $Au_{13}Ag_{12}$ -S). Typically, HAuCl<sub>4</sub>·4H<sub>2</sub>O (0.20 g/ml, 300 µl) was added to the 10 mL of ethanol under vigorous stirring. Then, 50 mg of PPh<sub>3</sub> and 50 µl of HSC<sub>2</sub>H<sub>5</sub>Ph were added to the reaction. After the solution turned colorless and transparent, 15mg of AgNO<sub>3</sub> (dissolved in 2mL of H<sub>2</sub>O) was added. After 20 minutes, a freshly prepared solution of NaBH<sub>4</sub> (20 mg of NaBH<sub>4</sub> in 2 mL of ethanol) was added, and the solution gradually changed to dark. The reaction lasted overnight at room temperature. The supernatant was collected by centrifugation. The crude product was washed with hexane three times to get the  $[Au_{13}Ag_{12}(SC_2H_4Ph)_5(PPh_3)_{10}Cl_2]^{2+}$  nanocluster.

**Preparation of**  $[Au_{13}Ag_{12}(PPh_3)_{10}Cl_8]^{2+}$  ( $Au_{13}Ag_{12}$ -Cl). The 50 µl of HSC<sub>2</sub>H<sub>5</sub>Ph reagent used to synthesize  $[Au_{13}Ag_{12}(SC_2H_4Ph)_5(PPh_3)_{10}Cl_2]^{2+}$  was substituted by 50 mg of HS-Adm. Other conditions remained unchanged, and the  $[Au_{13}Ag_{12}(PPh_3)_{10}Cl_8]^{2+}$  nanocluster was obtained.

**Preparation of [Au\_{13}(DPPM)\_6]^{3+} (Au\_{13}-DPPM).** The 50 mg of PPh<sub>3</sub> reagent used to synthesize  $[Au_{13}Ag_{12}(SC_2H_4Ph)_5(PPh_3)_{10}Cl_2]^{2+}$  was substituted by 50 mg of DPPM. Other conditions remained unchanged, and the  $[Au_{13}(DPPM)_6]^{3+}$  nanocluster was obtained.

**Preparation of**  $[Au_{19}Ag_{12}(S-Adm)_6(DPPM)_6Cl_7]^{2+}$  ( $Au_{19}Ag_{12}$ ). The 50 mg of PPh<sub>3</sub> and 50 µl of HSC<sub>2</sub>H<sub>5</sub>Ph reagents used to synthesize  $[Au_{13}Ag_{12}(SC_2H_4Ph)_5(PPh_3)_{10}Cl_2]^{2+}$  were substituted by 50 mg of DPPM and 50 mg of HS-Adm, respectively. Other conditions remained unchanged, and the  $[Au_{19}Ag_{12}(S-Adm)_6(DPPM)_6Cl_7]^{2+}$  nanocluster was obtained.

Of note, different metal-to-NaBH<sub>4</sub> ratios have been attempted in these synthesis systems. Specifically, the 20 mg of NaBH<sub>4</sub> has been changed to 10 or 40 mg. We found that the experiments with 10 mg of NaBH<sub>4</sub> also gave rise to the generation of such four nanoclusters, while the synthetic yields of these four nanoclusters were substantially reduced, which might result from the incomplete reduction in these synthesis systems. For the 40 mg NaBH<sub>4</sub> batch, first, we obtained these four nanoclusters in low yields; besides, some insoluble precipitates were observed, and such phenomena might result from the overreduction in these synthesis systems.

**Crystallization of nanoclusters.** Single crystals of the nanoclusters were cultivated at -4 °C by liquid-diffusing *n*-hexane into the CH<sub>2</sub>Cl<sub>2</sub> solution of each nanocluster. After a week, crystals of nanoclusters were collected, and the structures of these nanoclusters were determined. The CCDC number of  $[Au_{19}Ag_{12}(S-Adm)_6(DPPM)_6Cl_7]^{2+}$  is 2163804. The CCDC number of  $[Au_{13}Ag_{12}(SC_2H_4Ph)_5(PPh_3)_{10}Cl_2]^{2+}$  is 2183917. The CCDC number of  $[Au_{13}Ag_{12}(PPh_3)_{10}Cl_8]^{2+}$  is 2163571. The CCDC number of  $[Au_{13}(DPPM)_6]^{3+}$  is 2163572.

**Characterizations.** The optical absorption spectra of nanoclusters were recorded using an Agilent 8453 diode array spectrometer.

Electrospray ionization mass spectrometry (ESI-MS) measurements were performed by Waters XEVO G2-XS QTof mass spectrometer. The sample was directly infused into the chamber at 5  $\mu$ L/min. For preparing the ESI samples, nanoclusters were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (1 mg/mL) and diluted (v/v = 1:1) by CH<sub>3</sub>OH.

Photoluminescence (PL) spectra were measured on a FL-4500 spectrofluorometer with the same optical density of 0.1.

**X-Ray Crystallography.** The data collection for single-crystal X-ray diffraction (SC-XRD) of all nanocluster crystal samples was carried out on Stoe Stadivari diffractometer under nitrogen flow, using graphite-monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.54186$  Å). Data reductions and absorption corrections were performed using the SAINT and SADABS programs, respectively. The structure was solved by direct methods and refined with full-matrix least squares on F<sup>2</sup> using the SHELXTL software package. All non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were set in geometrically calculated positions and refined isotropically using a riding model. All crystal structures were treated with PLATON SQUEEZE. The diffuse electron densities from these residual solvent molecules were removed.



Fig. S1 ESI-MS results of the Au<sub>19</sub>Ag<sub>12</sub> nanocluster.



**Fig. S2** The overall structure of the  $Au_{19}Ag_{12}(S-Adm)_6(DPPM)_6Cl_7$  nanocluster. Color labels: orange sphere, Au; light blue sphere, Ag; green sphere, Cl; red sphere, S; magenta sphere, P; grey sphere, C; white sphere, H.



**Fig. S3** Packing of R-Au<sub>19</sub>Ag<sub>12</sub>(S-Adm)<sub>6</sub>(DPPM)<sub>6</sub>Cl<sub>7</sub> and S-Au<sub>19</sub>Ag<sub>12</sub>(S-Adm)<sub>6</sub>(DPPM)<sub>6</sub>Cl<sub>7</sub> nanocluster enantiomers in the crystal lattice. (A) The mirrored structures of R-nanocluster enantiomer and Snanocluster enantiomer. (B) The crystallographic packing of nanocluster enantiomers follows a "lamellar eutectic" pattern. (C-E) Packing of the Au<sub>19</sub>Ag<sub>12</sub>(S-Adm)<sub>6</sub>(DPPM)<sub>6</sub>Cl<sub>7</sub> nanocluster in the crystal lattice: view from the x axis (C), y axis (D), and z axis (E). Color labels: orange sphere, Au; light blue sphere, Ag; green sphere, Cl; red sphere, S; magenta sphere, P; pink sphere, C in Rnanocluster enantiomers; light green sphere, C in S-nanocluster enantiomers; white sphere, H.



**Fig. S4** Structural comparison among **Au**<sub>13</sub>**Ag**<sub>12</sub>**-S**, **Au**<sub>13</sub>**Ag**<sub>12</sub>**-Cl**, and **Au**<sub>19</sub>**Ag**<sub>12</sub> nanoclusters. (A) Comparison of the bond length of Au(kernel)---M(icosahedral surface). (B) Comparison of the bond length of M(icosahedral surface)---M(icosahedral surface). (C) Comparison of the bond length of Ag(icosahedral surface)---Cl(vertex). (D) Comparison of the bond length of Au(icosahedral surface)---P(shoulder). (E) Comparison of the bond length of Ag(icosahedral surface)---Cl(waist). (F) Comparison of the bond length of Ag(icosahedral surface)---S(waist). The compared bonds are highlighted in blue.



**Fig. S5** Crystalline packing and ligand-directed intercluster interactions of (A) Au<sub>13</sub>Ag<sub>12</sub>-S, (B) Au<sub>13</sub>Ag<sub>12</sub>-Cl, (C) Au<sub>13</sub>-DPPM, and (D) Au<sub>19</sub>Ag<sub>12</sub> nanoclusters.



Fig. S6 Optical absorption of the  $Au_{19}Ag_{12}$  nanocluster.



**Fig. S7** Comparison of UV-vis spectra of Au<sub>13</sub>-DPPM, Au<sub>13</sub>Ag<sub>12</sub>-S, Au<sub>13</sub>Ag<sub>12</sub>-Cl, and Au<sub>19</sub>Ag<sub>12</sub> nanoclusters. Optical absorptions of Au<sub>13</sub>-DPPM (green line), Au<sub>13</sub>Ag<sub>12</sub>-S (dark blue line), Au<sub>13</sub>Ag<sub>12</sub>-Cl (yellow line), and Au<sub>19</sub>Ag<sub>12</sub> (red line) nanoclusters.



**Fig. S8** Thermal stability test of the  $Au_{19}Ag_{12}$  nanocluster. (A) Time-dependent optical absorptions of the  $Au_{19}Ag_{12}$  nanocluster in  $CH_2CI_2$ . (B) Time-dependent optical absorptions of the  $Au_{19}Ag_{12}$ nanocluster in  $CH_2CI_2$  in a normalized way.



**Fig. S9** Comparison of the photoluminescent properties of Au<sub>13</sub>-DPPM, Au<sub>13</sub>Ag<sub>12</sub>-S, Au<sub>13</sub>Ag<sub>12</sub>-Cl, and Au<sub>19</sub>Ag<sub>12</sub> nanoclusters.

Table S1. Crystal data and structure refinement for	$r Au_{13}Ag_{12}(SC_2H_4Ph)_5(PPh_3)_{10}Cl_2$ .
---	---

ellipsoid plot	ADPs
0 1780 5 .eq P - 1 R = 0.07 RES= 0-153 X	
Formula	C <sub>220</sub> H <sub>195</sub> Ag <sub>8.92</sub> Au <sub>16.08</sub> Cl <sub>2</sub> P <sub>10</sub> S <sub>5</sub> , 38[H <sub>2</sub> O]
Formula sum	$C_{220}H_{271}Ag_{8.92}Au_{16.08}CI_2O_{38}P_{10}S_5$
Crystal system	triclinic
Space group	P-1
a/Å	20.3734(3)
b/Å	22.9783(3)
c/Å	32.3446(4)
α/°	70.7470(10)
β/°	83.8450(10)
γ/°	67.6260(10)
Volume/Å <sup>3</sup>	13216.1(3)
Z	2
pcalcg/cm <sup>3</sup>	2.059
µ/mm <sup>-1</sup>	23.065
F(000)	7697
Radiation	CuKα (λ = 1.54186)
Index ranges	-17 ≤ h ≤ 23, -22 ≤ k ≤ 26, -36 ≤ l ≤ 37
θ range (°)	4.695 – 62.499
Measured reflections and unique reflections	129140 / 34166(R <sub>int</sub> = 0.0425)
Goodness-of-fiton F <sup>2</sup>	1.027
Largest diff. peak/hole / e Å <sup>-3</sup>	3.617/-2.594
Final R indexes [I>=2σ (I)]	R1 = 0.0688, wR2 = 0.1975
Final R indexes [all data]	R1 = 0.0765, wR2 = 0.2068

ellipsoid plot	ADPs
10 1000 1000 1000 1000 1000 1000 1000	energia
Formula	C <sub>180</sub> H <sub>150</sub> Ag <sub>10.35</sub> Au <sub>12.65</sub> Cl <sub>6</sub> P <sub>10</sub> ,2(AgCl), 4(Cl), 38[H <sub>2</sub> O], 1[H <sub>2</sub> O]
Formula sum	$C_{180}H_{228}Ag_{12.35}Au_{12.65}CI_{12}O_{39}P_{10}$
Crystal system	monoclinic
Space group	l 1 2/a 1
a/Å	35.4973(10)
b/Å	16.6627(3)
c/Å	38.4422(12)
α/°	90
β/°	103.135(2)
γ/°	90
Volume/ų	22142.9(10)
Z	4
ρcalcg/cm <sup>3</sup>	2.272
µ/mm <sup>-1</sup>	26.373
F(000)	14215
Radiation	CuKα (λ = 1.54186)
Index ranges	$-40 \le h \le 36, -10 \le k \le 19, -44 \le l \le 40$
θ range (°)	6.109 – 62.500
Measured reflections and unique reflections	21321/11608 (R <sub>int</sub> = 0.0689)
Goodness-of-fiton F <sup>2</sup>	0.992
Largest diff. peak/hole / e Å <sup>-3</sup>	4.226/-6.592
Final R indexes [I>=2o (I)]	R1 = 0.0941, wR2 = 0.2431
Final R indexes [all data]	R1 = 0.1167, wR2 = 0.2664

Table S2. Crystal data and structure refinement for  $Au_{13}Ag_{12}(PPh_3)_{10}Cl_8$ .

## Table S3. Crystal data and structure refinement for $Au_{13}(DPPM)_6$ .

ellipsoid plot	ADPs
$r_{\rm res} = 100000 \text{ for set } 10000 \text{ for set } 100000 \text{ for set } 100000000000000000000000000000000000$	
Formula	C <sub>150</sub> H <sub>132</sub> Au <sub>13</sub> P <sub>12</sub> , 3(Cl), 43[H <sub>2</sub> O]
Formula sum	$C_{150}H_{218}Au_{13}CI_{3}O_{43}P_{12}$
Crystal system	trigonal
Space group	P -3 1 c
a/Å	19.7102(8)
b/Å	19.7102(8)
c/Å	27.4590(12)
α/°	90
β/°	90
γ/°	120
Volume/ų	9238.4(9)
Z	2
pcalcg/cm <sup>3</sup>	2.066
µ/mm <sup>-1</sup>	20.819
F(000)	5440
Radiation	CuKα (λ = 1.54186)
Index ranges	$-20 \le h \le 10, -22 \le k \le 23, -33 \le l \le 30$
θ range (°)	3.219– 69.597
Measured reflections and unique reflections	20149 /4988(R <sub>int</sub> = 0.0347)
Goodness-of-fiton F <sup>2</sup>	1.045
Largest diff. peak/hole / e Å <sup>-3</sup>	1.262/-2.462
Final R indexes [I>=2σ (I)]	R1 = 0.0345, wR2 = 0.0897
Final R indexes [all data]	R1 = 0.0402, wR2 = 0.0924

<b>Table 34.</b> Crystal data and structure refinement for $Au_{19}Ag_{17}(3 Au_{17})_6(D)$ i $W_{16}(C)$	e S4. Crystal data and structure refinement for Au <sub>19</sub> Ag <sub>12</sub> (S-Adm)	<sub>6</sub> (DPPM) <sub>6</sub> Cl <sub>7</sub>
---	---	--

ellipsoid plot	ADPs
Formula	C <sub>210</sub> H <sub>222</sub> Ag <sub>14.34</sub> Au <sub>16.66</sub> Cl <sub>7</sub> P <sub>12</sub> S <sub>6</sub> , 32[H <sub>2</sub> O]
Formula sum	$C_{210}H_{286}Ag_{14.34}Au_{16.66}CI_7O_{32}P_{12}S_6$
Crystal system	triclinic
Space group	P -1
a/Å	21.3747(4)
b/Å	21.9612(4)
c/Å	28.8966(6)
α/°	87.586(2)
β/°	74.5520(10)
γ/°	77.0140(10)
Volume/ų	12737.8(4)
Z	2
ρcalcg/cm <sup>3</sup>	2.337
µ/mm <sup>-1</sup>	28.438
F(000)	8374
Radiation	CuKα (λ = 1.54178)
Index ranges	-22 ≤ h ≤ 24, -25 ≤ k ≤ 24, -33 ≤ l ≤ 26
θ range (°)	6.073 – 62.499
Measured reflections and unique reflections	82334 / 29156(R <sub>int</sub> = 0.0351)
Goodness-of-fiton F <sup>2</sup>	0.923
Largest diff. peak/hole / e Å <sup>-3</sup>	2.077/-1.983
Final R indexes [I>=2σ (I)]	R1 = 0.0415, wR2 = 0.1019
Final R indexes [all data]	R1 = 0.0540, wR2 = 0.1063

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
Au	0.37	Au1	0.43	Ag3	0.69
Ag7	0.7	Au13	0.42	Ag14	0.67
Au15	0.38	Au16	0.37	Au17	0.37
Au18	0.49	Ag19	0.69	Ag1D	0.58
Ag1E	0.51	Au1F	0.33	Ag1G	0.63
Au1H	0.3	Ag1I	0.57	Ag1J	0.63
Au1K	0.31	Ag1L	0.62	Ag1M	0.63
Au1N	0.31				

**Table S5.** Atomic Occupancy for  $Au_{13}Ag_{12}(SC_2H_4Ph)_5(PPh_3)_{10}Cl_2$ .

**Notes:** The nanocluster is termed as  $Au_{13}Ag_{12}(SC_2H_4Ph)_5(PPh_3)_{10}Cl_2$  in the current work, although its crystal structure outcomes a composition of  $Au_{16.08}Ag_{8.92}(SC_2H_4Ph)_5(PPh_3)_{10}Cl_2$ . Actually, because of the Au/Ag co-occupation in some metal sites in the cluster framework, the chemical formula of this alloy nanocluster should be  $Au_xAg_{25-x}(SC_2H_4Ph)_5(PPh_3)_{10}Cl_2$ . However, all previous works used the " $Au_{13}Ag_{12}(SC_2H_4Ph)_5(PPh_3)_{10}Cl_2$ " formula for representing this alloy nanocluster system, by determining each alloying site as Au (or Ag) completely when such a site is occupied mainly by Au (or Ag). In this context, we also use the  $Au_{13}Ag_{12}(SC_2H_4Ph)_5(PPh_3)_{10}Cl_2$  chemical formula to represent this alloy nanocluster.

**Table S6.** Atomic Occupancy for Au<sub>13</sub>Ag<sub>12</sub>(PPh<sub>3</sub>)<sub>10</sub>Cl<sub>8</sub>.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
Cl	0.5	Cl1	0.5	Ag1B	0.35
Au1A	0.65	Cl2	0.5	Cl3	0.5

**Notes:** The nanocluster is termed as  $Au_{13}Ag_{12}(PPh_3)_{10}Cl_8$  in the current work, although its crystal structure outcomes a composition of  $Au_{12.65}Ag_{12.35}(PPh_3)_{10}Cl_8$ . Actually, because of the Au/Ag co-occupation in some metal sites in the cluster framework, the chemical formula of this alloy nanocluster should be  $Au_xAg_{25-x}(PPh_3)_{10}Cl_8$ . However, all previous works used the " $Au_{13}Ag_{12}(PPh_3)_{10}Cl_8$ " formula for representing this alloy nanocluster system, by determining each alloying site as Au (or Ag) completely when such a site is occupied mainly by Au (or Ag). In this context, we also use the  $Au_{13}Ag_{12}(PPh_3)_{10}Cl_8$  chemical formula to represent this alloy nanocluster.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
Au	0.62	Ag3A	0.54	Au1	0.51
Au2	0.5	Au3	0.57	Au1A	0.5
C01W	0.5	C51	0.5	H51A	0.5
H51B	0.5	C1AA	0.5	H1AA	0.5
H1AB	0.5	C59	0.5	H59A	0.5
Н59В	0.5	C62	0.5	H62A	0.5
H62B	0.5	C63	0.5	H63	0.5
C75	0.5	H75	0.5	C87	0.5
H87A	0.5	H87B	0.5	COAA	0.5
H0AA	0.5	C2AA	0.5	H2AA	0.5
H2AB	0.5	C20	0.5	H20A	0.5
H20B	0.5	C36	0.5	H36A	0.5
H36B	0.5	C39	0.5	C40	0.5
H40A	0.5	H40B	0.5	C45	0.5
H45A	0.5	H45B	0.5	C53	0.5
Н53	0.5	C103	0.5	H103	0.5
C125	0.5	H125	0.5	C152	0.5
H15A	0.5	H15B	0.5	C5AA	0.5
H5AA	0.5	H5AB	0.5	Au4	0.5
Ag0A	0.5	Ag1A	0.43	Ag2A	0.38
Au5	0.46	Ag	0.49		

**Table S7.** Atomic Occupancy for Au<sub>19</sub>Ag<sub>12</sub>(S-Adm)<sub>6</sub>(DPPM)<sub>6</sub>Cl<sub>7</sub>.

**Notes:** The nanocluster is termed as  $Au_{19}Ag_{12}(S-Adm)_6(DPPM)_6Cl_7$  in the current work, although its crystal structure outcomes a composition of  $Au_{16.66}Ag_{14.34}(S-Adm)_6(DPPM)_6Cl_7$ . Actually, because of the Au/Ag co-occupation in some metal sites in the cluster framework, the chemical formula of this alloy nanocluster should be  $Au_xAg_{31-x}(S-Adm)_6(DPPM)_6Cl_7$ . By analyzing the ESI-MS results, this  $Au_xAg_{31-x}(S-Adm)_6(DPPM)_6Cl_7$  alloy nanocluster was called  $Au_{19}Ag_{12}(S-Adm)_6(DPPM)_6Cl_7$  in this work, which also matched with the crystal data when we determined each alloying site as Au (or Ag) completely when such a site was occupied mainly by Au (or Ag).