## Supplementary Information

## Size Disproportionation among Nanocluster Transformations

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This Supporting Information file includes: Experimental Methods Figs. S1-S15 Tables S1-S4

## **Experimental Methods**

**Chemicals.** All following reagents were purchased from Sigma-Aldrich and used without further purification, including cupric acetylacetonate  $(Cu(C_5H_7O_2)_2, 98\%$  metal basis), silver nitrate (AgNO<sub>3</sub>, 99% metal basis), chloro(triphenylphosphine)gold(I) (Au(PPh<sub>3</sub>)Cl, 98%), 4-trifluoromethyl phenylthiophenol (C<sub>7</sub>H<sub>5</sub>F<sub>3</sub>S, 98%), triphenylphosphine (C<sub>18</sub>H<sub>15</sub>P, 99%), sodium borohydride (NaBH<sub>4</sub>, 99%), methanol (HPLC grade), dichloromethane (HPLC grade), hexane (HPLC grade), and toluene (HPLC grade).

**Preparation of (AgCu)**<sub>43</sub> **nanocluster.** 30 mg of AgNO<sub>3</sub> was dissolved in a mixed solution of 5 mL of MeOH and 20 mL of CH<sub>2</sub>Cl<sub>2</sub>, and 70 mg of Cu(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub> was added to this solution. After 20 minutes, 50 mg of PPh<sub>3</sub> and 50  $\mu$ L of 4-trifluoromethyl phenylthiophenol were added. Then, 5 mL of the aqueous solution of NaBH<sub>4</sub> (8 mg mL<sup>-1</sup>) was added. The reaction was proceeded for 12 hours. The obtained solution was centrifuged at 10000 rpm for 3 minutes, and the supernatant was collected and evaporated to get the crude product. The crude product was washed three times with hexane and methanol to get the (AgCu)<sub>43</sub> nanocluster.

**Preparation of**  $(AuAgCu)_{43}$ · $(AgCu)_{14}$  **nanocluster.** The as-prepared  $(AgCu)_{43}$  nanocluster (10 mg) was dissolved in 50 mL of toluene. The solution was vigorously stirred with a magnetic stir bar for 10 minutes. Then, 150 µL of Au(PPh<sub>3</sub>)Cl solution (dissolved in toluene, 5mg/mL) was added. The reaction was allowed to proceed for two hours. After that, the organic phase was rotavaporated under vacuum, and the precipitate was redissolved in CH<sub>2</sub>Cl<sub>2</sub>, producing the (AuAgCu)<sub>43</sub>·(AgCu)<sub>14</sub> nanocluster as determined by SC-XRD.

**Preparation of (AuAgCu)**<sub>33</sub> and (AuAgCu)<sub>56</sub> nanoclusters. The as-prepared (AgCu)<sub>43</sub> nanocluster (10 mg) was dissolved in 50 mL of toluene. The solution was vigorously stirred with a magnetic stir bar for 10 min. Then, 800  $\mu$ L of Au(PPh<sub>3</sub>)Cl solution (dissolved in toluene, 5mg/mL) was added. The reaction was allowed to proceed for two hours. After that, the organic phase was rotavaporated under vacuum, and the precipitate was redissolved in CH<sub>2</sub>Cl<sub>2</sub>. Then, thin-layer chromatography was used to separate and obtain (AuAgCu)<sub>33</sub> and (AuAgCu)<sub>56</sub> nanoclusters.

**Crystallization of (AgCu)**<sub>43</sub>, (AuAgCu)<sub>43</sub>·(AgCu)<sub>14</sub>, (AuAgCu)<sub>33</sub> and (AuAgCu)<sub>56</sub> nanoclusters. Single crystals of (AgCu)<sub>43</sub>, (AuAgCu)<sub>43</sub>·(AgCu)<sub>14</sub>, (AuAgCu)<sub>33</sub>, and (AuAgCu)<sub>56</sub> nanoclusters were cultivated at room temperature by diffusing the *n*-hexane into the  $CH_2Cl_2$  solution of each nanocluster. After a week, crystals were collected, and the structures of these nanoclusters were determined.

**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.

X-ray photoelectron spectroscopy (XPS) was performed on Thermo ESCALAB 250 equipped with a monochromated Al K $\alpha$  (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  $1 \times 10^{-9}$  mbar. The data was collected with FAT = 20 eV.

## X-Ray Crystallography

The data collection for single-crystal X-ray diffraction (SC-XRD) of all nanocluster crystal samples was carried out on a 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** XPS results of (A)  $(AgCu)_{43}$ , (B)  $(AuAgCu)_{43} \cdot (AgCu)_{14}$ , (C)  $(AuAgCu)_{33}$ , and (D)  $(AuAgCu)_{56}$  nanoclusters.



**Fig. S2** Comparison of the (A) Au, (B) Ag, and (C) Cu binding energy of  $(AgCu)_{43}$ ,  $(AgCu)_{43}$ · $(AgCu)_{14}$ ,  $(AuAgCu)_{33}$ , and  $(AuAgCu)_{56}$  nanoclusters.



**Fig. S3** ESI-MS results of the  $(AgCu)_{43}$  nanocluster in the negative ion mode. A series of mass signals, corresponding to  $Ag_xCu_{43-x}(SR)_{30}(PPh_3)_6$  where x ranged from 14 to 38, were detected, demonstrating that a large number of metal positions were co-occupied by Ag and Cu.



**Fig. S4** ESI-MS results of the  $(AuAgCu)_{43}$  nanocluster in the negative ion mode. A series of mass signals, corresponding to  $Au_2Ag_xCu_{41-x}(SR)_{30}(PPh_3)_6$  where *x* ranged from 5 to 15, were detected, demonstrating that a large number of metal positions were co-occupied by Ag and Cu.



**Fig. S5** ESI-MS results of the  $(AuAgCu)_{33}$  nanocluster in the negative ion mode. A series of mass signals, corresponding to  $Au_1Ag_xCu_{32-x}(SR)_{24}(PPh_3)_6S_2$  where x ranged from 8 to 17, were detected, demonstrating that a large number of metal positions were co-occupied by Ag and Cu.



**Fig. S6** Comparison of the corresponding lengths of (A) M(icosahedral kernel)---Ag(icosahedral surface), (B) M(icosahedral surface)---Ag(icosahedral surface), (C) M(motif)---S, and (D) M(icosahedral surface)---S bonds between (AgCu)<sub>43</sub> and (AuAgCu)<sub>43</sub> nanoclusters.



**Fig. S7** Crystalline packing mode of  $(AuAgCu)_{43} \cdot (AgCu)_{14}$ . The packing mode in the crystal lattice: views from the *a*, *b*, and *c* axes. For clarity, the innermost Au/Cl atoms in  $(AuAgCu)_{43}$  and  $(AgCu)_{14}$  were highlighted in green and blue, respectively.



Fig. S8 X-ray crystal structure of  $(AuAgCu)_{43}$ · $(AgCu)_{14}$  in a crystalline unit cell.



**Fig. S9** Intramolecular interactions in  $(AuAgCu)_{43}$  and  $(AgCu)_{14}$  nanoclusters, including  $\pi$ --- $\pi$ , C-H--- $\pi$  and C-H---F interactions.



**Fig. S10** Intercluster interactions between  $(AuAgCu)_{43}$  and  $(AgCu)_{14}$  nanoclusters. C-H--- $\pi$  and C-H---F interactions were highlighted with pink and blue dotted lines, respectively.



**Fig. S11** Illustration of the  $C_3$  symmetry axis in  $(AuAgCu)_{33}$  and  $(AuAgCu)_{56}$  nanoclusters, which passed through the center of  $Au_1Ag_{12}$  and  $Au_2Ag_{21}$  kernels, respectively.



**Fig. S12** Comparison of the corresponding lengths of (A) M(icosahedral kernel)---Ag(icosahedral surface), (B) M(icosahedral surface)---Ag(icosahedral surface), (C) M(motif)---S/Cl, and (D) M(icosahedral surface)---S/Cl bonds between (AuAgCu)<sub>33</sub> and (AuAgCu)<sub>56</sub> nanoclusters.



**Fig. S13** Thin layer chromatography (TCL) result of the product separation of the transformation from  $(AuAgCu)_{43}$  to  $(AuAgCu)_{33}$  and  $(AuAgCu)_{56}$ . (A) TCL result. (B,D) UV-vis absorption of the crude product from TLC, matching well with the optical absorption of  $(AuAgCu)_{33}$ . (C,E) UV-vis absorption of the crude product from TLC, matching well with the optical absorption of  $(AuAgCu)_{33}$ . (C,E) UV-vis absorption of the crude product from TLC, matching well with the optical absorption of  $(AuAgCu)_{33}$ .



**Fig. S14** Thermal stability tests of (A)  $(AuAgCu)_{33}$  and (B)  $(AuAgCu)_{56}$  nanoclusters under temperatures ranging from 40 to 70 °C.



**Fig. S15** Experimental optical absorptions of (A)  $(AuAgCu)_{33}$  and (B)  $(AuAgCu)_{56}$  nanoclusters in the presence of  $Au(PPh_3)Cl$ .

Table S1. Crystal data and structure refinement for the  $(AgCu)_{43}$  nanoclusters.

Molecular formula	$C_{336}H_{225}Ag_{26}Cu_{17}F_{90}P_7S_{30}$
Crystal system	trigonal
Space group	R-3
a/Å	28.6272(9)
b/Å	28.6272(9)
c/Å	108.574(5)
α/°	90
β/°	90
γ/°	120
Volume/ų	77057(6)
Z	6
$\rho_{calc}g/cm^3$	1.427
μ/mm-1	10.415
F(000)	32106.0
Radiation	CuK\a (λ = 1.54186)
Index ranges	-34 ≤ h ≤ 30, -34 ≤ k ≤ 33, -77 ≤ l ≤ 132
2θ range (°)	11.772 to 140.1
Measured reflections and unique reflections	31928 [R <sub>int</sub> = 0.0399, R <sub>sigma</sub> = 0.0272]
Goodness-of-fiton F <sup>2</sup>	1.024
Largest diff. peak/hole / e Å <sup>-3</sup>	1.22/-2.59
Final R indexes [I>=2o (I)]	$R_1 = 0.0430, wR_2 = 0.1223$
Final R indexes [all data]	$R_1 = 0.0544, wR_2 = 0.1309$

Molecular formula	C <sub>864</sub> H <sub>588</sub> Ag <sub>56</sub> Au <sub>4</sub> ClCu <sub>40</sub> F <sub>216</sub> P <sub>20</sub> S <sub>72</sub>
Crystal system	trigonal
Space group	R-3
a/Å	34.523(4)
b/Å	34.523(4)
c/Å	82.326(9)
α/°	90
β/°	90
γ/°	120
Volume/ų	84971(21)
Z	3
$\rho_{calc}g/cm^3$	1.607
μ/mm-1	11.485
F(000)	39879.0
Radiation	CuK\a (λ = 1.54186)
Index ranges	-38 ≤ h ≤ 30, -36 ≤ k ≤ 39, -94 ≤ l ≤ 67
2θ range (°)	8.232 to 124.998
Measured reflections and unique reflections	29216 [R <sub>int</sub> = 0.0867, R <sub>sigma</sub> = 0.0971]
Goodness-of-fiton F <sup>2</sup>	1.023
Largest diff. peak/hole / e Å <sup>-3</sup>	1.86/-1.44
Final R indexes [I>=2o (I)]	$R_1 = 0.0954, wR_2 = 0.2882$
Final R indexes [all data]	$R_1 = 0.1489, wR_2 = 0.3291$

**Table S2.** Crystal data and structure refinement for the  $(AuAgCu)_{43} \cdot (AgCu)_{14}$  nanoclusters.

Table S3. Cry	/stal data and structure	e refinement for the	(AuAgCu) <sub>33</sub> nanoclusters.

Molecular formula	$C_{264.23}H_{177.12}Ag_{20}AuCu_{12}F_{68.11}P_{5.75}S_2$
Crystal system	triclinic
Space group	P-1
a/Å	20.3056(8)
b/Å	22.3996(9)
c/Å	37.5185(12)
α/°	82.015(3)
β/°	84.918(3)
γ/°	83.158(3)
Volume/ų	16733.9(11)
Z	2
$\rho_{calc}g/cm^3$	1.741
μ/mm-1	13.217
F(000)	8490.0
Radiation	CuK\a (λ = 1.54186)
Index ranges	-23 ≤ h ≤ 13, -25 ≤ k ≤ 22, -43 ≤ l ≤ 41
2θ range (°)	8.672 to 124.998
Measured reflections and unique reflections	52150 [R <sub>int</sub> = 0.0760, R <sub>sigma</sub> = 0.0966]
Goodness-of-fiton F <sup>2</sup>	1.015
Largest diff. peak/hole / e Å <sup>-3</sup>	4.39/-3.20
Final R indexes [I>=2 $\sigma$ (I)]	R <sub>1</sub> = 0.0997, wR <sub>2</sub> = 0.2746
Final R indexes [all data]	$R_1 = 0.1303, wR_2 = 0.3009$

Table S4. Crystal data and structure refinement for the  $(AuAgCu)_{56}$  nanoclusters.

Molecular formula	$C_{372}H_{255}Ag_{27}Au_2CI_{14}Cu_{28}F_{90}P_9S_{33}$
Crystal system	monoclinic
Space group	P21/c
a/Å	41.4184(15)
b/Å	29.7952(15)
c/Å	47.331(2)
α/°	90
β/°	91.097(3)
γ/°	90
Volume/ų	58399(5)
Z	4
$\rho_{calc}g/cm^3$	1.519
μ/mm-1	11.528
F(000)	25748.0
Radiation	CuK\a (λ = 1.54186)
Index ranges	-47 ≤ h ≤ 38, -34 ≤ k ≤ 33, -54 ≤ l ≤ 34
2θ range (°)	11.606 to 125
Measured reflections and unique reflections	90602 [R <sub>int</sub> = 0.1062, R <sub>sigma</sub> = 0.2686]
Goodness-of-fiton F <sup>2</sup>	0.713
Largest diff. peak/hole / e Å <sup>-3</sup>	2.66/-1.08
Final R indexes [I>=2o (I)]	$R_1 = 0.0708$ , $wR_2 = 0.1744$
Final R indexes [all data]	R <sub>1</sub> = 0.1678, wR <sub>2</sub> = 0.2025