Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Probing the Surface-Active Sites of Metal Nanoclusters with Atomic Precision: A Case Study of Au_5Ag_{11}

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This Supporting Information includes:

Chemical Materials

All the following reagents were purchased from Sigma-Aldrich and used without further purification. Silver nitrate ($AgNO_3$, 99%), tetrachloroauric (III) acid ($HAuCl_4 \cdot 4H_2O$, 99% metal basis), cupric chloride ($CuCl_2$, 99% metals basis), bis(2-diphenylphosphinophenyl)ether (DPPOE, 98%), 2,6-dimethylbenzenethiol ($HSPhMe_2$, 97%, DMBT), 2,6-dichlorobenzenethiol ($HSPhCl_2$, 97%, DCBT), sodiumborohydride ($NaBH_4$, 99%), methanol (MeOH, HPLC grade), dichloromethane (CH_2Cl_2, HPLC grade), ethyl alcohol (EtOH, HPLC grade), n-hexane (HPLC grade), and toluene (Tol, HPLC grade).

Preparation of $Au_5Ag_{11}(SPhMe_2)_8(DPPOE)_2$

The preparation of $Au_5Ag_9Cu_2(SPhMe_2)_8(DPPOE)_2$ nanocluster was referred to the reported literature (*Angew. Chem. Int. Ed.,* 2022, **61**, e202205947).

Preparation of Cu-$SPhMe_2$ complex

10 mg of $CuCl_2$ was dissolved in methanol, and 50 uL of 2,6-dimethylbenzenethiol was added under ultrasound. After 5 minutes, the product was washed with methanol several times and dried in the oven. The obtained product was dissolved in 5 mL of toluene for further use.

Preparation of $Au_5Ag_9Cu_2(SPhMe_2)_8(DPPOE)_2$

15 mg of $Au_5Ag_{11}(SPhMe_2)_8(DPPOE)_2$ crystals were dissolved in 10 mL of toluene, and the prepared Cu-$SPhMe_2$ complex solution was added to the solution at the rate of 25 uL/min. After the addition of 175 uL Cu-$SPhMe_2$ complex, the $Au_5Ag_9Cu_2(SPhMe_2)_8(DPPOE)_2$ nanocluster was obtained. The supernatant was then separated and washed several times with methanol. Black acicular single crystals were obtained via the dichloromethane/methanol two-phase diffusing crystallization method at room temperature.

Preparation of $Au_5Ag_{11}(SPhCl_2)_8(DPPOE)_2$

10 mg of $Au_5Ag_{11}(SPhMe_2)_8(DPPOE)_2$ crystals were dissolved in 5 mL of CH_2Cl_2, and 2,6-dichlorobenzenethiol (1 mg/mL in CH_2Cl_2) was added to this solution with at the rate of 50 uL/min. After 10 minutes, the $Au_5Ag_{11}(SPhMe_2)_8(DPPOE)_2$ nanocluster was obtained. The final supernatant was centrifugated and washed several times with methanol. Red cubical crystals were obtained by dichloromethane/methanol two-phase diffusing crystallization method at room temperature.

Preparation of $Au_5Ag_{11}(SPhMe_2)_{8-x}(SPhCl_2)_x(DPPOE)_2$

The preparation of $Au_5Ag_{11}(SPhMe_2)_{8-x}(SPhCl_2)_x(DPPOE)_2$ was similar to the operation method of the $Au_5Ag_{11}(SPhCl_2)_8(DPPOE)_2$ nanocluster, except that the addition of 2,6-dichlorobenzenethiol was suspended at 3 minutes (i.e., 150 uL solution was added). Red cubical crystals of $Au_5Ag_{11}(SPhMe_2)_{8-x}(SPhCl_2)_x(DPPOE)_2$ were obtained by dichloromethane/methanol two-phase diffusing crystallization method at room temperature.

Characterization

The UV-vis absorption spectra of the nanoclusters were recorded using an Agilent 8453.

Photoluminescence (PL) spectra were measured on a Horiba Fluoro max plus spectrophotometer with the same optical density of 0.1.

Electrospray ionization mass (ESI-MS) measurements were performed on Waters XEVO G2-XS QT of the mass spectrometer. The sample was directly infused into the chamber at 5 µl/min. For preparing the ESI samples, the crystals were dissolved in CH_2Cl_2 (1 mg/mL) and diluted (v/v=1:1) by CH_3OH.

Single crystal X-ray diffraction (SC-XRD)

The data collection was carried out on a Stoe Stadivari diffractometer under liquid nitrogen flow at 120 K, using graphite-monochromatized Cu Kα radiation (λ = 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^2 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.

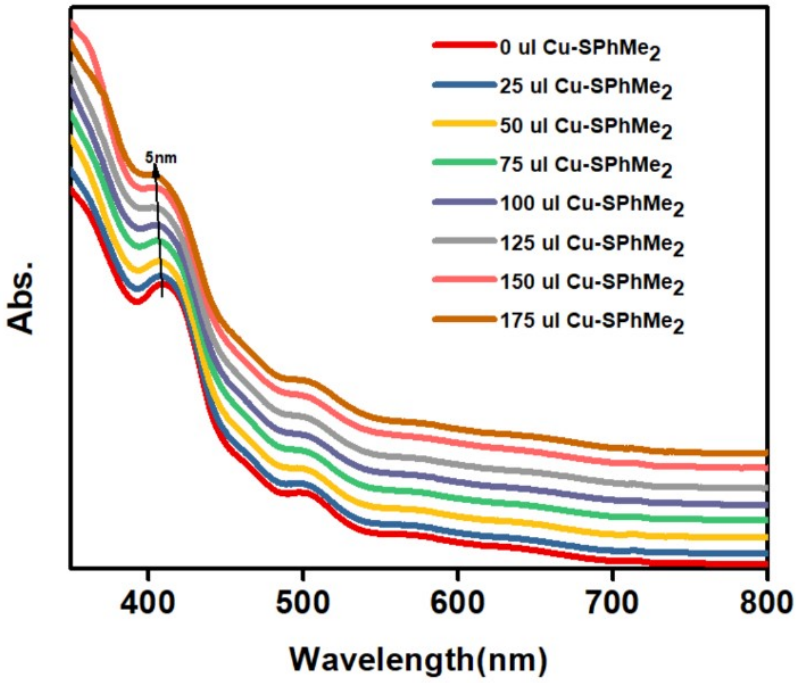

Figure S1. Time-dependent optical absorption spectra during the metal-exchange (Cu alloying) reaction beginning from **Au_5Ag_9-DMBT**.

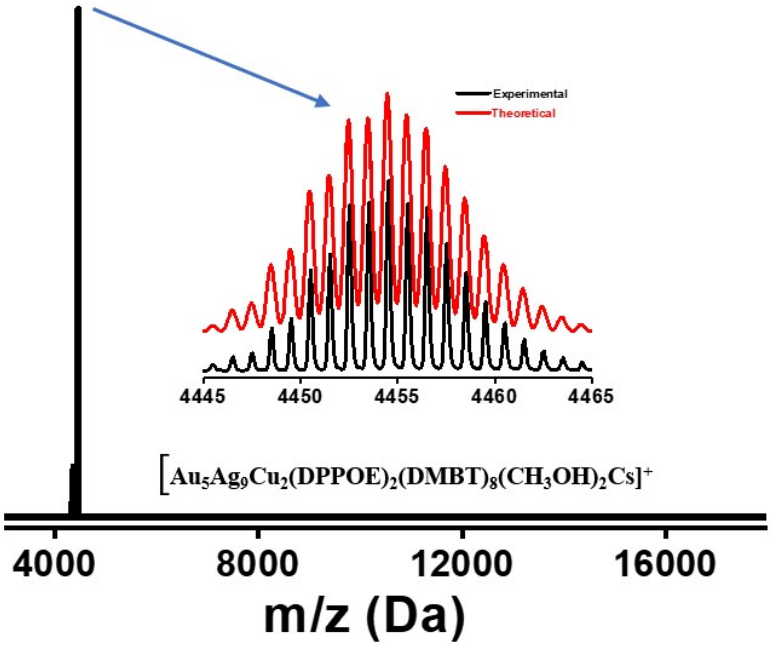

Figure S2. ESI-MS result of the **$Au_5Ag_9Cu_2$-DMBT** nanocluster.

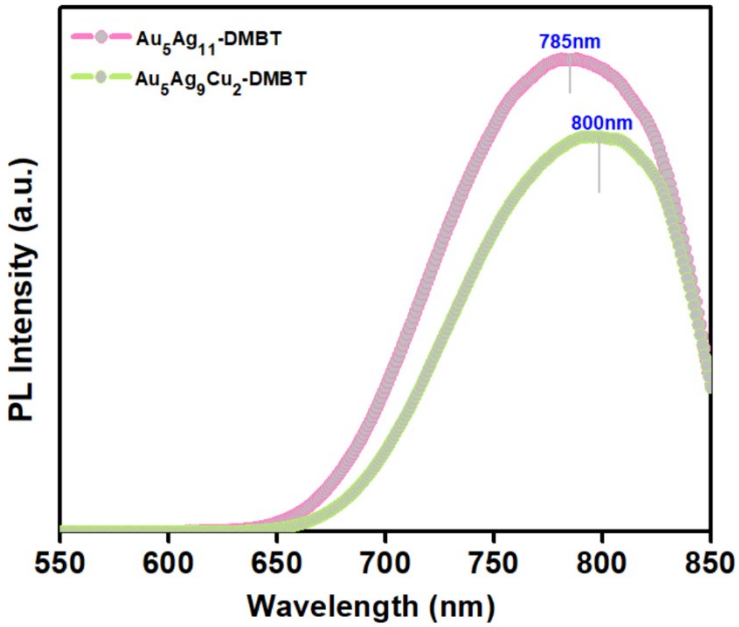

Figure S3. PL comparison between **Au_5Ag_{11}-DMBT** and **$Au_5Ag_9Cu_2$-DMBT** nanoclusters (dissolved in toluene).

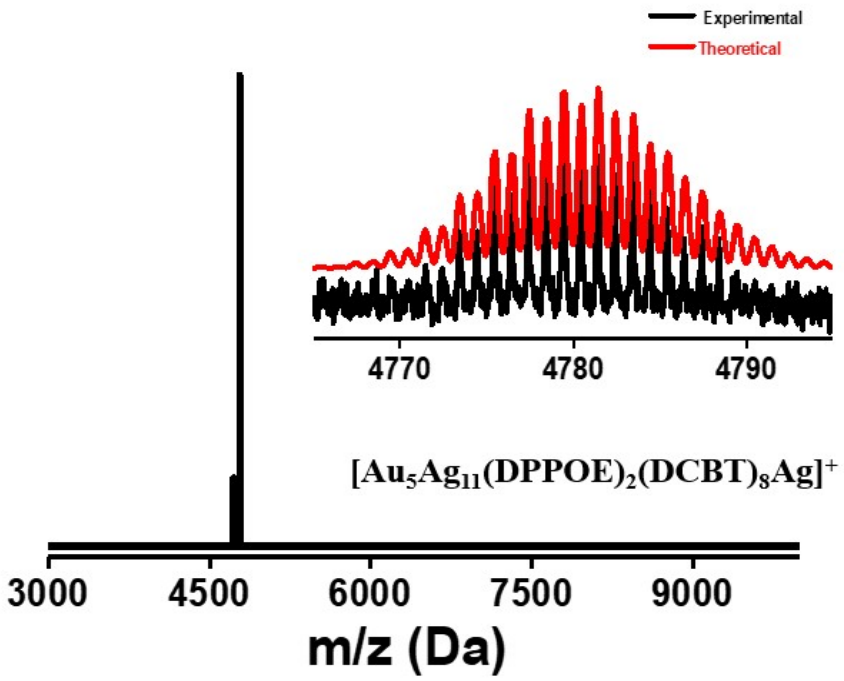

Figure S4. ESI-MS result of the **Au_5Ag_{11}-DCBT** nanocluster.

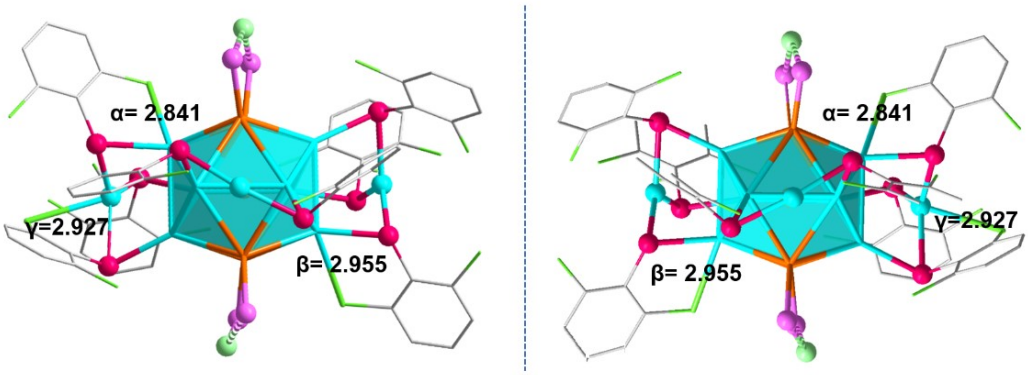

Figure S5. The three Ag-Cl bonds in a pair of enantiomer structures of **Au_5Ag_{11}-DCBT**.

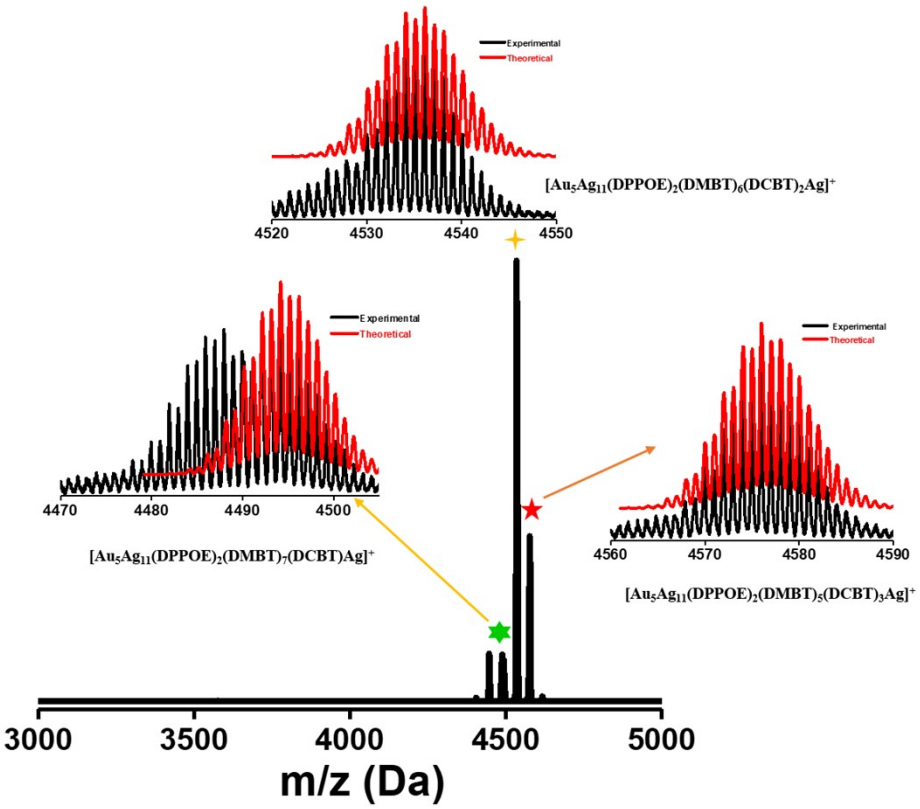

Figure S6. The ESI-MS results of the $Au_5Ag_{11}(DMBT)_{8-x}(DCBT)_x(DPPOE)_2$ (x = 1, 2, and 3) nanocluster.

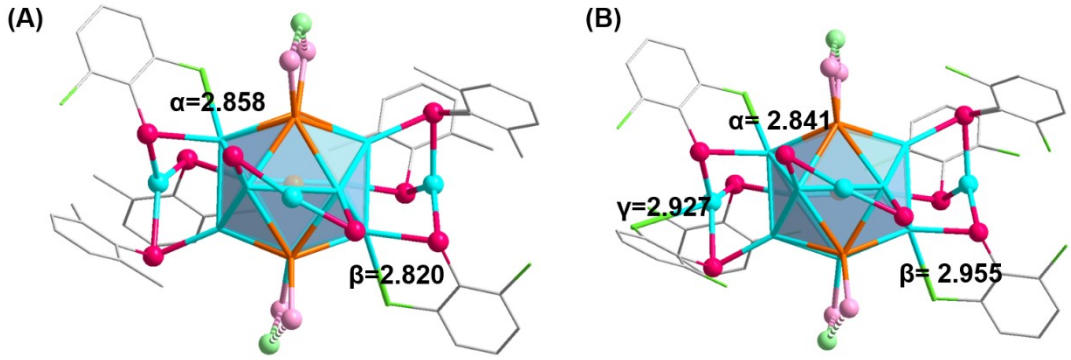

Figure S7. The Ag-Cl bonds in (A) **Au_5Ag_{11}-DMBT-DCBT** and (B) **Au_5Ag_{11}-DCBT** nanoclusters.

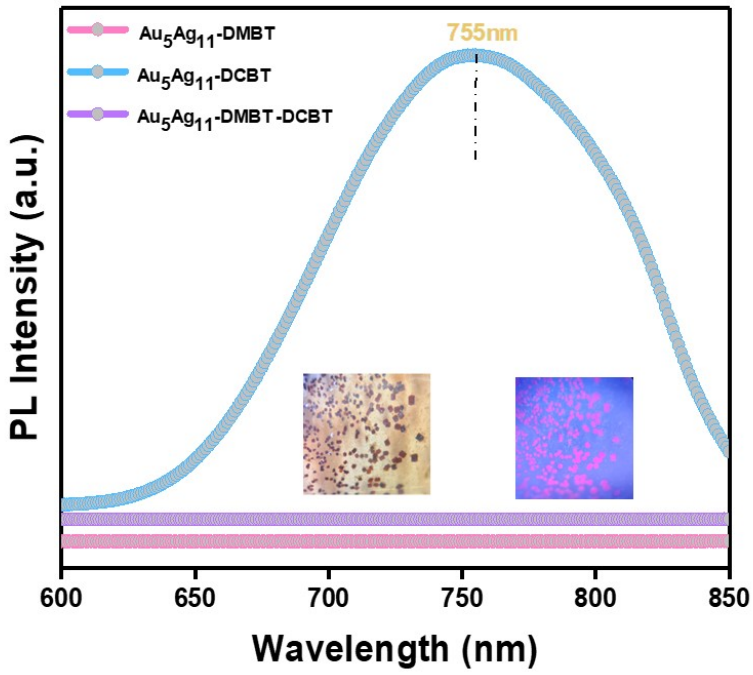

Figure S8. The crystal fluorescence characteristic of **Au_5Ag_{11}-DCBT**, **Au_5Ag_{11}-DMBT-DCBT**, and **Au_5Ag_{11}-DMBT** nanoclusters.

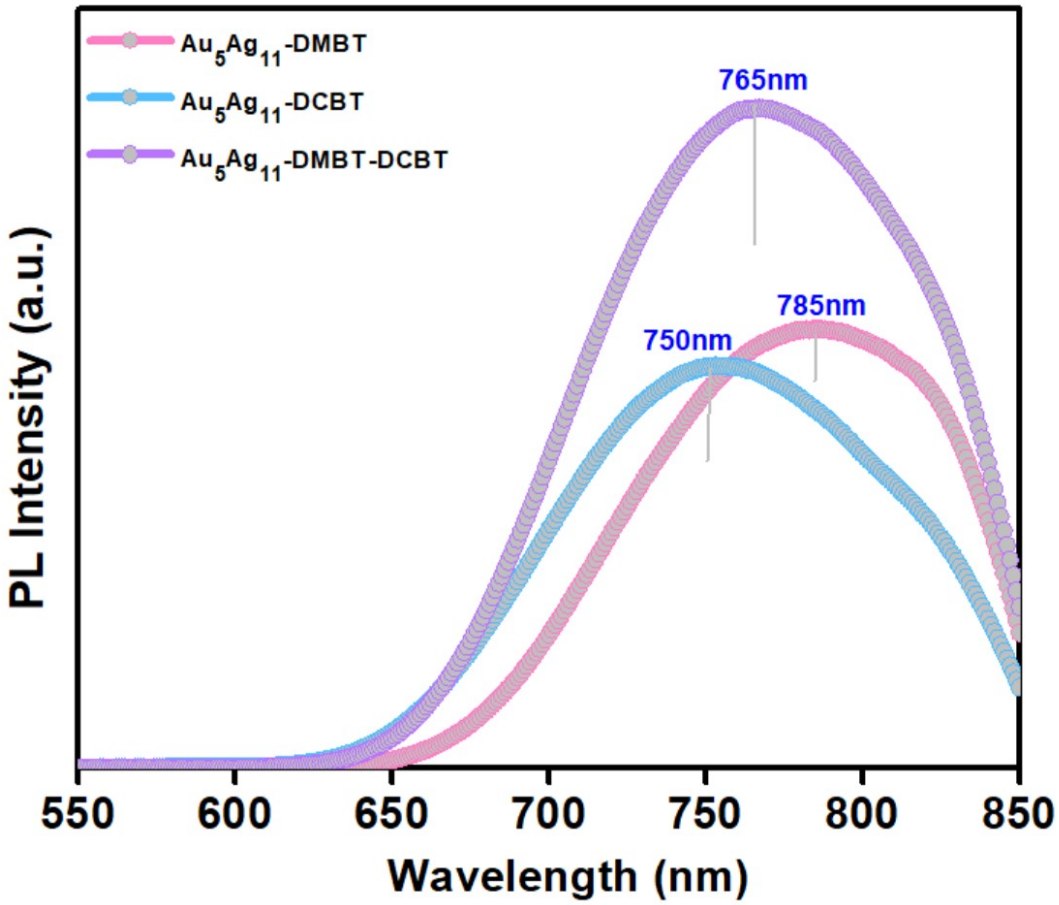

Figure S9. PL properties comparison among **Au_5Ag_{11}-DCBT**, **Au_5Ag_{11}-DMBT-DCBT**, and **Au_5Ag_{11}-DMBT** in toluene.

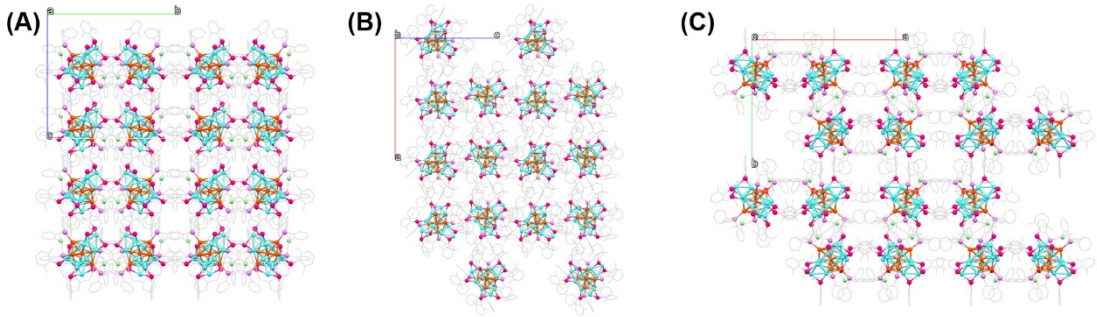

Figure S10. Stacking patterns of **Au_5Ag_{11}-DMBT** in the crystal lattice along *a*, *b*, and *c* axis.

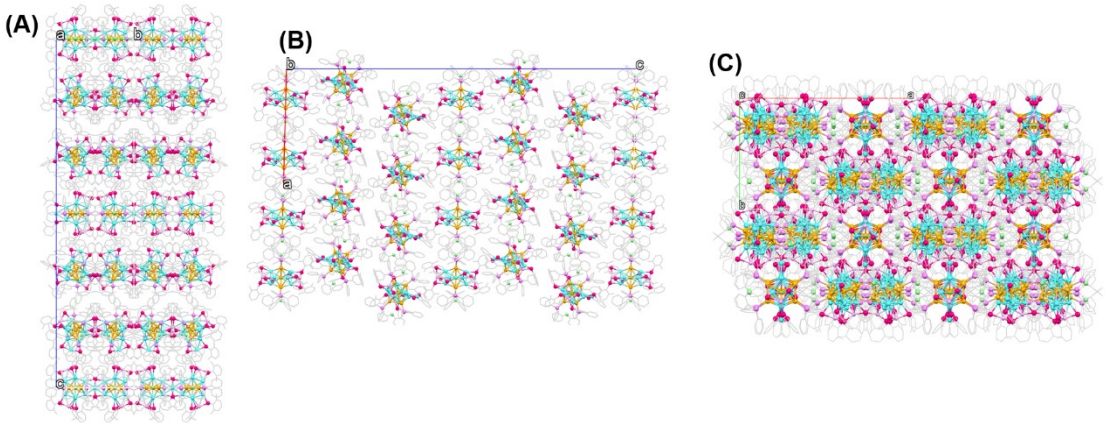

Figure S11. Stacking patterns of **$Au_5Ag_9Cu_2$-DMBT** in the crystal lattice along *a*, *b*, and *c* axis.

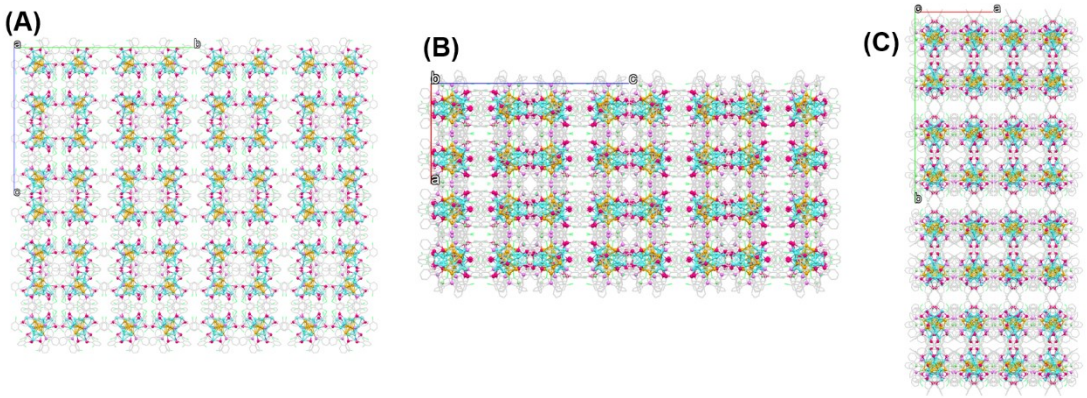

Figure S12. Stacking patterns of **Au_5Ag_{11}-DCBT** in the crystal lattice along *a*, *b*, and *c* axis.

Table S1. Crystal data and structure refinement for the $Au_5Ag_9Cu_2(SPhMe_2)_8(DPPOE)_2$ nanocluster.

Empirical formula	$C_{136}H_{128}Ag_9Au_5Cu_2O_2P_4S_8$
Formula weight	4257.48
Temperature/K	120
Crystal system	monoclinic
Space group	*I2/a*
a/Å	28.0881(3)
b/Å	18.3857(2)
c/Å	82.4807(10)
α/°	90
β/°	91.5410(10)
γ/°	90
Volume/Å^3	42579.2(8)
Z	12
ρ_{calc}g/cm^3	1.992
μ/mm^{-1}	21.347
F(000)	24288.0
Radiation	CuKα (λ = 1.54186)
2Θ range for data collection/°	8.018 to 139.282
Index ranges	-33 ≤ h ≤ 29, -22 ≤ k ≤ 20, -100 ≤ l ≤ 64
Reflections collected	196619
Independent reflections	39370 [R_{int} = 0.0905, R_{sigma} = 0.1024]
Data/restraints/parameters	39370/2448/2183
Goodness-of-fit on F^2	0.821
Final R indexes [I>=2σ (I)]	R_1 = 0.0423, wR_2 = 0.0892
Final R indexes [all data]	R_1 = 0.0753, wR_2 = 0.0952
Largest diff. peak/hole / e Å^{-3}	1.66/-1.08

Table S2. Crystal data and structure refinement for the $Au_5Ag_{11}(SPhCl_2)_8(DPPOE)_2$ nanocluster.

Empirical formula	$C_{120}H_{80}Ag_{11.27}Au_{4.73}Cl_{16}O_2P_4S_8$
Formula weight	4648.91
Temperature/K	120
Crystal system	orthorhombic
Space group	*Ccca*
a/Å	23.4047(7)
b/Å	56.3203(16)
c/Å	46.1622(18)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	60849(3)
Z	16
ρ_{calc}g/cm^3	2.030
μ/mm^{-1}	24.022
F(000)	34871.0
Radiation	CuKα (λ = 1.54186)
2Θ range for data collection/°	7.052 to 125
Index ranges	-20 ≤ h ≤ 26, -64 ≤ k ≤ 49, -49 ≤ l ≤ 53
Reflections collected	74458
Independent reflections	23986 [R_{int} = 0.1084, R_{sigma} = 0.1119]
Data/restraints/parameters	23986/1440/1256
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R1 = 0.1193, wR_2 = 0.3143
Final R indexes [all data]	R_1 = 0.1605, wR_2 = 0.3458
Largest diff. peak/hole / e Å^{-3}	2.27/-1.94

Table S3. Crystal data and structure refinement for the $Au_5Ag_{11}(SPhMe_2)_6(SPhCl_2)_2(DPPOE)_2$ nanocluster.

Empirical formula	$C_{127.66}H_{110.72}Ag_{11}Au_5Cl_{5.34}O_2P_4S_8$
Formula weight	4417.98
Temperature/K	120
Crystal system	triclinic
Space group	*P-1*
a/Å	15.839(2)
b/Å	21.943(3)
c/Å	23.474(2)
α/°	87.071(9)
β/°	83.398(9)
γ/°	78.741(10)
Volume/Å^3	7944.8(16)
Z	2
ρ_{calc}g/cm^3	1.847
μ/mm^{-1}	21.536
F(000)	4167.0
Radiation	CuKα (λ = 1.54186)
2Θ range for data collection/°	11.46 to 124.994
Index ranges	-11 ≤ h ≤ 18, -25 ≤ k ≤ 25, -22 ≤ l ≤ 27
Reflections collected	66857
Independent reflections	24655 [R_{int} = 0.0618, R_{sigma} = 0.0837]
Data/restraints/parameters	24655/1633/1490
Goodness-of-fit on F^2	0.925
Final R indexes [I>=2σ (I)]	R_1 = 0.0656, wR_2 = 0.1686
Final R indexes [all data]	R_1 = 0.0914, wR_2 = 0.1810
Largest diff. peak/hole / e Å^{-3}	2.70/-2.71