Supplementary Information

1. Experimental Section

**Synthesis of Au_{24}Ag_{20}(C_{12}H_{13})_{24}Cl_{2}:** AuSMe_{2}Cl was prepared according to literature methods.^{32} 60 mg AuSMe_{2}Cl and 30 mg CH_{3}COOAg were dissolved in 10 mL dichloromethane and 5 ml methanol. Then 1 mL of a methanol solution of 10 mg sodium methoxide and 30 μL 4-tert-butyl phenylacetylene were mixed together and sonicated for 5 minutes. Then the 4-tert-butyl phenylacetylene solution was added to the above solution under vigorous stirring. After 20 min, 10 mg tert-butylamineborane was added. The reaction was carried out at room temperature for 12 hours. After that, the reaction solution was centrifuged and the centrifugate precipitate was discarded, and the liquid was then washed with methanol several times to remove excess salts, alkynes and reducing agents. The target nanoclusters were extracted with dichloromethane. Finally, single crystal of Au_{24}Ag_{20}(C_{12}H_{13})_{24}Cl_{2} was obtained by diffusing methanol into toluene solution of the nanoclusters for two weeks.

**Synthesis of Au_{43}Ag_{38}(C_{12}H_{13})_{36}Cl_{12}:** 60 mg AuSMe_{2}Cl and 30 mg CH_{3}COOAg were dissolved in 10 mL dichloromethane and 5 ml methanol. Then 1 mL of a methanol solution of 10 mg sodium methoxide and 30 μL 4-tert-butyl phenylacetylene were mixed together and sonicated for 5 minutes. Then the 4-tert-butyl phenylacetylene solution was added to the above solution under vigorous stirring. After 20 min, 10 mg tert-butylamineborane was added. The reaction was carried out at room temperature for 36 hours. After that, the reaction solution was centrifuged, the centrifugate precipitate was discarded, and the liquid was washed with methanol several times to remove excess salts, alkynes and reducing agents. The target nanoclusters were extracted with dichloromethane. Finally, single crystal of Au_{43}Ag_{38}(C_{12}H_{13})_{36}Cl_{12} was obtained by diffusing methanol into toluene solution of the nanoclusters for two weeks.

**Synthesis of Au_{24}Ag_{20}(C_{9}H_{7})_{24}Cl_{2}:** 60 mg AuSMe_{2}Cl and 30 mg CH_{3}COOAg were dissolved in 10 mL dichloromethane and 5 ml methanol. Then 1 mL of a methanol solution of 10 mg sodium methoxide and 30 μL 2-methyl phenylacetylene were mixed
together and sonicated for 5 minutes. Then the 2-methyl phenylacetylene solution was added to the above solution under vigorous stirring. After 20 min, 20 μL diphenylsilane was added. The reaction was carried out at room temperature for 36 hours. After that, the reaction solution was centrifuged, the centrifugate precipitate was discarded, and the liquid was washed with methanol several times to remove excess salts, alkynes and reducing agents. The target nanoclusters were extracted with dichloromethane. Finally, single crystal of Au$_{24}$Ag$_{20}$(C$_9$H$_7$)$_{24}$Cl$_2$ was obtained by diffusing n-hexane into CH$_2$Cl$_2$ solution of the nanoclusters for two weeks.

**Synthesis of Au$_{43}$Ag$_{38}$(C$_9$H$_7$)$_{36}$Cl$_9$:** 60 mg AuSMe$_2$Cl and 30 mg CH$_3$COOAg were dissolved in 10 mL dichloromethane and 5 ml methanol. Then 1 mL of a methanol solution of 10 mg sodium methoxide and 30 μL 2-methyl phenylacetylene were mixed together and sonicated for 5 minutes. Then the 2-methyl phenylacetylene solution was added to the above solution under vigorous stirring. After 20 min, 20 μL diphenylsilane was added. The reaction was carried out at room temperature for 36 hours. After that, the reaction solution was centrifuged, the centrifugate precipitate was discarded, and the liquid was washed with methanol several times to remove excess salts, alkynes and reducing agents. The target nanoclusters were extracted with dichloromethane. Finally, single crystal of Au$_{43}$Ag$_{38}$(C$_9$H$_7$)$_{36}$Cl$_9$ was obtained by diffusing n-hexane into CH$_2$Cl$_2$ solution of the nanoclusters for two weeks.

**Characterization:** The UV-vis absorption spectra with a range of 300-1000 nm were recorded on a UV-1800 spectrophotometer (Shimadzu, Japan). For Au$_{24}$Ag$_{20}$(C$_{12}$H$_{13}$)$_{24}$Cl$_2$, Au$_{24}$Ag$_{20}$(C$_9$H$_7$)$_{24}$Cl$_2$ and Au$_{43}$Ag$_{38}$(C$_9$H$_7$)$_{36}$Cl$_9$, the diffraction data were collected on a Bruker D8 VENTURE with Mo Kα radiation (λ = 0.71073 Å). For Au$_{43}$Ag$_{38}$(C$_{12}$H$_{14}$)$_{36}$Cl$_{12}$, the X-ray crystallography was performed on a Bruker D8 VENTURE with Ga Kα radiation (λ = 1.34139 Å). Electrospray ionization (ESI) mass spectra were collected on a Waters Q-TOF mass spectrometer using a Z-spray source. The Au$_{24}$Ag$_{20}$(C$_{12}$H$_{13}$)$_{24}$Cl$_2$ sample was first dissolved in toluene (~ 0.5 mg/mL) and then diluted (2:1 v/v) with a methanol solution containing 50 mM CsCO$_3$. The Au$_{24}$Ag$_{20}$(C$_9$H$_7$)$_{24}$Cl$_2$ sample was first dissolved in toluene (~ 1 mg/mL) and then directly infused into the chamber at 5 μL/min. Chemical compositions of the
Au_{43}Ag_{38}(C_{12}H_{13})_{36}Cl_{12} and Au_{43}Ag_{38}(C_{9}H_{7})_{36}Cl_{9} nanoclusters were determined by matrix-assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry in positive-ion mode with trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as the matrix. A three-electrode system was employed for EIS (electrochemical impedance spectroscopy) experiments performed on a CHI660B electrochemical workstation, with working electrode (WE) of platinum foil, counter electrode (CE) of a glassy carbon and reference electrode of saturated Ag/AgCl. The experiments were carried out in 1 mol/L KHCO₃ at room temperature.

**Catalytic test:** All electrochemical tests were carried out in a customized H-type electrolytic cell, in which the anode and cathode compartments were separated by Nafion 117 membrane. The sample of each cluster uniformly coated on 1 cm×cm carbon paper (Toray TGP-H-090) was used as the working electrode, and the electrochemical workstation of Shanghai Chenhua CHI660D was used for electroreduction CO₂ test. Ag/AgCl electrode and platinum wire electrode were respectively used as reference electrode and counter electrode. Through \( E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.21 \text{ V} + 0.0591 \times \text{pH} \), all the electrode potentials in this study were converted to the reversible hydrogen electrode potential (RHE). The electrolyte was a 0.5 M KHCO₃ aqueous solution. Gas chromatography (GC) and nuclear magnetic resonance (NMR) techniques were selected to analyze the gas and liquid products, respectively.

Before the CO₂ electroreduction reaction, the KHCO₃ solution was purified with 30 mL/min CO₂ for 30 minutes to saturate the electrolyte and remove the air in the electrolytic cell. Linear voltammetry curve (LSV) was measured at a scanning rate of 10 mV/s from -0.3 to -1.2 V vs RHE at room temperature. During the reaction, the electrolyte in the cathode chamber was stirred at a speed of 300 rpm, and CO₂ gas was continuously and constantly introduced at a gas flow rate of 30 mL/min to purify and saturate it. The exhaust gas from the cathode chamber was analyzed at 20 min intervals using a gas chromatograph fitted with a thermal conductivity detector (TCD) and a hydrogen flame ionization detector (FID). The liquid product was detected by Bruker Avance 400 MHz $^1$H NMR with dimethyl sulfoxide (DMSO) as the internal standard.
2. Computational Methods
All structural optimizations are implemented in ORCA 5.0 quantum chemistry program package\textsuperscript{52} at the level of PBE/def2-SVP.\textsuperscript{53,54} The calculation of single-point energy is instigated using higher-level PBE0/Def2-TZVP\textsuperscript{53} to obtain more accurate wave function information. The dispersion effect was considered in the structural optimization and calculations of single point energy by utilizes the atom-pairwise dispersion correction with the Becke-Johnson damping scheme (D3BJ).\textsuperscript{55,56} It is worth mentioning that we use RI approximation in ORCA, so each basis set needs an auxiliary basis set, which can make the calculation easier when the accuracy sacrifice is negligible. In this study, Def2/J\textsuperscript{57} corresponding to the def2SVP and Def2-TZVP basis sets were used as auxiliary basis sets. In order to save computational resources, alkynyl groups have been simplified to methyl groups.
3. Supporting Figures and Tables

Fig. S1 (A) ESI-MS data for the Au$_{24}$Ag$_{20}$(C$_{12}$H$_{13}$)$_{24}$Cl$_{2}$ nanocluster. (B) Comparison of the experiment and the simulated isotopic patterns of Au$_{24}$Ag$_{20}$(C$_{12}$H$_{13}$)$_{24}$Cl$_{2}$ nanocluster. (C) ESI-MS data for the Au$_{24}$Ag$_{20}$(C$_{9}$H$_{7}$)$_{24}$Cl$_{2}$ nanocluster. (D) Comparison of the experiment and the simulated isotopic patterns of Au$_{24}$Ag$_{20}$(C$_{9}$H$_{7}$)$_{24}$Cl$_{2}$ nanocluster.
Fig. S2 MALDI-TOF-MS spectra of (A) \( \text{Au}_{43}\text{Ag}_{38}(\text{C}_{12}\text{H}_{13})_{36}\text{Cl}_{12} \) and (B) \( \text{Au}_{43}\text{Ag}_{38}(\text{C}_{9}\text{H}_{7})_{36}\text{Cl}_{9} \). Note that the ESI-MS data of the two \( \text{Au}_{43}\text{Ag}_{38} \) nanoclusters were difficult to be obtained and hence their MALDI-MS data were provided. Besides, one alkyne ligand for \( \text{Au}_{43}\text{Ag}_{38} \) was removed during the MALDI-TOF-MS measurements.
Fig. S3  Average bond lengths in (A) Au$_{24}$Ag$_{20}$(C$_{12}$H$_{13}$)$_{24}$Cl$_2$ and (B) Au$_{24}$Ag$_{20}$(C$_{6}$H$_{7}$)$_{24}$Cl$_2$. 
Fig. S4 Binding motifs in (A-D) $\text{Au}_{24}\text{Ag}_{20}(\text{C}_{12}\text{H}_{13})_{24}\text{Cl}_{2}$ and (E-G) $\text{Au}_{24}\text{Ag}_{20}(\text{C}_{9}\text{H}_{7})_{24}\text{Cl}_{2}$. 
Fig. S5 Distances between the central Au atom and the neighbor Au atoms in (A, B) \( \text{Au}_{43}\text{Ag}_{38}(\text{C}_{12}\text{H}_{13})_{36}\text{Cl}_{12} \) and (C, D) \( \text{Au}_{43}\text{Ag}_{38}(\text{C}_{9}\text{H}_{7})_{36}\text{Cl}_{9} \).
Fig. S6 Binding motifs in the Au$_{43}$Ag$_{38}$(C$_{12}$H$_{13}$)$_{36}$Cl$_{12}$ nanocluster.
Fig. S7 Binding motifs in the $\text{Au}_{43}\text{Ag}_{38}(\text{C}_9\text{H}_7)_{36}\text{Cl}_9$ nanocluster.
**Fig. S8** UV-vis absorption spectra of the four nanoclusters.
Fig. S9 Kohn-Sham MO diagrams of the inner cores of (A) Au$_{25}$(SR)$_{18}^-$, (B) Au$_{24}$Ag$_{20}$, (C) Au$_{38}$(SR)$_{24}$ and (D) Au$_{43}$Ag$_{38}$. 
Fig. S10 The electrochemical impedance spectra (EIS) of the four clusters.
Table S1. Crystal data and structure refinement for the Au$_{24}$Ag$_{20}$($C_{12}H_{13}$)$_{24}$Cl$_2$ nanocluster.

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Empirical formula                             | C288H312Ag20Au24Cl2                        |
| Formula weight                                | 10728.854                                  |
| Temperature                                   | 296(2) K                                  |
| Wavelength                                    | 0.71073 Å                                  |
| Crystal system                                | Triclinic                                  |
| Space group                                   | P -1                                       |
| Unit cell dimensions                          | a = 19.2914(15) Å, α = 97.077(2)°          |
|                                              | b = 24.9197(18) Å, β = 105.131(2)°         |
|                                              | c = 34.987(3) Å, γ = 100.118(2)°           |
| Volume                                        | 15729(2) Å                                  |
| Z                                             | 2                                          |
| Density (calculated)                          | 2.265 g/cm$^3$                             |
| Absorption coefficient                        | 12.411 mm$^{-1}$                           |
| F(000)                                        | 9820                                       |
| Theta range for data collection               | 2.003 to 24.034°.                          |
| Index ranges                                  | -22≤h≤22, -29≤k≤28, -41≤l≤41               |
| Reflections collected                         | 110558                                     |
| Independent reflections                       | 24722 [R(int)= 0.0909]                     |
| Max. and min. transmission                    | 0.370 and 0.190                            |
| Absorption correction                        | Multi-Scan                                 |
| Refinement method                             | Full-matrix least-squares on F$^2$         |
| Refinement program                            | SHELXL-2018/3(Sheldrick,2018)              |
| Function minimized                            | $\sum w(F_o^2 - F_c)^2$                    |
| Data / restraints / parameters                | 55123 / 13854 / 3092                       |
| Goodness-of-fit on F$^2$                      | 0.964                                      |
| $\Delta/\sigma_{max}$                        | 0.010                                      |
| Final R indices [I>2sigma(I)]                 | R1 = 0.0741, wR2 = 0.1757                  |
| R indices (all data)                          | R1 = 0.1685, wR2 = 0.2228                  |
| Largest diff. peak and hole                   | 1.730 and -2.060 eÅ$^{-3}$                |
**Table S2.** Crystal data and structure refinement for the Au$_{43}$Ag$_{38}$(C$_{12}$H$_{13}$)$_{36}$Cl$_{12}$ nanocluster.

| Property                                      | Value                        |
|-----------------------------------------------|------------------------------|
| **Empirical formula**                         | C864H942Ag76Au86Cl24         |
| **Formula weight**                            | 37314.16                     |
| **Temperature**                               | 193(2) K                     |
| **Wavelength**                                | 1.34139 Å                    |
| **Crystal system**                            | Trigonal                     |
| **Space group**                               | R -3                         |
| **Unit cell dimensions**                      |                             |
| a                                             | 26.1589(15) Å                |
| α = 90°                                       |                              |
| b                                             | 26.1589(15) Å                |
| β = 90°                                       |                              |
| c                                             | 148.875(12) Å                |
| γ = 120°                                      |                              |
| **Volume**                                    | 88225(12) Å³                 |
| **Z**                                         | 3                            |
| **Density (calculated)**                      | 2.107 g/cm³                  |
| **Absorption coefficient**                    | 20.715 mm⁻¹                  |
| **F(000)**                                    | 50700                        |
| **Theta range for data collection**           | 1.716 to 59.599°             |
| **Index ranges**                              | -33<=h<=31, -33<=k<=31, -191<=l<=172 |
| **Reflections collected**                     | 356807                       |
| **Independent reflections**                   | 43247 [R(int)=0.1214]        |
| **Absorption correction**                     | Multi-Scan                   |
| **Refinement method**                         | Full-matrix least-squares on F² |
| **Refinement program**                        | SHELXL-2018/3(Sheldrick,2018) |
| **Function minimized**                        | Σ w(Fo² - Fc²)²              |
| **Data / restraints / parameters**            | 43247 / 6612 / 1550          |
| **Goodness-of-fit on F²**                     | 1.014                        |
| **Δ/σmax**                                    | 0.014                        |
| **Final R indices [I>2sigma(I)]**             | R1 = 0.0714, wR2 = 0.1780    |
| **R indices (all data)**                      | R1 = 0.1317, wR2 = 0.2160    |
| **Largest diff. peak and hole**               | 2.492 and -2.559 eÅ⁻³        |
Table S3. Crystal data and structure refinement for the Au$_{24}$Ag$_{20}$(C$_9$H$_7$)$_{24}$Cl$_2$ nanocluster.

| Property                              | Value                                      |
|---------------------------------------|--------------------------------------------|
| Empirical formula                     | C216H168Ag20Au24Cl4                        |
| Formula weight                        | 9789.89                                    |
| Temperature                           | 296(2) K                                   |
| Wavelength                            | 0.71073 Å                                  |
| Crystal system                        | Triclinic                                  |
| Space group                           | P -1                                       |
| Unit cell dimensions                  |                                           |
| a                                     | 18.9562(18) Å                             |
| α                                     | 78.295(3)°                                 |
| b                                     | 19.6527(18) Å                             |
| β                                     | 79.704(3)°                                 |
| c                                     | 33.671(3) Å                               |
| γ                                     | 63.881(2)°                                 |
| Volume                                | 10971.6(18) Å                             |
| Z                                     | 2                                          |
| Density (calculated)                  | 2.963 g/cm$^3$                             |
| Absorption coefficient                | 17.801 mm$^{-1}$                          |
| F(000)                                | 8736                                       |
| Theta range for data collection       | 1.995 to 25.000°                           |
| Index ranges                          | -22<=h<=22, -23<=k<=22, -40<=l<=30         |
| Reflections collected                 | 72467                                      |
| Independent reflections               | 38173 [R(int)=0.0688]                      |
| Max. and min. transmission            | 0.269 and 0.125                           |
| Absorption correction                 | Multi-Scan                                |
| Refinement method                     | Full-matrix least-squares on F$^2$        |
| Refinement program                    | SHELXL-2018/3(Sheldrick,2018)              |
| Function minimized                    | Σ w(F$_o^2$ - F$_c^2$)$^2$                 |
| Data / restraints / parameters        | 38173 / 11173 / 2339                      |
| Goodness-of-fit on F$^2$              | 1.025                                      |
| Δ/σ$_{max}$                           | 0.013                                      |
| Final R indices [I>2sigma(I)]         | R1 = 0.0882, wR2 = 0.2220                 |
| R indices (all data)                  | R1 = 0.1430, wR2 = 0.2571                 |
| Largest diff. peak and hole           | 4.088 and -2.860 eÅ$^{-3}$                 |
Table S4. Crystal data and structure refinement for the Au$_{43}$Ag$_{38}$(C$_9$H$_7$)$_{36}$Cl$_9$ nanocluster.

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Empirical formula                             | C324H251Ag38Au43Cl19                       |
| Formula weight                                | 17031.90                                   |
| Temperature                                   | 296(2) K                                   |
| Wavelength                                    | 0.71073 Å                                  |
| Crystal system                                | Triclinic                                  |
| Space group                                   | P -1                                       |
| Unit cell dimensions                          |                                           |
| $a = 25.413(2)$ Å                             | $\alpha = 77.099(3)^\circ$               |
| $b = 25.542(2)$ Å                             | $\beta = 83.178(3)^\circ$                |
| $c = 28.705(3)$ Å                             | $\gamma = 73.626(3)^\circ$               |
| Volume                                        | 17395(3) Å                                 |
| Density (calculated)                          | 3.252 g/cm$^3$                             |
| Absorption coefficient                        | 20.240 mm$^{-1}$                           |
| F(000)                                        | 15062                                      |
| Theta range for data collection               | 1.952 to 25.359°                           |
| Index ranges                                  |                                            |
| Reflections collected                         | 60772                                      |
| Independent reflections                       |                                            |
| Max. and min. transmission                    | 0.237 and 0.107                            |
| Absorption correction                         | Multi-Scan                                 |
| Refinement method                             | Full-matrix least-squares on F$^2$         |
| Refinement program                            | SHELXL-2018/3(Sheldrick,2018)              |
| Function minimized                            | $\sum w(F_o^2 - F_c^2)^2$                  |
| Data / restraints / parameters                |                                            |
| Goodness-of-fit on F$^2$                      | 1.053                                      |
| $\Delta/\sigma_{max}$                        | 0.007                                      |
| Final R indices [I>2sigma(I)]                 |                                            |
| R1 = 0.0912, wR2 = 0.1983                     |                                            |
| R indices (all data)                          |                                            |
| R1 = 0.2172, wR2 = 0.2526                     |                                            |
| Largest diff. peak and hole                   |                                            |
| 2.815 and -2.771 eÅ$^{-3}$                    |                                            |
Supporting References

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