Electronic Supplementary Information for

Atomically precise alkynyl-protected $Ag_{19}Cu_2$ nanoclusters: Synthesis, structure analysis, and electrocatalytic CO_2 reduction application

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Experimental section

Materials and reagents. All chemicals and reagents were used as received without further purification. Methanol (MeOH), ethanol (EtOH), dichloromethane (DCM), trichloromethane ($CHCl_3$), *n*-hexane, and toluene were purchased from Caiyunfei Chemical Reagents (Tianjin, China). Triethylamine (Et_3N, 99.5%), sodium cyanoborohydride ($NaBH_3CN$, 95%), silver trifluoroacetate (CF_3CO_2Ag), copper powder, copper (II) trifluoroacetate hydrate ($Cu(CF_3CO_2)_2$), triphenylphosphine (PPh_3), and 3, 5-bis(trifluoromethyl)phenylacetylene (3, 5-$(CF_3)_2$PhCuCH) were purchased from Energy Chemical (Shanghai, China). Deionized water with a resistivity of 18.3 MΩ cm^{-1} was obtained using a Barnstead Nanopure water system.

Physical measurements and instrumentation. The surface chemical compositions and valence states were examined by X-ray photoelectron spectroscopy (XPS, Phi X-tool instrument). UV-visible absorption spectra of the clusters were recorded by a Shimadzu 2600 spectrophotometer. The data collection for the $Ag_{19}Cu_2(C{\equiv}CAr^F)_{12}(PPh_3)_6Cl_6$ nanoclusters was performed on an Agilent Technologies Super Nova single-crystal diffractometer using 100 Mo Kα radiation (λ= 0.71073Å), respectively. In the Olex2 graphical interface, SHELXT was used for structural solution and SHELXL for refinement. All non-hydrogen atoms were first subjected to isotropic refinement and then to anisotropic refinement. All hydrogen atoms of the ligand are placed at computational positions with fixed isotropic thermal parameters and are included in the final stage of the structure factor calculation for the full matrix least squares refinement.

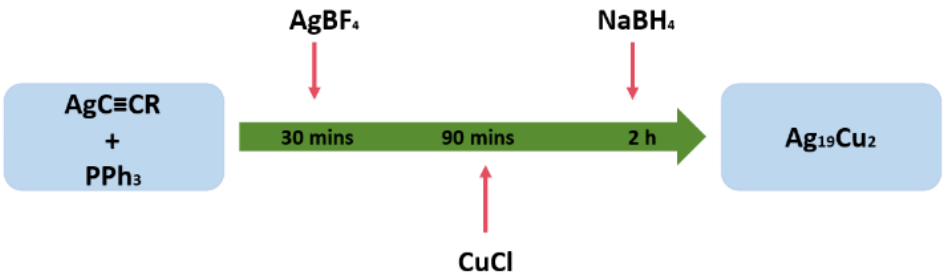
Synthesis of $Ag_{19}Cu_2(C{\equiv}CAr^F)_{12}(PPh_3)_6Cl_6$ nanoclusters. The $Ag_{19}Cu_2$ nanoclusters were synthesized by a direct reduction method from the mixed precursors (Scheme S1). Briefly, 60 mg of AgC≡CR and 30 mg of $AgBF_4$ were first co-dispersed in dichloromethane (CH_2Cl_2) for 30 mins, then 10 mg of CuCl was added, then the mixture was reduced using a borane tert-butylamine complex as the reducing agent in the presence of the PPh_3 ligand (60 mg) at 25 °C. After the reaction is completed, the organic layer is washed with deionized water, and then, *n*-hexane is diffused into the CH_2Cl_2 layer of the nanoclusters at 0 °C for 2h. The dark-red block-like single crystals (See Figure S1 for the microscope photo) suitable for the X-ray diffraction are obtained after about 15 days. The yield of $Ag_{19}Cu_2$ clusters is calculated as 12.6% (based on Cu). The CCDC number of the $Ag_{19}Cu_2(C{\equiv}CAr^F)_{12}(PPh_3)_6Cl_6$ cluster is 2366717.

Preparation of the $Ag_{19}Cu_2$/CNTs catalyst. In a typical trial, 2 mg of $Ag_{19}Cu_2$ and 1 mg of carbon nanotubes were co-dissolved in 0.5 mL of ethanol, and were sonicated for 30 mins to prepare a catalyst ink.

Electrochemical measurements. The eCO_2RR measurement was tested using a three-electrode system at the electrochemical workstation (CHI 660C, Shanghai). The gases are monitored by gas chromatography (GC, Hua ai 9560). To prepare the catalytic electrode, 666 μL of the ink and 30 μL of the nafion solution were dropwisely cast onto the gas diffusion carbon paper with an area of 2 cm * 0.5 cm, and the coating mass is calculated as 2 mg/cm^2. The working electrode was a gas diffusion carbon paper, the counter electrode was a platinum sheet, the reference electrode was an Ag/AgCl electrode, and the anion exchange membrane was used in the center to separate the anion and cation chambers. Carbon dioxide gas was introduced at a flow rate of 24 mL/min, and the cathode electrolyte was 1 M KOH (pH= 14).

The potentials in this study are converted into reversible hydrogen electrode (RHE) potentials according to the following equation:

$$E_{\mathrm{RHE}} = E_{\mathrm{Ag/AgCl}} + 0.0591\ \mathrm{pH} + 0.197$$



Scheme S1. The synthetic route for $Ag_{19}Cu_2$ NCs.

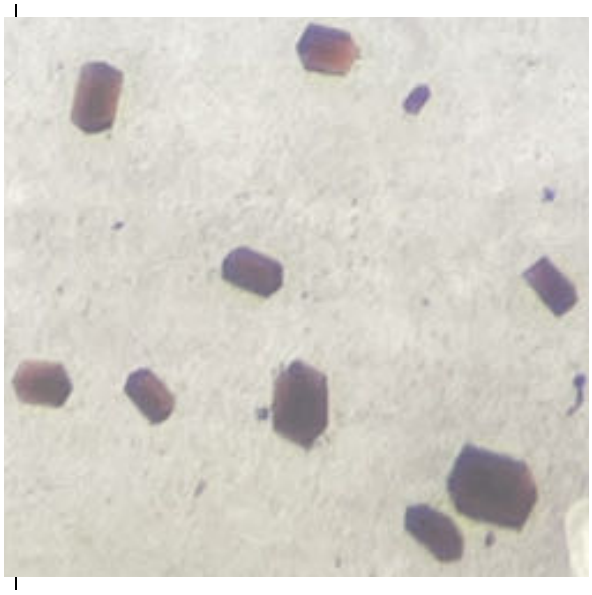


Figure S1. The image of $Ag_{19}Cu_2$ crystals under an optical microscope.

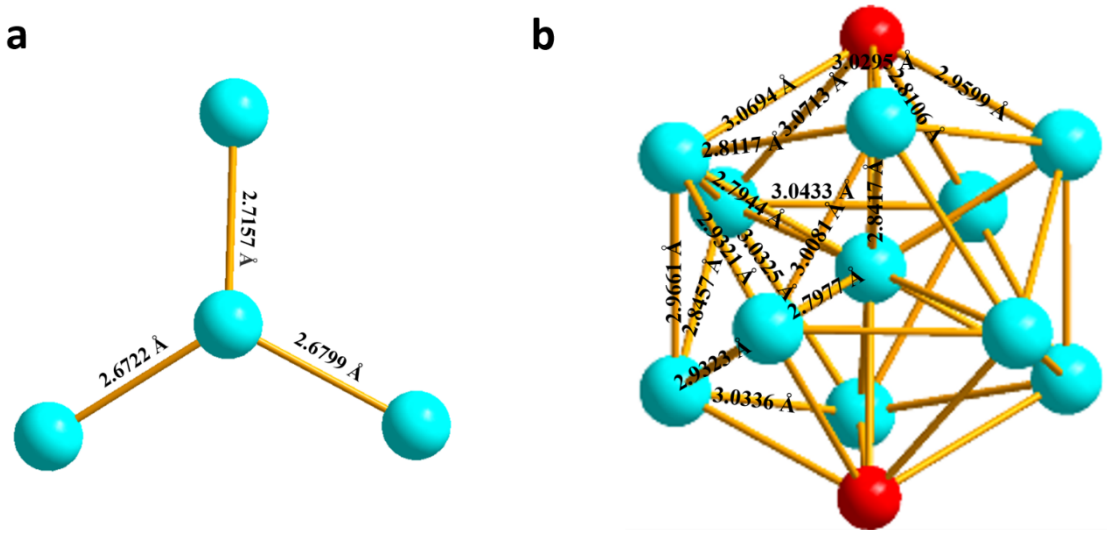


Figure S2. Metal bond length in (a) Ag_4 unit and (b) $Ag_{11}Cu_2$ unit. Color labels: Ag, blue; Cu, red; Cl, tan.

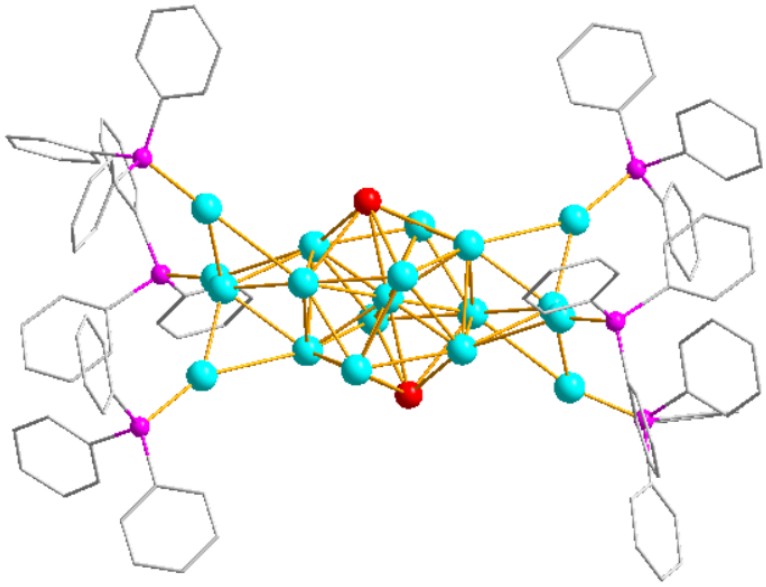


Figure S3. Coordination between the 6 PPh_3 ligands and Ag atoms in $Ag_{19}Cu_2$. Color code: Ag, blue; Cu, red; C, white; P, pink. All hydrogen atoms are omitted for clarity.

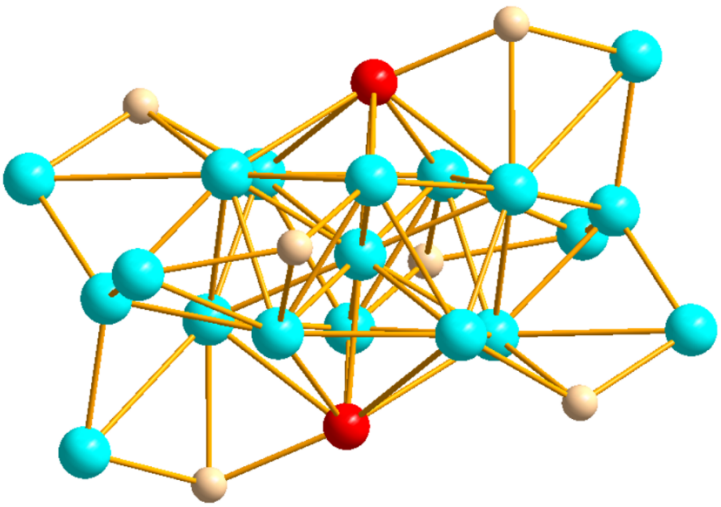


Figure S4. Coordination between the 6 Cl and Ag atoms in $Ag_{19}Cu_2$. Color code: Ag, blue; Cu, red; C, white; Cl, tan. All hydrogen atoms are omitted for clarity.

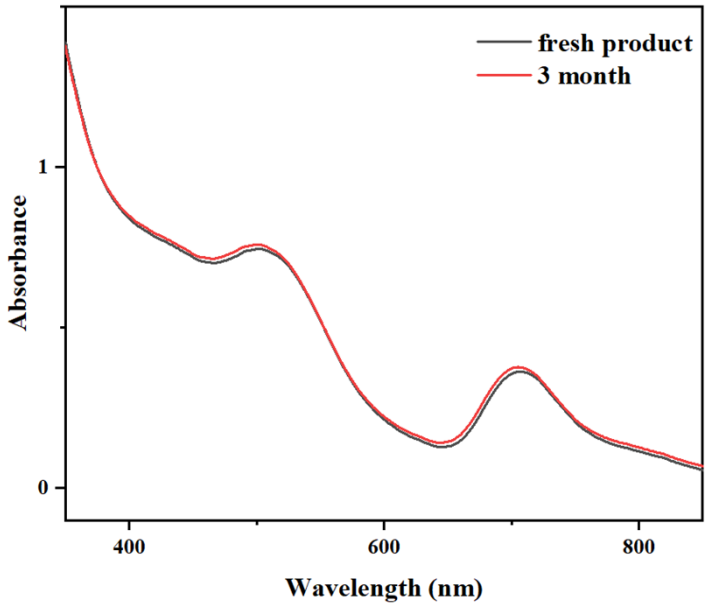


Figure S5. Absorption spectra of $Ag_{19}Cu_2$ clusters before and after 3 months.

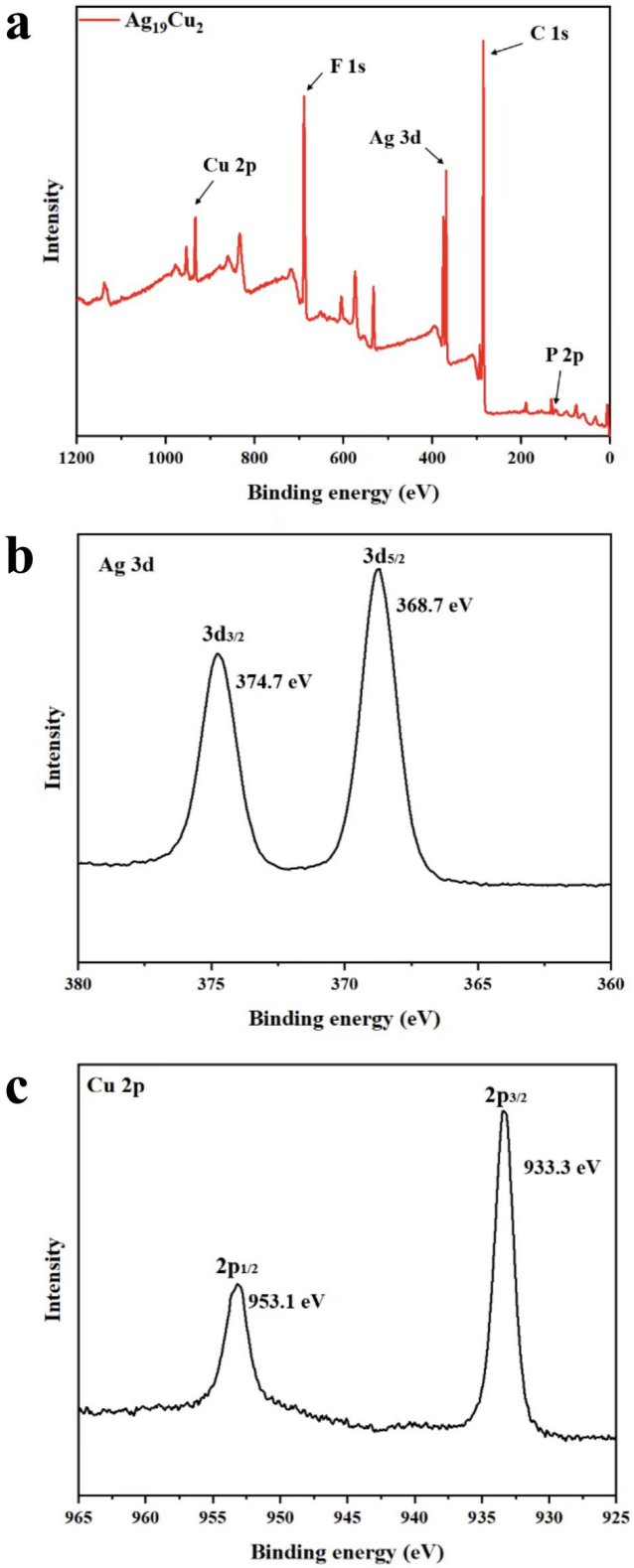


Figure S6. (a) XPS survey-scan spectra of the $Ag_{19}Cu_2$ nanoclusters, (b) High resolution XPS spectra of Ag3d, (c) Cu2p of the $Ag_{19}Cu_2$ nanoclusters.

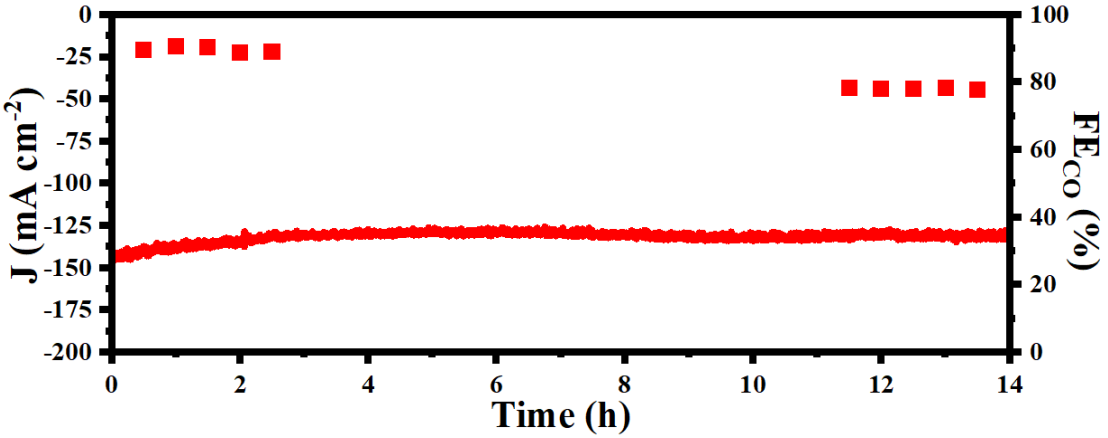


Figure S7. Long term stability test of the $Ag_{19}Cu_2$/CNTs catalyst in eCO_2RR.

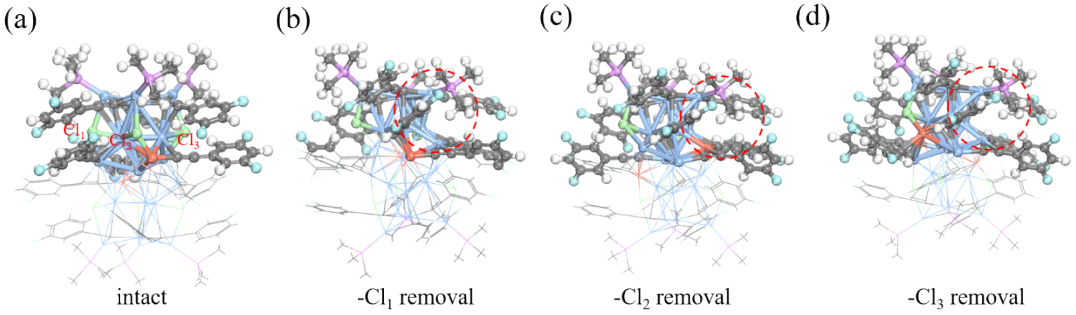


Figure S8. Schematic presentation of intact $Ag_{19}Cu_2$ nanoclusters (a) and $Ag_{19}Cu_2$ nanoclusters with different -Cl ligands removed respectively (b-d). Color legend: Ag, baby blue; Cu, dark orange; C, grey; Cl, light green; F, cyan; P, purple; H, white. For clarity, some of the ligands and metals are represented by line modes.

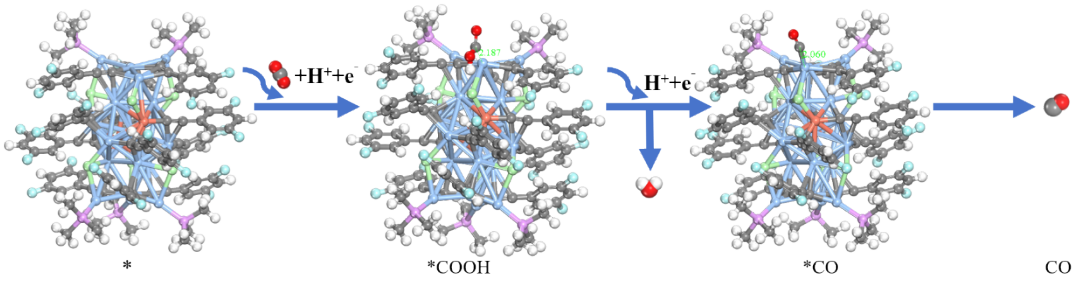


Figure S9. Schematic presentation of the electrocatalytic CO_2 reduction process on the $[Ag_{19}Cu_2(C{\equiv}CR)_{12}(P(CH_3)_3)_5Cl_6]^+$ cluster. Color legend: Ag, baby blue; Cu, dark orange; C, grey; Cl, light green; F, cyan; P, purple; H, white; O, red.

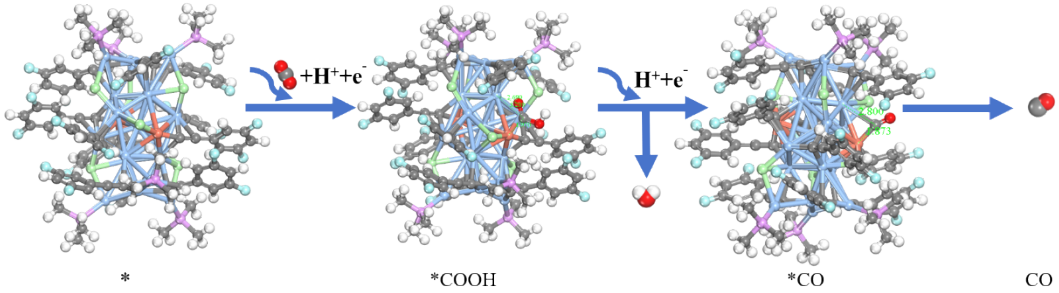


Figure S10. Schematic presentation of the electrocatalytic CO_2 reduction process on the $Ag_{19}Cu_2(C{\equiv}CR)_{11}(P(CH_3)_3)_6Cl_6^+$-(1) cluster. Color legend: Ag, baby blue; Cu, dark orange; C, grey; Cl, light green; F, cyan; P, purple; H, white; O, red.

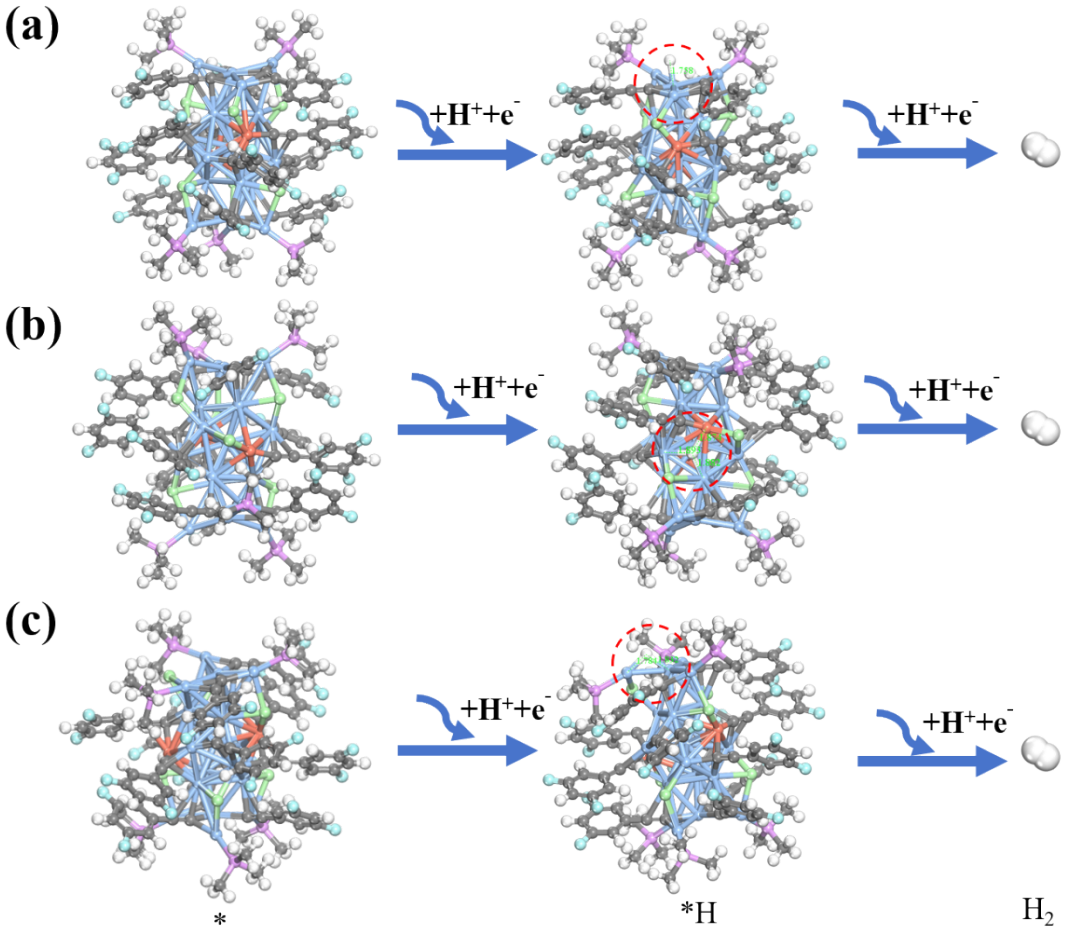


Figure S11. (a)-(c) Schematic presentation of the electrocatalytic hydrogen evolution process on the $[Ag_{19}Cu_2(C{\equiv}CR)_{12}(P(CH_3)_3)_5Cl_6]^+$, $[Ag_{19}Cu_2(C{\equiv}CR)_{11}(P(CH_3)_3)_6Cl_6]^+$-(1), $[Ag_{19}Cu_2(C{\equiv}CR)_{11}(P(CH_3)_3)_6Cl_6]^+$-(2) clusters respectively. Color legend: Ag, baby blue; Cu, dark orange; C, green; Cl, light green; F, cyan; P, purple; H, white.

Table S1. The structure parameters for $Ag_{19}Cu_2$.

Identification code	$Ag_{19}Cu_2(C{\equiv}CAr^F)_{12}(PPh_3)_6Cl_6$	
Empirical formula	$C_{232}\ H_{128}\ Ag_{19}\ C_{l6}\ Cu_2\ F_{72}\ P_6$	
Formula weight	6858.470	
Temperature/K	100	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 19.6392(2) Å	α = 67.042(1)°
	b = 19.8263(2) Å	β = 62.657(1)°
	c = 20.3821(2) Å	γ = 75.865(1)°
Volume	6470.59(10) $Å^3$	
Z	1	
Density (calculated)	1.760 g/cm^3	
Absorption coefficient	1.463mm^{-1}	
F(000)	3311	
Crystal size	0.2× 0.2× 0.06 mm^3	
Radiation	Mo K_α (λ = 0.71073)	
2θ range for data collection	2.3470 to 30.6000	
Index range	$-26 \le h \le 27$, $-25 \le k \le 28$, $-28 \le l \le 29$	
Reflections collected	200745	
Largest diff. peak/hole	3.393/-4.116e $Å^{-3}$	

Table S2. The detailed electronic energy (E_*), zero-point energy (E_{ZPE}), entropy corrections (TS), and free energy (G) of isolated molecule during electrochemical CO_2RR and HER.

Species	E_*	E_{ZPE}	TS	G
CO_2	-23.11	0.31	0.66	-23.36
CO	-14.81	0.13	0.61	-15.63
H_2	-6.76	0.27	0.40	-6.89