Supporting Information

Polymolybdate-Guided Assembly of a Thiacalix[4]arene-Protected Ag Nanocluster for Electrocatalytic CO₂ Reduction

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1. experimental section

Materials and Characterization. All reagents were purchased commercially and were not further purified when used. Powder X-ray diffraction (PXRD) analysis were performed on a Rigaku Mini Flex II diffractometer at a 2 θ range of 3–50° (5° min⁻¹) with CuK α radiation (λ =1.54056 Å). The solid-state UV/Vis spectra data of the cluster samples were obtained on UV-4000 spectrophotometer. Electrospray ionization mass spectrometry (ESI-MS) were performed on a Bruker Daltonik GmbH (Bruker, Germany). Thermogravimetric (TGA) patterns were recorded on a Mettler Toledo TGA/SDTA 851e analyzer in a N₂ atmosphere. FT-IR spectra using KBr pellets were taken on a Bruker Vertex 70 Spectrometer.

X-ray Crystal Structure Determination. Single crystal diffraction data was collected on Bruker D8 Venture diffractometer with liquid metal Ga K α radiation. The structures were solved using intrinsic phasing methods in ShelXT program and then refined by full-matrix least-squares on F2 using ShelXL-2014 in Olex² program. The hydrogen atoms were introduced at their geometric positions and refined as riding atom, and the positions of non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Due to the rotation disorder of tert-butyl groups, in all cases the ISOR, DELU and SIMU constraints were necessary to achieve convergence. The SQUEEZE operation was used to eliminate the contribution of disordered solvent molecule to the reflection intensity. A summary of the crystallographic data for the reported clusters is listed in Table S1. CCDC **2178163** contain the crystallographic data herein.

Synthesis for compound $[(Mo_6O_{22})@H_3Ag_{49}(MO_3)_9(MoO_4)(TC4A)_6(^{i}PrS)_{18}(CH_3CN)_2(H_2O)]$ {Ag₄₉Mo₁₆}: TC4A (8 mg, 0.011 mmol), ⁱPrSAg(5mg, 0.027 mmol), Silver acetate (8 mg, 0.048 mmol), (NH₄)_6Mo_7O_{24}·4H_2O (5 mg, 0.004 mmol) were added in a 15mL reaction vessel with 5 mL acetonitrile. 50 µL triethylamine were added dropwise. The resulting mixtures were sonicated for 5 min, then were transferred to a preheated oven at 80 °C for 3 days. Light brown colored crystals were obtained after cooling to 25 °C in a yield of ~65%.

Photocurrent responses. Photoelectrochemical tests were carried out on a CHI 660E electrochemical workstation. The platinum plate was used as the counter electrode, and the saturated calomel electrode was used as the reference electrode. 5 mg crystal samples were ultrasonically dispersed in 1 ml ethanol, and then the dispersion was dropped on ITO glass to prepare the working electrode. The electrodes were immersed in the 0.2 M Na_2SO_4 aqueous solution. A 300 W Xe lamp with UV cut-off filter was used as a full-wavelength light source.

Electrochemical Measurements. The electrochemical performance was tested on CHI 660E (Shanghai) electrochemical workstation. All electrochemical measurements were carried out in a gastight H-cell separated by Nafion 117 membrane between the two compartments. Each part has 60 ml 0.5 M KHCO₃ electrolyte and 40 mL headspace. The test system uses a standard three-electrode system, an Ag/AgCl electrode is used as the reference electrode, carbon rod is the counter electrode, and catalysts modified carbon cloth electrodes were used as the working electrode. 100 µL catalysts suspension (20 wt% loading on acetylene black) and 0.5wt% Nafion solution were dropped on carbon cloth (1×1 cm²). Before electrolysis measurement of CO₂ reduction, carbon dioxide was purged into the reaction system. Linear sweep voltammetry (LSV) was performed with a scan rate of 5 mV s⁻¹ from 0 V to -1.2 V vs. Ag/AgCl in Ar-saturated and CO₂-saturated conditions. CO₂ atmosphere has been maintained during the

testing process at rate of 20 mL/min. Gas phase products was analysis quantitatively using a Shimadzu GC-2014C Gas Chromatograph (Ar as gas carrier). ECSA measurement was estimated by performing cyclic voltammograms (CV) at different scan rates from 10 to 100 mV s⁻¹ under the potential window of -0.18 V to -0.06 V (vs. RHE) to measure the double-layer capacitance (C_{dl}). EIS measurement was carried out on the electrochemical analyzer in a frequency range from 100 kHz to 10 mHz at an overpotential of-0.80 V vs. RHE.



Figure S1. Pictures of fresh crystals of $\{Ag_{49}Mo_{16}\}$ separated from the solution.

Compound	{Ag ₄₉ Mo ₁₆ }
CCDC	2178163
Formula	$C_{298}H_{396}Ag_{49}Mo_{16}N_2O_{78}S_{42}$
T(K)	150
$F_{ m w}$	13421.33
Crystal system	triclinic
Space group	P-1
<i>a</i> , Å	26.048(3)
b, Å	27.800(3)
<i>c</i> , Å	35.912(4)
α/ °	82.533(5)
$eta / ^{ m o}$	83.882(6)
γ/°	76.420(5)
$V/Å^3$	24986(5)
Ζ	2
$ ho_{ m calcd}/ m gcm^{-3})$	1.784
$\mu/mm^{-1})$	13.734
<i>F</i> (000)	12938.0
Data/restraints/parameters	94341/1240/4467
Goof	0.963
$R_1/\mathrm{wR}_2(\mathrm{I} \geq 2\sigma(\mathrm{I}))$	0.1339/0.3417
R_1/wR_2 (all data)	0.1812/0.3799

2. Structure of Compounds



Figure S2. Three-dimensional packing structure of {Ag₄₉Mo₁₆}.

3. Powder X-ray diffraction



Figure S3. The XRD pattern of {Ag₄₉Mo₁₆}.

4. IR spectrum



Figure S4. IR spectrum of crystal sample of {Ag₄₉Mo₁₆}.

5. TG-Measurement



Figure S5. The TGA and DSC curves of {Ag₄₉Mo₁₆}.



6. XPS Analysis

Figure S6. (A) XPS survey of $\{Ag_{49}Mo_{16}\}$. (B) Ag 3d, (C) Mo 3d, and (D) S 2p high-resolution XPS spectra.

7. Energy Dispersive X-ray (EDX) Spectroscopic Analysis



Figure S7. The EDS pattern of {Ag₄₉Mo₁₆}.

8. Inductively coupled plasma (ICP) measurements of {Ag₄₉Mo₁₆}.

Table S1. The atom ratio of $\{Ag_{49}Mo_{16}\}$ nanoclusters calculated from inductively coupled plasma (ICP) measurements.

	Ag atom	Mo atom
ICP Experiment ratio of {Ag ₄₉ Mo ₁₆ }	73.7%	26.3%
Theoretical ratio of {Ag ₄₉ Mo ₁₆ }	75.4%	24.6%

9. Liquid UV-Vis absorption spectra of {Ag₄₉Mo₁₆}.



Figure S8. The liquid UV-Vis absorption spectra of {Ag₄₉Mo₁₆}.



Figure S9. Fragments identified in ESI-MS of $\{Ag_{49}Mo_{16}\}$ upon adding stronger base MeOK.

11. TEM images



Figure S10. TEM overview image of $\{Ag_{49}Mo_{16}\}$, scale bar: 50 nm (A), 20 nm (B), 10 nm (C) and 5 nm (D).

12. Solid-state absorption spectra



Figure S11. Solid-state absorption spectra of $({}^{i}PrSAg)_{n}$ and $\{Ag_{49}Mo_{16}\}$.

13. Photocurrent responses



Figure S12. Photocurrent responses of {Ag₄₉Mo₁₆} under 300W Xe light irradiation. **14. Electrocatalytic CO₂ reduction**



Figure S13. Cyclic voltammetry of $\{Ag_{49}Mo_{16}\}$ in CO₂ and Ar-saturated 0.1 M anhydrous acetronitrile solution of tetrabutyl ammonium bromide.



Figure S14. Gas chromatogram spectra of the CO and H_2 products signal measured in range of -0.6 V to -1.0 V vs. RHE from electrochemistry CO₂RR by using {Ag₄₉Mo₁₆} as electrocatalyst in CO₂ or Ar, respectively.



Figure S15. ¹H NMR spectra of liquid product after electrolysis using $\{Ag_{49}Mo_{16}\}$ as electrocatalyst in 0.5M KHCO₃ electrolyte.



Figure S16. FECO and FEH₂ values of $({}^{i}PrSAg)_{n}$ at different voltage in CO₂- saturated 0.5 M KHCO₃ electrolyte.



Figure S17. FECO and FEH₂ values of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ at different voltage in CO₂- saturated 0.5 M KHCO₃ electrolyte.



Figure S18. Tafel slopes of $(^{i}PrSAg)_{n}$ and $\{Ag_{49}Mo_{16}\}.$



Figure S19. Nyquist plots of electrocatalysts over the frequency ranging from 100 kHz to 10mHz at -0.9 V vs. RHE.





Figure S20. (A) The cyclic voltammograms (CVs) measurements with various scan rates for $\{Ag_{49}Mo_{16}\}$ in CO₂-saturated 0.5 M KHCO₃ electrolyte; (B) the capacitive current density $(J_a/2-J_c/2)$ as a function of scan rate.



Figure S21. Chronoamperometry curve of $\{Ag_{49}Mo_{16}\}$ in CO₂-saturated 0.5 M KHCO₃ electrolyte at a potential of -0.8V vs. RHE for 5 hours.



Figure S22. XRD pattern of {Ag₄₉Mo₁₆} after electrocatalysis experiment.



Figure S23. IR pattern of {Ag₄₉Mo₁₆} after electrocatalysis experiment.