Supplementary Information (SI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information for

Atomically precise Cu_{14} and Cu_{13} nanoclusters for oxygen evolution reaction: One additional Cu atom matters

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Experimental section

Materials and reagents

Methanol (CH_3OH), acetonitrile (CH_3CN), dichloromethane (CH_2Cl_2), *n*-hexane, and ethyl acetate were purchased from Zhiyuan Chemical Reagents (Tianjin, China). Trichloromethane ($CHCl_3$) and sodium borohydride ($NaBH_4$) were purchased from Kelong Chemical Reagents (Chengdu, China). Tetrakis(acetonitrile) copper(I) Tetrafluoroborate ($Cu(CH_3CN)_4BF_4$), 2-methyl-3-furanethiol (Fur-H) and triphenylphosphine (PPh_3) were bought from Energy Chemical (Shanghai, China). 1-Thionaphthol was purchased from Tokyo Chemical Industry (Japan). All chemicals and reagents were used as received without further purification. 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 (Japan). The single crystal data collection for the $[Cu_{14}(Fur)_3(PPh_3)_8H_{10}]^+$ nanoclusters (Cu_{14} NC) was performed on an Agilent Technologies Super Nova single-crystal diffractometer using 100 Cu K_α radiation (λ= 1.54184 Å). In the Olex 2 graphical interface, SHELXT was used to solve the structure and to refine. All non-hydrogen atoms were first refined isotropically followed by anisotropic refinement. All of the hydrogen atoms of the ligand are placed at computational positions with fixed isotropic thermal parameters and are included in the final stage of the calculation of the structure factors for the full matrix least squares refinement.

Synthesis of $[Cu_{14}(Fur)_3(PPh_3)_8H_{10}]^+$ nanocluster

In a typical trail, 100 mg of $Cu(CH_3CN)_4BF_4$ and 100 mg of PPh_3 were added into a 40 mL vial, dissolved with 4 mL of CH_3CN and 1 mL of $CHCl_3$, and the mixture was kept stirring for 5 mins. Then, 32 μL of Fur-H was added dropwisely. After stirring for 10 min, 100 mg of $NaBH_4$ dissolved in 5 mL of CH_3OH was added and the solution changed from light yellow into orange in 2 h of stirring. The reaction mixture was centrifuged, and the precipitate was collected, dried properly, dissolved in ethyl acetate and diffused by evaporation with hexane for more than 7 days to form yellow single crystals suitable for single crystal X-ray diffraction test at low temperature (Fig. S1). The CCDC number of the $[Cu_{14}(Fur)_3(PPh_3)_8H_{10}]^+$ cluster is 2417373.

Synthesis of $Cu_1(PPh_3)_2(OH)$ nanocluster

The synthesis was similar to that of Cu_{14} NC, except that no thiols were used and the amount of PPh_3 was increased to 164 mg to obtain clear crystals. Crystallization was carried out by diffusion of dichloromethane solution with hexane at low temperature. The CCDC number of the $Cu_1(PPh_3)_2(OH)$ is 2417860.

Synthesis of $[Cu_{13}(Nap)_3(PPh_3)_7H_{10}]^0$ nanocluster

Cu_{13} NC was synthesized by following the method in a previous report.[1]

Preparation of the Cu-based catalyst

The mixtures of nanoclusters and carbon black were first weighed, ensuring the same copper equivalent for two clusters. The mixtures were then dissolved separately in 0.5 mL of ethanol. Then it was sonicated for more than 30 mins to prepare the catalyst ink.

Electrochemical measurements

The electrocatalytic tests are carried out on a CHI750 electrochemical workstation coupled to a conventional three-electrode system. In the 1 M KOH aqueous solution, a platinum sheet electrode holder with carbon cloth clamped onto it was used as the working electrode, while a carbon rod and a Hg/HgO electrode were used as the counter and reference electrodes, respectively. Linear sweep voltammetry (LSV) curves were obtained at a rate of 5 mV s^{-1} with 90% iR compensation.

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

$$E_{\mathrm{RHE}} = E_{\mathrm{Hg/HgO}} + 0.0591{*}\mathrm{pH} + 0.098$$

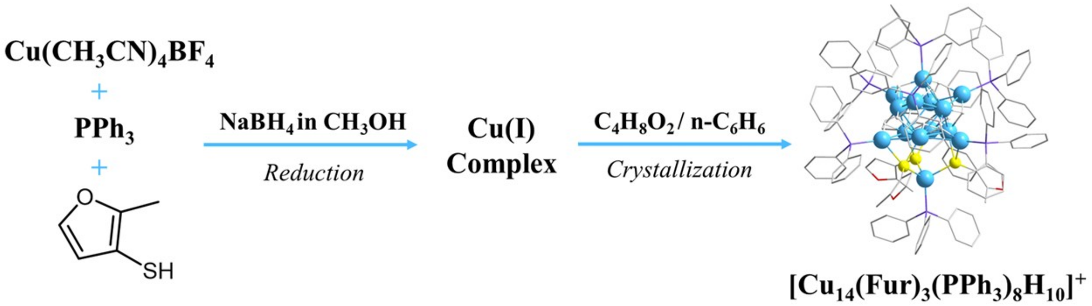
Computational details

All spin-polarized density functional theory (DFT) calculations were carried out by Vienna ab initio simulation package (VASP5.4.4)[2]. The Cu_{14} and Cu_{13} NCs were put in a cubic box (24 Å × 24Å × 24 Å), and their structures were optimized. The generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof (PBE) functional is adopted to handle the exchange-correlation energy[3]. The wave functions of all the computations were extended by a plane-wave cutoff energy of 400 eV and the projector augmented-wave (PAW) method[4] was applied to describe the ion-electron interactions. The Γ point was used to sample the Brillouin zone, and the convergence criteria for energy and force was set as 10^{-4} eV and -0.05 eV/ Å, respectively. The empirical density functional dispersion (DFT-D3) method[5] was utilized to account for the non-negligible van der Walls interactions between ligands.

Based on the computational hydrogen electrode (CHE) model[6], the change of Gibbs free energy (ΔG) for each elementary step of the OER can be calculated as follows:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S$$

where ΔE donate the change of the total energy. ΔE_{ZPE}, ΔS are the zero-point energy difference and entropy difference at T=298.15K. For the adsorbed intermediates, only the vibrational entropy calculated from the vibrational frequencies is considered.



Scheme S1. The synthetic route for Cu_{14} NC (blue, Cu; yellow, S; dark purple, P; red, O; grey, C; white, H).

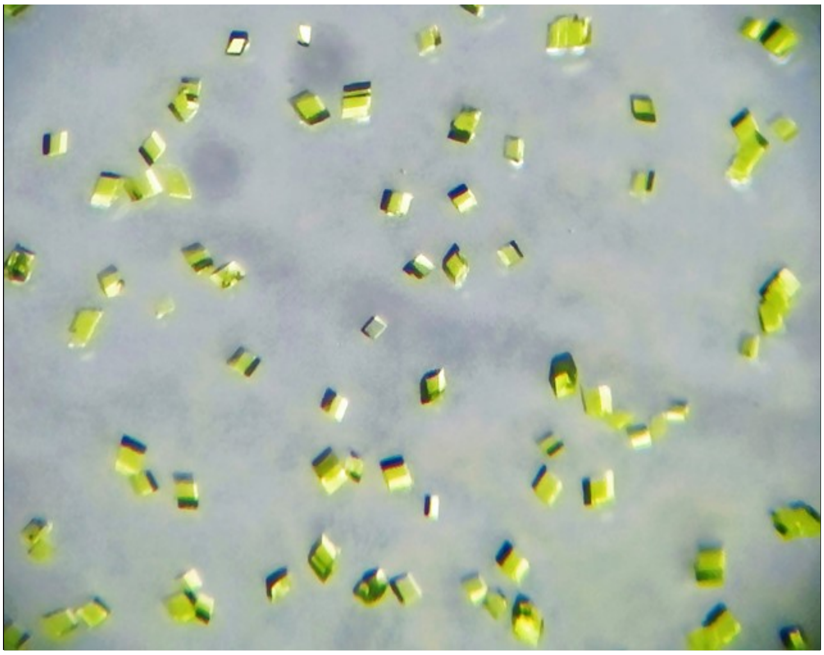


Fig. S1 The typical image of Cu_{14} crystals under an optical microscope.

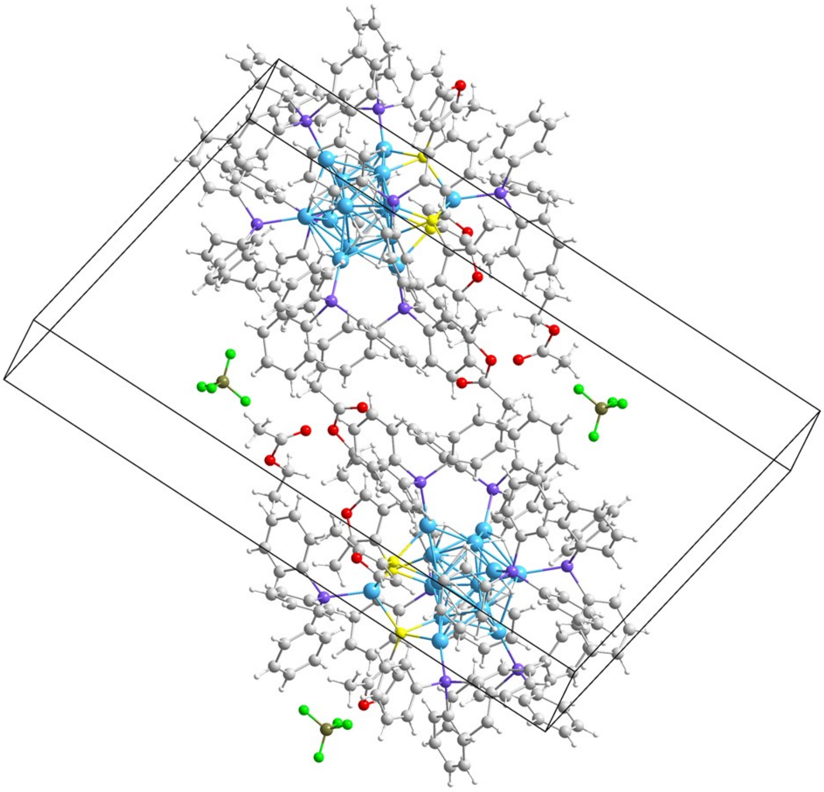


Fig. S2 Unit cell diagram of Cu_{14} (blue, Cu; yellow, S; dark purple, P; red, O; grey, C; white, H; dark green, B; light green, F).

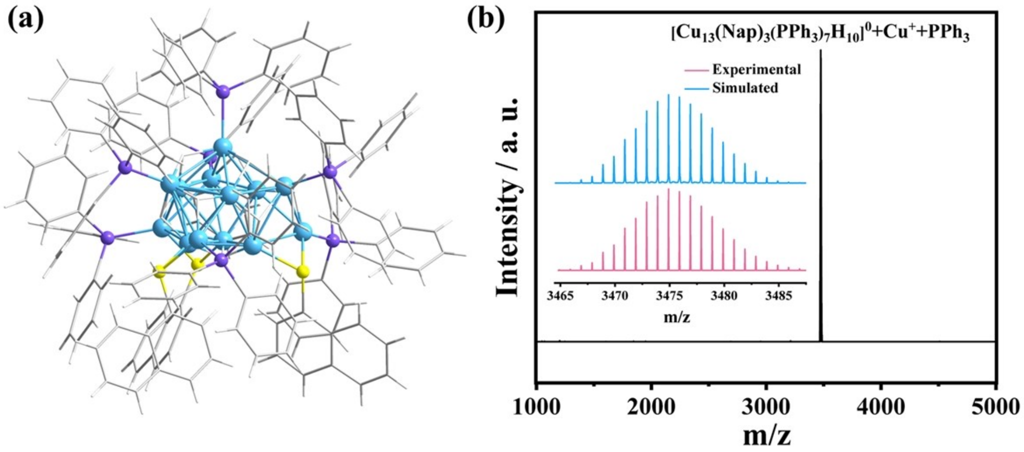


Fig. S3 (a) The total molecular structure of Cu_{13} NC.[1] (blue, Cu; yellow, S; dark purple, P; grey, C; white, H). (b) EIS-MS spectra for $[Cu_{13}(Nap)_3(PPh_3)_7H_{10}]^0$+$Cu^+$+$PPh_3$ in positive ion mode. Inset: isotopic experimental (blue) and simulated (pink) distribution pattern of $[Cu_{13}(Nap)_3(PPh_3)_7H_{10}]^0$.

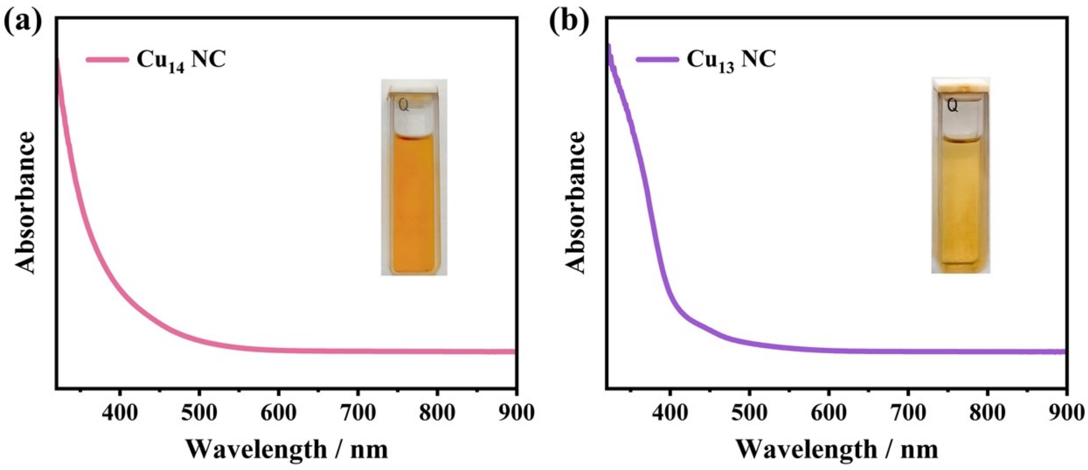


Fig. S4 UV-Vis absorption spectra of (a) Cu_{14} and (b) Cu_{13}; inset: photographs of Cu_{14} and Cu_{13} dissolved in CH_2Cl_2.

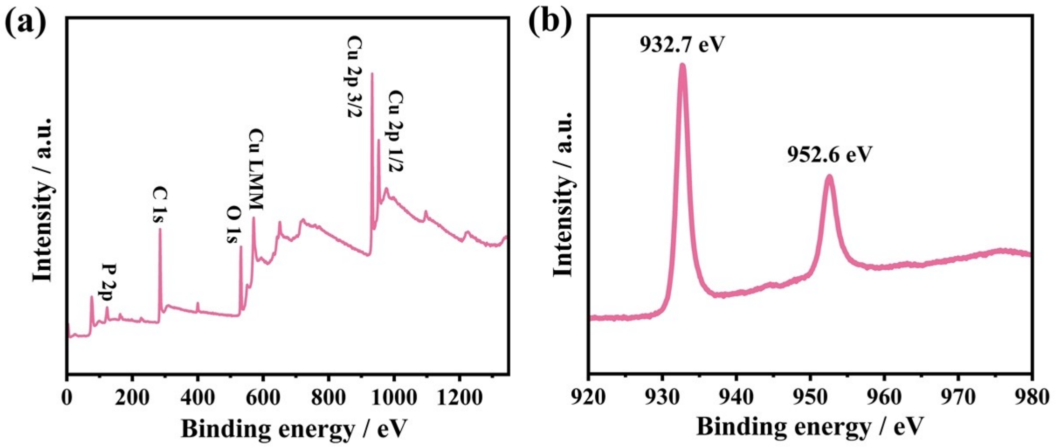


Fig. S5 (a) The X-ray photoelectron survey-scan spectrum of Cu_{14}; (b) The Cu 2p high-resolution XPS spectrum of Cu_{14}.

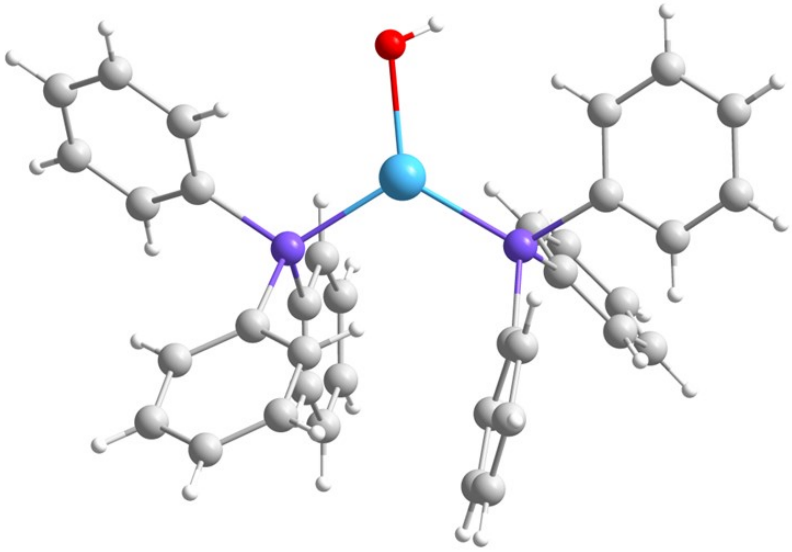


Fig. S6 The molecular structure of $Cu_1(PPh_3)_2(OH)$ (blue, Cu; dark purple, P; red, O; grey, C; white, H).

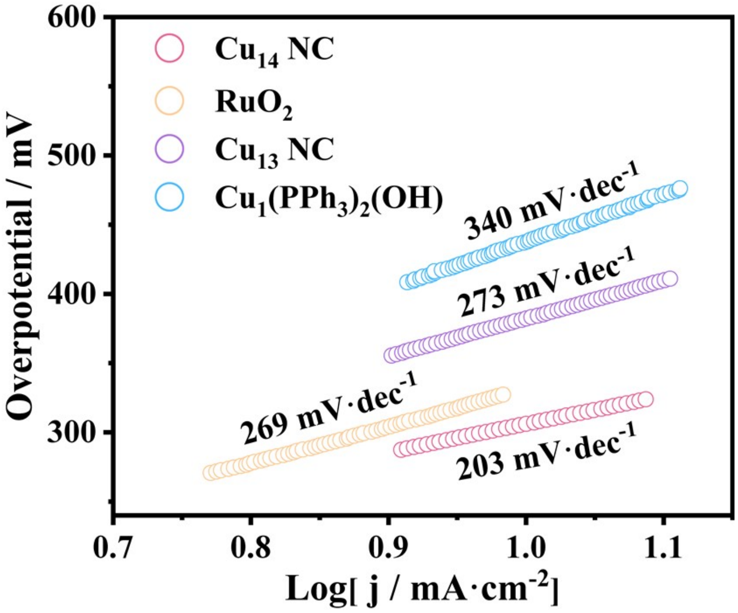


Fig. S7 The Tafel plots of Cu_{14} NC, Cu_{13} NC, RuO_2 and $Cu_1(PPh_3)_2(OH)$. The calculated Tafel slope values are marked.

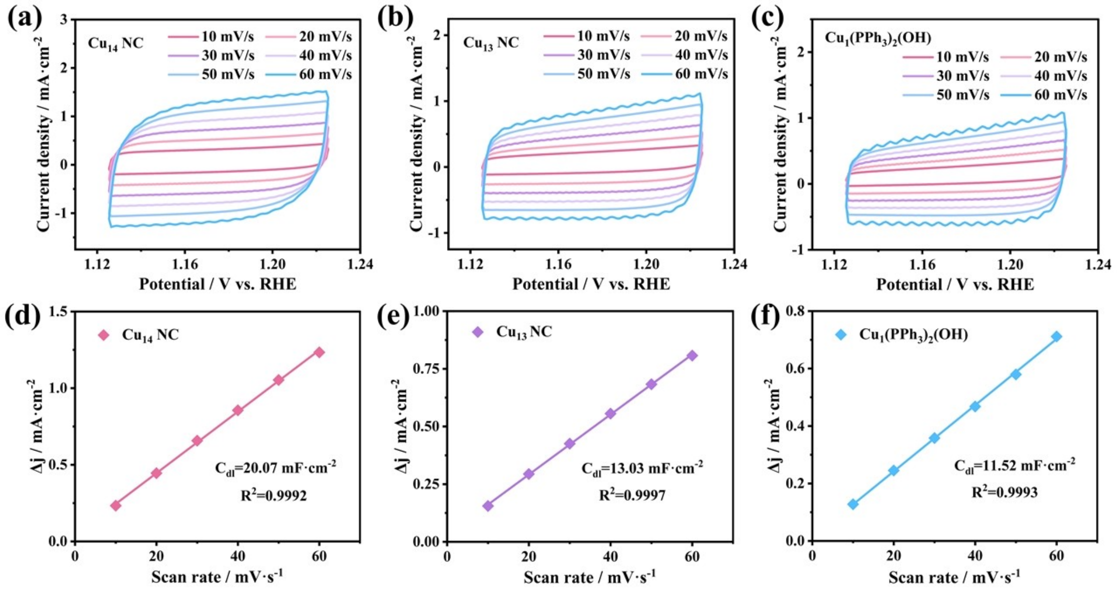
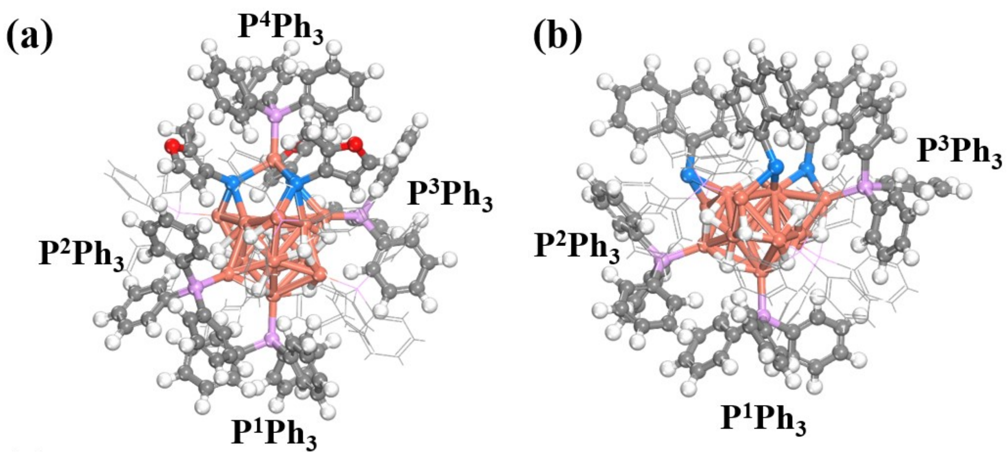


Fig. S8 (a-c) CV curves of different Cu-based metal catalysts measured in a non-Faradaic region of the voltammograms at scan rates of 10, 20, 30, 40, 50 and 60 mV s^{-1} in 1 M KOH and (d-f) corresponding linear fitting curves of current density vs. scan rate.



(c)

species the removed ligand	Cu_{14}	Cu_{13}
P^1Ph_3	-1869.59 eV	-1784.71 eV
P^2Ph_3	-1869.56 eV	-1784.53 eV
P^3Ph_3	-1869.69 eV	-1784.67 eV
P^4Ph_3	-1870.11 eV	

Fig. S9 The different coordination environments of -PPh_3 ligands in (a) Cu_{14} and (b) Cu_{13} NCs. For clarity, partial -PPh_3 ligands are represented by line modes. (c) The energy of Cu_{14} and Cu_{13} NCs after the removal of a -PPh_3 ligand. Colour legend: Cu, dark orange; C, grey; S, blue; P, purple; H, white; O, red.

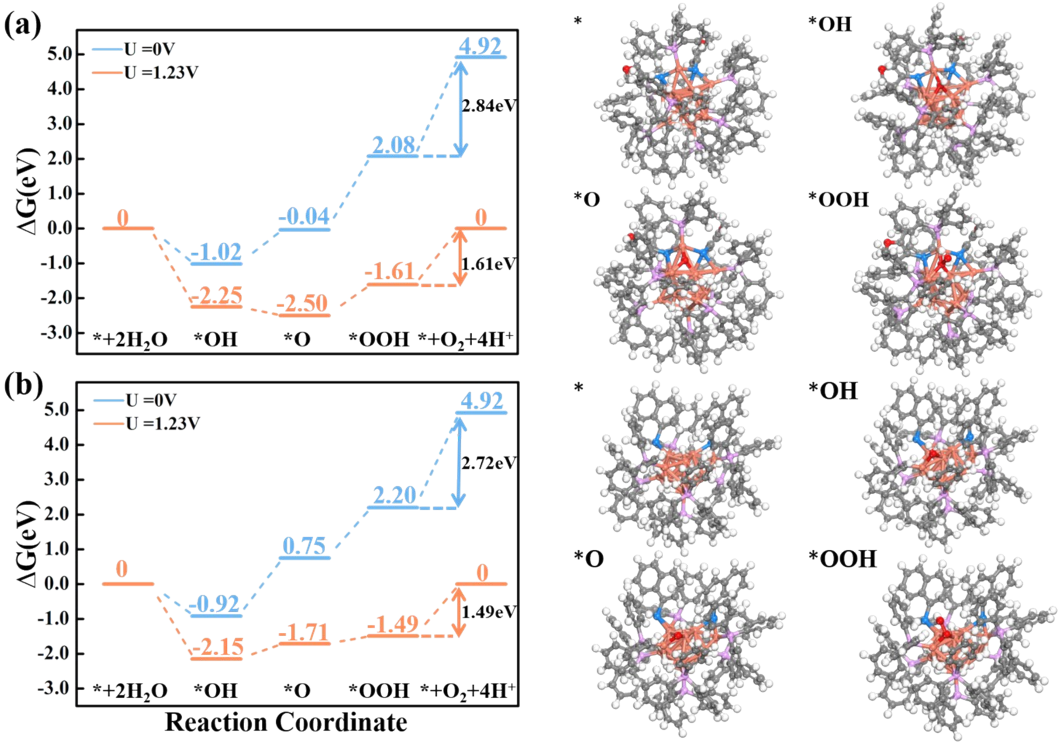


Fig. S10 The free energy diagrams (ΔG) for O_2 evolution and corresponding absorption structures of (a) Cu_{14} and (b) Cu_{13} NCs after removal of a -SR ligand at U = 0 V and U = 1.23V. Colour legend: Cu, dark orange; C, grey; S, blue; P, purple; H, white; O, red.

Table S1. The structure parameters for Cu_{14}.

Identification code	$[Cu_{14}(C_5H_5OS)_3(PPh_3)_8H_{10}]^+$	
Empirical formula	$Cu_{14}C_{167}H_{161}BF_4O_7P_8S_3$	
Formula weight	3600.260	
Temperature/K	100.00(11)	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 16.80840(10) Å	α = 97.8660(10)°
	b = 17.00600(10) Å	β = 95.7900(10)°
	c = 29.8137(2) Å	γ = 95.2100(10)°
Volume	8351.35(9) $Å^3$	
Z	2	
Density (calculated)	1.432 g cm^{-3}	
Absorption coefficient	3.396 mm^{-1}	
F(000)	3668	
Crystal size	0.12× 0.1× 0.08 mm^3	
Radiation	Cu K_α (λ = 1.54184)	
2θ range for data collection	5.276 to 146.746	
Index ranges	$-20 \leq h \leq 20$, $-20 \leq k \leq 21$, $-36 \leq l \leq 36$	
Reflections collected	280592	
Independent reflections	32539[R(int)=0.0813, R(sigma)=0.0437]	
Data/restraints/parameters	32539 / 0 / 1883	
Goodness-of-fit on F^2	1.061	
Final R indexes [$I \geq 2\sigma(I)$]	R_1= 0.0458, wR_2=0.1074	
Final R indexes (all data)	R_1= 0.0621, wR_2= 0.1141	
Largest diff. peak/hole	1.357 / -0.653 e $Å^{-3}$	

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