Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

An hourglass-shaped nickel-based polyoxometalate crystalline material as a highly-efficient bifunctional electrocatalyst for the oxygen evolution reaction and detection of H_2O_2

Yajie Li [ab], Na Zhu [ab], Zhixuan Su [ab], Xiaoli Hu[*a,b], Zhiyu Dou[*a], ZhongminSu[*a,b,c]

[a]School of Chemistry and Environmental Engineering, Changchun University of Science and Technology, Changchun, 130022, China.

[b]Jilin Provincial Science and Technology Innovation Center of Optical Materials and Chemistry, Changchun, 130022, China.

[c]State Key Laboratory of Supramolecular Structure and Materials, Institute of Theoretical Chemistry, College of Chemistry, Jilin University, Changchun, 130021, China.

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Table S3 Bond Angles for CUST-576.

EXPERIMENTAL SECTION

Materials

All chemicals used were commercially obtained and used without any additional purification. Reagents: $Na_2MoO_4{\cdot}2H_2O$, $NiCl_2{\cdot}6H_2O$, 1,3,5-Tri(1H-imidazol-1-yl)benzene (timb), NaOH, Carbon black(AB), Methanol(CH_3OH), Deionized water, H_3PO_4 (85%), Isopropanol (IPA) and 5 w% Nafion solution.

Synthesis of CUST-576 and CUST-576(Ni_0)

$Na_2MoO_4{\cdot}2H_2O$ (0.436 g, 1 mmol), $NiCl_2{\cdot}6H_2O$ (0.153 g, 0.65 mmol), timb (0.07 g, 0.2 mmol), and H_3PO_4 (0.1 mL) were accurately weighed, and added deionized water (5 mL), and CH_3OH (1 mL) at room temperature and stirred for 1h. The pH of the solution was then adjusted to 1.5 using 1 M NaOH, and the mixed solution was transferred to a 15 mL Teflon-lined autoclave and heated at 180 °C for 3 days in a constant-temperature blast dryer and then lowered to room temperature at 10 °C/h. After the solution was washed and dried with deionized water, orange block crystrals of CUST-576 were isolated. The optical microscopic images of CUST-576 was shown in **Fig.S18a†**. Anal. Found: C, 11.27; H, 1.0; N, 5.26.

The synthesis process of CUST-576(Ni_0) was similar to that of CUST-576, except that not add $NiCl_2{\cdot}6H_2O$. After the solution was washed and dried with deionized water, reddish-brown crystrals of CUST-576(Ni_0) were isolated. The optical microscopic image of CUST-576(Ni_0) was shown in **Fig.S18b†**.

There are some activation processes during our synthesis of CUST-576. The dissolution of the metal-oxygen clusters and ligands is further accelerated by adjusting the pH of the solution (flocculent precipitation occurs if the pH is too high or too low) and heating it up to a temperature of 180 °C (the orange-red color with a fair shape but very small grains is obtained at temperatures of 160 °C and 170 °C) to promote the assembly of metal-oxygen clusters with the ligands. The metal-oxygen clusters and the ligands are crystallized in the process of programmed cooling thus obtaining the target material.

Preparation of working electrode

The inclusion of CUST-576 with carbon black was conducted by grinding 10 mg of CUST-576 crystals with carbon black.𝒆𝒇The mass ratios employed were 1:1, 1:2, 1:4, 2:1, and 4:1 for CUST-576 to carbon black, respectively. Subsequently, the resulting ground samples were dispersed in a 0.2 mL solution of containing 5% Nafion solution. &10 mg of crystals were milled with carbon black in mass ratio of 1:2, and the milled samples were dispersed into 0.4 mL of 5% Nafion solution, the dispersion was subjected to sonication for efficient mixing. Then, 5 µL of the resulting ink was carefully dripped onto glassy carbon electrodes. Finally, the electrodes with the ink deposit were left to dry under ambient air conditions and dried to produce a working electrode with loads of 0.28 and 0.78 mg·cm^{-2}, respectively.

Instrumentation and characterization

Single-crystal X-diffraction data for CUST-576 were collected by using a Bruker APEX II diffractometer with Mo Kα radiation (λ = 0.71073 Å) at the temperature of 298(2) K. The structure was analyzed using the SHELXL-14 software and refined using the weighted matrix least squares method. Crystal data and structural refinement for CUST-576 are listed in **Table S1**. The partial bond lengths and angles of CUST-576 are listed in **Tables S2 -S3**. The CCDC code for CUST-576 is 2258244.

Fourier Transform Infrared (FTIR) spectra were analyzed in the wavelength range of 4000 - 400 cm^{-1} using a Nicolet 380 FTIR spectrophotometer. Thermogravimetric analysis (TGA) was performed using a DTG 60AH instrument, with a heating temperature of 30-800 °C and a heating rate of 10 °C min^{-1}. Powder X-ray diffraction (PXRD) patterns were analyzed on a Rigaku D-max 2550 instrument using Cu Kα (λ = 1.5406 Å) radiation. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo ESCALAB 250 instrument. The samples were characterized morphologically and analyzed by energy spectrum using Scanning Electron Microscopy (SU8000).

Electrochemical measurements

Electrochemical measurements were conducted at ambient temperature (25°C) employing a conventional three-electrode system. The synthesized catalyst material was used as the working electrode; the Hg/HgO and graphite rod were used as the reference electrode and the counter electrode, respectively. Cyclic voltammetry (CV),

impedance (AC), linear scanning voltammetry (LSV), and stability (I-T) tests were performed on the CHI760E workstation.

All the potentials measured against the SCE electrode were converted to potentials versus the reversible hydrogen electrode (RHE) according to the equation $E_{(RHE)} = E_{(vs.\ SCE)} + 0.098V+0.059pH$. The Tafel slope is obtained by fitting the linear region of the Tafel curve according to the Tafel equation ($\eta = a + b\log(j)$). The long-term stability was measured by using a chronoamperometric method and a multistep chronoamperometric method. The long-term chronoamperometric measurement was carried out at a given constant potential. All of the electrochemical data were offered without iR correction.

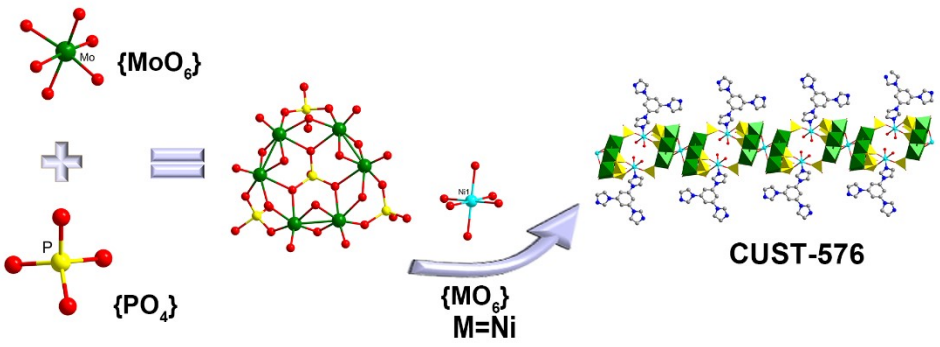

Fig. S1 Assembly process of **CUST-576**.

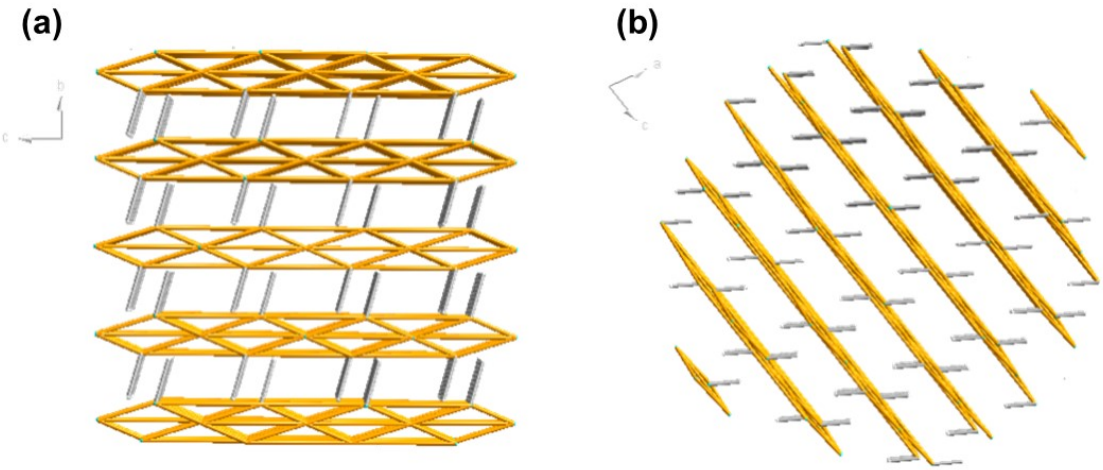

Fig. S2 The Topographies of CUST-576 in 1-D chain-like structure.

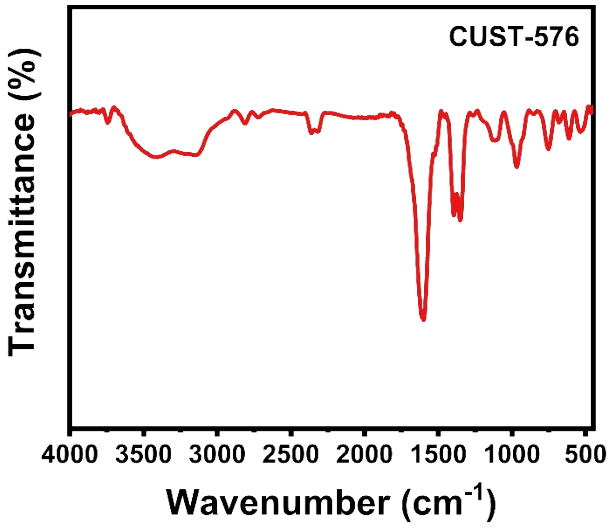

Fig. S3 The IR spectrum of **CUST-576**.

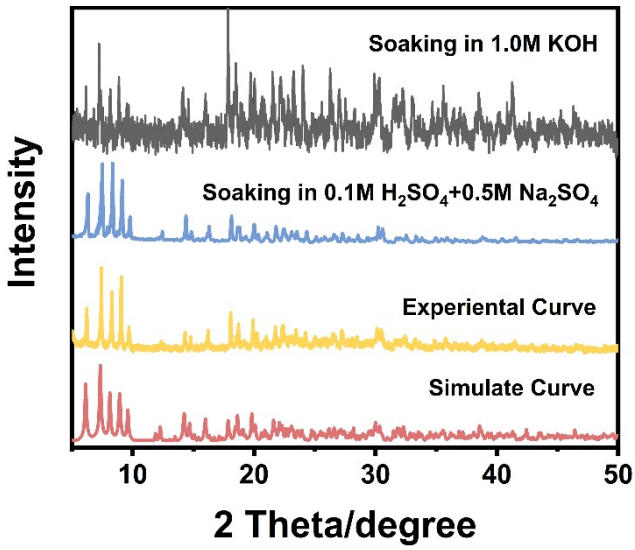

Fig. S4 Powder X-ray diffraction patterns of CUST-576.

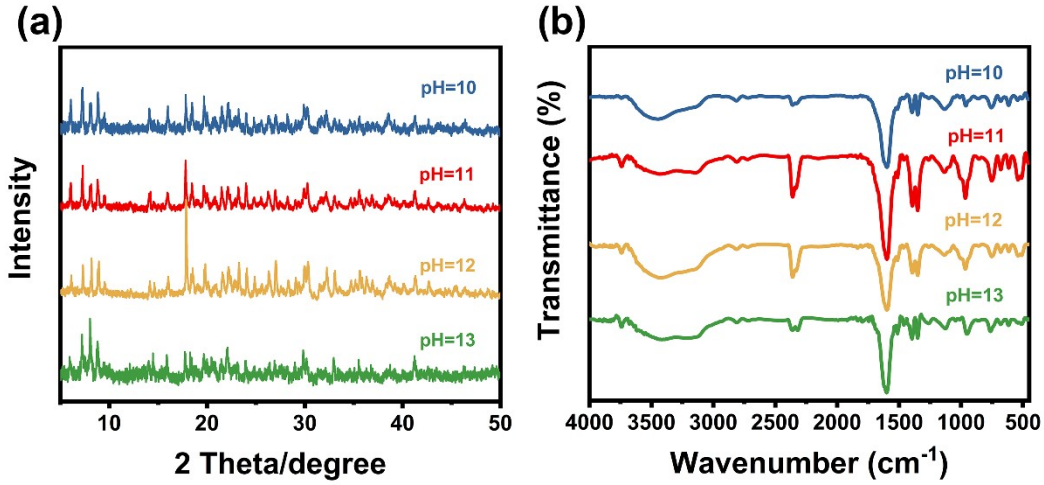

Fig. S5 (a) XRD and (b) FTIR spectra of CUST-576 in different pH aqueous solutions(pH=10-13).

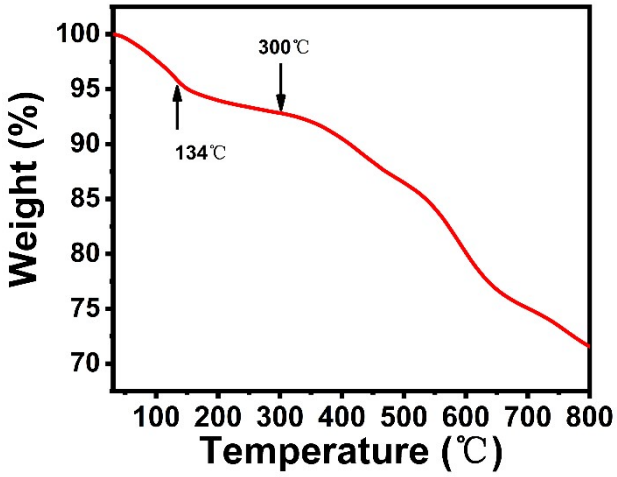

Fig. S6 The TGA curves of CUST-576.

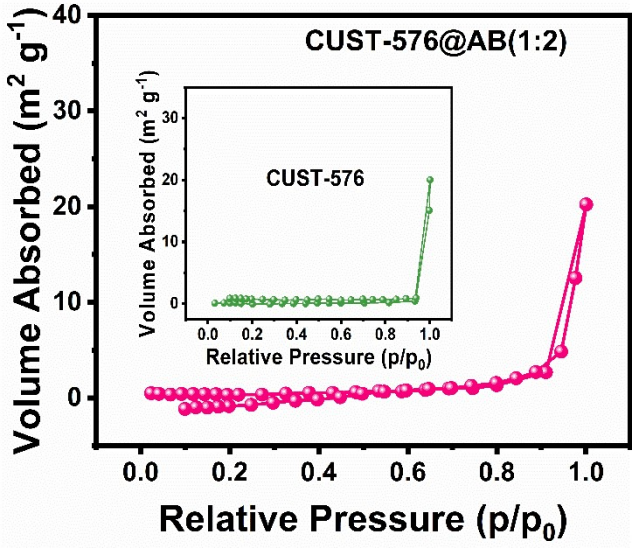

Fig. S7 N_2 adsorption isotherms of CUST-576 and CUST-576@AB (1:2) hybrids at 77 K.

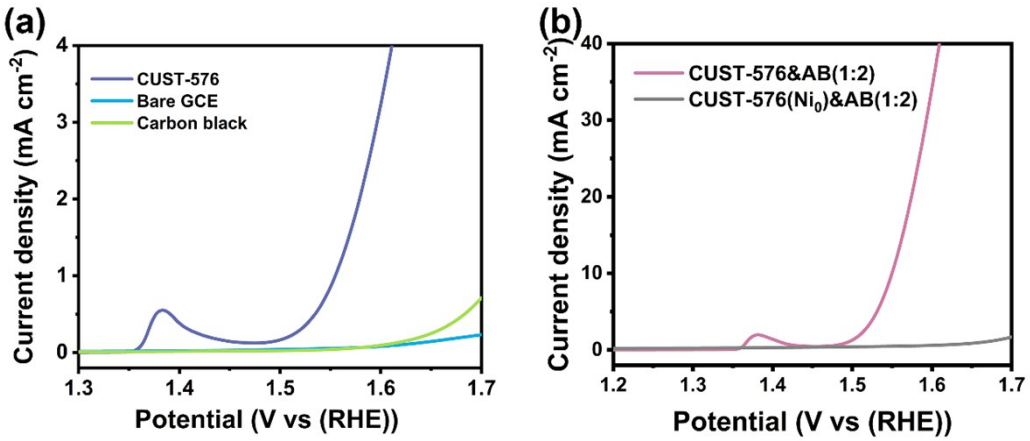

Fig. S8 (a) Polarization curve of CUST-576, Bare GCE and Carbon black in 1M KOH solution, (b) Polarization curve of CUST-576&AB and CUST-576(Ni_0)&AB.

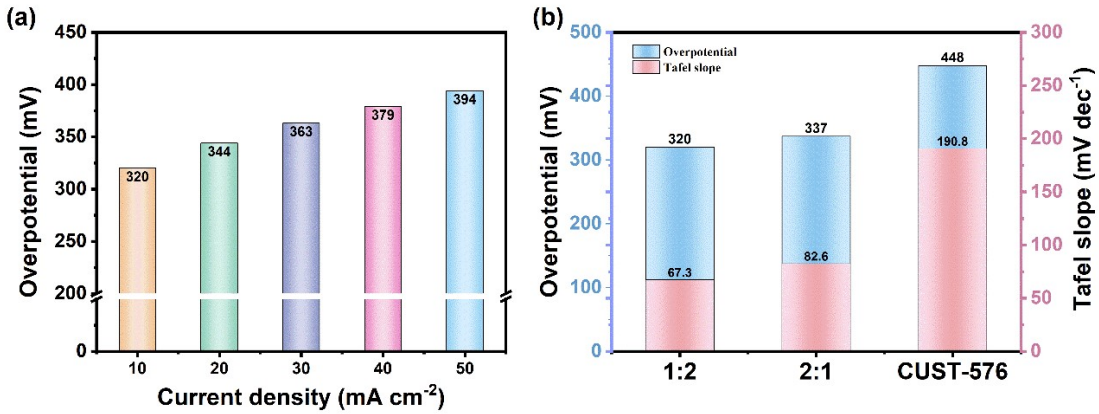

Fig. S9 (a) Comparison of Overpotential and Tafel slope in CUST-576, CUST-576&AB (1:2、2:1).

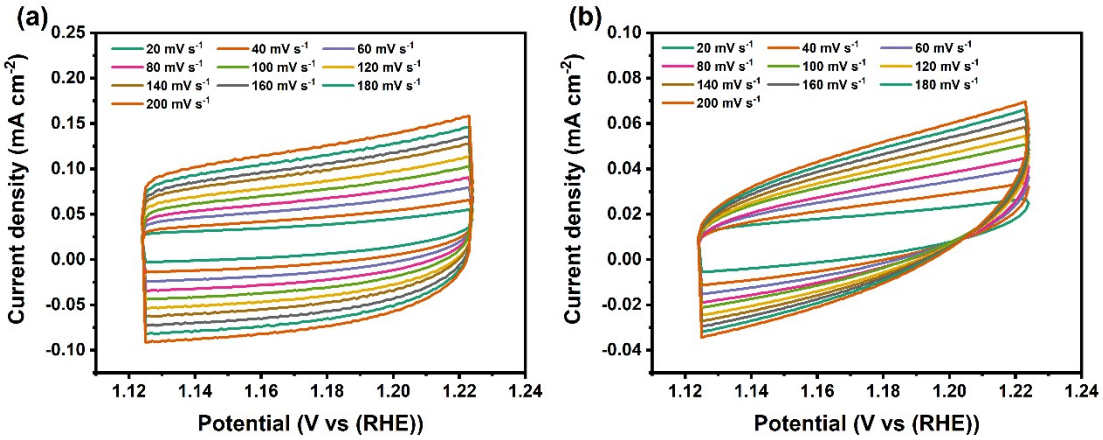

Fig. S10 (a) CV curve of CUST-576&AB (1:2) in 1M KOH (20-200mV s^{-1}), (b) CV curve of CUST-576 in 1M KOH (20-200mV s^{-1}).

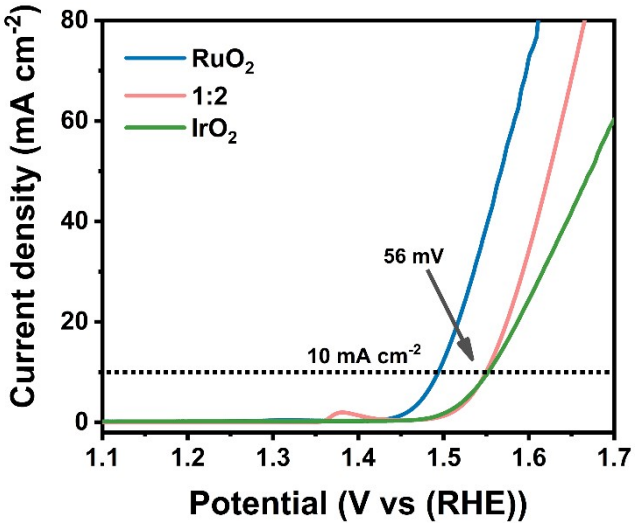

Fig. S11 (a) CV curve of CUST-576&AB (1:2), RuO_2, and IrO_2 in 1M KOH.

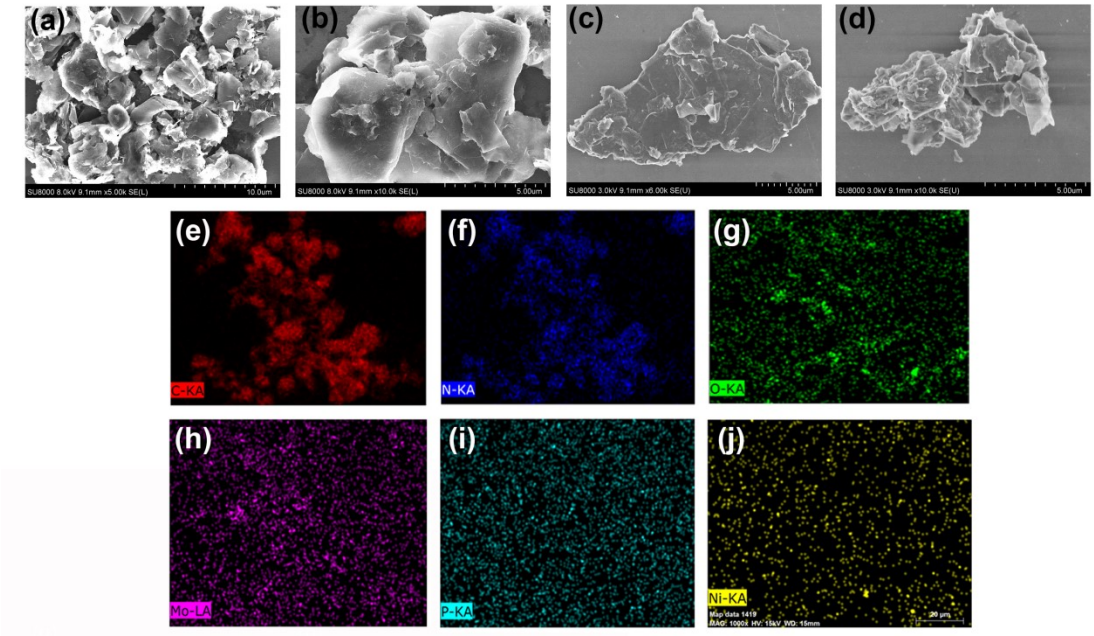

Fig. S12 SEM image of CUST-576&AB**:** (a-b) after OER and (c-d) after the long-term stability, EDX elemental mapping images of CUST-576&AB after OER (e-j).

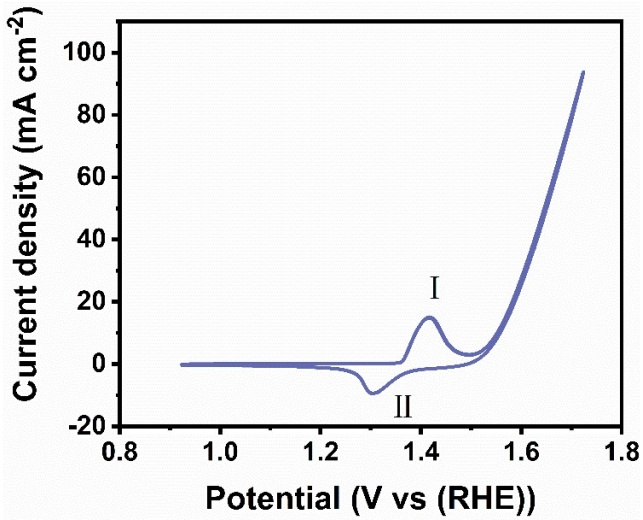

Fig. S13 Cyclic voltammetry curve of CUST-576&AB in 1.0 M KOH.

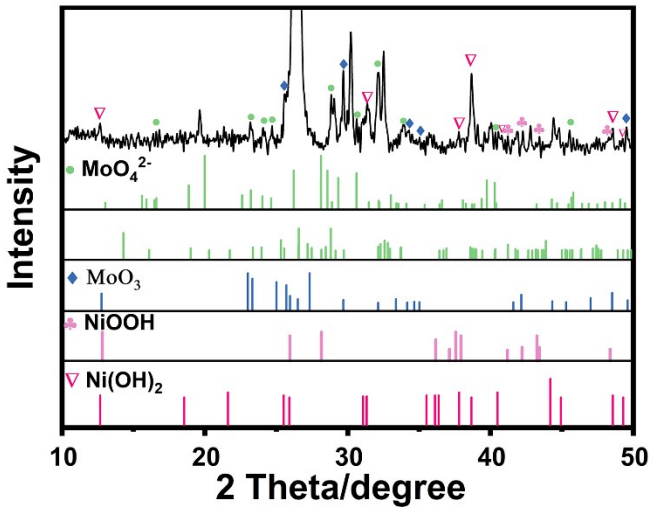

Fig. S14 PXRD pattern of CUST-576&AB after OER.

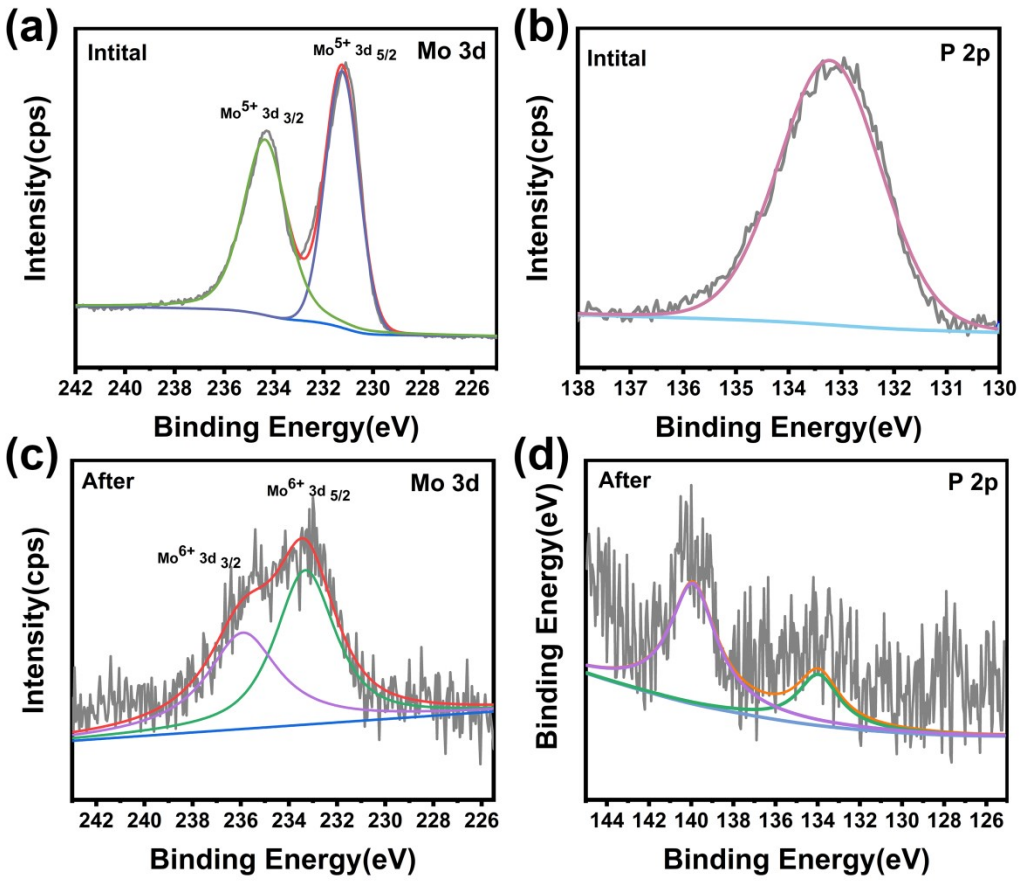

Fig. S15 XPS image of CUST-576 and CUST-576&AB. Initial: (a) Mo 3d, (b) P 2p. After:(c) Mo 3d, (d) P 2p. The dotted curve was used to demonstrate the experimental data, while the solid line was used to illustrate the fitting results.

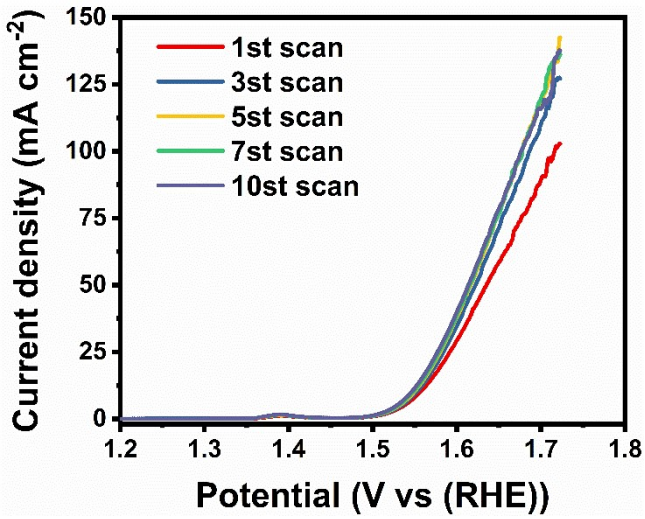

Fig. S16 The first-ten-cycle LSV curves in 1 M KOH after OER.

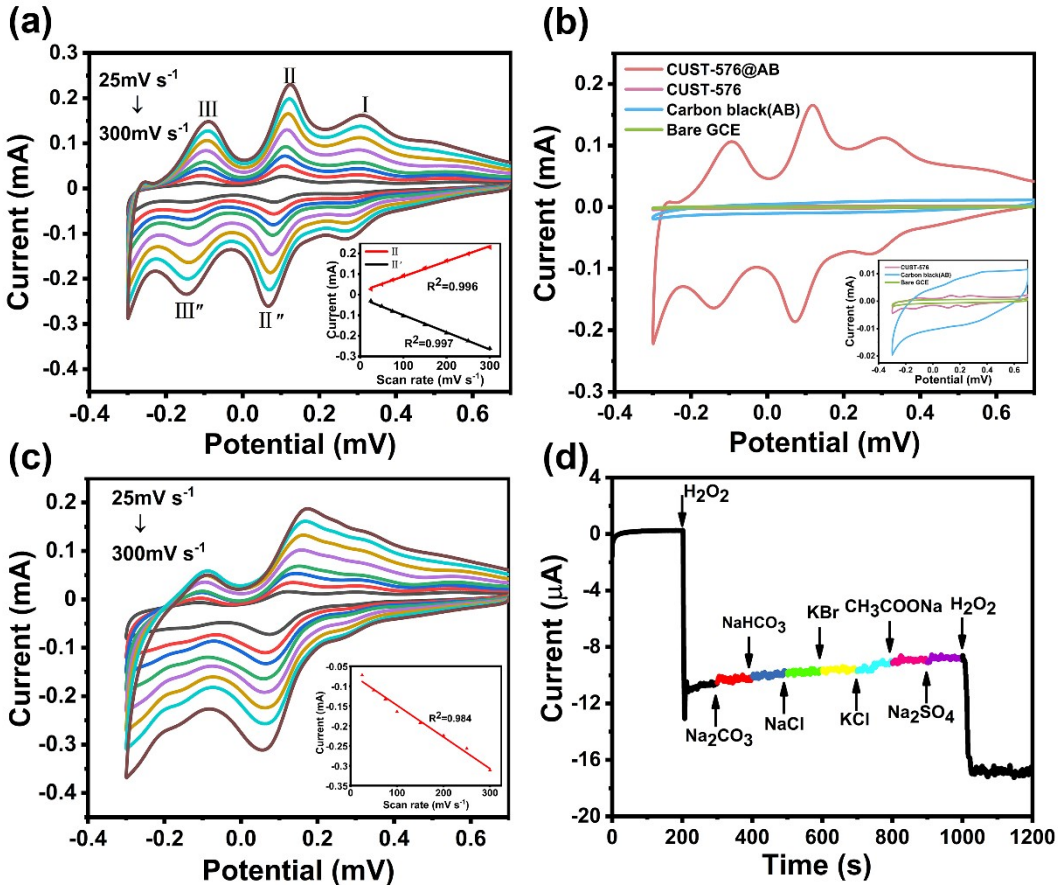

Fig. S17 (a) CVs (Cyclic Voltammograms) of $\{P_4Mo_6\}$-GCE at different scanning rates, (b) CV comparison of GCE, AB, CUST-576, and CUST-576@AB, (c) CVs of $\{P_4Mo_6\}$-GCE at different scanning rates in 4 mM H_2O_2, (d) Interference testing.

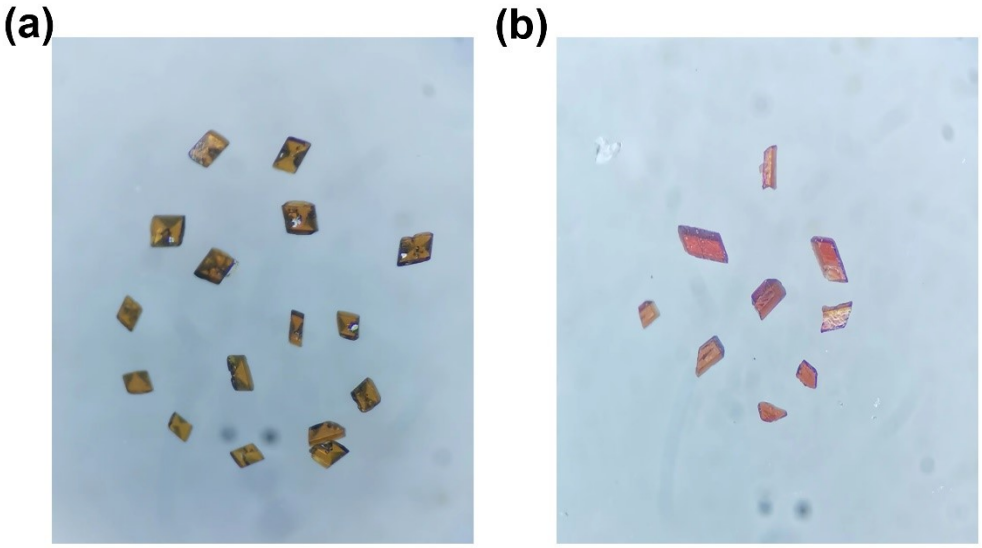

Fig. S18 Optical microscopic images of CUST-576 and CUST-576(Ni_0): (a) and (b).

Table S1. Crystal data and structure refinement for CUST-576

Identification code	CUST-576
CCDC Number	2258244
Empirical formula	$C_{30}H_{42}Mo_{12}N_{12}Ni_3O_{66}P_8$
Formula weight	3191.84
Temperature / K	283(2)
Crystal system	triclinic
Space group	P-1
a/Å	11.951(6)
b/Å	12.870(5)
c/Å	14.901(7)
α/°	84.43(2)
β/°	75.38(3)
γ/°	69.44(2)
Volume/Å^3	2076.3(17)
Z	1
ρ_{calc} g/cm^3	2.553
μ/mm^{-1}	2.684
F (000)	1532.0
Crystal size/mm^3	0.24 × 0.22 × 0.2
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	5.192 to 50.082
Index ranges	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -17 ≤ l ≤ 17 ≤ l ≤ 11
Reflections collected	27577
Independent reflections	7254 [Rint = 0.0865, Rsigma = 0.0735]
Data/restraints/parameters	7254/6/555
GOF on F^2	1.024
Final $R_{indexes}$ [I>= 2σ (I)]	R_1 = 0.0430, wR_2 = 0.0882
Final $R_{indexes}$[all data]	R_1 = 0.0736, wR_2 = 0.0984

Table S2. Bond Lengths for **CUST-576**.

Mo1	Mo4	2.5943(13)	Ni2	O242	2.124(5)
Mo1	O3	2.324(5)	Ni2	O29	2.030(6)
Mo1	O4	1.973(5)	Ni2	O30	2.042(6)
Mo1	O7	2.088(5)	Ni2	O32	2.091(6)
Mo1	O10	1.944(5)	Ni2	N6	2.023(4)
Mo1	O13	2.065(5)	P1	O3	1.538(5)
Mo1	O27	1.691(5)	P1	O5	1.555(5)
Mo2	Mo5	2.5964(16)	P1	O9	1.550(5)
Mo2	O2	1.996(5)	P1	O17	1.509(5)
Mo2	O6	2.109(5)	P2	O14	1.548(5)
Mo2	O9	2.309(5)	P2	O18	1.538(5)
Mo2	O12	1.938(5)	P2	O29	1.508(6)
Mo2	O18	2.073(5)	P2	O33	1.579(6)
Mo2	O28	1.669(5)	P3	O13	1.559(5)
Mo3	Mo6	2.5860(14)	P3	O15	1.534(5)
Mo3	O1	1.980(5)	P3	O24	1.497(5)
Mo3	O5	2.250(5)	P3	O26	1.570(5)
Mo3	O8	2.088(5)	P4	O16	1.518(6)
Mo3	O11	1.937(5)	P4	O21	1.522(6)
Mo3	O21	2.091(5)	P4	O23	1.572(6)
Mo3	O22	1.686(5)	P4	O31	1.551(6)
Mo4	O4	1.991(5)	C1	C2	1.4200
Mo4	O6	2.082(5)	C1	N2	1.4200
Mo4	O9	2.260(5)	C2	N1	1.4200
Mo4	O10	1.936(5)	N1	C3	1.4200
Mo4	O14	2.058(5)	C3	N2	1.4200
Mo4	O25	1.680(5)	N2	C12	1.378(5)
Mo5	O2	1.993(5)	C4	N3	1.4200
Mo5	O5	2.278(5)	C4	N4	1.4200
Mo5	O8	2.119(5)	N3	C5	1.4200
Mo5	O12	1.934(5)	N3	C10	1.354(5)
Mo5	O16	2.094(5)	C5	C6	1.4200
Mo5	O19	1.668(5)	C6	N4	1.4200
Mo6	O1	1.975(5)	C7	C8	1.3900
Mo6	O3	2.322(5)	C7	C12	1.3900
Mo6	O7	2.098(5)	C8	C9	1.3900
Mo6	O11	1.945(5)	C8	N5	1.359(5)
Mo6	O15	2.083(5)	C9	C10	1.3900
Mo6	O20	1.671(5)	C10	C11	1.3900

Ni1	O1	2.160(5)	C11	C12	1.3900
Ni1	O11	2.160(5)	C13	N5	1.4200
Ni1	O21	2.148(5)	C13	N6	1.4200
Ni1	O2	2.148(5)	N5	C14	1.4200
Ni1	O4	2.113(5)	C14	C15	1.4200
Ni1	O41	2.113(5)	C15	N6	1.4200
Ni2	O17	2.068(5)			

Table S3. Bond Angles for **CUST-576**.

O3	Mo1	Mo4	88.22(12)	O20	Mo6	O11	105.6(2)
O4	Mo1	Mo4	49.42(14)	O20	Mo6	O15	97.7(2)
O4	Mo1	O3	81.03(18)	O11	Ni1	O1	180.00(19)
O4	Mo1	O7	86.05(19)	O2	Ni1	O11	83.83(18)
O4	Mo1	O13	159.5(2)	O2	Ni1	O1	96.18(18)
O7	Mo1	Mo4	134.47(13)	O21	Ni1	O1	83.83(18)
O7	Mo1	O3	73.84(18)	O21	Ni1	O11	96.17(18)
O10	Mo1	Mo4	47.91(15)	O21	Ni1	O2	180.0
O10	Mo1	O3	82.60(19)	O41	Ni1	O1	83.41(18)
O10	Mo1	O4	95.6(2)	O41	Ni1	O11	96.59(18)
O10	Mo1	O7	155.8(2)	O4	Ni1	O11	83.41(18)
O10	Mo1	O13	87.6(2)	O4	Ni1	O1	96.59(18)
O13	Mo1	Mo4	135.21(14)	O4	Ni1	O21	84.44(18)
O13	Mo1	O3	79.35(18)	O41	Ni1	O21	95.56(18)
O13	Mo1	O7	82.9(2)	O4	Ni1	O2	95.55(18)
O27	Mo1	Mo4	99.23(18)	O41	Ni1	O2	84.44(18)
O27	Mo1	O3	172.2(2)	O41	Ni1	O4	180.0
O27	Mo1	O4	102.1(2)	O17	Ni2	O242	173.6(2)
O27	Mo1	O7	99.1(2)	O17	Ni2	O32	92.8(2)
O27	Mo1	O10	104.1(2)	O29	Ni2	O17	97.1(2)
O27	Mo1	O13	96.7(2)	O29	Ni2	O242	86.7(2)
O2	Mo2	Mo5	49.35(14)	O29	Ni2	O30	177.6(2)
O2	Mo2	O6	85.27(19)	O29	Ni2	O32	87.4(2)
O2	Mo2	O9	79.66(18)	O30	Ni2	O17	84.4(2)
O2	Mo2	O18	157.93(19)	O30	Ni2	O242	91.6(2)
O6	Mo2	Mo5	133.69(14)	O30	Ni2	O32	90.6(2)
O6	Mo2	O9	72.72(18)	O32	Ni2	O242	82.2(2)
O9	Mo2	Mo5	88.25(12)	N6	Ni2	O17	91.9(2)
O12	Mo2	Mo5	47.83(15)	N6	Ni2	O242	93.1(2)
O12	Mo2	O2	95.3(2)	N6	Ni2	O29	92.5(2)
O12	Mo2	O6	155.6(2)	N6	Ni2	O30	89.3(2)
O12	Mo2	O9	83.38(19)	N6	Ni2	O32	175.3(2)
O12	Mo2	O18	85.7(2)	O3	P1	O5	108.3(3)
O18	Mo2	Mo5	133.04(15)	O3	P1	O9	107.8(3)
O18	Mo2	O6	84.9(2)	O9	P1	O5	108.1(3)
O18	Mo2	O9	78.56(18)	O17	P1	O3	113.4(3)
O28	Mo2	Mo5	101.2(2)	O17	P1	O5	106.5(3)
O28	Mo2	O2	102.9(2)	O17	P1	O9	112.4(3)
O28	Mo2	O6	97.2(2)	O14	P2	O33	105.4(3)

O28	Mo2	O9	169.5(2)	O18	P2	O14	109.7(3)
O28	Mo2	O12	106.4(2)	O18	P2	O33	104.6(3)
O28	Mo2	O18	97.9(2)	O29	P2	O14	114.9(3)
O1	Mo3	Mo6	49.09(13)	O29	P2	O18	113.0(3)
O1	Mo3	O5	79.97(19)	O29	P2	O33	108.4(3)
O1	Mo3	O8	86.67(19)	O13	P3	O26	109.2(3)
O1	Mo3	O21	158.6(2)	O15	P3	O13	110.9(3)
O5	Mo3	Mo6	89.36(13)	O15	P3	O26	108.5(3)
O8	Mo3	Mo6	135.05(14)	O24	P3	O13	109.7(3)
O8	Mo3	O5	73.06(18)	O24	P3	O15	111.5(3)
O8	Mo3	O21	84.4(2)	O24	P3	O26	107.0(3)
O11	Mo3	Mo6	48.36(15)	O16	P4	O21	113.0(3)
O11	Mo3	O1	95.8(2)	O16	P4	O23	112.5(3)
O11	Mo3	O5	85.3(2)	O16	P4	O31	108.5(3)
O11	Mo3	O8	157.5(2)	O21	P4	O23	110.6(3)
O11	Mo3	O21	85.4(2)	O21	P4	O31	110.7(3)
O21	Mo3	Mo6	133.26(15)	O31	P4	O23	100.8(3)
O21	Mo3	O5	78.83(19)	Mo3	O1	Ni1	135.7(2)
O22	Mo3	Mo6	101.54(19)	Mo6	O1	Mo3	81.67(19)
O22	Mo3	O1	104.7(2)	Mo6	O1	Ni1	134.0(2)
O22	Mo3	O5	168.6(2)	Mo2	O2	Ni1	135.7(2)
O22	Mo3	O8	96.7(2)	Mo5	O2	Mo2	81.22(18)
O22	Mo3	O11	104.3(2)	Mo5	O2	Ni1	134.2(2)
O22	Mo3	O21	95.6(2)	Mo6	O3	Mo1	98.10(18)
O4	Mo4	Mo1	48.82(14)	P1	O3	Mo1	126.2(3)
O4	Mo4	O6	86.17(19)	P1	O3	Mo6	125.2(3)
O4	Mo4	O9	80.25(18)	Mo1	O4	Mo4	81.76(18)
O4	Mo4	O14	159.4(2)	Mo1	O4	Ni1	135.0(2)
O6	Mo4	Mo1	134.45(14)	Mo4	O4	Ni1	135.6(2)
O6	Mo4	O9	74.23(18)	Mo3	O5	Mo5	101.54(19)
O9	Mo4	Mo1	89.29(12)	P1	O5	Mo3	126.9(3)
O10	Mo4	Mo1	48.17(15)	P1	O5	Mo5	125.7(3)
O10	Mo4	O4	95.3(2)	Mo4	O6	Mo2	112.8(2)
O10	Mo4	O6	158.5(2)	Mo1	O7	Mo6	113.9(2)
O10	Mo4	O9	84.83(19)	Mo3	O8	Mo5	113.0(2)
O10	Mo4	O14	86.4(2)	Mo4	O9	Mo2	99.58(18)
O14	Mo4	Mo1	134.15(15)	P1	O9	Mo2	126.0(3)
O14	Mo4	O6	85.0(2)	P1	O9	Mo4	127.5(3)
O14	Mo4	O9	79.46(19)	Mo4	O10	Mo1	83.92(19)
O25	Mo4	Mo1	101.34(18)	Mo3	O11	Mo6	83.5(2)

O25	Mo4	O4	103.3(2)	Mo5	O12	Mo2	84.23(19)
O25	Mo4	O6	94.9(2)	P3	O13	Mo1	134.7(3)
O25	Mo4	O9	168.5(2)	P2	O14	Mo4	129.7(3)
O25	Mo4	O10	105.5(2)	P3	O15	Mo6	131.5(3)
O25	Mo4	O14	95.9(2)	P4	O16	Mo5	129.7(3)
O2	Mo5	Mo2	49.43(14)	P1	O17	Ni2	133.5(3)
O2	Mo5	O5	80.42(19)	P2	O18	Mo2	130.2(3)
O2	Mo5	O8	87.92(19)	P4	O21	Mo3	129.3(3)
O2	Mo5	O16	158.8(2)	P3	O24	Ni22	136.7(3)
O5	Mo5	Mo2	89.72(13)	P2	O29	Ni2	158.3(4)
O8	Mo5	Mo2	136.37(14)	N2	C1	C2	108.0
O8	Mo5	O5	71.93(18)	N1	C2	C1	108.0
O12	Mo5	Mo2	47.95(16)	C3	N1	C2	108.0
O12	Mo5	O2	95.5(2)	N2	C3	N1	108.0
O12	Mo5	O5	84.56(19)	C1	N2	C3	108.0
O12	Mo5	O8	155.4(2)	C12	N2	C1	127.1(4)
O12	Mo5	O16	84.1(2)	C12	N2	C3	124.9(4)
O16	Mo5	Mo2	131.63(16)	N3	C4	N4	108.0
O16	Mo5	O5	78.43(19)	C5	N3	C4	108.0
O16	Mo5	O8	84.1(2)	C10	N3	C4	125.3(4)
O19	Mo5	Mo2	101.7(2)	C10	N3	C5	126.7(4)
O19	Mo5	O2	103.8(2)	C6	C5	N3	108.0
O19	Mo5	O5	167.9(2)	C5	C6	N4	108.0
O19	Mo5	O8	96.7(2)	C6	N4	C4	108.0
O19	Mo5	O12	106.1(2)	C8	C7	C12	120.0