Supporting Information

Two 2D layered P_4Mo_6 clusters with the potential bifunctional properties: proton conduction and CO_2 photoreduction

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Impedance analysis. The samples were put into a homemade mould with a radius of 0.2 cm to get circular pellets. The thickness was measured by a vernier caliper. And then the pellets were smeared by silver colloid on two sides which were fixed on the sample stage with gold wires. The value of proton conduction were measured through an impedance/gain-phase analyzer (Solartron S1 1260) over a frequency range from 1 Hz to 1 MHz with an input voltage range from 100 mV to 3000 mV. The measurements were operated at temperatures (25 to 60 °C), with different relative humidities (40% to 98% RH). The proton conductivity was calculated using the following equation:

$$\sigma = \frac{l}{\mathrm{SR}},$$

where σ is the conductivity (S cm^{-1}), l is the thickness (cm) of the pellet, S is the cross-sectional area (cm^2) of the pellet and R is the bulk resistance (Ω). The activation energy (Ea) was calculated from the following equation:

$$\ln\sigma_T = \ln\sigma_0 - \frac{\mathrm{E}_a}{\mathrm{KT}} \qquad (\mathrm{K}=8.6\times10^{-5}\ \mathrm{eV/K}),$$

where σ is the conductivity (S cm^{-1}), K is the Boltzmann constant (eV/K) and T is the temperature (K).

Photocatalytic CO_2 reduction experiments. The photocatalytic performance of compound **1** and **2** was evaluated by applying it to the photocatalytic reduction of CO_2 (CEL-SPH2N-S9, AULTT, China). The experiments were carried out in a 100 mL Pyrex flask. A 300 W xenon arc lamp (CEL-PF300-T8, AULTT, China) (photocurrent: 14.5A) was employed as a visible-light source through a UV-cutoff filter with a wavelength greater than 420 nm, which was installed 10 cm away from the reaction solution. In the system of CO_2 photocatalytic reduction, we put photocatalyst (10mg) into a mixed solvent of triethanolamine (TEAOH, as a sacrificial base) and acetonitrile (1:4 v/v, 50 mL), and used $[Ru(bpy)_3]Cl_2{\bullet}6H_2O$ (11.3mg) as photosensitizer. The products were analyzed by performing gas chromatography (GC7920-TF2Z, AULTT, China).

Electrochemical measurements. The Mott–Schottky spots were carried out at ambient environment via using the electrochemical workstation (CHI 760e) in a

standard three-electrode system: The carbon cloth (CC, 1 cm×1 cm) modified with catalyst samples, carbon rod and Ag/AgCl were used as the working electrode, counter electrode and the reference electrode, respectively. The catalyst of 5 mg were grinded to powder and then dispersed in 1 mL of 0.5% Nafion solvent by ultrasonication to form a homogeneous ink. Subsequently, 200 μL of the ink were deposited onto the carbon cloth, and dried in room temperature for Mott-Schottky spots measurements. The Mott-Schottky plots were measured over an alternating current (AC) frequency of 1000 Hz, 1500 Hz and 2000 Hz, and three electrodes were immersed in the 0.2 M Na_2SO_4 aqueous solution.

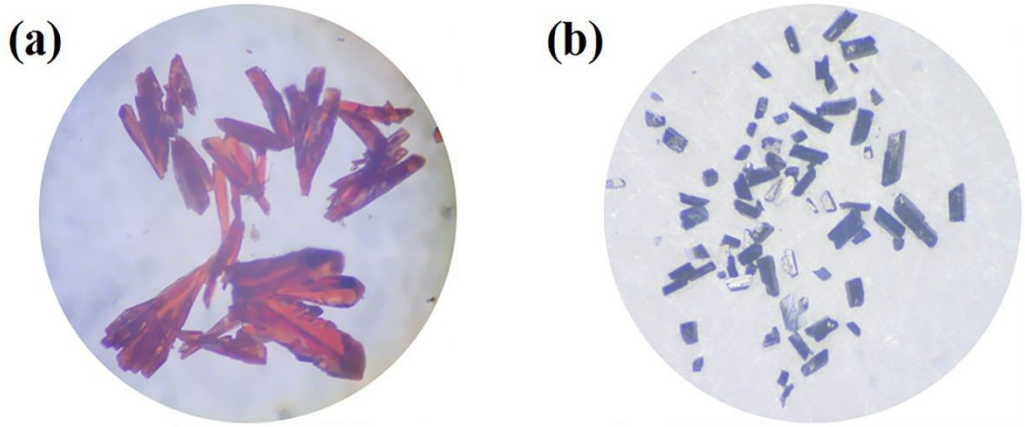

Fig. S1. (a) The image of compound **1** crystal under optical microscope.; (b) The image of compound **2** crystal under optical microscope.

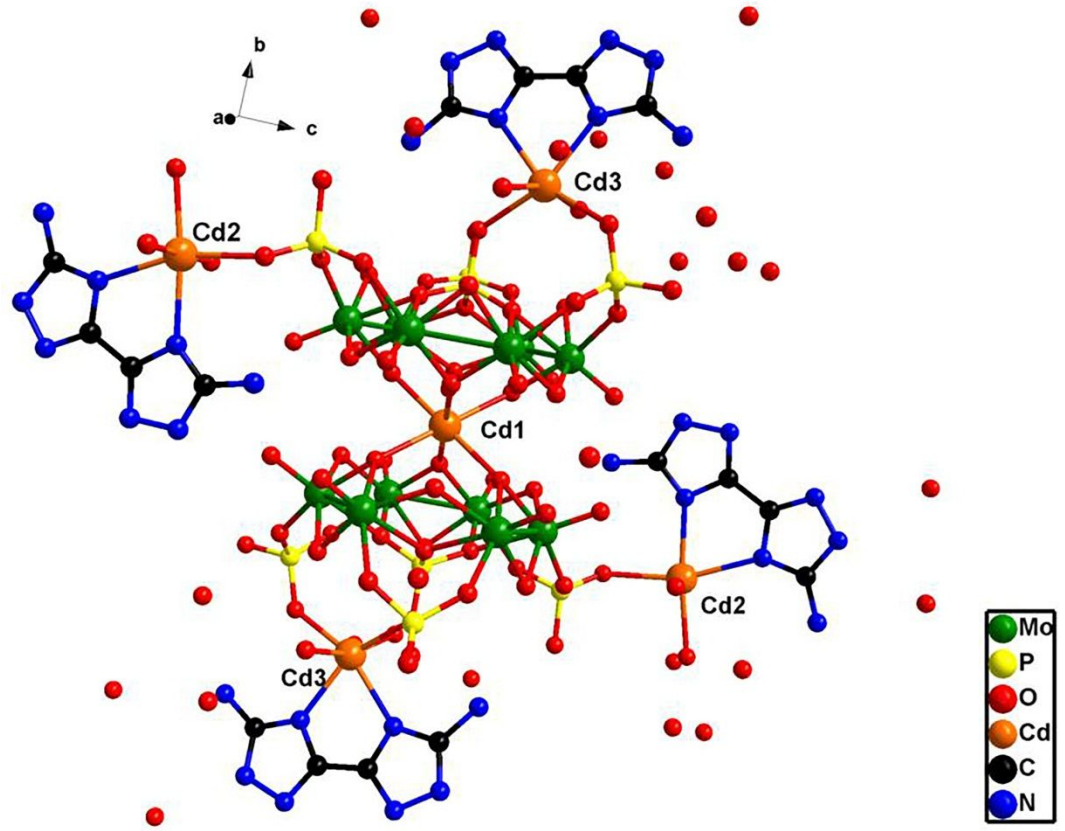

Fig. S2. Ball and stick representation of the basic crystallographic unit in compound **1**. Hydrogen atoms are omitted for clarity.

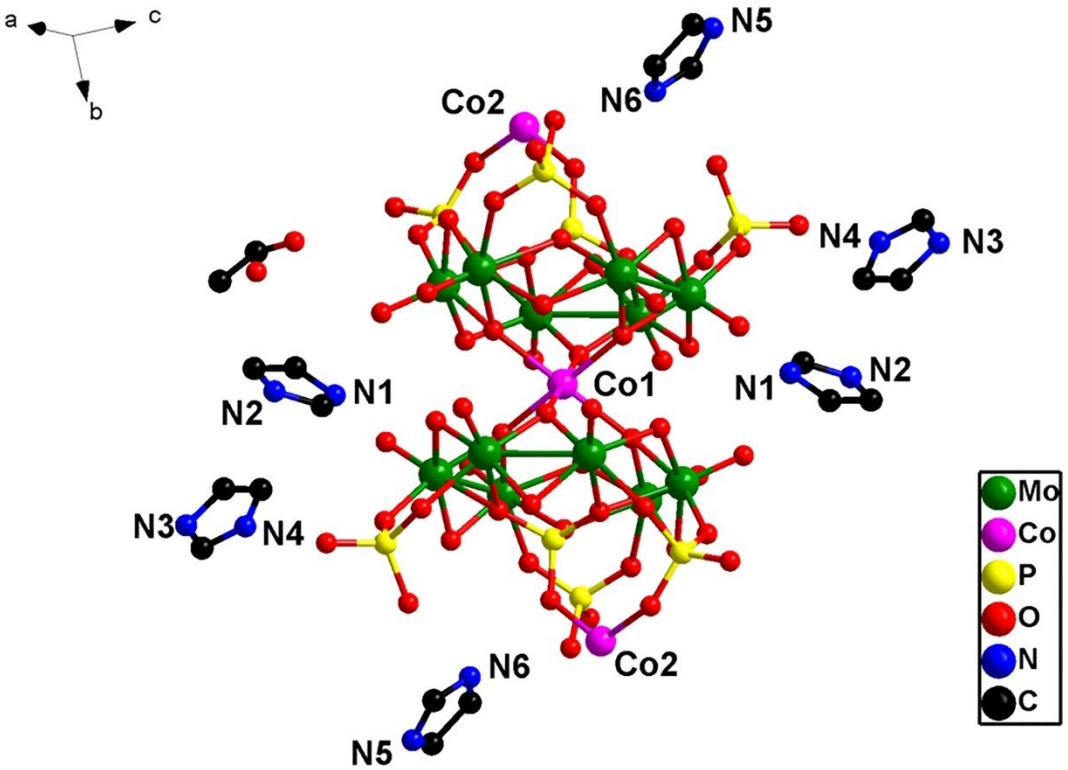

Fig. S3. Ball and stick representation of the basic crystallographic unit in compound **2**. Hydrogen atoms are omitted for clarity.

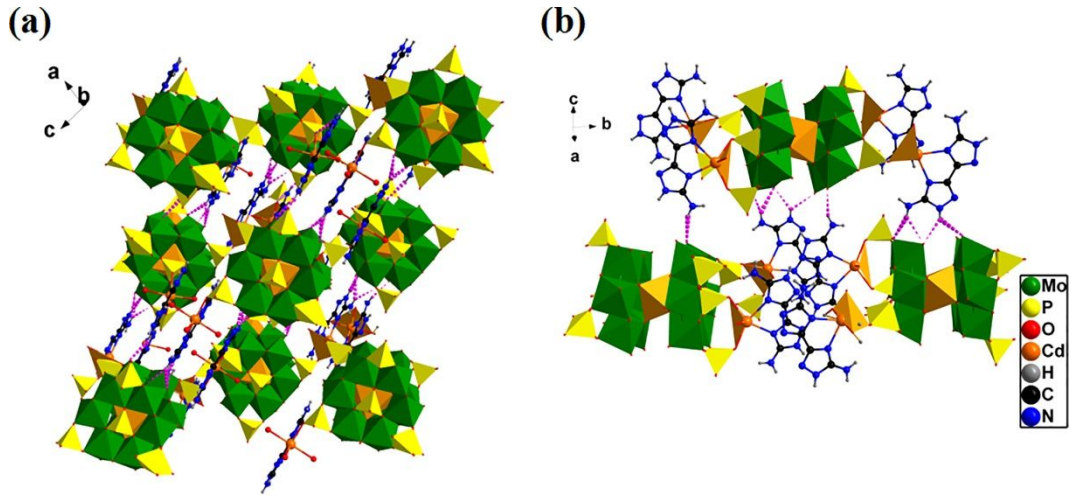

Fig. S4. (a) The 3D supramolecular structure of compound **1** along the b-axis. (b) Three $\{M[P_4Mo_6]_2\}$ units are connected with each other by hydrogen bonds. Free water molecules are omitted for clarity.

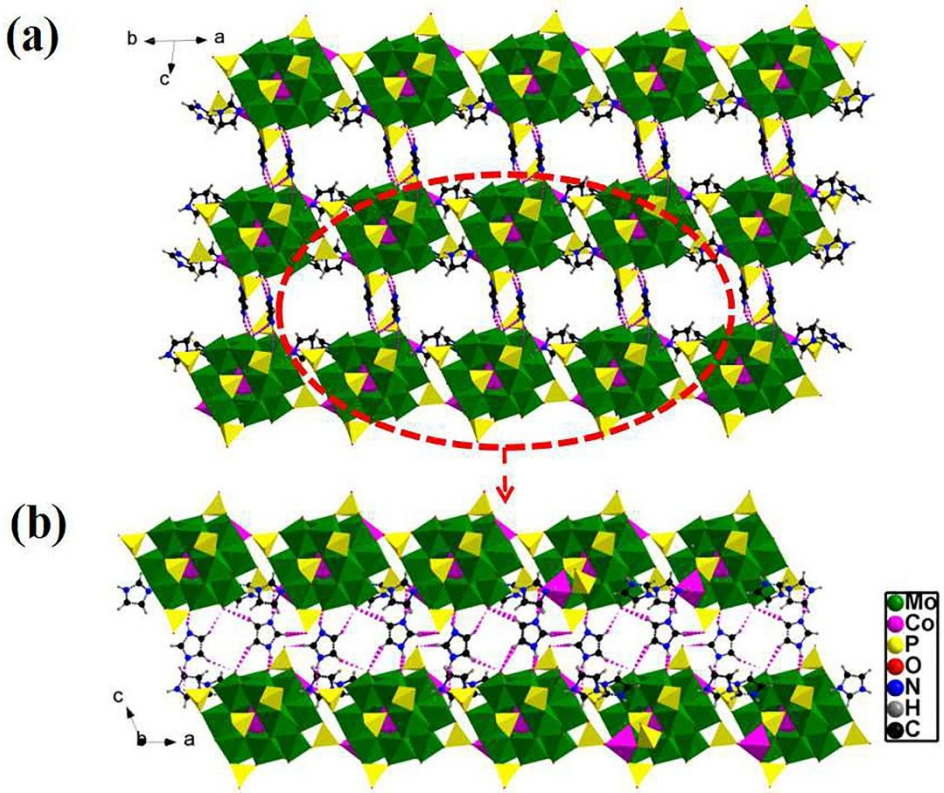

Fig. S5. (a) The 3D supramolecular structure of compound **2**. (b) The hydrogen bonding interactions in compound **2** along the b-axis. Free water and ethanol molecules are omitted for clarity.

IR Spectra

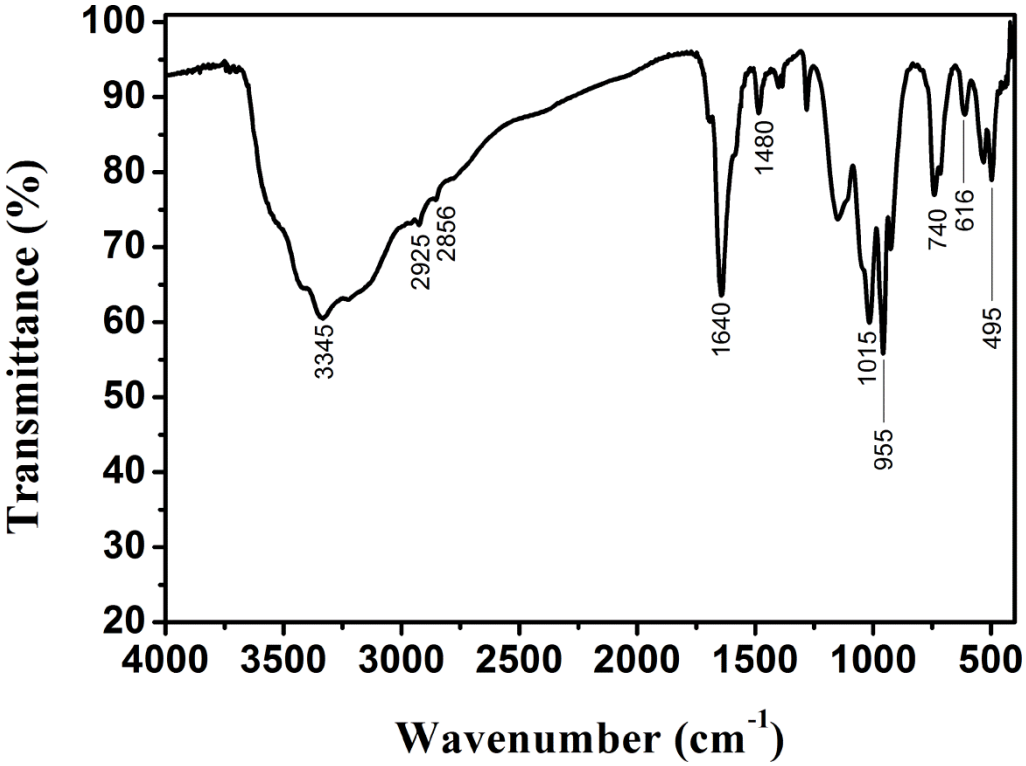

Fig. S6. The IR spectrum of compound **1.**

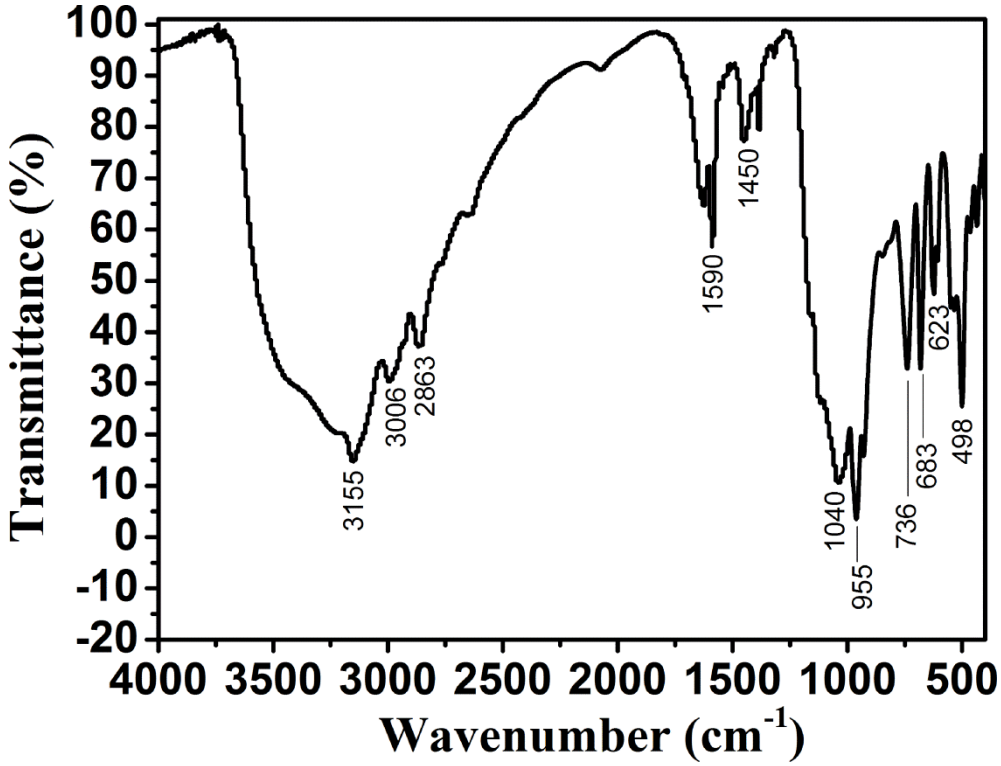

Fig. S7. The IR spectrum of compound **2.**

Powder X-ray Diffraction (PXRD)

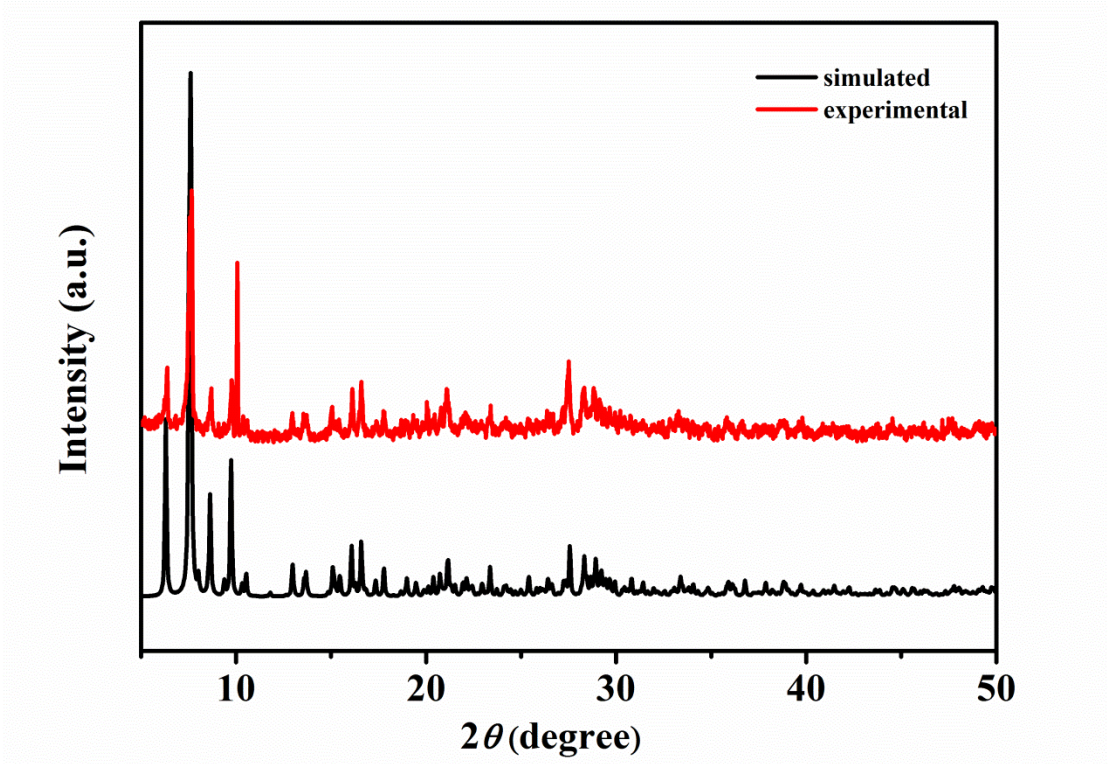

Fig. S8. Experimental and simulated PXRD patterns of compound **1.**

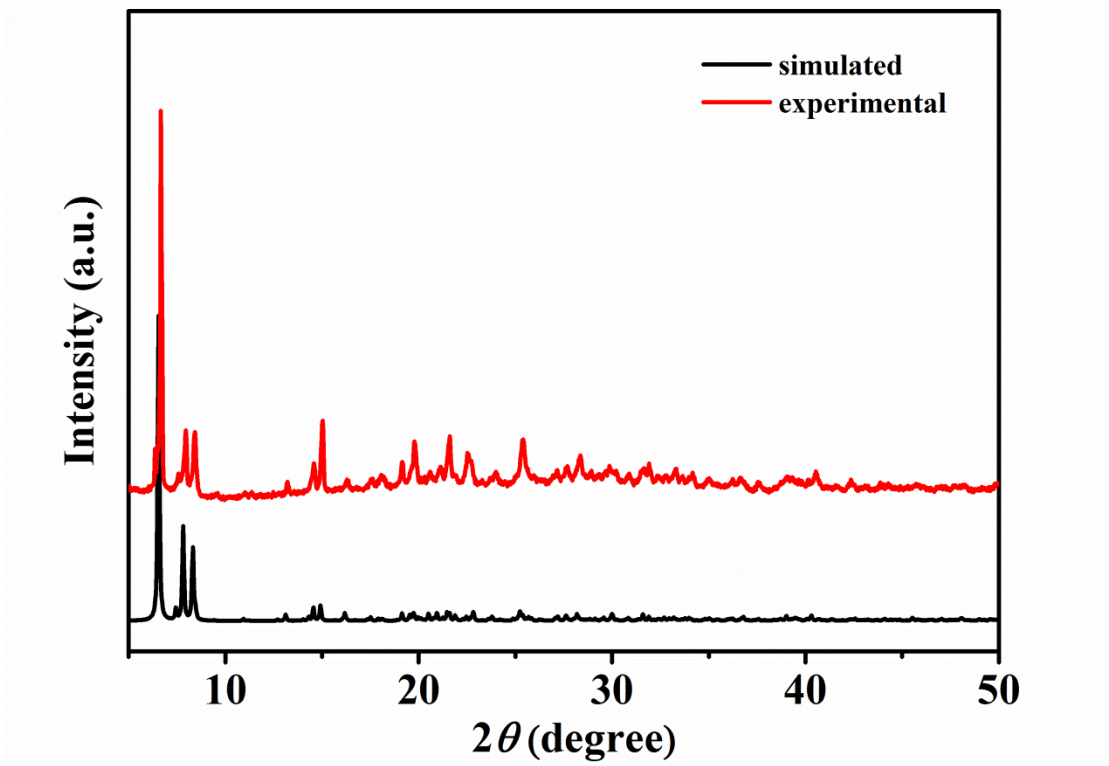

Fig. S9. Experimental and simulated PXRD patterns of compound **2.**

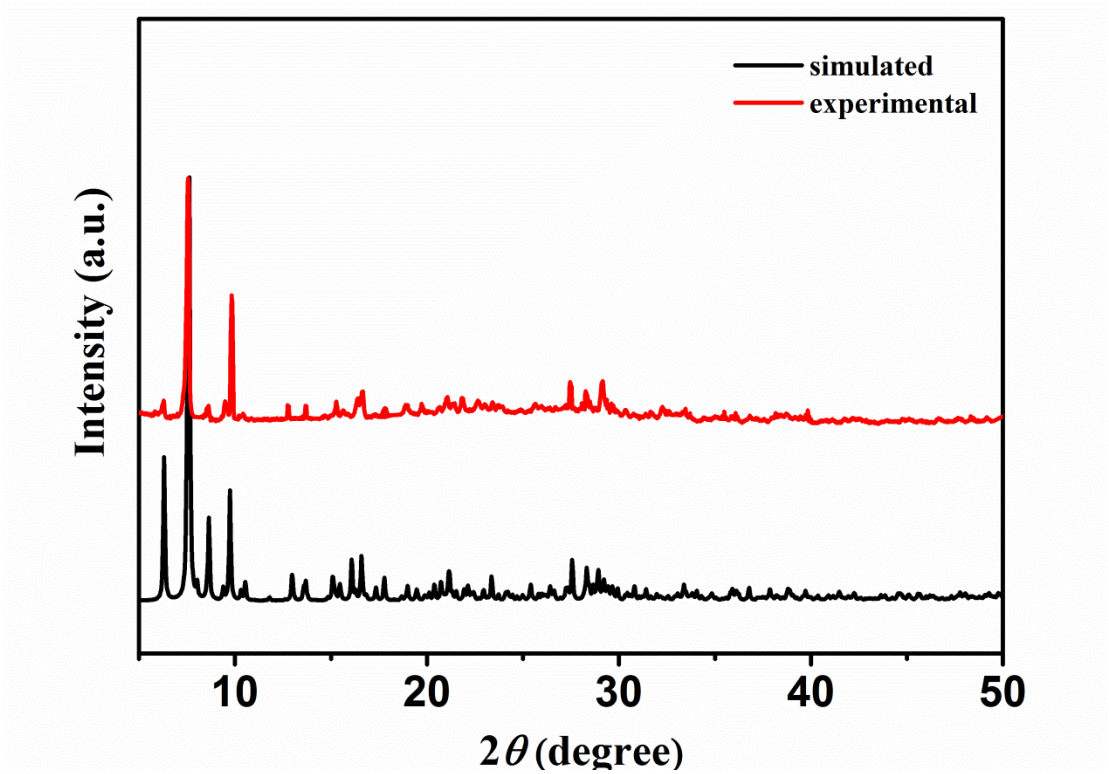

Fig. S10. The powder XRD patterns of compound **1** after impedance measurement.

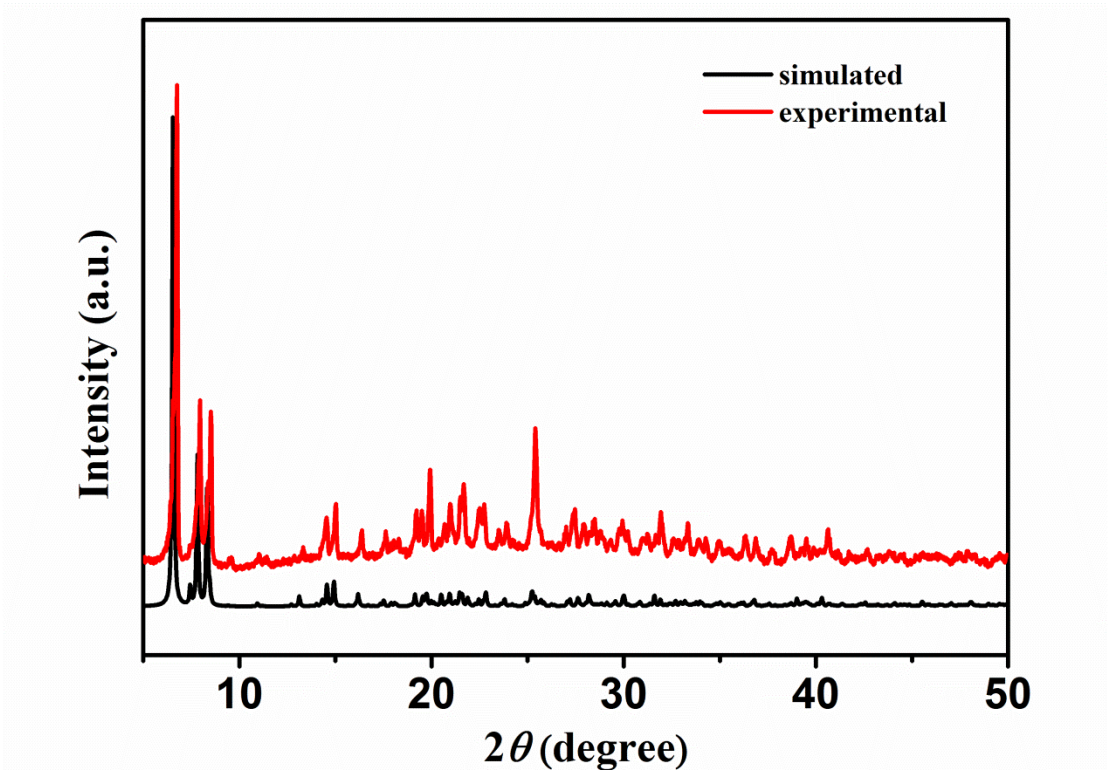

Fig. S11. The powder XRD patterns of compound **2** after impedance measurement.

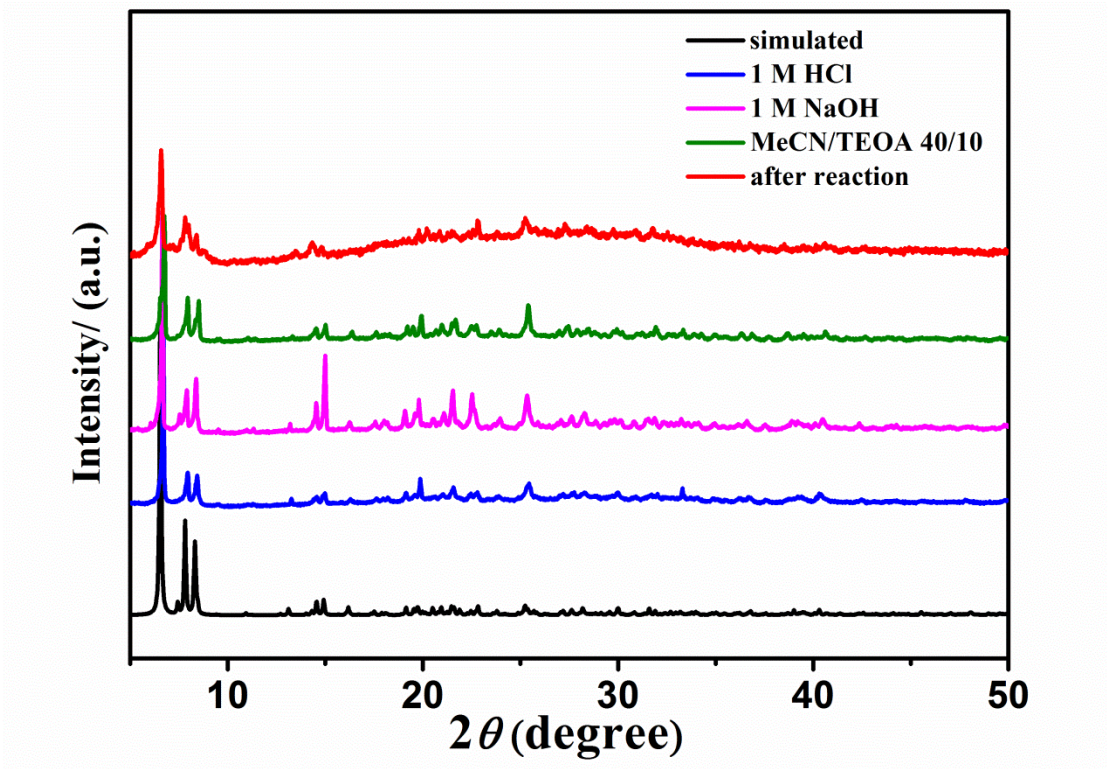

Fig. S12. The powder XRD patterns of compound **2** in different solutions compared with simulated curves.

Thermogravimetric Analysis (TGA)

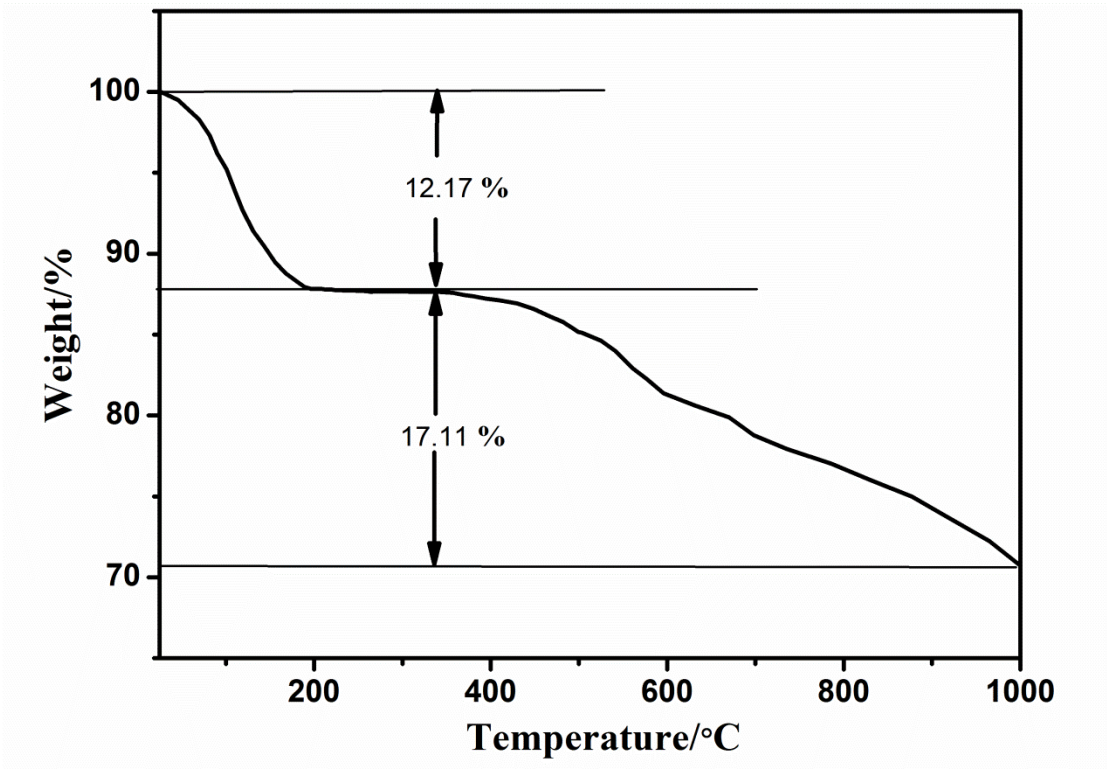

Fig. S13. The TG curve for compound **1**.

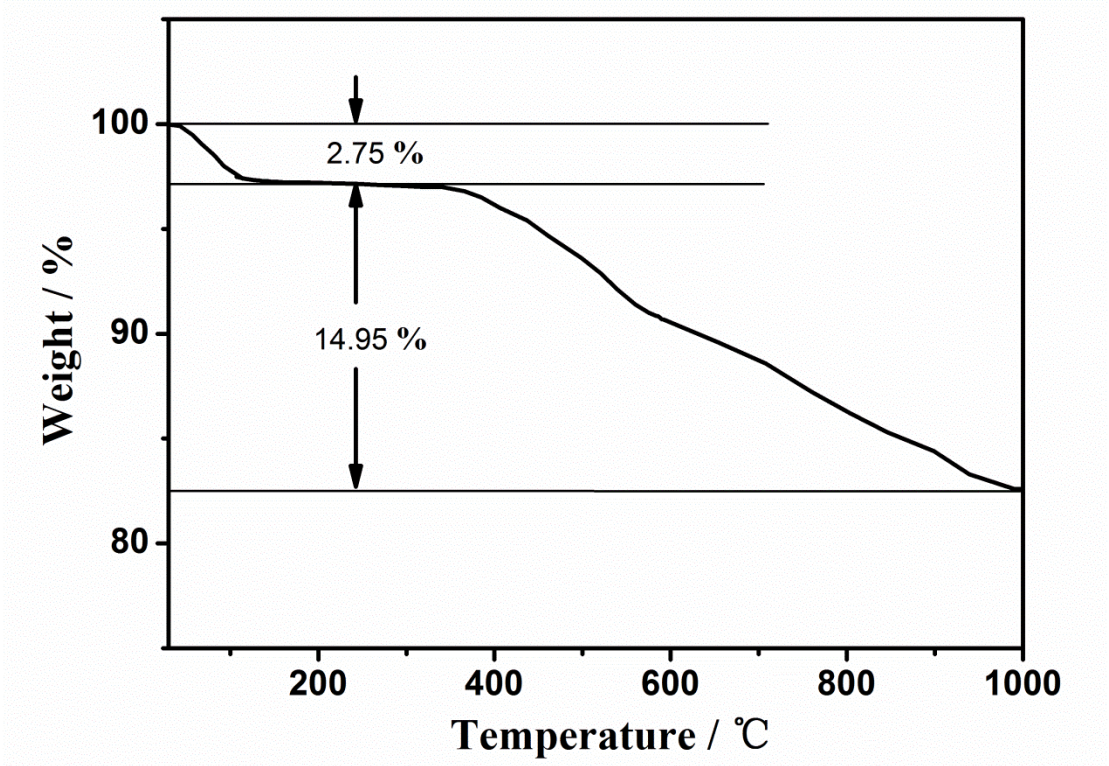

Fig. S14. The TG curve for compound **2**.

CO_2 photocatalytic reduction

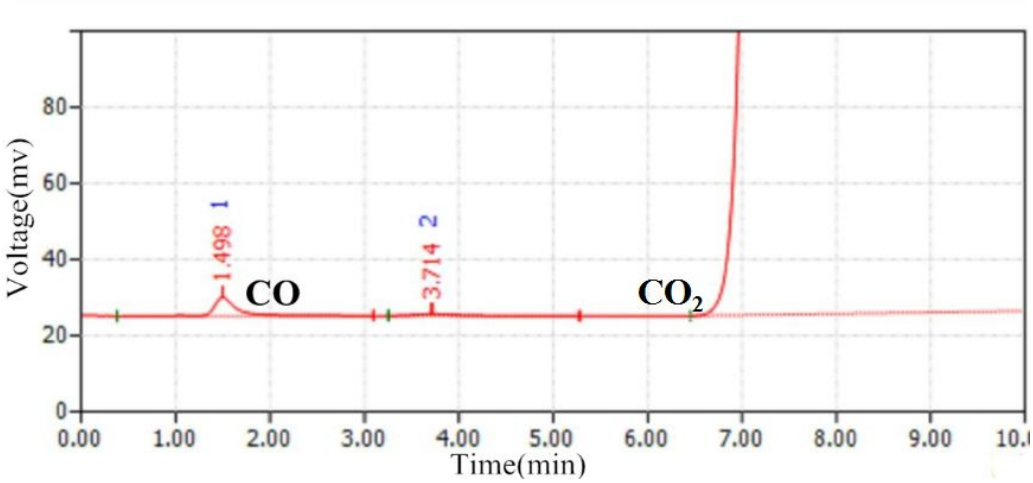

Fig. S15. GC profiles of CO_2 reduction to CO without catalyst after reaction 8h.

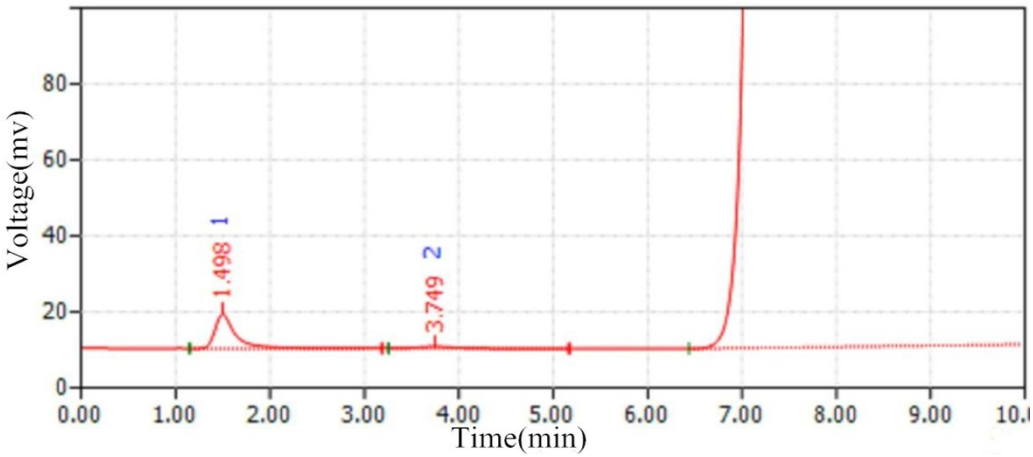

Fig. S16. GC profiles of CO_2 reduction to CO with compound **1** as catalyst after reaction 8h.

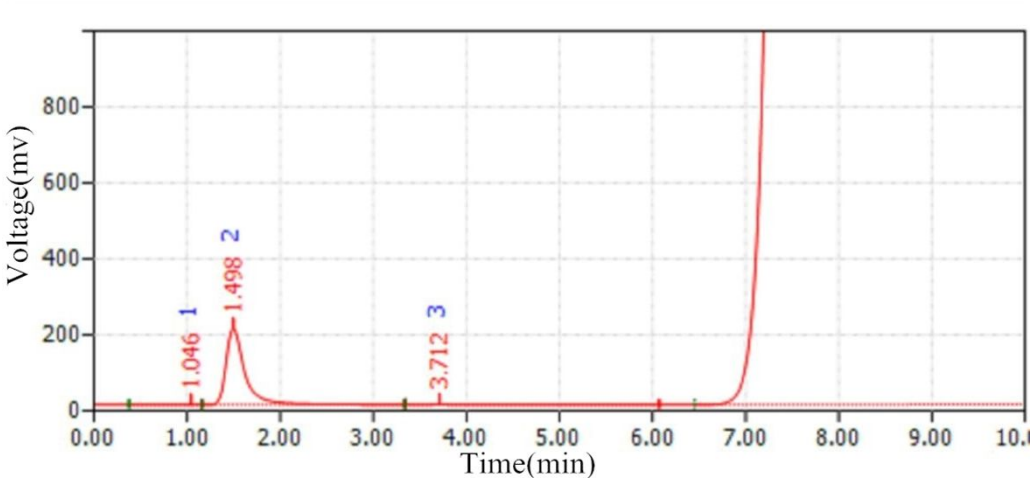

Fig. S17. GC profiles of CO_2 reduction to CO with compound **2** as catalyst after reaction 8h.

Table S1. Bond lengths (Å) of main atoms for compound **1**.

Mo(1)-O(33)	1.683(5)	P(1)-O(9)	1.502(5)
Mo(1)-O(6)	1.931(5)	P(1)-O(24)	1.545(5)
Mo(1)-O(3)	1.976(5)	P(1)-O(22)	1.549(5)
Mo(1)-O(21)	2.063(5)	P(1)-O(13)	1.553(5)
Mo(1)-O(7)	2.095(5)	P(2)-O(31)	1.490(6)
Mo(1)-O(22)	2.290(5)	P(2)-O(15)	1.526(5)
Mo(2)-O(19)	1.689(5)	P(2)-O(21)	1.539(6)
Mo(2)-O(11)	1.934(5)	P(2)-O(28)	1.594(6)
Mo(2)-O(2)	1.960(5)	P(3)-O(35)	1.508(6)
Mo(2)-O(16)	2.054(5)	P(3)-O(18)	1.523(6)
Mo(2)-O(4)	2.120(5)	P(3)-O(16)	1.533(6)
Mo(2)-O(24)	2.289(5)	P(3)-O(34)	1.586(6)
Mo(3)-O(8)	1.681(5)	P(4)-O(32)	1.455(7)
Mo(3)-O(11)	1.935(5)	P(4)-O(37)	1.517(7)
Mo(3)-O(2)	1.968(5)	P(4)-O(10)	1.525(7)
Mo(3)-O(37)	2.099(5)	P(4)-O(1A)	1.646(8)
Mo(3)-O(1)	2.110(5)	Cd(1)-O(5)	2.237(5)
Mo(3)-O(13)	2.248(5)	Cd(1)-O(5)#1	2.239(5)
Mo(4)-O(27)	1.697(6)	Cd(1)-O(2)	2.239(5)
Mo(4)-O(14)	1.948(5)	Cd(1)-O(2)#1	2.285(5)
Mo(4)-O(5)	1.959(5)	Cd(1)-O(3)#1	2.285(5)
Mo(4)-O(18)	2.049(5)	Cd(1)-O(3)	2.287(5)
Mo(4)-O(4)	2.127(5)	Cd(2)-O(32)#2	2.237(5)
Mo(4)-O(24)	2.305(5)	Cd(2)-O(31)	2.275(5)
Mo(5)-O(36)	1.683(5)	Cd(2)-N(1)	2.318(6)
Mo(5)-O(14)	1.947(5)	Cd(2)-O(2W)	2.324(7)
Mo(5)-O(5)	1.963(5)	Cd(2)-O(1W)	2.344(7)
Mo(5)-O(15)	2.067(6)	Cd(2)-N(5)	2.374(6)
Mo(5)-O(7)	2.112(5)	Cd(3)-O(35)	2.227(6)
Mo(5)-O(22)	2.274(5)	Cd(3)-O(9)	2.281(5)
Mo(6)-O(30)	1.686(6)	Cd(3)-O(4W)	2.290(6)
Mo(6)-O(6)	1.940(5)	Cd(3)-N(9)	2.305(7)
Mo(6)-O(3)	1.968(5)	Cd(3)-N(13)	2.343(8)
Mo(6)-O(10)	2.078(5)	Cd(3)-O(3W)	2.345(8)
Mo(6)-O(1)	2.117(5)		
Mo(6)-O(13)	2.273(5)		

Table S2. Bond angles (°) of main atoms for compound **1**.

O(33)-Mo(1)-O(6)	106.8(3)	O(11)-Mo(3)-O(1)	155.7(2)
O(33)-Mo(1)-O(3)	101.1(2)	O(2)-Mo(3)-O(1)	86.6(2)
O(6)-Mo(1)-O(3)	95.2(2)	O(37)-Mo(3)-O(1)	86.6(2)
O(33)-Mo(1)-O(21)	96.5(2)	O(8)-Mo(3)-O(13)	168.2(2)
O(6)-Mo(1)-O(21)	85.3(2)	O(11)-Mo(3)-O(13)	84.8(2)
O(3)-Mo(1)-O(21)	161.4(2)	O(2)-Mo(3)-O(13)	80.8(2)
O(33)-Mo(1)-O(7)	97.7(2)	O(37)-Mo(3)-O(13)	79.3(2)
O(6)-Mo(1)-O(7)	154.6(2)	O(1)-Mo(3)-O(13)	71.44(19)
O(3)-Mo(1)-O(7)	86.6 (2)	O(18)-Mo(4)-O(24)	79.1(2)
O(21)-Mo(1)-O(7)	85.2(2)	O(4)-Mo(4)-O(24)	71.83(18)
O(33)-Mo(1)-O(22)	168.4(2)	O(27)-Mo(4)-O(14)	106(3)
O(6)-Mo(1)-O(22)	83.8(2)	O(27)-Mo(4)-O(5)	102.5(2)
O(3)-Mo(1)-O(22)	82.18(19)	O(14)-Mo(4)-O(5)	95.0(2)
O(21)-Mo(1)-O(22)	79.4(2)	O(27)-Mo(4)-O(18)	96.6(3)
O(7)-Mo(1)-O(22)	71.35(19)	O(14)-Mo(4)-O(18)	86.8(2)
O(19)-Mo(2)-O(11)	107.3(2)	O(5)-Mo(4)-O(18)	159.5(2)
O(19)-Mo(2)-O(2)	101.3(2)	O(27)-Mo(4)-O(4)	97.6(2)
O(11)-Mo(2)-O(2)	94.9(2)	O(14)-Mo(4)-O(4)	155.5(2)
O(19)-Mo(2)-O(16)	94.1(2)	O(5)-Mo(4)-O(4)	86.2(2)
O(11)-Mo(2)-O(16)	87.7(2)	O(18)-Mo(4)-O(4)	83.9(2)
O(2)-Mo(2)-O(16)	162.8(2)	O(27)-Mo(4)-O(24)	169.1(2)
O(19)-Mo(2)-O(4)	96.9(2)	O(14)-Mo(4)-O(24)	84.0(2)
O(11)-Mo(2)-O(4)	154.7(2)	O(5)-Mo(4)-O(24)	80.8(2)
O(2)-Mo(2)-O(4)	87.2(2)	O(36)-Mo(5)-O(14)	106.7(3)
O(16)-Mo(2)-O(4)	83.4(2)	O(36)-Mo(5)-O(5)	102.2(3)
O(19)-Mo(2)-O(24)	168.5(2)	O(14)-Mo(5)-O(5)	94.8(2)
O(11)-Mo(2)-O(24)	82.7(2)	O(36)-Mo(5)-O(15)	96.6(3)
O(2)-Mo(2)-O(24)	83.0(2)	O(14)-Mo(5)-O(15)	86.4(2)
O(16)-Mo(2)-O(24)	80.5 (2)	O(5)-Mo(5)-O(15)	159.8(2)
O(4)-Mo(2)-O(24)	72.49(19)	O(36)-Mo(5)-O(7)	95.9(2)
O(8)-Mo(3)-O(11)	105.6(2)	O(14)-Mo(5)-O(7)	156.5(2)
O(8)-Mo(3)-O(2)	103.4(2)	O(5)-Mo(5)-O(7)	86.0(2)
O(11)-Mo(3)-O(2)	94.6(2)	O(15)-Mo(5)-O(7)	85.1(2)
O(8)-Mo(3)-O(37)	96.0(2)	O(36)-Mo(5)-O(22)	166.9(2)
O(11)-Mo(3)-O(37)	84.1(2)	O(14)-Mo(5)-O(22)	85.5(2)
O(2)-Mo(3)-O(37)	160.1(2)	O(5)-Mo(5)-O(22)	80.8(2)
O(8)-Mo(3)-O(1)	97.6(2)	O(15)-Mo(5)-O(22)	79.2(2)

O(7)-Mo(5)-O(22)	71.39(2)	O(37)-P(4)-O(1A)	107.4(4)
O(30)-Mo(6)-O(6)	105.6(2)	O(10)-P(4)-O(1A)	107.1(4)
O(30)-Mo(6)-O(3)	102.7(2)	O(5)-Cd(1)-O(5)#1	180.0
O(6)-Mo(6)-O(3)	95.2(2)	O(5)-Cd(1)-O(2)	96.96(18)
O(30)-Mo(6)-O(10)	96.5(2)	O(5)#1-Cd(1)-O(2)	83.04(18)
O(6)-Mo(6)-O(10)	85.7(2)	O(5)-Cd(1)-O(2)#1	83.04(18)
O(3)-Mo(6)-O(10)	159.8(2)	O(5)#1-Cd(1)-O(2)#1	96.96(18)
O(30)-Mo(6)-O(1)	98.8(2)	O(2)-Cd(1)-O(2)#1	180.0
O(6)-Mo(6)-O(1)	154.3(2)	O(5)-Cd(1)-O(3)#1	83.83(18)
O(3)-Mo(6)-O(1)	87.3(2)	O(5)#1-Cd(1)-O(3)#1	96.17(18)
O(10)-Mo(6)-O(1)	83.5(2)	O(2)-Cd(1)-O(3)#1	84.82(18)
O(30)-Mo(6)-O(13)	169.1(2)	O(2)#1-Cd(1)-O(3)#1	95.18(18)
O(6)-Mo(6)-O(13)	84.3(2)	O(5)-Cd(1)-O(3)	96.17(18)
O(3)-Mo(6)-O(13)	80.66(19)	O(5)#1-Cd(1)-O(3)	83.83(18)
O(10)-Mo(6)-O(13)	79.4(2)	O(2)-Cd(1)-O(3)	95.18(18)
O(1)-Mo(6)-O(13)	70.82(19)	O(2)#1-Cd(1)-O(3)	84.82(18)
O(9)-P(1)-O(24)	111.3(3)	O(3)#1-Cd(1)-O(3)	180.0
O(9)-P(1)-O(22)	112.5(3)	O(32)#2-Cd(2)-O(31)	96.5(2)
O(24)-P(1)-O(22)	108.4(3)	O(32)#2-Cd(2)-N(1)	174.0(2)
O(9)-P(1)-O(13)	108.8(3)	O(31)-Cd(2)-N(1)	89.6(2)
O(24)-P(1)-O(13)	108.4(3)	O(32)#2-Cd(2)-O(2W)	91.2(2)
O(22)-P(1)-O(13)	107.2(3)	O(31)-Cd(2)-O(2W)	87.8(3)
O(31)-P(2)-O(15)	112.6(3)	N(1)-Cd(2)-O(2W)	89.1(2)
O(31)-P(2)-O(21)	111.8(3)	O(32)#2-Cd(2)-O(1W)	87.3(2)
O(15)-P(2)-O(21)	111.5(3)	O(31)-Cd(2)-O(1W)	92.2(2)
O(31)-P(2)-O(28)	109.2(3)	N(1)-Cd(2)-O(1W)	92.3(2)
O(15)-P(2)-O(28)	104.7(3)	O(2W)-Cd(2)-O(1W)	178.5(2)
O(21)-P(2)-O(28)	106.5(3)	O(32)#2-Cd(2)-N(5)	101.6(2)
O(35)-P(3)-O(18)	112.3(4)	O(31)-Cd(2)-N(5)	161.9(2)
O(35)-P(3)-O(16)	112.5(4)	N(1)-Cd(2)-N(5)	72.4(2)
O(18)-P(3)-O(16)	111.1(3)	O(2W)-Cd(2)-N(5)	91.8(3)
O(35)-P(3)-O(34)	109.9(3)	O(1W)-Cd(2)-N(5)	88.6(2)
O(18)-P(3)-O(34)	106.2(4)	O(35)-Cd(3)-O(9)	121.5(2)
O(16)-P(3)-O(34)	104.2(3)	O(35)-Cd(3)-O(4W)	85.2(2)
O(32)-P(4)-O(37)	114.2(4)	O(9)-Cd(3)-O(4W)	86.1(2)
O(32)-P(4)-O(10)	112.5(4)	O(35)-Cd(3)-N(9)	87.3(2)
O(37)-P(4)-O(10)	110.9(4)	O(9)-Cd(3)-N(9)	147.3(2)
O(32)-P(4)-O(1A)	104.2(4)	O(4W)-Cd(3)-N(9)	113.5(2)

O(35)-Cd(3)-N(13)	156.6(2)	O(9)-Cd(3)-O(3W)	83.1(3)
O(9)-Cd(3)-N(13)	81.6(2)	O(4W)-Cd(3)-O(3W)	162.7(2)
O(4W)-Cd(3)-N(13)	94.2(3)	N(9)-Cd(3)-O(3W)	82.4(3)
N(9)-Cd(3)-N(13)	71.4(3)	N(13)-Cd(3)-O(3W)	97.5(3)
O(35)-Cd(3)-O(3W)	89.0(3)		

Table S3. Bond lengths (Å) of main atoms for compound **2**.

Mo(1)-O(28)	1.676(6)	Mo(6)-O(1)	1.983(5)
Mo(1)-O(8)	1.923(5)	Mo(6)-O(14)	2.033(5)
Mo(1)-O(1)	1.968(5)	Mo(6)-O(7)	2.113(5)
Mo(1)-O(27)	2.062(5)	Mo(6)-O(25)	2.291(5)
Mo(1)-O(5)	2.111(5)	Co(1)-O(4)#1	2.120(5)
Mo(1)-O(6)	2.256(5)	Co(1)-O(4)	2.120(5)
Mo(2)-O(19)	1.680(6)	Co(1)-O(1)	2.146(5)
Mo(2)-O(10)	1.928(5)	Co(1)-O(1)#1	2.146(5)
Mo(2)-O(2)	1.973(5)	Co(1)-O(2)#1	2.167(5)
Mo(2)-O(17)	2.043(5)	Co(1)-O(2)	2.167(5)
Mo(2)-O(3)	2.120(5)	Co(2)-O(29)	1.937(6)
Mo(2)-O(13)	2.287(5)	Co(2)-O(31)	1.944(6)
Mo(3)-O(21)	1.684(6)	Co(2)-O(20)	1.950(6)
Mo(3)-O(12)	1.936(6)	Co(2)-O(9)	1.951(5)
Mo(3)-O(4)	1.989(5)	P(1)-O(9)	1.500(6)
Mo(3)-O(11)	2.042(6)	P(1)-O(13)	1.542(5)
Mo(3)-O(3)	2.115(5)	P(1)-O(25)	1.544(5)
Mo(3)-O(13)	2.287(5)	P(1)-O(6)	1.550(5)
Mo(4)-O(24)	1.671(5)	P(2)-O(29)	1.502(6)
Mo(4)-O(12)	1.930(6)	P(2)-O(16)	1.527(6)
Mo(4)-O(4)	1.983(5)	P(2)-O(30)	1.537(6)
Mo(4)-O(15)	2.046(6)	P(2)-O(14)	1.542(6)
Mo(4)-O(5)	2.113(5)	P(3)-O(20)#2	1.516(6)
Mo(4)-O(6)	2.292(5)	P(3)-O(27)	1.520(6)
Mo(5)-O(26)	1.676(6)	P(3)-O(15)	1.523(6)
Mo(5)-O(10)	1.944(5)	P(3)-O(18)	1.560(7)
Mo(5)-O(2)	1.989(5)	P(4)-O(31)#3	1.475(7)
Mo(5)-O(16)	2.046(5)	P(4)-O(11)	1.517(6)
Mo(5)-O(7)	2.115(5)	P(4)-O(17)	1.525(6)
Mo(5)-O(25)	2.265(5)	P(4)-O(22)	1.570(7)
Mo(6)-O(23)	1.662(6)		
Mo(6)-O(8)	1.922(5)		

Table S4. Bond angles (°) of main atoms for compound **2**.

O(28)-Mo(1)-O(8)	106.0(3)	O(21)-Mo(3)-O(4)	101.3(3)
O(28)-Mo(1)-O(1)	102.4(3)	O(12)-Mo(3)-O(4)	95.8(2)
O(8)-Mo(1)-O(1)	95.7(2)	O(21)-Mo(3)-O(11)	96.6(3)
O(28)-Mo(1)-O(27)	95.4(3)	O(12)-Mo(3)-O(11)	87.5(2)
O(8)-Mo(1)-O(27)	87.4(2)	O(4)-Mo(3)-O(11)	160.2(2)
O(1)-Mo(1)-O(27)	160.3(2)	O(21)-Mo(3)-O(3)	96.5(3)
O(28)-Mo(1)-O(5)	94.4(3)	O(12)-Mo(3)-O(3)	157.0(2)
O(8)-Mo(1)-O(5)	158.8(2)	O(4)-Mo(3)-O(3)	85.8(2)
O(1)-Mo(1)-O(5)	85.4(2)	O(11)-Mo(3)-O(3)	83.7(2)
O(27)-Mo(1)-O(5)	84.9(2)	O(21)-Mo(3)-O(13)	170.3(2)
O(28)-Mo(1)-O(6)	167.8(2)	O(12)-Mo(3)-O(13)	83.6(2)
O(8)-Mo(1)-O(6)	84.9(2)	O(4)-Mo(3)-O(13)	80.40(19)
O(1)-Mo(1)-O(6)	81.6(2)	O(11)-Mo(3)-O(13)	80.6(2)
O(27)-Mo(1)-O(6)	79.2(2)	O(3)-Mo(3)-O(13)	74.04(19)
O(5)-Mo(1)-O(6)	74.3(2)	O(24)-Mo(4)-O(12)	105.3(3)
O(19)-Mo(2)-O(10)	105.8(3)	O(24)-Mo(4)-O(4)	102.1(3)
O(19)-Mo(2)-O(2)	102.6(3)	O(12)-Mo(4)-O(4)	96.2(2)
O(10)-Mo(2)-O(2)	96.1(2)	O(24)-Mo(4)-O(15)	96.2(3)
O(19)-Mo(2)-O(17)	95.4(3)	O(12)-Mo(4)-O(15)	87.0(2)
O(10)-Mo(2)-O(17)	87.2(2)	O(4)-Mo(4)-O(15)	159.9(2)
O(2)-Mo(2)-O(17)	159.9(2)	O(24)-Mo(4)-O(5)	96.7(3)
O(19)-Mo(2)-O(3)	96.2(2)	O(12)-Mo(4)-O(5)	156.9(2)
O(10)-Mo(2)-O(3)	156.7(2)	O(4)-Mo(4)-O(5)	85.8(2)
O(2)-Mo(2)-O(3)	86.0(2)	O(15)-Mo(4)-O(5)	83.7(2)
O(17)-Mo(2)-O(3)	83.3(2)	O(24)-Mo(4)-O(6)	169.8(2)
O(19)-Mo(2)-O(13)	169.3(2)	O(12)-Mo(4)-O(6)	84.0(2)
O(10)-Mo(2)-O(13)	83.4(2)	O(4)-Mo(4)-O(6)	80.7(2)
O(2)-Mo(2)-O(13)	81.1(2)	O(15)-Mo(4)-O(6)	79.9(2)
O(17)-Mo(2)-O(13)	79.5(2)	O(5)-Mo(4)-O(6)	73.55(19)
O(3)-Mo(2)-O(13)	73.95(19)	O(26)-Mo(5)-O(10)	105.4(3)
O(21)-Mo(3)-O(12)	105.6(3)	O(26)-Mo(5)-O(2)	102.1(3)
O(10)-Mo(5)-O(2)	95.1(2)	O(4)-Co(1)-O(1)#1	83.7(2)
O(26)-Mo(5)-O(16)	97.3(3)	O(1)-Co(1)-O(1)#1	180.0
O(10)-Mo(5)-O(16)	87.0(2)	O(4)#1-Co(1)-O(2)#1	96.42(19)
O(2)-Mo(5)-O(16)	159.1(2)	O(4)-Co(1)-O(2)#1	83.58(19)
O(26)-Mo(5)-O(7)	97.2(2)	O(1)-Co(1)-O(2)#1	83.4(2)
O(10)-Mo(5)-O(7)	156.8(2)	O(1)#1-Co(1)-O(2)#1	96.6(2)

O(2)-Mo(5)-O(7)	85.2(2)	O(4)#1-Co(1)-O(2)	83.58(19)
O(16)-Mo(5)-O(7)	84.9(2)	O(4)-Co(1)-O(2)	96.42(19)
O(26)-Mo(5)-O(25)	170.0(2)	O(1)-Co(1)-O(2)	96.6(2)
O(10)-Mo(5)-O(25)	83.9(2)	O(1)#1-Co(1)-O(2)	83.4(2)
O(2)-Mo(5)-O(25)	80.2(2)	O(2)#1-Co(1)-O(2)	180.0(2)
O(16)-Mo(5)-O(25)	79.4(2)	O(29)-Co(2)-O(31)	101.4(3)
O(7)-Mo(5)-O(25)	73.23(19)	O(29)-Co(2)-O(20)	98.7(3)
O(23)-Mo(6)-O(8)	105.4(3)	O(31)-Co(2)-O(20)	103.7(3)
O(23)-Mo(6)-O(1)	101.7(3)	O(29)-Co(2)-O(9)	123.0(2)
O(8)-Mo(6)-O(1)	95.2(2)	O(31)-Co(2)-O(9)	115.8(3)
O(23)-Mo(6)-O(14)	95.2(3)	O(20)-Co(2)-O(9)	111.5(2)
O(8)-Mo(6)-O(14)	89.2(2)	O(9)-P(1)-O(13)	111.6(3)
O(1)-Mo(6)-O(14)	160.6(2)	O(9)-P(1)-O(25)	110.0(3)
O(23)-Mo(6)-O(7)	98.5(2)	O(13)-P(1)-O(25)	108.7(3)
O(8)-Mo(6)-O(7)	155.1(2)	O(9)-P(1)-O(6)	111.4(3)
O(1)-Mo(6)-O(7)	86.5(2)	O(13)-P(1)-O(6)	107.2(3)
O(14)-Mo(6)-O(7)	81.7(2)	O(25)-P(1)-O(6)	107.9(3)
O(23)-Mo(6)-O(25)	171.0(2)	O(29)-P(2)-O(16)	112.9(4)
O(8)-Mo(6)-O(25)	83.1(2)	O(29)-P(2)-O(30)	109.1(3)
O(1)-Mo(6)-O(25)	80.0(2)	O(16)-P(2)-O(30)	106.0(3)
O(14)-Mo(6)-O(25)	81.9(2)	O(29)-P(2)-O(14)	110.6(4)
O(7)-Mo(6)-O(25)	72.73(19)	O(16)-P(2)-O(14)	110.4(3)
O(4)#1-Co(1)-O(4)	180.0	O(30)-P(2)-O(14)	107.6(3)
O(4)#1-Co(1)-O(1)	83.7(2)	O(20)#2-P(3)-O(27)	110.1(4)
O(4)-Co(1)-O(1)	96.3(2)	O(20)#2-P(3)-O(15)	107.3(3)
O(4)#1-Co(1)-O(1)#1	96.3(2)	O(27)-P(3)-O(15)	112.5(3)
O(11)-P(4)-O(17)	112.2(3)	O(17)-P(4)-O(22)	106.6(4)
O(31)#3-P(4)-O(22)	109.1(4)	O(20)#2-P(3)-O(18)	110.1(4)
O(11)-P(4)-O(22)	106.4(4)	O(27)-P(3)-O(18)	109.1(4)
O(31)#3-P(4)-O(11)	109.6(4)	O(15)-P(3)-O(18)	107.7(4)
O(31)#3-P(4)-O(17)	112.7(4)		

Table S5. Hydrogen bonds for compound **1** [Å and °].

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1WA···O21	0.87	2.36	3.091(9)	141
O1W—H1WA···O13W	0.87	2.48	3.22(2)	143
O1W—H1WB···O10W	0.87	2.01	2.858(19)	165
N2—H2A···O31	0.86	2.46	3.225(8)	147
N2—H2B···O8	0.86	2.13	2.981(9)	170
O2W—H2WA···N12	0.87	2.07	2.938(12)	173
N3—H3A···O5W	0.86	1.98	2.842(9)	168
O2W—H2WB···O1A	0.85	2.02	2.689(9)	133
O3W—H3WA···O11	0.91	1.84	2.738(10)	171
O3W—H3WB···O7W	0.90	2.44	3.116(14)	132
O3W—H3WB···O8WA	0.90	2.19	2.99(4)	146
O4W—H4WA···O5W	0.90	1.88	2.735(8)	158
N7—H7A···O19	0.86	2.29	2.976(9)	136
N7—H7A···O33	0.86	2.38	3.004(9)	129
O4W—H4WB···O5W	0.92	2.12	2.761(8)	126
N8—H8A···O9W	0.86	2.37	2.976(18)	128
N8—H8B···O16	0.86	2.38	3.160(9)	151
N8—H8B···O19	0.86	2.43	3.108(10)	137
O5W—H5WB···O28	0.83	2.30	2.887(9)	129
N10—H10A···O35	0.86	2.30	3.059(11)	148
N10—H10B···O30	0.86	2.36	3.155(11)	154
N11—H11A···O6W	0.86	1.92	2.782(13)	176
O11W—H11B···O27	0.85	2.56	3.31(2)	147
O12W—H12B···O6W	0.86	2.57	3.35(2)	150
O7W—H7WA···O9WA	0.83	1.92	2.67(3)	148
O7W—H7WA···O8WA	0.83	1.99	2.78(4)	158
N15—H15A···O14W	0.86	1.91	2.75(3)	168
O8W—H8WB···O31	0.83	1.92	2.727(14)	163
N16—H16B···O9	0.86	2.32	3.003(16)	137
O9W—H9WA···O7W	0.83	2.06	2.63(2)	125
O34—H34···O13W	0.85	1.91	2.57(2)	134

Table S6. Hydrogen bonds for compound **2** [Å and °].

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O5	0.86	2.00	2.860(16)	175
N2—H2···O3	0.86	2.02	2.850(11)	163
N3—H3A···O7	0.86	2.11	2.932(8)	159
N4—H4···O20	0.86	2.02	2.854(5)	163
N6—H6A···O9	0.86	2.32	3.126(10)	156
C1A—H1AA ···O12	0.96	2.13	2.858(15)	132
C1A—H1AA···O15	0.96	2.48	3.087(15)	121
C4—H4A···O24	0.93	2.60	3.40(2)	144
C5—H5···O24	0.93	2.38	3.205(10)	147
C2A—H2AB··· N5	0.97	2.50	3.347(15)	146
C6—H6···O30	0.93	2.48	3.349(12)	155
C8—H8···O18	0.93	2.32	3.028(11)	133
C8—H8···O8	0.93	2.19	2.830(10)	125
C8—H8···O27	0.93	2.31	2.916(9)	122
C9—H9···O22	0.93	2.21	2.881(3)	128

Table S7. Proton conductivities of the reported POM-based materials.

Compound	Condition (Temp., RH)	Conductivity [S cm^{-1}]	Ref
$(Na_8K_4(H_2pip)_8H_{21}[\{Cu(pip)_2\}_{52}\{La_{29}Ge_{10}W_{106}O_{406}(OH)_4(H_2O)_{28}\}]$	85 °C, 98%	5.3×10^{-3}	1
$(C_2H_6O)(C_3H_5N_2)_6[Co_3(H_6P_4Mo_6O_{31})_2]\bullet H_2O$	**60 °C, 98%**	**3.78×10^{-3}**	**This work**
$\{[Cu(H_2bpdc)(H_2O)_{2.5}]_2[SiW_{12}O_{40}]\}\cdot10H_2O$	100 °C, 98%	1.77×10^{-3}	2
$[Co(bpz)(Hbpz)][Co(SO_4)_{0.5}(H_2O)_2(bpz)]_4[PMo^{VI}_8Mo^{V}_4V^{IV}_4O_{42}]\cdot13H_2O$	75 °C,98%	1.5×10^{-3}	3
$\{H[Ni(Hbpdc)(H_2O)_2]_2[PW_{12}O_{40}]\cdot8H_2O\}_n$	100 °C,98%	1.35×10^{-3}	4
$[M(H_2O)_8][H(H_2O)_{2\text{-}3}](HINO)_4[PXO_{40}]$ M=Zn, Mn, Cu; X=W, Mo	100 °C,98%	1.3×10^{-3}	5
$Na_5[H_7\{N(CH_2PO_3)_3\}Mo_6O_{16}(OH)(H_2O)_4]_4$	60 °C, 98%	7.6×10^{-4}	6
$\{[Cu_3(L)_2(H_2O)_4][Cu(DMF)_4(SiW_{12}O_{40})]\cdot9H_2O\}_n$	100 °C, 98%	5.97×10^{-4}	7
$[Zn_{12}(trz)_{20}][SiW_{12}O_{40}]\cdot11H_2O$	95 °C, 95%	1.2×10^{-4}	8
$[Cu_{12}(BTC)_8(H_2O)_{12}][H_3PW_{12}O_{40}]\cdot nH_2O$	90 °C, 70%	4.76×10^{-5}	9
$[Cu(phen)(H_2O)]_3[P_2Mo_5O_{23}]\cdot5H_2O$	28 °C, 98%	2.2×10^{-5}	10
$[H_2en]_4[Ni_5(OH)_3(trzS)_3(en)(H_2O)(PW_9O_{34})]\cdot6H_2O$	85 °C, 98%	1.3×10^{-5}	11
$Cu_6(Trz)_{10}(H_2O)_4[H_2SiW_{12}O_{40}]\cdot8H_2O$	95 °C, 95%	1.84×10^{-6}	12

Table S8. CO_2 photoreduction of the reported POM-based materials.

Catalyst	Main product	Side product	Efficiency of main product (μmol g^{-1})	Ref
$[Co_{2.67}(SiW_{12}O_{40})(H_2O)_4(Htrz)_4]\cdot Cl_{1.33}$	CO	H_2	15705	13
$(C_2H_6O)(C_3H_5N_2)_6[Co_3(H_6P_4Mo_6O_{31})_2]\bullet H_2O$	**CO**	**None**	5789	**This work**
$Na_{10}Co_4(H_2O)_2(PW_9O_{34})_2$@g-$C_3N_4$	CO	H_2	896	14
$K_4Na_{28}[\{Co_4(O\text{-}H)_3(VO_4)\}_4(SiW_9O_{34})_4]\cdot 66H_2O$	CO	H_2	839.2	15
Au@ $[Cu_2(BTC)_{4/3}(H_2O)_2]_6[H_5PTi_2W_{10}O_{40}]\cdot(C_4H_{12}N)_2\cdot 24H_2O$	CO	CH_4	64	16
$(H_2bib)_{2.5}\{HCo[Mo_6O_{14}(OH)(HPO_4)_4]_2\}\cdot 4H_2O$	CO	CH_4	10.76	17
$H\{[Na_6CoMn_3(PO_4)(H_2O)_4]_3\{[Mo_6O_{12}(OH)_3(HPO_4)_3(PO_4)]_4[Co_{1.5}Mn_{4.5}]\}\cdot 21H_2O$	CH_4	CO	40.2	18

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