Supporting Information

Two Three-Dimensional Polyanionic Clusters $[M(P_4Mo_6)_2]$ (M = Co, Zn) Exhibiting Excellent Photocatalytic CO_2 Reduction Performance

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Photoluminescence Properties

The solid-state emission/excitation spectra were measured with an FP-6500 spectrofluorimeter equipped with a 450 W xenon lamp as the excitation source. As shown in Fig. S1, compound **2** exhibits photoluminescence with an emission maximum at 420 nm upon excitation at 201 nm. Based on emission spectrum of bbi ligand in room temperature exhibiting one emmision maximun at 398 nm.[1,2] In contrast to free ligands, red shifts of 22 nm have been observed upon the formation of compound **2** and the maximun emission band of **2** dose not belong to intraligands charge transfer while should be possibly assigned to ligand-to-metal charge transfer.

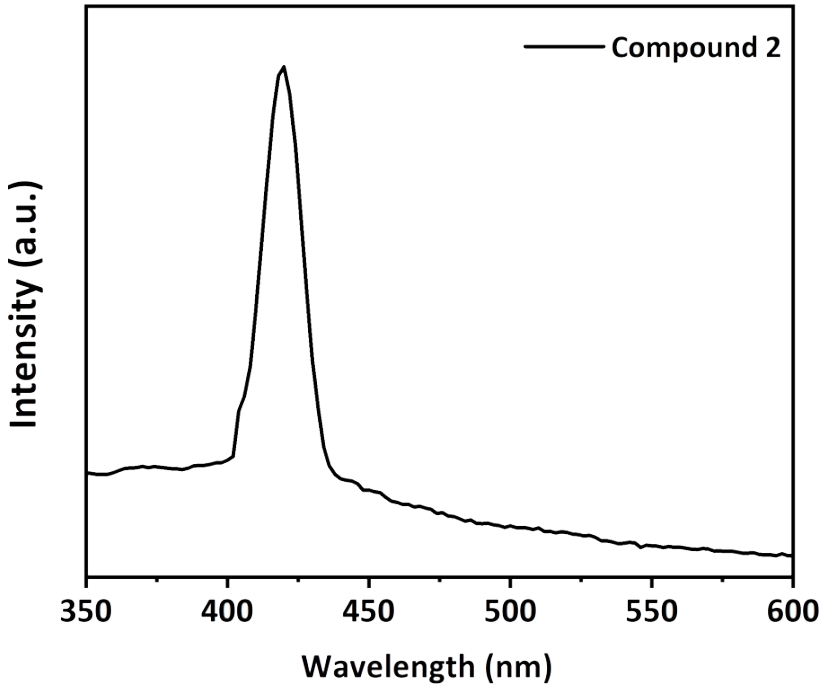

Fig. S1 Solid-state photoluminescent spectra of **2** at room temperature.

Experimental Section

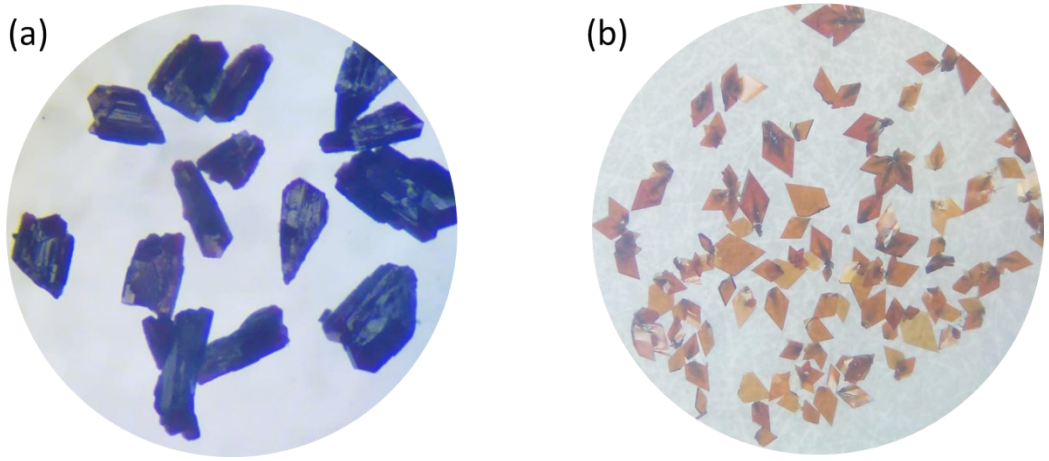

Fig. S2 The images of compounds **1** and **2** under optical microscope.

Structure

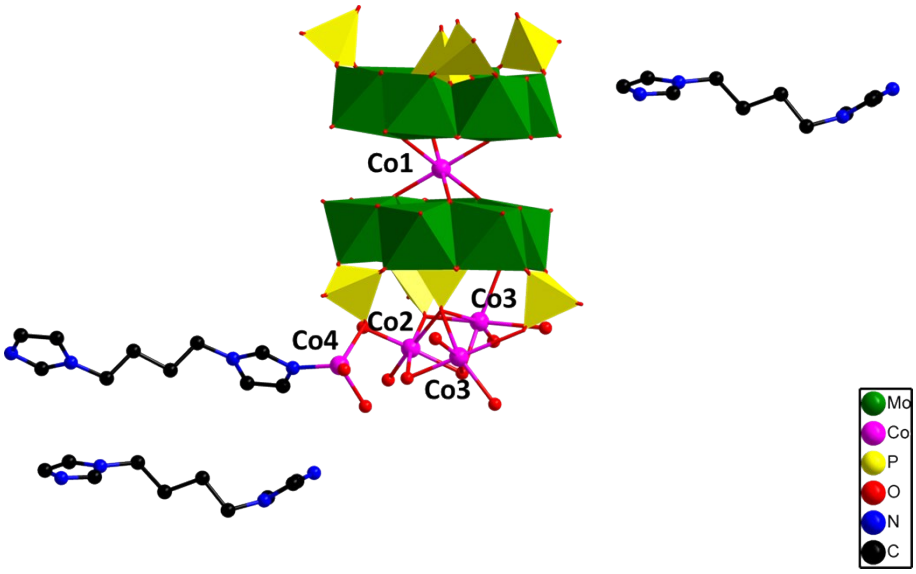

Fig. S3 The basic unit of compound **1**.

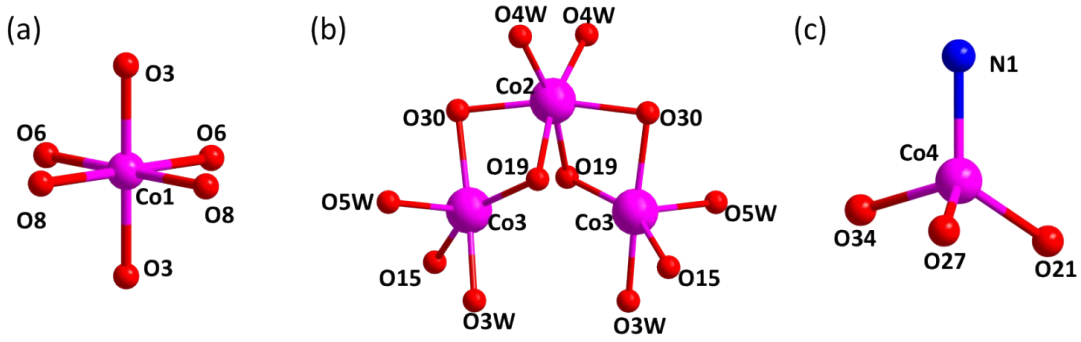

Fig. S4 The coordination mode of Co atoms of compound **1**.

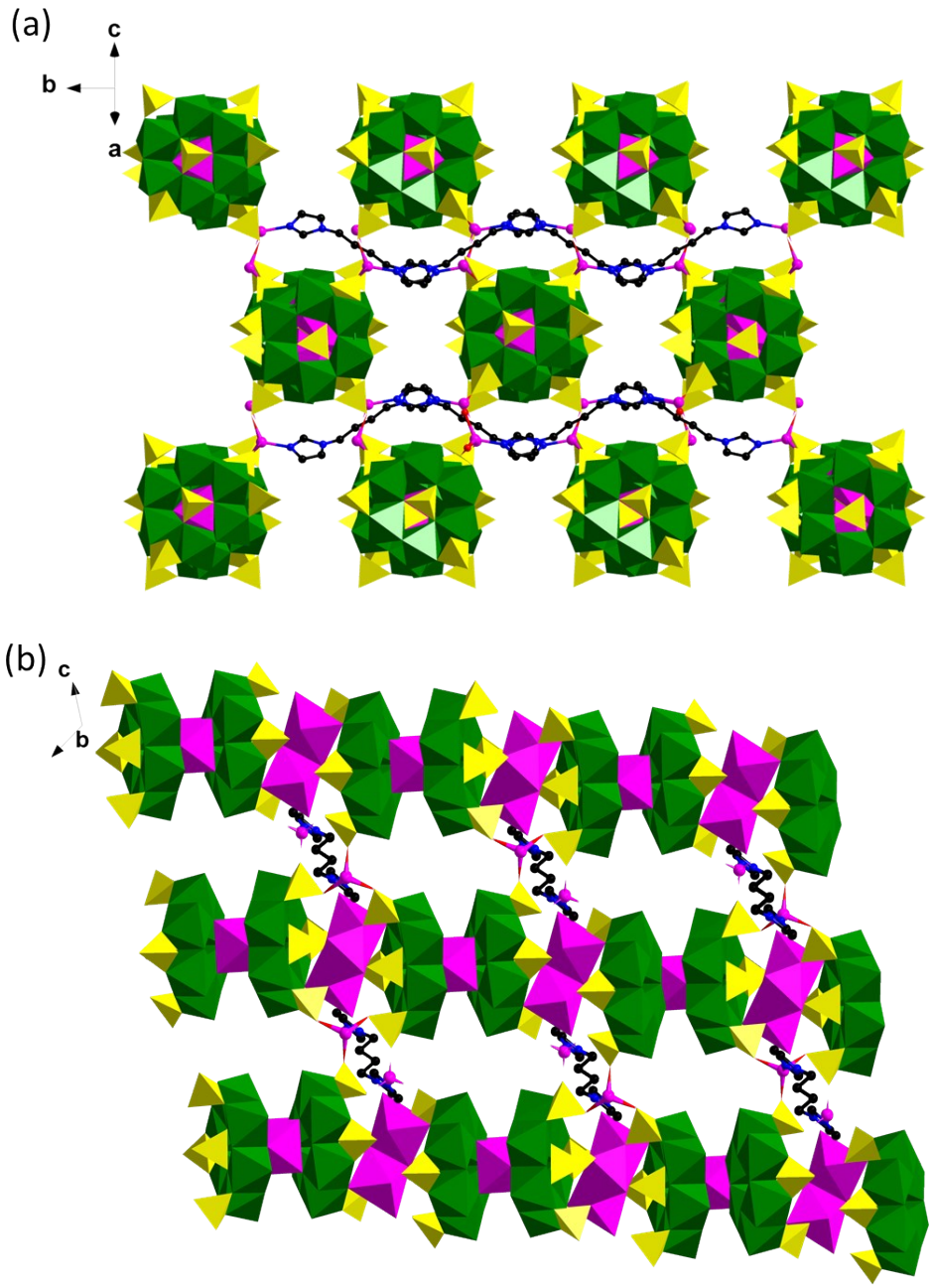

Fig. S5 Different views of the 3D perspective of compound **1**.

Topological structure of compound 1. As shown in Fig. S6, each $[H_{9.33}CoP_8Mo_{12}O_{62}]$ polyoxoanion and three Co^{2+} are regarded as a node, connected to each other to form an infinite inorganic chain. The adjacent 1D chains were linked by $\{Co_2P_2\}$ units (Co4) to form a 2D layer. Furthermore, bbi act as a bridging ligands by providing two apical N donors to coordinate with Co4 atoms, staggered connection to form a 4,8-connected 3D framework.

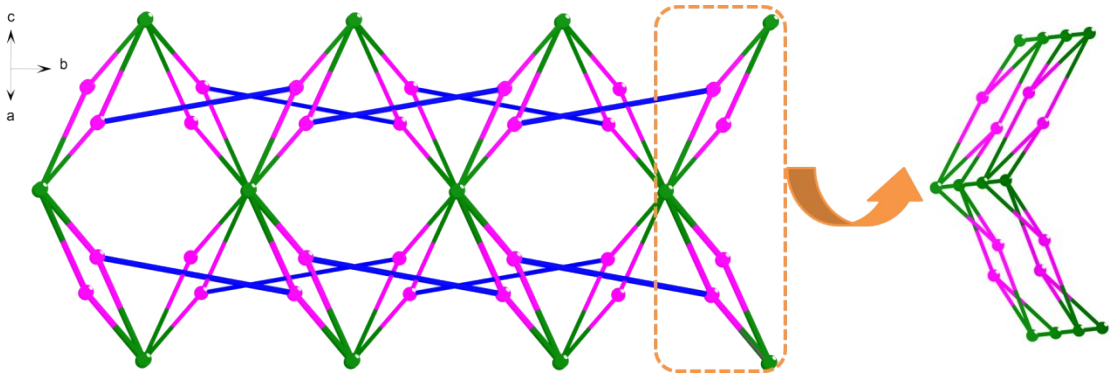

Fig. S6 Topological view of the 3D framework in **1**. Color code: pink balls, Co4 bridges; green balls, {[$H_{9.33}CoP_8Mo_{12}O_{62}$][$Co_{2.33}(H_2O)_4$]} nodes; green rods, schematic view of the 1D chain; blue rods, bbi linkers.

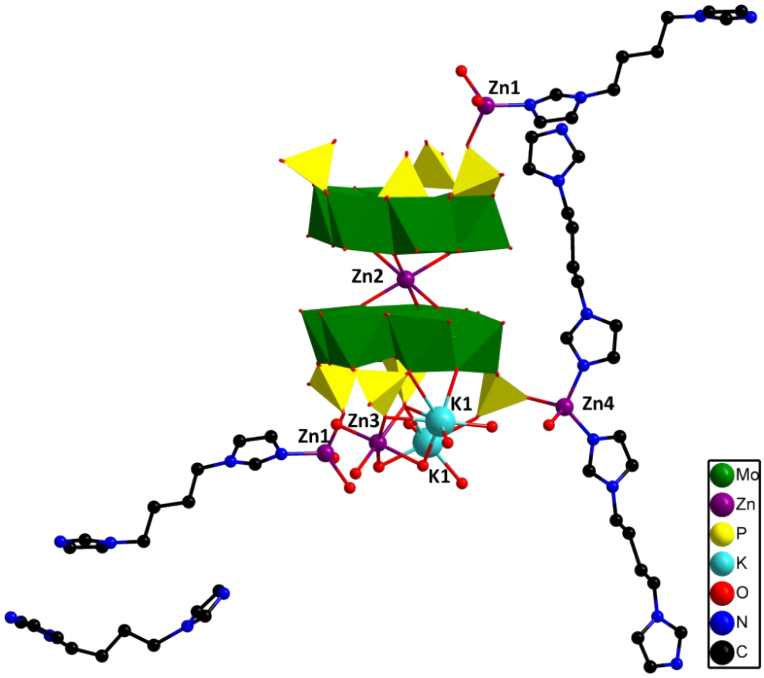

Fig. S7 The basic unit of compound **2**.

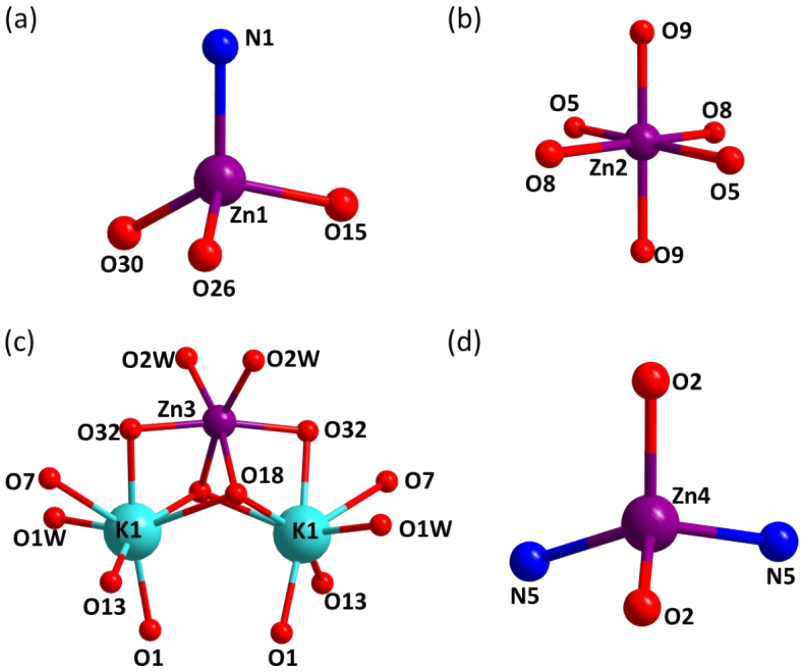

Fig. S8 The coordination mode of Zn atoms of compound **2**.

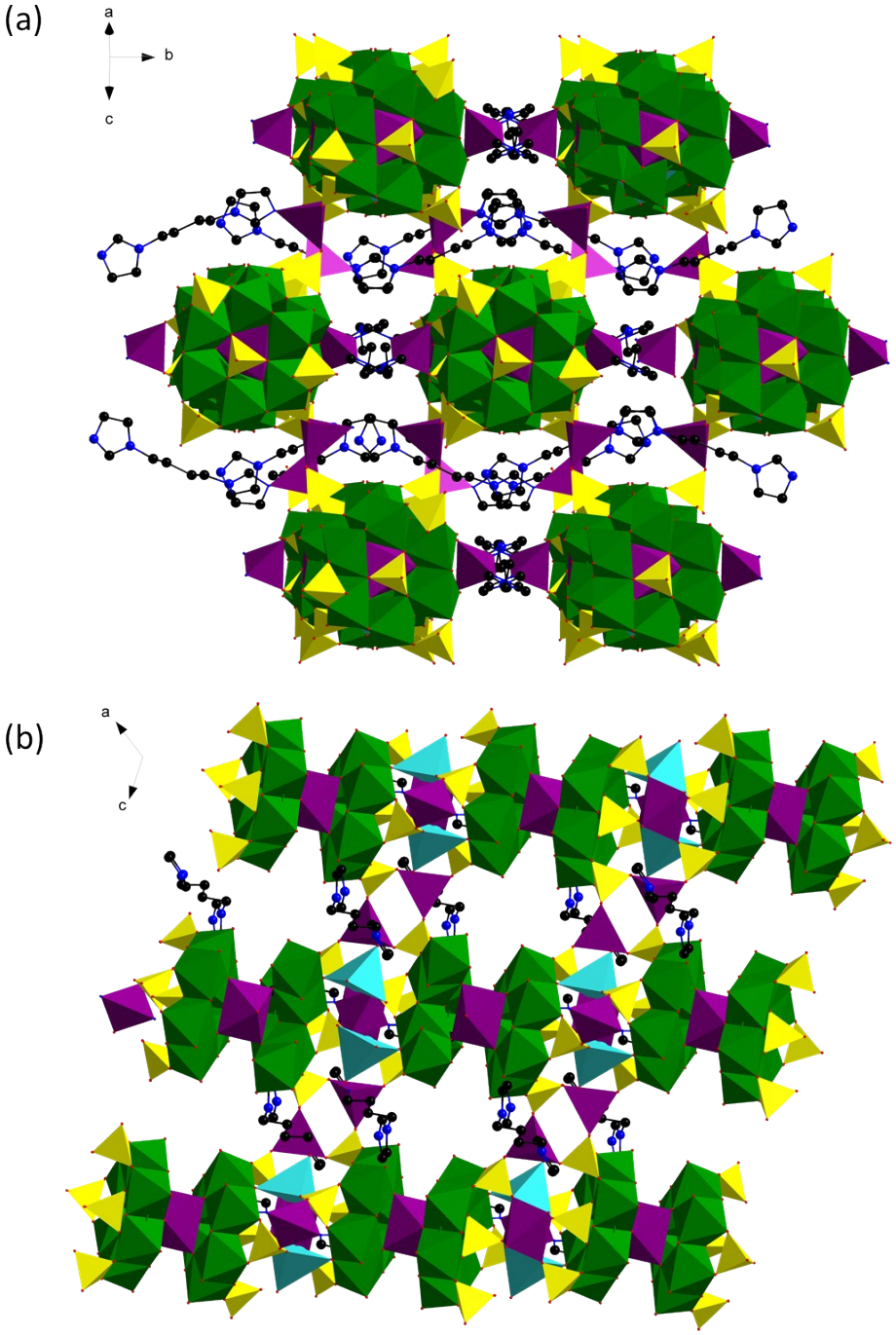

Fig. S9 Different views of the 3D perspective of compound **2**.

IR spectra

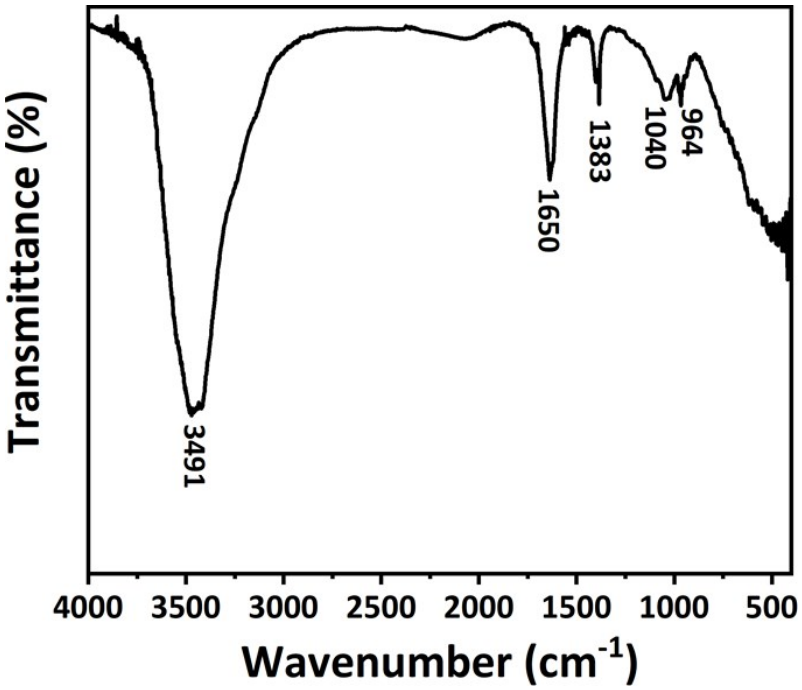

Fig. S10 IR spectra of compound **1**.

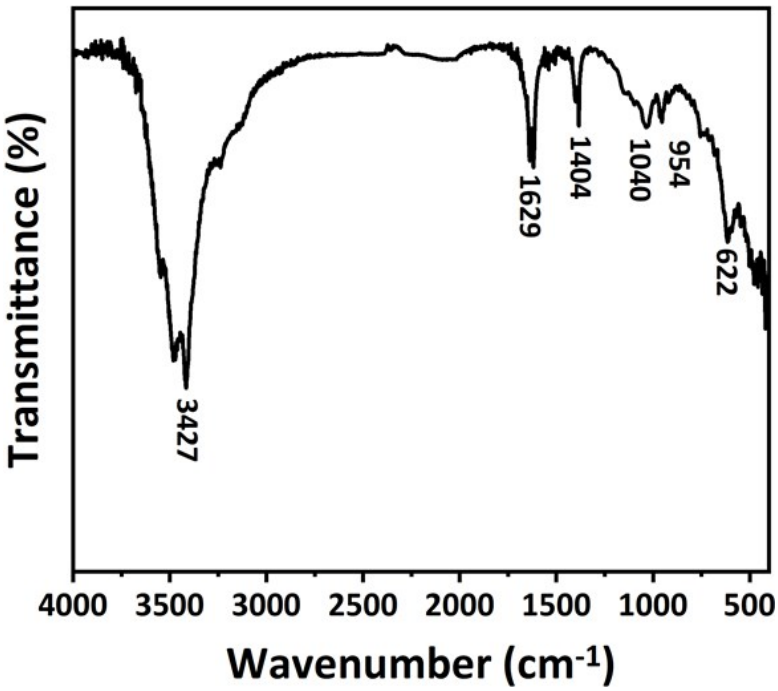

Fig. S11 IR spectra of compound **2**.

PXRD patterns

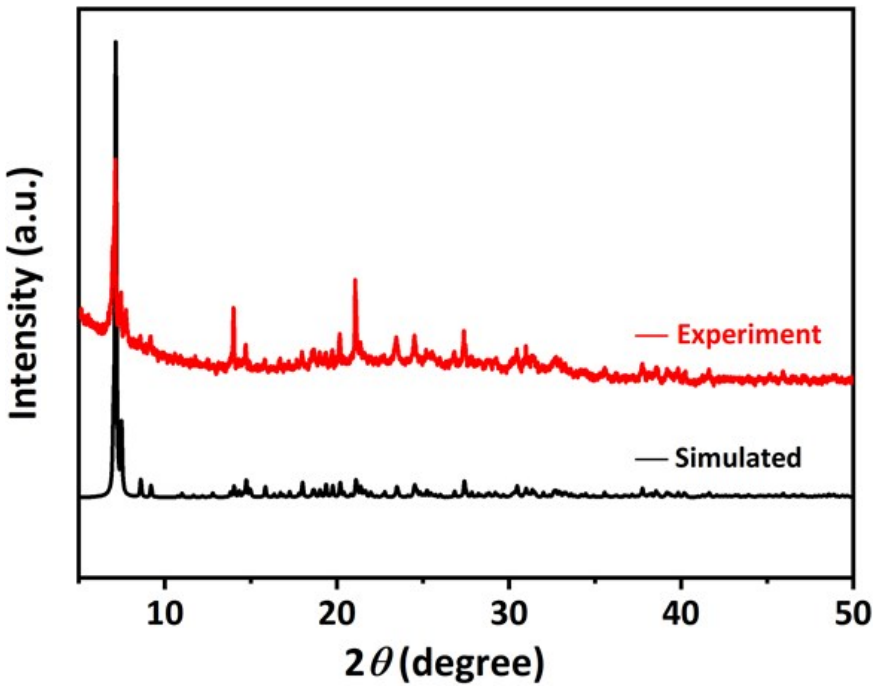

Fig. S12 PXRD patterns of compound **1**.

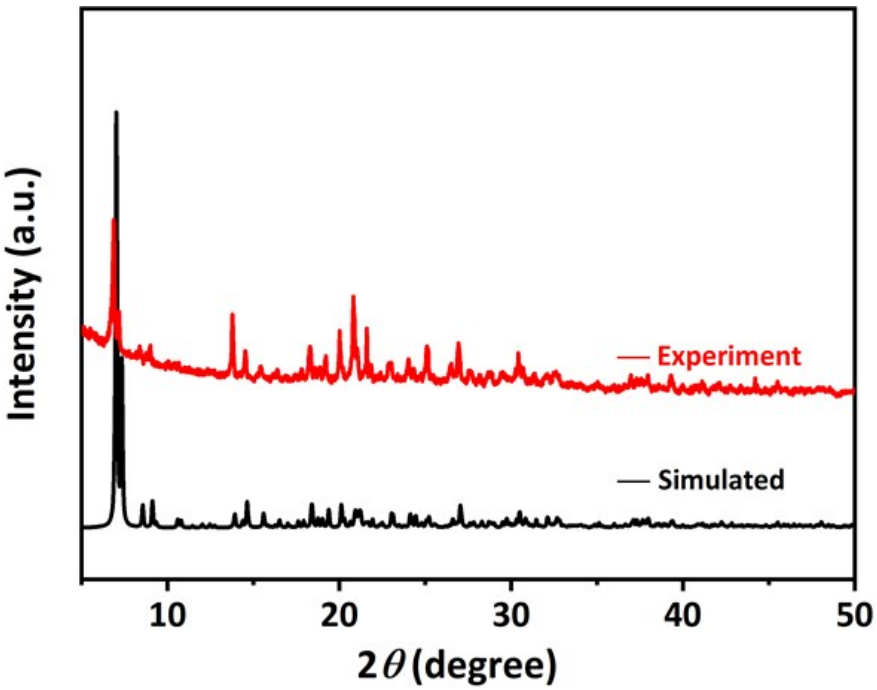

Fig. S13 PXRD patterns of compound **2**.

TG

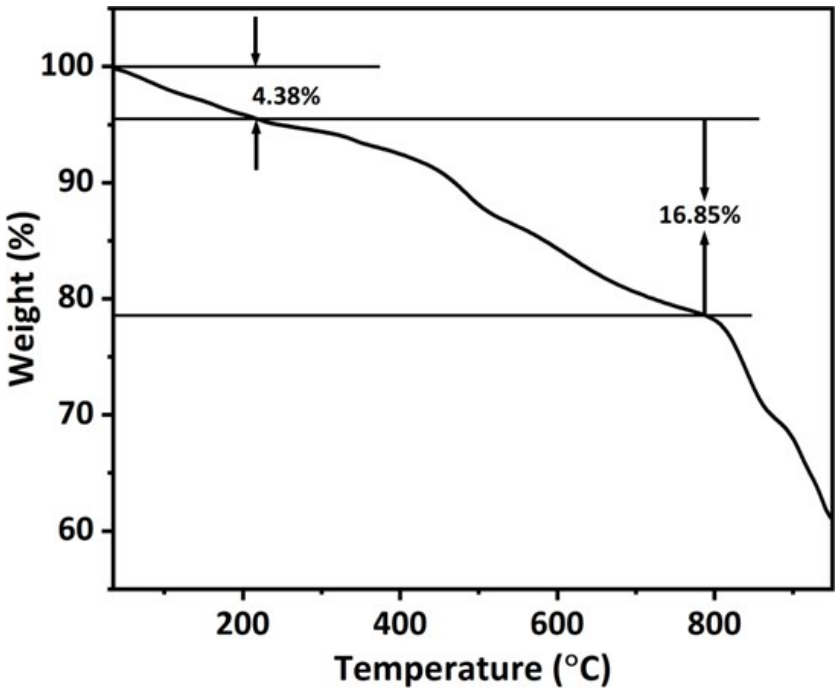

Fig. S14 TG curve of compound **1**.

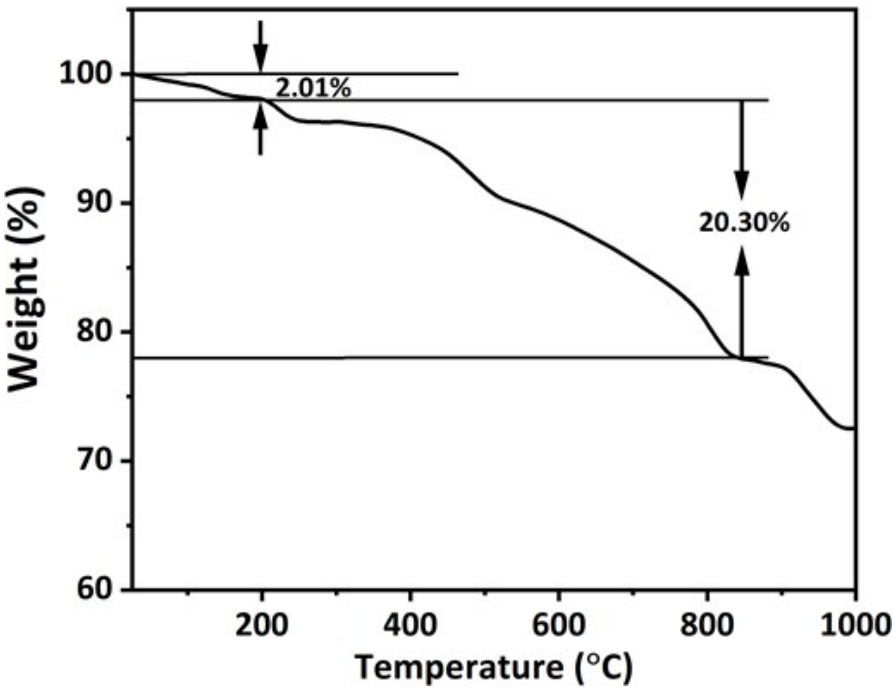

Fig. S15 TG curve of compound **2**.

Stability Test

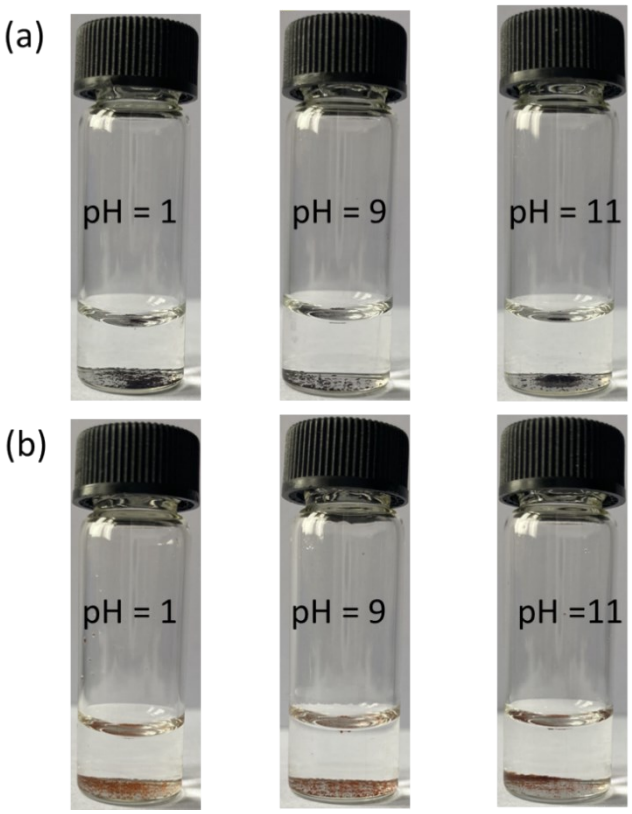

Fig. S16 The Images of compounds **1** and **2** soaked for 24 hours at different pH conditions.

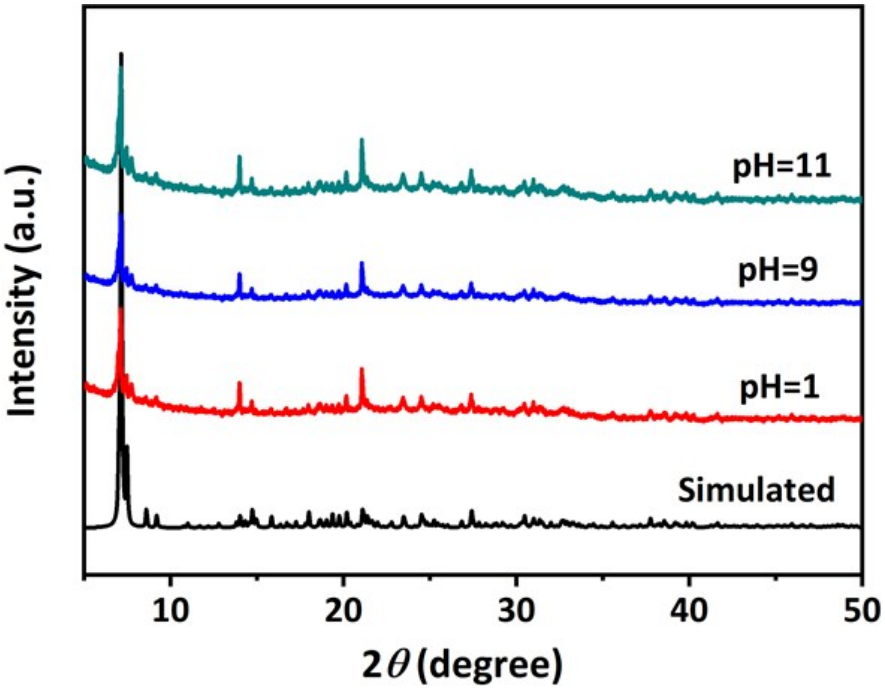

Fig. S17 The PXRD patterns of compound 1 in different solutions compared with simulated curves.

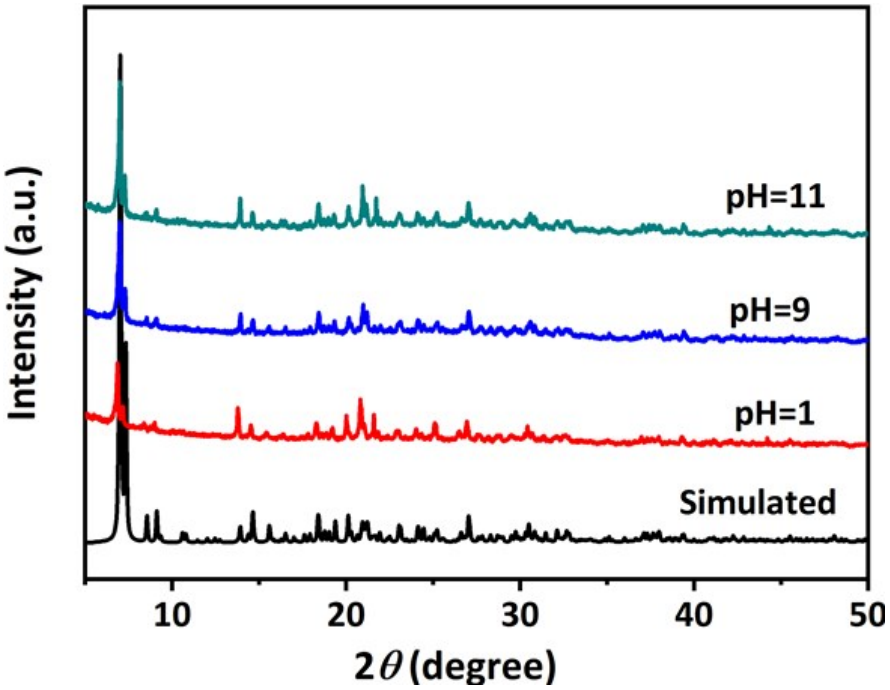

Fig. S18 The PXRD patterns of compound **2** in different solutions compared with simulated curves.

SEM and EDS

The as-prepared compounds **1** and **2** exhibited a morphology of block-shaped crystals and rhomboid-massive shaped crystals based on the SEM, respectively (Figure S19). The energy-dispersive spectrometry (EDS) data of the two compounds prove that C, N, O, P and transition metal elements are present (Figures S20 and S21).

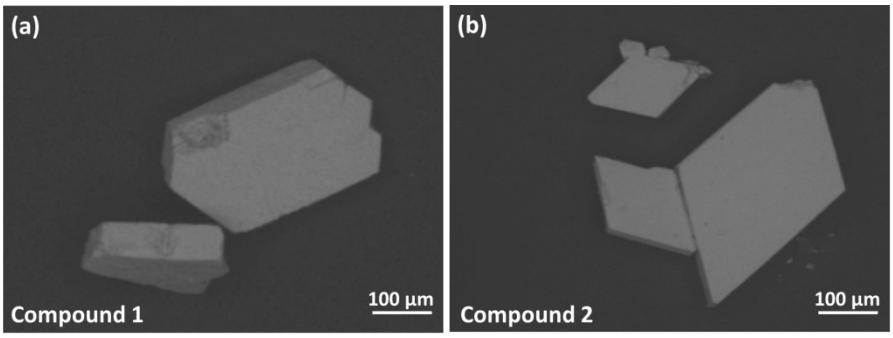

Fig. S19 SEM images of compound **1** (a) and compound **2** (b).

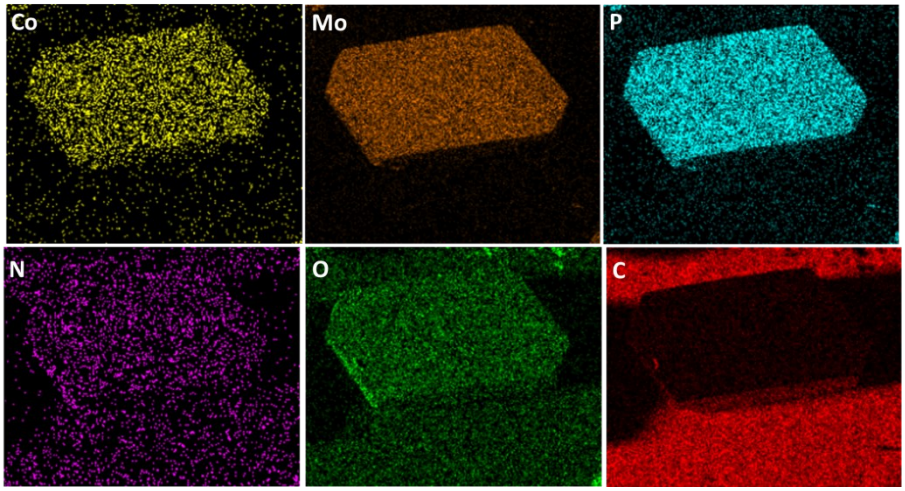

Fig. S20 EDS mapping images of compound **1**.

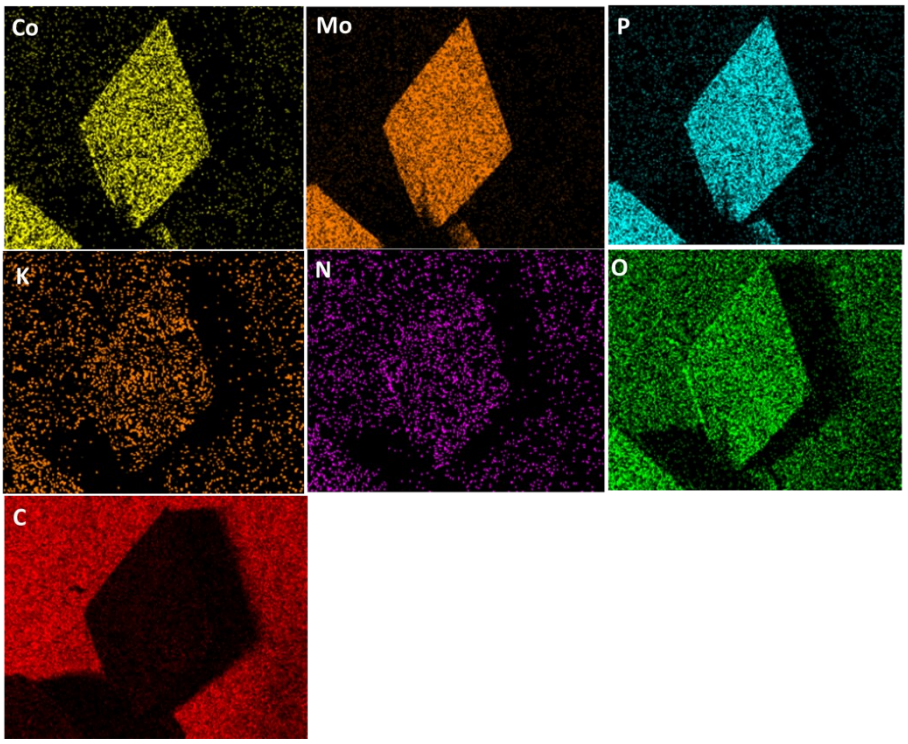

Fig. S21 EDS mapping images of compound 2.

Photographs of the CO_2 reduction devices

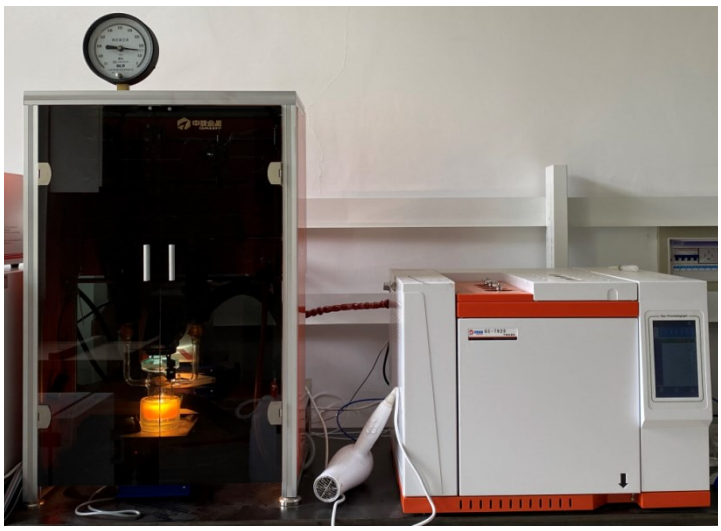

Fig. S22 Photographs of the photocatalytic CO_2 reduction devices.

GC profiles

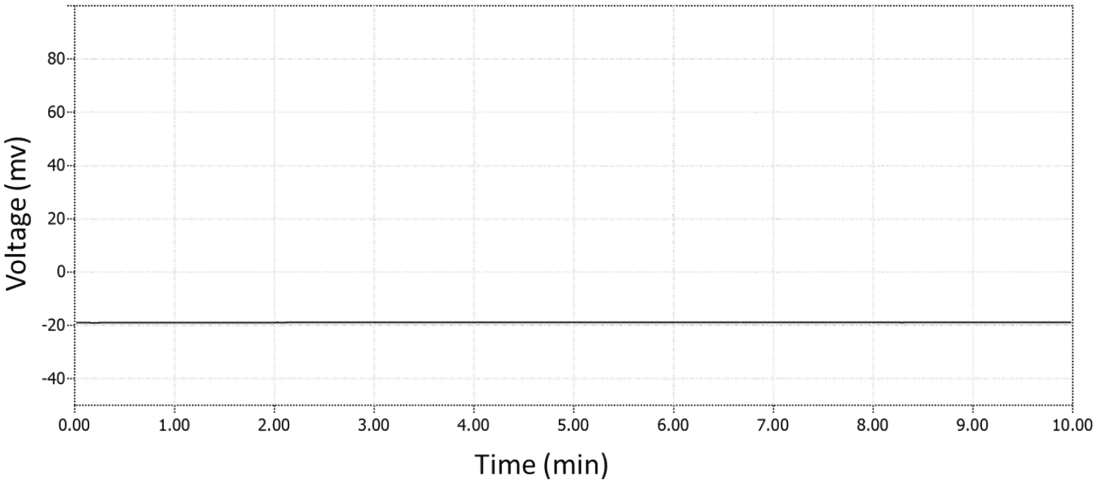

Fig. S23 GC profiles of the gaseous reaction products with compound **1** as catalyst by using the TCD.

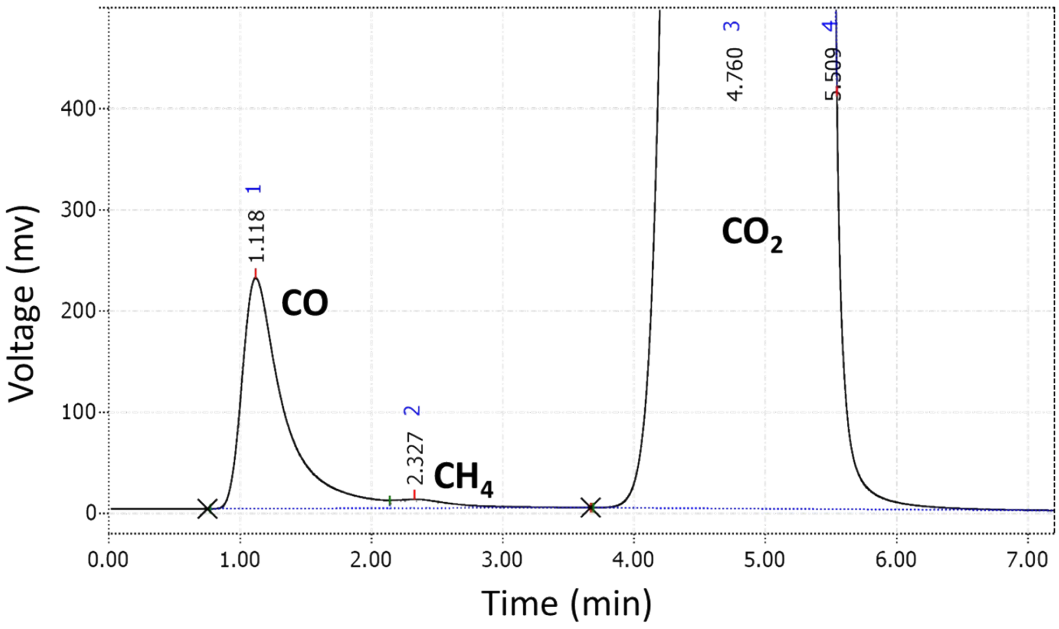

Fig. S24 GC profiles of CO_2 reduction to CO with compound **1** as catalyst after reaction 8 h.

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

Mo(1)-O(18)	1.674(6)	Co(1)-O(3)#1	2.155(6)
Mo(1)-O(14)	1.931(6)	Co(1)-O(6)	2.186(5)
Mo(1)-O(3)	1.982(6)	Co(1)-O(6)#1	2.186(5)
Mo(1)-O(7)	2.084(6)	Co(2)-O(4W)	2.066(7)
Mo(1)-O(4)	2.102(6)	Co(2)-O(4W)#2	2.066(7)
Mo(1)-O(12)	2.283(6)	Co(2)-O(30)	2.105(7)
Mo(2)-O(20)	1.673(6)	Co(2)-O(30)#2	2.105(7)
Mo(2)-O(10)	1.928(6)	Co(2)-O(19)#2	2.174(6)
Mo(2)-O(8)	1.987(5)	Co(2)-O(19)	2.174(6)
Mo(2)-O(17)	2.048(6)	Co(3)-O(3W)	2.004(17)
Mo(2)-O(13)	2.112(6)	Co(3)-O(19)#2	2.167(6)
Mo(2)-O(9)	2.264(6)	Co(3)-O(30)	2.181(7)
Mo(3)-O(32)	1.682(6)	Co(3)-O(5W)	2.247(11)
Mo(3)-O(14)	1.946(6)	Co(3)-O(15)	2.283(8)
Mo(3)-O(3)	1.975(6)	Co(4)-O(21)	1.941(7)
Mo(3)-O(11)	2.040(6)	Co(4)-O(34)	1.942(7)
Mo(3)-O(5)	2.097(6)	Co(4)-O(27)	1.966(6)
Mo(3)-O(25)	2.328(5)	Co(4)-N(1)	1.981(8)
Mo(4)-O(29)	1.675(7)	P(1A)-O(31)	1.459(9)
Mo(4)-O(10)	1.937(6)	P(1A)-O(24)	1.575(9)
Mo(4)-O(8)	1.973(6)	P(1A)-O(1)	1.578(15)
Mo(4)-O(28)	2.037(6)	P(1A)-O(7)	1.652(9)
Mo(4)-O(5)	2.089(6)	P(1B)-O(7)	1.454(8)
Mo(4)-O(25)	2.375(6)	P(1B)-O(2)	1.501(9)
Mo(5)-O(26)	1.687(7)	P(1B)-O(31)	1.571(9)
Mo(5)-O(15)	1.945(6)	P(1B)-O(24)	1.641(10)
Mo(5)-O(6)	1.981(5)	P(2)-O(19)	1.516(6)
Mo(5)-O(23)	2.046(6)	P(2)-O(25)	1.531(6)
Mo(5)-O(13)	2.084(6)	P(2)-O(9)	1.546(6)
Mo(5)-O(9)	2.281(6)	P(2)-O(12)	1.553(6)
Mo(6)-O(33)	1.677(8)	P(3)-O(28)	1.532(7)
Mo(6)-O(15)	1.951(7)	P(3)-O(21)#3	1.533(7)
Mo(6)-O(6)	1.969(6)	P(3)-O(11)	1.537(7)
Mo(6)-O(24)	2.081(7)	P(3)-O(27)	1.540(7)
Mo(6)-O(4)	2.085(6)	P(4)-O(30)	1.526(7)
Mo(6)-O(12)	2.264(6)	P(4)-O(34)#2	1.528(7)
Co(1)-O(8)#1	2.112(6)	P(4)-O(17)	1.537(7)
Co(1)-O(8)	2.112(6)	P(4)-O(23)	1.541(8)
Co(1)-O(3)	2.155(6)		

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

O(18)-Mo(1)-O(14)	105.1(3)	O(6)-Mo(5)-O(13)	86.3(2)
O(18)-Mo(1)-O(3)	102.4(3)	O(23)-Mo(5)-O(13)	84.2(3)
O(14)-Mo(1)-O(3)	95.8(3)	O(26)-Mo(5)-O(9)	172.1(3)
O(18)-Mo(1)-O(7)	95.2(3)	O(15)-Mo(5)-O(9)	81.5(3)
O(14)-Mo(1)-O(7)	87.5(3)	O(6)-Mo(5)-O(9)	79.9(2)
O(3)-Mo(1)-O(7)	160.4(2)	O(23)-Mo(5)-O(9)	80.3(2)
O(18)-Mo(1)-O(4)	98.5(3)	O(13)-Mo(5)-O(9)	73.7(2)
O(14)-Mo(1)-O(4)	155.2(2)	O(33)-Mo(6)-O(15)	105.4(4)
O(3)-Mo(1)-O(4)	86.4(2)	O(33)-Mo(6)-O(6)	102.0(4)
O(7)-Mo(1)-O(4)	82.7(3)	O(15)-Mo(6)-O(6)	95.4(3)
O(18)-Mo(1)-O(12)	170.8(3)	O(33)-Mo(6)-O(24)	95.8(4)
O(14)-Mo(1)-O(12)	83.1(2)	O(15)-Mo(6)-O(24)	86.2(3)
O(3)-Mo(1)-O(12)	80.5(2)	O(6)-Mo(6)-O(24)	160.9(3)
O(7)-Mo(1)-O(12)	80.8(2)	O(33)-Mo(6)-O(4)	98.0(3)
O(4)-Mo(1)-O(12)	72.8(2)	O(15)-Mo(6)-O(4)	155.7(3)
O(20)-Mo(2)-O(10)	104.2(3)	O(6)-Mo(6)-O(4)	85.9(2)
O(20)-Mo(2)-O(8)	102.9(3)	O(24)-Mo(6)-O(4)	84.9(3)
O(10)-Mo(2)-O(8)	95.6(3)	O(33)-Mo(6)-O(12)	170.2(3)
O(20)-Mo(2)-O(17)	98.4(3)	O(15)-Mo(6)-O(12)	82.6(3)
O(10)-Mo(2)-O(17)	84.8(3)	O(6)-Mo(6)-O(12)	82.5(2)
O(8)-Mo(2)-O(17)	158.0(2)	O(24)-Mo(6)-O(12)	78.9(3)
O(20)-Mo(2)-O(13)	94.7(3)	O(4)-Mo(6)-O(12)	73.5(2)
O(10)-Mo(2)-O(13)	159.8(2)	O(8)#1-Co(1)-O(8)	180
O(8)-Mo(2)-O(13)	86.9(2)	O(8)#1-Co(1)-O(3)	84.7(2)
O(17)-Mo(2)-O(13)	85.6(3)	O(8)-Co(1)-O(3)	95.3(2)
O(20)-Mo(2)-O(9)	168.0(3)	O(8)#1-Co(1)-O(3)#1	95.3(2)
O(10)-Mo(2)-O(9)	87.1(2)	O(8)-Co(1)-O(3)#1	84.7(2)
O(8)-Mo(2)-O(9)	79.4(2)	O(3)-Co(1)-O(3)#1	180
O(17)-Mo(2)-O(9)	78.6(2)	O(8)#1-Co(1)-O(6)	84.0(2)
O(13)-Mo(2)-O(9)	73.6(2)	O(8)-Co(1)-O(6)	96.0(2)
O(32)-Mo(3)-O(14)	104.4(3)	O(3)-Co(1)-O(6)	96.0(2)
O(32)-Mo(3)-O(3)	102.3(3)	O(3)#1-Co(1)-O(6)	84.0(2)
O(14)-Mo(3)-O(3)	95.5(2)	O(8)#1-Co(1)-O(6)#1	96.0(2)
O(32)-Mo(3)-O(11)	97.1(3)	O(8)-Co(1)-O(6)#1	84.0(2)
O(14)-Mo(3)-O(11)	88.8(3)	O(3)-Co(1)-O(6)#1	84.0(2)
O(3)-Mo(3)-O(11)	158.3(3)	O(3)#1-Co(1)-O(6)#1	96.0(2)
O(32)-Mo(3)-O(5)	96.8(3)	O(6)-Co(1)-O(6)#1	180
O(14)-Mo(3)-O(5)	158.1(2)	O(4W)-Co(2)-O(4W)#2	95.1(4)
O(3)-Mo(3)-O(5)	85.2(2)	O(4W)-Co(2)-O(30)	84.0(3)
O(11)-Mo(3)-O(5)	83.0(3)	O(4W)#2-Co(2)-O(30)	104.5(3)
O(32)-Mo(3)-O(25)	170.2(3)	O(4W)-Co(2)-O(30)#2	104.5(3)
O(14)-Mo(3)-O(25)	83.7(2)	O(4W)#2-Co(2)-O(30)#2	84.0(3)

O(3)-Mo(3)-O(25)	82.0(2)	O(30)-Co(2)-O(30)#2	167.5(4)
O(11)-Mo(3)-O(25)	77.3(2)	O(4W)-Co(2)-O(19)#2	92.5(2)
O(5)-Mo(3)-O(25)	74.7(2)	O(4W)#2-Co(2)-O(19)#2	167.6(3)
O(29)-Mo(4)-O(10)	104.3(3)	O(30)-Co(2)-O(19)#2	86.0(2)
O(29)-Mo(4)-O(8)	102.3(3)	O(30)#2-Co(2)-O(19)#2	84.6(2)
O(10)-Mo(4)-O(8)	95.7(3)	O(4W)-Co(2)-O(19)	167.6(3)
O(29)-Mo(4)-O(28)	97.4(3)	O(4W)#2-Co(2)-O(19)	92.5(2)
O(10)-Mo(4)-O(28)	86.6(3)	O(30)-Co(2)-O(19)	84.6(2)
O(8)-Mo(4)-O(28)	158.8(2)	O(30)#2-Co(2)-O(19)	86.0(2)
O(29)-Mo(4)-O(5)	98.0(3)	O(19)#2-Co(2)-O(19)	81.8(3)
O(10)-Mo(4)-O(5)	156.6(2)	O(3W)-Co(3)-O(19)#2	94.1(5)
O(8)-Mo(4)-O(5)	86.3(2)	O(3W)-Co(3)-O(30)	174.1(5)
O(28)-Mo(4)-O(5)	83.4(2)	O(19)#2-Co(3)-O(30)	84.3(2)
O(29)-Mo(4)-O(25)	171.2(3)	O(3W)-Co(3)-O(5W)	86.8(5)
O(10)-Mo(4)-O(25)	83.4(2)	O(19)#2-Co(3)-O(5W)	94.0(3)
O(8)-Mo(4)-O(25)	80.8(2)	O(30)-Co(3)-O(5W)	87.7(3)
O(28)-Mo(4)-O(25)	78.6(2)	O(3W)-Co(3)-O(15)	77.3(5)
O(5)-Mo(4)-O(25)	73.8(2)	O(19)#2-Co(3)-O(15)	155.5(2)
O(26)-Mo(5)-O(15)	105.6(3)	O(30)-Co(3)-O(15)	106.3(3)
O(26)-Mo(5)-O(6)	102.6(3)	O(5W)-Co(3)-O(15)	108.1(3)
O(15)-Mo(5)-O(6)	95.3(3)	O(21)-Co(4)-O(34)	102.1(4)
O(26)-Mo(5)-O(23)	96.5(3)	O(21)-Co(4)-O(27)	108.6(3)
O(15)-Mo(5)-O(23)	85.9(3)	O(34)-Co(4)-O(27)	107.4(3)
O(6)-Mo(5)-O(23)	159.8(3)	O(21)-Co(4)-N(1)	121.3(3)
O(26)-Mo(5)-O(13)	98.8(3)	O(34)-Co(4)-N(1)	105.3(4)
O(15)-Mo(5)-O(13)	154.5(3)	O(27)-Co(4)-N(1)	111.0(3)

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

Mo(1)-O(28)	1.677(4)	Zn(1)-O(26)#1	1.930(4)
Mo(1)-O(20)	1.936(4)	Zn(1)-O(30)#2	1.954(5)
Mo(1)-O(8)	1.975(4)	Zn(1)-O(15)	1.974(5)
Mo(1)-O(25)	2.068(5)	Zn(1)-N(1)	2.015(6)
Mo(1)-O(6)	2.084(4)	Zn(2)-O(8)	2.144(4)
Mo(1)-O(29)	2.325(4)	Zn(2)-O(8)#3	2.145(4)
Mo(2)-O(24)	1.696(4)	Zn(2)-O(5)#3	2.190(5)
Mo(2)-O(20)	1.940(5)	Zn(2)-O(5)	2.190(5)
Mo(2)-O(8)	1.980(4)	Zn(2)-O(9)	2.218(5)
Mo(2)-O(11)	2.052(5)	Zn(2)-O(9)#3	2.218(5)
Mo(2)-O(21)	2.121(4)	Zn(3)-O(32)	2.060(5)
Mo(2)-O(23)	2.260(4)	Zn(3)-O(32)#1	2.060(5)
Mo(3)-O(27)	1.674(4)	Zn(3)-O(2W)#1	2.089(5)
Mo(3)-O(10)	1.940(4)	Zn(3)-O(2W)	2.089(5)
Mo(3)-O(5)	1.979(4)	Zn(3)-O(18)#1	2.207(4)
Mo(3)-O(14)	2.060(4)	Zn(3)-O(18)	2.207(4)
Mo(3)-O(12)	2.092(5)	Zn(4)-O(2)	1.943(6)
Mo(3)-O(4)	2.305(4)	Zn(4)-O(2)#1	1.944(6)
Mo(4)-O(19)	1.688(5)	Zn(4)-N(5)#1	1.955(9)
Mo(4)-O(10)	1.942(4)	Zn(4)-N(5)	1.955(9)
Mo(4)-O(5)	1.974(4)	P(1)-O(30)	1.532(5)
Mo(4)-O(22)	2.038(5)	P(1)-O(25)	1.539(5)
Mo(4)-O(6)	2.097(4)	P(1)-O(22)	1.539(4)
Mo(4)-O(29)	2.315(5)	P(1)-O(15)	1.542(4)
Mo(5)-O(3)	1.691(5)	P(2)-O(18)	1.504(4)
Mo(5)-O(13)	1.956(4)	P(2)-O(29)	1.547(4)
Mo(5)-O(9)	1.977(4)	P(2)-O(23)	1.557(4)
Mo(5)-O(16)	2.103(5)	P(2)-O(4)	1.555(4)
Mo(5)-O(12)	2.110(5)	P(3)-O(2)	1.516(5)
Mo(5)-O(4)	2.252(4)	P(3)-O(14)	1.522(5)
Mo(6)-O(17)	1.693(5)	P(3)-O(16)	1.549(5)
Mo(6)-O(13)	1.945(5)	P(3)-O(1)	1.580(5)
Mo(6)-O(9)	1.979(4)	P(4)-O(32)	1.491(5)
Mo(6)-O(7)	2.056(4)	P(4)-O(26)	1.511(4)
Mo(6)-O(21)	2.100(4)	P(4)-O(7)	1.545(5)
Mo(6)-O(23)	2.261(4)	P(4)-O(11)	1.551(4)

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

O(28)-Mo(1)-O(20)	105.1(2)	O(3)-Mo(5)-O(12)	96.2(2)
O(28)-Mo(1)-O(8)	102.4(2)	O(13)-Mo(5)-O(12)	157.72(17)
O(20)-Mo(1)-O(8)	95.52(18)	O(9)-Mo(5)-O(12)	86.03(17)
O(28)-Mo(1)-O(25)	95.4(2)	O(16)-Mo(5)-O(12)	86.14(17)
O(20)-Mo(1)-O(25)	86.98(18)	O(3)-Mo(5)-O(4)	167.7(2)
O(8)-Mo(1)-O(25)	160.64(16)	O(13)-Mo(5)-O(4)	84.27(18)
O(28)-Mo(1)-O(6)	96.3(2)	O(9)-Mo(5)-O(4)	83.01(18)
O(20)-Mo(1)-O(6)	157.86(17)	O(16)-Mo(5)-O(4)	77.58(17)
O(8)-Mo(1)-O(6)	84.91(17)	O(12)-Mo(5)-O(4)	73.83(16)
O(25)-Mo(1)-O(6)	85.66(17)	O(17)-Mo(6)-O(13)	106.3(2)
O(28)-Mo(1)-O(29)	169.63(18)	O(17)-Mo(6)-O(9)	102.5(2)
O(20)-Mo(1)-O(29)	83.58(16)	O(13)-Mo(6)-O(9)	95.73(17)
O(8)-Mo(1)-O(29)	82.01(18)	O(17)-Mo(6)-O(7)	96.1(2)
O(25)-Mo(1)-O(29)	79.20(17)	O(13)-Mo(6)-O(7)	85.14(18)
O(6)-Mo(1)-O(29)	74.54(16)	O(9)-Mo(6)-O(7)	160.27(16)
O(24)-Mo(2)-O(20)	104.8(2)	O(17)-Mo(6)-O(21)	98.1(2)
O(24)-Mo(2)-O(8)	102.49(19)	O(13)-Mo(6)-O(21)	154.50(17)
O(20)-Mo(2)-O(8)	95.21(18)	O(9)-Mo(6)-O(21)	85.95(17)
O(24)-Mo(2)-O(11)	96.1(2)	O(7)-Mo(6)-O(21)	85.01(17)
O(20)-Mo(2)-O(11)	86.82(19)	O(17)-Mo(6)-O(23)	169.90(19)
O(8)-Mo(2)-O(11)	160.06(17)	O(13)-Mo(6)-O(23)	82.98(18)
O(24)-Mo(2)-O(21)	97.0(2)	O(9)-Mo(6)-O(23)	80.19(17)
O(20)-Mo(2)-O(21)	157.08(16)	O(7)-Mo(6)-O(23)	80.35(17)
O(8)-Mo(2)-O(21)	86.77(17)	O(21)-Mo(6)-O(23)	72.21(17)
O(11)-Mo(2)-O(21)	83.88(18)	O(26)#1-Zn(1)-O(30)#2	99.1(2)
O(24)-Mo(2)-O(23)	168.61(18)	O(26)#1-Zn(1)-O(15)	108.19(19)
O(20)-Mo(2)-O(23)	85.96(18)	O(30)#2-Zn(1)-O(15)	111.0(2)
O(8)-Mo(2)-O(23)	79.96(16)	O(26)#1-Zn(1)-N(1)	111.8(2)
O(11)-Mo(2)-O(23)	80.41(16)	O(30)#2-Zn(1)-N(1)	121.2(2)
O(21)-Mo(2)-O(23)	71.87(17)	O(15)-Zn(1)-N(1)	105.0(2)
O(27)-Mo(3)-O(10)	105.7(2)	O(8)-Zn(2)-O(8)#3	180
O(27)-Mo(3)-O(5)	101.9(2)	O(8)-Zn(2)-O(5)#3	84.68(16)
O(10)-Mo(3)-O(5)	95.57(19)	O(8)#3-Zn(2)-O(5)#3	95.32(16)
O(27)-Mo(3)-O(14)	96.2(2)	O(8)-Zn(2)-O(5)	95.32(16)
O(10)-Mo(3)-O(14)	85.7(2)	O(8)#3-Zn(2)-O(5)	84.68(16)
O(5)-Mo(3)-O(14)	160.73(17)	O(5)#3-Zn(2)-O(5)	180.00(8)
O(27)-Mo(3)-O(12)	97.9(2)	O(8)-Zn(2)-O(9)	98.48(15)
O(10)-Mo(3)-O(12)	155.24(17)	O(8)#3-Zn(2)-O(9)	81.53(15)
O(5)-Mo(3)-O(12)	86.88(19)	O(5)#3-Zn(2)-O(9)	85.15(17)
O(14)-Mo(3)-O(12)	84.2(2)	O(5)-Zn(2)-O(9)	94.86(17)
O(27)-Mo(3)-O(4)	170.72(19)	O(8)-Zn(2)-O(9)#3	81.53(15)
O(10)-Mo(3)-O(4)	83.12(17)	O(8)#3-Zn(2)-O(9)#3	98.47(15)

O(5)-Mo(3)-O(4)	79.78(16)	O(5)#3-Zn(2)-O(9)#3	94.85(17)
O(14)-Mo(3)-O(4)	81.29(17)	O(5)-Zn(2)-O(9)#3	85.14(17)
O(12)-Mo(3)-O(4)	73.05(16)	O(9)-Zn(2)-O(9)#3	180
O(19)-Mo(4)-O(10)	104.5(2)	O(32)-Zn(3)-O(32)#1	169.9(3)
O(19)-Mo(4)-O(5)	101.1(2)	O(32)-Zn(3)-O(2W)#1	82.3(2)
O(10)-Mo(4)-O(5)	95.68(19)	O(32)#1-Zn(3)-O(2W)#1	104.6(2)
O(19)-Mo(4)-O(22)	98.36(19)	O(32)-Zn(3)-O(2W)	104.6(2)
O(10)-Mo(4)-O(22)	86.5(2)	O(32)#1-Zn(3)-O(2W)	82.3(2)
O(5)-Mo(4)-O(22)	159.20(17)	O(2W)#1-Zn(3)-O(2W)	96.0(3)
O(19)-Mo(4)-O(6)	96.3(2)	O(32)-Zn(3)-O(18)#1	85.62(19)
O(10)-Mo(4)-O(6)	158.37(17)	O(32)#1-Zn(3)-O(18)#1	87.09(19)
O(5)-Mo(4)-O(6)	85.93(19)	O(2W)#1-Zn(3)-O(18)#1	88.93(18)
O(22)-Mo(4)-O(6)	84.64(19)	O(2W)-Zn(3)-O(18)#1	169.16(17)
O(19)-Mo(4)-O(29)	170.04(18)	O(32)-Zn(3)-O(18)	87.08(19)
O(10)-Mo(4)-O(29)	84.31(17)	O(32)#1-Zn(3)-O(18)	85.62(19)
O(5)-Mo(4)-O(29)	82.28(16)	O(2W)#1-Zn(3)-O(18)	169.16(17)
O(22)-Mo(4)-O(29)	77.35(16)	O(2W)-Zn(3)-O(18)	88.93(18)
O(6)-Mo(4)-O(29)	74.51(15)	O(18)#1-Zn(3)-O(18)	87.9(2)
O(3)-Mo(5)-O(13)	104.9(2)	O(2)-Zn(4)-O(2)#1	112.0(3)
O(3)-Mo(5)-O(9)	103.9(2)	O(2)-Zn(4)-N(5)#1	112.0(3)
O(13)-Mo(5)-O(9)	95.47(18)	O(2)#1-Zn(4)-N(5)#1	102.1(3)
O(3)-Mo(5)-O(16)	94.7(2)	O(2)-Zn(4)-N(5)	102.1(3)
O(13)-Mo(5)-O(16)	85.20(18)	O(2)#1-Zn(4)-N(5)	112.0(3)
O(9)-Mo(5)-O(16)	160.42(17)	N(5)#1-Zn(4)-N(5)	116.9(5)

Table S5. The BVS calculation[3] result of Mo and Co atoms in **1**.

Code	Bond Valence	Code	Bond Valence
Mo1	5.20	Mo6	5.22
Mo2	5.27	Co1	1.74
Mo3	5.19	Co2	1.93
Mo4	5.23	Co3	1.51
Mo5	5.20	Co4	2.18

Table S6. The BVS calculation[3] result of Mo and Zn atoms in **2**.

Code	Bond Valence	Code	Bond Valence
Mo1	5.21	Mo6	5.15
Mo2	5.13	Zn1	1.97
Mo3	5.22	Zn2	1.64
Mo4	5.18	Zn3	1.98
Mo5	5.06	Zn4	2.06

Table S7. The ICP result of the compounds **1** and **2**.

Compound **1**	Co (mmol/L)	Co (found (%))	Co (Calc. (%))
Content	2.672×10^{-4}	9.20	9.40
Compound **2**	Zn (mmol/L)	Zn (found (%))	Zn (Calc. (%))
Content	2.380×10^{-4}	8.63	8.56

The ICP results show that the experimental values are in good agreement with the theoretical values of single crystal X - ray diffraction.

Table S8. Comparison of reported $\{P_4Mo_6\}$-based materials of CO_2 photoreduction.

Photocatalyst	Main product	Side product	Efficiency of main product (μmol g^{-1})	Time	Ref
$(C_2H_5OH)(C_3H_5N_2)_6[Co_3(H_6P_4Mo_6O_{31})_2]\cdot H_2O$	CO	None	5789	8h	4
$(H_2bbi)_2\{[Co_2(bbi)][Co_{2.33}(H_2O)_4][H_{9.33}CoP_8Mo_{12}O_{62}]\}\cdot 4H_2O$	**CO**	**CH_4**	**3261**	**8h**	**This work**
$Na_6[Co(H_2O)_2(H_2tib)]_2\{Co[Mo_6O_{15}(HPO_4)_4]_2\}\cdot 5H_2O$	CO	CH_4	10.76	10h	5
$Na_3[Co(H_2O)_3][Co_2(bib)](H_2bib)_{2.5}\{HCo[Mo_6O_{14}(OH)(HPO_4)_4]_2\}\cdot 4H_2O$	CO	CH_4	9.39	10h	
$H\{[Na_2K_4Mn_4(PO_4)(H_2O)_4]_3\{[Mo_6O_{12}(OH)_3(HPO_4)_3(PO_4)]_4[Mn_6(H_2O)_4]\}\cdot 16H_2O$	CH_4	CO	17	19h	6
$H\{[Na_6CoMn_3(PO_4)(H_2O)_4]_3\{[Mo_6O_{12}(OH)_3(HPO_4)_3(PO_4)]_4[Co_{1.5}Mn_{4.5}]\}\cdot 21H_2O$	CH_4	CO	40.2	23h	

Table S9. The research of reaction conditions.

entry	CO (μmol)	CH_4 (μmol)	selectivity (%)
1[a]	32.61	2.35	93.3
2[b]	none	none	-
3[c]	1.43	0.91	61.1
4[d]	none	none	-
5[e]	none	none	-
6[f]	none	none	-

[a]Reaction conditions: photocatalyst (10 mg), $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (11.3 mg), solvent (50 mL, MeCN/TEOA, 4/1), CO_2 (1 atm), λ ≥ 420 nm, 298 K, 8 h reaction time; selectivity = (n(CO))/(n(CO + CH_4)) × 100%. [b]Dark condition. [c]No catalyst. [d]No $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$. [e]No TEOA. [f]Ar replaced CO_2.

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