Metal-doped polyoxometalates with dual-ligand for efficient CO_2 photoreduction

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1. Experimental section

1.1 Materials

The chemical reagents in this work were commercially available and utilized directly to synthesize the catalysts and evaluate their photocatalytic CO_2 reduction activities without further purification.

1.2 Synthesis

Hydro-/solvothermal synthesis has been established as a predominate method for constructing novel POM-based hybrid complexes recently. Nonetheless, the development of POM-base compounds is complicated, which is influenced by various parameters during the synthesis process, including temperature, solvent diversity, reaction duration, and pH values. Consequntly, it is practical to differentiate them based on their colour and shape, as demonstrated in Figure S1. Table 1 presents the complete crystallographic information for these three compounds.

1.3 X-ray crystallography

The crystal PXRD data of compounds was collected at 296(3) K on Bruker Apex II CCD with Mo-Kα radiation (λ = 0.71073 Å). The SHELX software package was utilized to resolve and refine the structure of three compounds through the direct method and full-matrix least-squares method on F^2 in the SHELX-2018/3 program package. In addition, the non-H atoms were refined by anisotropic thermal parameters. The detailed crystallographic data of three compounds are summarized in Table S1. Main bond lengths and bond angles of compounds were provided in Tables S2-S4.

1.4 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: conductive glass, carbon rod and saturated Ag/AgCl electrode were considered as the working electrode, counter electrode, and reference electrode, respectively. The preparation of the working electrode was given as follows: catalyst of 2 mg was ground to powder and then dispersed in anhydrous ethanol (990 μL) in the presence of 10 μL

5% Nafion solution by ultrasonication to form a homogeneous ink. Subsequently, 200 μL of the ink was deposited onto the carbon cloth (CC, 1 cm × 2 cm), and dried at room temperature for Mott–Schottky spots measurements. The Mott–Schottky plots were measured over an alternating current (AC) frequency of 2000 Hz, 2500 Hz and 3000 Hz, and electrodes were immersed in the 0.2 M Na_2SO_4 aqueous solution.

1.5 Photocatalytic CO_2 reduction measurement

The photocatalytic performance of compounds was evaluated by applying it to the photocatalytic reduction of CO_2 (CEL-PAEM-D8, AULTT, China), in a 100 mL quartz container, and irradiated with a 300 W Xe lamp which intensity of light is 5.2×10^5 cd ($420 \leq \lambda \leq 800$ nm). A specific amount of catalysts were dispersed in a mixed solvent of acetonitrile (MeCN) and triethanolamine (TEOA, as a sacrificial reagent) (v/v = 4:1, 50 mL), $[Ru(bpy)_3]Cl_2\cdot6H_2O$ (0.015 mmol) as a photosensitizer, and transferred them into a glass container. Then, the container was saturated with high-purity CO_2 gas, repeated three times, and the reaction system temperature was ensured at 6 ℃ via a circulating water-cooling system outside the container. After reaction finished, the amounts of gaseous products were analyzed using a gas chromatography equipped with a flame ionization detector (FID), and the H_2 was analyzed by thermal conductivity detector (TCD).

$$\text{CO selectivity} = \frac{n(CO)}{n(CO) + n(CH_4) + n(H_2)} \times 100\%$$

$$TON_{CO} = \frac{n(CO)}{n(catalyst)} \times 100\%$$

Recycling experiments

Reusability and stability are important indicators to evaluate catalysts, after each reaction, the catalyst was recovered by centrifugation and washed several times with deionized water, and then dried at 80 ℃ for 10 h before the next reaction.

Table S1. Crystal data and structure refinements for **1**, **2** and **3**

Compound	**1**	**2**	**3**
Formula	$C_{24}H_{55}Co_{3.5}N_{19}O_{53}PW_{11}$	$C_{25}H_{44}CoN_{15}O_{46}PV_2W_{10}$	$C_{42}H_{70}Co_2N_{22}O_{50}PV_{0.5}W_{11.5}$
Formula weight	3717.44	3321.03	3971.77
T (K)	293(2)	296(2)	273(2)
Crystal system	Triclinic	Orthorhombic	Triclinic
Space group	*P*-1	*P*bca	*P*-1
a(Å)	13.4083(5)	18.618(2)	12.2487(15)
b(Å)	17.6628(7)	16.868(5)	12.5099(15)
c(Å)	18.934(6)	39.902(2)	14.8406(18)
α(°)	78.786(3)	90	84.891(10)
β(°)	86.23(3)	90	87.839(2)
γ(°)	74.431(3)	90	65.168(10)
V(Å^3)	4236.7(3)	12531(3)	2055.6(4)
Z	2	8	1
D_c (mg m^{-3})	2.914	3.512	3.208
μ (mm^{-1})	15.647	18.956	16.590
F (000)	3359	11960	1808
θ range (deg)	1.905 to 25.024	1.021 to 25.500	1.378 to 25.498
Limiting indices	-15≤h≤15 -21≤k≤21 -22≤l≤22	-22≤h≤22 -20≤k≤20 -48≤l≤44	-14≤h≤13 -15≤k≤15 -17≤l≤17
Reflections collected	45313	90023	15330
Independent reflection/unique	14942 [R(int) = 0.1084]	11680 [R(int) = 0.1639]	7548 [R(int) = 0.0475]
Data/restraints/parameters	14942/501/1037	11680/90/913	7548/420/603
GOF	1.044	1.056	1.198
R_1[a]	0.0945	0.0500	0.0818
wR_2[b] [$I> 2\sigma(I)$]	0.2218	0.1225	0.2195
R_1, wR_2 (all data)	R_1 = 0.1413 wR_2 = 0.2396	R_1 = 0.0590 wR_2 = 0.1299	R_1 = 0.0928 wR_2 = 0.2248

[a]$R_1=\Sigma||F_0|-|F_c||/\Sigma|F_0|$, [b]$wR_2=\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0^2)^2]^{1/2}$

Table S2. Bond lengths (Å) and angles (deg) of main metal atoms for compound **1**.

Co(1)-N(5A)	1.96(3)	Co(4)-O(8W)	2.101(5)
Co(1)-O(4)	2.42(18)	Co(4)-O(9W)	2.101(5)
Co(1)-O(18)	1.97(2)	Co(5)-O(36)	1.68(3)
Co(1)-O(39)	1.99(2)	Co(5)-O(20)	1.88(2)
Co(1)-O(17)	2.09(2)	Co(5)-O(8)	1.88(2)
Co(1)-O(13)	2.122(18)	Co(5)-O(42)	1.95(3)
Co(2)-N(4)	2.14(2)	Co(5)-O(30)	1.96(2)
Co(2)-O(2W)	2.16(3)	Co(5)-O(10)	2.359(18)
Co(2)-O(1W)	2.17(3)	W(1)-O(14)	1.743(19)
Co(2)-O(1A)	2.183(19)	W(1)-O(13)	1.755(19)
Co(2)-N(3)	2.19(3)	W(1)-O(7)	1.891(19)
Co(2)-O(2A)	2.19(2)	W(1)-O(1)	1.953(17)
Co(2)-N(5)	2.20(2)	W(1)-O(3)	1.999(18)
Co(3)-O(3W)	2.12(4)	W(1)-O(4)	2.397(16)
Co(3)-O(3A)	2.17(3)	W(2)-O(24)	1.737(19)
Co(3)-O(4W)	2.19(3)	W(2)-O(17)	1.738(19)
Co(3)-O(5A)	2.20(3)	W(2)-O(23)	1.86(2)
Co(3)-N(12)	2.20(3)	W(2)-O(12)	1.931(17)
Co(3)-N(11)	2.22(4)	W(2)-O(6)	2.044(18)
Co(3)-N(10)	2.38(4)	W(2)-O(2)	2.425(16)
Co(4)-O(5W)	2.101(5)	P(1)-O(5)	1.518(18)
Co(4)-O(6W)	2.103(5)	P(1)-O(2)	1.526(18)
Co(4)#1-O(7WA)	2.32(4)	P(1)-O(4)	1.545(18)
Co(4)-O(7WB)	2.100(5)	P(1)-O(10)	1.58(2)
N(5A)-Co(1)-O(18)	105.0(11)	O(7WB)-Co(4)-O(6W)	144.8(15)
N(5A)-Co(1)-O(39)	103.3(11)	O(5W)-Co(4)-O(6W)	90.6(16)
O(18)-Co(1)-O(39)	92.9(10)	O(9W)-Co(4)-O(6W)	88.8(15)
N(5A)-Co(1)-O(17)	97.8(10)	O(8W)-Co(4)-O(6W)	68.2(16)
O(18)-Co(1)-O(17)	85.3(9)	O(5W)-Co(4)-O(7WA)#1	97.6(15)
O(39)-Co(1)-O(17)	158.6(7)	O(9W)-Co(4)-O(7WA)#1	83.9(14)
N(5A)-Co(1)-O(13)	95.9(11)	O(8W)-Co(4)-O(7WA)#1	145.3(15)
O(18)-Co(1)-O(13)	158.8(9)	O(36)-Co(5)-O(20)	104.7(13)
O(39)-Co(1)-O(13)	85.7(9)	O(36)-Co(5)-O(8)	103.2(11)
O(17)-Co(1)-O(13)	88.4(7)	O(20)-Co(5)-O(8)	85.4(9)
N(4)-Co(2)-O(2W)	90.9(11)	O(36)-Co(5)-O(42)	98.2(13)
N(4)-Co(2)-O(1W)	92.6(11)	O(20)-Co(5)-O(42)	156.9(9)
O(2W)-Co(2)-O(1W)	176.4(11)	O(8)-Co(5)-O(42)	92.1(9)
N(4)-Co(2)-O(1A)	142.7(9)	O(36)-Co(5)-O(30)	97.3(11)
O(2W)-Co(2)-O(1A)	90.2(10)	O(20)-Co(5)-O(30)	88.5(10)
O(1W)-Co(2)-O(1A)	86.4(11)	O(8)-Co(5)-O(30)	159.5(9)
N(4)-Co(2)-N(3)	70.2(10)	O(42)-Co(5)-O(30)	85.9(10)

O(2W)-Co(2)-N(3)	92.3(11)	O(36)-Co(5)-O(10)	169.0(11)
O(1W)-Co(2)-N(3)	89.8(12)	O(20)-Co(5)-O(10)	83.6(8)
O(1A)-Co(2)-N(3)	147.0(9)	O(8)-Co(5)-O(10)	84.5(7)
N(4)-Co(2)-O(2A)	142.3(9)	O(42)-Co(5)-O(10)	73.3(8)
O(2W)-Co(2)-O(2A)	88.5(10)	O(30)-Co(5)-O(10)	75.4(8)
O(1W)-Co(2)-O(2A)	89.3(11)	O(14)-W(1)-O(13)	102.5(9)
O(1A)-Co(2)-O(2A)	75.1(8)	O(14)-W(1)-O(7)	104.8(10)
N(3)-Co(2)-O(2A)	72.1(9)	O(13)-W(1)-O(7)	92.7(9)
N(4)-Co(2)-N(5)	70.3(10)	O(14)-W(1)-O(1)	99.5(9)
O(2W)-Co(2)-N(5)	88.8(11)	O(13)-W(1)-O(1)	92.0(8)
O(1W)-Co(2)-N(5)	91.4(12)	O(7)-W(1)-O(1)	153.6(8)
O(1A)-Co(2)-N(5)	72.4(9)	O(14)-W(1)-O(3)	98.1(8)
N(3)-Co(2)-N(5)	140.5(10)	O(13)-W(1)-O(3)	159.4(8)
O(2A)-Co(2)-N(5)	147.4(9)	O(7)-W(1)-O(3)	81.1(7)
O(3W)-Co(3)-O(3A)	80.7(14)	O(1)-W(1)-O(3)	85.5(7)
O(3W)-Co(3)-O(4W)	167.8(14)	O(14)-W(1)-O(4)	172.3(9)
O(3A)-Co(3)-O(4W)	91.6(10)	O(13)-W(1)-O(4)	78.1(7)
O(3W)-Co(3)-O(5A)	81.7(14)	O(7)-W(1)-O(4)	82.8(7)
O(3A)-Co(3)-O(5A)	76.6(10)	O(1)-W(1)-O(4)	72.8(6)
O(4W)-Co(3)-O(5A)	87.3(11)	O(3)-W(1)-O(4)	81.7(6)
O(3W)-Co(3)-N(12)	92.2(13)	O(24)-W(2)-O(17)	101.6(9)
O(3A)-Co(3)-N(12)	71.6(10)	O(24)-W(2)-O(23)	103.0(9)
O(4W)-Co(3)-N(12)	94.5(11)	O(17)-W(2)-O(23)	92.3(9)
O(5A)-Co(3)-N(12)	148.1(12)	O(24)-W(2)-O(12)	102.7(9)
O(3W)-Co(3)-N(11)	102.9(16)	O(17)-W(2)-O(12)	91.8(8)
O(3A)-Co(3)-N(11)	142.5(10)	O(23)-W(2)-O(12)	152.6(8)
O(4W)-Co(3)-N(11)	89.0(11)	O(24)-W(2)-O(6)	100.2(9)
O(5A)-Co(3)-N(11)	140.8(12)	O(17)-W(2)-O(6)	158.2(7)
N(12)-Co(3)-N(11)	71.0(12)	O(23)-W(2)-O(6)	83.9(9)
O(3W)-Co(3)-N(10)	96.3(14)	O(12)-W(2)-O(6)	82.3(8)
O(3A)-Co(3)-N(10)	151.8(11)	O(24)-W(2)-O(2)	168.0(9)
O(4W)-Co(3)-N(10)	86.0(12)	O(17)-W(2)-O(2)	89.0(7)
O(5A)-Co(3)-N(10)	75.2(12)	O(23)-W(2)-O(2)	81.9(8)
N(12)-Co(3)-N(10)	136.6(13)	O(12)-W(2)-O(2)	71.0(7)
N(11)-Co(3)-N(10)	65.6(13)	O(6)-W(2)-O(2)	69.2(6)
O(7WB)-Co(4)-O(5W)	92.0(17)	O(5)-P(1)-O(2)	111.3(10)
O(7WB)-Co(4)-O(9W)	87.5(17)	O(5)-P(1)-O(4)	109.6(10)
O(5W)-Co(4)-O(9W)	178.3(17)	O(2)-P(1)-O(4)	112.7(10)
O(7WB)-Co(4)-O(8W)	76.7(16)	O(5)-P(1)-O(10)	106.1(10)
O(5W)-Co(4)-O(8W)	91.0(17)	O(2)-P(1)-O(10)	109.4(10)
O(9W)-Co(4)-O(8W)	87.3(16)	O(4)-P(1)-O(10)	107.6(10)

Symmetry transformations used to generate equivalent atoms: #1 (#1 -x, -y+1, -z), #2 (x+1, y, z)

Table S3. Bond lengths (Å) and angles (deg) of main metal atoms for compound **2.**

Co(1)-N(8)	2.116(10)	V(4)-O(10)	1.926(9)
Co(1)-O(2A)	2.139(9)	V(4)-O(5)	2.450(7)
Co(1)-N(3)	2.150(11)	V(5)-O(28)	1.710(8)
Co(1)-N(4)	2.166(9)	V(5)-O(40)	1.903(8)
Co(1)-N(5)	2.189(10)	V(5)-O(20)	1.910(8)
Co(1)-O(1A)	2.254(9)	V(5)-O(11)	1.926(8)
Co(1)-O(12)	2.257(8)	V(5)-O(35)	1.956(8)
W(1)-O(13)	1.697(9)	V(5)-O(16)	2.430(7)
W(1)-O(11)	1.897(8)	V(6)-O(39)	1.702(8)
W(1)-O(21)	1.905(8)	V(6)-O(14)	1.895(8)
W(1)-O(6)	1.914(8)	V(6)-O(24)	1.905(9)
W(1)-O(10)	1.931(8)	V(6)-O(36)	1.914(8)
W(1)-O(5)	2.405(7)	V(6)-O(9)	1.918(8)
W(2)-O(18)	1.692(8)	V(6)-O(26)	2.460(7)
W(2)-O(1)	1.882(8)	V(7)-O(29)	1.687(9)
W(2)-O(4)	1.906(7)	V(7)-O(4)	1.891(7)
W(2)-O(32)	1.911(8)	V(7)-O(19)	1.902(8)
W(2)-O(17)	1.926(8)	V(7)-O(14)	1.938(8)
W(2)-O(22)	2.440(8)	V(7)-O(3)	1.948(7)
W(3)-O(27)	1.681(9)	V(7)-O(26)	2.413(8)
W(3)-O(25)	1.894(8)	V(8)-O(33)	1.704(8)
W(3)-O(30)	1.911(8)	V(8)-O(8)	1.891(8)
W(3)-O(6)	1.922(7)	V(8)-O(2)	1.913(8)
W(3)-O(8)	1.930(8)	V(8)-O(37)	1.918(8)
W(3)-O(5)	2.433(8)	V(8)-O(35)	1.919(7)
P(1)-O(26)	1.531(8)	V(8)-O(16)	2.398(7)
P(1)-O(5)	1.545(8)	V(9)-O(15)	1.697(8)
P(1)-O(22)	1.548(8)	V(9)-O(37)	1.891(8)
P(1)-O(16)	1.552(8)	V(9)-O(25)	1.923(9)
V(1)-O(13)	1.697(9)	V(9)-O(34)	1.926(8)
V(1)-O(11)	1.897(8)	V(9)-O(1)	1.938(8)
V(1)-O(21)	1.905(8)	V(9)-O(22)	2.409(7)
V(1)-O(6)	1.914(8)	V(10)-O(12)	1.707(8)
V(1)-O(10)	1.931(8)	V(10)-O(2)	1.901(8)
V(1)-O(5)	2.405(7)	V(10)-O(32)	1.907(8)
V(2)-O(18)	1.692(8)	V(10)-O(20)	1.908(8)
V(2)-O(1)	1.882(8)	V(10)-O(19)	1.910(8)
V(2)-O(4)	1.906(7)	V(10)-O(16)	2.408(8)
V(2)-O(32)	1.911(8)	V(11)-O(31)	1.714(8)
V(2)-O(17)	1.926(8)	V(11)-O(34)	1.888(8)
V(2)-O(22)	2.440(8)	V(11)-O(7)	1.902(9)
V(3)-O(27)	1.681(9)	V(11)-O(9)	1.922(8)

V(3)-O(25)	1.894(8)	V(11)-O(17)	1.949(8)
V(3)-O(30)	1.911(8)	V(11)-O(22)	2.433(7)
V(3)-O(6)	1.922(7)	V(12)-O(23)	1.702(9)
V(3)-O(8)	1.930(8)	V(12)-O(40)	1.900(8)
V(3)-O(5)	2.433(8)	V(12)-O(21)	1.909(9)
V(4)-O(38)	1.697(9)	V(12)-O(3)	1.922(8)
V(4)-O(24)	1.905(9)	V(12)-O(36)	1.941(8)
V(4)-O(7)	1.906(8)	V(12)-O(26)	2.436(7)
V(4)-O(30)	1.922(9)		

O(2A)-Co(1)-O(12)	86.4(3)	O(24)-V(6)-O(9)	85.3(4)
N(3)-Co(1)-O(12)	85.0(4)	O(36)-V(6)-O(9)	155.9(3)
N(4)-Co(1)-O(12)	83.5(3)	O(39)-V(6)-O(26)	172.1(3)
N(5)-Co(1)-O(12)	91.0(3)	O(14)-V(6)-O(26)	72.6(3)
O(1A)-Co(1)-O(12)	94.3(3)	O(24)-V(6)-O(26)	83.1(3)
N(8)-Co(1)-O(2A)	93.3(4)	O(36)-V(6)-O(26)	72.7(3)
N(8)-Co(1)-N(3)	95.1(4)	O(9)-V(6)-O(26)	83.3(3)
O(2A)-Co(1)-N(3)	145.3(4)	O(29)-V(7)-O(4)	101.7(4)
N(8)-Co(1)-N(4)	96.8(4)	O(29)-V(7)-O(19)	102.5(4)
O(2A)-Co(1)-N(4)	139.9(4)	O(4)-V(7)-O(19)	86.5(3)
N(3)-Co(1)-N(4)	72.1(4)	O(29)-V(7)-O(14)	100.2(4)
N(8)-Co(1)-N(5)	89.1(4)	O(4)-V(7)-O(14)	89.6(3)
O(2A)-Co(1)-N(5)	72.1(3)	O(19)-V(7)-O(14)	157.3(3)
N(3)-Co(1)-N(5)	141.6(4)	O(29)-V(7)-O(3)	101.6(4)
N(4)-Co(1)-N(5)	69.5(4)	O(4)-V(7)-O(3)	156.7(3)
N(8)-Co(1)-O(1A)	85.4(4)	O(19)-V(7)-O(3)	88.6(3)
O(2A)-Co(1)-O(1A)	76.0(3)	O(14)-V(7)-O(3)	86.2(3)
N(3)-Co(1)-O(1A)	71.2(4)	O(29)-V(7)-O(26)	171.3(3)
N(4)-Co(1)-O(1A)	143.3(4)	O(4)-V(7)-O(26)	84.0(3)
N(5)-Co(1)-O(1A)	147.2(3)	O(19)-V(7)-O(26)	84.3(3)
N(8)-Co(1)-O(12)	179.6(4)	O(14)-V(7)-O(26)	73.0(3)
O(13)-V(1)-O(11)	100.7(4)	O(3)-V(7)-O(26)	72.9(3)
O(13)-V(1)-O(21)	102.2(4)	O(33)-V(8)-O(8)	101.7(4)
O(11)-V(1)-O(21)	86.6(3)	O(33)-V(8)-O(2)	101.5(4)
O(13)-V(1)-O(6)	101.2(4)	O(8)-V(8)-O(2)	156.8(3)
O(11)-V(1)-O(6)	89.5(3)	O(33)-V(8)-O(37)	102.6(4)
O(21)-V(1)-O(6)	156.6(3)	O(8)-V(8)-O(37)	86.4(3)
O(13)-V(1)-O(10)	102.3(4)	O(2)-V(8)-O(37)	87.7(3)
O(11)-V(1)-O(10)	157.0(3)	O(33)-V(8)-O(35)	100.1(4)
O(21)-V(1)-O(10)	88.5(3)	O(8)-V(8)-O(35)	88.1(3)
O(6)-V(1)-O(10)	86.1(3)	O(2)-V(8)-O(35)	88.7(3)
O(13)-V(1)-O(5)	172.0(3)	O(37)-V(8)-O(35)	157.3(3)
O(11)-V(1)-O(5)	84.1(3)	O(33)-V(8)-O(16)	171.5(3)
O(21)-V(1)-O(5)	84.3(3)	O(8)-V(8)-O(16)	84.6(3)

O(6)-V(1)-O(5)	72.3(3)	O(2)-V(8)-O(16)	72.5(3)
O(10)-V(1)-O(5)	73.1(3)	O(37)-V(8)-O(16)	83.4(3)
O(18)-V(2)-O(1)	101.6(4)	O(35)-V(8)-O(16)	74.2(3)
O(18)-V(2)-O(4)	103.7(4)	O(15)-V(9)-O(37)	102.6(4)
O(1)-V(2)-O(4)	154.8(4)	O(15)-V(9)-O(25)	100.3(4)
O(18)-V(2)-O(32)	102.9(4)	O(37)-V(9)-O(25)	86.8(4)
O(1)-V(2)-O(32)	90.1(3)	O(15)-V(9)-O(34)	102.0(4)
O(4)-V(2)-O(32)	84.8(3)	O(37)-V(9)-O(34)	155.4(3)
O(18)-V(2)-O(17)	101.7(4)	O(25)-V(9)-O(34)	88.2(4)
O(1)-V(2)-O(17)	87.6(3)	O(15)-V(9)-O(1)	102.3(4)
O(4)-V(2)-O(17)	86.8(3)	O(37)-V(9)-O(1)	89.5(3)
O(32)-V(2)-O(17)	155.3(3)	O(25)-V(9)-O(1)	157.3(3)
O(18)-V(2)-O(22)	171.9(3)	O(34)-V(9)-O(1)	85.8(4)
O(1)-V(2)-O(22)	73.1(3)	O(15)-V(9)-O(22)	172.4(3)
O(4)-V(2)-O(22)	81.8(3)	O(37)-V(9)-O(22)	83.5(3)
O(32)-V(2)-O(22)	83.5(3)	O(25)-V(9)-O(22)	84.3(3)
O(17)-V(2)-O(22)	72.3(3)	O(34)-V(9)-O(22)	72.0(3)
O(27)-V(3)-O(25)	101.9(4)	O(1)-V(9)-O(22)	73.0(3)
O(27)-V(3)-O(30)	101.8(4)	O(12)-V(10)-O(2)	100.1(4)
O(25)-V(3)-O(30)	89.1(4)	O(12)-V(10)-O(32)	100.8(4)
O(27)-V(3)-O(6)	102.3(4)	O(2)-V(10)-O(32)	89.5(3)
O(25)-V(3)-O(6)	155.8(3)	O(12)-V(10)-O(20)	102.5(4)
O(30)-V(3)-O(6)	86.6(3)	O(2)-V(10)-O(20)	87.9(3)
O(27)-V(3)-O(8)	103.2(4)	O(32)-V(10)-O(20)	156.7(3)
O(25)-V(3)-O(8)	86.6(3)	O(12)-V(10)-O(19)	104.0(4)
O(30)-V(3)-O(8)	155.0(4)	O(2)-V(10)-O(19)	155.9(3)
O(6)-V(3)-O(8)	87.3(3)	O(32)-V(10)-O(19)	84.9(3)
O(27)-V(3)-O(5)	171.7(4)	O(20)-V(10)-O(19)	88.1(3)
O(25)-V(3)-O(5)	84.5(3)	O(12)-V(10)-O(16)	171.1(3)
O(30)-V(3)-O(5)	72.7(3)	O(2)-V(10)-O(16)	72.4(3)
O(6)-V(3)-O(5)	71.5(3)	O(32)-V(10)-O(16)	84.3(3)
O(8)-V(3)-O(5)	82.4(3)	O(20)-V(10)-O(16)	72.9(3)
O(38)-V(4)-O(24)	102.2(4)	O(19)-V(10)-O(16)	83.6(3)
O(38)-V(4)-O(7)	102.8(4)	O(31)-V(11)-O(34)	103.0(4)
O(24)-V(4)-O(7)	85.5(4)	O(31)-V(11)-O(7)	103.1(4)
O(38)-V(4)-O(30)	102.2(4)	O(34)-V(11)-O(7)	90.6(4)
O(24)-V(4)-O(30)	155.6(4)	O(31)-V(11)-O(9)	101.6(4)
O(7)-V(4)-O(30)	88.3(4)	O(34)-V(11)-O(9)	155.4(4)
O(38)-V(4)-O(10)	101.4(4)	O(7)-V(11)-O(9)	85.1(4)
O(24)-V(4)-O(10)	89.4(4)	O(31)-V(11)-O(17)	100.9(4)
O(7)-V(4)-O(10)	155.8(3)	O(34)-V(11)-O(17)	86.7(4)
O(30)-V(4)-O(10)	86.7(4)	O(7)-V(11)-O(17)	155.8(3)
O(38)-V(4)-O(5)	171.3(4)	O(9)-V(11)-O(17)	87.4(3)
O(24)-V(4)-O(5)	83.8(3)	O(31)-V(11)-O(22)	171.4(4)

O(7)-V(4)-O(5)	83.8(3)	O(34)-V(11)-O(22)	72.0(3)
O(30)-V(4)-O(5)	72.1(3)	O(7)-V(11)-O(22)	84.2(3)
O(10)-V(4)-O(5)	72.1(3)	O(9)-V(11)-O(22)	83.4(3)
O(28)-V(5)-O(40)	102.6(4)	O(17)-V(11)-O(22)	72.1(3)
O(28)-V(5)-O(20)	102.9(4)	O(23)-V(12)-O(40)	103.2(4)
O(40)-V(5)-O(20)	89.0(4)	O(23)-V(12)-O(21)	104.1(4)
O(28)-V(5)-O(11)	101.7(4)	O(40)-V(12)-O(21)	86.5(4)
O(40)-V(5)-O(11)	86.5(4)	O(23)-V(12)-O(3)	99.8(4)
O(20)-V(5)-O(11)	155.4(3)	O(40)-V(12)-O(3)	87.9(3)
O(28)-V(5)-O(35)	100.7(4)	O(21)-V(12)-O(3)	156.0(3)
O(40)-V(5)-O(35)	156.4(3)	O(23)-V(12)-O(36)	100.6(4)
O(20)-V(5)-O(35)	88.9(3)	O(40)-V(12)-O(36)	156.2(3)
O(11)-V(5)-O(35)	85.7(3)	O(21)-V(12)-O(36)	89.1(4)
O(28)-V(5)-O(16)	171.8(3)	O(3)-V(12)-O(36)	86.7(4)
O(40)-V(5)-O(16)	84.2(3)	O(23)-V(12)-O(26)	170.1(4)
O(20)-V(5)-O(16)	72.3(3)	O(40)-V(12)-O(26)	83.4(3)
O(11)-V(5)-O(16)	83.2(3)	O(21)-V(12)-O(26)	83.5(3)
O(35)-V(5)-O(16)	72.8(3)	O(3)-V(12)-O(26)	72.7(3)
O(39)-V(6)-O(14)	101.4(4)	O(36)-V(12)-O(26)	72.9(3)
O(39)-V(6)-O(24)	103.1(4)	O(26)-P(1)-O(5)	108.9(4)
O(14)-V(6)-O(24)	155.5(4)	O(26)-P(1)-O(22)	109.8(4)
O(39)-V(6)-O(36)	102.2(4)	O(5)-P(1)-O(22)	110.1(4)
O(14)-V(6)-O(36)	86.7(3)	O(26)-P(1)-O(16)	108.9(4)
O(24)-V(6)-O(36)	89.0(4)	O(5)-P(1)-O(16)	109.4(4)
O(39)-V(6)-O(9)	102.0(4)	O(22)-P(1)-O(16)	109.8(4)
O(14)-V(6)-O(9)	88.8(3)		

Symmetry transformations used to generate equivalent atoms: #1 (-x, -y+1, -z), #2 (x+1, y, z)

Table S4. Bond lengths (Å) and angles (deg) of main metal atoms for compound **3.**

Co(1)-N(9)	2.123(19)	W(2)-O(11)	1.847(18)
Co(1)-O(1W)	2.164(18)	W(2)-O(18)	1.897(17)
Co(1)-N(4)	2.17(2)	W(2)-O(17)	1.90(2)
Co(1)-N(3)	2.180(18)	W(2)-O(10)	1.93(2)
Co(1)-O(2A)	2.197(15)	W(2)-O(20)#1	2.37(3)
Co(1)-N(5)	2.208(19)	W(2)-O(19)	2.45(3)
Co(1)-O(1A)	2.222(15)	P(1)-O(19)	1.45(3)
W(1)-O(4)	1.691(19)	P(1)-O(19)#1	1.45(3)
W(1)-O(2)#1	1.88(2)	P(1)-O(20)#1	1.52(3)
W(1)-O(14)	1.899(18)	P(1)-O(20)	1.52(3)
W(1)-O(18)	1.913(18)	P(1)-O(22)	1.55(3)
W(1)-O(15)	1.92(2)	P(1)-O(22)#1	1.55(3)

W(1)-O(22)	2.42(4)	P(1)-O(21)	1.60(3)
W(2)-O(3)	1.702(16)	P(1)-O(21)#1	1.60(3)
N(9)-Co(1)-O(1W)	178.8(7)	O(19)#1-P(1)-O(20)	65.3(14)
N(9)-Co(1)-N(4)	92.8(8)	O(20)#1-P(1)-O(20)	180
O(1W)-Co(1)-N(4)	87.5(7)	O(19)-P(1)-O(22)	70.2(16)
N(9)-Co(1)-N(3)	90.3(7)	O(19)#1-P(1)-O(22)	109.8(16)
O(1W)-Co(1)-N(3)	88.7(7)	O(20)#1-P(1)-O(22)	109.5(16)
N(4)-Co(1)-N(3)	71.0(7)	O(20)-P(1)-O(22)	70.5(16)
N(9)-Co(1)-O(2A)	88.1(8)	O(19)-P(1)-O(22)#1	109.8(16)
O(1W)-Co(1)-O(2A)	90.9(7)	O(19)#1-P(1)-O(22)#1	70.2(16)
N(4)-Co(1)-O(2A)	143.1(6)	O(20)#1-P(1)-O(22)#1	70.5(16)
N(3)-Co(1)-O(2A)	72.1(7)	O(20)-P(1)-O(22)#1	109.5(16)
N(9)-Co(1)-N(5)	95.2(7)	O(22)-P(1)-O(22)#1	180
O(1W)-Co(1)-N(5)	86.1(7)	O(19)-P(1)-O(21)	111.6(14)
N(4)-Co(1)-N(5)	70.0(7)	O(19)#1-P(1)-O(21)	68.4(14)
N(3)-Co(1)-N(5)	140.8(8)	O(20)#1-P(1)-O(21)	73.4(14)
O(2A)-Co(1)-N(5)	146.7(7)	O(20)-P(1)-O(21)	106.6(14)
N(9)-Co(1)-O(1A)	88.3(7)	O(22)-P(1)-O(21)	75.9(16)
O(1W)-Co(1)-O(1A)	92.2(7)	O(22)#1-P(1)-O(21)	104.1(16)
N(4)-Co(1)-O(1A)	140.5(6)	O(19)-P(1)-O(21)#1	68.4(14)
N(3)-Co(1)-O(1A)	148.6(7)	O(19)#1-P(1)-O(21)#1	111.6(14)
O(2A)-Co(1)-O(1A)	76.4(6)	O(20)#1-P(1)-O(21)#1	106.6(14)
N(5)-Co(1)-O(1A)	70.6(7)	O(20)-P(1)-O(21)#1	73.4(14)
O(19)-P(1)-O(19)#1	180	O(22)-P(1)-O(21)#1	104.1(16)
O(19)-P(1)-O(20)#1	65.3(14)	O(22)#1-P(1)-O(21)#1	75.8(16)
O(19)#1-P(1)-O(20)#1	114.7(14)	O(21)-P(1)-O(21)#1	180
O(19)-P(1)-O(20)	114.7(14)		

Symmetry transformations used to generate equivalent atoms: #1 (-x+1, -y+1, -z-1), #2 (x+1, y, z)

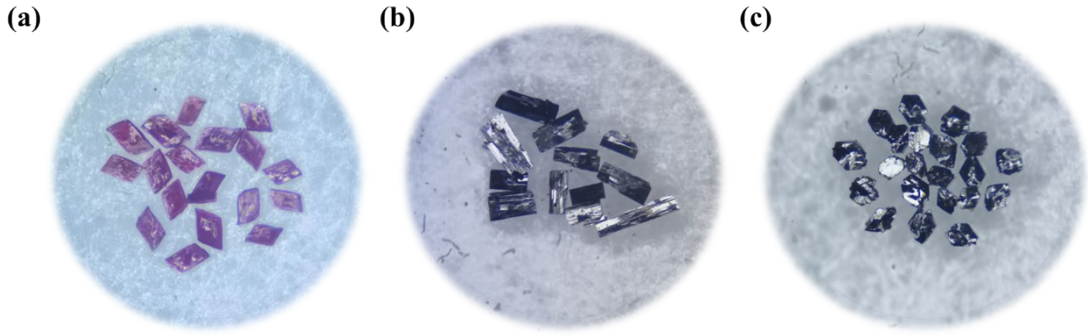

Figure S1. The image of crystal morphology for (a) **1**, (b) **2** and (c) **3**.

2. Crystal structures

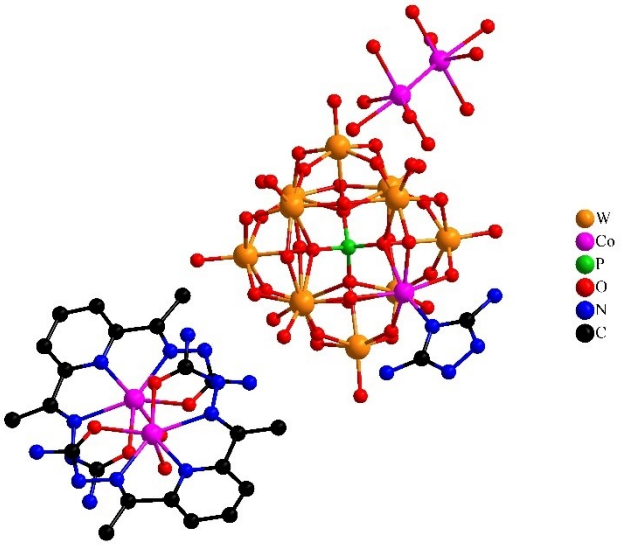

Figure S2. Ball and stick representation of the basic unit in compound **1**. Hydrogen atoms are omitted for clarity.

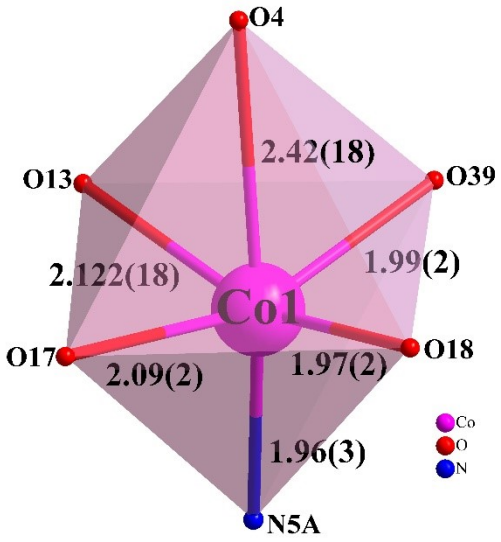

Figure S3. Coordination polyhedron of Co1 in compound **1**.

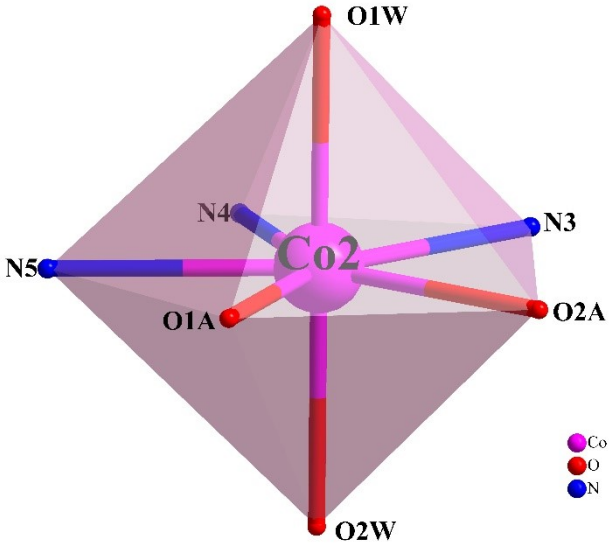

Figure S4. Coordination polyhedron of Co2 in compound **1**.

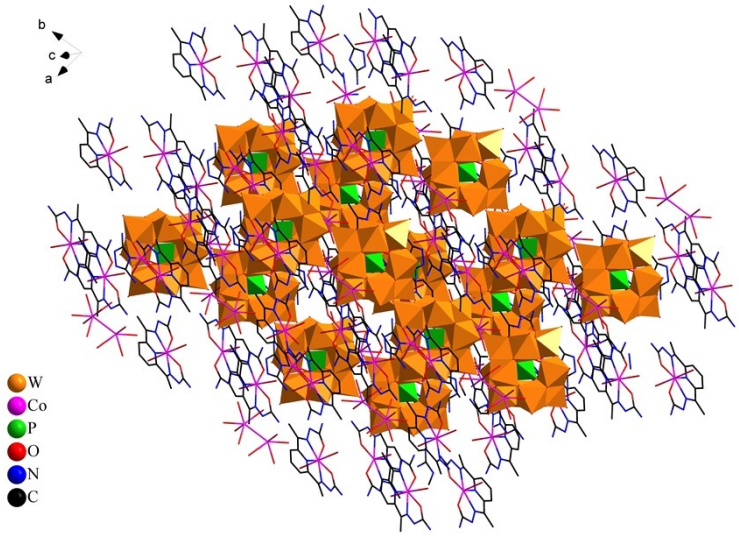

Figure S5. The 3D supramolecular structure of compound **1** with view in the direction of *c* axis. Free water molecules are omitted for clarity.

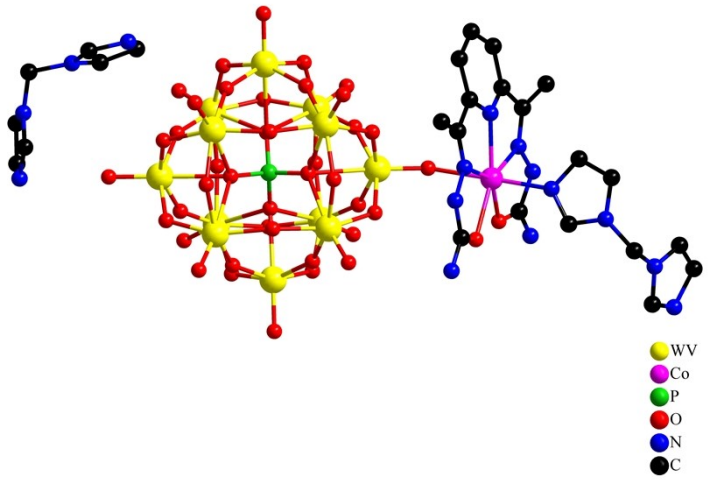

Figure S6. Ball and stick representation of the basic unit in compound **2**. Hydrogen atoms are omitted for clarity.

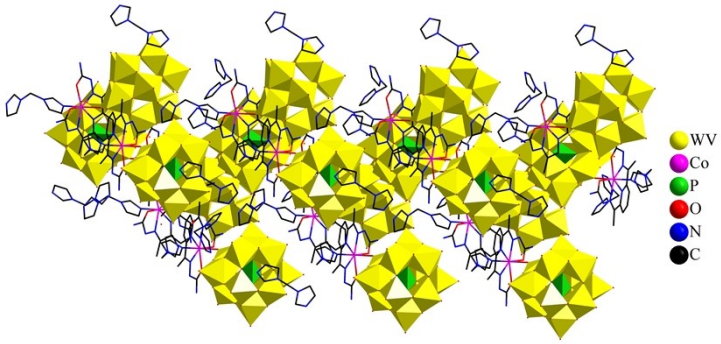

Figure S7. The 3D supramolecular structure of compound **2**. Free water molecules are omitted for clarity.

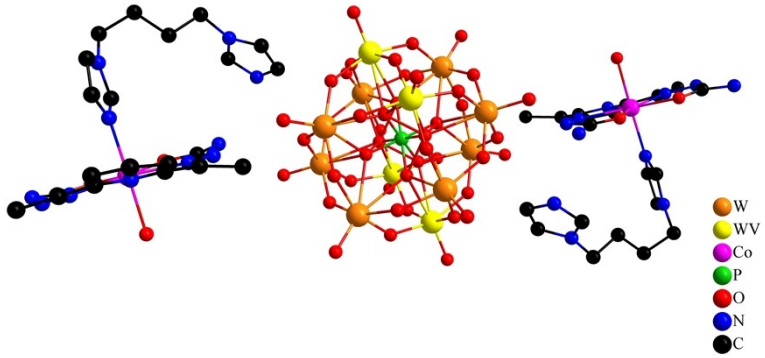

Figure S8. Ball and stick representation of the basic unit in compound **3**. Hydrogen atoms are omitted for clarity.

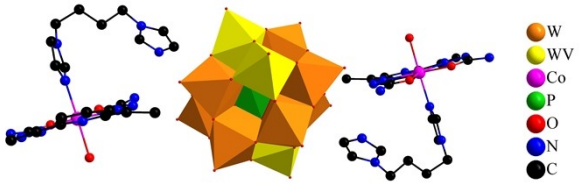

Figure S9. Polyhedral presentation of the compound **3**. Free water molecules are omitted for clarity.

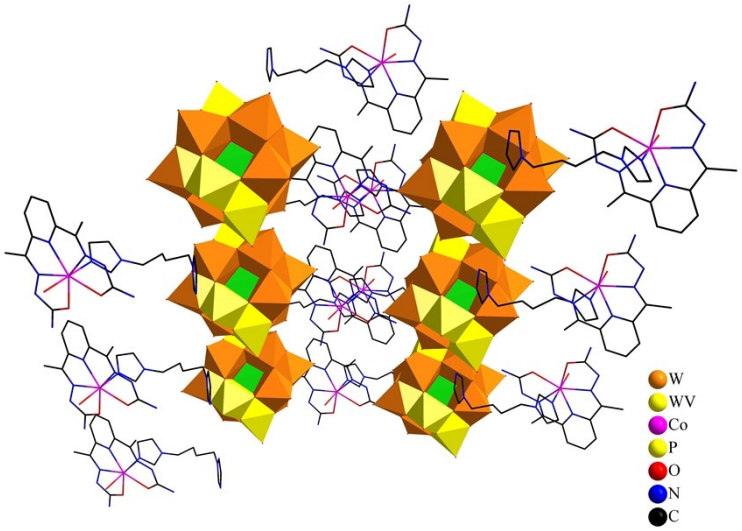

Figure S10. The 2D supramolecular structure of compound **3**. Free water molecules are omitted for clarity.

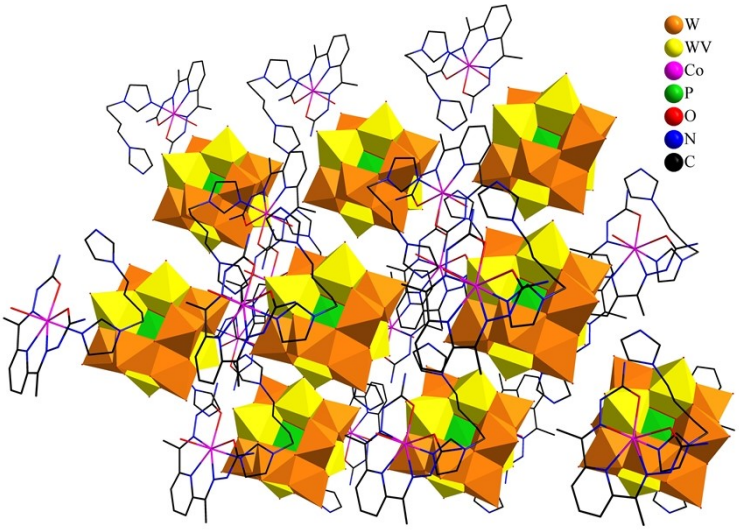

Figure S11. The 3D supramolecular structure of compound **3**. Free water molecules are omitted for clarity.

3. Characterizations

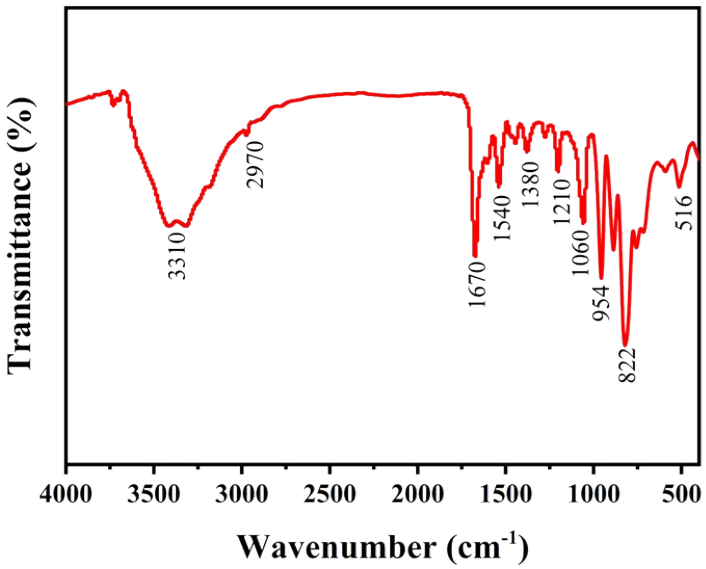

Figure S12. The IR spectrum of **1**.

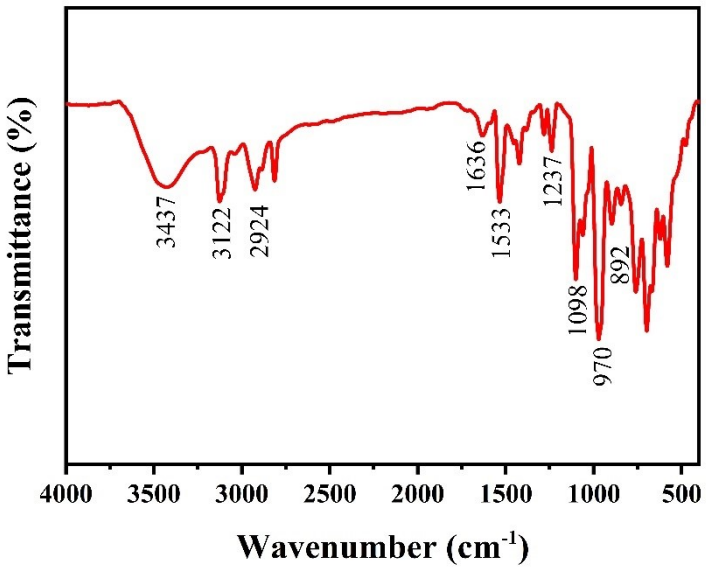

Figure S13. The IR spectrum of **2**.

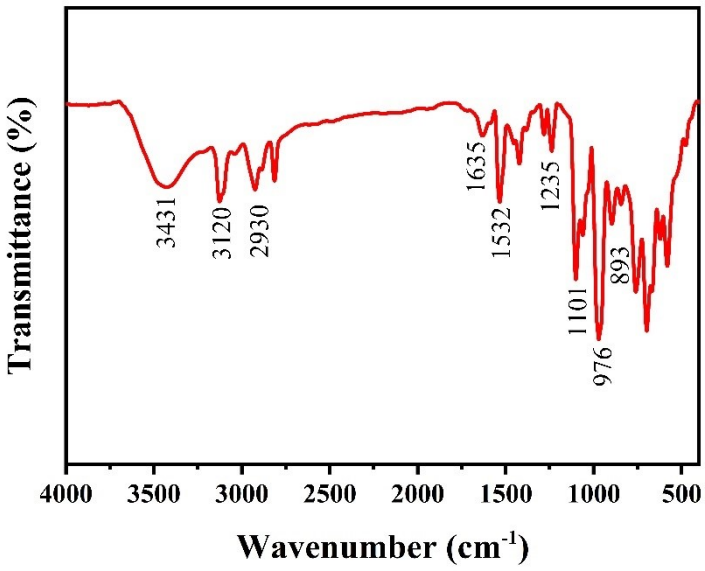

Figure S14. The IR spectrum of **3**.

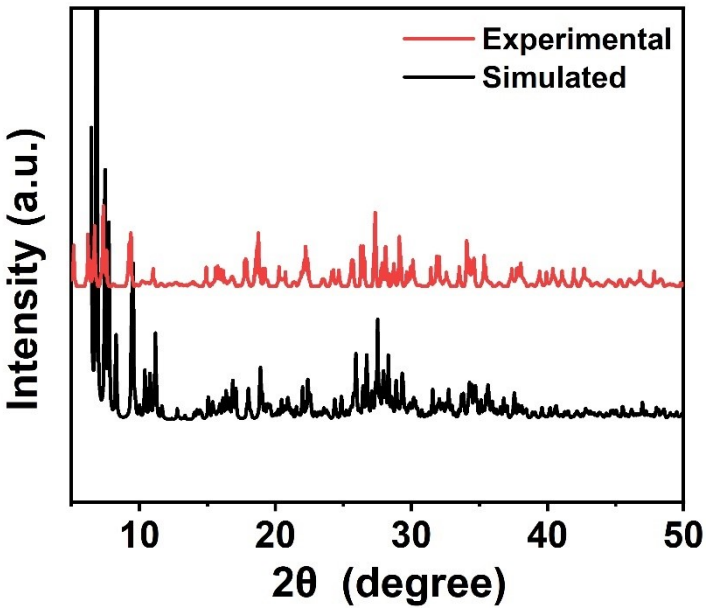

Figure S15. Experimental and simulated PXRD patterns of **1**.

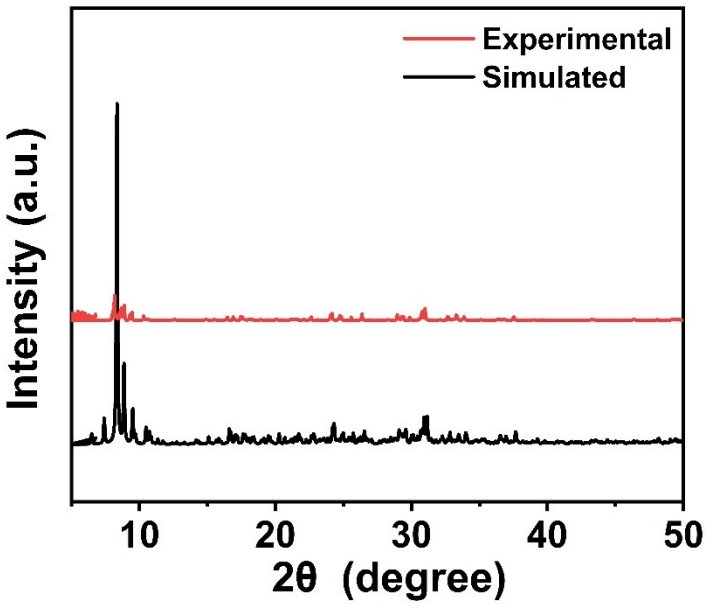

Figure S16. Experimental and simulated PXRD patterns of **2**.

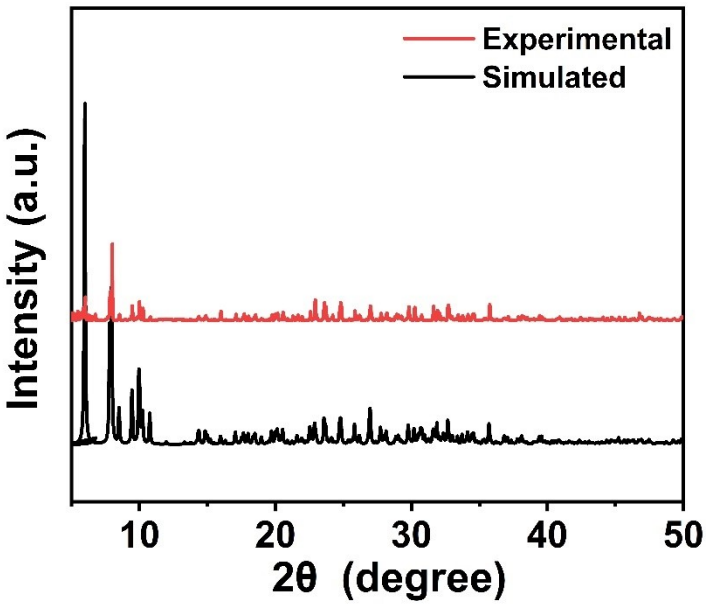

Figure S17. Experimental and simulated PXRD patterns of **3**.

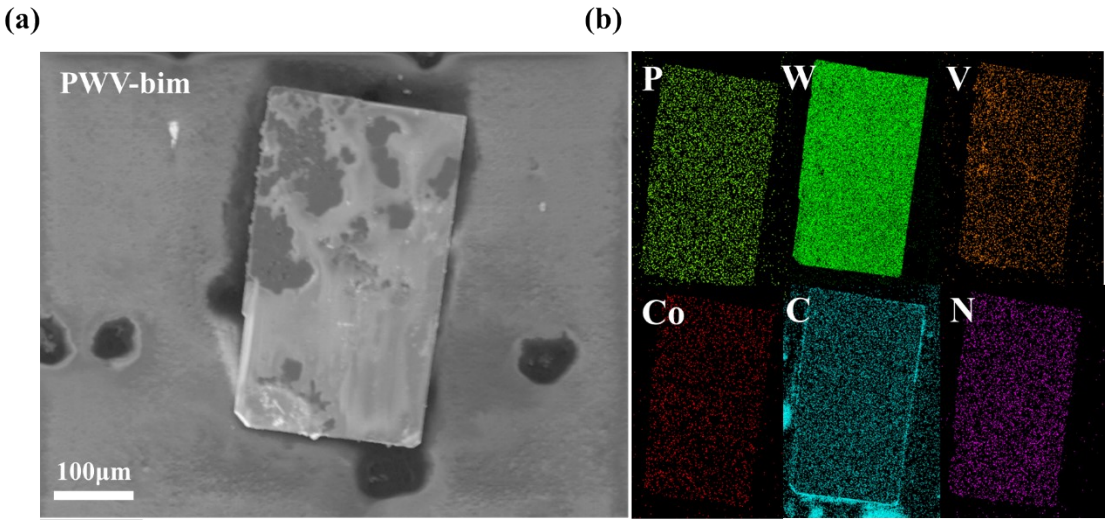

Figure S18. (a) TEM image and (b) EDX mapping of the various elements contained of **2**.

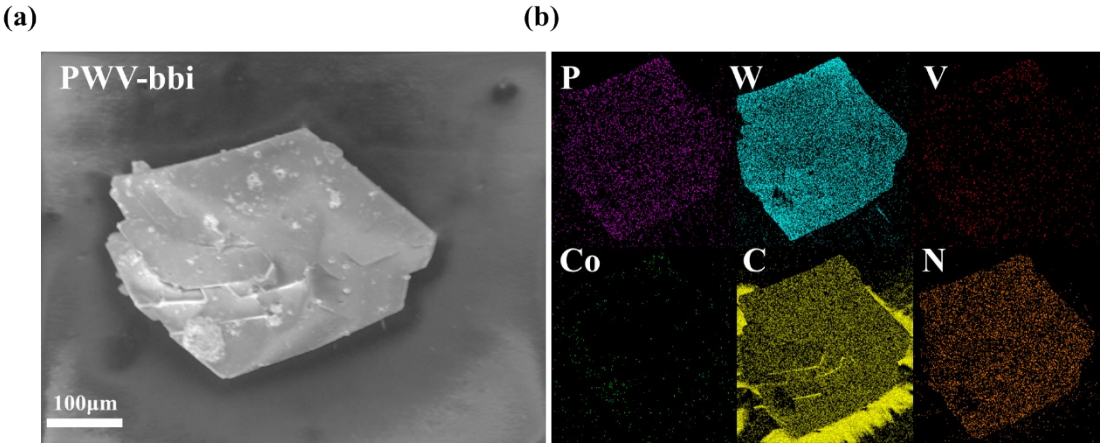

Figure S19. (a) TEM image and (b) EDX mapping of the various elements contained of **3**.

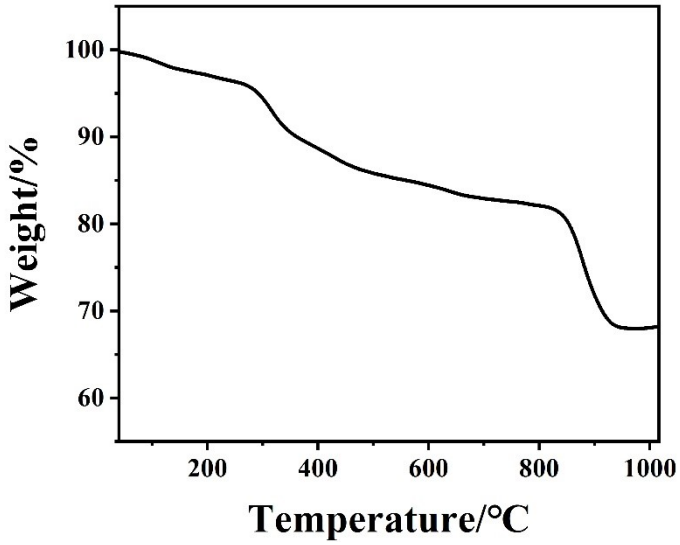

Figure S20. The TGA thermogram of as-synthesized **1**.

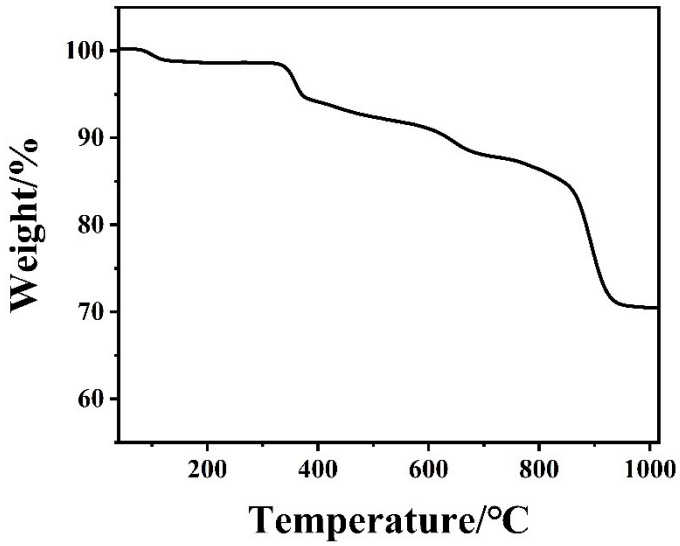

Figure S21. The TGA thermogram of as-synthesized **2**.

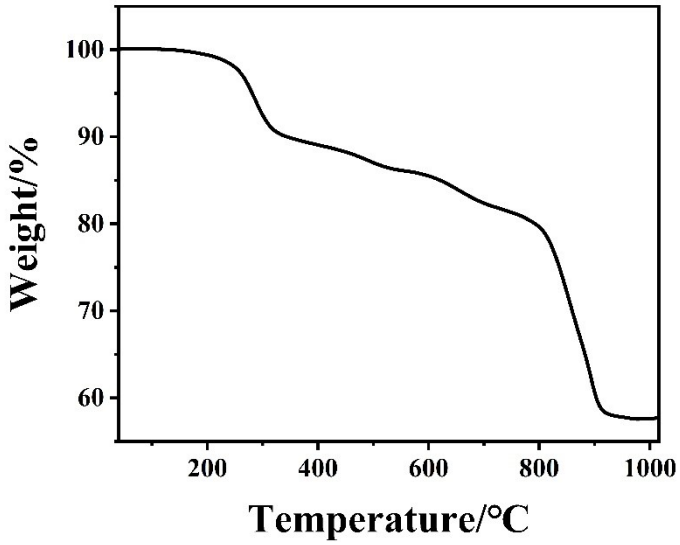

Figure S22. The TGA thermogram of as-synthesized **3**.

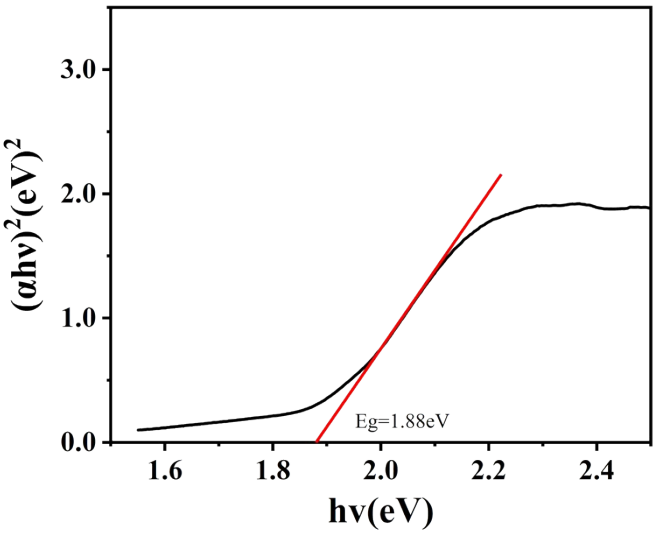

Figure S23. Tauc plot of **1**.

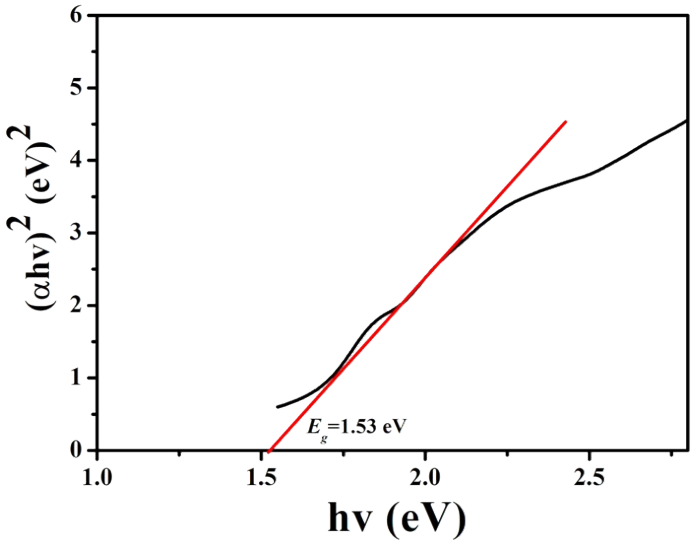

Figure S24. Tauc plot of **3**.

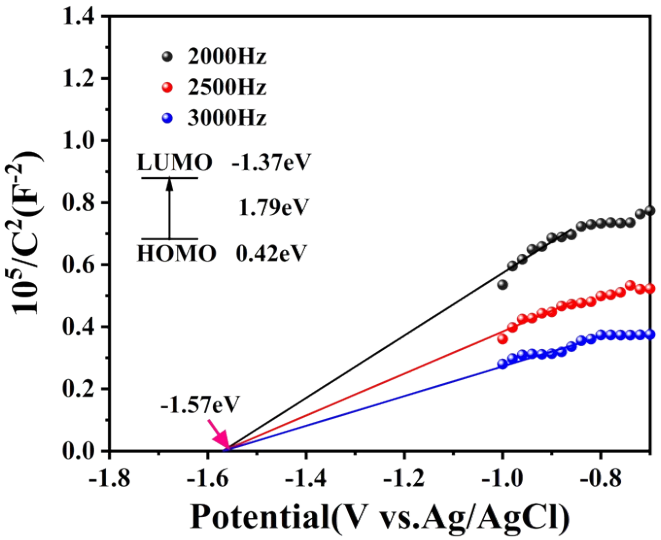

Figure S25. Mott−Schottky plot of **1**.

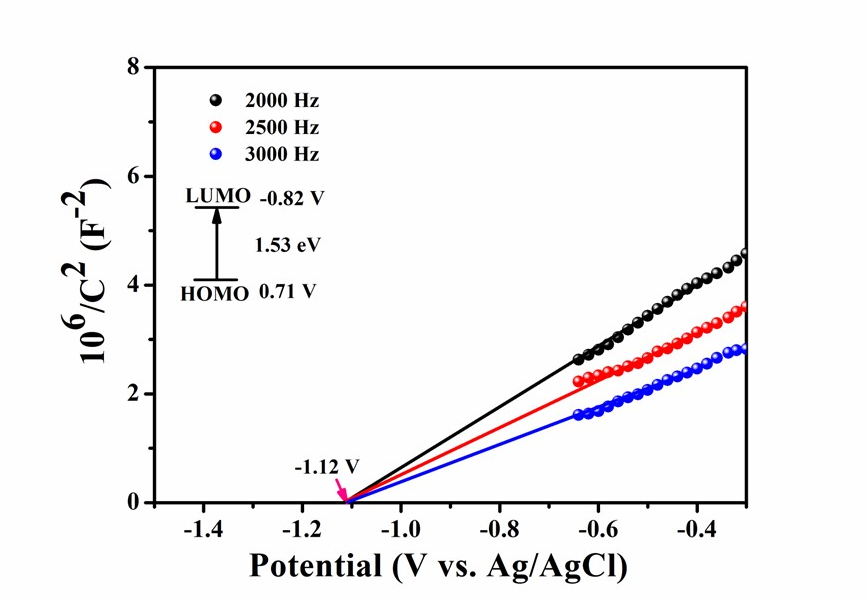

Figure S26. Mott−Schottky plot of **3**.

Figure S27. Photographs of the photocatalytic CO_2 reduction devices.

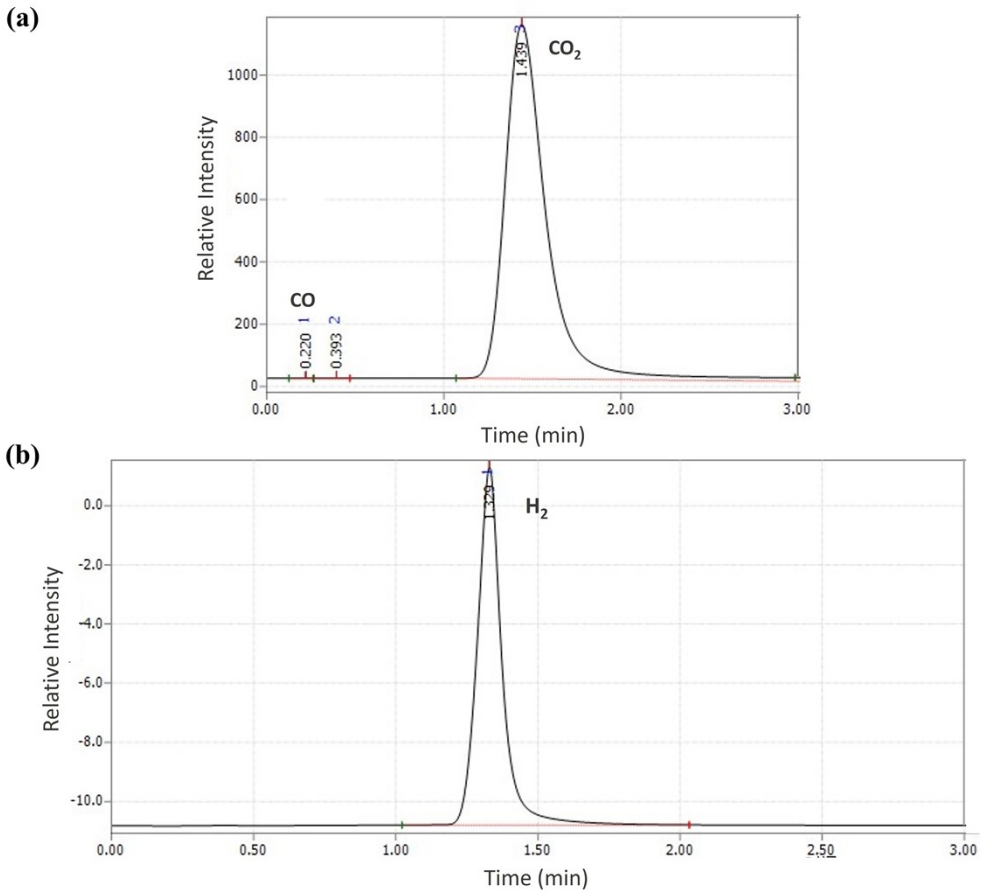

Figure S28. GC profiles of CO_2 reduction to CO with compound **2** as catalyst after reaction 8 h.

Table S5. Comparison of the photocatalytic activity of reported POM-based hybrid materials for converting CO_2 to CO.

Photocatalyst	Main product	$Rate_{CO}$ (μmol g^{-1} h^{-1})	Selectivity (%)	Light (nm)	Ref.
$[Co(DAPSC)(H_2O)_2]_2[Co(H_2O)_5]_{0.5}[PW_{11}CoO_{39}(Hdatrz)]\cdot 3.5H_2O$ (**1**)[a]	CO	4875.2	84.6	>420	This work
$H_2(bim)[H_3Co(DAPSC)(bim)(PW_{10}V^{IV}_2O_{40})]\cdot 4H_2O$ (**2**)[a]	CO	11003.3	91.5	>420	This work
$[Co(DAPSC)(bbi)(H_2O)]_2(PW_{11.5}V^{IV}_{0.5}O_{40})\cdot 4H_2O$ (**3**)[a]	CO	4882.3	82.5	>420	This work
DQTP COF-Co[b]	CO	1020	90.0	400~800	1
V_{18}-Co[c]	CO	10371	93.1	>420	2
Co-PO_4-PW_{12}[a]	CO	13676	94.5	450~700	3
$(H_2bbi)_2\{[Co_2(bbi)][Co_{2.33}(H_2O)_4][H_{9.33}CoP_8Mo_{12}O_{62}]\}\cdot 4H_2O$[a]	CO	3261	--	--	4
CUST-804[d]	CO	2710	82.8	>420	5
Zr-MBA-Ru/Mn-MOF[e]	CO	39.5	>99	>450	6

Reaction condition: (a) $[Ru(bpy)_3]Cl_2\cdot 6H_2O$ (11.3 mg), solvent (MeCN = 40 mL, TEOA = 10 mL), CO_2 atmosphere (1.0 MPa, 6 °C), 8 h. (b)$[Ru(bpy)_3]Cl_2\cdot 6H_2O$ (22.5 mg), solvent (MeCN = 40 mL, TEOA = 10 mL), CO_2 atmosphere (1.0 MPa, 20 °C). (c) $[Ru(bpy)_3]Cl_2\cdot 6H_2O$ (7 mg), solvent (MeCN = 40 mL, H_2O = 10 mL, TEOA = 1.12 mL), CO_2 atmosphere (1.0 MPa, 25 °C). (d) $[Ru(bpy)_3]Cl_2\cdot 6H_2O$ (66 μM), solvent (MeCN = 40 mL, TEOA = 10 mL), CO_2 atmosphere (1.0 MPa). (e) H_2O, no photosensitizer.

Table S6. Comparison of CO and H_2 production yields of catalyst **2**, control conditions, and control samples.

Catalysts	Dosage(mg)	CO(μmol)	H_2(μmol)	Note
2	5	402.9	35.8	Heterogeneous
$H_5PW_{10}V_2O_{40}$	3.94	0.27	0.35	Homogeneous
$Co(OAc)_2\cdot 4H_2O$	0.38	128.0	58.1	Homogeneous
$H_5PW_{10}V_2O_{40}$ + $Co(OAc)_2\cdot 4H_2O$	4.32	136.7	43.7	Homogeneous
DAPSC + bim	0.14+0.15	0.04	0.11	Homogeneous

Reaction condition: $[Ru(bpy)_3]Cl_2\cdot 6H_2O$ (11.3 mg), solvent (MeCN = 40 mL, TEOA = 10 mL), CO_2 atmosphere (1.0 MPa, 6 °C), 8 h.

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