Supplementary Information

Efficient visible light-driven water oxidation catalysts based on B-β-{BiW_8O_{30}} and unique 14-nuclear hetero-metal sandwich unit

Lige Gong[1], Li Yu[2], Kai Yu*[1], Yong Ding*[2], Jinhua Lv[1], Chunmei Wang[1], Zhanhua Su[1], Baibin Zhou *[1]

Contents

Experimental Section:

Supporting Figures:

Materials and physical measurements

All reagents were purchased and used without further purification. Elemental analysis (H) was performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Na, Bi, Co and W were performed by a Leaman inductively coupled plasma (ICP) spectrometer. IR spectra were recorded in the range of 4000–400 cm^{-1} on an Alpha Centaurt FT/IR Spectrophotometer with pressed KBr pellets. The X-ray powder diffraction data was collected on a Bruker AXS D8 Advance diffractometer using Cu-Kα radiation (λ=1.5418 Å) in the 2θ range of 5 – 50° with a step size of 0.02°. TG analyses were performed on a Perkin-Elmer TGA7 instrument in flowing N_2 at a heating rate of 10 ℃/min. UV−vis−NIR absorption spectroscopy was measured with a Cary 500 spectrophotometer. Diffuse reflectivity spectra were collected on a finely ground sample with a Cary 500 spectrophotometer equipped with a 110 mm diameter integrating sphere and were measured from 200 to 800 nm using barium sulfate ($BaSO_4$) as a standard with 100% reflectance. The electrochemical measurement was carried out on a CHI 660 electrochemical workstation at room temperature (25–30 ℃). X-ray photoelectron spectrum (XPS) analyses were performed on a VG ESCALAB MK II spectrometer with aMg Kα (1253.6 eV) achromatic X-ray source. The working electrode was a glassy carbon electrode. Platinum gauze was used as a counter electrode and Ag/AgCl as a reference electrode. Dynamic light scattering (DLS) measurements were carried out using a Zatasizer Nano 3600 instrument (Malvern Instruments Ltd.). Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were performed with a JEOL JSM 4800F scanning electron microscope.

Synthetic procedures

All common laboratory chemicals were reagent grade, purchased from commercial sources and used without further purification. $Bi(NO_3)_3{\cdot}5H_2O$ (0.228 g, 1.0 mmol), dissolved in 1 mL of 6M HCl was added to a solution of $Na_2WO_4{\cdot}2H_2O$ (3.300 g, 10.0 mmol) in 20 mL of deionized water, and the mixture was heated to 60 ℃ for about 10 min. Then, $Co(Ac)_2{\cdot}4H_2O$ (1.0 mmol)

dissolved in 4 mL water and dmap(1.0mmol)were added to the clear solution. The pH value of the solution was adjusted to 6.7 at room temperature by the addition of 1M HCl (The title compound can be prepared in the range of pH from 6.2 to 7.8, and the crystal size and geometry are ideal when pH is controlled at 6.7). The mixture was kept 90 ℃ for about 1 h and then cooled to room temperature and filtered. The purple crystal was obtained after 22 days (Yield: 45.2% based on W). In addition, parallel experiment displays that no crystals could be obtained when organic ligands are absent from the reaction system. Thus, it is supposed that the ligand could be the necessary template to provide sites of hydrogen bonding and π–π stacking interactions for the isolation of compound. Elemental Analysis (EA). For $(Hdmap)_2[\{Na(H_2O)_2\}_2\{CoNa_2(H_2O)_9\}_2\{B\text{-}a\text{-}BiW_8O_{30}\}_2\{Na_2Co_2W_2(H_2O)_6\}]\bullet 10H_2O$(dmap=N-(4-Pyridyl)dimethylamine)(**CoBiW-DMAP**): Calcd for C, 2.69 N, 0.90; H, 1.58; Co, 3.95; Bi, 6.70; W, 59.38; Na, 3.08%. Found for C, 2.73 N, 0.84 ; H, 1.60; Co, 3.91; Bi, 6.86; W, 59.32; Na, 3.02%. EA for reisolated **CoBiW-DMAP** after photocatalytic reaction: C, 2.70% N, 0.85 %; H, 1.57%; Co, 3.86; Bi, 6.86; W, 59.25; Na, 3.17%

Crystallography details

Crystal data for **CoBiW-DMAP** with the size of 0.28×0.28×0.24 mm was mounted on a glass fiber, and the data were collected at 293(2) K on Bruker APEX-Ⅱ CCD detector with graphite monochromatic Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined by fullmatrix least-squares on F2 using the SHELX program.1 Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at the calculated positions. CCDC-1510425 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crytallographic Data Centre, 12, Union Road,Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

The measurement of Quantum Yield

The quantum yields of O_2 evolution were determined for the photocatalytic water oxidation under the following conditions. A quartz flask containing a borate buffer solution (80 mM, pH 9.0, 15 mL) with **CoBiW-DMAP** (4 μM), $[Ru(bpy)_3]Cl_2$ (1 mM) and $Na_2S_2O_8$ (5 mM) was irradiated by an interference filtered (Asahi spectra SV 490) from a LED source ($420 < \lambda < 490$ nm) described above. The photon flux of the incident light was determined using a Ray virtual

radiation actinometer (FU 100, silicon ray detector, light spectrum, 400-700 nm; sensitivity, 10-50 μV μmol^{-1} m^{-2} s^{-1}), affording a value to be 1650 μmol m^{-2} s^{-1}.

Quantum Yield Calculation:

Initial O_2 formation rate = 0.044 μmol·s^{-1}

Irradiation radius = 1 cm = 0.01 m

Photon flux = π × (0.01m)^2 ×1650 μmol·m^{-2}·s^{-1} = 0.518 μmol·s^{-1}

$$\Phi_{QY(initial)} = 2 \times \frac{\text{initial } O_2 \text{formation rate}}{\text{Photon flux}} \times 100\%$$

$$= \frac{2 \times 0.044\,\text{umol}_{O_2}\text{s}^{-1}}{0.518\,\text{umol}_{\text{ph}}\text{s}^{-1}} \times 100\% = 17\%$$

Photocatalytic Water Oxidation

Photocatalytic water oxidation was performed as follows: the desired concentration of catalyst **CoBiW-DMAP** (0.5–8 μM) was prepared by dissolving the appropriate amount of catalyst in a buffer solution (80 mM, pH 4.8–10.0 for borate buffer) containing $[Ru(bpy)_3]Cl_2$ (0.25–1.5 mM) and $Na_2S_2O_8$ (1.0–7.5 mM). The above solution was deaerated by purging with Ar gas for 5 min in a flask (28 mL) sealed with a rubber septum (the total volume of the reaction solution was 15 mL). The reaction was then started by irradiating the solution with a LED light source (light intensity 16 mW, beam diameter 2 cm) through a transmitting glass filter (λ ≥ 420 nm) at room temperature. The spectrographic range of LED light is shown in the following picture. After each sampling time, 150 μL of Ar was injected into the flask and then the same volume of gas sample in the headspace of the flask was withdrawn by a SGE gas-tight syringe and analyzed by gas chromatography (GC). The O_2 in the sampled gas was separated by passing through a 2 m × 3 mm packed molecular sieve 5A column with an Ar carrier gas and quantified by a Thermal Conductivity Detector (TCD) (Shimadzu GC-9A). The total amount of evolved O_2 was calculated based on the concentration of O_2 in the headspace gas. Contamination of the head-space with air was corrected by measuring the N_2 concentration present in the head-space (from the N_2 peak in the GC traces). The solution pH was monitored after the reaction by a METTLER TOLEDO FEP20 pH meter.

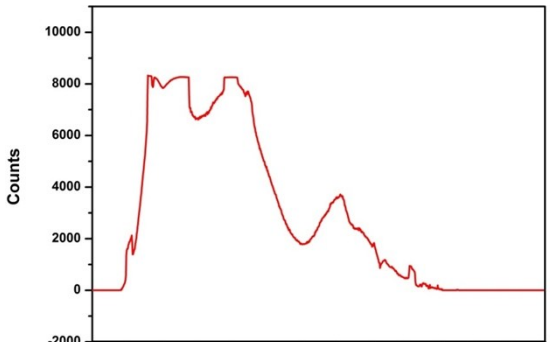


Table S1 The summary of visible light-driven water oxidation of POM-WOCs($[Ru(bpy)_3]^{2+}$ was used as photosensitizer,$S_2O_8^{2-}$as sacrificial electron acceptor)

POM-WOCs	Reaction conditions	TON	TOF	Ref
α-$K_6Na[\{Ru_3O_3(H_2O)Cl_2\}(SiW_9O_{34})]$	LED lamp (470nm), 50 μmol/L catalyst,1mmol/L$[Ru(bpy)_3]Cl_2$,5 mmol/L $Na_2S_2O_8$, 20 mmol/L Na_2SiF_6 buffer (pH 5.8)	23	0.7 s^{-1}	[1]
α-$K_{11}Na_1[Co_4(H_2O)_2(SiW_9O_{34})_2]$	LED lamp (470 nm), 42 μmol/L catalyst,1mmol/L$[Ru(bpy)_3]Cl_2$, 5mmol/L $Na_2S_2O_8$, 20 mmol/L Na_2SiF_6 buffer (pH 5.8)	24 (20 μmol/L CAT)	0.4 s^{-1} (42 μmol/L CAT)	[1]
$[\{Co_4(OH)_3(PO_4)\}_4(SiW_9O_{34})_4]^{32-}$	in 20 mL of borate buffer solution (80 mM, pH 7.5−9.0), and $Na_2S_2O_8$, $[Ru(bpy)_3]Cl_2$	44.5	0.053	[2]
$[(SiW_9O_{34})_2Co_8(OH)_6(H_2O)_2(CO_3)_3]^{16-a}$	300 W Xe lamp equipped with a long-pass filter (420 nm cutoff); catalyst concentration (1mM), $[Ru(bpy)_3]^{2+}$ (1.0 mM), $Na_2S_2O_8$ (5.0 mM), sodium borate buffer (80 mM, pH 8.0), total reaction solution volume: 20 mL	128.1	0.12	[3]
$[Cu_5(OH)_4(H_2O)_2(A\text{-}a\text{-}SiW_9O_{33})_2]^{10-}$	Conditions: LED lamp (≥ 420 nm); 5 mM catalyst, 1.0 mM $[Ru(bpy)_3]Cl_2$,5.0mM$Na_2S_2O_8$, 80mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.	91		[4]
$Na_{24}[Ni_{12}(OH)_9(CO_3)_3(PO_4)(SiW_9O_{34})_3]\cdot 56H_2O$	$[Ru(bpy)_3]^{2+}$ was used as photosensitizer,$S_2O_8^{2-}$as sacrificial electron acceptor	128.2	0.20s^{-1}	[5]
$Na_{25}[Ni_{13}(H_2O)_3(OH)_9(PO_4)_4(SiW_9O_{34})_3]\cdot 50H_2O$	$Ru(bpy)_3]^{2+}$ was used as photosensitizer, $S_2O_8^{2-}$ as sacrificial electron acceptor	147.6	0.25s^{-1}	[5]
$Na_{50}[Ni_{25}(H_2O)_2OH)_{18}(CO_3)_2(PO_4)_6(SiW_9O_{34})_6]\cdot 85H_2O$	$Ru(bpy)_3]^{2+}$ was used as photosensitizer, $S_2O_8^{2-}$ as sacrificial electron acceptor	204.5	0.34s^{-1}	[5]
$Na_{12}[\{Co^{II}_7As^{III}_6O_9(OH)_6\}$	300 W Xe lamp equipped with a	115.2	0.14	[6]

$(A\text{-}a\text{-}SiW_9O_{34})_2]\cdot 8H_2O$	long-pass filter (420 nm cutoff); catalyst concentration(1mM), $[Ru(bpy)_3]^{2+}$ (1.0 mM), $Na_2S_2O_8$ (5.0 mM), sodium borate buffer (80 mM, pH 8.0), total reaction solution volume: 20 mL;			
$[Mn_3^{III}Mn^{IV}O_3(CH_3COO)_3$ (A-α- $SiW_9O_{34})]^{6-}$	$[Ru(bpy)_3]^{2+}$ and $S_2O_8^{2-}$	5.2	0.0007 s^{-1}	[7]
$[\{Ru_4O_4(OH)_2(H_2O)_4\}$-(γ-$SiW_{10}O_{36})_2]^{10-}$	Conditions: Xe lamp, 420-520 nm bandpass filter, 50 mW light beam with a diameter of ~1.5 cm focused on the reaction solution, 1.0 mM $[Ru(bpy)_3]^{2+}$, 5.0 mM $Na_2S_2O_8$, 5.0 μM 1, 20 mM sodium phosphate buffer (initial pH 7.2), total reaction volume 8mL	~3.5×10^2	~8×10^{-2} s^{-1}	[8]
$Cs_{10}[Ru_4(m\text{-}O)_4(m\text{-}OH)_2(H_2O)_4(g\text{-}SiW_{10}O_{36})_2]$	Surelite Continuum Surelite II Nd:YAG laser (excitation at 355 nm and 532nm, half-width 8 ns), 47.6 mM $[Ru(bpy)_3]^{2+}$, 5.0mM $Na_2S_2O_8$, varying [cat.], 10mM phosphate buffer (pH 7.0) or TiO_2 film sensitized with $[Ru(bpy)_2(dpb)]^{2+}$		N/A	[9]
$Cs_{10}[Ru_4(m\text{-}O)_4(m\text{-}OH)_2(H_2O)_4(g\text{-}SiW_{10}O_{36})_2]$	50 W halogen lamp (l > 550 nm), 60 mM catalyst, 0.1 mM $[Ru\{(m\text{-}dpp)Ru(bpy)_2\}_3](PF_6)_8$, 10 mM $Na_2S_2O_8$ and 50 mM Na_2SO_4,10 mM KH_2PO_4 buffer (pH 7.2)		TOF = 8×10^{-3} s^{-1} @ 60mM catalyst	[10]
$K_{10}[Co(H_2O)_2(g\text{-}SiW_{10}O_{35})_2]\cdot 23H_2O$	A LED light (≥420nm, 16mW), $[Ru(bpy)_3]Cl_2$, $Na_2S_2O_8$, and borate buffer (0.08m, pH 9.0)	313	3.2 s^{-1}	[11]
$Cs_5[Ru^{III}(H_2O)SiW_{11}O_{39}]$	0.3mM catalyst,6mM $(NH_4)_2[Ce^{IV}(NO_3)_6]$ in 0.1 M HNO_3	20		[12]
$K_{10.2}Na_{0.8}[\{Co_4(\mu\text{-}OH)(H_2O)_3\}(Si_2W_{19}O_{70})]$	Xe lamp (420～520 nm),10 μmmol/L catalyst,1.0 mmol/L $[Ru(bpy)_3]Cl_2$,5mmol/L,$Na_2S_2O_8$, 25 mmol/L sodium borate buffer (pH 9.0)	80	0.1 s^{-1}	[13]
$[\{\beta\text{-}SiNi_2W_{10}O_{36}(OH)_2(H_2O)\}_4]^{24-}$	0.5 mM $[Ru(bpy)_3]^{2+}$ and 10 mM $Na_2S_2O_8$. Conditions: ≥420 nm	335	1.7 s^{-1}	[14]

	LED light (17 mW, beam diameter ~0.4cm), 80mM sodium borate buffer initial pH 9.0, total solution volume15 mL.			
$[\{Co_4(OH)_3(PO_4)\}_4(GeW_9O_{34})_4]^{32-}$	in 20 mL of borate buffer solution (80 mM, pH 7.5−9.0), and $Na_2S_2O_8$,$[Ru(bpy)_3]Cl_2$	38.75	15.5 μmol	[13]
$Cs_9[(c\text{-}PW_{10}O_{36})_2Ru_4O_5(OH)(H_2O)_4]$	Xe lamp, 420–520nm bandpass filter, 1.0 mM $[Ru(bpy)_3]Cl_2$, 5 mM $Na_2S_2O_8$,20 mM Na_2SiF_6 buffer pH 5.8	120	5.1 mM	[15]
$Na_{10}[Co_4(H_2O)_2(\alpha\text{-}PW_9O_{34})_2]$	Xe lamp (420～470 nm), 5 μmol/Lcatalyst,1.0mmol/L $[Ru(bpy)_3]Cl_2$,5.0mmol/L $Na_2S_2O_8$, 80 mmol/L sodium borate buffer (pH 8.0)	224		[16]
$[\{Co_4(OH)_3(PO_4)\}_4(PW_9O_{34})_4]^{28-}$	in 20 mL of borate buffer solution (80 mM, pH 7.5−9.0), and $Na_2S_2O_8$, $[Ru(bpy)_3]Cl_2$	20.25	8.7μmol	[16]
$[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$	Conditions: 455 nm LED light (17mW, beam diameter ~0.5 cm), 5.0mM $Na_2S_2O_8$, 1.0mM $[Ru(bpy)_3]Cl_2$,2.0μM Co_4POM (blue), 2.0 μM Co_4POM + 0.15 μM $Co(NO_3)_2$ (red), 0.15 μM $Co(NO_3)_2$ (black) all in 120 mM borate buffer, and 0.15 μM $Co(NO_3)_2$ (green) in 80 mM borate buffer.	TON = 302 ± 1		[17]
$[\{Co_4(OH)_3(PO_4)\}_4(AsW_9O_{34})_4]^{28-}$	in 20 mL of borate buffer solution (80 mM, pH 7.5−9.0), and $Na_2S_2O_8$, $[Ru(bpy)_3]Cl_2$	33.0	13.2 μmol	[16]
$[Mn_3(H_2O)_3(SbW_9O_{33})_2]^{12-}$	1.0 mM $[Ru(bpy)_3]Cl_2$ and 5.0 mM $Na_2S_2O_8$. Conditions: >420 nm LED light (17 mW, beam diameter ~0.4cm), 80mM sodium borate buffer initial pH 9.0, total solution volume15 mL.	103	0.4 s^{-1}	[18]
$[Fe_{11}(H_2O)_{14}(OH)_2(W_3O_{10})_2(a\text{-}SbW_9O_{33})_6]^{27-}$	LED lamp (≥420 nm), 1.0 mM $[Ru(bpy)_3](ClO_4)_2$,5.0mM $Na_2S_2O_8$, 80 mM sodium borate buffer (initial pH 10.0),	1815 ± 50	6.3 s^{-1}	[19]
$[\{Co(H_2O)_3\}_2\{CoBi_2W_{19}O_{66}(OH)_4\}]^{10-}$	$[Ru(bpy)_3]^{2+}$ as photosensitizer (PS) and $S_2O_8^{2-}$ as a sacrificial	21	115 μM	[20]

	electron acceptor in different buffer media: NaOAc/HOAc (40 mM, pH 4.7),NaPi (40 mM, pH 7 and 8), and Na_2SiF_6/$NaHCO_3$ buffer(20 mM, pH 5.8)			
$Na_9H_5[Co_2Bi_2(\alpha\text{-B-}CoW_9O_{34})_2]$	Xe lamp (＞400 nm), 10 μmol/L catalyst,1.0mmol/L$[Ru(bpy)_3]Cl_2$,5mmol/L$Na_2S_2O_8$,50mmol/L sodium phosphate buffer (pH 7.4)	9.5		[21]
$Na_{14}[Co_2Bi_2(\beta\text{-B-}CoW_9O_{34})_2]$	Xe lamp (＞400 nm), 10 μmol/L catalyst,1.0mmol/L$[Ru(bpy)_3]Cl_2$,5mmol/L $Na_2S_2O_8$, 50 mmol/L sodium phosphate buffer (pH 7.4)	30		[21]
$K_7[Co^{III}Co^{II}(H_2O)W_{11}O_{39}]$	LED lamp, ≥420 nm, 1.0 mmol/L $[Ru(bpy)_3]Cl_2$,5mmol/L $Na_2S_2O_8$, 80mmol/L sodium borate buffer (pH 8.0)	360 (1 μmol/L CAT)	0.5 s^{-1} (5 μmol/L CAT)	[22]
$(NH_4)_3[CoMo_6O_{24}H_6]\cdot 7H_2O$	300 W Xe lamp (400–490/800 nm), 20 mM catalyst, 0.4 mM $[Ru(bpy)_3](NO_3)_2$,3mM $Na_2S_2O_8$, 0.1 M borate buffer solution (pH 8.0)		TOF initial = 0.11 s^{-1}	[23]
$(NH_4)_6[Co_2Mo_{10}O_{38}H_4]\cdot 7H_2O$	300 W Xe lamp (400–490/800 nm), 10 mM catalyst, 0.4 mM $[Ru(bpy)_3](NO_3)_2$,3mM $Na_2S_2O_8$, 0.1 M borate buffer solution (pH 8.0)		TOF initial = 0.16 s^{-1}	[23]
$Na_{10}[Co_4(H_2O)_2(VW_9O_{34})_2]\cdot 35H_2O$	1.0 mM $[Ru(bpy)_3]Cl_2$ and 5.0 mM $Na_2S_2O_8$. Conditions: 455 nm LED light (17 mW, beam diameter ~0.4cm), 80mM sodium borate buffer initial pH 9.0, total solution volume 2.0 mL.	~ 35	> 1 × 10^3 s^{-1}	[24]
$[(V^{IV}{}_5V^{V}{}_1)O_7(OCH_3)_{12}]^-$	$Ru(bpy)_3{}^{2+}$ (2 × 10^{-4} M), 1 (6 × 10^{-5} M), and $Na_2S_2O_8$ (10 mM) in 2mL of acetonitrile/phosphate buffer, and excitation at λ = 450 nm			[25]
$[Mn_4V_4O_{17}(OAc)_3]^{3-}$	$Ru(bpy)_3{}^{2+}$ (2 × 10^{-4} M), 1 (6 × 10^{-5} M), and $Na_2S_2O_8$ (10 mM) in MeCN/H_2O (9:1)	1150	1.75s^{-1}	[26]
$[Co^{II}(Me_6tren)(OH_2)]^{2+}$	1.0 mM $[Ru(bpy)_3]Cl_2$ and 5.0	54		[27]

	mM $Na_2S_2O_8$. Conditions: ≥420 nm Xe lamp , 2 mL 100mM borate buffer initial pH 9.0			
$[Co^{III}(Cp^*)(bpy)(OH_2)]^{2+}$	1.0 mM $[Ru(bpy)_3]^{2+}$ and 5.0 mM $Na_2S_2O_8$. Conditions: ≥420 nm Xe lamp , 2 mL 100mM borate buffer initial pH 9.0	29		[27]
$Co(NO_3)_2$	1.0 mM $[Ru(bpy)_3]^{2+}$ and 5.0 mM $Na_2S_2O_8$. Conditions: ≥420 nm Xe lamp , 2 mL 100mM borate buffer initial pH 9.0	52		[27]
$Co_4O_4(py)_4(Ac)_4$	$[Ru(bpy)_3]^{2+}$ and $S_2O_8^{2-}$	40±2	$0.02s^{-1}$	[28]
$[Co^{II}_4(dpy\{OH\}O)_4(OAc)_2(H_2O)_2](ClO_4)_2$	LED lamp, 470 nm, 1.0 mmol/L $[Ru(bpy)_3]Cl_2$, 5mmol/L $Na_2S_2O_8$, 80mmol/L sodium borate buffer (pH 8.5)	20	$0.24s^{-1}$	[29]

Table S2 Crystallographic parameters for **CoBiW-DMAP.**

Compound	**CoBiW-DMAP**
Formula	$C_7H_{20}Bi\ Co_2N_2Na_4O_{49}W_9$
Mr	2989.61
Crystal. size, mm^3	0.28 ×0.28×0.24
Crystal system	Monoclinic
Space group	C2/c
a, Å	43.399(17)
b, Å	18.242(7)
c, Å	17.078(7)
β, deg	103.322(5)
V ($Å^3$)	13157(9)
Z	8
D_{calcd}, Kg m^{-3}	3.019
μ(MoKα), mm^{-1}	18.935
F(000), e	10520.0
θ range, deg/°	2.38-28.57
Reflections collected / unique/ Rint	16778 / 16421/ 0.0000
Data/restraints/parameters	16410 / 43 / 678
R_1/ wR_2 $[I \geq 2\sigma(I)]^a$	0.0641/ 0.1284
$R(F)/wR(F^2)^a$ (all refl.)	0.1099/ 0.1385
GoF $(F^2)^a$	1.000
Δρfin (max/min), e $Å^{-3}$	1.097/-0.607

$^aR_1 = \sum||F_0|-|F_C||/\sum|F_0|$; $wR_2 = \sum[w(F_0^2-F_C^2)^2]/\sum[w(F_0^2)^2]^{1/2}$, $w=[\sigma^2(F_0^2)+(0.484P)^2+24.2999P]^{-1}$, where $P=(Max(F_0^2,0)+2\ F_C^2)/3$, $GoF=[\sum w(F_0^2-F_C^2)^2/(n_{obs}-n_{param})]^{1/2}$.

Table S3 The selected bond lengths for **CoBiW-DMAP**.

Bi(1)-O(5)	2.086(14)	Bi(1)-O(14)	2.158(11)	Bi(1)-O(22)	2.124(12)
W(1)-O(2)	1.919(11)	W(1)-O(8)	1.774(12)	W(1)-O(12)	1.955(11)
W(1)-O(14)	2.248(12)	W(1)-O(20)	2.041(13)	W(1)-O(24)	1.722(13)
W(2)-O(3)	1.910(13)	W(2)-O(4)	1.899(13)	W(2)-O(5)	2.280(13)
W(2)-O(16)	1.884(12)	W(2)-O(21)	1.920(12)	W(2)-O(30)	1.727(13)
W(3)-O(3)	1.935(13)	W(3)-O(6)	1.812(12)	W(3)-O(12)	1.965(12)
W(3)-O(13)	2.000(12)	W(3)-O(14)	2.218(11)	W(3)-O(36)	1.736(12)
W(4)-O(4)	1.925(12)	W(4)-O(5)	2.348(13)	W(4)-O(10)	1.877(12)
W(4)-O(15)	1.983(13)	W(4)-O(17)	1.707(13)	W(4)-O(23)	1.857(13)
W(5)-O(9)	1.923(12)	W(5)-O(10)	1.975(13)	W(5)-O(11)	1.975(12)
W(5)-O(22)	2.244(11)	W(5)-O(29)	1.777(13)	W(5)-O(33)	1.744(13)
W(6)-O(2)	1.944(11)	W(6)-O(9)	1.967(11)	W(6)-O(18)	1.789(12)
W(6)-O(22)	2.179(12)	W(6)-O(25)	1.736(13)	W(6)-O(27)	1.973(13)
W(7)-O(5)	2.197(12)	W(7)-O(7)	1.764(13)	W(7)-O(19)	1.767(12)
W(7)-O(21)	2.063(14)	W(7)-O(23)	2.116(13)	W(7)-O(26)	1.771(12)
W(8)-O(1)	1.907(12)	W(8)-O(11)	1.936(12)	W(8)-O(15)	1.890(14)
W(8)-O(22)	2.242(13)	W(8)-O(27)	1.922(13)	W(8)-O(37)	1.716(14)
W(9)-O(1)	1.889(12)	W(9)-O(13)	1.908(12)	W(9)-O(14)	2.263(12)
W(9)-O(16)	1.955(13)	W(9)-O(20)	1.866(14)	W(9)-O(32)	1.709(13)
Co(1)-O(8)	2.097(12)	Co(1)-O(18)	2.035(13)	Co(1)-O(26)#1	2.024(13)
Co(1)-O(34)	2.103(13)	Co(1)-O(35)	2.191(14)	Co(1)-O(38)	2.120(15)
Co(1)#1- O(26)	2.024(13)	Co(2)-O(6)#1	2.035(12)	Co(2)-O(7)	2.041(13)
Co(2)-O(19)#1	2.021(14)	Co(2)-O(28)	2.190(13)	Co(2)-O(29)	2.050(13)
Co(2)-O(31)	2.128(15)	Co(2)#1- O(6)	2.034(12)	Co(2)#1- O(19)	2.021(14)
Na(1) - O(6)	2.443(17)	Na(1) - O(8)	2.417(15)	Na(1)-O(9)#3	2.427(14)
Na(1)-O(12)	2.762(16)	Na(1)-O(31)#1	2.530(16)	Na(1)-O(39)	2.363(19)
Na(1)#2-O(9)	2.427(14)	Na(1)#2-O(31)	2.530(16)	Na(2)-O(28)	2.437(18)
Na(2)-O(42)	2.44(2)	Na(2)-O(44)	2.325(17)	Na(2)-O(3)#1	2.541(14)
Na(2)-O(19)#1	2.660(16)	Na(2)-O(21)#1	2.576(15)	Na(2)-O(43)#1	2.58(2)
Na(2)#1-O(19)	2.660(16)	Na(2)#1-O(21)	2.576(15)	Na(2)#1-O(43)	2.58(2)
Na(3)-O(34)#3	2.373(18)	Na(3)-O(35)#3	2.511(19)	Na(3)-O(36)	2.383(17)
Na(3)-O(40)	2.35(3)	Na(3)-O(41)	2.43(3)	Na(3)-O(43)	2.30(2)
Na(3)#2-O(34)	2.373(18)	Na(3)#2-O(35)	2.511(19)	Na(3)#2-O(38)	2.477(18)
Na(4)-O(38)#2	2.477(18)	Na(4)-O(45)	2.36(2)	Na(4)-O(46)	2.48(2)
Na(4)-O(47)	2.35(2)	Na(4)-O(48)	2.46(2)		
O(5)-Bi(1)-O(14)	87.3(5)	O(5)-Bi(1)-O(22)	89.6(5)	O(22) -Bi(1)-O(14)	84.1(4)
O(24)-W(1)-O(2)	101.7(6)	O(24)-W(1)-O(8)	103.4(7)	O(24)-W(1)-O(12)	97.2(5)
O(24)-W(1)-O(14)	161.7(5)	O(24)-W(1)-O(20)	92.7(6)	O(30)-W(2)-O(3)	101.0(6)
O(30)-W(2)-O(4)	99.5(6)	O(30)-W(2)-O(5)	171.4(5)	O(30)-W(2)-O(16)	101.0(6)
O(30)-W(2)-O(21)	97.1(6)	O(36)-W(3)-O(3)	100.4(6)	O(36)-W(3)-O(6)	103.8(6)
O(36)-W(3)-O(12)	97.1(6)	O(36)-W(3)-O(13)	98.2(6)	O(24)-W(3)-O(14)	169.2(5)
O(17)-W(4)-O(4)	97.9(6)	O(17)-W(4)-O(5)	170.0(5)	O(17)-W(4)-O(10)	92.0(5)
O(17)-W(4)-O(15)	100.5(6)	O(17)-W(4)-O(23)	99.9(6)	O(33)-W(5)-O(9)	100.1(6)
O(33)-W(5)-O(10)	100.6(6)	O(33)-W(5)-O(11)	97.8(6)	O(33)-W(5)-O(22)	171.8(6)
O(33)-W(5)-O(29)	104.3(6)	O(25)-W(6)-O(2)	96.4(6)	O(25)-W(6)-O(9)	95.7(5)

O(25)-W(6)-O(18)	105.0(7)	O(25)-W(6)-O(22)	167.5(6)	O(25)-W(6)-O(27)	97.7(7)
O(7)-W(7)-O(5)	80.1(6)	O(7)-W(7)-O(19)	96.9(6)	O(7)-W(7)-O(21)	154.2(6)
O(7)-W(7)-O(23)	90.9(6)	O(7)-W(7)-O(26)	102.8(6)	O(37)-W(8)-O(1)	98.7(6)
O(37)-W(8)-O(11)	98.1(6)	O(37)-W(8)-O(15)	102.7(7)	O(37)-W(8)-O(22)	170.7(6)
O(37)-W(8)-O(27)	100.4(7)	O(32)-W(9)-O(1)	98.8(6)	O(32)-W(9)-O(13)	99.0(6)
O(32)-W(9)-O(14)	173.4(6)	O(32)-W(9)-O(16)	101.0(7)	O(32)-W(9)-O(20)	101.5(6)
O(26)-Co(1)-O(8)	90.8(5)	O(26)-Co(1)-O(18)	97.9(6)	O(26)-Co(1)-O(34)	85.6(5)
O(26)-Co(1)-O(35)	167.0(6)	O(26)-Co(1)-O(38)	92.4(6)	O(19)-Co(2)-O(6)	89.5(5)
O(19)-Co(2)-O(7)	89.5(5)	O(19) -Co(2)-O(28)	95.1(5)	O(19) -Co(2)-O(29)	88.8(5)
O(19)-Co(2)-O(31)	175.5(5)	O(39)-Na(1)-O(6)	142.2(6)	O(39)-Na(1)-O(8)	106.2(6)
O(39)-Na(1)-O(9)	88.7(5)	O(39)-Na(1)-O(12)	153.5(6)	O(39)-Na(1)-	82.2(6)
O(44) -Na(2)-O(3)	144.8(6)	O(44) -Na(2)-O(21)	102.2(5)	O(44)-Na(2)-O(28)	78.1(6)
O(44)-Na(2)-O(42)	80.7(7)	O(44)-Na(2)-	110.2(6)	O(43) -Na(3)-O(34)	167.3(9)
O(43)-Na(3)-O(35)	97.0(7)	O(43)-Na(3)-O(36)	96.9(7)	O(43) -Na(3)-O(40)	93.3(9)
O(43)-Na(3)-O(41)	97.8(8)	O(47)-Na(4)-O(33)	91.4(8)	O(47)-Na(4)-	163.1(8)
O(47)-Na(4)-O(45)	108.1(8)	O(47)-Na(4)-O(46)	83.2(9)	O(47) -Na(4)-O(48)	84.6(9)

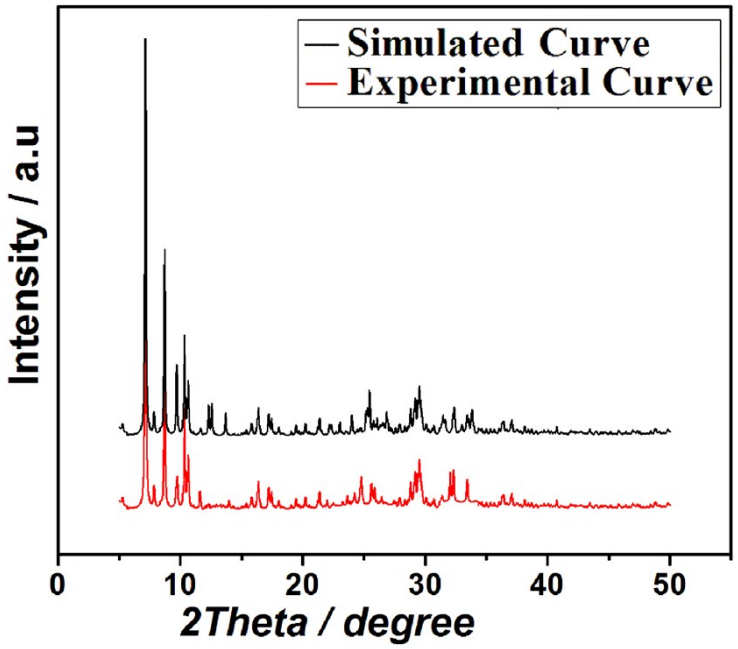


Fig. S1 The XRD pattern of **CoBiW-DMAP**. The phase purity of **CoBiW-DMAP** was confirmed by the well match of the experimental pattern (line in red) with the simulated one (line in black). The diffraction peaks of both simulated and experimental patterns match in the key positions, indicating the phase purity of the compound. The difference in intensity may be due to the preferred orientation of the powder samples.

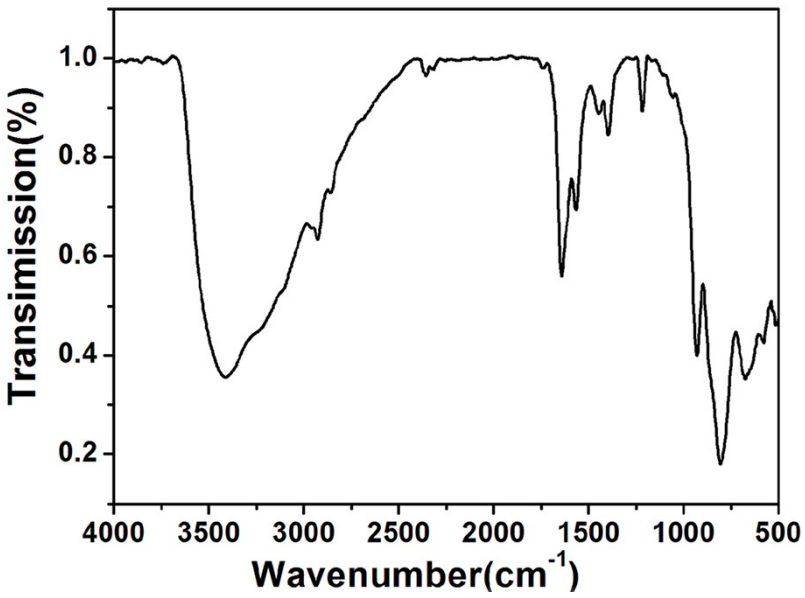


Fig. S2 The FT-IR spectrum in the range 4000-500 cm^{-1} for **CoBiW-DMAP**. Peaks at 515 cm^{-1} and 933 cm^{-1} can be attributed to ν(W-Oa) and ν(W=Od) vibrations. The characteristic peaks 809 cm^{-1} and associated with ν(W-Ob-W), and 677 cm^{-1} attributed to ν(W-Oc-W), respectively. In addition, bands in the 1217-1642 cm^{-1} regions can be assigned to characteristic peaks of the dmap ligands.

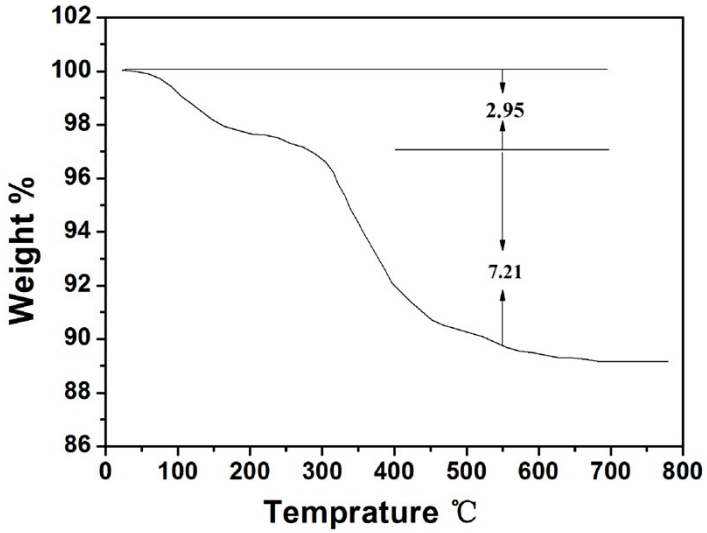


Fig. S3 Thermal gravimetric analysis has been performed for the three compounds between 20 and 800 ℃. The first weight loss of 2.95% in the temperature range of 60 – 280 °C corresponds to the release of all lattice water molecules, which is in accordance with the calculated value of 2.87 %. The second weight loss of 7.21 % in the temperature range of 280 – 550 °C are attributed to the loss of all dmap organic ligands in the **CoBiW-DMAP**. The value is close to the calculated value of 7.53%.

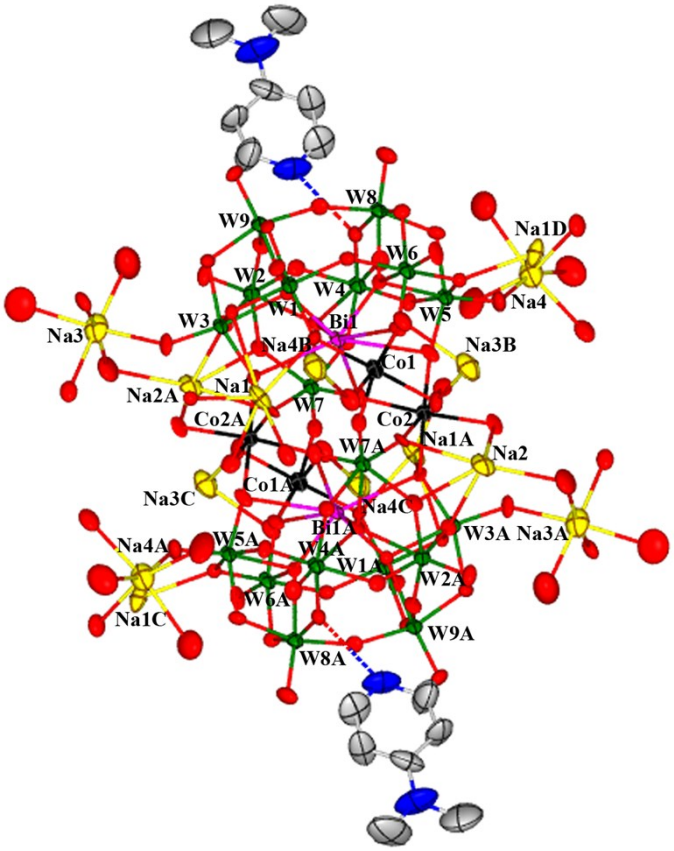


Fig. S4 ORTEP view of the basic units in **CoBiW-DMAP** with 50% thermal ellipsoid.

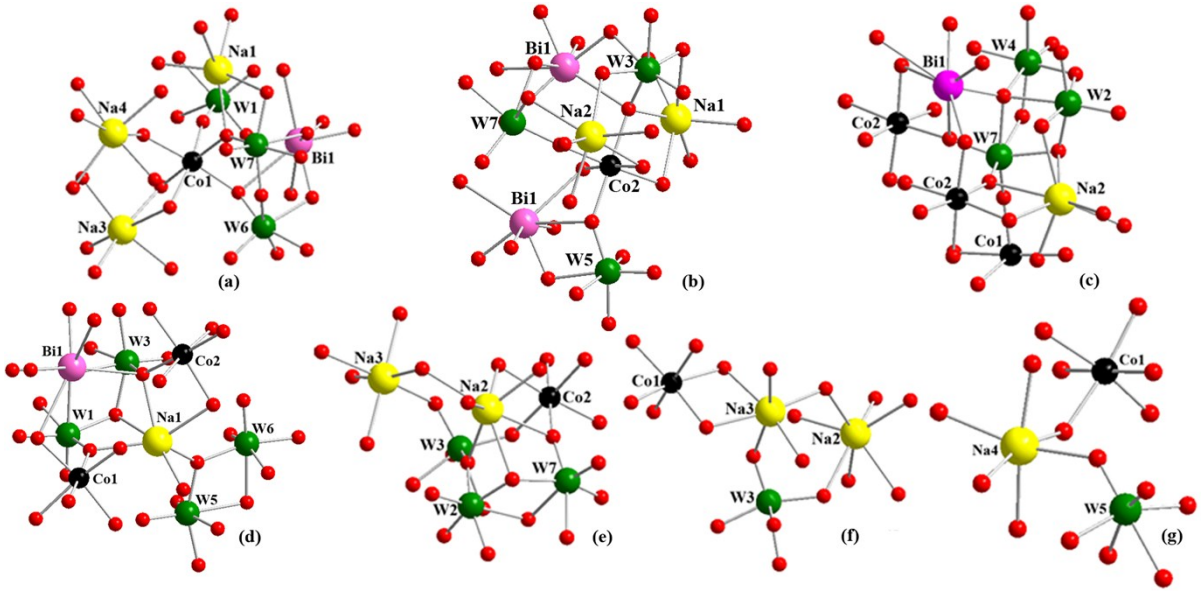


Fig. S5 The coordination environments of the Co1, Co2, W7, Na1, Na2, Na3, and Na4 atoms in **CoBiW-DMAP**.

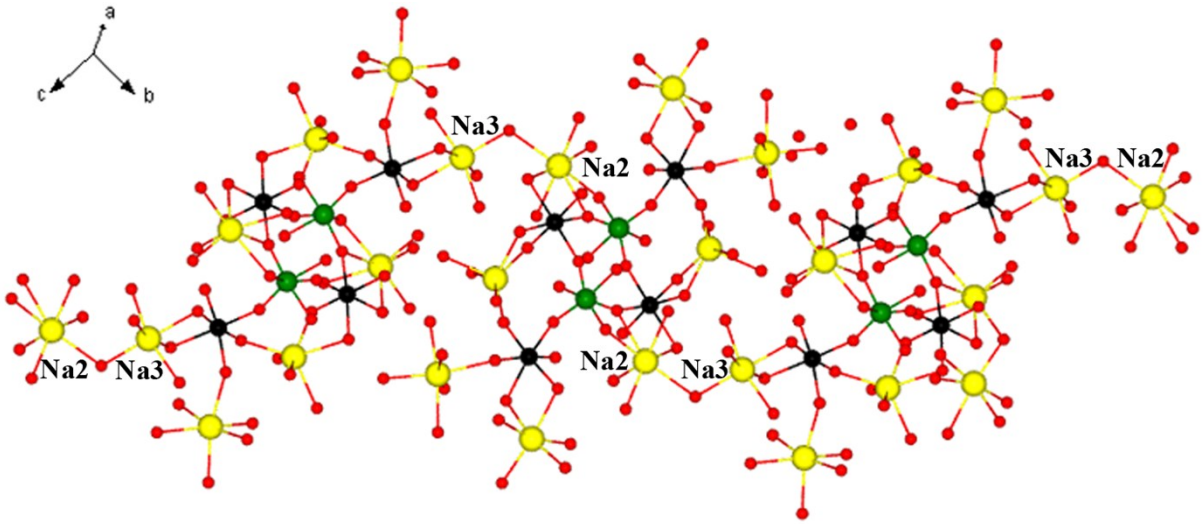


Fig. S6 The infinite 1-D chain based on fourteen-nuclear units for **CoBiW-DMAP.**

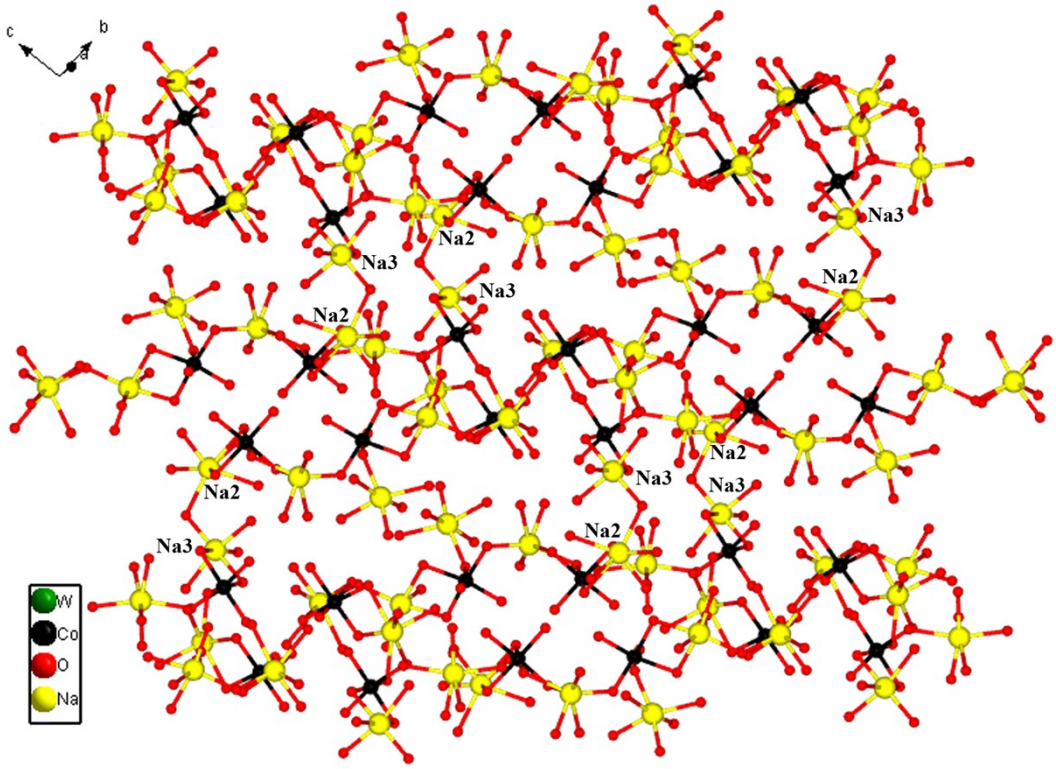


Fig. S7 The infinite 2-D layer linked by Na-O-Na liker for **CoBiW-DMAP**.

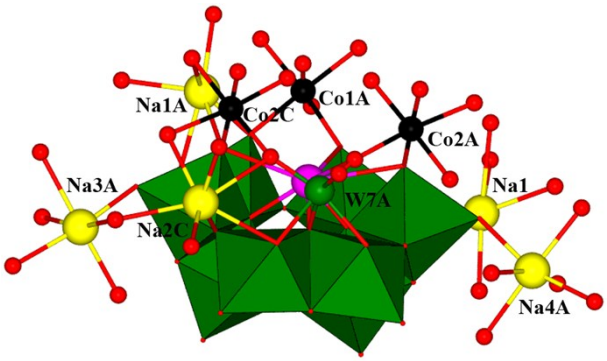


Fig. S8 The Coordination environment of {BiW_8} polyoxoanions for **CoBiW-DMAP**.

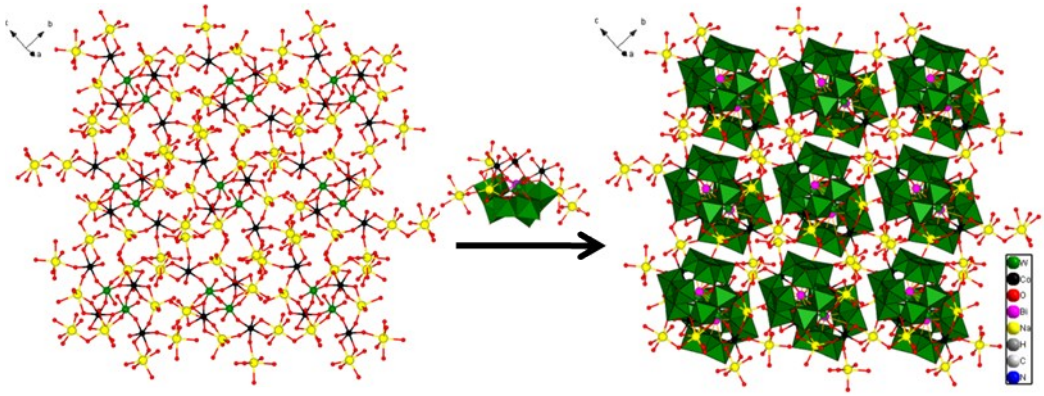


Fig. S9 (a) The unique 2D mixed metal oxide layer based on 14-nucler sandwich unit; (b) The 2D layer of **CoBiW-DMAP** based on {B-β-BiW_8O_{30}} clusters and 14-nucler sandwich units.

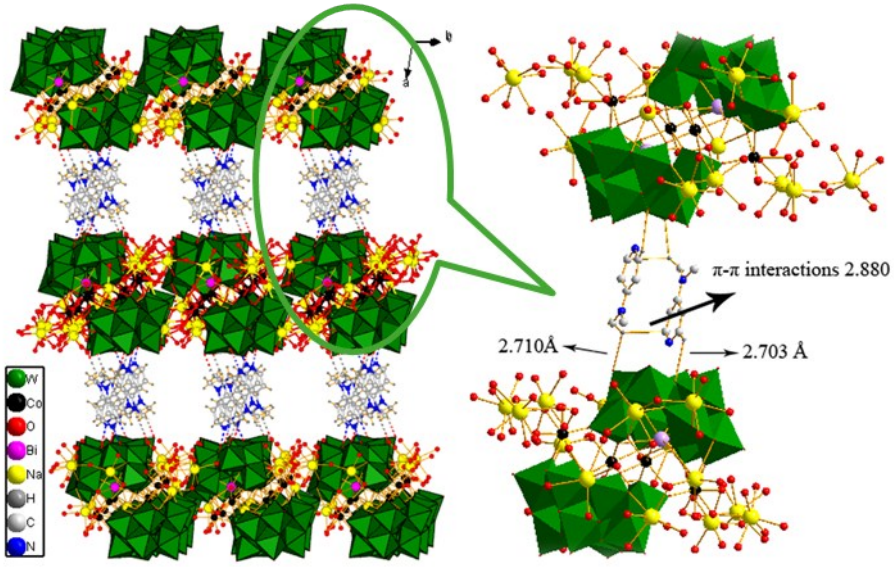


Fig. S10 The schematic view of the 3D structure of **CoBiW-DMAP**.

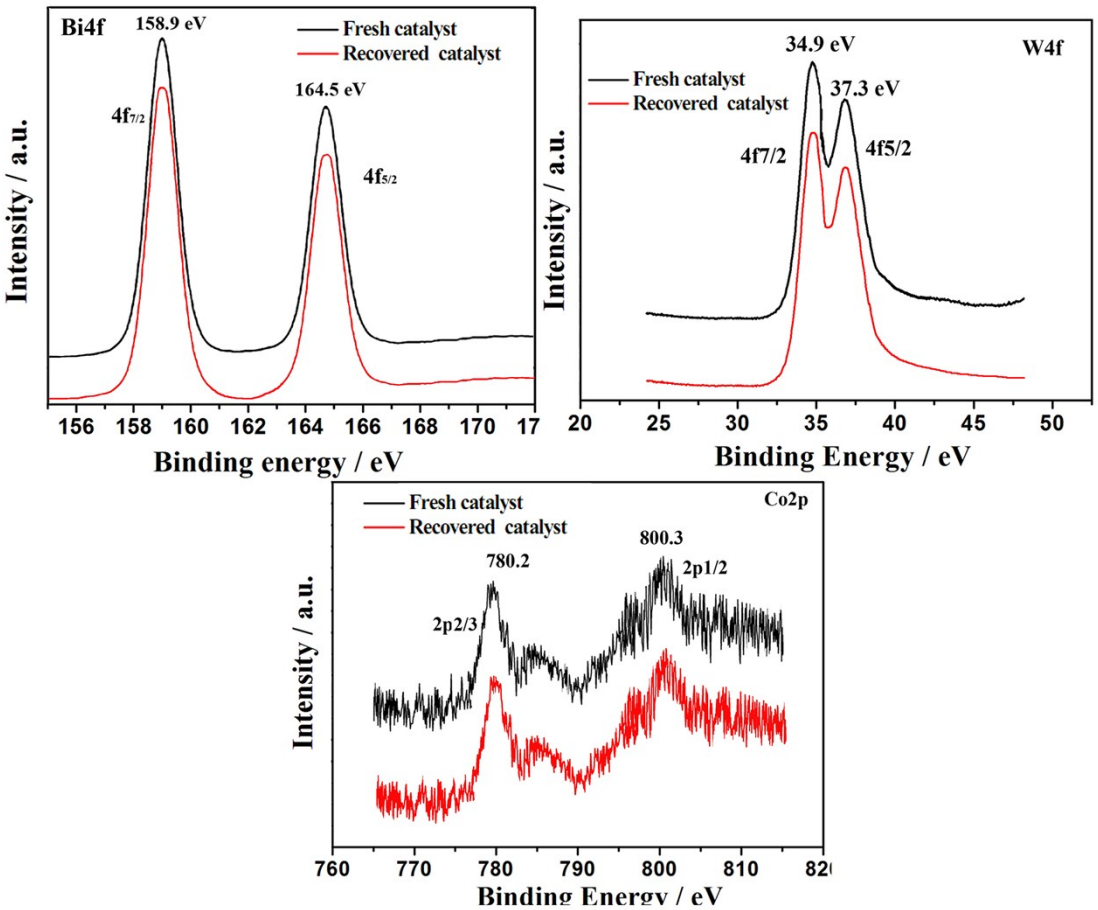
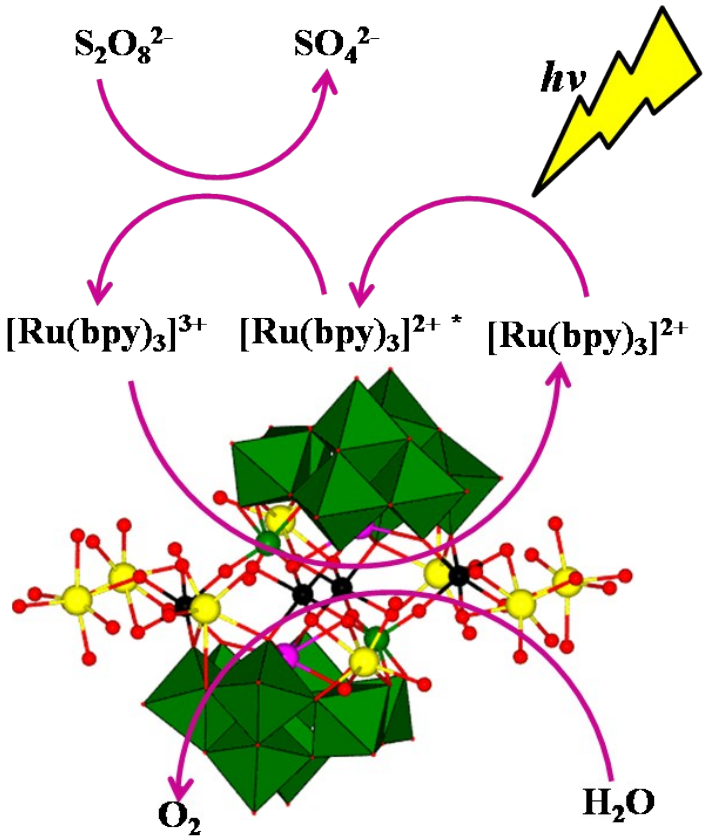


Fig. S11 The X-ray photoelectron spectra (XPS) of **CoBiW-DMAP** before and after the photocatalytic water oxidation reaction. (The $Bi4f_{7/2}$ and $Bi4f_{5/2}$ binding energies of 158.9 and 164.5 eV, the $W4f_{7/2}$ and $W4f_{5/2}$ binding energies of 34.9 and 37.3 eV, and the $Co2p_{3/2}$ and $Co2p_{1/2}$ binding energies of 780.2 and 800.3 eV for CoBiW-DMAP indicate that the oxidation state for Bi, W, and Co centers are +3, +6, and +2, respectively.)



Scheme S1. Photochemical water oxidation cycle in presence of **CoBiW-DMAP**, photosensitizer, and electron acceptor.

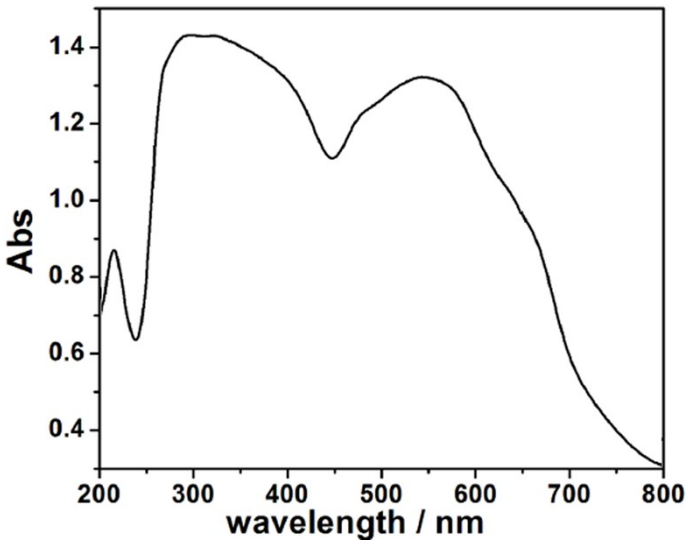


Fig.S12 UV-Vis diffuse reflectance spectrum of **CoBiW-DMAP.**

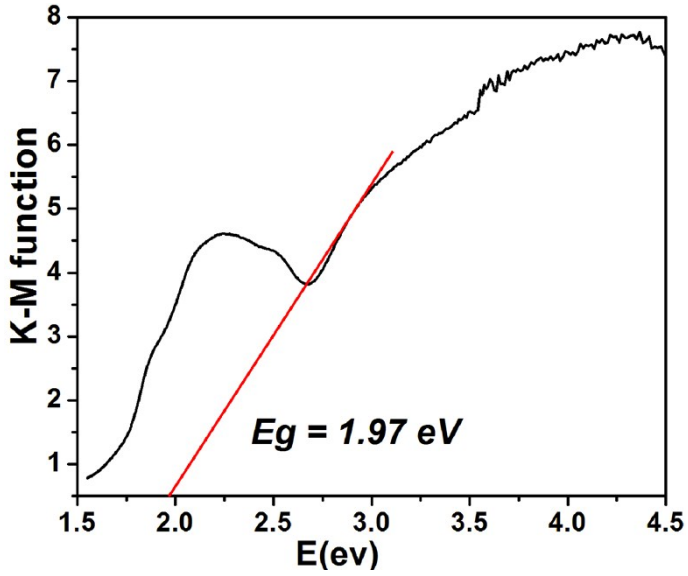


Fig.S13 K-M function versus E(ev) curve of **CoBiW-DMAP**. The red dashed lines are the tangents of the curves. The intersection value is the band gap**.**

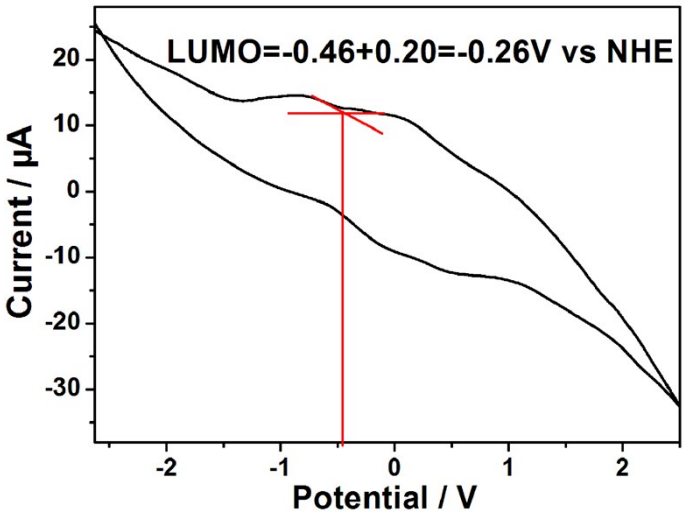


Fig.S14 Cyclic voltammogram of 2.5×10^{-4} M **CoBiW-DMAP** in pure water (pH = 7.0) at a scan rate of 100mV/s. The working electrode was glassy carbon and the reference electrode was Ag/AgCl.

With Ag/AgCl electrode as reference electrode, relative to that NHE potential of 0.20 eV, the formula for calculating level:

E_{HOMO}= -(eE^{ox}+4.5 +0.20) eV = -(eE^{ox}+4.70) eV

E_{LUMO}= -(eE^{red}+4.5 +0.20) eV = -(eE^{red}+4.70) eV

$Eg=E_{HOMO}-E_{LUMO}$ E^{red}= -0.26 V

E_{LUMO}= -(Ee^{red}+4.6+0.20) eV = -(-0.26+4.70) eV = -4.44 eV Eg = 1.97 eV

E_{HOMO} = -(1.97+4.44) eV= -6.41 eV

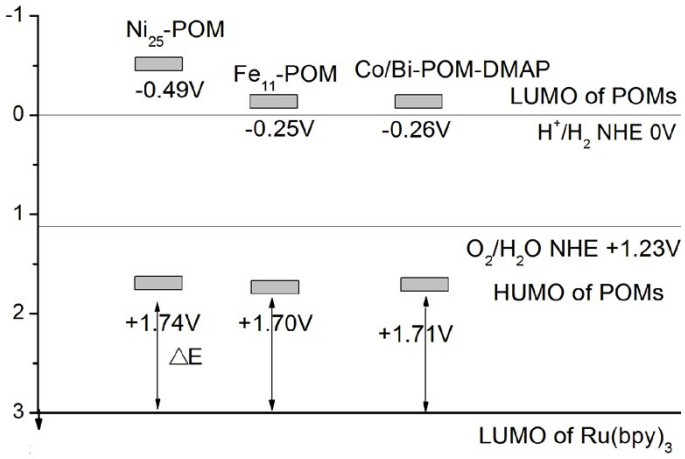


Fig.S15 The band gap structures of Ni_{25}-POM , Fe_{11}-POM and CoBiW-DMAP. △E = HOMO ($[Ru(bpy)_3]^{3+}$)–HOMO(POMs).

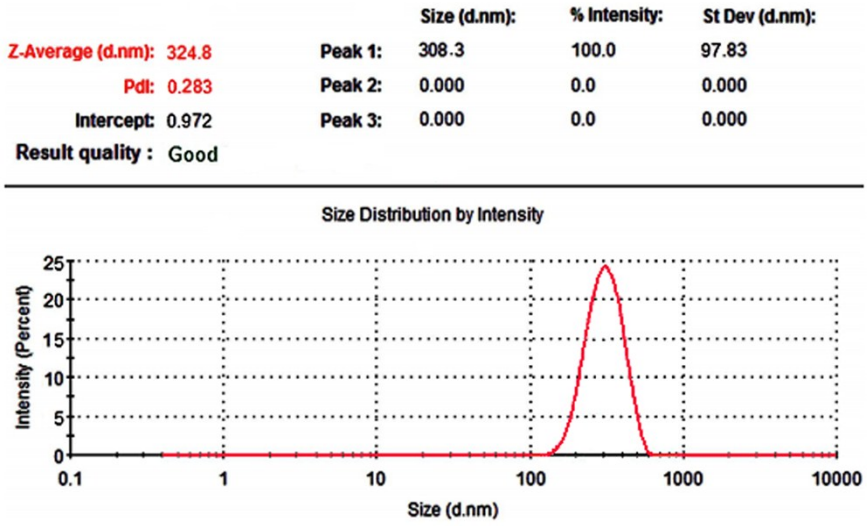


Fig.S16 DLS curve of the solution obtained by re-distributing the POM-dye precipitate in distilled water.

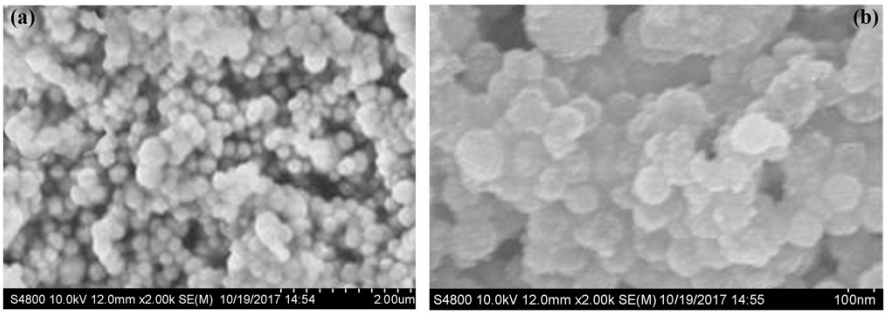


Fig.S17 (a) and (b) SEM images of the precipitate formed from **CoBiW-DMAP**

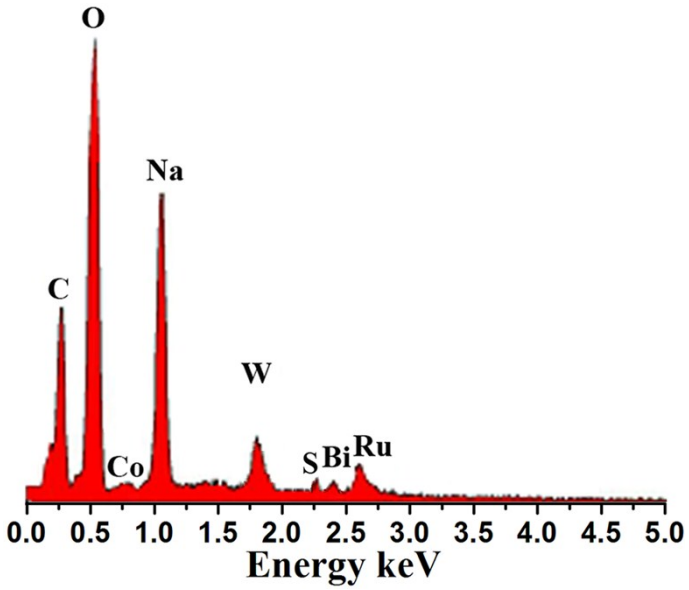


Fig.S18 EDX analysis of the ion-pairing salt precipitates obtained from the photocatalytic water oxidation solution of **CoBiW-DMAP**.

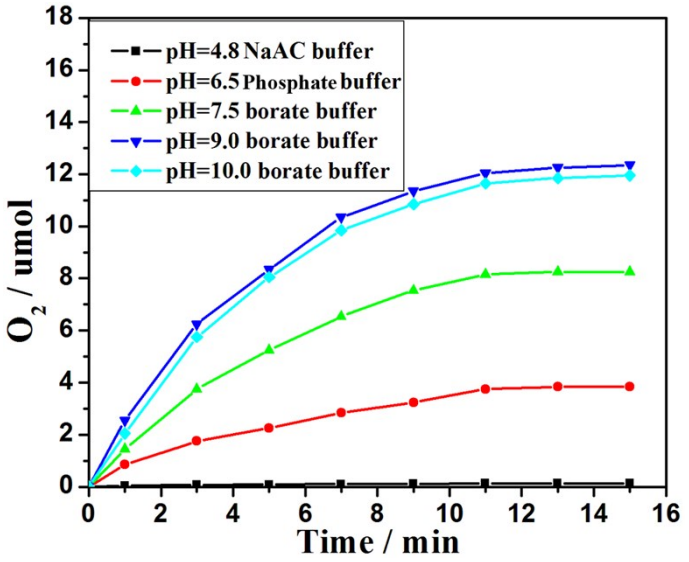


Fig. S19 Kinetics of O_2 formation in the photocatalytic system under various pH conditions. Conditions: LED lamp ($\lambda \geq 420$ nm), 1.0 mM $[Ru(bpy)_3]Cl_2$, 5.0 mM $Na_2S_2O_8$, 4 μM **CoBiW-DMAP**, total reaction volume is 15 mL.

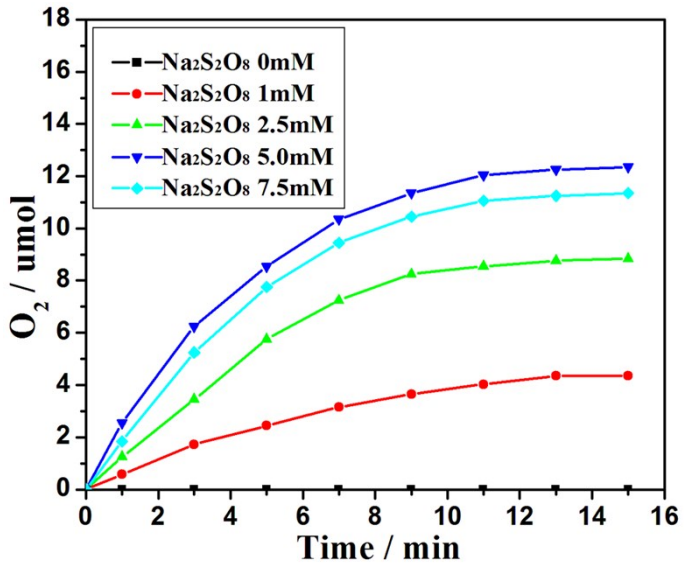


Fig. S20 Kinetics of O_2 formation in the photocatalytic system using different concentrations of $Na_2S_2O_8$. Conditions: LED lamp ($\lambda \geqslant 420$ nm), 1.0 mM $[Ru(bpy)_3]Cl_2$, 4 μM **CoBiW-DMAP**, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.

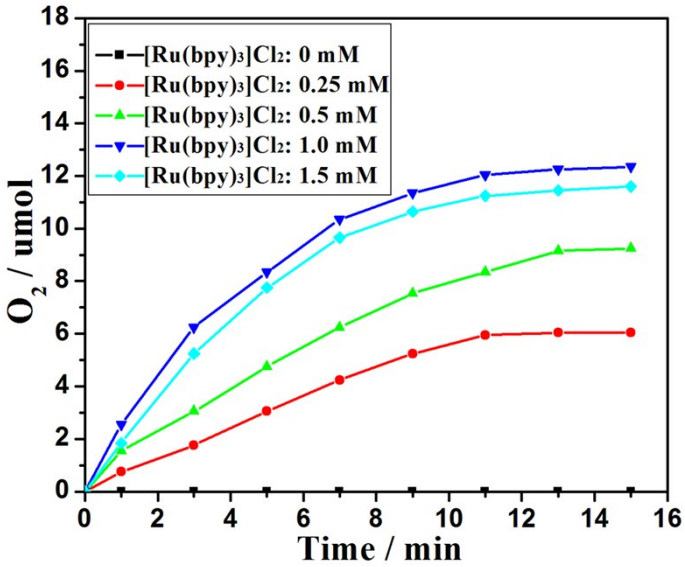


Fig. S21 Kinetics of O_2 formation in the photocatalytic system using different concentrations of $[Ru(bpy)_3]Cl_2$. Conditions: LED lamp ($\lambda \geqslant 420$ nm), 5.0 mM $Na_2S_2O_8$, 4 μM CoBiW-DMAP, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.

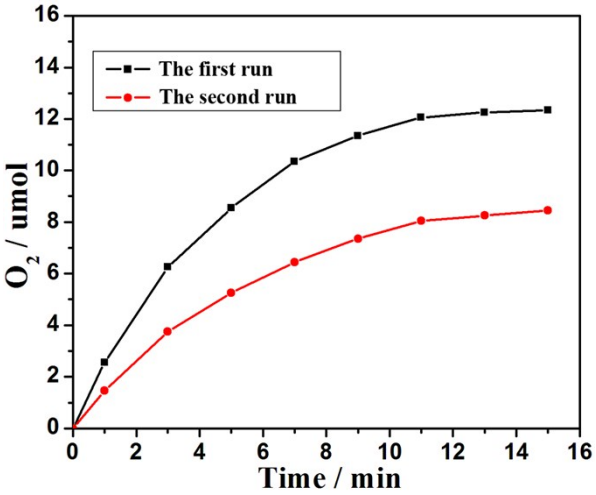


Fig. S22 Kinetics of O_2 formation for the first run and the second run. After completion of the first run, 17.8 mg $Na_2S_2O_8$ was added to the second run. Conditions: LED lamp ($\lambda \geqslant 420$ nm), 1.0 mM $[Ru(bpy)_3]Cl_2$, 5.0 mM $Na_2S_2O_8$, 4 μM CoBiW-DMAP, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.

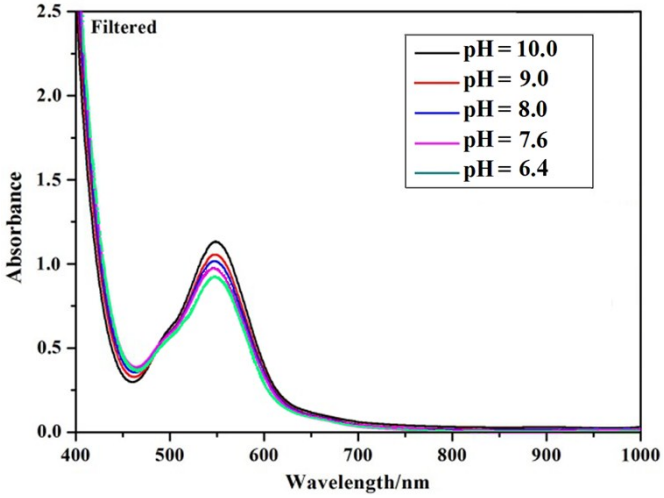


Fig. S23 The UV-Vis spectra of **CoBiW-DMAP** (0.5 mM) in sodium borate buffer (pH = 10, 9, 8, and 7.6) and phosphate buffer solutions (pH = 6.4).

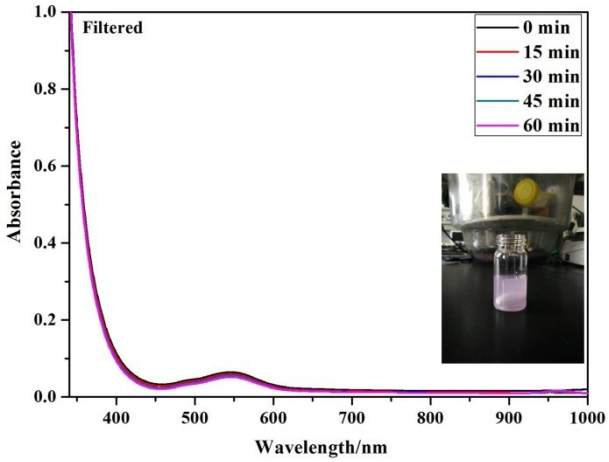


Fig. S24 Time-dependent UV-Vis spectra of CoBiW-DMAP (0.5 mM) in the pH 9.0 sodium borate buffer solution (80 mM) with $Na_2S_2O_8$ (5 mM).

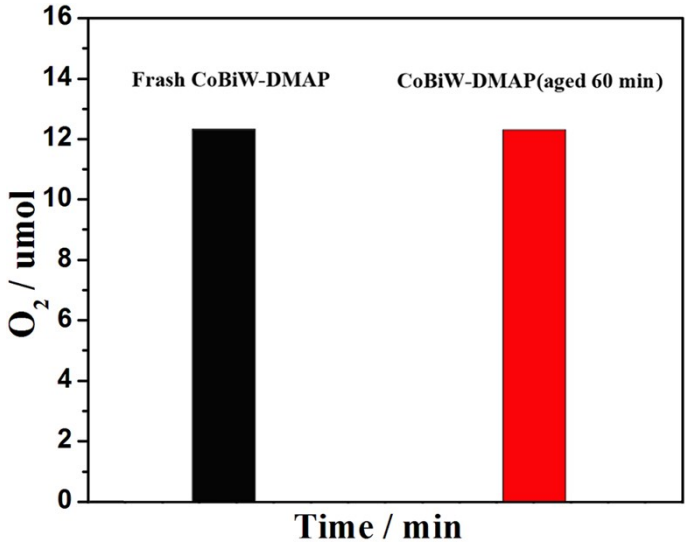


Fig. S25 O_2 evolution in the photocatalytic system using 4 μM of fresh (black) and 60 min aged **CoBiW-DMAP** (red). Conditions: LED lamp (λ≥420 nm), 1.0 mM $[Ru(bpy)_3]Cl_2$, 5.0 mM $Na_2S_2O_8$, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.

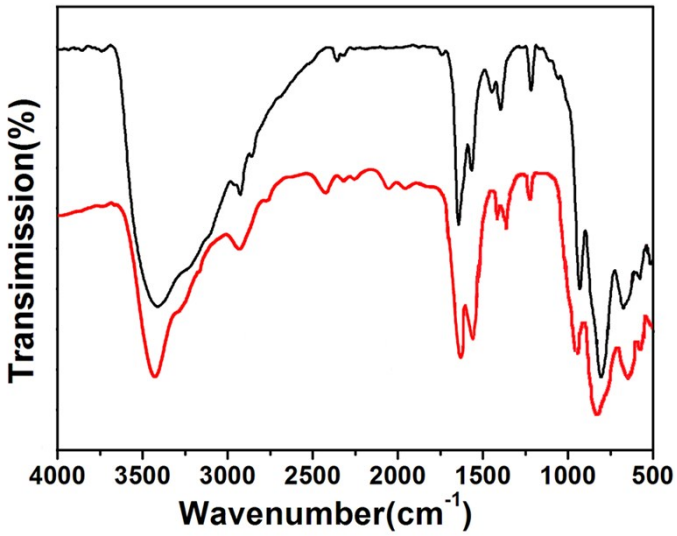


Fig. S26 FT-IR spectra of fresh (black curve) and the recycled **CoBiW-DMAP** (red curve) obtained from the photocatalytic water oxidation solution using acetone.

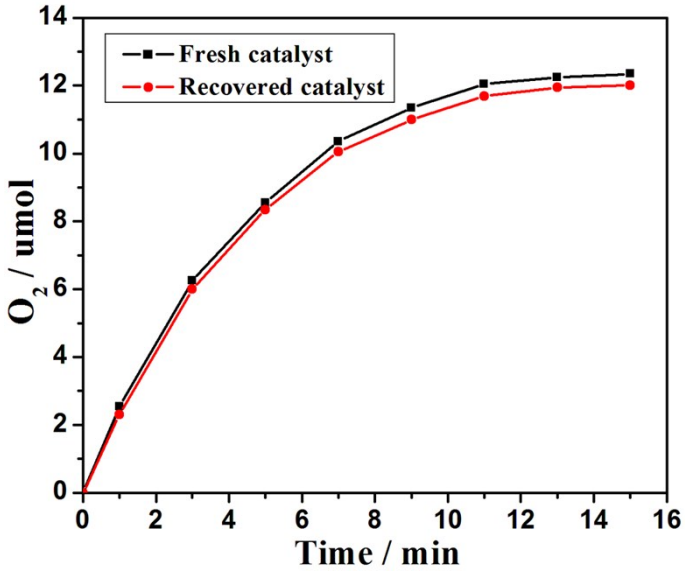


Fig. 27. Kinetics of O_2 formation in the photocatalytic system using fresh and recovered **CoBiW-DMAP**. Conditions: LED lamp ($\lambda \geq 420$ nm), 1.0 mM $[Ru(bpy)_3]Cl_2$, 5.0 mM $Na_2S_2O_8$, 4 μM **CoBiW-DMAP**, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL.

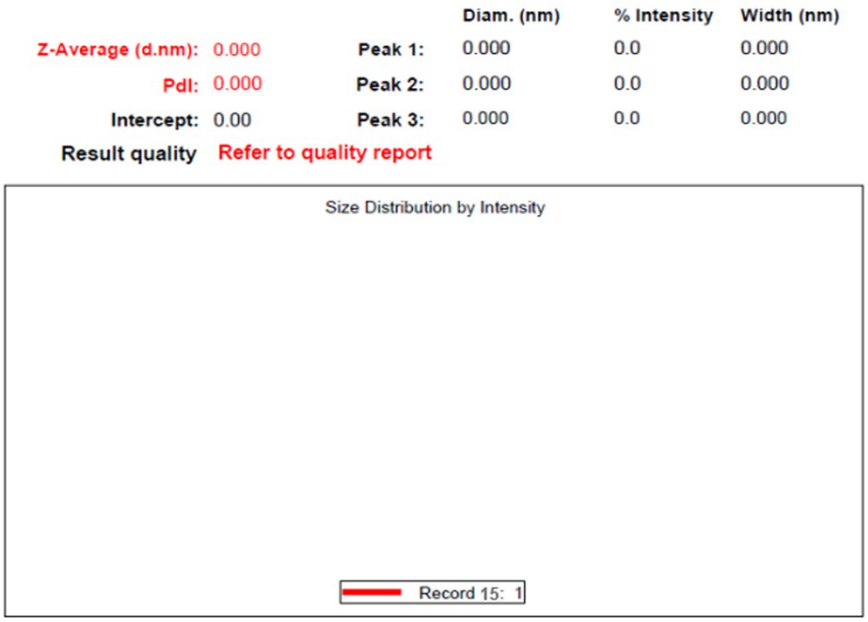


Fig. S28. Particle size distribution measured by DLS in a solution of **CoBiW-DMAP** (4.0 μM), $[Ru(bpy)_3](ClO_4)_2$ (1.0 mM), $Na_2S_2O_8$ (5.0 mM) in 80 mM, pH = 9.0 borate buffer after 15 min of irradiation.

Table S4 Catalytic water oxidation activity of CoBiW-DMAP and Co^{2+} (aq) under various pH

Entry	Complex	Complex concentration (μM)	pH	TON	O_2 yield (%)	pH after the photocatalysis	buffer (mM)
1	CoBiW-DMAP	4	9.0	206	16.4	8.8	80 NaB_i
2	CoBiW-DMAP*	4	9.0	142	22.7	8.3	80 NaB_i
3	CoBiW-DMAP	2	9.0	363	29.1	8.7	80 NaB_i
4	CoBiW-DMAP	2	8.0	307	24.5	5.8	80 NaB_i
5	CoBiW-DMAP	2	7.6	253	20.3	3.9	120 NaB_i
6	CoBiW-DMAP	2	6.4	113	9.1	5.0	100NaP_i
7	$Co(NO_3)_2$	2	9.0	538	43.1	8.6	80 NaB_i
8	$Co(NO_3)_2$	2	8.0	402	32.2	2.9	80 NaB_i
9	$Co(NO_3)_2$	2	7.6	54	4.3	2.7	120 NaB_i
10	$Co(NO_3)_2$	2	6.4	0.47	0.04	5.2	100NaP_i

Conditions: LED light (16 mW, ⩾420 nm, beam diameter 2 cm), $[Ru(bpy)_3]Cl_2$ (1.0 mM), $Na_2S_2O_8$ (5.0 mM), 15 mL total solution volume, all stock solutions prepared in DI water. *Catalyst reusability test: 17.8 mg $Na_2S_2O_8$ was added for the second run.

Table S5 Inductively coupled plasma mass spectrometry for solution with **CoBiW-DMAP** before and after the photocatalytic water oxidation reaction (Conditions: **CoBiW-DMAP** (4 μM), $[Ru(bpy)_3]^{2+}$ (1 mM), $Na_2S_2O_8$ (5 mM) in a 80 mM sodium borate buffer solution 15 mL (pH = 9.0)).

Entry	Aged time (min)	Reaction time (min)	Concentration of catalysts (uM)	Elements	Co/W after extraction (uM)
1	60	0	4	Co	0
				W	0
2	0	30	4	Co	0.12
				W	0.26

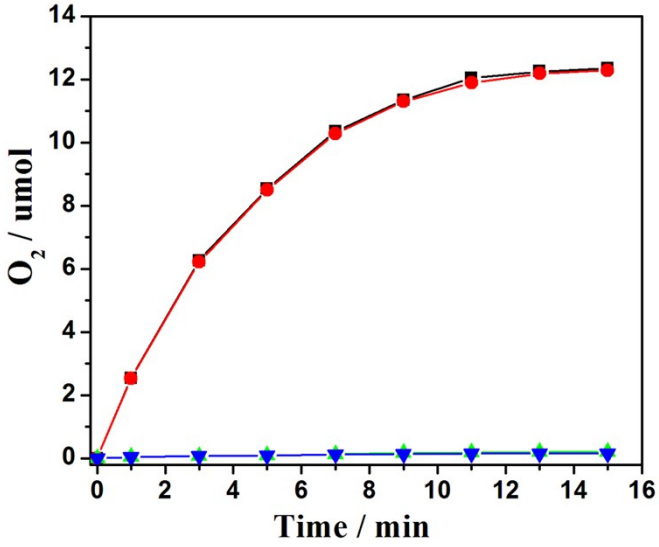


Fig. S29. Kinetics of light-driven catalytic O_2 evolution from water catalyzed by **CoBiW-DMAP** and $Co(NO_3)_2$. Conditions: LED lamp ($\lambda \geq 420$ nm), 1.0 mM $[Ru(bpy)_3]Cl_2$, 5.0 mM $Na_2S_2O_8$, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume is 15 mL. 4.0 μM CoBiW-DMAP(black), 4.0 μM CoBiW-DMAP+0.12 μM $Co(NO_3)_2$ (red), 0.12 μM $Co(NO_3)_2$ (green), residual solution after the first run followed by extraction using a toluene solution of $THpANO_3$ (blue).

References

[1] P. -E. Car, M. Guttentag, K. K. Baldridge, R. Alberto, Patzke, *G. R. Green Chem*. 2012, **14**, 1680-1688.

[2] X. -B. Han, Z. -M. Zhang, T. Zhang, Y. -G. Li, W. -B. Lin, W. -S You, Z. -M. Su, E. -B. Wang, *J. Am. Chem. Soc*. 2014, **136**, 5359−5366.

[3] J. Wei, Y. -Y. Feng, P. -P. Zhou, Y. Liu, J. -Y. Xu, R. Xiang, Y. Ding, C. -C. Zhao, L. -Y. Fan, C. -W. Hu, *ChemSusChem*, 2015, **8**, 2630–2634.

[4] L. Yu, X.-Q. Du, Y. Ding, H. -L. Chena, P. -P. Zhou, *Chem. Commun.*, 2015,**51**, 17443.

[5] X. -B. Han, Y. -G. Li, Z. -M. Zhang, H. -Q. Tan, Y. Lu, E. -B. Wang, *J. Am. Chem. Soc.* 2015, **137**, 5486−5493.

[6] W. -C. Chen, X. -L. Wang, C. Qin, K. -Z. Shao, Z. -M. Su ,E. -B. Wang, *Chem. Commun.*, 2016, **52**, 9514.

[7] R. Al-Oweini, A. Sartorel, B. S. Bassil, M. Natali, S. Berardi, F. Scandola, U. Kortz, M. Bonchio, *Angew. Chem. Int. Ed.,* 2014, **126**, 11364–11367.

[8] Y. V. Geletii, Z. -Q Huang, Y. Hou, D. G. Musaev, T. -Q. Lian, C. L. Hill, *J. AM. CHEM. SOC.* 2009, **131**, 7522-7523.

[9] M. Orlandi, R. Argazzi, A. Sartorel, M. Carraro, G. Scorrano, M. Bonchio and F. Scandola, *Chem. Commun.*, 2010, **46**, 3152-3154.

[10] F. Puntoriero, G. L. Ganga, A. Sartorel,M. Carraro, G. Scorrano, M. Bonchio and S. Campagna, *Chem. Commun.*, 2010, **46**,4725-4227.

[11] R. Xiang, Y. Ding, J. -W. Zhao,*Chem. Asian J*. 2014, **9**, 3228-3237.

[12] G. Zhu, E. N. Glass, C. Zhao, H. Lv,; J. W. Vickers, I. Geletii, D. G.. Musaev, J. Song, C. L.

Hill, *Dalton Trans*. 2012, **41**, 13043.
[13] G. Zhu, Y. V. Geletii, P. Kogerler, H.Schilder, J. Song, S. Lense, C. Zhao, K. I. Hardcastle, D. G. Musaev, C. L. Hill, *Dalton Trans*. 2012, **41**, 2084-2090.
[14] L. Yu, Y. Ding, M. Zheng, H. Chen and J. Zhao, *Chem.Commun.*, 2016, **52**, 14494.
[15] C. Besson, Z. -Q. Huang, Y. V. Geletii, S. Lense, K. I. Hardcastle, D. G. Musaev, T. -Q. Lian, A. Proustac, C. L. Hill. *Chem. Commun.*, 2010, **46**, 2784-2786.
[16] Z. Huang, Z. Luo, Y. V. Geletii, J. W. Vickers, Q. Yin,; D. Wu, Y. Hou, Y. Ding, J. Song, D. G. Musaev, C. L. Hill, T. Lian, *J.Am. Chem. Soc.* 2011, **133**, 2068-2071.
[17] J. W. Vickers, H. -J. Lv, J. M. Sumliner, G. -B. Zhu, Z. Luo, D. G. Musaev, Y. V. Geletii, C. L. Hill, *J. Am. Chem. Soc*. 2013, **135**, 14110−14118.
[18] L. Yu, Y. Ding and M. Zheng, *Appl. Catal., B*, 2017, **209**, 45.
[19] X. -Q. Du, Y. Ding, F. -Y. Song, B. -C Ma, J. -W Zhao, J. Song, *Chem. Commun.*, 2015, **51**, 13925-3928.
[20] F. Evangelisti, P. –E. Car, O. Blacque, G. R. Patzke. Catal. Sci. Technol. 2013, **3**, 3117-3129.
[21] D. Guo, S. Teng, Z. Liu, W. You, L. Zhang, *J. Clust. Sci*. 2012, **24**, 549.
[22] F. Song, Y. Ding, B. Ma, C.Wang, Q. Wang, X. Du, S. Fu, J. Song, *Energy Environ. Sci*. 2013, **6**, 1170.–1184.
[23] S. Tanaka, M. Annaka and K. Sakai, *Chem. Commun.*, 2012, **48**, 1653-1655.
[24] H. -J. Lv, J. Song, Y. V. Geletii, J. W. Vickers, J. M. Sumliner, D. G. Musaev, P. Kögerler, P. F. Zhuk, J. Bacsa, G. -B. Zhu, C. L. Hill, *J. Am. Chem. Soc*. 2014, **136**, 9268-9271.
[25] M. -P. Santoni, G. L. Ganga, V. M. Nardo, M. Natali, F. Puntoriero, F. Scandola, S. Campagna, *J. Am. Chem. Soc*. 2014, **136**, 8189-8192.
[26] B. Schwarz, J. Forster, M. K. Goetz，D. Yücel, C. Berger, T. Jacob, C. Streb, *Angew.Chem. Int. Ed.*, 2016, **55**, 6329-6333
[27] D. Hong, J. Jung, J. Park, Y. Yamada, T. Suenobu, Y. -M. Lee,W. Nam and S. Fukuzumi, *Energy Environ. Sci.*, 2012, **5**, 7606.
[28] G. C. Dismukes, N. S. McCool, D. M. Robinson and J. E. Sheats, *J. Am. Chem. Soc.*, 2011,**133**,11446
[29] F. Y.Song,R. Moré, M. Schilling, G. Smolentsev, N. Azzaroli, T. Fox, S. Luber and G. R. Patzke, *J. Am. Chem. Soc.*,2017,139, 14198-14208