Electronic Supplementary Information (ESI)

Exposing Coordination-Unsaturated Co sites in Co-MOF for Efficient Photocatalytic Water Oxidation

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Ligand synthesis

The ligand 1,2-bis((5H-imidazol-4-yl)methylene)hydrazine (H_2BIM) was prepared by the reported method.[S1]

Crystallographic studies

Single crystal structures of **CoBIM-1** and **CoBIM-2** were measured by X-ray diffraction. Data collection were performed on an Agilent Technologies Gemini A System (Cu Kα, λ = 1.54178 Å; Mo Kα, λ = 0.71073 Å). Crystals of **CoBIM-1** and **CoBIM-2** were measured at 100 K. The data were processed using CrysAlis$^{Pro.1}$. The structures were solved by direct methods and refined by full-matrix least-squares refinements based on F_2. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms were generated geometrically. The crystallographic calculations were conducted using SHELXL-2018/3 program. All the crystal structures contain lots of unknow residual electron density belong to solvent molecules. The treatment for the solvent molecules in the cavities involves the use of the SQUEEZE program of PLATON, which can provide a better refinement data. A summary of crystal data and structure refinement parameters is listed in Tables S1.

Table S1. Crystal data and structure refinement parameters for **CoBIM-1** and **CoBIM-2**

Parameter	**CoBIM-1**	**CoBIM-2**
Chemical formula	$C_8H_8N_6OCo$	$C_{24}H_{18}N_{18}Co_2$
Formula weight	263.13	676.42
Temperature (K)	100(2)	100(2)
Crystal system	cubic	cubic
Space group	*Ia*-3*d*	*Im*-3
a (Å)	32.7620(3)	23.6941(6)
b (Å)	32.7620(3)	23.6941(6)
c (Å)	32.7620(3)	23.6941(6)
α (deg)	90.00	90.00
β (deg)	90.00	90.00
γ (deg)	90.00	90.00
Volume (Å^3)	35165.1(10)	13302.1(10)
Z	96	16
D_{calcd} (g cm^{-3})	1.193	1.351
μ (mm^{-1})	9.136	8.189
Reflections collected	15378	5829
Unique reflections	2116	1984
R_{int}	0.0356	0.0876
Goodness-of-fit on F^2	1.086	1.011
R_1[a] [I > 2σ(I)]	0.0738	0.0587
wR_2[b] [I > 2σ(I)]	0.2201	0.1240
R_1[a] [all refl.]	0.0864	0.1411
wR_2[b] [all refl.]	0.2315	0.1496
CCDC number	2203264	2204131

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

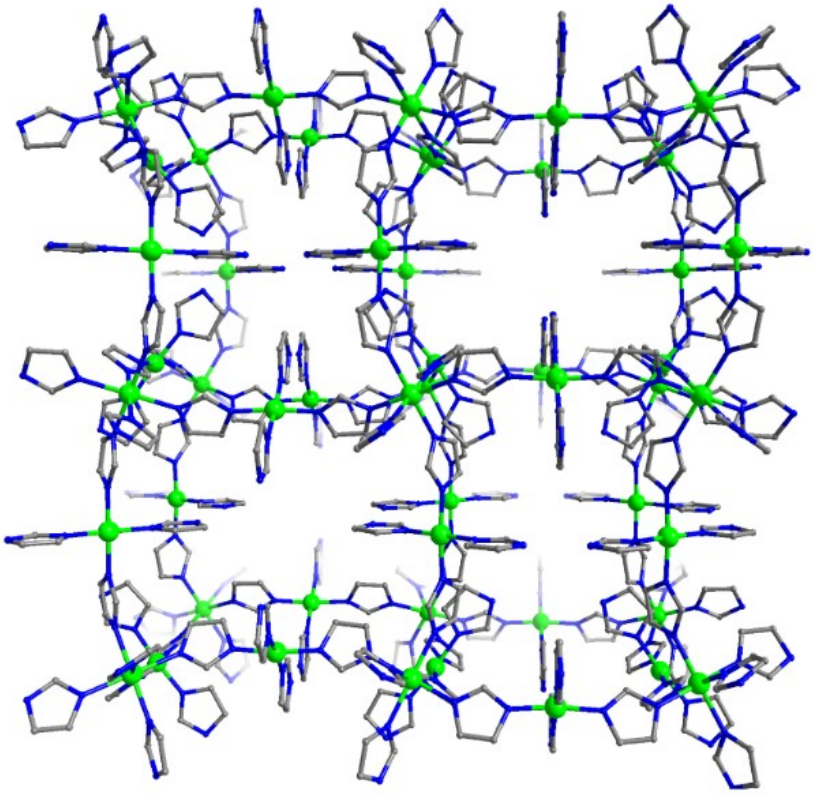

Figure S1. The simplified crystal structure of **CoBIM-2** (only include imidazole parts and cobalt atoms). Colour codes: Co green, N blue, and C grey.

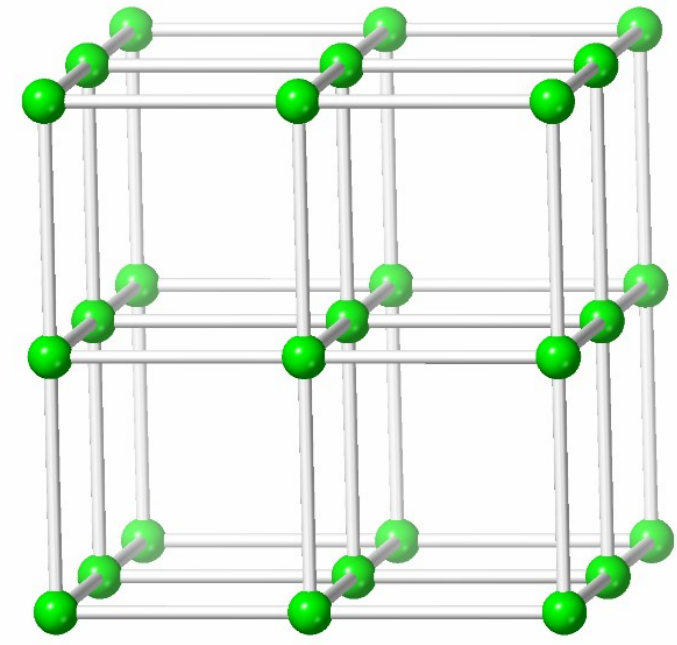

Figure S2. The **pcu** topology of **CoBIM-2**.

Additional Characterizations

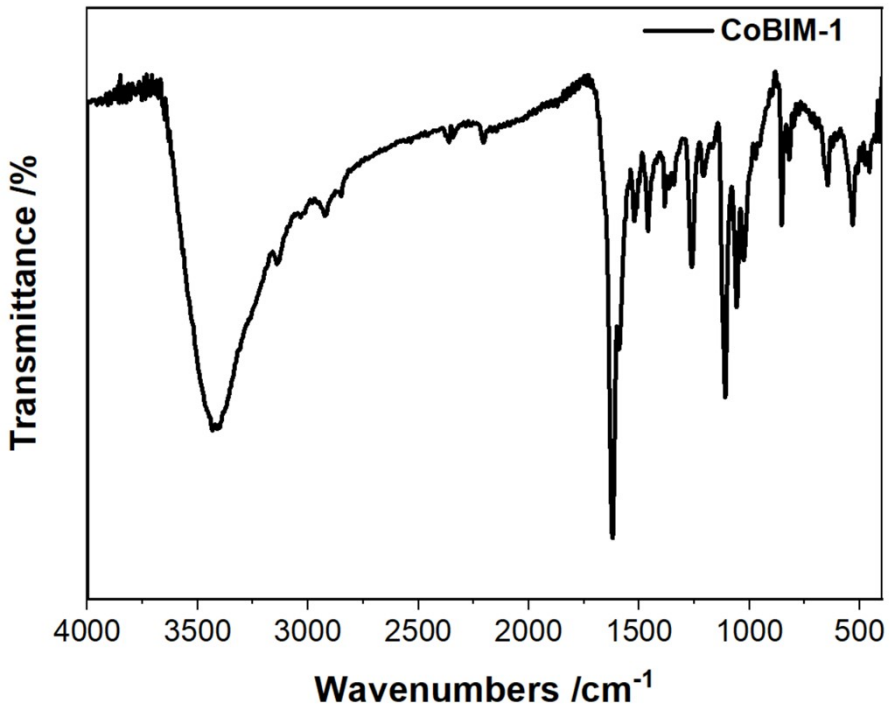

Figure S3. FT-IR spectrum of **CoBIM-1**.

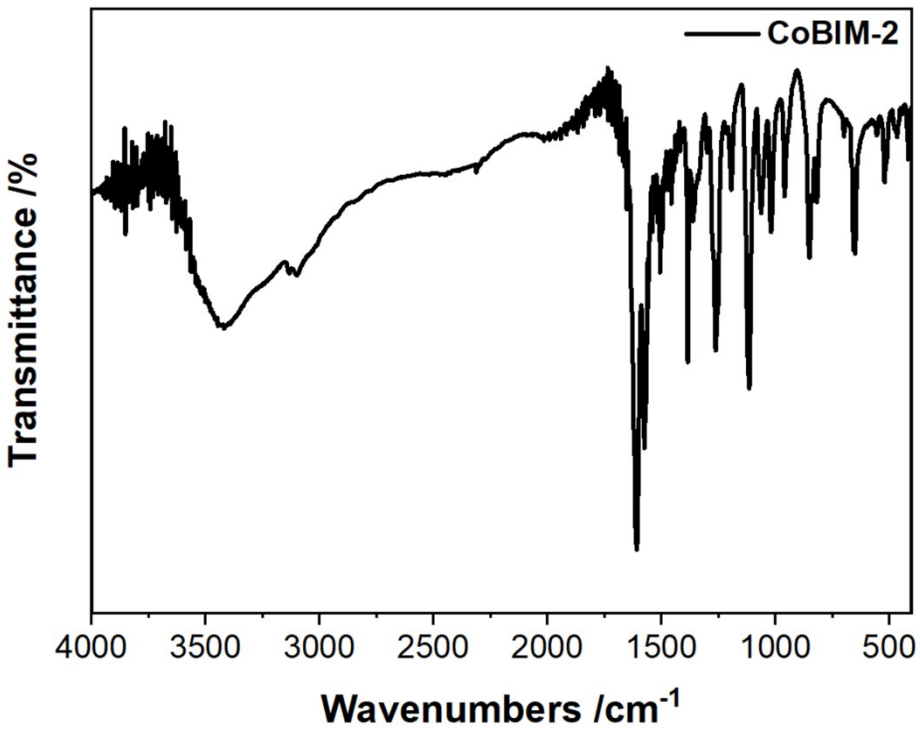

Figure S4. FT-IR of **CoBIM-2**.

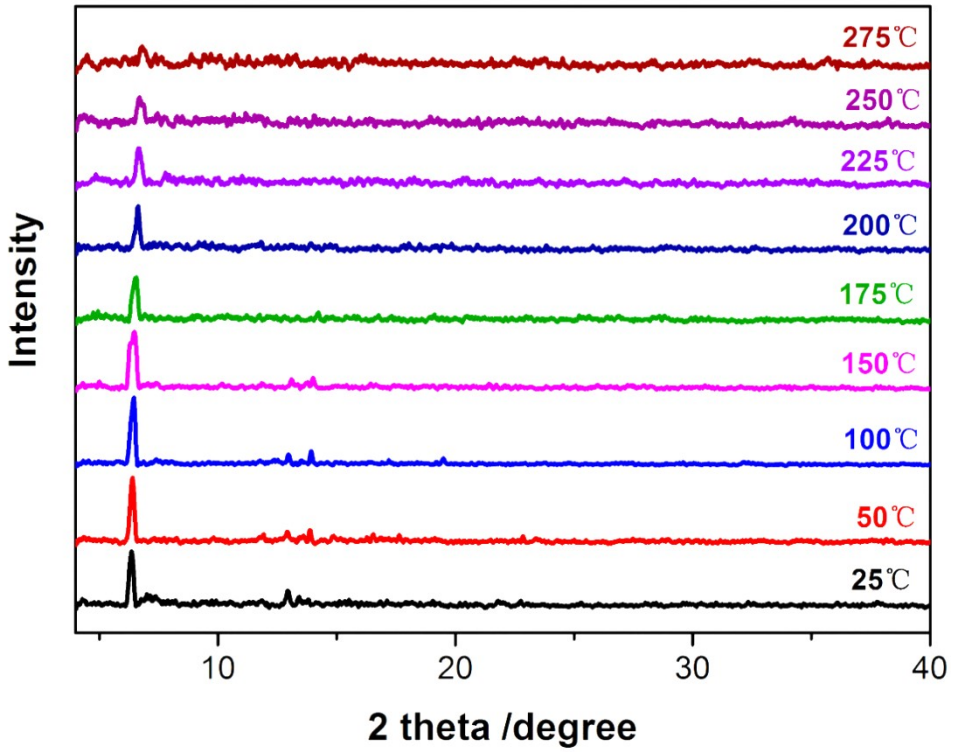

Figure S5. The variable temperature PXRD patterns of **CoBIM-1** in an air atmosphere.

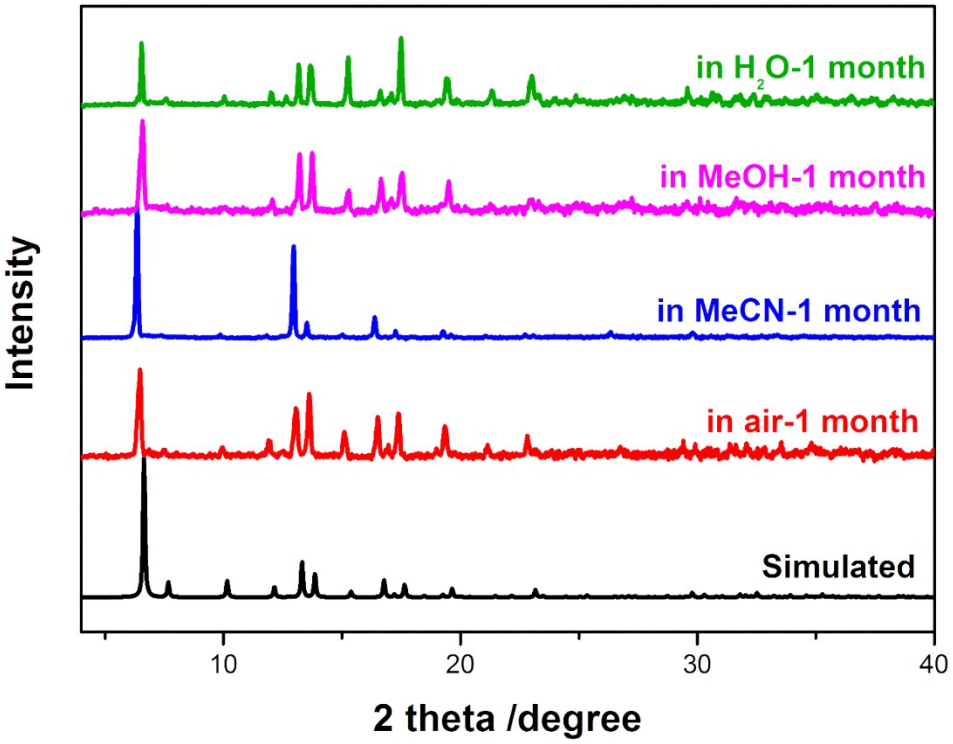

Figure S6. The PXRD patterns of **CoBIM-1** immersed in different solvents for one month at room temperature.

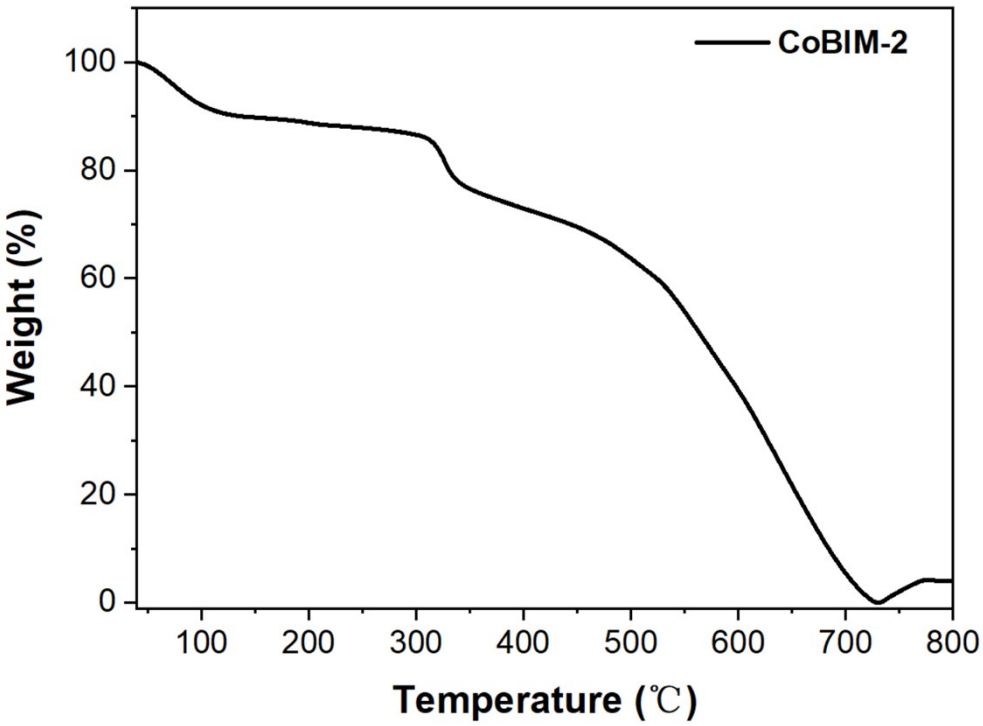

Figure S7. TGA plot of **CoBIM-2** in a N_2 atmosphere.

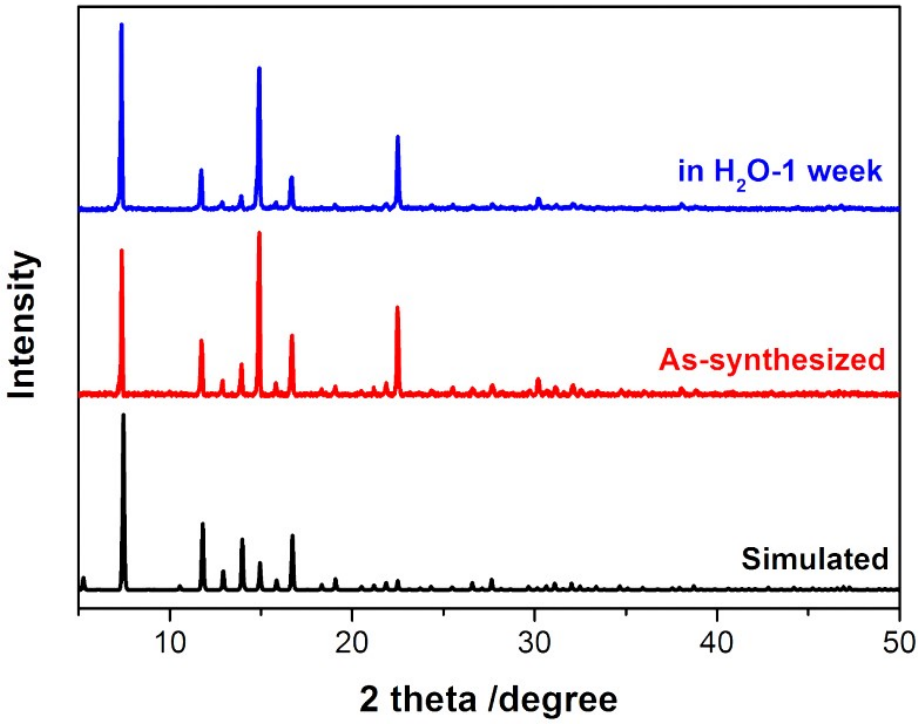

Figure S8. Powder X-ray diffraction patterns (PXRD, Cu Kα, λ = 1.5418 Å) of simulated, as-synthesized, and water immersed (for one week) **CoBIM-2** at room temperature.

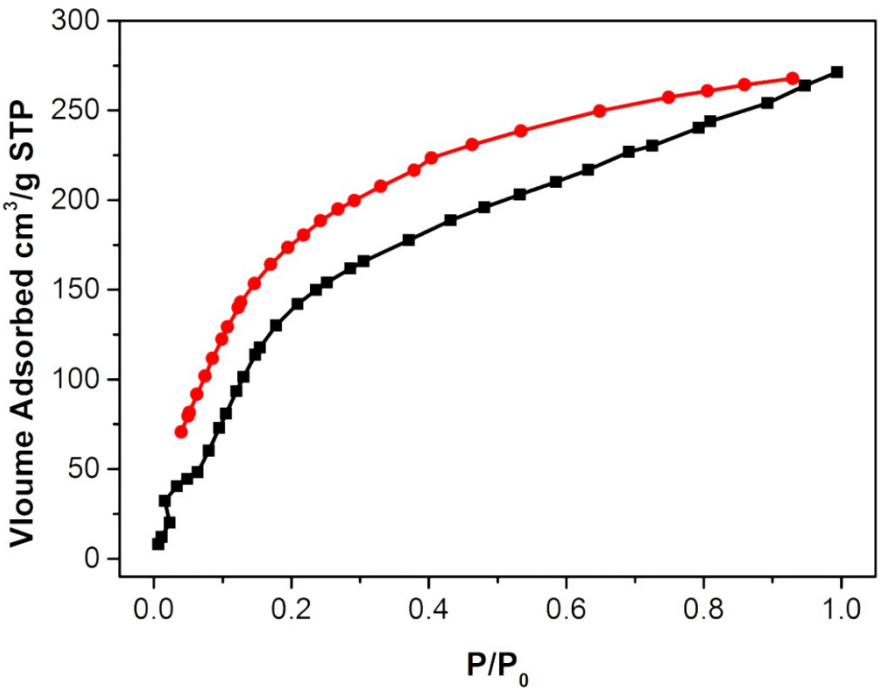

Figure S9. H_2O adsorption and desorption isotherms of **CoBIM-1** at 298K. The solid black squares and red circles represent adsorption and desorption isotherms, respectively.

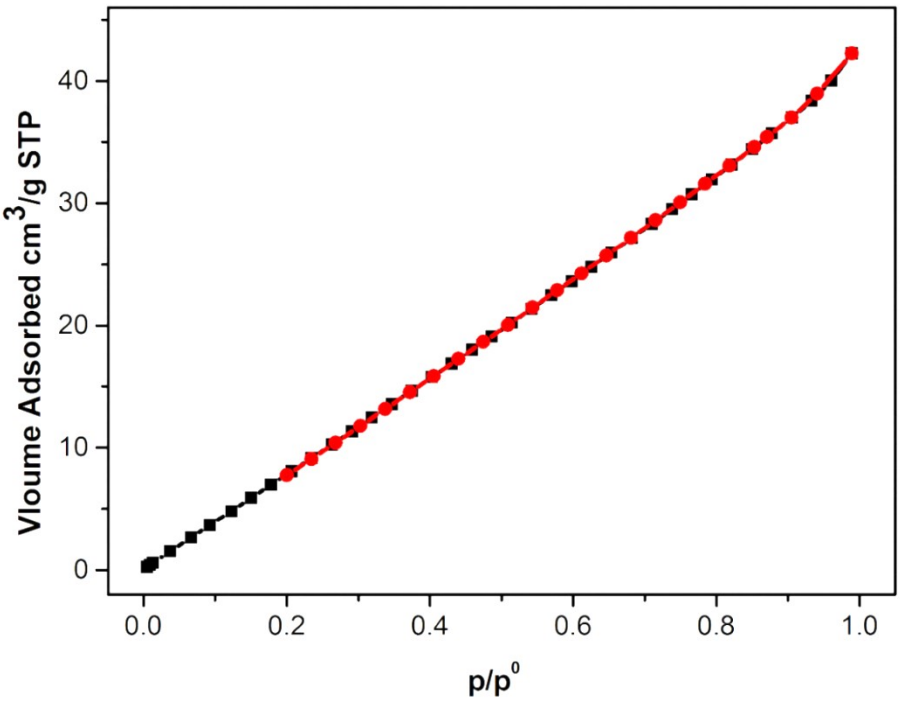

Figure S10. N_2 adsorption and desorption isotherms of **CoBIM-2** at 77 K. The solid black squares and red circles represent adsorption and desorption isotherms, respectively.

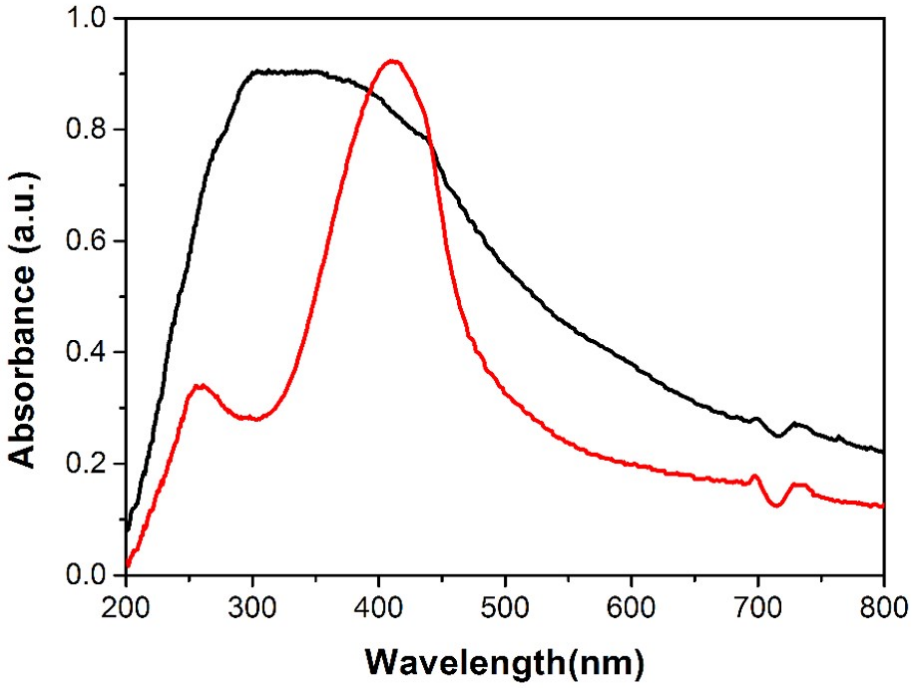

Figure S11. The solid-state UV-vis absorption spectra of **CoBIM-1** (black line) and **CoBIM-2** (red line), respectively.

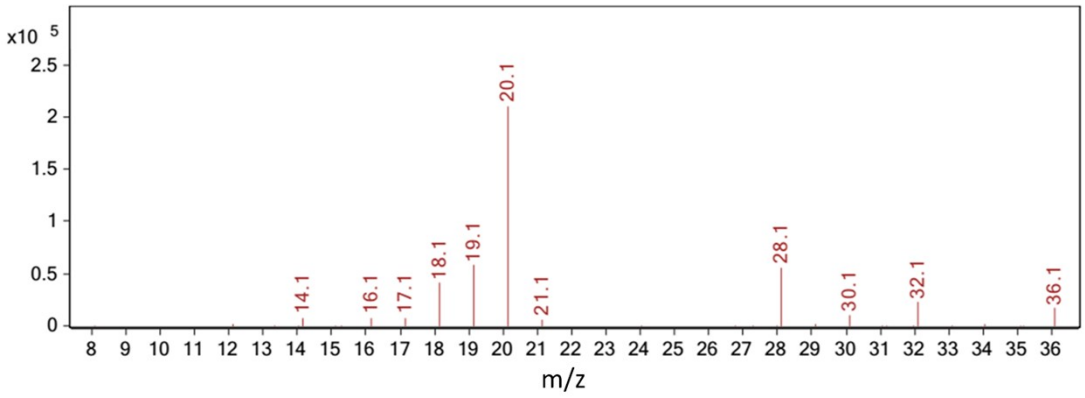

Figure S12. The GC-MS data from the photocatalytic water oxidation experiment using **CoBIM-1** as a catalyst and $H_2{}^{18}O$ as the solvent for a reaction time of 90 minutes.

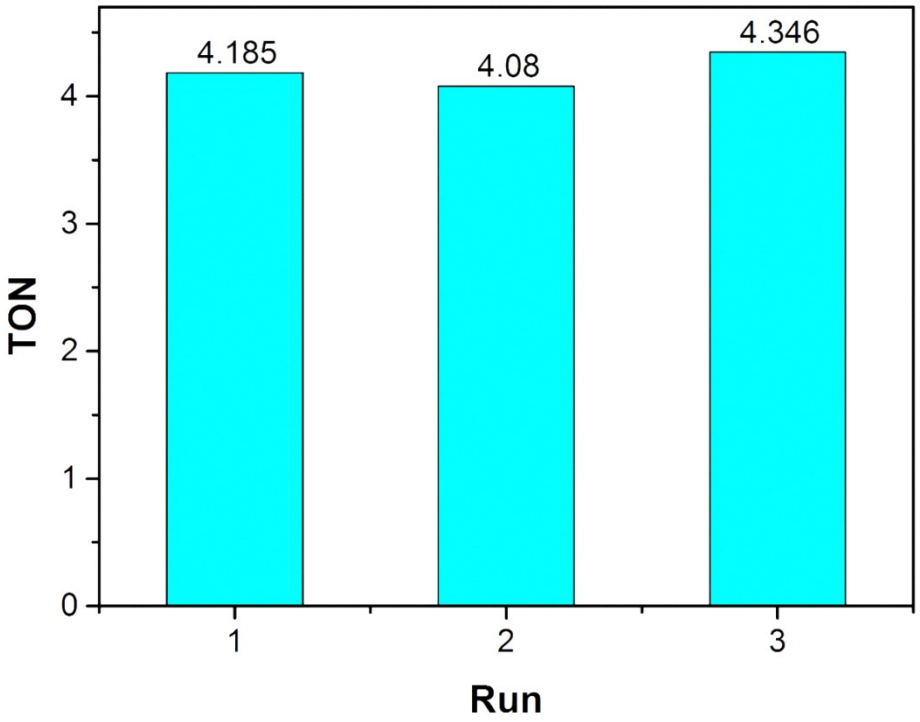

Figure S13. The TON of **CoBIM-1** during three catalytic runs.

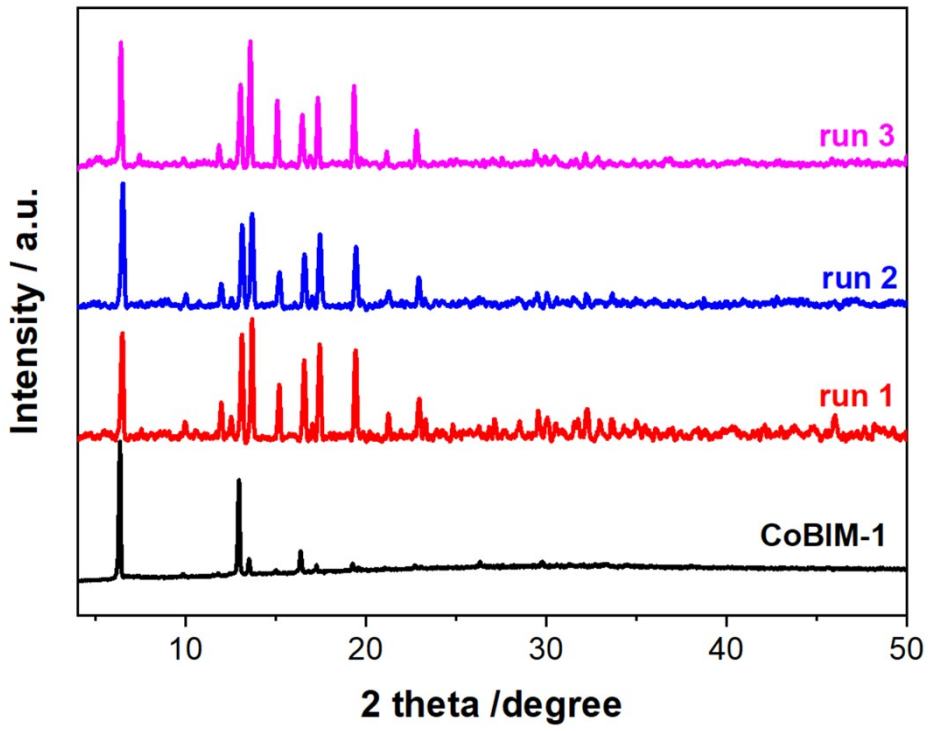

Figure S14. The PXRD patterns of **CoBIM-1** during three catalytic runs.

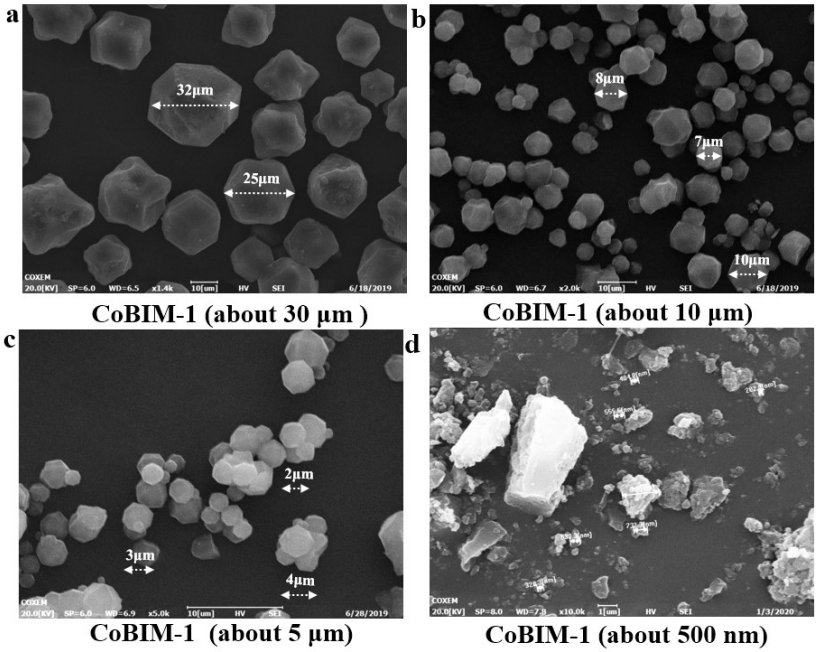

Figure S15. The SEM of **CoBIM-1** with size of around (a) 30 μm, (b) 10 μm, (c) 5 μm, and (d) 500 nm.

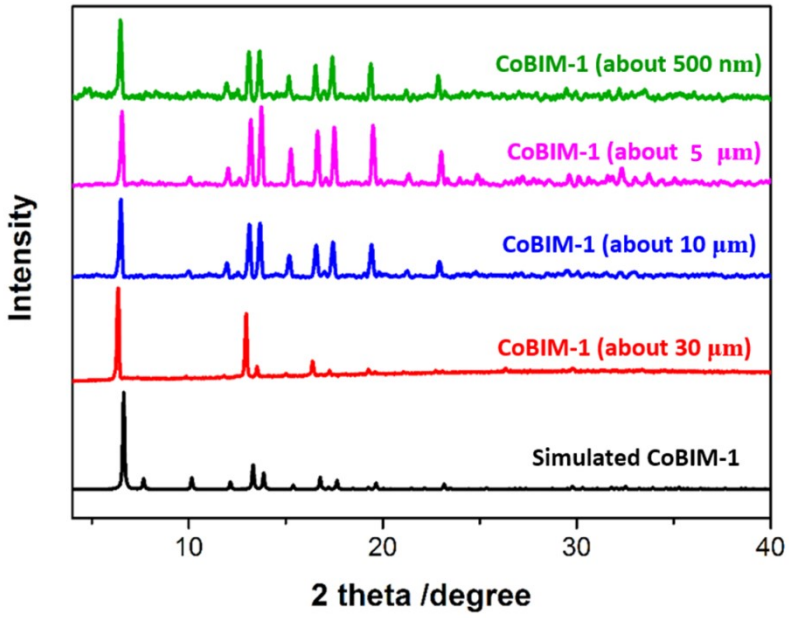

Figure S16. The PXRD patterns of **CoBIM-1** with different size.

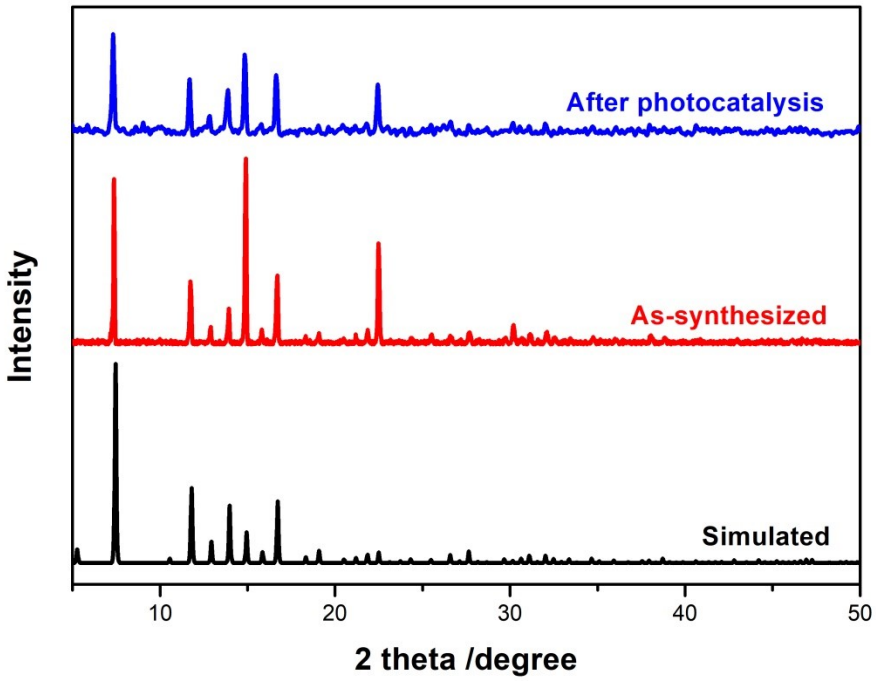

Figure S17. Powder X-ray diffraction patterns (PXRD, Cu Kα, λ = 1.5418 Å) of simulated, as-synthesized, and after photocatalyzed **CoBIM-2** at room temperature.

Table S2. The O_2 evolution and turnover number (TON) of **CoBIM-1** with different particle sizes

Catalysts	O_2 (μmol)	TON
CoBIM-1	40.0	4.2
CoBIM-1 (about 10 μm)	50.6	5.3
CoBIM-1 (about 5 μm)	51.3	5.4
CoBIM-1 (about 500 nm)	51.6	5.4

Conditions: degassed borate buffer solution, 10 mL; catalysts, 10 mg; $Ru(bpy)_3Cl_2$, 6 mM; $Na_2S_2O_8$, 30 mM; reaction time, 2 h; pH, 8.2; light source, 470 nm LED.

Reference

S1 X.-P. Zhou, M. Li, J. Liu and D. Li, Gyroidal metal–organic frameworks, *J. Am. Chem. Soc.* 2012, **134**, 67-70.