Supplementary Information

Synthesis of Boron Imidazolate Framework with Cobalt Clusters for the Efficient Visible-Light Driven CO_2 Reduction

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Experiment section

Materials and methods. All chemical reagents for syntheses were used as purchased without further purification. All the solvents used were of analytical grade. Field Emission Transmission Electron Microscope (FETEM) images were recorded by FEI Tecnai F20. Powder X-ray diffraction (PXRD) analyses were recorded on a Rigaku Dmax2500 diffractometer (MiniFlex-II)with Cu Kα radiation (λ = 1.54056 Å). A UV-visible spectrophotometer (Lambda 950, PerkinElmer) was used to measure the absorption spectra of the as-prepared samples. Surface chemical analyses were performed by X-ray photoelectron spectroscopy (XPS, Thermo Fisher, ESCALAB 250Xi). Steady-state PL were recorded on a Multi-Mode Microplate Readers (BioTek, Synergy neo2). Time-resolved PL spectra were investigated by a fluorescent spectrophotometer (Edinburgh, FLS980).

Synthesis of BIF-101 crystals. $KBH(2\text{-mim})_3$ (0.035 g), nitroterephthalic acid (0.015g) and $Co(NO_3)_2$ (0.050 g) were mixed in H_2O (1 mL)/2-propanol (1 mL)/DMA (2 mL) solution in a 20 mL vial and stirred for half an hour. The mixture was heated at 80 °C for 5 days, followed by cooling to room temperature. The orange red block crystals were obtained. Yield, 58% (based on B).

Photocatalytic CO_2 reduction experiments. The photocatalytic reduction of CO_2 was carried out in a 400 mL reactor and irradiated under a 300-W (PLS-SXE300D)Xe lamp with a 420 nm cutoff filter. Prior to light illumination, the whole reaction setup was vacuumed and then the high-purity CO_2 gas was bubbled into the reaction setup to reach a pressure of 1 atm. In a typical reaction system, the catalyst BIF-101 (10 mg, 24.6 μmol based on cobalt) was suspended in acetonitrile/H_2O (v/v = 4:1) containing 5% (v/v) TEOA (90 mL, pH = 9.3 adjusted with HNO_3) and $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (75 mg), by stirring with a magnetic stirrer. The generated gas products were analyzed by a gas chromatography analyzer (FULI 9790II) equipped with the flame ionization detector (FID) and thermal conductivity detector (TCD). Each reaction was repeated three times to ensure the reliability of the experiment data. The turnover number (TON) is defined as the numder of produced product that occer per catalyst.

PL Characterization. Steady-state photoluminescence (PL) spectra were recorded on a Multi-Mode Microplate Readers (BioTek, Synergy neo2). Time-resolved PL decay spectra were recorded on a FLS980 Spectrometer. The photoluminescent quenching of $[Ru(bpy)_3]Cl_2$ (66 μM, 10 mL) were performed in the reaction system solution (CH_3CN/H_2O = 4:1, with TEOA 5%) upon the addition of increasing amounts of BIF-101 (0.00, 0.25, 0.50, 0.75, and 1.00 mg) or TEOA (0.0, 0.25, 0.5, 1.0, and 1.5 mL). The samples were excited at λ_{ex} = 375 nm. The solution of

$[Ru(bpy)_3]Cl_2$ (66 μM, 10 mL) and after addition of BIF-101 (1.00 mg) were used for time-resolved PL decay testing, respectively, excited at λ_{ex} = 375 nm.

Electrochemical measurements. The measurements were studied on an electrochemical analyzer (CHI 760E) in a standard three-electrode cell, with working electrode (indium tin oxide, ITO), reference electrode Ag/AgCl (KCl saturated) and counter electrode platinum plate. Mott-Schottkey measurements were conducted at frenquencies of 500, 1500 Hz in the potential range from -1 to 1 V. Photocurrent tests were performed at the potential 0.3 V (vs Ag/AgCl) excited by a 300-W Xe lamp with a 420 nm cutoff filter. **Preparation of working electrodes:** (1) BIF-101 powder (5 mg) were dispersed in the solution cantaing ethanol (0.5 mL), acetonitrile (0.5 mL) and nafion (10 μL) then ultrasonication for 30 min. 20 μL of the prepared suspension was pipetted onto the ITO (0.25 cm^2) and dried at ambient temperature. (2) For the addition of $[Ru(bpy)_3]Cl_2$, the prepared working electrode BIF-101 (1) was immersed in $[Ru(bpy)_3]Cl_2$ solution (1 mg/mL, 16 mL, CH_3CN/H_2O = 4:1) for 1 hour, and then the photocurrent was measured.

Quantum efficiency (QE) measurements. The quantum efficiencies of CO generation were measured under the same photocatalytic reaction condition irradiated by the Xe lamp equipped with a band-pass filter centered at 450 nm. QE values were calculated according to the following equation:

$$QE = \frac{2 \times \mathrm{CO}}{\text{incident photons}} \times 100\%$$

The flux of incident photons was measrued by a photoradiometer (PL-MW2000, PerfectLight). The light intensity (I) was measured to be 33 mW/cm^2 at 450 nm and the illuminated area (S) was 41.83 cm^2. The incident photons flux were calculated using the equation:

$$\text{Photon flux} = \frac{\mathrm{I} \times \mathrm{S}}{(\mathrm{h} \times \mathrm{c}/\lambda) \times \mathrm{N_A}} = 5.19 \times 10^{-6}\, mol/s$$

h is Plank constant = $6.62606957 \times 10^{-34}$ J·S, c is velocity of light = 2.99792458×10^8 m/S, N_A is the Avogadro constant = $6.02214076 \times 10^{23}$. After 5 h, the yield of CO was 61.5 μmol. Based on equations, QE was calculated as 0.132%.

Table S1. Summary of crystal data and structural refinements for BIF-101

Compound reference	BIF-101
Chemical formula	$Co_{1.5}(OiPr)_{0.5}(OH)_{0.5}(H_2O)(HBH(mim)_3)(NBDC)$
Formula mass	1219.27
Crystal system	monoclinic
a [Å]	26.697(8)
b [Å]	11.981(3)
c [Å]	22.084(4)
α [°]	90.00
β[°]	92.738
γ [°]	90.00
Unit cell volume [$Å^3$]	7056(3)
Temperature [K]	293(2)
Space group	*C*2/c
No. of formula units per unit cell, Z	4
No. of reflections measured	29596
No. of independent reflections	8074
R_{int}	0.1186
Final R1 values (I > 2σ(I))	0.1230
Final wR(F^2) values (I > 2σ(I))	0.3714
Goodness of fit on F^2	1.114

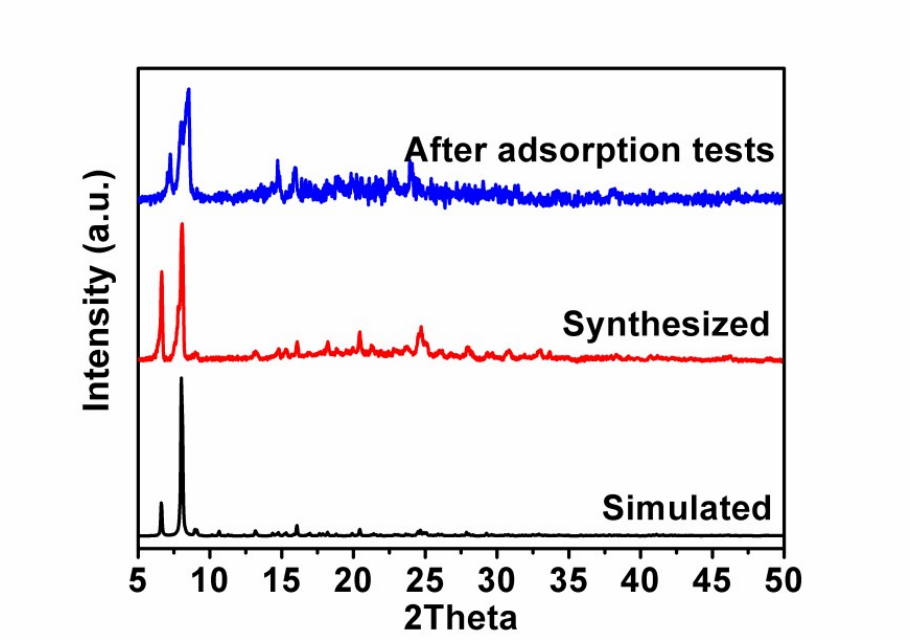

Figure S1. The Powder XRD patterns of **BIF-101** (simulated, synthesized and after adsorption tests).

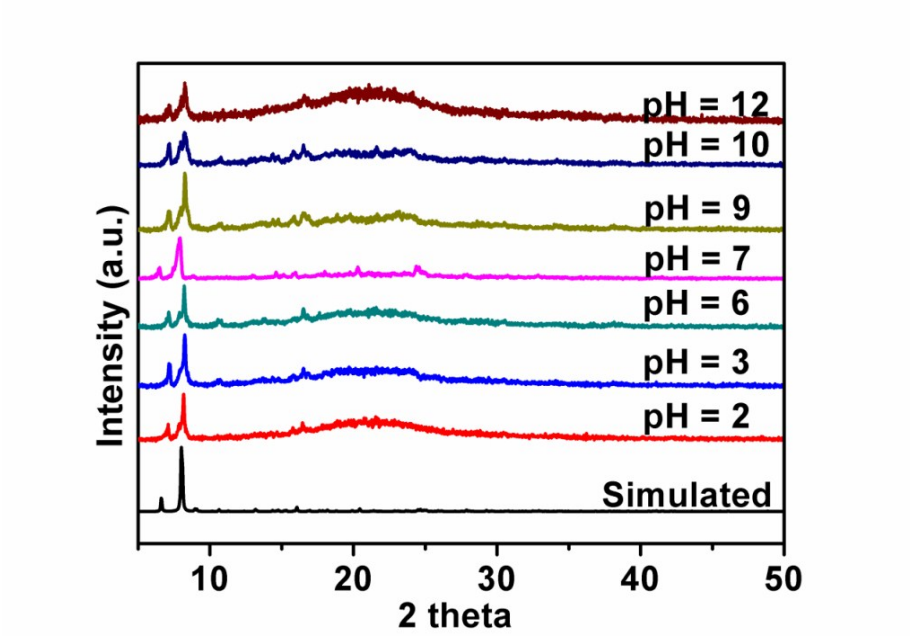

Figure S2. The Powder XRD patterns of **BIF-101** (simulated, immersed in pH = 2, 3, 6, 7, 9, 10, 12 aqueous solution for 10 h with HNO_3 or NaOH adjusted)

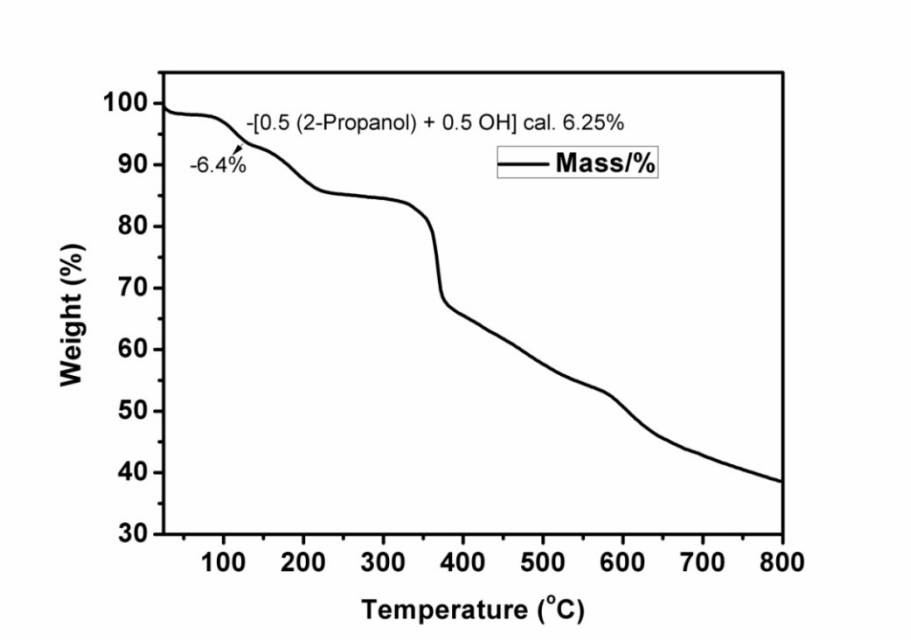

***Figure S3*.** The TGA plot of BIF-101.

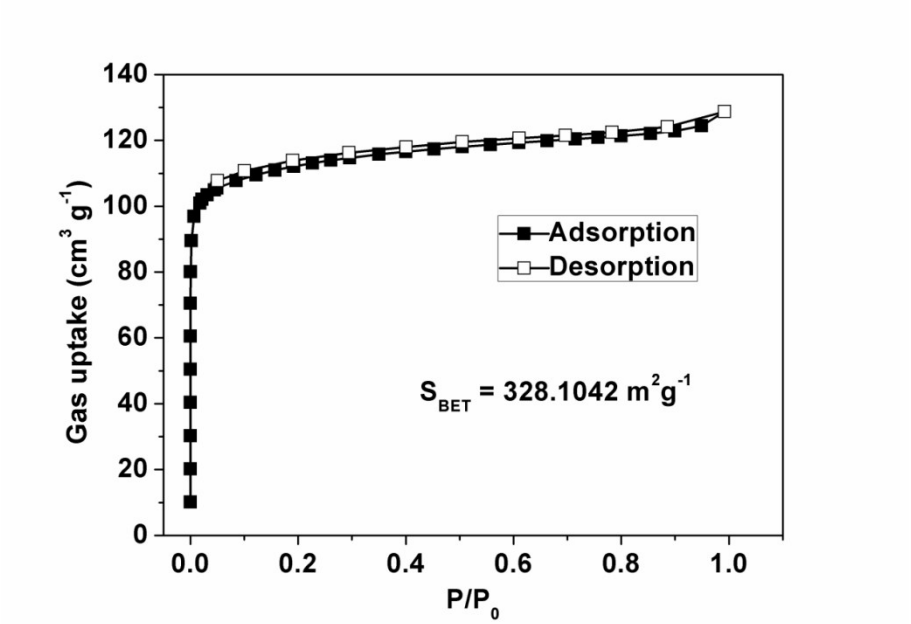

Figure S4. The N_2 isotherms of BIF-101 at 77 K.

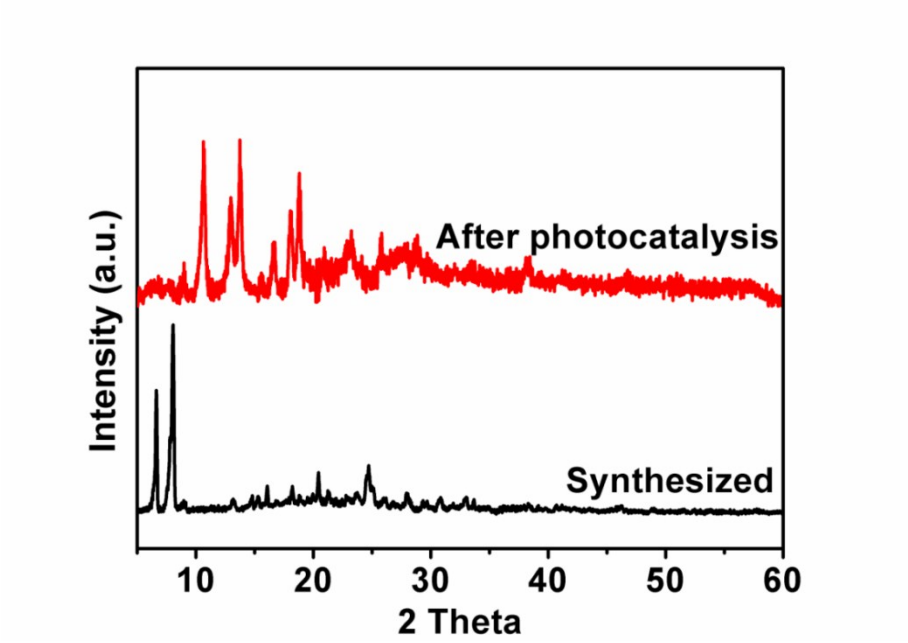

Figure S5. The Powder XRD patterns of BIF-101 after photocatalysis for CO_2, which reveals that the structure has changed.

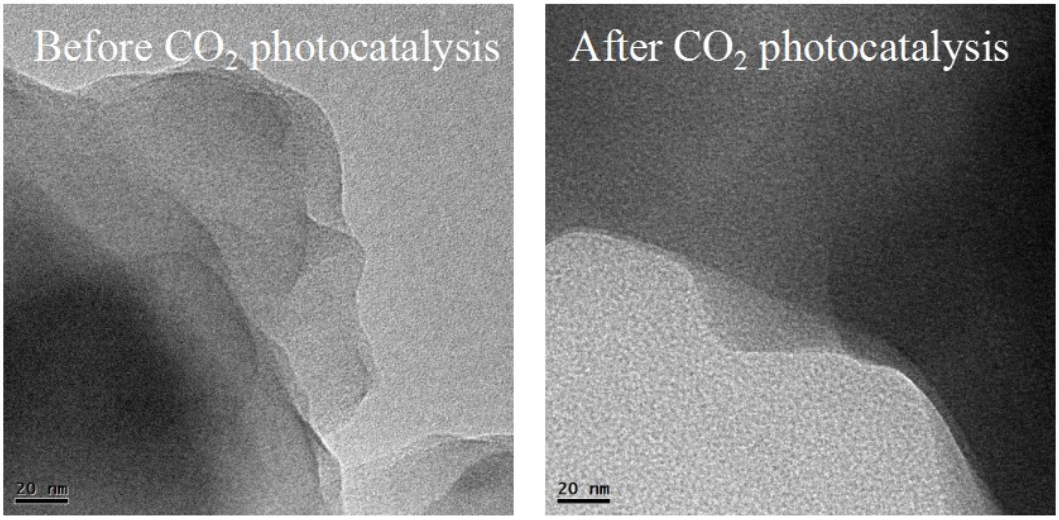

Figure S6. HR-TEM images of BIF-101 before and after CO_2 photoreduction, it turns out that no metal nanoparticles are formed.

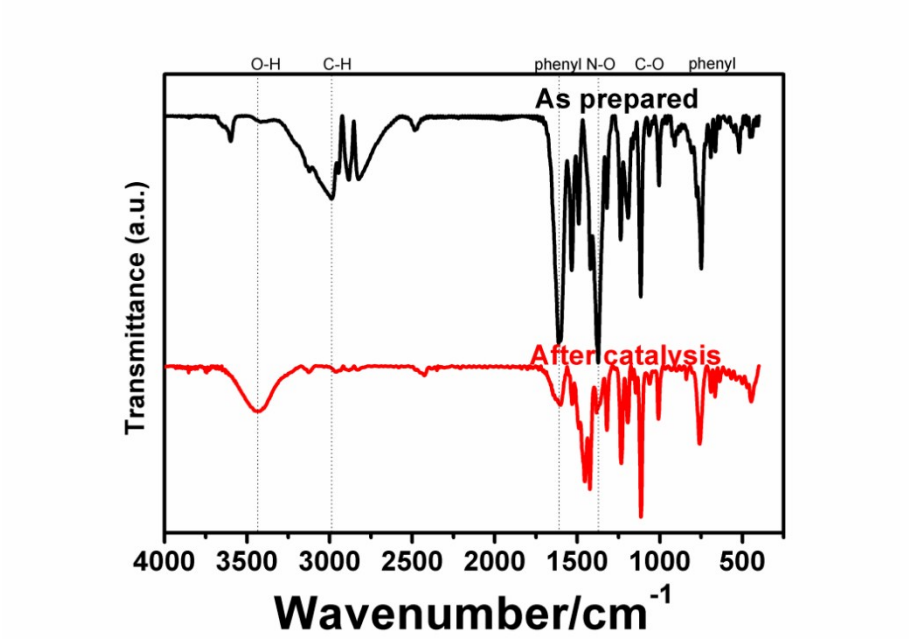

Figure S7. FT-IR analysis to relate BIF-101 atomic bonding before and after photocatalysis for CO_2, the spectra reveal that NBDC are released from the framwork.

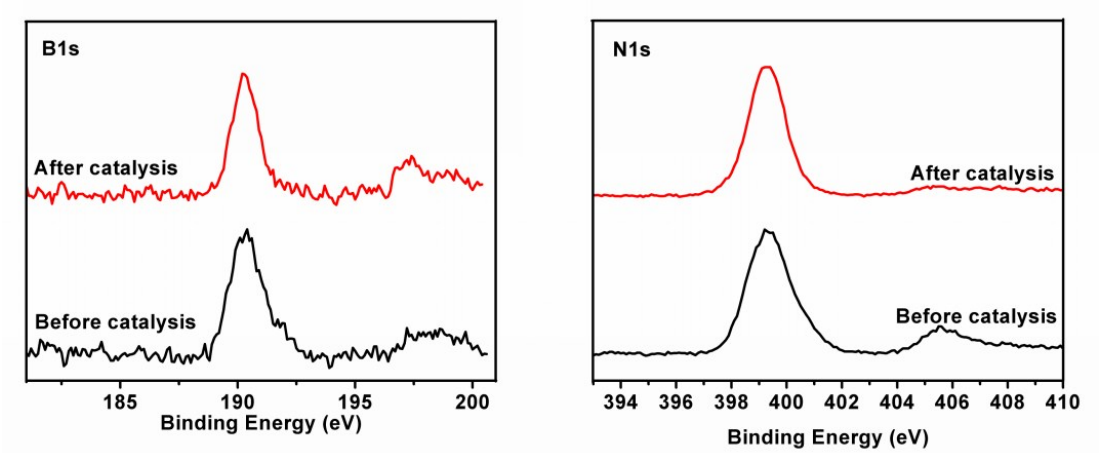

Figure S8. The XPS spectra of B1s and N1s in BIF-101 before and after CO_2 photoreduction.

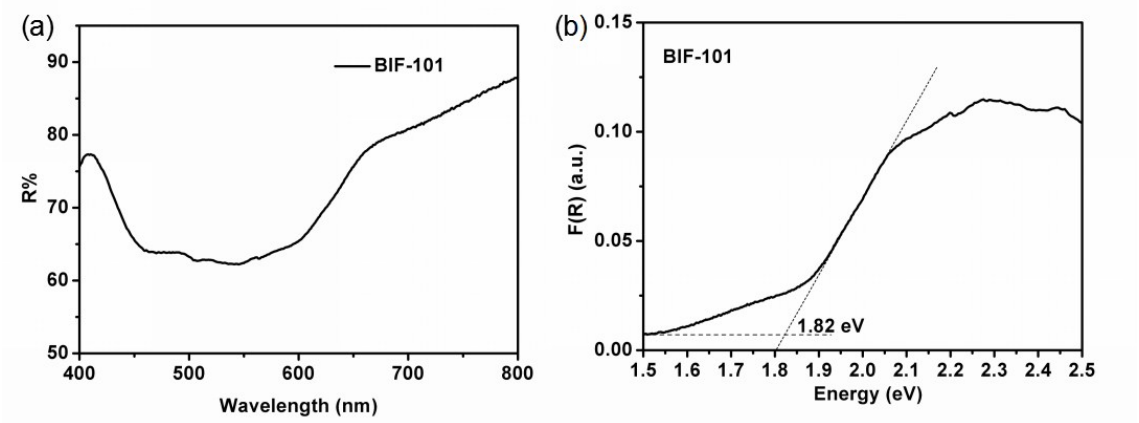

Figure S9. a) The UV-Vis diffusion spectrum of BIF-101. b) Tauc plots of BIF-101 for band gap calculation based on UV-Vis spectrum.

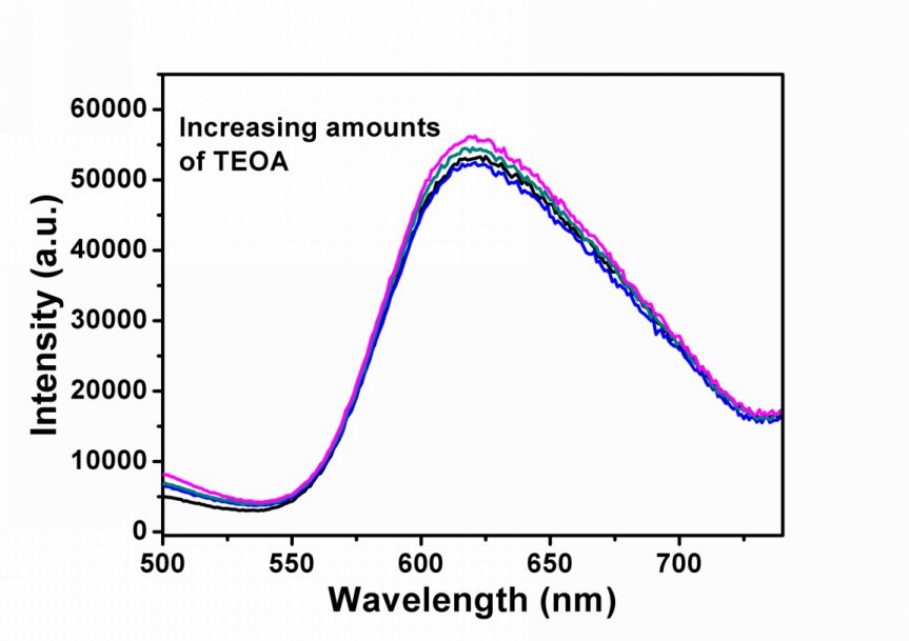

Figure S10. Steady state fluorescence spectra of $[Ru(bpy)_3]Cl_2$ (66 µM) upon the addition of TEOA (λ_{ex} = 375 nm).

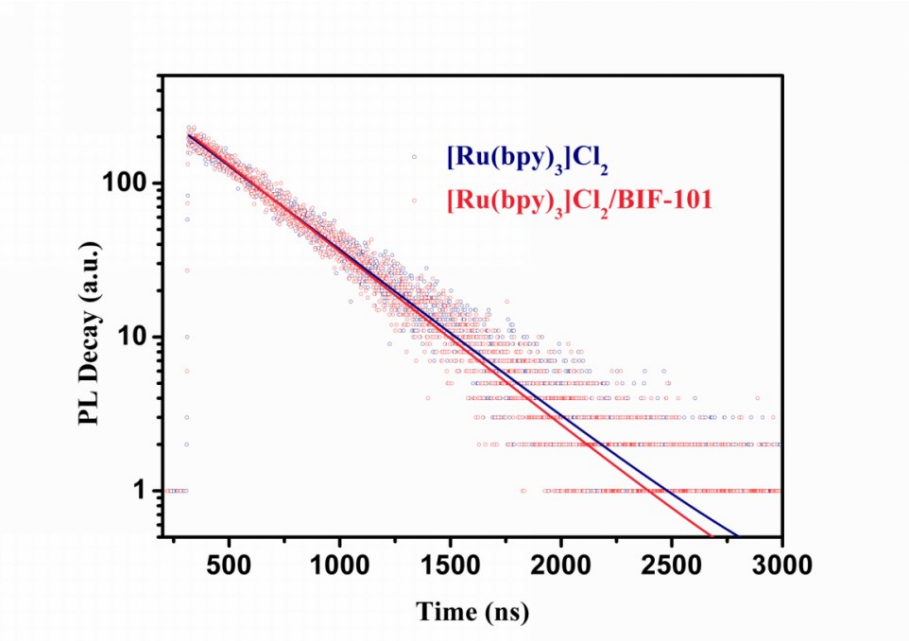

Figure S11. Time-resolved fluorescence decay spectra of $[Ru(bpy)_3]Cl_2$ with and without BIF-101.

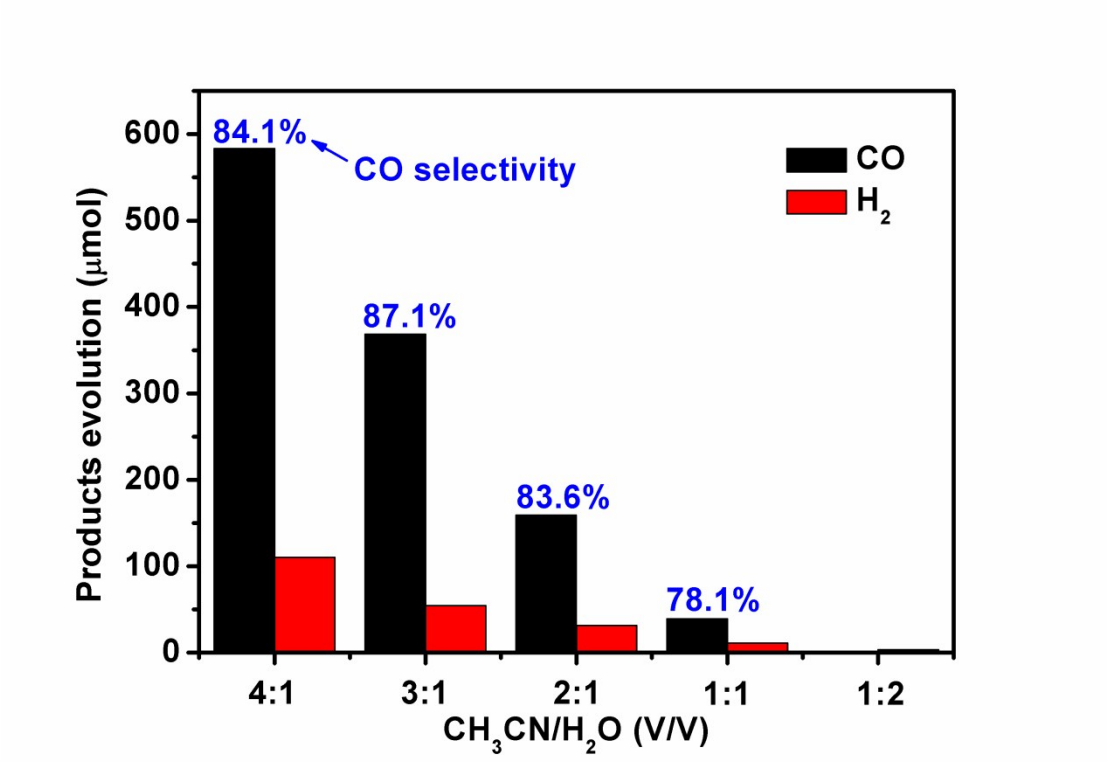

Figure S12. The effect of volume ratio of CH_3CN/H_2O on CO_2 photoreduction. (10 mg BIF-101, 90 mL CH_3CN/H_2O solution with 5% TEOA, 75 mg $[Ru(bpy)_3]Cl_2$, 300 W Xe lamp with a 420 nm cutoff filter).

Table S2. Performance comparison of our sample with state-of-the-art catalysts for CO_2 photoreduction.

Catalyst (used amount)	Photosensitizer	Electron donor	Solvent	Light source (nm)	Major Product rate[a] ($\mu mol\ g^{-1}\ h^{-1}$)	Ref.
ZrPP-1-Co	/	TEOA	MeCN	λ>420 (300 W Xe lamp)	CO 14.5	*Adv. Mater.* **2018**, 30, 1704388.
MAF-X27l-OH (30 nmol)	$[Ru(bpy)_3]Cl_2$	TEOA	MeCN / H_2O	λ=420 (LED light)	CO 6.37 ($\mu mol\ h^{-1}$)	*J. Am. Chem. Soc.* **2018**, 140, 38.
Co-ZIF-9 (0.8 μmol)	$[Ru(bpy)_3]Cl_2$	TEOA	MeCN / H_2O	λ>420 (Xe lamp)	CO 83.6 ($\mu mol\ h^{-1}$)	*Angew. Chem. Int. Ed.* **2014**, 53, 1034.

Ni(TPA/TEG) (L)	$[Ru(bpy)_3]Cl_2$	TEOA	MeCN / H_2O	λ>420 (300 W Xe lamp)	CO 15866	*Sci. Adv.* **2017**, 3: e1700921.
Co_3O_4 platelets	$[Ru(bpy)_3]Cl_2$	TEOA	MeCN / H_2O	λ>420 (300 W Xe lamp)	CO 3523	*Adv. Mater.* **2016**, 28, 6485.
$[Ni(bpet)]^{2+}$	$[Ru(bpy)_3]^{2+}$	BIH	DMA / H_2O	λ=450 (6 W LED lamp)	CO 84.5	J. *Am. Chem. Soc.* **2017**, 139, 6538.
MOF-525-Co	/	TEOA	MeCN	400<λ<800 (300 W Xe lamp)	CO 201.6 CH_4 36.67	*Angew. Chem. Int. Ed.* **2016**, 128, 14522-14526.
NH_2-UiO-66		TEOA	MeCN	420<λ<800 (500 W Xe lamp)	$HCOO^-$ 26.4	*Chem.-Eur. J.* **2013**, 19, 14279.
UiO-66/CNNS	/	TEOA	MeCN	400<λ<800 (300 W Xe lamp)	CO 9.9	*Adv. Funct. Mater.* **2015**, 25, 5360.
NH_2-MIL-101(Fe)	/	TEOA	MeCN	400<λ<800 (300 W Xe lamp)	$HCOO^-$ 445	*ACS Catal.* **2014**, 4, 4254.
NH_2-MIL-125(Ti)	/	TEOA	MeCN	400<λ<800 (500 W Xe lamp)	$HCOO^-$ 16.3	*Angew. Chem. Int. Ed.* **2012**, 51, 3364.
PCN-222	/	TEOA	MeCN	400<λ<800 (300 W Xe lamp)	$HCOO^-$ 60	*J. Am. Chem. Soc.* **2015**, 137, 13440.
MOF-253-$Ru(CO)_2Cl_2$	/	TEOA	MeCN	400<λ<800 (Xe lamp)	$HCOO^-$ 16.75 CO 46.5	*Chem. Commun.* **2015**, 51, 2645.

(Y[Ir(ppy)$_2$(dcbpy)]$_2$[OH])	/	TEOA	MeCN	Visible light (500 W Xe lamp)	$HCOO^-$ 158.3	*Chem. Sci.* **2014**, 5, 3808.
Eu-Ru(phen)$_3$-MOF	/	TEOA	MeCN	420<λ<800 (300 W Xe lamp)	$HCOO^-$ 94.0	*Nat. Commun.* **2018**, 9, 3353.
BIF-20@g-C_3N_4(20%)	/	TEOA	MeCN	400<λ<800 (300 W Xe lamp)	CO 53.9 CH_4 15.5	*ACS Nano* **2018**, 12, 5333.
BIF-101	[Ru(bpy)$_3$]Cl_2	TEOA	MeCN	λ>420 (300 W Xe lamp)	CO 5830	*This work*