Supplementary Information

Local protons enhance photocatalytic CO_2 reduction by porphyrinic zirconium-organic frameworks

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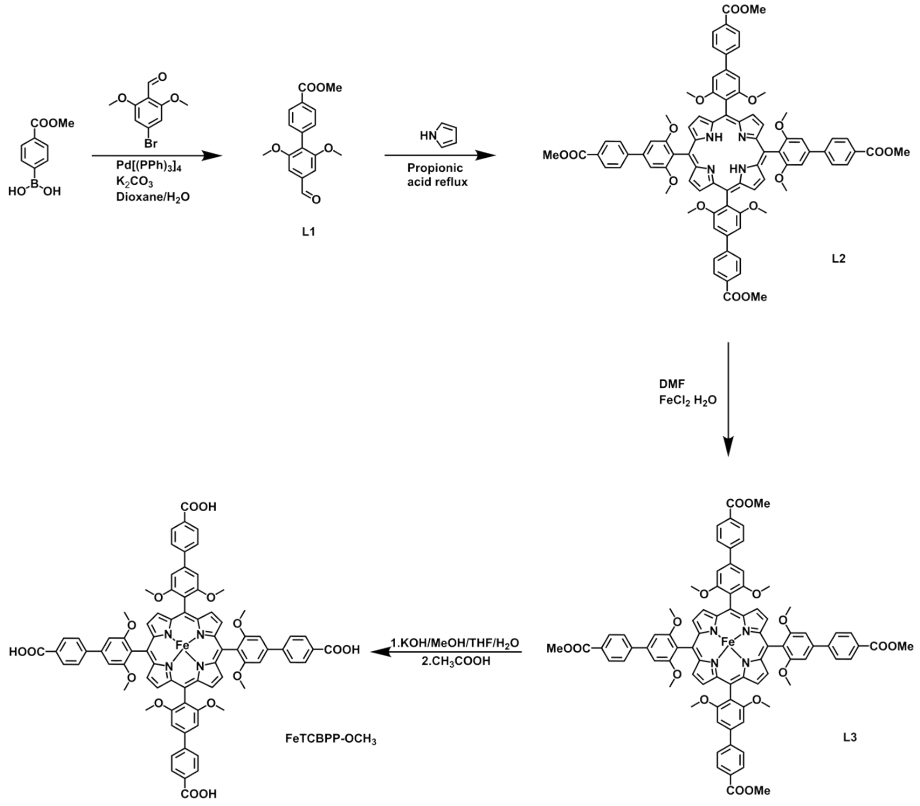
Section S1. Materials and instrumentation

All chemicals were used as purchased without further purification. Powder X-ray diffraction (PXRD) was carried out with a Bruker D8-Focus Bragg-Brentano X-ray Powder Diffractometer. ^{1}H Nuclear magnetic resonance (^{1}H NMR) spectra were collected on a Varian 300 MHz NMR spectrometer. Mass spectra (MS) were measured by Bruker Autoflex speed TOF/TOF. Gas sorption measurements were conducted using a PhysiChem iPore 620 automated surface area and micropore analyzer. The ultraviolet-visible (UV-vis) diffuse reflectance was measured by a SHIMADZU U-4100 UV-vis spectrophotometer using barium sulfate ($BaSO_4$) as a standard. Gas chromatography was performed using GC-2014 gas chromatography. The thermogravimetric analysis (TGA) curves of the samples were carried out using a TGA Q500 analyzer heated from room temperature to 800 °C in air with the heating rate of 10 $°C \cdot min^{-1}$. The femtosecond time-resolved transient absorption (fs-TA) spectra were measured by Helios Fire Transient Absorption spectrometer (Ultrafast Systems LLC).

Section S2. Experimental details

Syntheses of linkers

Scheme S1. The synthetic strategy for FeTCBPP-OCH_3.



Synthesis of L1. 4-Bromo-2,6-dimethoxybenzaldehyde (25 g, 102 mmol) and 4-methoxy carbonylphenylboronic acid (18.36 g, 102 mmol) were dissolved in a degassed *p*-dioxane/H_2O mixture (v/v 4:1, 500 mL). K_2CO_3 (28.19 g, 204 mmol) and Pd[(PPh)$_3$]$_4$ (1 g, 0.86 mmol) were continuously added to the mixture and heated under reflux for

12 h. The reaction was monitored by TLC (thin-layer chromatography). After the mixture was cooled to ambient temperature, it was extracted with CH_2Cl_2 and H_2O. The aqueous phase was washed twice with CH_2Cl_2. The combined organic phases were dried (Na_2SO_4), filtrated and evaporated. The crude product was absorbed on silica-gel and subjected to column chromatography (petroleum ether : EtOAc = 100:5) to give the product as a white solid (L1). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 10.54$ (s, 1H), 8.14 (d, 2H), 7.66 (d, 2H), 6.77 (s, 2H), 3.98 (s, 6H), 3.96 (s, 3H) ppm.

Synthesis of L2. L1 (1 g, 3.33 mmol) was dissolved in propionic acid (30 mL). The resulted solution was heated to 130 °C. A solution of pyrrole (0.23 mL, 3.33 mmol) in propionic acid (0.84 mL) was then added dropwise slowly, and the solution was stirred for 12 h. After the mixture was cooled to room temperature, H_2O was introduced. Then, dark red solid was collected by filtration. The crude product was absorbed on silica-gel and subjected to column chromatography (CH_2Cl_2 : MeOH = 100:1) to give the product as a purple solid (L2). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 8.77$ (s, 8H), 8.26 (d, 8H), 7.99 (d, 8H), 7.23 (d, 8H), 4.01 (s, 12H), 3.63 (S, 24H), -2.44 (s, 2H) ppm.

Syntheses of L3 and FeTCBPP-OCH$_3$. A mixture of L2 (1 g, 0.7 mmol) and $FeCl_2 \cdot 4H_2O$ (0.28 mg, 1.4 mmol) was added into DMF, and the resultant mixture was refluxed for 18 h. After the mixture was cooled to room temperature, H_2O was introduced. The resultant precipitate was filtered and washed with HCl (0.01 M) and H_2O twice, to give the product as a dark red solid (L3). And then L3 was added and stirred in a mixed solvent of THF (35 mL) and MeOH (35 mL), to which a solution of KOH (2.98 g, 53.2 mmol) in H_2O (35 mL) was added. The mixture was then refluxed for 48 h. After the mixture was cooled to room temperature, THF and MeOH were evaporated. Additional water was added to the resultant water phase. The resulting mixture was acidified with CH_3COOH until pH < 3. The red/black solid (FeTCBPP-OCH$_3$) was collected by filtration, washed with water three times, and then dried in vacuum.

Syntheses of ***MOF-OCH$_3$*** *and* ***MOF-OH***

Synthesis of MOF-OCH$_3$. A mixture of 10 mg of $ZrCl_4$, 200 mg of benzoic acid and 10 mg of FeTCBPP-OCH$_3$ were dissolved with 2 mL DEF in a 5 mL vial. The vial was sealed and sonicated for about 10 min until the formation of a homogeneous solution. The reaction was heated in an isothermal oven at 120 °C for 48 h, yielding dark red cubic crystals. For ^1H NMR measurement, the crystals of **MOF-OCH$_3$** (no Fe) were digested by 10 M H_2SO_4 aqueous solution, and then the mixture was centrifugated and washed with water for three times. The resulted solid was dried in 100 °C oven and then dissolved in 0.5 mL DMSO-*d*$_6$.

Synthesis of MOF-OH. MOF-OCH_3 (400 mg) in dry dichloromethane (25 mL) at −20 °C was added to BBr_3 (500 mL). The mixture was stirred for 12 h at room temperature, then placed in ice water and filtered. The resulting black crystals of **MOF-OH** were washed with methanol for three times. For ^1H NMR measurement, the crystals of **MOF-OH** (no Fe) were digested by 10 M H_2SO_4 aqueous solution, and then the mixture was centrifuged and washed with water for three times. The resulted solid was dried in 100 °C oven and then dissolved in 0.5 mL DMSO-d_6. For MS measurement, the treatment of samples was same as that for NMR, but tetrahydrofuran was used as the solvent.

Section S3. Catalyst characterization

Ultrafast Transient Absorption (TA) Measurement

Femtosecond TA measurements were performed at room temperature in a Helios Fire spectrometer (Ultrafast Systems LLC) with pump and probe beams derived from an amplified Ti: sapphire laser system (Coherent Astrella, 800 nm, 5.5 mJ pulse^{-1}, 35 fs, and 1 kHz repetition rate). Custom designed fiber-coupled alignment-free spectrometer with a 1024 pixel CMOS sensor (spectral response: 200 − 1000 nm) was used as VIS/UV-VIS detector. Spectral acquisition rate up to 2400 spectra·s^{-1}. ADC resolution 16 bit. White light continuum (420 − 760 nm) generated by rotated CaF_2 plate was used as probe beam. The experimental data were fitted to a multiexponential decay function convoluted with the instrument response function.

Samples for TA experiments were prepared by dispersing 1 mg of MOFs in 1 mL of DMF.

Electrochemical measurements

All the electrochemical measurements were conducted in a three-electrode cell connected to an electrochemical workstation (CHI660E). To prepare working electrodes, 1 mg of samples were dispersed in a mixture consisting of 1 mL ethanol and 100 μL 5% Nafion by ultrasonication for 2 h. For the test of Mott-Schottky plot, 80 μL suspension was casted in a 1×1 cm^2 window on an FTO glass and dried at room temperature to serve as the working electrode, Ag/AgCl electrode and Pt electrode were used as the reference electrode and counter electrode, respectively. 0.2 M Na_2SO_4 aqueous solution was used as the electrolyte.

Photocatalytic CO_2 reduction

1 mg photocatalyst was evacuated and purged with CO_2 for several times. A mixture of 5 mL MeCN, 3% TFE and 0.025 M BIH solution that pre-degassed with CO_2 to remove the dissolved O_2, was injected into the reaction flask. Then the solution was irradiated with a LED lamp ($\lambda = 420$ nm). The catalytic system was kept at room temperature by circulating condensate. The yields of reaction products were examined by using the

flame ionization detector (FID, for detecting CO) and thermal conductivity detector (TCD, for detecting H_2) of a gas chromatograph S7 (GC2014, Ar carrier, Shimadzu).

In-situ Attenuated Total Reflection Fourier-Transform Infrared Spectroscopy

In-situ infrared testing was performed on a Bruker infrared meter. The total reflection accessory was VeeMaxTMIII. First, a layer of catalyst was loaded on the germanium crystal of the ATR fitting. Then carbon dioxide atmosphere was introduced after adding a trace amount of water. At last, visible light was turned on and the IR signal was in situ collected through an MCT detector along with the reaction.

Section S4. Computational details

Spin-polarized density functional theory (DFT)[1] calculations were performed using the Vienna ab initio simulation package (VASP).[2] Generalized gradient approximation with Perdew-Burke-Ernzerhof functional was used for describing the exchange-correlation potential.[3] The fully relaxed geometric optimization of **MOF-OH** and **MOF-OCH_3** was conducted until meeting the convergence criterion (10^{-5} eV for total energy change and 0.05 eV $Å^{-1}$ for the maximum forces on each atom). The energy cutoff was set as 400 eV. The DFT-D3 method was used for van der Waals corrections.[4] The Gibbs free energy diagram for CO_2 reduction reaction was calculated using the computational hydrogen electrode (CHE) model developed by Nørskov et al.[5, 6] The Gibbs free energy change (ΔG) of each elementary step was computed by the following equation:

$$\Delta G = \Delta E + \Delta E_{zpe} - T\Delta S$$

where ΔE_{zpe} and ΔS represented zero-point energy and entropy, respectively, T was set at room temperature (298.15 K).

Section S5. Supplementary figures

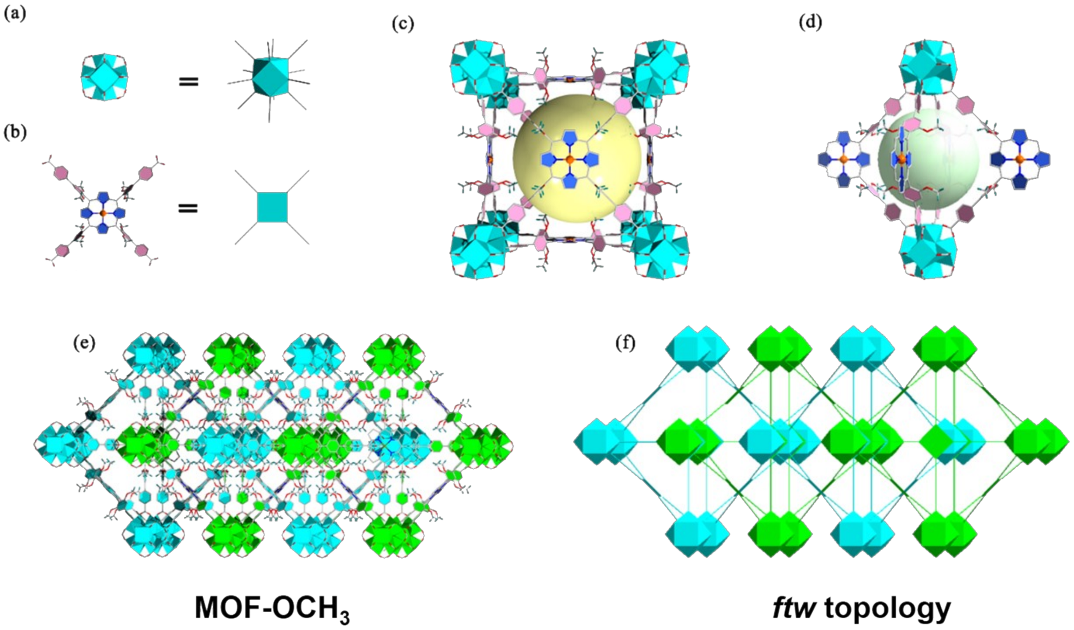


Fig. S1. The structure of **MOF-OCH$_3$**: (a) 12-connected $Zr_6O_4(OH)_4$ unit, (b) 4-connected organic linker, (c) the cubic cage constructed from six FeTCBPP-OCH$_3$ fragments and eight $Zr_6O_4(OH)_4$ clusters, and (d) the octahedral cage constructed from four FeTCBPP-OCH$_3$ fragments and two $Zr_6O_4(OH)_4$ clusters, (e) and (f) 3D structure and *ftw* topology, respectively. Color codes: ZrO_8 polyhedron, cyan polyhedra; C, gray; O, red; N, blue; Fe, orange; H, olive or omitted for clarity.

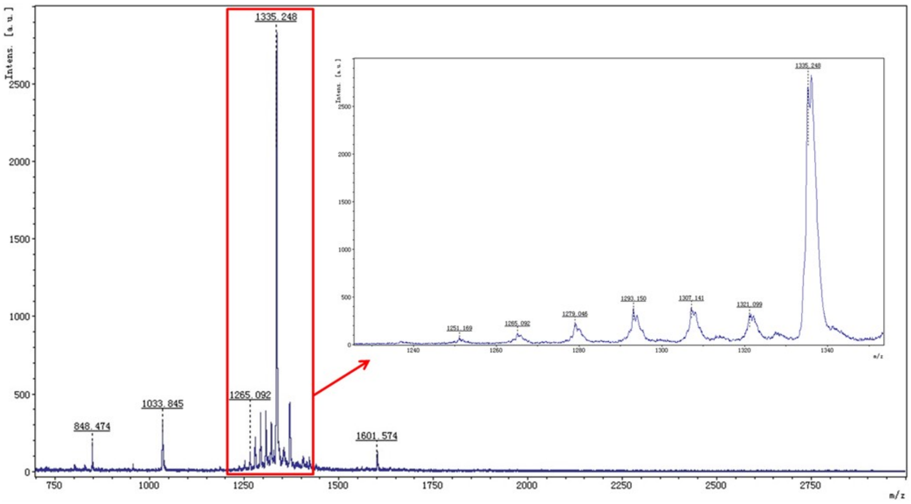


Fig. S2. Mass spectrum of **MOF-OH**. Inset: partial enlargement.

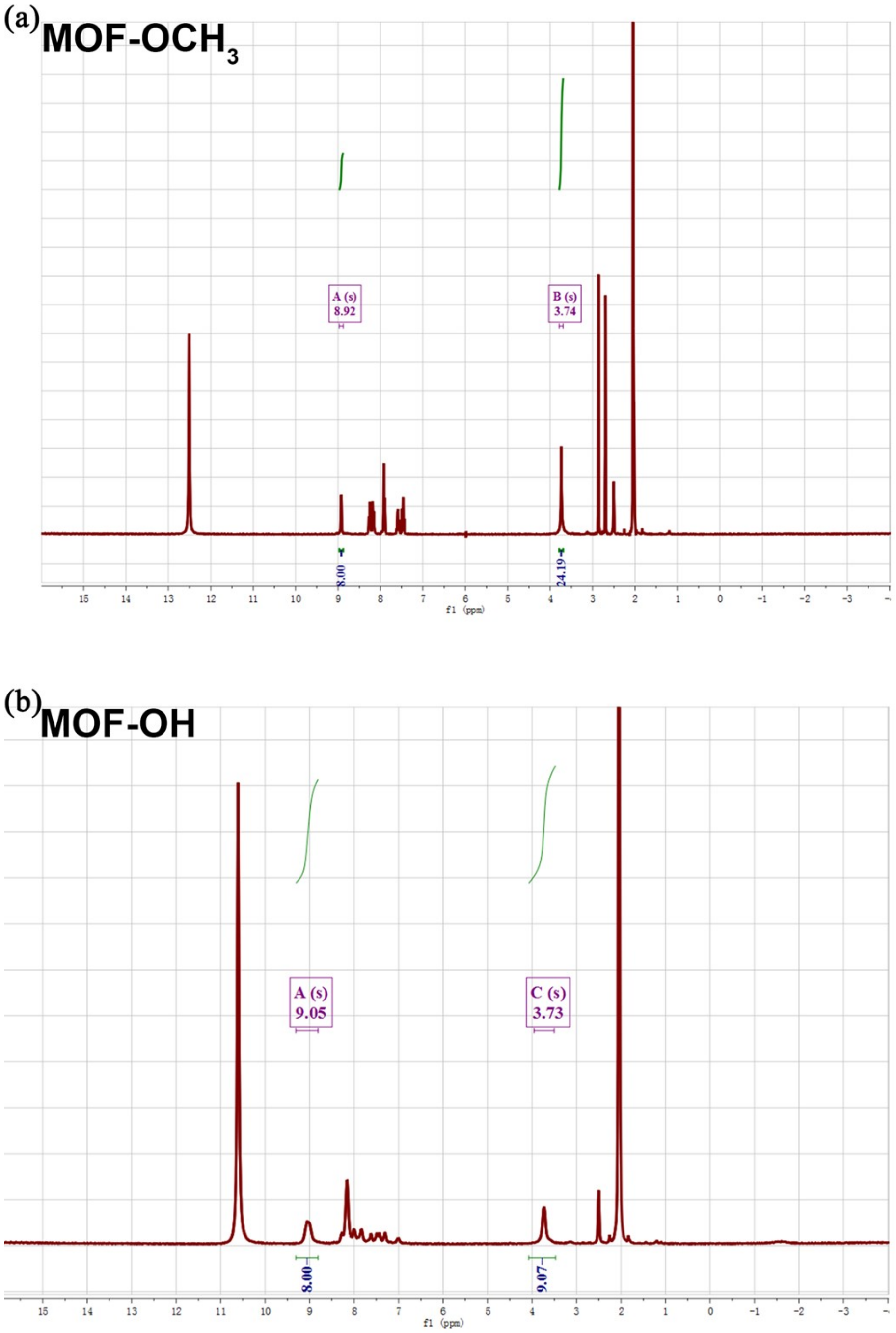


Fig. S3. ^{1}H NMR spectra of (a) **MOF-OCH$_3$** and (b) **MOF-OH**, respectively.

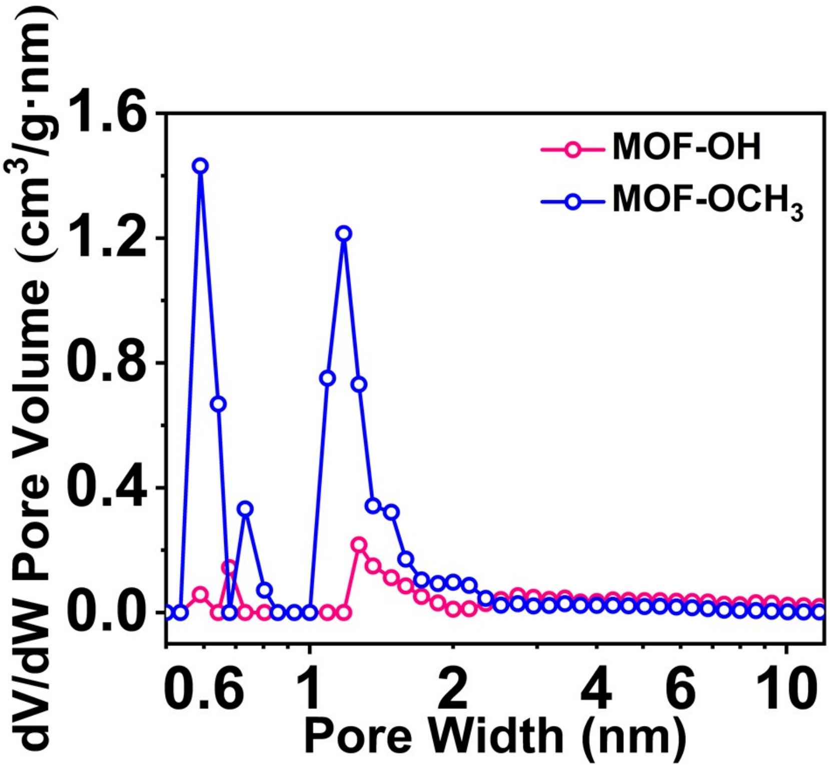


Fig. S4. The corresponding pore size distribution of **MOF-OCH$_3$** and **MOF-OH**, respectively.

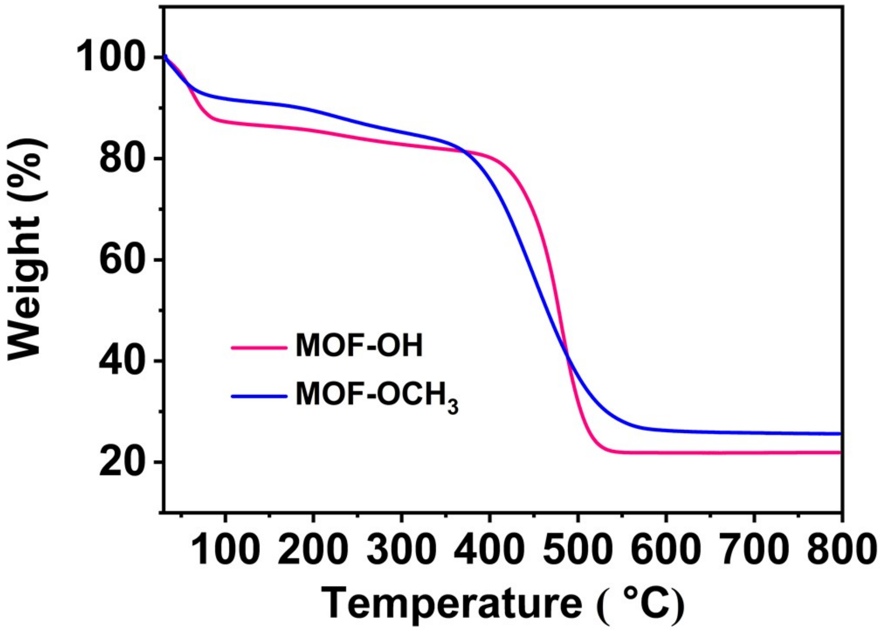


Fig. S5. TGA curves of as-prepared **MOF-OCH$_3$** and **MOF-OH**, respectively.

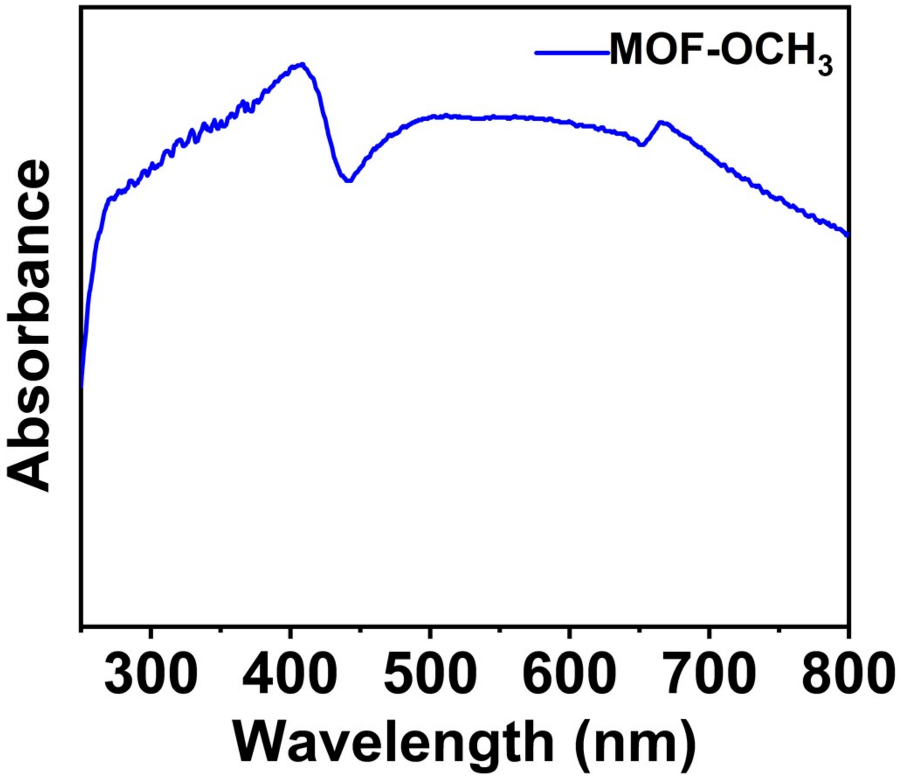


Fig. S6. UV-vis spectrum of **MOF-OCH$_3$**.

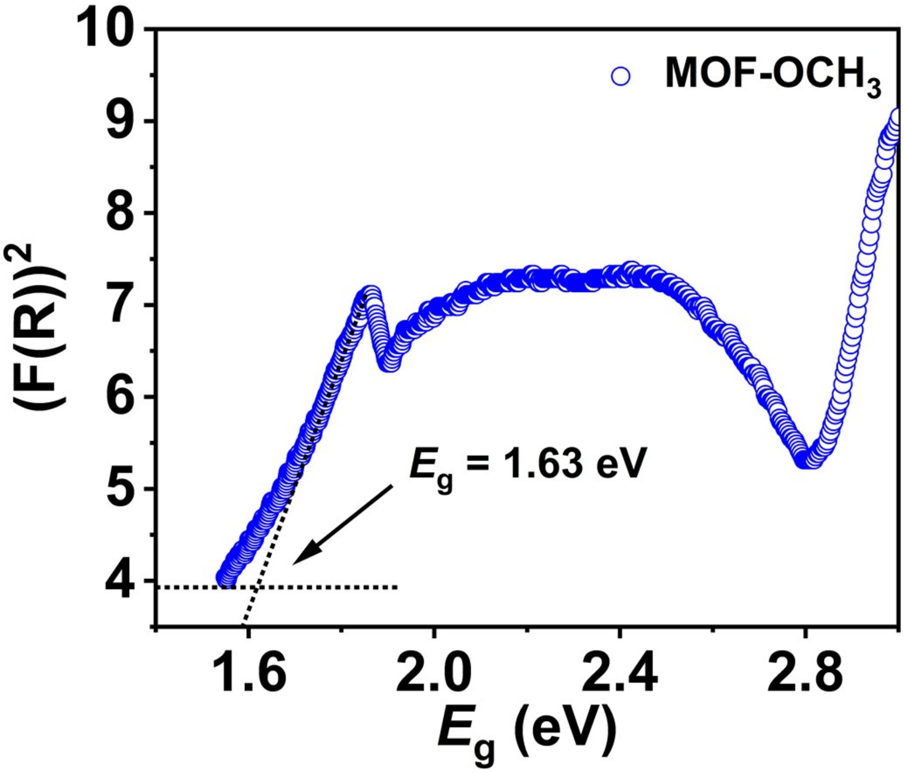


Fig. S7. DRS of **MOF-OCH$_3$** via K-M transformation.

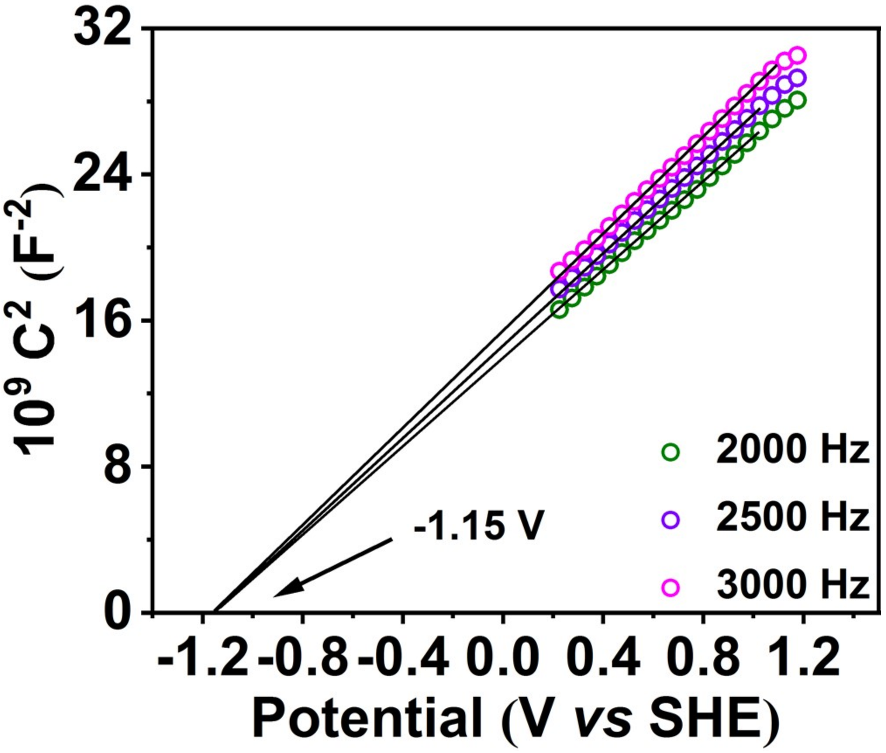


Fig. S8. Mott−Schottky plots of the as-prepared **MOF-OCH$_3$** electrode.

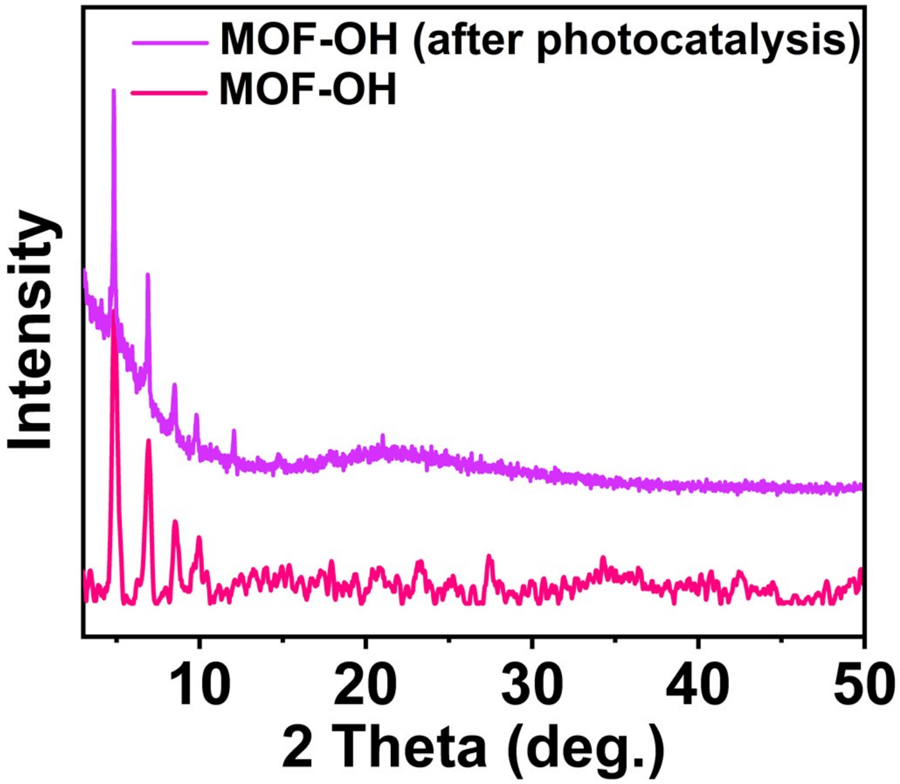


Fig. S9. PXRD patterns of **MOF-OH** before and after the photocatalytic CO$_2$ reduction.

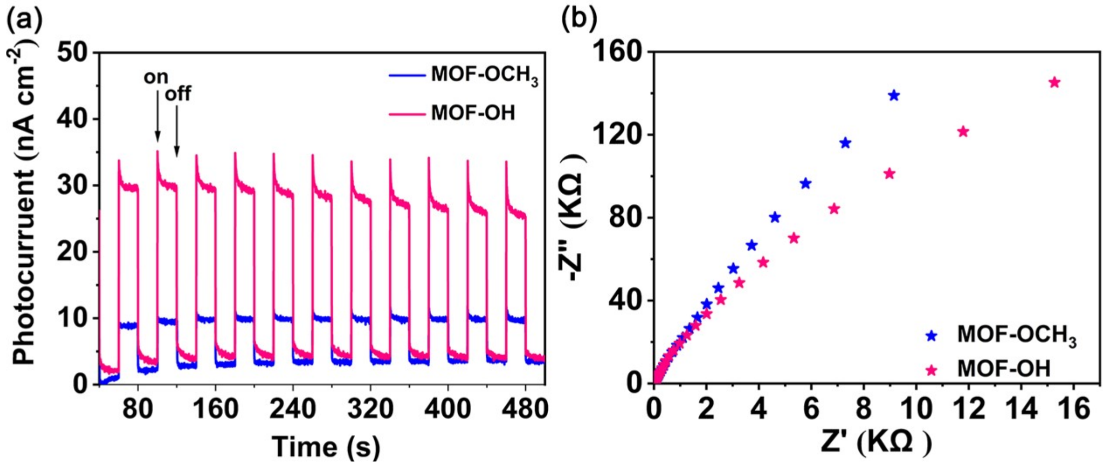


Fig. S10. Transient photocurrent responses of **MOF-OH** and **MOF-OCH$_3$**, and (b) EIS Nyquist plots of **MOF-OH** and **MOF-OCH$_3$**, respectively.

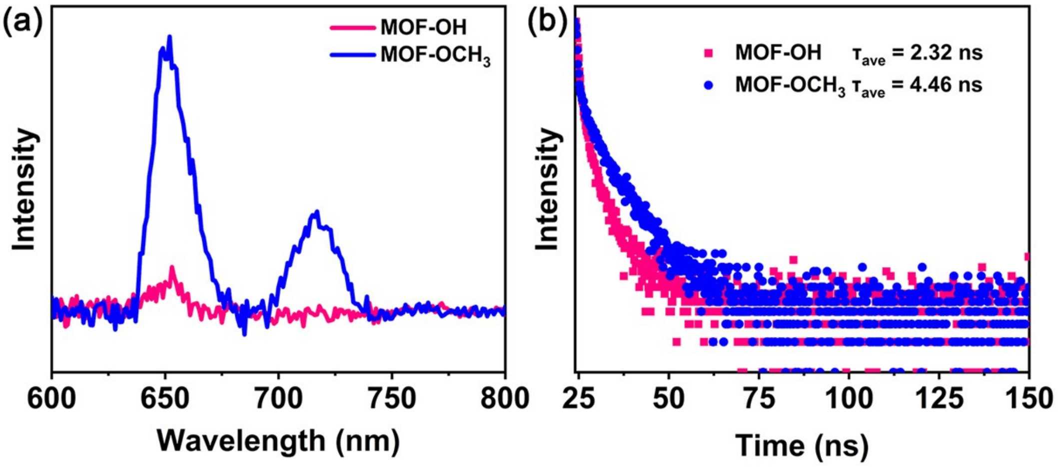


Fig. S11. (a) PL spectra and (b) time-resolved absorption spectra of **MOF-OH** and **MOF-OCH$_3$**, respectively.

References

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