Supporting Information

Visible-light-driven photocatalytic CO$_2$ reduction to formate over zirconium-porphyrin metal-organic framework with shp-a topology

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Materials

CH$_3$CN (99.9%, for HPLC, Acros), TEOA (99%, Acros), Zirconium (IV) chloride (ZrCl$_4$) (99%, TCI), Zirconium propoxide solution (70 wt.% in n-propanol, Acros), acetic acid (99.5%, Innochem), methylacrylic acid (99.0%, Aladdin), tetrais(4-carboxyphenyl)-porphyrin (TCPP, Jinan Henghua Sci. & Tec. Co., Ltd.), $^{13}$CO$_2$ (99%, Wuhan newreid Special Gas Co., Ltd.). Other reagents were of analytical grade and used without further purification.

Characterization

The powder X-ray diffraction (PXRD) patterns were recorded with a Rigaku D-MAX 2550 diffractometer using Cu-Kα radiation ($\lambda = 0.15417$ nm) with 2θ ranging from 3 to 40°. The morphologies of samples were characterized by a field emission scanning electron microscopy (XL30ESEM-FEG, USA). N$_2$ adsorption were measured by using Micromeritics ASAP 2020 instrument. UV-vis spectra of solid state samples were measured on a HITACHI U-4100 spectrophotometer. Mott-Schottky measurement was conducted using Pt and Ag/AgCl electrodes as the counter electrode and reference electrode, respectively. The working electrode was prepared on a fluorine-doped tin oxide (FTO) glass, and 0.2 M of Na$_2$SO$_4$ solution was used as electrolyte. Photocurrent measurements were conducted on electrochemical workstation CHI 660E (ChenHua Instrument, Shanghai). The $^{13}$C Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker AVANCE III 600M system (600 MHz). The fluorescence emission was recorded on an LS-55 fluorescence spectrometer made by PerkinElmer. FT-IR were recorded on a Mattson Alpha-Centauri spectrometer within 400–4000 cm$^{-1}$ using the samples prepared as pellets with KBr. The formed formate was detected by using a Metrohm 940 Professional IC Vario. EPR spectra were obtained on a JES-FA 200 EPR spectrometer; scanning frequency: 9.45 GHz; scanning power: 0.998 mW; scanning temperature: 25 °C. The in situ EPR experiments were carried out using a 500 W xenon arc lamp where a 420 nm optical filter was used to cut off ultraviolet light. The stable radical of 2,2-diphenyl-1-picrylhydrazyl (DPPH) was used as a standard for the calculation of g values. In the molecular docking study part, the 3D structures of CO$_2$, Zr clusters and TCPP ligand were first prepared through Discovery Studio (Biovia Inc. San Diego, CA, USA) by referring to the crystal structures of PCN-223. Docking modeling used the CDOCKER method in Discovery Studio. Combining CDocker Energy and CDocker Interaction Energy values, a reasonable docking conformation is selected.
Synthesis of $\text{Zr}_6$ methacrylate oxoclusters $\text{Zr}_6(\text{OH})_4\text{O}_4(\text{OMc})_{12}(\text{PrOH})$

2 mL of Zirconium(IV) propoxide (ca. 70%, solution in $n$-propanol, 4.95 mmol) was mixed under an $\text{N}_2$ atmosphere with 2.5 mL of methacrylic acid and stored in a closed Schlenk tube at ambient temperature for 11 days. After washed with $n$-propanol, the resulted samples were dried at 60 °C.

**Figure S1.** Two kinds of coordination modes for carboxyl group of TCPP ligand in PCN-223.

**Figure S2.** The ion chromatograms of $\text{HCOO}^-$ standard solution.
Figure S3. Calibration curve of HCOO⁻ solution.

Figure S4. PXRD patterns of PCN-223 after 10 h photocatalytic reaction and the simulated PCN-223.
**Figure S5.** SEM image of PCN-223 after 10 h photocatalytic reaction.

**Figure S6.** The cyclic tests of PCN-223 for photocatalytic CO$_2$ reduction under 10 h visible light irradiation.
Figure S7. PXRD patterns of Zr$_6$ methacrylate oxoclusters and the simulated one.

Figure S8. Solid UV-Vis absorption spectra of Zr$_6$ methacrylate oxoclusters.
Figure S9. Amounts of HCOO⁻ produced by Zr₆₆ methacrylate oxoclusters as a function of visible-light irradiation time (the solution were irradiated by a 300 W Xe lamp with a 420 nm cut-off filter (black) or six 10 W LED lamp (260-280 nm, blue)).

Figure S10. EPR spectra with g values for PCN-223.
Figure S11. IR spectra of PCN-223 under different conditions.

Figure S12. The optimal molecular docking conformation of CO$_2$ and TCPP ligand (cdocker energy = -3.72 kcal·mol$^{-1}$, cdocker interaction energy = 3.72 kcal·mol$^{-1}$).