Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Visible-light-driven photocatalytic CO_2 reduction to formate over zirconium-porphyrin metal-organic framework with *shp-a* topology

Dashu Chen,[a] Zhifen Guo,[b] Bin Li[a] and Hongzhu Xing*[b]*

[a]*College of Chemistry, Chemical Engineering and Resource Utilization; Post-doctoral Mobile Research Station of Forestry Engineering, Northeast Forestry University, No. 26 Hexing Road, Harbin 150040, China*

[b]*Provincial Key Laboratory of Advanced Energy Materials, College of Chemistry, Northeast Normal University, No. 5268 Renmin Street, Changchun, 130024, China*

E-mail: libinzh62@163.com (B. Li)

E-mail: xinghz223@nenu.edu.cn (H. Xing)

Materials

CH_3CN (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), tetrakis(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 (λ = 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_2SO_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 Zr_6 methacrylate oxoclusters $Zr_6(OH)_4O_4(OMc)_{12}(PrOH)$

2 mL of Zirconium(IV) propoxide (ca. 70%, solution in *n*-propanol, 4.95 mmol) was mixed under an 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.

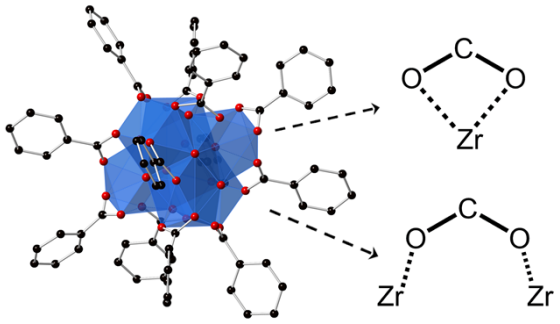

Figure S1. Two kinds of coordination modes for carboxyl group of TCPP ligand in PCN-223.

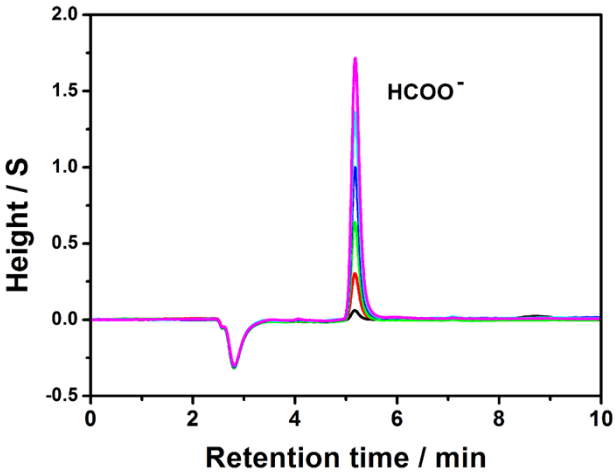

Figure S2. The ion chromatograms of $HCOO^-$ standard solution.

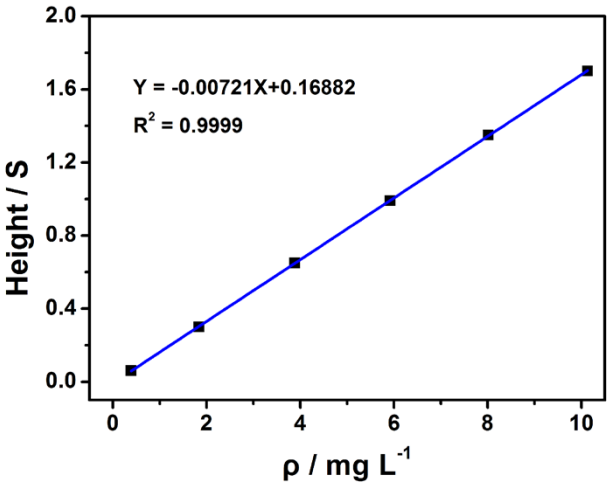

Figure S3. Calibration curve of $HCOO^-$ solution.

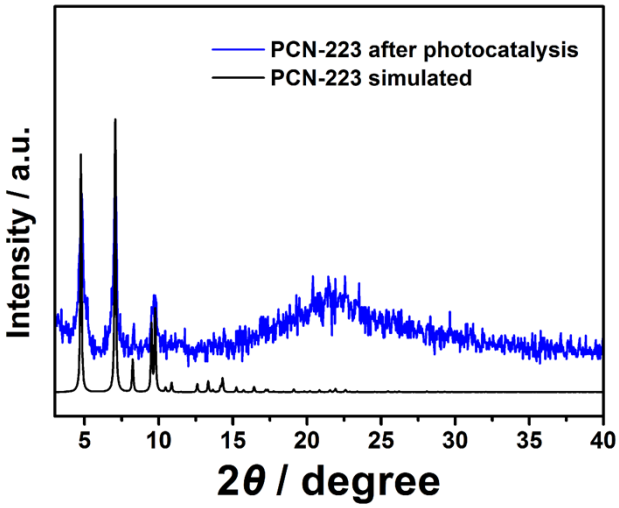

Figure S4. PXRD patterns of PCN-223 after 10 h photocatalytic reaction and the simulated PCN-223.

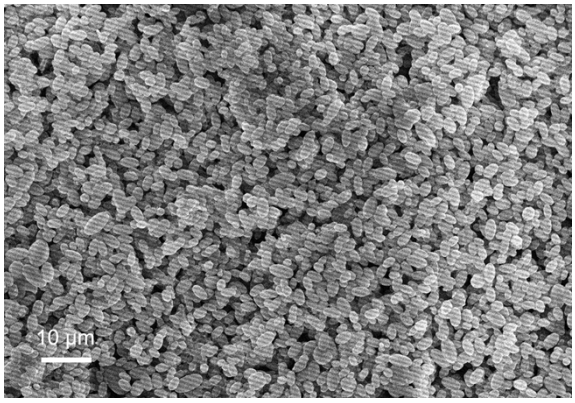

Figure S5. SEM image of PCN-223 after 10 h photocatalytic reaction.

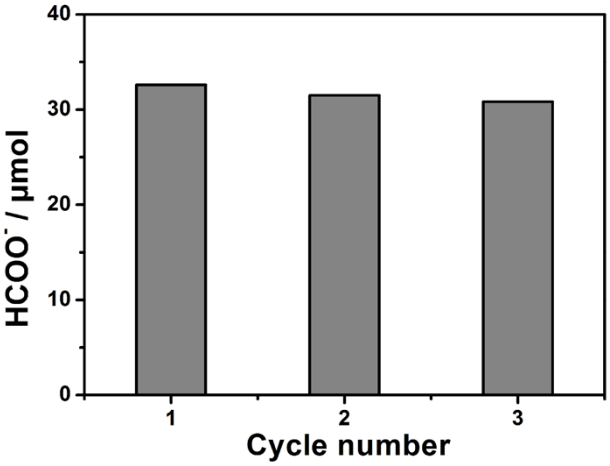

Figure S6. The cyclic tests of PCN-223 for photocatalytic CO_2 reduction under 10 h visible light irradiation.

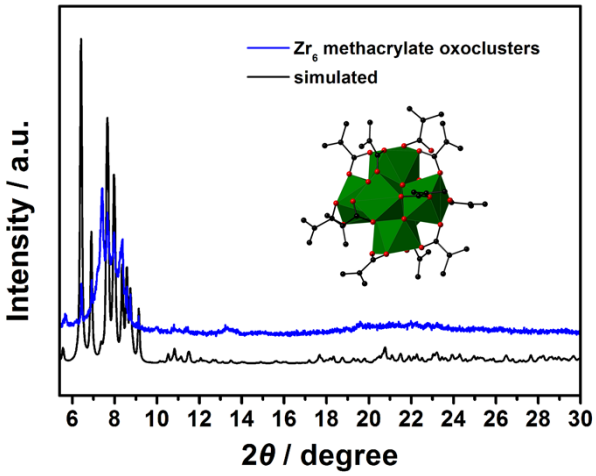

Figure S7. PXRD patterns of Zr_6 methacrylate oxoclusters and the simulated one.

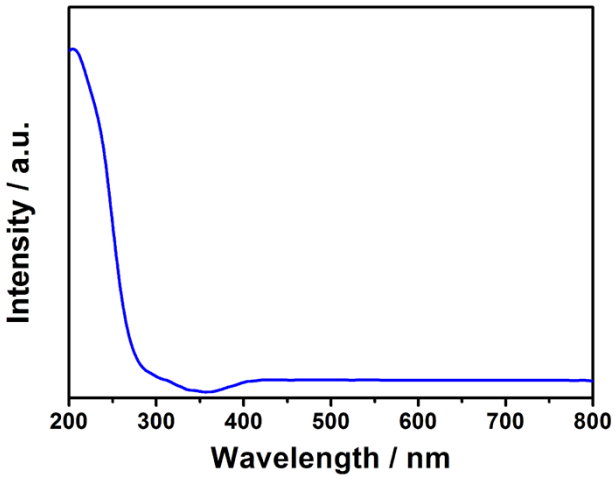

Figure S8. Solid UV-Vis absorption spectra of Zr_6 methacrylate oxoclusters.

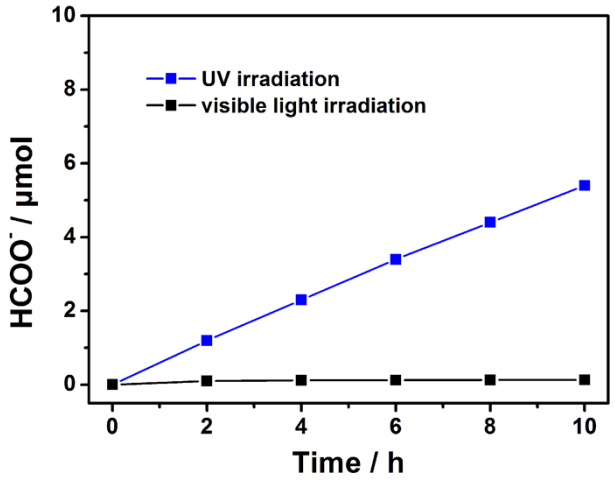

Figure S9. Amounts of $HCOO^-$ produced by Zr_6 methacrylate oxoclusters as a function of visible-light irradiation time {the solution were irradiated by a 300 W Xe lamp with a 420 nm cut-off filter (black) or six 10 W LED lamp (260-280 nm, blue)}.

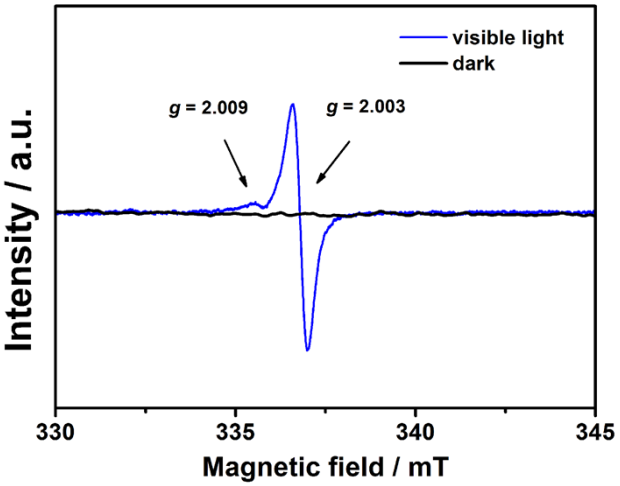

Figure S10. EPR spectra with *g* values for PCN-223.

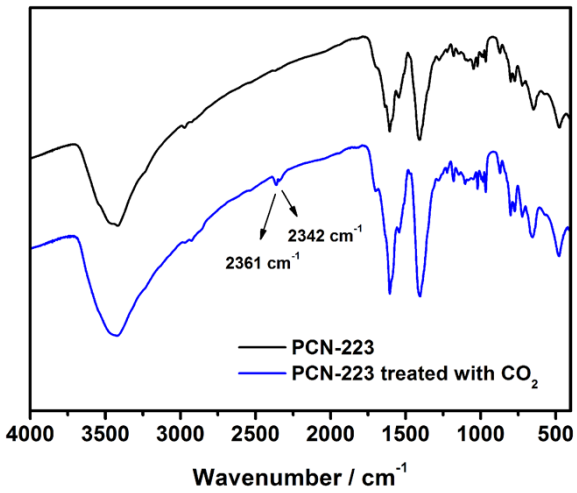

Figure S11. IR spectra of PCN-223 under different conditions.

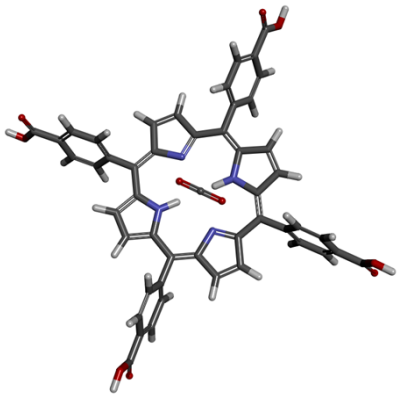

Figure S12. The optimal molecular docking conformation of CO_2 and TCPP ligand (cdocker energy = -3.72 kacl·mol^{-1}, cdocker interaction energy = 3.72 kacl·mol^{-1}).