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Local protons enhance photocatalytic CO₂ reduction by porphyrinic zirconium-organic frameworks[†]

Xue Zhao,^a Chang-Yan Zhu,^b Jun-Sheng Qin, ^b*^{ac} Heng Rao, ^{ac} Dong-Ying Du, ^b^b Min Zhang, ^{*} Ping She, ^{ac} Li Li^a and Zhong-Min Su*^a

The immobilization of molecular catalysts based on porphyrin fragments within metal-organic frameworks (MOFs) offers a promising approach for achieving sustainable and stable photocatalytic activity. In this study, we presented the synthesis of a phenolic hydroxy-modified iron-porphyrinic zirconium-based MOF, $Zr_{6}O_{4}(OH)_{4}$ (FeTCBPP-OH)₃, named **MOF-OH** (FeTCBPP-OH = iron 5,10,15,20-tetrakis[4-(4'-carboxyphenyl)-2,6-dihydroxylphenyl]porphyrin), through post-synthetic modification of a precursor MOF called **MOF-OCH**₃ $(Zr_6O_4(OH)_4(FeTCBPP-OCH_3)_3)$, FeTCBPP-OCH₃ = iron 5,10,15,20-tetrakis[4-(4'-carboxyphenyl)-2,6-dimethoxyphenyl]porphyrin). Initially, we attempted the direct assembly of Zr^{4+} centers and FeTCBPP-OH ligands; however, this approach was unsuccessful in obtaining MOF-OH. This perhaps resulted from the high number of hydroxyl groups on the polyphenolic porphyrinic fragments, which exhibited a stronger binding affinity towards zirconium centers. Consequently, we achieved MOF-OH by selectively modifying the partial methoxy positions of the FeTCBPP-OCH₃ fragments in MOF-OCH₃ through demethylation. To evaluate the photocatalytic performance of MOF-OH, we conducted CO2 reduction experiments without any additional photosensitizer. Remarkably, after 72 hours, the yield of CO reached a high value of 26.8 mmol g⁻¹. Notably, the CO production of MOF-OH was significantly higher than that of MOF-OCH₃, possibly due to the presence of phenolic hydroxyl substituents, which led to higher local proton concentrations. Furthermore, MOF-OH exhibited excellent stability, as demonstrated by the consistent CO production observed during four consecutive runs of CO2 reduction. To gain insights into the photocatalytic CO2 reduction process, we conducted a comprehensive series of characterizations and density functional theory calculations, which provided a deeper understanding of the mechanism involved.

Introduction

The conversion of CO_2 into high-energy C1 products has the potential to reduce atmospheric CO_2 levels while enabling sustainable strategies for obtaining valuable chemicals such as CO, HCOOH, CH_3OH , and CH_4 .¹⁻³ One promising pathway for this conversion is the photochemical reduction of CO_2 , which utilizes light instead of electricity. Sunlight, an abundant and free energy source, makes this approach particularly attractive.^{4,5} Researchers have dedicated considerable efforts

to exploring photocatalysts capable of capturing and reducing CO_2 . In the past few decades, various homogeneous catalysts, including transition metal complexes,⁶ ionic liquids,⁷ and organocatalysts,⁸ have been employed for CO₂ reduction. However, challenges related to catalyst recovery and product separation need to be overcome. Heterogeneous catalysts, such as TiO₂-based systems9 and metal-doped zeolites,10 have been developed, but their practical applications were limited by the high cost of noble metal catalysts. CO₂ can be reduced to CO through a two-electron and two-proton transfer reaction.¹¹⁻¹³ However, CO₂ is a highly stable molecule as it represents the most oxidized state of carbon, requiring considerable energy input for its transformation.¹⁴ Comparatively, photocatalytic systems based on non-precious metal photosensitizers and catalysts hold promise for large-scale applications. Therefore, it is particularly attractive to explore efficient and highly selective photocatalytic systems for CO₂ reduction.^{15,16}

Homogeneous catalysts, such as iron tetraphenylporphyrin and its derivatives, have been used for CO₂ photoreduction and have demonstrated high catalytic activities and selectivities.^{17,18}



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^a State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130012, P. R. China. E-mail: qin@jlu.edu.cn, suzhongmin@jlu.edu.cn

^b Department of Chemistry, Northeast Normal University, Changchun 130024, P. R. China. E-mail: mzhang@nenu.edu.cn

^c International Center of Future Science, Jilin University, Changchun 130012, P. R. China

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This can be attributed to the favourable binding of metal active sites with CO₂ and the homogeneity of the photocatalytic systems.¹⁹ Recent studies have shown that hydroxyl functionalization of the macrocyclic benzene ring greatly enhances the selectivity and redox catalytic activity for CO2 reduction to CO.^{20–22} The hydroxyl substituents in the second coordination sphere near the catalytic centres can increase the local proton concentrations, thereby accelerate catalysis. However, homogeneous catalysts often face limitations in terms of their solubility in organic media and interfacial electron/mass transfer. In recent years, metal-organic frameworks (MOFs) have gained increasing attention as photocatalysts due to their high porosity, chemical stability, and synthetic tunability.²³⁻²⁹ Especially, zirconium-based MOFs can be custom-designed for specific applications under harsh conditions,³⁰ making them potential platforms for the construction of site-isolated light-absorbing entities and single-site CO2 reduction catalysts.^{23,28} In this context, the immobilization of hydroxyl-modified porphyrinic fragments into Zr-MOF skeletons appears to be a judicious choice for the construction of potential photocatalysts for CO₂ reduction.31,32

While the search for reusable and stable catalysts for visible light-promoted CO₂ reduction continues, there is a growing gap between design and preparation that represents a critical limitation. In this study, we presented a couple of structural models in which molecular catalysts are successfully incorporated into Zr-MOFs for photocatalytic CO2 reduction. One such model is an iron porphyrin-based MOF with phenolic hydroxyl modification, called **MOF-OH** $(Zr_6O_4(OH)_4(FeTCBPP-OH)_3, FeTCBPP-OH = iron$ 5,10,15,20-tetrakis[4-(4'-carboxyphenyl)-2,6-dihydroxylphenyl]porphyrin). MOF-OH can be obtained through the post-synthetic modification of MOF-OCH₃ (Zr₆O₄(OH)₄(FeTCBPP-OCH₃)₃, FeT- $CBPP-OCH_3 = iron 5,10,15,20-tetrakis[4-(4'-carboxyphenyl)-2,6$ dimethoxyphenyl]porphyrin). Direct synthesis of MOF-OH through the assembly of precursors was not possible due to the higher binding affinity of hydroxyl groups on the polyphenolic porphyrinic fragments towards zirconium centers.^{33,34} The resulting 3D microporous MOF-OH, with numerous local proton sources, was employed as a heterogeneous photocatalyst, demonstrating effective integration of CO₂ capture and reduction under visible-light irradiation. For comparison, photocatalytic CO2 reduction of MOF-OCH₃ was also explored to elucidate the role of hydroxyl groups attached to the skeletons between MOF-OH and MOF-OCH₃. Furthermore, a comprehensive series of experimental characterizations and density functional theory (DFT) calculations were conducted to propose a mechanism for CO₂ photoreduction.

Results and discussion

Syntheses and characterization

The solvothermal reaction of FeTCBPP-OCH₃, ZrCl₄, and benzoic acid in *N*,*N*-diethylformamide (DEF) at 120 °C for 48 h yielded dark purple cubic crystals with the framework formula of $[Zr_6O_4(OH)_4(FeTCBPP-OCH_3)_3]$ (noted as **MOF-OCH**₃, Fig. 1). Furthermore, the direct assembly of the Zr⁴⁺ centres and the

FeTCBPP-OH fragments under similar conditions was unsuccessful. Fortunately, MOF-OH ([Zr₆O₄(OH)₄(FeTCBPP-OH)₃]) was achieved by post-synthetic modification of MOF-OCH₃ with demethylation reaction. There are two types of cages constructed by Zr₆O₄(OH)₄ clusters (Zr₆, Fig. S1a, ESI[†]) and FeTCBPP-OCH₃ fragments (Fig. S1b, ESI[†]) in MOF-OCH₃: (i) large cubic cages (Fig. S1c, ESI⁺), in which each vertex is occupied by a typical 12-connected Zr₆ cluster, and each face is a 4-connected FeTCBPP-OCH₃, and (ii) small cages (Fig. S1d, ESI^{\dagger}), which consist of two Zr_6 clusters on the axial sites and four FeTCBPP-OCH₃ on the longitude positions. Thus, the expected (4,12)-connected ftw topology is formed when the Zr₆ units are considered as 12-c nodes and the organic linkers as 4-c nodes. Furthermore, the space of an individual net is large enough to result in a two-fold interpenetration in MOF-OCH₃ (Fig. S1e and f, ESI[†]). MOF-OH is conformationally identical to MOF-OCH₃, except that part of the methoxy groups of the FeTCBPP-OCH₃ fragments was demethylated in MOF-**OH**. After demethylation, the microenvironment was changed, resulting in a couple of structural models with the introduction of iron tetraphenylporphyrin fragments into Zr-MOFs for a potential study on photocatalytic CO₂ reduction.

After the analysis of mass spectra and ¹H NMR spectra of MOF-OH and MOF-OCH₃ (Fig. S2 and S3, ESI[†]), it was observed that FeTCBPP-OCH3 was partially converted to FeTCBPP-OH in MOF-OH. According to quantitative calculations from ¹H NMR results, approximately 62.5% of the methoxy groups in MOF-OCH₃ were converted to hydroxyl groups. The powder X-ray diffraction (PXRD) patterns of MOF-OCH₃ and MOF-OH matched well with the simulated ones, which confirmed the purities of these two MOFs (Fig. 2a). The porosities of these MOFs were confirmed by N_2 adsorption at 77 K (Fig. 2b). MOF-OCH₃ and MOF-OH exhibited type I isotherms, due to the micropore nature of the interpenetrated structures. The Brunauer-Emmett-Teller (BET) surface areas were 1613 and 493 $m^2 g^{-1}$ for **MOF-OCH₃** and **MOF-OH**, respectively. The pore size and BET surface area of MOF-OH were reduced after the post-synthetic modification (Fig. S4, ESI⁺), which could be attributed to capillary-force-driven pore collapsing during

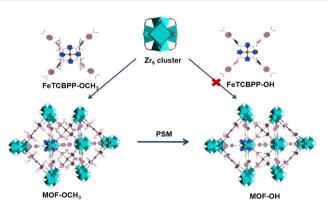


Fig. 1 Schematic diagram for the preparation of $MOF-OCH_3$ and MOF-OH. Colour codes: ZrO_8 polyhedron, cyan polyhedra; C, gray; O, red; N, blue; Fe, orange; H, olive or omitted for clarity.

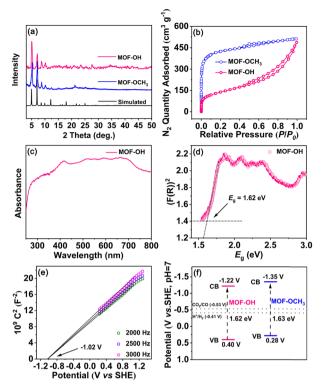


Fig. 2 (a) PXRD patterns and (b) N_2 isotherms at 77 K of **MOF-OH** and **MOF-OCH**₃, respectively. (c) UV-vis spectrum and (d) diffuse reflectance spectrum *via* K–M transformation of **MOF-OH**, (e) Mott–Schottky plots of the as-prepared **MOF-OH** electrode, and (f) calculated redox potentials of **MOF-OH** and **MOF-OCH**₃, respectively.

desorption.^{35,36} This result can be assigned to the preparation conditions of **MOF-OH**, which was synthesized from **MOF-OCH**₃ through BBr₃ cleavage ether reaction and post-treatment with water. Thermal-gravimetric analysis (TGA) confirmed that both **MOF-OH** and **MOF-OCH**₃ exhibited excellent thermal stabilities, and no obvious weight loss was observed until 400 °C (Fig. S5, ESI†).

Thermodynamic feasibility for CO₂ reduction

In the UV-vis spectra of MOF-OH and MOF-OCH₃ (Fig. 2c and Fig. S6, ESI[†]), a broad and strong absorption was observed in the range from 250 to 800 nm, which inherits the feature of the porphyrin fragments. These results perhaps allowed for promoting the electrons of MOF-OH and MOF-OCH₃ to an excited state upon visible-light irradiation.³⁷ The band gap (E_g) was tested by fitting the Tauc function to the K-M absorbance above the Urbach tail.³⁸ Accordingly, the E_g values of **MOF-OH** and MOF-OCH₃ can be estimated to ~1.62 and ~1.63 eV (Fig. 2d and Fig. S7, ESI[†]), indicating the semiconductivities of these two materials. In addition, Mott-Schottky measurements of MOF-OH and MOF-OCH₃ were conducted at frequencies of 2000, 2500, and 3000 Hz (Fig. 2e and Fig. S8, ESI⁺), respectively. Furthermore, the conduction-band (CB) position was estimated by measuring the flatband potential $(E_{\rm fb})$ via Mott-Schottky plots. The positive slope of the plots indicates the n-type semiconductors of MOF-OH and MOF-OCH₃,³⁹ and $E_{\rm fb}$ were evaluated to be approx. -1.02 and -1.15 V vs. SHE, respectively.

Since $E_{\rm fb}$ of n-type semiconductors was considered to be ~0.2 V more negative than the CB minima,⁴⁰ the CB of **MOF-OH** and **MOF-OCH**₃ were estimated to be approx. -1.22 and -1.35 V vs. SHE (Fig. 2f), which is more negative than the redox potentials of CO/CO₂ (-0.53 V vs. SHE, pH 7).⁴¹ Thus, **MOF-OH** and **MOF-OCH**₃ possess strong thermodynamic driving forces to realize CO₂ reduction.

Catalytic performance in overall CO₂ photoreduction

In light of the good semiconductor characteristics and excellent stabilities of Zr-MOFs, MOF-OH and MOF-OCH3 were utilized as photocatalysts for CO₂ reduction. Photocatalytic reduction of CO₂ over MOF-OH was conducted with 0.025 M BIH and 3 vol% 2,2,2trifluoroethanol (TFE) in a 5 mL acetonitrile (MeCN) as solvent under an LED lamp irradiation ($\lambda = 420$ nm). Remarkably, **MOF**-OH exhibited significant photocatalytic CO₂ reduction activity. The yield of CO increased with time and was up to 26.8 mmol g^{-1} at 72 h (Fig. 3a), which was much higher than those of the homogeneous molecular systems.⁴² In addition, only a minor amount of H₂ was observed by gas chromatography. No other products could be detected in either the gas or liquid phases, suggesting that MOF-OH possessed a high CO selectivity of 93% toward the CO_2 conversion. As a comparison, the performance of MOF-OCH₃ was also carried out under the same conditions. The photocatalytic activity of MOF-OH was much higher than that of MOF-OCH₃, which suggested the critical role of the phenol substituents on the phenyl rings in orienting the photocatalysis towards CO2 reduction. Furthermore, no CO was detected without MOF-OH (Fig. 3b), demonstrating the crucial role in the reaction. In the absence of BIH, no CO was produced, proving that BIH was essential as a sacrificial electron donor for CO₂ reduction.⁴³ A decrease in CO production was observed without TFE, suggesting that proper weak Brønsted acids significantly improved the catalytic process.44,45 Moreover, no CO was produced when the parallel

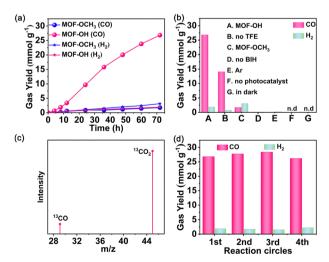


Fig. 3 Visible-light-driven CO₂ reduction performance of **MOF-OH** and **MOF-OCH₃**: (a) time-dependent CO/H₂ yields over **MOF-OH** (pink) and **MOF-OCH₃** (blue), (b) the yields of CO/H₂ under different conditions, (c) mass spectrum of produced ¹³CO *via* isotope ¹³CO₂ reduction under visible light, and (d) the yields of CO/H₂ over **MOF-OH** of four runs.

reaction was carried out in the dark, revealing a truly photocatalytic behaviour. To confirm the origin of CO, Ar as a reactant was added to the reaction system instead of CO_2 under a similar condition. However, no CO was detected.

In addition, isotope labelling experiments were performed by using ¹³CO₂ under the same conditions (Fig. 3c). A clear signal at an m/z ratio of 29 was observed that corresponding to ¹³CO, which verified the source of CO. No obvious change in CO production occurred during the four runs, demonstrated the stability of **MOF-OH** (Fig. 3d). The PXRD patterns further manifested that the skeleton of **MOF-OH** was retained after CO₂ reduction (Fig. S9, ESI†).

Mechanism study

The charge separation efficiency is considered to be of paramount importance for determining the photocatalytic activity.⁴⁶ The photoelectrochemical properties were performed with the combination of transient photocurrent measurements and electrochemical impedance spectroscopy (EIS). Both MOF-OCH₃ and MOF-OH exhibited obvious photocurrent signals and demonstrated excellent reproducibility of the response intensity throughout the on-off cycles (Fig. S10a, ESI[†]). However, the transient photocurrent intensity of MOF-OH is ~ 3 times that of MOF-OCH₃. In addition, the EIS spectra revealed that MOF-OH exhibited a smaller semicircle radius compared to MOF-OCH₃ (Fig. S10b, ESI[†]). These results indicated the presence of a higher separation and transfer efficiency of charge carriers in MOF-OH. In addition, photoluminescence (PL) spectra and timeresolved PL spectra were analysed to investigate the charge migration dynamics. The fluorescence intensity of MOF-OH was lower than that of **MOF-OCH**₃ (Fig. S11a, ESI[†]), indicating that the charge recombination was suppressed in MOF-OH. The average lifetime of **MOF-OH** (2.32 ns) was shorter compared to **MOF-OCH**₃ (4.46 ns) (Fig. S11b, ESI[†]), suggesting that the efficient electron-hole pairs separation in **MOF-OH** and therefore more favourable for photocatalytic CO₂ reduction.^{47,48}

To further investigate the rapid charge separation of photocatalysts, we recorded the femtosecond time-resolved transient absorption (fs-TA) spectra that is a powerful tool for tracking carrier dynamics in nanosystems in real time. For the measurements, a pump-probe scheme with visible-light pumping and white-light continuous probing was used. The fs-TA spectra of MOF-OH and MOF-OCH₃ were recorded in the wavelength range of 450-750 nm under the excitation with a 400 nm laser pulse (Fig. 4a and b). For MOF-OH, pulsed laser excitation resulted in a bleaching signal in 500-530 nm, which was a ground-state bleaching. The absorption signal in the excited state appeared at 530-750 nm. By probing the absorption intensity at λ = 700 nm after band edge excitation, the kinetic curves for MOF-OH and MOF-OCH3 were shown in Fig. 4c and d. Most importantly, the average lifetime (τ_{ave}) of **MOF-OH** (94.0 \pm 8.1 ps) was shorter than that of **MOF-OCH₃** (225.6 \pm 15.5 ps). The fast component may be attributed to fast electron transfer from the conduction-band minimum of the MOF to the trap state, suggesting that the accelerated TA decay kinetics suppressed electron-hole binding. This result was also consistent with the transient photocurrent measurements and EIS results.

To investigate the conversion pathway and mechanism of CO_2 in **MOF-OH**, the intermediates on the surface of the photocatalysts were analysed by using *in situ* attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR). As shown in Fig. 4e, the carbonate species, *i.e.* monodentate carbonate (m- CO_3^{2-} , at 1345 cm⁻¹), bidentate carbonate (b- CO_3^{2-} , at 1598 and 1282 cm⁻¹),⁴⁹ and bicarbonate (c- CO_3^{2-} , at

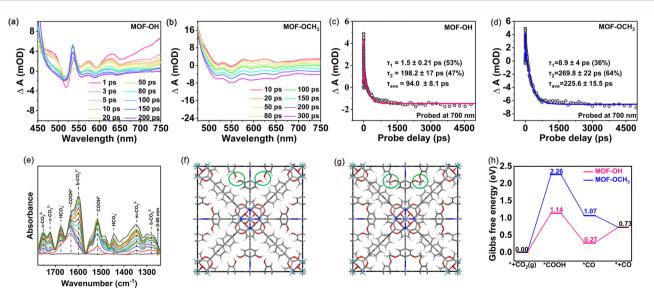
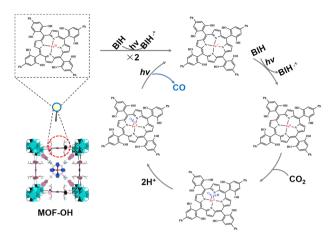


Fig. 4 (a) and (b) fs-TA data of **MOF-OH** and **MOF-OCH₃** excited at 400 nm showing the temporal changes at different time constants. (c) and (d) Representative TA kinetics of **MOF-OH** and **MOF-OCH₃** taken at the probing wavelength of 700 nm. (e) *In situ* ATR-FTIR measurement using MOF-OH as a catalyst in the presence of CO₂ and H₂O vapor under visible light irradiation (Xe lamp, $\lambda > 420$ nm). Optimized structural models of (f) **MOF-OH** and **(g) MOF-OCH₃**. The green circles indicated the hydroxy and methoxy. (h) Gibbs free energy diagrams for CO₂ reduction on **MOF-OH** and **MOF-OCH₃**, respectively.



 $\label{eq:scheme1} \begin{array}{l} \mbox{Proposed mechanism for the overall CO}_2 \mbox{ photoreduction of } \\ \mbox{MOF-OH}. \end{array}$

1752 and 1721 cm⁻¹) were identified. Additionally, the peaks at 1676 and 1444 cm⁻¹ can be assigned to asymmetric stretching of * HCO_3^- and symmetric stretching of * HCO_3^- , respectively.⁵⁰ The peaks at 1631, 1515 cm⁻¹ emerged, which were attributed to the formation of COOH*,^{49,51} a critical intermediate during the photoreduction of CO₂ to CO.

Furthermore, DFT calculations were carried out to investigate the mechanism of CO₂ reduction to CO over MOF-OH and MOF-OCH₃ (computational details can be found in the ESI[†]). The fully optimized geometric models of MOF-OH and MOF-OCH₃ were shown in Fig. 4f and g, where their difference of building groups was marked in green circles. The central Fe atom of the porphyrin ring was well-accepted to be the active site for CO₂ reduction, which was consistent with previous reports.^{52,53} The second coordination spheres of polyhydroxy groups offer a high local concentration of protons, which enhanced the photocatalytic efficiencies in terms of both rate constant and catalytic selectivity. To further understand the better catalytic performance of MOF-OH than that of MOF-OCH₃, the Gibbs free energy diagrams for CO₂ reduction to CO were systematically considered and explored (Fig. 4h). The CO₂ reduction starts with forming *C-Fe bonding at the active site and the subsequent proton-coupled electron transfer process to produce *COOH intermediate. The computed ΔG values for this elementary reaction on MOF-OH and MOF-OCH₃ were 1.14 and 2.26 eV, respectively. Subsequently, the *COOH intermediate was further hydrogenated to generate *CO intermediate. This process is exothermic in the Gibbs free energy diagram. The formed *CO intermediate on MOF-OH can easily release the CO gas by overcoming a small barrier by 0.46 eV. These results confirmed the better catalytic activity of MOF-OH, which further explained the much higher CO yield of MOF-OH than that of MOF-OCH₃.

On the basis of the above investigations, we proposed the mechanism of overall CO_2 photoreduction over **MOF-OH** (Scheme 1). CO_2 was first complexed with the triply reduced Fe^0 species (forming $Fe^{II}CO_2$), which after protonation, produced a $Fe^{II}CO$ intermediate, which is stabilized by internal

hydrogen bonding.^{54,55} The release of CO requires the breaking of the C–O bond and therefore an additional electron. In addition, it was noted that the electron-rich Fe^0 species can react with H⁺ to generate Fe^{II} and the unrequired byproduct H₂, although it remained a minor pathway in optimized conditions. On the other hand, a high concentration of Fe^0 active species in solution that would ensue from highly efficient electron transfers from the sensitizer can also support H₂ evolution.

Conclusions

In conclusion, we achieved the production of **MOF-OH** through a demethylation-driven post-synthetic modification process. This involved modifying the methoxy groups of the FeTCBPP-OCH₃ fragments in MOF-OCH₃. The yield of CO reached an impressive 26.8 mmol g^{-1} after 72 hours using **MOF-OH** as the photocatalyst for CO2 reduction, even without any photosensitizer. This yield was significantly higher than that achieved with MOF-OCH₃. Comprehensive studies on the kinetic mechanism revealed that the exceptional photocatalytic performance of MOF-OH can be primarily attributed to the iron porphyrin ligand with phenolic hydroxyl groups. These groups successfully immobilized the catalytic centre within the MOFs, facilitating ultrafast electron migration and efficient charge separation. Furthermore, the introduction of phenolic hydroxyl groups resulted in a high concentration of local protons, greatly enhancing the photocatalytic efficiencies. Additionally, DFT calculations demonstrated that MOF-OH can easily release CO gas by overcoming a small potential barrier in the formed *CO intermediate, compared to MOF-OCH₃. This work not only provides a solid foundation for the accurate design of MOF photocatalysts at the molecular level but also presents successful MOF models that can be used to investigate the relationship between structures and photocatalytic performances. These findings strongly emphasize the need for further studies to explore the multifunctional coordination sphere of MOF photocatalysts. Moreover, ongoing investigations in our laboratory aim to delve into the design and performance of the pore microenvironment.

Author contributions

Xue Zhao: validation, formal analysis, investigation, data curation, writing – original draft. Chang-Yan Zhu: data curation, writing – original draft. Jun-Sheng Qin: conceptualization, funding acquisition, project administration. Heng Rao: conceptualization, funding acquisition. Dong-Ying Du: conceptualization, validation, writing – review & editing. Min Zhang: data curation, conceptualization. Ping She: conceptualization, funding acquisition. Li Li: conceptualization. Zhong-Min Su: project administration.

Conflicts of interest

The authors declare no competing financial interest.

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