Supporting Information for

Neighboring Zn-Zr Sites in a Metal-Organic Framework for CO₂

hydrogenation

Jingzheng Zhang,^{†,§} Bing An,^{†,§} Zhe Li,^{†,§} Yonghua Cao,[†] Yiheng Dai,[†] Wangyang Wang,[†] Lingzhen Zeng,[†] Wenbin Lin,[‡] and Cheng Wang^{*,†}

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Section S1. General Experimental

The post-synthetic modifications of MOF-catalysts were carried out in a glovebox filled with Argon. All the solvents used in the preparation are dried, oxygen-free, and stored under Ar atmosphere. All of the other reagents and solvents are commercially available and used as received.

¹H NMR analysis was recorded on a Bruker NMR 500 DRX spectrometer at 500 MHz and referenced to the proton resonance resulting from incomplete deuteration of DMSO- d_6 ($\delta = 2.50$). ¹³C NMR spectra were recorded at 125 MHz, and all of the chemical shifts are reported downfield in ppm relative to the carbon resonance of deuterated solution. Infrared spectra (IR) were recorded on a Nicolet 6700 FTIR spectrometer equipped with an MCT detector using ATR mode. Thermogravimetric analysis (TGA) was performed in air using a NETZSCH TG 209 F1 equipped with an Alumina pan. TGA-MS was performed in air using TA Instruments SDT 650 equipped with Alumina pan and Discovery MS. Inductively coupled plasma-optical emission spectrometry (ICP-OES) analyses were performed on an Agilent ICP-OES instrument. Inductively coupled plasma-mass spectrometry (ICP-MS) analyses were performed on an Agilent 7700x ICP-MS and analyzed using ICP-MS Mass Hunter version B01.03. Samples were diluted in a 5% HNO₃ matrix and analyzed with a ¹⁵⁹Tb internal standard against a six-point standard curve over the range from 1 ppm to 100 ppm. The correlation coefficient was >0.9997 for all analytes of interest. Powder X-ray diffraction (PXRD) was carried out on a Japan Rigaku DMax-yA rotating anode X-ray diffractometer equipped with graphite monochromatized Cu K α radiation ($\lambda = 1.54$ Å). Nitrogen sorption measurements were conducted using a Micromeritics ASAP 2460 system at 77 K. The samples were prepared at 150 °C in a vacuum for 10 h. The surface area was calculated using the Brunauer-Emmett-Teller (BET) method in the range of $P/P_0 = 0.05-0.3$. Microporous surface areas, pore volumes, and mean pore diameters of micropores were evaluated by the HK method from the adsorption branches of isotherms. Transmission electron microscopy (TEM) and EDX mapping were performed on Phillips Analytical FEI Tecnai F30 electron microscope operated at an electron acceleration voltage of 300 kV. The samples were suspended in the anhydrous THF solvent, and the specimens are sample powders deposited onto a Cu microgrid coated with a holey carbon film for EDX-mapping. GC-MS spectral analyses were performed on a Shimadzu GCMS-QP2010 Plus equipped with SH-Rxi-5Sil MS 30 m \times 0.5 mm \times 0.25 µm column. H₂-Temperature-programmed desorption (H₂-TPD) measurements were obtained using a Micromeritics AutoChem II 2920

instrument. The samples were reduced *in situ* under flowing 5% H₂-Ar at 150°C for 1 h. After that, the reduced catalyst was cooled to 50 °C and then exposed to 1 atm of H₂ for 1 h, followed by purging with Ar for 30 min to remove any physisorbed molecules. H₂-TPD experiment was then operated when the temperature is increased to 250 °C at a heating rate of 5 °C min⁻¹ and holding at 250 °C for 1 h. H₂ is monitored using Mass Spectroscopy (MS, m/z=2). CO₂-Temperature-programmed desorption (CO₂-TPD) measurements were obtained using a Micromeritics AutoChem II 2920 instrument. The samples were pre-heated at 150 °C for 1 h to clean the surface of the sample from moisture and other adsorbed gas. After that, the sample was cooled down to 50 °C and then equilibrated in a CO₂ flow for 1 h, followed by flushing in Ar for 30 min to remove any physisorbed molecules. The CO₂-TPD experiment was then operated at 50-250 °C with a heating rate of 5 °C min⁻¹ and holding at 250 °C for 1 h. CO₂ is monitored using MS (m/z=44). H₂-D₂ exchange experiments were conducted using a Micromeritics AutoChem II 2920 instrument. The sample was first pretreated with Argon at 250 °C for 60 min and hydrogen for 30 min, then a flow of deuterium gas was injected. The injection was conducted 5 times. The gas component in the effluent is monitored and recorded by MS. The m/z values are 3 for HD. In situ Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFTS) of the samples was performed with a Nicolet 6700 instrument equipped with an MCT detector at 50 scans and a 4 cm⁻¹ resolution.

Section S2. Preparation and Characterization of Catalysts

2.1 Synthesis of catalysts.

2.1.1 MOF-808. MOF-808 was synthesized following the reported procedure with slight modification^[1]. 1,3,5-benzenetricarboxylic acid (BTC, 210 mg) and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (970 mg) in a solution containing N,N'-dimethylformamide (DMF) (30 mL) and formic acid (30 mL) are dissolved in a 50 mL capped bottle. The bottle is sealed and heated in a 100 °C isothermal oven for one day. The white powder is collected by centrifugation (9000 rpm, 2 min), washed with DMF three times (30 mL × 3), and acetone three times (30 mL × 3), then soaked in acetone and solvent exchange three times per day in three days. Finally, MOF-808 is dried under a dynamic vacuum overnight at 60 °C (Yield: 76%).



Figure S1. TEM images of MOF-808.

Analysis of the composition of MOF-808 by ¹H-NMR.

2 mg of MOF-808 was digested in 50 μ L of D₃PO₄. Then 50 μ L of D₂O and 300 μ L of DMSO-d₆ are added to the digested solution. The sample is then analyzed by ¹H-NMR. The ratio of BTC ligand and formate is approximately 1:1 by integrating the corresponding peaks of each ligand (Figure S2). The molar ratio between BTC and Zr determined by TGA analysis is 1/3. We thus deduce a formula for MOF-808 as Zr₆(μ ₃-O)₄(μ ₃-OH)₄(BTC)₂(HCO₂)₆, based on the molar ratio of Zr/BTC/HCO₂⁻ = 3/1/3.





Figure S3. TGA curve of MOF-808 in the 200-700 °C range. In the temperature range of 220-350 °C, there is 14.4% weight loss corresponding to the decomposition of six capping formate, leaving six hydroxyl groups on the SBU (calculated 12.3%). In the range of 350-600 °C, there is 28.2% weight loss corresponding to the decomposition of BTC ligand (calculated 30.3%). And the weight loss from 220 °C to 600 °C is 42.6% which matches the conversion of MOF-808 to ZrO_2 (calculated 42.6%).

2.1.2 Post-synthetic metalation of MOF-808 with ZnEt₂

The post-synthetic metalation process was conducted in a glove box filled with nitrogen. MOF-808 (100.0 mg, 69.8 μ mol) was weighted on a filter paper, washed with THF several times, and added 30 mL of dried THF solvent and stirred. 1.4 mL of ZnEt₂ (1 M in hexane) was dropwise added to the suspension. The mixture was stirred for 2-3 h, and the white solid was then centrifuged out and washed with THF 5-8 times. MOF-808-ZnEt was dried in a Schlenk tube under vacuum and stored in a glovebox for further use.

The synthesis of MOF-808-Zn-x (x = 1-4) was through the same method, but the amount of ZnEt₂ added was different. We obtained the corresponding MOF-808-Zn-x (x = 1-4) by adding 0.08 mL, 0.15 mL, 0.3 mL and 1.4 mL of ZnEt₂ respectively. The max loading of Zn is 15.2 wt%, which corresponds to the fully occupied $Zr_6(\mu_3-O)_4(\mu_3-OZnEt)_4$ clusters, and the corresponding catalyst was denoted MOF-808-Zn-4 (Table S1).



Figure S4. PXRD patterns of MOF-808-Zn-x with different Zn content.



Figure S5. TEM images of MOF-808-Zn-4.



Figure S6. High-resolution TEM images of MOF-808-Zn-4.

MOF-808-Zn-4 was then analyzed by ¹H-NMR. The ratio between BTC ligand and formate is approximately 1:1 by integrating peaks corresponding to each ligand (Figure S7).

Approximately 1 mg of vacuum-dried MOF samples were precisely weighed and transferred to a 22 mL Teflon-lined stainless steel reaction vessel. 9 mL of 5% HNO₃ aqueous solution and 100 μ L of HF were added to the vessel and heated in a 150 °C oven for 8 h. After the steel reactor was cooled to room temperature, the clear solution was transferred to a 10 mL tube. The solution was first diluted to 10 mL. Then 10 μ L of this solution was pipetted and further diluted to 10 mL for ICP-MS analysis. For ICP-OES, the samples after digestion were diluted to 10 mL for analysis. Each sample was prepared in duplicates for the test. The Zn content is 15.2 wt% based on ICP-OES analysis, corresponding to a ratio between Zn and Zr₆(μ ₃-OH)₄ sites around 4. As a result, the formula for MOF-808-Zn is Zr₆(μ ₃-OZn)₄(BTC)₂(HCO₂)₆, based on the molar ratio of Zr/BTC/HCO₂⁻ =

3/1/3. Different Zn content in MOF-808-Zn is varied by changing the amount of added ZnEt₂. The contents of Zn in different MOF-808 samples are listed in Table S1.



Figure S7. The ¹H-NMR spectrum of MOF-808-Zn-4 digested in D₃PO₄/D₂O/DMSO-d₆.



Figure S8. TGA curve of MOF-808-Zn-4 in the 200-700 °C range. In the temperature range of 220-320 °C, there is 10.4% weight loss corresponding to the decomposition of six capping formate, leaving six hydroxyl groups on the SBU (calculated 9.9%). In the range of 320-630 °C, there is 25.7%

weight loss corresponding to the decomposition of BTC ligand and two hydroxyl groups retained by formate decomposition (calculated 24.5%). And the all weight loss from 220 °C to 630 °C is 36.1% which matches the conversion of MOF-808-Zn-4 to ZrO_2 and ZnO (calculated 34.4%).

Catalyst	Zn Content (%)	The number of Zn per Zr ₆ cluster
MOF-808-Zn-1	4.3	1
MOF-808-Zn-2	8.2	2
MOF-808-Zn-3	11.5	3
MOF-808-Zn-4	15.2	4

Table S1. Different Zn Content in MOF-808-Zn.



Figure S9. The Zn number per Zr_6 cluster in MOF-808-Zn measured by ICP analysis against the amount of ZnEt₂ added in the metalation step.

2.2 Nitrogen sorption experiments



Figure S10. Nitrogen sorption isotherms (77K) for MOF-808 ($S_{BET} = 1511 \text{ m}^2/\text{g}$).



Figure S11. DFT simulated cylinder-shaped pore size distribution of MOF-808. The pore size is about 14 - 22 Å.



Figure S12. Nitrogen sorption isotherms (77K) for MOF-808-Zn-1 (S_{BET} =831 m²/g).



Figure S13. DFT simulated cylinder-shaped pore size distribution of MOF-808-Zn-1. The pore size is about 13 – 18 Å.



Figure S14. Nitrogen sorption isotherms (77K) for MOF-808-ZnEt-4 ($S_{BET} = 326 \text{ m}^2/\text{g}$).



Figure S15. DFT simulated cylinder-shaped pore size distribution of MOF-808-Zn-4. The pore size is about 12 - 21 Å.

Section S3. Evaluation of catalytic performance

3.1 Catalytic test

Activity evaluation for CO₂ hydrogenation was carried out in a continuous-flow, high-pressure, fixed-bed reactor. The samples (0.1-0.2 g) were loaded in a reactor with an inner diameter of 7 mm. The reaction temperature was programmed to increase from room temperature at the heating rate of 5°C min⁻¹. After reaching the target temperature, the products of CO₂ hydrogenation were analyzed under reaction conditions at 250 °C and a gas pressure of 4.0 MPa, H₂/CO₂ = 3, GHSV = 4500-18000 h⁻¹. At a concentration of 5% in the gas, Argon was used as an internal standard for calculating CO₂ conversion. The steady-state activity was recorded after at least 20 h on stream. Products were quantified by gas chromatography with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The columns are TDX-01 for Ar, CO, CO₂, and Propake-Q for methanol and other organic products. The CO₂ conversion (X_{CO2}) and the carbon-based selectivity (S_i) for MeOH and CO were calculated using an internal normalization method and mass balance method.

$$X_{CO_2} = (1 - \frac{A_{CO_2,out}}{A_{CO_2,in}} \cdot \frac{A_{Ar,in}}{A_{Ar,out}}) \times 100\%$$
 (Eq 1)

 $A_{CO2, in}$ and $A_{Ar, in}$ are the peak areas of the corresponding gases in the TCD chromatographs of the gas (CO_2/H_2) feed before catalysis. $A_{CO2, out}$ and $A_{Ar, out}$ are the peak areas of the exit gas composition during catalysis.

The yield of product i (i = CO or MeOH), Y_i , is determined by applying the following equations:

$$\mathbf{Y}_i = \frac{A_i}{A_{Ar} f_{i,Ar}} \times 100\% \quad (\text{Eq 2})$$

Where $f_{i,Ar}$ is the calibration factor determined for compound *i*. The selectivity (*S_i*) was calculated using equation Eq 3:

$$S_i = \frac{Y_i}{X_{CO_2}} \times 100\%$$
 (Eq 3)

Section S4. Characterization of Catalysts After Reaction.

The reusability of MOF-808-Zn was tested, and the results were shown in Figure S16. In the first run, initially, high activity was obtained due to the conversion of capping formates on the SBU. In the second run, the methanol STY was stable during the 15 hours on stream. The initial high activity was not observed. There was no decrease of methanol STY from the 1st run to the 2nd run, demonstrating the reusability of the MOF-808-Zn catalyst.



Figure S16. STY_{MeOH} of MOF-808-Zn vs reaction time in two consecutive runs. Reaction conditions: GHSV = 4500 h⁻¹, temperature = 250 °C, $H_2/CO_2 = 3$, P = 4 MPa.

4.1 Characterization of catalysts after the reaction.



Figure S17. PXRD patterns of MOF-808-Zn-4 before the reaction and after a 20-h run of CO_2 hydrogenation.



Figure S18. TEM and EDX mapping images of MOF-808-Zn-4 after a 100-h run of CO_2 hydrogenation.



Figure S19. High-resolution TEM images of MOF-808-Zn-4 after the reaction.

4.2 Additional catalytic data.

7.		Reaction conditions			Catalytic performance			
Catalyst ^{Zn} (%)	Zh (%)	Temp. (°C)	Pressure (MPa)	GHSV (mL/(g h))	Conv. (%)	MeOH Select.(%)	STY (mg.g ⁻¹ h ⁻¹)	Refs.
ae-ZnO-ZrO	6.1	340	4.0	21176	10.0	70.9	493.3	[2]
ZnO-ZrO ₂	/	340	3.0	14400	6.0	<50	138.9	[3]
ZnO-ZrO ₂ solid solution	10.4	320	5.0	24000	10.0	86.0	/	[4]
ZnZrO	10.4	330	2.0	3600	7.5	50.0	46.3	[5]
ZnZrO	10.4	320	4.0	2400	10.0	60.0	50.0	[6]
ZnO-ZrO ₂	31.7	320	3.0	18000	5.7	70.0	246.2	[7]
15ZnZr-600	15.0	300	2.0	9000	5.5	75.1	106.0	[8]
ZnZr	13.0	290	4.5	10800	2.1	80.5	58.7	[9]
MOF-808-Zn-4	15.2	250	4.0	4500	2.1	>99	30.4	This work

Table S2. Activity comparison of reported ZrZn catalysts and the MOF catalysts in CO_2 hydrogenation to methanol reaction.

Reaction conditions: $H_2/CO_2 = 3$.

Catalyst	Temp (GHSV	CO ₂ conv.	Select	. (%)	STY
(°C) (h ⁻¹)	(%)	МеОН	СО	$\left(\mathrm{mg}_{\mathrm{MeOH}}\mathrm{g_{Zn}^{-1}}\mathrm{h^{-1}}\right)$		
MOF-808-Zn-1	250	4500	0.6	94.3	5.7	190.7
MOF-808-Zn-2	250	4500	1.1	>99	0	178.1
MOF-808-Zn-3	250	4500	1.6	>99	0	185.1
MOF-808-Zn-4	250	4500	2.1	>99	0	182.9
UiO-66-Zn-4	250	4714	0	0	0	0
UiO-66-HCO ₂ H- Zn-4	250	4500	1.29	>99	0	135.2
UiO-67-HCO ₂ H- Zn-4	250	4800	1.53	>99	0	156.6

Table S3. Catalytic performances in CO₂ hydrogenation.

Reaction conditions: $H_2/CO_2 = 3$, P = 4 MPa, Time = 20 h.



Figure S20. CO₂ conversion and MeOH selectivity as a function of reaction temperature of MOF-808-Zn-4 for CO₂ hydrogenation to methanol. Reaction conditions: GHSV = 4500 h⁻¹, H₂/CO₂ = 3, P = 4 MPa, Time = 20 h

4.3 Additional characterization of the ¹³C-labeled experiment.



Figure S21. GC-MS spectra of the liquid products catalyzed by MOF-808-Zn using ¹³C-labeled ${}^{13}CO_2/H_2$ as the feed gas. The peak m/z = 33 is attributed to ${}^{13}CH_3OH$, indicating the carbon source in methanol product is all from CO₂ gas.



Figure S22. The ¹H-NMR spectrum of the liquid products using MOF-808-Zn-4 as the catalyst and ¹³C-labeled ¹³CO₂/H₂ as the feed gas. After the reaction, the catalyst was washed out by THF. Peaks at $\delta = 3.21$ and 3.49 correspond to ¹³CH₃OH, and peaks at $\delta = 1.88$ and 3.73 are attributed to THF. D₂O is added for field locking.

Section S5. Synthesis and Characterization of Other Catalysts

5.1 Synthesis and characterization of UiO-66 and UiO-66-Zn-4

UiO-66 was synthesized following the literature procedure.^[11] ZrCl₄ (0.053 g, 0.227 mmol) and 1,4-benzenedicarboxylic acid (H₂BDC) (0.034 g, 0.227 mmol) were dissolved in DMF (24.9 g, 340 mmol) at room temperature. The obtained mixture was sealed and placed in a pre-heated oven at 120 °C for 24 hours. After cooling in air to room temperature, the resulting white powder was collected by centrifugation (9000 rpm, 2 min), washed with DMF three times (30 mL \times 3), and acetone three times (30 mL \times 3), then soaked in acetone for solvent exchange three times per day in three days. Finally, UiO-66 was dried under a dynamic vacuum overnight at 60 °C (Yield: **70** %).

2 mg of UiO-66 was digested in 50 µL of D₃PO₄ to determine the ratio of the capping formates to BDC. Then 50 µL of D₂O and 300 µL of DMSO-d₆ were added to the digested solution. The sample was then analyzed by ¹H-NMR (Figure S25), and the ratio of BDC ligand and formate is determined to be approximately 30.09:1 by the integrating corresponding peaks of each ligand. We thus deduce a formula for UiO-66 as $Zr_6(\mu_3-O)_4(\mu_3-OH)_4(BDC)_{5.91}(HCO_2)_{0.19}$, based on the molar ratio of Zr/BDC/HCO₂⁻ = 6/5.91/0.19. The TGA of UiO-66 (Figure S27) gave 53.7% weight loss in the temperature range of 200-540 °C, due to the mass loss from conversion of $Zr_6(\mu_3-O)_4(\mu_3-OH)_4(BDC)_{5.91}(HCO_2)_{0.19}$ to ZrO_2 (theoretical mass loss: 55.3%).

The post-synthetic metalation of UiO-66 MOF was similar to that of MOF-808. UiO-66 (100.0 mg, 60.8 µmol) was weighted on a filter paper, washed with THF several times, and added 30 mL of dried THF solvent and stirred. 1.2 mL of ZnEt₂ (1 M in hexane) was dropwise added to the suspension. The mixture was stirred for 2-3 h, and the white solid was then centrifuged out and washed with THF 5-8 times. UiO-66-Zn-4 was then dried in a Schlenk tube under vacuum and stored in a glovebox for further use. The sample was analyzed by ¹H-NMR, and the ratio of BDC ligand and formate is determined by the integrations corresponding to each ligand to be approximately 32.75:1 (Figure S26). A small amount of formate is possibly produced from DMF decomposition in the synthesis. The Zn content is 12.9 wt% based on ICP-MS analysis, which corresponds to four Zn per $Zr_6(\mu_3-OH)_4$ site. As a result, the formula for UiO-66-Zn-4 is $Zr_6(\mu_3-O)_4(\mu_3-OZn)_4(BDC)_{5.92}(HCO_2)_{0.18}$, based on the molar ratio of Zr/BDC/HCO₂⁻ = 6/5.92/0.18.



Figure S23. Preparation and structure of UiO-66-Zn-4.



Figure S24. PXRD patterns of UiO-66 and UiO-66-Zn-4.



Figure S25. The ¹H-NMR spectrum of UiO-66 digested in $D_3PO_4/D_2O/DMSO-d_6$.





Figure S27. TGA curve of UiO-66 in the 200 - 800 °C range.



Figure S28. TEM images of UiO-66-Zn-4.



Figure S29. TGA curve of UiO-66-Zn-4 in the 200 - 700 °C range.

5.2 Synthesis and characterization of UiO-66-HCO₂H and UiO-66-HCO₂H-Zn-4

UiO-66-HCO₂H was synthesized following the literature procedure.^[12] 0.24 g of ZrOCl₂·8H₂O was dissolved in 20 mL of DMF/ 0.8 mL of HCO₂H under 5 min sonication. H₂BDC (0.136 g, 0.82 mmol) was then added, and the mixture was sonicated for another 5 min and placed into a 120 °C pre-heated oven for 1 day. After cooling in air to room temperature, the resulting white powder was collected by centrifugation (9000 rpm, 2 min), washed with DMF three times (30 mL × 3), and acetone three times (30 mL × 3), then soaked in acetone for solvent exchange three times per day in three days. Finally, UiO-66 was dried under a dynamic vacuum overnight at 60 °C (Yield: **58**%).

The post-synthetic metalation of UiO-66-HCO₂H MOF was similar to that of MOF-808. UiO-66-HCO₂H (100.0 mg, 66.1 µmol) was weighted on a filter paper, washed with THF several times, and added 30 mL of dried THF solvent stirred. 1.3 mL of ZnEt₂ (1 M in hexane) was dropwise added to the suspension. The mixture was stirred for 2-3 h, and the white solid was then centrifuged out and washed with THF 5-8 times. UiO-66-HCO₂H-Zn was then dried in a Schlenk tube under vacuum and stored in a glovebox for further use. The sample was then analyzed by ¹H-NMR, and the ratio between BDC ligand and formate is determined by the integrations corresponding to each ligand to be approximately 1.11:1 (Figure S31). The Zn content is 13.8 wt% based on ICP-MS analysis, which corresponds to four Zn per $Zr_6(\mu_3$ -OH)₄ sites. As a result, the formula for UiO-66-HCO₂H-Zn-4 is $Zr_6(\mu_3$ -OZn)₄(BDC)_{4.14}(HCO₂)_{3.72}, based on the molar ratio of Zr/BDC/HCO₂⁻ = 6/4.14/3.72.



Figure S30. PXRD patterns of UiO-66-HCO₂H and UiO-66-HCO₂H-Zn-4.



Figure S31. The ¹H-NMR spectrum of UiO-66-HCO₂H-Zn-4 digested in D₃PO₄/D₂O/DMSO-*d*₆.



Figure S32. TEM images of UiO-66-HCO₂H-Zn-4.

5.3 Synthesis and characterization of UiO-67-HCO₂H and UiO-67-HCO₂H-Zn-4

UiO-67-HCO₂H was synthesized by a slightly modified literature procedure^[12]. 1.2 g of ZrOCl₂·8H₂O was dissolved in 100 mL of DMF / 4 mL of HCO₂H under sonication for 5 min. 4,4' -biphenyldicarboxylic acid (H₂BPDC, 1 g) was added, and the mixture was sonicated for another 5 min and placed into 120 °C pre-heated oven for 1 day. After cooling in air to room temperature, the resulting white powder was collected by centrifugation (9000 rpm, 2 min), washed with DMF three times (30 mL × 3), and acetone three times (30 mL × 3), then soaked in acetone for solvent exchange three times per day in three days. Finally, UiO-67-HCO₂H was dried under dynamic vacuum overnight at 60 °C (Yield: **75** %).

The post-synthetic metalation of UiO-67-HCO₂H MOF was the same as above. The sample was then digested and analyzed by ¹H-NMR, and the ratio between bpdc ligand and formate is determined to be approximately 3.25:1. The Zn content is 12.2 wt% based on ICP-MS analysis, which corresponds to four Zn per $Zr_6(\mu_3$ -OH)_4 site. We thus deduce a formula for UiO-67-HCO₂H-Zn-4 as $Zr_6(\mu_3$ -OJ₄(μ_3 -OZn)_4(bpdc)_{5.2}(HCO_2)_{1.6}.



Figure S33. Preparation and structure of UiO-67-HCO₂H-Zn-4.



Figure S34. PXRD pattern of UiO-67-HCO₂H and UiO-67-HCO₂H-Zn-4.





Figure S36. TEM images of UiO-67-HCO₂H-Zn-4.

Section S6. Varies of Profiles to Probing the Zn-(µ₃-O)-Zr-OH Active Site

6.1 X-Ray Absorption Spectroscopic (XAS) Analysis

The general procedure of XAS data analysis

X-ray absorption data were collected at Beamline 10-BM-A, B at the Advanced Photon Source (APS) at Argonne National Laboratory. Spectra were collected at the zinc K-edge (9659 eV) in the transmission mode. The X-ray beam was monochromatized by a Si (111) monochromator and detuned by 50% to reduce the contribution of higher-order harmonics below the noise level. A metallic zinc foil standard was used as a reference for energy calibration and was measured simultaneously with experimental samples. The incident beam intensity (I₀), transmitted beam intensity (I₁), and reference (I_{ref}) were measured by 20 cm ionization chambers with gas compositions of 90% N₂ and 10% Ar, 66% N₂ and 34% Ar, and 100% N₂, respectively. Data were collected over six regions: -250 to -30 eV (10 eV step size, dwell time of 0.25 s), -30 to -12 eV (5 eV step size, dwell time of 0.5 s), -12 to 30 eV (1.1 eV step size, dwell time of 1 s), 30 eV to 6 Å⁻¹, (0.05 Å⁻¹ step size, dwell time of 2 s), 6 Å⁻¹ to 12 Å⁻¹, (0.05 Å⁻¹ step size, dwell time of 2 s), 12 Å⁻¹ to 15 Å⁻¹, (0.05 Å⁻¹ step size, dwell time of 2 s), 2 Å⁻¹ to 15 Å⁻¹, (0.05 Å⁻¹ step size, dwell time of 2 s), 2 Å⁻¹ to 15 Å⁻¹, (0.05 Å⁻¹ step size, dwell time of 2 s), 2 Å⁻¹ to 15 Å⁻¹, (0.05 Å⁻¹ step size, dwell time of 2 s), 2 Å⁻¹ to 15 Å⁻¹, (0.05 Å⁻¹ step size, dwell time of 2 s), 2 Å⁻¹ to 15 Å⁻¹, (0.05 Å⁻¹ step size, dwell time of 2 s), 2 Å⁻¹ to 15 Å⁻¹, (0.05 Å⁻¹ step size, dwell time of 2 s), 2 Å⁻¹ to 15 Å⁻¹, (0.05 Å⁻¹ step size, dwell time of 4 s). Multiple X-ray absorption spectra were collected at room temperature for each sample. Samples were grounded and mixed with polyethyleneglycol (PEG) and packed in a 6-shooter sample holder to achieve adequate absorption length.

Data were processed using the Athena and Artemis programs of the IFEFFIT package based on FEFF 6.1. Before merging, spectra were calibrated against the reference spectra and aligned to the first peak in the smoothed first derivative of the absorption spectrum. The background noise was removed, and the spectra were processed to obtain a normalized unit edge step.

Fitting of the EXAFS region was performed using the Artemis program of the IFEFFIT package. Fitting was performed in R space with a k-weight of 2 for Zn samples. Refinement was performed by optimizing an amplitude factor S0² and energy shift ΔE_0 which are common to all paths, in addition to parameters for bond length (ΔR) and Debye-Waller factor (σ^2).

Full multiple scattering (FMS) was used to simulate Zn K-edge XANES spectra by solving the Schrödinger equation. FMS within the muffin-tin (MT) approximation - the potential is spherical shape around the atoms and is constant in the remaining space - is performed by the FEFF9.6 program.^[13, 14] The overall simulated spectra are shifted to align their first-derivative maximum with

EXAFS study of MOF-808-Zn-BR and MOF-808-Zn-AR

X-ray absorption data of MOF-808-Zn sample before and after the reaction was collected and processed through identical protocols at Beamline 10-BM-A, B at the Advanced Photon Source (APS) Argonne National Laboratory. The fitting model was optimized using Gaussian 09 program. Fitting results were shown in Figure 3, and fitting parameters were shown in Tables S4-5.

Sample	MOF-808-Zn-BR
Fitting range	<i>k</i> 2.3 – 9.2 Å ⁻¹
	R 1.0 - 4.0 Å
Independent points	13
Variables	9
R-factor	0.022
S_0^{2}	0.953
$\Delta E_0(\mathrm{eV})$	-1.86±1.76
CN (Zn-C ₁)	1
<i>R</i> (Zn-C ₁) (Å)	2.029±0.05
σ^2 (Zn-C ₁) (Å ²)	0.005±0.001
CN (Zn-O ₁)	1
<i>R</i> (Zn-O ₁) (Å)	2.060±0.05
$\sigma^2 \left(\text{Zn-O}_1 \right) \left(\text{\AA}^2 \right)$	0.005±0.001
CN (Zn-C ₂)	2
R (Zn-C ₂) (Å)	2.619±0.18
σ^2 (Zn-C ₂) (Å ²)	0.001±0.006
CN (Zn-C ₃)	1
<i>R</i> (Zn-C ₃) (Å)	2.649±0.18
$\sigma^2 \left(\text{Zn-C}_3 \right) \left(\text{\AA}^2 \right)$	0.001±0.006
CN (Zn-O ₂)	4
R (Zn-O ₂) (Å)	2.707±0.09
σ^2 (Zn-O ₂) (Å ²)	0.002±0.004
CN (Zn-O ₃)	2
<i>R</i> (Zn-O ₃) (Å)	2.732±0.09
σ^2 (Zn-O ₃) (Å ²)	0.002±0.004
$CN(Zn-C_4)$	1
<i>R</i> (Zn-C ₄) (Å)	3.084±0.18
σ^2 (Zn-C ₄) (Å ²)	0.001±0.006
CN (Zn-Zr ₁)	3
<i>R</i> (Zn-Zr ₁) (Å)	3.410±0.12

Table S4. Summary of EXAFS fitting parameters for MOF-808-Zn-BR.

σ^2 (Zn-Zr ₁) (Å ²)	0.011±0.006
CN (Zn-C ₅)	2
R (Zn-C ₅) (Å)	3.495±0.18
σ^2 (Zn-C ₅) (Å ²)	0.001±0.006

Table S5. Summary of EXAFS fitting parameters for MOF-808-Zn-AR.

Sample	MOF808-Zn-AR
Fitting range	<i>k</i> 2.4 – 8.3 Å ⁻¹
	<i>R</i> 1.1 – 4.0 Å
Independent points	13
Variables	9
R-factor	0.014
S_0^2	0.953
$\Delta E_0(\mathrm{eV})$	5.18±1.48
CN (Zn-O ₁)	1
<i>R</i> (Zn-O ₁) (Å)	1.911±0.03
σ^2 (Zn-O ₁) (Å ²)	0.0002±0.001
CN (Zn-O ₂)	1
<i>R</i> (Zn-O ₂) (Å)	1.959±0.03
σ^2 (Zn-O ₂) (Å ²)	0.0002±0.001
CN (Zn-O ₃)	2
<i>R</i> (Zn-O ₃) (Å)	2.129±0.02
σ^2 (Zn-O ₃) (Å ²)	0.001±0.008
CN (Zn-Zr ₁)	1
<i>R</i> (Zn-Zr ₁) (Å)	3.005±0.11
σ^2 (Zn-Zr ₁) (Å ²)	0.013±0.007
CN (Zn-O ₄)	1
<i>R</i> (Zn-O ₄) (Å)	3.599±0.15
σ^2 (Zn-O ₄) (Å ²)	0.005±0.011
<i>CN</i> (Zn-O ₅)	1
R (Zn-O ₅) (Å)	3.728±0.15
σ^2 (Zn-O ₅) (Å ²)	0.005±0.011
CN (Zn-Zr ₂)	1
<i>R</i> (Zn-Zr ₂) (Å)	3.752±0.11
σ^2 (Zn-Zr ₂) (Å ²)	0.013±0.007
CN (Zn-C ₁)	1
<i>R</i> (Zn-C ₁) (Å)	3.832±0.15
$\sigma^2 (Zn-C_1) (Å^2)$	0.005±0.011
CN (Zn-Zr ₃)	1
R (Zn-Zr ₃) (Å)	3.956±0.11
σ^2 (Zn-Zr ₃) (Å ²)	0.013±0.007
CN (Zn-O ₆)	2

<i>R</i> (Zn-O ₆) (Å)	3.988±0.15
σ^2 (Zn-O ₆) (Å ²)	0.005±0.011

XANES calculation for MOF-808-Zn-AR sample

To confirm the first shell coordination environment of the MOF-808-Zn-AR sample, XANES calculation using FEFF 9.6 code was performed.

The standard sample ZnO was first simulated. As shown below, the simulated data and the experimental data gave roughly the same characteristic peaks.



Figure S37. The XANES simulation and the experiment data of standard sample ZnO.

XANES spectra of the MOF-808-Zn with different Zn coordination numbers (CN = $2\sim4$, capping with water molecular) were simulated. The models were optimized by the DFT method before the simulation. As shown in Figure S38, with increasing Zn coordination number, the intensity of the pre-edge peak around 9664.4 eV (highlight by red line) decreases due to a more symmetric first shell coordination environment of the Zn.

In the CN = 4 model, the first coordination shell of Zn is of tetrahedral geometry. Such a structure causes the pre-edge peak to be weak in the simulated XANES spectrum, which best matches the experimental data.



Figure S38. The XANES simulation of MOF-808-Zn with different coordination numbers.

XAS of some control samples of MOF-808-Zn

We also plotted the Zn K-edge EXAFS data of ZnO and Zn foil in R space in Figure S39. The comparison clearly showed that the Zn-O path in the MOF-808-Zn system is similar to that in ZnO. Instead, the MOF-808-Zn sample has a weak Zn-Zr path in the second shell, while the Zn-Zn path in ZnO is very strong. Zn foil only showed a Zn-Zn path, and this signal was not observed in the other two samples. This comparison indicates that the Zn centers in the MOF-808-Zn sample remain single sites without forming ZnO or Zn NPs.



Figure S39. Zn K-edge EXAFS of MOF-808-Zn (red), ZnO (blue) and Zn foil (green) in R space.

6.2 DED Process

HKL Generation from the theoretical structure of MOF-808

The PXRD pattern of MOF-808 was calculated from its theoretical structure in CCDC Mercury software,^[15] which was put into GSAS software^[16] together with the structure of MOF-808 to undergo Rietveld refinement. The intensities of diffraction of crystal planes, F_{calc} , and the phase angles φ_{calc} were extracted from Rietveld refinement by GSAS into RFL format.

Theoretical structure factor generated from structure model of MOF-808

The structure model of MOF-808 was generated from the reported CIF file^[17] by manually deleting all guest molecules to keep only SBUs and ligands as the skeleton of MOF in the unit cell. Its theoretical PXRD pattern was calculated by CCDC Mercury software,^[18] which was then refined against the model itself using the Rietveld method and GSAS software. The purpose of this step is to obtain theoretical structure factors of different diffraction peaks from fitted intensity information (F_{calc}) and phase angles (φ_{calc}) and automatically convert them into the RFL format by GSAS.

Note that attempts to extract F_{calc} and φ_{calc} by an alternative route from PLATON^[19] and SHELXL would give significantly fewer usable diffraction intensities that lead to poorer DED analysis quality. This alternative route includes calculating intensities of diffraction by PLATON stored in an HKL format with an INS file, which was put into SHELXL for refinement to obtain the F_{calc} and φ_{calc} in an FCF format. However, most of the obtained F_{calc} did not share the same *hkl* indexes as that of the F_{obs} extracted by Le Bail refinements in GSAS. We thus recommend directly using the GSAS refinement to obtain F_{calc} .

PXRD Refinement of MOF-808: Le Bail Refinement

Diffraction patterns of bare MOF-808, MOF-808-Zn-1, and MOF-808-Zn-4 were collected on a Japan Rigaku DMax- γ A rotating anode X-ray diffractometer equipped with graphite monochromatized Cu K α radiation ($\lambda = 1.54$ Å) in a collecting rate of 0.2 °/min. These patterns were sent into GSAS software with the cell parameters from the CIF file for Le Bail refinement over the 20 range of 3 - 30 ° (Figure S40).^[20] The cell parameters, profiles of pseudo-Voigt functions, and other parameters were refined. Then F_{obs} was extracted and saved in RFL format. The result of Le Bail refinements was shown in Figure S40.



Figure S40. The result of Le Bail refinements on MOF-808 with or without loadings of zinc.

Structure Envelope (SE) Densities Generation by SUPERFLIP

A Python code was used to extract F_{calc} and F_{obs} with the same Miller Indexes, together with the phase angles φ_{calc} to prepare the inputs in INFLP format for SUPERFLIP software.^[21] Then SE densities ρ_{obs} of MOF-808, MOF-808-Zn-1, and MOF-808-Zn-4 were calculated by SUPERFLIP software and saved in XPLOR format. More details and the contents of INFLP files were displayed below.

Contents of INFLP files as inputs of SUPERFLIP software

From F_{obs}: MOF-808-NoZn title MOF-808-NoZn

crystallographic data #----cell 35.1364 35.1364 35.1364 90.000 90.000 90.000

spacegroup Fd-3m spacegroup Fd-3m centro yes centers 0.000000 0.000000 0.000000 endcenters symmetry x y z 3/4-x 1/4-y 1/2+z 1/4-x 1/2+y 3/4-z 1/2+x 3/4-y 1/4-z z x y 1/2+z 3/4-x 1/4-y 3/4-z 1/4-x 1/2+y 1/4-z 1/2+x 3/4-y y z x 1/4-y 1/2+z 3/4-x 1/2+y 3/4-z 1/4-x 3/4-y 1/4-z 1/2+x 3/4+y 1/4+x 1/2-z -y -x -z 1/4+y 1/2-x 3/4+z 1/2-y 3/4+x 1/4+z 3/4+x 1/4+z 1/2-y 1/2-x 3/4+z 1/4+y -x -z -y 1/4+x 1/2-z 3/4+y 3/4+z 1/4+y 1/2-x 1/4+z 1/2-y 3/4+x 1/2-z 3/4+y 1/4+x -z -y -x -x -y -z 1/4+x 3/4+y 1/2-z 3/4+x 1/2-y 1/4+z 1/2-x 1/4+y 3/4+z -z -x -y 1/2-z 1/4+x 3/4+y 1/4+z 3/4+x 1/2-y 3/4+z 1/2-x 1/4+y -y -z -x 3/4+y 1/2-z 1/4+x 1/2-y 1/4+z 3/4+x 1/4+y 3/4+z 1/2-x 1/4-y 3/4-x 1/2+z ухz 3/4-y 1/2+x 1/4-z 1/2+y 1/4-x 3/4-z 1/4-x 3/4-z 1/2+y 1/2+x 1/4-z 3/4-y xzy 3/4-x 1/2+z 1/4-y 1/4-z 3/4-y 1/2+x 3/4-z 1/2+y 1/4-x 1/2+z 1/4-y 3/4-x z y x

x 1/2+y 1/2+z 3/4-x 3/4-y z 1/4-x y 1/4-z 1/2+x 1/4-y 3/4-z z 1/2+x 1/2+y 1/2+z 1/4-x 3/4-y 3/4-z 3/4-x y 1/4-z x 1/4-y y 1/2+z 1/2+x 1/4-y z 1/4-x 1/2+y 1/4-z 3/4-x 3/4-y 3/4-z x 3/4+y 3/4+x -z-y 1/2-x 1/2-z 1/4+y -x 1/4+z1/2-y 1/4+x 3/4+z 3/4+x 3/4+z -y 1/2-x 1/4+z 3/4+y -x 1/2-z 1/2-y 1/4+x -z 1/4+y 3/4+z 3/4+y -x 1/4+z -y 1/4+x 1/2-z 1/4+y 3/4+x -z 1/2-y 1/2-x -x 1/2-y 1/2-z 1/4+x 1/4+y -z 3/4+x -y 3/4+z 1/2-x 3/4+y 1/4+z -z 1/2-x 1/2-y 1/2-z 3/4+x 1/4+y 1/4+z 1/4+x -y3/4+z - x 3/4+y-y 1/2-z 1/2-x 3/4+y -z 3/4+x 1/2-y 3/4+z 1/4+x1/4+y 1/4+z -x 1/4-y 1/4-x z y 1/2+x 1/2+z 3/4-y x 3/4-z 1/2+y 3/4-x 1/4-z 1/4-x 1/4-z y 1/2+x 3/4-z 1/4-y x 1/2+z 1/2+y 3/4-x z 3/4-y

1/4-z 1/4-y x 3/4-z y 3/4-x 1/2+z 3/4-y 1/4-x z 1/2+y 1/2+x 1/2+x y 1/2+z 1/4-x 1/4-y z 3/4-x 1/2+y 1/4-z x 3/4-y 3/4-z $1/2+z \ge 1/2+y$ z 3/4-x 3/4-y 1/4-z 1/4-x y 3/4-z 1/2+x 1/4-y 1/2+y z 1/2+x 3/4-y 1/2+z 1/4-x y 3/4-z 3/4-x 1/4-y 1/4-z x 1/4+y 1/4+x -z 1/2-y -x 1/2-z 3/4+y 1/2-x 1/4+z -y 3/4+x 3/4+z 1/4+x 1/4+z -y-x 3/4+z 3/4+y 1/2-x -z 1/2-y 3/4+x 1/2-z 1/4+y 1/4+z 1/4+y -x 3/4+z 1/2-y 1/4+x -z 3/4+y 3/4+x 1/2-z -y 1/2-x 1/2-x -y 1/2-z 3/4+x 3/4+y -z 1/4+x 1/2-y 3/4+z -x 1/4+y 1/4+z 1/2-z -x 1/2-y -z 1/4+x 1/4+y 3/4+z 3/4+x -y 1/4+z 1/2-x 3/4+y 1/2-y -z 1/2-x 1/4+y 1/2-z 3/4+x -y 1/4+z 1/4+x 3/4+y 3/4+z -x 3/4-y 3/4-x z $1/2+y \ge 1/2+z$ 1/4-y 1/2+x 3/4-z y 1/4-x 1/4-z

3/4-x 3/4-z y x 1/4-z 1/4-y 1/2+x z 1/2+y 1/4-x 1/2+z 3/4-y 3/4-z 3/4-y x 1/4-z 1/2+y 3/4-x z 1/4-y 1/4-x 1/2+z y 1/2+x1/2+x 1/2+y z 1/4-x 3/4-y 1/2+z 3/4-x y 3/4-z x 1/4-y 1/4-z 1/2+z 1/2+x y z 1/4-x 1/4-y 1/4-z 3/4-x 1/2+y 3/4-z x 3/4-y 1/2+y 1/2+z x3/4-y z 3/4-x y 1/4-z 1/4-x 1/4-y 3/4-z 1/2+x 1/4+y 3/4+x 1/2-z 1/2-y 1/2-x -z 3/4+y - x 3/4+z-y 1/4+x 1/4+z 1/4+x 3/4+z 1/2-y -x 1/4+z 1/4+y 1/2-x 1/2-z -y 3/4+x -z 3/4+y 1/4+z 3/4+y 1/2-x 3/4+z - y 3/4+x-z 1/4+y 1/4+x 1/2-z 1/2-y -x 1/2-x 1/2-y -z 3/4+x 1/4+y 1/2-z 1/4+x - y 1/4+z-x 3/4+y 3/4+z 1/2-z 1/2-x -y -z 3/4+x 3/4+y 3/4+z 1/4+x 1/2-y 1/4+z - x 1/4+y1/2-y 1/2-z -x 1/4+y -z 1/4+x -y 3/4+z 3/4+x 3/4+y 1/4+z 1/2-x

3/4-y 1/4-x 1/2+z 1/2+y 1/2+x z 1/4-y x 1/4-z y 3/4-x 3/4-z 3/4-x 1/4-z 1/2+y x 3/4-z 3/4-y 1/2+x 1/2+z y 1/4-x z 1/4-y 3/4-z 1/4-y 1/2+x 1/4-z y 1/4-x z 3/4-y 3/4-x 1/2+z 1/2+y x endsymmetry

Grid definition for density maps #-----dimension 3 voxel AUTO

control parameters for Superflip run #-----maxcycles 10000 repeatmode 1 bestdensities 1

outputfile MOF-808-NoZn.xplor expandedlog yes

Keywords for charge flipping #----perform fourier delta AUTO weakratio 0.0 Biso 0.0 randomseed AUTO searchsymmetry average

input data
#----dataformat intensity phase
fbegin
h k l F^2obs phase
1 1 1 7270233.22 0
2 2 0 235357.91 0.5

From F_{obs}: MOF-808-Zn

title MOF-808-Zn

crystallographic data #----cell 35.1364 35.1364 35.1364 90.000 90.000 90.000

spacegroup Fd-3m spacegroup Fd-3m centro yes centers $0.000000 \quad 0.000000 \quad 0.000000$ endcenters symmetry хyz 3/4-x 1/4-y 1/2+z 1/4-x 1/2+y 3/4-z 1/2+x 3/4-y 1/4-z z x y 1/2+z 3/4-x 1/4-y 3/4-z 1/4-x 1/2+y 1/4-z 1/2+x 3/4-y y z x 1/4-y 1/2+z 3/4-x 1/2+y 3/4-z 1/4-x 3/4-y 1/4-z 1/2+x 3/4+y 1/4+x 1/2-z

-y -x -z 1/4+y 1/2-x 3/4+z 1/2-y 3/4+x 1/4+z 3/4+x 1/4+z 1/2-y 1/2-x 3/4+z 1/4+y -x -z -y 1/4+x 1/2-z 3/4+y 3/4+z 1/4+y 1/2-x 1/4+z 1/2-y 3/4+x 1/2-z 3/4+y 1/4+x -z -y -x -x -y -z 1/4+x 3/4+y 1/2-z 3/4+x 1/2-y 1/4+z 1/2-x 1/4+y 3/4+z -z -x -y 1/2-z 1/4+x 3/4+y 1/4+z 3/4+x 1/2-y 3/4+z 1/2-x 1/4+y -y -z -x 3/4+y 1/2-z 1/4+x 1/2-y 1/4+z 3/4+x 1/4+y 3/4+z 1/2-x 1/4-y 3/4-x 1/2+z ухz 3/4-y 1/2+x 1/4-z 1/2+y 1/4-x 3/4-z 1/4-x 3/4-z 1/2+y 1/2+x 1/4-z 3/4-y хzy 3/4-x 1/2+z 1/4-y 1/4-z 3/4-y 1/2+x 3/4-z 1/2+y 1/4-x 1/2+z 1/4-y 3/4-x z y x x 1/2+y 1/2+z 3/4-x 3/4-y z 1/4-x y 1/4-z 1/2+x 1/4-y 3/4-z z 1/2+x 1/2+y 1/2+z 1/4-x 3/4-y 3/4-z 3/4-x y 1/4-z x 1/4-y y 1/2+z 1/2+x

1/4-y z 1/4-x 1/2+y 1/4-z 3/4-x 3/4-y 3/4-z x 3/4+y 3/4+x -z-y 1/2-x 1/2-z 1/4+y -x 1/4+z 1/2-y 1/4+x 3/4+z3/4+x 3/4+z -y 1/2-x 1/4+z 3/4+y -x 1/2-z 1/2-y 1/4+x -z 1/4+y 3/4+z 3/4+y -x 1/4+z - y 1/4+x1/2-z 1/4+y 3/4+x -z 1/2-y 1/2-x -x 1/2-y 1/2-z 1/4+x 1/4+y -z3/4+x -y 3/4+z 1/2-x 3/4+y 1/4+z -z 1/2-x 1/2-y 1/2-z 3/4+x 1/4+y 1/4+z 1/4+x -y 3/4+z -x 3/4+y -y 1/2-z 1/2-x 3/4+y -z 3/4+x 1/2-y 3/4+z 1/4+x1/4+y 1/4+z -x 1/4-y 1/4-x z y 1/2+x 1/2+z 3/4-y x 3/4-z 1/2+y 3/4-x 1/4-z 1/4-x 1/4-z y 1/2+x 3/4-z 1/4-y x 1/2+z 1/2+y 3/4-x z 3/4-y 1/4-z 1/4-y x 3/4-z y 3/4-x 1/2+z 3/4-y 1/4-x z 1/2+y 1/2+x 1/2+x y 1/2+z 1/4-x 1/4-y z 3/4-x 1/2+y 1/4-z x 3/4-y 3/4-z 1/2+z x 1/2+y

z 3/4-x 3/4-y 1/4-z 1/4-x y 3/4-z 1/2+x 1/4-y 1/2+y z 1/2+x 3/4-y 1/2+z 1/4-x y 3/4-z 3/4-x 1/4-y 1/4-z x 1/4+y 1/4+x -z 1/2-y -x 1/2-z 3/4+y 1/2-x 1/4+z -y 3/4+x 3/4+z 1/4+x 1/4+z -y -x 3/4+z 3/4+y 1/2-x -z 1/2-y 3/4+x 1/2-z 1/4+y 1/4+z 1/4+y -x 3/4+z 1/2-y 1/4+x -z 3/4+y 3/4+x 1/2-z -y 1/2-x 1/2-x -y 1/2-z 3/4+x 3/4+y -z 1/4+x 1/2-y 3/4+z -x 1/4+y 1/4+z 1/2-z -x 1/2-y -z 1/4+x 1/4+y 3/4+z 3/4+x -y 1/4+z 1/2-x 3/4+y 1/2-y -z 1/2-x 1/4+y 1/2-z 3/4+x -y 1/4+z 1/4+x 3/4+y 3/4+z -x 3/4-y 3/4-x z $1/2+y \ge 1/2+z$ 1/4-y 1/2+x 3/4-z y 1/4-x 1/4-z 3/4-x 3/4-z y x 1/4-z 1/4-y 1/2+x z 1/2+y 1/4-x 1/2+z 3/4-y 3/4-z 3/4-y x 1/4-z 1/2+y 3/4-x z 1/4-y 1/4-x 1/2+z y 1/2+x 1/2+x 1/2+y z

1/4-x 3/4-y 1/2+z 3/4-x y 3/4-z x 1/4-y 1/4-z 1/2+z 1/2+x y z 1/4-x 1/4-y 1/4-z 3/4-x 1/2+y 3/4-z x 3/4-y 1/2+y 1/2+z x3/4-y z 3/4-x y 1/4-z 1/4-x 1/4-y 3/4-z 1/2+x 1/4+y 3/4+x 1/2-z 1/2-y 1/2-x -z 3/4+y - x 3/4+z-y 1/4+x 1/4+z 1/4+x 3/4+z 1/2-y -x 1/4+z 1/4+y 1/2-x 1/2-z -y 3/4+x -z 3/4+y 1/4+z 3/4+y 1/2-x 3/4+z - y 3/4+x-z 1/4+y 1/4+x 1/2-z 1/2-y -x 1/2-x 1/2-y -z 3/4+x 1/4+y 1/2-z 1/4+x - y 1/4+z-x 3/4+y 3/4+z 1/2-z 1/2-x -y -z 3/4+x 3/4+y 3/4+z 1/4+x 1/2-y 1/4+z -x 1/4+y 1/2-y 1/2-z -x 1/4+y -z 1/4+x -y 3/4+z 3/4+x 3/4+y 1/4+z 1/2-x 3/4-y 1/4-x 1/2+z 1/2+y 1/2+x z 1/4-y x 1/4-z y 3/4-x 3/4-z 3/4-x 1/4-z 1/2+y x 3/4-z 3/4-y 1/2+x 1/2+z y1/4-x z 1/4-y 3/4-z 1/4-y 1/2+x

1/4-z y 1/4-x z 3/4-y 3/4-x 1/2+z 1/2+y x endsymmetry

Grid definition for density maps #-----dimension 3 voxel AUTO

control parameters for Superflip run
#----maxcycles 10000
repeatmode 1
bestdensities 1

outputfile MOF-808-Zn.xplor expandedlog yes

Keywords for charge flipping #----perform fourier delta AUTO weakratio 0.0 Biso 0.0 randomseed AUTO searchsymmetry average # input data #----dataformat intensity phase fbegin # F^2obs phase h k 1 1 1 1 11879313.5 0 2 2 0 629488.32 0.5 3 1 1 3066529.82 0.5 2 2 2 10618552.17 0 4 0 0 4386523.93 0 3 3 1 1122709.78 0.5 4 2 2 60762.74 0.5 3 3 3 709850.06 0 5 1 1 394002.27 0 4 4 0 690374.87 0 5 3 1 192598.1 0.5

Structure Envelope Plots

UCSF Chimera^[22] was used to visualize these SE densities and their differences. For example, the difference between SE densities of MOF-808-Zn-4 and MOF-808 can hint at possible positions of zinc atoms. A scale factor defined by the ratio of the maxima of ρ (MOF-808-Zn-4) and ρ (MOF-808) is needed to calculate the difference to completely remove diffraction contributions from the framework. The result of difference envelope density visualization of MOF-808-Zn-4 and MOF-808, ρ_{Δ} , was shown in Figure S41.



Figure S41. Difference envelope density plot of MOF-808-Zn-4 and MOF-808.

6.3 Probe the Formation of HO-Zr⁴⁺-O-Zn²⁺ Active Sites



Figure S42. IR spectrum of MOF-808 after 250 °C heating for 20 h.



Figure S43. The ¹H-NMR spectrum of MOF-808 after 250 °C heating for 20 h treatment digested in $D_3PO_4/D_2O/DMSO-d_6$.



Figure S44. The ¹H-NMR spectrum of MOF-808-Zn-4-AR after a 100-h run of CO₂ hydrogenation, digested in $D_3PO_4/D_2O/DMSO-d_6$.



9.10 9.00 8.90 8.80 8.70 8.60 8.50 8.40 8.30 8.20 8.10 8.00 7.90 7.80 7.70

Figure S45. The ¹H-NMR spectrum of MOF-808-Zn-4 after a 20-h run under pure H₂, digested in $D_3PO_4/D_2O/DMSO-d_6$ (the red line). The green line corresponds to MOF-808-Zn-4 after a 100-h run under CO₂/H₂=1:3 for CO₂ hydrogenation, digested at the same conditions.



Figure S46. TGA-MS of MOF-808-HCO₃⁻ in the 35 – 700 °C range. The upper curve is the TGA curve of MOF-808-HCO₃⁻, and the one below is mass spectrometry trace tracking m/z= 44 and m/z= 18 (CO₂ and H₂O).



Figure S47. TGA-MS of MOF-808 in the 35 – 700 °C range. The upper curve is the TGA curve of MOF-808, and the one below is mass spectrometry trace tracking m/z= 44 and m/z = 18 (CO₂ and H₂O). as a control, there was no significant signal at about 250 °C.



Figure S48. H/D exchange profiles of UiO-66-Zn-4. The light orange line is mass = 2, the pink line is mass = 3, the light green is mass = 4.

Section S7. DFT Calculation

Computational Setup

All density functional theory (DFT) calculations were carried out using the Gaussian 09 program.^[23] The structures of chemical species were fully optimized by using the B3LYP functional.^[24-26] The 6-31G (d) basis set was used for C, H, and O, and LanL2DZ (Lanl-2-double-zeta) was used for Zn and Zr. The corresponding energy calculation was based on def2TZVP basis set to ensure accuracy. The catalyst structure was modeled using the Zr₆-SBU with Zn loaded on μ_3 -OH. Zr₆ cluster structure was modeled using the Zr₆ species from the single crystal structure of MOF-808 and was optimized before use in further calculation tasks. The transition states (TSs) of CO₂ hydrogenation (shown in Figure 10 of the manuscript) were found by using the TS method and further confirmed by the intrinsic reaction coordinate (IRC) method. The TSs were validated by imaginary vibrational frequencies along the reaction coordinates and their reasonable geometries bridging the reactants and products.

Optimization of the Zr₆(µ₃-O)₄(µ₃-OH)₄(BTC)₆(OH)₆(H₂O)₆ cluster

 $Zr_6(\mu_3-O)_4(\mu_3-OH)_4(BTC)_6(OH)_6(H_2O)_6$ cluster in MOF-808 was first optimized. The formic capped Zr_6 cluster was obtained from the MOF-808 crystal structure reported in the literature.^[1] The capping formate was removed and modified to the terminal water and hydroxyl groups, while the terminal carboxylate groups were protonated to ensure the charge balance of the cluster. The optimized Zr_6 structure was shown below.



Figure S49. Structure of the optimized $Zr_6(\mu_3-O)_4(\mu_3-OH)_4(BTC)_2(OH)_6$ cluster.

Construction of the MOF-808-Zn model

Three models with a Zn^{2+} ion bonded to a terminal μ_1 -OH group on Zr^{4+} , a μ_3 -O⁻ group, and carboxylate O were used as the initial trial structure for geometry optimization. The Zr_6 framework was frozen to ensure the stability of the support. Only the Zn and bonded O atoms were allowed to move. After the optimization, the three initial trial models converge to the same structure with Zn^{2+} coordinated to one μ_3 -O⁻, one μ_2 -O⁻ (bridging the Zn²⁺ and a Zr⁴⁺), and one terminal μ_1 -OH (on a Zr⁴⁺).



Figure S50. Structure of the optimized MOF-808-Zn cluster.



Figure S51. The scheme of active sites for three hydrogen dissociation and their activation energies.

Calculation of the energy profile

We calculated the energy profile of the CO_2 -hydrogenation-to-methanol process. During the calculation, all the Zr_6 -Zn cluster was frozen, and the reactant (CO_2 and H_2) and intermediate (HCO_2H et al.) were free to move. According to the experimental results, only the HCO_2H intermediate pathway was calculated. Figure 10 in the manuscript gave the corresponding energy levels and the intermediates in the process. The oxygenate intermediates, such as formate and formaldehyde, were adsorbed on the Zn center.



Figure S52. DFT-computed mechanism of CO_2 hydrogenation to methanol on MOF-808-Zn catalyst in the ball-and-stick structural model. Viewed from the sideway of the SBU.

The reaction pathway on pristine MOF-808

We have considered the H_2 activation process on the Zr site of MOF-808 and calculated the energy profile for this step. As shown in Figure S54, the barrier for the heterolytic splitting of H_2 on the Zr-OH site was 35.8 kcal/mol, which is much higher than that on the Zn-O-Zr center in MOF-808-Zn (17.2 kcal/mol). Meanwhile, the Zr-H generation from H_2 is thermodynamically unfavorable (28.6 kcal/mol), while the enthalpy of Zn-H formation is -1.9 kcal/mol. Thus, the formation of Zr-H is both kinetically and thermodynamically unfavorable compared to the formation of Zn-H.

Besides, we also considered the possibility that Zr-H formation through the hydride transfer pathway from Zn-H. We tried to obtain the energy barrier for this hydride transfer process (Figure S55). However, when we optimized the structure containing Zr-O-Zn site and Zr-H species, the hydride species on Zr-H automatically moved to the Zn center to form Zn-H.



Reaction Coordinate

Figure S53. Energy diagram for heterolytic H_2 splitting on MOF-808-Zn and pristine MOF-808, showing that H_2 activation on Zn-O-Zr center is both thermodynamically and kinetically favorable.



Figure S54. Optimization of the model containing Zr-H species and Zn vacancy. The atoms in ball-and-stick models: aqua blue: Zr, red: O, gray: C, white: H, bluish violet: Zn.

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