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Supplementary Information

Zirconium vs. Hafnium: A Comparative Study of Mesoporous MOF Stability

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Section S1. Materials and Characterization

1.1. Chemicals

All reagents and solvents used were of commercially available grade and used without any additional purification. Hafnium(IV) chloride (HfCl_4 , 98%), hafnium(IV) oxychloride hydrate ($\text{HfOCl}_2 \cdot x\text{H}_2\text{O}$, 99.99%) were purchased from Sigma Aldrich. Zirconium(IV) oxychloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 98%), zirconium(IV) chloride (ZrCl_4 , 98%), terephthalic acid (>99%), benzoic acid (99.5%), 1,3,5-benzenetricarboxylic acid (98%) were purchased from Acros Organics. Isophthalic acid (99.94%), 4,4',4'',4'''-(Pyrene-1,3,6,8-tetrayl)tetrabenzoic acid (H_4TBAPy , 97%) were purchased from BLDpharm. Formic acid (>99%), hydrochloric acid (37%), N,N-dimethylformamide (DMF, >99.9%), methanol (MeOH, >99.8%), ethanol (EtOH, 99.5%, <0.2% H₂O), acetone (99.8%) were purchased from LABKEM.

1.2. Characterization

1.2.1. Powder X-ray diffraction (PXRD)

X-ray powder diffraction patterns were obtained using a Panalytical X'pert PRO. The instrument operated at 40 kV and 40 mA in theta-theta configuration, employing a secondary monochromator with Cu K- α radiation ($\lambda = 1.5418 \text{ \AA}$) and a Pixel solid-state detector with an active length in $2\theta - 3.347^\circ$. Data collection occurred over a range of 2 to $75^\circ 2\theta$ with a step size of 0.026° and a time per step of 700s at RT (total time 2h). To ensure consistent sample illumination, 1° fixed soller and divergence slits were employed, maintaining a constant volume of sample illumination.

1.2.2. Temperature-dependent Powder X-ray Diffraction (TD-PXRD)

Temperature dependent XRD diffractograms were obtained using a Bruker D8 Advance diffractometer operating at 30 kV and 20 mA, equipped with a Cu tube ($\lambda = 1.5418 \text{ \AA}$), a Vantec-1 PSD detector, and an Anton Parr HTK2000 high-temperature furnace. Powder X-ray diffraction (XRD) patterns were recorded in 2θ steps of 0.033° in the $4 \leq 2\theta \leq 38$ range, counting for 1s per step (total time for each temperature 20min). Data sets were recorded from 30 to 550 °C with the step 15°C at 0.0166 °C s⁻¹ heating rate.

1.2.3. Thermogravimetric analysis (TGA)

TGA was performed with a simultaneous differential scanning calorimetry (DSC)/TGA thermal analysis instrument Mettler-Toledo TGA/SDTA 851e thermobalance under a 50 cm³ min⁻¹ flow of synthetic air, and a heating rate 1°C min⁻¹.

1.2.4. Scanning electron microscopy (SEM)

The surface morphology of the samples was examined using a Hitachi S-4800 field emission scanning electron microscope (FEG-SEM) operating at an accelerating voltage of 5 kV. Prior to imaging, the samples were coated with a 10 nm layer of gold using an Emitech K550x ion sputter to enhance conductivity and minimize charging effects during imaging.

1.2.5. Energy-dispersive X-ray spectroscopy (EDX)

The morphological characterization and elemental composition of your samples were analyzed by SEM-EDS using a JEOL JSM-6400 equipped with an Oxford Instrument X-sight Serie Si(Li) pentaFET detector. The

observation and measurement conditions were high vacuum, a voltage of 20 kV, a current of 1000 pA and a working distance of 15 mm. The sample was mounted on an aluminium sample holder with graphite tape (electrically conductive) and coated with gold.

Section S2. Synthesis

2.1. Synthesis of Zr UiO-66

ZrCl₄ (886 mg, 3.726 mmol), terephthalic acid (623 mg, 3.713 mmol) were weighted into a 250 mL GL bottle. Then, DMF (100 mL) and formic acid (14 mL) were added and the mixture was sonicated for 20 min until all components fully dissolved. The transparent solution was put into the oven and gradually heated to 120 °C and stored for 24 h. The white powder recovered at 10 000 rpm for 10 min. Washed 3 times with DMF over 2 days. Washed with MeOH once per day over 3 days. Evaporated under high vacuum overnight. Yield: 976 mg (95% calculated based on the linker).

2.2. Synthesis of Hf UiO-66

HfCl₄ (886 mg, 3.726 mmol), terephthalic acid (623 mg, 3.713 mmol) were weighted into a 250 mL GL bottle. Then, DMF (100 mL) and formic acid (14 mL) were added and the mixture was sonicated 20 min until uniform cloudy suspension formed. The suspension was put into the oven and gradually heated to 120 °C and stored for 24 h. The white powder recovered at 10 000 rpm for 10 min. Washed 3 times with DMF over 2 days. Washed with MeOH once per day over 3 days. Yield: 1.252 g (93% calculated based on the linker).

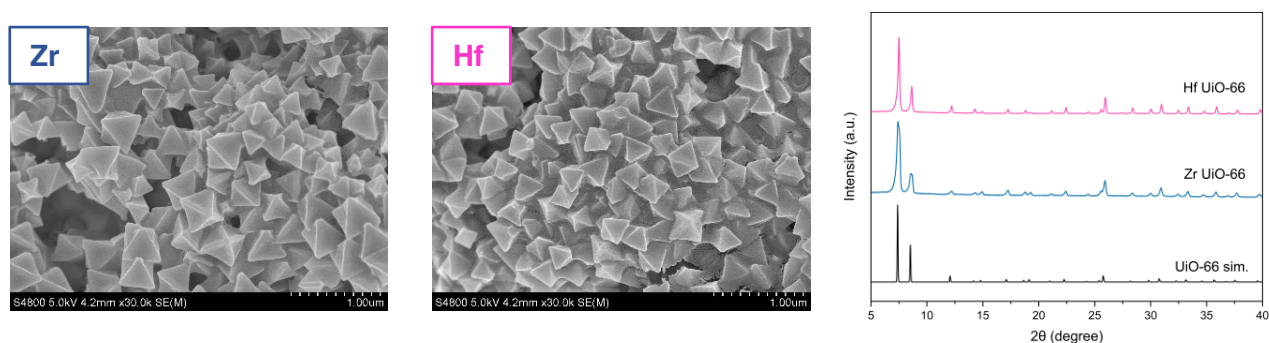


Figure S1. SEM images and PXRD patterns of Zr and Hf UiO-66.

2.3. Synthesis of Zr MOF-808

The synthesis was modified from ref. [1]. ZrCl₄ (1.213 g, 5.1 mmol), 1,3,5-benzenetricarboxylic acid (1.072 g, 5 mmol) were weighted into a 250 mL GL bottle. Formic acid (20 mL) and H₂O (30 mL) were added and all components were mixed by sonication for 20 min. The suspension was put into the oven and gradually heated to 100 °C and stored for 24 h. The white powder recovered at 10 000 rpm for 10 min. Washed 3 times with DMF over 2 days. Washed with MeOH once per day over 3 days. Evaporated under high vacuum overnight. Yield: 1.402 g (>99% calculated based on metal salt).

2.4. Synthesis of Hf MOF-808

The synthesis was modified from ref. [1]. HfCl₄ (1.667 g, 5.1 mmol), 1,3,5-benzenetricarboxylic acid (1.072 g, 5 mmol) were weighted into a 250 mL GL bottle. Formic acid (20 mL) and H₂O (30 mL) and all components were mixed by sonication for 20 min. The suspension was put into the oven and gradually heated to 100 °C and stored for 24 h. The white powder recovered at 10 000 rpm for 10 min. Washed 3 times with DMF over 2 days. Washed with MeOH once per day over 3 days. Evaporated under high vacuum overnight. Yield: 1.704 g (>99% calculated based on metal salt).

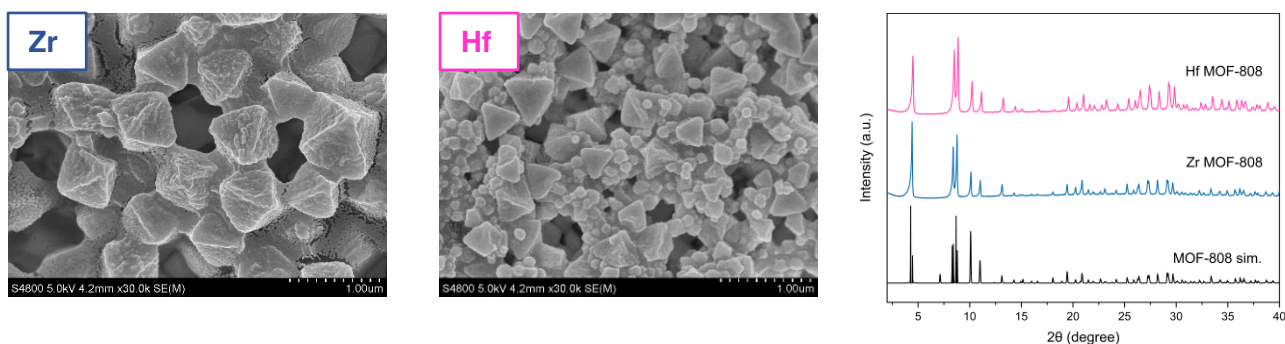


Figure S2. SEM images and PXRD patterns of Zr and Hf MOF-808.

2.5. Synthesis of Zr NU-1000

The synthesis was reproduced from ref. [2]. $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (1.94 g, 6 mmol), benzoic acid (54 g) and DMF (120 mL) were weighted into a 500 mL GL bottle and sonicated until reagents fully dissolved. The solution was heated at 100 °C for 1h. H_4TBAPy (800 mg, 1.17 mmol) was weighted into a 100 mL GL bottle and 40 mL DMF was added. Then, the bottle was placed in the oven at 100 °C for 1h. Further, the linker solution was poured into the metal salt solution. The reaction mixture was placed into an oven pre-heated to 120 °C for 24 h. After the product cooled down, the yellow powder was recovered at 20 000 rpm 10 min. Washed 3 times in DMF over 4 hours. Transferred into the 250 mL GL bottle, added 130 mL DMF and 4 mL of 12M $\text{HCl}_{\text{conc.}}$. Heated at 100 °C for 18h. Washed 3 times with DMF over 2 days. Washed 3 times with EtOH over 2 days. Evaporated under high vacuum overnight. Yield: 915 mg (72% calculated based on the linker).

2.6. Synthesis of Hf NU-1000

The synthesis was modified from ref. [3]. $\text{HfOCl}_2 \cdot 8\text{H}_2\text{O}$ (500 mg, 1.22 mmol), benzoic acid (10.80 g, 88.4 mmol), and 32 mL of DMF were added to a 100-mL media bottle and the solids were dissolved via sonication. The resulting cloudy solution was incubated in an oven at 80 °C for 1 h, then removed from the oven and cooled to room temperature. H_4TBAPy (160 mg, 0.234 mmol) was then added to the reaction solution and the mixture was sonicated for 10 min to yield a yellow suspension. The reaction mixture was placed in a 100 °C oven for 24 h, during which time yellow powder precipitated from the solution. After 24 h, the reaction was removed from the oven and cooled to room temperature. The solid was isolated by centrifugation, washed three times with 25 mL of DMF through repeated centrifugation and redispersion, and then soaked in 40 mL of DMF for 8 h. After 8 h, the yellow solid was isolated by centrifugation and re-suspended in 25 mL of DMF, transferred back into a 100-mL media bottle and 1.33 mL of 12M HCl were added. The reaction mixture was incubated in a 100 °C oven for 18 h, then removed from the oven and cooled to room temperature. The solid was isolated by centrifugation, washed three times with 25 mL of DMF, washed three times with 40 mL of acetone, and then soaked in 40 mL of acetone for 18 h. The solid was activated at 120 °C under vacuum for 18 h. Yield: 210 mg (66% calculated based on the linker).

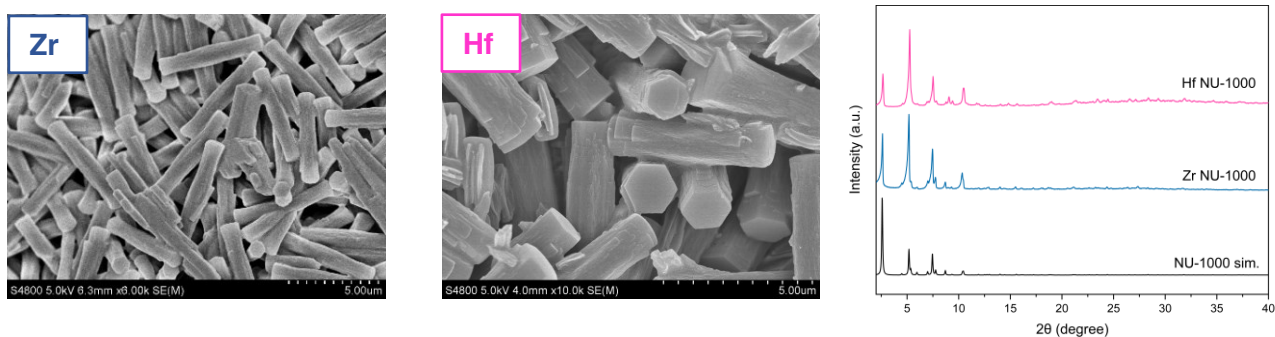


Figure S3. SEM images and PXRD patterns of Zr and Hf NU-1000.

2.7. Synthesis of Zr MIP-206

The synthesis was reproduced from ref. [4]. ZrCl_4 (10.4 g, 44.4 mmol), isophthalic acid (5 g, 30 mmol) and formic acid (30 mL) were weighted into a 120 mL autoclave. Magnetic stirring bar was added and components were stirred at 600 rpm for 10 min to disperse the components uniformly. Then the stirring bar was taken out. The suspension was put into the oven and gradually heated to 180 °C and stored for 24 h. After the autoclave cooled down, the white suspension was recovered at 10 000 rpm 10 min. The product was washed with acetone once per day over 7 days. Evaporated under high vacuum overnight. Yield: 10.2 g (94% calculated based on metal salt).

Smaller scale Zr MIP-206 synthesis: ZrCl_4 (5.2 g, 22.22 mmol), isophthalic acid (2.5 g, 15 mmol) and formic acid (15 mL) were weighted into a 100 mL autoclave. Magnetic stirring bar was added and components were stirred at 600 rpm for 10 min to disperse the components uniformly. Then the stirring bar was taken out. The suspension was put into the oven and gradually heated to 180 °C and stored for 24 h. After the autoclave cooled down, the white suspension was recovered at 10 000 rpm 10 min. Washed with acetone once per day over 7 days. Evaporated under high vacuum overnight.

2.8. Synthesis of Hf MIP-206

The synthesis was modified from ref. [3]. HfCl_4 (14.511 g, 44.4 mmol), isophthalic acid (5 g, 30 mmol) and formic acid (30 mL) were weighted into a 120 mL autoclave. Magnetic stirring bar was added and components were stirred at 600 rpm for 10 min to disperse the components uniformly. Then the stirring bar was taken out. The suspension was put into the oven and gradually heated to 180 °C and stored for 24 h. After the autoclave cooled down, the white suspension was recovered at 10 000 rpm 10 min. Washed with acetone once per day over 7 days. Evaporated under high vacuum overnight. Yield: 14.3 g (97% calculated based on metal salt).

Smaller scale Hf MIP-206 synthesis: HfCl_4 (7.256 g, 22.22 mmol), isophthalic acid (2.5 g, 15 mmol) and formic acid (15 mL) were weighted into a 100 mL autoclave. Magnetic stirring bar was added and components were stirred at 600 rpm for 10 min to disperse the components uniformly. Then the stirring bar was taken out. The suspension was put into the oven and gradually heated to 180 °C and stored for 24 h. After the autoclave cooled down, the white suspension was recovered at 10 000 rpm 10 min. Washed with acetone once per day over 7 days. Evaporated under high vacuum overnight.

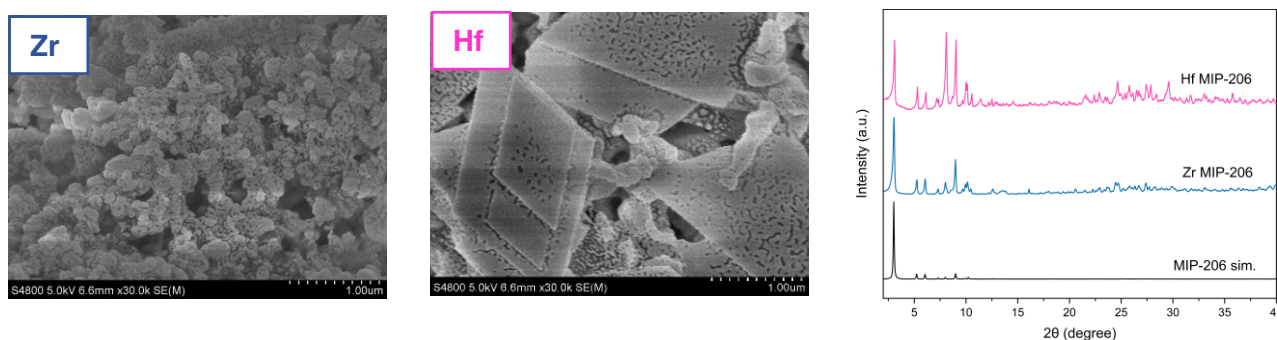
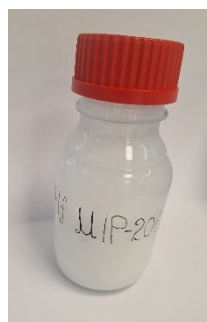


Figure S4. SEM images and PXRD patterns of Zr and Hf MIP-206. The PXRD patterns of Zr and Hf MIP-206 vary slightly depending on the guest molecules present in the pores. When the samples were washed in DMF, or DMSO, additional peaks were observed in the range of 20-35°.

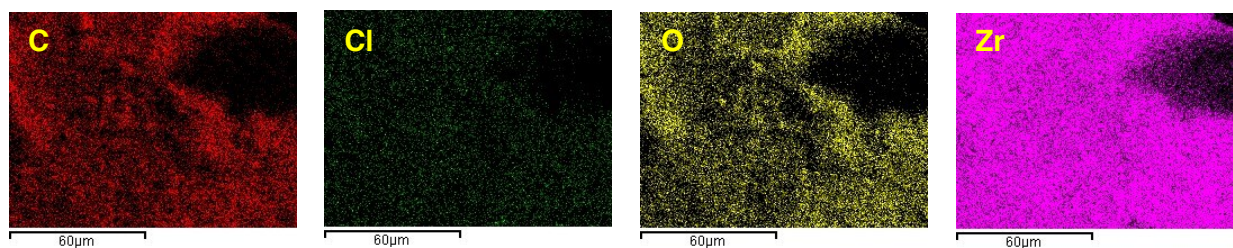
2.9. Yield of MOF synthesis and a representative scale of the reaction

MOF	Mass	Yield
Zr UiO-66	0.976 g	95%
Hf UiO-66	1.252 g	93%
Zr MOF-808	1.402 g	>99%
Hf MOF-808	1.704 g	>99%
Zr NU-1000	0.915 g	72%
Hf NU-1000	0.500 g	63%
Zr MIP-206	10.2 g	94%
Hf MIP-206	14.3 g	97%

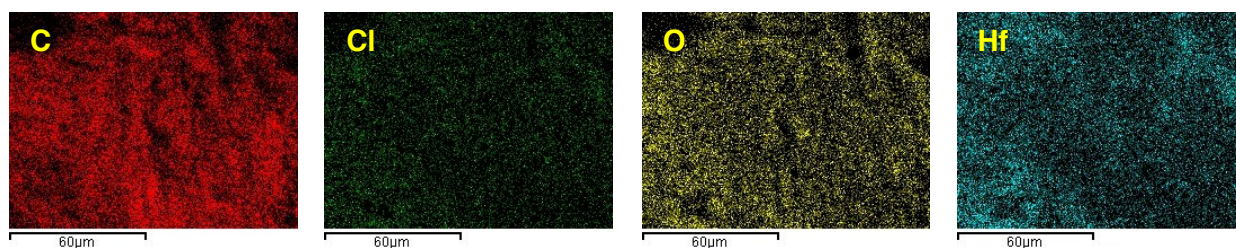


Section S3. Energy-dispersive X-ray spectroscopy

Zr UiO-66



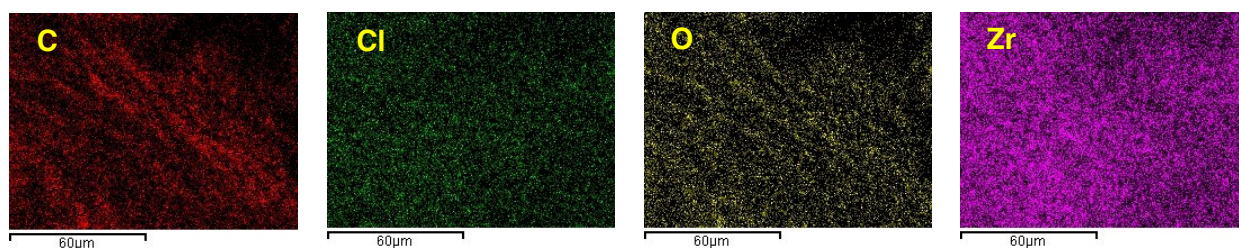
Hf UiO-66



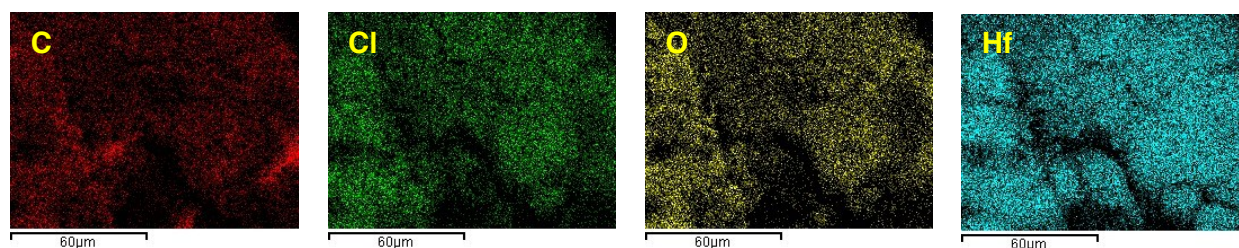
Element	C	O	Cl	Hf
Zr UiO-66, weight%	48.39	33.75	0.15	17.71
Hf UiO-66, weight%	50.95	30.36	0.48	18.21

Figure S5. EDX analysis of Zr and Hf UiO-66.

Zr MOF-808



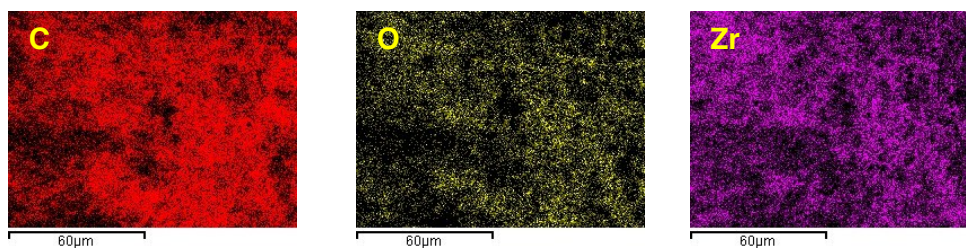
Hf MOF-808



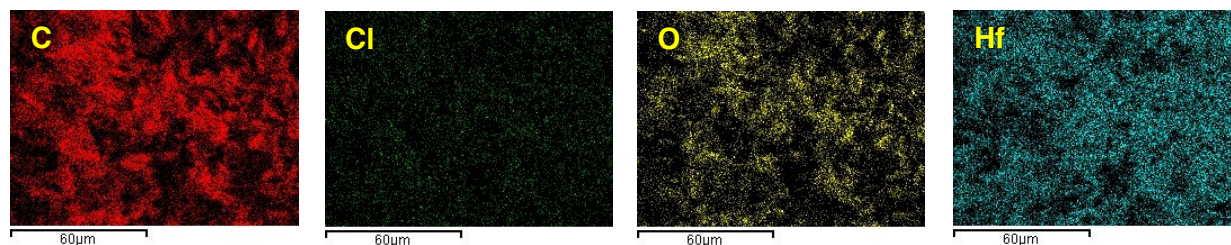
Element	C	O	Cl	Hf
Zr MOF-808, weight%	54.35	33.07	1.62	10.96
Hf MOF-808, weight%	30.79	24.68	2.36	42.17

Figure S6. EDX analysis of Zr and Hf MOF-808.

Zr NU-1000



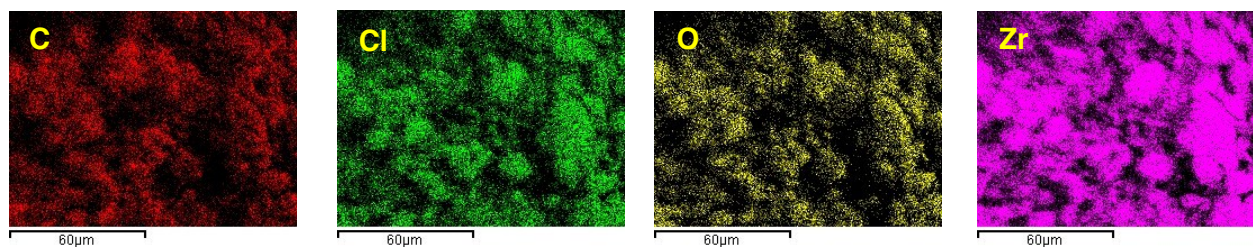
Hf NU-1000



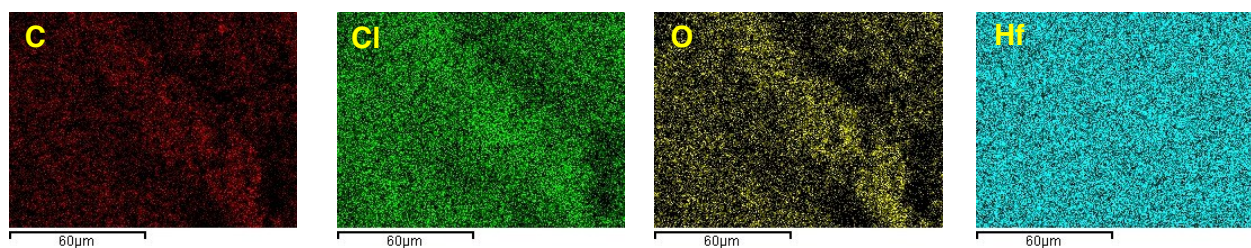
Element	C	O	Cl	Zr
Zr NU-1000, weight%	68.71	27.09	0	4.2
Hf NU-1000, weight%	51.49	23.11	0.06	25.34

Figure S7. EDX analysis of Zr and Hf NU-1000.

Zr MIP-206



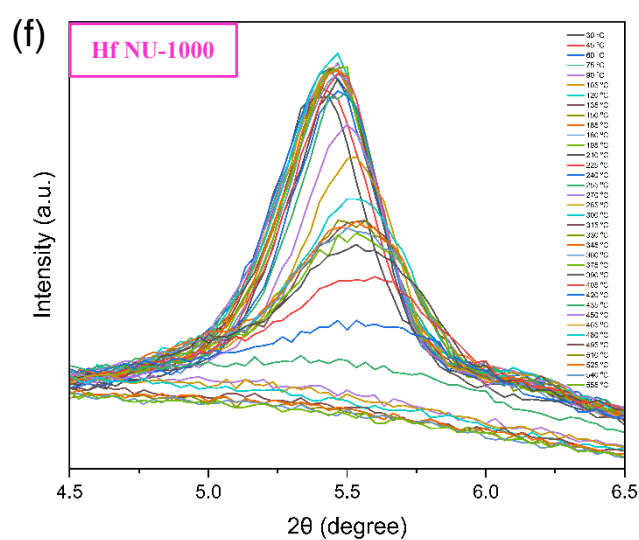
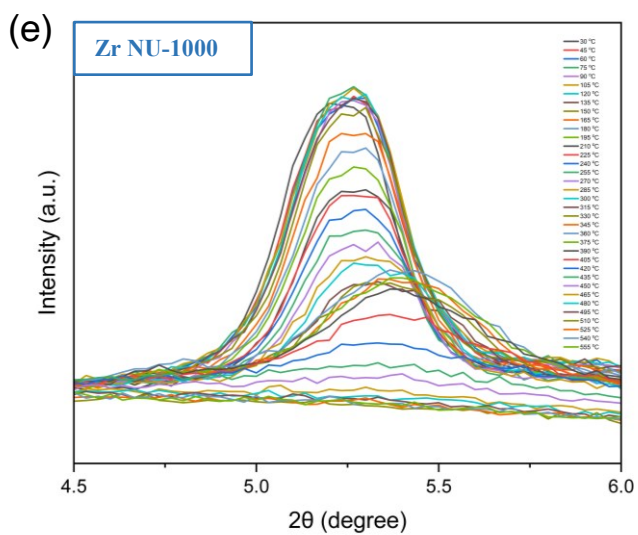
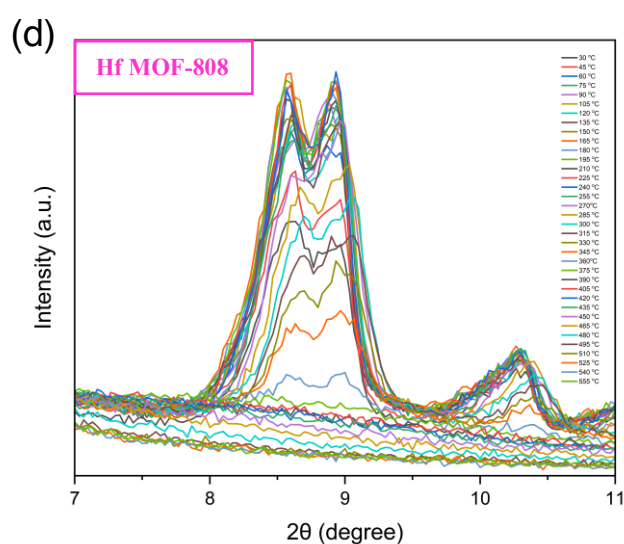
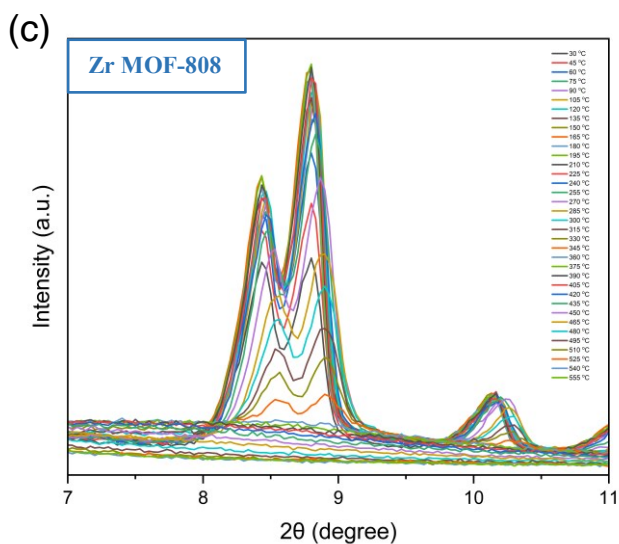
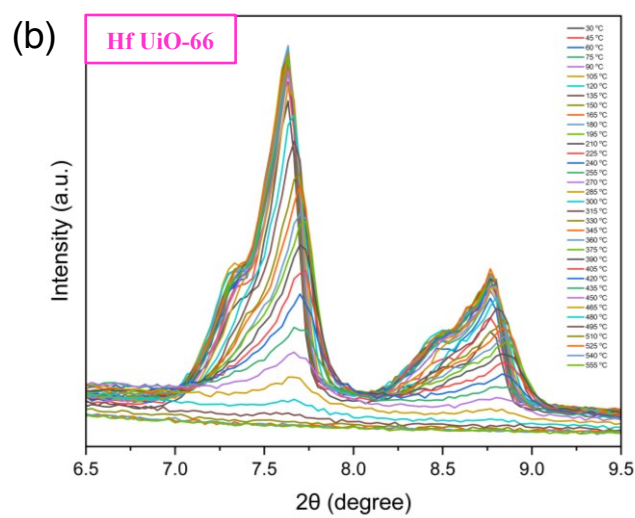
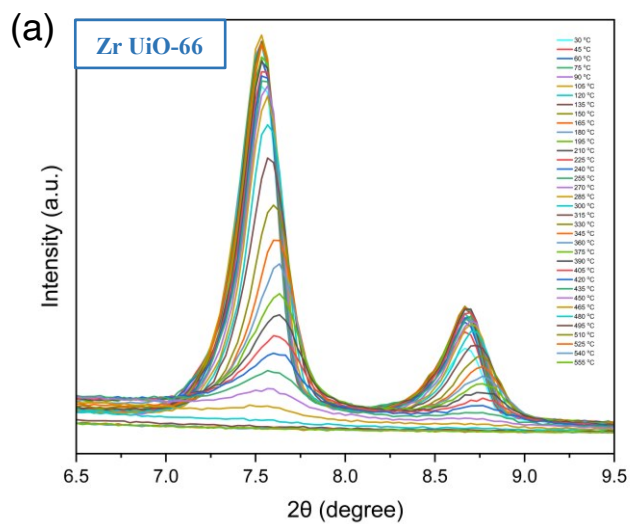
Hf MIP-206



Element	C	O	Cl	Zr
Zr MIP-206, weight%	50.75	30.26	3.04	15.95
Hf MIP-206, weight%	23.56	20.67	4.26	51.51

Figure S8. EDX analysis of Zr and Hf MIP-206.

Section S4. Temperature-dependent Powder X-ray Diffractograms



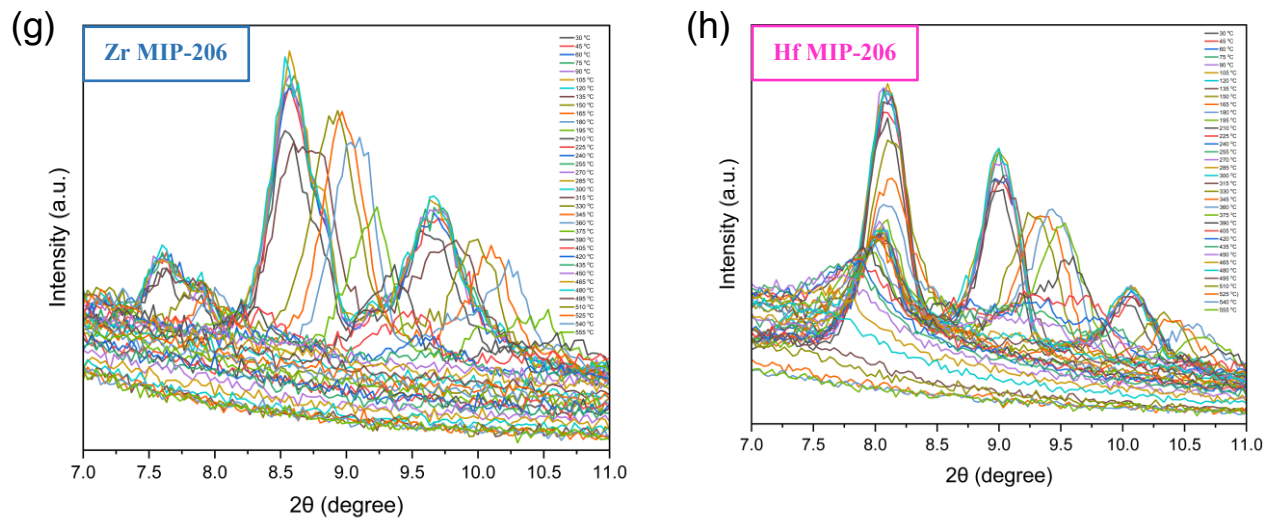
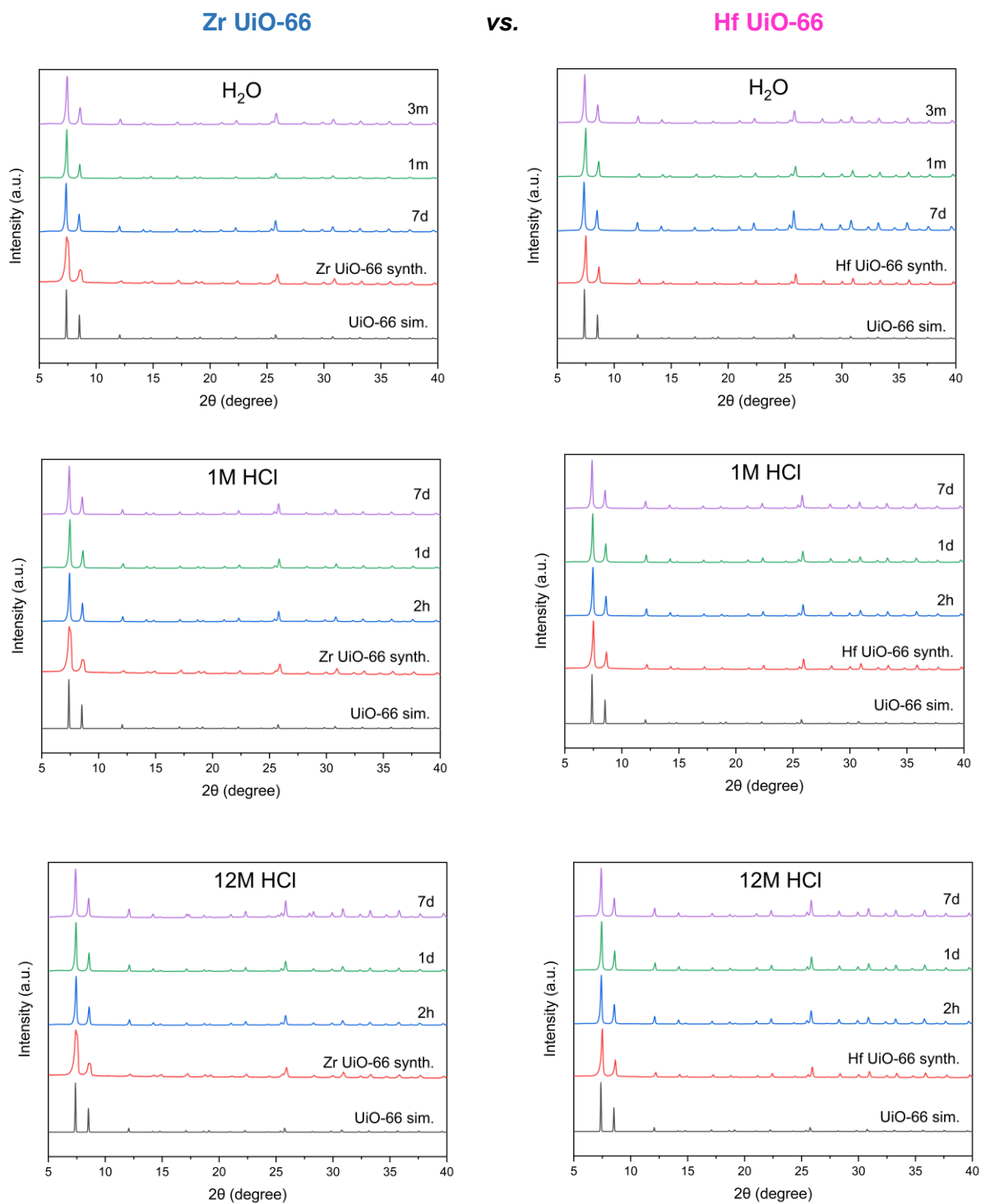


Figure S9. Temperature-dependent diffractograms of (a) Zr UiO-66; (b) Hf UiO-66; (c) Zr MOF-808; (d) Hf MOF-808; (e) Zr NU-1000; (f) Hf NU-1000; (g) Zr MIP-206; (h) Hf MIP-206.

Section S5. Chemical Stability

The procedure to measure chemical stability was as follows: 100 mg of MOF was weighed into a 16 mL vial. The MOF was then immersed in 10 mL of various solutions: 12M HCl (pH ~ -1.1), 1M HCl (pH ~ 1), 1 μ M KOH (pH ~ 8), 1M KOH (pH ~ 14), or H₂O (pH ~ 7). The suspension was briefly sonicated to uniformly disperse the particles and then left undisturbed at room temperature. At specified time intervals (2 hours, 1 day, 7 days, 1 month, 3 months), 2 mL of the suspension was extracted, centrifuged at 15 000 rpm for 10 minutes, and washed five times with water followed by ethanol. Finally, the powder was evaporated under dynamic high vacuum (10⁻⁵ bar) for 2 hours and characterized by PXRD.

5.1. Chemical stability of Zr vs. Hf UiO-66



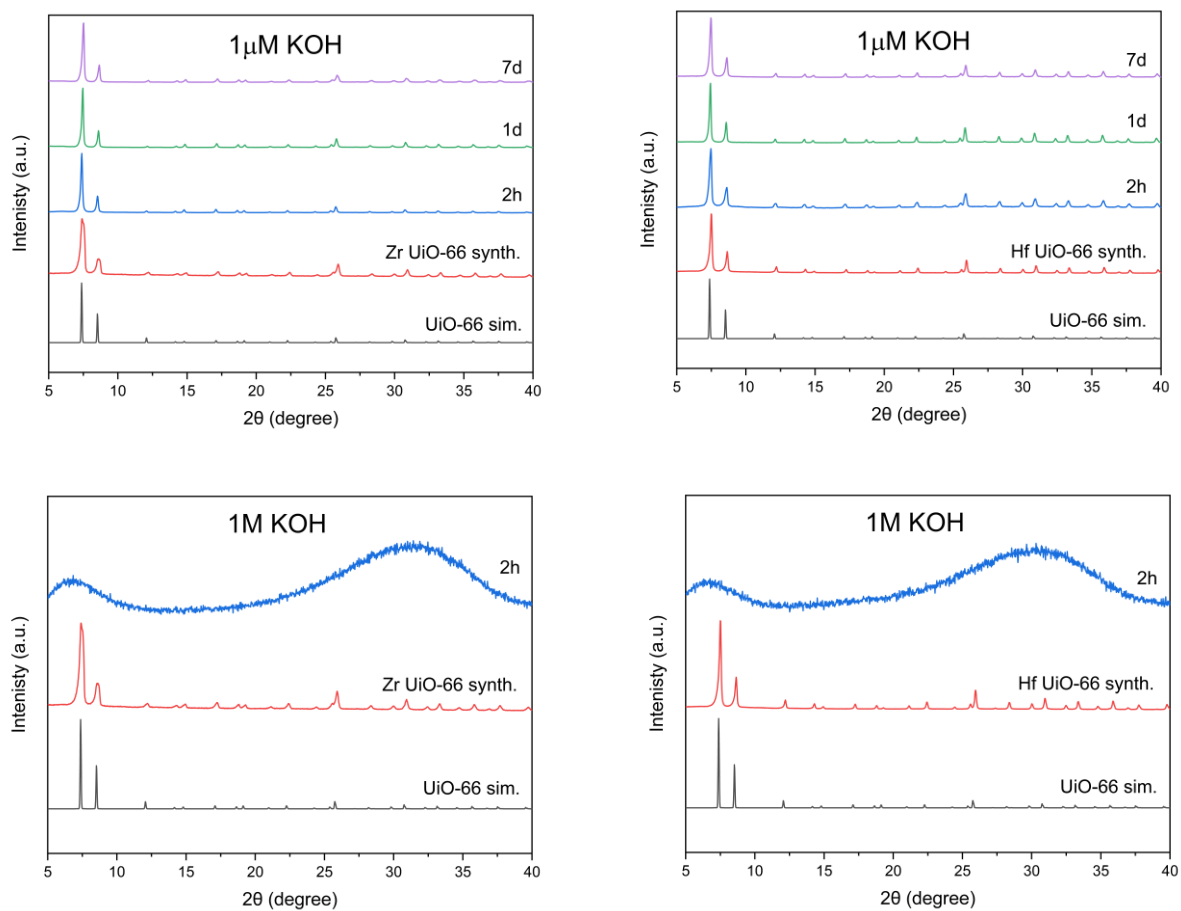


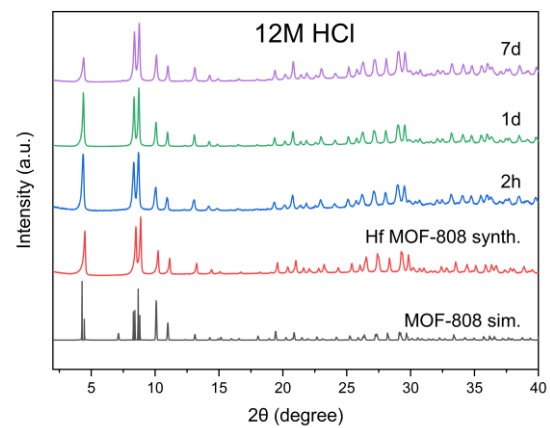
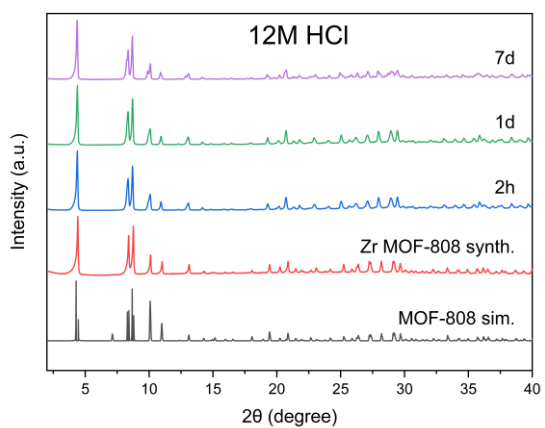
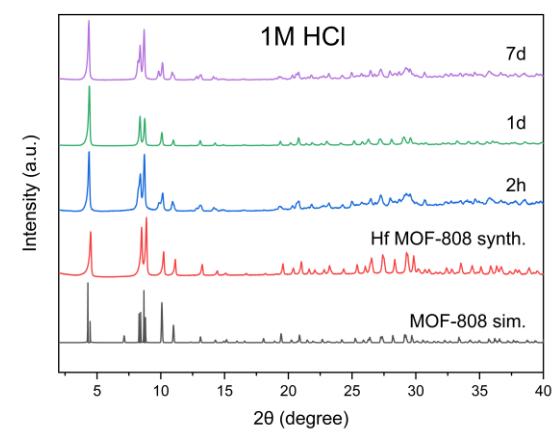
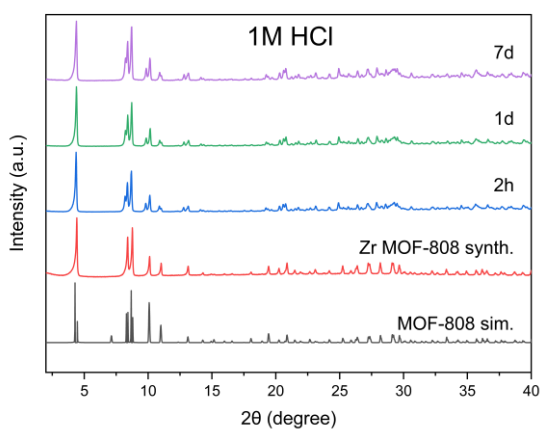
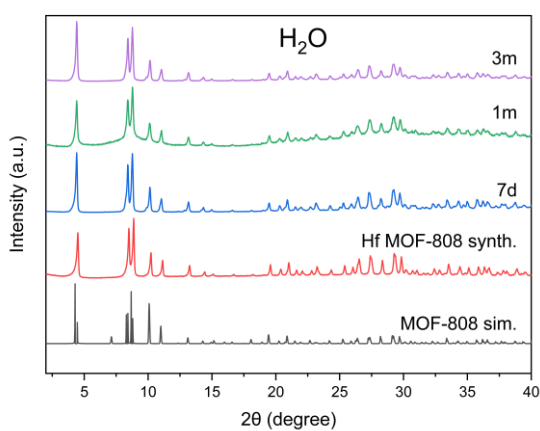
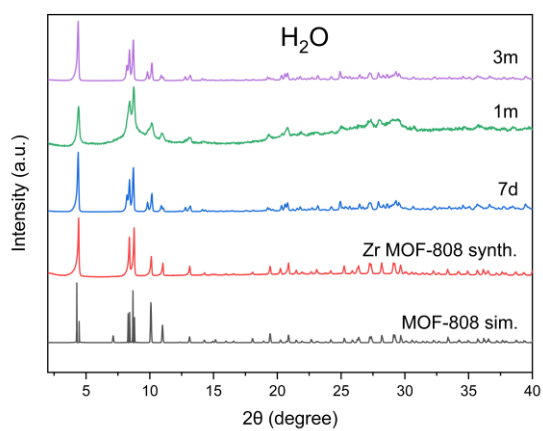
Figure S10. Chemical stability of Zr vs. Hf UiO-66 in H_2O (7 days, 1 month, 3 months), and in 1M HCl, 12M HCl, $1\ \mu\text{M}$ KOH, 1M KOH (2 hours, 1 day, 7 days).

5.2. Chemical stability of Zr vs. Hf MOF-808

Zr MOF-808

vs.

Hf MOF-808



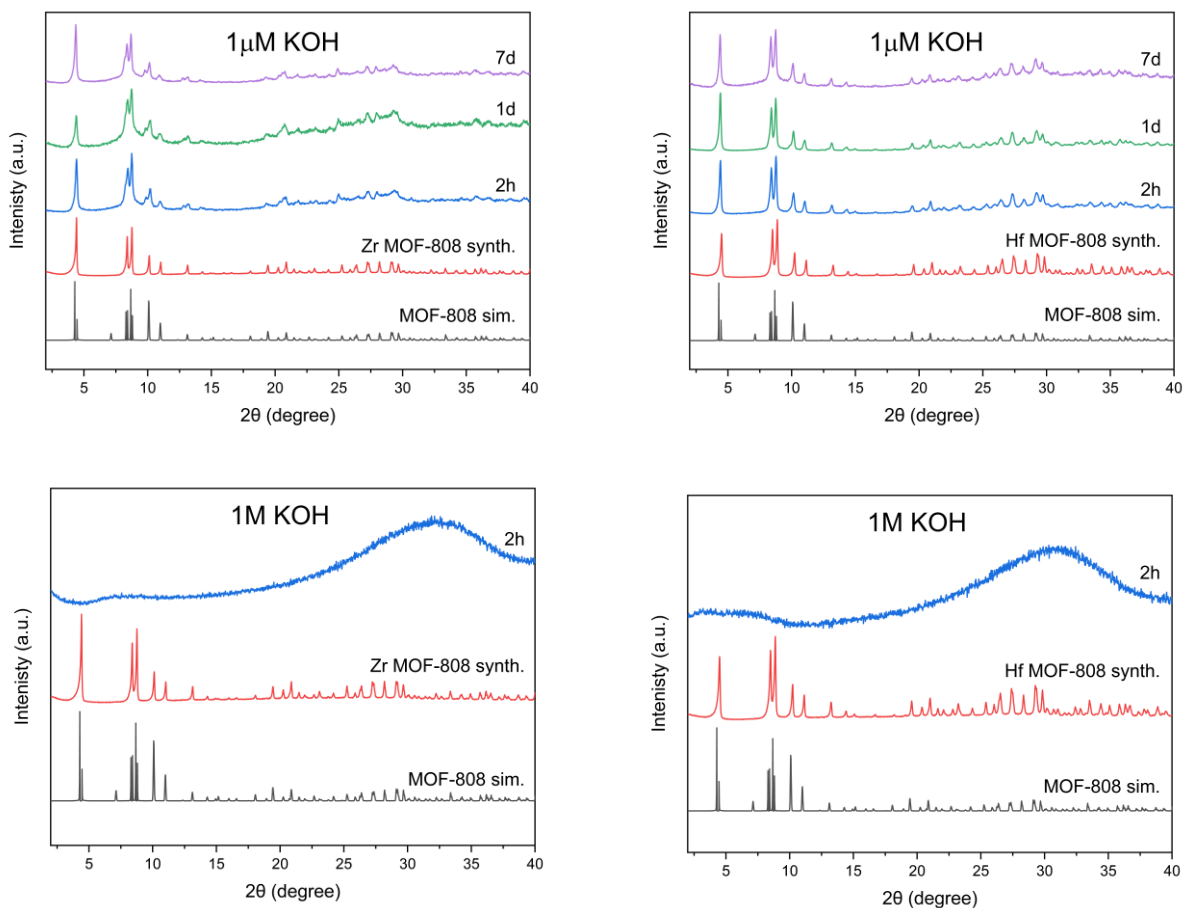


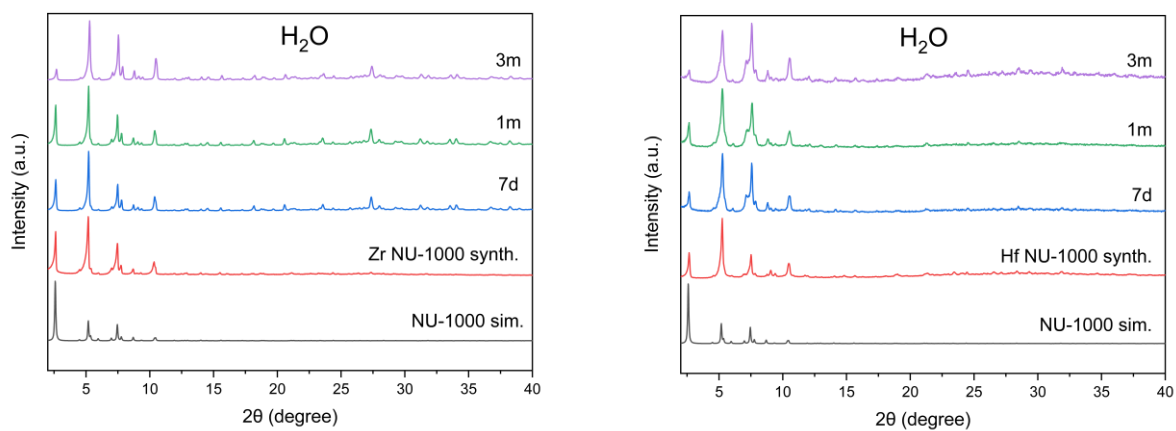
Figure S11. Chemical stability of Zr vs. Hf MOF-808 in H₂O (7 days, 1 month, 3 months), and in 1M HCl, 12M HCl, 1μM KOH, 1M KOH (2 hours, 1 day, 7 days).

5.3. Chemical stability of Zr vs. Hf NU-1000

Zr NU-1000

vs.

Hf NU-1000



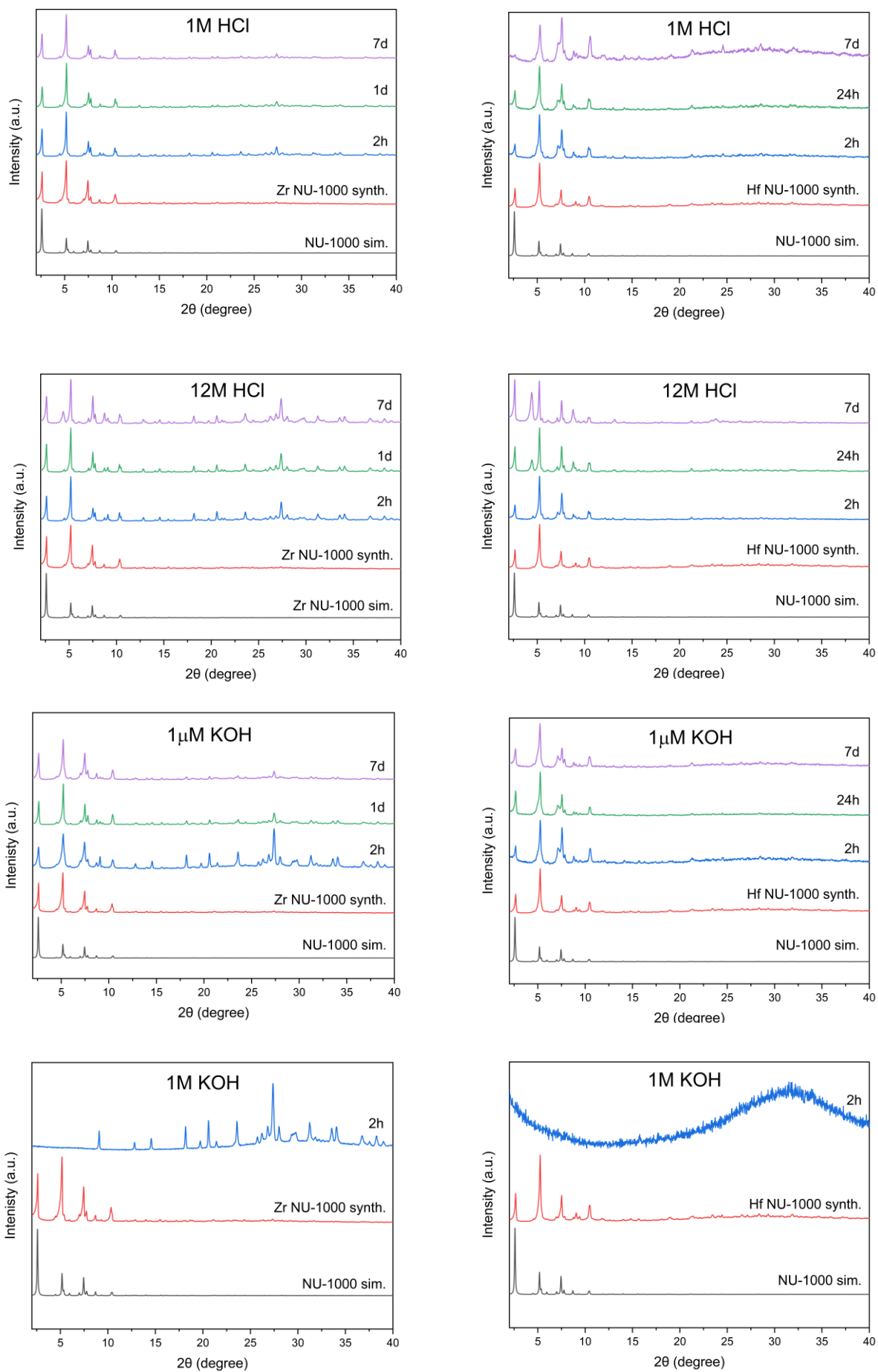


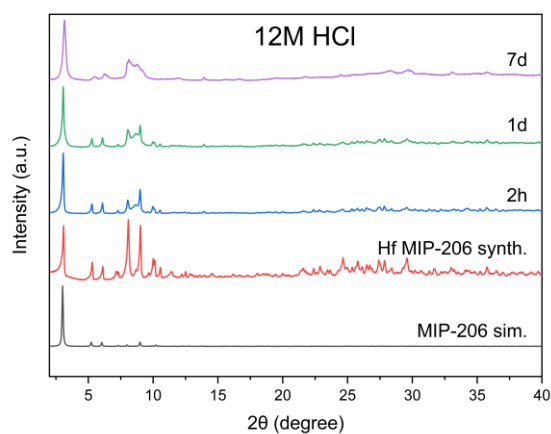
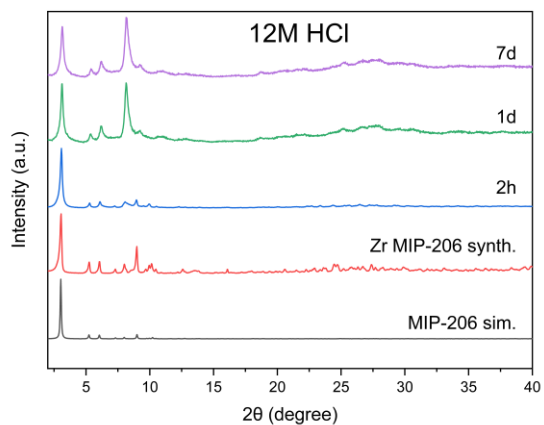
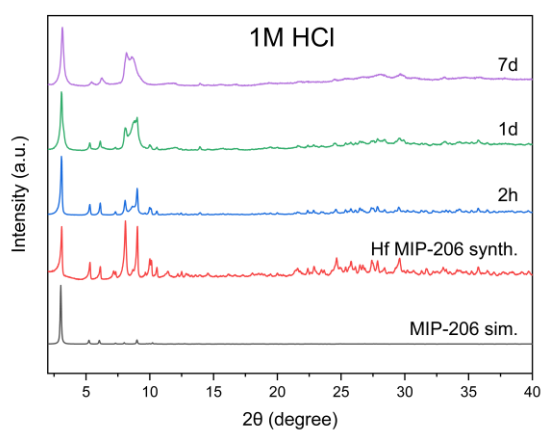
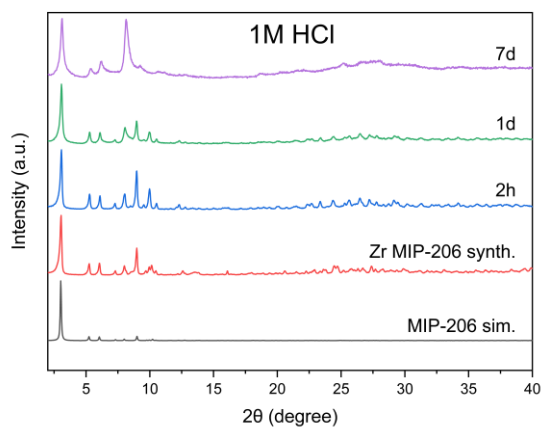
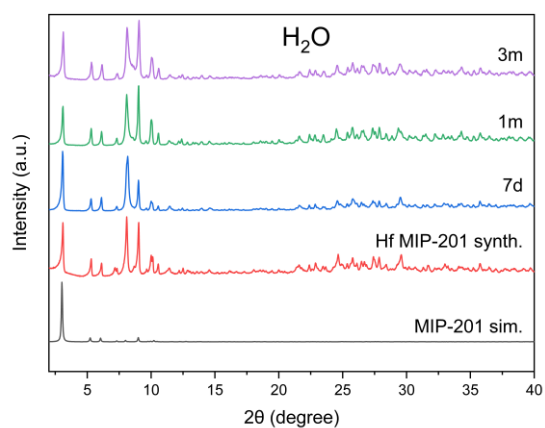
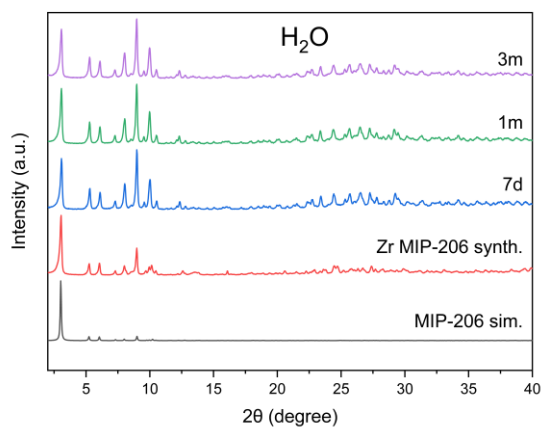
Figure S12. Chemical stability of Zr vs. Hf NU-1000 in H₂O (7 days, 1 month, 3 months), and in 1M HCl, 12M HCl, 1μM KOH, 1M KOH (2 hours, 1 day, 7 days).

5.4. Chemical stability of Zr vs. Hf MIP-206

Zr MIP-206

vs.

Hf MIP-206



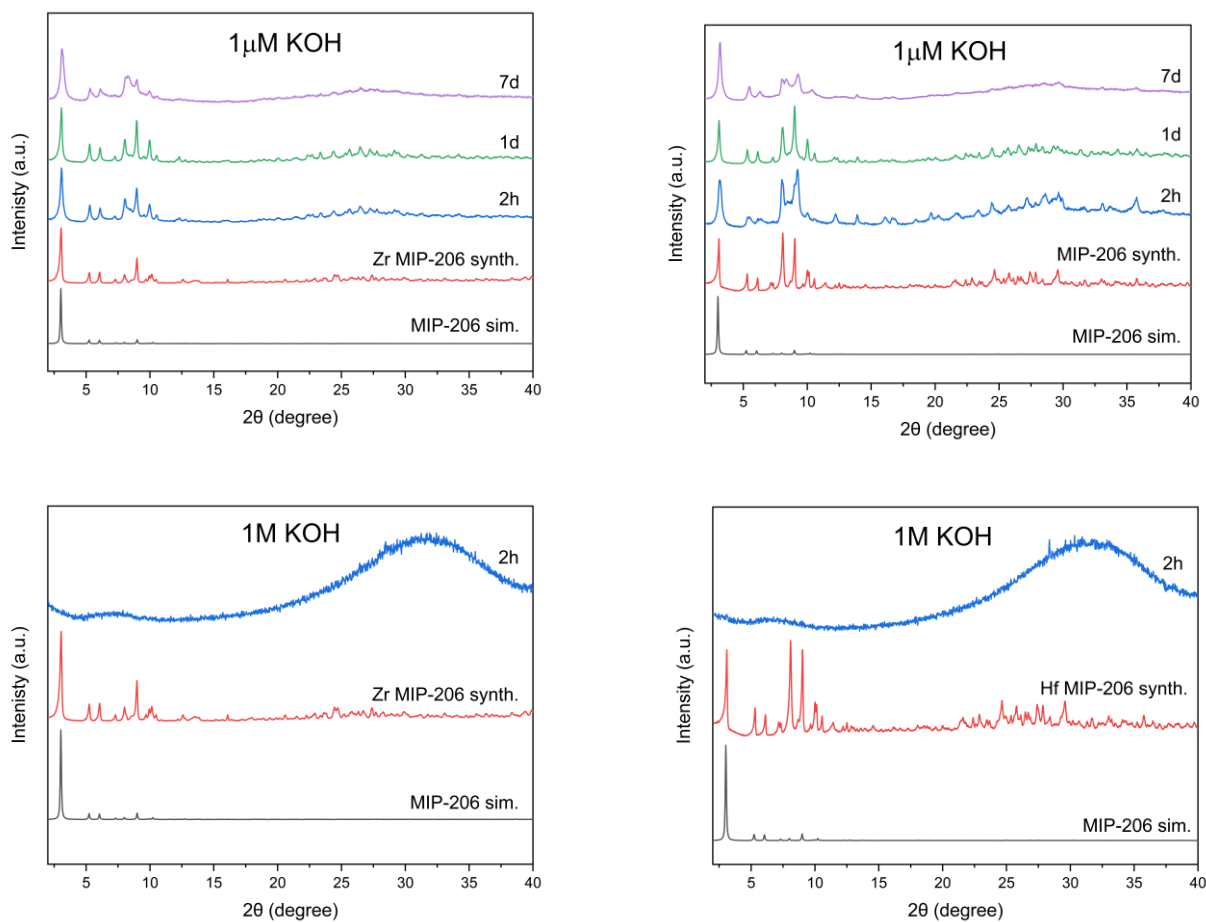


Figure S13. Chemical stability of Zr vs. Hf MIP-206 in H₂O (7 days, 1 month, 3 months), and in 1M HCl, 12M HCl, 1 μM KOH, 1M KOH (2 hours, 1 day, 7 days).

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