Supplementary Information

Small Molecules, Big Effects: Tuning Adsorption and Catalytic

Properties of Metal-Organic Frameworks

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1. Chemicals and Instruments

$ZrOCl_2 \cdot 8H_2O$, 1,3,5-benzenetricarboxylic acid (H_3BTC), formic acid (FA), acetic acid (AA), and trifluoroacetic acid (TFA) were purchased from Sigma-Aldrich. The linear polyethylenimine (MW 2500) was bought from Polysciences, Inc (Lot number of 708172) and used without any modification. Other chemicals were purchased from commercial sources and used without any further purification.

Powder X-ray diffraction (PXRD) data were collected at room temperature on a STOE-STADI-P powder diffractometer equipped with an asymmetric curved Germanium monochromator ($CuK\alpha1$ radiation, λ = 1.54056 Å) and one-dimensional silicon strip detector (MYTHEN2 1K from DECTRIS). The line focused Cu X-ray tube was operated at 40 kV and 40 mA. The powder was packed in a 3 metallic mask and sandwiched between two polyimide layers of tape. Intensity data from 2 to 40 degrees two theta were collected for 8 mins. The instrument was calibrated against a NIST Silicon standard (640d) before the measurement.

N_2 adsorption and desorption isotherms on activated materials were measured at Northwestern University on a TriStar (Micromeritics) instrument at 77 K. Activations of MOFs were performed under a dynamic vacuum for 12 h on SmartVapPrep (SVP) from Micromertics at 120 °C (heating rate: 2 °C /min).About 50 mg of the sample was used in each measurement.

Water isotherms were measured on a Micromeritics 3Flex. Before the water adsorption measurements, water (analyte) was flash-frozen under liquid nitrogen and then evacuated under a dynamic vacuum at least 3 times to remove any gases in the water reservoir. P_0 reading was compared to P_0 of water at room temperature before measurements. The measurement temperature was controlled with a Micromeritics temperature controller (Isocontroller). Activation of MOFs was performed under a dynamic vacuum for 12 h on SmartVapPrep (SVP) from Micromertics at 120 °C (heating rate: 2 °C /min).About 30 mg of sample was used in each measurement.

All ^{1}H NMR spectra were collected on a Bruker Avance III 500 MHz system equipped with DCH CryoProbe and automated with a BACS-60 autosampler. [19]F spectra were collected on a fully automated 400 MHz Bruker Avance III HD system equipped with SampleXpress autosampler.

2. General Procedures

2.1 Activation of samples:

The as-synthesized samples were immersed in water (20 mL water for small scale and 120 mL water for large scale) and water was replaced for six times over the course of 24 h. Then the resulting powder was washed with ethanol (15 mL water for small scale and 60 mL water for large scale) three times and dried in vacuum oven at 80 °C for 1 h. The activation of MOFs was for sorption analysis was performed under a dynamic vacuum for 12 h on SmartVapPrep (SVP) from Micromertics at 120 °C (heating rate: 2 °C /min).

2.2 Digestion of samples for NMR:

For ^{1}H NMR, as-synthesized samples were digested with D_3PO_4/DMSO-d6 or K_3PO_4 D_2O solution. For ^{19}F NMR, 5 µL of 1 vol% 1-bromo-3,5-bis(trifluoromethyl)benzene in the DMSO-d6 solution was added and used as the internal standard to calculate the amount of the TFA modulator in the MOF-808.

2.3 Liquid-state catalytic hydrolysis of DMNP:

The liquid phase hydrolysis of DMNP was carried out at room temperature and monitored by in situ ^{31}P NMR spectroscopy. First, the MOF-808-X catalyst (0.375 µmol, 1.5 mol%), N-ethylmorpholine (50 µL), DI water (0.9 mL), and D_2O (0.1 mL) were put into a 1.5-dram vial and sonicated for 5 mins to form a uniform dispersion. Then, DMNP (4 µL, 25 µmol) was added into the MOF dispersion and the vial was shaken for 10 seconds. The mixture was transferred into an NMR tube quickly and the ^{31}P NMR spectrum was immediately collected. The first spectrum was collected 2 minutes after the start of the catalytic reaction, and subsequent spectra were obtained every 1 min to construct kinetic profiles.

2.4 Solid-state catalytic hydrolysis of DMNP:

The solid phase hydrolysis of DMNP was carried out at 25 °C under 50% relative humidity (RH) controlled by a humidity oven (Memmert HPP 110, 115 Volt 50/60 Hz) (Figure S13). MOF catalysts (1.5 µmol, 6 mol%) and PEI (17 mg) were added to a 1.5-dram vial. The MOF/PEI composites were then formed by vortex-mixing for 30 seconds. DMNP (4 µL, 0.025 mmol) was carefully added onto the composite with multiple contact spots and then vortex-mixing for 30 seconds. The uncapped vial was put into the humidity oven at 50% RH for a specified time before digestion. At the designated time, 0.7 mL of D_2SO_4/DMSO-d$_6$ (15/100) was added into the vial, and the vial was sonicated for 5 minutes and then transferred into an NMR tube for collection of ^{31}P NMR data.

Notes:

MOFs reported here were synthesized by Xinyao Liu at Northwestern University, Evanston, IL.
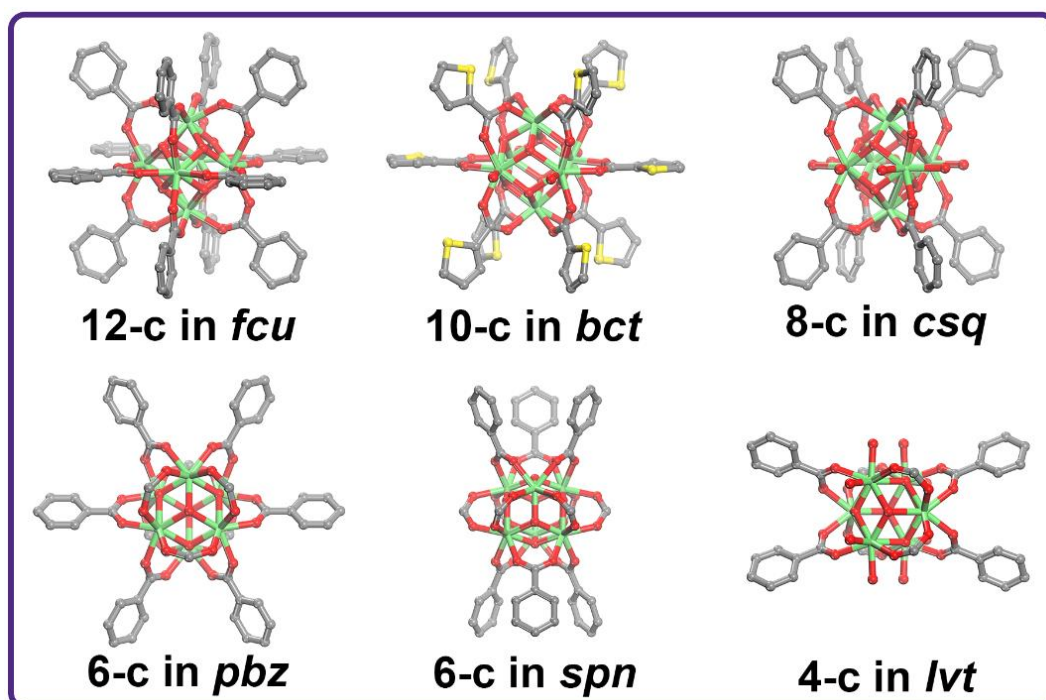
3. Supporting Figures:

Figure S1. Illustration of the various node connectivities possible for the Zr_6 cluster and representative topologies for each example.[1-5]
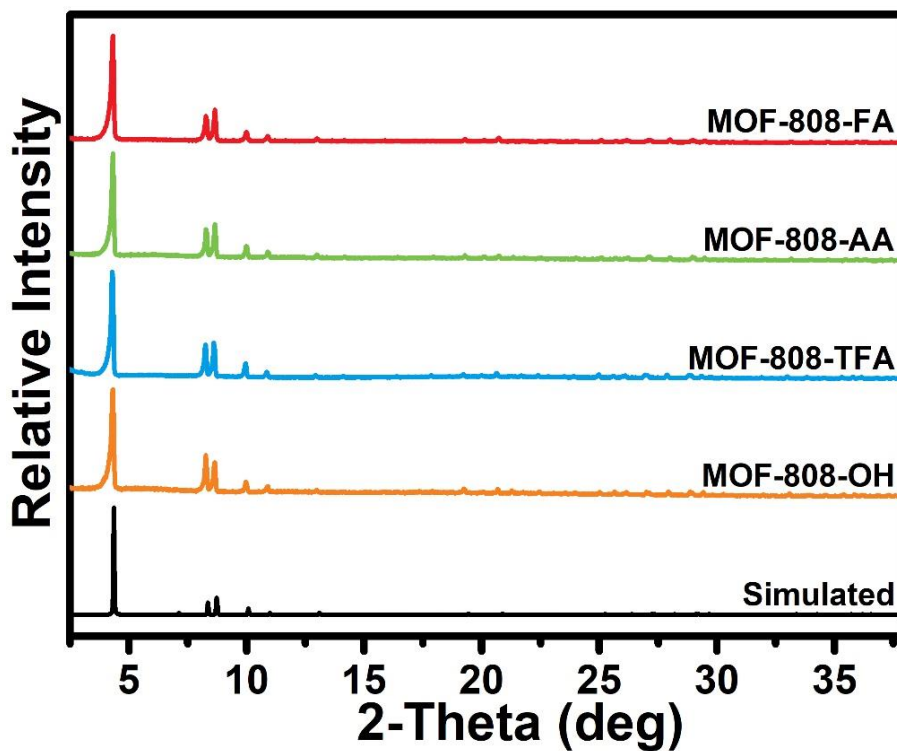

Figure S2. PXRD patterns of synthesized MOF-808-X (X = FA, AA, TFA, and OH) and the simulated one.
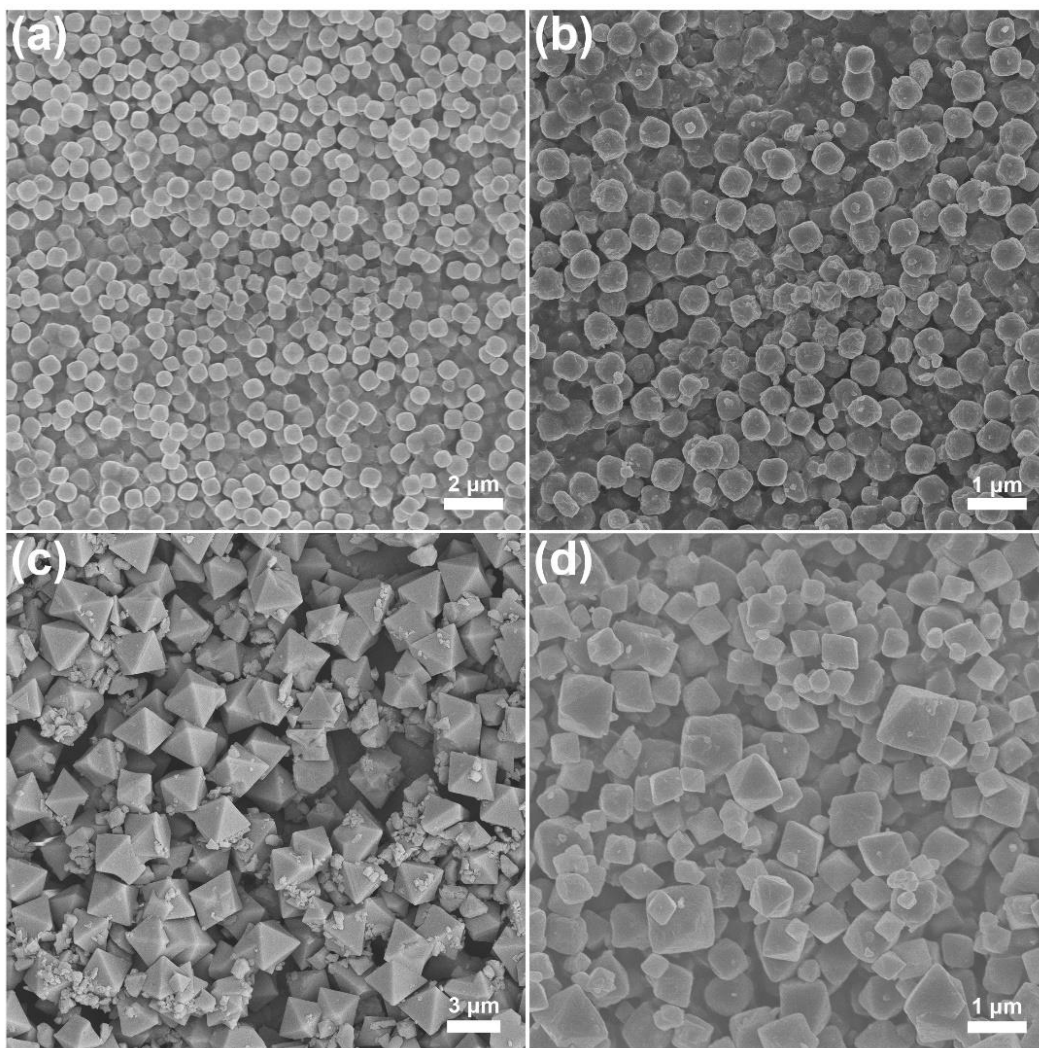
Figure S3. SEM images of (a) MOF-808-FA; (b) MOF-808-AA; (c) MOF-808-TFA (H_2O:TFA = 10:5); (d) MOF-808-TFA (H_2O:TFA = 10:3).
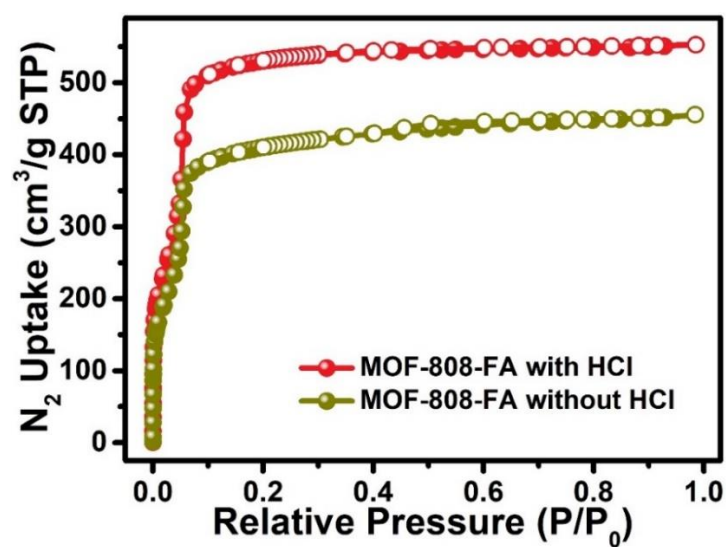
Figure S4. N_2 isotherms of MOF-808-FA with and without HCl used as an additive during the aqueous synthesis.
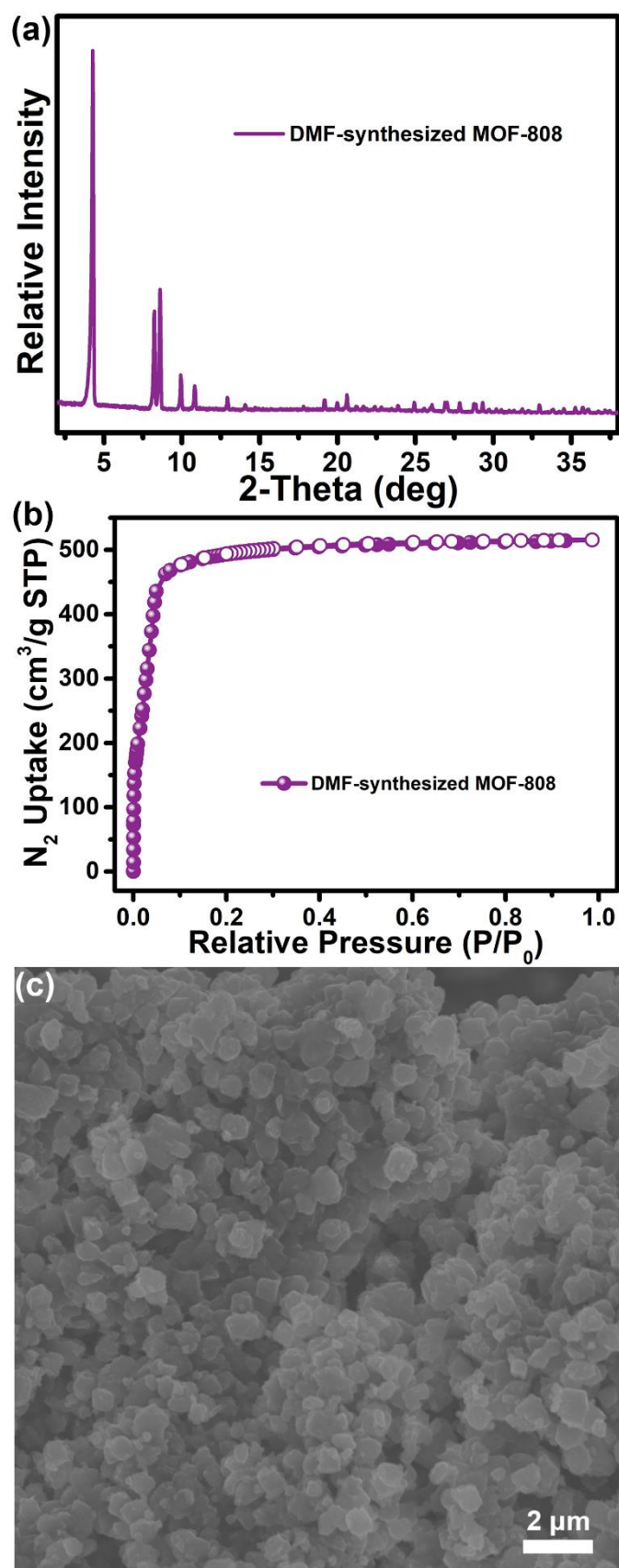
Figure S5. The (a) PXRD pattern, (b) N2 isotherm, and (c) SEM image of MOF-808 powder synthesized in DMF.

Figure S6. The pictures of water-synthesis of MOF-808-TFA, in which more than 7 grams of activated samples can be obtained from a single reaction at the 150 mL scale.
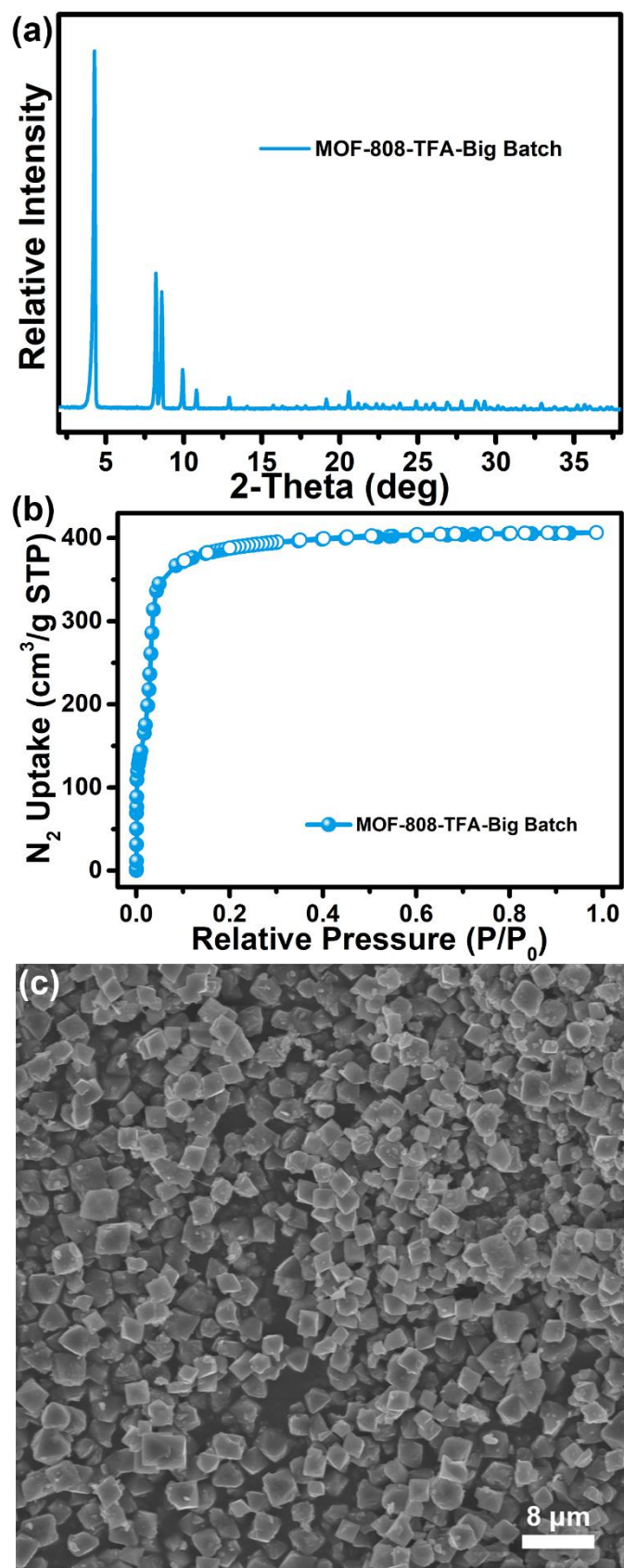
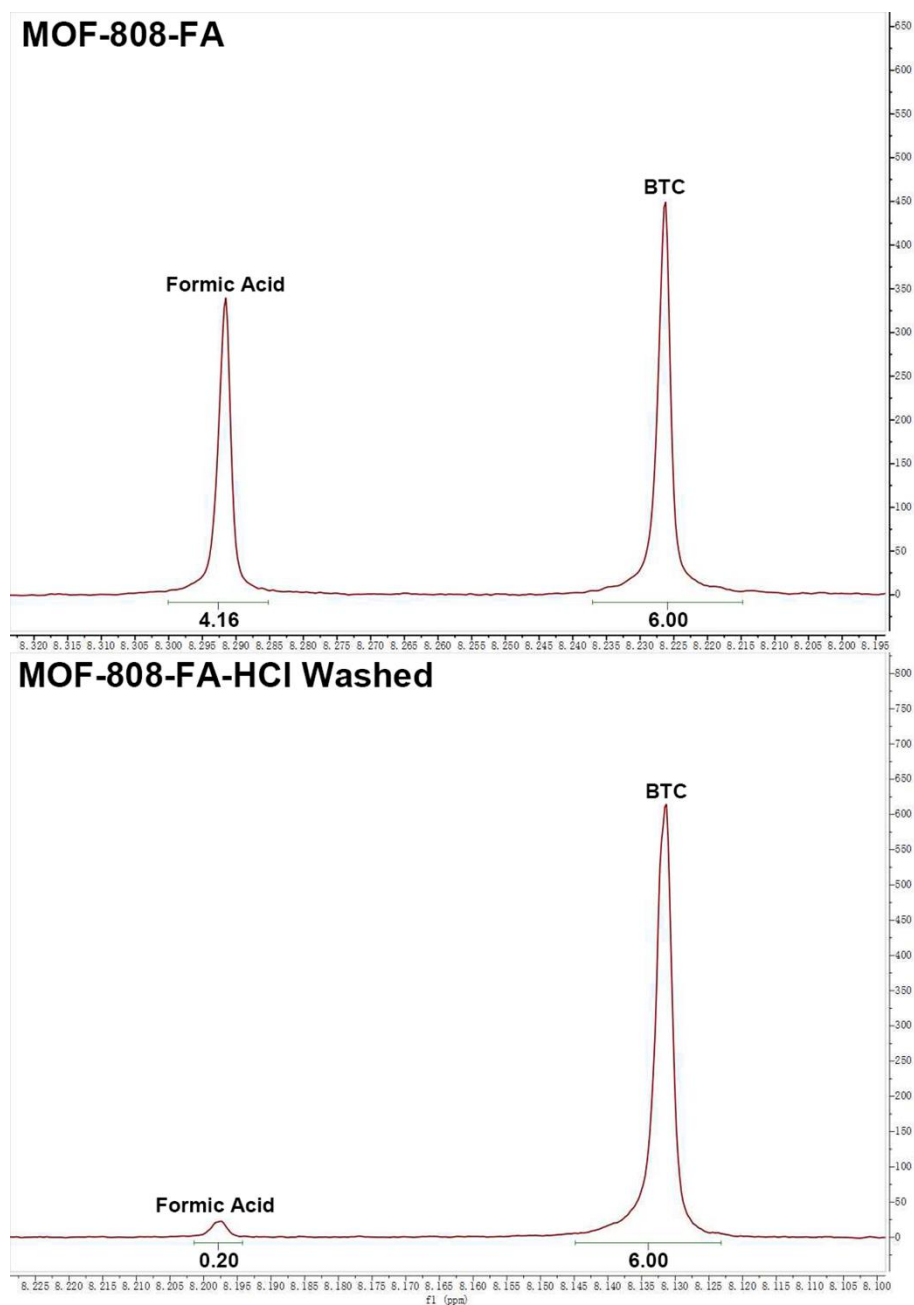**Figure S7.** The (a) PXRD pattern, (b) N$_2$ isotherm, and (c) SEM image of scale-up batch of MOF-808-TFA.
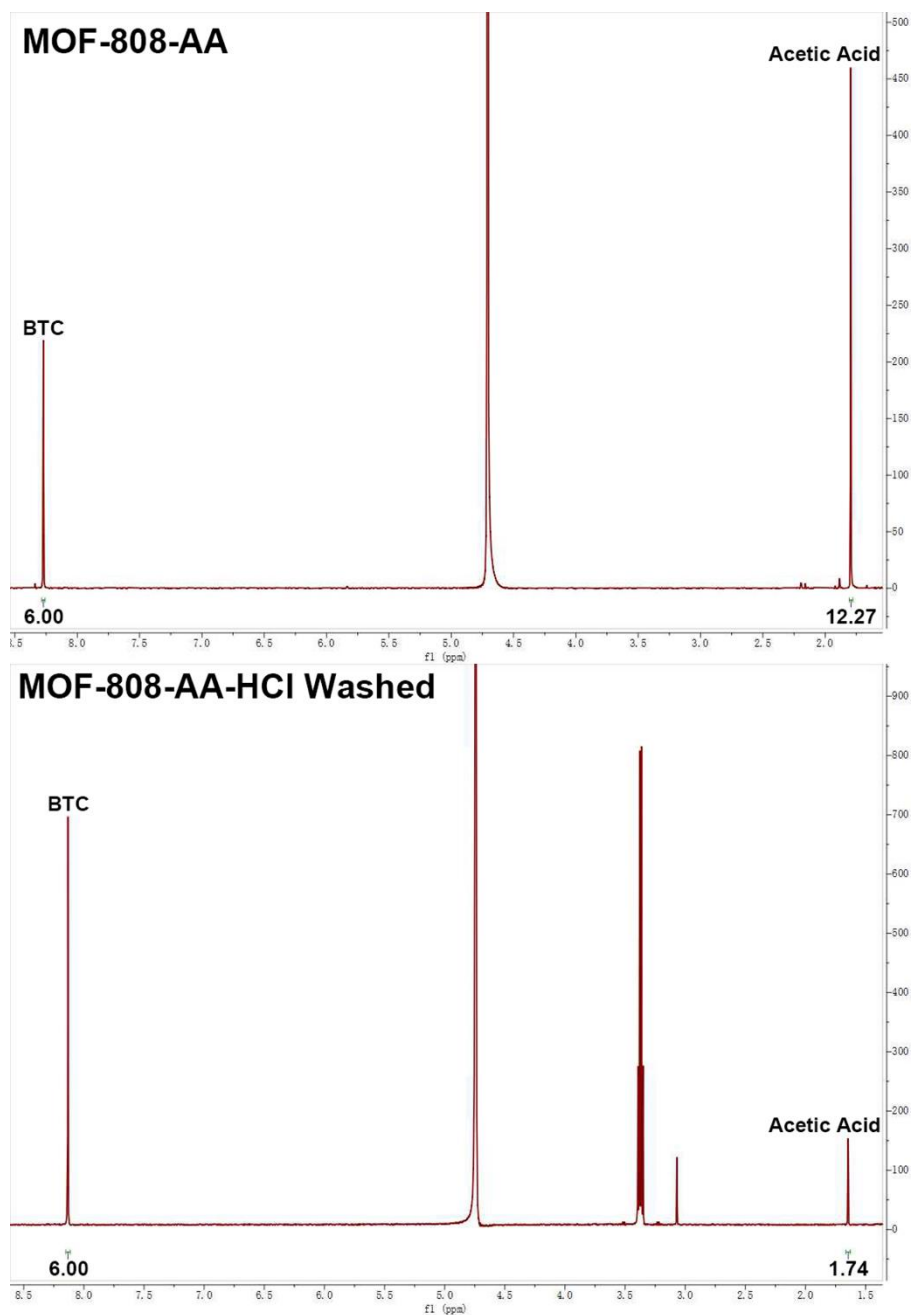
Figure S8. ^{1}H NMR spectra of MOF-808-FA (top) and MOF-808-OH washed from MOF-808-FA (bottom). To calculate the number of FA, the integration of H atom in BTC linker is set to 6 instead of 3 (in the chemical formula of MOF-808, there are 2 BTC linkers per Zr-node).
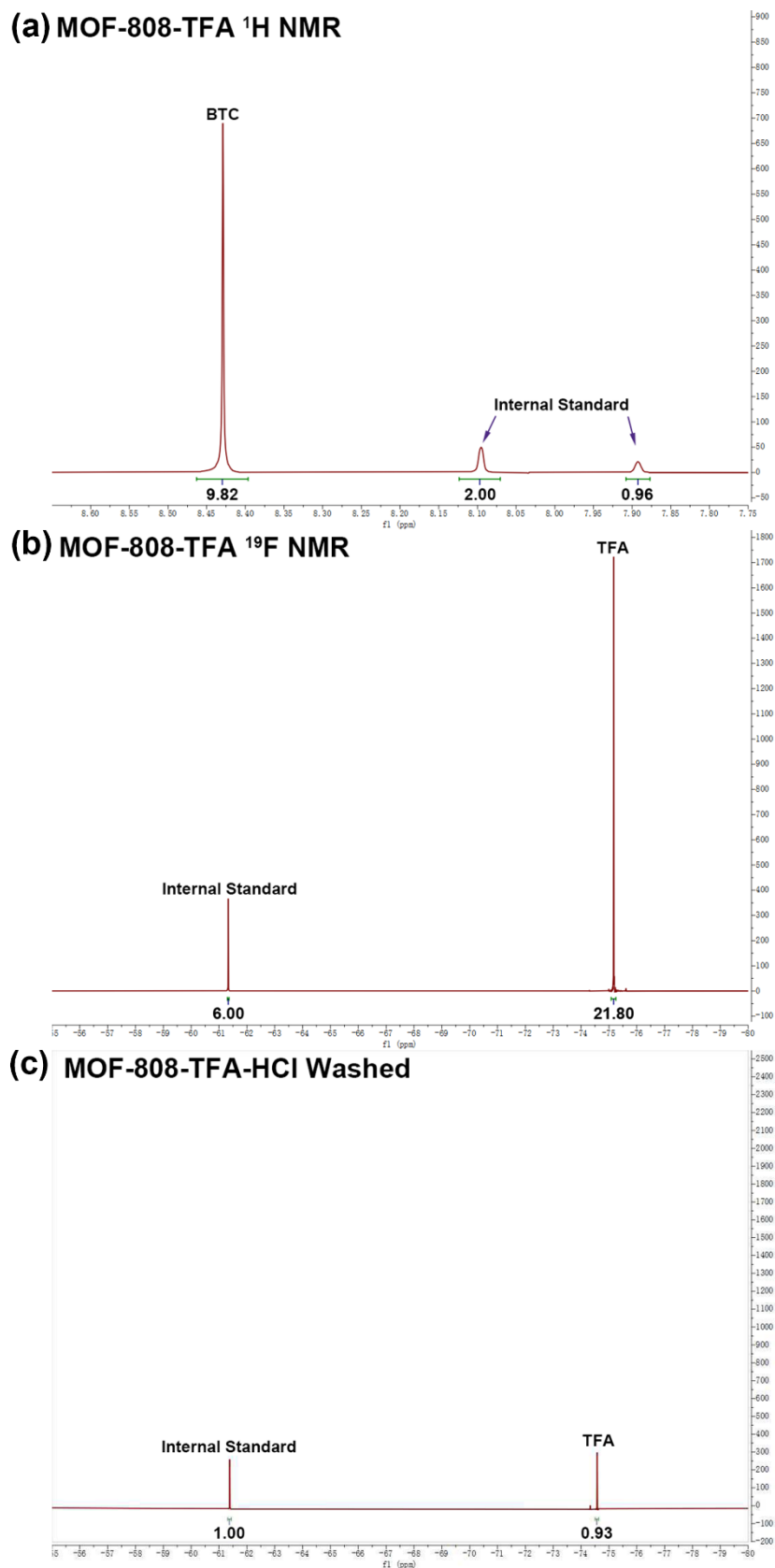
Figure S9. ^{1}H NMR spectra of MOF-808-AA (top) and MOF-808-OH washed from MOF-808-AA (bottom). To calculate the number of AA, the integration of H atom in BTC linker is set to 6 instead of 3 (in the chemical formula of MOF-808, there are 2 BTC linkers per Zr-node).

Figure S10. (a) ^{1}H NMR spectrum of MOF-808-TFA. ^{19}F NMR spectra of (b) MOF-808-TFA and (c) MOF-808-OH washed from MOF-808-TFA. The internal standard is 1-bromo-3,5-bis(trifluoromethyl)benzene.
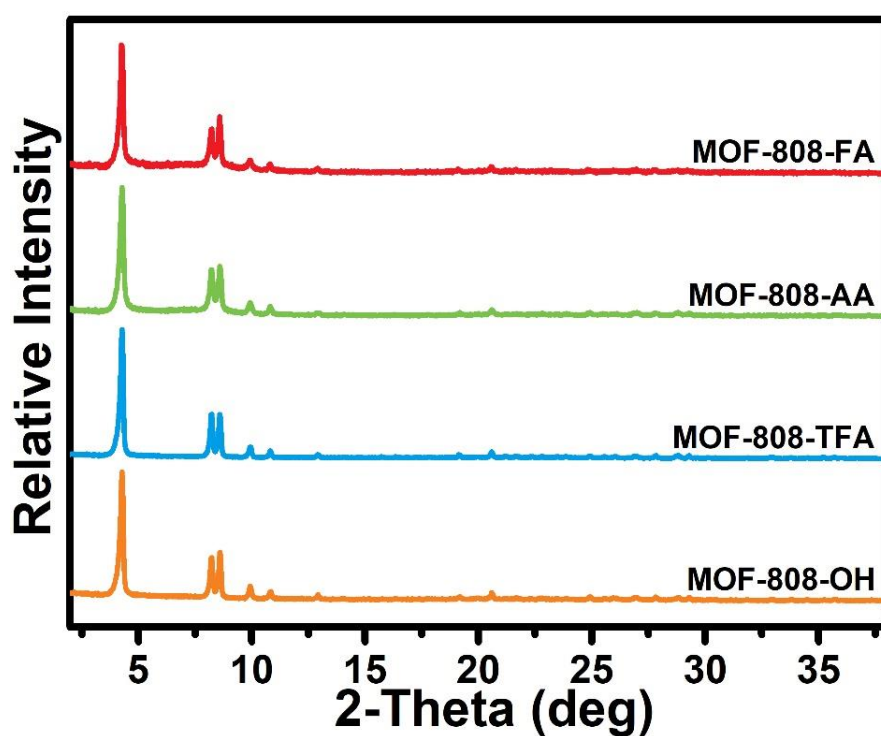
Figure S11. The PXRD patterns of MOF-808-X (X = FA, AA, TFA, and OH) after water treatment.
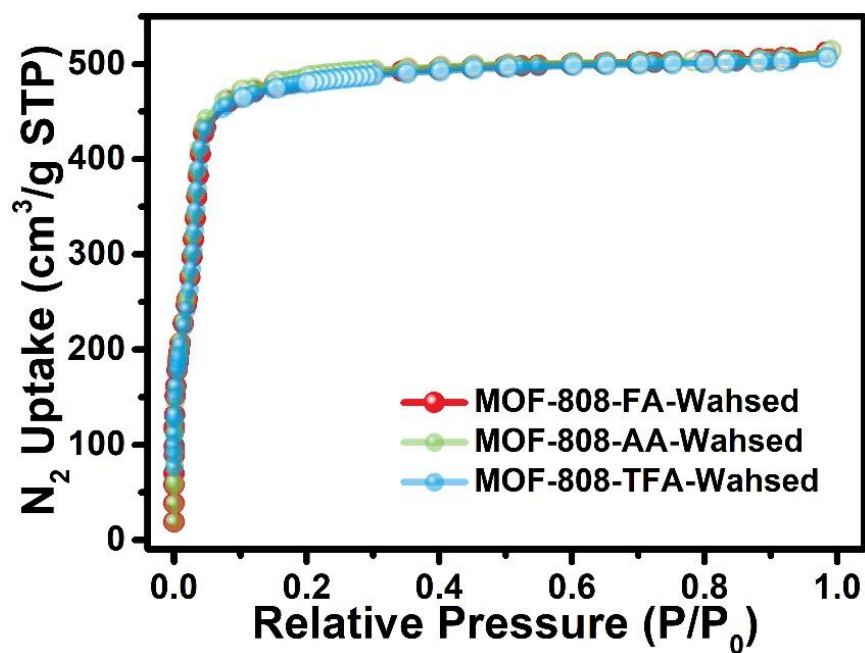

Figure S12. N_2 isotherms of MOF-808-OH washed from MOF-808-X (X = FA, AA, and TFA).
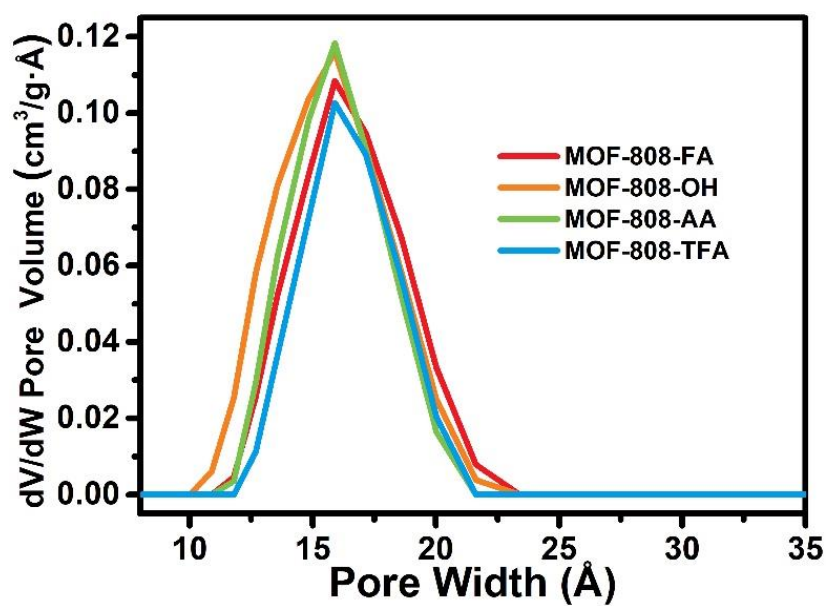
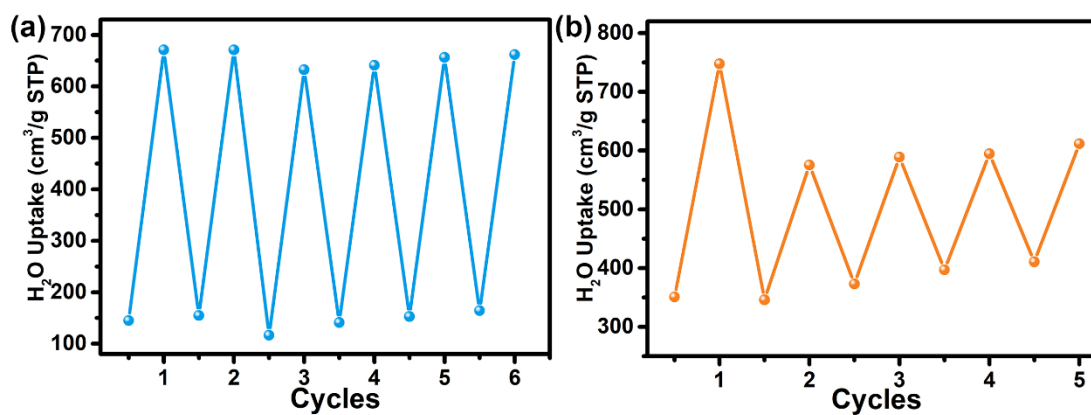**Figure S13.** DFT pore size distribution of MOF-808-X (X = FA, AA, TFA, and OH).

Figure S14. The water adsorption cycling test of (a) MOF-808-TFA and (b) MOF-808-OH.
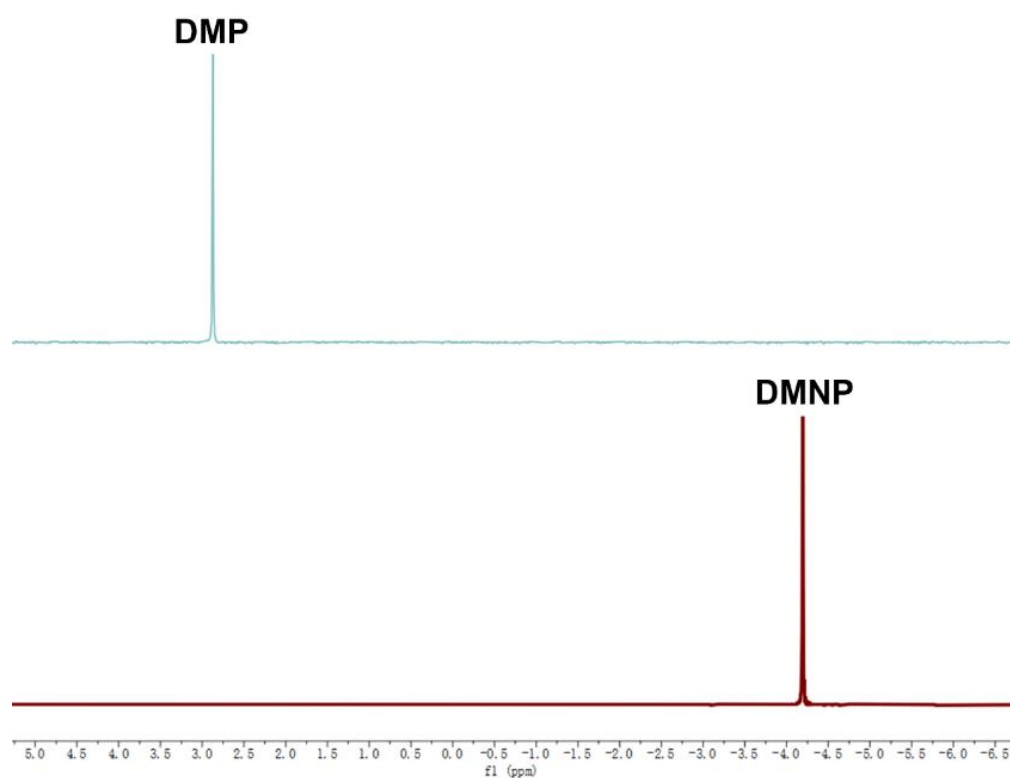
Figure S15. Representative example of the ^{31}P NMR spectra obtained for the liquid-state hydrolysis of DMNP using MOF-808-X (X = FA, AA, TFA, and OH) after 5 minutes.
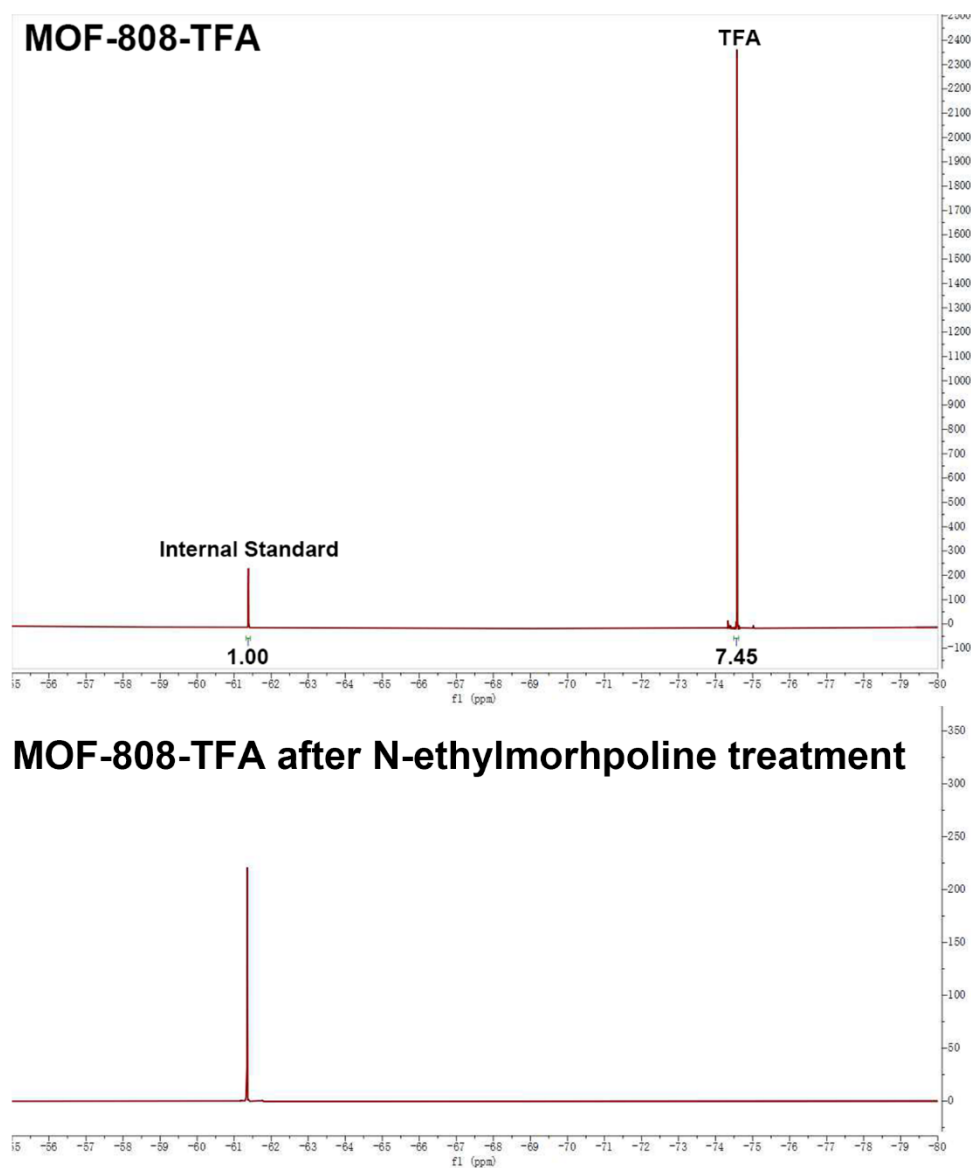
Figure S16. ^{19}F NMR spectra for a digested sample of MOF-808-TFA (top) and a digested sample of MOF-808-TFA after soaking in *N*-ethylmorpholine (50 µL in 1 mL water) for 5 min (bottom).

Figure S17. Left: the home-designed humidity chamber which used in the previous work. Right: the humidity oven which used for solid-state hydrolysis in this work.
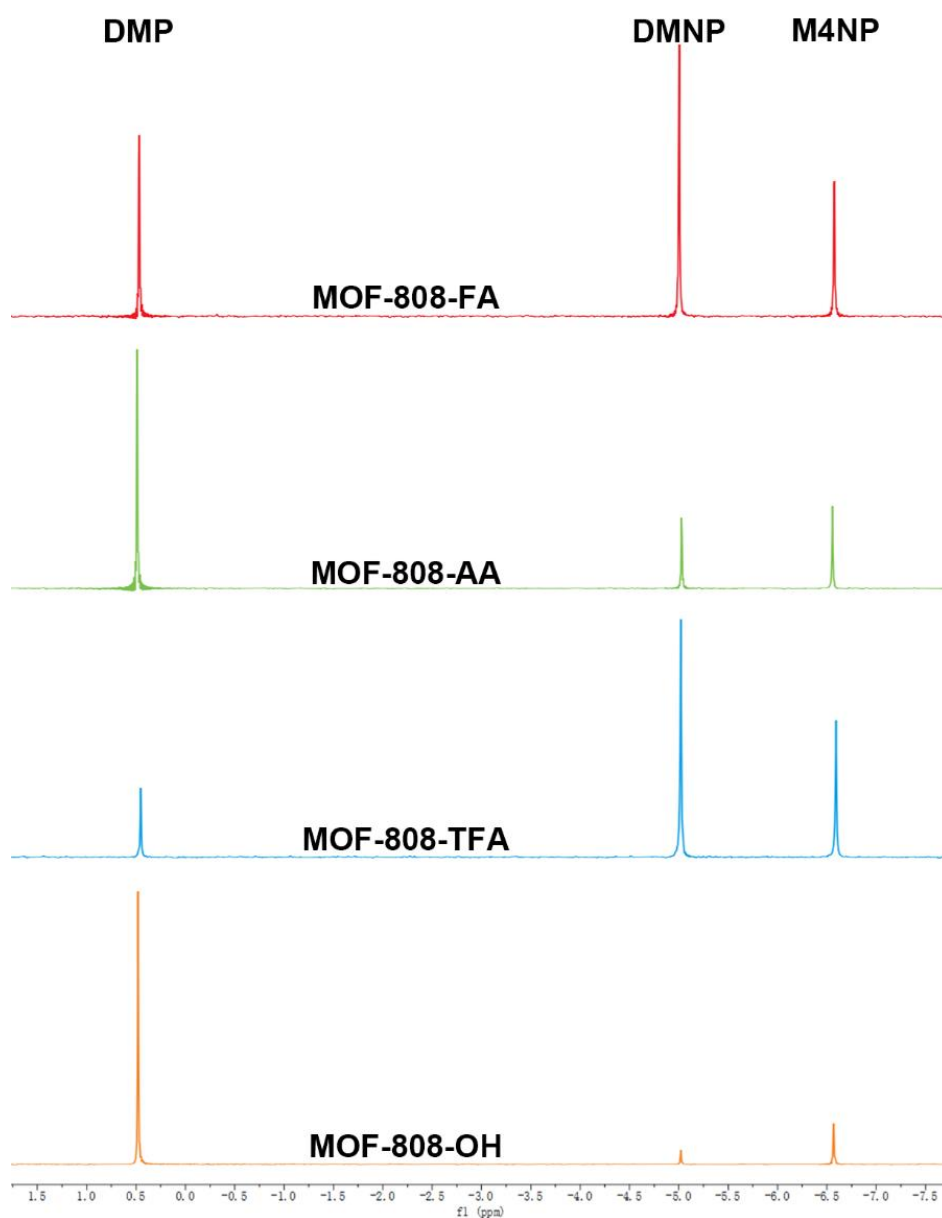
Figure S18. ^{31}P NMR spectra for the solid-state hydrolysis of DMNP using MOF-808-X/PEI composites (X = FA, AA, TFA, and OH) after 2 hours.
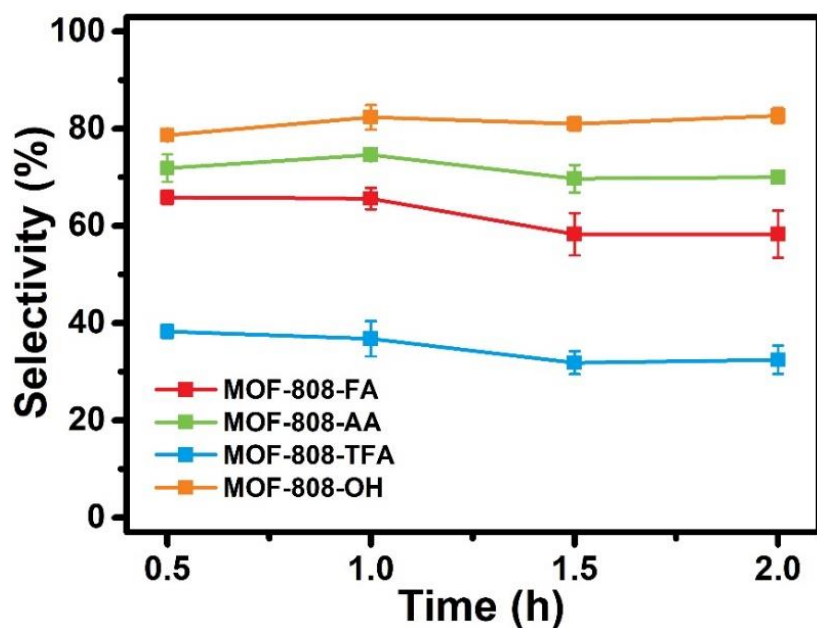
Figure S19. The selectivity of DMP for the solid-state hydrolysis of DMNP using MOF-808-X/PEI composites (X = FA, AA, TFA, and OH).
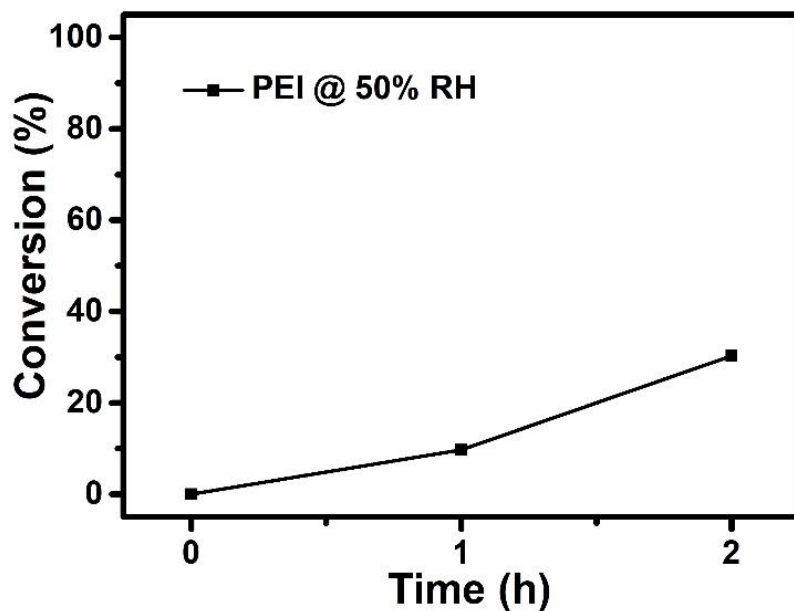

Figure S20. Conversion profile for the solid-state DMNP hydrolysis reaction performed with bulk PEI at 50% RH in the absence of MOF-808-X. Only M4NP is observed in the ^{31}P NMR spectra.

4. Supporting References

(1) Alezi, D.; Spanopoulos, I.; Tsangarakis, C.; Shkurenko, A.; Adil, K.; Belmabkhout, Y.; O'Keeffe, M.; Eddaoudi, M.; Trikalitis, P. N., Reticular Chemistry at Its Best: Directed Assembly of Hexagonal Building Units into the Awaited Metal-Organic Framework with the Intricate Polybenzene Topology, pbz-MOF. *J. Am. Chem. Soc.* **2016,** 138, 12767-12770.

(2) Bon, V.; Senkovska, I.; Baburin, I. A.; Kaskel, S., Zr- and Hf-Based Metal–Organic Frameworks: Tracking Down the Polymorphism. *Cryst. Growth Des.* **2013,** 13, 1231-1237.

(3) Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. P., A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability. *J. Am. Chem. Soc.* **2008,** 130, 13850-13851.

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(5) Zhang, Y.; Zhang, X.; Lyu, J.; Otake, K.-i.; Wang, X.; Redfern, L. R.; Malliakas, C. D.; Li, Z.; Islamoglu, T.; Wang, B.; Farha, O. K., A Flexible Metal–Organic Framework with 4-Connected Zr6 Nodes. *J. Am. Chem. Soc.* **2018,** 140, 11179-11183.