Supporting Information for

Modular Functionalization of Metal-Organic Frameworks for Nitrogen Recovery from Fresh Urine

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S1. General Information

Chemicals.

Chemical reagents were purchased from Sigma-Aldrich, Fisher Scientific, and TCI America. Unless otherwise noted, all commercial reagents were used without further purification.

Instruments.

Powder X-ray diffraction data for unit cell determination were collected using a Panalytical X'Pert Pro and a Rigaku SmartLab. FT-IR spectra were obtained from a Nicolet™ iS50 FTIR Spectrometer. Digested MOF samples were prepared by dissolving 5 mg powder in 20 L of HF solution and 480 L of $(CD_3)_2SO$, followed by 5 min of sonication (and heating, if needed) to ensure all the solids were fully dissolved. Final clear solutions were used for ^1H NMR measurement. Solution ^1H NMR spectra were acquired on a Bruker DRX500 NMR spectrometer. Samples for SEM study were prepared by dropcasting the MOF-methanol suspension onto a silicon wafer. SEM/EDS analysis was carried out on a ZEISS 1550VP Field Emission SEM - Oxford EDS - HKL EBSD system. During the SEM measurement, the accelerating voltage was 5 kV and the working distance was kept at 6 mm. For the SEM/EDS measurement of MOF-808-Cu, the accelerating voltage was 15 kV and the working distance was kept at 6 mm. UV−vis diffuse reflectance measurement was carried out on Cary 5000. X-ray absorption spectroscopy data was collected at the Stanford Synchrotron Radiation Lightsource (SSRL) using beam line 4-1.

Analytical methods.

Concentration of ammonium was determined by the colorimetric assay adapted from the Berthelot method.[12,51] 50 L of sample was added to a mixture (pH 11.0) of 6.95 mL of Milli-Q water, 0.5 mL of phenol (3%) solution, and 2 mL of Na_2HPO_4 solution, and 0.25 mL of nitroprusside solution (0.50 g/L). After complete mixing, 250 L of NaClO (2.5%) solution was added, and the final solution was put in a 80^{o}C water bath for 10 min, followed by cooling with water to room temperature. Full spectrum was collected with a NanoDrop 2000 spectrometer and absorbance at 628 nm was used to quantify the amount of ammonium in solutions.

Concentration of urea was determined by the colorimetric assay adapted from a previous report.[64] Sample solution (1 mL) was first mixed with a potassium phosphate buffer (50 mM, pH 7.2, 1 mL), and p-dimethylaminobenzaldehyde solution (0.1 M in 10:1 ethanol and concentrated HCl (v/v), 0.5 mL) was then added. Mixture was mixed at room temperature for 30 min and UV-Vis spectra was taken with a NanoDrop 2000 spectrometer. Absorbance at 435 nm was recorded to determine urea concentrations.

S2. Synthesis Procedures

MOF-808: Microcrystalline MOF-808 was synthesized and activated following the previous procedure.[65] Organic component of MOF-808 was quantified with ^{1}H NMR spectrum of the digested sample and the chemical formula of synthesized MOF-808 was determined as $Zr_6O_{7.2}(OH)_{0.8}(C_9H_3O_6)_2(HCOO)_{2.8}$.

MOF-808-U: Urease was covalently immobilized onto MOF-808 backbone *via* the carbodiimide coupling reaction and the condition was optimized from the reported procedure.[35] MOF-808 (10 mg) was immersed in an anhydrous DMF solution (1 mL) containing EDC·HCl (9.6 mg), DMAP (1.5 mg), and NHS (5.8 mg). The suspension was completely mixed at 37^{o}C for 30 min, and the solids were separated and washed with DMF and H_2O. The amine-active-NHS ester intermediate was then immersed in urease solution (1 mL, 20000 ppm in 50 mM HEPES solution, pH 7.0), and the mixture was allowed to rotate at a revolver at 10 rpm at room temperature overnight for complete coupling. Solids were then separated and washed with 50 mM HEPES solution. Supernatant in the second step of coupling was collected and added into cold acetone (4 times of the volume), fully mixed, and stored in a -20^{o}C freezer overnight. On the next day, the precipitated protein was centrifuged, separated, and dried under vacuum, and quantified with Pierce BCA protein colorimetric assay. The immobilization yield of urease onto MOF-808 was determined as 1.7g/g.

MOF-808-no FA: MOF-808-no FA was synthesized as an intermediate for incorporation of the dicarboxylate. Activated MOF-808 was suspended in a HCl solution and heated at 80^{o}C for 2 days. Over a period of 24 hours, MOF powders were separated and the supernatant was decanted and replaced with fresh HCl solution. The solids were washed with water and were carried onto the following post-synthetic modification.

MOF-808-OA: MOF-808-no FA was added into a sodium oxalate (OA) aqueous solution and stirred at room temperature for 2 days. Over a period of 24 hours, MOF powders were separated and the supernatant was decanted and replaced with fresh sodium oxalate solution. The solids were washed with water and anhydrous acetone and dried under vacuum. Successful incorporation of oxalate was confirmed and quantified by a reported colorimetric assay procedure,[46] and chemical formula was determined as $Zr_6O_7(OH)(C_9H_3O_6)_2(O_2CCO_2Na)_3$.

MOF-808-MA: MOF-808-no FA was added into a malonic acid (MA) aqueous solution for 2 days. Over a period of 24 hours, MOF powders were separated and the supernatant was decanted and replaced with fresh malonic acid solution. The solids were washed with water and anhydrous acetone and dried under vacuum. Successful incorporation of malonic acid was confirmed and quantified with the ^{1}H NMR spectrum of the digested sample, and chemical formula was determined as $Zr_6O_{4.2}(OH)_{3.8}(C_9H_3O_6)_2(MA)_{5.8}$.

MOF-808-SA: MOF-808-no FA was added into a succinic acid (SA) aqueous solution for 2 days. Over a period of 24 hours, MOF powders were separated and the supernatant was decanted and replaced with fresh succinic acid solution. The solids were washed with water and anhydrous acetone and dried under vacuum. Successful incorporation of succinic acid was confirmed and quantified with the ^{1}H NMR spectrum of the digested sample, and chemical formula was determined as $Zr_6O_{4.7}(OH)_{3.3}(C_9H_3O_6)_2(SA)_{5.3}$.

MOF-808-Cu: MOF-808 was added into a $CuSO_4$ methanolic solution. The suspension was rotated at 10 rpm at room temperature overnight for complete mixing. Solids were separated by centrifuge, washed with MeOH, and dried under vacuum. Successful incorporation of Cu was confirmed and quantified with ICPMS. Chemical formula of MOF-808-Cu was determined as $Zr_6O_{7.25}(OH)_{0.75}(C_9H_3O_6)_2(O)_{2.75}(CuSO_4)_{2.75}$.

S3. FT-IR Spectra

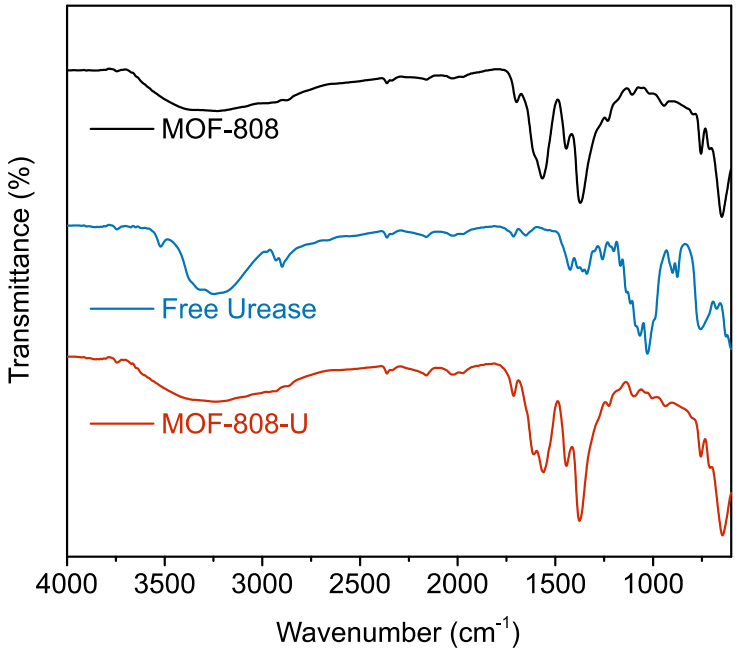

Figure S1. FT-IR spectra of MOF-808, free urease, and MOF-808-U.

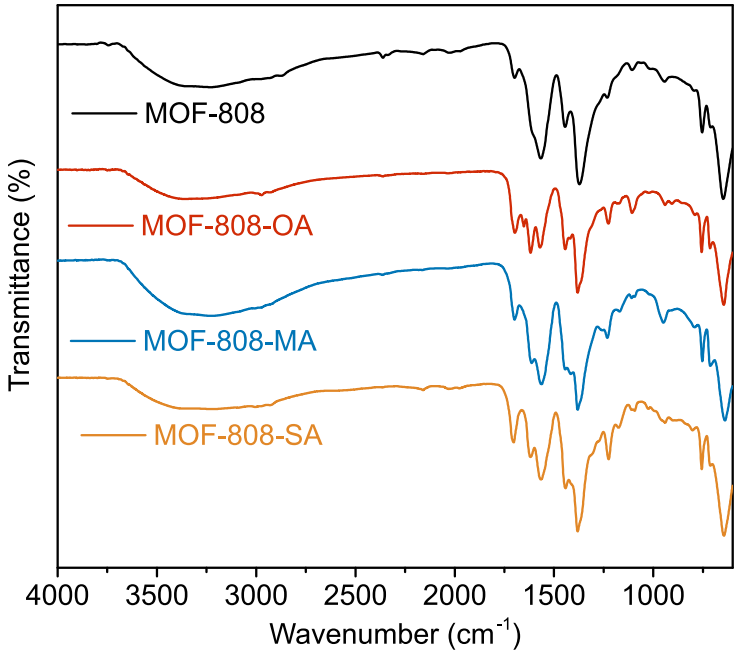

Figure S2. FT-IR spectra of MOF-808 and the dicarboxylate functionalized derivatives.

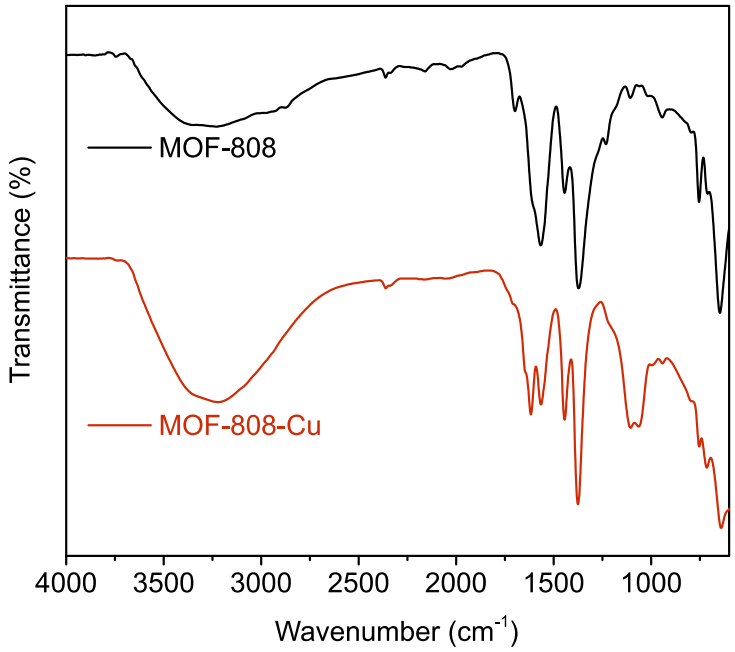

Figure S3. FT-IR spectra of MOF-808 and MOF-808-Cu.

S4. ^{1}H NMR Spectra of Digested MOF Samples

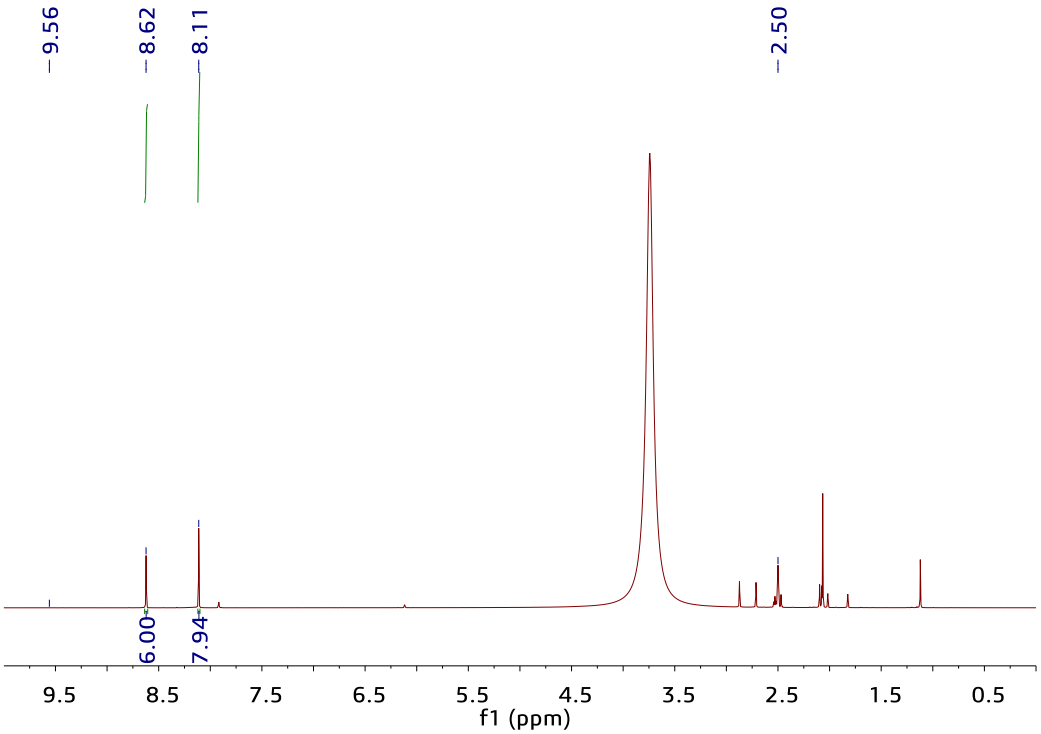

Figure S4. ^{1}H NMR spectrum of digested MOF-808. Peak with the chemical shift of 8.08 ppm is assigned to formic acid (FA). Ratio of BTC and FA was determined as 2:2.82.

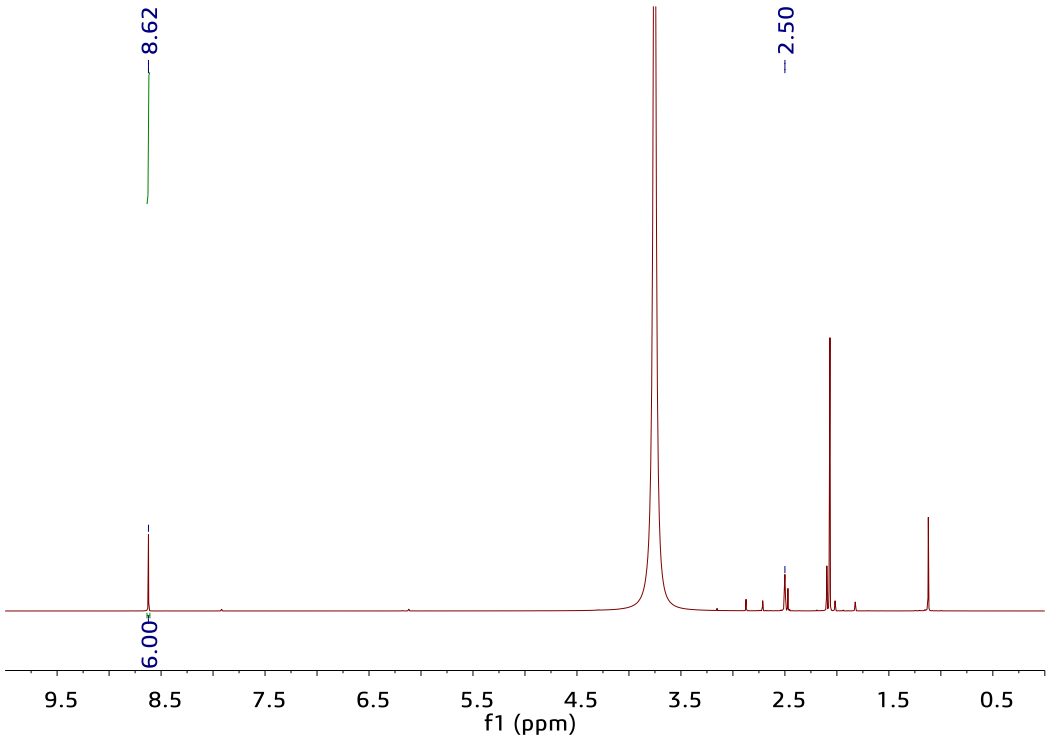

Figure S5. ^{1}H NMR spectrum of digested MOF-808-OA.

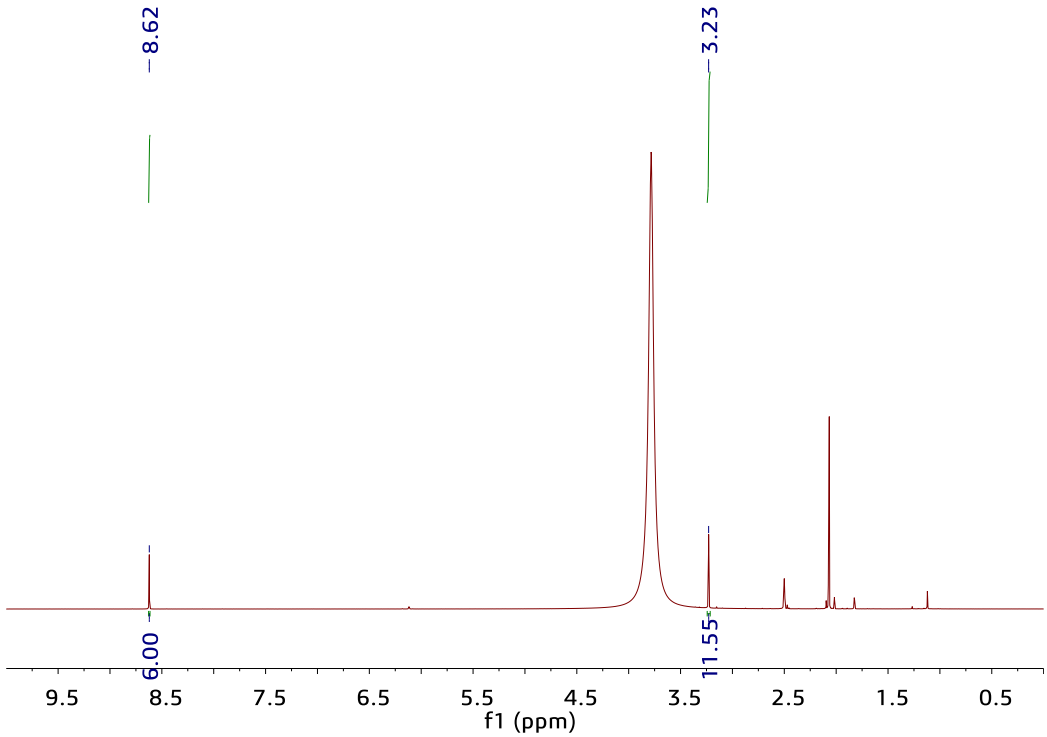

Figure S6. ^{1}H NMR spectrum of digested MOF-808-MA. Peak with the chemical shift of 3.23 ppm is assigned to malonic acid (MA). Ratio of BTC and MA was determined as 2:5.78.

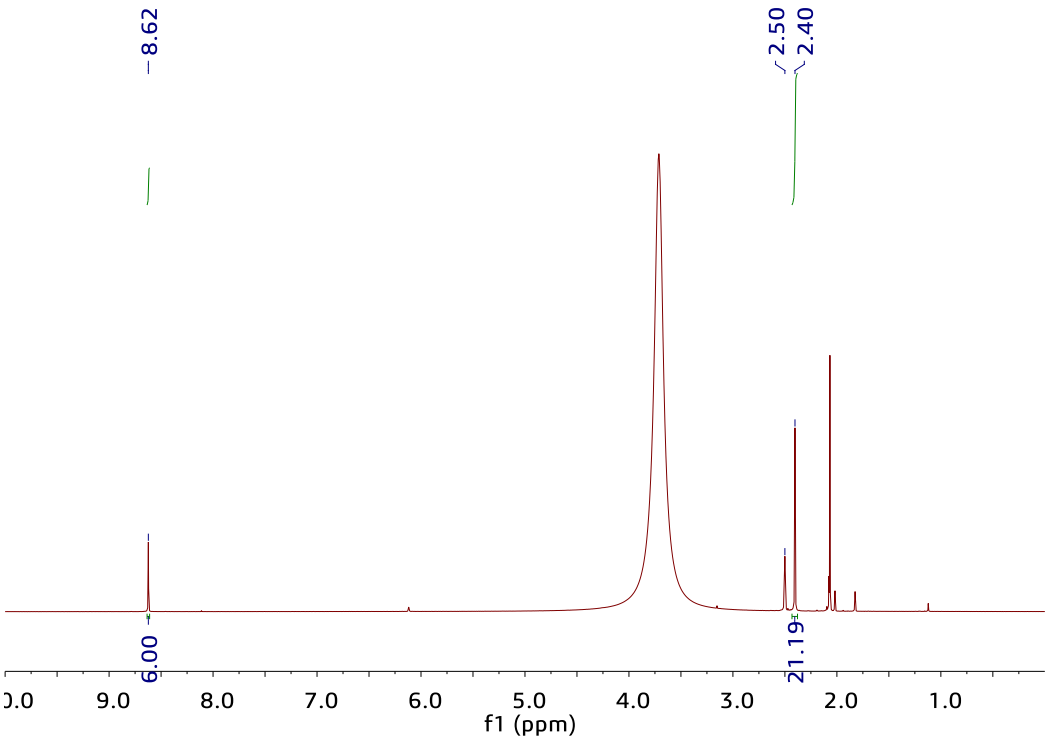

Figure S7. ^{1}H NMR spectrum of digested MOF-808-SA. Peak with the chemical shift of 2.40 ppm is assigned to succinic acid (SA). Ratio of BTC and SA was determined as 2:5.30.

S5. SEM Images

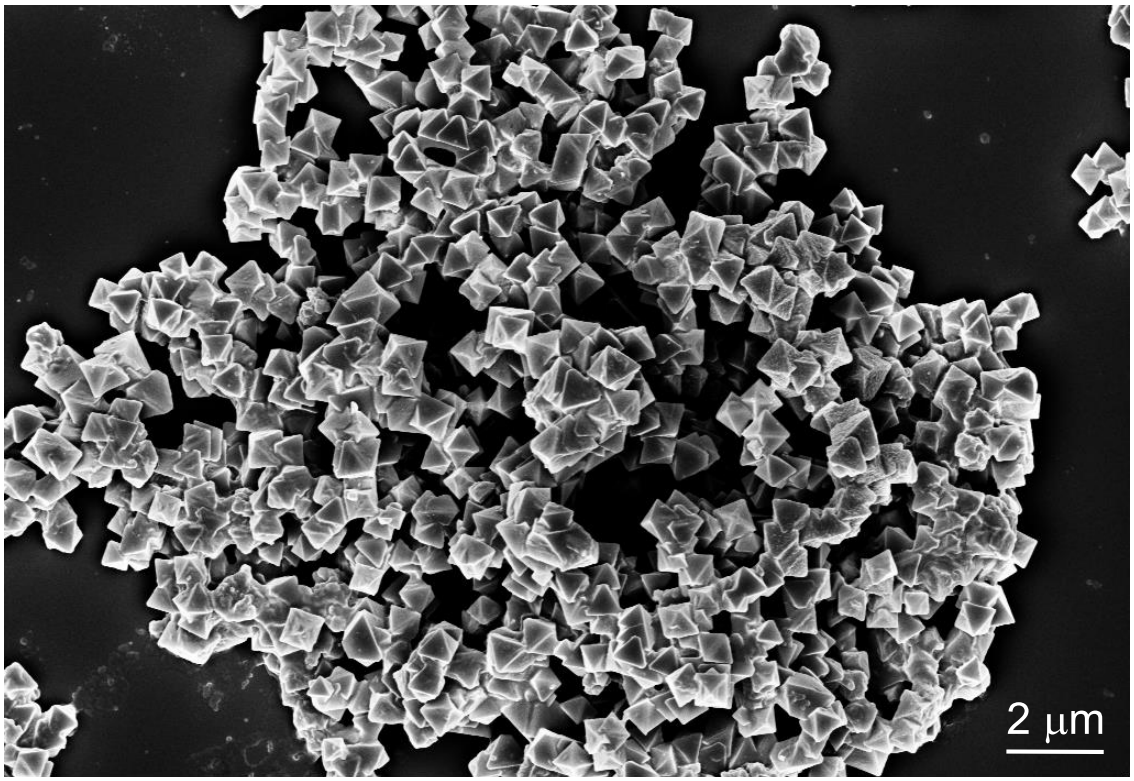

Figure S8. SEM image of MOF-808.

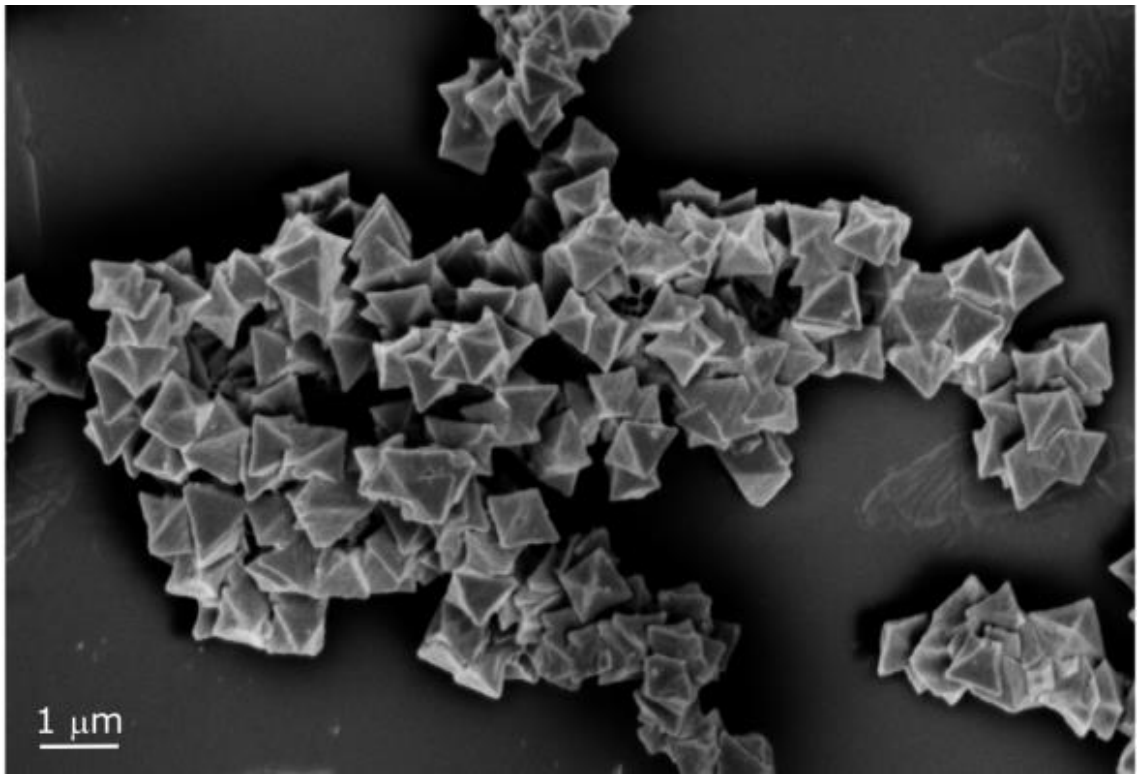

Figure S9. SEM image of MOF-808-U.

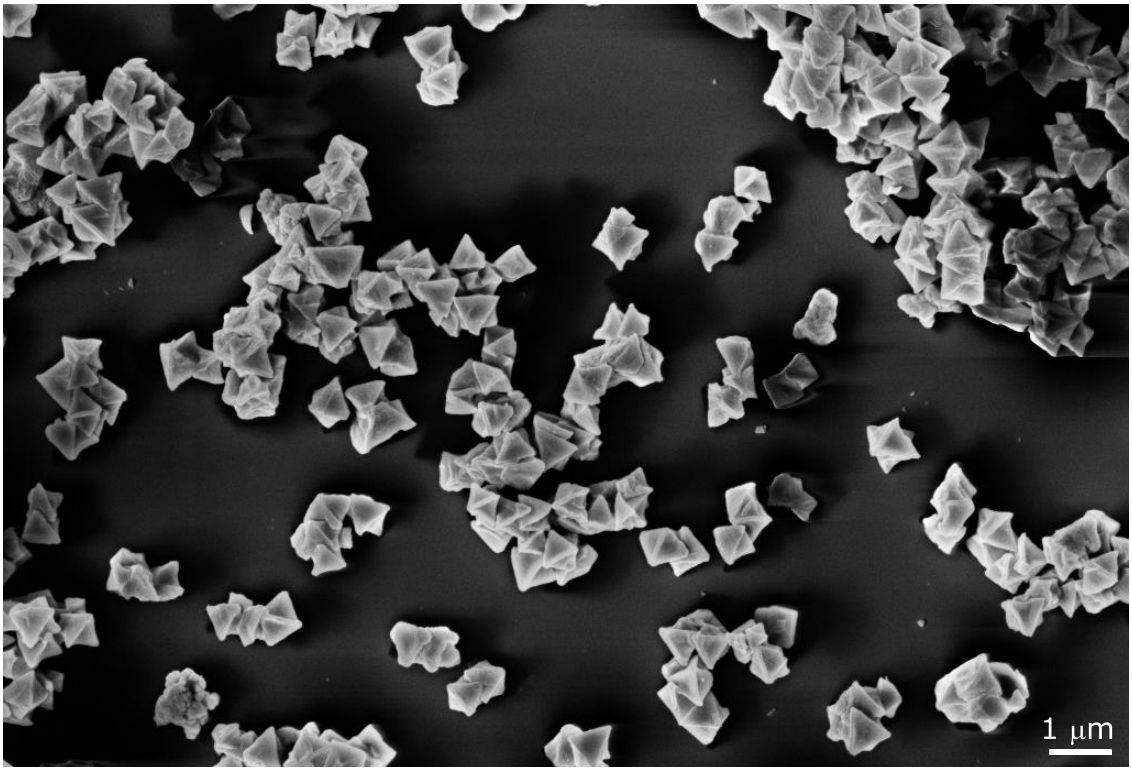

Figure S10. SEM image of MOF-808-OA.

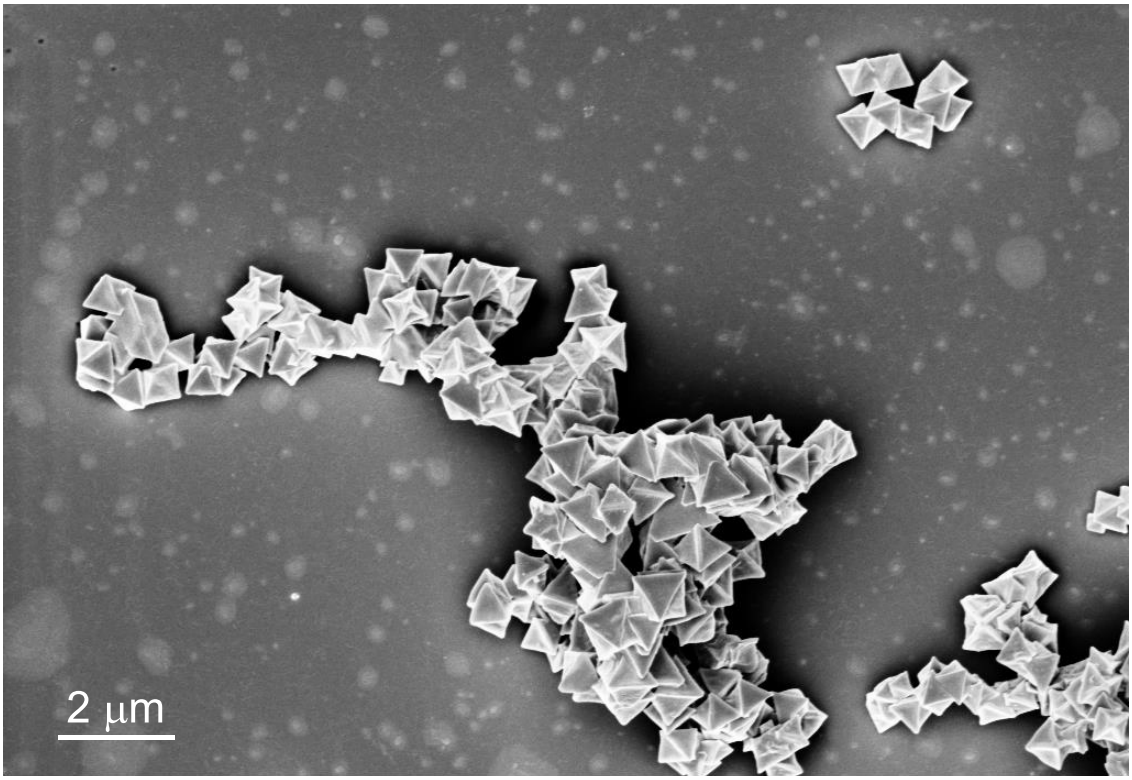

Figure S11. SEM image of MOF-808-MA.

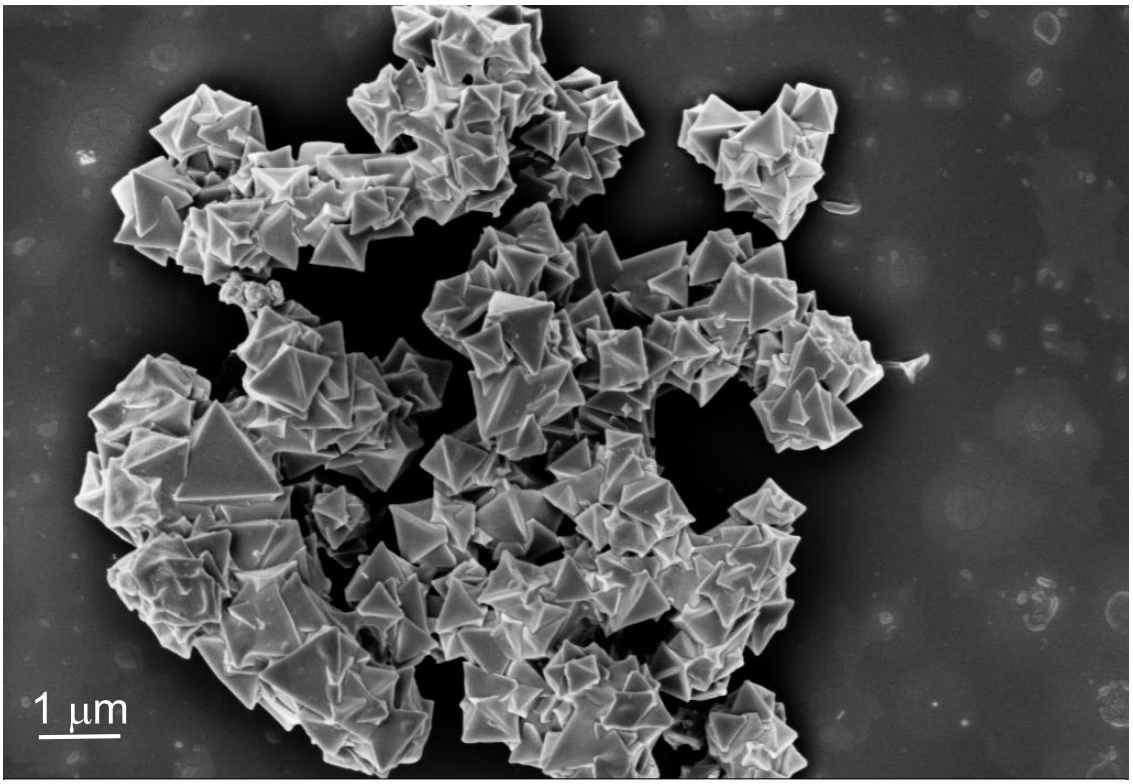

Figure S12. SEM image of MOF-808-SA.

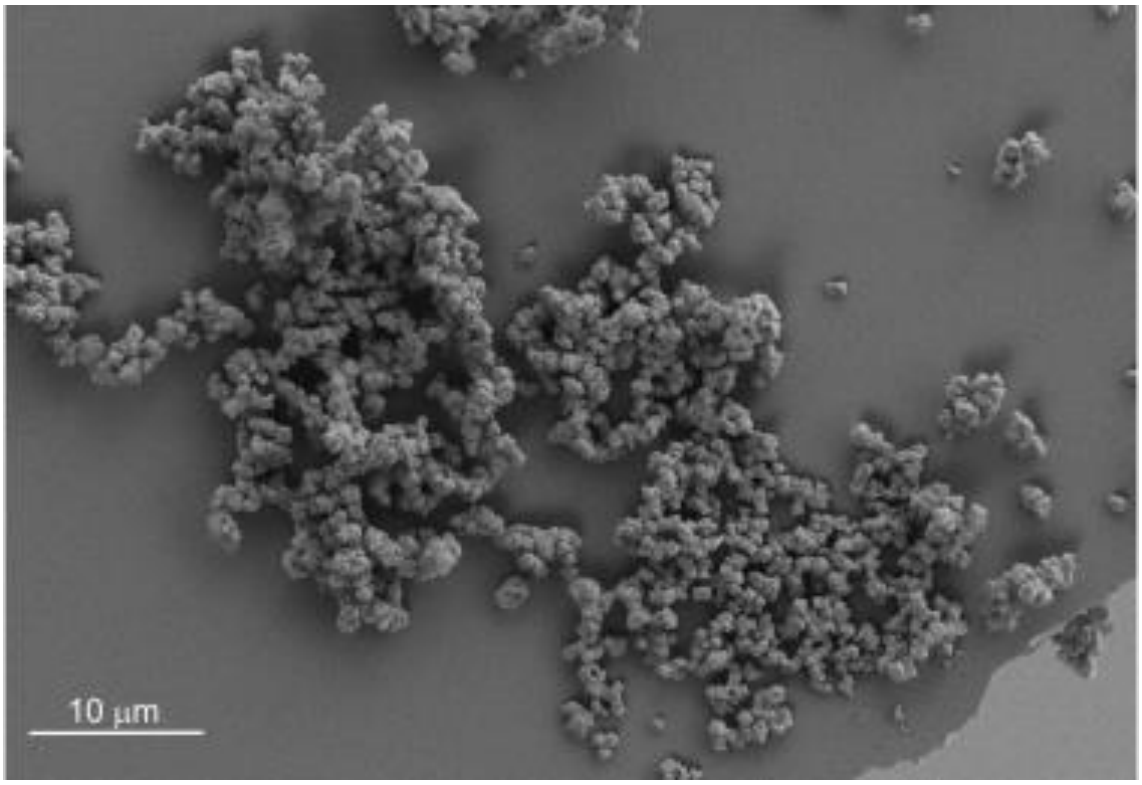

Figure S13. SEM image of MOF-808-Cu.

S6. Characterization of MOF-808-U

Michaelis–Menten kinetics experiments

As-synthesized MOF-808-U (10 mg) was added to urea solutions of various concentrations. Upon complete mixing, the suspensions were further rotated at 10 rpm at room temperature for 10 min. Mixtures were centrifuged, and the ammonium concentration of the supernatant was determined to evaluate the hydrolysis efficiency. For free urease, the procedures were similar except that 50 L of the urease solution (20000 ppm in 10 mM HEPES, pH 7.0) was used as the enzyme source, and ammonium concentration was determined after 1 min of reaction.

Table S1. Enzymatic kinetic parameters determined from the Michaelis–Menten plot.

	K_m (mM)	k_{cat} (mM s^{-1} g^{-1})
MOF-808-U	25.15	0.1825
Free Urease	24.80	0.3565

Stability tests

MOF-808-U (10 mg) was added to a urea solution (250 mM, 1 mL). Suspension was left at a rotator (10 rpm) for 24 h, and urea concentration was measured to calculate the amount of consumed substrate. Free urea solution was then added to the separated MOF-808-U for the measurement of the immobilized urease's activity on the following day. To determine the stability of free urease in the solution (10 mM HEPES, pH 7.0), a stock solution was firstly made (20000 ppm) and kept at room temperature. For each day's measurement, 50 L of urease solution was taken from the stock solution and added to a urea solution. The mixture was left at a rotator for 24 h before urea concentration was determined.

S7. Characterization of MOF-808-Based Adsorbents

Ammonium adsorption isotherms measurements

Aqueous solutions of ammonium bicarbonate (NH_4HCO_3) of different concentrations were prepared by dissolving the salt of proper amount in Milli-Q water. NH_4HCO_3 was selected for the isotherm measurement as the pH of the solutions was well-maintained in a wide range of concentrations of the solute (pH: 8.20±0.04).

MOF powders were added into different concentration ammonium solutions with a final suspension concentration of 10 g/L. The mixtures were left at a rotate revolver at 10 rpm at room temperature overnight to ensure adsorption equilibrium was reached. Suspensions were centrifuged, and the supernatant was directly used for the quantification of ammonium.

Q_{eq}, ammonium capture capacity was calculated using the following equation:

$$Q_{eq} = \frac{(C_i - C_e) \times V}{m}$$

where V is the volume of the solution (mL), m is the mass of adsorbents (mg), and C_i and C_e are initial and final concentrations of solution, respectively.

Three adsorption isotherm models, Langmuir, Freundlich, and Langmuir–Freundlich models were applied to fit the experimental data. Fitting parameters of three models for MOF-808, MOF-808-SA, MOF-808-MA, and MOF-808-OA were summarized in the following table (Table S2). The Langmuir–Freundlich model yielded the best fit for all adsorbents.

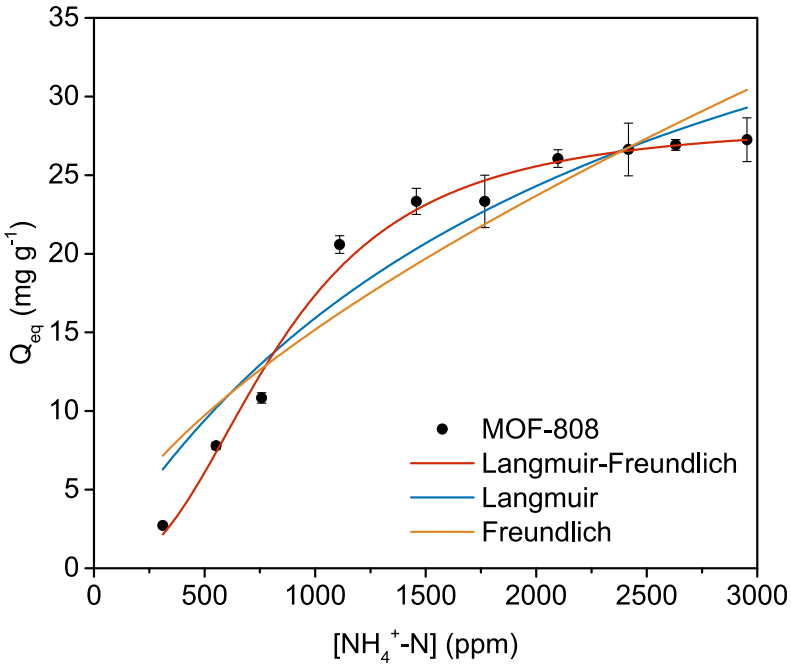

Figure S14. Comparison of Langmuir, Freundlich, and Langmuir–Freundlich models of MOF-808 for fitting the

experimental uptake data.

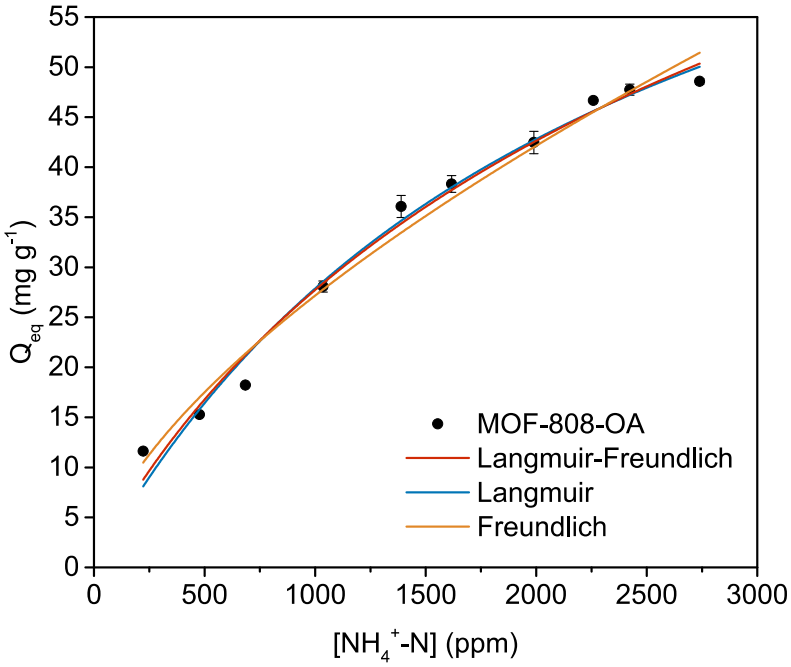

Figure S15. Comparison of Langmuir, Freundlich, and Langmuir–Freundlich models of MOF-808-OA for fitting the experimental uptake data.

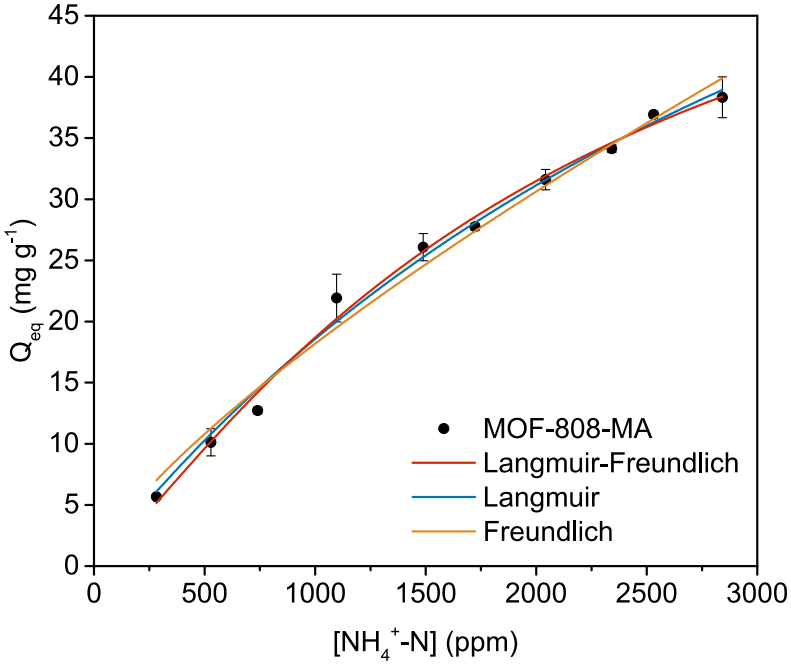

Figure S16. Comparison of Langmuir, Freundlich, and Langmuir–Freundlich models of MOF-808-MA for fitting the

experimental uptake data.

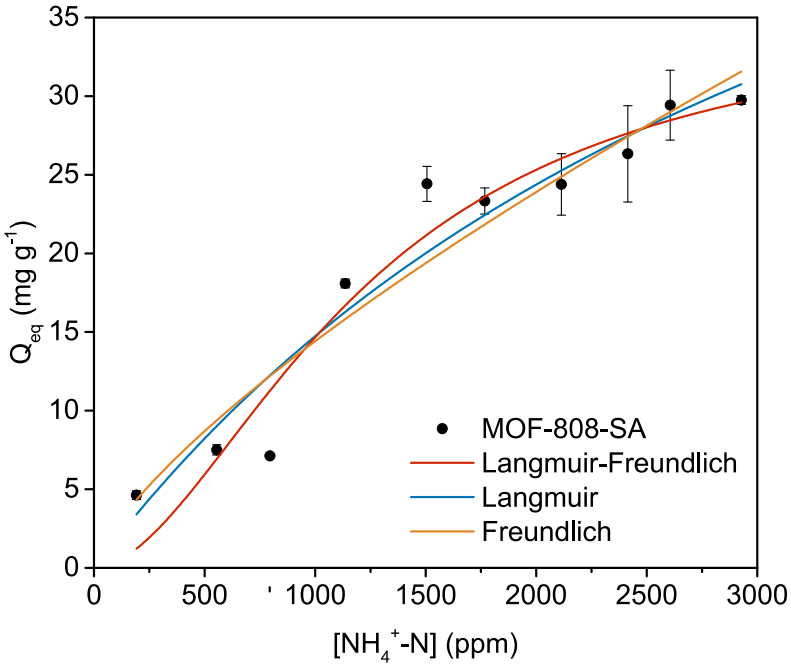

Figure S17. Comparison of Langmuir, Freundlich, and Langmuir–Freundlich models of MOF-808-SA for fitting the experimental uptake data.

Table S2. Fitting parameters of three different models for MOF-808-based adsorbents.

Langmuir, $Q_{eq} = \frac{Q_{sat}K_LC_e}{1+K_LC_e}$			
	Q_{sat} (mg g^{-1})	K_L (L mg^{-1})	R^2
MOF-808	51.47106	4.7151*10^{-4}	0.92128
MOF-808-SA	70.63362	2.63402*10^{-4}	0.92361
MOF-808-MA	96.24274	2.39109*10^{-4}	0.99152
MOF-808-OA	92.17529	4.33557*10^{-4}	0.98305
Freundlich, $Q_{eq} = K_F C_e^{\frac{1}{n}}$			
	K_F (L$^{1/n}$ mg$^{-1/n}$)	n	R^2
MOF-808	0.17906	1.55601	0.87519
MOF-808-SA	0.09316	1.37022	0.91011
MOF-808-MA	0.10093	1.32989	0.98358
MOF-808-OA	0.34153	1.57846	0.97915

Langmuir- Freundlich, $Q_{eq} = \frac{Q_{sat}(K_{LF}C_e)^{\frac{1}{n}}}{1+(K_{LF}C_e)^{\frac{1}{n}}}$				
	Q_{sat} (mg g^{-1})	K_{LF} (L$^{1/n}$ mg$^{-1/n}$)	n	R^2
MOF-808	28.35427	4.02817*10^{-8}	0.39507	0.98696
MOF-808-SA	35.71255	2.66543*10^{-6}	0.55382	0.92753
MOF-808-MA	65.28451	9.03994*10^{-5}	0.82257	0.99253
MOF-808-OA	112.58567	2.88443*10^{-4}	1.11177	0.98545

Adsorption kinetics experiment

MOF-based adsorbents were added into a 50 mM ammonium bicarbonate solution with a loading of 50 g/L. The mixtures were rotated at 10 rpm at room temperature for 90 min, during which aliquots were taken at intervals. MOF powders were separated and ammonium levels in the resulting solutions were analyzed with the colorimetric assay.

Regeneration of MOF-808-OA and ammonium recovery

Exhausted MOF-808-OA was mixed with $NaNO_3$ solution (1M, 10g/L) and left at a rotate revolver at 10 rpm overnight. Suspension was centrifuged and concentration of ammonium in the supernatant was measurement. Nitrogen recovery efficiency was calculated using the following equation:

$$\text{Recovery Efficiency} = \frac{C_r \times V_r}{m} \times 100\%$$

where C_r is the ammonium concentration in the regeneration reagent after the treatment, V is the volume of the regeneration reagent, and m is the mass of adsorbed nitrogen.

S8. Computation Studies on Adsorption of Ammonium by MOF-808-Based Adsorbents

System preparation

A unit cell with dimension 3.5 nm x 3.5 nm x 3.5 nm was created to accommodate 96 Zr MOF-808 clusters. The pristine MOF-808 structure[28] was modified to incorporate oxalic acid, malonic acid, or succinic acid for MOF-808-OA, MOF-808-MA, or MOF-808-SA, respectively. To simulate actual experimental conditions, all hydrogen (H) atoms of the carboxylic acid groups that serve as ammonium adsorption sites were removed. The amount of acids present in the unit cell reflect the experimental measured amount of 3 acids per pore for OA, 6 for MA and 6 for SA, respectively. The unit cell was then solvated with water molecules, as described with the SPC model. In order to reproduce the experimental condition of the highest absorption concentration (around 2700 ppm), various numbers of ammonium ions were added to the solvated system. In particular, 73, 66, 54 and 38 ammonium cations per cell were added for MOF-808-OA, MOF-808-MA, MOF-808-SA and MPOF-808, respectively. To assure neutrality of the whole system, a balanced number of bicarbonate and hydronium ions were added.

Molecular dynamic simulations

For all four different systems, we used the following protocol for the molecular dynamics (MD) simulations. First, we performed a 500 steps of steepest descents minimization followed by 500 steps of conjugate gradient minimization. Then, the system was heated to 298 K using the NVT ensemble for 10 ps, followed by a 2 ns equilibration in the NPT ensemble. Finally, a 15 ns NVT of MD was followed with geometrical analyses preformed. We used the LAMMPS software[66] with the UFF force field for all MD simulations,[67] with default atom types and charge. A timestep of 0.5 fs was used for all systems and the coordinates and velocity were saved every ns.

The same MD protocol was used to obtain the production dynamics for the ions when solvated in water but without the MOF. The same amount of ions as described before (73, 66, 54 and 38 ammonium cations and bicarbonates ions per cell, for the four systems) were considered.

Two-phase thermodynamic (2PT) simulations

The last frame of the production MD simulation was used as input to run three 20 ps long NVT MD simulations at room temperature, which were subsequently used for the 2PT analysis,[66] for each system. The same software, forcefield and parameters as the MD protocol described before were considered. A timestep of 0.5 fs was used for all systems and the coordinates and velocity were saved every fs.

We refer to the previous reports for a detailed description of the 2PT method and theory.[48–50] Briefly, from the classical MD simulation the program calculates the velocity autocorrelation function of each saved time step and takes the Fourier transform to obtain the vibrational density of states (DOS). Finally, the DOS is used as the partition function to calculate various thermodynamic properties, including the free energy to assess the strength of the ionic interactions in the systems. Thus, we compute the free energy from three 20 ps MD for each system and reported the average values and uncertainty. The 2PT analysis allows the free energy of the whole system to be partitioned into that for each molecular group, where we report the values for ammonium as a separate group from the rest.

The same MD protocol and 2PT analysis were also used for the ions immersed in water, without the presence of the MOF, but in the same concentration to have a reference point for each system studied. The final difference in free energy is obtained by subtracting the energy of the ions in water from those in the MOF.

Radial distribution function and cumulative distribution function analyses

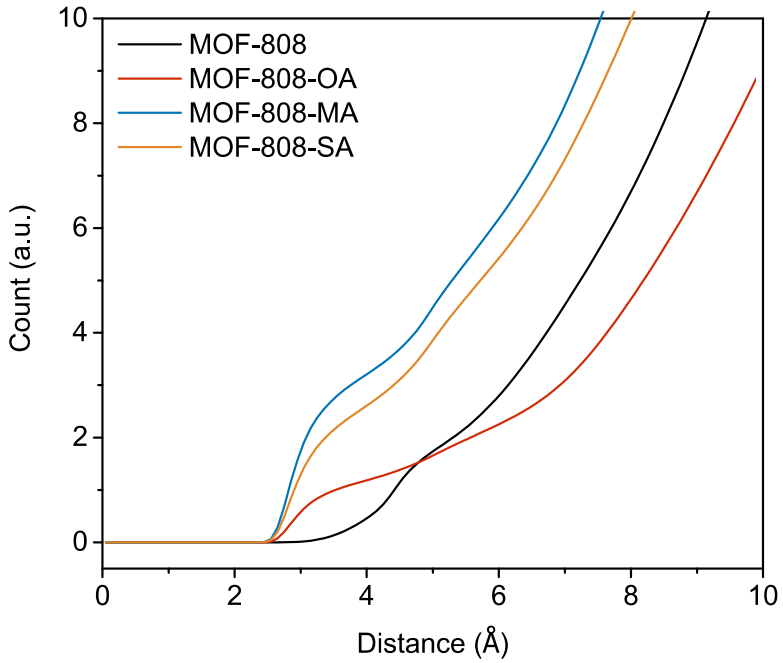

Figure S18. Cumulative distribution function (CDF) analyses of four MOF systems. For MOF-808-OA, MOF-808-MA, and MOF-808-SA, the RDF intensity of carboxylate oxygen and ammonium nitrogen was integrated, whereas for MOF-808, the RDF intensity of formate hydrogen and ammonium nitrogen was integrated.

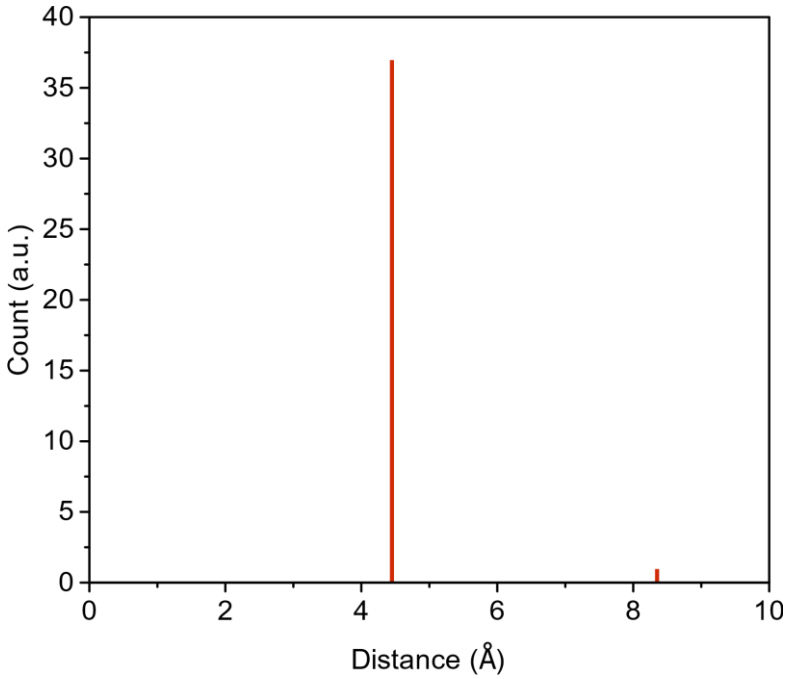

Figure S19. Histogram of the RDF analysis for each ammonium-H pair present in the MOF-808 system.

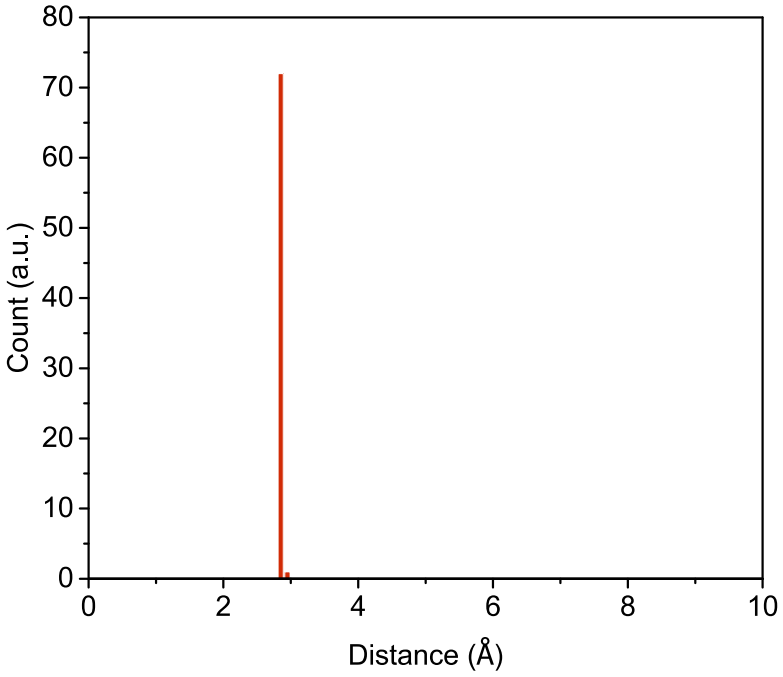

Figure S20. Histogram of the RDF analysis for each ammonium-oxygen pair present in the MOF-808-OA system.

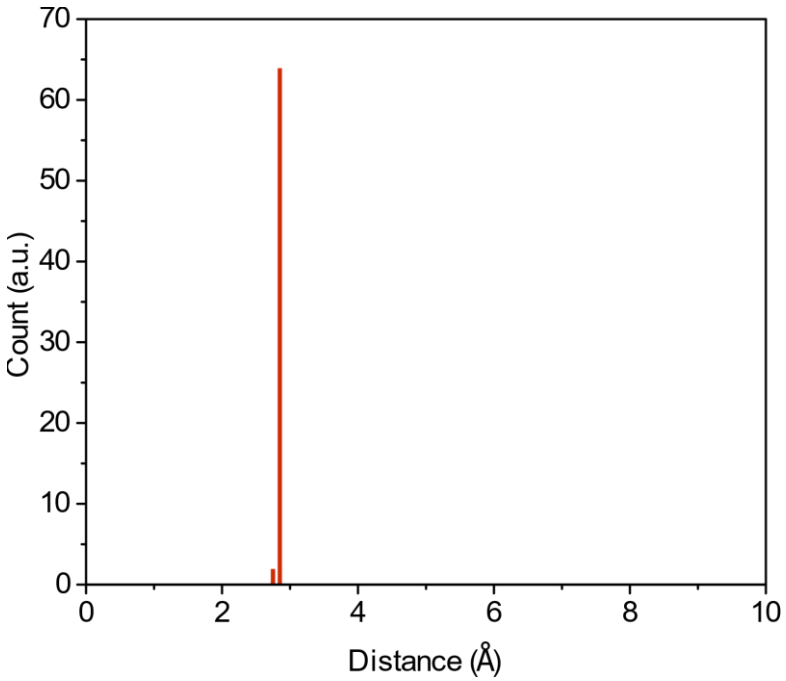

Figure S21. Histogram of the RDF analysis for each ammonium-oxygen pair present in the MOF-808-MA system.

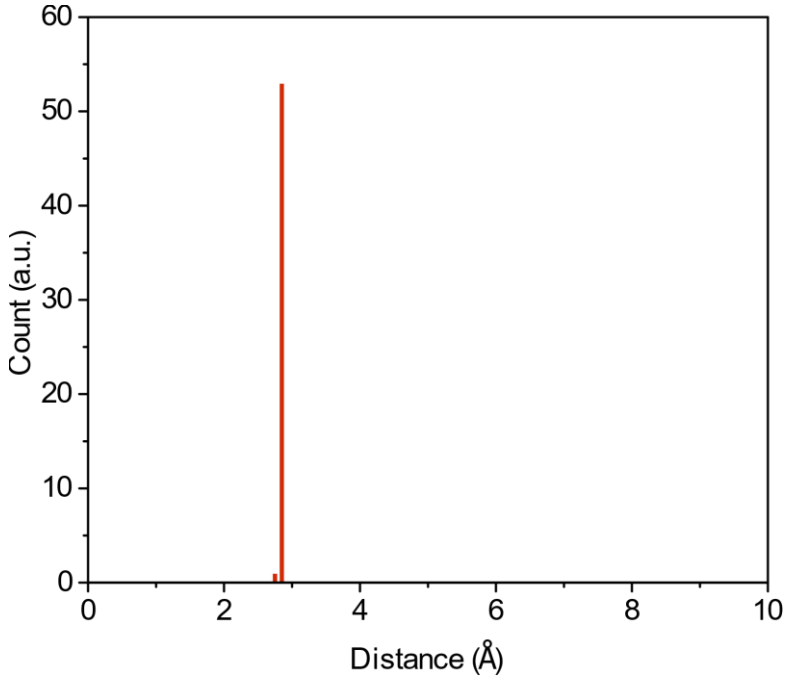

Figure S22. Histogram of the RDF analysis for each ammonium-oxygen pair present in the MOF-808-SA system.

2PT free energy analysis

The adsorption free energy for ammonium uptake by MOF systems Q was calculated with the following equation:

$$Q_{adsorption} = E_{MOF\text{-}ammonium} - E_{ammonium(aq)}$$

Free energy values are reported in Table S3.

Table S3. Adsorption free energies of all MOF systems

Free Energy (kcal/mol)	MOF-808	MOF-808-OA	MOF-808-MA	MOF-808-SA
$E_{MOF\text{-}ammonium}$	-1138	-2181	-2246	-1527
$E_{ammonium(aq)}$	1034	2356	2057	1582
$Q_{adsorption}$	-2172	-4537	-4303	-3109

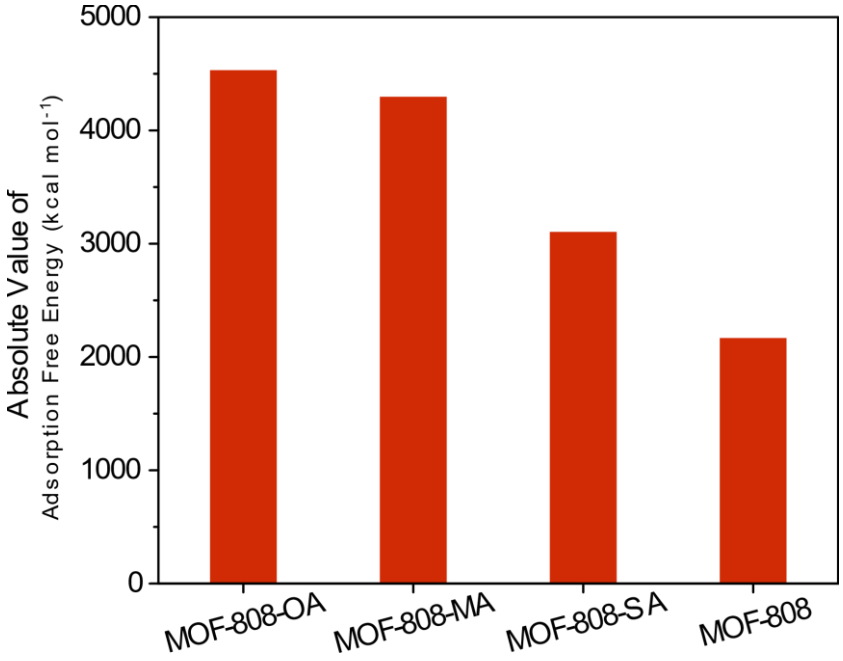

Figure S23. Histogram of the adsorption free energy (absolute value) of all MOF systems.

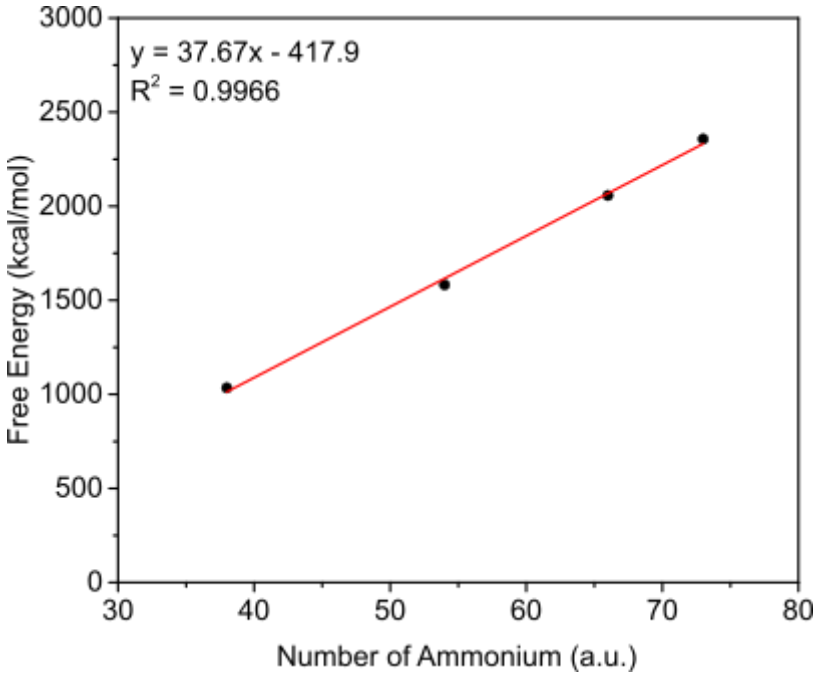

Figure S24. Free energy of different amount of ammonium ions in water solution. The high linearity of the curve indicates the validity of the 2PT analysis.

Table S4. Summary of simulation results of ammonium binding onto MOF-based adsorbents

System	MOF-808	MOF-808-OA	MOF-808-MA	MOF-808-SA
# of carboxylate O per ammonium-N	-	1.24	3.33	2.74
Distance between carboxylate O and ammonium-N (nm)	0.445 (formate-H and ammonium-N)	0.285	0.285	0.285
Adsorption free energy (kcal/mol)	-2172	-4537	-4303	-3109
Pore radius (nm)	1.84-1.91	1.74-1.81	1.56-1.62	1.49-1.55

Pore size analysis

In order to assess the pore size distribution, MD simulations using the same protocol as described above but at 77K were performed on the four different acid modified and solvated MOF systems. After the 15 ns MD calculation, the last frame of the simulation was extracted and used as input for the void analysis. The Free Volume Calculator tool of the Maestro software[13] was used, considering a probe radius of 0.15 nm and a grid spacing of 0.025 nm. The results of the analysis are reported in Table S5.

Table S5. Pore size analysis of all MOF systems

System	MOF-808	MOF-808-OA	MOF-808-MA	MOF-808-SA
Free volume (%)	52.08	44.56	32.67	28.95
Mean void size (nm^3)	0.331	0.244	0.112	0.0978
Radius (nm)	1.84-1.91	1.74-1.81	1.56-1.62	1.49-1.55

S9. Detection of Ammonium with MOF-808-Cu

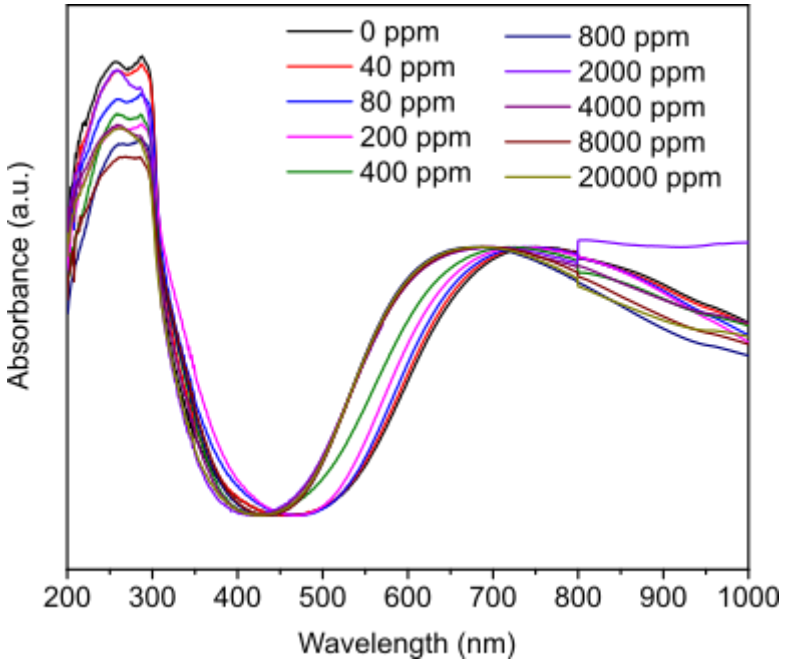

Figure S25. UV−vis diffuse reflectance spectra for MOF-808-Cu after exposing to ammonium hydroxide solutions of different concentrations.

Colorimetric response of MOF-808-Cu with ammonium

MOF-808-Cu was suspended in ammonium hydroxide solutions (40 g/L) and an immediate color change was detected from pale green to blue. RGB channels were extracted from the digital images of the samples taken with an iPhone SE2 using an online application Color Picker (https://imagecolorpicker.com/en).

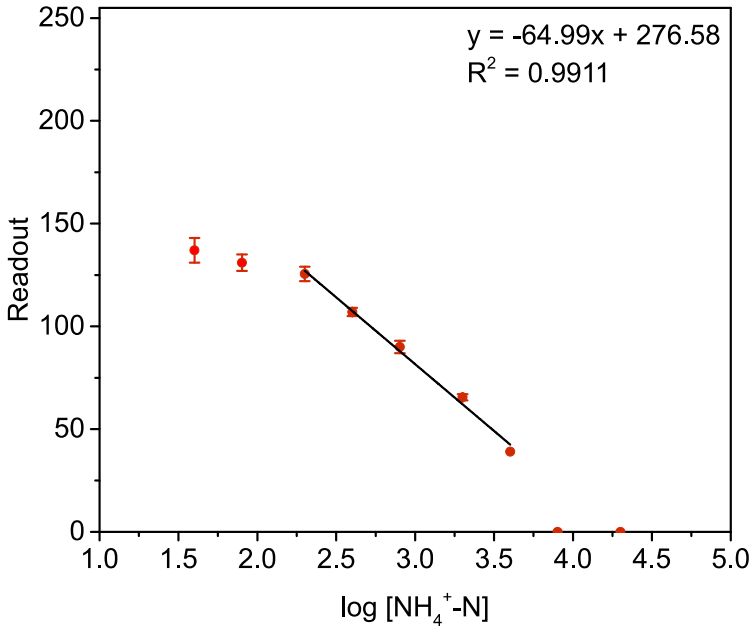

Figure S26. Relationship between ammonium concentrations vs. R value of MOF-808-Cu upon exposure to ammonium hydroxide solutions.

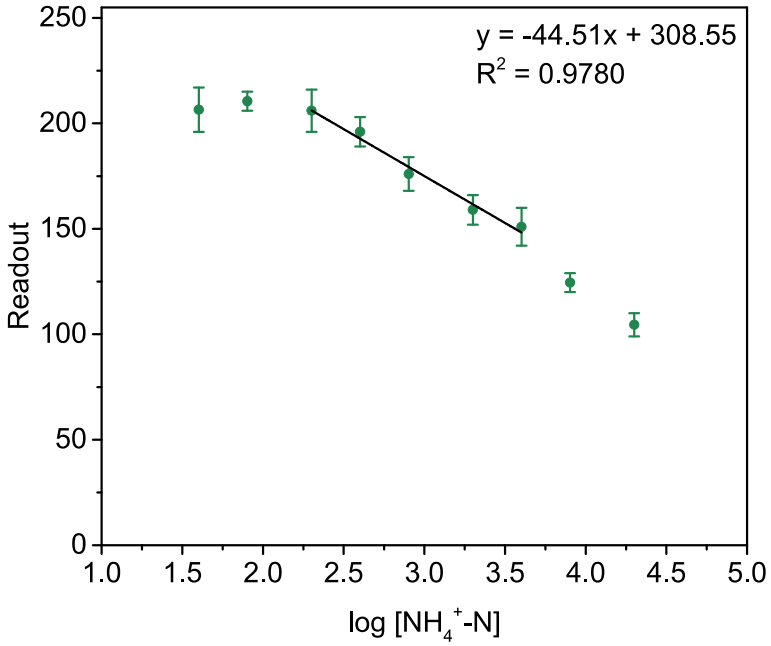

Figure S27. Relationship between ammonium concentrations vs. G value of MOF-808-Cu upon exposure to ammonium hydroxide solutions.

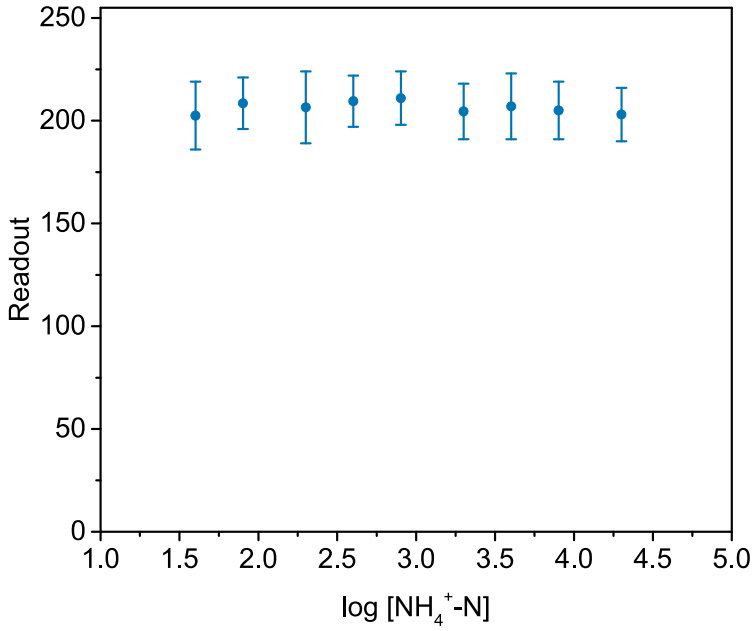

Figure S28. Relationship between ammonium concentrations vs. B value of MOF-808-Cu upon exposure to ammonium hydroxide solutions.

S10. XAS Analysis for MOF-808-Cu

Bulk X-ray spectroscopy was collected at the Stanford Synchrotron Radiation Lightsource (SSRL) using beamline 4-1. The incident x-ray energy was obtained using a Si (220) double crystal monochromator, with the Stanford Positron Electron Accelerating Ring (SPEAR) storage ring containing 500 mA at 3.0 GeV in top-off mode. Samples were prepared by depositing a few mg of sample into an Al sample holder slot and sealed with mylar tape. Samples were mounted in the beam with a motorized sample positioning system. The incident and transmitted x-ray intensities were measured with nitrogen-filled ion chambers. Energy calibration of the monochromator was monitored using a Cu foil measured in transmission geometry between two ion chambers after the sample. The maximum of the first derivative of the Cu foil was defined to be 8989 eV. Fluorescence detection of Cu K-alpha fluorescence was measured using a PIPS photodiode detector. Samples were mounted at 45° to the incident x-ray beam to minimize scattering. The spectra were collected from 200 eV below the Cu K-edge to ~1200 eV above the edge, with a minimum counting time of 1 s per point below the edge, up to 30 s per point at the end of the scan. Each scan had a length of approximately 25 minutes. For each sample, approximately 5-15 replicates were measured, depending on the Cu concentration in the sample, to achieve the desired counting statistics and check for potential beam damage. Spectroscopy data were analyzed using standard methods with the SIXPACK software package.[68] The amplitude reduction factor was determined using a $CuSO_4$ $5H_2O$ standard with known Cu-O coordination and fixed for the extended x-ray absorption fine structure (EXAFS) fitting of the samples. Calculations of the theoretical EXAFS for Cu-O and Cu-Zr shells were performed using the FEFF7 package.[69]

Table S6. EXAFS fitting results for MOF-808-Cu and MOF-808-Cu-NH_3.

	Shell	Coordination number	Distance (Å)	Debye-Waller factor ($\Delta\sigma^2$, Å^2)
MOF-808-Cu	Cu-O	4.2±0.9	1.92±0.01	0.001±0.001
	Cu-Zr	1.75±1.2	3.19±0.09	0.015±0.01
	R factor: 0.0709, E_0: -6.87 eV, S_0^2: 0.63			
MOF-808-Cu-NH_3	Cu-O	3.9±0.3	1.951±0.005	0.003±0.001
	Cu-Zr	1.30±1.0	3.28±0.02	0.008±0.005
	R factor: 0.0114, E_0: 0.65 eV, S_0^2: 0.63			

In the EXAFS analysis of MOF-808-Cu, since O and N are of similar Z, they cannot be effectively distinguished at similar bind distances to the Cu metal. However, although the EXAFS fitting was only performed with O ligands, the Cu-O distance lengthens by 0.03 Å, and the Debye-Waller parameter for the first shell increases by a factor of three. This is suggestive of a mixed coordination compared to the sample without NH_3, showing higher disorder and longer distances (the Cu-N bond is longer than the Cu-O bond). Interestingly, for the fitting of the Cu-Zr shell in this sample, the bond distance increases by 0.09 Å and its disorder parameter decreases in half, as seen by an increase in the overall amplitude of the second shell of the EXAFS. This suggests that the NH_3 coordination to the Cu metal decreases its static disorder, likely due to steric effects of the larger NH_3 ligand vs. OH.

S11. Nitrogen Recovery from Fresh Urine with Functionalized MOFs

The relevant performances of all three functional MOFs were studied carefully during treatment. Near-complete conversion of urea was achieved for first three cycles with MOF-808-U with the hydrolysis activity decreasing slightly to 70% after five successive cycles (Figure S27). In the case of MOF-808-OA, ammonium uptake was influenced by the presences of competing ions (e.g., Na^{+}, Ca^{2+}) (Figure S28). Uptake of urea was also observed with MOF-808-OA, probably due to sorption via Van der Waals interactions and hydrogen bonding between urea and the MOF backbone.[70–72] Even though adsorbed urea competes with the uptake of ammonium, the total nitrogen capture capacity was not significantly influenced since urea is also a nitrogen rich species. We also found the nitrogen recovery efficiency focusing on the adsorption process (MOF-808-OA) to be efficient (Figure S29).

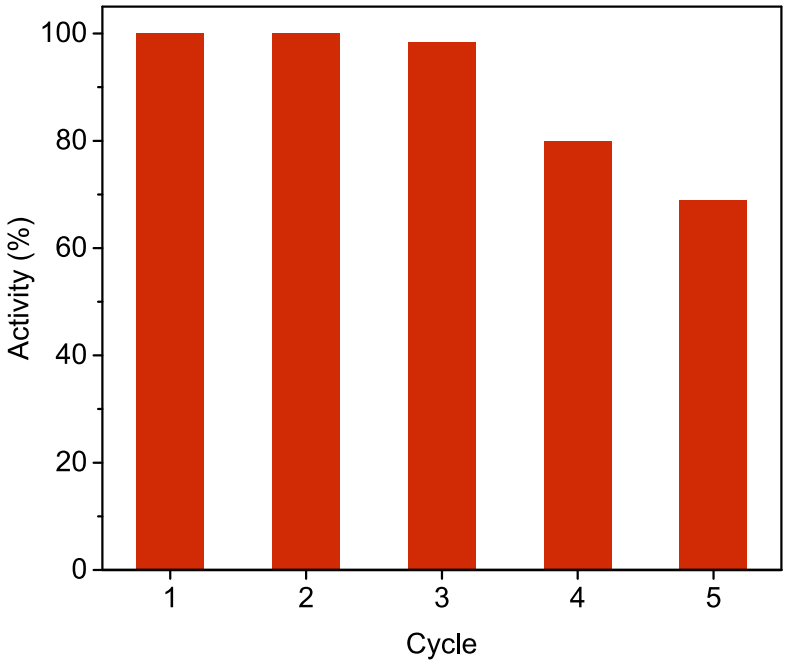

Figure S28. Catalytic activity of MOF-808-U in five successive cycles.

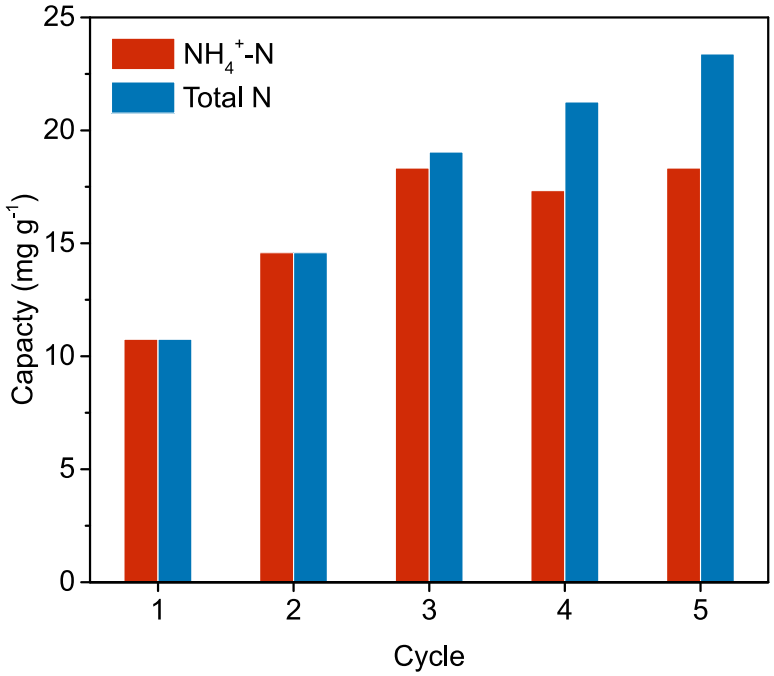

Figure S29. Ammonium and total nitrogen (including urea) capture capacity of MOF-808-OA in five cycles of treatment.

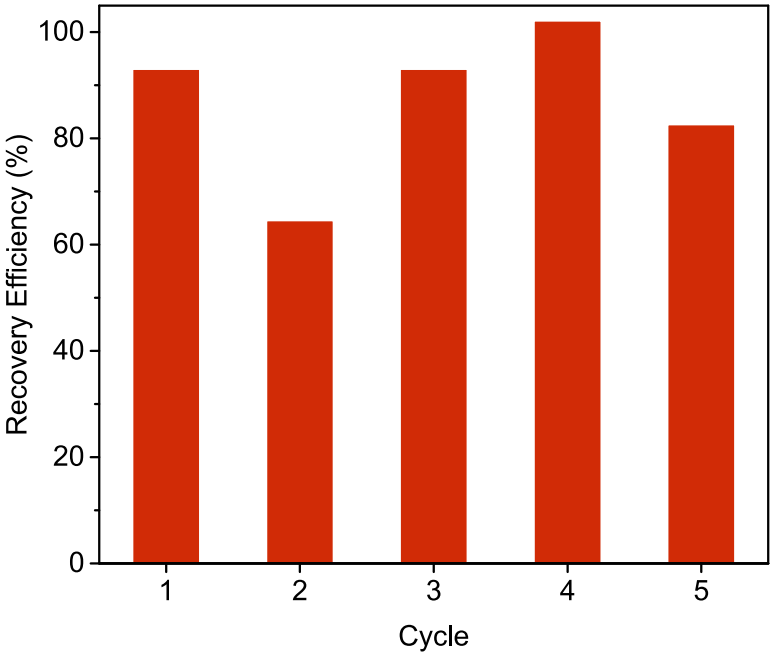

Figure S30. Total nitrogen (NH_4^+-N and urea) recovery efficiency of MOF-808-OA in five cycles of treatment.

S12. Cost analysis of current and alternate N recovery processes

Cost analysis of MOF production.

Costs for reagents for functionalized MOF synthesis are listed in **Table S7**. In order to estimate the annual cost of all materials and to cover all possible application scenarios, we herein apply a factor of 10-1000 to the price of pristine MOF substrates by considering reloading of urease, costs of other chemicals, and adjustment of production costs as manufacturing scale increases. Cost analysis of MOF-808-Cu is not considered here as usage of MOF-808-Cu as sensors is minimal compared to MOF-808-U and MOF-808-OA.

Table S7. Costs for reagents for functionalized MOF synthesis.

	Cost ($/kg)	References or Notes
MOF Substrate	30	[73]
Urease	65	https://wap.china.cn/Food-Additives/sentian2/
Oxalic Acid	0.6	https://www.intratec.us/chemical-markets
Functionalized MOFs for annual operation	300-30000	A factor of 10 to the price of pristine MOF substrates for annual usage of functionalized MOFs

Cost analysis of N recovery in this work.

In the current treatment process, 1L urine requires 200 g MOF materials and yields 45% of N recovery product. Considering 1L urine generally contains about 250 mM urea [60], 18 g ammonium nitrate can be produced every 30 min with our process. We therefore extrapolate that 315.36 kg ammonium nitrate can be produced annually with 200 g MOF materials. With the estimated cost of MOF materials listed in Table S7, we further extrapolate that the costs for producing a metric ton of ammonium nitrate in our process is $0.15-15/kg N.

Cost analysis of alternate urine N recovery techniques

We herein refer multiple works treating fresh urine with the recovery products as urea and stored urine by recovering ammonium products. Additionally, we also list here costs for conventional process for ammonia/ammonium production/recovery. Based on the data from this table, our developed N recovery process is comparable to alternate technologies. It is also important to highlight that given our treatment process encompasses both N conversion and recovery, it will greatly save the capital and operation costs for urine collection, transportation, and storage, therefore it further reduces potential costs and much more suitable for decentralized treatment.

Table S8. Cost comparison on current N production/recovery techniques.

Techniques	N Sources	Cost	Products	References
Haber-Bosch process		10.3−12.5 kWh/kg N	Ammonia	[14]
Conventional gas stripping		3.9−28.2 kWh/kg N	Ammonia	[14]
Electrolysis cell with strip/bacteria	Stored urine	2.6−13. kWh/kg N	Ammonium	[14]
Electrolysis cell with strip/acid	Stored urine	8−13.7 kWh/kg N	Ammonium	[74]
Adsorption	Stored urine	$7.40/kg N with clinoptilolite used once	Ammonium	[11]
		$6.00/kg N with Dowex Mac 3 used 100 times	Ammonium	[11]
Ammonia stripping–acid absorption	Stored urine	$13.7 per 10 000 L urine (pH 9.2, 22 °C)	Ammonium	[15]
		$94 per 10 000 L urine (pH 10.2, 22 °C)	Ammonium	[15]
		$100 per 10 000 L urine (pH 10.2, 70C)	Ammonium	[15]
Microbial fuel cell	Stored urine	3.46 MJ/kg N	Ammonium	[17]
Evaporation and recrystallization	Fresh urine	35.5 MJ/kg N	Urea	[5]
Forward osmosis and membrane distillation	Fresh urine	$143–238 /100 m^3 urine	Urea	[6]
		-$2.05–-84.65 (profit)/100 m^3 urine (50% N recovery efficiency and alternative energy use is included	Urea	[6]
MOF-facilitated N recovery	**Fresh urine**	**$0.15-15/kg N**	**Ammonium**	**This work**

S13. References

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