Supporting Information

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Section S1 General Methods and Materials

Chemicals. Zirconium oxychloride octahydrate ($ZrOCl_2 \cdot 8H_2O$, purity ≥ 98%), tetrahydrofuran (THF), dimethyl sulfoxide-d_6 (DMSO-d_6, 99.9% atom % D), hydrofluoric acid (HF, 48 wt % in water), and deuterium chloride (DCl, 20% solution in deuterium oxide) were obtained from Sigma-Aldrich. 1,3,5-Benzenetricarboxylic acid (H_3BTC) and tris(3-aminopropyl)amine (TAPA, >97%) was obtained from TCI America. Anhydrous *N, N*-dimethylformamide (DMF), formic acid (purity > 98%), acetone (ACS grade), methanol (ACS grade), and hydrochloric acid (HCl, 37% in water) were obtained from Fisher Scientific. Glycine (99%) was obtained Santa Cruz Biotechnology. DL-proline (95%), L-lysine hydrochloride (98%), L-arginine hydrochloride (98%), 3-chloropropionic acid (95%), ethylenediamine (EDA, 95%), 1,3-diaminopropane (DAP, 95%), and tris(2-aminoethyl)amine (TAEA, 95%) were obtained from AK Scientifics. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was obtained from Oakwood Products, Inc. All chemicals were used without further purification.

Sample activation. The MOF samples were activated using a Micromeritics Accelerated Surface Area and Porosimetry (ASAP) 2420 System or under a dynamic vacuum (< 0.05 Torr) with a Schlenk. Full activation details are provided in **Section S2**.

Liquid-state Nuclear magnetic resonance (NMR) spectroscopy. Liquid-state ^1H NMR spectra were acquired on Bruker Avance NEO 500 (500 MHz) spectrometer at 297–300 K at the NMR facility of the College of Chemistry, University of California, Berkeley.

To investigate the amounts of loaded molecules in MOF-808, all samples were washed and activated by the procedure described in **Section S2** for the sample digestion. Activated MOF samples (ca. 10 mg) were digested and sonicated in the mixture of HF (20 μL, 48 wt % in water), DCl (150 μL, 20% solution in deuterium oxide), and DMSO-d_6 (580 μL). This process is termed as "digest NMR" in the context of this work. The loaded molecules in the MOF sample can be identified by adding a small portion of pure molecules to the MOF samples, which are then analyzed by digest NMR with same parameters. The peaks of the targeted molecules in the spectrums can be distinguished with increased integration.

Potentiometric titrations. Potentiometric titrations were conducted using a Metrohm Titrando 905 instrument, which was equipped with a Dosino 800 20 mL dosing unit set to collect the equilibrium pH data. The calibration process involved using commercial pH buffers with values of 2.00, 4.00, 7.00, and 9.00 (Metrohm). Before each titration, the MOF sample was ground using a mortar and pestle. Subsequently,

approximately 50 mg of the sample was dispersed in around 60 mL of a 0.01 M aqueous $NaNO_3$ solution and allowed to reach equilibrium for a duration of 5 minutes. During the titration procedure, a magnetic stir bar was introduced into the titration solution, and the pH was adjusted to a range of 10.5-11 using 0.1 M aqueous NaOH solution. The titration was carried out by adding 0.1 M aqueous HCl solution in increments of 0.025 mL at an injection rate of 0.01 mL min^{-1} until the pH reached 3.

Powder X-ray diffraction (PXRD) analyses. PXRD data were collected on a Bruker D8 Advance or Rigaku Miniflex 600 X-ray diffractometer equipped with a Cu anode (CuKa radiation radiation, $\lambda = 1.54184$ Å, with a 0.6 mm slit and Ni filter) in Bragg-Brentano geometry. For PXRD measurements, the crystalline, powderous samples were mounted on zero-background holders and leveled with a spatula. The PXRD patterns were recorded between 2 and 50° (0.02° per step).

Nitrogen sorption isotherms. Nitrogen sorption isotherms were measured by a Micromeritics ASAP 2420 System with liquid nitrogen bath to maintain the temperature at 77 K for each measurement. Ultra-high-purity (>99.998%, from Praxair) nitrogen and helium (>99%, from Praxair) gases were used throughout the adsorption experiments.

Water vapor sorption isotherms. Water vapor isotherms were measured by a BELSORP MAX II. Before the measurements, the sample was activated at 120 °C for 12 hours and the vapor source was degassed through five cycles of freeze-pump-thaw. The measurement temperature was maintained in a water bath equipped with a thermostatic circulator. UHP-grade helium was used for free space corrections.

CO_2 sorption isotherms. CO_2 sorption isotherms were measured by a Micromeritics 3Flex Adsorption Analyzer with a water circulation bath to maintain the temperature at 288, 298, and 308K. Research-grade CO_2 (99.998%, from Praxair) was used throughout the adsorption experiments.

Dynamic CO_2 breakthrough measurement. Dynamic CO_2 breakthrough measurement were conducted on a Micromeritics Breakthrough Analyzer equipped with an oil circulation bath for sample activation up to 180 °C, a CO_2 sensor (detection limit = 0.6 to 984 ppm), and a humidity sensor. Argon (>99.998%, from Praxair), CO_2 air mixture (1000 ppm, from Praxair), and compressed dry air (79% N_2, 21% O_2, from Praxair) were used throughout the measurements. The humidified compressed air can be obtained by passing the dry air through a water bath, and different relative humidity ranging from 0% to 50% can be fine-tuned by adjusting the blend ratio of the humidified and dry compressed air.

Before the dynamic breakthrough measurement, around 100 mg of the sample powder was placed in the sample column reactor (i.d. 4.9 mm, length 309 mm) and was activated at 140 °C with argon flow (50 sccm) until the detected outlet CO_2 concentration is lower than 5 ± 1 ppm, and the whole system was cooled down to 25 °C before the measurement. The designated gas feed of 400 ppm CO_2 (50 sccm) with different relative humidity (0-50%) was tuned and monitored by humidity sensor and CO_2 sensor until reach equilibrium (outlet CO_2 concentration = 395 ± 5 ppm, relative humidity = 0, 10, 25, or 50 within 5% deviation), and the gas value was then switched to the column reactor for the measurement. The measurement was terminated 30 minutes after the detected outlet CO_2 concentration was reached 395 ± 5 ppm.

For cycling test with breakthrough analyzer, the sample was activated at 60°C for 15 minutes, followed by at 140 °C with argon flow (50 sccm) until the detected outlet CO_2 concentration is lower than 20 ppm. The gas value was then switched to the column reactor for the measurement, which was terminated once the detected outlet CO_2 concentration was reached 380 ppm.

Solid-state NMR spectroscopy. Solid-state ^{13}C NMR experiments were conducted on a Bruker AV-500 (500 MHz) or a Bruker Avance NEO 400 (400 MHz) spectrometer at 297–300 K at the NMR facility of the College of Chemistry, University of California, Berkeley. The MOF samples were washed, activated by the procedure described in **Section S2**. Following this, the solid-state NMR spectra of these samples were measured under three distinct conditions: (1) activated samples, (2) adsorption of CO_2 under dry condition, and (3) adsorption of CO_2 with 50% RH. To facilitate sample humidification, Micromeritics Breakthrough Analyzer was employed. Approximately 50 mg of sample powder was loaded into a column reactor, where it was activated and exposed to humid air with 50% RH until saturation was reached. For CO_2 adsorption, the sample was exposed to $^{13}CO_2$ gas (2.47 atm, Sigma Aldrich, 99% atom ^{13}C) with the home-built gas dosing apparatus for 24 hours at room temperature. Next, the solid was evacuated (< 0.1 Torr) under dynamic vacuum at room temperature for 3 h to remove excess CO_2.

Section S2 Synthetic Procedures

Synthesis and activation of MOF-808. Microcrystalline MOF-808 was synthesized and activated slightly modified from our previous reported procedure[1, 2]. In a 1000 mL Pyrex media storage bottle (polypropylene plug sealed screw cap), $ZrOCl_2 \cdot 8H_2O$ (9.7 g, 30 mmol) and H_3BTC (2.1 g, 10 mmol) are fully dissolved in 450 mL DMF. Afterwards, 450 mL formic acid is further introduced, and the reaction mixture is shaken to homogeneity, sealed, and incubated in a pre-heated oven at 130 °C for 48 h. After cooling to room temperature, the supernatant is decanted, and the obtained white solid is collected into a 125 mL Nalgene HDPE lab sample bottle, centrifuged, and decanted. The remaining slurry is resubmerged with DMF (100 mL) and shaken to a fine dispersion, which are repeated three times per day over 3 days. The same procedure is carried out with deionized water for 3 days followed by acetone for 1 day. Next, the solid is centrifuged and dried at room temperature by a rotary evaporator and evacuated (< 0.1 Torr) under dynamic vacuum at 60 °C for 3 h, followed by at 140 °C for 24 h to yield the activated product. After cooling to room temperature, the solid is transferred into a glovebox or immediately used.

Synthesis and activation of MOF-808-FR. Activated MOF-808 powder (5 g) is placed in a clean 125 mL Nalgene HDPE bottle, and 100 mL 1 mol L^{-1} hydrochloric acid (HCl) aqueous solution is introduced. The mixture is shaken vigorously by an orbital shaker for 30 min, and then heated in a pre-heated oven at 85 °C for 5 days. During this period, the mixture is cooled to room temperature, centrifuged, decanted the supernatant, and replaced with fresh 1 mol L^{-1} HCl aqueous solution three times a day. Next, after cooling to room temperature, the remaining slurry is centrifuged, decanted, and treated with the same procedure using deionized water three times a day over a period of 3 days followed by acetone three times a day for 1 day. Next, the solid is centrifuged and dried at room temperature by a rotary evaporator and evacuated (< 0.1 Torr) under dynamic vacuum at 60 °C for 3 h, followed by at 140 °C for 24 h to yield the activated product. After cooling to room temperature, the solid is transferred into a glovebox or immediately used.

Synthesis and activation of MOF-808-Gly. In a 250 mL Pyrex media storage bottle (polypropylene plug sealed screw cap), to the activated MOF-808-FR powder (1 g) is introduced a freshly-prepared aqueous glycine solution (3 mol L^{-1}, 200 mL). The mixture is shaken gently and heated in a pre-heated oven at 85 °C for 3 days. During this period, the supernatant is decanted and replaced with the same freshly-prepared aqueous glycine solutions, which is repeated twice a day over a period of 3 days. The sample is then cooled to room temperature, centrifuged, and decanted. The resulting solid was collected by centrifugation and washed with deionized water (40 mL) three times a day over a period of 3 days. The solid is further treated with acetone (40 mL) three times in 1 day, followed by a 10% solution of DBU in THF (40 mL) twice a

day in 1 day for amine deprotonation, and fresh THF (40 mL) three times a day in 1 day prior to activation. Afterwards, the solid is isolated by centrifugation, and dried under a dynamic vacuum at 30 °C for 3 h, 60 °C for 2 h, and 140 °C for 20 h to obtain activated MOF-808-Gly. After cooling to room temperature, the solid is transferred into a glovebox or immediately used.

Synthesis and activation of MOF-808-Pro. In a 250 mL Pyrex media storage bottle (polypropylene plug sealed screw cap), to the activated MOF-808-FR powder (1 g) is introduced a freshly-prepared aqueous DL-proline solution (3 mol L^{-1}, 200 mL). The mixture is shaken gently and heated in a pre-heated oven at 85 °C for 3 days. During this period, the supernatant is decanted and replaced with the same freshly-prepared aqueous DL-proline solutions, which is repeated twice a day over a period of 3 days. The sample is then cooled to room temperature, centrifuged, and decanted. The resulting solid was collected by centrifugation and washed with deionized water (40 mL) three times a day over a period of 3 days. The solid is further treated with acetone (40 mL) three times in 1 day, followed by a 10% solution of DBU in THF (40 mL) twice a day in 1 day for amine deprotonation, and fresh THF (40 mL) three times a day in 1 day prior to activation. Afterwards, the solid is isolated by centrifugation, and dried under a dynamic vacuum at 30 °C for 3 h, 60 °C for 2 h, and 140 °C for 20 h to obtain activated MOF-808-Pro. After cooling to room temperature, the solid is transferred into a glovebox or immediately used.

Synthesis and activation of MOF-808-Lys. In a 250 mL Pyrex media storage bottle (polypropylene plug sealed screw cap), to the activated MOF-808-FR powder (1 g) is introduced a freshly-prepared L-lysine hydrochloride ethylene glycol solution (0.684 mol L^{-1}, 200 mL). The mixture is shaken gently and heated in a pre-heated oven at 120 °C for 1 day. During this period, the supernatant is decanted and replaced with the same freshly-prepared L-lysine hydrochloride solutions, which is repeated twice a day. The sample is then cooled to room temperature, centrifuged, and decanted. The resulting solid was collected by centrifugation and washed with ethylene glycol (40 mL) three times a day over 1 day, followed by deionized water (40 mL) three times a day over a period of 4 days. The solid is further treated with acetone (40 mL) three times in 1 day, followed by a 10% solution of DBU in THF (40 mL) twice a day in 1 day for amine deprotonation, and fresh THF (40 mL) three times a day in 1 day prior to activation. Afterwards, the solid is isolated by centrifugation, and dried under a dynamic vacuum at 30 °C for 3 h, 60 °C for 2 h, and 140 °C for 20 h to obtain activated MOF-808-Lys. After cooling to room temperature, the solid is transferred into a glovebox or immediately used.

Synthesis and activation of MOF-808-Arg. In a 250 mL Pyrex media storage bottle (polypropylene plug sealed screw cap), to the activated MOF-808-FR powder (1 g) is introduced a freshly-prepared L-arginine

hydrochloride ethylene glycol solution (0.684 mol L^{-1}, 200 mL). The mixture is shaken gently and heated in a pre-heated oven at 120 °C for 1 day. During this period, the supernatant is decanted and replaced with the same freshly-prepared L-arginine hydrochloride solutions, which is repeated twice a day. The sample is then cooled to room temperature, centrifuged, and decanted. The resulting solid was collected by centrifugation and washed with ethylene glycol (40 mL) three times a day over 1 day, followed by deionized water (40 mL) three times a day over a period of 4 days. The solid is further treated with acetone (40 mL) three times in 1 day, followed by a 10% solution of DBU in THF (40 mL) twice a day in 1 day for amine deprotonation, and fresh THF (40 mL) three times a day in 1 day prior to activation. Afterwards, the solid is isolated by centrifugation, and dried under a dynamic vacuum at 30 °C for 3 h, 60 °C for 2 h, and 140 °C for 20 h to obtain activated MOF-808-Arg. After cooling to room temperature, the solid is transferred into a glovebox or immediately used.

Synthesis and activation of MOF-808-EtCl. In a 250 mL Pyrex media storage bottle (polypropylene plug sealed screw cap), to the activated MOF-808-FR powder (1 g) is introduced a freshly-prepared aqueous 3-chloropropionic acid solution (3 mol L^{-1}, 200 mL). The mixture is shaken gently and heated in a pre-heated oven at 85 °C for 3 days. During this period, the supernatant is decanted and replaced with the same freshly-prepared aqueous 3-chloropropionic acid solutions, which is repeated twice a day over a period of 3 days. The sample is then cooled to room temperature, centrifuged, and decanted. The resulting solid was collected by centrifugation and washed with deionized water (40 mL) three times a day over a period of 3 days followed by acetone (40 mL) three times a day in 1 day. Afterwards, the solid is isolated by centrifugation, and dried under a dynamic vacuum at 30 °C for 3 h, 60 °C for 2 h, and 140 °C for 20 h to obtain activated MOF-808-EtCl. After cooling to room temperature, the solid is transferred into a glovebox or immediately used.

Synthesis and activation of MOF-808-EDA. In a 4 mL glass vial (PTFE sealed screw cap), to the activated MOF-808-EtCl powder (100 mg) is introduced 50% of EDA solution in DMF (2.0 mL) under argon. The mixture is shaken gently and heated in a pre-heated oven at 85 ˚C for 24 h. After cooling down to room temperature, the sample is collected and washed with methanol (10 mL) three times and acetone (10 mL) three times for 1 day. Afterwards, the solid is isolated by centrifugation, and dried under a dynamic vacuum at 30 °C for 3 h, 60 °C for 2 h, and 140 °C for 20 h to obtain activated MOF-808-EDA. After cooling to room temperature, the solid is transferred into a glovebox or immediately used.

Synthesis and activation of MOF-808-DAP. In a 4 mL glass vial (PTFE sealed screw cap), to the activated MOF-808-EtCl powder (100 mg) is introduced 50% of EDA solution in DMF (2.0 mL) under argon. The

mixture is shaken gently and heated in a pre-heated oven at 85 °C for 24 h. After cooling down to room temperature, the sample is collected and washed with methanol (10 mL) three times and acetone (10 mL) three times for 1 day. Afterwards, the solid is isolated by centrifugation, and dried under a dynamic vacuum at 30 °C for 3 h, 60 °C for 2 h, and 140 °C for 20 h to obtain activated MOF-808-DAP. After cooling to room temperature, the solid is transferred into a glovebox or immediately used.

Synthesis and activation of MOF-808-TAEA. In a 4 mL glass vial (PTFE sealed screw cap), to the activated MOF-808-EtCl powder (100 mg) is introduced 50% of TAEA solution in DMF (2.0 mL) under argon. The mixture is shaken gently and heated in a pre-heated oven at 85 °C for 24 h. After cooling down to room temperature, the sample is collected and washed with methanol (10 mL) three times and acetone (10 mL) three times for 1 day. Afterwards, the solid is isolated by centrifugation, and dried under a dynamic vacuum at 30 °C for 3 h, 60 °C for 2 h, and 140 °C for 20 h to obtain activated MOF-808-TAEA. After cooling to room temperature, the solid is transferred into a glovebox or immediately used.

Synthesis and activation of MOF-808-TAPA. In a 4 mL glass vial (PTFE sealed screw cap), to the activated MOF-808-EtCl powder (100 mg) is introduced 50% of TAPA solution in DMF (2.0 mL) under argon. The mixture is shaken gently and heated in a pre-heated oven at 85 °C for 24 h. After cooling down to room temperature, the sample is collected and washed with methanol (10 mL) three times and acetone (10 mL) three times for 1 day. Afterwards, the solid is isolated by centrifugation, and dried under a dynamic vacuum at 30 °C for 3 h, 60 °C for 2 h, and 140 °C for 20 h to obtain activated MOF-808-TAPA. After cooling to room temperature, the solid is transferred into a glovebox or immediately used.

Section S3 Nuclear Magnetic Resonance Analyses of Digested Samples

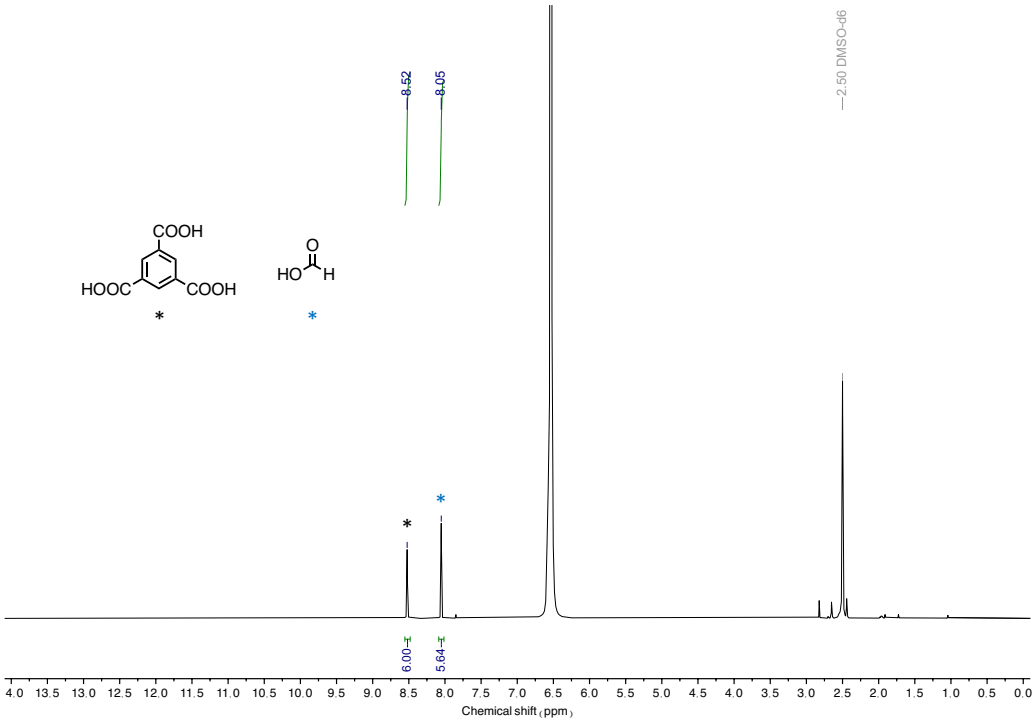

Figure S1. ^{1}H NMR spectrum of digested MOF-808.

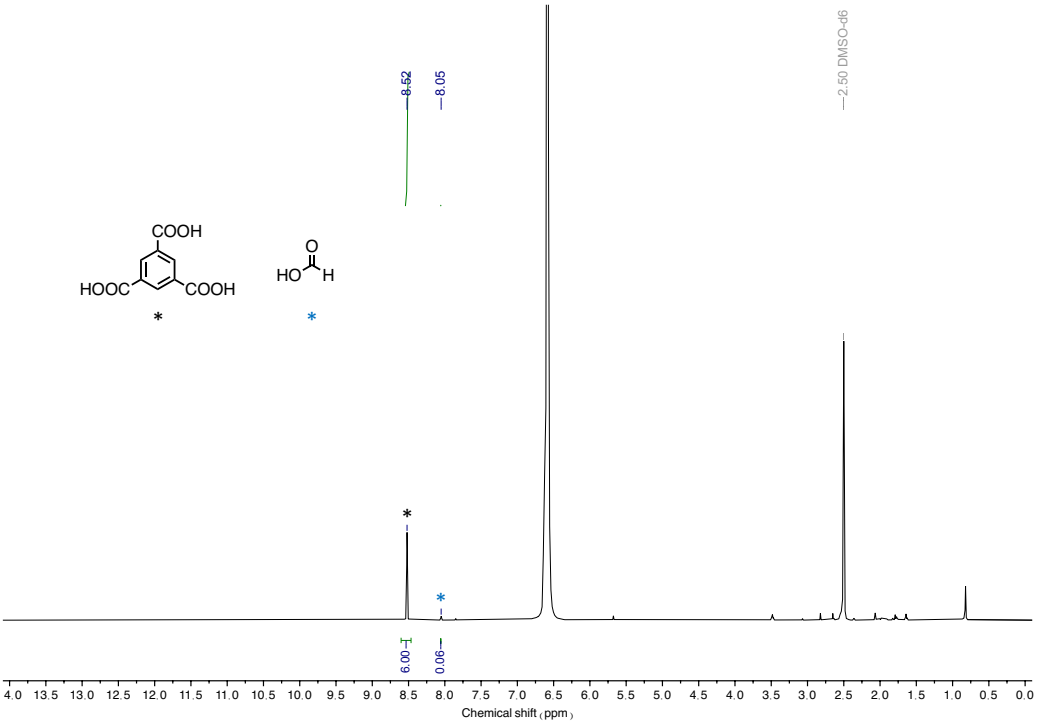

Figure S2. ^{1}H NMR spectrum of digested MOF-808-FR.

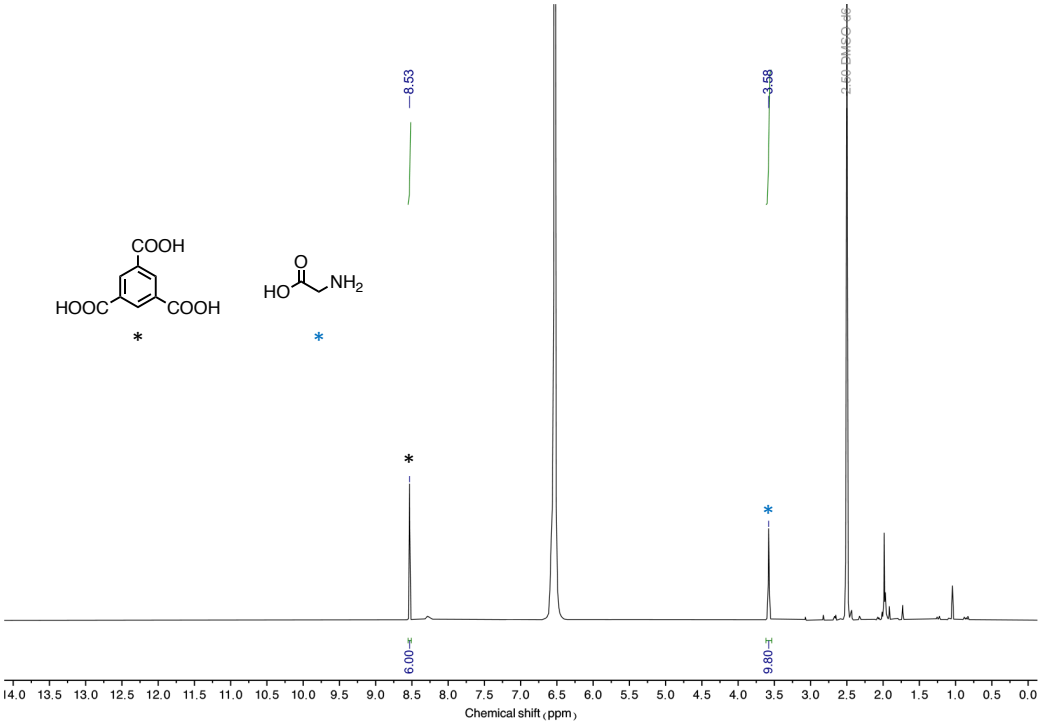

Figure S3. ^{1}H NMR spectrum of digested MOF-808-Gly.

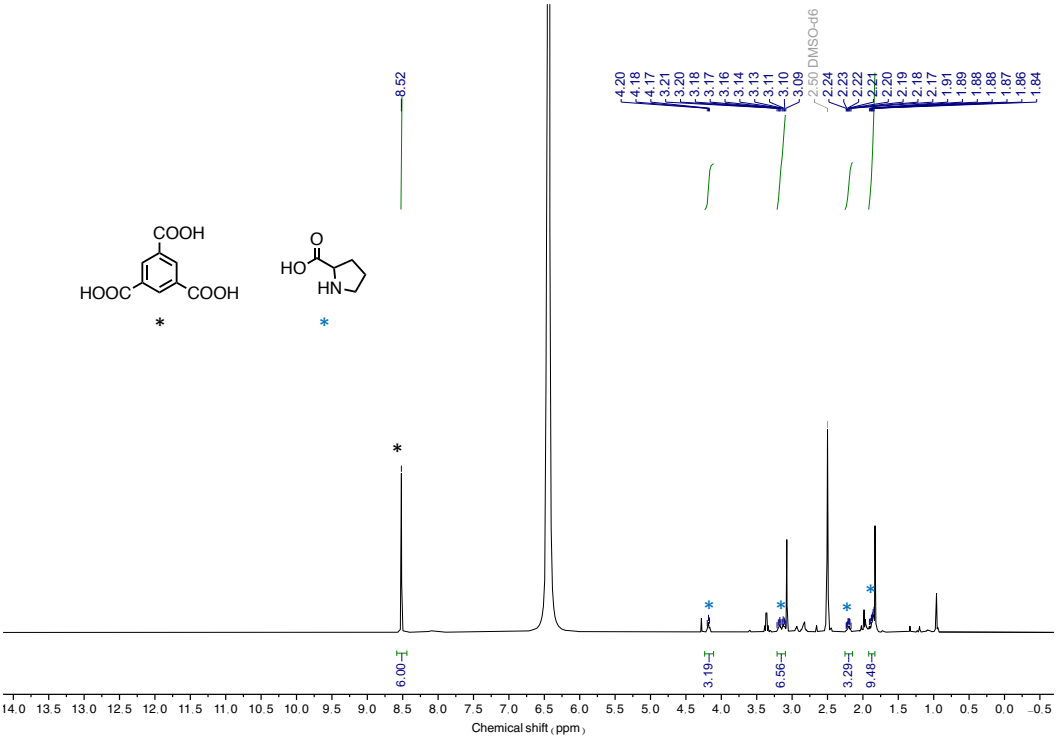

Figure S4. ^{1}H NMR spectrum of digested MOF-808-Pro.

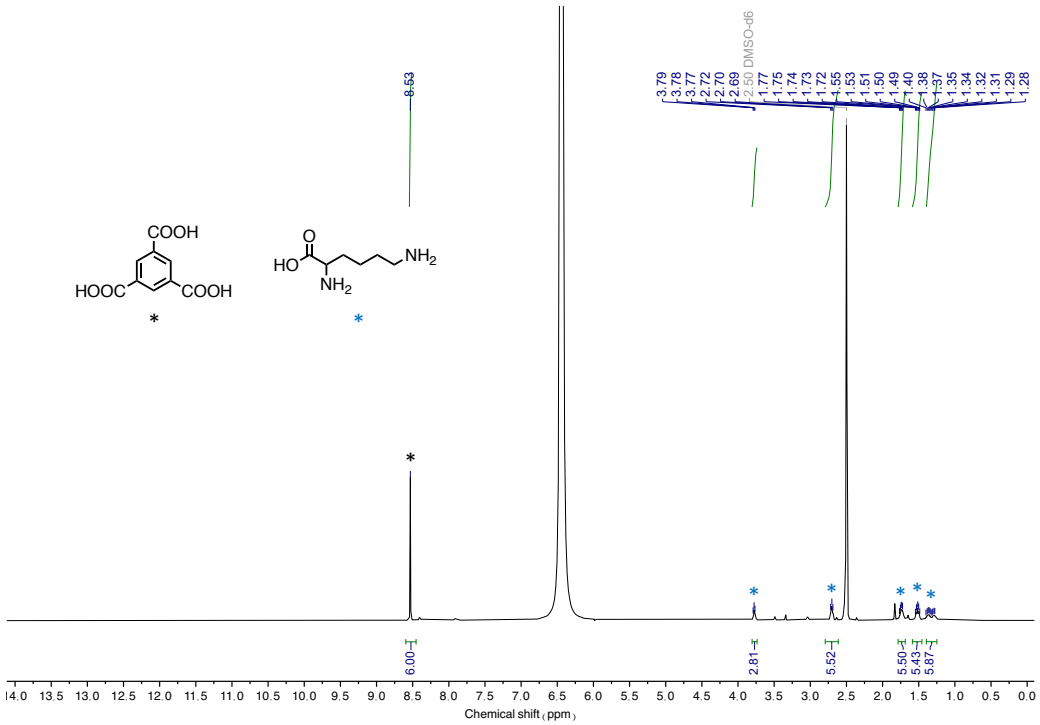

Figure S5. [1]H NMR spectrum of digested MOF-808-Lys.

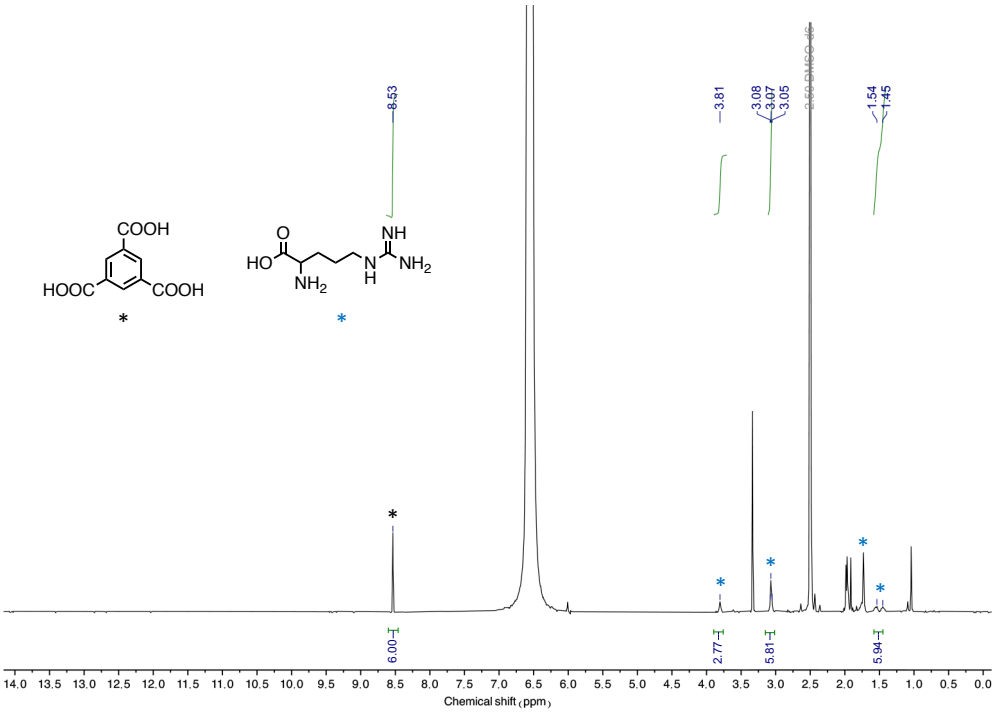

Figure S6. [1]H NMR spectrum of digested MOF-808-Arg. Some peaks of DL-arginine in the digested sample are overlapped with the peaks attributed to residual ethylene glycol (1.76 and 3.33).

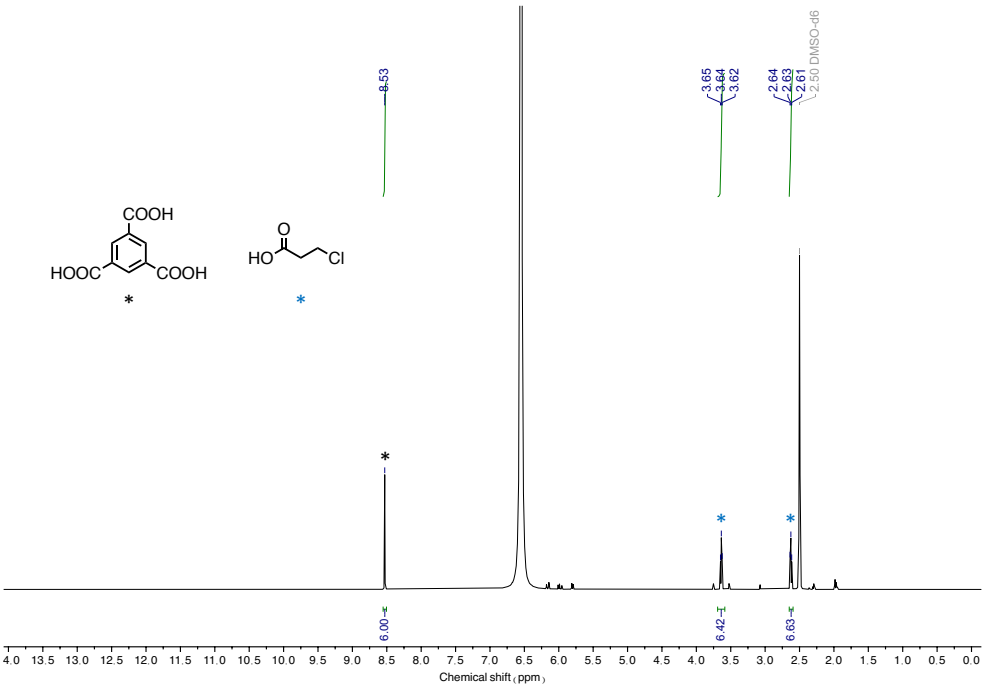

Figure S7. ^{1}H NMR spectrum of digested MOF-808-EtCl.

Section S4 Potentiometric Acid-Base Titration Analyses

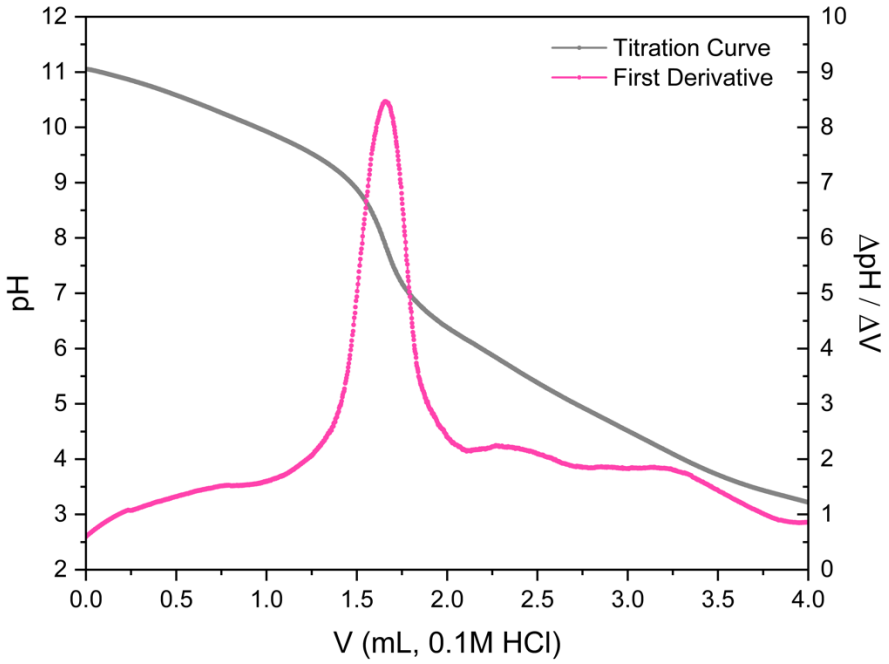

Figure S8. Acid-base titration curve of MOF-808-Gly and the first derivative.

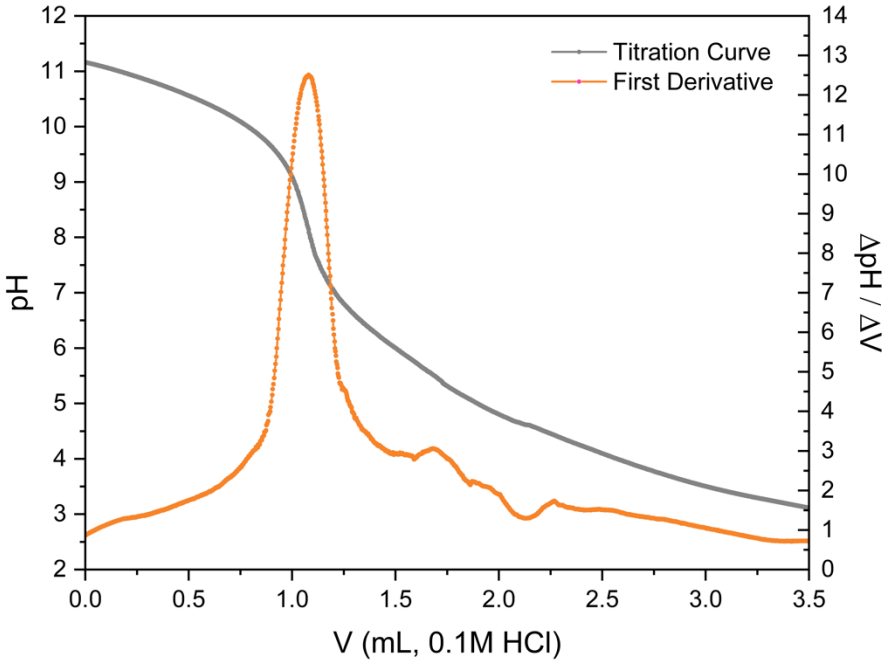

Figure S9. Acid-base titration curve of MOF-808-Pro and the first derivative.

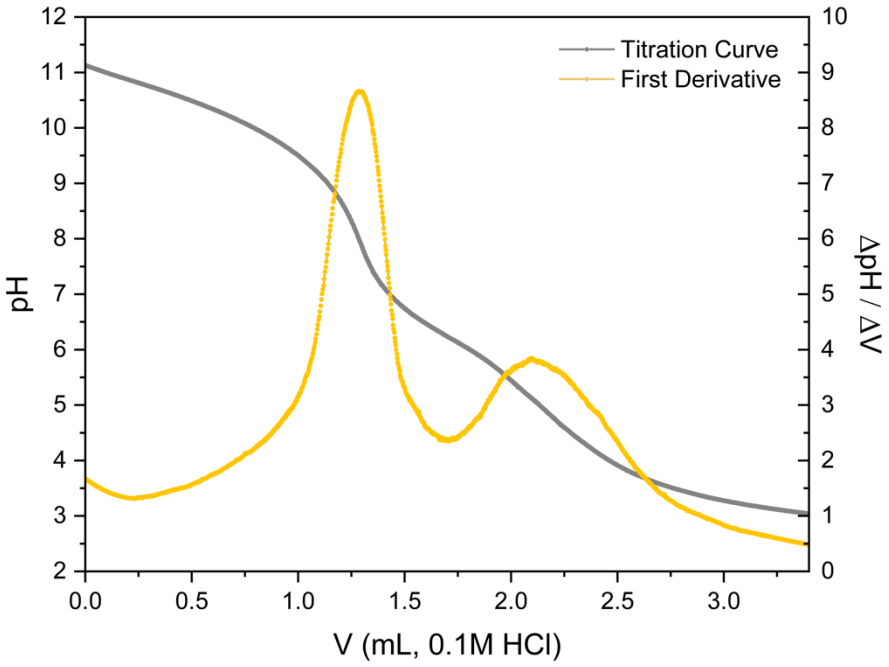

Figure S10. Acid-base titration curve of MOF-808-Lys and the first derivative.

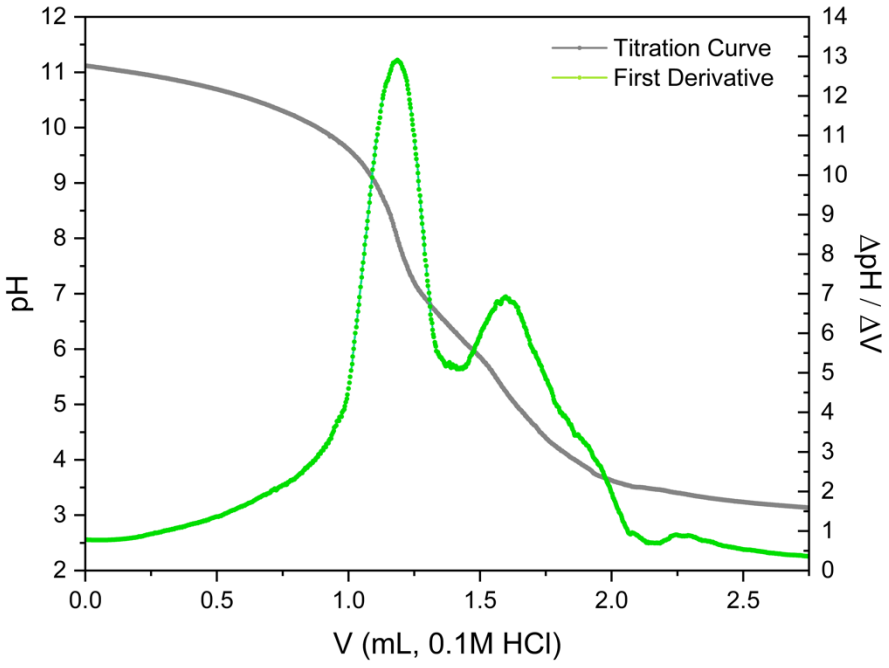

Figure S11. Acid-base titration curve of MOF-808-Arg and the first derivative.

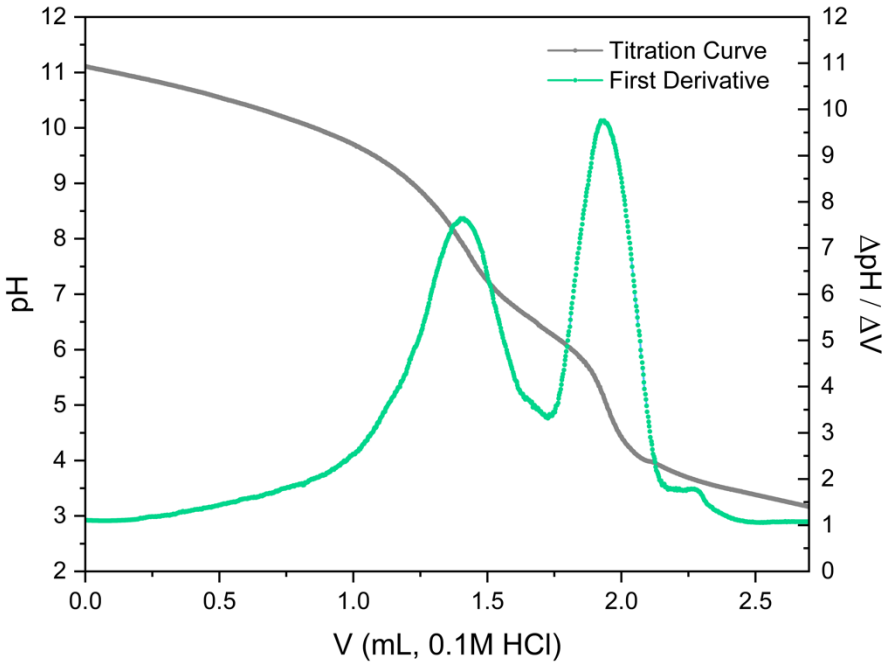

Figure S12. Acid-base titration curve of MOF-808-EDA and the first derivative.

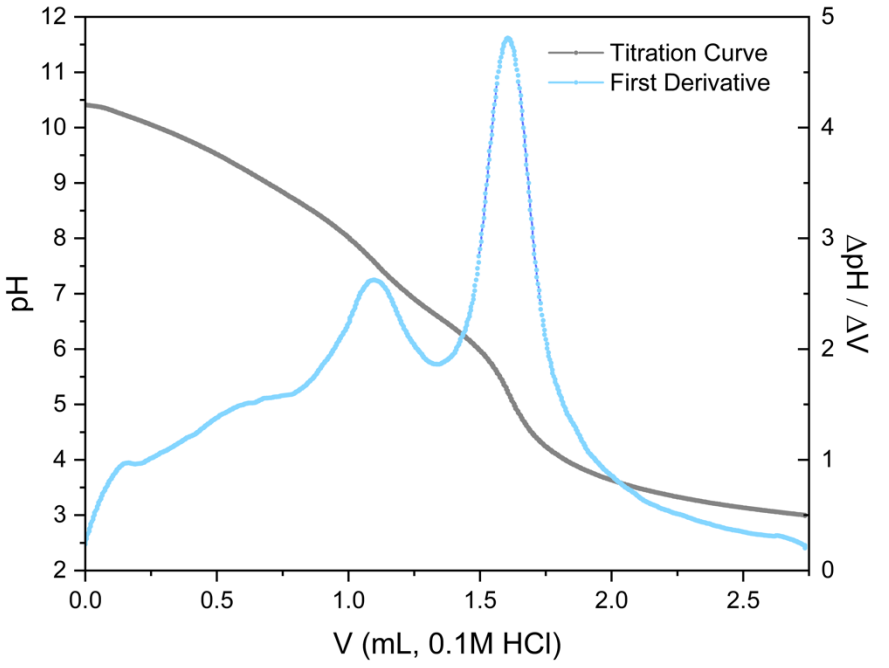

Figure S13. Acid-base titration curve of MOF-808-DAP and the first derivative.

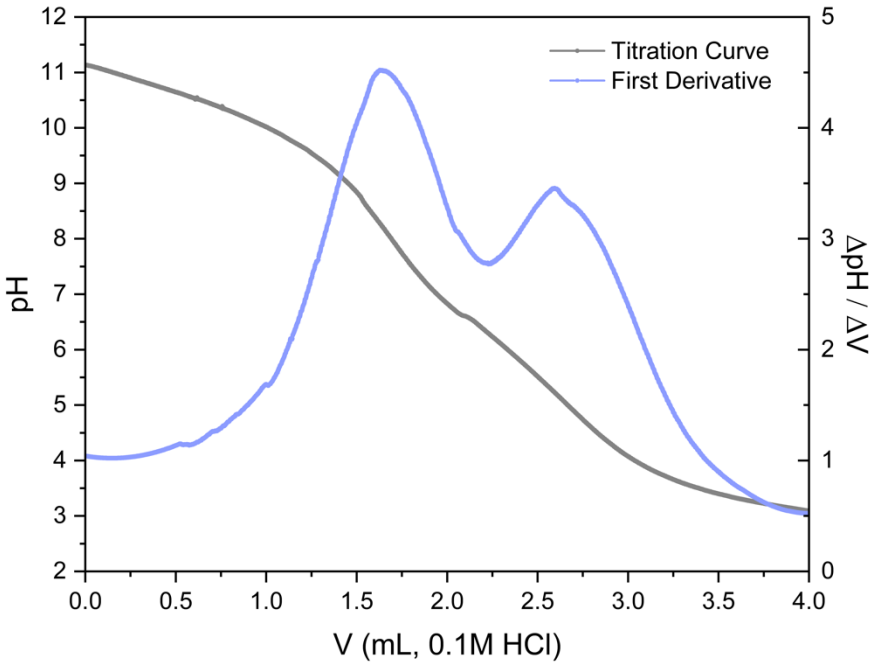

Figure S14. Acid-base titration curve of MOF-808-TAEA and the first derivative.

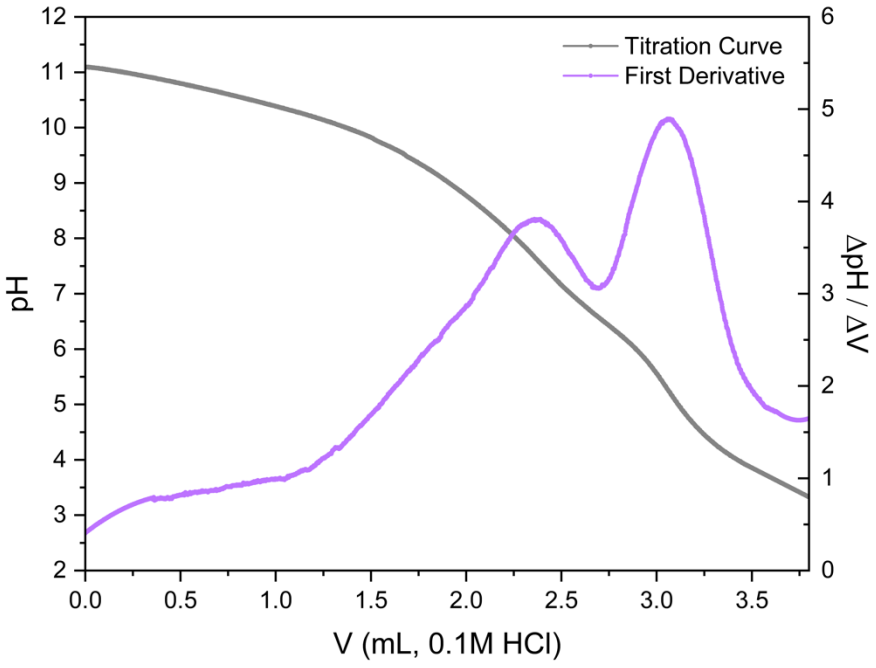

Figure S15. Acid-base titration curve of MOF-808-TAPA and the first derivative.

Table S1. Summary of the acid-base titration of MOF-808-AA and MOF-808-PA series.

Sample	Volume to eq. point (mL)	Number of basic sites g^{-1}	pK_{a1}	pK_{a2}
MOF-808-Gly	1.658	2.00×10^{21}	10.2	-
MOF-808-Pro	2.096	1.30×10^{21}	10.2	-
MOF-808-Lys	1.594	2.52×10^{21}	10.3	9.4
MOF-808-Arg	1.080	1.92×10^{21}	10.6	10.2
MOF-808-EDA	1.936	2.33×10^{21}	10.3	9.8
MOF-808-DAP	1.610	1.94×10^{21}	10.2	9.4
MOF-808-TAEA	2.594	3.12×10^{21}	10.3	9.4
MOF-808-TAPA	3.070	3.70×10^{21}	10.2	9.8

Table S2. Comparison of loaded amino acids in MOF-808-AA series by employing acid-base titration and ^{1}H digest NMR. The amount of loaded amino acids in MOF samples from titration is determined under consideration of number of effective amine groups in each of amino acids.

Sample	Observed by titration		Observed by digest NMR	
	Number of basic sites g^{-1}	Number of AAs in mmol g^{-1}	Number of AAs per SBU	Number of AAs in mmol g^{-1}
MOF-808-Gly	2.00×10^{21}	3.32	4.90	3.28
MOF-808-Pro	1.30×10^{21}	2.16	3.19	2.05
MOF-808-Lys	2.52×10^{21}	2.09	2.81	1.99
MOF-808-Arg	1.92×10^{21}	1.59	2.77	1.64

Table S3. Determination of loaded polyamines in MOF-808-PA series by employing acid-base titration. The conversion rate of amination is determined by the ratio of number of polyamines in MOF-808-PA series to number of 3-chloropropionic acid in MOF-808-EtCl obtained by ^{1}H digest NMR (2.09 mmol g^{-1}).

Sample	Number of basic sites g^{-1}	Number of PAs in mmol g^{-1}	Gravimetric primary amine loading in mmol g^{-1}	Conversion rate from MOF-808-EtCl
MOF-808-EDA	2.33×10^{21}	1.93	1.93	92.3%
MOF-808-DAP	1.94×10^{21}	1.61	1.61	77.0%
MOF-808-TAEA	3.12×10^{21}	1.73	3.46	82.8%
MOF-808-TAPA	3.70×10^{21}	2.05	4.10	98.1%

Section S5 Powder X-ray Diffraction Analyses

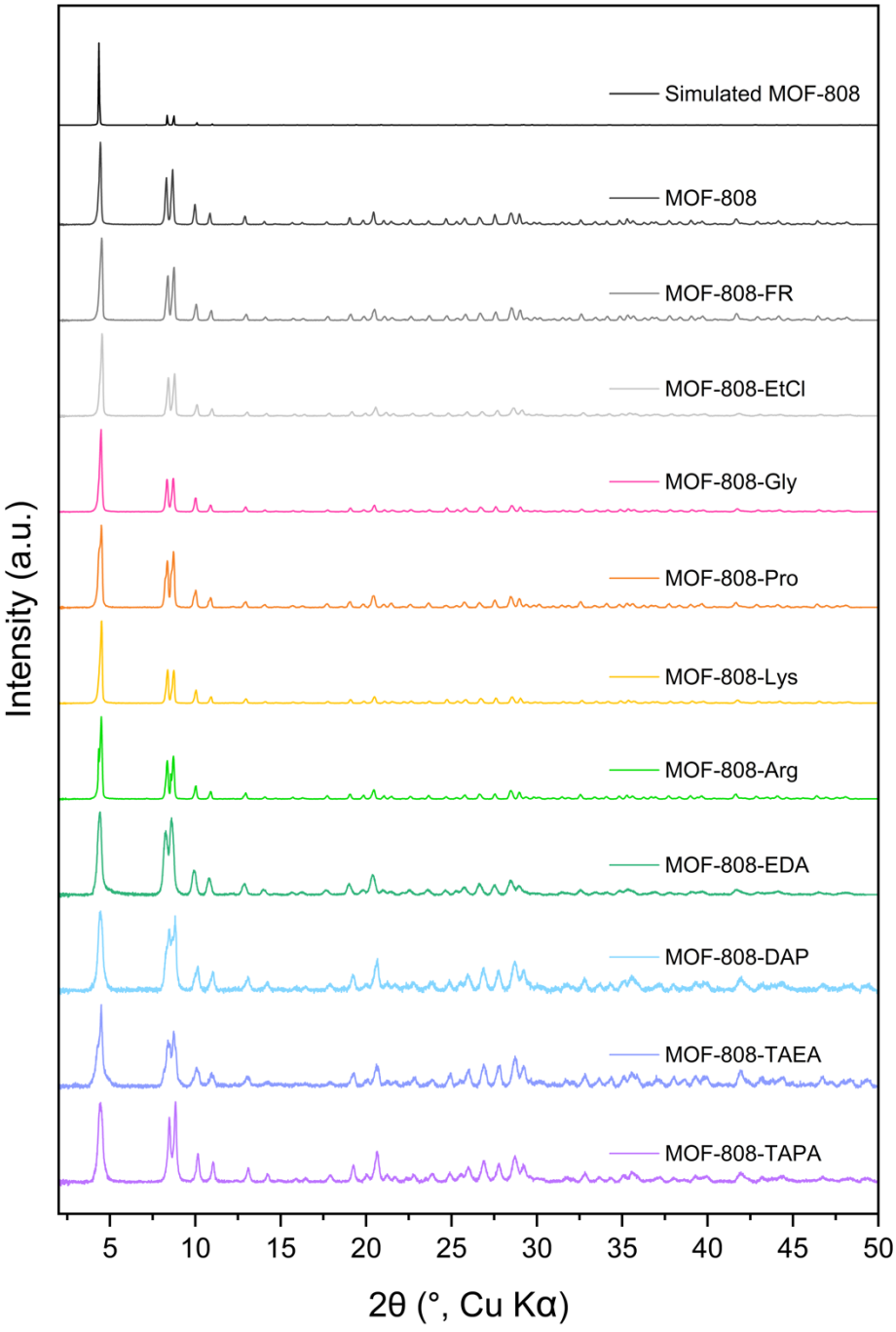

Figure S17. PXRD patterns of simulated MOF-808, activated MOF-808, MOF-808-FR, MOF-808-EtCl, MOF-808-AA series (Gly, Pro, Lys, and Arg), and MOF-808-PA series (EDA, DAP, TAEA, and TAPA).

Section S6 Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy

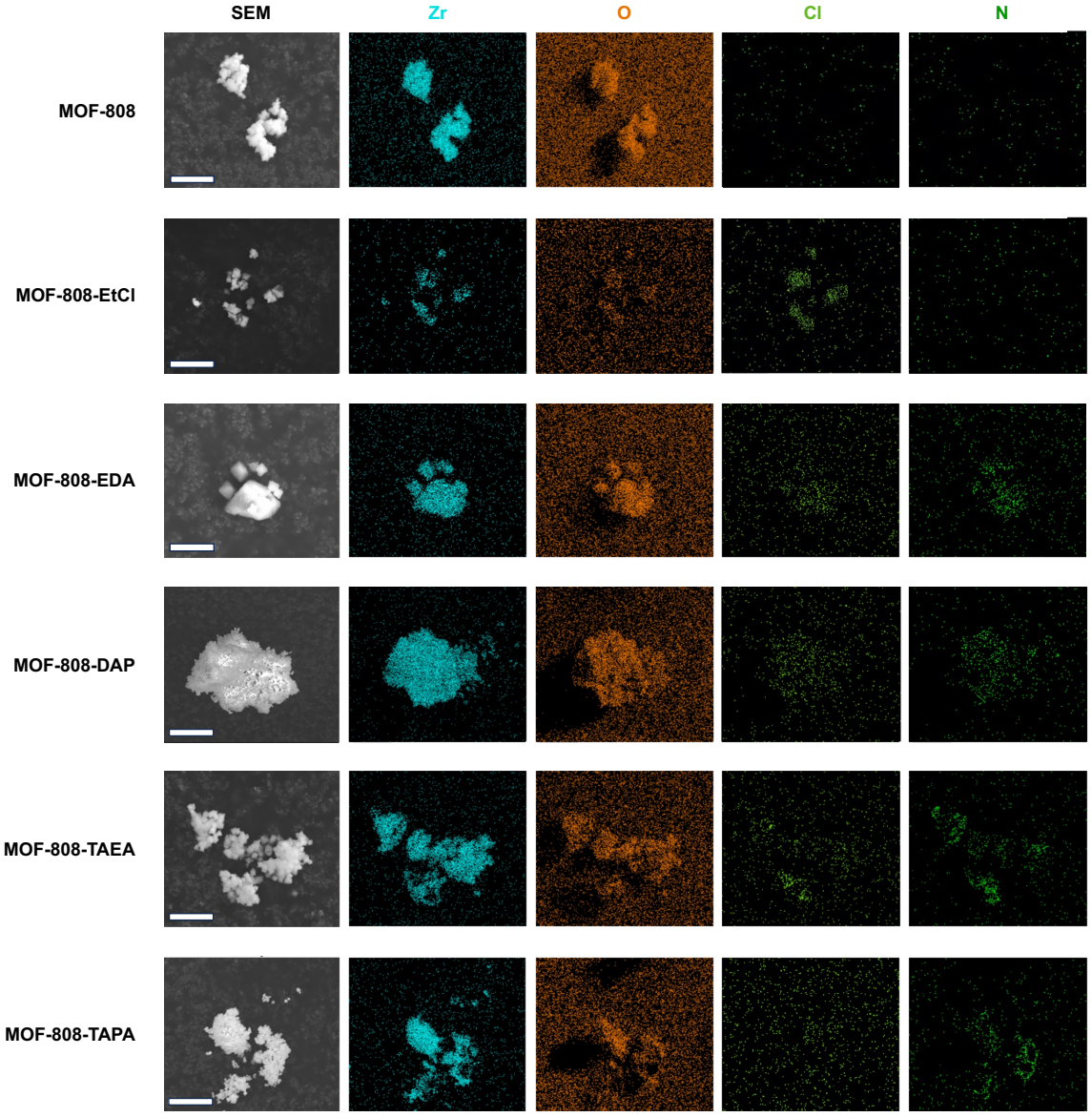

Figure S18. SEM images with EDS of MOF-808, MOF-808-EtCl, and MOF-808-PA series (EDA, DAP, TAEA, and TAPA). All samples were washed and activated before imaging. Scale bar = 10 μm.

Section S7 Nitrogen Sorption Analyses

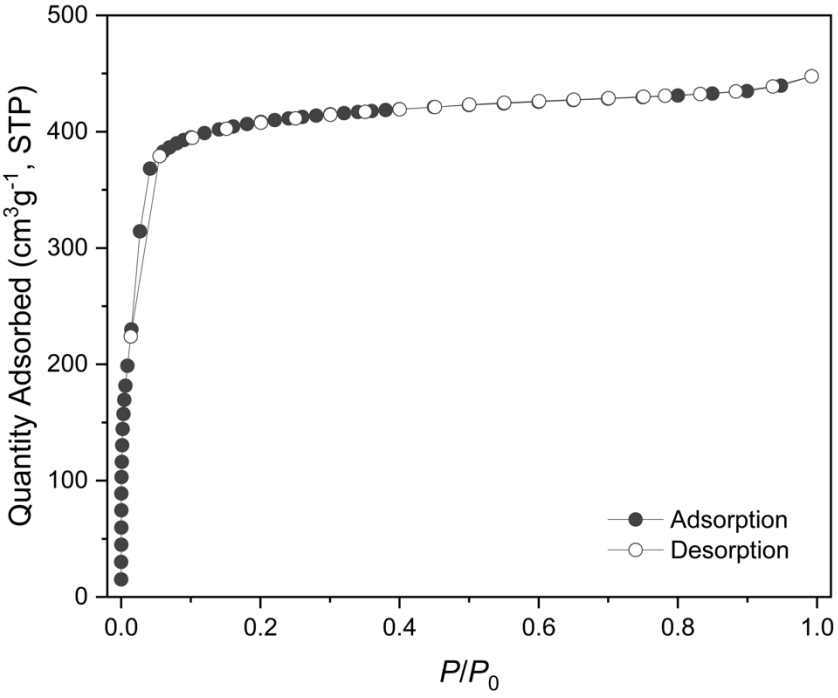

Figure S19. N_2 sorption isotherm of MOF-808 at 77 K.

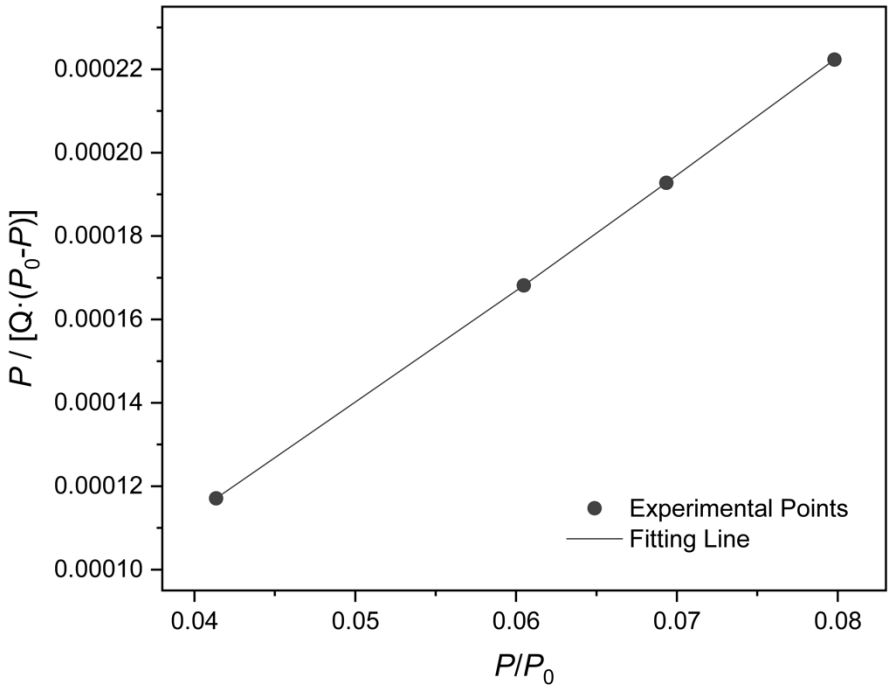

Figure S20. BET plot of MOF-808 derived from N_2 sorption isotherm at 77 K. The calculated BET surface area is 1545 $m^2 g^{-1}$. Correlation coefficient r = 0.9999.

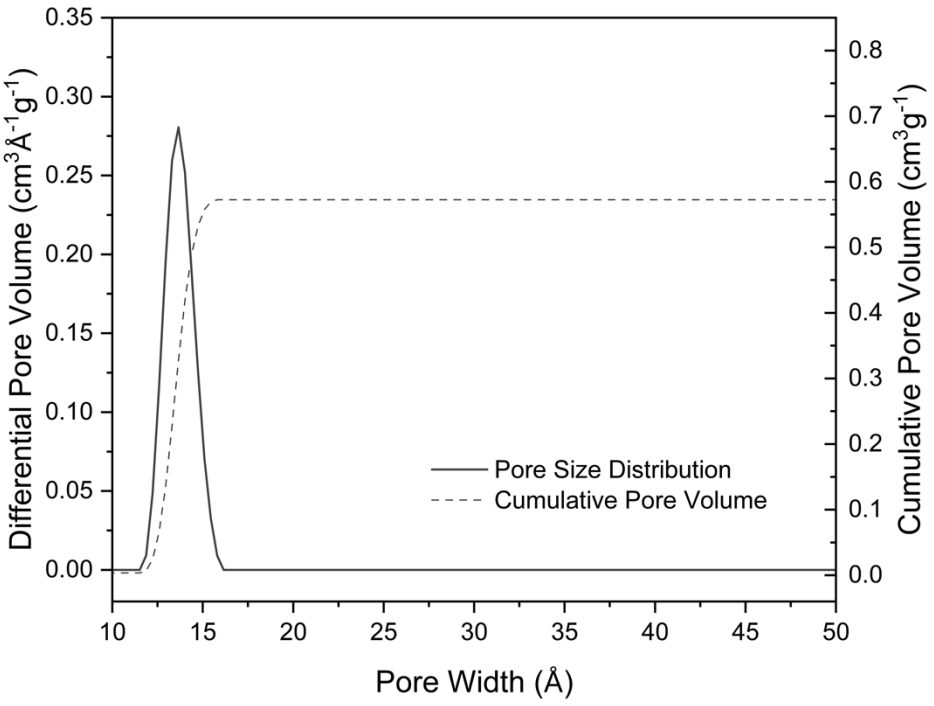

Figure S21. Differential and cumulative pore volume of MOF-808 derived from its N_2 sorption isotherm at 77 K.

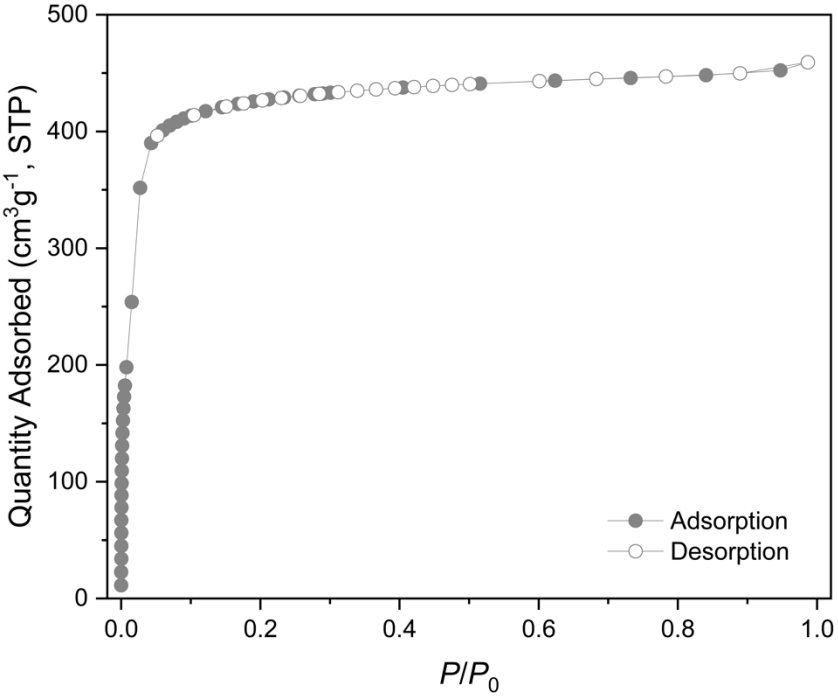

Figure S22. N_2 sorption isotherm of MOF-808-FR at 77 K.

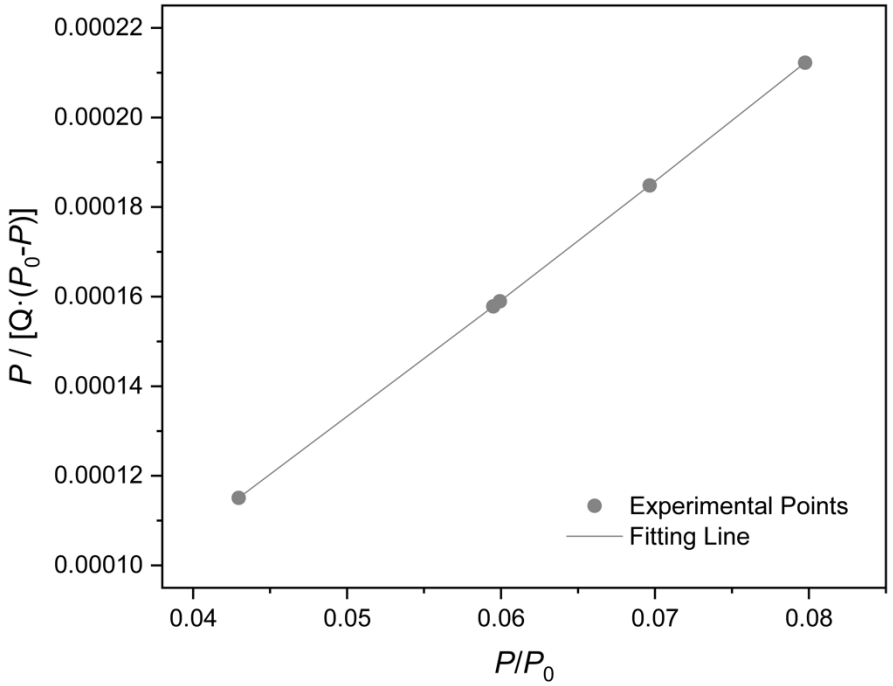

Figure S23. BET plot of MOF-808-FR derived from N_2 sorption isotherm at 77 K. The calculated BET surface area is 1610 m^2g^{-1}. Correlation coefficient r = 0.9998.

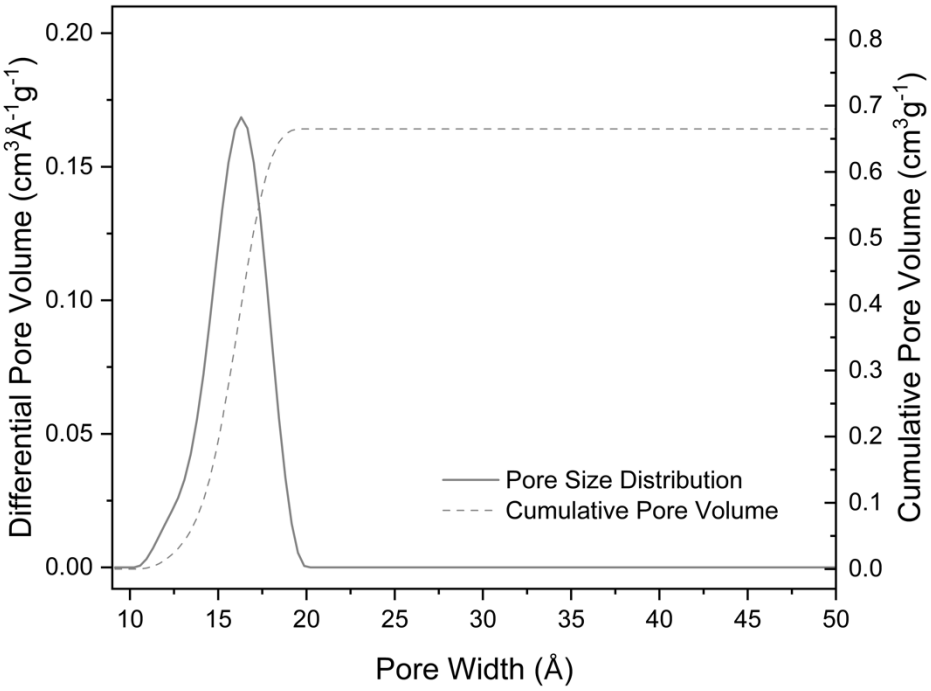

Figure S24. Differential and cumulative pore volume of MOF-808-FR derived from its N_2 sorption isotherm at 77 K.

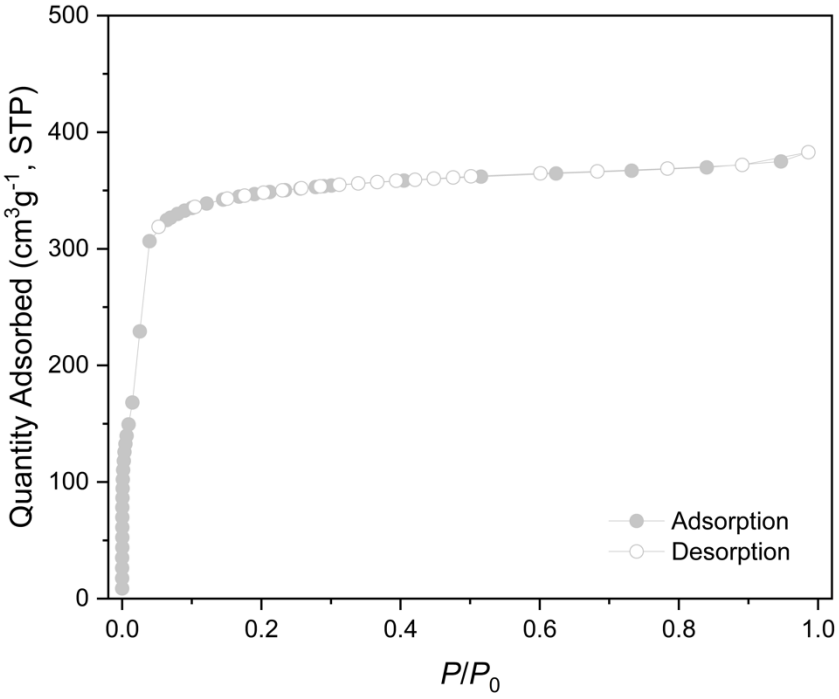

Figure S25. N_2 sorption isotherm of MOF-808-EtCl at 77 K.

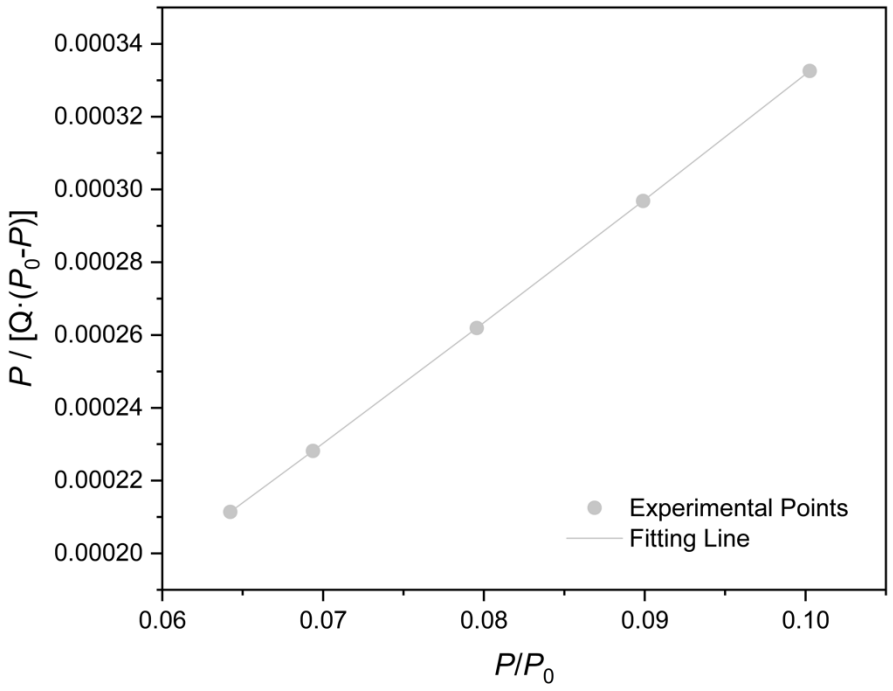

Figure S26. BET plot of MOF-808-EtCl derived from N_2 sorption isotherm at 77 K. The calculated BET surface area is 1297 m^2 g^{-1}. Correlation coefficient r = 0.9999.

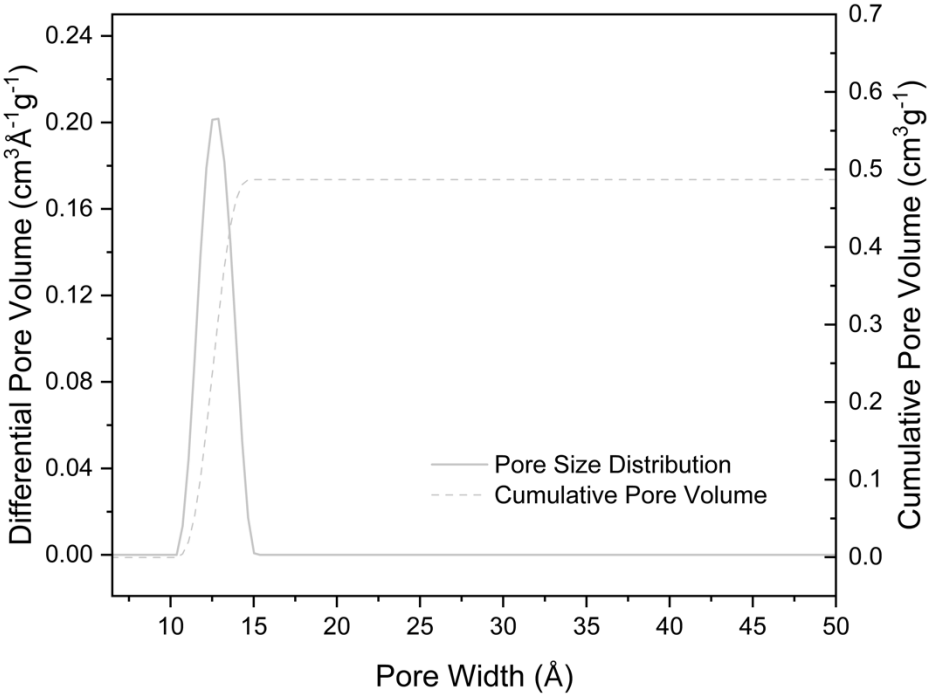

Figure S27. Differential and cumulative pore volume of MOF-808-EtCl derived from its N_2 sorption isotherm at 77 K.

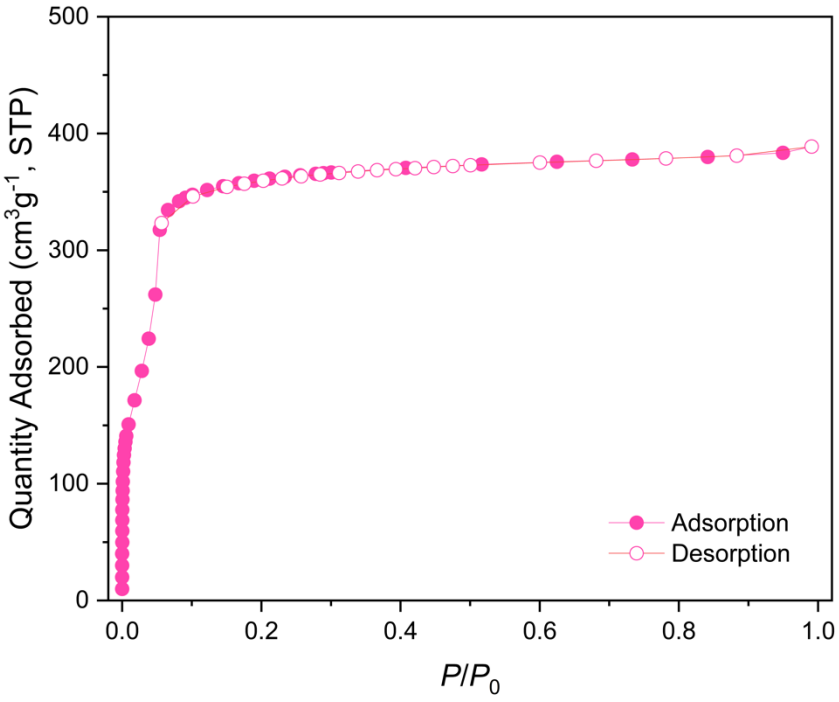

Figure S28. N_2 sorption isotherm of MOF-808-Gly at 77 K.

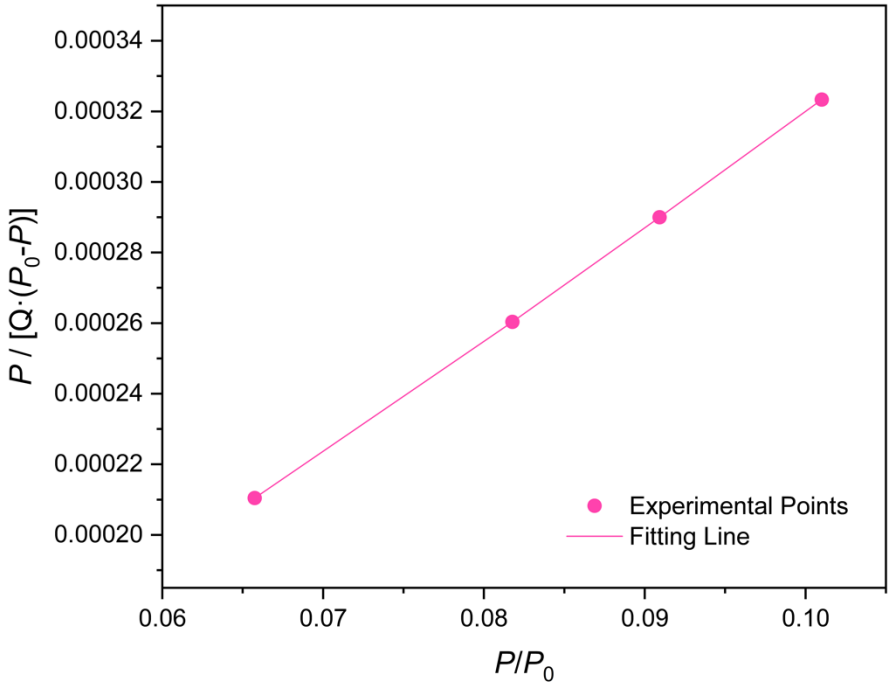

Figure S29. BET plot of MOF-808-Gly derived from N_2 sorption isotherm at 77 K. The calculated BET surface area is 1361 m^2g^{-1}. Correlation coefficient r = 0.9998.

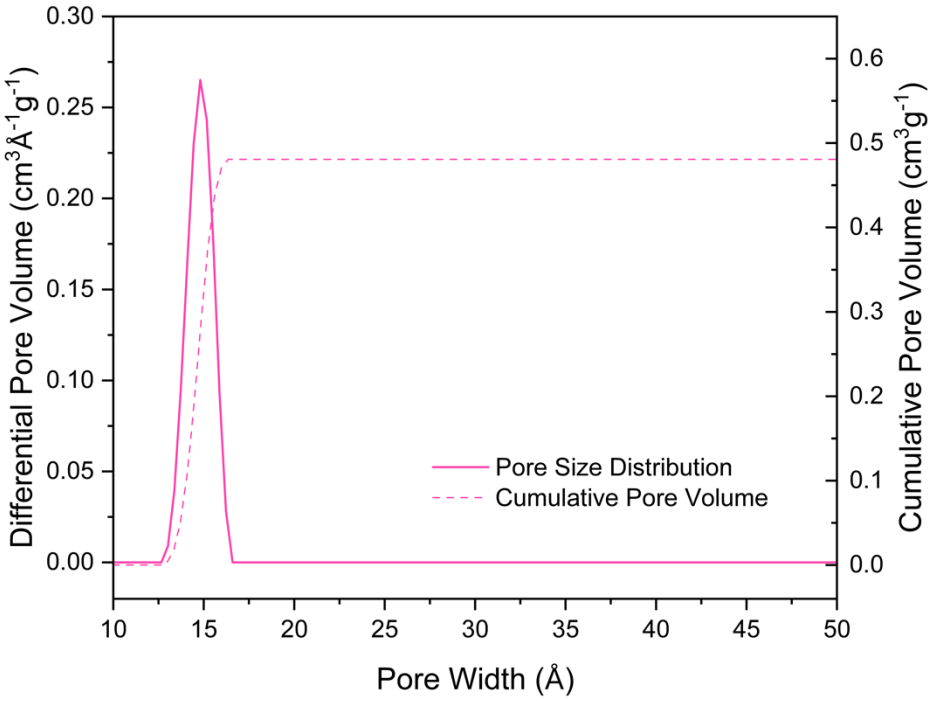

Figure S30. Differential and cumulative pore volume of MOF-808-Gly derived from its N_2 sorption isotherm at 77 K.

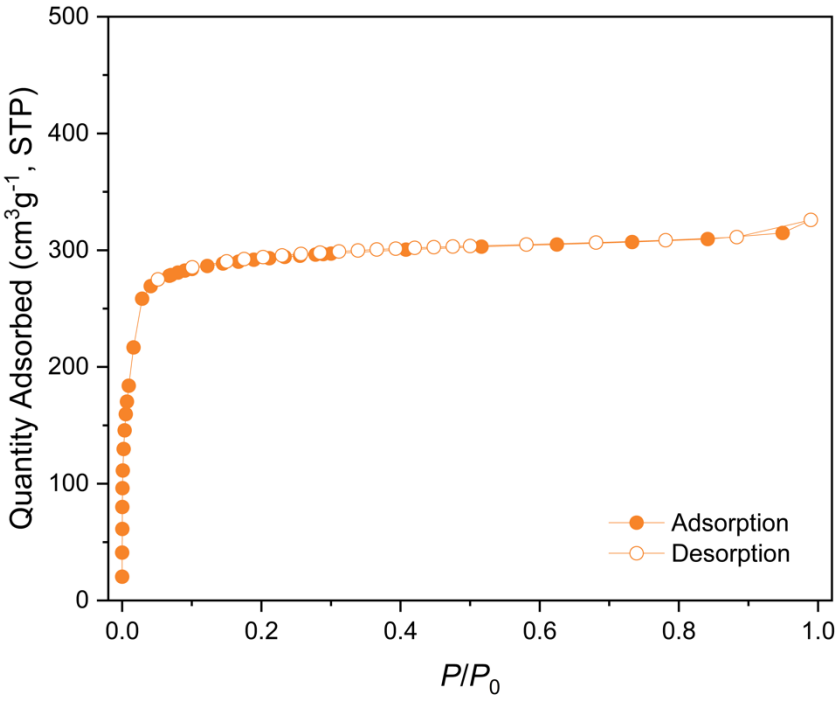

Figure S31. N_2 sorption isotherm of MOF-808-Pro at 77 K.

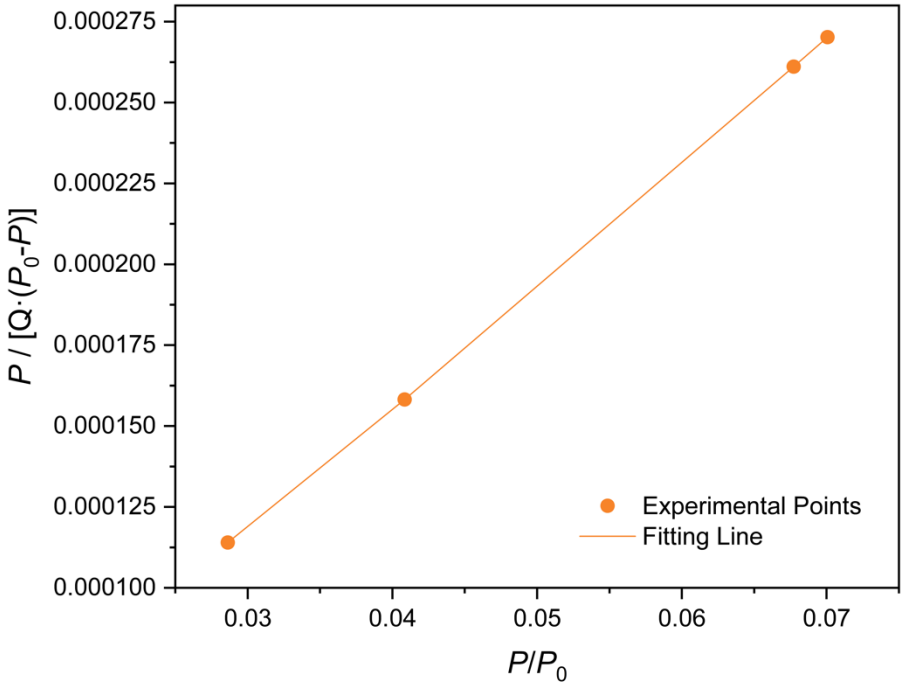

Figure S32. BET plot of MOF-808-Pro derived from N_2 sorption isotherm at 77 K. The calculated BET surface area is 1149 $m^2 g^{-1}$. Correlation coefficient r = 0.9999.

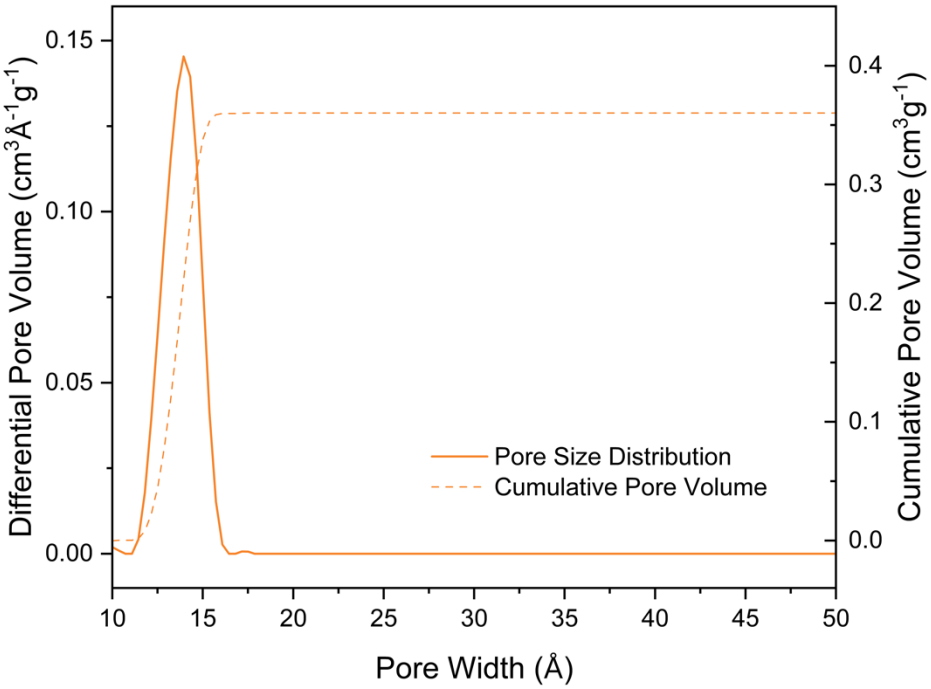

Figure S33. Differential and cumulative pore volume of MOF-808-Pro derived from its N_2 sorption isotherm at 77 K.

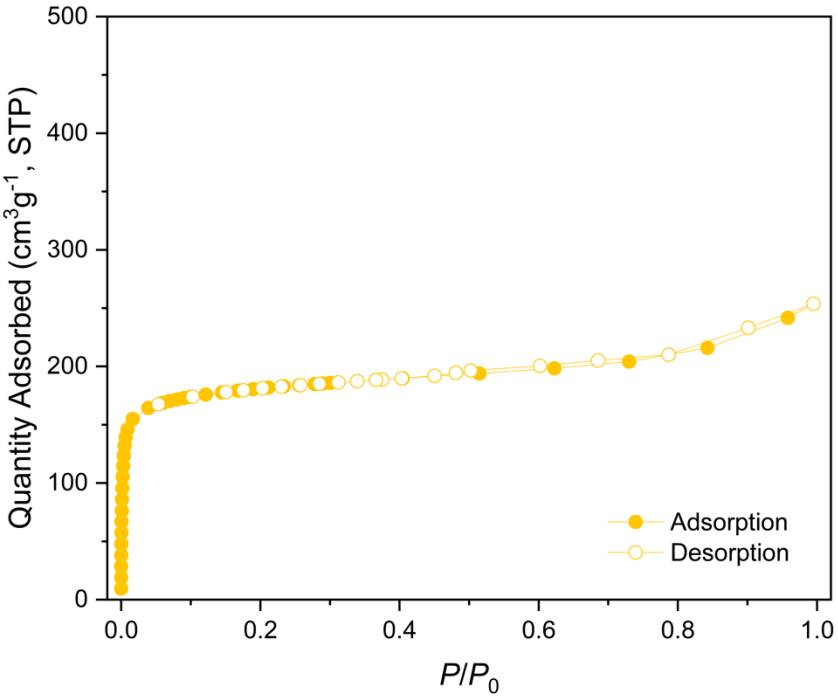

Figure S34. N_2 sorption isotherm of MOF-808-Lys at 77 K.

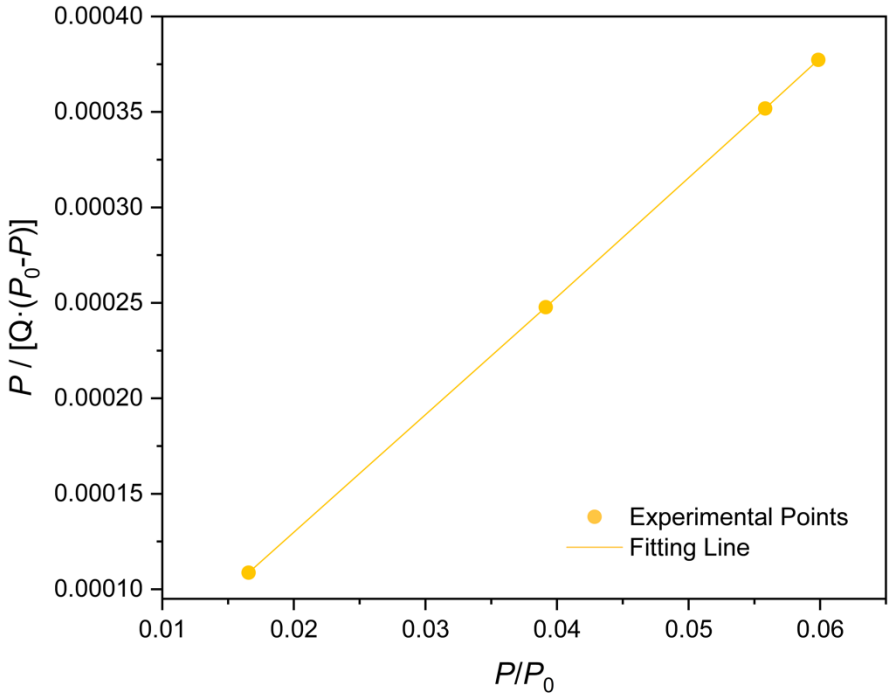

Figure S35. BET plot of MOF-808-Lys derived from N_2 sorption isotherm at 77 K. The calculated BET surface area is 701 $m^2 g^{-1}$. Correlation coefficient r = 0.9998.

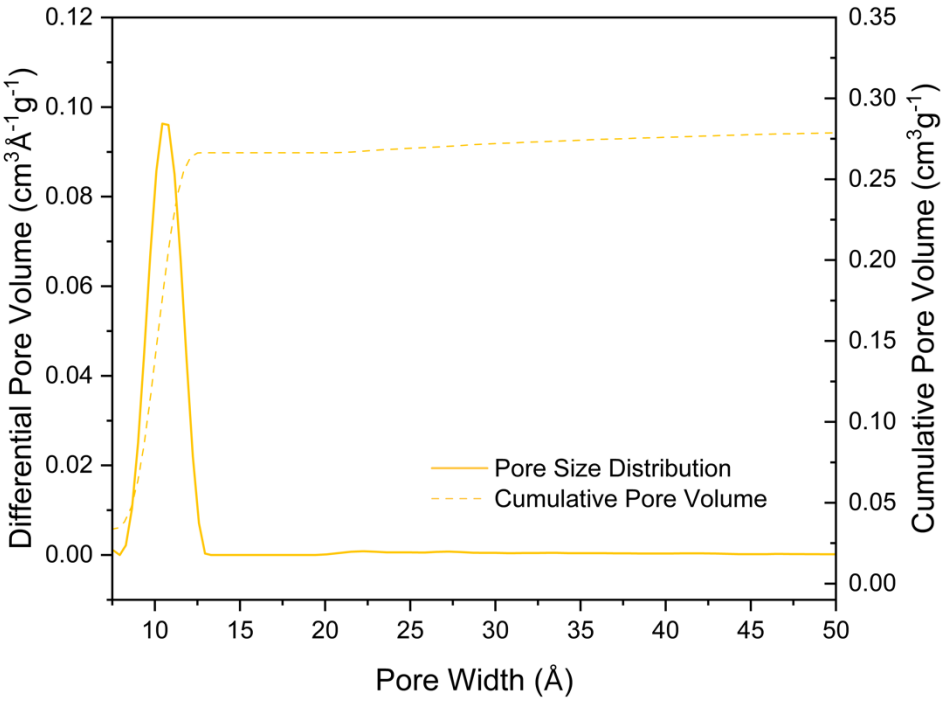

Figure S36. Differential and cumulative pore volume of MOF-808-Lys derived from its N_2 sorption isotherm at 77 K.

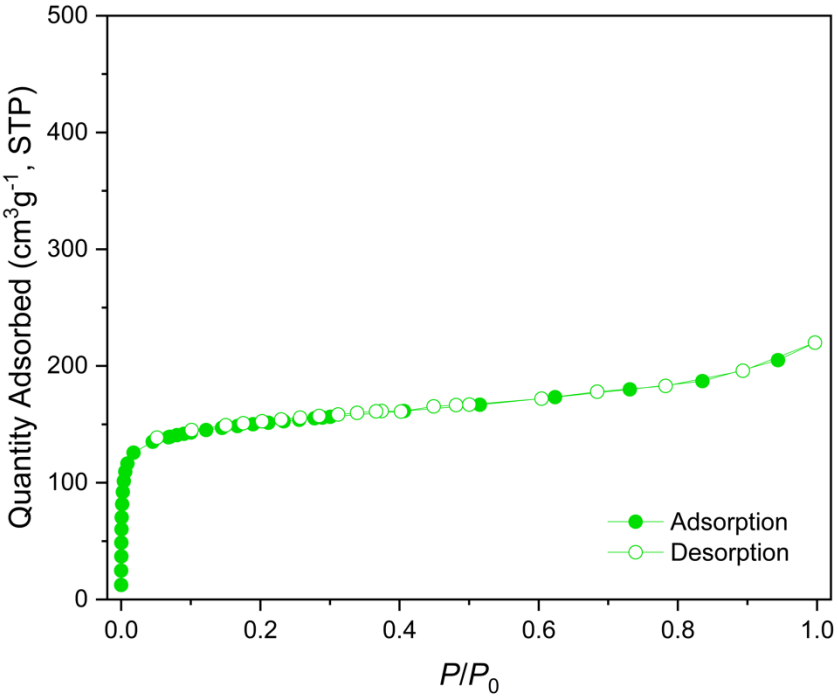

Figure S37. N_2 sorption isotherm of MOF-808-Arg at 77 K.

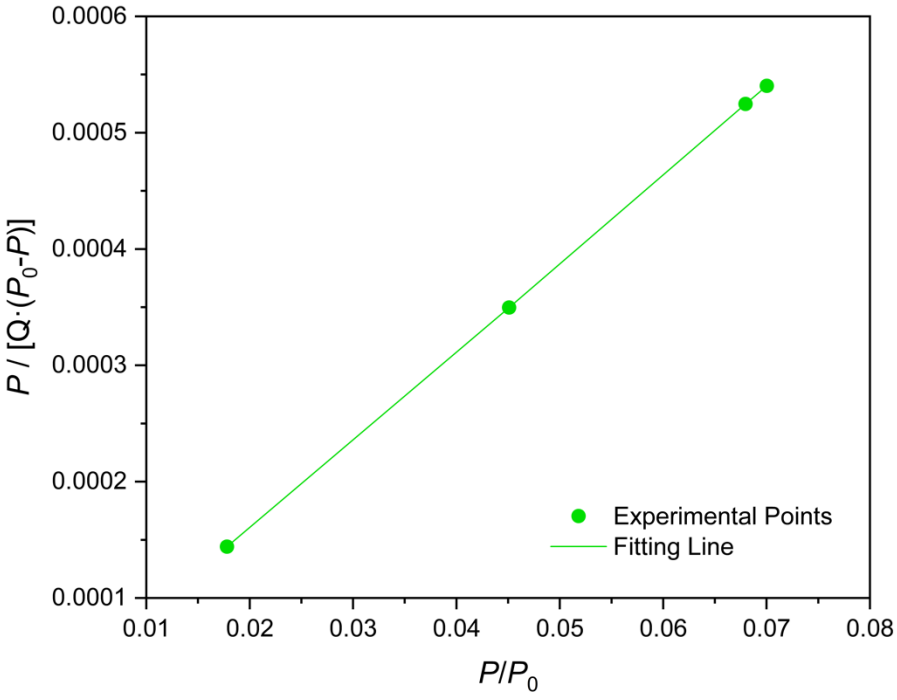

Figure S38. BET plot of MOF-808-Arg derived from N_2 sorption isotherm at 77 K. The calculated BET surface area is 573 $m^2 g^{-1}$. Correlation coefficient r = 0.9999.

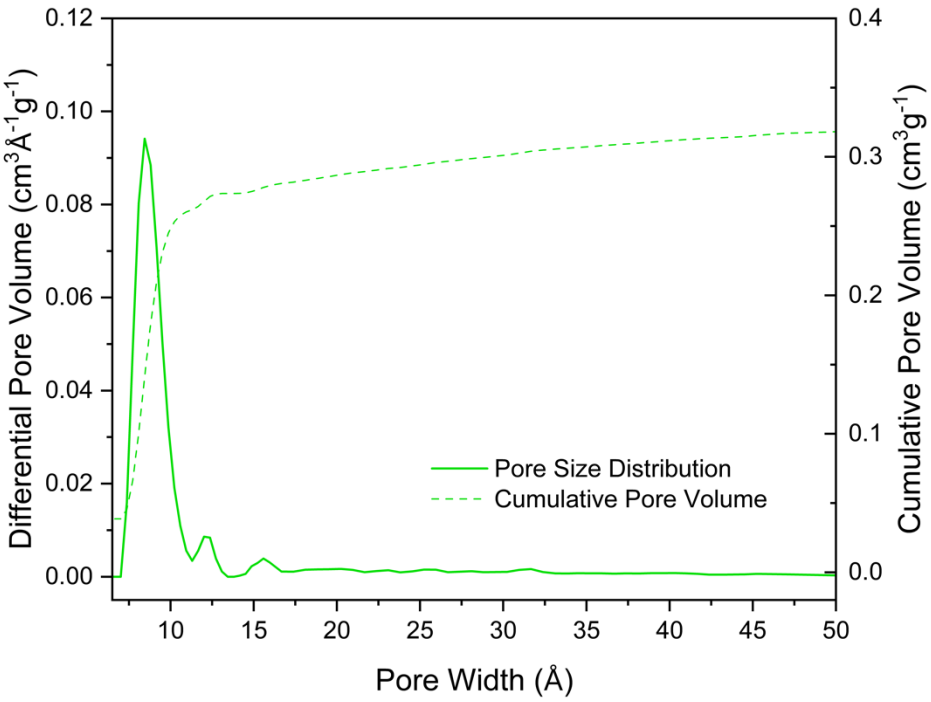

Figure S39. Differential and cumulative pore volume of MOF-808-Arg derived from its N_2 sorption isotherm at 77 K.

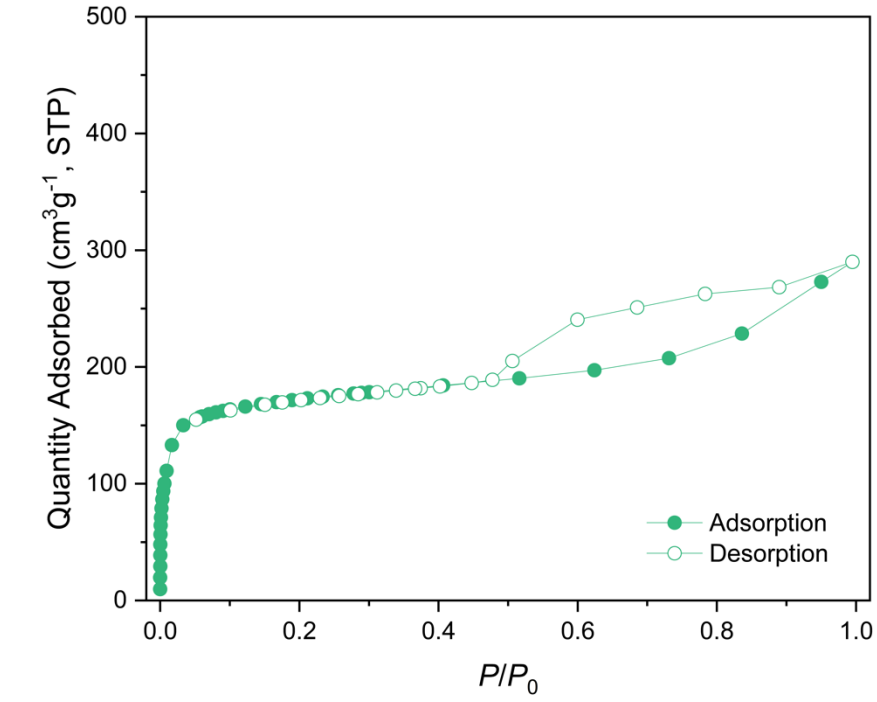

Figure S40. N_2 sorption isotherm of MOF-808-EDA at 77 K.

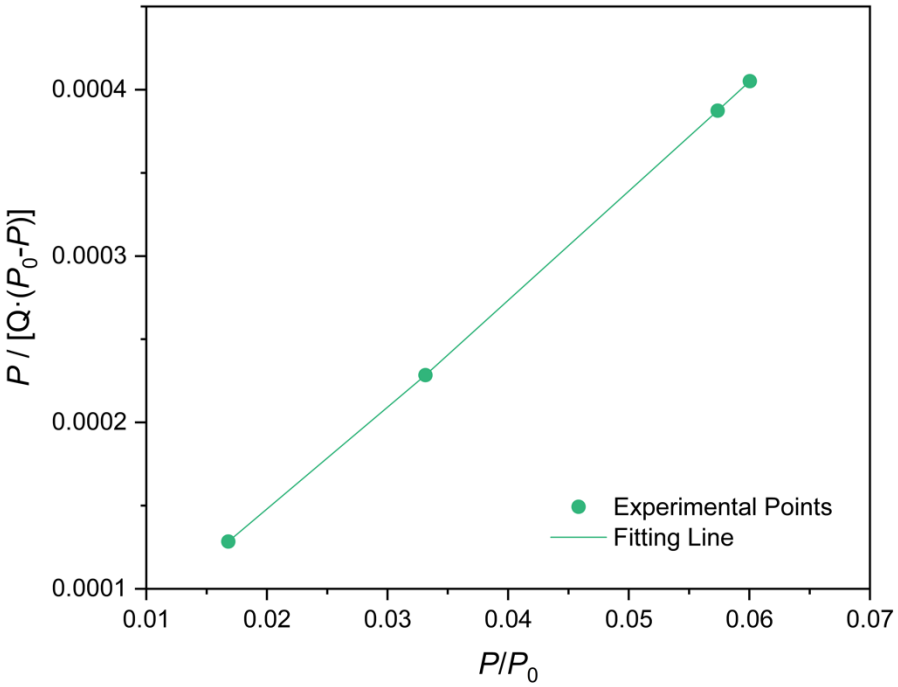

Figure S41. BET plot of MOF-808-EDA derived from N_2 sorption isotherm at 77 K. The calculated BET surface area is 676 $m^2 g^{-1}$. Correlation coefficient r = 0.9999.

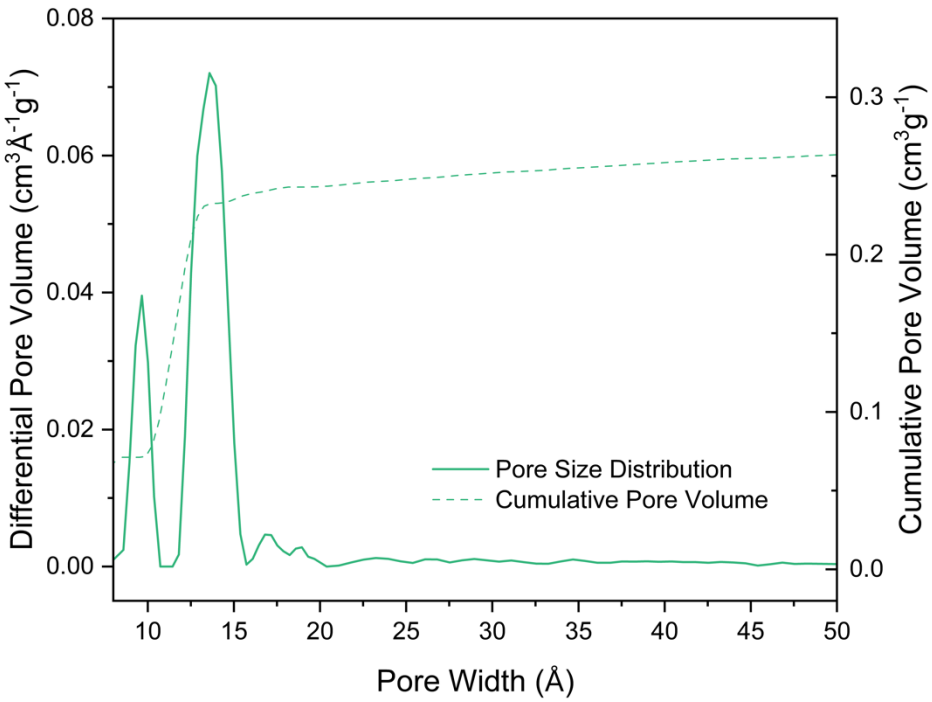

Figure S42. Differential and cumulative pore volume of MOF-808-EDA derived from its N_2 sorption isotherm at 77 K.

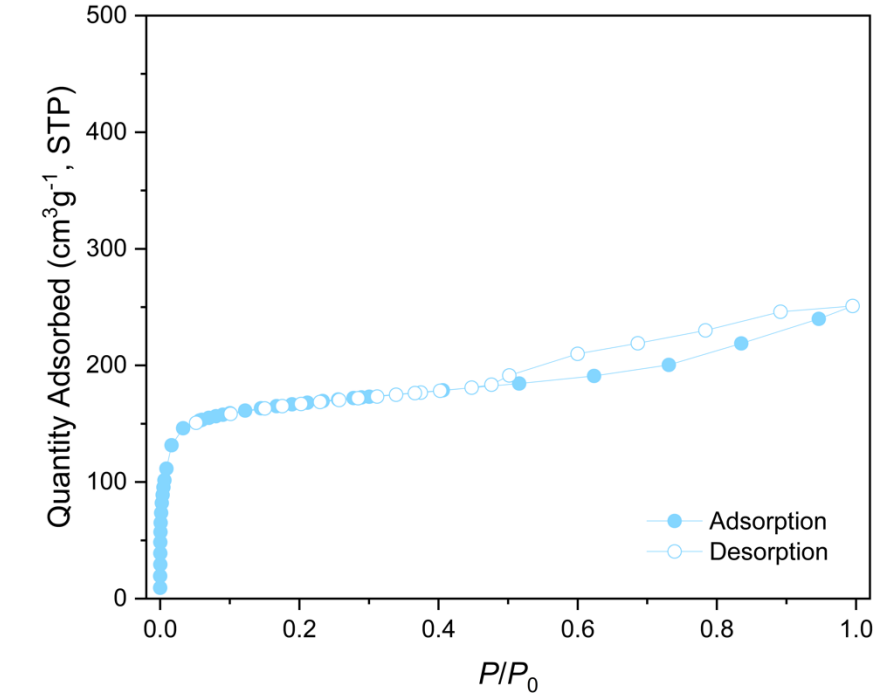

Figure S43. N_2 sorption isotherm of MOF-808-DAP at 77 K.

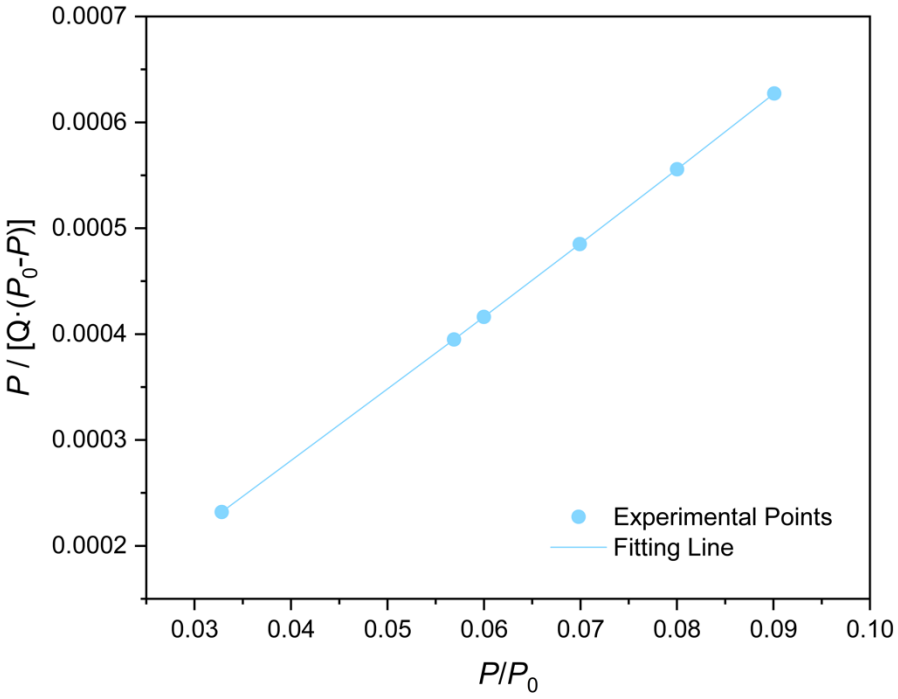

Figure S44. BET plot of MOF-808-DAP derived from N_2 sorption isotherm at 77 K. The calculated BET surface area is 630 $m^2 g^{-1}$. Correlation coefficient r = 0.9999.

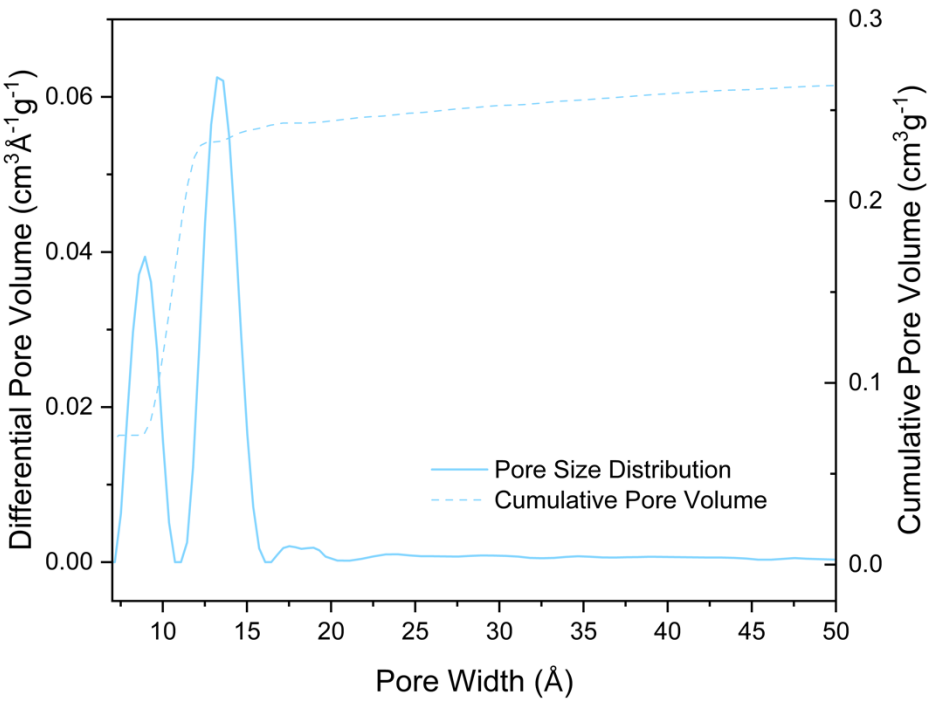

Figure S45. Differential and cumulative pore volume of MOF-808-DAP derived from its N_2 sorption isotherm at 77 K.

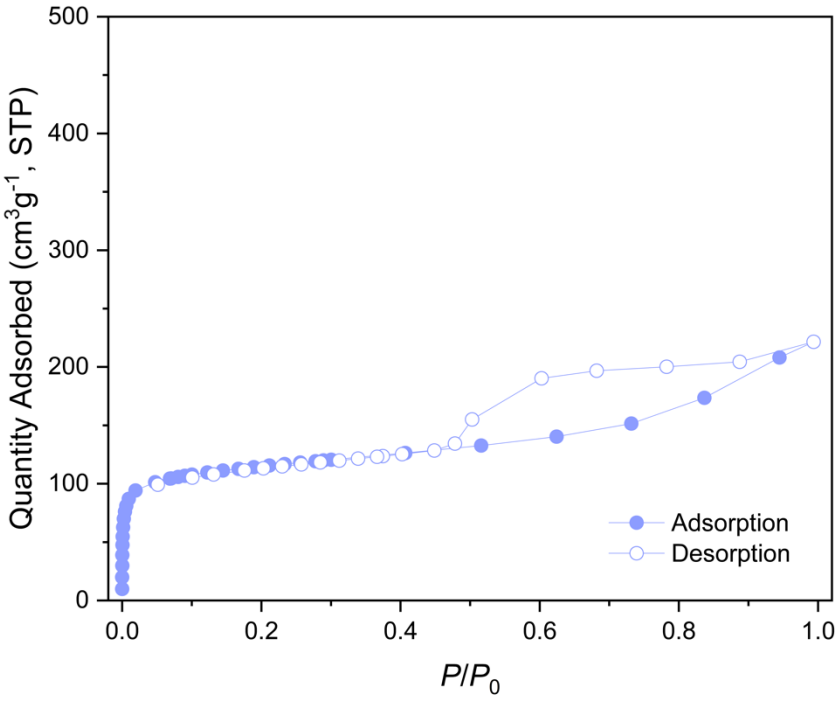

Figure S46. N_2 sorption isotherm of MOF-808-TAEA at 77 K.

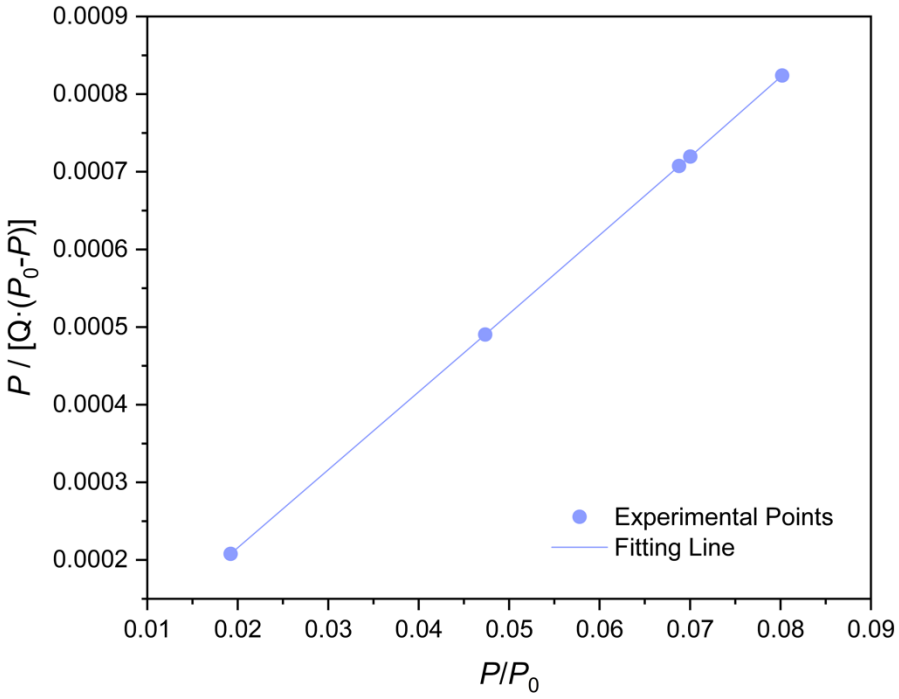

Figure S47. BET plot of MOF-808-TAEA derived from N_2 sorption isotherm at 77 K. The calculated BET surface area is 430 $m^2 g^{-1}$. Correlation coefficient r = 0.9999.

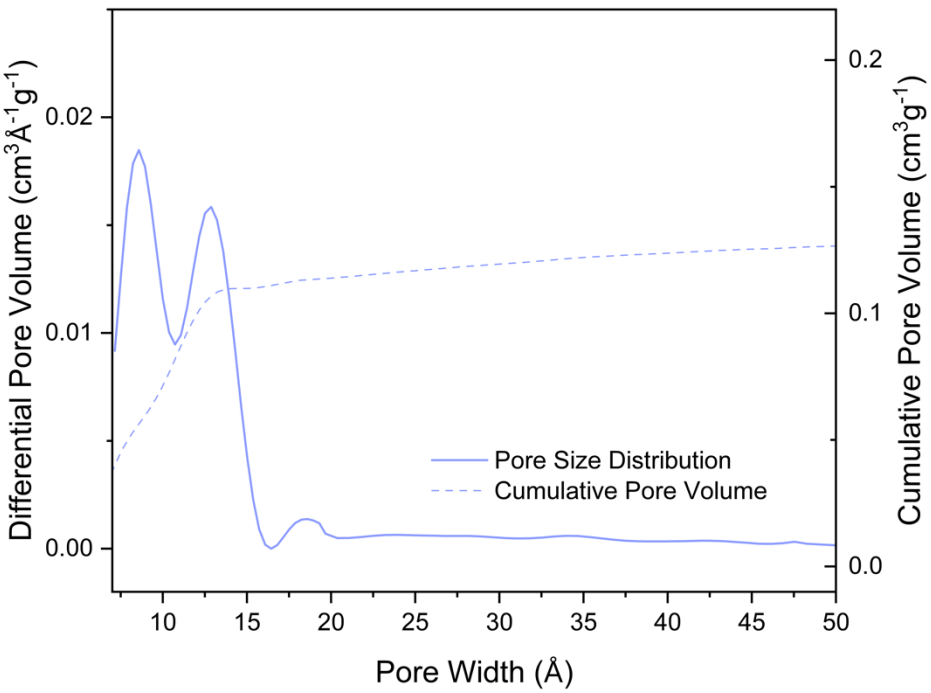

Figure S48. Differential and cumulative pore volume of MOF-808-TAEA derived from its N_2 sorption isotherm at 77 K.

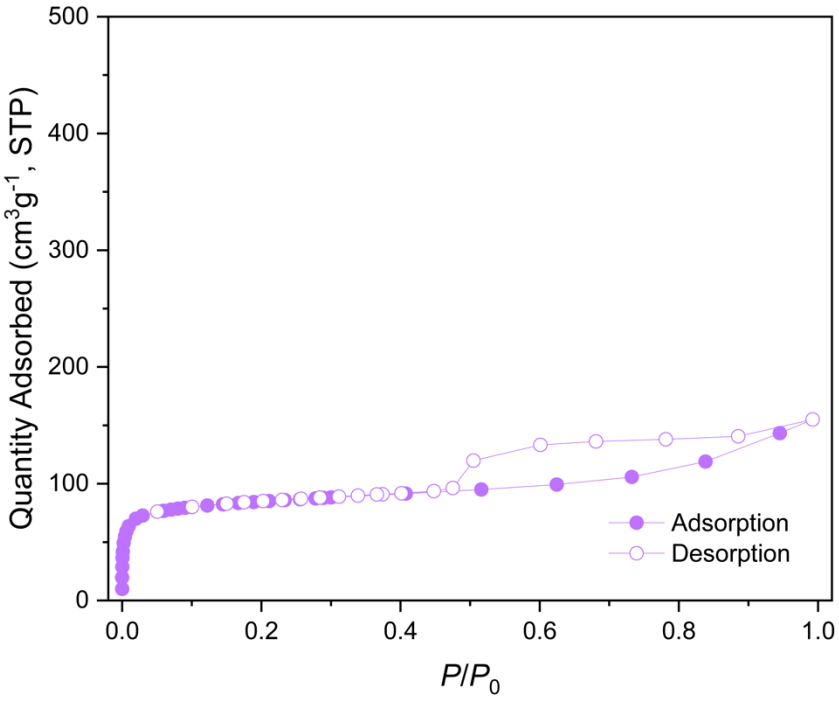

Figure S49. N_2 sorption isotherm of MOF-808-TAPA at 77 K.

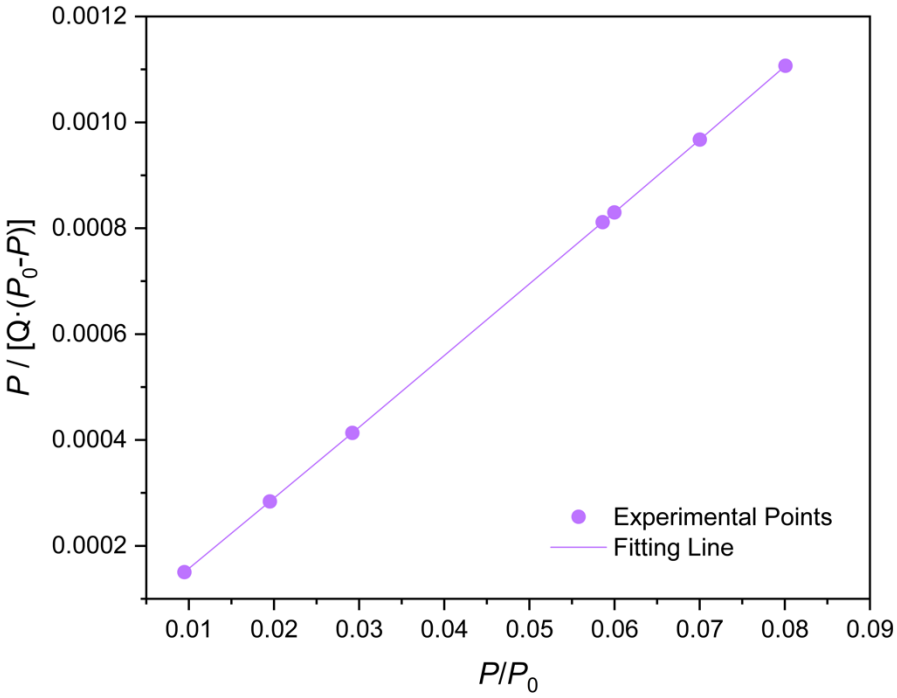

Figure S50. BET plot of MOF-808-TAPA derived from N_2 sorption isotherm at 77 K. The calculated BET surface area is 321 $m^2 g^{-1}$. Correlation coefficient r = 0.9999.

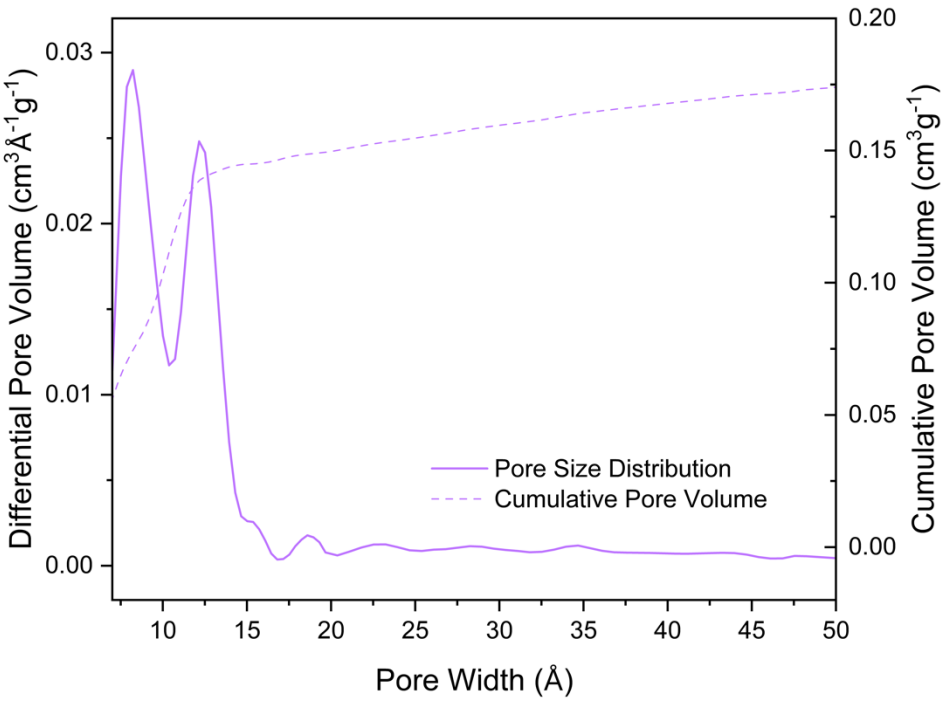

Figure S51. Differential and cumulative pore volume of MOF-808-TAPA derived from its N_2 sorption isotherm at 77 K.

Section S8 Water Vapor Sorption Analyses

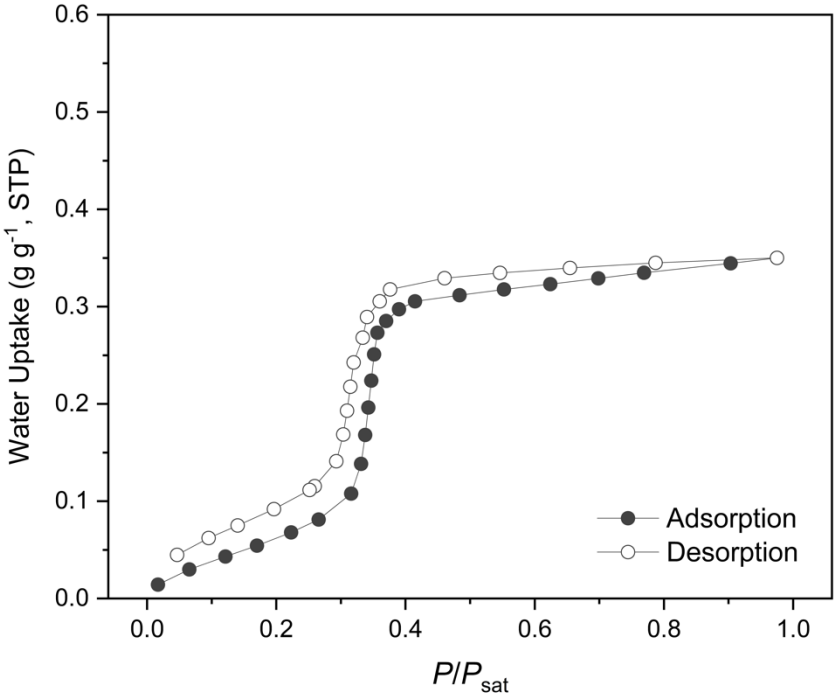

Figure S52. Water sorption isotherm of MOF-808 at 25 °C.

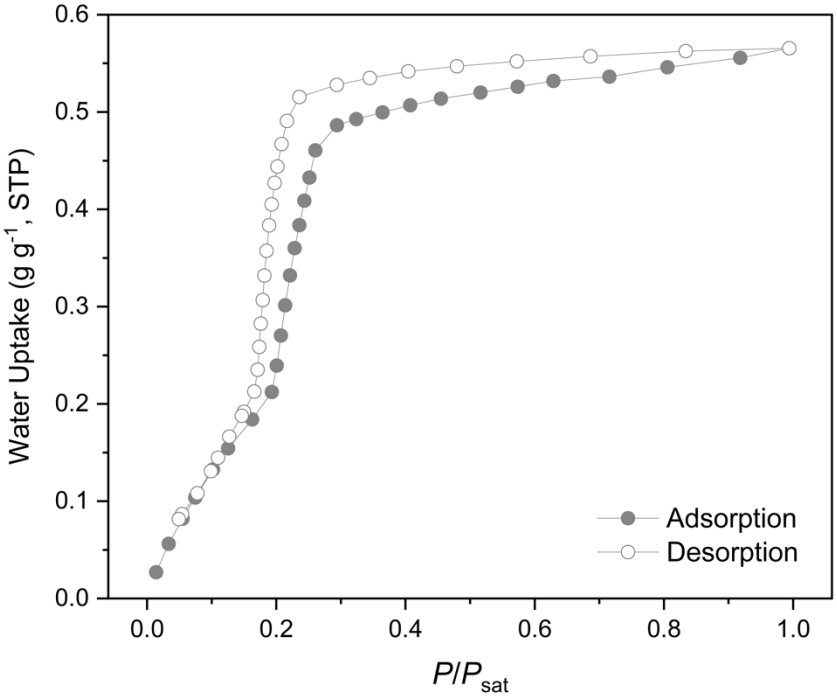

Figure S53. Water sorption isotherm of MOF-808-FR at 25 °C.

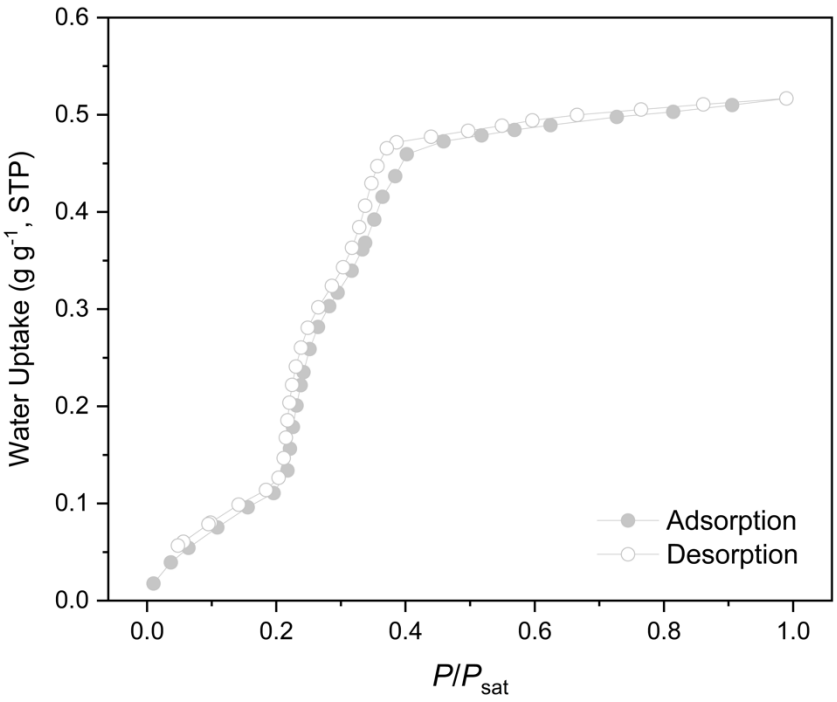

Figure S54. Water sorption isotherm of MOF-808-EtCl at 25 °C.

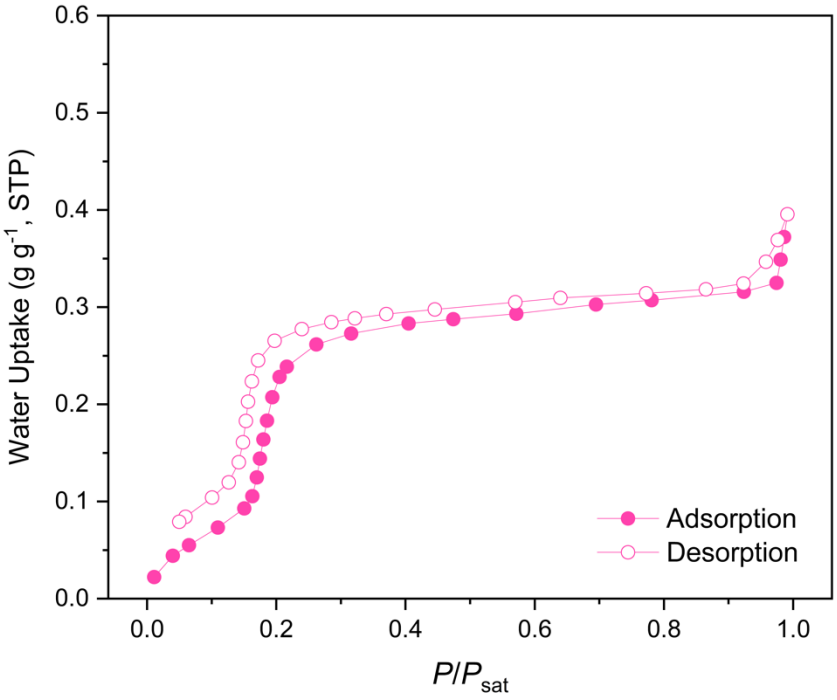

Figure S55. Water sorption isotherm of MOF-808-Gly at 25 °C.

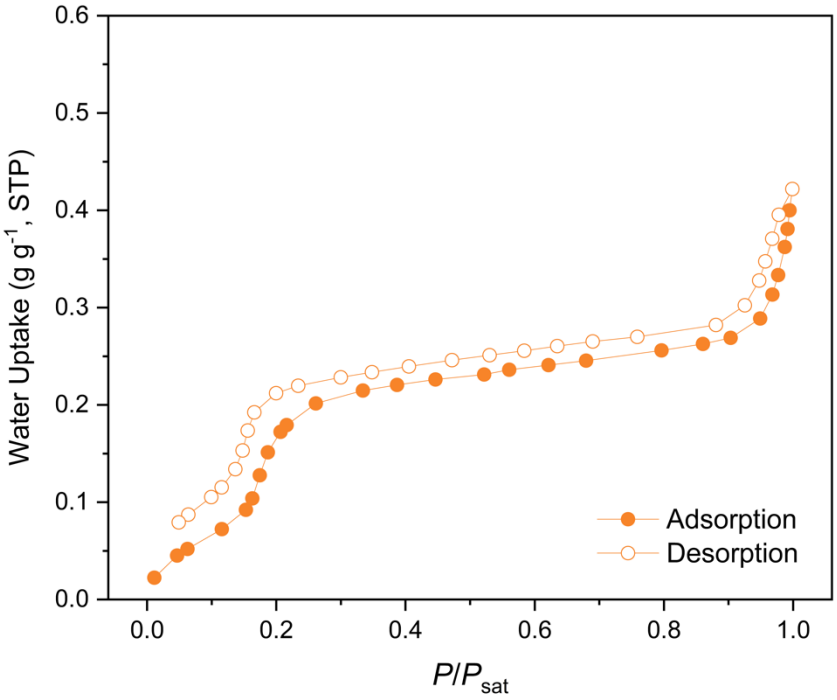

Figure S56. Water sorption isotherm of MOF-808-Pro at 25 °C.

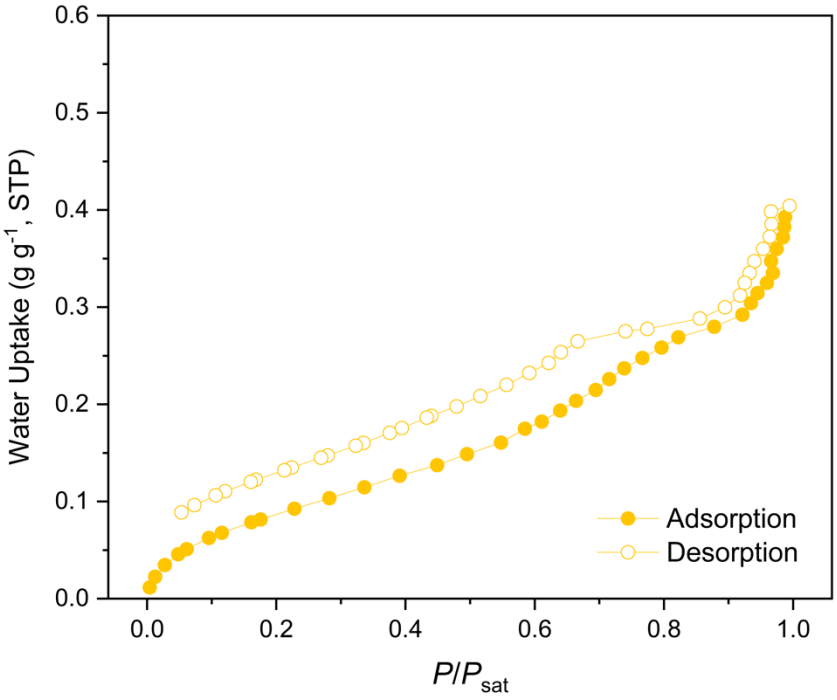

Figure S57. Water sorption isotherm of MOF-808-Lys at 25 °C.

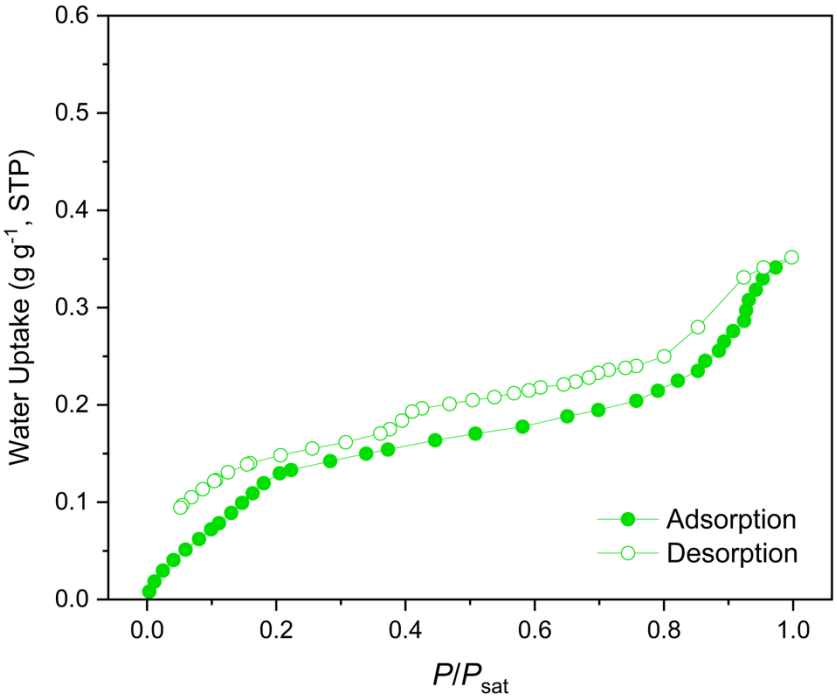

Figure S58. Water sorption isotherm of MOF-808-Arg at 25 °C.

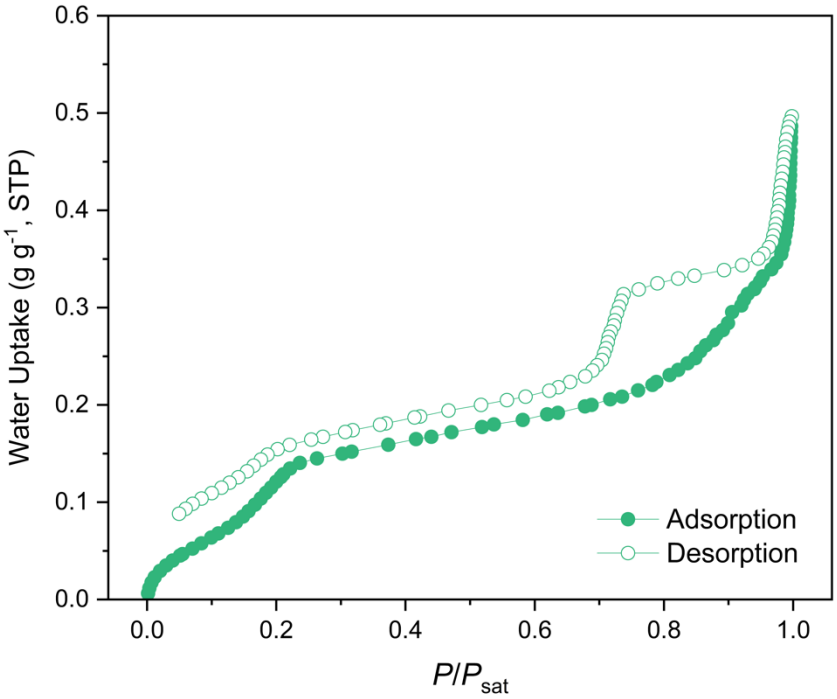

Figure S59. Water sorption isotherm of MOF-808-EDA at 25 °C.

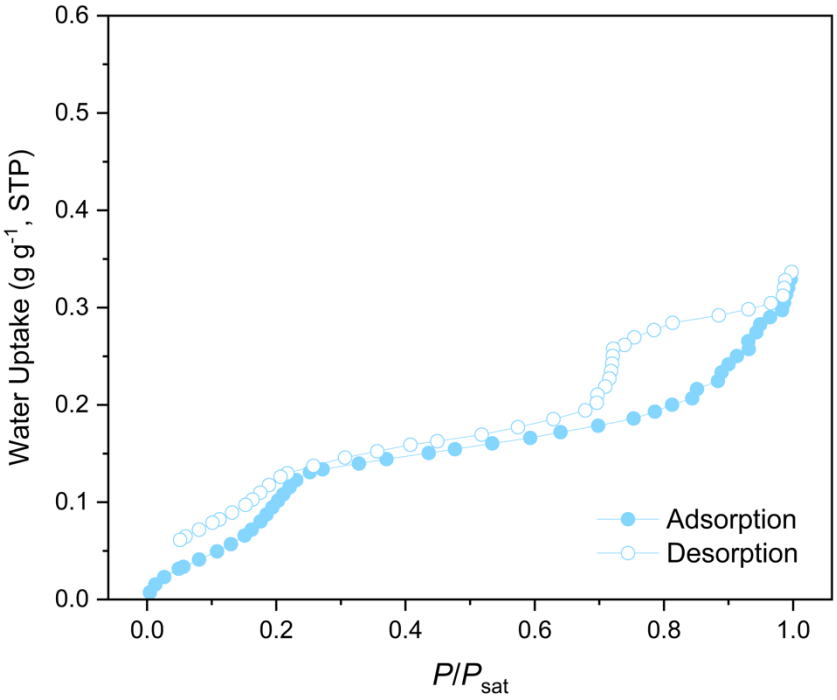

Figure S60. Water sorption isotherm of MOF-808 at 25 °C.

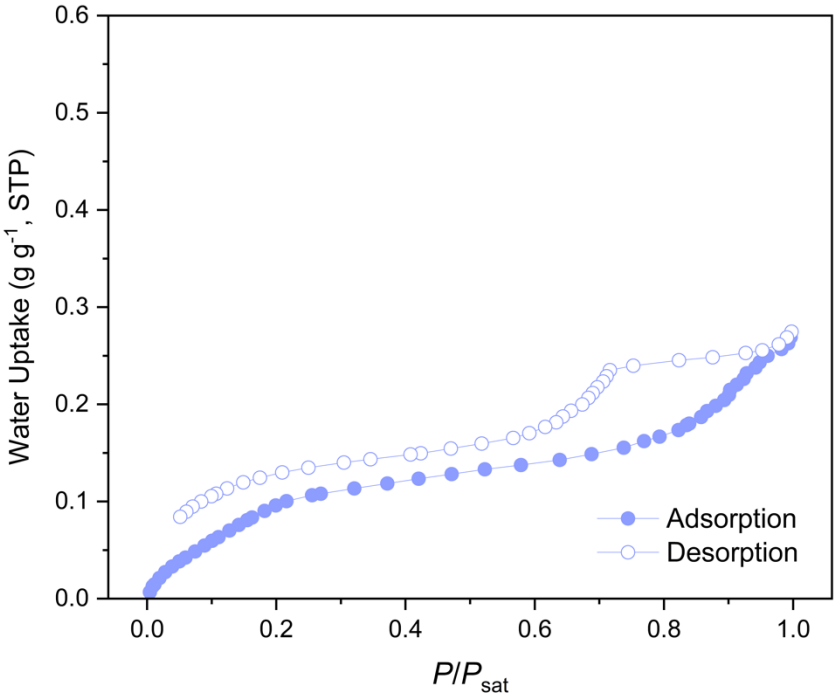

Figure S61. Water sorption isotherm of MOF-808-FR at 25 °C.

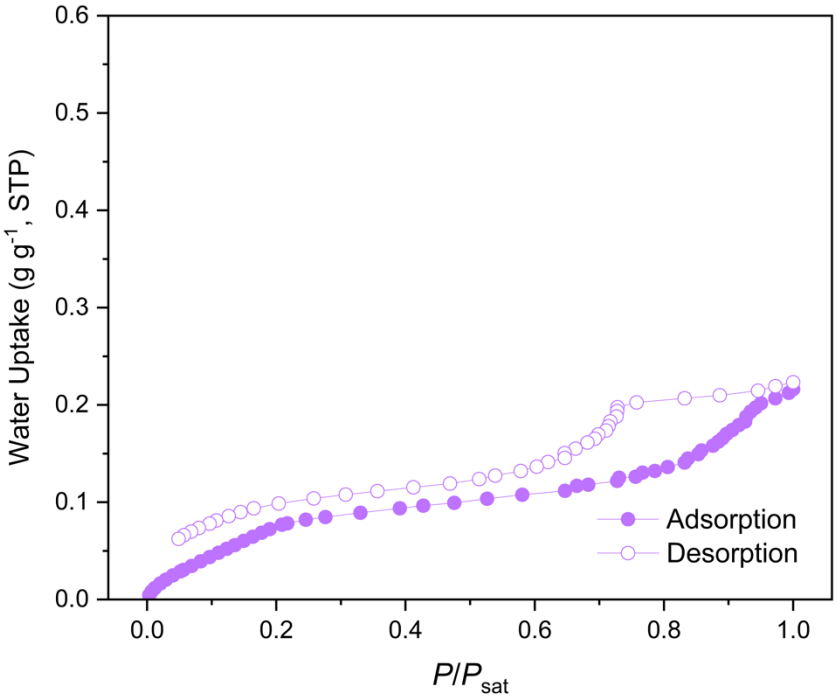

Figure S62. Water sorption isotherm of MOF-808 at 25 °C.

Section S9 Single-Component Carbon Dioxide Sorption Analyses

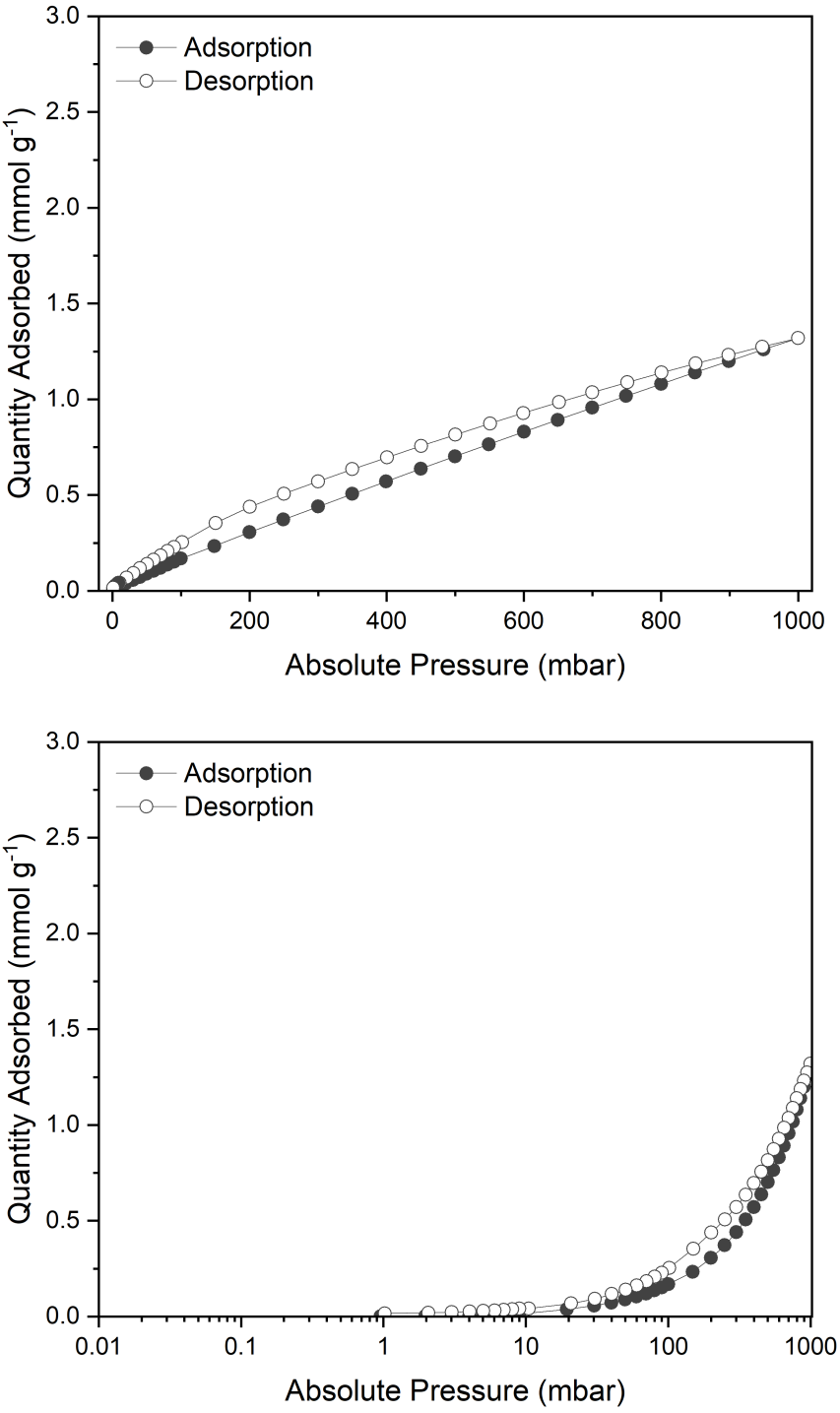

Figure S63. Single-component CO_2 sorption isotherm of MOF-808 at 25 °C with pressure plotted on a linear (top) and a logarithmic scale (bottom).

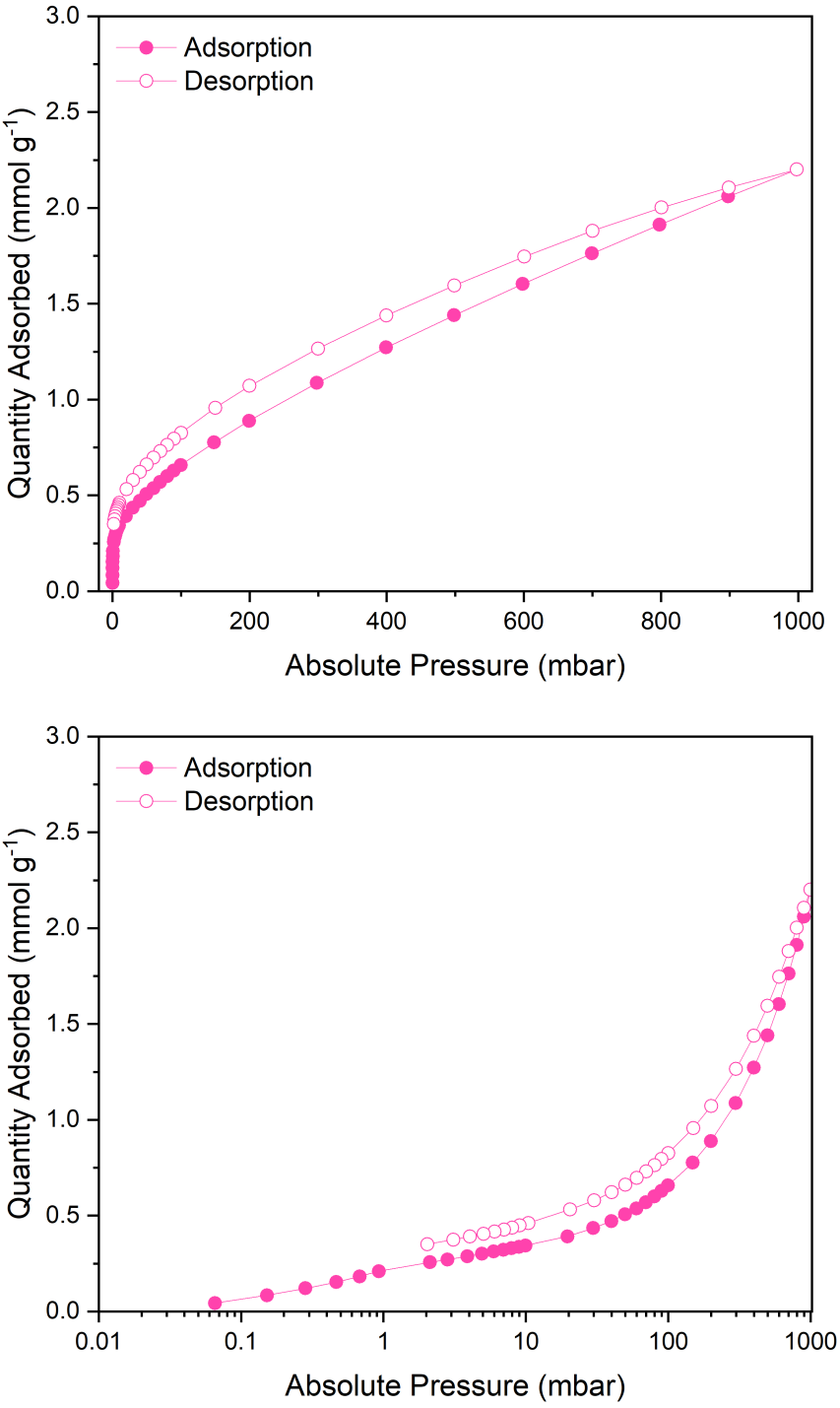

Figure S64. Single-component CO_2 sorption isotherm of MOF-808-Gly at 25 °C with pressure plotted on a linear (top) and a logarithmic scale (bottom).

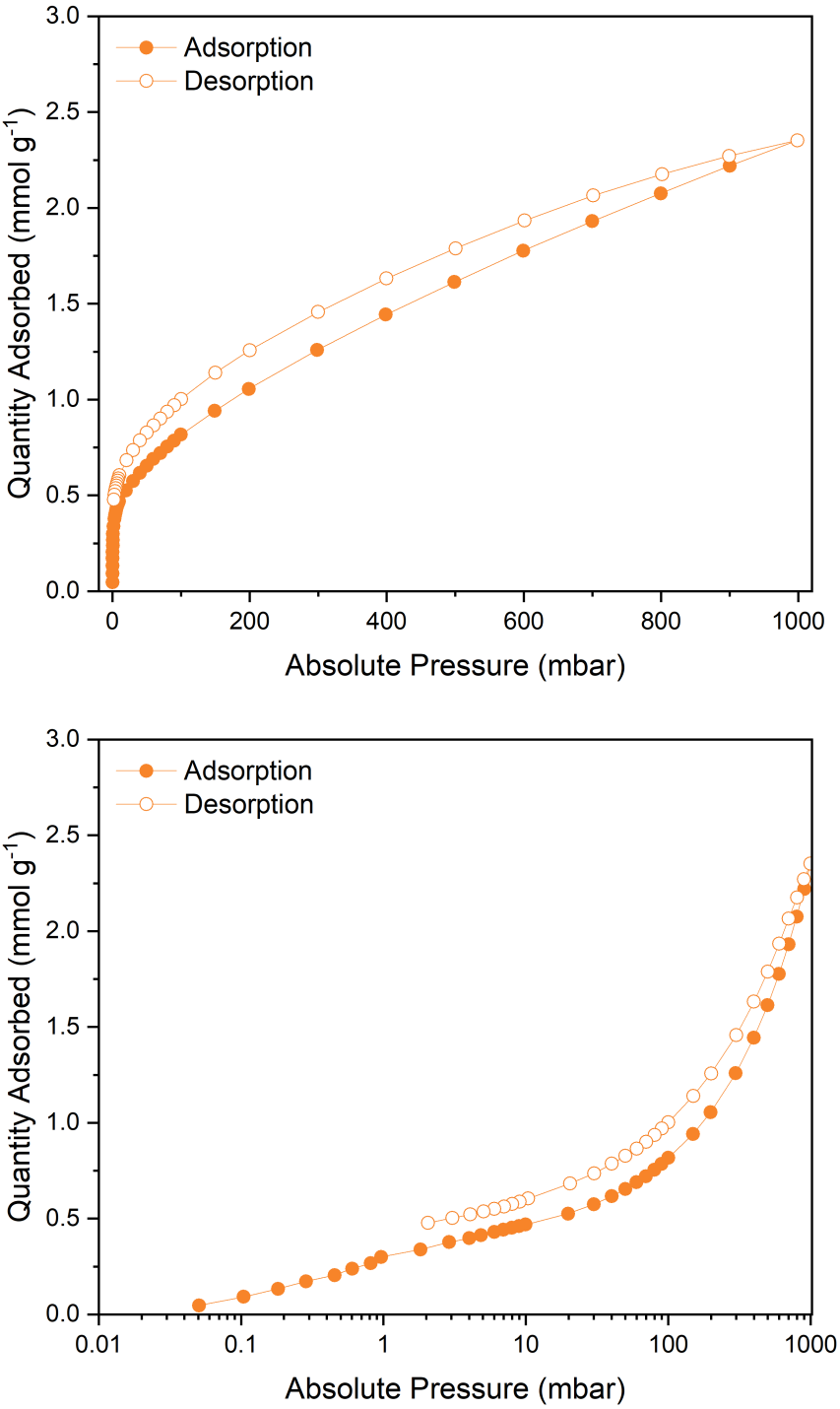

Figure S65. Single-component CO_2 sorption isotherm of MOF-808-Pro at 25 °C with pressure plotted on a linear (top) and a logarithmic scale (bottom).

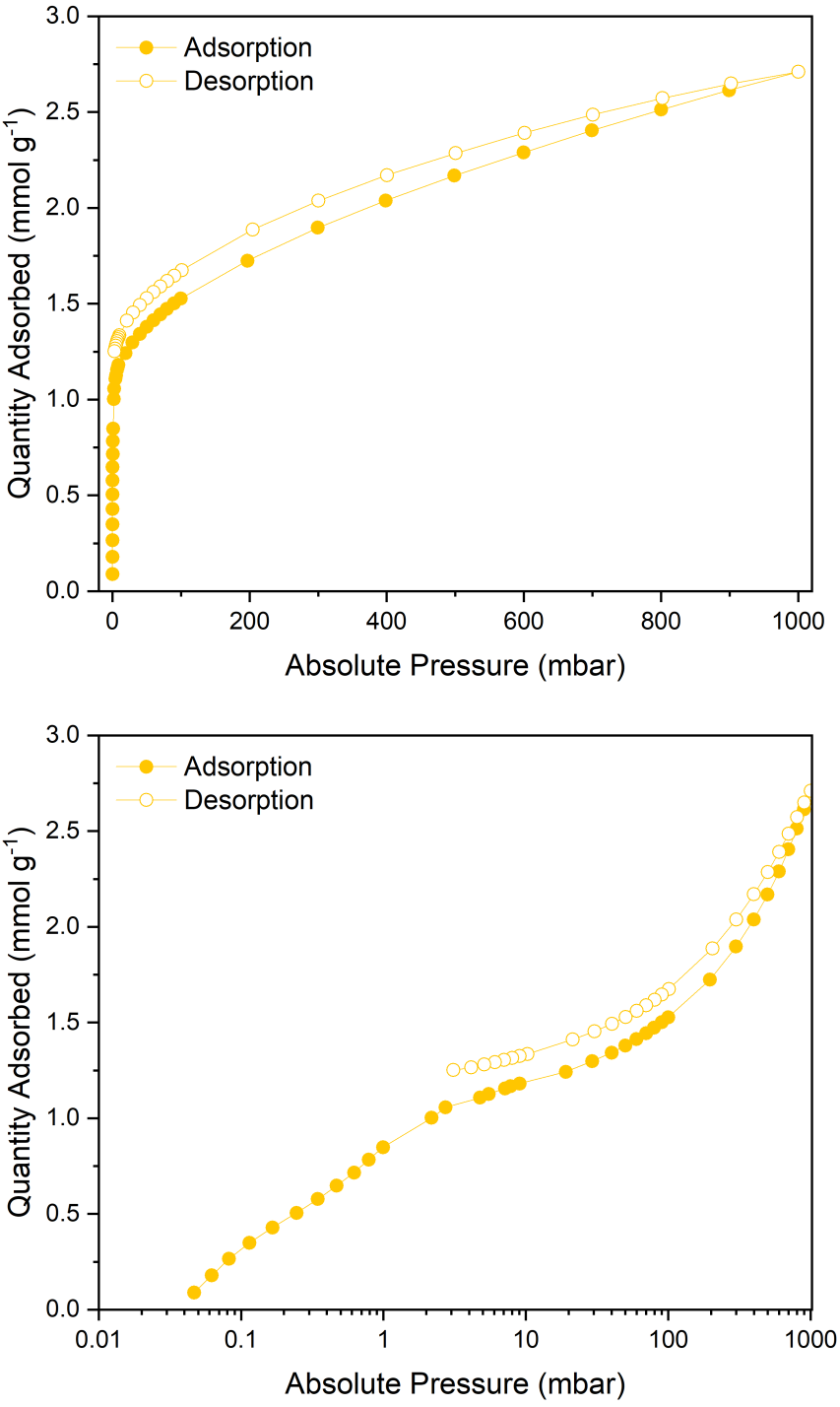

Figure S66. Single-component CO_2 sorption isotherm of MOF-808-Lys at 25 °C with pressure plotted on a linear (top) and a logarithmic scale (bottom).

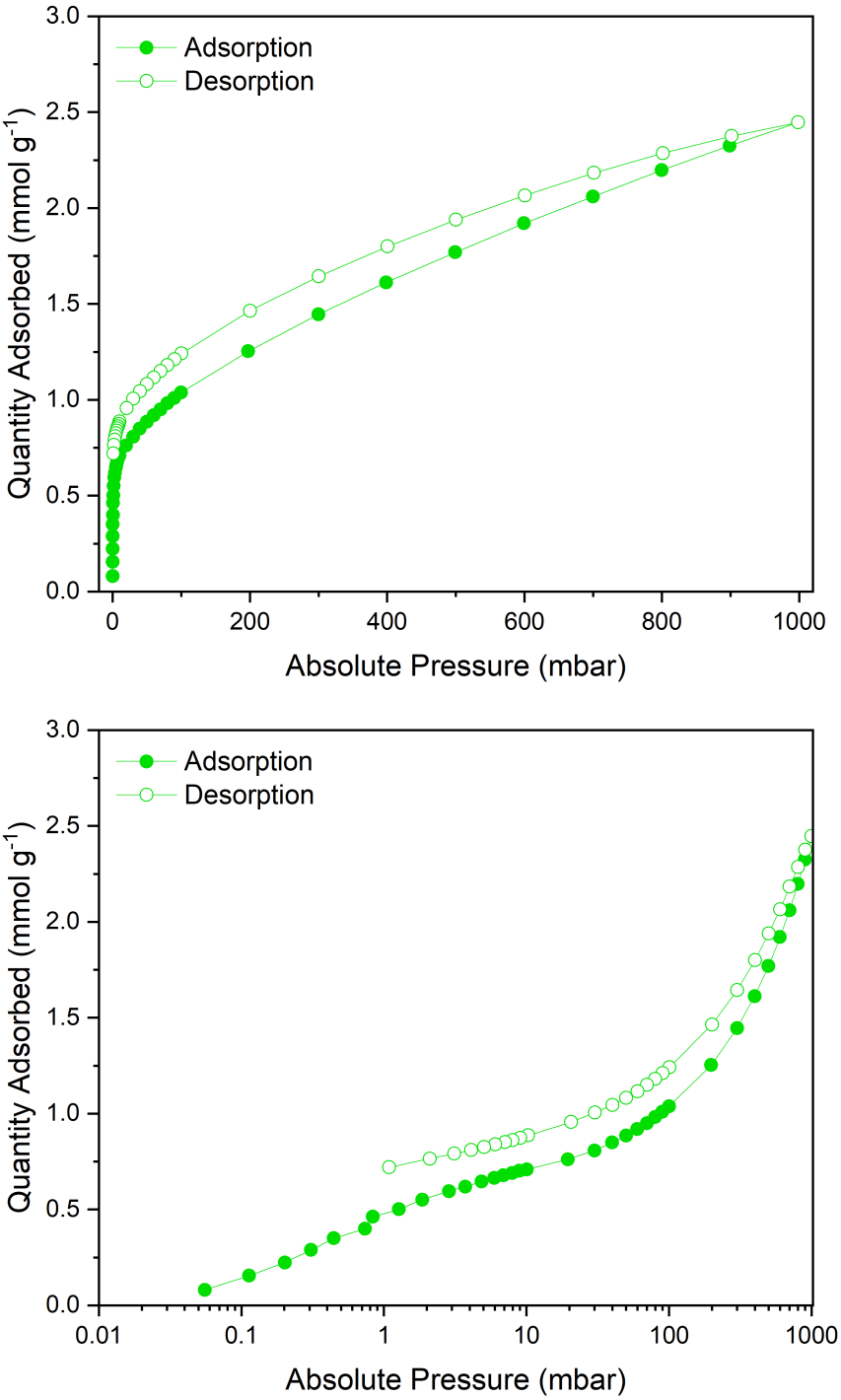

Figure S67. Single-component CO_2 sorption isotherm of MOF-808-Arg at 25 °C with pressure plotted on a linear (top) and a logarithmic scale (bottom).

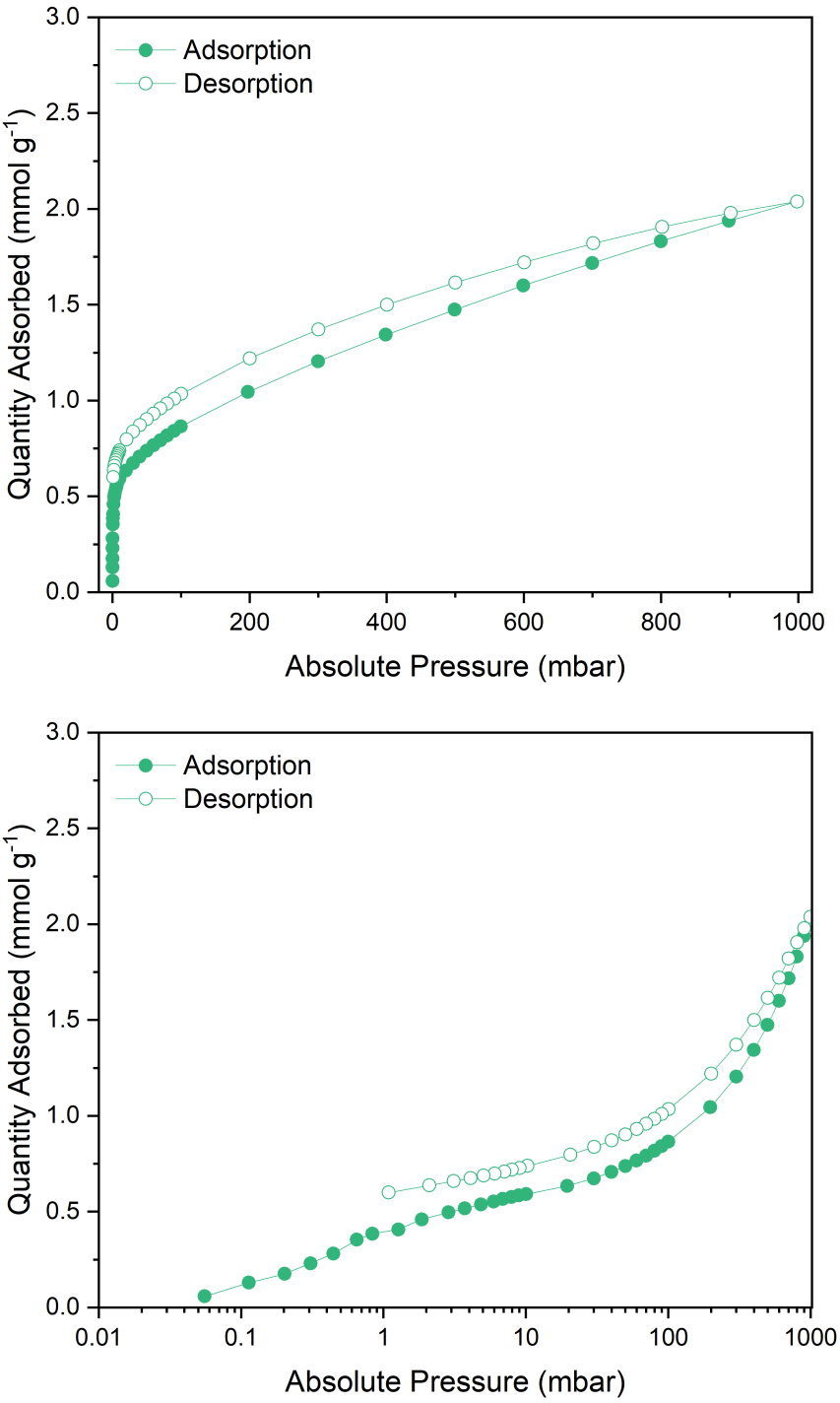

Figure S68. Single-component CO_2 sorption isotherm of MOF-808-EDA at 25 °C with pressure plotted on a linear (top) and a logarithmic scale (bottom).

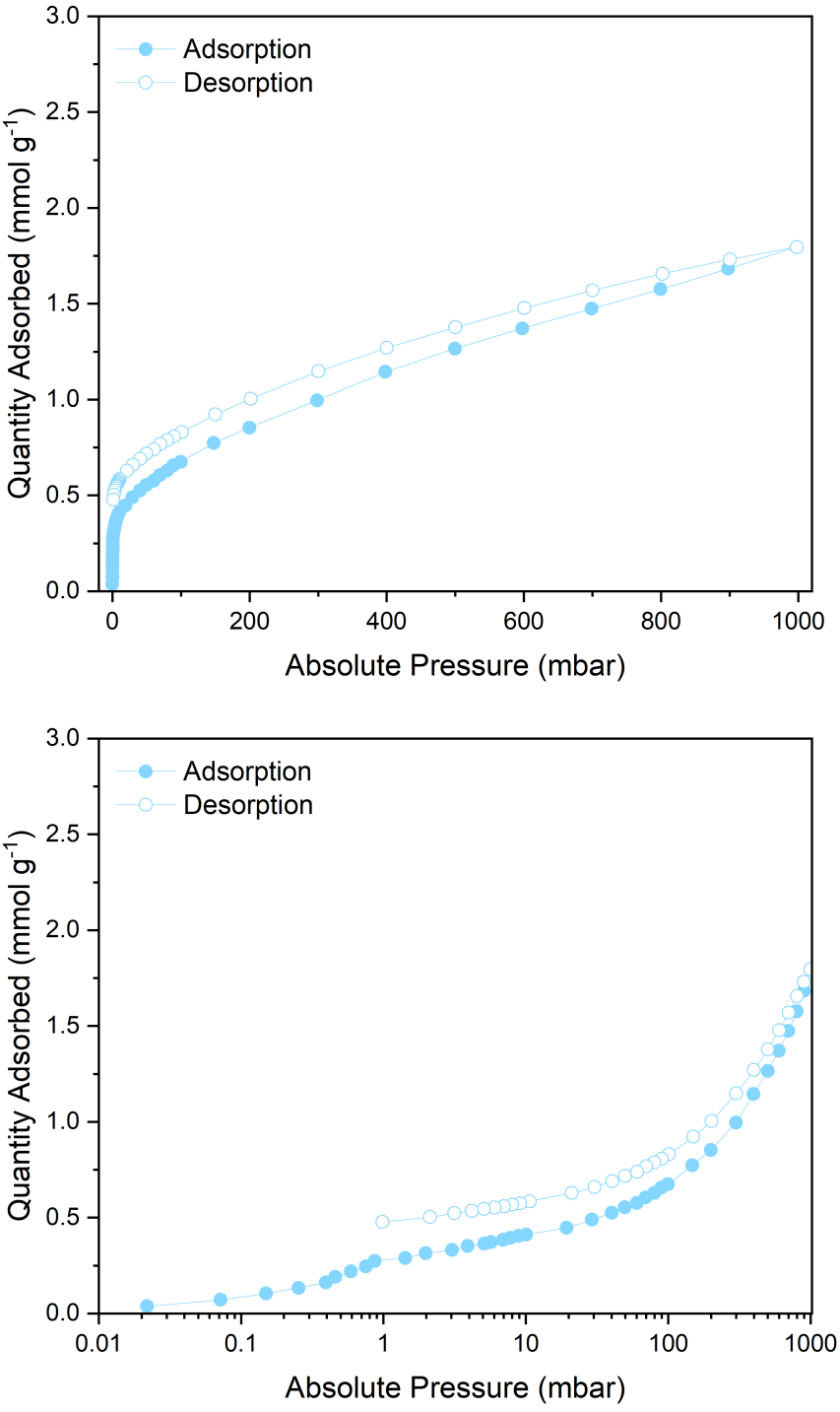

Figure S69. Single-component CO_2 sorption isotherm of MOF-808-DAP at 25 °C with pressure plotted on a linear (top) and a logarithmic scale (bottom).

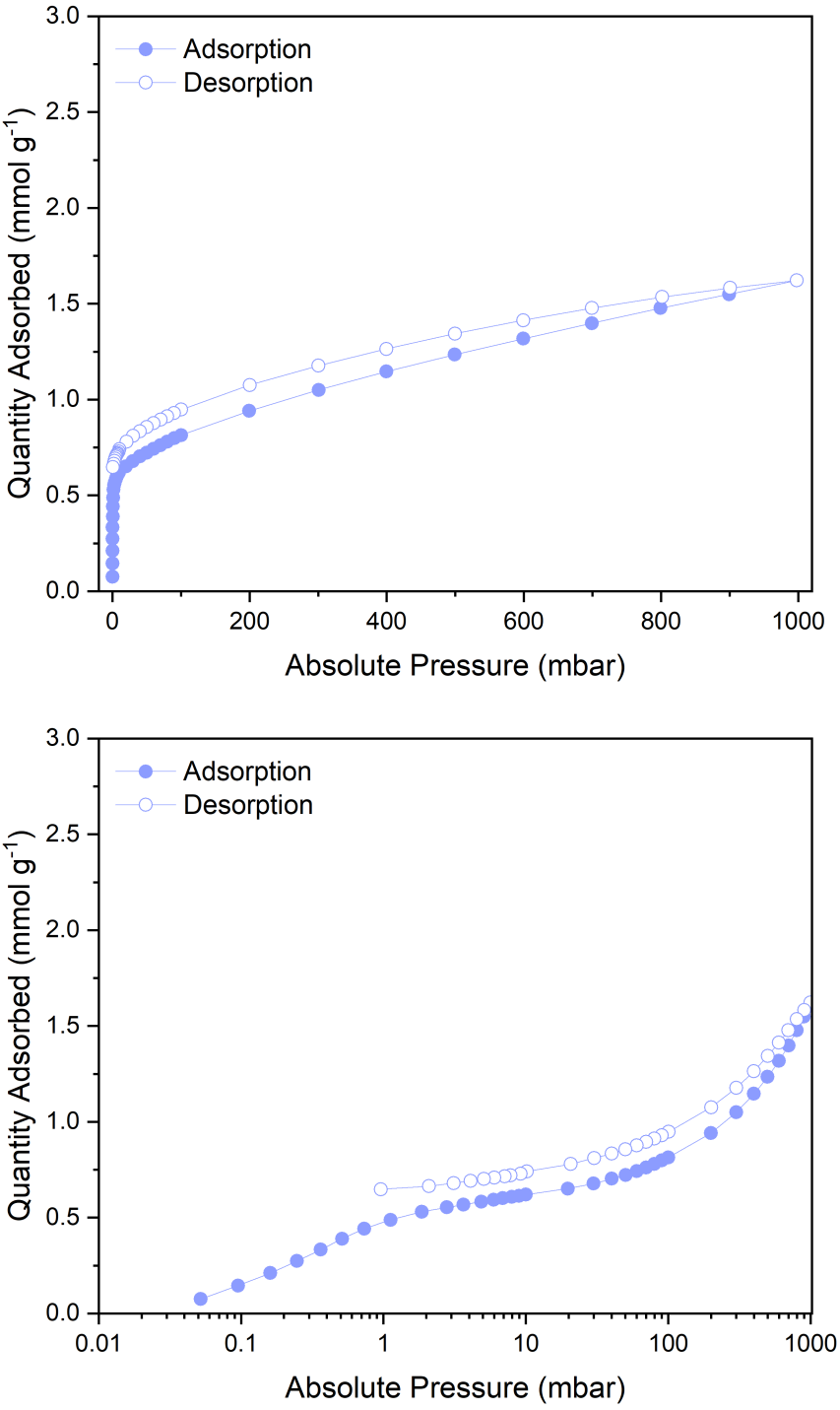

Figure S70. Single-component CO_2 sorption isotherm of MOF-808-TAEA at 25 °C with pressure plotted on a linear (top) and a logarithmic scale (bottom).

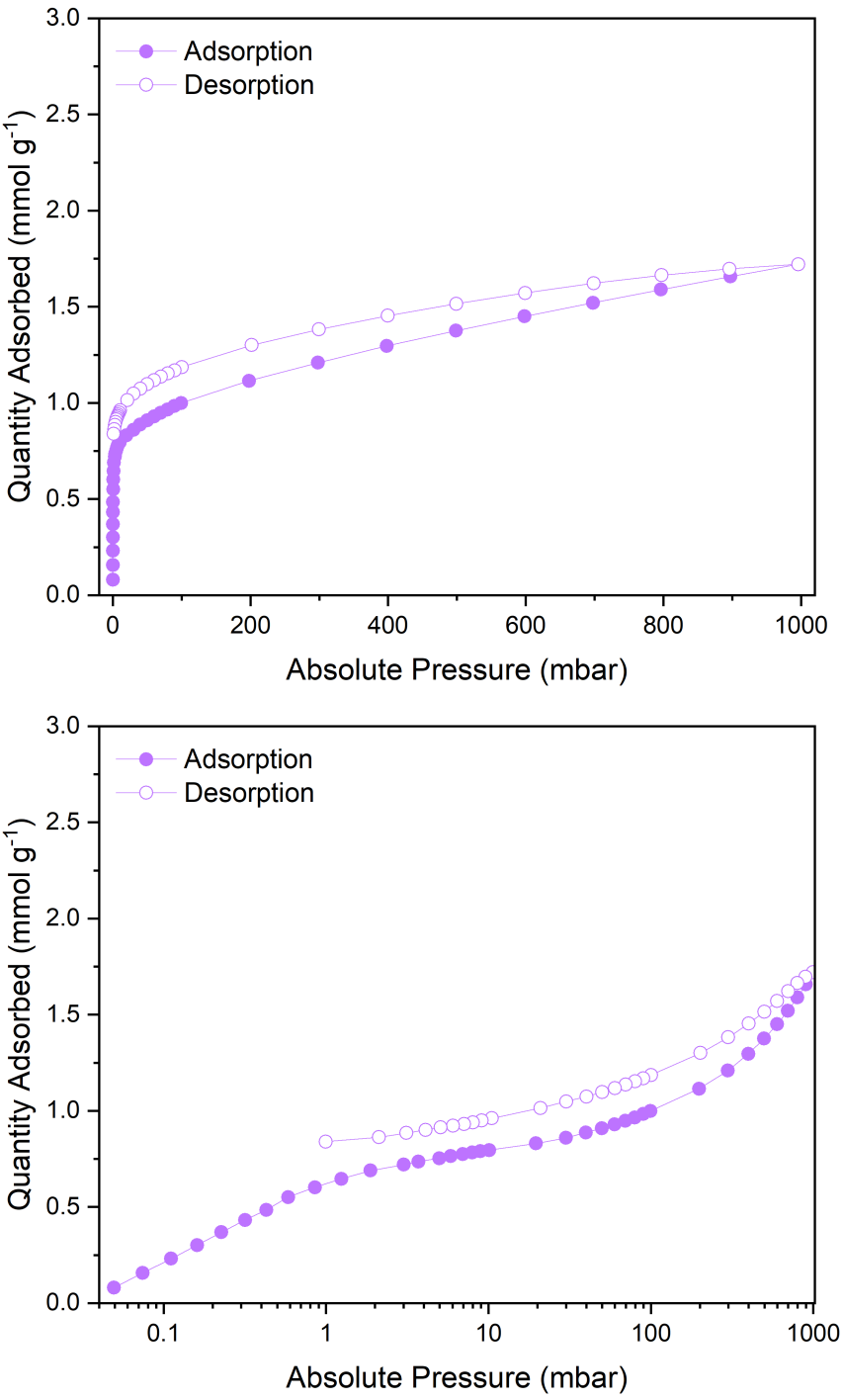

Figure S71. Single-component CO_2 sorption isotherm of MOF-808-TAPA at 25 °C with pressure plotted on a linear (top) and a logarithmic scale (bottom).

Section S10 Dynamic Breakthrough Sorption Analyses

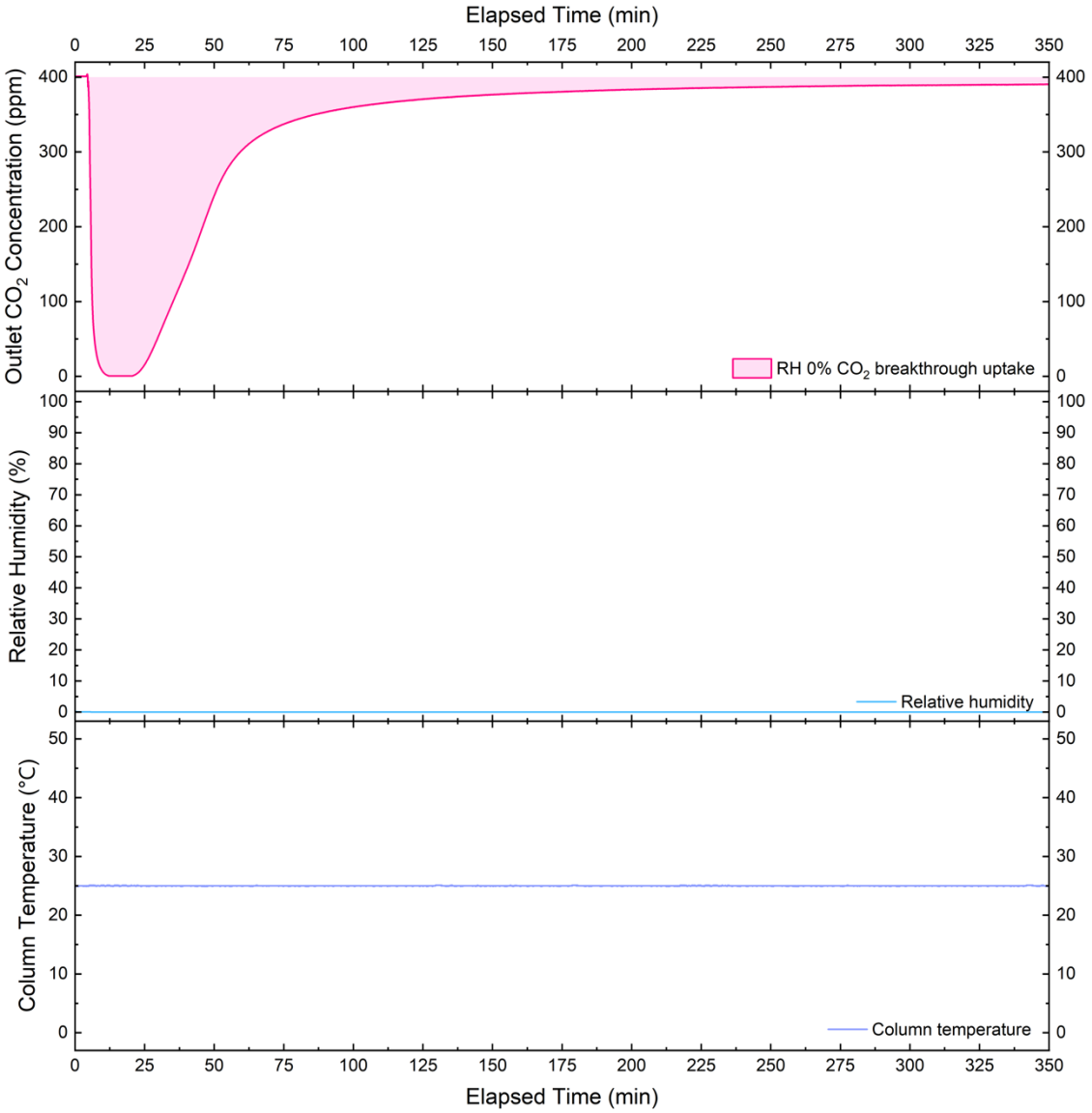

Figure S72. Dynamic breakthrough measurement of MOF-808-Lys at 0% RH and 25 °C. In the plot of the outlet CO_2 concentration, the CO_2 uptake can be derived through numerical integration of the marked area as 0.556 mmol g^{-1}.

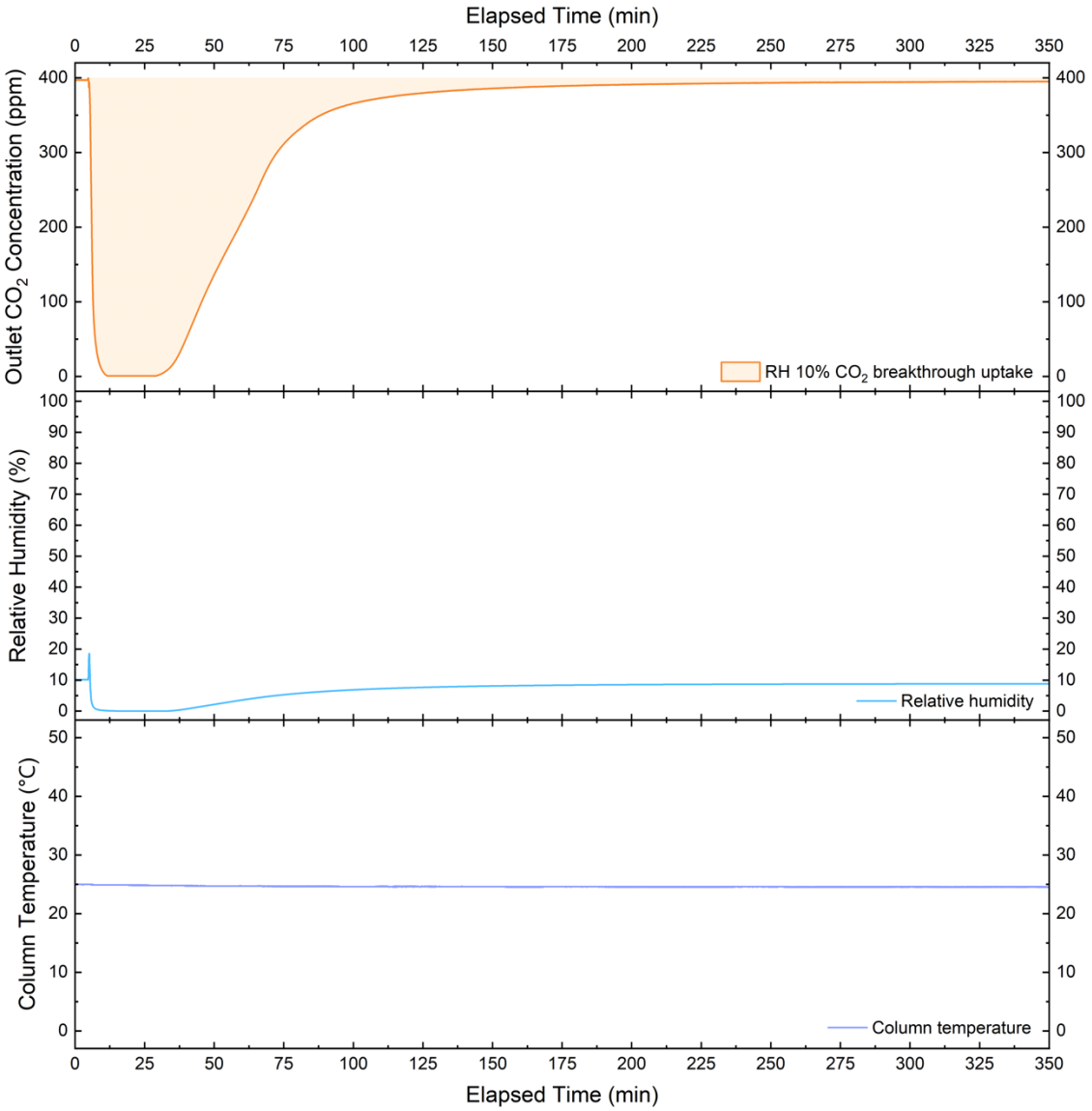

Figure S73. Dynamic breakthrough measurement of MOF-808-Lys at 10% RH and 25 °C. In the plot of the outlet CO_2 concentration, the CO_2 uptake can be derived through numerical integration of the marked area as 0.612 mmol g^{-1}.

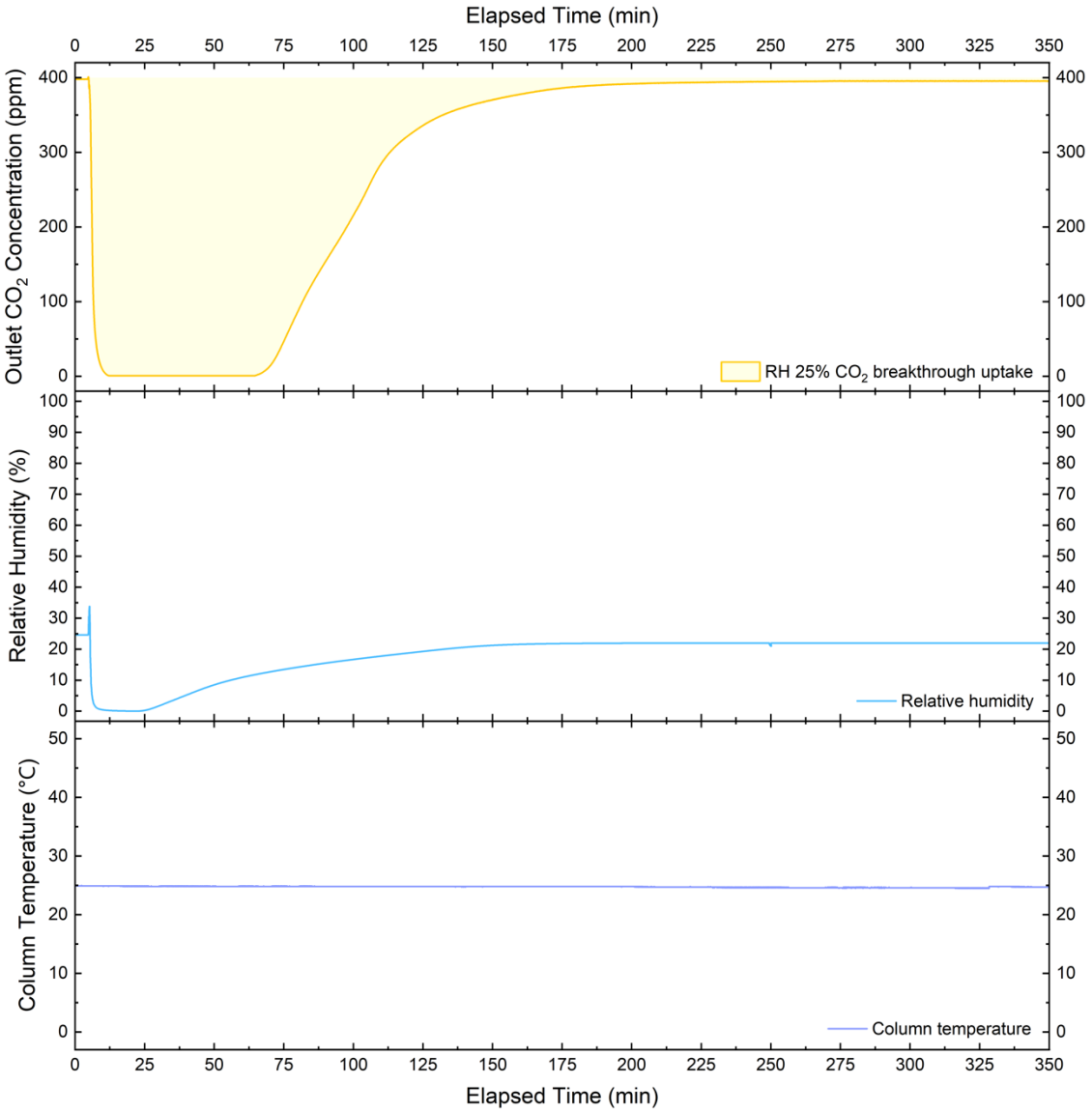

Figure S74. Dynamic breakthrough measurement of MOF-808-Lys at 25% RH and 25 °C. In the plot of the outlet CO_2 concentration, the CO_2 uptake can be derived through numerical integration of the marked area as 0.865 mmol g^{-1}.

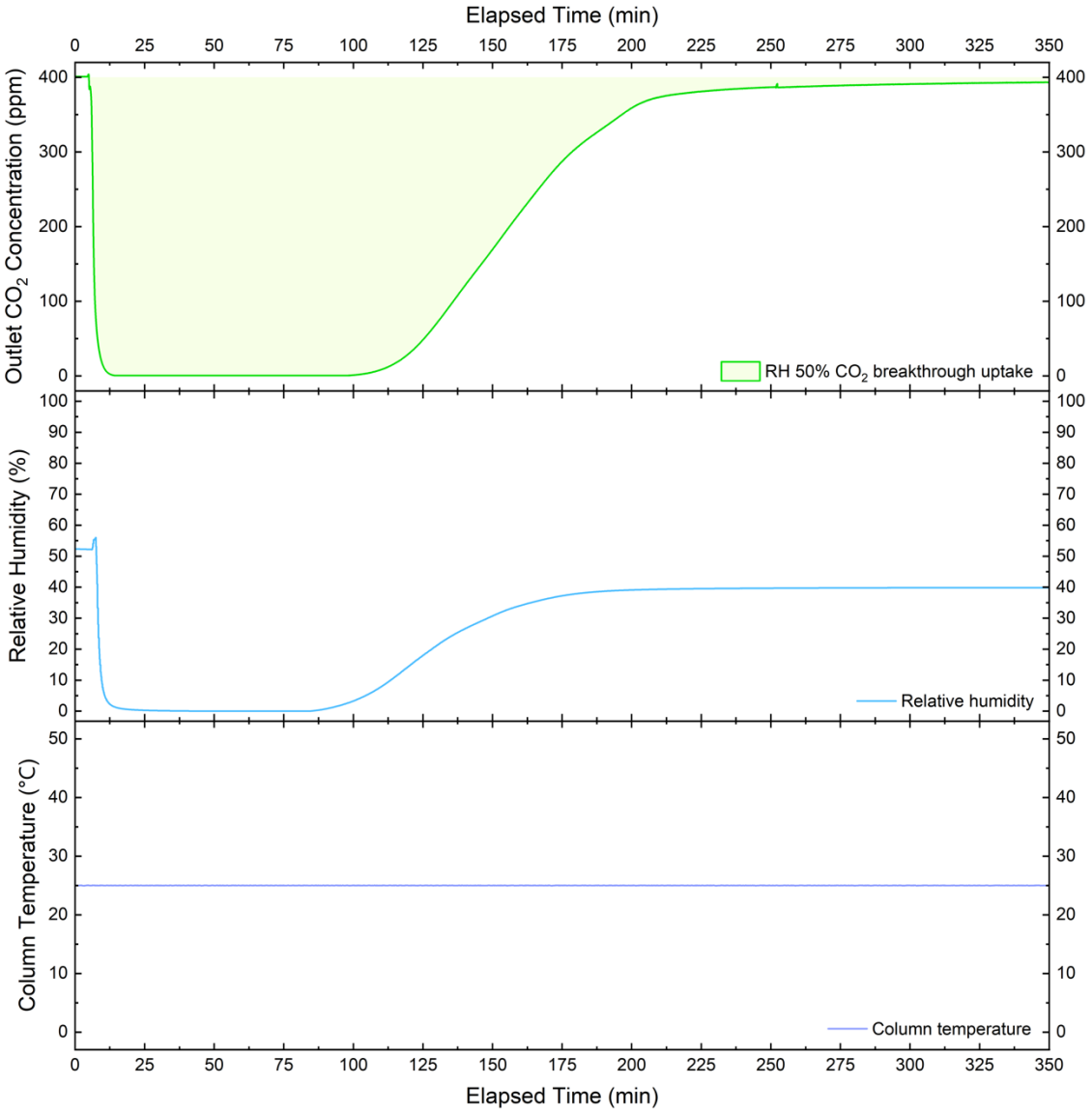

Figure S75. Dynamic breakthrough measurement of MOF-808-Lys at 50% RH and 25 °C. In the plot of the outlet CO_2 concentration, the CO_2 uptake can be derived through numerical integration of the marked area as 1.205 mmol g^{-1}.

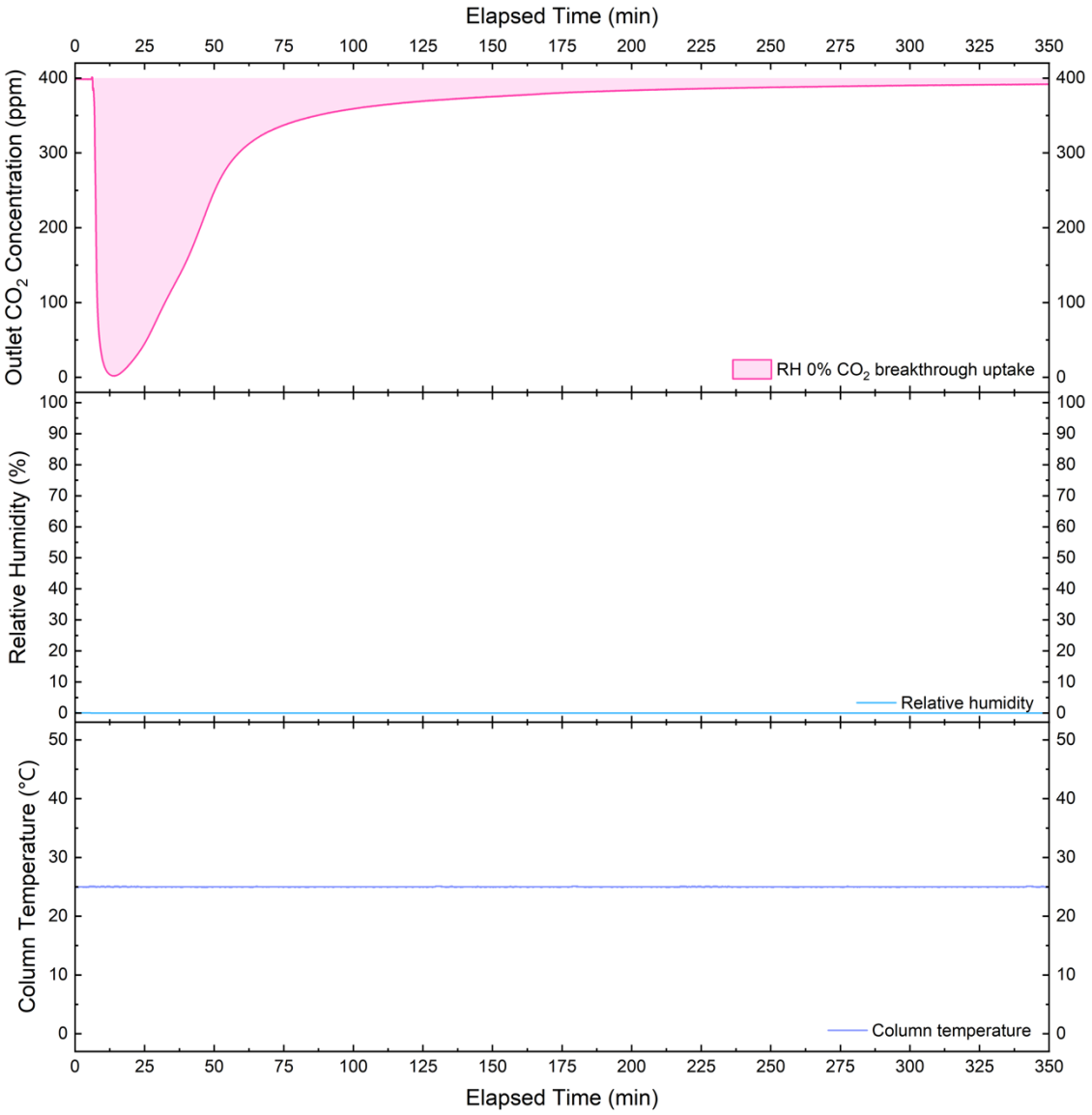

Figure S76. Dynamic breakthrough measurement of MOF-808-TAPA at 0% RH and 25 °C. In the plot of the outlet CO_2 concentration, the CO_2 uptake can be derived through numerical integration of the marked area as 0.454 mmol g^{-1}.

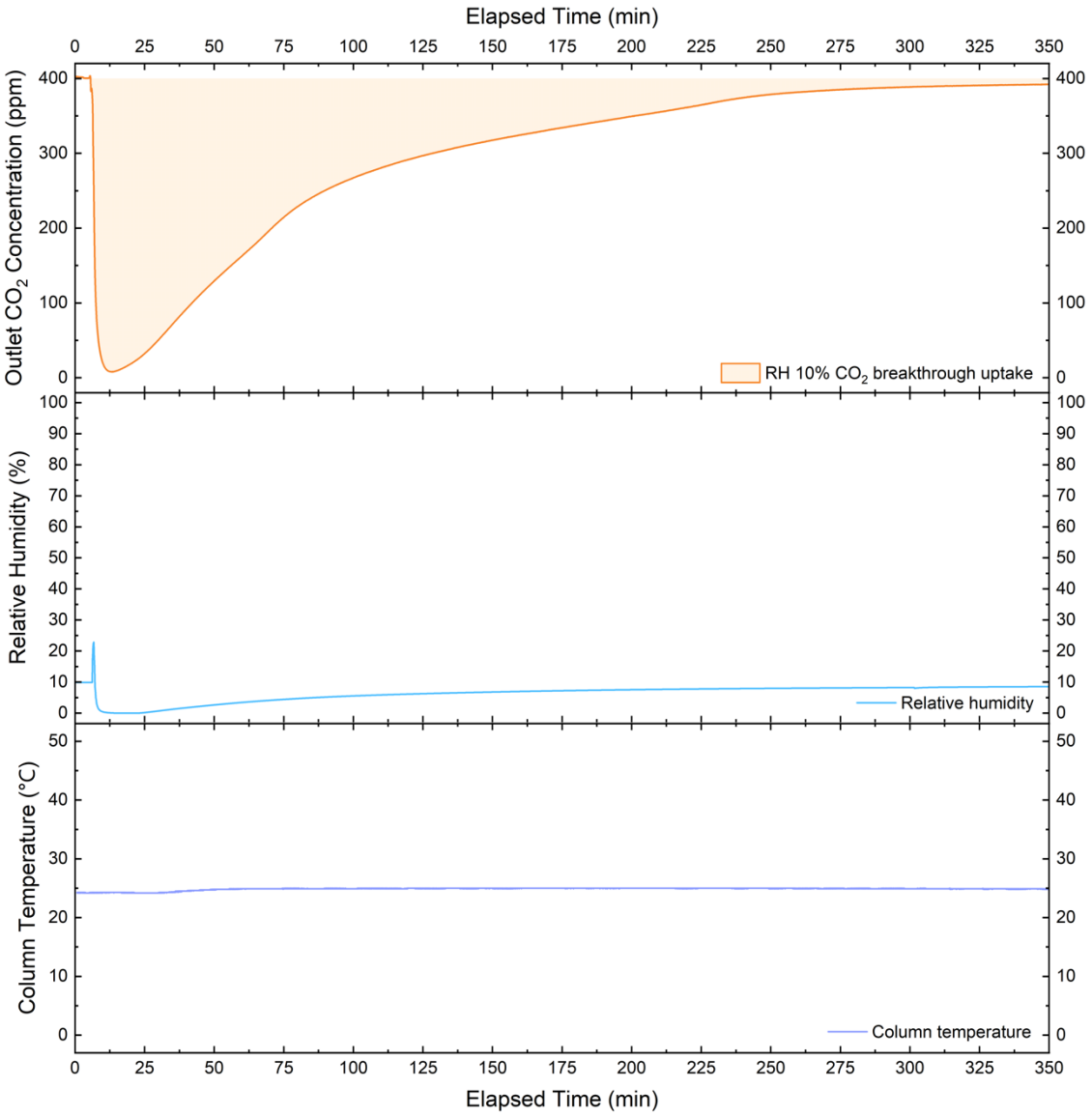

Figure S77. Dynamic breakthrough measurement of MOF-808-TAPA at 10% RH and 25 °C. In the plot of the outlet CO_2 concentration, the CO_2 uptake can be derived through numerical integration of the marked area as 0.757 mmol g^{-1}.

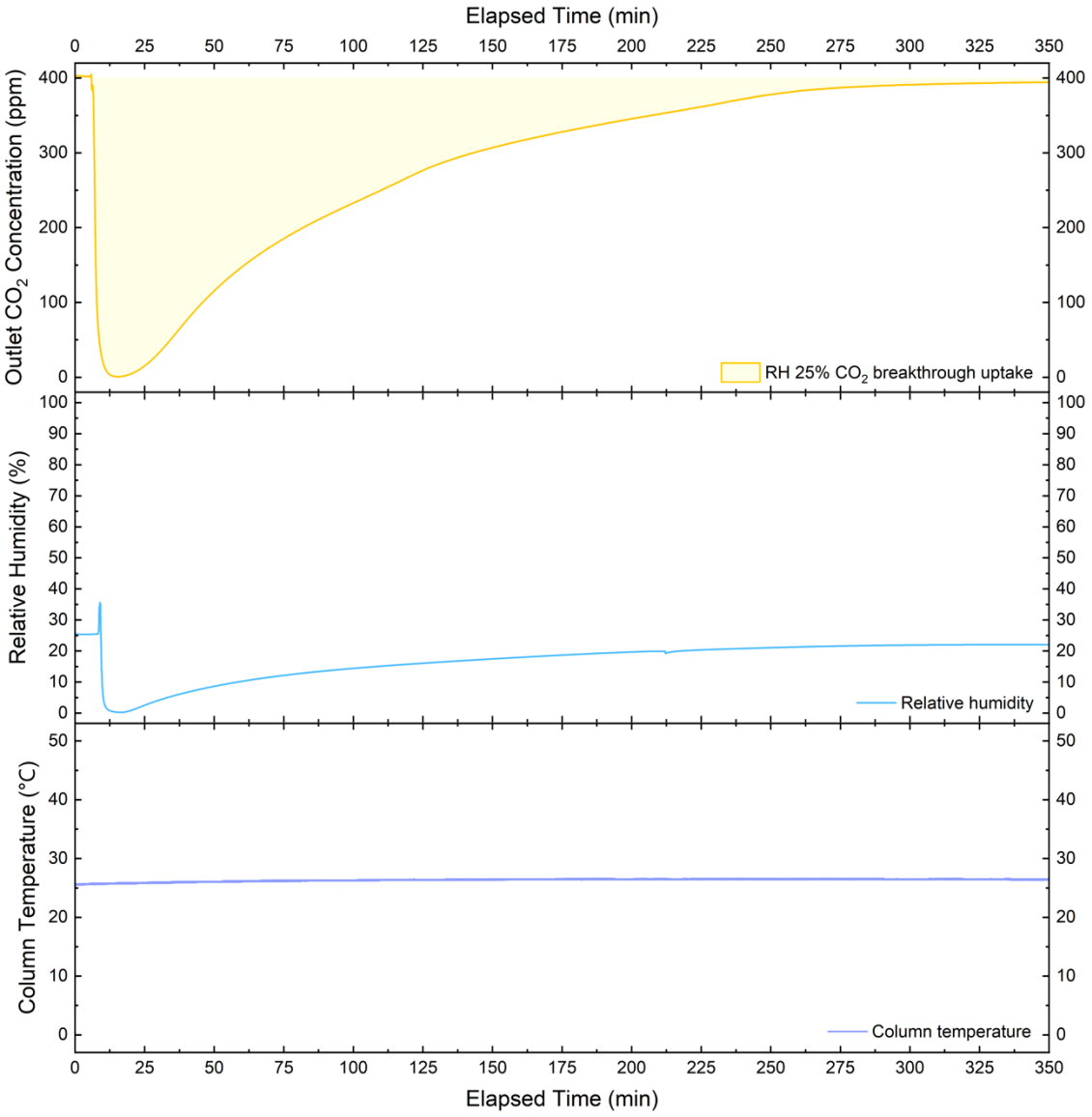

Figure S78. Dynamic breakthrough measurement of MOF-808-TAPA at 25% RH and 25 °C. In the plot of the outlet CO_2 concentration, the CO_2 uptake can be derived through numerical integration of the marked area as 0.796 mmol g^{-1}.

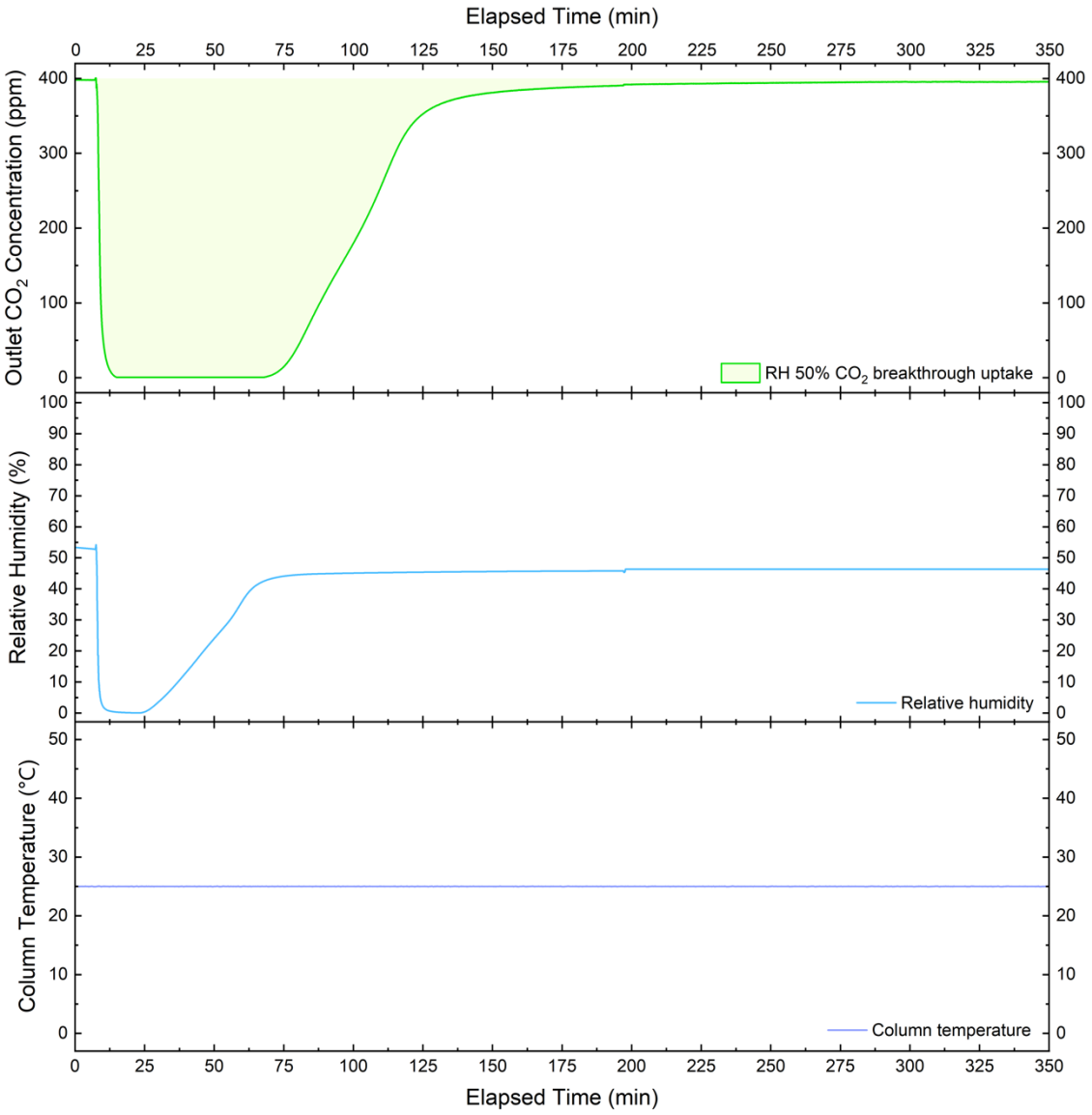

Figure S79. Dynamic breakthrough measurement of MOF-808-TAPA at 50% RH and 25 °C. In the plot of the outlet CO_2 concentration, the CO_2 uptake can be derived through numerical integration of the marked area as 0.872 mmol g^{-1}.

Section S11 Cycling Performance

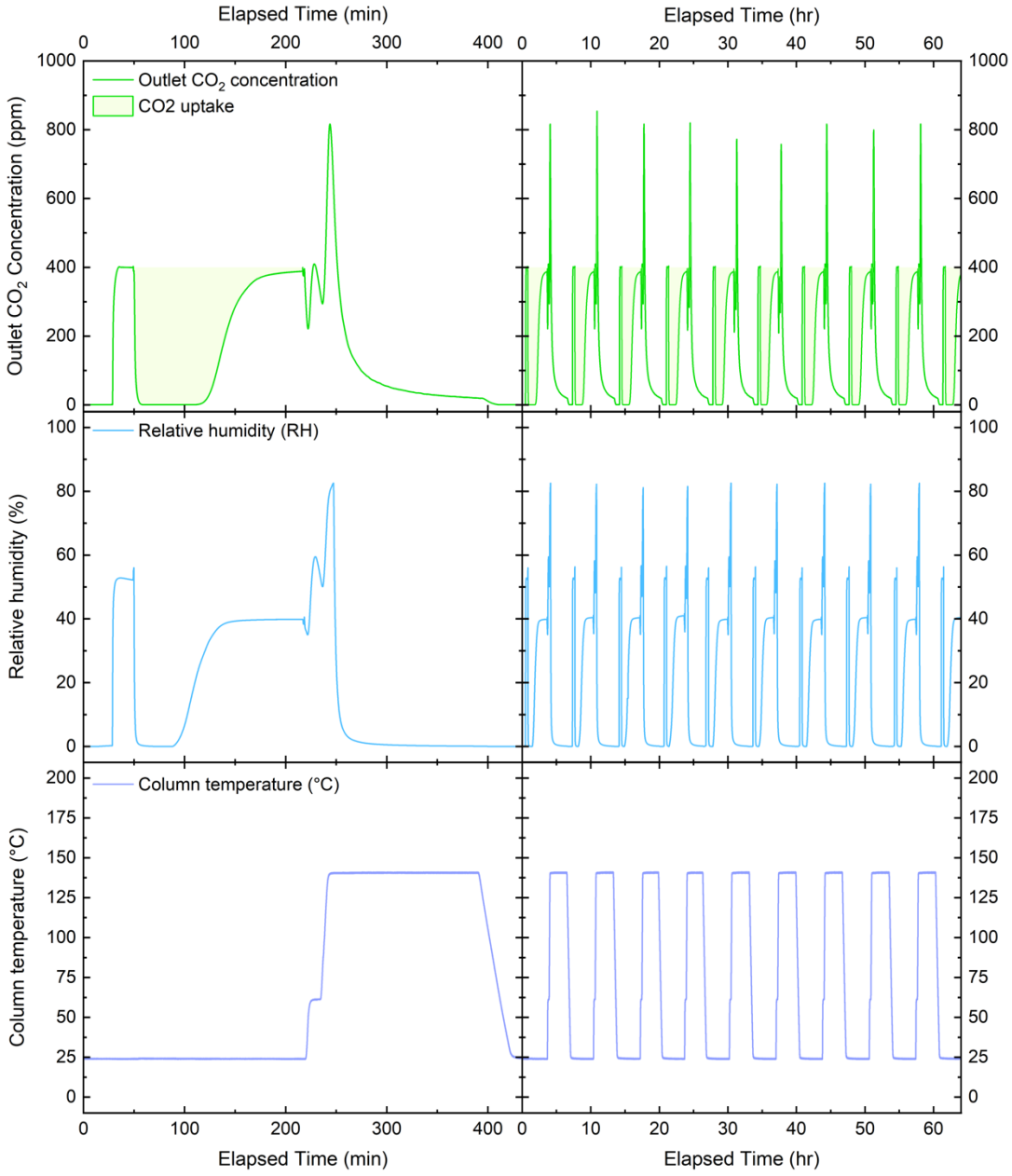

Figure S80. Temperature-swing cycles (left: 1 cycle; right: 10 cycles) conducted on MOF-808-Lys at 50% RH. In the plot of the outlet CO_2 concentration, the CO_2 uptake can be derived through numerical integration of the marked area.

Section S12 Reference

1. Jiang, J.; Gándara, F.; Zhang, Y.-B.; Na, K.; Yaghi, O. M.; Klemperer, W. G., Superacidity in Sulfated Metal–Organic Framework-808. *J. Am. Chem. Soc.* **2014,** *136*, 12844-12847.

2. Lyu, H.; Chen, O. I.-F.; Hanikel, N.; Hossain, M. I.; Flaig, R. W.; Pei, X.; Amin, A.; Doherty, M. D.; Impastato, R. K.; Glover, T. G., Carbon Dioxide Capture Chemistry of Amino Acid Functionalized Metal–Organic Frameworks in Humid Flue Gas. *J. Am. Chem. Soc.* **2022,** *144*, 2387-2396.