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Supporting Information

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Section S1: Materials and Methods

Chemicals

Hydroxylamine hydrochloride ($NH_2OH \cdot HCl$, purity ≥ 99%), dimethyl terephthalate (purity ≥ 98%), yttrium (III) nitrate hexahydrate ($Y(NO_3)_3 \cdot 6\ H_2O$, purity ≥ 99%), sodium hydroxide (NaOH, purity ≥ 98%) were purchased from AK Scientific Inc. Methanol (EtOH, purity ≥ 99.8%) and formic acid (HCOOH, ≥ 98%) was purchased from Sigma Aldrich. Deuterated solvents were obtained from Cambridge Isotope Laboratories. Ultrahigh-purity (UHP) grade (99.999%) argon, nitrogen, and helium were obtained from Praxair. All chemicals were used without further purification.

Analytical techniques and instruments

Powder X-ray diffraction (PXRD) patterns were recorded using a Rigaku Miniflex 600 diffractometer (Bragg-Brentano geometry, Cu Kα radiation $\lambda = 1.54056$ Å).

^1H NMR and ^{13}C NMR spectra were acquired on a Bruker AVQ-500 NMR spectrometer and internally referenced to the residual solvent signals

Thermogravimetric analysis (TGA) curves were recorded on a TA Q500 thermal analysis system under nitrogen flow, ramping at 5 °C min^{-1} from room temperature to 800 ˚C. Ultrahigh-purity-grade N_2 was used in TGA measurement.

Elemental analysis measurements were performed using a Perkin Elmer 2400 Series II CHNS elemental analyzer at the Microanalytical Laboratory of the College of Chemistry, University of California, Berkeley.

Scanning electron micrographs were collected using a FEI Quanta 3d FEG scanning electron microscope with an accelerating voltage of 5 - 10 kV and a working distance of 10 mm. Samples were dispersed on carbon tape on top of stainless-steel sample holders.

Optical microscope image was taken from HRX-01 digital microscope with the transmission mode. The sample was dispersed on a piece of glass slide and the polarizer was slightly turned on for creating a contrast between the crystals and the background.

Single-crystal X-ray diffraction (SXRD) measurement on MOF-419 was performed on a Rigaku XtaLAB P200 equipped with a MicroMax 007HF rotating anode and a Pilatus 200K hybrid pixel array detector. Data were collected using Cu Kα radiation ($\lambda = 1.5406$ Å). Crystal was mounted on a Kapton® MiTeGen MicroMount™ and kept at 250 K throughout the collection. Data collection was performed with CrysAlisPro.[1] Data processing was done with CrysAlisPro and included a multi-scan absorption correction applied using the SCALE3 ABSPACK scaling algorithm within CrysAlisPro.

Nitrogen sorption experiments were conducted using a Micromeritics Accelerated Surface Area and Porosimetry (ASAP) 2420 System. Before the measurement, the sample was activated at 120°C for 12 hours. The sample was cooled to 77 K using a liquid nitrogen bath during the measurement. The data analyses were carried out using the Micromeritics MicroActive software.[2]

Water vapor sorption experiments were carried out on a BEL Japan BELSORP-aqua-3. 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.

Section S2: Synthesis of Linker H_2BDH and MOF-419

Synthesis of 1,4-benzo-dihydroxamic acid (H_2BDH)

The synthesis of H_2BDH was carried out based on a modified procedure reported in the previous literature.[3] Briefly, in a 250 mL round bottom flask, 90 mL deionized water was added to dissolve sodium hydroxide (14.4 g, 360 mmol) and hydroxylamine hydrochloride (12.6 g, 180 mmol), followed by the addition of a suspension of dimethyl terephthalate (11.6 g, 60 mmol) in 100 mL methanol. The mixture was stirred vigorously for 24 hours at room temperature. After cooling down to room temperature, the crude product was acidified with HCl to pH = 5.5. The white solid was filtered, washed with deionized saturated solution of $NaHCO_3$ and deionized water, and dried under vacuum overnight (61 % yield). ^1H-NMR (500 MHz, DMSO-d_6): 11.35 (brs), 9.20 (brs), 7.81 (s, 4H). ^{13}C NMR (500 MHz, DMSO-d_6) δ: 163.51 (C), 135.13 (C), 127.05 (CH).

Synthesis of MOF-419 in DMF

In a 20 mL scintillation vial, H_2BDH (98 mg, 0.5 mmol) was dispersed in DMF (10 mL). The resulting mixture was heated for 30 min in a preheated oven at 100 °C to yield a clear solution. Yttrium (III) nitrate hexahydrate (191 mg, 0.5 mmol) was dissolved in DMF (2 mL) and added to the H_2BDH solution. The combined solution was sonicated for 10 min and formic acid (4 mL, 100 mmol) was added. The vial was placed in an oven at 100 °C for 90 min. The resulting solid was collected via filtration. The single crystals were washed with DMF (10.0 mL) three times to remove the unreacted reagents in the pores. DMF solvent was removed by washing the crystals with acetone (10.0 mL) for three times. The obtained solid was collected via filtration and dried under vacuum to yield MOF-419 (148 mg, 90% based on linker). Elemental Analysis: for $YC_9H_7N_2O_6$: Calcd. C 32.95%, H 2.15%, N 8.54%; Found C 32.59%, H 2.54%, N 8.51%.

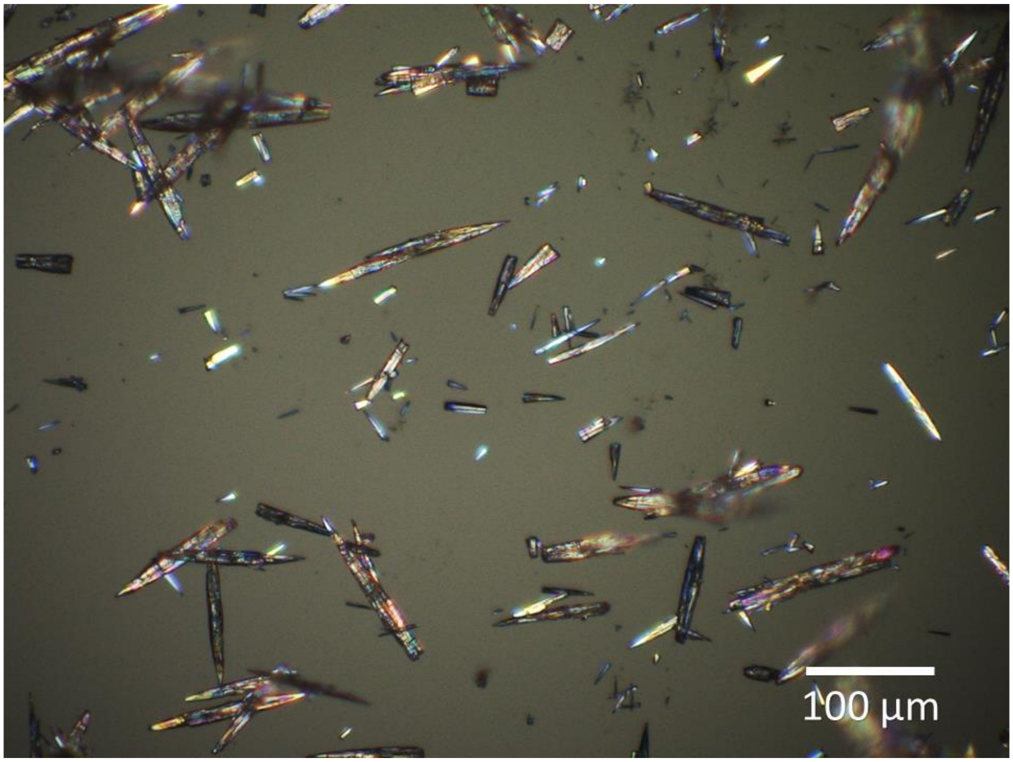


Figure S1. Optical image of needle-shaped crystals of MOF-419.

Synthesis of MOF-419 in water

In a 20 mL scintillation vial, yttrium (III) nitrate hexahydrate (191 mg, 0.5 mmol) and H_2BDH (98 mg, 0.5 mmol) were dispersed in deionized water (12 mL). The mixture was sonicated for 10 min and formic acid (4 mL, 100 mmol) was added to the solution. The vial was placed in an oven at 100 °C overnight. The resulting solid was collected via filtration. The single crystals were washed with deionized water (10.0 mL) and acetone (10.0 mL) three times per day for two days, respectively. The obtained solid was collected via filtration and dried under vacuum to yield MOF-419 (122 mg, 72% based on linker). Elemental Analysis: for $YC_9H_7N_2O_6$: Calcd. C 32.95%, H 2.15%, N 8.54%; Found C 32.57%, H 2.43%, N 8.42%.

Table S1 Summary of the elemental analysis results

Elements	C (%)	H (%)	N (%)	S (%)
Calculated	32.95	2.15	8.54	0
MOF-419 (DMF)	32.59	2.54	8.51	0
MOF-419 (H_2O)	32.57	2.43	8.42	0

Section S3: Single-Crystal X-ray Diffraction Analyses

The structural solutions were determined by using intrinsic phasing (SHELXT) and refined by the principle of least squares on F^2 (SHELXL) using the Olex2 software package.[4] Olex2 solvent mask procedure was applied,[5] and the masked volume and the total number of masked electrons are 180 Å^3 and 55 e$^-$, respectively.

Table S2 Measurement details, data quality, and refinement quality of the single-crystal structure of MOF-419.

	Before SQUEEZE	After SQUEEZE
Empirical formula	$C_9H_7N_2O_6Y$	$C_9H_7N_2O_6Y$
Formula weight	328.08	328.08
Temperature/K	250	250
Crystal system	tetragonal	tetragonal
Space group	$I4_122$	$I4_122$
a/Å	17.20550(10)	17.20550(10)
b/Å	17.20550(10)	17.20550(10)
c/Å	15.70790(10)	15.70790(10)
α/°	90	90
β/°	90	90
γ/°	90	90
Volume/Å^3	4650.00(6)	4650.00(6)
Z	8	8
ρ_{calc}g/cm^3	0.937	0.937
μ/mm^{-1}	3.662	3.662
F(000)	1296.0	1296.0
Crystal size/mm^3	0.1 × 0.05 × 0.01	0.1 × 0.05 × 0.01
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.266 to 158.008	7.266 to 158.008
Index ranges	$-21 \le h \le 21$, $-21 \le k \le 21$, $-15 \le l \le 19$	$-21 \le h \le 21$, $-21 \le k \le 21$, $-15 \le l \le 19$
Reflections collected	50171	50171
Independent reflections	2517 [R_{int} = 0.0475, R_{sigma} = 0.0126]	2517 [R_{int} = 0.0475, R_{sigma} = 0.0126]
Data/restraints/parameters	2517/9/88	2517/9/87
Goodness-of-fit on F^2	1.245	1.109
Final R indexes [I>=2σ (I)]	R_1 = 0.0560, wR_2 = 0.1782	R_1 = 0.0345, wR_2 = 0.0944
Final R indexes [all data]	R_1 = 0.0562, wR_2 = 0.1784	R_1 = 0.0346, wR_2 = 0.0946
Largest diff. peak/hole / e Å^{-3}	1.94/-1.12	1.94/-0.94
Flack parameter	0.51(6)	0.53(3)

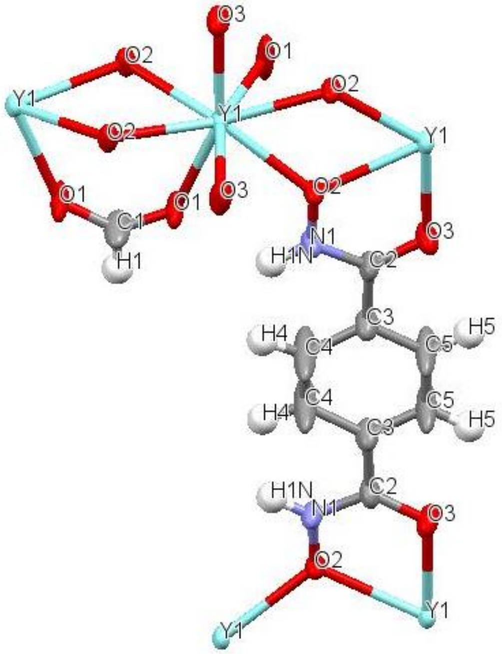


Figure S2. The connectivity between the yttrium secondary building units (SBUs) and organic linker H_2BDH in the single crystal structure of MOF-419. The bonding between the metal center and the hydroxamate groups allow for flexibility. Y, cyan sphere; O, red sphere; N, deep-blue sphere; C, gray sphere. H, white sphere.

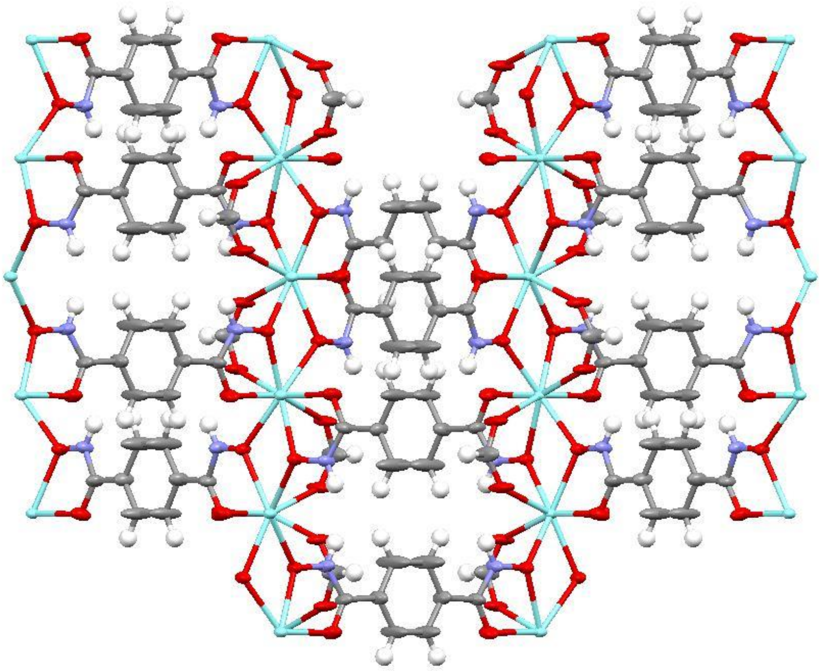


Figure S3. Packing in the single crystal structure of MOF-419 viewed along the a-axis. Y, cyan sphere; O, red sphere; N, deep-blue sphere; C, gray sphere. H, white sphere.

Section S4: Powder X-Ray Diffraction Analysis

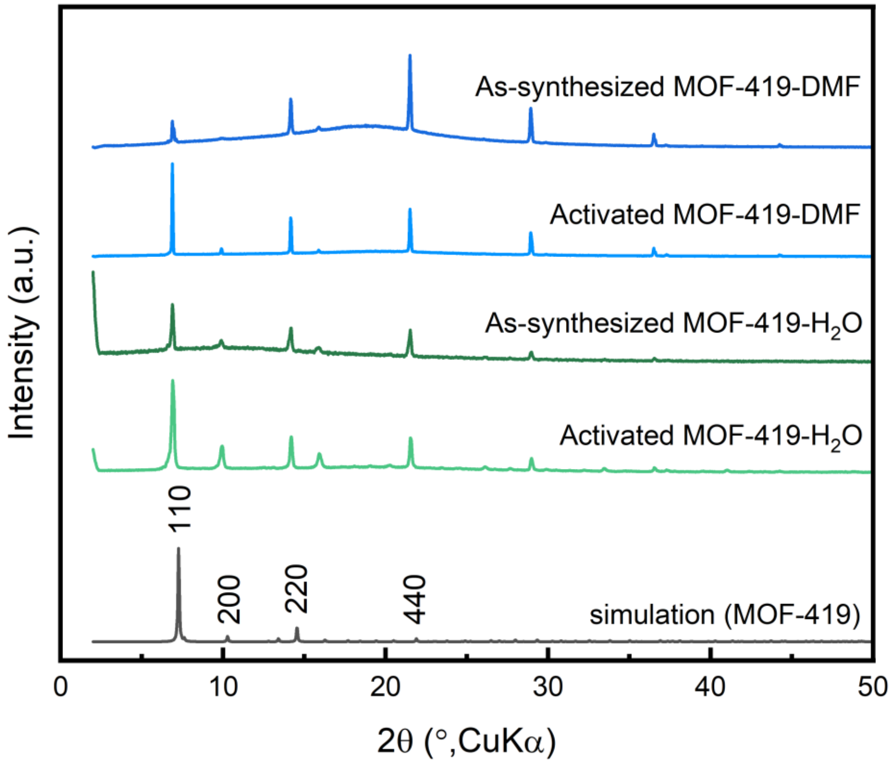


Figure S4. Powder x-ray diffraction pattern of as-synthesized and activated MOF-419 samples prepared by different solvents. The simulated patterns at the bottom were generated using the single crystal structure of MOF-419 obtained from DMF.

Section S5: Nuclear Magnetic Resonance Spectroscopy

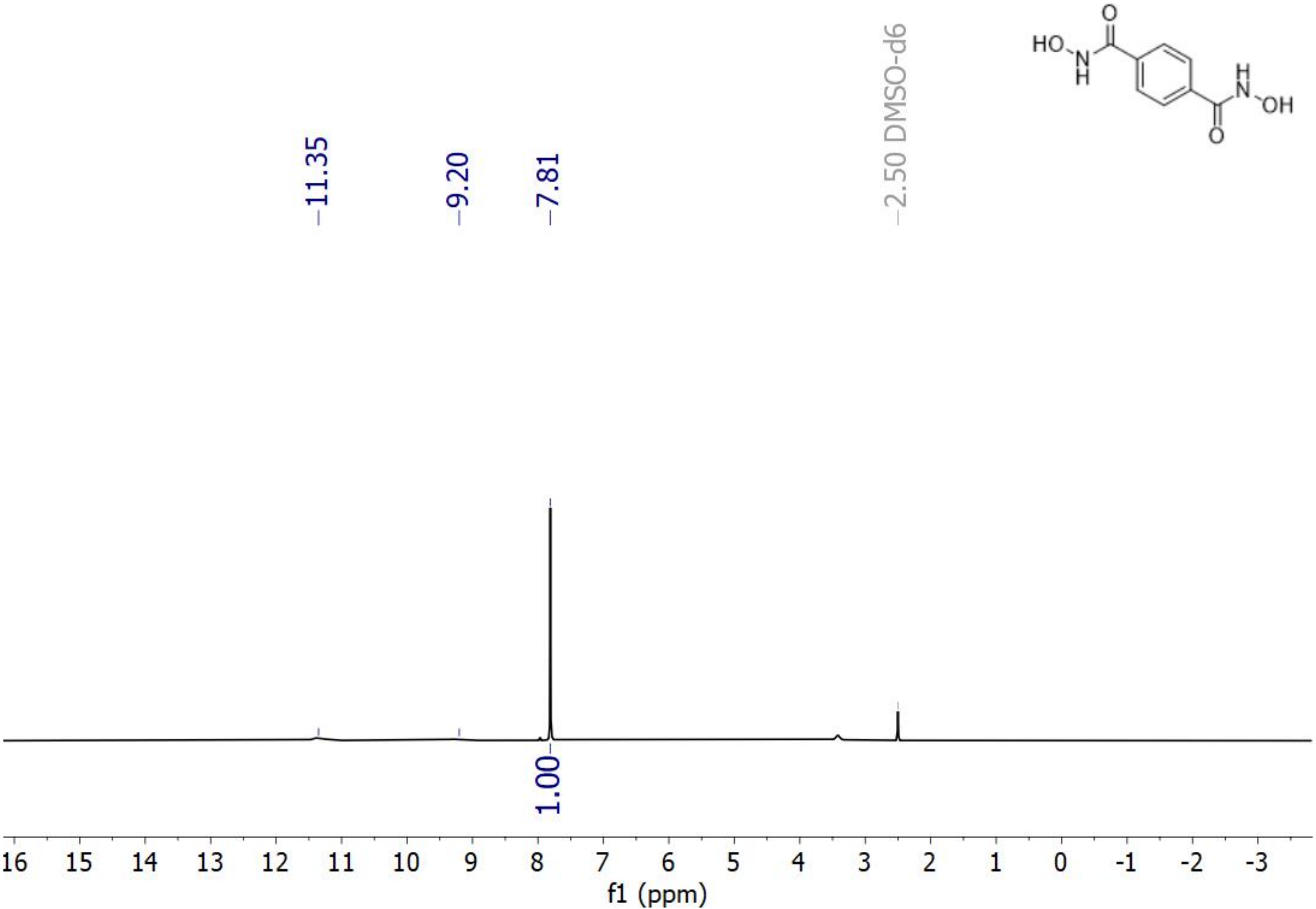


Figure S5. ^{1}H-NMR spectrum of linker H_2BDH in DMSO-d_6.

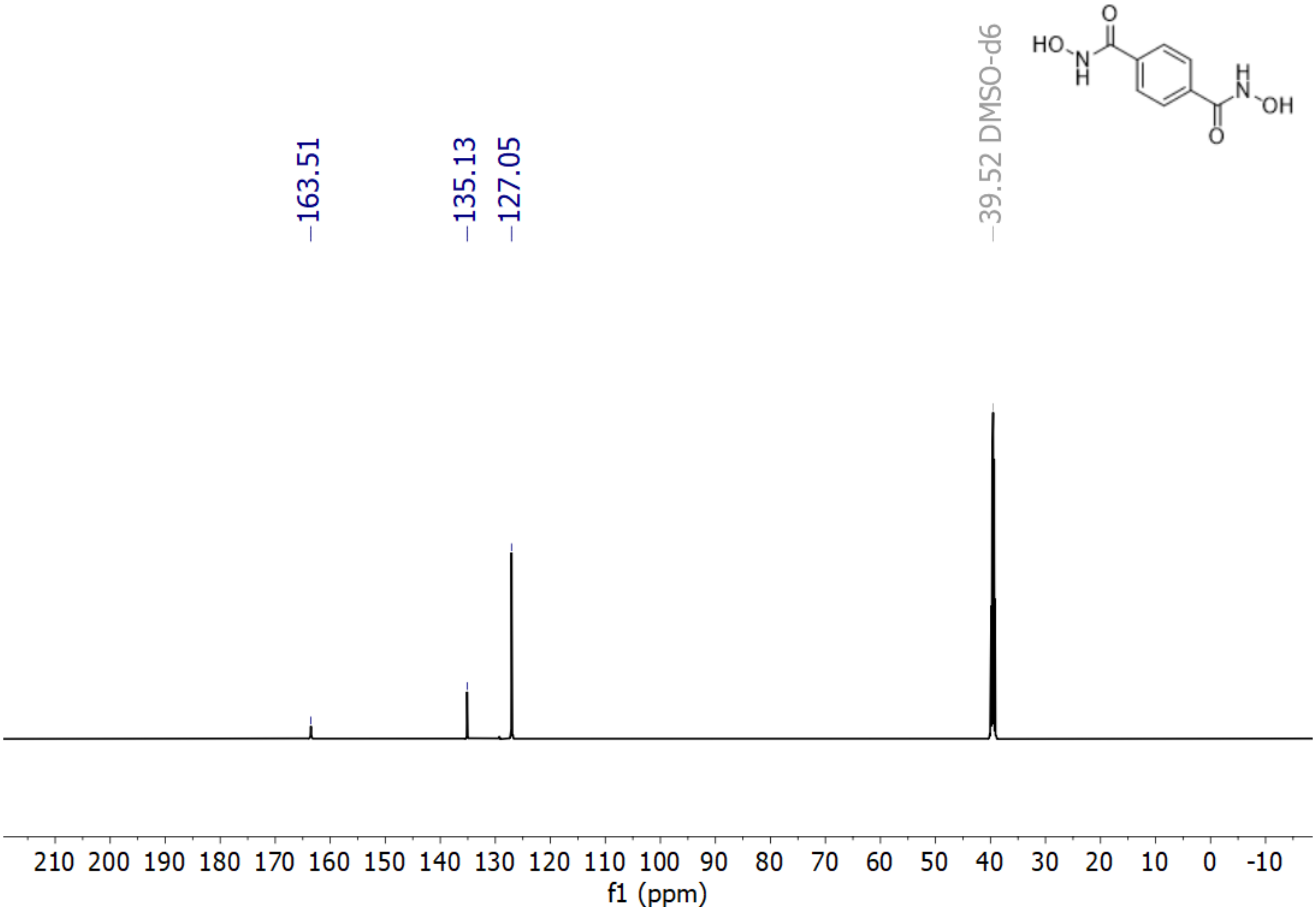


Figure S6. ^{13}C-NMR spectrum of linker H_2BDH in DMSO-d_6.

MOF-419 was digested in a mixture of 60 µL 35 % DCl in D_2O and 600 µL of deuterated dimethylsulfoxide (DMSO-d_6) for ^{1}H-NMR analysis. The proton signal from the hydrogen atom on formic acid and aromatic hydrogen atoms H_2BDH linker showed a 1:4 ratio, suggesting a 1:1 ratio between $HCOO^-$ and BDH^{2-} in MOF-419. The proton signal at 6.37 ppm corresponds to the proton in DCl/D_2O and the signal at 2.50 was from the DMSO-d_6 solvent. No signal from DMF and acetone was found, suggesting the washing and activation were completed.

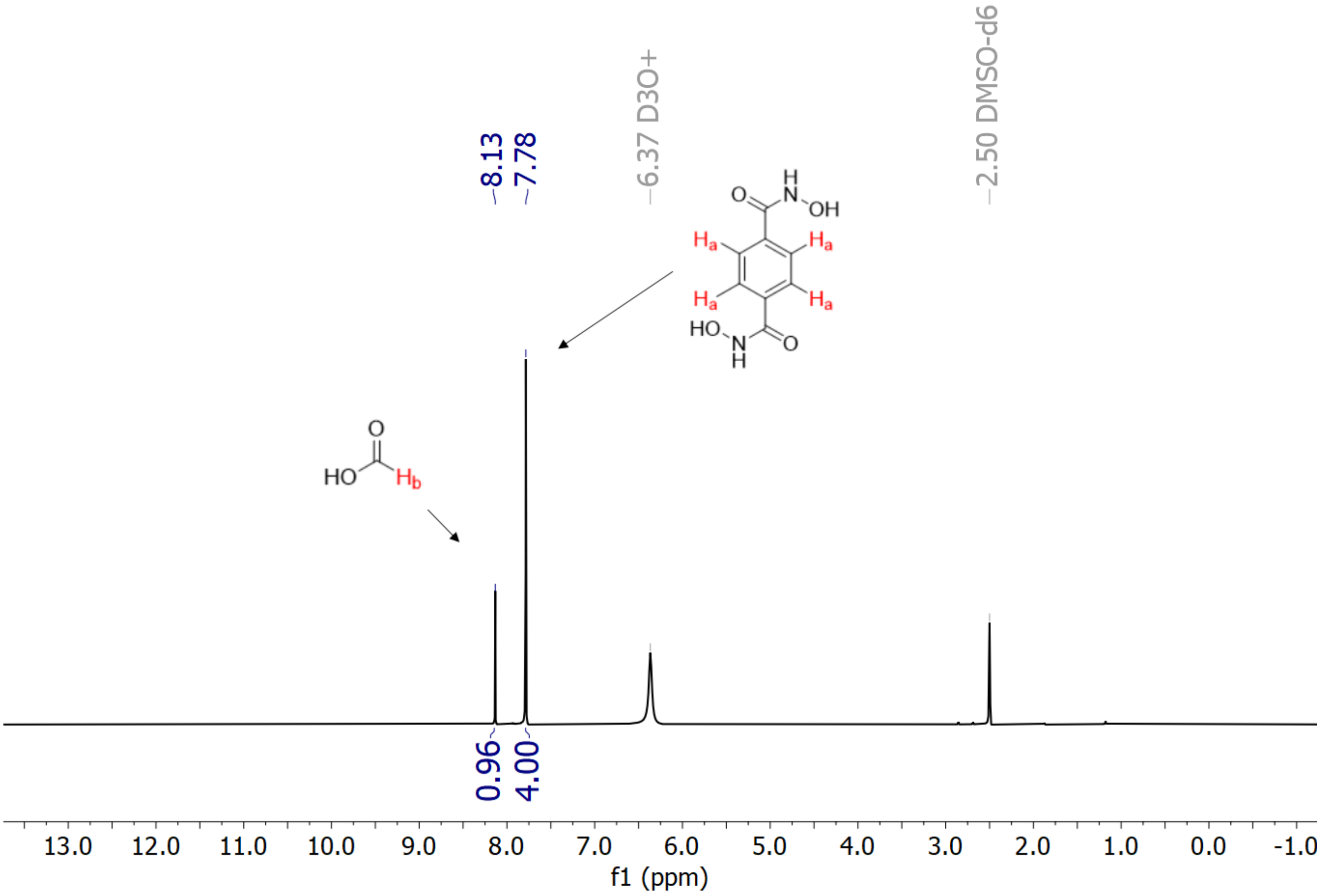


Figure S7. ^{1}H-NMR spectrum of MOF-419 after being thoroughly washed with acetone and digested in DCl/D_2O/DMSO-d_6 solvent mixture.

Section S6: Thermogravimetric Analysis

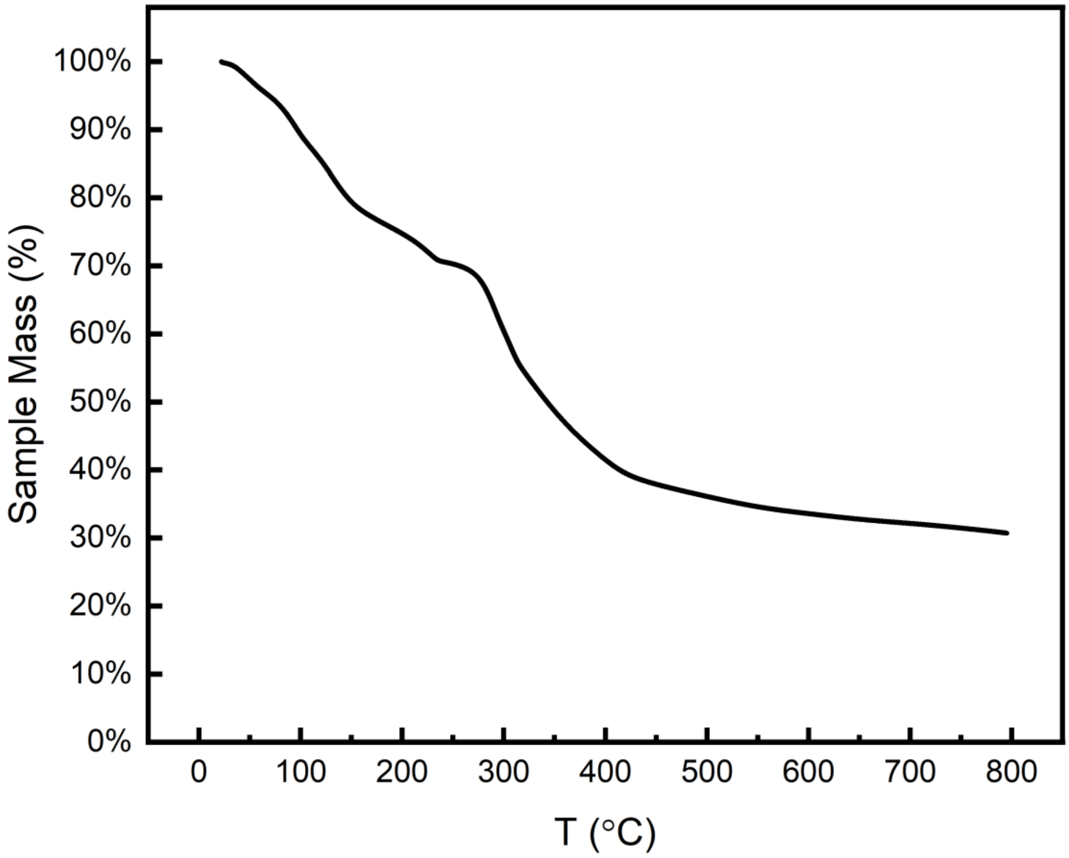


Figure S8. TGA profile of as-synthesized MOF-419 measured under N_2 flow.

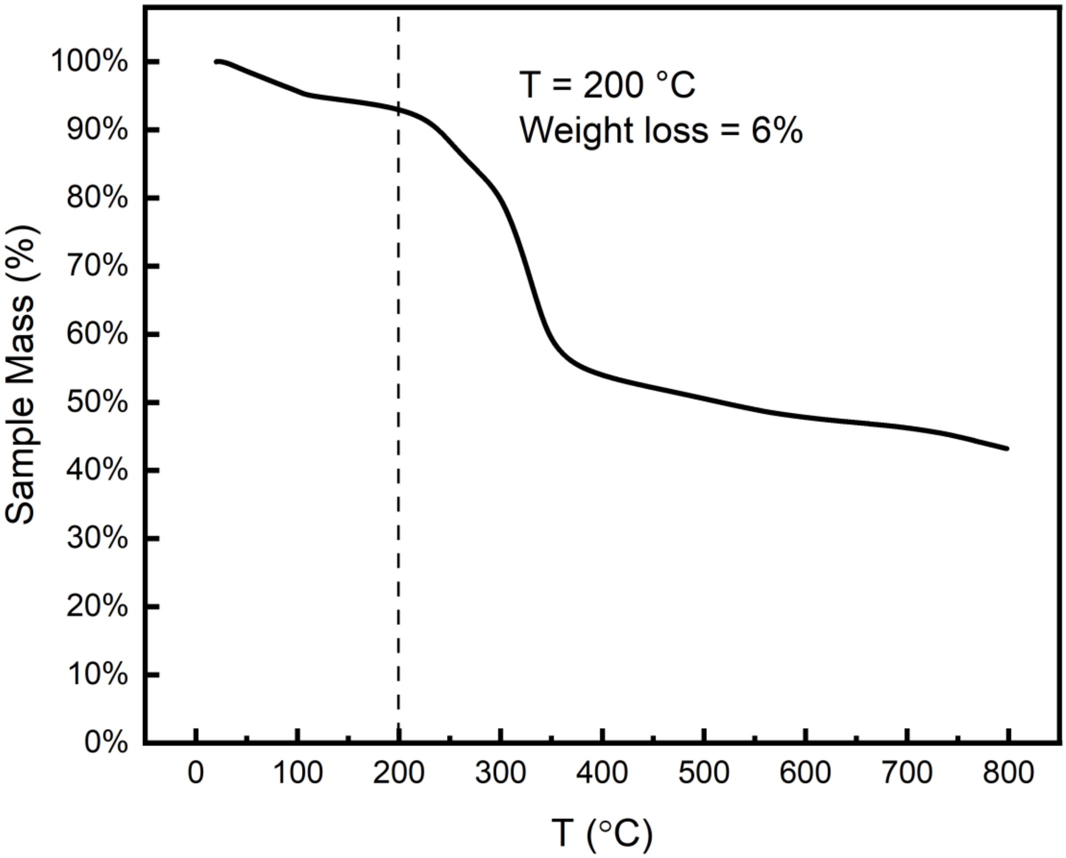
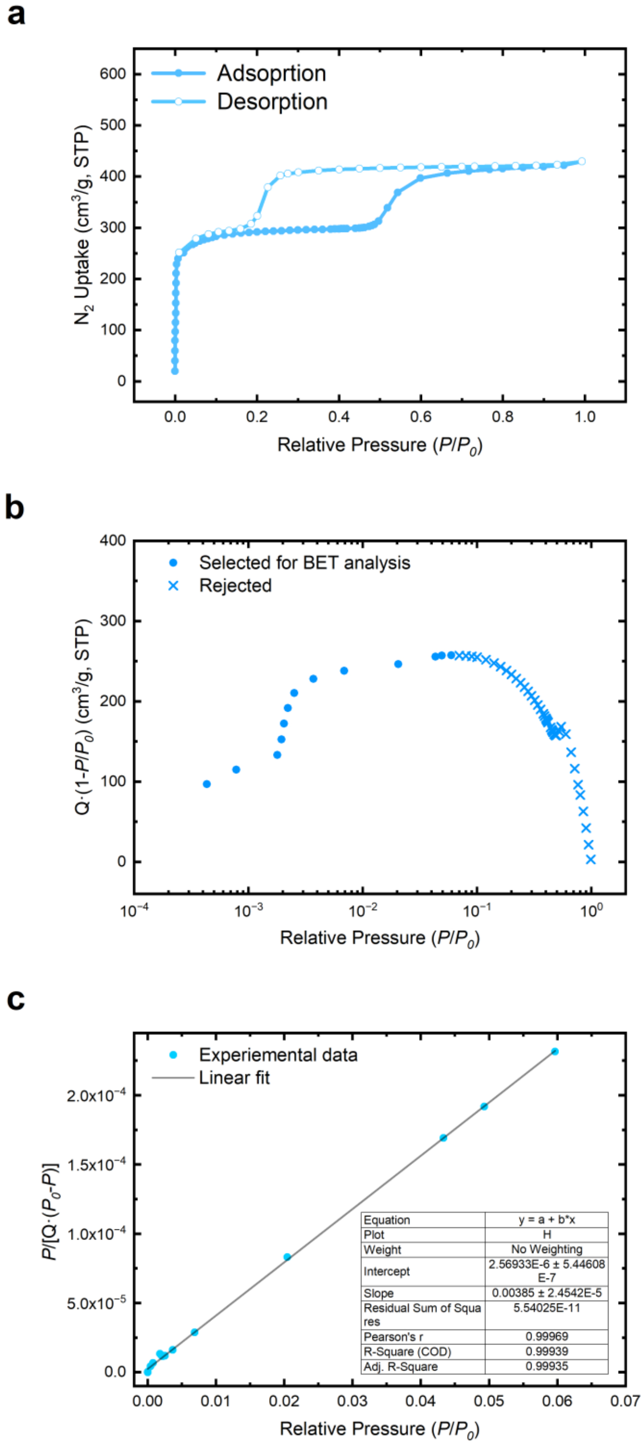


Figure S9. TGA profile of activated MOF-419 measured under N_2 flow.

Section S7: Nitrogen Sorption Analysis



Equation	y = a + b*x
Plot	H
Weight	No Weighting
Intercept	2.56933E-6 ± 5.44608 E-7
Slope	0.00385 ± 2.4542E-5
Residual Sum of Squa res	5.54025E-11
Pearson's r	0.99969
R-Square (COD)	0.99939
Adj. R-Square	0.99935

Figure S10. Nitrogen sorption analysis of MOF-419. (**a**) N_2 sorption isotherm at 77 K. (b) Rouquerol plot for determination of the appropriate pressure range for BET analysis. (c) BET plot (correlation co-efficient = 0.99969) yielding a BET surface area of 1130 m^2/g; P: partial pressure of argon, P_0 = 1 atm, STP: standard temperature and pressure).

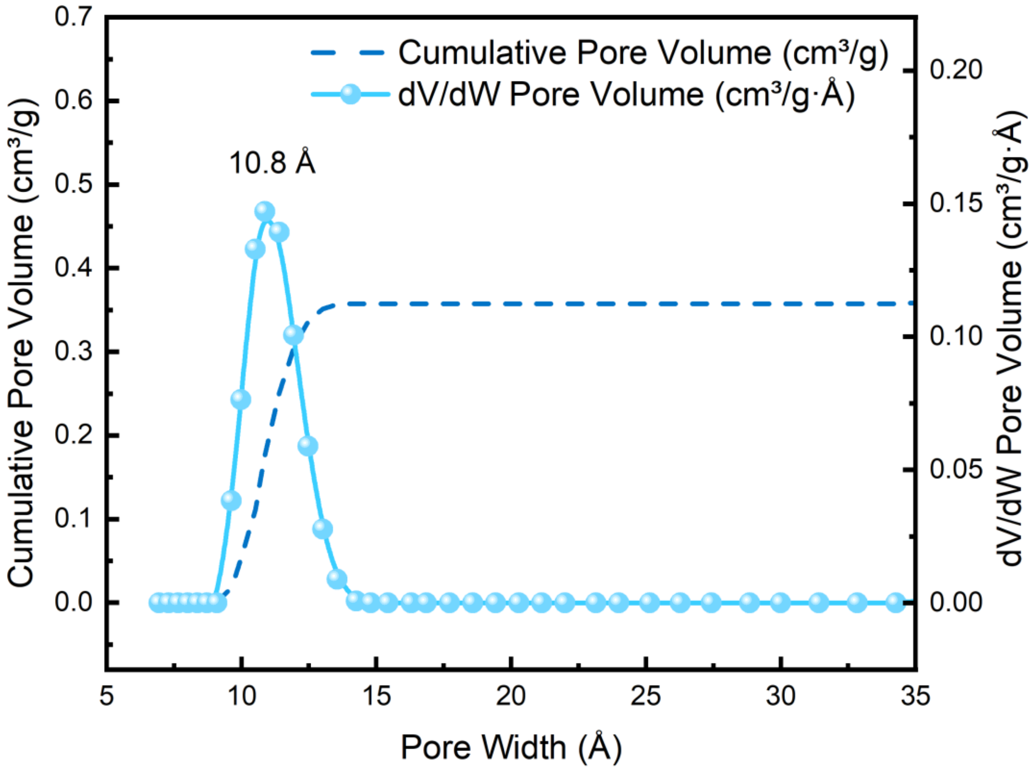


Figure S11. Pore size distribution plot of MOF-419 estimated from its nitrogen sorption isotherm at 77 K (cumulative pore volume = 0.363 cm^3/g).

Section S8: Scanning Electron Microscopy

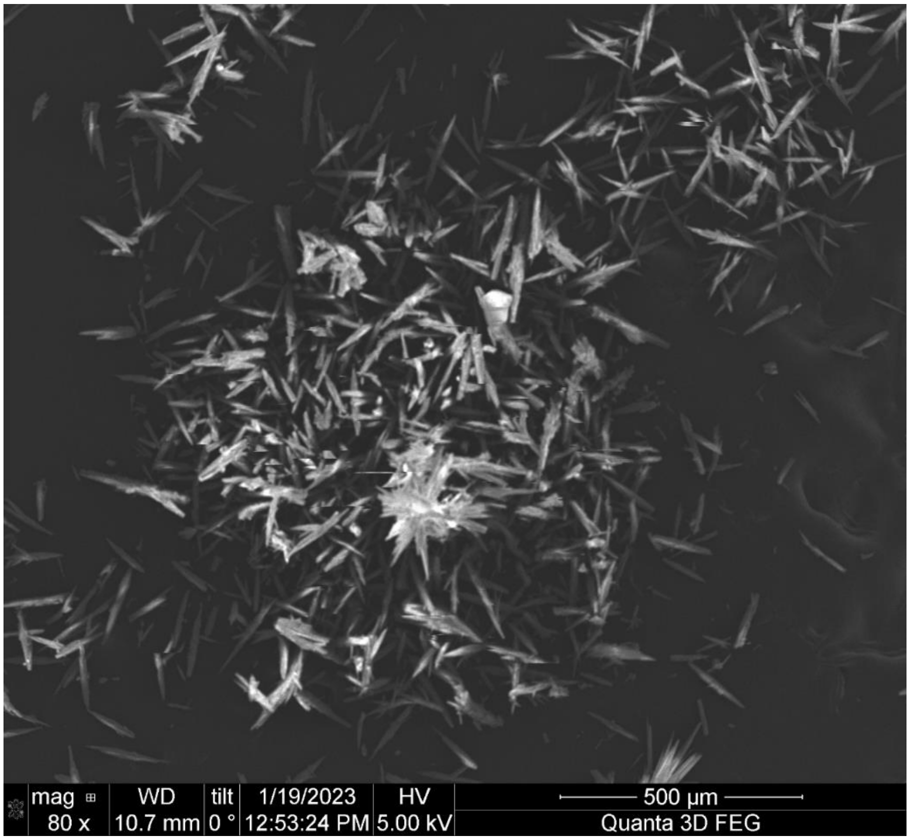


Figure S12. Representative scanning electron microscopy micrograph of MOF-419 crystallites.

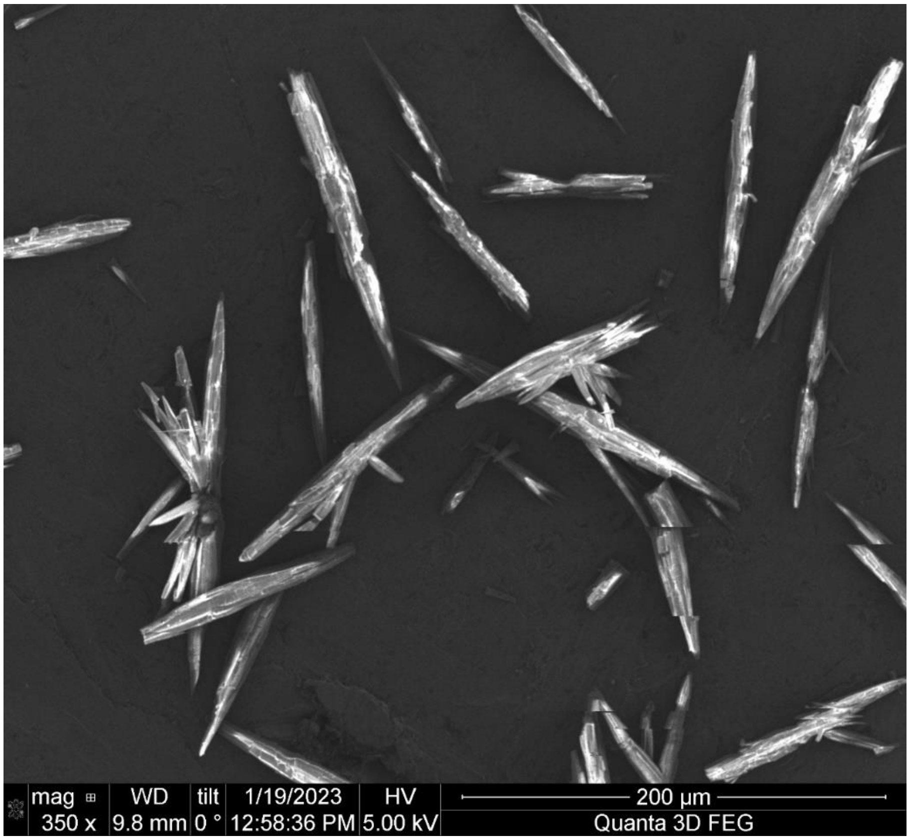


Figure S13.Needle-like morphology of MOF-419 crystals.

References

[1] Rigaku Corporation. Oxford, UK, **2015**, CrysAlisPro Software system.

[2] Micromeritics Instruments Corporation. Norcross, GA, USA, **2018**, MicroActive.

[3] N. M. Padial, J. Castells-Gil, N. Almora-Barrios, M. Romero-Angel, I. Da Silva, M. Barawi, A. Garcia-Sanchez, V. c. A. de la Peña O'Shea, C. Marti-Gastaldo, *J. Am. Chem. Soc.* **2019**, 141, 13124.

[4] a) G. M. Sheldrick, *Acta Crystallographica Section A: Foundations of Crystallography* **2008**, 64, 112; b) G. M. Sheldrick, *Acta Crystallographica Section C: Structural Chemistry* **2015**, 71, 3; c) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, 42, 339.

[5] P. Van der Sluis, A. Spek, *Acta Crystallographica Section A: Foundations of Crystallography* **1990**, 46, 194.