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Structural Analysis of and Selective CO_2 Adsorption in Mixed-Ligand Hydroxamate-based Metal-organic Frameworks

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*Keywords:*Hydroxamate, Coordination Polymer, Metal-organic Framework, X-ray Structural Analysis, Gas Sorption

Table of Contents

1. General Procedures

Powder X-ray powder diffraction (PXRD) patterns were recorded on a Rigaku Miniflex (scanning range: 3-30°; scanning increments: 0.01°). Carbon, nitrogen and hydrogen contents were determined by microanalytical procedures using a Elementar vario EL cube. Thermogravimetric analyses were carried out with a Hitachi TG/DTA 6200, X-DSC7000 apparatus between 25 and 500 °C (10 $°C\cdot min^{-1}$ scan rate and under N_2 atmosphere). IR spectra were recorded in a JASCO FT/IR-4200 type A fourier transform infrared spectrometers with KBr pellets. Gas Sorption isotherms for pressures in the range 0-1.0 bar were measured by a volumetric method using Micromeritics Tristar-II instruments. >99.999% purity He, H_2 and N_2 were used for all measurements. >99.999% H_2 gas was generated0 by Yanaco RHG-200 hydrogen generator. A typical sample of 30-100 mg of MOF **1-3** was transferred to a pre-weighed analysis tube and evacuated by heating at either 135 °C under dynamic vacuum for 6 h. The evacuated analysis tube containing the degassed sample was weighed again to determine the mass of sample. The tube was mounted on the analysis port of the gas sorption instrument. For all isotherms, warm and cold free space correction measurements were performed using ultra-high purity He gas. Nitrogen gas sorption isotherms at 77 K were measured in liquid nitrogen. Brunauer, Emmett and Teller (BET) surface areas were determined from N_2 adsorption data at 77 K using Micromeritics software.

2. Experimental section

2.1 Synthesis of MOF-1

A mixture of H_2BDHA (98 mg, 0.50 mmol), HINA (62 mg, 0.50 mmol), $Zn(NO_3)_2\cdot 6H_2O$ (149 mg, 0.50 mmol), DMF 3 mL and H_2O 1 mL was placed in a 20 mL of screw cap vial. The mixture was heated at 120 °C for 24 h. After cooling down to room temperature, the precipitates were separated by centrifuge and washed with DMF. The solid was washed with $CHCl_3$ to remove the remaining DMF and immersed in 20 mL of $CHCl_3$ for overnight. The precipitates were separated by centrifuged and evacuated at 150 °C for 6 h under high vacuum to give **MOF-1** $[Zn_2(BDHA)_{0.5}(INA)_3]$ (115 mg, 1.9 mmol, 77%) as colorless crystals. Elemental Analysis: Found. C, 44.49; H, 2.47; N, 9.37; Calcd for $C_{22}H_{15}N_4O_8Zn$: C, 44.47; H, 2.54; N, 9.43.

2.2 Synthesis of MOF-2

The above procedure was followed using $Co(NO_3)_2\cdot 6H_2O$ (146 mg, 0.50 mmol) instead of $Zn(NO_3)_2\cdot 6H_2O$ and DMF 4 mL as solvent. The precipitates were separated by centrifuged to give **MOF-2** [$Co_2(BDHA)_{0.5}(INA)_3(DMF)$] as red crystals for SXRD analysis and evacuated at 150 °C for 6 h under high vacuum to give for gas sorption analyses **MOF-2** [$Co_2(BDHA)_{0.5}(INA)_3(H_2O)$] (65.9 mg, 1.1 mmol, 43%). Elemental Analysis: Found. C, 44.12; H, 3.00; N, 9.67; Calcd for $C_{22}H_{17}Co_2N_4O_9$: C, 44.09; H, 2.86; N, 9.35.

3. Single crystals

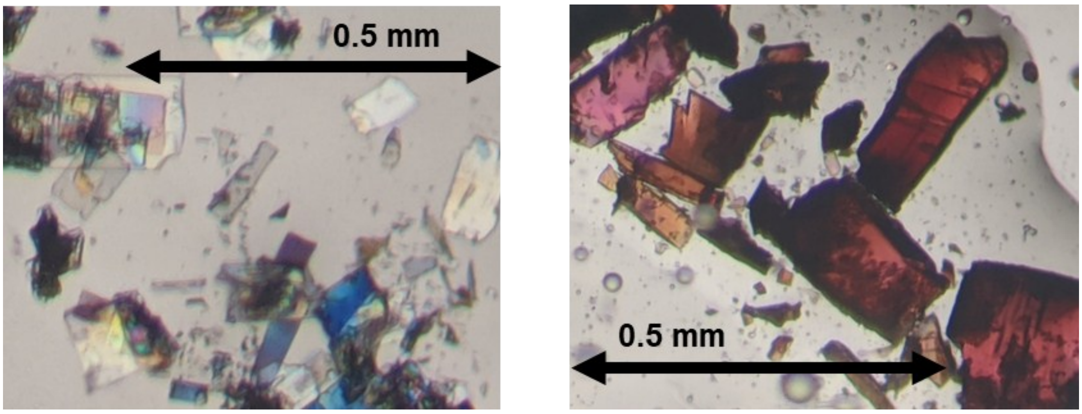


Fig S1 Single crystals of **MOF-1** (left) and **MOF-2** (right).

4. Single X-ray structure analyses

Single crystals of **MOF-1** and **MOF-2** suitable for X-ray diffraction were obtained by solvothermal synthesis. The diffraction data for **MOF-1** was collected at the BL40XU beamline of Spring-8 (2018A1167, 2018A1405, 2018B1084, 2018B1275, 2019A1057, 2019A1677, 2019B1129, 2019B1774, and 2019B1784.) on an EIGER X Ditector (Dectris) using synchrotron radiation, while that for **MOF-2** was collected using a Bruker APEX II diffractometer equipped with a APEX II CCD detector with Mo-Kα radiation (λ = 0.71073 Å). The structures were solved using a direct method (SHELXT)[S1] and refined by a full-matrix least-squares method on F^2 for all reflections using the programs of SHELXL-2016.[S2] All hydrogen atoms were placed using AFIX instructions, while all other atoms were refined anisotropically. Moreover, the diffused electron densities resulting from these residual solvent molecules were removed from the data set using the SQUEEZE routine of PLATON and refined further using the data generated.[S3] Supplementary crystallographic data were deposited at the Cambridge Crystallographic Data Centre (CCDC) under the numbers CCDC-1971703 and 1971704, respectively, and can be obtained free of charge from *via* www.ccdc.cam.ac.uk/data_request.cif. The crystal data, data correction and selected refinement details are summarized in Table S1.

Table S1 Crystal data and structure refinements of **MOF-1** and **MOF-2**

	MOF-1	**MOF-2**
empirical formula	$C_{22}H_{15}N_4O_8Zn_2$	$C_{25}H_{21}Co_2N_5O_9$
formula weight	594.12	653.33
color	colorless	red
crystal system	monoclinic	monoclinic
unit-cell dimentions		
(a = Å), (b = Å), (c = Å)	a = 8.5509(9)	a = 37.3165(17)
	b = 29.906(3)	b = 11.9989(5)
	c = 8.8030(8)	c = 17.9499(9)
α (deg)	90.0000	90.0000
β (deg)	92.190(6)	102.058(2)
γ (deg)	90.0000	90.0000
volume of unit cell (Å^3)	2249.5(4)	7859.9(6)
space group	$P2_1/n$ (#14)	$C2/c$ (#15)
Z value	4	8
D_{calc} (g/cm^3)	1.754	1.104
crystal size (mm)	0.02 x 0.02 x 0.01	0.05 x 0.05 x 0.01
temp (°C)	-183	-173
λ(Å)	0.78291	0.71073
Reflections collected	11461	28390
Independent reflections	3767	7317
Completeness (%)	97.4	99.9
Parameters	325	370
$R1$, $wR2$	0.0462, 0.1219	0.0551, 0.1793
goodness-of-fit on F^2	1.063	1.119
CCDC	1971703	1971704

5. Powder x-ray diffraction analyses

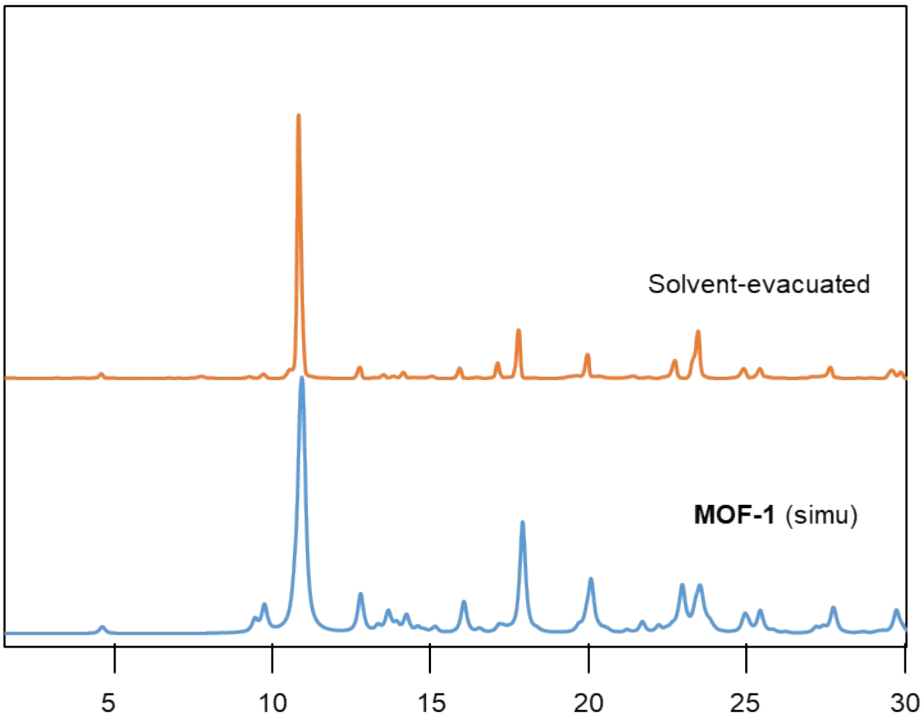


Fig S2 Experimental (top) and simulated (bottom) PXRD patterns of bulk **MOF-1**.

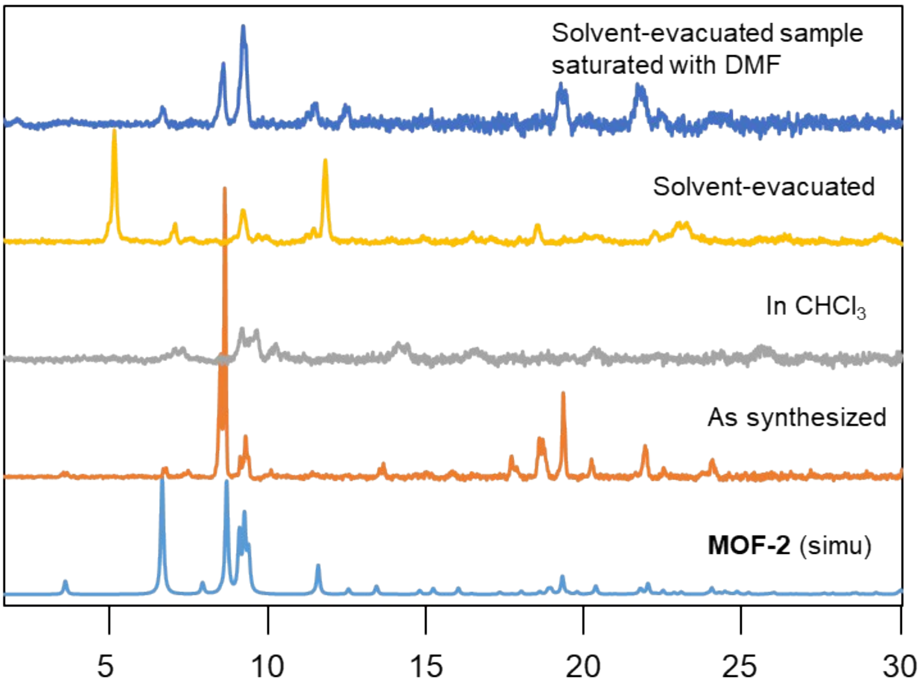


Fig S3 PXRD patterns of bulk **MOF-2**: Simulated PXRD pattern (light blue), the pattern of the as-synthesized sample in DMF (orange), the pattern of a sample upon changing the solvent from DMF to $CHCl_3$ (gray), the pattern of the solvent-evacuated sample (yellow), and the pattern of a sample re-saturated with DMF (dark blue). The gray and yellow patterns indicate that the sample loses the original crystal structure upon removal of the solvent molecules. The dark blue pattern confirms partial restoration of the crystal structure upon soaking the solvent-free sample in DMF.

6. Stability in H_2O

The PXRD analysis of **MOF-2**, immersed in H_2O at room temperature was measured. As shown in Fig. S4, the PXRD pattern of **MOF-2** changed upon addition of H_2O at room temperature suggests the decomposition of **MOF-2** upon immersing in water under concomitant formation of a new crystalline phase (yellow pattern in Fig. S4).

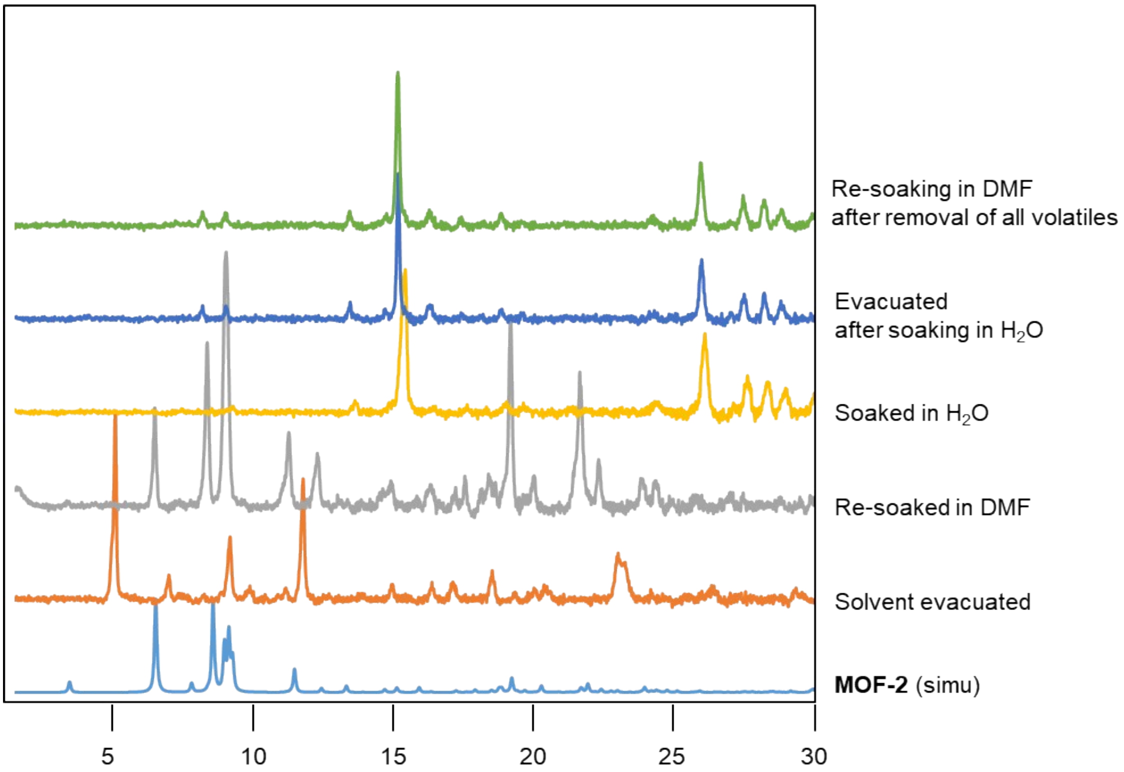


Fig S4 PXRD patterns of bulk **MOF-2**: Simulated PXRD pattern (light blue), the pattern of the as-synthesized sample in DMF (orange), the pattern of a sample upon changing the solvent from DMF to $CHCl_3$ (gray), the pattern of the solvent-evacuated sample (yellow), and the pattern of a sample re-saturated with DMF (dark blue). The gray and yellow patterns indicate that the sample loses the original crystal structure upon removal of the solvent molecules. The dark blue pattern confirms partial restoration of the crystal structure upon soaking the solvent-free sample in DMF.

7. Infrared Spectroscopic Analyses

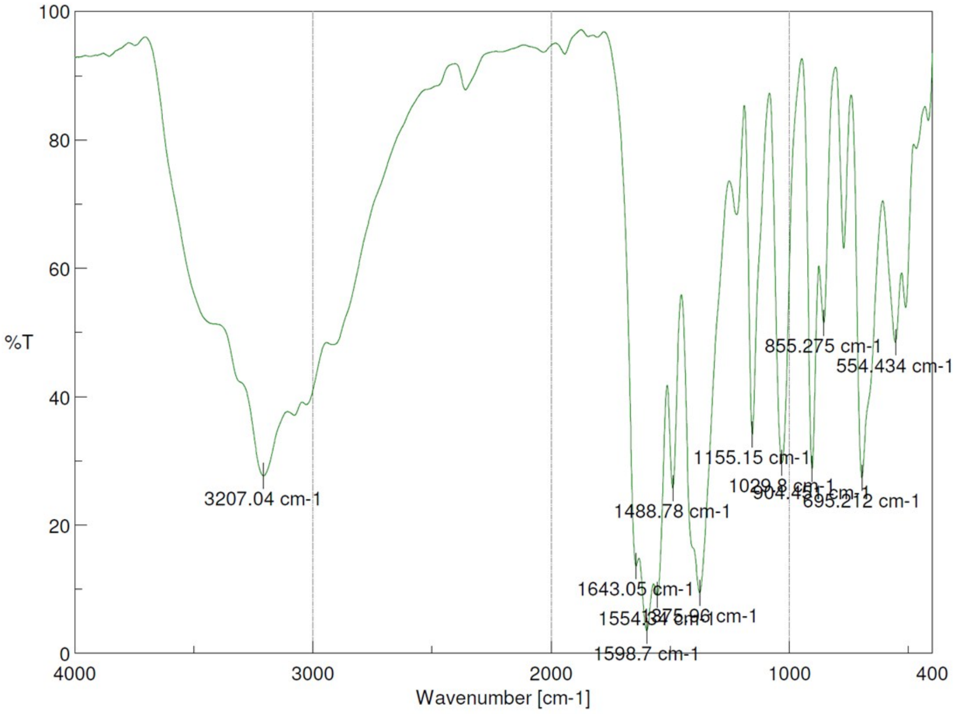


Fig S5 FT-IR spectrum of **MOF-1**.

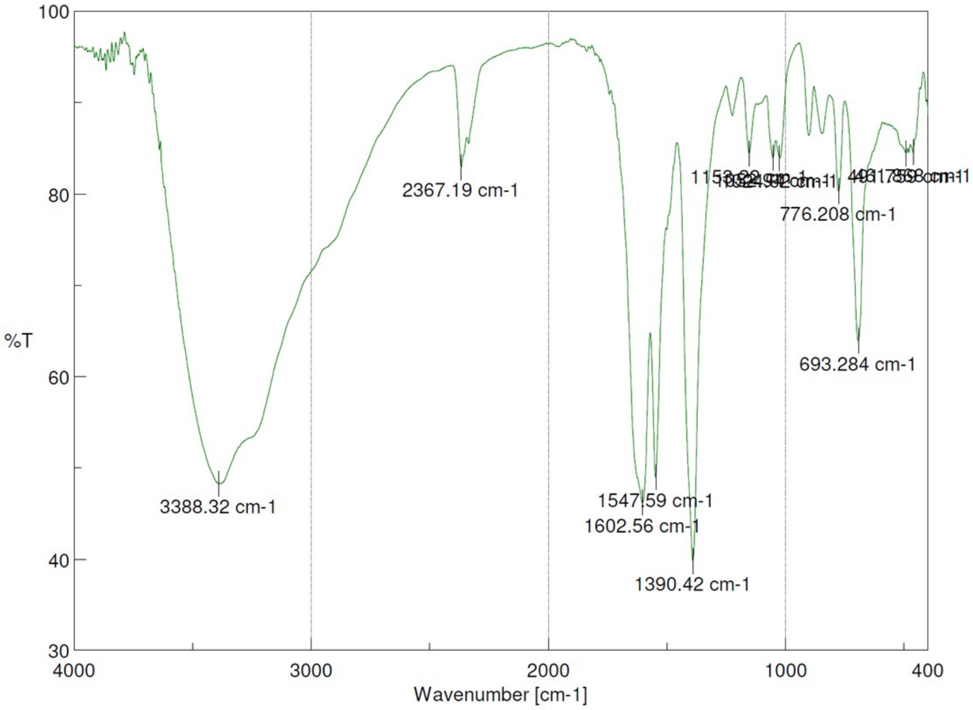


Fig S6 FT-IR spectrum of **MOF-2**.

8. Thermogravimetric Analyses

The thermal stability of **MOF-1** and **MOF-2** was evaluated using TGA (r.t. to 550 °C) (Figs S7 and S8). **MOF-1** exhibits high thermal stability up to 320 °C. Conversely, the TGA curves of **MOF-2** indicate a continuous mass loss below 500 °C. The first weight loss (<100 °C) is due to the removal of solvent molecules in the pores. During the second weight loss (225-250 °C), **MOF-2** loses 3.5% of its mass, which corresponds to the loss of a water molecule (calcd 3.0%). This result indicates that the cobalt centers in **MOF-2** are coordinated to water instead of DMF upon activation. An elemental analysis of **MOF-2** also suggested the presence of coordinated water instead of DMF.

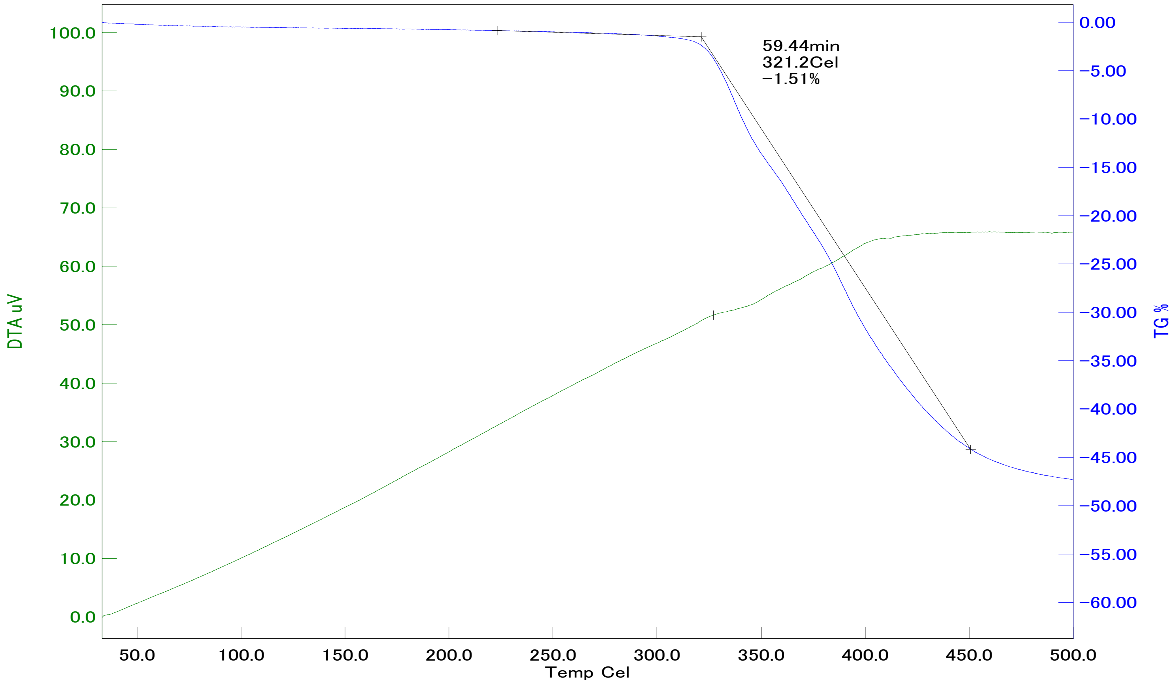


Fig S7 TG/DTA curve of bulk **MOF-1**

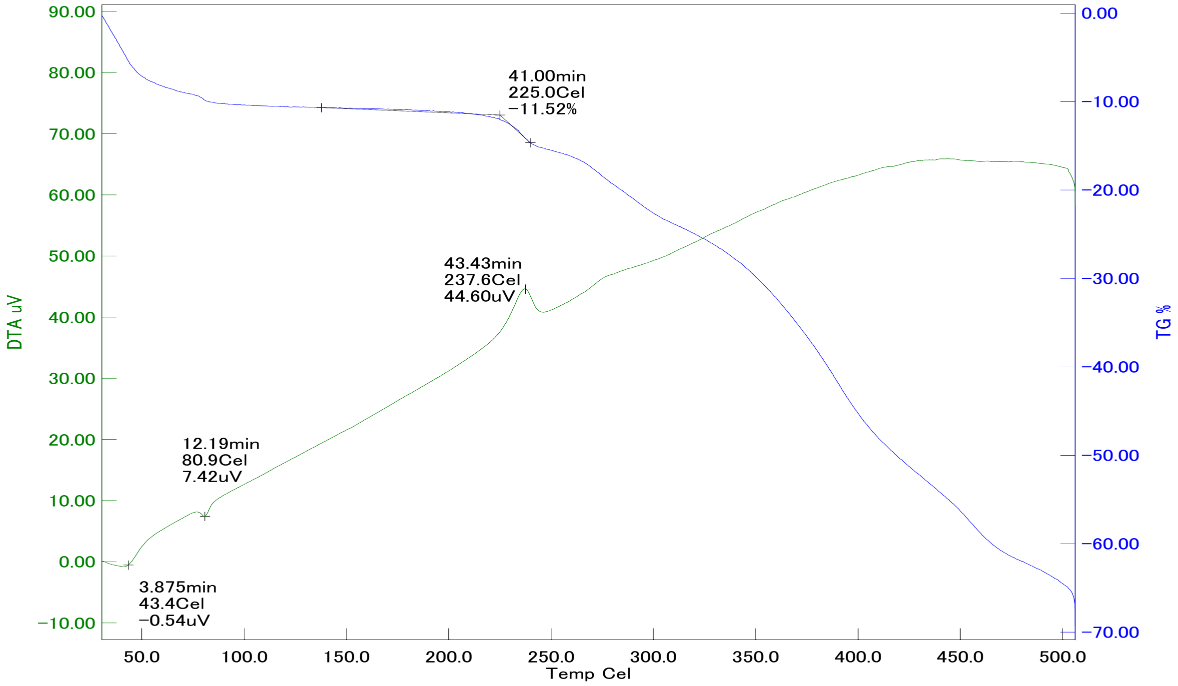


Fig S8 TG/DTA curve of bulk **MOF-2**

9. Gas Sorption Analyses

Low-pressure gas adsorption measurements. Gas Sorption isotherms for pressures in the range 0-1.0 bar were measured by a volumetric method using Micromeritics Tristar-II instruments. >99.999% purity He, H_2, N_2, CO_2 were used for all measurements. >99.999% H_2 gas was generated by Yanaco RHG-200 hydrogen generator. A typical sample of 30-100 mg of **MOF-1** and **MOF-2** was transferred to a pre-weighed analysis tube and evacuated by heating at either 135 °C under dynamic vacuum for 6 h. The evacuated analysis tube containing the degassed sample was weighed again to determine the mass of sample. The tube was mounted on the analysis port of the gas sorption instrument. For all isotherms, warm and cold free space correction measurements were performed using ultra-high purity He gas. Nitrogen gas sorption isotherms at 77 K were measured in liquid nitrogen. Brunauer, Emmett and Teller (BET) surface areas were determined from N_2 adsorption data at 77 K using Micromeritics software. The heat of adsorption can be directly calculated for each isostere on plot by using a derivation of the van’t Hoff equation:

$$\ln(P) = \frac{-\Delta(H)}{RT} + \frac{\Delta S}{R}$$

where: ΔH is heat of adsorption in kJ/mol, ΔS is entropy of sorption in kJ/mol*K, P is the pressure in Torr, and R is the gas constant, 0.0083144 kJ/mol*K.

9-1. CO_2 sorption isotherms of **MOF-2** at 258 K, 273 K, and 298 K

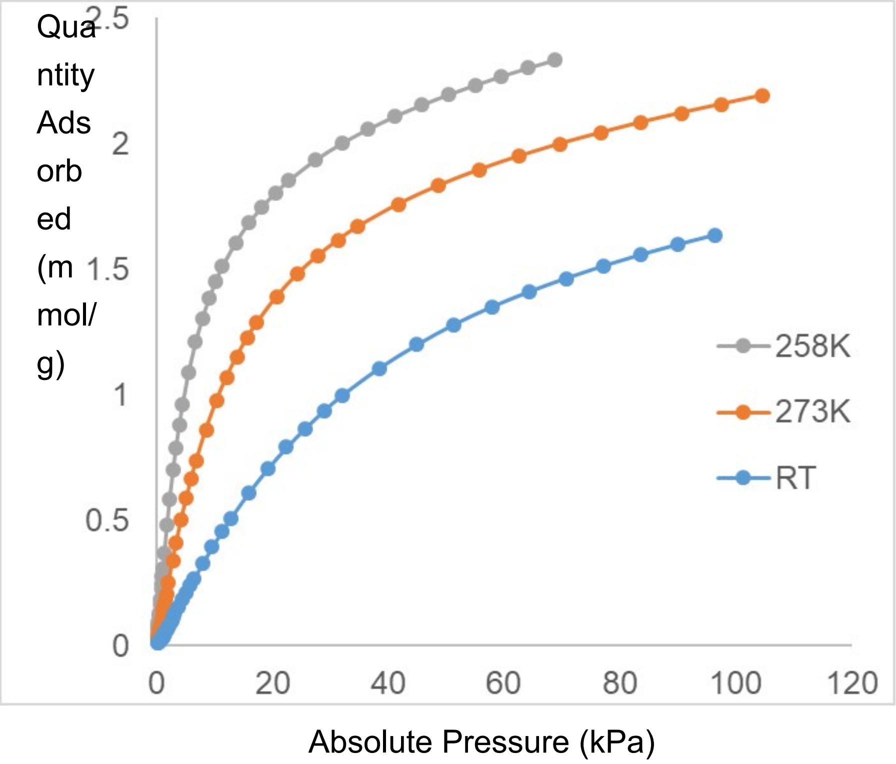
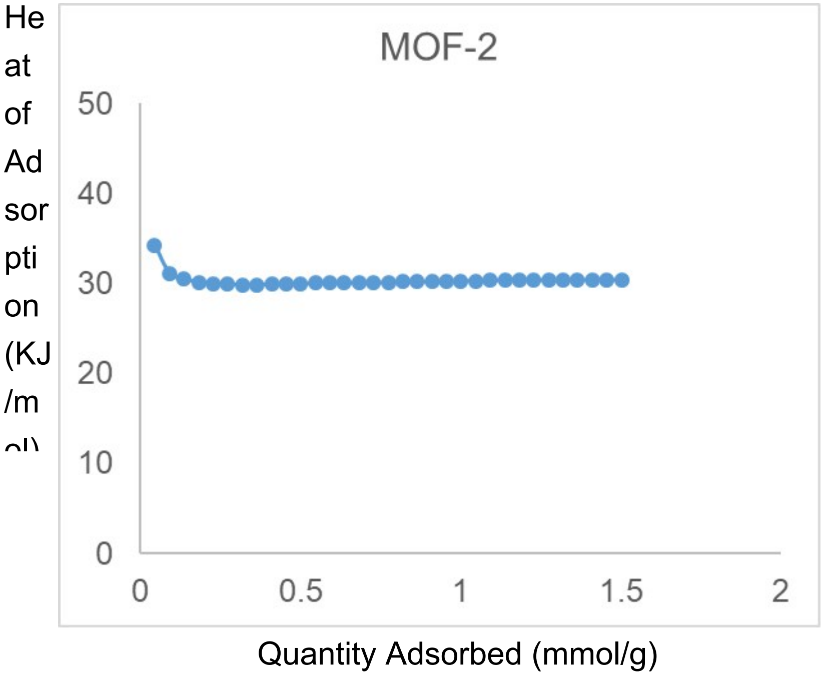


Fig S9 CO_2 adsorption isotherms for **MOF-2** at 258 K, 273 K, and 298 K.



9-2. Heat of Adsorption (Q_{ST}) of **MOF-2**

Fig S10. Heat of Adsorption for CO_2 of **MOF-2**

10. References

S1. Sheldrick, G. M. Acta Crystallogr. Sect. A, **2015**, 71, 3-8.

S2. Sheldrick, G. M. Acta Crystallogr. Sect. C, **2015**, 71, 3-8.

S3. Spek, A. L. Acta Cryst. Sect. D, **2009**, 65, 145-155.