Supporting Information

Dynamic DMF binding in MOF-5 enables the formation of metastable cobalt-substituted MOF-5 analogs

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Contents include: 17 pages, 10 figures, and 1 table.

Materials: Dry, deaerated dichloromethane (DCM, HPLC grade, Honeywell) and *N,N*-dimethylformamide (DMF, 99.8%, VWR) were obtained by degassing with a flow of argon gas for 30 min and by passing the solvent through two silica columns in a Glass Contour Solvent System. 70% HNO_3 (ICP-AES grade, EMD), $Zn(NO_3)_2 \cdot 6H_2O$ (99%, Alfa Aesar), $Co(NO_3)_2 \cdot 6H_2O$ (99.9%, Strem), $CoCl_2 \cdot 6H_2O$ (98%, Strem), ^{67}Zn metal (97% enriched, Trace Sciences International), and terephthalic acid (Sigma-Aldrich) were used without further modification. Anhydrous $CoCl_2$ was prepared by placing powder of $CoCl_2 \cdot 6H_2O$ under reduced pressure on a Schlenk line at 100 ºC for 12 h. Natural abundance MOF-5 was prepared according to literature.[1]

Preparation of ^{67}Zn-enriched $Zn(NO_3)_2 \cdot x H_2O$: ^{67}Zn metal flakes (0.100 g, 1.5 mmol) were suspended in 1 mL of deionized water in a glass vial and placed in a –20 °C fridge for 15 min. This vial was then held in an ice bath and 1.00 mL of 70% aqueous HNO_3 that was cooled to –20 °C was added drop-wise in two portions. After adding 600 μL the reaction suspension and remaining HNO_3 was placed back into the freezer. After 20 min, the remaining acid was added dropwise. The solution was then kept at 10^{-6} torr on a Schlenk line overnight and 370 mg of white powder was recovered and used without further purification for the synthesis of enriched MOF-5.

Preparation of ^{67}Zn-enriched MOF-5: This preparation followed the procedure reported for natural abundance MOF-5.[1] The white powder described above was dissolved in 41 mL of anhydrous DMF and 500 μL of deionized water in a 100-mL Teflon-capped glass jar. Terephthalic acid (69 mg, 0.42 mmol) was added and sonicated until completely dissolved and two glass slides were added to increase the surface area available for crystallization. After heating at 100 °C for 7 h, cubic crystals were collected by gravity filtration in an N_2-filled bench-

top glovebox. These were washed in fresh DMF for 8 h, repeated six times, and soaked in DCM following directions as indicated for natural abundance MOF-5.[1] The phase purity of this material, partially solvated by DMF and DCM, was confirmed by PXRD (Figure S6).

Synthesis of $Co_xZn_{4-x}O(C_8H_4O_4)_3$ by cation exchange: Anhydrous $CoCl_2$ (0.30 mmol) was dissolved in 10 mL of dry, deaerated DMF and added at room temperature to freshly evacuated crystals of $Zn_4O_{13}C_{24}H_{12}$ (MOF-5) (50 mg, 6.5 x 10^{-2} mmol). These suspensions were stirred gently for one minute, thirty minutes, one hour, one day, one week, two weeks, or one month, before replacing the solution with fresh DMF until UV-Vis traces of the mother liquor indicated the absence of Co^{2+} in solution.

Attempt at Solvothermal Synthesis of $Co_xZn_{4-x}O(C_8H_4O_4)_3$ (1<x<4): See also Table S1. *Method 1A*. In a Teflon-capped glass jar, $Co(NO_3)_2 \cdot 6H_2O$ or $CoCl_2 \cdot 6H_2O$ (0.75 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (0.75 mmol), and terephthalic acid (0.5 mmol) were dissolved in 49 mL of anhydrous DMF and 1 mL of deionized water. The jar was then kept in a 100 ºC oven for 7 h, after which point powder was collected by gravity filtration under an inert atmosphere, washed with fresh DMF, and analyzed by PXRD. *Method 1B*. In a Teflon-capped glass jar, $Co(NO_3)_2 \cdot 6H_2O$ or $CoCl_2 \cdot 6H_2O$ (1.125 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (0.375 mmol), and terephthalic acid (0.5 mmol) were dissolved in 49 mL of anhydrous DMF and 1 mL of deionized water. The jar was then kept in a 100 ºC oven for 7 h, after which point powder was collected by gravity filtration under an inert atmosphere, washed with fresh DMF, and analyzed by PXRD. *Method 2A*. In a Teflon-capped glass jar, $Co(NO_3)_2 \cdot 6H_2O$ (1.5 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (1.5 mmol), and terephthalic acid (0.5 mmol) were dissolved in 49 mL of anhydrous DMF and 1 mL of deionized water. The jar was then kept in a 100 ºC oven for 7 h, after which point powder was collected by gravity filtration under an inert atmosphere, washed with fresh DMF, and analyzed by PXRD.

Method 2B. In a Teflon-capped glass jar, $Co(NO_3)_2 \cdot 6H_2O$ (15 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (1.5 mmol), and terephthalic acid (0.5 mmol) were dissolved in 49 mL of anhydrous DMF and 1 mL of deionized water. The jar was then kept in a 100 ºC oven for 7 h, after which point powder was collected by gravity filtration under an inert atmosphere, washed with fresh DMF, and analyzed by PXRD.

Table S1. Summary of reaction conditions employed for attempting to synthesize $Co_xZn_{4-x}O(BDC)_3$, $1<x<4$, and subsequent analysis by ICP-AES and PXRD. The leftmost column includes in parentheses the identity of X in the cobaltous salt of the reaction mixture. Zn:Co was determined by ICP-AES.

Entry (X)	mmol of $CoX_2 \cdot 6H_2O$	mmol of $Zn(NO_3)_2 \cdot 6H_2O$	Zn:Co ratio	PXRD analysis
1 (NO_3^{2-})	0.375	1.125	6.23	MOF-5
2 (NO_3^{2-})	0.75	0.75	3.60	MOF-5
3 (NO_3^{2-})	1.125	0.375	1.66	Unknown phase
4 (Cl^-)	0.375	1.125	4.10	MOF-5
5 (Cl^-)	0.75	0.75	0.19	Unknown phase
6 (Cl^-)	1.125	0.375	Not measured	Amorphous
7 (NO_3^{2-})	1.5	1.5	1.33	Unknown phase
8 (NO_3^{2-})	15	1.5	Not measured	Unknown phase

Sample Preparation for Nuclear Magnetic Resonance: Zn-MOF samples were prepared as described above using natural abundant ^{67}Zn (4.1 %) for MOF solvated with DMF or desolvated without DMF. Enriched solvated Zn-MOF sample was prepared using 97 % enriched

[67]Zn. Samples were packed in a glovebox under dry Ar or N_2 gas into zirconia (ZrO_2) magic angle spinning (MAS) rotors with outer diameters of either 4 mm or 7 mm (100 or 400 µl, respectively). The enriched sample was sealed using epoxy to inhibit any reaction with the atmosphere. For the solvated sample, desolvated Zn-MOF was packed into ZrO_2 rotors and solvated *in situ* using > 99 % dry DMF.

Solid-state Nuclear Magnetic Resonance Analysis of Activated MOF-5: Natural abundance non-solvated MOF-5 was analyzed using solid-state NMR under spinning and non-spinning conditions to characterize its structure and NMR properties at 21.1 T. Under MAS the chemical shift anisotropy (CSA) and dipolar coupling interactions are attenuated leaving only the residual second order quadrupolar broadening of the central transition, which is the dominant interaction for [67]Zn, being solely responsible for the observed linewidth and shape. The spectrum represented within Figure S3a was simulated (inset) with the following parameters: isotropic chemical shift (δ_{iso}) = 158 ppm, quadrupolar coupling constant (C_Q) = 1.65 MHz, and asymmetry parameter (η) = 0.

Under non-spinning conditions, all the anisotropic interactions are present. Figure S3b and S3c are the non-spinning spectra without and with ^{1}H decoupling, respectively. In Figure S3c, the "horns" of the spectrum are narrowed compared to Figure S3b, denoting the effect of the ^{1}H radio frequency field that decouples the ^{1}H dipolar interaction. The observed CSA is significant, leading to the characteristic shape with the span (Ω) = 87 ppm and skew (κ) = 1. The near tetrahedral symmetry of the Zn-MOF, combined with the reduction of the second order quadrupolar broadening at ultrahigh magnetic fields, creates a unique circumstance whereby the breadth of the lineshape begins to be dominated by the CSA rather than by the quadrupolar interaction. This is more clearly shown in Figure S4 where the non-

spinning experimental spectrum (Fig. S4a) cannot be simulated solely using the quadrupolar coupling parameters determined from the MAS experiment (Fig. S4b). A CSA interaction of considerable magnitude is required to provide excellent agreement between the simulation and experimental data (Fig. S4c).

Solid-state Nuclear Magnetic Resonance Analysis of DMF-Solvated ^{67}Zn Enriched MOF-5: The non-spinning spectrum of the evacuated MOF-5 spectra revealed that the powdered lineshape was affected by dipolar, chemical shift anisotropy (CSA), and quadrupolar interactions. Magic-angle spinning (MAS) NMR was acquired to attenuate the first two interactions and partially reduce the second-order quadrupolar broadening of the central transition (Figure S1B). Surprisingly, the linewidth of the resulting spectrum was nearly identical to the spectrum under non-spinning conditions, while the "horns" attributed to the solvated site disappeared (Figure S1B). This result indicates that the linewidth of the unsolvated site is no longer dominated by quadrupolar broadening at ultrahigh magnetic fields, while the FWHM of the linewidth of the solvated site reduces from ~21 kHz to an expected value of ~6 kHz, thereby obscuring it by the main resonance of the unsolvated site (~14 kHz). This contraction indicates the solvated site is still the dominated by quadrupolar broadening, although disorder could also impact its signal.

Other Physical Measurements: Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 Thermogravimetric Analyzer at a heating rate of 0.5 °C/min under a nitrogen gas flow of 90 mL/min. Fourier-transform infrared spectroscopic measurements were performed in a N_2-filled glovebox using a Bruker Alfa spectrometer. The data was averaged over 32 scans at 4-cm^{-1} resolution between 8000-500 cm^{-1}. Mass-spectrometry was conducted in multi-ion detection mode using a Hiden Analytical HPR20 QIC benchtop gas analysis system.

The exhaust gas from a TGA measurement of DMF-soaked natural abundance MOF-5 was sampled *in situ* using the N_2 flow as a carrier gas. The TGA was connected to the QIC capillary inlet using standard Swagelok fittings, with the capillary held at 160 °C and 3 mbar. Diffuse reflectance UV-Vis spectra were collected between on a Varian Cary 5000 UV-Vis-NIR spectrometer equipped with a Praying Mantis diffuse reflectance accessory and an environmental chamber (Harrick Scientific Products) and referenced to $BaSO_4$. Cobalt, nickel, and zinc analyses were conducted at the MIT Center for Materials Science and Engineering Shared Experimental Facility (CSME-SEF) using a HORIBA Jobin ACTIVA inductively coupled plasma atomic emission spectrometer (ICP-AES). Standards were prepared from solutions purchased from ULTRA Scientific©, designated suitable for ICP analysis.
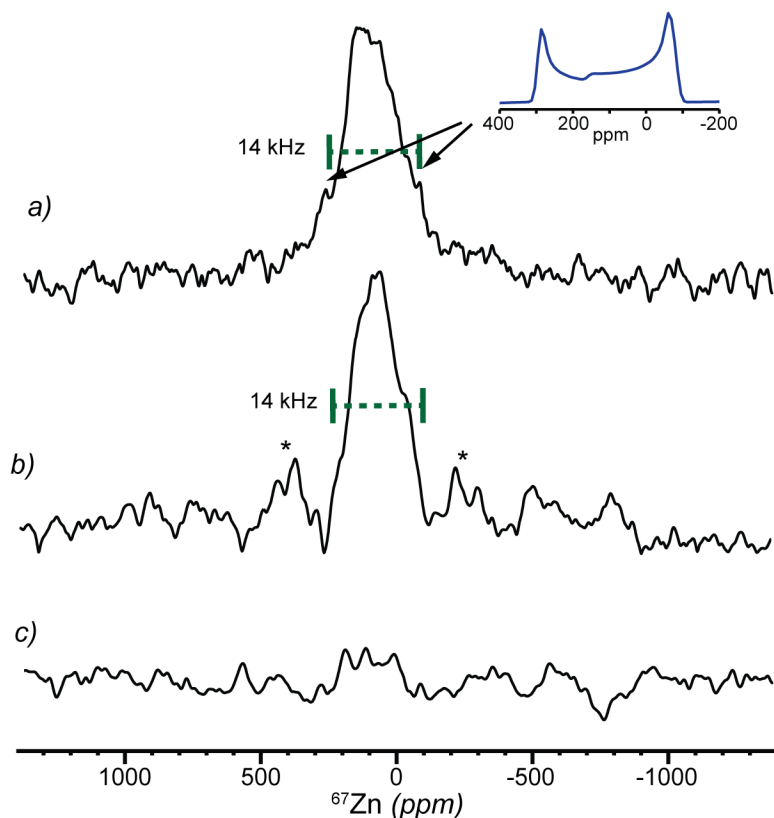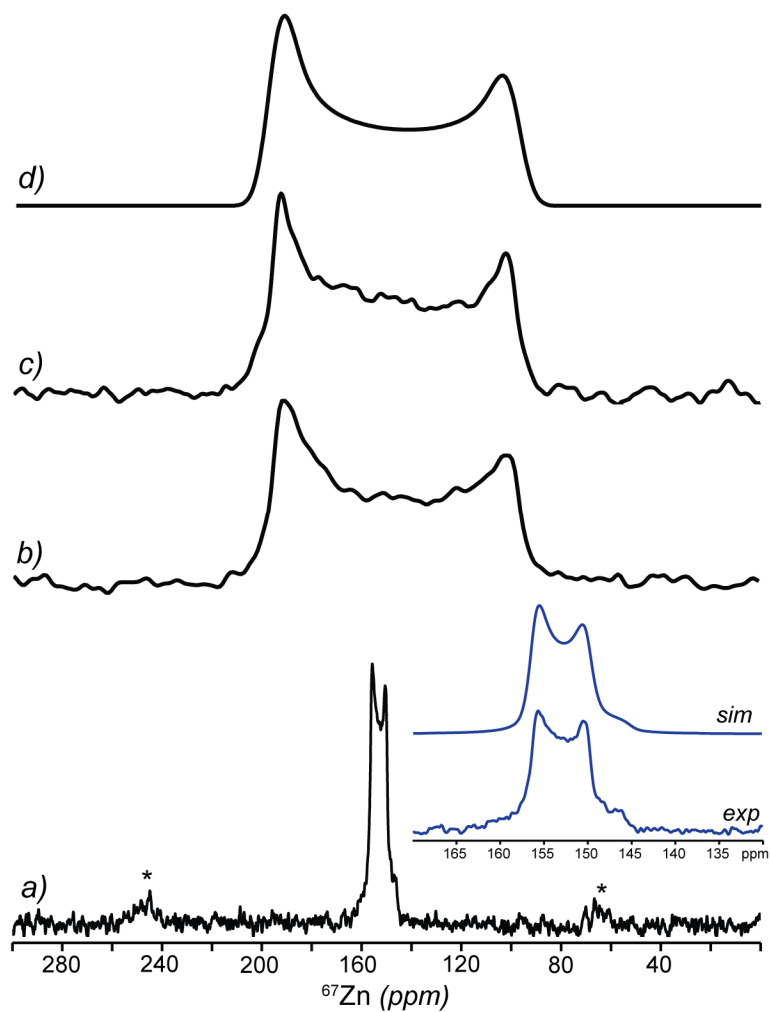
Fig. S1. [67]Zn NMR spectra acquired at 21.1 T (900 MHz, ^{1}H) using (a) [67]Zn isotopically labeled DMF-solvated MOF-5 under non-spinning (a) and MAS (b) conditions ("*" denotes the location of the spinning sidebands). Natural-abundance DMF-solvated MOF-5 gave spectrum (c), under non-spinning conditions. The spectral inset (blue) illustrates the secondary site present within the solvated system.
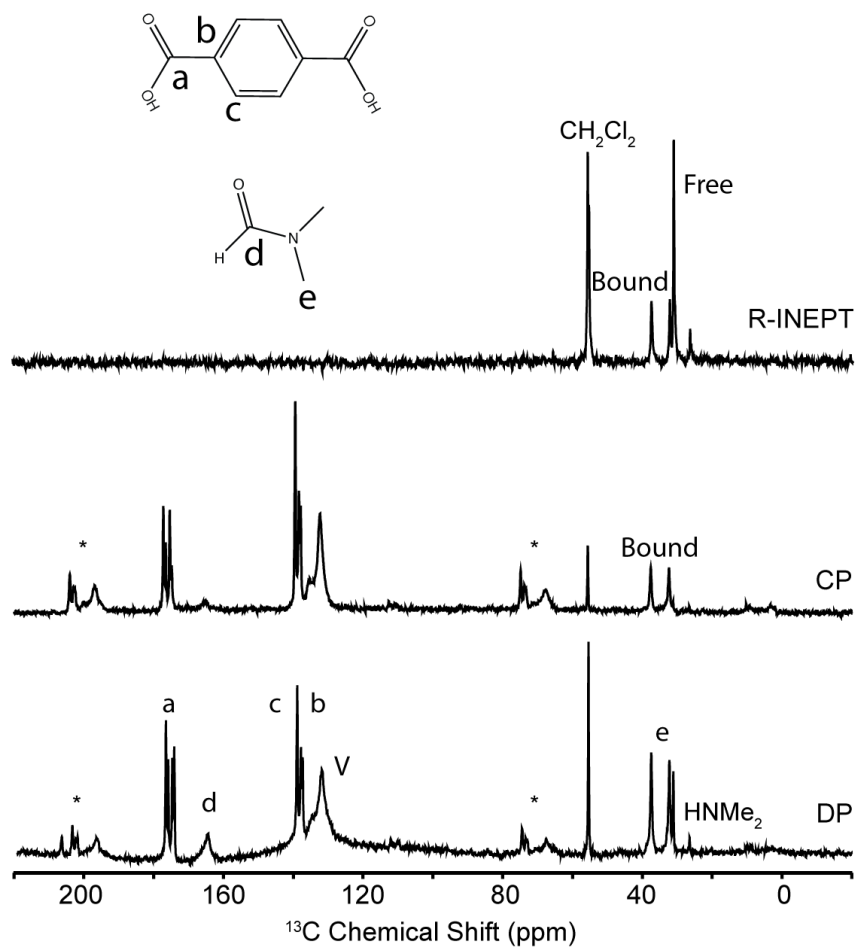
Fig. S2. ^{13}C MAS NMR of DMF-solvated MOF-5 at 303 K using Bloch (DP), cross-polarization (CP) and refocused-INEPT (R-INEPT). Lower case letters denote the identity of the resonances according to the species illustrated at the top. V corresponds to Vespel® present within the rotor and stator housing and * denotes spinning sidebands. Dimethylamine and dichloromethane impurities are assigned as well.

Fig. S3. ^{67}Zn NMR spectra of natural abundance desolvated MOF-5 acquired at 21.1 T (900 MHz, ^{1}H). (a) MAS spectrum (inset (blue) – expanded region of the experimental (exp) MAS NMR spectrum and simulation (sim) using the following parameters, δ_{iso} = 158 ppm, C_Q = 1.65 MHz and η = 0, (b) non-spinning spectrum, (c) non-spinning with ^{1}H decoupling, and (d) complete spectral simulation using the following parameters, C_Q = 1.65 MHz, η = 0, δ_{iso} = 158 ppm, Ω = 87 ppm and κ = 1.
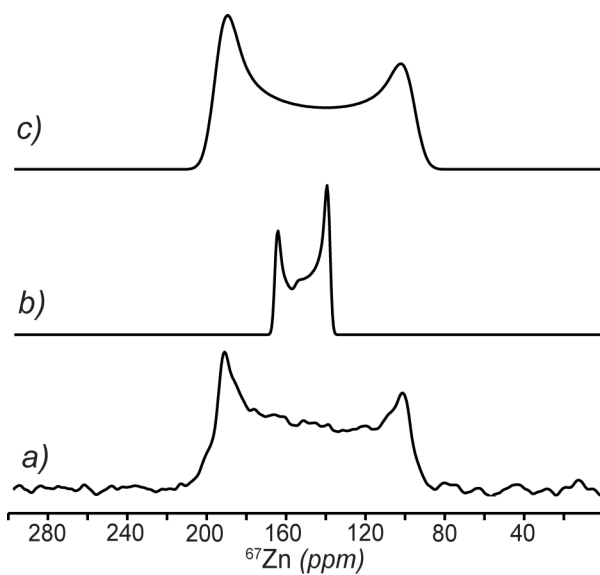
Fig. S4. ^{67}Zn NMR spectrum of natural abundance desolvated Zn-MOF acquired at 21.1 T (900 MHz, ^{1}H), (a) the experimental spectrum under non-spinning conditions, (b) the corresponding quadrupolar simulation (C_Q = 1.65 MHz and η = 0, determined from MAS NMR) under non-spinning conditions (with no consideration of CSA), and (c) the complete simulation incorporating both the chemical shift anisotropy and quadrupolar coupling.
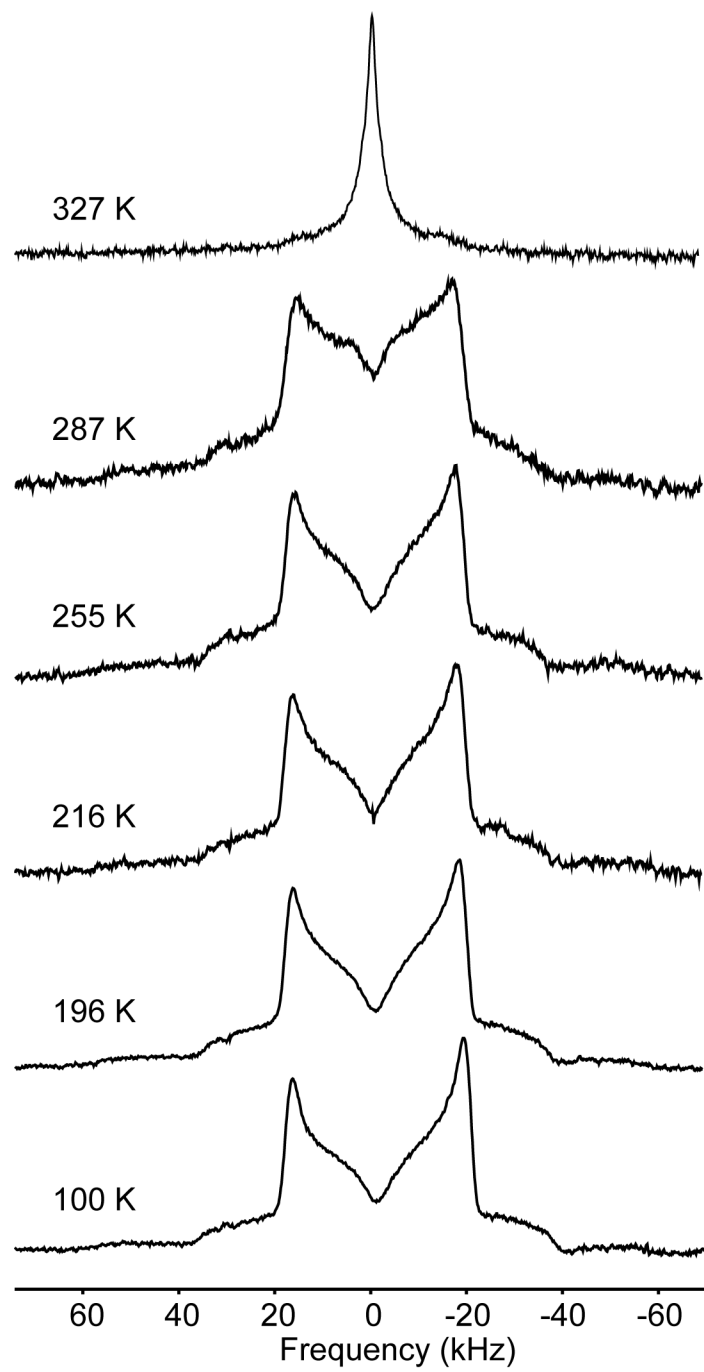
**Fig. S5.** Variable temperature non-spinning ^{2}H NMR spectra of d_7-DMF bound to MOF-5.
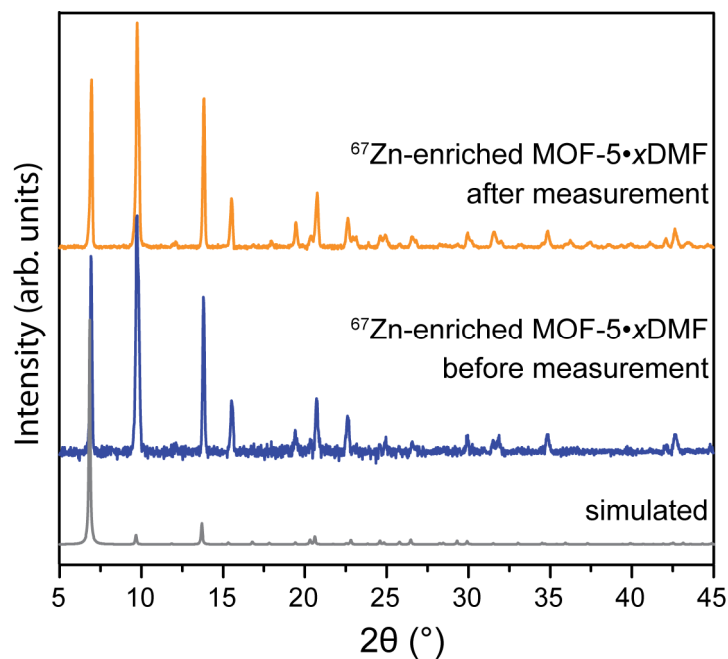
Fig. S6. Powder X-ray diffraction pattern of the ^{67}Zn-enriched DMF-solvated MOF-5 sample that was used for ^{67}Zn NMR experiments before (middle) and after (top) measurements compared to the simulated pattern of evacuated MOF-5 (bottom). Note that discrepancies in peak intensities are due to the sample being solvated.
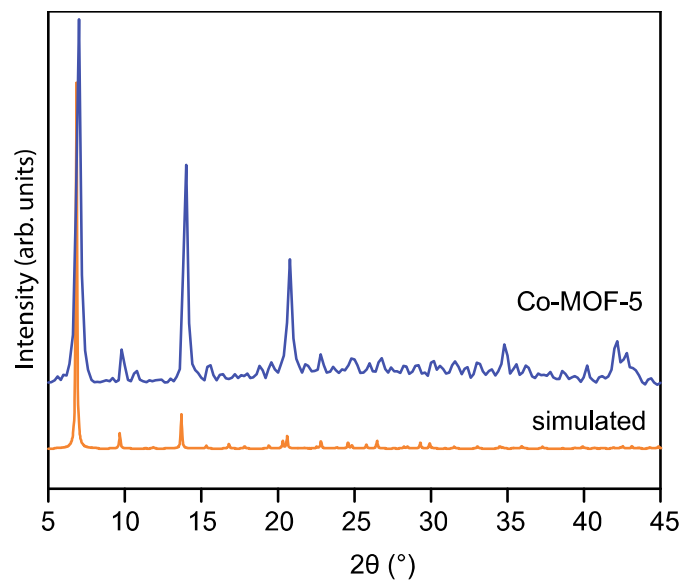
Figure S7. PXRD pattern of 1-month-soaked Co-MOF-5 and the simulated pattern of MOF-5.
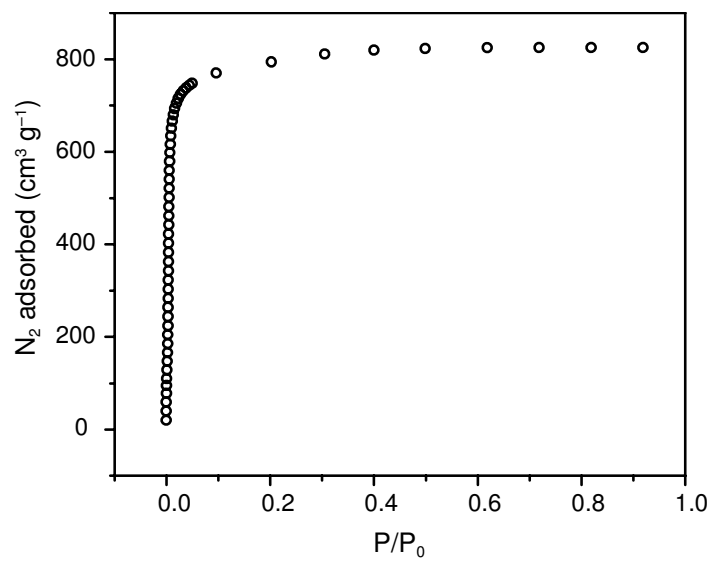
Figure S8. N_2 isotherm of 1-month soaked Co-MOF-5 collected at 77 K.
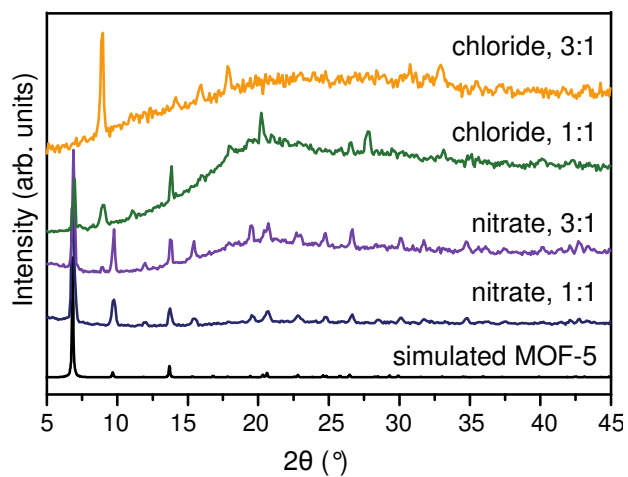
Figure S9. PXRD patterns of materials obtained from attempting the direct synthesis of Co-MOF-5 while keeping the metal content constant in the reaction mixture. The corresponding reaction conditions are denoted by whether cobalt nitrate or chloride salts were used, and the relative ratio of Co to Zn in solution.
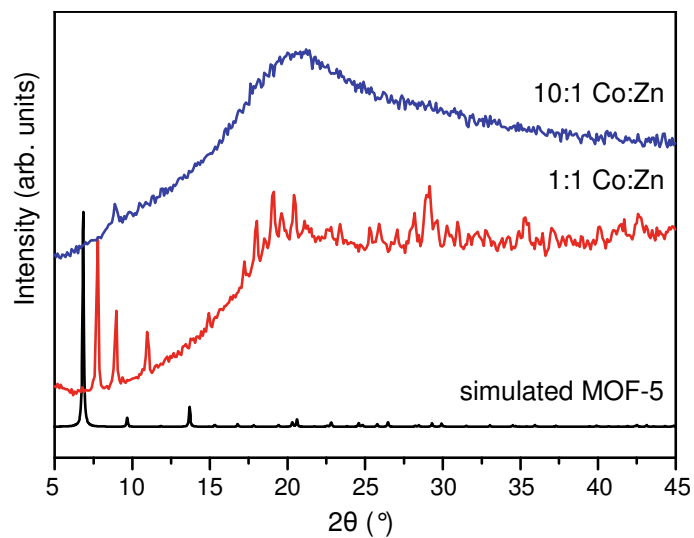
Figure S10. PXRD patterns of the materials resulting from the attempt at direct synthesis of Co-MOF-5 where additional metal was added in the form of cobalt nitrate hexahydrate. The relative cobalt to zinc ratio in the initial solution is written by the corresponding PXRD pattern.

(1)   Kaye, S. S.; Dailly, A.; Yaghi, O. M.; Long, J. R. Impact of Preparation and Handling on the Hydrogen Storage Properties of $Zn_4O(1,4-benzenedicarboxylate)_3$ (MOF-5). *J. Am. Chem. Soc.* **2007**, *129*, 14176.