Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information for:

Comprehensive study of carbon dioxide adsorption in the metal-organic frameworks M_2(dobdc) (M = Mg, Mn, Fe, Co, Ni, Cu, Zn)

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Chemical deuteration of 2,5-dihydroxy-1,4-benzendicarboxylic-d_2 acid

Additional Information:

Chemicals and reagents of the highest grade were purchased from Sigma Aldrich and were used without further purification. Solvents were purchased from Sigma Aldrich and Merck (St. Louis, MO, USA) and were purified by established methods. NMR solvents were purchased from Cambridge Isotope Laboratories Inc. (MA, USA) and Sigma Aldrich and were used without further purification. D_2O (99.8 %) was supplied by AECL (Ontario, Canada). Thin-layer chromatography (TLC) was performed on Fluka Analytical silica gel aluminium sheets (25 F254) (product of Sigma Aldrich, St. Louis, MO, USA). Davisil® silica gel (LC60Å 40-63 micron) (product of W. R. Grace & Co.-Conn, Columbia, USA) was used for bench-top column chromatography.**

Hydrothermal reactions were performed using a Mini Benchtop 4560 Parr Reactor (600 mL vessel capacity, 3000 psi maximum pressure, 350 °C maximum temperature). Thin layer chromatography was used (referenced with the protonated compound) to estimate the purity and to develop separation protocols. ^{1}H NMR (400 MHz) and ^{2}H NMR (61.4 MHz) spectra were recorded on a Bruker 400 MHz spectrometer at 298 K. Chemical shifts, in ppm, were referenced to the residual signal of the corresponding NMR solvent. Deuterium NMR was performed using the probe's lock channel for direct observation.

Electrospray ionization mass spectra (ESI-MS) were recorded on a 4000 QTrap AB Sciex spectrometer. The overall percentage deuteration of the molecules was calculated by NMR and MS using the isotope distribution analysis of the different isotopologues in MS.

**Commercial materials and equipment are identified in this paper only to specify adequately the experimental procedure. In no case does such identification imply recommendation by NIST nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

Figure S1. NMR Spectra of 2,5-dihydroxy-1,4-benzendicarboxylic-d_2 acid. Bottom (in red): ^{1}H NMR (400 MHz, acetone-d_6) showing small residual proton signal at 7.43 ppm. Top (in black): ^{2}H NMR (61.4 MHz, acetone-d_6) showing a broad deuterium signal at 7.46 ppm.

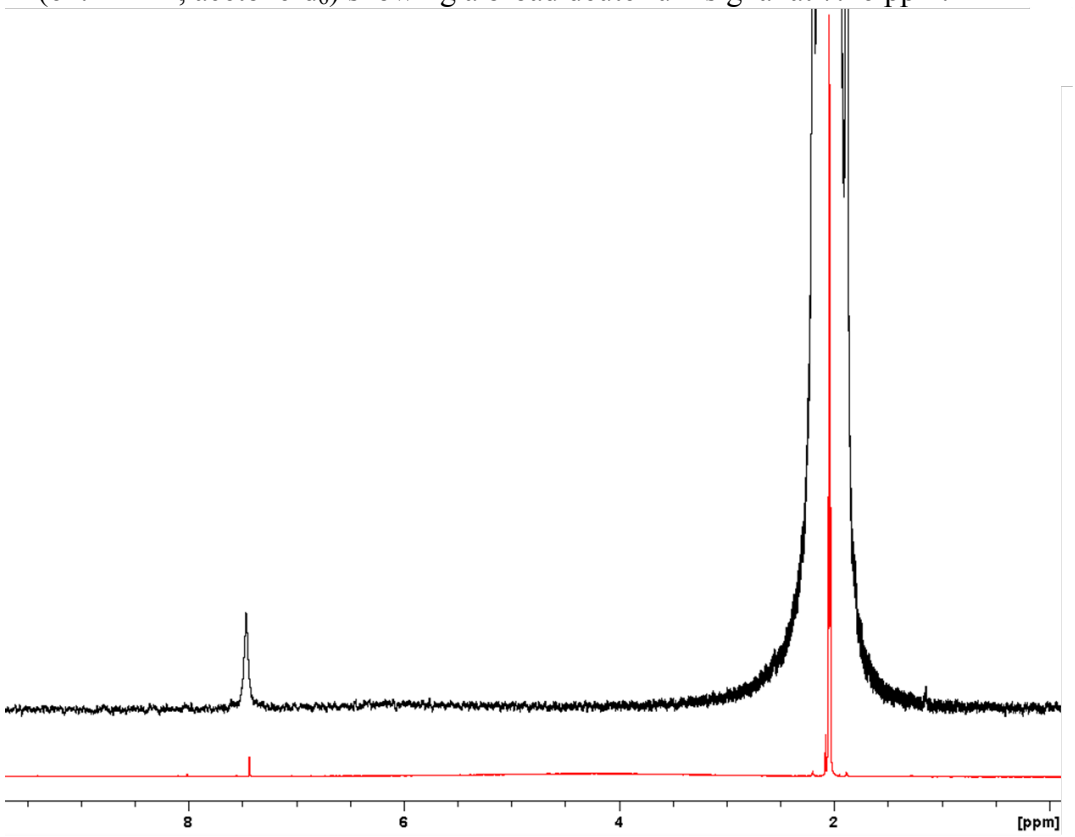


Figure S2. ^{13}C NMR (in acetone-d_6) spectra of 2,5-dihydroxy-1,4-benzendicarboxylic-d_2 acid. Top (in black): ^{13}C $\{^{1}H\}$ (proton decoupled only) spectrum showing triplet for the carbon baring D; bottom (in red): ^{13}C $\{^{1}H, ^{2}H\}$ (decoupling both ^{1}H and ^{2}H with D1 = 20 s) where the triplet is resolved into singlet, confirming C-D, and a residual peak integrating 1 to 0.02, respectively.

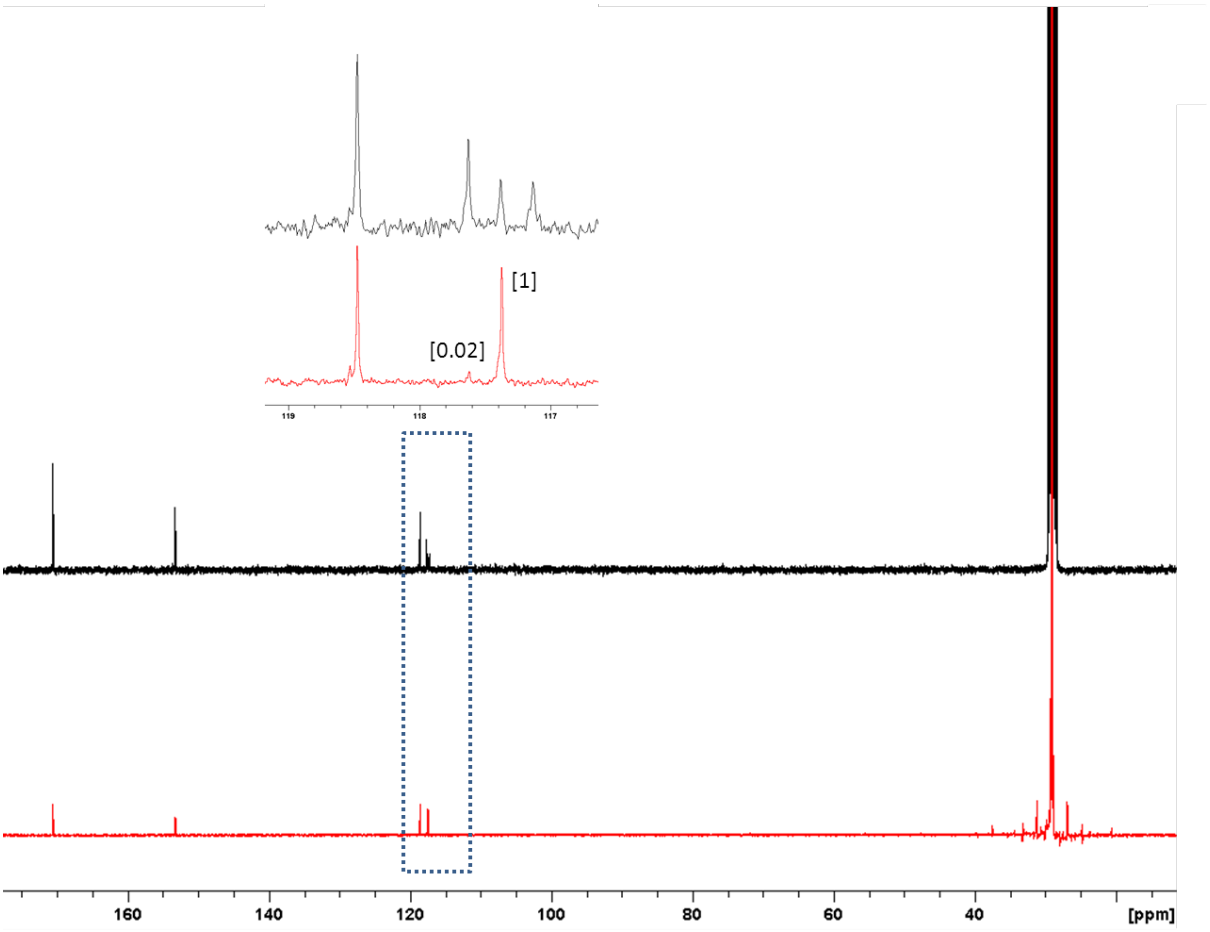


Figure S3. ESI-MS (negative mode) of 2,5-dihydroxy-1,4-benzenedicarboxylic-d_2 acid (deuterated, Mw = 200) showed two signals at m/e 199 (M^{-1}) and 198 (M^{-2}).

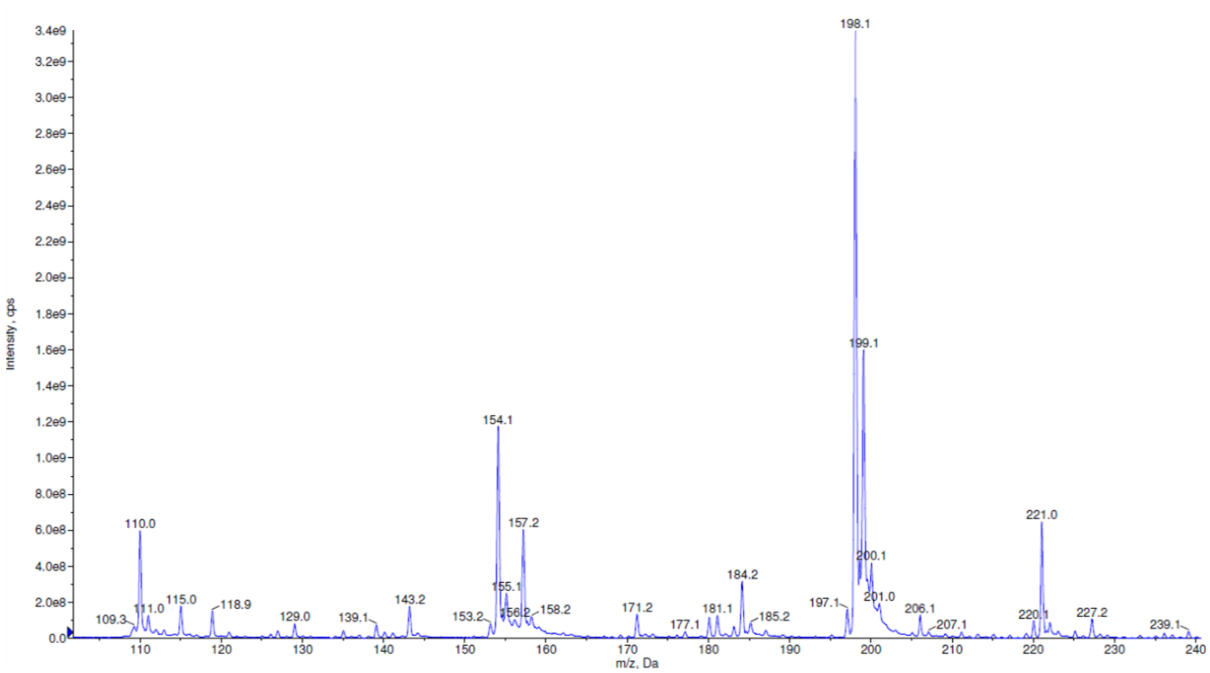
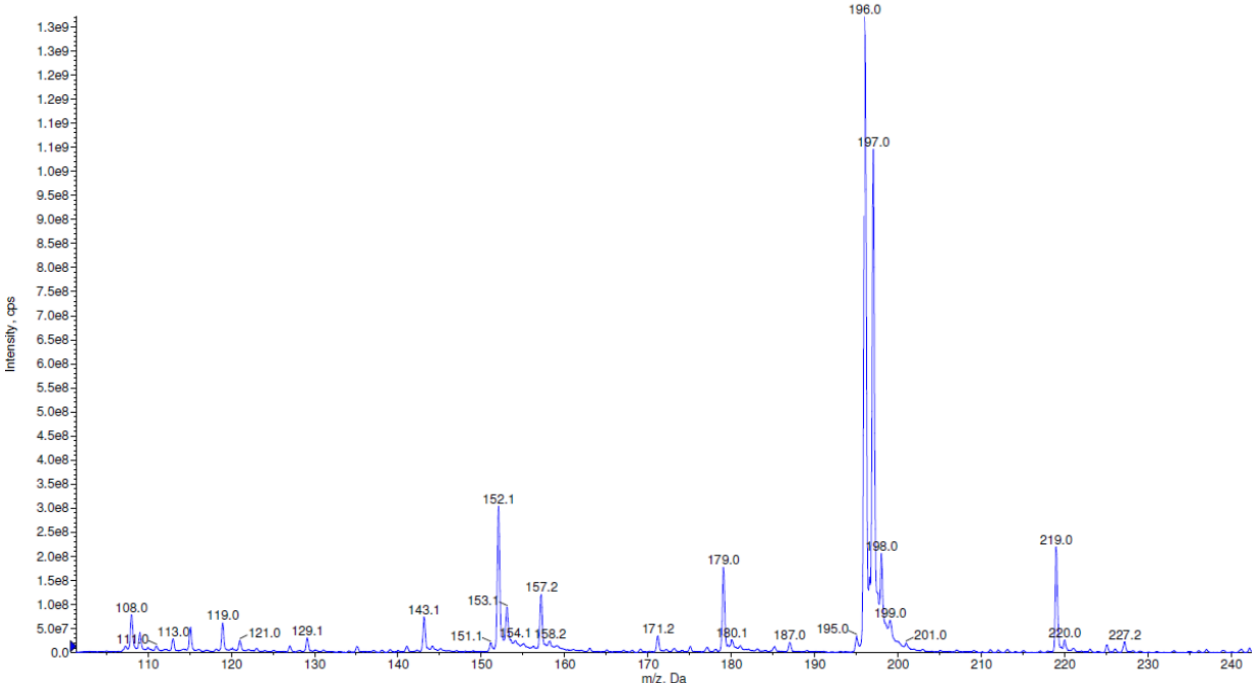


Figure S4. ESI-MS (negative mode) of protonated 2,5-dihydroxy-1,4-benzenedicarboxylic (protonated, Mw = 198) showed two signals at m/e 197 (M^{-1}) and 196 (M^{-2}).



Low pressure gas adsorption of the M_2(dobdc) series

UHP-grade (99.999 % purity) helium, nitrogen, and carbon dioxide were used for all adsorption measurements. Gas adsorption isotherms for pressures in the range 0 – 1.1 bar were measured using a Micromeritics ASAP 2020 instrument. For standard measurements in ASAP low-pressure glass sample holders, activated samples were transferred under a N_2 atmosphere to preweighed analysis tubes, which were capped with a Transeal. The samples were evacuated on the ASAP until the outgas rate was less than 3 μbar/min. The evacuated analysis tubes containing degassed samples were then carefully transferred to an electronic balance and weighed to determine the mass of sample (typically 100 – 200 mg). For cryogenic measurements, the tube was fitted with an isothermal jacket and transferred back to the analysis port of the gas adsorption instrument. The outgas rate was again confirmed to be less than 3 μbar/min. Langmuir surface areas and pore volumes were determined by measuring N_2 adsorption isotherms in a 77 K liquid N_2 bath and calculated using the Micromeritics software, assuming a value of 16.2 $Å^2$ for the molecular cross-sectional area of N_2. Adsorption isotherms between 25 and 45 °C were measured using a recirculating dewar (Micromeritics) connected to a Julabo F32-MC isothermal bath.

Figure S5. Excess CO_2 adsorption isotherms at 298 K for all M_2(dobdc) frameworks.

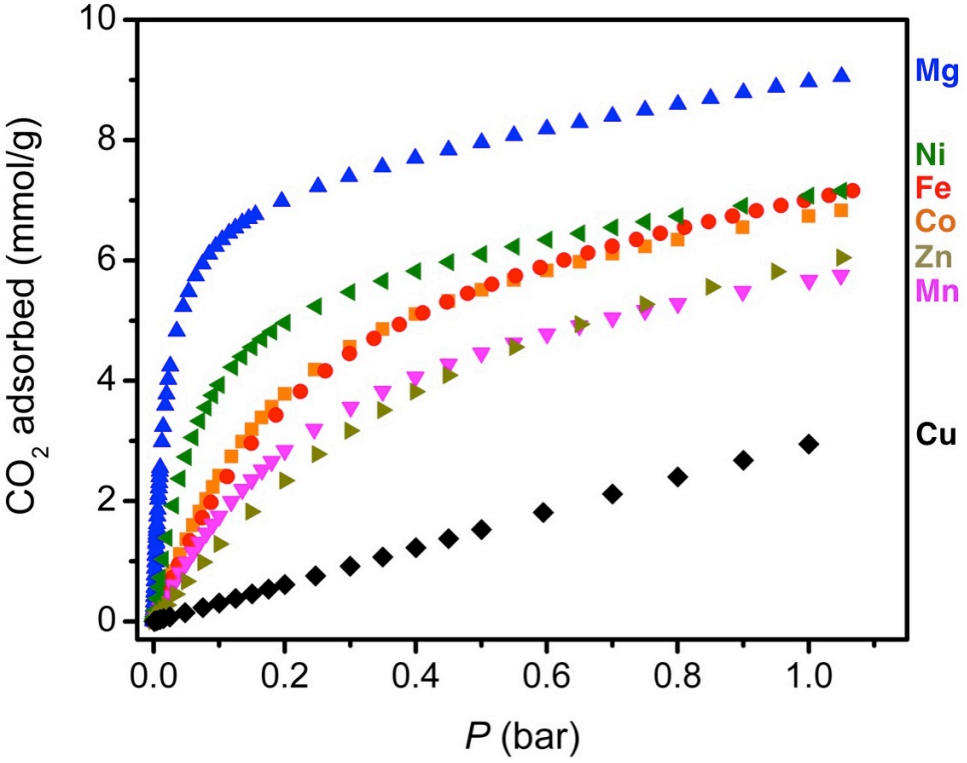
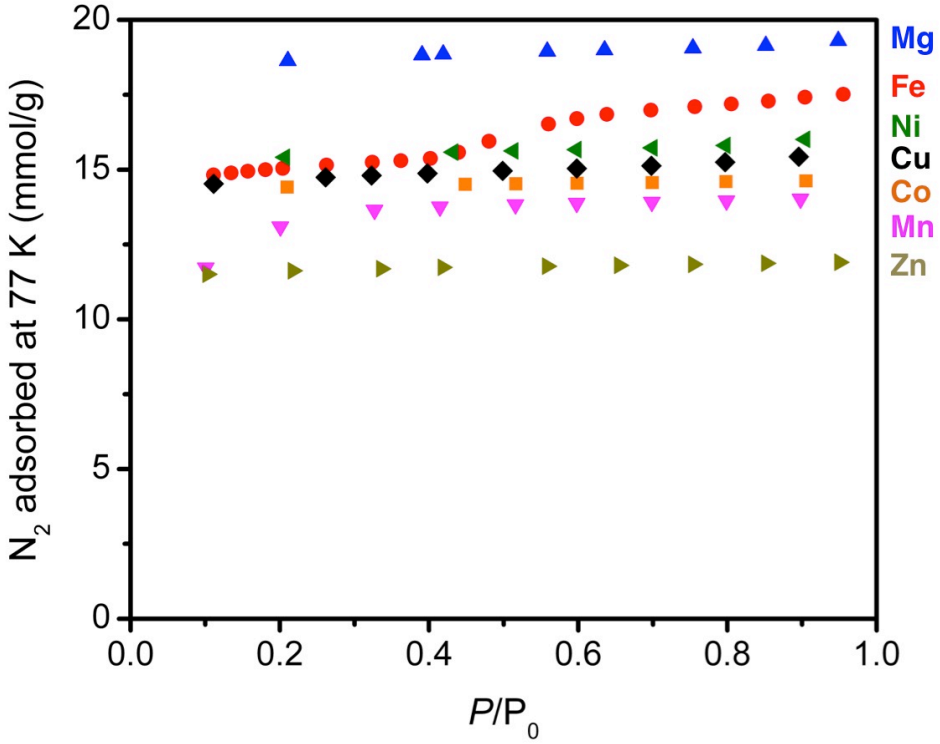


Figure S6. N_2 adsorption at 77 K for all M_2(dobdc) frameworks.



Fitting CO_2 adsorption isotherms for M_2(dobdc) series

The CO_2 adsorption isotherms were fit with a dual-site Langmuir-Freundlich model (Eqn. 1), where n is the absolute amount adsorbed in mmol/g, P is the pressure in bar, $q_{sat,i}$ is the saturation capacity in mmol/g, b_i is the Langmuir parameter in bar^{-1}, and v_i is the Freundlich parameter for two sites 1 and 2. The fitted parameters for each adsorption isotherm can be found in Tables S1-S7. Plots of the CO_2 adsorption isotherms with the corresponding dual-site Langmuir-Freundlich fits can be found in Fig. S7-S13. Several recent studies have demonstrated the ability of Langmuir-type equations to successfully model adsorption in metal-organic frameworks, especially those that have well-defined adsorption sites on the pore surface.[i]

$$n = \frac{q_{sat,1} b_1 P^{v_1}}{1 + b_1 P^{v_1}} + \frac{q_{sat,2} b_2 P^{v_2}}{1 + b_2 P^{v_2}} \quad (1)$$

Table S1. Dual-site Langmuir-Freundlich parameters for CO_2 adsorption in Co_2(dobdc) at 25, 35, and 45 ºC.

	25 ºC	35 ºC	45 ºC
$q_{sat,1}$	7.2	7.2	7.2
b_1	6.4	3.9	2.5
v_1	1.1	1.1	1.1
$q_{sat,2}$	2.8	2.8	2.3
b_2	0.23	0.13	0.11
v_2	2.2	1.9	1.6

Table S2. Dual-site Langmuir-Freundlich parameters for CO_2 adsorption in Fe_2(dobdc) at 25, 35, and 45 ºC.

	25 ºC	35 ºC	45 ºC
$q_{sat,1}$	8.3	8.3	8.3
b_1	4.1	2.6	1.7
v_1	1.1	1.1	1.1
$q_{sat,2}$	3.1	3.1	3.1
b_2	0.12	0.086	0.064
v_2	2.5	2.5	2.5

Table S3. Dual-site Langmuir-Freundlich parameters for CO_2 adsorption in Mg_2(dobdc) at 25, 35, and 45 ºC.

	25 ºC	35 ºC	45 ºC
$q_{sat,1}$	7.2	7.1	7.2
b_1	56.5	33.4	18.2
v_1	1	1	1
$q_{sat,2}$	7.0	7.7	7.1
b_2	0.36	0.22	0.15
v_2	1.2	1.1	1.2

Table S4. Dual-site Langmuir-Freundlich parameters for CO_2 adsorption in Mn_2(dobdc) at 25, 35, and 45 ºC.

	25 ºC	35 ºC	45 ºC
$q_{sat,1}$	7	7	7
b_1	3.3	2.1	1.4
v_1	1	1	1
$q_{sat,2}$	10	10	10
b_2	0.031	0.024	0.019
v_2	1	1	1

Table S5. Dual-site Langmuir-Freundlich parameters for CO_2 adsorption in Ni_2(dobdc) at 25, 35, and 45 ºC.

	25 ºC	35 ºC	45 ºC
$q_{sat,1}$	6.2	6.3	6.1
b_1	22.0	12.1	7.5
v_1	1.1	1.1	1.1
$q_{sat,2}$	3.0	3.0	3.1
b_2	0.64	0.32	0.24
v_2	1.7	1.8	1.4

Table S6. Dual-site Langmuir-Freundlich parameters for CO_2 adsorption in Zn_2(dobdc) at 25, 35, and 45 ºC.

	25 ºC	35 ºC	45 ºC
$q_{sat,1}$	6.7	6.7	6.7
b_1	2.2	1.5	1.0
v_1	1.1	1.1	1.1
$q_{sat,2}$	3.3	3.3	3.3
b_2	0.68	0.51	0.39
v_2	0.82	0.82	0.82

Table S7. Dual-site Langmuir-Freundlich parameters for CO_2 adsorption in Cu_2(dobdc) at 25, 35, and 45 ºC.

	25 ºC	35 ºC	45 ºC
$q_{sat,1}$	3.2	3.2	3.2
b_1	0.35	0.19	0.10
v_1	1.8	1.8	1.8
$q_{sat,2}$	7.2	7.2	7.20
b_2	0.41	0.31	0.24
v_2	1.00	1.0	1.0

Figure S7. Dual-site Langmuir-Freundlich fits for CO_2 adsorption in Co_2(dobdc) at 25, 35, and 45 ºC.

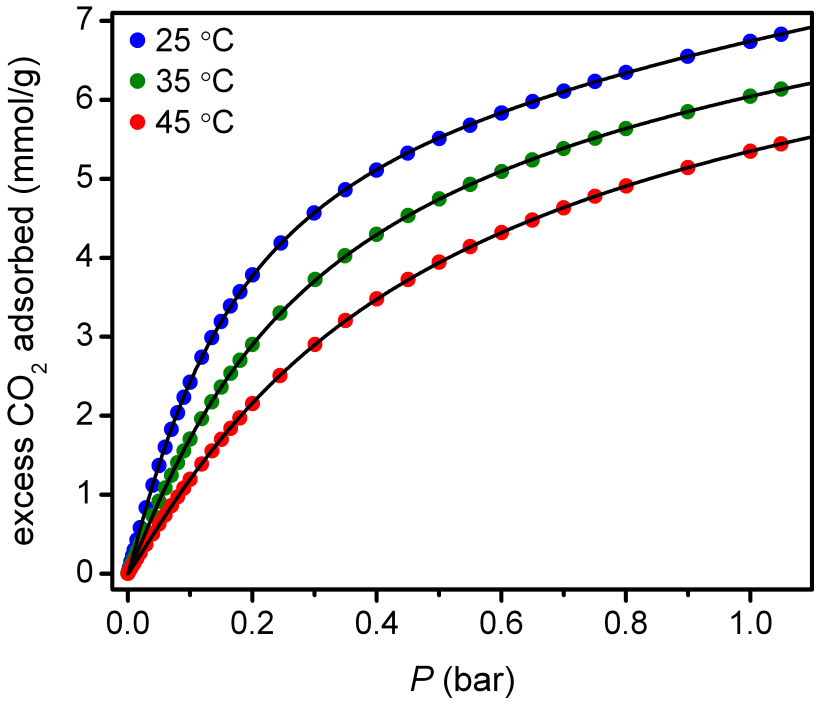


Figure S8. Dual-site Langmuir-Freundlich fits for CO_2 adsorption in Fe_2(dobdc) at 25, 35, and 45 ºC.

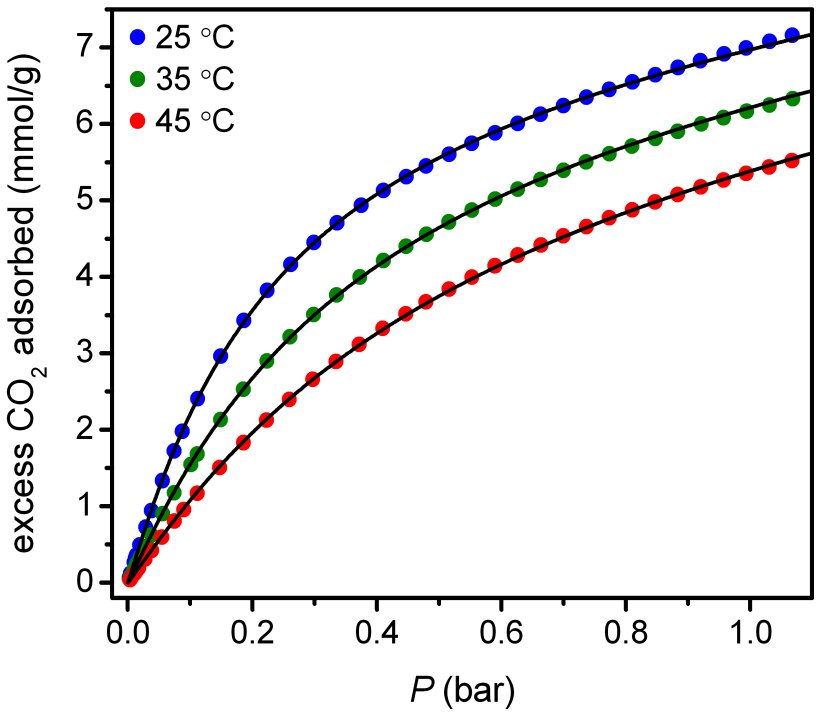


Figure S9. Dual-site Langmuir-Freundlich fits for CO_2 adsorption in Mg_2(dobdc) at 25, 35, and 45 ºC.

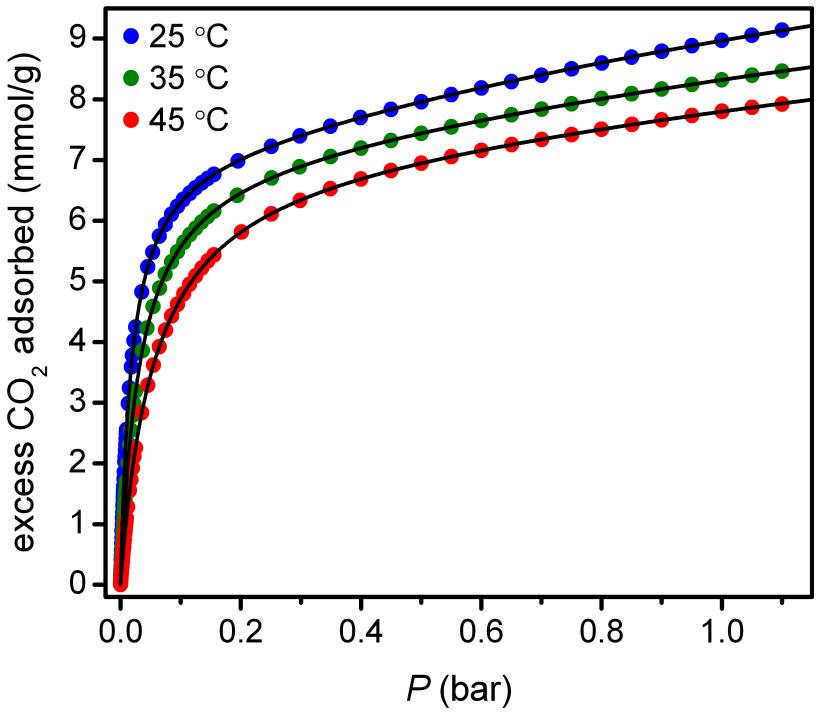


Figure S10. Dual-site Langmuir-Freundlich fits for CO_2 adsorption in Mn_2(dobdc) at 25, 35, and 45 ºC.

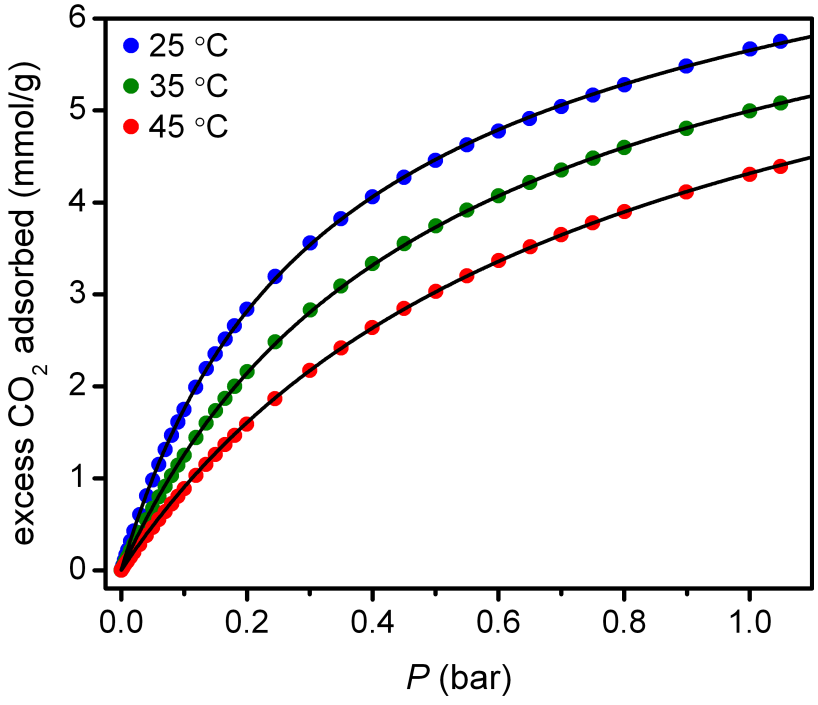


Figure S11. Dual-site Langmuir-Freundlich fits for CO_2 adsorption in Ni_2(dobdc) at 25, 35, and 45 ºC.

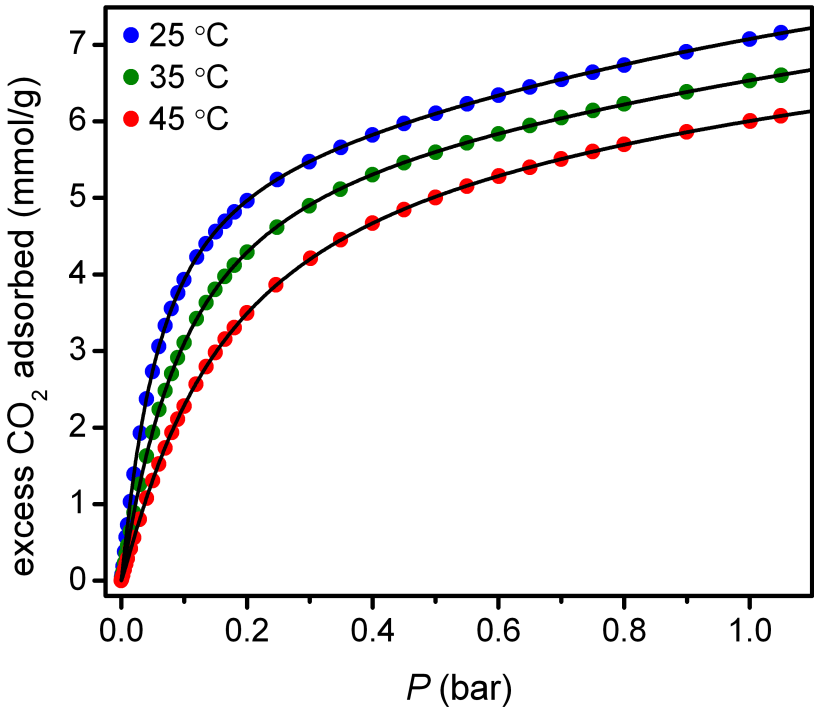


Figure S12. Dual-site Langmuir-Freundlich fits for CO_2 adsorption in Zn_2(dobdc) at 25, 35, and 45 ºC.

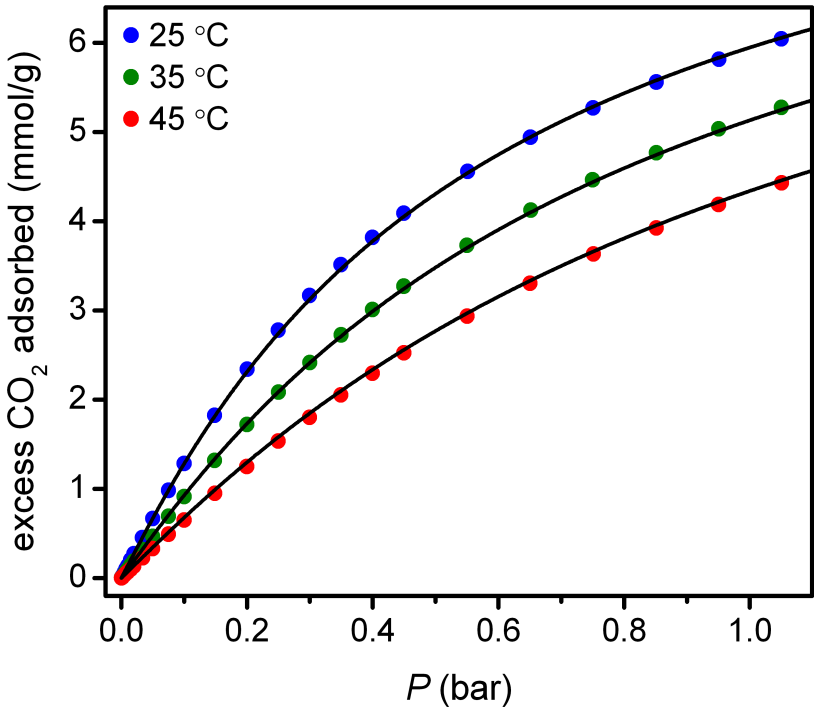
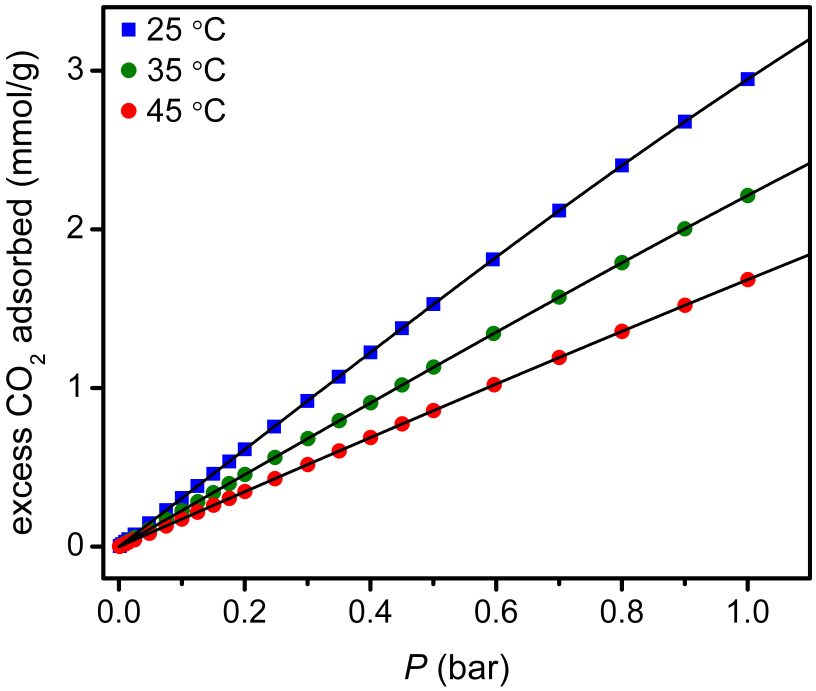


Figure S13. Dual-site Langmuir-Freundlich fits for CO_2 adsorption in Cu_2(dobdc) at 25, 35, and 45 ºC.



Calculating Isosteric heats of adsorption

The Clausius-Clapeyron equation (Eqn. 2) was used to calculate the isosteric heats of adsorption, $-Q_{st}$, for CO_2 in each M_2(dobdc) analog, using the dual-site Langmuir-Freundlich fits for each material at 25, 35, and 45 ºC to calculate the pressures that correspond to a given CO_2 loading at each temperature.[ii]

$$\ln P = -\frac{Q_{st}}{R}\left(\frac{1}{T}\right) + C \qquad (2)$$

Here, P is the pressure, n is the amount adsorbed, T is the temperature, R is the universal gas constant, and C is a constant. The isosteric heat of adsorption, $-Q_{st}$, was obtained from the slope of plots of $(\ln P)_n$ as a function of $1/T$. An error in the isosteric heat for a given loading can be calculated from the standard error in slope of the best-fit line. Fundamentally, this error describes the quality of agreement between the fitted isotherms and the Clausius-Clapeyron relation. The isosteric heats of adsorption as a function of loading for CO_2 in M_2(dobdc) can be found in Figure 2. Note that while it is most appropriate to use absolute adsorption in thermodynamic calculations,[iii] the isosteric heats of adsorption reported here were calculated from experimentally measured excess adsorption isotherms since the difference between the excess and absolute CO_2 uptake at the highest measured pressures (≈ 1 bar) is less than 0.03 mmol/g, which is within the error of the experimental measurement. As such, the isosteric of adsorption is only calculated up to the highest CO_2 loading that was measured at 45 °C, as the isotherm fits have only been experimentally verified in this region and difference between excess and absolute adsorption will become significant at higher loadings.

Neutron powder diffraction data for the bare and CO_2 dosed M_2(dobdc) series

Figure S14. Neutron powder diffraction data for bare Zn_2(dobdc), 10 K. The green line, crosses, and red line represent the background, experimental, and calculated diffraction patterns, respectively. The blue line represents the difference between experimental and calculated patterns.

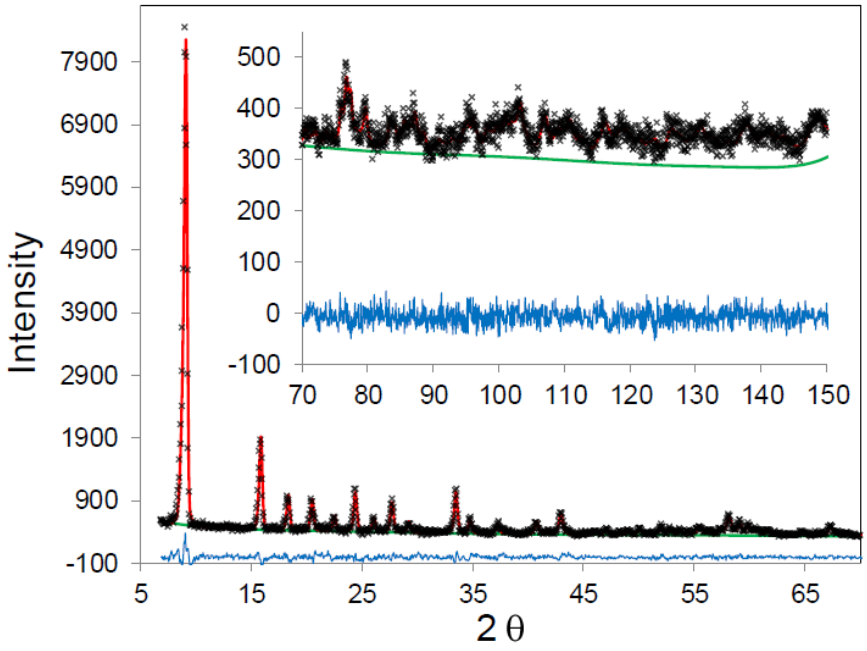


Figure S15. Neutron powder diffraction data for bare Co_2(dobdc), 10 K. The green line, crosses, and red line represent the background, experimental, and calculated diffraction patterns, respectively. The blue line represents the difference between experimental and calculated patterns.

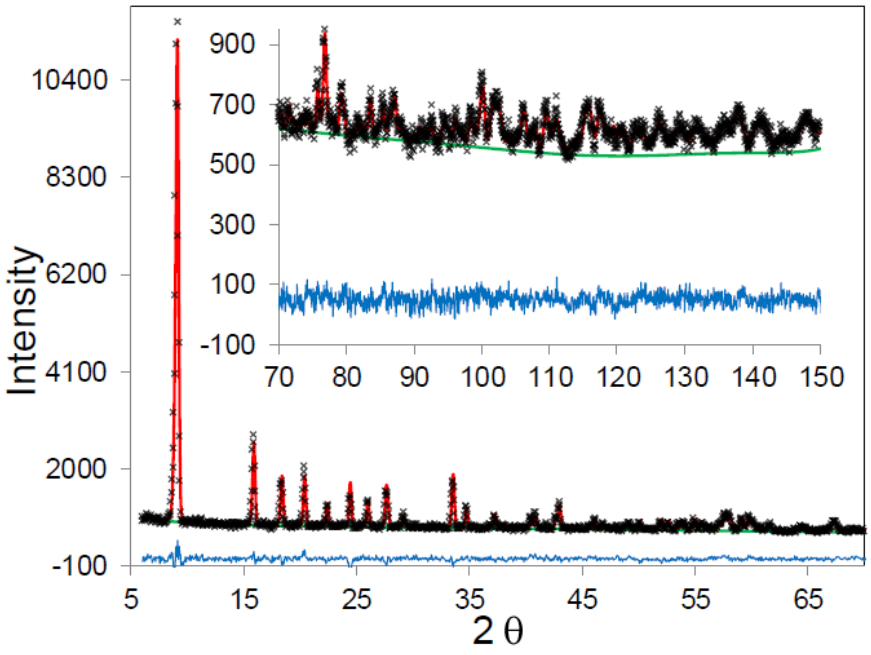


Figure S16. Neutron powder diffraction data for bare Fe_2(dobdc), 10 K. The green line, crosses, and red line represent the background, experimental, and calculated diffraction patterns, respectively. The blue line represents the difference between experimental and calculated patterns.

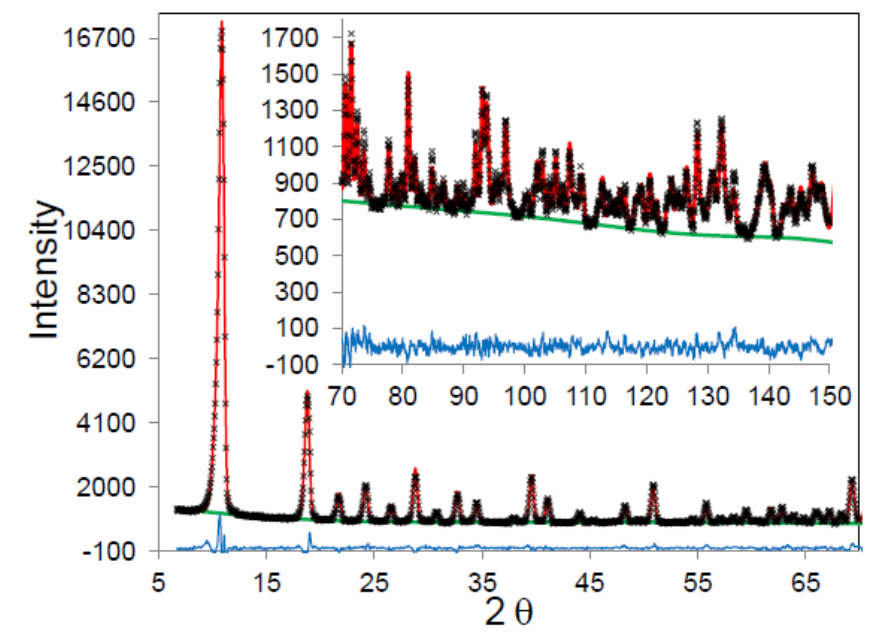


Figure S17. Neutron powder diffraction data for bare Mn_2(dobdc), 10 K. The green line, crosses, and red line represent the background, experimental, and calculated diffraction patterns, respectively. The blue line represents the difference between experimental and calculated patterns.

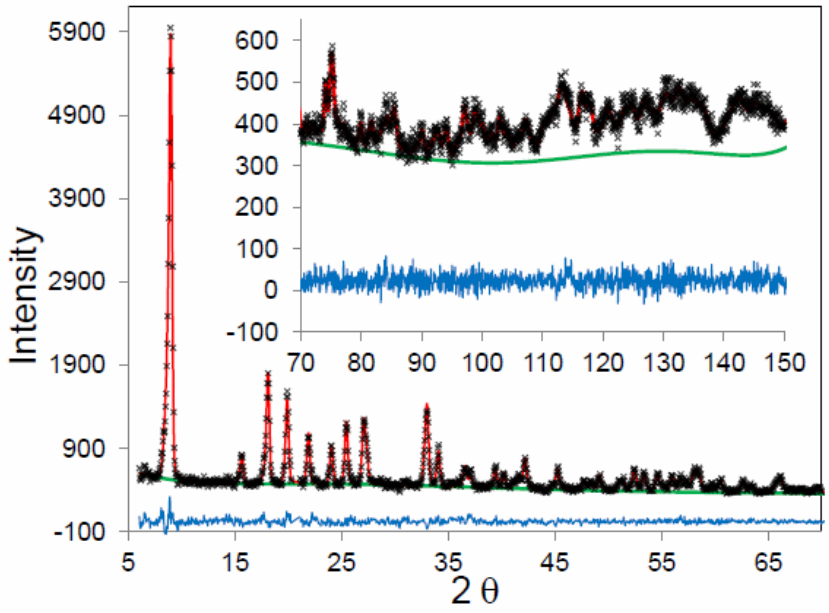


Figure S18. Neutron powder diffraction data for Mg_2(dobdc) with 0.75 CO_2 per Mg site, 10 K. The green line, crosses, and red line represent the background, experimental, and calculated diffraction patterns, respectively. The blue line represents the difference between experimental and calculated patterns.

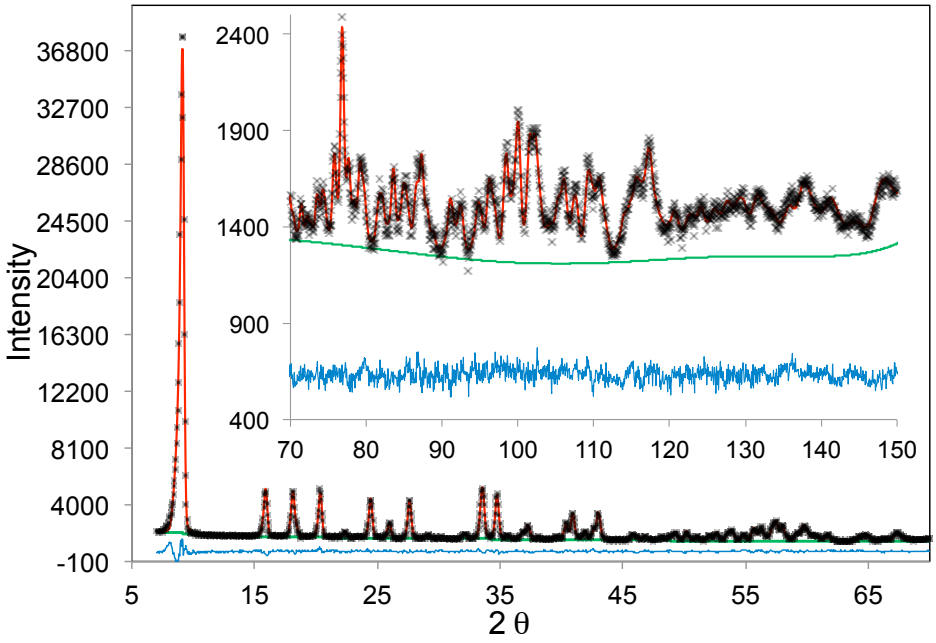


Figure S19. Neutron powder diffraction data for bare Cu_2(dobdc), 10K. The green line, crosses, and red line represent the background, experimental, and calculated diffraction patterns, respectively. The blue line represents the difference between experimental and calculated patterns.

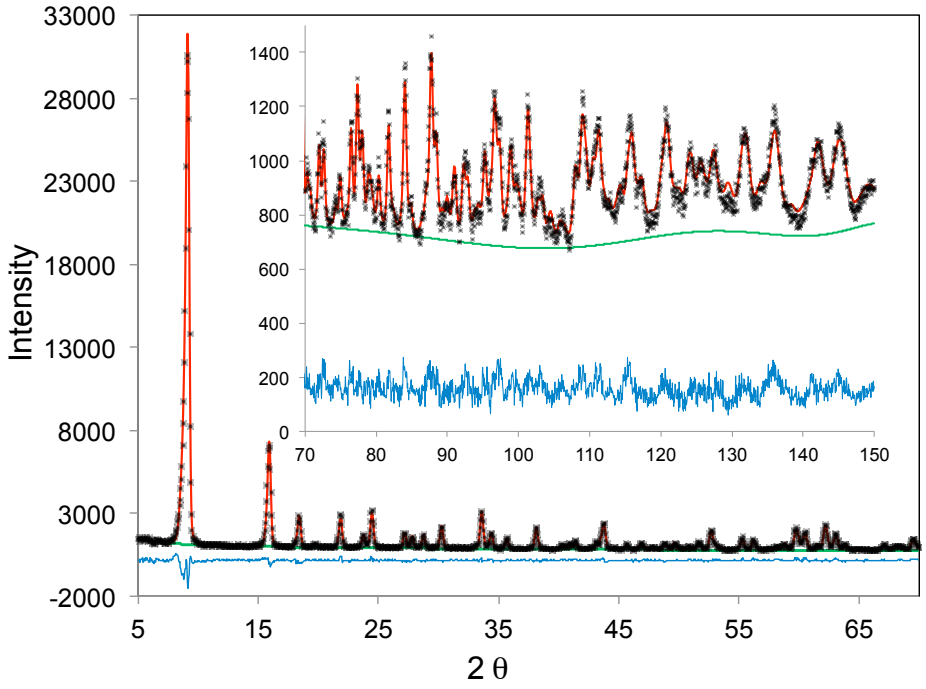


Table S8. Fractional atomic coordinates, occupancies, and isotropic displacement parameters obtained from Rietveld refinement of structural model of activated Mn_2(dobdc) framework, 10 K, Trigonal, R-3, a = 26.333(2) Å, c = 7.0477(5) Å, V = 4232.3(5) Å^3. Values in parentheses indicate one standard deviation in the refined value. Goodness-of-fit parameters: χ^2 = 0.9049, wRp = 0.0440, Rp = 0.0361.

Atom	X	Y	Z	Occupancy	$U_{(ISO)}$ (Å^2)	Multiplicity
Mn	0.3854(7)	0.3606(9)	0.142(3)	1	0.007(5)	18
O1	0.3280(6)	0.2935(6)	0.360(2)	1	0.023(2)	18
O2	0.2999(7)	0.2282(7)	0.591(2)	1	0.023(2)	18
O3	0.3544(7)	0.2745(7)	0.014(3)	1	0.023(2)	18
C1	0.3186(5)	0.2441(5)	0.420(2)	1	0.014(1)	18
C2	0.3289(5)	0.2055(5)	0.288(2)	1	0.014(1)	18
C3	0.3443(6)	0.2219(5)	0.089(1)	1	0.014(1)	18
C4	0.3523(5)	0.1841(5)	-0.018(1)	1	0.014(1)	18
H	0.3599(9)	0.1921(8)	-0.157(3)	1	0.010(6)	18

Table S9. Fractional atomic coordinates, occupancies, and isotropic displacement parameters obtained from Rietveld refinement of structural model of activated Fe_2(dobdc) framework, 10 K, Trigonal, R-3, a = 26.0983(4) Å, c = 6.8512(2) Å, V = 4041.3(1) Å^3. Values in parentheses indicate one standard deviation in the refined value. Goodness-of-fit parameters: χ^2 = 2.936, wRp = 0.0359, Rp = 0.0282.

Atom	X	Y	Z	Occupancy	$U_{(ISO)}$ (Å^2)	Multiplicity
Fe	0.3824(2)	0.3521(2)	0.1430(6)	1	0.012(2)	18
O1	0.3272(3)	0.2938(4)	0.363(1)	1	0.003(3)	18
O2	0.3010(4)	0.2272(4)	0.599(1)	1	0.024(3)	18
O3	0.3549(4)	0.2732(3)	0.007(1)	1	0.009(2)	18
C1	0.3161(4)	0.2440(3)	0.423(1)	1	0.022(2)	18
C2	0.3259(3)	0.2038(3)	0.287(1)	1	0.002(2)	18
C3	0.3430(3)	0.2226(4)	0.095(1)	1	0.012(2)	18
C4	0.3487(3)	0.1819(4)	-0.034(1)	1	0.003(2)	18
H	0.3613(6)	0.1919(6)	-0.168(2)	1	0.013(7)	18

Table S10. Fractional atomic coordinates, occupancies, and isotropic displacement parameters obtained from Rietveld refinement of structural model of activated Co_2(dobdc) framework, 10 K, Trigonal, R-3, a = 25.9067(9)Å, c = 6.8548(5)Å, V = 3984.3(3) Å^3. Values in parentheses indicate one standard deviation in the refined value. Goodness-of-fit parameters: χ^2 = 1.044, wRp = 0.0379, Rp = 0.0316.

Atom	X	Y	Z	Occupancy	$U_{(ISO)}$ (Å^2)	Multiplicity
Co	0.385(1)	0.349(1)	0.136(4)	1	0.003(7)	18
O1	0.3283(6)	0.2968(6)	0.367(2)	1	0.018(3)	18
O2	0.3011(6)	0.2279(6)	0.603(2)	1	0.001(3)	18
O3	0.3547(6)	0.2749(6)	0.011(2)	1	0.001(3)	18
C1	0.3160(6)	0.2470(6)	0.424(2)	1	0.029(4)	18
C2	0.3290(6)	0.2075(5)	0.288(2)	1	0.020(4)	18
C3	0.3477(6)	0.2257(7)	0.089(2)	1	0.028(4)	18
C4	0.3503(6)	0.1810(5)	-0.026(2)	1	0.008(3)	18
H	0.3647(9)	0.1951(7)	-0.175(3)	1	0.001(4)	18

Table S11. Fractional atomic coordinates, occupancies, and isotropic displacement parameters obtained from Rietveld refinement of structural model of activated Zn_2(dobdc) framework, 10 K, Trigonal, R-3, a = 25.929(2) Å, c = 6.7962(9)Å, V = 3957.1(6) Å^3. Values in parentheses indicate one standard deviation in the refined value. Goodness-of-fit parameters: χ^2 = 0.9577, wRp = 0.0484, Rp = 0.0402.

Atom	X	Y	Z	Occupancy	$U_{(ISO)}$ (Å^2)	Multiplicity
Zn	0.3833(9)	0.353(1)	0.139(3)	1	0.021(6)	18
O1	0.3305(9)	0.2968(8)	0.382(3)	1	0.014(3)	18
O2	0.300(1)	0.227(1)	0.603(3)	1	0.014(3)	18
O3	0.3541(9)	0.272(1)	0.001(3)	1	0.014(3)	18
C1	0.3166(9)	0.2450(9)	0.429(3)	1	0.015(2)	18
C2	0.3267(9)	0.2058(9)	0.286(3)	1	0.015(2)	18
C3	0.3441(9)	0.224(1)	0.094(3)	1	0.015(2)	18
C4	0.3521(9)	0.185(1)	-0.029(3)	1	0.015(2)	18
H	0.365(2)	0.194(2)	-0.158(7)	1	0.05(2)	18

Table S12. Fractional atomic coordinates, occupancies, and isotropic displacement parameters obtained from Rietveld refinement of structural model of activated Cu_2(dobdc) framework, 10 K, Trigonal, R-3, a = 25.8733(7) Å, c = 6.2577(2) Å, V = 3627.8(2) Å^3. Values in parentheses indicate one standard deviation in the refined value. Goodness-of-fit parameters: χ^2 = 1.187, wRp = 0.0276, Rp = 0.0337.

Atom	X	Y	Z	Occupancy	$U_{(ISO)}$ (Å^2)	Multiplicity
Cu	0.3864(2)	0.3484(2)	0.1754(8)	1	0.001(1)	18
O1	0.3551(3)	0.3026(3)	0.437(1)	1	0.012(1)	18
O2	0.2920(3)	0.2243(3)	0.628(1)	1	0.012(1)	18
O3	0.3591(3)	0.2759(3)	0.005(1)	1	0.012(1)	18
C1	0.3236(3)	0.2480(3)	0.465(1)	1	0.0106(5)	18
C2	0.3267(3)	0.2064(3)	0.303(1)	1	0.0106(5)	18
C3	0.3480(3)	0.2235(3)	0.093(1)	1	0.0106(5)	18
C4	0.3545(3)	0.1840(3)	-0.040(1)	1	0.0106(5)	18
H	0.3687(5)	0.1963(5)	-0.204(2)	1	0.021(3)	18

Table S13. Fractional atomic coordinates, occupancies, and isotropic displacement parameters obtained from Rietveld refinement of structural model of Mg_2(dobdc) framework dosed with 0.75 CO_2 per Mg, 10 K, Trigonal, R-3, a = 25.8728(8) Å, c = 6.8700(3) Å, V = 3982.7(3) Å^3. Values in parentheses indicate one standard deviation in the refined value. Goodness-of-fit parameters: χ^2 = 1.303, wRp = 0.0273, Rp = 0.0223.

Atom	X	Y	Z	Occupancy	$U_{(ISO)}$ (Å^2)	Multiplicity
Mg	0.3804(4)	0.3515(4)	0.138(1)	1	0.011(2)	18
O1	0.3252(3)	0.2956(3)	0.362(1)	1	0.012(1)	18
O2	0.3028(3)	0.2288(4)	0.598(1)	1	0.012(1)	18
O3	0.3539(4)	0.2744(4)	0.002(1)	1	0.012(1)	18
C1	0.3158(3)	0.2466(3)	0.4239(9)	1	0.0203(6)	18
C2	0.3289(3)	0.2087(3)	0.2858(9)	1	0.0203(6)	18
C3	0.3459(3)	0.2239(3)	0.092(1)	1	0.0203(6)	18
C4	0.3526(3)	0.1825(3)	-0.0272(9)	1	0.0203(6)	18
H	0.3606(5)	0.1904(5)	-0.174(2)	1	0.007(3)	18
O2b	0.2283(8)	0.7573(8)	0.602(2)	0.825(7)	0.097(6)	18
C2a	0.1773(6)	0.7214(5)	0.600(2)	0.825(7)	0.052(4)	18
O2a	0.1283(4)	0.6856(4)	0.600(1)	0.825(7)	0.011(3)	18

Table S14. Fractional atomic coordinates, occupancies, and isotropic displacement parameters obtained from Rietveld refinement of structural model of Mn_2(dobdc) framework dosed with 0.5 CO_2 per Mn, 10 K, Trigonal, R-3, a = 26.326(2) Å, c = 7.0440(5) Å, V = 4227.9(5) Å^3. Values in parentheses indicate one standard deviation in the refined value. Goodness-of-fit parameters: χ^2 = 0.9695, wRp = 0.0436, Rp = 0.0355.

Atom	X	Y	Z	Occupancy	$U_{(ISO)}$ (Å^2)	Multiplicity
Mn	0.386(1)	0.361(1)	0.142(4)	1	0.033(7)	18
O1	0.3292(6)	0.2945(6)	0.362(2)	1	0.019(2)	18
O2	0.3007(7)	0.2278(7)	0.589(2)	1	0.019(2)	18
O3	0.3572(6)	0.2768(7)	0.011(2)	1	0.019(2)	18
C1	0.3202(5)	0.2457(5)	0.419(2)	1	0.017(1)	18
C2	0.3288(6)	0.2053(5)	0.288(2)	1	0.017(1)	18
C3	0.3453(6)	0.2235(6)	0.090(2)	1	0.017(1)	18
C4	0.3524(6)	0.1832(6)	-0.021(2)	1	0.017(1)	18
H	0.361(1)	0.1919(8)	-0.161(3)	1	0.004(5)	18
O2b	0.234(2)	0.777(2)	0.470(5)	0.54(1)	0.05(1)	18
C2a	0.191(1)	0.738(1)	0.529(4)	0.54(1)	0.030(9)	18
O2a	0.146(1)	0.7000(9)	0.583(4)	0.54(1)	0.005(7)	18

Table S15. Fractional atomic coordinates, occupancies, and isotropic displacement parameters obtained from Rietveld refinement of structural model of Fe_2(dobdc) framework dosed with 0.35 CO_2 per Fe, 10 K, Trigonal, R-3, a = 26.0349(5) Å, c = 6.8508(2) Å, V = 4021.4(2) Å^3. Values in parentheses indicate one standard deviation in the refined value. Goodness-of-fit parameters: χ^2 = 3.161, wRp = 0.0399, Rp = 0.0307.

Atom	X	Y	Z	Occupancy	$U_{(ISO)}$ (Å^2)	Multiplicity
Fe	0.3844(2)	0.3531(2)	0.1400(5)	1	0.0061(7)	18
O1	0.3256(3)	0.2936(3)	0.362(1)	1	0.0050(8)	18
O2	0.3020(3)	0.2293(3)	0.603(1)	1	0.0050(8)	18
O3	0.3537(3)	0.2727(3)	0.012(1)	1	0.0050(8)	18
C1	0.3174(3)	0.2460(2)	0.4200(9)	1	0.0041(4)	18
C2	0.3278(3)	0.2040(3)	0.2893(9)	1	0.0041(4)	18
C3	0.3448(2)	0.2237(3)	0.0916(8)	1	0.0041(4)	18
C4	0.3501(3)	0.1824(3)	-0.0239(8)	1	0.0041(4)	18
H	0.3609(5)	0.1934(4)	-0.173(2)	1	0.002(3)	18
O2b	0.212(1)	0.756(1)	0.510(4)	0.350(6)	0.0434*	18
C2a	0.1686(9)	0.714(1)	0.552(4)	0.350(6)	0.0468*	18
O2a	0.1253(9)	0.6725(9)	0.592(3)	0.350(6)	0.010(6)	18

*Uaniso O2b=[U11,U12,U13,U22,U23,U33] = [0.04(2),0.02(1),0.000(1),0.04(2),-0.00(2),0.04(2)]
Uaniso C2a=[U11,U12,U13,U22,U23,U33] = [0.05(1),0.025(9),0.00(1),0.05(1),0.00(1),0.05(2)]

Table S16. Fractional atomic coordinates, occupancies, and isotropic displacement parameters obtained from Rietveld refinement of structural model of Co_2(dobdc) framework dosed with 0.5 CO_2 per Co, 10 K, Trigonal, R-3, a = 25.8977(9) Å, c = 6.8460(4) Å, V = 3976.4(3) Å^3. Values in parentheses indicate one standard deviation in the refined value. Goodness-of-fit parameters: χ^2 = 0.8989, wRp = 0.0345, Rp = 0.0278.

Atom	X	Y	Z	Occupancy	$U_{(ISO)}$ (Å^2)	Multiplicity
Co	0.382(1)	0.349(1)	0.133(4)	1	0.004(9)	18
O1	0.3260(5)	0.2973(6)	0.372(2)	1	0.001(2)	18
O2	0.3022(6)	0.2275(6)	0.601(2)	1	0.001(2)	18
O3	0.3562(6)	0.2740(6)	0.005(2)	1	0.001(2)	18
C1	0.3165(5)	0.2470(6)	0.428(2)	1	0.008(1)	18
C2	0.3302(5)	0.2082(5)	0.288(2)	1	0.008(1)	18
C3	0.3473(5)	0.2255(6)	0.089(2)	1	0.008(1)	18
C4	0.3517(6)	0.1809(6)	-0.028(2)	1	0.008(1)	18
H	0.3616(9)	0.1928(8)	-0.174(3)	1	0.004(5)	18
O2b	0.218(2)	0.757(2)	0.504(5)	0.62(2)	0.09(2)	18
C2a	0.172(1)	0.718(1)	0.558(4)	0.62(2)	0.037(8)	18
O2a	0.127(1)	0.6848(9)	0.611(3)	0.62(2)	0.001(6)	18

Table S17. Fractional atomic coordinates, occupancies, and isotropic displacement parameters obtained from Rietveld refinement of structural model of Zn_2(dobdc) framework dosed with 0.5 CO_2 per Zn, 10 K, Trigonal, R-3, a = 25.914(2) Å, c = 6.7986(6) Å, V = 3953.8(5) Å^3. Values in parentheses indicate one standard deviation in the refined value. Goodness-of-fit parameters: χ^2 = 1.088, wRp = 0.0345, Rp = 0.0279.

Atom	X	Y	Z	Occupancy	$U_{(ISO)}$ (Å^2)	Multiplicity
Zn	0.3836(8)	0.3546(9)	0.144(2)	1	0.029(5)	18
O1	0.3281(6)	0.2966(7)	0.375(2)	1	0.015(3)	18
O2	0.3001(7)	0.2267(7)	0.611(2)	1	0.015(3)	18
O3	0.3537(8)	0.2743(8)	0.017(2)	1	0.015(3)	18
C1	0.3157(7)	0.2448(7)	0.434(2)	1	0.016(1)	18
C2	0.3270(7)	0.2064(6)	0.284(2)	1	0.016(1)	18
C3	0.3431(6)	0.2212(6)	0.092(2)	1	0.016(1)	18
C4	0.3525(7)	0.1841(8)	-0.036(2)	1	0.016(1)	18
H	0.361(1)	0.191(1)	-0.165(4)	1	0.032(8)	18
O2b	0.229(3)	0.766(3)	0.538(9)	0.54(2)	0.10(2)	18
C2a	0.182(2)	0.724(2)	0.577(6)	0.54(2)	0.053(1)	18
O2a	0.1356(2)	0.685(1)	0.614(4)	0.54(2)	0.01(1)	18

Table S18. Fractional atomic coordinates, occupancies, and isotropic displacement parameters obtained from Rietveld refinement of structural model of Cu_2(dobdc) framework dosed with 0.5 CO_2 per Cu, 10 K, Trigonal, R-3, a = 25.8582(7) Å, c = 6.2615(2) Å, V = 3625.8(2) Å^3. Values in parentheses indicate one standard deviation in the refined value. Goodness-of-fit parameters: χ^2 = 1.271, wRp = 0.0321, Rp = 0.0266.

Atom	X	Y	Z	Occupancy	$U_{(ISO)}$ (Å^2)	Multiplicity
Cu	0.3865(2)	0.3491(2)	0.1761(8)	1	0.002(1)	18
O1	0.3544(3)	0.3031(3)	0.434(1)	1	0.006(1)	18
O2	0.2922(3)	0.2240(3)	0.629(1)	1	0.006(1)	18
O3	0.3605(3)	0.2770(3)	0.008(1)	1	0.006(1)	18
C1	0.3246(3)	0.2478(3)	0.466(1)	1	0.0098(6)	18
C2	0.3277(3)	0.2062(3)	0.299(1)	1	0.0098(6)	18
C3	0.3481(3)	0.2247(3)	0.093(1)	1	0.0098(6)	18
C4	0.3541(3)	0.1841(3)	-0.043(1)	1	0.0098(6)	18
H	0.3672(5)	0.1955(5)	-0.198(2)	1	0.011(3)	18
O1a	0.251(2)	0.787(1)	0.468(8)	0.172(6)	0.02(2)	18
C1a	0.210(2)	0.747(2)	0.550(8)	0.172(6)	0.08(2)	18
O1b	0.170(2)	0.707(2)	0.634(7)	0.172(6)	0.008(2)	18
O2a	0.149(3)	0.045(4)	0.30(1)	0.142(5)	0.10(4)	18
C2a	0.153(2)	0.020(3)	0.449(8)	0.142(5)	0.06(3)	18
O2b	0.156(2)	-0.005(3)	0.598(8)	0.142(5)	0.02(2)	18
O3a	0.0	0.0	0.314(2)	0.152(8)	0.06(4)	6
C3a	0.0	0.0	0.5	0.152(8)	0.3(1)	3

Table S19. Fractional atomic coordinates, occupancies, and isotropic displacement parameters obtained from Rietveld refinement of structural model of Fe_2(dobdc) framework dosed with 1.3 CO_2 per Fe, 10 K, Trigonal, R-3, a = 26.0010(5) Å, c = 6.8607(2) Å, V = 4016.8(2) Å^3. Values in parentheses indicate one standard deviation in the refined value. Goodness-of-fit parameters: χ^2 = 1.862, wRp = 0.0417, Rp = 0.0334.

Atom	X	Y	Z	Occupancy	$U_{(ISO)}$ (Å^2)	Multiplicity
Fe	0.3856(2)	0.3529(2)	0.1427(6)	1	0.0055(8)	18
O1	0.3255(3)	0.2932(3)	0.352(1)	1	0.014(1)	18
O2	0.3033(3)	0.2262(4)	0.600(1)	1	0.014(1)	18
O3	0.3534(4)	0.2708(3)	0.008(1)	1	0.014(1)	18
C1	0.3161(3)	0.2447(3)	0.4228(9)	1	0.0077(5)	18
C2	0.3254(3)	0.2036(3)	0.2909(9)	1	0.0077(5)	18
C3	0.3429(3)	0.2209(3)	0.0961(9)	1	0.0077(5)	18
C4	0.3514(3)	0.1828(3)	-0.0248(9)	1	0.0077(5)	18
H	0.3606(5)	0.1954(5)	-0.171(2)	1	0.01(3)	18
O2b	0.2213(4)	0.7566(5)	0.552(2)	0.856(6)	0.142(8)	18
C2a	0.1746(3)	0.7160(4)	0.581(2)	0.856(6)	0.068(4)	18
O2a	0.1280(3)	0.6796(4)	0.615(1)	0.856(6)	0.012(2)	18
O3b	0.2006(8)	0.0157(4)	0.678(2)	0.407(6)	0.09(1)	18
C3a	0.1848(2)	0.0209(2)	0.524(1)	0.407(6)	0.028(6)	18
O3a	0.1699(7)	0.0267(4)	0.374(2)	0.407(6)	0.048(7)	18

Table S20. Fractional atomic coordinates, occupancies, and isotropic displacement parameters obtained from Rietveld refinement of structural model of Co_2(dobdc) framework dosed with 1.5 CO_2 per Co, 10 K, Trigonal, R-3, a = 25.874(1)Å, c = 6.8486(4)Å, V = 3970.5(4) Å^3. Values in parentheses indicate one standard deviation in the refined value. Goodness-of-fit parameters: χ^2 = 0.9775, wRp = 0.0355, Rp = 0.0290.

Atom	X	Y	Z	Occupancy	$U_{(ISO)}$ (Å^2)	Multiplicity
Co	0.379(1)	0.349(1)	0.151(4)	1	0.001(9)	18
O1	0.3287(6)	0.2959(7)	0.364(2)	1	0.005(2)	18
O2	0.3026(7)	0.2291(7)	0.599(2)	1	0.005(2)	18
O3	0.3577(7)	0.2758(7)	0.002(2)	1	0.005(2)	18
C1	0.3191(6)	0.2476(6)	0.429(2)	1	0.016(2)	18
C2	0.3282(7)	0.2069(6)	0.290(2)	1	0.016(2)	18
C3	0.3465(6)	0.2239(7)	0.091(2)	1	0.016(2)	18
C4	0.3506(6)	0.1816(7)	-0.024(2)	1	0.016(2)	18
H	0.358(1)	0.191(1)	-0.168(4)	1	0.012(7)	18
O2b	0.232(2)	0.747(2)	0.651(6)	0.73(2)	0.13(2)	18
C2a	0.179(1)	0.715(1)	0.625(3)	0.73(2)	0.028(7)	18
O2a	0.130(1)	0.6839(9)	0.605(3)	0.73(2)	0.011(7)	18
O3b	0.206(1)	0.024(1)	0.657(5)	0.78(2)	0.07(1)	18
C3a	0.184(1)	0.024(1)	0.511(5)	0.78(2)	0.07(1)	18
O3a	0.164(1)	0.029(1)	0.369(6)	0.78(2)	0.09(1)	18

Table S21. Fractional atomic coordinates, occupancies, and isotropic displacement parameters obtained from Rietveld refinement of structural model of Zn_2(dobdc) framework dosed with 1.5 CO_2 per Zn, 10 K, Trigonal, R-3, a = 25.850(2) Å, c = 6.8072(8) Å, V = 3939.4(6) Å^3. Values in parentheses indicate one standard deviation in the refined value. Goodness-of-fit parameters: χ^2 = 1.255, wRp = 0.0369, Rp = 0.0309.

Atom	X	Y	Z	Occupancy	$U_{(ISO)}$ (Å^2)	Multiplicity
Zn	0.382(1)	0.351(1)	0.145(2)	1	0.007(6)	18
O1	0.3325(8)	0.2955(9)	0.372(3)	1	0.004(3)	18
O2	0.3040(8)	0.2280(9)	0.600(3)	1	0.004(3)	18
O3	0.356(1)	0.2742(9)	0.010(3)	1	0.004(3)	18
C1	0.316(1)	0.245(1)	0.429(2)	1	0.018(3)	18
C2	0.327(1)	0.2081(8)	0.288(2)	1	0.018(3)	18
C3	0.3456(8)	0.2212(9)	0.097(3)	1	0.018(3)	18
C4	0.3503(9)	0.182(1)	-0.030(3)	1	0.018(3)	18
H	0.363(2)	0.190(1)	-0.155(6)	1	0.01(1)	18
O2b	0.233(3)	0.747(3)	0.626(8)	0.69(2)	0.12(3)	18
C2a	0.183(2)	0.711(2)	0.618(5)	0.69(2)	0.05(3)	18
O2a	0.134(2)	0.680(1)	0.615(4)	0.69(2)	0.01(1)	18
O3b	0.203(2)	0.024(3)	0.690(9)	0.60(2)	0.08(2)	18
C3a	0.181(2)	0.025(2)	0.530(6)	0.60(2)	0.06(2)	18
O3a	0.160(2)	0.028(2)	0.389(9)	0.60(2)	0.07(2)	18

Table S22. Fractional atomic coordinates, occupancies, and isotropic displacement parameters obtained from Rietveld refinement of structural model of Fe_2(dobdc) framework dosed with 1.5 CO_2 per Fe, 298 K, 0.67 bar residual pressure, Trigonal, R-3, a = 26.082(1) Å, c = 6.8783(6) Å, V = 4052.1(5) Å^3. Values in parentheses indicate one standard deviation in the refined value. Goodness-of-fit parameters: χ^2 = 2.435, wRp = 0.0225, Rp = 0.0176.

Atom	X	Y	Z	Occupancy	$U_{(ISO)}$ (Å^2)	Multiplicity
Fe	0.3862(3)	0.3557(4)	0.134(1)	1	0.014(2)	18
O1	0.3256(5)	0.2966(5)	0.370(2)	1	0.020(2)	18
O2	0.3034(5)	0.2294(5)	0.590(2)	1	0.020(2)	18
O3	0.3573(6)	0.2668(5)	0.011(2)	1	0.020(2)	18
C1	0.3206(5)	0.2494(4)	0.420(2)	1	0.009(1)	18
C2	0.3157(5)	0.1994(4)	0.300(2)	1	0.009(1)	18
C3	0.3410(5)	0.2164(4)	0.117(2)	1	0.009(1)	18
C4	0.3451(5)	0.1818(4)	-0.025(2)	1	0.009(1)	18
H	.3613(8)	0.1928(8)	-0.161(3)	1	0.006(8)	18
O2b	0.210(1)	0.740(1)	0.571(5)	0.645(8)	0.14(2)	18
C2a	0.1620(9)	0.6993(8)	0.598(3)	0.645(8)	0.050(9)	18
O2a	0.1164(9)	0.660(1)	0.623(3)	0.645(8)	0.04(1)	18
O3b	0.191(4)	0.043(5)	0.66(2)	0.124(6)	0.05(5)	18
C3a	0.174(3)	0.038(4)	0.51(1)	0.124(6)	0.01(4)	18
O3a	0.159(4)	0.036(4)	0.36(2)	0.124(6)	0.01(5)	18

Table S23. Fractional atomic coordinates, occupancies, and isotropic displacement parameters obtained from Rietveld refinement of structural model of Zn_2(dobdc) framework dosed with 1.5 CO_2 per Zn, 298 K, 0.6 bar residual pressure, Trigonal, R-3, a = 25.887(2) Å, c = 6.8210(6) Å, V = 3958.6(5) Å^3. Values in parentheses indicate one standard deviation in the refined value. Goodness-of-fit parameters: χ^2 = 1.169, wRp = 0.0296, Rp = 0.0246.

Atom	X	Y	Z	Occupancy	$U_{(ISO)}$ (Å^2)	Multiplicity
Zn	0.3836(9)	0.3524(9)	0.136(2)	1	0.023(5)	18
O1	0.3271(7)	0.2944(8)	0.362(3)	1	0.027(3)	18
O2	0.3033(8)	0.2283(8)	0.608(3)	1	0.027(3)	18
O3	0.3542(9)	0.2738(8)	0.003(3)	1	0.027(3)	18
C1	0.3160(8)	0.2447(8)	0.430(2)	1	0.026(2)	18
C2	0.3259(8)	0.2064(8)	0.283(2)	1	0.026(2)	18
C3	0.3412(8)	0.2202(8)	0.0939(2)	1	0.026(2)	18
C4	0.3493(8)	0.1807(9)	-0.028(2)	1	0.026(2)	18
H	0.364(1)	0.194(1)	-0.153(4)	1	0.022(9)	18
O2b	0.223(4)	0.749(4)	0.54(1)	0.46(2)	0.14(3)	18
C2a	0.177(3)	0.708(2)	0.584(8)	0.46(2)	0.09(2)	18
O2a	0.131(2)	0.669(2)	0.617(5)	0.46(2)	0.02(1)	18
O3b	0.175(7)	0.004(8)	0.75(3)	0.16(1)	0.09(5)	18
C3a	0.174(5)	0.018(5)	0.58(2)	0.16(1)	0.05(5)	18
O3a	0.172(6)	0.032(6)	0.42(3)	0.16(1)	0.07(5)	18

Single crystal analysis of CO_2 in Co_2(dobdc)

Table S24. Single crystal X-ray diffraction data and structure refinement for activated Co_2(dobdc) dosed with 5 torr CO_2 at 150 K.

Empirical formula	$Co_2C_{10.94}H_2O_{11.88}$
Formula weight	441.35 g/mol
Temperature	150(2) K
Wavelength	0.7749 Å
Crystal system	Trigonal
Space group	R–3 :H
Unit cell dimensions	a = 25.994(7) Å, α = 90° b = 25.994(7) Å, β = 90° c = 6.8127(18) Å, γ = 120°
Volume	3987(2) Å^3
Z	9
Density (calculated)	1.653 Mg/m^3
Absorption coefficient	2.428 mm^{-1}
F_{000}	1948
Crystal color	Violet
Crystal size	0.200 x 0.050 x 0.050 mm^3
θ range	3.406 to 32.075°
Index ranges	$-35 \leq h \leq 16$, $0 \leq k \leq 35$, $0 \leq l \leq 8$
Reflections collected	2236
Independent reflections	2236 [R_{int} = 0.0925]
Completeness to θ = 27.706°	96.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.888 and 0.287
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2236 / 19 / 117
Goodness-of-fit on F^{2a}	1.130
Final R indices [I > 2σ(I)]^b	R_1 = 0.0977, wR_2 = 0.2437
R indices (all data)	R_1 = 0.1284, wR_2 = 0.2628
Largest diff. peak and hole	1.564 and –1.346 e.Å^{-3}

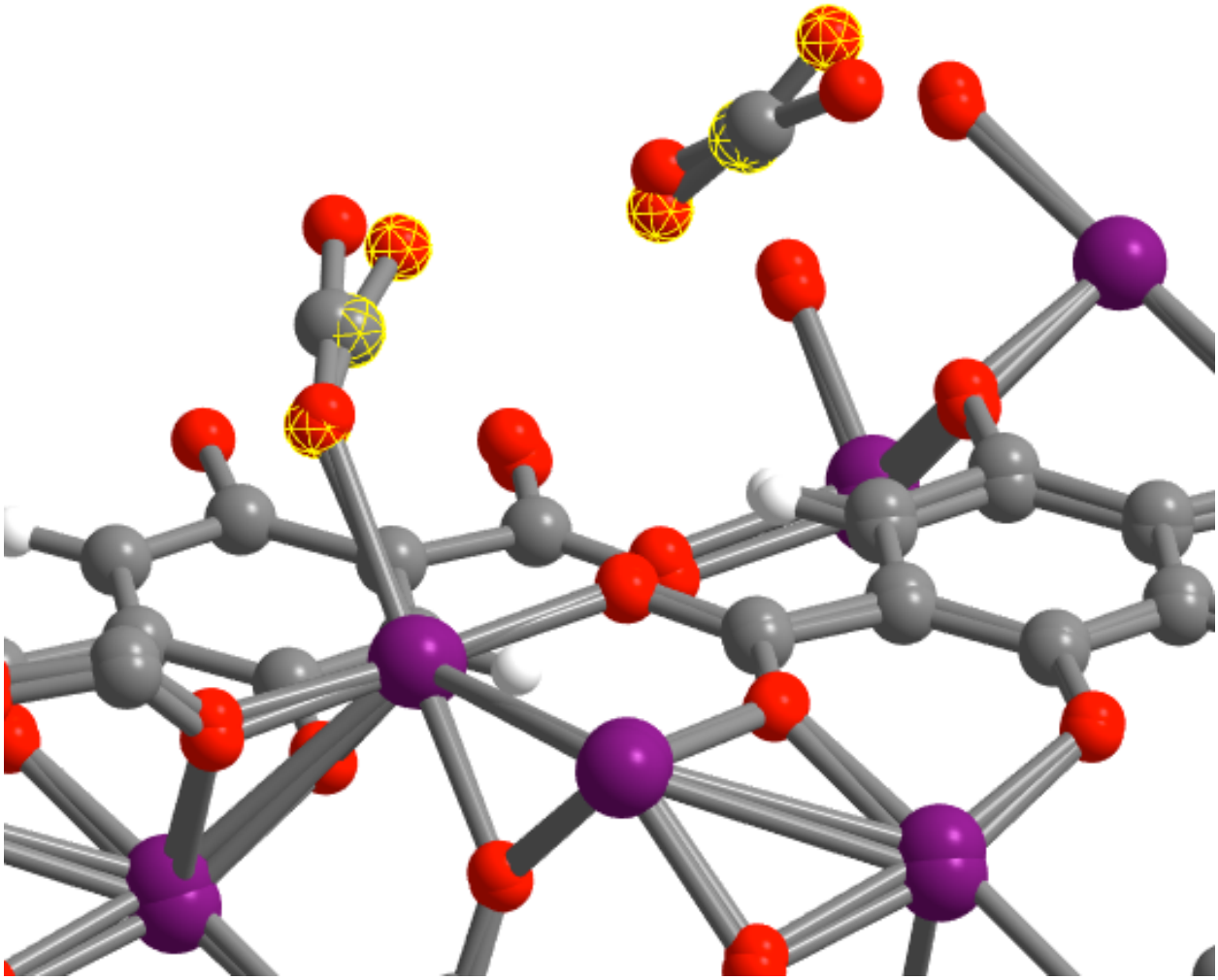
[a]GooF = $\{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$ where n is the number of reflections and p is the total number of parameters refinded. [b]$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$

Table S25. Fractional atomic coordinates, occupancies, and equivalent isotropic displacement parameters obtained from single crystal X-ray diffraction data and structure refinement of activated Co_2(dobdc) dosed with 5 torr CO_2 at 150 K.

Atom	X	Y	Z	Occupancy	$U_{(eq)}$ (Å^2)[a]	Multiplicity
Co	0.9495(1)	0.6347(1)	0.187(2)	1	0.021(1)	18
O1	0.9407(2)	0.6902(3)	0.8309(8)	1	0.022(1)	18
O2	0.9628(3)	0.6594(3)	0.4697(9)	1	0.023(1)	18
O3	0.8953(3)	0.6335(3)	0.2350(9)	1	0.025(1)	18
C1	0.8889(4)	0.6777(4)	0.743(1)	1	0.022(2)	18
C2	0.8742(4)	0.6610(4)	0.547(1)	1	0.025(2)	18
C3	0.8191(4)	0.6502(4)	0.475(1)	1	0.024(2)	18
C4	0.9131(4)	0.6510(4)	0.408(1)	1	0.022(2)	18
O4	0.8710(5)	0.5537(4)	–0.114(2)	0.85(3)	0.055(4)	18
C5	0.820(1)	0.5347(19)	–0.106(8)	0.85(3)	0.181(15)	18
O5	0.770(2)	0.521(3)	–0.08(1)	0.85(3)	0.45(3)	18
O6	0.882(2)	0.518(2)	0.502(6)	0.62(3)	0.22(2)	18
C6	0.851(2)	0.496(2)	0.368(7)	0.62(3)	0.22(2)	18
O7	0.814(2)	0.481(2)	0.245(5)	0.62(3)	0.22(2)	18

[a] $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Figure S20. Structural overlay of the models obtained from powder neutron diffraction (10 K) and single crystal X-ray diffraction (150 K) obtained from samples of Co_2(dobdc). The highlighted CO_2 molecules are from the single crystal model. We have shown that the CO_2 angles with respect to the framework surface are loading dependent. Despite differences in loading level and difference in data collection temperatures, the models show good agreement.



Additional images

Figure S21. Fourier difference map showing the Zn bound CO_2 molecule at (a) 10 K and (b) 298 K and (c) secondary adsorption site at 10 K.

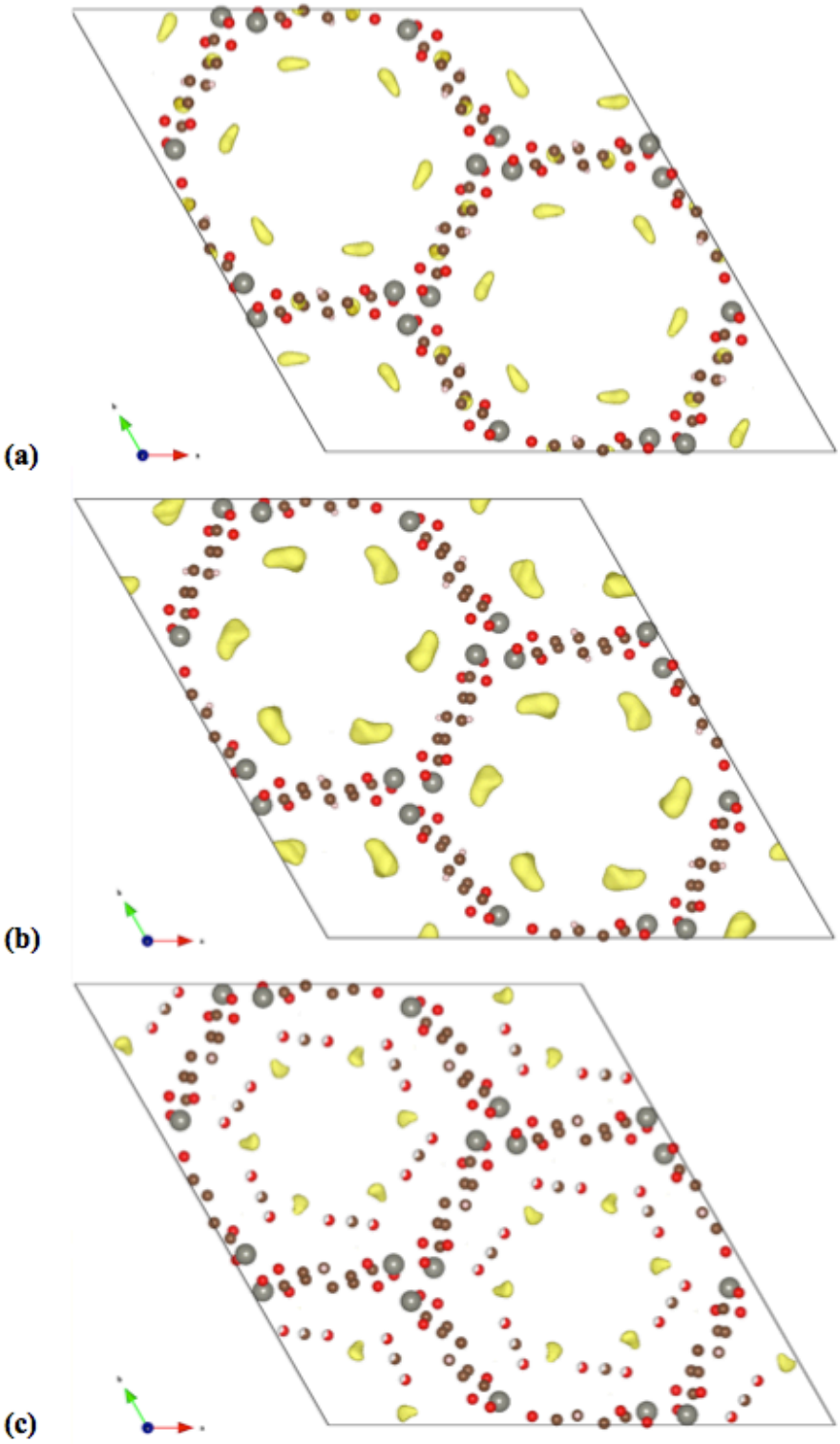


Figure S22. The black data points represent the total number of CO_2 adsorbed in sites I and II for the 1.5 CO_2 per iron (II) loading at temperatures ranging from 10 K to 300 K (black dashed line represents ideal adsorption). The data were acquired using a high-intensity powder neutron diffractometer, Wombat. The error bars represent a single standard deviation. The red data points show the residual pressure of CO_2 as a function of temperature revealing significant desorption that begins at a temperature of approximately 178 K.

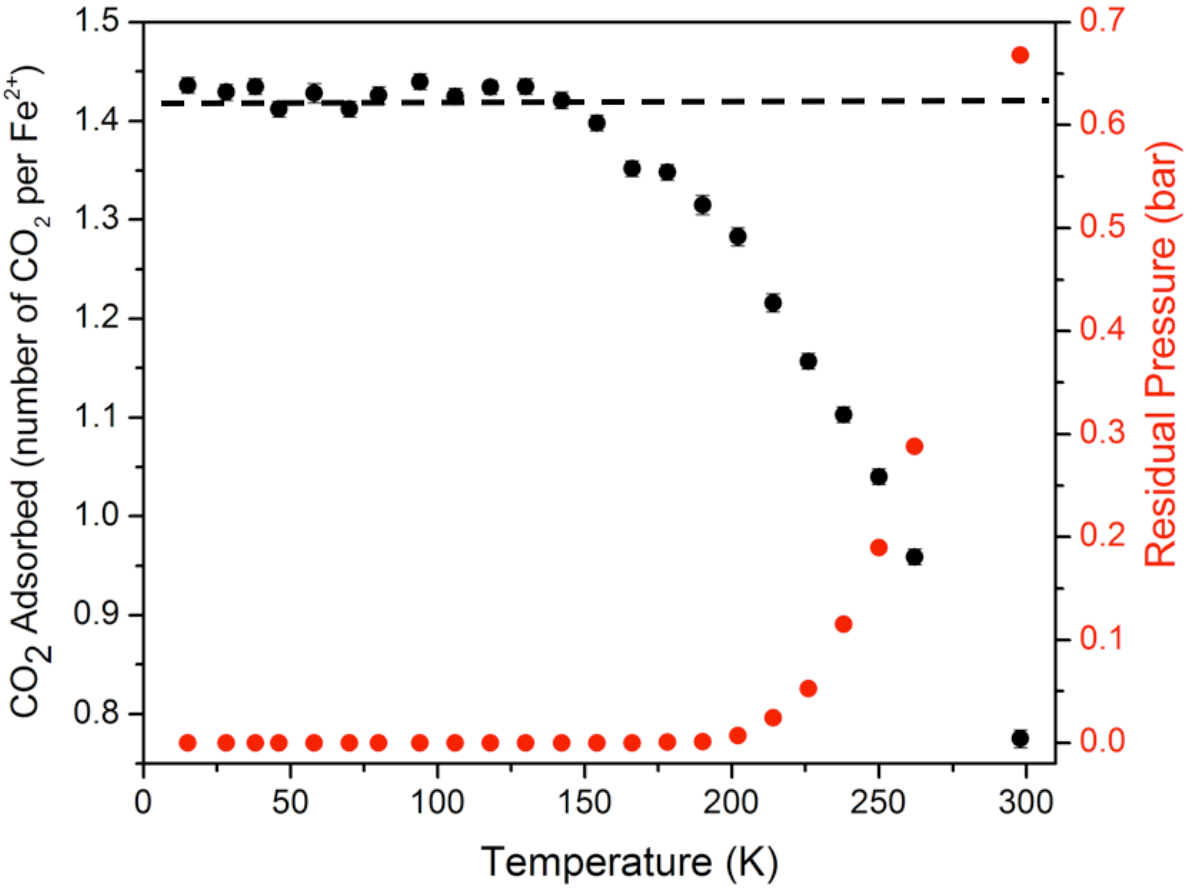


Figure S23. Unit cell parameters of Fe_2(dobdc) loaded with 0.5 CO_2 per iron (II) (left) and then 1.5 CO_2 per iron(II) (right) plotted as a function of temperature.

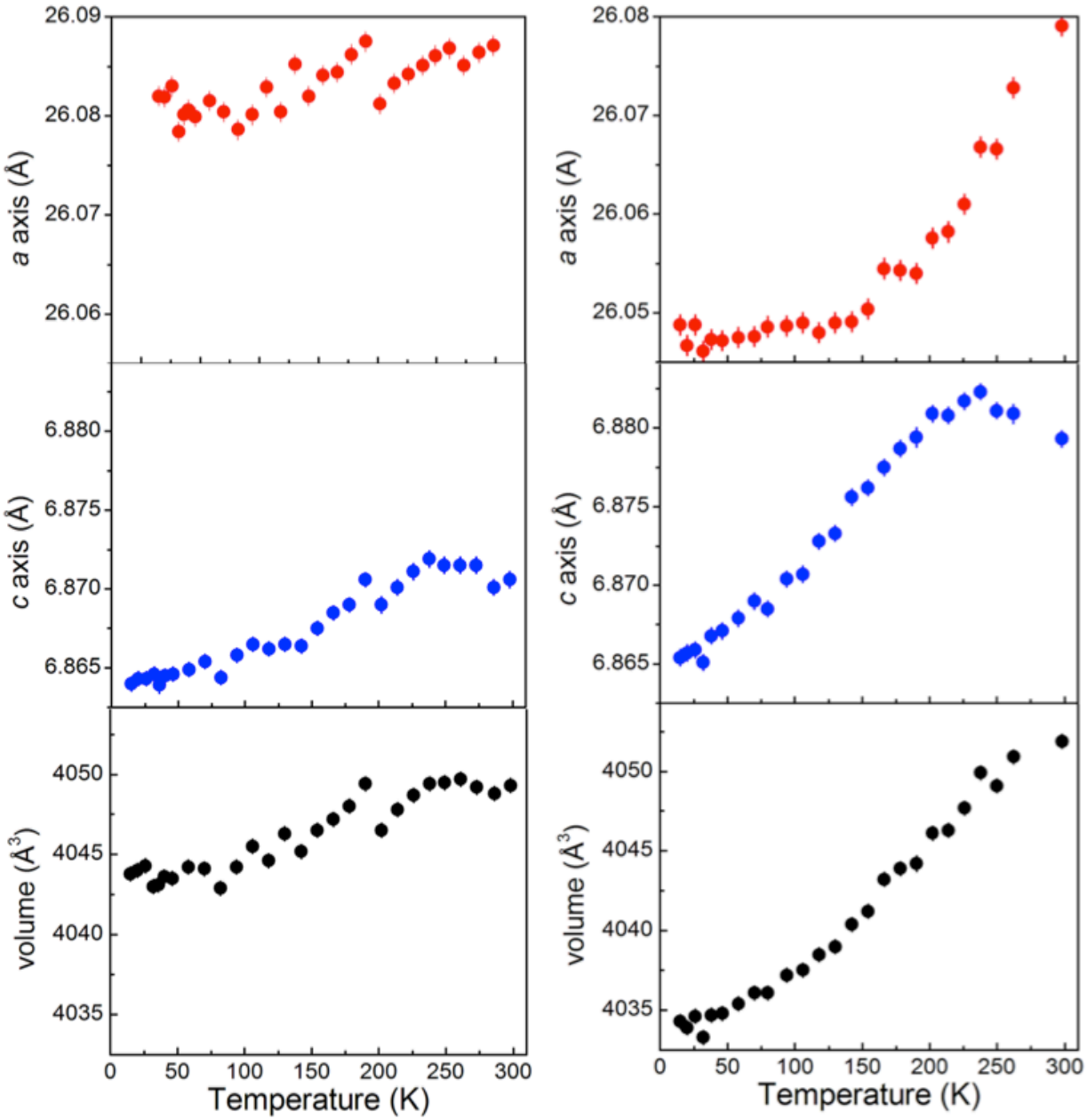


Figure S24. (a) Inelastic neutron scattering data of bare Fe_2(dobdc) and then loaded with 0.75 CO_2 per iron. (b) Inelastic scattering data after the data obtained from the bare framework was subtracted from the CO_2 loaded sample.

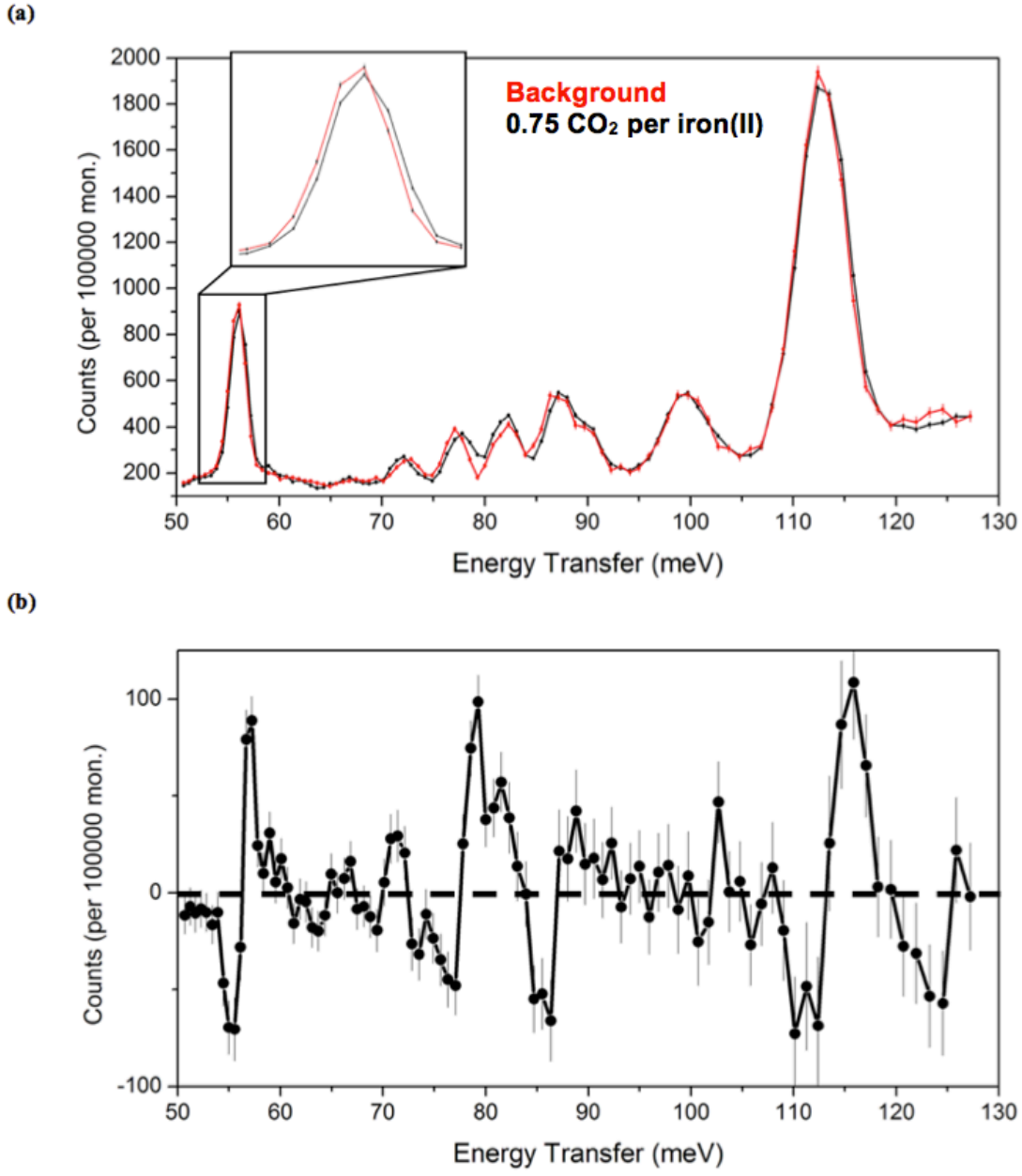


Figure S25. (a) Space filling model of Fe_2(dobdc) loaded with 1.3 CO_2 per Fe^{2+} viewed along the channel axis, *c*, and (b) then along the *b*-axis, with the framework removed for clarity.

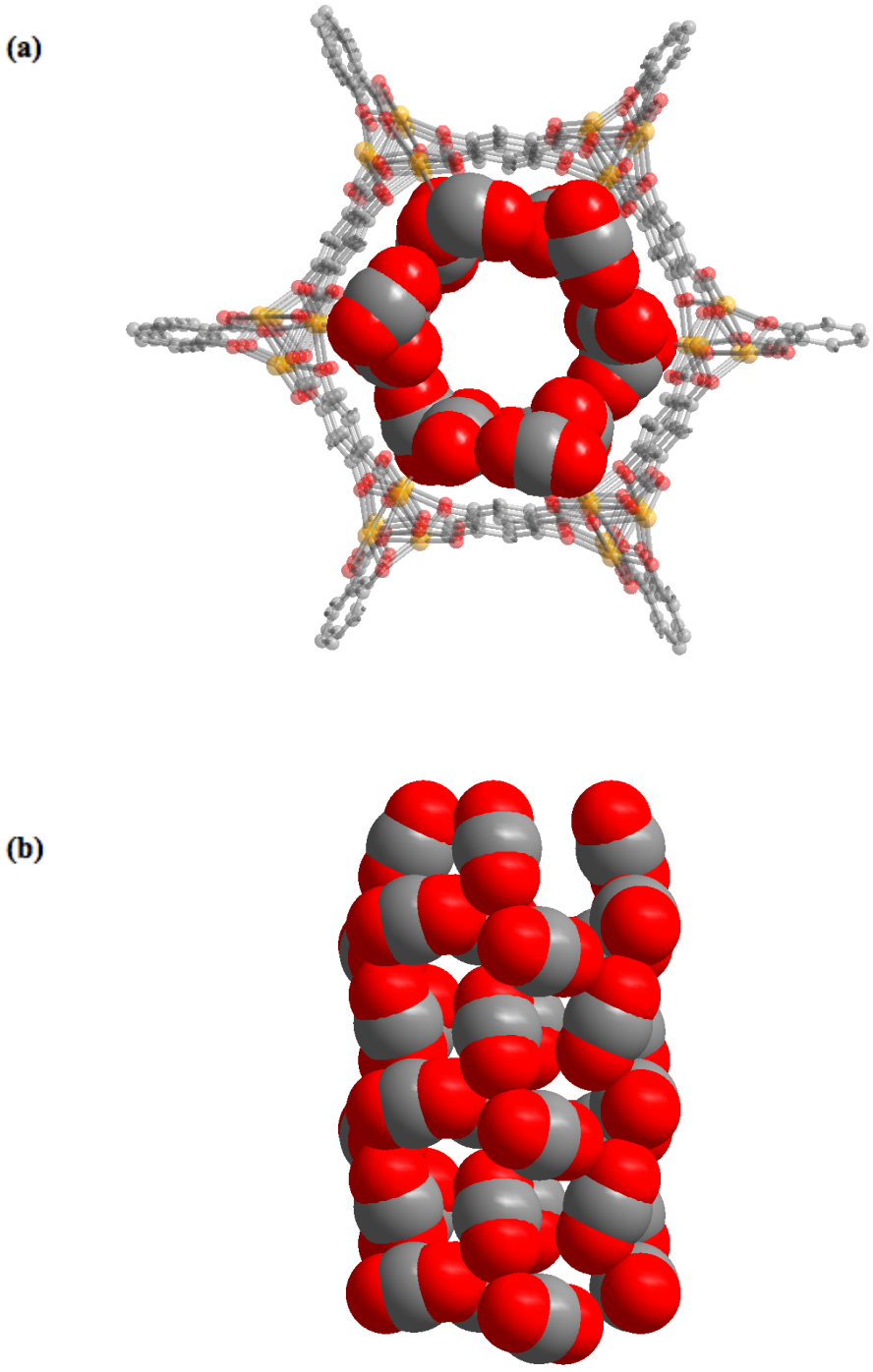
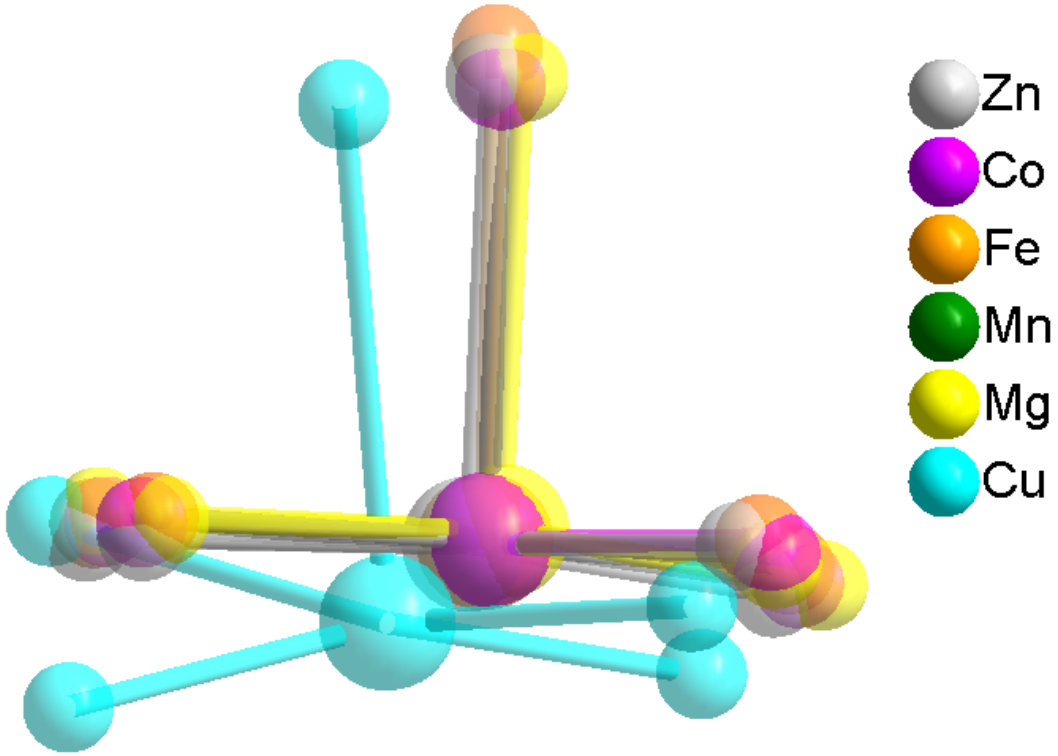


Figure S26. Ball and stick model showing an overlay of the MO_5 polyhedra for the M_2(dobdc) analogs for M = Mg, Mn, Fe, Co, Cu, and Zn. The top, (a), and bottom images, (b) reveal a significant distortion in CuO_5 and MnO_5 polyhedra relative to the other analogs. The two are presented separately for clarity.

(a)



(b)

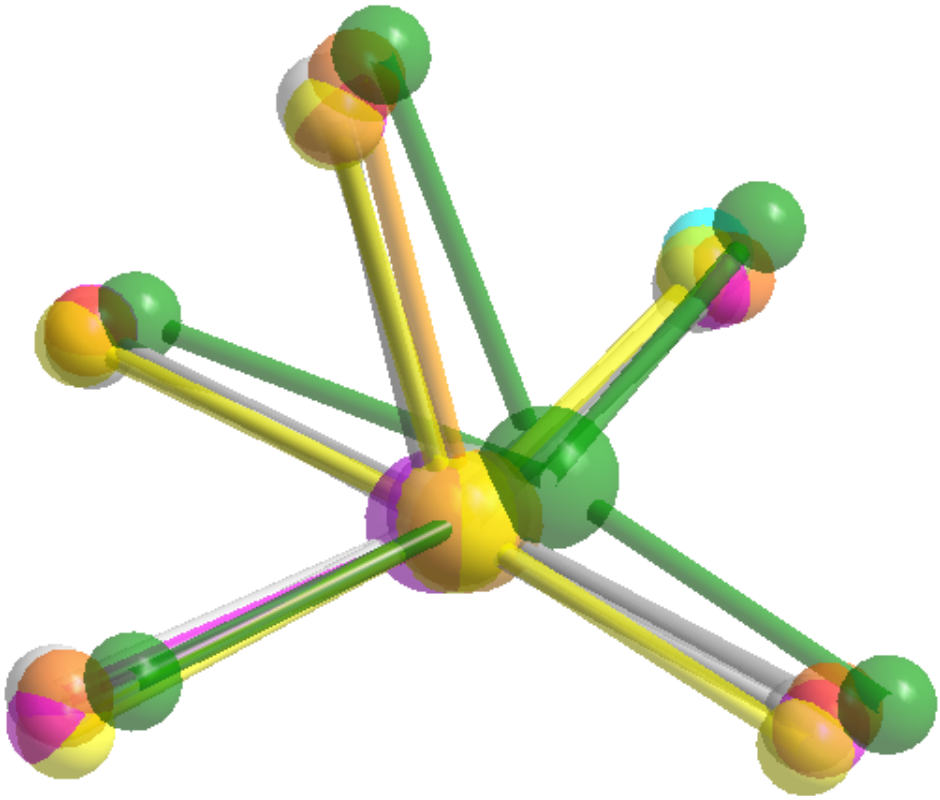


Figure S27. Ball and stick model showing the first structure solution of CO_2 adsorption in the Cu_2(dobdc) framework with two CO_2 adsorption sites. This model was the result of a false minimum, a problem that was resolved once the third CO_2 adsorption site was identified.

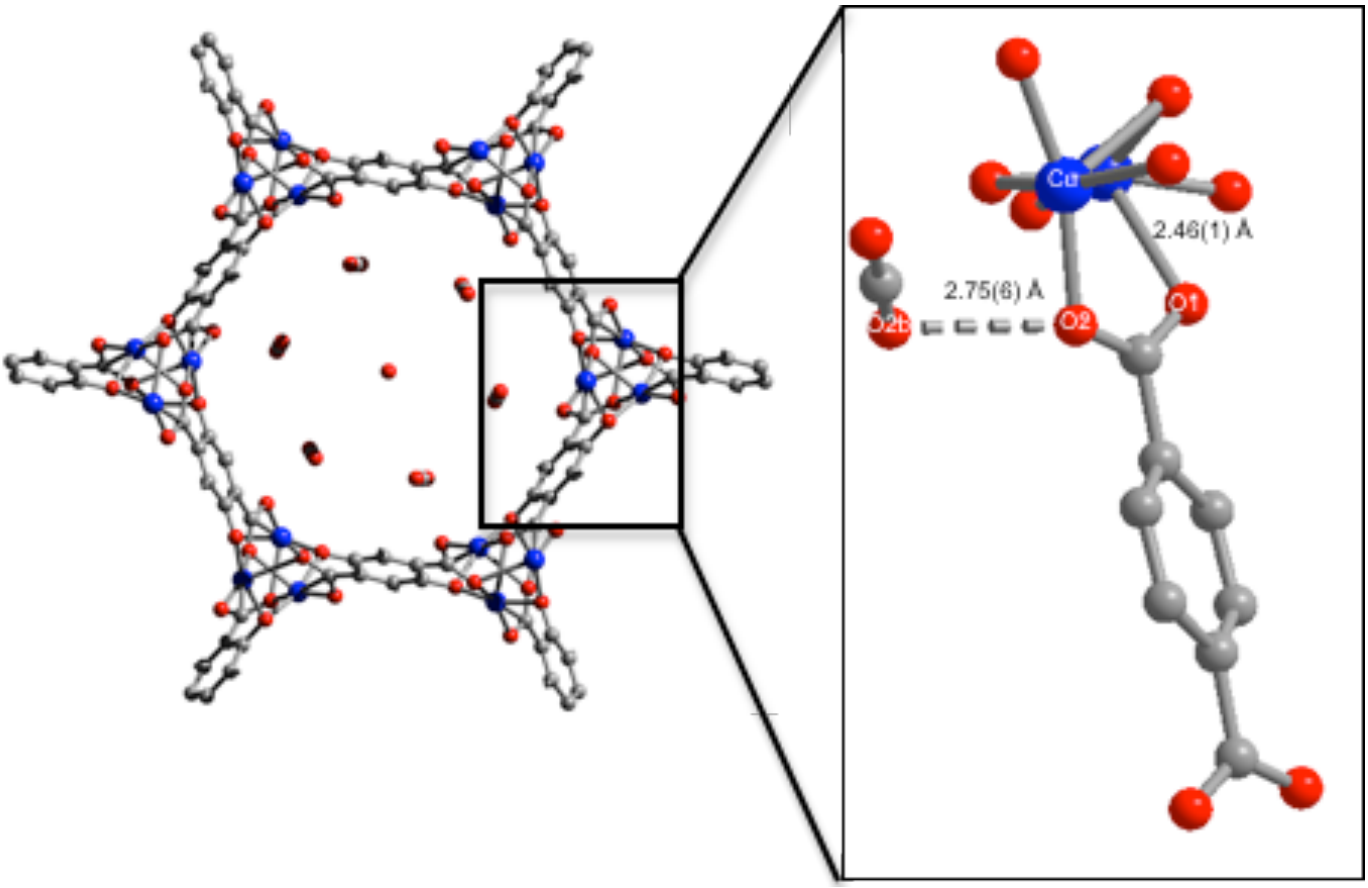


Figure S28. Ball and stick model showing the Cu polyhedron with respect to the site I CO_2. Comparison of experimental structural results (black) with theoretical DFT simulations (red) reveals excellent agreement.

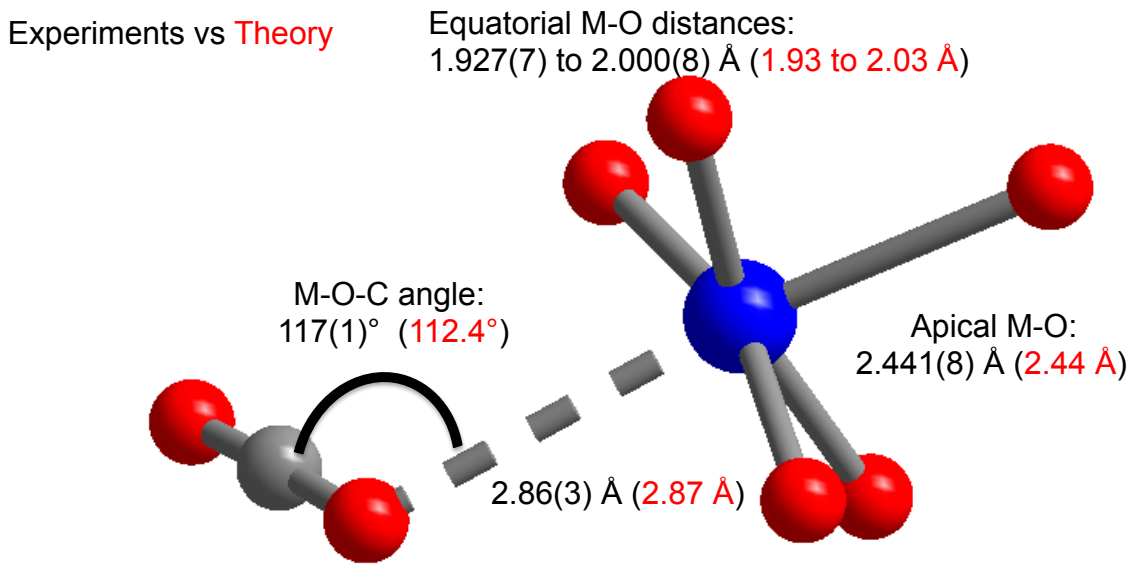
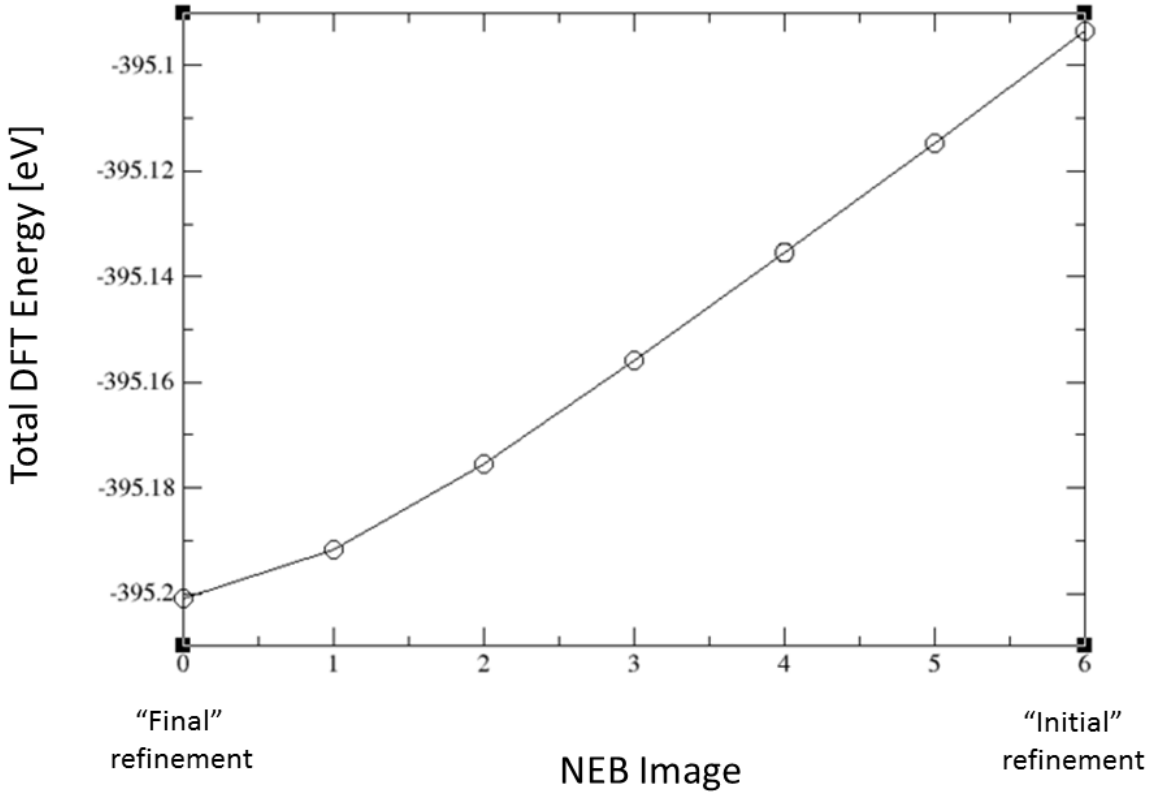


Figure S29. Nudged elastic band calculations, performed within DFT using vdW-DF2+*U* in line with all other calculations in this manuscript, show no barrier between the initial refinement structure and final refinement structure, supporting that the final refinement is likely the only "primary" binding site for CO_2 in Cu_2(dobdc). Initial refinement structure is relaxed using DFT using a quasi-Newton relaxation scheme for 20 ionic steps to provide a starting image near the initial refinement; final refinement structure is taken as the vdW-DF2+*U*-predicted binding geometry, which agrees well with the final experimental refinement. Image structures for NEB are constructed using linear interpolation between the "initial" and "final" refinement structures as a starting point and allowed to relax.



Synchrotron X-ray diffraction data for CO_2 dosed Cu_2(dobdc)

Figure S30. Synchrotron X-ray powder diffraction data for CO_2 adsorbed in Cu_2(dobdc). The green line, crosses, and red line represent the background, experimental, and calculated diffraction patterns, respectively. The blue line represents the difference between experimental and calculated patterns.

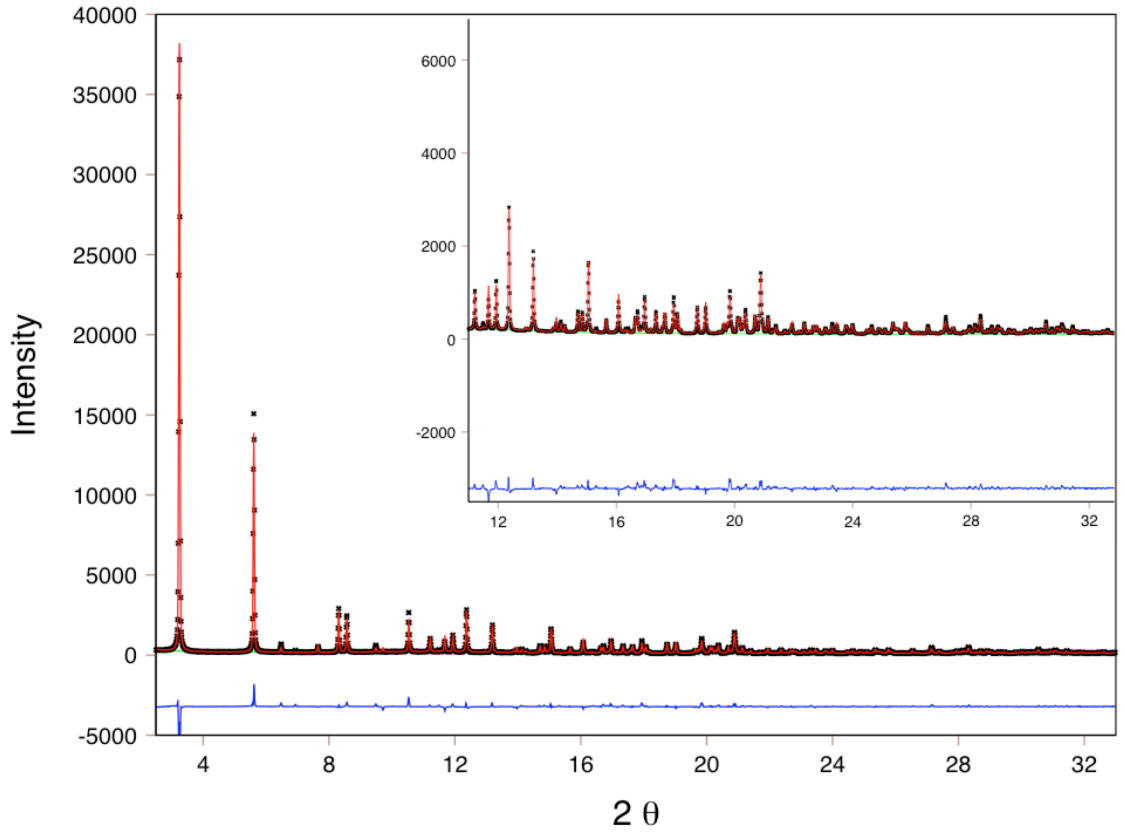


Table S26. Fractional atomic coordinates, occupancies, and isotropic displacement parameters obtained from Rietveld refinement of structural model of Cu_2(dobdc) framework dosed with refined dose of 1.5 CO_2 per Cu, 150 K, Trigonal, R-3, a = 25.8978(3) Å, c = 6.2785(1)Å, V = 3646.76(8) Å^3. Values in parentheses indicate one standard deviation in the refined value. Goodness-of-fit parameters: χ^2 =1.176, wRp = 0.0597, Rp = 0.0442

Atom	X	Y	Z	Occupancy	$U_{(ISO)}$ (Å^2)	Multiplicity
Cu	0.3874(1)	0.3492(1)	0.1751(4)	1.0	0.0126(6)	18
O1	0.3544(4)	0.3004(4)	0.426(2)	1.0	0.014(2)	18
O2	0.2899(4)	0.2255(4)	0.633(2)	1.0	0.014(2)	18
O3	0.3624(4)	0.2781(4)	0.012(2)	1.0	0.014(2)	18
C1	0.3284(8)	0.2478(6)	0.485(2)	1.0	0.011(4)	18
C2	0.3289(8)	0.2082(8)	0.304(3)	1.0	0.011(4)	18
C3	0.3479(8)	0.2225(5)	0.091(3)	1.0	0.011(4)	18
C4	0.3546(6)	0.1838(8)	-0.024(2)	1.0	0.011(4)	18
C1a	0.271(1)	0.749(2)	0.527(6)	0.53(1)	0.18(2)	18
O1a	0.221(1)	0.727(2)	0.564(9)	0.53(1)	0.16(3)	18
O1b	0.1711(9)	0.702(1)	0.615(5)	0.53(1)	0.10(2)	18
C2a	0.148(1)	0.002(1)	0.349(4)	0.51(1)	0.12(1)	18
O2a	0.154(2)	0.001(2)	0.530(4)	0.51(1)	0.12(1)	18
O2b	0.160(1)	0.004(2)	0.711(4)	0.51(1)	0.11(2)	18
C3b	0.0	0.0	0.3163(9)	0.58(2)	0.16(2)	3
O3b	0.0	0.0	0.5	0.58(2)	0.35(9)	6

Coordinate files for DFT structures of CO_2 in M_2(dobdc)

Coordinates are provided in the format of VASP POSCAR files with nuclear coordinates provided as fractional (Direct) coordinates in terms of the crystallographic basis vectors. Selective Dynamics are enabled to allow only the CO2 molecule to relax (with vdW-DF2+*U*) within the rigid (PBE+*U*) M_2(dobdc).

```
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    -7.0913762758806689   13.4745115715249604    0.0182226035629158
    -7.0916724110859466  -11.7516324991570080    6.5928931085496609
   C    H    O    Mg
    25     6    20     6
Selective dynamics
Direct
  0.7482245082990033  0.3534019561877599  0.1812378289473671   F   F   F
  0.6178686864118532  0.1681233715252830  0.0821353813181318   F   F   F
  0.4357333985898890  0.9695266986682114  0.8683503946494255   F   F   F
  0.3242964642812183  0.8076126796414442  0.7941651238854277   F   F   F
  0.1812417570426135  0.7482124708854769  0.3533874975116333   F   F   F
  0.0821432447687300  0.6178660181570308  0.1681074617961187   F   F   F
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  0.7941780484555920  0.3243099013687001  0.8075985077022096   F   F   F
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  0.1681051383648509  0.0821450806675372  0.6178521899197094   F   F   F
  0.9695102304529257  0.8683608555517210  0.4357129975650480   F   F   F
  0.8075933403174815  0.7941779831051718  0.3242669341483122   F   F   F
  0.2518079787588334  0.6466360641850599  0.8187536189884810   F   F   F
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  0.5643066165282917  0.0305157504412321  0.1316440805260584   F   F   F
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  0.1924063837065262  0.2058395520413114  0.6757204995273725   F   F   F
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  0.9043833218257902  0.5264829859982925  0.3701530491344798   F   F   F
  0.3662307749504663  0.9306573408865049  0.7366377267545516   F   F   F
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  0.7366440236451126  0.3662253009791741  0.9306487282664975   F   F   F
  0.3333867003273170  0.0692587353055814  0.6981855480007439   F   F   F
  0.5264653972743858  0.3701612556937306  0.9043783722804832   F   F   F
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0.9307653118267609	0.3018601266864636	0.6666226325414897	F	F	F
0.6298659855286601	0.0956917531533250	0.4735391504587838	F	F	F
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0.0693631109866644	0.2633795254480518	0.6337875662267436	F	F	F
0.2797886042429261	0.8601593501446280	0.1047223474090337	T	T	T
0.2771921593065050	0.9786977964833398	0.2702874042150862	T	T	T
0.5197348673738986	0.1144740833773241	0.7873118502351915	F	F	F
0.7873126286326126	0.5197330899686392	0.1144702234295565	F	F	F
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   1.00000000000000
    15.5129570444968383    0.0199324128806612    0.0317033892838443
    -7.2060776324217928   13.6874753160057345    0.0549078577108840
    -7.2254709284679297  -11.9118042507125974    6.7625285861417348
   C    H    O    Mn
    25     6    20     6
Selective dynamics
Direct
  0.0306008559147841  0.1297024176357624  0.5651282874262407   F   F   F
  0.0769903566474781  0.6125416226700082  0.1623329971843503   F   F   F
  0.1296233121273929  0.5645235596485776  0.0307817472222851   F   F   F
  0.1624415613546546  0.0769694871596798  0.6121108053498432   F   F   F
  0.1725356950349592  0.7387697072001131  0.3426765273500152   F   F   F
  0.1868126950803415  0.1990470305111387  0.6711105959414070   F   F   F
  0.1989897728008572  0.6709508580959849  0.1868847047478965   F   F   F
  0.2611848572977635  0.6571104216220007  0.8278062181302559   F   F   F
  0.3289965668931387  0.8132083359259710  0.8010643276113001   F   F   F
  0.3428652600948112  0.1724988400199408  0.7380093146367699   F   F   F
  0.3874293546228387  0.8375528167763093  0.9231736200095639   F   F   F
  0.4354514306002031  0.9694324076567327  0.8702707416854381   F   F   F
  0.5645485393997305  0.0305676113433222  0.1297292583145477   F   F   F
  0.6125706453770547  0.1624471982236813  0.0768264029904628   F   F   F
  0.6571347699052410  0.8275011449799052  0.2619907153632823   F   F   F
  0.6710034331067476  0.1867916640740432  0.1989356873887616   F   F   F
  0.7388151727022674  0.3428895783781059  0.1721938118696897   F   F   F
  0.8010102271990860  0.3290491719040389  0.8131153102520798   F   F   F
  0.8131872909197142  0.8009529694889324  0.3288894040586143   F   F   F
  0.8274642899649862  0.2612302927998158  0.6573234426500250   F   F   F
  0.8375584236453193  0.9230304978402728  0.3878891656500798   F   F   F
  0.8703766878726071  0.4354764403512661  0.9692182427777070   F   F   F
  0.9230096203524667  0.3874583773300415  0.8376669878156733   F   F   F
  0.9693991680850544  0.8702975823641808  0.4348717125738020   F   F   F
  0.2867182211167814  0.9354465838047624  0.2125142070049808   T   T   T
  0.1940454050261522  0.6651274496466328  0.6443221110308102   F   F   F
  0.3348912587779722  0.3558814371571231  0.8061346793294391   F   F   F
  0.3557770387169938  0.8058644704015023  0.3350362596523766   F   F   F
  0.6442229612829138  0.1941355145985426  0.6649637703476472   F   F   F
  0.6651087412220207  0.6441185628429764  0.1938653056705988   F   F   F
  0.8059545949738691  0.3348725203533789  0.3556778889692609   F   F   F
  0.0654193243573928  0.6917182316764610  0.3263381856069429   F   F   F
  0.0706773255873543  0.2605559818555179  0.6358047063260415   F   F   F
  0.1103187855966183  0.4912819694054136  0.6439953899449193   F   F   F
  0.2604757202878503  0.6347512241579594  0.0711149603623156   F   F   F
  0.3082612291379974  0.6732228614026212  0.9350065998597827   F   F   F
  0.3267432165123125  0.0653793421435935  0.6908672570424201   F   F   F
  0.3652231352544320  0.9293321004963317  0.7393490240948353   F   F   F
  0.3563869472215231  0.8895852114165166  0.5086274953045802   F   F   F
  0.4913401911702024  0.6436544465356349  0.1113032507203258   F   F   F
  0.5086598088296341  0.3563455234644337  0.8886967262797043   F   F   F
  0.6436130527784982  0.1104147955834733  0.4913724746954813   F   F   F
  0.6347768647455894  0.0706678845037061  0.2606509759052145   F   F   F
  0.6732568134877539  0.9346206798563159  0.3091327719575716   F   F   F
  0.6917388008618772  0.3267771085974118  0.0649934071401930   F   F   F
  0.7395242797122776  0.3652487758420548  0.9288850396377342   F   F   F
  0.8896812294034646  0.5087180605946457  0.3560046390550085   F   F   F
  0.9293226964127186  0.7394440181445319  0.3641953236739610   F   F   F
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0.9345806976428079	0.3082817983235628	0.6736618443929459	F	F	F
0.2922521256672325	0.9957364714278554	0.3003452131594808	T	T	T
0.2793387081643409	0.8743010856453193	0.1219770622603664	T	T	T
0.1053119502892983	0.7781768366533797	0.5154049616204972	F	F	F
0.2217813908492374	0.4840053959488202	0.8954769451737477	F	F	F
0.4839927394766903	0.8946664789977561	0.2220590064470755	F	F	F
0.5160072605233523	0.1053335140022611	0.7779409635529504	F	F	F
0.7782186241507389	0.5159946040512295	0.1045230478262980	F	F	F
0.8946880427107047	0.2218231633466061	0.4845950083794008	F	F	F

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FeMOF74-CO2
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    15.4545641719544555    0.0070457894495687   -0.0240572322099241
    -7.1903018448809917   13.6184022160005789    0.0023475278054387
    -7.2125667559608564  -11.8788526292561869    6.6845211247248297
   C    H    O    Fe
    25     6    20     6
Selective dynamics
Direct
  0.0319829952171773  0.1314413009281239  0.5662083736980463   F   F   F
  0.0810330893083417  0.6177681586549113  0.1660647822298813   F   F   F
  0.1313729932887568  0.5655286979596781  0.0322419307980653   F   F   F
  0.1662293188708617  0.0810420954600204  0.6172554641843675   F   F   F
  0.1794476037161274  0.7487115038387273  0.3495089527043120   F   F   F
  0.1921438721906057  0.2049156727429065  0.6771965956873629   F   F   F
  0.2048328249440345  0.6770390507102135  0.1922448081645030   F   F   F
  0.2512907366009358  0.6501990799956232  0.8209418832497448   F   F   F
  0.3229006585434959  0.8078568150945600  0.7952188557193978   F   F   F
  0.3497837425251689  0.1794559623153589  0.7477905179389595   F   F   F
  0.3822323894418105  0.8337809692271918  0.9191546289617136   F   F   F
  0.4344224187409722  0.9680240952654273  0.8685000440575124   F   F   F
  0.5655775512590466  0.0319759237345565  0.1314999559424663   F   F   F
  0.6177676105581540  0.1662190457727988  0.0808453940382492   F   F   F
  0.6502162874748336  0.8205440226846434  0.2522095120610786   F   F   F
  0.6770993414564614  0.1921431849054045  0.2047811592806141   F   F   F
  0.7487092933990667  0.3498009200044194  0.1790581467502790   F   F   F
  0.7951671750559370  0.3229609792897890  0.8077552068354947   F   F   F
  0.8078561138094500  0.7950843272571575  0.3228034043126087   F   F   F
  0.8205523812838535  0.2512884961612443  0.6504910172957210   F   F   F
  0.8337706661290980  0.9189578895399464  0.3827445068156266   F   F   F
  0.8686270067112005  0.4344713020403148  0.9677580592018984   F   F   F
  0.9189668876916599  0.3822318413451171  0.8339352027701210   F   F   F
  0.9680170287828602  0.8685586990718548  0.4337916263019608   F   F   F
  0.2908047246193611  0.9395630015804269  0.2158201710183315   T   T   T
  0.1834535634726180  0.6558912638242731  0.6342536669692151   F   F   F
  0.3440709735056018  0.3659906796779779  0.8166848394496355   F   F   F
  0.3658421239398990  0.8164387503069079  0.3442934229879739   F   F   F
  0.6341578760600584  0.1835612346930944  0.6557066070120356   F   F   F
  0.6559290264943627  0.6340093203220576  0.1833151455503739   F   F   F
  0.8165464365273536  0.3441087061757528  0.3657463330307849   F   F   F
  0.0691363158154772  0.7005406935938439  0.3294508408723473   F   F   F
  0.0732493421441092  0.2640932822156685  0.6381365187916757   F   F   F
  0.0964263242752921  0.4786175197364599  0.6329592202100969   F   F   F
  0.2640208495994543  0.6369561247723965  0.0738115184107784   F   F   F
  0.2995626735591799  0.6699755653385111  0.9313557165855428   F   F   F
  0.3299821249769579  0.0691018490264881  0.6994129247946219   F   F   F
  0.3630137044856738  0.9267370615894919  0.7357719853726792   F   F   F
  0.3674508054094048  0.9034441945545026  0.5212223148496236   F   F   F
  0.4786785599016099  0.6325061378083774  0.0975532677800928   F   F   F
  0.5213214400983688  0.3674938321916059  0.9024467092198734   F   F   F
  0.6325491945906734  0.0965558124455157  0.4787776551503882   F   F   F
  0.6369862955143333  0.0732629234104820  0.2642280146273137   F   F   F
  0.6700179050230304  0.9308981729734498  0.3005871042053840   F   F   F
  0.7004373564408013  0.3300244046614580  0.0686442904144471   F   F   F
  0.7359791504005671  0.3630438752276106  0.9261884815892429   F   F   F
  0.9035736907247269  0.5213825102635425  0.3670408087898807   F   F   F
  0.9267506798559495  0.7359067177843244  0.3618635112083197   F   F   F
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0.9308637061845602	0.2994593364061302	0.6705491891276409	F	F	F
0.3026164101381867	0.0035544311197617	0.3100686995920389	T	T	T
0.2765200929552958	0.8742449748185608	0.1185463829756990	T	T	T
0.1080689075125250	0.7837676131637252	0.5160718035140377	F	F	F
0.2162072558736199	0.4831830759801790	0.8928891785043618	F	F	F
0.4831982614024994	0.8919137128118848	0.2165299760004942	F	F	F
0.5168017385975006	0.1080862801880969	0.7834699939995033	F	F	F
0.7837927591263707	0.5168169240197926	0.1071108144956554	F	F	F
0.8919310854874567	0.2162323868362535	0.4839281664859598	F	F	F

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CoMOF74-CO2
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    15.2999234049848614   -0.0025964635924967   -0.0152724116282011
    -7.1265714412560213   13.5240970429364609   -0.0076107863835677
    -7.1290723882713749  -11.7911518743697279    6.6270129221598237
   C    H    O    Co
    25     6    20     6
Selective dynamics
Direct
  0.0307235812173445  0.1312458441701807  0.5620598820746352   F   F   F
  0.0841817790693042  0.6204342775496485  0.1698760448156378   F   F   F
  0.1311721904240812  0.5619138975952040  0.0307982752504543   F   F   F
  0.1699170226882671  0.0841158998703762  0.6205270926759354   F   F   F
  0.1857671906184493  0.7542745520685088  0.3571364768236762   F   F   F
  0.1950231400610178  0.2082580885759313  0.6766254383150709   F   F   F
  0.2082051092836750  0.6763332562595892  0.1950120788918142   F   F   F
  0.2455281974276744  0.6428975560187311  0.8144166959135788   F   F   F
  0.3237935595509569  0.8050165920011239  0.7918770082607622   F   F   F
  0.3571941110299974  0.1855937201221849  0.7543442944170948   F   F   F
  0.3794938455400612  0.8301496225816294  0.9159240211438799   F   F   F
  0.4382826237317232  0.9692055775168882  0.8688045163577414   F   F   F
  0.5617173462682814  0.0307944414831027  0.1311954836422586   F   F   F
  0.6205061544599388  0.1698503924183683  0.0840760018561184   F   F   F
  0.6428059189700051  0.8144062648778103  0.2456557355829077   F   F   F
  0.6762064404490360  0.1949834079988761  0.2081230067392354   F   F   F
  0.7544718325723281  0.3571024439812689  0.1855833340864237   F   F   F
  0.7917948907163250  0.3236667737404133  0.8049879361081906   F   F   F
  0.8049768459389881  0.7917419114240758  0.3233745616849220   F   F   F
  0.8142327943815459  0.2457254479314912  0.6428634931763213   F   F   F
  0.8300829623117281  0.9158840851296262  0.3794728783240657   F   F   F
  0.8688278095759188  0.4380861024047960  0.9692017147495449   F   F   F
  0.9158181979306974  0.3795657224503444  0.8301239401843716   F   F   F
  0.9692764427826575  0.8687541558298193  0.4379401179253577   F   F   F
  0.2812196075268043  0.9269058190439682  0.2048837803493750   T   T   T
  0.1851591590794470  0.6511083735234280  0.6284814218952164   F   F   F
  0.3489323117785332  0.3717368281163047  0.8155608132923859   F   F   F
  0.3716801542269721  0.8150572370820726  0.3489346412903060   F   F   F
  0.6283198457730279  0.1849427479179298  0.6510653887096964   F   F   F
  0.6510676882214668  0.6282631718836953  0.1844391717076093   F   F   F
  0.8148408409205530  0.3488915964765766  0.3715185781047836   F   F   F
  0.0772833544378813  0.7110349214399392  0.3402363262213797   F   F   F
  0.0713084109012243  0.2644051961879157  0.6311257215992470   F   F   F
  0.0914714003741111  0.4695233405337689  0.6236129423727874   F   F   F
  0.2643709552435638  0.6309798998328588  0.0715899320038744   F   F   F
  0.2883905986596247  0.6597005735624393  0.9228102054134908   F   F   F
  0.3404223493790326  0.0770924929049883  0.7111422475710469   F   F   F
  0.3693546415197559  0.9284002445913089  0.7355621701304287   F   F   F
  0.3767015655319810  0.9085438774675296  0.5305712298972978   F   F   F
  0.4694754238837220  0.6235532475533176  0.0914690978097425   F   F   F
  0.5305245761162780  0.3764467224466870  0.9085308791902520   F   F   F
  0.6232984344680190  0.0914561295324674  0.4694287401027069   F   F   F
  0.6306453584802370  0.0715997404086863  0.2644378298695713   F   F   F
  0.6595776806209699  0.9229075290950135  0.2888577814289519   F   F   F
  0.7116094313403778  0.3402993964375582  0.0771898015865062   F   F   F
  0.7356290447564362  0.3690201001671412  0.9284100679961256   F   F   F
  0.9085286146258866  0.5304766894662336  0.3763870866272043   F   F   F
  0.9286916110987775  0.7355948038120914  0.3688743084007484   F   F   F
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0.9227166675621135	0.2889651085600562	0.6597637037786228	F	F	F
0.2987196771073407	0.9973874809012497	0.3044153781234868	T	T	T
0.2607767970338190	0.8546568080282415	0.1019204056595665	T	T	T
0.1193058017889683	0.7911076347622554	0.5271431754193827	F	F	F
0.2087340834764362	0.4728736100863884	0.8810431605153184	F	F	F
0.4725798471553020	0.8809420118155700	0.2088285666762175	F	F	F
0.5274201528446980	0.1190579811844330	0.7911714033237800	F	F	F
0.7912659315235615	0.5271263899136116	0.1189568324846846	F	F	F
0.8806941912110275	0.2088923652377446	0.4728567945806148	F	F	F

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NiMOF74-CO2
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    15.1665707574288984   -0.0056678327150128   -0.0154456877922552
    -7.0674392096184029   13.4120106915082538   -0.0120535880838855
    -7.0649648953754909  -11.6929598734154112    6.5662448745405122
   C    H    O    Ni
    25     6    20     6
Selective dynamics
Direct
  0.0311529640848534  0.1327372115865018  0.5592486767310945   F   F   F
  0.0851849946379062  0.6236813093347635  0.1719589348439001   F   F   F
  0.1327024795773113  0.5589254726416826  0.0313713097080281   F   F   F
  0.1720654272343083  0.0852460438923330  0.6234008179399595   F   F   F
  0.1922170318993039  0.7651698581488162  0.3641974748487371   F   F   F
  0.1966744230243194  0.2095437347987428  0.6755729320798238   F   F   F
  0.2094470613717263  0.6755272320352290  0.1968069828779591   F   F   F
  0.2345676376142123  0.6355130849341961  0.8077835412822338   F   F   F
  0.3240837200333857  0.8032251669041983  0.7904289717343431   F   F   F
  0.3643734818897784  0.1923281867180293  0.7646049382074622   F   F   F
  0.3760284249939119  0.8278513381072585  0.9147498406739558   F   F   F
  0.4410177975149665  0.9688574841893782  0.8672611230711169   F   F   F
  0.5589835262841945  0.0311439830858617  0.1327400964222889   F   F   F
  0.6239705268604681  0.1721480197956424  0.0852498244490647   F   F   F
  0.6356264904946869  0.8076719292202341  0.2353947326224173   F   F   F
  0.6759158986586655  0.1967741930181006  0.2095706956504273   F   F   F
  0.7654333324925418  0.3644876263250865  0.1922176747660558   F   F   F
  0.7905539087350206  0.3244734792240465  0.8031942331703377   F   F   F
  0.8033251956677390  0.7904556251235562  0.3244267353049395   F   F   F
  0.8077829404851613  0.2348302577894472  0.6358021959811424   F   F   F
  0.8279341914577500  0.9147533160299659  0.3765988494448038   F   F   F
  0.8672984905294427  0.4410752386175858  0.9686299063402686   F   F   F
  0.9148146240541521  0.3763180505875354  0.8280407325408703   F   F   F
  0.9688466546072050  0.8672621483357972  0.4407509906536689   F   F   F
  0.2767025602661601  0.9216083842447368  0.1988911562392541   T   T   T
  0.1850500206660897  0.6474589815376532  0.6254129441446992   F   F   F
  0.3523560513138762  0.3745380416843389  0.8143303035338931   F   F   F
  0.3743466998090668  0.8142448865205125  0.3526264054442620   F   F   F
  0.6256542702976802  0.1857558247387630  0.6473748106040276   F   F   F
  0.6476435673781751  0.6254613182379600  0.1856693638508773   F   F   F
  0.8149499517183756  0.3525411344006173  0.3745867266851803   F   F   F
  0.0866692984104276  0.7303736335935582  0.3512202293873585   F   F   F
  0.0761796359770273  0.2700048820363534  0.6288119716154696   F   F   F
  0.0803810584160658  0.4610852703408526  0.6157757080486164   F   F   F
  0.2698818016026934  0.6281799071168521  0.0765369258877016   F   F   F
  0.2698928023035592  0.6484122957759908  0.9135798352097098   F   F   F
  0.3515324114222551  0.0867066663380527  0.7296785966310182   F   F   F
  0.3717874067502791  0.9239244101945090  0.7300645869663711   F   F   F
  0.3840961400444627  0.9190060028508711  0.5386676979118903   F   F   F
  0.4613083829502571  0.6157732132911846  0.0817037550663642   F   F   F
  0.5386912357417941  0.3842261466311143  0.9182959123184062   F   F   F
  0.6159034786475956  0.0809933570714279  0.4613319694728730   F   F   F
  0.6282125656341861  0.0760757057437544  0.2699350838635084   F   F   F
  0.6484685586844918  0.9132940449212299  0.2703226194172714   F   F   F
  0.7301071700809061  0.3515878201622797  0.0864198356201697   F   F   F
  0.7301181707817719  0.3718202088214113  0.9234627449421779   F   F   F
  0.9196185602759854  0.5389140895814464  0.3842239593361469   F   F   F
  0.9238199827150311  0.7299944778859526  0.3711876957693008   F   F   F
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0.9133303202816307	0.2696257263287407	0.6487794379974048	F	F	F
0.2977627224918176	0.9983284434669361	0.3012543655220274	T	T	T
0.2523835238425712	0.8428052525801015	0.0927611533721238	T	T	T
0.1256625102081657	0.8005563640885143	0.5328414664898844	F	F	F
0.1995185454526833	0.4667866508377756	0.8749607148974050	F	F	F
0.4668561668708335	0.8743289481447363	0.1996589056222007	F	F	F
0.5331434518212177	0.1256704117775627	0.8003407617625697	F	F	F
0.8004810732393750	0.5332127090845304	0.1250389524873654	F	F	F
0.8743374621762996	0.1994437518497492	0.4671582043399951	F	F	F

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CuMOF74-CO2
    1.000000000000000
    15.2489455497523032   -0.0475266532617733   -0.1841801506346098
    -7.1427936579844600   13.4679987913793848   -0.1819755501450751
    -7.1442677751025450  -11.8272175991350359    6.4468462915043547
   C    H    O    Cu
    25     6    20     6
Selective dynamics
Direct
  0.0363397651295756  0.1357807304996399  0.5649584299637596   F   F   F
  0.0915842000821101  0.6245426656135180  0.1776719716957516   F   F   F
  0.1357749449038224  0.5649129421464352  0.0363642529427253   F   F   F
  0.1776775069524561  0.0915850479358298  0.6244949243096301   F   F   F
  0.2050472149976343  0.7770202428997450  0.3764212513936229   F   F   F
  0.2082978788110594  0.2196895385592157  0.6816039384745309   F   F   F
  0.2196733744440564  0.6815989863515242  0.2083085591967659   F   F   F
  0.2229796323272879  0.6235497924860240  0.7949726935487220   F   F   F
  0.3183949370542720  0.7916970755408101  0.7803309171586363   F   F   F
  0.3764501841122296  0.2050606653733453  0.7769500582206561   F   F   F
  0.3754647005767708  0.8223220281733816  0.9084343376162920   F   F   F
  0.4350891502629324  0.9636663935061307  0.8642256210034560   F   F   F
  0.5649121735362428  0.0363350737691022  0.1357755984899356   F   F   F
  0.6245342512776020  0.1776773297295406  0.0915653275067143   F   F   F
  0.6235497882722214  0.7949394505649110  0.2230496126092163   F   F   F
  0.6816046816377721  0.2083022843815243  0.2196687502261199   F   F   F
  0.7770213377794448  0.3764509187732941  0.2050285224995747   F   F   F
  0.7803275956626550  0.3184017249077300  0.7916926568515734   F   F   F
  0.7917017398810060  0.7803098213630832  0.3183957289101969   F   F   F
  0.7949527573868309  0.2229798730385326  0.6235784194362353   F   F   F
  0.8223221117396378  0.9084143119865047  0.3755047430751119   F   F   F
  0.8642260252029459  0.4350877691128474  0.9636369631055572   F   F   F
  0.9084154186099340  0.3754566943087312  0.8223276956890189   F   F   F
  0.9636598535624827  0.8642186294226519  0.4350412374210038   F   F   F
  0.2508669139064027  0.9215385322472013  0.1955184898134235   T   T   T
  0.1747320071246676  0.6279375029125092  0.6078980218811765   F   F   F
  0.3720555896119961  0.3921398948332779  0.8252650502027379   F   F   F
  0.3921183310014626  0.8252643628569984  0.3720822693107664   F   F   F
  0.6078826391053269  0.1747363484022770  0.6279189467375019   F   F   F
  0.6279440290800551  0.6078594650890210  0.1747346171820396   F   F   F
  0.8252679652598047  0.3720626130257614  0.3921016489486959   F   F   F
  0.1226732090693048  0.7819267862613515  0.3750055034155224   F   F   F
  0.0829484745496529  0.2741411098580500  0.6403325365585175   F   F   F
  0.0888658688150699  0.4484444548347497  0.6084807857407029   F   F   F
  0.2741307534031563  0.6402506639258263  0.0829889756178304   F   F   F
  0.2180649304916713  0.6249232443420851  0.8773355345173499   F   F   F
  0.3750733569189393  0.1226747216912329  0.7818519650259574   F   F   F
  0.3597455317276754  0.9170551551912567  0.7258588175872021   F   F   F
  0.3915479670299078  0.9111345143622955  0.5515520609927478   F   F   F
  0.4484481151732709  0.6084352510562141  0.0889475580104033   F   F   F
  0.5515515035187875  0.3915641088660777  0.9110521093743600   F   F   F
  0.6084516516621434  0.0888648455600176  0.4484476063920226   F   F   F
  0.6402544406568254  0.0829449607469641  0.2741408532427130   F   F   F
  0.6249276131878148  0.8773259895680567  0.2181492510223393   F   F   F
  0.7819350418928153  0.3750768715962209  0.1226641363125580   F   F   F
  0.7258692189813232  0.3597494520124584  0.9170106952120562   F   F   F
  0.9111337498770240  0.5515549050875848  0.3915188816440249   F   F   F
  0.9170511441424125  0.7258582500642135  0.3596671308262529   F   F   F
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0.8773264096227464	0.2180725736609048	0.6249941639692409	F	F	F
0.2939474923103809	0.0036760334301538	0.3189373499393171	T	T	T
0.2048275427474507	0.8372978512257695	0.0695284776339858	T	T	T
0.1311401192118353	0.8208025050936243	0.5549787541826419	F	F	F
0.1791932572849930	0.4449604298710454	0.8689302597577182	F	F	F
0.4449657479187650	0.8688517549885688	0.1792063854443029	F	F	F
0.5550338707733005	0.1311476049337585	0.8207932819404817	F	F	F
0.8208063614070653	0.5550389300512606	0.1310694076270593	F	F	F
0.8688598531726655	0.1791976108446462	0.4450209166473087	F	F	F

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ZnMOF74-CO2
   1.00000000000000
    15.2439154824645406    0.0096688540602981    0.0385957437582283
    -7.0956567272266406   13.4918402437420184    0.0377689953887450
    -7.0950190972763432  -11.7567279111508967    6.6193482706989686
   C    H    O    Zn
    25     6    20     6
Selective dynamics
Direct
  0.7429966507110777  0.3527355326125701  0.1814537092950133   F   F   F
  0.6143076949952260  0.1676559665477058  0.0821830680629319   F   F   F
  0.4360812802994758  0.9726672922706143  0.8713626107554759   F   F   F
  0.3274353813610418  0.8105584335412388  0.7960720254665432   F   F   F
  0.1814398393681813  0.7429868934398840  0.3527026170229348   F   F   F
  0.0822060437256198  0.6143246040535502  0.1676420111897201   F   F   F
  0.8713664246340045  0.4360857529896478  0.9726477628719223   F   F   F
  0.7960851053077249  0.3274451869216932  0.8105386495272811   F   F   F
  0.3527131771599201  0.1814585395910413  0.7429772358697448   F   F   F
  0.1676496712942921  0.0822092505958736  0.6143036733840148   F   F   F
  0.9726481988238973  0.8713739904698841  0.4360644222521302   F   F   F
  0.8105542365610958  0.7961003481050426  0.3274305988282222   F   F   F
  0.2570353561903147  0.6473068396434911  0.8185517684852286   F   F   F
  0.3857183454994413  0.8323804097263192  0.9178113509721300   F   F   F
  0.5639463901302122  0.0273714078996932  0.1286346835360845   F   F   F
  0.6725933993346231  0.1894803195321799  0.2039254524652563   F   F   F
  0.8185794446766650  0.2570628437787406  0.6472949655914420   F   F   F
  0.9178127708025841  0.3857263244493723  0.8323557694827386   F   F   F
  0.1286513809080105  0.5639658750925491  0.0273525055884889   F   F   F
  0.2039210895986372  0.6725962013317854  0.1894494606858004   F   F   F
  0.6473033850647241  0.8185868813316333  0.2570333374332989   F   F   F
  0.8323637830854409  0.9178254946963307  0.3857021687176214   F   F   F
  0.0273663987250643  0.1286649130452560  0.5639432586845459   F   F   F
  0.1894651711464306  0.2039413794979339  0.6725808936144659   F   F   F
  0.0520446007725882  0.7608749733144781  0.7065071967601010   T   T   T
  0.1913016680352797  0.6606463707992916  0.6356097262428904   F   F   F
  0.6356185077589771  0.1913086837801572  0.6606297179384271   F   F   F
  0.6606315764770940  0.6356253462911141  0.1912846597929345   F   F   F
  0.8087261900166567  0.3393913209191410  0.3643861179391834   F   F   F
  0.3644005256268485  0.8087432442175313  0.3393701427839204   F   F   F
  0.3393817235467154  0.3644103209379352  0.8087207573751911   F   F   F
  0.6835517681103340  0.3307110014254917  0.0678262623019492   F   F   F
  0.9046249406505282  0.5234055249551801  0.3713583793226078   F   F   F
  0.3655898280863639  0.9342288006152657  0.7393865861915785   F   F   F
  0.0678421513085112  0.6835629808024848  0.3306951644312974   F   F   F
  0.3713781553311364  0.9046372789143220  0.5233930551433588   F   F   F
  0.7393966448214400  0.3655955268339852  0.9342129192867787   F   F   F
  0.3307007325971156  0.0678409918196294  0.6835450462613082   F   F   F
  0.5234036332396244  0.3713867293556277  0.9046234911400575   F   F   F
  0.9342164803618473  0.7394022387707366  0.3655789551170514   F   F   F
  0.3164741897258239  0.6693291887780575  0.9321694504412363   F   F   F
  0.0953983838334693  0.4766297043285235  0.6286361880835827   F   F   F
  0.6344342617643548  0.0658090658455279  0.2606088124933876   F   F   F
  0.9321758580590256  0.3164873805777759  0.6693052729354960   F   F   F
  0.6286369597071797  0.0954084644052102  0.4766018068896258   F   F   F
  0.2606173087737531  0.6344505895493384  0.0657822039828204   F   F   F
  0.6693169684394178  0.9321949773922142  0.3164623179811272   F   F   F
  0.4766119594619624  0.6286520453646673  0.0953821885296833   F   F   F
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0.0657977475218274	0.2606337047427232	0.6344257580178692	F	F	F
0.1235336912278654	0.8735177814466958	0.7372562217839020	T	T	T
0.9815369721584614	0.6507597754224782	0.6782742337878298	T	T	T
0.5155174752552796	0.1091377339312558	0.7800341732974516	F	F	F
0.7800434927646123	0.5155266282709832	0.1091257554190648	F	F	F
0.1091327420163424	0.7800543308086816	0.5155103126675868	F	F	F
0.4845039322343894	0.8909076460700263	0.2199650095904175	F	F	F
0.2199758544933061	0.4845175898298137	0.8908785684000975	F	F	F
0.8908900213520283	0.2199874595275233	0.4844925251477576	F	F	F

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