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# Influence of Pore Size on Carbon Dioxide Diffusion in Two Isoreticular Metal–Organic Frameworks

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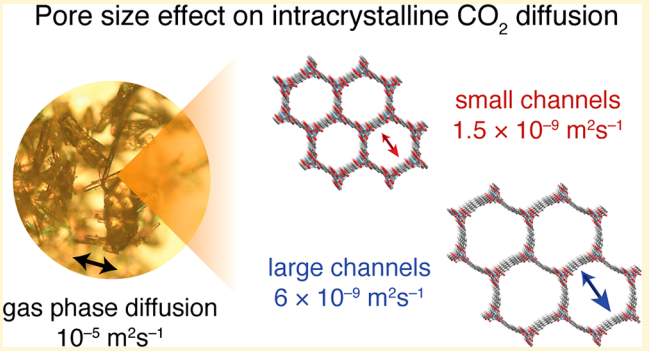
**ABSTRACT:** The rapid diffusion of molecules in porous materials is critical for numerous applications including separations, energy storage, sensing, and catalysis. A common strategy for tuning guest diffusion rates is to vary the material pore size, although detailed studies that isolate the effect of changing this particular variable are lacking. Here, we begin to address this challenge by measuring the diffusion of carbon dioxide in two isoreticular metal–organic frameworks featuring channels with different diameters, $Zn_2$(dobdc) (dobdc$^{4-}$ = 2,5-dioxidobenzene-1,4-dicarboxylate) and $Zn_2$(dobpdc) (dobpdc$^{4-}$ = 4,4′-dioxidobiphenyl-3,3′-dicarboxylate), using pulsed field gradient NMR spectroscopy. An increase in the pore diameter from 15 Å in $Zn_2$(dobdc) to 22 Å in $Zn_2$(dobpdc) is accompanied by an increase in the self-diffusion of $CO_2$ by a factor of 4 to 6, depending on the gas pressure. Analysis of the diffusion anisotropy in $Zn_2$(dobdc) reveals that the self-diffusion coefficient for motion of $CO_2$ along the framework channels is at least 10000 times greater than for motion between the framework channels. Our findings should aid the design of improved porous materials for a range of applications where diffusion plays a critical role in determining performance.




## INTRODUCTION

The diffusion of molecules in porous materials underpins numerous technologies, including electrochemical energy storage,[1] catalysis,[2,3] and molecular separations.[4] In the context of separations, diffusion can limit the rate at which adsorption–desorption cycles can be performed in adsorption-based processes, and it directly influences the selectivity for different products in membrane separations. Regardless of the application, pore size plays a critical role in determining diffusion in porous materials. Early studies of a series of carbon-based molecular sieves showed that the self-diffusion of water and ethanol increases as a function of pore size,[5] and more recent work on electrolyte ion diffusion in porous carbon electrodes has shown similar effects.[1,6] These carbon materials have highly disordered structures, however, and it is very challenging to probe the effect of pore size while keeping all other structural features constant.

This difficulty has motivated the use of crystalline metal–organic frameworks (MOFs) as model systems for diffusion studies, as these microporous materials have well-defined and tunable pore geometries.[7−10] Some frameworks can be prepared with different pore sizes by expansion of the parent organic linkers to form families of materials with the same framework topology (known as isoreticular MOFs),[11,12] making them excellent model systems for diffusion studies. For example, $Zn_2$(dobdc) (dobdc$^{4-}$ = 2,5-dioxidobenzene-1,4-dicarboxylate) and $Zn_2$(dobpdc) (dobpdc$^{4-}$ = 4,4′-dioxidobiphenyl-3,3′-dicarboxylate) have very similar crystal structures, but their different linker lengths give rise to pore diameters of approximately 15 and 22 Å, respectively (Figure 1). Importantly, these materials, along with their diamine-functionalized variants, have been shown to be promising candidates for $CO_2$ capture.[13−19] Many $^{13}$C NMR studies have established the utility of $^{13}CO_2$ as a probe of molecular motion in MOFs,[20−27] and we have previously studied diffusion of adsorbed $^{13}CO_2$ in $Zn_2$(dobpdc) using pulsed field gradient (PFG) NMR spectroscopy.[29] Here, we extend this work to explore the diffusion of adsorbed $^{13}CO_2$ in both $Zn_2$(dobdc) and $Zn_2$(dobpdc) to examine the influence of pore size on this diffusion. We find that a relatively small increase in the pore diameter can have significant impacts on $CO_2$ diffusion, and we quantify the very large diffusion anisotropies in $Zn_2$(dobdc) and $Zn_2$(dobpdc).

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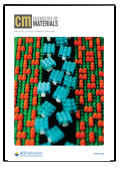

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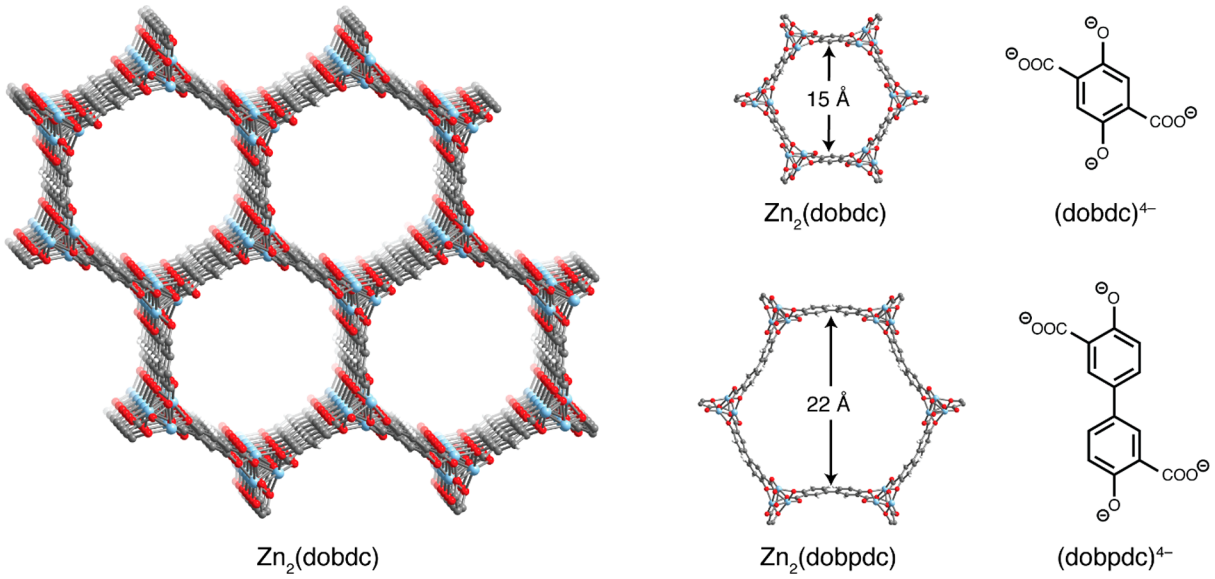


**Figure 1.** Two metal−organic frameworks with different pore sizes. Left: a portion of the crystal structure of $Zn_2$(dobdc). Right: views of a single pore of $Zn_2$(dobdc) and $Zn_2$(dobpdc) alongside illustrations of their respective ligands. Pale blue, gray, red, and white spheres represent Zn, C, O, and H atoms, respectively.

## RESULTS AND DISCUSSION

The metal−organic frameworks $Zn_2$(dobdc) and $Zn_2$(dobpdc) were synthesized as large crystals (Figure S1) suitable for single-crystal X-ray diffraction studies and measurement of intracrystalline diffusion via PFG NMR spectroscopy. Diffraction studies of $CO_2$ adsorption in both materials at 298 K confirmed that the open $Zn^{2+}$ coordination sites exposed upon activation of the materials provide the primary binding site for $CO_2$, in agreement with previous work (Figure S2).[28] At a lower temperature of 100 K, it was also possible to resolve a secondary binding site in $Zn_2$(dobdc) where $CO_2$ is adsorbed adjacent to the primary site (see the crystallographic information files). At 298 K, the $M-O_{CO_2}$ distances are 2.44(3) and 2.528(12) Å in $Zn_2$(dobdc) and $Zn_2$(dobpdc), respectively, suggesting slightly weaker adsorption of $CO_2$ in the larger pore material—an observation that is further supported by $CO_2$ adsorption isotherm data (Figure S3).

Carbon-13 NMR spectra collected for $Zn_2$(dobdc) samples dosed with varying pressures of $^{13}CO_2$ show residual chemical shift anisotropy line shapes (Figure 2 and Figure S4), with the magnitude of the residual anisotropy depending on the $CO_2$ pressure, as observed previously for $Mg_2$(dobdc) and $Mg_2$(dobpdc) variants.[20−22] Importantly, the spectral contributions of $CO_2$ molecules occupying crystals with different orientations relative to the applied magnetic field (Figure 2a) appear at different NMR frequencies, providing the opportunity to study anisotropic diffusion,[25,26,29,30] i.e., the self-diffusion coefficients parallel to ($D_\parallel$) and perpendicular to ($D_\perp$) the one-dimensional channels running along the $c$-axes within the MOF crystal structures (Figure 2b).

PFG NMR spectra were first collected for $Zn_2$(dobdc) dosed with 492 mbar of $^{13}CO_2$ with the magnetic field gradients applied along the $z$-direction. These data revealed that $CO_2$ diffusion in $Zn_2$(dobdc) is highly anisotropic (Figure 2c), with the signal intensities decaying at vastly different rates, depending on the chemical shift (i.e., depending on the crystallite orientation). Applying our recently developed analysis method,[30] we extracted a self-diffusion coefficient of $D_\parallel = 1.5(4) \times 10^{-9}$ m$^2$ s$^{-1}$ for diffusion along the MOF channels (Figure 2d and Figure S5). The value for $D_\parallel$ is comparable to the self-diffusion coefficient of liquid water under ambient conditions[31] ($2.3 \times 10^{-9}$ m$^2$ s$^{-1}$) and smaller than the diffusion of free $CO_2$ gas[32] ($D = 1.1 \times 10^{-5}$ m$^2$ s$^{-1}$ at 25 °C and 1 bar) by 4 orders of magnitude.

From our PFG NMR experiments, we were unable to definitively determine whether $D_\perp$ is zero or nonzero (Figure S6), and on the basis of our analysis we estimate an upper limit for $D_\perp$ of $10^{-13}$ m$^2$ s$^{-1}$, at least 8 orders of magnitude smaller than the diffusion of free $CO_2$.[31] Using these values of $D_\parallel$ and $D_\perp$, we obtained simulated NMR spectra that show good agreement with the experimental spectra (Figure 2d and Figure S6). From the results of our PFG NMR experiments, we also calculate a root-mean-square displacement of 10 $\mu$m along the MOF channels, which is much smaller than the typical crystal sizes of on the order of 100 $\mu$m employed in the experiments (Figure S1). Thus, exchange with the gas phase is expected to be minimal on the time scale of the measurement. Experiments performed with $^{13}CO_2$ pressures of 282 and 3578 mbar gave very similar results to the experiments at 492 mbar (Figures S5 and S8−S10), with $D_\parallel = 1.0(3) \times 10^{-9}$ and $1.4(4) \times 10^{-9}$ m$^2$ s$^{-1}$, respectively (Figure 3); for both pressures we again estimated $D_\perp < 1 \times 10^{-13}$ m$^2$ s$^{-1}$. Finally, PFG NMR experiments and simulations performed with the magnetic field gradient applied in the laboratory $x$-direction also yielded consistent values for $D_\parallel$ and $D_\perp$ (Figure S7).

Given the upper bound for $D_\perp$, the ratio $D_\parallel/D_\perp$ is at least $10^4$, illustrating that $CO_2$ diffusion in $Zn_2$(dobdc) is highly anisotropic. This result is consistent with our prior investigation of $CO_2$ diffusion in $Zn_2$(dobpdc)[29,30] as well as a recent study of proton conductivity in single crystals of $Co_2$(dobdc), which found that conductivity along the channels was 1200 times greater than the conductivity in the perpendicular direction.[33] Such large transport anisotropies can be well understood by considering the structure of the $M_2$(dobdc) materials, wherein the walls of the one-dimensional channels are expected to be largely impermeable (Figure 1, left). The substantial diffusion anisotropy may also support a


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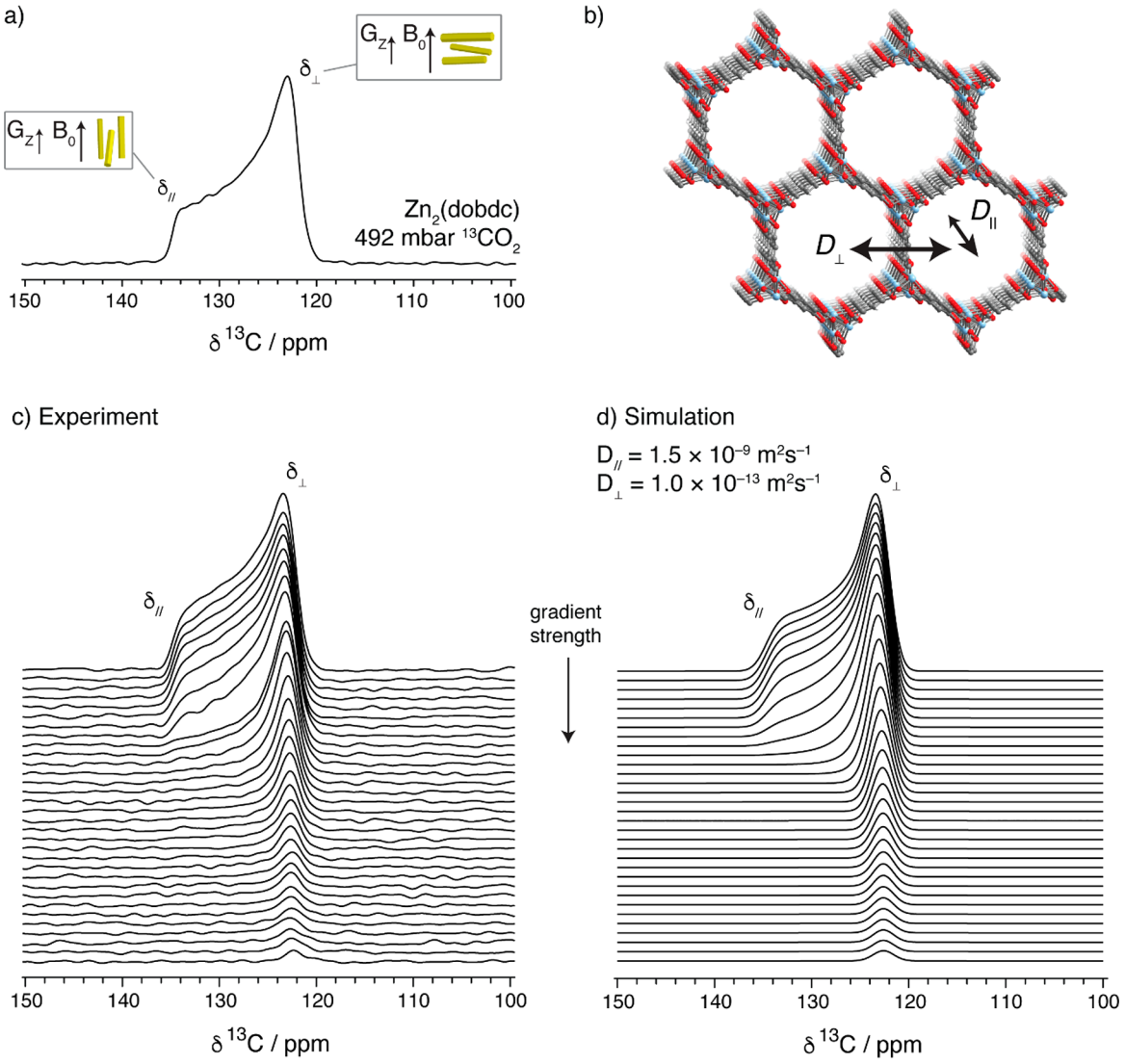


**Figure 2.** Highly anisotropic $CO_2$ diffusion in $Zn_2$(dobdc). (a) Static quantitative $^{13}$C NMR (7.1 T, 25 °C) spectrum of $Zn_2$(dobdc) dosed with 492 mbar of $^{13}CO_2$. (b) A portion of the crystal structure of $Zn_2$(dobdc) showing how $D_\parallel$ and $D_\perp$ are defined. (c) PFG NMR spectra with the applied magnetic field gradient in the $z$-direction (parameters: $\Delta$ = 31.4 ms, $\delta'$ = 2 ms, gradient pulse stabilization time ($t_s$) = 1 ms, $\tau$ = 5.2 ms, and maximum $g$ = 18.0 T m$^{-1}$). (d) Simulated PFG NMR spectra with $D_\parallel$ = 1.5 × 10$^{-9}$ m$^2$ s$^{-1}$, $D_\perp$ = 1.0 × 10$^{-13}$ m$^2$ s$^{-1}$, $\delta_\parallel$ = 134.7 ppm, and $\delta_\perp$ = 122.4 ppm; Gaussian peaks with a FWHM of 2.2 ppm were used to model the homogeneous line shape.

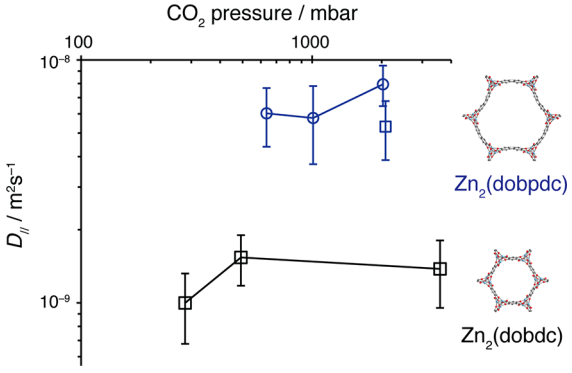


**Figure 3.** Effect of pore diameter upon diffusion. Self-diffusion coefficients for $CO_2$ diffusion parallel to the channels within $Zn_2$(dobdc) and $Zn_2$(dobpdc). Two data sets are shown for two independent $Zn_2$(dobpdc) samples, circles are data from our previous work,[29,30] and the data point from this work is shown as a square. Errors represent 95% confidence bounds.

previous hypothesis that pore obstruction (e.g., resulting from unreacted ligand or crystal defects) accounts for the inaccessibility of some adsorption sites in $M_2$(dobdc) compounds;[28] indeed, negligible cross-pore diffusion combined with partially occluded channels could render some adsorption sites completely inaccessible on the time scale of adsorption experiments. We note that previous studies of diffusion in materials with nominally one-dimensional pores have generally shown nonzero $D_\perp$, which is usually attributed to the presence of defects that enable diffusion between neighboring one-dimensional channels.[34,35] We note that the very high diffusion anisotropies obtained in this study are consistent with a high level of crystallinity.

Analogous measurements performed with the larger pore $Zn_2$(dobpdc) framework under 2078 mbar of $^{13}CO_2$ afforded $D_\parallel$ = 5.3(1) × 10$^{-9}$ m$^2$ s$^{-1}$ (Figure 3, Figures S5 and S11), similar to our previous work.[29,30] We also measured $D_\perp$ < 6 × 10$^{-13}$ m$^2$ s$^{-1}$ (Figure S12), which is significantly smaller than the $D_\perp$ values we determined in our previous analysis of this


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material ((1.6−4.6) × $10^{-11}$ $m^2$ $s^{-1}$).[30] In our previous work, we postulated that structural defects led to diffusion within the *ab*-plane (between the channels) of the framework. The discrepancies between our two studies most likely arise from the different synthesis methods used for $Zn_2$(dobpdc), which may have led to different defect levels in the two materials. We note that the Langmuir surface area of the $Zn_2$(dobpdc) sample studied in the present work is greater than that of the material in our previous work (3440 vs 2605 $m^2$/g),[29] which is consistent with high crystallinity and likely a lower level of defects.

Compared to the value of $D_{\parallel}$ determined for $Zn_2$(dobdc), $D_{\parallel}$ is consistently greater for $Zn_2$(dobpdc) by a factor of 4−6 (Figure 3). This difference is significant, given the relatively small difference in the pore sizes of these materials (15 vs 22 Å). Previous density functional theory (DFT) calculations of molecular diffusion within $Mg_2$(dobdc) showed that diffusive pathways down the middle of the channel have considerably lower activation barriers than diffusion between the open metal sites located on the channel walls.[36] We therefore postulate that the presence of additional pore volume in $Zn_2$(dobpdc) (in the pore center, remote from open metal sites) favors these lower-barrier pathways and accounts for the greater observed self-diffusion. As we noted above, the $CO_2$−Zn interaction at the primary binding sites also appears to be slightly stronger in $Zn_2$(dobdc) than in $Zn_2$(dobpdc), which will also partly account for the lower $CO_2$ diffusion rate in $Zn_2$(dobdc). Indeed, previous DFT work also showed that $CO_2$ hopping between primary binding sites is another important diffusion mode.[36]

We note the Langmuir surface area measured for $Zn_2$(dobdc) in this work is slightly lower than typical literature values (920 $m^2$/g vs 1000−1280 $m^2$/g, respectively),[28,37,38] while our measured Langmuir surface area for $Zn_2$(dobpdc) compares favorably to literature values (3440 $m^2$/g vs 2970−3100 $m^2$/g, respectively).[14,15,39] The lower surface area measured here for $Zn_2$(dobdc) could indicate either the presence of defects or unwanted molecules (e.g., unreacted ligand) in the pores of our large crystals, which could then decrease $CO_2$ self-diffusion and accentuate the differences in diffusion between the two frameworks. We do, however, expect this effect to be minor, especially given the similar $D_{\parallel}$ values for our two independent $Zn_2$(dobpdc) samples (Figure 3), which have markedly different Langmuir surface areas (3440 vs 2605 $m^2$/g). Lastly, we note that there is relatively little variation in $D_{\parallel}$ as a function of pressure from 282−3578 mbar for $Zn_2$(dobdc) and 635−2078 mbar for $Zn_2$(dobpdc).[29,30] This is despite significant changes in $CO_2$ adsorption amounts; e.g., for $Zn_2$(dobdc) the adsorbed quantity varies from 3.7 to 5.0 to >6.4 mmol/g for $CO_2$ pressures of 282, 492, and 3578 mbar, respectively (Figure S3). Future experiments with a better signal-to-noise ratio and at more extreme pressures may allow for pressure-dependent diffusion behavior to be observed, as recently reported for methane diffusion in $M_2$(dobdc) materials.[40]

## CONCLUSION

The foregoing results reveal the highly anisotropic nature of self-diffusion of $CO_2$ in $Zn_2$(dobdc) and demonstrate that diffusion along the MOF channels ($D_{\parallel}$) is reduced by at least 4 orders of magnitude compared to free $CO_2$ gas, with values comparable to that of liquid water diffusion at ambient conditions. We further estimated an upper limit for the diffusion of $CO_2$ between the channels ($D_{\perp}$) in $Zn_2$(dobdc) and found that the self-diffusion coefficient in this perpendicular crystal direction is at least 4 orders of magnitude smaller than $D_{\parallel}$. By comparing self-diffusion in two isoreticular frameworks with different pore sizes, $Zn_2$(dobdc) and $Zn_2$(dobpdc), we have been able quantify the important role of pore size on $CO_2$ diffusion. In particular, a relatively small change of pore size from 15 to 22 Å leads to increases in the self-diffusion coefficient $D_{\parallel}$ by a factor of 4−6, depending on the $CO_2$ pressure. Future efforts will focus on expanding this analysis to explore a larger family of isoreticular frameworks with differing pore sizes, such that a quantitative relationship between pore size and diffusion can be determined. Future efforts would also benefit from analysis of diffusion under mixed-gas conditions that are more relevant to real-world applications.[41−43] Insights from studies of this type and related foregoing work will ultimately assist in the design of improved adsorbents and membranes for gas separations.

## EXPERIMENTAL SECTION

**Synthesis of $Zn_2$(dobdc).** $H_4$dobdc (500 mg, 2.52 mmol) was dissolved in 250 mL of ethanol. Separately, $Zn(CH_3CO_2)_2{\cdot}2H_2O$ (1950 mg, 8.88 mmol) was dissolved in 250 mL of deionized water. Then, 5 mL aliquots of each solution were combined in a 20 mL scintillation vial. To seal the vial, Teflon tape was first wrapped around the glass thread, and the plastic lid was then tightly closed. The vial was further sealed using electrical tape. The vial was placed in a 75 °C oven for ∼2 h, at which point yellow, needle-shaped crystals had formed. The contents of approximately 20−30 vials prepared in this manner were combined in a glass jar and were washed with deionized water three times and then with methanol six times. For all washes, the solution above the sedimented crystals was decanted and then replaced with pure solvent (∼40 mL), and the resulting crystal/fresh solvent mixture was heated at 60 °C for at least 1 h before the next wash. The crystals were stored in a jar of methanol until they needed to be used for further experiments. For NMR experiments, the crystals were transferred to 8 mm diameter valved NMR tubes (Norell) while still solvated by methanol, and they were then activated for 39 h at 180 °C under high vacuum by using a turbomolecular pump. Activated $Zn_2$(dobdc) crystals were obtained as yellow needles. A Langmuir surface area of 920 $m^2$/g was determined from $N_2$ adsorption isotherm measurements performed at 77 K.

**Synthesis of $Zn_2$(dobpdc).** $H_4$dobpdc (280 mg, 1.03 mmol) was dissolved in 100 mL of ethanol in a Schlenk flask. Separately, $Zn(CH_3CO_2)_2{\cdot}2H_2O$ (780 mg, 3.55 mmol) was dissolved in 100 mL of deionized water in a 500 mL round-bottom flask, which had been silanized with chlorotrimethylsilane (2% in toluene). The solutions were both sparged for 1 h with nitrogen gas, at which point the ligand/ethanol solution was cannula-transferred into the 500 mL round-bottom flask containing the zinc acetate solution. The combined solution was then heated at 75 °C in an oil bath for 12 h, after which time white needle-shaped crystals had formed. This procedure was performed twice, and the crystalline products were combined. The reaction liquid was decanted and was replaced with fresh *N*,*N*-dimethylformamide (DMF) and left to stand for 12 h. Next, two 3 h washes were performed sequentially with each of the following solvents: DMF, MeOH, and $CH_2Cl_2$. Washes were performed at room temperature in a glovebox (95% $N_2$, 5% $H_2$). The crystals were then transferred to a valved NMR tube and activated for 63 h at 180 °C under high vacuum by using a turbomolecular pump. The $Zn_2$(dobpdc) crystals were obtained as off-white needles. A Langmuir surface area of 3440 $m^2$/g was determined from $N_2$ adsorption isotherm measurements performed at 77 K.

**Sample Preparation for NMR Experiments.** MOF crystals were transferred to valved NMR tubes, as described above, and were


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then activated inside the NMR tubes. Note that the as-purchased valved 5 mm NMR tubes were modified to have an outer diameter of 8 mm so they could best fill the 8 mm detection coil used for NMR experiments. Samples were evacuated on a custom gas dosing manifold[29] and then dosed with $^{13}CO_2$ gas (Sigma-Aldrich, 99 atom % $^{13}C$, <3 atom % $^{18}O$) at ambient temperature, with at least 30 min allowed for equilibration. Finally, the pressure was recorded by using a capacitance manometer (MKS instruments, model 722B), and the Teflon valve on the NMR tube was closed before detaching the tube from the manifold and performing NMR experiments.

**Pulsed Field Gradient NMR Measurements and Data Analysis.** All NMR experiments were performed in static mode with a 7.0 T horizontal magnet and using a Bruker solution-state NMR probe equipped with an 8 mm coil. Diff30 and microimaging (Mic5) attachments were used for experiments with magnetic field gradients applied along the $z$- and $x$-directions, respectively. A 90° pulse length of 35 $\mu$s for $^{13}C$ gave a radio-frequency field strength of 7.1 kHz. $^{13}C$ NMR chemical shifts were referenced to the ethylene carbon of neat ethanol at 57.4 ppm as a secondary reference relative to tetramethylsilane (1 vol % in deuterated chloroform) at 0.0 ppm. Sine-shaped gradient pulses were used in all PFG NMR measurements. Initial calibration of the gradient strength was carried out via stimulated echo $^1H$ PFG NMR experiments performed on water at 25 °C with a known self-diffusion coefficient of $2.3 \times 10^{-9}$ m$^2$ s$^{-1}$.[31] Additional PFG NMR experiments were performed on ethylene glycol and glycerol at 298 K to confirm that the known self-diffusion coefficients[44,45] could be reproduced.

For PFG NMR experiments performed on $CO_2$-dosed MOF samples, the 13-interval pulse sequence with bipolar magnetic field gradient pulses (sine-shaped) was used (Figure S13).[46] The effective durations of the individual magnetic field gradient pulses ($\delta'$), the delays between the RF pulses ($\tau$), the gradient pulse stabilization times ($t_s$), and diffusion delays ($\Delta$) are given in the figure captions and are defined graphically in Figure S13. Diffusion delays were set to integer multiples of the period (20 ms) of the 50 Hz mains alternating current to mitigate potential issues from residual mains hum.[47]

We define $\theta$ as the angle between the long axis of the needle-shaped crystals and the applied magnetic field, $B_0$, direction. The decay of the NMR signal with the applied gradient applied along the $z$-direction is then governed by the following equations:

$$\delta = \delta_{\parallel} \cos^2\theta + \delta_{\perp} \sin^2\theta \quad (1)$$

$$D_{\mathrm{eff},z} = D_{\parallel} \cos^2\theta + D_{\perp} \sin^2\theta \quad (2)$$

$$\frac{I(b)}{I(b_0)} = a \exp(-bD_{\mathrm{eff},z}) \quad (3)$$

$$b = (2\delta'\gamma g)^2\left(\Delta + \frac{3\tau}{2} - \frac{\delta'}{6}\right) \quad (4)$$

where eq 1 gives the chemical shift ($\delta$) of $CO_2$ located in a crystal at angle $\theta$ relative to $B_0$, given residual chemical shift anisotropy parameters $\delta_{\parallel}$ and $\delta_{\perp}$. Equation 2 gives the effective diffusion coefficient for $CO_2$ in a given crystal obtained from PFG NMR measurements, where the magnetic field gradient is applied along the $z$-direction ($D_{\mathrm{eff},z}$). Equations 3 and 4 give the signal decay observed in pulsed-field gradient NMR experiments performed with the 13-interval sequence,[46] where $I(b)$ is the integrated signal intensity for a given $b$ value, $g$ is the applied magnet field gradient strength, $b_0$ is the $b$ value at the smallest $g$ used, and $\gamma$ is the gyromagnetic ratio of the studied nucleus (see also Figure S13).

Analysis of the PFG NMR data was undertaken in a manner very similar to our previous approach.[30] First, $D_{\parallel}$ values were obtained by fits of the PFG NMR signal intensities integrated over a small range of chemical shifts at $\delta_{\parallel}$. Second, spectral simulations in a Matlab code[30] were performed to estimate the magnitude $D_{\perp}$. Third, additional experiments that probe larger $b$ values (i.e., experiments with stronger gradients, larger $g$) were performed and analyzed to estimate a lower-limit value of $D_{\perp}$. We simulated the NMR response from $CO_2$ in 28656 crystallites with different orientations ($\varphi$, $\theta$), relative to $B_0$, according to the Zaremba, Conroy, and Wolfsberg scheme for sampling the spherical coordinate space, as implemented in Simpson software.[48] Gaussian peaks with a FWHM of 2.2 ppm were used to model the homogeneous line shape (i.e., the line shape from the spectral contribution of $CO_2$ in a single crystal). Additional details on these simulations are given in our previous work.[30]

**X-ray Diffraction.** A methanol-solvated crystal of $Zn_2$(dobdc) was mounted on a borosilicate glass fiber by using a minimal amount of epoxy in air, ensuring that the crystal pores at the two ends of the crystal remained accessible. The glass fiber was then inserted into a 1.0 mm borosilicate glass capillary, which was connected to a HiP Taper Seal valve using a Swagelok Ultra-Torr vacuum fitting with a Viton O-ring. The capillary-dosing assembly was then attached to a port on a Micromeretics ASAP 2420 instrument by using a Cajon VCO fitting. The capillary was evacuated under reduced pressure at 180 °C for 24 h to remove solvent molecules that fill the pores and coordinate to the Zn centers within the crystal. The capillary was dosed with 900 mbar of $CO_2$ and was then flame-sealed using a methane/oxygen torch. Details of diffraction experiments on $Zn_2$(dobpdc) are provided in our previous work.[29]

X-ray diffraction data were collected at Beamline 12.2.1 at the Advanced Light Source, Lawrence Berkeley National Laboratory, by using synchrotron radiation ($\lambda$ = 0.7288 Å) with a Bruker Photon II CMOS detector. Data were collected at 100 K (for $Zn_2$(dobdc)·2.0$CO_2$) and 298 K (for $Zn_2$(dobdc)·1.0$CO_2$), with the sample temperature maintained by using an Oxford Cryosystems cryostream.

The crystals of each compound were found to be non-merohedral twins based on analysis of diffraction patterns. For each structure, CELL_NOW[49] was used to determine the orientation matrices. Raw data for both twin matrices were integrated and corrected for Lorentz and polarization effects by using Bruker AXS SAINT software[50] and corrected for absorption by using TWINABS.[51] TWINABS was used to produce a merged HKLF4 file for structure solution and initial refinement and an HKLF5 file for final structure refinement. The structures were solved by using direct methods with SHELXS[52,53] and refined by using SHELXL[54,55] operated in the OLEX2 interface.[56] Thermal parameters were refined anisotropically for all non-hydrogen atoms. Disorder and thermal motion of the bound gas molecules required the use of displacement parameter and distance restraints. All hydrogen atoms were refined by using the riding model.

**Gas Adsorption Measurements.** Gas adsorption measurements were performed using a Micromeritics ASAP 2420 instrument. Nitrogen adsorption isotherms at 77 K are shown in Figure S3 and were used to determine Langmuir surface areas. Carbon dioxide adsorption isotherms at 21 °C are also shown Figure S3.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.0c00745.

Microscope images of crystals, gas adsorption data, additional NMR spectra and simulations, additional crystallographic data (PDF)

Crystallographic data for $Zn_2$(dobdc)·$(CO_2)_{1.0}$ at 298 K (CIF)

Crystallographic data for $Zn_2$(dobdc)·$(CO_2)_{2.0}$ at 100 K (CIF)

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## Notes

The authors declare no competing financial interest.

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