

Buffered Coordination Modulation as a Means of Controlling Crystal Morphology and Molecular Diffusion in an Anisotropic Metal-Organic Framework

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ABSTRACT: Significant advances have been made in the synthesis of chemically selective environments within metal-organic frameworks, yet materials development and industrial implementation have been hindered by the inability to predictively control crystallite size and shape. One common strategy to control crystal growth is the inclusion of coordination modulators, which are molecular species designed to compete with the linker for metal coordination during synthesis. However, these modulators can simultaneously alter the pH of the reaction solution, an effect that can also significantly influence crystal morphology. Herein, non-coordinating buffers are used to independently control reaction pH during metal-organic framework synthesis, enabling direct interrogation of the role of the coordinating species on crystal growth. We demonstrate the efficacy of this strategy in the synthesis of low-dispersity single-crystals of the framework $\text{Co}_2(\text{dobdc})$ ($\text{dobdc}^{4-} = 2,5\text{-dioxido-1,4-benzenedicarboxylate}$) in a pH 7-buffered solution using cobalt(II) acetate as the metal source. Density functional theory calculations reveal the anisotropic nature of competitive acetate binding, and by using a series of cobalt(II) salts with carboxylate anions of varying coordination strength, it is possible to control crystal growth along the *c*-direction. Finally, we use zero length column chromatography to show that crystal morphology has a direct impact on guest diffusional path length for the industrially-important hydrocarbon *m*-xylene. Together, these results provide molecular-level insight into the use of modulators in governing crystallite morphology and a powerful strategy for the control of molecular diffusion rates within metal-organic frameworks.

INTRODUCTION

Metal-organic frameworks (MOFs) are a promising class of porous coordination solids with numerous potential applications, including in gas and liquid separations,¹⁻³ catalysis,⁴⁻⁶ drug delivery,^{7,8} energy storage,^{9,10} and sensing.¹¹⁻¹³ Indeed, the judicious selection of metal cations and organic linkers enables optimization of pore size, shape, and functionality for a given application. However, the use of frameworks in pelletized materials, mixed-matrix membranes, and packed beds is highly dependent on the distributions of crystal size and shape.¹⁴ Therefore, successful implementation of this class of materials on an industrial scale demands additional control over macroscopic characteristics such as crystallite size and morphology.

For an individual crystallite, morphology defines surface-area-to-volume ratios and intracrystalline mass transfer resistances. As crystallite size and shape are consequences of the crystallization process, precise understanding and control over the variables involved in crystallization is required to optimize MOF crystals for industrial applications. Toward this end, a number of successful strategies have been reported in the literature to manipulate the size and shape of MOF crystallites.¹⁵ One of the most common strategies, referred to as coordination modulation, involves the addition of molecules to the reaction that can

interfere with the crystallization process but are not significantly incorporated into the framework structure.¹⁶ To date, the morphologies of many different framework types and topologies have been successfully altered by adding modulators.¹⁷⁻²⁰ These modulators often feature one or more of the same functional groups present on the framework linker and therefore compete with the linker during crystal growth, imposing kinetic limitations on the growth rate along different crystallographic directions.

While the addition of a modulator is generally expected to change crystal morphology, it can be difficult to predict the exact nature of that change. At a fundamental level, all MOFs can be described as being composed of Lewis acidic metal ions or clusters bridged by Lewis basic ligands that act as linkers. For the vast majority of reported frameworks, the organic linkers also behave as Brønsted-Lowry acids and/or bases during synthesis. Modulators with mimicking functionalities will also behave as Brønsted-Lowry acids or bases and change the protonation equilibrium in solution (pH in water or pH* in non-aqueous media). Addition of modulators thus alters coordination and protonation equilibria simultaneously: increasing the concentration of modulator may increase competitive binding at metal sites, but it will also change the pH of the solution. Although

this correlation has been described in the literature, the most common strategy employed to counterbalance these effects is the addition of a modulator followed by a pH-compensating Bronsted-Lowry acid or base, which increases the ionic strength of solution.²¹⁻²³ However, this strategy introduces a new variable into the reaction conditions, as the dramatic increase in ion concentration changes dissociation constants and reactant solubility.²⁴⁻²⁶ This complication is exacerbated by the solvothermal nature of many framework syntheses, in which linker deprotonation occurs via the thermal decomposition of an amidic solvent, most commonly *N,N*-dimethylformamide (DMF). In these syntheses, DMF will readily decompose at elevated temperatures to yield an amine and either a carbonyl species or a carboxylic acid via thermolysis or hydrolysis, respectively.²⁷ In this case, the solution pH and the number and identity of coordinating molecules change as a function of time, following a non-constant and complex rate. The development of buffered, aqueous synthesis conditions would importantly enable deconvolution of the roles the modulator plays as a coordinative species and as a base.

The challenge of independently controlling pH and metal ion complexation has long been prevalent in biochemical and biological research. In 1966, Good and coworkers introduced a set of twelve buffers designed for use in biological studies near physiological pH,²⁸ among these are various zwitterionic *N*-substituted aminosulfonic acids. The buffers were selected based on a number of criteria, including the key requirement that the buffers do not coordinate metal cations *or* that they coordinate to form soluble salts with known binding constants. Indeed, controlling pH is necessary for the measurement of physiologically relevant properties, but for processes involving metallocofactors, it is crucial that the buffer molecules do not preferentially form complexes with the metal ions. Given that metallocofactors play an important role in regulating the kinetic and thermodynamic pathways of many biological processes,²⁹⁻³¹ unintended metal complexation by buffer molecules can interfere with or fundamentally alter the physiological property being measured. Recognition that Good's molecules and a number of other common biological buffers can still engage in disruptive metal complexation motivated the identification of guidelines for optimal metal ion and buffer combinations³² as well as development of truly non-coordinating buffers.^{33,34}

The use of nominally or non-coordinating buffers similarly offers an intriguing means of controlling MOF crystal formation, given that most syntheses rely on the indirect and convoluted interplay of pH and metal complexation. The well-known series of frameworks $M_2(\text{dobdc})$ ($M = \text{Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd}$; $\text{dobdc}^{4-} = 2,5\text{-dioxido-1,4-benzenedicarboxylate}$; Figure 1)³⁵⁻³⁸ present an interesting test case in this regard. These materials feature a high density of coordinatively-unsaturated metal(II) sites that can interact strongly and selectively with a variety of guest molecules and have accordingly been demonstrated as promising adsorbents for numerous gas separations applications.^{37,39-42} The traditional solvothermal routes used to prepare these frameworks generate either significantly polycrystalline samples or long rod-like crystallites, wherein the longest crystallite direction aligns with the one-dimensional channels propagating along the *c*-axis.⁴³⁻⁵² Guest transport along the one-dimensional channels of the long crystals has been shown to be much faster than diffusion across the channels,⁵³ rendering much of the external surface inaccessible to molecules. Thus, developing a controlled means of synthesizing these crystals with optimal morphologies presents a highly desirable target.

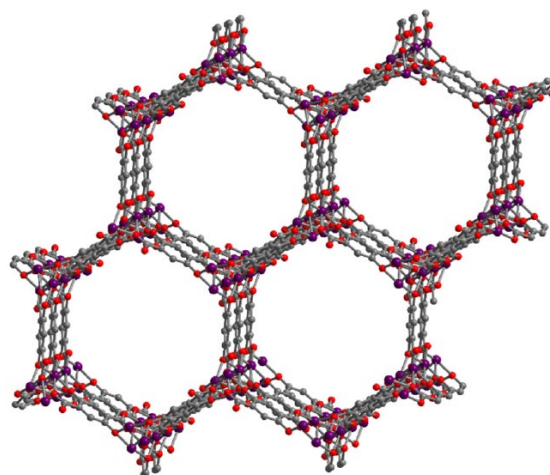


Figure 1. Portion of the crystal structure of $\text{Co}_2(\text{dobdc})$ illustrating the hexagonal pores along the *c*-axis. Purple, red, and gray spheres represent Co, O, and C atoms, respectively; H atoms are omitted for clarity.

Herein, we demonstrate that the synthesis of $\text{Co}_2(\text{dobdc})$ under mild conditions starting from cobalt(II) acetate results in the formation of regular, well-faceted single crystals that are compressed along the *c*-axis relative to crystals prepared via traditional routes. Use of a non-coordinating buffer to control pH during synthesis further reveals that acetate modulates crystal growth by competing with the dobdc^{4-} linker for coordination, a result that is borne out by computations. By varying the coordination strength of competing anion and the solution pH, it is possible to generate crystallites with varying sizes and morphologies, giving rise to a previously unprecedented level of control over framework crystal growth. Zero length column chromatography experiments demonstrate that diffusion of the industrially-important molecule *m*-xylene is more favorable in crystals that are compressed along the *c*-axis, highlighting the importance of fine-tuned control over crystal growth for real-world applications.

RESULTS AND DISCUSSION

Morphology of Non-Buffered $\text{Co}_2(\text{dobdc})$. The synthesis of $M_2(\text{dobdc})$ has been reported in a range of solvent systems, including pure water,^{54,55} water/tetrahydrofuran mixtures, alcohol mixtures,⁵⁶⁻⁵⁸ and DMF.^{35,37} Since we were interested in developing methods to probe the effects of pH and metal complexation separately, we chose to avoid DMF, which decomposes during synthesis, making it challenging to quantify base concentration at each point during the reaction. Water is a clear choice to enable a quantitative measure of pH; however, the low solubility of H_4dobdc in water would severely limit the maximum concentration of reactants in solution. The use of ethanol as a co-solvent with water promotes the solubility of all reactants while still enabling the quantitation of pH.⁵⁹⁻⁶¹ Moreover, water/ethanol mixtures have the potential to offer more environmentally-conscious syntheses for industrial applications. Finally, given the precedent for the use of acetate as a base in the synthesis of $M_2(\text{dobdc})$ ($M = \text{Co, Ni, Zn}$),^{54,62,63} cobalt(II) acetate was selected as the metal precursor.

The non-buffered synthesis of $\text{Co}_2(\text{dobdc})$ was carried out by combining $\text{Co}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ and H_4dobdc in a 1:1 (v/v) water/ethanol mixture in a 20-mL scintillation vial and heating the mixture to 75 °C in an oil bath for at least 2 h. These conditions yield readily dispersible orange crystalline particles, and powder X-ray diffraction data for this solid are consistent with the

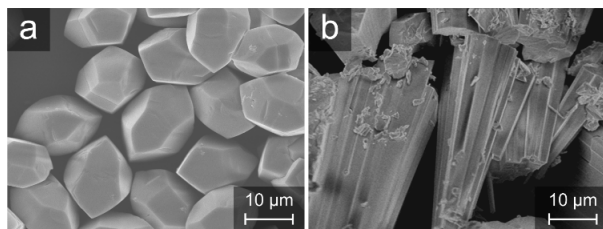


Figure 2. SEM images of $\text{Co}_2(\text{dobdc})$ synthesized from H_4dobdc and cobalt(II) acetate in (a) 1:1 water/ethanol, and (b) using a published single-crystal solvothermal route.³⁷

expected $\text{Co}_2(\text{dobdc})$ phase (Figure S1). Optical microscopy characterization of the particles indicated that they have uniform size and morphology, and the uniform reflectance or transmittance of polarized light across individual crystallites showed them to be single crystals (Figure S2). Scanning electron microscopy (SEM) images of the crystallites revealed low-dispersity polyhedra with clearly-defined facets (Figure 2a). We found that using an oven instead of an oil bath during synthesis produces slightly larger crystallites with much greater polydispersity (Figure S3). To ensure reproducibility and enable reliable comparison across all samples, all subsequent reactions were performed using an oil bath. Significantly, our synthesis route affords access to regular, well-faceted single crystals with a characteristic length of $\sim 10\ \mu\text{m}$, which is important for obtaining accurate diffusion measurements (see below). In marked contrast, crystallites of $\text{Co}_2(\text{dobdc})$ synthesized via the reported solvothermal route³⁷ using $\text{Co}(\text{NO}_3)_2(\text{H}_2\text{O})_6$ and a 1:1:1 (v/v/v) mixture of DMF, ethanol, and water generates clusters of long, rod-like crystallites (Figure 2b). Similarly, the preparation of $\text{Co}_2(\text{dobdc})$ at room temperature starting from cobalt(II) acetate previously yielded nanoparticles on the order of $20\ \text{nm}$.⁶¹

The narrow-dispersity polyhedra resulting from synthesis in water/ethanol are pentagonal dodecahedra that are elongated along a three-fold axis (Figure 3, left). Notably, the crystallites do not possess the expected long rod-like morphology. Instead, they exhibit a shorter, more truncated shape that is consistent with S_6 symmetry within the space group $R\bar{3}$.⁶⁴ The only three-fold axis of symmetry apparent in the crystal morphology corresponds to the three-fold c -axis found in $R\bar{3}$. A self-consistent set of Miller indices can be generated with symmetry operators and the correct choice of one of each of the side faces and the top face. Here, the $\{100\}$ and $\{401\}$ families of planes describe the morphology of the pentagonal dodecahedra (Figure 3, right), while the other planes are generated by symmetry. The full set of planes generated in this manner is a set of six indices to describe the facets parallel to the c -axis, $\{(1-10), (-110), (100), (-100), (010), (0-10)\}$, and a set of six indices describing facets that intersect the c -axis to cap the crystallite, $\{(401), (-40-1), (0-41), (04-1), (4-41), (4-4-1)\}$ (teal and violet, respectively, in Figure 3). Geometric overlays from multiple angles enabled assignment of morphology, but it is important to stress that this assignment does not provide information about specific surface chemistry and is merely a recreation of the three-dimensional shape. Some care must be taken with this approach, as the method reconstructs polyhedra from two-dimensional projections of crystals oriented at many angles relative to the viewing axis. For example, nearly all information about faces intersecting the c -axis is lost when the crystals are aligned directly along the three-fold axis (Figures S4 and S5). Given sufficient randomly distributed particles, crystallite morphology may be reconstructed with confidence.

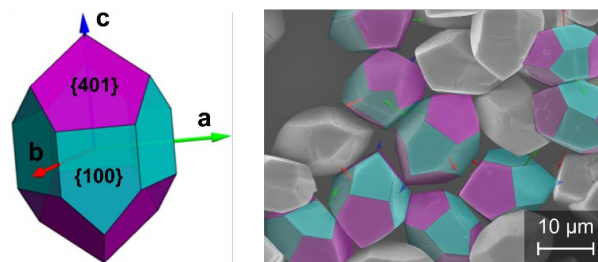


Figure 3. (Left) Illustration of the morphology of $\text{Co}_2(\text{dobdc})$ pentagonal dodecahedra with axes and generating faces overlaid. (Right) Projection of this morphology onto the SEM image of $\text{Co}_2(\text{dobdc})$ from Figure 2a, with crystallites arranged at different angles.

Non-Coordinating Buffers. Most solvothermal syntheses reported for $\text{Co}_2(\text{dobdc})$ result in polydisperse mixtures containing rod-like crystallites extending along the c -axis.⁴³⁻⁵² The ability to access homogeneous, low-aspect ratio crystallites as reported here is therefore notable and suggests that the non-buffered synthesis route affords a level of morphological control that is typically absent in solvothermal reactions. A key difference between our synthesis and the typical literature solvothermal syntheses of MOF single crystals is the use of an acetate salt as the metal precursor, suggesting that acetate may play a role in determining crystallite shape. Previous reports of coordination modulation in the synthesis of various frameworks, including $\text{Ni}_2(\text{dobdc})$ and $\text{Mg}_2(\text{dobdc})$, have shown that acetate can interact with metal ions as a Lewis base, thereby influencing the interactions between the metal ions and linker molecules.⁶⁵⁻⁶⁹ By design, acetate here also acts as a Brønsted base to deprotonate the linker. However, pH also plays an important role in morphology,^{68,69} and it is impossible to know *a priori* if the presence of acetate is also important for the synthesis of narrow-dispersity, low-aspect ratio crystallites without eliminating acetate from the reaction. If the presence of acetate is required for uniform crystallites, it could be acting either as a director of crystallite shape through metal coordination or as a pH-altering base, such that the consequent extent of linker deprotonation is optimal for generating the observed crystallite shape. The independent evaluation of both of these possibilities requires the use of a non-coordinating buffer in $\text{Co}_2(\text{dobdc})$ synthesis.

Toward this end, we first examined the effect of including a nominally non-coordinating buffer on crystallite morphology with acetate still present in solution. In general, the addition of a buffer will increase the ionic strength of the reaction solution while maintaining the pH at a constant value relative to the non-buffered solution. The molecule 4-morpholinepropanesulfonic acid (MOPS)²⁸ was chosen as a suitable buffer for neutral-pH reaction conditions, given that it has a pK_a of 7.2 and that numerous studies have established that it interacts very weakly or negligibly with metal ions in solution.³² As a control to account for any metal ion–buffer interaction, the synthesis of $\text{Co}_2(\text{dobdc})$ was carried out using the same reaction conditions in the presence and absence of buffer near neutral pH (see the Supporting Information for details). In the presence of MOPS, the reaction mixture was maintained at a constant $\text{pH} = 7$, while the pH of the non-buffered reaction decreased slightly from 6.7(1) to 5.5(1) as H_4dobdc was deprotonated. SEM images of the crystallites resulting from both reactions are shown in Figure 4a and b. Importantly, there is no discernable difference in the crystal morphology, suggesting that MOPS buffer may be

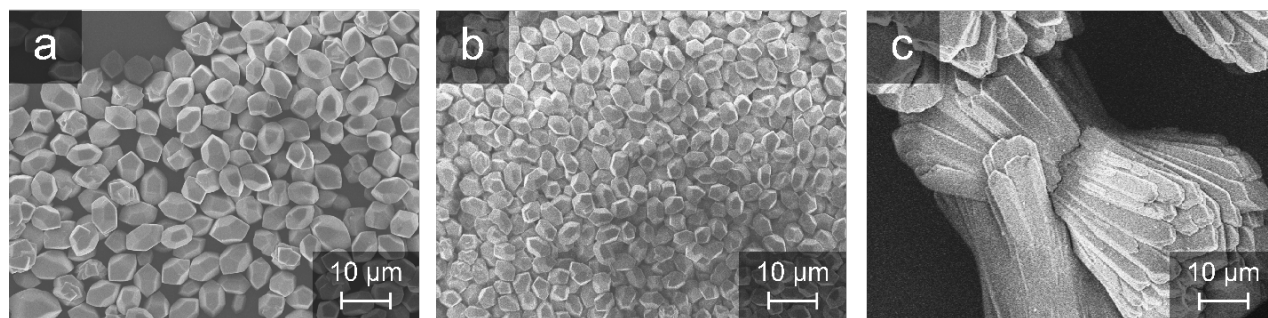


Figure 2. $\text{Co}_2(\text{dobdc})$ crystallites synthesized with (a) H_4dobdc and cobalt(II) acetate without buffer; (b) H_4dobdc and cobalt(II) acetate with MOPS buffer (pH = 7); and (c) H_4dobdc and cobalt(II) tetrafluoroborate with MOPS buffer.

used to control pH with negligible participation in metal complexation under these reaction conditions. Of note, it was also found that by carrying out the buffered framework synthesis in silanized glassware, the sensitivity of crystallite size and morphology to heating method is significantly minimized (Figure S6). Finally, there is no evidence of buffer incorporation into the framework via infrared spectroscopy (Figures S7 and S8).

The use of MOPS buffer further enabled the synthesis of $\text{Co}_2(\text{dobdc})$ in the presence of diverse cobalt(II) salts while maintaining neutral pH (Figures 4c and S9). Interestingly, substituting weakly-coordinating tetrafluoroborate for acetate as the counteranion produces long, polycrystalline and polydisperse rods (Figure 4c), indicating that acetate plays a key role in controlling $\text{Co}_2(\text{dobdc})$ crystallite morphology. The use of cobalt(II) salts featuring anions with differing coordinating ability further resulted in uniform changes to the crystal morphology and apparent facets (Figure S9).

Using cobalt(II) acetate as the metal precursor, we also varied the reaction conditions by buffering the solution to pH values of 6.5 (using MOPS) or 5.5 and 6 (using 2-ethanesulfonic acid, MES). Although pH values ranging from 3 to 11 are accessible using noncoordinating buffers, cobalt hydroxide readily forms at pH ~ 8 ,⁷⁰ and reactions buffered below the pK_a of the carboxylate functionalities (<5) will not proceed in appreciable amounts. We found that decreasing the reaction pH increases crystal size and aspect ratio in the presence of acetate (Figure S10) but has no effect in the presence of tetrafluoroborate (Figure S11). Lowering the pH affects the protonation state of both acetate and H_4dobdc in solution and appears to slow overall formation. This result is also consistent with our observation that $\text{Co}_2(\text{dobdc})$ crystallites synthesized with cobalt(II) acetate without buffer are larger than crystallites synthesized with cobalt(II) acetate at pH 7 (Figure 4a and b). Thus, we can ascribe the pH-induced morphological changes to the $\text{Co}_2(\text{dobdc})$ crystallites to acetate protonation. Indeed, as acetate is protonated, it is less able to compete with the linker during crystal growth, leading to longer crystallites. This lack of coordination control also leads to greater morphological dispersity.

Computational Modeling. Density functional theory (DFT) calculations were carried out to study the competitive binding of acetate and dobdc^{4-} during $\text{Co}_2(\text{dobdc})$ crystallite formation, using a 125-atom helical cluster model consisting of five neighboring cobalt centers coordinated by seven linkers (Figure 5a–c). This cluster was constructed based on a previously reported 106-atom cluster developed to model $\text{C}_1\text{--C}_3$ hydrocarbon binding in $\text{Fe}_2(\text{dobdc})$.⁷¹ While both models feature five adjacent metal centers and seven linkers, a key difference in our cluster is that all of the linkers are derived from salicylic acid, whereas in the iron cluster, two of the linkers are truncated. The mixed-linker choice was suitable for the iron cluster because there is

no substitution of the primary metal coordination sphere upon hydrocarbon binding, and the modeled gas adsorption site is far removed from the sites with truncated linkers. In contrast, a quantitative analysis of acetate and linker binding at various positions in the cobalt helix model requires the use of identical linkers. Finally, the coordination spheres of all unsaturated Co sites in our model were completed by a water molecule to better reflect the solvated environment in which the metal helices are formed.

Starting from the aforementioned 125-atom cluster, terminal or central linker molecules were replaced by bidentate acetate or monodentate acetate and a water molecule (Figure 5d–f). Binding energies were determined for each scenario and are given in

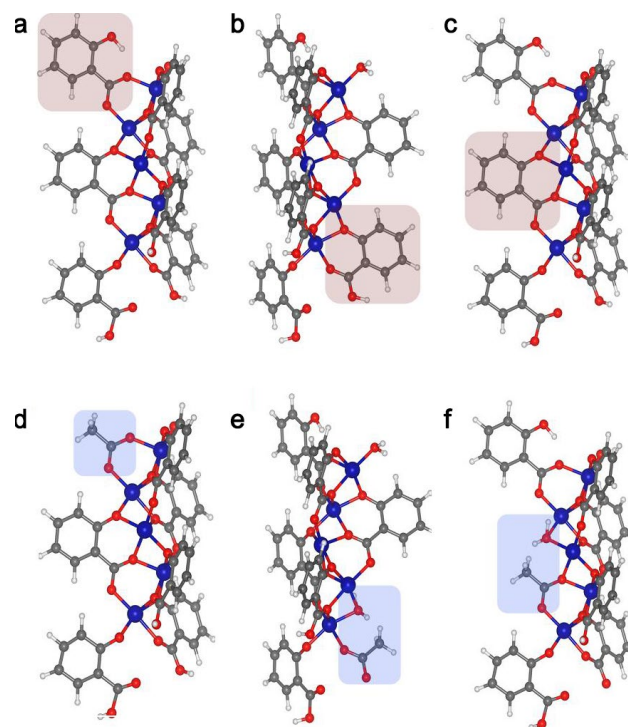


Figure 3. Helices used for DFT binding energy calculations. Co, O, C, and H atoms are shown in blue, red, grey, and white, respectively. Replaced bidentate terminal, monodentate terminal, and middle-helix linker molecules are highlighted in red in (a)–(c), respectively, while target binding molecules are highlighted in blue in (d)–(f). In (d), the linker is replaced by acetate, while in (e) and (f) the linker is replaced by a combination of acetate and water.

Table 1. Binding of terminal bidentate- and terminal monodentate-bound acetate + water can compete favorably with binding of terminal linkers (Figure 5d and e). For instance, the binding of terminal bidentate acetate is 28 kJ/mol more favorable than terminal salicylate (binding energies of -113 versus -85 kJ/mol, respectively). The binding of terminal monodentate acetate + water is even more competitive, with a binding energy of -125 kJ/mol. It is interesting to additionally compare terminal monodentate acetate + water binding to *central bidentate* acetate + water binding (Figure 5e and f). The computed binding energies indicate that competitive binding of terminal acetate + water is 25 kJ/mol more favorable than competitive binding of bidentate acetate + water in the center of the helix. Likewise, the binding of terminal acetate + water is 12 kJ/mol more favorable than competitive binding of terminal bidentate acetate. Thus, depending on the manner in which acetate binds, its competitive advantage over the linker can double. This finding has interesting implications for the mechanism of cluster growth in solution. While monodentate acetate and water binding is the most energetically competitive scenario, monodentate acetate may be dislodged more readily than a bidentate acetate. However, the monodentate binding scenario is likely stabilized by the co-adsorption of water, which could also play a role in determining the kinetics of replacement. We note that in all cases, it is more favorable for acetate than for H₄dobdc to bind to Co, consistent with our hypothesis that acetate governs crystallite morphology by coordinating to the Co centers during crystal growth.

Table 1. Computed Binding Energies (E_b) and Binding Energy Differences (ΔE) in kJ/mol for Terminal and Central Linkers and Acetate (or Acetate + Water) Molecules in the Cobalt Helix^a

Terminal coordination	E_b	ΔE_b
[C ₇ O ₃ H ₅] ⁻	-85	—
Bidentate [CH ₃ COO] ⁻	-113	-28
Monodentate [CH ₃ COO] ⁻ + H ₂ O	-125	-40
Central coordination	E_b	ΔE_b
[C ₇ O ₃ H ₄] ²⁻	-583	—
Bidentate [CH ₃ COO] ⁻ + H ₂ O	-598	-15

$$^a \Delta E = E_b - E_b(\text{linker})$$

Counter Ions as Modulators for Controlled Morphologies.

Given the evidence that acetate controls Co₂(dobdc) crystallite morphology via coordination during crystal growth, we sought to tune the morphology by changing the acetate binding strength. Acetate is readily modified by replacing the methyl group with more electron-donating or -withdrawing functionalities. The pK_a value of each conjugate acid can be used as a

proxy for coordination strength, given that the acidity of the carboxylate increases with the addition of electronegative substituents through inductive electron withdrawal.⁷² Formate, chloroacetate, and trichloroacetate were chosen as alternative counterions to probe the effects of binding strength on crystallite morphology. The pK_a values of all the corresponding acids are < 5 (Table S1),^{73,74} and thus each anion will be fully deprotonated in MOPS buffer solution. Cobalt(II) formate is commercially available, and cobalt(II) chloroacetate and cobalt(II) trichloroacetate were prepared via salt metathesis of cobalt carbonate and the corresponding haloacetic acid (see the Supporting Information). Some care needs to be taken in synthesizing and using trichloroacetate, which can undergo hydrolysis via the haloform reaction at elevated temperature in water. However, on the time scale and temperature scale of the Co₂(dobdc) synthesis, this side reaction is negligible.⁷⁵

The synthesis of Co₂(dobdc) starting from cobalt(II) acetate, formate, chloroacetate, or trichloroacetate in buffered solution produced monodisperse crystallites of varying aspect ratios (Figure 6). Powder X-ray diffraction (PXRD) analysis of the resulting crystallites confirmed the formation of Co₂(dobdc) (Figure S12), and N₂ adsorption isotherms confirmed that all samples are highly porous. Quantification of modulator incorporation by ¹H nuclear magnetic resonance (NMR) across three batches of Co₂(dobdc) showed an average incorporation 0.01 ± 0.01 acetate:H₄dobdc and 0.06 ± 0.02 formate:H₄(dobdc) (molar ratios). No quantifiable chloroacetate was incorporated (Table S2). Together, the PXRD data, surface area measurements, and analysis of digested MOF by NMR indicate that the modulators did not significantly alter the bulk structure or defect density of Co₂(dobdc). The crystal aspect ratio increases in the order acetate < formate < chloroacetate < trichloroacetate and is therefore inversely related to the pK_a of the corresponding conjugate acid (Table S1). Notably, because all reaction solutions were buffered to the same pH, the trend in crystal morphology can be ascribed directly to coordination modulation during growth. In particular, more electron-withdrawing groups diminish the ability of the carboxylate to compete with linker binding, resulting in longer crystallites. This observation indicates that the carboxylate-based modulators investigated preferentially bind along the *c*-axis of the crystal during crystal growth. Interestingly, the crystallite facets are the same for all crystals in the series, indicating that their surface energies are minimized irrespective of the competing anion (Figure S13). However, crystals prepared in the presence of trichloroacetate exhibit noticeably smoother facets than the other samples, suggesting that anion coordination may become negligible at very low conjugate acid pK_a values. We note that the modulator does not need to be the sole counteranion in solution to observe these

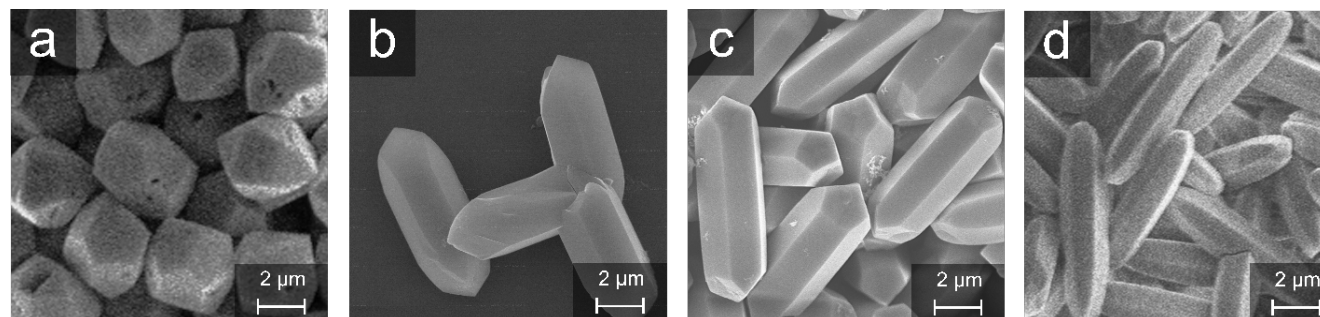


Figure 4. Co₂(dobdc) synthesized in water/ethanol buffered to pH 7 with different carboxylate metal salts: (a) cobalt(II) acetate (b) cobalt(II) formate (c) cobalt(II) chloroacetate (d) cobalt(II) trichloroacetate.

effects. Reaction conditions that utilized $\text{Co}(\text{NO}_3)_2$ starting material in conjunction with sodium acetate, sodium formate, or sodium chloroacetate gave rise to crystals of approximately the same size and aspect ratio as those synthesized with the coordination modulator as the anion in the Co starting material (Figure S14). Interestingly, the modulator concentration does not have a significant effect on the size or aspect ratio of the resulting crystals over a wide range of concentrations. By using $\text{Co}(\text{NO}_3)_2$ as a starting material, we were able to vary the acetate concentration in solution, and varying the acetate concentration across four concentrations ranging from 5 mM to 100 mM had a negligible impact on the resulting crystal size or aspect ratio (Figure S15). Furthermore, as discussed above, in the presence of even more weakly coordinating anions, morphological monodispersity is completely lost (Figure 4c). In general, the crystallite volume is similar across samples although it increases slightly with decreasing conjugate acid $\text{p}K_a$, which could imply a subtle lowering of the nucleation rate. Finally, we note the crystal yields are very high and nearly identical (~95%).

Aspect Ratio Dependent Diffusion of *m*-Xylene. Morphological control of MOF crystals has direct consequences on system-level adsorbent performance. For instance, the diffusion of guest molecules within $\text{M}_2(\text{dobdc})$ frameworks is highly favored along the *c*-axis (i.e. through the hexagonal pores shown in Figure 1),⁵³ and thus the methods introduced in this study to control crystal aspect ratio should enable direct control over the diffusional path length under conditions wherein the limiting mass transfer resistance is intracrystalline diffusion. Specifically, we anticipated that gas diffusion will be faster in crystals with shorter dimensions along the *c*-axis because those crystals would have a shorter diffusional path length (see the *c*-axis shown Figure 3).

To test this hypothesis, we utilized zero length column (ZLC) chromatography to measure differences in the diffusion of *m*-xylene in the lowest and highest aspect ratio crystallites of $\text{Co}_2(\text{dobdc})$, prepared from cobalt(II) acetate and trichloroacetate, respectively, in MOPS buffer (see Figure 6 and the Supporting Information for details). ZLC chromatography is an established technique that enables differentiation between equilibrium- and kinetically-controlled regimes and can be used to measure intracrystalline diffusion once the latter regime has been established.^{76,77} We chose *m*-xylene as a suitable probe molecule, given the high affinity of $\text{Co}_2(\text{dobdc})$ for the C_8 alkylaromatics and the importance of their separation in industry.³⁹ The characteristic width of both the long and short aspect ratio crystals used for this experiment was ~2.5 μm (Figure 6a and d), and thus their dimensions only differ along the *c*-axis.

In line with our hypothesis, *m*-xylene desorption from the longer crystals (~8 μm in length) exhibited a pronounced dependence on the purge gas flow rate, indicating that *m*-xylene diffusion in longer crystals is under kinetic control (Figure 7a). In contrast, the desorption rate in shorter crystals (~4 μm in length) was negligibly impacted by flow rate, even under the highest flow rates attainable, indicating that *m*-xylene diffusion in shorter crystals is under equilibrium control (Figure 7b). Additional details and discussion of the ZLC experiment and data analysis are given in the Supporting Information. These results indicate that the shorter crystallites are better-suited for process use, as the material selectivity remains unchanged but the adsorbate flux increases, due to a decrease in diffusional path length. More broadly, the ability to control MOF crystal morphology—and thereby adsorbate diffusion in MOFs—via modulated, buffered syntheses is a powerful new approach for the tailored synthesis of these adsorbents for industrially relevant applications.

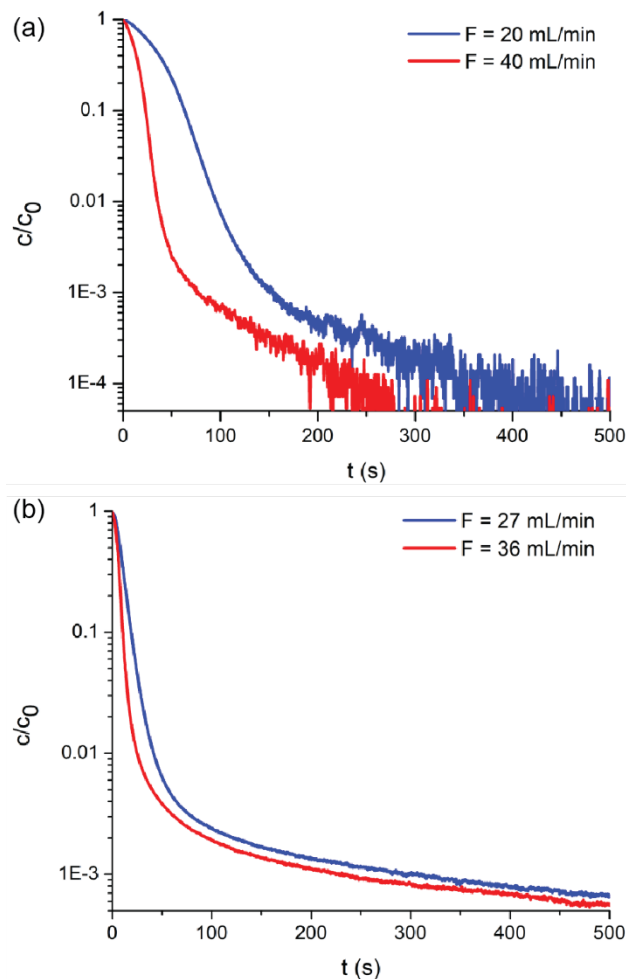


Figure 7. Comparison of desorption curves at two different He flow rates (F) for (a) long aspect ratio $\text{Co}_2(\text{dobdc})$ (path length = 2.5 microns) and (b) the short aspect ratio $\text{Co}_2(\text{dobdc})$ crystallites; the steep drop-off is due to the non-linear isotherm. See Supporting Information for detailed discussion of zero length column chromatography theory and experiments.

CONCLUSIONS

By employing non-coordinating buffers in the synthesis of the metal-organic framework $\text{Co}_2(\text{dobdc})$, we have been able to deconvolute the effects of reaction pH and coordinating anion on crystal morphology. Theory and experiment both indicate that morphological control stems from coordinating anions in solution, which engage in anisotropic competitive binding during crystallite growth. The degree of interaction can be tuned by varying the electron density on the interacting functional group of the anion, allowing access to monodisperse sets of crystallites with varying aspect ratios. Diffusional studies indicate that path length control enables the minimization of diffusional resistances for the industrially-important molecule *m*-xylene, highlighting the power of this synthetic approach for tuning framework crystallites to suit a given process. We anticipate that the high level of precision and rational control over MOF crystallite morphology demonstrated here can be extended beyond aqueous solvents to establish the use of noncoordinating buffers for precise pH control in nonaqueous and water-incompatible syntheses.

ASSOCIATED CONTENT

Supporting Information. Experimental details, gas adsorption measurements, morphological indexing, DFT, additional crystal

characterization, and ZLC details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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