

# SELECTIVE CH<sub>4</sub>/CO<sub>2</sub> GAS SEPARATION OF AN ANISOTROPIC ZINC BASED METAL ORGANIC FRAMEWORK<sup>1</sup>

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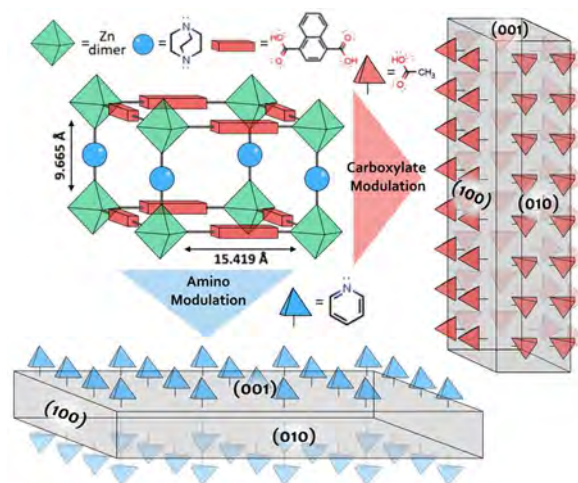
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## Abstract

This work investigates the morphological control and CO<sub>2</sub>/CH<sub>4</sub> adsorption characteristics of an anisotropic MOF, [Zn<sub>2</sub>(NDC)<sub>2</sub>(DABCO)]<sub>n</sub>. Rod and plate morphologies are acquired through changing the modulating species to acetic acid or pyridine during synthesis, respectively. Each morphology is rationalized to expose a different major surface pore aperture which in turn should present different mass transport characteristics. To study this effect, single-component equilibrium and kinetic adsorption data for CO<sub>2</sub> and CH<sub>4</sub> were collected in order to determine diffusion and transport characteristics of gases through each surface pore type. Equilibrium analysis indicates a slight selectivity towards CO<sub>2</sub> whereas kinetic data unexpectedly shows lower diffusion time constants for CO<sub>2</sub> compared to CH<sub>4</sub>. Mass transfer resistances on each species is discussed to explain the observed trend.

## Introduction

The efficient separation of CO<sub>2</sub> from CH<sub>4</sub> is critical for the technoeconomic success of the natural and biogas industries, however current industrial separation techniques are energy intensive or require high capital and operational expenses.<sup>2,3</sup> Common separation processes such as cryogenic distillation require a significant amount of energy, highlighting the need to find alternative approaches.<sup>2,3</sup> Recent



**Figure 1.** Schematic of the modulation process for the [Zn<sub>2</sub>(NDC)<sub>2</sub>(DABCO)]<sub>n</sub> MOF. Acetic acid (red pyramids) competitively coordinates with 1,4-naphthalene dicarboxylate (red rods) to direct growth in the [001] direction, while pyridine (blue pyramids) competitively coordinates with DABCO (blue spheres) to direct growth in the [100] and [010] direction. Reprinted with permission from [1].

attempts at making these separations more efficient involve the use of polymer membranes. While these membrane systems require a lower energy input, a lower concentration of feed CO<sub>2</sub> is required to prevent the membrane from plasticizing.<sup>4</sup> Other approaches use zeolites, but these materials are often synthesized with non-ideal particle morphologies, offer a limited range of pore sizes and chemistry, and can require energy and capital-intensive synthesis conditions.<sup>5</sup> An ideal separation platform would use easily synthesized and readily tunable materials, and would be effective regardless of intake quantities and concentrations.

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1. Text and figures reprinted with permission from: Huelsenbeck, L.; Westendorff, K.S.; Gu, Y.; Marino, S.; Jung, S.; Epling, W.S.; Giri, G. Modulating and Orienting an Anisotropic Zn-Based Metal Organic Framework for Selective CH<sub>4</sub>/CO<sub>2</sub> Gas Separation. Crystals 2019, 9, 20.

Metal organic frameworks (MOFs) are novel materials and could potentially fulfill these requirements. MOFs consist of metal ion clusters bound together by coordinating organic linkers to form a porous, periodic structure<sup>6,7</sup>. Their key features include high surface areas ( $> 1000 \text{ m}^2/\text{g}$ ), chemical customizability, and relatively easy and low temperature synthesis, which enable their application in a wide range of areas including catalysis, fuel cell development, drug delivery, data storage, and gas separations.<sup>6,8–12</sup>

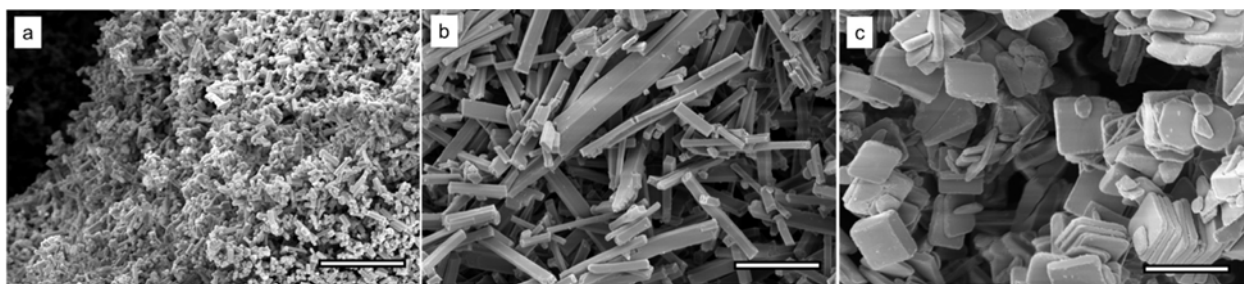
MOFs have shown promise as selective gas separators due to their ability to sterically and chemically restrict the species that pass through their pores. MOFs have previously been used in combination with a polymer matrix to demonstrate a high selectivity in a  $\text{CO}_2/\text{CH}_4$  gas mixture.<sup>3</sup> It was hypothesized that the selective permeation was due to the well-defined sorption properties of the microporous, crystalline MOF.<sup>3</sup> Additionally, it has been shown that the unmodulated  $[\text{Cu}_2(\text{NDC})_2(\text{DABCO})]_n$  MOF can separate gases in a  $\text{CO}_2/\text{CH}_4$  system where  $\text{CO}_2$  and  $\text{CH}_4$  have differing kinetic diameters of 3.3 Å and 3.8 Å, respectively<sup>13,14</sup>. This system is interesting for gas sorption kinetics due to its different lattice dimensions leading to anisotropic pore sizes ( $a = b = 10.819 \text{ Å}$ ,  $c = 9.635 \text{ Å}$ ).

Recent studies have shown that these gas adsorption capabilities can be further enhanced through the introduction of modulators during MOF synthesis, by altering the overall crystal growth process.<sup>15</sup> In anisotropic MOFs, such as those in the  $\text{M}_2(\text{dicarboxylate})_2(\text{N-ligand})$  series, the modulator-based growth control is dramatic and can significantly alter crystal aspect ratios.<sup>16–18</sup> The introduction of modulators during synthesis can target either the carboxylate ( $h00$ ,  $0k0$ ) or the amino ( $00l$ ) planes, inhibiting crystal growth along these planes and directing MOF crystal growth

along unmodulated axes (**Figure 1**).<sup>16–18</sup> Previous work has demonstrated the  $[\text{Cu}_2(\text{NDC})_2(\text{DABCO})]_n$  (NDC=1,4-naphthalene dicarboxylate; DABCO=1,4-diazabicyclo[2.2.2]-octane) member of the  $[\text{M}_2(\text{dicarboxylate})_2(\text{N-ligand})]_n$  MOF series can be modulated to obtain rod or plate morphologies with the use of acetic acid (carboxylate) or pyridine (amino) modulators.<sup>19</sup>

The anisotropy of the unit cell, combined with modifying the crystal aspect ratio, exposes pore apertures of different dimensions on the crystal surface. The choice of modulator determines which pore aperture is exposed as the major pore aperture on the crystal surface, allowing for selection of the surface pore dimension, as well as the total internal channel length of each pore type. For example, the use of an amino modulator creates a plate morphology where a carboxylate-carboxylate aperture predominates on the crystal surface, while the use of a carboxylate modulator creates a rod morphology where more of the carboxylate-amino aperture is present on the surface of the crystal. These morphologies and their subsequent major surface pores can be used to create and tune molecular sieves for specific separation applications within the same topology.

In this work, we synthesized and characterized the  $[\text{Zn}_2(\text{NDC})_2(\text{DABCO})]_n$  MOF and controlled its morphology using pyridine and acetic acid as modulators to form plates and rods, respectively. We then demonstrated the change in separation selectivity using these two crystal morphologies in a single component adsorption system for both  $\text{CO}_2$  and  $\text{CH}_4$ .



**Figure 2.** SEM image of  $[\text{Zn}_2(\text{NDC})_2(\text{DABCO})]_n$  (a) unmodulated resulting in bulk morphology (b) 1.6 M acetic acid as a modulator resulting in rod morphology and (c) 1.6 M pyridine as a modulator resulting in plate morphology. Scale bars are 5  $\mu\text{m}$ . Reprinted with permission from [1].

**Table 1.** Minor axis, major axis, and aspect ratio measurements for different morphologies of  $[\text{Zn}_2(\text{NDC})_2(\text{DABCO})]_n$ . Reprinted with permission from [1].

| Morphology | Minor Axis ( $\mu\text{m}$ ) | Major Axis ( $\mu\text{m}$ ) | Aspect Ratio   | Major Surface Plane(s) |
|------------|------------------------------|------------------------------|----------------|------------------------|
| Bulk       | $0.3 \pm 0.1$                | $0.6 \pm 0.3$                | $2.1 \pm 1.1$  | N/A                    |
| Rod        | $1.2 \pm 0.5$                | $10.5 \pm 5.4$               | $10.1 \pm 5.3$ | (100), (010)           |
| Plate      | $0.4 \pm 0.1$                | $2.7 \pm 0.4$                | $6.9 \pm 2.5$  | (001)                  |

## Results and Discussion

### Characterization of modulated $[\text{Zn}_2(\text{NDC})_2(\text{DABCO})]_n$

By extending the rationale developed by Pham et al., rod and plate morphologies of  $[\text{Zn}_2(\text{NDC})_2(\text{DABCO})]$  can be created with the use of acetic acid (carboxylate) or pyridine (amine) modulators, respectively<sup>19</sup>. **Figure 2** shows scanning electron microscope (SEM) images of particles synthesized with no modulator, 1.6 M acetic acid as modulator, and 1.6 M pyridine as modulator. Compared to the unmodulated synthesis, the modulated syntheses show larger crystals. The acetic acid modulator shows the formation of rod like crystals, and the pyridine modulator shows the formation of plate like crystals. This confirms that modulating for different coordination modes in a MOF composed of two distinct linkers can yield drastically different morphologies. Aspect ratios of these crystals are described in **Table 1** showing both modulators increase the aspect ratio of their respective morphologies. The unmodulated MOF shows slight preferential growth to a rod-like

morphology. While the major axis for the rod morphology is in the [001] direction, the major axes for the plate morphology are in the [100] and [010] directions (**Figure 1**). It should be noted the major planes on each particle (i.e. the surfaces parallel to the major axis or axes) are associated with the carboxylate-carboxylate or carboxylate-amine pore aperture as a result of the anisotropic crystal structure.

Powder x-ray diffraction (PXRD) data was collected for  $[\text{Zn}_2(\text{NDC})_2(\text{DABCO})]_n$  MOF synthesis with and without the presence of the amine and carboxylate modulators compared to a simulated diffraction pattern (cite). These patterns show that the modulators do not alter the crystal structure. It should be noted that texture in the bulk powder sample is observed. Differing relative intensities in the peaks, specifically in those matching the (001) and (110) planes, are recorded for different morphologies. Since particle orientation affects the relative intensity of diffraction peaks, these patterns indicate a preferential crystal orientation for

a bulk powder. This is likely due to particle morphology influencing packing, orienting particles along their major axes and with respect to the substrate.<sup>20</sup> This effect is highlighted in **Figure 2c**, where plates are observed to orient in stacks.

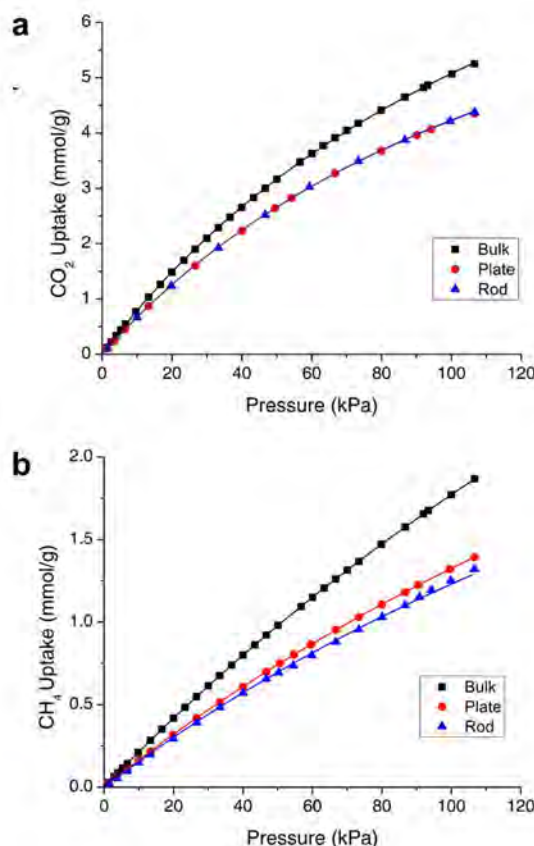
### Adsorption Isotherms

Nitrogen isotherms of the synthesized  $[\text{Zn}_2(\text{NDC})_2(\text{DABCO})]_n$  MOF were used to verify the microporosity of the synthesized material for the bulk and modulated samples.<sup>1</sup> The BET surface area (**Table 2**) and isotherms are comparable to that of reported values for the Zn and Cu analog of  $[\text{M}_2(\text{NDC})_2(\text{DABCO})]_n$  (M=Zn,Cu).<sup>16,19</sup> Experiments show that the  $[\text{Zn}_2(\text{NDC})_2(\text{DABCO})]_n$  surface area measurements are highly sensitive to the drying procedure.<sup>1</sup> The sensitivity is likely due to solvent stabilization effects observed in the  $[\text{Zn}_2(\text{dicarboxylate})_2(\text{N-ligand})]_n$  MOF family<sup>16</sup>. Previous results have shown that a MOF with a similar zinc-based topology had reduced crystallinity after activation, indicating a partial collapse of the framework<sup>16</sup>. Given this information, it is difficult to ascertain surface area contributions from defects due to modulation (i.e. defect engineering) or degradation from activation for the different modulated syntheses. However, a similarity in measured surface area between morphologies shows that any effect is similar in all three cases.

**Figure 3** shows the single-component isotherms for  $\text{CO}_2$  and  $\text{CH}_4$  of  $[\text{Zn}_2(\text{NDC})_2(\text{DABCO})]_n$  at 273 K for different morphologies. The total uptake of each species follows the same trend as BET surface area measurements, where lower quantities of  $\text{CO}_2$  and  $\text{CH}_4$  are adsorbed by lower surface area morphologies. This

**Table 2.** Brunauer, Emmet, Teller (BET) surface areas calculated from nitrogen isotherms at 77 K for different morphologies of  $[\text{Zn}_2(\text{NDC})_2(\text{DABCO})]_n$  and a reference value. Reprinted with permission from [1].

| Morphology                                                             | BET Surface Area (m <sup>2</sup> /g) |
|------------------------------------------------------------------------|--------------------------------------|
| $\text{Zn}_2(\text{NDC})_2(\text{DABCO})$<br><i>Bulk</i> <sup>33</sup> | 1000                                 |
| <i>Bulk</i>                                                            | 1226 ± 16                            |
| <i>Rod</i>                                                             | 1082 ± 76                            |



**Figure 3.** Adsorption isotherms for bulk, plate and rod morphologies of  $[\text{Zn}_2(\text{NDC})_2(\text{DABCO})]_n$  at 273 K for (a)  $\text{CO}_2$  and (b)  $\text{CH}_4$ . Reprinted with permission from [1].

**Table 3.** Langmuir isotherm fitting parameters ( $a_m$  and  $b$ ), Henry's constant ( $K$ ) and CO<sub>2</sub>/CH<sub>4</sub> selectivity for different morphologies of [Zn<sub>2</sub>(NDC)<sub>2</sub>(DABCO)]<sub>n</sub>. Reprinted with permission from [1].

| Morphology   | Adsorbate       | $a_m$<br>(mmol/g) | $b$<br>(kPa <sup>-1</sup> ) | $K$<br>(mmol/g<br>kPa) | CO <sub>2</sub> /CH <sub>4</sub><br>Selectivity, $\alpha$ |
|--------------|-----------------|-------------------|-----------------------------|------------------------|-----------------------------------------------------------|
| <i>Bulk</i>  | CO <sub>2</sub> | 12.78             | 0.0066                      | 0.0842                 | 3.85                                                      |
|              | CH <sub>4</sub> | 9.38              | 0.0023                      | 0.0219                 |                                                           |
| <i>Rod</i>   | CO <sub>2</sub> | 10.35             | 0.0069                      | 0.0716                 | 4.46                                                      |
|              | CH <sub>4</sub> | 5.26              | 0.0031                      | 0.0161                 |                                                           |
| <i>Plate</i> | CO <sub>2</sub> | 10.21             | 0.0070                      | 0.0719                 | 4.26                                                      |
|              | CH <sub>4</sub> | 6.16              | 0.0027                      | 0.0169                 |                                                           |

behavior is expected for physisorption as the quantity adsorbed is a function of the accessible surface area. The Langmuir isotherm model (Eq. 1) provides an accurate approximation of the adsorption with fitting parameters listed in **Table 3**.

$$q = a_m \frac{bP}{1 + bP} \quad (1)$$

Where  $q$  is the quantity adsorbed per mass of adsorbate,  $a_m$  is the maximum adsorbed quantity per adsorbate mass to form a complete monolayer,  $b$  is the affinity or Langmuir constant and  $P$  is the dosing pressure.

The product of  $a_m$  and  $b$  yield another constant termed Henry's constant ( $K$ ), which provides a linear approximation of the adsorption isotherm. The ratio of Henry's constants for CO<sub>2</sub> and CH<sub>4</sub> provides an equilibrium selectivity,  $\alpha$ .

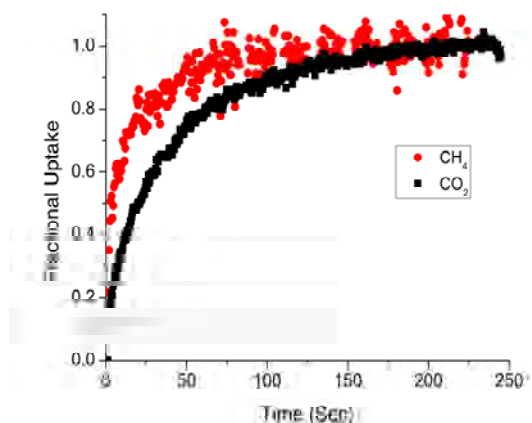
[Zn<sub>2</sub>(NDC)<sub>2</sub>(DABCO)] demonstrates moderate selectivity towards CO<sub>2</sub> compared to CH<sub>4</sub>. This value is comparable to selectivity for other MOFs under similar conditions such as the ZIF family (3.9-10.1)<sup>21</sup>, MIL-101 (3-5)<sup>22</sup> and MOF-177 (4.43).<sup>23</sup> The higher affinity of CO<sub>2</sub> to adsorb on the surface is likely due to a higher quadrupole moment.<sup>22,24</sup> Both modulated morphologies (amine and carboxylate) show a moderate increase in selectivity compared to the bulk. This may be because more defect sites are

preferentially interacting with CO<sub>2</sub><sup>25</sup>, however more work is required to confirm this interaction.

#### Surface Pore Aperture and CO<sub>2</sub>/CH<sub>4</sub> Kinetic Selectivity

As previously mentioned, the major surface for each crystal morphology, defined as the surfaces parallel to the crystal major axes, is associated with a crystallographic plane. More specifically, the plate morphology will have a major surface with a pore entrance aperture defined by the carboxylate-carboxylate frame, whereas the rod morphology will have a major surface with a pore entrance aperture defined by the carboxylate-amine frame (**Figure 1**). Each pore aperture is expected to present different mass transfer resistances.<sup>26</sup> Therefore, diffusional differences between carboxylate-carboxylate and carboxylate-amine pore apertures will exist and variation in kinetic selectivity between morphologies can be expected for the differently sized adsorbates CO<sub>2</sub> and CH<sub>4</sub>. Given the high aspect ratio of each morphology, a significant portion of diffusion is expected to occur through the major surface pore.

**Figure 4** shows representative data taken for the uptake of CO<sub>2</sub> and CH<sub>4</sub> for the bulk morphology. CH<sub>4</sub> is adsorbed more quickly,



1k  
morphology of  $[\text{Zn}_2(\text{NDC})_2(\text{DABCO})]_n$  at 273 K for  $\text{CO}_2$  and  $\text{CH}_4$ . Reprinted with permission from [1].

reaching 90% of the total uptake at around 50 seconds compared to about 125 seconds for the  $\text{CO}_2$ . This contradicts other work in microporous MOFs, which determined the diffusion of  $\text{CO}_2$  is much quicker than  $\text{CH}_4$  due to the difference in kinetic diameter.<sup>27</sup> However, such a trend agrees with the Knudsen diffusion model, which states molecules with larger mass will diffuse more slowly in pores with a diameter below that of the mean free path, as is the case for gas in microporous materials. To better understand the diffusion of each species with respect to morphologies, we apply a single-component adsorption micropore diffusion control model developed by Ruthven *et al.*<sup>28</sup> to adsorption rate data collected for  $\text{CO}_2$  and  $\text{CH}_4$  that has successfully been applied to several MOF particle systems.<sup>22,29</sup>

$$\frac{m}{m_\infty} \approx \frac{6}{\sqrt{\pi}} \sqrt{\frac{D_c t}{r_c^2}} - 3 \frac{D_c t}{r_c^2} \quad (2)$$

Where  $m/m_\infty$  is the mass uptake relative to the equilibrium uptake mass,  $D_c$  is the intracrystalline diffusivity,  $r_c$  is the crystal radius, and  $t$  is time. It should be noted *Eq. 2* is valid for  $\frac{m}{m_\infty} < 0.85$ .<sup>28</sup> This model assumes the intracrystalline diffusion resistances are much greater than

macroporous resistances in particle aggregates, diffusion is constant within the crystalline material, and the concentration of adsorbate is constant outside of the particle. All of these assumptions are valid given that the free diffusivity of gases in macropores are much greater than those in the micropores<sup>28</sup>, the gases do not condense in the micropores under the sampling conditions, and the sample tube volume can be approximated as an infinite reservoir compared to the volume adsorbed.

**Table 4** shows the diffusion time constants,  $D_c/r_c^2$ , found by fitting *Eq. 2* to multiple uptake curves for each gas species and morphology at 94 kPa (700 mmHg). Kinetic selectivity was found by dividing the diffusion time constant for  $\text{CO}_2$  by the diffusion time constant for  $\text{CH}_4$ . It can be seen that kinetic selectivity exists for  $\text{CO}_2/\text{CH}_4$  as a function of morphology. Interestingly, the  $\text{CO}_2$  diffusion time constant remains relatively constant across the different morphologies. This implies that the diffusional resistances on  $\text{CO}_2$  within the framework are not highly dependent on diffusion direction (i.e. the pore aperture size or frame chemistry) and may be dominated by more complex electrostatic interactions with the framework.<sup>30,31</sup> A two-fold increase in diffusion time constant is observed for  $\text{CH}_4$  between the plate and rod, suggesting the different pore apertures have a significant effect on diffusion through the framework. These data show the diffusion through the carboxylate-amine frame (rod) is nearly twice as fast as the carboxylate-carboxylate frame (plate). Since  $\text{CH}_4$  is thought to have little chemical or intermolecular interactions with the framework, the diffusion is likely determined by pore aperture size.<sup>32</sup> Given the linker geometry and bond rotation of 1,4-

**Table 4.** Diffusion time constants from fitting Eq. 2 to kinetic adsorption data of CO<sub>2</sub> and CH<sub>4</sub> and kinetic selectivity for varied morphologies. Reprinted with permission from [1].

| Morphology   | CO <sub>2</sub>                  | CH <sub>4</sub>                  | CO <sub>2</sub> /CH <sub>4</sub> |
|--------------|----------------------------------|----------------------------------|----------------------------------|
|              | $D_e/r_c(s^{-1}) \times 10^{-3}$ | $D_e/r_c(s^{-1}) \times 10^{-3}$ | Kinetic Selectivity              |
| <i>Bulk</i>  | <b>1.57 ± 0.07</b>               | <b>5.24 ± 0.44</b>               | <b>0.300 ± 0.028</b>             |
| <i>Rod</i>   | <b>1.73 ± 0.13</b>               | <b>8.75 ± 0.74</b>               | <b>0.197 ± 0.022</b>             |
| <i>Plate</i> | <b>1.88 ± 0.15</b>               | <b>4.72 ± 0.27</b>               | <b>0.399 ± 0.039</b>             |

naphthalenedicarboxylate, the pore aperture in the carboxylate-carboxylate frame may be significantly smaller than the carboxylate-amine frame. Such a geometry could explain why the diffusion is faster through the carboxylate-amine frame, however more work is required to understand the chemistry and structure around each pore aperture.

#### Conclusion

The anisotropic MOF [Zn<sub>2</sub>(NDC)<sub>2</sub>(DABCO)]<sub>n</sub> in the [M<sub>2</sub>(NDC)<sub>2</sub>(DABCO)]<sub>n</sub> (M=metal) family can be modulated in a similar fashion to other metal analogs. Modulation yielded high aspect ratio crystals with different pore apertures on the major surface of a given morphology. XRD and BET characterization showed modulation had little effect on the crystallinity and microporosity of the resulting materials. Furthermore, it was demonstrated [Zn<sub>2</sub>(NDC)<sub>2</sub>(DABCO)]<sub>n</sub> has a moderate equilibrium selectivity of around 4 for all morphologies, which is comparable to other MOFs. Kinetic selectivity experiments showed the diffusion of CH<sub>4</sub> into the framework as measured by a diffusion time constant was much faster than CO<sub>2</sub>. We hypothesize this may be due to other interactions controlling the CO<sub>2</sub> diffusion as the diffusion constant did not change appreciably between different morphologies

(i.e. pore apertures). We further hypothesized the pore aperture defined by the carboxylate-amine frame may be larger, as it allows for faster diffusion of CH<sub>4</sub>. Finally, oriented films were fabricated using a convective deposition technique termed solution shearing<sup>1</sup>, which can be used for creating high performance selective membranes of oriented thin film MOFs.

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1. Text and figures reprinted with permission from: Huelsenbeck, L.; Westendorff, K.S.; Gu, Y.; Marino, S.; Jung, S.; Epling, W.S.; Giri, G. Modulating and Orienting an Anisotropic Zn-Based Metal Organic Framework for Selective CH<sub>4</sub>/CO<sub>2</sub> Gas Separation. *Crystals* 2019, 9, 20.
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