

Background: Roughly one third of all human-generated carbon dioxide (CO₂) comes from coal-fired power plants¹. Due to the role of CO₂ in global climate change, reducing emissions is imperative, and its capture and sequestration at the source is highly attractive. While scrubbing technologies are currently employed as the industrial standard, they are inefficient and regeneration of the amine reagent used for CO₂ capture is expensive.¹

Several classes of adsorbent materials have been proposed as alternatives for CO₂ capture, but metal-organic frameworks (MOFs) are one of the most promising. As porous, crystalline solids, their robustness, chemical tunability, and void space for guest occlusion, i.e. a gas or solvent molecule within the pore, make MOFs highly attractive for such applications. Designing a porous material such as a MOF to replace reagent-based methods is a challenge, as it must exhibit superior selectivity for CO₂ at elevated temperatures and low partial pressures, from a mostly nitrogen-rich atmosphere. In addition to excellent CO₂ adsorption under challenging conditions, the MOF must possess a high tolerance to water, straightforward regeneration, and robustness over thousands of cycles.²

Selective gas or solvent adsorption in a static MOFs is attributed to size exclusion and/or favorable host-guest interactions.² MOFs that exhibit framework distortion upon guest addition or removal offer an additional route for tuning selectivity. Termed “breathing MOFs”, they were pioneered by Ferey and Kitagawa in the early 2000s.³ Though their body of literature has grown significantly, the ability to rationally design new breathing MOFs has yet to be demonstrated, contrary to their static counterparts.⁴ Selectivity in breathing MOFs is attributed to a “gate-opening” pressure in which the pore expands, allowing the guest to enter. This unique property could offer a superior method for designing new, more efficient materials for CO₂ capture. Thoroughly understanding how chemical environment, pore aperture, and breathing ability affect selectivity for CO₂ could yield a great leap toward designing an industrially viable material.

Objective: Utilizing isorecticular synthesis⁵, I will develop a series of porous, breathing MOFs tailored for CO₂ capture. Exceptional guest selectivity will be achieved through optimizing a synergistic relationship between functionality, pore availability (i.e. aperture), and breathing motif. By tuning the pore environment in such a way, it will be possible to enhance the initial framework-CO₂ attraction and reduce the available “gate-opening” pressure to that of CO₂.

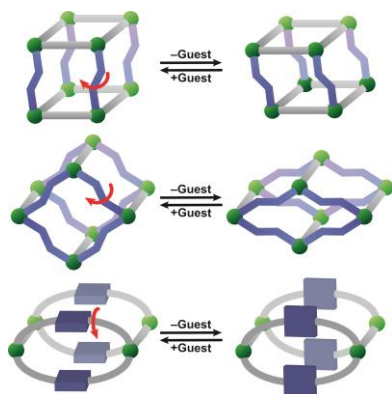


Figure 1: Illustration depicting ligand rotation in breathing MOFs.

Methodology: Using a set of semi-rigid, organic linkers where size, shape, and functional groups have been altered, I will synthesize 2-pillared, 2D sheet MOFs or 1D tube MOFs, which are also referred to as metal-organic nanotubes (MONTs). Continuing work started in the [redacted] group⁶, these breathing MOFs will exhibit guest-dependent rotation of the ligand (Figure 1). Characterization using X-ray diffraction methods will be employed. For MOFs in which breathing is a result of rotation of phenyl rings in the ligand, breathing can be verified by ¹³C CP MAS NMR, as demonstrated in a publication currently under revision by the [redacted] group.

Tuning pore size and functionality within a framework has been well documented⁵. Triazole ligands of increasing size that adopt a *syn*-geometry will be incorporated into the frameworks, and isorecticular synthesis will be exploited by adorning the non-triazole moiety with amino, nitrile, hydroxyl, methyl, halide, and ester groups, similar to previous reports (Figure 2).^{5,7} Experimental evidence show that these alterations can affect a framework’s selectivity for CO₂

over CH₄, N₂, and O₂; moreover, nitrogen-containing functional groups tend to enhance the framework-gas attraction via a Lewis acid-base interaction.⁸ My first aim is to identify the functional groups that enhance framework interaction with CO₂ in breathing MOFs. From there, I will determine the role of pore aperture by systematically increasing the ligand size. The final variable to evaluate if breathing mechanism influences selective CO₂ adsorption. The effects of these alterations can be understood by single and multi-component gas adsorption studies. Selectivity will be evaluated according to previously-published methods that evaluate the role of kinetic favorability in mixed-gas systems.⁷

Anticipated Results: My work will result in the development of a porous, breathing MOF that will outperform the most highly-selective materials to date for selective CO₂ adsorption in mixed-gas systems.⁷ Preparation of such a MOF could form a platform for newer, more efficient materials to be developed. My findings will be presented at regional and national conferences, and published in relevant peer-reviewed journal articles.

Broader Impacts: Because of the correlation between increased atmospheric CO₂ levels and rising global temperatures, curbing anthropogenic CO₂ emissions is a goal of utmost importance for our society; capturing these emissions at the source is highly attractive. In addition, synthetic chemists are seeking routes to convert CO₂ to valuable commercial commodities like plastics⁹ and synthetic fuels.¹⁰ Efficient capture of CO₂ will help advance these processes, as CO₂ is an abundant C₁-feedstock. Development of a highly selective and efficient porous, adsorbent material for CO₂ capture from coal-fired power plants would be invaluable for its environmental and economic benefits.

Intellectual Merit: My relevant experience working with gas storage materials at both [REDACTED] and [REDACTED] has prepared me well for graduate work at the University of [REDACTED], where I will work under Dr. [REDACTED]. I possess strong synthetic skills and a familiarity with an array of characterization techniques (see personal statement). I have presented posters and oral presentations at several regional and national conferences, and was recently published¹¹ as a co-author for my work at [REDACTED].

As a Latino in science, I hope to mentor young scientists from underrepresented backgrounds in STEM fields through tutoring and educational outreach initiatives. My leadership role at a non-profit organization (see personal statement) has left me with the experience to engage the general public in educational discourse, and I hope to foster an understanding of basic science in our society. Whether I pursue academia, industry, or government-employment, I look forward to joining the generations of scientists who will solve the greatest issues of our age.

References

- [1] *Science* **2007**, 317 (5835), 184-186. [2] *Coord. Chem. Rev.* **2011**, 255 (15-16), 1791-1823. [3] *Chem. Soc. Rev.* **2009**, 38 (5), 1380-1399. [4] *Coord. Chem. Rev.* **2014**, 258-259 (0), 119-136. [5] *Science* **2002**, 295 (5554), 469-472. [6] [REDACTED]. [7] *Proc. Natl. Acad. Sci. USA* **2009**, 106 (49), 20637-20640. [8] *J. Am. Chem. Soc.* **2009**, 131 (11), 3875-3877. [9] <http://www.research.bayer.com/en/CO2.aspx>, 2012. [10] *Chem. Ing. Tech.* **2013**, 85 (4), 489-499. [11] [REDACTED].

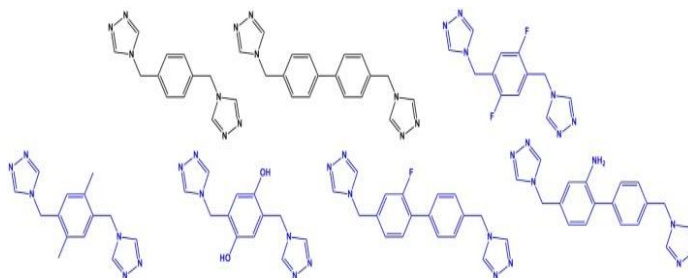


Figure 2: Representative ligands for MOF synthesis.