

## Design and Synthesis of Metalated Porous Organic Cages

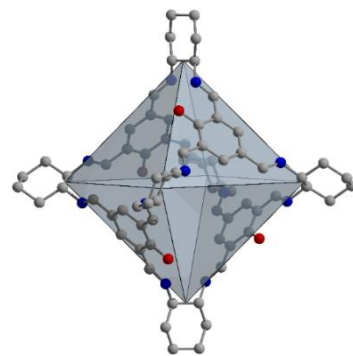
**Motivation:** Since the mid-1970s, global natural gas production has steadily risen to its current all-time high, and is projected to continue until at least 2040.<sup>1</sup> Although natural gas is a cleaner burning fuel than gasoline, its implementation in the transportation sector has been stymied by its significantly lower volumetric energy density.<sup>2</sup> Densification strategies, including liquefaction or high-pressure storage, have inherent safety and cost issues that are widely viewed as prohibitive for passenger vehicles.<sup>3</sup>

**Introduction:** Adsorbed natural gas systems that employ porous materials, such as metal-organic frameworks (MOFs) and covalent organic frameworks (COFs), have received considerable attention as potential alternatives to higher pressure and/or cryogenic storage methods.<sup>4,5</sup> In these systems, favorable interactions between the gas and the porous solid increase the amount of gas that can be stored at a given temperature and pressure as compared to an empty tank.<sup>4</sup> However, the non-molecular nature of these extended structures makes solubility non-existent, reducing compatibility with post-synthetic functionalization and modification that can be leveraged to increase gas adsorption capacity and bulk material properties, such as density and thermal conductivity.

Hybrid metal-organic or all-organic molecular analogs of these porous materials, coined porous coordination cages (PCCs) and porous organic cages (POCs), respectively, directly address this issue while retaining the highly sought after permanent porosity and tunability of their expanded, 3-D counterparts.<sup>6,7</sup> PCCs often contain open metal sites that provide favorable interactions for increased gas storage as compared to all-organic structures.<sup>6</sup> However, these molecules tend to display surface areas that pale in comparison to MOFs and POCs. On the other hand, POCs display surface areas that are on par with many MOFs, but lack the tunable metal cation-gas molecule interactions seen in hybrid metal-organic systems.<sup>8</sup> To address these issues, *I propose the design, synthesis, and application of novel porous organic cages with integrated metal sites toward the selective adsorption and/or storage of small molecules.*

**Preliminary Results:** Although porous organic cages have been heavily investigated over the past decade, the study of the high-pressure storage of gases in these materials is still well in its infancy.<sup>7</sup> As a result, relatively little is known about their utility as gas storage materials. Similarly, post-synthetic metalation of these systems to introduce sites with catalytic activity or selective gas adsorption has been unexplored. The standard metric for porous materials, gravimetric surface area, is a simplistic representation of a material's ability to store a gas. While the high surface areas that POCs have displayed provide a basis for using such materials as gas storage media, investigations into these materials for the specific task of gas storage is surprisingly limited. Incorporation of metal chelating sites within molecular cages will allow for the precise insertion of a specific metal post-synthetically. Metal cations can play an important role in tuning metal-gas interactions, which is necessary for creating a material for selective gas adsorption or high-pressure storage. I targeted a known POC based on triformylphenol and 1,2-diaminocyclohexane, where a half-salen unit is formed when the cage is constructed (Figure 1).<sup>9</sup> Confirmed *via* SEM-EDX and XPS, initial results show coordination of a Ni<sup>2+</sup> center into the cage's structure, while retaining permanent porosity (Figure 2). Further gas adsorption studies to better understand the selectivity of the metal-integrated POC are currently underway.

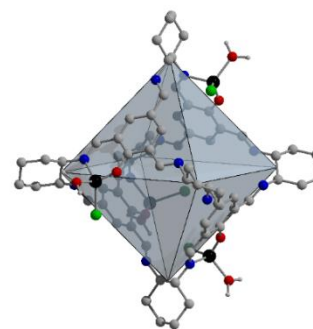
**Aim 1:** *Create a library of ligands and cage topologies that are conducive to metal integration.* Inspiration for this approach can be drawn from recent literature on the reported topologies of cages, where the most straightforward methods involve imine or boronic ester formation to create the covalently linked cage. Although specific angles must be considered within the ligands in order to access these desired topologies, functional groups and sizes of the ligands are typically tunable. Understanding this, cages will be



**Figure 1:** Known POC targeted for preliminary work

functionalized and built around traditional multi-dentate ligands, such as salen, catechol, and 2,2'-bipyridine to form metal complexes after cage isolation.

**Aim 2:** *Isolate porous organic cages and introduce metals to their chelating sites.* Typically, solution-based syntheses produce cages. The purity of isolated cages can be confirmed through several techniques due to their molecular nature, most readily being high-resolution mass spectrometry, NMR, and IR spectroscopy. For more complex cages, such as cages containing chiral centers, additional efforts will be put forth to obtain diffraction quality single crystals, utilizing techniques such as vapor diffusion and liquid/liquid diffusion, to further confirm cage formation. After successful isolation, the porous organic cages will then



**Figure 2:** Model representing the integration of  $\text{Ni}^{2+}$

be introduced to metal salts to obtain their metalated counterparts *via* solvothermal methods and solid-state metalations. A plethora of techniques are available at the University of Delaware for the characterization of the metalated POCs, including SEM-EDX, XPS, EPR, and the previously mentioned techniques.

**Aim 3:** *Perform gas adsorption studies and identify the roles that both cages and metal-sites play in selective gas uptake and storage.* Gas adsorption studies will be performed on both the base cage and the metalated cage to decipher the interplay of porosity and selective gas uptake. Surface area analyses will be performed in the Bloch Lab, using both  $\text{CO}_2$  and  $\text{N}_2$  as probe molecules, along with systematic high-pressure gas storage studies (hydrocarbons,  $\text{H}_2$ , etc.) and enthalpy of adsorption calculations.

**Intellectual Merit:** While small molecule storage has been heavily studied in extended frameworks like MOFs and COFs, much less is known for porous *molecular* materials. These materials retain the sought after permanent porosity of expanded frameworks, as well as impart solubility that can lead to advantageous post-synthetic modification. This project will elucidate how POCs can be utilized as gas storage media and develop the novel field of metalated POCs, including their design, synthesis, and utilization as adsorbed natural gas materials.

**Broader Impacts:** My proposed project has opportunities for collaborations that I will pursue heavily to better understand these systems. Collaboration with computational groups will help predict gas storage capacities and suggest more favorable interactions based on metals and ligands, and work with catalysis-focused groups can utilize my metalated cages as a homogenous setting for catalytic reactions. Just as importantly, I will continue to mentor undergraduate researchers and first year graduate students to teach them essential and advanced laboratory skills. I will share my findings at local, national, and international meetings when they are deemed safe, and until then, I will present my work virtually and continue to publish results.

## References

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