Introduction:
The need for materials that can selectively separate carbon dioxide from other gases is great. The impacts of global climate change are becoming more evident, and isolation of carbon dioxide at the point of generation is one of the proposed methods of mediating this global challenge. According to the United Nations Intergovernmental Panel on Climate Change in its Fifth Assessment Report, human activity is “extremely likely (95-100%) to have been the dominant cause of the observed warming since the mid-20th century.” It further states that the results of this climate change will have impacts that “include alteration of ecosystems, disruption of food production and water supply, damage to infrastructure and settlements, human morbidity and mortality and consequences for mental health and human well-being.” One method to offset human production of greenhouse gas is carbon dioxide capture and sequestration (CCS). The current industrial standard is wet scrubbing, where alkanolamines capture carbon dioxide through carbamate formation. While this method is effective, release of the carbon dioxide and regeneration of the capture media could increase overall energy consumption by as much as 40%.

New materials are being investigated as potential carbon capture media, which must selectively adsorb carbon dioxide over other gases present in the atmosphere and in waste streams. It must be easy to regenerate, requiring a small energy input to release the pure carbon dioxide for sequestration or as a chemical feedstock. Metal-organic frameworks (MOFs) are emerging as promising materials for carbon capture. MOFs are crystalline, porous solids composed of metal ions and polyfunctional organic linkers. One major advantage of MOFs is that pore shape and size can be varied, and the functionality of the pores can also be controlled through ligand design and the coordination environment of metal centers.

Our strategy for the selective capture of carbon dioxide is to incorporate open Lewis base sites within the pores of MOFs. While carbon dioxide is a non-polar molecule, it does possess two polar C=O bonds, resulting in a partial positive charge on its carbon atom which can interact with an electron donor. The major components of the atmosphere (N₂, O₂) are homonuclear diatomics and nonpolar, precluding such an interaction. An additional benefit of our strategy is that the interaction we are seeking to employ is strictly physical in nature (physisorption), which should be reversible at a lower energy
cost than that observed in wet-scrubbing where a chemical change occurs (chemisorption) upon carbamate formation. Generating open Lewis base sites within MOFs is not trivial given the propensity of these functional groups to act as ligands, resulting in a relative scarcity of such solids in the literature.3,4

**Linker Design, Synthesis and Structure:**

Our lab has been exploring 9H-carbazole-2,7-dicarboxylate as a linker, generating frameworks from a variety of metals and with an assortment of structures.5 Cadmium, zinc and zirconium networks have been reported in the literature.6,7,8 In analyzing the gas sorption properties of networks with this linker, we have observed a relatively low selectivity for the adsorption of carbon dioxide versus dinitrogen. To increase this selectivity, we have been working to produce frameworks incorporating stronger Lewis base groups. The nitrogen atom of the carbazole presents a point of functionalization, and we have begun to couple pyridyl groups to this atom to yield a significantly more basic 4-aminopyridyl functionality. The strong basicity presents the problem that the pyridyl group can compete with the carboxylate for binding to the metal center. To help avoid this competitive binding, we have incorporated 2,6-substitution of the pyridyl ring, such that the steric hindrance could reduce the competence of the pyridine as a ligand, while maintaining the basicity for adsorption of carbon dioxide.

Synthesis of the desired pyridyl-carbazole starts with the commercially available dimethyl-4,4′-biphenyldicarboxylate and 2,6-dimethyl-4-hydroxypyridine via a multistep process (Scheme 1). The biphenyl dicarboxylate is mono-nitrated via literature procedure, 9,10 and the carbazole is generated via a ring-closing Cadogan reaction to yield dimethyl 9H-carbazole-2,7-dicarboxylate.11,12 2,6-dimethyl-4-hydroxypyridine13 is converted to the 4-iodopyridine through the triflate complex via literature procedure,1415-16 which is then coupled to the carbazole diester via a Buchwald-Hartwig cross coupling reaction.17 Refluxing one equivalent of the carbazole di-ester with two equivalents of the iodopyridine, three equivalents of cesium carbonate and five mole percent of bis(tri-tert-butylphosphine)palladium in toluene under an inert nitrogen atmosphere yields a white/gray solid in 85% yield after washing with ethyl acetate. For use in solvothermal syntheses of coordination polymers, the carbazole ester is converted to the dicarboxylic acid via standard base hydrolysis methods in 92% yield.
Single crystals of the pyridyl-carbazole ester suitable for an X-ray diffraction study were grown from the slow evaporation of dichloromethane. In the solid state, the compound crystallizes with half a molecule in the asymmetric unit; the carbazole and ester groups lie in a plane that varies from the plane of the pyridine ring by 43.3 degrees. The molecules are aligned in the solid-state by intermolecular π-π interactions between the six-membered rings of the carbazoles and those of the pyridines. Figure 1 shows the molecular structure of the compound, and the packing of the molecule.

Figure 1. The molecular structure (left) and packing (right) of the pyridyl-carbazole ester.

**Coordination Polymer Synthesis and Structure**

A cadmium coordination polymer was synthesized in a thick-walled glass tube, when 0.0239 mmol of the pyridyl-carbazole diacid and 2 equivalents of cadmium (II) nitrate tetrahydrate were combined in 3 mL of dimethylformamide. The tube was degassed via three freeze-pump-thaw cycles. The evacuated tube was sealed with a methane-oxygen torch and placed in a 110 °C oven for two days, after which pale gold needle crystals had formed. The crystals were isolated and analyzed by X-ray diffraction.
The crystalline network has a linear trimetallic cadmium secondary building unit with six bridging carboxylates and two dimethylformamide molecules (Figure 2). The cluster is capped by two pyridine groups from the carbazole. We have observed similar SBUs in cobalt and manganese coordination polymers using the parent carbazole linker, and similar SBUs have been reported in the literature.\textsuperscript{18,19,20,21} The packing of

\textbf{Figure 2.} The secondary building unit of the Cadmium coordination polymer

the framework is shown in Figure 3. The trimeric SBUs are connected by the carboxylate linkages to generate two dimensional sheets. The coordination of the pyridine groups at the two terminal cadmium atoms joins these sheets together to generate a three dimensional network. While two of the pyridine groups are coordinated to cadmium centers, one out of every three is still left open the structure. Unfortunately, the binding observed in this structure leads to a structure that is not porous, with a void volume of only 11.6%.

\textbf{Figure 3.} The packing of the Cadmium coordination polymer shown along the A face (top left), the B face (right) and the C face (bottom left).

\textbf{Future Directions}

While we have managed to synthesize our targeted ligand and structurally characterize a cadmium coordination polymer with this linker, the resulting solid does not possess the porous structure that we desire. To address this, we are exploring solvo-thermal syntheses
with a variety of metal ions, including transition metals and lanthanides, to produce secondary building units that yield a porous material. As our other target is to have open Lewis base sites within the network, the reported structure having two out of three pyridines coordinated to metal centers is not desirable. To address this issue, we are altering the 2,6-substitution of the pyridine (Ph, tBu), such that the steric hindrance reduces the competence of the pyridyl group as a ligand, while still being accessible for carbon dioxide. When we gain our targeted network – porous with open pyridine groups – the gas adsorption properties, selectivities and heats of adsorption will be analyzed using a Micromeretics ASAP2020 Physisorption analyzer. We have also begun ab initio calculations to examine the interactions of carbon dioxide with our linkers.

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References: