Summer Scholar Report

Carbazole-based metal-organic frameworks for gas separations

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Introduction

The United Nations Intergovernmental Panel on Climate Change recently released its Fifth Assessment Report, in which they stated with 95% certainty that human activity was responsible for the climate change observed over the past half century. Since the beginning of the Industrial Revolution, the concentration of carbon dioxide in the atmosphere has increased by 40%, the greater part of which is attributed to the burning of fossil fuels.[1] One method to offset human production of green house gas is carbon dioxide capture and sequestration. The current industrial standard is wet scrubbing, where alkanolamines capture carbon dioxide through carbamate formation. While this method is effective in the capture of carbon dioxide, release of the CO_2 and regeneration of the capture media could increase overall energy input by as much as 40%.[2]

New technologies are being investigated as potential carbon capture media, with metal-organic frameworks (MOFs) emerging as one possible solution. MOFs provide many advantages over other materials, including large open pores and structural regularity. Perhaps most beneficial is that the materials can be readily modified through the judicious selection of metal ions and organic linkers. Pore shape and size can be varied, and the functionality of the pores can also be controlled.

Our approach to carbon dioxide capture is the inclusion of open Lewis base sites within the pores of an MOF. Primary atmospheric gases (N_2, O_2) possess non-polar bonds, while carbon dioxide's polar bonds result in a partial positive charge on the carbon atom. Materials with open Lewis base sites included should selectively adsorb carbon dioxide due to a Lewis acid/base interaction. If this interaction is strictly physical in nature (physisorption), then the reversibility would have a lower energy cost than observed in wet- scrubbing where a chemical change occurs (chemisorption). Generating open Lewis base sites within MOFs is not trivial, given the propensity of these functional groups to act as ligands. This has resulted in a relative scarcity of such solids in the literature. Herein are described some efforts towards producing such materials.

Linker Synthesis

The structure and functionality of an MOF is greatly impacted by the selected organic linker. For this project, derivatives of carbazole dicarboxylates were chosen. The dicarboxylate motif has demonstrated great success in the production of highly porous MOFs.[3] The carbazole group provides a single Lewis base site sufficiently removed from the carboxylates to avoid chelation

or competition for binding. Additionally, the nitrogen-containing carbazole provides a site for interaction with carbon dioxide and can also be substituted with other functionalities to enhance the Lewis base character in the pores.

Synthesis of the desired carbazole from commercially available dimethyl biphenyl-4,4' - dicarboxylate can be accomplished via two routes, both of which begin with mono-nitration of the biphenyl, as reported by Olkhovik, et al. [4] The literature method for carbazole formation involves three steps, the first of which is reduction of the nitro group to an aniline, a reaction that runs for ten days. The amino group is converted to an azide, which then undergoes a thermal ring closure to carbazole over 40 hours. To avoid the use of an azide and long reaction times, alternative reaction conditions were explored.

One method for the generation of carbazoles is a Cadogan reaction; the reaction of 2-nitrobiphenyls with organophosphorous reagents.[5] One previous attempt to synthesize the targeted carbazole via a Cadogan reaction was reported using triphenyl phosphine, but demonstrated low yield and low purity.[4] We were able to optimize a Cadogan reaction to produce pure dimethyl 9H-carbazole-2,7-dicarboxylate in 45% yield (Scheme 1). Refluxing 4,4'-dimethyl-2-nitrophenyl dicarboxylate in neat triethyl phosphite for 12 hours, followed by cooling of the reaction mixture, resulted in precipitate formation. After filtration and washing with benzene, an off-white solid was isolated that proved to be the pure carbazole. While the yield for this reaction is lower than that of the azide route (45% vs. 79%), we feel that the quickness, ease of purification, and removal of the azide step make it a favorable alternative. For use in solvothermal MOF syntheses, the carbazole ester was hydrolyzed to its acid form. This was accomplished via standard base hydrolysis methods in 94% yield.
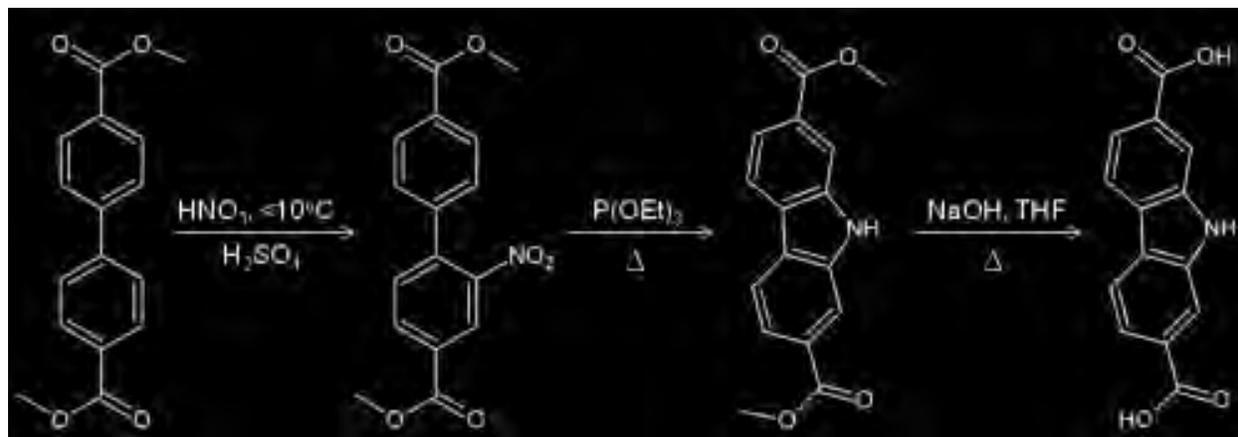
Scheme 1. Synthesis of 9H-carbazole-2,7-dicarboxylate accomplished via nitration, a Cadogan reaction, and base hydrolysis.

Metal-Organic Framework Synthesis and Structure

Utilizing this carbazole acid, a manganese MOF was synthesized in a thick-walled glass tube, when 0.125 mmol of 9H-carbazole-2,7-dicarboxylic acid and 1 equivalent of manganese(II) nitrate tetrahydrate were combined in 3mL of dimethylacetamide. The tube was degassed via three freeze-pump-thaw cycles. The evacuated tube was sealed with a methane-oxygen
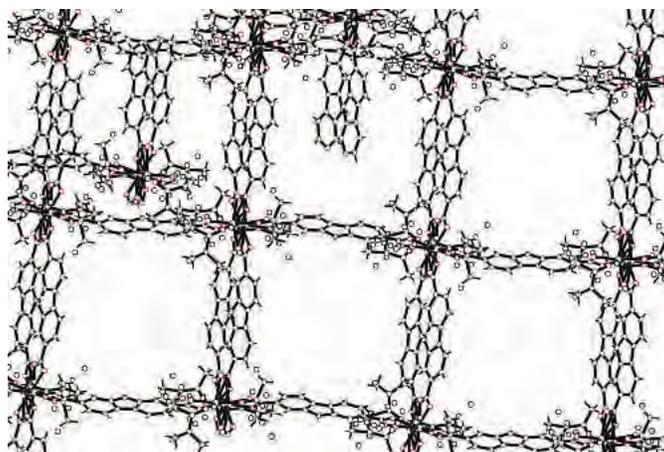

Figure 1. The solid state structure of the carbazole-based Mn MOF.

torch and placed in a 110°C oven for seven days, at which point tan to pale orange rectangular crystals had formed. The crystals were isolated and analyzed by X-ray diffraction (Figure 1).[6] In the asymmetric unit, there are three distinct metal centers arranged in a linear trinuclear cluster. The two terminal manganese centers are bound by four oxygen atoms from three carboxylates and two solvent oxygen atoms each. The central manganese atom is bound by six oxygen atoms from six carboxylates. All three metal centers are in pseudo-octahedral configuration. Similar Mn$_3$ secondary building units (SBUs) have been previously observed.[7-10] The trimanganese hexacarboxylate units combine to form two-dimensional sheets that are connected through N– HO hydrogen bonds. The Platon program SQUEEZE[11] was used to address unrefined solvent, which was treated as 12 dimethylacetamide molecules that when removed generate a void volume of 2064 Å.^{3} Gas adsorption studies are currently being performed on this material and will be reported at a later date.

Future Directions

Beyond producing MOFs with 9H-carbazole ligands, we are seeking to couple pyridyl groups at these positions to generate linkers with the motif proposed in Figure 2. The 4-aminopyridyl functionality of this linker would enhance the basicity of the open Lewis base site. The addition of 2,6- dialkyl substitution on the pyridyl ring should temper the ability of the pyridine to

compete with the carboxylate as a metal binder. The steric hindrance should not greatly impact interaction with small molecules like carbon dioxide.

To this end, I began to explore the coupling of 2,6- lutidines to the carbazole. This began with the production of 2,6-dimethyl-4-triflatopyridine from 4-hydroxy-2,6- dimethylpyridine.[12] The utilization of this yellow oil proved to be difficult, as it decomposed to form the dipyridinium ether 4,4'-oxybis(2,6-dimethylpyridinium)bis(trifluo- romethanesulfonate) (Figure 3). Colorless crystals of this decomposition product were isolated and analyzed by X-ray diffraction.[13]
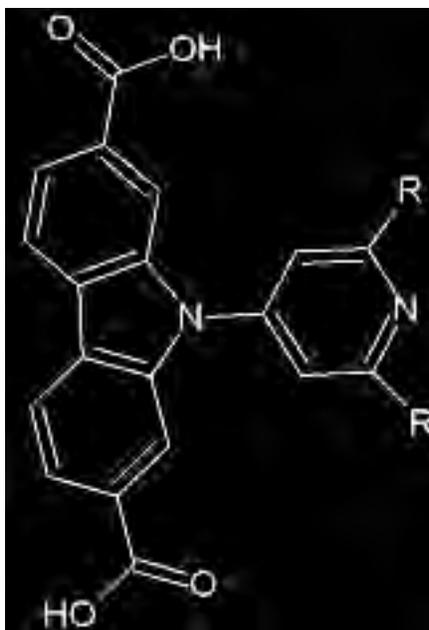

Figure 2. Proposed organic linker with a 2,6-disubstituted- 4-aminopyridine motif. (R=alkyl)
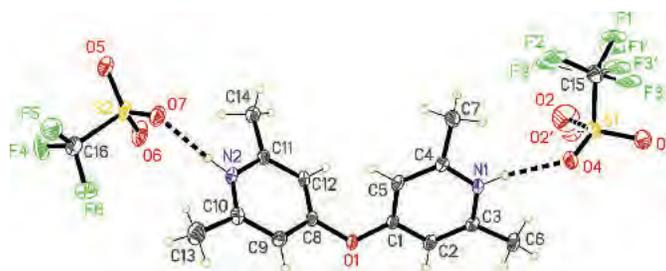

Figure 3. The molecular structure of the 4,4'-oxybis(2,6-dimethylpyridinium) bis (trifluoromethanesulfonate), with displacement ellipsoids drawn at the 50% probability level.
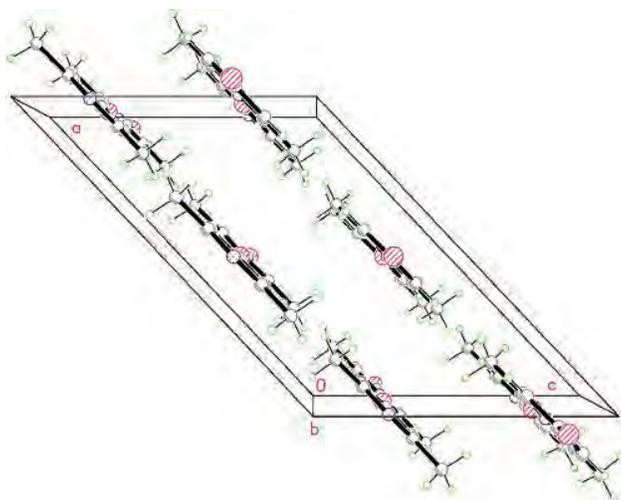
Figure 4. The unit cell of 4-iodo-2,6-dimethylpyridine along the b-face.

The structure is typical of a dipyridyl ether, with a C–O–C bond angle of 119.3$^{\text{o}}$ and C–O bond lengths of 1.364 Å and 1.389 Å.[14] The dissimilar C–O–C–C torsion angle of 61.5$^{\text{o}}$ and 15.1$^{\text{o}}$ result in what is defined as a skew conformation for bridged diaryls.[15]

To avoid the stability issues associated with the pyridyl triflate, it was converted to the 4-iodo-2,6-dimethylpyridine (Scheme 2).[16] The crystal structure of the resulting solid was also determined. The structure of the pyridyl ring is as expected, but the molecules arrange in sheets (Figure 4) held together by short N–I contacts of 3.161Å. The coupling reaction conditions are still being optimized, and work is being done to modify the 2,6-alkyl groups to bulkier substituents.
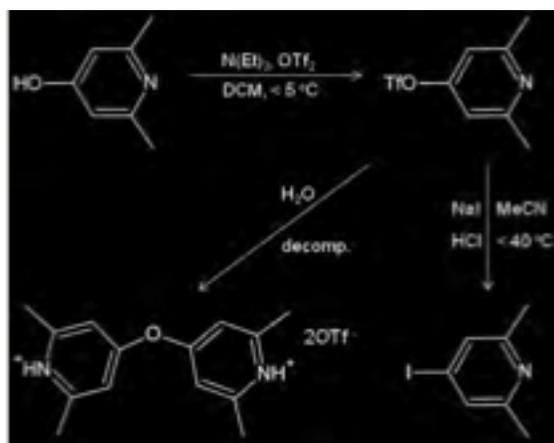
Scheme 2. Synthesis of 2,6-dimethyl-4-triflatopyridine, its decomposition in the presence of moist air, and its conversion to 4-iodo-2,6-dimethylpyridine.

Acknowledgements

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