The Synthesis and Characterization of Corannulene-Based Metal-Organic Frameworks

MaryGrace H. Rainsford

South Carolina Governor’s School for Science and Mathematics

Due to the great demands within the energy community, the need to develop materials that can significantly alter the vitality of different substances is one of the top priorities of researchers. In recent years, metal-organic frameworks (MOFs) have been synthesized to potentially be used as these advances. The objective of this project is to specifically alter the synthetic route of corannulene-based MOFs to create a new anode for a Li-ion battery used in hybrid cars. Due to the crystalline materials porosity and high surface area, the rate performance of this battery can effectively be improved. To do this, a three step synthetic route resulting in dimethyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaboralon-2-yl)-isophthale was proposed with the goal of successfully improving the anode material for Li-ion batteries as compared to the previously used graphite. The crystals were tested for crystallinity using nuclear magnetic resonance (NMR). Results from the NMR graphs from each step of the synthetic route convey that the desired crystals were successfully made with the correct alignment of hydrogens throughout the product. From this work it can be deduced that additional work with corannulene-based metal-organic frameworks is promising because of their advantageous properties. In the future, the viability of its synthetic route can continue to be improved so it can be used within even more applications.

Introduction

Metal-organic frameworks (MOFs) are crystalline hybrid materials constructed of metal nodes coordinated to organic linkers in order to form one, two, or three, dimensional frameworks. They have significant potential for use in Li-ion hybrid car batteries due to the fact that they are porous, crystalline materials, with a high surface area and a great degree of structural integrity. Since their discovery in 1988 by Yaghi, porous MOFs have attracted a great deal of research activity. In particular, researchers have sought to increase the viability of their synthetic route (Cook et al, 2012). In the past, the Shustova Group successfully synthesized a two-dimensional MOF. Now, we aim to successfully produce a synthetic route that can make the necessary three-dimensional MOF that will provide the possibility of many advances within the energy community.

To produce such advances, we propose the use of corannulene-based metal-organic frameworks with the goal of successfully creating a complete and more viable synthetic route of the crystalline material. Corannulene, C_{20}H_{16}, is a bowl-shaped polyaromatic hydrocarbon and is the smallest subunit of fullerene, its parent molecule, to retain a curved surface. It can accept four electrons to form a tetraanion compared to fullerene which can accept six electrons. This smaller number of accepted electrons implies that corannulene is more electron rich per carbon than fullerene (Fellows, 2016). Another advantage is that this corannulene-based MOF has the potential to act as the anode material in Li-ion batteries. Due to its porosity and high surface area, the anode can allow faster diffusion of the Li⁺ ion improving rate performance of the battery (Han, 2015). It is also possible someday to incorporate them into devices such as organic-light emitting diodes (OLED) and solar panels due to their fluorescence and high surface area. Additional work is promising because of MOFs advantageous properties as well as their potential to be used in so many applications.

Methods

To complete the overall synthesis of 3,5-bis(methoxycarbonyl)phenylboronic acid, we must divide the process into three steps as shown in Figure 1. First, we must start with purifying a solution that we can then turn into solid crystals through the process of recrystallization. To confirm crystallinity, analysis is done through purified x-ray diffraction (PXRD) which characterizes the crystals and where the electrons are located within it. Then we must repeat the process of filtering and purification in the reverse order to turn the solution back to a liquid state. Lastly, we transform this liquid solution through extraction, washing, and drying to produce a final solid crystal. The crystallinity of these solids are once again tested using PXRD.

Step One-Dimethyl 5-aminooiso phthalate

To create a solution that could be purified, a beginning solution of dimethyl 5-aminooiso phthalate was dissolved in 134 mL of 6 M hydrochloric acid. A container was then prepared with ice and water, creating an ice bath for the solution to sit in and be cooled to 0°C. A separate solution of sodium nitrate in 33.5 mL of water was prepared and then added to the beginning solution. Remaining at 0°C, it was then stirred for two hours. Another separate solution of potassium iodide in 108.8 mL of water was also cooled to 0°C in an ice bath and then slowly added dropwise with the periodical addition of 228 mL dichloromethane (DCM). The solution could then be purified using a silica plug. The top of the condenser was filled with one inch of silica using a funnel. This powder was then wet with DCM. With an empty round bottom flask below, the material was then added to the top of the plug. DCM was continuously added until the solution finally turned a clear color. When the solution was clear, the solution was evaporated using a rotovap. With a solid solution in the round bottom flask, the recrystallization process could then be performed. A small amount of methanol was added while swirling the flask to ultimately dissolve the powder. If all of the powder could not dissolve with just methanol, a heat gun was used to dissolve more. The goal was to add the minimum amount possible of methanol and still have the powder dissolve. After allowing the solution to cool, the crystals then started to form. It was then filtered and the crystals were collected.

Confirmation of Crystallinity

Nuclear Magnetic Resonance (NMR) is a commonly used method for characterizing crystalline material. NMR identifies the carbon-hydrogen framework of an organic compound. In the compound, a magnetic field is generated by the atomic nucleus as a spinning charged particle and with an external magnetic field present, the nuclei align themselves either move with or against the field of the external magnet. The crystallinity of the collected crystals was confirmed through the use of NMR.

Step Two-Dimethyl 5-iodoisophthalate

A solution of 8.45 g of dimethyl 5-iodoisophthalate resulted from the previous step. This was then added to a round bottom flask along with the addition of 6.71 g of bis(pinaeolato) diboron, 0.16 g of Pd(acetate)$_2$, 7.67 g of potassium acetate, and 58.64 mL of dimethylformamide DMF. This
was then heated to 90°C for twelve hours. After this, 160 mL of water was added and it was stirred for ten minutes allowing it to precipitate. It was then filtered. To precipitate the black palladium, DCM was dissolved in the solution. This was then filtered to collect the extra unneeded black part of the product. This step was repeated until all of the palladium was gone. To purify this solution, a silica plug was once again used. The top of the condenser was filled with one inch of silica using a funnel. A separate solution of 100 mL of ethyl acetate and 400 mL of hexane was made to add to the plug. This solution was added to create the final needed product for step three.

**Step Three-Dimethyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-isophthalate**

A solution of 5.32 g of dimethyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-isophthalate resulted from the previous step. To this boronic ester, 108 mL of tetrahydrofuran, 27 mL of water, and 10.65 g of sodium periodate was added. This was then stirred for thirty minutes. After thirty minutes 12 mL of 1 M hydrochloric acid was added. It was then stirred for seventeen hours. An equal volume of water compared to the solution was then added. This was then extracted with ethyl acetate using a separatory funnel. The ethyl acetate is denser than the water so it collected the product and rose to the top. Only the top part of the solution was kept. The extraction process was repeated until all of the unwanted thicker liquid was gone. The wanted product was then washed twice with a 1:1 solution of brine to water. It was then dried with sodium sulfate and filtered. The solution was then evaporated using the rotovap. The powder product was washed with hexane and it was filtered to collect the final crystal product. Using PXRD again, we analyzed the crystallinity of the crystalline material.

**Results**

**Nuclear Magnetic Resonance**

From our nuclear magnetic resonance (NMR) we found some basic apparent patterns. As shown in Figures 2, 4 and 5, the molecular structure of the compound is shown as well as the NMR graph of the structure. For each step in the synthesis process we used NMR to characterize what we made. The goal was to determine the number of equivalent protons within the compound. The product from the first step, dimethyl 5-iodoisophthalate, corresponds to Figure 2. A smaller peak was observed where the double bonded carbons are at around 8.22 and 8.56 parts per million of the compound and a larger peak was observed around 3.89 ppm where the covalent bond with carbon and oxygen is. The actual crystal product of the dimethyl 5-iodoisophthalate is shown in Figure 1.

The HNMR results from the product from the second step, dimethyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isophthalate, corresponds to Figure 3. A smaller peak was observed around 8.25 ppm where the double bonded carbons are. A slightly larger peak was then noticed around 3.89 ppm where the covalent bonds between the carbon and oxygen’s are. The largest peak was observed around 1.20 ppm where the methyl group bonds in the boronic ester.

Finally, the product of the third step, (3,5-bis(methoxycarbonyl)phenyl)boronic acid, corresponds to Figure 4. A small peak was observed around 8.25 ppm where the double bonded carbons are. A very small barely observable peak was noticed around 4.2 ppm where the boron bonds to the hydroxides. A large peak was observed around 3.89 ppm where the carbonyl bond to the oxygen’s. The final crystal product of the dimethyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isophthalate is shown in Figure 5.

**Discussion**

We made significant progress synthesizing the corannulene-based metal-organic framework. The results demonstrate this progress through the results of each of the steps in the three-step synthetic route that we used to make the organic linker. This organic linker will eventually be coordinated to the necessary corannulene derivative in the final 11 step synthetic route as shown in Figure 6. This ligand attached to the organic linker will eventually result in the final crystalline material that can be used to enhance various applications in the energy community.

With the nuclear magnetic resonance, it revealed that the peaks on the molecule match what is in the spectrum so we have determined that we know we made what we wanted to. The presence of the peaks matches the protons associated with the compound. For the dimethyl 5-iodoisophthalate, there were two small peaks and one large peak. In this example, there are six different protons that are associated with the three different numbers labeling the hydrogens on the molecular structure (3.89, 8.20, and 8.56). The large peak at 3.89 represents those six protons. There are three protons per each 3.89 written since it is a methyl group (CH$_3$), which also means that it integrates for six. Since the integration number is 6, the peak is high as evident in the spectrum. This peak is a singlet since it has no neighboring protons based on the n+1 rule.

In terms of the two smaller peaks, the integration is smaller, which explains why the peaks are smaller. Two protons are associated with 8.56 so it integrates for two and is also a singlet. The peak at 8.25 is associated with two protons so it integrates for six. It is also a singlet. The peak at 3.89 is associated with twelve protons so it integrates for twelve. It is also a singlet like the peaks in the previous compound since it has no neighboring protons based on the n+1 rule.

For the dimethyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isophthalate, there was one very large peak, one average peak, and two very small peaks. The high peak at 1.20 is associated with twelve protons. There are three protons per every 1.20 written on the structure, which means that it integrates for twelve. It is also a singlet like the peaks in the previous compound since it has no neighboring protons. The peak at 3.89 is associated with six protons so it integrates for six. It is also a singlet. The peak at 8.25 is associated with two protons so it integrates for two and is also a singlet. Finally, the peak at 8.23 is associated with one proton so it integrates for one and is also a singlet. Since this compound has four equivalent protons, four peaks were expected on the spectrum. The results with four peaks show that it is what we wanted.

For the (3,5-bis(methoxycarbonyl)phenyl)boronic acid, there was one very large peak and three very small peaks. The high peak at 3.89 is associated with six protons so it integrates for six. It is a singlet like all previous components due to its lack of a neighboring proton. The very small peak at 4.2 is associated with two protons so it integrates for two and is also a singlet. The peak at 8.25 is associated with two protons so it integrates for two and is also a singlet. Finally, the peak at 8.23 is associated with one proton so it integrates for one and is also a singlet. Four peaks were expected since there are four equivalent protons so the peaks in the spectrum prove we got the product we wanted.

In the future, we hope to get to the point where the crystalline material can be used for various applications. Due to the fluorescence and high surface area of the corannulene-based MOFs, it possible someday to incorporate them into devices such as organic-light emitting diodes (OLEDs) and solar panels. The main goal of our research group is to apply the material as anodes for Li-ion batteries. Previously, graphite was used as the anode but due to corannulene’s great reversible capacity and the porosity and high surface area of MOFs, it acts as the better organic linker.
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Notes and References


Figure 1. Synthesis of diboronic acid.

Figure 2. NMR of dimethyl 5-iodoisophthalate
Figure 3. NMR of dimethyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isophthalate

Figure 4. NMR of (3,5-bis(methoxycarbonyl)phenyl)boronic acid

Figure 5. Crystal product of (3,5-bis(methoxycarbonyl)phenyl)boronic acid
Figure 6. 11 step synthetic route for future necessary corannulene derivative.