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Metal-Organic Framework Development for the Treatment of Enviromental Pollutants

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Dedication

The paper is dedicated to my parents for their continued support of my academics, Rosa Mauro for assisting with experimentation, and Dr. Jie Ling for his guidance with regards to my proposal and finalization of the project.

Abstract

For several years, the development of Metal-Organic Frameworks has been on the rise due to their adaptability and wide-ranging functions. This experiment serves as a means to test the capabilities of two Metal-Organic Frameworks, ZIF-8 and UIO-67, in their potential role as filters for anionic pollutants. After synthesis and verification of structures, each Metal-Organic Framework was tested against three anionic pollutants commonly found in the environment.

Introduction

Metal-Organic Frameworks, or MOFs, are a relatively new invention with their prominence not appearing until the last decade when significant thought was put into the possible products of Metal-Organic Frameworks. Recent research has highlighted the unique mix of properties that MOFs possess (8). These properties are well-defined pore aperture, tailorable composition and structure, tunable size, versatile functionality, high agent loading (8). This combination of properties is unique for each type of MOF synthesized based upon the chemical components. This high adaptability and stability with pores make the MOF ideal for holding or collecting different molecule or compounds. In many cases, it has been shown that MOFs are porous and can absorb substances from their respective surrounding environments if the substances can meet certain requirements like the pore size of the MOF (7). The porous nature and use of differing pore sizes allows for some MOFs to serve as filters (7). Two such Metal-Organic Frameworks that are capable of filtration in theory are UIO-67 and ZIF-8. These two have differing structures and pore sizes.

UIO-67: Uses and Potential

UIO-67 is a special MOF that has been shown to be capable of extreme adaptability and utility. The use of Zirconium as the base metal ion allows for a wide range of variability of pore sizes. One such structure is shown in Figure One. They have already proven themselves to be capable of filtration of some acids and bases (9). Additional research has shown that they are capable of being reused as many as ten times before any drop in performance is detected (6). UIO-67 has only recently synthesized within the past twenty years, so there is limited information as to functions. Despite this, research shows that UIO-66, a family member of UIO-67, is capable of collecting and storing uranium from a mixed sample of differing metal ions (3). This makes it incredibly valuable as the reduction of nuclear waste and reuse of uranium could save significant amounts of energy and work to preserve the natural environment from radioactive waste.

ZIF-8: Uses and Potential

ZIF-8 is a classic MOF synthesized in laboratories as it is notably easier to synthesize than the majority of other MOFs. ZIF-8 has been shown to capable of not only filtration via its pores of liquids, but also gases. In a recent study, it was found that ZIF-8 was capable of absorbing specific gases from a large mix (1). In the aforementioned experiment, it was found that ZIF-8 could readily absorb Carbon Dioxide from the air or with minor alteration other gases like propane and butane by adjusting its pore from the ones shown in Figure Two. In a different study, ZIF-8 was shown to be capable of absorbing one of the most environmentally harmful gases, ozone (5). With its ability to absorb ozone and its easier synthesis than other MOFs, it is possible that given enough ZIF-8 synthesis and use, a positive change with regards to climate change could result.

Summary of Work Completed

Synthesis of ZIF-8 and UIO-67 were attempted as the two MOFs chosen for experimentation. The ZIF-8 synthesis attempt was completed using 0.893g of $Zn(NO_3)_2 \cdot 6H_2O$, 0.985g of 2-MIM being dissolved in 30ml of methanol respectively (10). The samples were then placed in Teflon-lined autoclaves and heated for 24 hours. After this, the powder crystals that formed were washed and dried before being sent for X-ray analysis. The UIO-67 synthesis involved 1.2mmol $ZrCl_4$, 1.2mmol 4,4'-Biphenyl dicarboxylic acid, 30 equivalents of acetic acid, and 30ml of DMF being mixed in Teflon-lined autoclaves and heated for 48 hours (4). After this, the powder crystals that formed were washed and dried before being sent for X-ray analysis.

Although the entirety of research was not completed, there were circumstances beyond control that prevented completion of the project. These began with the lack of necessary lab equipment due to broken equipment. The primary machine that caused problems was an X-Ray Diffractometer. This device emits X-rays at a sample and uses the feedback to determine the shape of the sample and its components. The figures below are the results of such work. Since these MOFs are acting as filters, their structures are critical to their function. Without verification of the structure of the MOF, no research can be completed as the metal-organic framework being tested would no longer serve as a control to the experimentation. The X-Ray Diffractometer remains broken to this point, but the chemical engineering department eventually agreed to allow use of their device to the graduate student in the laboratory. In order for samples to be tested, all samples were given to the graduate student so that they could test them and send the results.

The next delay in research occurred at this phase of experimentation as the graduate

student who was given the sample for testing, which normally takes less than twenty-four hours, did not send results for almost one month. Without knowledge of if the samples synthesized were the right MOFs, synthesis of MOFs would only serve to waste university funding and chemicals as it would be impossible to know how to adjust the reactants for synthesis without the X-ray data.

Planned Research

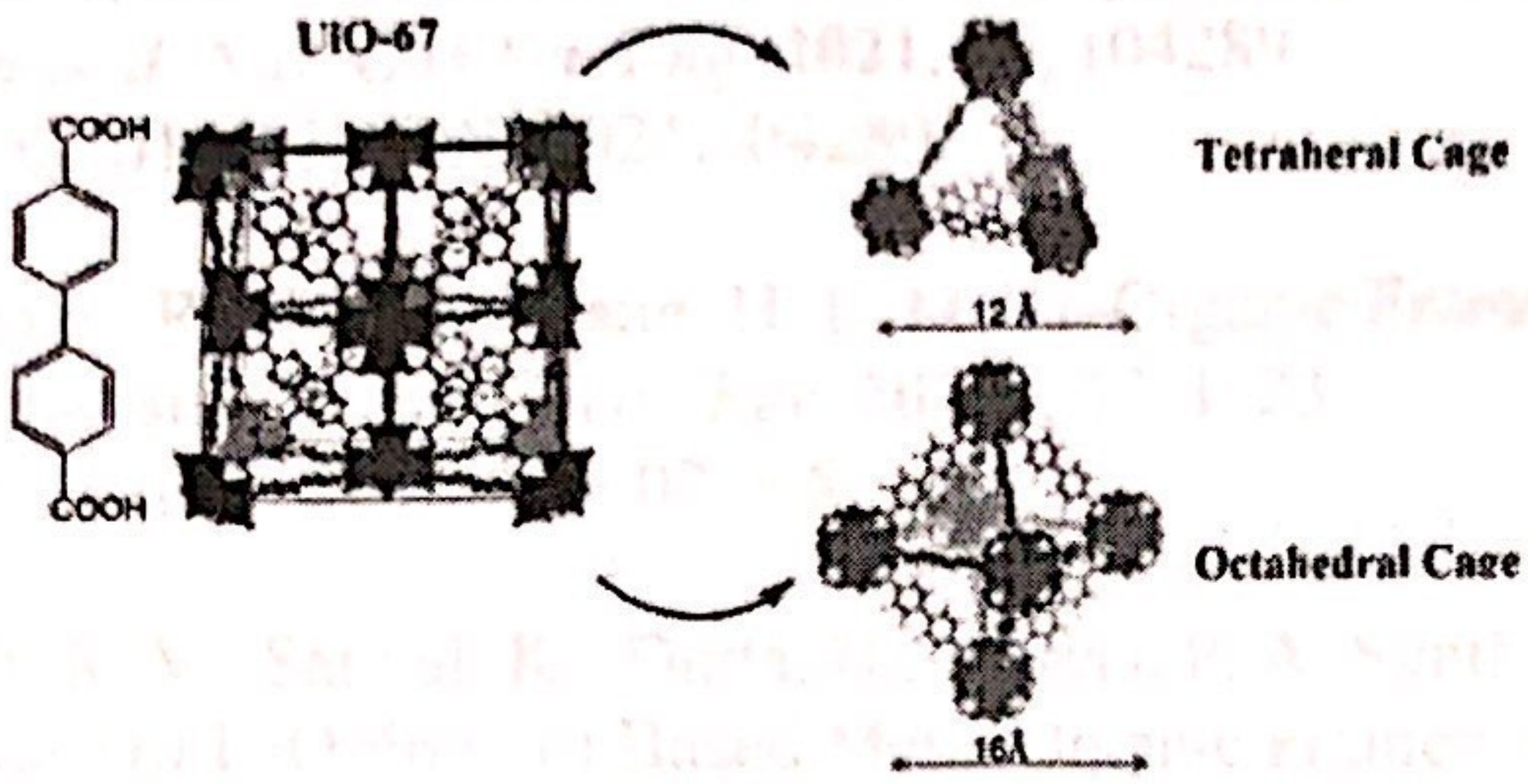
The plan was to synthesize the MOFs and test them against varying environmental pollutants. The pollutants tested would then be measured to determine what remain after interaction with the MOFs. Multiple trials would be completed in order to help verify results.

Lessons and Recommendations

The primary lesson that I learned was to determine the functionality of the equipment before beginning experimentation. I should have also worked towards being able to operate the X-Ray Diffractometer myself. This would have helped with the speed of the process. I would recommend the repair of the X-Ray Diffractometer that the UAH Chemistry Department has. I would also recommend that more effort be placed into faster synthesis so that the experiment can be completed in a rapid fashion.

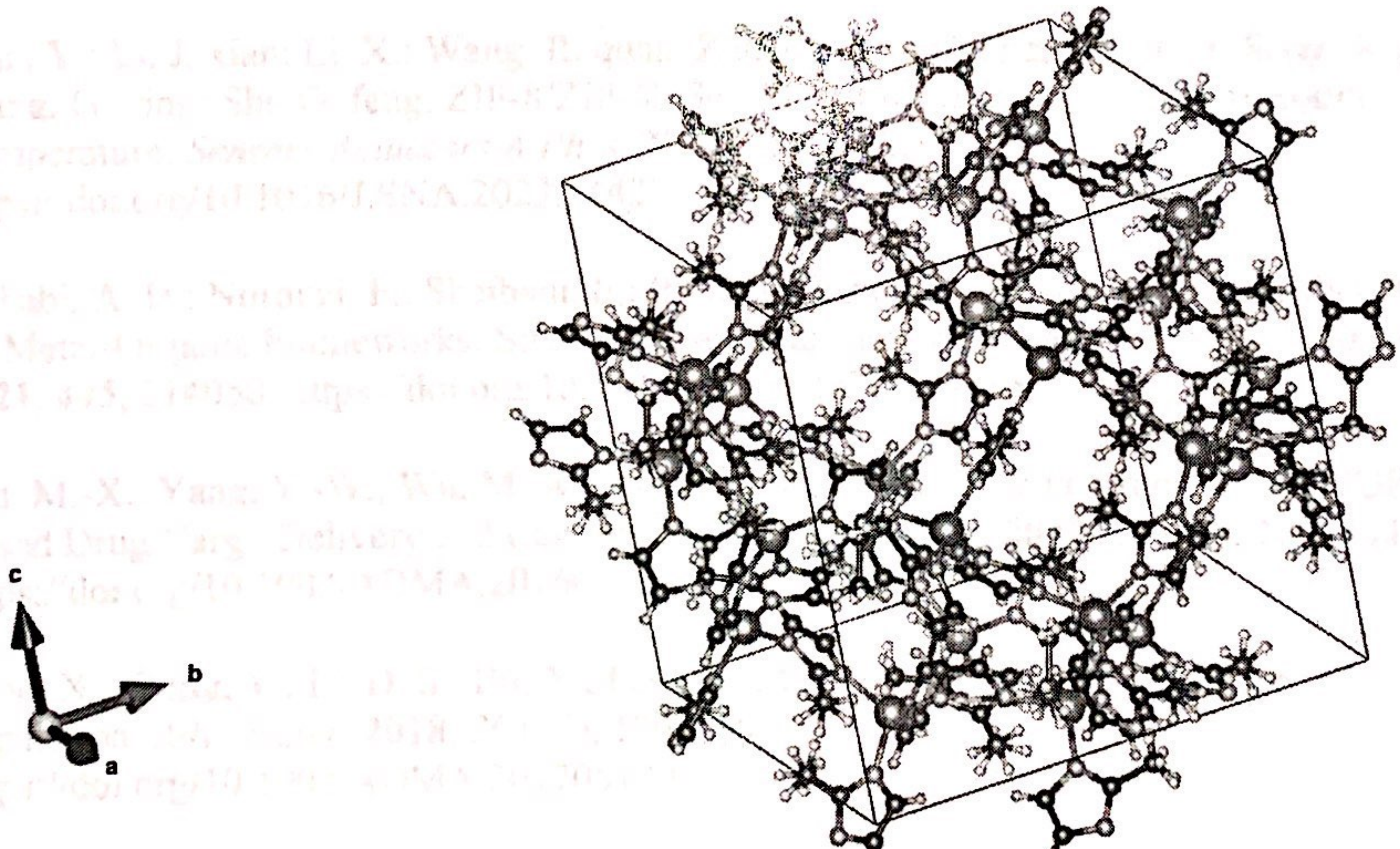
Figures

Figure One



The figure above shows the three-dimensional structure of UIO-67.

Figure Two



The above figure shows the three-dimensional structure of ZIF-8.

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