METAL ORGANIC FRAMEWORK CAP AND GUEST INTERPLAY

WPI

A Major Qualifying Project Report
Submitted to the Faculty of
WORCESTER POLYTECHNIC INSTITUTE
in partial fulfillment of the requirements for the
Degree of Bachelor of Science in Chemical Engineering

By:

Kweku Sam Colecraft

Approved:

Assistant Professor Ronald L. Grimm,
Research Advisor

Approved:

Professor Stephen J. Kmiotek,
Major Advisor

ABSTRACT

Over the past 20 years Metal Organic Frameworks have been a hot topic of research due to having the largest surface areas and porosities of all the microporous materials. These features have made MOFs to be desirable for applications in fields such as drug delivery, carbon capture, catalysis, storage, and separations processes. The Grimm, Burdette, and McDonald groups have developed a mechanism for coordinating capping molecules onto the surface of MOF–5 via a hydrothermal process to seal in guest molecules that are introduced into the pores. In the previous studies, Crystal Violet, a large sterically bulky dye, was successfully trapped within the pores of MOF–5 by various capping reagents. This study explores the next step in the development of the capping and trapping mechanism which is to understand the cap and guest relationship between caps and smaller guest molecules. We hypothesized that the large sterically bulky cap triphenyl acetic acid would trap methylene blue, a smaller dye, in MOF–5 and that the less bulky cap methylene blue would fail to trap the methylene blue within MOF–5. Overall, this study advances the field of research further towards MOFs being used for drug delivery.

TABLE OF CONTENTS

1 INTRODUCTION

1.1 Origins of Metal Organic Frameworks: A highly ordered, microporous, crystalline material

Beginning in the 1860s, a new class of materials emerged and became a widespread of interest, led by zeolites. This new class consisted of microporous materials which were desired for their porosity, surface area, ordered crystalline nature, and surface functionality among other features. They were desired for many different applications, notably separations, gas storage, drug delivery, and catalysis.[6] The primary materials of interest among this class were zeolites which are aluminosilicates that are known commonly as molecular sieves. They are 3D materials consisting of orthosilicate tetrahedra.[6]

Then, in 1999, the Metal Organic Framework (MOF) became established as a widely researched area of microporous materials.[7-8] MOFs are highly ordered crystalline materials comprising of metal clusters that are linked together by organic ligands. This new class of materials had record-breaking porosity levels and surface areas with highly tunable structures. Compared to previous microporous materials, they have larger potential Langmuir surface areas, (1000-10000m^2/g) [9] opposed to the previous (300-2000m^2/g).[6] Furthermore, their porosities reach up to 90% of the material being comprised of free volume, typically at least comprising 50% of the material.

1.2 Metal Organic Frameworks for Drug Delivery

Due to the combination of high surface area, porosity and tunability, they are being researched for their potential to provide superior results in applications such as storage and transport, one of these being drug delivery. For over 100 years, it has been a major goal in the science and health fields to engineer nanoscale drug carriers such that they could deliver treatments directly to diseased tissues. These engineered carriers need to fulfill the following criteria as defined by Chapter 21 of “Metal Organic Frameworks for Biomedical Applications”

- Biodegradability to avoid accumulation in the living organism.
- Lack of toxicity and excretion of the degradation products
- High drug payloads and good incorporation yields of the active molecules
- Controlled release of the cargo
- Selective targeting of diseased cells or organs
- Possibilities of surface modifications to control in vivo fate and ensure stability
- Good detection by imaging techniques
- "Green", reproducible, and scalable synthesis [10]

MOFs' surface areas and porosity make them viable candidates for this biomedical feat as they have been shown to have the capacity to deliver drug payloads that have been greater than 25%.[10] Along with these upsides come the challenges of fully encapsulating drugs until release at specific locations within the body. Furthermore, MOFs need to be produced that have highly specific chemical stabilities, both biodegradable yet sturdy enough to reach the desired target. These are the obstacles between the field of MOFs and the next potential largest breakthrough in medicine, materials science biomedical engineering.

1.3 Previous Contributions: MOF–5 Guest Trapping Mechanism

1.3.1 Capping and Trapping Guests in MOF

The McDonald, Burdette, and Grimm groups at WPI have made significant strides in fulfilling the criteria of both controlling the in-vivo fate of payloads and controlling the release of the cargo.[10] Over the previous years, a mechanism has been developed by which guests can be sealed within MOFs. The procedure was pioneered with MOF–5 due to its framework and pore sizes being ideal for a range of organic guest molecules, and well-developed crystal structure that allow orthogonal binding of capping reagents.[5] Furthermore, this MOF has a relatively simple synthesis and there exists a wide variety of literature on this MOF despite it not meeting the criteria necessary for a MOF to be used for this application. It was found that carboxylic acid groups could coordinate with the metal ions of MOF–5 and would effectively bind to each metal cluster.[5] Figure 1 shows how the capping groups bind to a MOF surface.

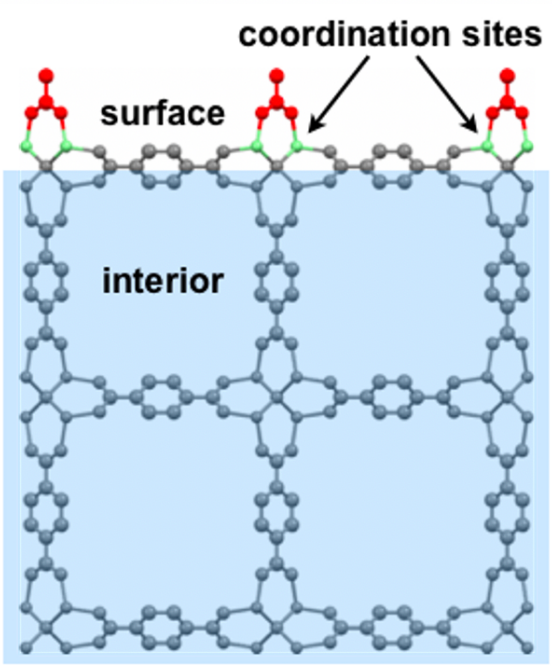

Figure 1: Coordination of capping reagents onto the metal ions of MOF–5. The red molecules indicate the coordination sites to which capping reagents will orthogonally bind and trap molecules.[5]

To test the feasibility of this mechanism, MOF–5 would be loaded with a guest molecule, a capping molecule would be coordinated onto its surface, and then the release of the guests in a solution would be monitored to confirm trapping.

1.3.2 Crystal Violet (CV) as a Guest in MOF–5

Due to this mechanism of the binding of capping groups to the coordination sites, it was hypothesized that larger, sterically bulky capping groups that still allowed for the occupation of each coordination site would be ideal to block leaching from the pores of MOF–5.

Crystal Violet (CV) was used as the preliminary guest to verify the possibility of trapping due to its large aromatic rings having high enough surface area to interact with the interior of MOF–5 and simultaneously being small enough to diffuse out of MOF–5 and large enough to be trapped by guest molecules within the pores.[5] Furthermore, CV showed high solubility in all used solvents while being easily quantifiable by way of UV-Visible Spectroscopy

1.3.3 Carboxylic Acid and Alkyl Amines as Capping Reagents

There were 7 different capping reagents that were coordinated onto the MOF–5 pores. These included triphenyl acetic acid (TPAA), diphenyl acetic acid (DPAA), Phenyl Acetic Acid (PAA) diisopropylethylamine (DIPEA), triethylamine (TEA), trimethyl acetic acid (TMAA), and acetic acid (AA). Below in Figure 2 is a schematic showing the structures of the caps along with their Van der Waals radii (excluding PAA).[5]

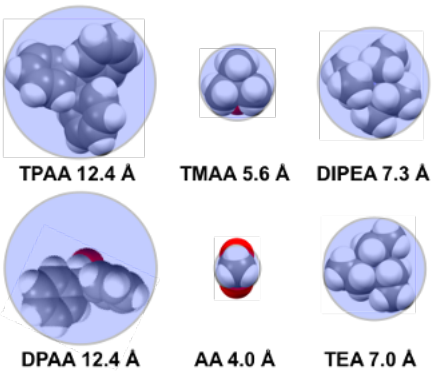

Figure 2: Relative sizes of capping reagents with Van der Waals radii. The size of these molecules largest to smallest is TPAA, DPAA, DIPEA, TEA, TMAA, and AA. Note that PAA was used but not reported and would go directly after DPAA in size.[5]

1.3.4 Results of CV Trapping

From the CV release profiles, it was determined that each of the different capping groups provided a significant blockage of the pores and prevented the leakage of CV into solution. The three caps that completely trapped CV were TPAA, DPAA and PAA where the others provided

partial coverage as evidenced by some leakage from the pores.[5] These results provided the foundational understanding for the mechanism and scope of MOF guest capping and trapping, prompting many questions that need to be answered to further along this manipulation of MOFs towards the eventual implementation of drug delivery.

1.4 Project goal: Elucidate the interplay between pore, guest, and cap sizes in successfully trapping guests in MOF–5

CV was successfully trapped within MOF–5 but as previously mentioned, it is a large, sterically bulky guest dye. This leaves the following questions to be answered:

- Is it possible for dyes smaller than crystal violet to be trapped within MOF–5 pores?
- What are the limits to the sizes of guests that can be trapped by each size of cap?

This project begins to answer these questions by attempting to cap and trap the guest dye Methylene Blue (MB) within the pores of MOF–5 with two different capping reagents.

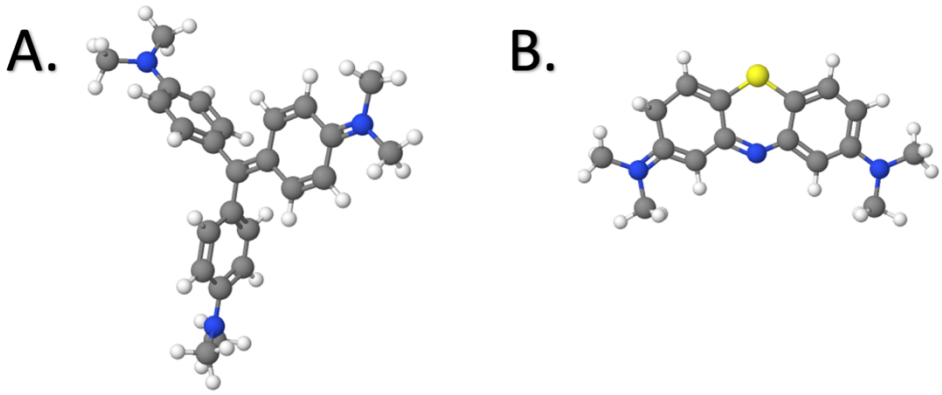

Figure 3: The molecular structures of (**A**) Crystal Violet and (**B**) Methylene Blue. Crystal Violet has 3 aromatic rings compared to the two observed in Methylene Blue Making it larger and more sterically bulky.

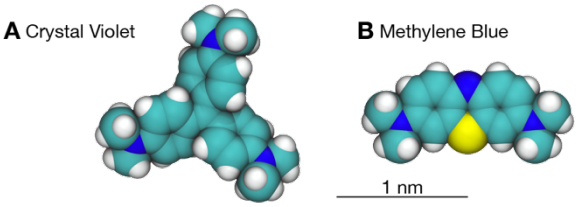

Figure 4: (**A**) Crystal Violet and (**B**) Methylene Blue Van der Waal sizes

Figure 3 shows the relative sizes of CV and MB visually based on their chemical structures and Figure 4 shows the Van der Waals dimensions of MB compared to CV. As can be clearly seen, MB is smaller and less sterically bulky. It also was easily identifiable by UV-Visible Spectroscopy, making it an ideal gust candidate. The two different capping reagents that will be used are TPAA and PAA, the largest and smallest caps that were able to completely tap crystal violet in MOF–5. Figure 5 shows the relative sizes of these two capping reagents.

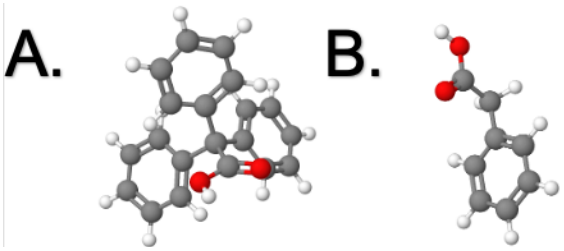

Figure 5: The molecular structures of (**A**) Triphenyl Acetic Acid and (**B**) Phenyl Acetic Acid.

It is hypothesized that TPAA will successfully trap MB while smaller caps PAA would not have the steric bulk to successfully seal MB within the pores of MOF–5. The plan for executing the project goal is as follows:

1. Optimize growth to yield high-quality MOF–5
2. Study the Dye Release profile of MOF–5 loaded with varying cap and dye sizes

2 EXPERIMENTAL SECTION

2.1 MOF–5 synthesis

MOF–5 was prepared through a hydrothermal procedure derived from the established procedure with with some modifications to increase crystal output. 0.9 g (3 mmol) of zinc acetate hexahydrate, 0.371 g (2.25 mmol) of terepthalic acid (benzene dicarboxylic acid), and 25 ml diethyl formamide (DEF) or dimethyl fornamide (DMF) was added to a 25 ml microwave vial and sealed with a teflon cap.[5,7] The mixture was then sonicated until the terepthalic acid and zinc acetate were dissolved in the DEF. Then, the microwave vial was placed in a 6" tube furnace (see Appendix A) and was heated according to the following heating program:

- Ramp up to 120 ºC over 5 hours
- Soak at 120 ºC for 24 hours
- Ramp down to 25 ºC (room temperature) over 7 hours.

In total, this heating program lasted 36 hours. (1 day and 12 hours). The crystals were kept in the solvent until ready for dye loading.

2.2 Loading Guest Dye in MOF–5

Dye was loaded into the pores MOF–5 by loading them into a solution containing 90% saturated dye. The 90% saturated solution was made by loading dye into 10 ml of ethanol (100%), thoroughly mixing, and repeating until the ehanol was unable to dissolve any more dye and thus a saturated solution had been created. Then, a 9 mL of this saturated solution was added to 1mL of ethanol to form a 90% saturated solution (note that a 1:10 ration may be achieved through any combination of saturated dye solution and ethanol). 75.0mg (97.4 µmol) of MOF–5 was then added to 3mL of the 90% saturated solution and stored at room temperature for 24 hours. [5]Prior to use, the crystals were removed and blotted dry on filter paper prior to dye leakage testing.

2.3 Coordination of capping reagents onto MOF–5

Capping reagents were coordinated onto MOF–5 by a second solvothermal process adapted from previous efforts. [5]The dye loaded crystals (75.0 mg, 97.4 µmol) were added to 20 mg (0.67 mmol) of additional zinc acetate hexahydrate, 0.033 mmol of capping reagent (9.51 mg TPAA

and 4.49 mg PAA), 0.33mmol of additional dye (135 mg CV and 105 mg MB) , and 5mL of DEF in a 25 mL microwave vial. These were then heated in a 6" tube furnace according to the following heating program:

- Heat at 120 ºC for 48 hours
- Ramp down to 25 ºC (room temperature) over 6 hours.

In total, this procedure lasted 54 hours (2 days and 6 hours). The resulting capped crystals were then washed with ethanol and dried on filter paper to remove external dye that may linger from the capping procedure.

2.4 Calibration curve for dye leakage quantification

A calibration curve was created from which the concentration of dye and subsequently the mass or moles of dye leached into solution could be determined to quantify the amount of dye that is released in total. To create the calibration curve, the maximum absorbance was first determined by measuring the spectra of CV and MB. Then, the absorbance was taken at 31.25 μM along with the absorbances of solutions with concentrations that are half of the previous solution until a solution a solution with concentration 0.9766 μM was measured. These absorbance values were plotted, and the linear equation found was used to determine the concentration of dye in the leakage tests.

2.5 Testing capping efficacy by UV-Visible Spectroscopy

The UV-Vis Spectroscopy machine was first calibrated with a blank ethanol sample. Then, previously washed Capped crystals (75.0 mg) were placed in 3.0 mL of ethanol and the absorbance of the solution at the maximum wavelength (589 nm for CV and 655 nm for MB) was measured and recorded at 1 s intervals over the course of 120 minutes.

3. RESULTS

3.1 MOF–5 synthesis

3.1.1 Synthesis with DEF as Solvent

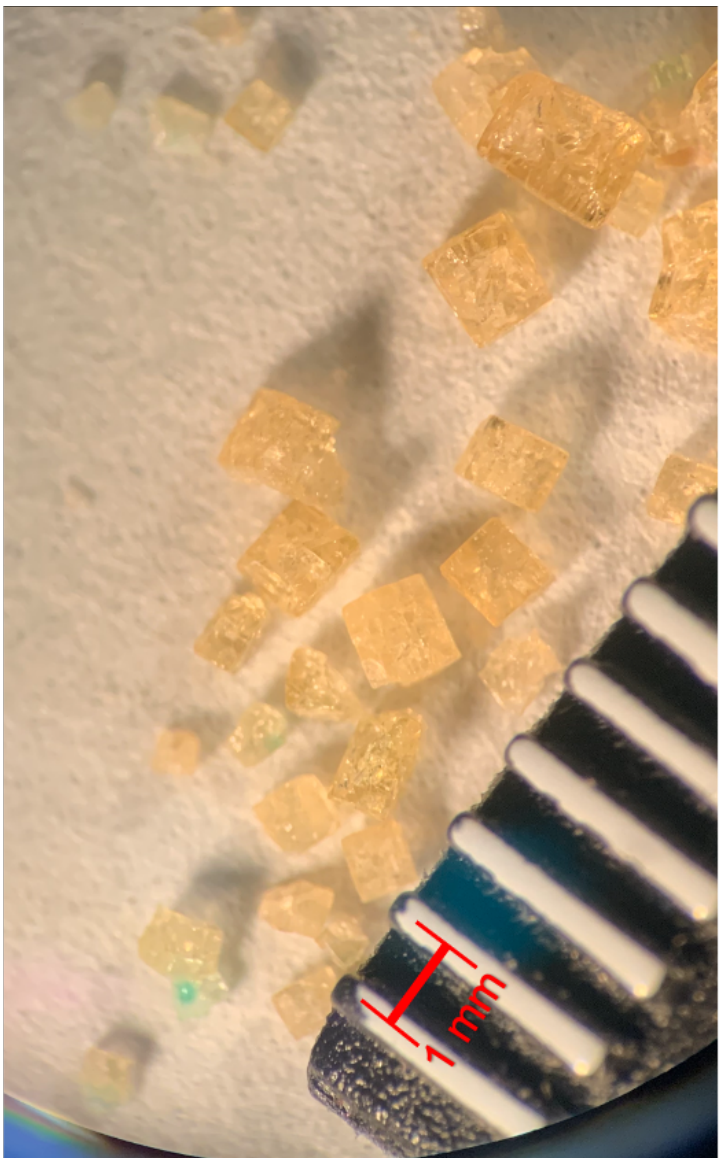

Figure 6: The size and appearance of MOF–5 synthesized in DEF. The crystals have a slight yellow tint and range in size from 0.5 to 1.5 mm.

Figure 6 above shows the appearance of synthesized crystals. Crystals of MOF–5 appear slightly tinged orange but are otherwise white. Most crystals range between 0.5mm and 1 mm. The resultant crystals range in color from clear to having a slightly yellowish orange tint. The solvent

ranged in color from tinted yellow to tinted yellowish orange to brown following synthesis. The variation experienced is dependent on the time since opening of the DEF and its dryness.

3.1.2 Synthesis with DMF as Solvent

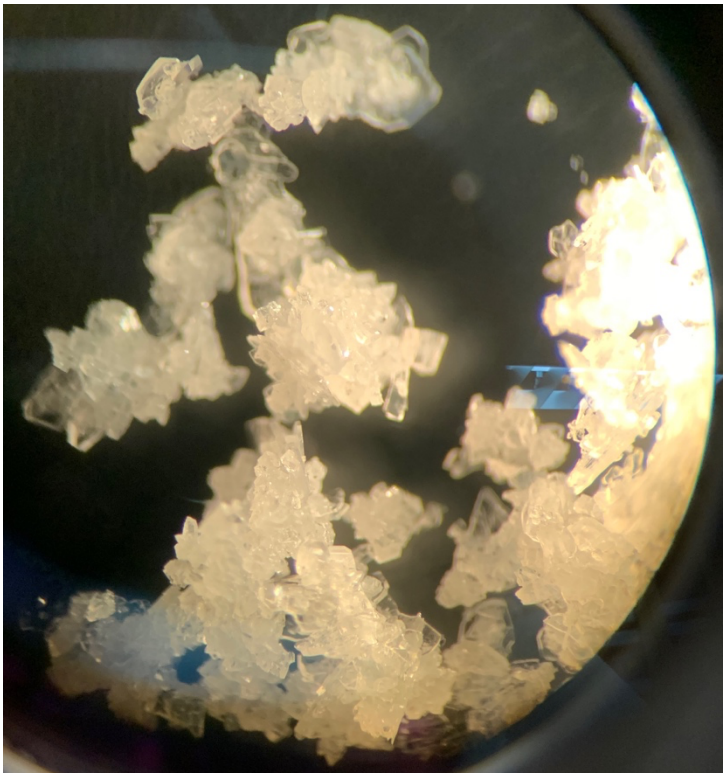

Figure 7: Microscope enhanced image of MOF–5 synthesized in DMF. The crystals are clear and white but smaller and less defined than MOF–5 synthesized in DEF.

Figure 7 above shows the appearance of DMF synthesized crystals. These crystals are white, clear, and range between the 100 µm and 1mm size.

4.1 Calibration Curves for Dye Leakage Quantification

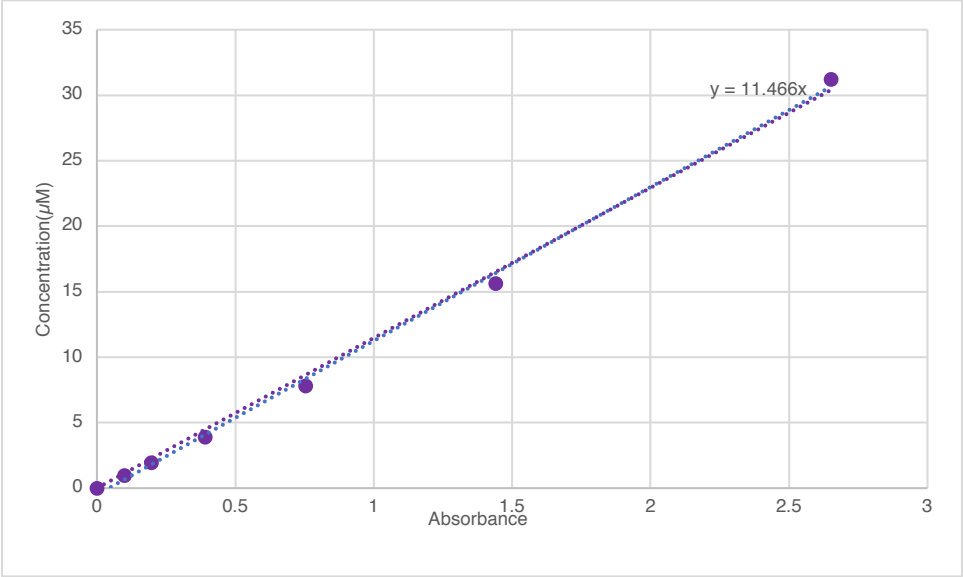

Figure 8: Calibration Curve for the quantification of CV leakage from MOF–5. The equation shown is that which outputs concentration (Y) based on the observed absorbance (X).

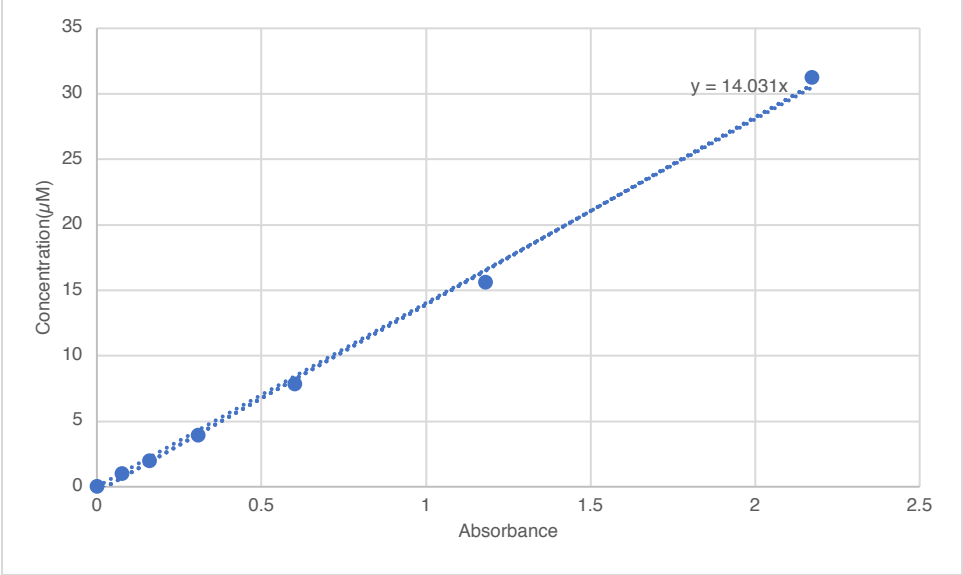

Figure 9: Calibration Curve for the quantification of MB leakage from MOF–5. The equation shown is that which outputs concentration (Y) based on the observed absorbance (X).

Figures 8 and 9 show the calibration curves that were created from various concentrations of Crystal Violet (top) and Methylene Blue (bottom) in ethanol. Using the equations from these graphs, the dye release tests were performed and afterwards, the mole fraction per gram of CV or MB that leached out of the pores of MOF–5 could be calculated.

4.1 Testing capping efficacy by UV-Visible Spectroscopy

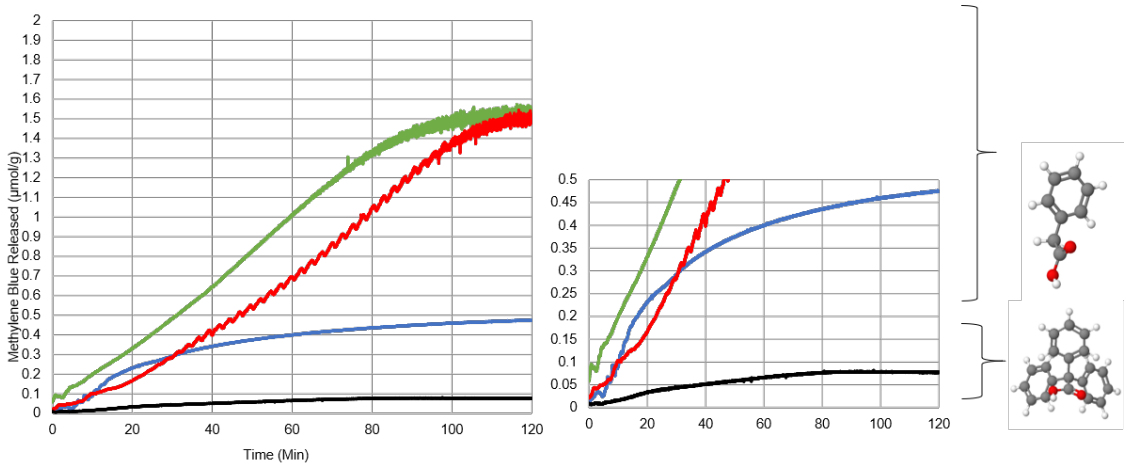

Figure 10 Results of Dye Release tests with MB in MOF–5 capped by PAA and TPAA.MOF–5 capped with TPAA leaches out minimal MB. MOF–5 capped with PAA leaches out significant MB.

From Figure 10, MOF–5 released <0.09 μmol g^{-1} when TPAA was coordinated onto the structure of MOF–5. On the other hand, when PAA was used, between 0.4 and 1.5 μmol/g of dye leached into solution. It should be noted that there were some inconsistencies in the levels of MB that leached into solution when capped with PAA. This phenomenon will be further addressed in the discussion section of paper. Below in Figure 11 is an example of Methylene Blue leaching out of capped MOF–5.

Figure 11: Image of MB loaded MOF–5 in ethanol with dye leaking out into solution, turning it blue.

4. DISCUSSION

4.1 MOF–5 Synthesis Breakthrough: Large Crystal Synthesis

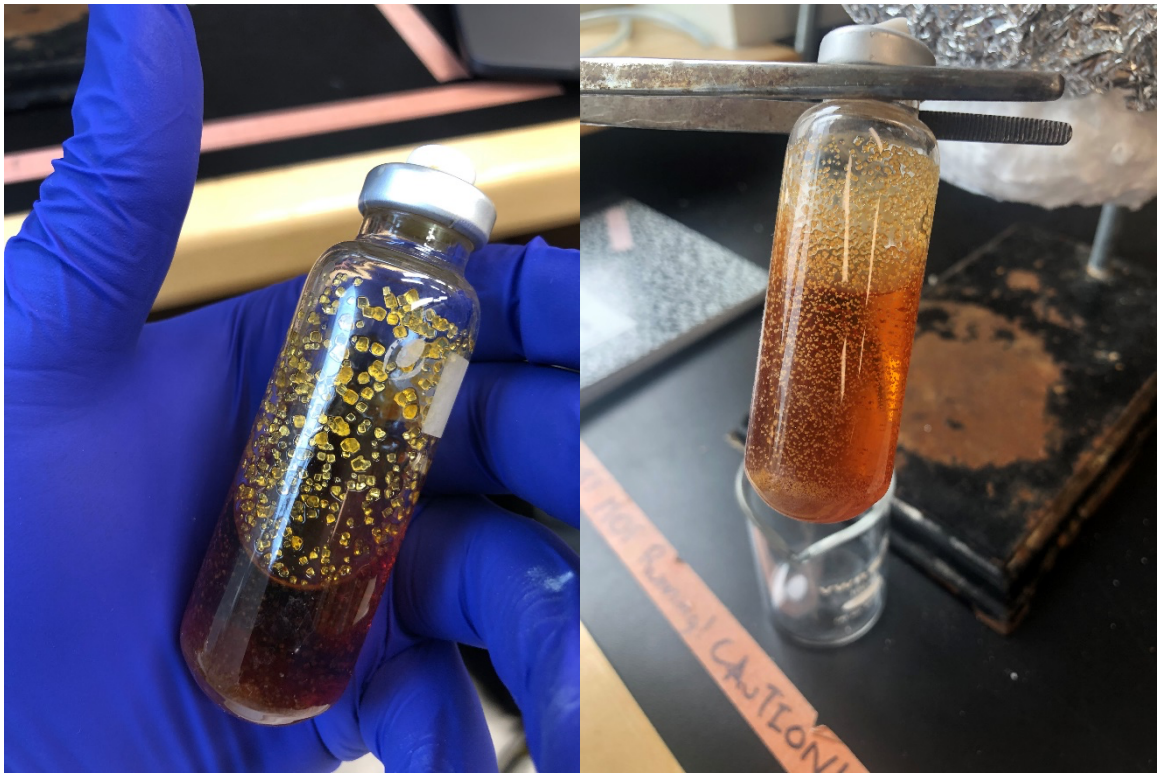

Figure 12: MOF–5 synthesized following the adjustment to the synthesis procedure. (Left) MOF–5 made by the previously stablished synthesis procedure.

In the first phase of this project, the optimization of the growth of MOF–5, great time was spent adjusting the synthesis procedure to yield larger crystals of MOF–5. The zinc acetate: terephthalic acid ratio that had been established originally was 3:1. Under those conditions, crystals on the scale of the photo on the right were being produced; very uncoordinated and small crystals nonetheless showing the necessary peaks in XRD scans. However, the synthesis ratio was changed to 4:3 zinc acetate: terephthalic acid and the results yielded some of the largest crystals that had been produced in the lab. Figure 12 shows side by side the yield of the initial procedure (left) to the adjusted procedure (right).

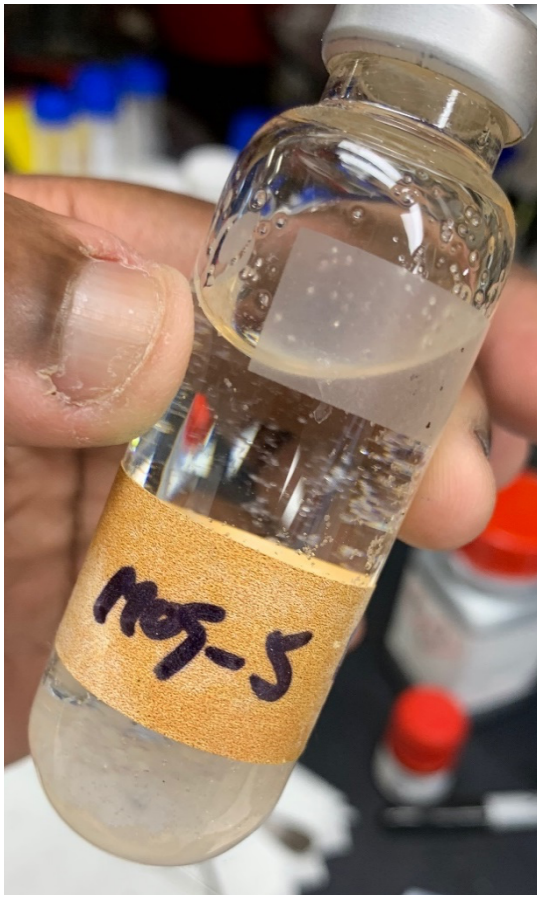

Figure 13: MOF–5 synthesized in DMF in solution.

In the final days of experimentation, the useable DEF was exhausted and was substituted with DMF. As previously seen, these yield crystals on the 20-500 µm scale as opposed to the 1000+ µm crystals that are seen when MOF–5 is synthesized with DEF. The size difference can be seen by the above figure. After these larger scale crystals were able to be consistently produced from this new procedure, the dye loading, and capping experiments were undertaken.

4.1 Capping Efficacy: TPAA trapped Methylene Blue within MOF–5 but PAA did not

When Crystal Violet was trapped within MOF–5 with various caps, each of the capping reagents tested proved to provide significant pore blockage as TPAA, DPAA and PAA all completely trapped Crystal Violet within MOF–5.

With Methylene Blue, TPAA was the only cap that provided substantial pore coverage. However, it still allowed some methylene blue, though a miniscule amount, to leak out of the pores of MOF–5. This indicates that though significant blockage was attained, complete trapping was not achieved.

The hypothesis was supported that only the most sterically bulky cap would be successful in sealing Methylene Blue within MOF–5. This is likely due to the lack of steric hinderance of methylene blue faces within the pores of MOF–5. It requires less realigning within the pores to diffuse out due to its smaller size. These results have given a deeper understanding of the relationship between dye guest sizes and cap sizes in the development of the MOF guest capping and trapping field and leaves clear direction for the next steps that need to be undertaken to apply this mechanism to drugs and eventually within the human body.

5. CONCLUSION AND NEXT STEPS

5.1 How did this study advance the field?

The questions that were intended to be explored by this study were:

- Is it possible for dyes smaller than crystal violet to be trapped within MOF–5 pores?
- What are the limits to the sizes of guests that can be trapped by each size of cap?

This study suggests that smaller dyes can be trapped within the pores of MOF–5 with larger, more sterically bulky capping reagents like TPAA. Though a small amount of MB leached out of the pores of MOF–5, the quality of MOF used in that trial was likely worse and this would have hindered the positioning and efficacy of the capping reagents in how they were coordinated onto the surface of the MOF–5. Future trials with MOF–5 synthesized in DEF may be able to report complete trapping of MB by TPAA.

This study also gave insight into the interplay between guest and cap sizes and the limits of sizes of guests that can be capped by sizes of traps. Methylene blue was significantly trapped by TPAA while the three different runs of MOF capped with PAA each resulted in significant dye leakage., TPAA, DPAA and PAA all completely trapped CV in MOF–5 but only TPAA trapped MB in MOF–5. A relationship is developing between caps and guests in that smaller guests are only able to be trapped by larger, sterically bulky caps that can seal the aperture pf the MOF pores most completely. These findings provide a clear direction into the next steps.

5.2 Next Steps: First, confirm results. Then, Change the Variables (Guest/Cap/MOF)

The results of this study have provided the preliminary answers to the design questions, but further experimentation is needed to both confirm the results of this experiment and drive the field to the successful MOF facilitated delivery of drugs. Below is the suggested process:

1. Establish the Cap/trapping efficacy relationship with Methylene Blue in MOF–5 by determining that MB can indeed be trapped.
    a. Retest TPAA to confirm trapping.
    b. Determine whether DPAA also traps MB in MOF–5

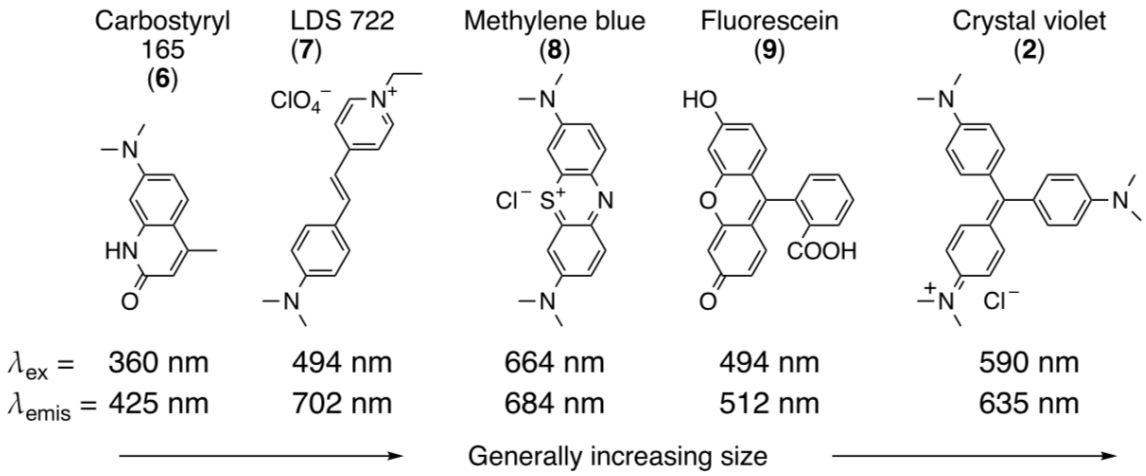

Figure 14: List of dyes proposed for trapping within MOF–5 organized by size.[1]

c. Confirm that PAA is unable to trap MOF–5.

   i. In the process test other smaller experienced caps i.e., DIPEA, TEA and TMAA to ensure that the results hold true based on size of cap.

2. If PAA is confirmed not to trap MB, compare with Fluorescein to quantify the differences in guest size that determine capping efficacy, then continue to smaller dyes.
3. In the case that PAA is found to trap MB, Establish the Cap/trapping efficacy relationship with a smaller guest in MOF–5.
   a. Start with Carbostyryl 165, see Figure 14.
   b. Continue decreasing the guest sizes until there is no longer a practical application to drug delivery or the capping/trapping mechanism fails.
4. For each guest size that is trapped, establish the minimum cap size that achieves trapping (beginning with Crystal Violet)
5. Explore the feasibility of the Cap/trapping mechanism with other MOFs to the end that it is either established that this process is applicable to a variety of MOFs or determined that it is not.
6. In the case that this mechanism applies to other MOFs, expand Photo-cleavable cap testing and Bio-Compatible MOF capping.

6. REFERENCES

1. Grimm, R.L. and Burdette, S.C. NIH R15 Grant Proposal 2019.
2. Bui, A., How Can We Tell We've Capped a MOF? Grimmgroup, REU Report 2019.
3. Bui, A., HKUST-1. Ronald Grimm: Grimmgroup REU Report 2019.
4. Bui, A., XPS Sputtering of MOF–5 and HKUST-1 with and without Capping Groups. Grimmgroup, REU Report 2019.
5. Homan, R. A.; Hendricks, D. S.; Rayder, T. M.; Thein, U. S.; Fossum, K. J.; Claudio Vázquez, A. P.; Yan, J.; Grimm, R. L.; Burdette, S. C.; MacDonald, J. C., A Strategy for Trapping Molecular Guests in MOF–5 Utilizing Surface-Capping Groups. *Cryst. Growth Des.* **2019**, *19*, 6331-6338.
6. Chowdhury, A. H.; Salam, N.; Debnath, R.; Islam, S. M.; Saha, T., Chapter 8 - Design and Fabrication of Porous Nanostructures and Their Applications. *In* Nanomaterials Synthesis, Beeran Pottathara, Y.; Thomas, S.; Kalarikkal, N.; Grohens, Y.; Kokol, V., Eds. Elsevier: 2019; 265-294.
7. Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M., Design and Synthesis of an Exceptionally Stable and Highly Porous Metal-Organic Framework. *Nature* **1999**, *402*, 276-279.
8. Zhang, X.; Chen, Z.; Liu, X.; Hanna, S. L.; Wang, X.; Taheri-Ledari, R.; Maleki, A.; Li, P.; Farha, O. K., A Historical Overview of the Activation and Porosity of Metal–Organic Frameworks. *Chem. Soc. Rev.* **2020**, *49*, 7406-7427.
9. Nazari, Z.; Taher, M. A.; Fazelirad, H., A Zn Based Metal Organic Framework Nanocomposite: Synthesis, Characterization and Application for Preconcentration of Cadmium Prior to Its Determination by FAAS. *RSC Adv*. **2017**, *7*, 44890-44895.
10. Christodoulou, I.; Serre, C.; Gref, R., Chapter 21 - Metal-Organic Frameworks for Drug Delivery: Degradation Mechanism and in Vivo Fate. In Metal-Organic Frameworks for Biomedical Applications, Mozafari, M., Ed. Woodhead Publishing: 2020; pp 467-489.
11. Engineering, O. Cylinder Shaped Ceramic Heaters 1800°F Max and 4 Kw Max. https://www.omega.com/en-us/industrial-heaters/radiant-heaters/ceramic-radiant-heaters/crfc/p/CRFC-26-120-A.
12. Amazon K-Type Thermocouple Wire AWG 24 Solid W. Braided Fiberglass Insulation - 10 Yard Roll. https://www.amazon.com/K-Type-Thermocouple-Braided-Fiberglass-Insulation/dp/B0768JJT4R.
13. Zoro, Ceramic Fiber Insulation.
14. Engineering, O. Ceramic Beads.
15. Fossum, K. Determination of Capping Location and Guest Quantification of MOF–5; Worcester Polytechnic Institute: Burdette Lab MQP Report, 2017.
16. Dawley, R., Elucidating the Surface Sites and Reactivity of a Zirconium-Based MOF for Future Capping and Trapping of Molecular Guests. Grimmgroup WPI MQP Report 2021.

7. APPENDIX

7.1 APPENDIX A: DEVELOPMENT OF A FURNACE DESIGNED TO SYNTHESIZE MOF

The furnace that was used to synthesize the MOF–5 in this paper was previously developed and tailored to fit the solvothermal processes that MOFs require. Below are the schematics of the designed furnace in Figures 15 and 16.

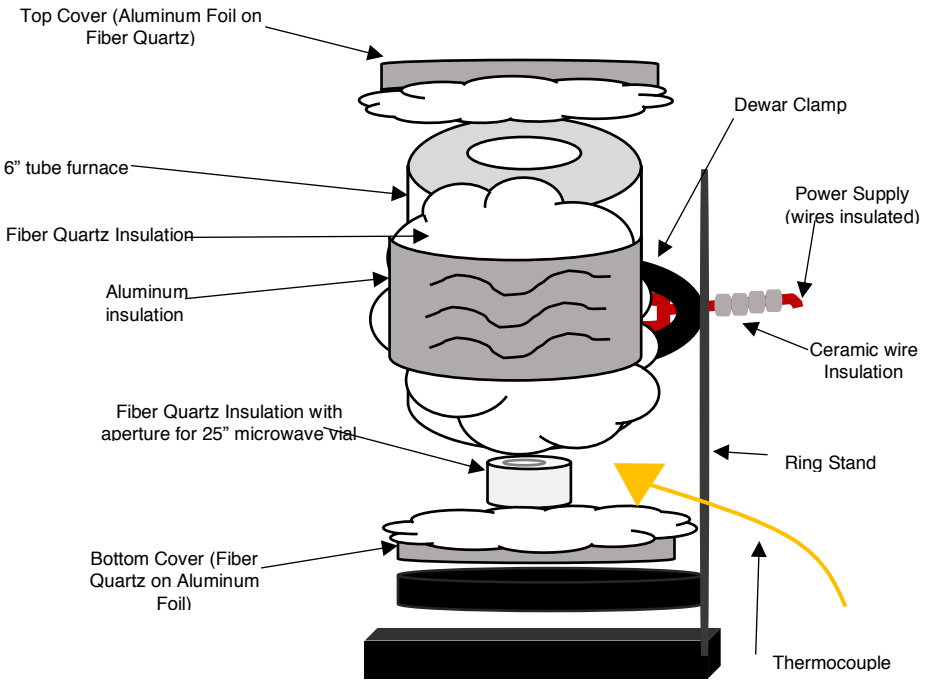

Figure 15: Schematic of tube furnace used to synthesize MOFs (exterior view).

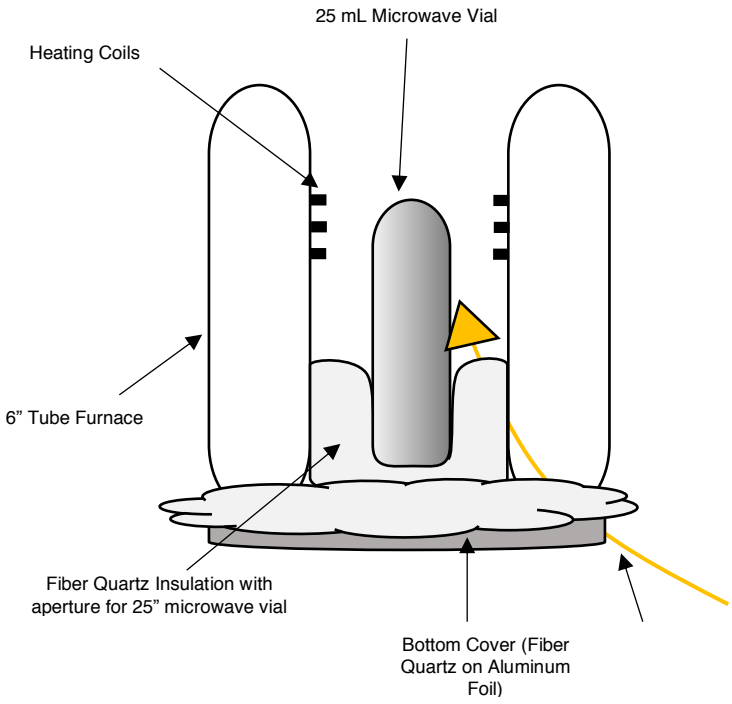

Figure 16: Schematic of tube furnace used to synthesize MOFs (interior view).

- The heater used was a cylinder-shaped ceramic heater. It was the OMEGA CRFC-26/120-A model cylinder without vestibules. It was 6 in. in length with a maximum operating temperature of 982°C (1800°F) with a Power of 435 W and supply voltage of 120V. The dimensions of this cylinder are 6" in length, 2" inner diameter and a 4" outer diameter. [11]
- The thermocouple that was placed inside the heater is a K-Type thermocouple wire AWG braided with high temperature fiberglass that insulates up to 700°C (1300°F).[12]
- The insulation that was used around the heater and exposed wiring was High Temperature Quartz Fiber Wool insulation. [13]
- Ceramic fish spine beads were used around the wires connecting the furnace to the power supply to prevent any wires to be exposed during the use of this furnace. [14]
- Standard aluminum foil was wrapped around the Quartz Fiber Wool insulation to both hold the top and bottom furnace covers in place and provide additional thermal insulation. Below in Figures 17,18,19 are images of the furnace set up.

Figure 17: Love Controls model 32B-23 Temperature Process Controller

Figure 18: Top view of the MOF–5 furnace with aperture, braided thermocouple, quartz fiber, aluminum foil and ring stand in view.

Figure 19: Interior view of the furnace with heating coils and quartz fiber molded vial slot in view. Thermocouple can be seen protruding from the bottom of the setup.

7.2 APPENDIX B: DETERMINATION OF THE CAPPING REAGENT LOCATION ON THE SURFACE OF MOF–5

7.2.1 SYNTHESIS OF HKUST-1

In the process of determining the location of the caping reagent on the surface of MOF–5, the water stable MOF HKUST-1 was successfully synthesized. This is important to note as it has not yet been applied to capping and trapping. This is a potential candidate for future caping and trapping research with air and water stable MOFs. Figure 20 shows a schematic and live photo of HKUST-1 side by side.

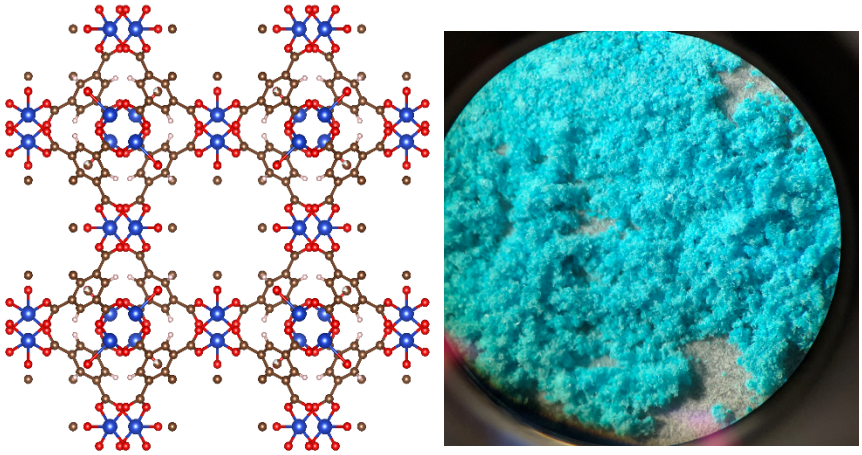

Figure 20: Schematic of HKUST-1 showing copper ions coordinated by benzene 1,3,5 tricarboxylic acid linkers (Left) Live image of HKUST-1 (Right).[3-4]

7.2.2 CONFIRMATION OF CAP LOCATION ON MOF–5 SURFACE

Although from McDonald's foundational paper [5]it was established that capping reagents could be successfully introduced to MOF–5 and obstruct the leakage of dye molecules; it was uncertain that the proposed coordination of the capping reagents with the metal ion sites was how the capping reagents were achieving the desired results. As a result, several studies over the span of 3 different REU programs facilitated by the Grimm Group determined that the capping reagents were indeed blocking channels by remaining on the surface of the MOF and not entering its pores. These studies used fluorinated capping reagents for their visibility in the X-ray

Photoelectron Spectroscopy machine to confirm that the capping reagents would remain on the surface of MOF–5 and not in the pores.[2,15] This collective study confirmed the feasibility of capping and trapping guests in MOF and the proposed mechanism of surface coordination. It also supported the hypothesis of sterically bulky capping groups being more likely to successfully trap guests because the mechanism of coordination was indeed occurring. Figure 21 shows the XPS images of both capped and uncapped HKUST-1 and MOF–5. The XPS shows concentration of the fluorinated capping groups on the pores, supporting the postulated coordination mechanism of capping groups.

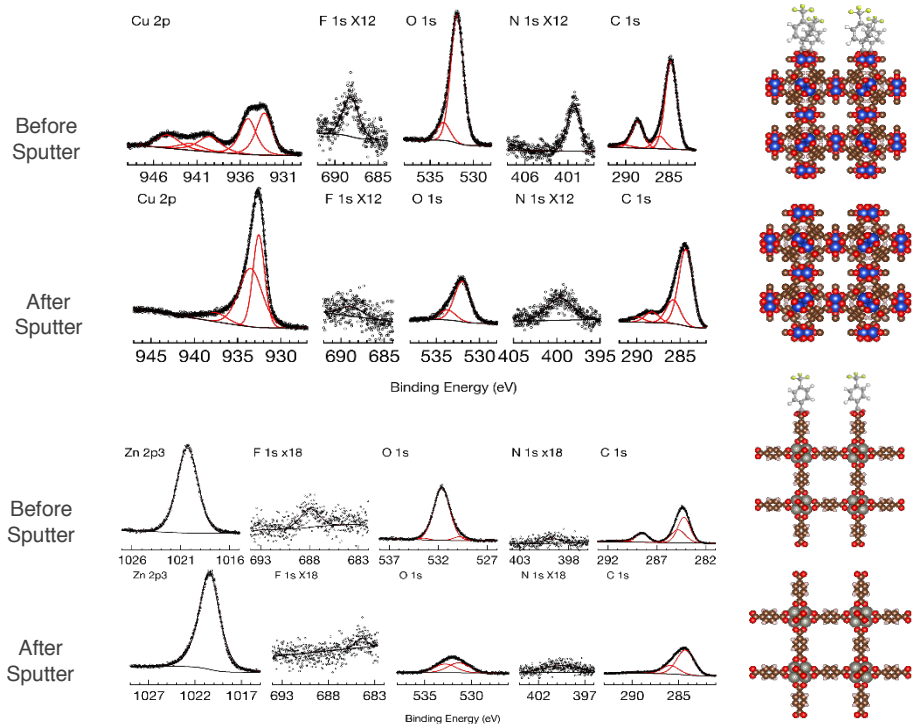

Figure 21: X-ray Photo Electron Spectroscopy results of capped vs. uncapped HKUST-1 and MOF–5. Sputtering shows the fluorinated groups situated on the surface of the MOFs as opposed to in the pores.[2]

7.3 APPENDIX C: THE STATE OF CAPPING/TRAPPING WITH ZIRCONIUM MOF UIO–66

UiO–66 is a water-stable Zirconium based MOF that is concurrently being researched to be adapted for the capping and trapping of guests. Currently, the Grimm and Burdette groups have succeeded in synthesizing UiO–66 and project work has been done to validate the feasibility of attaching a silane group to the surface of the MOF for capping and trapping purposes.[16] The surface attachment and XPS methods used have supported the feasibility of using silane groups to cap UIO–66. The future work of this field entails:

1. Optimizing the synthesis of UiO–66
2. Confirming Silane attachment to the surface of UiO–66
3. Capping and trapping of guest molecules within the pores of UiO–66.[16]

7.4 APPENDIX D: CHALLENGES AND ABANDONED PROCEDURES.

Over the course of this project, there were some challenges that are elucidated below.

1. CV trapping control failure and procedure adjustment

   Several attempts were made with no avail to trap CV in MOF-4 capped with TPAA as a control to determine that the capping coordination process was successful. In the past, the capping was done at 100°C but the procedure had to be adjusted to 120°C after which capping was successful.

2. Synthesis of MOF–5 with distilled DEF

   In the past, crystals of MOF–5 were obtained despite using distilled and recycled DEF. However, over the course of this project, no MOF–5 was able to be synthesized with distilled DEF. The product would appear decomposed or crystals would be miniscule. For this reason, the solvent was switched to DMF following the exhaustion of DEF from the bottle.

3. Dye Leakage rate determination of uncapped MOF–5

   An attempt was made to quantify the rate of dye leakage in uncapped MOF–5 to compare it to the rate of leakage when various capping molecules are introduced. The attempt was unsuccessful as it seemed that residual MB on the surface of MOF–5 mad e it impossible to measure the rate of leakage by immediately saturating the Ethanol.

4. Digestion of Capped and trapped Methylene Blue in TPAA

   An attempt was made to digest MB trapped in MOF–5 by TPAA. This attempt yielded unreasonable values for the total amount of MB in the pores of MOF–5. This experiment must be completed to understand the mass% loss of dye over time rather than measuring it in μmol/g as this study was forced to resort to.