

Investigation of Triphenylacetic Acid as a Trapping Agent for  
Sealing Molecular Guests Within Porous Metal-Organic  
Frameworks

A Major Qualifying Project Report

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## I. Introduction

Metal-organic frameworks (MOFs) consisting of crystalline coordination polymers have been of interest as porous host materials for molecular sorption, storage, and heterogeneous catalysis for the past decade due to the high surface areas and large void volumes of channels permeating the solids.<sup>1</sup> MOFs exhibit permanent porosity, high thermal stability, and feature continuous channels with surface areas, pore volumes, and surface properties that can be modified via synthesis of appropriate molecular building blocks, or post-synthetically by introducing substituents at reactive sites on the backbone of the framework.<sup>1</sup> Those unique properties render MOFs useful as porous hosts for applications involving sorption, separation, and reaction between molecules because the dimensions of pores are large enough (ranging from 6 Å to over 500 Å)<sup>2</sup> to permit guest molecules to diffuse into channels and interact with the organic components comprising the framework.<sup>1</sup> For example, recent studies focusing on organic synthesis have demonstrated that MOFs that incorporate catalytic groups within or pendant on the MOF backbone are able to adsorb organic reactants and function efficiently as heterogeneous catalysts for a range of synthetic transformations.<sup>1</sup>

To date, research on MOFs has focused primarily in two areas: (1) exploring synthetic strategies to achieve different framework architectures (e.g., cubic, diamond, etc.), and (2) investigating the behavior of MOFs in the context of molecular sorption, separation, and reactivity of guests within the confines of MOFs. We currently are exploring a strategy to trap adsorbed molecular guests inside of MOF particles in order to prevent diffusion of guests out of the porous host. Establishing a reliable method to seal guests within MOFs is a necessary requirement for developing and assessing the utility of

MOFs as host materials for long-term storage of guests, and ultimately for release/delivery of guests from MOFs in response to external stimuli (e.g., delivery of drugs). Toward that goal, the focus of this project was to test our hypothesis that a carboxylic acid featuring a large, sterically demanding substituent should serve as an effective trapping agent when attached to the surface of MOF particles. We reasoned that blocking the openings of pores exposed on the surface of MOFs should prevent guest molecules adsorbed within channels from diffusing out. In this study, a MOF known as MOF-5<sup>3</sup> was prepared via hydrothermal synthesis from benzene-1,4-dicarboxylic acid and zinc nitrate, the structure and porous behavior of MOF-5 was characterized, sorption and desorption of rhodamine B dye guest molecules by untreated MOF-5 was examined using UV-Visible spectroscopy, a trapping agent, triphenylacetic acid, was bonded to the surface of particles of MOF-5 in the presence of rhodamine B, and the resulting treated MOF was examined using UV-Visible spectroscopy to determine if the trapping agent was effective in preventing rhodamine from diffusing out of the MOF. An overview of this approach is illustrated in Figure 1.

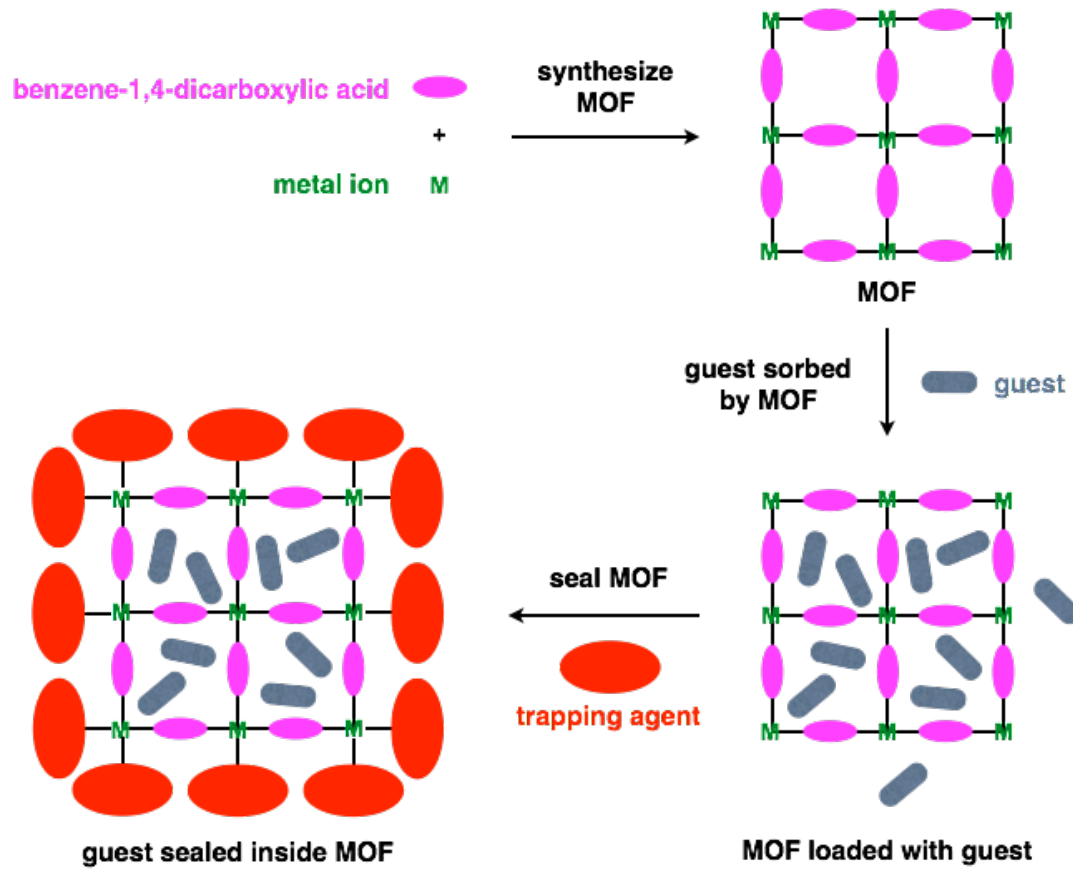


Figure 1. Overview of the approach utilized to seal guest molecules within a MOF.

## **II. Background**

### **2.1 Metal-Organic Frameworks**

We selected a metal-organic framework as the host material for the guest in this project. To understand the advantages of this decision and its impact, one should first understand what these materials are and what their intrinsic properties are.

#### **2.1.1 Coordination Networks**

A coordination network is a polymer composed of alternating units of organic ligands coordinated to metal ions where individual polymer chains are crosslinked via additional coordination between chains to form a two- or three-dimensional network.<sup>4</sup> Coordination networks generally form solids that may be amorphous (disordered) or crystalline (ordered), and that may nonporous or porous depending on the size, shape, rigidity, and number of coordinating functional groups present on the ligand, the valence and coordination geometry of the metal ion, and the conditions used to form the coordination network.

#### **2.1.2 Metal-Organic Frameworks**

A metal-organic framework is a coordination network in which rigid ligands and metal ions form a highly-ordered “framework” with a repeating architecture (e.g., cubic, diamond, etc.) such that the resulting solid is crystalline and often porous due to channels formed by void space within the framework.<sup>4</sup> Porous MOFs frequently exhibit permanent porosity, high thermal stability, and feature channels with high surface areas, large pore volumes, and surface properties that can be modified through synthesis. Those properties and the wide range of framework architectures that can be tailored make MOFs attractive



as host materials for applications involving molecular sorption, separation, and storage, and heterogeneous catalysis.<sup>1</sup>

### 2.1.3 MOF-5

Shown in Figure 2,  $Zn_4O(1,4\text{-benzenedicarboxylate})_3$ , better known as MOF-5, is a cubic metal-organic framework developed by Omar Yaghi et al.<sup>3</sup> Due to the remarkable stability of the crystal structure up to 400°C, this MOF has been widely investigated in regard to its guest storage and adsorption properties.<sup>1</sup> As shown in Figure 3, MOF-5 features large, highly-ordered 13 Å open channels throughout the framework that result in a high internal surface area of 4400 m<sup>2</sup>/g and crystalline structure made of more than 50% void space,<sup>5</sup> which allows for high storage capacity and passive diffusion of a range of guest molecules into and out of the crystal.

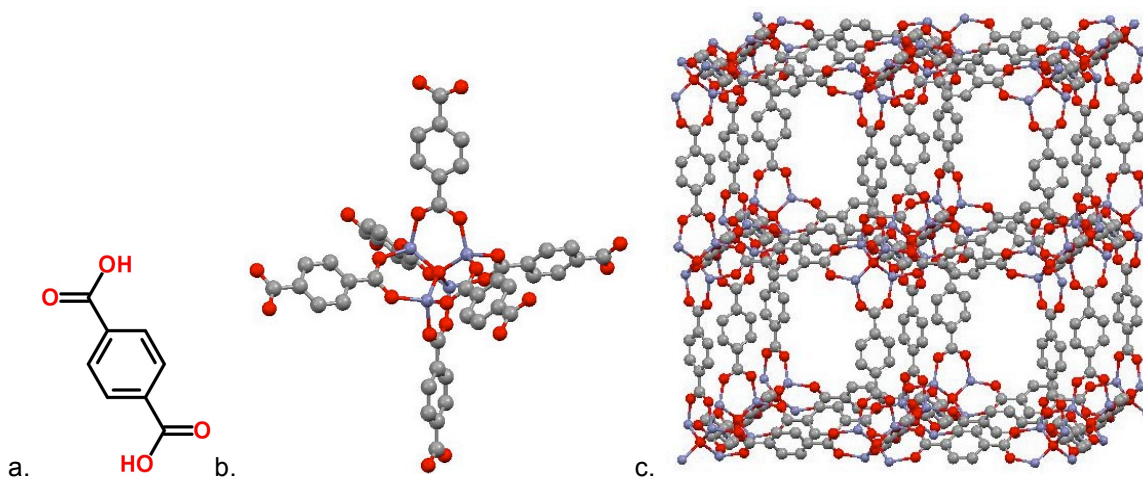


Figure 2. Depiction of a) benzenedicarboxylic acid, the organic ligand component of MOF-5, b) the coordination of organic ligands around the metal centers present in the structure, and c) the structure of MOF-5 formed from these coordination centers

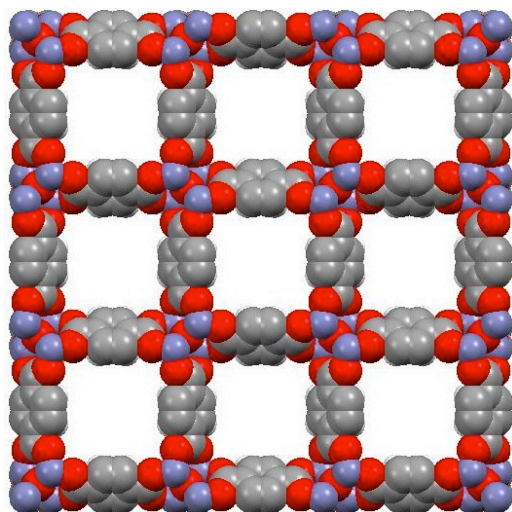


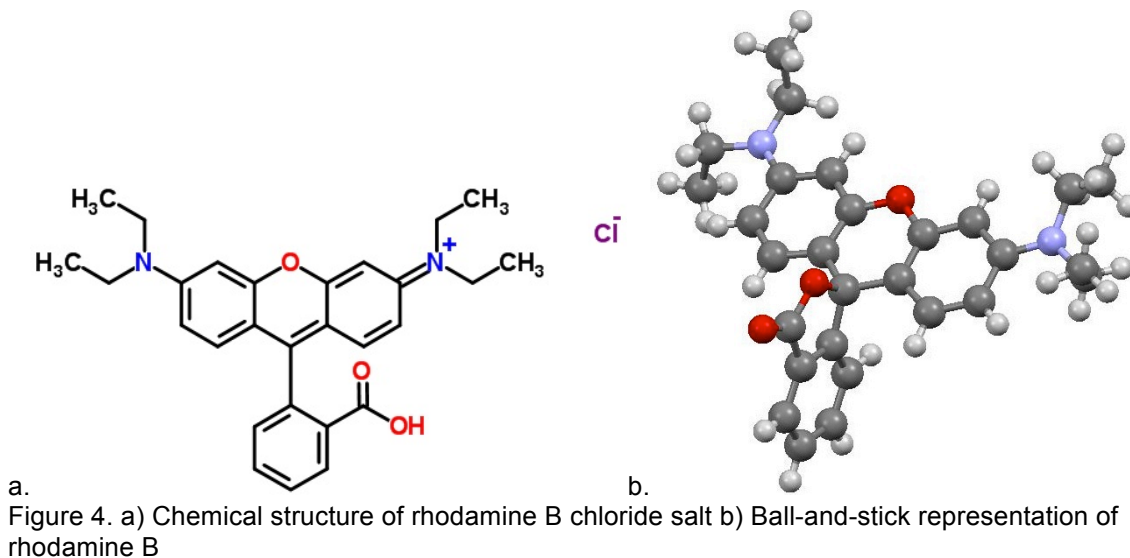
Figure 3. Representation of MOF-5 perpendicular to one face of the crystal showing the porosity of the crystal

## 2.2 Rhodamine B

We chose to use a dye as a guest in this project, as this would allow us to monitor the presence of the guest in the host both qualitatively via microscope observation and quantitatively via UV-Visible spectroscopy. In our selection of a dye we had three parameters that should be met for it to be deemed suitable. These consisted of the vibrancy of the dye, its size, and its reactivity with the exposed groups within the pores of the host. Rhodamine B is a chemical dye of a red or violet color typically used to trace flow of a solution. Its color in solution is very noticeable and vibrant.<sup>6</sup> This vibrancy allows for easy observation of a qualitative change of the dye's concentration in a stock solution.

The structure of rhodamine B is shown in Figure 4. The dimensions of the dye are 13.4 Å x 12.3 Å x 6.1 Å in terms of length, width, and thickness, respectively. We reasoned that those dimensions, along with the mostly flat structure of the large aromatic ring system, should allow the dye to diffuse through the 13 Å pores of MOF-5. Though a carboxylic acid group is present on the structure of rhodamine B, we reasoned that this

group is inhibited from reacting with the metal centers in the host by its position on the structure and its tendency to form a ring perpendicular to the rest of the molecule rather than remain a chloride salt. The UV-Visible spectrum of this dye also allows for easy determination of the dye's presence in solution, exhibiting a strong absorbance peak at 545 nm even at very low concentrations.



### 2.3 Ferrocene

Shown in figure 5, the second dye we selected for use in our study was ferrocene, an organometallic compound with the formula  $\text{Fe}(\text{C}_5\text{H}_5)_2$ . It is the prototypical metallocene, a type of organometallic chemical compound consisting of two cyclopentadienyl rings bound on opposite sides of a central metal atom.<sup>7</sup> Though ferrocene is less vibrant than rhodamine B, it still exhibits a strong yellow coloration in solution. At its largest size diagonally, it is only about 6 Å across, which should theoretically allow it to diffuse readily through the large pores of MOF-5. Its structure is made up of only one metal ion and two stable five-membered rings, meaning it should interact weakly with the inner surface of MOF-5. Ferrocene's spectral properties,

however, are less desirable than those of rhodamine B, exhibiting a characteristic absorbance peak far less intense at 435 nm. For this reason, investigation of ferrocene as a guest was delayed until the conclusion of our experimentation with rhodamine B.

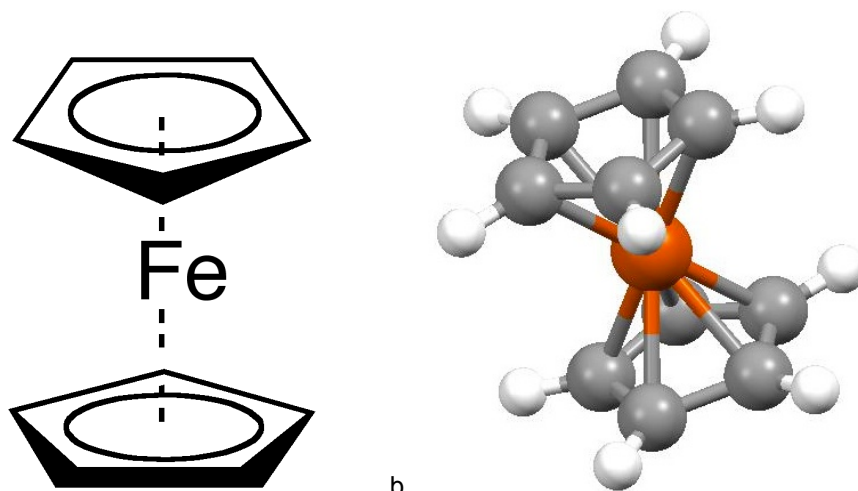


Figure 5. a) Chemical structure of ferrocene, b) Ball-and-stick representation of the structure of ferrocene.

## 2.4 Adsorption

The method through which the guest should theoretically diffuse into and interact with the internal surface of the host is called adsorption, which can be divided into two distinct categories. Physical adsorption is the attraction of particles of gases or dissolved compounds onto the surface of a solid, without chemically bonding them to the surface. This adsorption occurs as a result of surface interactions between the adsorbent and the surface to which it adsorbs, such as van der Waals forces, hydrogen bonding, and electrostatic attraction. Porous solids tend to attract more adsorbent, due to their larger surface area and thus larger probability of intermolecular interaction. Chemical adsorption results in the compound being bonded to the surface covalently rather than via weaker interactions, and therefore typically takes longer to occur than physical

adsorption.<sup>8</sup> The latter process does not involve any chemical alteration to the guest or host, allowing passive diffusion both into and out of the host. This process, also known as physisorption, occurs in MOFs and was thus the form of adsorption that we focused on in this project. In our particular case, physisorption occurred largely as a consequence of van der Waals interactions between the dye and the host structure, due to the nonpolar nature of the MOF and the weak dipole moment in the dye. This adsorption tends to occur until the dye is no longer able to diffuse into the structure or the inner surface of the crystal is entirely occupied, at which point the interactions between the dye and host are minimized. For this reason, the dye was allowed to diffuse into the MOF in a saturated solution for a time period longer than deemed necessary for physisorption to occur to be sure that the host had been loaded with the highest concentration of dye possible under standard conditions.

## **2.4 Characterization Techniques**

### **2.4.1 Thermal Gravimetric Analysis**

Thermal gravimetric analysis (TGA) is a method of thermal analysis in which loss of mass from a material is measured as a function of increasing temperature with constant heating rate, or as a function of time with constant temperature and/or constant mass loss.<sup>9</sup> This method of characterization is typically used to identify a MOF by the percentage of its initial weight lost, and thus the percentage of its structure made up of available void space for guests. Each MOF has a specific TGA pattern representing its porosity and thermal stability. The initial mass loss shown in these patterns usually shows loss of the solvent present in its pores as it evaporates at its boiling point. Secondary mass loss in a MOF loaded only with pure solvent usually indicates the structure at which its

structure decomposes. The different temperatures at which mass loss occurs correspond to the boiling point of the solvent and the loss of structural integrity in the MOF and thus shift with changes in the solvent present and the crystal for which the pattern is obtained.

#### **2.4.2 Powder Diffraction**

Powder diffraction is a scientific technique using X-ray, neutron, or electron diffraction on powder or microcrystalline samples for structural characterization of materials.<sup>10</sup>

#### **2.4.3 Powder X-Ray Diffraction (PXRD)**

Powder X-ray diffraction (PXRD) results in a diffraction pattern that is unique to the bulk material of a crystalline solid. This method involves irradiating a bulk sample of crystals (i.e., a powder) with X-rays continuously over a range of incident angles, resulting in peaks of different intensity representing all of the unique crystalline planes. The X-rays diffract in a pattern characteristic of the crystalline structure.<sup>11</sup> This method obtains a trace unique to each different crystal structure, therefore it is invaluable in determining the structure of a synthesized crystal. This unique trace is a result of the spacing of the metal centers in the structure and as a result can be compared to calculated data obtained from the known crystal structure, as well as traces obtained from the crystal in previous literature to confirm the identity of the product.

#### **2.4.5 Ultraviolet-Visible Spectroscopy**

Ultraviolet-visible (UV-Vis) spectroscopy shows the absorption of energy by a compound in the ultraviolet and visible light ranges of the electromagnetic spectrum. This type of spectroscopy is only useful in colored or fluorescent compounds. This is because other compounds are transparent in these regions and will show no absorption.<sup>8</sup>

These measurements are obtained by first obtaining a baseline measurement for the absorbance of the solvent in a given range and subsequently obtaining absorbance measurements for the solution with a given concentration of a dye. In the case of this project, these subsequent readings were obtained as a function of time in which the host loaded with dye was exposed to the solvent. Beer's Law (Absorbance = molar extinction coefficient  $\times$  path length of container in cm  $\times$  concentration of solute) allows us to determine the concentration of the dye in solution at a given time. From this law, we can conclude that under conditions of a constant path length and molar extinction coefficient the absorbance of a solution is proportional to the concentration of the solute. Using this information, we were able to determine whether the concentration of dye in solution increased in time by observing the change in absorbance.

### III. Objective

The main objective of this project was to determine whether a molecular guest could be sealed within a MOF by bonding a bulky monocarboxylic acid to the surface of MOF crystals such that the sterically demanding substituent of the acid would block the openings of pores and prevent diffusion of the guest out of the MOF channels. Previous research has shown that guests can be trapped within the pores of MOFs via interaction with reactive or attractive groups on the inner surface of the framework<sup>12</sup>, but no published work has determined whether sealing the surface of the crystal is a viable method for forcing the crystal to retain a guest.

We selected MOF-5 as the host material for this study due to its large pores (13 Å), which result in over 50 percent of the structure being void space, as well as its highly symmetric cubic structure resulting in consistent exposure of pores at each surface. Its thermal stability also allowed us to repeat the method of hydrothermal synthesis used to produce the MOF in order to bond the monocarboxylic acid to the surface of the crystal at its metal centers without the possibility of the host's structure decomposing.

Triphenylacetic acid was selected as the trapping agent because of the close match between its effective coverage radius (12.4 Å) and the pore size of MOF-5 as well as its theoretical ability to coordinate to the zinc centers at the crystal's surface via the carboxylic acid substituent of its structure. Assuming full coverage of the coordination sites on the surface, the triphenylmethyl substituent is large enough to block enough of the exposed channels on the surface to prevent rhodamine B from escaping the channels. Additionally, this substituent is not so large that steric repulsion would make it incapable of coordinating to every site, resulting in coverage of every pore at the surface.



Rhodamine B was selected as the primary dye of focus due to the close match between its dimensions (shown in Figure 6) and those of the pores of MOF-5, allowing it to diffuse through these pores while still being capable of desorbing from the structure in solution. This close match gave us the best chance to prove our hypothesis that a guest could be sealed within the MOF via bonding of a trapping agent at the host's surface, as rhodamine B would be the less likely to diffuse through small gaps in pore coverage like smaller guests might. Its strong absorbance at 545 nm also allowed us to determine easily whether the dye diffused from the sealed MOF in solution.

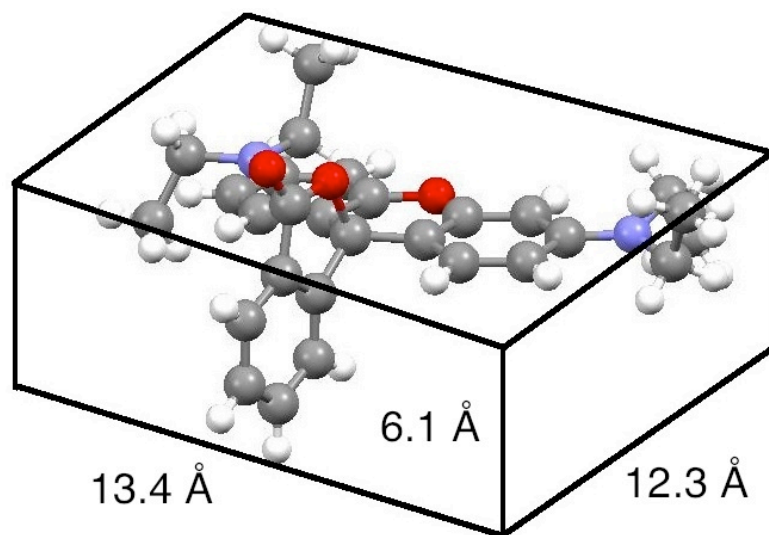


Figure 6. Structural measurements from Mercury showing the size in three dimensions of Rhodamine B in angstroms.

We chose ferrocene as a second candidate because of its small size and strong absorbance in the UV-visible spectrum, which would allow us to determine its presence in solution easily. The size of this guest would allow us to determine whether the trapping agent was capable of sealing a much smaller guest within the host. Its lack of reactivity with the internal structure of the MOF should also prevent any chemical bonds from forming between the guest and host, meaning that it could only be trapped within the structure by the monocarboxylic acid at the surface.

Guests of two different sizes were tested to observe the effectiveness of the trapping agent in preventing desorption of guests of varying size and structure and thus the size of the gaps in its coverage of the host's surface. This would allow us to determine what guests might be effectively trapped by triphenylacetic acid and test other guests to determine the exact size of these gaps.

Figure 7 shows a hypothetical model of triphenylacetic acid (shown in red) coordinated to zinc ions exposed on the surface of MOF-5 (shown in grey). The space-filling structures of triphenylacetic acid and MOF-5, which were generated from the known crystal structures, indicate the relative sizes of the trapping agent (12.4 Å) and the pore openings in MOF-5 (12.8 Å). As shown on the left in Figure 7, bulky triphenylmethyl headgroup of triphenylacetic acid is just small enough to permit triphenylacetic acid to coordinate to all of the zinc metal centers exposed on the surface of MOF-5, and thus allow full coverage on the surface. As shown on the right in Figure 7, access to the openings of channels on the surface of MOF-5 is reduced sufficiently when the surface is saturated with the trapping agent that rhodamine B guests adsorbed within the channels should remain sealed inside. We chose to test triphenylacetic acid as the trapping agent on the basis of that analysis.

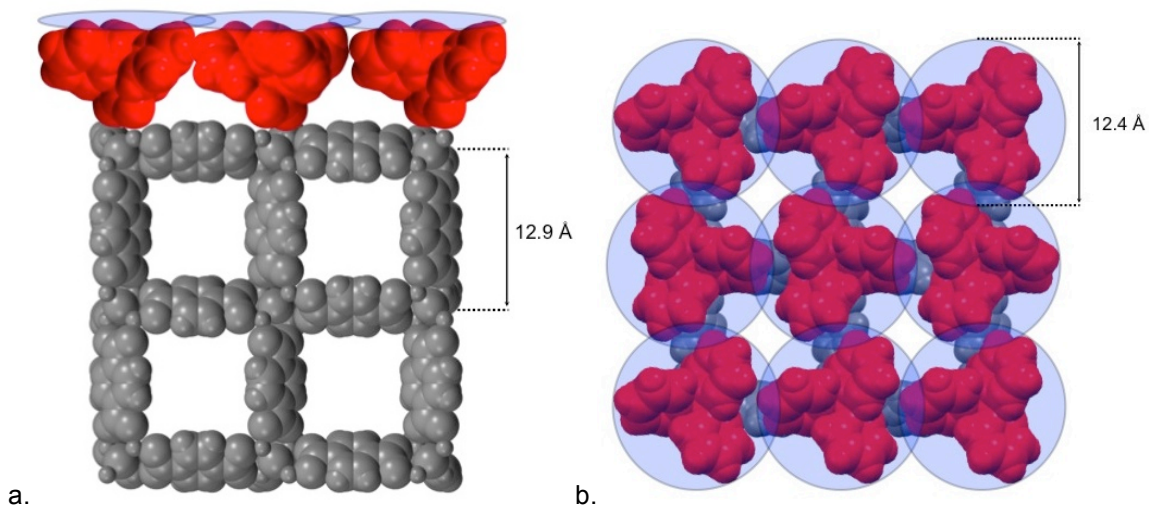


Figure 7. Structural data from Mercury showing theoretical seal of MOF-5 by triphenylacetic acid via a) side view and b) top view including measurements confirming large enough pores for rhodamine to diffuse in. and enough coverage of pores to prevent diffusion out once sealed

To assess our hypothesis, it was necessary to determine whether the dye in use can diffuse both into and out of the crystal. Once this is confirmed, a method must be decided upon to seal the MOF at its outer surface. This can be performed by bonding a monocarboxylic acid to the exposed metal centers at the surface of the crystal. Upon sealing the MOF, the same test used to determine whether passive diffusion was possible in an unsealed MOF can be used to determine whether the dye will diffuse similarly with the surface sealed.

## IV. Experimental

All experiments were conducted under standard ambient conditions.

Hydrothermal synthesis was conducted using a preheated oven at 100°C with time of heating preset. Loading of crystals with dye was performed in saturated ethanol solution at room temperature and pressure. Thermal gravimetric analysis was conducted using a Hi-Res TGA 2950 Thermogravimetric Analyzer (TA Instruments) under a nitrogen atmosphere at a rate of 10°C/min. Powder X-ray diffraction was performed using a Bruker AXS D8 Focus with a Cu source.

### 4.1.1 Synthesis of MOF-5

0.306g (0.00103 moles) of zinc nitrate hexahydrate, 0.140 g (0.000843 moles) of 1,4-benzenedicarboxylic acid (BDC), and 20 mL of diethylformamide (DEF) were sealed in a 125 mL high pressure microwave vial, heated to 100 °C for 41 hours, and then allowed to cool to room temperature. Clear cubic crystals were present in solution at elevated temperature and remained present as solution cooled. Crystals of MOF-5 were isolated by removing the reaction solution with a pipette and then sealing the crystals in the microwave vial to prevent guest DEF from evaporating out of the MOF crystals.

### 4.1.2 Failed Syntheses of MOF-5

1. 1.213g (0.00401 moles) of zinc nitrate hexahydrate, 0.343g (0.00206 moles) of BDC, and 40 mL of N,N'-dimethylformamide (DMF) were sealed in a 125 mL high pressure microwave vial, heated to 80 °C for 24 hours, and then allowed to cool to room temperature. Clear crystals were present in solution at elevated temperature and remained present as solution cooled. Crystals were isolated by removing the reaction solution with

a pipette and then sealing the crystals in the microwave vial to prevent guest DMF from evaporating out of the MOF crystals.

2. 0.7422g (0.00249 moles) of zinc nitrate hexahydrate, 1.572g (0.00946 moles) of BDC, and 30 mL of DMF were sealed in a 125 mL high pressure microwave vial, heated to 80 °C for 72 hours, and then allowed to cool to room temperature. Clear monoclinic crystals were present in solution at elevated temperature and remained present as solution cooled. Crystals were isolated by removing the reaction solution with a pipette and then sealing the crystals in the microwave vial to prevent guest DMF from evaporating out of the MOF crystals.

## **4.2 Characterization of MOF-5**

### **4.2.1 Thermal Gravimetric Analysis**

As a general procedure for thermal gravimetric analysis, crystals of MOF-5 were stored in a sealed microwave vial prior to analysis by TGA in order to prevent guest DEF solvent from evaporating out of the crystals. Samples of solvated MOF-5 were removed from the vial, blotted dry on filter paper to remove external solvent, and then were loaded immediately into a pre-tared Pt TGA pan and heated from RT to 600 °C at a rate of 10 °C per minute.

### **4.2.2 Powder X-Ray Diffraction**

As a general procedure for PXRD analysis, MOF-5 wet with excess solvent was ground using a mortar and pestle. The resultant powder was loaded into a PXRD pan and scanned from 3° to 50° in 2 $\theta$ .

### **4.3 Adsorption of Dye into MOF-5**

#### **4.3.1 Adsorption of Rhodamine B**

Saturated solution of rhodamine B dye in ethanol was prepared in a 2-dram vial. Crystals were blotted dry on filter paper until they were no longer transparent and placed in prepared solution for 24 hours. Procedure was repeated with DEF in place of ethanol.

#### **4.3.2 Adsorption of Ferrocene**

Saturated solution of ferrocene dye in ethanol was prepared in a covered 50 mL beaker. Crystals were blotted dry on filter paper until they were no longer transparent and placed in prepared solution for 72 hours.

### **4.4 Determination of Sorption and Desorption of Guest Dyes from Unsealed MOF-5**

#### **4.4.1 Rhodamine B**

Microscope observation revealed that crystals had become red. UV-vis spectrometer was prepared by obtaining a baseline reading for the absorbance of ethanol. Dyed crystals were placed in a cuvette filled with ethanol and readings were obtained over the course of 30 minutes. Change in the color of solution was qualitatively observed before each reading was obtained.

#### **4.4.2 Ferrocene**

Microscope observation revealed that crystals seemed to become yellow. UV-vis spectrometer was prepared by obtaining a baseline reading for the absorbance of ethanol. Dyed crystals were placed in a cuvette filled with ethanol and readings were obtained over the course of 30 minutes.

## **4.5 Sealing of MOF-5**

Unsealed, dyed crystals were placed in saturated solution of rhodamine B in DEF in a 125-mL microwave vial. 0.0194g (0.0000652 moles) of zinc nitrate and 0.010g (0.0000347 moles) of triphenylacetic acid were added to this solution, which was then heated to 100°C for 41 hours and then allowed to cool to room temperature. Removed excess solvent with pipette and sealed flask. Crystals were isolated by removing the reaction solution with a pipette and then sealing the crystals in the microwave vial to prevent guest DEF from evaporating out of the crystals.

### **4.5.1 Determination of Sorption and Desorption of Dye from Sealed MOF-5**

Microscope observation revealed that crystals remained vibrant red after sealing procedure. The UV-vis spectrometer was prepared by obtaining a baseline reading for the absorbance of ethanol. Dyed, sealed crystals were placed in a cuvette filled with ethanol and readings were obtained over the course of 60 minutes.

## **4.6 Determination of Sorption and Desorption of Dye from MOF with Temperature**

### **4.6.1 TGA Analysis of Rhodamine B**

The TGA instrument was prepared and calibrated as previously stated. Rhodamine B powder was loaded into a pre-tared Pt TGA pan and heated from RT to 300 °C at a rate of 10 °C per minute.

### **4.6.2 TGA Analysis of Ferrocene**

The TGA instrument was prepared and calibrated as previously stated. Ferrocene powder was loaded into a pre-tared Pt TGA pan and heated from RT to full decomposition at a rate of 10 °C per minute.

#### **4.6.3 TGA Analysis of Unsealed MOF-5 Loaded With Rhodamine in Ethanol**

The TGA instrument was prepared and calibrated as previously stated. Samples of loaded, unsealed MOF-5 were removed from the vial, blotted dry on filter paper to remove external solvent, and then were loaded immediately into a pre-tared Pt TGA pan and heated from RT to 300 °C at a rate of 10 °C per minute.

#### **4.6.4 TGA Analysis of Unsealed MOF-5 loaded with Rhodamine in DEF**

Crystals dyed in ethanol were transferred to a rhodamine B solution in DEF and left for sorption to occur for 48 hours. The TGA instrument was prepared and calibrated as previously stated. Samples of loaded, unsealed MOF-5 were removed from the vial, blotted dry on filter paper to remove external solvent, and then were loaded immediately into a pre-tared Pt TGA pan and heated from RT to 300 °C at a rate of 10 °C per minute.

#### **4.6.5 TGA Analysis of Unsealed MOF-5 loaded with Ferrocene in Ethanol**

The TGA instrument was prepared and calibrated as previously stated. Samples of unsealed MOF-5 loaded with ferrocene were removed from the beaker, blotted dry on filter paper to remove external solvent, and then were loaded immediately into a pre-tared Pt TGA pan and heated from RT to 300 °C at a rate of 10 °C per minute.

#### **4.6.6 TGA Analysis of Sealed MOF-5 loaded with Rhodamine B**

The TGA instrument was prepared and calibrated as previously stated. Samples of loaded, sealed MOF-5 were removed from the vial, blotted dry on filter paper to remove external solvent, and then were loaded immediately into a pre-tared Pt TGA pan and heated from RT to 300 °C at a rate of 10 °C per minute.



## **4.7 Preparation of Control Solutions**

### **4.7.1 Rhodamine, Zinc Nitrate, and Monocarboxylic Acid**

0.025g (0.000084 moles) of zinc nitrate hexahydrate, 0.036g (0.00013 moles) of triphenylacetic acid and a saturated solution of rhodamine B in 10 mL of DEF were sealed in a 50 mL high pressure microwave vial, heated to 100 °C for 41 hours, and then allowed to cool to room temperature.

### **4.7.2 Rhodamine and Zinc Nitrate**

0.025g (0.000084 Moles) of zinc nitrate hexahydrate, and a saturated solution of rhodamine B in 10 mL of DEF were sealed in a 50 mL high pressure microwave vial, heated to 100 °C for 41 hours, and then allowed to cool to room temperature.

## V. Results and Discussion

### 5.1 Synthesis and Characterization of MOF-5

The theoretical work setting the foundation for this experimentation called for the host material to be MOF-5, so the crystals had to be identified positively as such before further investigation could take place. After determining a consistent and successful method of synthesis, it was possible to synthesize larger batches of the crystal for testing. The crystals appeared to have a predominantly cubic structure under view of a microscope, suggesting that the MOF synthesized was MOF-5. Shown in Figure 8, TGA data showed significant initial mass loss of 52% between room temperature and 220 °C corresponds to loss of diethylformamide (boiling point 176-177 °C). DEF is lost immediately starting at room temperature because the pores are large enough to contain a significant amount of DEF, some of which is in contact with the surface of the MOF backbone, but the majority of which is present in the middle of the void space. The 13 Å channels are exposed to air on the surface of the MOF particles and large enough that DEF easily can evaporate out of the pores on exposure to air. This volatility is the primary reason for loading the sample in a pre-tared pan as quickly as possible following extraction of the crystals from solution. The mass loss becomes less intense at 140 °C and the slope of the graph becomes less steep, signifying slower loss of mass, likely due to more energy being required to drive out DEF on the internal surface of the MOF. Mass continues to be lost beyond the boiling point of DEF, due either to DEF that interacts more strongly with the surface of the MOF than with other molecules of DEF in bulk solvent, or because unreacted starting materials with higher boiling points than DEF also are present in the MOF and are desorbing. The mass loss of 52% is typical for MOF-5

and reflects the large internal void space present in that structure. The empty MOF solid remains stable up to 450 °C, as indicated by no further loss in mass. The MOF crystals start to decompose above 450 °C, as indicated by the steep mass loss of 30% above that temperature. This behavior is consistent with the behavior of MOF-5 reported in previous literature.

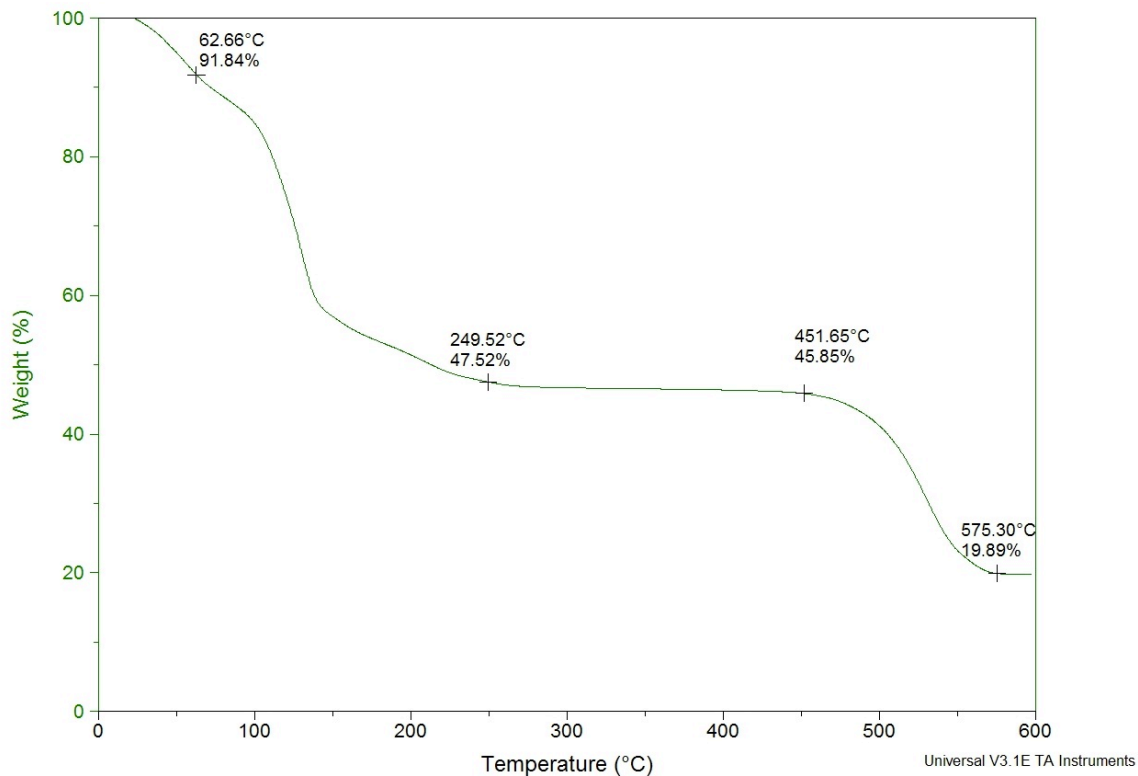


Figure 8. Thermal gravimetric analysis of MOF-5 via temperature ramp from room temperature to 600°C at a rate of 20°C per minute

The PXRD trace shown in Figure 9 shows peak positions and intensities consistent with those reported for MOF-5 in previous literature.<sup>13</sup> Each of the peaks in a PXRD trace correspond to a unique set of lattice planes present in the crystal structure, meaning that synthesis of a crystal that was not MOF-5 would yield an entirely different trace, as we found in failed syntheses of the host material. The components used to synthesize MOF-5 are known to form other crystals under different synthesis conditions, each of which results in a different PXRD trace. MOF-5 itself is known to undergo phase

transitions to form slightly different structures over time when exposed to water vapor or bulk liquid water, meaning a PXRD trace had to be obtained soon after extraction of the crystals from solution. It was important to determine that the material synthesized was MOF-5, otherwise the bonding of the triphenylacetic acid to the host's surface would not occur as theorized; this means that the trapping of a guest within the host would not occur as theorized and thus conditions not pertaining to sealing of the crystal at its surface could cause resistance to desorption of the guest.

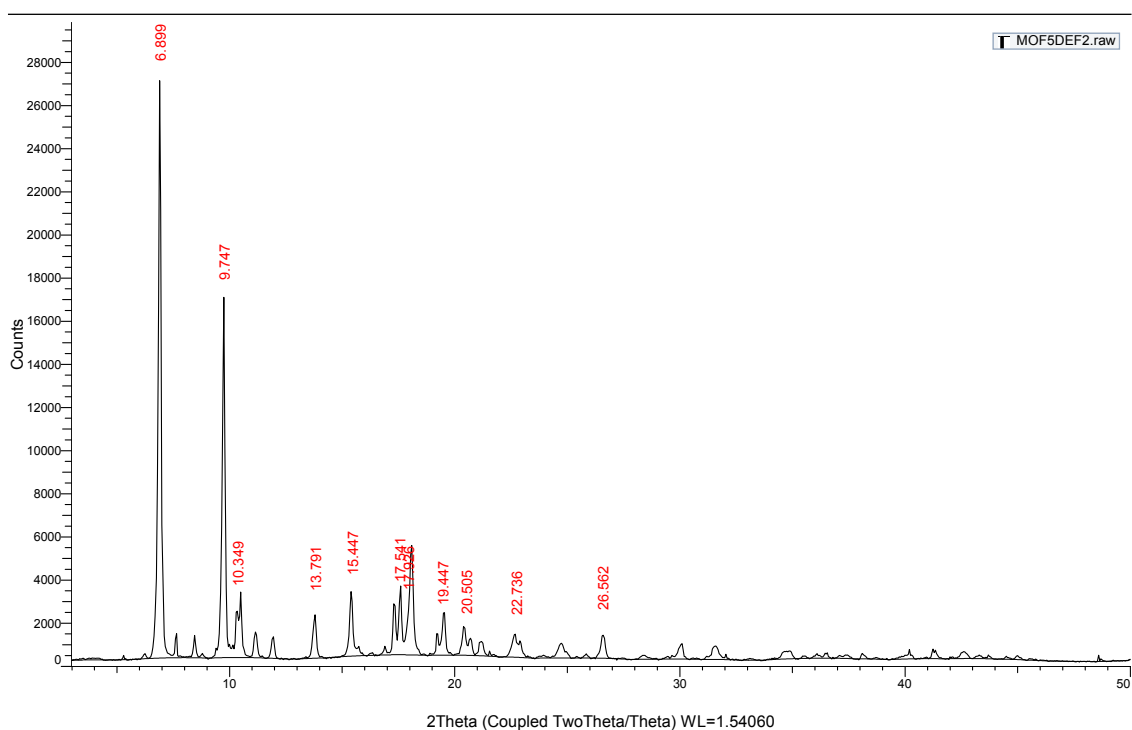


Figure 9. Powder X-ray diffraction data confirming the identity of the product crystal as MOF-5

## 5.2 Unsealed MOF-5

Before assessing the effect of the trapping agent, it was necessary to investigate both sorption and desorption of the guest, rhodamine B, in solution by MOF-5. It was important to demonstrate that the dimensions of rhodamine were small enough to allow the dye to diffuse into the channels of MOF-5 and to load within the MOF in a high enough concentration to be observed visually within crystals of MOF-5, and to ensure

enough rhodamine was absorbed to be detected. More importantly, it was essential to show that rhodamine B present in loaded crystals of MOF-5 would diffuse back out of the MOF into solution and in a high enough concentration to be detected and quantified by UV-visible spectroscopy. Under conditions of constant path length and molar extinction coefficient, desorption of the guest from the host material should be evident from an increase in the absorption of the solution with time when unsealed crystals were placed in a stock solution of the solvent in which the dye was adsorbed into the MOF and thus an increase of the concentration of the dye in solution. The adsorption of the dye into the crystal proved successful under microscope observation. The data collected in the UV-Vis spectrometry test shown in Figure 10 over the course of thirty minutes proved that the dye diffused from the framework and into the solution at a near constant rate if the crystal was left unsealed.

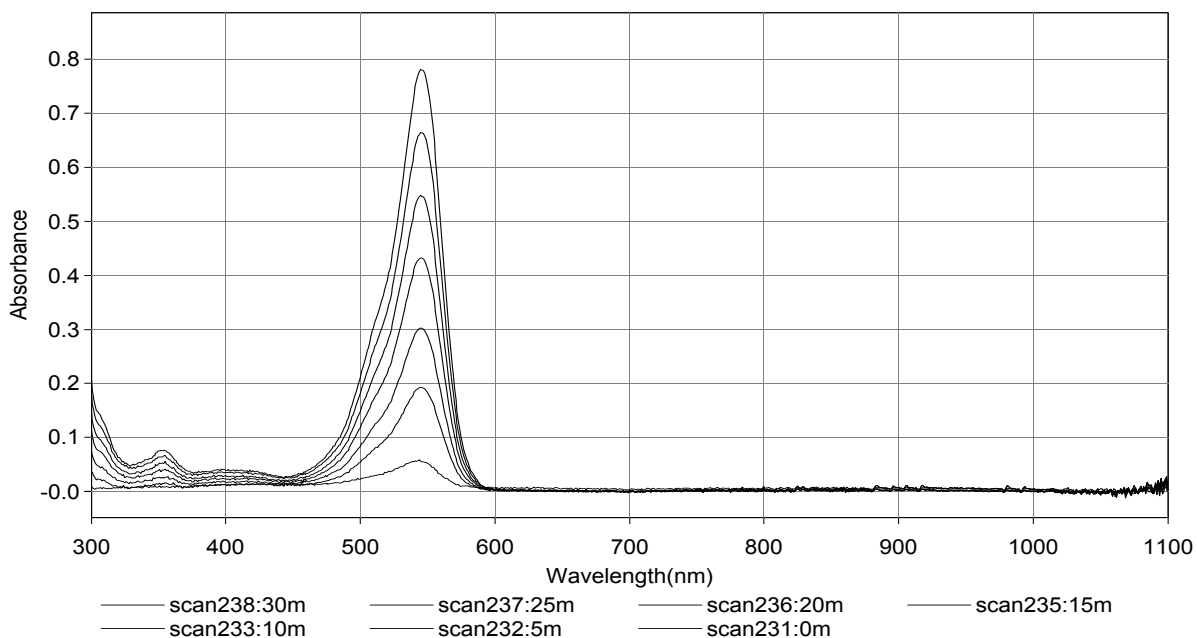


Figure 10. UV-Visible spectrometry readings displaying the increase in absorbance of the solution due to release of rhodamine B from the crystal over the course of thirty minutes.

As shown in Figure 10, the main absorbance peak of rhodamine B occurs at and around 545 nm. A steady, almost constant increase in absorbance at this wavelength occurred with time as the dye flowed out of the crystal and into the solution. Taking this data into account, it can be concluded that rhodamine B passively diffuses out of MOF-5 in an ethanol solution when the crystal is left unsealed. Observation of the color of the solution further strengthened this conclusion, as the ordinarily clear ethanol solution had become a pink color readily visible to the naked eye even without comparing it to stock ethanol.

Loaded samples of MOF-5 isolated after exposing MOF crystals to saturated solutions of rhodamine B in ethanol also were tested using thermal gravimetric analysis to determine if the amount of rhodamine B absorbed could be quantified thermally on the basis of the mass of guest lost. A thermal gravimetric analysis of the unsealed MOF loaded with the dye in ethanol was performed (shown in Figure 11) and the data showed behavior suggesting that rhodamine B diffused from the unsealed crystal separate from the ethanol in the structure at around the temperature at which the dye begins to decompose. This decomposition temperature was confirmed by the TGA data shown in Figure 13. It could be argued that this mass loss was a result of decarboxylation of the dye; if this were the case, the same behavior would be observed in the sealed MOF. Data discussed later proved that this is not the case.

A test, shown in Figure 12, was also performed assessing the diffusion of the dye with heat in an unsealed MOF loaded in DEF to ensure that the secondary mass loss was not a result of the presence of different solvents. This data showed slightly different behavior than that in ethanol, but exhibited a similar increase in mass loss around the

decomposition temperature of rhodamine B. There was also a far higher mass percentage loss. This is likely, however, to be due to excess external solvent that increased the mass of the sample. This could also have led to the smaller size of the mass loss peak in the DEF sample.

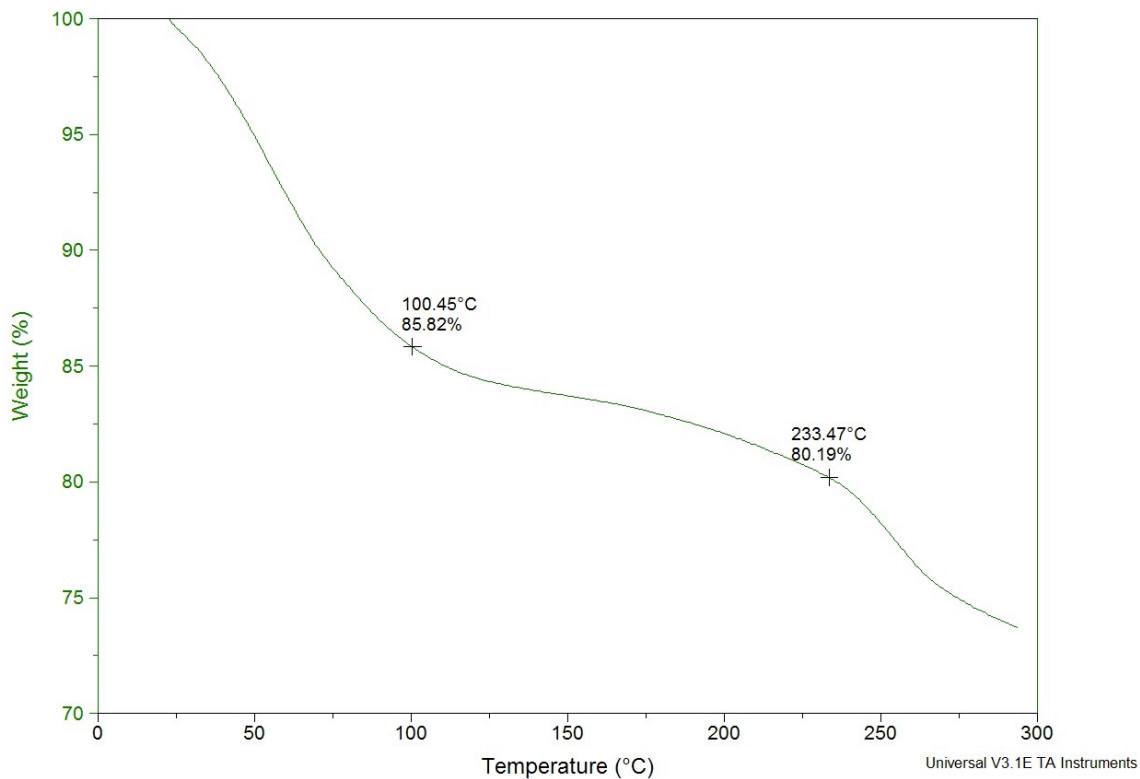


Figure 11. Thermal gravimetric analysis of MOF-5 loaded with rhodamine B in ethanol showing mass loss separate from the immediate loss of ethanol

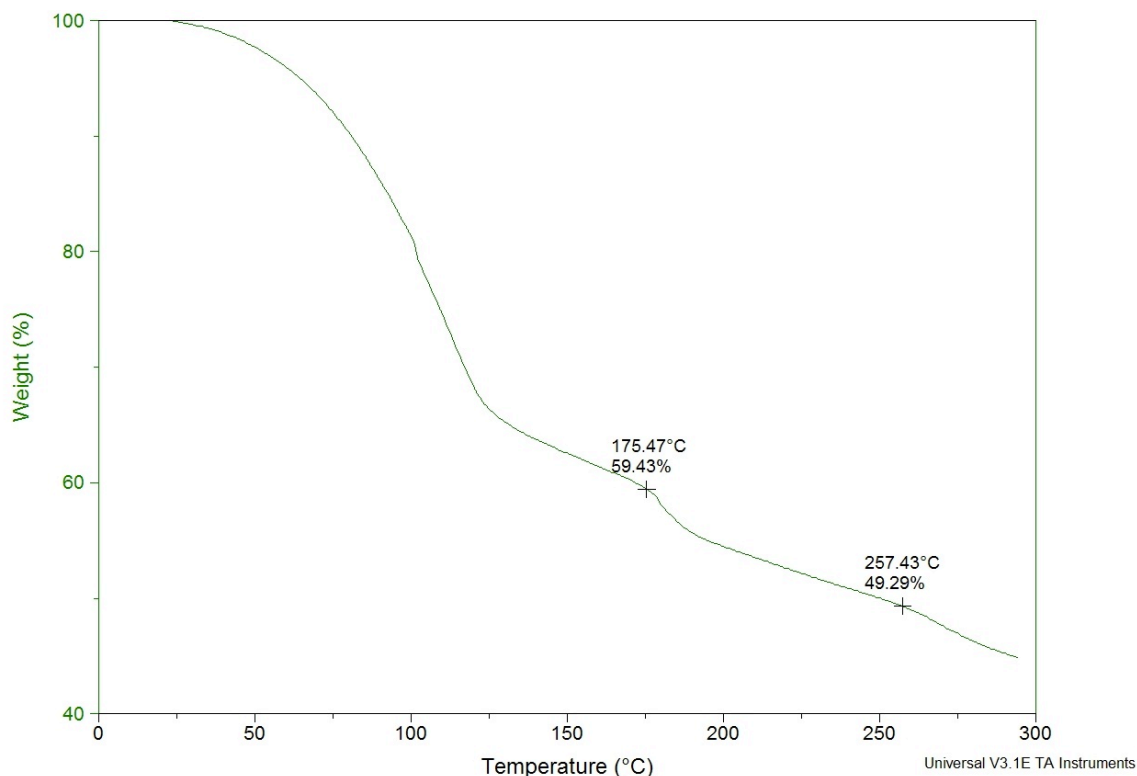


Figure 12: Thermal gravimetric analysis of MOF-5 loaded with rhodamine B in DEF showing mass loss separate from the loss of the solvent

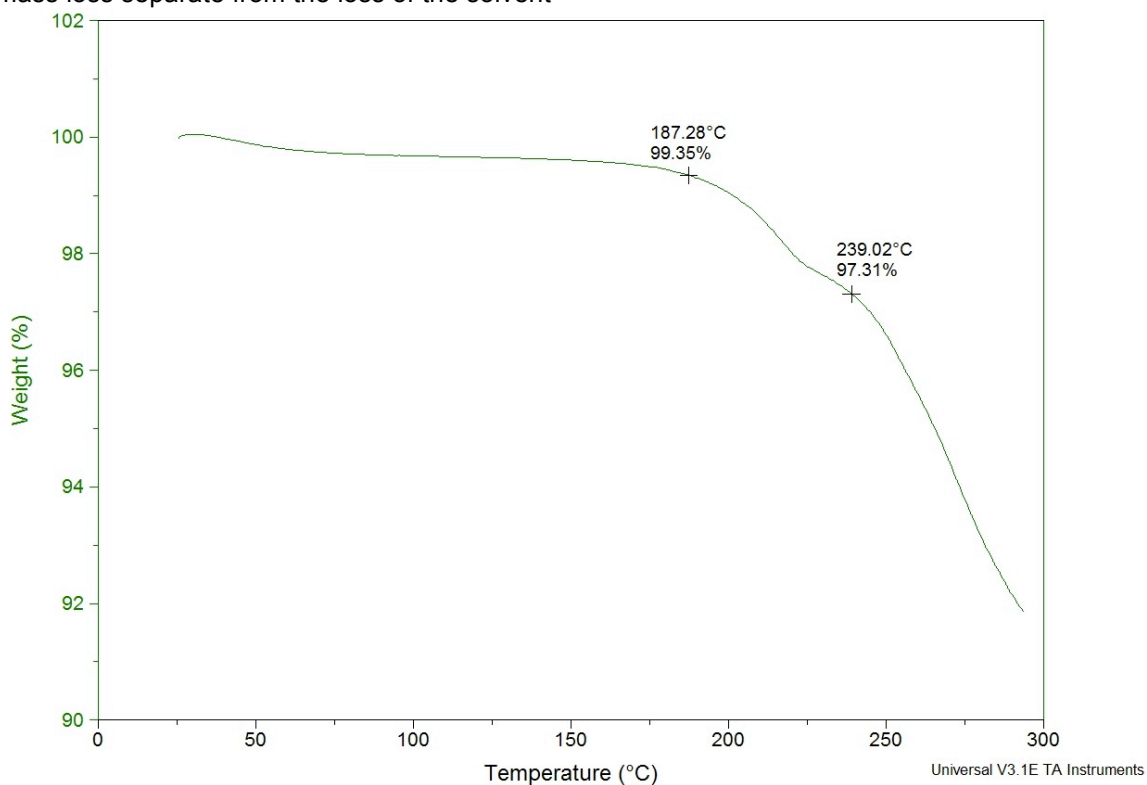


Figure 13. Thermal gravimetric analysis of rhodamine B powder showing its approximate decomposition temperature



When tested with ferrocene, a much smaller dye, the TGA data shown in Figure 14 showed similar behavior. After a small diffusion of ethanol out of the structure, likely so low due to delay in the start of the test, the data showed mass reduction between about 165°C and 315°C not observed in the unloaded MOF. This may correspond to diffusion of DEF from the structure after an initial loss of ethanol, as UV-Vis analysis (shown in Figure 16) showed that the dye did not diffuse out of the framework in a stock ethanol solution. This might suggest that the dye did not adsorb to the crystal. Due to this finding, ferrocene was deemed unfit as a dye with which to test this trapping method and sealing of the MOF was not performed.

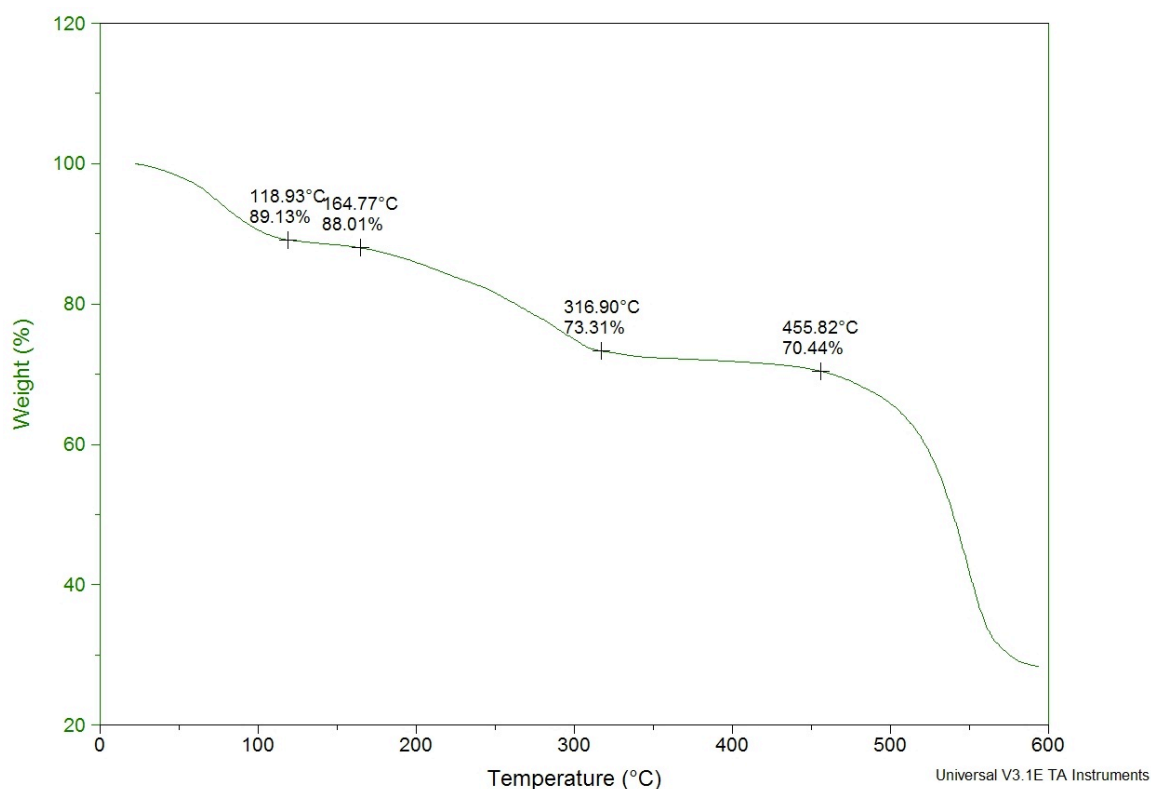


Figure 14. Thermal gravimetric analysis of MOF-5 loaded with ferrocene in ethanol showing mass loss of ferrocene between 165°C and 315°C

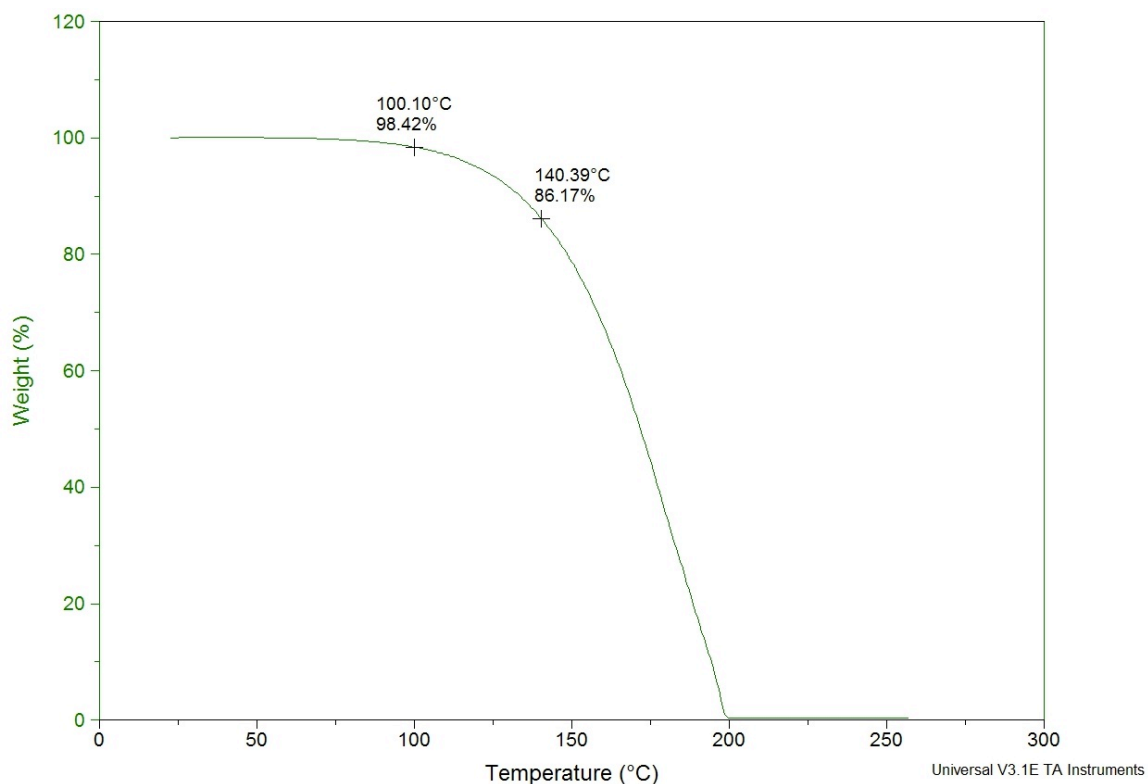


Figure 15. Thermal gravimetric analysis of ferrocene showing complete decomposition by 200°C

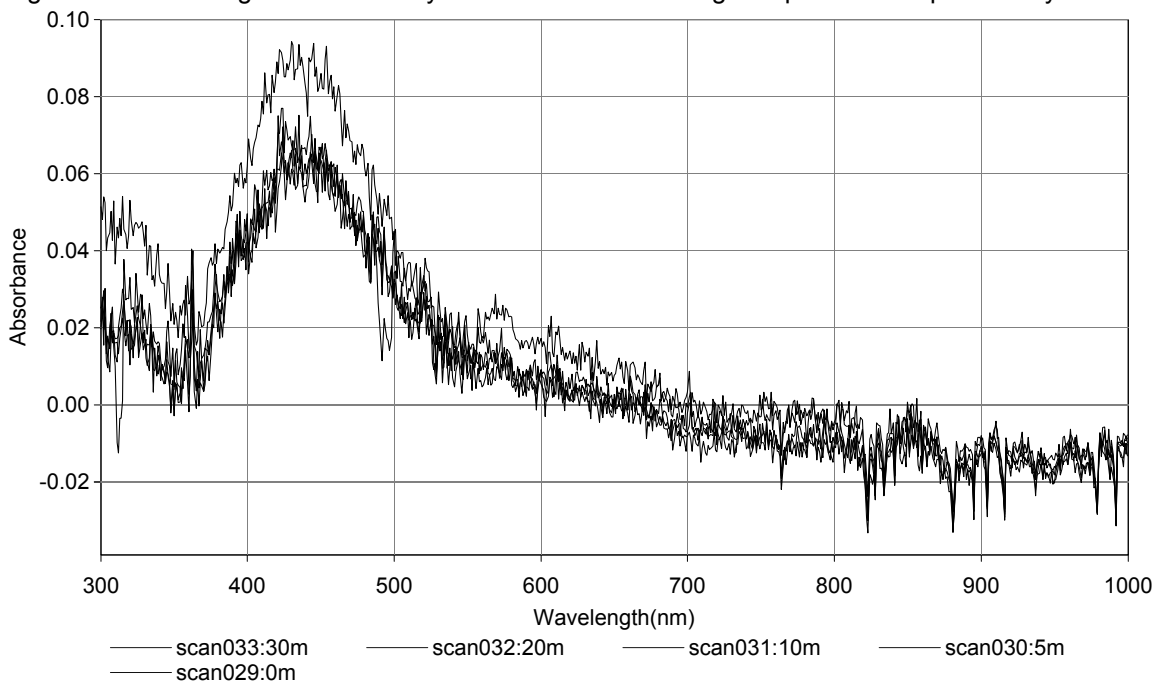


Figure 16. UV-Visible scan of unsealed MOF loaded with ferrocene in ethanol. Highest peak corresponds to zero-minute reading, likely due to ferrocene dye present on the surface of the crystal.

### 5.3 Sealed MOF-5

Several tests had to be performed to prove the accomplishment of the project's initial objective of proving that a guest can be sealed within MOF-5 by bonding a trapping agent to the MOF's surface. This seal was performed by exposing MOF-5 loaded with rhodamine B to hydrothermal conditions identical to those in its synthesis with triphenylacetic acid in place of the dicarboxylic acid present as an organic ligand in the crystal structure in a saturated solution of rhodamine B in DEF. To show this, the behavior of the sealed host had to behave similarly to the MOF not loaded with dye. For this data to be valid, we had to ensure that dye was not present on the surface of the MOF, therefore we blotted the crystals dry on filter paper prior to performing these tests. The first method for observing this behavior was UV-Vis spectroscopy, which would show whether the guest dye diffused into solution from the sealed host as it had from the host not treated with triphenylacetic acid. During this test the crystal remained the same red color after it was sealed as it had when unsealed and no change in absorption at any wavelength was observed, suggesting that the absorbance of the solution remained the same and therefore that the concentration of the dye in solution did not change.

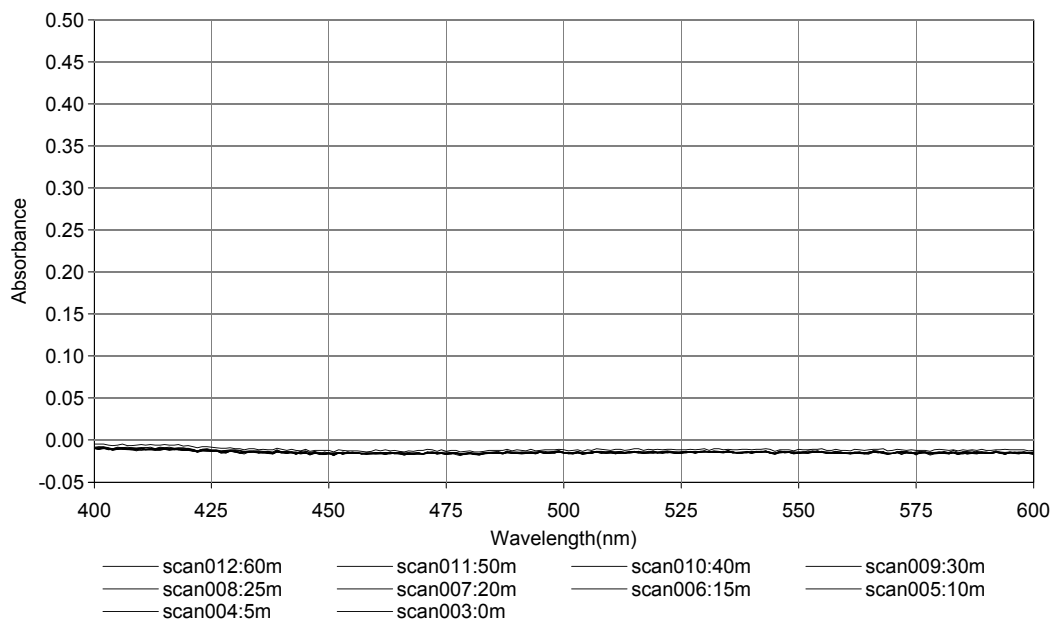


Figure 17. UV-Visible spectrometry data showing that the absorbance of the solution did not change over the course of 60 minutes despite dyed sealed crystals being added to the cuvette.

Rhodamine B exhibits a strong absorbance peak at 545 nm. Thus, it was expected that if it were to diffuse out of the sealed crystal, such a peak would exist on the readings in this case as well. Figure 17 shows that this was not the case, as no change in absorbance occurred over twice the timeframe of the unsealed test, even on the scale of hundredths of absorbance units. The absence of this peak suggested that the dye has been sealed inside the crystal by the monocarboxylic acid on the surface, as that was the only alteration made to the crystal between this test and that of the unsealed MOF. Visually, this suspicion was confirmed, as the ethanol solution remained the clear color that it was originally and the crystals exhibited the same red color despite being submerged in a solvent that had previously reduced the vibrancy of their red coloration over a much shorter period of time.

We then performed a thermal gravimetric analysis of the sealed MOF-5 to determine whether the sealed host exhibited the same secondary mass loss due to

rhodamine B desorption as the unsealed host. This test heating the product from room temperature to 300°C showed behavior similar to that of a crystal not containing any dye with slightly less mass loss, suggesting that the dye remained within the crystal structure despite being heated above its decomposition temperature and the temperature at which it diffused out of the unsealed MOF. This showed that decarboxylation of the dye did not occur in either case, as the resultant carbon dioxide would be able to diffuse from the structure similarly to the ethanol solvent.

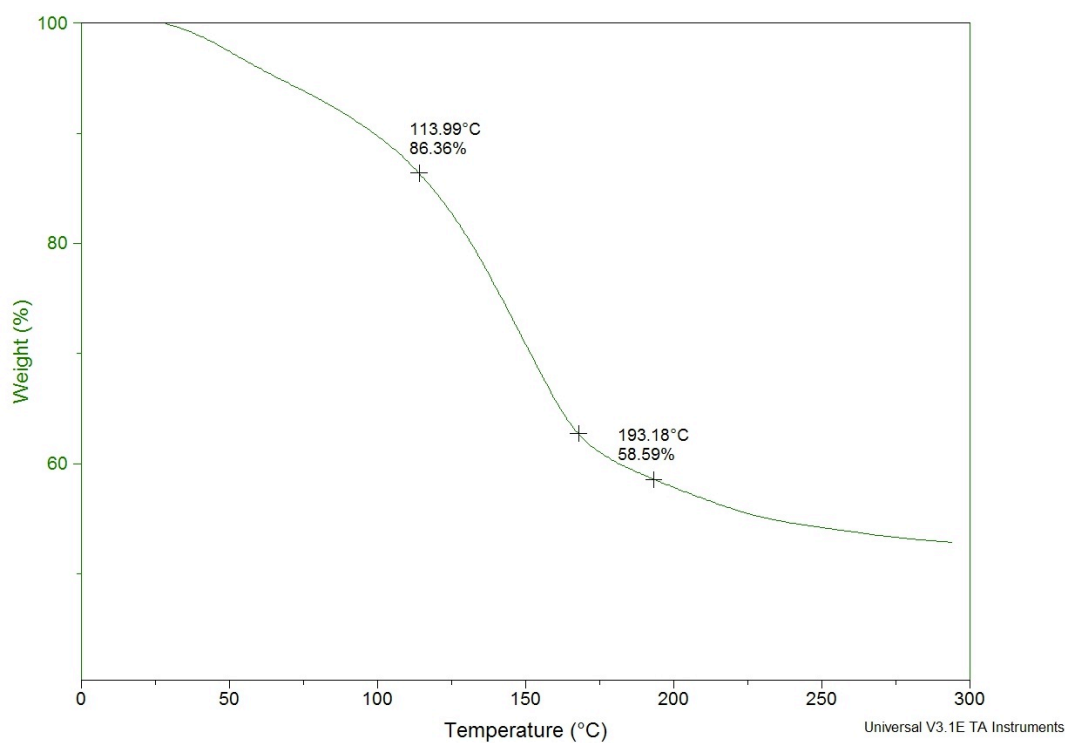


Figure 18. Thermal gravimetric analysis of sealed MOF-5 loaded with rhodamine B exhibiting the absence of increased mass loss around the decomposition temperature of the dye

## VI. Conclusions

The results of this project confirmed our original hypothesis that a guest could be sealed within the pores of MOF-5 by adsorbing a bulky monocarboxylic acid to its surface. Triphenylacetic acid was found to be effective in preventing the desorption of rhodamine B from the host both when the sealed crystals were placed in a stock solution of the solvent used in adsorption of the guest into the MOF and with increasing temperature to a point at which the dye should decompose and the MOF should remain stable.

In the early stages of experimentation, we found that DEF was required for the synthesis of MOF-5, as attempts at synthesis using DMF failed to yield the correct crystal. This finding should discourage those attempting to synthesize this MOF in the future from using an ineffective solvent in hydrothermal synthesis.

These findings show that a guest can be retained within a MOF without reaction of the guest with the internal surface of the crystal, meaning that it can be released from the host by controlled removal of the trapping agent from its surface. This seal could be effective in containment of catalysts, medicinal drugs, and gases, as well as guests of types that may not have been previously investigated with respect to adsorption and desorption in MOFs.

Despite these conclusions, it still remains to be seen whether this trapping method would be effective in MOFs with pore arrangements less symmetrical and consistent than that of MOF-5. Other hosts may be more compatible with conditions necessary for application of trapping and controlled release of a guest in application to pertinent issues and future research.

## **VII. Recommendations for Future Experimentation**

The discovery that a guest can be sealed inside MOF-5 opens the door for a bevy of new experimentation. Though only one monocarboxylic acid was investigated as a sealing agent, future research could be conducted to determine whether a different trapping agent would be more effective at sealing the MOF. These trapping agents should be large enough to exhibit a similar effective coverage radius to triphenylacetic acid, but not so large that the steric repulsion between each molecule of the capping agent causes a larger opening for the guest to diffuse from the pores of the MOF.

Similarly, current experimentation did not investigate the possibility of controlled release of the guest from the crystal. Future research should test trapping agents that can undergo conformational change to open pores upon a change in the pH level or ultraviolet radiation. Likewise, a trapping agent whose bonds with the surface of the crystal break upon controlled conditions could be investigated.

Further investigation should be conducted with regard to what other guests can be trapped. Present research only recorded results for two candidates, but exactly how effective the discussed methods can be could be determined by researching precisely what size the guest in question must be for the seal to remain functional.

Upon completion of this research, the viability of these sealed MOFs as drug delivery agents could be determined based on their stability and toxicity levels in conditions matching those of the human body. This could provide an alternative to those who are allergic to current medication hosts.

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