# Synthesizing and Post-Synthetically Modifying Metal-Organic Frameworks Anna Robert, Kristine Tanabe, Corinne Allen and Seth Cohen

### Purpose

The purpose of these experiments is to construct core shell metalorganic frameworks and post-synthetically modify them through metallation.

### Introduction

Metal-organic frameworks (MOFs,) are porous, crystalline materials that can be used for catalysis, sensing, gas storage, and separation. They are made of organic ligands and metal ions and are synthesized through solvothermal complexation. They are stable under a variety of conditions and can maintain their porosity as seen by their chemical and thermal robustness. While there are a large variety of MOFs and their uses, these frameworks can also be enhanced through post synthetic modification, or PSM, and covalent modifications. This allows tailoring of functional groups and metal binding sites that are not compatible with standard solvothermal conditions. These modifications allow the functions and uses of MOFs to be even more diverse.

## **Experimental Procedures:**

# IRMOF-3 Zn(NO<sub>3</sub>)<sub>2</sub>\*6H<sub>2</sub>O 2-aminoterephthalic acid (NH<sub>2</sub>-BDC)

First, 0.75 g of NH<sub>2</sub>BDC and 3.39 g of  $Zn(NO_3)_2$  is added to a 125 mL Erlenmeyer flask. Then 100 mL of dimethylformamide (DMF) is added to the mixture. The flask is placed in the sonicator for 5 minutes. The solution is then divided into 10 mL portions and transferred to 10 scintillation vials. The vials are then placed into a sand bath, and then transferred to the oven. The solution is heated at a rate of 2.5 °C per minute from 35 ° C to 100 ° C. The temperature is held for 18 hours. Then the solution cools at a rate of 2.5 ° C per minute to a final temperature of 35 ° C. Crystals form at the bottom of the vials.

# AM1-BDC



AM1-BDC is a ligand that is used in synthesizing IRMOF-3-AM1. First 1g of NH<sub>2</sub>BDC, 18.2 mL of acetic anhydride, and 100 mL of ethanol is measured and added to a round bottom flask. The solution is heated while attached to a reflux condenser. The solution is left to reflux, continual boiling and condensing, over night. The next day the solution is allowed to cool and then it is placed on the rotor evaporator (rotovap) to remove the ethanol. Methanol is added as a co-rinse and the solution is placed on the rotovap to remove any extra solvent. The mixture is placed in a Buchner funnel and undergoes vacuum filtration. The mixture is rinsed with methanol to get a solid. The product is gently scraped off of the Buchner funnel and placed in a vial. The rest of the solution is placed on the rotovap to remove the solvent. It is placed on the filter flask with the vacuum while using water as a co-rinse. The solution is left to dry overnight. The next day the solution is placed in the filter flask with the vacuum and is washed with methanol. The product is then scraped off of the Buchner funnel and placed in the vial.

# <sup>1</sup>H Nuclear Magnetic Resonance





# Shell: IRMOF-1

IRMOF-3





IRMOF-3-AM1 outer core: Then .29g of AM1-BDC and 1.12g of  $Zn(NO_3)_2$  is measured and placed into a 125 mL Erlenmeyer flask. 50 mL of DMF is added to the mixture and the flask is placed in the sonicator for 5 minutes dissolve the solution. The remaining 5 vials are decanted of their mother liquor. The solution is divided into 10 mL portions and transferred to the 5 vials. The 10 vials are transferred to a sand bath and then to the oven. They heat at a rate of 2.5 °C per minute from 35 °C to 100 °C, and the temperature is held for 15 hours. The solution then cools at a rate of 2.5 °C per minute to the final temperature of 35 °C.

Nuclear Magnetic Resonance (NMR) helps identify the purity of the ligand. Based on the location of the peaks, chemicals can be identified, which helps detect traces of solvent or other unwanted chemicals.



In the synthesis of IRMOF-3-AMCupz, IRMOF-3-AMpz is modified through PSM to become IRMOF-3-AMCupz. First chloroform is decanted from one vial of IRMOF-3-Ampz. Then 2 mL of chloroform is measured and added to the vial. 0.054 g of copper is measured and added to the vial. The liquid turns a dark blue color. The vial sits for 24 hours. After several rinses in chloroform, the crystals are ready.

For the synthesis of IRMOF-3-AMFepz, PSM modifies IRMOF-3-AMpz with iron to become IRMOF-3-AMFepz. . Chloroform is decanted from one vial of IRMOF-3. 2 mL of chloroform is added to the vial. 0.0706g of iron is added to the vial and the liquid turns a dark red color. The vial sits for 24 hours, and is rinsed in chloroform.





In the synthesis of IRMOF-3-AMpz, the Core Shell MOFs (IRMOF-3-Ampz inner core and IRMOF-1 outer core) are modified with copper or iron. Chloroform is decanted from two vials of the IRMOF-3-Ampz inner core, IRMOF-1 outer core Core Shell MOF. Then 2 mL of chloroform and 0.0706g of iron is added to the vial. 2 mL of chloroform and 0.054g of copper is added to another vial. It sits for 24 hours, and is rinsed in chloroform.

# Core: IRMOF-3-AM(M<sup>+</sup>)pz, Shell: IRMOF-3-AM1



The Core Shell MOF with an IRMOF-3-Ampz inner core and IRMOF-3-AM1 outer core is modified with copper or iron. Chloroform is decanted from two vials of the Core Shell MOFs. 2 mL of chloroform and 0.0706g of iron is added to one vial. Then 2 mL of chloroform and 0.054g of copper is added to the other vial. It sits for 24 hours, and it is rinsed in chloroform.



First the chemicals are measured to make IRMOF-3 as the inner core: 0.48 g of NH<sub>2</sub>BDC and 2.24 g of  $Zn(NO_3)_2$ . Then 100 mL of DMF is added to the mixture in a 125 mL Erlenmeyer flask. The mixture is placed in the sonicator for 5 minutes to dissolve the mixture into the DMF. The solution is divided into 10 mL portions and transferred to 10 scintillation vials. The vials are placed in a sand bath and transferred to an oven. The vials are heated at a rate of 2.5 °C per minute from 35 to 100 °C. The temperature is held for 18 hours. Then the solution cools at a rate of 2.5 °C per minute to final temperature of 35 °C. Amber colored cubed crystals form at the bottom of the vials.



Core (inside): IRMOF-3 Shell (outside): IRMOF-1

IRMOF-1 outer core: Then .22g of  $H_2BDC$  and 1.12g of  $Zn(NO_3)_2$  is measured and placed into a 125 mL Erlenmeyer flask, and 50 mL of DMF is added to the mixture. The flask is placed in the sonicator for 5 minutes to dissolve the chemicals into the DMF. Then the solution is divided into 5 10 mL portions. 5 of the scintillation vials are decanted of their IRMOF-3 mother liquor and the new solution is added to each

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# Core: IRMOF-3-AM(M<sup>+</sup>)pz, Shell: IRMOF-1

Copper modified on left. Iron modified on right.







For this experiment, the UMCM-3 MOFs are synthesized in a heat block.  $NH_2$ -BDC (.04941g), BTB (.04268g), and  $Zn(NO_3)_2$ (.32281g) are measured and added to a 125 mL Erlenmeyer flask. 10 mL of DMF is added to the mixture. The ingredients are dissolved in DMF while in the sonicator for 5 minutes. 2 mL of the solution is added to each of the 5 vials. They are placed in a heat block at 100 °C for 18 hours. Clear needle crystals are present.

# Conclusion

In conclusion two types of crystals were synthesized. UMCM-3, which are tiny needle like crystals, were synthesized in a heat block versus using an isothermal oven. IRMOF-3 was synthesized resulting in small amber cubed crystals. The ligand, AM1-BDC, was made to be used in the synthesis of Core Shell MOFs. IRMOF-1 and IRMOF-3-AM1 crystals were grown over IRMOF-3 crystals to make Core Shell MOFs. Amber cubed crystals were seen on the inside of lighter, clearer cubed crystals. The inner core was then post synthetically modified in tandem with a metal binding group, pyrazine dicarboxylate. Then the MOFs were metallated with iron and copper. Therefore, Core Shell MOFs were successfully synthesized.

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