



# Molecular Organic Framework: Encapsulation effects on Diels-Alder kinetics

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## Introduction:

Molecular Organic Frameworks (MOF) are a class of porous materials that have versatile applications for storing and transporting molecules. MOFs are easily tunable in terms of chemical and structural properties which allows for a variety of methods to encapsulate guest molecules within its different cavities. Unlike the pores, the functionalized capsules of a MOF (Figure 1) provide a very protective environment for accommodating these guest molecules. Unusual chemical properties such as stabilization of intermediates, suppression of dimerization, and thermal stability have been observed in the capsules.<sup>1</sup> In this experiment,  $\text{Co}(\text{NCS})_2$ , and 2,4,6-tris(3-pyridyl)-1,3,5-triazine were used to build the framework.

Thiophene, furan, and toluene were the guest molecules used for encapsulation. Assembly of the MOF was varied by a guest molecule and a reaction condition while a control of only the metal and ligand was used to test if the guest molecule perturbs MOF crystal growth.

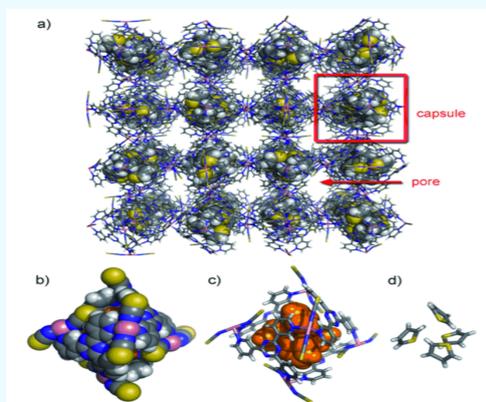
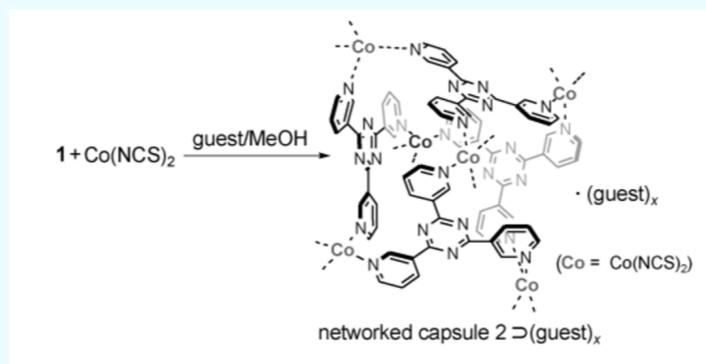


Figure 1. A) Crystalline structure of the  $\text{M}_6\text{L}_4$  MOF. The capsule and pores are shown. B) A close up the complex. C) Shows encapsulation of the guest molecules. D) Orientation of encapsulated guest molecules.

## Experimental Design:

A solution of 2,4,6-tris(3-pyridyl)-1,3,5-triazine in a mixture of guest and methanol was placed in a test tube. Absolute methanol was layered on top of the solution as a buffer. Then, a solution of  $\text{Co}(\text{NCS})_2$  in methanol was carefully layered on the top of the resultant solution. The test tube was covered with para-film and left for 7 days.



Scheme 1. Synthesis of MOF with various guests.

## Results & Discussion:

No crystals were formed under any of the reaction conditions tested, however, some of the reaction vessels changed color indicating a chemical reaction. Initially, all of the test tubes had a clear bottom layer and a pink top layer. After sitting at room temperature for a week, two thiophene solutions and three toluene solutions turned blue. This could be due to the excess of guest molecules used to ensure encapsulation during MOF formation. The high concentration may have made the coordination of the guest molecules more favorable than the ligand. Another possible explanation could be that over time, the methanol solvent reacted with the air to produce water. The water may have coordinated to the metal instead of the ligand. This makes sense as water is a weaker field ligand than  $\text{NCS}^-$  and there is a shift in the blue solutions spectra to 625nm.

Table 1. Color change for each guest.

	Thiophene	Furan	Toluene
Scale Up	Light pink/purple	Pink	Teal
Double Buffer	Lavender	Pink	Teal
Fridge	Light pink purple	Light pink	Light pink
Scint-Vial	Dark blue	Dark teal Evaporated	Light pink
Scale Down	Blue	Pink	Light pink top Faint blue bottom
No Buffer	Light pink top Faint blue bottom	Pink	Teal
Decreased MeOH	Blue	Little solvent Dark purple	Light pink top Faint blue bottom
No Guest	Pink	Pink	Pink

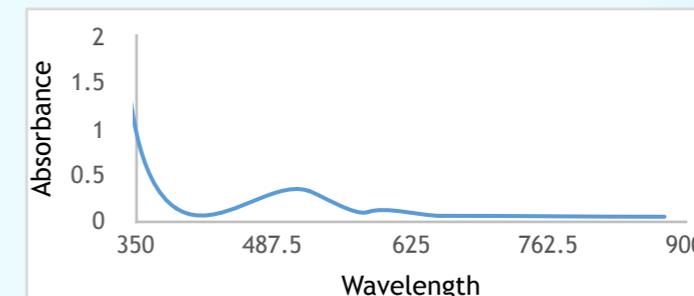


Figure 3. UV/Vis spectrum for  $\text{Co}(\text{NCS})_2$  & Linker.

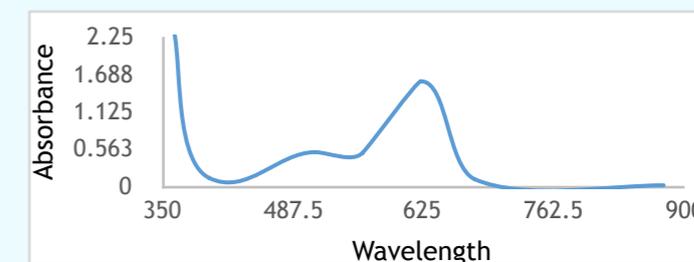


Figure 4. UV/Vis spectra for thiophene in a scint. vial.

## Future Work:

Keeping the reaction vessels air tight, using dry solvents, sonification, or heating may help promote crystal formation. Once crystals have been formed, a diels-alder reaction can be performed and the MOF can be broken down for analysis.

## Conclusion:

The desired MOF was not successfully synthesized in this experiment however the drastic color change of certain solution allude to what may have prevented crystal formation.

## Acknowledgements:

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## References:

- Inokuma, Y.; Yoshioka, S.; Fujita, M., A molecular Capsule Network: Guest Encapsulation and Control of Diels-Alder Chemistry. *Angew. Chem. Int. Ed.*, 2010, 49, 8912-8914.