

Synthesis and Characterization of Metal Organic Frameworks Utilizing a Bi-Functional Acetylacetonate Organic Linker

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Abstract

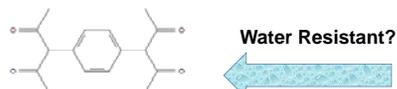
Metal-organic frameworks (MOFs), crystalline materials constructed from organic linkers bridging metal centers, remains an active research area due to the enormous design flexibility associated with the innumerable combinations of the constituent building blocks (2). The key property of these solids, their permanent porosity, makes them excellent materials for a diverse range of applications including CO₂ sequestration, chemical separations, fuel storage and drug delivery(1).

We posited that chemically stable MOFs might be achieved through acac-based organic linkers. We've recently completed the synthesis of the ditopic organic linker bis(1,4-diacetylacetonate) benzene. Work is currently underway to characterize the crystalline materials generated by the reaction of a wide variety of metal centers and the bifunctional acac linker. Details of the synthesis, will be presented.

Motivation

Currently, carboxylates are one of the most popular functional groups for binding linkers to the metal centers. Unfortunately carboxylates are readily hydrolyze by water which in turn leads to decomposition of the MOF lattice. The decomposition of the MOF by water voids many of the potential applications of MOFs such as CO₂ sequestration (for industrial use).

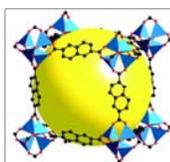
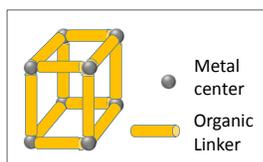
Groups working on dye-sensitized solar cells (DSSCs) have recently overcome similar hydrolytic stability issues by exchanging the carboxylate binding group for acetylacetonate (acac). In efforts to create a more robust MOF, acac linkers will be utilized.



Acetylacetonate Linker

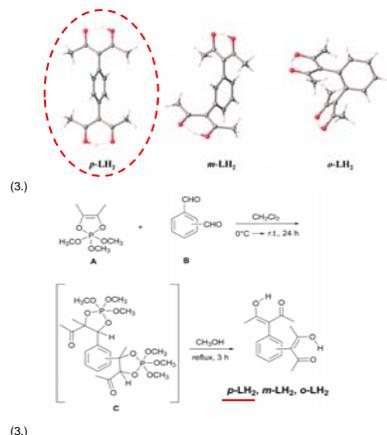
Introduction to Metal Organic Frameworks

Metal Organic Frameworks (MOFs) are permanently porous crystalline coordination networks composed of two main components (organic linkers and metal centers)(2). Appealing features of MOFs include its ability to be chemically altered to perform task such as chemical sequestration or MOFs incredible synthetic flexibility. MOFs in a sense can act as "chemical cages"



(4)

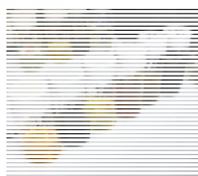
Synthesis of Acetylacetonate Linker



(3)

- Dissolved in CH₂Cl₂, 2,2,2-trimethoxy-4,5-dimethyl-1,3 Dioxaphospholene (A) reacts with bis-aldehyde (B)(3)
- bis-pentaoxophosphorane (c) is formed which is later hydrolyzed under 3 hour reflux in CH₃OH to later yield bis-(3-acetylacetonate)benzene (p-LH₂)(3)

MOF Synthesis



- Acac linker was deprotonated with aqueous sodium hydroxide
- After, various hydrated metal chlorides solutions were treated with the basic acac solution
- Solutions were then incubated in an oven for several days.

Metal centers used: Ru³⁺ Fe³⁺ Ni²⁺ Cr³⁺

- Crystallinity was initially assessed using optical methods. Using a polarized light microscope, the materials were characterized based on their outward appearance and the possible presence of uniform extinction



What's Next?

Once crystals of suitable size and quality are obtained, they will be analyzed using single crystal X-ray diffraction which will yield the structure of the solid at atomic resolution.



- After assessing the structural properties of the MOF the next step would be assessing other characteristics such as optical properties and porosity.
- Most importantly, the robustness of the MOF will also be assessed. Utilizing the acac linker (instead of the typical carboxylate linkers) it was predicted that a more stable MOF would be made. A MOF that can withstand aqueous environments without being hydrolyzed and ultimately decomposing.

Additionally, for future research, since MOF design is incredibly flexible, we hope to expand the variety of metal centers used with the acac linker to heavier metal centers such as Europium and Gadolinium. Or utilize other acac derivatives such as m-LH₂.

Acknowledgements

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Benedict Research Labs

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