Metal-Sulfur Cubane Functionalized Frameworks

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Overview

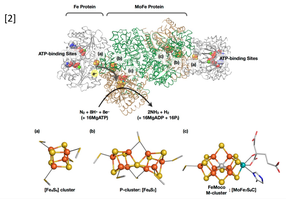
CMS teachers apply to the Summer Research Experience for Teachers (SRET) program to be partnered with university researchers and undergraduate students at the University of North Carolina at Charlotte. SRET focuses on providing mastery and vicarious experiences to teachers with the goal of increasing confidence in science education.

Abstract

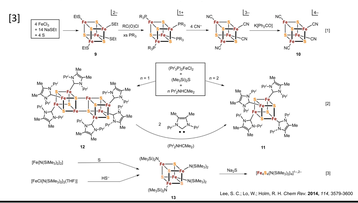
Fe_4S_4 clusters are naturally occurring compounds that are involved in redox processes, which are processes where electrons are transferred. There are molecularly similar synthetic compounds known with M=Co, Fe and can be stabilized by a variety of organic ligands (an ion or molecule attached to a metal atom by coordinate bonding). However, their use as building blocks for functional, solid-state materials remains limited due to lack of synthetic protocols. Here, we explore the use of a covalent organic framework (COF) as a solid-state scaffold for attaching M_4S_4 clusters. Specifically, we prepare a two-dimensional (2D) COF with *N*-heterocyclic carbene (NHC) ligands. These NHC ligands serve as points of attachment for M_4S_4 clusters, which will be bound via ligand exchange reactions. The COF and phosphine-ligated M_4S_4 clusters are prepared according to literature protocols. Instrumentation will be used to characterize the products conductivity, thermal stability, and crystallinity.. These cluster-COFs may be useful for catalytic and energy storage applications.

Background - M_4S_4 Cubane Clusters

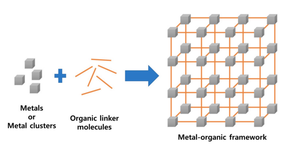
Naturally Occurring Clusters



Synthetic M_4S_4 Clusters



Background - Metal Organic Frameworks (MOFs)



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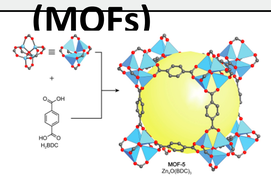

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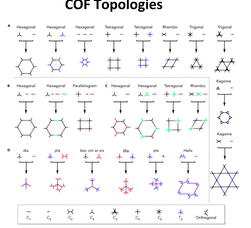
Omar Yaghi

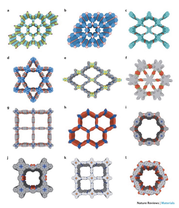
https://www.forbes.com/forbes/2009/0907/opinions-environment-consumption-ideas-opinions.html?sh=1482cd0dba5c

Background - Covalent Organic Frameworks (COFs)

- Crystalline porous polymers
- Highly ordered structures
- Atomically precise
- Customizable topology
- Contain ordered nanopores

COF Topologies





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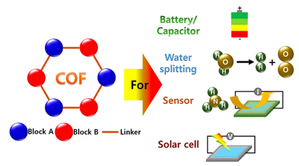
COF Applications



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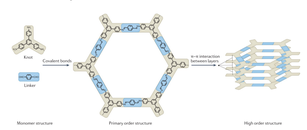
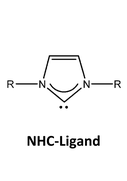
Imine COF Synthesis

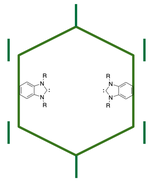


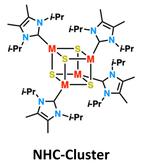
N-Heterocyclic Carbene (NHC) COFs

NHC Ligands

- Strong sigma-donors
- Proven ligand for M4S4 clusters
- Can displace phosphine ligands
- Tunable synthesis
- Easily modified



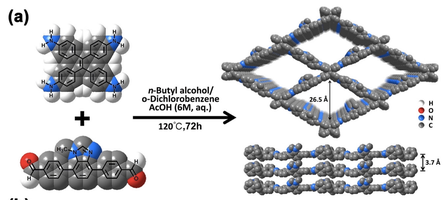




Question: Can we prepare an NHC-Cluster-COF hybrid?

We targeted two known NHC-containing COFs as scaffolds to host M4S4 clusters

I. IM-COF-1 : Sidewall of COF functionalized with NHC ligands



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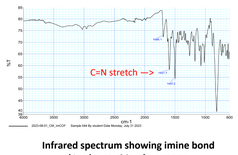
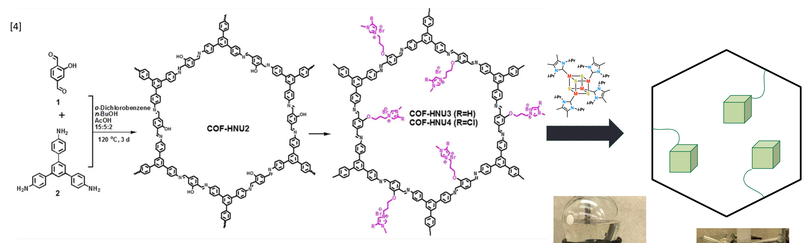
COF-NHC with dimethyl carbonate.

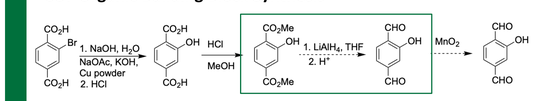


Infrared spectrum showing imine bond (C=N) stretching frequency.

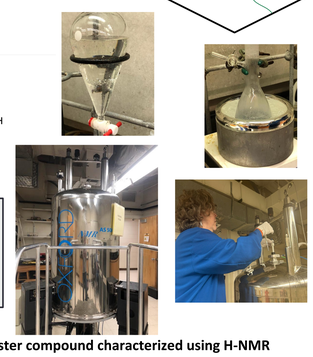
II. COF-HNU2 : Dangling NHC ligands inside pore



COF Organic Building Block Synthesis

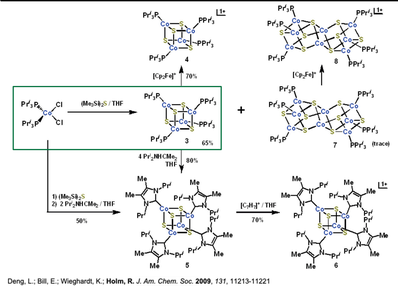


- Bis(hydroxymethyl)phenol (7): To dimethyl-2-Hydroxy-terephthalate 6 (6.30 g, 30.0 mmol) in dry THF (250 mL) were added in portion under argon lithium aluminum hydride (5.15 g, 135 mmol).
- The mixture was stirred (with mechanical stirrer) under reflux for 2 d.
- Ethyl acetate, water and 10% sulfuric acid were added very carefully to the mixture in an ice-water bath.
- The solution was extracted with ethyl acetate, washed with brine, and dried over MgSO4.
- After filtration, the solvent was evaporated to afford a crude oil.
- After the addition of small amount of benzene, a pure white solid was precipitated (3.06 g, 78%)



Diester compound characterized using H-NMR spectroscopy

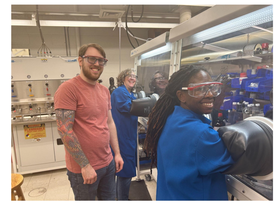
Synthesis of Co_4S_4 Cluster



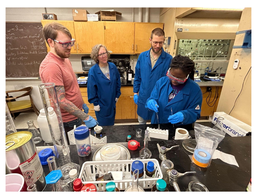
$Co_4S_4(PR_3)_4$ Synthesis inside nitrogen glovebox.

Conclusions & Future Work

- Teachers obtained hands on laboratory experience with organic synthesis, polymer (COF) synthesis, and air-free inorganic/organometallic cluster preparation and characterization.
- A known COF with CO2-protected NHC ligands (IM-COF-1)was prepared.
- Organic building blocks for COF-HNU2 were synthesized.
- The phosphine ligated Co4S4 cluster was synthesized and crystallized.
- The final attachment of the cluster to the COF is currently underway.



Human Factor



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"I love reaching into the unknown." -Connor

"Whether it's a single problem you solve in the lab or trying new reactions; creativity and science go hand in hand." -Dr. Bejger

"Science is more like tools. It gives you the how to do things, but you have to use creativity to inspire the work. The science doesn't tell us what to do only how to do it." -Jonathan

"You have to reinvent yourself every 5 or 10 years to stay relevant." -Dr. Bejger

"We work together because if they have succeeded, then I have succeeded." -Jonathan

"The job has many different hats: writing, problem solving, teaching, fundraising, group leader, project manager, training. You're learning something new everyday." -Dr. Bejger

"You have all these known pathways that do different things and you have to synthesize new compounds, mix and match, do things that haven't been done before. You have to be creative." -Connor

"This lab is all about determination, patience, passion and creativity. I have witnessed first hand the qualities that make great scientist! We work hard and learn from every mistake. I look forward to bringing my scholars real world evidence of the Scientific Method in action to be able to spark their science curiosity." -Krystal

"I dropped chemistry as an undergrad, overwhelmed. I never had chemistry in high school. Only the boys took it, encouraged by the golf coach who was also the chemistry teacher. The boys were on the golf team. 41 years later I have my chance! No question denied. My presence, welcome. Perhaps I'll pursue another degree! I've already started sharing the thrill of discovery with my students!"-Evelyn

References

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(3) Lee, S.; Lo, W.; Holm, R. H. Developments in the biomimetic chemistry of cubane-type and higher ... https://pubs.acs.org/doi/10.1021/cr40040f67 (accessed Aug 1, 2023).

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Footnotes

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[4]*Executive Director, CTI*

Photos by Evelyn King Metcalf Dr. Chris Bejger Scott Garland