

Developing Highly Porous Metal-Organic Frameworks and Composite Materials for Hydrogen Storage

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DOE Hydrogen Program
2024 Annual Merit Review and Peer Evaluation Meeting

AMR Project ID: ST251



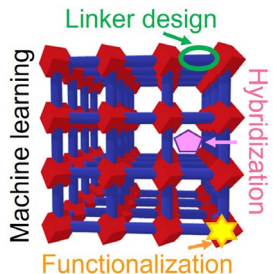
CAL STATE LA
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Project Goal

- Develop novel hydrogen storage materials that exceed the capabilities of current storage materials (>2.9 wt% and 8.4 g H_2/L) near room temperatures and low pressure (up to 100 bar).
- Discover strategies to meet the Department of Energy (DOE) targets for on-board vehicular hydrogen storage (5.5 wt%, 40 g H_2/L near room temperature at 100 bar).
- Enhance the education and training of minority students from underrepresented/disadvantaged communities and develop a diverse and highly skilled next-generation workforce.



Metal-organic frameworks (MOFs)

Metal hydrides

Overview

Timeline

- Project Start: 8/1/2023
- Project End: 7/31/2025

Partners

- PI: Yangyang Liu, Cal State LA (lead)
- Sandia National Laboratory
- Lawrence Livermore National Laboratory

Budget

- Total Project Budget#: \$300,000
 - Total DOE Share: \$300,000
 - Total Cost Share: \$0
 - Total DOE Funds Spent*: \$69,323.90
- *as of 03/01/2024

Barriers

- Materials Construction and Yield – Optimize reaction conditions
- Stability and Durability – Develop highly robust materials
- Deliverable Efficiency – Employ various design strategies to improve H₂-framework interaction and hydrogen storage capacity

Potential Impact

- Development of novel porous materials and/or hybrid materials with hydrogen storage capacities exceeding gravimetric/volumetric deliverable hydrogen capacities exceeding 2.9 wt% and 8.4 g H₂/L (current state of the art) near room temperature up to 100 bar.
- Discover a material with the hydrogen binding affinity of 15 – 25 kJ/mol with functionalization and/or hybridization.
- Discover strategies and pathways to get closer to or meet 2025 DOE storage targets for onboard vehicular hydrogen storage (5.5 wt%, 40 g H₂/L near room temperature at 100 bar).
- Enhance the education and training of underrepresented students from disadvantaged/minority communities by engaging students in research, incorporating research into current academic courses, research seminars/workshops, outreach activities, research collaboration and networking with national laboratories, and student internships.

Approach

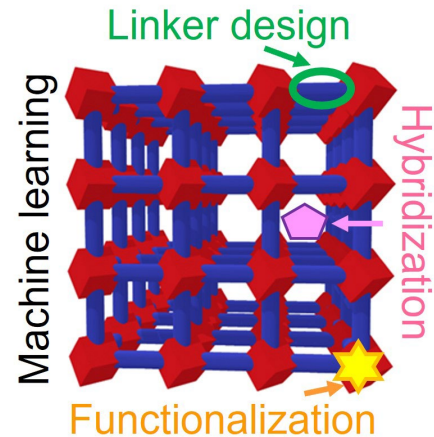
Research Strategies:

- Optimize MOF structures for hydrogen storage through multitopic ligand design, linker elongation, and machine learning
- Increase framework-hydrogen interactions by introducing additional binding sites in MOFs.
- Develop MOF/hydride composite materials through nanoconfinement for enhanced hydrogen storage properties.

Education and Workforce Development:

- Engage minority students from underrepresented communities in hydrogen storage research and train them to be the next generation of scientists and engineers.

Collaboration with HyMARC teams will allow us to access their state-of-the-art facilities for materials testing and characterizations to achieve accelerated materials discovery. The simulation and computational team at HyMARC will provide theoretical prediction and validation for new materials discovery.



High-pressure hydrogen testing apparatus (Sandia) 5

Approach – Safety Planning and Culture

- This project was not required to submit a safety plan for review by the HSP.
- Prioritizing Safety/Analyzing Safety Hazards
 - All lab members must pass safety training before conducting research
 - All hydrogen cylinders will be closed fully when not in use
 - Specific team member assigned to manage lab safety duties, such as waste management, lab inspections and assessments
 - A hydrogen alarm was installed in the lab and closely monitored
- Best Practices/Lesson Learned
 - Discuss incidents and near misses during weekly group meetings
 - Make plans and adjustments to avoid future incidents
 - Communicate lessons learned to all members and collaborating partners



A hydrogen alarm

Accomplishments and Progress

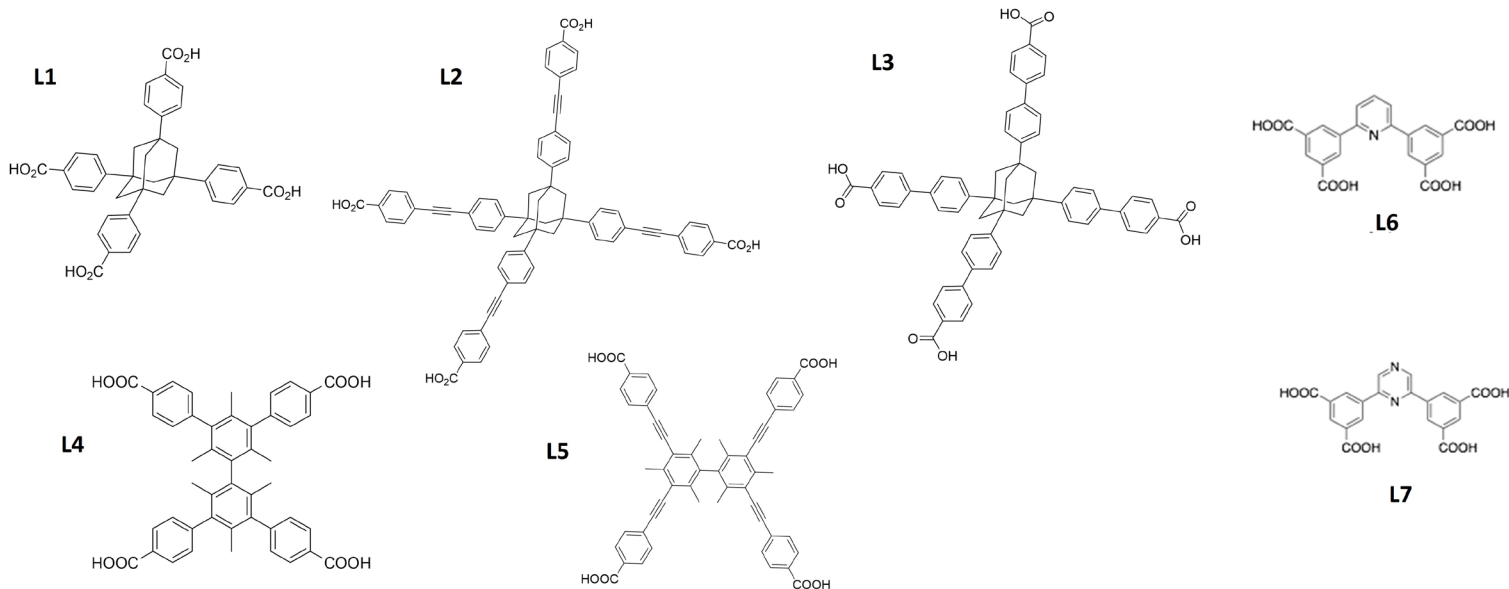
New Ligands Synthesized, Purified and Characterized

- Seven (7) ligands with high purity were synthesized.
- The conditions of multi-step synthesis were optimized to improve yields.
- The ligand structures were confirmed using NMR.



Milestone 1:

New ligands and new MOFs synthesized



NOTE: This is a **new project** started on 08/01/2023

Accomplishments and Progress

New MOFs were Synthesized and Characterized

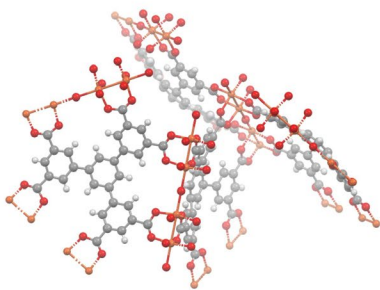
- *Five (5)* MOFs were synthesized.
- The MOF crystal structures were analyzed using X-ray crystallography.
- MOF phase purity was confirmed using powder X-ray diffraction (PXRD).
- All MOFs were activated, and one with extremely high porosity required supercritical CO₂ activation
- The surface areas of all MOFs were characterized using N₂ sorption at 77 K
- H₂ adsorption up to 1 bar was measured for all MOFs at Cal State LA.

Milestone 1:

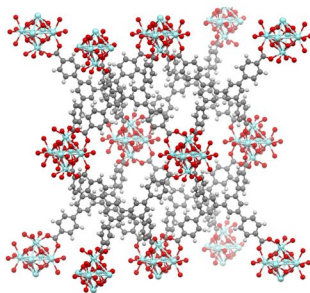
New ligands and new MOFs synthesized

Milestone 2:

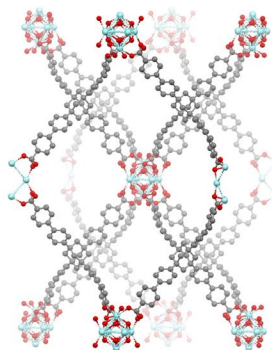
New MOF structures characterized and hydrogen storage properties studied



CSLA 1 & 2



CSLA-3 & 4

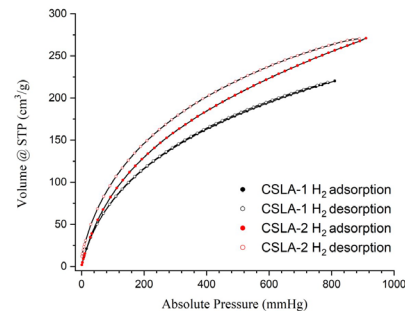
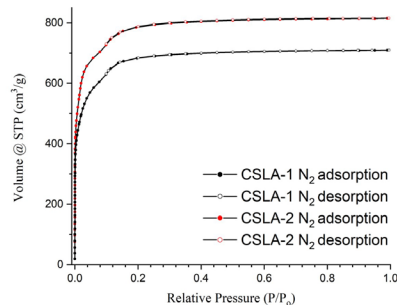
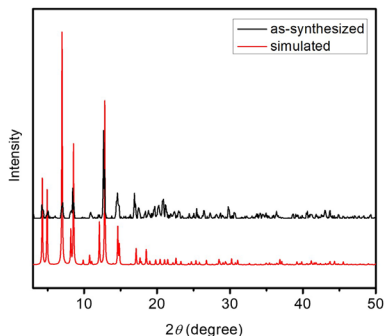
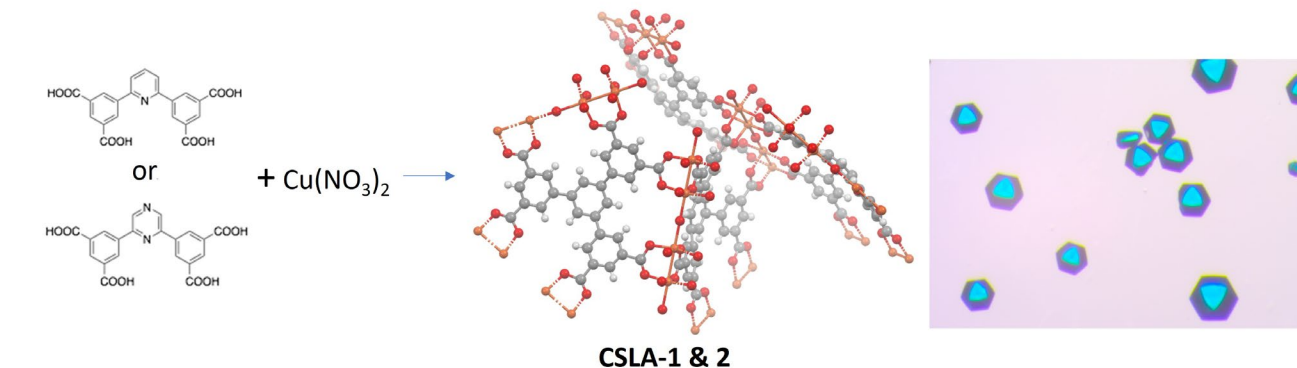


CSLA-11

Accomplishments and Progress

New MOFs were Synthesized and Characterized

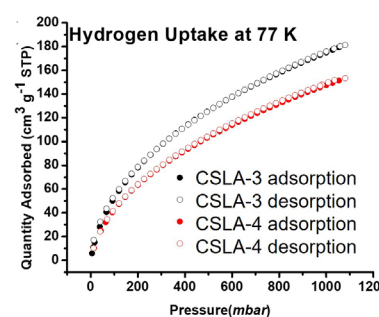
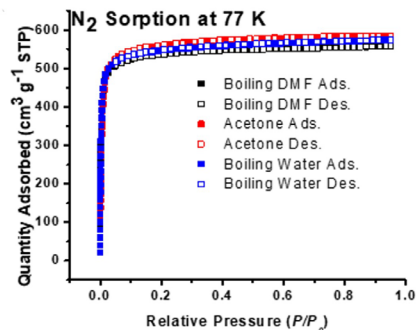
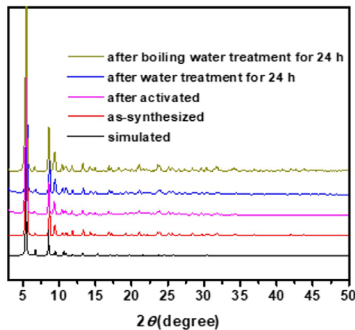
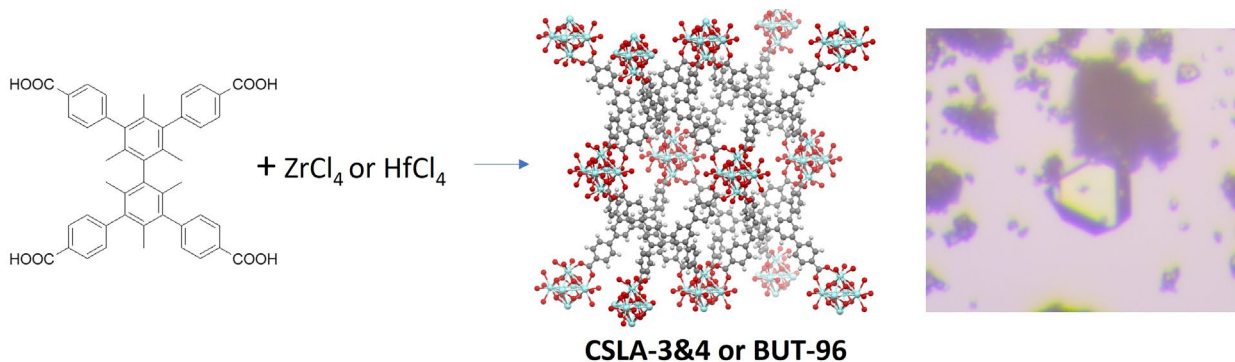
MOF1+2. Isostructural copper MOFs with rationally designed pore vacancies



Accomplishments and Progress

New MOFs were Synthesized and Characterized

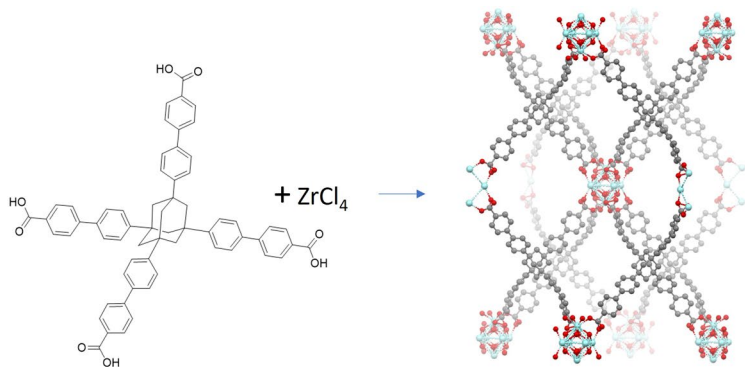
MOF3&4. Highly stable MOF systems as a platform for functionalization



Accomplishments and Progress

New MOFs were Synthesized and Characterized

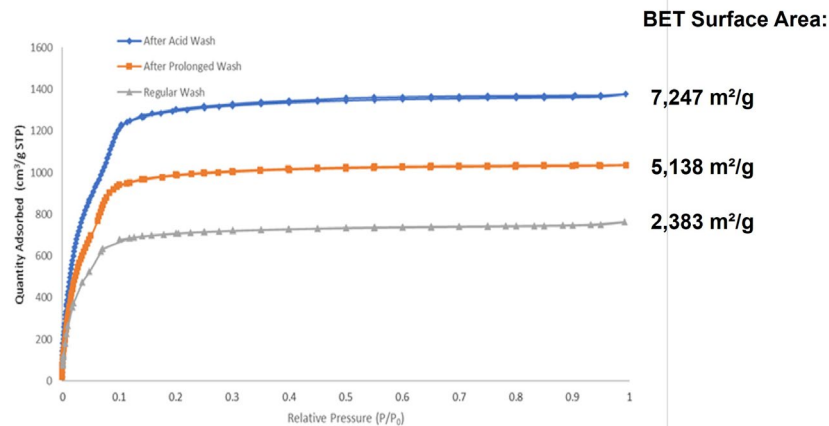
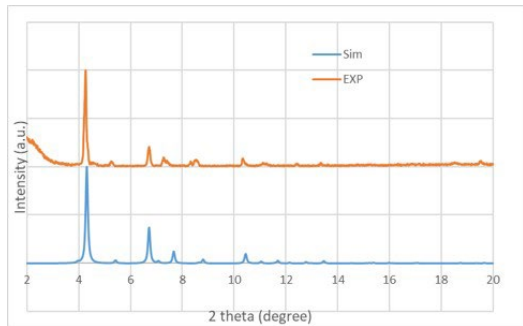
MOF5. A Zr-MOF with an extremely high surface area ($>7,000 \text{ m}^2/\text{g}$)



CSLA-11

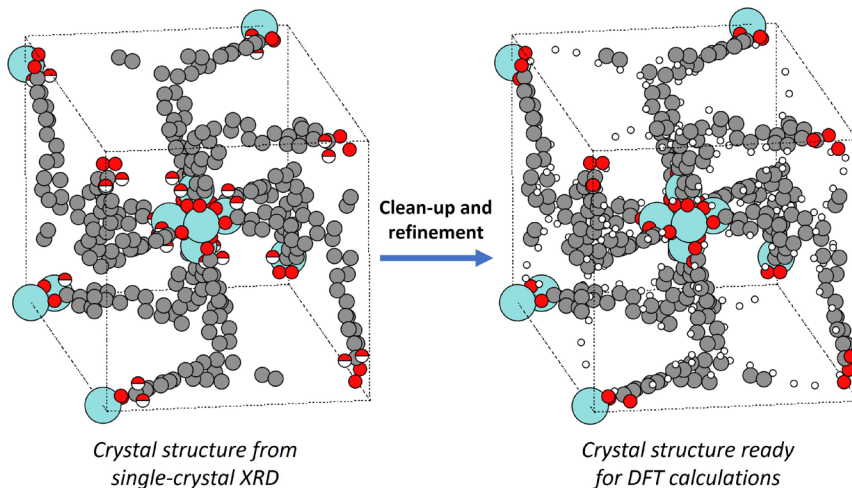


Required supercritical CO_2 drying to fully activate (due to its high porosity)



Progress

- MOF scaleup is in progress
 - 300 mg samples are needed for high-pressure H_2 studies at Sandia National Laboratory
- MOF functionalization is in progress
- The H_2 binding sites in these MOFs are being studied using molecular simulation at Lawrence Livermore National Laboratory

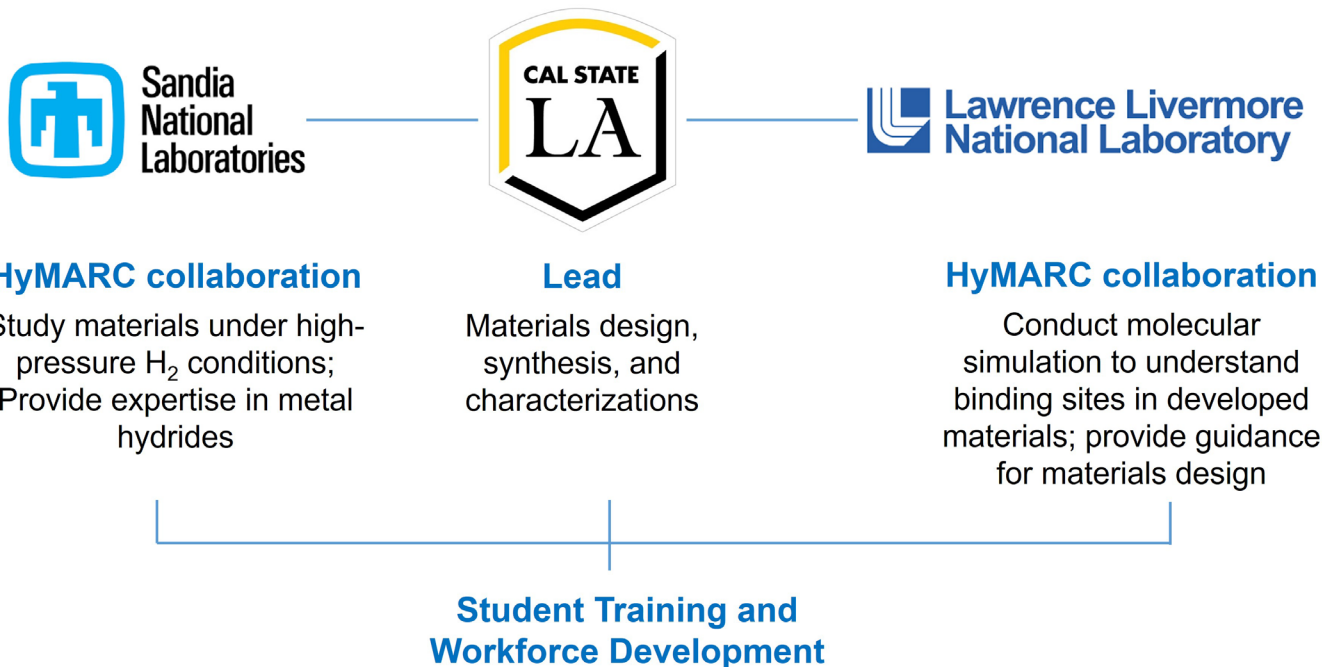


By Dr. Sichi Li (LLNL)

Accomplishments and Progress: Response to Previous Year Reviewers' Comments

- This project was not reviewed last year

Collaboration and Coordination



DEIA/Community Benefits Plans and Activities

- Underrepresented Student Recruitment and Retention
 - Recruited and engaged three students (one graduate student and two undergraduate students) from underrepresented groups to conduct research supported by this project. Both undergraduate students were inspired to pursue a Master's degree in Materials Science and Engineering or Chemistry and will continue working on this project during their Master's studies.
- Outreach to local community universities and high schools
 - Hosted one underrepresented community college student and one underrepresented high school student to conduct summer research on this project.
- Student internship, training, and workforce development
 - Students from underrepresented groups will be conducting research at our partnering national laboratories and receive training from national lab scientists.

Remaining Challenges and Barriers

- Scaling up MOFs takes time. Some of the linkers and MOFs have relatively low yields, which makes the synthesis of > 300 mg MOFs challenging.
 - The synthetic conditions for these MOFs and linkers are being optimized.
- Some of the synthesized linkers did not produce MOFs after many trials of solvothermal synthesis under different conditions.
 - Varying metal ions and synthesis methods may be explored.
- The stability of MOFs varies depending on the metal-ligand combinations.

Proposed Future Work

- Explore the synthesis of other new MOFs with the obtained linkers. High-pressure hydrogen sorption experiments will be conducted for all MOFs. Binding sites will be studied using molecular simulation.
 - Try different metal-linker combinations for new MOF synthesis
 - To complete milestone 3: Identified top-performing MOF structures and established structure-property relationships
- MOFs will be functionalized with additional binding sites to increase H₂-framework interactions. The binding affinity will be measured and compared to the simulation.
 - MOFs will be doped with metal cations and oxygen-rich functional groups. Their hydrogen affinity will be measured.
 - To achieve milestone 4: MOFs functionalized with additional binding sites
 - To achieve milestone 5: Identify functionalized MOFs with increased affinity for H₂ (Q_{st} between 15-25 kJ/mol)
- MOF/hydride composites will be synthesized and studied for their H₂ adsorption and release properties.

Summary

- Seven new ligands and five MOFs were synthesized, and their structures were characterized.
- The stability and activation of MOFs were evaluated and optimized.
- The porosity and surface areas of synthesized MOFs were measured. Low-pressure hydrogen adsorption measurements were conducted.
- Samples are being prepared for high-pressure hydrogen sorption experiments. MOF functionalization and hydrogen affinity studies are underway.
- All milestones up to this date were met.