Metal-Organic Frameworks Containing Frustrated Lewis Pairs for Hydrogen Storage at Ambient Temperature

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Project ID: ST210

Overview

Timeline

- Project start: Dec. 2019
- Phase I end: Dec. 2020
- Phase II end: Sept. 2022

Barriers

- Barriers to be addressed
  A. Hydrogen binding energies
  B. Hydrogen physisorption capacity at ambient temperature
  C. New H_2 adsorption mechanism

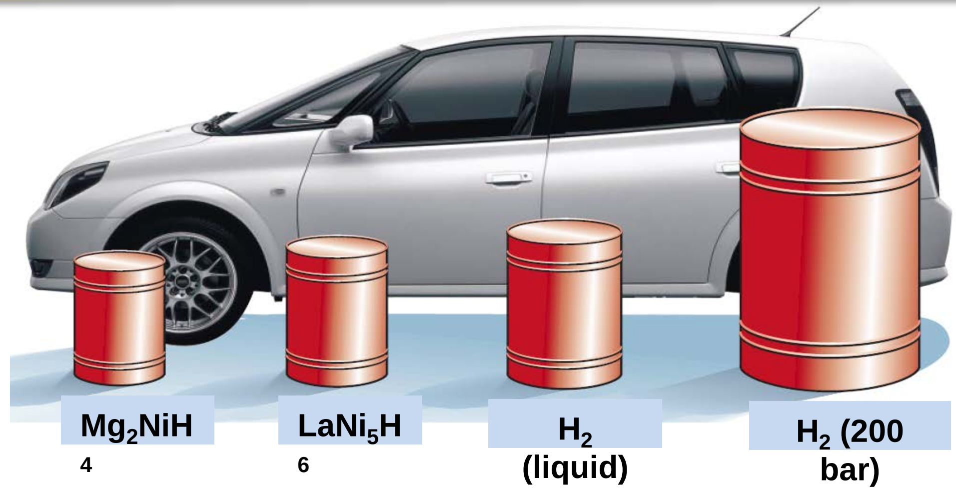
Budget

- Total project requested: $850K
  - DOE share: $680K
  - Contractor share: $170 K
- Funding received in FY2020 (Phase I)
  - $ 300 K

Partners

- Interactions/collaborations
  - University of South Florida (Lead)
  - Argonne National Laboratory (Subcontractor)
  - HyMARC

Current Technology Options for on-board H_2 Storage



- Compressed hydrogen gas (**high pressure >700 bar**)
- Cryogenic storage of liquid hydrogen (**energy consuming**)
- Chemisorption using metal hydrides and chemical hydrides (**irreversible and poor kinetics of hydrogen recharging**)
- Physisorption using porous materials (**fast charge-recharge process but very low uptake capacity at room temperature**)

To reach high storage capacity for porous materials at ambient temperature, H_2 binding energy needs to be in the range of <u>15 to 25 kJ/mol</u>.

Objective – Relevance

Table 1. Technical System Targets: Onboard Hydrogen Storage for Light-Duty Fuel Cell Vehicles

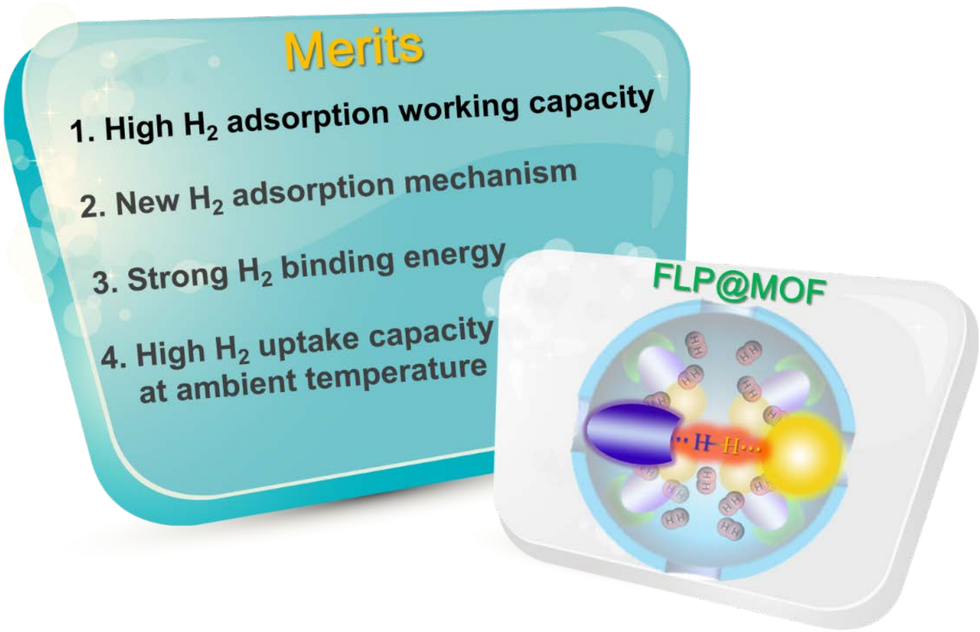
Storage Parameter	Units	2025	Ultimate
System Gravimetric Capacity:	kWh/kg ($kg\ H_2$/kg system)	1.8 (0.055)	2.2 (0.065)
System Volumetric Capacity:	kWh/L ($kg\ H_2$/L system)	1.3 (0.040)	1.7 (0.050)

Energy Environ. Sci., **2018**, *11*, 2784—2812.

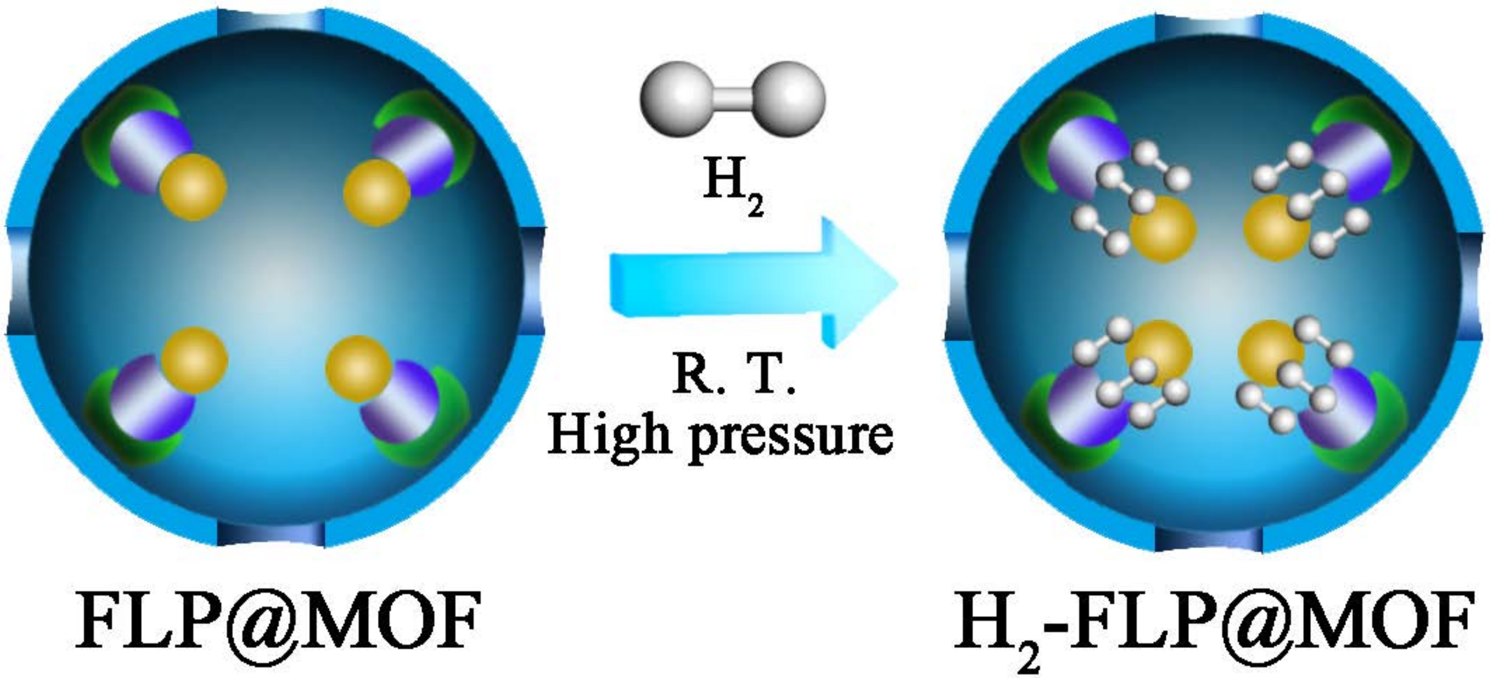
Objective - Relevance

- ***Phase I –*** to demonstrate and deliver one FLP@MOF with reversible total gravimetric capacity ≥ 1.5 wt % and total volumetric capacity ≥ 0.012 kg H_2/L at H_2 pressure of ≤100 bar at room temperature.
- ***Overall*** – to produce one or more FLP@MOF that that meets or exceeds the DOE's 2025 goal of H_2 storage gravimetric density (GD) of 5.5 wt.% and volumetric density (VD) of 0.040 kg H_2/L.

Merits of FLP@MOFs & Their Impact on Technology Barriers



Approach: Encapsulating FLP into MOF (FLP@MOF) for Hydrogen Storage at Ambient Temperature



Approach – Development Strategy

FLP@MOF Design and Synthesis (USF)	Characterization & Modeling (USF/ANL/HyMARC)	Optimization & Engineering (USF/ANL)
▪ Develop various approaches to synthesize new FLP@MOF ▪ Structure characterization of FLP@MOF ▪ High throughput synthesis of FLP@MOF	▪ H_2 storage capacity & reversibility measurements ▪ Advanced characterization of H_2-FLP@MOF ▪ Computational modelling of H_2-FLP@MOF	▪ Volumetric capacity enhancement of H_2 adsorption in FLP@MOF

- New FLP@MOFs with high H_2 storage capacities
- Enhancing H_2 hydrogen binding energy to 15-25 kJ/mol
- Unveiling possibly new H_2 adsorption mechanism
- Improving volumetric H_2 adsorption capacity by preparing monolithic FLP@MOF

Collaborating with HyMARC/others and leveraging existing experimental / theoretic supports are essential to the project success!

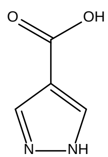
Approach: Phase I Milestone Status

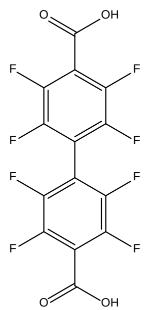
Milestone #	Milestones/Go-NoGo DP	Milestone Verification	Percent Complete
M 1.1.1	Complete synthesize at least six meso-MOFs for the incorporation of FLP	MOF synthesis will be carried out at USF based on literature reported method	100%
M 1.1.2	Design and synthesize a series of FLP@MOF using step-wise anchoring approach	FLP@MOF synthesis will be carried out at USF	20%
M 2.1.1	Complete high-pressure hydrogen storage measurements for stepwise synthesized FLP@MOFs	Isotherm of H_2 at different pressures will be measured by USF and ANL teams	0%
M 2.2.1	Complete structural studies of the first batch of FLP@MOF	Conventional analytic tools will be applied to study selected FLP@MOF at USF/ANL	10%
GNG 1.2.3	At least one FLP@MOF with reversible total gravimetric capacity ≥ 1.5 wt % and total volumetric capacity ≥ 0.012 kg H_2/L at H_2 pressure of ≤ 100 bar at room temperature	To be delivered to DOE designated lab for certification after initial measurement at USF/ANL	0%

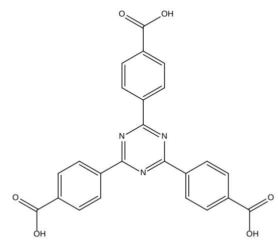
The focus of Phase I is to deliver one FLP@MOF with reversible total gravimetric capacity ≥ 1.5 wt %.

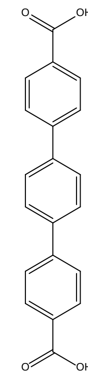
Accomplishments: Ligand Synthesis

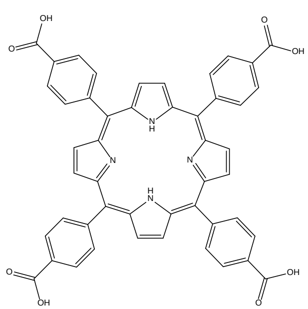
- The following ligands have been synthesized for the construction of MOFs.

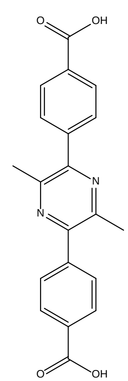


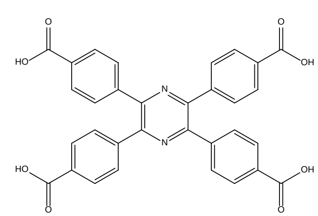


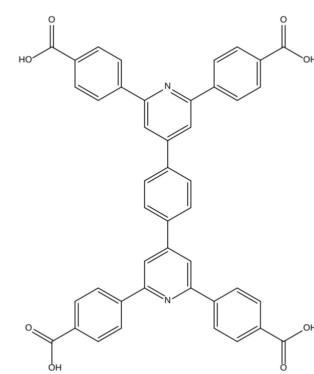






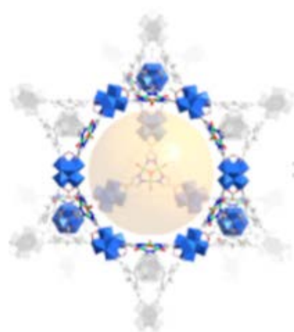




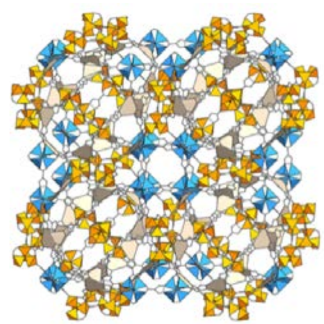


Accomplishments: Preparation of meso-MOFs.

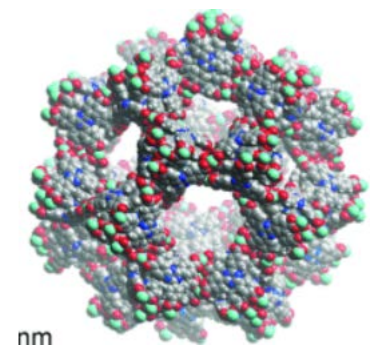
- Meso-MOFs: MOF818, FDM-3, Tb-TATB, Zr-UIO-68, Zr-UIO-67-8F, PCN-333(Fe), PCN-333(Cr), UIO-68, MIL-101(Cr), MIL-101-4F and MIL-101-Br(Cr) with the structures shown below have been prepared as planned.



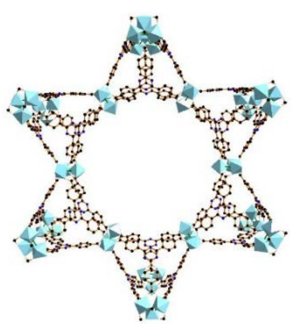
MOF-818



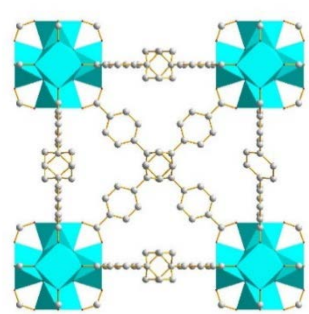
FDM-3



Tb-TATB



PCN-333

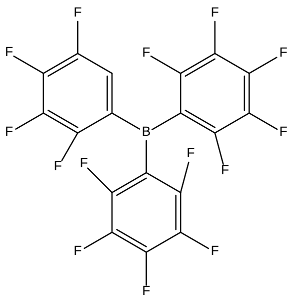


UIO-68

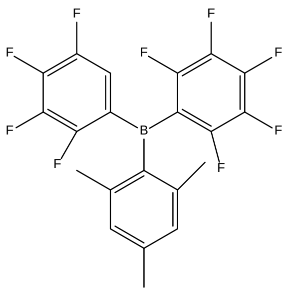
MIL-101

Accomplishments: Synthesis of Lewis acids and Lewis bases for FLP

- The following two Lewis acids have been prepared.

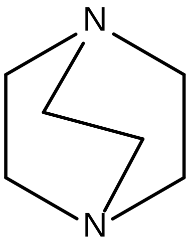


$B(C_6F_5)_3$

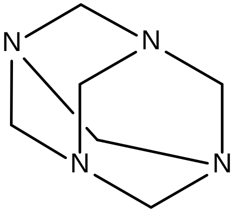


$MesB(C_6F_5)_2$

- The following two Lewis bases have been prepared.

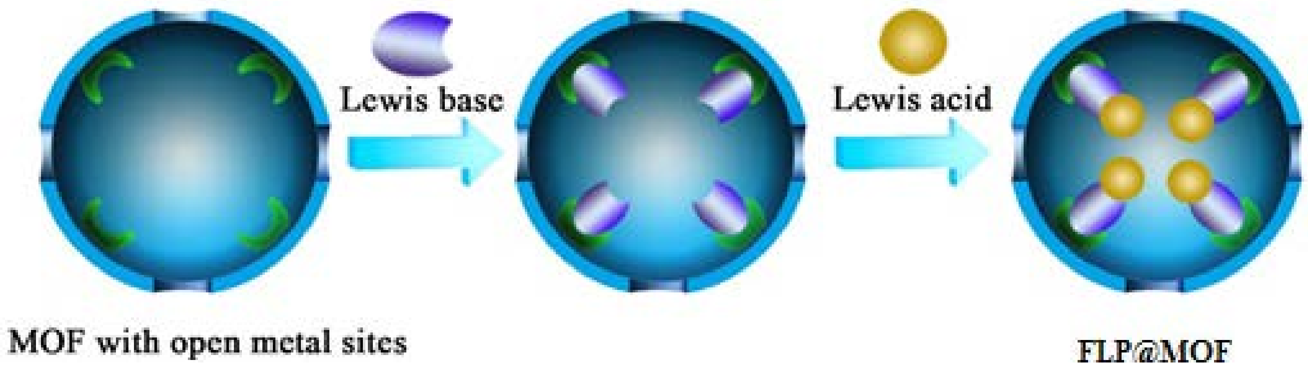


DABCO

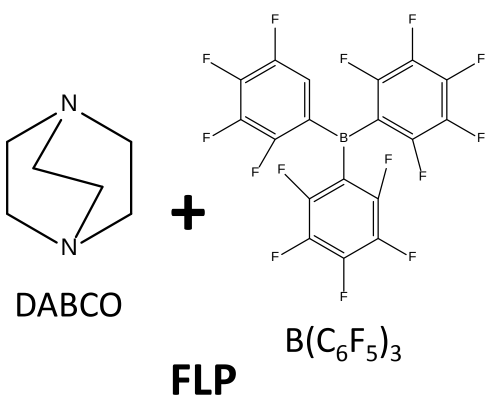


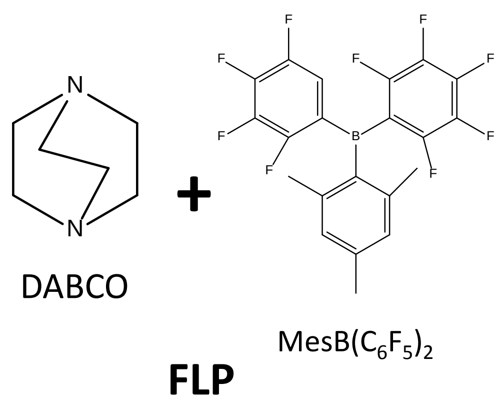
HMTA

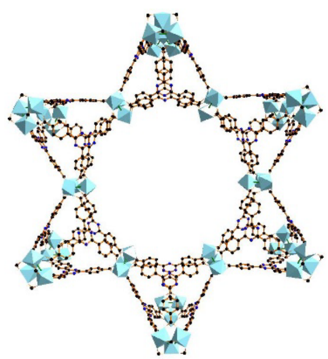
Accomplishments: Step-wise anchoring of FLP on MOF through coordination interaction



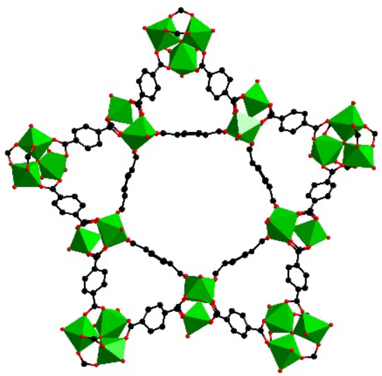
- The following two sets of FLPs have been encapsulated in PCN-333(Cr) and MIL-101(Cr) using step-wise anchoring approach.







PCN-333 (Cr)



MIL-101 (Cr)

Collaborations: Working with HyMARC

- HyMARC – SNL
  - High pressure analysis
  - Surface characterization tools
- HyMARC – PNNL
  - In situ NMR study
- HyMARC – LLNL
  - Modeling/simulation of H_2-FLP@MOF Surface XPS
- HyMARC - NREL
  - Measurements of Qst for H2 adsorption in FLP@MOF
  - Capacity certification

Looking forward to formulating detailed experimental plan through the discussion with HyMARC members!

Challenges and Barriers

- The high-pressure sorption instrument at USF will need to be well calibrated to collect reliable high-pressure H_2 sorption isotherms particularly at pressure close to 100 bar.

Proposed Future Work

- **Remaining Phase I Activities**
  - Synthesis of a series of mesoporous MOFs
  - Incorporation of FLPs into the synthesized mesoporous MOFs via step-wise anchoring approach
  - Optimize FLP vs MOF formulation through high throughput synthesis
  - Structural characterizations of the prepared FLP@MOFs with conventional and advanced tools
  - High pressure H2 storage capacity measurements
- **Planned Phase II Activities**
  - Developing other approaches to incorporate FLPs into MOFs
  - Continue high throughput synthesis/screening of FLP@MOFs and optimization of FLP@MOFs
  - High pressure hydrogen storage measurements
  - Advanced characterizations and mechanistic studies of H2 adsorption in FLP@MOFs
  - Computational modeling/simulation support
  - Process engineering of FLP@MOF

Any proposed future work is subject to change based on funding levels.

Technology Transfer Activities

- **A Provisional Patent Application entitled "FRUSTRATED LEWIS PAIR-IMPREGNATED POROUS MATERIALS AND USES THEREOF" has been filed.**

Summary

- Eight ligands have been synthesized for the construction of MOFs.
- Six meso-MOFs: MOF818, FDM-3, Tb-TATB, Zr-UIO-68, Zr-UIO-67-8F, PCN-333(Fe), PCN-333(Cr), UIO-68, MIL-101(Cr), MIL-101-4F and MIL-101-Br(Cr) with the structures shown below have been prepared.
- Two Lewis acids and two Lewis bases have been prepared for FLPs.
- Two sets of FLPs have been encapsulated in PCN-333(Cr) and MIL-101(Cr) using step-wise anchoring approach.

Acknowledgements

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- Technology Manager: Zeric Hulvey

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