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

Shengqian Ma (Lead)
University of South Florida/University of North Texas
Di-Jia Liu (Sub)
Argonne National Laboratory

June 7-11, 2021

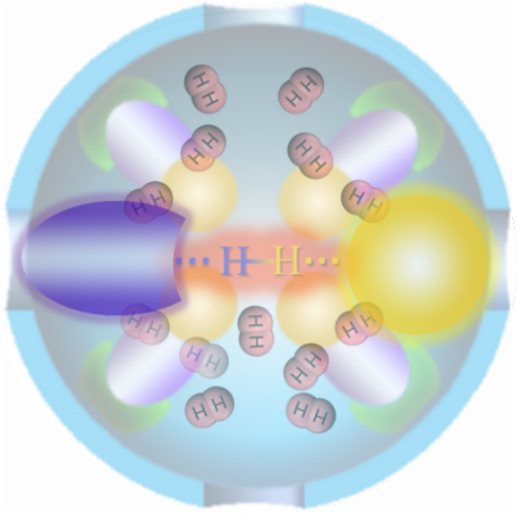
Project ID: ST210

This presentation does not contain any proprietary, confidential, or otherwise restricted information

2021 DOE Hydrogen and Fuel Cells Program Annual Merit Review Meeting

Project Goal

- **The goal** of this project is to develop new materials based on metal-organic framework (MOF) incorporated with frustrated Lewis pairs (FLP), FLP@MOF, as next-generation of hydrogen storage sorbent that can meet or exceed DOE's 2025 performance target of H_2 storage gravimetric density (GD) of 5.5 wt.% and volumetric density (VD) of 0.040 kg H_2/L.



FLP@MOF for Hydrogen Storage at Ambient Temperature

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

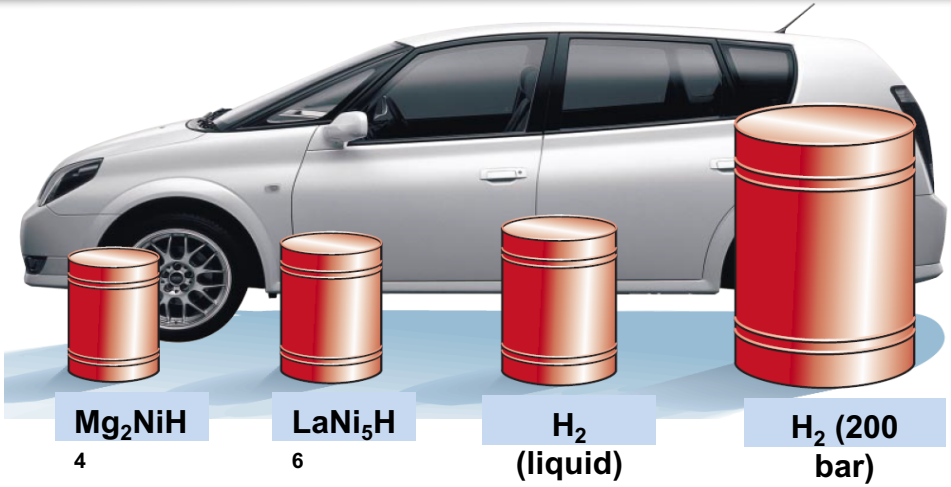
Budget

- 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 15 to 25 kJ/mol.

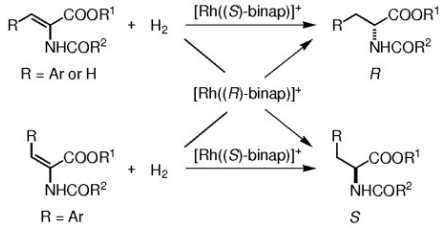
Objective – Relevance

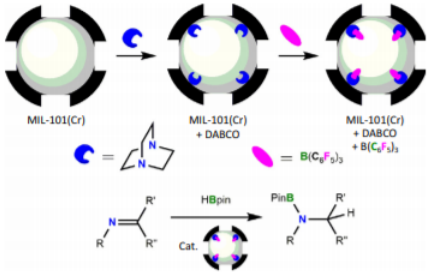
Table 1. Technical System Targets: Onboard Hydrogen Storage for Light-Duty Fuel Cell Vehicles

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.

Frustrated Lewis Pairs





Transition metal for hydrogenation

Rh- and Ru-based catalysts for asymmetric hydrogenation

Metal-free hydrogenation (FLP)

the first MOF-supported FLPs

1897

1912 Noble prize

1970s

2001 Noble prize

2006

2018

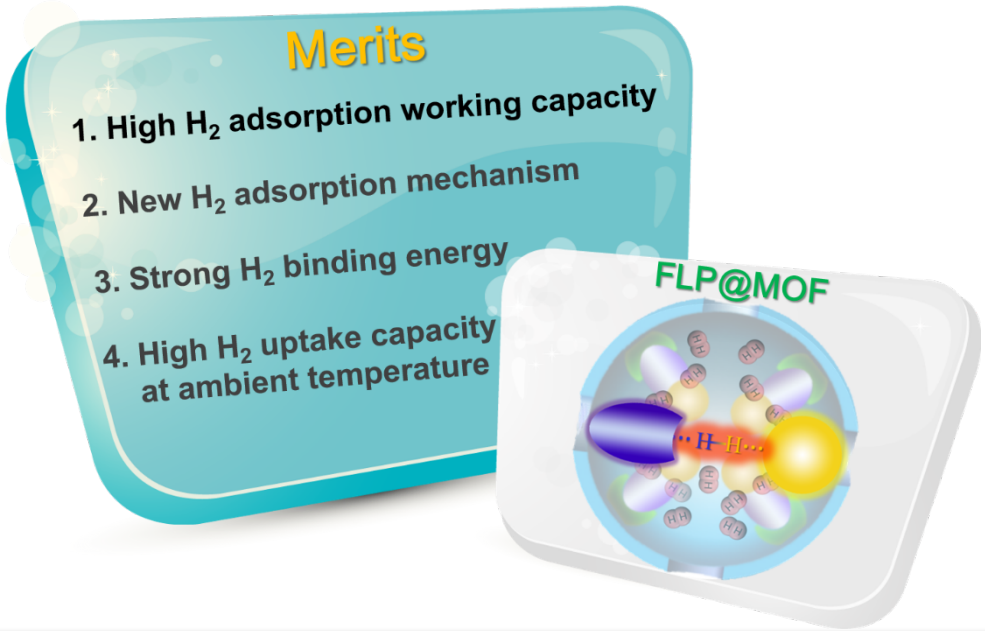
▶ Interaction between FLP and H_2 is strong

Ind. Eng. Chem., 1926, 18, 1005. Angew. Chem. Int. Ed., 2002, 41, 2008. Science, 2006, 314, 1124.
Chem 2018, 4, 2587. Angew. Chem. Int. Ed., 2019, 58, 7420.

Objective - Relevance

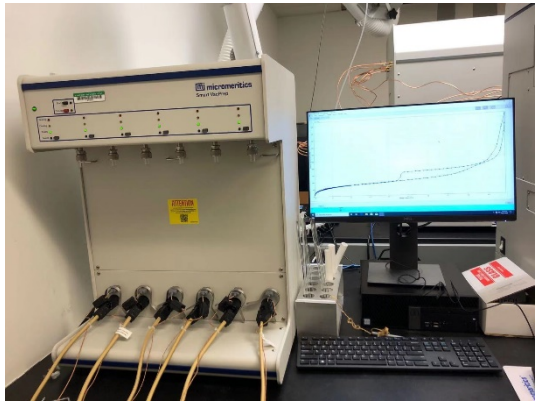
- ***Phase I*** – to demonstrate and deliver one FLP@MOF with reversible total gravimetric capacity ≥ 1.5 wt % and total volumetric capacity ≥ 0.012 kg H_2/L at H_2 pressure of ≤100 bar at room temperature.
- ***Overall*** – to produce one or more FLP@MOF that that meets or exceeds the DOE's 2025 goal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

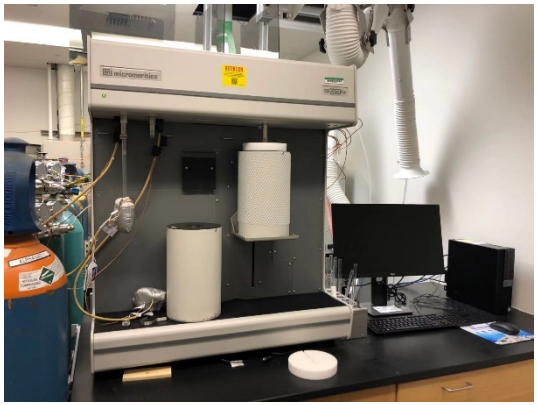


Gas Sorption Instruments in UNT Lab

Multi-port degas equipment



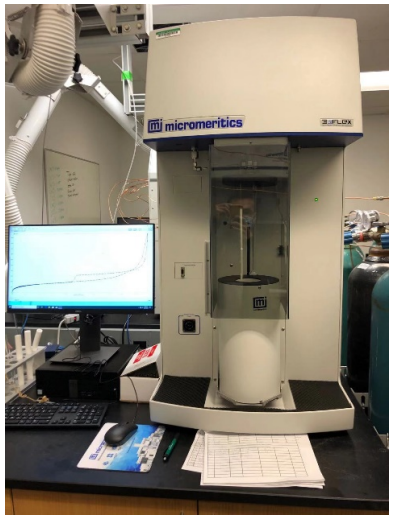
ASAP 2020 Plus physisorption



HPVA II high pressure adsorption analyzer



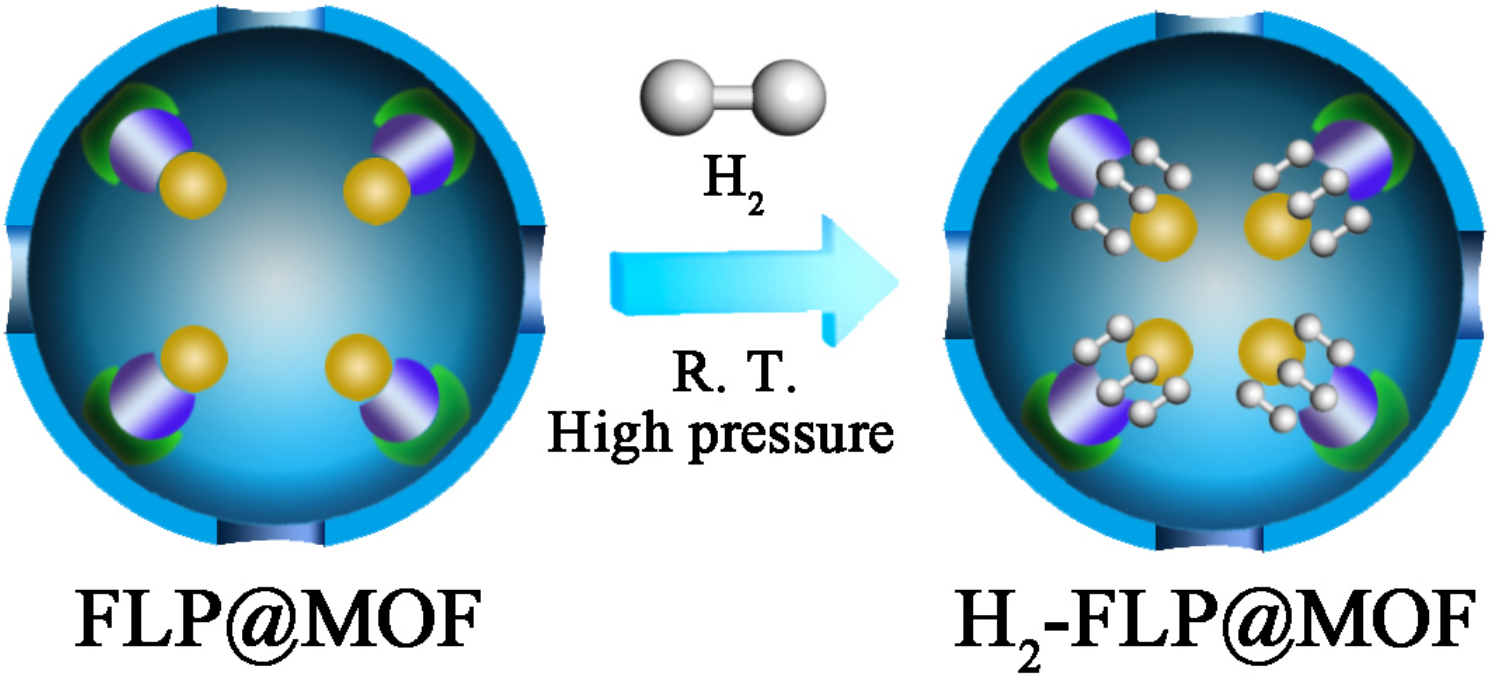
3 FLEX multi-channel physisorption



Glovebox



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



Approach – Development Strategy

FLP@MOF Design and Synthesis (USF)

- Develop various approaches to synthesize new FLP@MOF
- Structure characterization of FLP@MOF
- High throughput synthesis of FLP@MOF

Characterization & Modeling (USF/ANL/HyMARC)

- H_2 storage capacity & reversibility measurements
- Advanced characterization of H_2-FLP@MOF
- Computational modelling of H_2-FLP@MOF

Optimization & Engineering (USF/ANL)

- 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

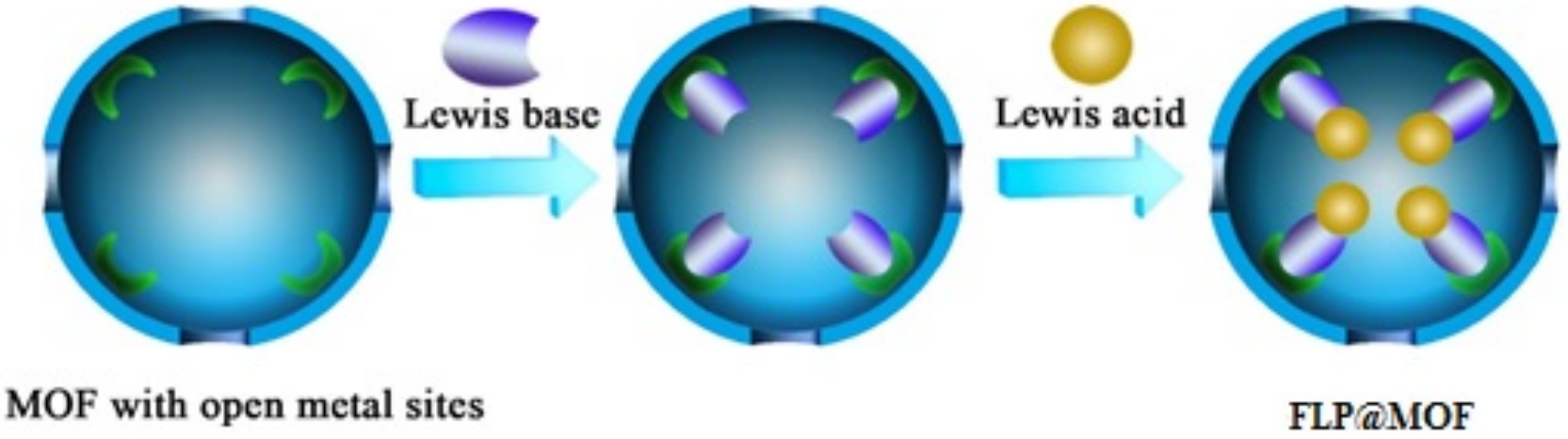
Milestone #	Milestones/Go-NoGo DP	Milestone Verification	Percent Complete
M 1.1.1	Complete synthesize at least six meso-MOFs for the incorporation of FLP	MOF synthesis will be carried out at USF based on literature reported method	100%
M 1.1.2	Design and synthesize a series of FLP@MOF using step-wise anchoring approach	FLP@MOF synthesis will be carried out at USF	80%
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	30%
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 and Progress

Project was not reviewed last year.

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



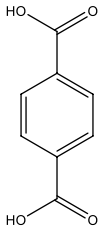
Robust framework

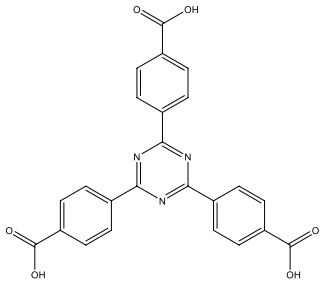
Big pore

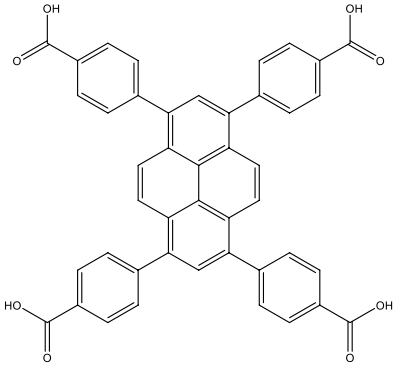
High surface area

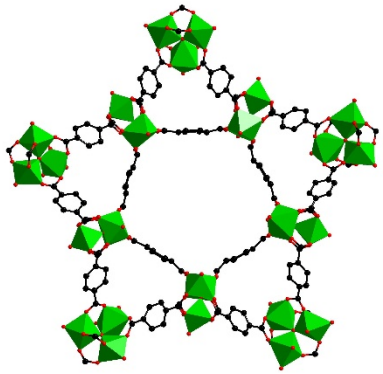
Open metal site

Preparations of ligands and MOFs

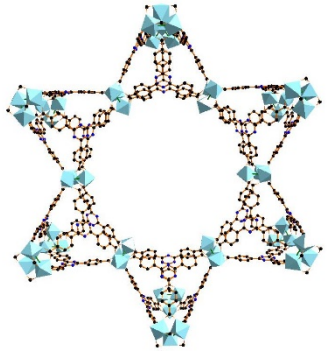




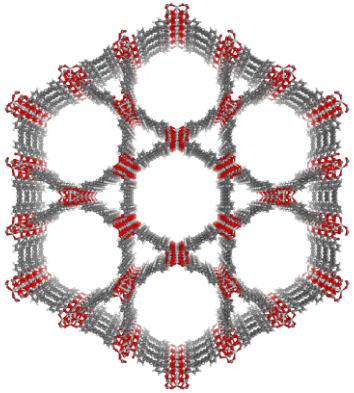




MIL-101 (Cr)

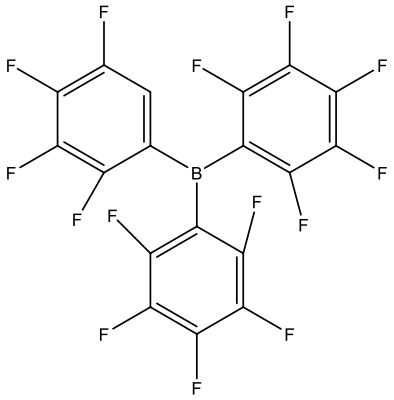


PCN-333 (Cr)

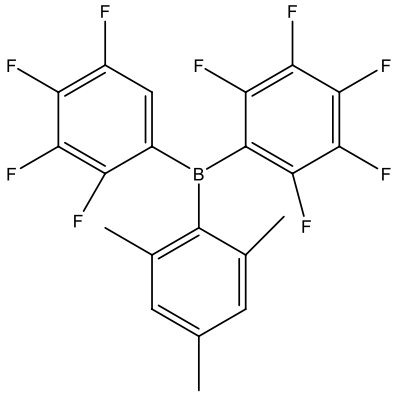


NU-1000 (Zr)

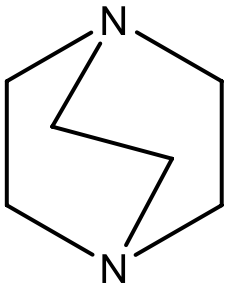
Synthesis of Lewis acids and Lewis bases for FLPs



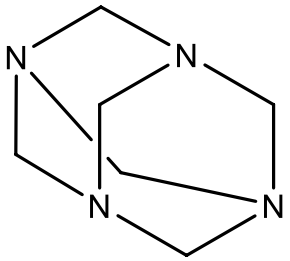
$B(C_6F_5)_3$



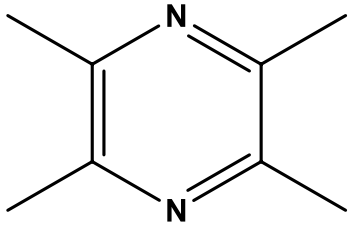
$MesB(C_6F_5)_2$



DABCO



HMTA

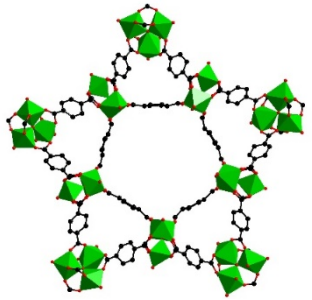


TMPA

Preparation of FLP@MIL-101(Cr)

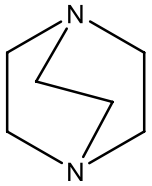
Number	Samples
1	N1-B1@MIL-101(Cr)
2	N1-B2@MIL-101(Cr)
3	N2-B1@MIL-101(Cr)
4	N2-B2@MIL-101(Cr)
5	N3-B1@MIL-101(Cr)
6	N3-B2@MIL-101(Cr)

MOF:

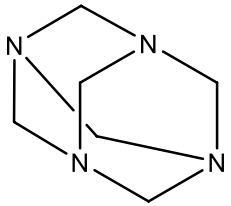


MIL-101 (Cr)

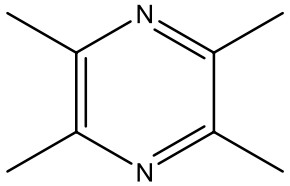
Lewis base:



N1: DABCO

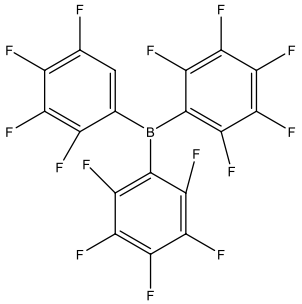


N2: HMTA

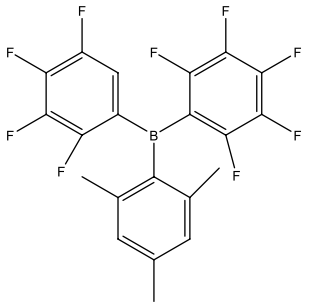


N3: TMPA

Lewis acid:

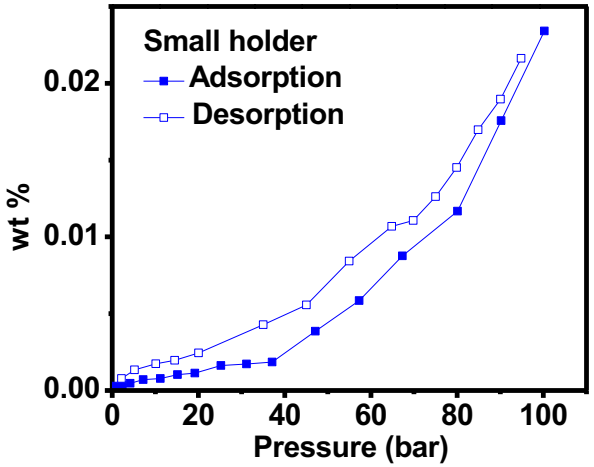


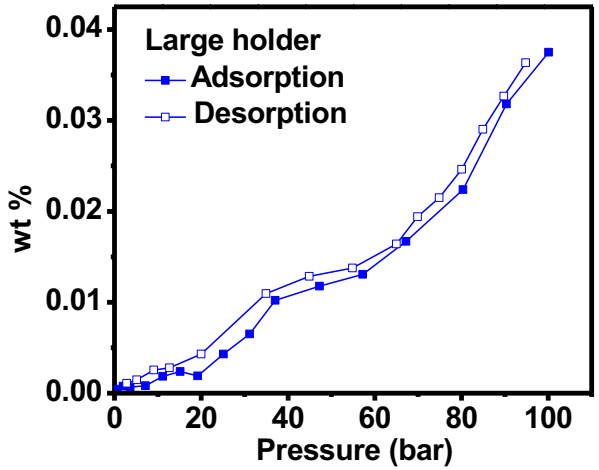
B1: $B(C_6F_5)_3$

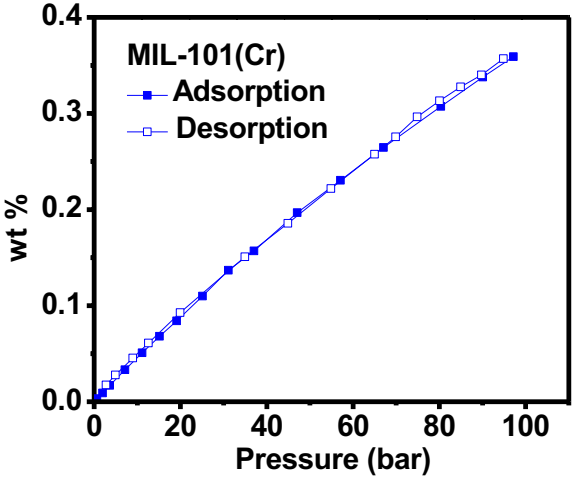


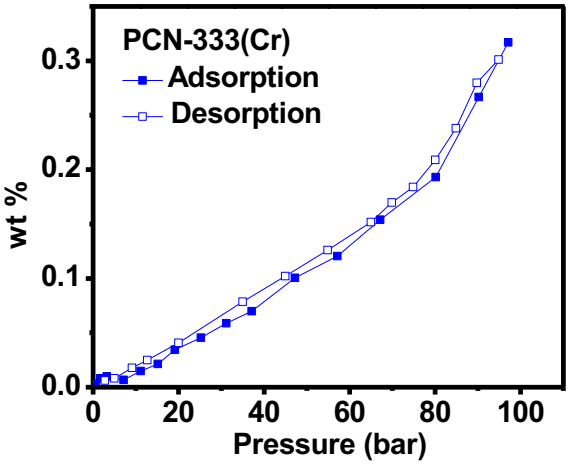
B2: $MesB(C_6F_5)_2$

High-pressure H_2 Adsorption Measurements on Sample Holders and Pure MOFs (wt %)

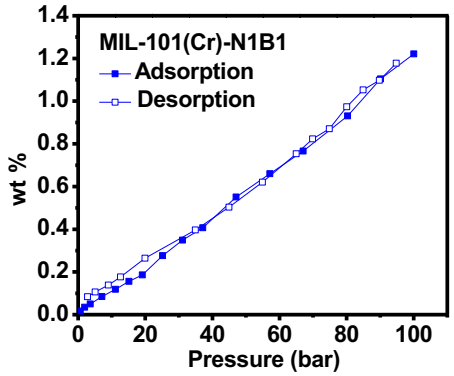


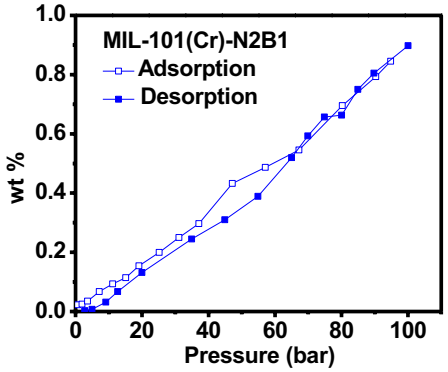


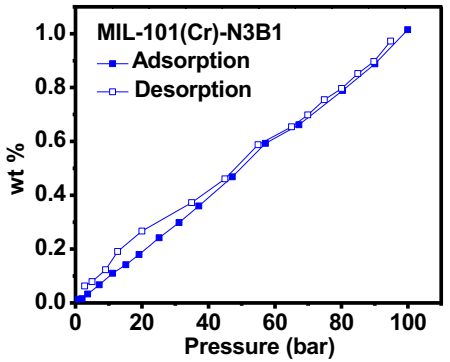


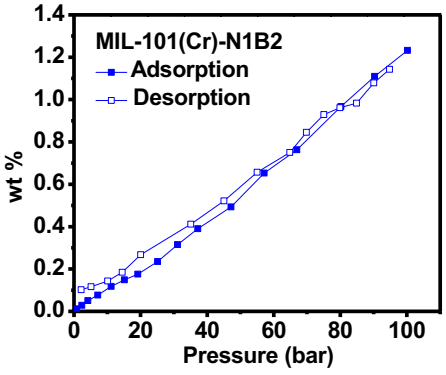


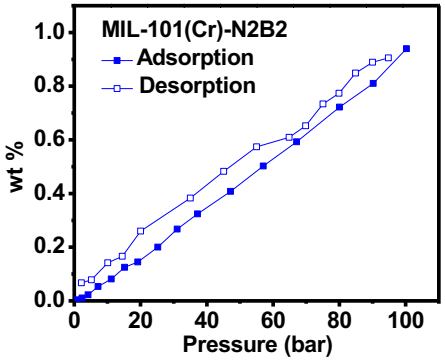
High-pressure H_2 Adsorption Measurements on MIL-101(Cr)-FLPs (1 mmol/g), wt %

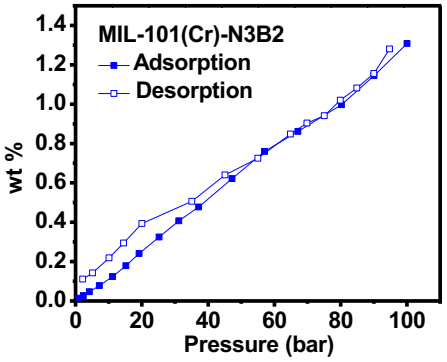




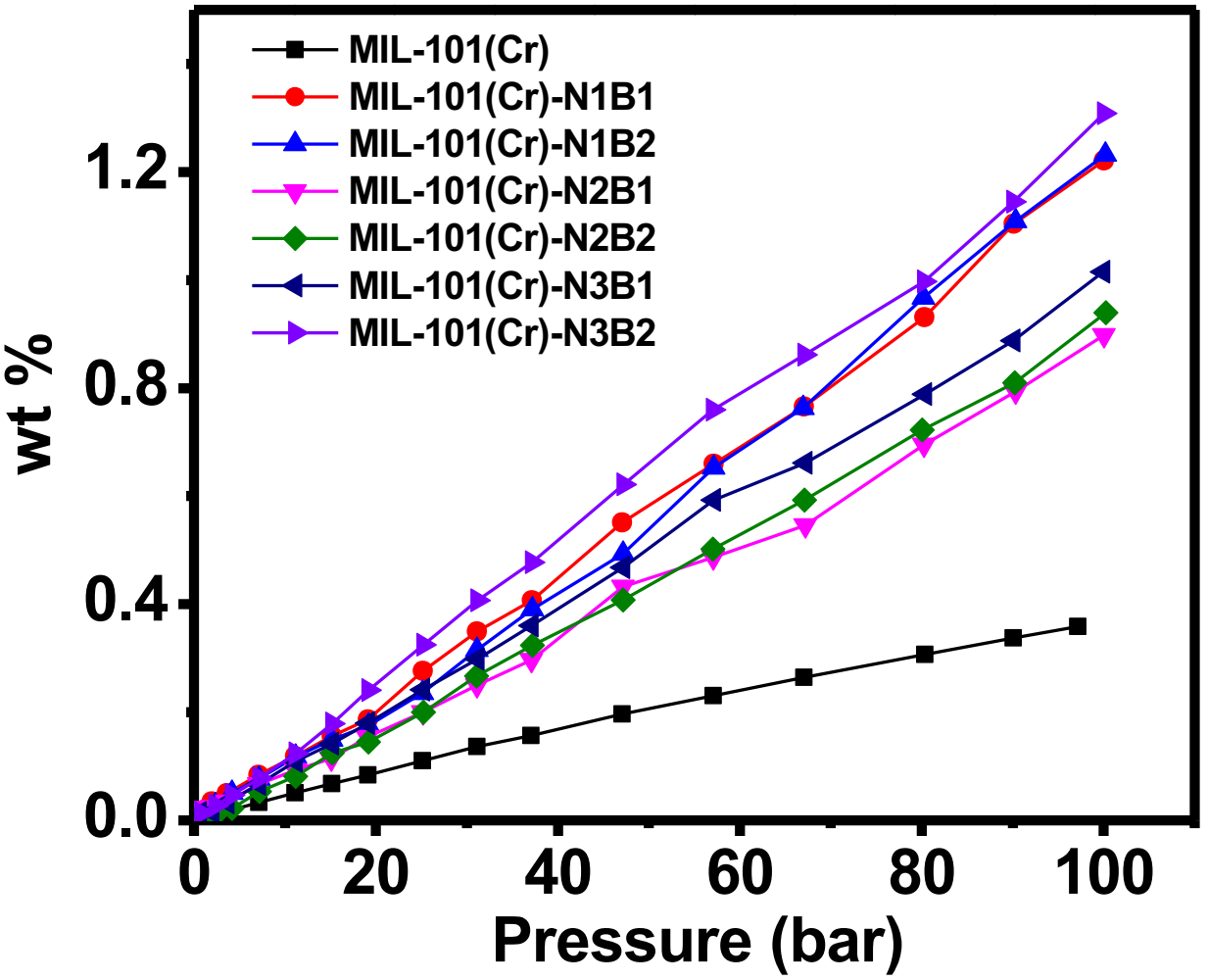








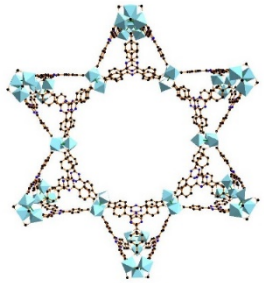
Summary for MIL-101(Cr)-FLPs (1 mmol/g) performances wt %



Preparation of FLP@PCN-333(Cr)

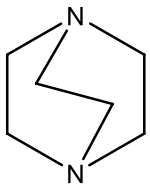
Number	elements
1	N1-B1@PCN-333(Cr)
2	N1-B2@PCN-333(Cr)
3	N2-B1@PCN-333(Cr)
4	N2-B2@PCN-333(Cr)
5	N3-B1@PCN-333(Cr)
6	N3-B2@PCN-333(Cr)

MOF:

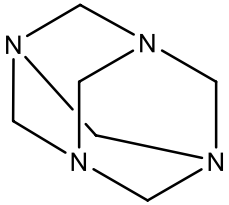


PCN-333 (Cr)

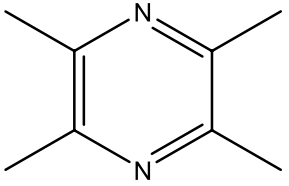
Lewis base:



N1: DABCO

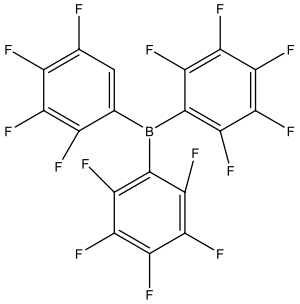


N2: HMTA

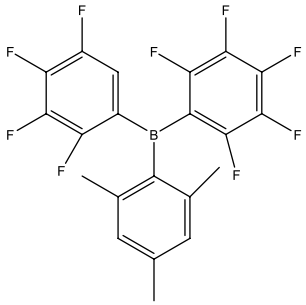


N3: TMPA

Lewis acid:

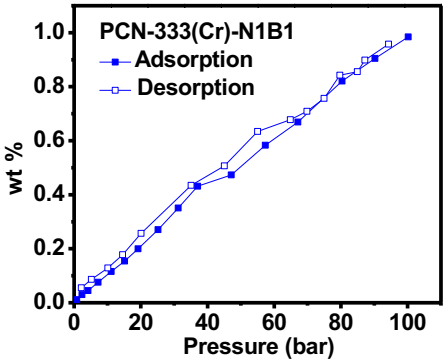


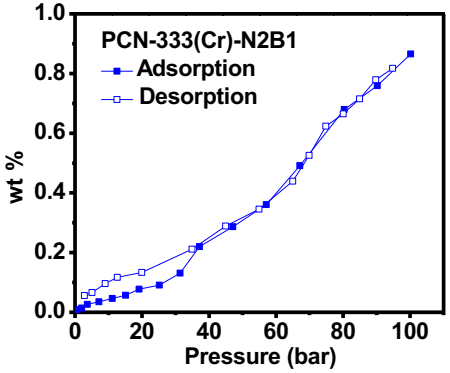
B1: $B(C_6F_5)_3$

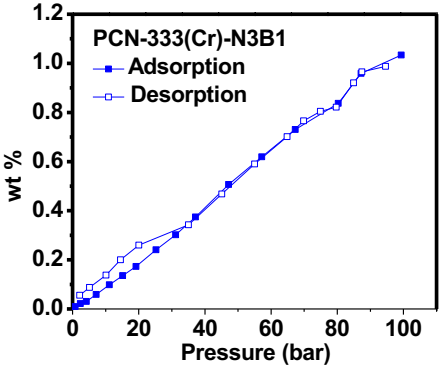


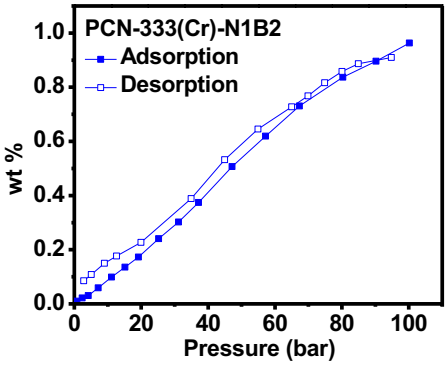
B2: $MesB(C_6F_5)_2$

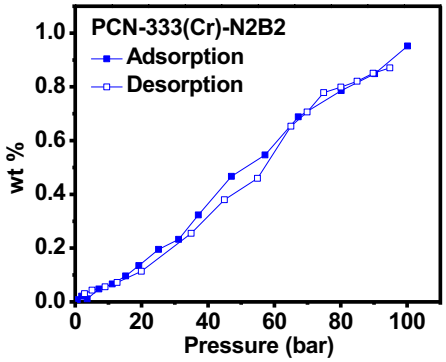
High-pressure H_2 Adsorption Measurements on PCN-333(Cr)-FLPs (1 mmol/g), wt %

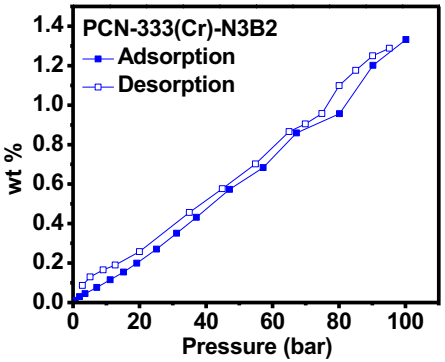




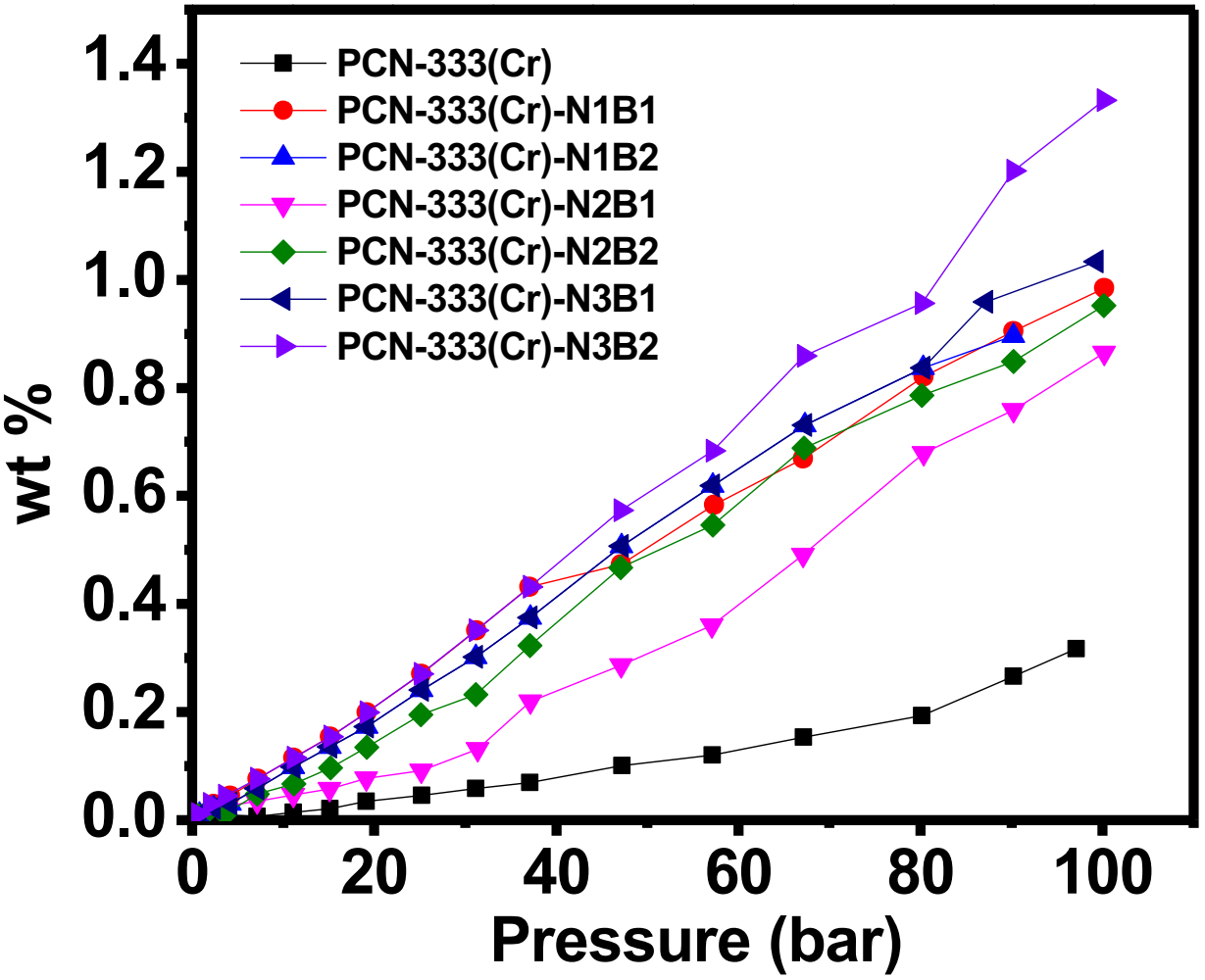








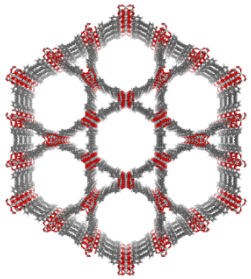
Summary for PCN-333(Cr)-FLPs (1 mmol/g) performances, wt %



Preparation of FLP@NU-1000(Zr)

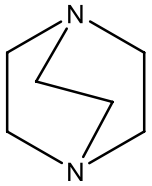
Number	elements
1	N1-B1@NU-1000(Zr)
2	N1-B2@NU-1000(Zr)
3	N2-B1@NU-1000(Zr)
4	N2-B2@NU-1000(Zr)
5	N3-B1@NU-1000(Zr)
6	N3-B2@NU-1000(Zr)

MOF:

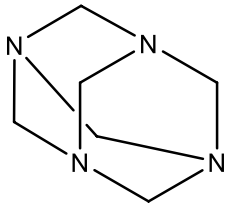


NU-1000 (Zr)

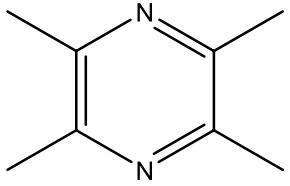
Lewis base:



N1: DABCO

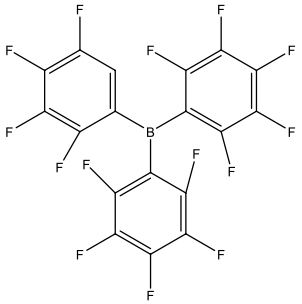


N2: HMTA

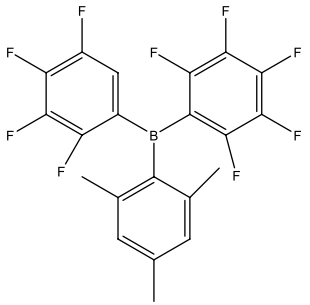


N3: TMPA

Lewis acid:



B1: $B(C_6F_5)_3$

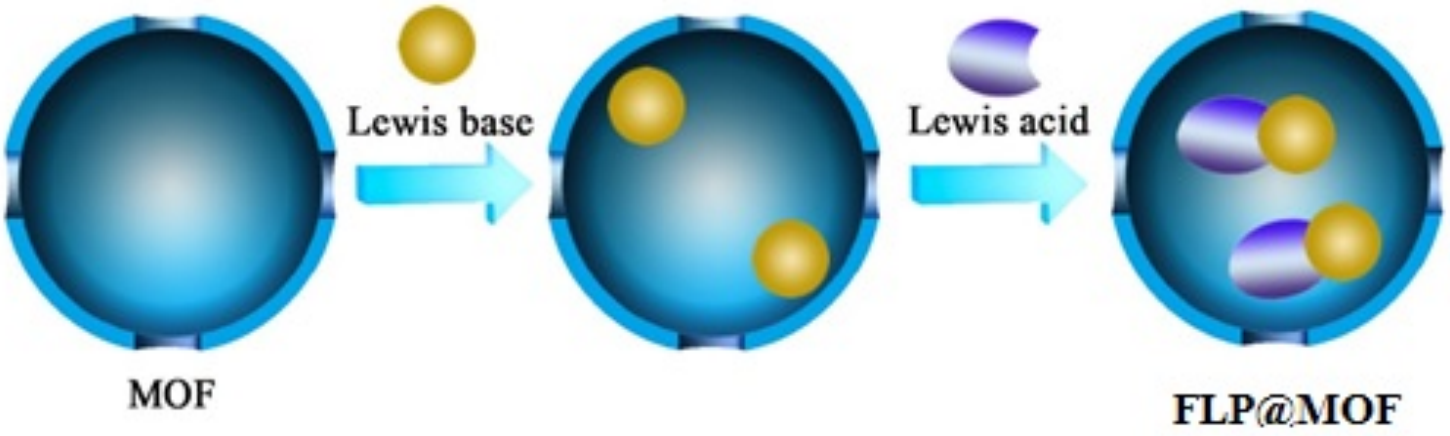


B2: $MesB(C_6F_5)_2$

Summary for strategy 1

- The test sample holders have negligible influence on the sorption results
- Different MOFs exhibit different H_2 adsorption performances
- The anchoring of FLP to MOFs can increase the H_2 sorption performances substantially
- The loading amount of FLP in FLP@MOFs has significant influence on the H_2 adsorption performances

Ongoing: *De novo* assembly of FLP within the nanospace of MOFs

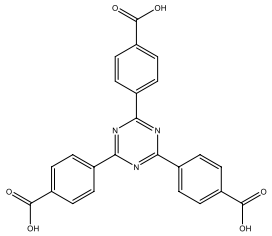


Solid framework

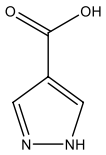
Big pore

High surface area

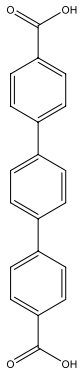
Ligand Preparation



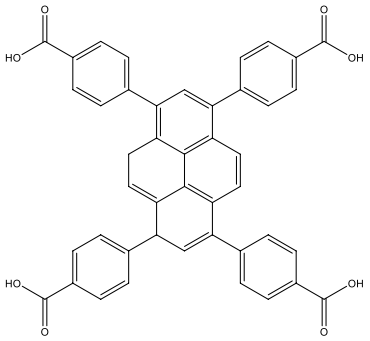
For PCN-333(Fe)
Tb-TATB



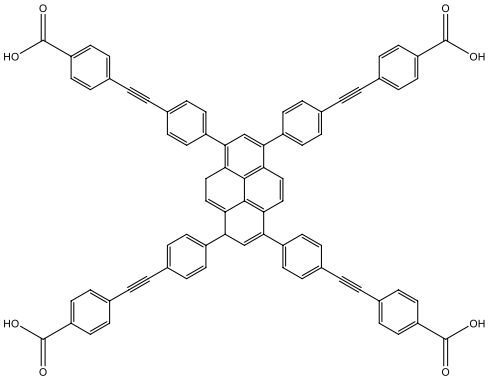
For MOF-818
FDM-3



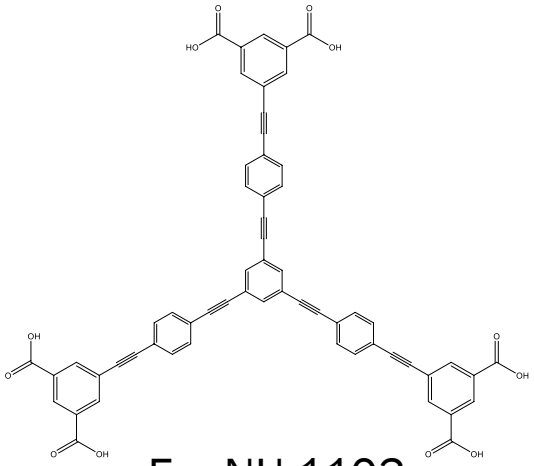
For UIO-68



For NU-1000



For NU-100



For NU-1103

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!

Proposed Future Work

- Remaining Phase I Activities
  - 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.

Acknowledgements

- This work is supported by the Award **DE-EE0008810**.
- Technology Manager: Zeric Hulvey
- Project Manager: Jesse Adams
- Hydrogen Fuel R&D Program Manager: Ned Stetson



Postdoc: Dr. Yin Zhang



Ma Research Group at UNT

30