
Uniting Theory and Experiment to Deliver Flexible MOFs for Superior Methane (NG) Storage

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Project ID: **ST213**

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Overview

Timeline

- Project start: Nov. 2019
- Phase I end: Sep. 2020
- Phase II end: Sep. 2022

Budget

- Total project requested: \$1,000,000
 - DOE share: \$800,000
 - Contractor share: \$200,000
- Funding received in FY2019 (Phase I)
 - \$300,000

Barriers

- Barriers addressed
 - A. System Weight and Volume
 - B. System cost
 - C. Efficiency
 - D. Durability/Operability

Partners

- Interactions/collaborations
 - University of South Florida
 - HyMARC



Objective – Relevance

- **Phase I** – Demonstrate a FlexMOF with total CH₄ deliverable capacity of ≥ 200 v/v (5-65 bar, room temperature) with evaluation for H₂ storage.
- **Overall** – Demonstrate a FlexMOF with total CH₄ deliverable capacity of ≥ 300 v/v (5-65 bar, room temperature) with evaluation for H₂ storage.

Potential Advantages of FlexMOFs & Their Impact on Technology Barriers

- **System Weight and Volume** – FlexMOFs have potential to reach both gravimetric and volumetric uptake capacities based on theory and preliminary experimental data
 - **System Cost** – FlexMOFs are based on low-cost linkers and synthesis processes scalable industrially
 - **Efficiency** – The induction of flexibility in the FlexMOFs through gas loading has both thermodynamic and kinetically favorable properties for NG storage .
 - **Durability/Operability** – FlexMOFs show promise to improve CH₄ uptake capacities with tunable gate opening in the 5–35/65 bar range.
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Current Technology Options for On-board CH₄ Storage



Physical Properties	CNG	LNG
Physical state	compressed gas	cryogenic liquid
Temperature in vehicle tank	ambient	-162 °C (-259 °F)
Typical pressure in tank	2500–3600 psig (17.3–24.9 MPa)	10–50 psig (170–446 kPa)
Typical density in tank	1.1–1.6 lb/gallon	3.5 lb/gallon
Typical specific gravity	0.13–0.19	0.42
Typical energy density (LHV)	23,000–34,000 BTU/gallon	75,000 BTU/gallon (21,000 MJ/L)
LHV = lower heating value	(6500–9500 MJ/L)	



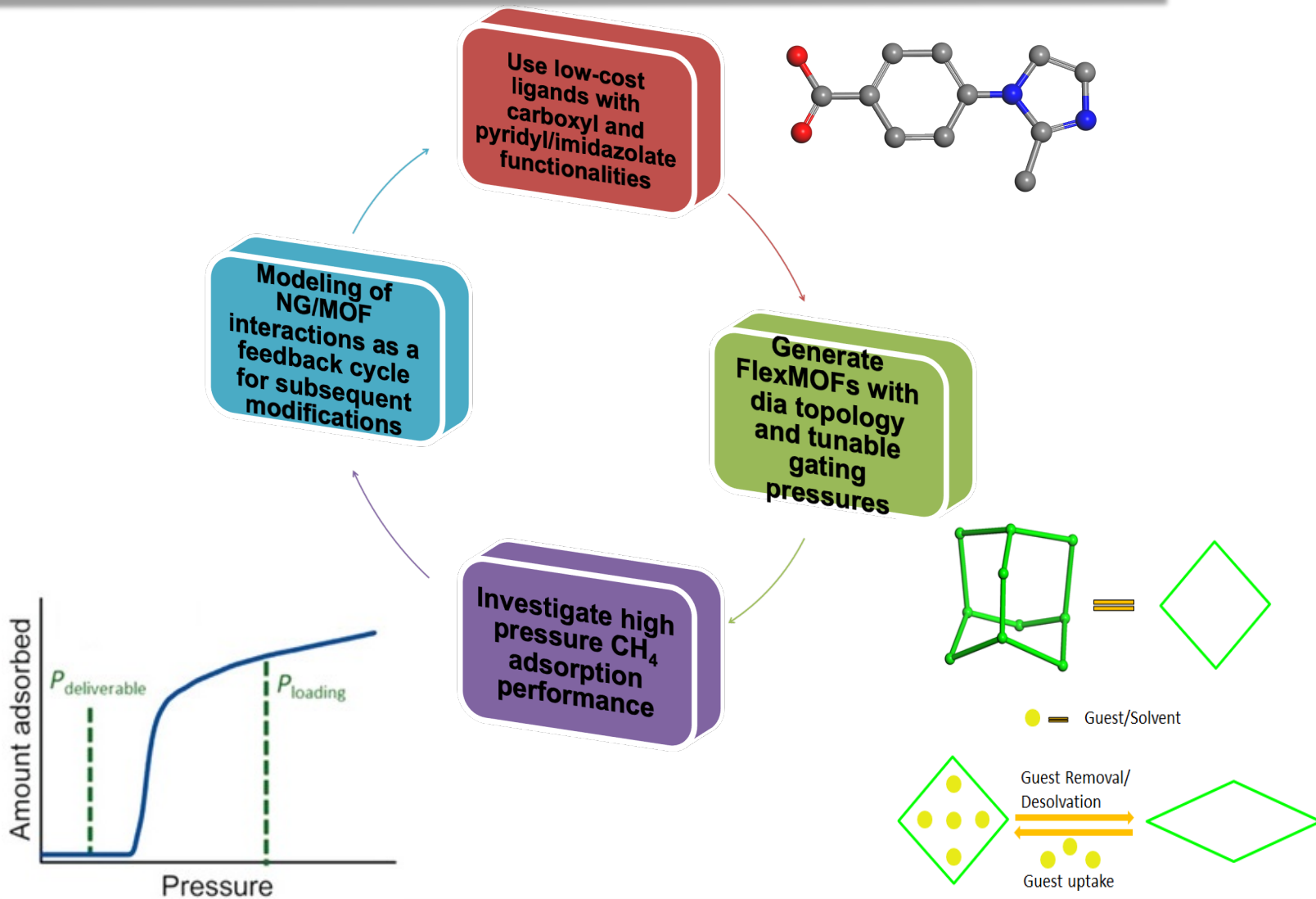
DOE Methane Storage Technology Targets

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

Storage Parameter	Units	Target
Gravimetric Capacity	g (CH ₄)/g	0.5
Volumetric Capacity	cm ³ (STP)/cm ³	350



Approach: Uniting Theory and Experiment to Design FlexMOFs





Approach: Phase I Activities

- Design and synthesis of a series of new FlexMOFs with **dia** topology
 - Screening existing FlexMOFs
 - CH₄ storage capacity measurement and structural characterization
 - Preliminary modeling/simulation effort
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Instrumentation for High Pressure Measurements

High-Pressure Gas Sorption Apparatus ASAP 2020 Surface Area Analyzer





MOF Parametrization

- Repulsion and dispersion parameters:

- Universal Force Field (UFF) Lennard-Jones 12–6 parameters

$$U_{rd} = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$

- Electrostatic parameters:

- Extended Charge Equilibration (EQ_{eq}) partial charges

1.) Rappe, A. K.; Casewit, C. J.; Skiff, W. M. UFF: A Full Periodic Table Force Field for Molecular Mechanics and Molecular Dynamic Simulations. *J. Am. Chem. Soc.* **1992**, *114*, 10024–10035.

2.) Wilmer, C. E.; Kim, K. C.; Snurr, R. Q. An Extended Charge Equilibration Method. *J. Chem. Phys. Lett.* **2012**, *3*, 2506–2511.



CH₄ Potential Parameters

Model	Atomic Site	Mass (amu)	Partial Charge (e ⁻)	ε (K)	σ (Å)
CH ₄ -PHAST	CHG	12.0110	-0.5868	58.5387	2.2242
	HCE	1.0079	0.1467	0.0000	0.0000
	HCE	1.0079	0.1467	0.0000	0.0000
	HCE	1.0079	0.1467	0.0000	0.0000
	HCE	1.0079	0.1467	0.0000	0.0000
	MOV	0.0000	0.0000	16.8542	2.9629
	MOV	0.0000	0.0000	16.8542	2.9629
	MOV	0.0000	0.0000	16.8542	2.9629
	MOV	0.0000	0.0000	16.8542	2.9629
TraPPE	CH4	16.0426	0.0000	148.0000	3.7300

1.) Cioce, C. R. Computational Investigations of Potential Energy Function Development for Metal–Organic Framework Simulations, Metal Carbenes, and Chemical Warfare Agents. Ph.D. Thesis, University of South Florida, 2015.

2.) Martin, M. G.; Siepmann, J. I. Transferable Potentials for Phase Equilibria. 1. United-Atom Description of *n*-Alkanes. *J. Phys. Chem. B* **1998**, *102*, 2569–2577.



Simulation Details

- Grand canonical Monte Carlo (GCMC) simulations were carried out using the in-house Massively Parallel Monte Carlo (MPMC) code.
- Chemical potential, volume, and temperature were kept constant (grand canonical (μVT) ensemble).
- Using the Metropolis Method, four types of moves (insertion, deletion, translation, and rotation) were performed on randomly selected CH_4 molecules using the Monte Carlo (MC) process.
- MC process continued until the total potential energy and particle number oscillated around a constant value.



Approach: Phase I Milestone Status

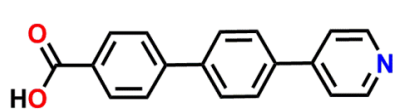
Milestone #	Milestones/Go-NoGo DP	Milestone Verification	Percent Complete
1.1.1	Design and synthesize series of ligands with carboxylate and pyridyl/imidazole moieties	Experiments at USF by Ma group parallel with Space group simulations	100%
1.1.2	Synthesize a series of flexible MOFs with varying pore sizes and degree of interpenetration	Experiments at USF by Ma group parallel with Space group simulations	10%
1.2.1	Carry out high-pressure CH ₄ storage measurements and calculate CH ₄ binding energies with H ₂ modeling in parallel	Experiments at USF by Ma group parallel with Space group simulations	0%
3.1.1	Advanced empirical modeling to facilitate discovery	Simulations at USF by Space group	10%
GNG 1.2.3	Demonstrate a FlexMOF with total CH ₄ deliverable capacity of ≥ 200 v/v (5-65 bar, room temperature) with evaluation for H ₂ storage	Experiments at USF by Ma group	0%

The focus of Phase I is to produce and demonstrate a FlexMOF with total CH₄ deliverable capacity of ≥ 200 v/v.

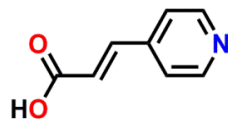


Accomplishments: Ligand Synthesis

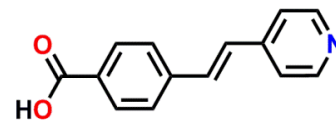
- Ligands containing carboxylate and pyridyl/imidazolate moieties shown below have been synthesized.



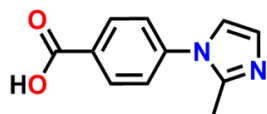
(L1)



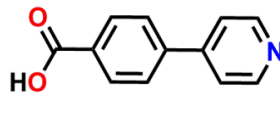
(L2)



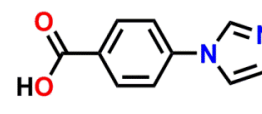
(L3)



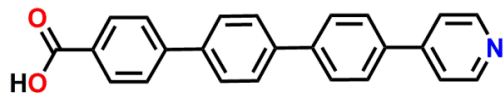
(L4)



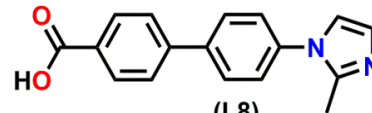
(L5)



(L6)



(L7)



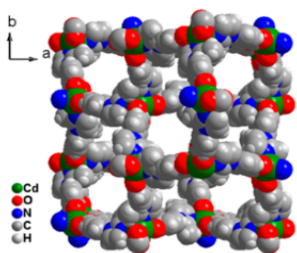
(L8)

- FlexMOFs consisting of the ligands **L1** and **L4** have already been synthesized.

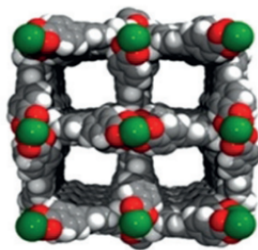


Accomplishments: Synthesis of FlexMOFs

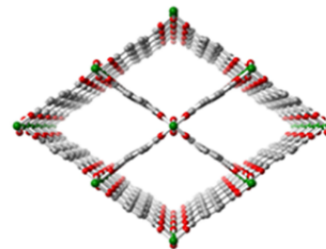
- The MOFs shown below have been synthesized experimentally in the lab and will be tested for their CH₄ adsorption properties.



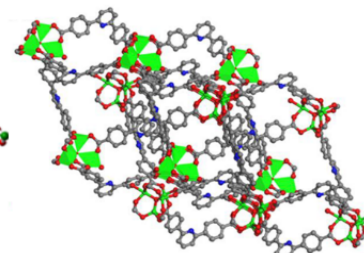
Cd-MOF



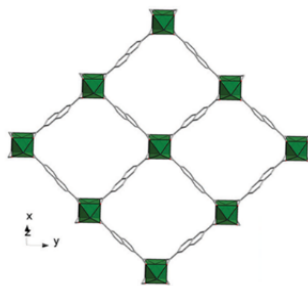
X-dia-1-Ni



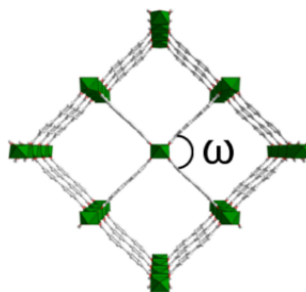
MIL-53



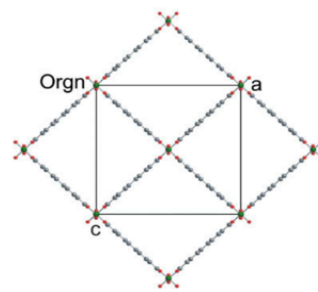
Zn-PDDA



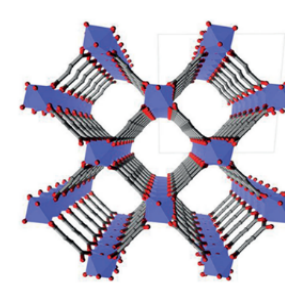
DUT-8 (Ni)



COMOC-2



DUT-5

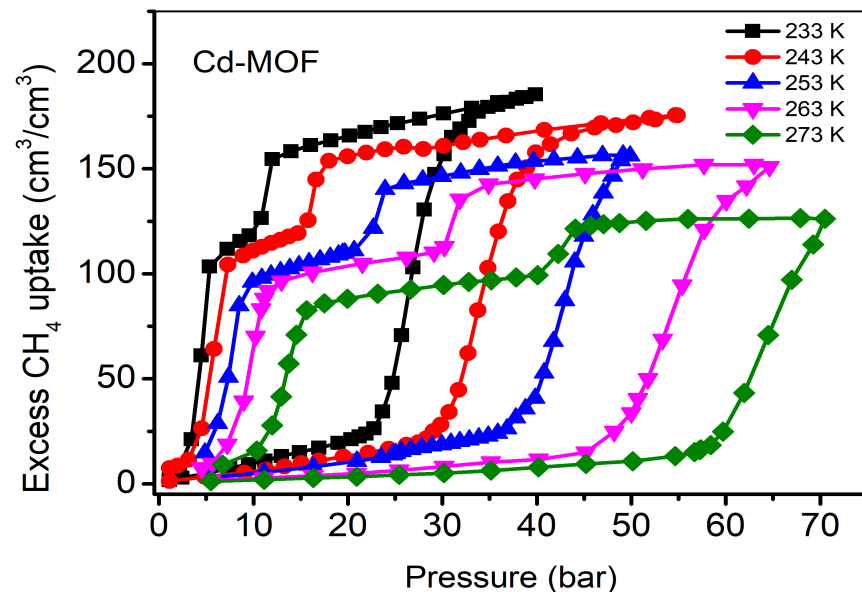
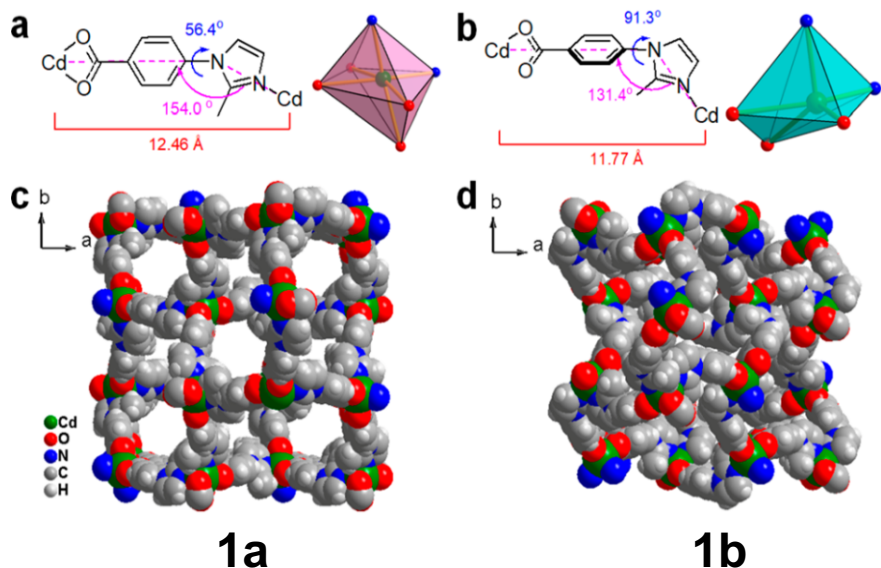


MIL-53-FA (Al)



Cd-MOF

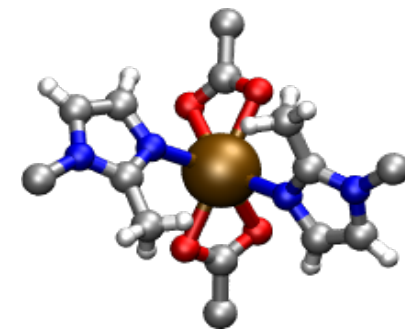
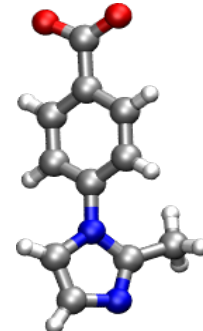
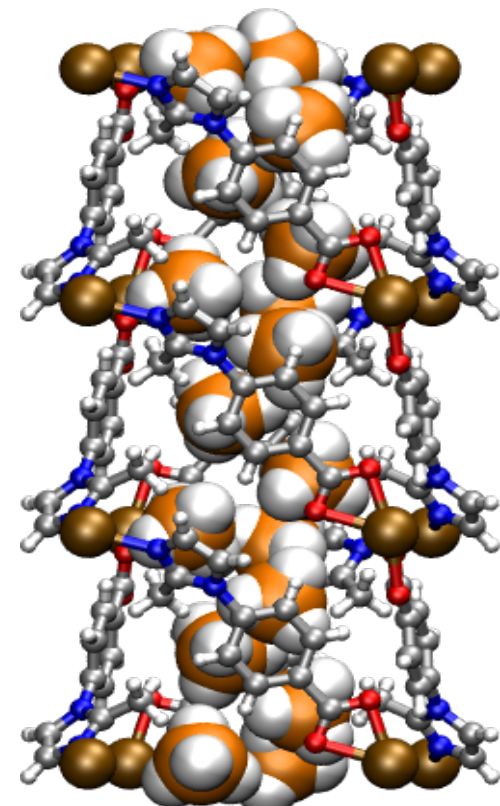
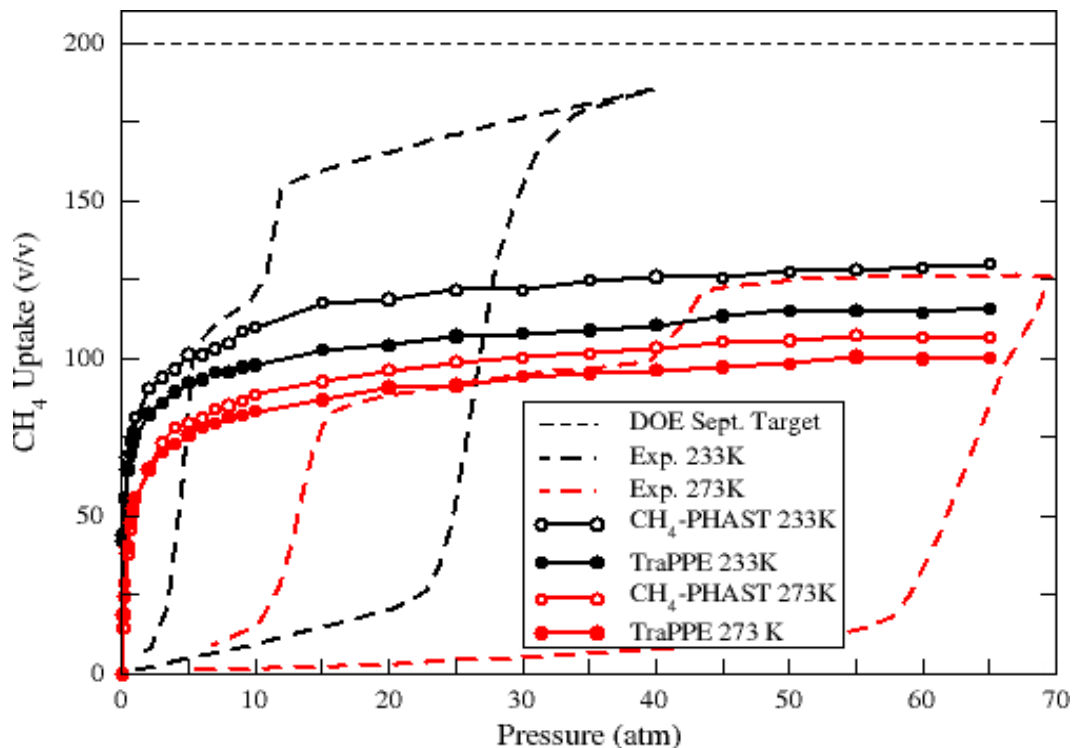
- Experimental CH₄ adsorption studies have been performed in the Cd-MOF.
- The MOF undergoes gate opening upon CH₄ adsorption at lower pressures as the temperature decreases. The measured 5–65 bar working capacity is around 150 v/v at 263 K.



Yang, H.; Guo, F.; Lama, P.; Gao, W.-Y.; Wu, H.; Barbour, L. J.; Zhou, W.; Zhang, J.; Aguila, B. Ma, S. Visualizing Structural Transformation and Guest Binding in a Flexible Metal–Organic Framework under High Pressure and Room Temperature *ACS Cent. Sci.* **2018**, *4*, 1194–1200.

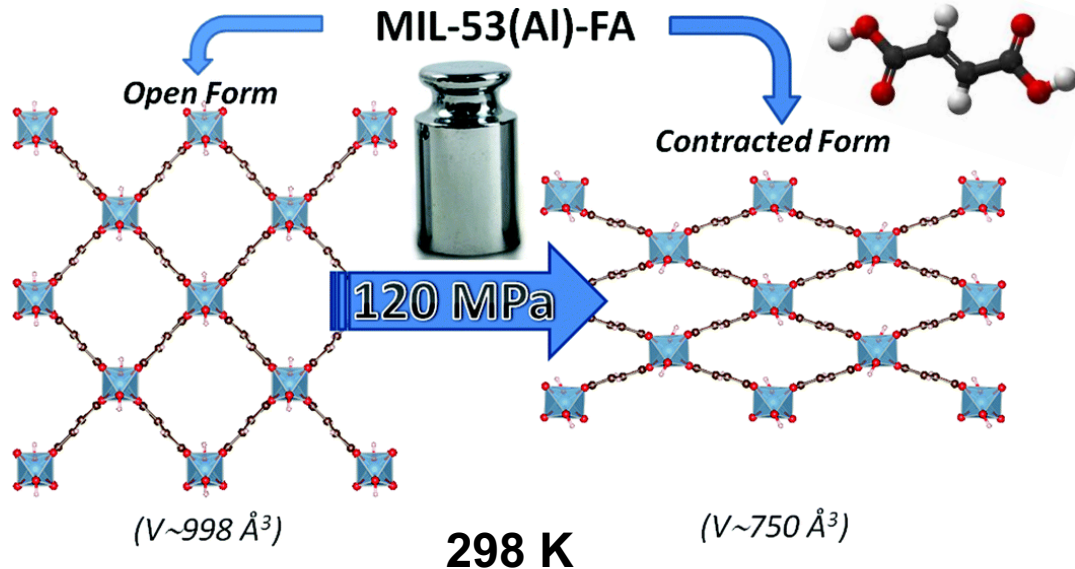


Simulations in Cd-MOF



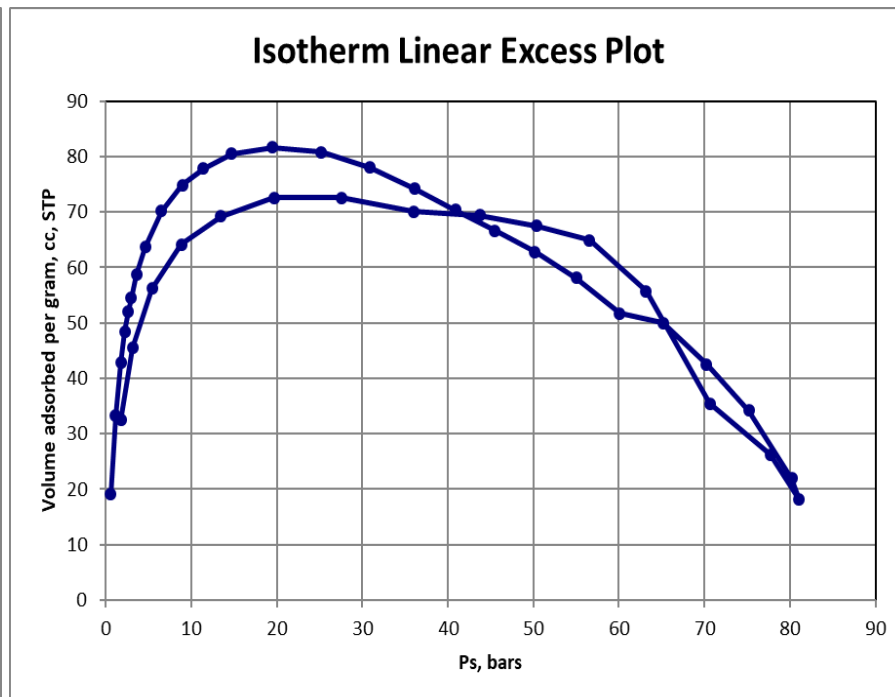
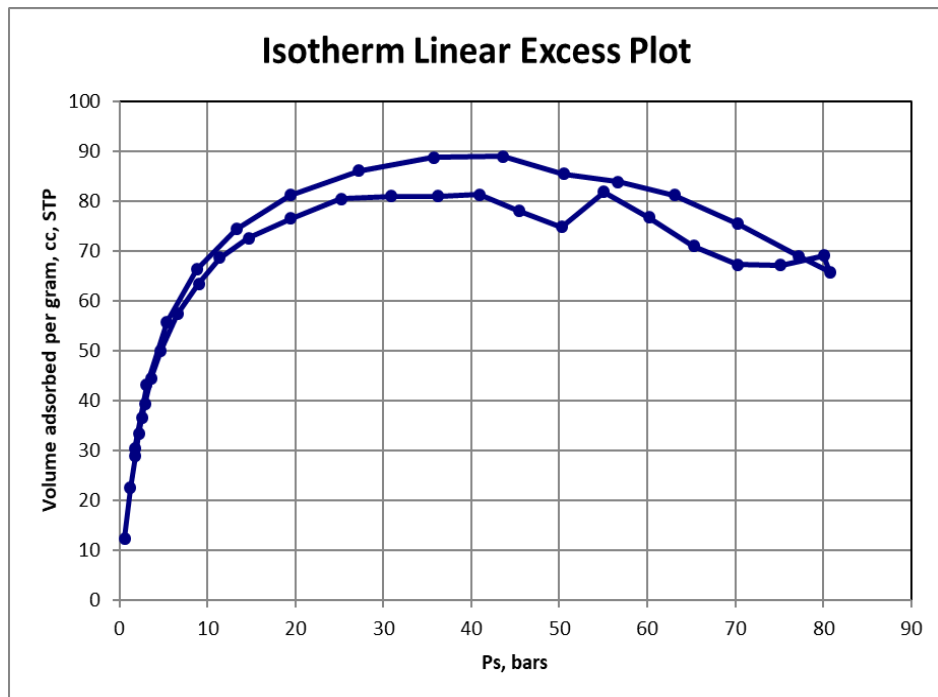
- Simulations of CH₄ adsorption at 273 and 233 K reproduced the first step of the corresponding experimental desorption isotherms.
- Simulations revealed that the CH₄ molecules prefer to localize near the imidazolate rings.

MIL-53-FA (Al)



Yot, P. G.; Vanduyfhuys, L.; Alvare, E.; Rodriguez, J.; Itié, J.-P.; Fabry, P.; Guillou, G.; Devic, T.; Beurroies, I.; Llewellyn, P. L.; Van Speybroeck, V.; Serre, C.; Maurin, G. Mechanical energy storage performance of an aluminum fumarate metal-organic framework. *Chem. Sci.* **2016**, *7*, 446–450.

- Experimental CH_4 adsorption studies have been performed in MIL-53-FA (Al).
- The shape of isotherms reveal that the MOF does not exhibit flexibility.





Collaborations: Working with HyMARC

- **HyMARC**
 - High pressure adsorption studies
 - Virtuous Evaluation and Feedback Loop for Superior Materials

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



Challenges and Barriers

- The high-pressure adsorption instrument needs to be well-calibrated in order to collect reliable high-pressure CH₄ adsorption isotherms at pressures above 60 bar.
- Computational time and resources on supercomputers are limited due to the COVID-19 pandemic.

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* * * * * ATTENTION * * * * *  
Due to Bridges contributing to our understanding of the COVID-19 pandemic, we  
are requesting that all Bridges RM users submit jobs with a maximum time limit  
of 12 hours.  
Longer jobs are unlikely to run. Thank you for your understanding.  
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Proposed Future Work

■ Remainder of FY2020

- Milestone 1.1.2: Synthesize a series of flexible MOFs with varying pore sizes and degree of interpenetration.
- Milestone 1.2.1: Carry out high-pressure CH₄ storage measurements and calculate CH₄ binding energies with H₂ modeling in parallel.
- Milestone 3.1.1: Advanced empirical modeling to facilitate discovery.

■ FY2021

- Milestone 1.2.2: Identify at least four FlexMOFs with tunable gating pressures and high working capacity.
- Milestone 3.1.2: Modeling of CH₄ or H₂–MOF interactions as a feedback cycle for subsequent modifications.
- Milestone 1.1.3: Synthesize new FlexMOF with high CH₄ working capacities in the 5–65 bar regime with evaluation for H₂.
- Milestone 2.1: Identify CH₄ or H₂ binding sites and map the gas within the MOF by single crystal X-ray diffraction and neutron diffraction measurements.

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



Summary

- **Objective:** Demonstrate a FlexMOF with total CH₄ deliverable capacity of ≥ 300 v/v (5–65 bar, room temperature) with evaluation for H₂ storage.
 - **Relevance:** The dynamic nature of FlexMOFs allows them to display thermodynamic and kinetically favorable properties for CH₄ adsorption. They have the potential to reach both the gravimetric and volumetric uptake targets for on-board CH₄ storage.
 - **Approach:**
 - Design and synthesis of a series of new FlexMOFs and screening of existing FlexMOFs.
 - Evaluate CH₄ adsorption performance at high pressures.
 - Modeling of MOF–CH₄ interactions as a feedback cycle for subsequent modifications
 - **Accomplishments:**
 - Milestone 1.1.1: Design and synthesize series of ligands with carboxylate and pyridyl/imidazolate moieties. (Completed)
 - Milestone 1.1.2: Synthesize a series of flexible MOFs with varying pore sizes and degree of interpenetration. (Partial)
 - Milestone 3.1.1: Advanced empirical modeling to facilitate discovery. (Partial)
 - **Collaborations:** HyMarc for high pressure adsorption studies and characterization.
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Publications and Presentations

- **Publications:**

- Verma, G.; Kumar, S.; Vardhan, V.; Ren, J.; Niu, Z.; Pham, T.; Wojtas, L.; Butikofer, S.; Garcia, J. C. E.; Chen, Y.-S.; Space, B.; Ma, S. A robust **soc**-MOF platform exhibiting high gravimetric uptake and volumetric deliverable capacity for on-board methane storage. *Nano Res.* **2020**, DOI: 10.1007/s12274-020-2794-9.
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Acknowledgments

Thank you all for your attention and this opportunity!

We would like to thank the Central X-ray facility at USF for help provided with structural characterization of the MOFs using Single Crystal and Powder X-ray Diffractometers.

We would also like to thank Jason Exley (Sales Engineer) from Micromeritics Inc. for help with calibration and troubleshooting of the High-Pressure Adsorption HPVA-100 instrument.

We also extend our gratitude for the computational resources made available by an XSEDE Grant (TG-DMR090028) as well as those provided by Research Computing at USF.

