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# Metallation of Metal–Organic Frameworks: En Route to Ambient Temperature Storage of Molecular H<sub>2</sub>

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Mentors: Professor Joseph T. Hupp & Omar K. Farha

Northwestern University

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Project ID #  
**ST108**

# Overview

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## Timeline

- Project start date: Nov. 2011
- Project end date: Nov. 2013
- Percent completed: 75%

## Budget

- Total project funding
  - DOE share: \$150K
- Funding received in FY12: \$75K
- Funding for FY13: \$75K

## Barriers

- Barriers addressed:
  - Develop functionalized sorbents for metallation
  - Deposit metal ions by solution & atomic layer deposition
  - Materials characterization and performance
- **Target:**  $Q_{st} \sim 15-25$  kJ/mol

## Partners

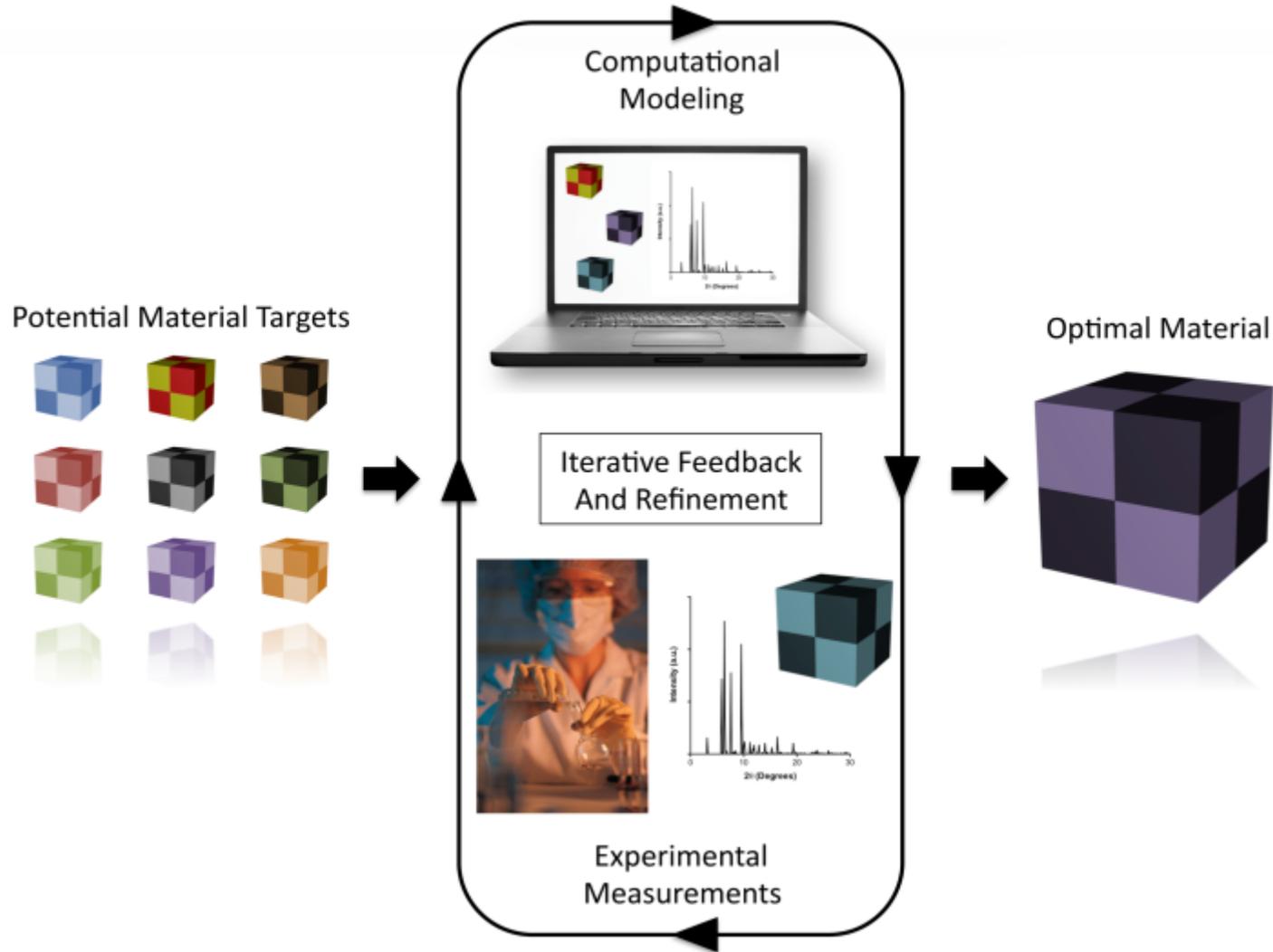
- Professors Joseph T. Hupp & Omar K. Farha – Mentors
- Northwestern University – Host Site

# Relevance

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- Address barriers to move towards the *ambient temperature storage of molecular H<sub>2</sub>*
  - Couple to DOE's 2017 gravimetric and volumetric targets
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- Barriers addressed:
    - Develop functionalized sorbents for metallation
    - Deposit metal ions by solution and atomic layer deposition
    - Materials characterization and performance (Target:  $Q_{st} \sim 15-25$  kJ/mol)

# Approach: Iterative Experimental/Computational Materials Development



# Approach: Ultra-High Surface Area MOFs

Storage Targets	Total Gravimetric (kg H <sub>2</sub> /kg System)	Excess Gravimetric (kg H <sub>2</sub> /kg System)	Total Volumetric (kg H <sub>2</sub> /L System)	Excess Volumetric (kg H <sub>2</sub> /L System)	Pressure (Bar)
2010	-	0.045	-	0.028	-
2017	-	0.055	-	0.040	-
Ultimate	-	0.075	-	0.070	-
<b>NU Materials</b>					
NU-100	0.164	<b>0.0995</b>	0.048	0.029	70
NU-111	0.12	0.075	0.052	0.032	65
NU-125	0.075	0.058	0.046	<b>0.035</b>	65
NU-109*	<b>0.219</b>	0.089	0.044	0.018	100

- A handful of promising sorbents are available in the NU lab for storage at *cryogenic temperatures (materials only basis)*. \* Computationally predicted.

Farha, O.K. et al. *Nat. Chem.* **2010**, 2, 944.

Farha, O.K. et al. *J. Am. Chem. Soc.* **2012**, 134, 9860.

Peng, Y. et al. *Chem. Commun.* **2013**, 49, 2992.

Wilmer, C.E. *Energy Environ. Sci.* **2013**, DOI: 10.1039/c3ee24506c.

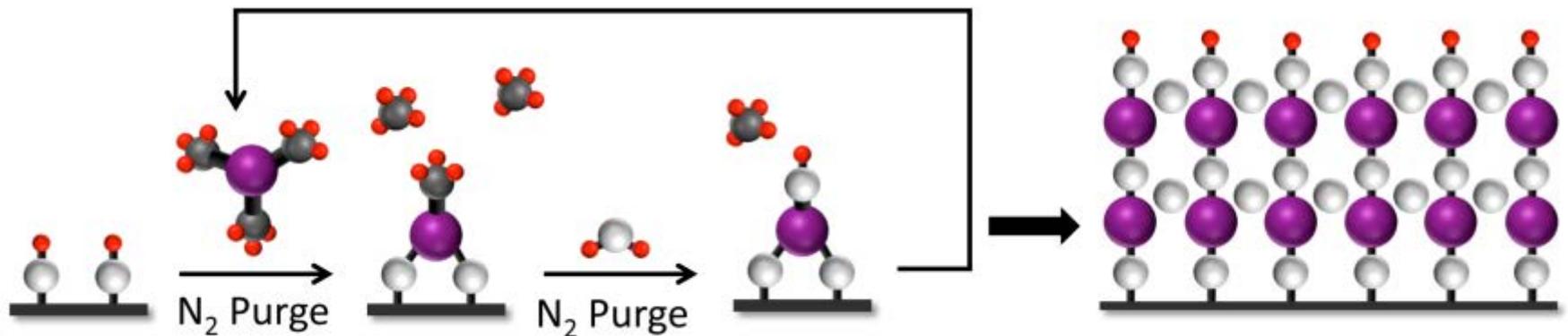
Fairen-Jimenez, D. *Chem. Commun.* **2012**, 48, 10496.

# Approach: Milestones

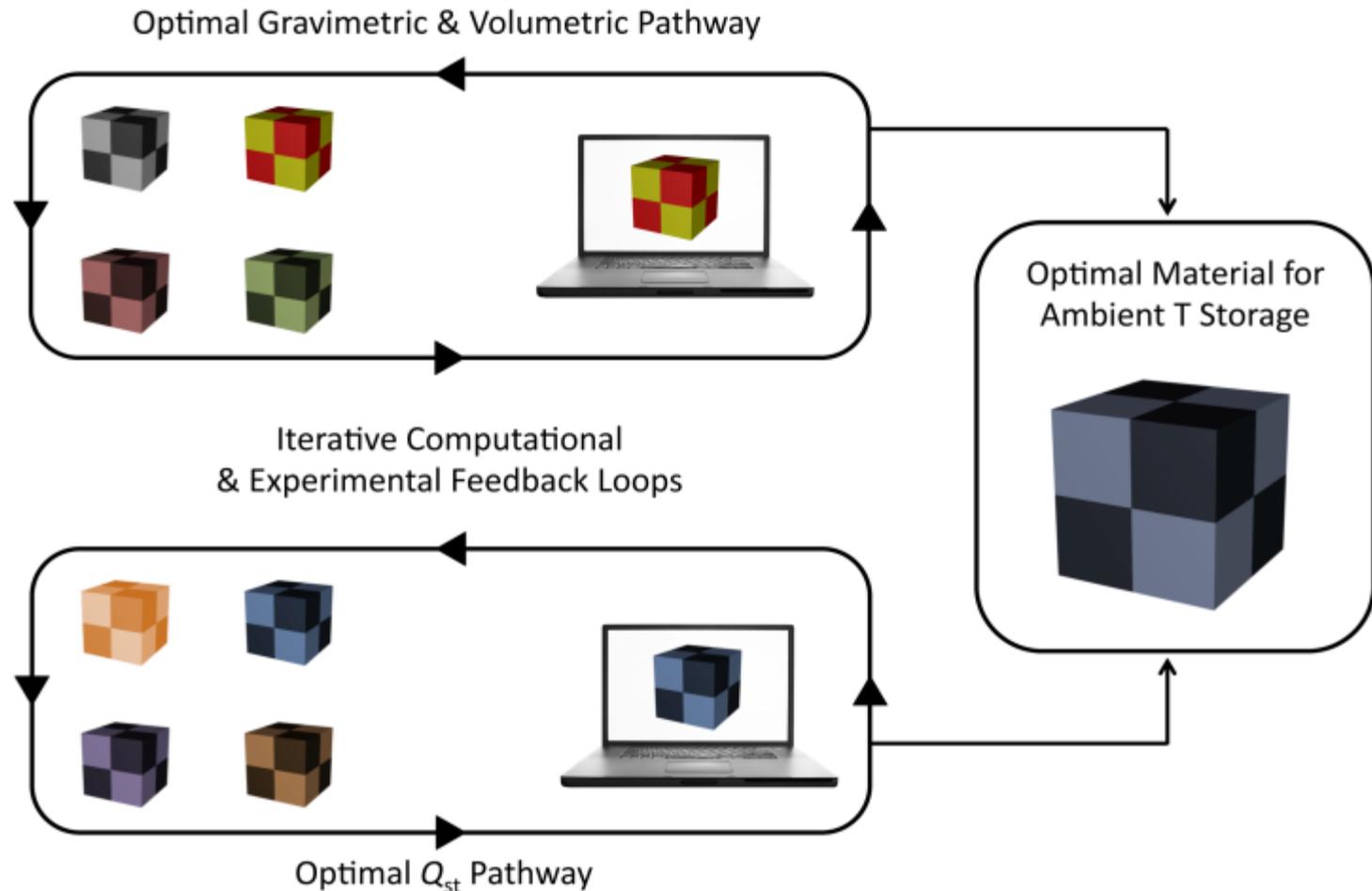
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- Deposit coordinatively unsaturated metal ions into MOFs by solution and ALD
  - Develop functionalized sorbents
  - Deposit metal ions
  - Materials characterization and performance

## Atomic Layer Deposition (ALD)

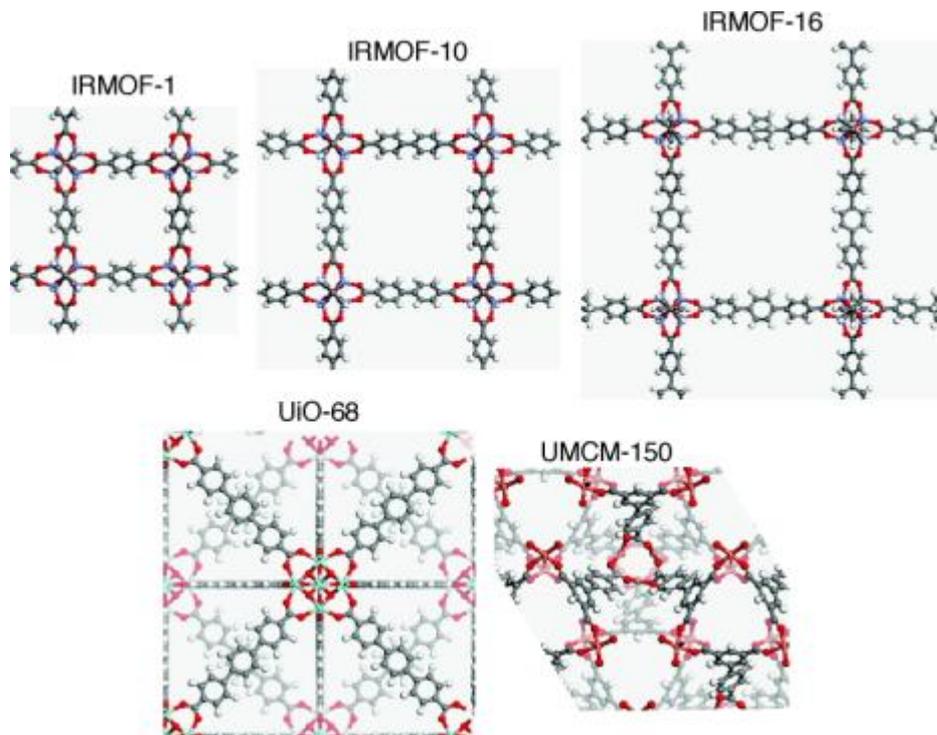


# Approach: Iterative Computational & Experimental Approach Towards High $Q_{st}$



# Approach: Functional Porous Materials for Incorporation of Divalent Metal Ions

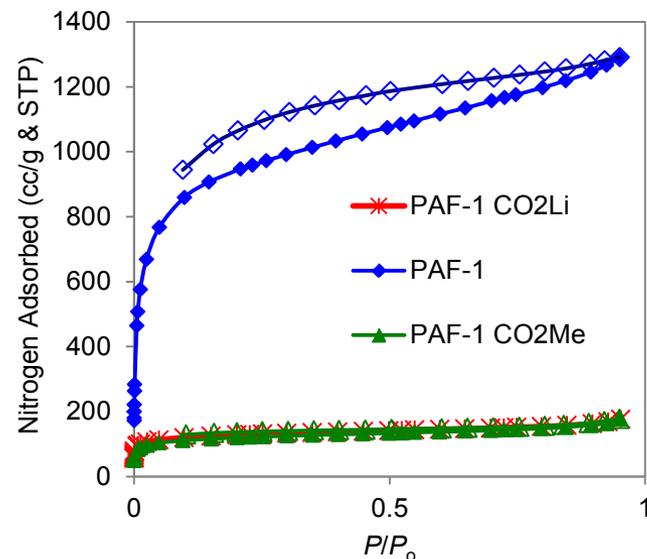
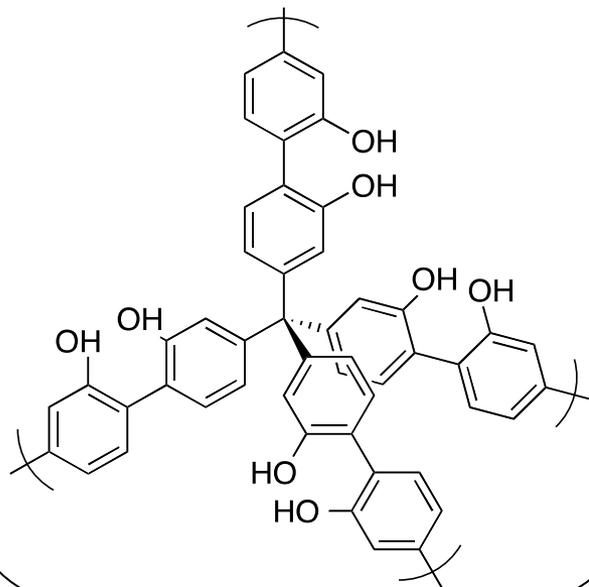
- Functionalized sorbents allow for an easy route to metallation, which have been *computationally* predicted to have high  $Q_{st}$  values



Metal	$Q_{st}$ (kJ/mol)
$\text{Li}^+$	-10
$\text{Mn}^{2+}$	-20
$\text{Mg}^{2+}$	-22
$\text{Ni}^{2+}$	-78
$\text{Cu}^{2+}$	-84

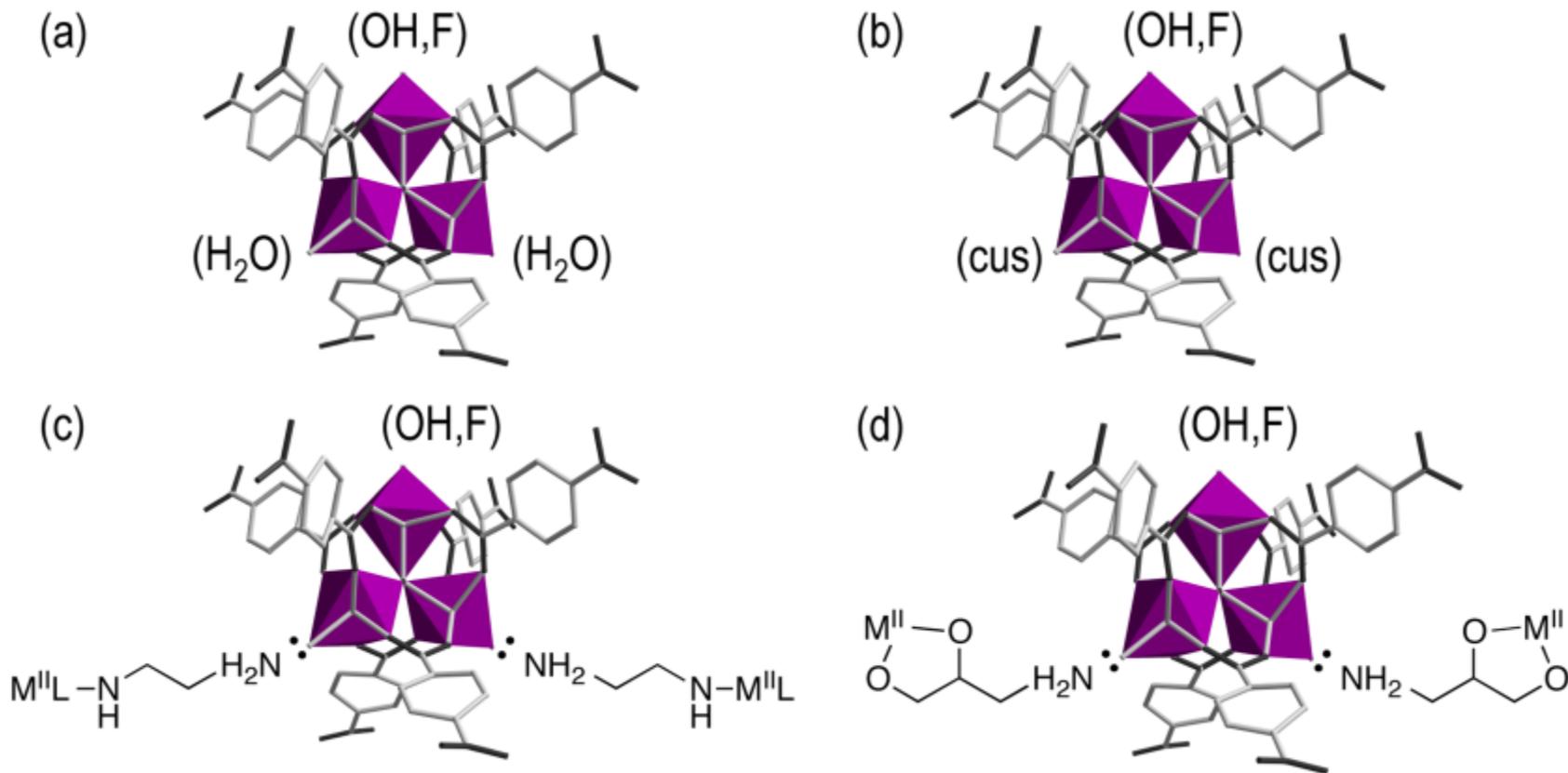
# Accomplishments and Progress: Attempts to Functionalize PAF-1

## Initial Materials Target

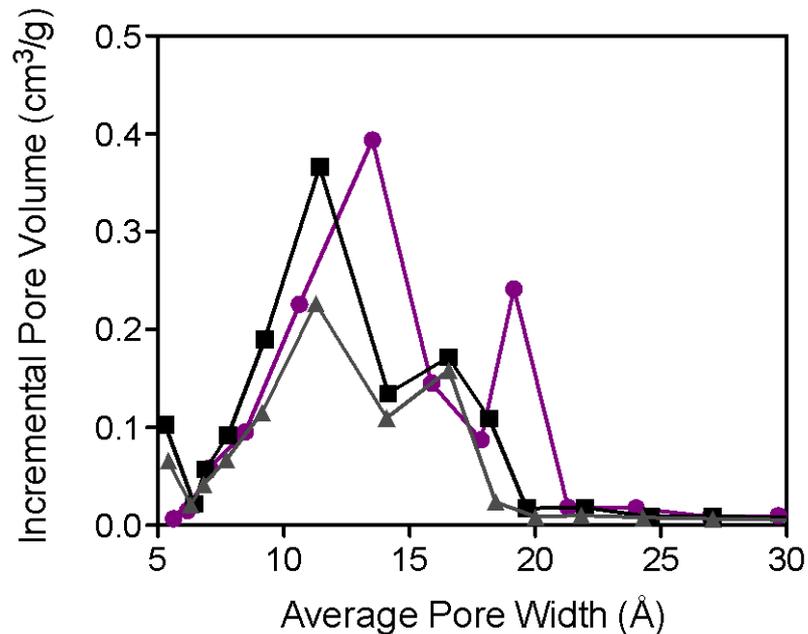
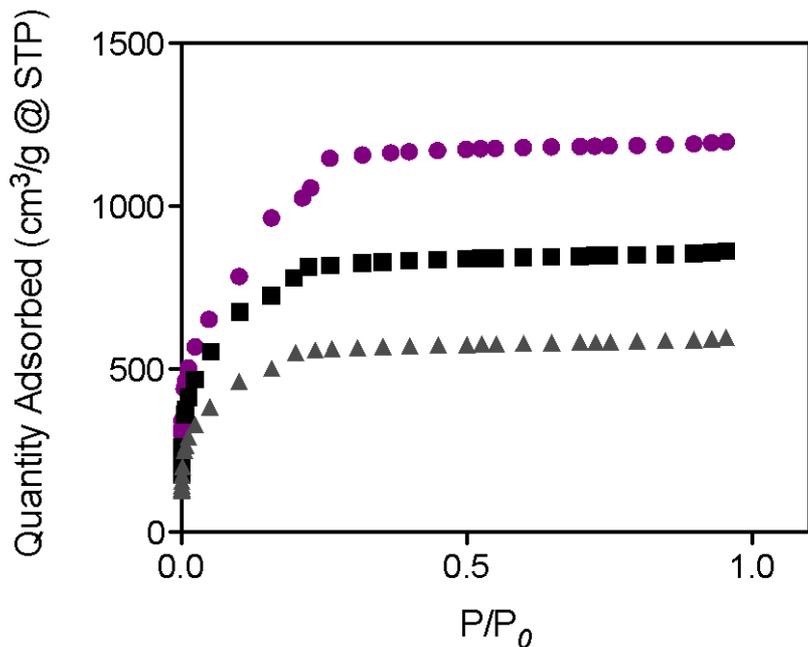


- All attempts to functionalize PAF-1 have led to drastic decreases in observed surface areas
- Metallation has proven to be difficult

# Accomplishments and Progress: $-NH_2$ and $-OH$ MIL-101 Functionalized MOF Platform



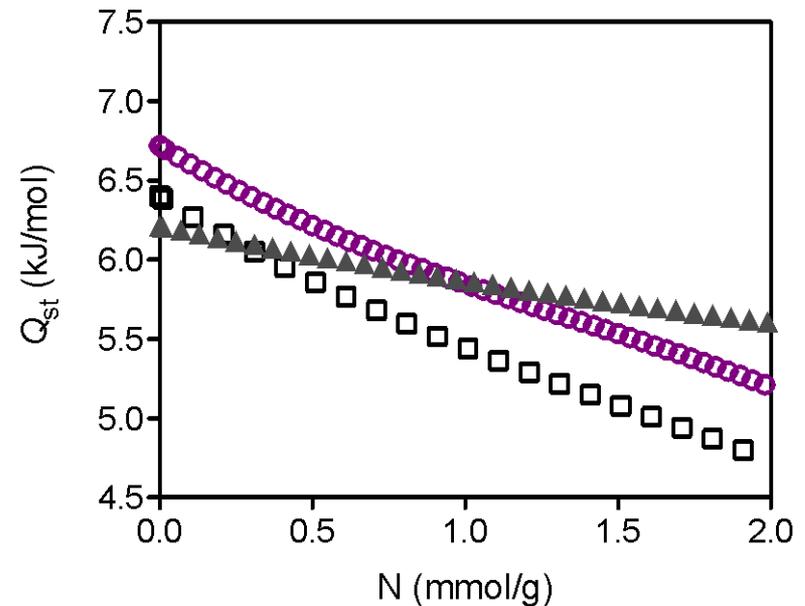
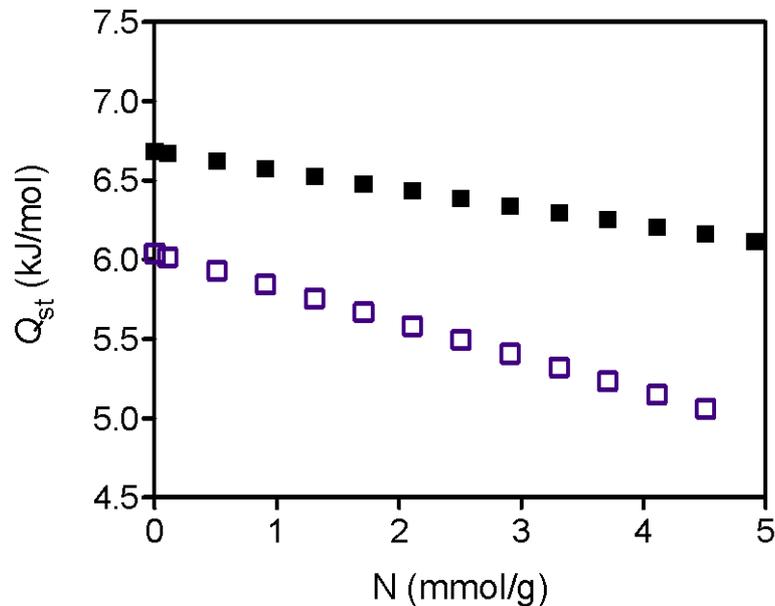
# Accomplishments and Progress: Characterization of Functionalized MIL-101 MOF Derivatives



- The -NH<sub>2</sub> and -OH functionalized MIL-101 derivatives remain porous, however crystallinity can be compromised

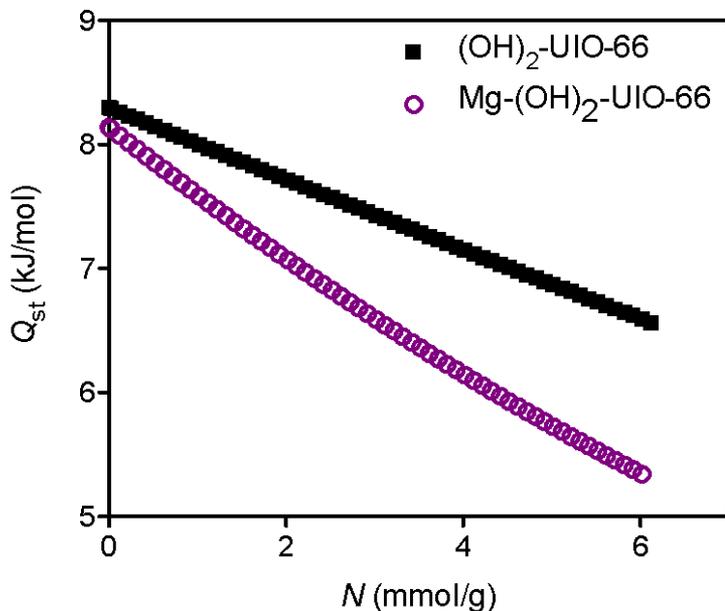
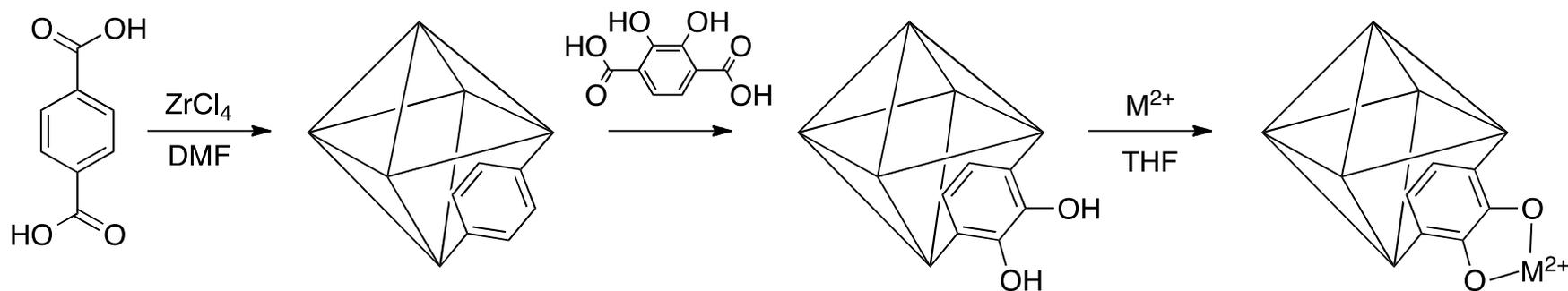
# Accomplishments and Progress: Materials Performance for Functionalized MIL-101 Derivatives

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- No significant increase in the  $Q_{st}$  values were observed for  $Zn^{2+}$  and  $Mg^{2+}$  metallated materials

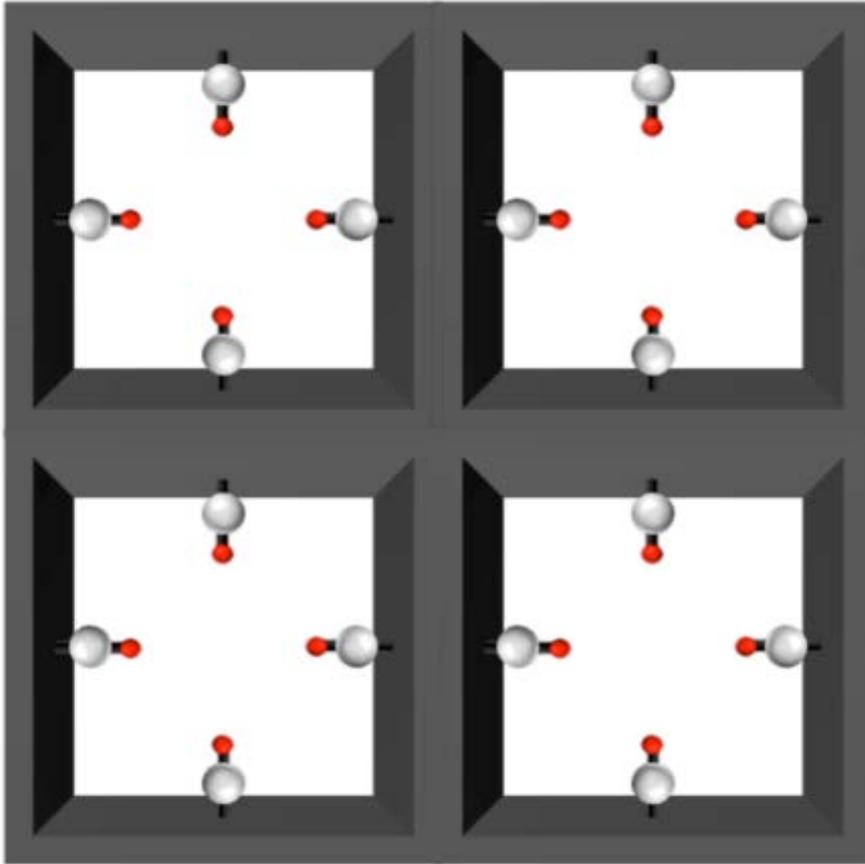
# Accomplishments and Progress: Catechol Functionalized MOF



- Metallation remains a challenge, presumably due to small aperture sizes

# Accomplishments and Progress: Functionalized MOF Platform

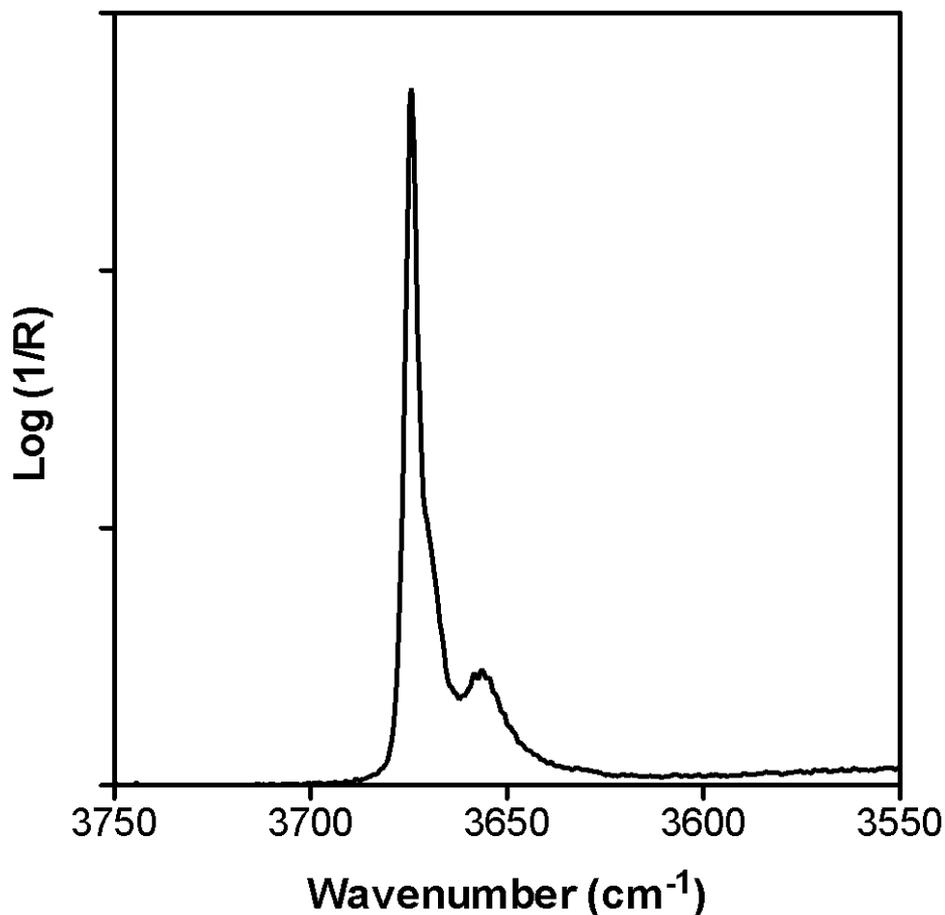
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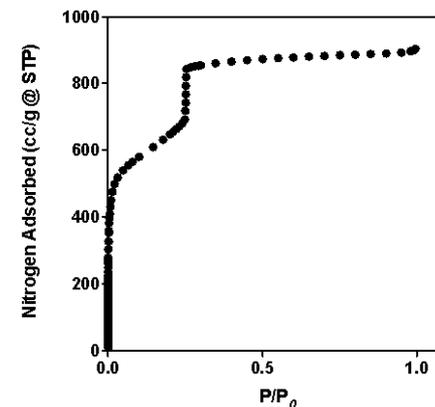
- Our MOF has several attractive features, including:
  - High thermal, hydrothermal and chemical stability
  - Large pores and apertures
  - Functionalized pores
  - Adequate surface area and pore volume

# Accomplishments and Progress: Characterization of Parent MOF

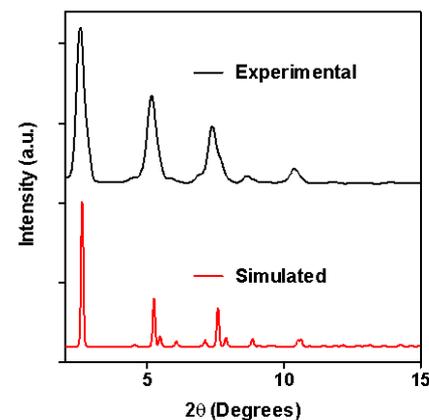
IR Spectroscopy: Functional groups for metallation



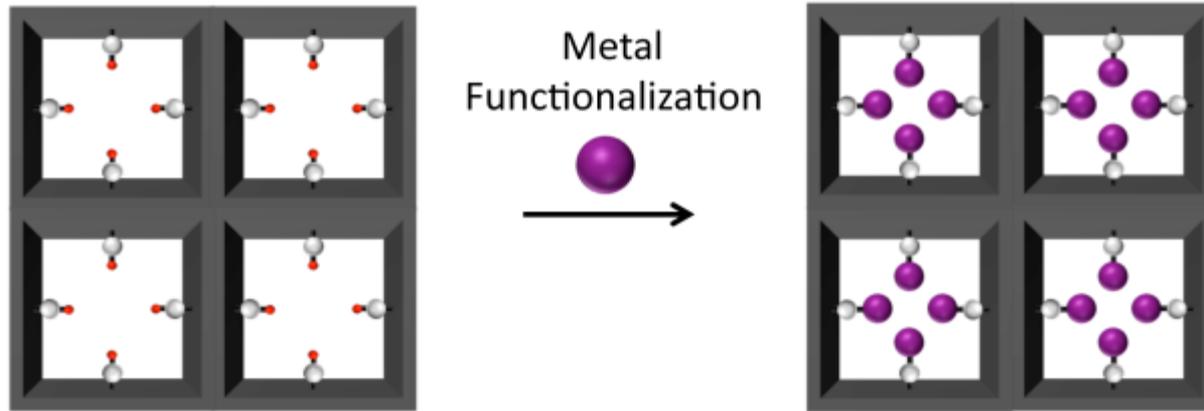
Porous



Crystalline

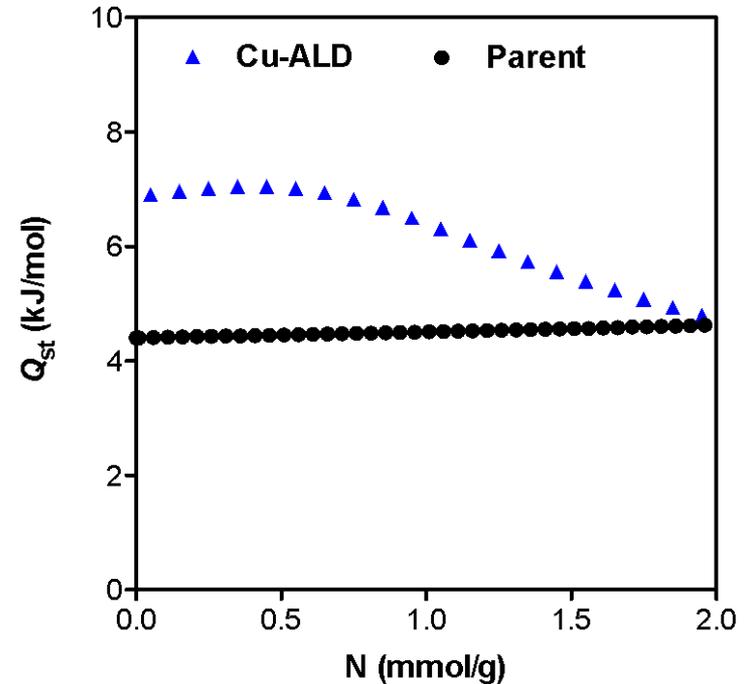
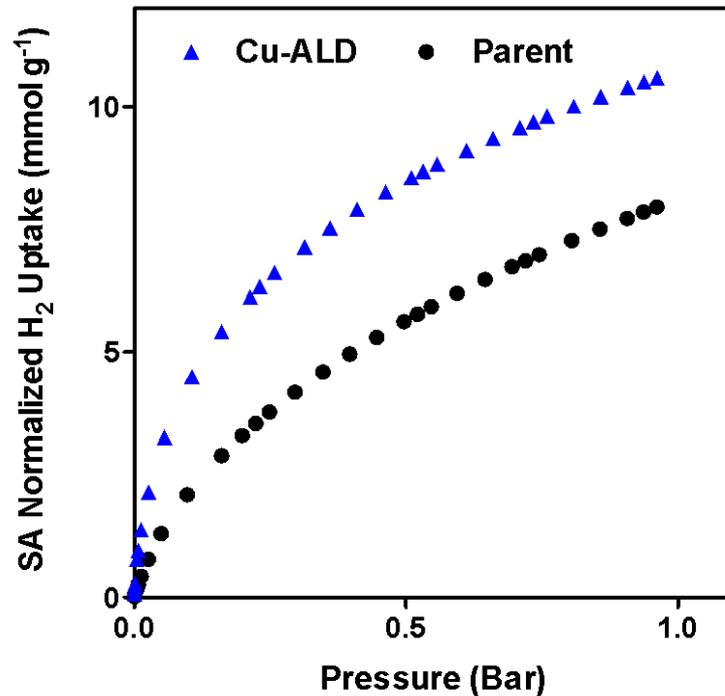


# Accomplishments and Progress: Deposit Metal Ions by Solution & ALD



MOF	Metal:Zr	Metal:Zr <sub>6</sub>	BET Surface Area (m <sup>2</sup> g <sup>-1</sup> )	Pore Volume (cm <sup>3</sup> g <sup>-1</sup> )
Parent MOF	-	-	2230	1.30
Zn-ALD	0.6(1)	4	1460	0.85
Al-ALD	1.3(2)	8	1620	0.91
Cu-ALD	1	6	-	-
Zn-Solution	0.6	4	1670	0.98
Al-Solution	1.6	10	1200	0.75

# Accomplishments and Progress: Materials Performance for Metallated Materials



- Q<sub>st</sub> ~60% improvement over parent—but still only ~ 7 kJ/mol

# Collaborations

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- Professor Randall Q. Snurr – Computational (Northwestern University)
- David Fairen-Jimenez – Computational (Northwestern University/Cambridge University)
- Philip A. Parilla – Experimental/Sorption (National Renewable Energy Laboratory/HS-CoE)
- Taner Yildirim – Experimental/Sorption (National Institute of Standards and Technology)
- Alex B. F. Martinson – Experimental/ALD (Argonne National Laboratory)
- Jeffrey T. Miller – Experimental/Physical Characterization (Argonne National Laboratory/Advanced Photon Source)
- Karen L. Mulfort – Experimental/Physical Characterization (Argonne National Laboratory/Advanced Photon Source)
- David M. Tiede – Experimental/Physical Characterization (Argonne National Laboratory/Advanced Photon Source)

# Proposed Future Work

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H																He		
Li	Be	Element included in at least one ALD material										B	C	N	O	F	Ne	
Na	Mg	Element not included in any ALD material										Al	Si	P	S	Cl	Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	Ac																
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

- Iterative materials feedback for ALD metallated MOFs
- Study H<sub>2</sub> adsorption dynamics *in situ* (Jeffrey T. Miller, ANL)

# Summary Slide

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- **Relevance:**

- Address barriers to move towards the *ambient temperature storage of molecular H<sub>2</sub>*

- **Approach:**

- Iterative computational and experimental approach to depositing coordinatively unsaturated metal ions on functionalized sorbents

- **Technical Accomplishments & Progress:**

- Functionalized sorbents have been synthesized and metallated
- 60% improvement in  $Q_{st}$  vs parent material

- **Collaborations:**

- Active computational and experimental collaborations

- **Proposed Future Research**

- Use computational guidance to further metallate our functional MOF (*in situ* studies of most promising system)

# Acknowledgement

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- Dr. Wojciech Bury
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