Metallation of Metal–Organic Frameworks: En Route to Ambient Temperature Storage of Molecular H_2

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

Northwestern University

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Project ID #
ST108

Overview

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} ~15−25 kJ/mol

Partners

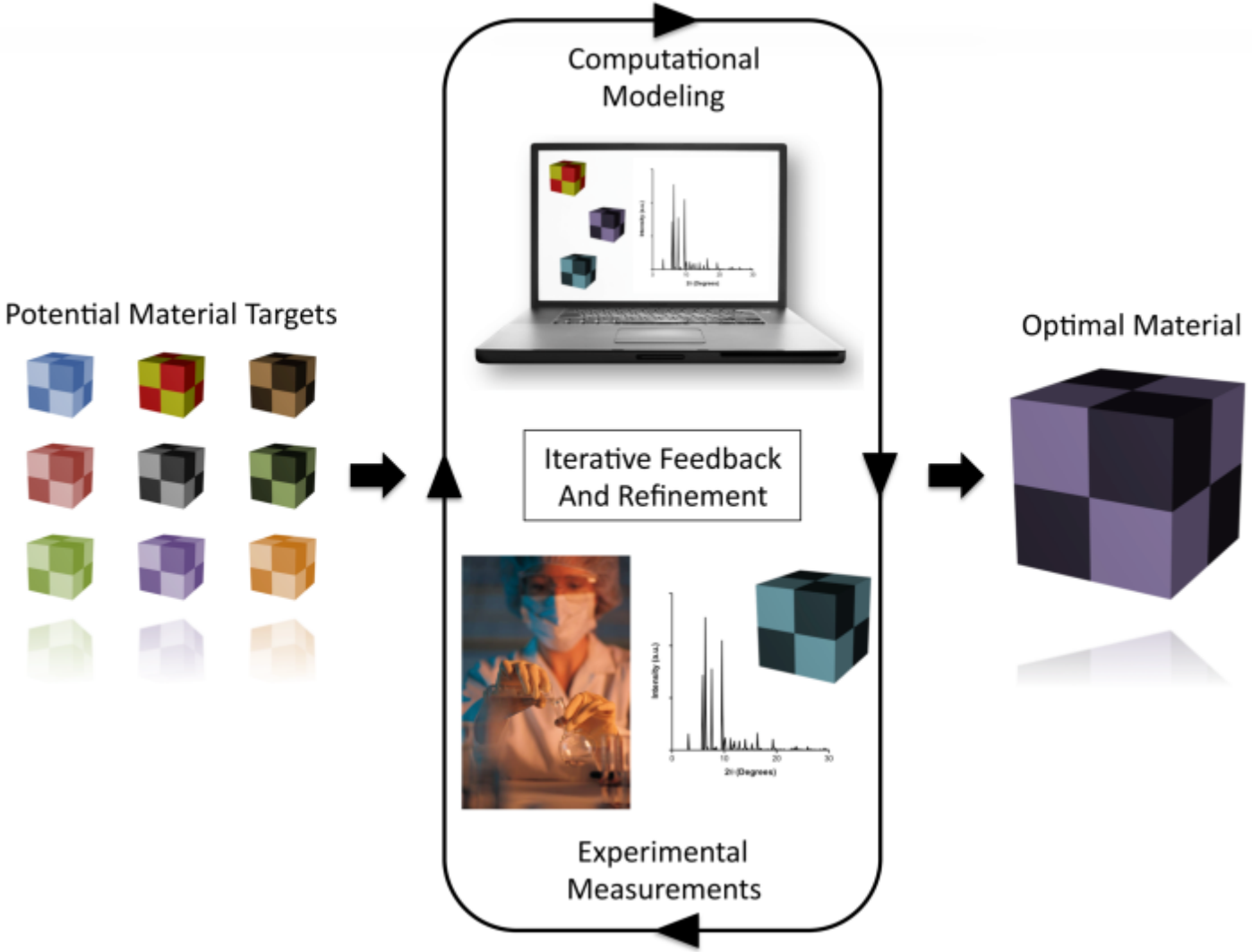
- Professors Joseph T. Hupp & Omar K. Farha – Mentors
- Northwestern University – Host Site

Relevance

- **Address barriers to move towards the *ambient temperature storage of molecular H_2***
- **Couple to DOE's 2017 gravimetric and volumetric targets**

- Barriers addressed:
  - Develop functionalized sorbents for metallation
  - Deposit metal ions by solution and atomic layer deposition
  - Materials characterization and performance (Target: Q_{st} ~15−25 kJ/mol)

Approach: Iterative Experimental/Computational Materials Development



Wilmer, C.E. et al. *Nature Chem.* **2012,** *4,* 83.

Approach:Ultra-High Surface Area MOFs

Storage Targets	Total Gravimetric (kg H_2/kg System)	Excess Gravimetric (kg H_2/kg System)	Total Volumetric (kg H_2/L System)	Excess Volumetric (kg H_2/L System)	Pressure (Bar)
2010	-	0.045	-	0.028	-
2017	-	0.055	-	0.040	-
Ultimate	-	0.075	-	0.070	-
NU Materials					
NU-100	0.164	**0.0995**	0.048	0.029	70
NU-111	0.12	0.075	0.052	0.032	65
NU-125	0.075	0.058	0.046	**0.035**	65
NU-109*	**0.219**	0.089	0.044	0.018	100

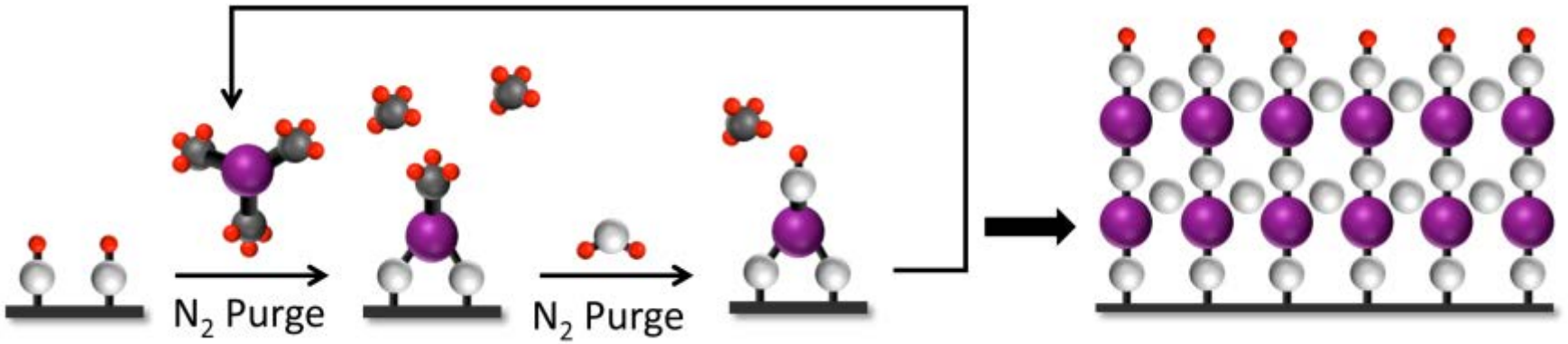
- A handful of promising sorbents are available in the NU lab for storage at *cryogenic temperatures (materials only basis).* * Computationally predicted.

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.

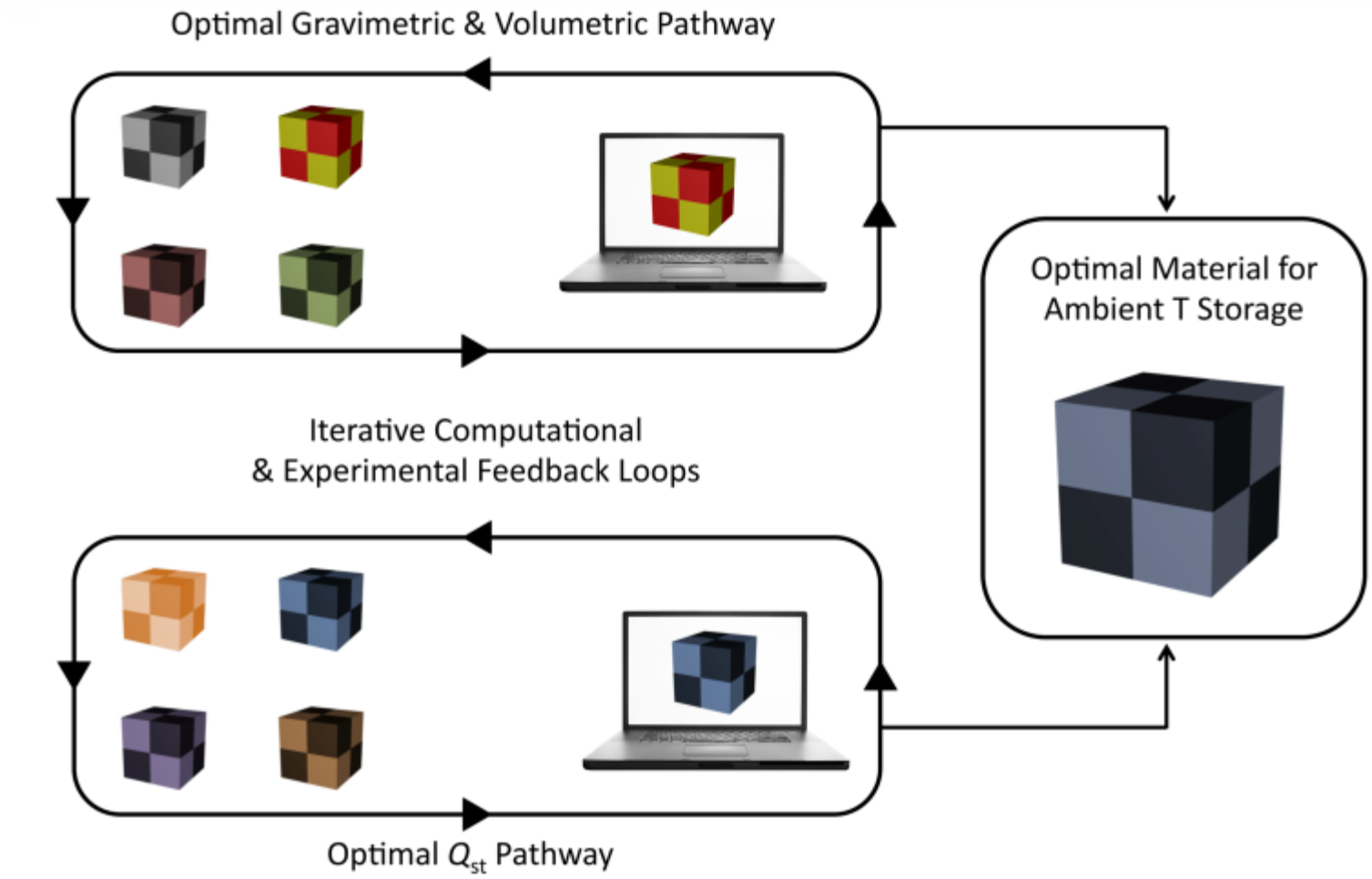
Approach: Milestones

- 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)



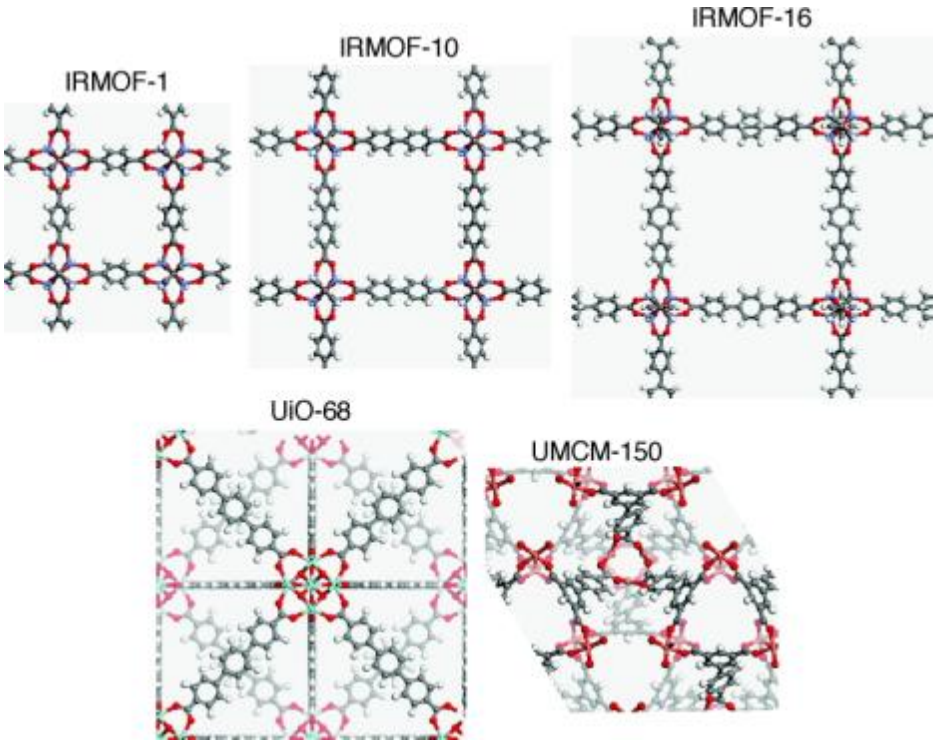
Approach: Iterative Computational & Experimental Approach Towards High Q_{st}



In collaboration with Prof. Randall Q. Snurr (Northwestern University).

Approach: Functional Porous Materials for Incorporation of Divalent Metal Ions

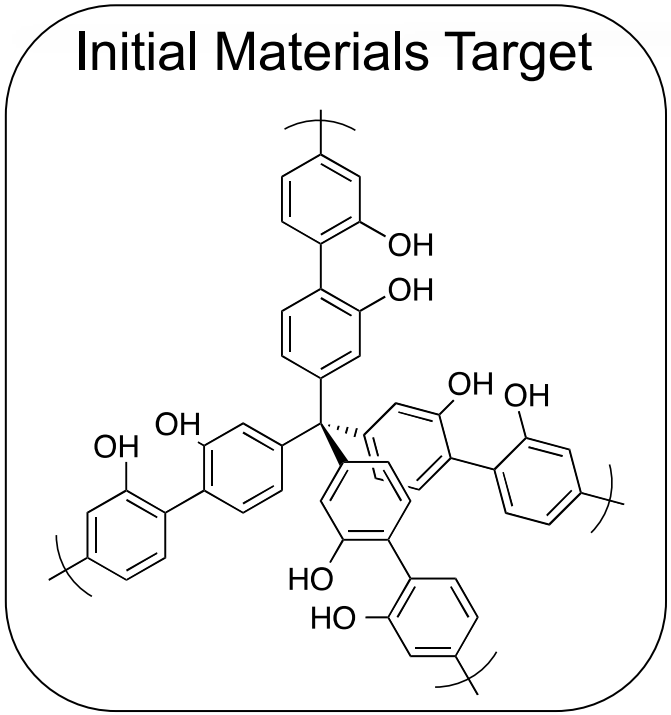
- Functionalized sorbents allow for an easy route to metallation, which have been *computationally* predicted to have high Q_{st} values

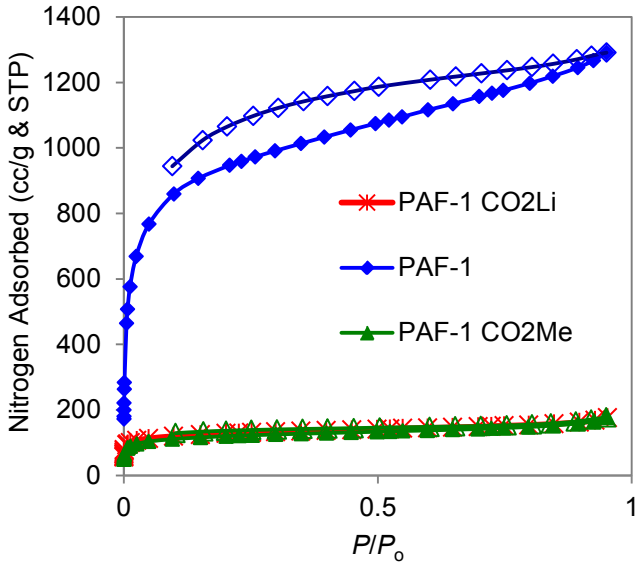


Metal	Q_{st} (kJ/mol)
Li^{+}	-10
Mn^{2+}	-20
Mg^{2+}	-22
Ni^{2+}	-78
Cu^{2+}	-84

Getman, R.B.; Miller, J.H.; Wang, K.; Snurr, R.Q. *J. Phys. Chem. C* **2011,** *115,* 2066.

Accomplishments and Progress: Attempts to Functionalize PAF-1

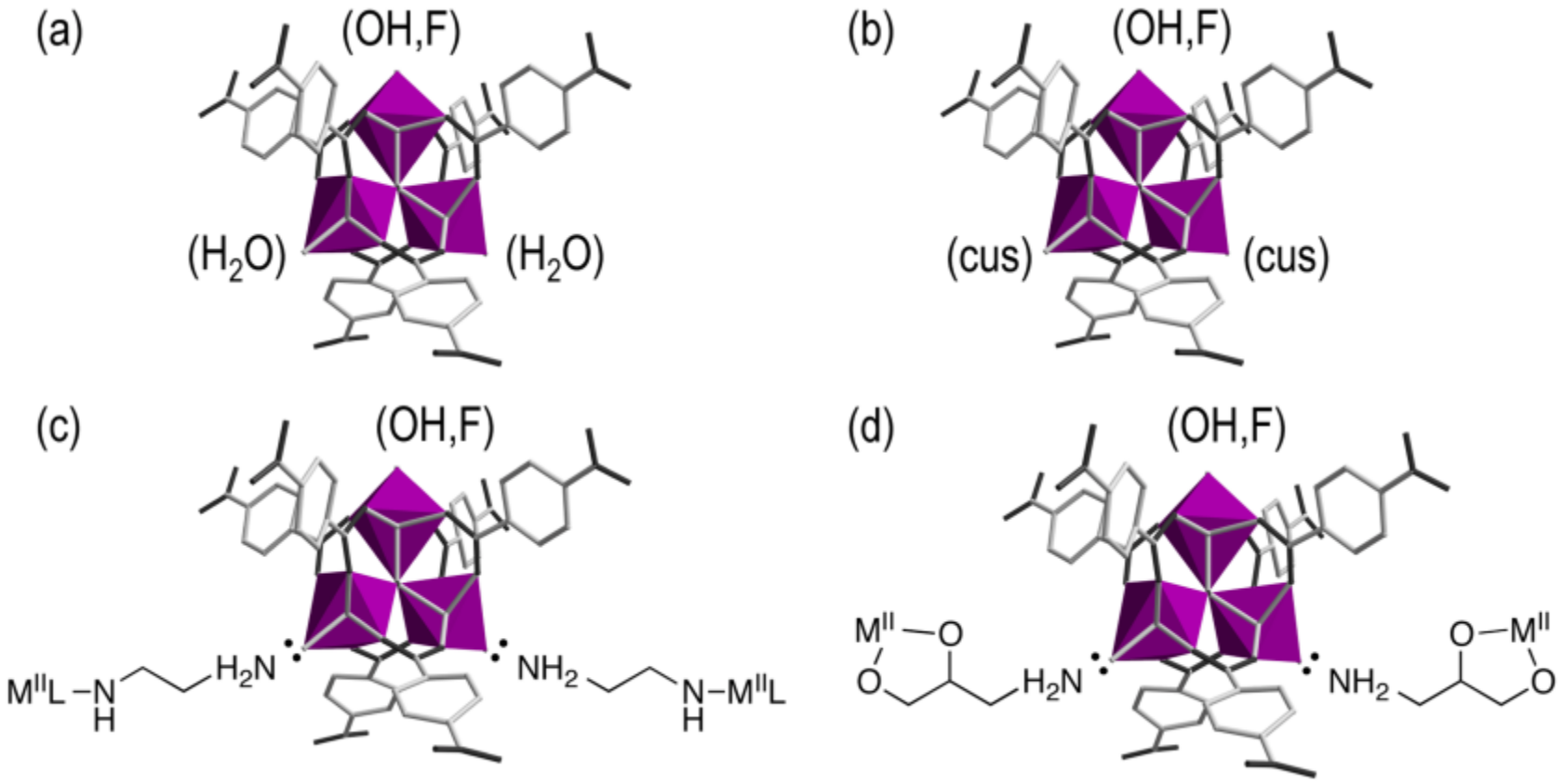




- All attempts to functionalize PAF-1 have led to drastic decreases in observed surface areas
- Metallation has proven to be difficult

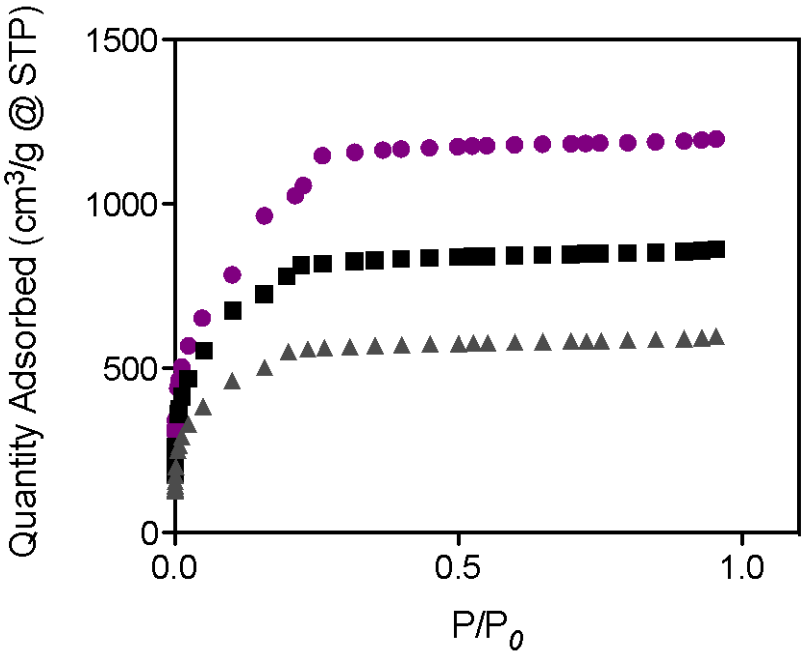
Ben, T.; Ren, H.; Ma, S.; Cao, D.; Lan, J.; Jing, X.; Wang, W.; Xu, J.; Deng, F.; Simmons, J.M.; Qiu, S.; Zhu, G. *Angew. Chem. Int. Ed.* **2009,** *48,* 9457.

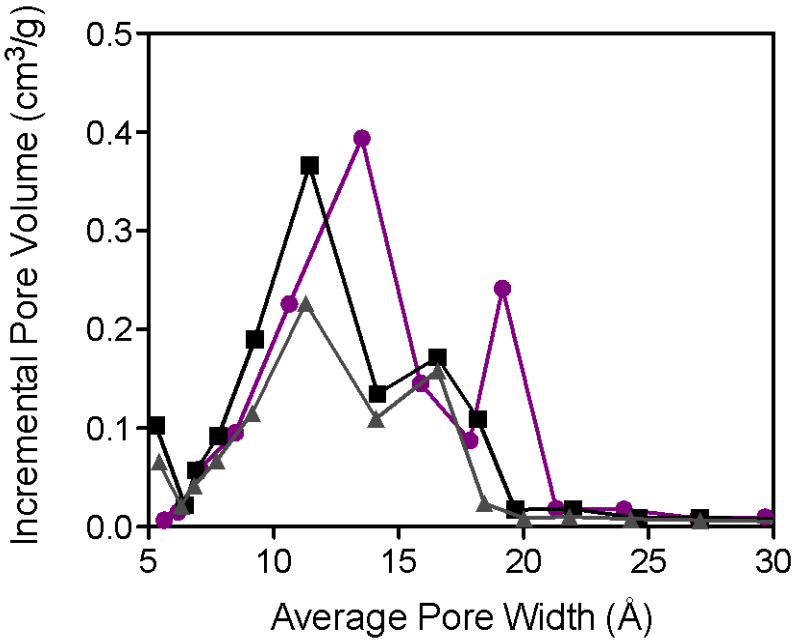
Accomplishments and Progress: $-NH_2$ and $-OH$ MIL-101 Functionalized MOF Platform



Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surblé, S.; Margiolaki, I. *Science*, **2005,** *309,* 2040.

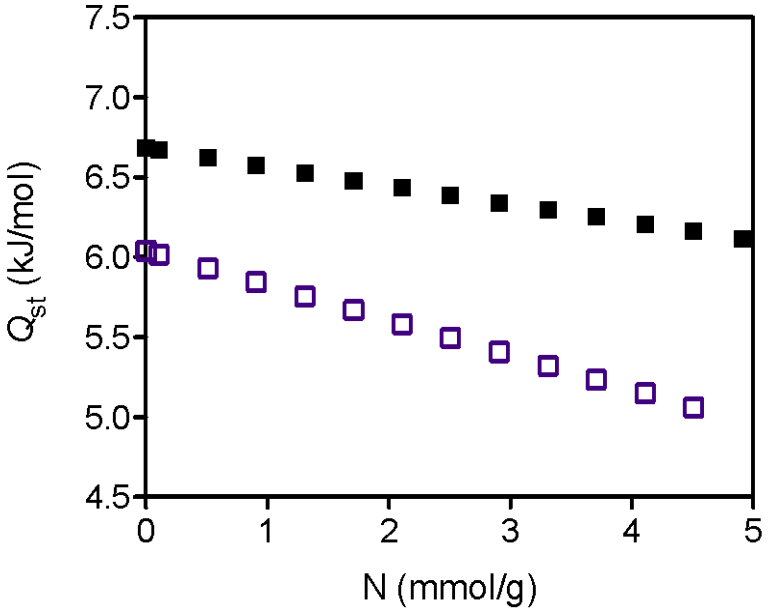
Accomplishments and Progress: Characterization of Functionalized MIL-101 MOF Derivatives

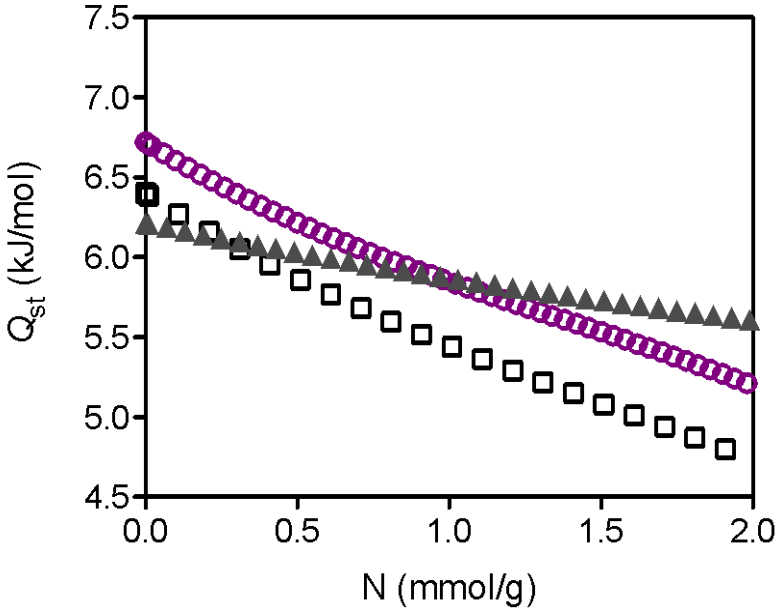




- The $-NH_2$ and $-OH$ functionalized MIL-101 derivatives remain porous, however crystallinity can be compromised

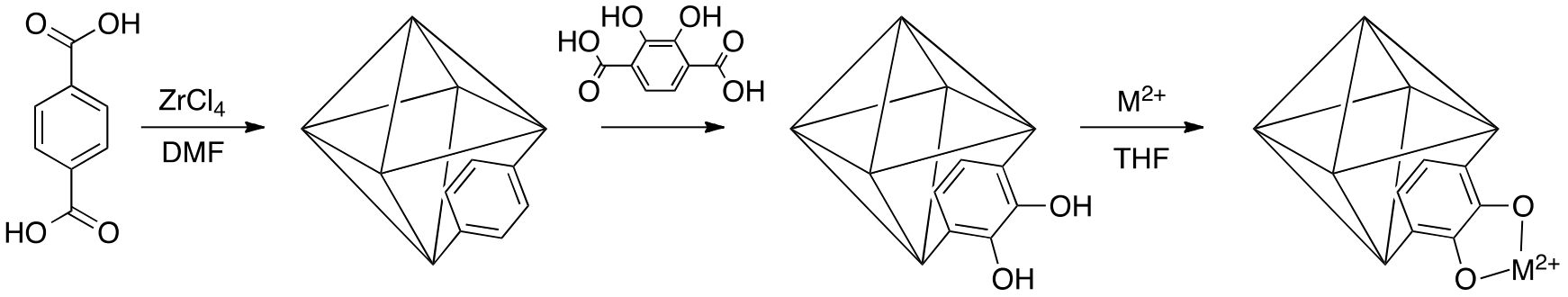
Accomplishments and Progress: Materials Performance for Functionalized MIL-101 Derivatives

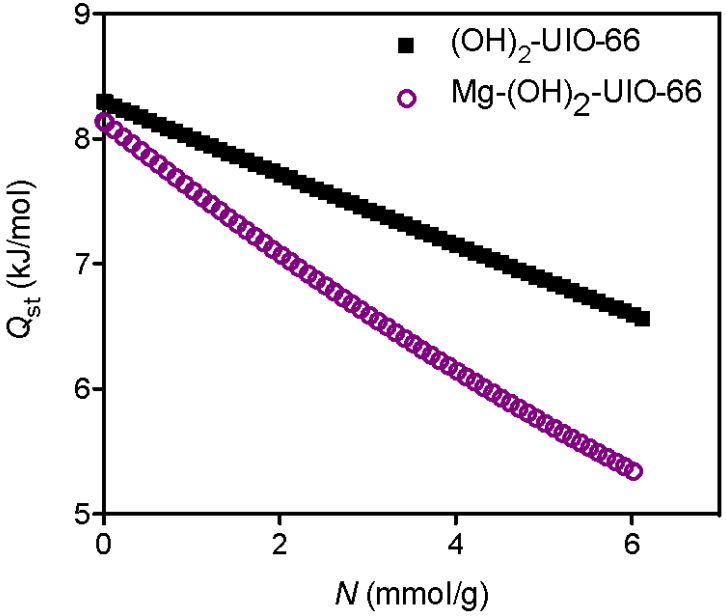




- No significant increase in the Q_{st} values were observed for Zn^{2+} and Mg^{2+} metallated materials

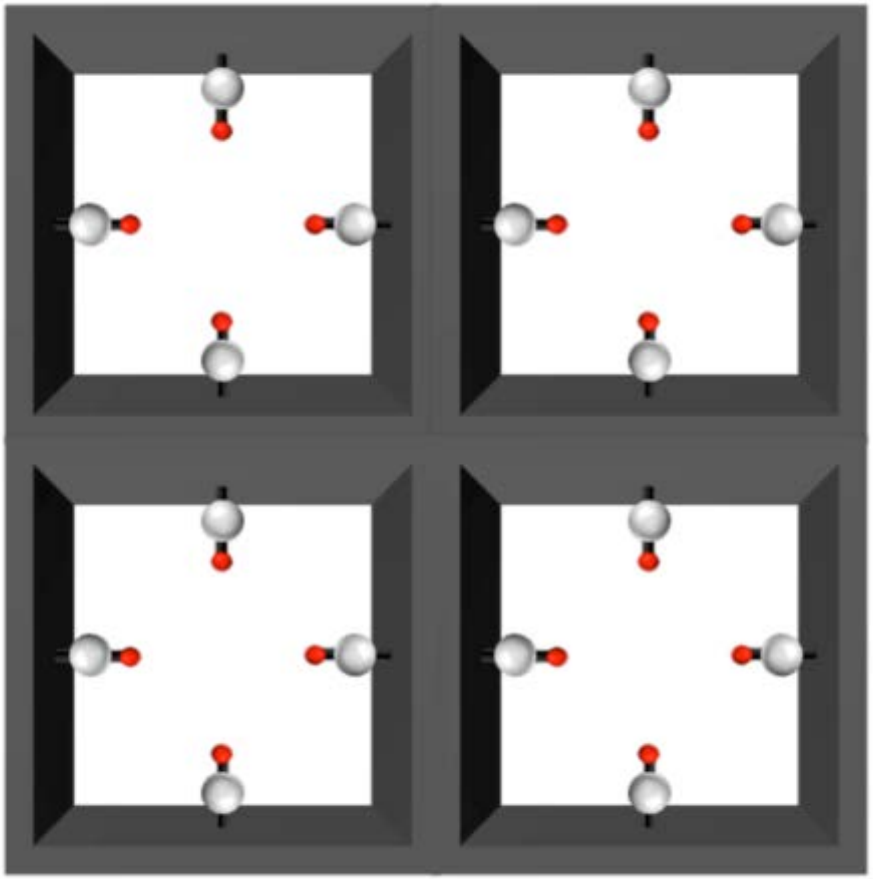
Accomplishments and Progress: Catechol Functionalized MOF





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

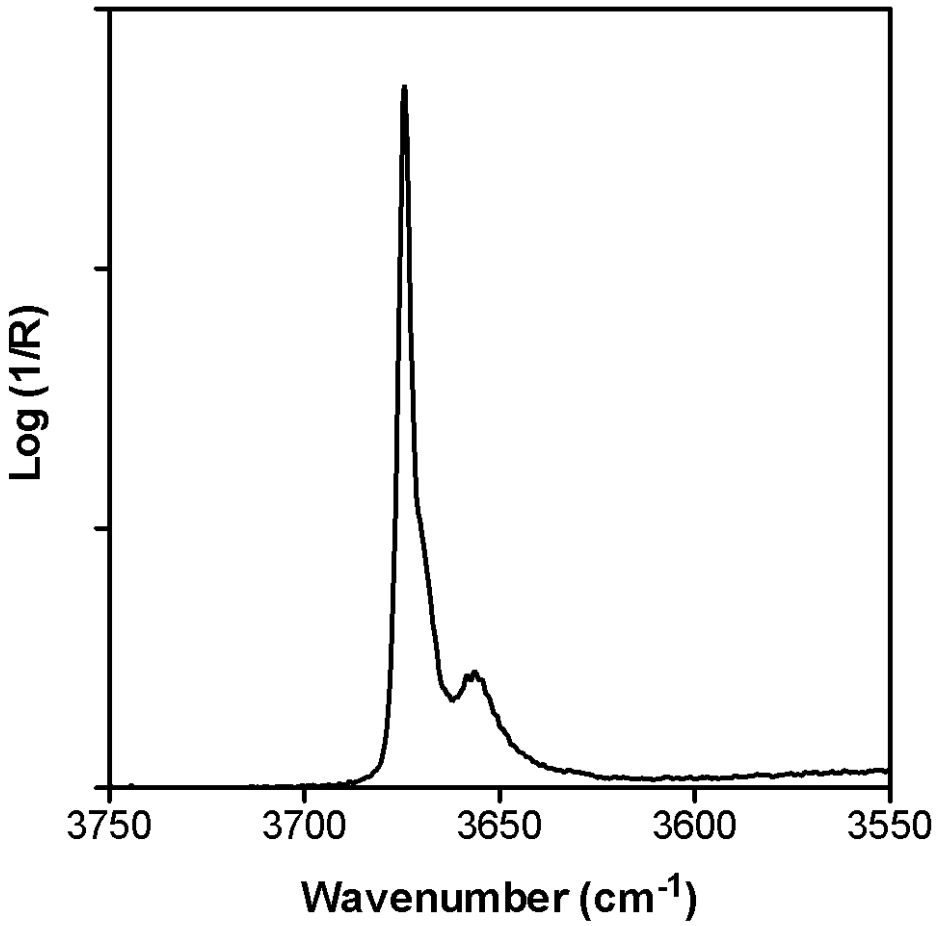
Accomplishments and Progress: Functionalized MOF Platform



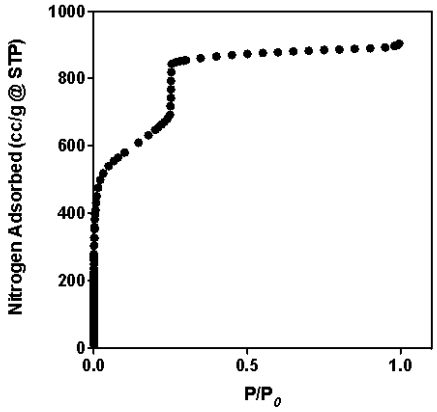
- Our MOF has several attractive features, including:
  - High thermal, hydrothermal and chemical stability
  - Large pores and apertures
  - Functionalized pores
  - Adequate surface area and pore volume

Accomplishments and Progress: Characterization of Parent MOF

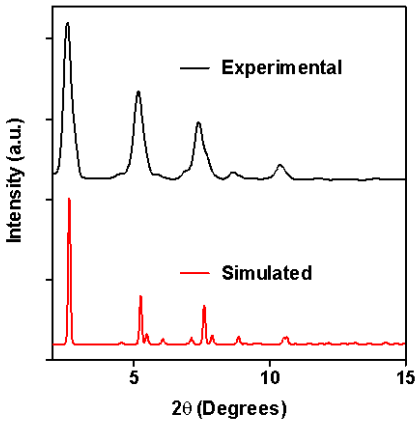
IR Spectroscopy: Functional groups for metallation



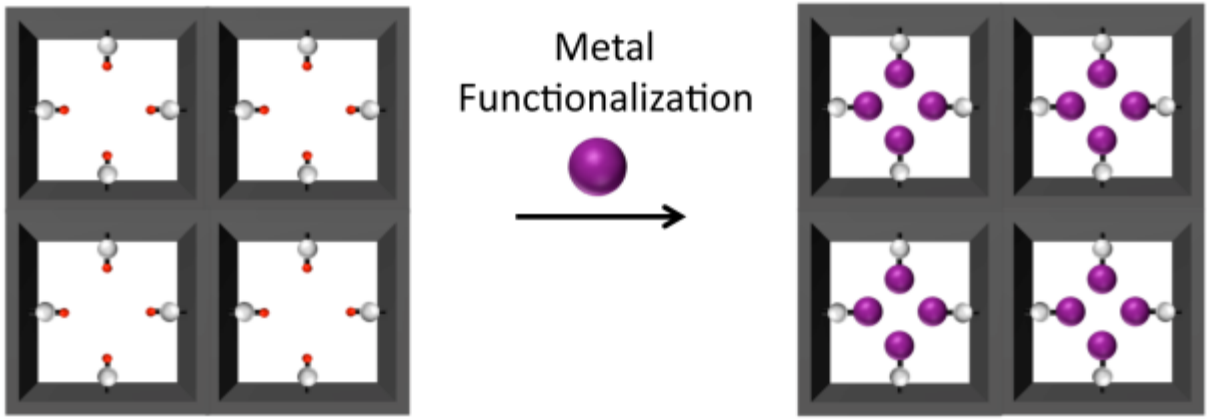
Porous



Crystalline

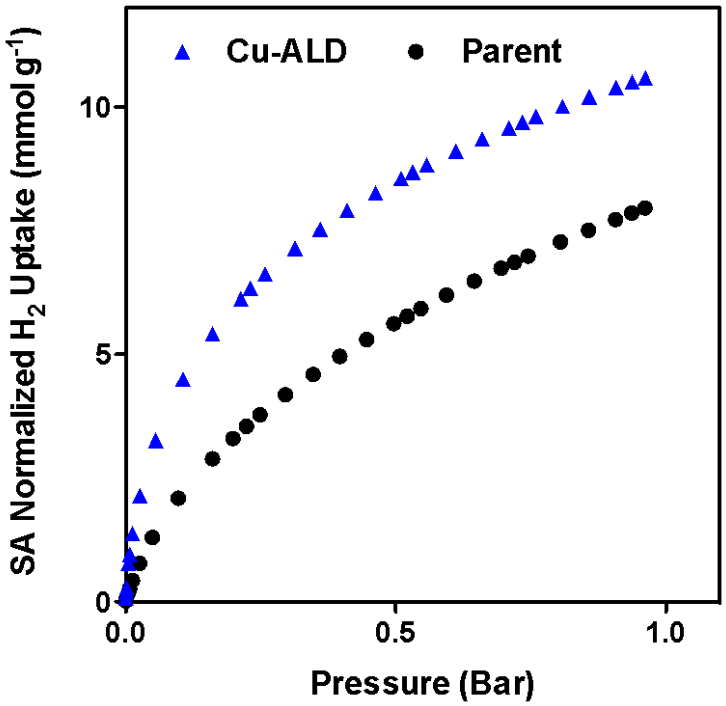


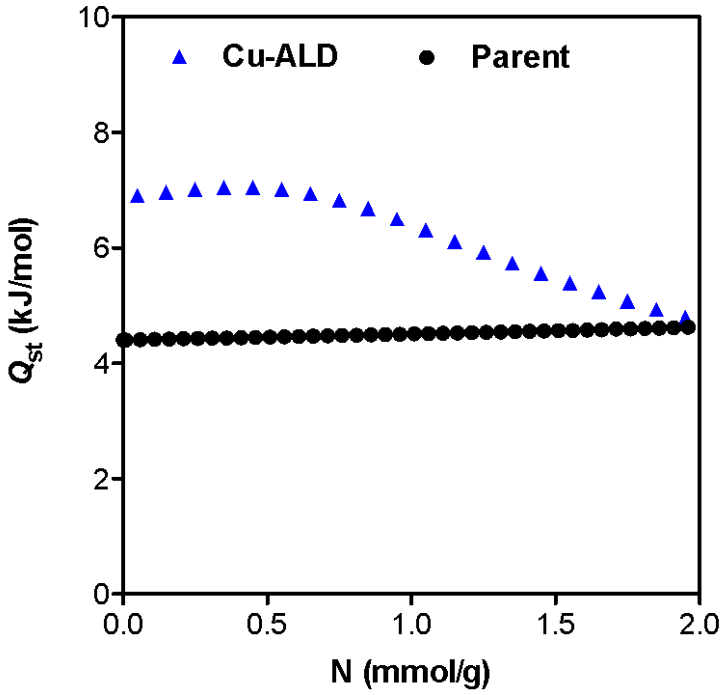
Accomplishments and Progress: Deposit Metal Ions by Solution & ALD



MOF	Metal:Zr	Metal:Zr_6	BET Surface Area (m^2 g^{-1})	Pore Volume (cm^3 g^{-1})
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



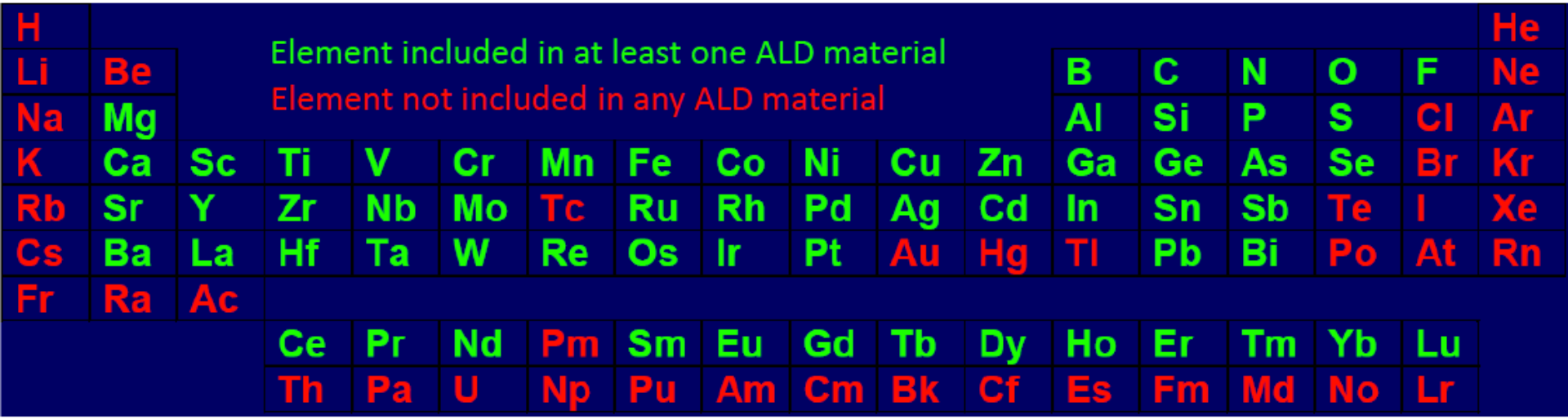


- Q_{st} ~60% improvement over parent—but still only ~ 7 kJ/mol

Collaborations

- 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



- Iterative materials feedback for ALD metallated MOFs
- Study H_2 adsorption dynamics *in situ* (Jeffrey T. Miller, ANL)

Summary Slide

- Relevance:
  - Address barriers to move towards the *ambient temperature storage of molecular* H_2
- 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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