New Carbon-Based Porous Materials with Increased Heats of Adsorption for Hydrogen Storage

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Northwestern University

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Project ID: ST023

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Overview

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Timeline

- Start date: 9/1/2008*
- End date: 8/31/2012
- 60% complete*

Barriers Addressed

- Hydrogen storage
  - Gravimetric target
  - Volumetric target
  - Increased heat of adsorption

Budget

- Total project funding
  - DOE share: $1,295,493
  - Contractor share: $321,833
- FY10 Funding: $350,000
- FY11 Funding: $300,000

Partners

- Juergen Eckert (UCSB)
- NREL

* 9/1/2008 is official start date. Initial funding received March 2009.

Relevance

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Overall Project Objectives

- Develop new materials to meet DOE volumetric and gravimetric targets for hydrogen storage
  - Metal-organic frameworks (MOFs)
  - Polymer-organic frameworks (POFs)

- Our view is that hydrogen storage sorbents must have **both**
  - High heats of adsorption and
  - High surface area

Relevance

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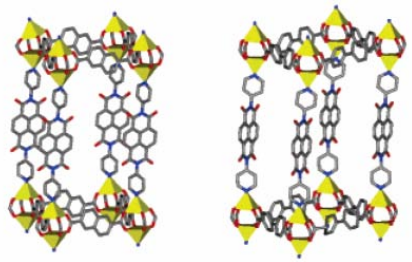
Objectives for Current Year

- MOFs and POFs
  - Develop materials with very high surface area
  - Develop materials containing functional groups that can bind hydrogen
  - Measure heats of adsorption and hydrogen uptake

- Modeling
  - Aid in the development of high surface area materials
  - Develop models for cation-containing MOFs
  - Screen different cations and cation environments for their ability to bind hydrogen and the resulting storage capacities

Approach

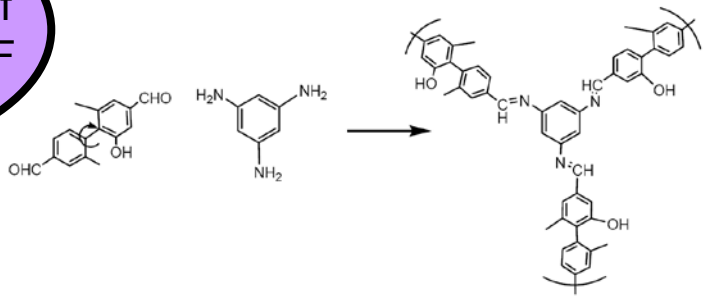


Snurr
Computational elucidation, design and modeling

Hupp
Synthesis and characterization of MOFs

Kanatzidis
Synthesis and characterization of POFs

Nguyen
Design and synthesis of SBUs for MOF and POF assembly



Approach

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1. Enhance heats of adsorption via introduction of cations

   Two approaches for introducing cations

   - Framework reduction
   - Alkoxide functionalization

   Both of these techniques were pioneered by members of our team at Northwestern University

2. Enhance H_2 capacity by increasing surface area

3. Combine chemistries for high heats of adsorption and high surface areas to increase room temperature hydrogen storage

Status

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Go/No-Go Decision: August 2010 → Go

Some Key Milestones Achieved:

- Synthesized POFs with surface areas of >1500 m^2/g.
- Achieved 10 kJ/mol heat of adsorption with little or no drop-off at higher coverages (no less than 6 kJ/mol at highest coverage).
- Determined that catenation is generally not beneficial for hydrogen uptake in MOFs without cations.
- Developed model for MOFs containing cations.
- Achieved material gravimetric capacity of >6 wt.% at 77 K and 100 bar.
- Achieved material volumetric capacity of >30 g/L at 77 K and 100 bar.

Technical Accomplishments: Outline

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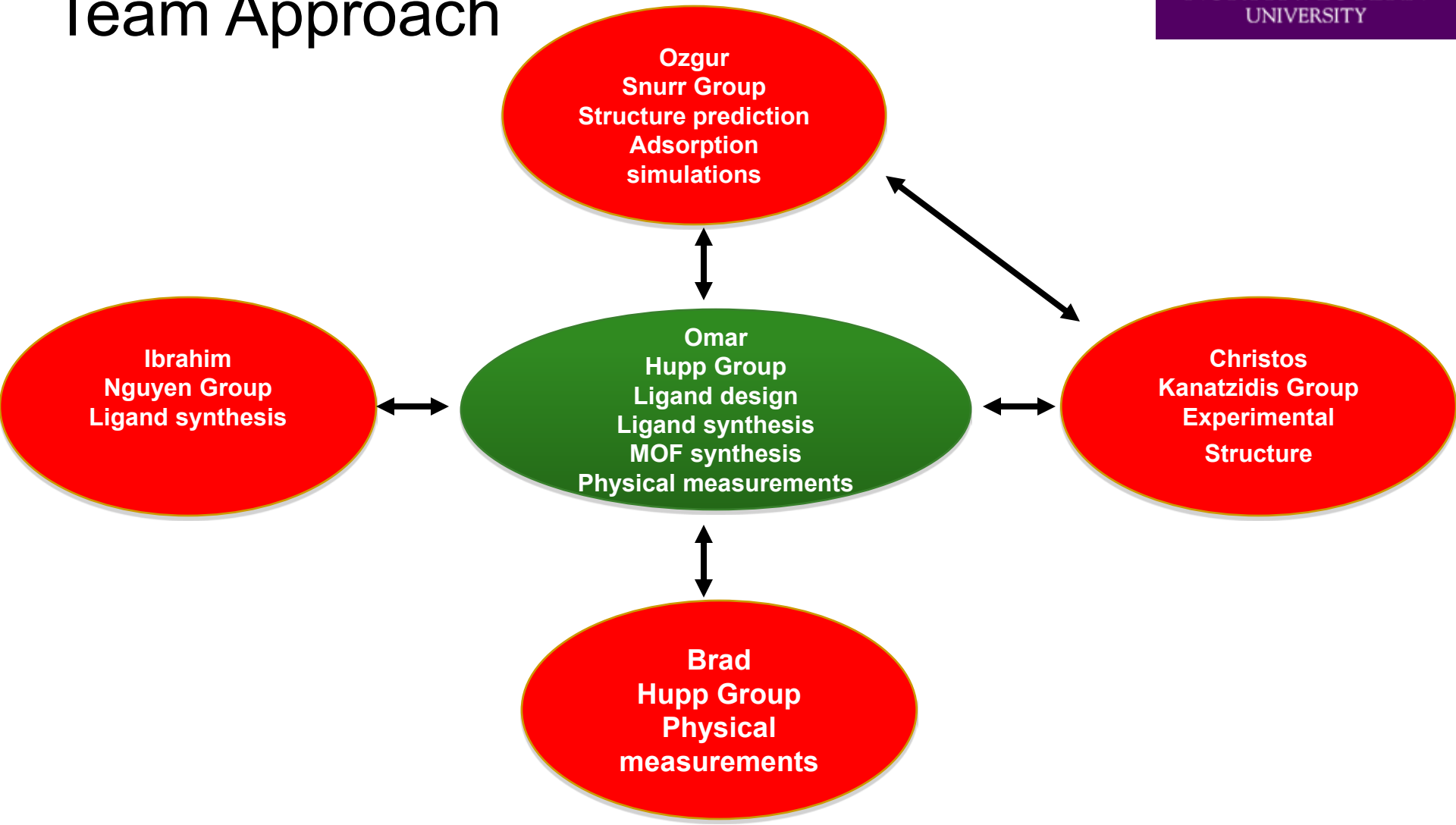
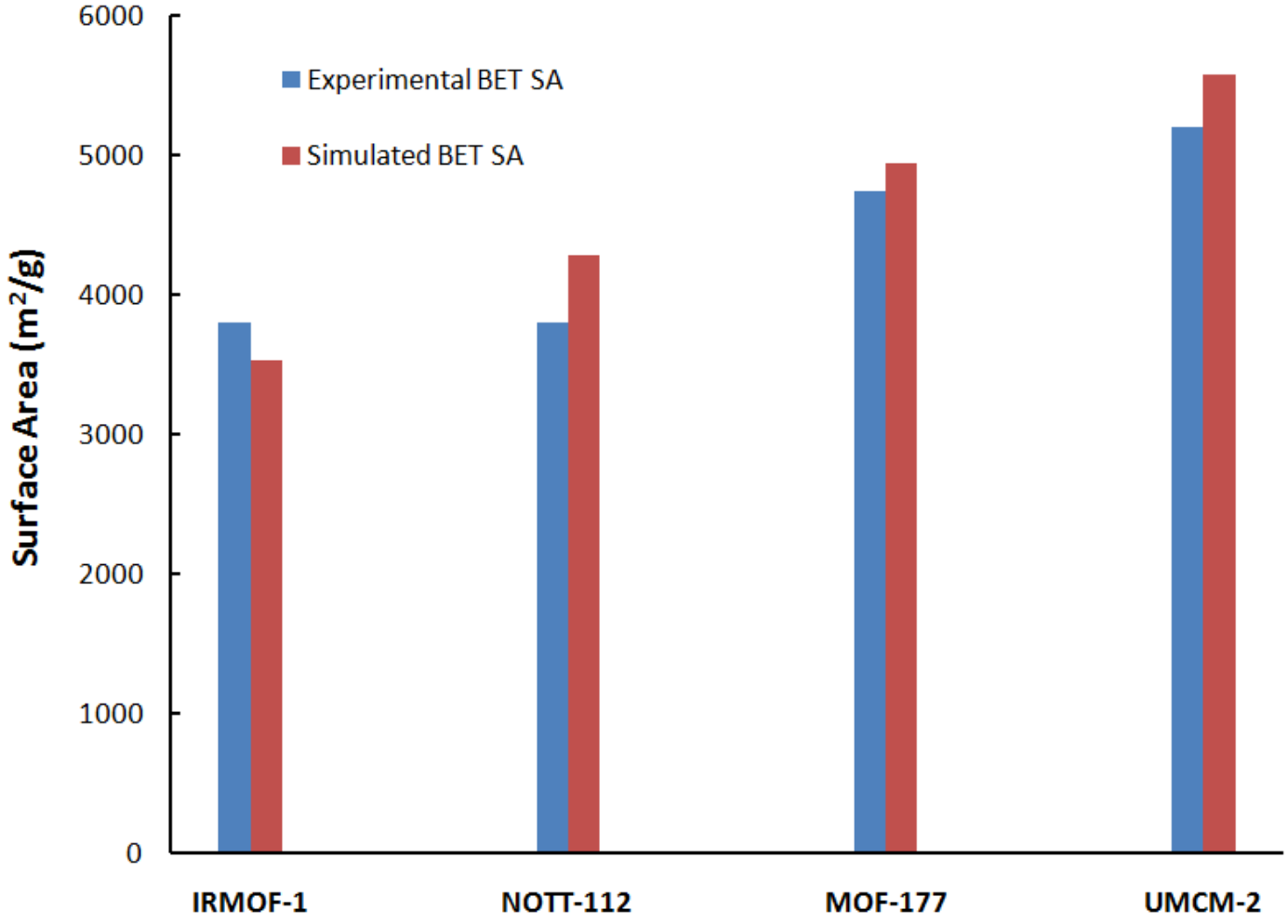
- Metal-organic frameworks (MOFs)
  - Achieving very high surface areas and cryogenic hydrogen uptake
  - Achieving high heats of adsorption
    - zwitterionic MOFs (last year)
    - Alkoxide functionalization

- Polymer-organic frameworks (POFs)
  - New synthetic chemistries
  - Achieving high surface areas
  - Achieving high heats of adsorption

High Surface Area MOFs: Team Approach



Literature: High Surface Area MOFs

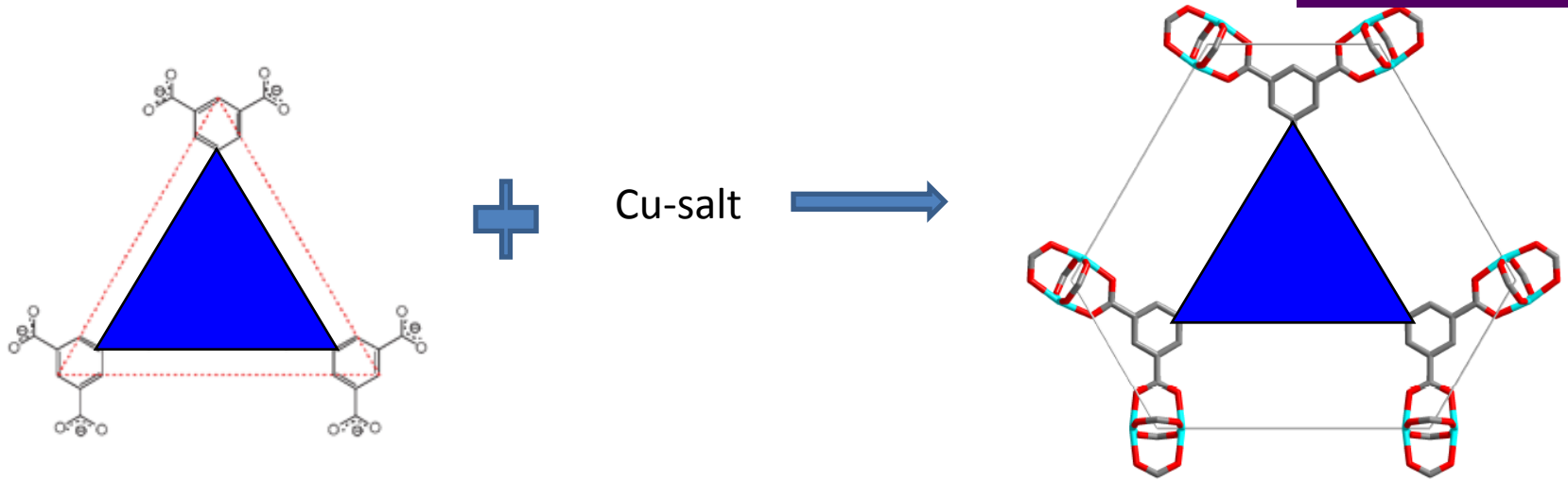


Some high surface area MOFs from the literature as of early 2010.

From Modeling to Reality

Farha, Yazaydin, Eryazici, Malliakas, Hauser, Kanatzidis, Nguyen, Snurr, Hupp, *Nature Chem.,* 2010.

Target Coordination and Topology



Why this topology:

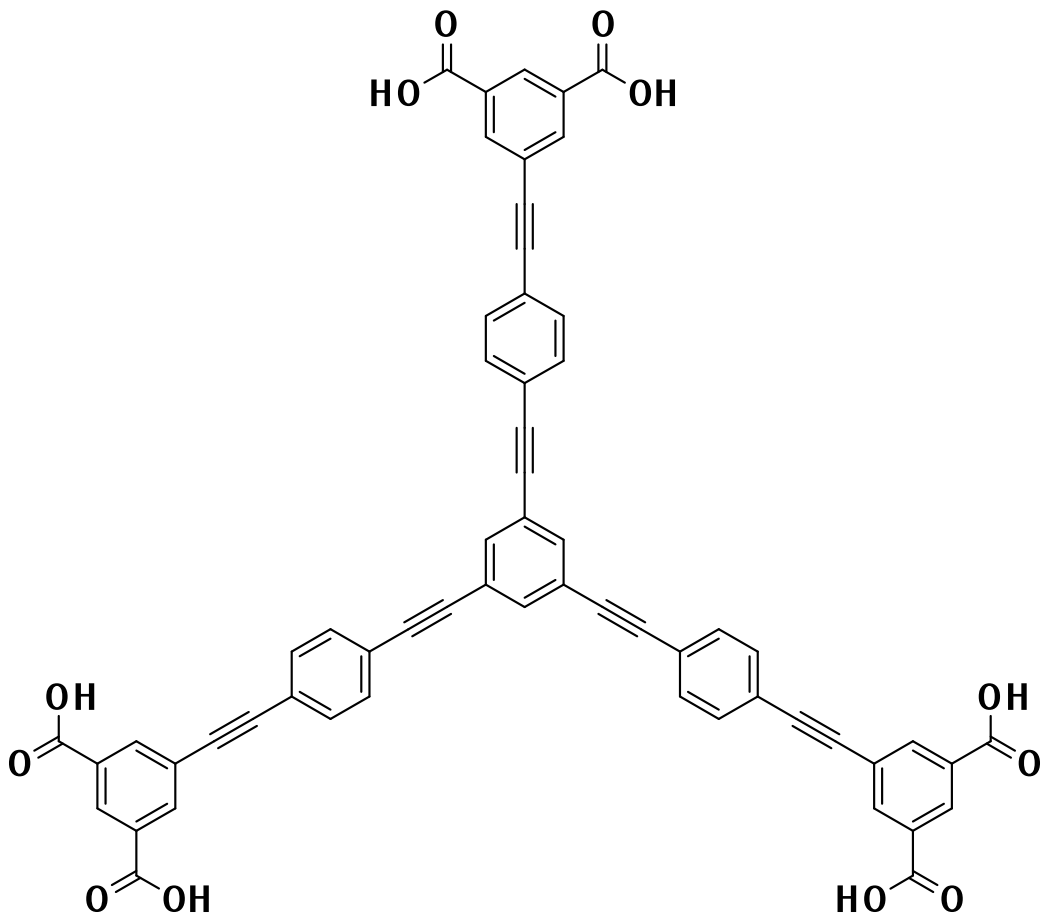
(a) high stability under ambient conditions

(b) unsaturated coordination sites (Cu(II) sites)

(c) impossibility of forming interpenetrated multi-network structures.

cf. M. Schroder et al. and H-C. Zhou, et al.

New Ligand



Structure Prediction

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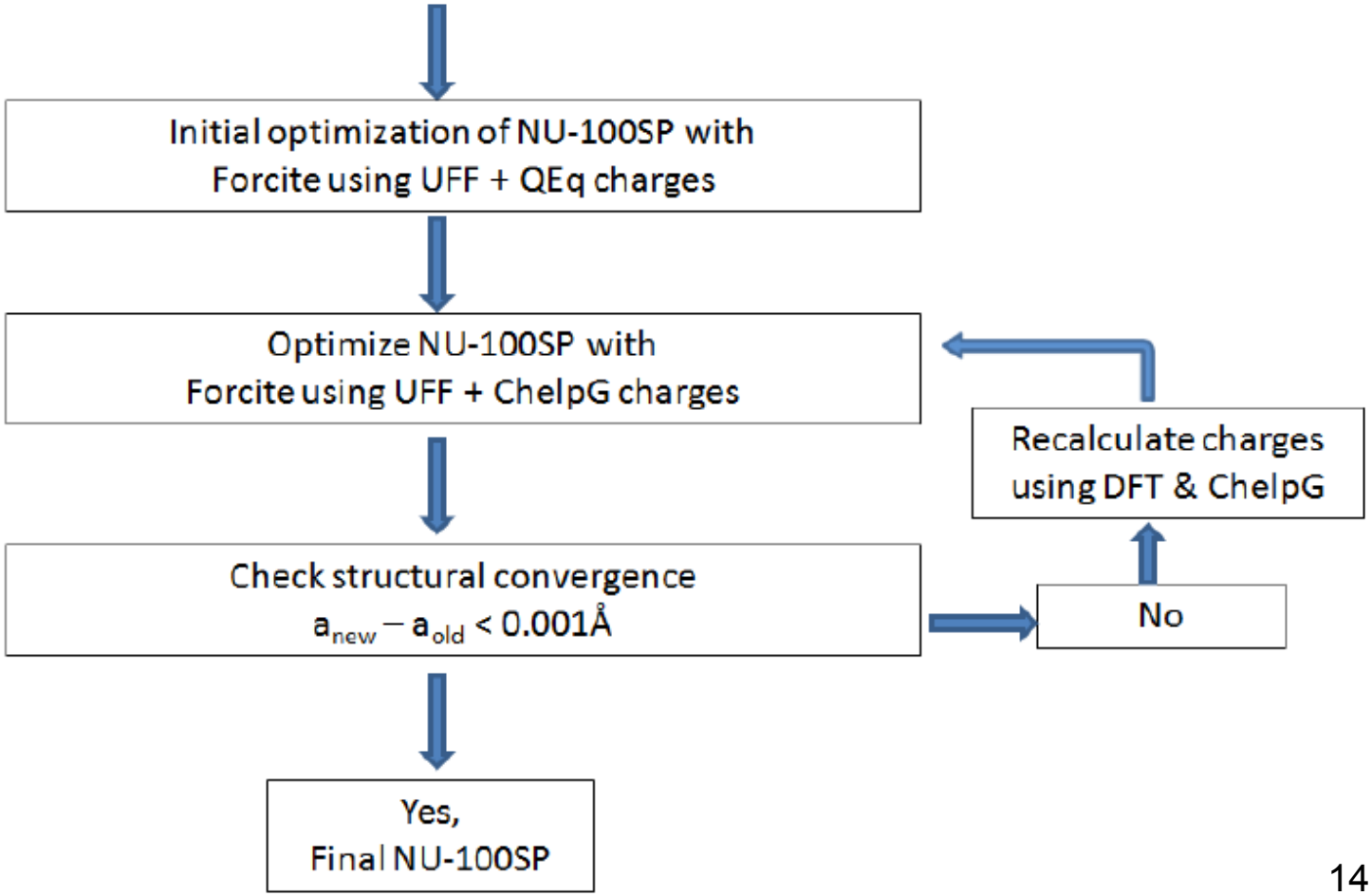
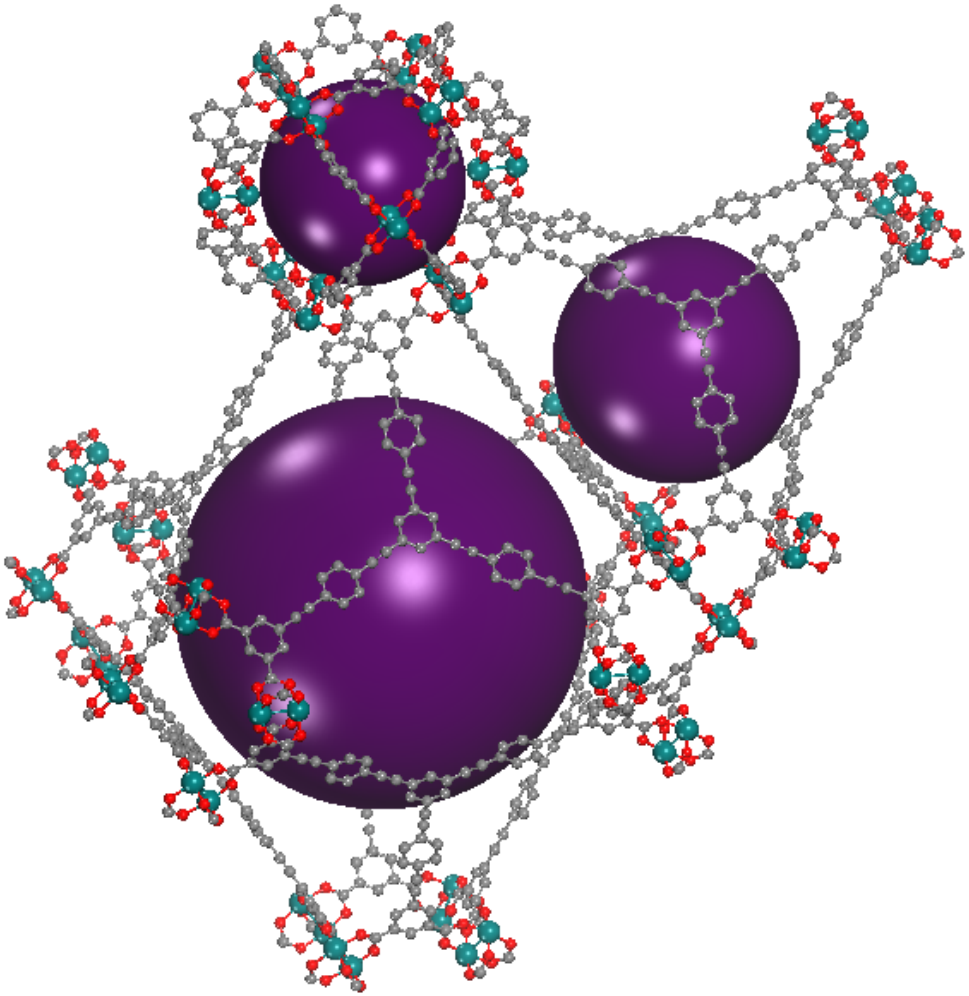
Combine this ligand with Cu-paddlewheels in Fm-3m space group

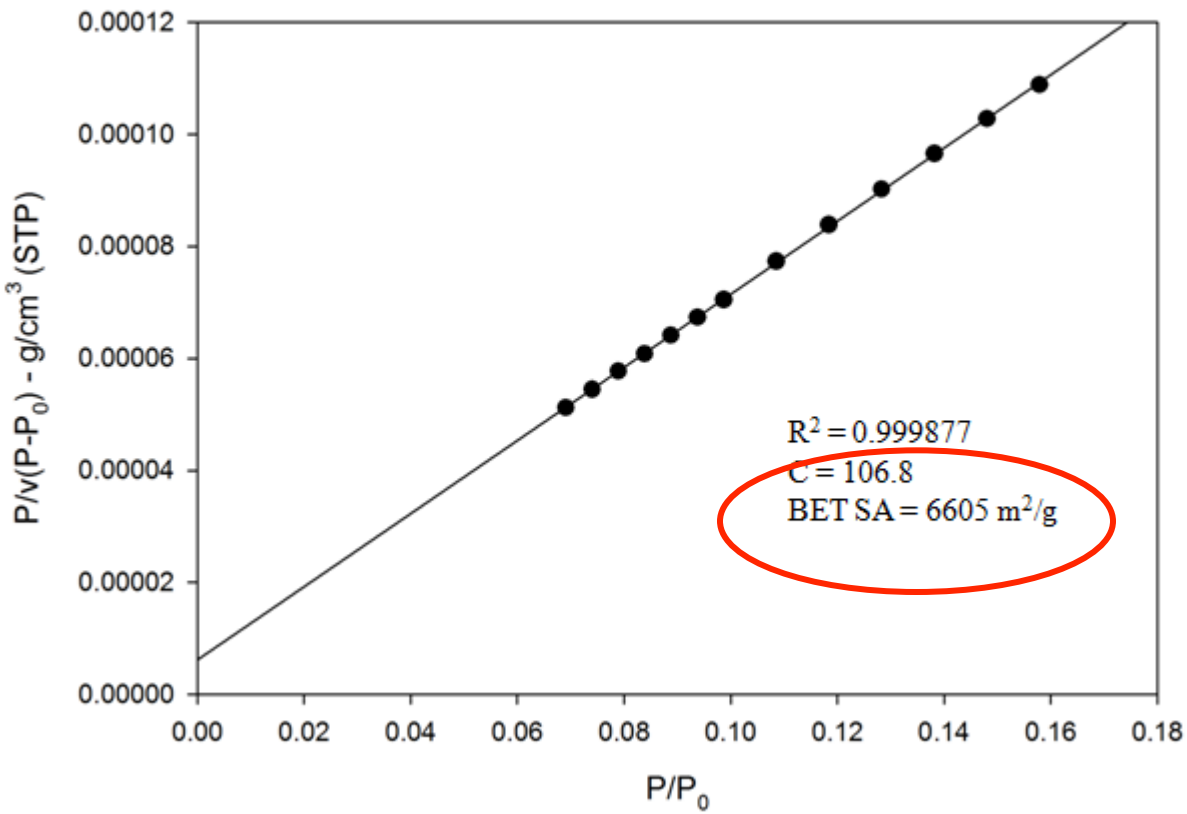


New Material: NU-100



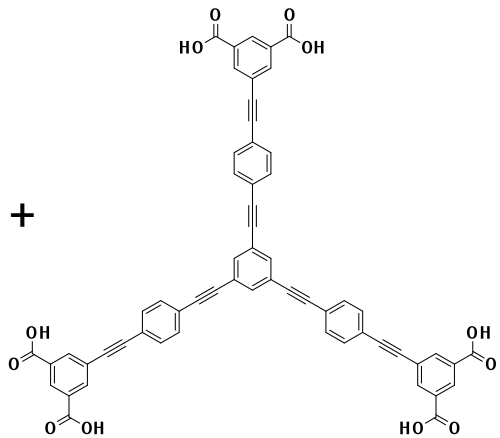
Predicted Surface Area of NU-100

Simulated Structure → Simulated N_2 isotherm → BET Model



MOF Synthesis

$Cu(NO_3)_2 \cdot 2.5H_2O$ +



$\xrightarrow[75°C/24hrs]{DMF/HBF_4}$ MOF

↓

Single crystal

↓

Matched with predicted structure

a=b=c=59.872002 Å

a=b=c=59.539389 Å

MOF Activation

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- Heating at 100 C under vacuum → Failed
- Solvent exchange, then room temperature evacuation → Failed
  - -ethanol
  - -acetone
  - -chloroform
- Modified supercritical drying →

This technique, developed by the Hupp group at NU, is now used by other groups to successfully activate MOFs.

New Material: NU-100

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truncated octahedron

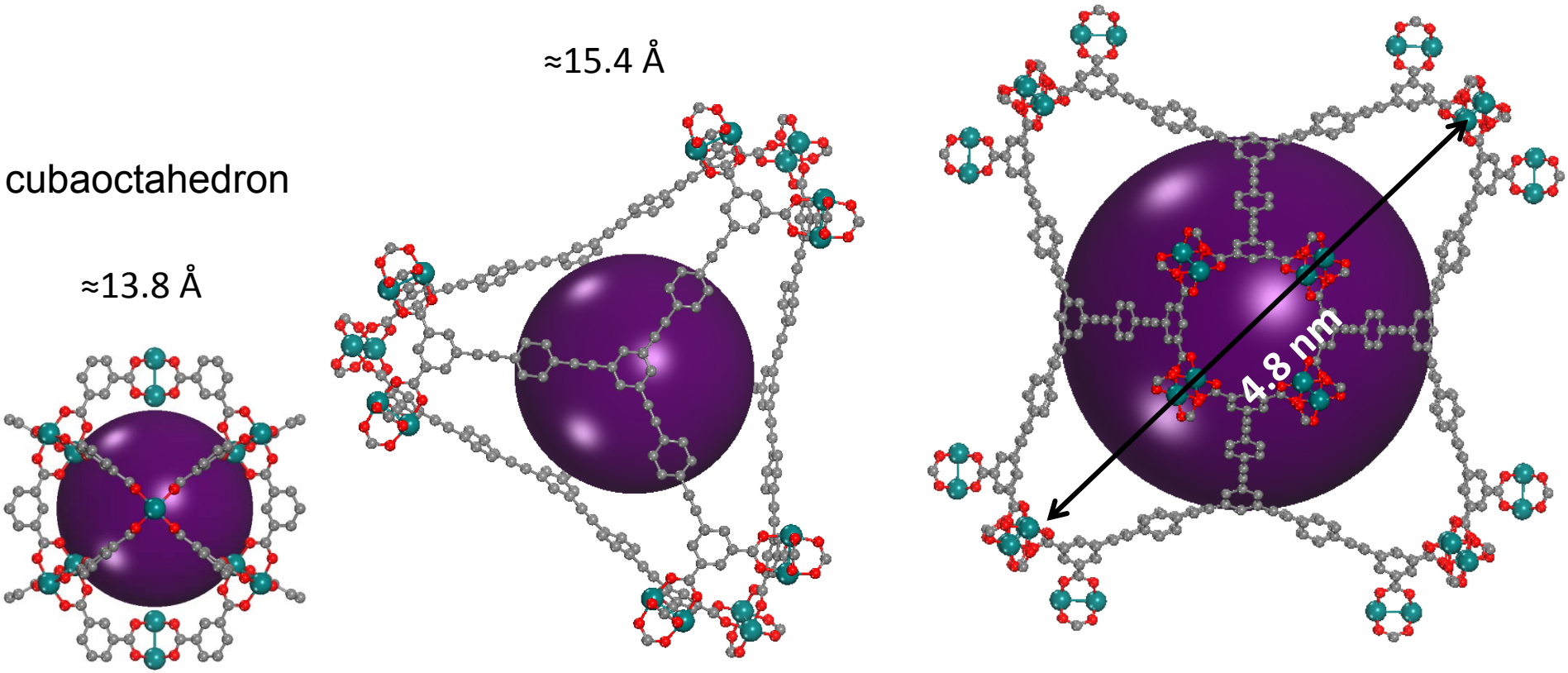
≈27.8 Å

truncated tetrahedron

≈15.4 Å

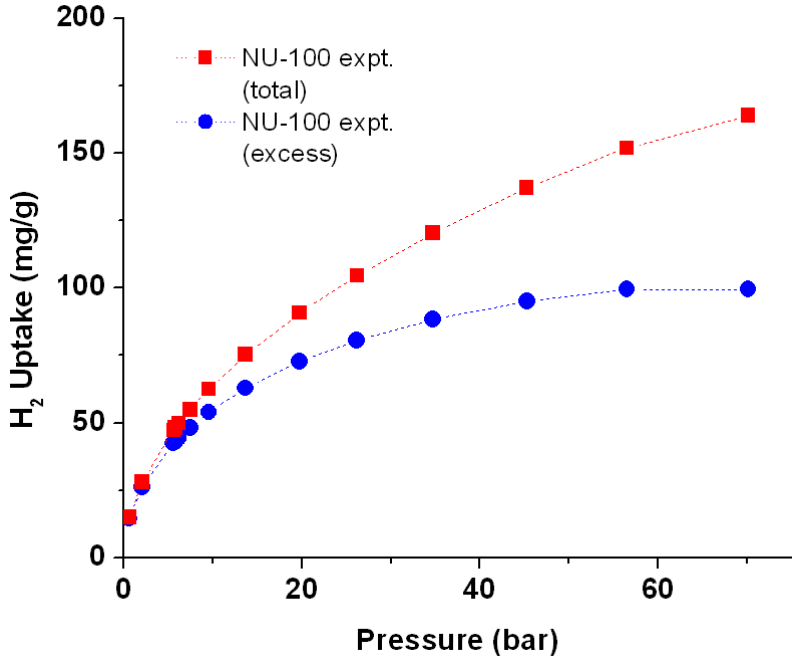
cubaoctahedron

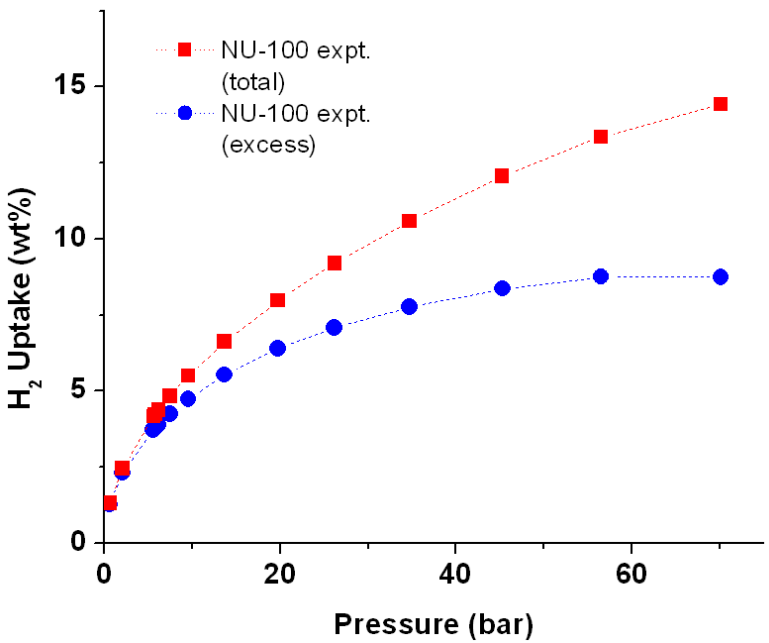
≈13.8 Å



Farha, Yazaydin, Eryazici, Malliakas, Hauser, Kanatzidis, Nguyen, Snurr, Hupp, *Nature Chem.*, 2010.

Hydrogen Storage





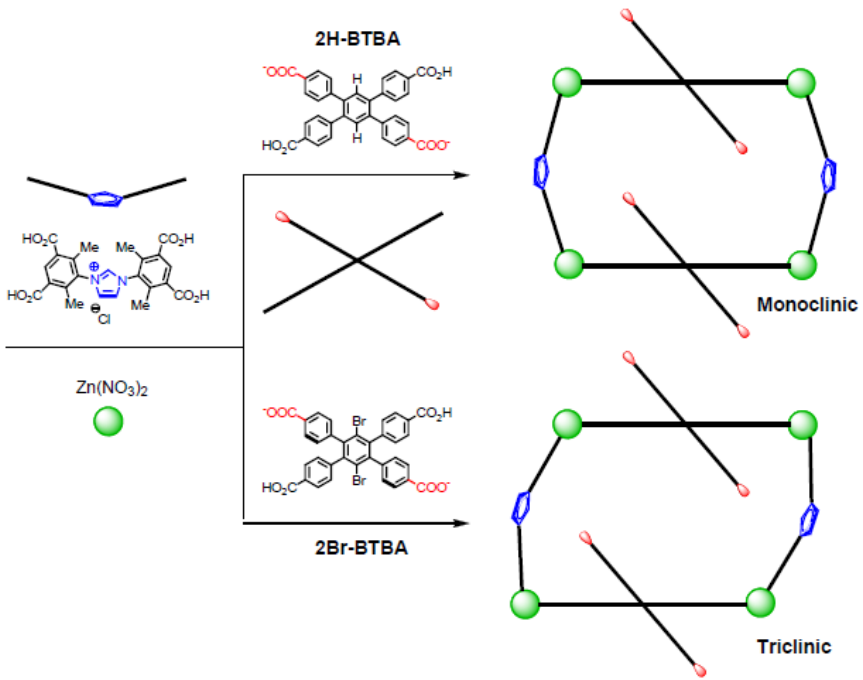
<u>Hydrogen uptake at 77 K</u>

Excess	99.5 mg / g	Total	164 mg / g
	9 wt%		14 wt%
	28 g/L		45 g/L

These excess values are the highest reported to date at 77 K.

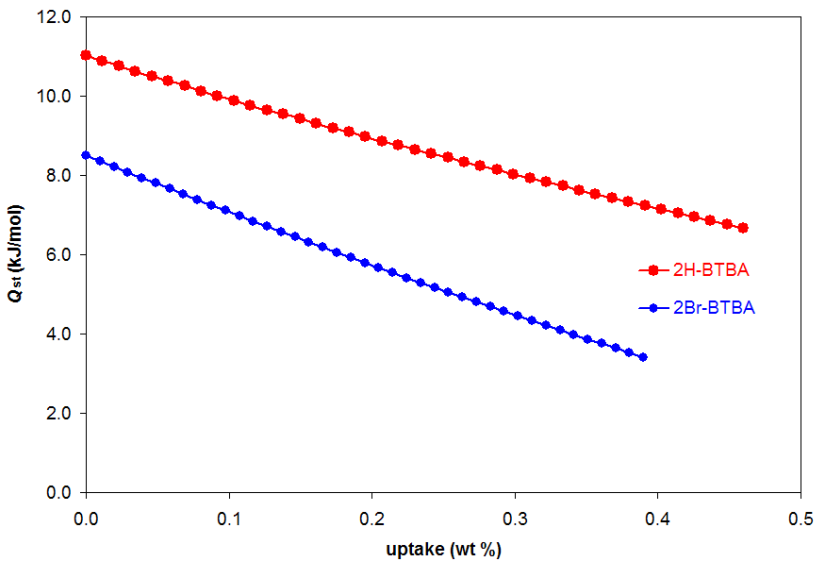
Improved Heats of Adsorption

Approach 1: Charged Cavities (last year)



We have conceived and synthesized a new class of zwitterionic MOFs

Isosteric heats of adsorption in new zwitterionic MOFs obtained from experimental isotherms at 77 and 87 K

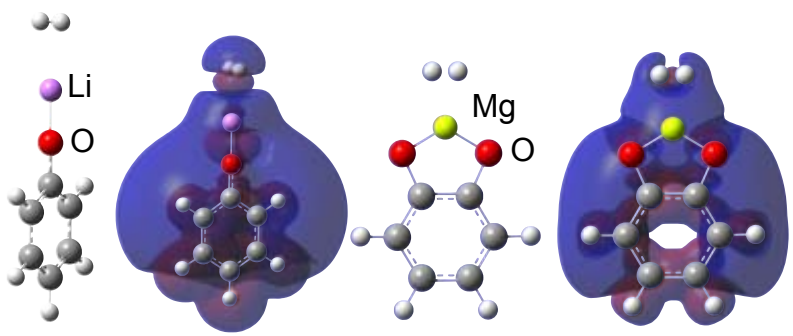


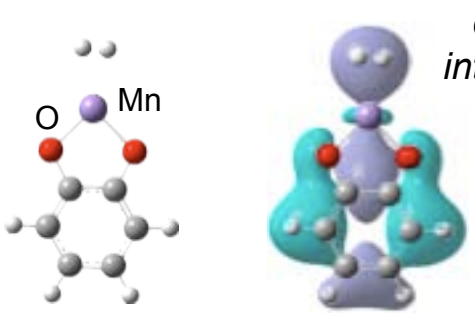
→ Over 10 kJ/mol heat of adsorption at low loading

Improved Heats of Adsorption

Approach 2: Linker functionalization with divalent cations

- Metal-alkoxide MOFs have been synthesized in our labs.
- Which metal is best?
  - Divalent cations have larger electric fields than Li.
  - Transition metals can interact strongly with hydrogen.
- We are studying this question computationally and experimentally.



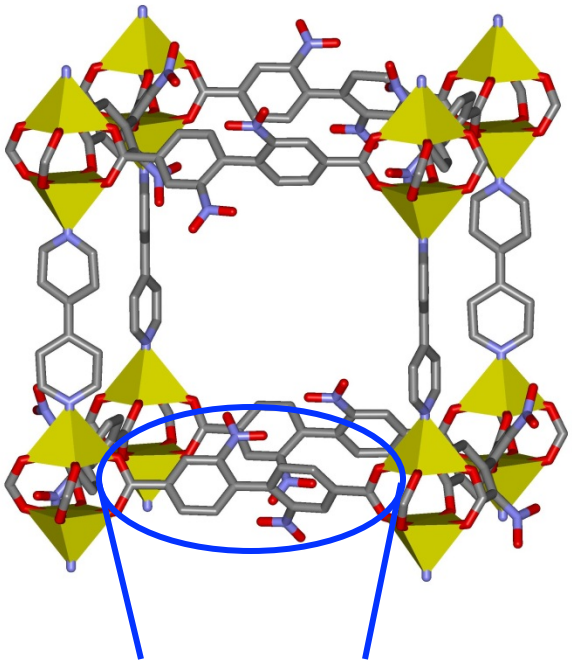


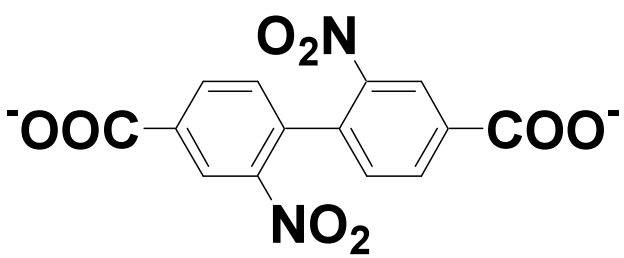
d orbital interactions

Getman, Miller, Wang, Snurr, *J. Phys. Chem. C*, 2011.

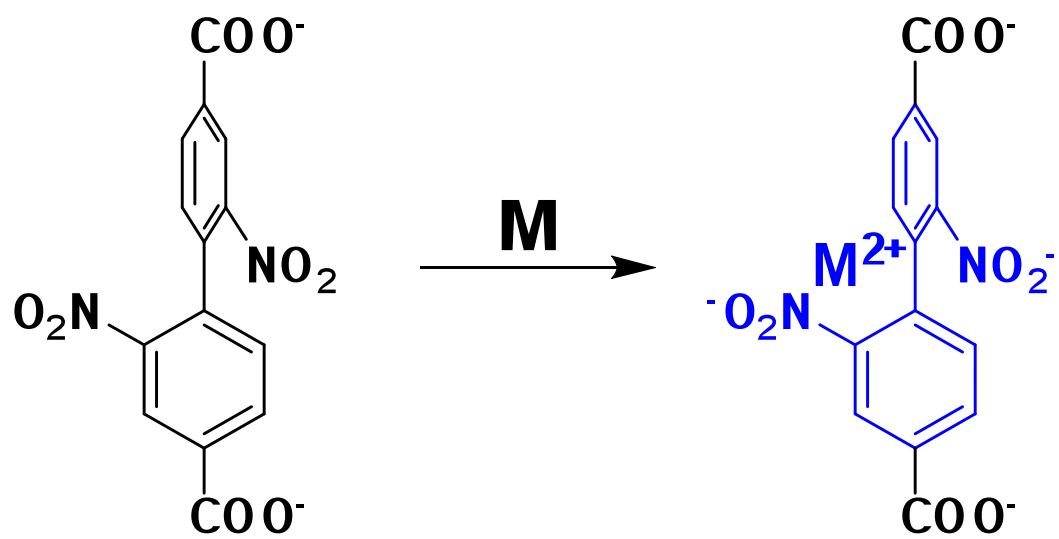
Improved Heats of Adsorption

Approach 2: Linker functionalization with divalent cations





Work in progress

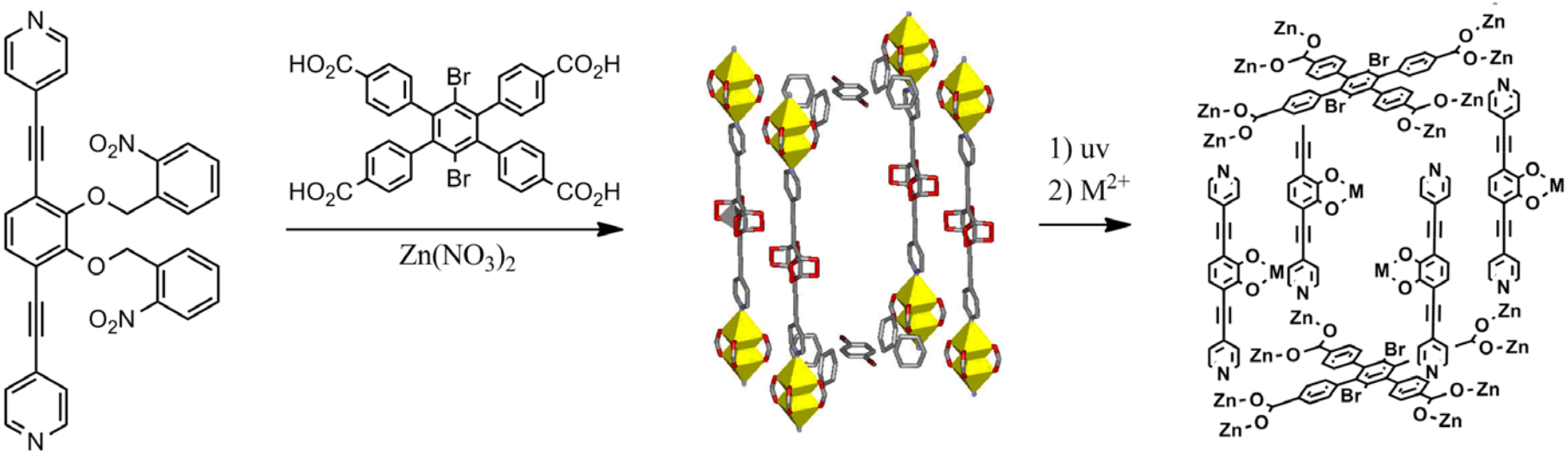


M = Mg, Ca, etc.

Improved Heats of Adsorption

Approach 2: Linker functionalization with divalent cations

Preliminary experimental results



- Rotational disorder prevents complete solution of the crystal structure
- 58% post-synthesis cleavage of photolabile *o*-nitrobenzyl groups
- Metalation of naked catechol struts is underway

Improved Heats of Adsorption

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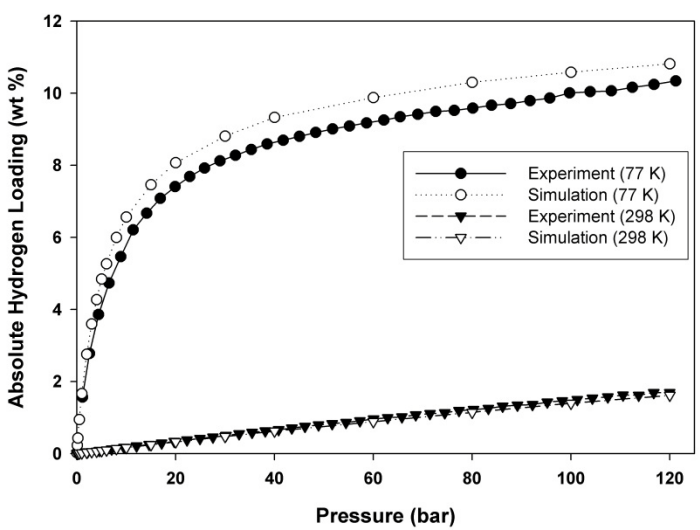
Molecular Modeling

- Determine H_2/cation interactions with high-level quantum chemical methods (MP2 with large basis set)
- Fit QM results to analytic forms for grand canonical Monte Carlo (GCMC) simulations
- Use GCMC to predict effects of different cations, cation loading, pore size, etc. on hydrogen uptake



Past work on unfunctionalized MOFs: Hydrogen in IRMOF-1

Simulations: Ryan, Broadbelt, Snurr, *Chem. Comm.*, 2008.
Experiments: Kaye, Dailly, Yaghi, Long, *J. Am. Chem. Soc.,* 2007.

Modeling H_2 Storage in Alkoxide Functionalized IRMOF-16

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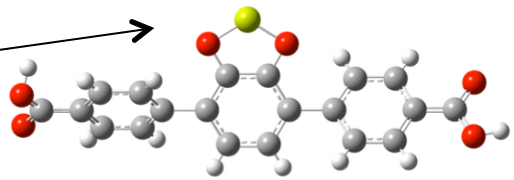
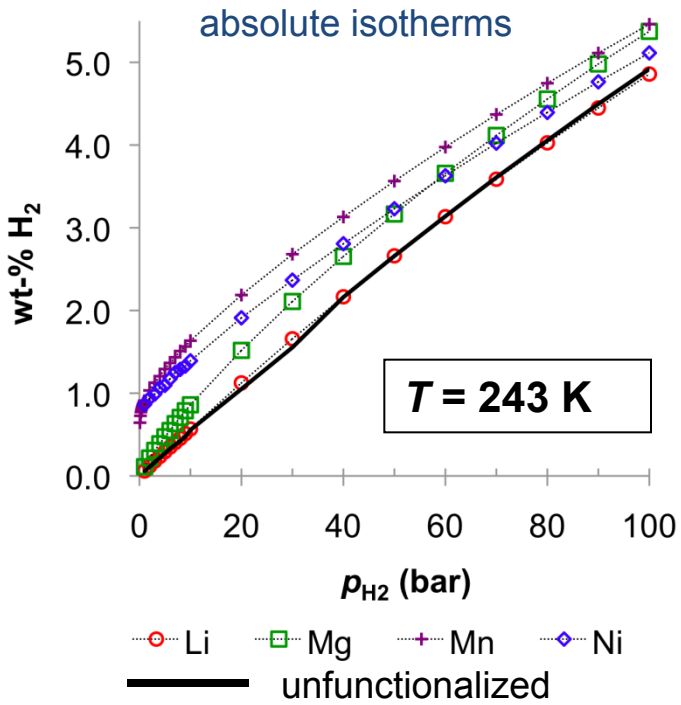
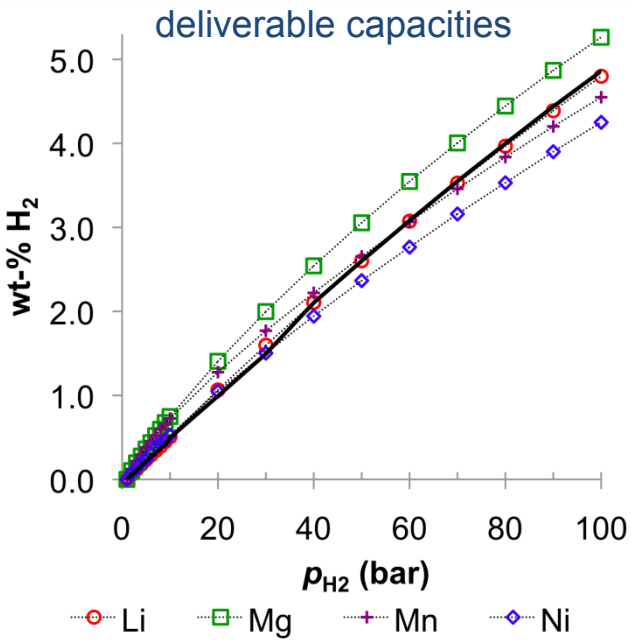
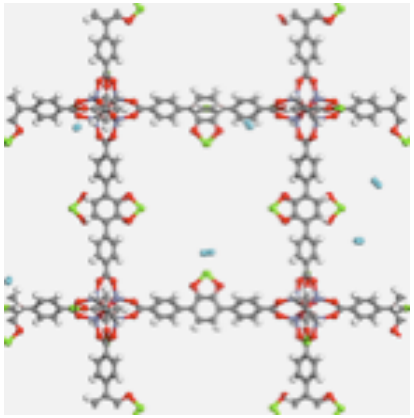
- Different metal alkoxide MOFs simulated
- First, one functional group per linker
- Enhanced deliverable capacity predicted for Mg-alkoxide functionalization







Results from grand canonical Monte Carlo (GCMC)



Getman, Miller, Wang, Snurr, *J. Phys. Chem. C*, 2011.

Modeling H_2 Storage in Alkoxide Functionalized IRMOF-16

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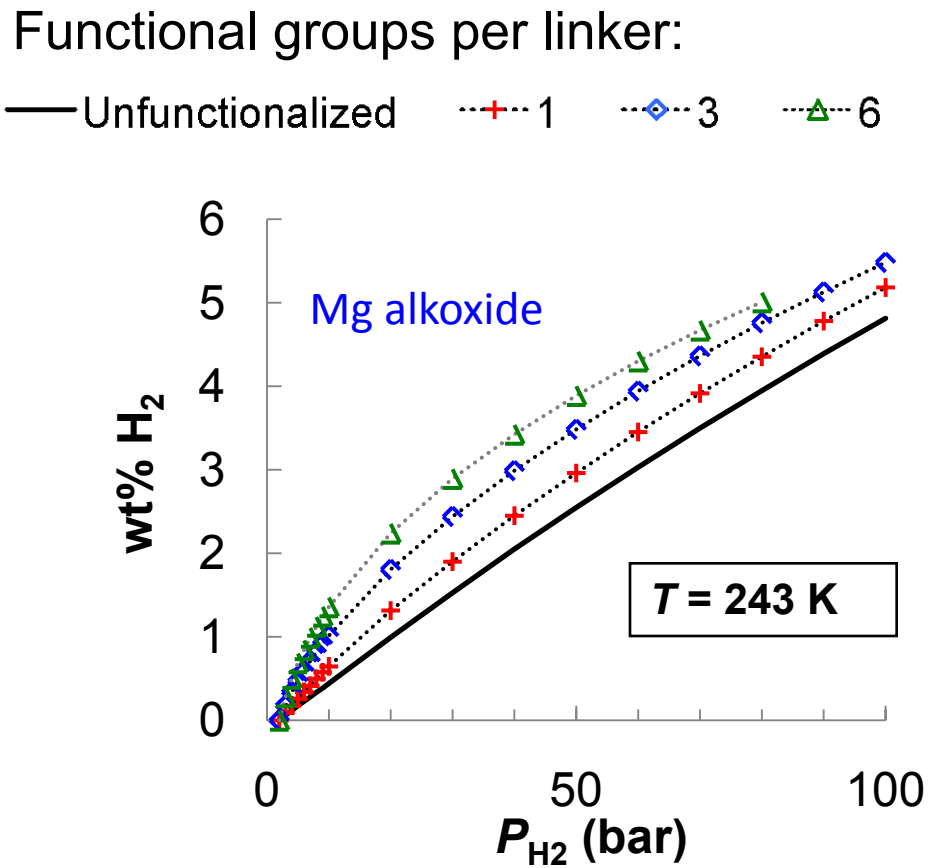
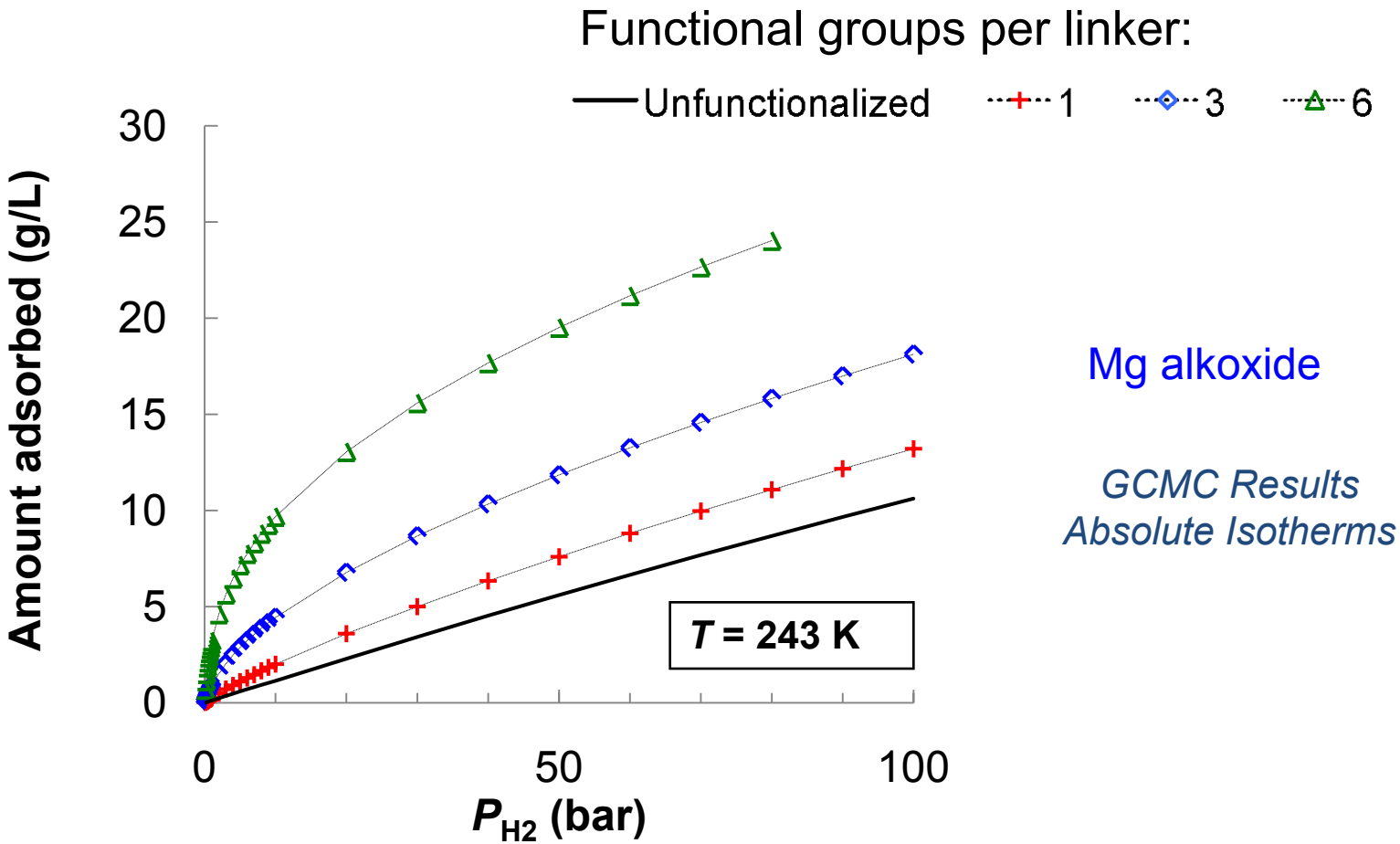
- Gravimetric adsorption is predicted to increase with increasing number of functional groups per linker.



GCMC Results
Absolute Isotherms

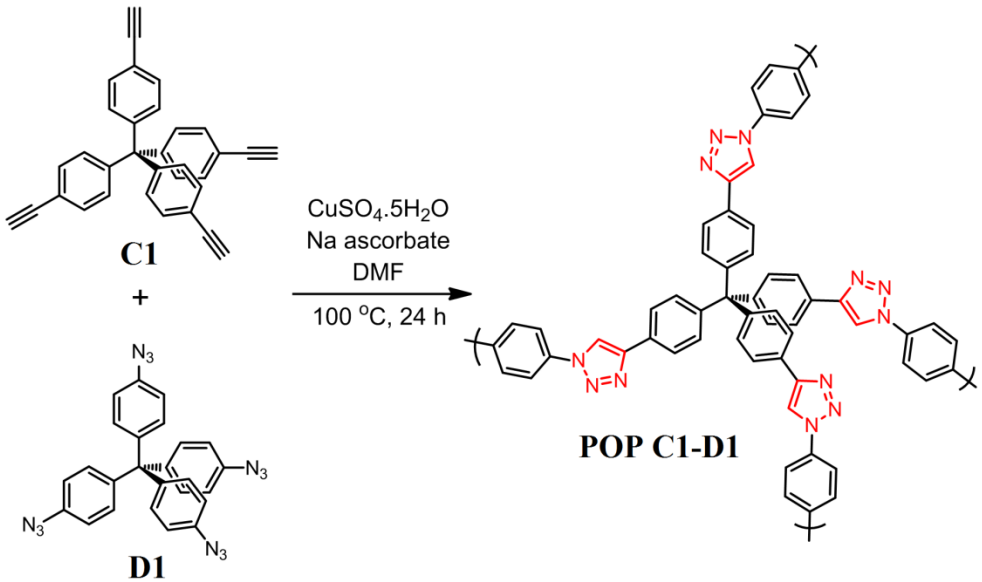
IRMOF-16 was chosen for modeling as an example of a high surface area MOF.

Modeling H_2 Storage in Alkoxide Functionalized IRMOF-16



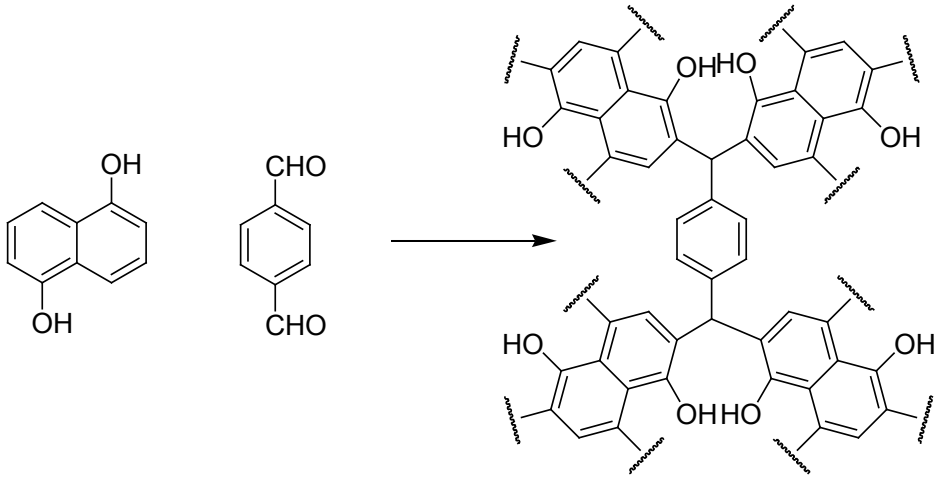
Adding more functional groups is predicted to lead to significant increases in volumetric storage.

Polymer-Organic Frameworks

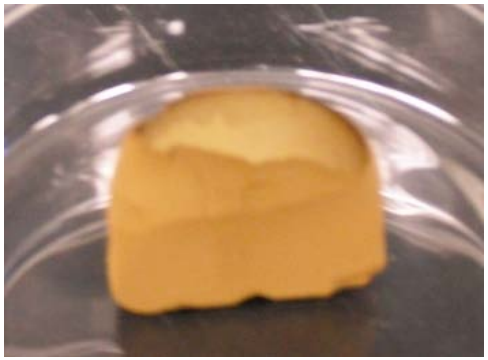


- Tailorable, microporous polymers made from rigid building blocks
- Modular construction
  - Schiff's base chemistry (FY 2010)
  - "Click" chemistry (FY 2011)
  - Components chosen to produce loosely-packed, extended 3D networks
- Surface area can be increased by tuning the synthesis conditions.
- We have achieved 1500 m^2/g.
- Extremely stable. POFs survive at pH 14.5 for days.

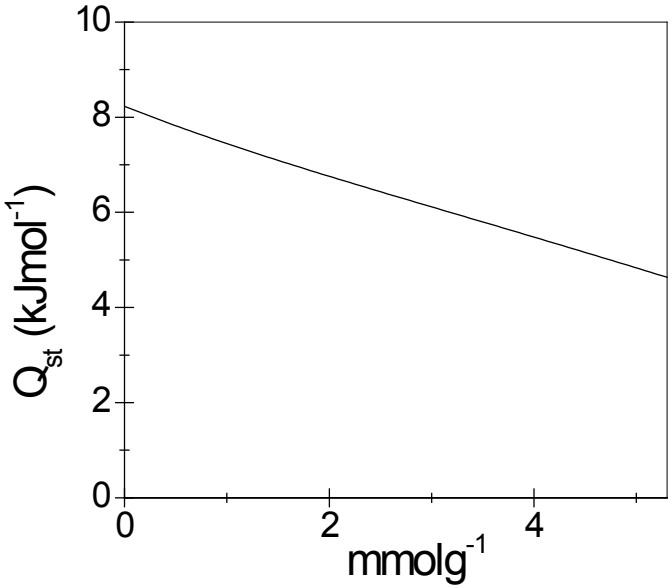
POFs with –OH functional groups



Obtained as powder or monolith



- POFs can be synthesized with a wide range of functional groups.
- Some of these functional groups can be metallated to create sites that may bind hydrogen strongly (in progress).



Heat of H_2 adsorption is 8.2 kJ/mol at low coverage in POF with –OH groups.

Collaborations

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- NREL
  - Lin Simpson, Philip Parilla
  - Validation of high pressure sorption measurements
  - Currently in progress
- University of California, Santa Barbara
  - Juergen Eckert
  - Neutron scattering
  - Beam time has been approved

Future Work

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Major Focus: Combine strategies for

- high surface area and high free volume
- high heats of adsorption

Planned work:

- Introduce Mg and other cations into MOFs and POFs
- Continue efforts to increase surface areas of POFs
- Continue to measure H_2 uptake and heats in new materials
- Measure high-pressure, room-temperature isotherms in most promising materials
- Validate model against experimental data
- Determine optimal combination of heat of adsorption and surface area

Summary

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- We are developing new materials to meet DOE hydrogen storage targets. The new concept is to introduce cations into MOFs and POFs to **improve heats of adsorption** (which will improve room temperature storage) along with **high surface areas** (which are needed for high hydrogen capacity).

- We have synthesized a variety of new MOFs
  - Functional groups can be tailored to increase the H_2 heat of adsorption
  - Achieved 11 kJ/mol heat of adsorption at low loading (zwitterionic MOF)
  - Achieved 14 wt% and 45 g/L at cryogenic temperatures (NU-100 MOF)

- We have synthesized a variety of new POFs
  - Functional groups can be tailored to increase the H_2 heat of adsorption
  - Achieved 1500 m^2/g
  - Achieved 8 kJ/mol heat of adsorption at low loading

- We have developed useful models for funtionalized MOFs
  - Alkaline earth and transition metal alkoxide groups are promising targets
  - Modeling can be used to design MOFs on the computer before their synthesis

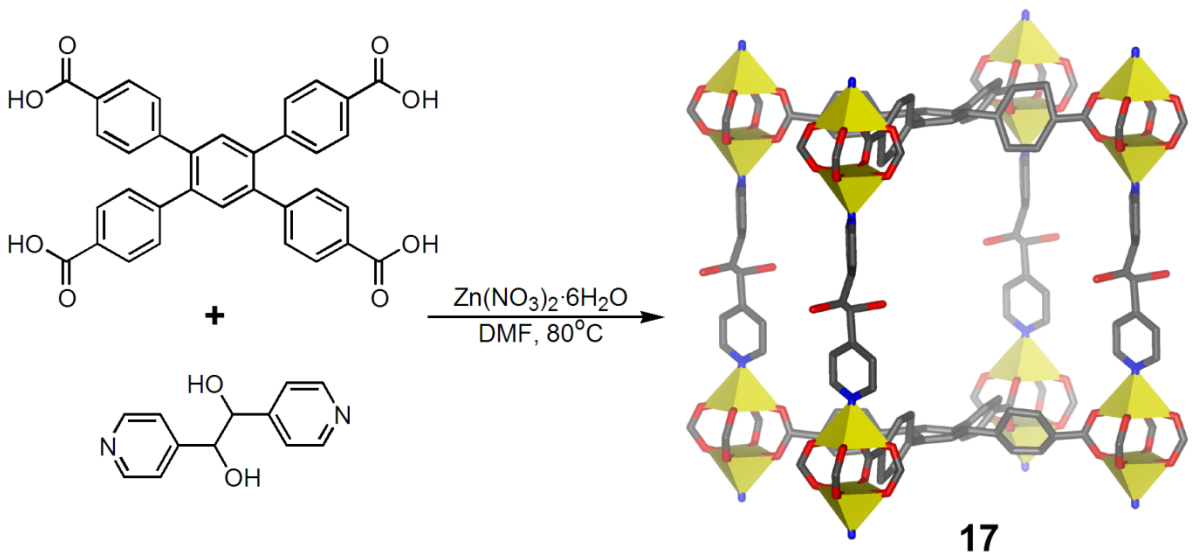
Summary

	April 2010	March 2011
Surface Area (m^2/g)	1521	6143
Isosteric Heat of Adsorption (kJ/mol)	11	11
Excess H_2 Uptake at 77 K and 1 bar (wt%)	1.5	1.6
Excess H_2 Uptake at 77 K and 70 bar (wt%)	Not measured	9
Excess H_2 Uptake at 77 K and 70 bar (g/L)	Not measured	28

Technical Backup Slides

Improved Heats of Adsorption

- Another approach: Metal-Alkoxide MOFs
- Previously synthesized in our labs:



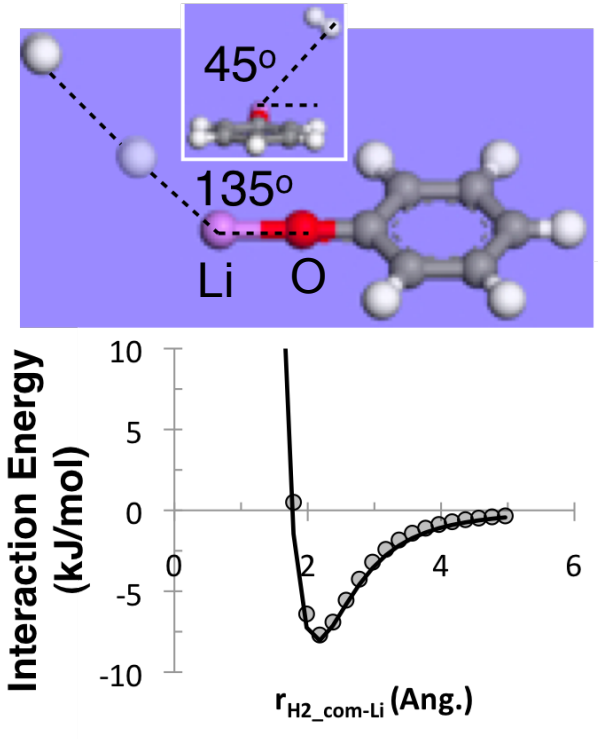
Li- functionalized MOFs

Mulfort, Farha, Stern, Sarjeant, Hupp, *J. Am. Chem. Soc.*, 2009.

Model for Cation-Containing MOFs

- *ab initio*-based force field for alkoxide groups
  - Morse, Coulomb potentials
  - Fit to 200 single points
  - Li, Mg, Mn: MP2/6-311+G**
  - Ni, Cu: M06/6-311++G**

- Lennard-Jones potentials from DREIDING force field for other framework atoms



points: QM energies, lines: fitted force fields. Force fields based on 12 'approaches.'

Getman, Miller, Wang, Snurr, *J. Phys Chem. C*, 2011.

H_2 Adsorption on Metal Alkoxides

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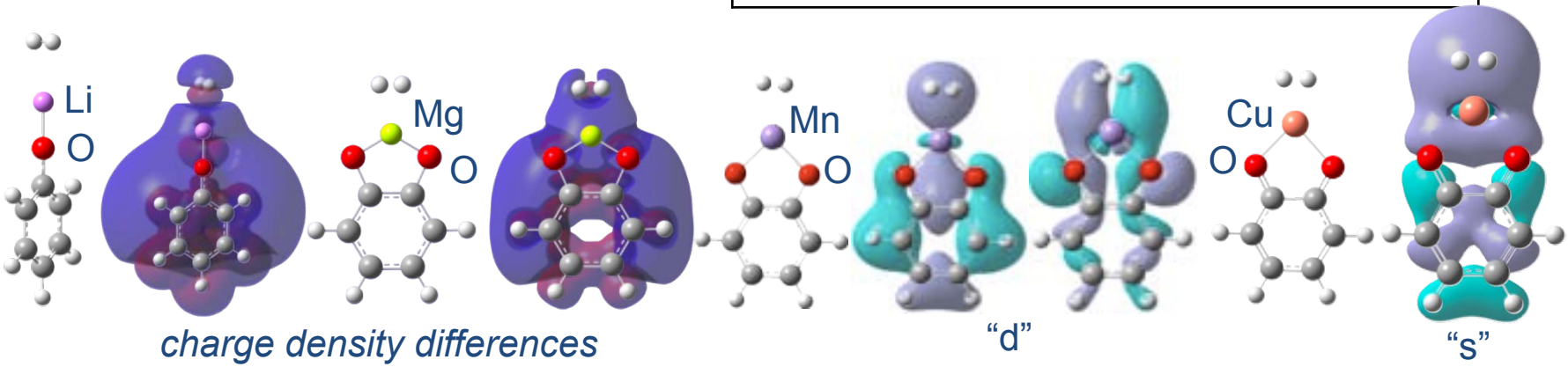
- Metals have large positive charges, H_2 binds "side-on"
- Li, Mg: physical adsorption
- Mn, Ni, Cu: chemical bonds
- Predicted binding energies on all but Li are larger than highest to date observed in literature
  - Ni-CPO-27: 13.5 kJ/mol

$$H_2 + MO_x\text{-}C_6H_{(6-x)} \rightarrow H_2\text{—}MO_x\text{-}C_6H_{(6-x)}$$

	Charge	H_2 binding energy (kJ/mol)
Li	+0.9	−10
Mg	+1.2	−22
Mn	+1.0	−46
Ni	+0.6	−78
Cu	+0.6	−84



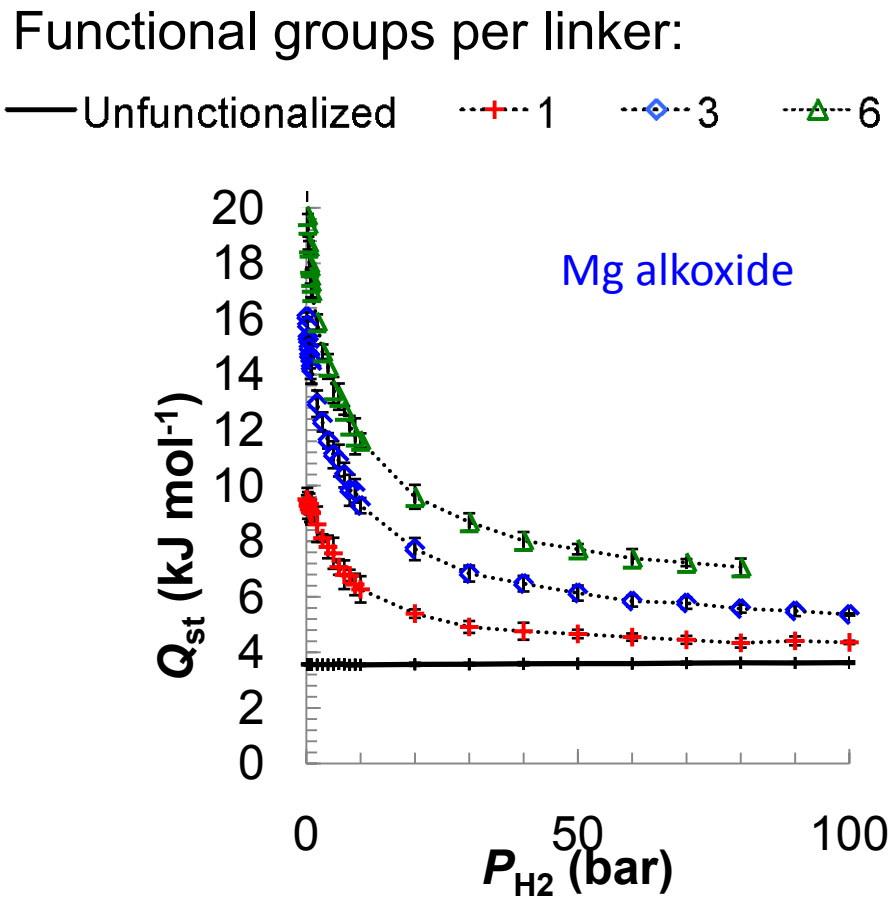
charge density differences

accumulation = red, depletion = blue

molecular orbitals

Modeling H_2 Storage in Alkoxide Functionalized IRMOF-16

- Initial heats of adsorption are larger in MOFs with more functional groups.
- MOFs with more functional groups sustain higher heats of adsorption over the full pressure range.



GCMC Results