

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

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Project ID:
st023

Overview



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Timeline

- Start date: 9/1/2008*
- End date: 8/31/2012
- 35% complete*

Budget

- Total project funding
 - DOE share: \$1,295,491
 - Contractor share: \$323,875
- FY09 Funding: \$350,000
- FY10 Funding: \$350,000

Barriers Addressed

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

Partners

- No official partners
- Collaborators listed at end of talk

* 9/1/2008 is official start date. Funding not received until March 2009.

Relevance



Overall Project Objectives

- Develop new materials to meet DOE volumetric and gravimetric targets for hydrogen storage
 - Metal-organic frameworks (MOFs)
 - Polymer-organic frameworks (POFs)
 - Tight integration of synthesis, characterization, and modeling
- **Increase heats of adsorption** as a means to meet volumetric and gravimetric targets at ambient conditions

Relevance



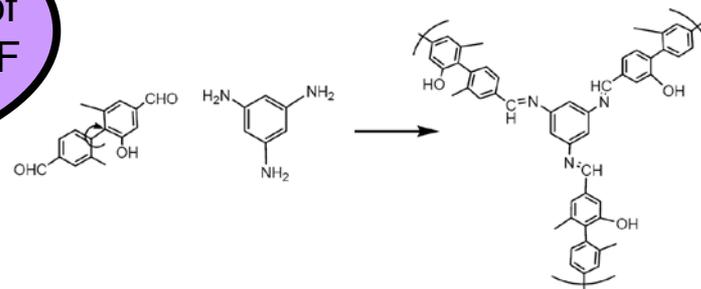
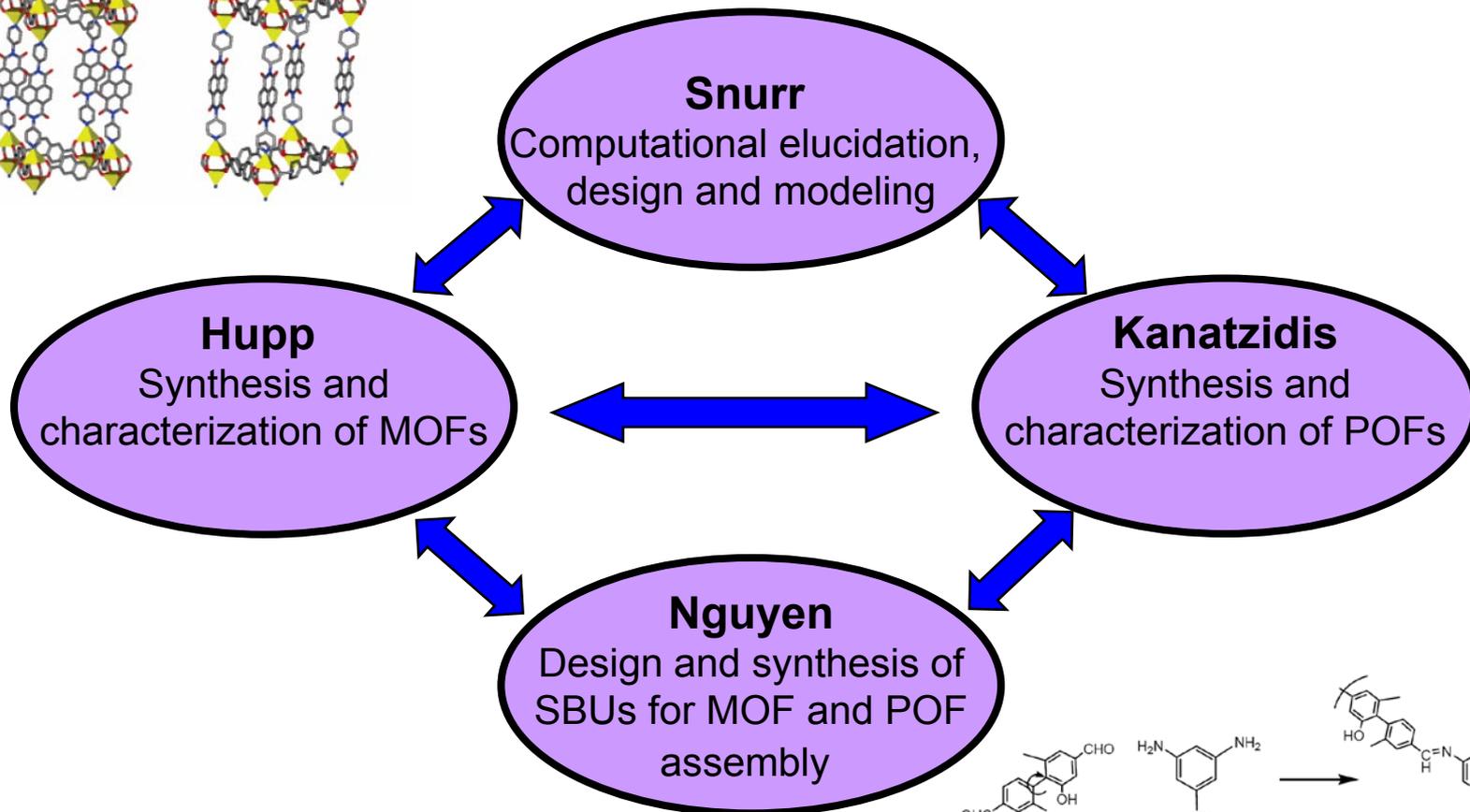
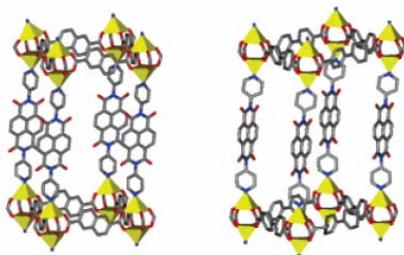
Objectives for Current Year

- Metal-organic frameworks
 - Develop MOFs containing functional groups that can bind hydrogen
 - Measure heats of adsorption and hydrogen uptake
- Polymer-organic frameworks
 - Develop new POFs with high heats of adsorption
 - Use building blocks that increase microporosity and can bind lithium and other ions
- Modeling
 - Determine whether catenation is beneficial
 - Develop model for cation-containing MOFs

Approach



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Approach



Enhance H₂ uptake via introduction of cations

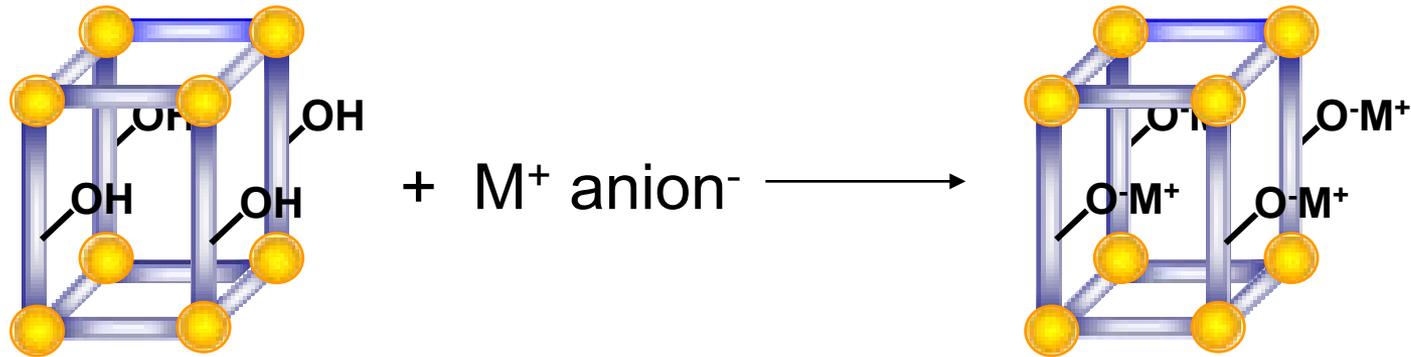
- Two approaches for introducing cations
 - Framework reduction
 - Alkoxide functionalization
- Mechanisms for increased uptake
 - Enhanced London dispersion interactions due to enhanced framework polarizability?
 - Enhanced adsorption due to increase in electric field?
 - Enhanced adsorption due to charge/quadrupole interactions?
 - Enhanced adsorption due to ion-induced displacement of catenated frameworks?

Approach



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Metal-organic Frameworks



- Introduce charge via desirable cations located on the organic linkers
- Cation placement known and controllable

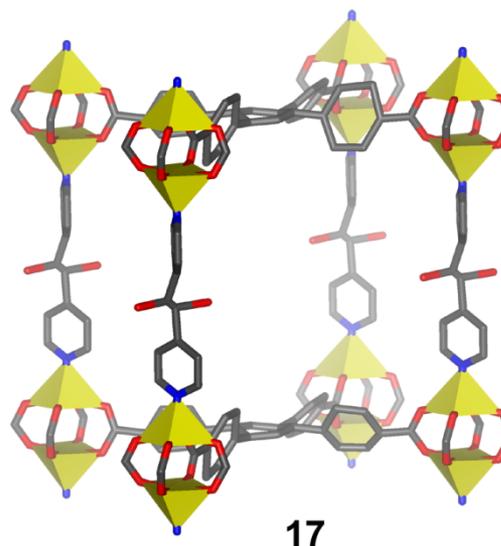
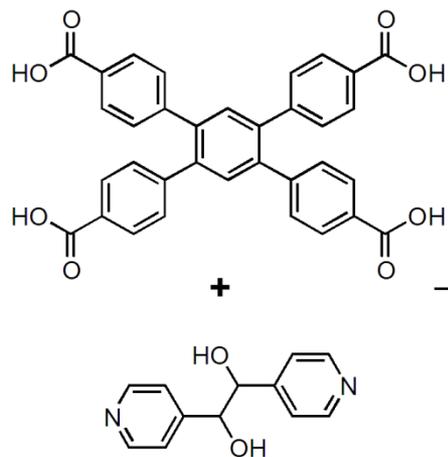
Approach



Metal-organic Frameworks

Key Milestones for FY 10

- Achieve 8 kJ/mol heat of adsorption at low coverage ✓
- Achieve 10 kJ/mol heat of adsorption at low coverage ✓
- Achieve 10 kJ/mol heat of adsorption with little drop-off at higher coverages (no less than 6 kJ/mol at highest coverage) ✓



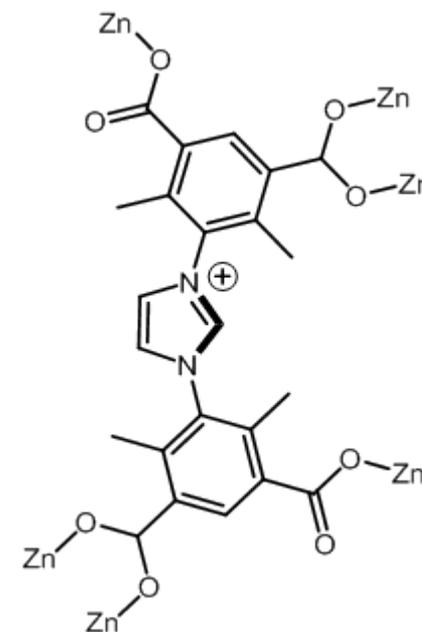
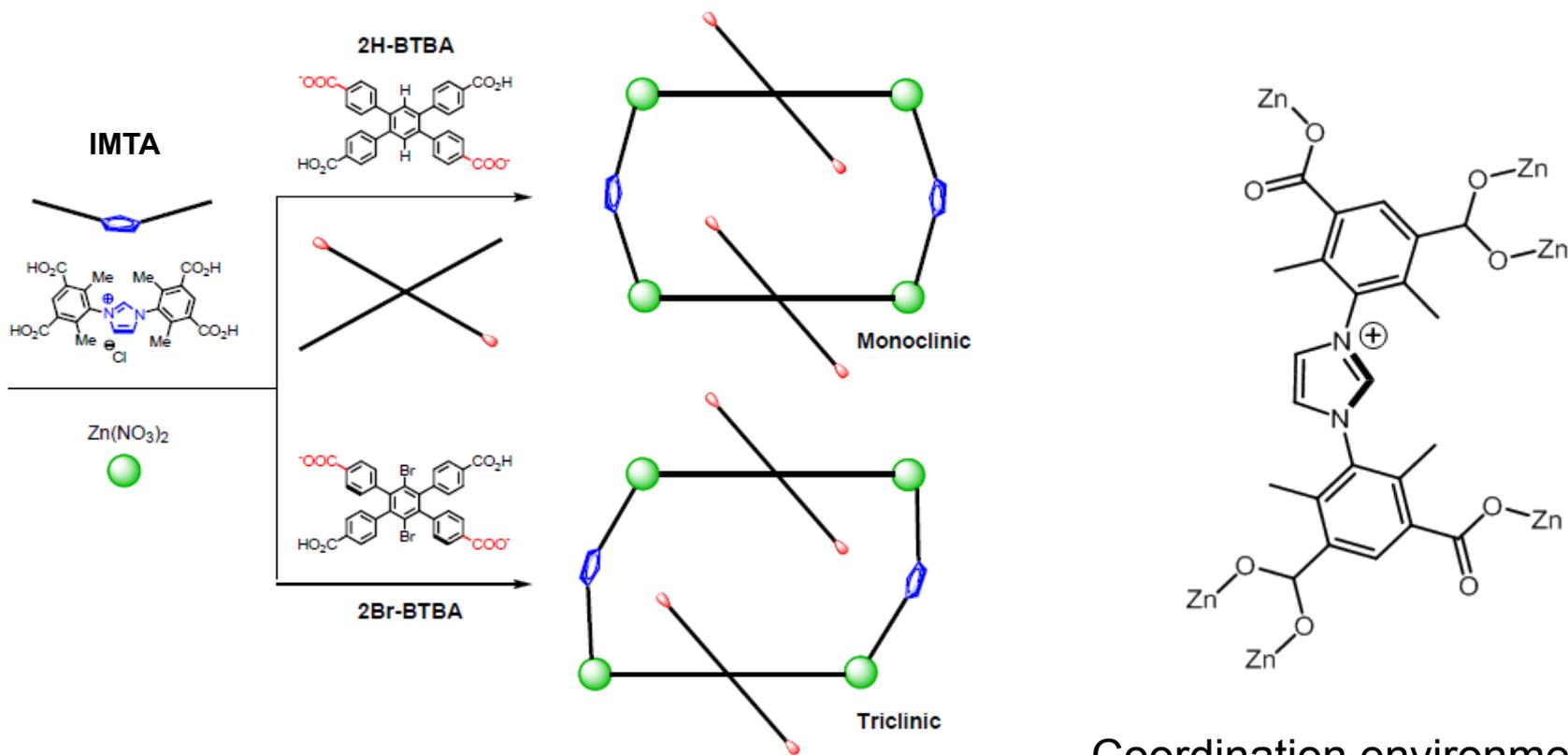
Hydroxyl-
functionalized MOFs

Technical Accomplishments

Another Approach: Charged Cavities



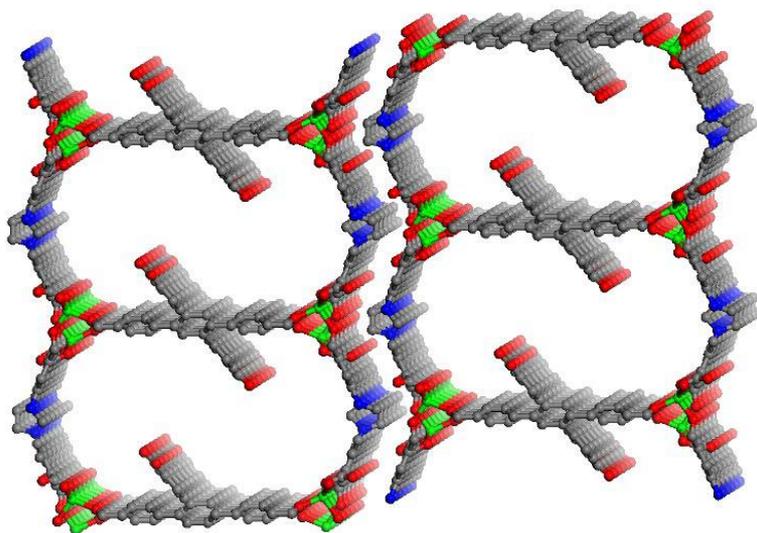
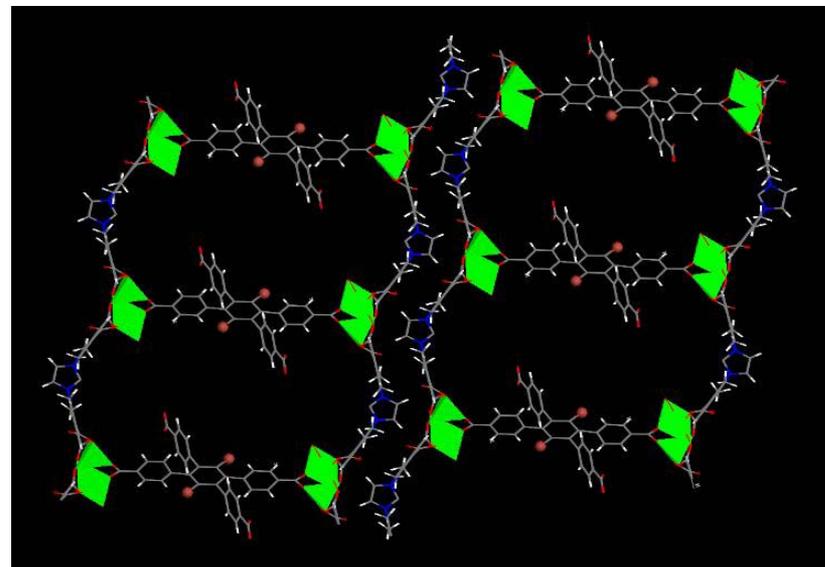
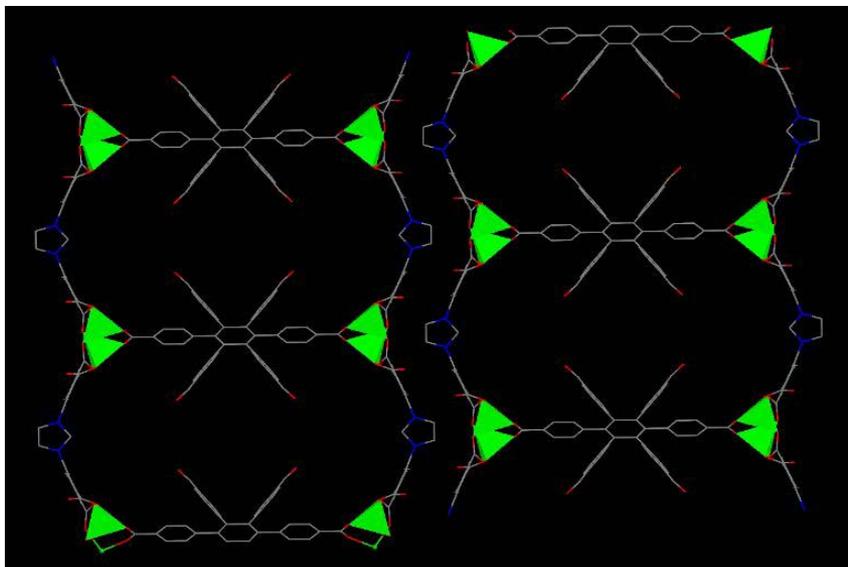
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Coordination environment
around IMTA linker

We have conceived and
synthesized a new class of
zwitterionic MOFs

Technical Accomplishments: Zwitterionic MOF - cavity and channel view



Pore Sizes based on linker lengths: 18 x 11 Å

BET Surface Area: 631 m²/g
Pore Volume: 27 cm³/g

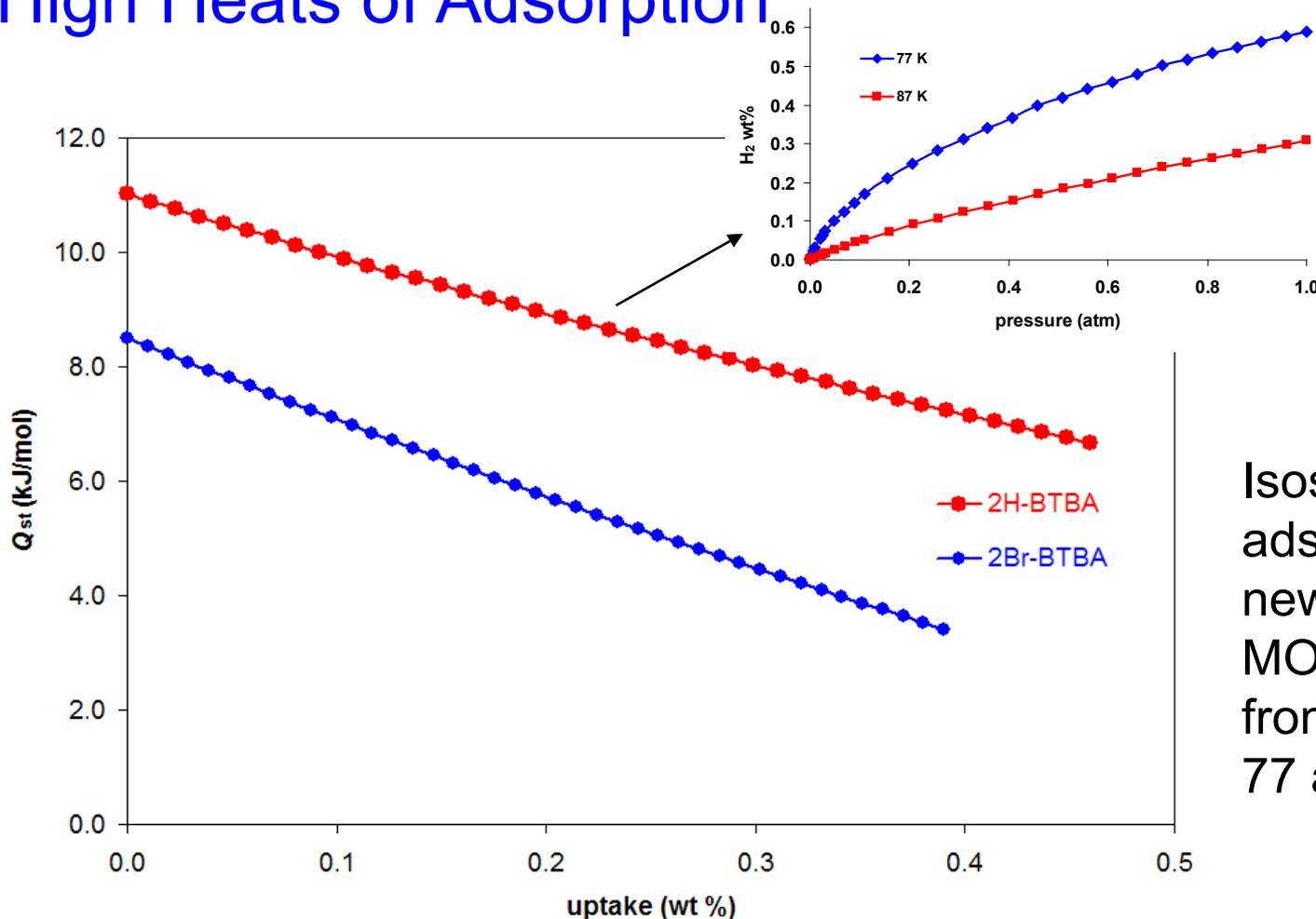
H-K Pore Size Distribution:
pores between 4-12 Å, with maximum around 6 Å

Technical Accomplishments

High Heats of Adsorption



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Excess H₂
isotherms in
2H-BTBA
zwitterionic MOF

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

Milestone for FY 10

Achieve 10 kJ/mol heat of adsorption

Approach



Polymer-organic Frameworks

- Tailorable, microporous polymers containing π -conjugated phenyl groups linked together
- Modular construction
 - Two synthesis methods
 - Schiff's base chemistry
 - "Click" chemistry
 - Unique class of materials not studied elsewhere
 - Components chosen to produce loosely-packed, extended 3D networks
- Attributes of POFs that make them attractive for hydrogen storage
 - Very low density
 - Three-dimensional semi-rigid character
 - Designed microporosity through inefficient packing of polymer chains
 - Built-in functional groups for tuning H_2 interaction
 - Ability to generate systematic series of materials will provide increased understanding of gas adsorption and ultimately optimization

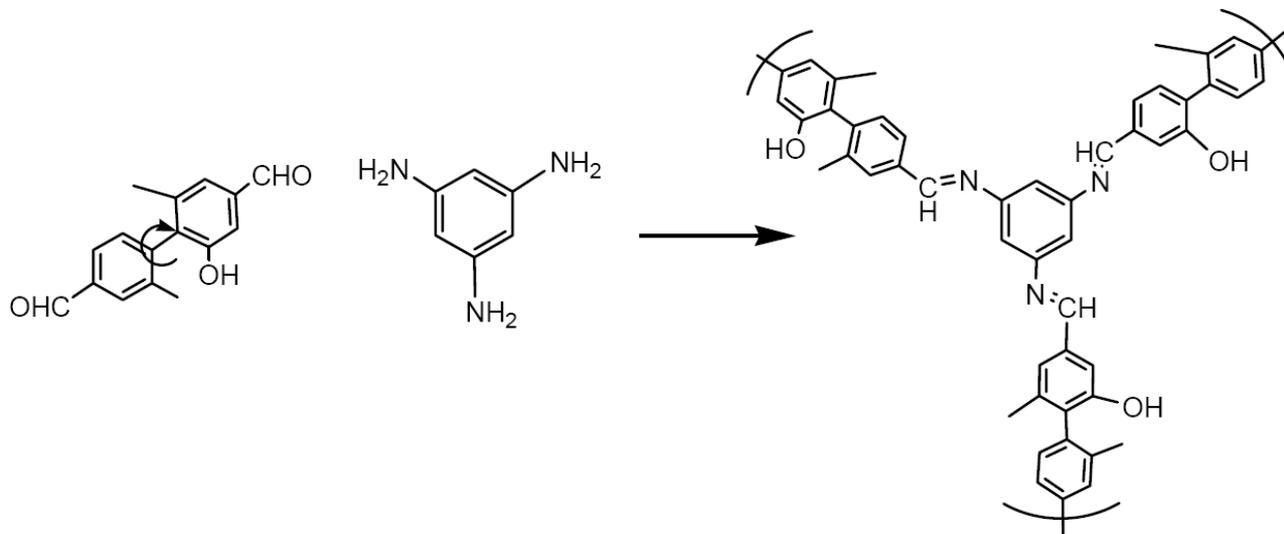
Approach



Polymer-organic Frameworks

Key Milestones for FY 10

- Synthesize POFs with surface areas $> 1500 \text{ m}^2/\text{g}$ ✓
- Introduce Li ions into POFs
- Achieve 8 kJ/mol heat of adsorption at low coverage ✓
- Achieve 10 kJ/mol heat of adsorption at low coverage

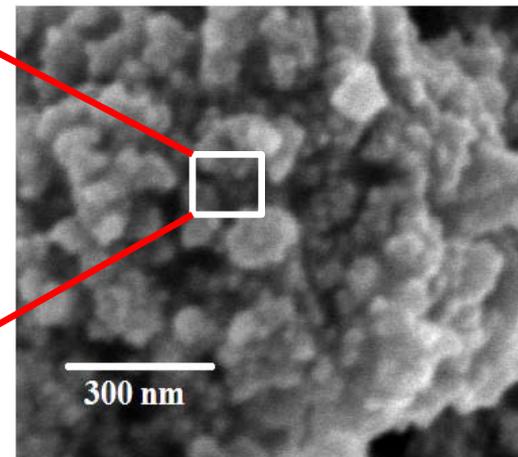
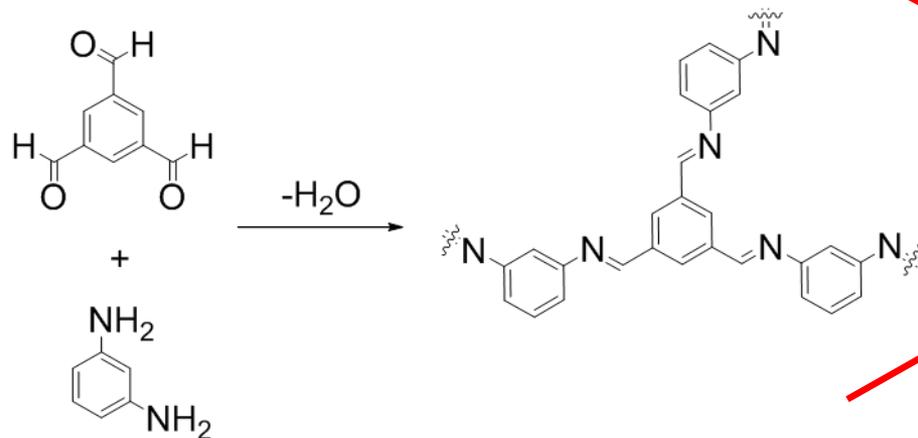


Technical Accomplishments

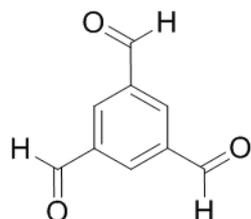
POFs based on Schiff base chemistry



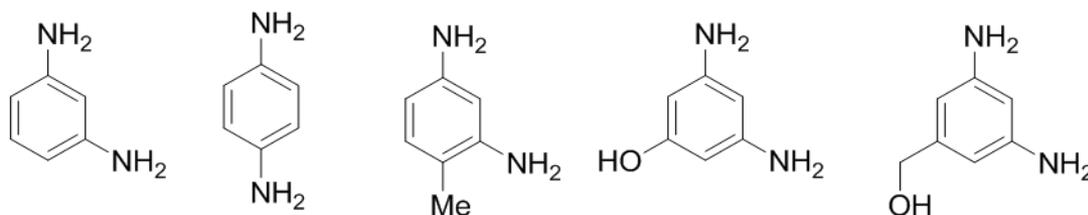
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1,3,5-triformylbenzene

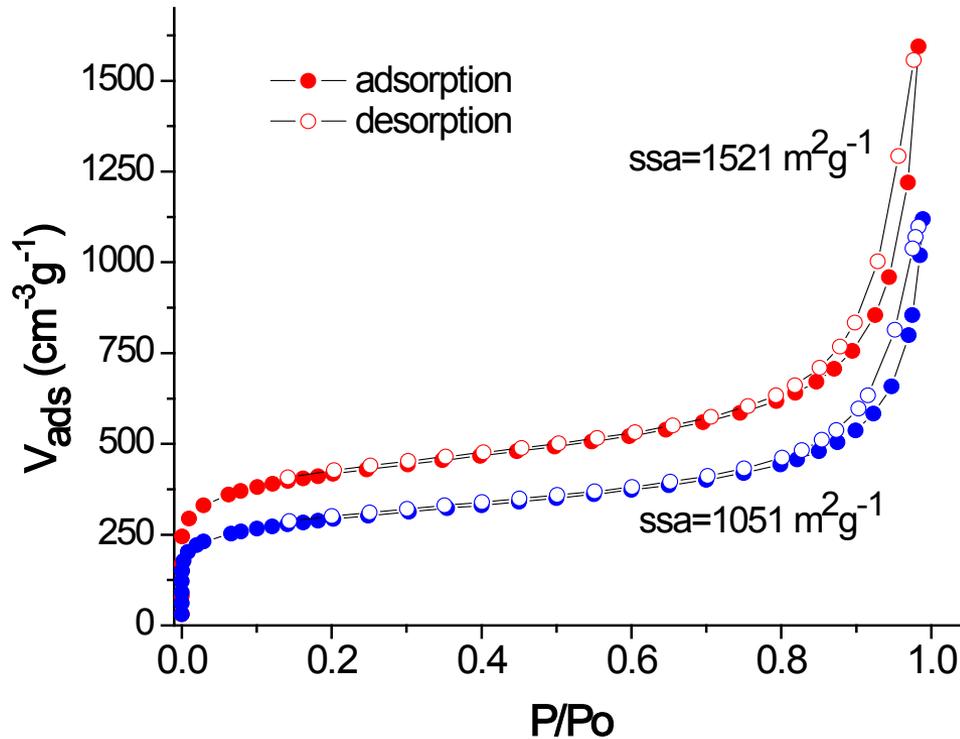


Amine monomers



- Simple reaction conditions
- Readily available starting materials and reagents
- Formation of product in high yields

Surface Area and Porosity of POFs



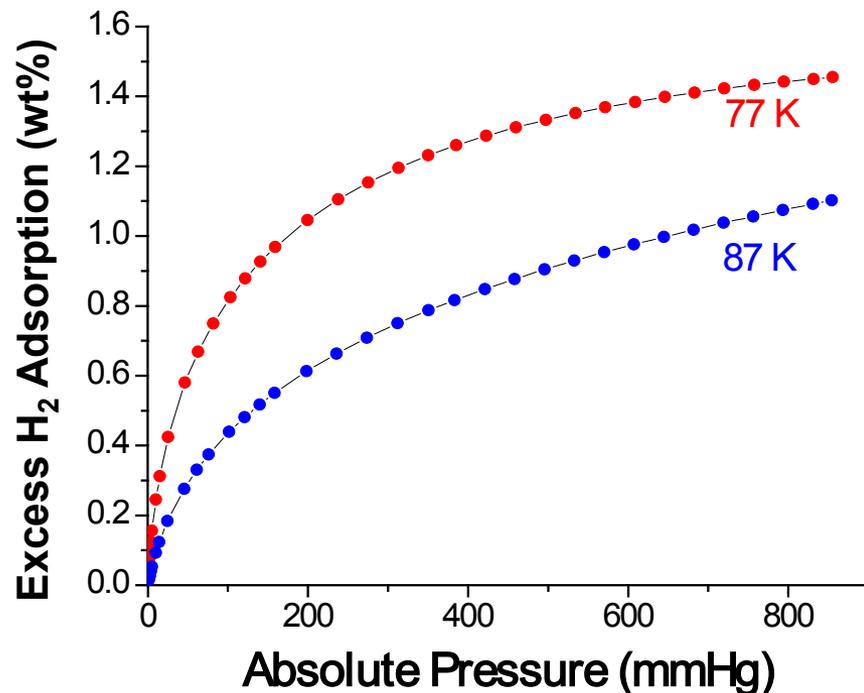
N₂ sorption at 77 K

Milestone for FY 10
Synthesize POFs with
surface areas > 1500 m²/g

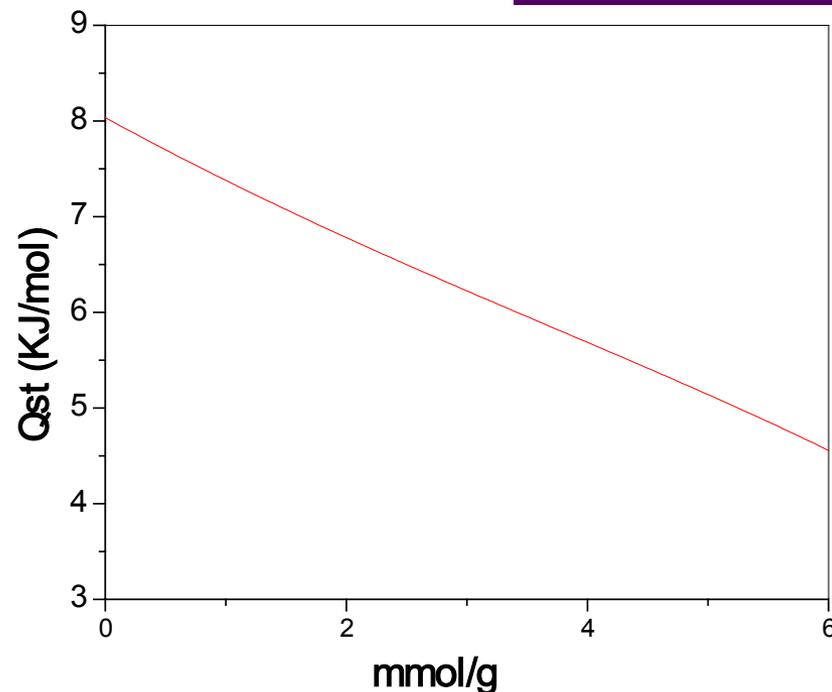
Sample	Specific surface area (m ² g ⁻¹)	Micropore volume (cm ³ g ⁻¹)	Total pore volume (cm ³ g ⁻¹)
POF-1	443	0.09	0.40
POF-2	1051	0.31	1.13
POF-3	1521	0.45	1.13

Technical Accomplishments

H₂ Storage and Heat of Adsorption



Hydrogen adsorption isotherm of **POF-3** at 77 K and 87 K.



Isosteric heat of H₂ adsorption of **POF-3**

- H₂ uptake up to 1.5 wt %
- **Milestone for FY 10:** Achieve 8 kJ/mol heat of adsorption at low coverage

Approach



Molecular Modeling

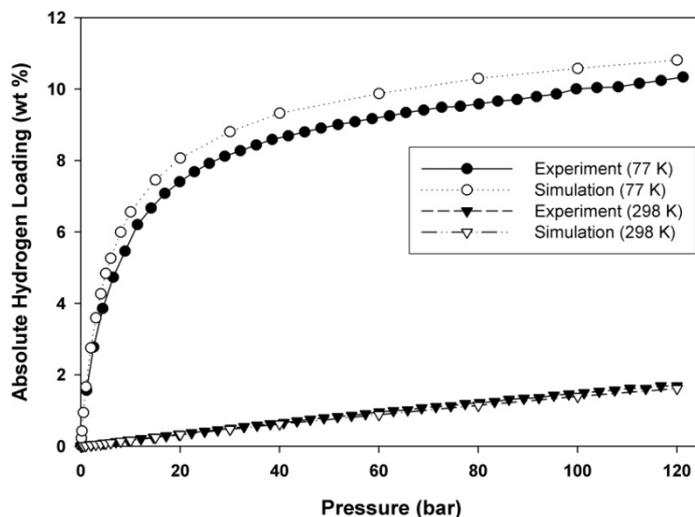
- Determine effect of catenation on H₂ adsorption in MOFs using
 - grand canonical Monte Carlo (GCMC) simulations
 - existing force fields that have been validated for other MOFs
- Develop model for cation-containing MOFs
 - Determine H₂/cation interactions with high-level quantum chemical methods (MP2 with large basis set)
 - Fit QM results to analytic forms for GCMC
 - Use GCMC to predict effects of different cations, cation loading, pore size, etc. on hydrogen uptake

Approach



Molecular Modeling

- Milestones for FY 10
 - Determine whether catenation is beneficial for hydrogen uptake in MOFs without cations ✓
 - Develop model for cation-containing MOFs ✓
 - Predict hydrogen isotherms, heats, and diffusivities in cation-containing MOFs



Past work: Hydrogen in IRMOF-1

Simulations: Ryan, Broadbelt, Snurr,
Chem. Comm., 2008.

Experiments: Kaye, Dailly, Yaghi, Long,
J. Am. Chem. Soc., 2007.

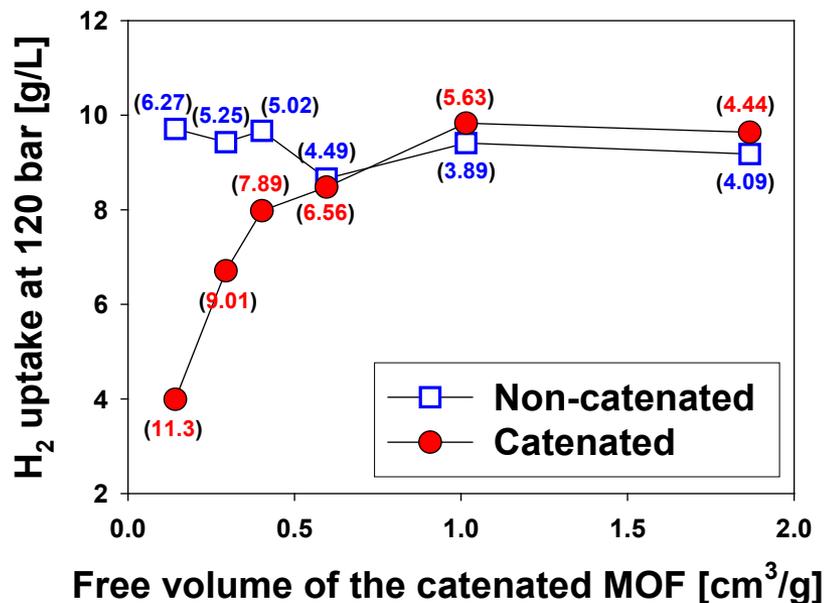
Technical Accomplishments

Is Catenation Beneficial for H₂ Storage?



Selected MOFs: 4 catenated MOFs synthesized at NU and their hypothetical non-catenated versions; 2 catenated IRMOFs (IRMOF-9 and IRMOF-15) and their non-catenated counterparts (IRMOF-10 and IRMOF-16). These materials have a wide range of pore sizes and free volumes.

Predicted Absolute Uptake at 298 K



Although catenation causes an increase in Q_{st} (numbers in parenthesis), the effect is not enough to compensate the loss of free volume that also arises from catenation.

→ Need strong binding sites

Technical Accomplishments

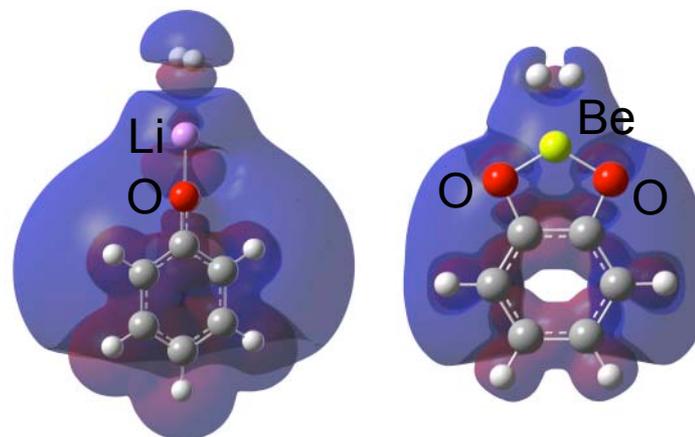
H₂ Adsorption on Alkoxide Aromatics



MP2/6-311+G**

- Binding energies
 - are caused by strong positive cation charges
 - are stronger in alkaline earths than alkalis
 - decrease as atomic number increases
- Predicted Be and Mg energies are larger than highest observed to date in literature
 - Ni-CPO-27: 13.5 kJ/mol

Metal alkoxide	Metal charge	H ₂ + * → H ₂ * Energy (kJ/mol)
O-Be-O	+1.2	-43
O-Mg-O	+1.6	-22
O-Li	+0.9	-10
O-Na	+0.9	-2



red: electron density accumulation, blue: depletion

Technical Accomplishments

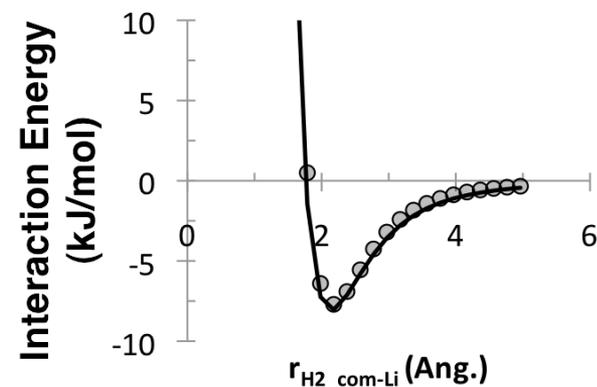
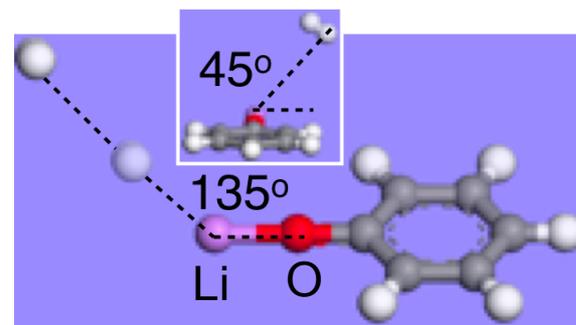
Model for Cation-Containing MOFs



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- *ab initio*-based force field for alkoxide groups
 - Morse, Coulomb potentials
 - Fit to 200 single points
 - MP2/6-311+G**
- Lennard-Jones potentials from DREIDING force field for other framework atoms

→ Model now finished



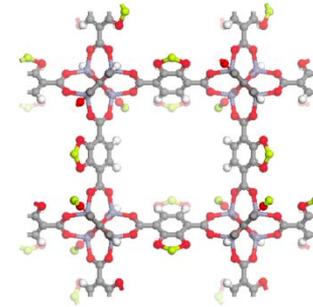
points: QM energies, lines: fitted force fields.
Force fields based on 12 'approaches.'

Technical Accomplishments

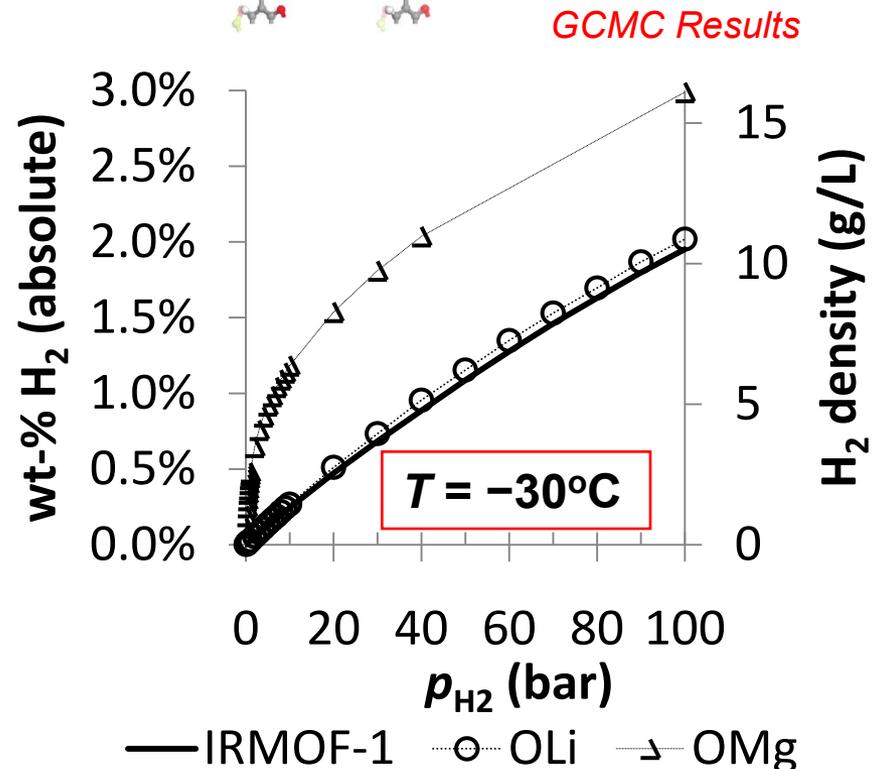
Modeling H₂ Storage in Alkoxide Functionalized IRMOF-1



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- Li- and Mg-alkoxide functionalization shown
 - One functional group per linker
 - Isotherm for unfunctionalized IRMOF-1 matches experiment at 77 K and 298 K (slide 18).
- Significant enhancement predicted for Mg-alkoxide functionalization
- H₂ molecules saturate the Mg sites ~ 40 bar and then adsorb on the rest of the MOF.





Collaborations

- Argonne National Laboratory
 - Dr. Karen Mulfort: SAXS and other characterization
 - Dr. Randy Winans: SAXS and WAXS characterization
 - Dr. Peter Stair: Raman characterization
- Universidade Federal Ceara, Fortaleza, Brazil
 - Profs. Celio Cavalcante, Diana Azabedo, Mardonio Lucena: high-pressure adsorption measurements, round-robin validation of uptake measurements
- Nature of the collaborations
 - We have existing relations with these groups, but the collaboration on hydrogen storage is just starting.
 - These groups are external to the DOE H₂ Program

Summary



- We are developing new materials to meet DOE hydrogen storage targets. New concept is to introduce cations into MOFs and POFs to **improve heats of adsorption**, which will improve room temperature storage. With these new chemistries in hand, we can combine them with methods for increasing surface area later.
- We have synthesized a new class of MOFs
 - Functional groups can be tailored to increase the H₂ heat of adsorption
 - Achieved 11 kJ/mol heat of adsorption
- We have synthesized a variety of new POFs
 - Functional groups can be tailored to increase the H₂ heat of adsorption
 - Achieved 1500 m²/g
 - Achieved 8 kJ/mol heat of adsorption
- We have developed useful models for catenated and functionalized MOFs
 - Modeling predicts that catenation alone is not a viable strategy for achieving DOE H₂ targets in MOFs
 - Alkaline earth alkoxide groups are promising targets

Proposed Future Work



- MOFs
 - Introduce Mg cations
 - Develop high-surface-area, cation-containing MOFs
 - Continue to measure H₂ uptake and heats in new materials
 - Measure high-pressure, room-temperature isotherms in most promising materials
- POFs
 - Introduce cations into POFs and optimize
 - Continue to measure H₂ uptake and heats in new materials
 - Continue efforts to further increase surface areas
 - Start “click” chemistry for making new POFs
- Modeling
 - Validate model against experimental data
 - Determine optimal combination of heat of adsorption and surface area
 - Extend modeling to POFs
- Go/No-Go Decision during FY 10
 - Heats of adsorption above 10 kJ/mol
 - The Phase 2 transition could include down selecting materials.



Summary

April 2010

Best Sample from Each Class	Surface Area (m²/g)	Total Pore Volume (cm³/g)	Excess H₂ Uptake at 77 K and 1 bar (wt%)	Isosteric Heat of Adsorption (kJ/mol)
Alkoxide MOF	840	0.46	1.3	6.6
Zwitterionic MOF	631	0.27	0.5	11
POF	1521	1.13	1.5	8

April 2009

Best Sample from Each Class	Surface Area (m²/g)	Total Pore Volume (cm³/g)	Excess H₂ Uptake at 77 K and 1 bar (wt%)	Isosteric Heat of Adsorption (kJ/mol)
Alkoxide MOF	840	0.46	NA	NA
Zwitterionic MOF	Material not yet conceived	NA	NA	NA
POF	Material being synthesized	NA	NA	NA