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EFRC-NETL Research on Carbon Capture and ARPA-e

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Center for Gas Separations Relevant to Clean Energy Technologies

an Office of Basic Energy Sciences
Energy Frontier Research Center

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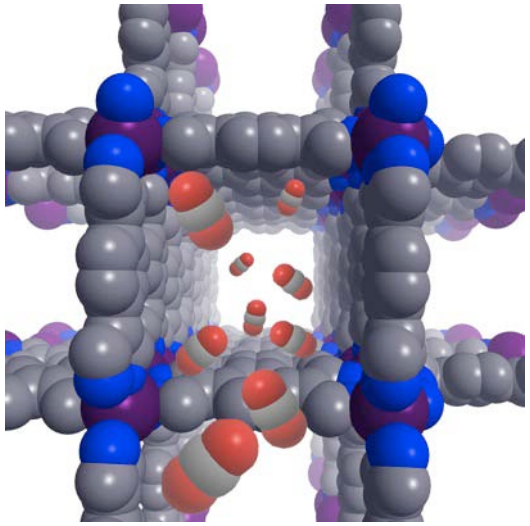
Center for Gas Separations Relevant to Clean Energy Technologies

Berend Smit and Jeff Long (UC Berkeley)

The aim of this EFRC is to develop new strategies and materials that allow for *energy efficient* selective *capture* or *separation* of CO_2 from gas mixtures based on molecule-specific chemical interactions.



RESEARCH PLAN AND DIRECTIONS

Capture of CO_2 from gas mixtures requires the molecular control offered by nanoscience to tailor-make those materials exhibiting exactly the right adsorption and diffusion selectivity to enable an economic separation process. Characterization methods and computational tools will be developed to guide and support this quest.

EFRC

- Solid Adsorbents
  - Jeffrey Long (UC Berkeley):
  - Omar Yaghi (UCLA)
  - Hong-Cai Zhou (Texas A&M)
- Polymer Membranes:
  - Frantisek Svec and Jean Frechet (LBNL)
  - Bret Helm and Ting Xu (LBNL)
  - Dave Luebke (NETL)
- Characterization
  - Resonance soft X-rays: Blandine Jerome and Jeff Kortright (LBNL)
  - X-ray crystallography: Simon Teat (LBNL)
  - NMR: Jeffrey Reimer (UC Berkeley)
- Computation
  - Adsorption and Diffusion: Berend Smit (UC Berkeley)
  - Electronic Structure calculation: Jeff Neaton (Molecular Foundry, LBNL) and Gullia Galli (UC Davis)
  - Quantum calculations: Laura Gagliardi (U Minessota)
  - Materials Screening: Maciej Haranczyk (LBNL)

Methods of Reducing Power Plant CO_2 Emissions

	primary separation
1. **Postcombustion CO_2 capture**:	**CO_2 from N_2**
2. Precombustion CO_2 capture:	CO_2 from H_2
3. Oxyfuel combustion:	O_2 from N_2

Long-group (Berkeley)

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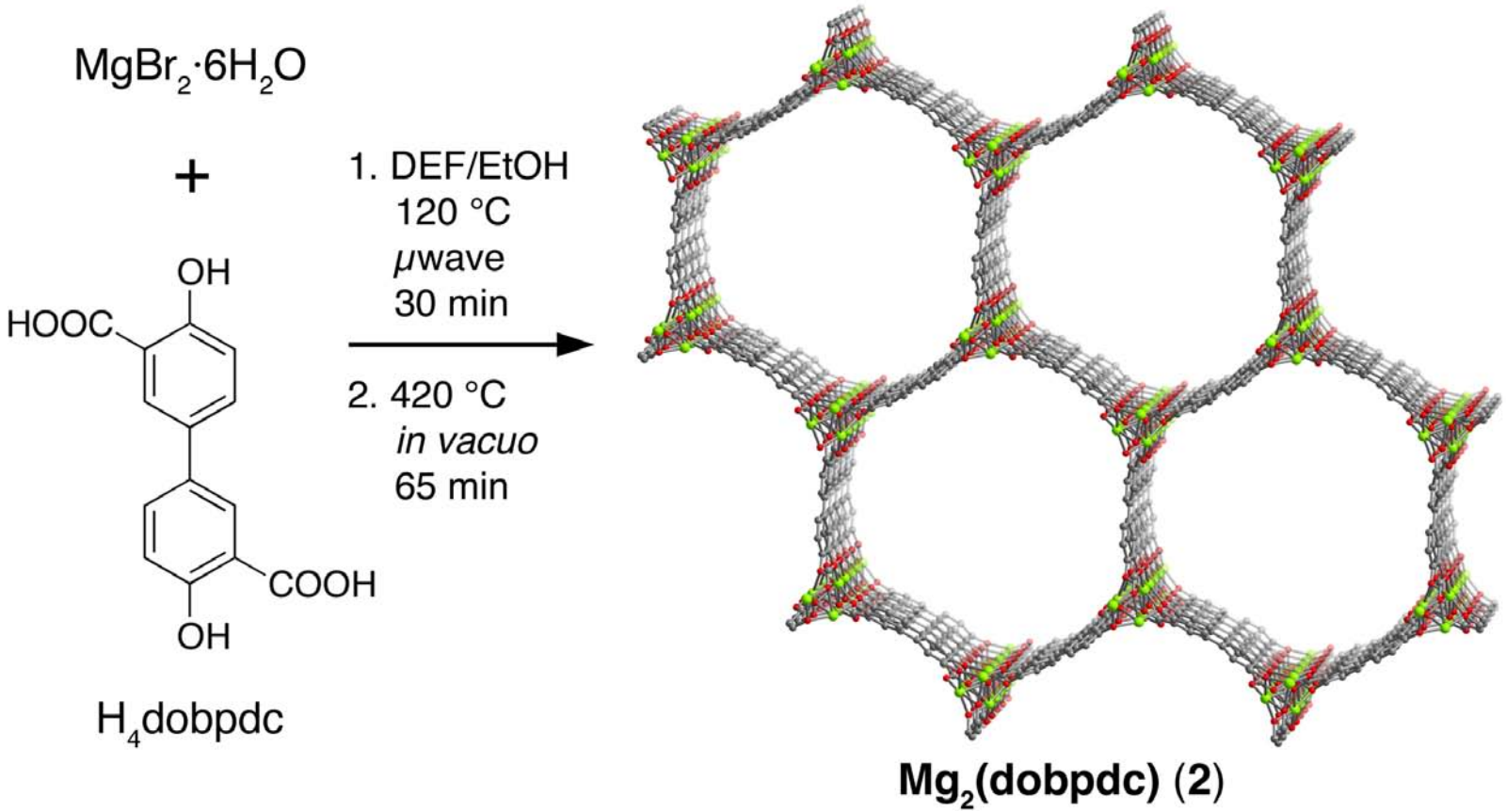
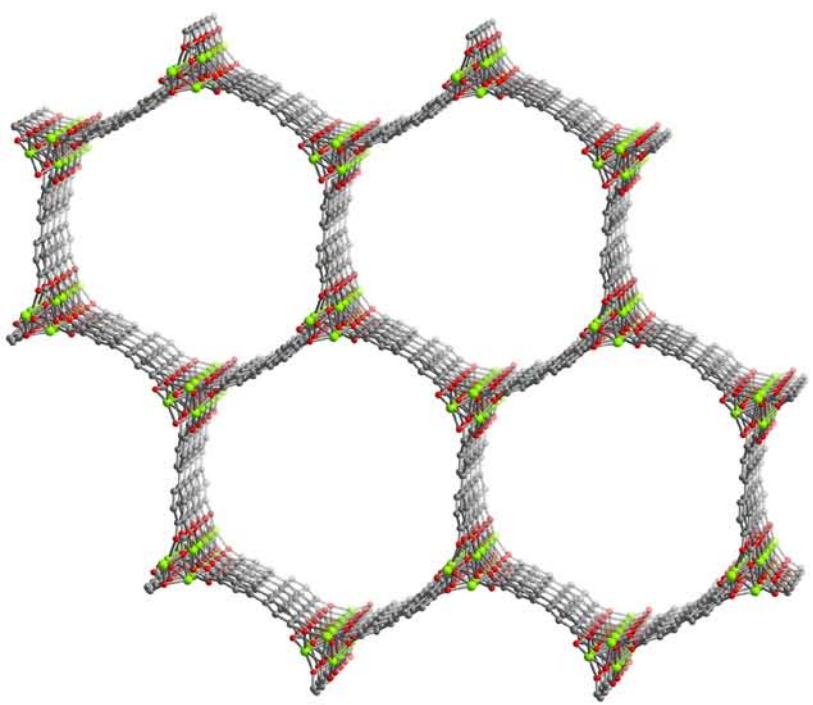
An Expanded Form of $Mg_2(dobdc)$ (Mg-MOF-74)



- Expanded channels have a diameter of 18 Å and are lined with open Mg^{2+} sites

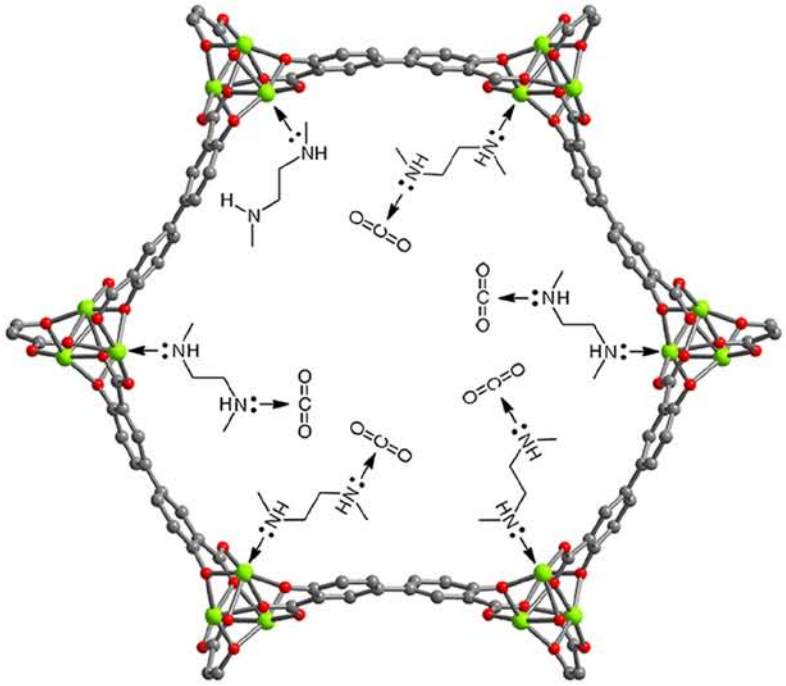
McDonald, Lee, Mason, Wiers, Hong, Long *J. Am. Chem. Soc.* **2012**, *134*, 7056

Appending Diamine Groups



$Mg_2(dobpdc)$

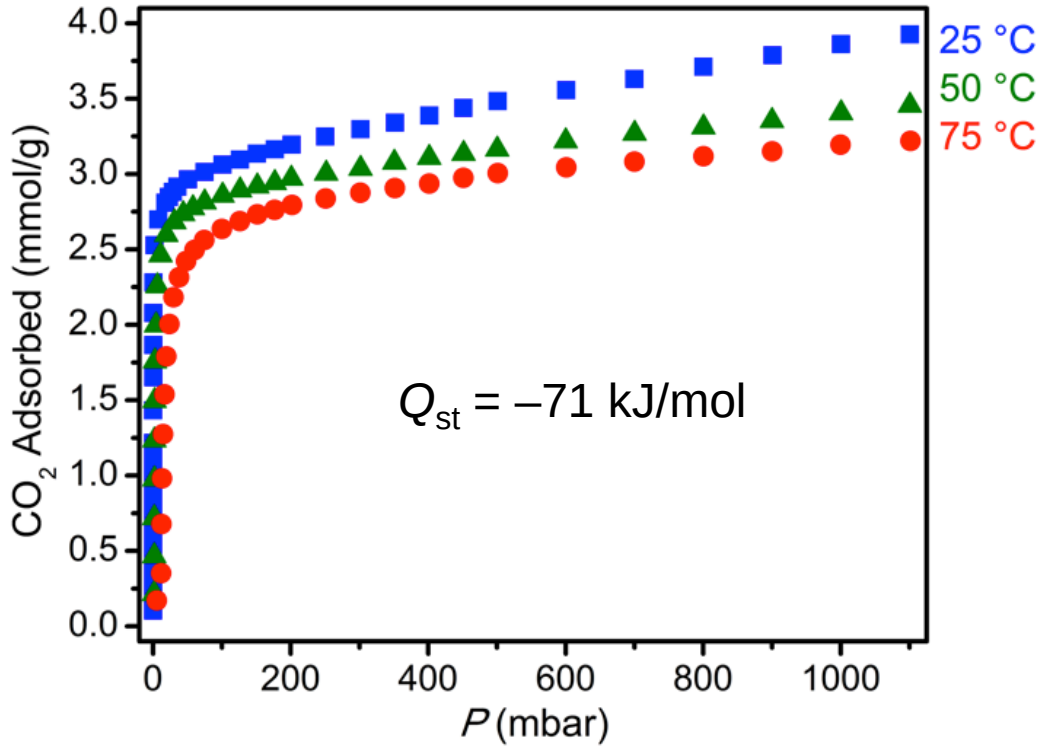
1. mmen
   C_6H_{14}
   24 h
2. 100 °C
   in vacuo
   6 h
3. CO_2



mmen-Mg_2(dobpdc) + CO_2

McDonald, Lee, Mason, Wiers, Hong, Long *J. Am. Chem. Soc.* **2012**, *134*, 7056

Strong CO_2 Binding



- High affinity of alkylamines for CO_2 results in high capacity at low pressure
- Very little N_2 uptake observed, leading to high selectivity of S = 200

McDonald, Lee, Mason, Wiers, Hong, Long *J. Am. Chem. Soc.* **2012**, *134*, 7056

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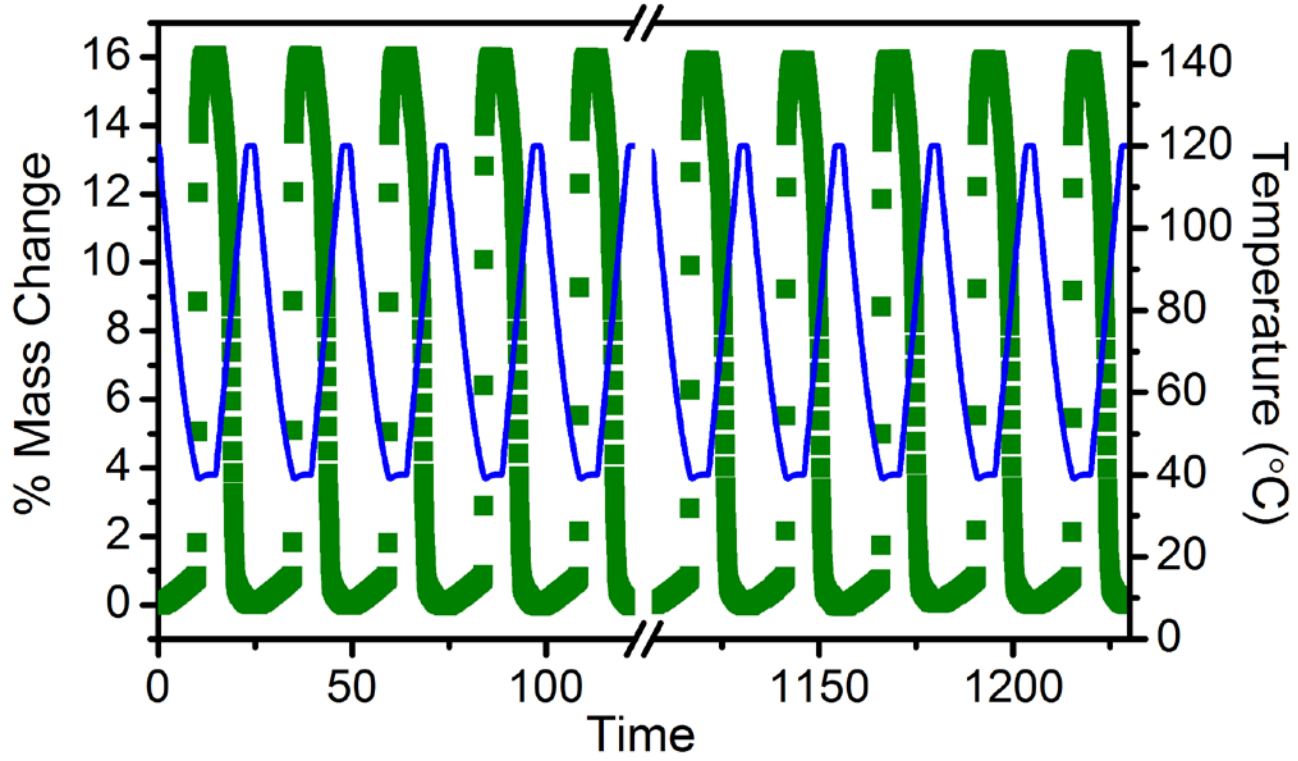
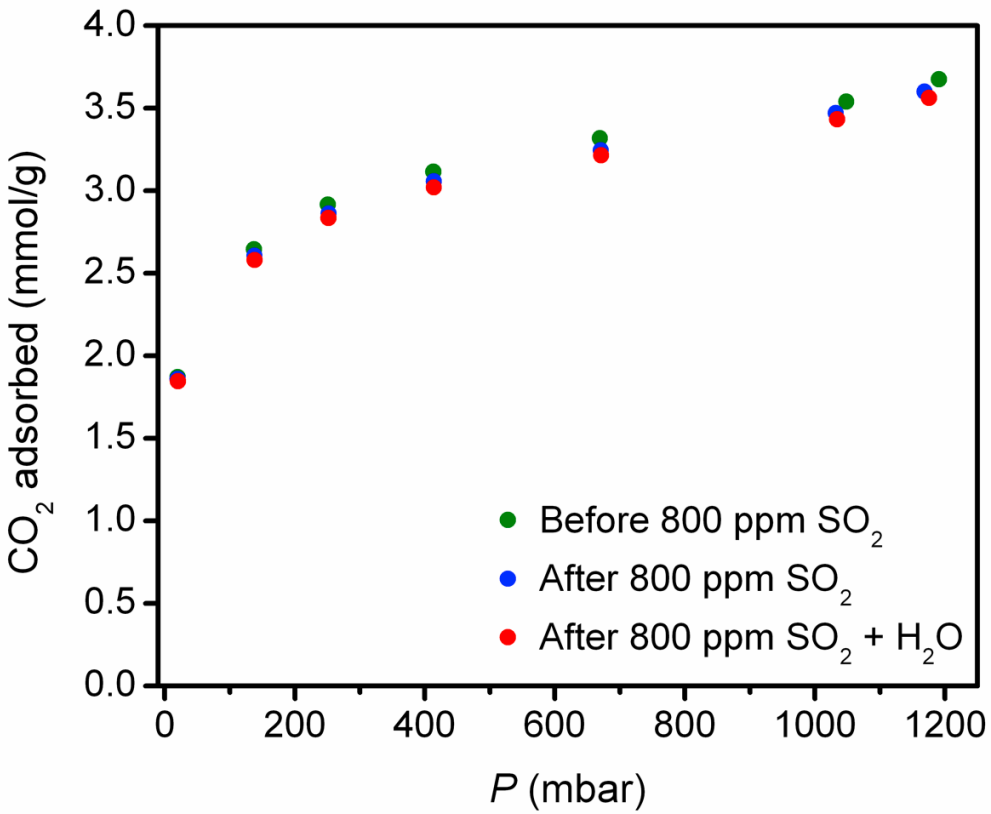
Cycling CO_2 Removal from 15% CO_2 in N_2



- Capacity of 14 wt % achieved with loss of at most 0.1 wt % after 50 cycles
- Performance in the presence of water needs to be investigated

McDonald, Lee, Mason, Wiers, Hong, Long *J. Am. Chem. Soc.* **2012**, *134*, 7056

Preliminary Study of Effects of SO_2 and Water



- Initial exposure to SO_2 and water do not greatly reduce CO_2 capacity
- **New ARPA-E instrument will enable cycling studies with realistic flue gas**

Methods of Reducing Power Plant CO_2 Emissions

		primary separation
1.	Postcombustion CO_2 capture:	CO_2 from N_2
2.	**Precombustion CO_2 capture:**	**CO_2 from H_2**
3.	Oxyfuel combustion:	O_2 from N_2

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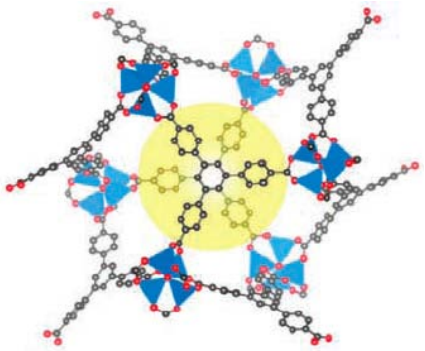
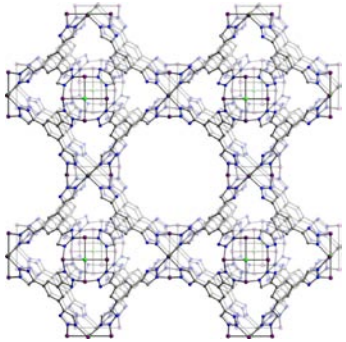
MOFs Tested for CO_2/H_2 Separation

MOF-177



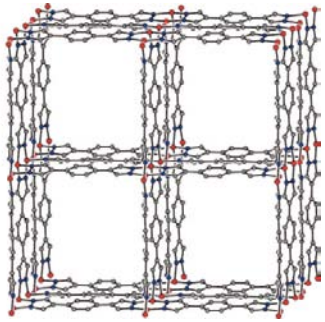
SA_{BET} = 4690 m^2/g

Cu-BTTri



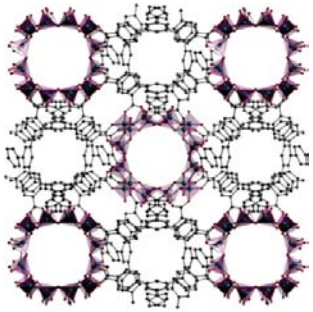
SA_{BET} = 1750 m^2/g

Co(BDP)



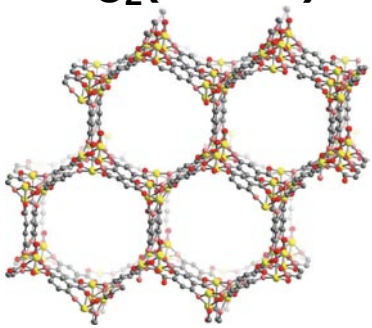
SA_{Lan} = 2670 m^2/g

Be-BTB



SA_{BET} = 4030 m^2/g

Mg_2(dobdc)



SA_{BET} = 1800 m^2/g

Investigate:

high surface area

open metal sites

flexibility

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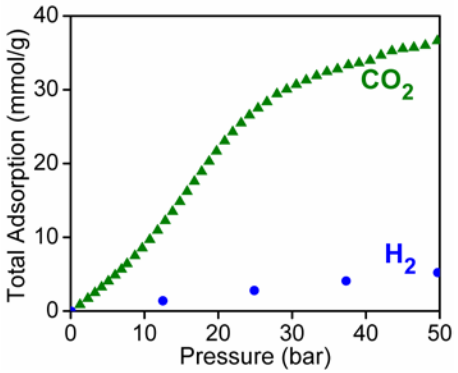
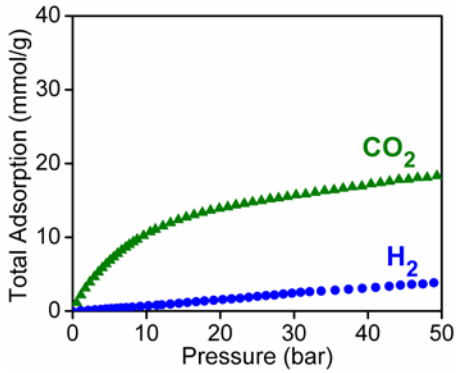
CO_2/H_2 Adsorption at 40 °C in Selected MOFs

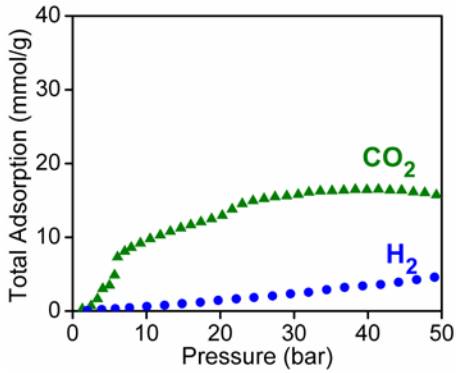
MOF-177



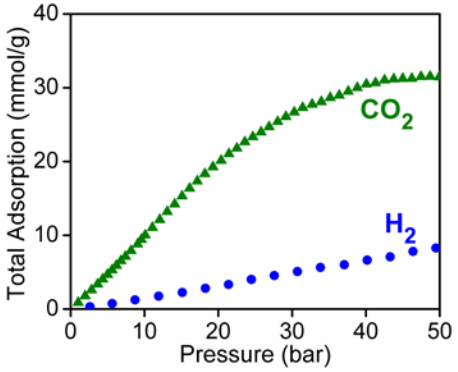
Cu-BTTri



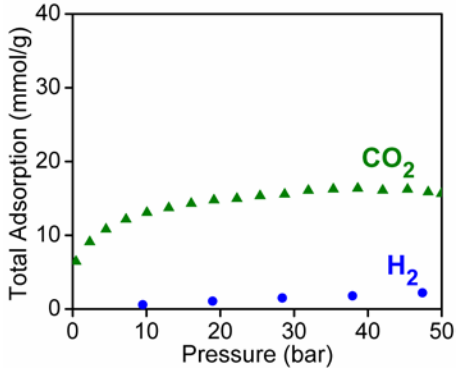
Co(BDP)



Be-BTB



$Mg_2(dobdc)$



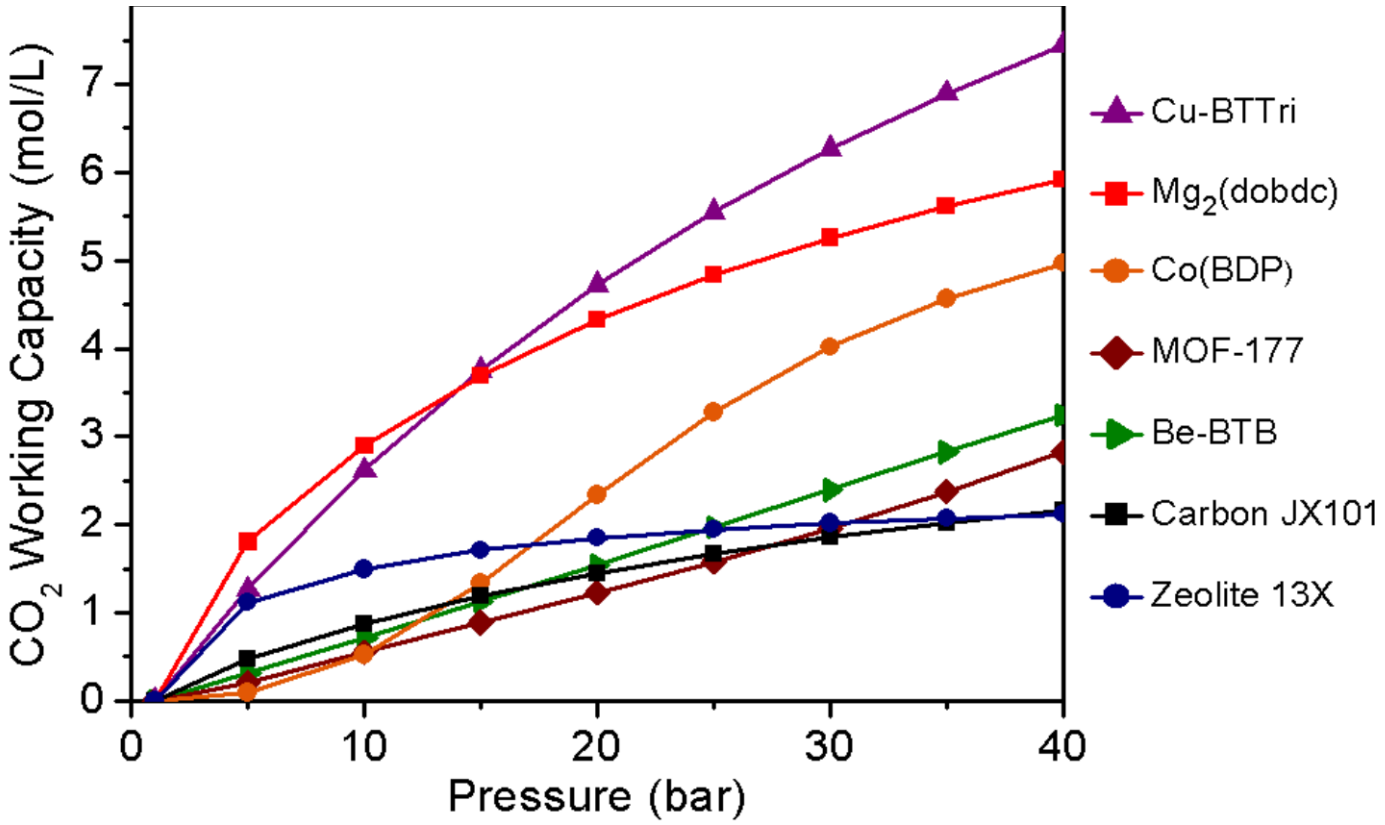
High surface area gives high CO_2 capacity

Open metal sites give better selectivity

Herm, Swisher, Smit, Krishna, Long *J. Am. Chem. Soc.* **2011**, *133*, 5664

CO_2 Working Capacity for 1:4 Mixture at 40 °C

Using Ideal Adsorbed Solution Theory (IAST) with 1 bar purge pressure:



Herm, Swisher, Smit, Krishna, Long *J. Am. Chem. Soc.* **2011**, *133*, 5664

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Methods of Reducing Power Plant CO_2 Emissions

	primary separation
1. Postcombustion CO_2 capture:	CO_2 from N_2
2. Precombustion CO_2 capture:	CO_2 from H_2
3. Oxyfuel combustion:	**O_2 from N_2**

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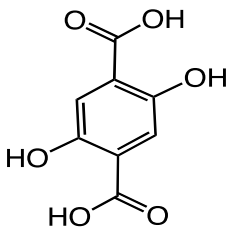
A Framework with Accessible Fe^{II} Sites

Can distinguish O_2 from N_2 by its greater propensity for accepting electrons transferred from a redox-active metal:

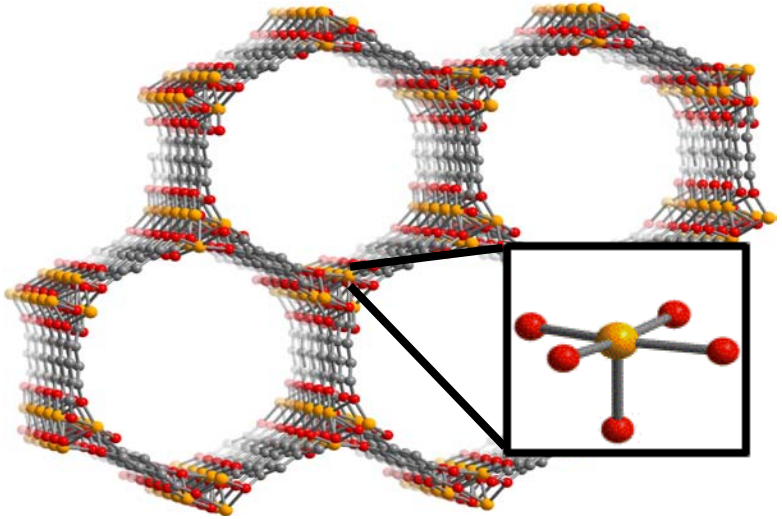
$$M^{n+} + O_2 \longrightarrow M^{(n+1)+}—O_2^-$$

$FeCl_2$

+



H_4dobdc



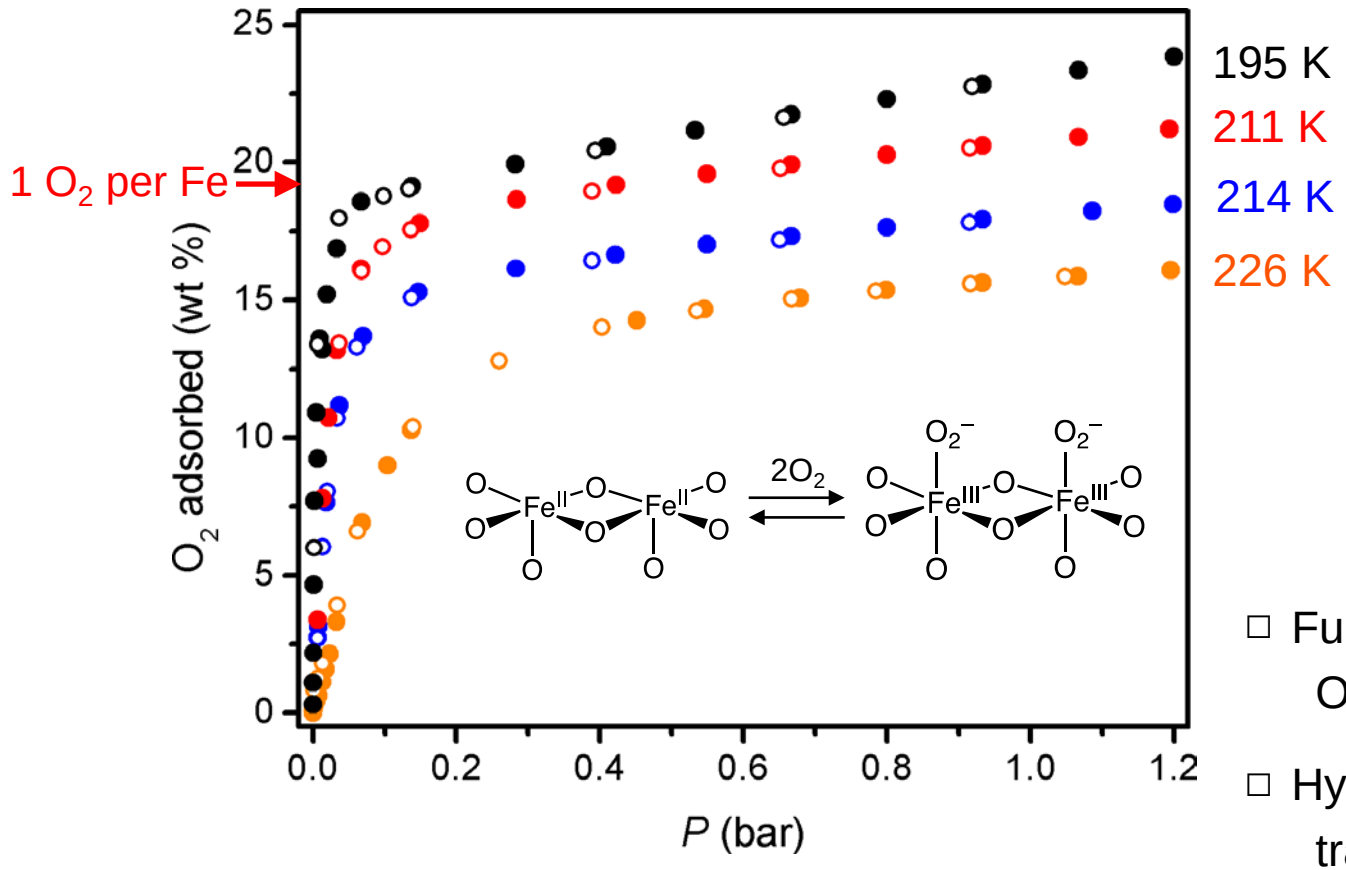
Fe_2(dobdc)

- Desolvation leads to square pyramidal Fe^{II} centers with open coordination site

Bloch, Murray, Queen, Maximoff, Chavan, Bigi, Krishna, Peterson, Grandjean, Long, Smit, Bordiga, Brown, Long

J. Am. Chem. Soc. **2011**, *133*, 14814

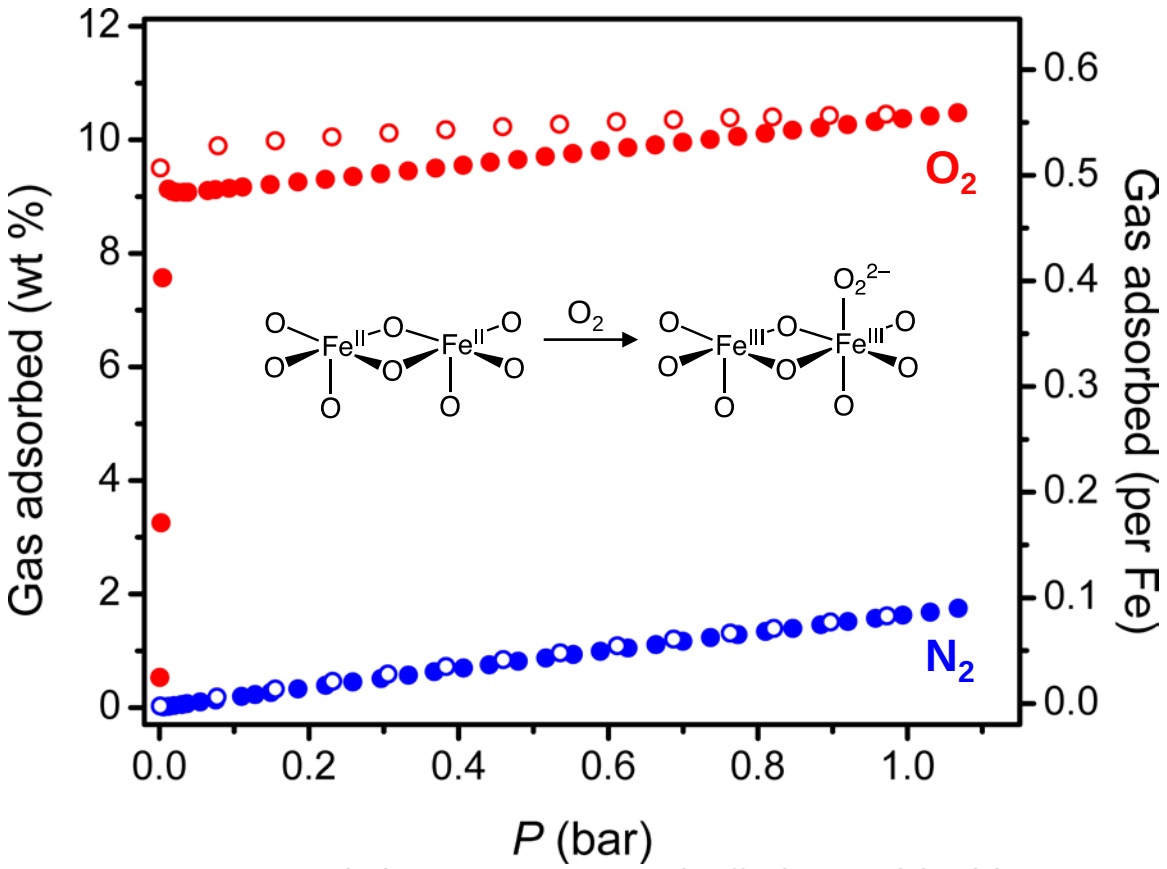
Reversible O_2 Binding at Lower Temperatures



Bloch, Murray, Queen, Maximoff, Chavan, Bigi, Krishna, Peterson, Grandjean, Long, Smit, Bordiga, Brown, Long
J. Am. Chem. Soc. **2011**, *133*, 14814

- Fully reversible uptake of one O_2 molecule per Fe center
- Hypothesis: one electron transfers from each Fe to give Fe^{III}—O_2^-

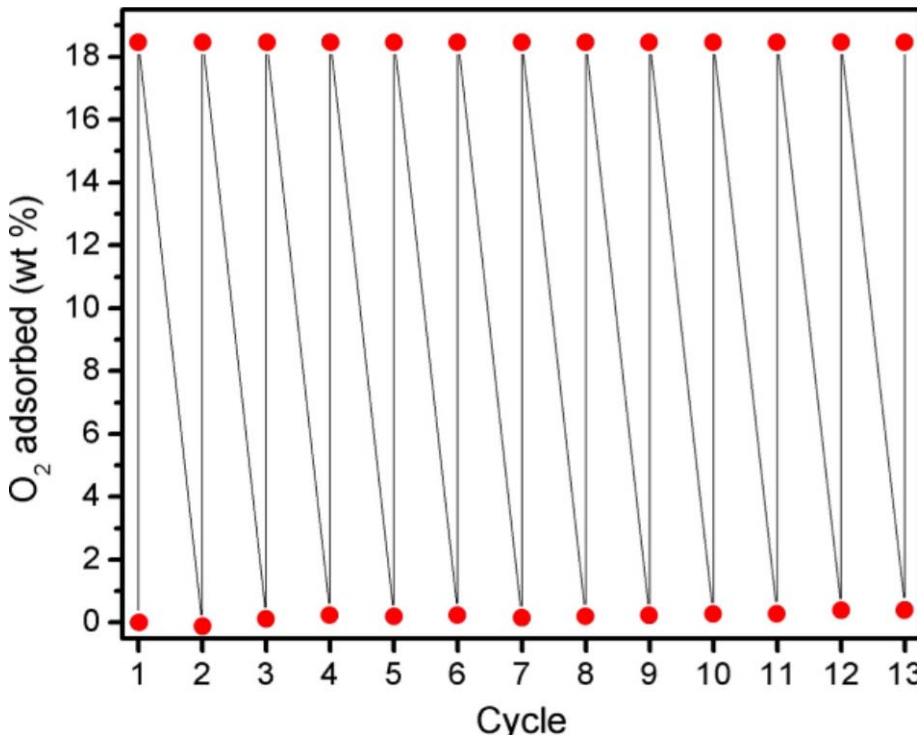
Irreversible O_2 Binding in Fe_2(dobdc) at 298 K



- Irreversible uptake of 1 O_2 molecule for every 2 Fe centers
- Hypothesis: two electrons transfer, one from each Fe, to give Fe^{III}—O_2^{2-}

Bloch, Murray, Queen, Maximoff, Chavan, Bigi, Krishna, Peterson, Grandjean, Long, Smit, Bordiga, Brown, Long
J. Am. Chem. Soc. **2011**, *133*, 14814

Rapid O_2 Adsorption/Desorption Cycling at 211 K



- Adsorption upon exposure to 0.2 bar O_2 for 2 min
- Desorption upon exposure to vacuum for 25 min

Bloch, Murray, Queen, Maximoff, Chavan, Bigi, Krishna, Peterson, Grandjean, Long, Smit, Bordiga, Brown, Long
J. Am. Chem. Soc. **2011**, *133*, 14814

High-Throughput Synthesis

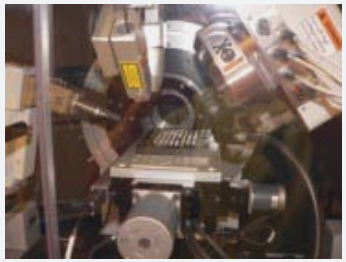
Highly-parallel, automated discovery of new MOFs

Automated Solid and Liquid Dosing

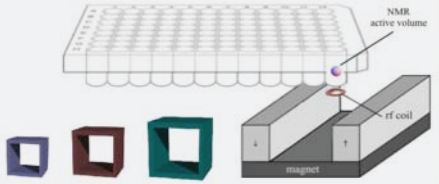
New Structure Types

High-Throughput Characterization

Rapid identification of new porous materials

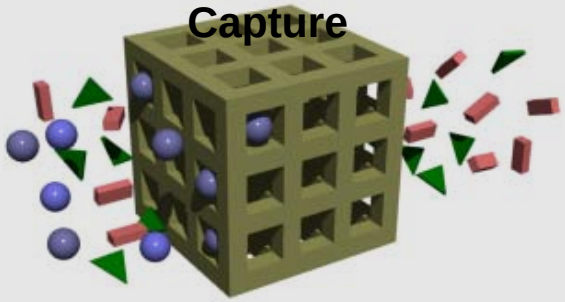


Powder X-ray Diffraction



NMR Porosity Screening

High-Throughput Discovery of Robust Metal-Organic Frameworks for CO_2 Capture



Berkeley Lab

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Eric R. Masanet

arpa·e
Advanced Research Projects Agency • ENERGY

Wildcat Discovery Technologies

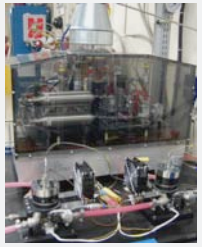
Steven S. Kaye

EPRI ELECTRIC POWER RESEARCH INSTITUTE

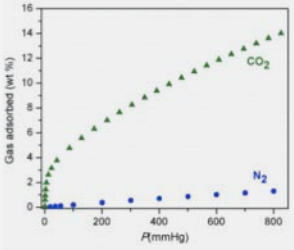
Abhoyjit S. Bhown

CO_2 Adsorption Screening

Rapid screening of CO_2 capture performance



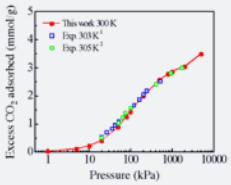
High-throughput Instrumentation

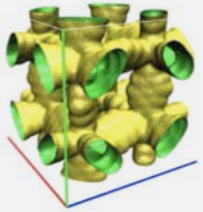


Adsorption Data

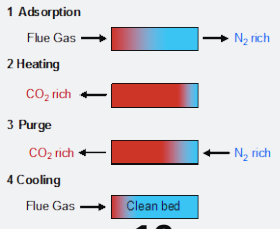
Computational Analysis

Data analysis, life cycle and sorbent performance analysis





Simulations



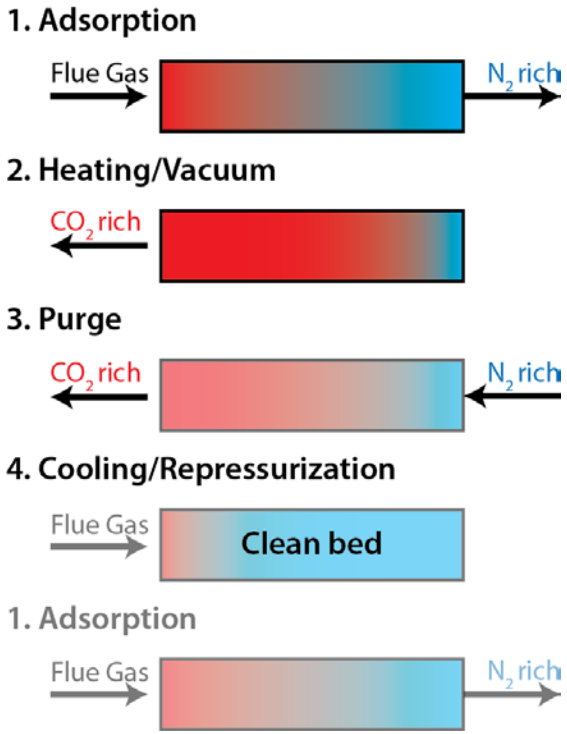
Sorbent Performance

Parasitic energy

Energy penalty for CCS can be divided into the compression work and the heating energy:

- **Heating energy (Q):** heat necessary to regenerate a given sorbent:
  - Sensible heat: heats and cools bed. Provides driving force to produce CO_2
  - Desorption heat: desorbs CO_2 (equal to heat of adsorption, Δh).

$$Q = \frac{\underbrace{(C_p \rho_{sorbent} \Delta T}_{\text{Sensible heat requirement}} + \underbrace{\Delta h_{CO2} \Delta q_{CO2} + \Delta h_{N2} \Delta q_{N2})}_{\text{Desorption heat requirement}}}{CO_{2\,\mathrm{Produced}}}$$

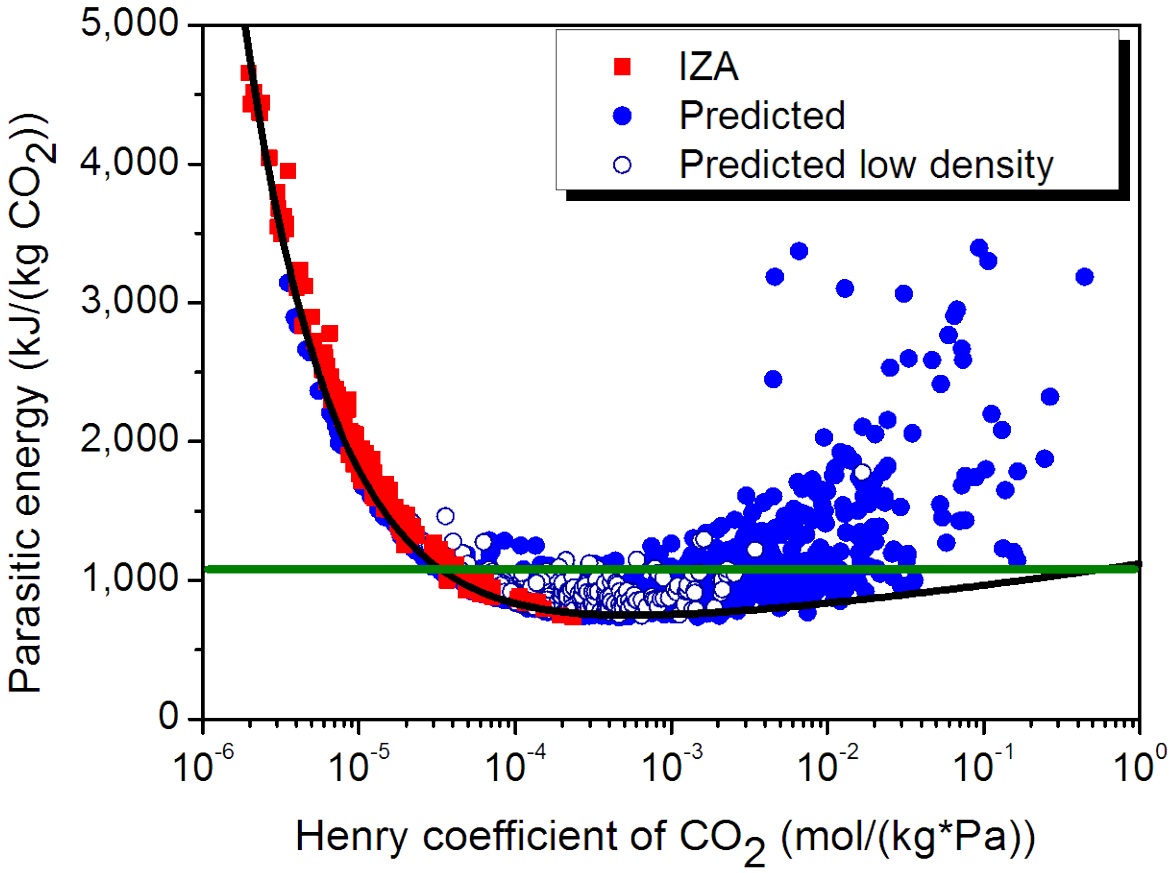


- **Compressor work (W_{comp}):** Work to compress CO_2 product to 150 bar (for transport)

- **Equivalent energy** calculated by discounting the heat requirement by the Carnot efficiency to simulate the effect of taking steam from a steam cycle

$$W_{eq} = \left(0.75Q \cdot \eta_{carnot} + W_{comp}\right)$$

Screening zeolite structures

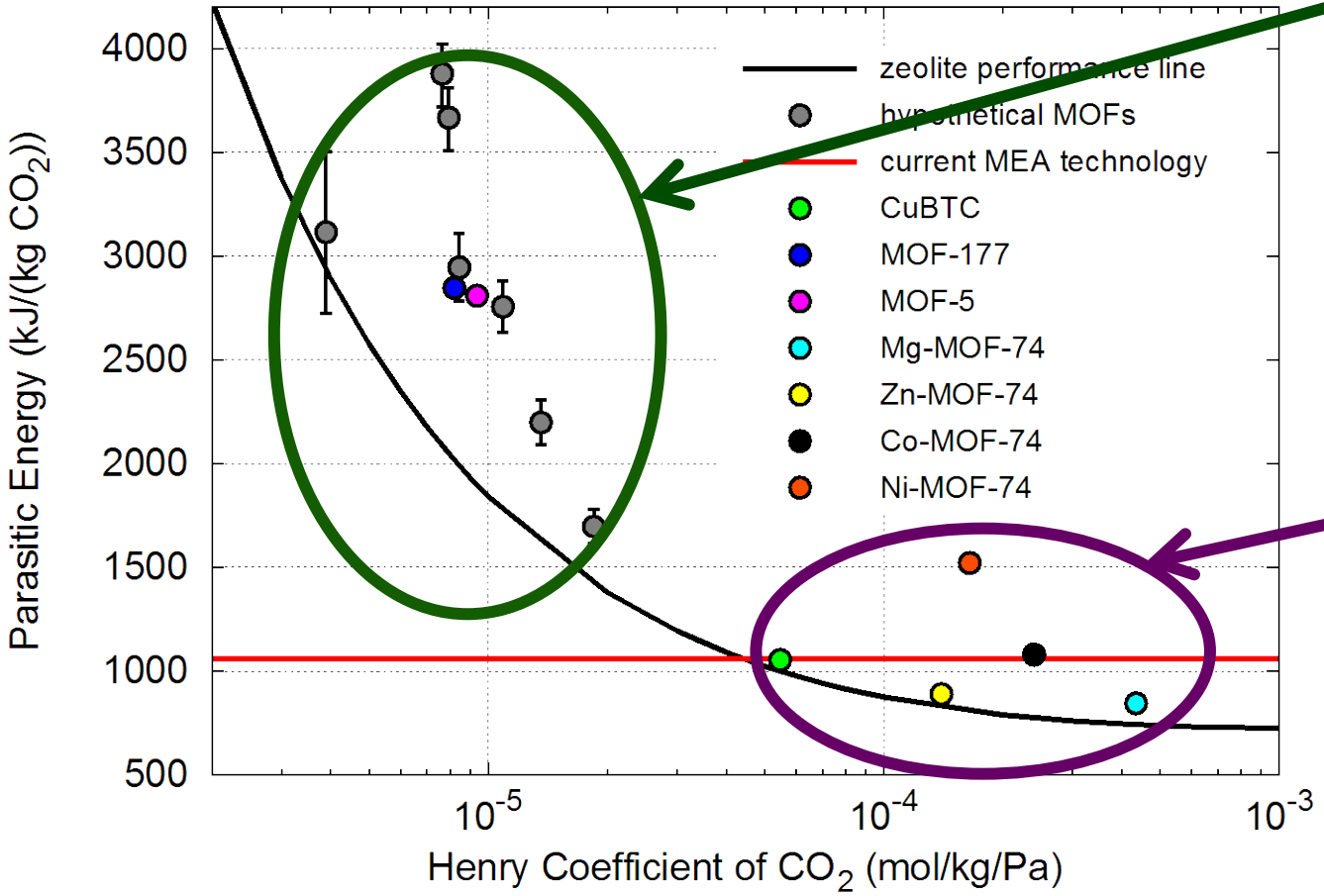


Screening

- All zeolites
- 3.M hypothetical structures

Lin, L.-C. *et al.* In silico screening of carbon-capture materials. *Nat. Mater.* 11, 633-641 (2012)

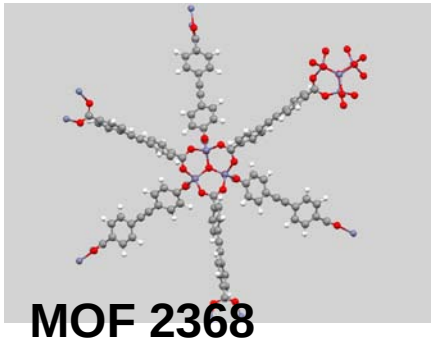
Screening MOFs



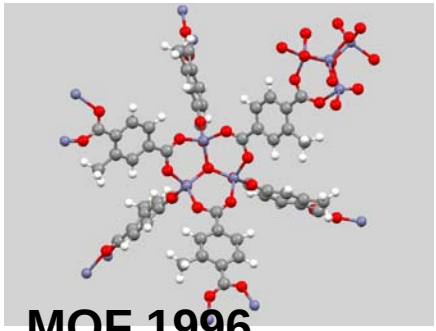
Effect of ligand (MOF-5 related)

Effect of metal: MOF-74

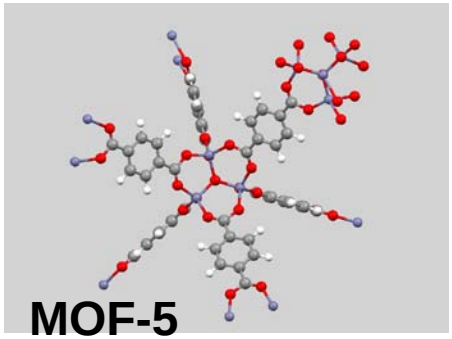
Effect of ligands



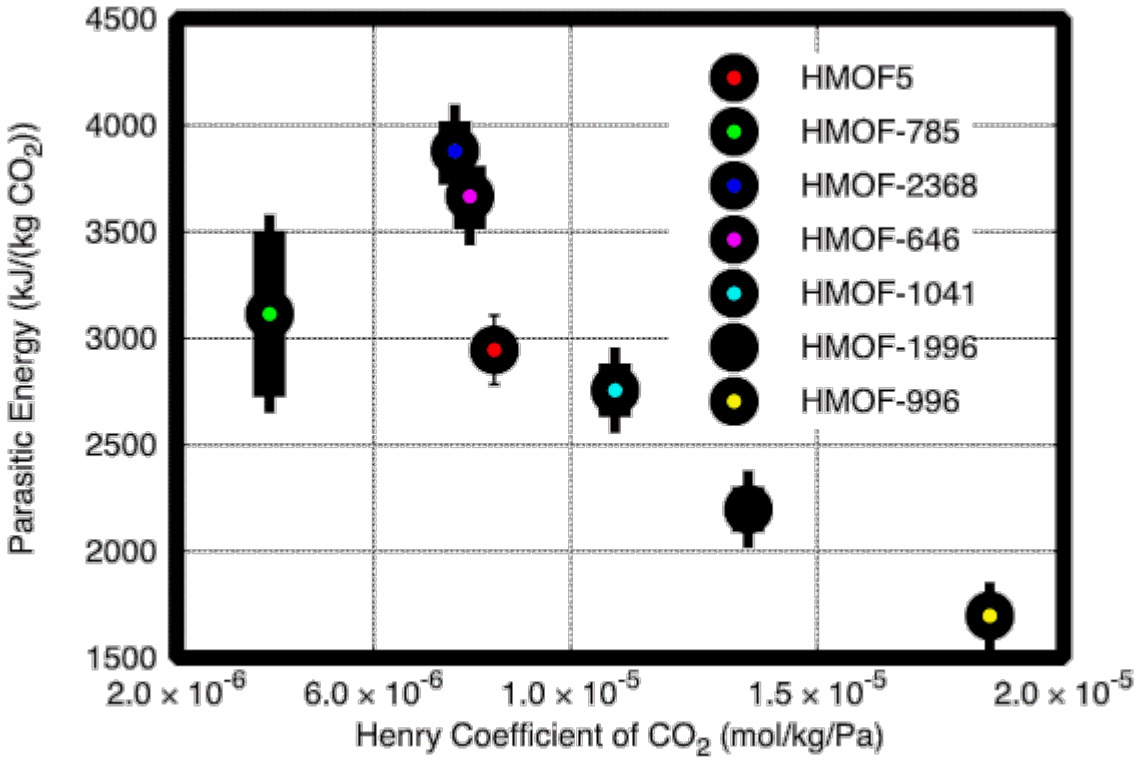
MOF 2368



MOF 1996



MOF-5



Generation of thousands of hypothetical MOFs structures

Concluding remarks

- **MOFs: beautiful chemistry and giving completely novel materials**
  - 11,000 new MOFs reported!
  - Promising leads for
    - Oxygen separations
    - Carbon capture
    - Hydrogen separation
  - Need to quickly evaluate these materials
    - High throughput experiments
    - Computational screening of possible structures