Cooperative Carbon Dioxide Capture in Metal-Organic Frameworks

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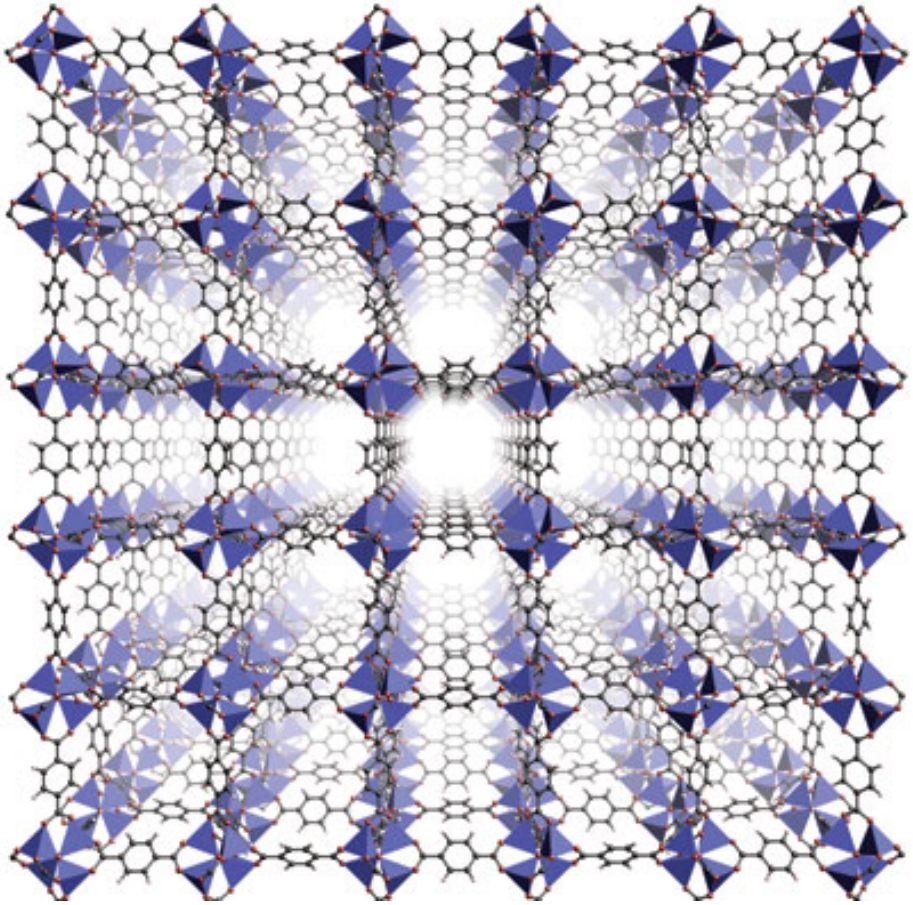
Metal-Organic Frameworks (MOFs)



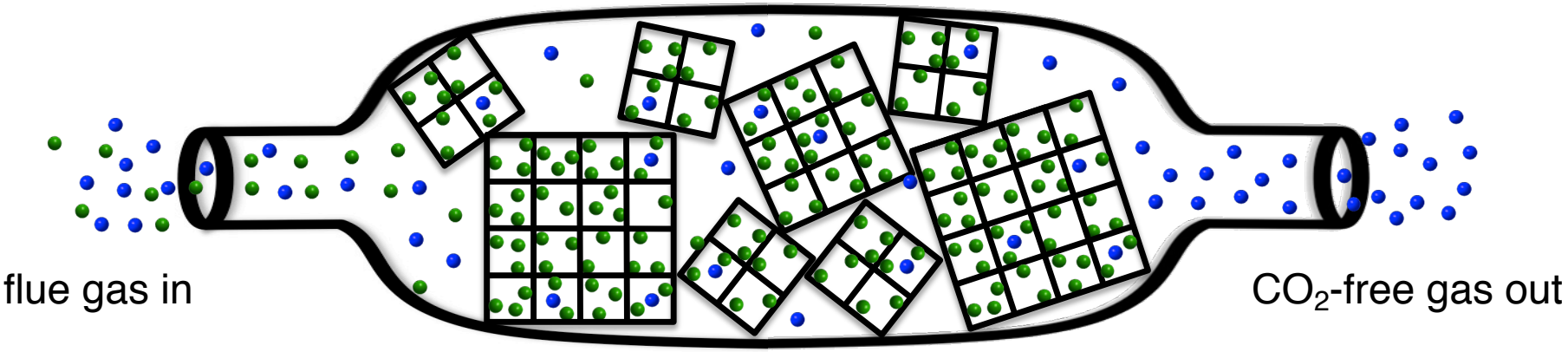
Zn_4O(1,4-benzenedicarboxylate)$_3$

MOF-5

- BET surface areas up to 7100 m^2/g
- Density as low as 0.13 g/cm^3
- Tunable pore sizes up to 10 nm
- Channels connected in 1-, 2-, or 3-D
- Internal surface can be functionalized
- BASF production on ton scale

Yaghi et al. *Nature* **2003**, *423*, 705
Kitagawa et al. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334
Férey *Chem. Soc. Rev.* **2008**, *37*, 191

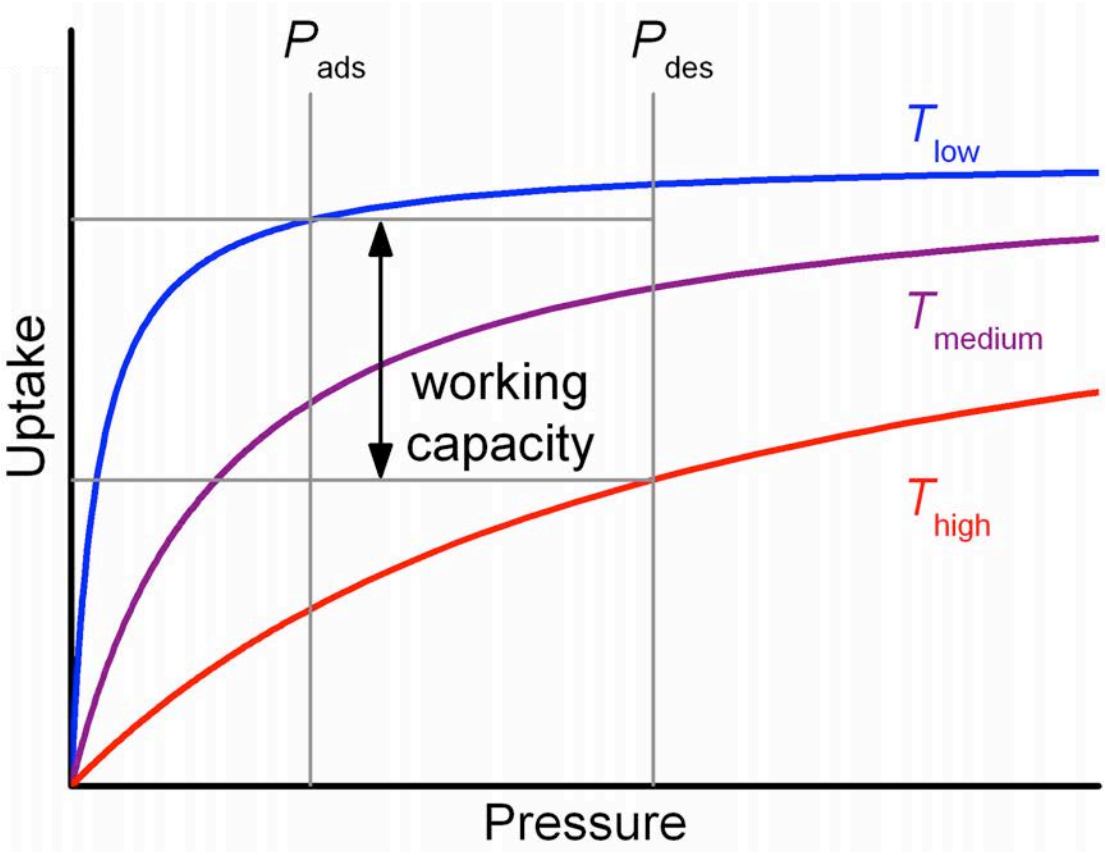
Utilizing MOFs for Carbon Dioxide Capture



MOF-loaded bed

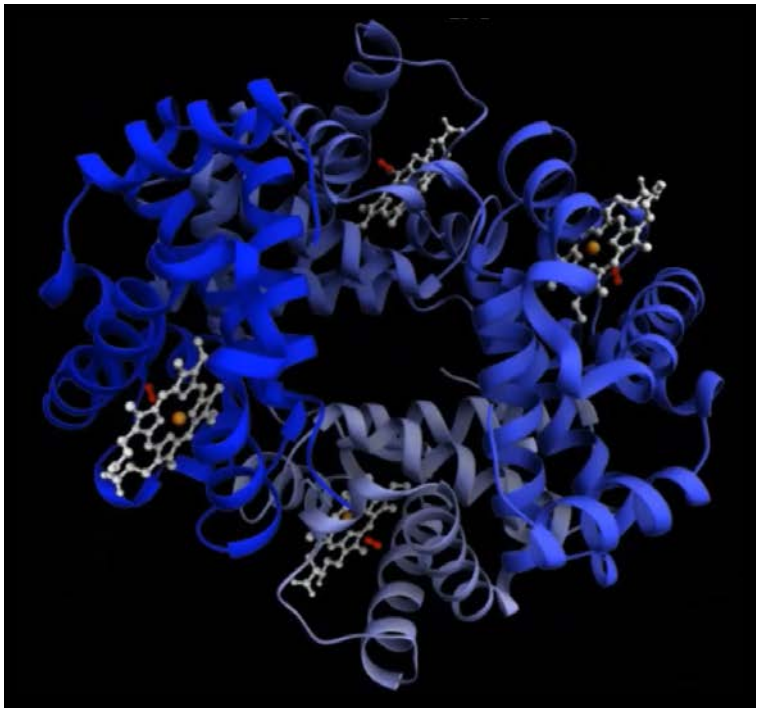
- Requires surface functionalization such that only CO_2 adsorbs in the MOF
- CO_2 released in pure form by raising the temperature or dropping the pressure
- High surface area leads to a high working capacity for removing CO_2

Classical Adsorbents: Langmuir Isotherms

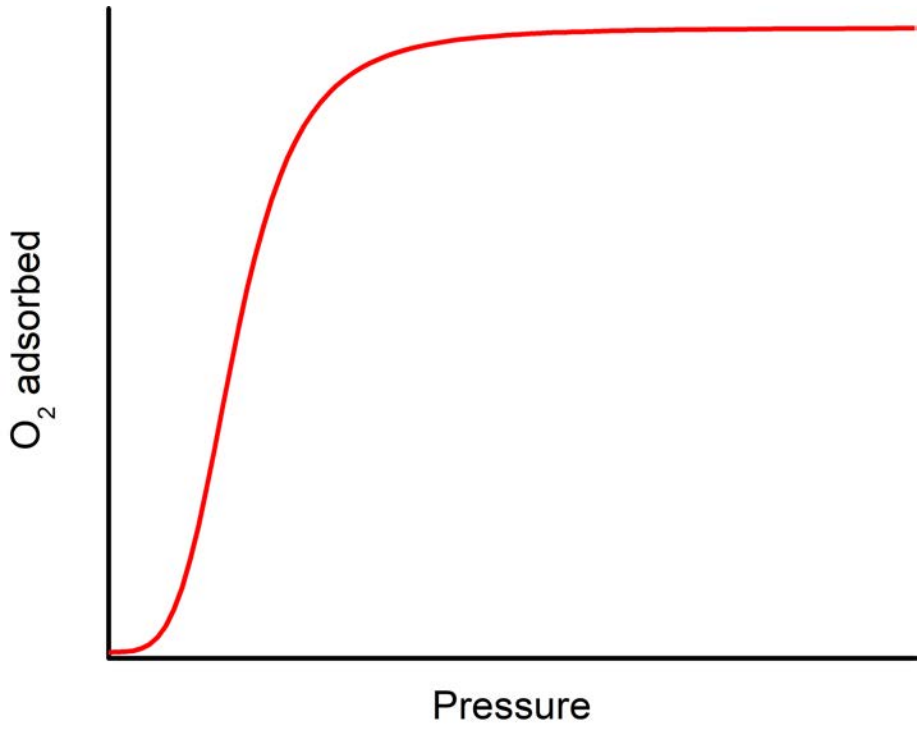


- Very large temperature (or pressure) swings are required to acheive a high working capacity

Cooperative Binding and Release of O_2 in Hemoglobin

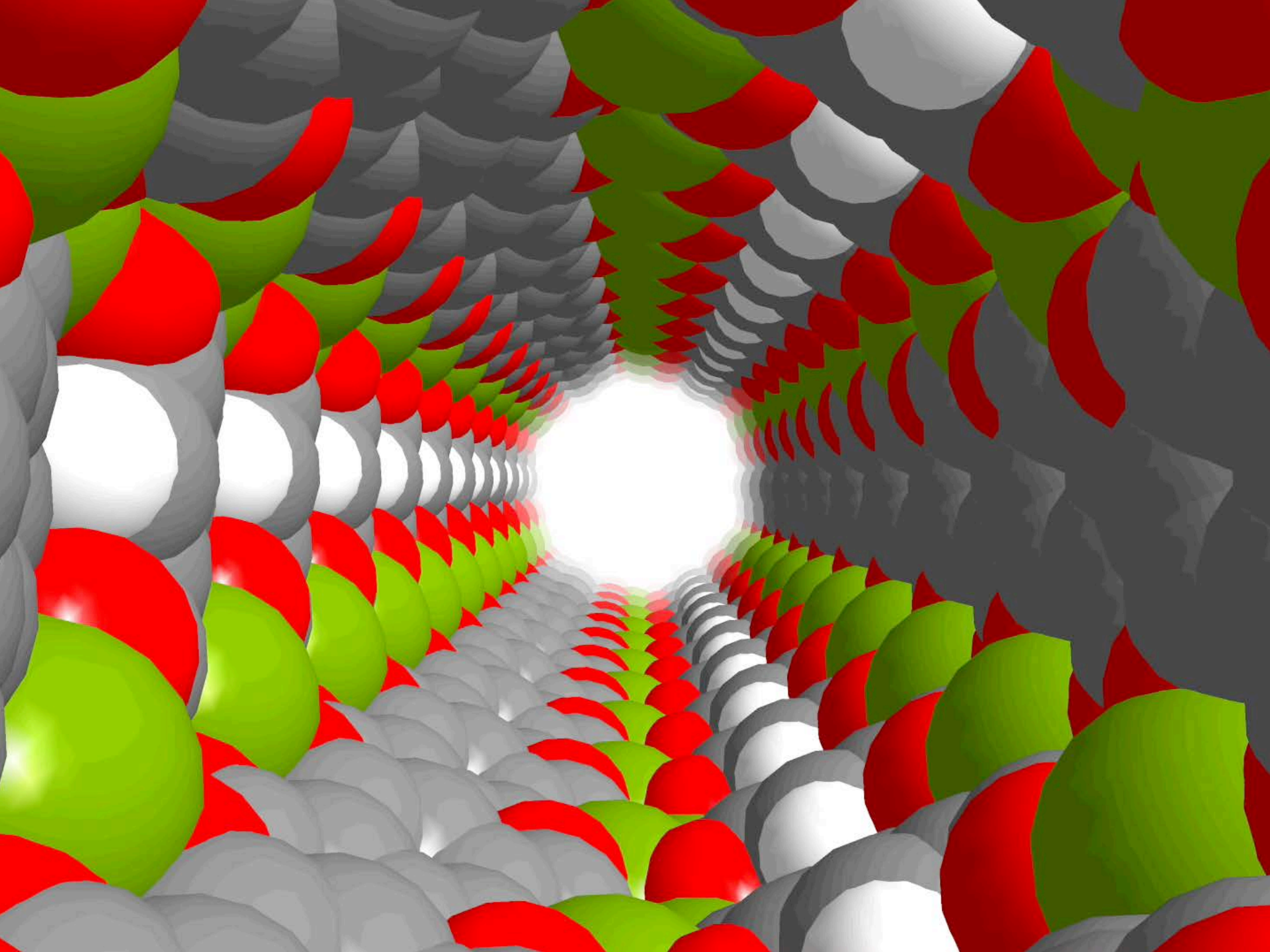


hemoglobin

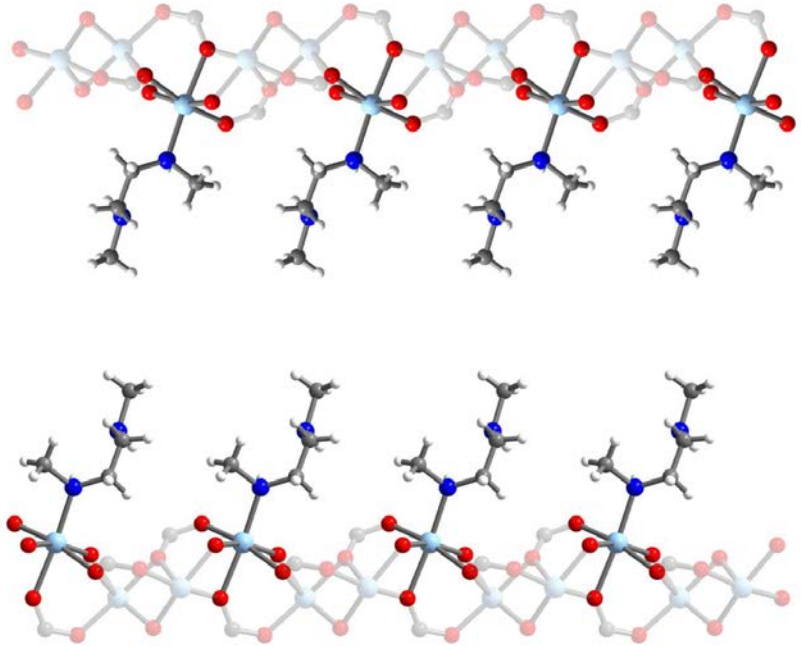


- Binding of O_2 at one iron site facilitates binding at three other iron sites

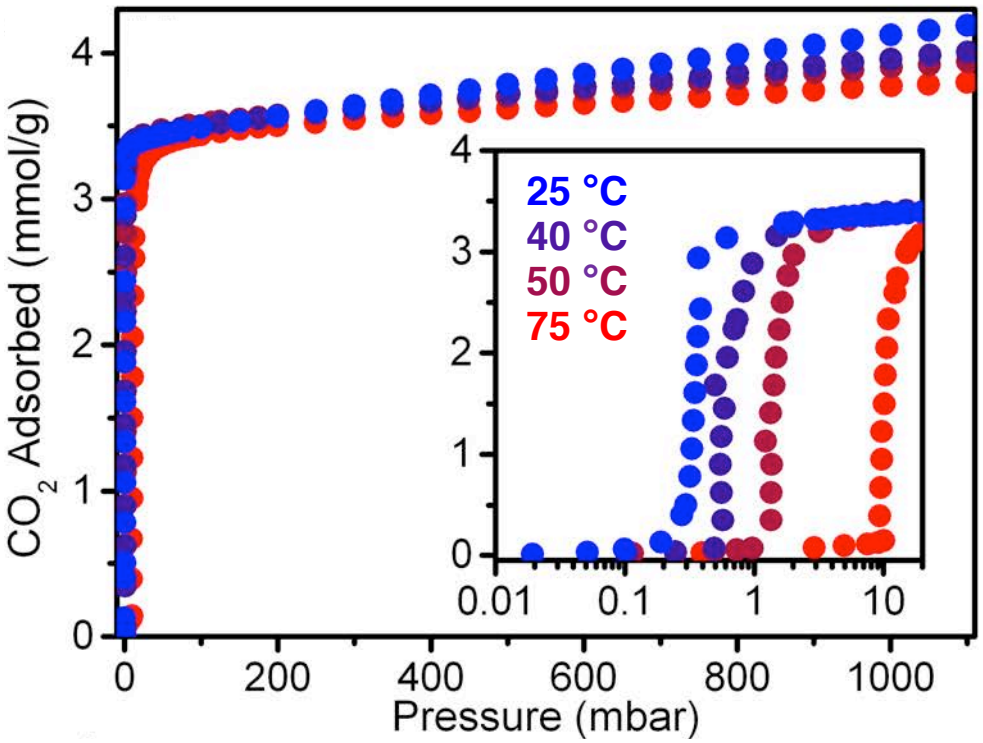
Imai, Yonetani *J. Biol. Chem.* **1974**, *250*, 2227



Cooperative Binding and Release of CO_2 in a MOF



mmen–Mg_2(dobpdc)

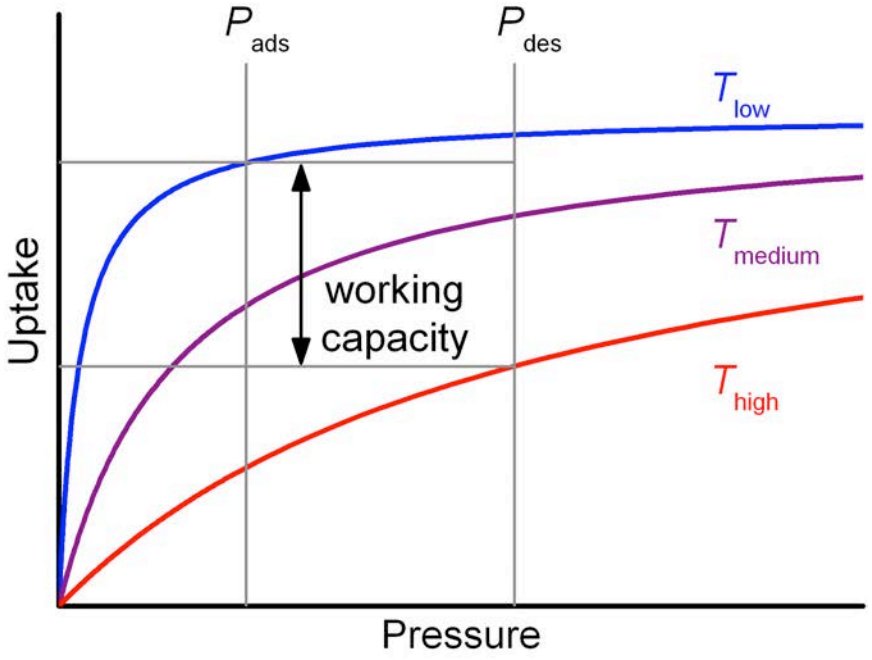


- Unprecedented switch-like mechanism for high-capacity CO_2 uptake and release

McDonald, Mason, Kong, Bloch, Gygi, Dani, Crocellà, Giordano, Odoh, Drisdell, Vlaisavljevich, Dzubak, Poloni, Schnell, Planas, Kyuho, Pascal, Prendergast, Neaton, Smit, Kortright, Gagliardi, Bordiga, Reimer, Long *Nature* **2015**, *519*, 303

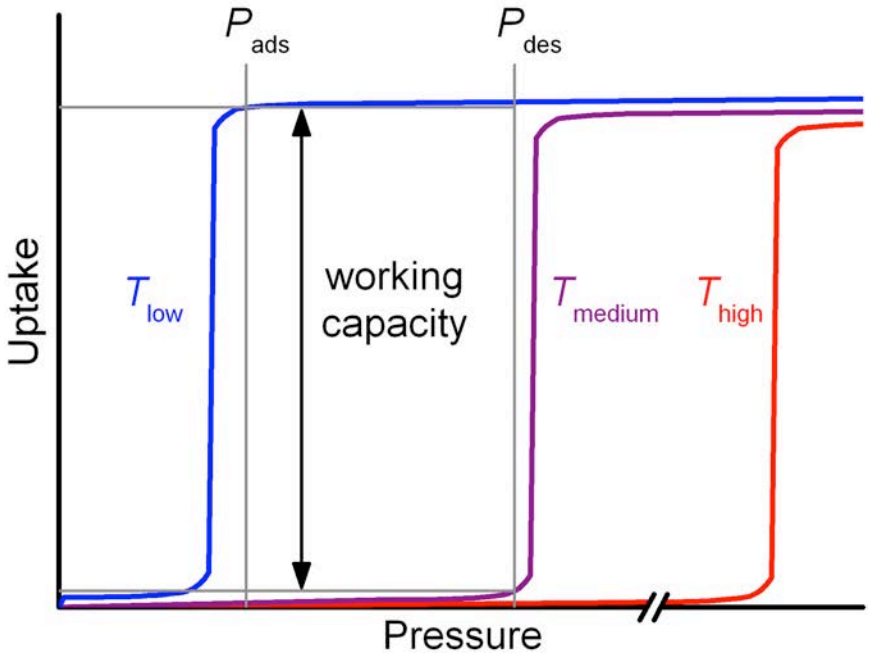
Classical versus Cooperative Adsorbents

amine solutions and other amine adsorbents



2 wt % CO_2 removed, $\Delta T = 100$ °C

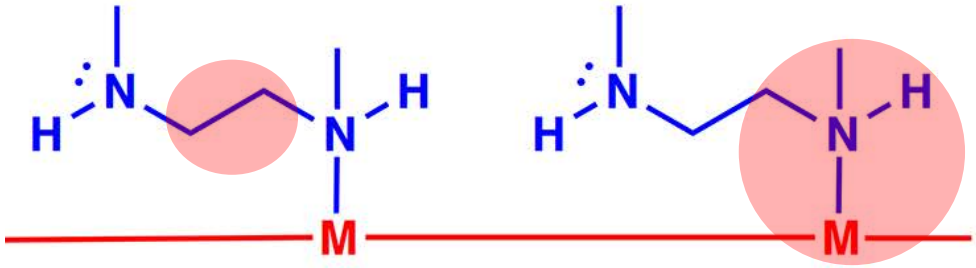
diamine-appended MOFs



15 wt % CO_2 removed, $\Delta T = 50$ °C

McDonald, Mason, Kong, Bloch, Gygi, Dani, Crocellà, Giordano, Odoh, Drisdell, Vlaisavljevich, Dzubak, Poloni, Schnell, Planas, Kyuho, Pascal, Prendergast, Neaton, Smit, Kortright, Gagliardi, Bordiga, Reimer, Long *Nature* **2015**, *519*, 303

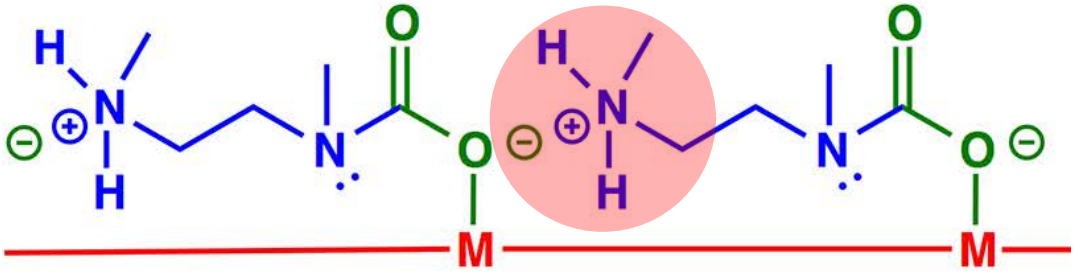
Manipulating the Adsorption Step Position



Substituents on diamine backbone

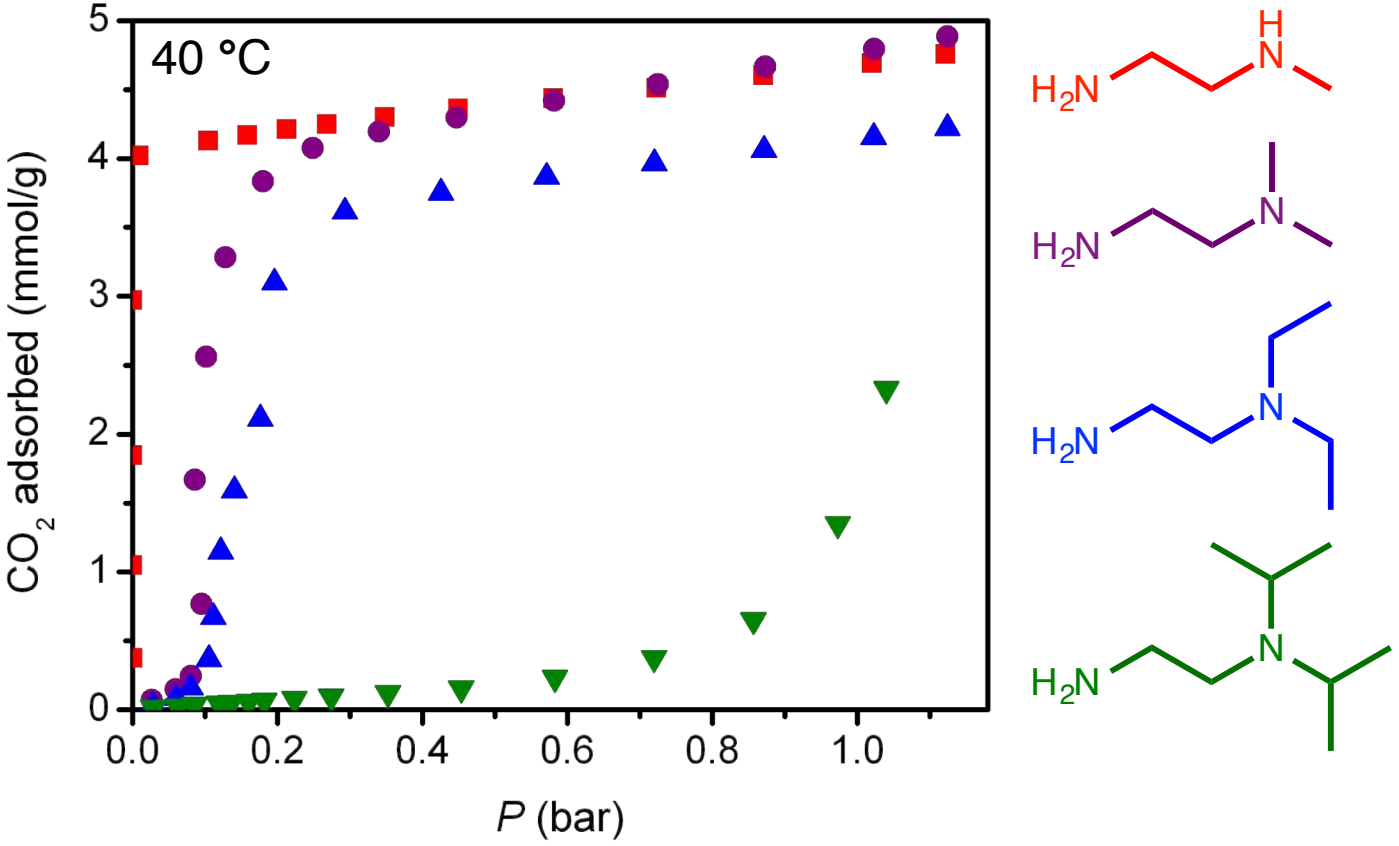
Substituents on metal-bound amine

$+CO_2$



Substituents on ammonium-forming amine

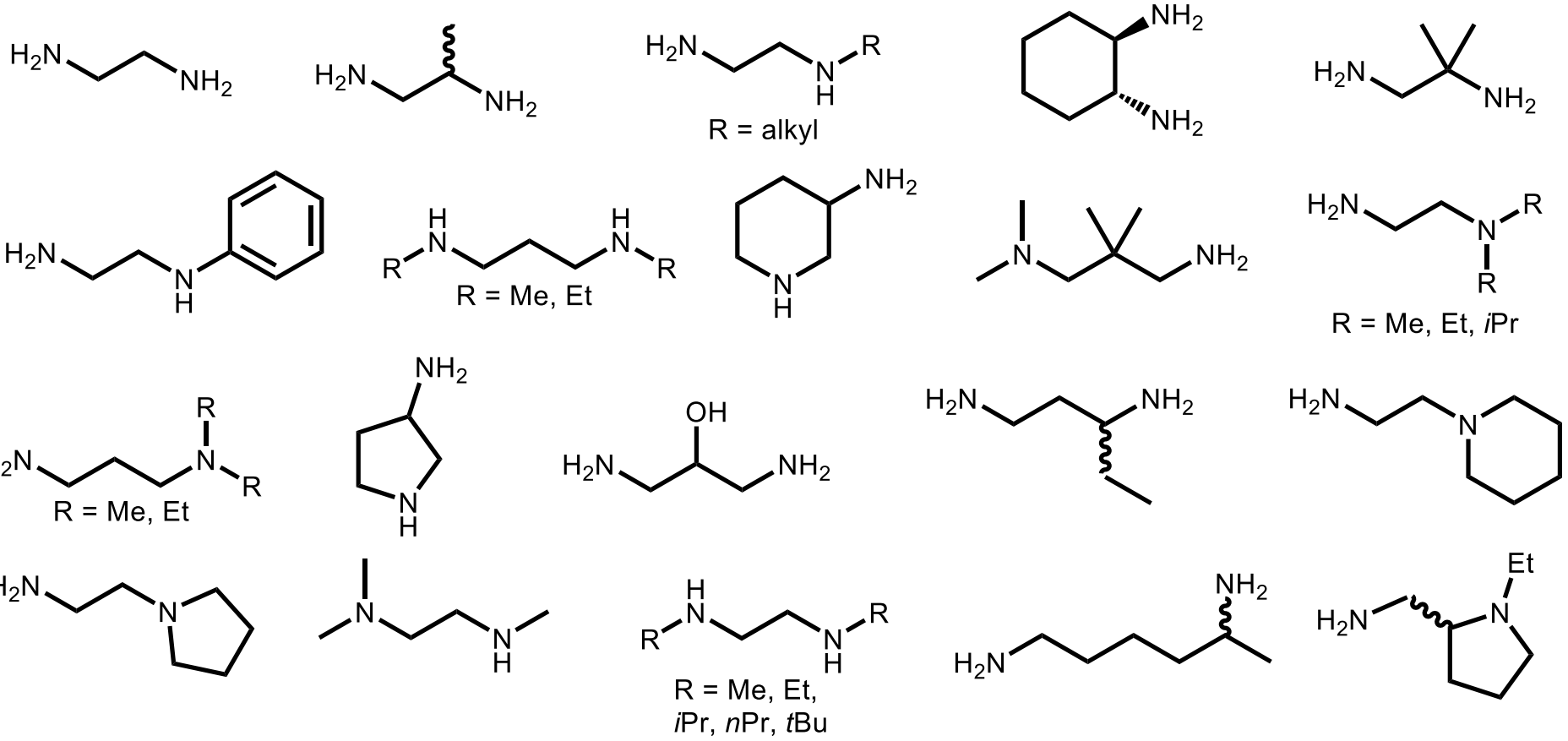
Varying Diamine Bulk in Mg_2(dobpdc)



- Increased hydrocarbon bulk shifts step and also suppresses water adsorption

Siegelman, McDonald, Gonzalez, Martell, Milner, Mason, Berger, Bhown, Long *J. Am. Chem. Soc.* **2017**, *139*, 10526

Variation of the Diamine Shifts the Step Position



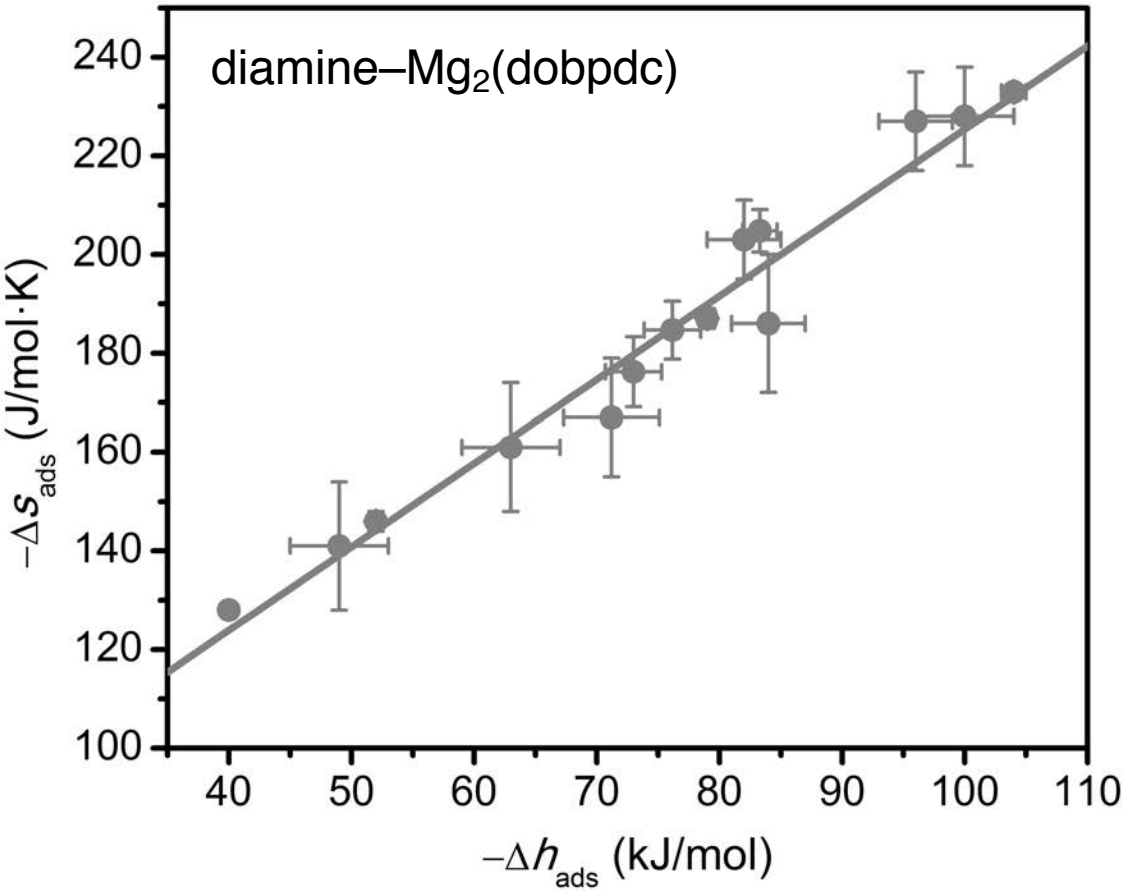
- More than 80 different diamines have now been tested in Mg_2(dobpdc)
- Step position at 40 °C varies from ~2 ppm to >2 bar

Siegelman, McDonald, Gonzalez, Martell, Milner, Mason, Berger, Bhown, Long *J. Am. Chem. Soc.* **2017**, *139*, 10526

Milner, Siegelman, Forse, Gonzalez, Runčevski, Martell, Reimer, Long *J. Am. Chem. Soc.* **2017**, *139*, 13541

Milner, Martell, Siegelman, Gygi, Weston, Long *Chem. Sci.* **2018**, *9*, 160

Varying the Thermodynamics of CO_2 Capture



- More exothermic CO_2 adsorption correlates with a larger entropic penalty

Siegelman, McDonald, Gonzalez, Martell, Milner, Mason, Berger, Bhown, Long *J. Am. Chem. Soc.* **2017**, *139*, 10526
Milner, Siegelman, Forse, Gonzalez, Runčevski, Martell, Reimer, Long *J. Am. Chem. Soc.* **2017**, *139*, 13541
Milner, Martell, Siegelman, Gygi, Weston, Long *Chem. Sci.* **2018**, *9*, 160

CO_2 Separations

Coal flue gas
0.15 bar

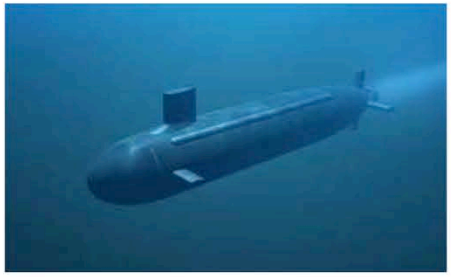
Natural gas flue gas
0.05 bar

Natural gas sweetening
1-5 bar

Cryogenic air distillation
410 ppm

Air capture for EOR
410 ppm

Biogas upgrading
0.5 bar



Air recycling
1-3 mbar

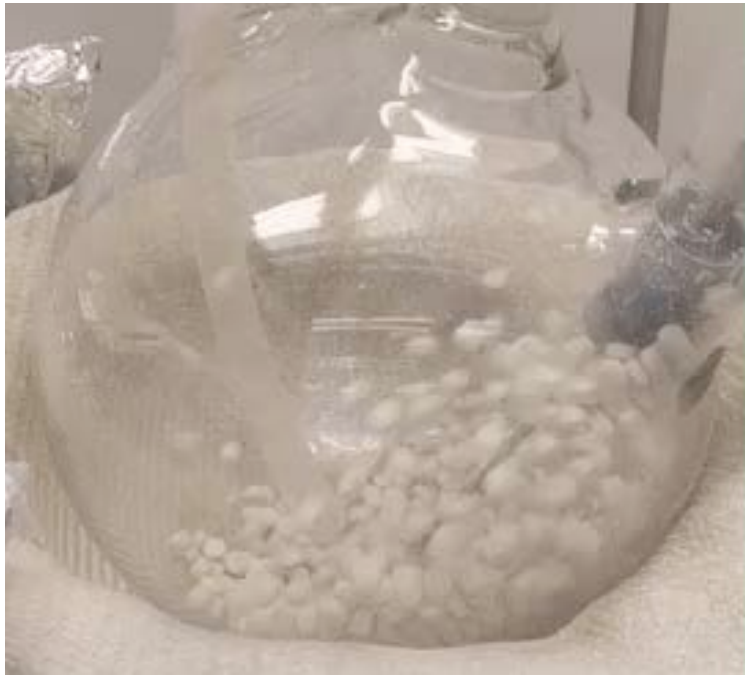
Hydrogen production
2-10 bar

Mosaic Materials, Inc.

Revolutionizing carbon dioxide separations

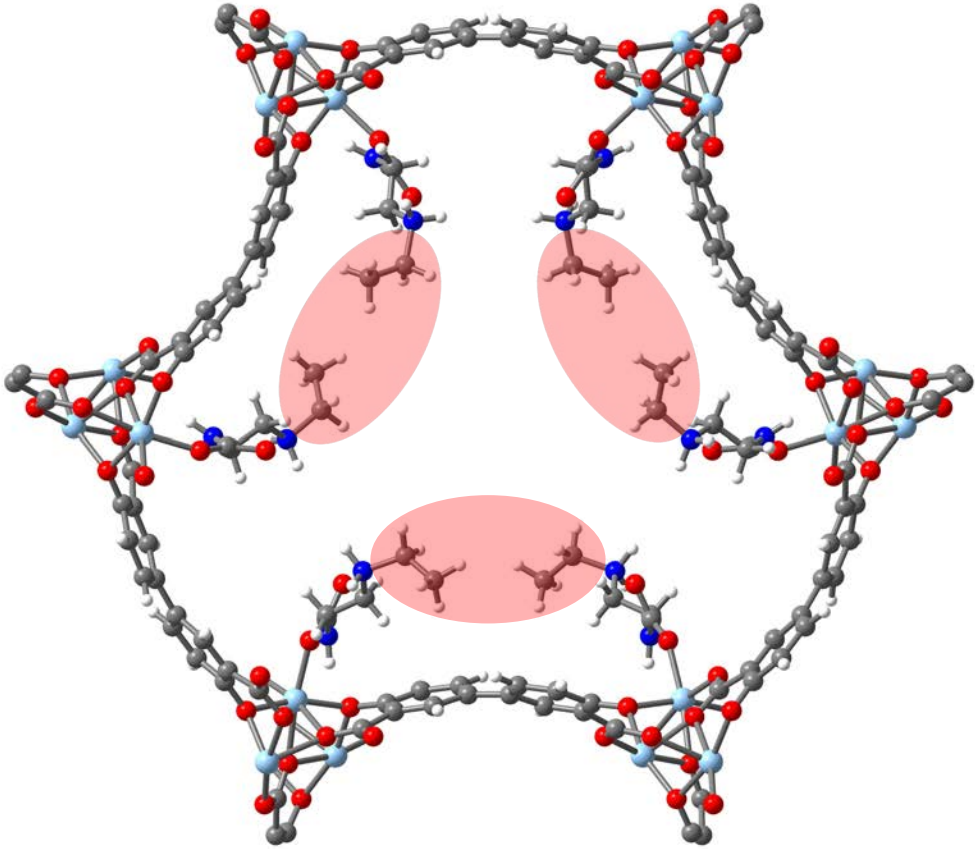
http://mosaicmaterials.com/

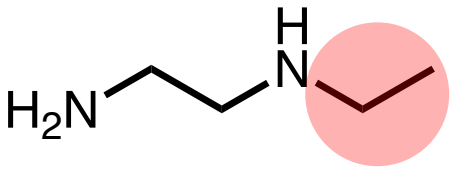
Mosaic Materials:
Manufacture of MOFs for CO_2 Capture



Scalable production of cooperative CO_2 adsorbents in various structured forms

A Strategy for Extreme Capture Conditions



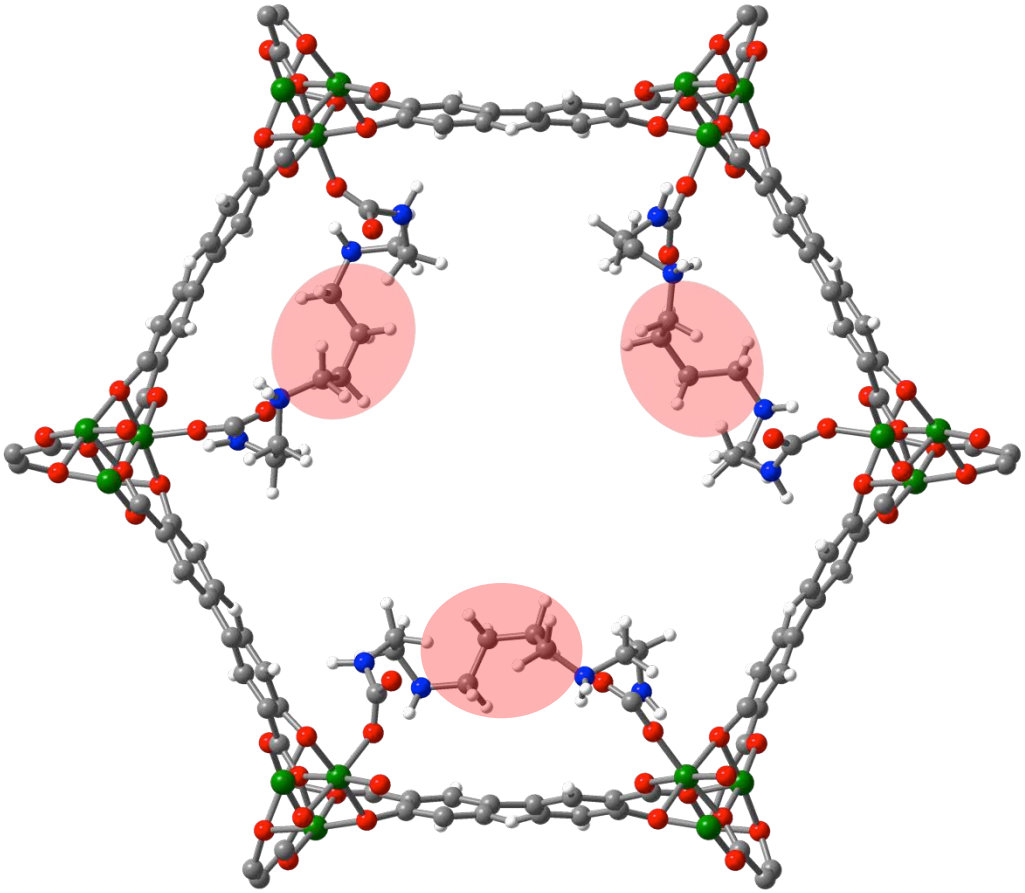


N-ethylethylenediamine

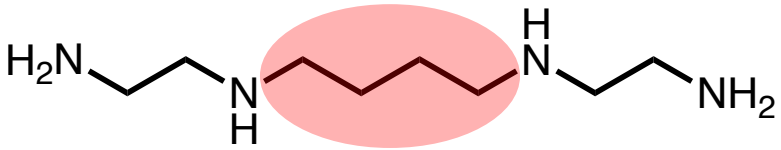
- Joining two diamines may still allow cooperative chain formation

Siegelman, McDonald, Gonzalez, Martell, Milner, Mason, Berger, Bhown, Long *J. Am. Chem. Soc.* **2017**, *139*, 10526

Tetraamine-Appended Mg_2(dobpdc)



geometry-optimized model

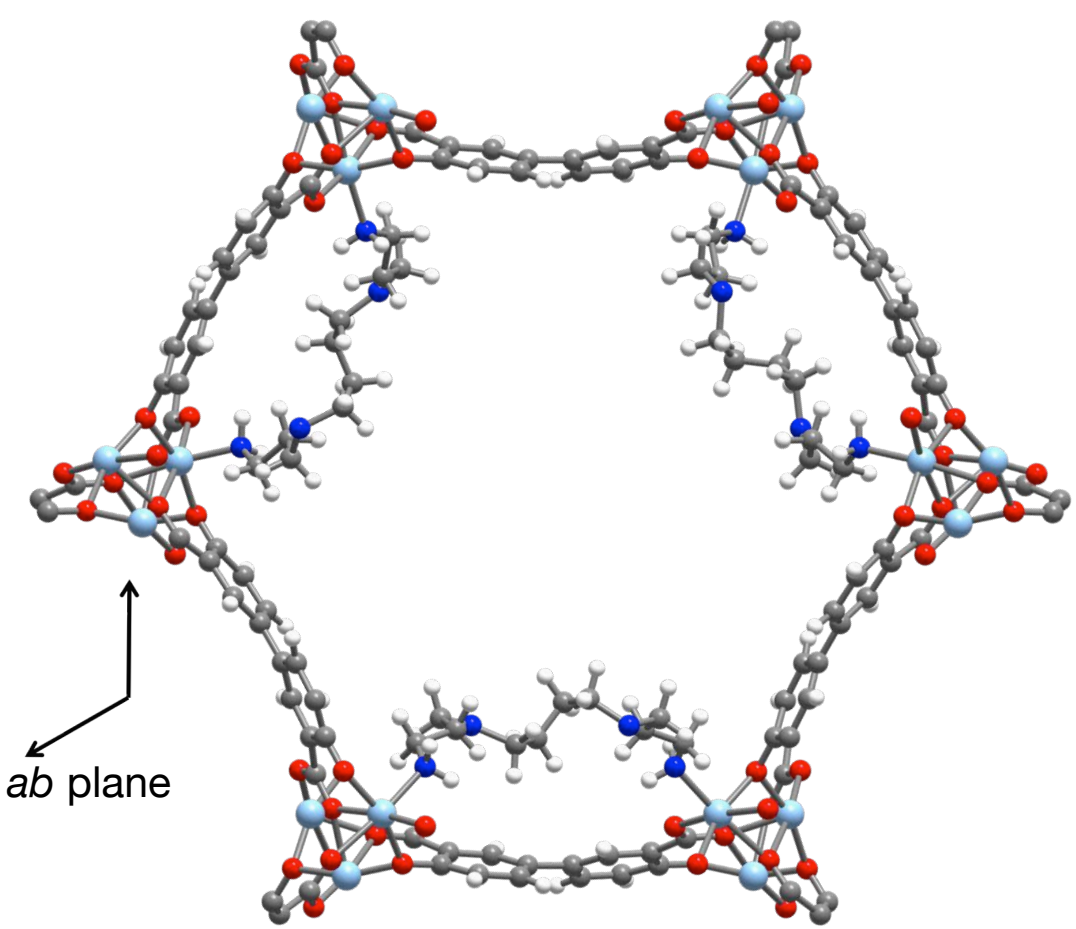


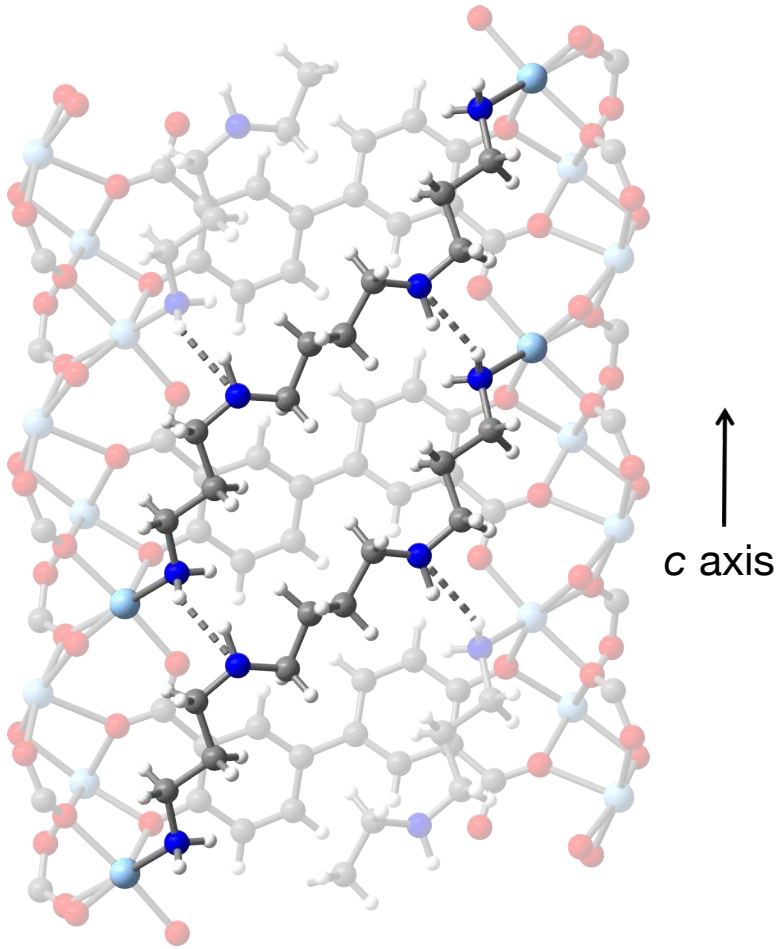
N,N′-bis(2-aminoethyl)-1,4-butanediamine

- Reduced volatility expected from greater weight and multi-metal coordination

Kim, Siegelman, Jiang, Forse, Lee, Martell, Milner, Falkowski, Neaton, Reimer, Weston, Long *Science* **2020,** *369*, 392

Confirmed Multi-Metal Coordination

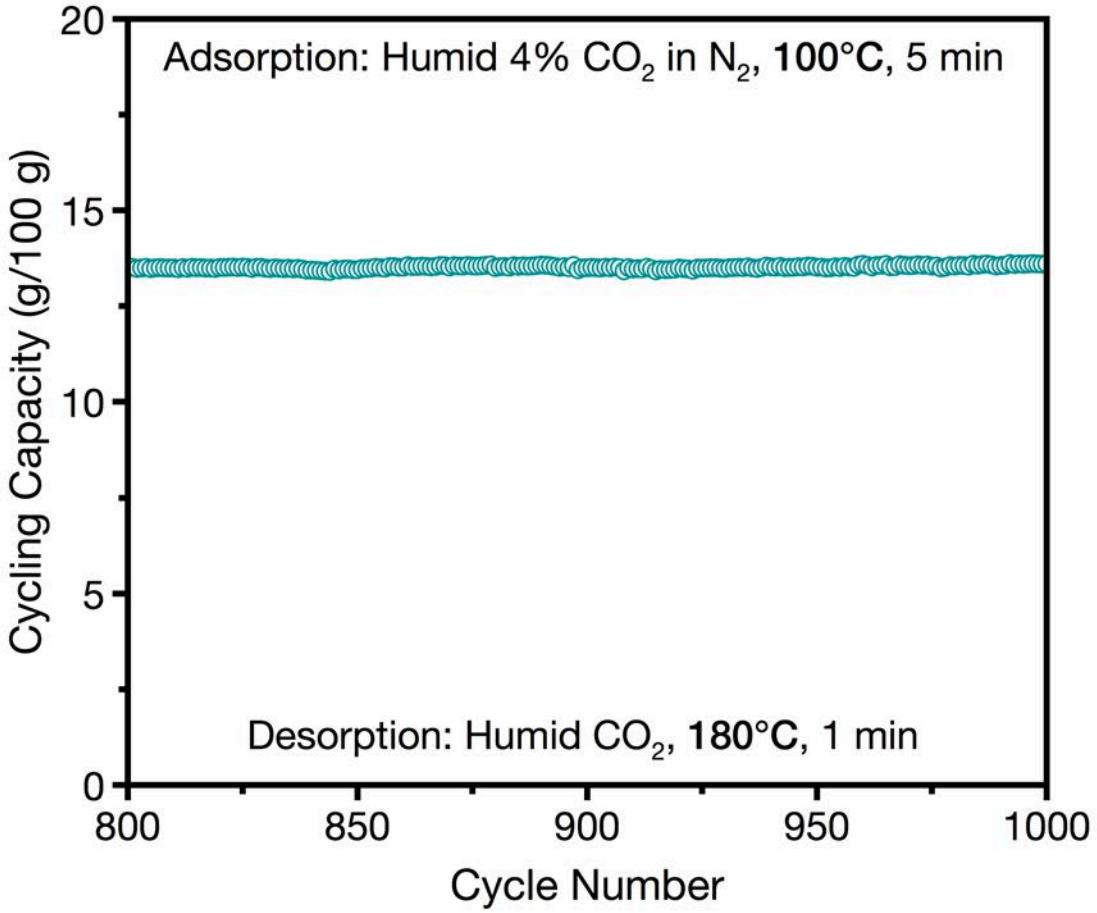




- Crystal structure shows coordination of tetraamines to metals bridging the *ab* plane

Kim, Siegelman, Jiang, Forse, Lee, Martell, Milner, Falkowski, Neaton, Reimer, Weston, Long *Science,* **2020,** *369*, 392

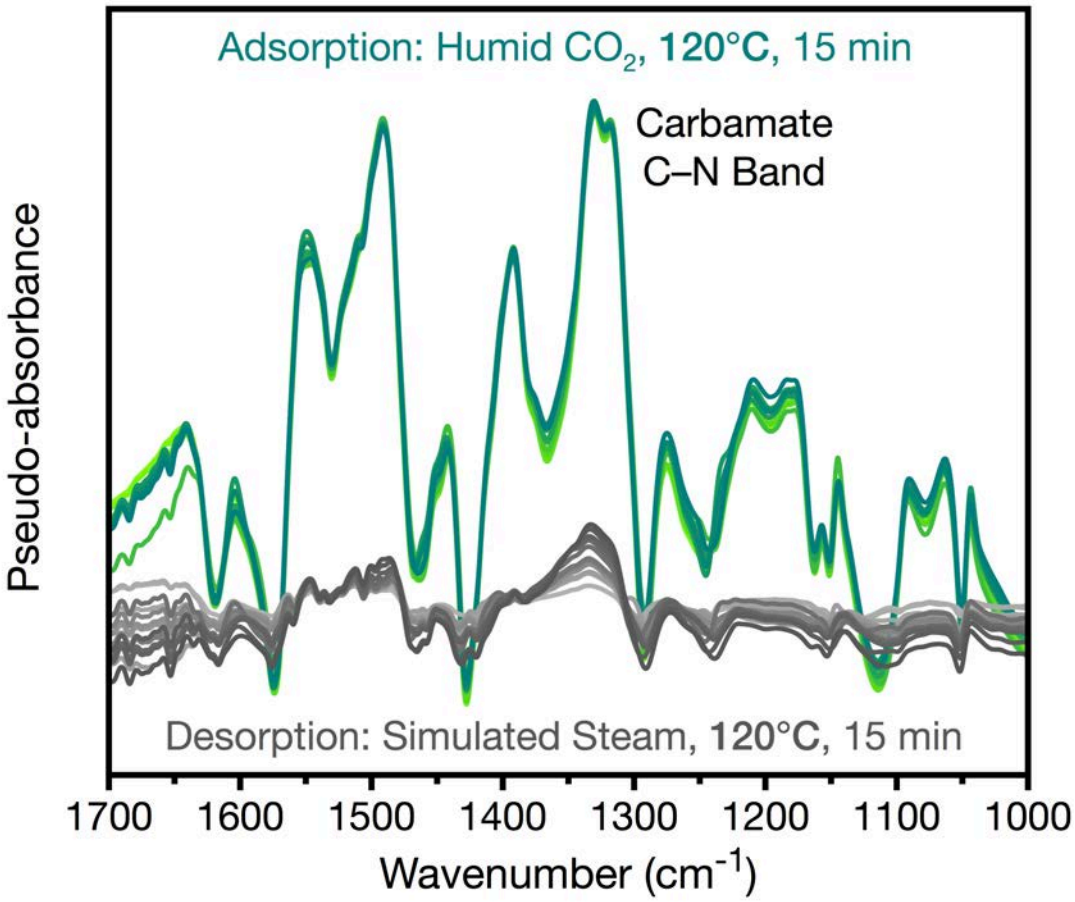
1000 Adsorption-Desorption Cycles



- NMR experiments indicate 100% tetraamine retention after 1000 cycles

Kim, Siegelman, Jiang, Forse, Lee, Martell, Milner, Falkowski, Neaton, Reimer, Weston, Long *Science* **2020,** *369*, 392

Regeneration via Direct Steam Stripping



- No change in the representative carbamate band over 15 cycles

Kim, Siegelman, Jiang, Forse, Lee, Martell, Milner, Falkowski, Neaton, Reimer, Weston, Long *Science* **2020,** *369*, 392

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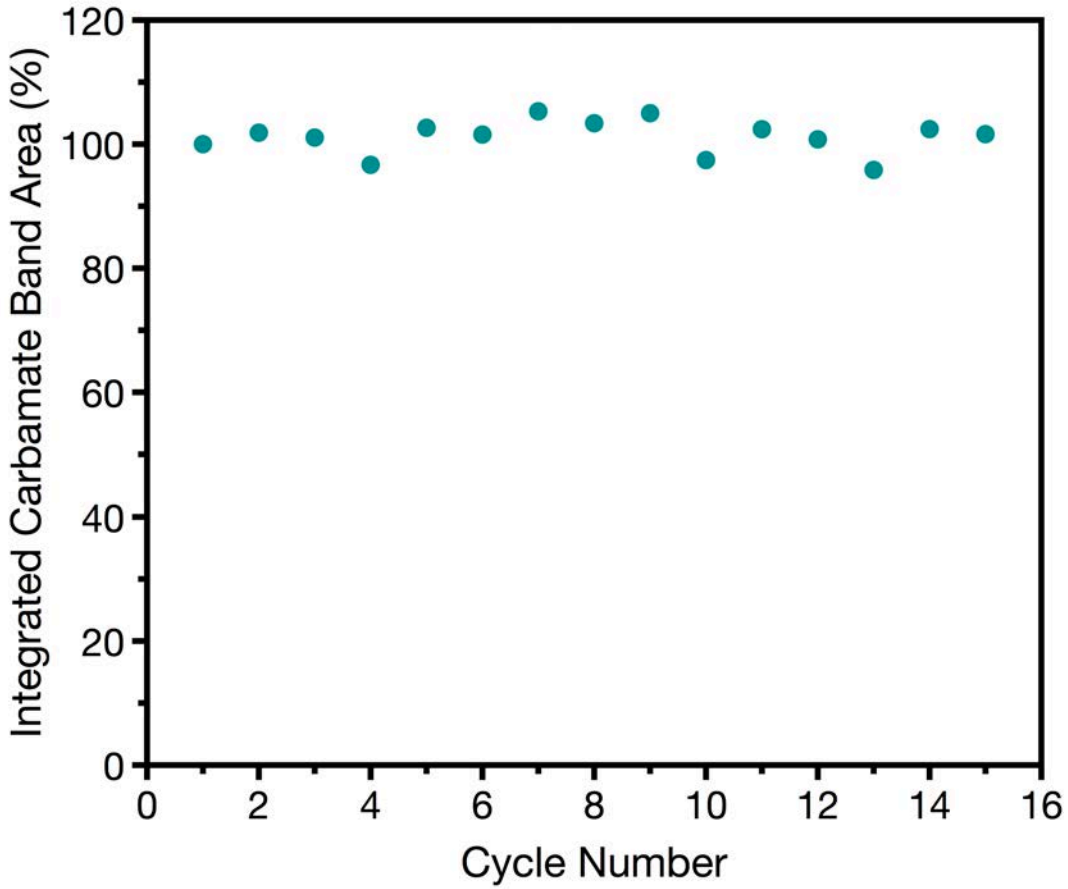

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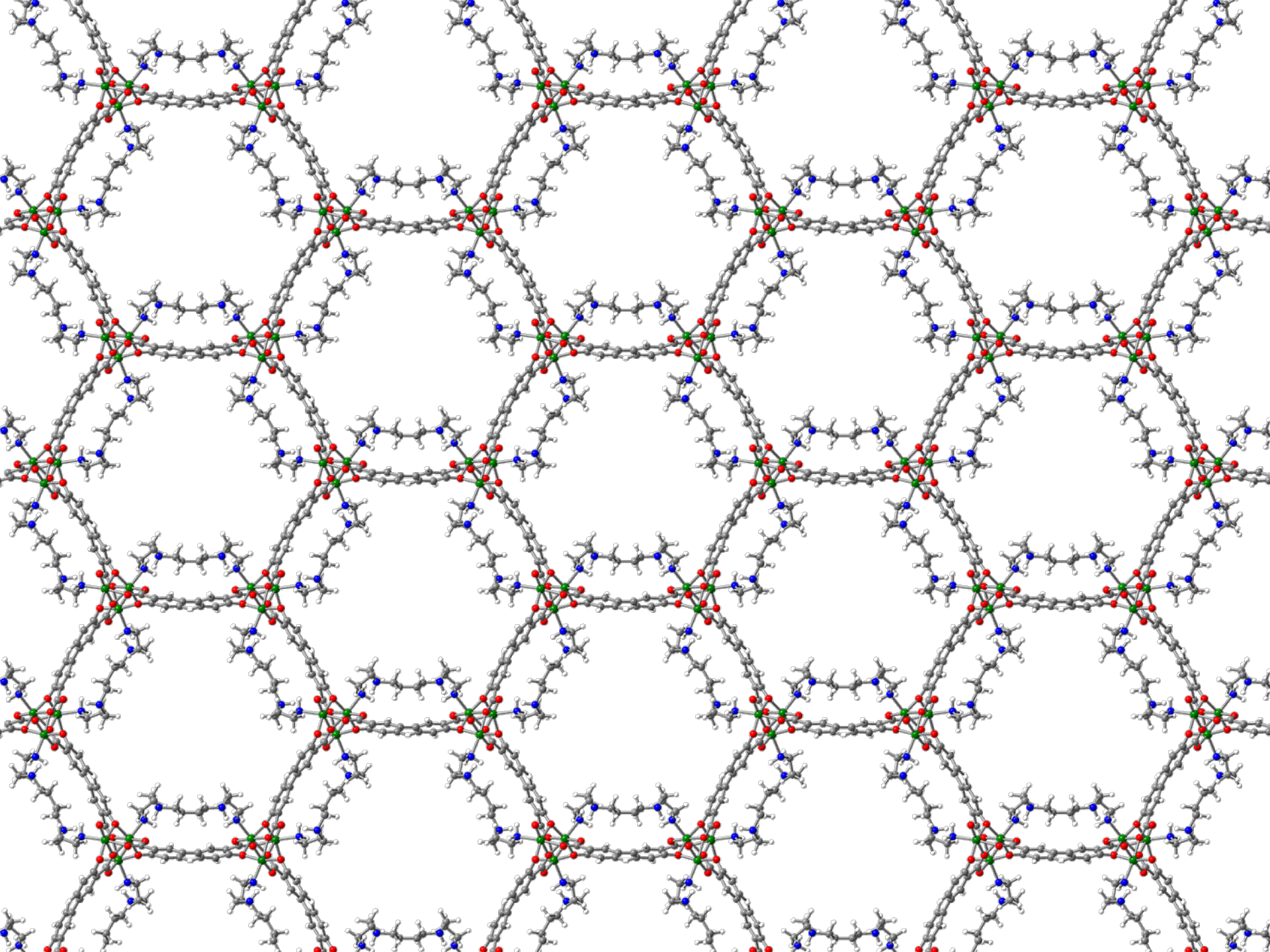
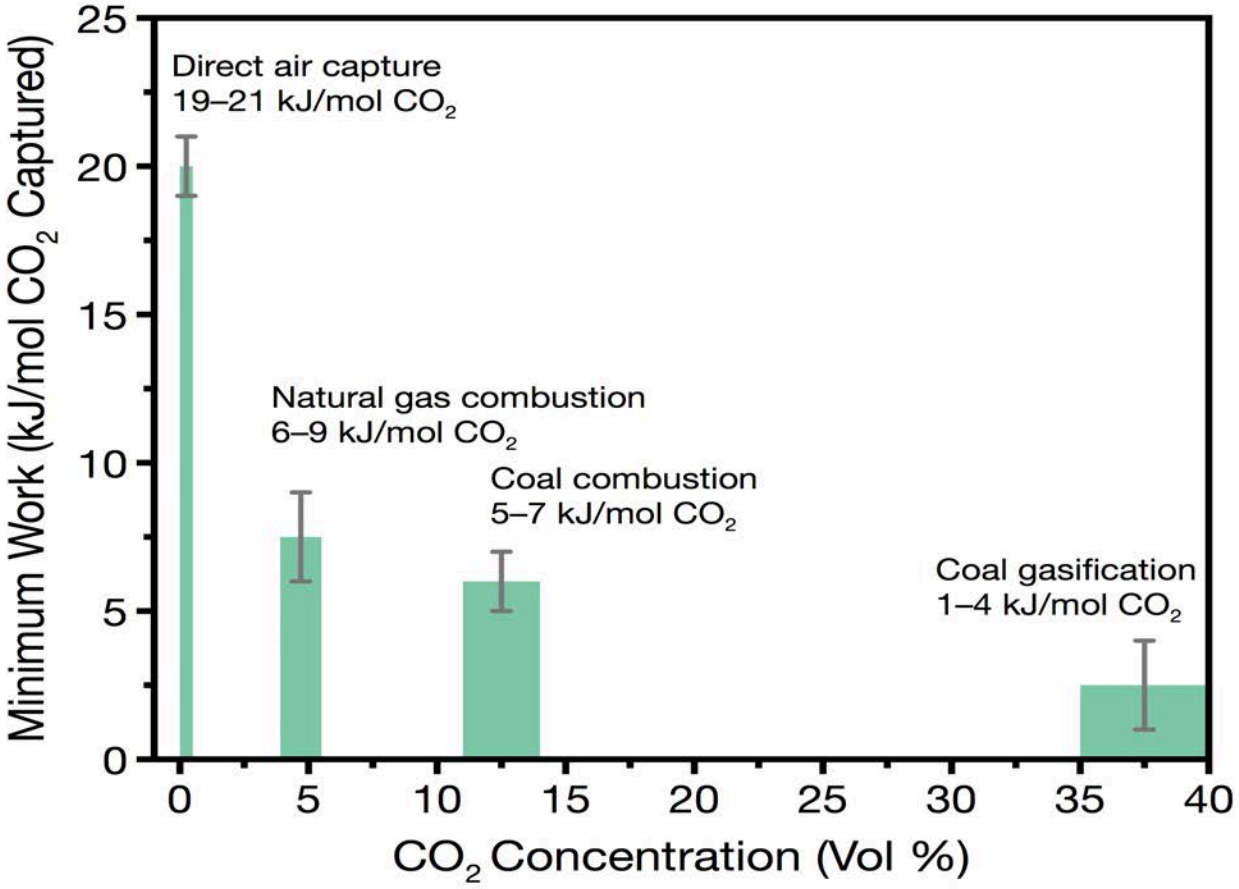


Minimum Work Required for CO_2 Capture



- Entropy penalty for unmixing CO_2 leads to increased minimum work for dilute mixtures such as air

Siegelman, Kim, Long, submitted

Acknowledgements

Graduate Students
Jonathan Bachman
Eric Bloch
Matthew Dods
Miguel Gonzalez
Henry Jiang
Eugene Kim
Jarad Mason
Thomas McDonald
Rebecca Siegelman

Postdoctoral Fellows
Dr. Alexander Forse
Dr. Jeffrey Martell
Dr. Phillip Milner

Undergraduate Student
David Gygi

Collaborators
Dr. Abhoyjit Bhown (EPRI)
Dr. Walter Drisdell (LBNL)
Dr. Joseph Falkowski (ExxonMobil)
Prof. Laura Gagliardi (U Chicago)
Dr. Steven Kaye (Apple)
Dr. Jeffrey Kortright (LBNL)
Dr. Jung-Hoon Lee (LBNL)
Prof. Jeffrey Neaton (UC Berkeley)
Dr. David Prendergast (LBNL)
Prof. Jeffrey Reimer (UC Berkeley)
Prof. Berend Smit (UC Berkeley)
Dr. Simon Weston (ExxonMobil)

Funding
Department of Energy:
Office of Science, EFRC Program
ARPA-E, CERC-WET, NETL
ExxonMobil, Chevron, Bakar Foundation