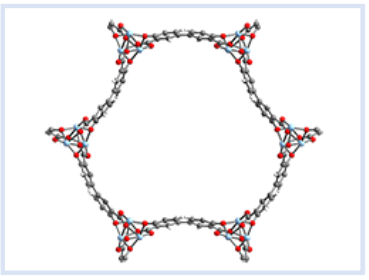
2017 NETL CO_2 Capture Technology Project Review Meeting

August 24, 2017



Amine-Appended Metal-Organic Frameworks as Switch-Like Adsorbents for Energy-Efficient Carbon Capture

Jeffrey R. Long, Jeffrey B. Neaton, and Maciej Haranczyk

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NATIONAL ENERGY TECHNOLOGY LABORATORY

U.S. DEPARTMENT OF ENERGY

BERKELEY LAB

Project Overview

Funding

- Total project funding
  - DoE share: $4.4M
- Funding for FY17: $1.4M

Project Participants

- PI: Jeffrey Long (LBNL)
- Co-PI: Jeffrey Neaton (LBNL)
- Co-PI: Maciej Haranczyk (LBNL)

Partners (unfunded under this program)

- MOF production (Mosaic Materials)
- System development (Inventys)
- Process modeling (CCSI^2, EPRI)

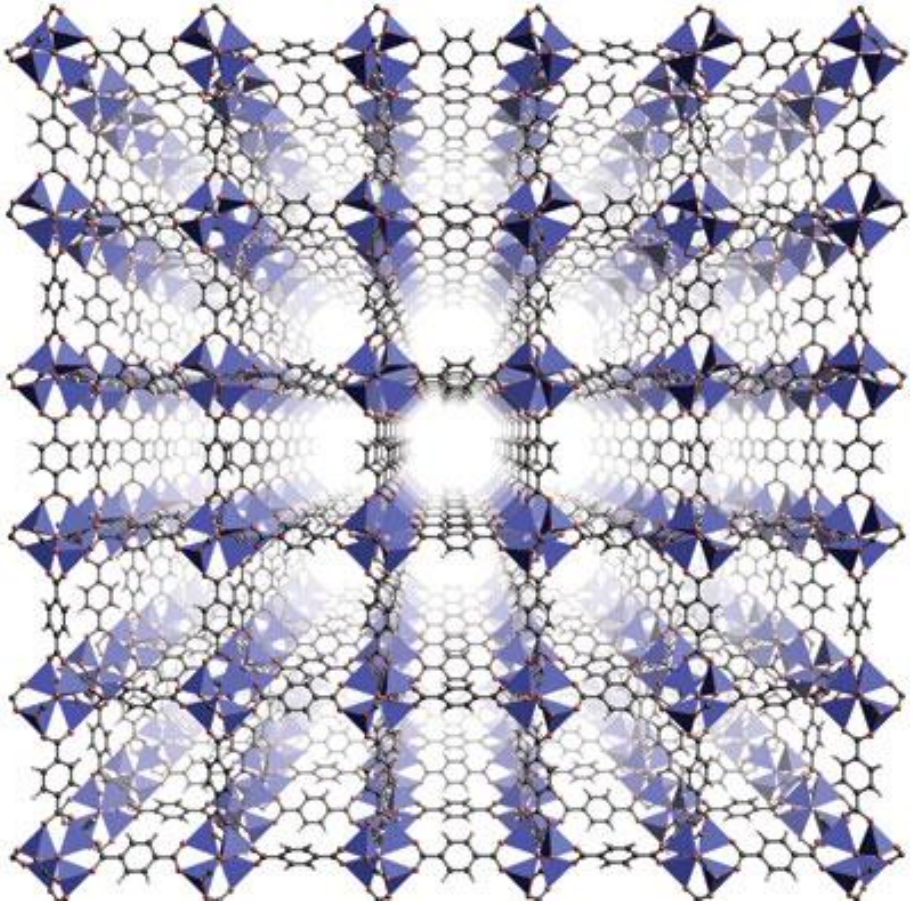
Overall Project Performance Dates

- Project start date: 6/1/2017 (funded from ?/?/2017)
- Project end date: 5/31/2021

Overall Project Objectives

Development of a transformational technology based upon a diamine-appended MOF for post-combustion CO_2 capture at a power plant

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

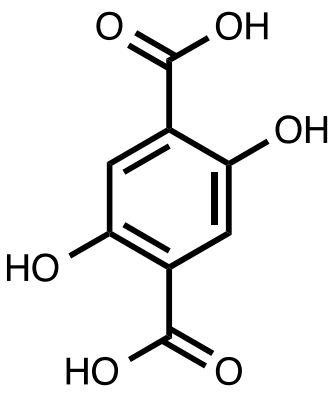
Can we make a MOF with surfaces densely coated with amine groups?

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

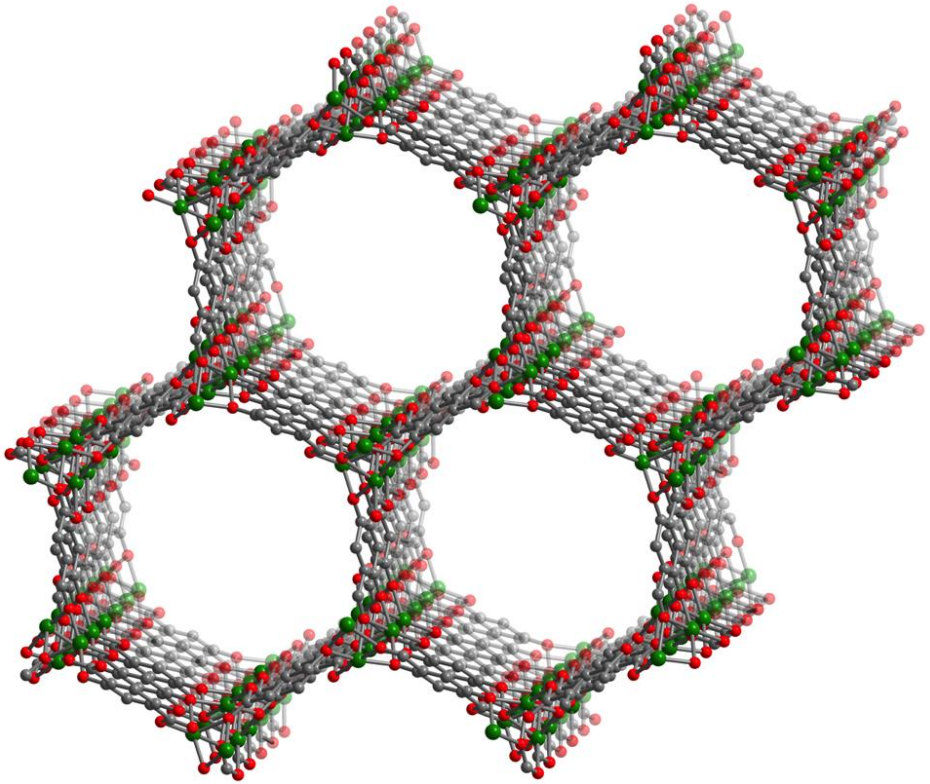
A MOF with a High Density of Exposed M^{2+} Sites

$MX_2 \cdot 6H_2O$

+



H_4dobdc



M_2(dobdc), M-MOF-74

(M = Mg, Mn, Fe, Co, Ni, Cu, Zn)

Rosi, Kim, Eddaoudi, Chen, O'Keeffe, Yaghi *J. Am. Chem. Soc.* **2005**, *127*, 1504

Dietzel, Morita, Blom, Fjellvåg *Angew. Chem., Int. Ed.* **2005**, *44*, 6354

Caskey, Wong-Foy, Matzger *J. Am. Chem. Soc*. **2008**, *130*, 10870

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

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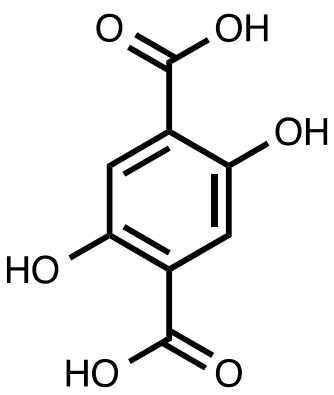
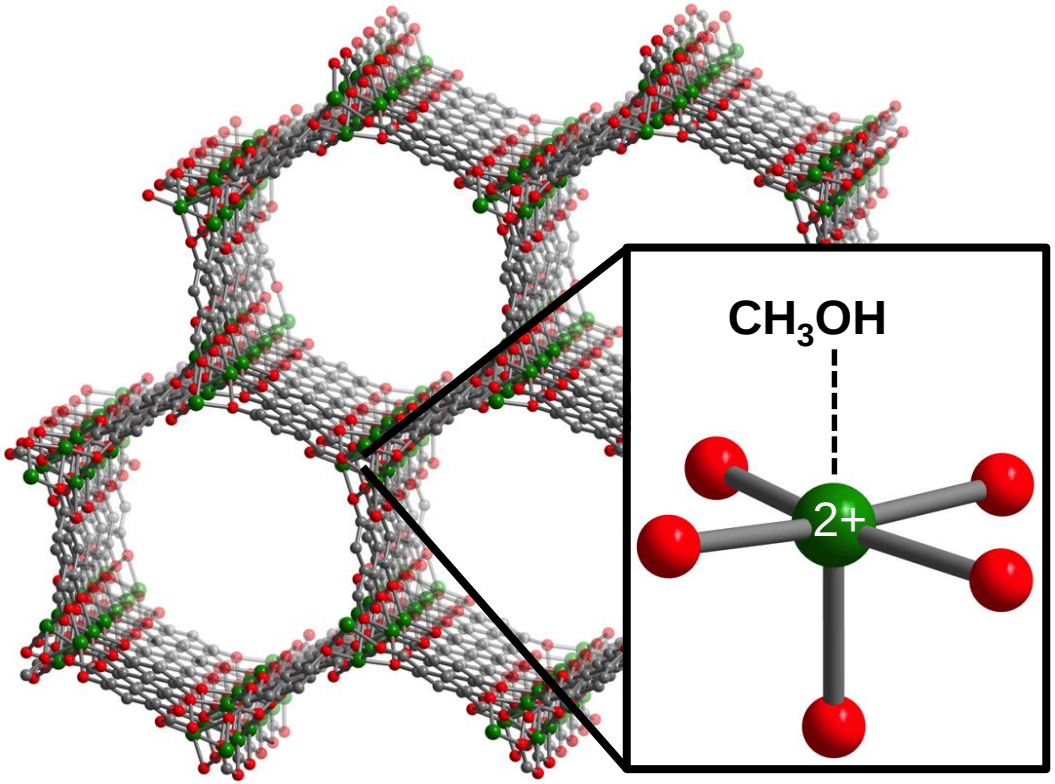


H_4dobdc



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A MOF with a High Density of Exposed M^{2+} Sites

$MX_2 \cdot 6H_2O$

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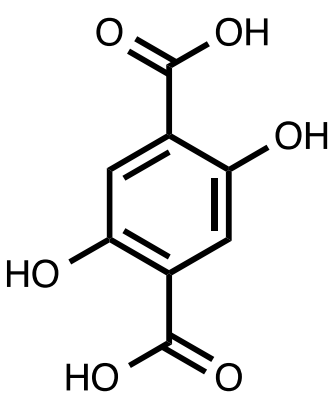
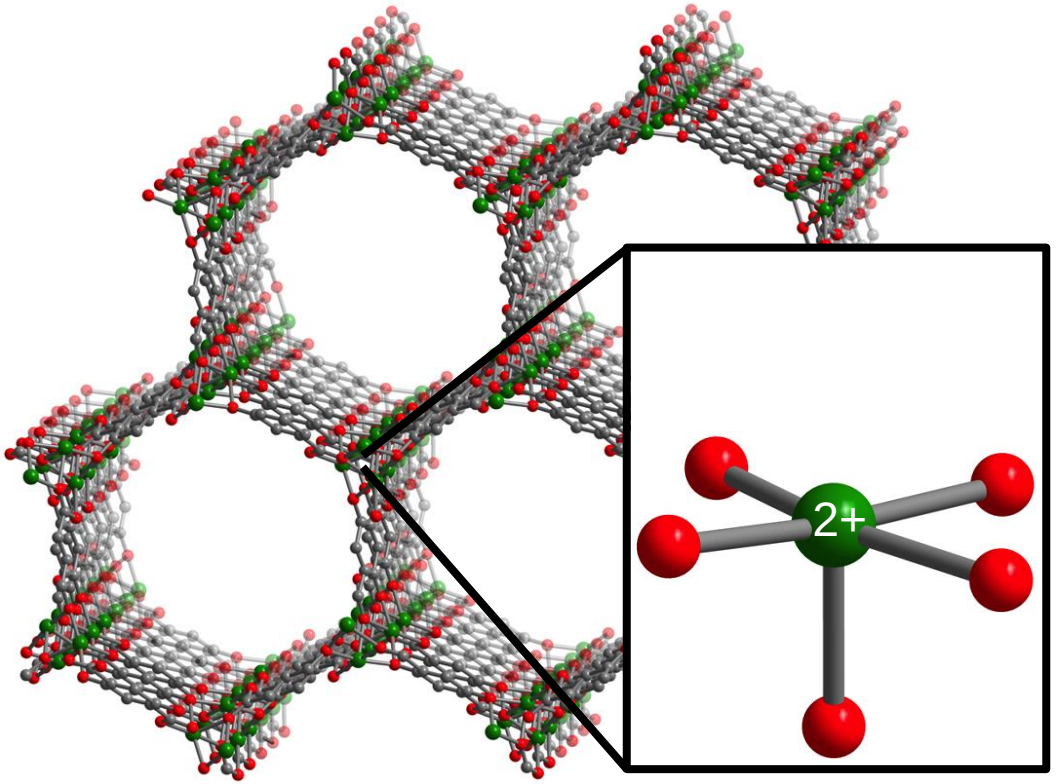


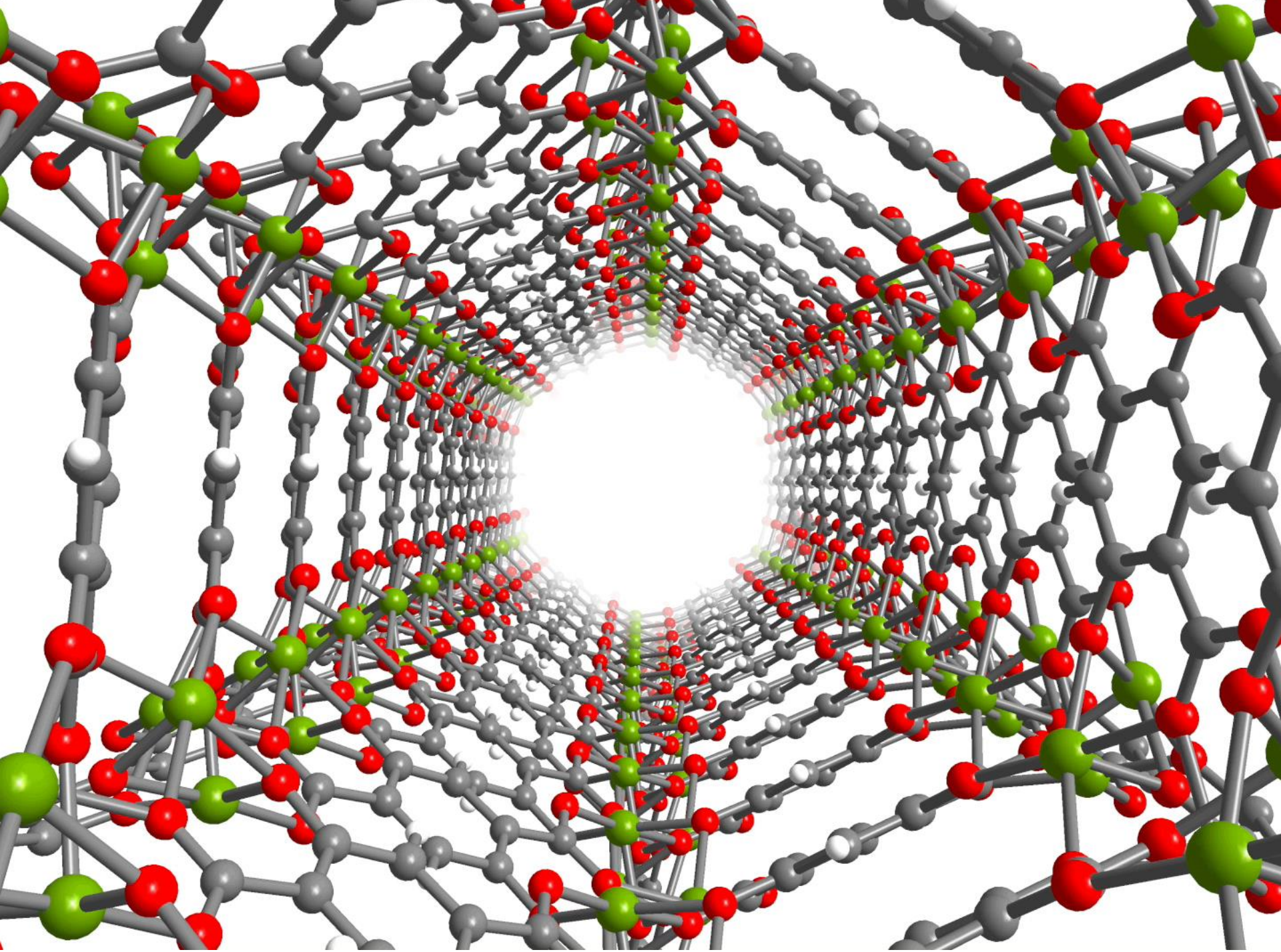
H_4dobdc

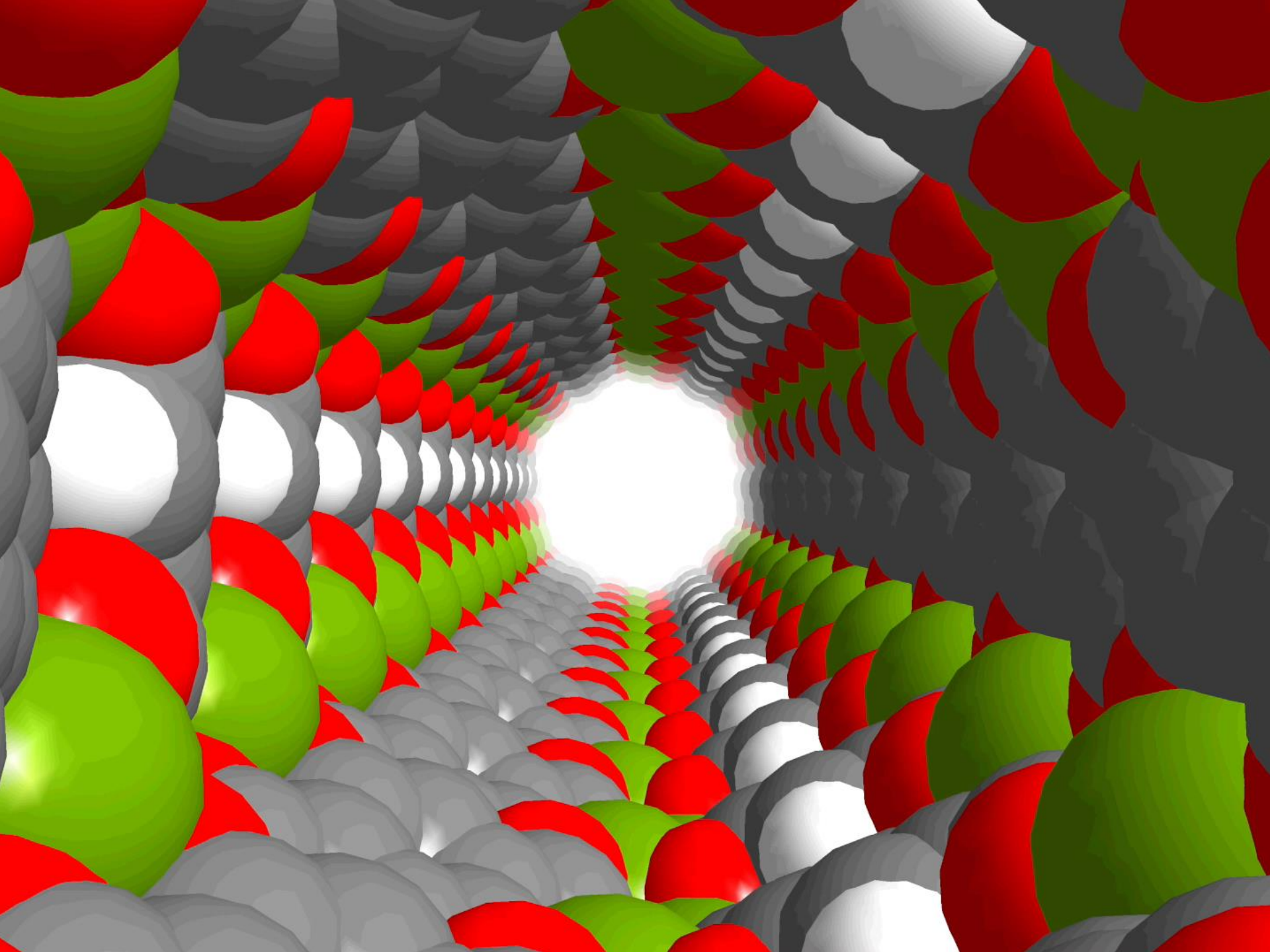


M_2(dobdc), M-MOF-74

(M = Mg, Mn, Fe, Co, Ni, Cu, Zn)

- Activated frameworks have Langmuir surface areas of 1280-2060 m^2/g
- Record high density of open metal coordination sites per unit mass or volume

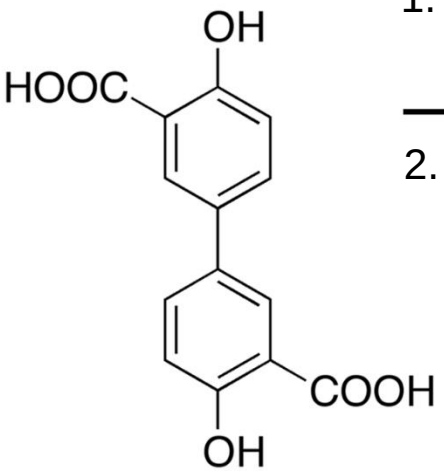




An Expanded Form of Mg_2(dobdc) (Mg-MOF-74)

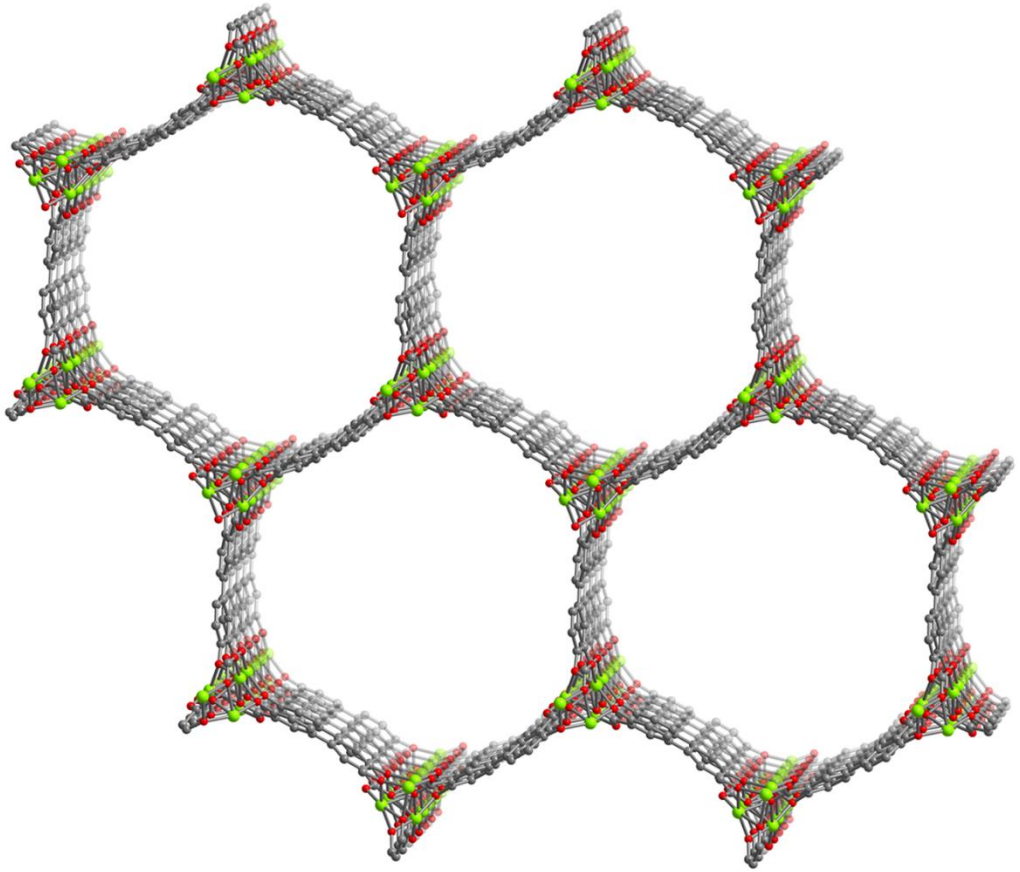
$Mg(NO_3)_2 \cdot 6H_2O$

+



H_4dobpdc

1. DMF/MeOH
   120 ° C
2. 100 ° C
   flowing CO_2

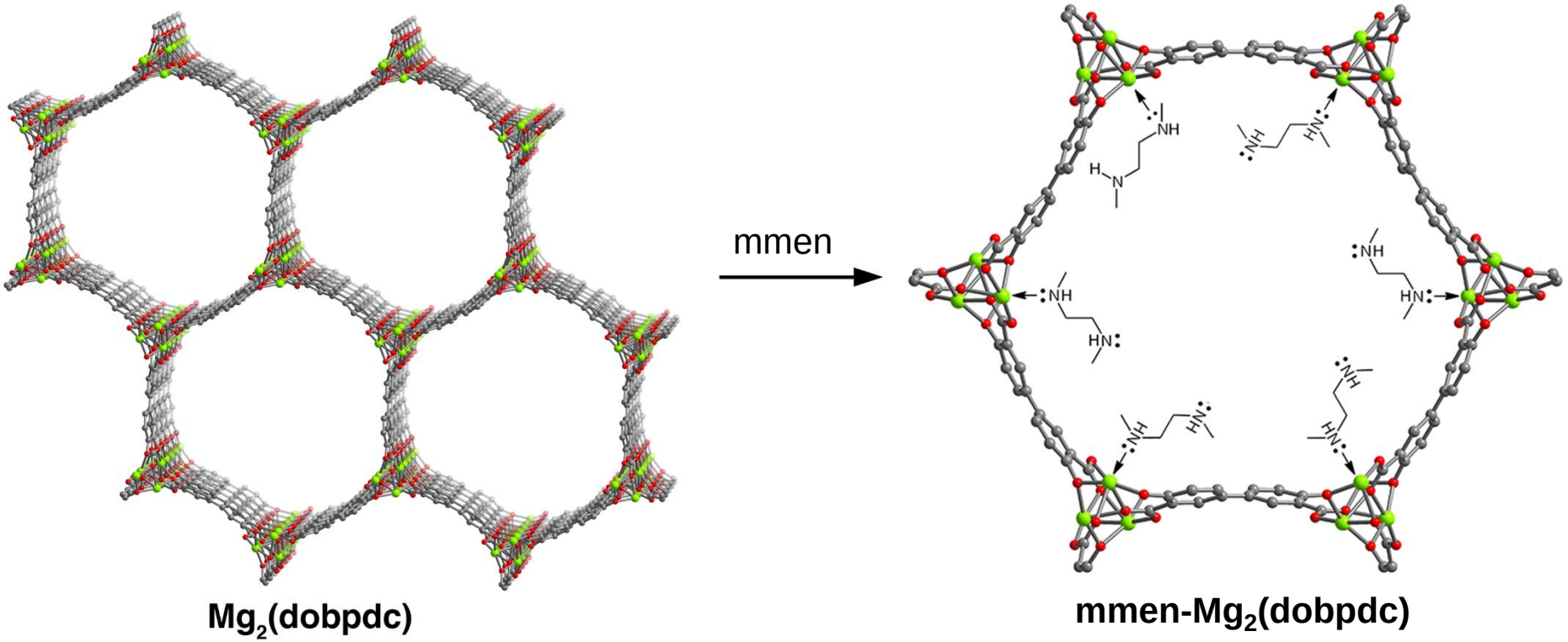


Mg_2(dobpdc)

- 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

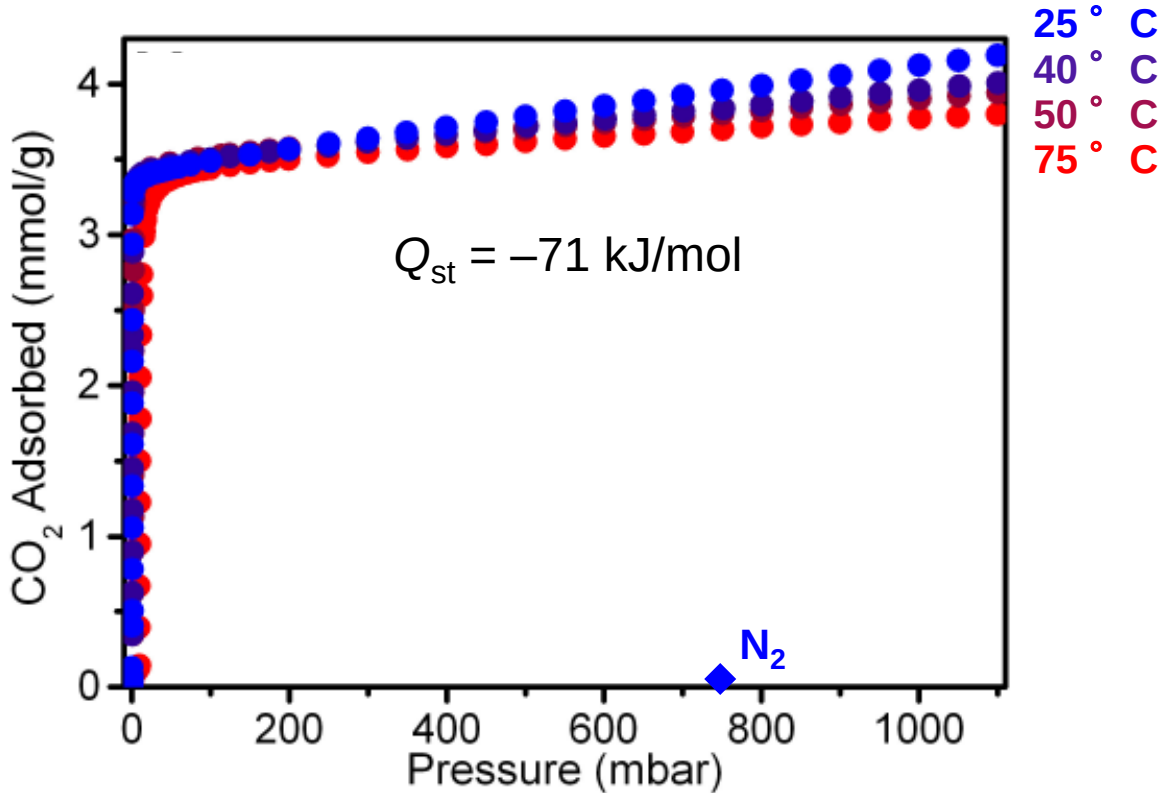
Appending Diamine Groups



- Dangling amines coat the periphery of the channel leaving space for rapid CO_2 diffusion

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

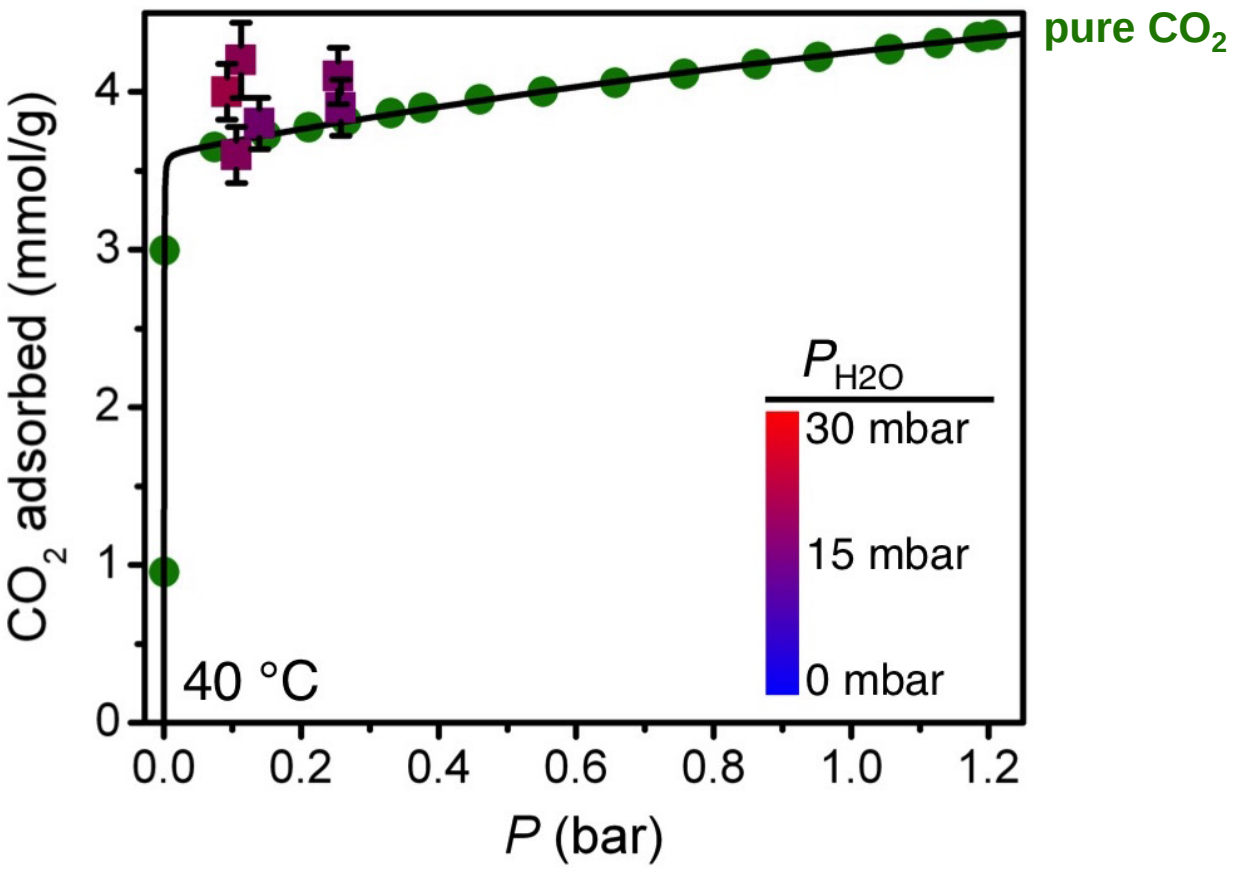
Strong, Selective CO_2 Adsorption



- High affinity of alkyl amines 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

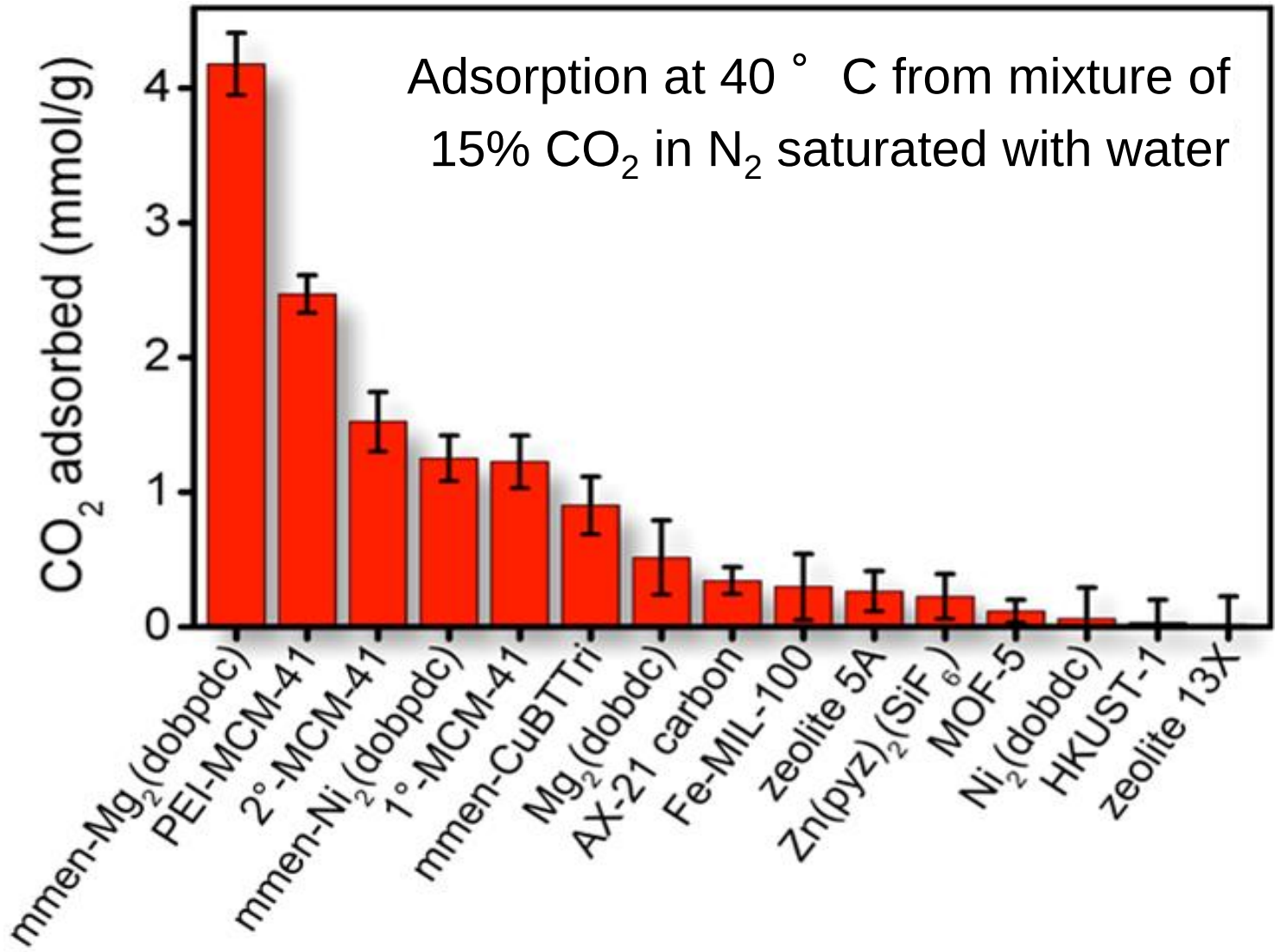
CO_2 Adsorption in the Presence of Water



- No loss of CO_2 capacity under wet flue gas conditions

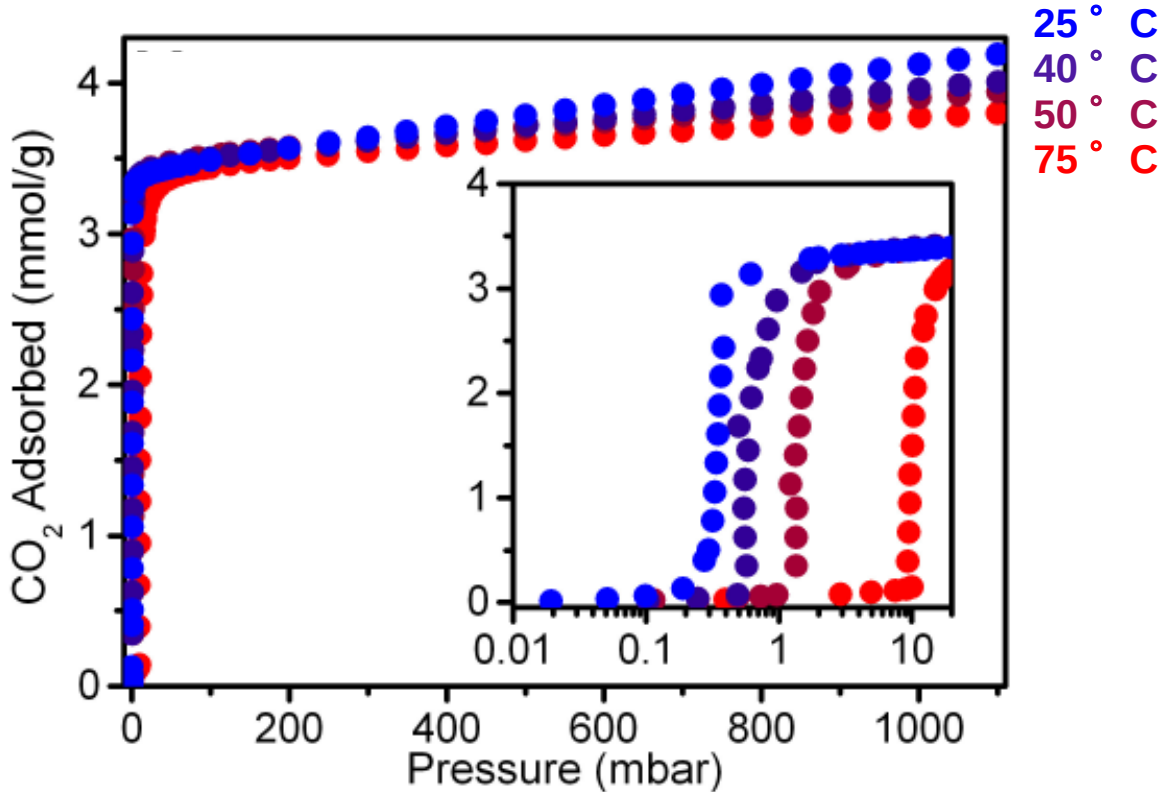
Mason, McDonald, Bae, Bachman, Sumida, Dutton, Kaye, Long, *J. Am Chem. Soc.* **2015**, *137*, 4787

CO_2 Adsorption from a Wet Simulated Flue Gas



Mason, McDonald, Bae, Bachman, Sumida, Dutton, Kaye, Long, *J. Am Chem. Soc.* **2015**, *137*, 4787

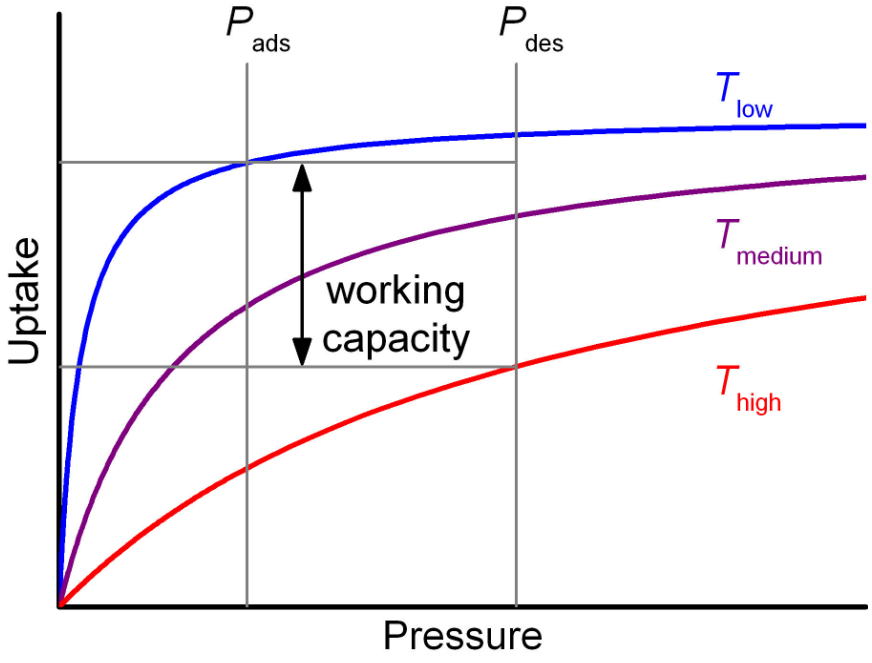
Step-Shaped Isotherms via Cooperative CO_2 Binding



- Very little hysteresis upon desorption of CO_2
- Step shifts rapidly to higher pressure with increasing temperature

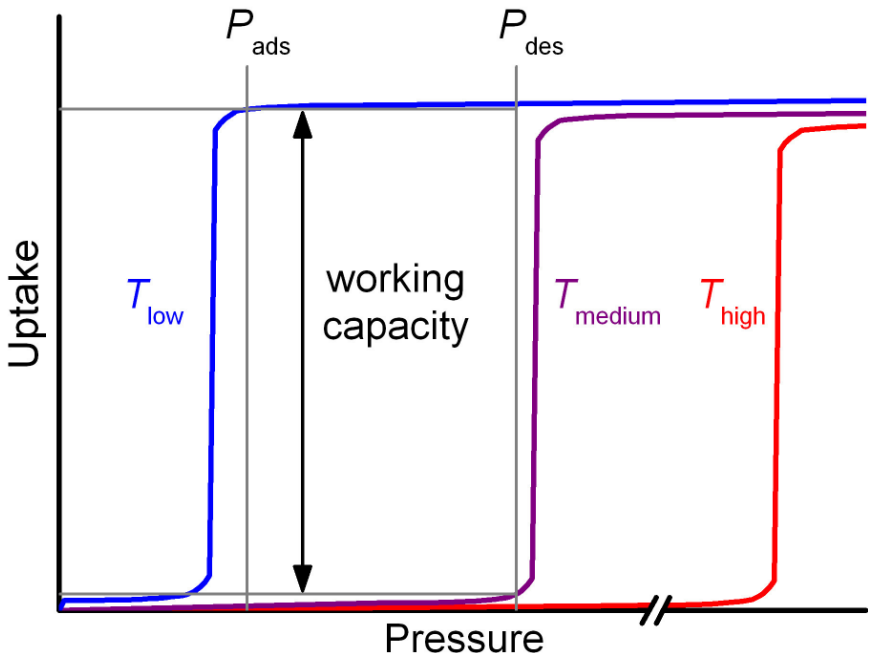
Classical versus Cooperative Adsorbents

amine solutions and other amine adsorbents



2 wt % CO_2 removed, ΔT = 100 ° C

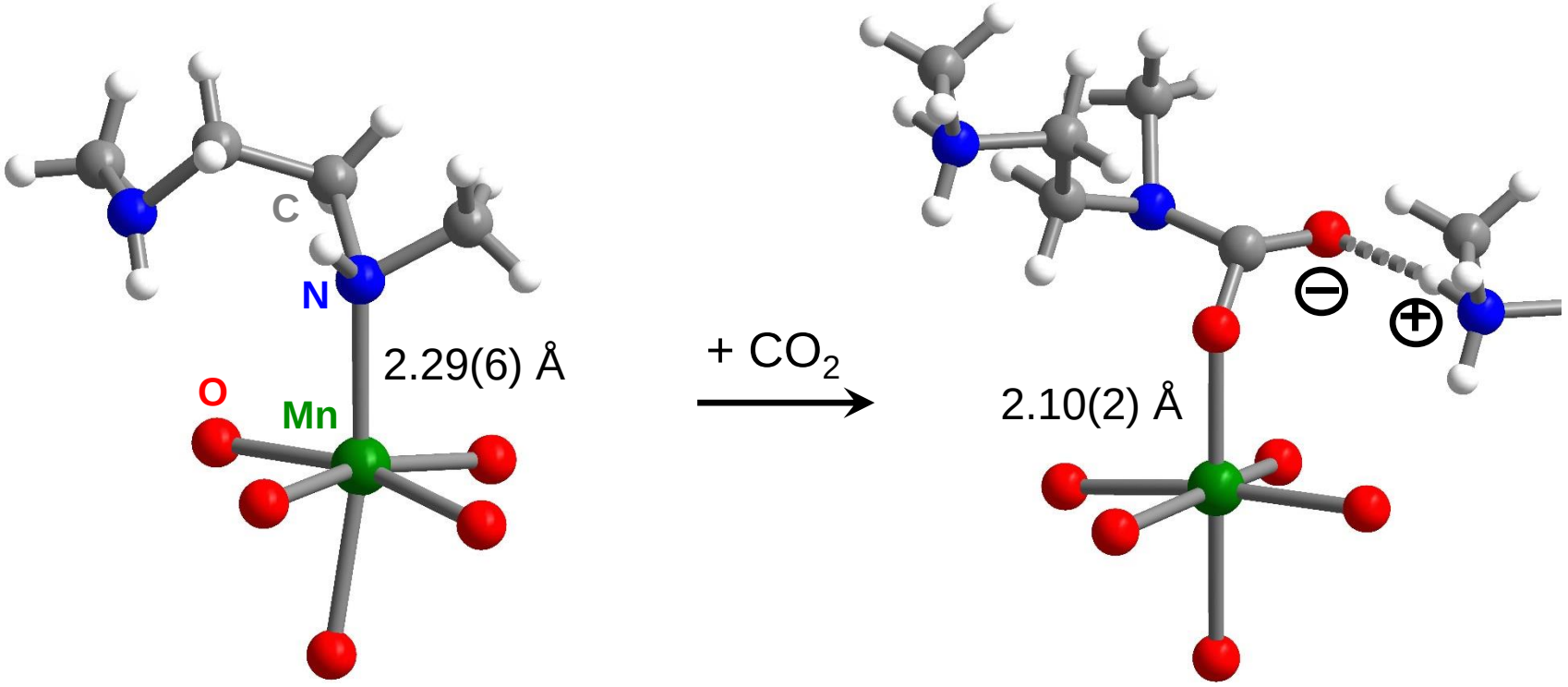
diamine-appended MOFs



15 wt % CO_2 removed, ΔT = 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

Structure Reveals Insertion of CO_2 into Mn-N Bond!

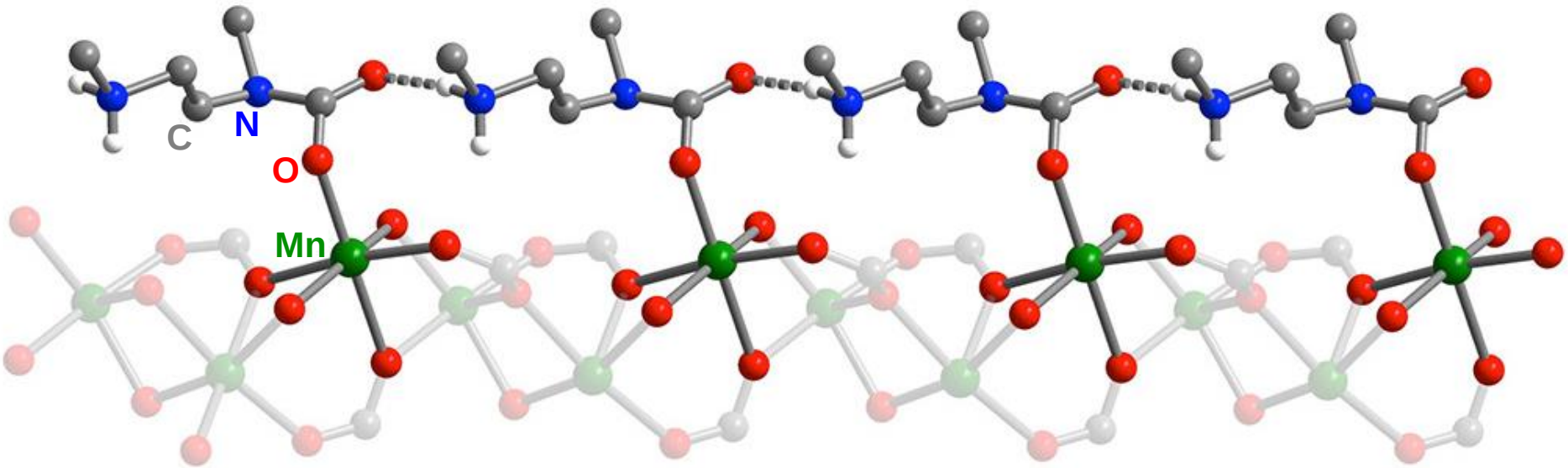


mmen-Mn_2(dobpdc) **mmenCO_2-Mn_2(dobpdc)**

- Insertion and proton transfer results in metal-bound carbamate
- Ammonium cation from neighboring site forms an ion pair with the carbamate

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

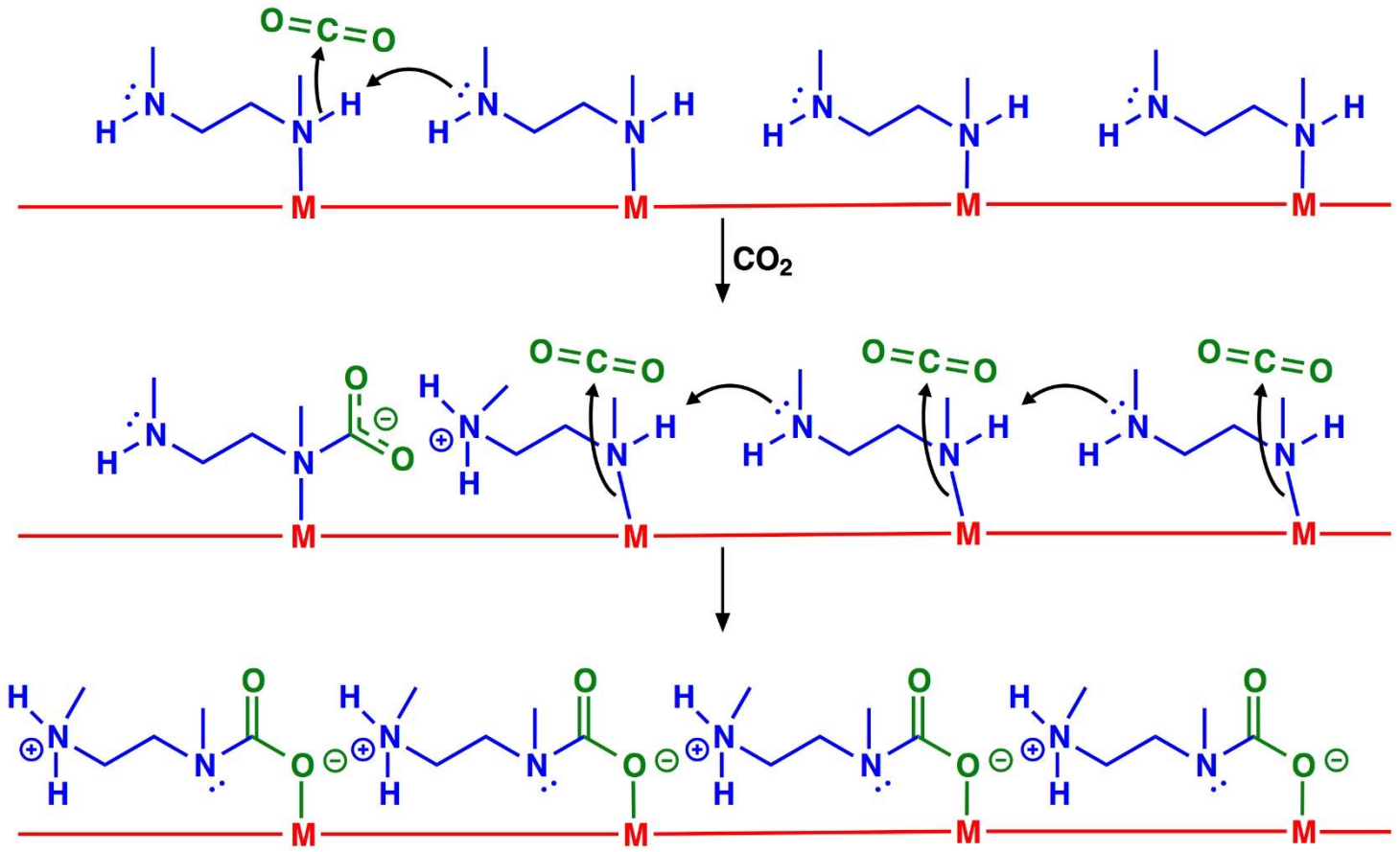
Ammonium Carbamate Chains



- Insertion of CO_2 into the metal-amine bond together with proton transfer
- One-dimensional ammonium carbamate chains indicate origins of cooperativity

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

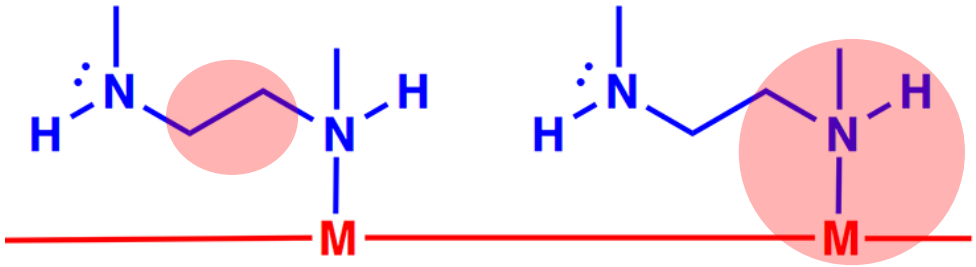
Cooperative CO_2 Adsorption Mechanism



- Position of the step should be influenced by metal-amine bond strength

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

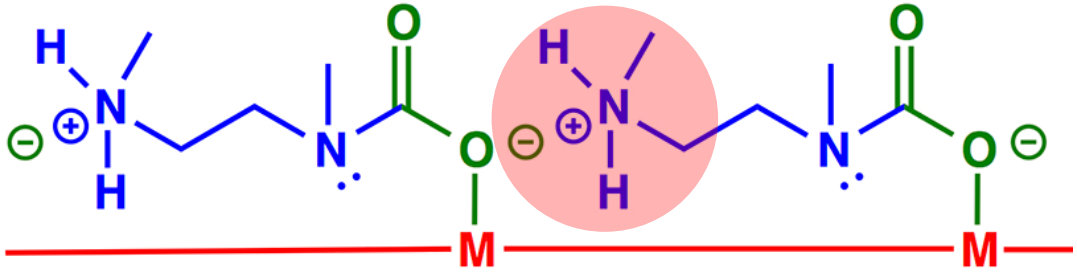
Manipulating the Adsorption Step Position



Substituents on diamine backbone

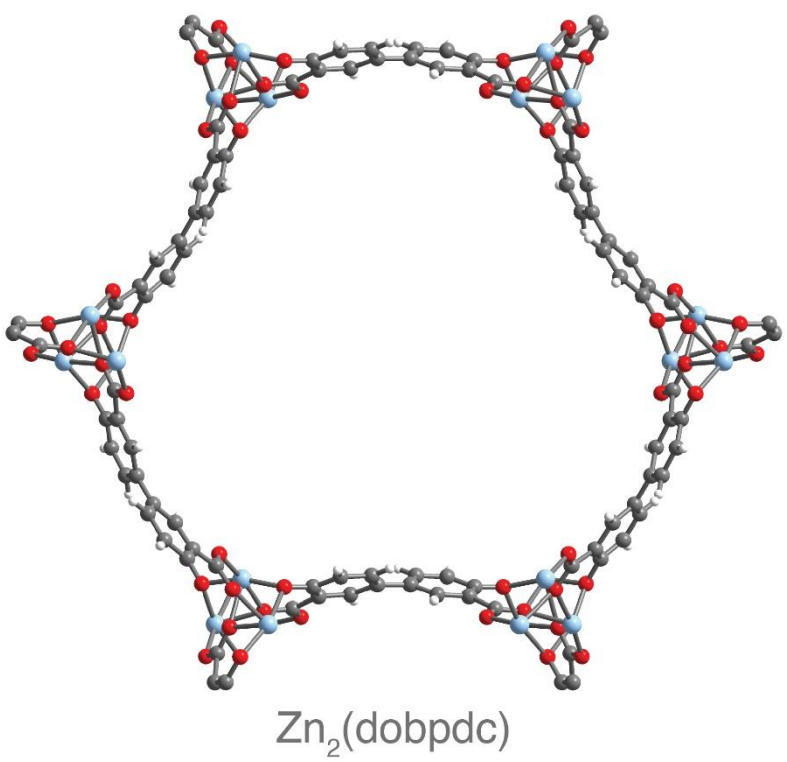
Substituents on metal-bound amine

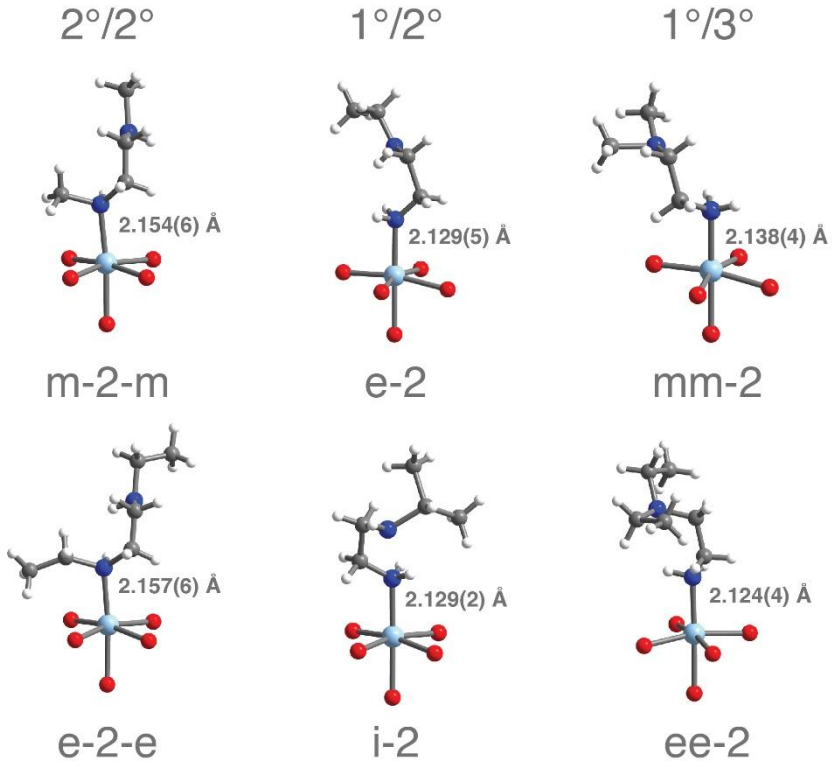
$+CO_2$



Substituents on ammonium-forming amine

Single Crystal Structures of $Zn_2(dobpdc)(diamine)_2$

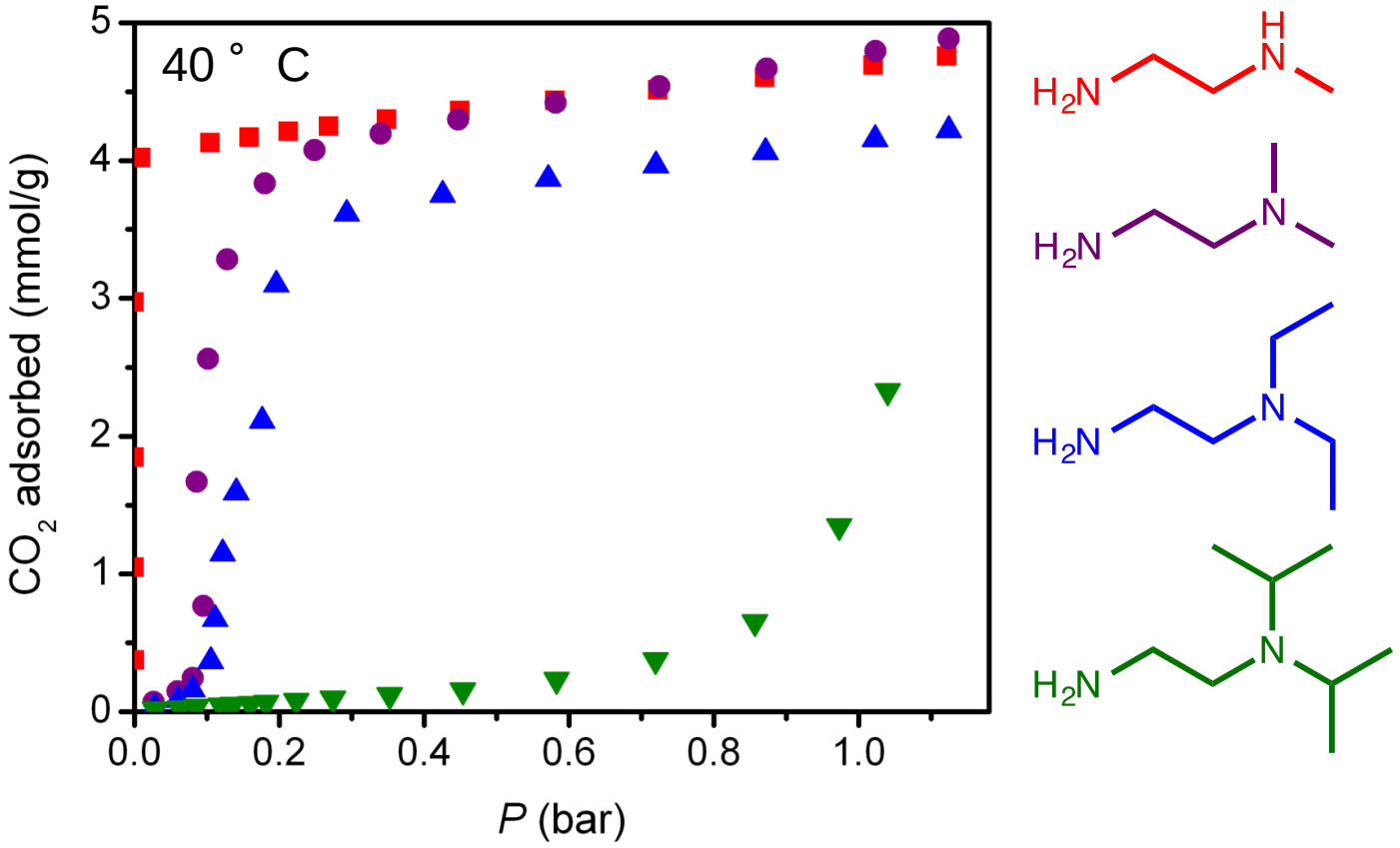




- Single crystals remain intact upon grafting diamines, activating, and adsorbing CO_2
- Primary amines preferentially bind to the metal center

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

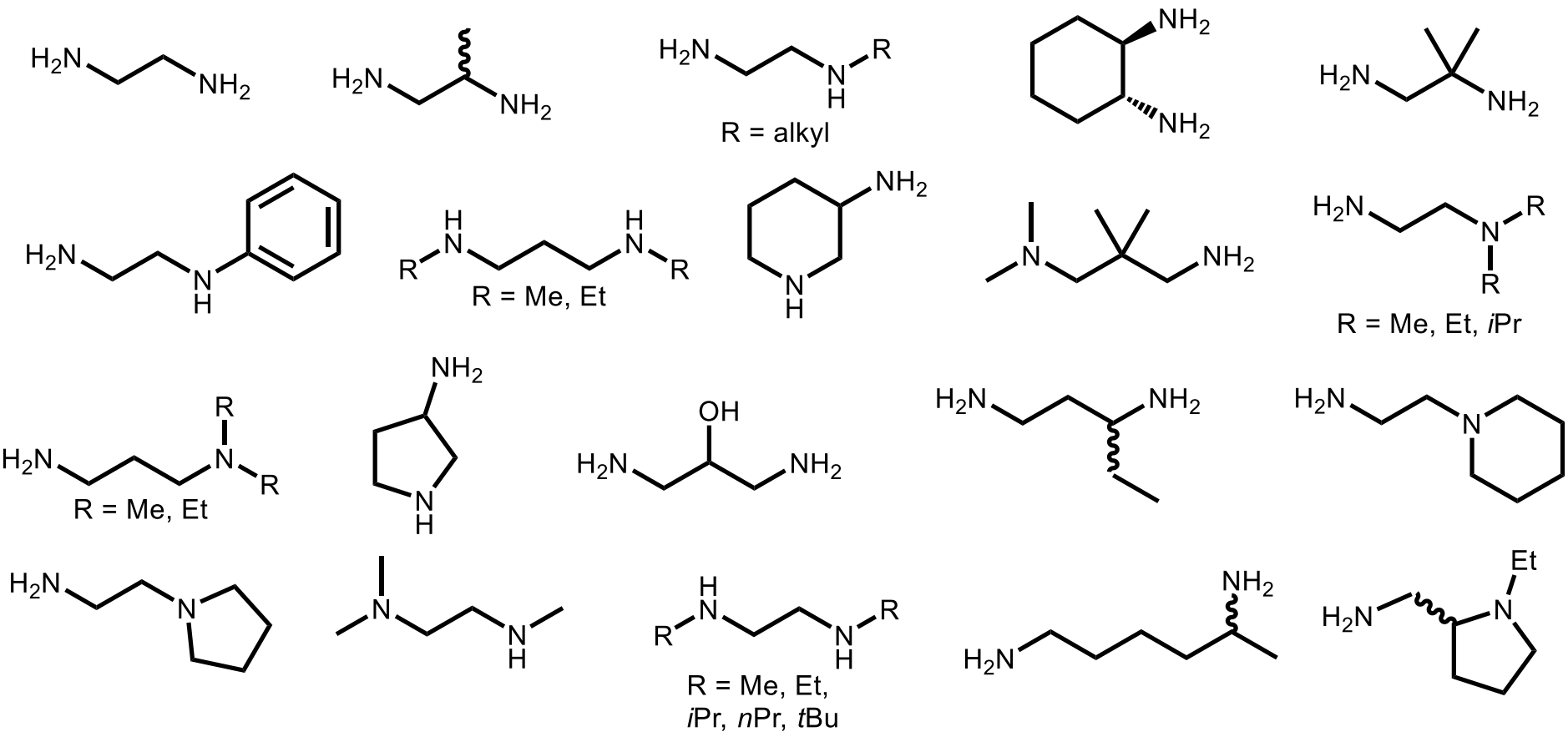
Varying Diamine Bulk in Mg_2(dobpdc)



- 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

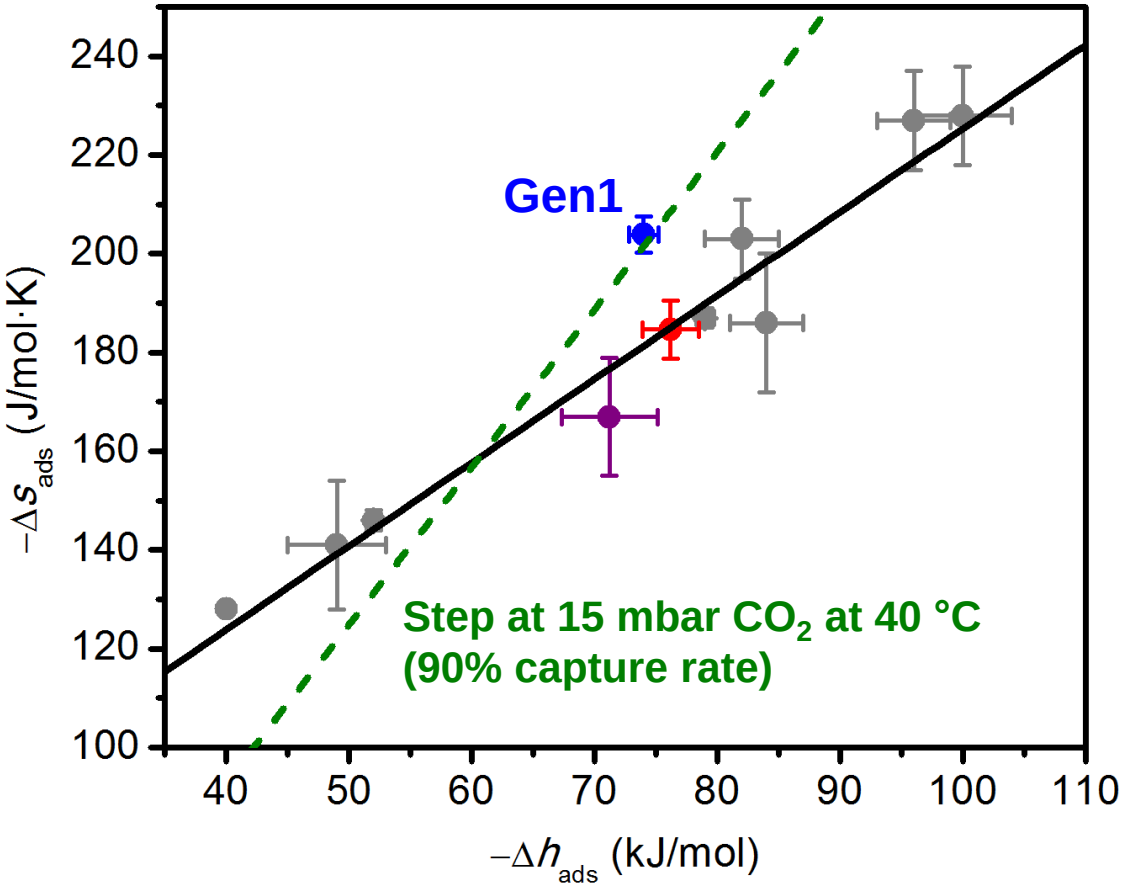
Variation of the Diamine Shifts the Step Position



- More than 80 different diamines have now been tested in Mg_2(dobpdc)
- Step position at 40 ° C varies from ~50 ppm to >1.2 bar

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

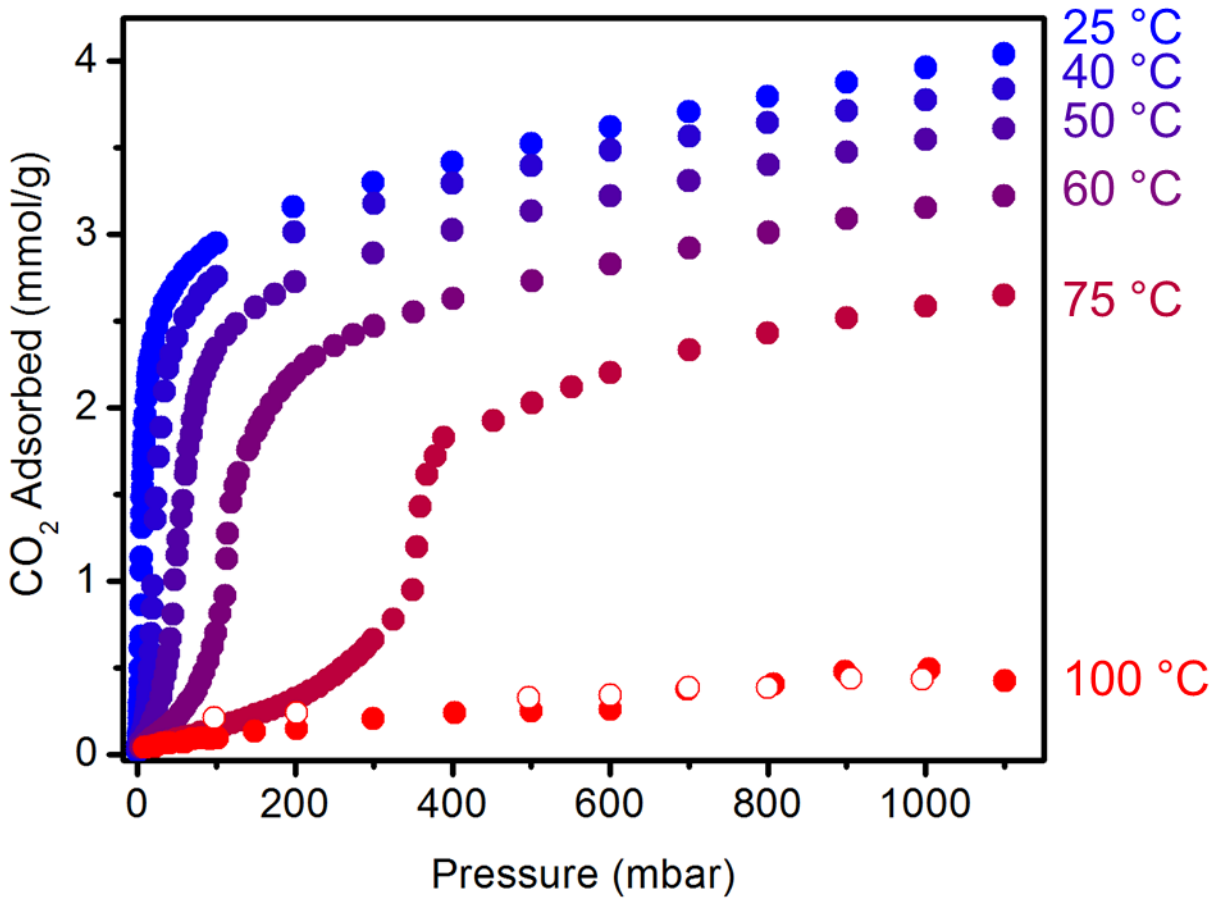
Manipulating the Thermodynamics of CO_2 Capture



- Molecular level tunability enables manipulation of enthalpy and entropy
- Gen1 adsorbent achieves 90% capture with small temperature swing

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

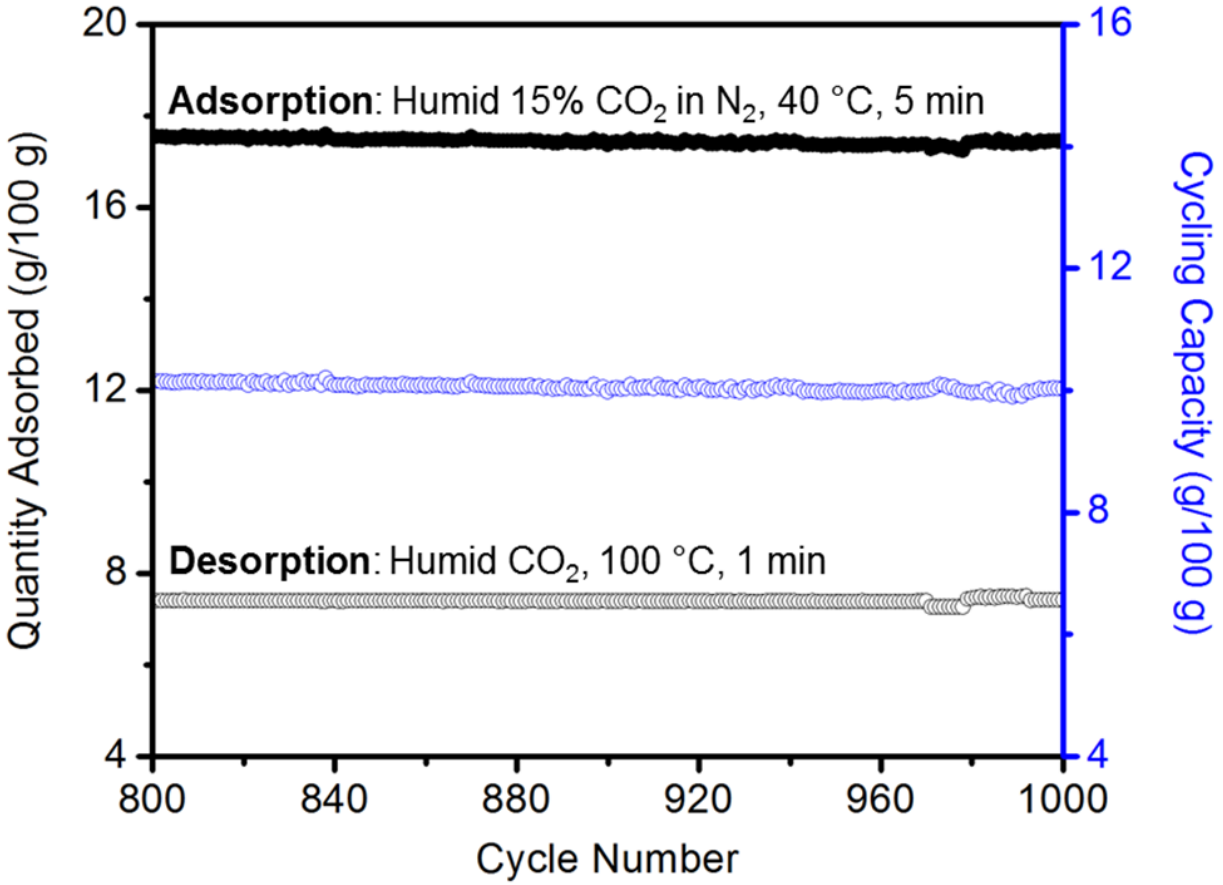
Gen1 Material for Coal Flue Gas Capture



- Step-shaped adsorption at 40 ºC and little adsorption at 100 ºC
- Working capacity of 2.4 mmol/g (9.1 wt%) with a 60 ºC temperature swing

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

Adsorption/Desorption Cycling in Gen1 Material



- TGA cycling experiments show no loss of capacity over 1000 cycles

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

Technical and Economic Advantages/Challenges

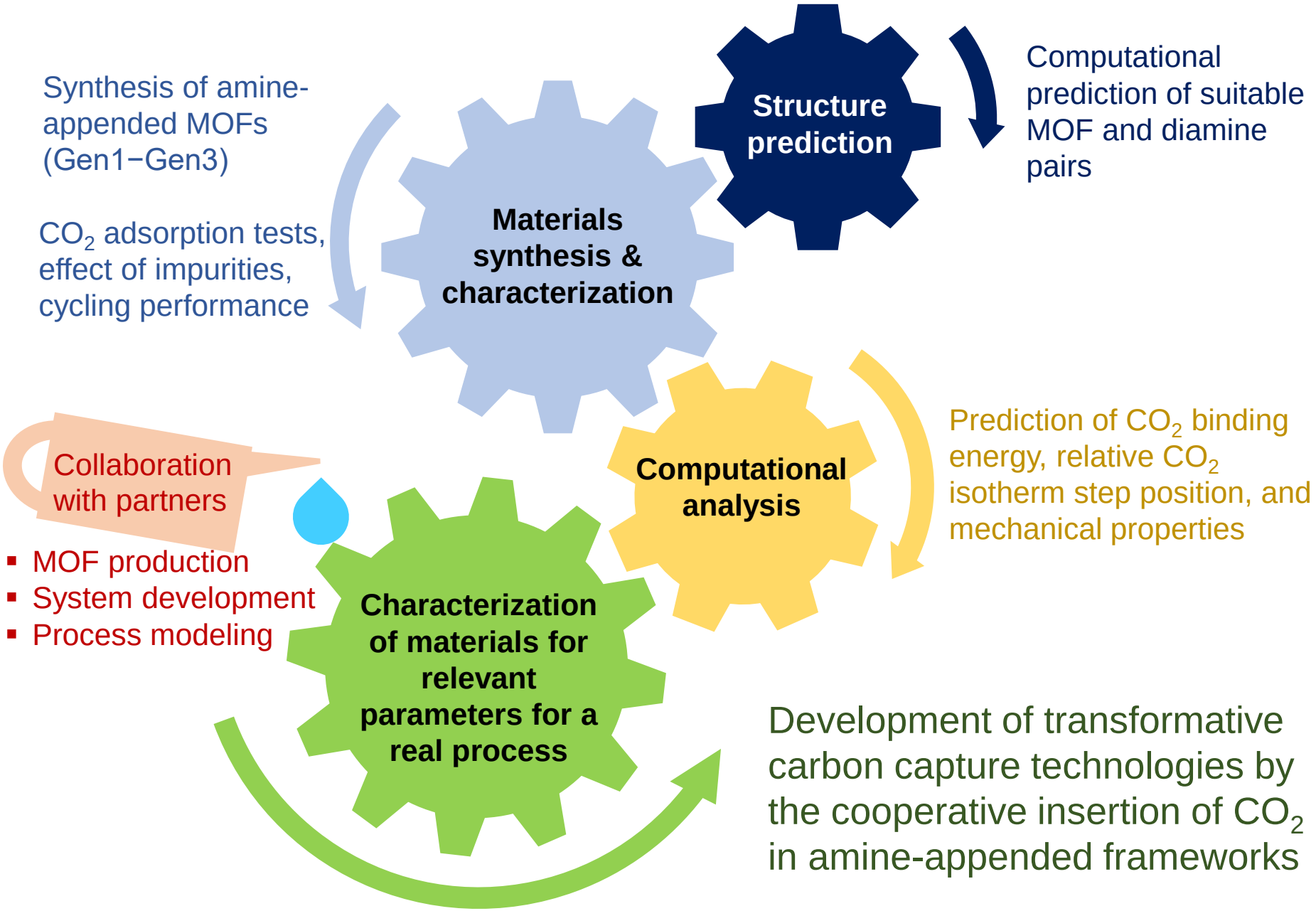
Advantages

- High tunability of diamine-appended framework materials
- Large working capacity due to step-shaped CO_2 adsorption
- High selectivity for CO_2 over N_2, O_2, and H_2O is possible
- Molecular level characterization is possible

Challenges

- Large scale production of the adsorbent
- Rendering the materials into a structured form
- Durability and chemical stability under real flue gas
- Reduction of regeneration cost (temperature swing)

Technical Approach and Project Scope



Experimental Design and Work Plan

Year 1

- Gen1 Amine-appended MOFs synthesis
- Effect of water, SO_x, and NO_x for Gen1 materials
- Computational prediction of suitable MOF and commercially available amine pairs

Year 2

- Synthesis of new amine-appended MOFs (Gen2)
- Stability and cycling performance tests
- Computational work to predict optimal amine-appended MOFs

Year 3

- Extensive characterization of Gen1/Gen2 materials
- Characterization of materials fabricated by industrial partners
- Expanded computational search

Year 4

- Gen3 materials synthesis and comprehensive characterization
- Characterization of materials tested on partners' site

- Project management and planning
- Literature survey and synthesis and testing of any relevant materials

- Collaboration with MOF production, system development, and process modeling partners

Project Schedule and Key Milestones (Year 1)

	Tasks	Milestones
Materials synthesis	Synthesis of amine-appended MOFs (Gen1 materials)	Deliver a new material with a working capacity of >2.5 mmol/g
	Characterization of the effect of water, SO_x, and NO_x on CO_2 adsorption properties of Gen1 materials	Deliver a material that retains >90% of original CO_2 uptake capacity after 20 cycles in the presence of water, SO_x, NO_x
Computation	Search optimal amine-appended MOFs within databases of reported materials	Propose 2 candidates whose CO_2 uptake capacity is greater than 3.0 mmol/g
	Prediction of CO_2 binding energies for amine-appended MOFs	Propose candidates having high CO_2 binding energies (>70 kJ/mol)

Project Schedule and Key Milestones (Year 2)

	Tasks	Milestones
Materials synthesis	Synthesis of new amine-appended MOFs (Gen2)	Deliver a new material with a working capacity of >3.0 mmol/g
	Characterization of the effect of water, SO_x, and NO_x on CO_2 adsorption properties of new adsorbents	Deliver a Gen2 material that retains more than 95% of the original CO_2 uptake capacity after exposure to a N_2/CO_2 (= 85/15) stream containing impurities for 3 days followed by cycling tests
Computation	Search optimal amine-appended MOFs (Gen2 materials) among computationally designed materials	Propose 2 candidates whose CO_2 uptake capacity is greater than 3.5 mmol/g
	Prediction of relative CO_2 isotherm step position	Based on the analyses, propose the promising candidates whose step position is lower than materials prepared in Year 1

Project Schedule and Key Milestones (Year 3)

	Tasks	Milestones
Materials synthesis	Comprehensive characterization of all relevant parameters for a real process	Deliver a Gen2 material that retains more than 95% of the original CO_2 uptake capacity after exposure to a N_2/CO_2 (= 85/15) stream containing impurities for a week followed by cycling tests
	Characterization of materials fabricated by industrial partners	Design shaped materials that maintain at >90% of CO_2 adsorption capacity
Computation	Extend the material design	Propose at least 1 candidate whose *volumetric* CO_2 uptake capacity is greater than 3.5 mmol/cm^3
	Prediction of mechanical strength for a real process	Based on the analyses, propose mechanically robust candidates (>10 GPa) for practical applications

Project Schedule and Key Milestones (Year 4)

	Tasks	Milestones
Materials synthesis	Synthesis and comprehensive characterization for new (Gen3) materials predicted in Year 3	Deliver a Gen3 material that demonstrates >3.2 mmol/g of CO_2 uptake capacity after exposure to a N_2/CO_2 (= 85/15) stream containing impurities for a week followed by cycling tests
	Characterization of materials tested by partners	Performance of tested materials maintains at least 90% of CO_2 adsorption capacity

Project Timeline

Tasks	Year 1				Year 2				Year 3				Year 4			
	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12	Q13	Q14	Q15	Q16
Synthesis of amine-appended MOFs (Gen1 materials)	■	■	■	■												
Characterization of the effect of water, SO_x, and NO_x on CO_2 adsorption properties of Gen1 materials	■	■	■	■												
Search optimal amine-appended MOFs within databases of reported materials	■	■	■	■												
Prediction of CO_2 binding energies for amine-appended MOFs	■	■	■	■												
Synthesis of new amine-appended MOFs (Gen2)					■	■	■	■								
Characterization of the effect of water, SO_x, and NO_x on CO_2 adsorption properties of new adsorbents					■	■	■	■								
Search optimal amine-appended MOFs (Gen2 materials) among computationally designed materials					■	■	■	■								
Prediction of relative CO_2 isotherm step position					■	■	■	■								
Comprehensive characterization of all relevant parameters for a real process									■	■	■	■				
Characterization of materials fabricated by industrial partners									■	■	■	■				
Extend the material design									■	■	■	■				
Prediction of mechanical strength for a real process									■	■	■	■				
Synthesis and comprehensive characterization for new (Gen3) materials predicted in Year 3													■	■	■	■
Characterization of materials tested by partners													■	■	■	■

Project Success Criteria

Year	Success Criteria
Year 1	Prepare an adsorbent with >90% CO_2 capture from N_2/CO_2 (= 85/15) gas mixtures and a working capacity of >2.5 mmol/g under temperature swing conditions.
Year 2	Prepare an adsorbent with >90% CO_2 capture from N_2/CO_2 (= 85/15) gas mixtures, a working capacity of >3 mmol/g with a smaller temperature swing than MEA (80 °C), and a regeneration energy less than 2.5 MJ/kg CO_2.
Year 3	Prepare an adsorbent that retains the same properties as that from Year 2 after extended high-temperature cycling in the presence of water and other flue gas contaminants(water, SO_x, NO_x = ~2%, 800 ppm, and 500 ppm). Synthetic cost (based on rough cost analysis) is less than $75/kg.
Year 4	Prepare an adsorbent with >90% CO_2 capture from flue gas, a working capacity of >3.2 mmol/g, and a regeneration energy less than 2.2 MJ/kg CO_2 after extended high-temperature exposure/cycling. Synthetic cost (based on rough cost analysis) is less than $50/kg.

High Impact Technical Risks and Mitigation Strategies

Description of Risk	Mitigation Strategies
Computationally proposed materials are difficult to synthesize.	Computational screening will predict multiple promising materials. If one of the proposed adsorbents is difficult to prepare, we will synthesize another promising material.
Challenges are encountered with gram-scale synthesis of a sorbent.	The Long group has extensive expertise with preparing MOFs at the gram scale. We will focus on scalability as a parameter when evaluating new adsorbents.
Sorbents with a specific process (fixed bed or Veloxo Therm) fail to show significant reductions in energy penalty and capital cost.	Computational investigation will be performed to evaluate if the palletization of materials under high-pressure affects the CO_2 adsorption properties. In addition, we plan to elucidate the reasons for this from the close collaboration with system modeling partners.
Calibration of sorbent performance and process limitations can impact the performance of this FWP success criteria.	Accurate data collection mitigates the inaccuracy/ indefinite of the modeling data. We will carry out analysis of new materials to minimize the uncertainty (e.g. use of large quantity of material, repeat analysis to confirm the reproducibility).
Sorbent performance and scalability impact the technology system economics.	Any issues related to the process design will be solved in close collaboration with the partners. We will also work with MOF synthesis partners to figure out how promising sorbents will be synthesized economically.

Progress and Current Status of Project: Facilities and Other Resources

Materials synthesis

- Fume hoods, benches and standard equipment for wet chemistry
- Gas/vapor adsorption analyzers (e.g. N_2, Ar, CO_2, water)
- Thermogravimetric analyzers (TGA) coupled with a mass spectrometer
- Laboratory built breakthrough setups
- Powder X-ray diffractometer (PXRD)
- FT-IR and UV-vis spectrometers
- Grove boxes, ovens, microscopes
- SEM, NMR (solution, solid-state), EA (CHN, ICP) are available at UC Berkeley Chemistry Department
- Access to ALS for single crystal XRD analysis

Computation

- Powerful GPU-equipped Linux workstations
- Mid-range computing clusters with multicore 2.5 GHz Ivy Bridge and 2.3 GHz Haswell nodes
- Access to DOE's the National Energy Resource Scientific Computing Center (NERSC) Cray XC30/XC40 "Cascade" system

Plans for Future Testing and Development

Prediction of MOF−diamine pairs

- Search optimal amine-appended MOFs within databases
- Propose 2 candidates whose CO_2 uptake capacity is greater than 3.0 mmol/g

Prediction of CO_2 binding energies

- Optimize structures and estimate CO_2 binding energies for Gen1 materials
- Calculate water, SO_x, and NO_x binding energies

Synthesis of diamine-appended MOFs (Gen1 materials)

- Synthesis and characterization of Gen1 materials
- Test CO_2 adsorption behaviors of Gen1 materials
- Characterization of the effect of water, SO_x, and NO_x on CO_2 adsorption properties on Gen1 materials

Collaboration with partners

- Discussion of technology information needs for MOF production, system development, and process modeling
- Collection and analysis of materials characterization data
- Incorporation of relevant data into design catalogue