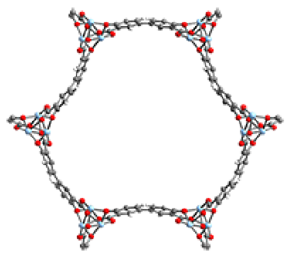
2018 NETL $CO_2$
Capture Technology
Project Review Meeting

*August 13, 2018*



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

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

*Lawrence Berkeley National Laboratory*

# Project Overview

## Funding

- Total project funding
  - DoE share: $7.4M
  - Cost share: $755k

## Project Participants

- PI: Jeffrey Neaton (LBNL)
- Co-PI: Jeffrey Long (LBNL)
- Co-PI: Maciej Haranczyk (LBNL)
- Mosaic Materials (MOF production)
- Inventys (System development)
- Electricore (System development)
- $CCSI^2$ (Process modeling – unfunded)

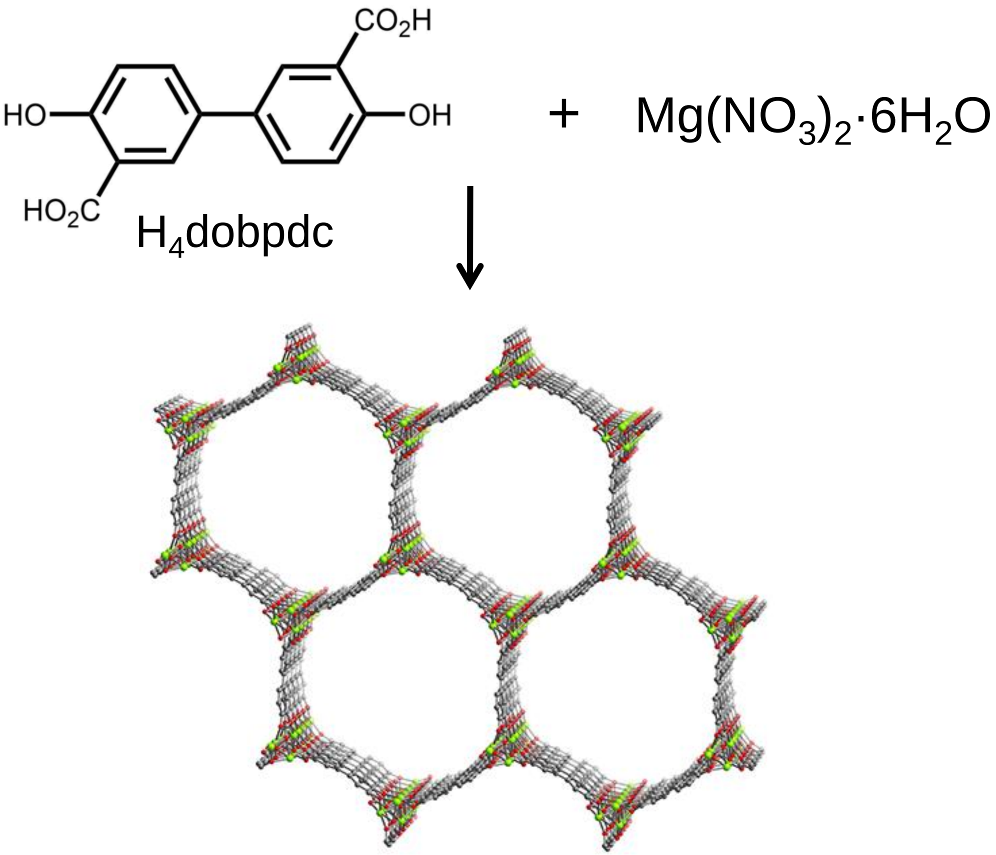
## Overall Project Performance Dates

- Project start date: 8/1/2017
- Industrial partners start date: 8/1/2018
- Project end date: 7/31/2021

## Overall Project Objectives

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

# Technology Background: MOFs for $CO_2$ Capture

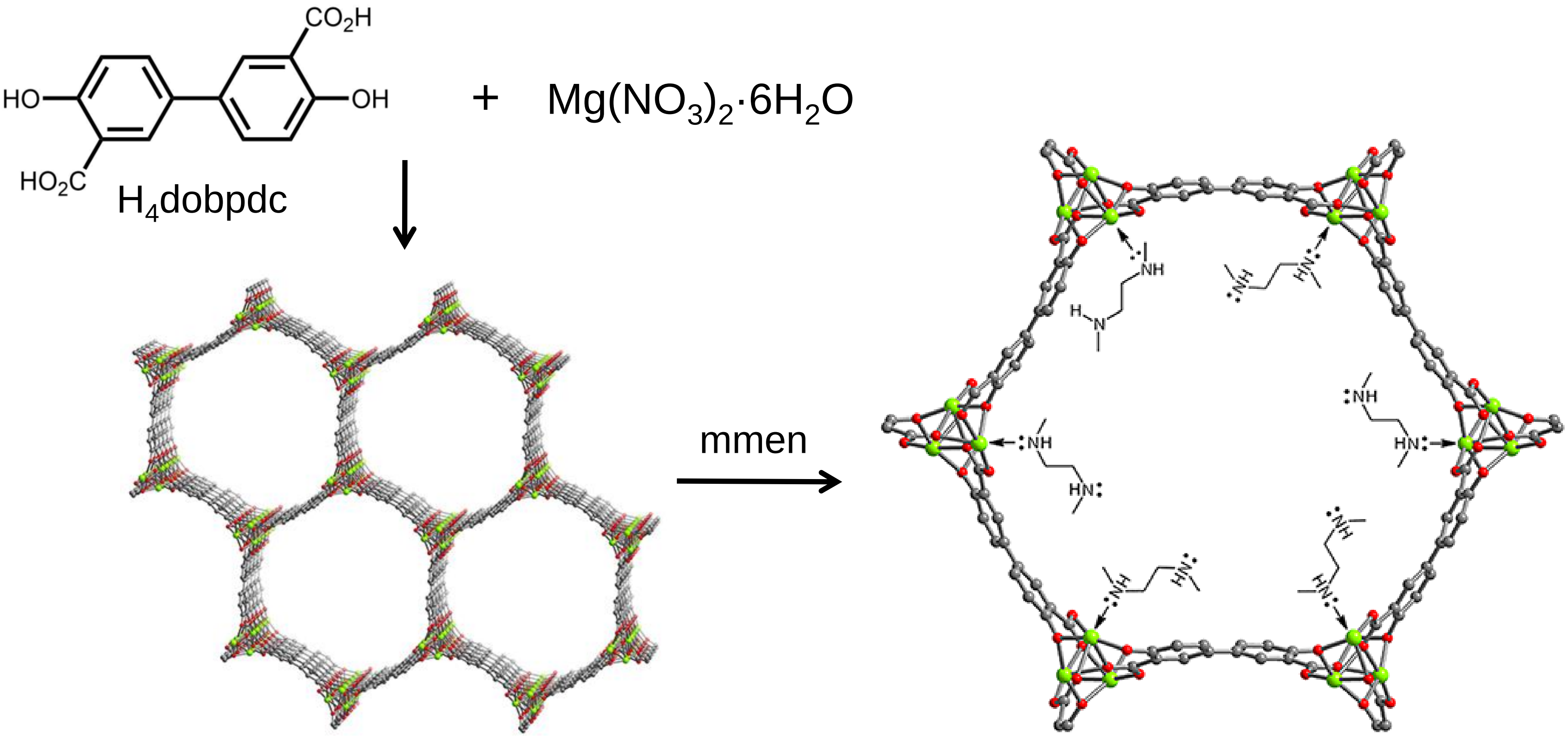



**$Mg_2$(dobpdc)** **mmen-$Mg_2$(dobpdc)**

- MOF channels have a diameter of 18 Å and are lined with open $Mg^{2+}$ sites
- Dangling amines coat periphery of the channel leaving space for rapid $CO_2$ diffusion

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

# Technology Background: MOFs for $CO_2$ Capture

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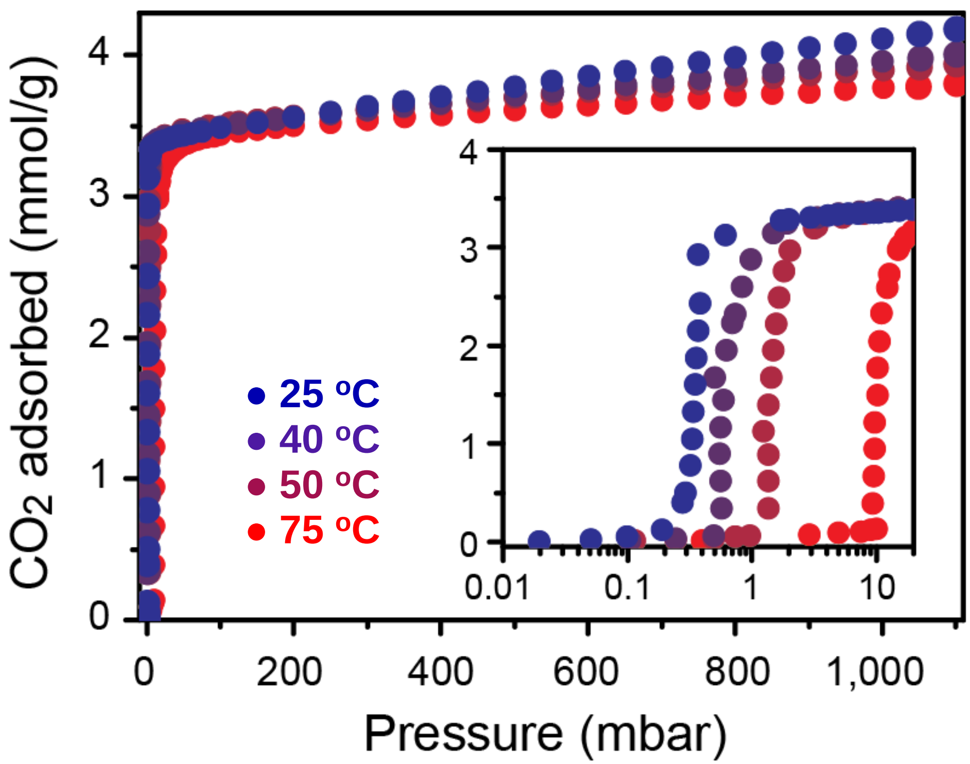
# Step-Shaped Isotherms via Cooperative $CO_2$ Binding




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


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

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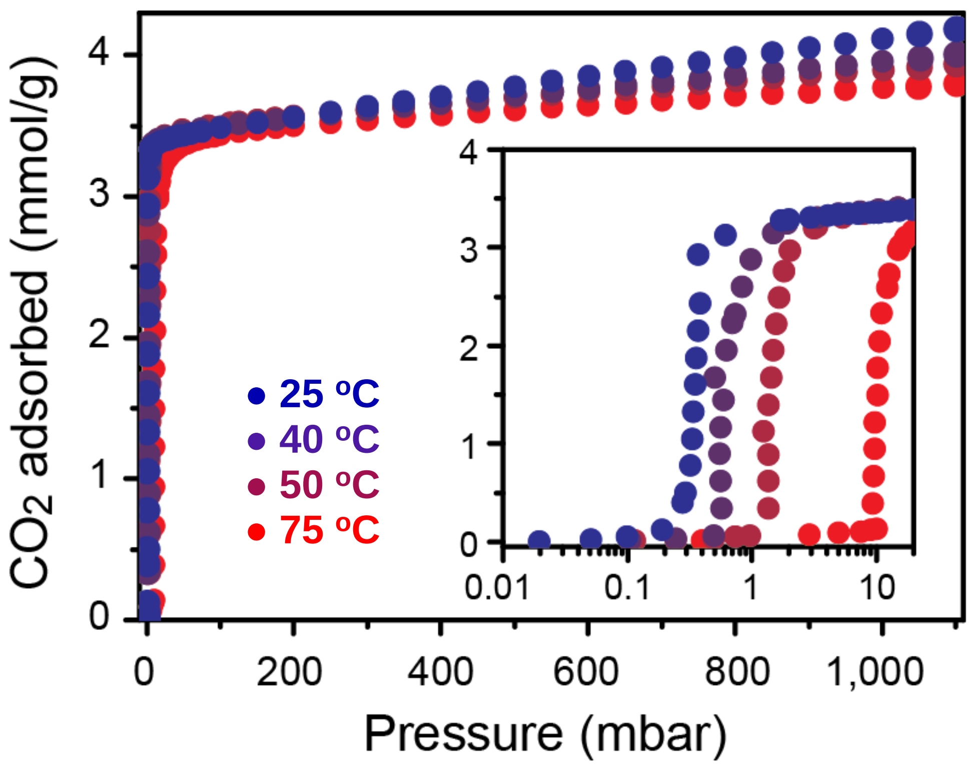


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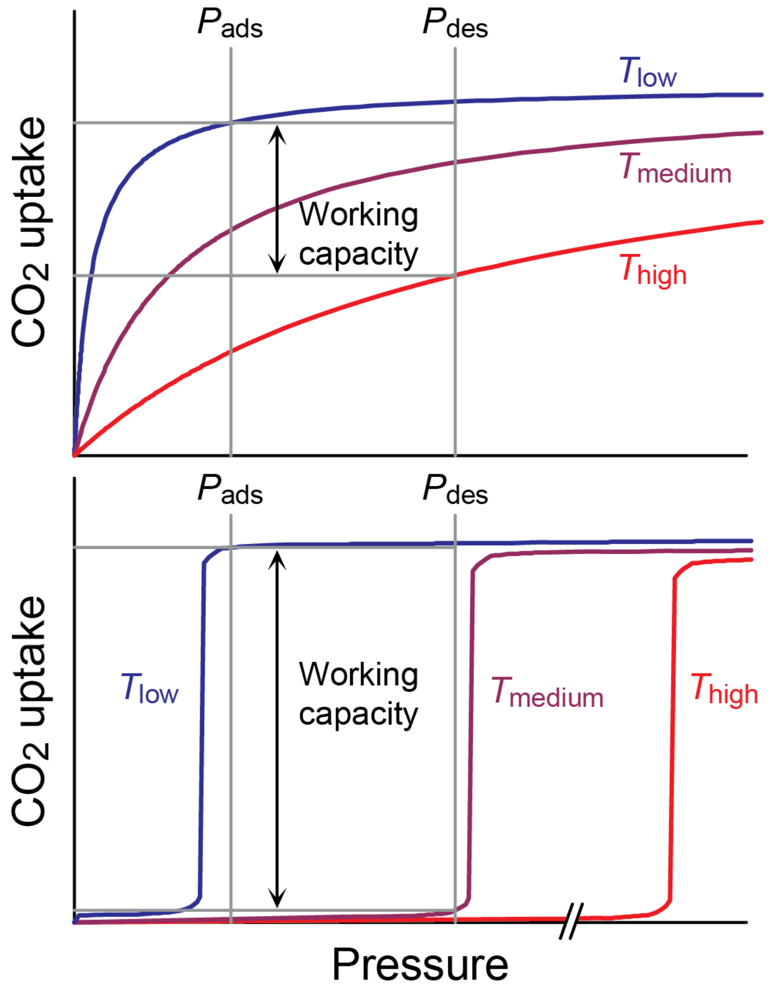
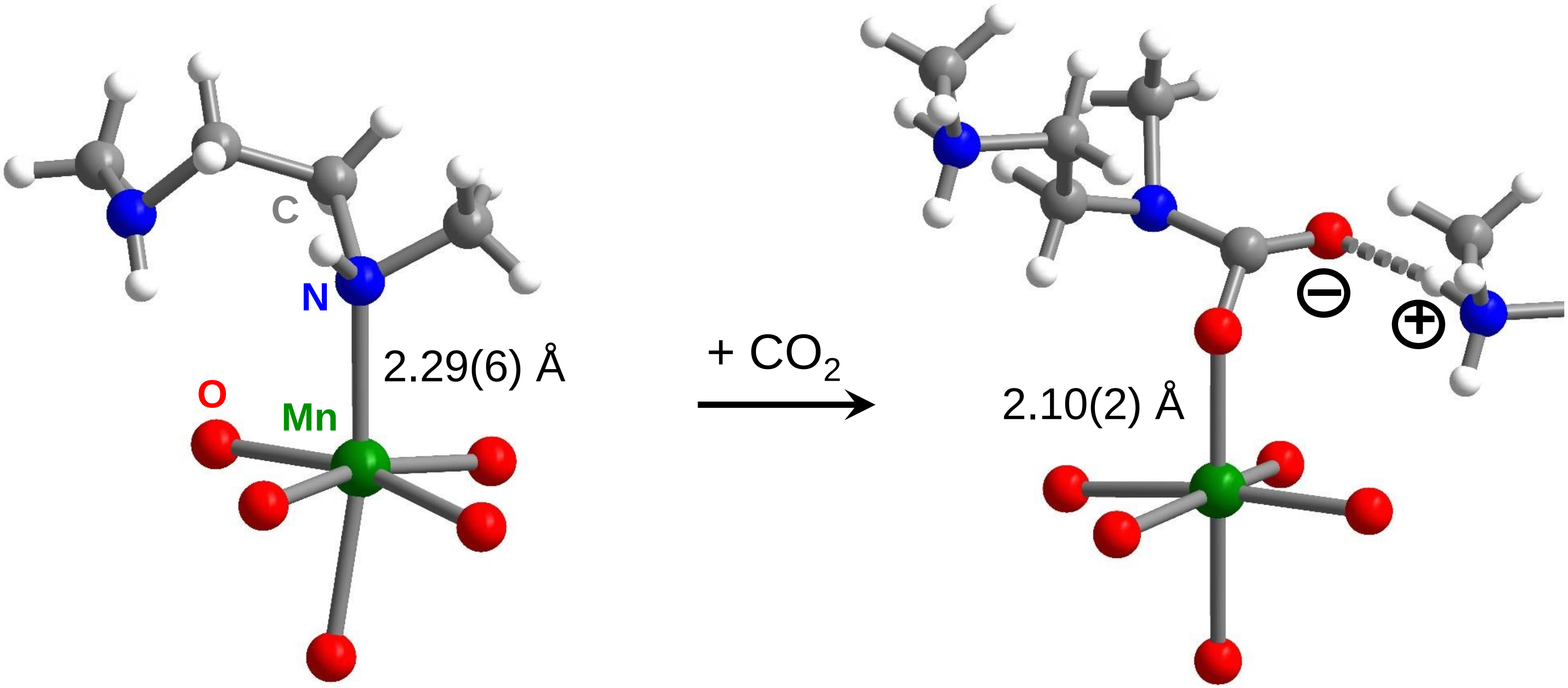




McDonald, Mason, Kong, Bloch, Gygi, Dani, Crocellà, Giordano, Odoh, Drisdell, Vlaisavljevich, Dzubak, Poloni, Schnell, Planas, Lee, Pascal, Prendergast, Neaton, Smit, Kortright, Gagliardi, Bordiga, Reimer, Long *Nature* **2015**, *519*, 303

# $CO_2$ Inserts into the Metal-Amine Bonds

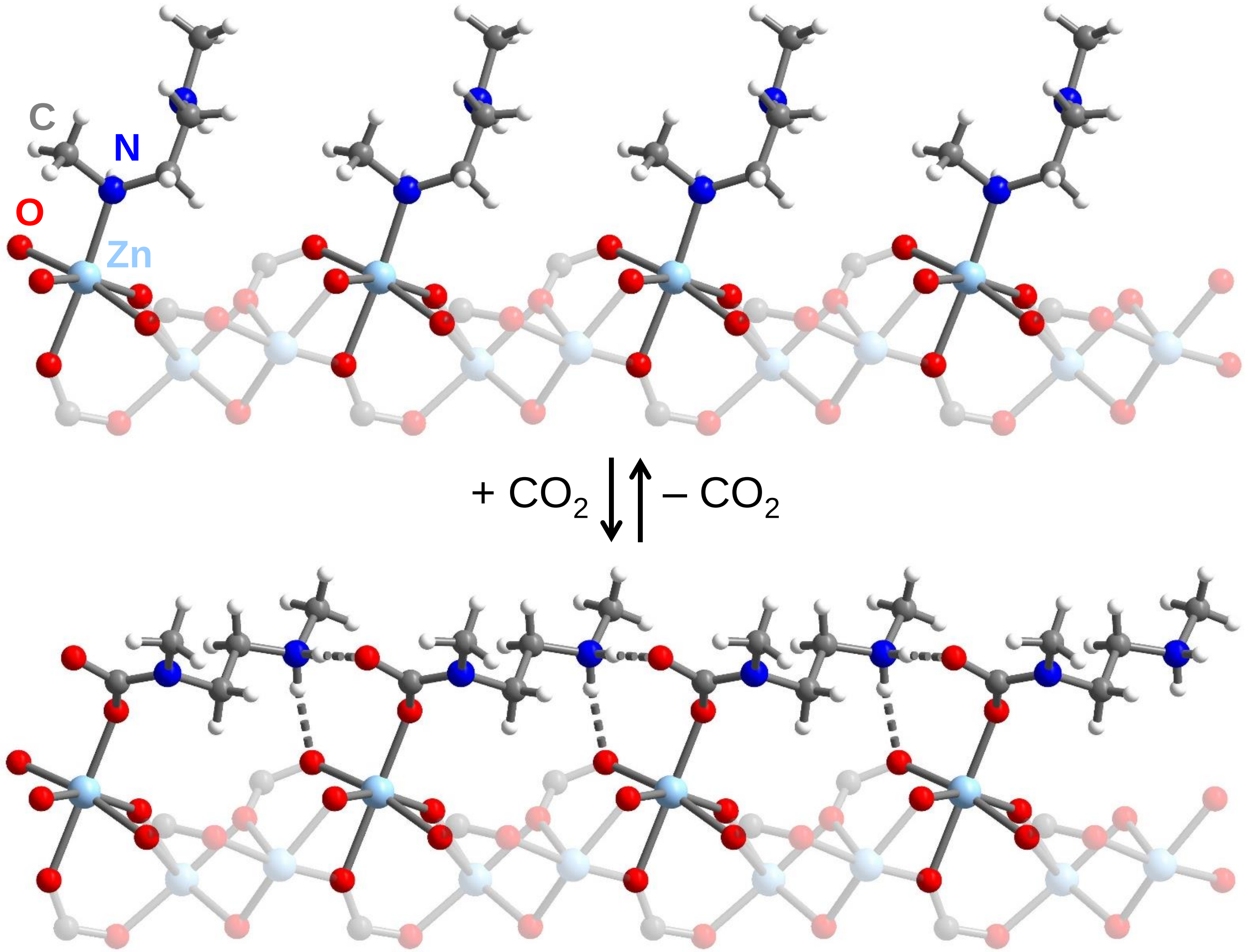



**mmen-$Mn_2$(dobpdc)** **mmen$CO_2$-$Mn_2$(dobpdc)**

- 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, Lee, Pascal, Prendergast, Neaton, Smit, Kortright, Gagliardi, Bordiga, Reimer, Long *Nature* **2015**, *519*, 303

# Cooperative $CO_2$ Adsorption Mechanism




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

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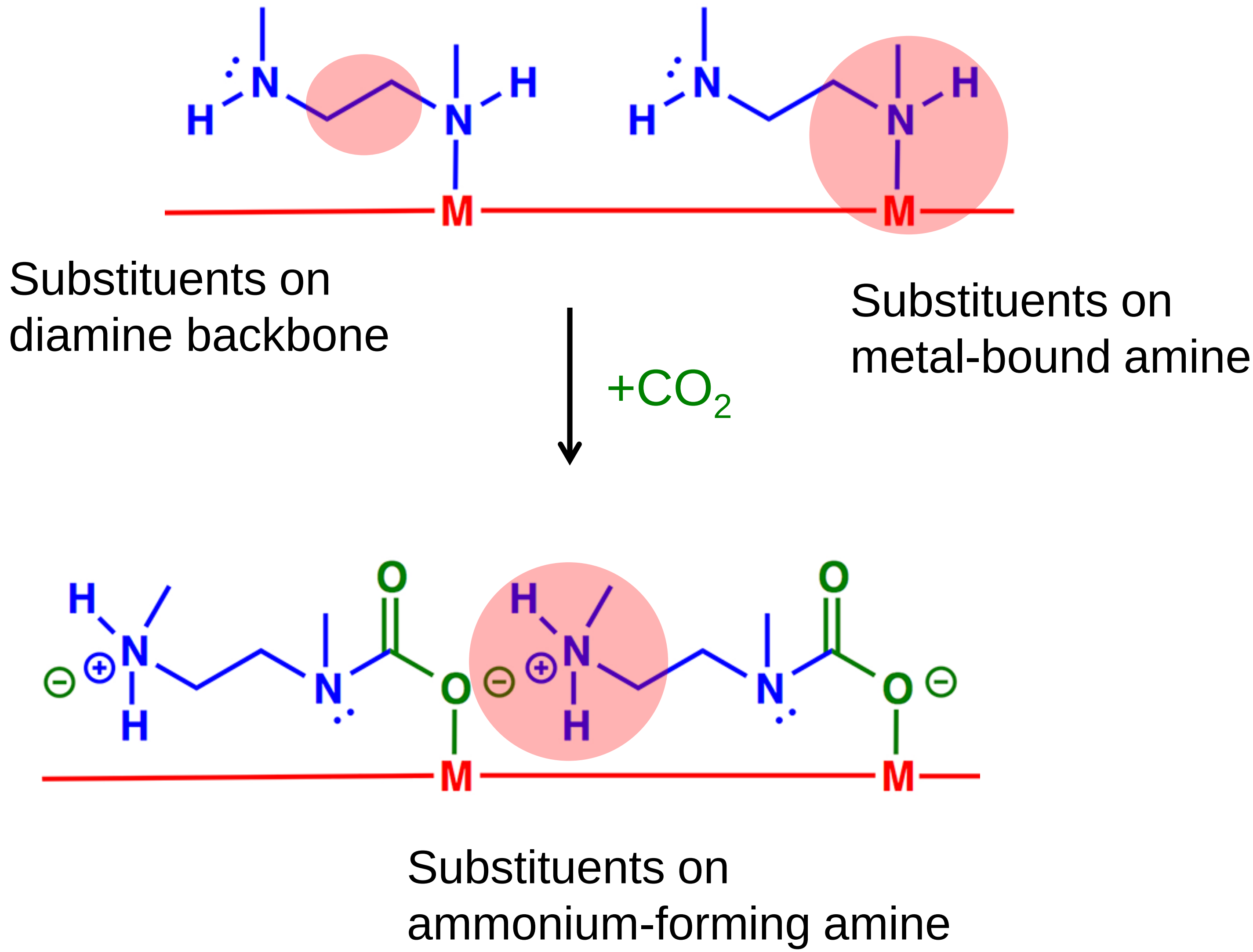
# Manipulating the Adsorption Step Position



# Technical and Economic Advantages/Challenges

## Advantages

- High tunability of amine-appended framework materials
- Large working capacity due to stepped $CO_2$ adsorption
- High $CO_2$ selectivity over $N_2$, $O_2$, and $H_2O$
- Molecular level characterization is possible

## Challenges

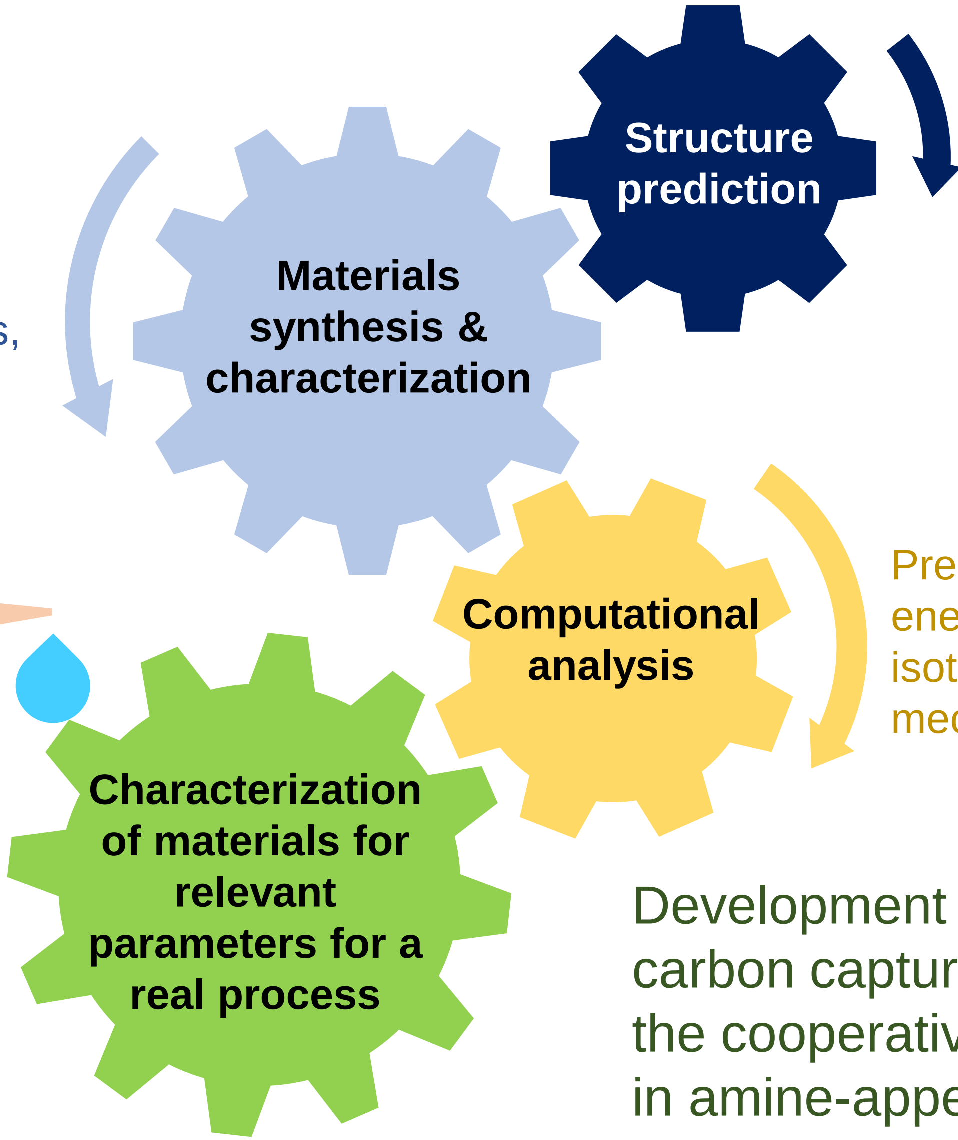
- Large scale and economical production of materials
- Durability and chemical stability is unknown
- Reduction of regeneration cost (temperature swing)

# Technical Approach and Project Scope

Synthesis of amine-appended MOFs (Gen1−Gen3)

$CO_2$ adsorption tests, effect of impurities, cycling performance

Computational prediction of suitable MOF and diamine pairs




Prediction of $CO_2$ binding energy, relative $CO_2$ isotherm step position, and mechanical properties

Collaboration with partners

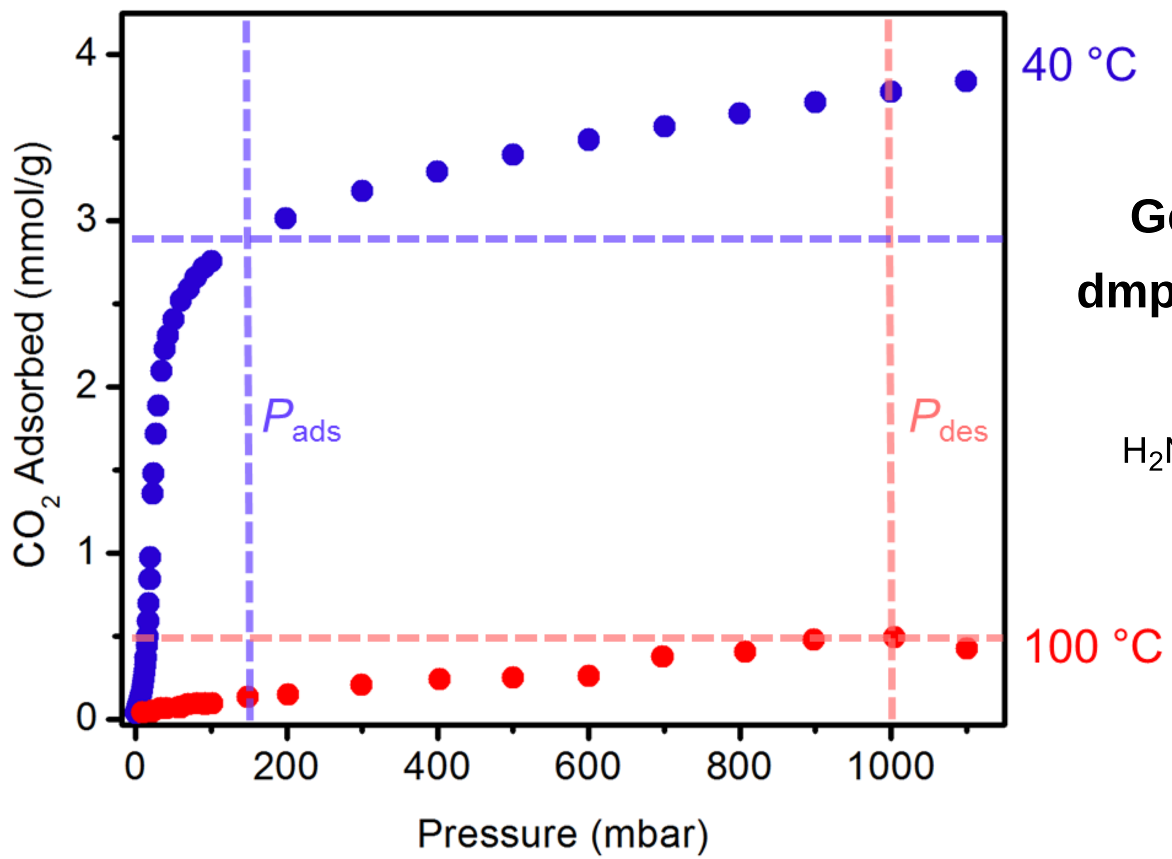
- MOF production
- System development
- Process modeling

Development of transformative carbon capture technologies by the cooperative insertion of $CO_2$ in amine-appended frameworks

# Project Schedule and Key Milestones (Year 1)

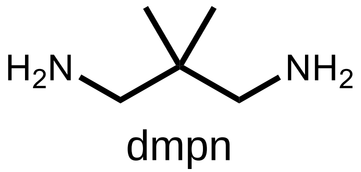
| | Tasks | Milestones | Progress |
|---|---|---|---|
| Materials synthesis | Synthesis of diamine-appended MOFs (Gen1 materials) | Deliver a new material with a working capacity of >2.5 mmol/g | Complete |
| Materials synthesis | Characterization of the effects of water, $SO_x$, and $NO_x$ on $CO_2$ adsorption properties of Gen1 materials | Deliver a material that retains >90% of original $CO_2$ uptake capacity after 20 cycles in the presence of $H_2O$, $SO_x$, $NO_x$ | Complete (97% capacity retained) |
| 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 | Pending |
| Computation | Prediction of $CO_2$ binding energies for amine-appended MOFs | Propose candidates having high $CO_2$ binding energies (>70 kJ/mol) | Complete |

# Year 1 Progress: Gen1 Material Identified




**Gen1 material:**

**dmpn-$Mg_2$(dobpdc)**




- 2.4 mmol/g (9.1 wt %) working capacity with only a 60 °C temperature swing
- Approximate regeneration energy: 2.4 MJ/kg $CO_2$

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

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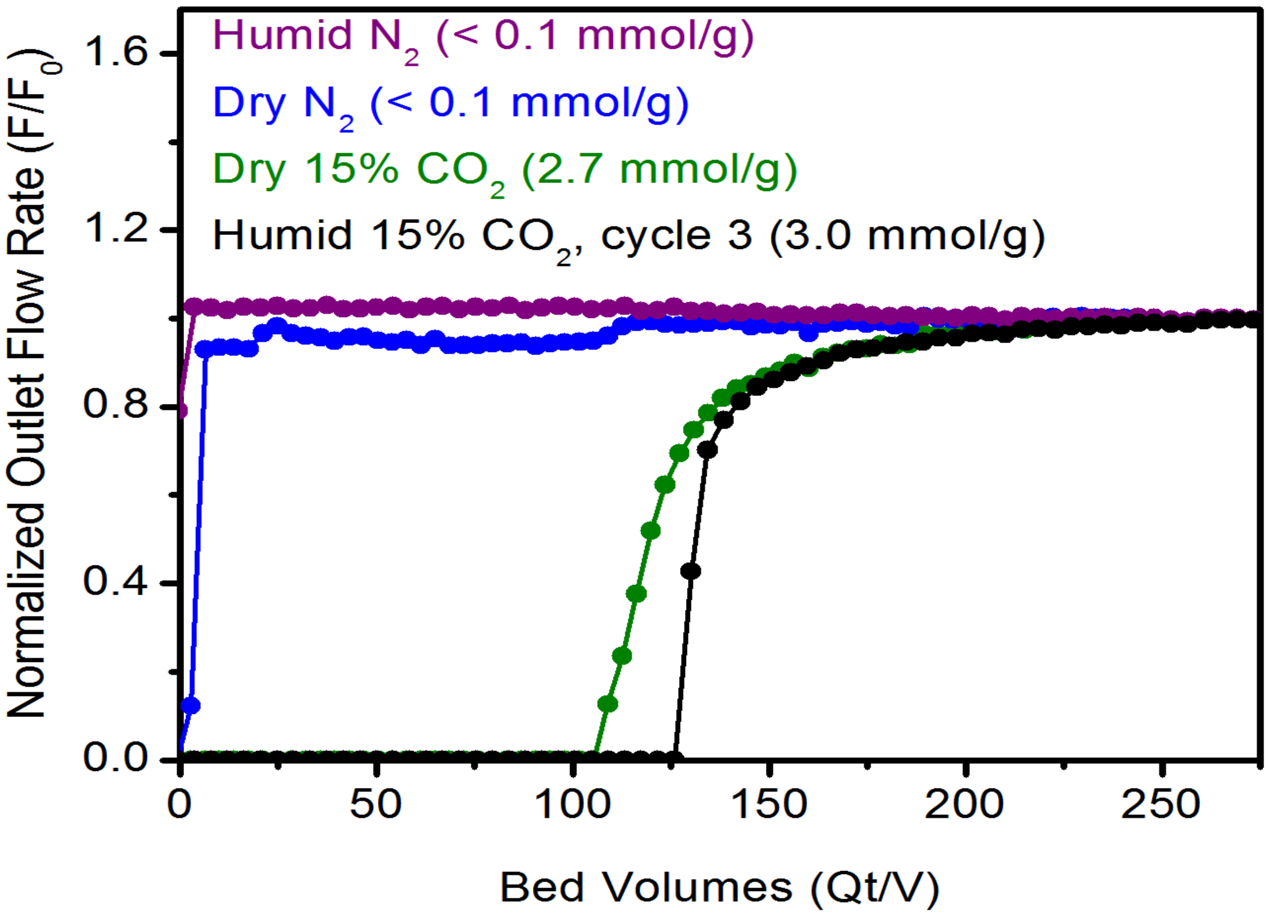
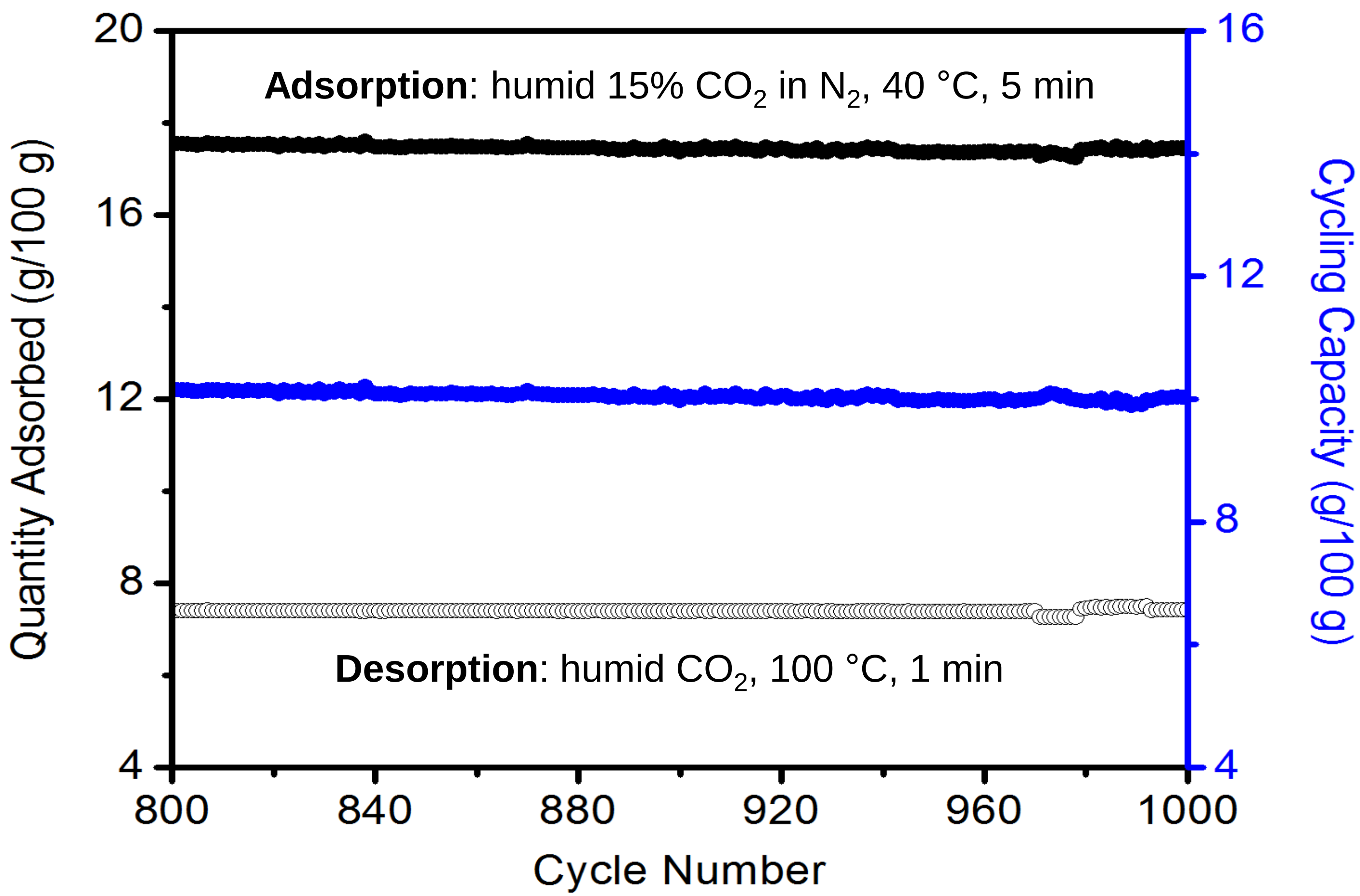
# Gen1: Humid Breakthrough Experiments



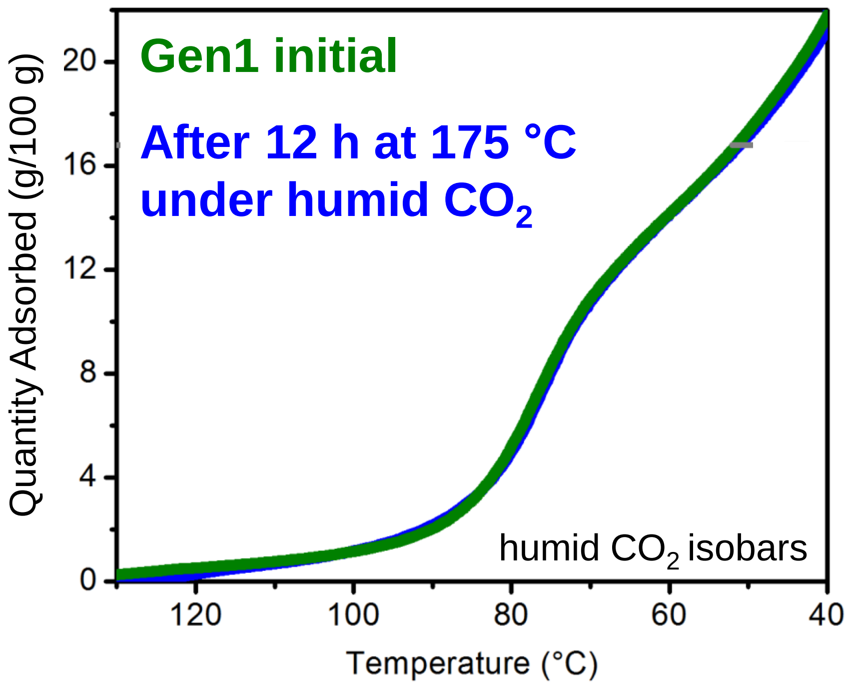

- Breakthrough experiments with pre-humidified column and gas stream show sharp $CO_2$ breakthrough and high capacity

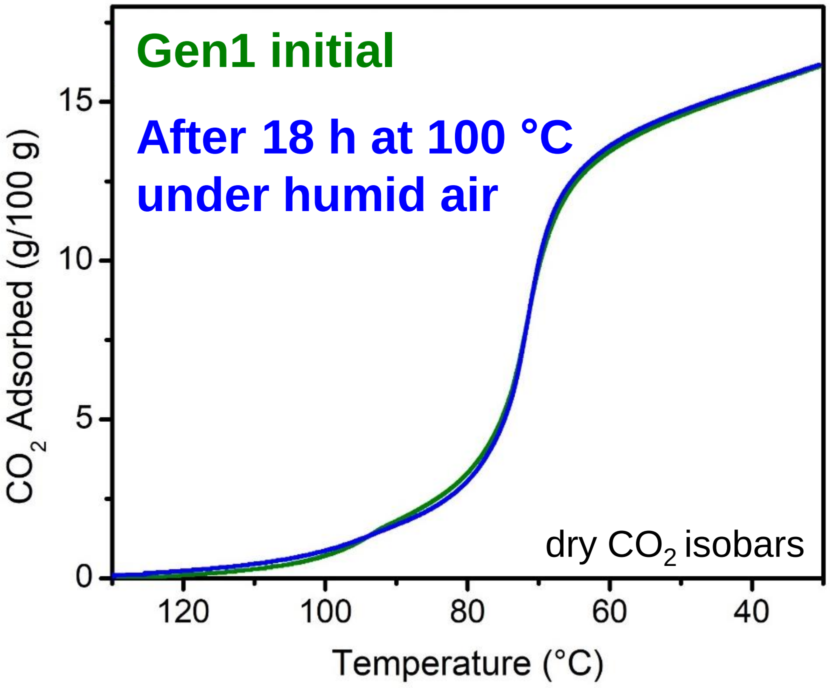
# Gen1: 1000 Adsorption/Desorption Cycles




- Stable to 1000 humid adsorption/desorption cycles under simulated flue gas conditions (diamine loading after experiment: 97%)

# Gen1: Thermal, $CO_2$, $H_2O$, and $O_2$ Stability

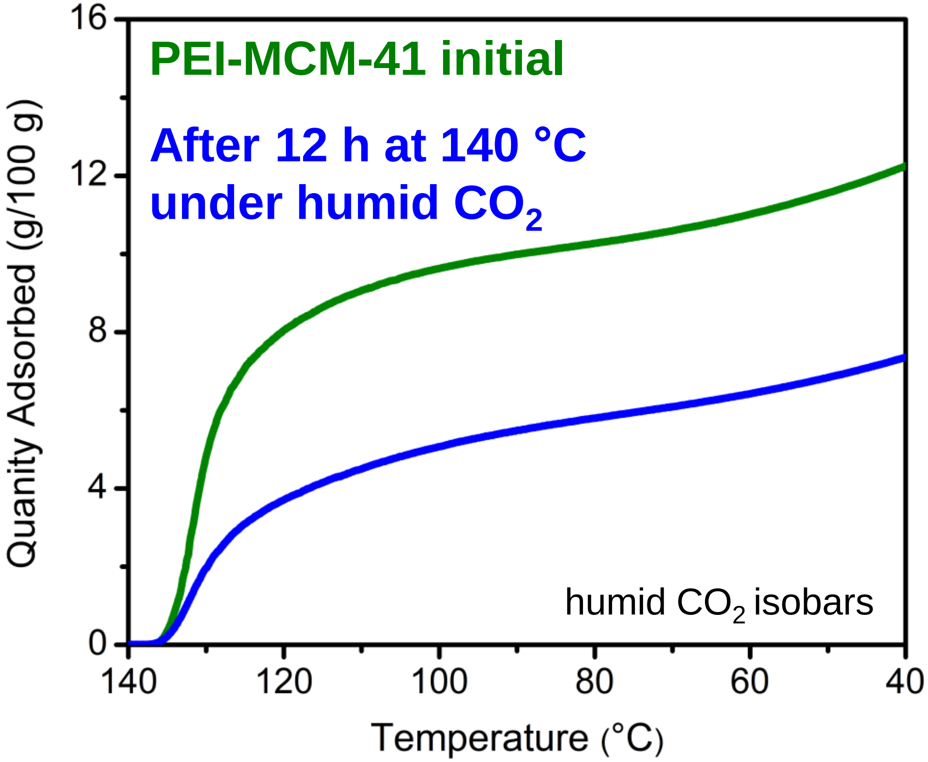


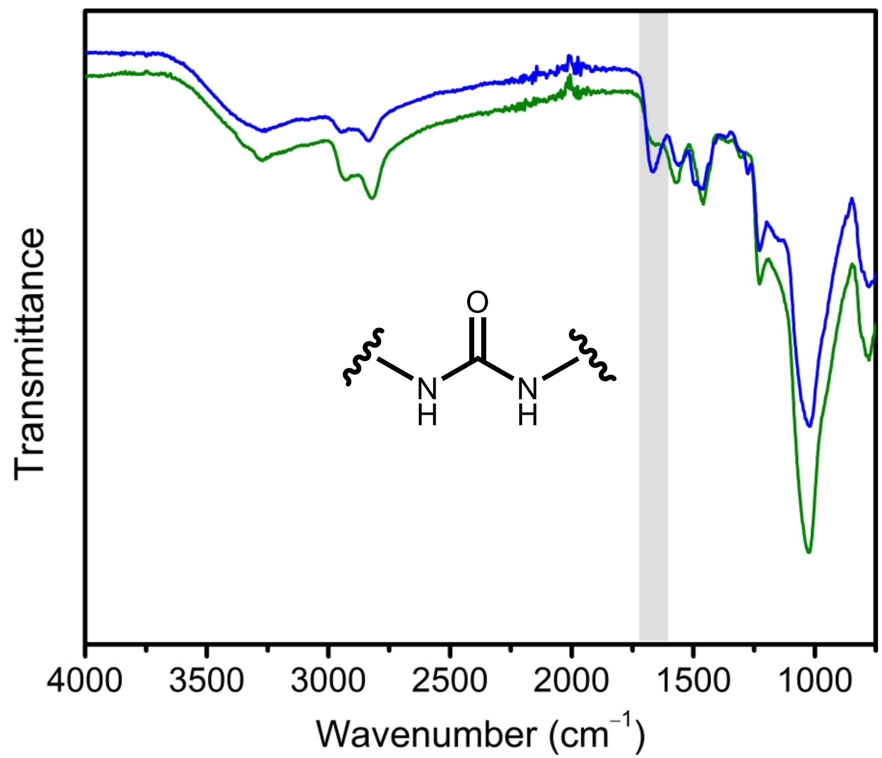




- Gen1 material shows excellent thermal stability under humid conditions, and stability to oxidation at high temperatures
- Infrared spectra show no evidence of urea formation
- Long-term storage in ambient conditions also reveals no change in performance

# Stability Comparison with PEI-MCM-41

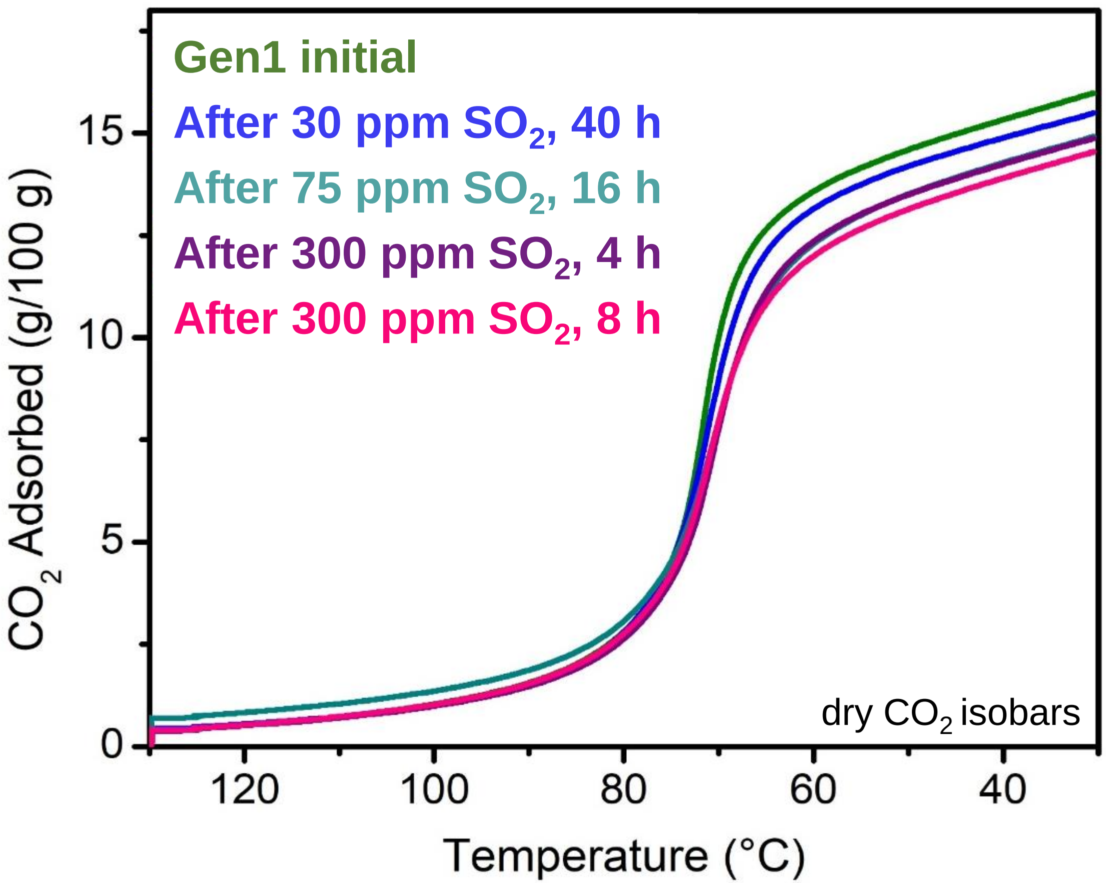
**50 wt % PEI-MCM-41**




- Substantial capacity loss for PEI-MCM-41 after accelerated decomposition test
- Infrared spectra indicate urea formation

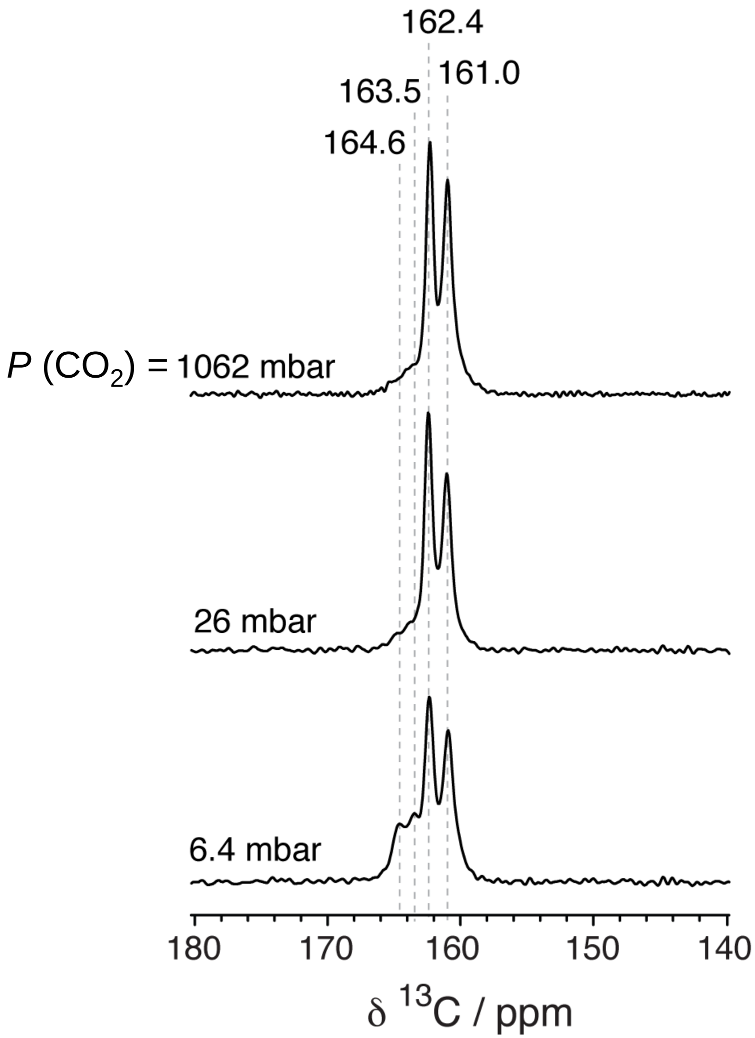
# Gen1 Stability: $SO_2$ Exposure Testing



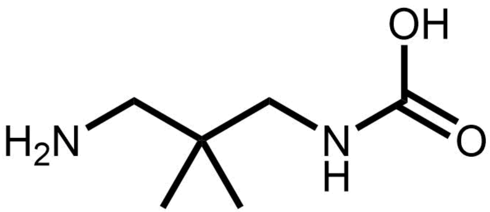

- Exposure time delivers 1 $SO_2$ per diamine or 2 $SO_2$ per diamine (300 ppm, 8 h)
- 89% of $CO_2$ uptake capacity retained in most aggressive test

# Gen1: A Mixed Mechanism for $CO_2$ Uptake

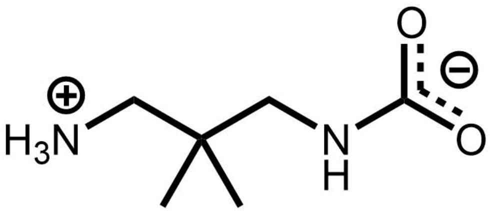
Solid-state NMR experiments allow form of adsorbed $CO_2$ to be determined




- Carbamic acid at 161.0 ppm

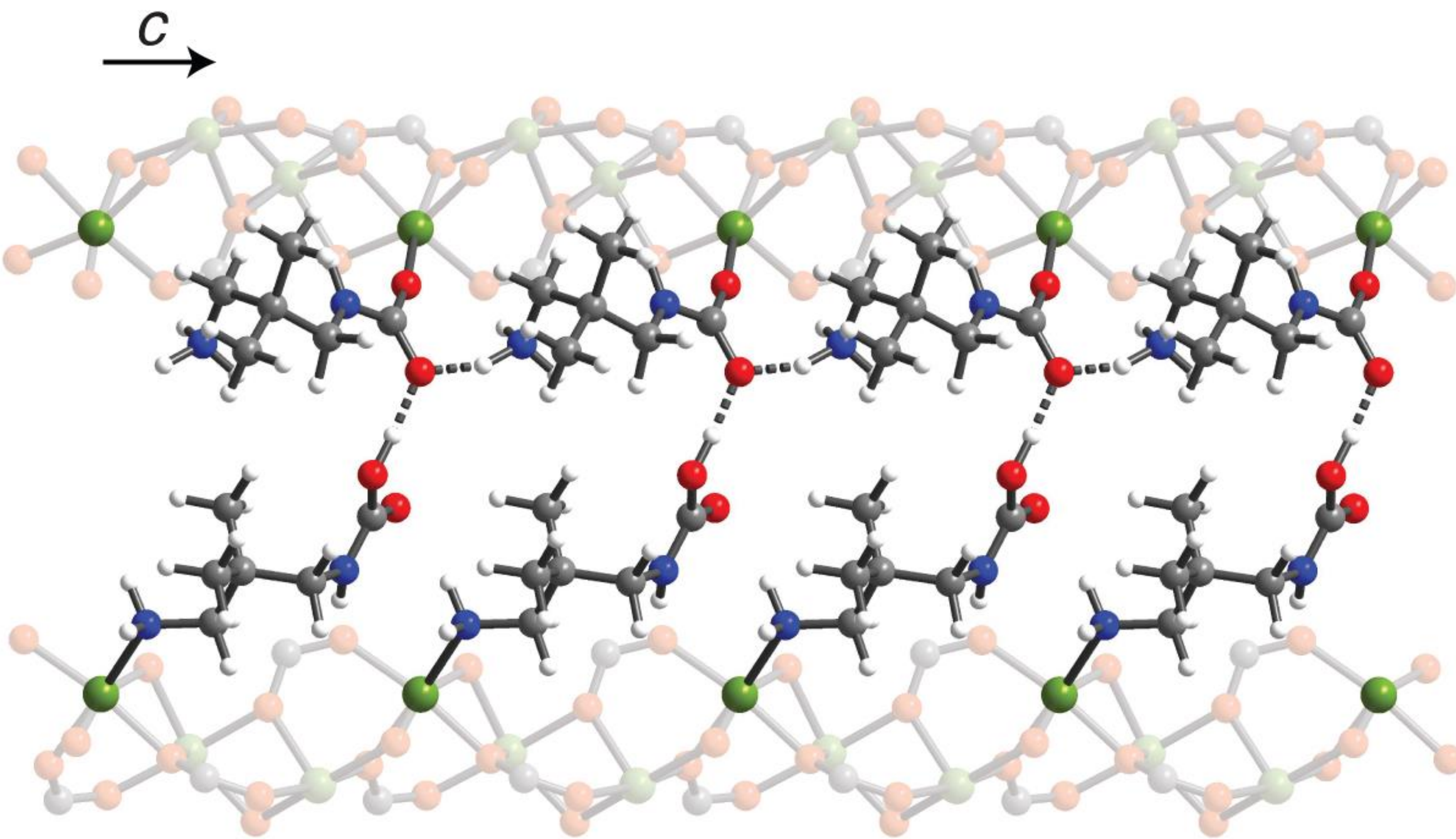



- Ammonium carbamate at 162.4 ppm



# Gen1: Proposed $CO_2$-Loaded Structure

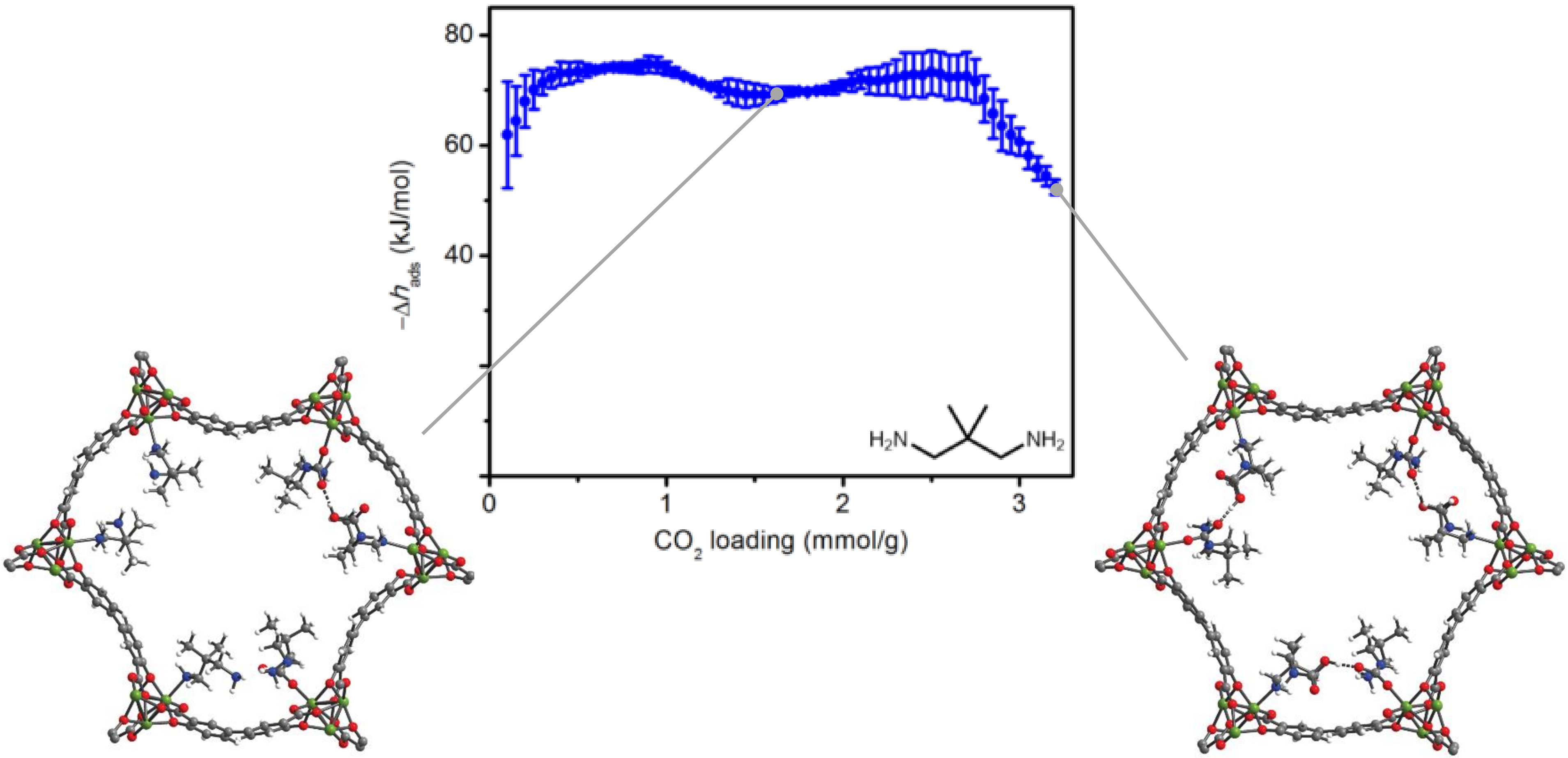
$CO_2$-loaded structure based upon NMR and IR spectra and DFT calculations contains a 1:1 mixture of ammonium carbamate and carbamic acid groups




**ammonium carbamate chain**

**H-bonded carbamic acid groups**

# DFT Predictions Match Measured Isosteric Heats




DFT: –73 kJ/mol (Exp: –71 kJ/mol)
50% $CO_2$ loading
(2 carbamate + 1 carbamic acid)

DFT: –54 kJ/mol (Exp: –52 kJ/mol)
100% $CO_2$ loading
(3 carbamate + 3 carbamic acid)

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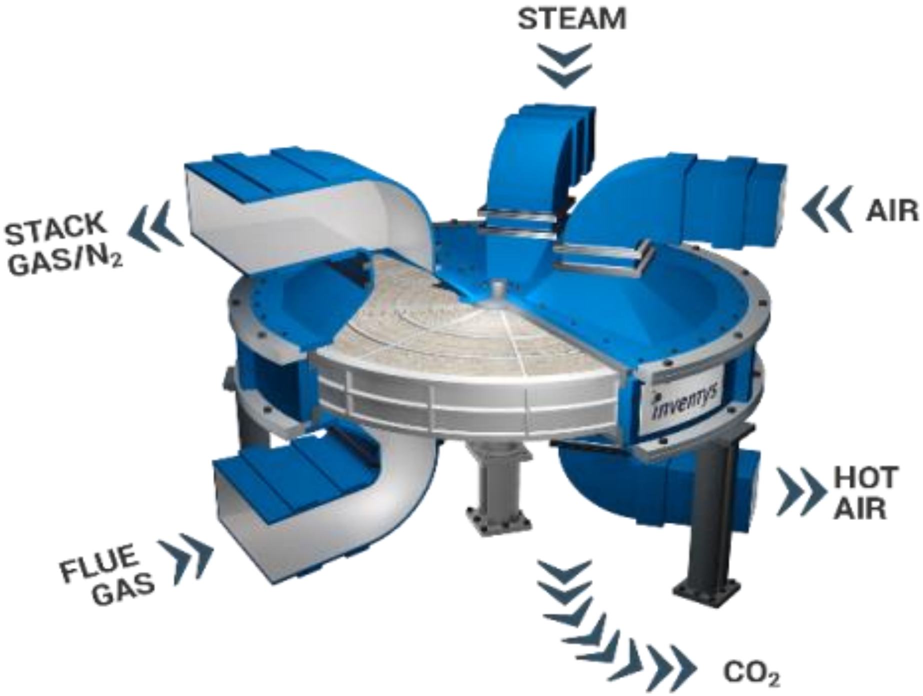
# Partners for Developing a Separation Process

## MOF Manufacturing: Mosaic Materials


## Separation System: Inventys (w/ Electricore)




- Total funding for industrial partners: $3M from DoE plus $775k in cost share
- Subcontracts and IP agreement are nearly finalized

# Mosaic Materials: Large-Scale MOF Production

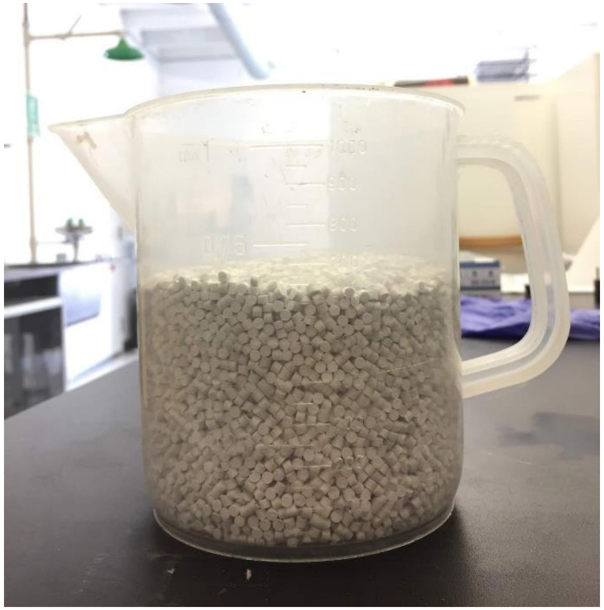
Founded in 2014 to commercialize MOFs for gas separations

Synthesis and testing laboratory in Berkeley, CA

Producing kg-scale quantities of patent-protected adsorbents for:

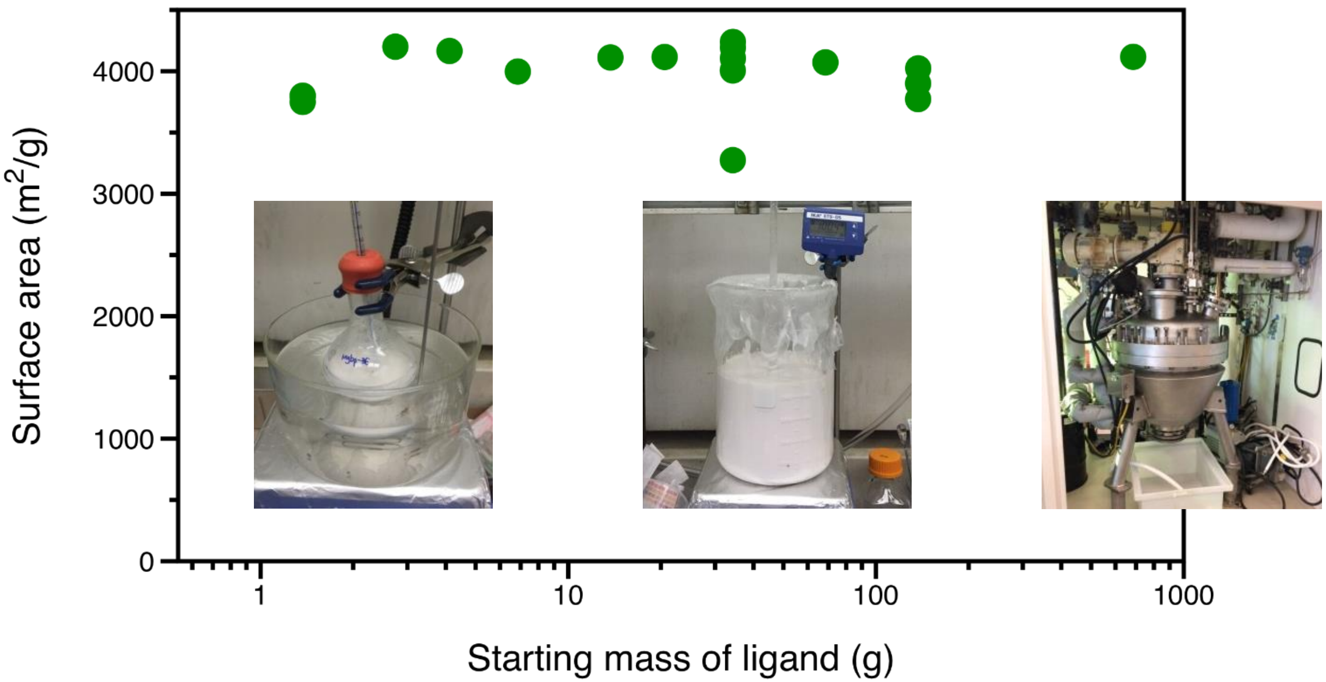
1. $CO_2$ separations: flue gases, biogas, natural gas, air
2. Industrial chemicals: ethylene, propylene, CO, $H_2S$

Production methods scalable to ton-scale production in structured forms



# Role of Mosaic Materials

- Tech transfer: Interface with LBNL and Inventys/Electricore
- Optimize scalable diamine-appended MOF production process
- Realize and test structured forms of the diamine-appended MOFs
- Deliver 10-kg batches of Gen1 and Gen2 materials to Inventys

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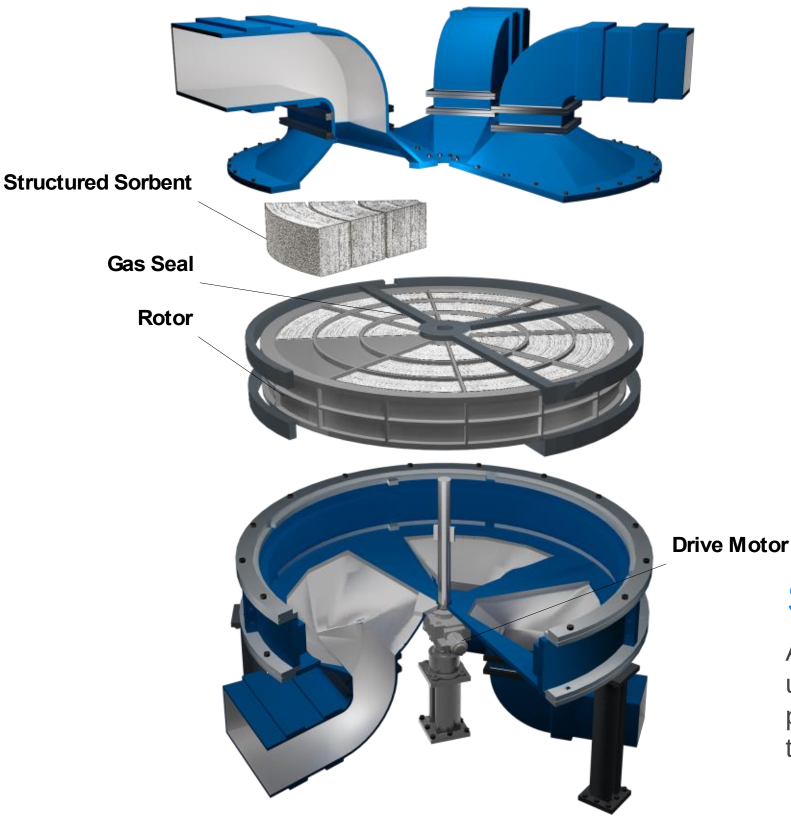
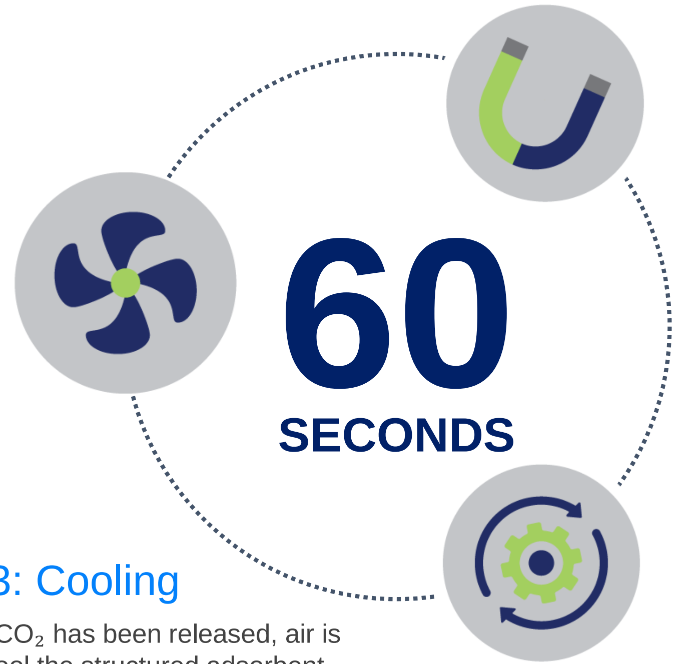
# Inventys: Rapid Cycle Temperature Swing Adsorption

## THREE SIMPLE STEPS




### Step 1: Adsorption

As flue gas passes through the VeloxoTherm™ Adsorbent Structure, $CO_2$ clings to the adsorbent while the other gases pass through.

### Step 2: Regeneration

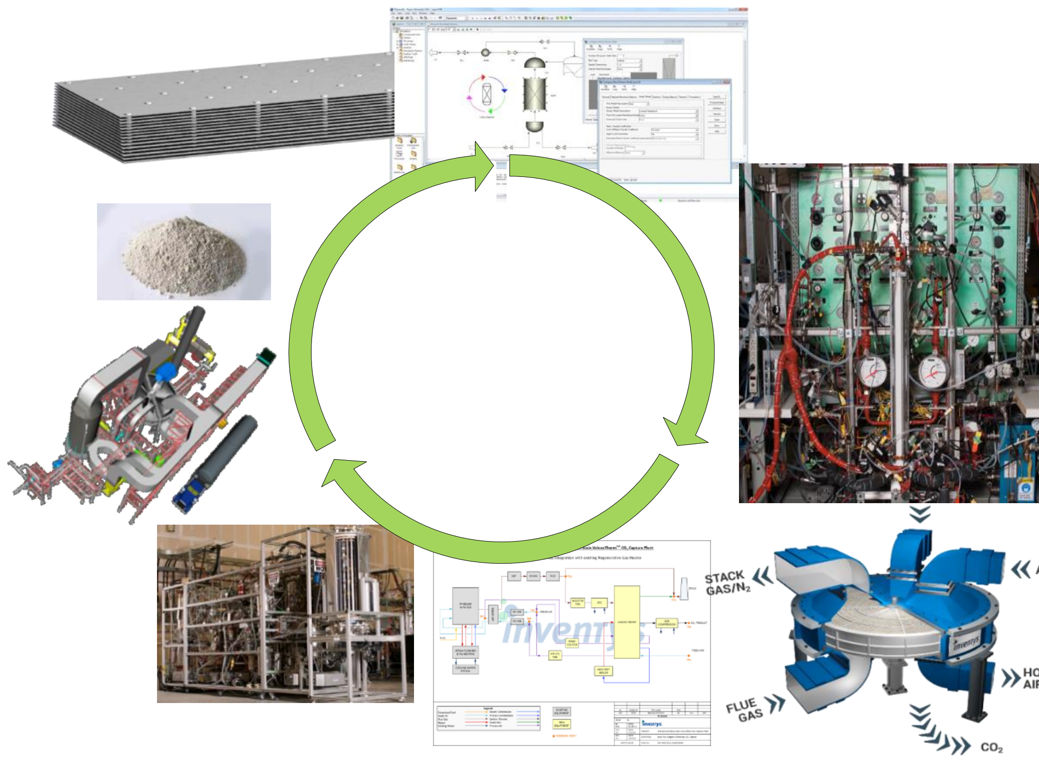
After the structured adsorbent becomes saturated with $CO_2$, it is regenerated. Low pressure steam is used to release the $CO_2$ from the adsorbent.

### Step 3: Cooling

After the $CO_2$ has been released, air is used to cool the structured adsorbent, preparing it for the adsorption step and the process is started over again.

# Role of Inventys

- Formation of structured adsorbent beds
- Process development and testing: powders → single bed test station (VTS) → multi-bed process demonstration unit (PDU) → pilot unit at NCCC to test at 0.1 TPD (RPV-RAM)
- Process modeling and validation: Process test data used to map performance of process and inform design of next stage test system (VTS→PDU→RPV-RAM)
- Preliminary analysis of NCCC test data: total life-cycle capture economics



# Updated Experimental Design and Work Plan

## Year 2

- Gen1 production at kg scale
- Testing & modeling of VeloxoTherm process
- Synthesis of new amine-appended MOFs (Gen2) & scale-up
- Stability and cycling performance tests
- Computational work to predict amine-appended MOFs

## Year 3

- Gen2 production at kg scale
- Bench skid construction & initial shakedown and baseline tests at NCCC
- Testing & modeling of VeloxoTherm process (Gen2)
- In house continuous PDU testing & characterization of Gen1/Gen2 materials
- Expanded computational search

## Year 4

- Bench scale testing at NCCC
- Life cycle and capture economics analysis
- Extensive characterization of materials tested
- Gen3 materials synthesis and comprehensive characterization. Scale-up to multigram.

---

- Project management and planning
- Literature survey and synthesis

# Project Timeline

| | Task Descriptions | YR 1 | YR 2 | YR 3 | YR 4 |
|---|---|---|---|---|---|
| Synthesis & characterization | 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 | ■ | | | |
| | 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 | | ■ | | |
| | Characterization of materials fabricated by industrial partners | | | ■ | |
| | Synthesis and comprehensive characterization for new (Gen3) materials predicted in Year 3 | | | | ■ |
| | Characterization of materials tested by partners | | | | ■ |
| Computation | Search optimal amine-appended MOFs within databases of reported materials | ■ | | | |
| | Prediction of $CO_2$ binding energies for amine-appended MOFs | ■ | | | |
| | Search optimal amine-appended MOFs (Gen2 materials) among computationally designed materials | | ■ | | |
| | Prediction of relative $CO_2$ isotherm step position | | ■ | | |
| | Extend the material design | | | ■ | |
| | Prediction of mechanical strength for a real process | | | ■ | |

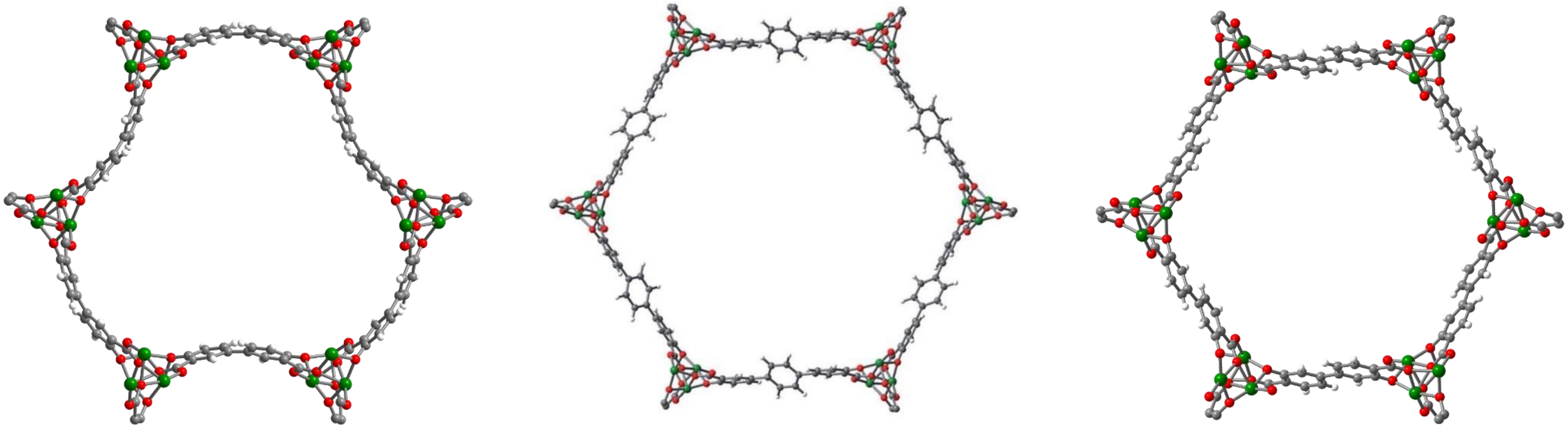
# Project Timeline

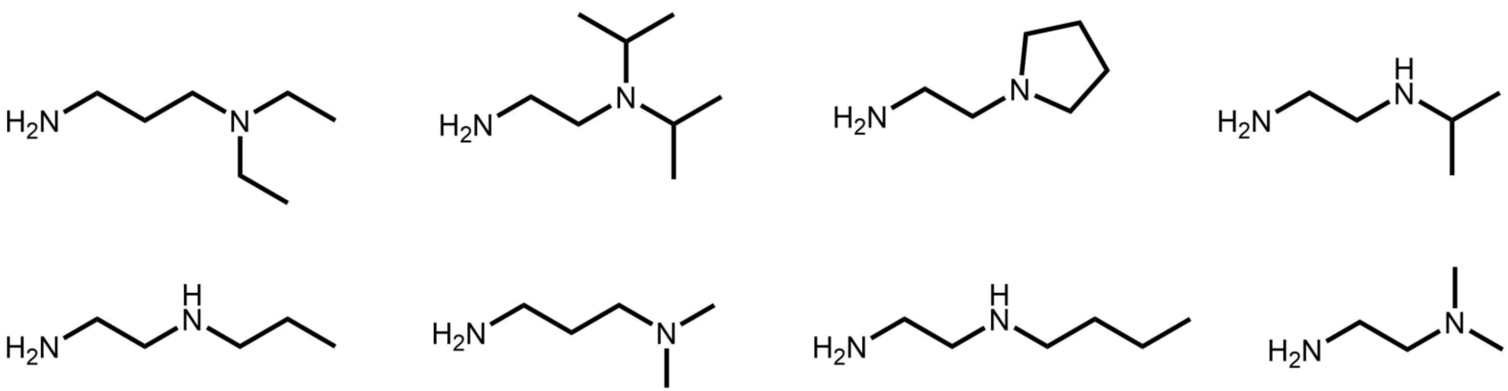
| | Task Descriptions | YR 1 | YR 2 | YR 3 | YR 4 |
|---|---|---|---|---|---|
| System Testing | Gen1 materials production for Inventys | | ■ | ■ | |
| | Concept development, modeling & testing | | ■ | ■ | |
| | Process & cycle design simulations | | ■ | ■ | |
| | Bench-scale unit design & construction | | ■ | ■ | |
| | Gen2 materials production for Inventys | | | ■ | ■ |
| | Comprehensive characterization of all relevant parameters for a real process | | ■ | ■ | ■ |
| | In-house continuous PDU performance testing | | | ■ | ■ |
| | Bench scale field performance & durability testing | | | ■ | ■ |

# Project Success Criteria

| Year | Success Criteria |
|---|---|
| **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(~2% $H_2O$, 30 ppm $SO_x$, 20 ppm $NO_x$). Synthetic cost (based on approximate cost analysis) is less than $75/kg. |
| **Year 4** | Demonstrate a unit adsorbent bed that exhibits Key Performance Indicators's (KPI's) consistent with the capture economics of DOE 2$^{nd}$ generation techno-economic targets for post-combustion capture after 500 hours of operation. |

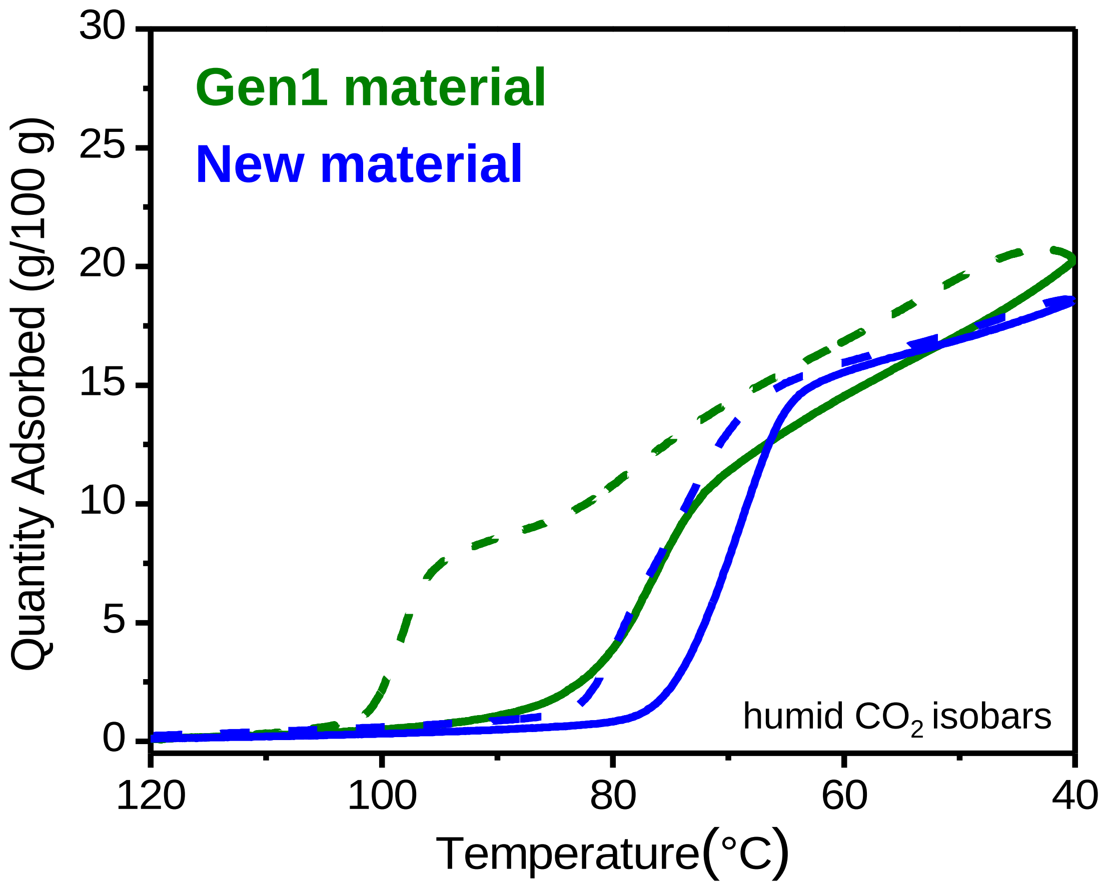
# Developing Gen2 Materials





Currently testing MOF-diamine combinations for improved performance

# A Promising Gen2 Material




- Sharper isobar with less hysteresis enables regeneration at 80-85 °C
- Initial stability tests show thermal stability at high temperatures and humidity

# Plans for Future Testing and Development

**Preliminary system testing of Gen1 material**

- Gen1 production at kg scale, baseline cost estimates
- Concept feasibility testing and modeling of VeloxoTherm process
- Initial planning and design of testing skid

**Synthesis of improved diamine-appended MOFs (Gen2 materials)**

- Synthesis and characterization of Gen2 materials → long term cycling, breakthrough, stability testing
- Scale-up evaluation of Gen2 materials

**Further materials improvements**

- Search for better diamine-appended MOFs within screening database
- Structure-stability studies of diamine-appended MOFs ($H_2O$, $SO_x$, $NO_x$)
- Calculate $H_2O$, $SO_x$, and $NO_x$ binding energies