Core-Shell MOFs for Direct Air Capture

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Prof. Chris Wilmer (Pitt, co-PI)
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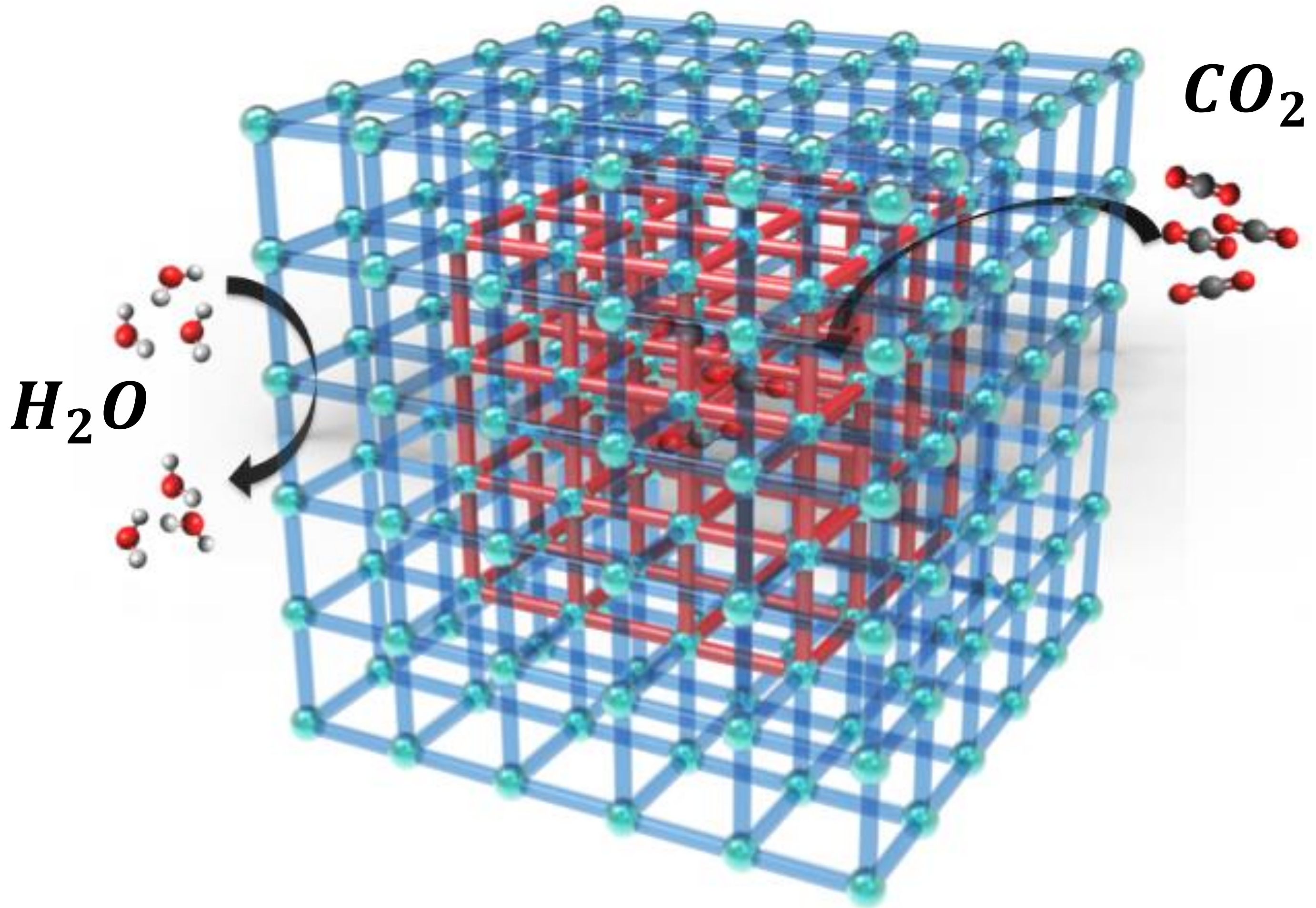

UCFER Task 05-UPitt-S1-22
Annual Project Review Meeting
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Who's on our team?

Dr. Katherine Hornbostel
Assistant Professor
MEMS & ChemE, Pitt

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Grad student, Chemistry

Project goal & objectives

Project goal: identify and characterize a core-shell MOF design that strongly binds CO_2 and has a high selectivity for CO_2 over $N_2/O_2/H_2O$

Project objectives:

1. Computationally identify optimal core-shell combinations for direct air capture.
2. Synthesize and characterize optimal core-shell MOFs.
3. Determine the optimal core-shell MOF packing structure.

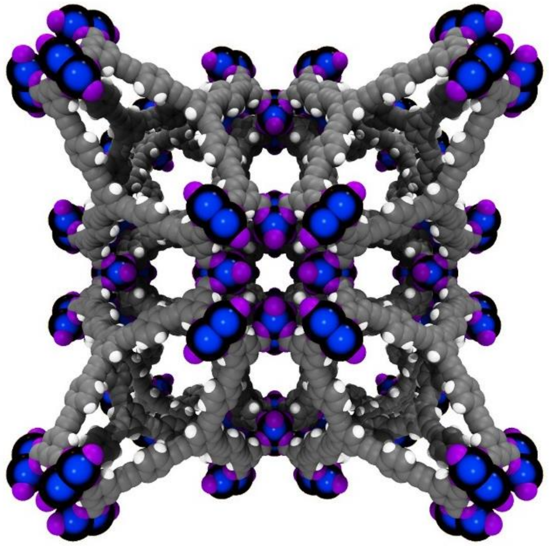
Dr. Wilmer's team

Dr. Rosi's team

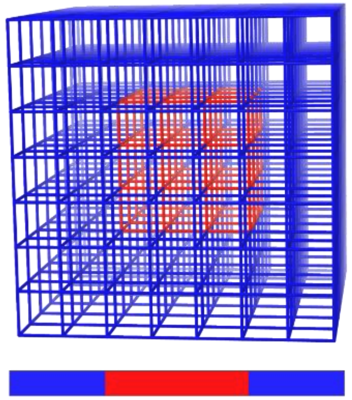
Dr. Hornbostel's team

What are core-shell MOFs?

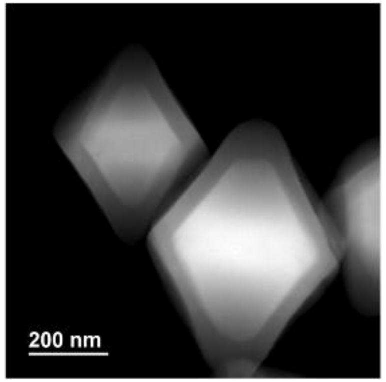
1. MOFs = Metal-Organic Frameworks
   1. organic-inorganic hybrid crystalline porous materials
   2. consist of a regular array of positively charged metal ions interconnected by organic 'linker' molecules



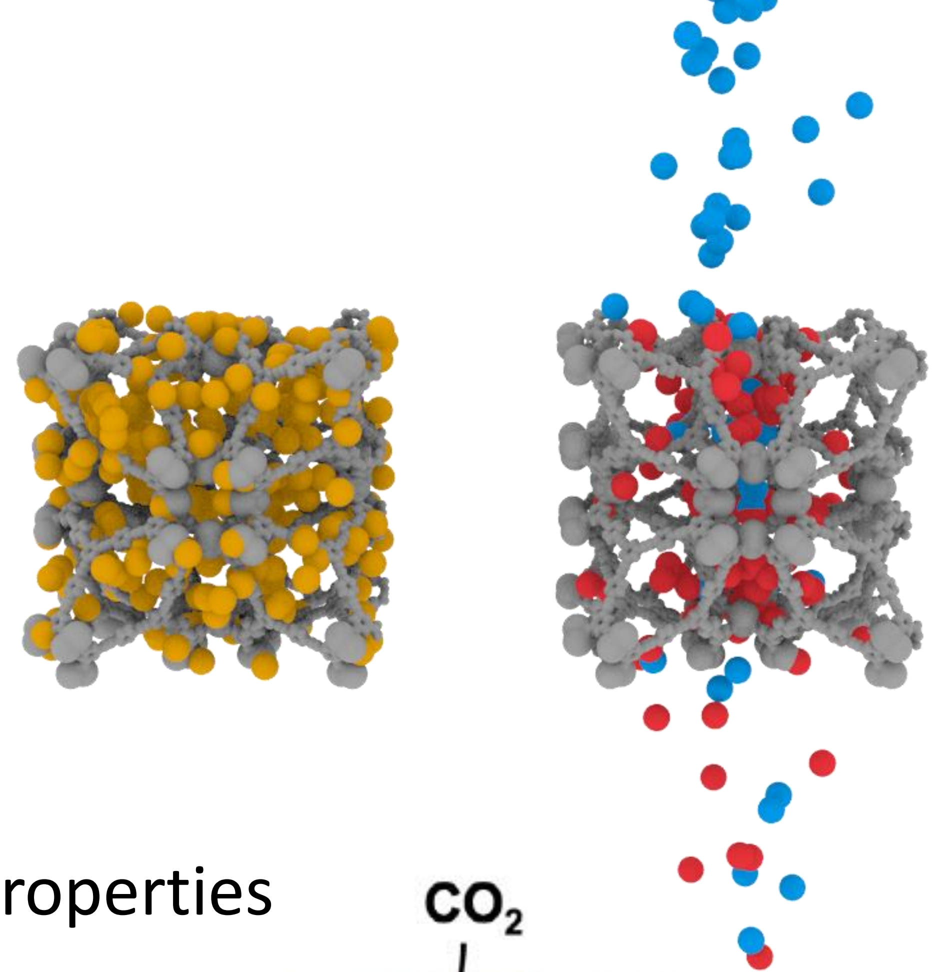
2. Core-Shell MOFs = Core MOF + Shell MOF
   1. Core MOF in center
   2. Different shell MOF grown around core MOF



Core-Shell

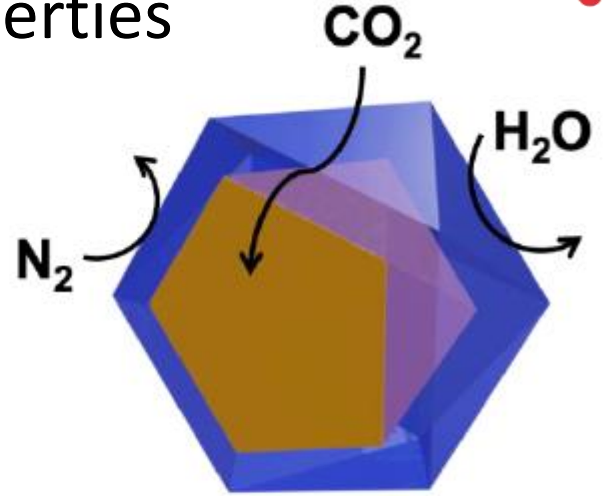


Why core-shell MOFs for DAC?



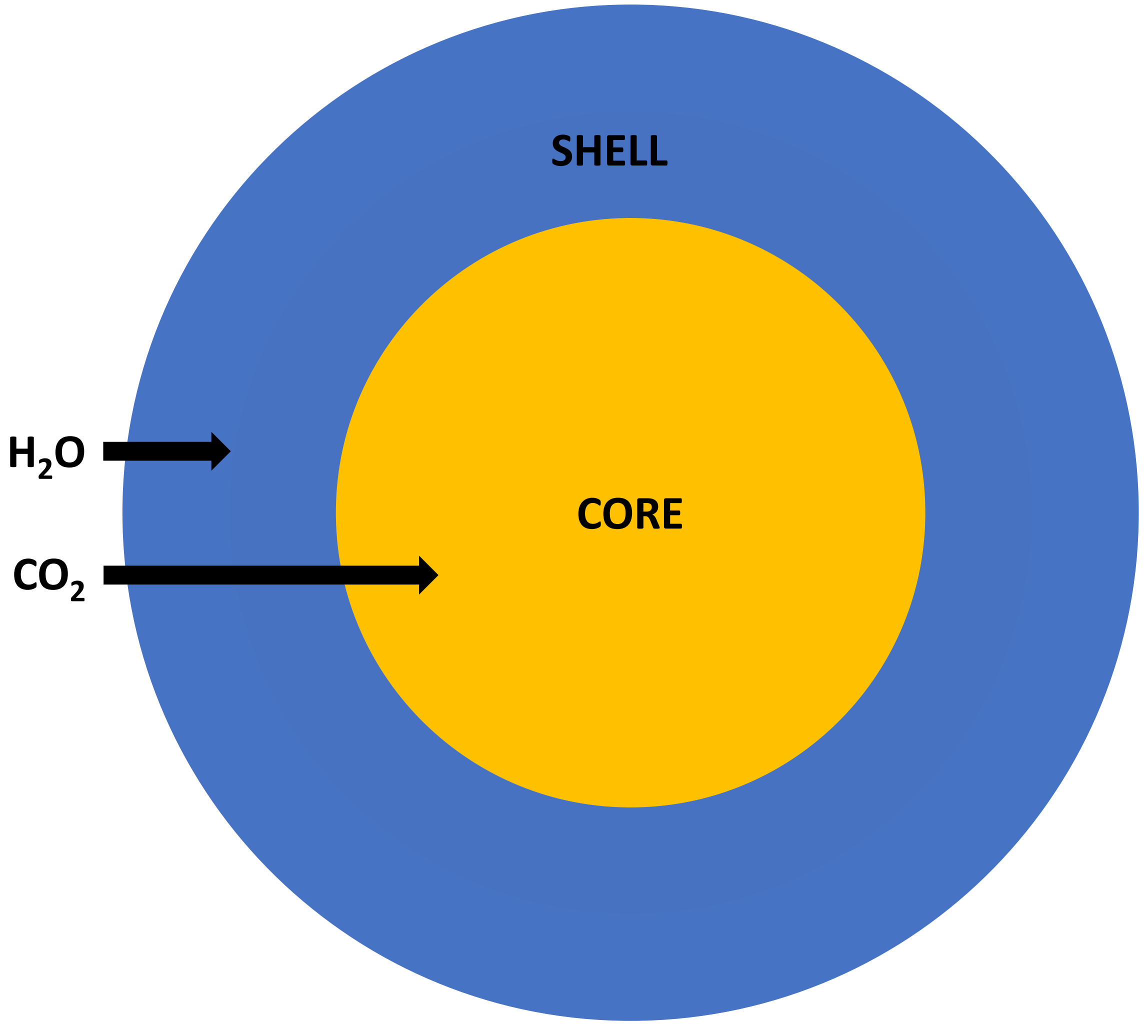
1. MOFs are great for traditional carbon capture
    1. Can pack lots of gas into small volume (i.e., great for gas *storage*)
    2. Can have high affinity to CO_2 over other species (i.e., great for gas *separations*)
    3. Scalable to industrial applications

2. Core-shell MOFs allow us to optimize for two properties
    1. Core MOF has high affinity to CO_2
    2. Shell MOF rejects H_2O



Basic core-shell MOF design

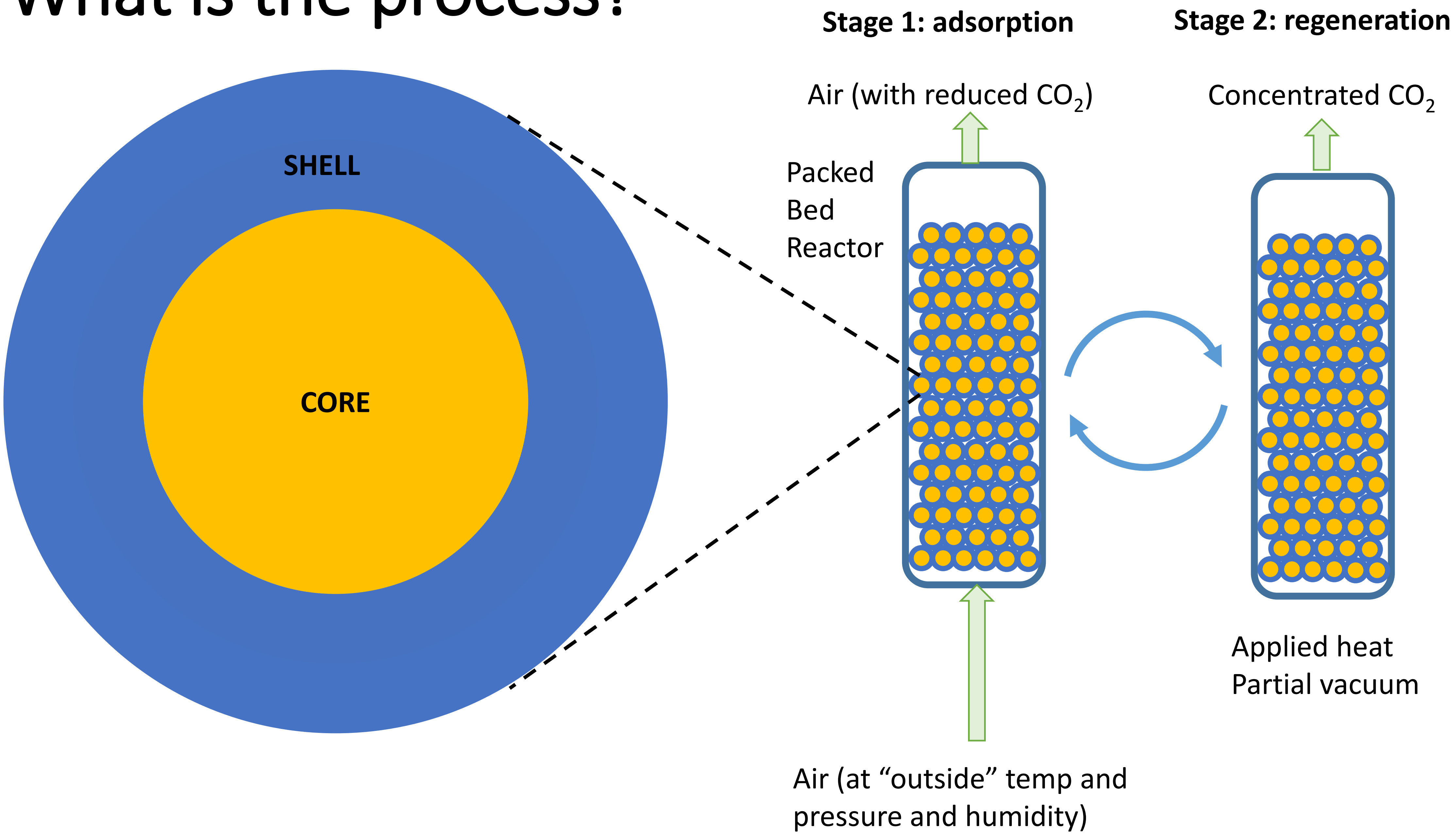
Ideal shell MOF:
- Low H_2O diffusivity
- High CO_2 diffusivity



Ideal core MOF:
- High CO_2 working capacity
- Low N_2 working capacity

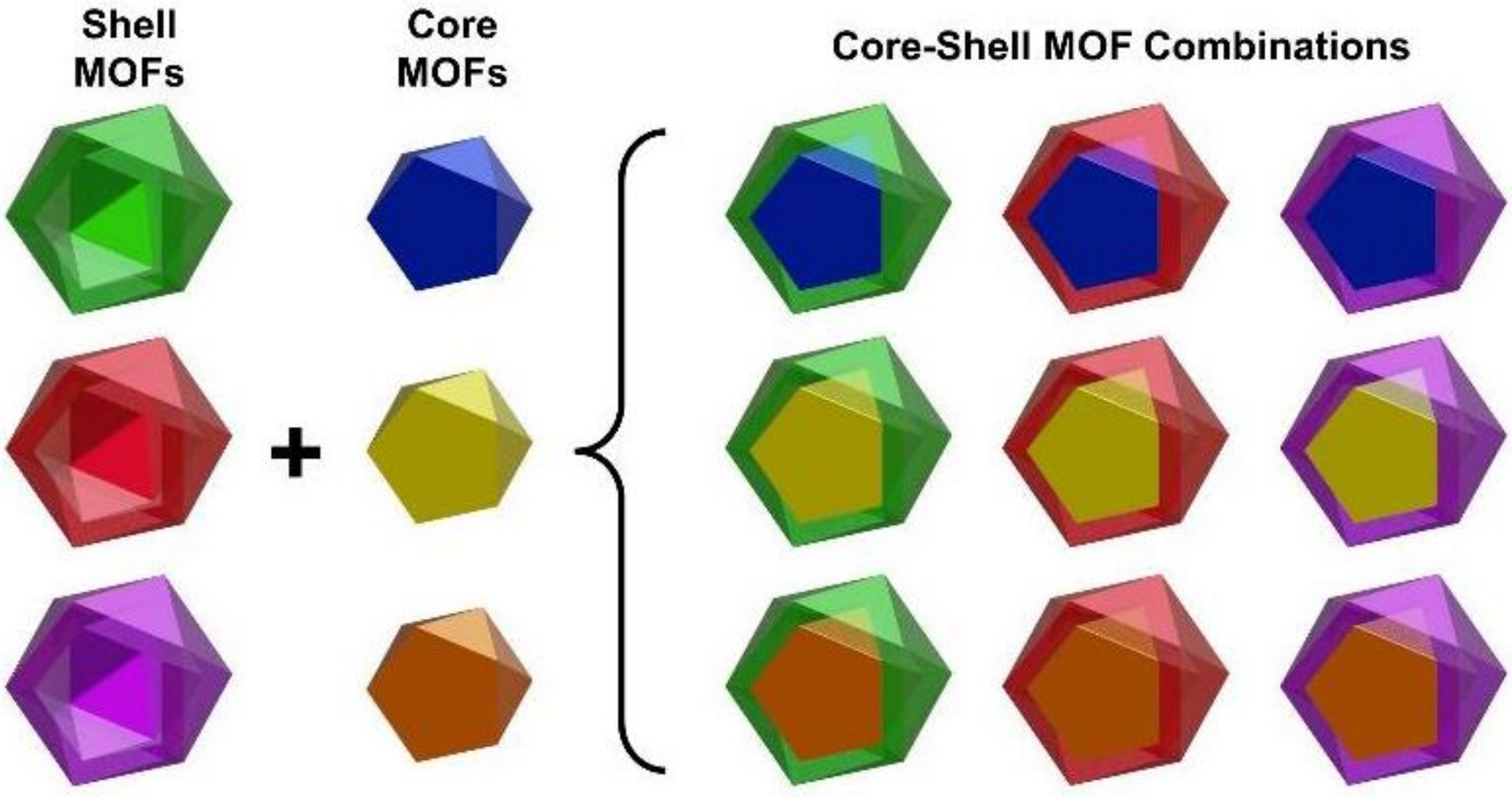
Size the thickness of the shell and the volume of the core so that by the time H_2O breaks through the shell into the core, the core is full of CO_2.

What is the process?



Objective 1: Computationally identify optimal core-shell combinations for direct air capture.

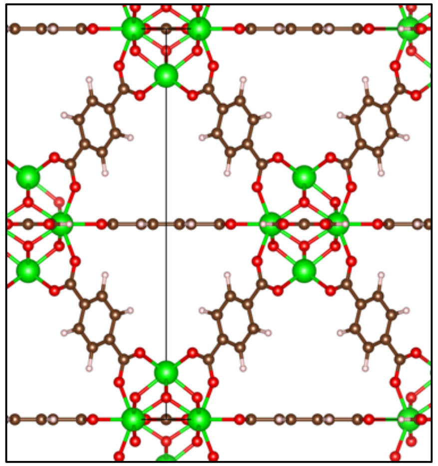
Dr. Chris Wilmer



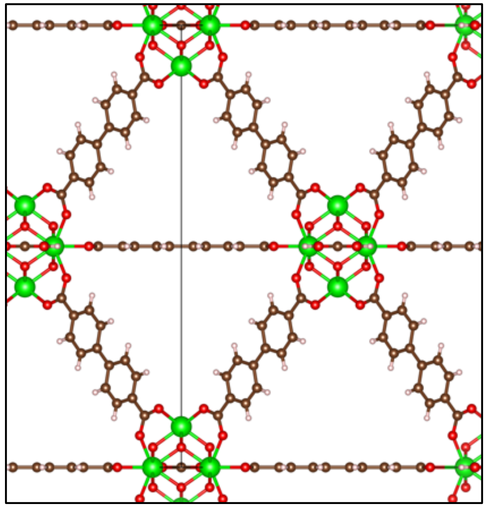
Screening Overview

Two MOFs

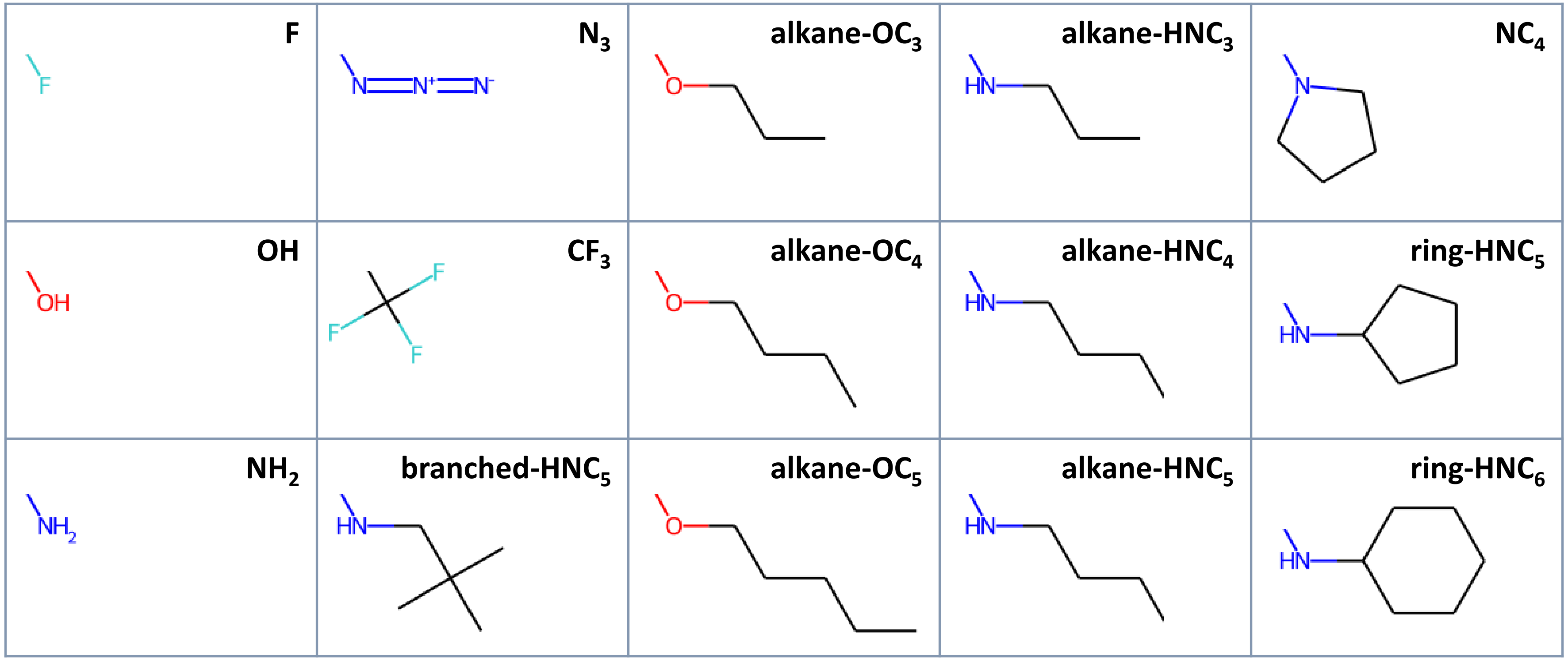
UIO-66



UIO-67



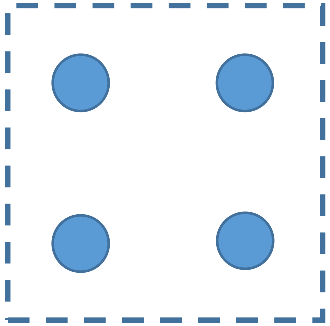
15 Functional Groups



Three Gases: CO_2, H_2O, N_2

Measure:

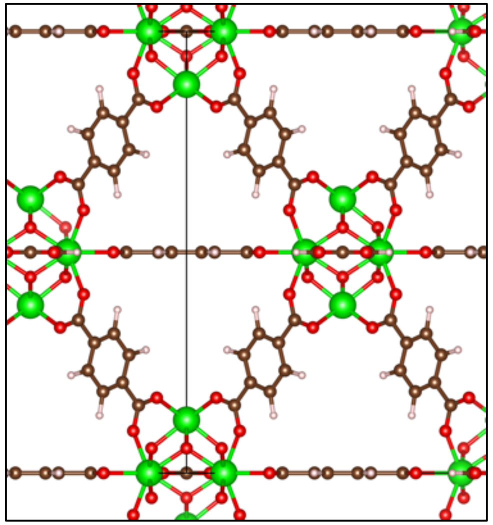
- Diffusion in LAMMPS (all gases)
- Adsorption in RASPA at two process conditions:
  - STP (1 atm, 298K)
  - 15 mbar, 373K



Fixed FF

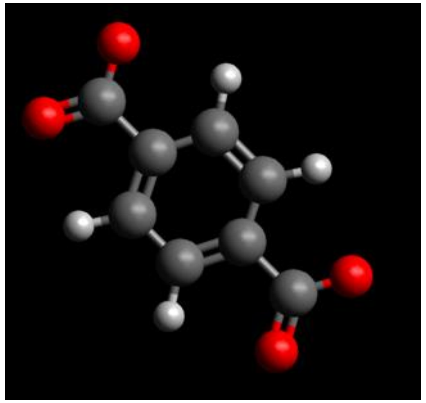
MOFUN: Find / Replace Functionalized Linkers

Structure



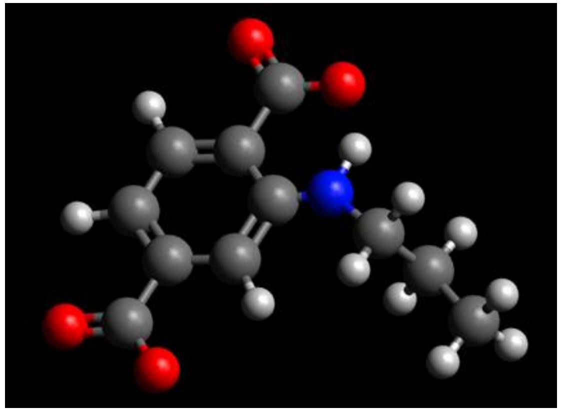
UIO-66

Linker



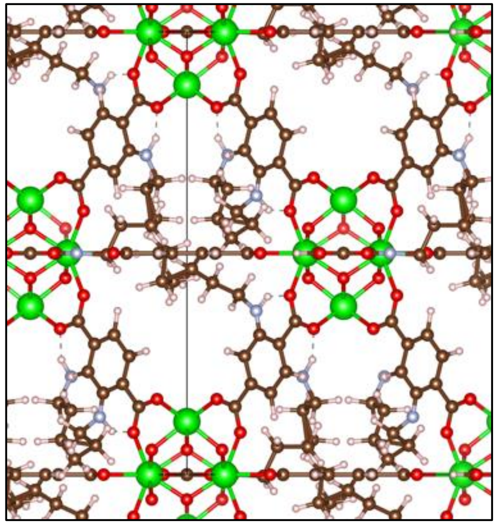
Linker UIO-66

Functionalized Linker



Linker UIO-66-HNC_3H_7

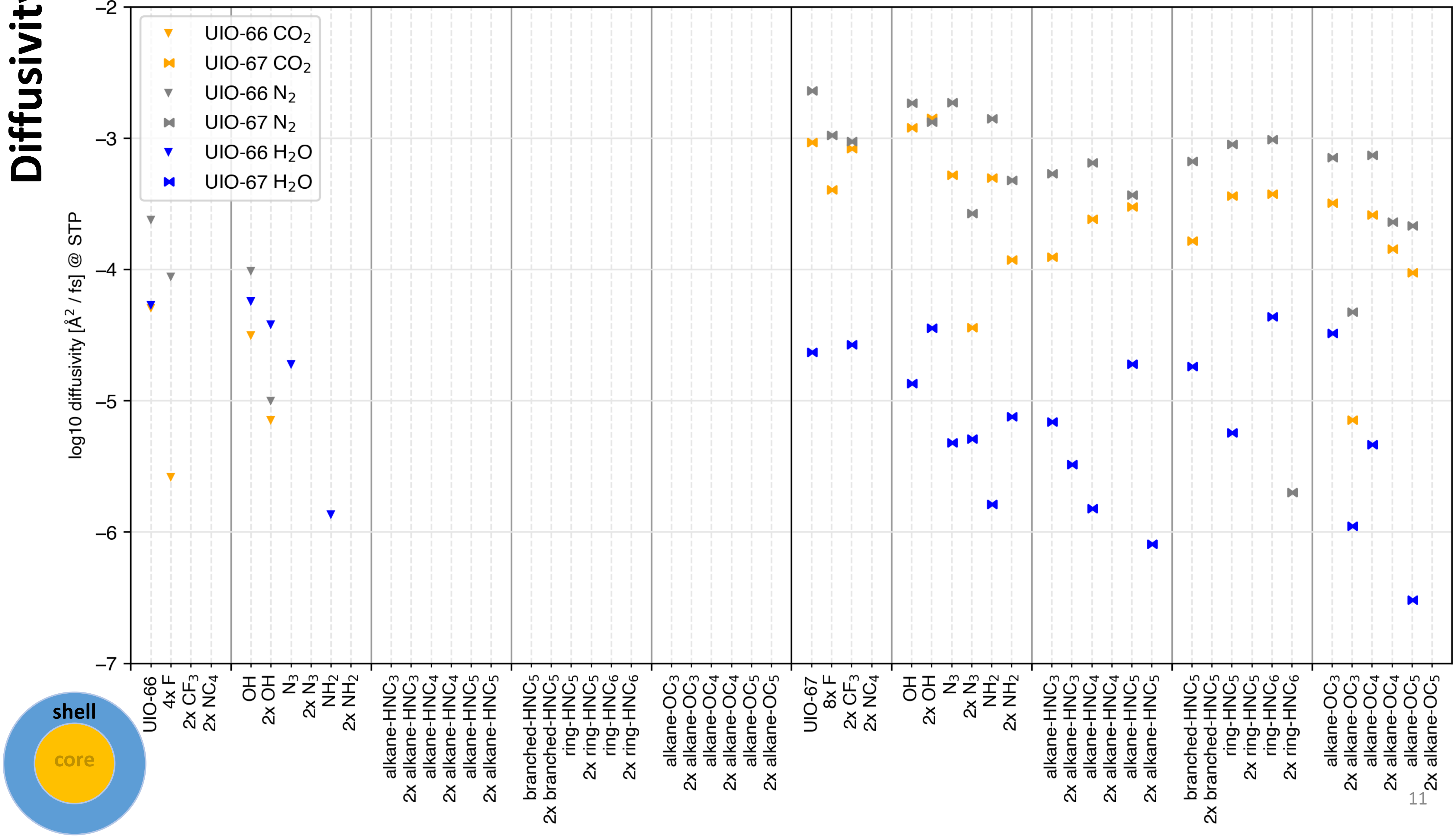
Find / replace functionalized linkers into structure



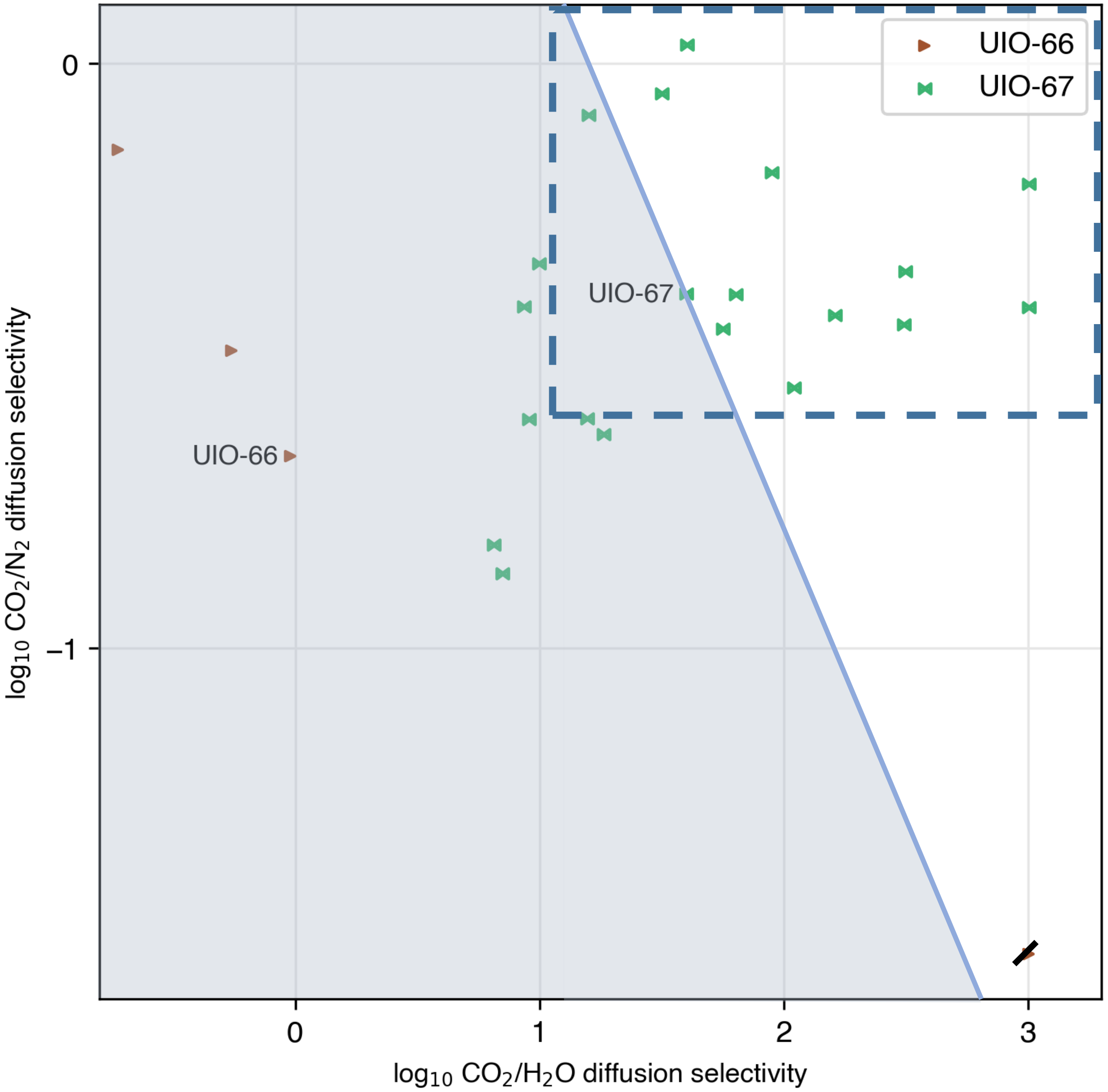
Often results in unrealistic functional group overlap!

Run NVT to relax functional group into more reasonable configuration.

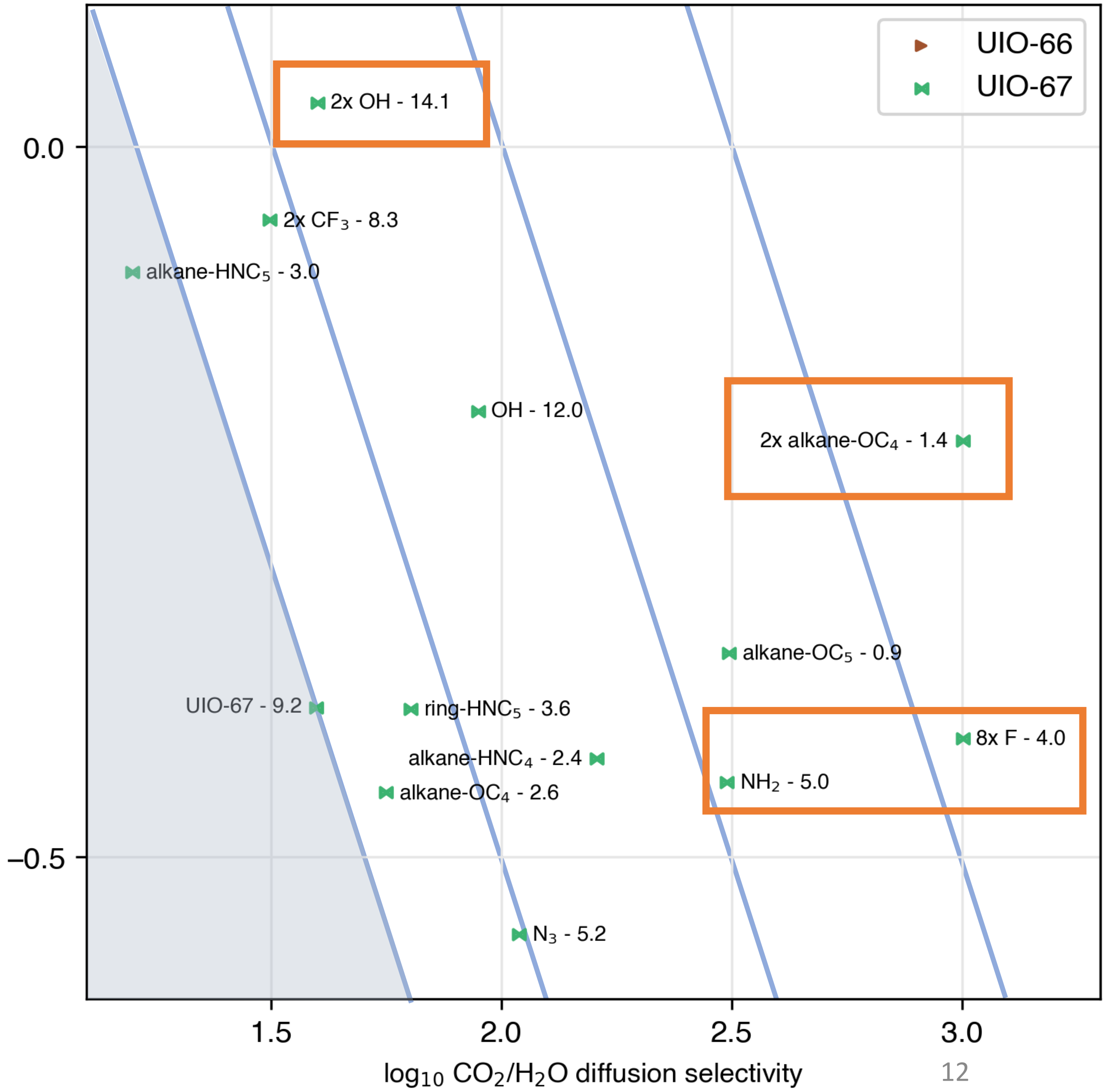
Diffusivity

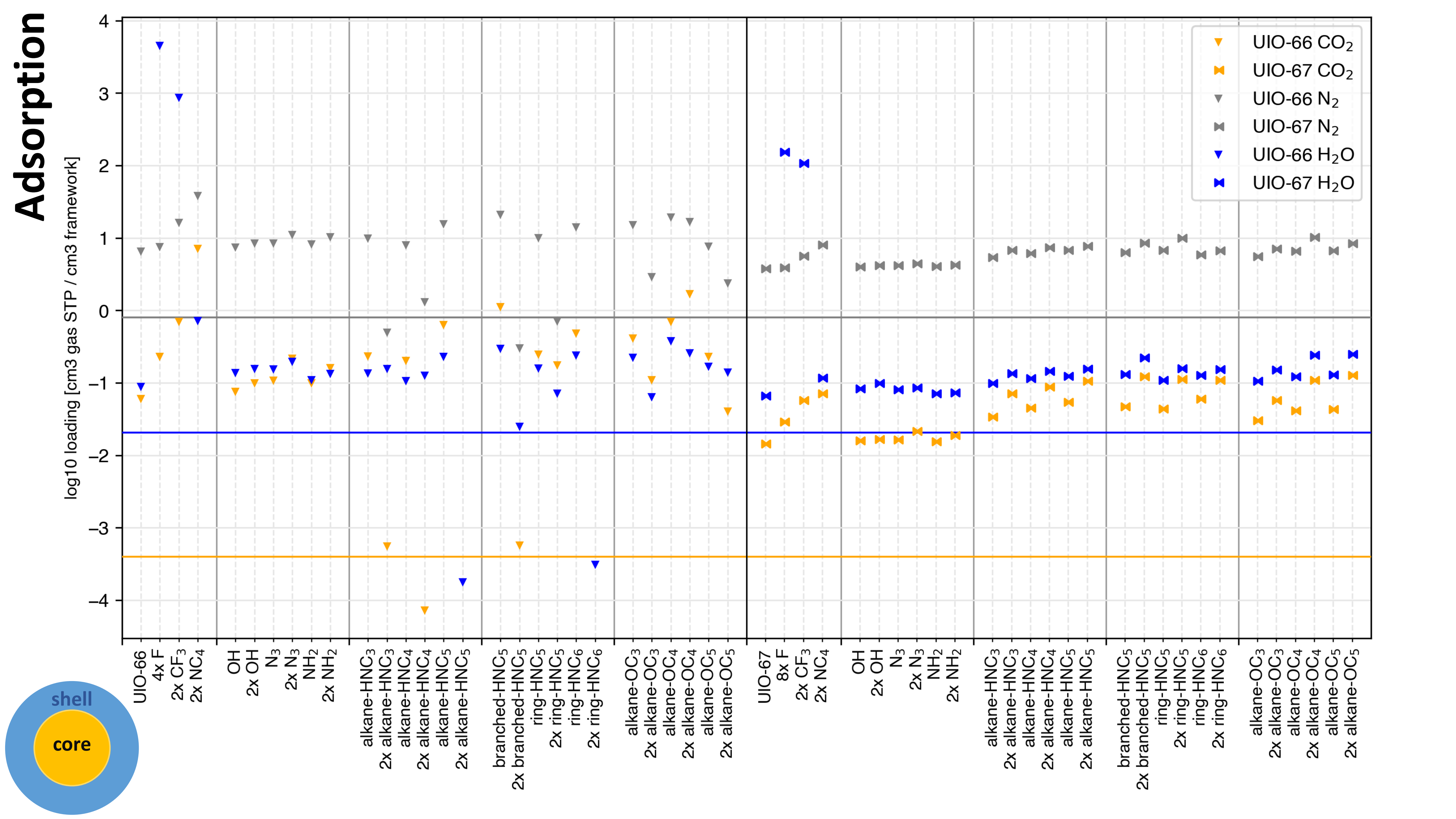


Diffusion Selectivities



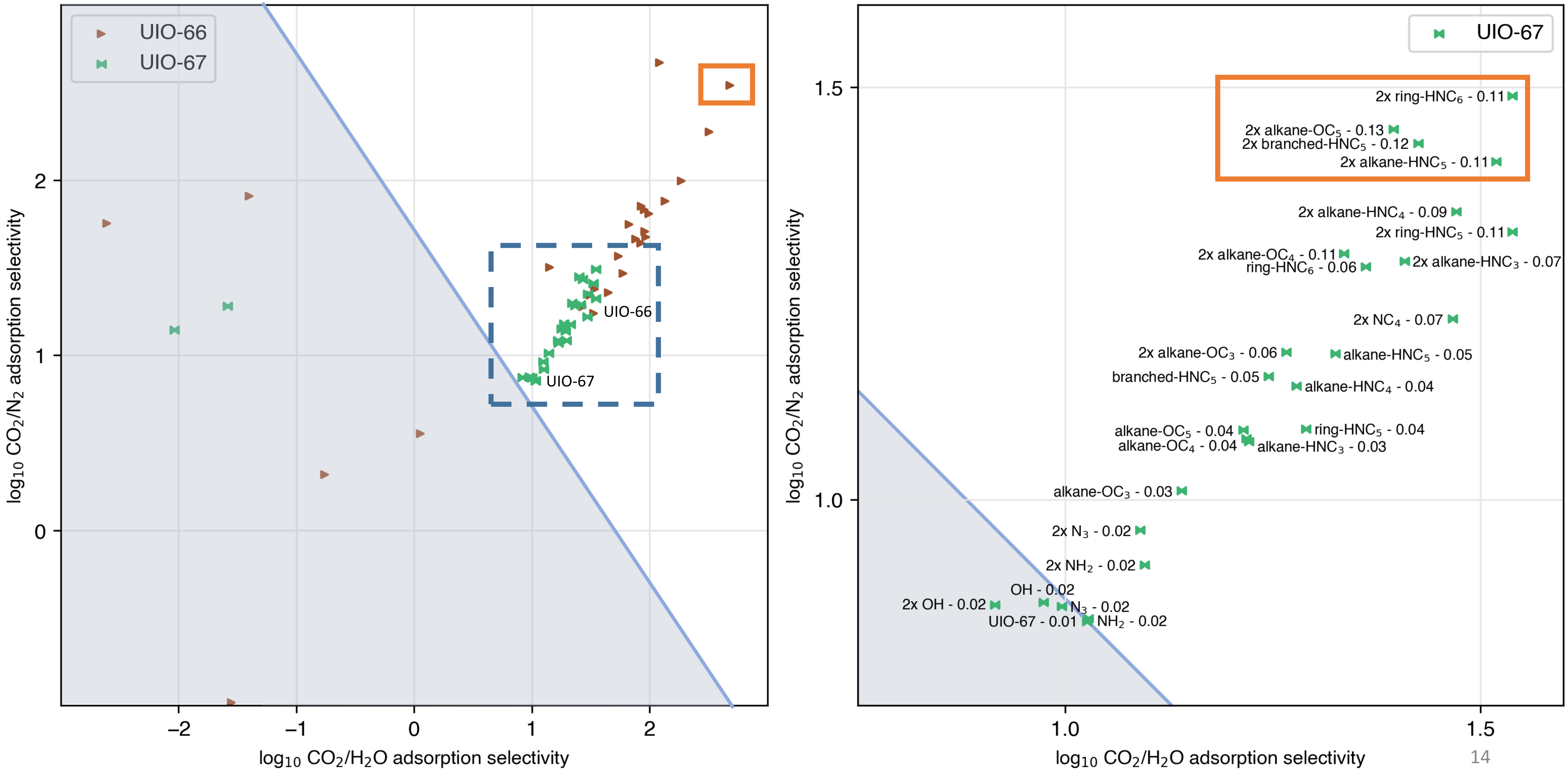
Functional Group - Diffusivity x 1e4 [Å^2 / fs]





Adsorption
log10 loading [cm3 gas STP / cm3 framework]
UIO-66 CO_2
UIO-67 CO_2
UIO-66 N_2
UIO-67 N_2
UIO-66 H_2O
UIO-67 H_2O
UIO-66
4x F
2x CF_3
2x NC_4
OH
2x OH
N_3
2x N_3
NH_2
2x NH_2
alkane-HNC_3
2x alkane-HNC_3
alkane-HNC_4
2x alkane-HNC_4
alkane-HNC_5
2x alkane-HNC_5
branched-HNC_5
2x branched-HNC_5
ring-HNC_5
2x ring-HNC_5
ring-HNC_6
2x ring-HNC_6
alkane-OC_3
2x alkane-OC_3
alkane-OC_4
2x alkane-OC_4
alkane-OC_5
2x alkane-OC_5
UIO-67
8x F
2x CF_3
2x NC_4
OH
2x OH
N_3
2x N_3
NH_2
2x NH_2
alkane-HNC_3
2x alkane-HNC_3
alkane-HNC_4
2x alkane-HNC_4
alkane-HNC_5
2x alkane-HNC_5
branched-HNC_5
2x branched-HNC_5
ring-HNC_5
2x ring-HNC_5
ring-HNC_6
2x ring-HNC_6
alkane-OC_3
2x alkane-OC_3
alkane-OC_4
2x alkane-OC_4
alkane-OC_5
2x alkane-OC_5
shell
core

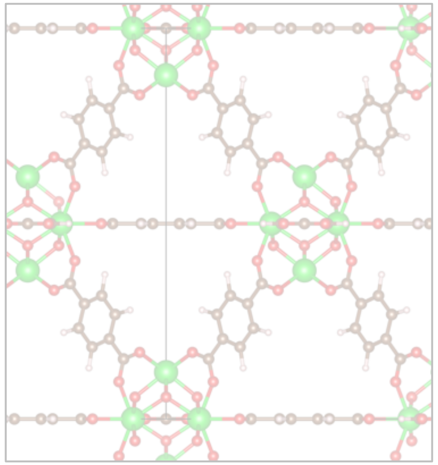
Adsorption Selectivities



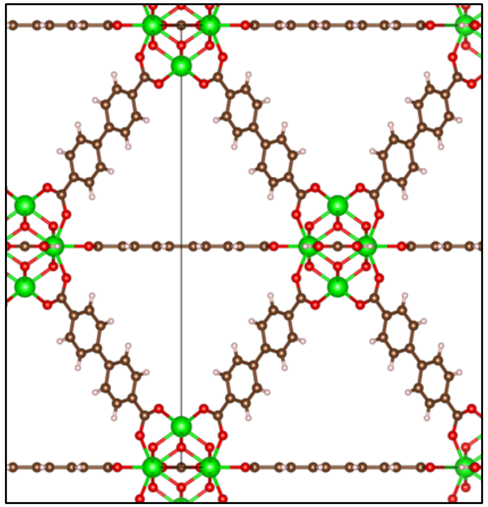
Screening Results

MOFs

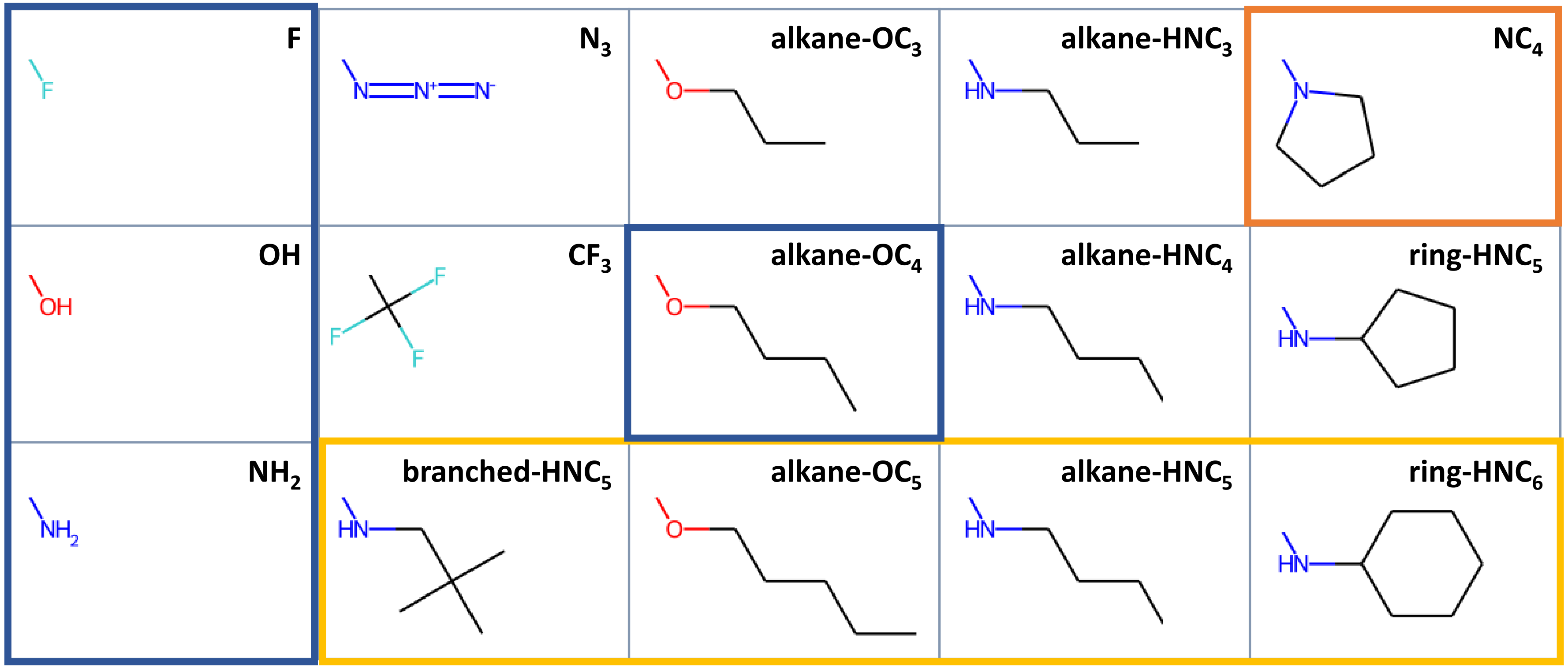
UIO-66

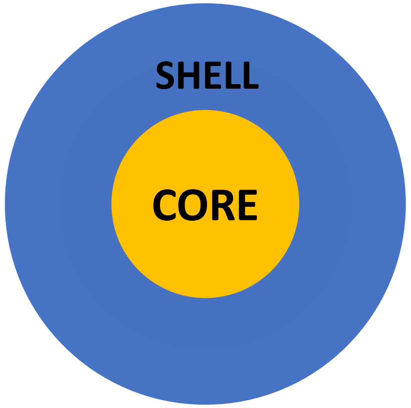


UIO-67



Functional Groups





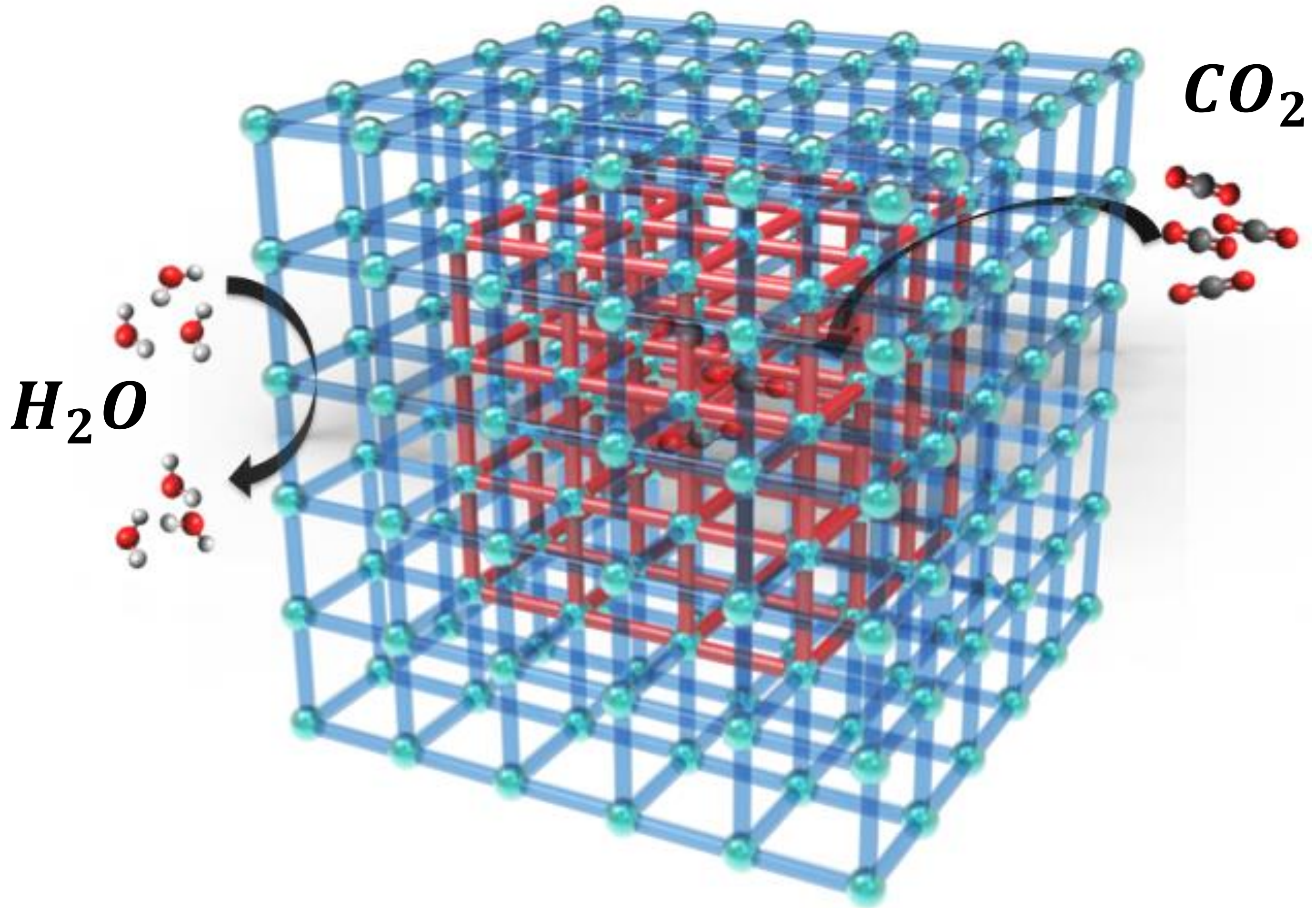
Best shell MOF candidates (UIO-67): F, OH, NH_2, alkane-OC$_4$

Best core MOF candidates (UIO-67): longest hydrocarbons

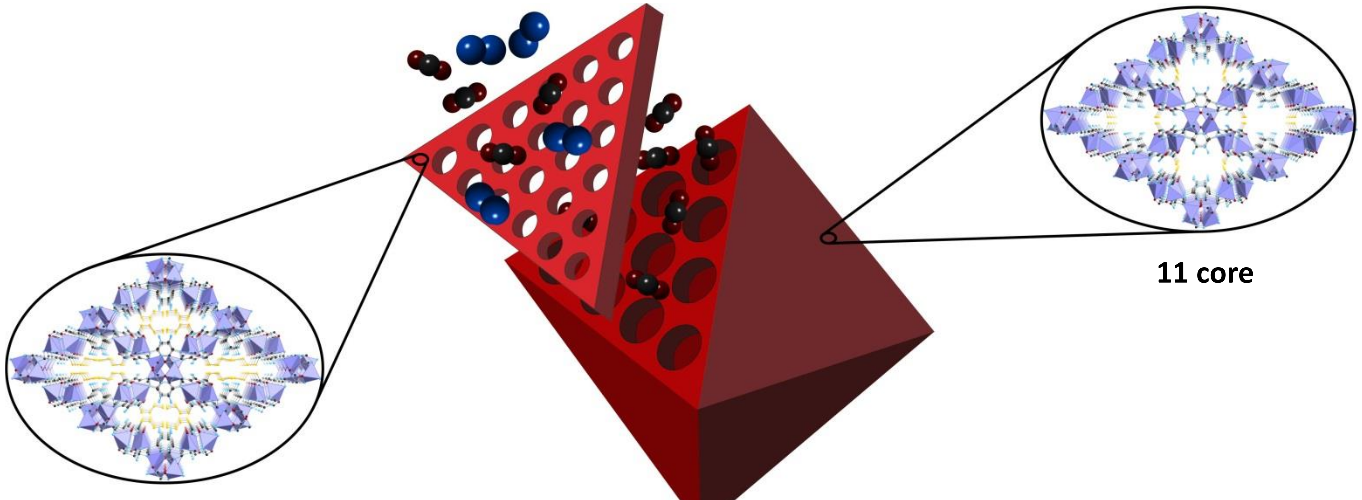
Best core MOF candidate: UIO66-NC$_4$

Objective 2: Synthesize & characterize optimal core-shell MOFs.

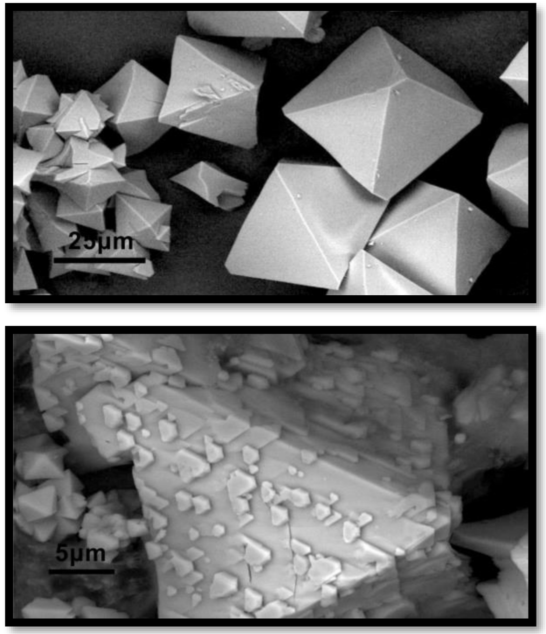
Dr. Nathaniel Rosi



Core-Shell MOFs for Molecular Separations



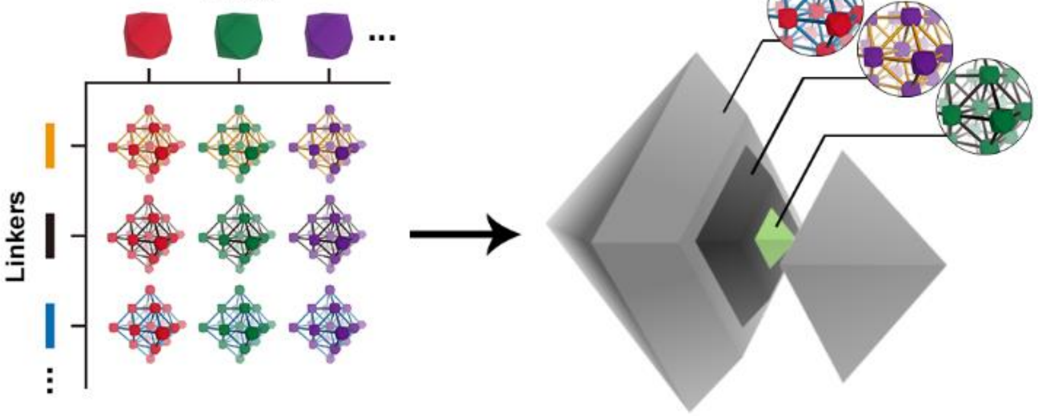
Li, Rosi, et al. *JACS* **2013**



Core

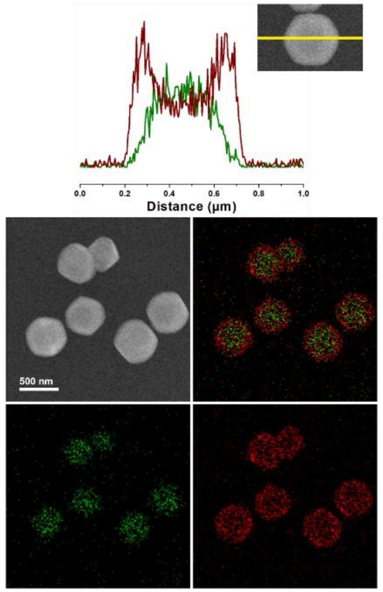
Core-shell

UiO-Based Core-Shell MOFs

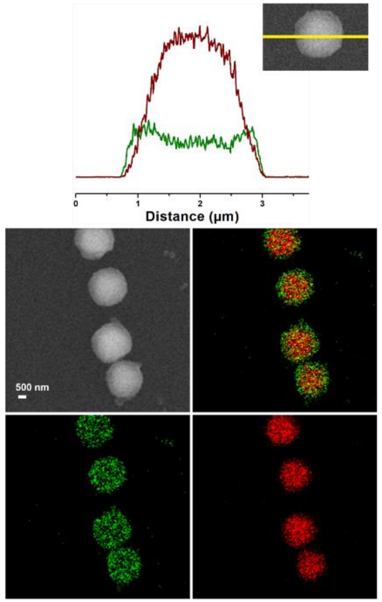


Luo, Rosi, et al. *JACS* **2019**

UiO-67(Zr)⊂UiO-67(Hf)



UiO-67(Hf)⊂UiO-67(Zr)



Ligand Design

Core ligand design strategy:

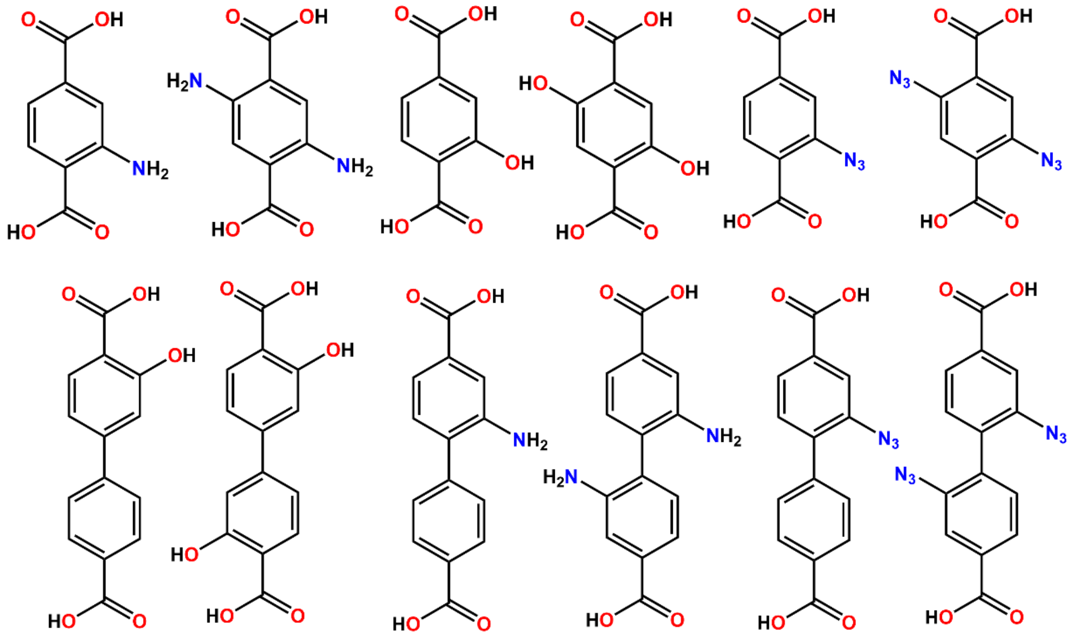
Lewis basic groups: NH_2-, OH-, N_3-

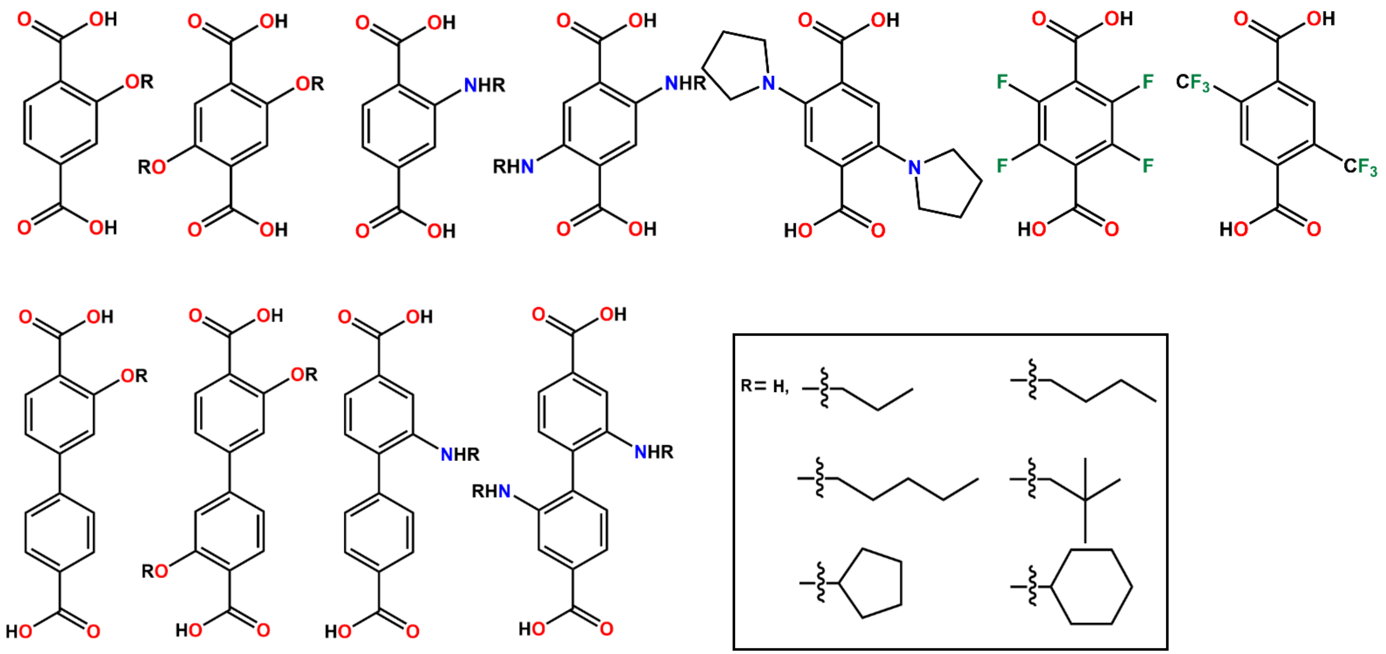
Forming Lewis acid-base pair with CO_2

Shell ligand design strategy:

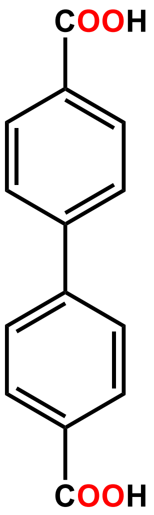
Hydrophobic groups: alkylamino, alkylhydroxyl, F-

Preventing water from entering core MOF

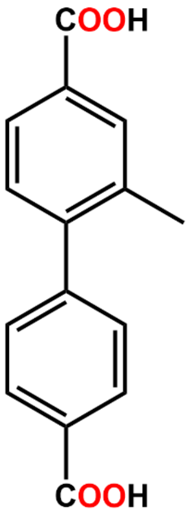




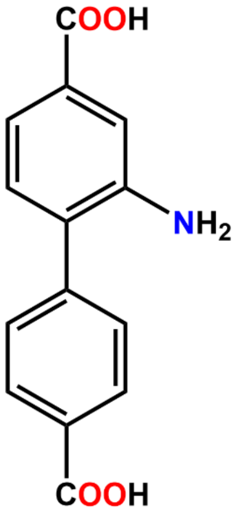
Synthesis of UiO-67 MOFs



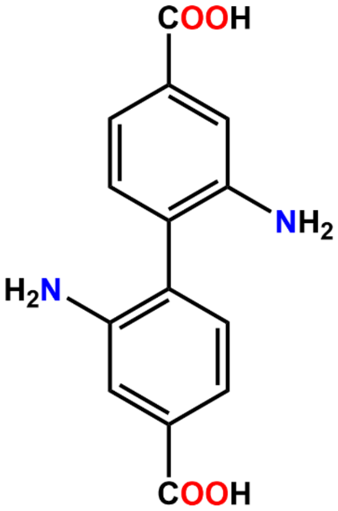
H_2-BPDC
(UiO-67)



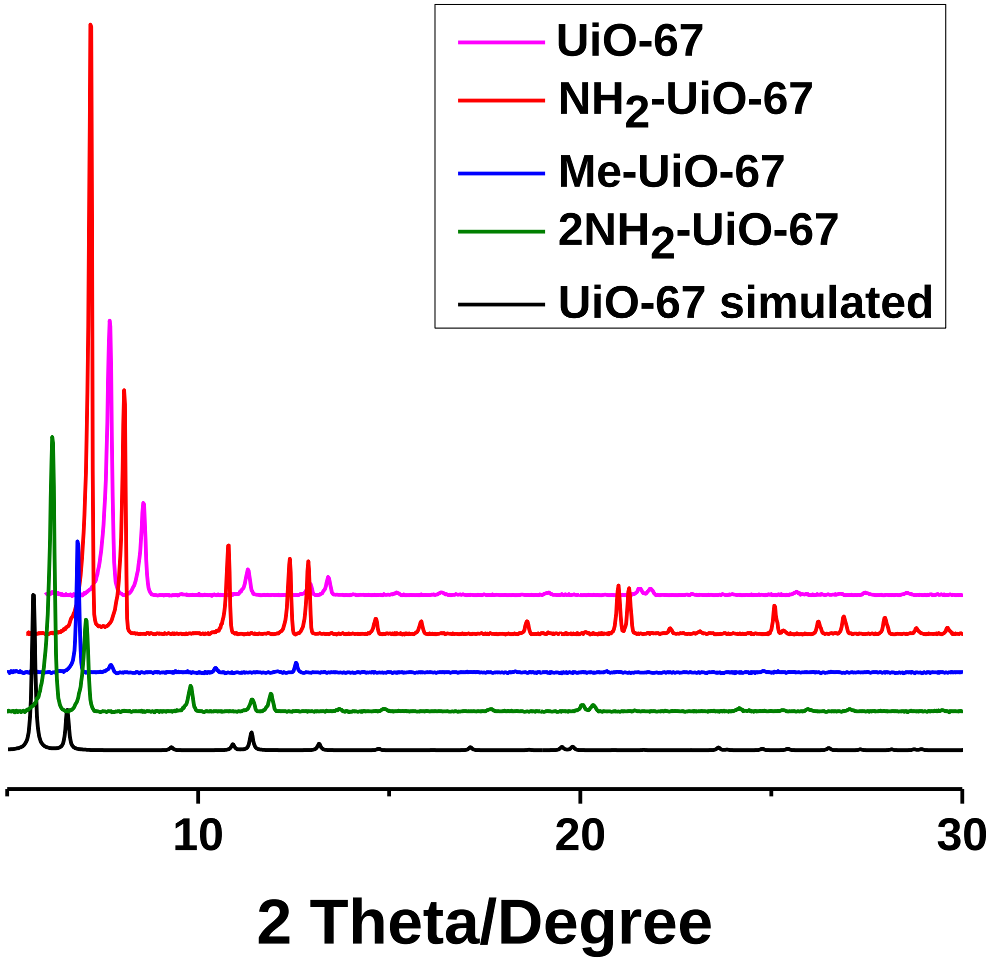
H_2-Me-BPDC
(Me-UiO-67)



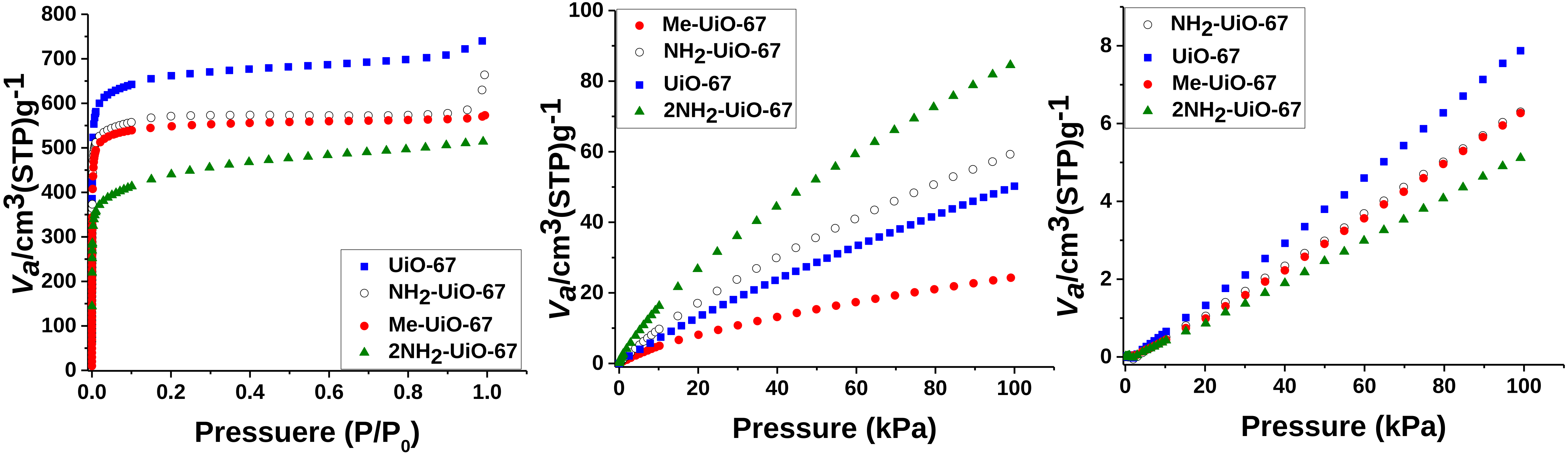
H_2-NH_2-BPDC
(NH_2-UiO-67)



H_2-2NH_2-BPDC
(2NH_2-UiO-67)



Characterizations of UiO-67 MOFs



N_2 adsorption isotherms at 77K

CO_2 adsorption isotherms at 298K

N_2 adsorption isotherms at 298K

Comparison of Experimental Results vs. Simulation Results

Adsorption @ STP:

CO_2 loading *a* cc/g at 4.2×10^{-4} bar, 298 K
N_2 loading *b* cc/g at 0.79 bar, 298 K

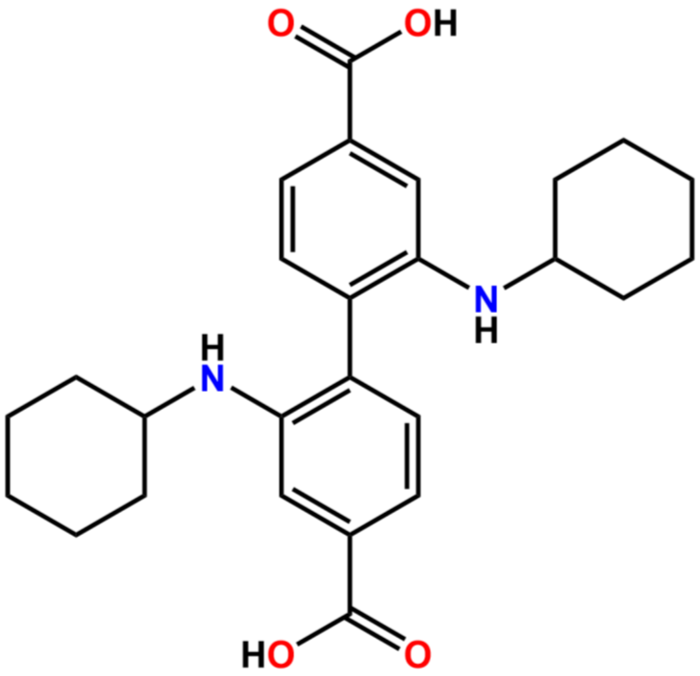
$$\text{Adsorption selectivity} = \frac{a / 4.2\text{x}10^{-4}}{b / 0.79}$$

	UiO-67	NH_2-UiO-67	$2NH_2$-UiO-67
Simulation Results	7.11	7.45	8.33
Experimental Results	7.20	28.9	133

Simulation results have lower selectivity but similar trend

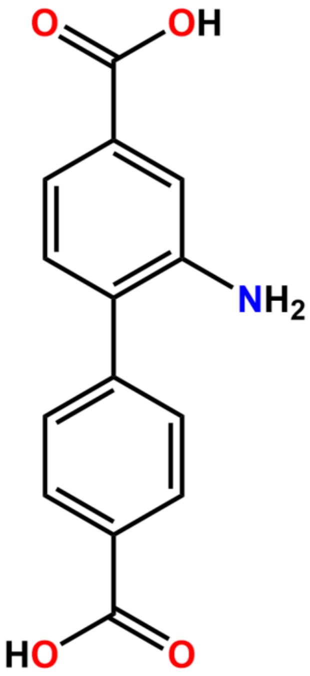
Selection of Core-shell MOF Pair

Core:



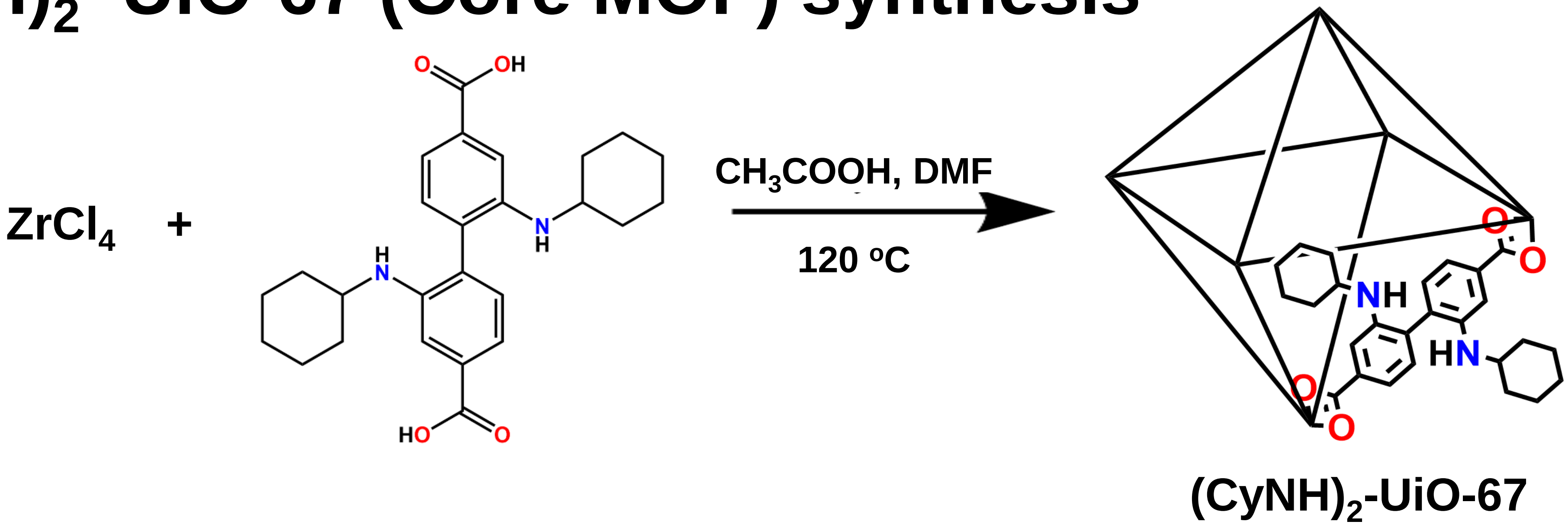
- Highest CO_2 over N_2 adsorption selectivity: 31
- High CO_2 capacity：0.0104 cm^3/g (STP, 42.18 Pa, 298K)

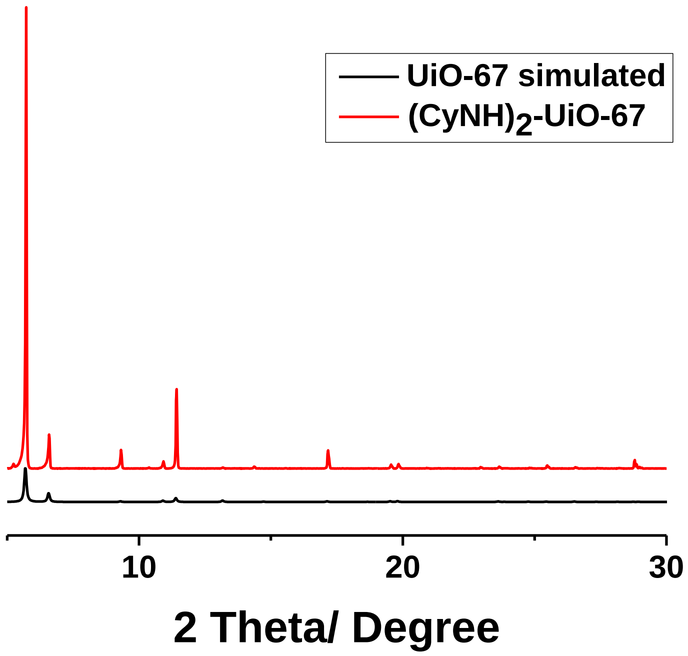
Shell:

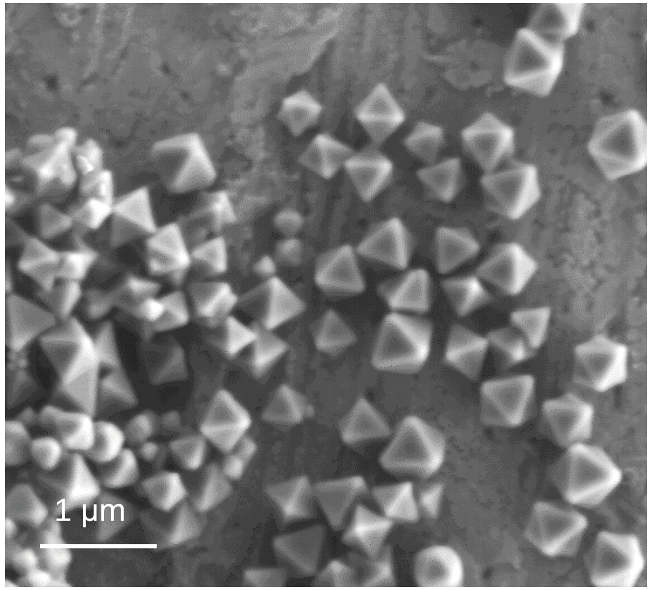


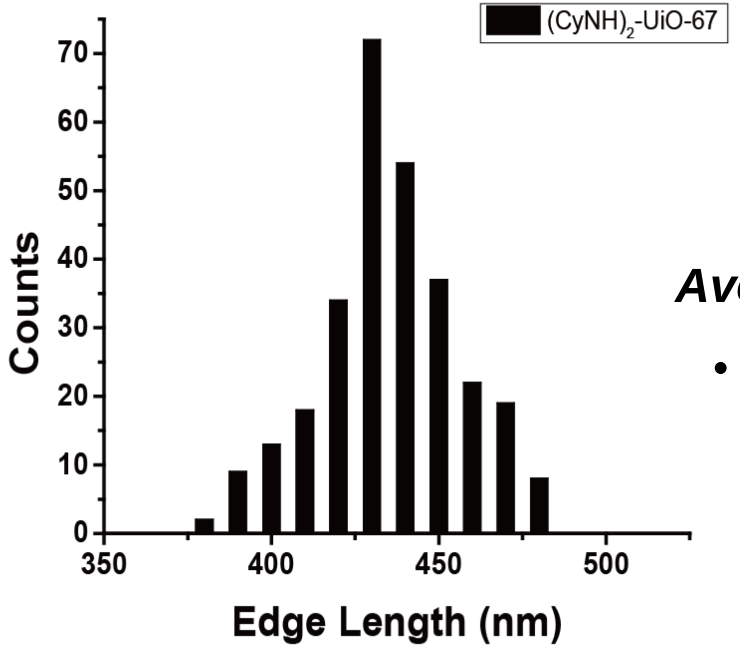
- High CO_2/H_2O diffusion selectivity: 307
- High CO_2 diffusivity: 4.98 $Å^2/fs$

$(CyNH)_2$–UiO-67 (Core MOF) synthesis







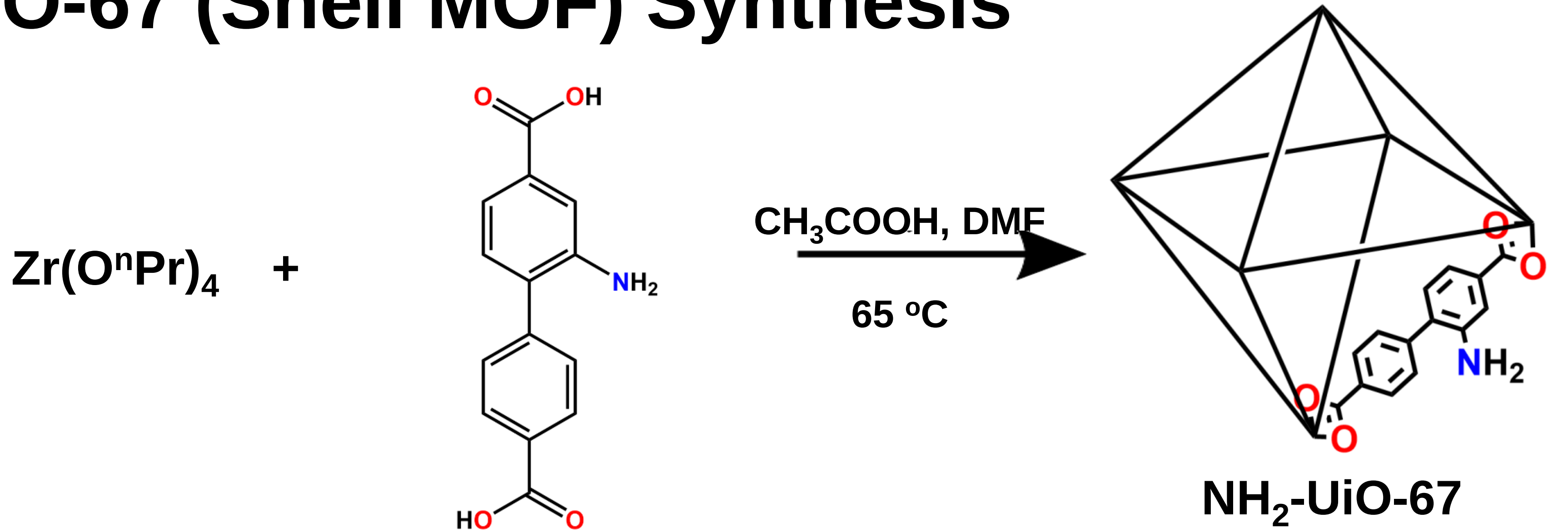


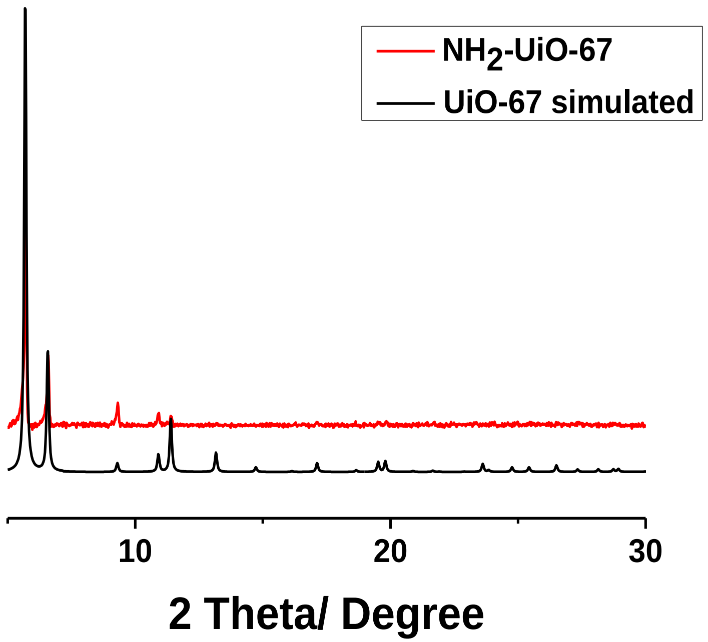
Size distributions (based on 300 counts)

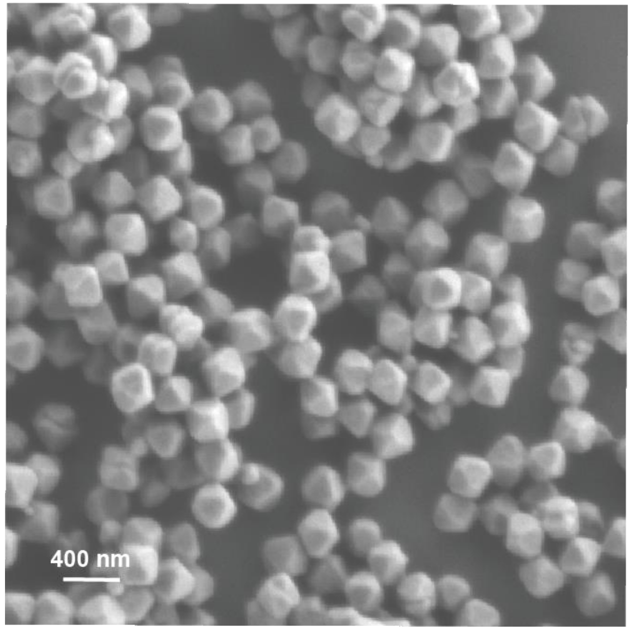
Average diameter :

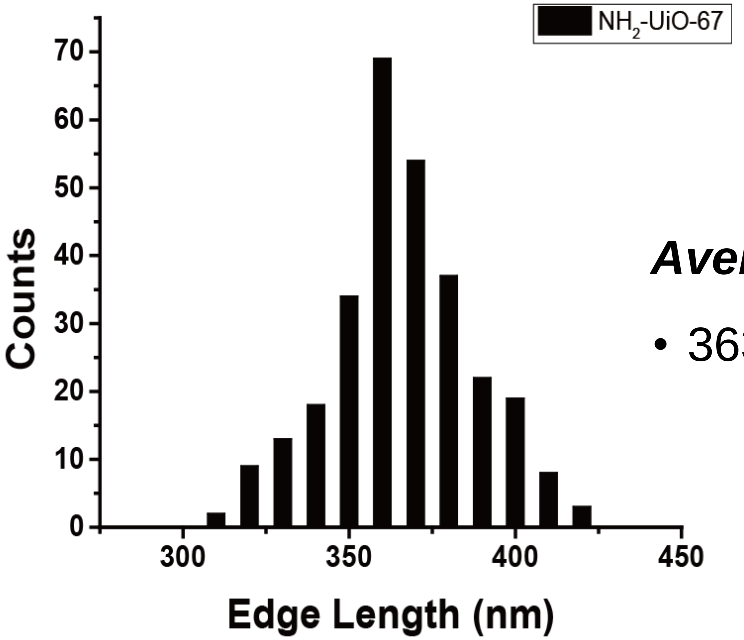
- 422±22 nm

NH_2-UiO-67 (Shell MOF) Synthesis









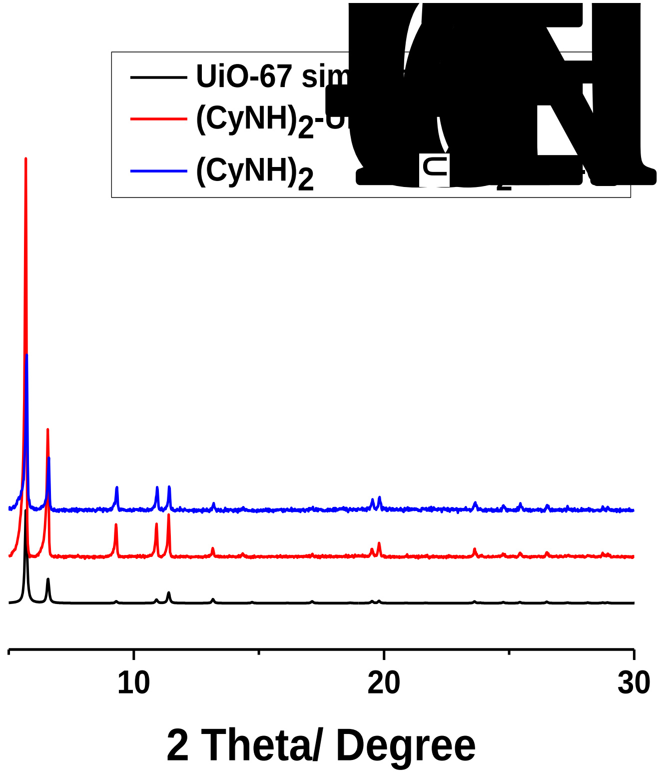
Size distributions (based on 300 counts)

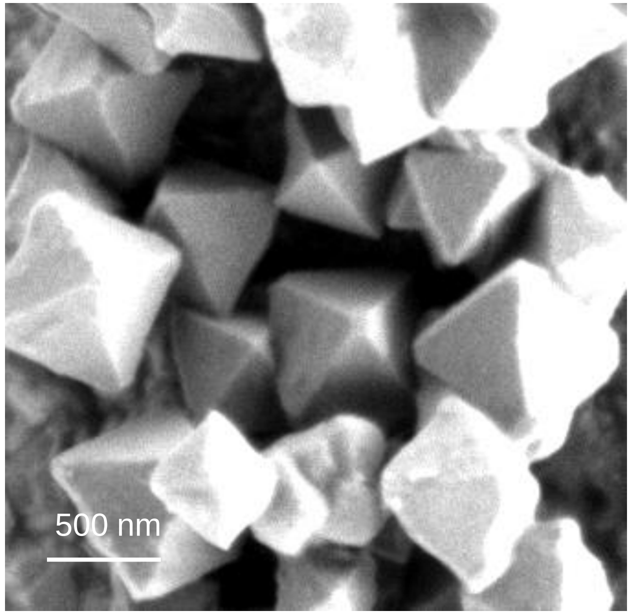
Average diameter :

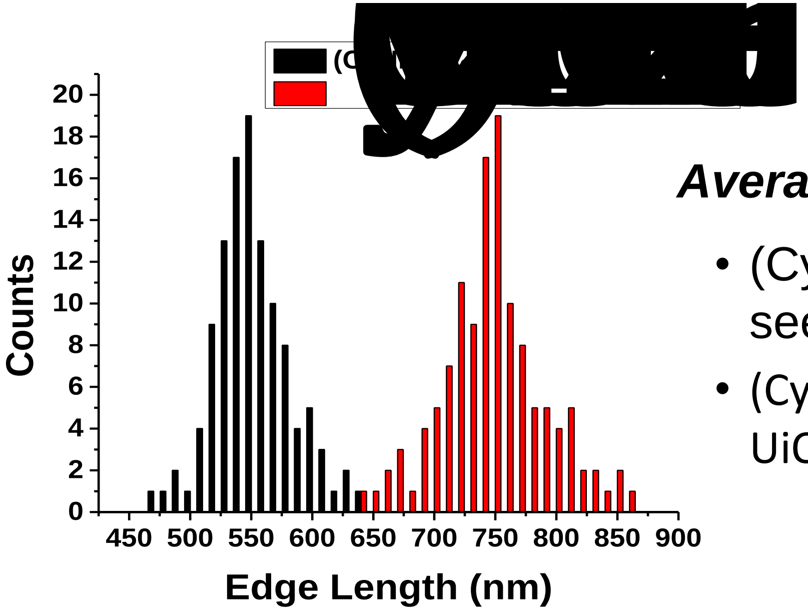
- 363±22 nm

Core-Shell MOF Synthesis

$$(CyNH)_2\text{-UiO-67 seeds} + Zr(O^nPr)_4 + NH_2\text{-BPDC} \xrightarrow[65\ ^{o}C]{CH_3COOH,\ DMF} (CyNH)_2\text{-UiO-67} \subset NH_2\text{-UiO-67}$$







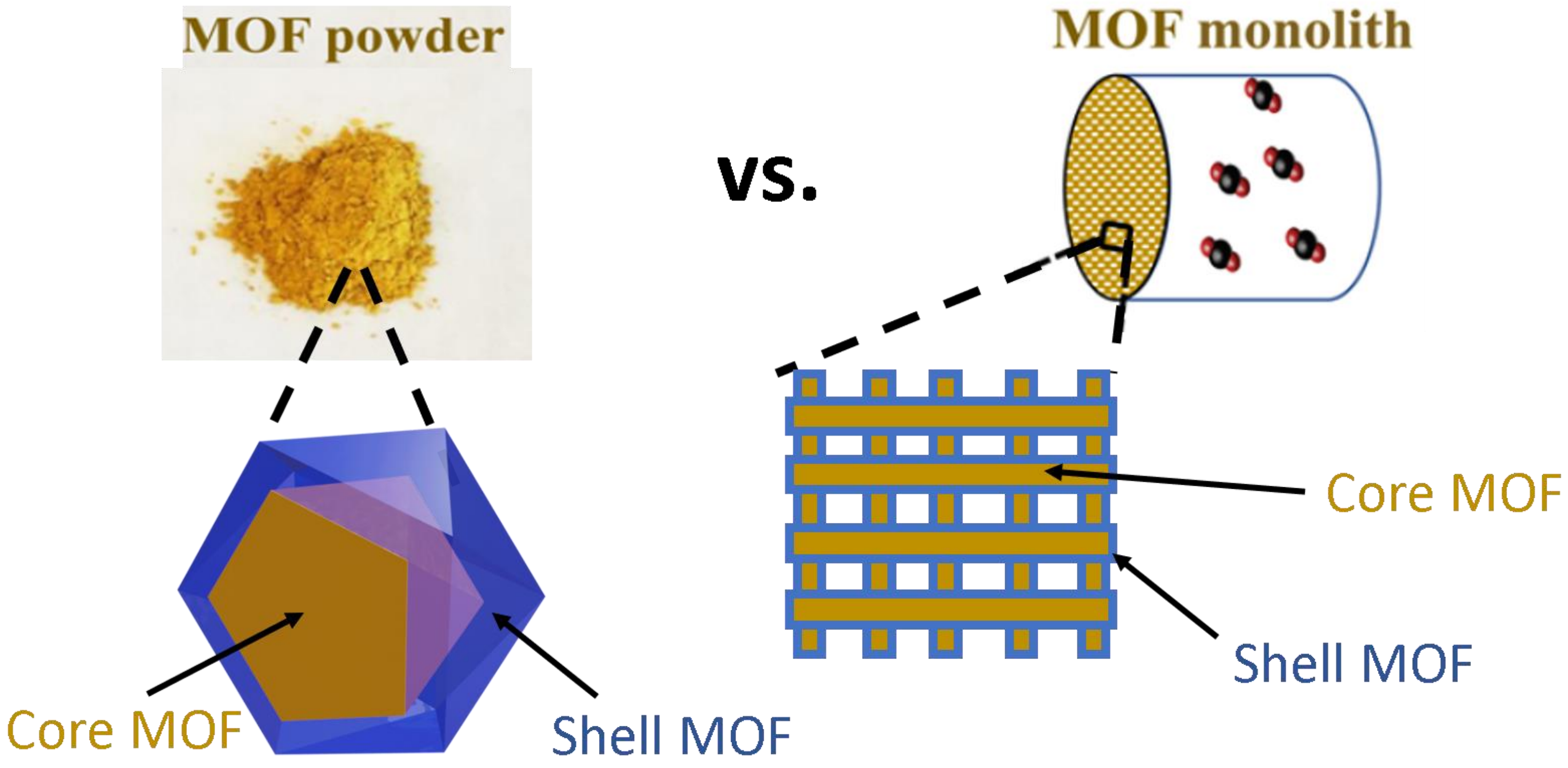
Size distributions (based on 300 counts)

Average diameter :

- $(CyNH)_2$-UiO-67 seeds: **546±61 nm**
- $(CyNH)_2$-UiO-67⊂NH_2-UiO-67: **746±78 nm**

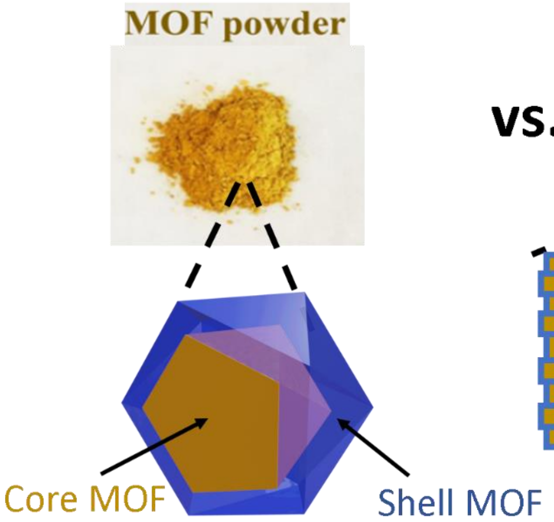
Objective 3: Determine the optimal core-shell MOF packing structure.

Dr. Katherine Hornbostel

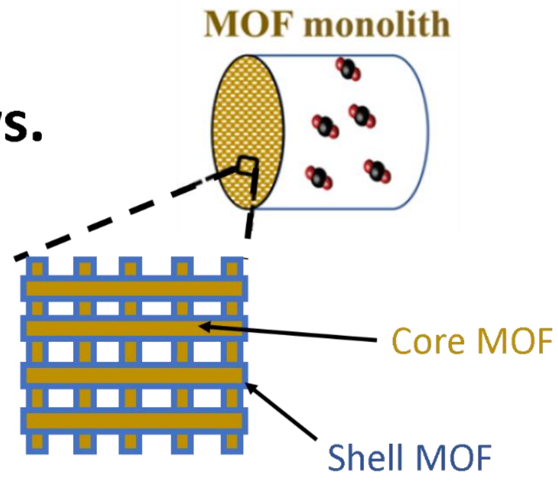


Goal: Optimize the particle and reactor designs for core-shell MOFs.

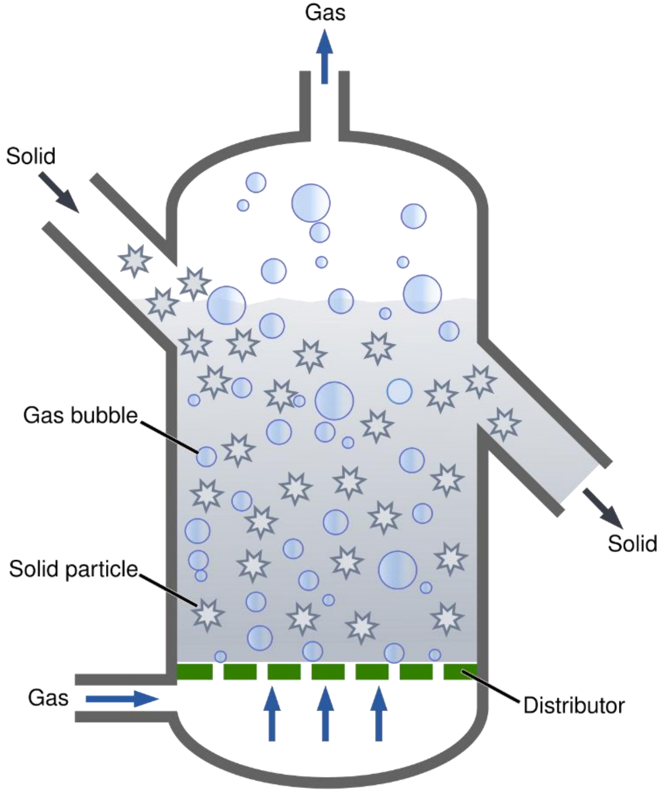
1. Optimize pellet/particle design



vs.

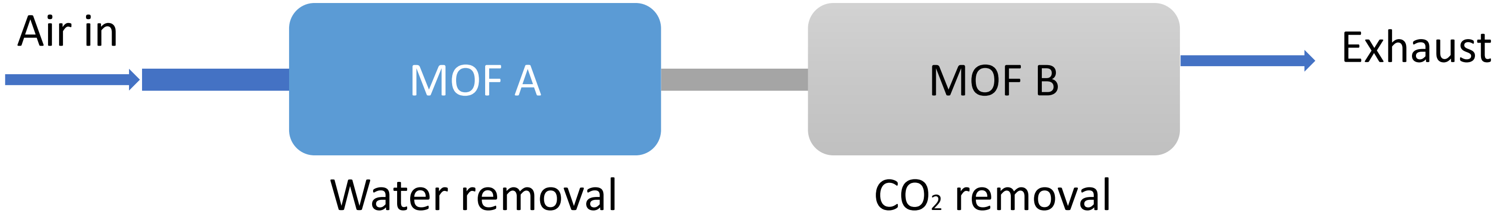


2. Optimize reactor design

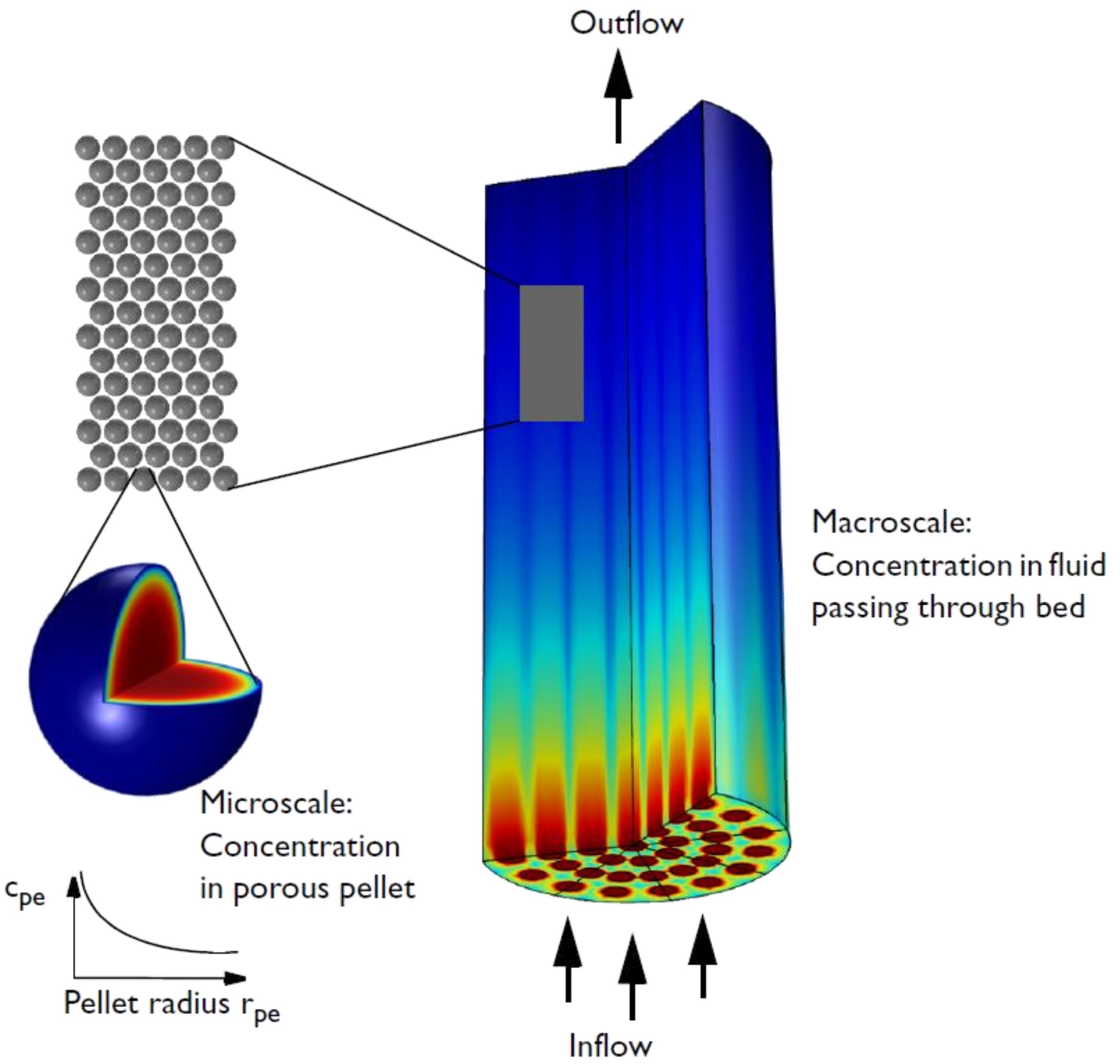


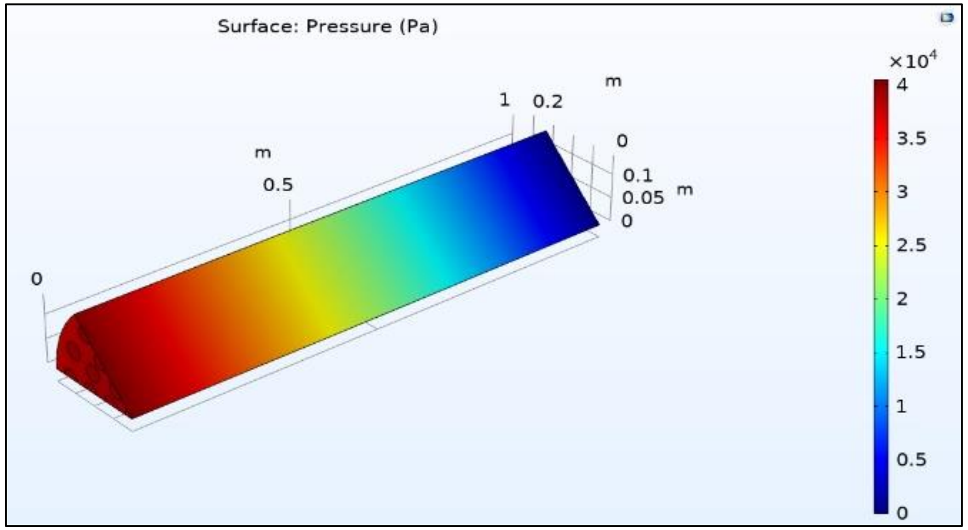
https://commons.wikimedia.org/wiki/File:Fluidized_Bed_Reactor_Graphic.JPG

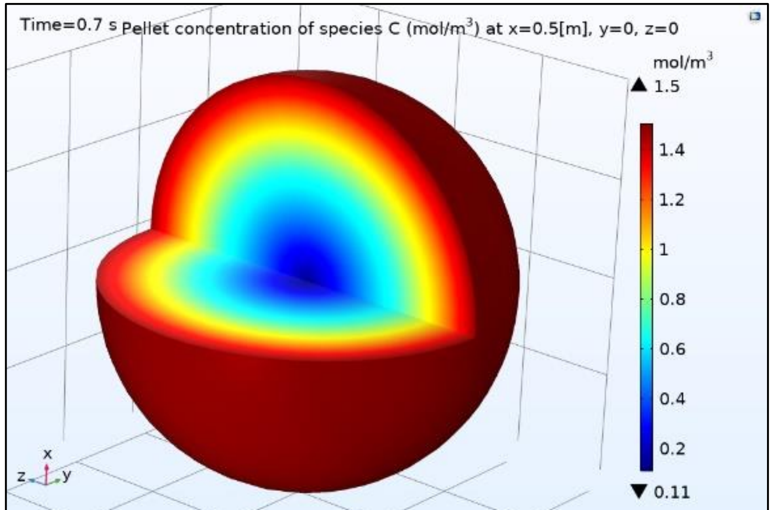
Benchmark: Separate MOF reactors



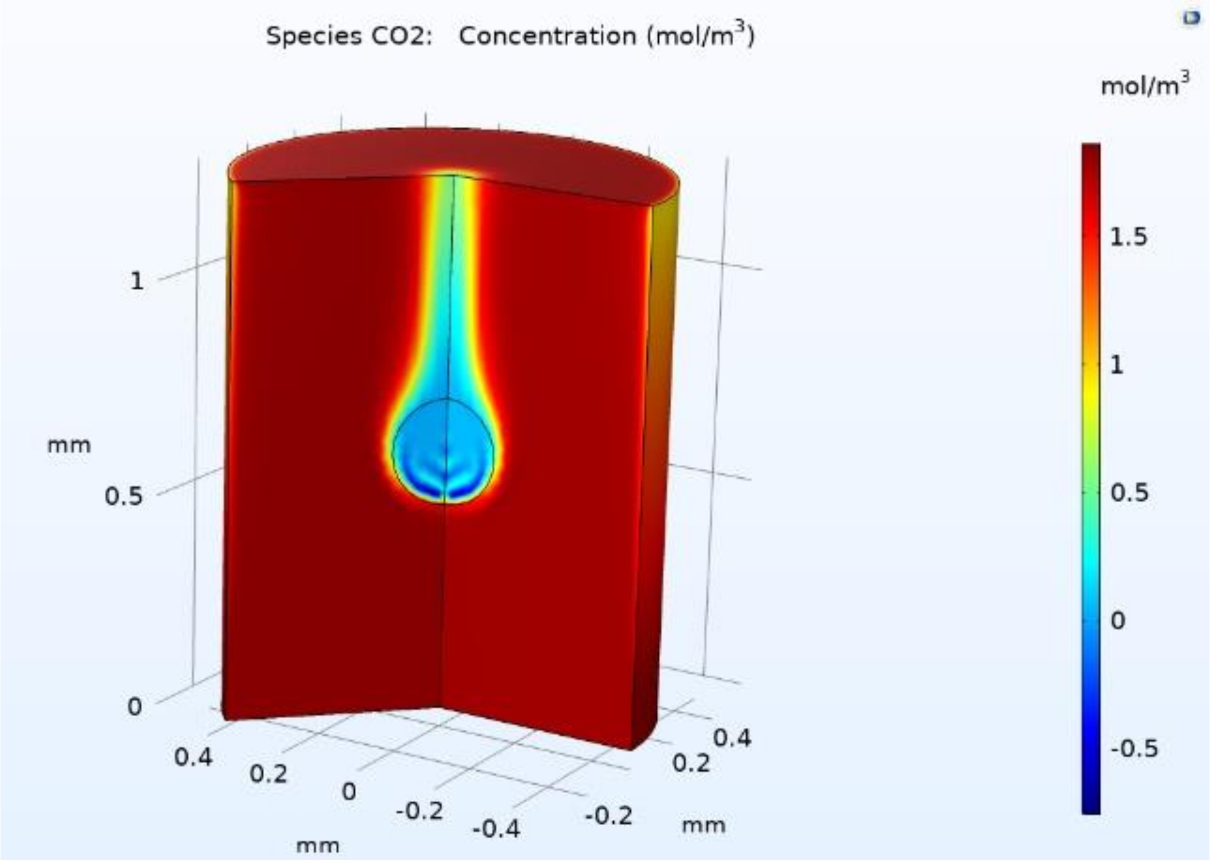
Q1: Developed COMSOL Multiphysics model of packed bed reactor filled with MOF pellets.



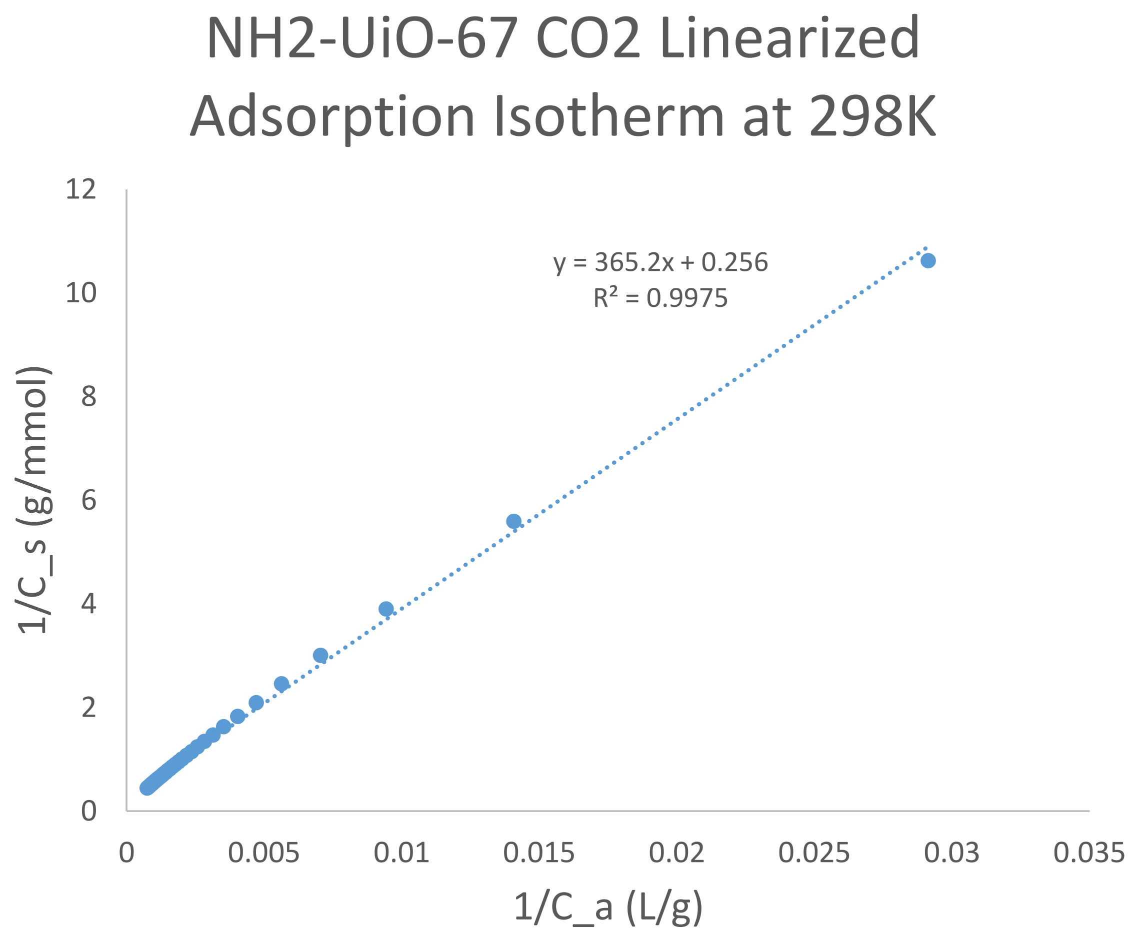


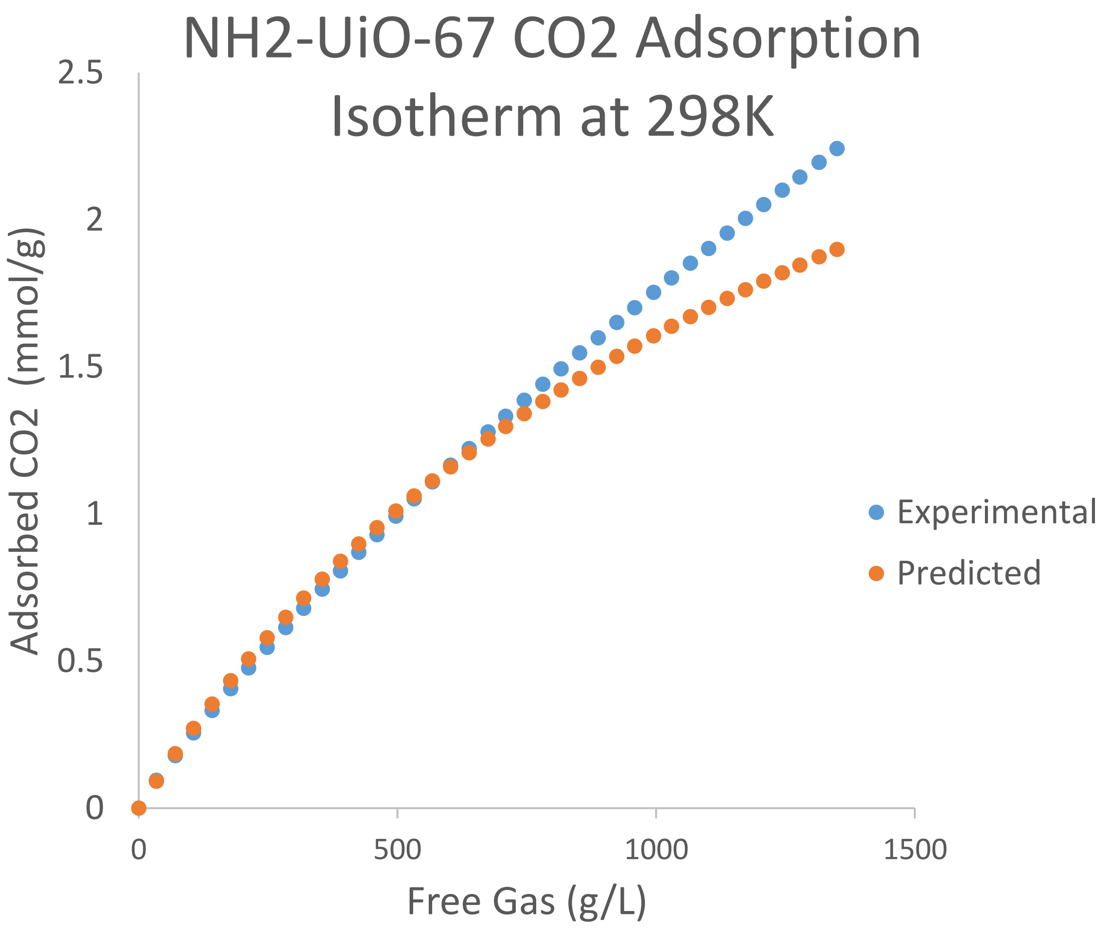


Q2: Developed COMSOL Multiphysics model of individual MOF pellet exposed to air flow.

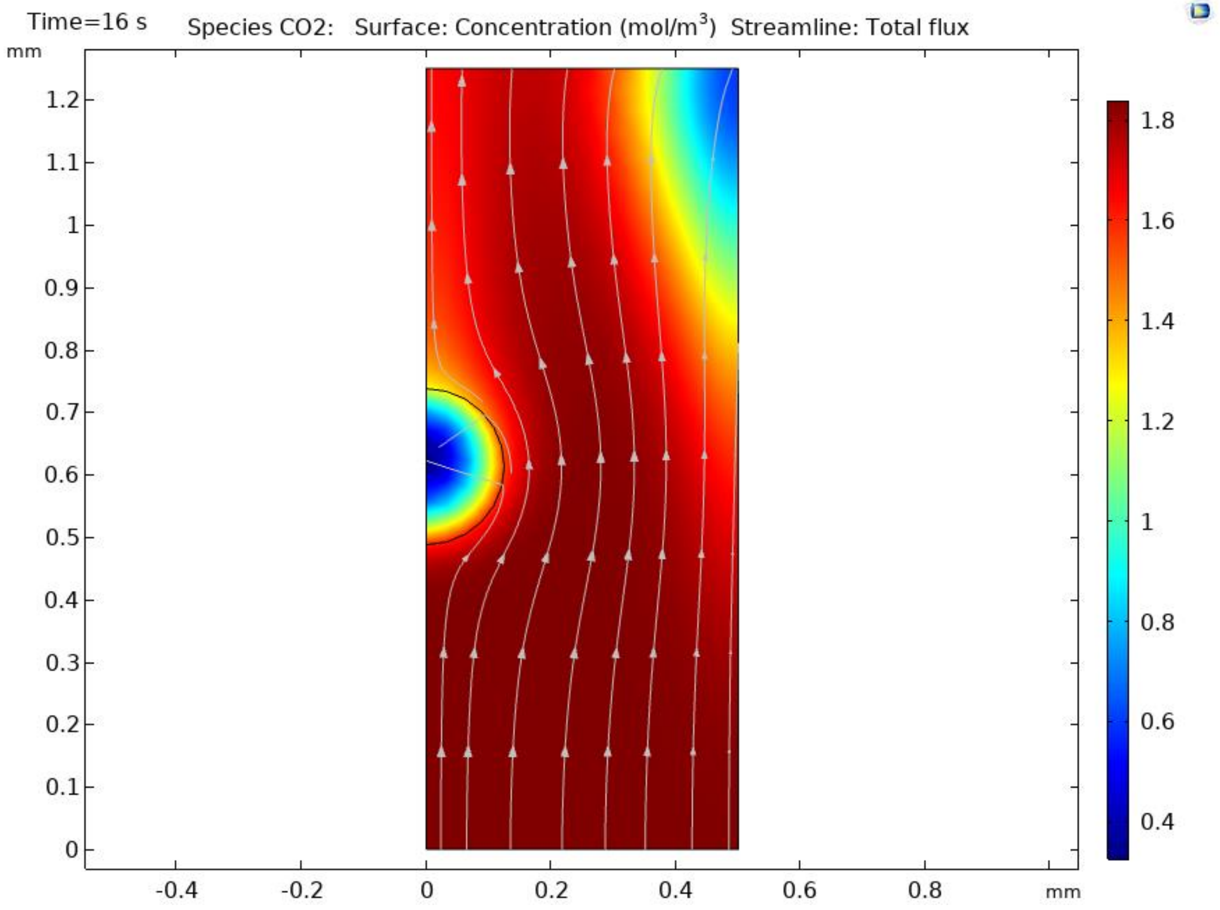


Q3: Langmuir constants were extrapolated from experimental data and incorporated into the single pellet model.





Q3: Initial modeling results using the predicted isotherm values show physical accuracy.

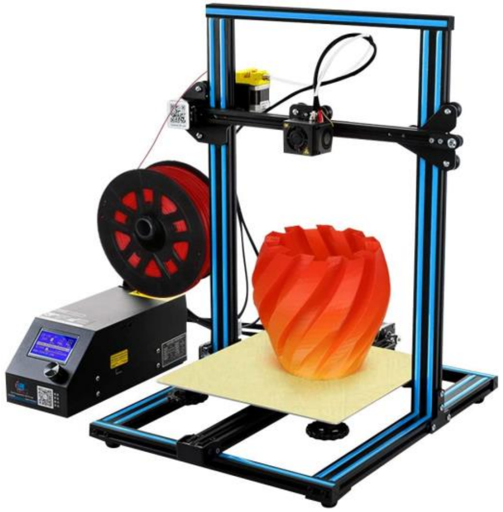


Q4: Investigated different options for 3D-printed MOF monoliths available at Pitt.

Printing Method

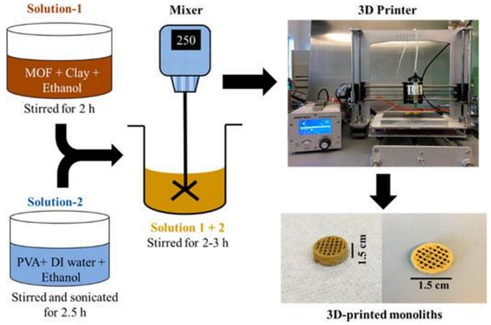
Shortcomings

Filament Printer



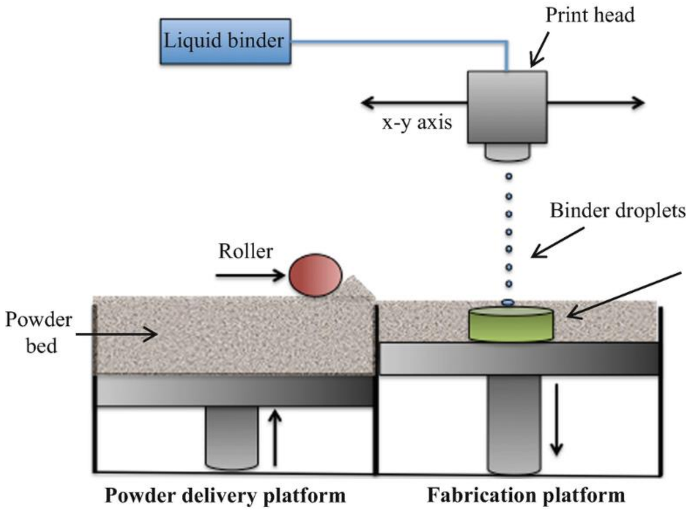
Filament Extruder

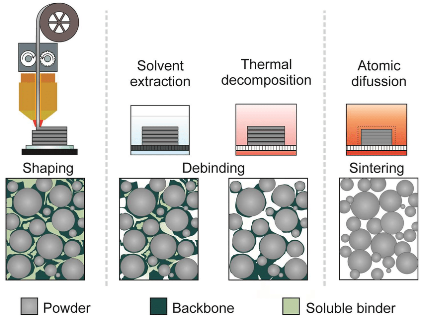
Food Printer



Current Industry Method

Binder Jet Printer





Laser Sintering Process

Project Schedule

		Year 1				Year 2			
Obj.	Task	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
1	1.1 Simulate $CO_2/N_2/H_2O$ adsorption in all CoRE database MOFs.								
	1.2 Simulate $CO_2/N_2/H_2O$ diffusivity in all CoRE database MOFs.								
	1.3 Identify optimal core-shell MOF pairs.								
	1.4 Model water stability in 5 highest ranked core-shell MOF candidates.								

Project Schedule (cont.)

		Year 1				Year 2			
		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
2	2.1 Prepare and characterize adsorption properties of target MOFs for core and shell domains.								
	2.2 Develop synthetic protocols for preparing core-shell MOFs with selected core and shell domains with optimal properties.								
	2.3 Characterize CO_2 capture performance of core-shell MOFs in dry and humid air.								
3	3.1 Create 3D-printed monolith with core MOF.								
	3.2 Coat monolith in shell MOF and test core-shell monolith.								
	3.3 Perform experiments on core-shell MOF powder.								

Next steps

1. Wilmer team:
   1. Score and rank core-shell MOF combinations based on combined adsorption/diffusion properties
   2. Screen smaller subset of candidate core-shell MOFs with higher fidelity simulations
2. Rosi team:
   1. Adsorption characterization of core-shell system
   2. Examination of properties as function of core and shell thickness
3. Hornbostel team:
   1. Finish developing single pellet core-shell model and perform parametric studies
   2. 3D-print first core-shell MOF monolith
4. Everyone: start drafting first journal paper(s) based on this work

Thank you! Questions?