Engineering Accessible Adsorption Sites in Metal Organic Frameworks for CO_2 Capture

Saki T. Golafale, Kennedi Trice, Taylor Sledge

Dr. Conrad W. Ingram (PI), Dr. Tandabany C. Dinadayalane (Co-PI)
Department of Chemistry*, *Clark Atlanta University, Atlanta, GA 30314

DOE contract No.: DE-FE0022952
2017 Crosscutting Research & Rare Earth Elements Portfolios Review
March 20-23, 2017 Pittsburgh, PA

Outline

- Background
- Research goal and objectives
- Progress
    - Diaza-crown ether MOFs
    - Ultra large pore stilbene based MOFs
    - Stilbene and pyrazine based MOFs
    - CO_2 adsorption studies
- Summary
- Acknowledgement

Background

Post-combustion Capture: capturing carbon dioxide from flue gas after fossil fuel combustion

Flue gas contains about 15% of CO_2,
75% of N_2, 5% of H_2O, 3% of O_2,

~14% CO_2 captured from flue gas

Current techniques pursued

- adsorption on a solid
- hybrid processes, such as adsorption/membrane systems
- absorption into a liquid

Adsorption into a liquid

state of the art technology

Drawback

large amounts of heat are needed to release absorbed CO_2

amine is corrosive and unstable, and the liquid is hard to handle.

Required characteristics for solid adsorbents

- High storage capacity,
- Excellent selectivity over other gases,
- Chemically stable under flue gas of power plants,
-
- Easy to regenerate with minimal energy input, and
-
- Easily synthesized with low capital cost

Examples of solid adsorbents

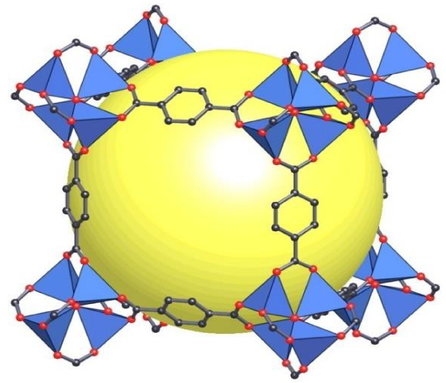
- Activated carbon
- Zeolites and other inorganic porous materials
- **Metal-organic frameworks**

Unique properties of MOFs

- Highly crystalline nature
- Permanent porosity
- Uniformed pore-size and large surface area (> 5,000 m^2/g)
- Tunable chemistry

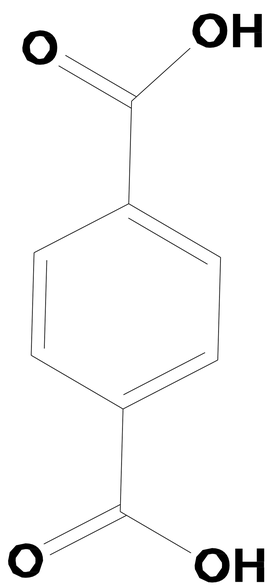
Metal organic frameworks

Metal ion + Organic linker → **MOF material**

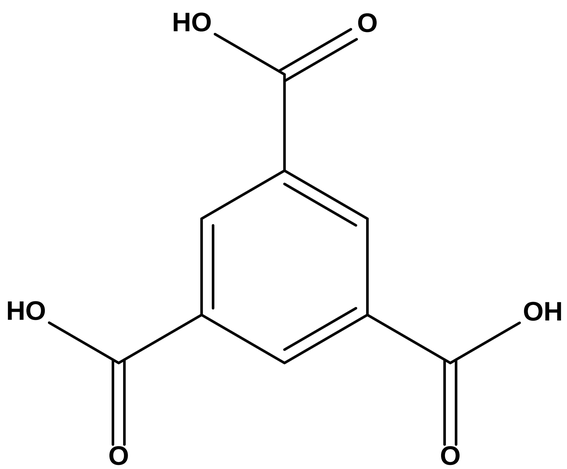


Metal salts

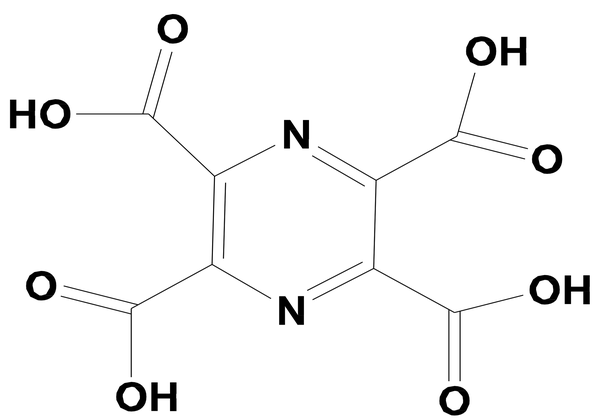
Examples of organic linkers



Ditopic linker



tritopic linker



polytopic linker

Examples of Metal salts

$Mg(NO_3)_2 . 6H_2O$

$Zn(NO_3)_2 . 6H_2O$

$ZrCl_4$

Goal and Objectives

Goal

To develop metal organic framework (MOFs) materials with improved sites accessibility, thus enhance their CO_2 adsorption and selectivity properties

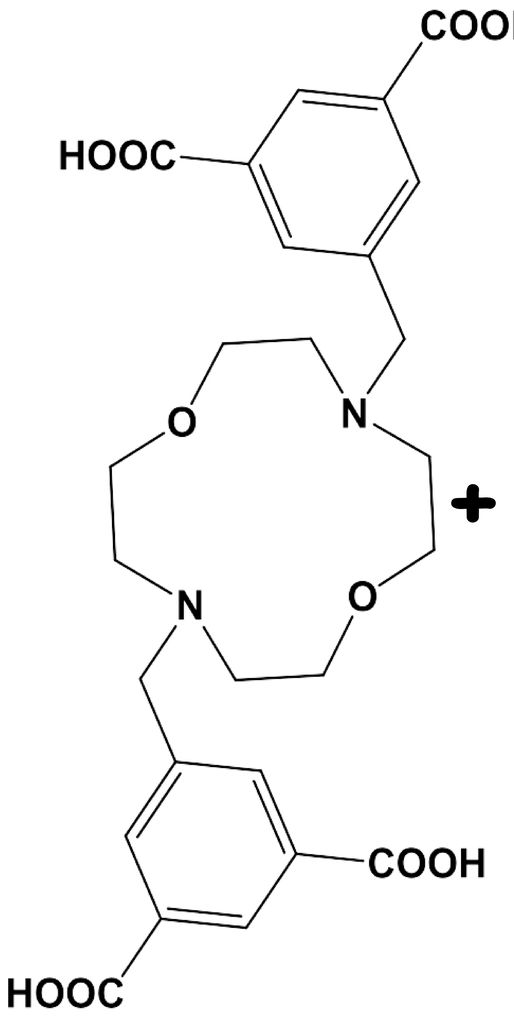
Objectives

- To synthesize MOFs with metal ions adsorption sites in more accessible locations

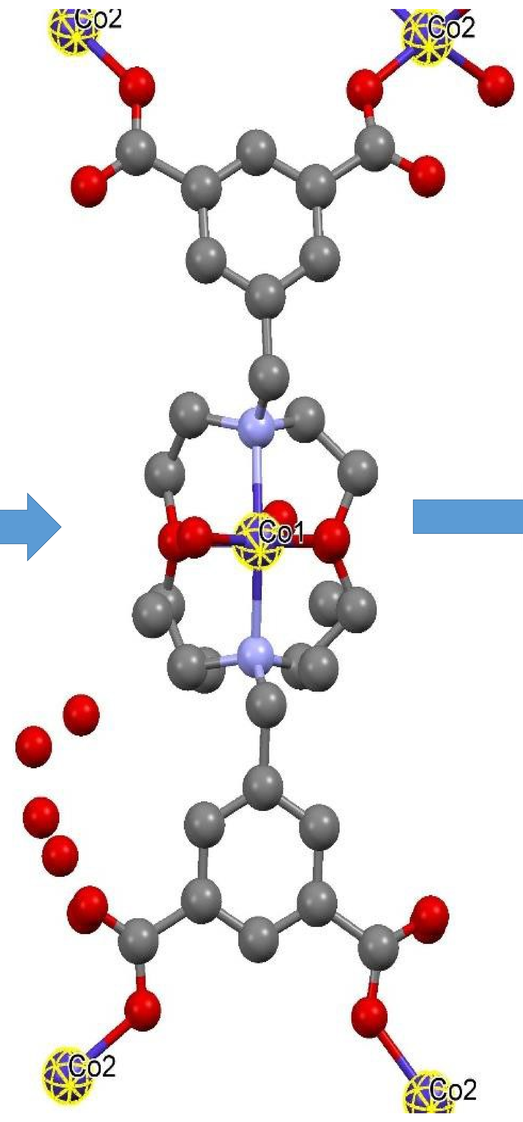
- To synthesize MOFs with nitrogen containing-ligand/linker as a possible improved alternative to amine-functionalized

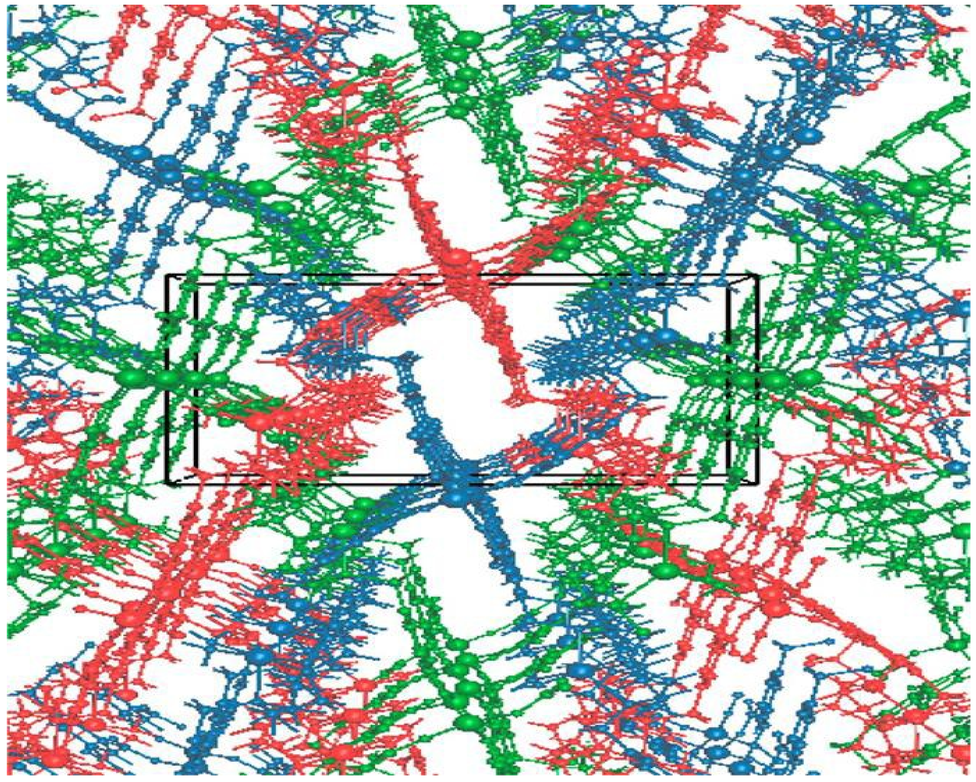
- To understand the nature of the adsorption sites and mechanism(s) by computational studies relevant to the adsorption of CO_2 within our metal organic frameworks

Synthesis of nitrogen diaza-crown containing MOFs with metal in center for CO_2 adsorption



+ Co^{2+}



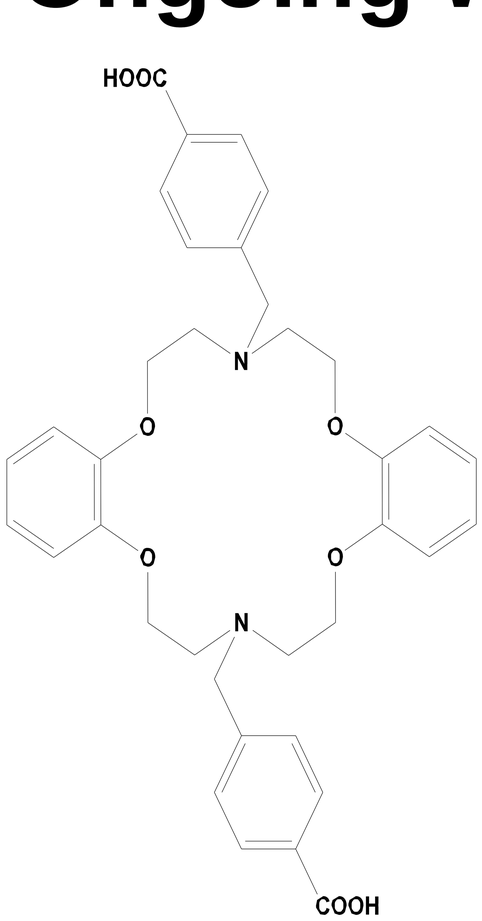


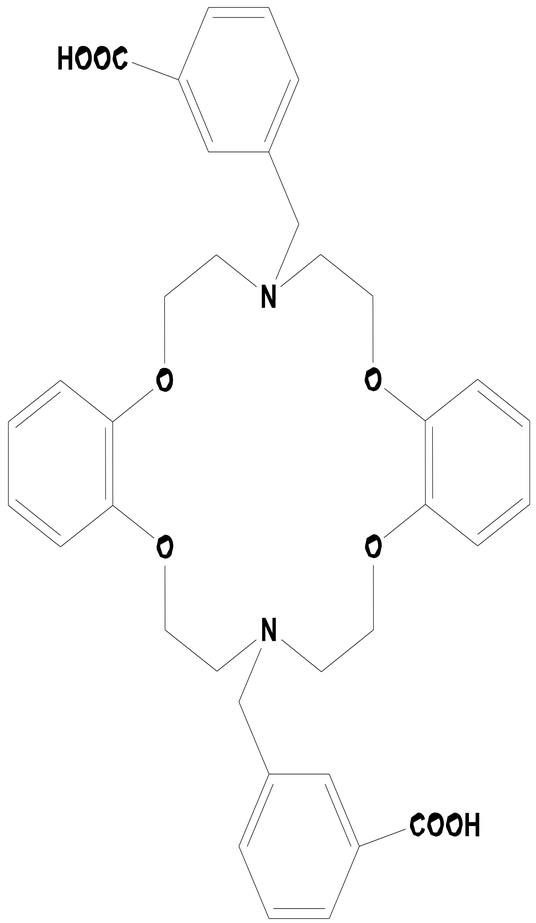
3D interpenetrated Cobalt MOF

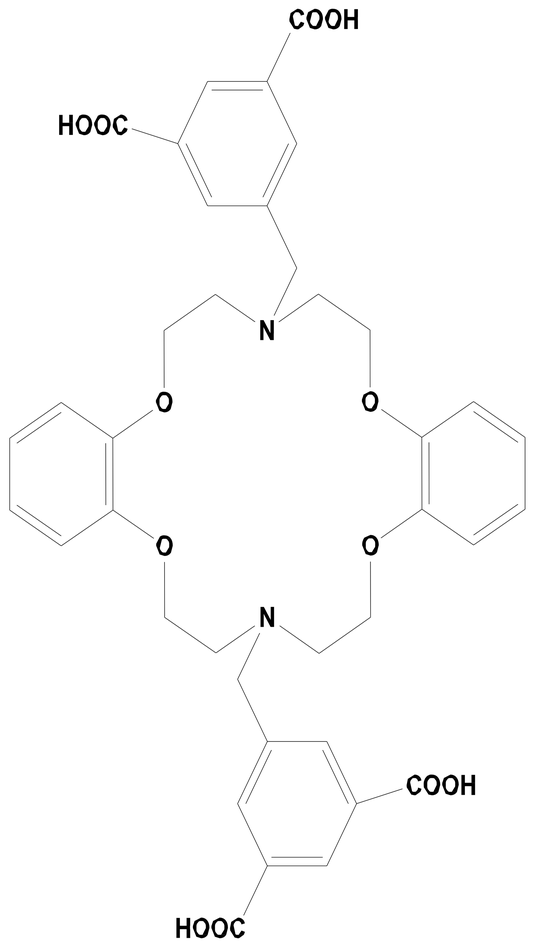
Summary of diaza-crown ether MOFs

3D MOFs using diaza crown ether ligand and with metal within center of crown ether but the structure is nonporous

Ongoing work

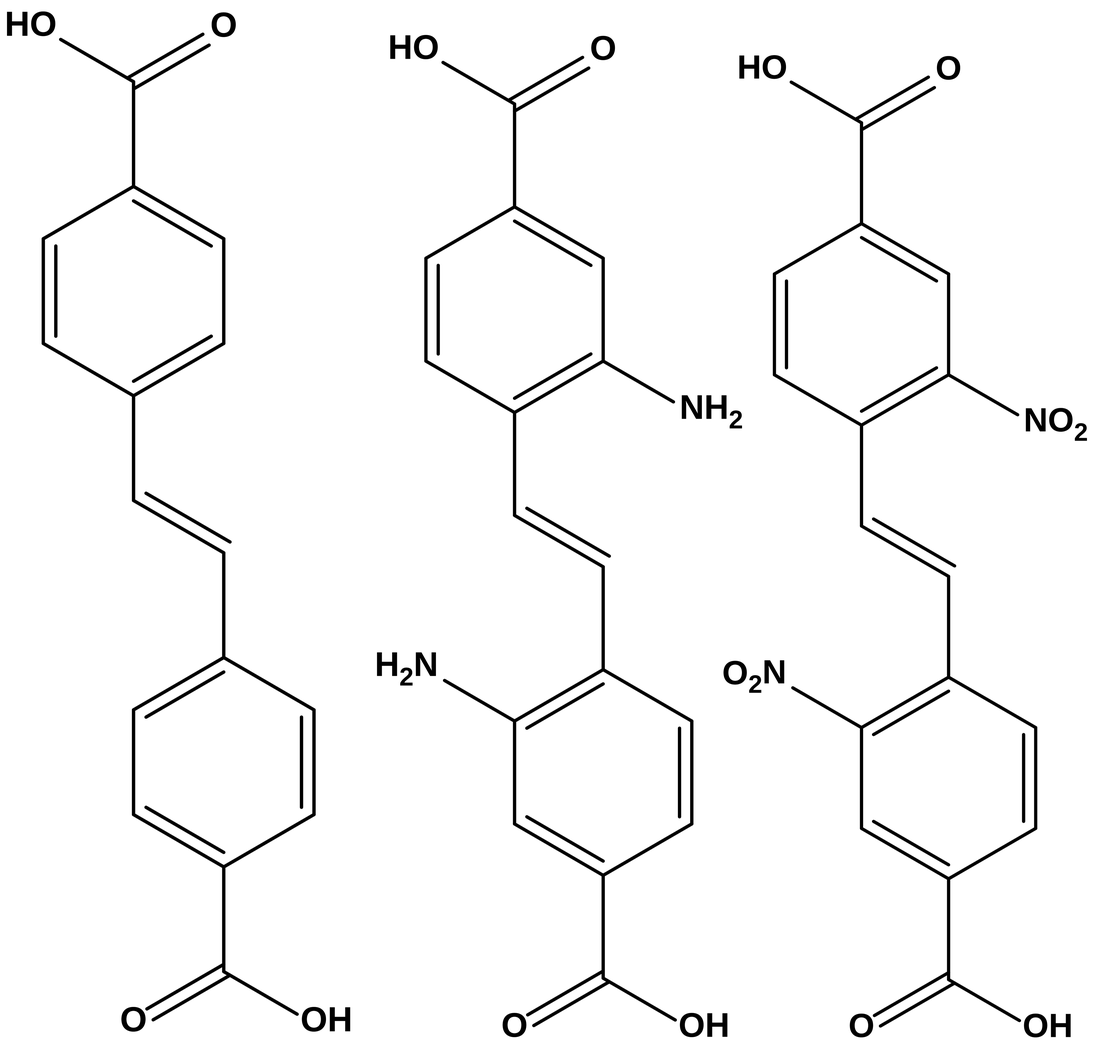




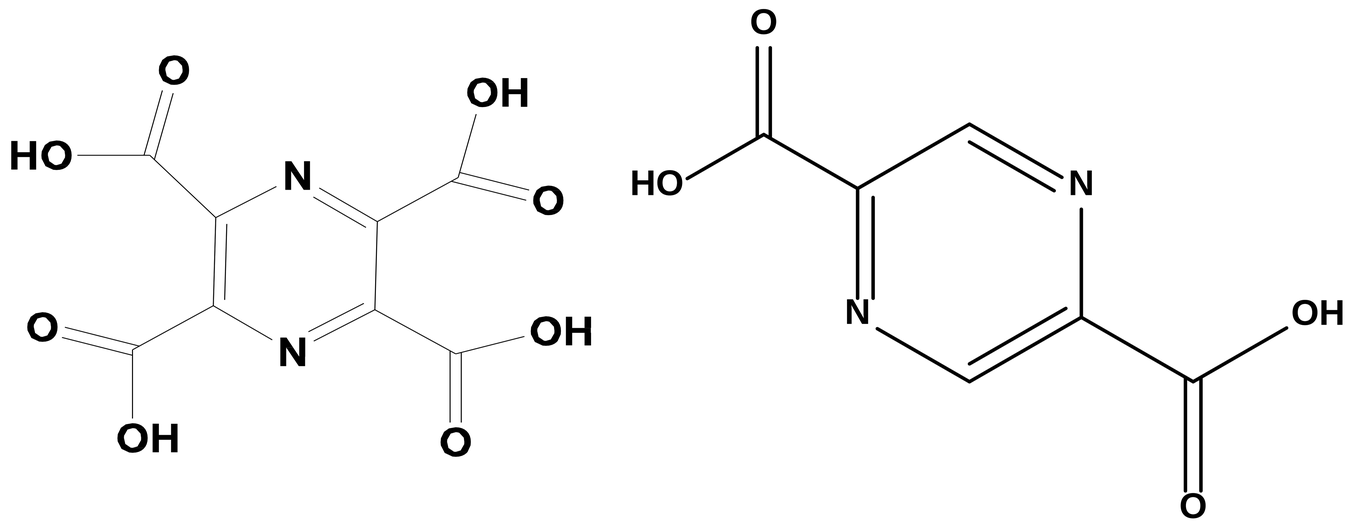


MOFs from stilbene and pyrazine linkers

Stilbene linkers

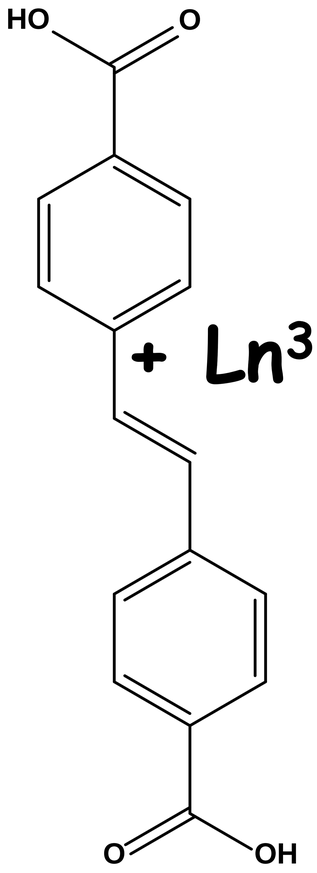


Pyrazine linkers

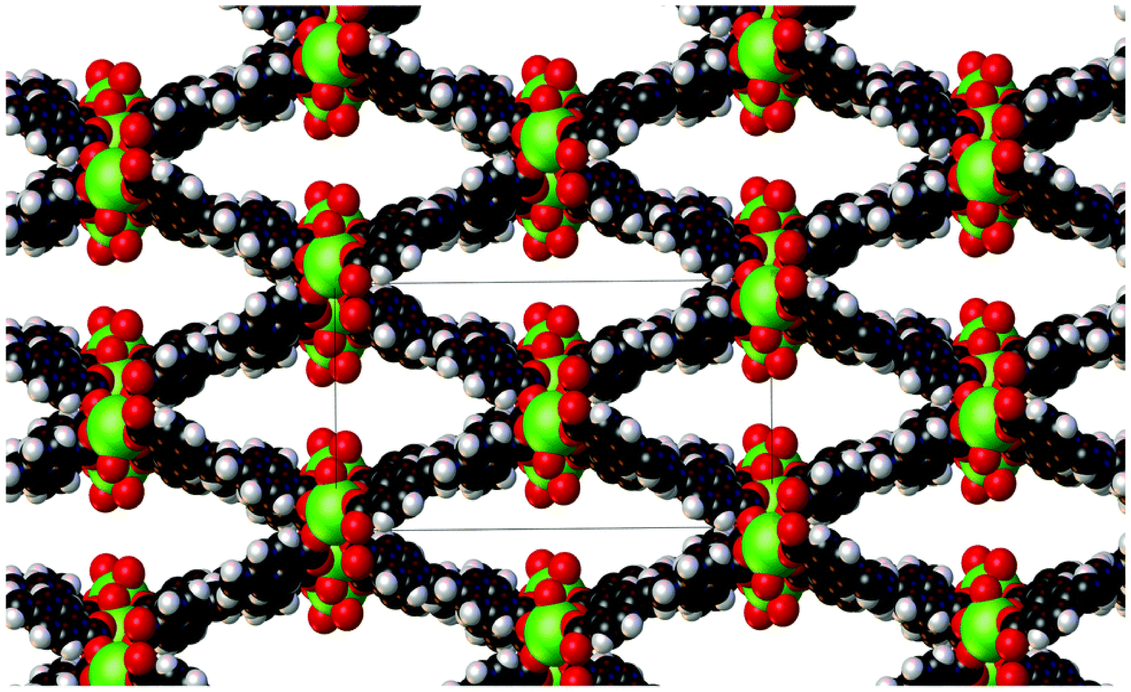


- **Rigid or flexible MOFs**
- **Non-interpenetration in MOFs**

Stilbene lanthanide MOFs



+ Ln^{3+} →



Non-interpenetrating structure

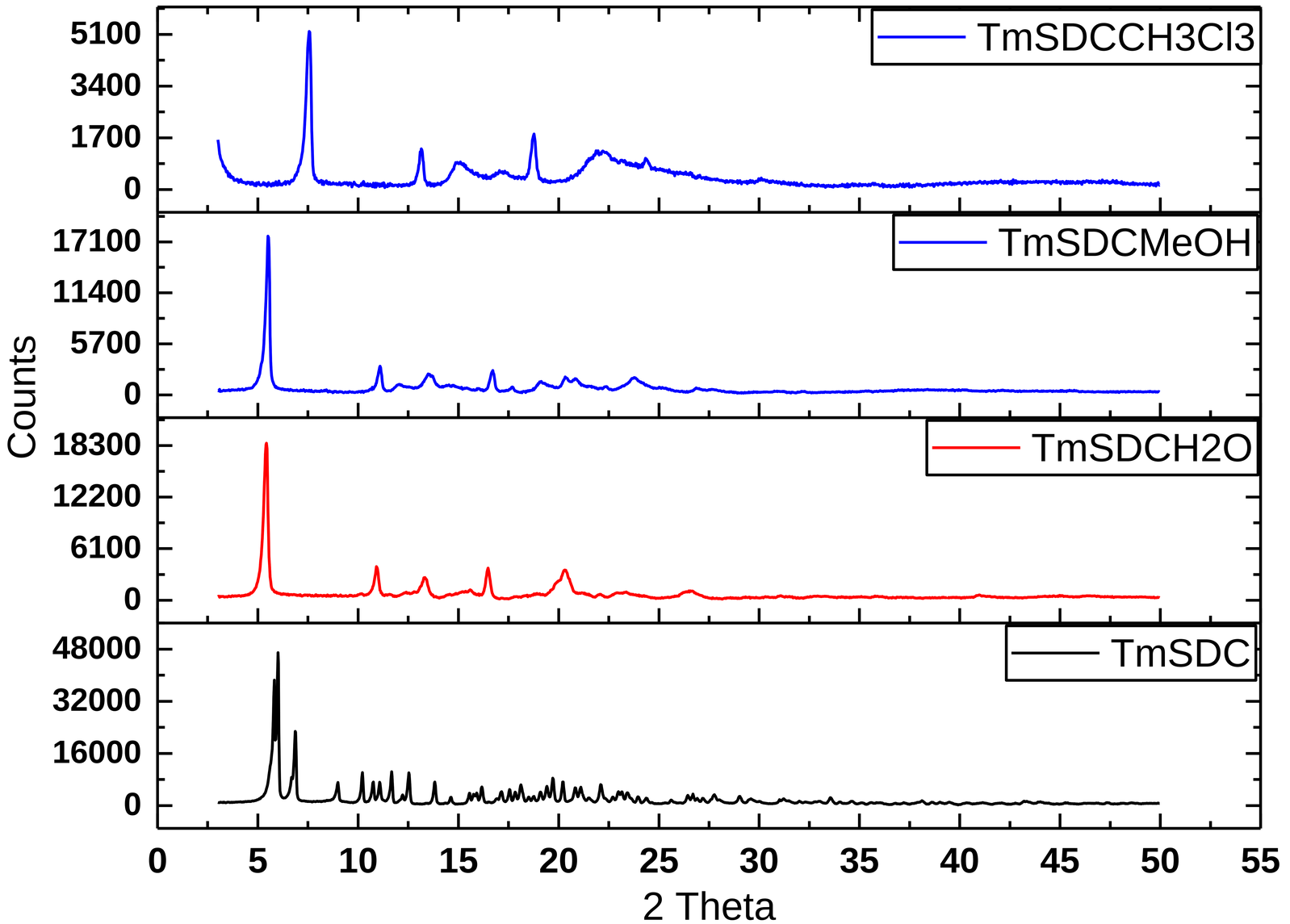
Ultra-large pores (dimensions of 23 Å x 12 Å)

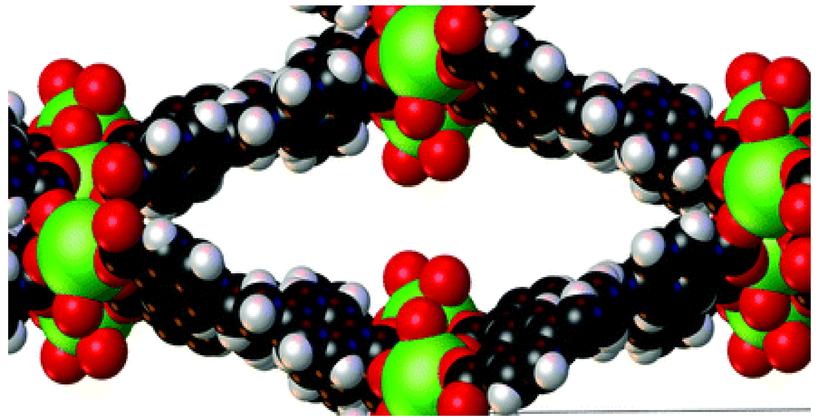
Accessible channels

Diamond-shaped open framework

*Mathis II, Stephan R., **Saki T. Golafale**, John Bacsa, Alexander Steiner, Conrad W. Ingram, F. Patrick Doty, Elizabeth Auden, and Khalid Hattar.* ***Dalton Transactions*** *46, no. 2 (2017): 491-500.*

X-ray diffraction patterns of solvent exchanged stilbene lanthanide MOFs





Framework could adjust depending on solvent used

CO_2 adsorption analysis

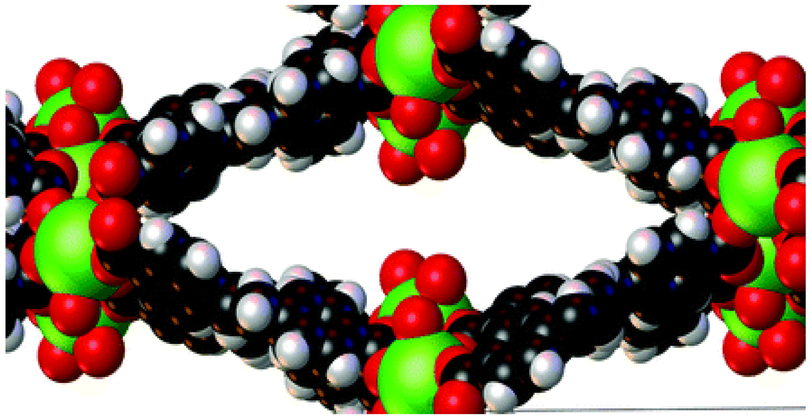
Micromeritics ASAP 2020

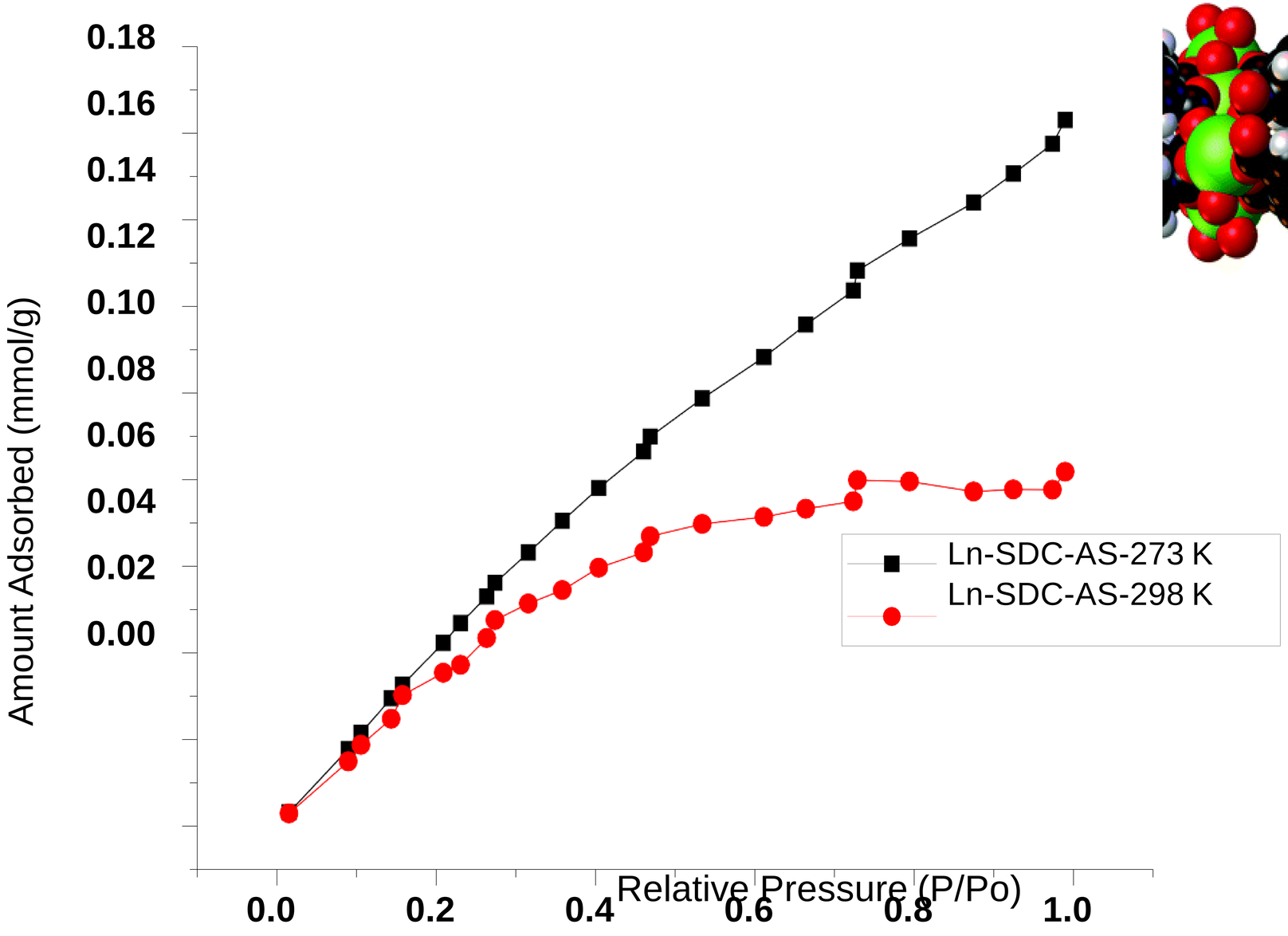
Samples are degassed at temperatures depending on thermal stability

Degassed samples are then analyzed at at 273K and 298K using CO2 as adsorbate gas

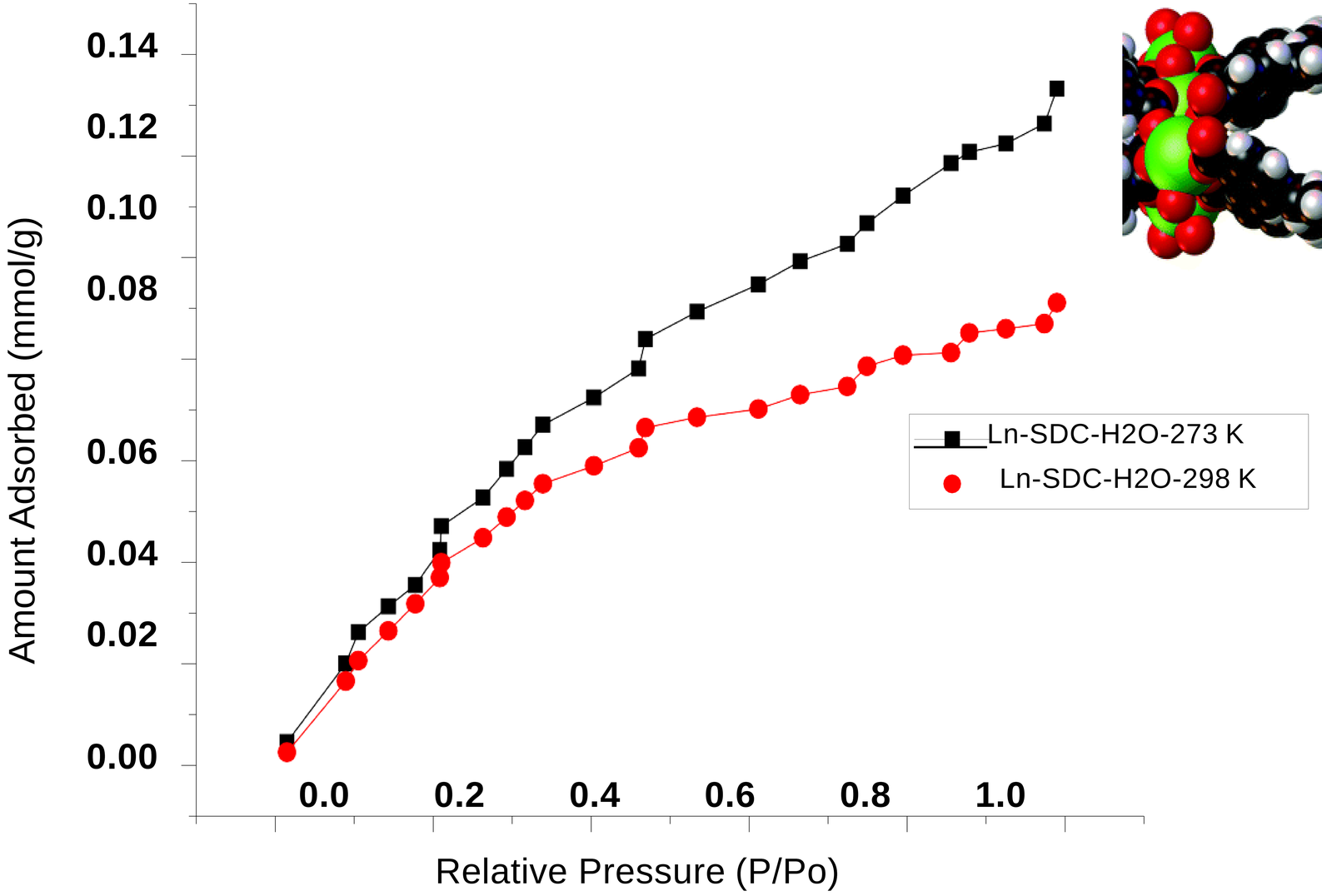
Analysis of CO2 capture shows amount adsorbed as a function of pressure (0 to 1 bar)

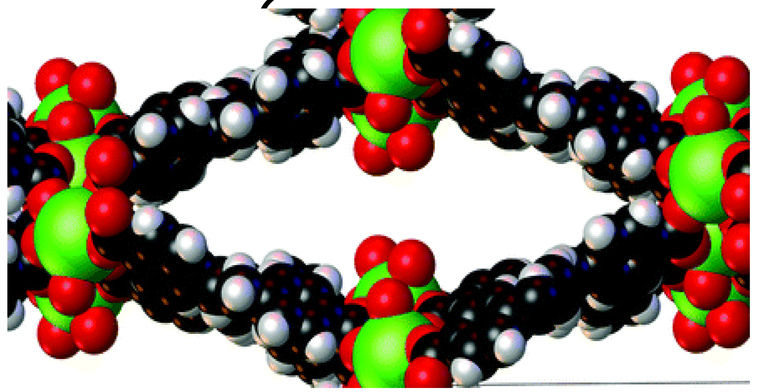
CO_2 adsorption isotherms of stilbene lanthanide MOF



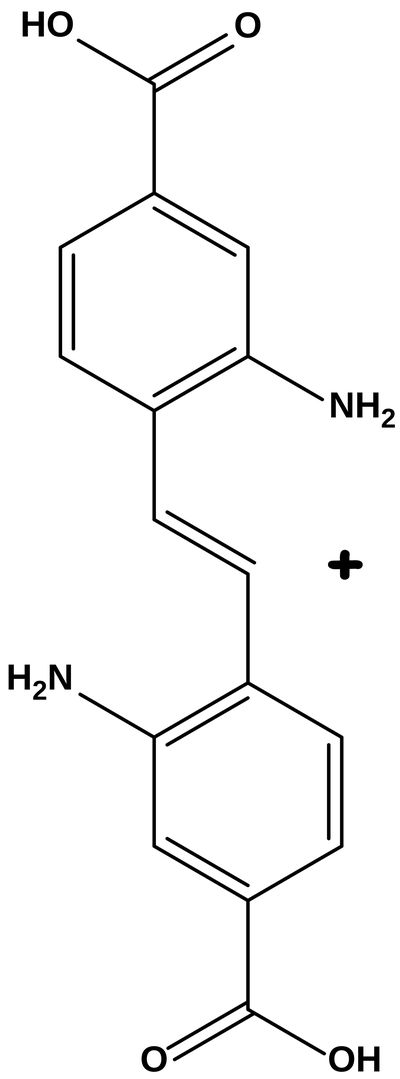


CO_2 adsorption isotherms of stilbene lanthanide stilbene MOF soaked in H_2O

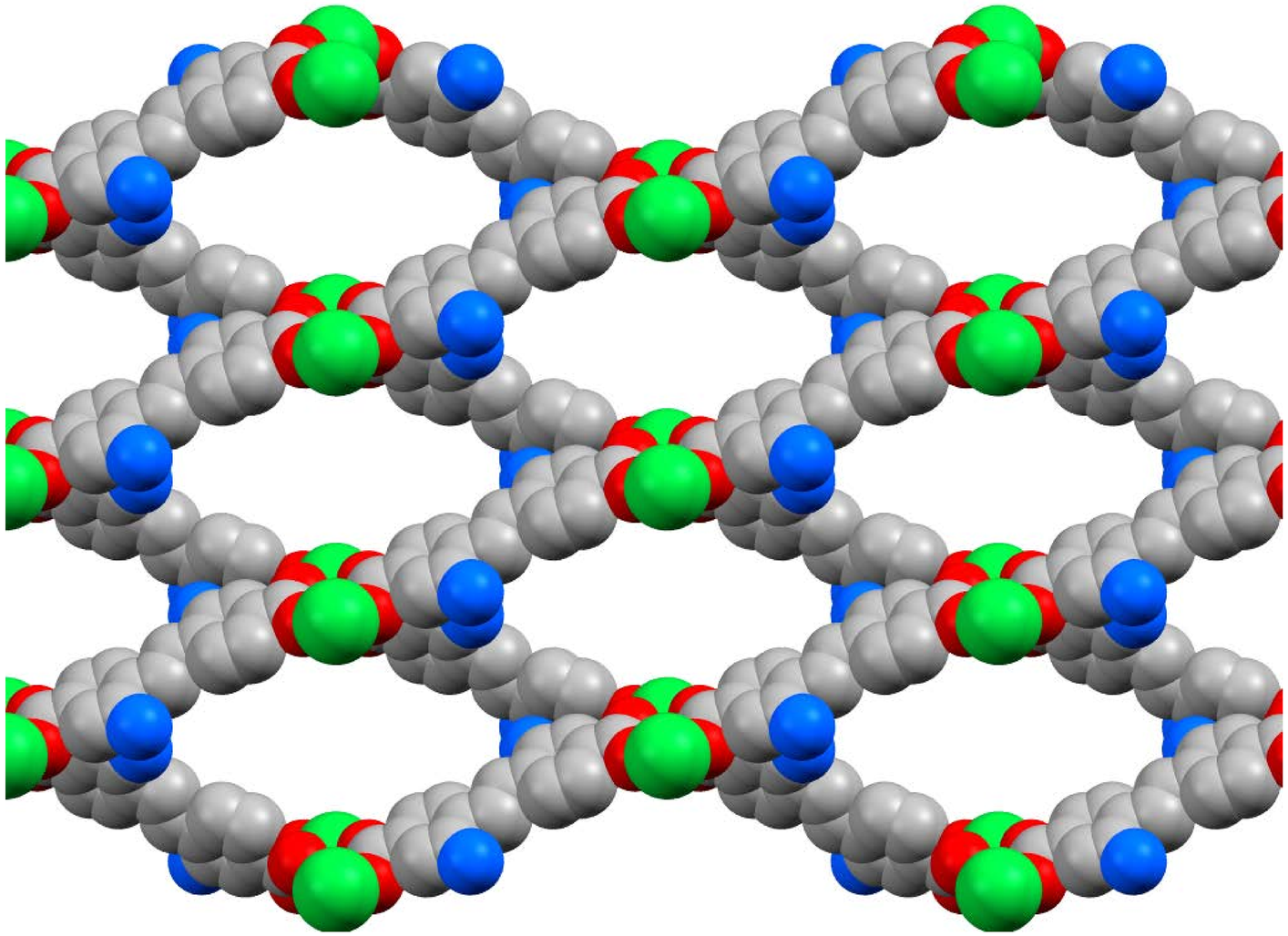




Amino-stilbene Lanthanide MOFs

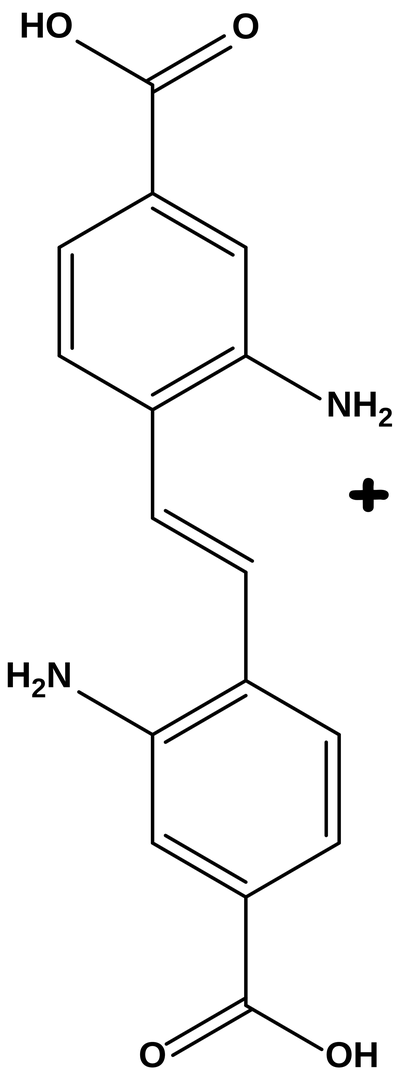


+ Ln^{3+}

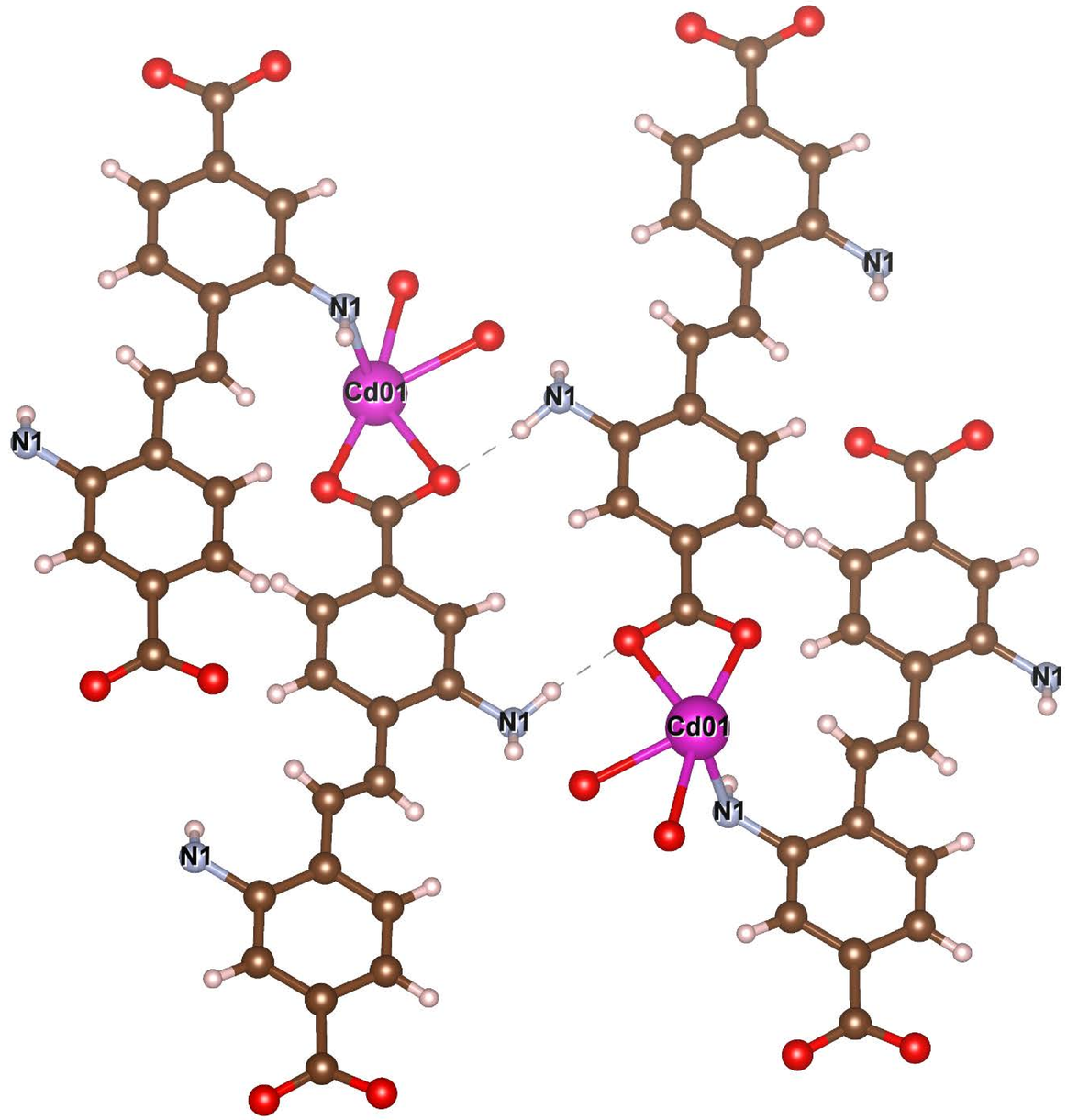


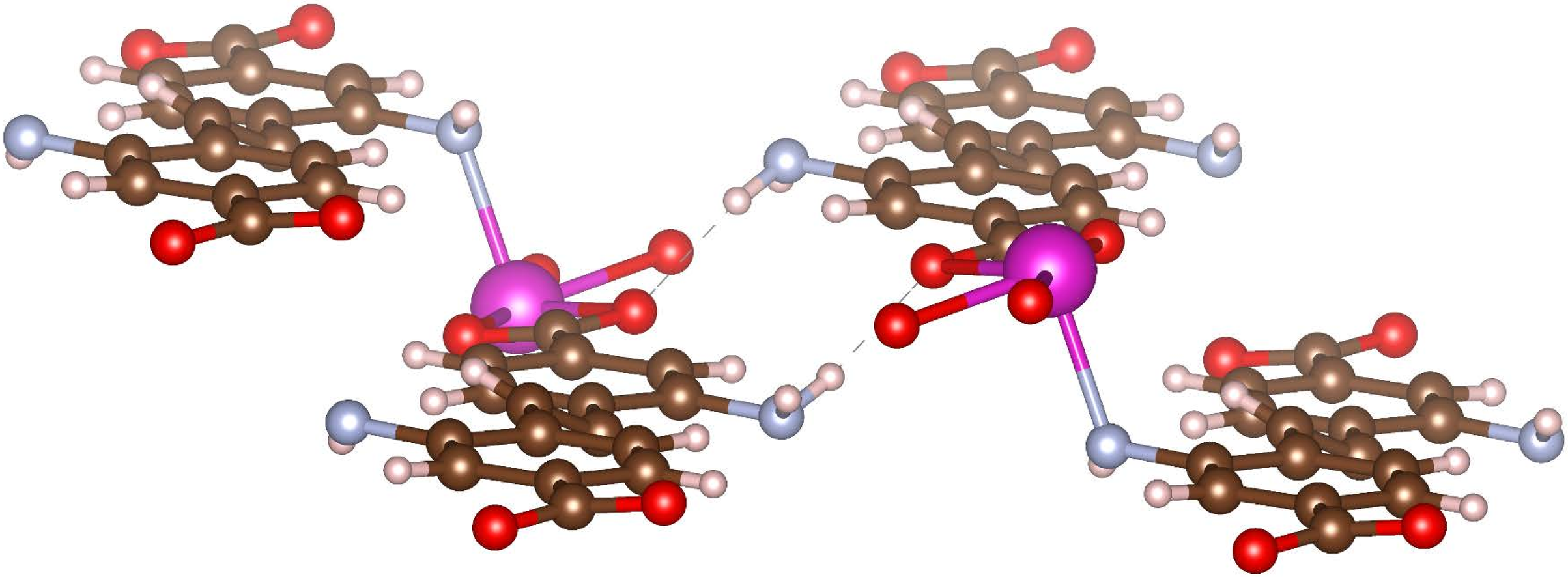
Contains amine functional groups
Open and accessible framework
CO_2 adsorption studies ongoing

Amino-stilbene based transition metal MOFs



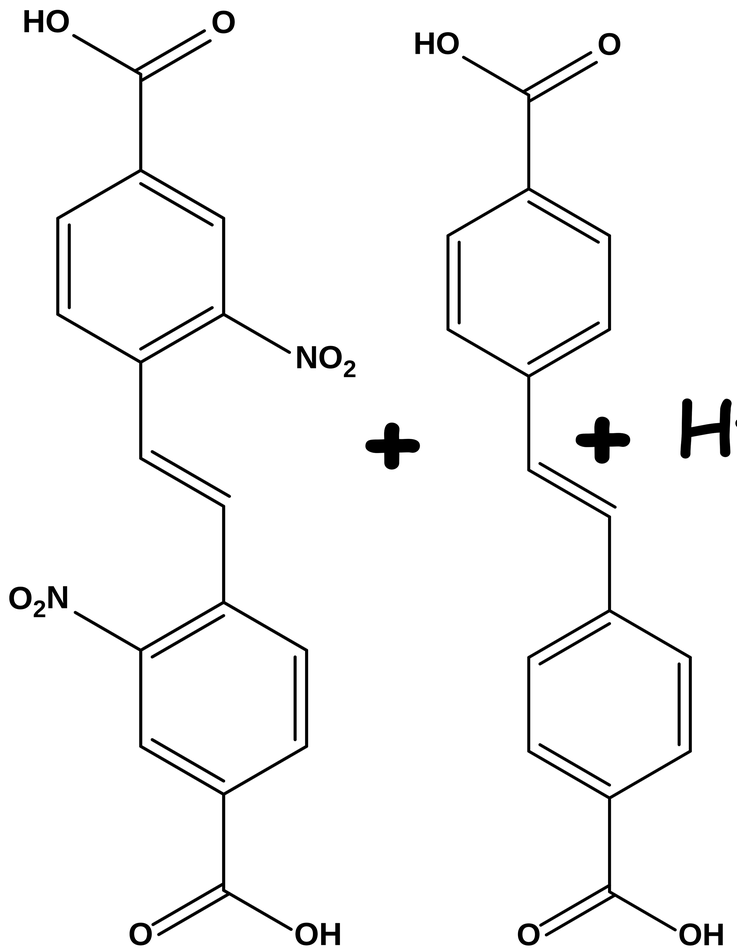
+ Cd^{2+}



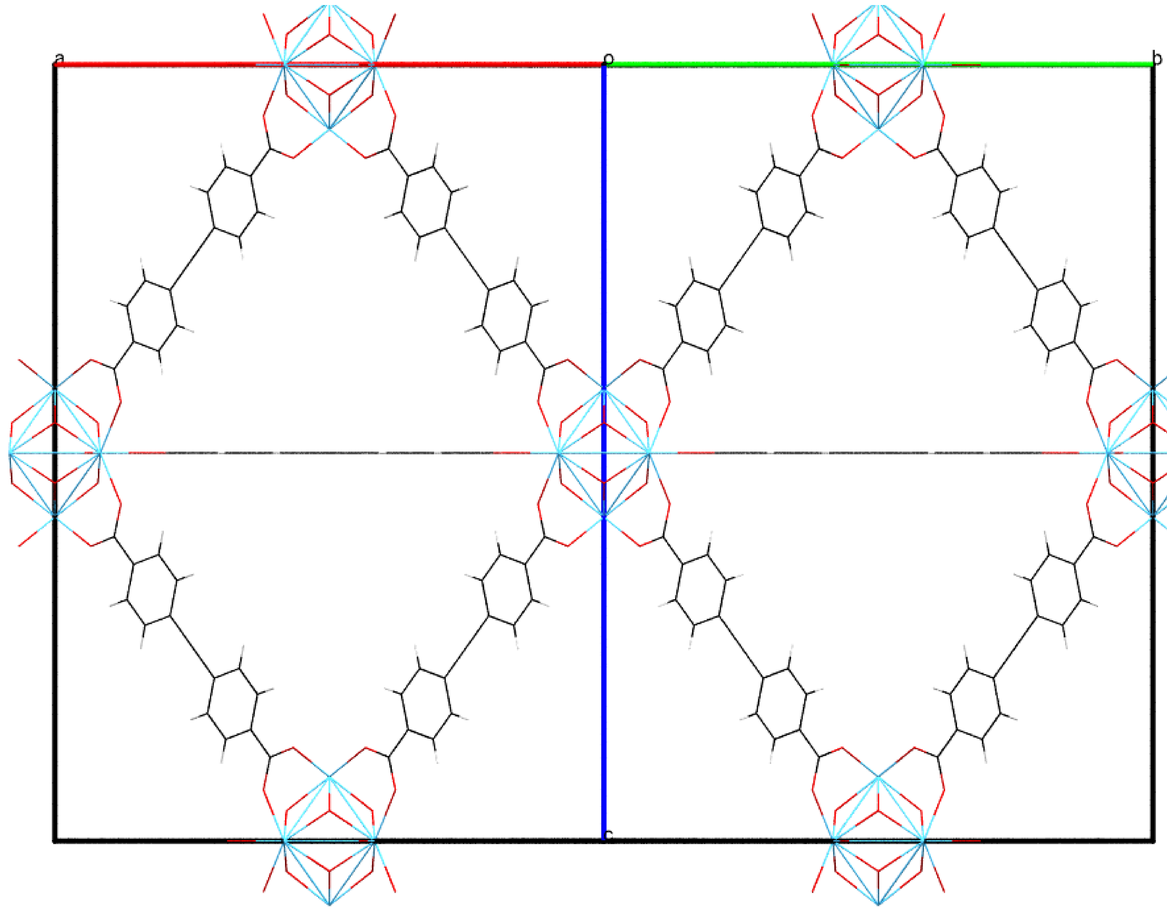


Layered structure bridged via H-bonding and metal-O/N coordination
Exploring different synthesis conditions

Mixed Ligand Hafnium MOF



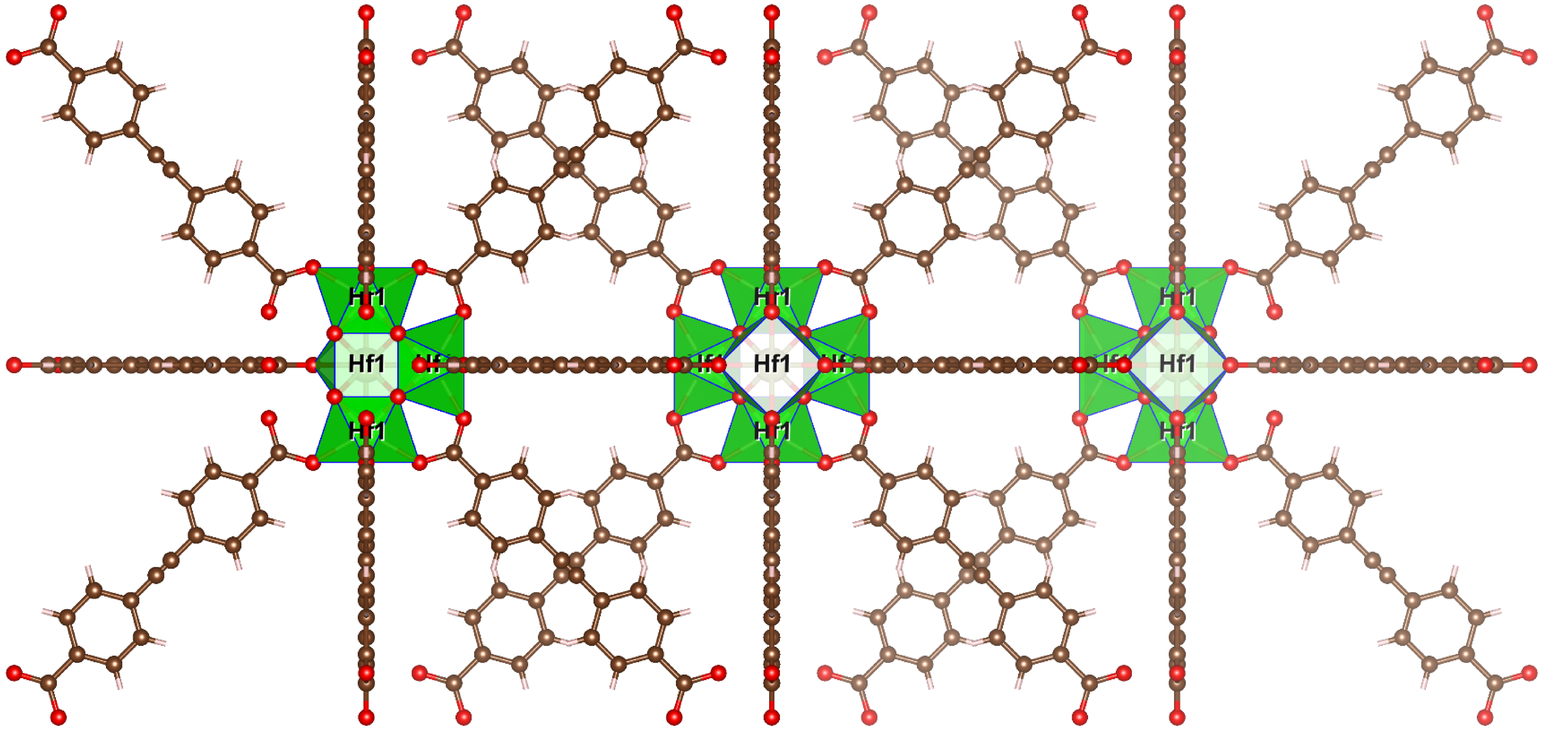
+ + Hf(IV)



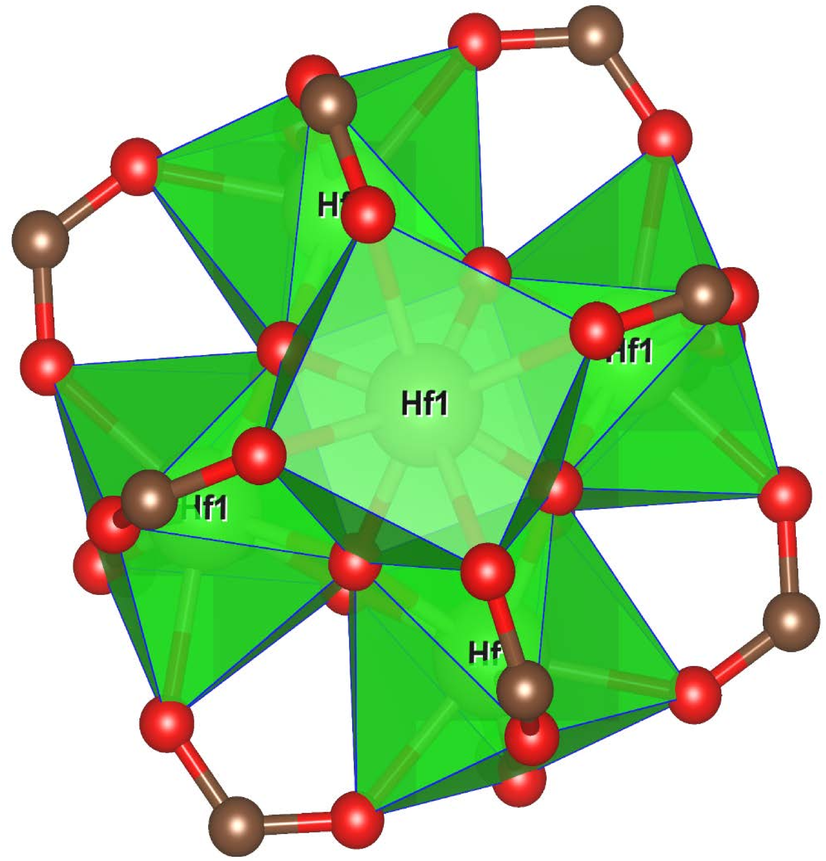
Very low density MOF ~0.73 g/cm^3

Average Hf-O bond length is 2.1 A

Mixed Ligand Hafnium MOF

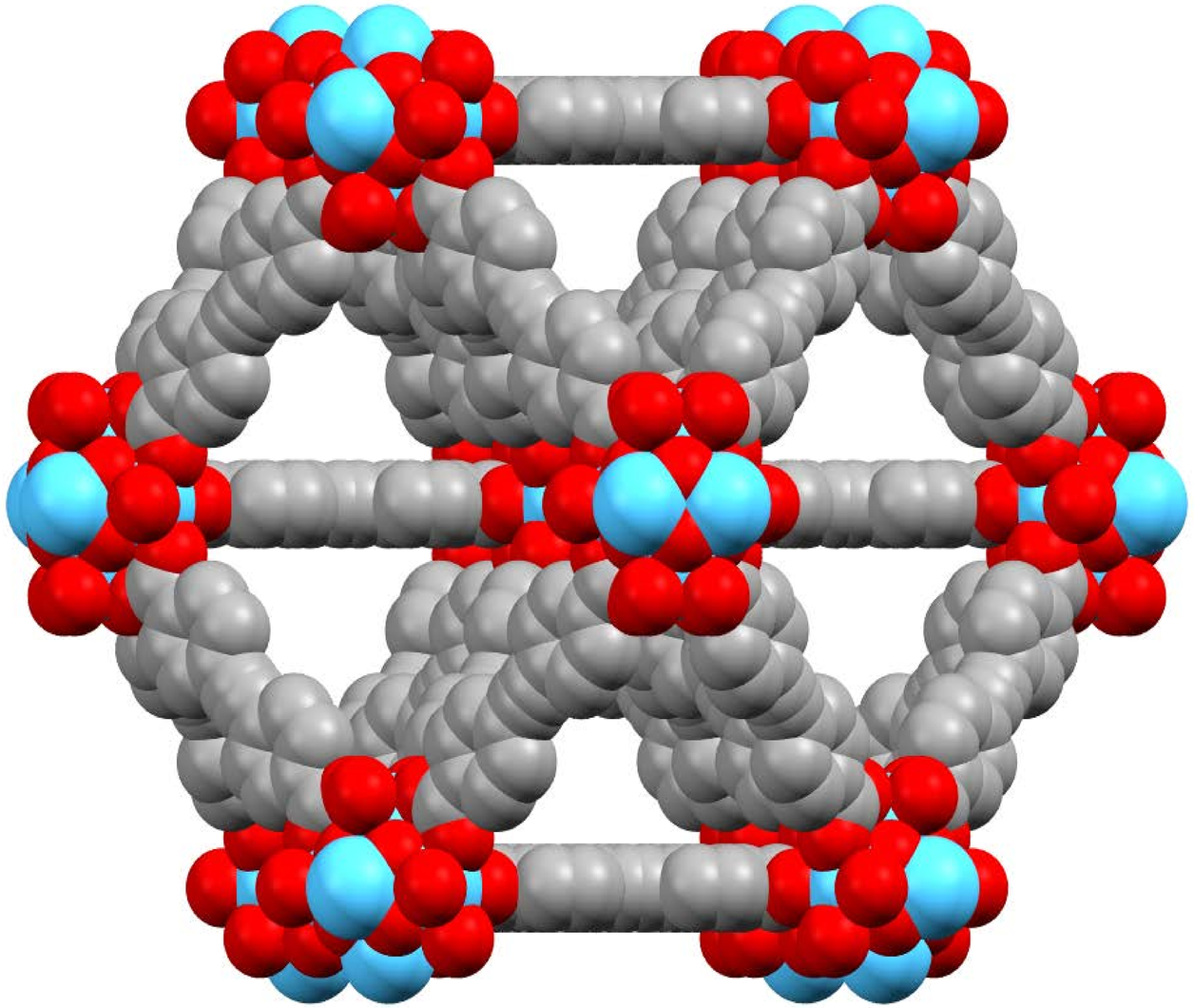


Hf-coordinated carboxylates



Inner core Hf_6-cluster with strong Hf-O bond key to stability

Mixed Ligand Hafnium MOF



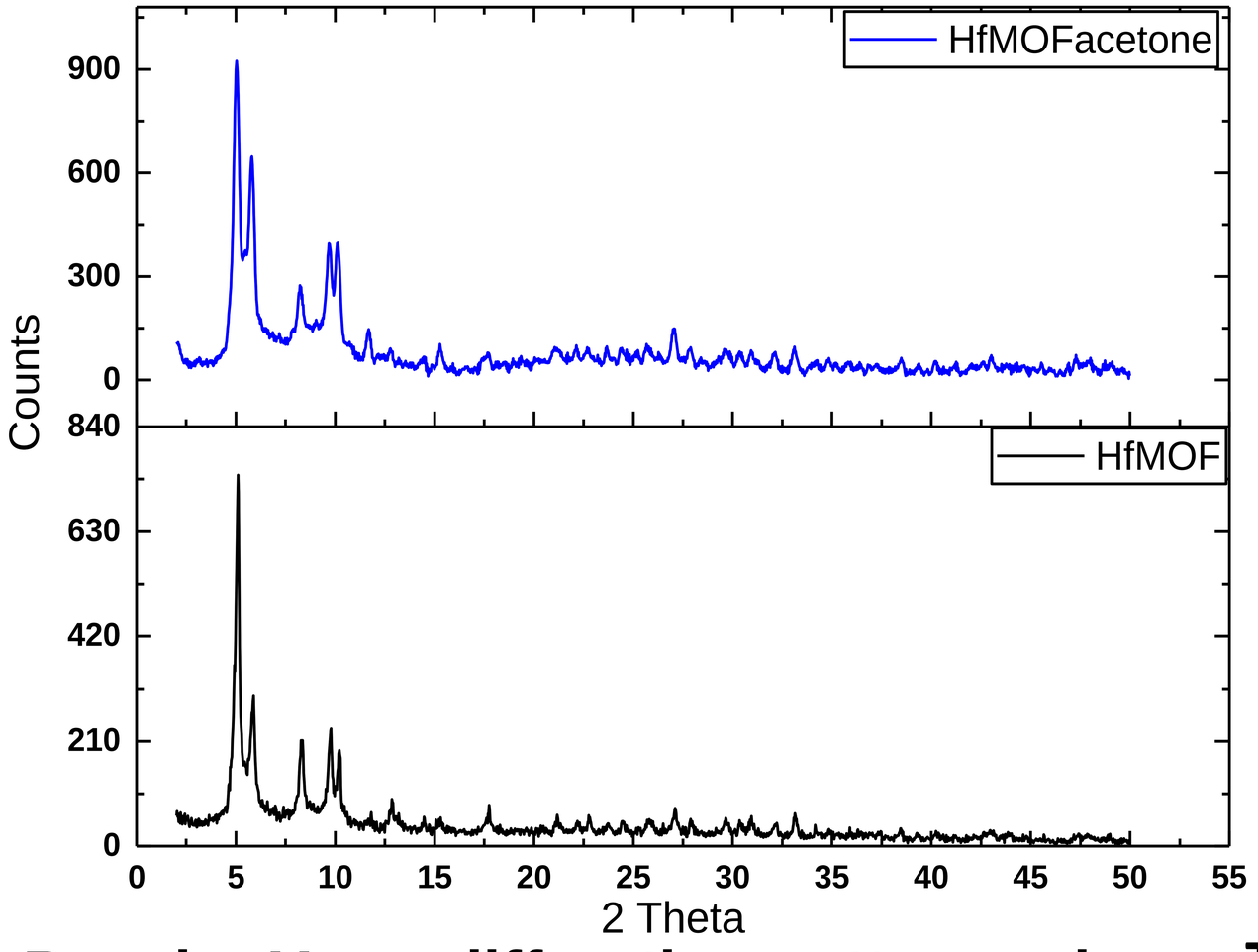
Space filling model

Very low density MOF ~0.73 g/cm^3

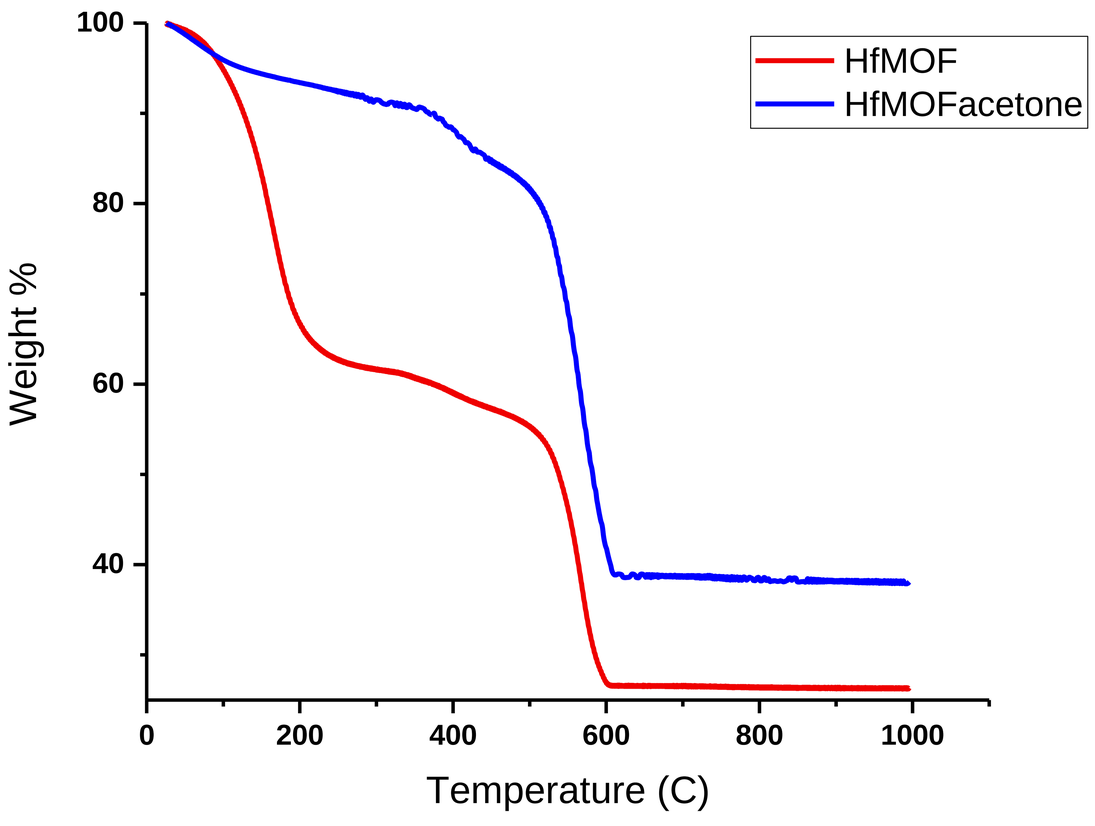
Average Hf-O bond length is 2.1 A

Thermally and structural stable when soaked in acetone for 12 h

Powder x-ray diffraction and TGA of fresh and solvent exchanged Hafnium MOF

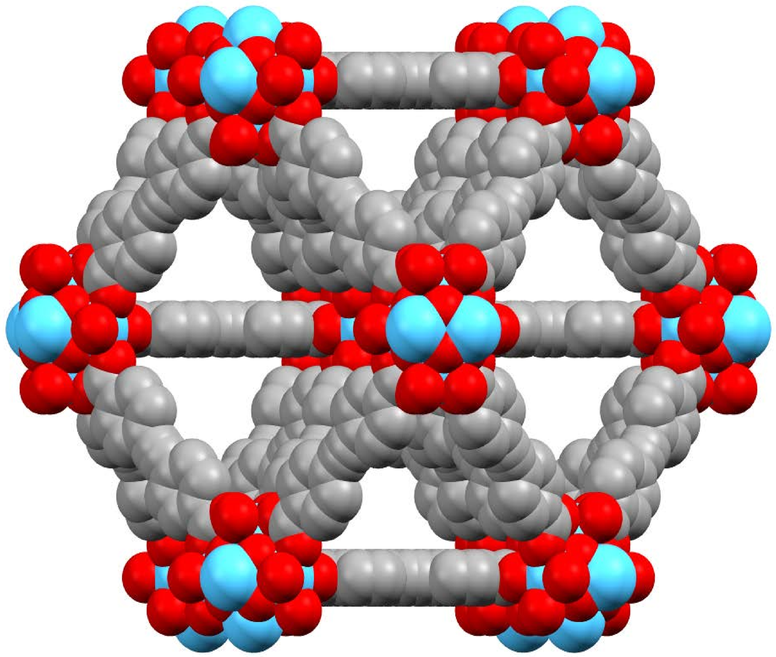


Powder X-ray diffraction patterns show no change in structure!

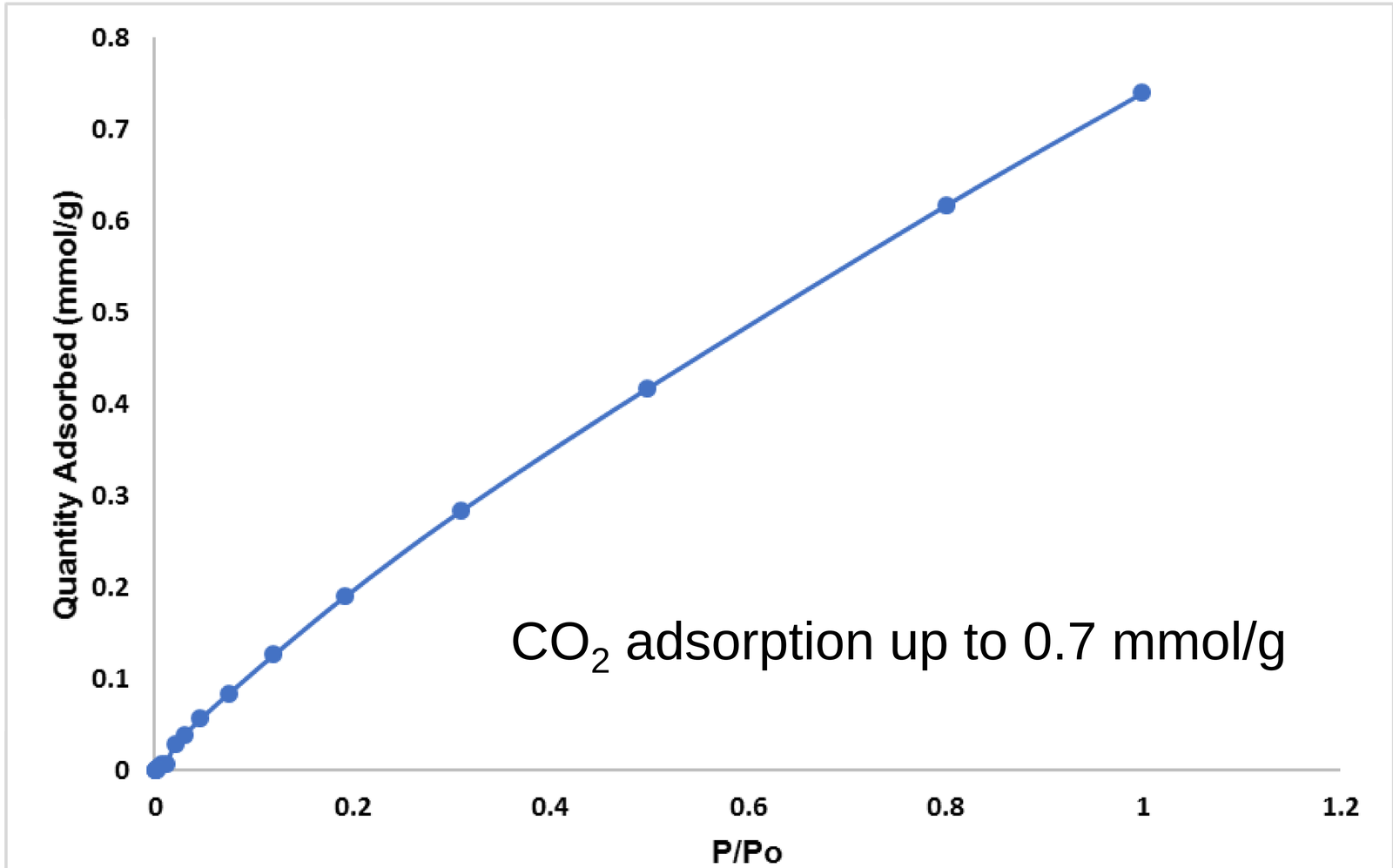


Thermograms of fresh and solvent exchanged HfMOF
Solvent exchange show more thermally stable material

CO_2 adsorption isotherm of HfMOF

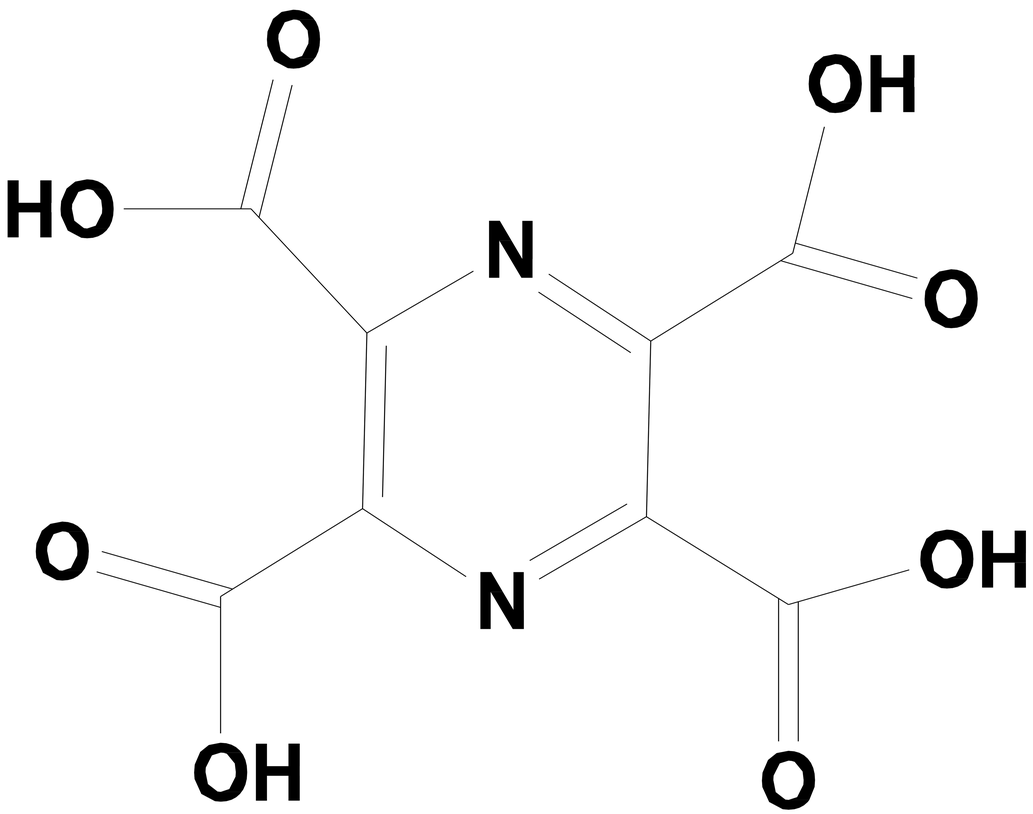


HfMOF

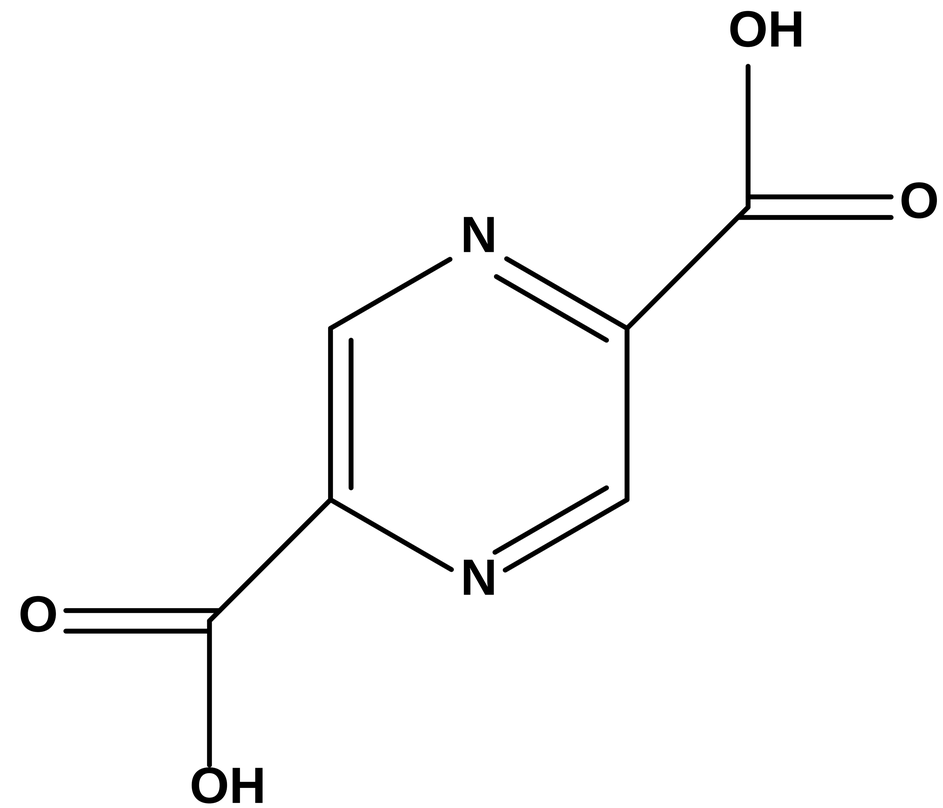


CO_2 adsorption isotherm at 25 degrees C showing increasing CO_2 adsorption as a function of pressure

Pyrazine based MOFs

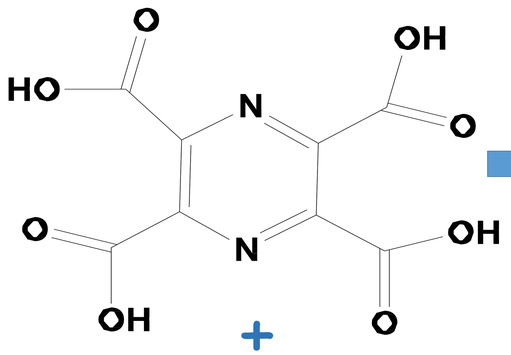


Metals used
Gd^{3+}, Eu^{2+},
Mn^{2+}, Zn^{2+} Ca^{2+}



Metals used
Zr(IV) and Hf(IV)

Gadolinium pyrazine MOF



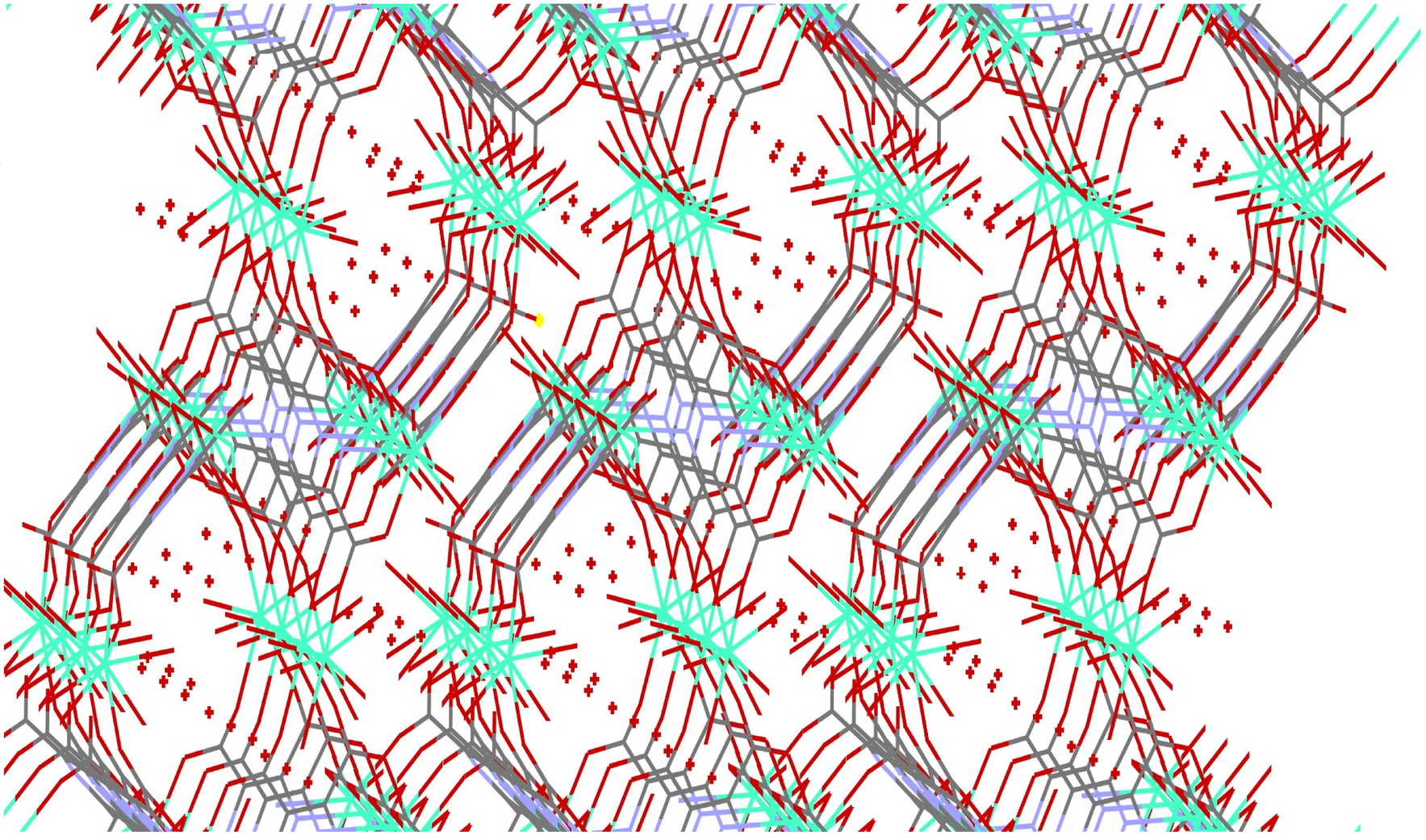
\+

Gd/or Tb

Open framework
Large channels ~ 12Å

Kinetic diameter CO_2
3.3Å

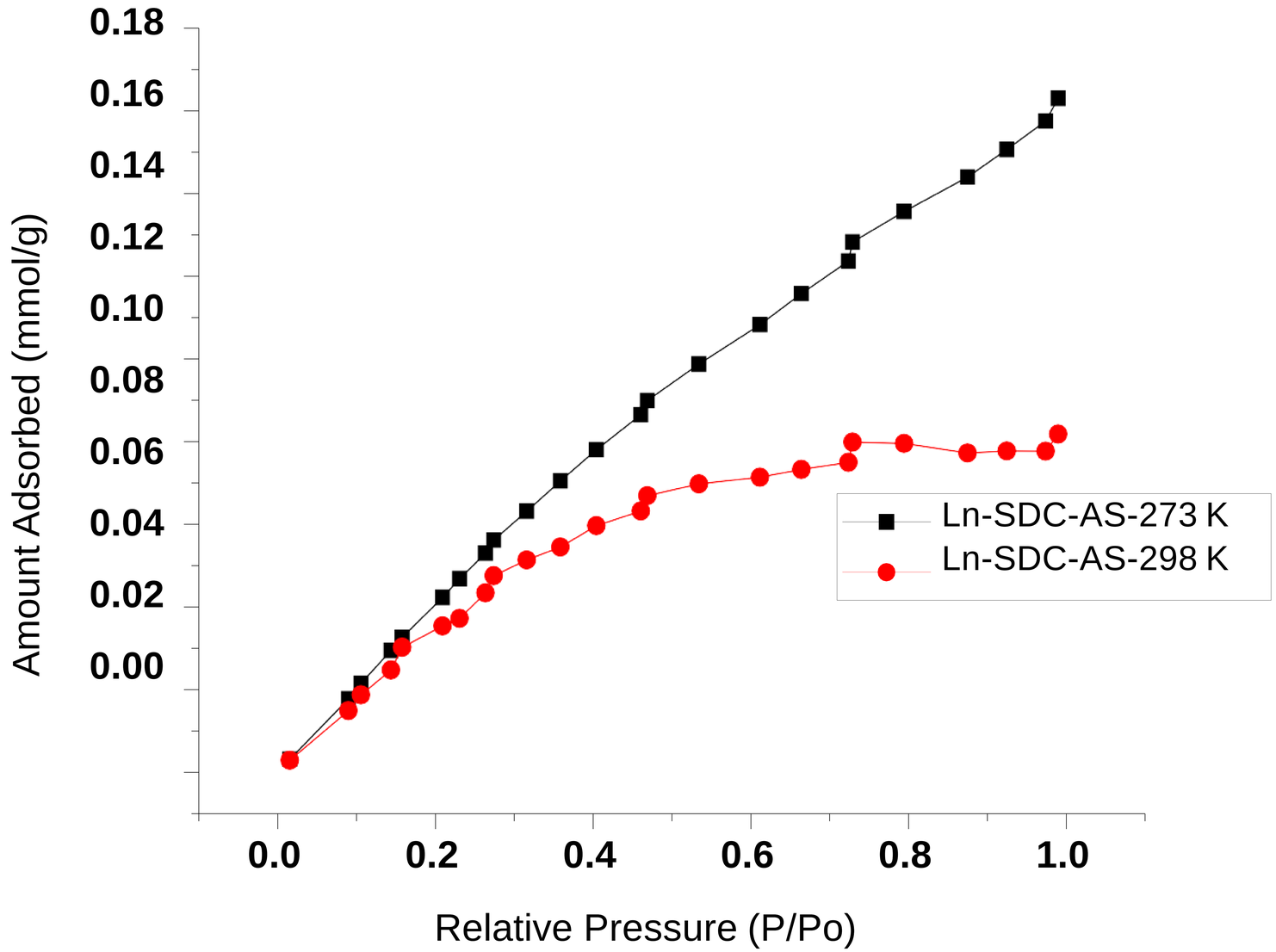
Channels contain non-coordinating water



$\{[Gd_4(C_8N_2O_8)_3(H_2O)_{11}]10H_20\}_n$

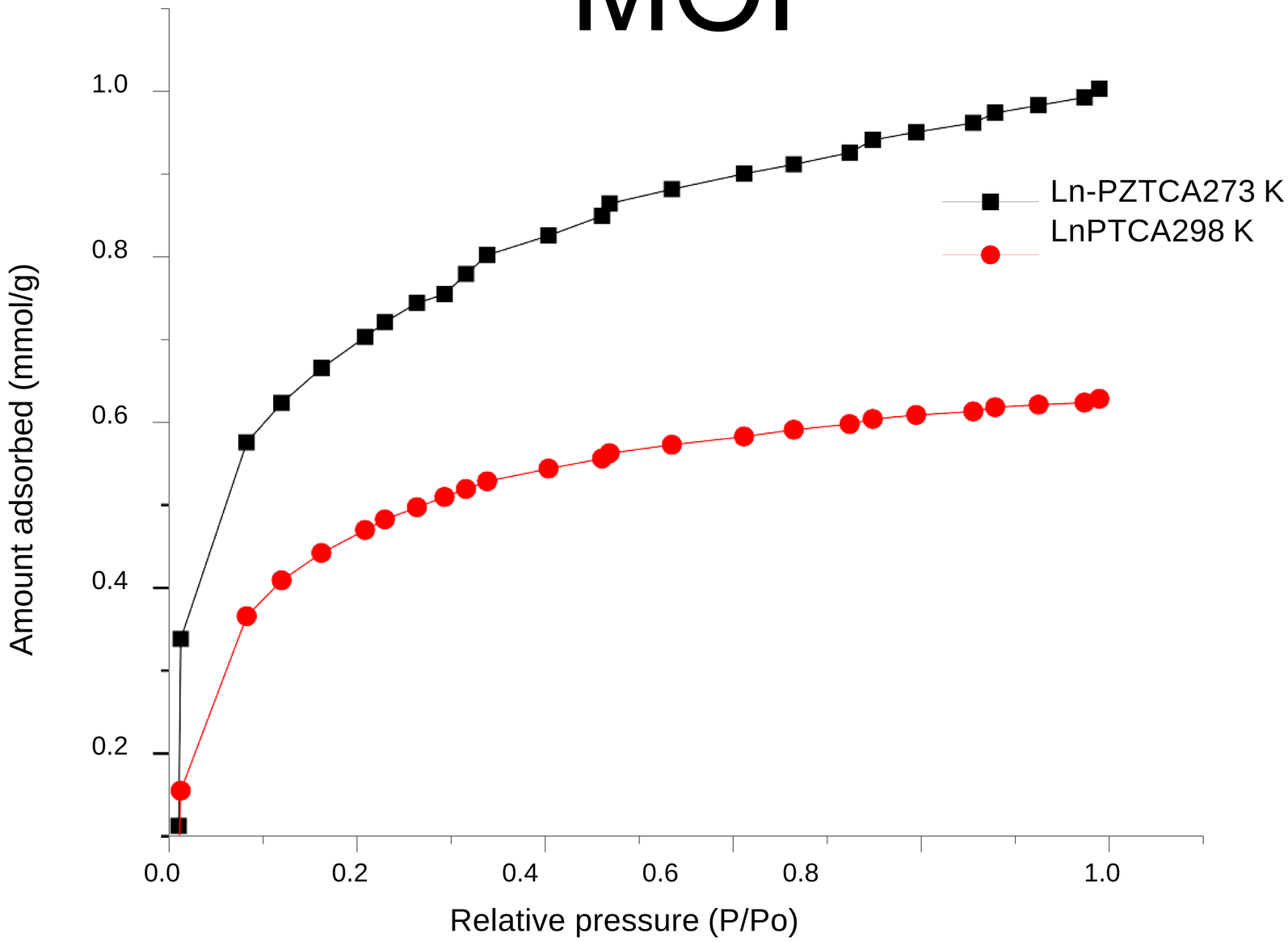
Ingram et al. Crystengcommun 2015

CO2 adsorption isotherm of Gdpztc MOF



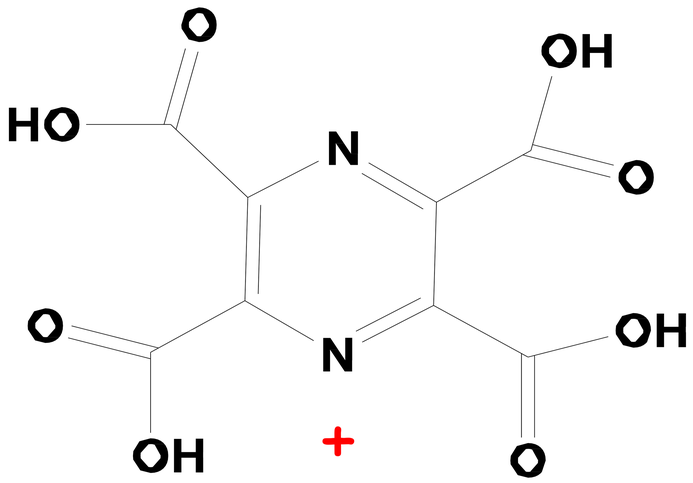
Gd-PZTC as synthesized

CO2 adsorption isotherm of Gdpztc MOF



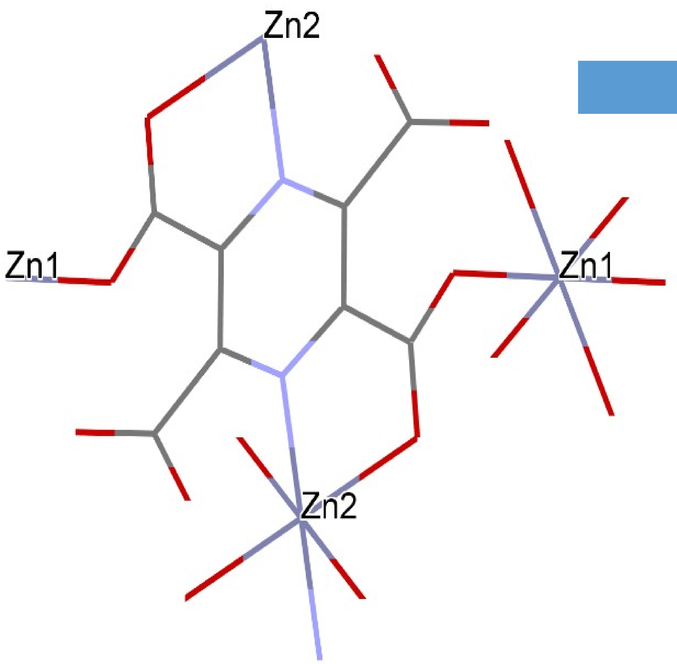
Gd-PZTC after solvent exchange with chloroform

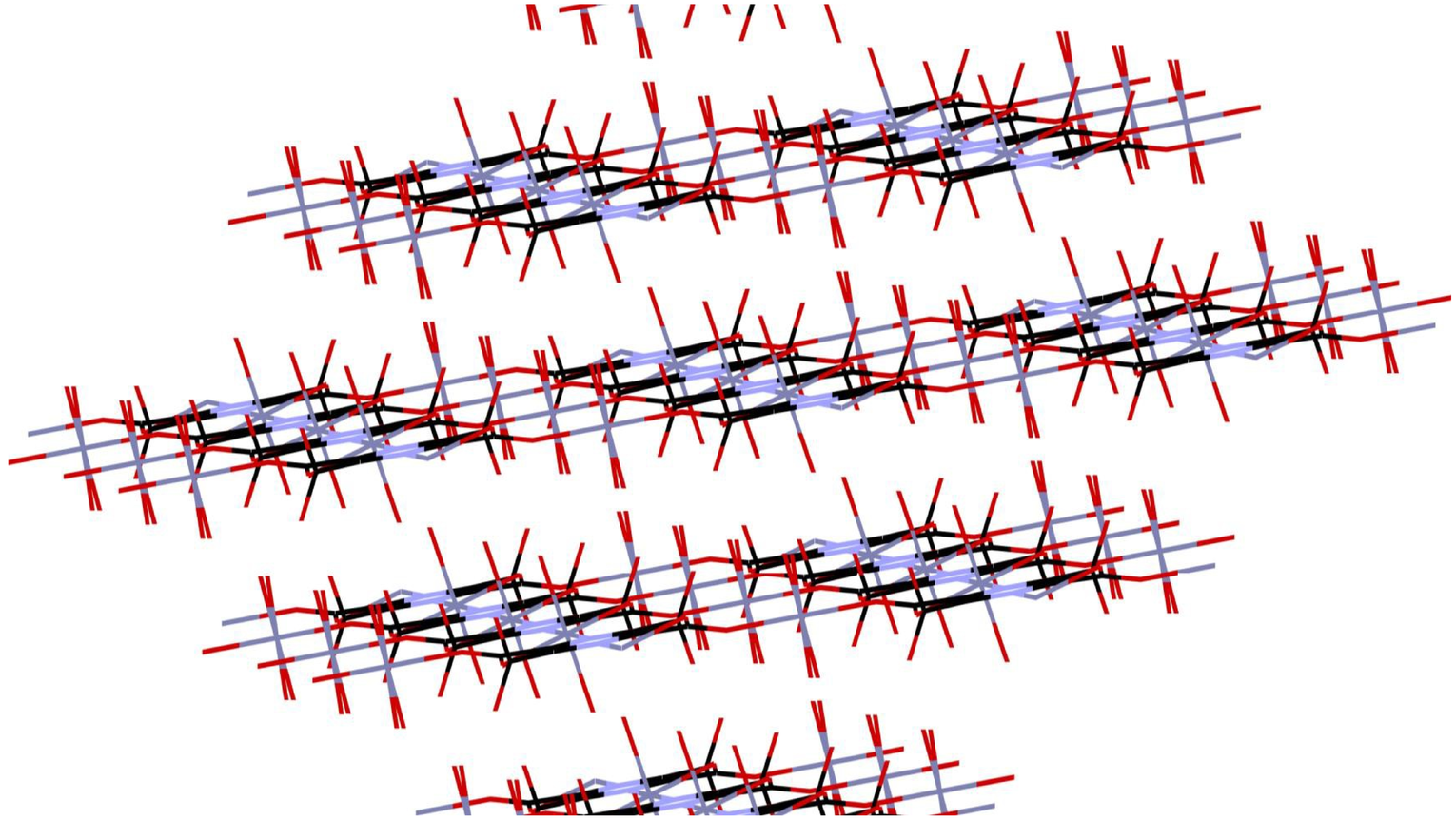
Zinc pyrazine MOF



+

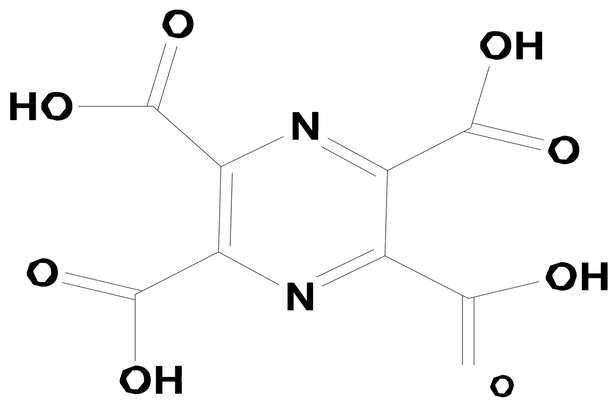
Zn^{2+}



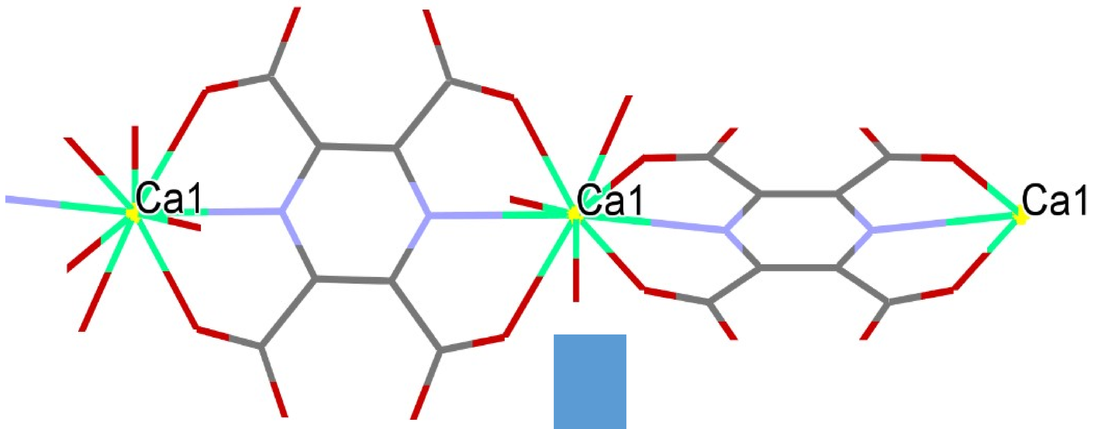


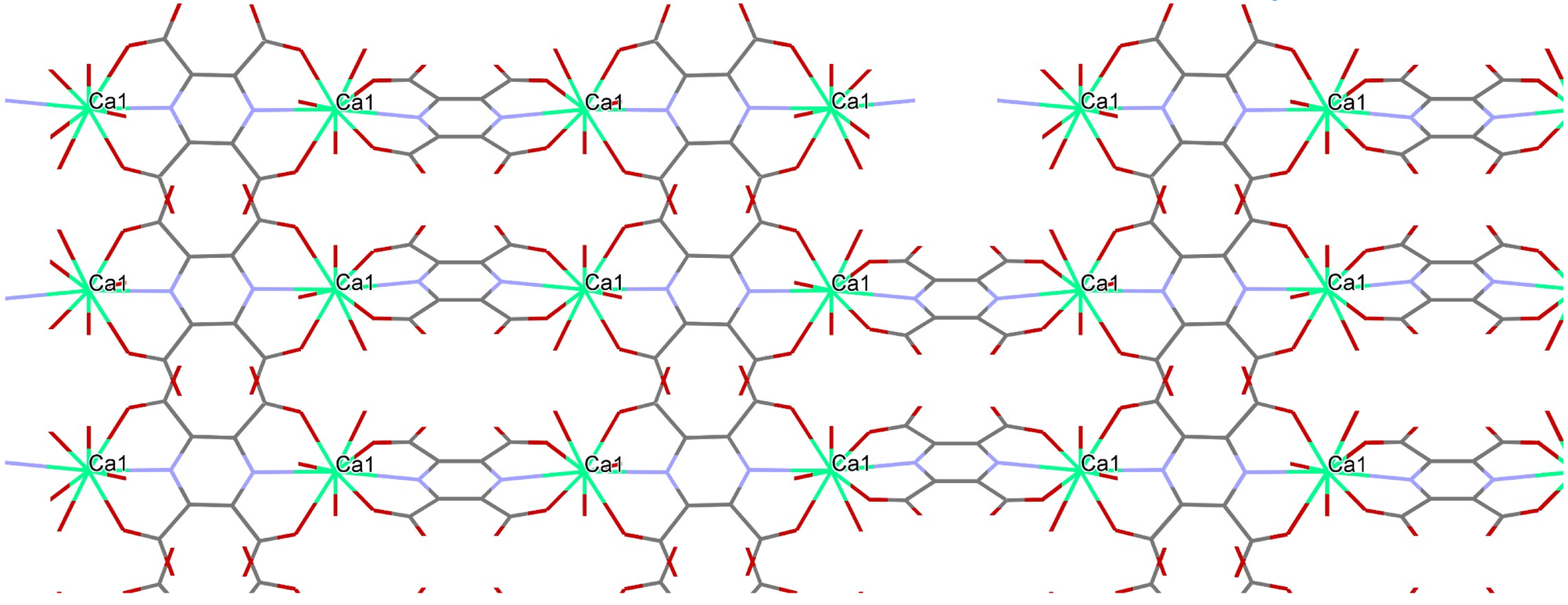
Golafale, Ingram et al. submitted 2017

Calcium pyrazine MOF



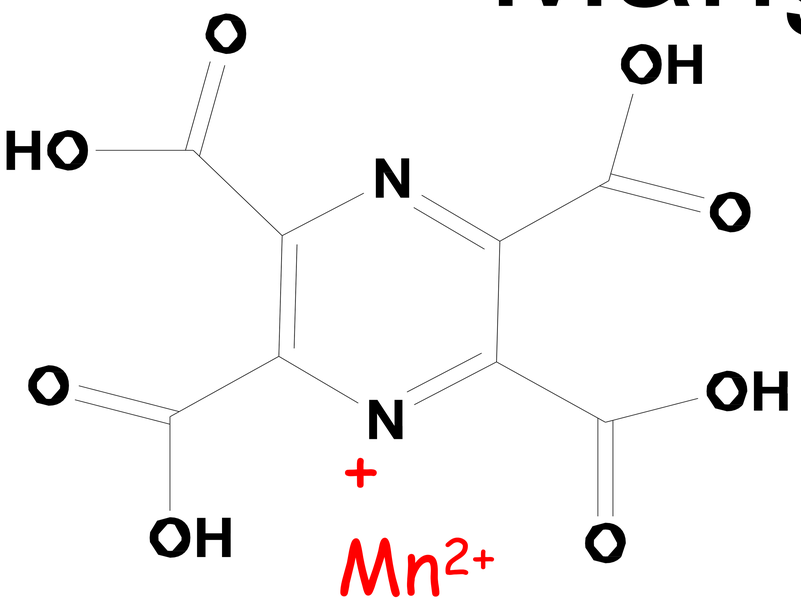
+ Ca^{2+}

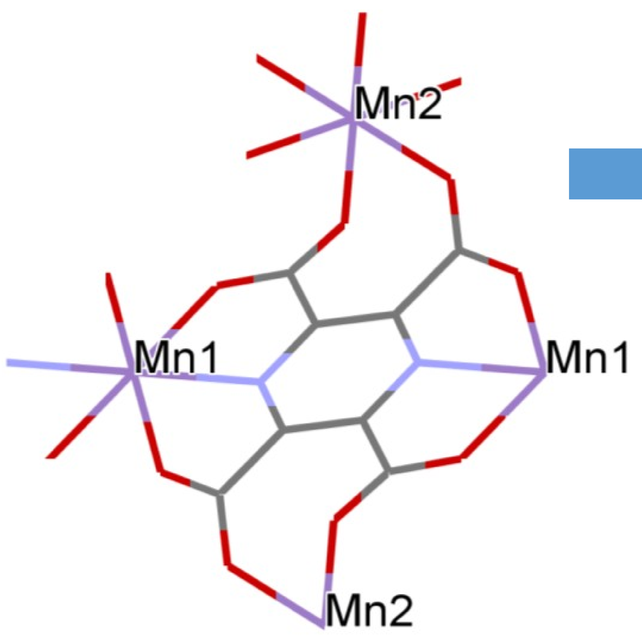


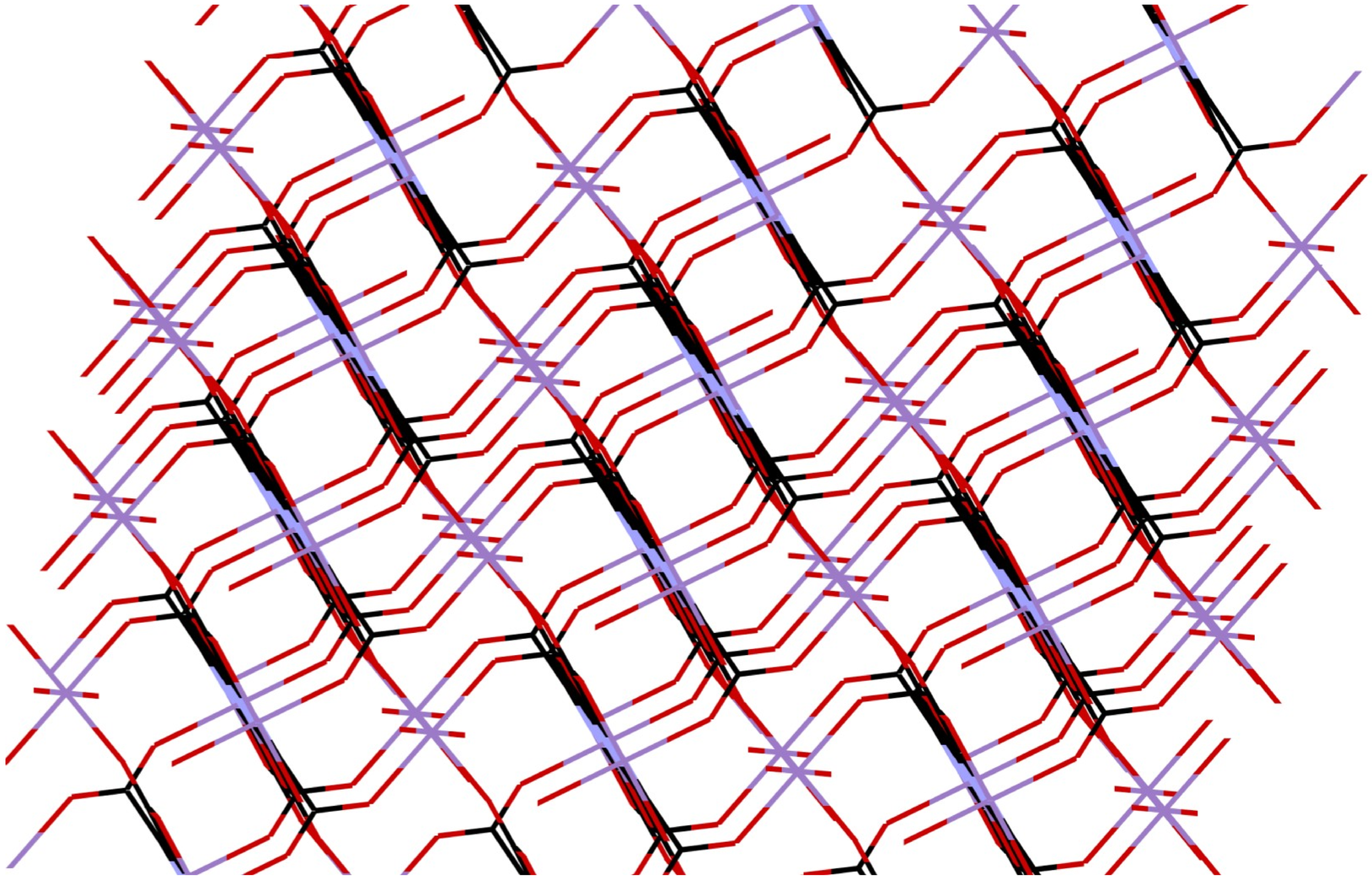


Golafale, Ingram et al. submitted 2017

Manganese pyrazine MOF

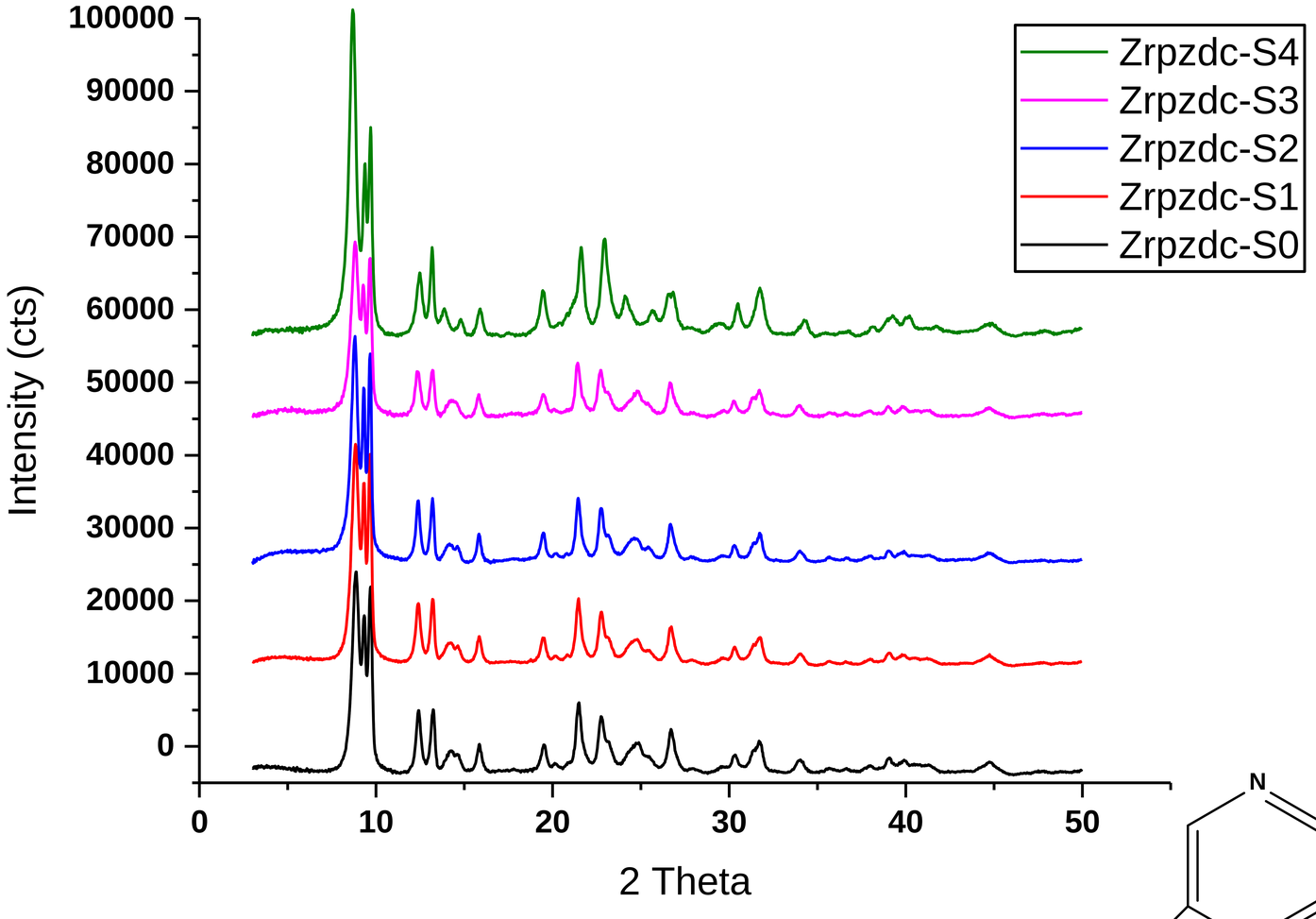






Golafale, Ingram et al. submitted 2017

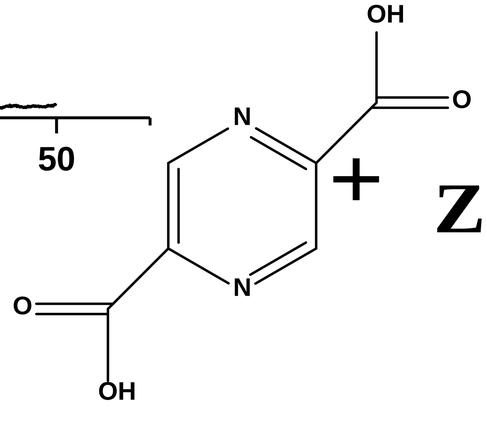
Zirconium Pyrazine MOF



Powder X-ray diffraction

S0 to S4 represent increasing volume of acetic acid added

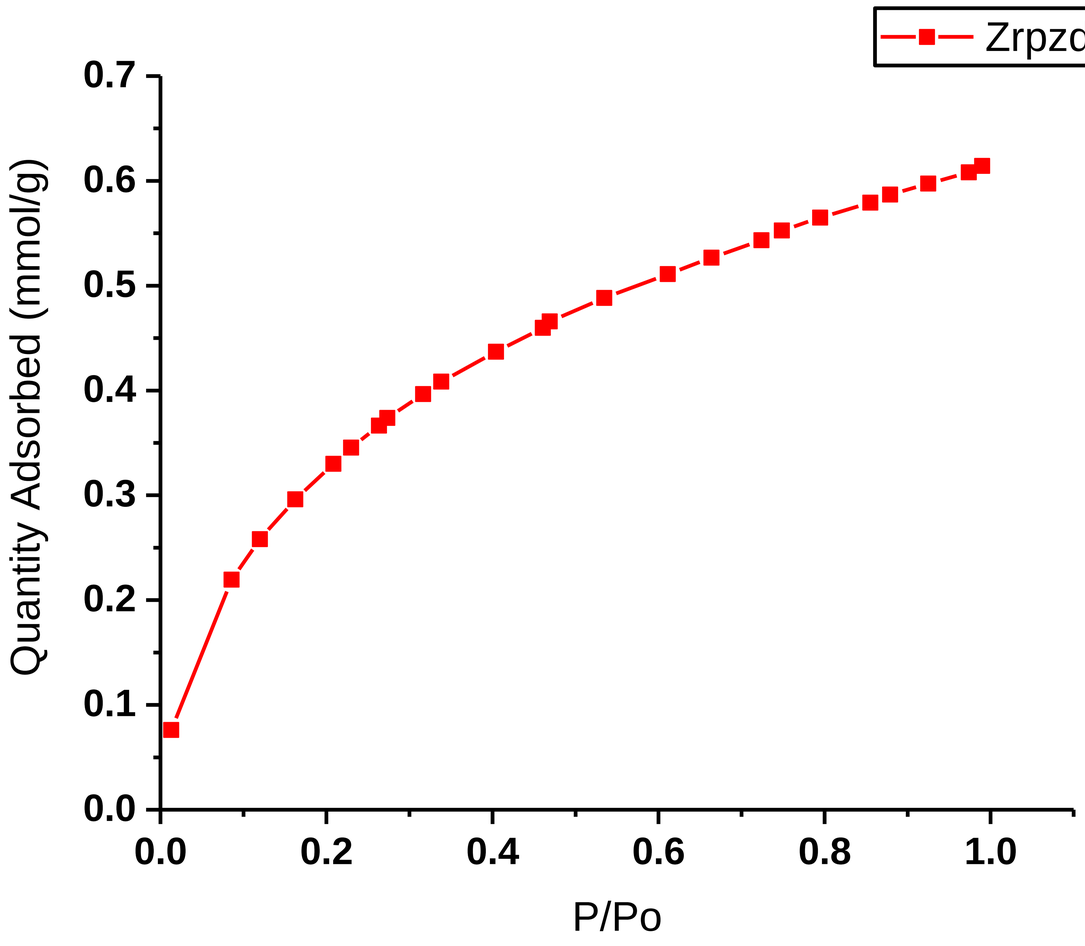
S0 = no acetic acid added



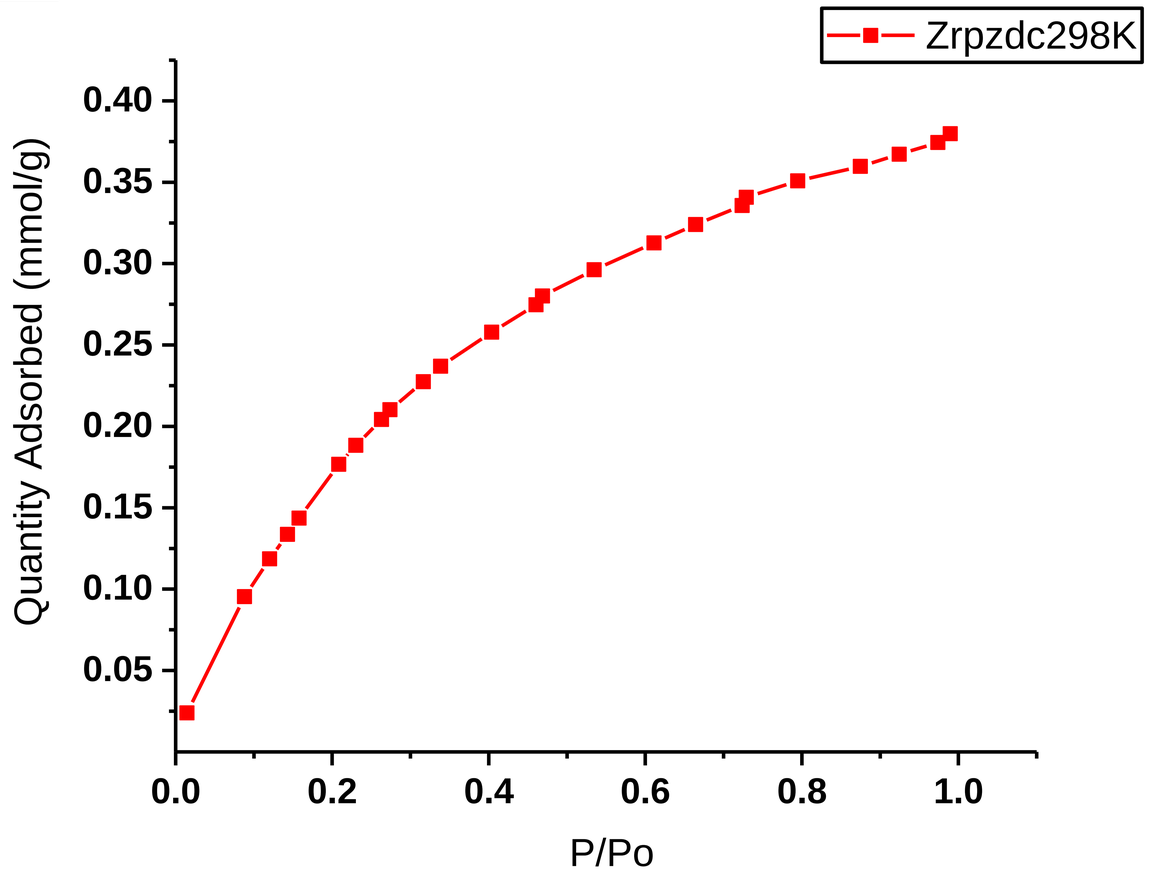
Zn(IV) → **Microcrystalline powder**

Acetic acid has been used as additive to enhance crystallinity of Zirconium MOF

CO_2 adsorption isotherms of Zrpzdc

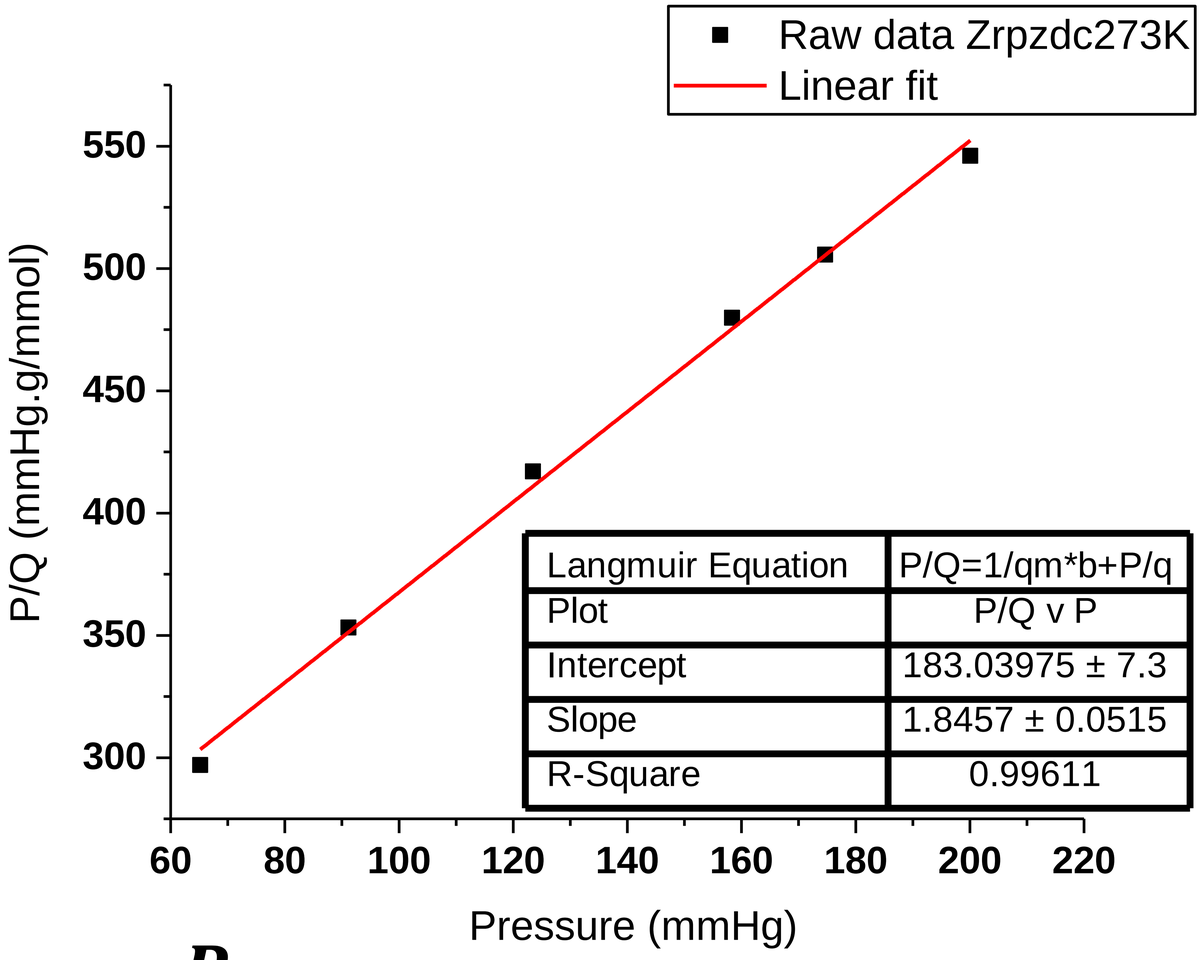


CO2 Adsorption isotherm at 0 degrees C

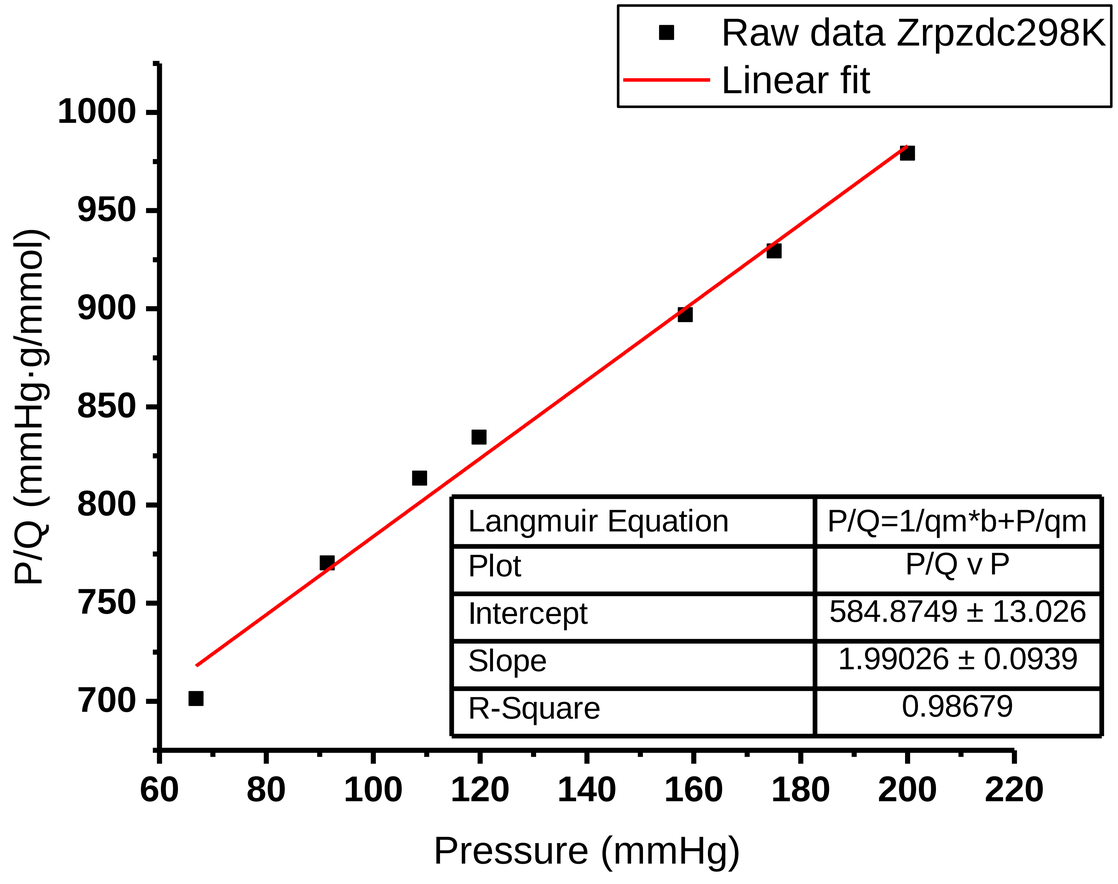


CO2 Adsorption isotherm at 25 degrees C

Langmuir Transform model



Langmuir Equation	P/Q=1/qm*b+P/q
Plot	P/Q v P
Intercept	183.03975 ± 7.3
Slope	1.8457 ± 0.0515
R-Square	0.99611



Langmuir Equation	P/Q=1/qm*b+P/qm
Plot	P/Q v P
Intercept	584.8749 ± 13.026
Slope	1.99026 ± 0.0939
R-Square	0.98679

$$\frac{P}{Q} = 1/qm * b + P/qm \qquad Slope = \frac{1}{qm} \qquad Intercept = \frac{1}{qm * b}$$

$$@\ 25\ degrees\ C, qm = 0.502\ \frac{mmol}{g}; @\ 0\ degree\ C\ qm = 0.542\ \frac{mmol}{g}$$

Adsorption models to be used

Quantity adsorbed

$$@\ \mathbf{25}\ \boldsymbol{degrees\ C}, \boldsymbol{qm} = \mathbf{0.502}\ \frac{\boldsymbol{mmol}}{\boldsymbol{g}}; @\ \mathbf{0}\ \boldsymbol{degree\ C}\ \boldsymbol{qm} = \mathbf{0.542}\ \frac{\boldsymbol{mmol}}{\boldsymbol{g}}$$

Langmuir constant

$$@\ \mathbf{25}\ \boldsymbol{degrees\ C}, \boldsymbol{b} = \mathbf{0.0034} \qquad @\ \mathbf{0}\ \boldsymbol{degree\ C}, \boldsymbol{b} = \mathbf{0.0101}$$

Finally, we can use the Langmuir constants and the temperatures at 0 and 25 degrees to determine the thermodynamics of adsorption

Gibbs free energy (G), enthalpy (H), and entropy (S)

Summary

- Synthesized MOFs with metals in accessible sites for CO_2 adsorption but no CO_2 capacity
- Synthesized nitrogen functionalized non-interpenetrating MOFs structure showing promising CO_2 capacity

Acknowledgements

US Department of Energy, National Energy Technology Laboratory

DOE Contract FE0022952

Chemistry Department, Clark Atlanta University

Dr. Conrad W. Ingram (PI)

Dr. Tandabany C. Dinadayalane (Co-PI)

Taylor Sledge (Undergraduate)

Kennedi Trice (Undergraduate)