Engineering Accessible Adsorption Sites in Metal Organic Frameworks for CO_2 Capture

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Outline

- Background
- Research goal and objectives
- Research Progress
  - Synthesis of nitrogen-containing metal-organic frameworks
  - Synthesis of nitro and amino metal-organic frameworks
  - Synthesis of zirconium and hafnium metal-organic frameworks
  - Carbon dioxide adsorption studies
- Publications
- Summary and future work

Background

Carbon dioxide (CO_2) capture and storage (CCS) is a process consisting of the separation of CO_2 from industrial and energy-related sources, transport to a storage location and long-term isolation from the atmosphere.

Post-combustion capture

Post-combustion CO_2 capture refers to removal of CO_2 from the flue gas produced from fossil fuel combustion

The Post-Combustion Technology Area includes three key technologies:

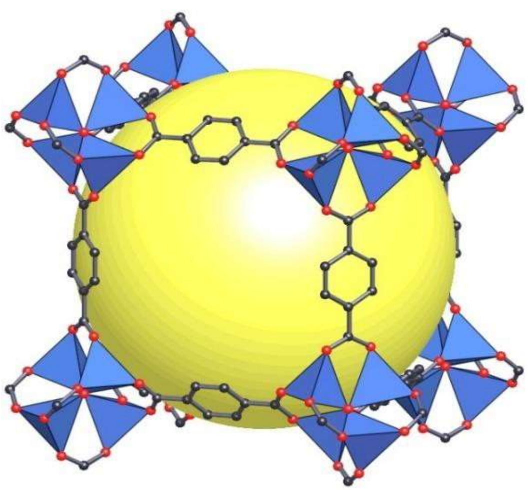
- Solvents
- Membranes
- Sorbents

Solid sorbent

Zeolites
Carbonates
Amine-rich sorbents
Metal-organic frameworks

Focus

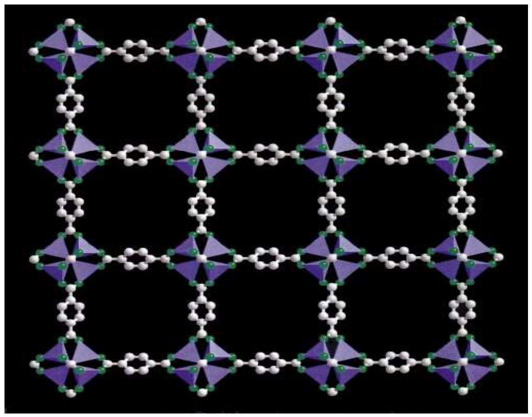
- Low-cost raw materials,
- thermal and chemical stability
- low attrition rates,
- low heat capacity,
- high CO_2 adsorption capacity, and high CO_2 selectivity



MOF-5: Yaghi and co-workers, Nature 1999 vol. 402

Background

Metal-organic frameworks are porous materials that can exhibit very high surface areas that have potential for applications such as gas storage and separation



MOF-5: Yaghi and co-workers, Nature 1999 vol. 402

Key MOF properties

- High surface areas (e.g. 10,000 m^2/g)
- Uniform channels,
- Thermal stability
- Adjustable chemical functionalities

Four crucial developments of MOF

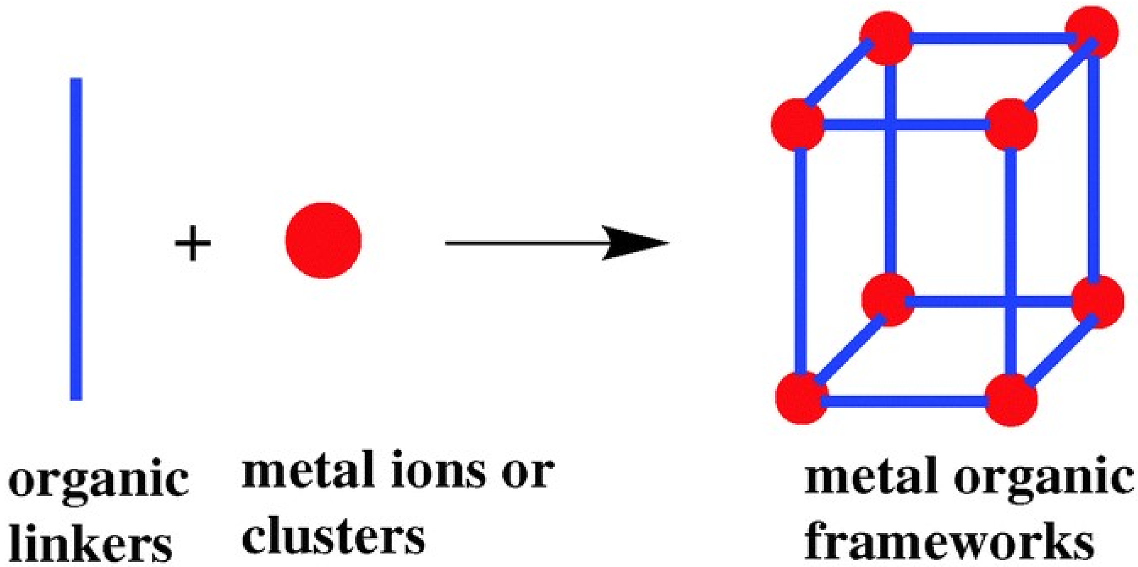
1. The invention and expansion of reticular chemistry

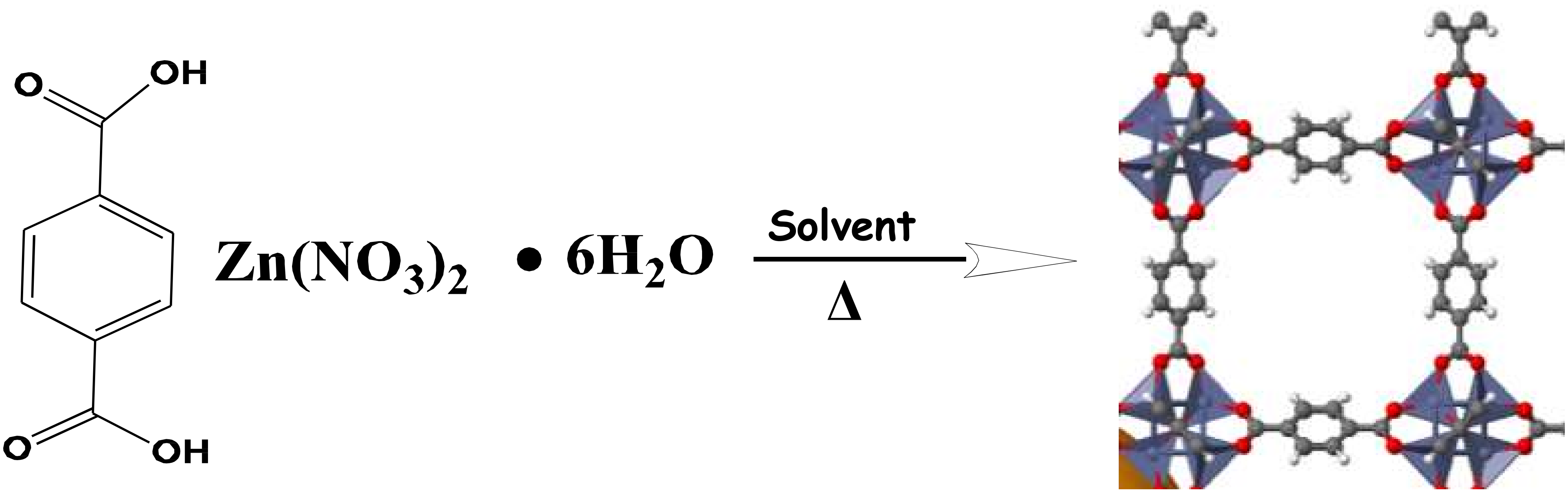
2. The marriage of molecular chemistry with framework chemistry

3. The discovery of ultra high surface area and porosity

4. The concept of "heterogeneity within order"

Metal-Organic Frameworks (MOFs)





MOF-5: Yaghi and co-workers, Nature 1999 vol. 402

Research goal and objectives

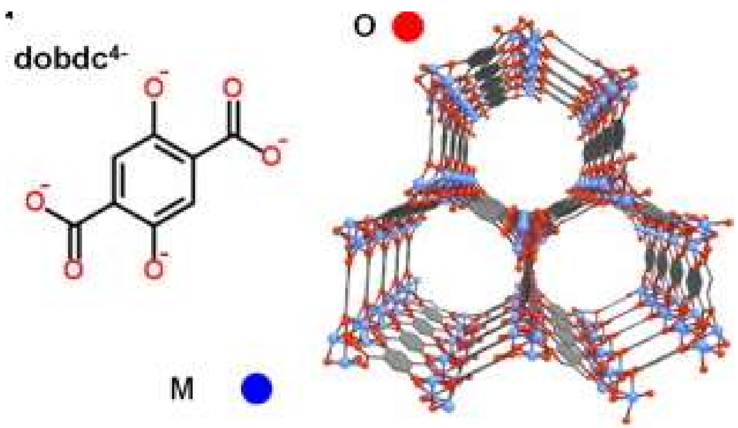
GOAL: To develop metal organic framework (MOFs) materials with improved sites accessibility, thus enhance their CO_2 adsorption and selectivity properties

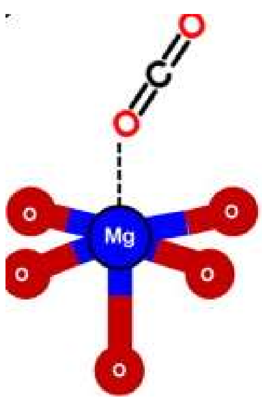
OBJECTIVES

- 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 sorbent; and
- 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.

MOFs with accessible adsorption sites

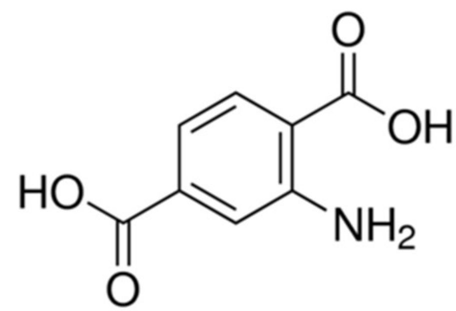
Coordinatively unsaturated metal sites

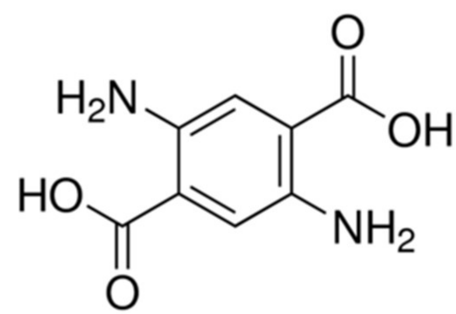




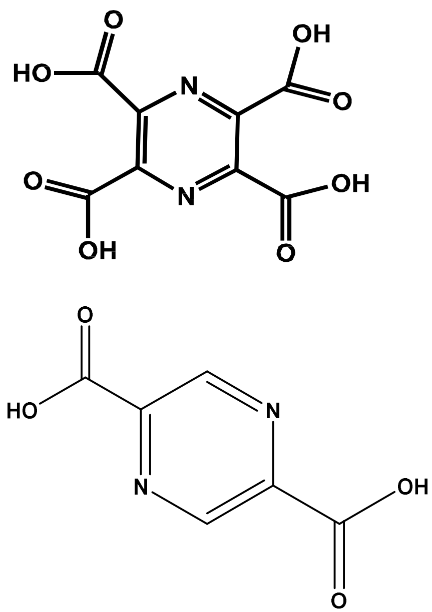
Chen, De-Li, et al. *Chemical Engineering Science*, vol. 117, 2014, pp. 407–415

Ligands with heteroatoms

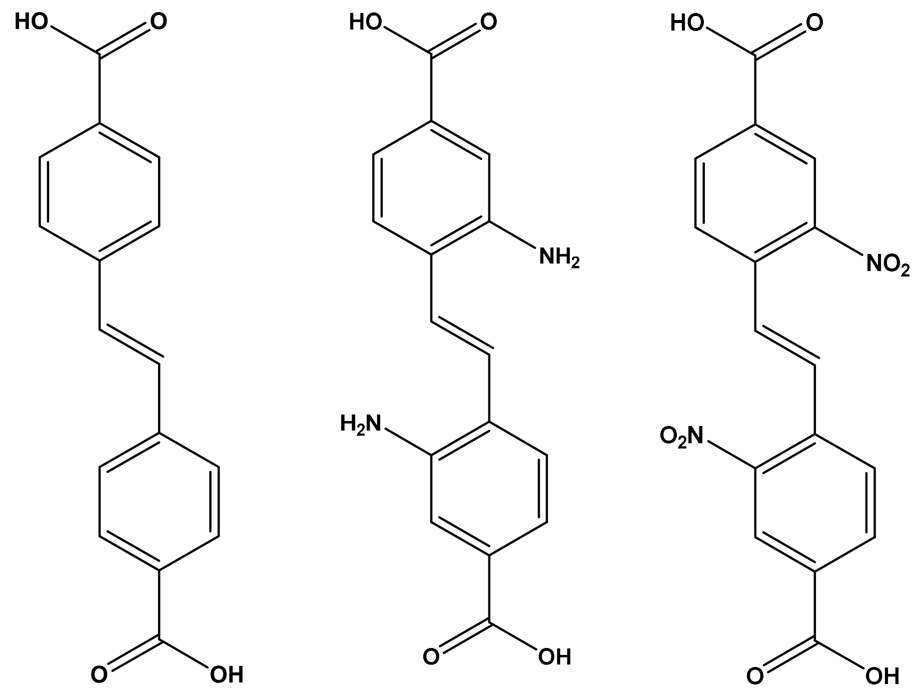




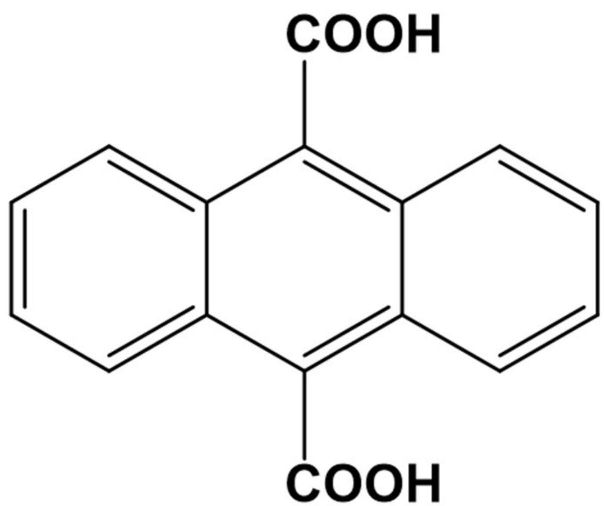
Ligands of interest



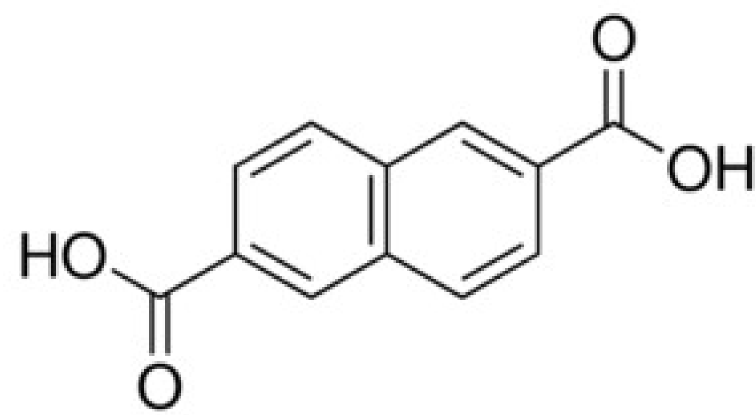
Pyrazines



Stilbenes

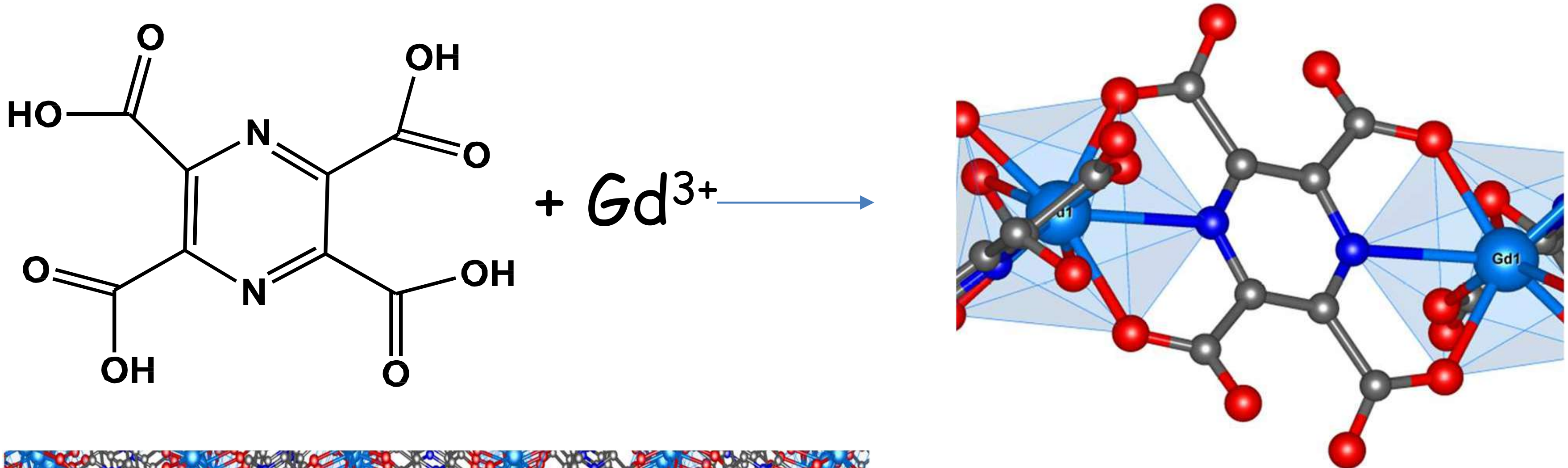


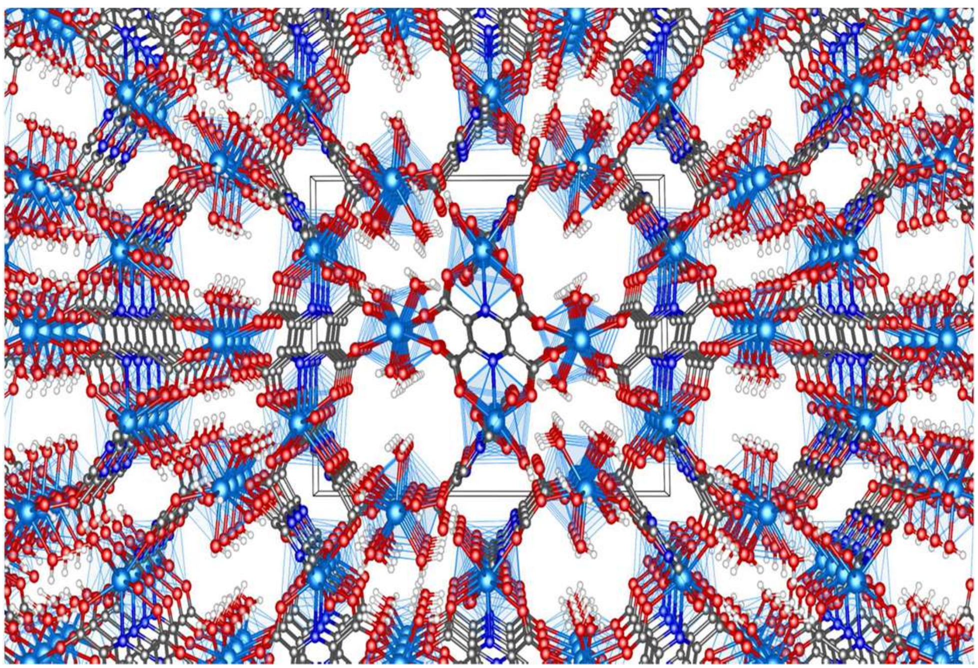
9,10-anthracene dicarboxylic acid



2,6-naphthalenedicarboxylic acid

Pyrazine based metal-organic frameworks





3D framework

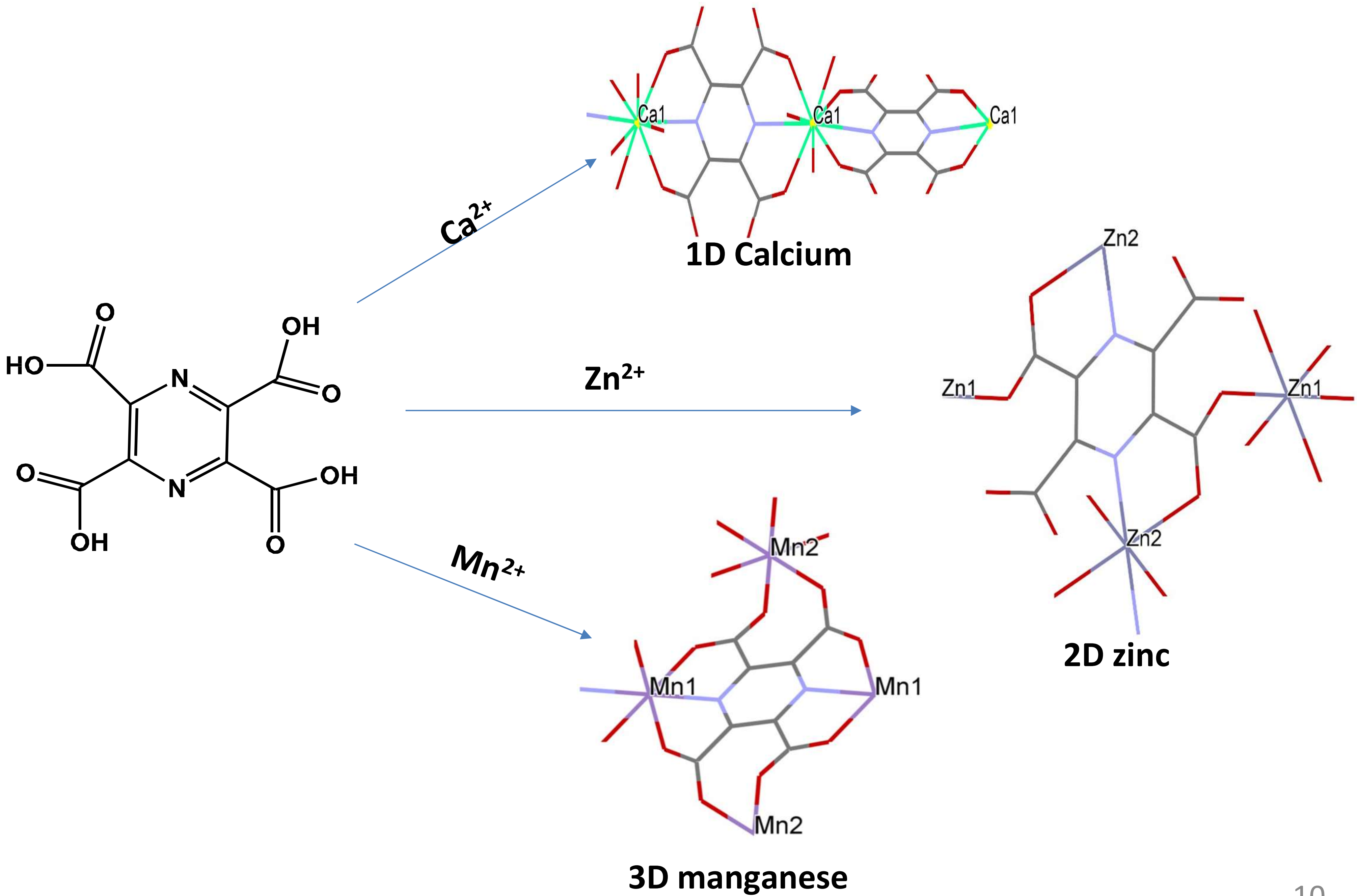
CO_2 adsorption capacity

1.36 mmol/g = 5.9 wt% at 273K

1.34 mmol/g = 5.8 wt% at 298K

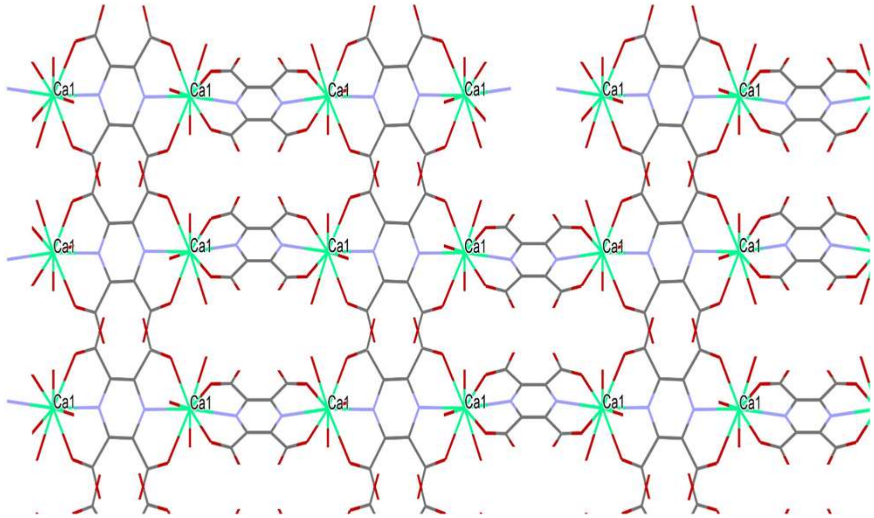
Ingram et al. CrystEngComm, 2015,**17**, 5377-5388

Pyrazine based metal-organic frameworks

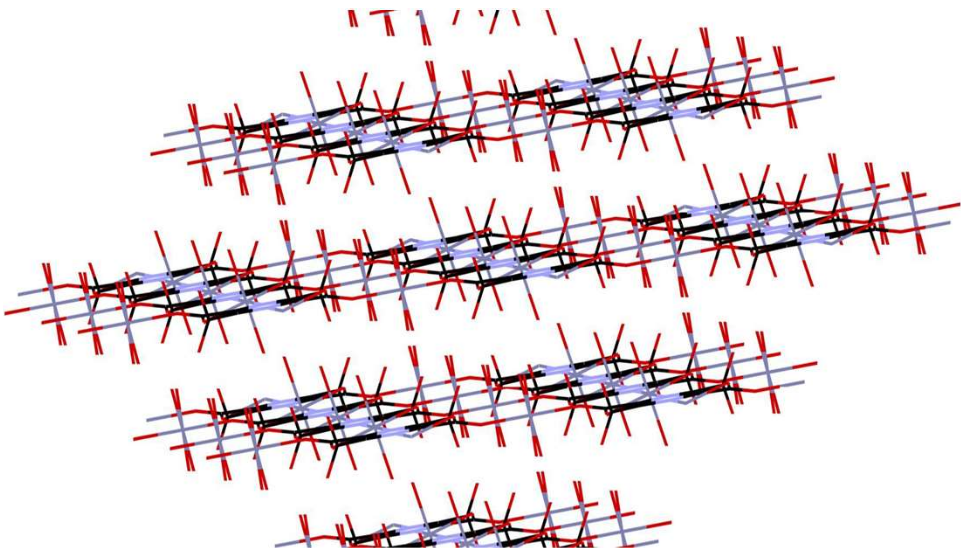


Golafale et al *Inorganica Chimica Acta*, *467*, 163-168.

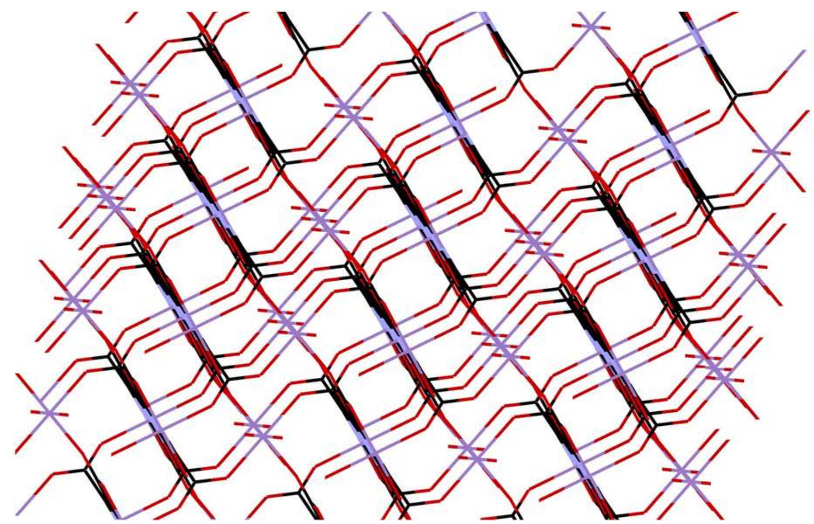
Pyrazine based metal-organic frameworks



1D Calcium



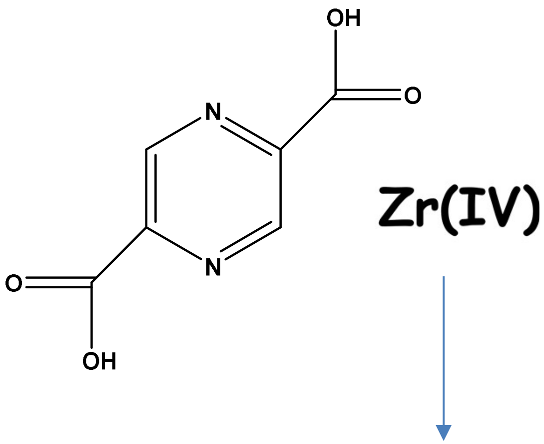
2D zinc



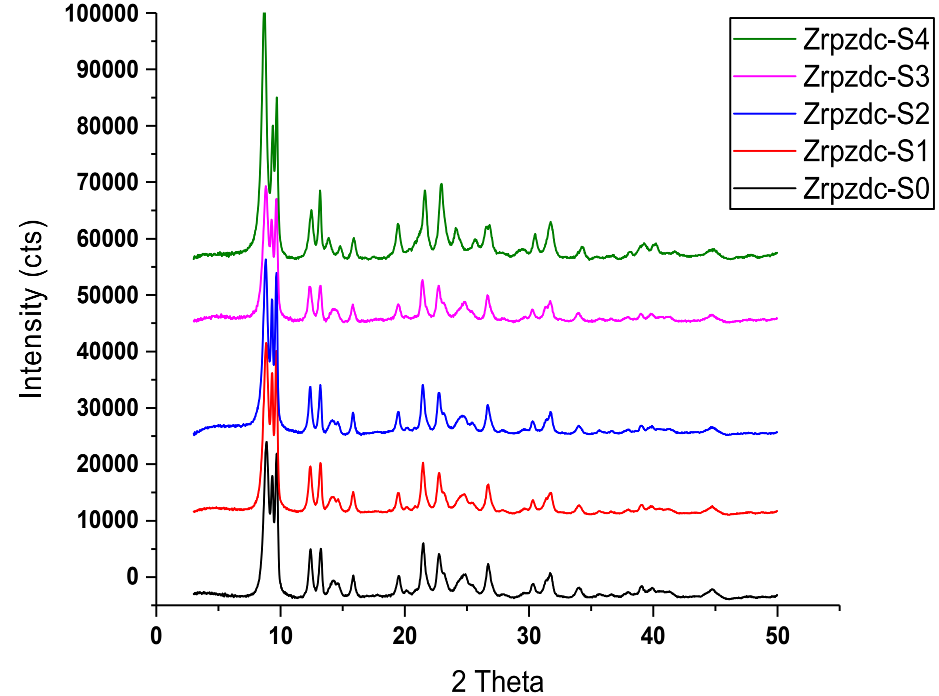
3D manganese

Golafale et al *Inorganica Chimica Acta*, 2017, *467*, 163-168.

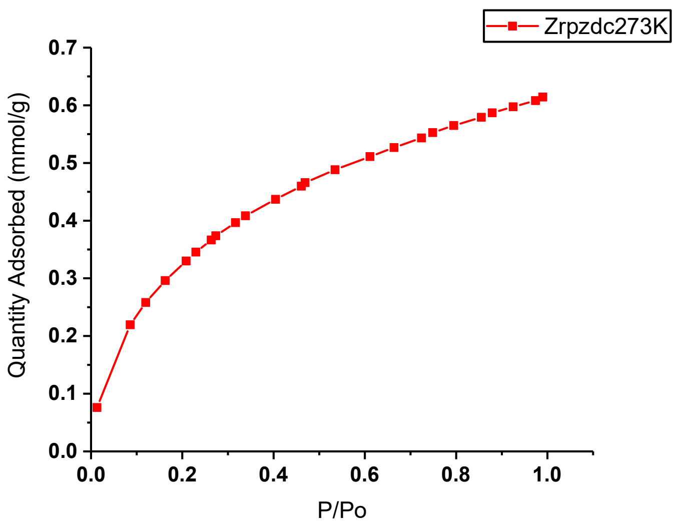
Pyrazine based zirconium metal-organic framework

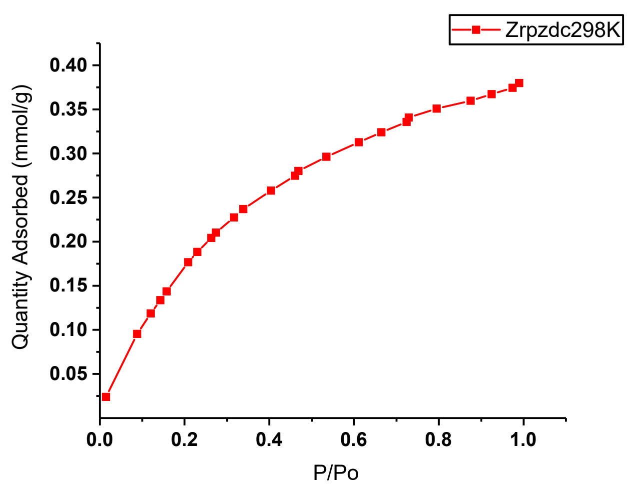


Microcrystalline powder



X-ray diffraction pattern

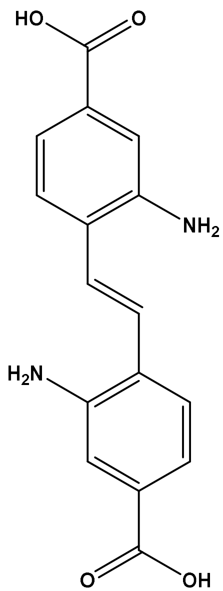




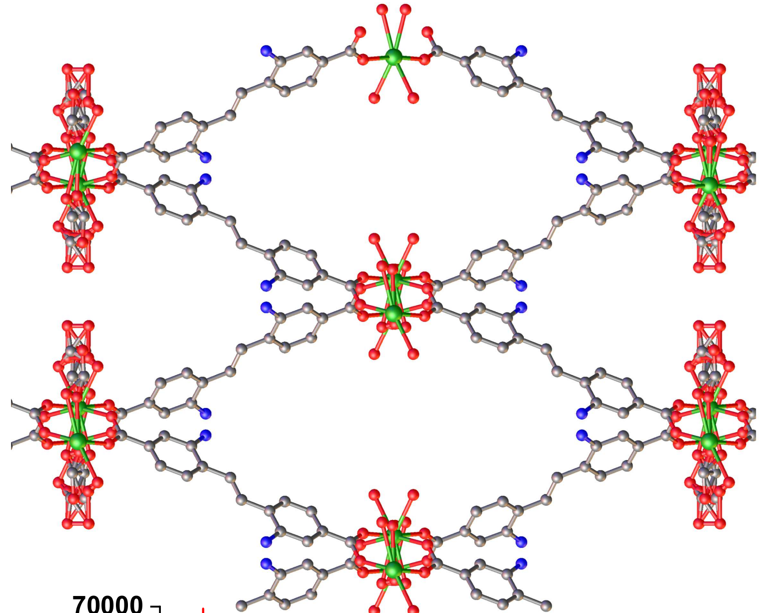
0.6 mmol/g = 2.6 wt% at 273K

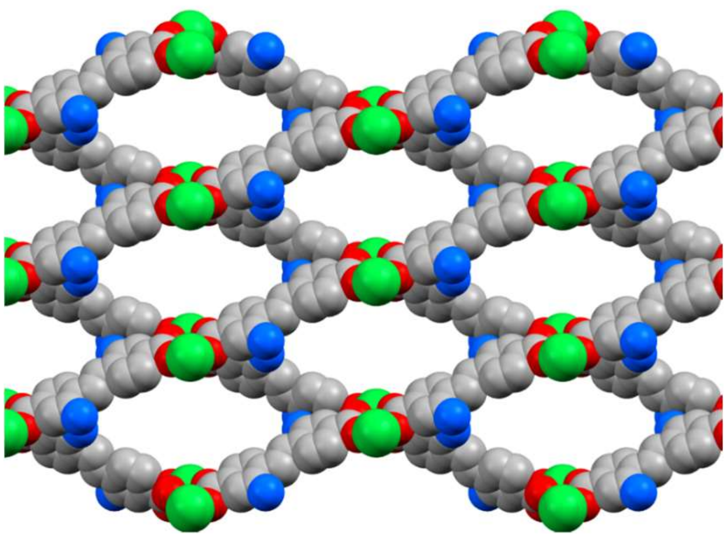
0.35 mmol/g = 1.5 wt% at 298K

Amine based stilbene metal-organic frameworks

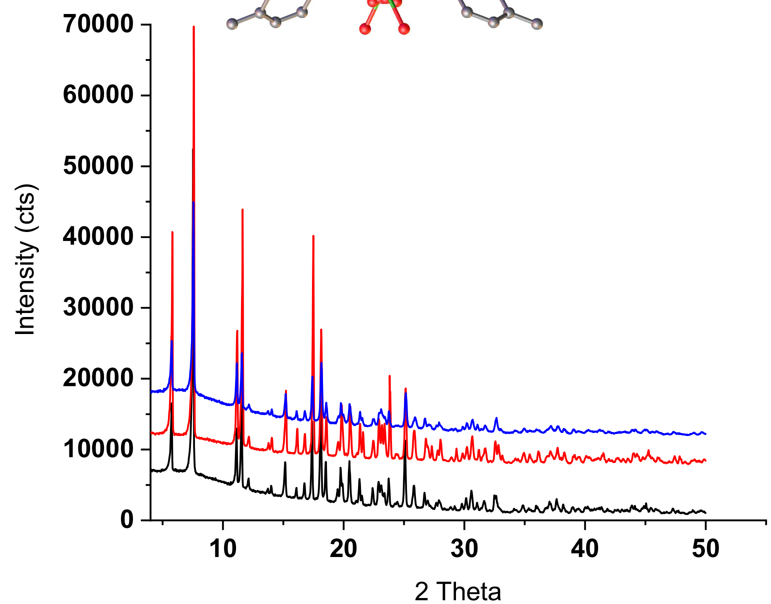


+ Ln^{3+} →





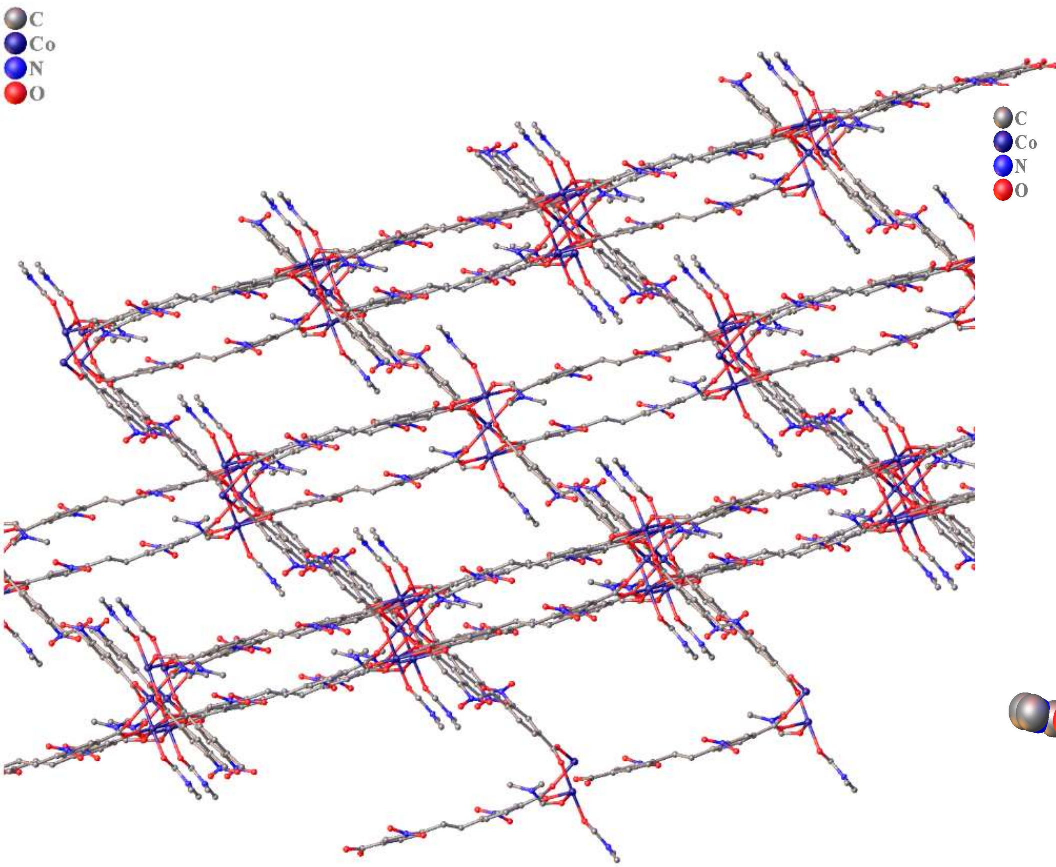
Space filling model

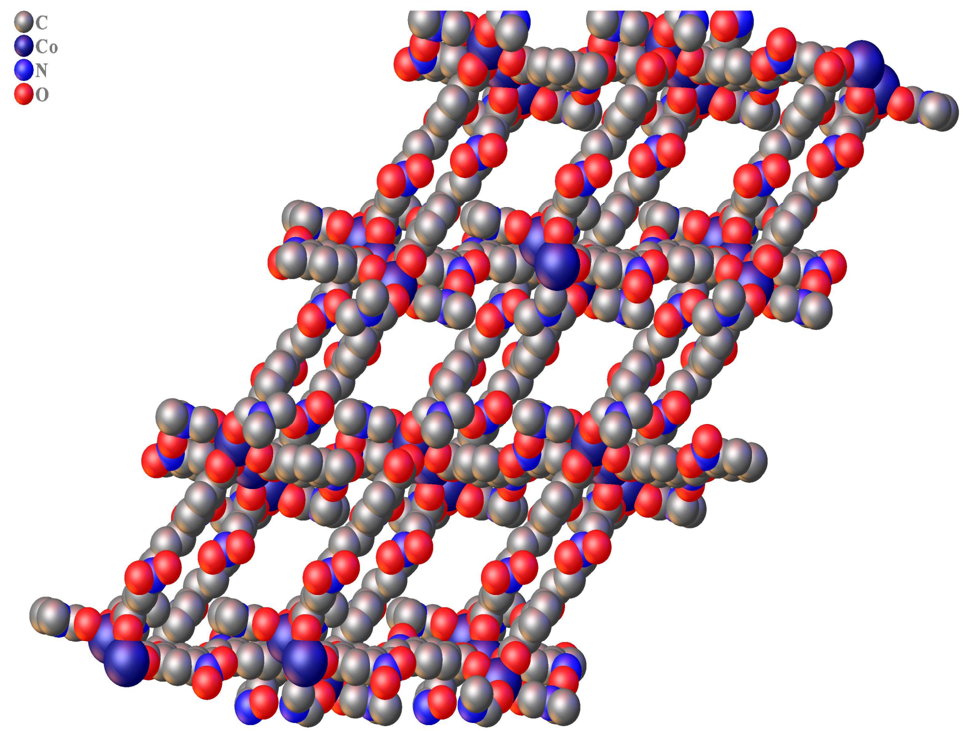


X-ray diffraction pattern

Golafale et al *Inorganica Chimica Acta*, 2018

Nitro based stilbene metal-organic frameworks



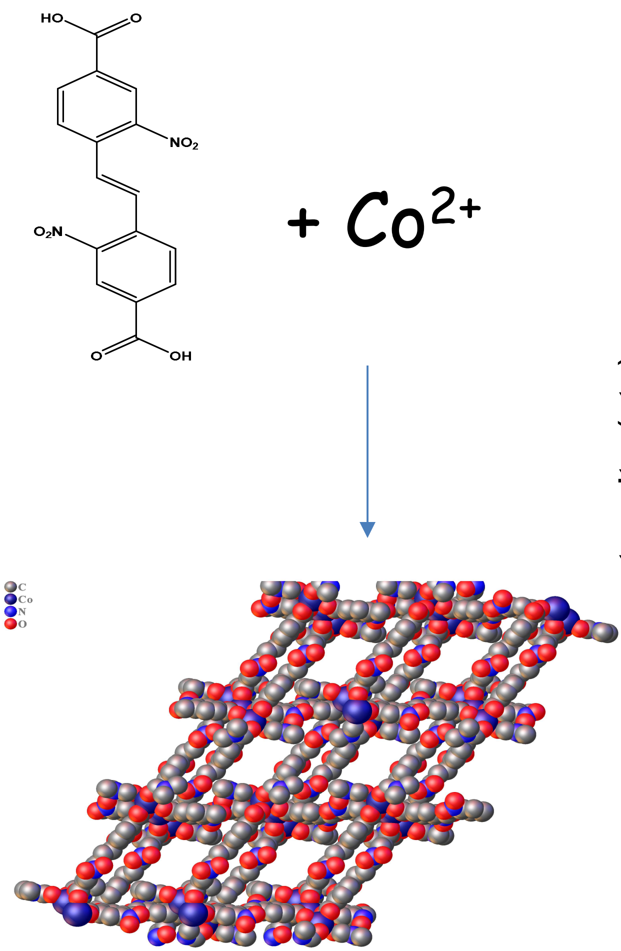


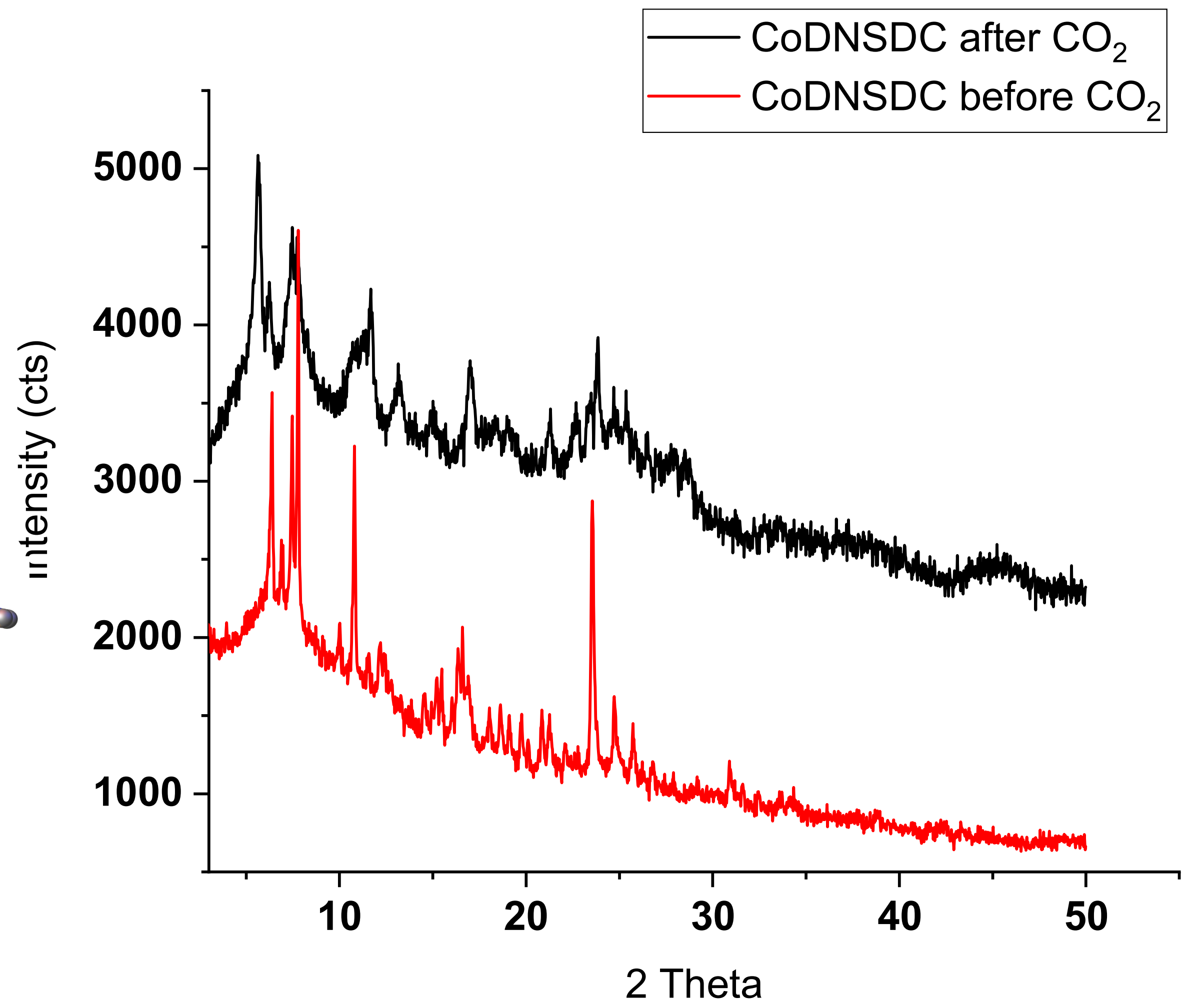
CO_2 adsorption studies

CO_2 adsorption

- CO_2 adsorption capacity
- Sample degassed at 120 degrees for 24 hours
- Analysis carried out at 273 and 298 K from 0 to 1 atm.
- Plot of quantity adsorbed vs pressure

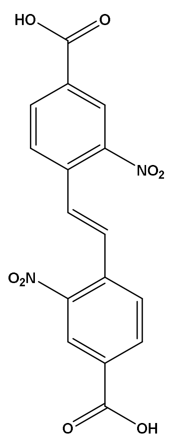
MOF after activation at 120 degrees Celsius and gas adsorption



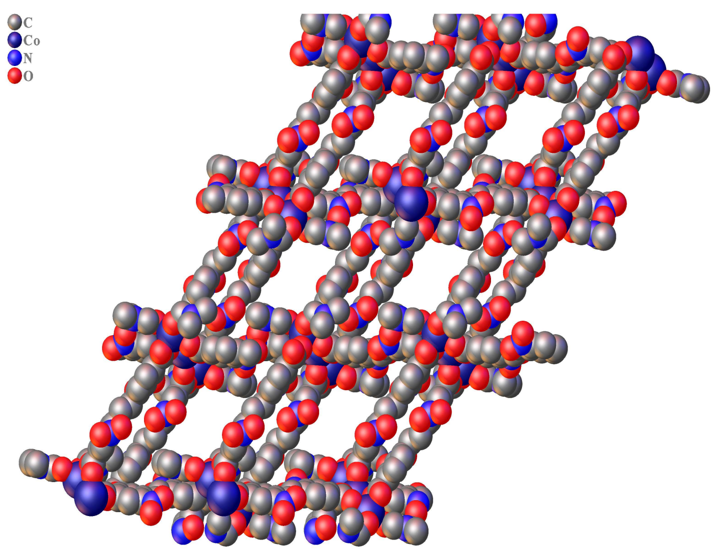


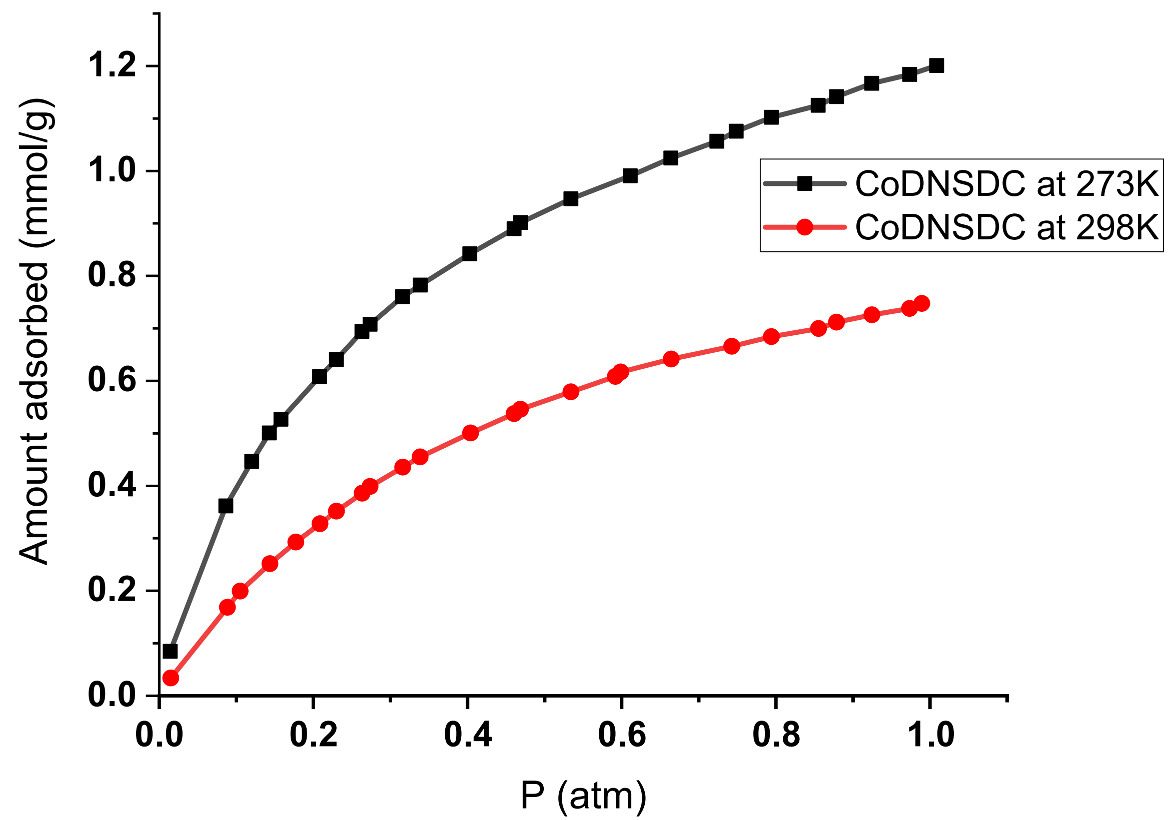
X-ray diffraction pattern

CO2 adsorption isotherms: nitrostilbene cobalt MOF



+ Co^{2+}



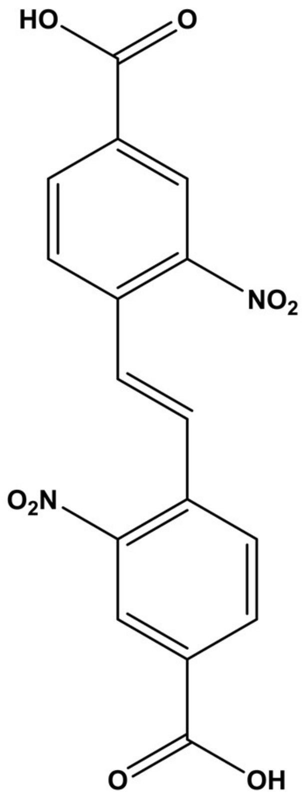


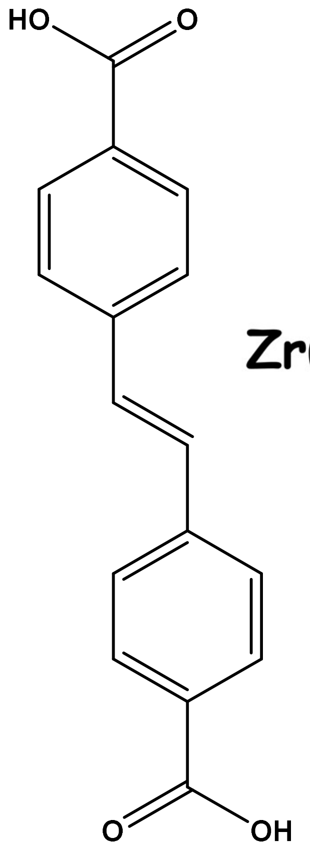
CO_2 adsorption capacity

1.2 mmol/g = 5.3 wt% at 273K

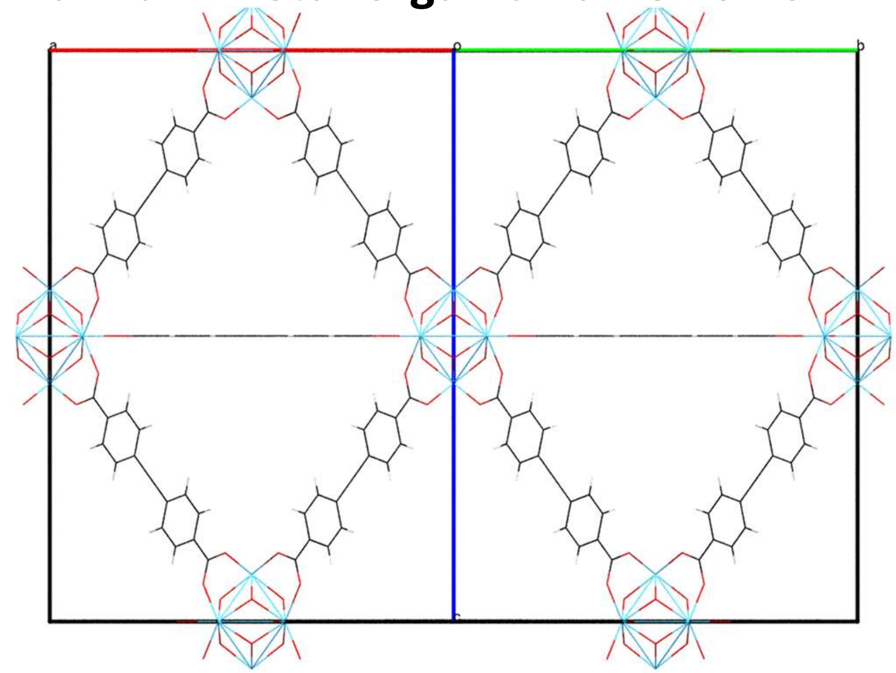
0.6 mmol/g = 2.6 wt% at 298

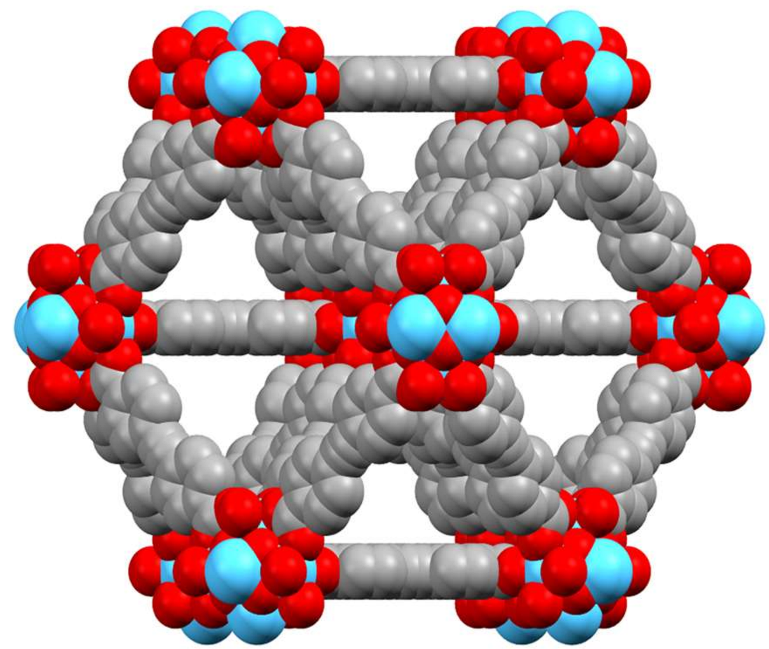
Mixed ligand zirconium and hafnium metal-organic frameworks





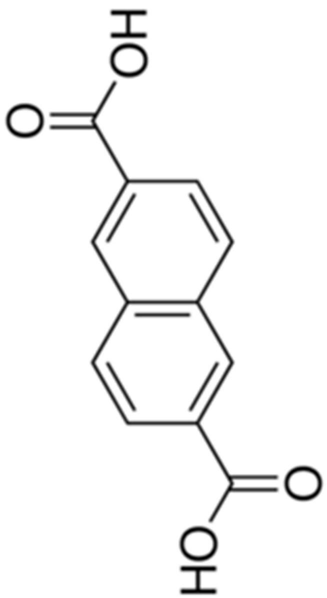
Zr(IV)/Hf(IV)





Zr = zirconium; Hf = hafnium

Naphthalene based zirconium and hafnium metal-organic frameworks

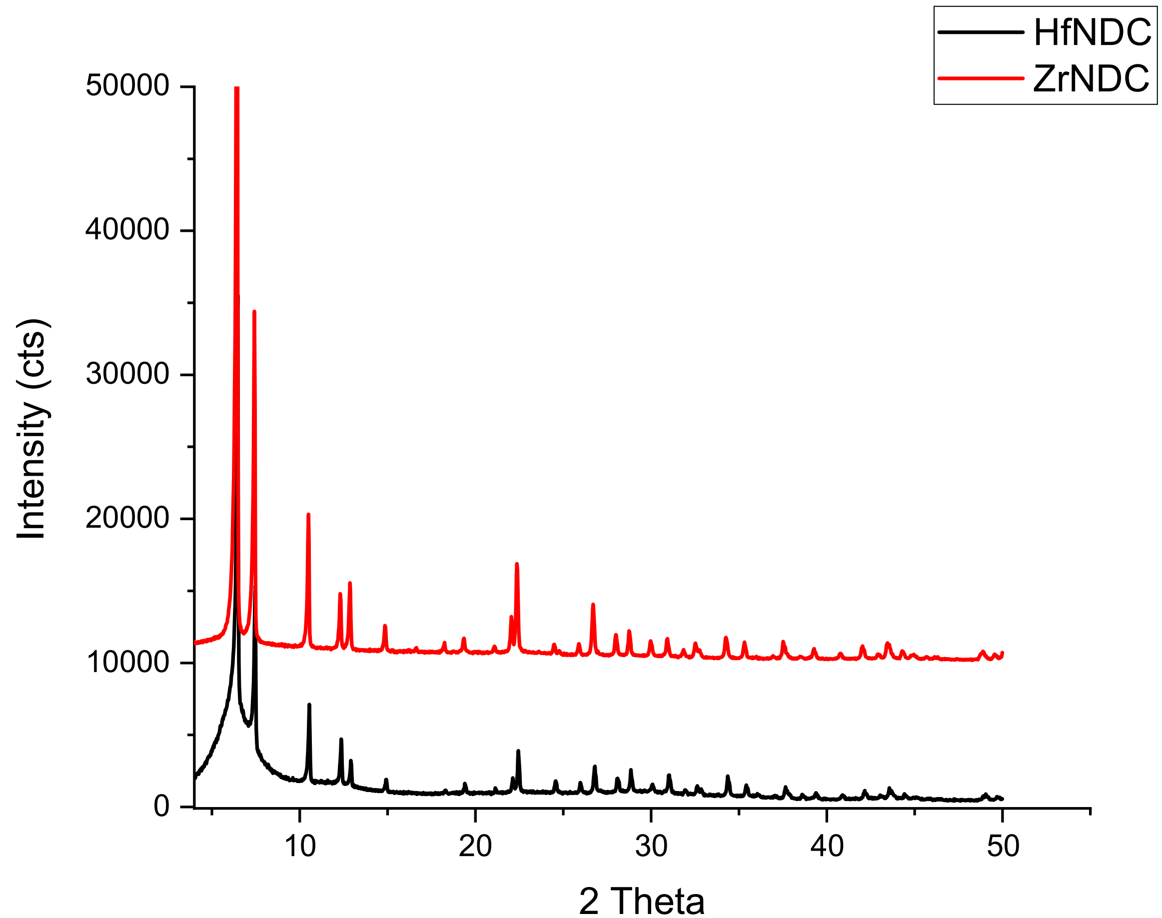


+

Zr(IV)/Hf(IV)

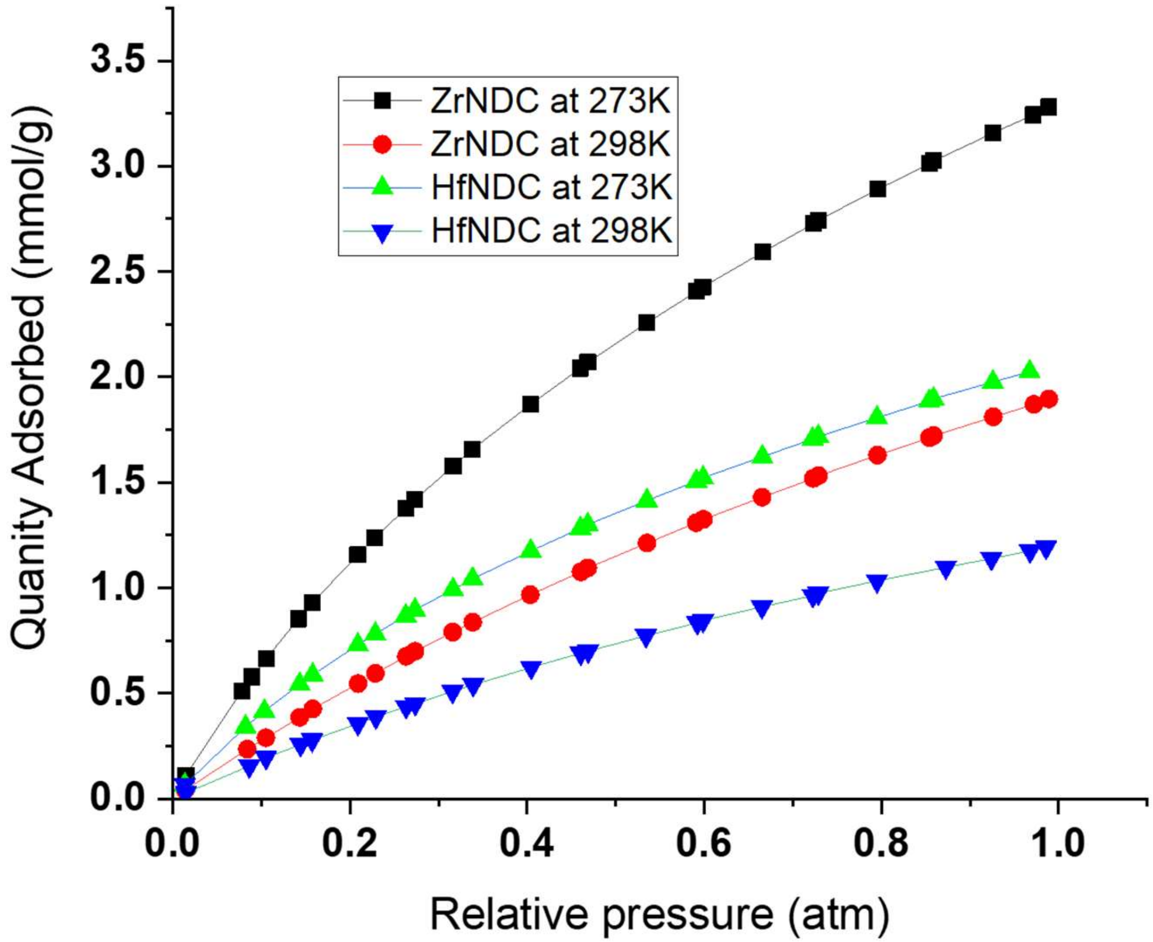
↓

Microcrystalline powder



Powder X-ray diffraction

Naphthalene based zirconium and hafnium CO2 adsorption isotherms



CO_2 adsorption capacity

3.3 mmol/g = 14.5 wt%

2.0 mmol/g = 8.8 wt%

1.5 mmol/g = 6.6 wt%

1.0 mmol/g = 4.4 wt%

Summary/Future work

Sample	Temperature (K)	Loading (mmol/g)	Loading (wt%)	Heat of adsorption (kJ/mol)
GdPZTC	273	1.36	5.9	28.5
GdPZTC	298	1.34	5.8	
CoDNSDC	273	1.2	5.3	27
CoDNSDC	298	0.6	2.6	
ZrNDC	273	3.3	14.5	24.6
ZrNDC	298	1.5	6.6	
HfNDC	273	2.0	8.8	24
HfNDC	298	1.0	4.4	
ZrPZDC	273	0.6	2.6	

All samples were analyzed in pressure range of 0 to 1 atmosphere

Summary/Future work

1. **Metal-organic frameworks with accessible adsorption sites have been successfully designed, synthesized and CO_2 adsorption capacity determined**

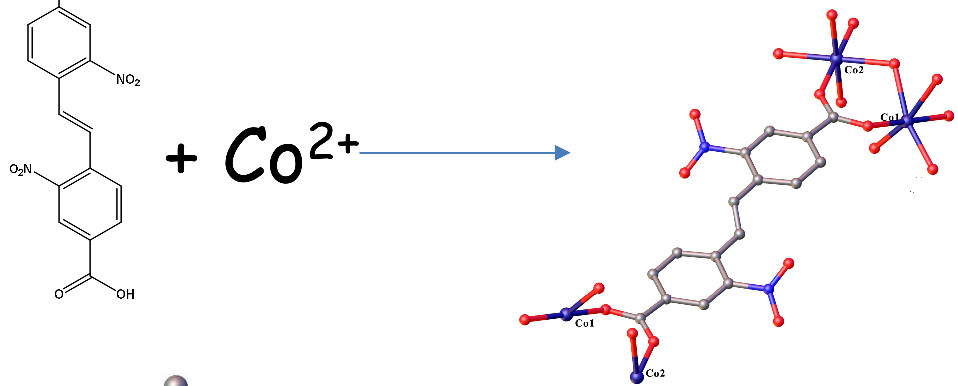
2. **Demonstrated the use of rigid and extended linkers/ligands to large pores MOFs**

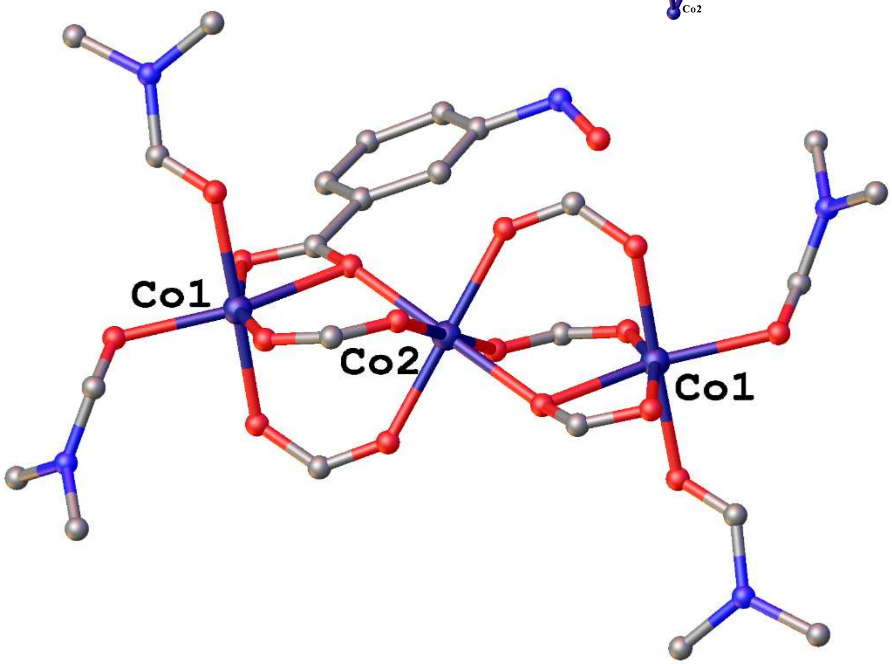
3. **Demonstrated the use of different heteroatoms in MOFs to improve CO_2 access to adsorption sites**

4. **Investigate specific adsorption sites within MOFs**

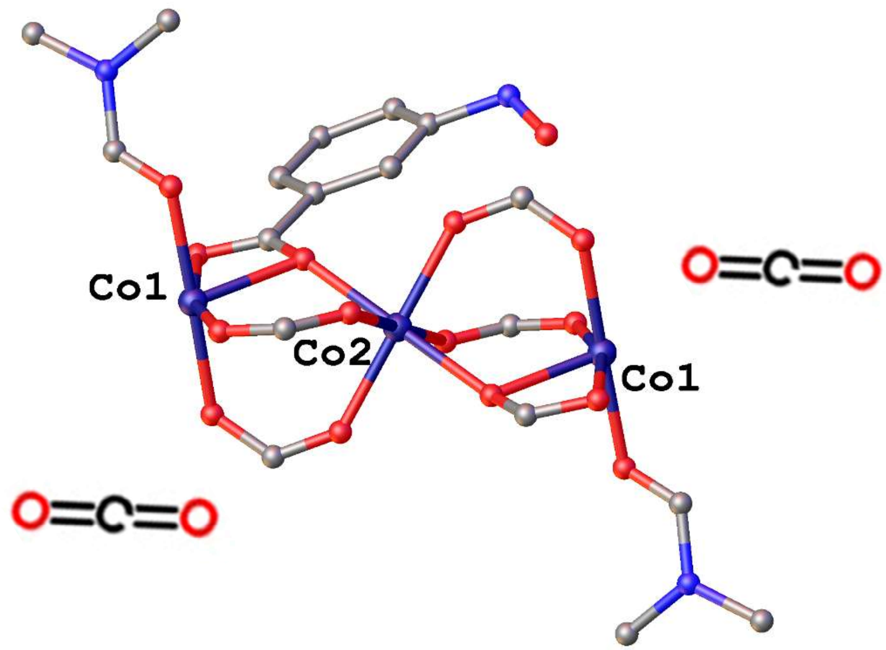
5. **Investigate nitrogen adsorption to determine surface area, pore size, etc.**

Summary/Future work





Coordination environment



MOF with open metal sites

Recent publications

Mathis II, S. R., **Golafale, S. T**., Bacsa, J., Steiner, A., Ingram, C. W., Doty, F. P., & Hattar, K. (2017). Mesoporous stilbene-based lanthanide metal organic frameworks: synthesis, photoluminescence and radioluminescence characteristics. *Dalton Transactions*, 2016, *46*(2), 491-500.

Golafale, S. T., Ingram, C. W., Holder, A. A., Chen, W. Y., & Zhang, Z. J. (2017). 1-D calcium, 2-D zinc and 3-D manganese coordination polymers derived from pyrazine-2, 3, 5, 6-tetracarboxylic acid. *Inorganica Chimica Acta*, 2017, *467*, 163-168.

Mathis, S.R., II; **Golafale, S.T**.; Solntsev, K.M.; Ingram, C.W. Anthracene-Based Lanthanide Metal-Organic Frameworks: Synthesis, Structure, Photoluminescence, and Radioluminescence Properties. *Crystals* **2018**, *8*, 53.

Accepted Manuscript
Golafale, S. T., Ingram, C. W., Bacsa, J., Steiner, A., Solntsev, K.M Synthesis, structure and photoluminescence properties of lanthanide based metal organic frameworks and a cadmium coordination polymer derived from 2,2’-diamino- trans 4,4’-stilbenedicarboxylate *Inorganica Chimica Acta,* 2018

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Undergraduates

Paris Napue, Tamia C. Middleton and Jamai Jackson

THANK YOU!