Engineering Accessible Sites in Metal Organic Frameworks for CO_2 Capture

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Post-combustion capture Processes

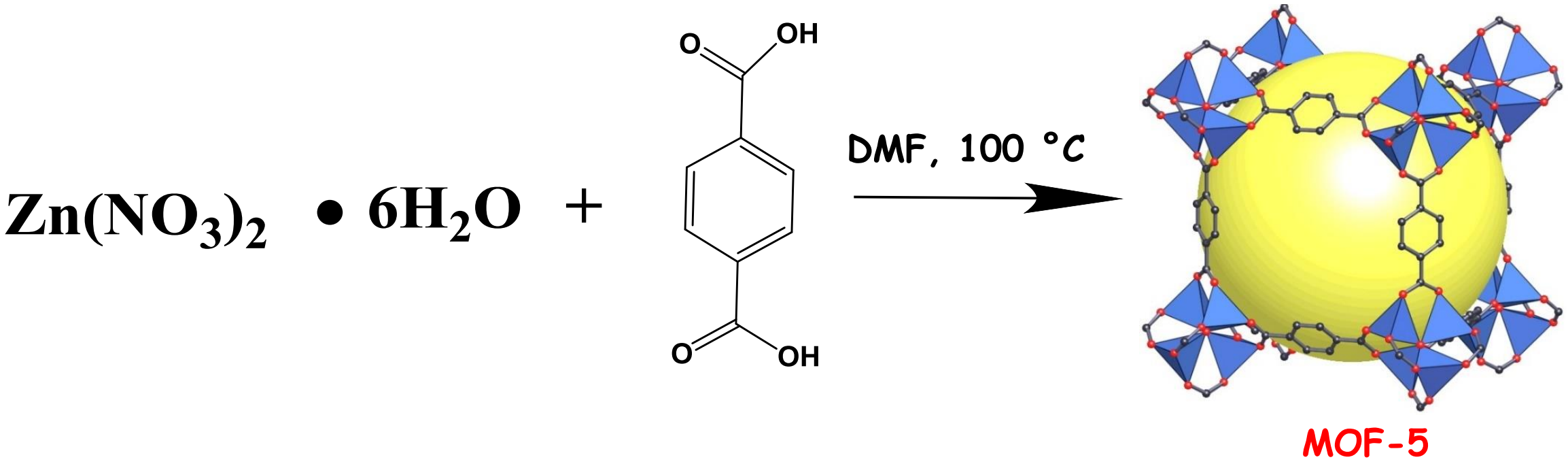
Hybrid processes
Adsorption/Membrane systems

Absorption into a liquid
Liquid amine

Adsorption on solids

Our approach: Metal organic frameworks as solid adsorbents for CO_2 capture

Metal organic frameworks



MOF-5

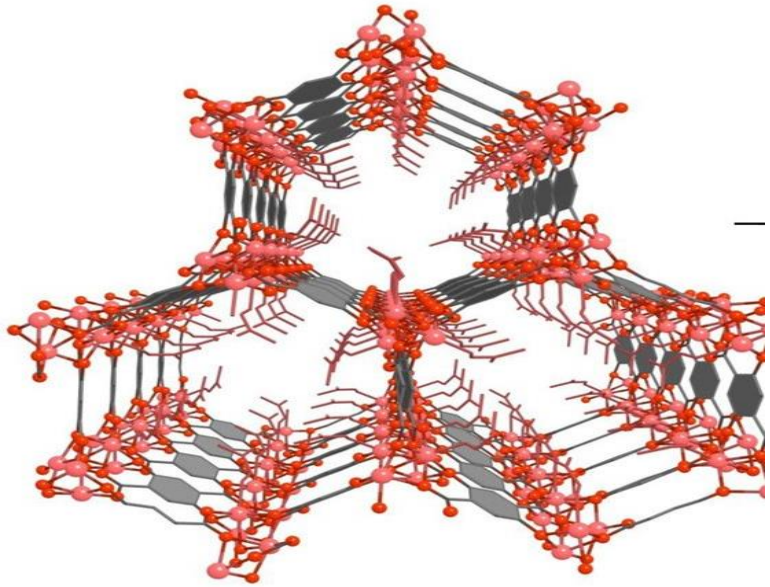
Yaghi et al. Nature **402**, 276-279

- Highly porous crystalline solids
- Very large surface area (~ 6000 m^2/g)
- Gas storage & separation
- Tunable chemistry

Metal organic frameworks

Other notable MOFs with high capacity CO_2

- Mg-MOF74
- MOF-200
- MOF-210



Mg-MOF-74·DMF

Britt et al. PNAS vol. 106 no. 49 **20637–20640**

There is a need to

- Isolate the metal sites to increase site accessibility
- Improve stability of MOFs
- Increase capacity

Research Goal and Plan

Goal

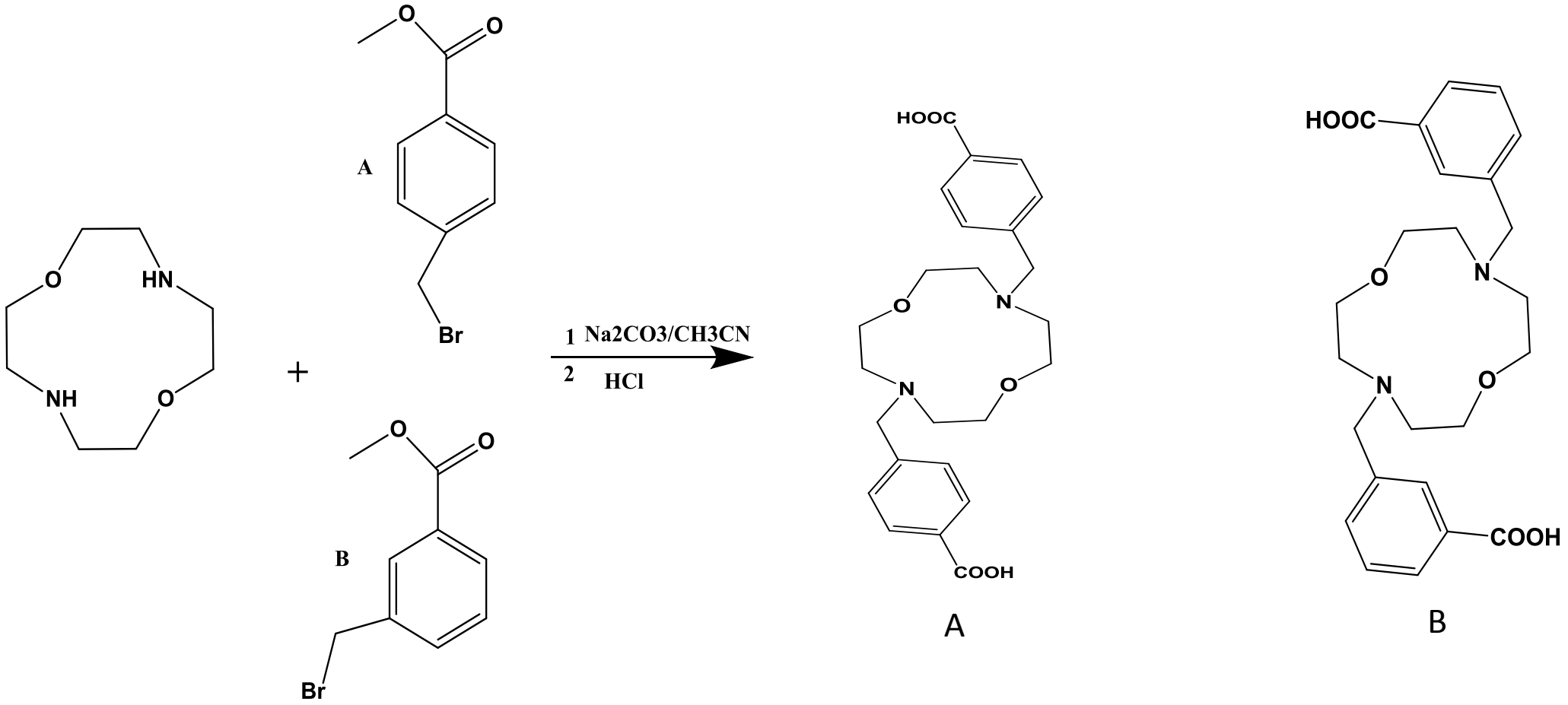
Synthesize metal organic frameworks (MOFs) with adsorption sites, improve capacity and stability for CO_2

Research plan

- MOFs with coordination sites within the center of the ligand [e.g., crown ether based ligands]
- MOFs with nitrogen or amine containing ligands [e.g., pyrazine based ligands]
- MOFs with stilbene and anthracene based ligands

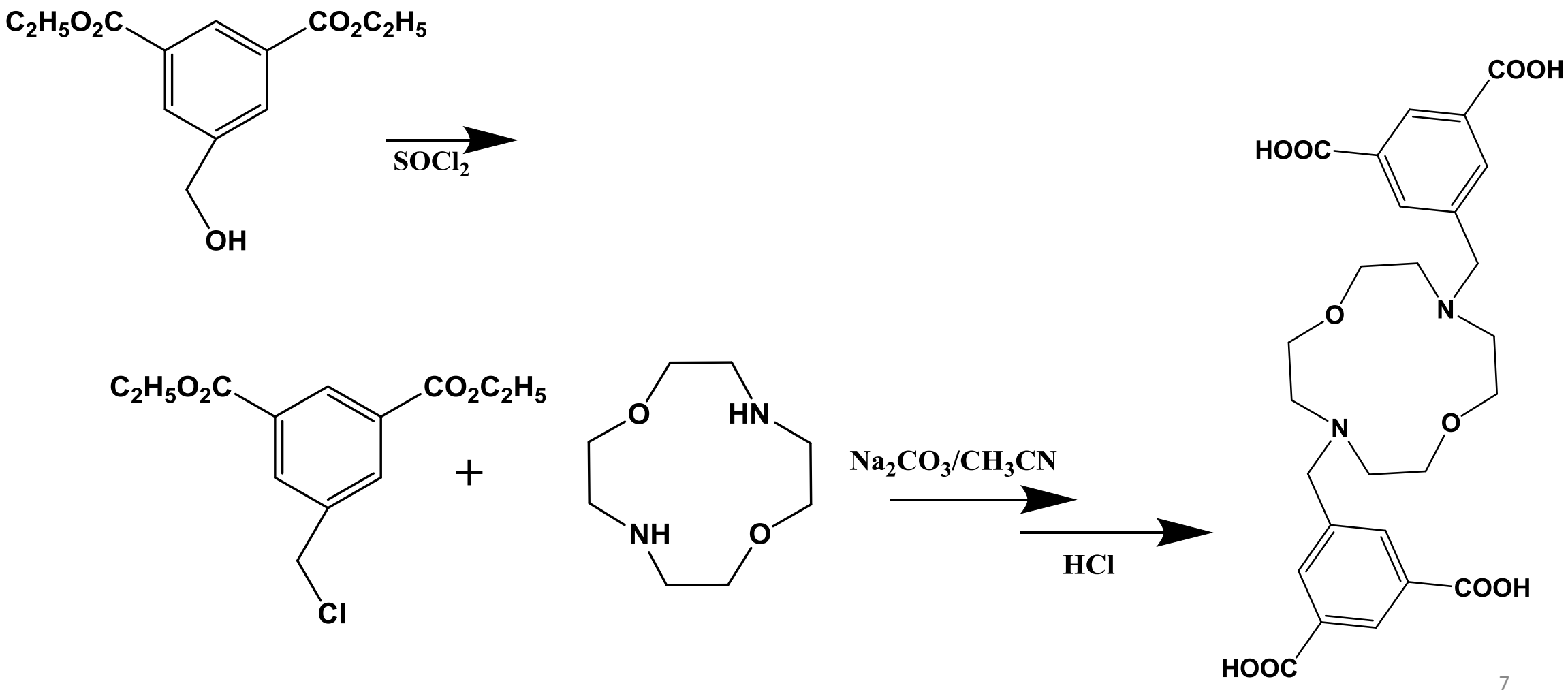
Research progress

Synthesis of diaza-crown ether ligands

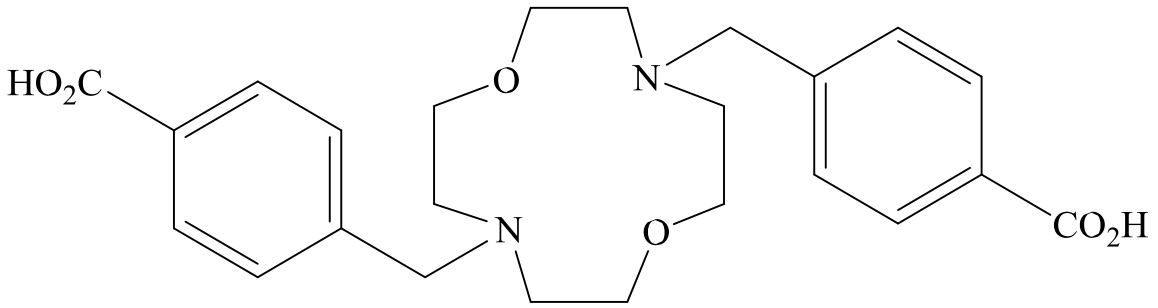


Research progress

Synthesis of diaza-crown ether ligands

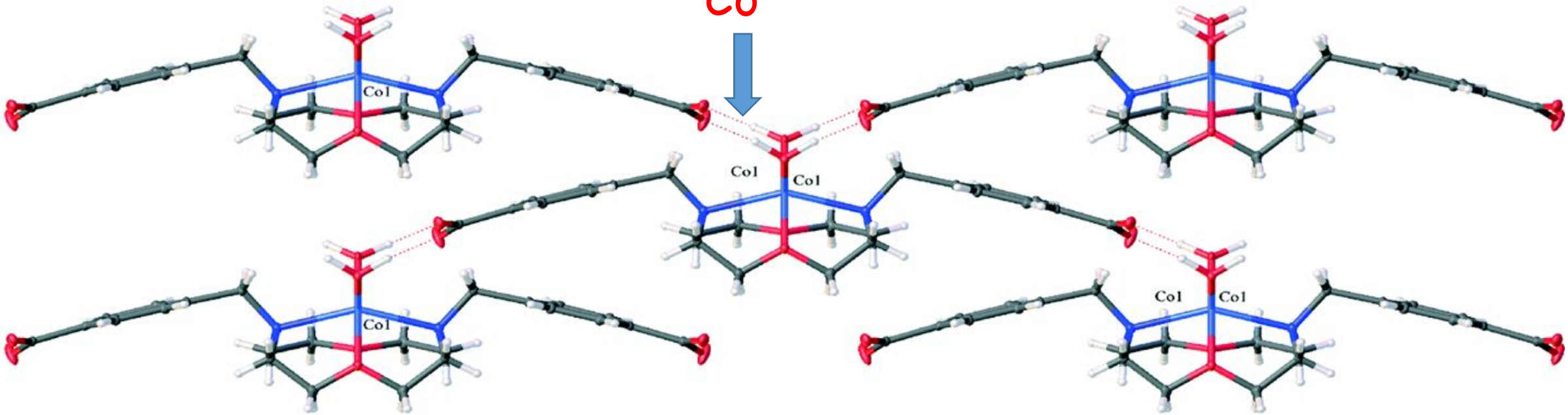


Transition metal diaza crown MOFs-0D



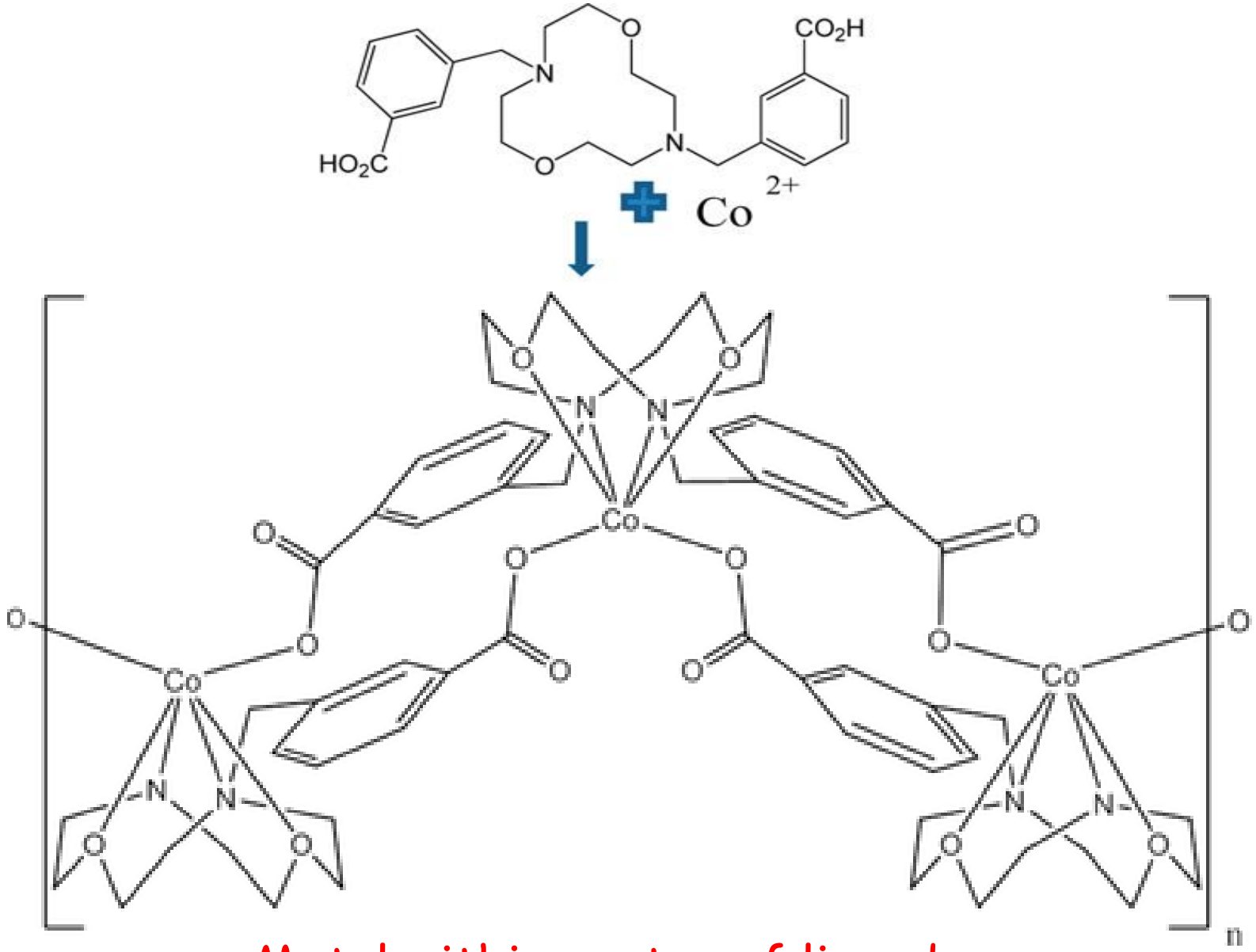
+

Co^{2+}



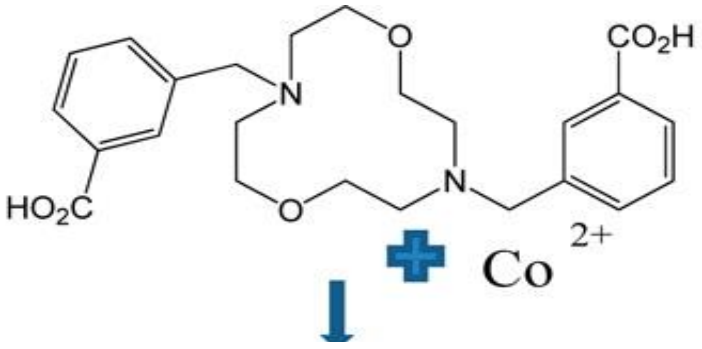
Metal within center of ligand

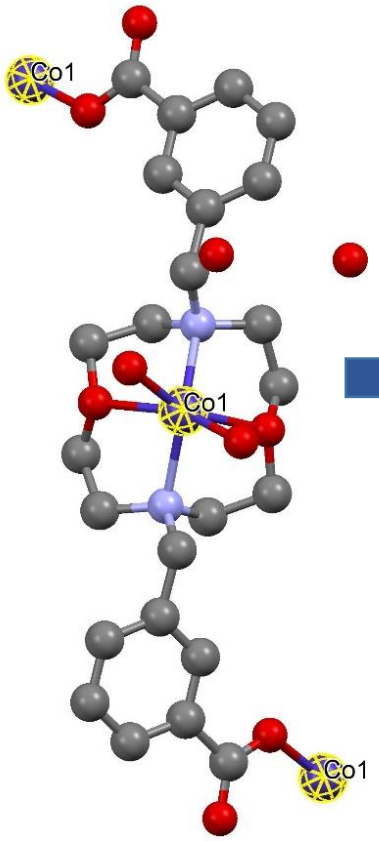
Transition metal diaza crown MOFs-1D

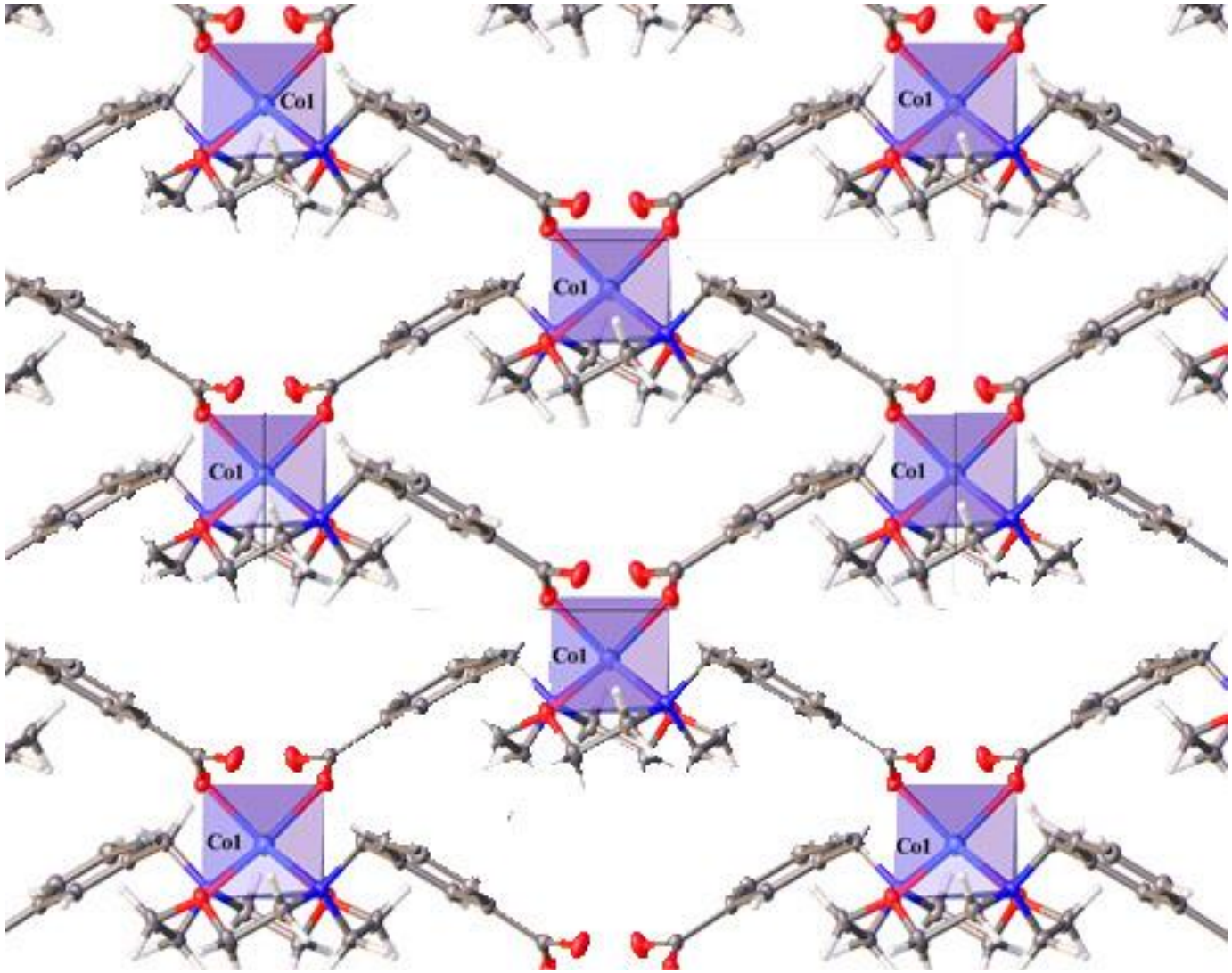


Metal within center of ligand

Transition metal diaza crown MOFs-2D

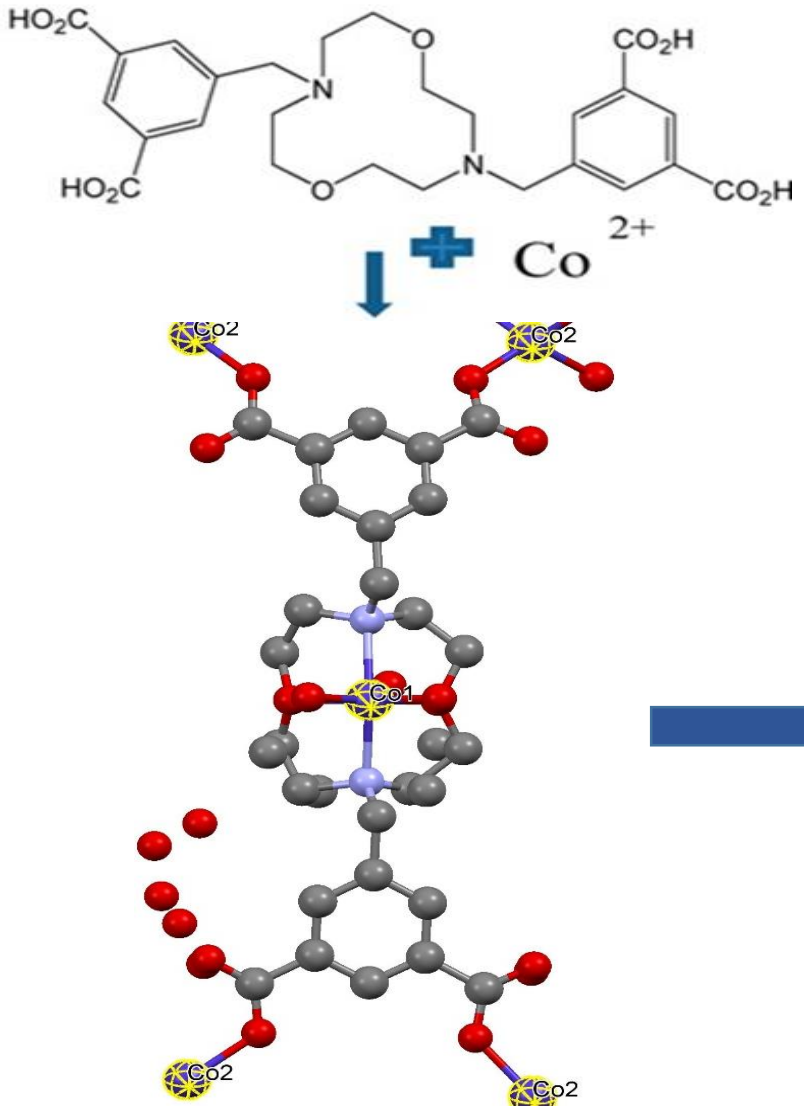


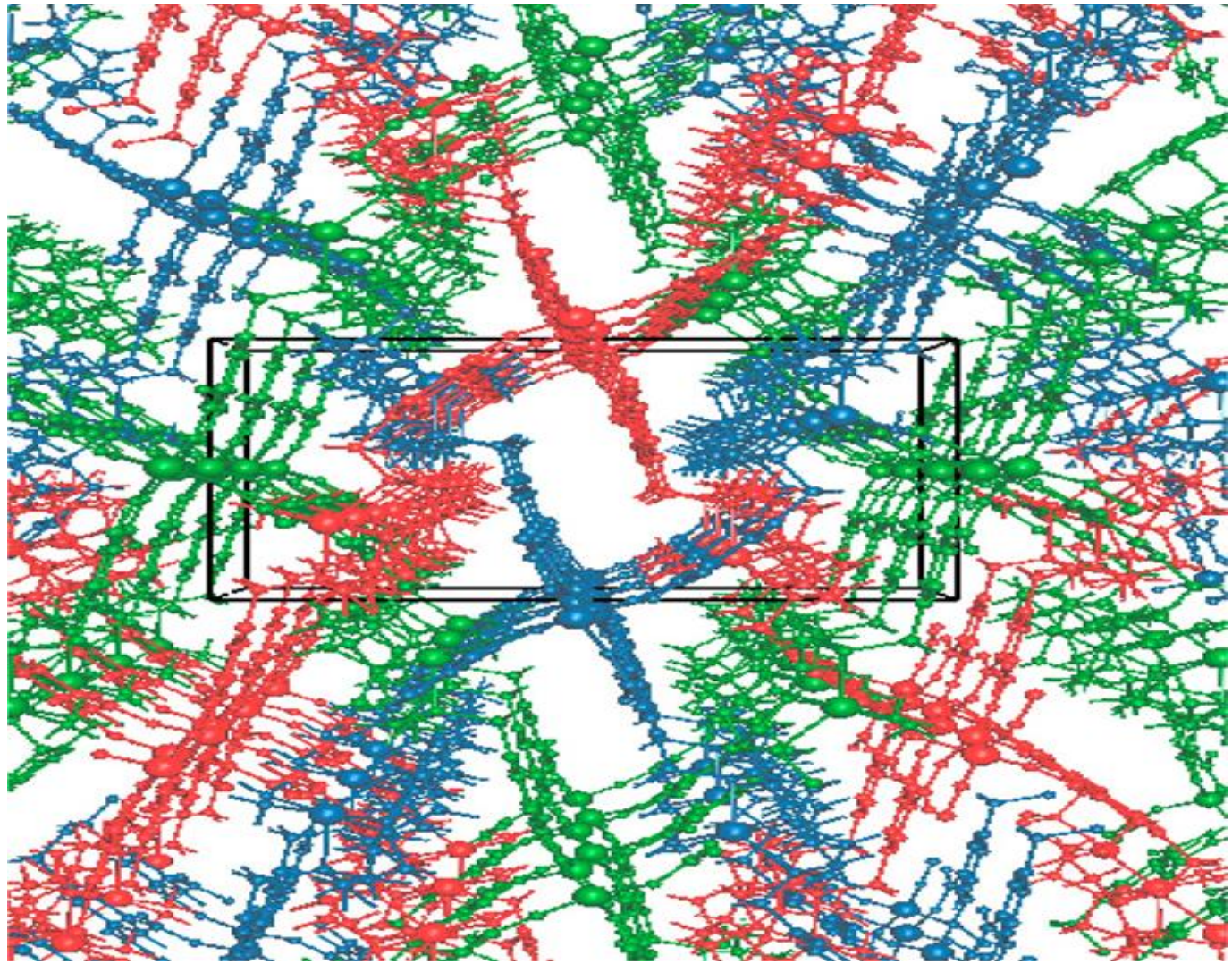




Metal within center of ligand

Transition metal diaza crown MOFs-3D

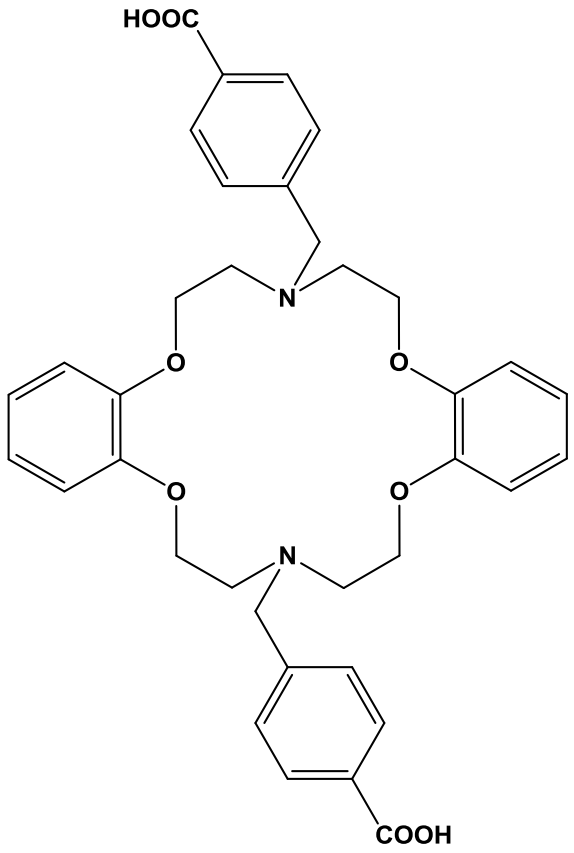


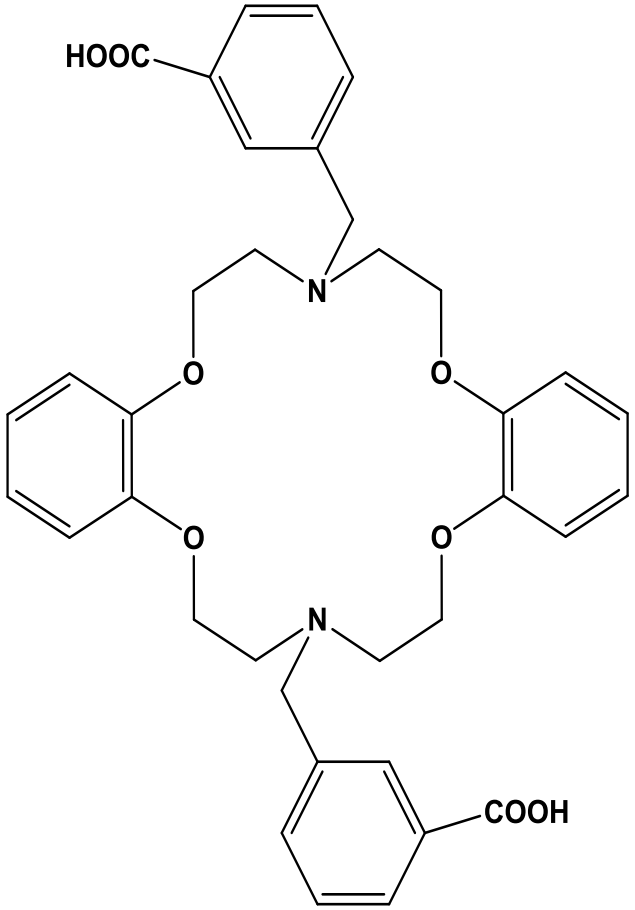


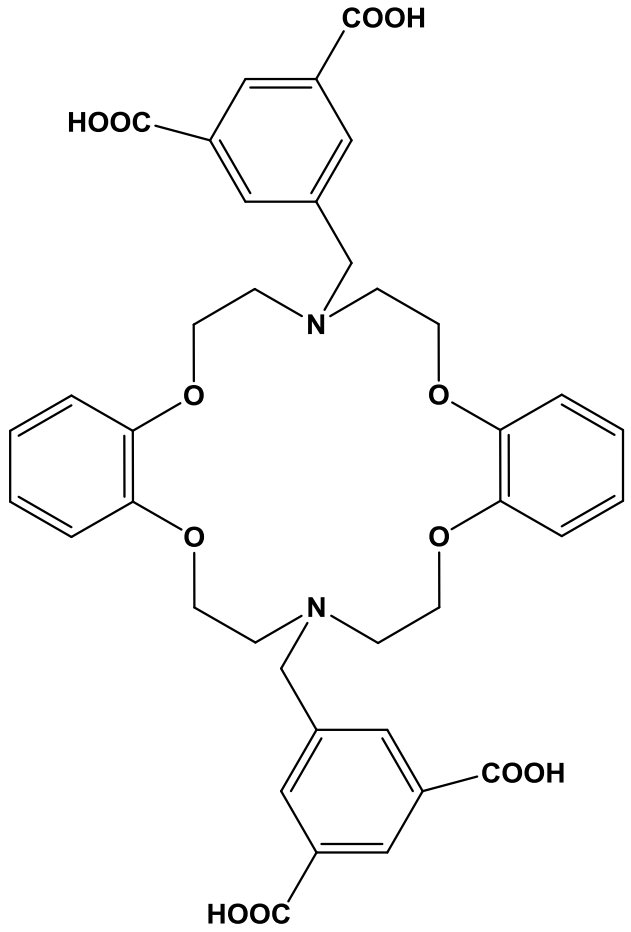
Metal within center of ligand

3 D triply interpenetrating

Modification of diaza-crown ether ligands





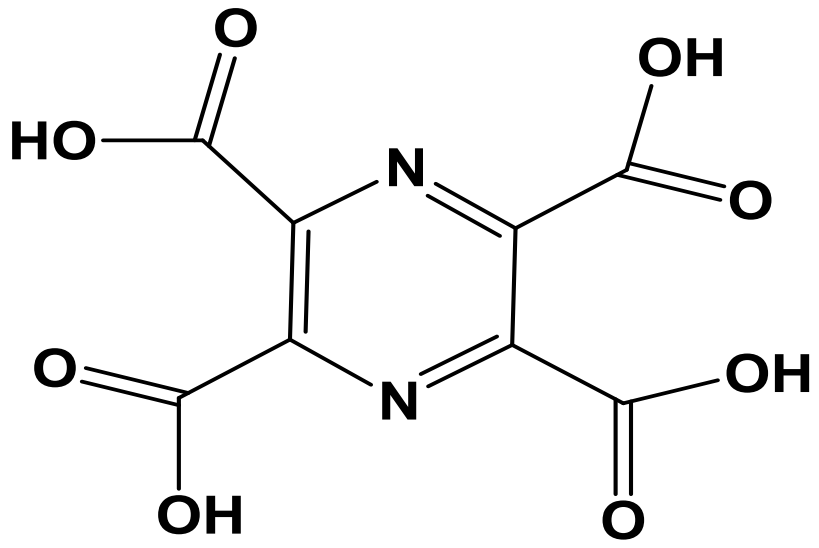


Introducing ligands with side-arms

Nitrogen-containing Pyrazine organic ligand

MOFs with nitrogen containing ligands has shown promise for CO_2

Our approach



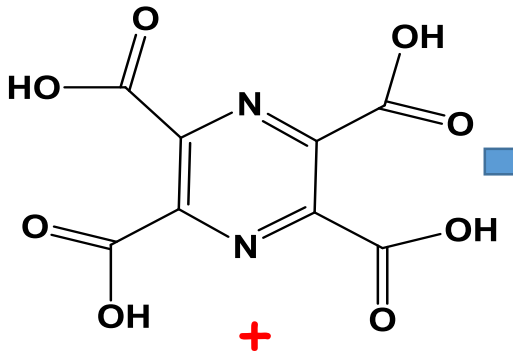
pyrazine-2,3,5,6-tetracarboxylic acid
PZTC

PZTC

- Is Multitopic
- Has High symmetry
- Is Rigid
- Has Ten N/O coordination sites

Focus on f, d, and s blocks metals

MOF based on pyrazine and f-block metal



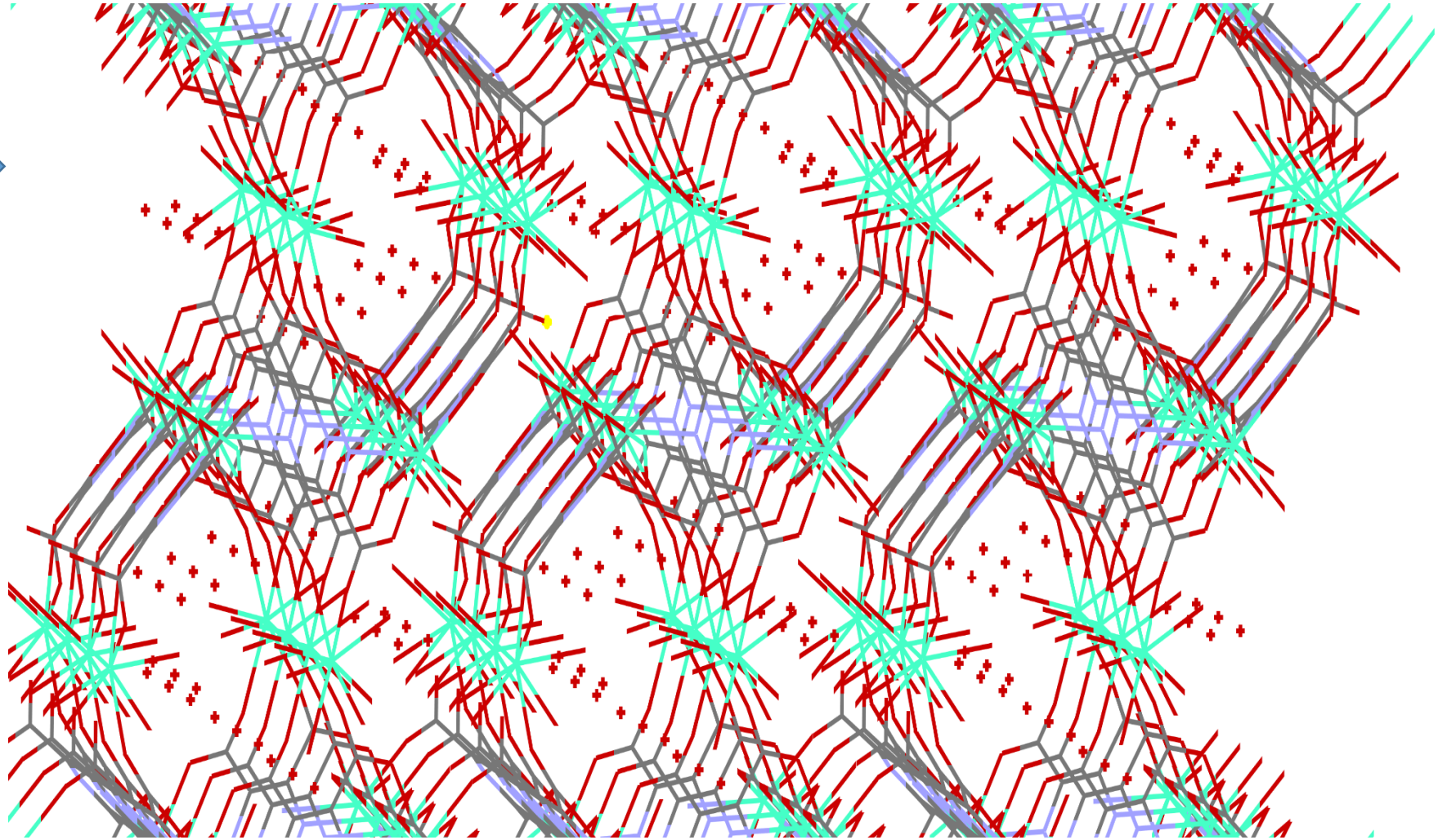
\+

Gd/or Tb

Open framework
Large channels ~ 12Å

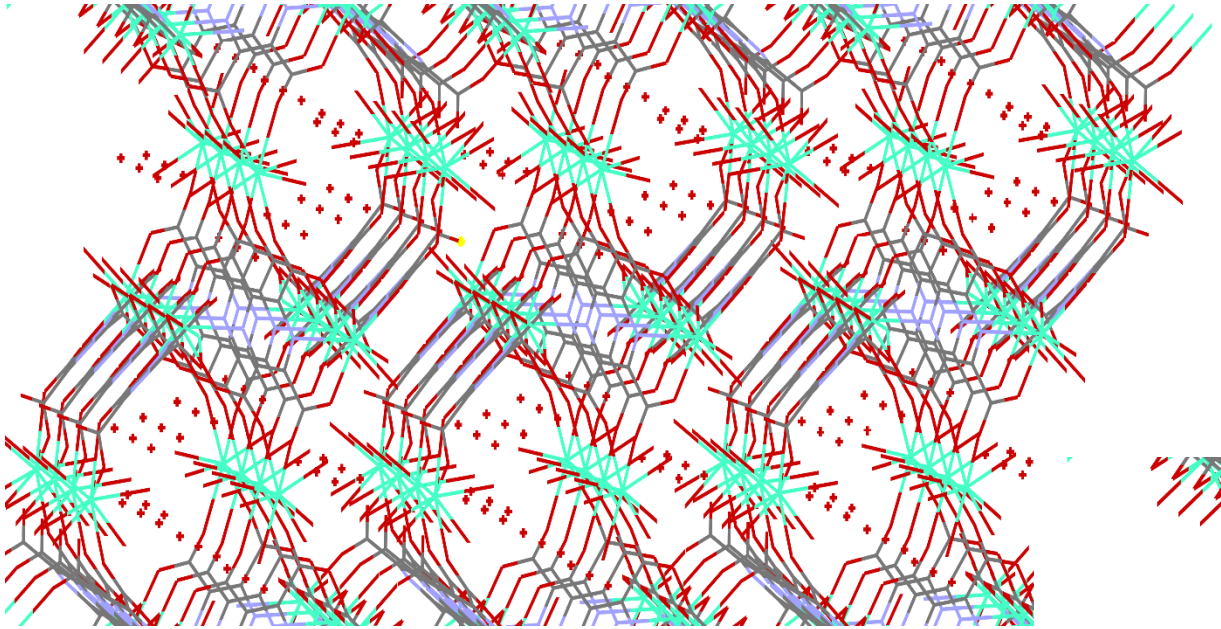
Kinetic diameter CO_2
3.3Å

Channels contain non-coordinating water



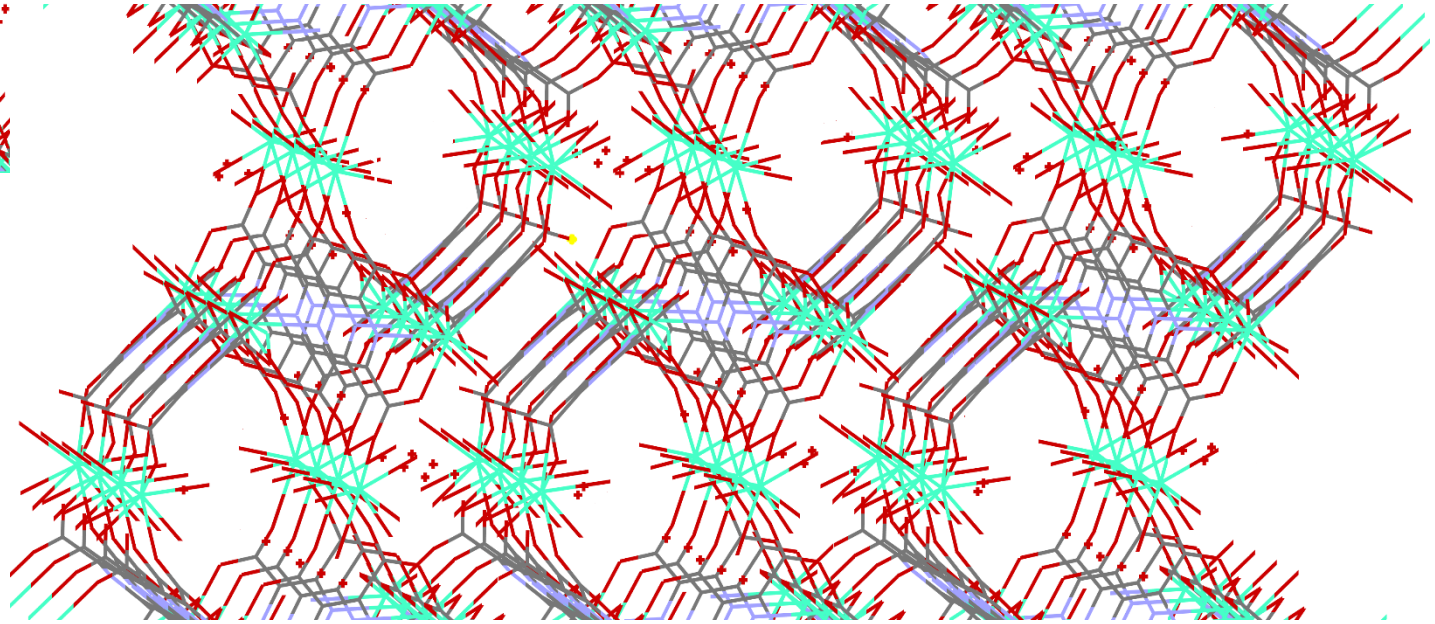
$\{[Ln_4(C_8N_2O_8)_3(H_2O)_{11}]10H_20\}_n$

Activation of f-block pyrazine MOF for CO_2



Solvent Exchange

Ethanol, chloroform

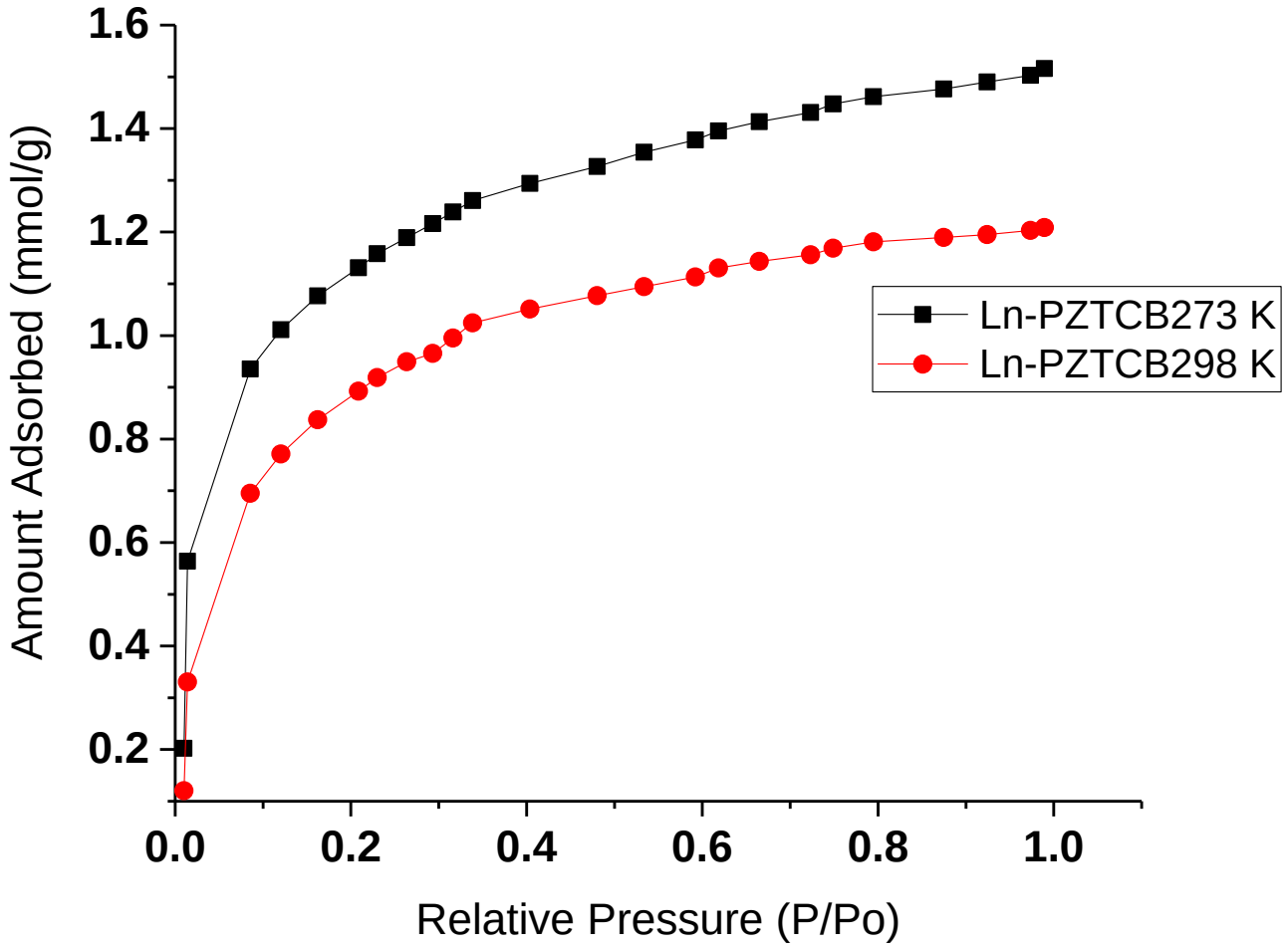


CO_2 adsorption behavior of Ln-PZTC MOF

Micromeritics ASAP 2020

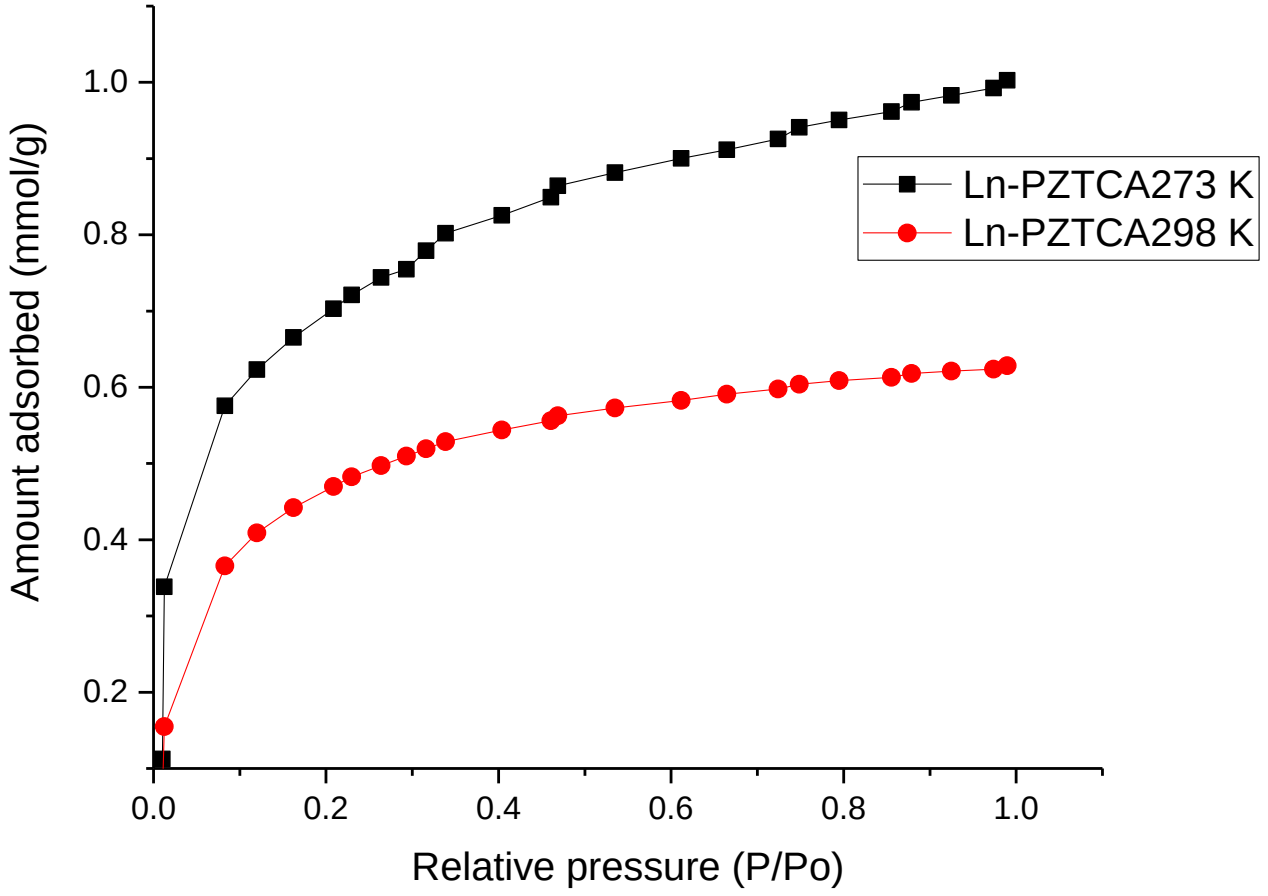
Analysis gas: CO_2, N_2, etc.

CO_2 adsorption isotherms of Ln-PZTC MOF



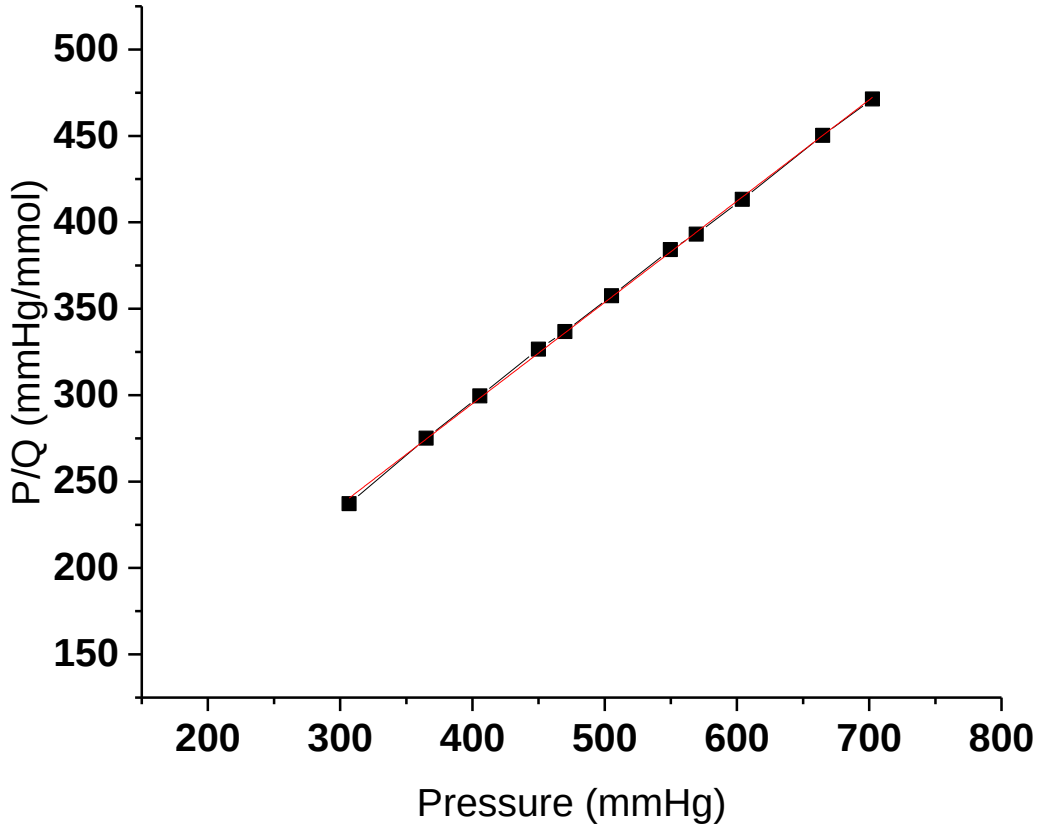
Ln-PZTC after solvent exchange with ethanol

CO_2 adsorption isotherms of Ln-PZTC MOF

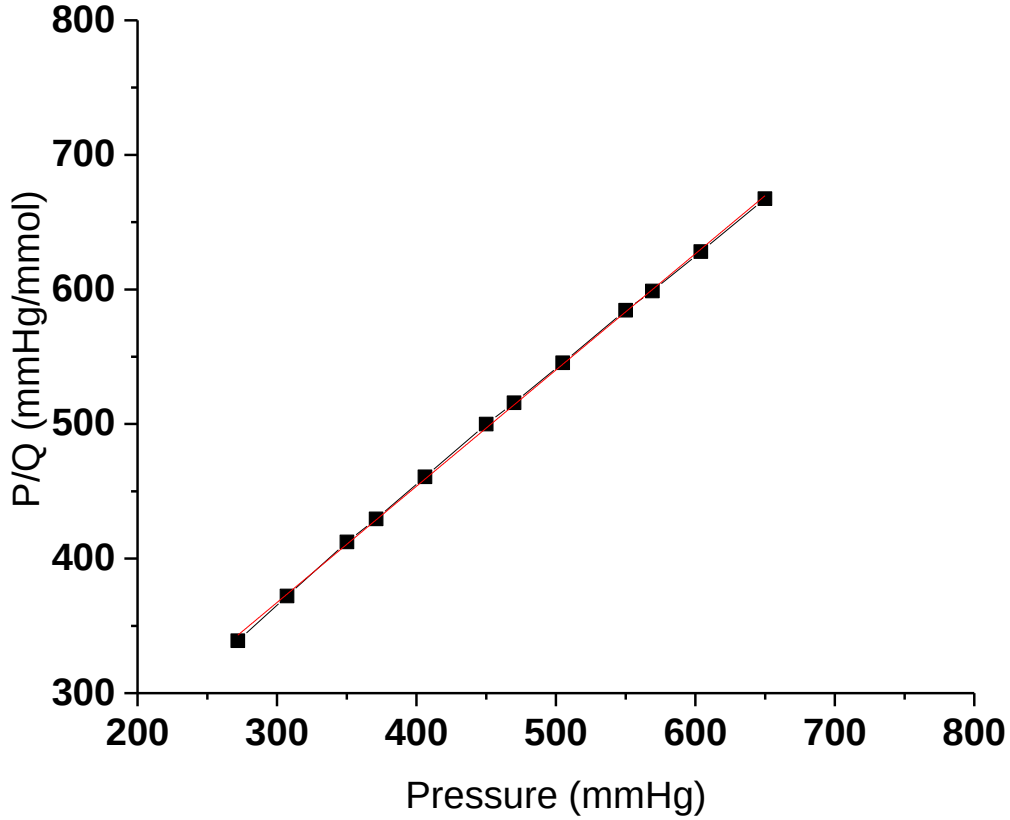


Ln-PZTC after solvent exchange with chloroform

Langmuir isotherm Linear fit



Ln-PZTCA273 K after solvent exchange with chloroform



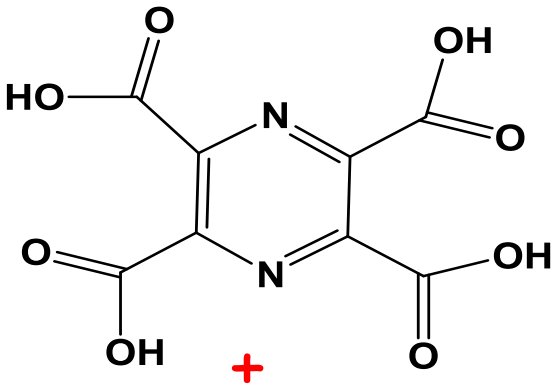
Ln-PZTCB 273 K after solvent exchange with ethanol

CO_2 adsorption behavior of Ln-PZTC MOF

Sample	Solvent exchange	Degas temp (°C)	Analysis Temp (K)	Amount Adsorbed (mmol/g)
LnpztcA273	Chloroform	65	273	1.13
LnpztcA298	Chloroform	65	298	0.66
LnpztcB273	Ethanol	85	273	1.65
LnpztcB298	Ethanol	85	298	1.36

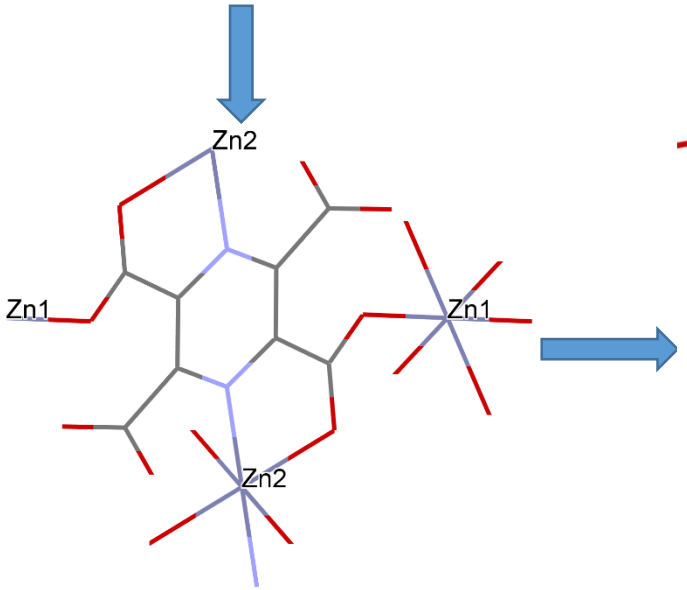
Adsorption capacity improved with ethanol at 273 K and 298 K

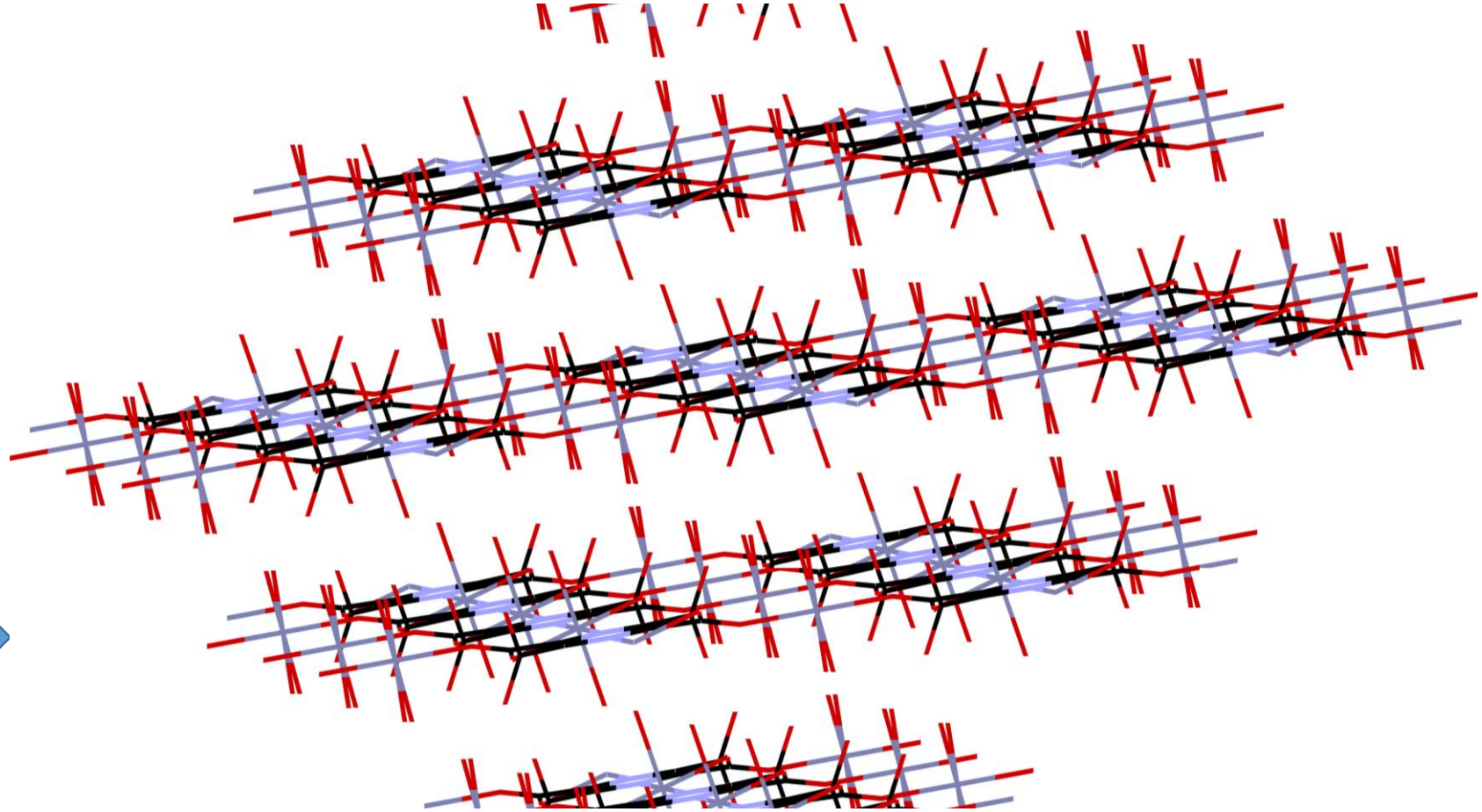
Pyrazine-zinc coordination polymer



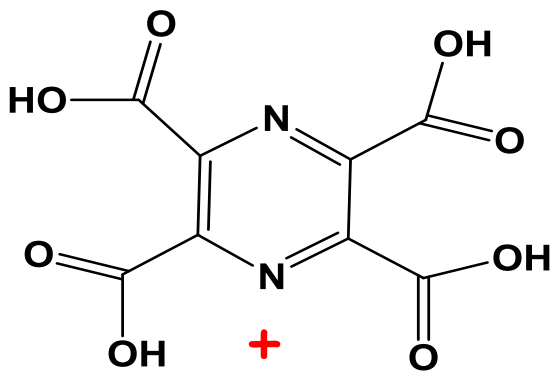
+

Zn^{2+}

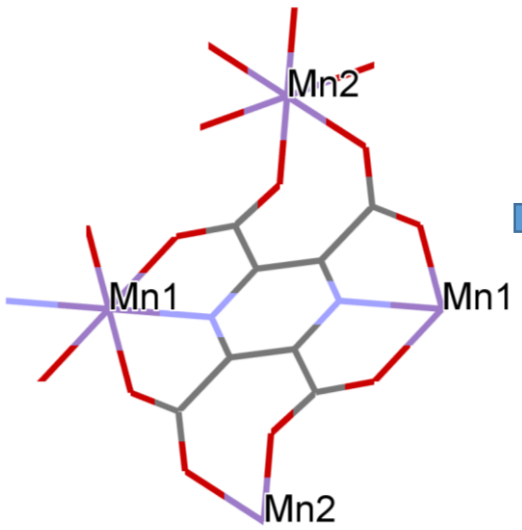


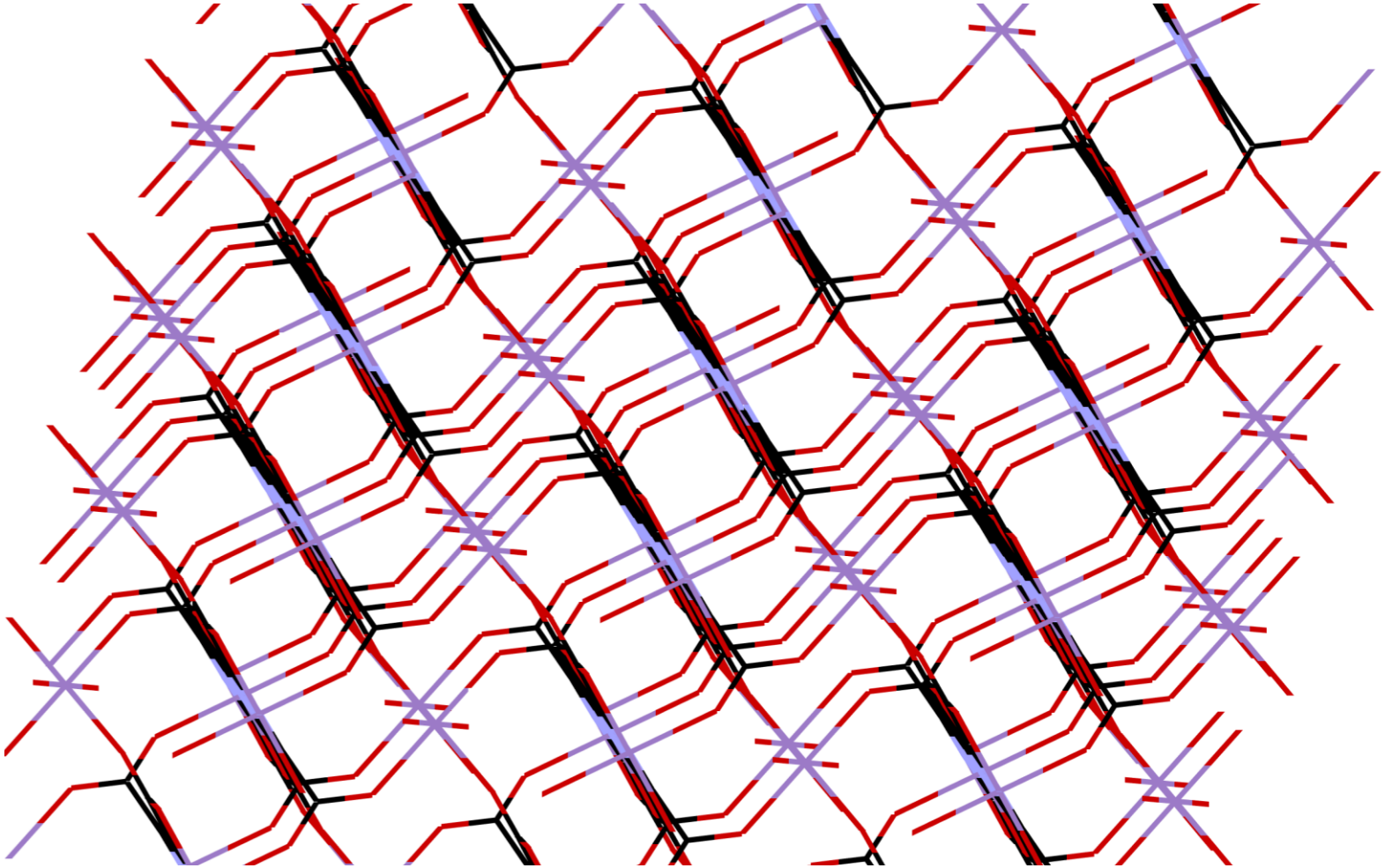


Pyrazine-manganese coordination polymer

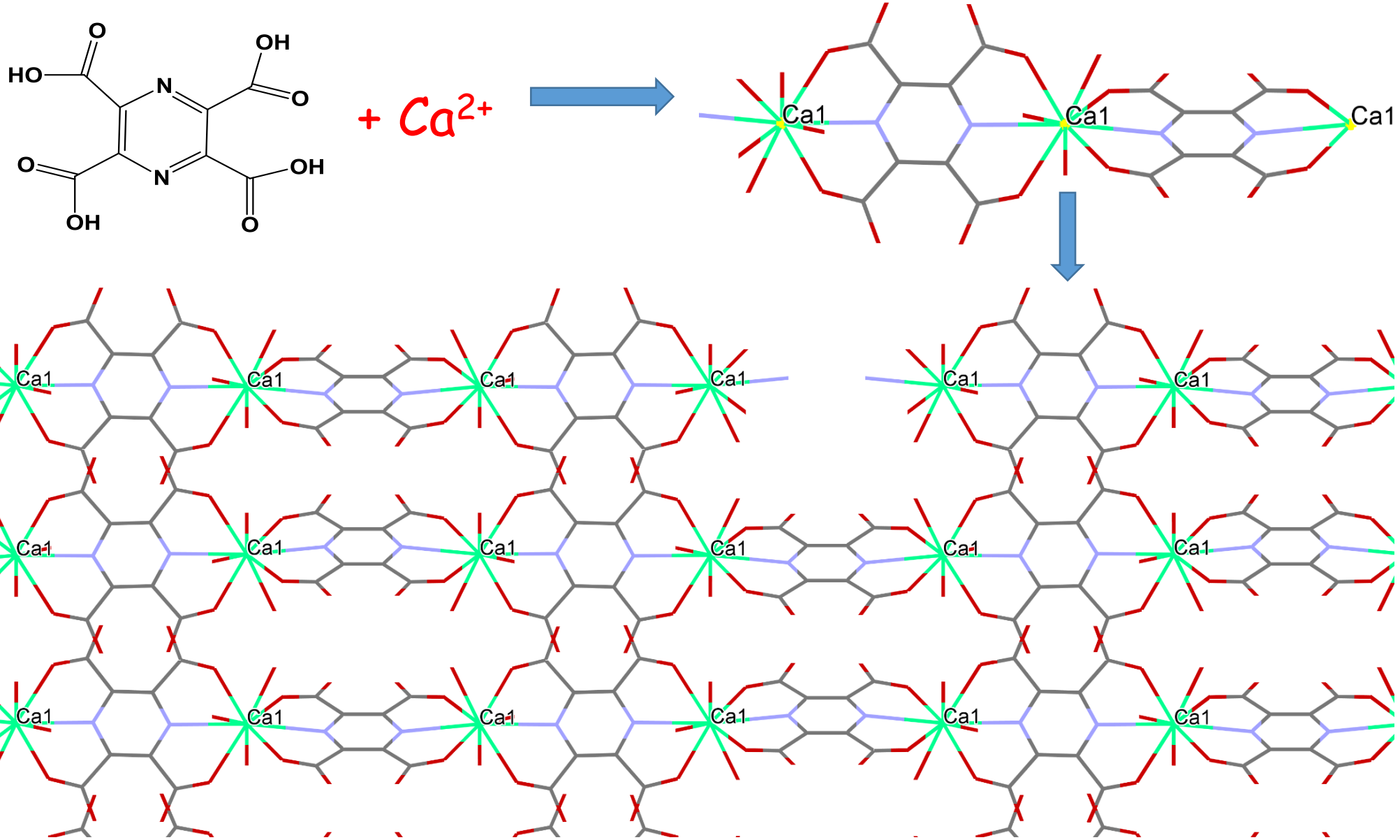


+ Mn^{2+}

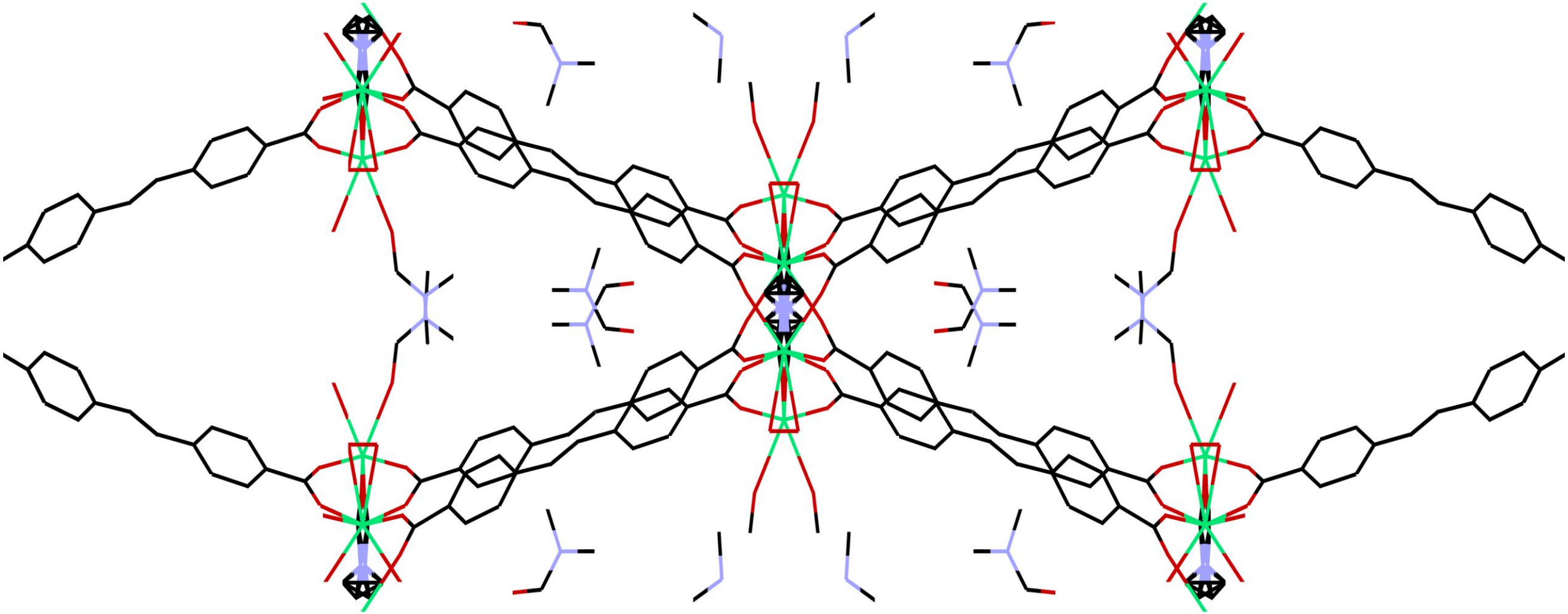




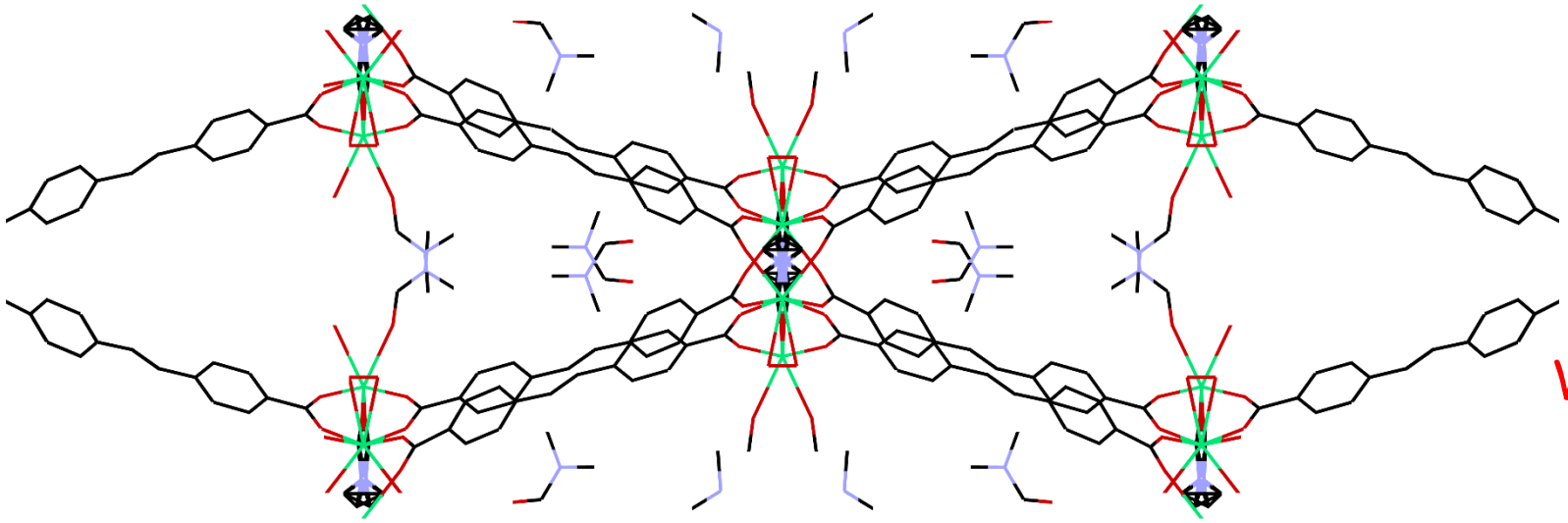
Pyrazine-calcium coordination polymer



Ultra-large Pore Lanthanide stilbene based MOF

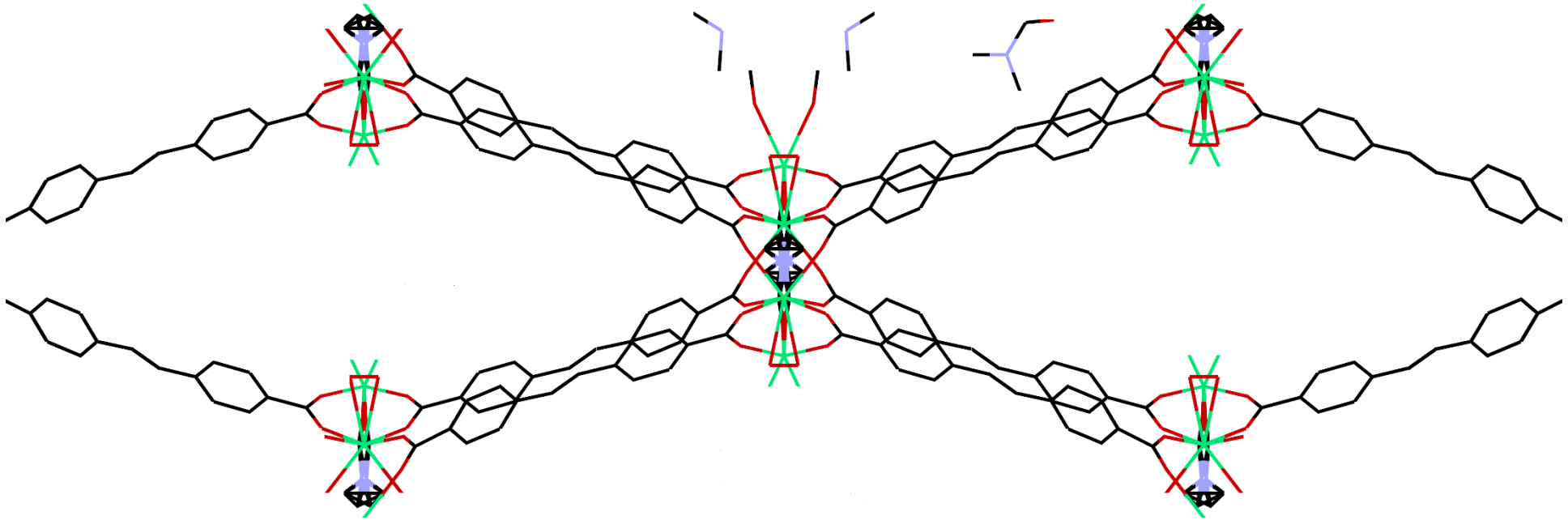


Activation of ultra-large pore Lanthanide stilbene based MOF

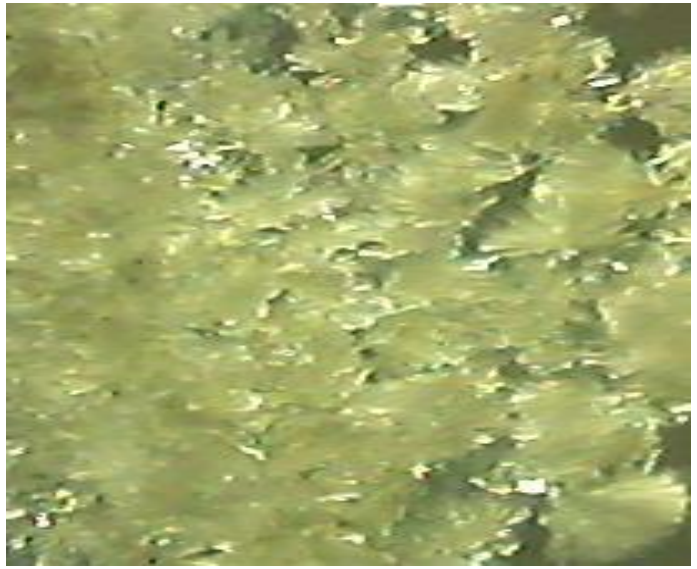


Solvent Exchange

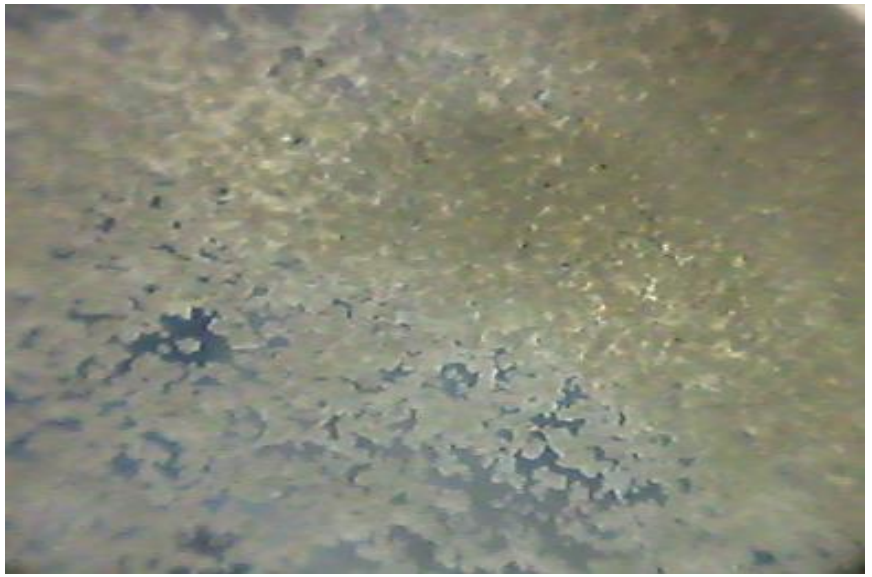
Water or dichloromethane



Optical images of Ln-SDC-AS and solvent exchanged samples



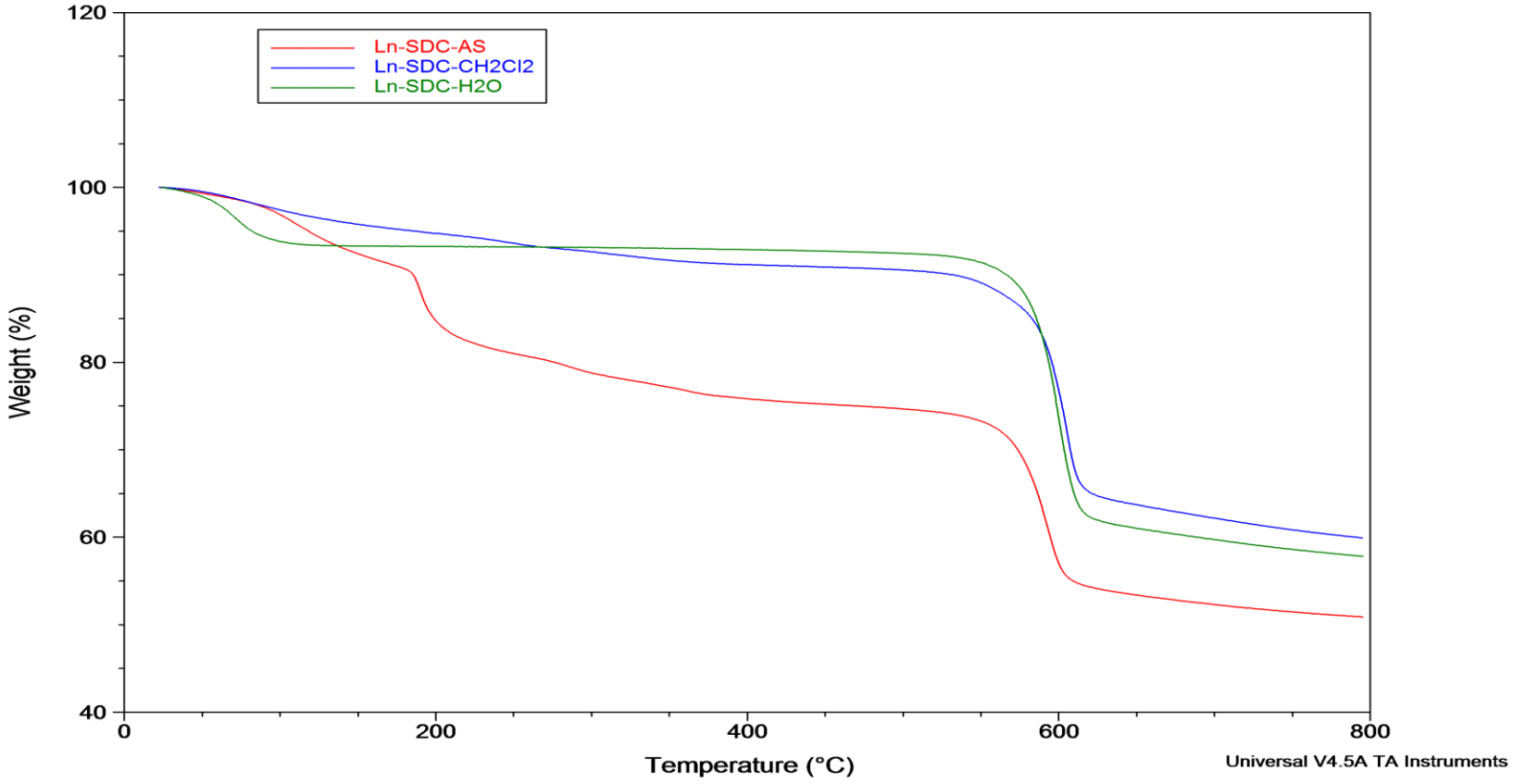
Ln-SDC-AS



Ln-SDC-H_2O

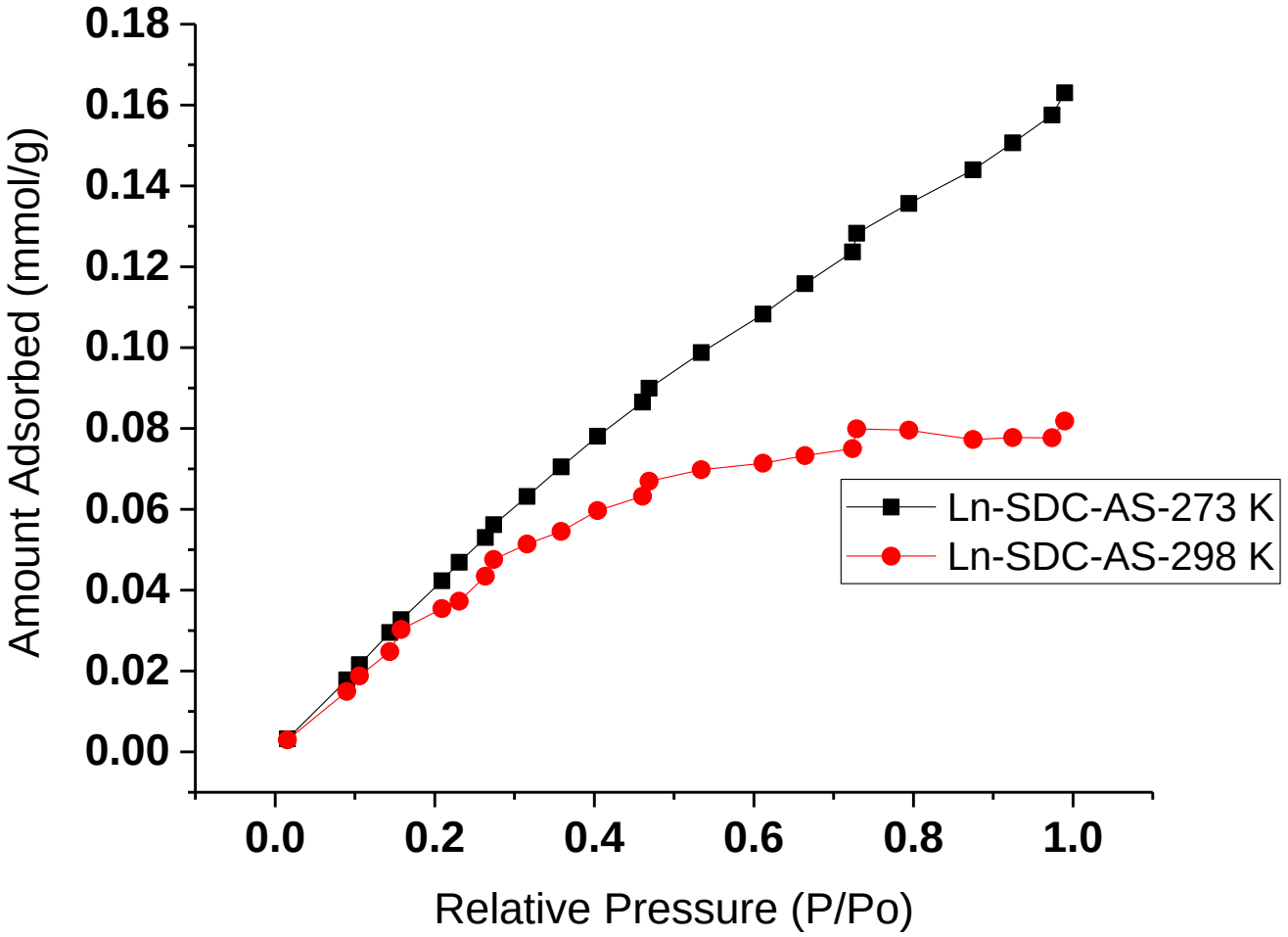
Ln-SDC-CH_2Cl_2

Thermal stability of Ln-SDC-AS and solvent exchanged samples



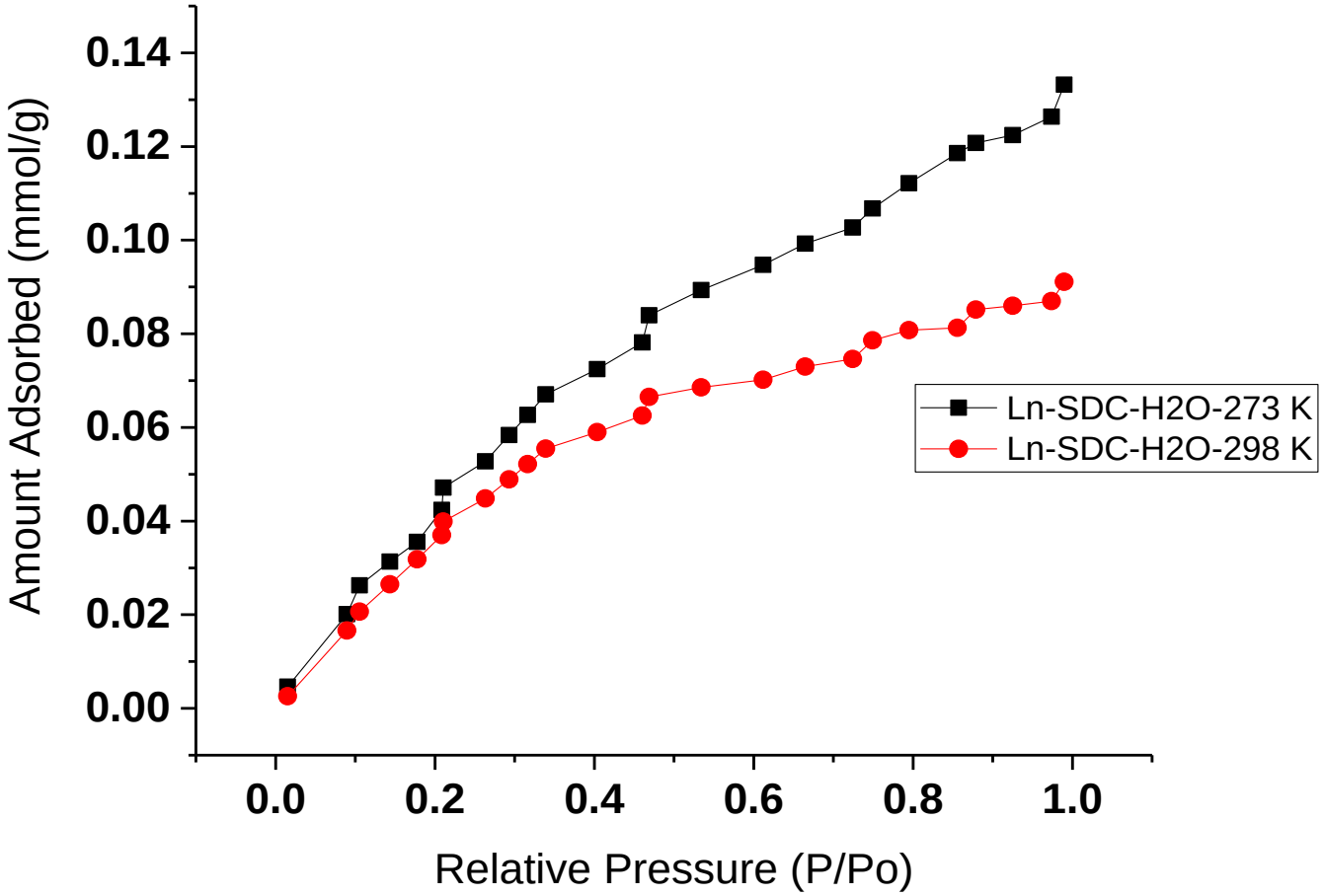
LnSDC-H_2O and LnSDC-CH_2Cl_2 seem more stable than as synthesized

CO_2 adsorption isotherms of Ln-SDC-AS at 273 and 298 K



Step-wise isotherms could indicate changes in framework structure

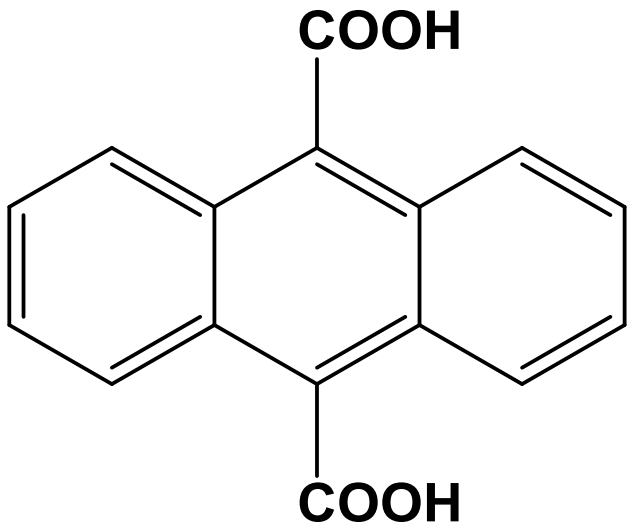
CO_2 adsorption isotherms of Ln-SDC-H_2O at 273 and 298 K

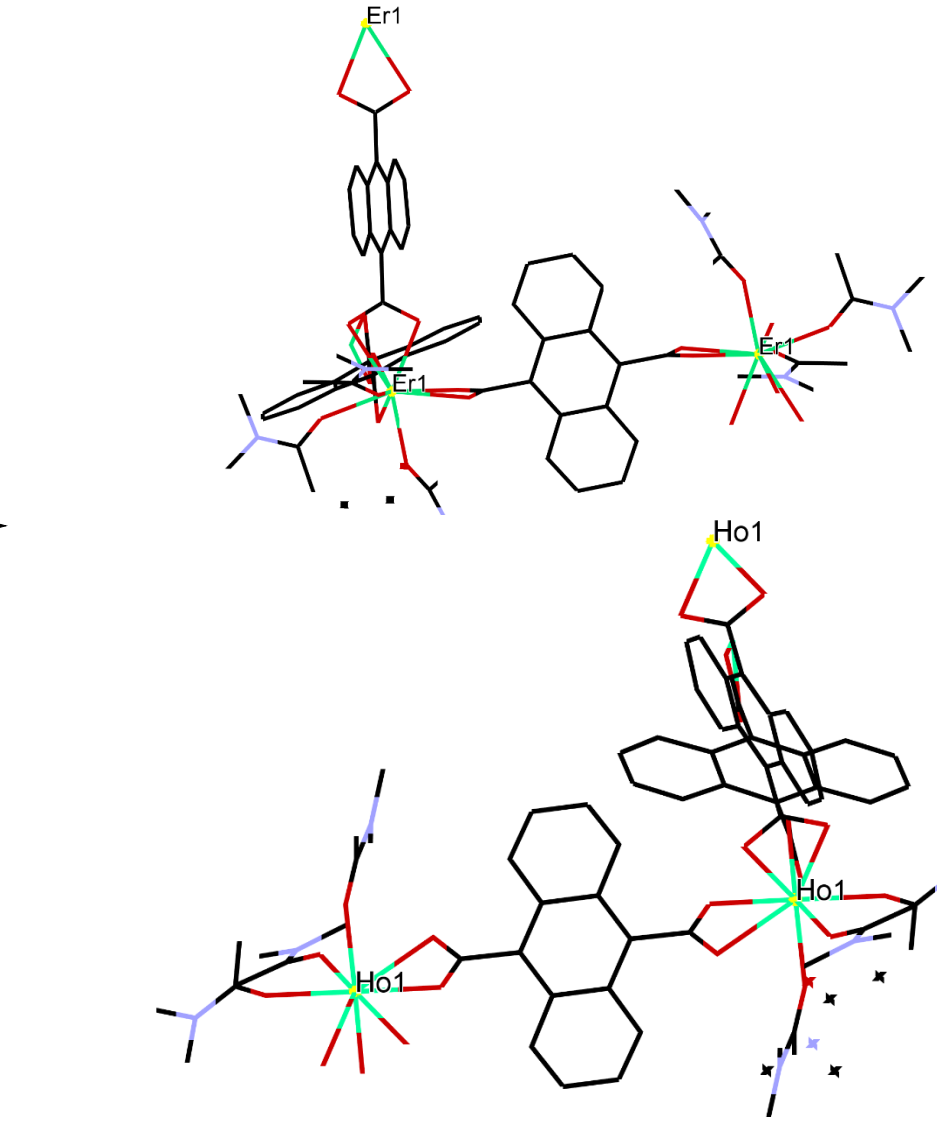


Step-wise isotherms could indicate changes in framework structure

Lanthanide Series of anthracene based MOFs

Ln +

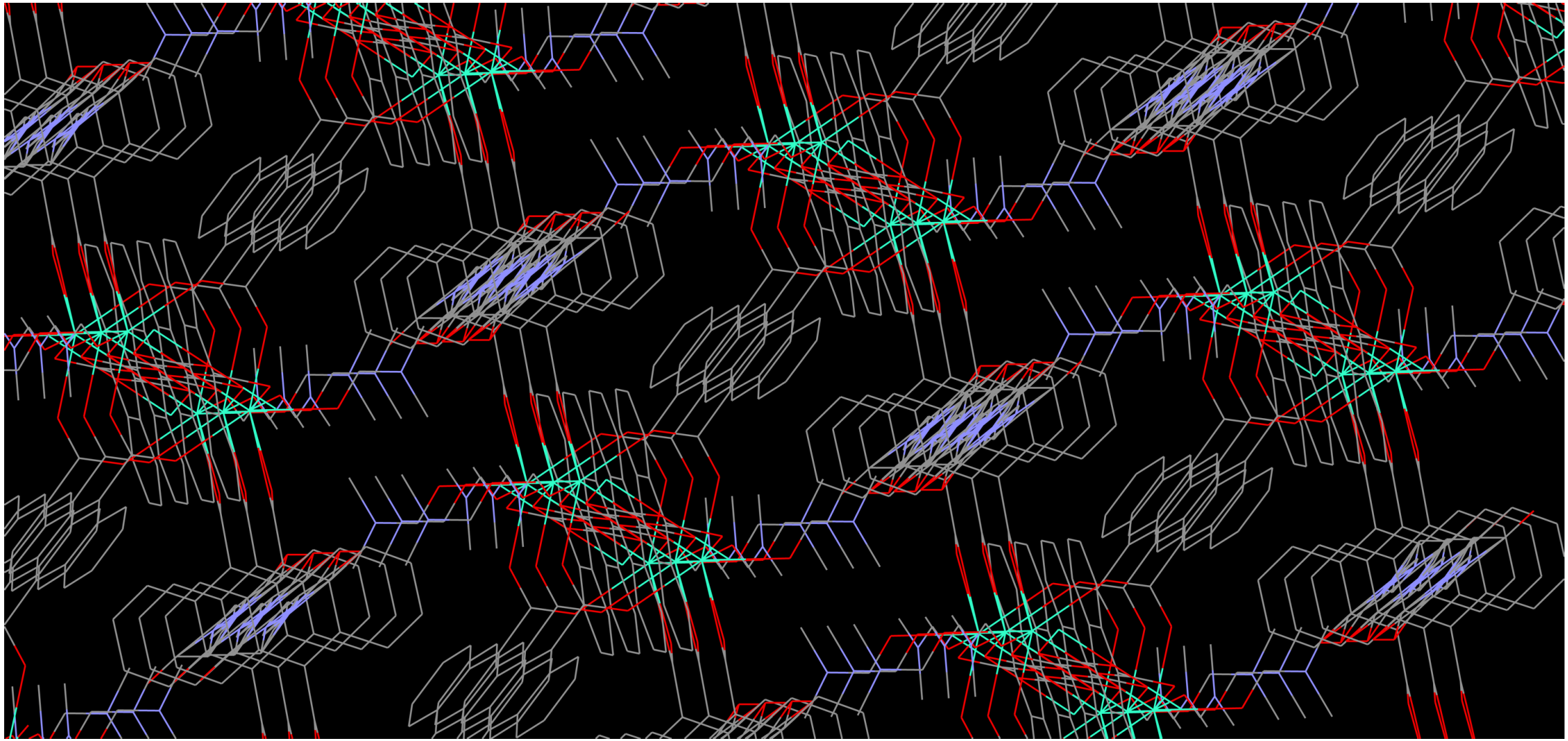




9,10-Anthracene dicarboxylic acid (ADC)

Ln = Pr, Nd, Sm, Gd, Tb, Eu, Dy, Ho, Tm, Er, Yb

Lanthanide series of anthracene based MOFs



Packing diagram showing the 3-D structure of Ln-ADC MOF

Conclusions

- Synthesized new crown-ether based ligands and new MOFs with coordination sites within the center of the ligand; structures will be further developed towards CO_2 adsorption.

- Synthesized new MOFs with of nitrogen-containing ligands that showed CO_2 adsorption capacity; structures will be further developed towards CO_2 adsorption

- Synthesized ultra-large pore stilbene based MOF which showed CO_2 adsorption potential; structures will be further developed towards CO_2 adsorption

- Studied CO_2 adsorption based on activation of metal sites to enhance adsorption

Acknowledgements

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Thank you.