Engineering Accessible Adsorption Sites in Metal Organic Frameworks for CO_2 Capture

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DE-FE0022952

Presentation Outline

- The project team
- Technical background/motivation for the project
- Potential significance of the results of the work
- Relevancy to fossil energy
- Statement of Project Objectives (SOPO)
- Project milestones, budget, and schedule as related to SOPO tasks
- Project management plan
- Project status and preliminary results

Project Team

Principal Investigator: Conrad W. Ingram, Ph. D.
Associate Professor of Chemistry
(Inorganic Chemistry, CAU)

Co-principal Investigator: Dinadanylane Tandabany, Ph. D.
Associate Professor of Chemistry
(Physical/computational chemistry, CAU)

Post Doc: Huayang Lee, Ph. D.

Students:
One graduate (Ph.D.) student
Two project funded undergraduate students
Many leverage-funded undergraduate students

Technical Background/Research Motivation

Department of Energy (DOE) is focused Improving the cost effectiveness of novel technologies for CO_2 capture so that fossil based systems with carbon capture are cost competitive.

Typically flue gas composition:

CO_2	3–15% (by vol.)
O_2	5%
N_2	81%

Adsorbents performance requirements for effective post combustion adsorption technology:

- **chemically stable**
- **high CO_2 capacity and selectivity**
- **easily regenerated with minimal energy input**
- **easily synthesized with low capital cost**

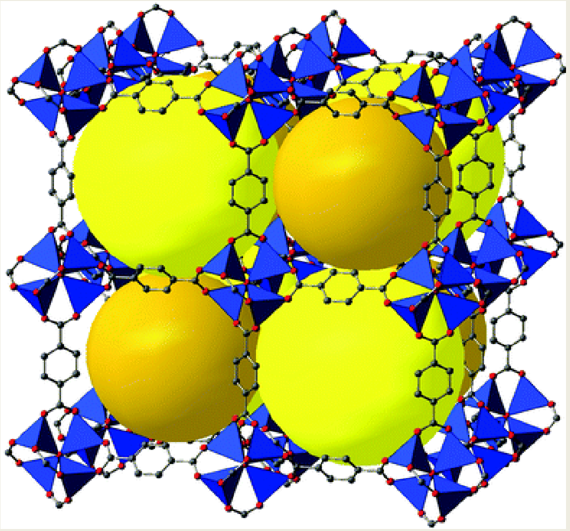
http://energy.gov/fe/science-innovation/carbon-capture-and-storage-research/carbon-capture-rd

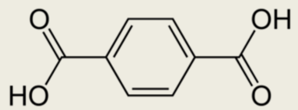
http://www.alrc.doe.gov/publications/proceedings/01/carbon_seq/p9.pdf

Technical Background/Research Motivation

Metal organic framework as CO_2 adsorbent

MOF = covalent linkage of metal ions as nodes + organic ligand as linker
(also defined as 3D coordination polymer with permanent porosity)





Commonly used ligand:
benzene dicarboxylate

Attributes

- Unprecedented high surface area –up to 5000 m^2/g
- Tunable surface chemistry and pore size
- Thermally stability (variability)
- Potential large concentration of adsorption sites

Drawbacks

- Limited accessible to sites
- Pore window less than 2 nm
- Thermally stability (variability)

http://yaghi.chem.ucla.edu/staticpages/research/01MOFs

Technical Background/Research Motivation

A combination of amine functionality and unsaturated metal sites to increase adsorption capacity

Examples of MOFs with metal center as CO_2 adsorption sites

Chemical Formula	Common Name	BET (m_2/g)	Langmuir (m_2/g)	CO_2 (Wt. %)	Press. (bar)	Temp (K)
$Mg_2(DOBDC)$	Mg-MOF-74	1800	2060	35.2	1	298
$Zn_4O(BBC)_2(H_2O)_3$	MOF-200	4530	10400	70.9	50	298

DOBDC: 2,5-dioxido-1,4-benzenedicarboxylate

BBC: 4,4′,4′′-(benzene-1,3,5-triyl-tris(benzene-4,1-iyl))tribenzoate

Furukawa H, et al., Science, 329, 424–428 (2010).
Britt D, et al. Proc Natl Acad Sci.USA ,106,:20637–20640 (2009).

Objectives

To synthesize metal organic framework (MOFs) with improved sites accessibility, thus enhanced CO_2 adsorption and selectivity properties.

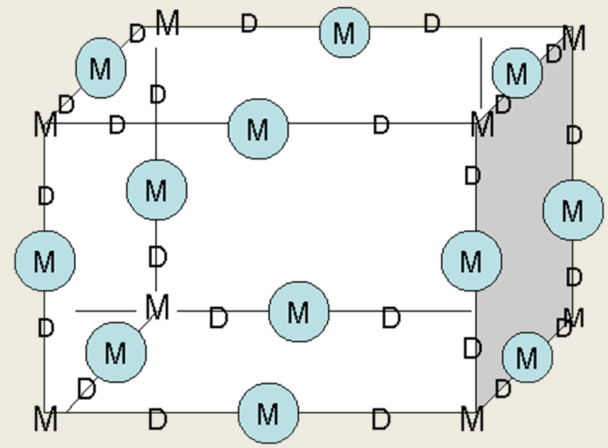
Specific objectives:

- **Synthesize MOFs with metal ions adsorption sites in more accessible locations**
- **Synthesize MOFs with nitrogen/amine containing-ligand linker as a possible improved alternative to amine-functionalized MOFs; and**
- **Understand the nature of the adsorption sites and mechanism(s) by computational studies relevant to the adsorption of CO_2 within the metal organic frameworks.**

Relevance-Outcomes and Potential Impacts

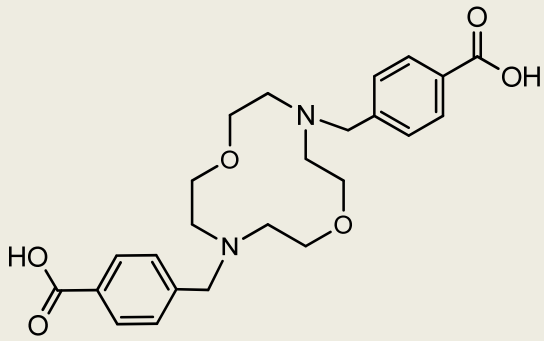
- **The proposed research supports the Department of Energy's (DOE) Office of Fossil Energy and the National Energy Technology Laboratory (NETL) mission**
  - **Advances in the science of coal/fossil fuel technologies, specifically carbon capture.**
- **The research will guide rational design/synthesis strategies towards producing advanced sorbents for CO_2 capture.**
- **Successful CO_2 adsorbent materials will have tremendous industrial and environmental (CO_2 mitigation) impact.**
- **Provide research opportunities for graduate and undergraduate students in the fields of chemistry, materials and science related to the use of fossil energy resources.**
  - **Develop the next generation of US scientists**

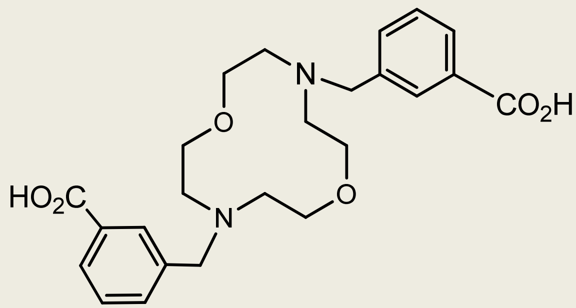
Approach

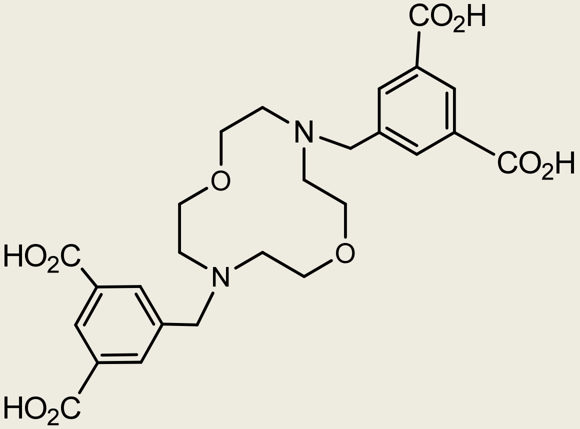


- Position metal in more accessible location.
- Increase thermal stability of resulting MOFs.
- Explore the effects of :
  - ➢ chemical compositions of synthesis mixtures (such as, organic linkers/functionalities and metals)
  - ➢ the synthesis conditions (such as temperature, and solvents)

Diaza crown ethers complexes as organic linkers







SCOPE OF WORK

Five main activities:

1. **Evaluate the CO_2 adsorption properties of diazo crown ether polycarboxylates based MOFs that were recently synthesized in our laboratory.**

2. **Synthesize new MOFs based on an expanded series of diazo crown ethers and judicious choice of metal ions, and, evaluate their CO_2 adsorption properties.**

3. **Evaluate the CO_2 adsorption properties of MOFs synthesized with the nitrogen-containing pyrazine linker, recently synthesized in our laboratory.**

4. Investigate the nature of the sites and mechanism(s) of adsorption by conducting density functional theory (DFT) - based computational studies relevant to the adsorption of CO_2 within the metal organic frameworks:

- Density functional theory (DFT) level using double -z basis set with appropriate effective core potential (ECP) for metal ion will be employed for designing the materials and the capture of CO_2.

- A double-layered ONIOM (Our own N-layered Integrated Molecular Orbital and molecular Mechanics) approach will be employed in the benchmarking calculations.

- The DFT level will be used for the important region (adsorption site) of CO_2 adsorption and semi-empirical method will be used for rest of the region and larger molecular systems of the proposed MOFs.

Tasks

Task 1.0 Project management and planning

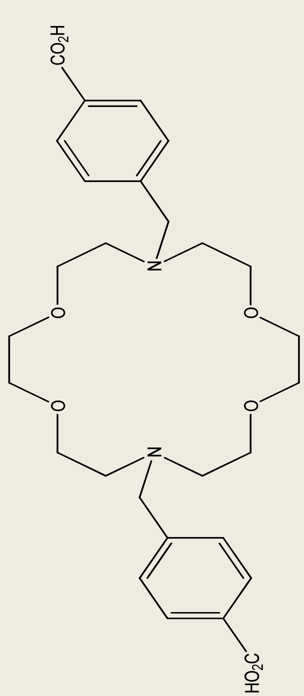
- Update the Project Management Plan
- Initiate project planning during kick-off meeting

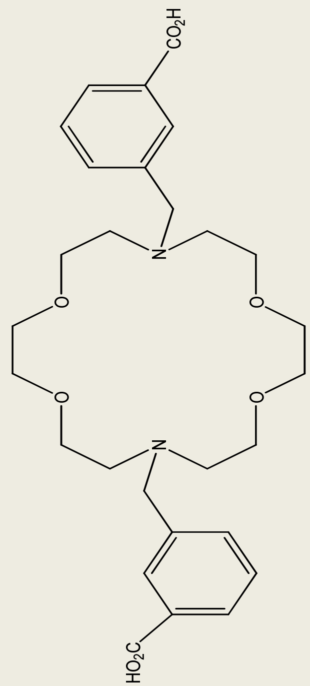
Task 2.1 CO_2 adsorption studies on our recently synthesized diaza crown ether carboxylates MOFs

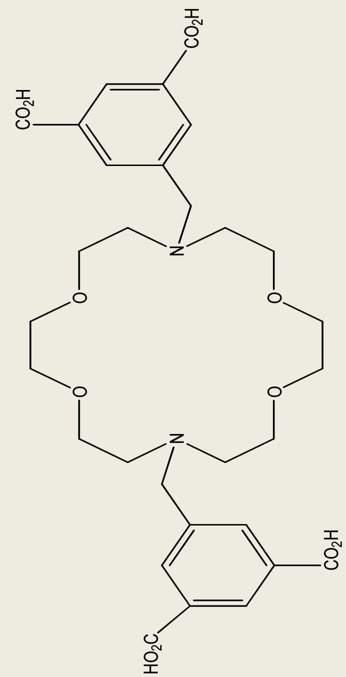
- Conduct CO_2 adsorption studies on the MOFs at temperatures between 273K and 298K and multiple dosing pressures between 0 and 1 atm.
- Generate single component adsorption-desorption isotherms and determine adsorption capacities from them.
- Determine selectivity factor from CO_2/N_2 ratios at the same temperature and pressure.

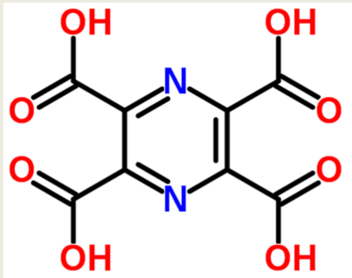
Task 2.2 Synthesis of MOFs with expanded diazo crown ether carboxylates

- Synthesis of diazo crown ethers polycarboxylates
- Synthesis of MOFs using expanded ligands of the ligands plus metals
- CO_2 adsorption properties and the CO_2/N_2 selectivity studies









- The metal ions will include at minimum s-block (Mg^{2+} and Li^{+}), transition (including, Mg^{2+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Cu^{2+} and Ni^{2+})

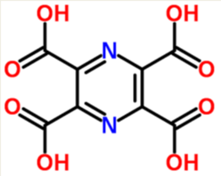
Task 2.3 Synthesis of MOFs with diazo crown ether carboxylates containing side-arm substituents towards increasing stability

Use diazo crown ethers polycarboxylates, with side arm substituents to:

- Avoid interpenetrating structures, and to improve the thermal stability of the resulting MOFs, and used in MOFs preparation.

- Impart hydrophobic characteristics, thus aiding in the prevention of structural collapse following the thermal desorption of intercalated synthesis-solvent molecules.

Task 2.4 Evaluation of the CO_2 adsorption properties of MOFs synthesized with a nitrogen-donor pyrazine ligand



Task 3.0 Investigate the nature of the sites and mechanism(s) of adsorption by conducting density functional theory (DFT) -based computational studies relevant to the adsorption of CO_2 within the metal organic frameworks.

Characterization of the resulting framework structures

• X-Ray crystallography:	MOFs framework structure and composition
• Powdered X-ray diffraction:	Phase crystallinity and phase purity
• Porosimetry:	Surface area and pore size, pore volume
• Thermogravimetric analysis:	Thermal behavior
• Infrared spectroscopy:	Chemical functionalities
• Porosimetry/ Surface area analyzer	Adsorption studies of CO_2 and nitrogen
• Inductively coupled plasma/ mass spectrometry:	Metal content

Tasks Schedule	Year 1				Year 2				Year 3			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
1.0 Project planning (select personnel, literature review, experiments design, procure chemicals).	+											
2.1 Adsorption of CO_2 on three crown ether polycarboxylate MOFs already synthesized in our lab		+	+	+	+	+						
2.2 Synthesis of new s &d block metal, expanded and side arm crown ether polycarboxylate			+	+	+	+						
2.3 Adsorption of CO_2 on new s & d block, metal expanded and side arm crown ether polycarboxylate MOFs					+	+	+	+	+	+	+	

Tasks and Schedule	Year 1				Year 2				Year 3			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
2.4 Adsorption studies of CO_2 on new pyrazine based MOFs			+	+	+	+						
3.0 Theoretical and computational studies of MOFs adsorption of CO_2 on MOFs			+	+	+	+	+	+	+	+	+	+
4.0 Periodic reports to DOE	+	+	+	+	+	+	+	+	+	+	+	+

Budget

CATEGORY	Year 1 Costs	Year 2 Costs	Year 3 Costs	Total Costs	Project Costs %
a. Personnel (include students)	$41,507	$41,867	$41,188	$124,562	49.8%
b. Fringe Benefits	$5,673	$5,776	$5,583	$17,032	6.8%
c. Travel	$2,270	$2,270	$2,270	$6,810	2.7%
e. Supplies	$2,468	$2,876	$1,446	$6,790	2.7%
h. Other Direct Costs	$2,120	$2,120	$1,855	$6,095	2.4%
Total Direct Costs	$54,038	$54,909	$52,342	$161,289	65%
i. Indirect Charges	$29,721	$30,200	$28,788	$88,709	35.5%
Total Project Costs	$83,759.6	$85,108	$81,130	$249,998	100%

Facilities and Equipment

Research Center for Science and Technology

Clark Atlanta University

- A private, historically black institution (HBCU)
- Formed in 1988 with the consolidation of ***Clark College*** (founded in 1869) and ***Atlanta University*** (founded in 1865).

CAU Thomas W. Cole, Jr. Research Center for Science and Technology

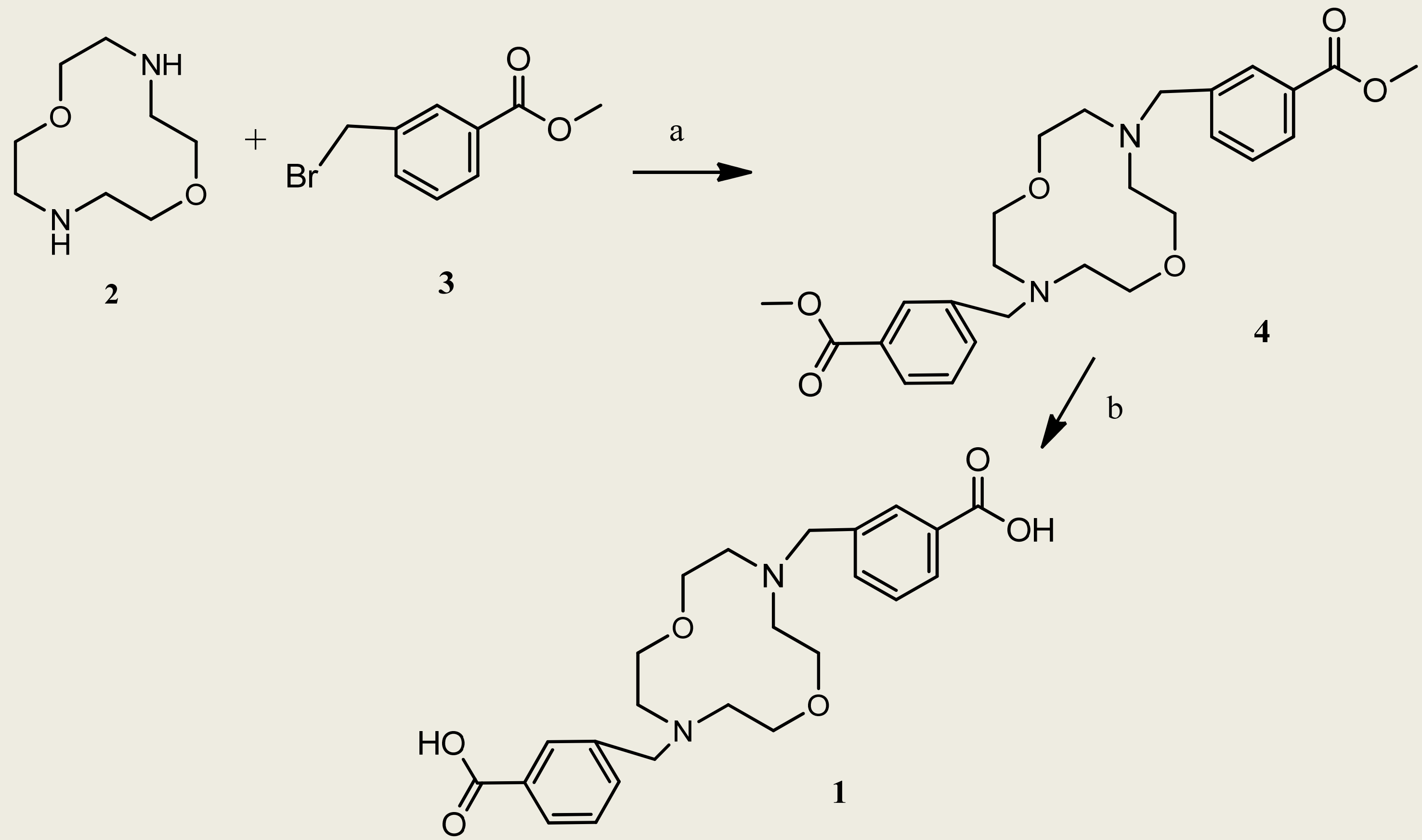
- Approximately 240,000 sq. ft. of state-of-the-art laboratories

Facilities and Equipment

Project status

- Project commencement October 1, 2014
- One Post Doc selection in process through leveraging from CAU CREST
- One current undergraduate selected: Ms. Kimberli Hill
- 2nd undergraduate student will be selected in November, 2014
- Graduate student to be selected in November 2014
- Background/literature review has commenced
- Laboratory training and familiarity with MOF synthesis and characterization procedures by student(s) have commenced

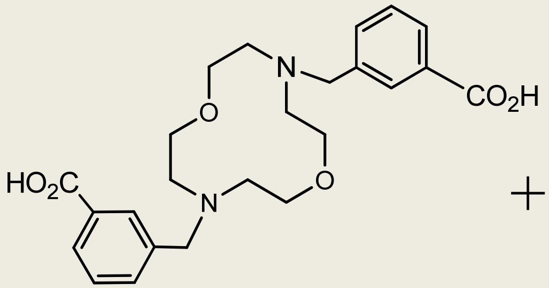
Diazo crown carboxylate ligands synthesis



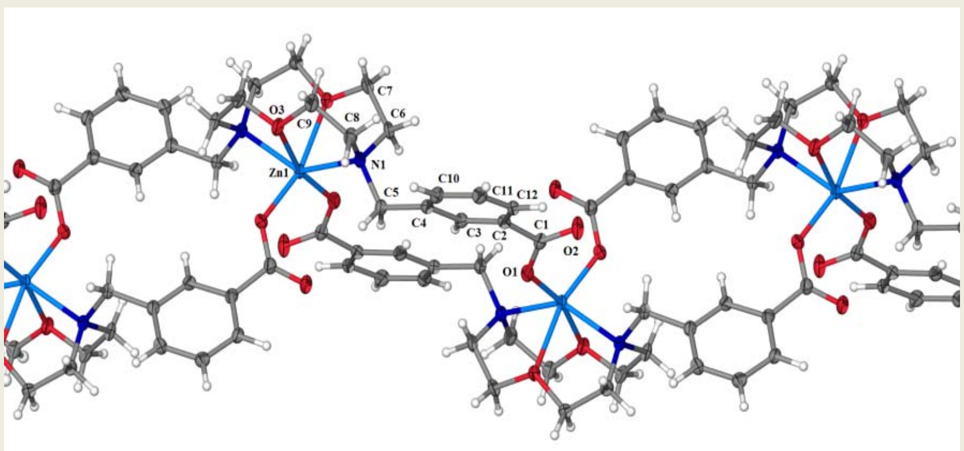
a). Na_2CO_3, CH_3CN, reflux, 1 d; b). HCl (aq. 6 N), 90 ^oC 5 h.

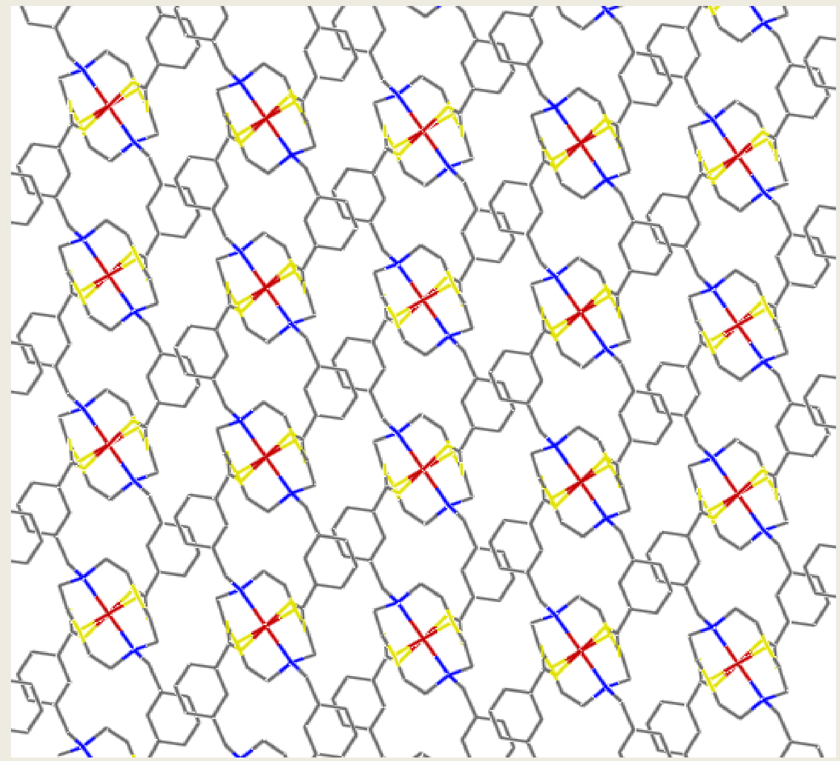
Scheme 1

1. New 1D chain-like Zn- diazo crown ether carboxylate coordination polymer



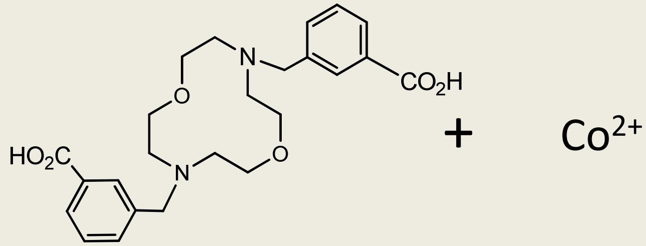
+ Zn^{2+} or Co^{2+} = 1D MOF

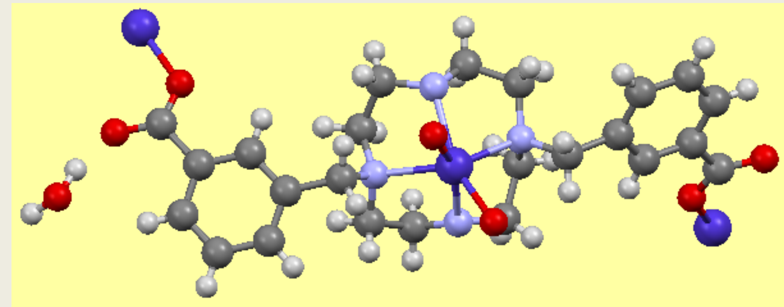


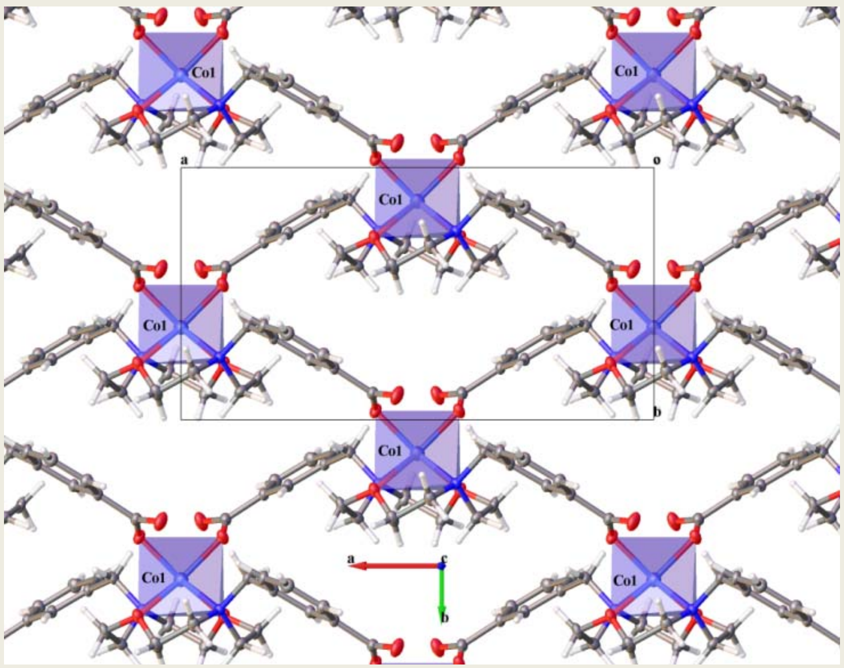


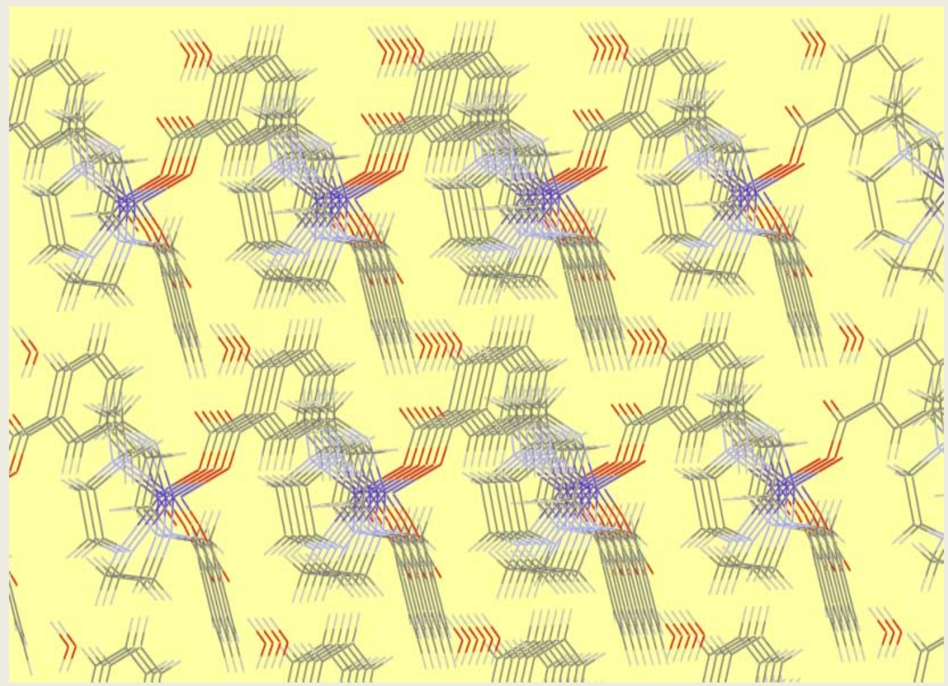
Liao, Ingram, et al, Acta Cryst, 2012
Liao, Ingram, et al, Acta Cryst 2014

2. New 2D cobalt- diazo crown ether carboxylate MOF

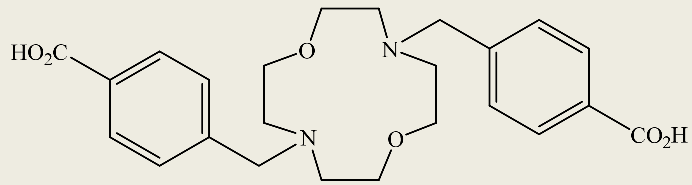


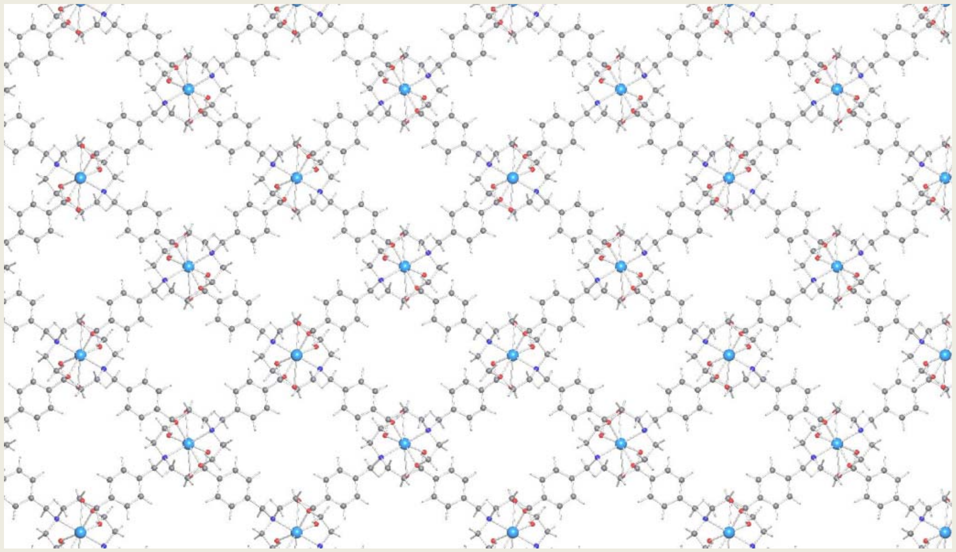


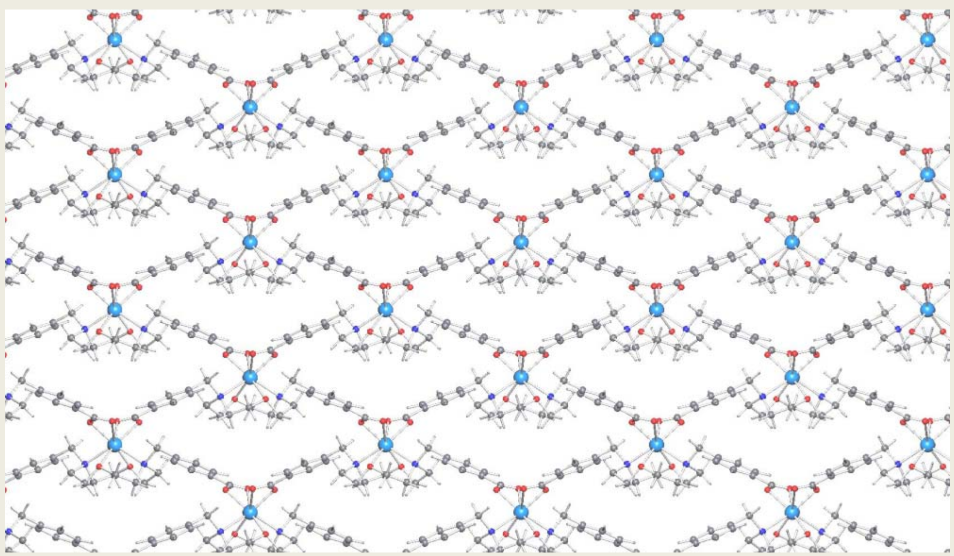




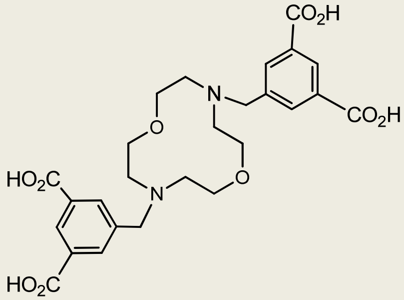
Ingram *et al*. 2013, Crystal Growth and Design.

4.  + M^{2+}

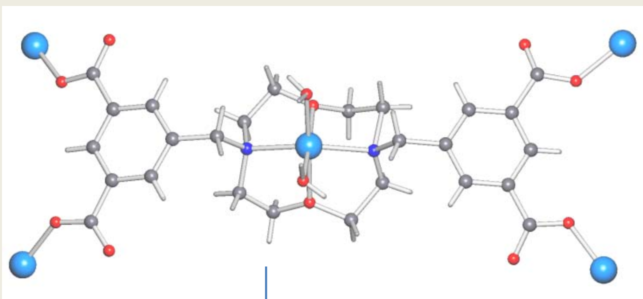


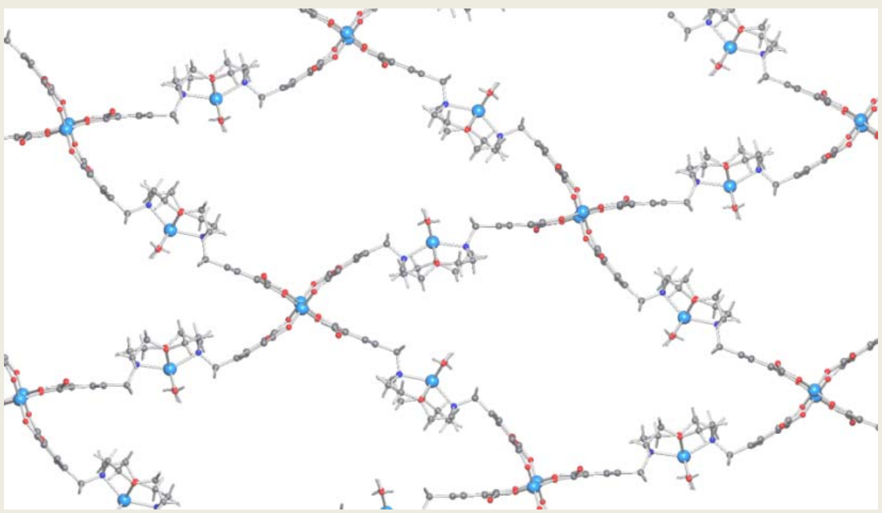


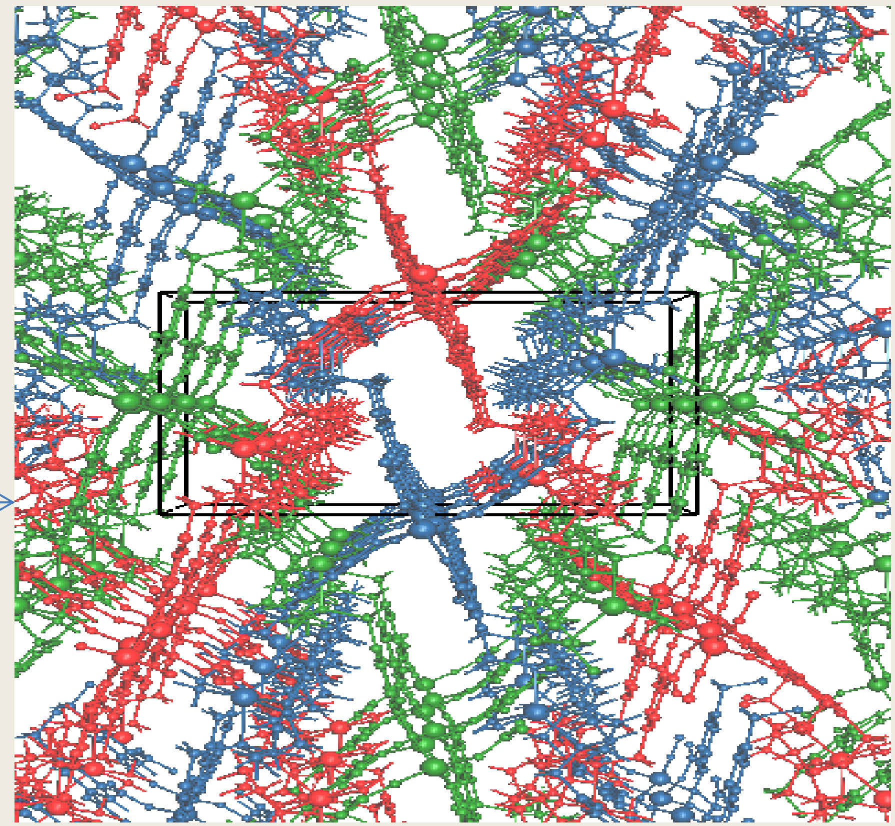
5. New 3D cobalt- diazo crown ether carboxylate MOF



$+ \quad Co^{2+} \quad = $ 3D MOF



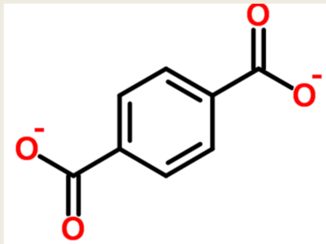




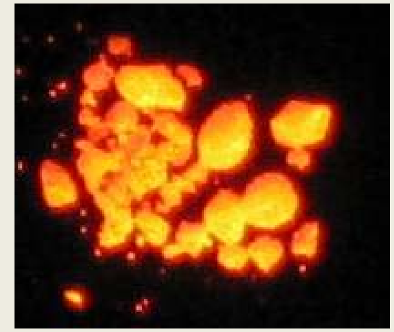
Ingram *et al*. 2013, Crystal Growth and Design.

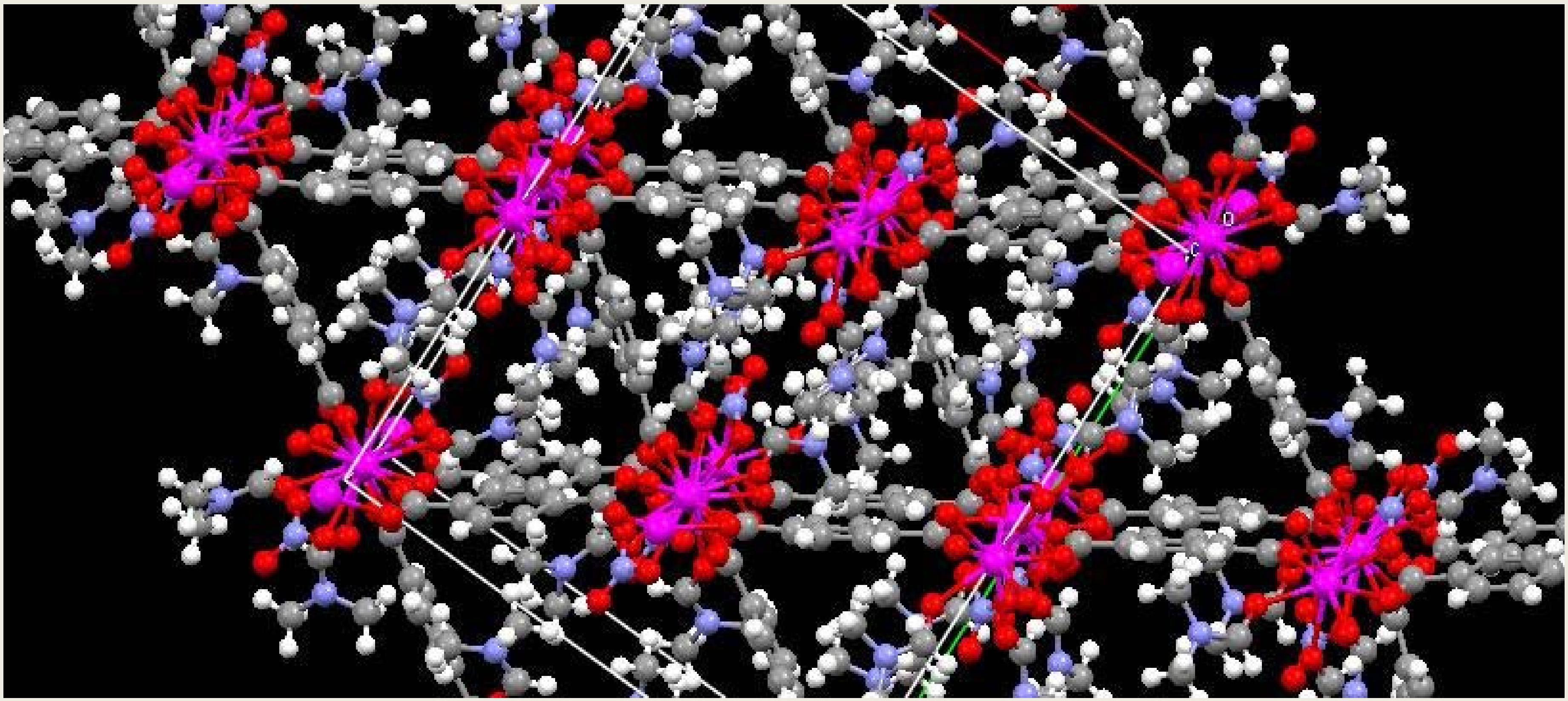
B. Paramagnetic 3D-MOF

6.



+ Gd^{2+}





Ingram *et al*. 2012, Inorganica Chimica Acta., 2012

Thank You!