Multiscale Simulations of Hydrogen Adsorption in Nanoporous Materials

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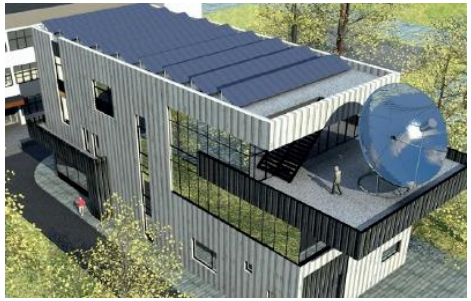
Hydrogen Storage

- Clean energy vector.
  $2H_2+O_2=2H_2O$ + 142MJ/kg

Energy density	MJ/kg
Hydrogen	142
Methane	55.5
Gasoline	46.4
Li battery	1.8

- Problem: renewable energy output fluctuations.

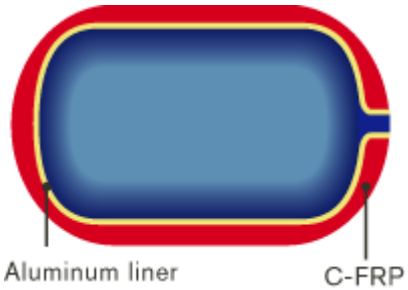



- Efficient H2 storage: maximize the use of renewables, significantly reduce the fossil fuels dependence, pollution-free cities, dependable energy supplies for remote communities.

Mature Hydrogen Storage Technologies

- Liquid H_2 (~30% loss with cooling) – few new developments.

- High-pressure (>700bar) tanks - still actively pursued.



- Car makers: BMW, Daimler, Ford, Honda Hyunday, Nissan, Volkswagen, Mercedes.

Hyunday Tucson FCV
$499/month, 36-mo lease

Hydrogen Refuelling Stations in Europe

ludwig bölkow systemtechnik

H2Stations.org

in operation
planned

Status January 2016

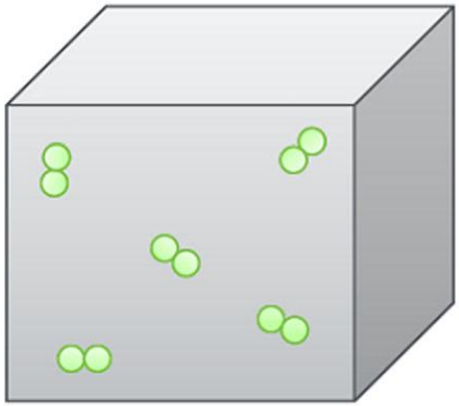
© Ludwig-Bölkow-Systemtechnik GmbH www.lbst.de

But,

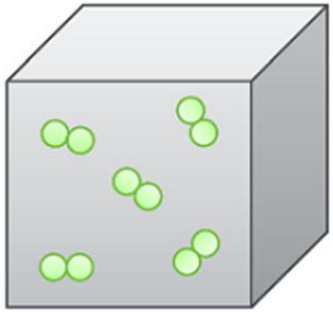
- Most (~96%) H_2 comes from fossil fuels.
- Established storage tanks: still energetically inefficient, still expensive, bulky, hard to scale up for onboard use.

Comparison Between Storage Methods

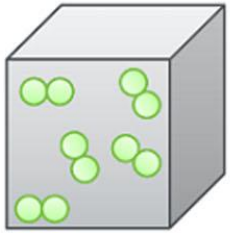
Physical Storage



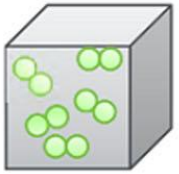
1 bar
normal
0.3 g/L



150 bar
lab cylinders
10 g/L



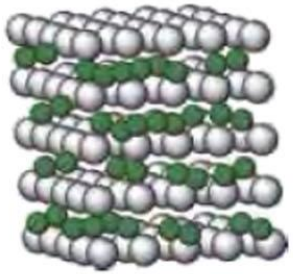
350 bar
Gen 1 vehicles
28 g/L



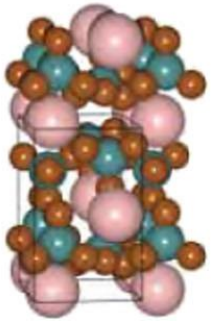
700 bar
Gen 2 vehicles
40g/L

liquid H_2
71 g H_2/L
@ 20 K

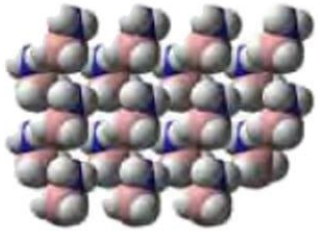
Materials -based Storage



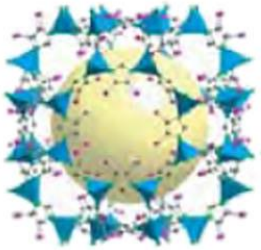
interstitial hydrides
~100-150 g H_2/L



complex hydrides
~70-150 g H_2/L



chemical storage
~70-150 g H_2/L



sorbents
≤ 70 g H_2/L

Reference

water
111 g H_2/L

Stetson N. An overview of U.S. DOE's activities for hydrogen fuel cell technologies. Clearwater, Florida, America, 2/27/2012.

Hydrogen Storage in Materials

- Chemisorption (metallic hydrides, complex hydrides, etc.).

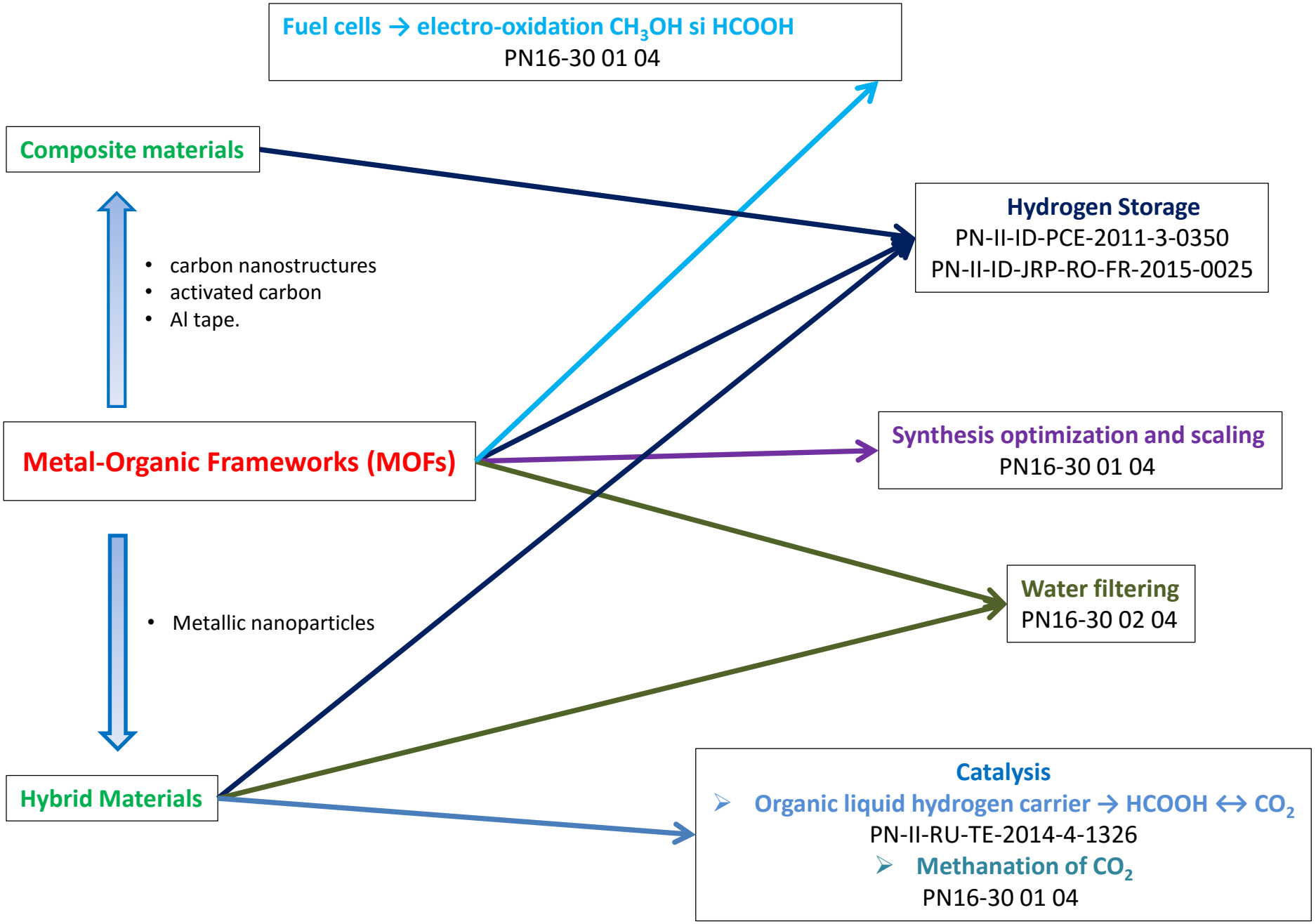
  pro: high volumetric absorption capacities;
  con: slow kinetics, complex heat management, faster degrading of the storage material, poor reversibility.

- **Physisorption** (metal-organic frameworks, zeolites, clathrates, activated carbons, etc.)

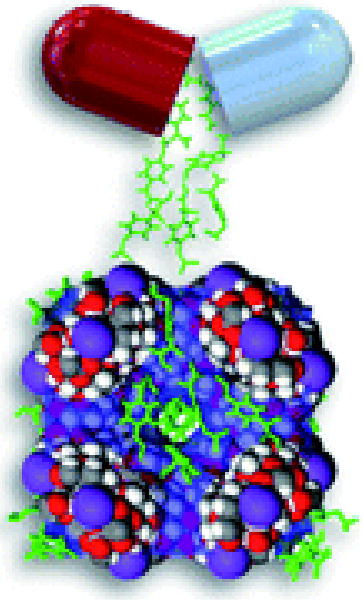
  pro: fast sorption kinetics, simple energy management, good reversibility.
  con: low adsorption capacities at room temperature (low adsorption enthalpies Q_{st}).

An Interdisciplinary Team

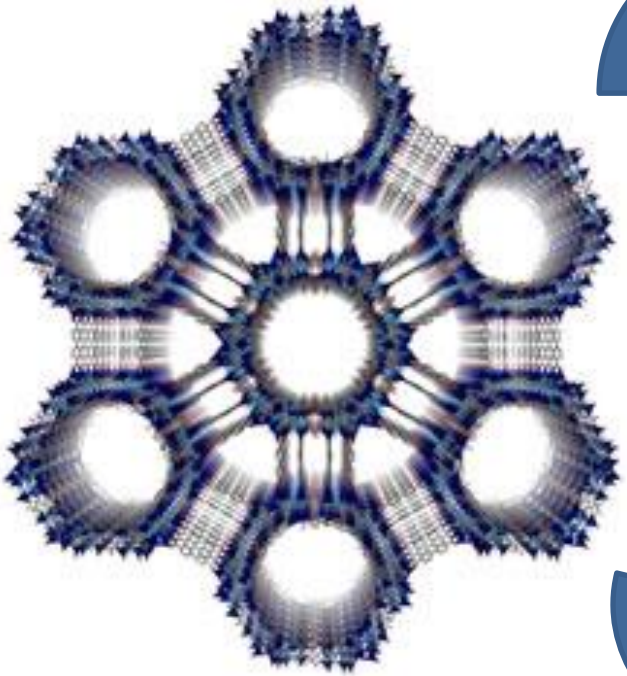
- Daniel Bîlc – theory (solid state computational chemistry),
- Marius Oancea – theory (computational chemistry),
- Ioana Grosu – chemistry (synthesis),
- Gabriela Blăniţă – chemistry (synthesis and adsorption measurements),
- Dan Lupu – chemistry (synthesis and adsorption measurements),
- Ioan Coldea – engineering (device construction and adsorption measurements),
- Xenia Filip – NMR measurements,
- Claudiu Filip – NMR measurements.
- Maria Miclăuş – X-ray scattering,
- Gheorghe Borodi – X-ray scattering.


Fuel cells → electro-oxidation CH_3OH si HCOOH
PN16-30 01 04
Composite materials
• carbon nanostructures
• activated carbon
• Al tape.
Hydrogen Storage
PN-II-ID-PCE-2011-3-0350
PN-II-ID-JRP-RO-FR-2015-0025
Metal-Organic Frameworks (MOFs)
Synthesis optimization and scaling
PN16-30 01 04
Water filtering
PN16-30 02 04
• Metallic nanoparticles
Hybrid Materials
Catalysis
➢ Organic liquid hydrogen carrier → HCOOH ↔ CO_2
PN-II-RU-TE-2014-4-1326
➢ Methanation of CO_2
PN16-30 01 04

Drug delivery

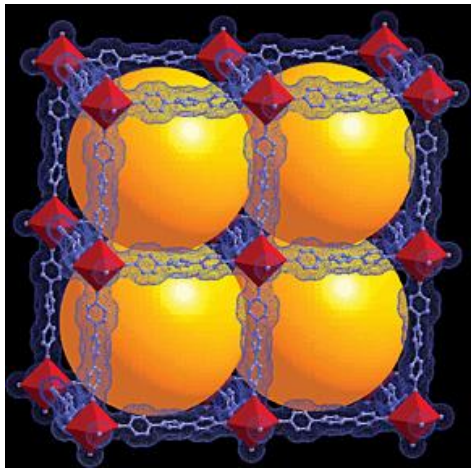


Bio-compatible polymers



Porous polymer MOF/COF

Gas storage/separation



Polymers decorated with polarizable moieties

Multiscale Adsorption Simulations Project

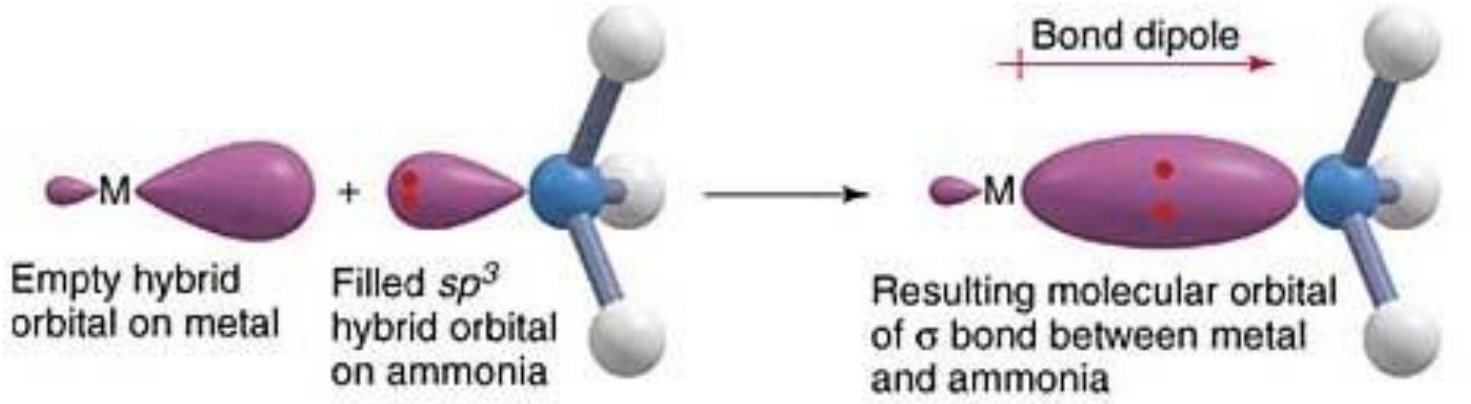
1. Nucleus project: develop the multiscale adsorption simulation methodology → new activity of the hydrogen storage group.

2. TE 2014 project: universal multiscale simulations for hydrogen storage.

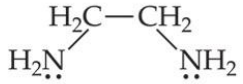
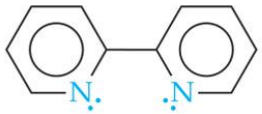
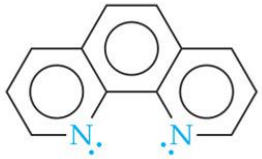
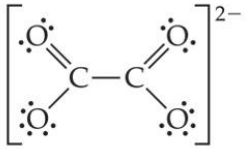
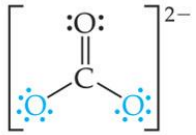
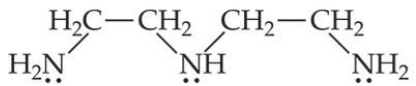
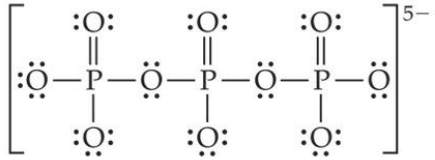
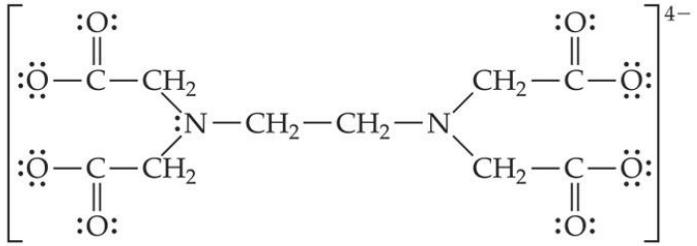
3. New research direction: electrically controlled adsorption in nanoporous solids.

Metal-Ligand Bond

- Lone pair electrons on the linker
- Empty metal orbitals.

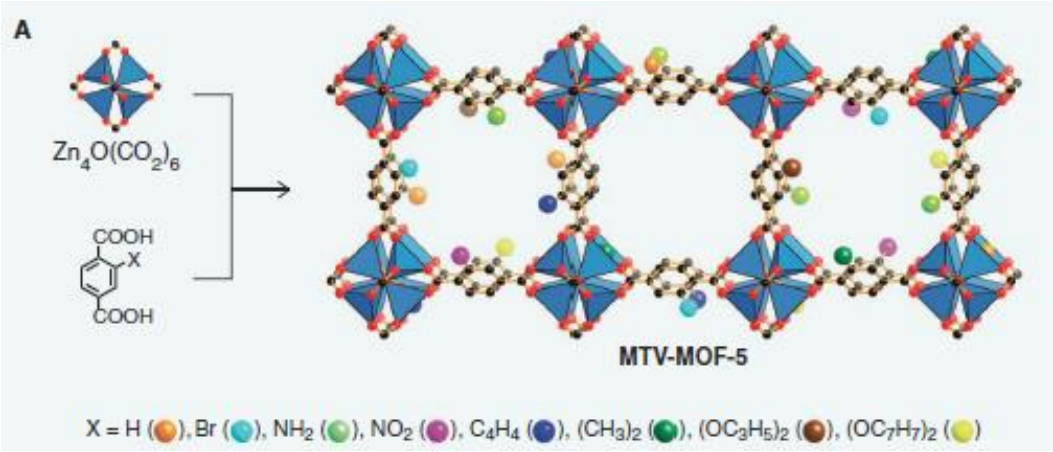


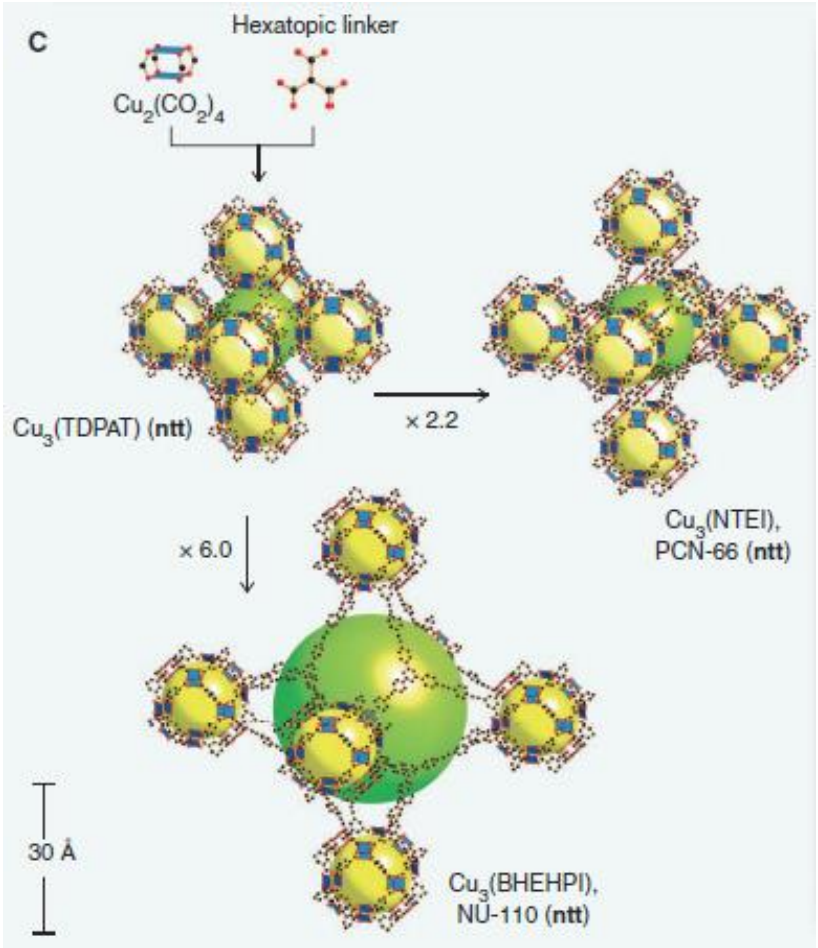
Organic linkers

Ligand Type	Examples							
Monodentate	H_2O: Water	$:F:^-$	Fluoride ion	$[:C\equiv N:]^-$	Cyanide ion	$[:O-H]^-$	Hydroxide ion
	$:NH_3$ Ammonia	$:Cl:^-$	Chloride ion	$[:S=C=N:]^-$ (or)	Thiocyanate ion	$[:O=N=O:]^-$ (or)	Nitrite ion
Bidentate	 Ethylenediamine (en)	 Bipyridine (bipy)	 *Ortho*-phenanthroline (*o*-phen)	 Oxalate ion	 Carbonate ion			
Polydentate	 Diethylenetriamine	 Triphosphate ion						
	 Ethylenediaminetetraacetate ion ($EDTA^{4-}$)							

Metal-Organic Frameworks (MOFs)

- Secondary building units (SBUs) connected by organic linkers.
- Practically unlimited topologies.
- Crystalline with large tunable pores → large surface areas.





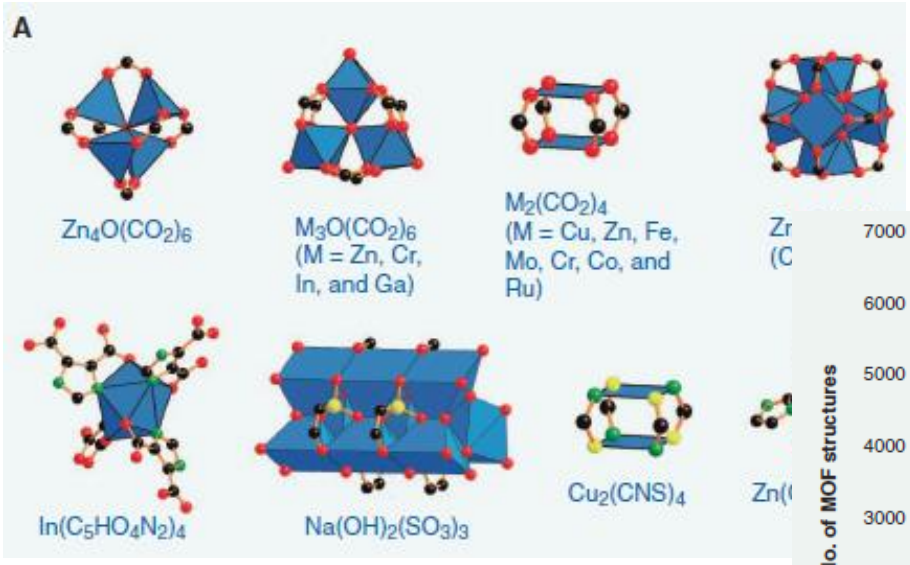
Science **341**, 974 (2013)

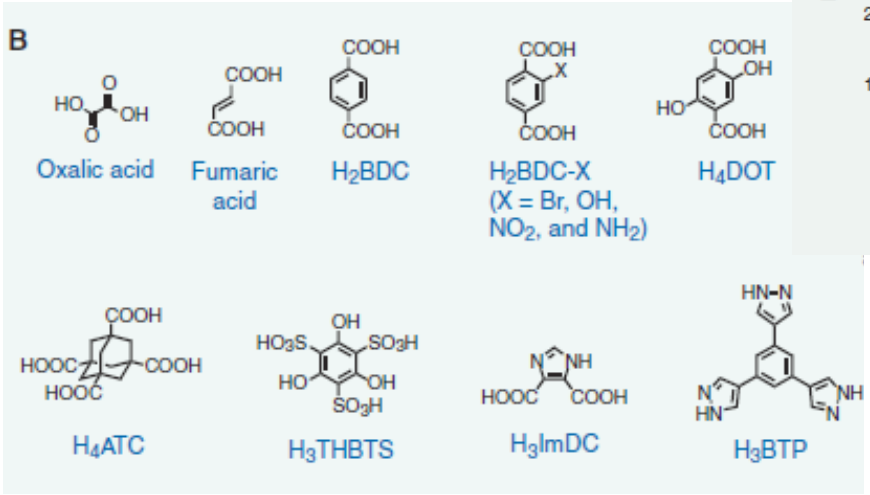
Unlimited MOF Topologies

SBUs

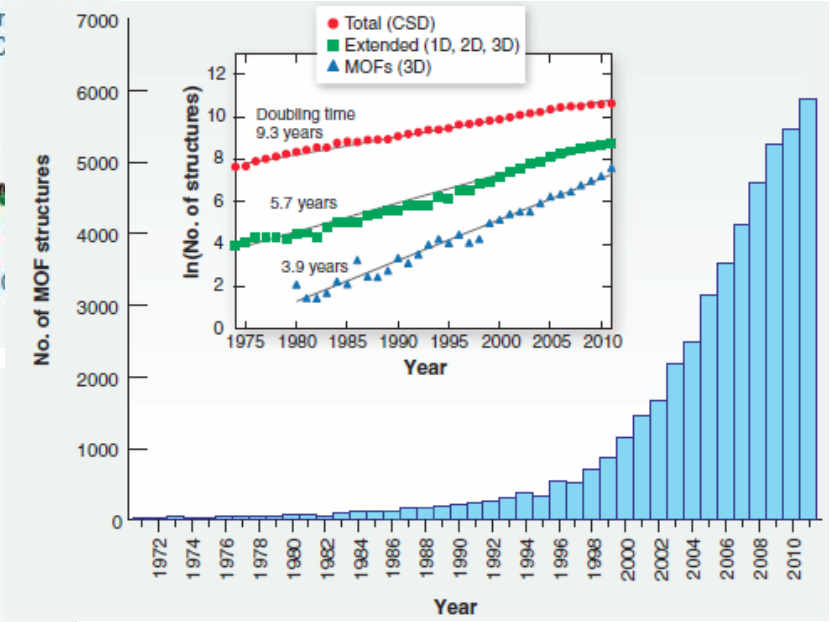
+

linkers





Over 38000 known MOFs



Science **341**, 974 (2013)

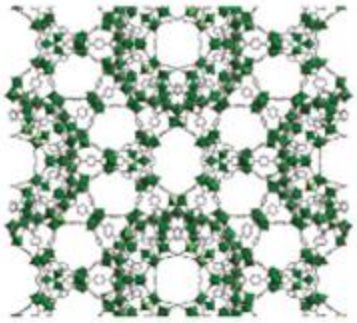
Adsorption in Metal-Organic Frameworks

- DOE benchmarks for hydrogen adsorption
  5.5wt%, 40g/l by 2020, 7.5wt%, 70g/l final
  quite ambitious!
  700bar hydrogen: 40g/l
  Liquid hydrogen: 70.8g/l
- Promising MOFs and COFs for hydrogen storage only at 77K and below.
- Still, Q_{st} too low (3-10kJ/mol), while optimum is at 15-20kJ/mol. How to increase Q_{st}?

Adsorption in Metal-Organic Frameworks

MOF	BET m^2/g	Langmuir m^2/g	P(bar)	T(K)	wt%	g/l	Q_{st} (kJ/mol)
MIL-101		5500	80	298	0.43	1.84	10
			80	77	6.1	26.1	
HKUST-1	1154	1958	50	77	3.6		4.5
			65	298	0.35		
IRMOF-6	2804	3305	45	77	4.63	31.7	

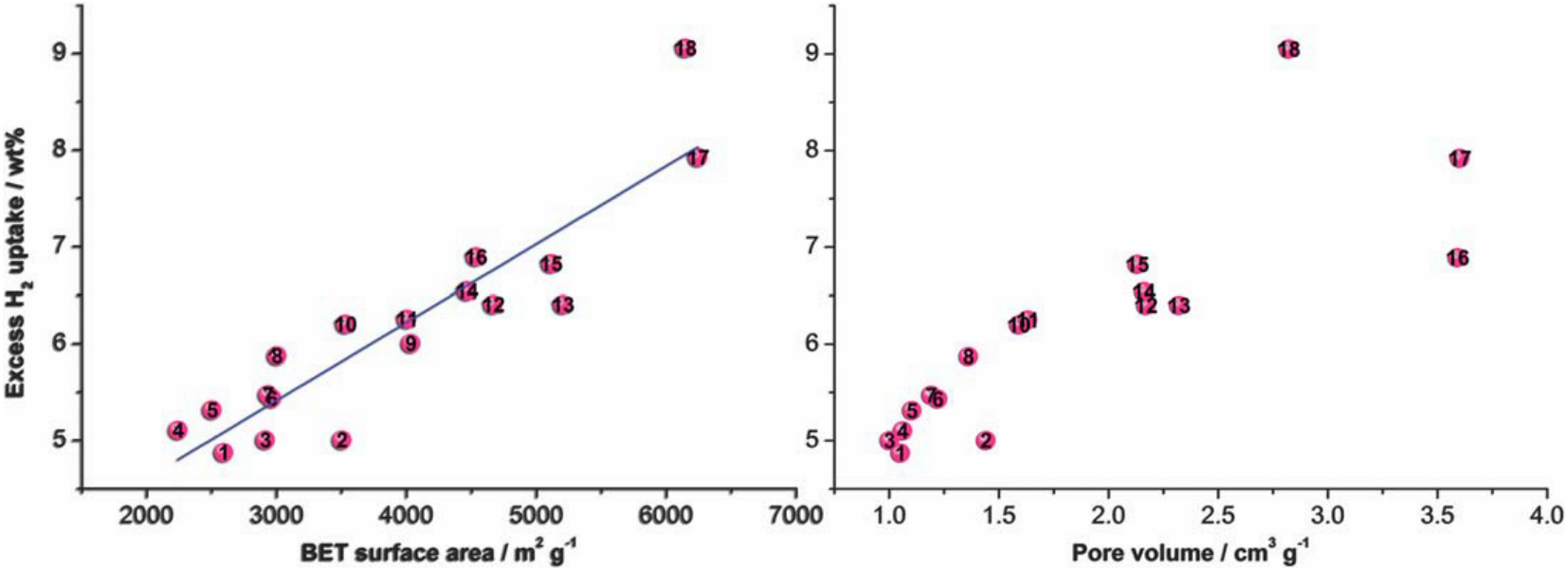
Chem. Soc. Rev. 38, 1294 (2009)



- Good performance at 77K
- Poor performance at SATP.
- Still far from DOE targets
- Adsorption enthalpy should be ~20kJ/mol

To increase adsorption in MOFs

- Design MOFs with large accessible surface area and pore volume;



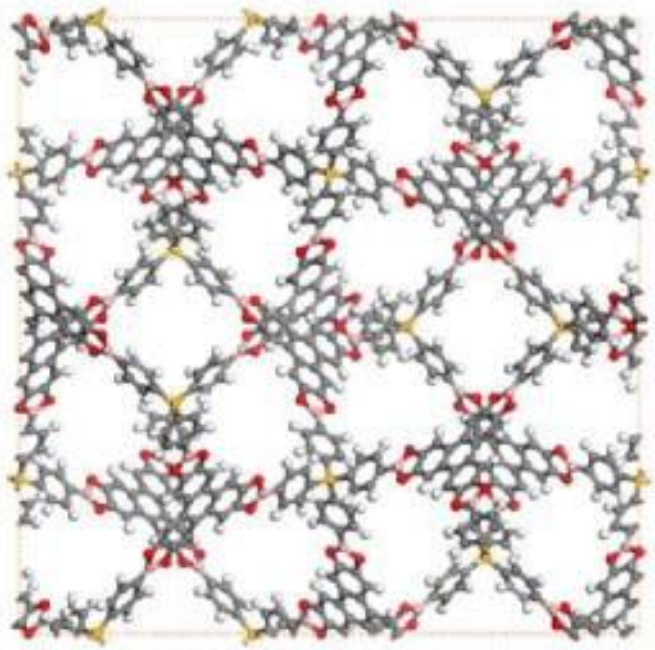
- linker functionalization, unsaturated metal sites, chemical doping (e.g. Li doping), etc.
- What about some physics idea?
  Use electric fields

Nucleus project: Multiscale Adsorption Simulations Methodology

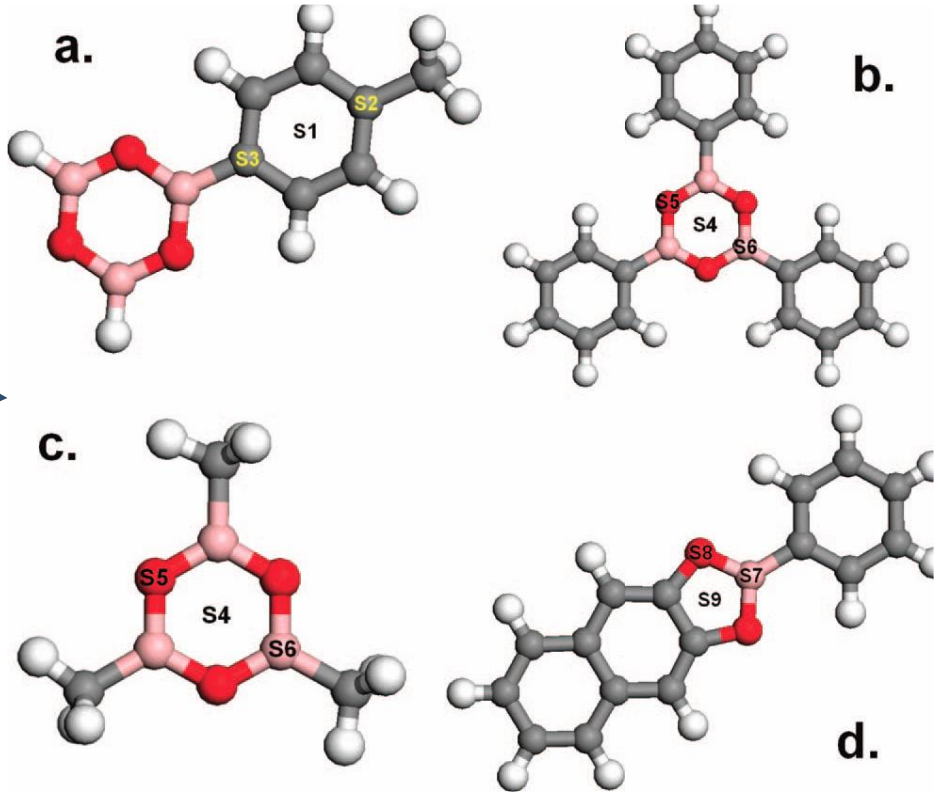
1. Ab initio simulations:
    1. Binding sites,
    2. Binding energies,
    3. Stability of MOF structure.
2. Adsorption isotherms
    1. Grand canonical Monte Carlo adsorption simulations.
    2. Direct comparison with experiments.

More on Ab Initio Simulations

- molecular models:



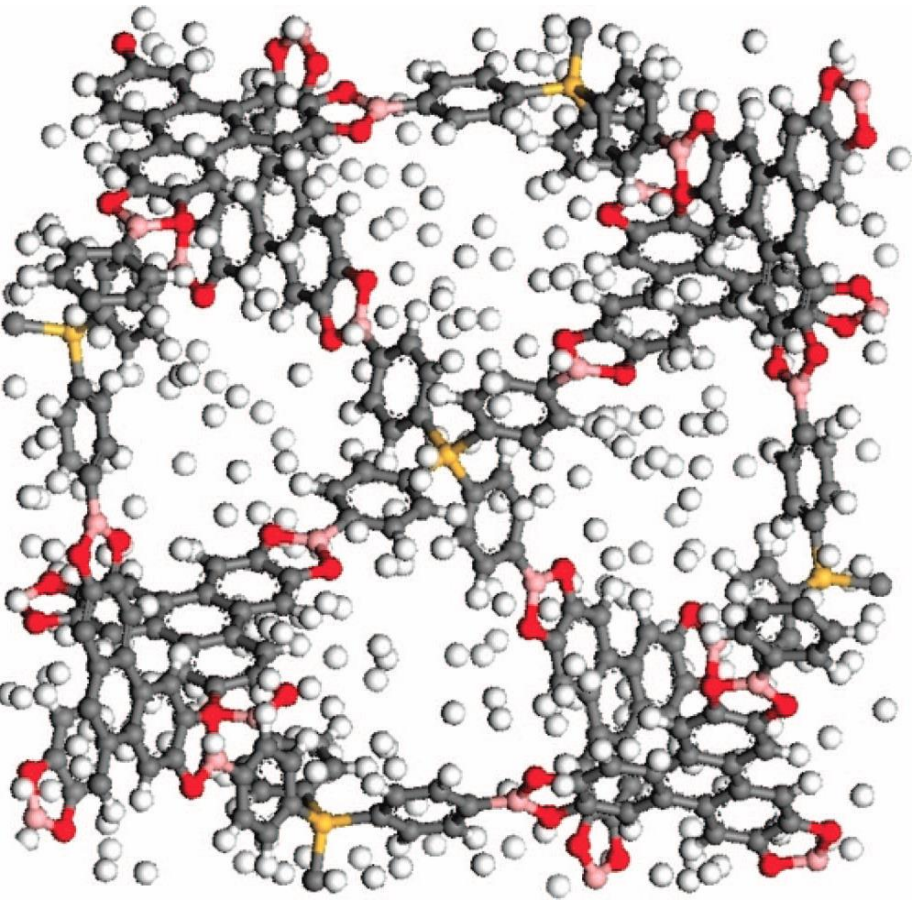
COF-105



J. Phys. Chem. C *112*, 9095 (2008)

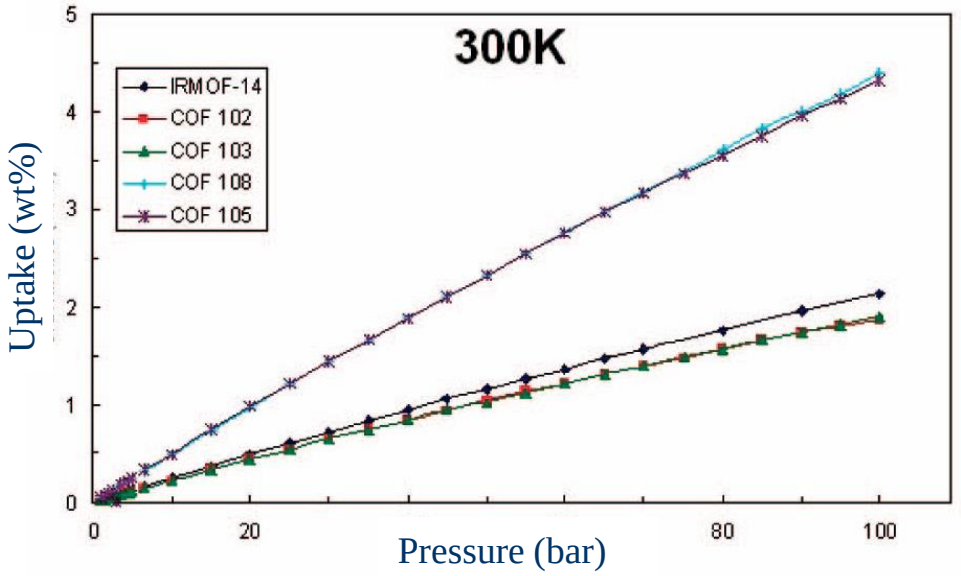
- binding sites S1, S2, etc.;
- Binding energies;
- Bulk properties, structural stability from periodic DFT;

Grand Canonical Monte Carlo



J. Phys. Chem. C
112, 9095 (2008)

- H_2 molecules in a MOF cell.
- H_2 >~< binding sites via van der Waals interactions (modeled by force fields);
- Operations: insertion, deletion, translation, rotation of H_2 molecules at each step;
- N becomes constant → convergence.
- Get adsorption isotherms.

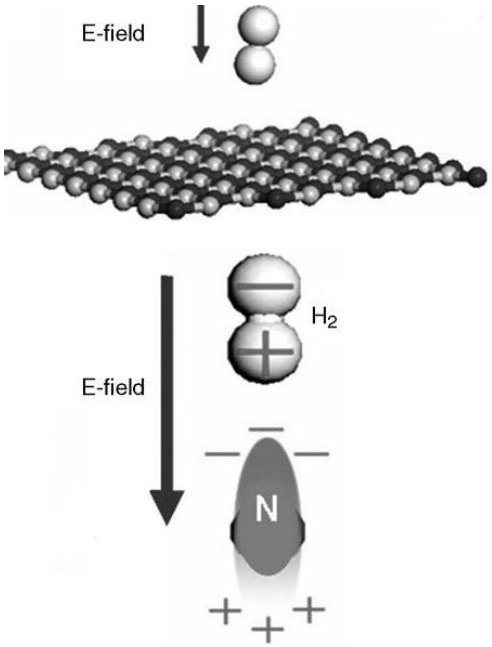


Adsorption in Electric Field

- Q_{st} increase: open metal sites, ions, linker functionalization, impurities… hard to control
- Alternative: E-field induced dipoles of H_2 and MOF.
- Pro: E easier to control than P, T, might take much less energy.
- Con: we need to find polarizable MOFs with large enough pores.

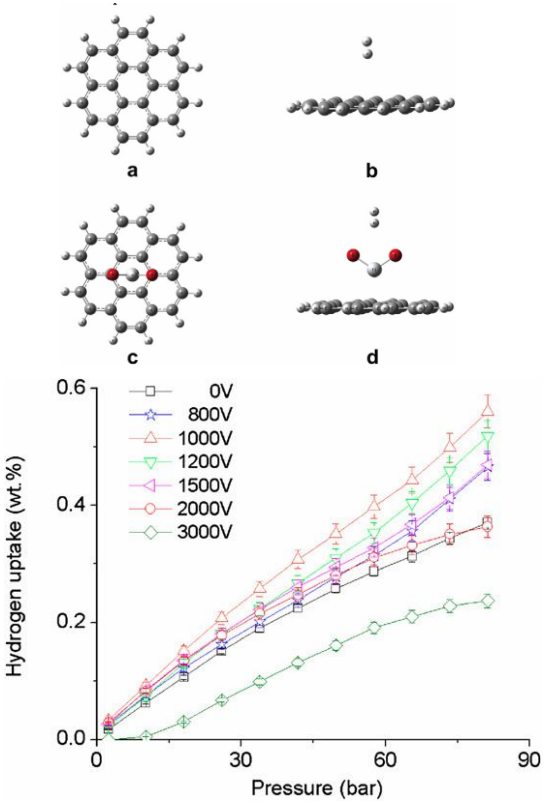
So Far on Electrically Controlled Adsorption

Adsorption on substrates
BN, AlN, graphene



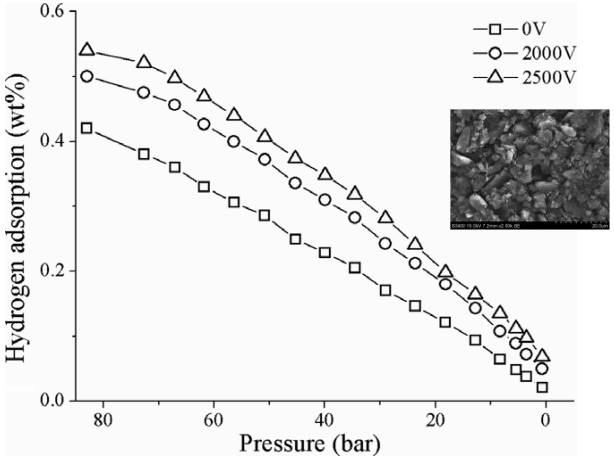
PNAS 107, 2801 (2010),
J. Nanopart. Res. 14, 1256 (2012),
Int. J. Hy. En. 37, 11842 (2012).

Exp: Adsorption on coronene and TiO_2



Int. J. Hy. En. 37, 16018 (2012)

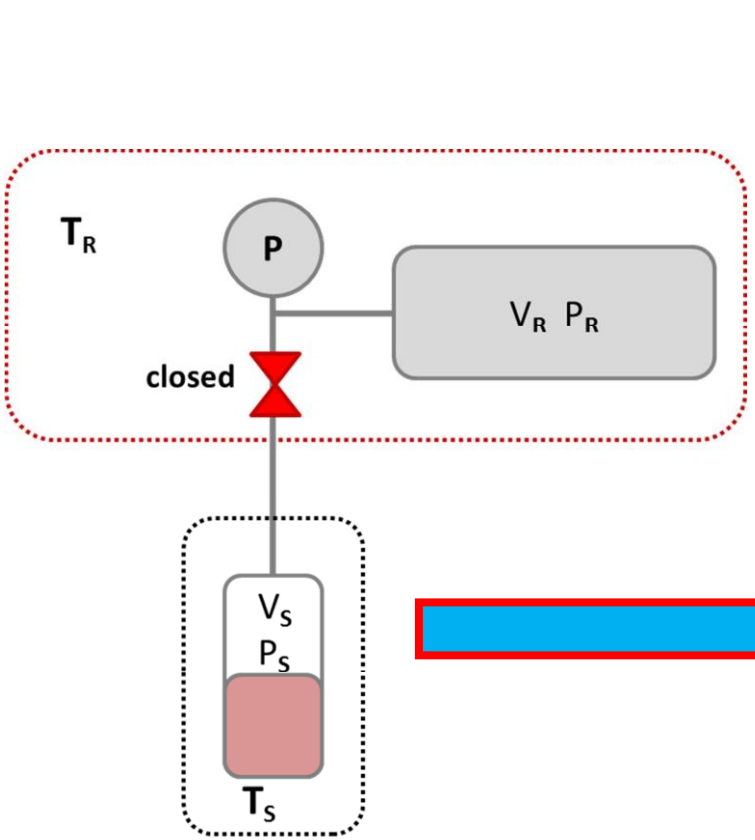
Exp. Adsorption on activated carbon

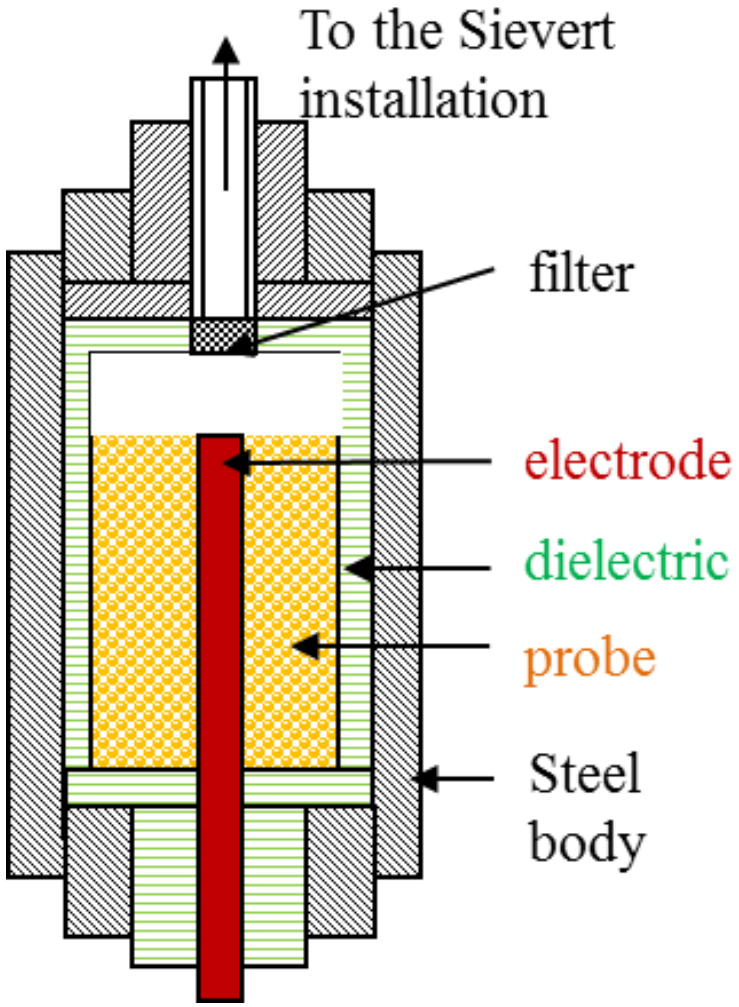


Carbon 48, 876 (2010)

- Too large fields (~23000MV/m)
- MOFs?

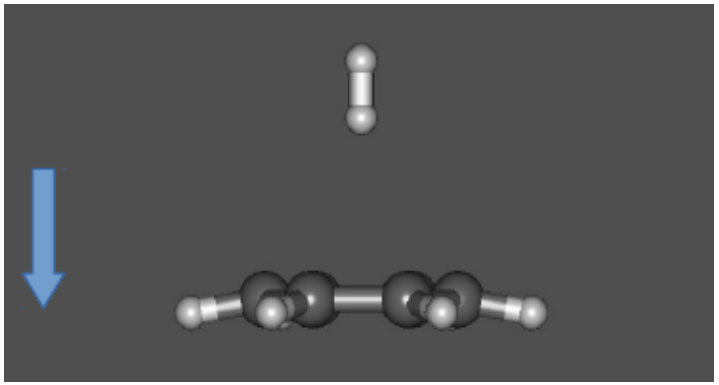
Reactor for Sievert Measurements in Electric Field

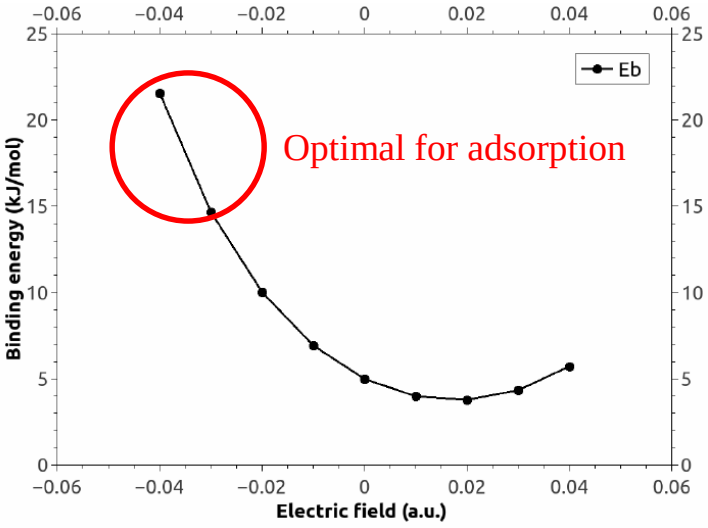




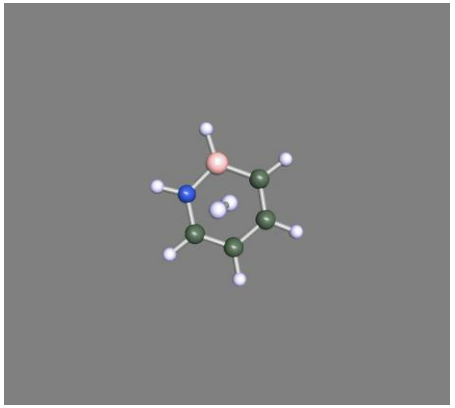
A Simple Test

H_2 on benzene

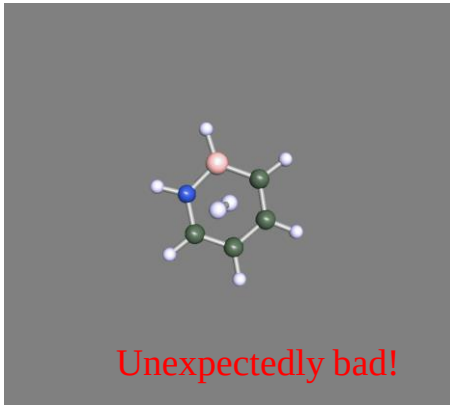


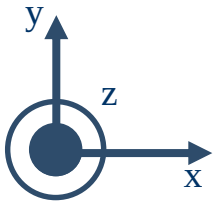


H_2 on azaborine



$E_b(E = 0) = 5.2kJ/mol$

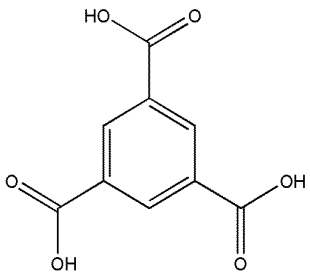


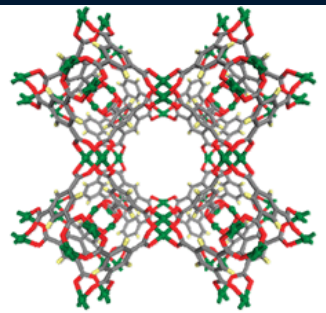


$E_b(E = 0.01) = 4.2kJ/mol$

What About MOFs?

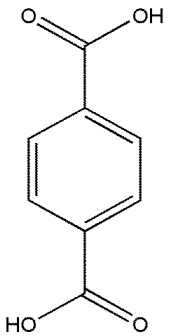
1,3,5 tricarboxylic acid (BTC)

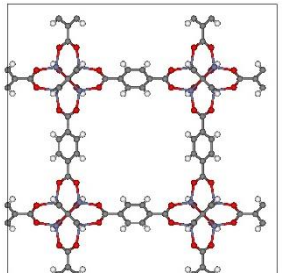




$[Cu_3(BTC)_2(H_2O)_3]_n$, HKUST-1

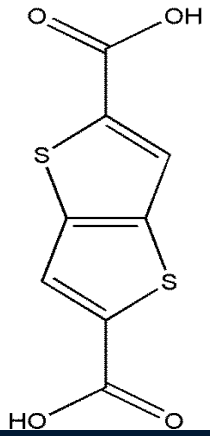
Terephtalic acid (BDC)

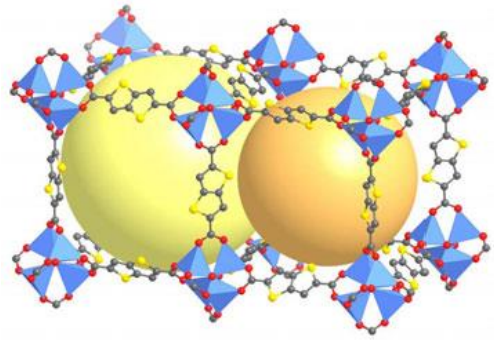




IRMOF-1

2,2':5',2''-terthiophene-5,5''-dicarboxylate (TTDC)

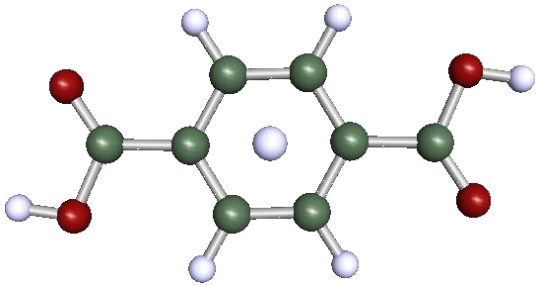




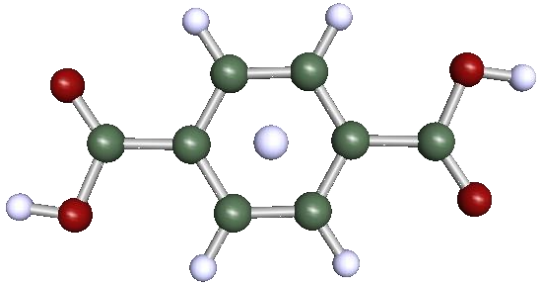
IRMOF-20

Molecular Models for Adsorption

BDC

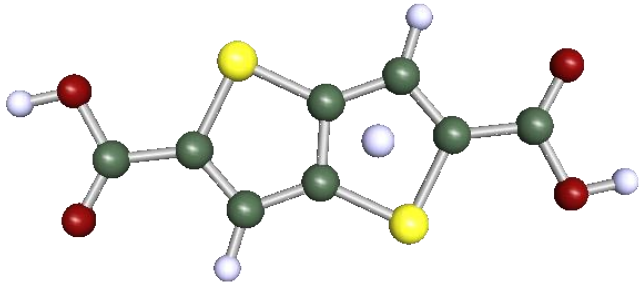


E_b=4.55kJ/mol

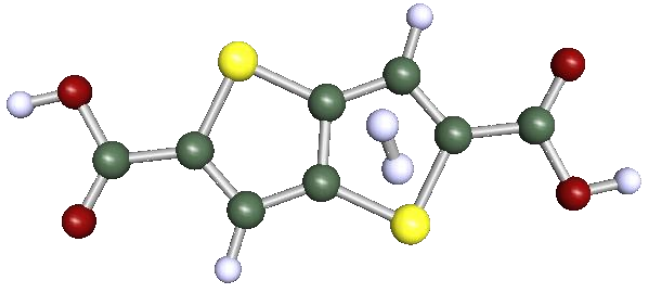


E_z= 0.01 E_b=4.33kJ/mol
E_z=-0.01 E_b=5.54kJ/mol

TTDC



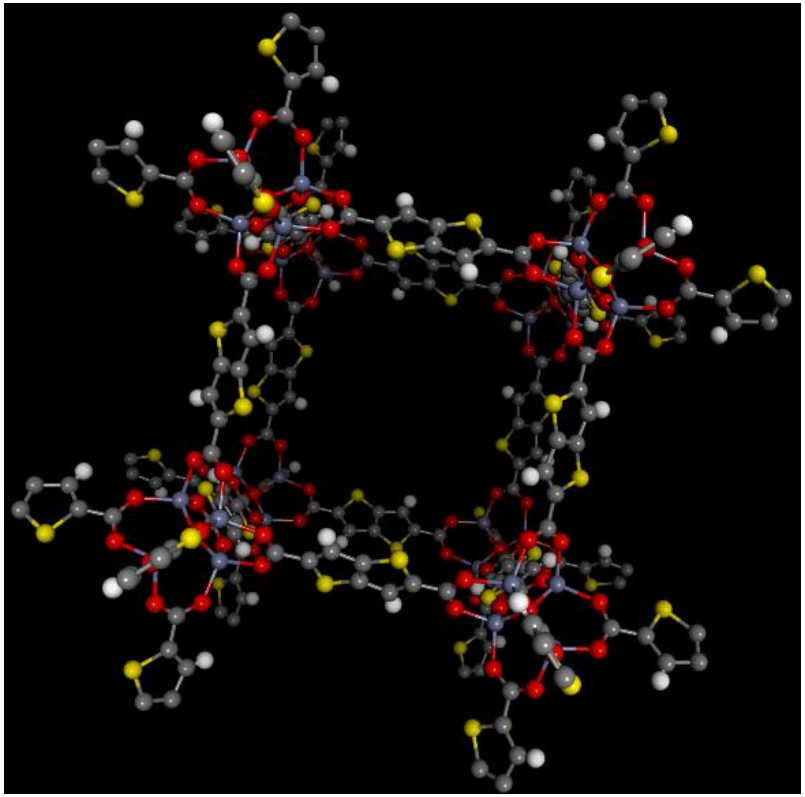
E_b=4.82kJ/mol

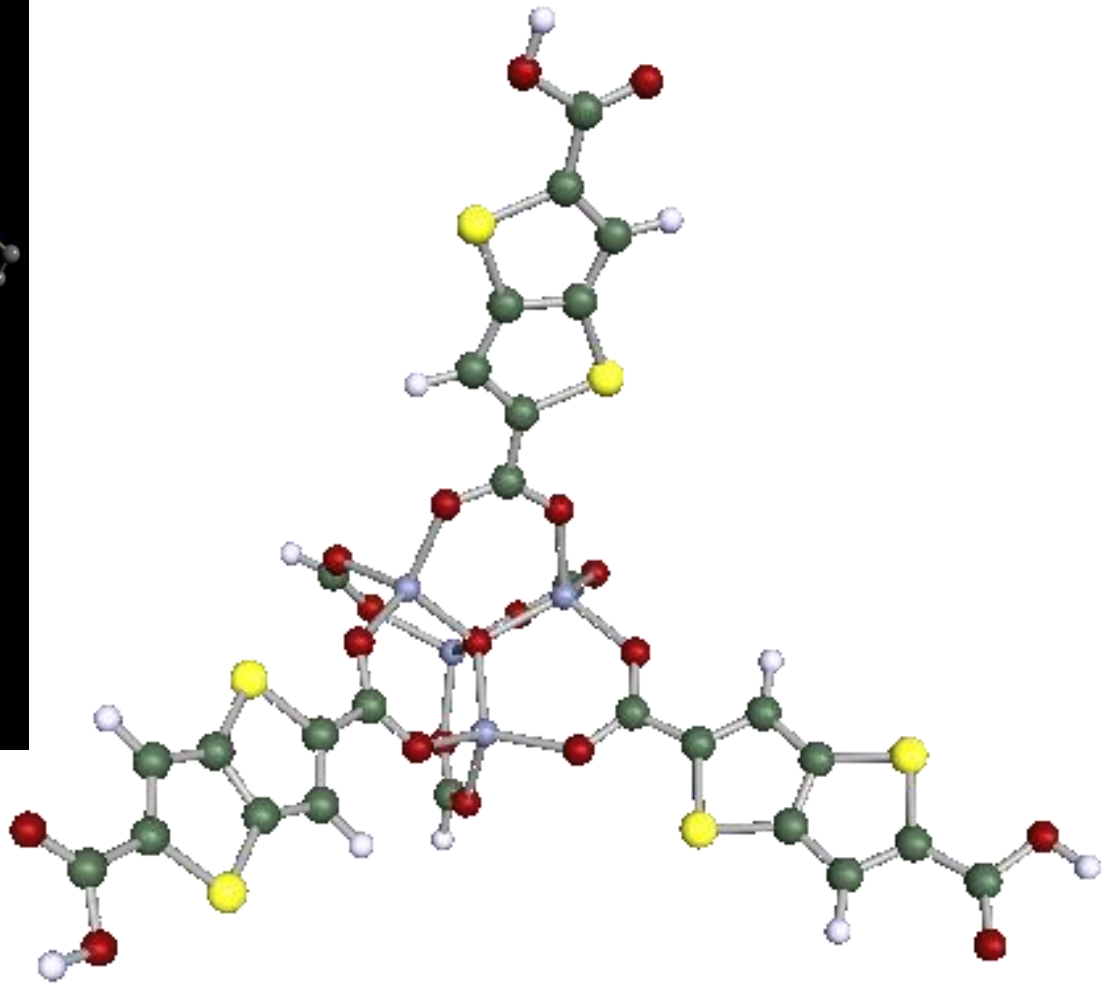


E_z= 0.01 E_b=4.78kJ/mol
E_z=-0.01 E_b=5.74kJ/mol

Isn't E_z too large?

Larger Molecular Models – IRMOF-20





Highly Polarizable Nanoporous Materials

- 2013 Daniel, Claudiu: combine high-k dielectrics + organic linkers → novel HPNM materials.
- But, higly polarizable MOFs do already exist.

CHEMICAL REVIEWS

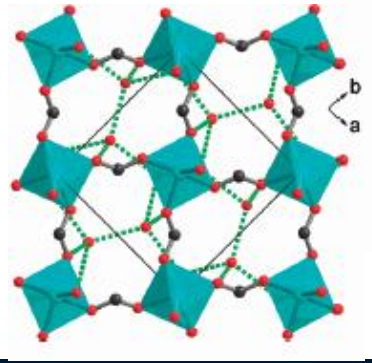
Ferroelectric Metal–Organic Frameworks

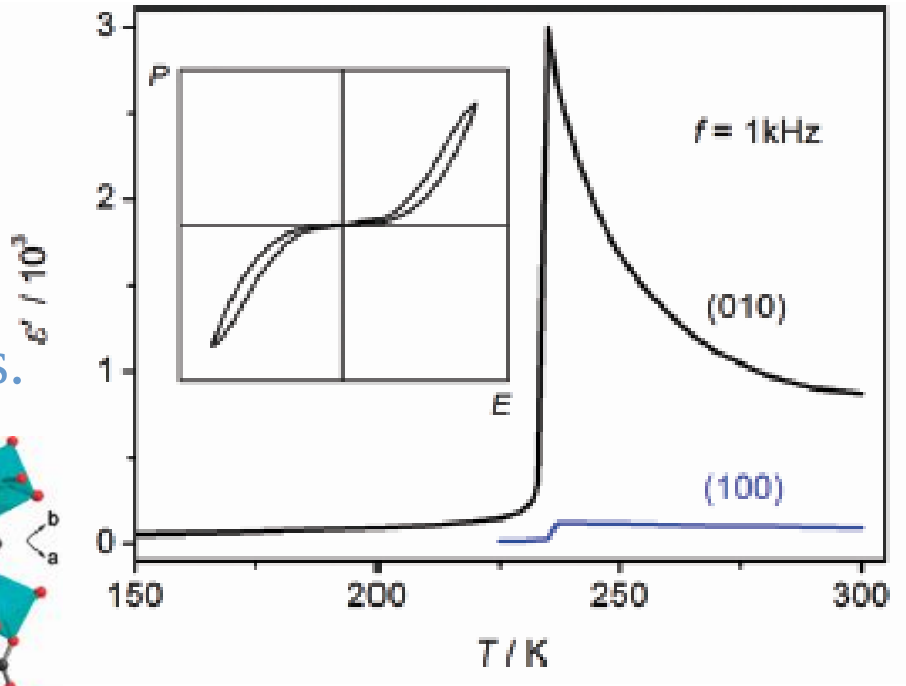
Wen Zhang* and Ren-Gen Xiong*

- Some are really good dielectrics.

$[Cu(HCOO)_2(H_2O)_2]\cdot 2H_2O$

$\epsilon \sim 1000$

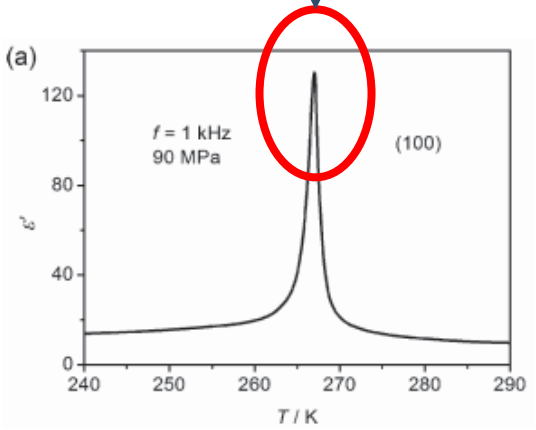




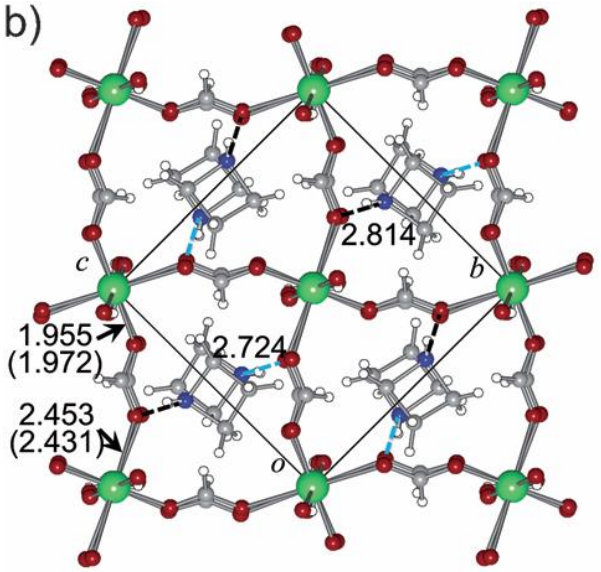
Why Is Ferroelectricity Desirable?

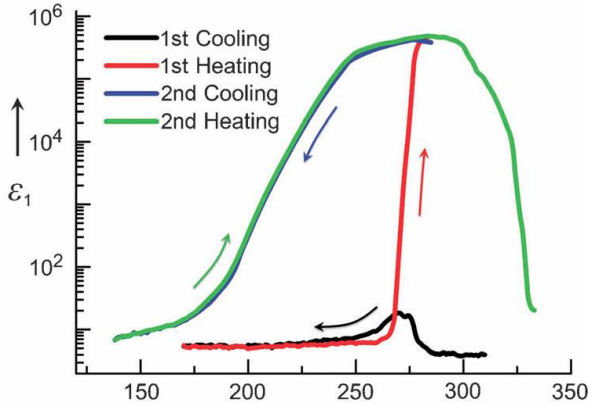
Dielectric Anomaly:

$$\epsilon = \epsilon_0 + \frac{C}{T - T_0}$$



A MOF perovskite:





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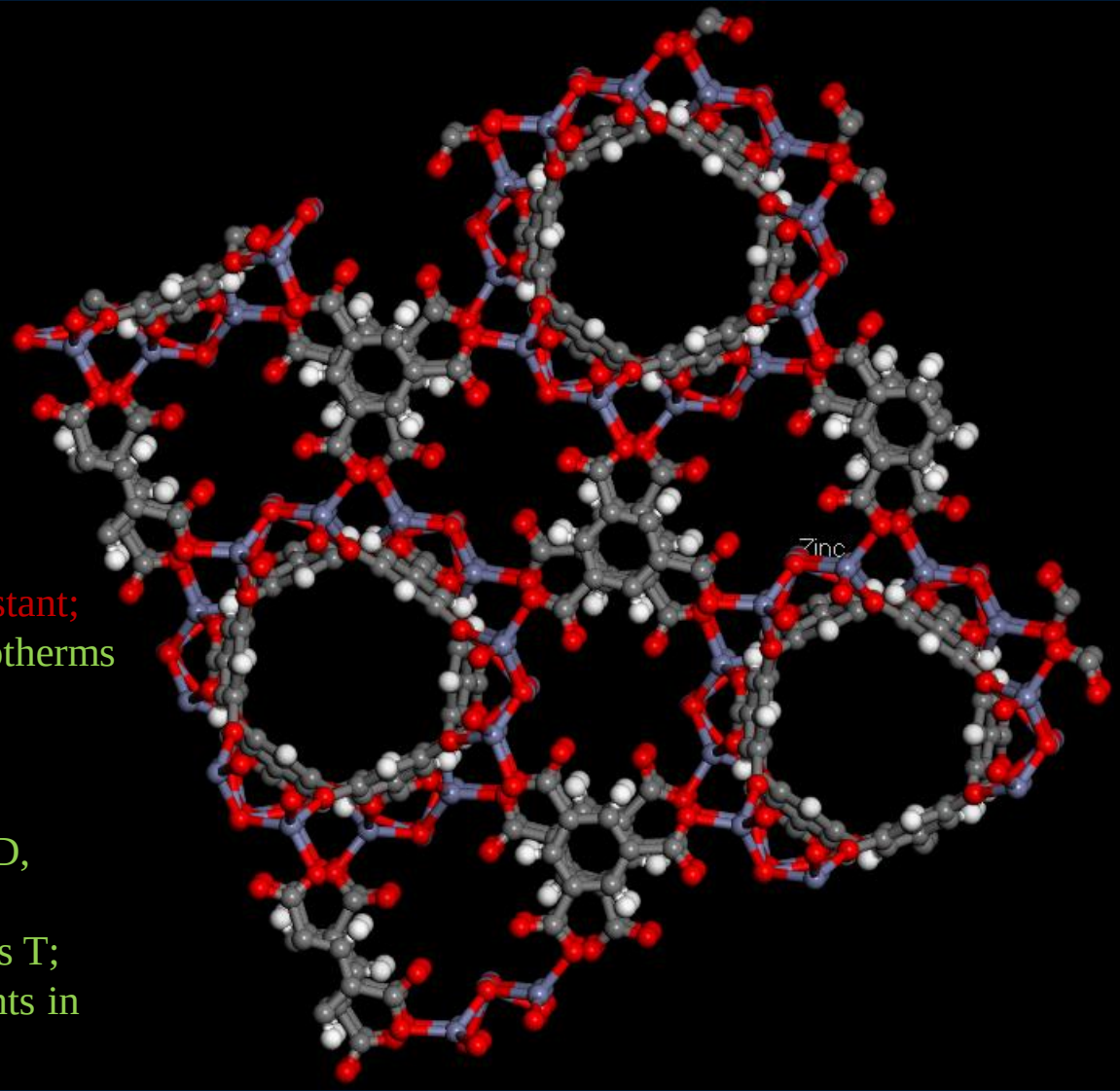
- Ferroelectricity from structural transition (orthorhombic – monoclinic).
- Needs slow heating/cooling.
- Too small pores.

A Ferroelectric MOF with Large Pores



P63cm →ferroelectric;
~18x18x17 → large pores.

- Compute dielectric constant;
- Calculate adsorption isotherms in electric field;
- Synthesize;
- Get the solvent out;
- Structural analysis: XRD, PXRD, NMR.
- Dielectric anomaly? ε vs T;
- Adsorption measurements in electric field.

The Rational Design Cycle for Gas Storage Materials