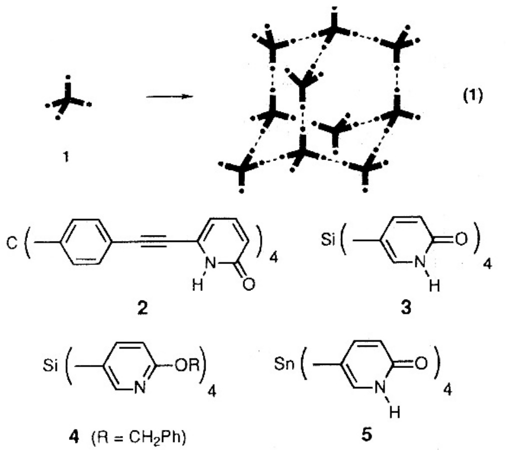
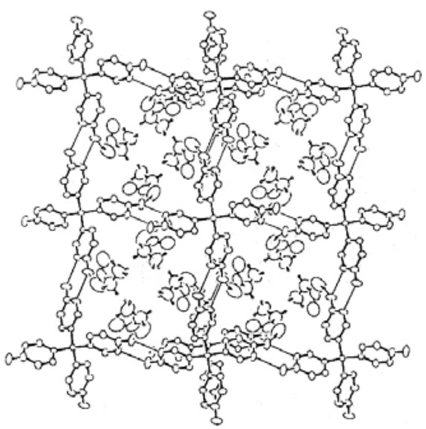
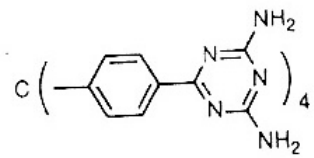
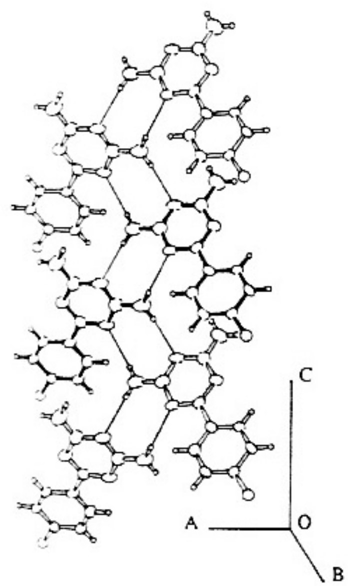
Porous solids: hydrogen-bonded networks

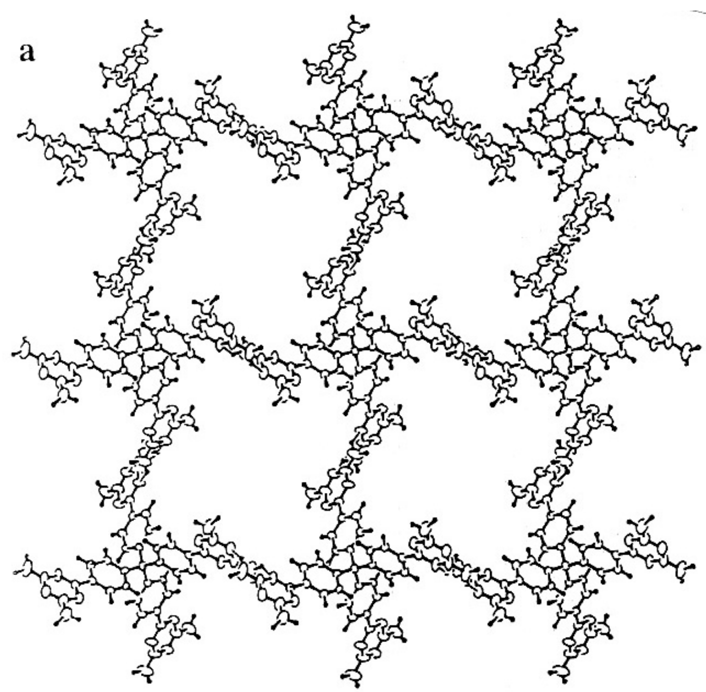
Molecular tectonics: 3D organic superlattices based on hydrogen bonding











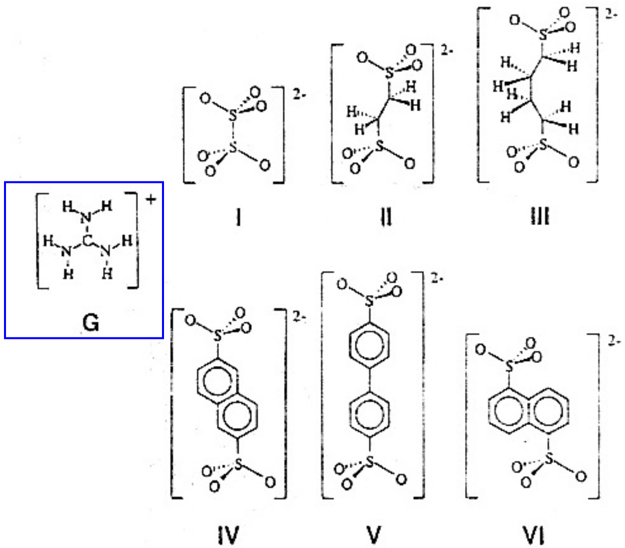
(Inclusion solvent molecules omitted for clarity)

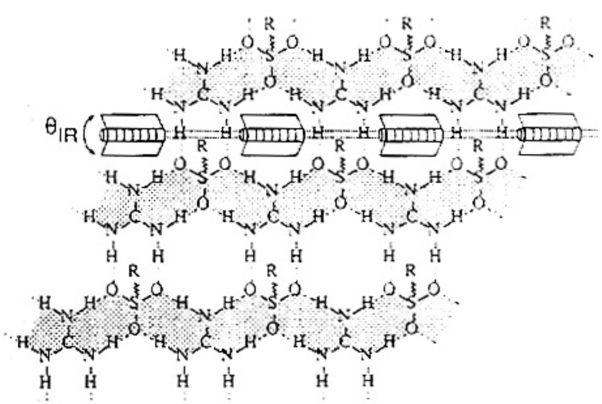
8 HB’s per molecule– can remove up to 63% of solvent molecules before structural integrity is affected

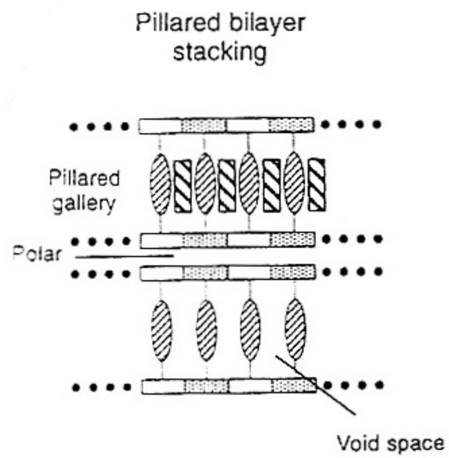
Wuest and coworkers, *JACS* **1994**, *116*, 12119
Wuest and coworkers, *JACS* **1997**, *119*, 2737

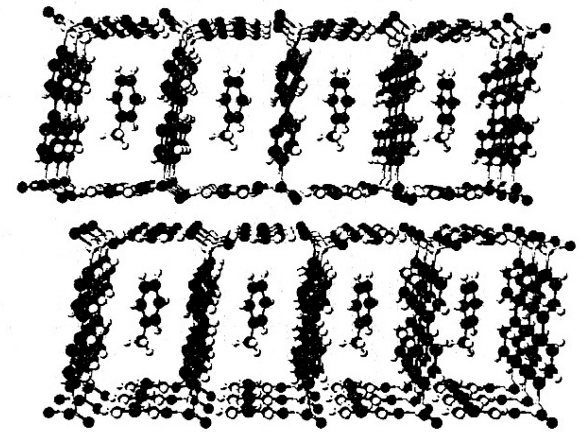
Porous solids: hydrogen-bonded networks

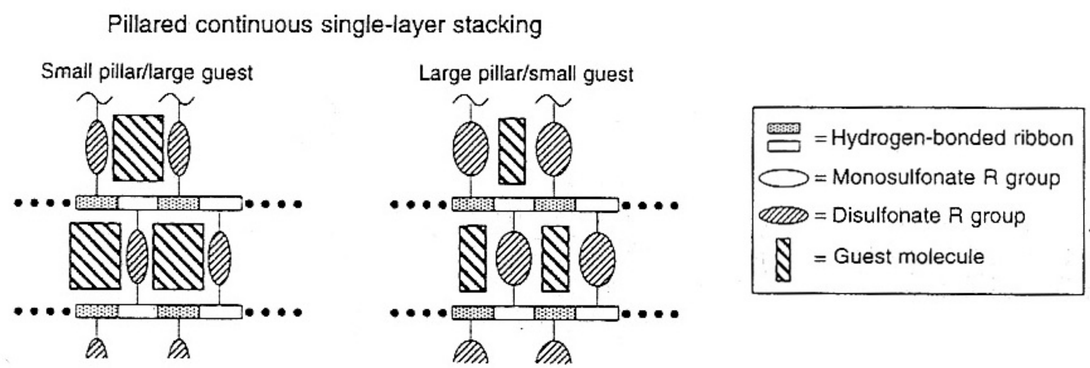
Molecular tectonics: Guanidinium-sulfonate networks











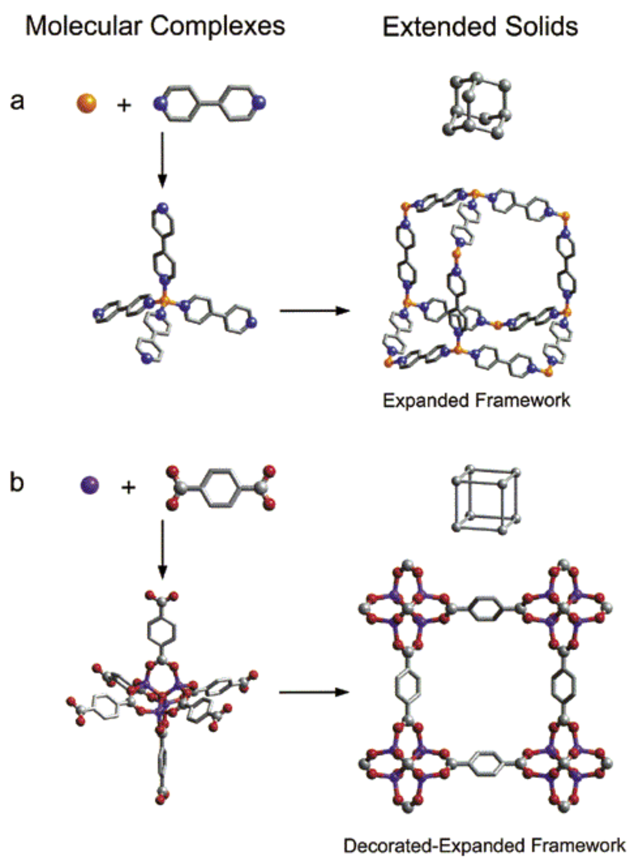
Ward and coworkers, *Science* **1997**, *276*, 575

Porous solids: Metal-organic frameworks (MOFs)

Recent reviews: *Chem. Soc. Rev*. **2009**, *38*, vol. 5 (special issue on MOFs);
Top. Curr. Chem. **2010**, Vol. 293 (monograph); *Adv. Mater.* **2011**, *23*, 249-267 (applications).

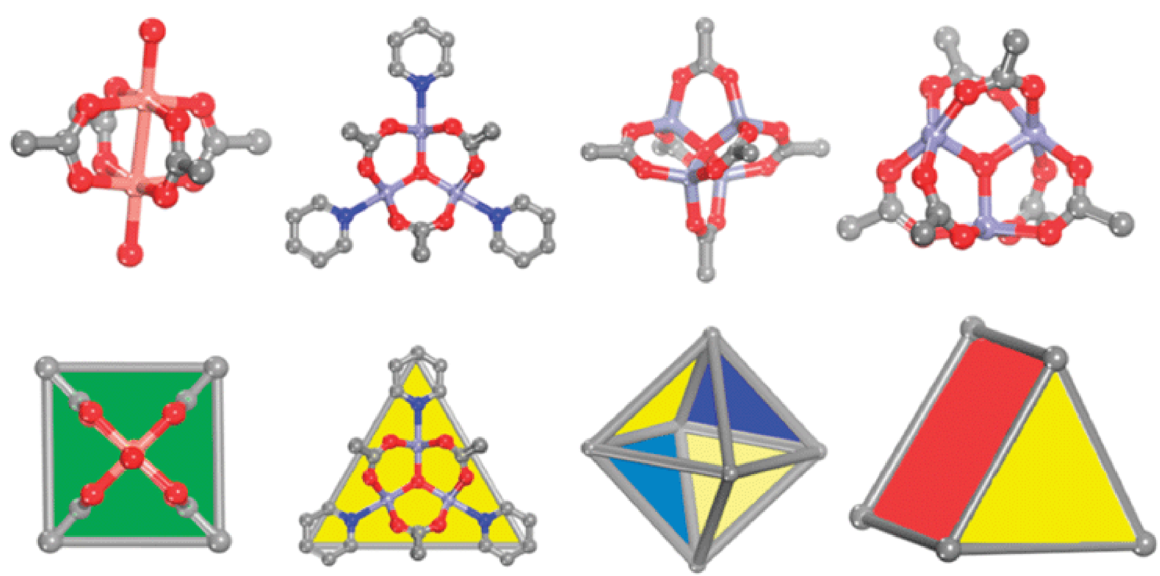
Reticular synthesis of MOFs (Yaghi and O'Keeffe): *Nature* **2003**, *423*, 705-714; also see CSR review (2009)

Key design element to non-interpenetrating frameworks: Secondary building units (SBUs) based on "decorated" metal-ligand clusters as framework vertices + rigid polydentate ligands (carboxylates)



dinuclear "paddle wheel" $(M_2C_4)L_2$

μ-oxo polynuclear carboxylate clusters: $(M_3OC_3)L_3$ (M_4OC_6) (M_3OC_6)

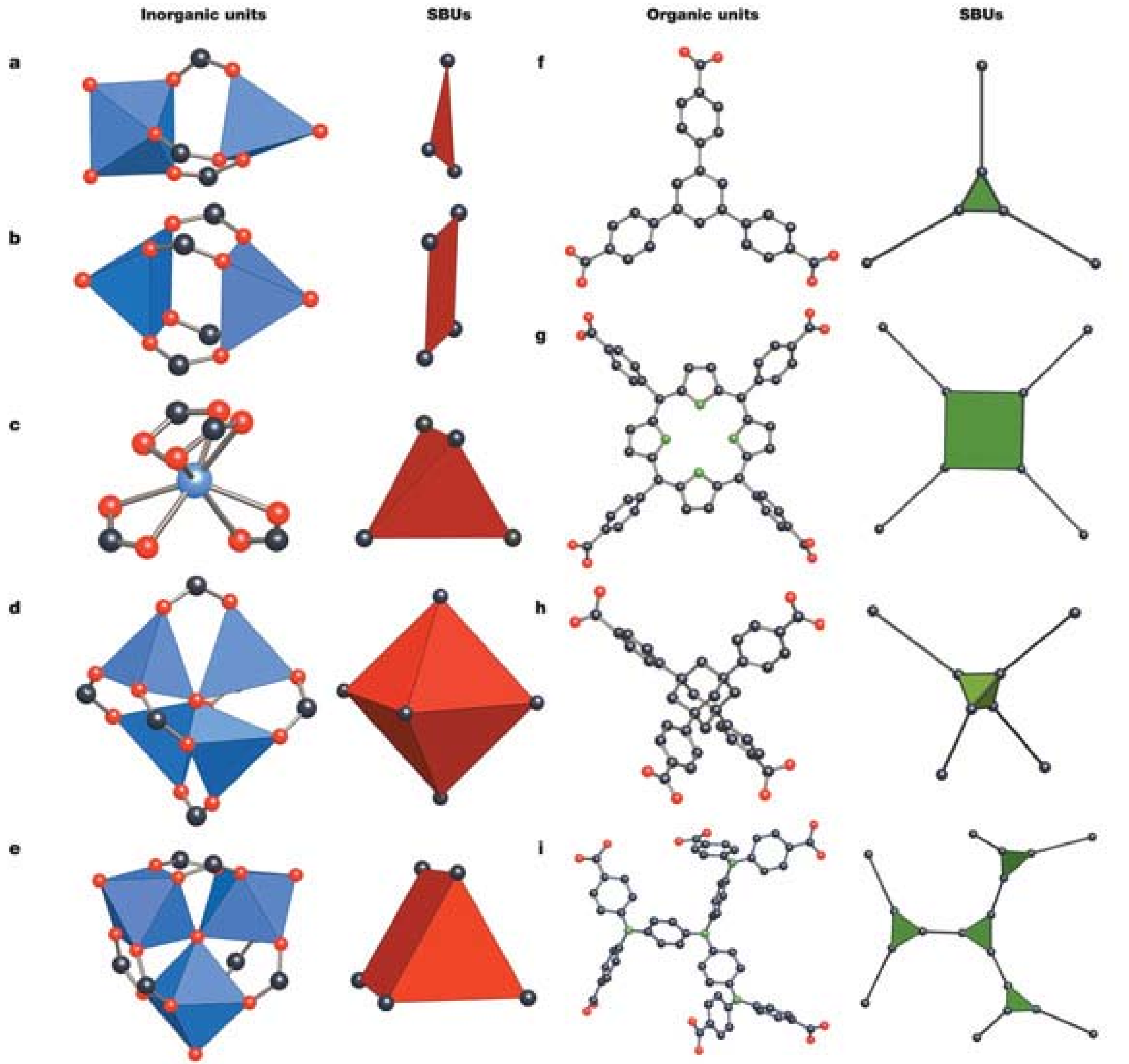


Secondary building units (SBUs) in MOF synthesis

Tetrahedron (neutral)

Square pyramidal
(fractional charge)

Polynuclear clusters
(e.g., Zn_4O)

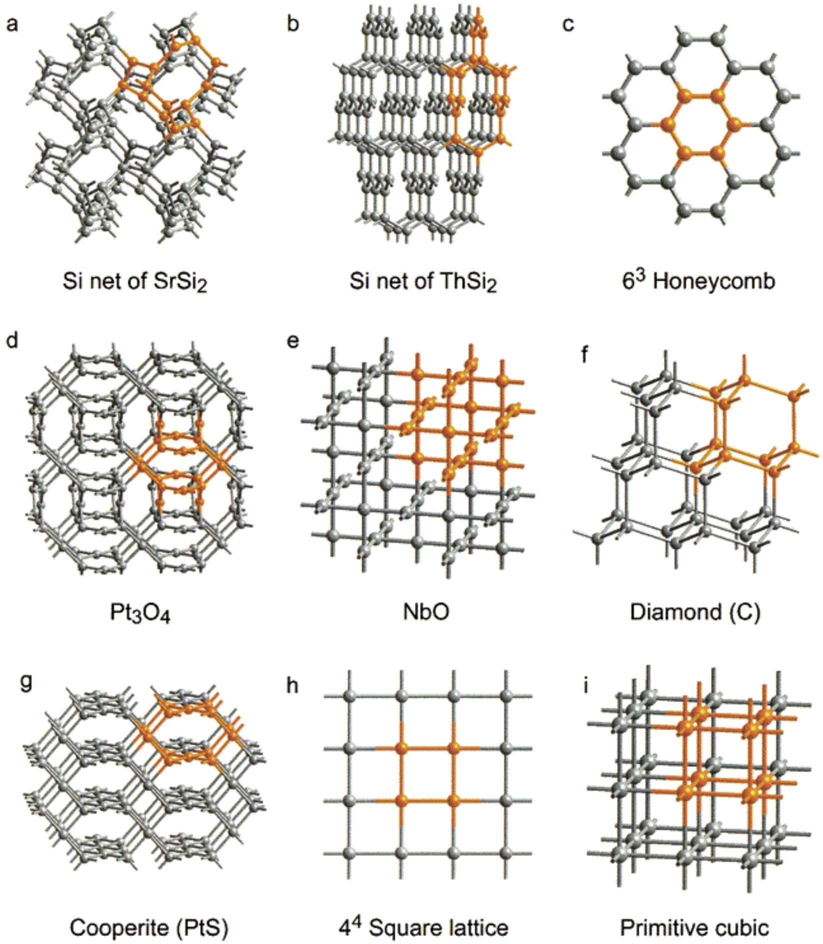


Nature **2003**, *423*, 705-714

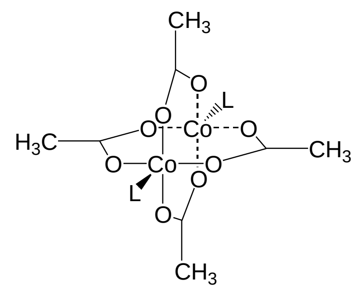
MOF synthesis is driven by network topologies

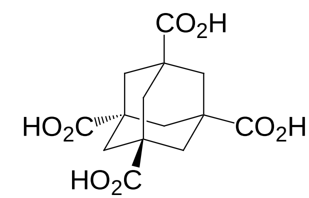
Growth is directed by cluster geometries and rigid framework components

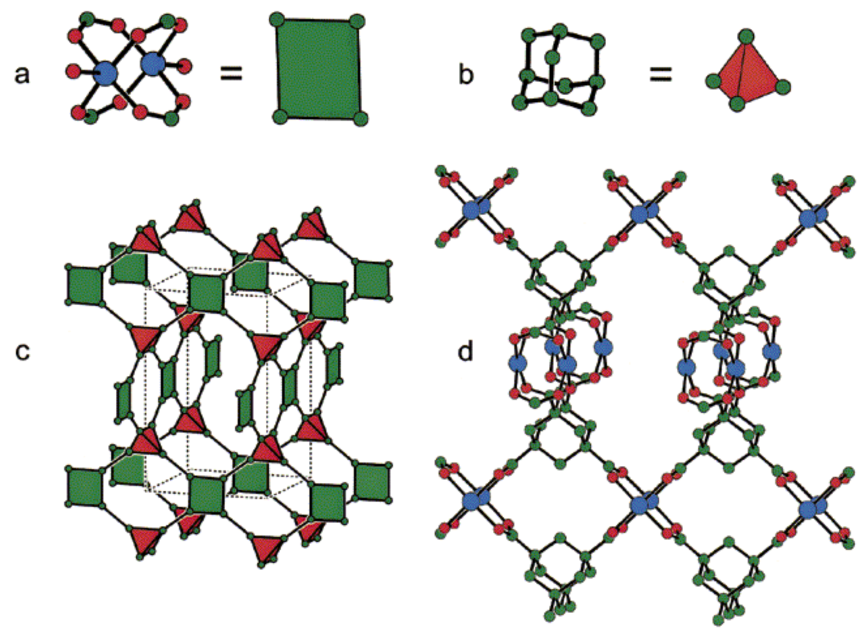
Some common networks observed in traditional crystalline materials:



Example of reticular MOF synthesis:





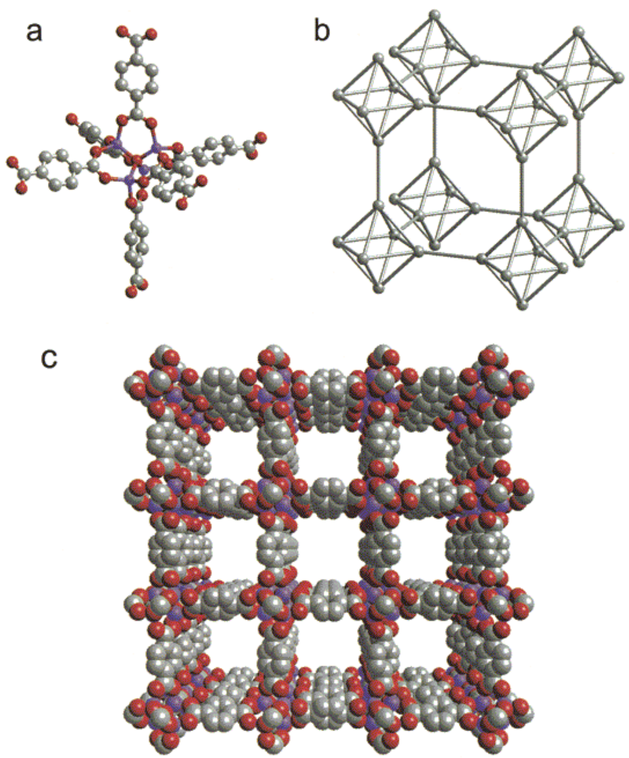


Eddaoudi et al., *Acc. Chem. Res.* **2001**, *34*, 319.

Isoreticular metal-organic frameworks (IRMOFs)

Reticular assembly is modular; permits growth of MOFs with unprecedented porosity

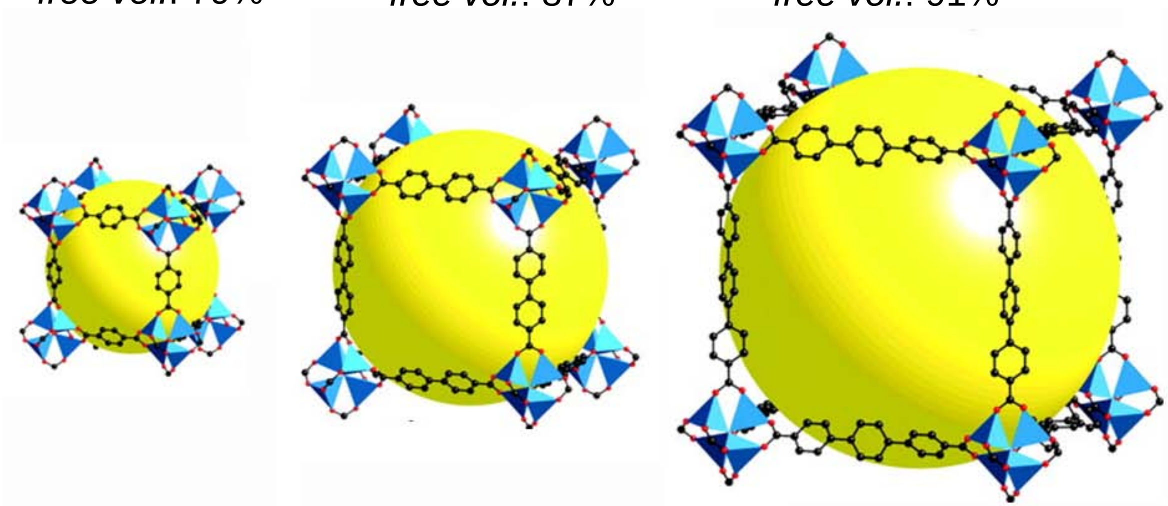
"MOF-5": Li et al., *Nature* **1999**, *402*, 276.



pore: 11.2 Å
sphere: 18.5 Å
free vol.: 79%

pore: 15.4 Å
sphere: 24.5 Å
free vol.: 87%

pore: 19.1 Å
sphere: 28.8 Å
free vol.: 91%



Structural characteristics of natural zeolite (faujasite):
pore: 7.4 Å
sphere: n/a
free vol.: <50%

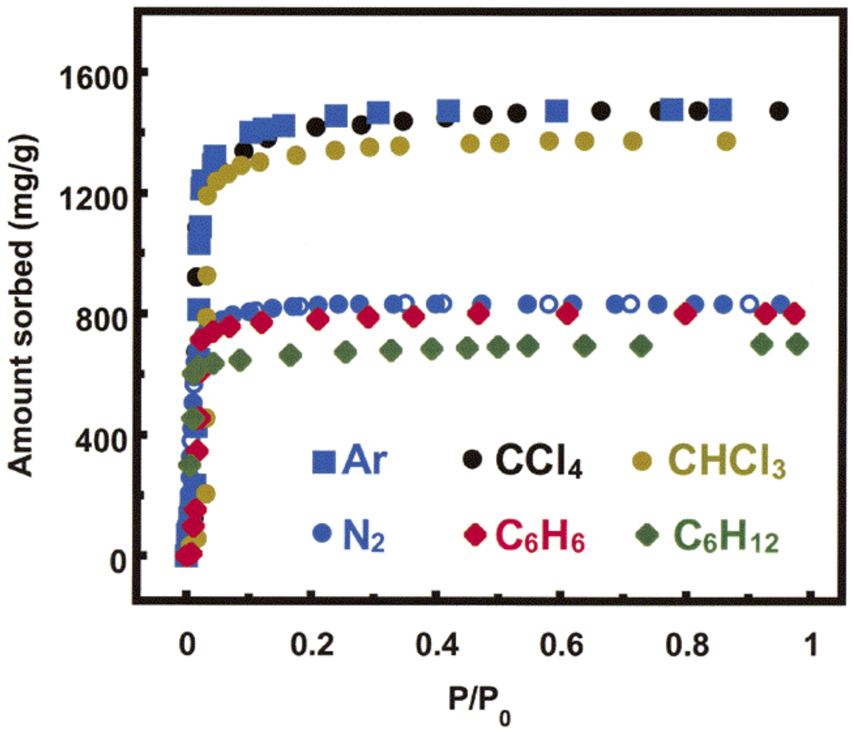
Eddaoudi et al. *Science* **2002,** *295,* 469.

<u>Note</u>: MOF syntheses are highly dependent on experimental parameters: proper stoichiometry; rapid and even heating (microwave); poor, bulky solvents (e.g., diethylformamide); nucleation conditions (e.g., slow addition of base). Many MOFs are non-interpenetrating, but not all.

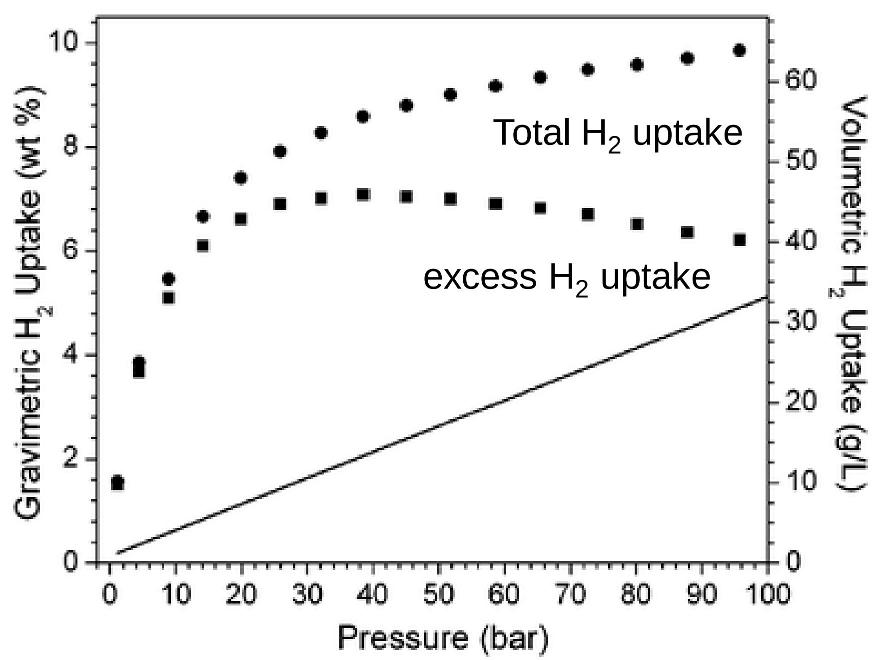
Applications of nanoporous MOFs

- Bonding enthalpy of carboxylates to Zn_4O clusters on the order of 100 kcal/mol
- Rigid organic "struts" enable MOFs to withstand evacuation of solvent at high temperatures, producing mesoporous solids with very high surface areas

MOF-5 storage capacity:



MOF-5 capacity for H_2 storage:



Reversible storage of (excess) H_2 up to 7 wt%

Eddaoudi et al., *Acc. Chem. Res.* **2001**, *34*, 319.

H$_2$ storage: *Science* **2003**, *300*, 1127; *J. Am. Chem. Soc.*, **2007**, *129*, 14176