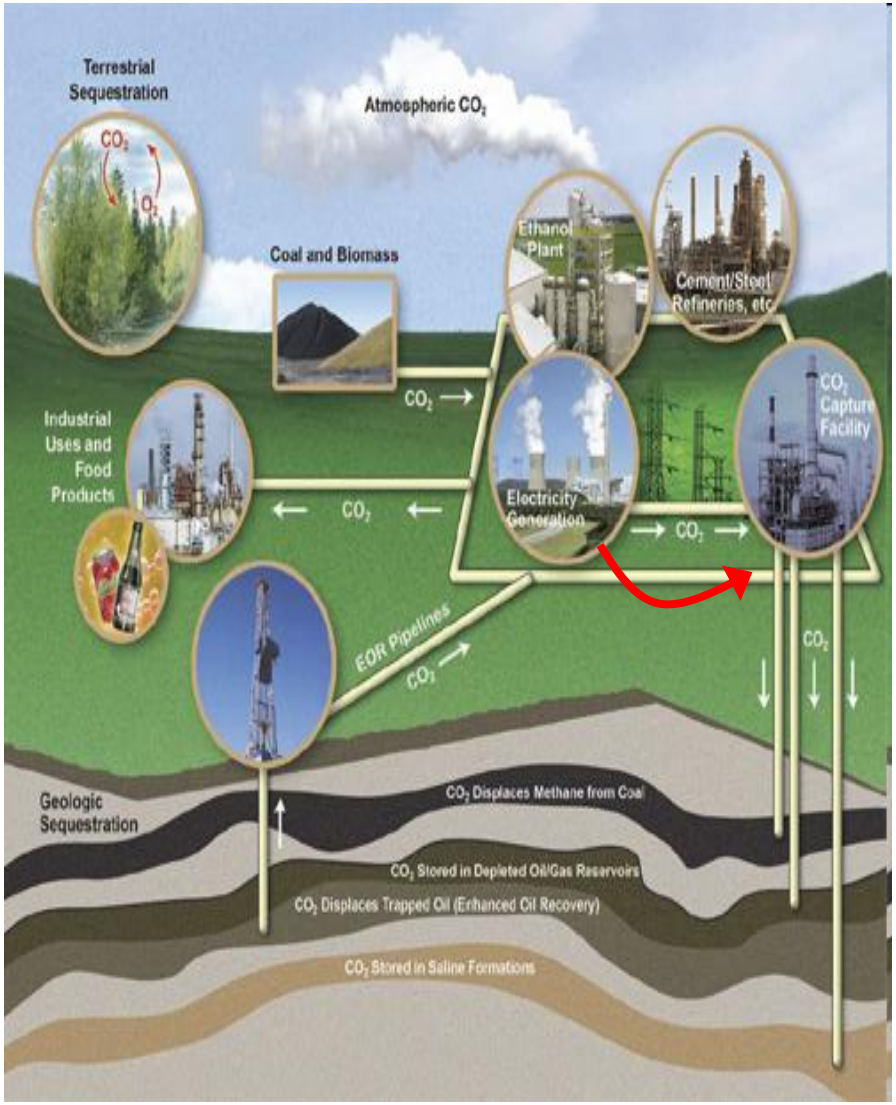
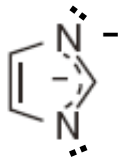
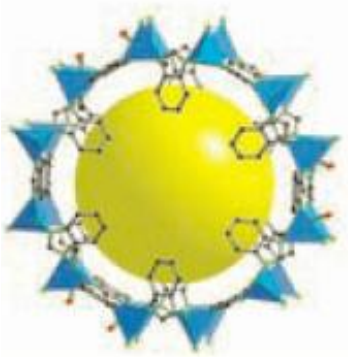
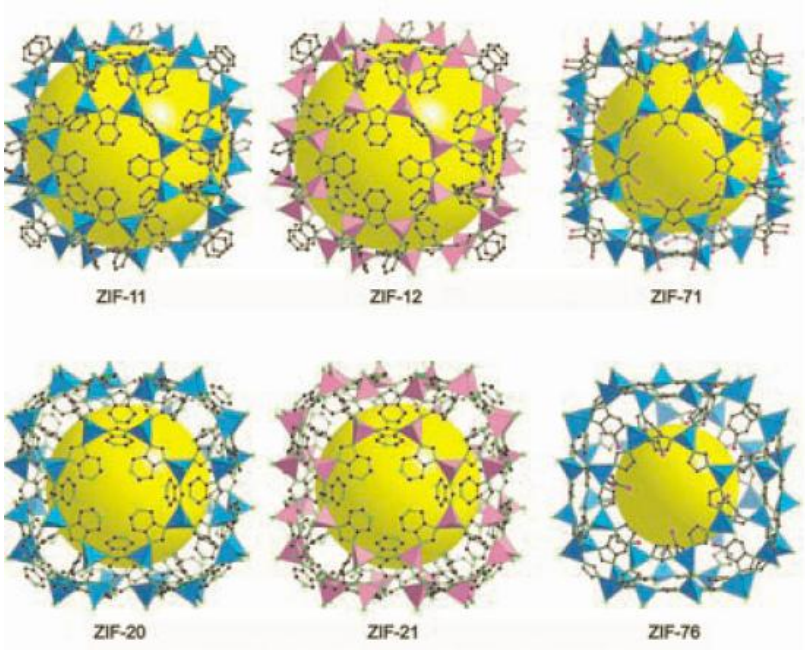
Zeolitic Imidazolate Frameworks for CO_2 Storage and Separation



Zn^{2+} + 4  ⟶ 

Imidazolate

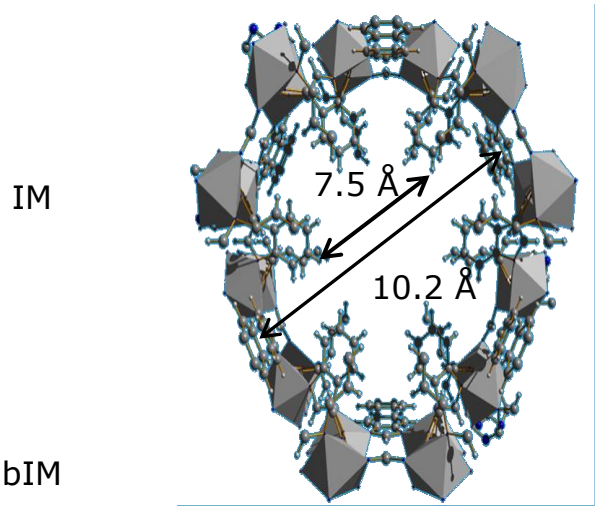


Yaghi et al, Science, **319**, 939 (2008)

Research Question

- Why do ZIFs absorb so much CO_2, and with such selectivity?
  - Absorption sites / mechanism
  - Selectivity mechanism
- Why are ZIFs so stable?
  - Thermal vs. solvent stability
  - Strong metal-ligand bonds vs. hydrophobic effect
- What determines the ZIF crystal structures?
  - Kinetics vs. thermodynamics
  - Ligand-ligand interactions
  - Reaction conditions

Modeling the CO_2 / ZIF interaction



Imidazolate ligands

ZIF-68

$$E_{\text{int}}^{SAPT(DFT)} = E_{elst}^{(1)} + E_{exch}^{(1)} + E_{ind}^{(1)} + E_{exch-ind}^{(1)} + E_{disp}^{(2)} + \ldots$$

- CO_2 / ZIF interaction is weak
- Important terms?
  - Electrostatics
  - Polarization
  - Exchange repulsion
  - Dispersion
- Must go beyond traditional DFT
  - Dispersion corrected DFT
  - SAPT(DFT)

Each term fit individually to create physically-motivated FF!