

Seventh Annual Conference on Carbon Capture & Sequestration

Novel Flexible Materials for Carbon Dioxide Capture

Bradley Bockrath, Jeffery Culp, Milton Smith, and Edward Bittner

National Energy Technology Center

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Ionic Metal-Organic Complexes for CO₂ Capture

A vast array of new materials is now available as potential CO₂ capture agents

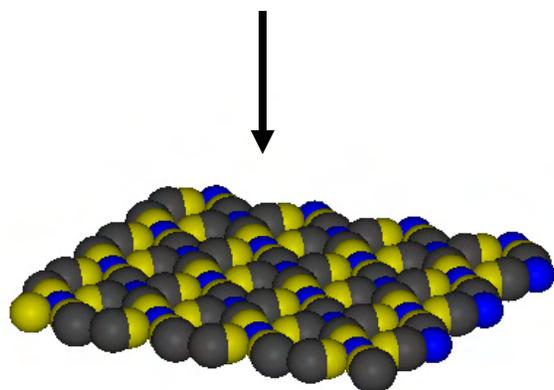
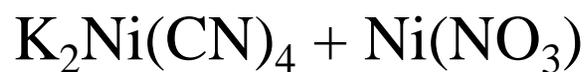
- Metal Organic Frameworks
- Prussian Blues
- Coordination Polymers
- Hofmann Clathrates (Layered-Pillared Complexes)

Layered-Pillared Complexes for CO₂ Capture (Hofmann Clathrates)

- Assembled from simple metal ions and organic “linkers”
- Regular crystalline structure
- Microporous
- Easily engineered by choice of metal and linker
- Potential dry sorbent for CO₂ in flue gas or from syngas at high pressure (IGCC)
 - High capacity
 - Reactivation with lower energy cost
 - Stable

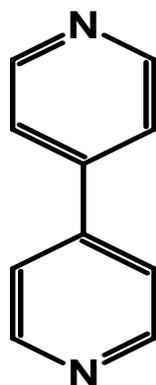
Assembling a Pillared Layered Complex

Easy Synthesis in High Yield



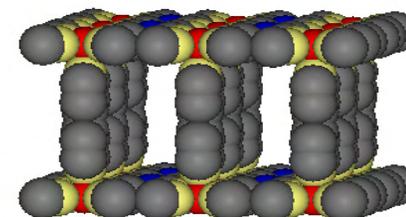
**METAL CYANIDE
SHEETS**

+

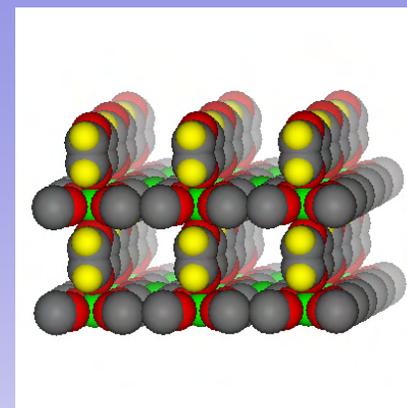
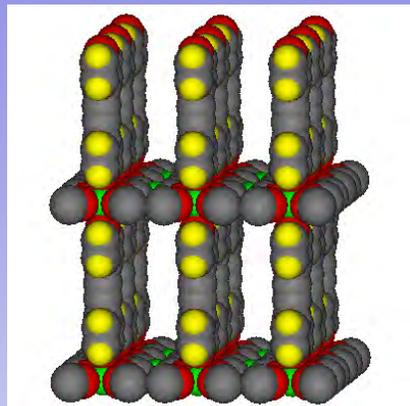


ORGANIC PILLARS

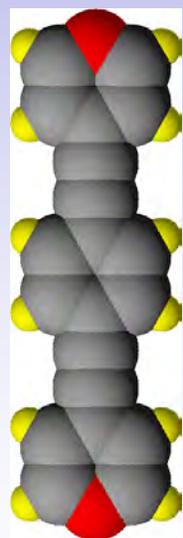
**Toluene (dry)
Reflux 24 hrs**



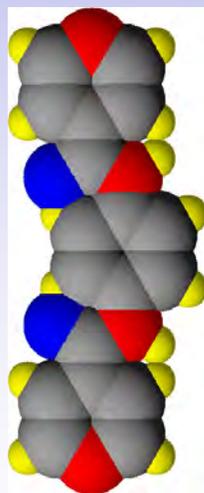
Layered-Pillared Complexes for CO₂ Capture (Hofmann Clathrates)



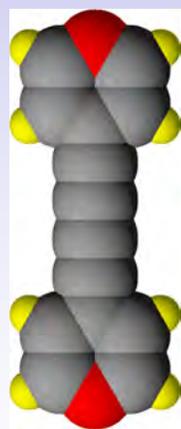
Bi-pyridyl Ligands Change Pore Height
Pore Width Remains ~ 6 Å



19.0 Å



17.0 Å



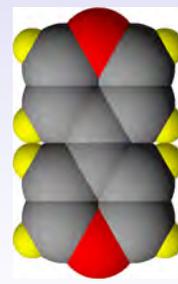
15.0 Å



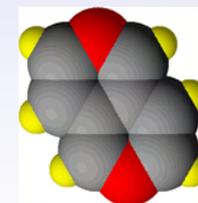
13.6 Å



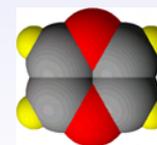
12.3 Å



9.8 Å



7.6 Å



5.6 Å

Micro-Porous Materials Characterization

Isotherms Available over a Wide Range of Temperature and Pressure Conditions



**High Pressure (0-80 atm)
Ultimate Gas Capacity**



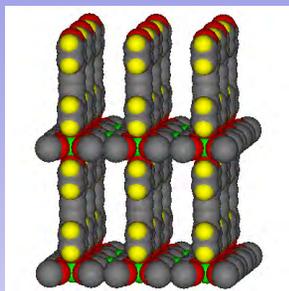
**Low Pressure (0-1 atm)
Pore Volume,
Surface Area**



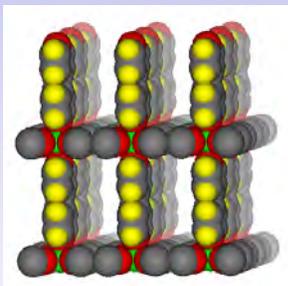
**Powder XRD
Structural Analysis**

CO₂ on Ni(L)[Ni(CN)₄] Slit Pore Materials

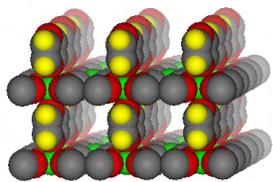
Storage Capacity Studies



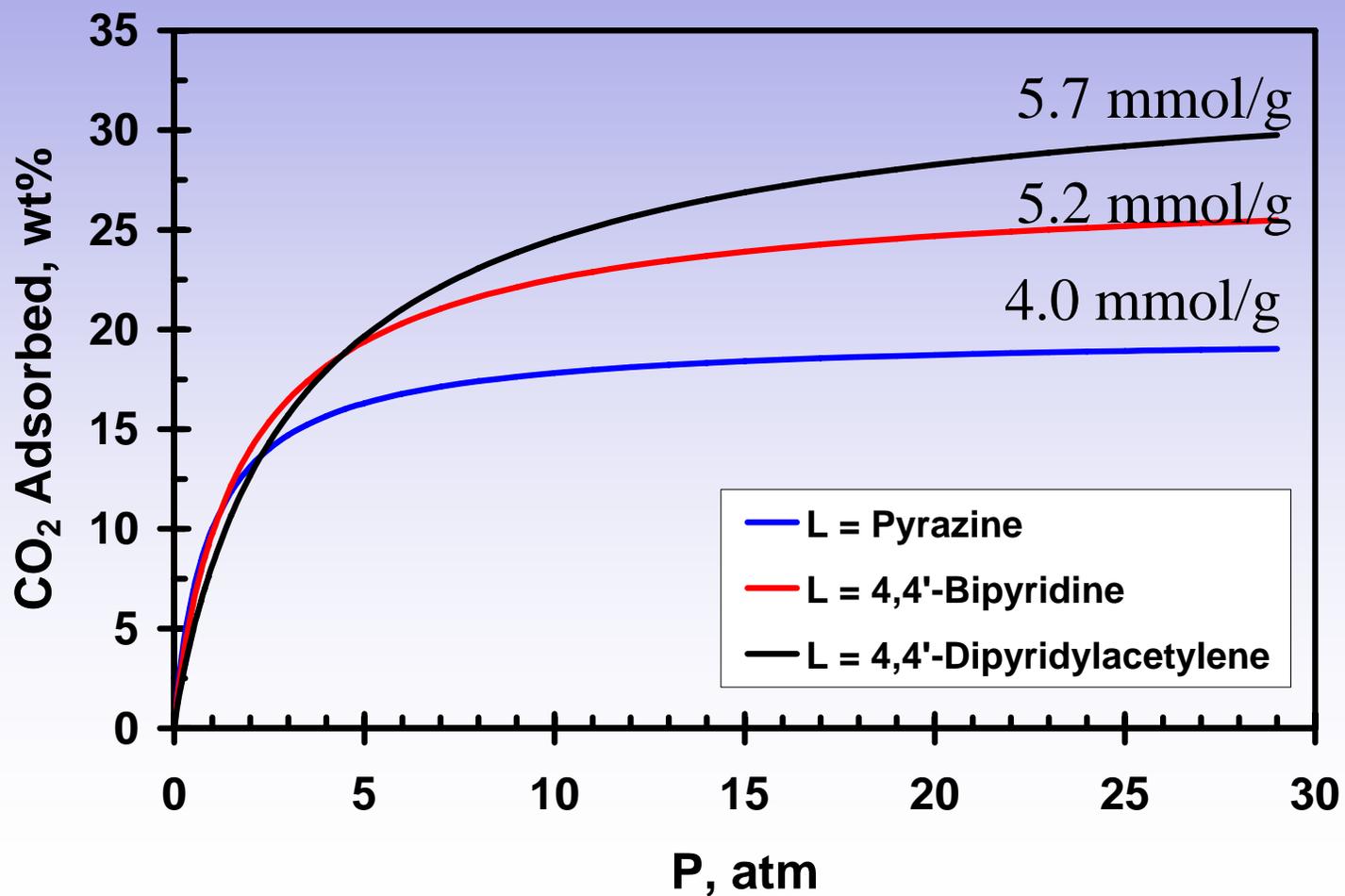
4,4'-Dipyridylacetylene



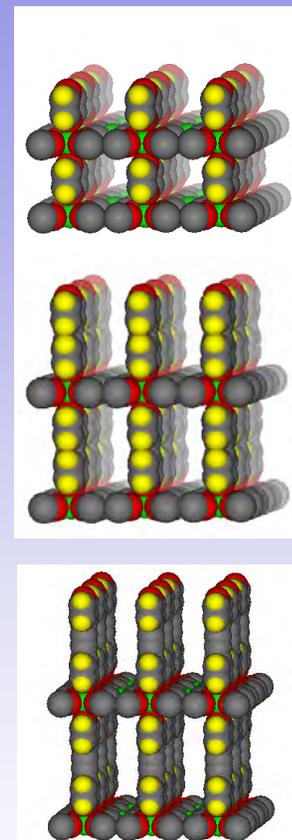
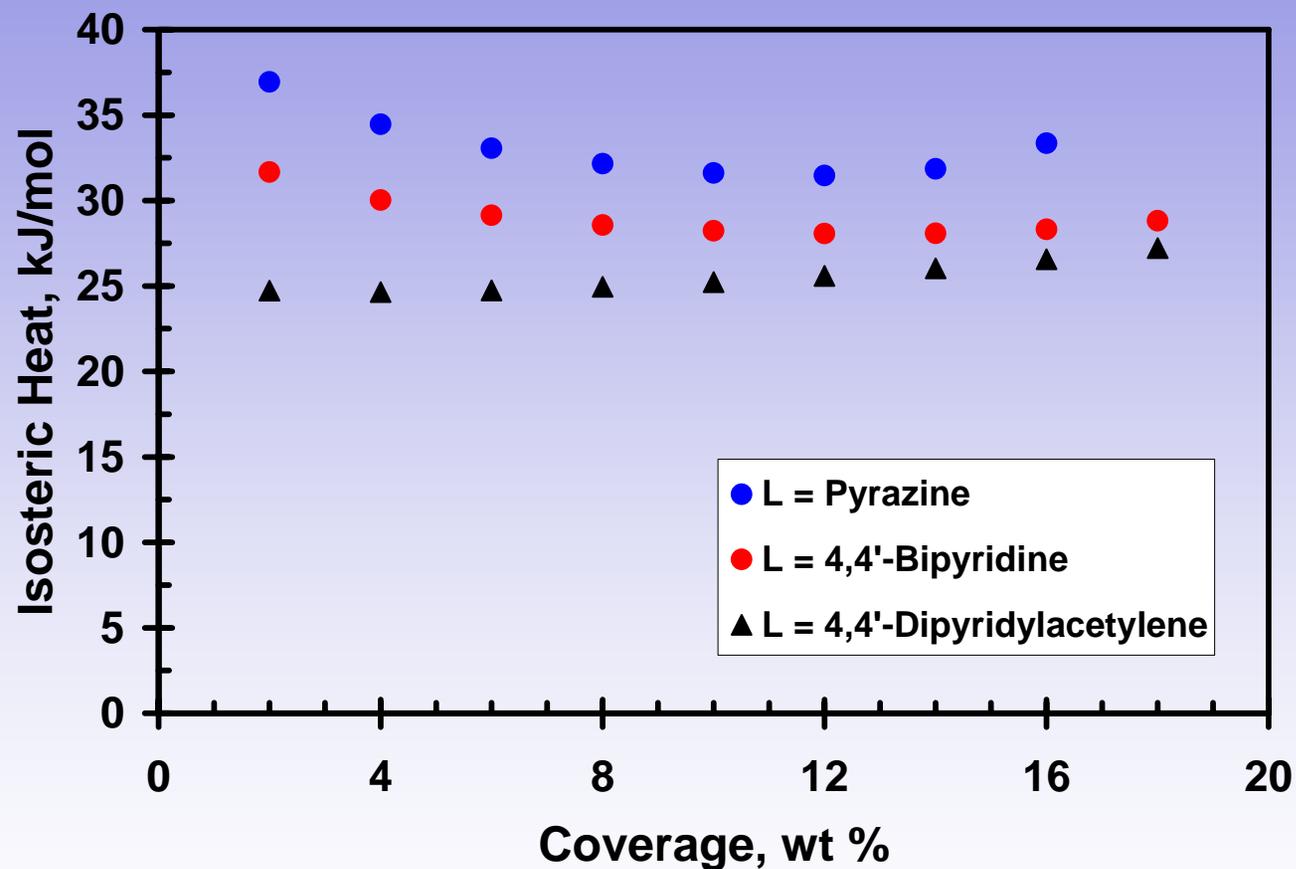
4,4-Bipyridine



Pyrazine

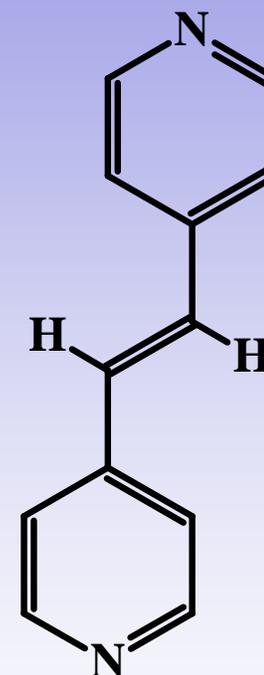
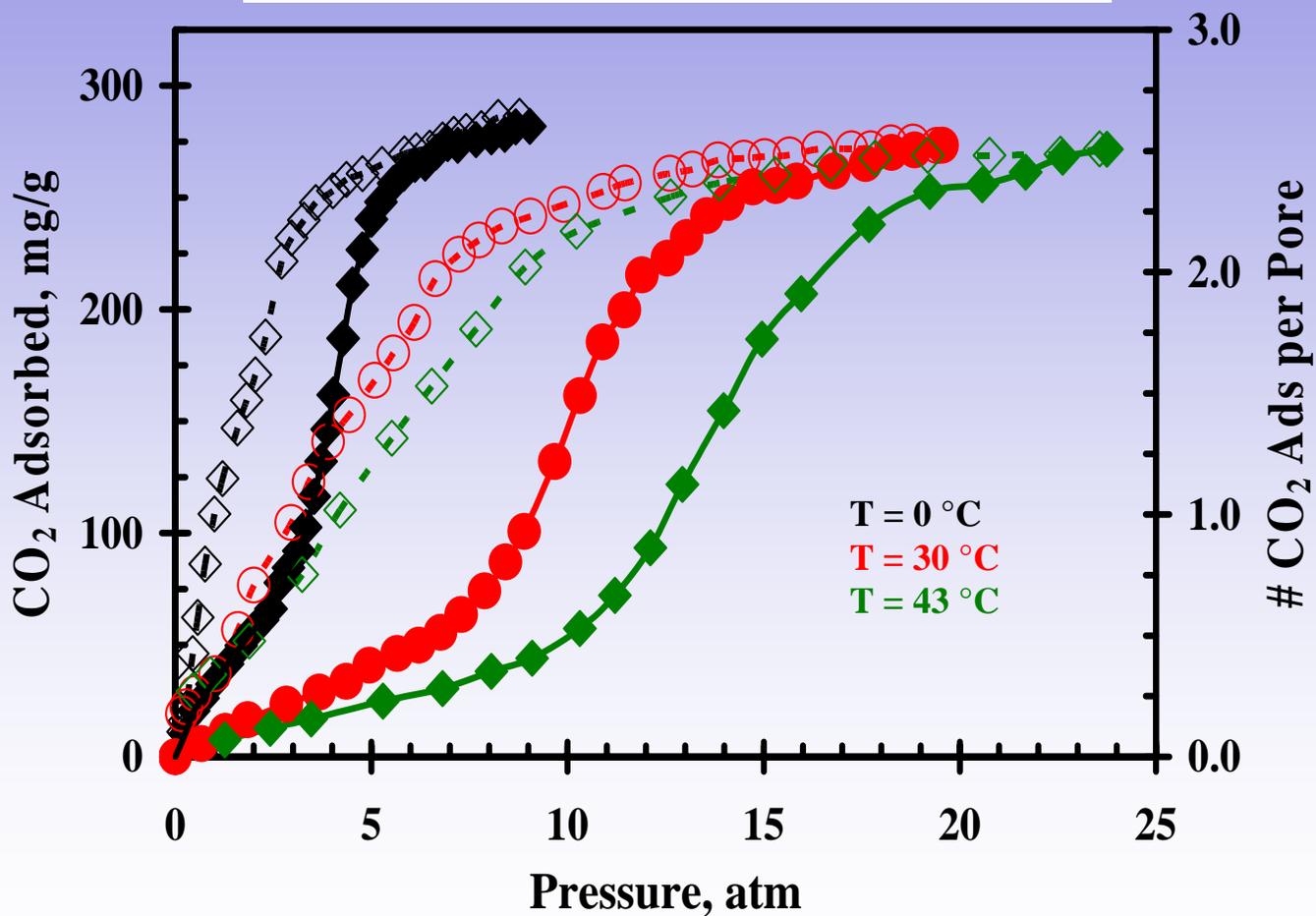


Heat of CO₂ Adsorption Depends on Pore Size



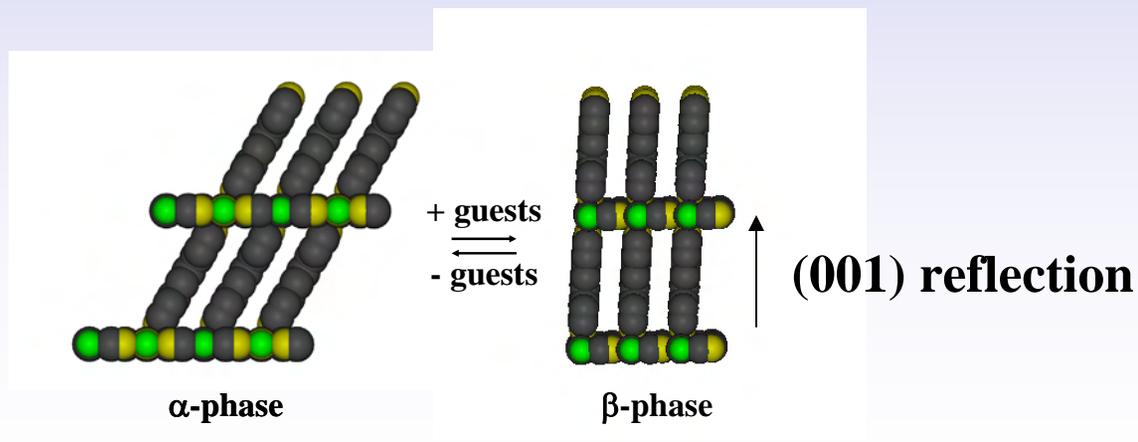
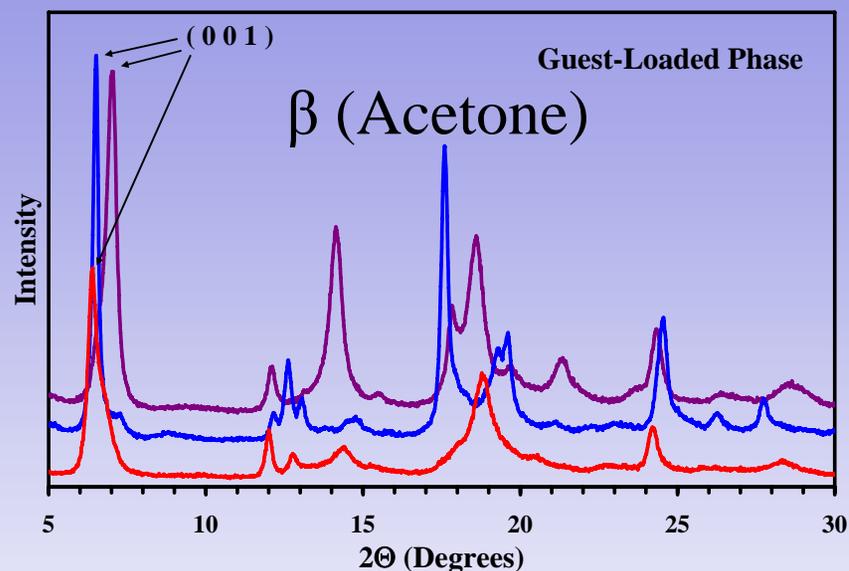
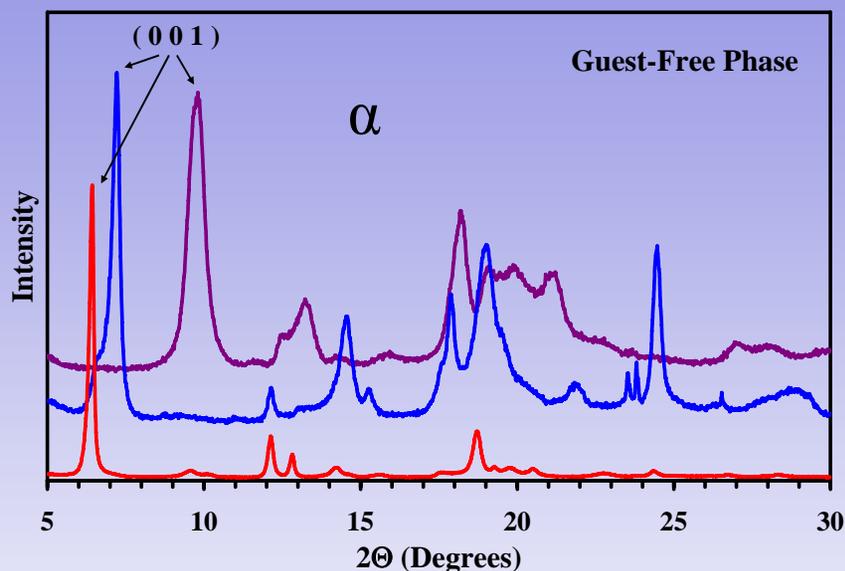
Non-Linear Pillar Generates Reactive Adsorbent

Step Isotherm with Hysteresis

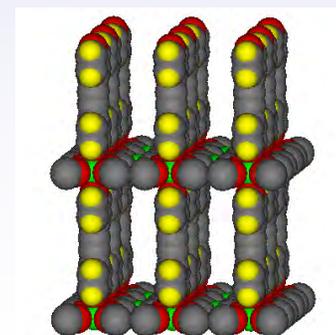
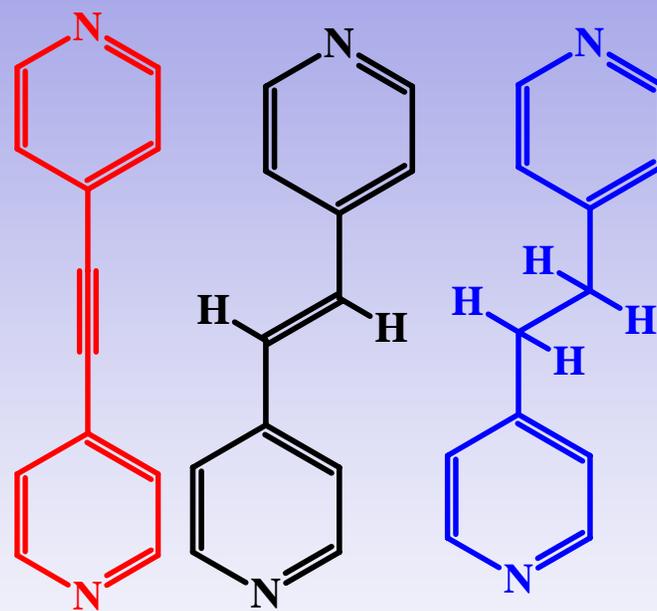
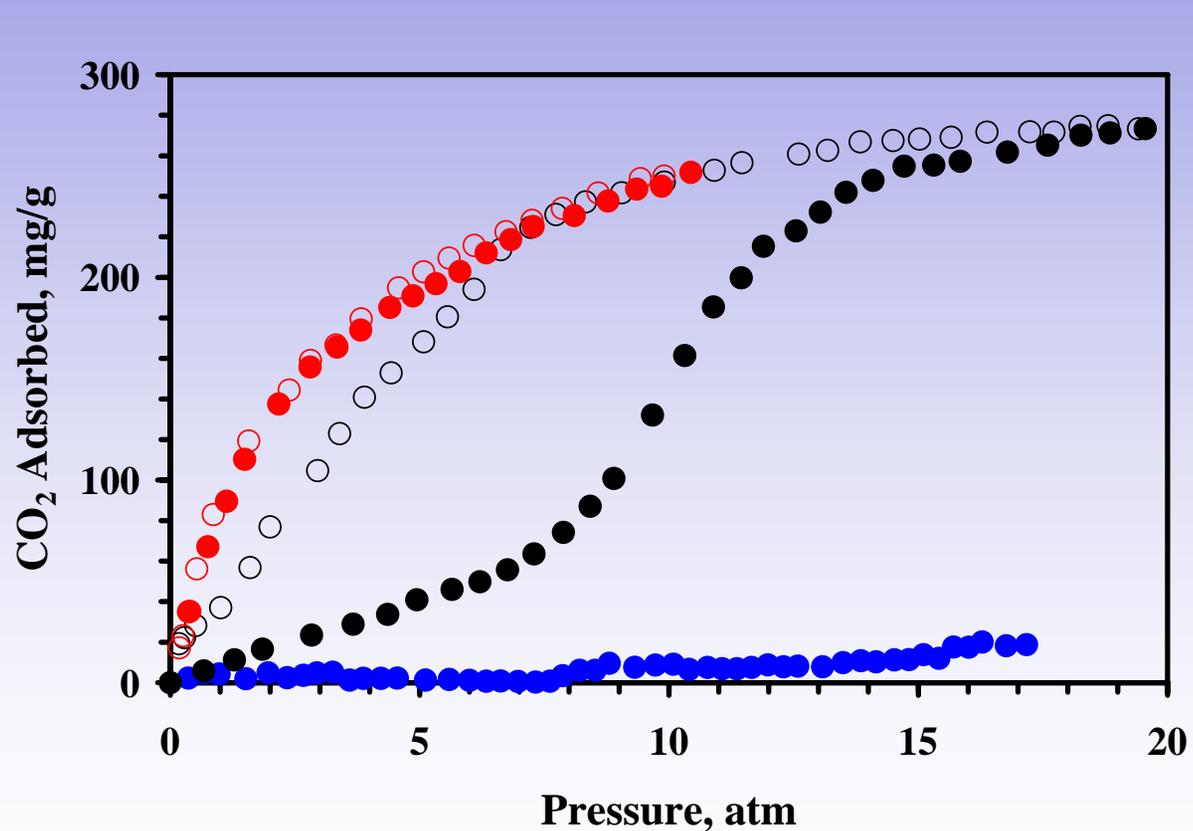


Addition of Guests Causes Phase Change

XRD Detects Lattice Expansion

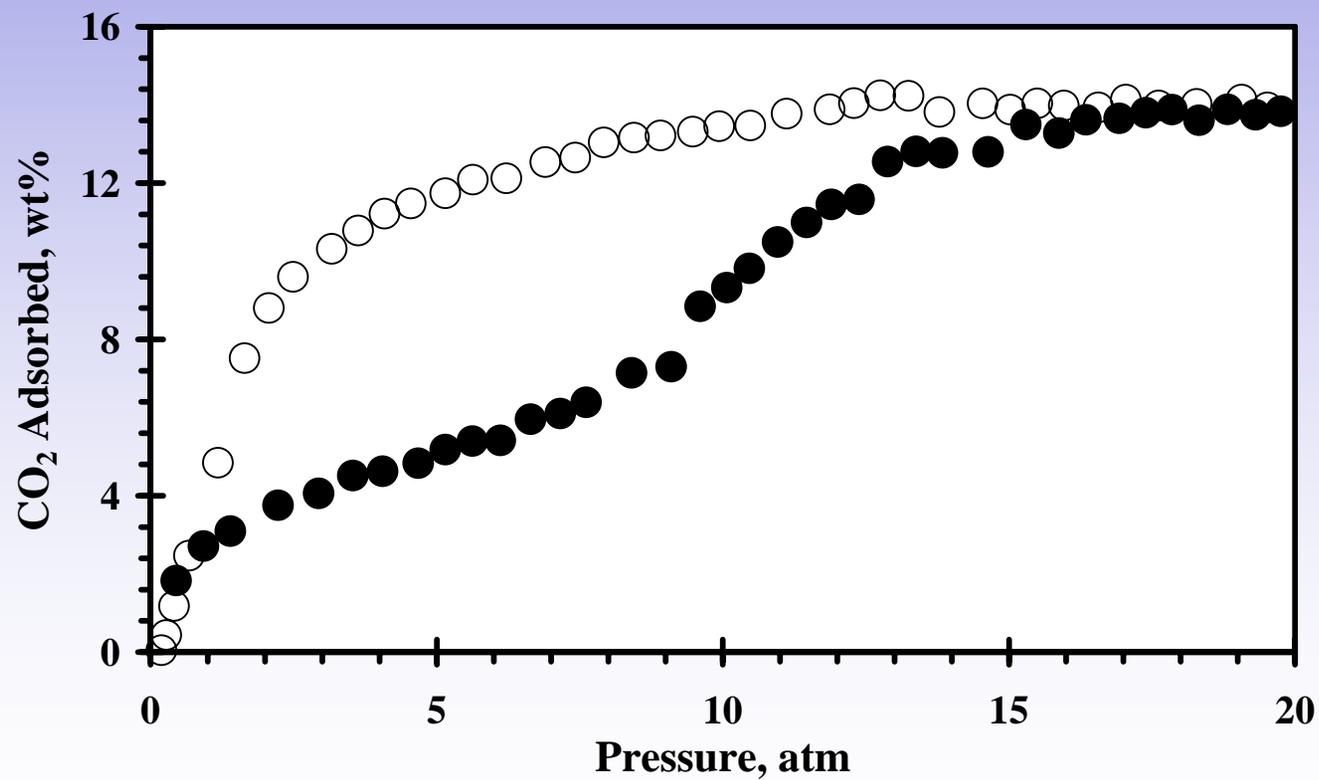
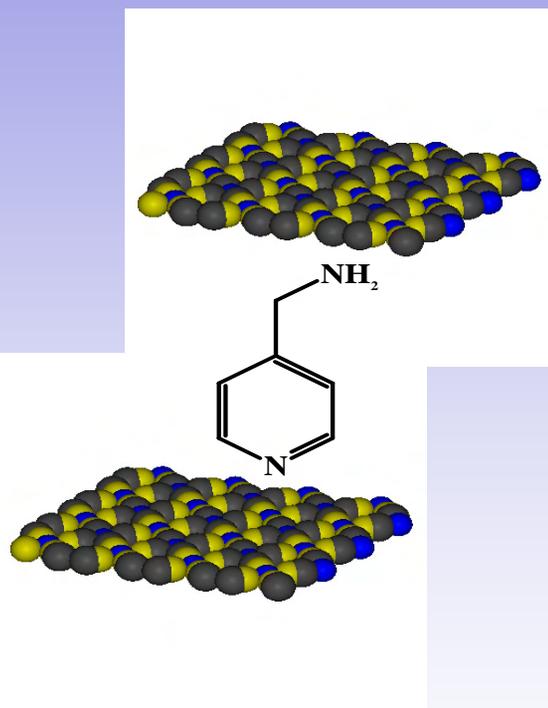


Choice of Pillar gives Rigid, Flexible, or Collapsed Pore Structure



Other Non-Linear Pillars Generate Similar Results

CO₂ Adsorption at 43 °C on Ni(L₆)[Ni(CN)₄]



Layered-Pillared Complexes for CO₂ Capture

- Crystalline Microporous Structure
- High Capacity for CO₂
- Tailoring of Pore Properties by Choice of Pillar
 - Rigid structure, Type I Isotherm
 - Flexible Structure, Pronounced Hysteresis
- Stable toward water
- Potential for Further Development