New Concepts for Optimized Hydrogen Storage in MOFs

Omar M. Yaghi and Adam J. Matzger
Department of Chemistry
University of Michigan
Ann Arbor, MI 48109

May 23, 2005

Project ID # STP52 Yaghi

Overview

Timeline

- Project start date
  1/1/2005
- Project end date
  12/31/2008
- Percent complete
  2%

Budget

- Total project funding
  - DOE share: $1.60M
  - Contractor share: $0.35M
- Funding received in FY04
  - $0.00
- Funding for FY05
  - $37,500 (estimated)

Barriers

- Technical barriers addressed
  - B) Weight and Volume
  - C) Efficiency
  - M) Hydrogen Capacity and Reversibility
- Technical targets by YR 2010
  - Gravimetric capacity: 6.0%
  - Volumetric capacity: 4.5%
  - Operating ambient temp.: -30/50 °C

Partners (planned FY06)

- Juergen Eckert (Los Alamos)
- Randall Q. Snurr (Northwestern University)
- Joseph T. Hupp (Northwestern University)

Objectives

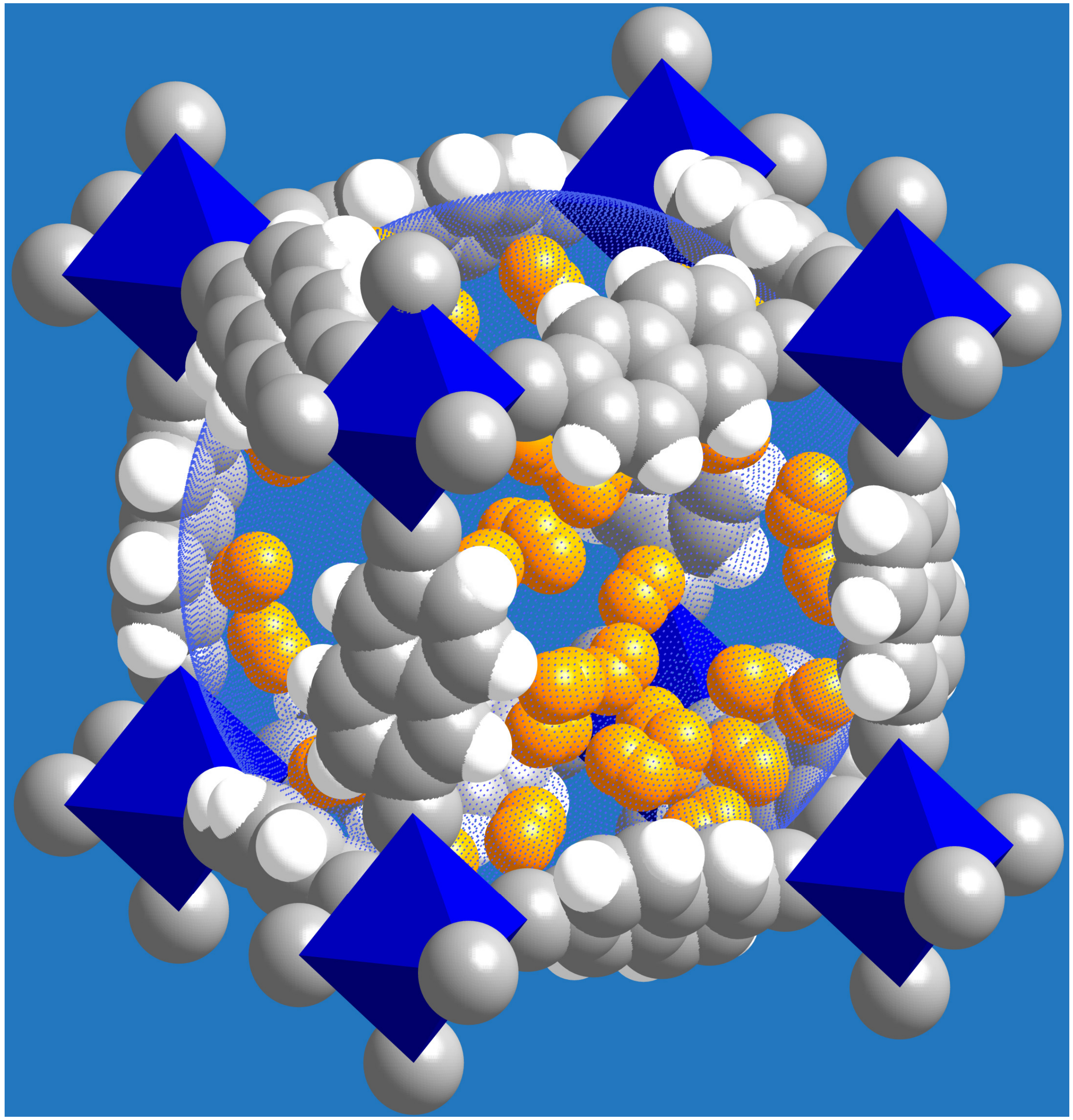
To develop next generation, highly porous metal-organic framework materials (MOFs) that meet or exceed DOE targets for on-board H_2 storage.

- ❑ Improve mass and volumetric H_2 density in MOFs.
  - Utilize strategies for design of materials with high thermal stability and architectural stability.
  - Utilize new concepts for synthesis of materials with extraordinary surface areas (>2000 m^2/g)
  - Develop strategies for synthesis of MOFs having minimal open space but very high surface areas.
- ❑ Employ MOFs in reversible H_2 storage systems.
  - Measure H_2 uptakes under full range of temperatures and pressures as specified in the DOE freedomCAR guidelines.
  - Down-select best materials for scale-up.

Design and Approach

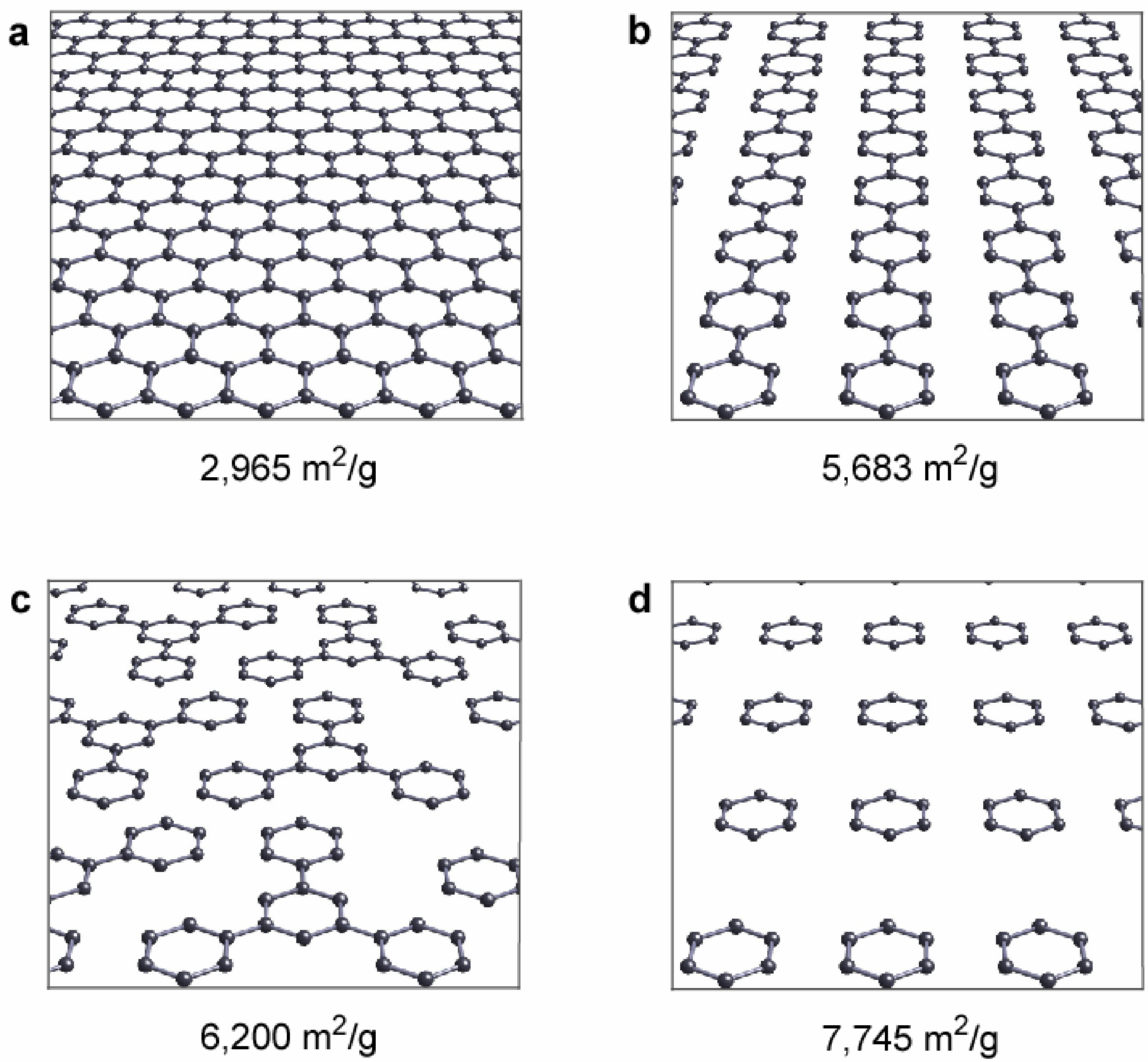
- Implement three major strategies that minimizes open space while increasing total surface area for H_2 binding.
  - Increase surface areas by increasing exposed edges in framework comprising MOF.
  - Use catenated networks.
  - Impregnation of large pores to produce new internal sorption sites and higher surface area.
- Equilibrium H_2 uptake as a function of structure.
  - Measure H_2 uptakes under full range of conditions designated in DOE YR 2010 targets.
  - Use Raman spectroscopy to elucidate H_2 interaction with new materials.

MOFs as H_2 Storage Materials

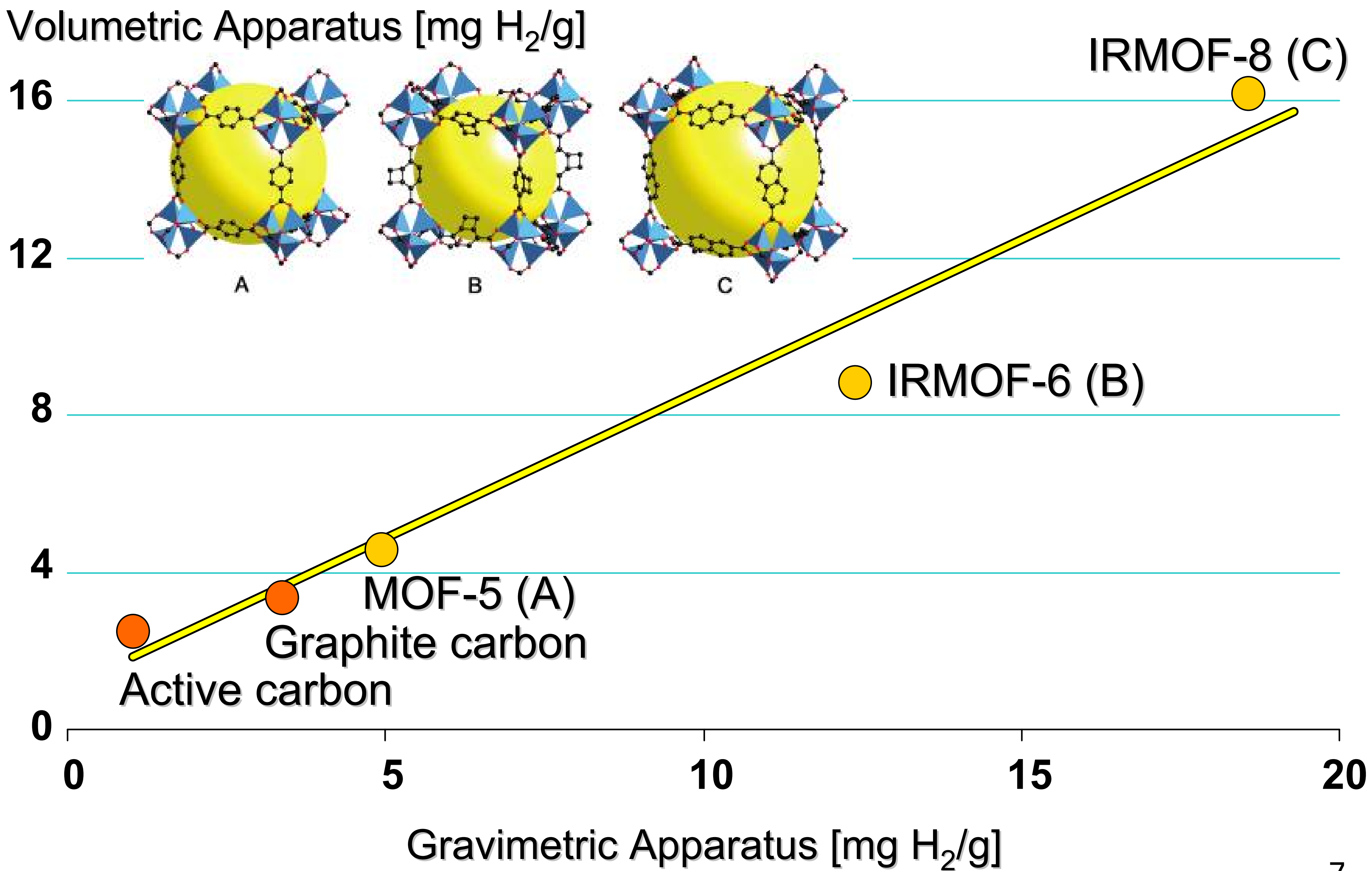


Synthetic Strategy to High Surface Area MOFs

Exposing latent edges dramatically increases surface area.

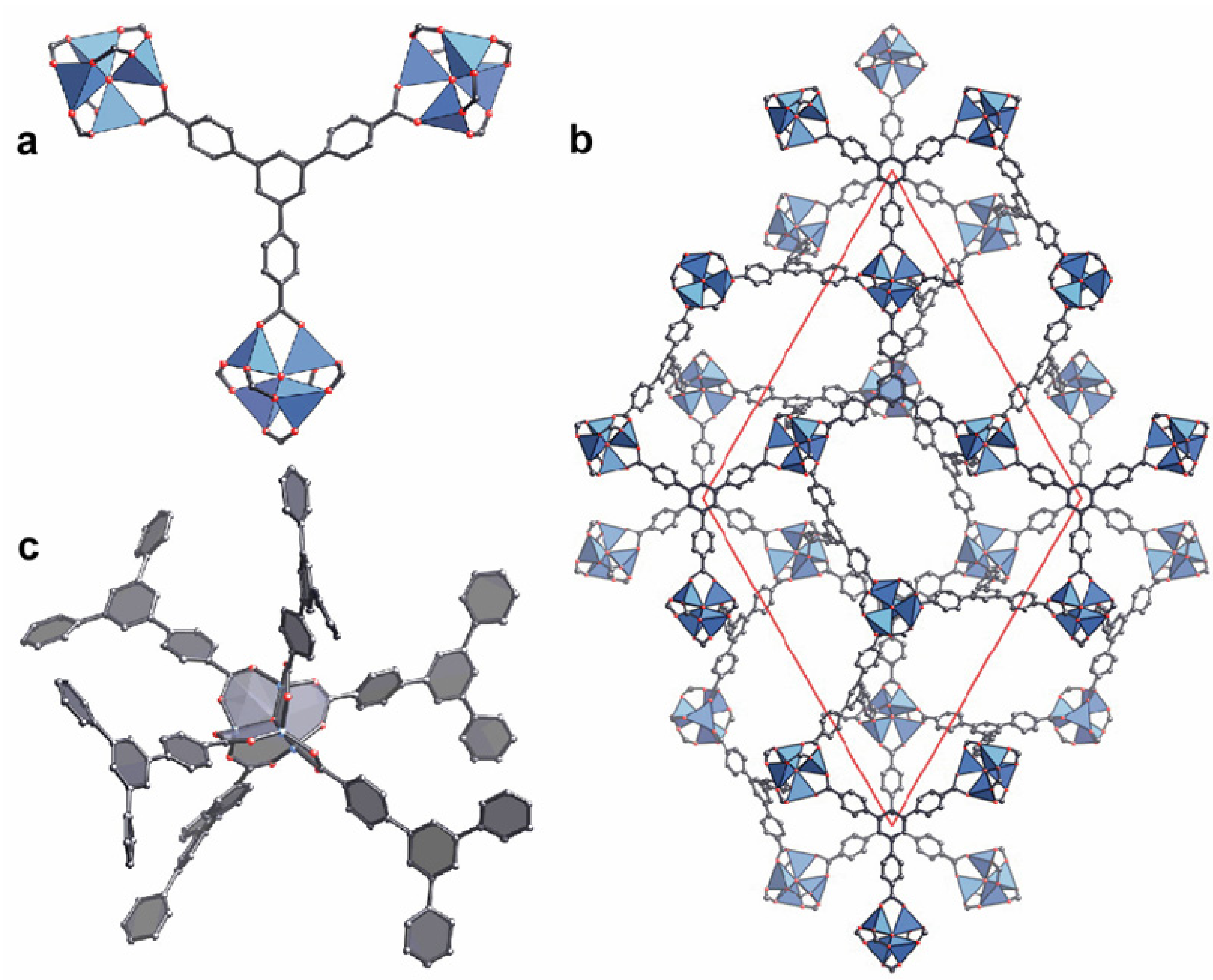


H_2 Storage Capacity at RT & 10 bar

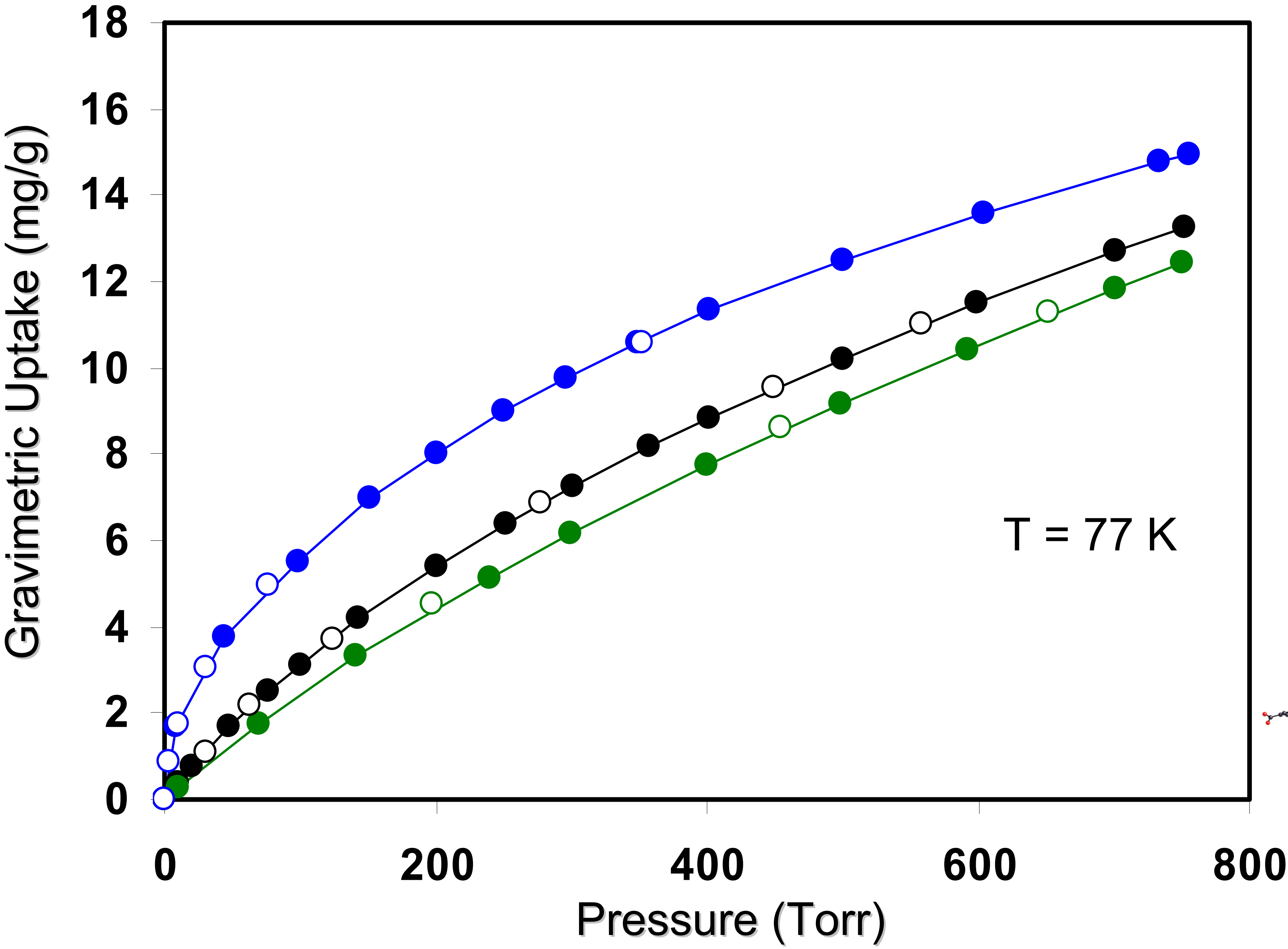


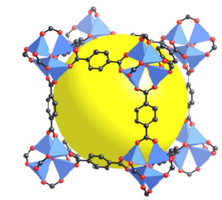
Structure of Zn_4O(1,3,5-benzenetribenzoate)$_3$

MOF-177: S_A (Langmuir) = 4,500 m^2/g, V_p = 1.59 cm^3/g

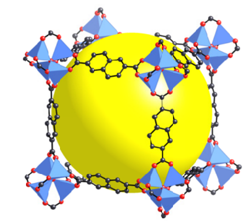


Low Pressure, Low Temperature H_2 Sorption

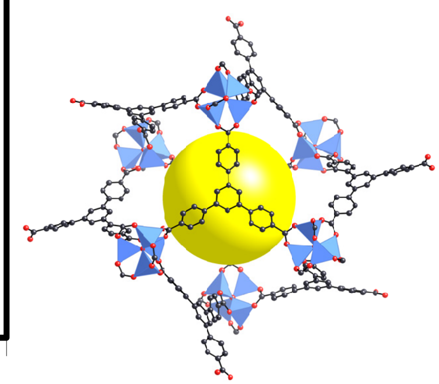




IRMOF-1

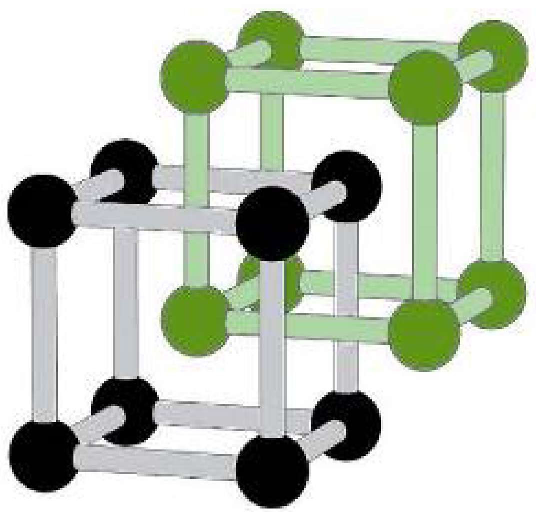


IRMOF-8



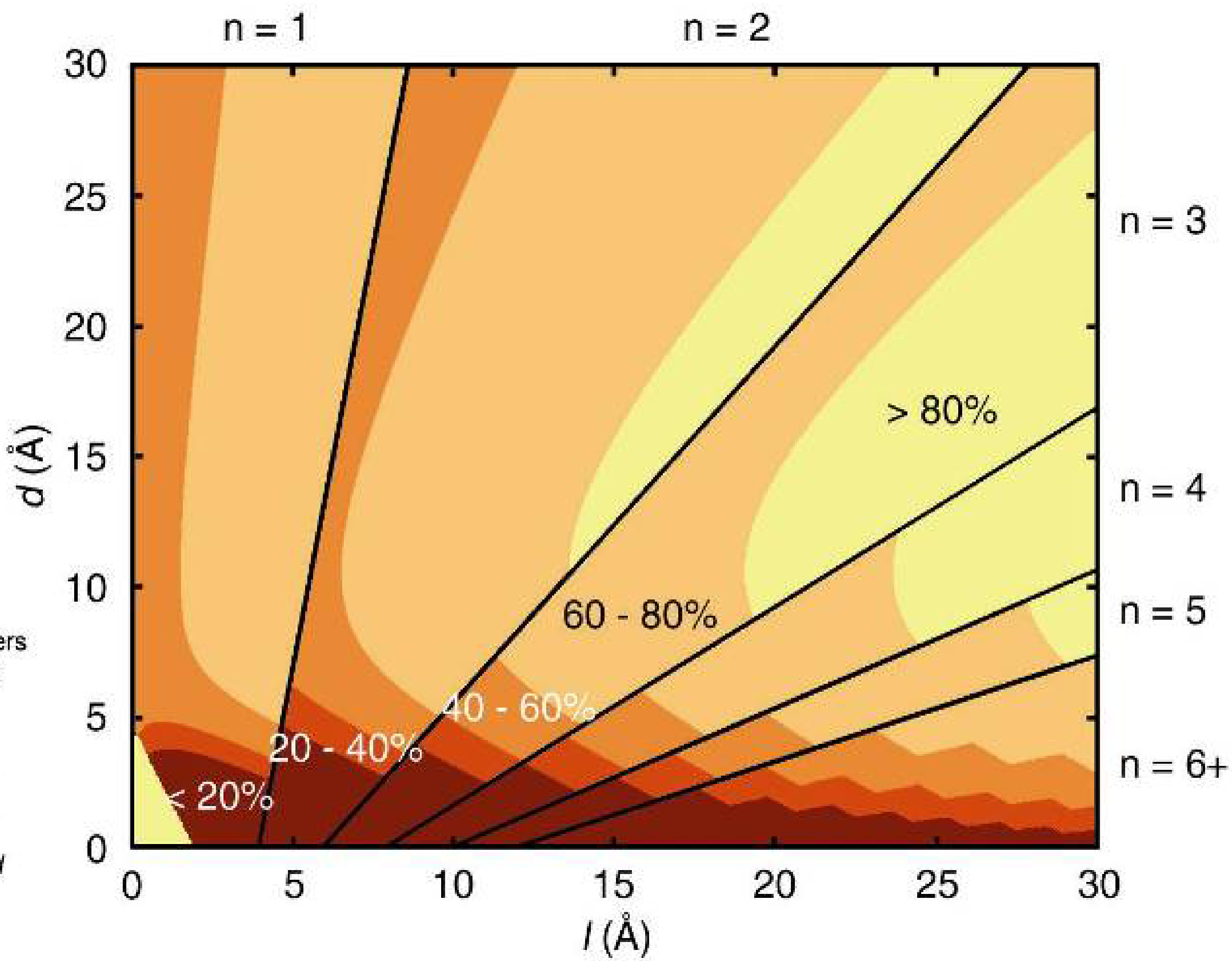
MOF-177

Large Free Volume in Catenated Networks: The role of Secondary Building Units

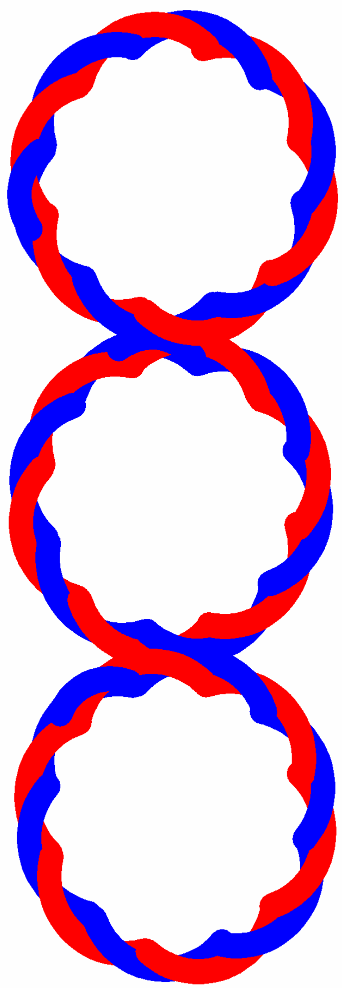


Cell edge: $a = d + l$
van der Waals Radius of SBU = $\delta / 2$
For n frameworks to interpenetrate with centers of the SBUs aligned along the body diagonal:
$n(d + \delta) \leq \sqrt{3}\, a$ thus $n \leq \sqrt{3}\,(d + l) / (d + \delta)$

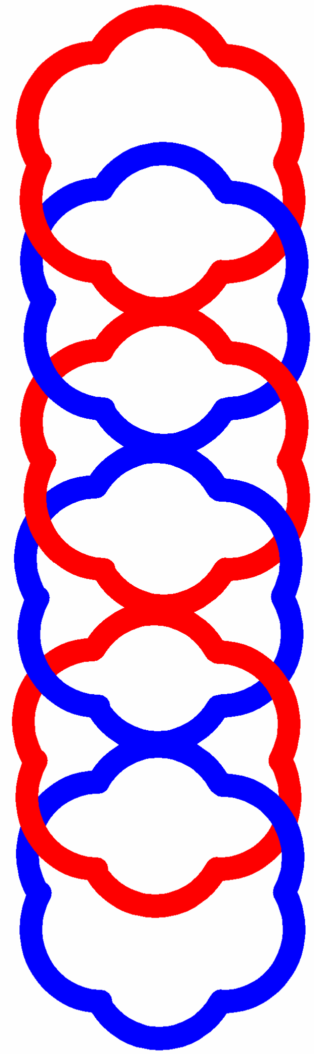
Volume of the cell = $(d + l)^3$
Volume occupied by SBUs / cell = $n(\pi / 6)d^3$
Volume of the linkers / cell = $3n(\pi r^2)l$
Free Volume = $(d + l)^3 - (n(\pi / 6)d^3 + 3n(\pi r^2)l$



Types of Catenation



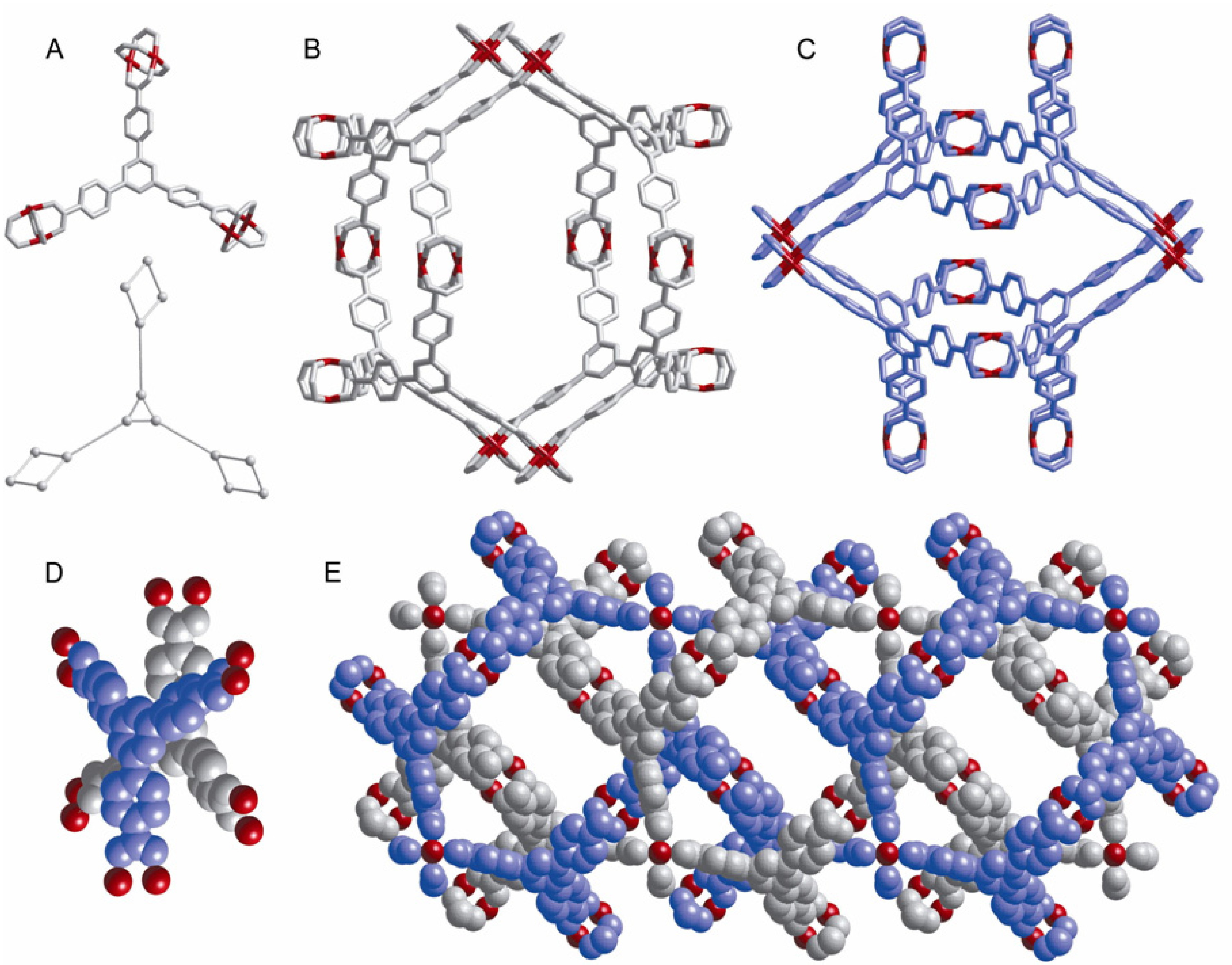
Interweaving



Interpenetrated

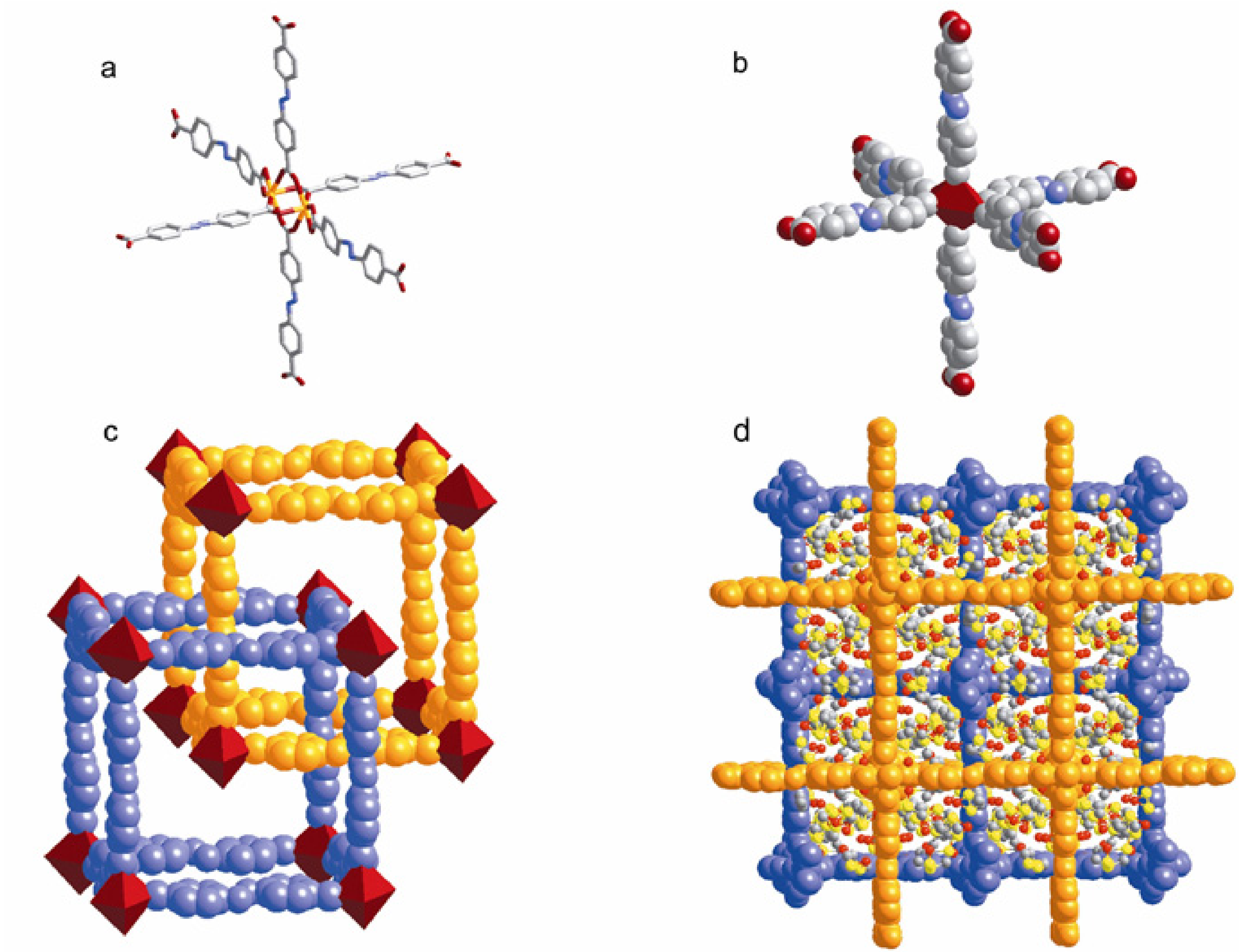
Structure of Interwoven Cu_3(1,3,5-benzenetribenzoate)$_2$(H_2O)$_3$

MOF-14: S_A (Langmuir) = 1,502 m^2/g; V_p = 0.53 cm^3/g

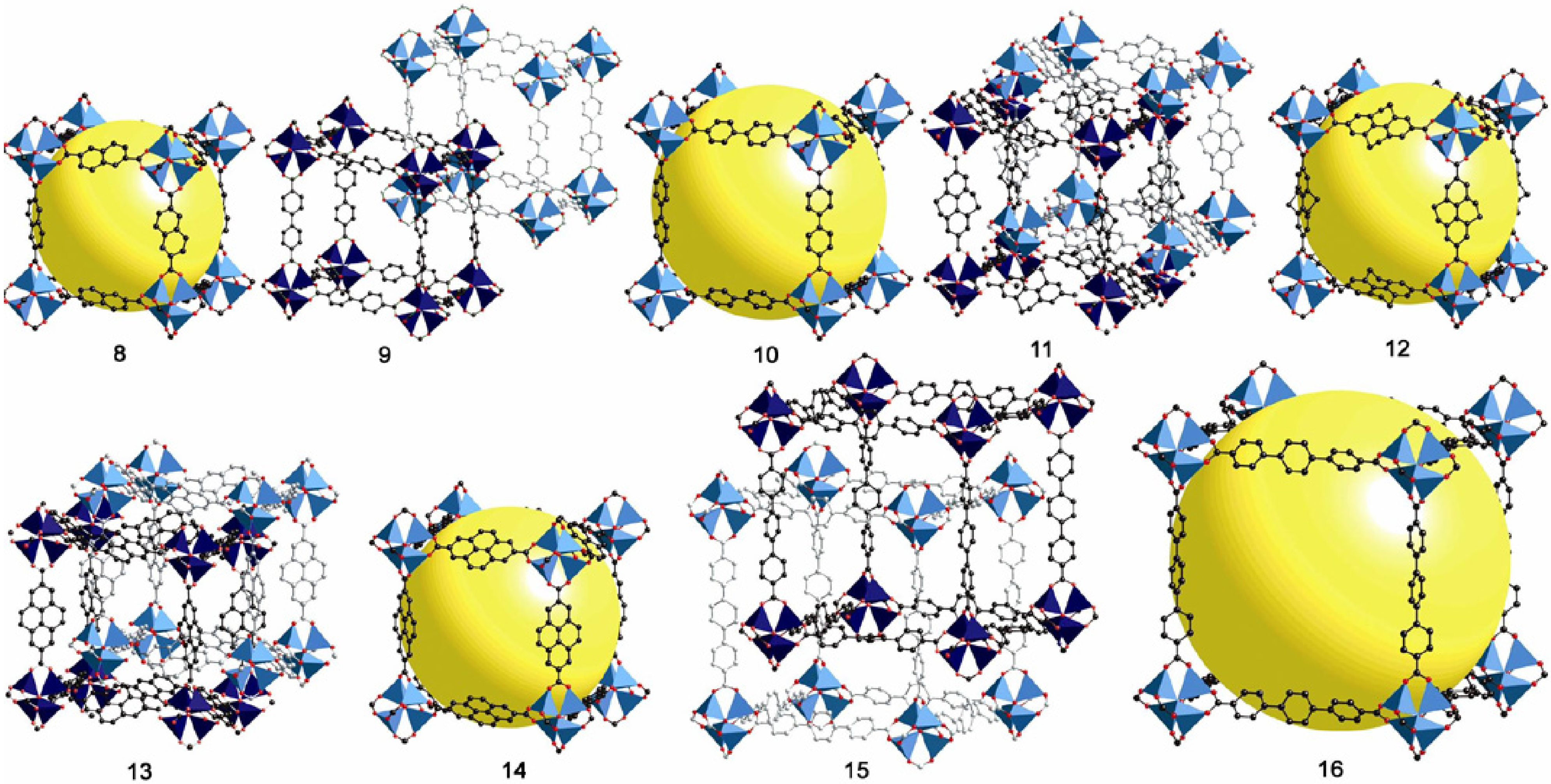


Structure of Interpenetrated $Tb_2(4,4'\text{-azodibenzoate})_3[(CH_3)_2SO]_3$

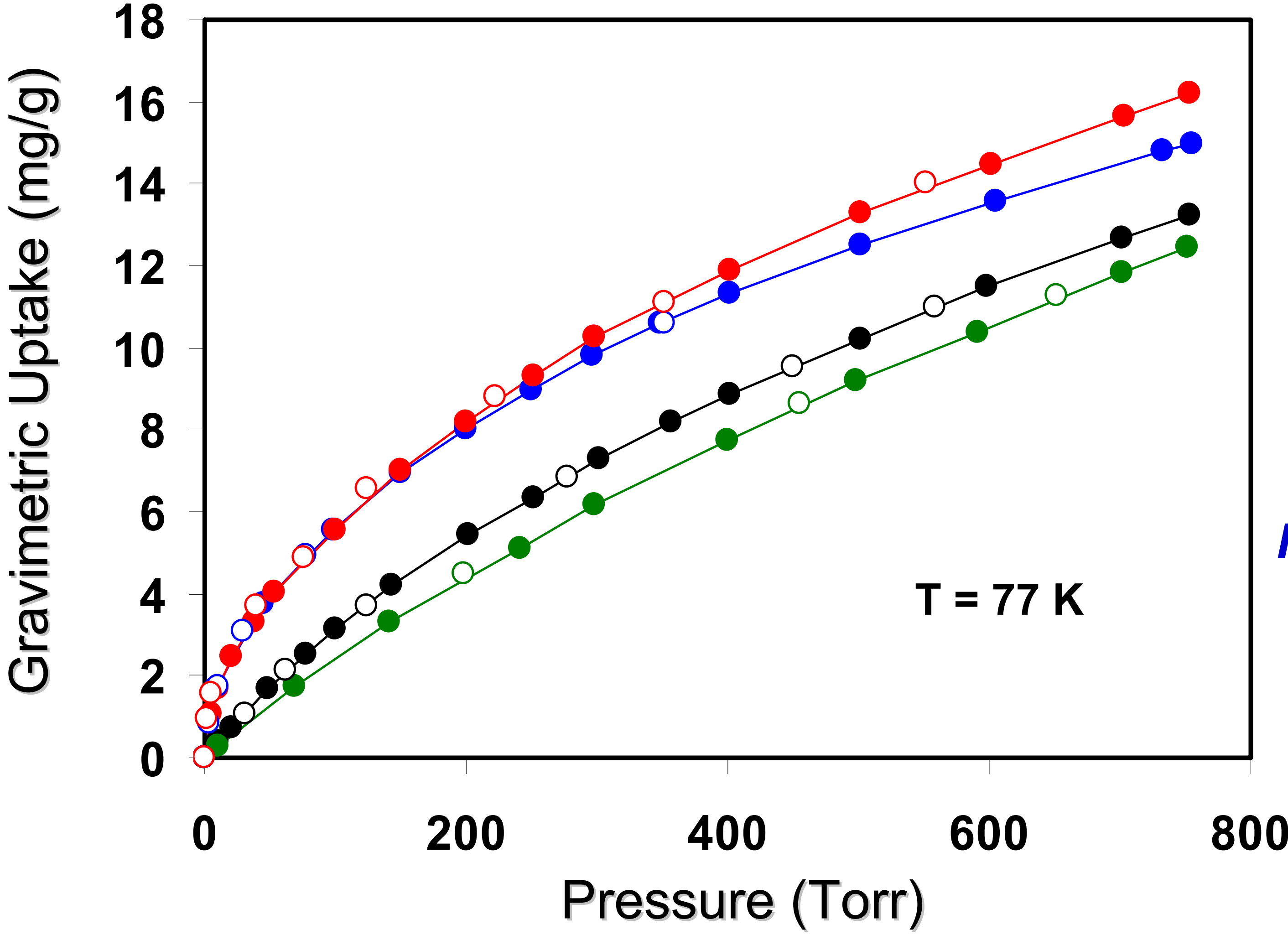
MOF-9: $V_{Free} = 71\%\ V_{Crystal}$; 16 $[(CH_3)_2SO]$/unit cell

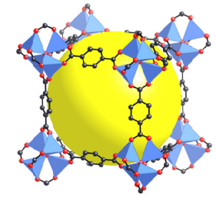


Interpenetrated Isoreticular MOFs

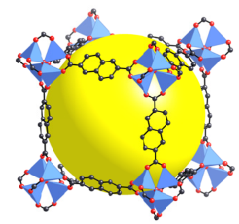


Low Pressure, Low Temperature H_2 Sorption

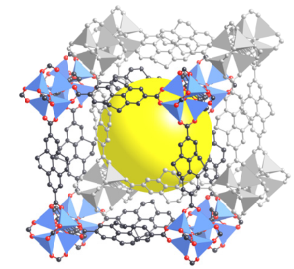




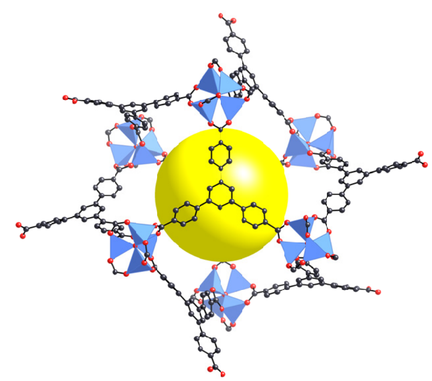
IRMOF-1



IRMOF-8

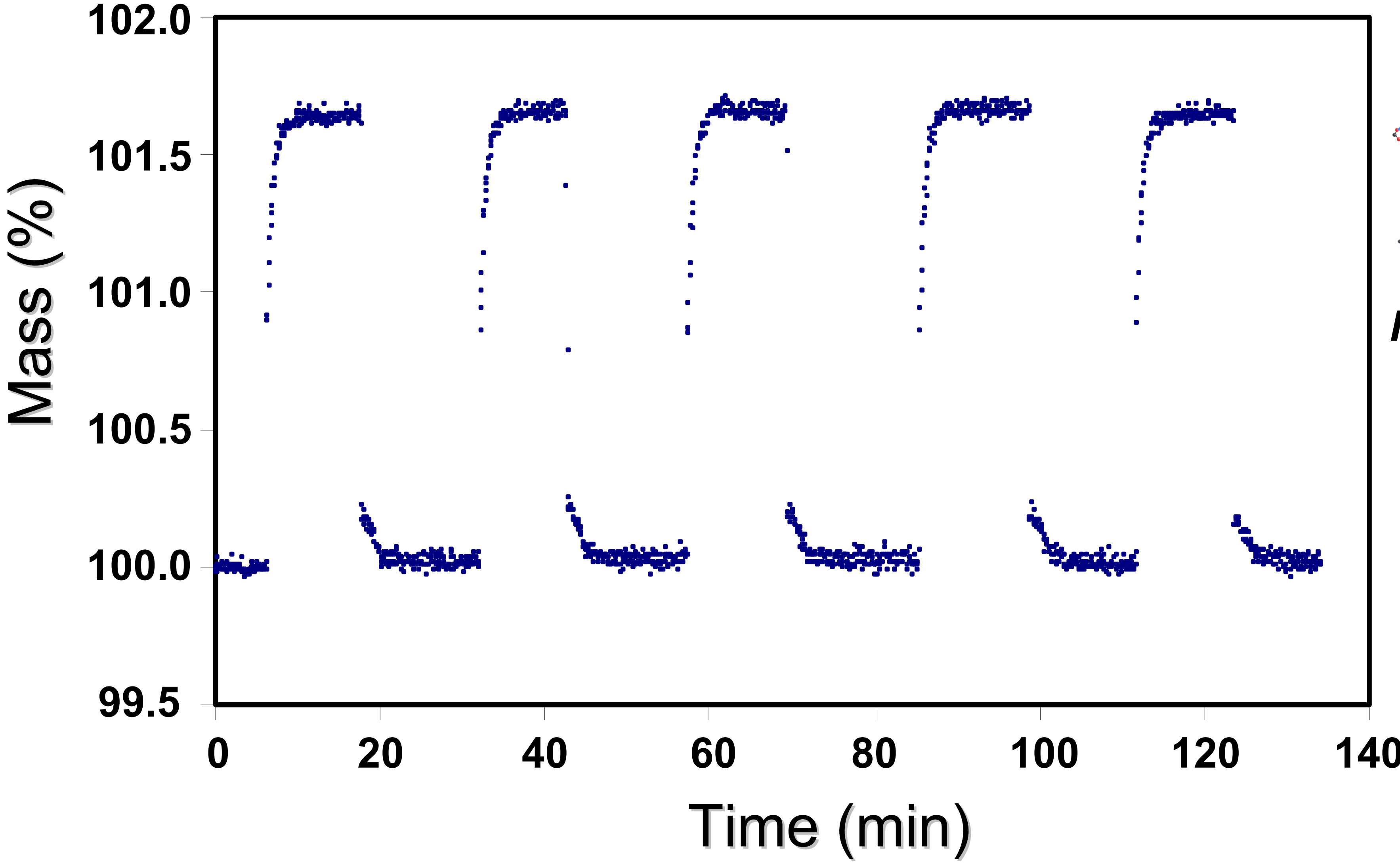


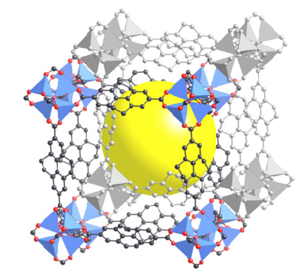
IRMOF-11



MOF-177

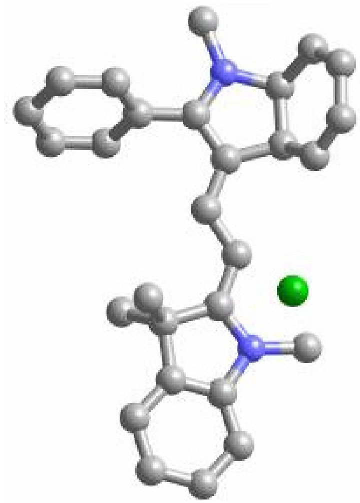
Reversible H_2 sorption in IRMOF-11 at 77K



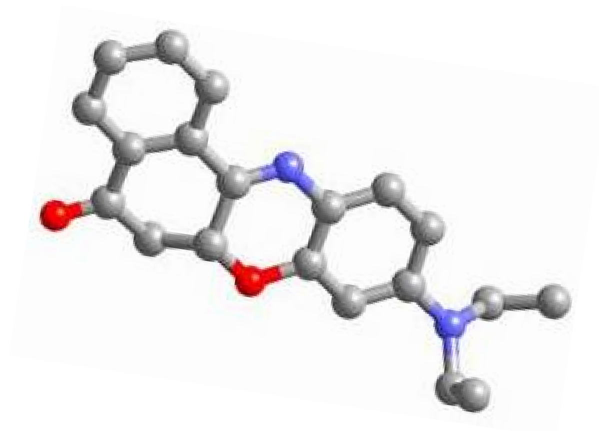


IRMOF-11

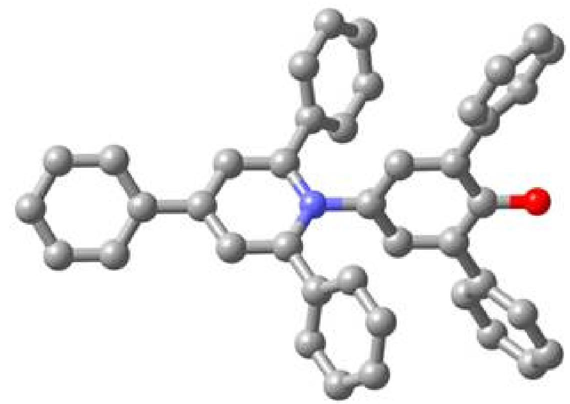
Impregnation of MOF-177



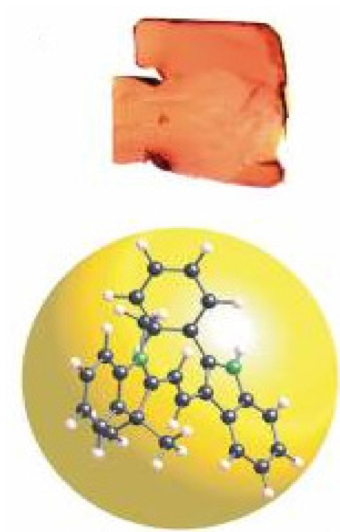
Astrazon orange



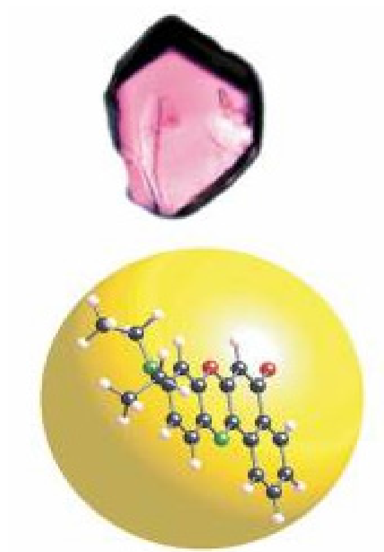
Nile red



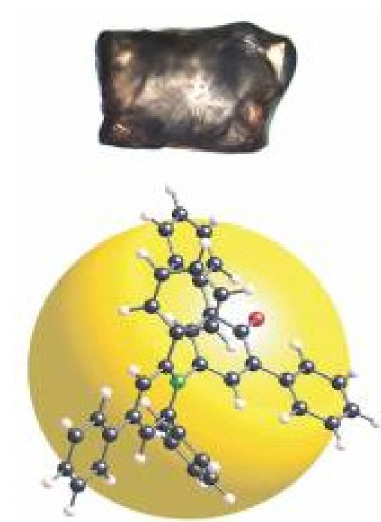
Reichardt's dye



Astrazon Orange R
16 molecules
per unit cell

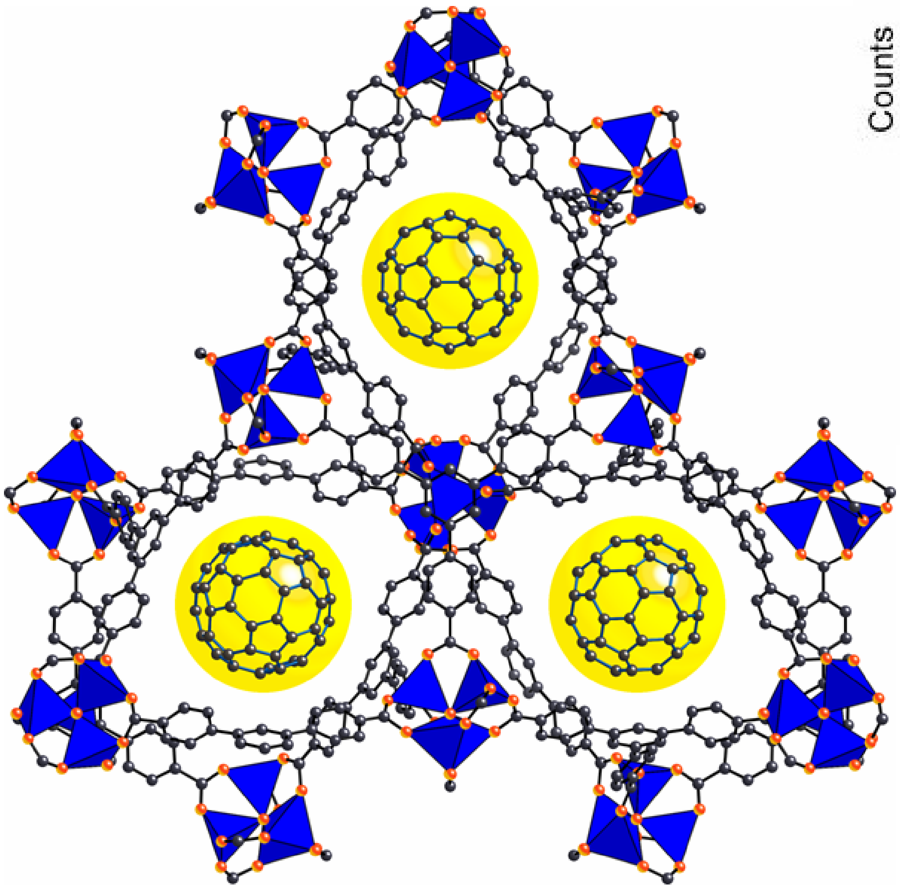


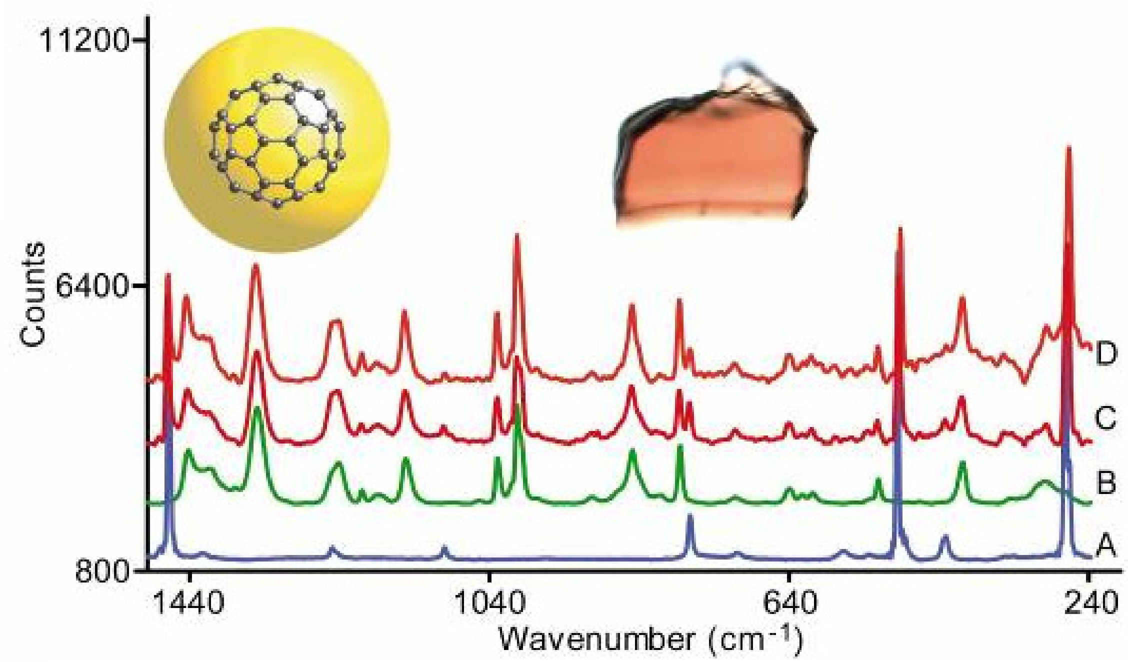
Nile Red
2 molecules
per unit cell



Reichardt's dye
1 molecule
per unit cell

Inclusion of C_{60} in MOF-177

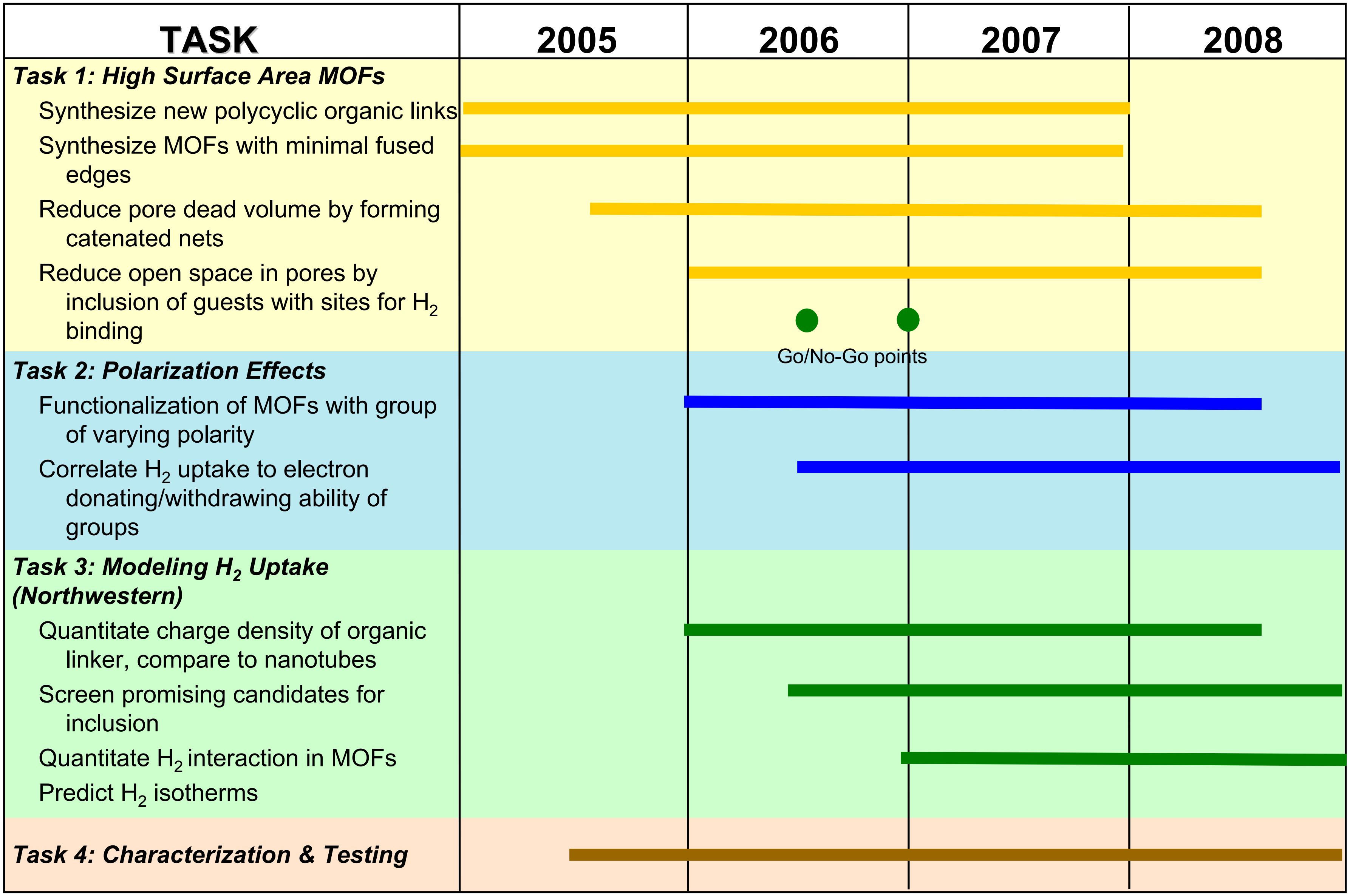




Raman Spectroscopy

- A) Bulk C_{60}
- B) Evacuated MOF-177
- C) Single crystal with C_{60}
- D) Single crystal with C_{60} cleaved in half

Future Work


TASK
2005
2006
2007
2008
Task 1: High Surface Area MOFs
Synthesize new polycyclic organic links
Synthesize MOFs with minimal fused edges
Reduce pore dead volume by forming catenated nets
Reduce open space in pores by inclusion of guests with sites for H_2 binding
Go/No-Go points
Task 2: Polarization Effects
Functionalization of MOFs with group of varying polarity
Correlate H_2 uptake to electron donating/withdrawing ability of groups
Task 3: Modeling H_2 Uptake (Northwestern)
Quantitate charge density of organic linker, compare to nanotubes
Screen promising candidates for inclusion
Quantitate H_2 interaction in MOFs
Predict H_2 isotherms
Task 4: Characterization & Testing

Publications and Presentations

Please list any publications and presentations that have resulted from work on this project.

- *No publications resulting from current funding.*

Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

- High exposure to H_2 gas with possibility of personal injury due to decreased oxygen content in the atmosphere.
- High concentrations of H_2 may pose a fire or explosion in and around instrumentation.

Hydrogen Safety

Our approach to deal with this hazard:

- Dedicated a single laboratory for all H_2 experiments.
- Installed active ventilation snorkles from laboratory hoods to all instrumentation consuming/ releasing H_2.
- Installed atmospheric H_2 detector (% level detection) outfitted with an alarm in the dedicated laboratory.

Acknowledgements