Metal-Organic Frameworks (MOFs)

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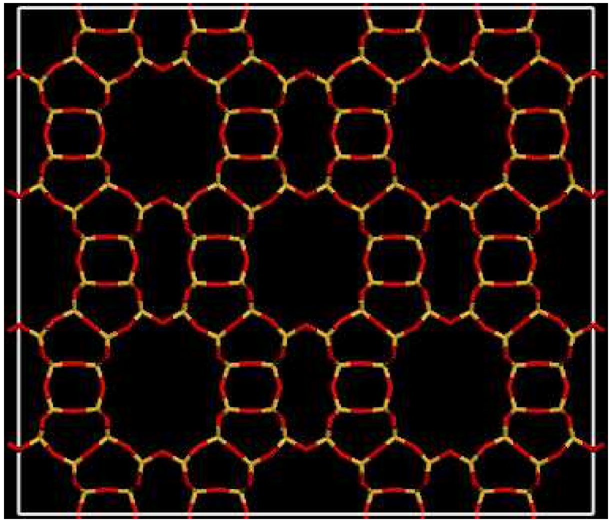
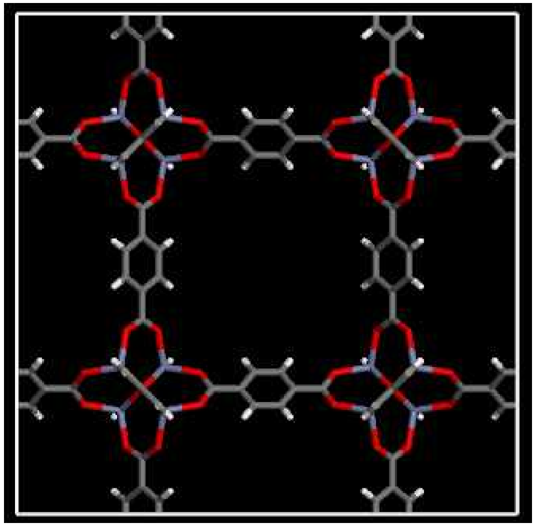
Sandia team: Mark Allendorf, Jeffery Greathouse, Patrick Doty



Mordenite (zeolite), $Na(AlO_2)(SiO_2)_{10}$



MOF-5, $Zn_4O(C_6H_4O_4)_3$

	Mordenite	MOF-5
Pore apertures	6.7 Å x 7.0 Å 2.9 Å x 5.7 Å	11.2 Å x 11.2 Å ➡ Gas diffusivity 100-1000X > molecular sieves ➡ faster, lower pressure PSA
Density	1.6 g/cm^3	0.6 g/cm^3 ➡ Lighter, more portable
Surface area	300 m^2/g	3500 m^2/g ➡ Highest gas sorption capacity

A Cu-based MOF selectively adsorbs Kr and Xe in air samples

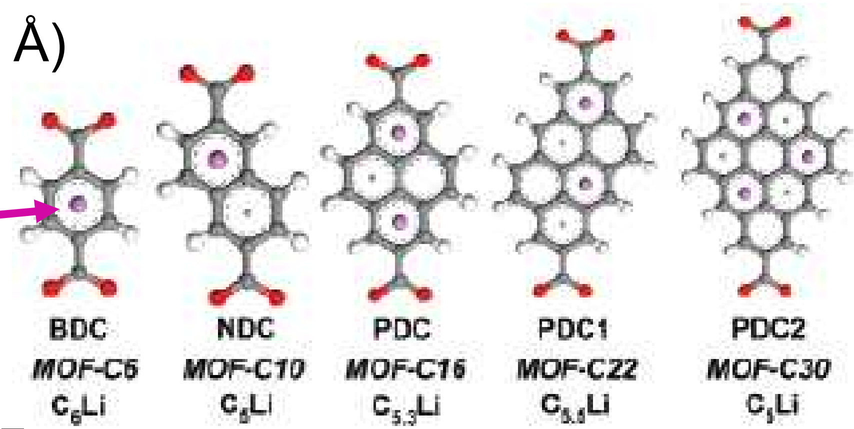
guest	y (gas)[a]	x (CuBTC)[b]	compression ratio (# adsorbed / # gas)
N_2	0.797	0.773	4.1
O_2	0.200	0.215	4.5
Xe	1.66×10^{-4}	2.80×10^{-3}	71.0
Kr	2.20×10^{-3}	8.87×10^{-3}	16.9

Greathouse et al, SAND Report **2008**

Kr adsorption may be enhanced by:

- ►Tailoring a MOF with pore aperture in between the atomic diameters of Kr (3.6 Å) and Xe (4.0 Å)
- ►Metal doping at linker ring sites

Li atom



Li-doped MOF's enhance H_2 adsorption.
Han and Goddard, *J. Am. Chem. Soc.* **2007**

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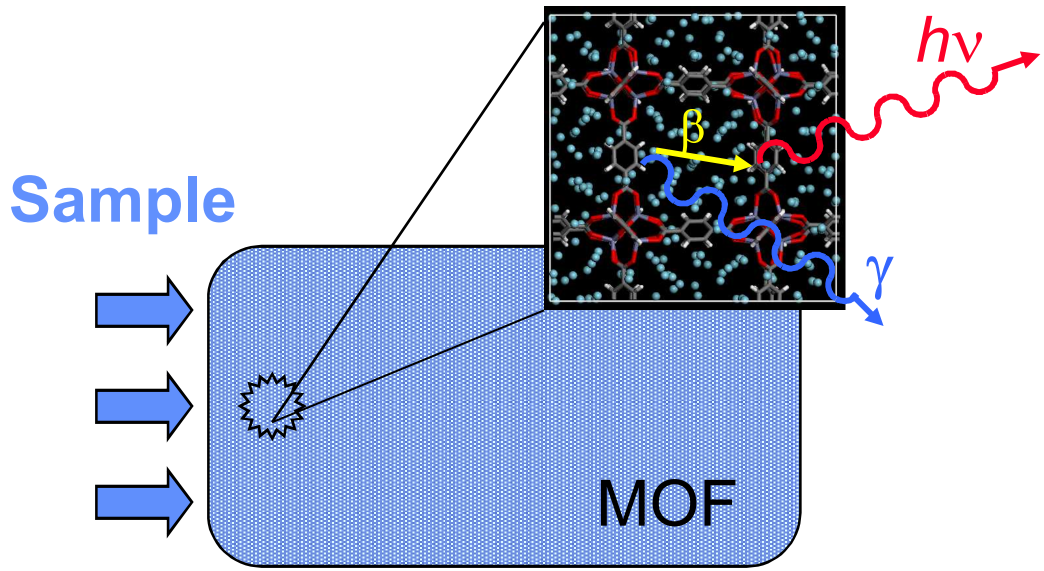
Simultaneous isotope collection and detection is feasible with Sandia's scintillating MOFs

- High surface-area MOF adsorbs isotopes
- Isotopes emit, yielding $\beta + \gamma$
- γ escapes and is detected
- β particle collides w/ fluor in MOF, causing it to scintillate
- Enables immediate detection of short-lived isotopes
- Eliminates need for optically coupled phoswich detector → increases detection efficiency
- Sample:
  - Preconcentrated by PSA or
  - Concentrated in situ with simultaneous detection

$Xe \rightarrow \gamma$ + fast electron



Bauer et al. *J. Am. Chem. Soc.* **2007**.

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NA-22 FY2009 plutonium detection proposal: noble gas collection and detection

Objective: exploit the structural versatility of nanoporous framework materials (NFM) and their unique physical properties to create multifunctional materials for noble gas collection and detection

- ***Atomistic modeling to guide synthesis through rational design***
  - Adsorption isotherms
  - Interferences and competitive adsorption
  - Temperature and pressure effects
- ***Synthesis: Optimize NFM through targeted modifications***
  - Goal 1: High surface-area, tailored sorbents for smaller, faster, low-pressure systems
  - Goal 2 (stretch goal): Nanoporous, scintillating NFM for simultaneous collection/adsorption
  - MOFs as starting point: synthetically versatile high-surface area NFM
- ***Materials screening, transport properties, scaleup issues***
  - Microporosimetry: surface areas, pore volumes, isotherms
  - PSA: bench-scale simulation of separation process
  - Electron-beam to simulate beta radiation: quantify light output and timing

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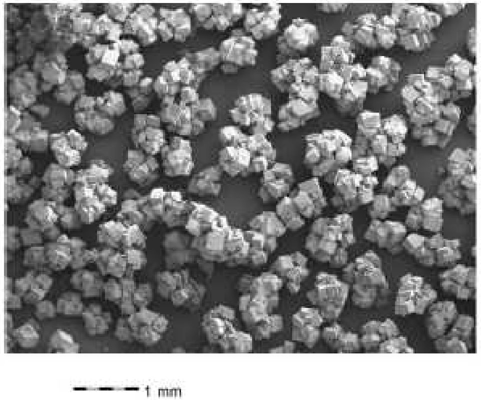
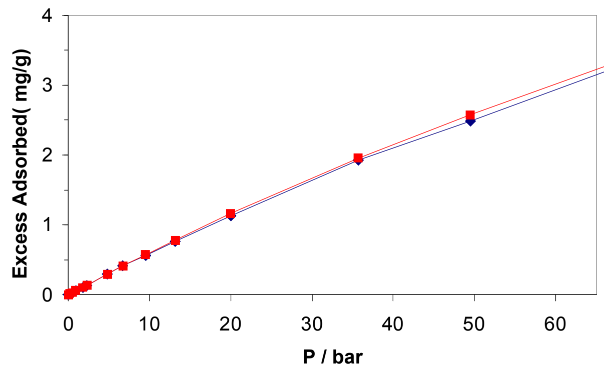
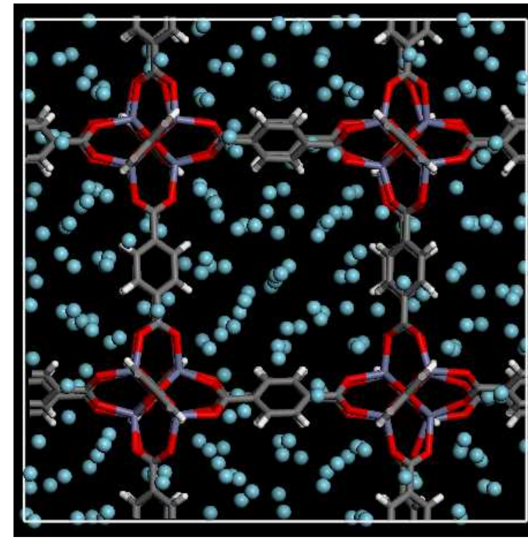
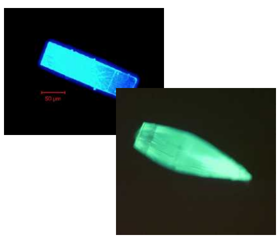
Sandia's established program in NFM has all the capabilities required to carry out this project



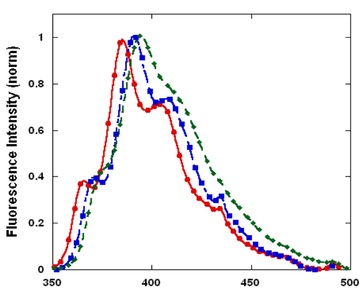


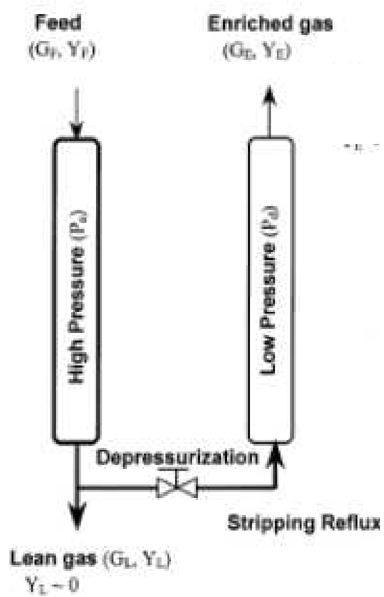




Synthesis & Characterization

- Hoods
- Glove boxes
- Ovens
- FTIR
- XRD
- NMR
- Fluorescence
- Raman
- SEM/TEM





Computational modeling

- Molecular dynamics
- Monte Carlo methods
- Quantum chemistry
- Massively parallel machines

Transport measurements

- PSA
- Microporosimeter

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