SAND2008-4976P

National Institute for Nano Engineering

Stress-Induced Chemical Detection Using Flexible Coordination Polymers

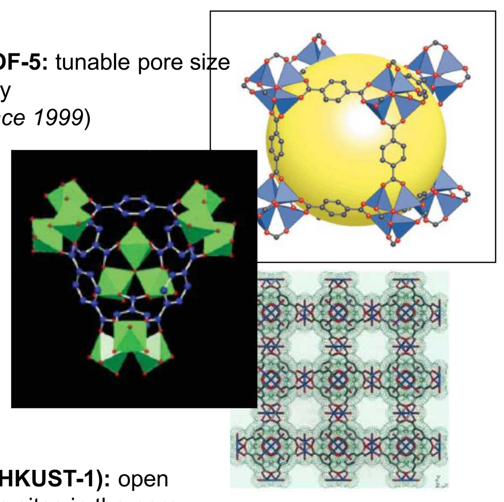
Jeffery A. Greathouse, Ronald J.T. Houk, Mark D. Allendorf
Sandia National Laboratories
Peter J. Hesketh, Leanne Andruszkiewicz
Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA

MOFs: "Molecular Tinker Toys" lead to record-breaking materials

Issues with nanoporous materials:
- Distribution of pore sizes, properties
- Surface chemistry is difficult to control
- Synthetic templates may be required
- Growth on surfaces is problematic

A Solution: Metal-organic frameworks
- Metal cations bridged by organic ligands
- Rigid structures, permanent porosity
- Tunable pore size (1-5 nm), chemistry
- Ultrahigh surface areas (up to 6,000 m^2/g)

Many potential applications:
- Chemical sensors
- Decontamination
- Water purification
- H_2 and CO_2 storage
- Nanoscale templates
- Drug delivery
- Catalysts
- Separations/chromatography



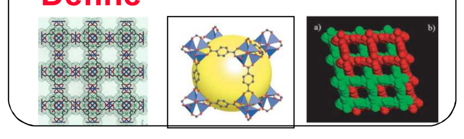
"Isoreticular" MOF-5: tunable pore size and pore chemistry (*Yaghi et al. Science 1999*)

Cr MIL: 6000 m^2/g (*Férey et al., Science 2005*)

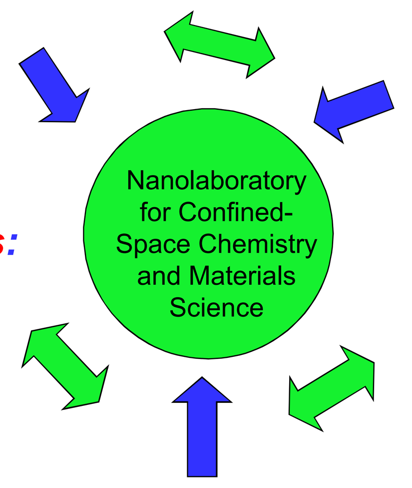
Cu MOF (HKUST-1): open coordination sites in the pore (*Chui et al. Science 1999*)

Approach: Define canonical MOFs, Leverage Sandia capabilties, Collaborate to accelerate startup

Define



Leverage
- Nanopore models (6316)
- Chemical synthesis (8700)
- Materials integration (8300)

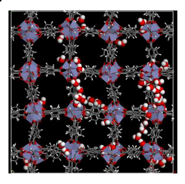


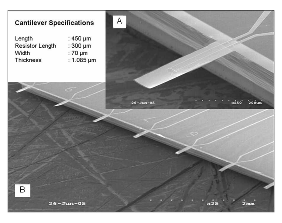
Task 1: Synthesis & Properties

Properties
Data for model validation
Identify MOF suites for SNL missions:
- ***Chem/bio/radiation detection***
- ***Water purification***
- ***Enhanced surveillance***
- ***Efficient separations***

Task 2: Validated confined-space models

Link nanoscale environment to observable properties
- **Ab initio calculations**
- **Force-field development**
- **Transport models**



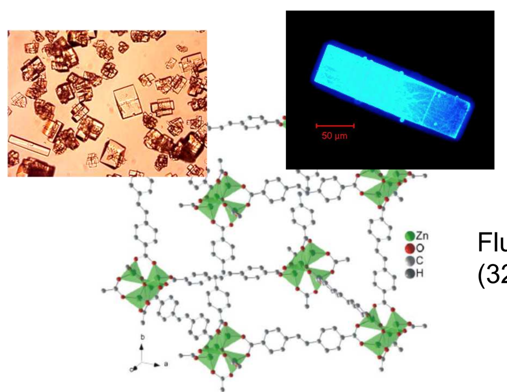


Reliable manufacturing and applications
- MOF films on surfaces
- Membranes
- Sensing platforms

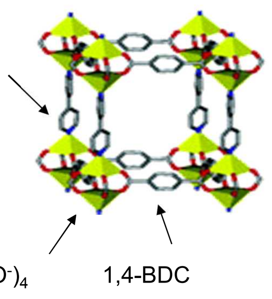
Collaborate

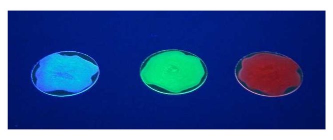
UNMHU · Georgia Institute of Technology · College of Chemistry

New fluorescent MOFs: nanoporous materials for selective chemical detection

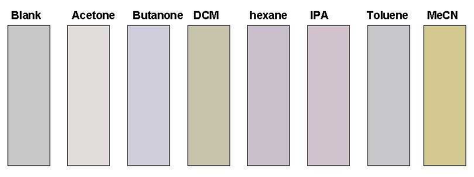


Fluorescence emission (325 nm excitation)





Above: Empty MOF (blue); infused with Tb (green) and Eu (red) immobilized in a polymer film under 254-nm light. **Below:** color signatures for various adsorbed organic solvents

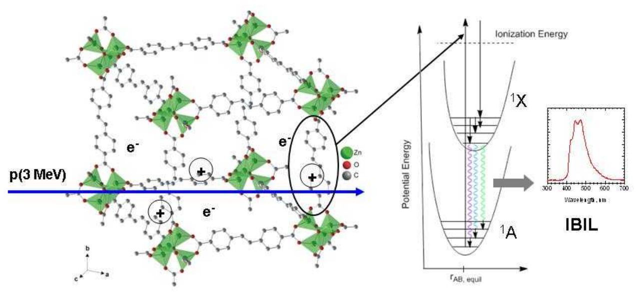


IRMOF-S1: An isotropic, nanoporous cage with a high-efficiency fluorophore

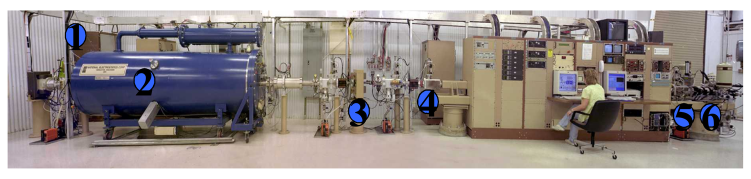
Bauer, Allendorf et al. *J. Amer. Chem. Soc.* **129** (2007), 7136

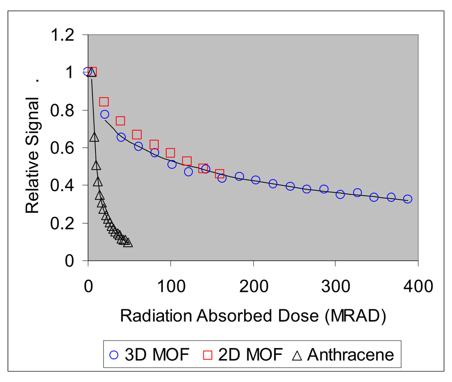
Infiltration with Lanthoid elements: adsorbed molecules generate unique color signatures
Allendorf and Houk, TA filed, 2008

Scintillating MOFs: first new class of radiation detection materials since 1950



Ion beam-induced luminescence (IBIL) used to characterize MOF response to ionizing radiation





MOFs are extremely radiation tolerant—more so than the anthracene standard

SAMPLE	Mass (mg)	Dose rate J/kg/s	Cts./J	Intensity
Anthracene	0.4	1.20E+04	1.13E+09	100%
2D MOF	0.38	9.33E+03	2.49E+08	22%
3D MOF 1	0.22	1.00E+04	9.62E+07	9%
3D MOF 2	0.49	9.33E+03	6.62E+07	6%
Stilbene				50%
BC422Q (commercial organic scintillator)				11%

Doty, Allendorf et al. subm. to *Adv. Mater.* 2008

First MOF compositions tested are comparable to commercial scintillators

Patent pending

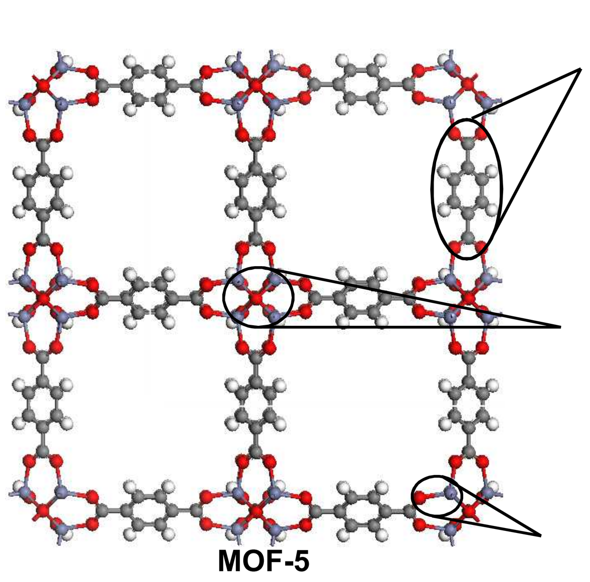
Structural non-rigidity in MOFs requires a radically different approach to atomistic modeling

First "Flexible" Force Field for MOFs

Allow some atoms in the framework to move

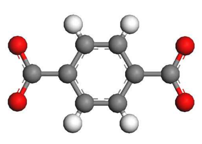
Covalently bonded atoms are rigid

Coordination (ionic) bonds are flexible

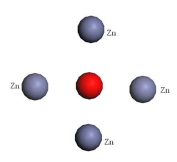


MOF-5

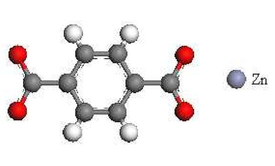
Rigid Bonding



Nonbonded Interactions

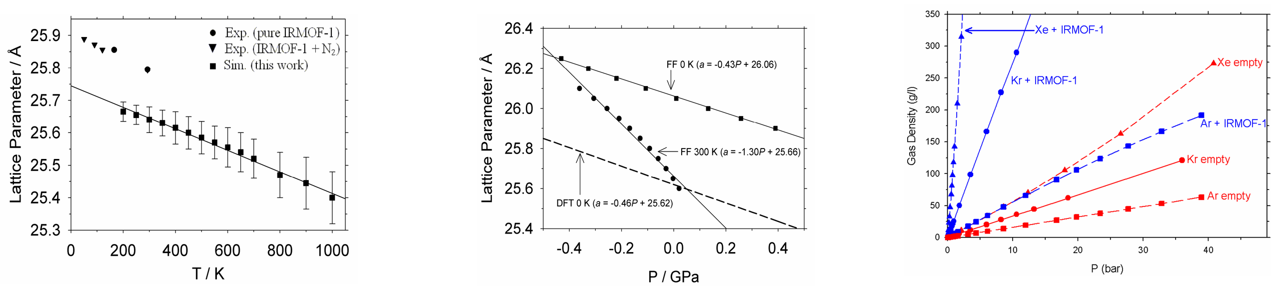


Zn and Inorganic Oxygen



Zn and O_{BDC}

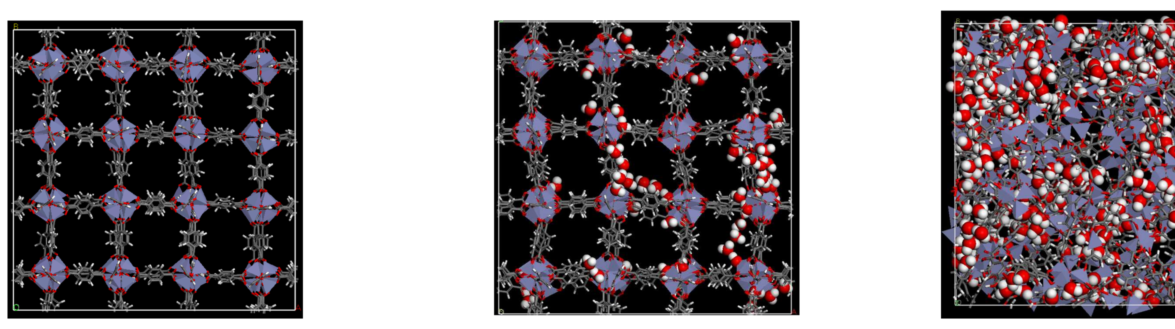
Flexible force field proves to be a robust tool for simulating a wide spectrum of MOF properties



Thermal properties · **Mechanical properties** · **Gas adsorption**

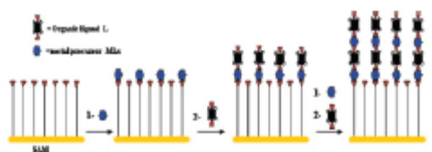
Greathouse and Allendorf *J. Phys. Chem. C* **2008,** 5795

- First simulation of MOF reactivity: collapse of MOF-5 upon reaction with water

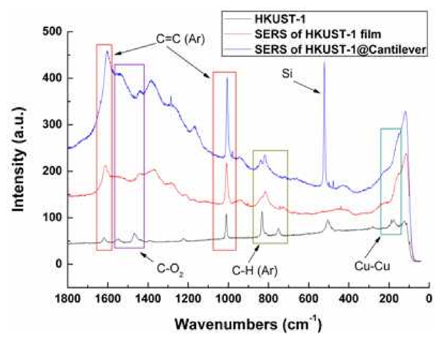


Greathouse and Allendorf *JACS* **2006**, *128*, 10678

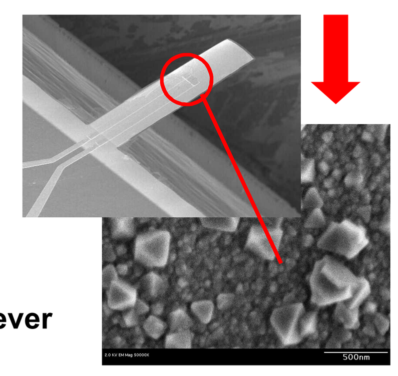
Integrating MOFs with surfaces is essential to incorporate MOFs into sensors and electronic devices



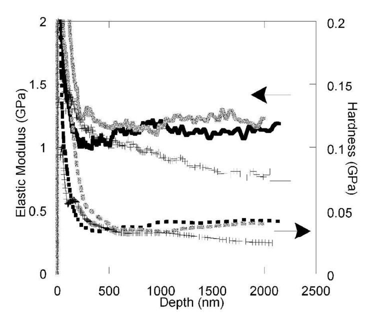
Step-by-step growth method implemented to adapt MOFs to MEMS and other devices



μ-Surface-Enhanced Raman used to characterize thin MOF films on cantilevers



MOF on a microcantilever

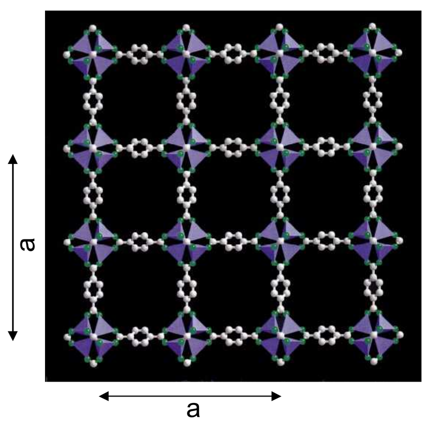


MOF mechanical properties measured (using nanoindent-ation) to predict device sensitivity

Bahr, Allendorf, et al. *Phys. Rev. B* **2007**, 76, 184106

Structural flexibility upon "guest" molecule adsorption enables stress-induced detection in microcantilevers

- **Example: IRMOF-1 (also known as MOF-5):**
  - a = 25:6690 Å post synthesis (8 DMF+ 1 C_6H_5Cl/pore)
  - a = 25:8849 Å evacuated → 0.8% change
- **Adsorption induces stress if MOF layer is mechanically coupled to microcantilever**
  - Calculated sensitivity
    - Known response function of microcantilever (0.04 mN/m)
    - 40 μm x 450 μm x 1 μm CP layer
    - Assume 10X S/N
  - Result: Calculated sensitivity = ~17 - 50 fmoles
  - General problem: elastic constants for MOFs must be known



Sandia is a multiprogram laboratory operated by Sandia Corporation a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000

Sandia National Laboratories