Creating a Discovery Platform for Confined-Space Chemistry and Materials: Metal Organic Frameworks

LABORATORY DIRECTED RESEARCH & DEVELOPMENT

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Problem

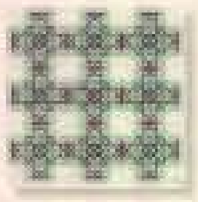
Control over the properties of nanoporous materials is a prerequisite for successful application of these materials

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)

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

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



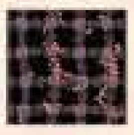
Cu MOF (HKUST-1): open coordination sites in the pore
(Chui et al. Science 1999)

"Isoreticular" IRMOF-1: tunable pore size and pore chemistry
(Yaghi et al. Science 1999)

Technical Approach:

Define Canonical MOFs

Leverage SNL Capabilities
- Nanopore models
- Chemical synthesis
- Materials integration



Task 1: Synthesis & Properties
- Data for model validation
- Identify MOF suites for SNL missions:
  - Chem/bio/radiation detection
  - Water purification
  - Enhanced surveillance
  - Efficient separations
  - Gas storage

Task 2: Validated confined-space models
- Link nanoscale environment to observable properties
  - Ab initio calculations
  - Force-field development
  - Transport models

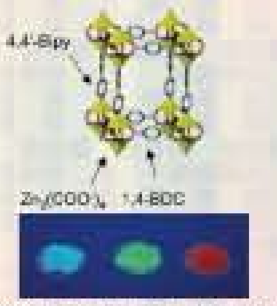
Task 3: Reliable manufacturing and applications
- MOF films on surfaces
- Membranes
- Sensing platforms

Collaborate-Accelerate
NMHU
Georgia Tech
College of Chemistry

New fluorescent MOFs: nanoporous materials for selective chemical detection

Fluorescence emission (325 nm excitation)

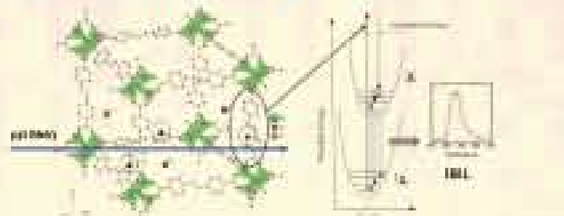
IRMOF-S1: An isotropic, nanoporous cage with a high-efficiency fluorophore
Bauer, Allendorf et al. *J. Amer. Chem. Soc.* **129** (2007), 7136



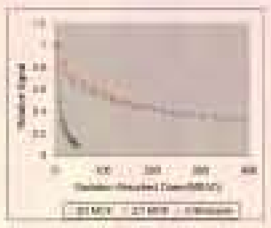
Above: Empty MOF (blue); infused with Tb (green) and Eu (red) immobilized in a polymer film under 254-nm light.
Below: color signatures for various adsorbed organic solvents

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	[illegible]	Intensity
Anthracene	0.4	1.20E+04	1.15E+09	100%
2D MOF	0.35	8.35E+03	2.49E+08	22%
3D MOF 1	0.22	1.00E+04	8.62E+07	9%
3D MOF 2	0.49	9.33E+03	8.62E+07	6%
Stilbene				50%
BC422Q (commercial organic scintillator)				11%

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

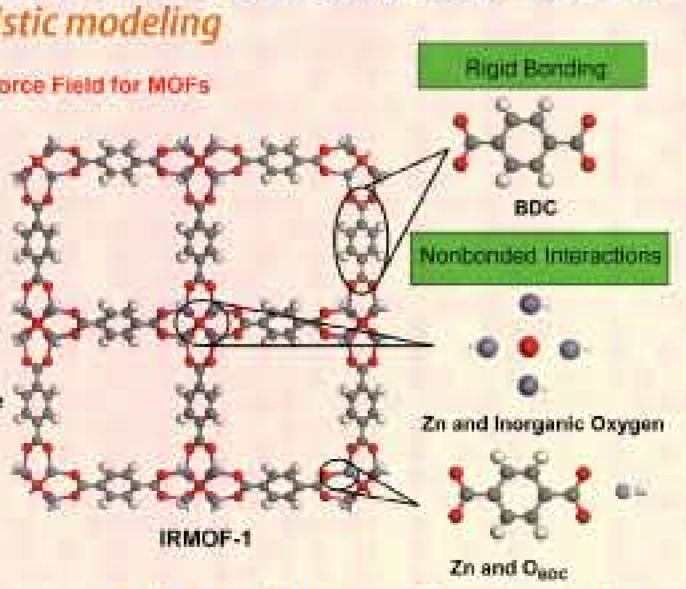
First MOF compositions tested are comparable to commercial scintillators

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

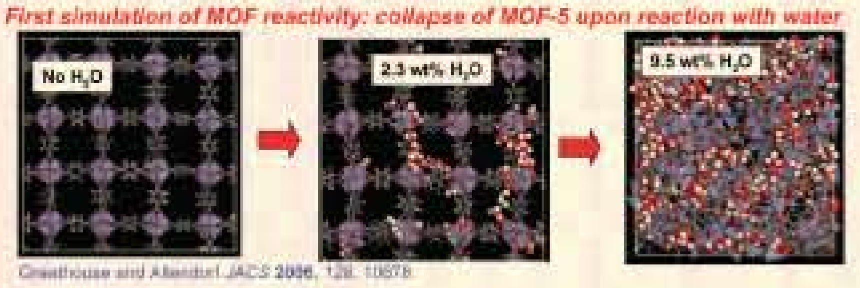


Flexible force field proves to be a robust tool for simulating a wide spectrum of MOF properties

Thermal properties | Mechanical properties | Gas sorption

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

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

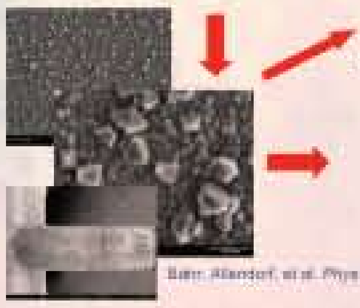


Greathouse and Allendorf *JACS* **2006**, 128, 10678

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

Micro-Surface-Enhanced Raman developed to characterize thin MOF films on micro-scale substrates

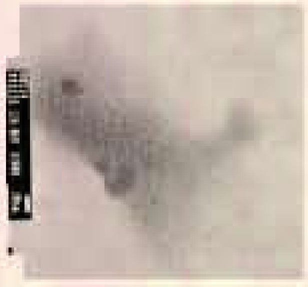


First measurement of MOF mechanical properties (using nanoindentation)

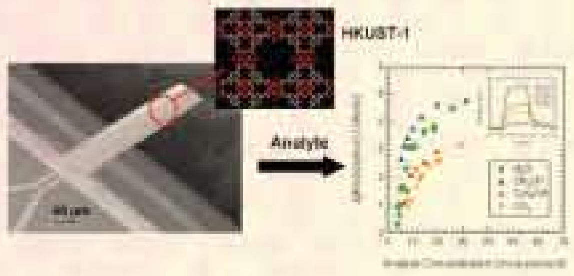
Bahr, Allendorf, et al. *Phys. Rev. B* **2007**, 76, 184106

Significance

- New radiation detection schemes
- MOFs on surfaces inspired a second LDRD that created the first MOF-on-MEMS sensor (patent filed)
- Faster H_2 desorption from MOF-templated hydride nanoparticles
- Portable, low-cost MOF-based breath sensors and personal exposure monitors



MgH_2 nanoparticles in a MOF template (small black dots in SEM image above) and MOF-coated microcantilever for chem detection (below)



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