

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

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

- 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

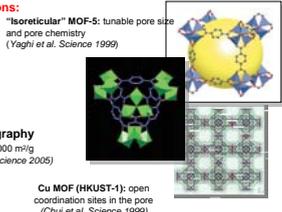
- A Solution: Metal-organic frameworks**
- Metal cations bridged by organic ligands
 - Rigid structures, permanent porosity
 - Tunable pore size (1-5 nm), chemistry
 - Ultrahigh surface areas (up to 6,000 m²/g)



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

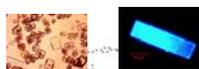
Many potential applications:

- Chemical sensors
- Decontamination
- Water purification
- H₂ and CO₂ storage
- Nanoscale templates
- Drug delivery
- Catalysts
- Separations/chromatography

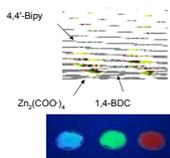


Cu MOF (HKUST-1): open coordination sites in the pore (Chui et al. Science 1999)

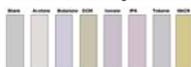
New fluorescent MOFs: nanoporous materials for selective chemical detection



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

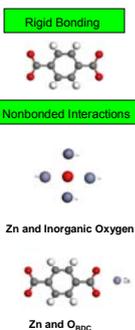
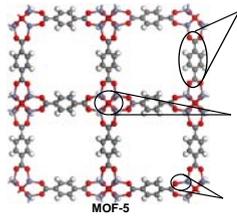
Bauer, Allendorf et al. J. Amer. Chem. Soc. 129 (2007), 7136

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

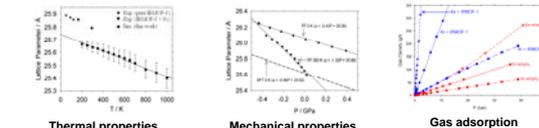
Structural non-rigidity in MOFs requires a radically different approach to atomistic modeling

First "Flexible" Force Field for MOFs

Allow some atoms in the framework to move
Covalently bonded atoms are rigid
Coordination (ionic) bonds are flexible

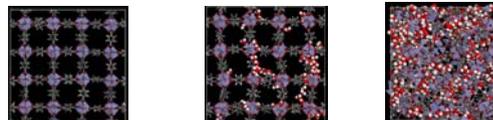


Flexible force field proves to be a robust tool for simulating a wide spectrum of MOF properties



Thermal properties Greathouse and Allendorf J. Phys. Chem. C 2008, 5795

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

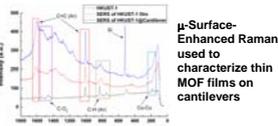


Greathouse and Allendorf JACS 2006, 128, 10678

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

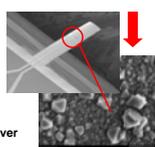


Step-by-step growth method implemented to adapt MOFs to MEMS and other devices



MOF mechanical properties measured (using nanoindentation) to predict device sensitivity

MOF on a microcantilever



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 C₆H₆Cl₆/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

