SAND2006-6708C

# Growth of Metal Organic Frameworks onto Microcantilever Substrate Materials

Renée Shediac,[a] Elaine Lai,[a] Christina Bauer,[a] Blake A. Simmons,[a] Arnab Choudhury,[b] Peter J. Hesketh[b], R. Stumpf,[a] D. Bahr,[c] Mark D. Allendorf[a]

The Electrochemical Society
National Meeting
Cancun, Mexico
10/31/2006

[a]Sandia National Laboratories
Livermore, California

[b]Georgia Institute of Technology
Atlanta, GA, USA

[c]Washington State University
Pullman, WA

Sandia National Laboratories

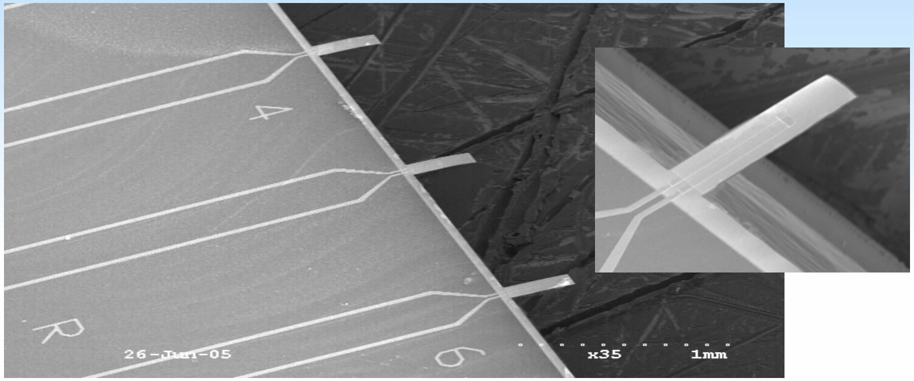
# Microcantilever Chemical Sensor Arrays

Motivation:

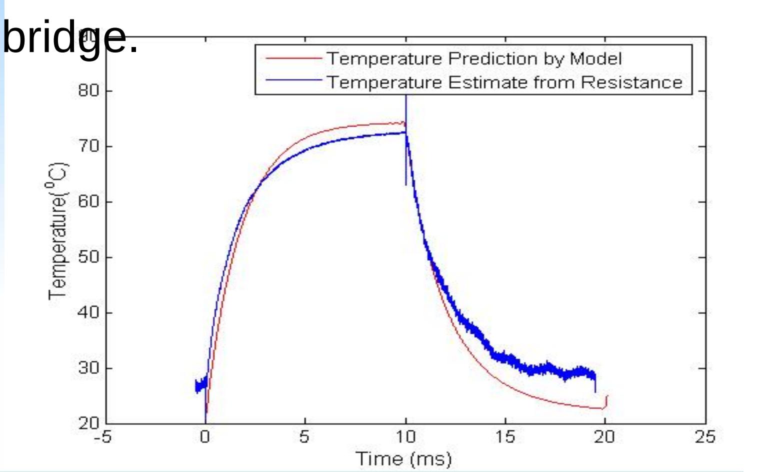
- Microcantilever sensors provide high sensitivity with simple design and fabrication
- Selective coatings can be defined with MOF layers on the cantilevers.
- Microcantilever arrays provide a built-in thermomechanical reference for chemical sensing
- Low cost, low power, platform for real-time label-free sensing.

Results:

- Thermal model has good agreement with the cantilever transient response.
- Deflection tests match up with analytical models for completed sensors.
- Low noise resistance measurements with AC bridge.




Cantilever chip with 5 measurement and 5 reference cantilevers




Comparison of experimental temperature variation with thermal model. $V_{DC}$= 2.75V, $V_{AC}$=2.25V, $f$ = 50 Hz

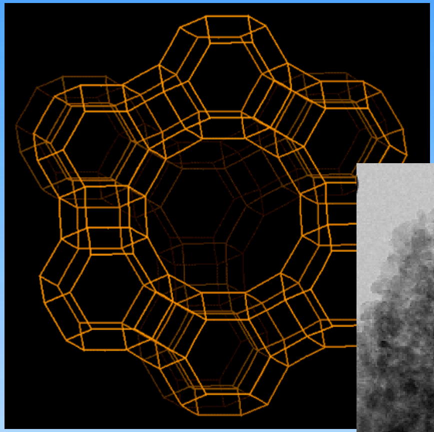
A. Choudhury, Prof. P.J. Hesketh (G-Tech), Z. Hu, T. Thundat (Oak-Ridge National Labs.)

Sandia National Laboratories

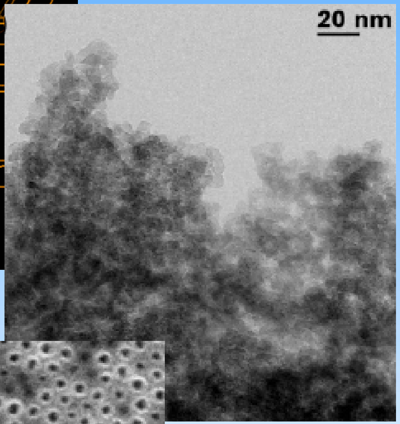
# Control over the properties of nanoporous materials is a prerequiste for successful application of these materials

Issues:

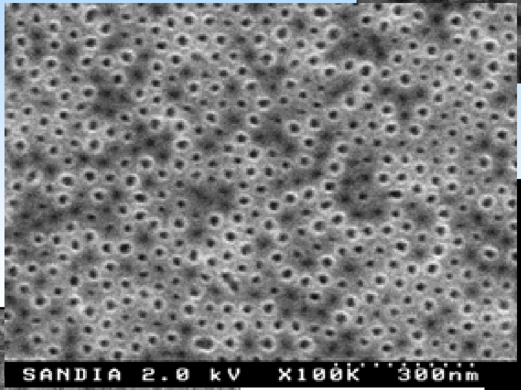
- Distribution of pore sizes, properties
- Surface chemistry is difficult to control
- Synthetic templates may be required
- Growth on substrate materials to create hybrid materials is problematic
- Novel materials may solve some of these problems:
  - Carbon nanotubes
  - Synthetic zeolites
  - Block copolymers
  - Anodized aluminum oxide
  - Aerogels
  - Metal organic frameworks



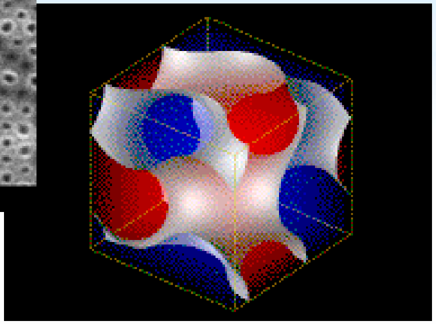
Zeolites



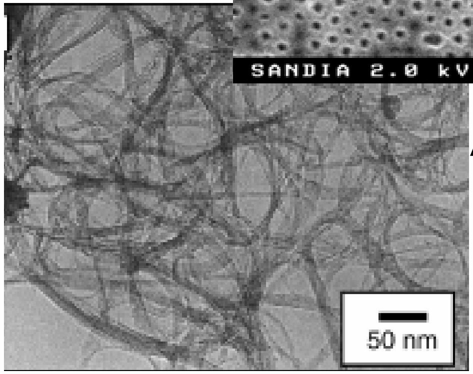

Alumina aerogel




Aluminum Oxide



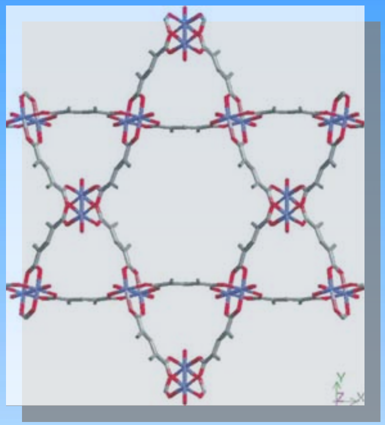
Block copolymers



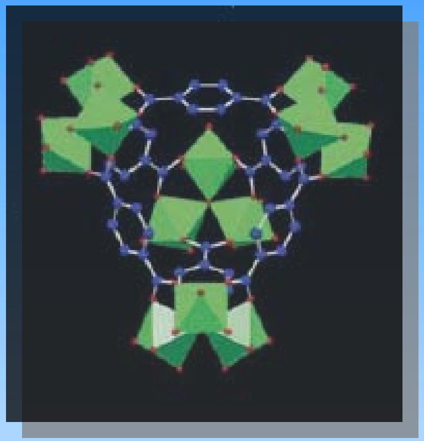

Single-walled CNT

Sandia National Laboratories

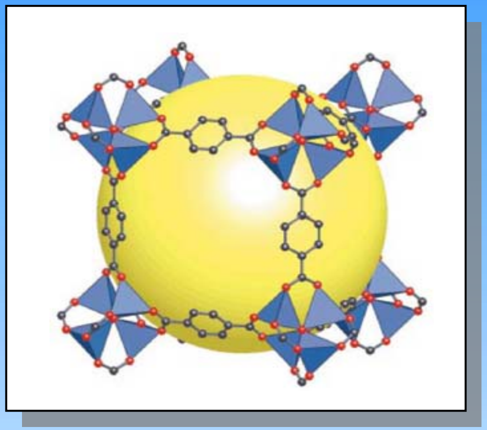
# Metal Organic Frameworks: self-assembled, hybrid materials with tailorable properties



**Cu MOF:** replaceable groups within the pore *(Chui et al. Science 1999)*



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

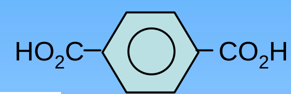


**"Isoreticular" MOF:** Rigid, open framework with tunable pore size, chemistry (Yaghi et al.)

- Inorganic clusters linked by coordinating organic ligands
- Crystalline materials
- 1D, 2D, or 3D structures
- Wide range of metals used, including Zn, Cu, Co, Ni, Ag, Cd, lanthanides
- Open coordination sites possible
- Rigid porosity in some structures, with pore diameters comparable to zeolites
- Chemically tailorable pore environment

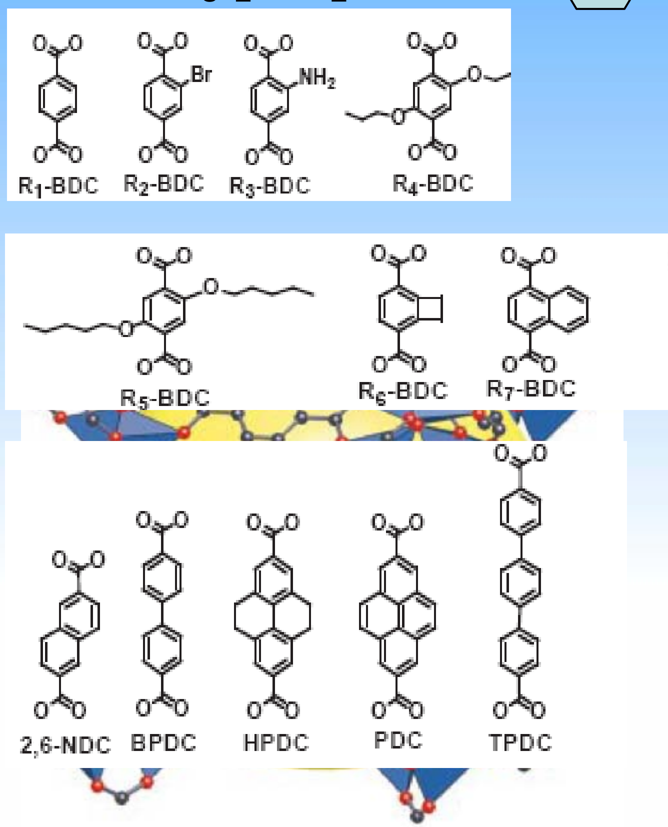
# IRMOF synthesis occurs by self assembly

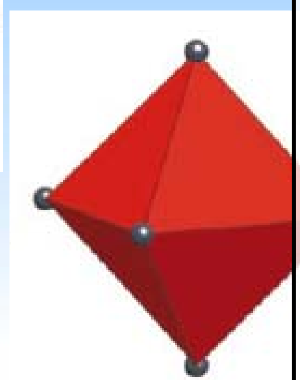
Example: IRMOF-1 (MOF-5)

$Zn(NO_3)_2 \cdot 6H_2O$ + 

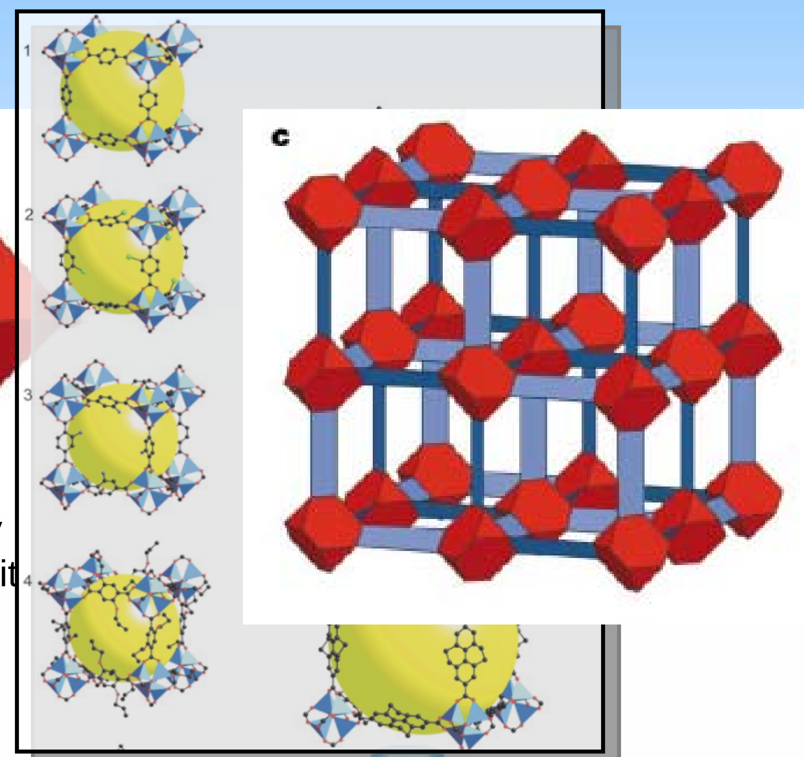

DEF

$\Delta$ 48 hrs, 70 °C



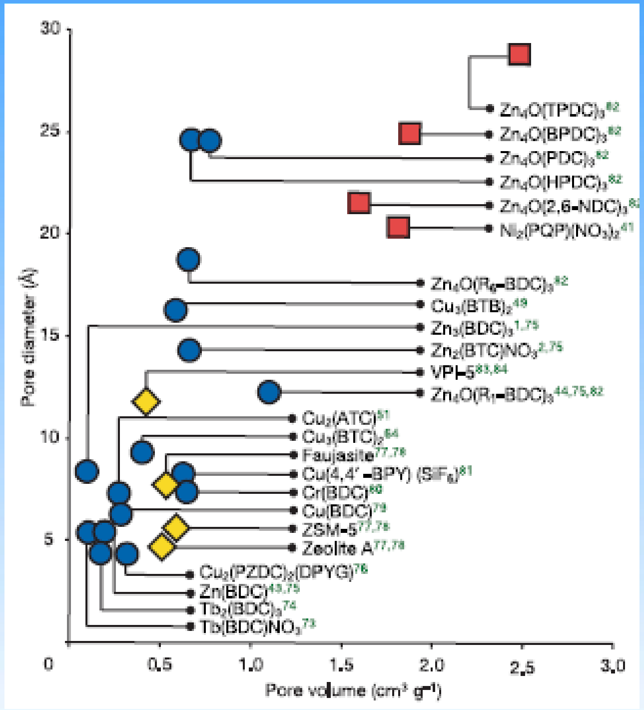



Secondary Building Unit

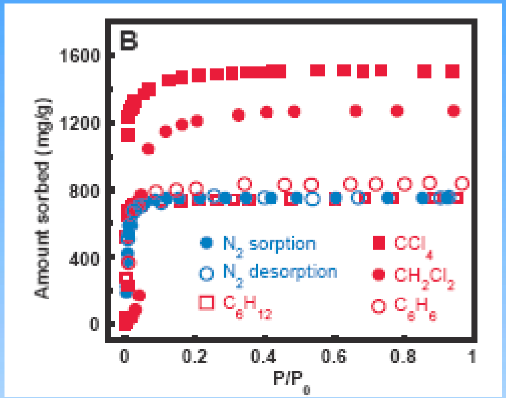



Yaghi et al. *Nature* 2003

# "Isoreticular" IRMOFs: Unique properties among crystalline porous materials



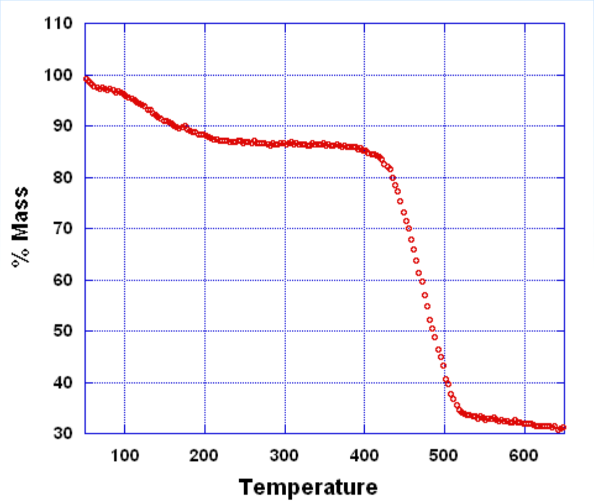

MOF porosity compared to zeolites.
MOFs: ● sorption; ■ XRD. ◆ : zeolites




• **Reversible Type 1 adsorption**

**Many potential applications:**

- **Sensors**
- **Sorbents**
- **Gas storage**
- **Chromatography**
- **Molecular templates**
- **Drug delivery**
- **Catalysts**




- **Homogeneous, periodic pores**
- **Lowest density**
- **Extremely high surface areas**
- **Functionalizable pores**

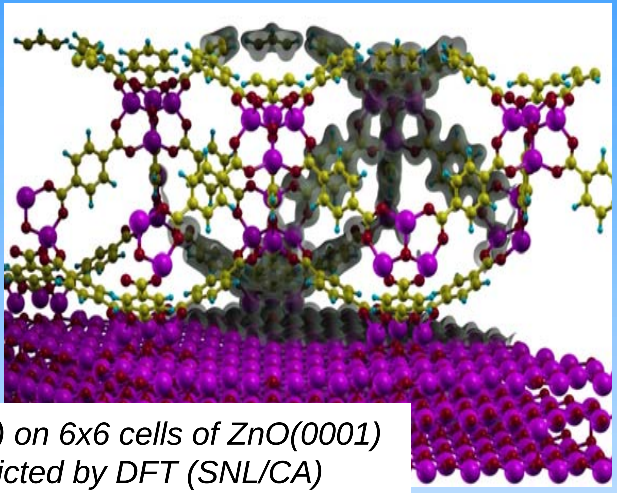
• **Thermally stable to > 400 ºC**

Sandia National Laboratories

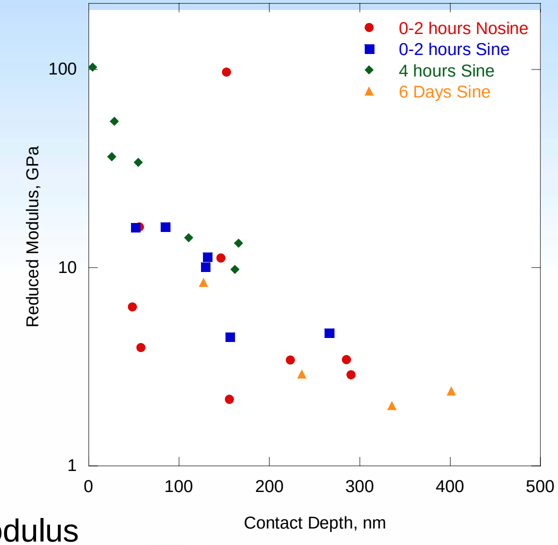
# The complexity of MOF structures makes it challenging to employ theory as a guide to MOF growth on surfaces

- Plane-wave DFT impractical as a screening tool for MOF substrates
  - 3000 CPU hours, 64 processors on Sandia "Thunderbird"
- DFT can predict bulk properties
  - Crystal structure (good agreement with expt)
  - Elastic constants:
    - reduced modulus = 21
    - Nanoindentation: 5 – 100 (avg ~ 18) Problems with the measurement:
      - –Crystal orientation
      - –Surface roughness
      - –Decomposition
    - $B/G_H$ = (fracture resist/plastic deform.) = 3.2 (ductile)

☞Suggests adaptability to substrates



*IRMOF-1(001) on 6x6 cells of ZnO(0001) structure predicted by DFT (SNL/CA)*

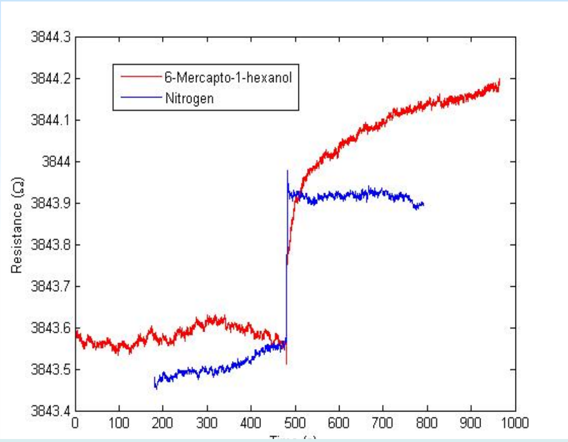



IRMOF-1 Reduced modulus measured by nanoindentation

Sandia National Laboratories

# Preliminary Results

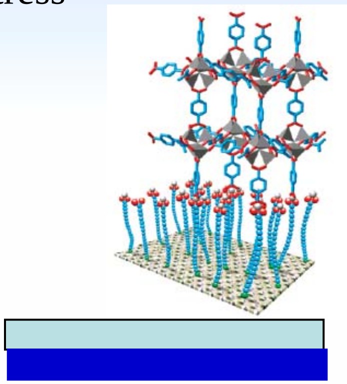
- The sensitivity based upon ac excitation of 1V pk-pk and lock-in-amplifier measurements at 50 kHz with a 100 mS time constant provides a resolution of 5 m$\Omega$ of resistance.
- Cantilever bridge sensitivity is calculated based upon AFM deflection tests of ~1 m$\Omega$/nm deflection, i.e. gauge factor $K_B$ = 117 which corresponds to a surface stress gauge factor of $K_S$ = 51 and therefore a **surface stress sensitivity 0.04 mN/m !**
- Surface stress induced by aminoethane-thiol reaction with gold 0.45mN/m [2].
- Measured response above with 315ppb mercaptahexanol corresponds to a resistance change of shown bellow can be compared to the calculated surface stress sensitivity.




Meassured cantilever resistance response exposed to 315 ppb of mercaptahexanol.

Estimate of sensitivity with MOF coating of 0.1 – 1 um thickness when a linear strain produced is 0.8%. Calculations using DF theory provide following properties for the MOF: Bulk modulus 1.58GPa; $C_{11}$=0 .264 $C_{12}$=0.107, $C_{44}$=0.036. The surface stress would be well within the sensitive range for the cantilever sensor of 5 m$\Omega$ Other groups have reported a 6% volumetric strain [3].

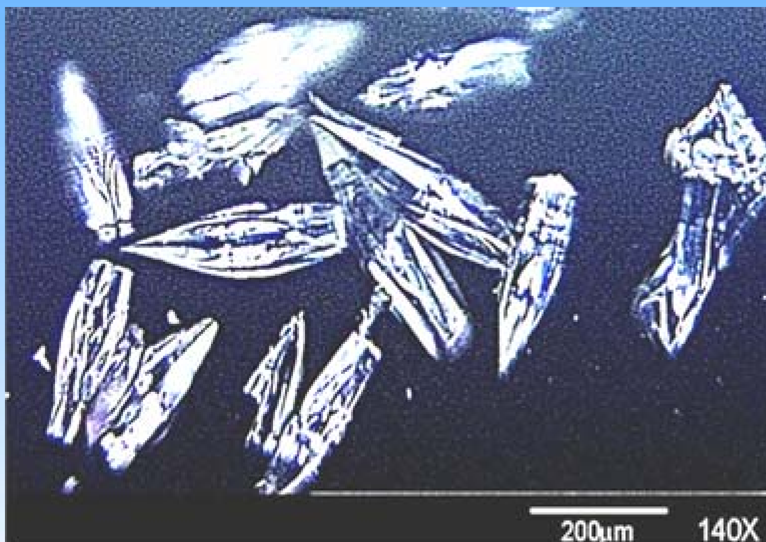
| MOF thickness ($\mu$m) | Tip deflection ($\mu$m) | Calculated resistance change ($\Omega$) |
|---|---|---|
| 0.1 | 5.3 | 5.3 |
| 1 | 83 | 83 |

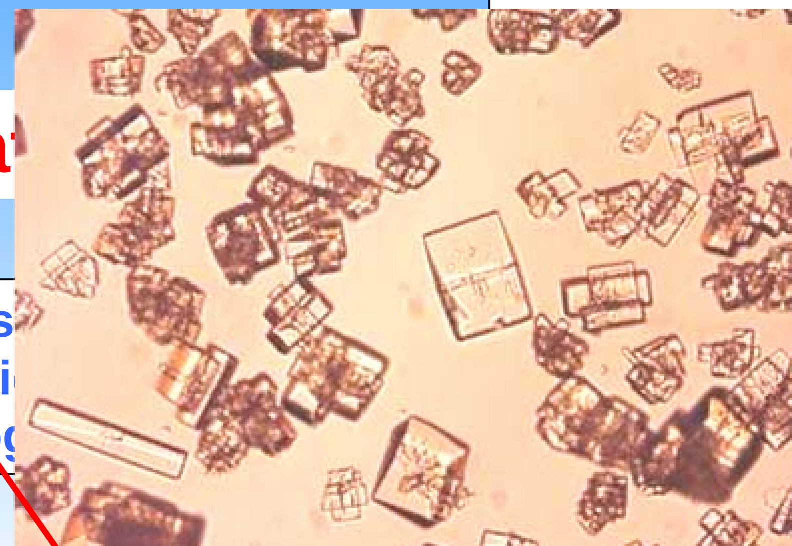


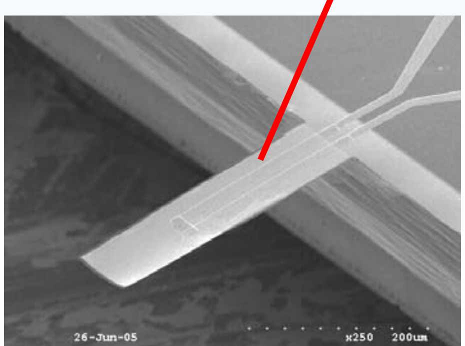
**[2]** McFarland *et al.* "Influence of surface stress on the resonance behavior of microcantilevers," Appl Phys. Lett., Vol. 87, 2005. [3] A. J. Fletcher, *et al.* "Flexibility in metal-organic framework materials: Impact on sorption properties," J. Solid State Chem., Vol. 178, pg. 2491, 2005.

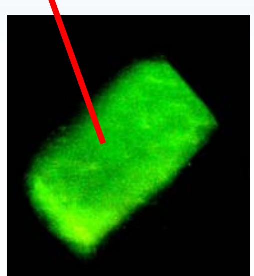
# MOFs must be adapted to substrate materials to realize the potential of their unique properties

**Surfaces**

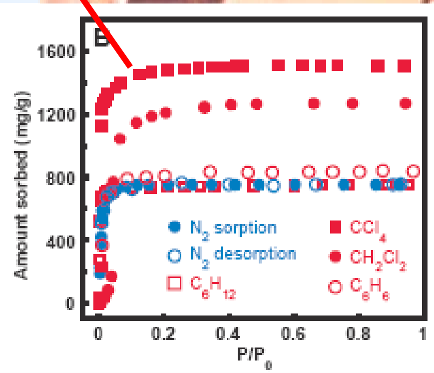




**Cubic Zn-Stilbene MOF**

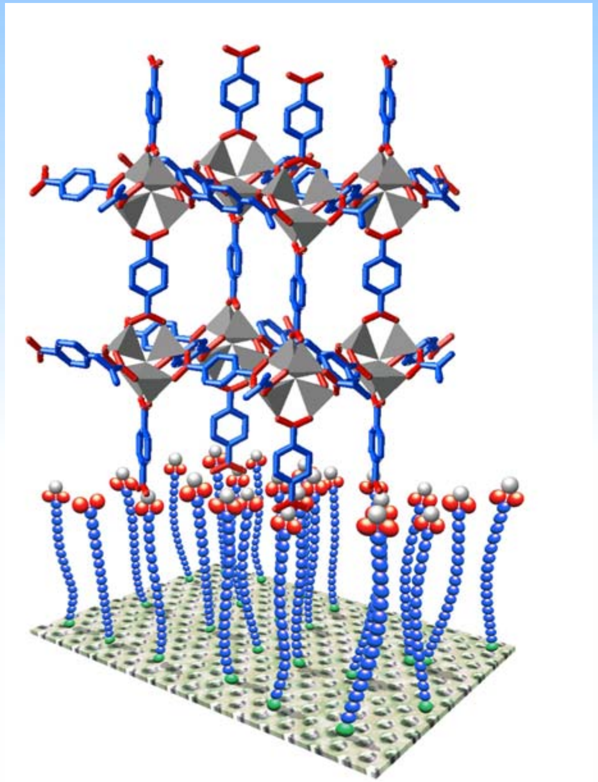



**Eddaoudi et al. *Science* 2002**

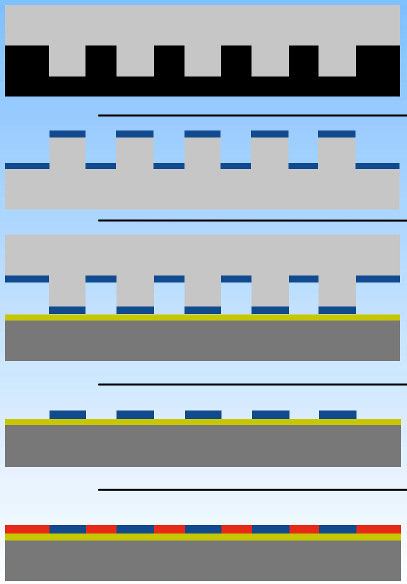
# MOF growth on SAMs: entry point for patterning and device fabrication

SAM termination determines growth:

- MOF growth on $CO_2H$ SAM
- No growth on $CF_3$ SAM



**Microcontact Printing**



Cast PDMS stamp from Master

Apply 16-MCHD to stamp

Apply stamp to Au substrate

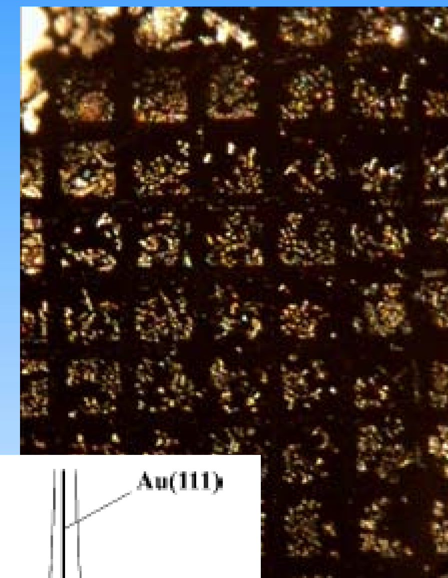
Rinse substrate with EtOH

Repeat with $CF_3$-Dodecane to create $2^{nd}$ SAM

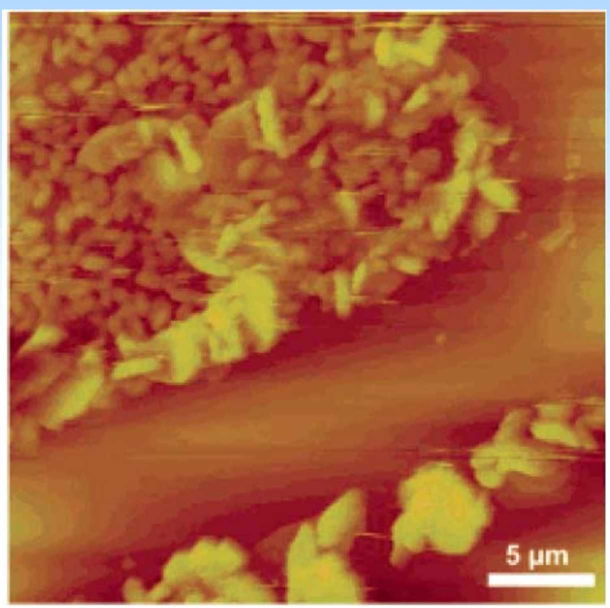
Sandia National Laboratories

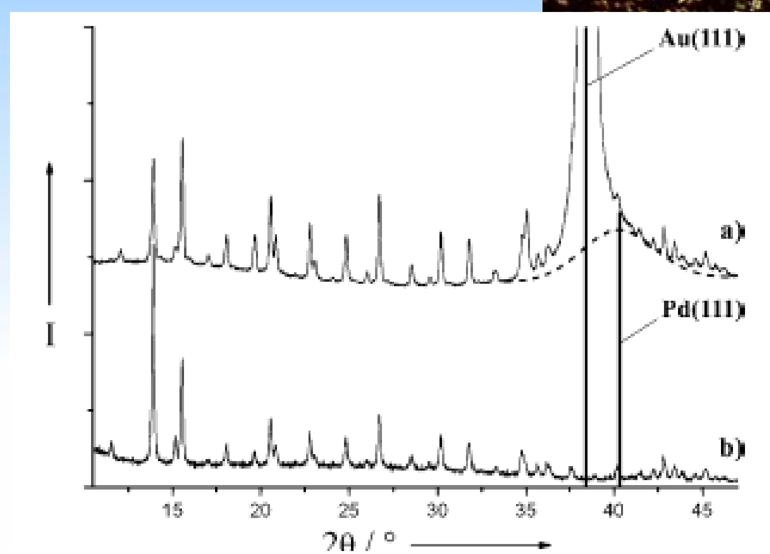
# IRMOF growth on self assembled monolayers has been demonstrated

- Polycrystalline growth on $CO_2H$-terminated Au(111)-SAM surface
- Confirmed by grazing incidence PXRD
- No growth on $CF_3$-terminated surface
- Patterning effective, but growth is not uniform

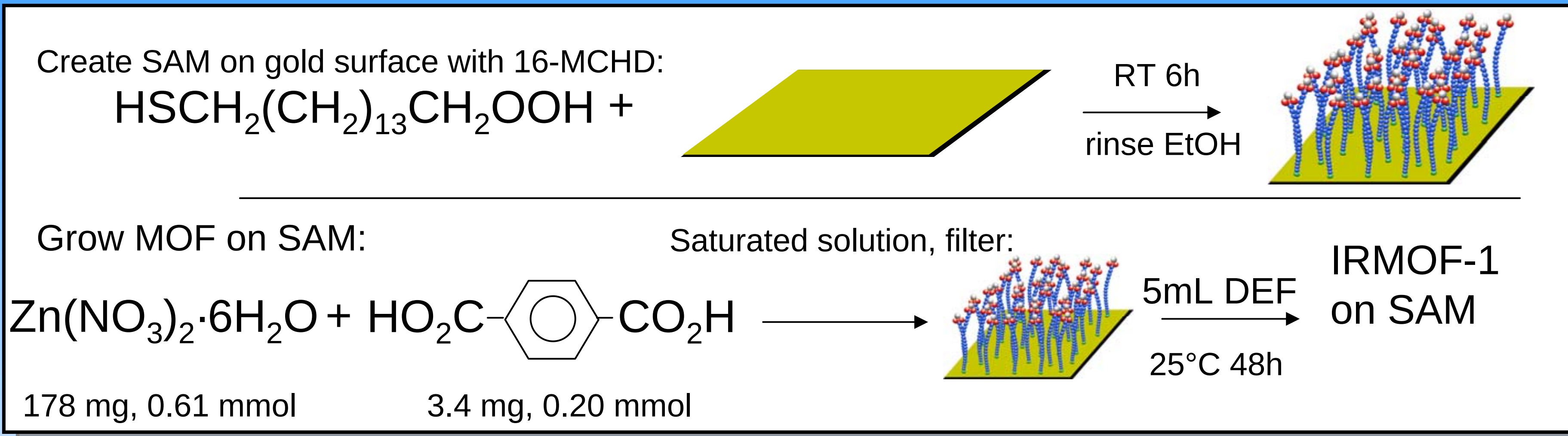


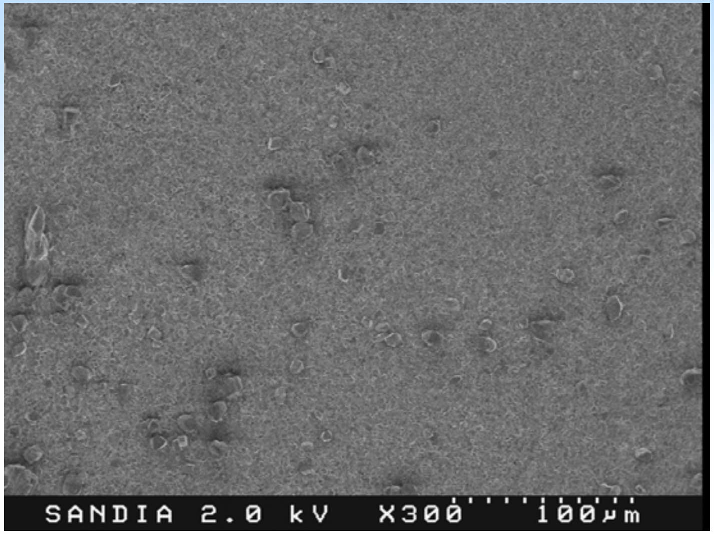
Hermes et al., *JACS*, **2005**, 13744-13745

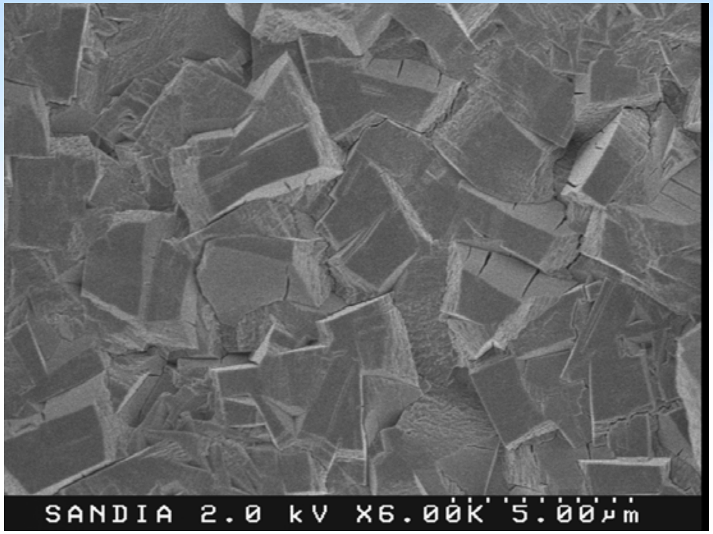


# Improved procedure results in dense, polycrystalline MOF-on-SAM films

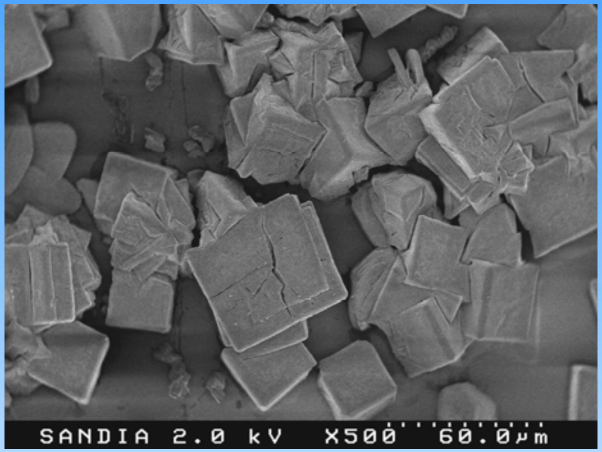


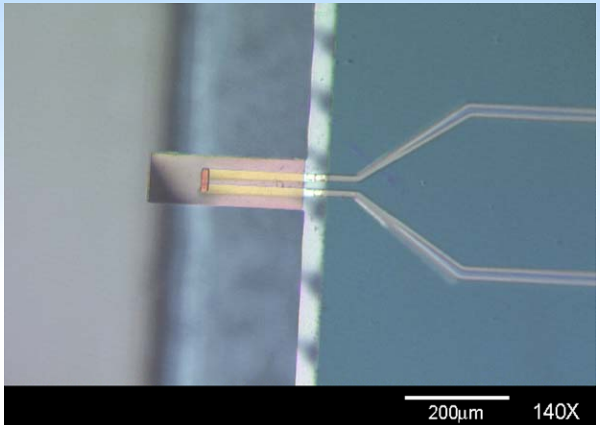



# Polycrystalline IRMOF growth can be achieved on surfaces, but layers are not uniform or dense

- MOFs on SAMs
  - Entry point to devices
  - Single crystal growth observed
  - Dimensions comparable to MEMs devices



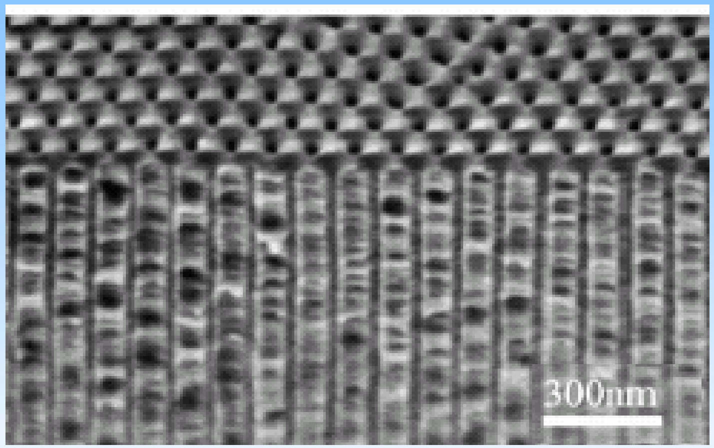

IRMOF-1 crystals on SAM/Au




Silicon piezoresistive cantilever beam (fabricated by GA Tech)

Sandia National Laboratories

# Growth on anodized aluminum oxide: departure point for using MOFs for separations

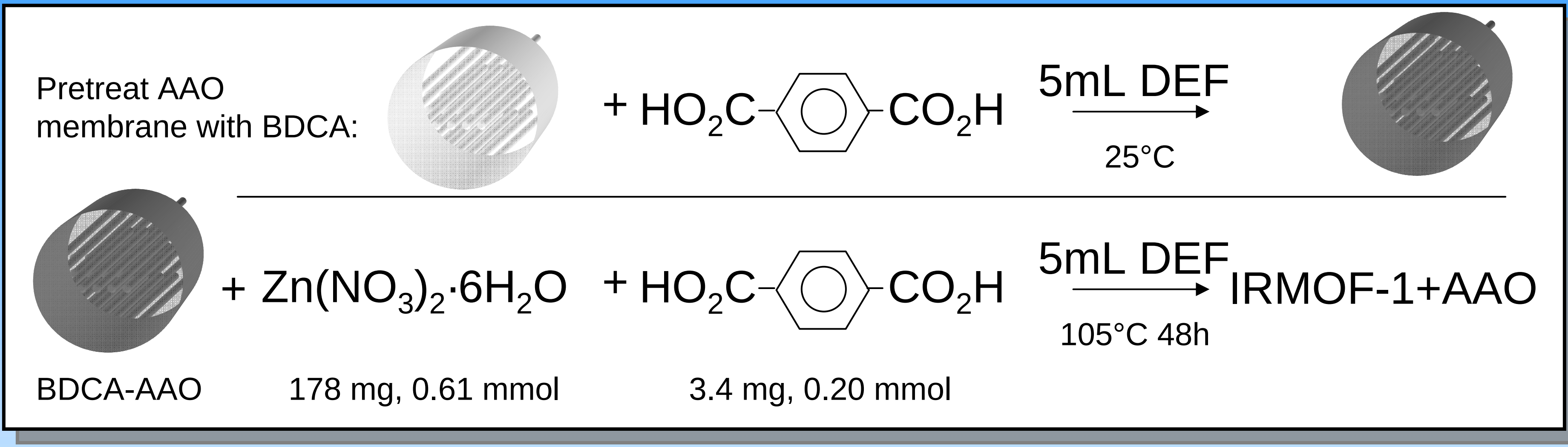



Anodized Aluminum Oxide membrane, side view

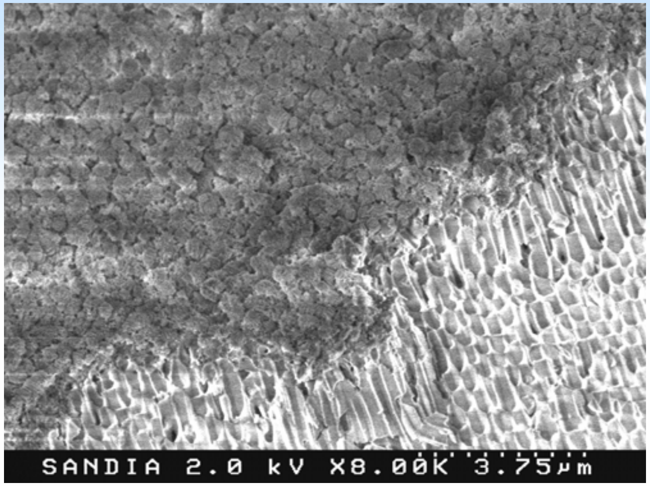
- **Advantages of MOFs for membrane-based separations**
  - Thermal stability >> polymer membranes
  - No swelling or decomposition by hydrocarbons
  - Low-cost synthesis
  - Tailorable pore environment
  - Catalytic separations feasible

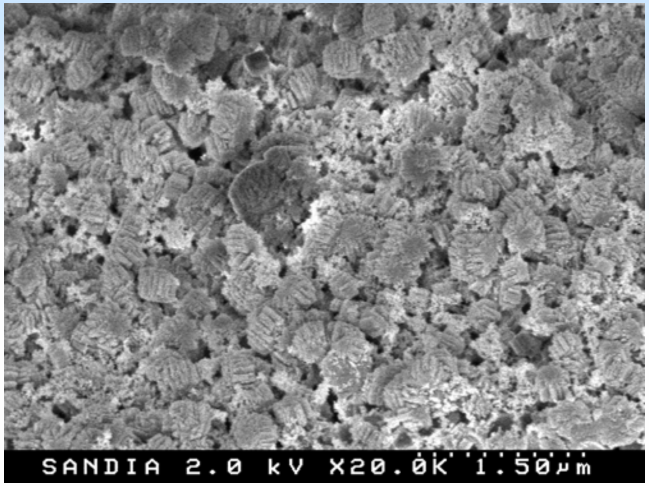
- **Anodized aluminum oxide (AAO)**
  - Potential MOF support material
  - Self-organized porosity controlled by processing conditions:
    - Uniform 20-200 nm diameter
    - Uniform 50-400 nm periodicity
    - Random pore paths or straight, uniform lengths available

# Carboxylate-based MOFs can be grown on AAO




Results in complete MOF coverage:



# Summary

• Hybrid MOF materials created
- MOF-SAMs for surface coatings or patterned MOF deposition
- MOF-AAO with near-pinhole free coverage: future filter technology

• Simulations predict mechanical properties of IRMOF-1 in agreement with nanoindentation measurements


## Acknowledgements

This work was funded by the Sandia National Laboratories Laboratory Directed Research and Development program


Sandia National Laboratories