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Novel Tuned Metal-Organic Frameworks for Environmental and Energy Applications

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UT Austin
Department of Chemistry Seminar
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Team Members

CSTs:

(Fukushima): Jim Krumhansl

(Relicensing): Bianca Thayer, Mark Rigali, UOP Colleagues (Edith Flanigen, Bob Bedard, Dennis Fennelly)

(Discovery, Development, 1993-1996)

Robert Dosch (SNL), Ray Anthony, CV Phillip (Texas A&M), John Sherman (UOP)

Linda McLaughlin, Jim Miller, Norm Brown, Larry Bustard, Elmer Klavetter, Howard Stevens, Jim Krumhansl…

Volatile Gases Separations (Zeolites and MOFs) & Waste Forms:

Dorina Sava, Mark Rodriguez, Terry Garino, Haiqing Liu, Ben Cipiti, Jim Krumhansl, David Rademacher, Jeff Greathouse, Paul Crozier

Karena Chapman, Peter Chupas, Haiyan Zhao (ANL/APS)

Sigma Volox Off-Gas Team:

Bob Jubin (ORNL), Denis Strachan (PNNL), Nick Soelberg (INL)

Light Emitting MOFs:

Dorina Sava, Mark Rodriguez, Lauren Rohwer

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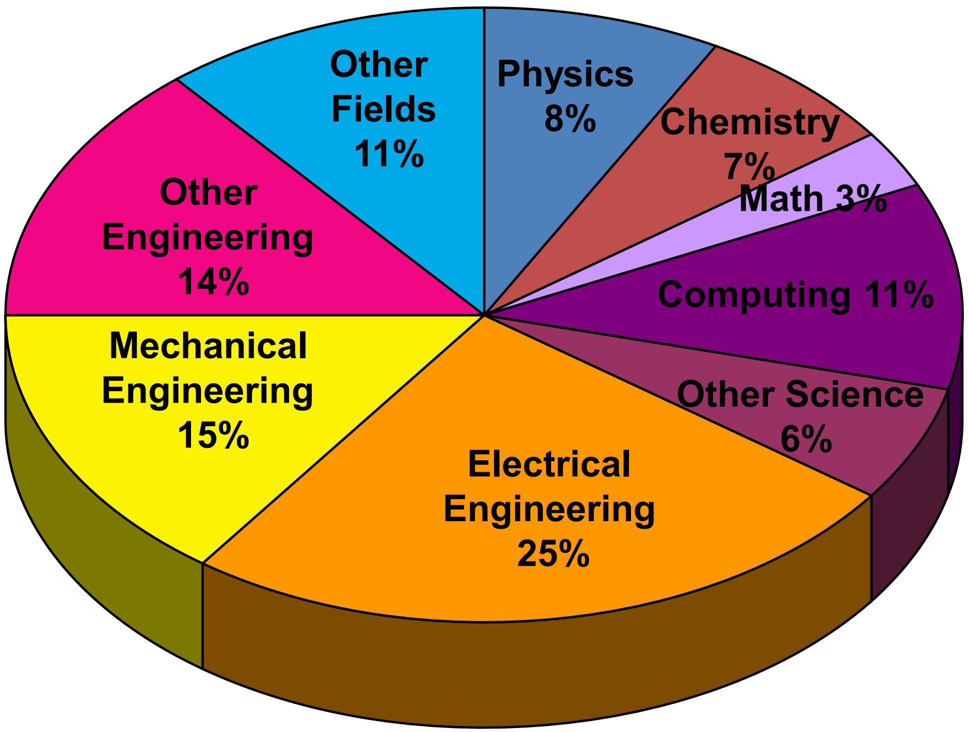
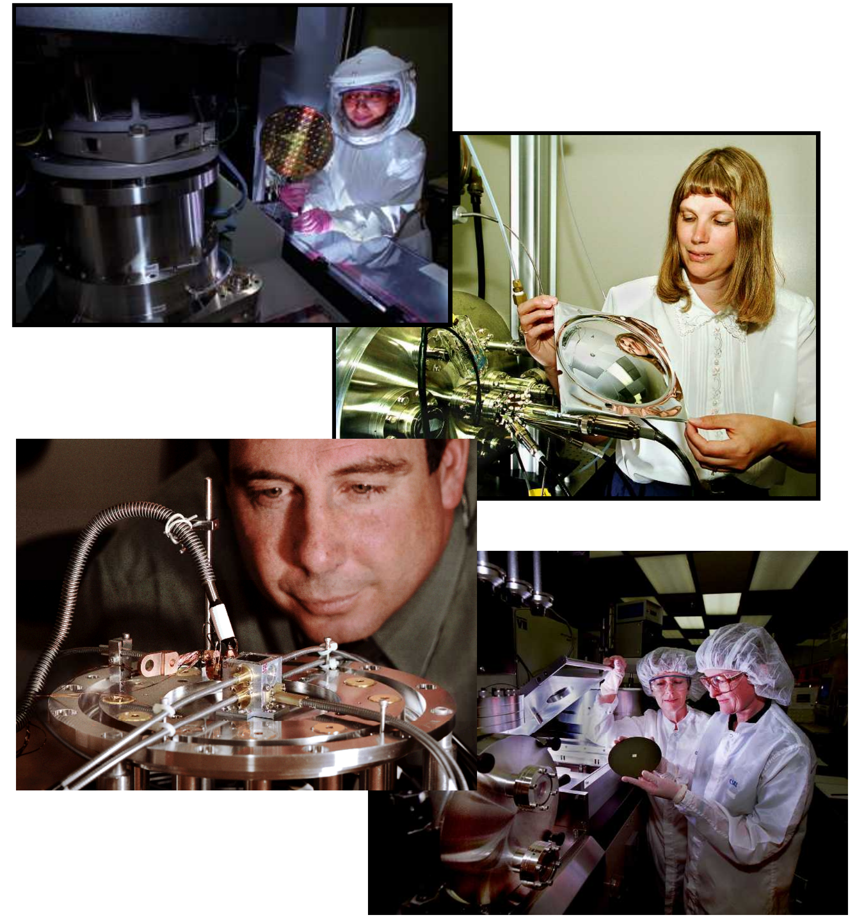
Additional Support: Work at Argonne and use of the Advanced Photon Source were supported by the US DOE Office of Science, Office of Basic Energy Sciences, under contract No. DE-AC02-06CH11357.

Sandia National Laboratories:
“Exceptional Service in the National Interest”

≈ $ 2.2B Operating Budget FY11





~8,200 full-time employees (~ 900 in California)
1,431 PhDs and 2,235 Masters

Sandia National Laboratories

Kauai Test Facility
Hawaii

Tonopah Test Range,
Nevada

Albuquerque, New Mexico

Yucca Mountain,
Nevada

WIPP,
New Mexico

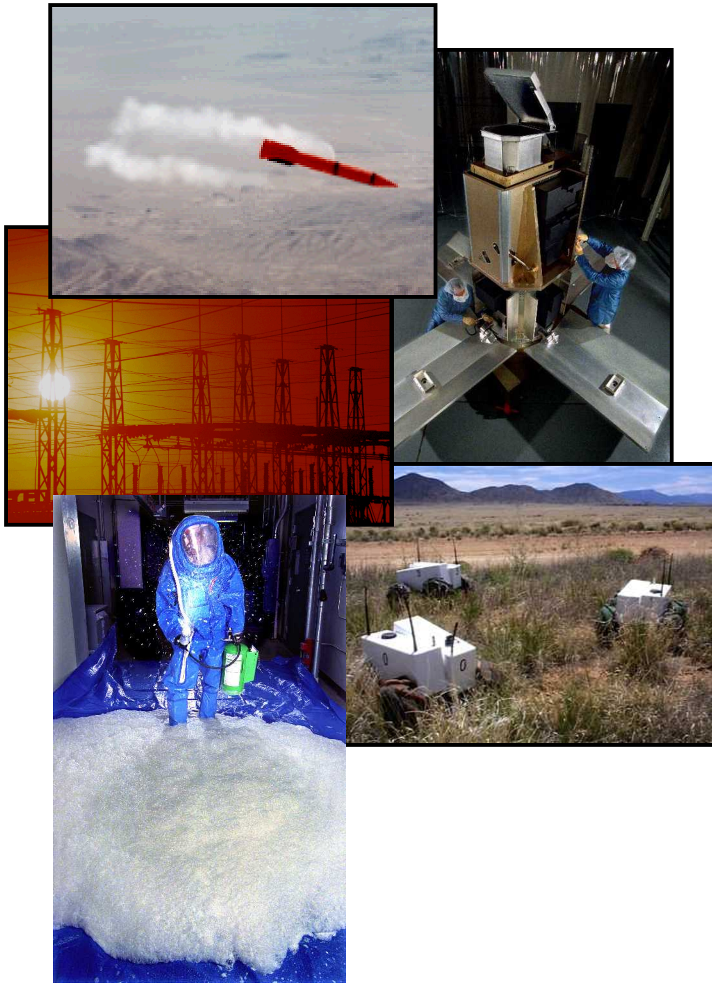
Pantex, Texas

Livermore,California

Sandia is organized into six Strategic Management Units (SMUs)

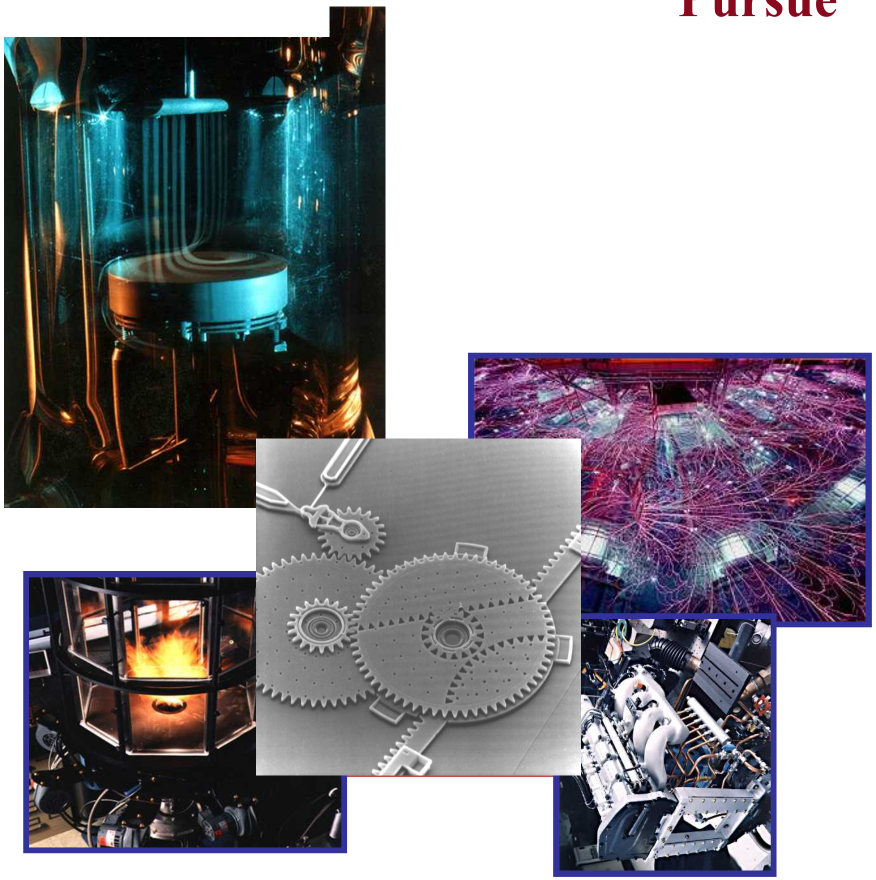
Our six Strategic Management Units:

- NW: Nuclear Weapons SMU
- DS&A: Defense Systems & Assessments SMU
- ST&E: Science, Technology, & Engineering SMU
- ECIS: Energy and Critical Infrastructure SMU
- HS&D: Homeland Security & Defense SMU
- IES: Integrated Enabling Services SMU



Science and Technology Engineering SMU Focus

Pursue "science with the mission in mind"



Energy Research

Basic Energy Sciences,
Combustion Research,
Nanotechnology, Fusion,
Biological & Environmental Research, Scientific Computing

Renewable & Fossil Energy

Solar, Photovoltaic, Thermal Wind, Oil & Gas,
Strategic Petroleum Reserve

Energy Efficiency

Electric Energy Storage, Hydrogen Research, Energy Conservation

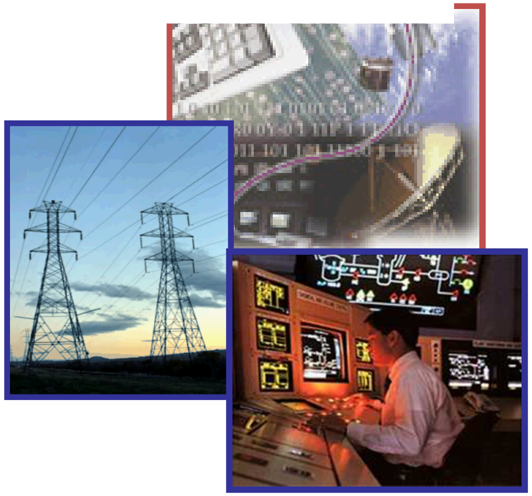
Waste Legacy

Waste Storage, Environmental Technology & Restoration

Nuclear Energy

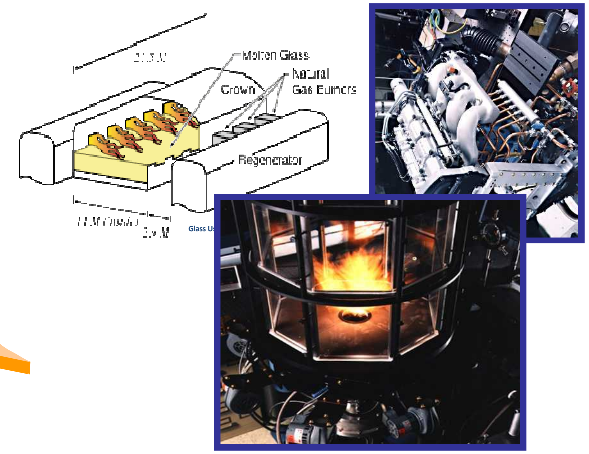
NRC, Risk & Reliability
Reactor Safety
Nuclear Energy R&D

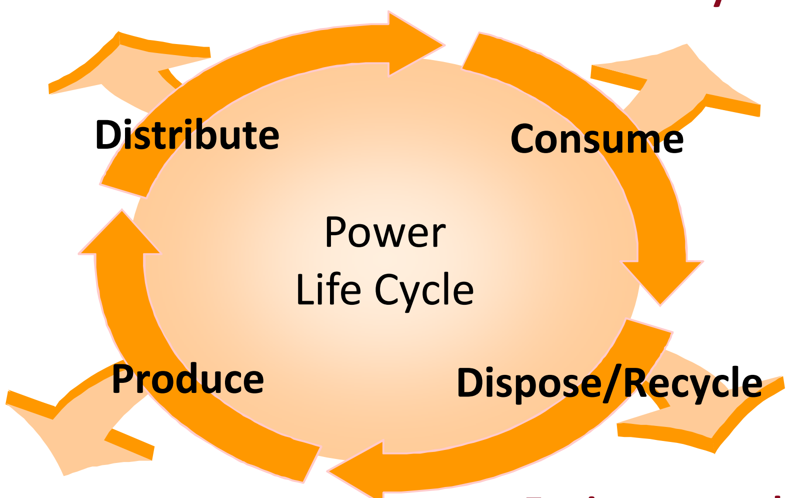
Energy and Critical Infrastructure SMU Focus



Safe, Secure, Reliable Systems Infrastructure

Efficiency / Productivity





Portfolio of Power Sources

Environmental Stewardship

E&CI_202_10/24/01

Sandia seeks high academic quality in ~13 technical disciplines.

- Information Technology
- Electrical Engineering
- Mechanical Engineering
- Computer Science
- Computer Engineering
- Chemistry
- Physics
- Math
- Materials Science Engineering
- Chemical Engineering
- Aeronautical/Aerospace Engineering
- Civil Engineering
- Industrial Engineering

Overview of Sandia's Student Programs

- **GPA**
  - 3.4 Cumulative GPA

- **Student Internship Program (SIP)**
  - The mission of SIP is to hire the best and brightest students and to provide them with valuable professional and personal development and to develop a strategic workforce pipeline.
  - 640 Year-round Students
  - 35 Telecommuting Students
  - ~600 Summer-only Students

- **Co-Op** Work Study program
- **Postdoctoral Associates**, advertised at Sandia web site, in major scientific society journals, and with individual PIs directly for ≈ October start-dates
- **Fellowships and One-Year-on-Campus (OYOC)**
  - National Physical Science Consortium (NPSC) fellowship
  - National Consortium for Graduate Degrees for Minorities in Engineering and Science, Inc. (GEM) fellowship
  - OYOC

http://www.sandia.gov/careers

Overview of Sandia's Truman Fellowship

Truman Fellowship

Sandia National Laboratories announces the establishment of the President Harry S. Truman Fellowship in National Security Science and Engineering to attract the best nationally recognized new Ph.D. scientists and engineers.

The Fellowship

The Fellowship provides the opportunity for recipients to pursue independent research of their own choosing that supports the national security mission of Sandia National Laboratories. The appointee is expected to foster creativity and to stimulate exploration of forefront science and technology and high-risk, potentially high-value R&D.

Truman Fellowship candidates are expected to have solved a major scientific or engineering problem in their thesis work as evidenced by a recognized impact in their field.

Benefits

The salary for Truman Fellows is $110,800.

Requirements

U.S. citizenship, the ability to obtain a DOE "Q" clearance; minimum GPA;
research in areas of interest to national security; the candidate must have been awarded a Ph.D.

http://www.sandia.gov/careers

I. Solid State Lighting (SSL): Towards Single Component Phosphors

- The ability to generate white light from a single phosphor:
  - an alternative to existing approaches that achieve white light through color mixing
  - a promising approach for next-generation SSL materials

- Current white LEDs for SSL are based on blue InGaN LEDs that excite a yellow-emitting YAG:Ce phosphor (cool white light) made warmer by incorporating a red-emitting phosphor

- Warm white LEDs can also be achieved by utilizing near-UV InGaN LEDs to excite blends of red-, green-, and blue-emitting phosphors. Unfortunately, the additional down-conversion step (near-UV to blue) *significantly lowers the conversion efficiency of the device.*

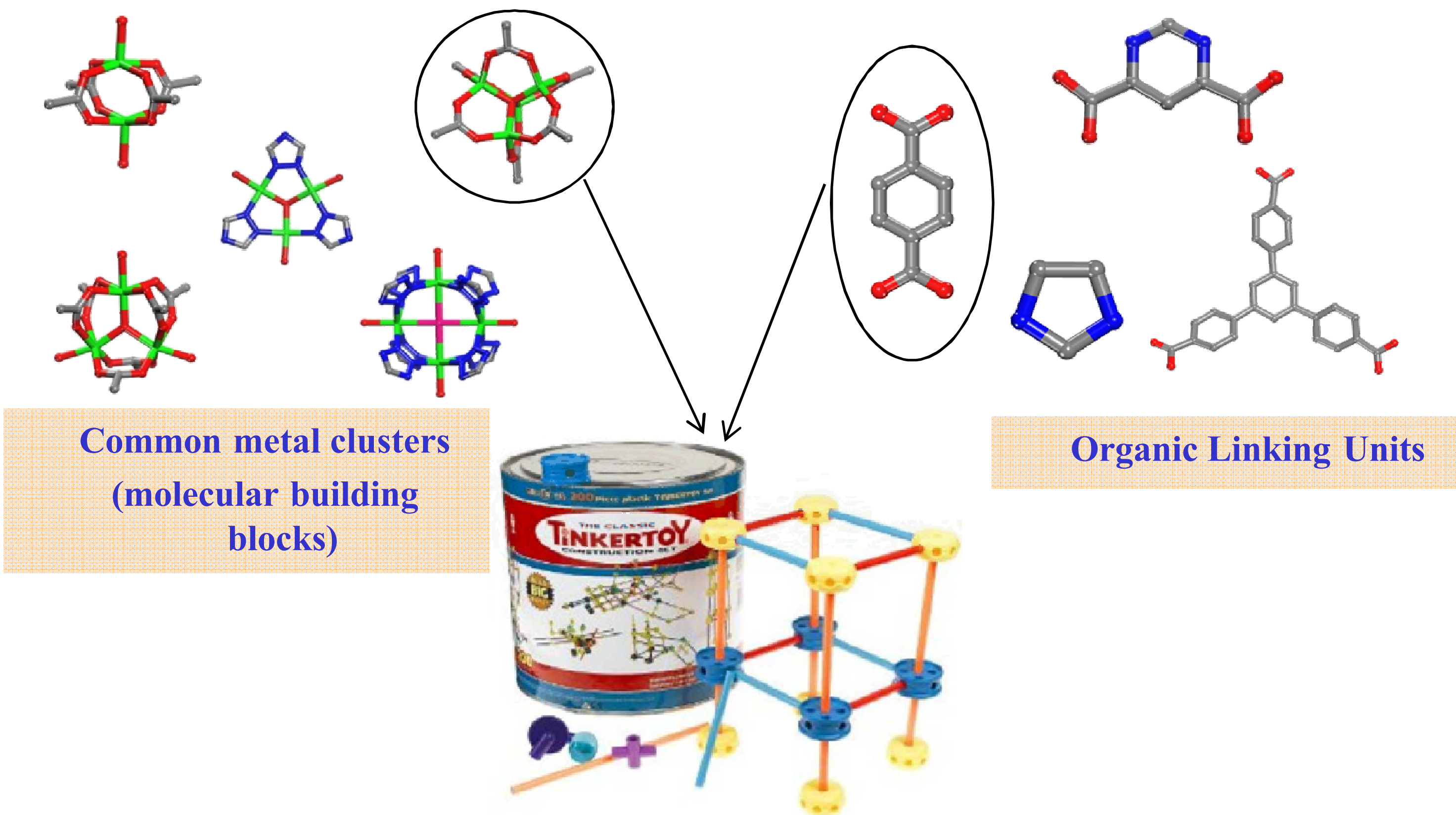
- In this context, MOFs are promising candidates for single component phosphors due to their highly tunability of both organic and inorganic component, pre- or post- synthesis

Metal-Organic Frameworks (MOFs)

"Tunable" frameworks for gas selectivity / high capacity due to high surface areas

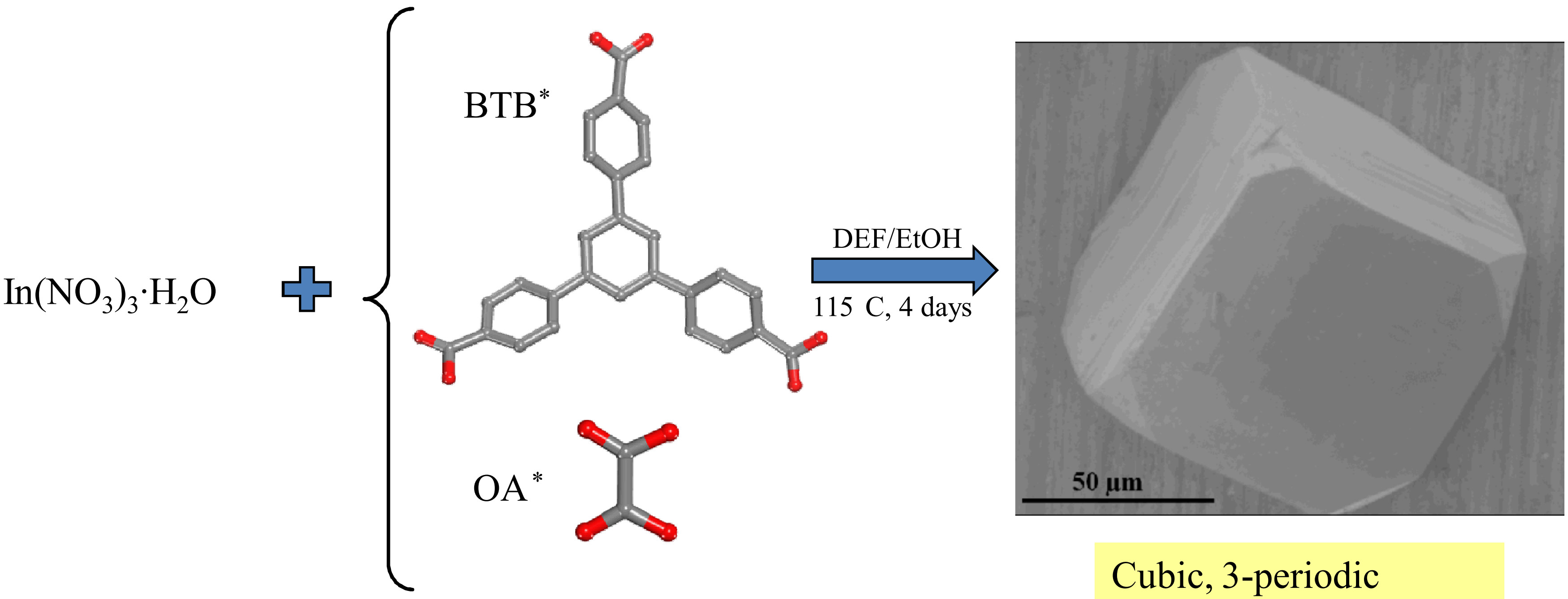
Novel Separations and Waste Forms Technologies via Structure – Property Determination using *Integrated Synthesis, Characterization and Modeling*

eg., Volatile gases/long-lived fission products pose *unique scientific issues* with regards to detection, storage, capture of volatile gases – including ^{129}I, ^{85}Kr, ^{14}C (CO_2), ^{3}H



SMOF-1 (Sandia Metal-Organic Framework-1): A Novel In-BTB framework

$In(NO_3)\bullet H_2O$ + 1,3,5-Tris(4-carboxyphenyl)benzene (BTB) + 1.5 oxalic acid (OA) + N,N'-diethylformamide(DEF) / EtOH mixture; 115°C, 4 days -> $In(BTB)_{2/3}(OA)(DEF)_{3/2}$

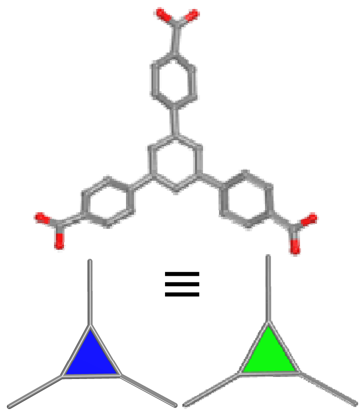


Cubic, 3-periodic
a= 33.975(3) Å, Ia-3
V= 39,217(10) $Å^3$

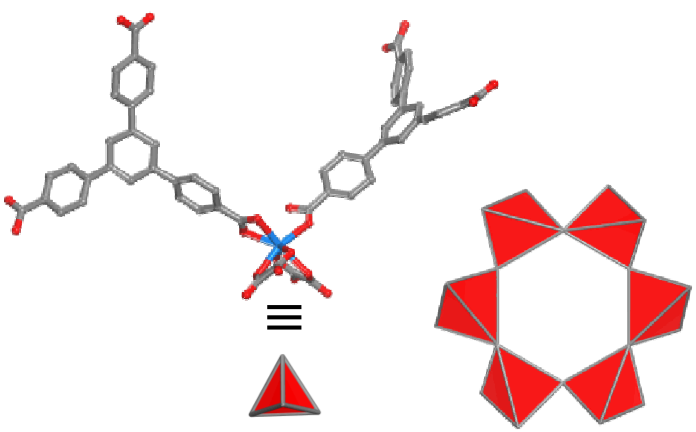
✓The first In-BTB reported net
✓The first oxalic acid-BTB system explored to date

J. Am. Chem. Soc. **2012,** 134 (9), 3983.

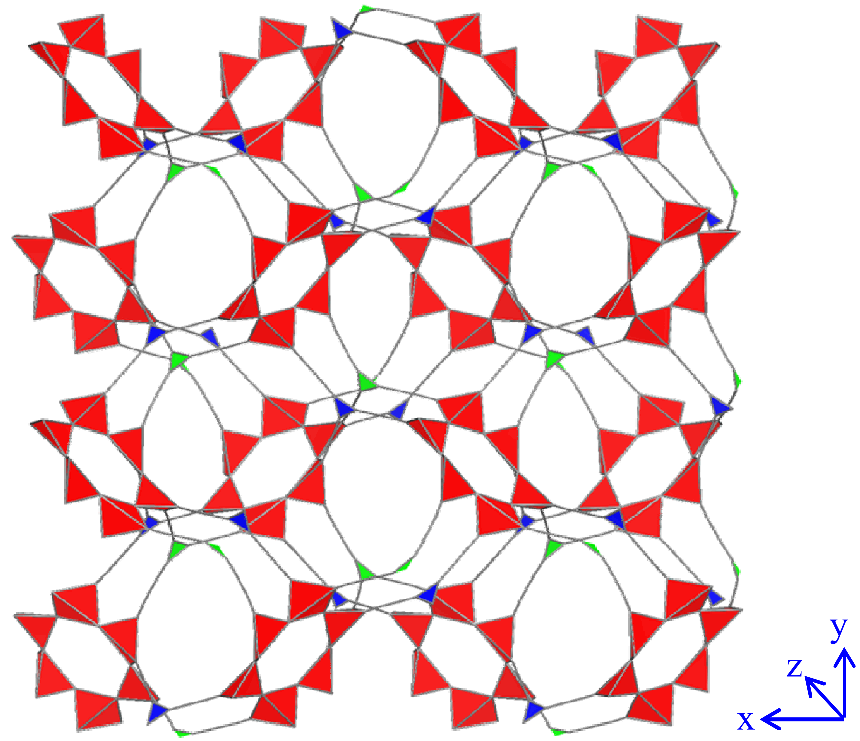
Structure Determined by Single Crystal X-ray Crystallography
Topological evaluation: Unprecedented (3,3,4) Trinodal Net



Two topologically distinct 3-connected nodes



4-connected node

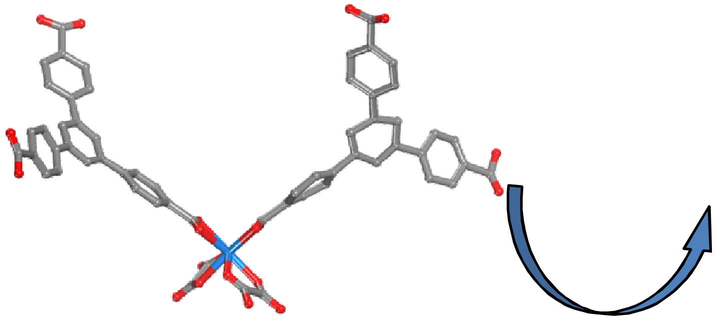


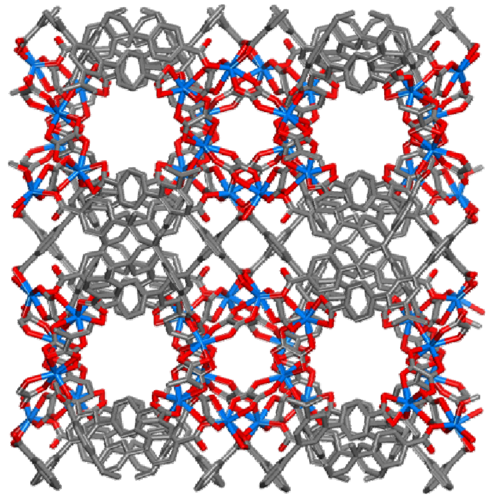
Coordination sequences:
V1 : 3 9 22 36 58 88 114 151 196 234
V2: 3 9 22 39 54 79 119 151 186 240
V3: 4 10 21 39 60 85 117 154 195 242

The short Schläfli (point) symbol: $\{6^3.8^3\}3\{6^3\}2$

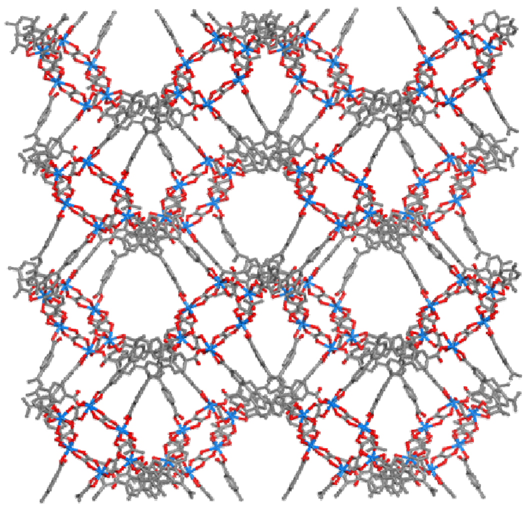
SMOF-1 (Sandia Metal-Organic Framework-1): A Novel In-BTB framework

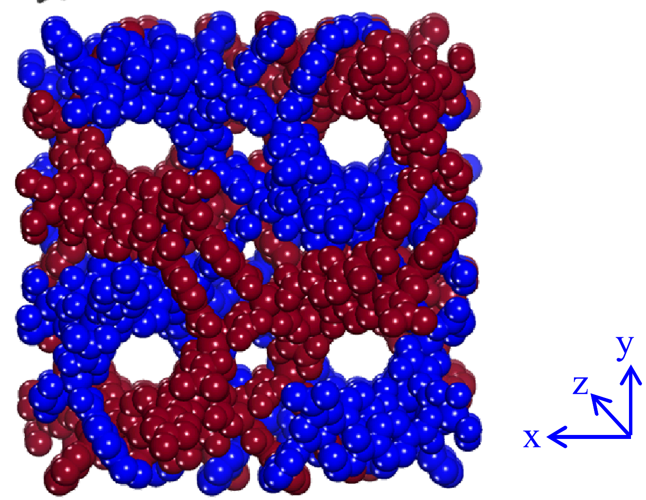
$In(BTB)_{2/3}(OA)(DEF)_{3/2}$





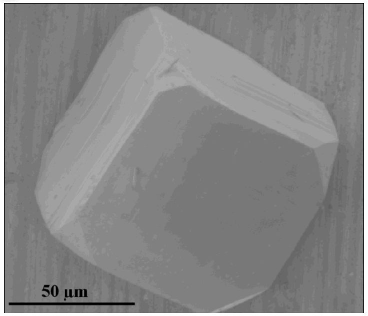
Potential open channels in all directions, accessible through passages of ~4.3Å

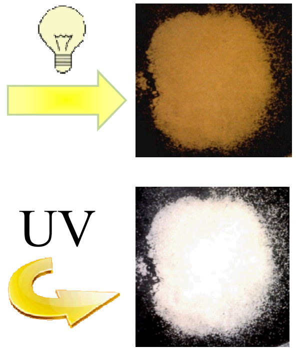




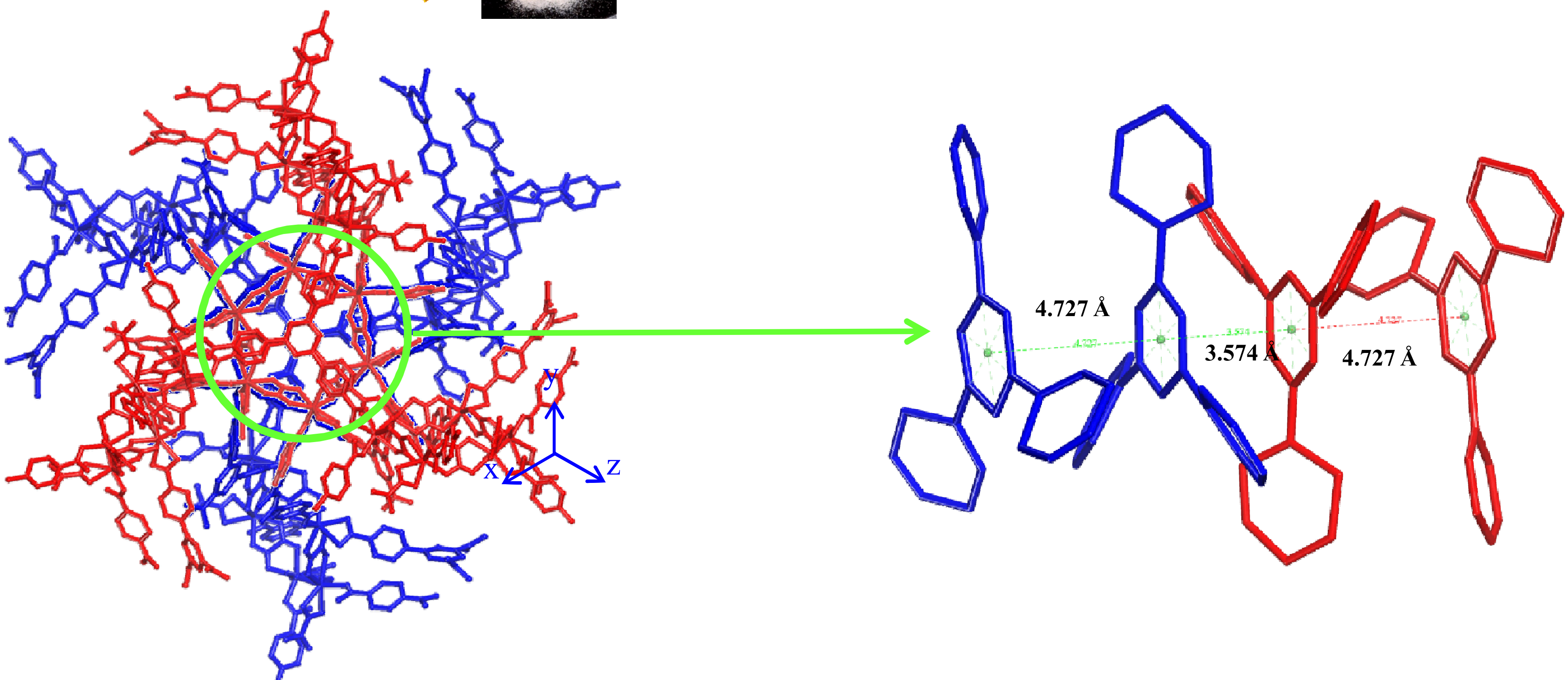
Corrugation ⟺ Interpenetration

SMOF-1: White Light Emitter Due to Framework Corrugation and Interpenetration

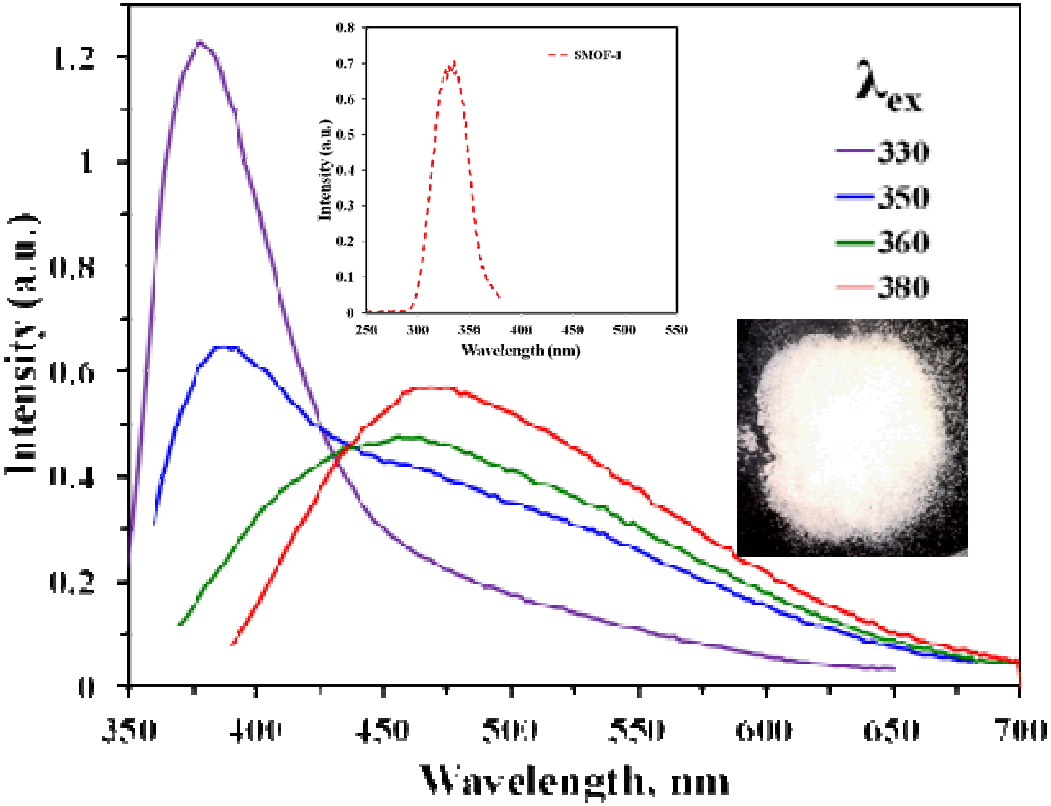




Unique arrangement of BTB linkers in SMOF-1 results in a cascade of π---π* aromatic interactions



Direct white-light broadband emission : Combination of π---π* aromatic interactions & Ligand to Metal charge transfer (LMCT)



Excitation and emission spectra in SMOF-1

*CRI (Color Rendering Index) ~ 90
*CCT (Correlated Color Temperature) ~ 3200

Color properties in SMOF-1

λ_{ex}	CRI*	CCT* (K)	x	y
330	77.4	34463	0.209	0.193
350	84.5	22413	0.241	0.268
360	85.1	33290	0.234	0.275
380	81.1	21642	0.235	0.387

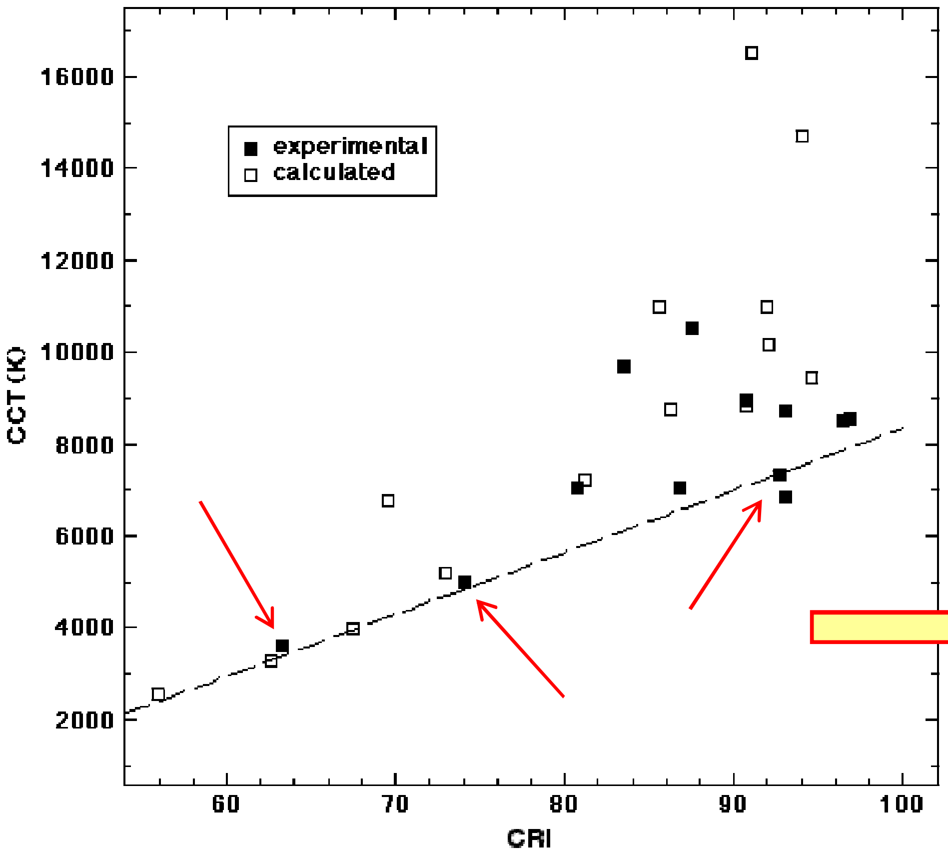
✓CRI values fall within intended ranges (81-85)

- High CCT (21642-33290 K)

Department of Energy; Solid-State Lighting
http://www1.eere.energy.gov/buildings/ssl/

Optimized Simulated Spectra Guides Successful In-framework Eu Co-doping

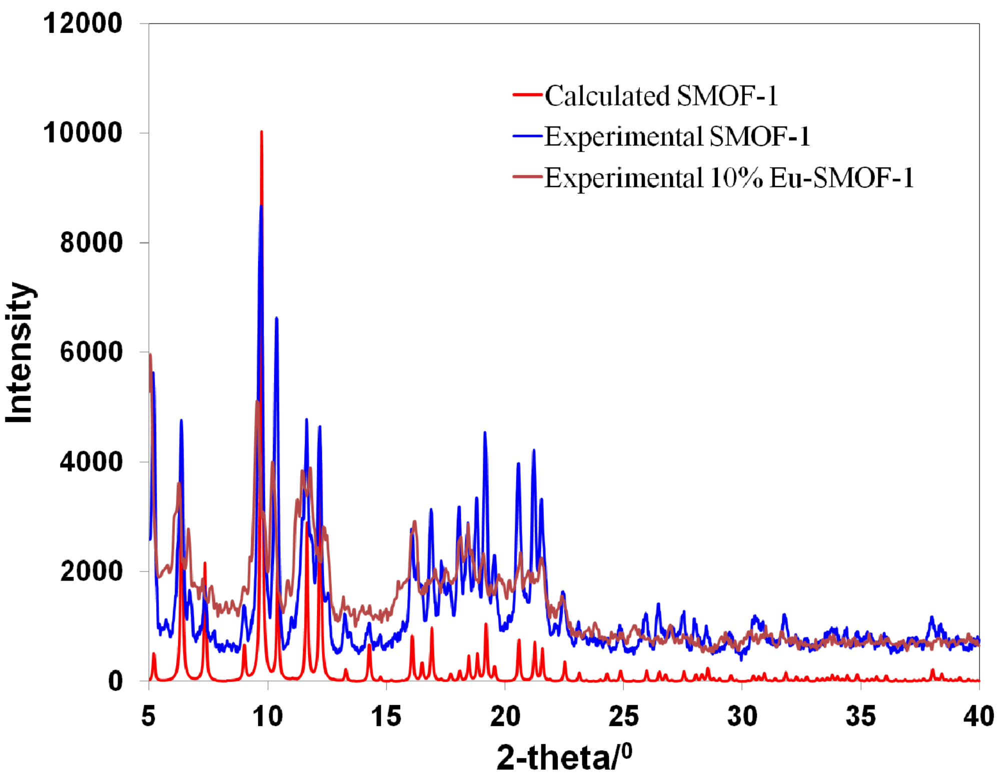
Calculated and experimental CCTs and CRIs for 2.5, 5, and 10% Eu-doped SMOF-1

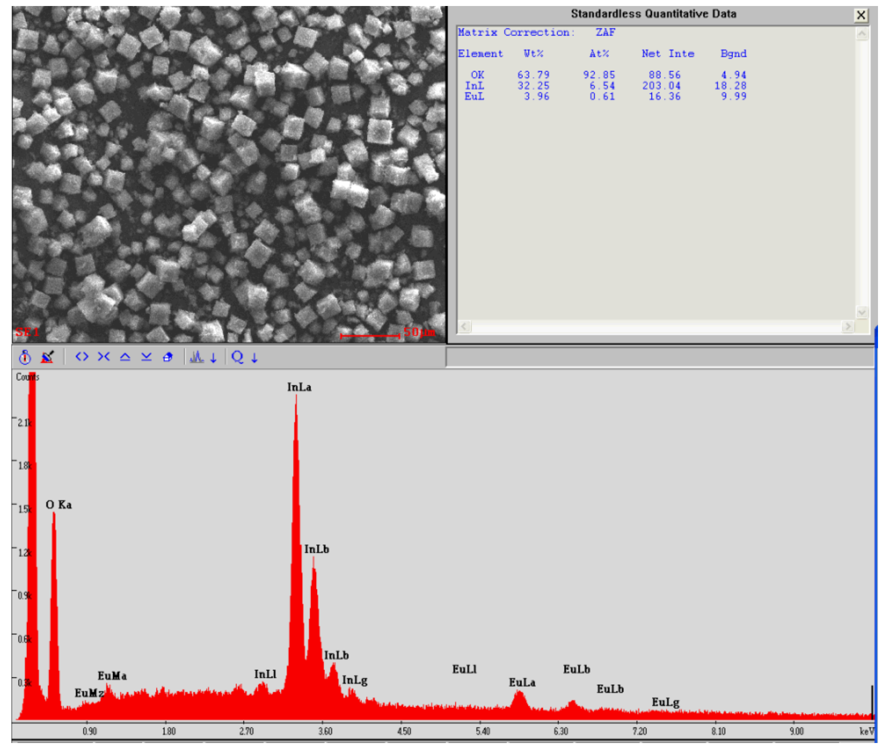


- *Simulated spectra* were generated by summing an SMOF-1 and Eu^{3+} spectra, at excitation wavelengths of 350, 360, and 380 nm, respectively.
- Then, the amplitudes of each spectra were varied to find the optimal color properties.
- The best values of CRI and CCT fall *along* or *below* the dashed line in the plot

By increasing the Eu^{3+} concentration to 10%, the CRI and CCT shift closer to the set target of CRI~90 and CCT~3200K

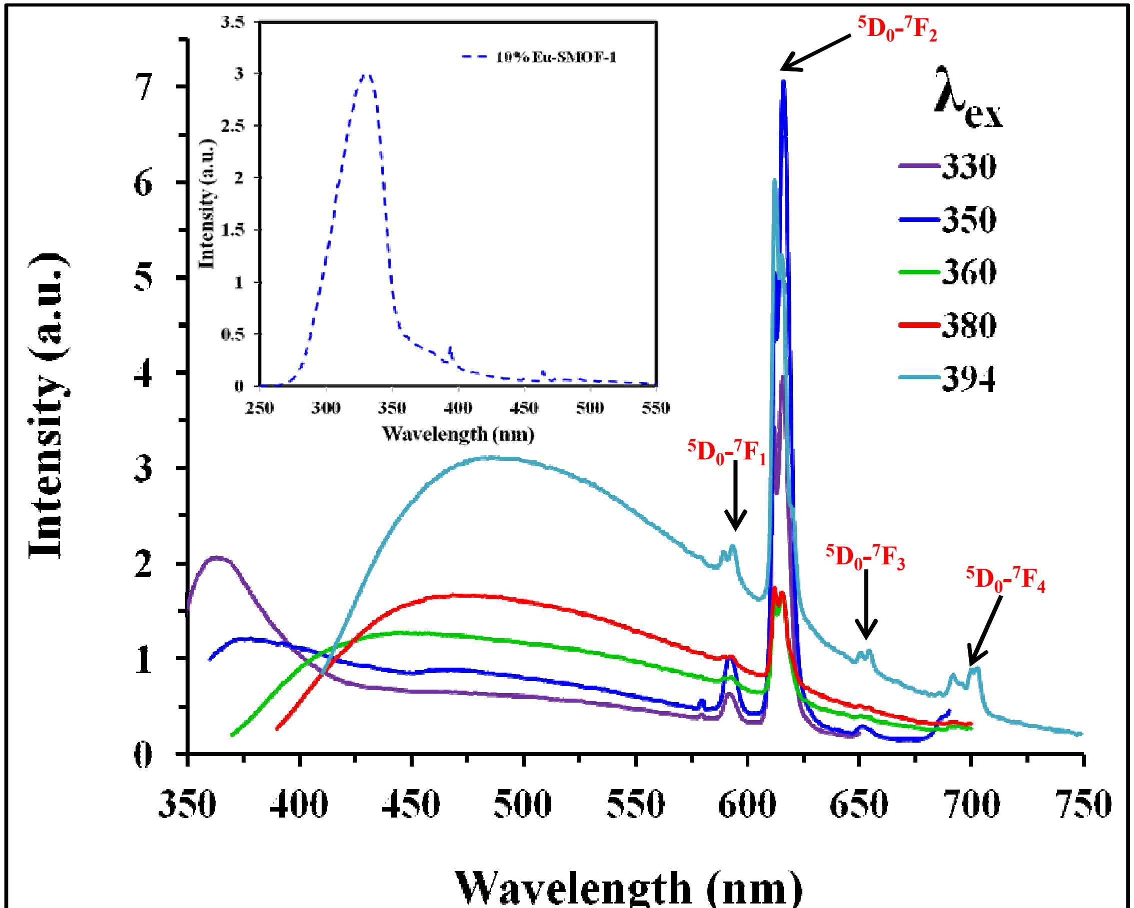
Successful In-framework Eu Co-Doping at 2.5, 5, and 10%





Unit cell refinement of the 10% Eu-doped SMOF-1 sample reveals *enlarged unit cell parameters* a=34.57(6) Å, compared to a=33.975(3) Å.

Enhanced System Tunability: Improved color Properties within Framework 10% Eu Co-doping



Color properties in 10% Eu-doped SMOF-1

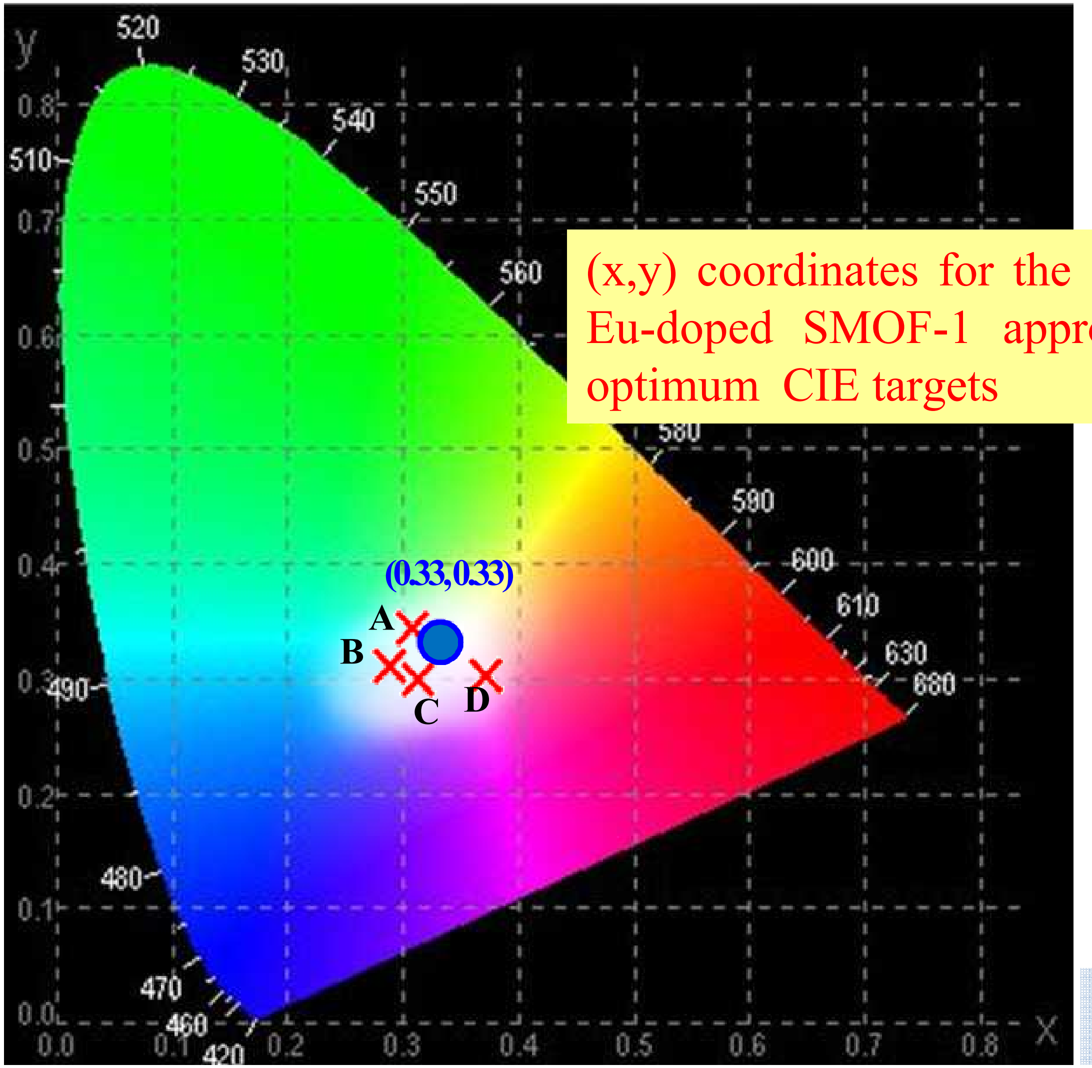
λ_{ex}	CRI	CCT (K)	x	y
350	63	3606	0.369	0.301
360	81	7068	0.309	0.298
380	93	8695	0.285	0.309
394	93	6839	0.304	0.343

✓CCT values are significantly improved

Absolute QY ~ 4.3% at 330 nm

Narrowband emission peaks observed from the Eu^{3+} component, attributed to the parity forbidden ^5D-^7F transitions, and electric dipole transitions

CIE* Optimum White-Light Chromaticity Coordinates Set at (0.33, 0.33)

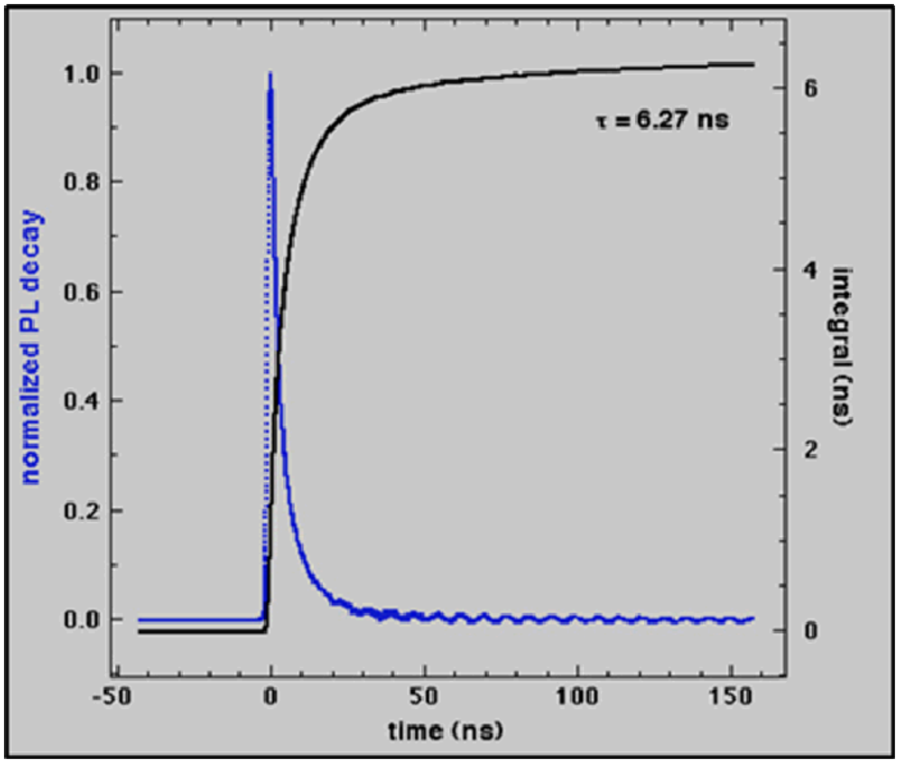


(x,y) coordinates for the 10% Eu-doped SMOF-1 approach optimum CIE targets

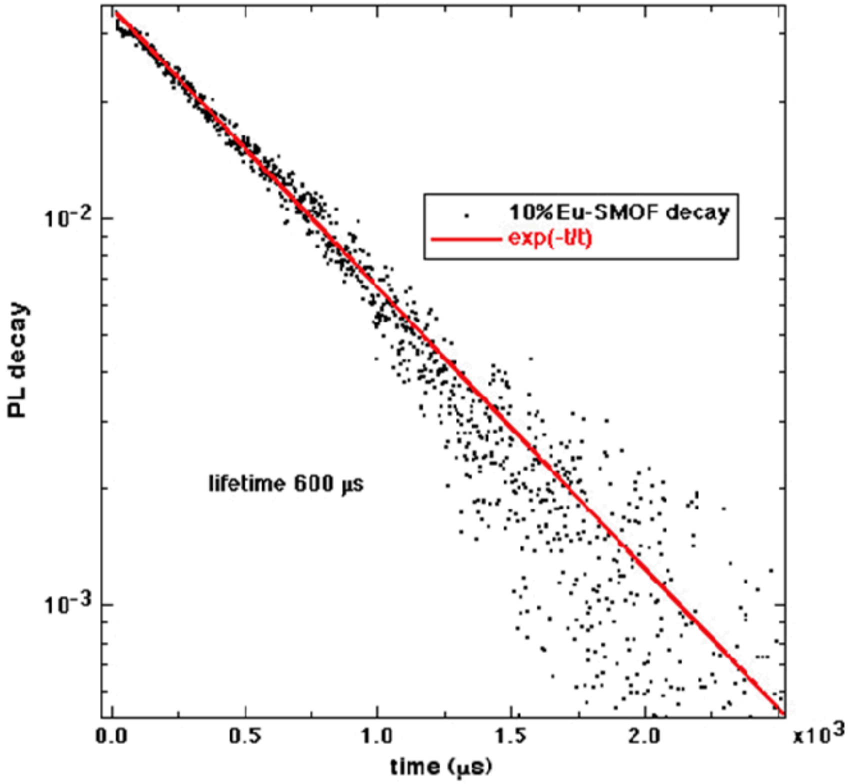
*CIE: Commission Internationale de l'Eclairage

A-D: (x, y) chromaticity coordinates for λ_{ex}= 394, 380, 360, 350 nm.

Framework Tunability is Reflected in the PL Lifetime



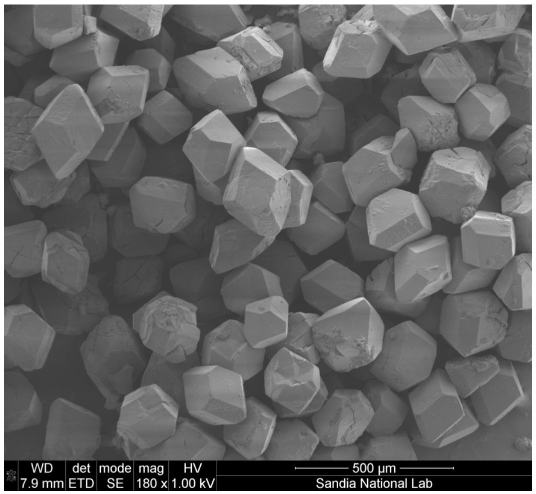
SMOF-1 harmonic average lifetime **6.27 ns**



10% doped Eu-SMOF-1 harmonic average lifetime **600 µs**
(long lifetime: low oscillator strength of 4f-4f transitions of Eu^{3+})

On-going studies SMOF-2: A Novel In-30% Eu- BTB Framework

$In(NO_3){\bullet}H_2O$ + $EuCl_3{\bullet}6H_2O$ + 1,3,5-Tris(4-carboxyphenyl)benzene (BTB) + oxalic acid + (DEF)/EtOH
115°C, 4 days



a= b= 43.671 Å

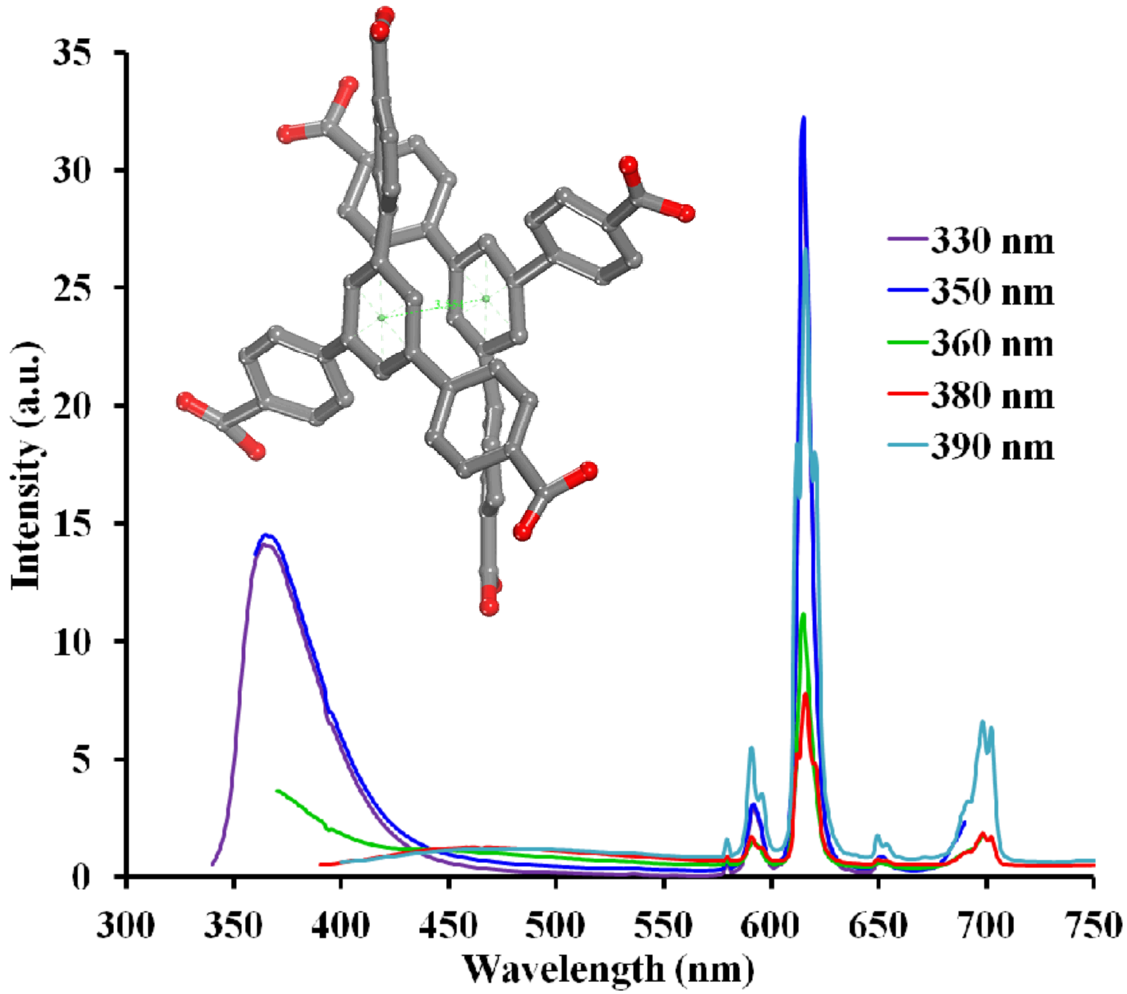
c = 41.867 Å

α= β= 90

γ= 120

Volume= 69149.5 $Å^3$

Absolute QY increases to ~ 11.2 %



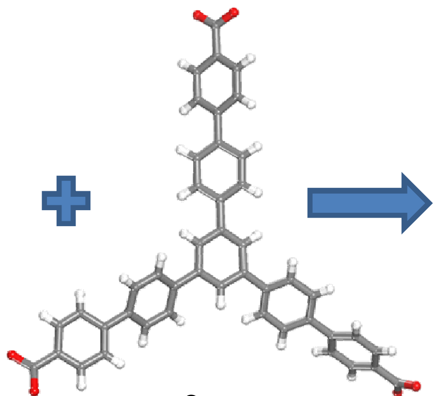
Sava, D.F. et.al, 2012, in preparation

Advanced Materials: SMOF-3
Novel MOF red light emitters

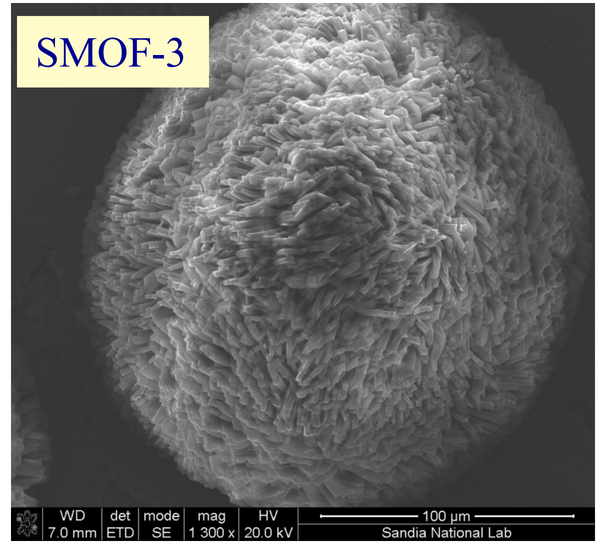
Another platform for tuning light emissions

Sava, D.F. et.al, 2012, in prep

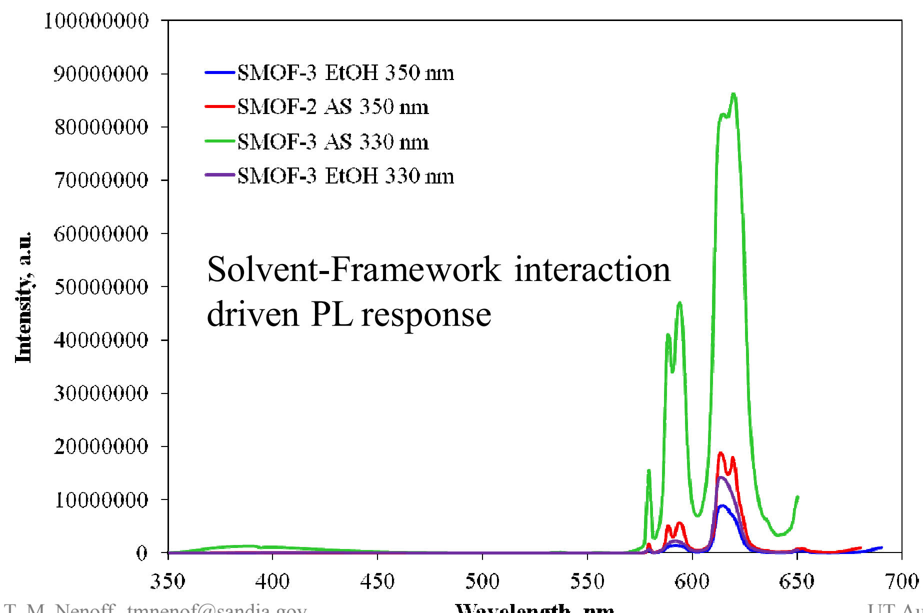
$EuCl_3 \cdot 6H_2O$ +



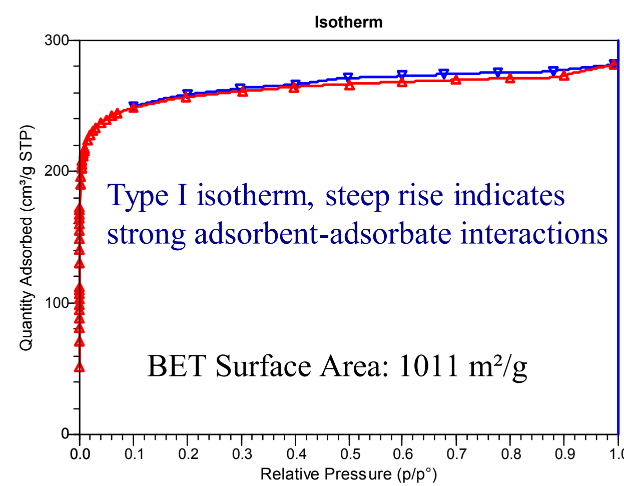
~ 2nm



Absolute QY increases to = 21 %



Solvent-Framework interaction driven PL response

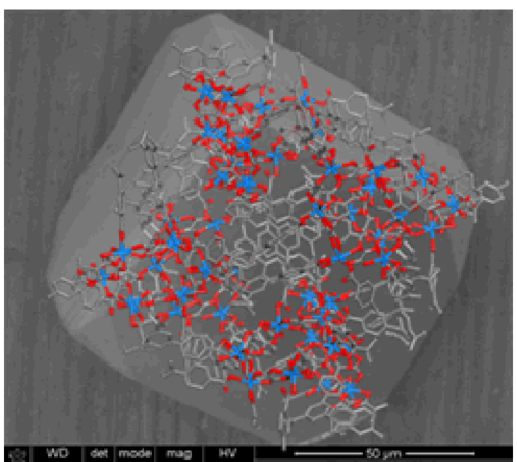


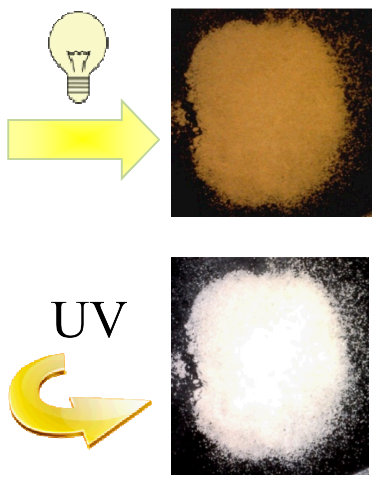
Type I isotherm, steep rise indicates strong adsorbent-adsorbate interactions

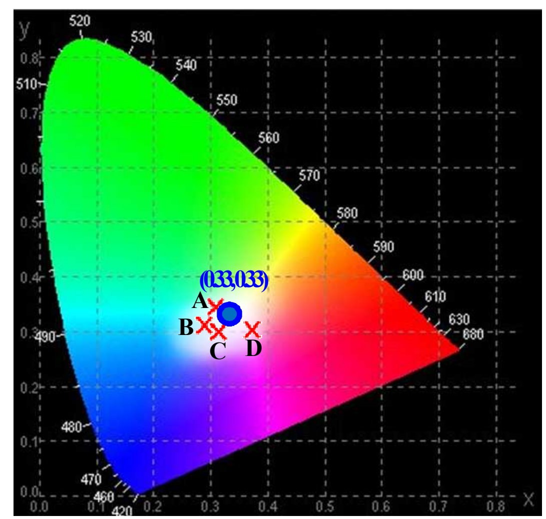
BET Surface Area: 1011 m^2/g

Summary

- Introduced a prototype novel MOF material featuring intrinsic broadband direct white light emission
- Tunable platform which allows for the significant enhancement of the associated color properties upon Eu^{3+} co-doping, approaching values required for SSL applications
- On-going studies into novel MOFs indicate enhanced absolute quantum yields for new framework structures (QY: SMOF-2 ~ 11.2 %, SMOF-3 ~ 21%)
- Current studies include thermal quenching stabilities of MOFs for SSL
- Future research is directed towards pre- or post-synthesis framework functionalization for enhanced SSL properties







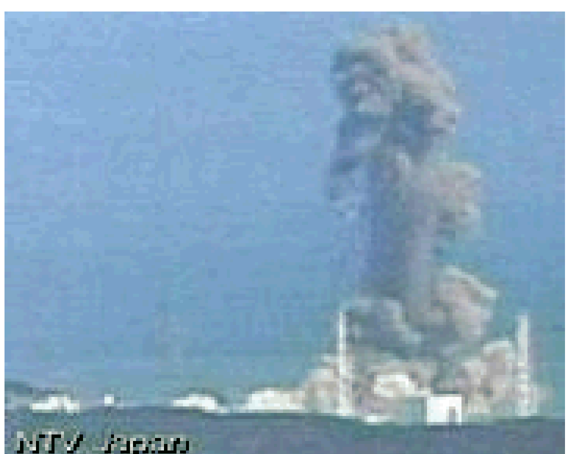
Global Environmental Gas Separations & Storage Needs

I. Nuclear Waste Legacy (EM, NE) for USA and the world

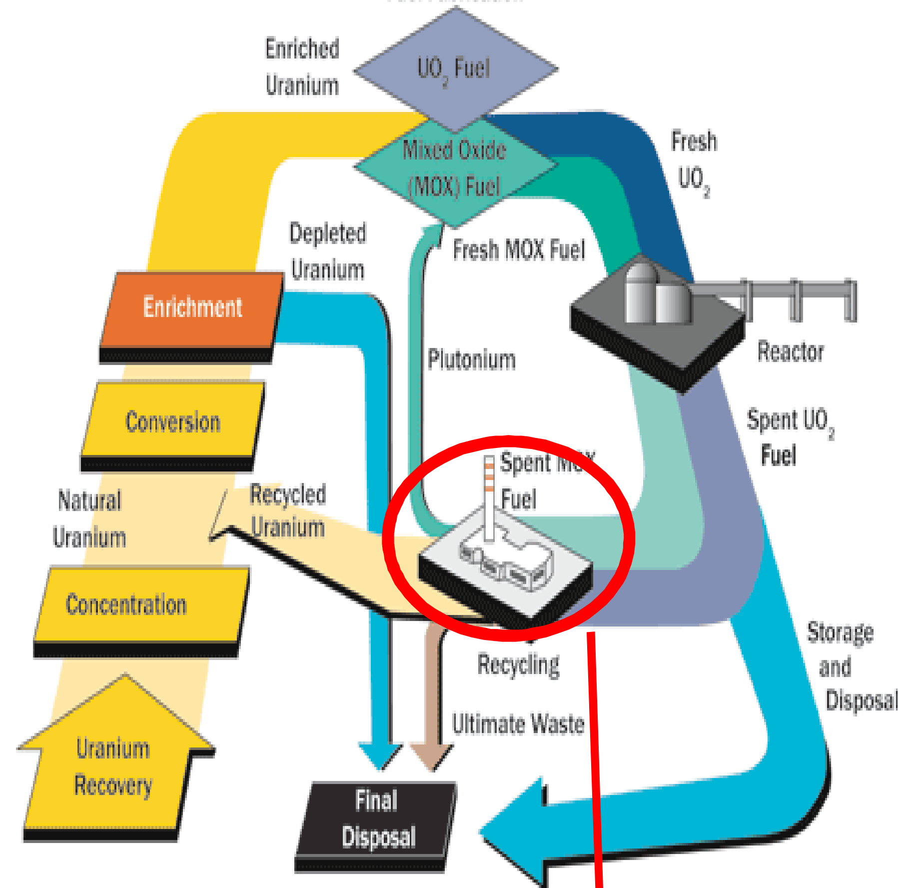
INL and Hanford Legacy Aqueous Waste

Elements, Dec 2006

Fukashima Daiichi Nuclear Power Plant explosion March 11, 2011: I^{129}, I^{131} volatile gas released; Cs^{135}, Cs^{137} aqueous released *(www.IAEA.org)*



II. Nuclear Fuel Reprocessing (NE)

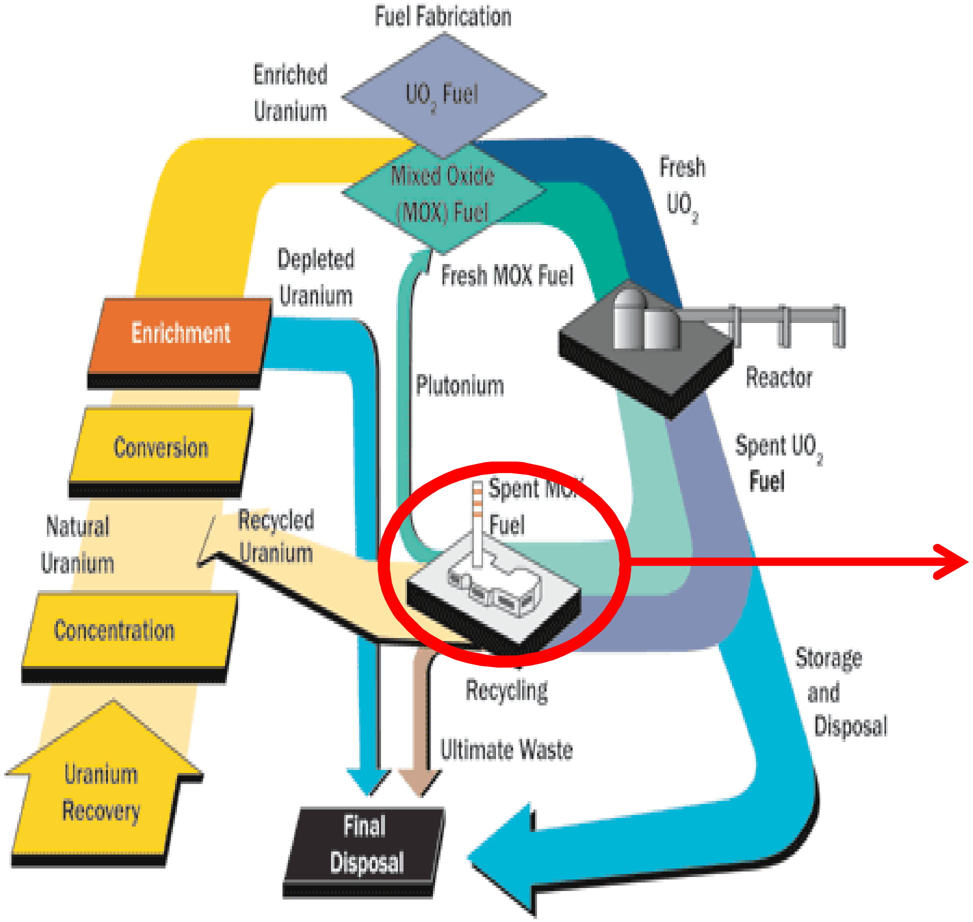


Source: U.S. Nuclear Regulatory Commission

Separations of non-burnable volatile fission products and lesser actinides

II. Capture and Storage of Volatile Fission Gas Products from Reprocessing and/or Nuclear Accidents

Nuclear Fuel Reprocessing (NE)



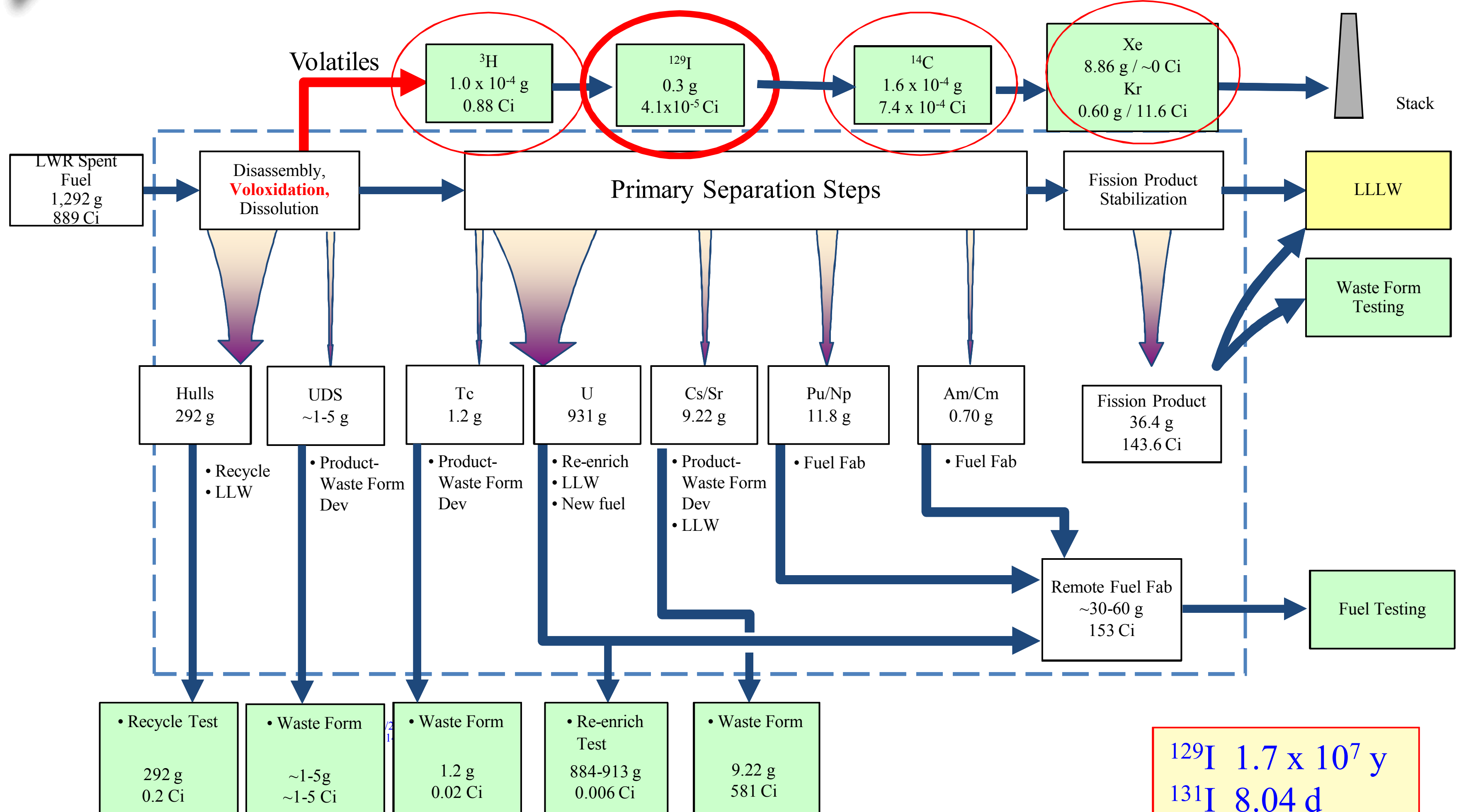
Source: U.S. Nuclear Regulatory Commission

Separations of non-burnable volatile fission products and lesser actinides

Fundamental materials studies into
- Why known materials work well
 and
- Synthesis and Development of new and improved separations materials

Utilizing state-of-the-art
- Predictive modeling
- Synthesis methods
- Characterization methods
- On-line testing in complex streams

Fuel Reprocessing Scheme
Sigma Off-Gas Team (ORNL, SNL, PNNL, INL)



^{129}I 1.7 x 10^{7} y
^{131}I 8.04 d

^{90}Sr 29 y
^{81}Kr 2.1 x 10^{5} y
^{133}Xe days

Mass Basis: 1 kg SNF; 55 GWD/MTIHM; 5 year Cooling

Provided by R. Jubin, ORNL

Use of Metal Organic Frameworks (MOFs) for Radiological Gas Sorption

Separations of non-burnable volatile fission products and lesser actinides

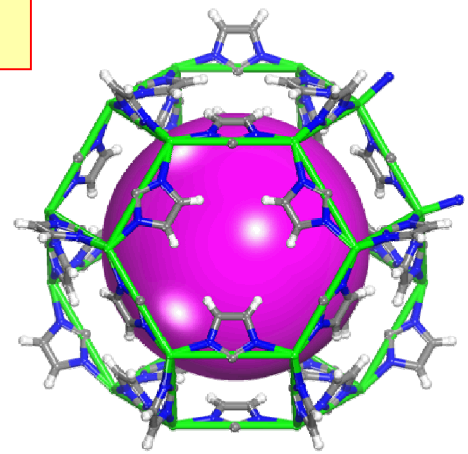
- Why known materials work well and
- Synthesis and Development of new and improved separations materials

Utilizing state-of-the-art
- Predictive modeling
- Synthesis methods
- Characterization methods
- On-line testing in complex streams

Hydrophobic vs Hydrophilic MOFs
For I_2 Sorption in complex stream (eg., H_2O)

Basolite Z1200, ZIF-8
Constricted Pore Opening (≈ 3.4Å)
1100 – 1600 m^2/g
Pore Volume = 0.636 cc/g
stable in Air & H_2O

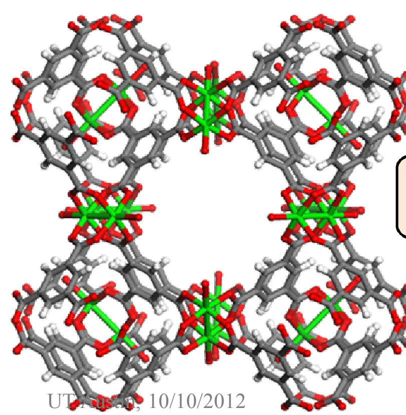
Park, K.S. et.al., *Proc. Natl. Acad. Sci*. **2006**, *103,* 10186.



I_2@ZIF-8 ~ 125 wt.% I_2

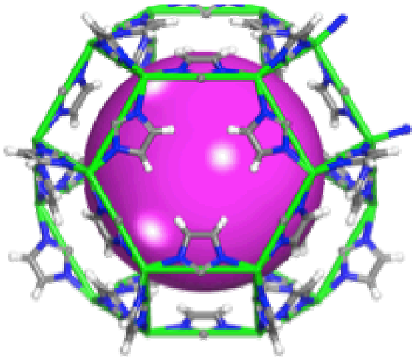
Basolite C300, Cu-BTC, HKUST-1
Open Channels, ≈ 1nm in 3D
1500-2100 m^2/g
Exposed Metal Sites of Framework

Chui, S. S. Y et.al, Science **1999**, 283, 1148.



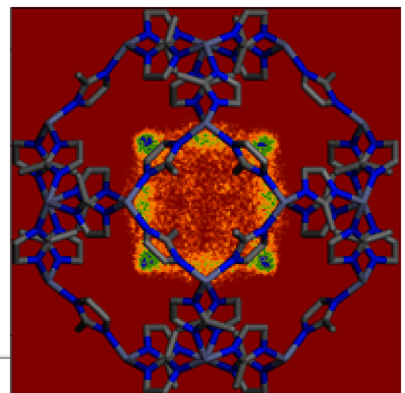
I_2@HKUST-1 ~ 175 wt.% I_2

Integration of Experiment & Modeling to Identify Chemical Reasons for I_2 Sorption

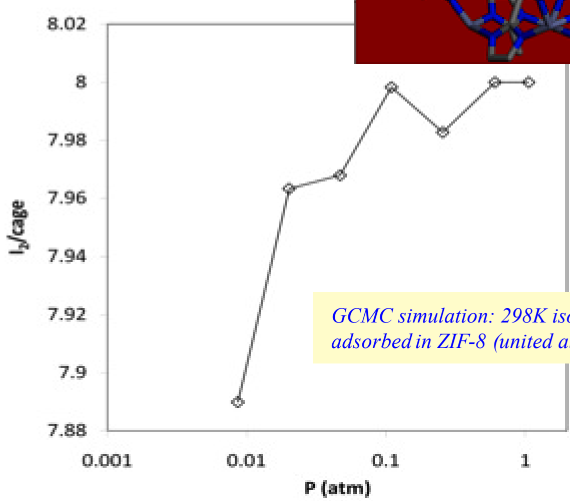


Molecular modeling

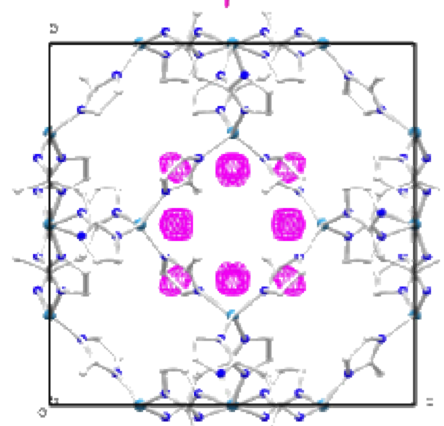
Complementary local and long-range structural probes



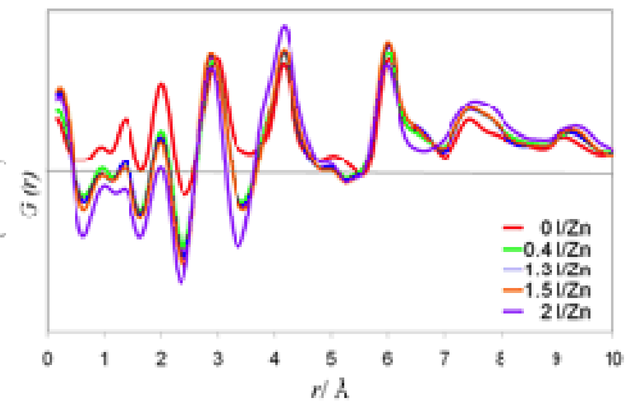
MD Simulation:
Electron density determined



GCMC simulation: 298K isotherm of I_2 adsorbed in ZIF-8 (united atom model)



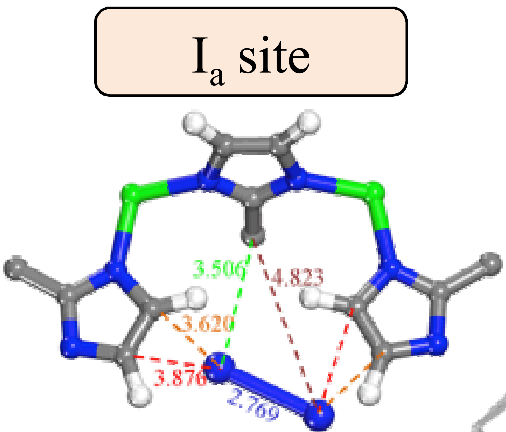
Difference-Fourier analysis map

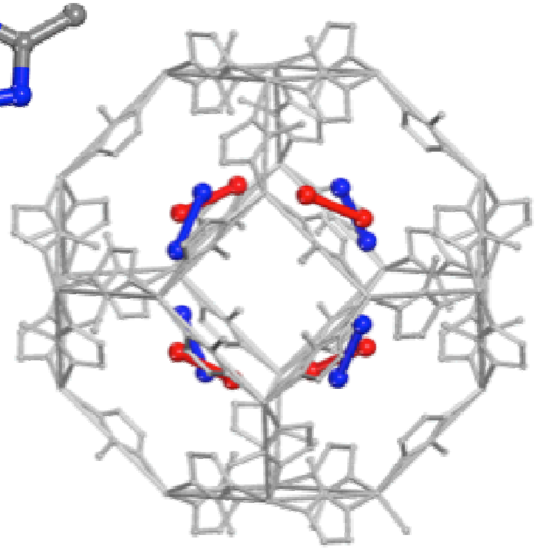


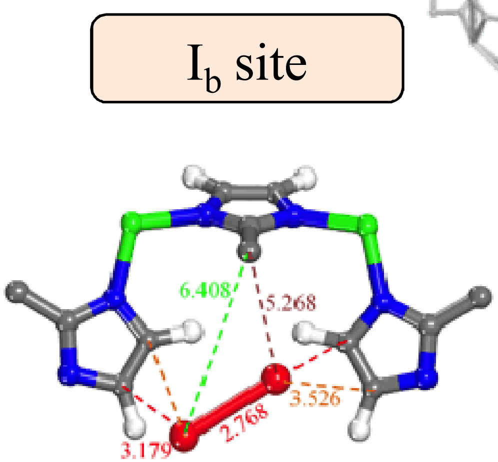
Pair Distribution Function analysis – ANL/APS synchrotron

J. Amer. Chem. Soc., **2011**, *133* (32), 12398.

Volatile Gas Sorption Defined by Pore Opening & Structure of ZIF-8 MOF





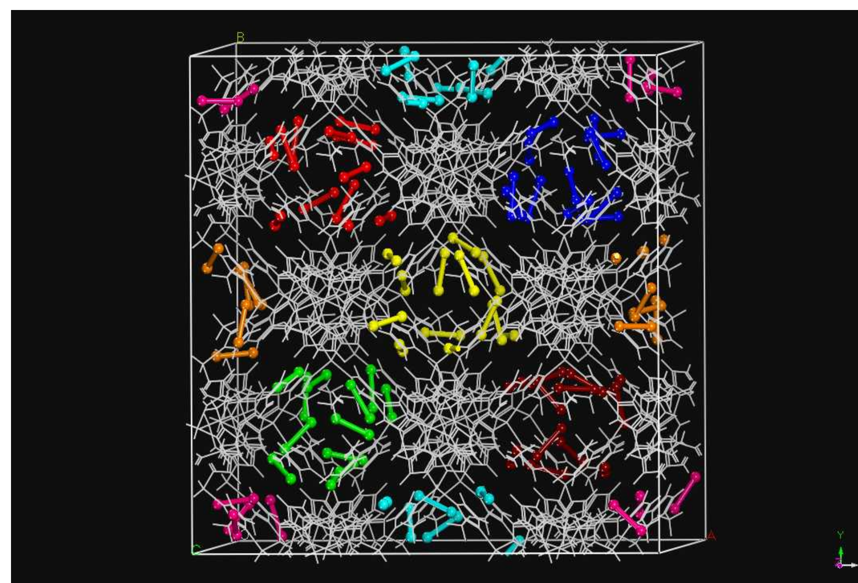


Structure – Property Characterization:
Able to combine initial X-ray diffraction data with GCMC simulations with all possible orientations of I_2 molecules from d-PDF/Synchrotron Data,

The 8 I_2 Binding Sites inside ZIF-8 Pore were determined; max 6/cage experimentally.

Physisorption into 2 sites, with site I_a having stronger preference of siting.

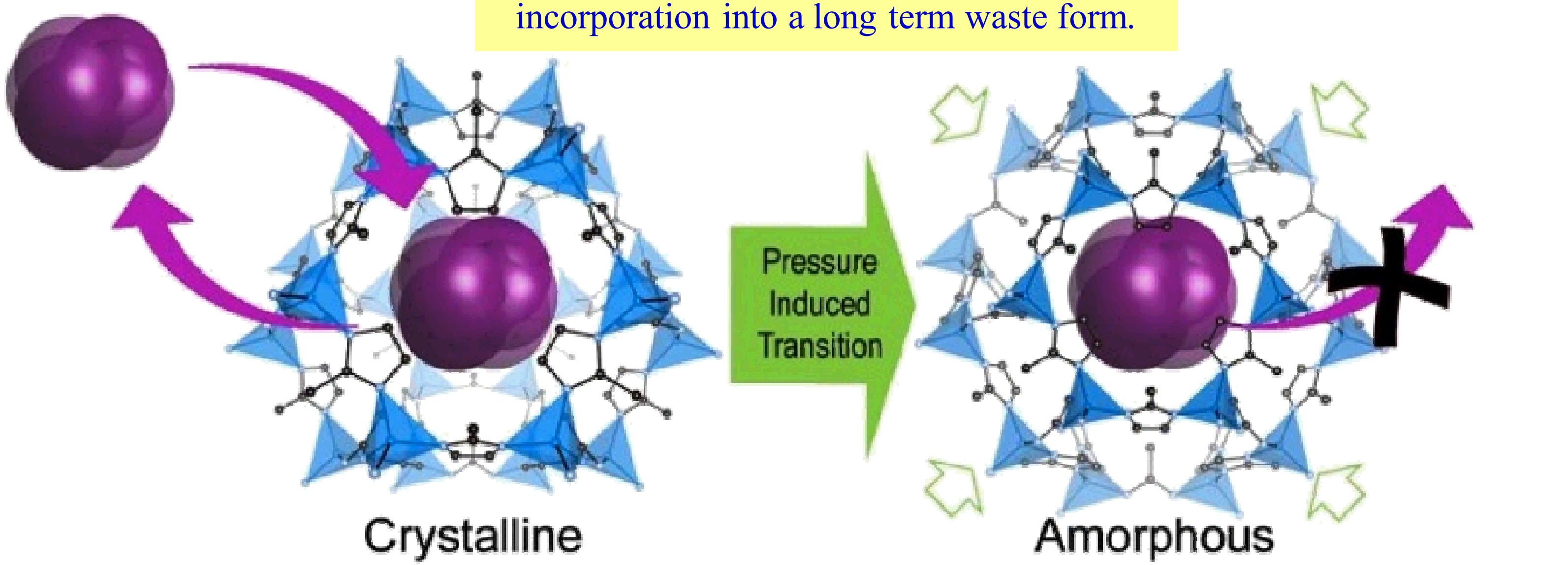
MD Simulations indicate entrapment of I_2 gas in pores

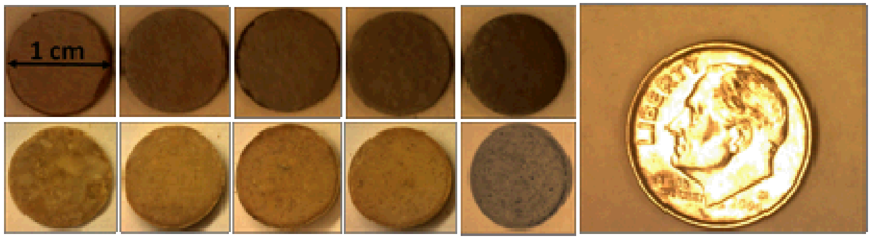


I_2@ZIF-8 Pressure-Induced Amorphization of Trapped Gases: Enhanced Retention

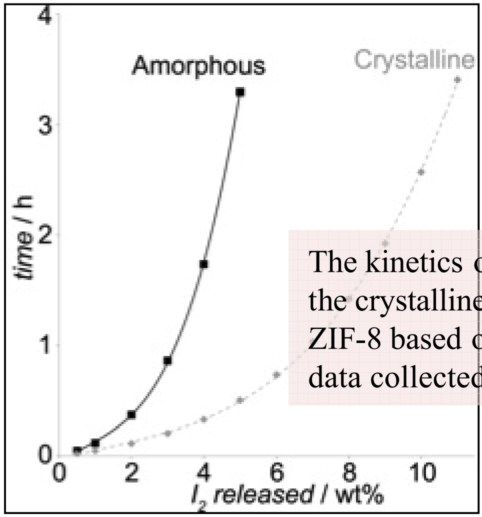
J. Amer. Chem. Soc. **2011**, *133*(46), 18583

Secure consolidated interim storage before incorporation into a long term waste form.



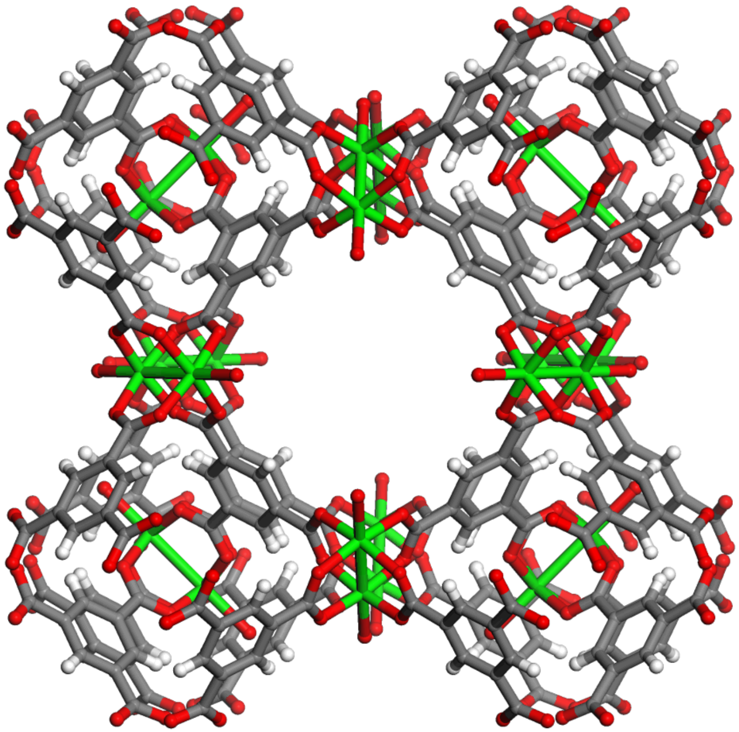


Crack free pellets of iodine loaded ZIF-8 powders were obtained by applying uniaxial mechanical pressure.



The kinetics of I_2 release from the crystalline and amorphized ZIF-8 based on isothermal TGA data collected at 200 C, 4hours

High Sorption Capacity and Reversible Release of I_2 Gas in the Presence of H_2O



Chui, S. S. Y et.al Science **1999**, 283, 1148.

Specific surface area = 1798 m^2 g^{-1}
Pore volume= 0.7 cc/g

In order to assess realistic reprocessing conditions*, the experiments were led under regular atmospheric conditions
350 K and ambient pressure
(I_2 vapor pressure= 0.014 atm).

The I_2 gas uptake was monitored gravimetrically.

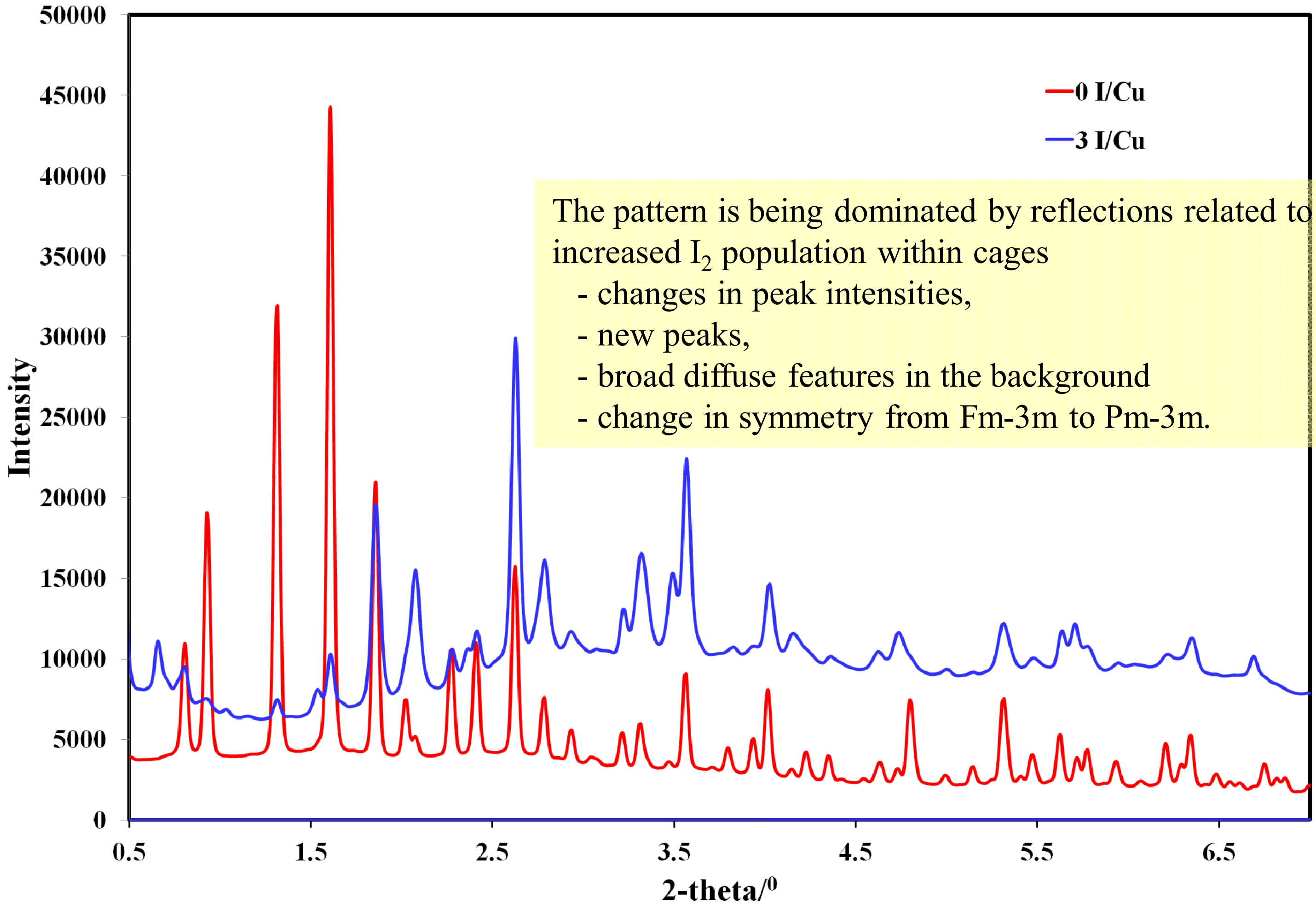
The material exhibits excellent capacity of up ~ 175 wt.% I_2 (3:1 I/Cu ratio) under atmospheric conditions, within close correlation with GCMC simulations, which predict maximum 200 wt.% I_2 (3.5:1 I/Cu ratio), under dry conditions.

Sample crystallinity is maintained up to maximum I_2 loading, as evidenced by high resolution synchrotron X-ray powder diffraction data.

I_2 sorption stable to 100°C

* Haefner, D.; Law, J.; Tranter, T. Idaho National Laboratory, INL-EXT-10-18845, 2010

Dramatic PXRD Data Changes with Iodine Loading, Modeling Required for Refinement



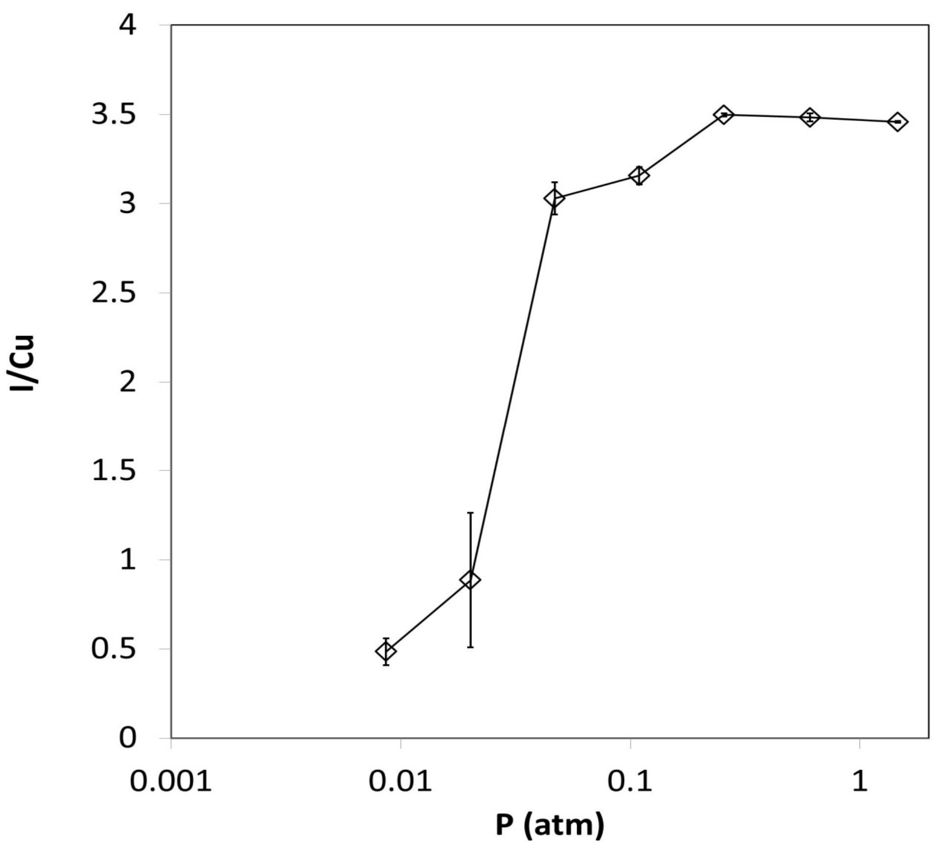
The pattern is being dominated by reflections related to increased I_2 population within cages

- changes in peak intensities,
- new peaks,
- broad diffuse features in the background
- change in symmetry from Fm-3m to Pm-3m.

Refinement before (red) and after (blue) I_2 loading
Maximum I_2 loading (3 I/Cu)

GCMC simulations Using the United-Atom Model of I_2 Adsorption Isotherms in HKUST-1 (Cu-BTC)

Grand Canonical Monte Carlo (GCMC) simulations: Using "fix GCMC" of LAAMPS.
I_2 molecules exchanged between cage and reservoir at 298K.
Range of chemical potentials corresponding to pressure range of 0.0086 atm – 1.5 atm.
HKUST-1 structure was held stationary.
I_2 insertion, deletion and translation attempts.
Total of 2 x 10^8 MC cycles for each start point

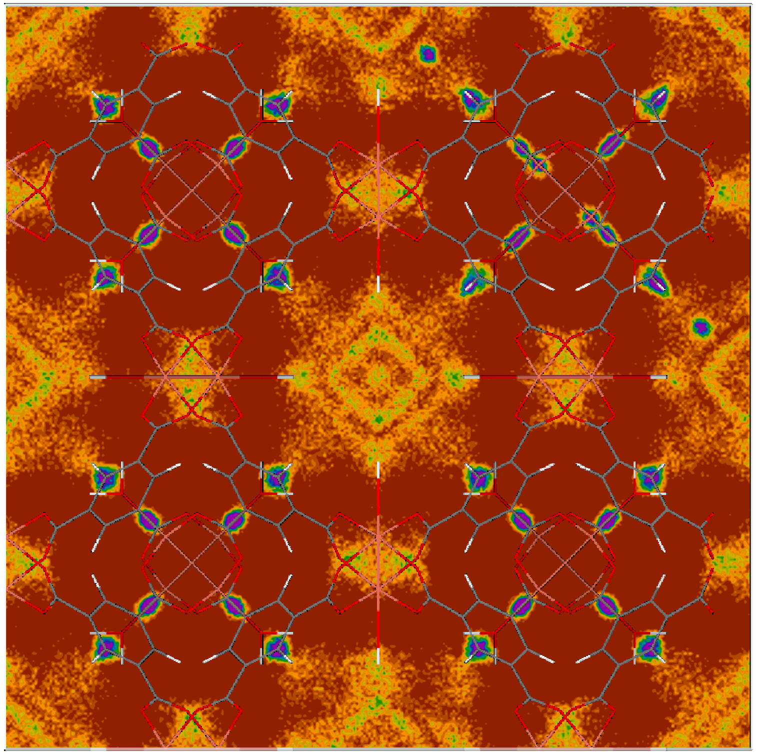


This model predicts the maximum loading of **3.5 I/Cu** (under "dry" conditions),

close correlation with the observed maximum experimental loading of **3.3 I/Cu** (under "wet" conditions).

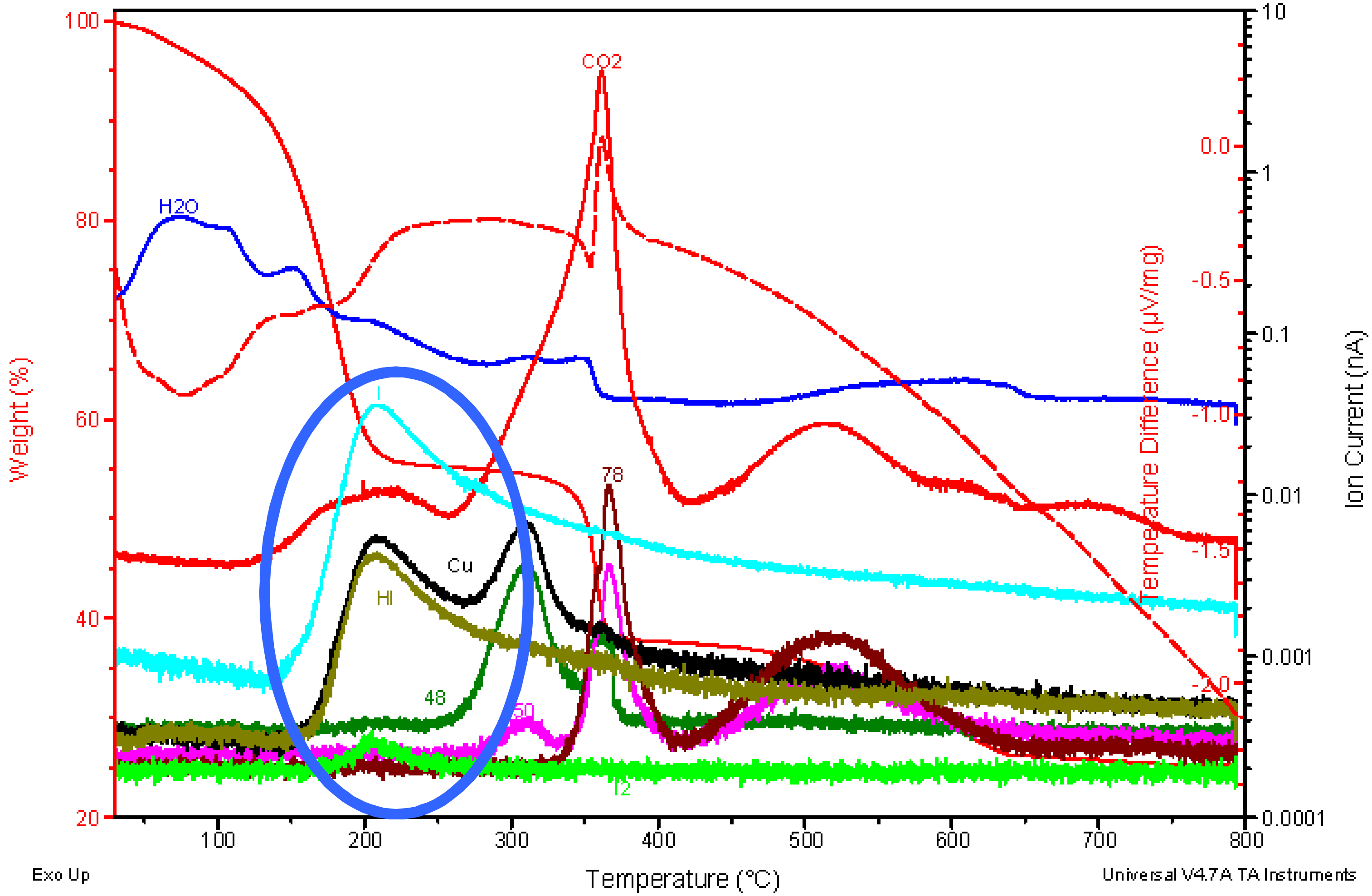
MD Simulations: 2D I_2 Density Contour Plot, Using the Explicit (diatomic) Model

MD Simulations: LAAMPS, 8 unit cell, framework atoms fixed.
Short-range van der Waals interactions, Universal Force Field (UFF) without modification
I_2: explicit and united-atom models in canonical ensemble, 298K, 10 fs timestep, steric approximations



Primary density sites are located in the tetrahedral cavities, as well as near the structural water molecules.

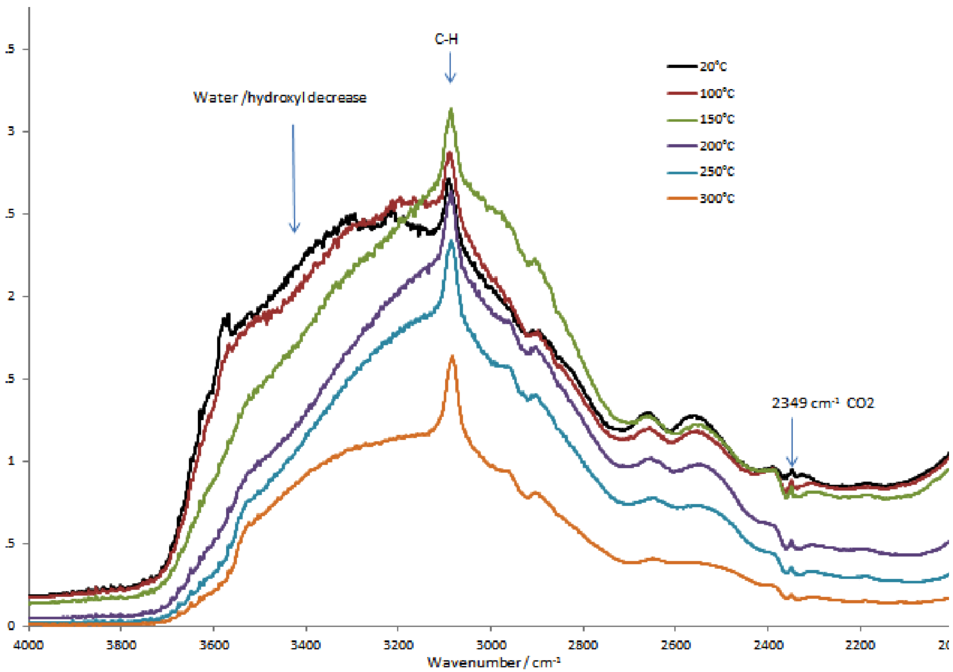
TGA-MS: Conflict with Modeling
Does HKUST-1 + H_2O + I_2 -> HI?

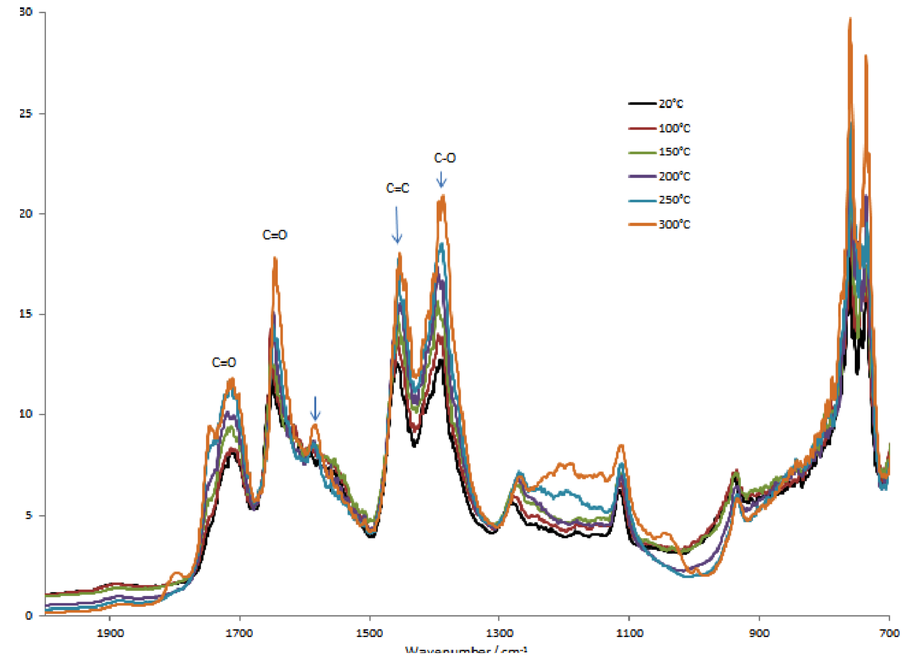


175wt% I_2 loading in HKUST-1

Variable Temperature IR of I_2 loaded HKUST-1

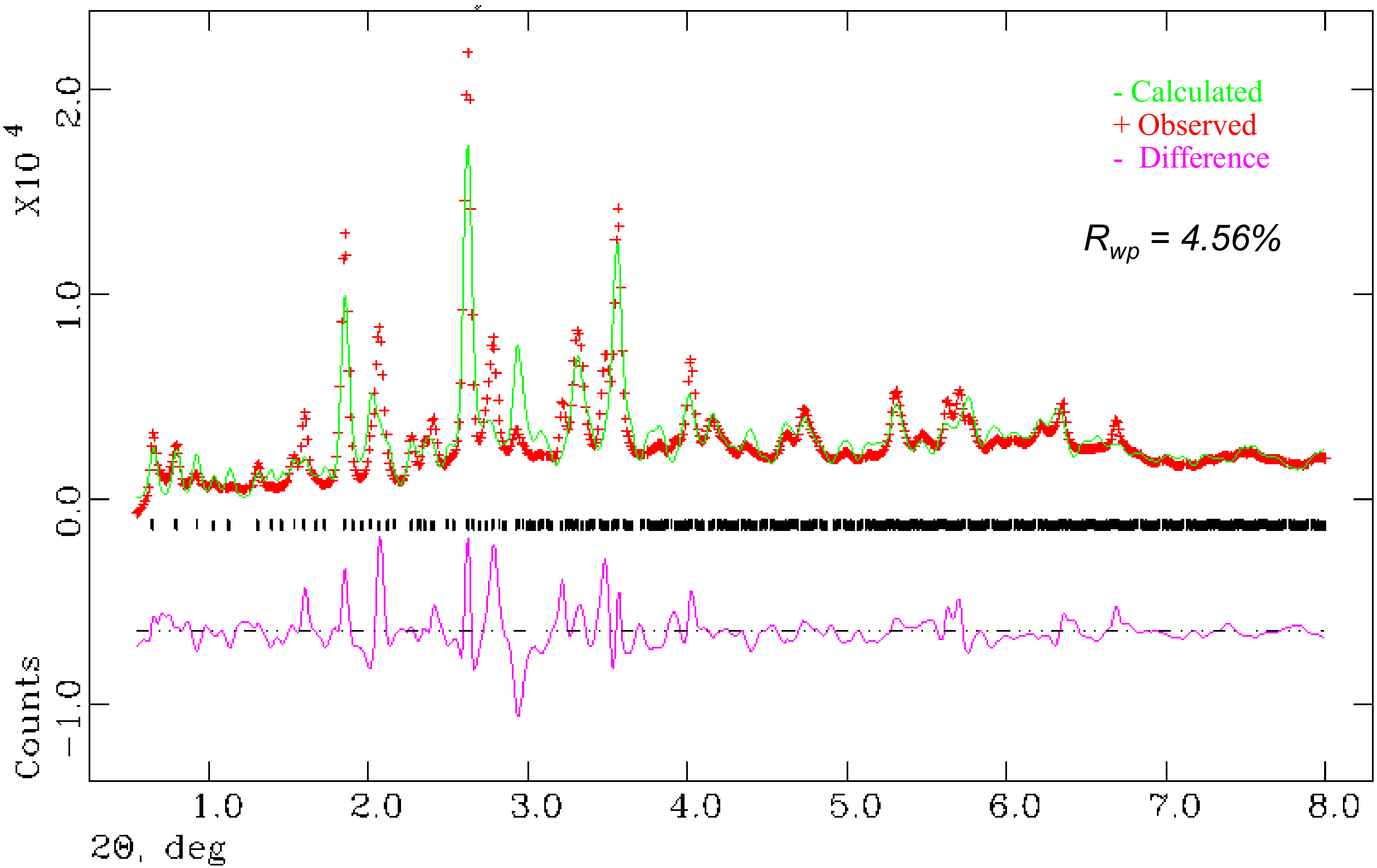
Attempt to emulate TGA-MS measurements using IR
Monitor temperature dependence of the intensities of different IR bands
50°C/min from 20°C to 300°C, IR measured at 1 min intervals





No clear peak at 2308 cm^{-1} for HI in I_2 loaded HKUST-1 (Phys. Rev. 2012, 47(8), 585)
HI probably formed upon release of I_2 at high temperatures
Mechanism studies on-going:
correlations of temperature vs. IR intensity changes for events at metal-centers

Rietveld Refinement I_2@HKUST-1 of Synchrotron Data (APS/ANL) using Model

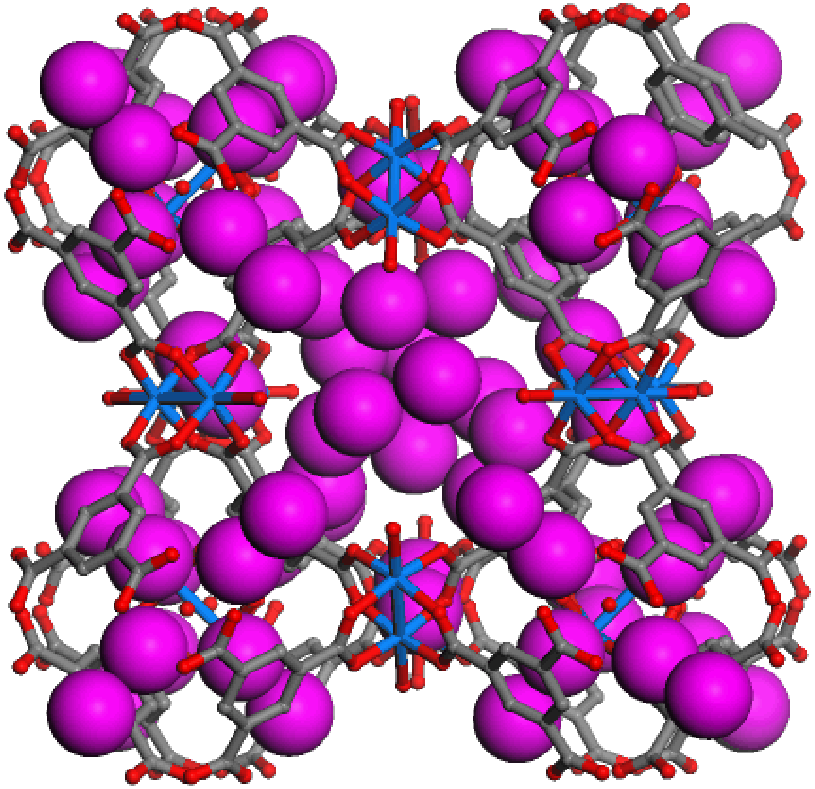


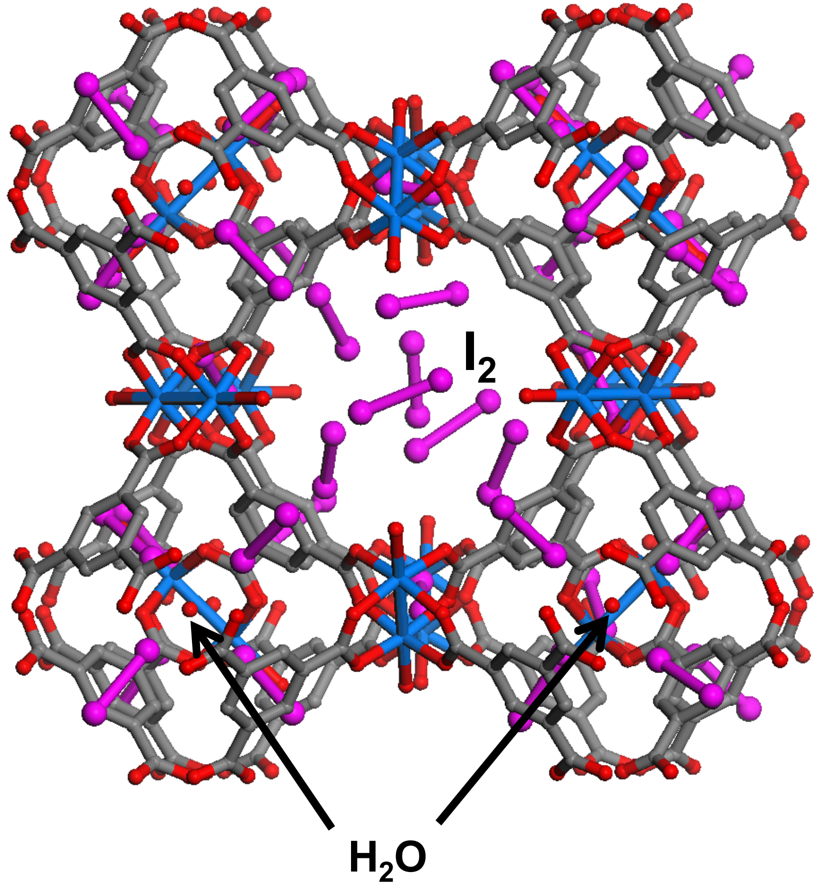
Including variable I_2 and $O(H_2)$ site occupancy with crystallographic disorder

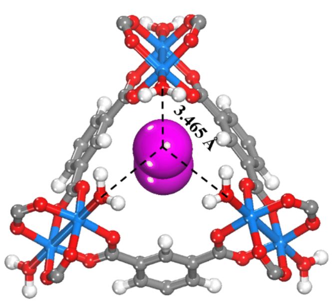
Crystal Structure of I_2@HKUST-1, co-adsorption of I_2 and H_2O

I_2/HKUST-1 **3.3 I/Cu**

Nenoff, Sava, et.al., **2012**, submitted.



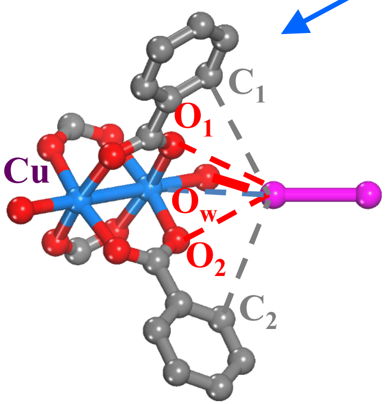




No Evidence of HI; possible combination of physi- and chemi-sorption of I_2
Iodine gas behaves *hydrophilic* in the HKUST-1 framework

A Combination of Physisorption & Chemisorption Of I_2 (Not HI) into HKUST-1

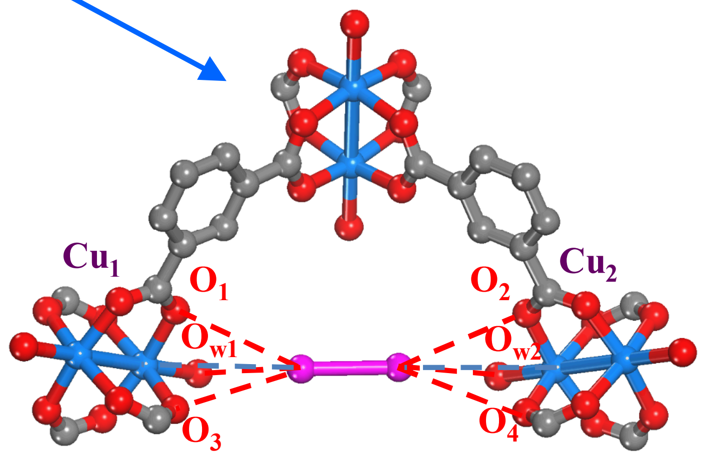
Strong interactions between I_2 and the dimetal cluster



I---C_1: 4.022 Å
I---C_2: 3.865 Å

I---O_w: 3.886 Å
I---O_1 : 3.306 Å
I---O_2 : 3.233 Å

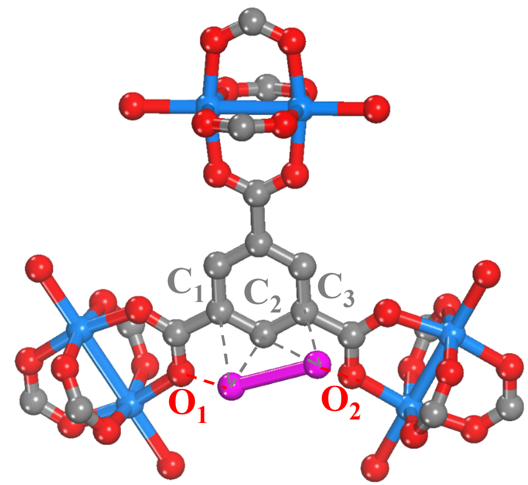
I---Cu: 4.093 Å



I---O_{w1}: 4.033 Å
I---O_{w2}: 3.853 Å
I---O_1 : 3.838 Å
I---O_2 : 3.833 Å
I---O_3 : 3.643 Å
I---O_4 : 3.720 Å

I---Cu_1: 4.515 Å
I---Cu_2: 4.480 Å

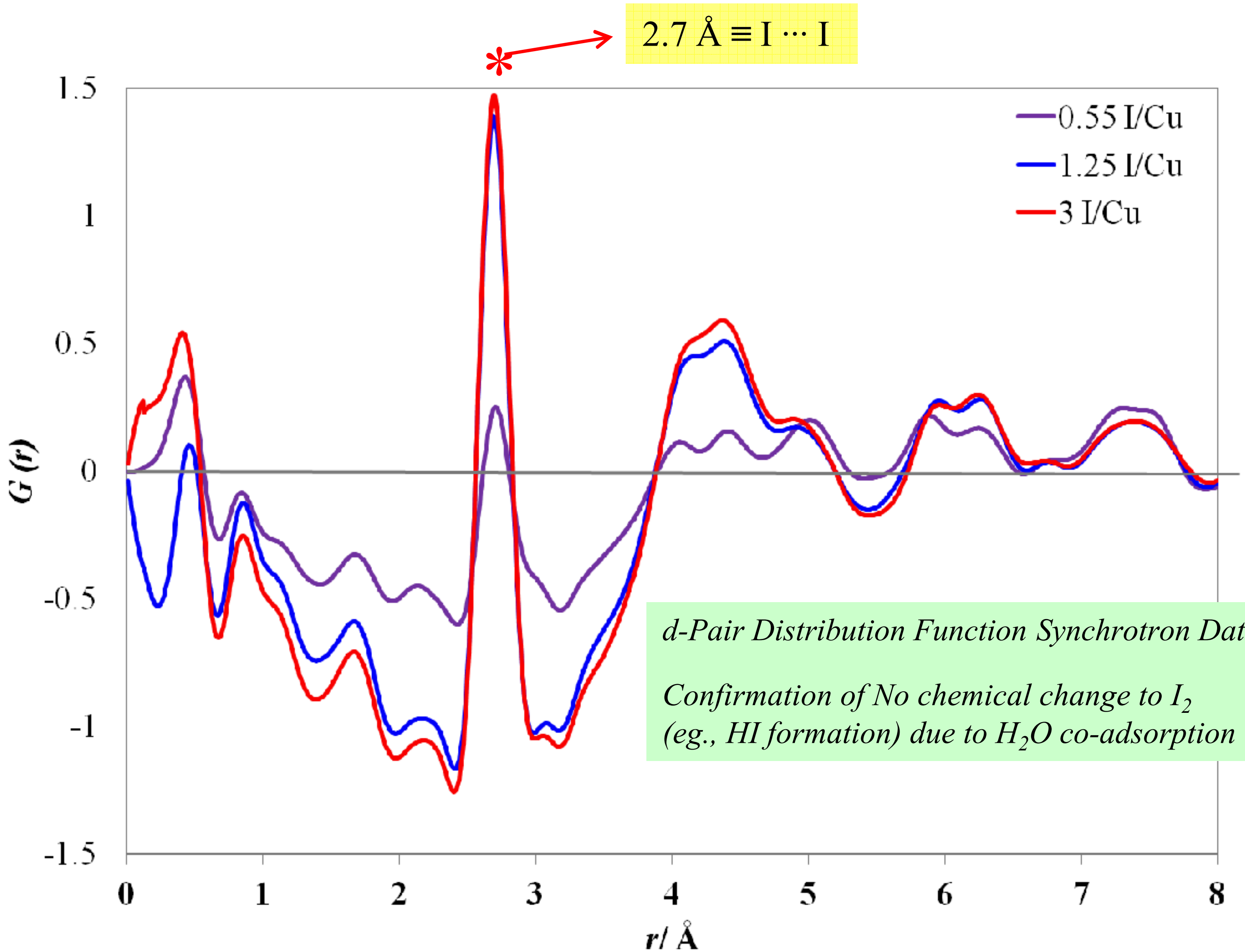
Close contacts between I_2 and the organic linker



I---C_1: 3.629 Å
I---C_2: 3.470 Å
I---C_3: 3.920 Å

I---O_w: 3.886 Å
I---O_1 : 4.283 Å
I---O_2 : 4.474 Å

Confirmation of I_2 Molecule Integrity Maintained, Independent of Weight Loading



d-Pair Distribution Function Synchrotron Data

Confirmation of No chemical change to I_2 (eg., HI formation) due to H_2O co-adsorption

Conclusions, On-going Studies

The high capacity and stability of MOFs allows for applications in

- nuclear fuel reprocessing
- nuclear accident remediation
- pre-concentrators for sensors

Structure – Property Relationship studies combining modeling, synthesis, testing allows for a feedback loop in the design, tuning and optimization of materials

- Incorporation of MD simulations and GCMC modeling with Structure Analysis to determine Iodine loading levels, and Iodine electron density to compliment X-ray Analysis

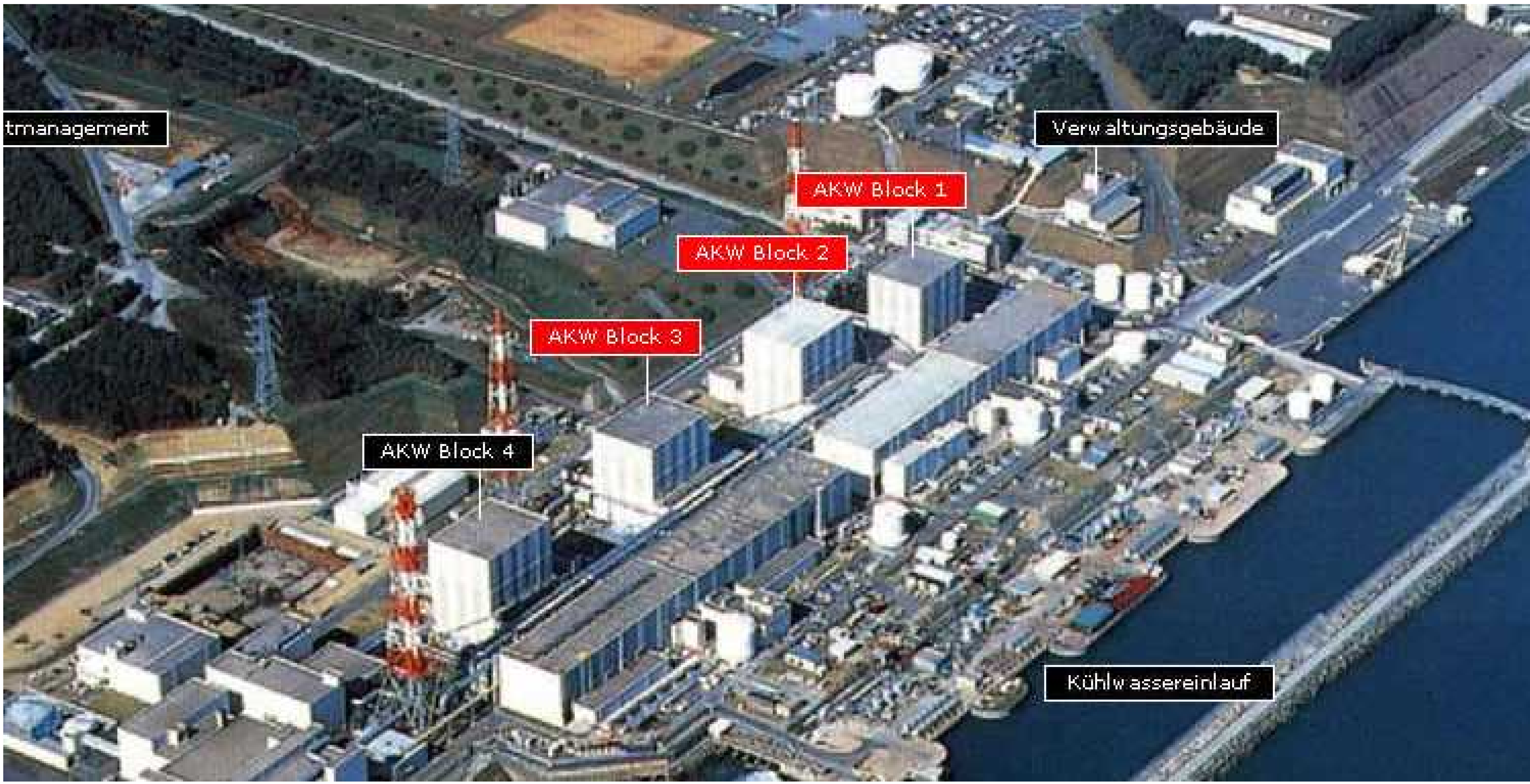
- The HKUST-1 framework structure (open pore, open metal center) allows for both chem- and physisorption, resulting in:
  high weight % loading, and controlled reversible desorption of I_2

- Preferential I_2 sorption over H_2O; no HI gases developed from interaction with Cu in MOF

- Optimization of MOFs from lessons learned with ZIF-8 and HKUST-1:
  - preference for metal and ligand interactions or pore restriction
  - programmatic needs dictate retention but need to release of I_2 in controlled manner

III. Fukushima Daiichi Nuclear Incident

- Fukushima Daiichi (Plant I)
  - Unit I - GE Mark I BWR (439 MW), Operating since 1971
  - Unit II-IV - GE Mark I BWR (760 MW), Operating since 1974



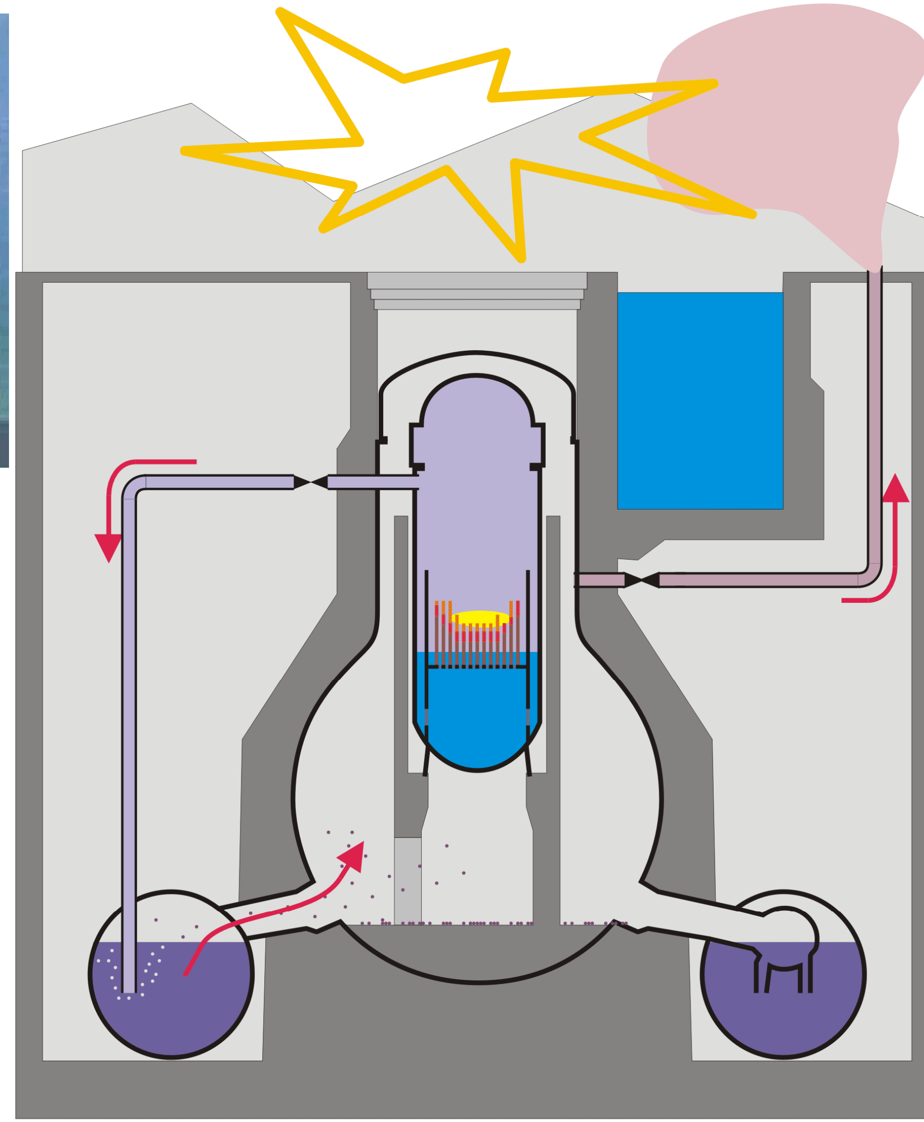
The Fukushima Daiichi Incident – Dr. Matthias Braun – AREVA

The Fukushima Daiichi Incident

Accident progression

- Day 2,

H_2 explosion at Unit 1

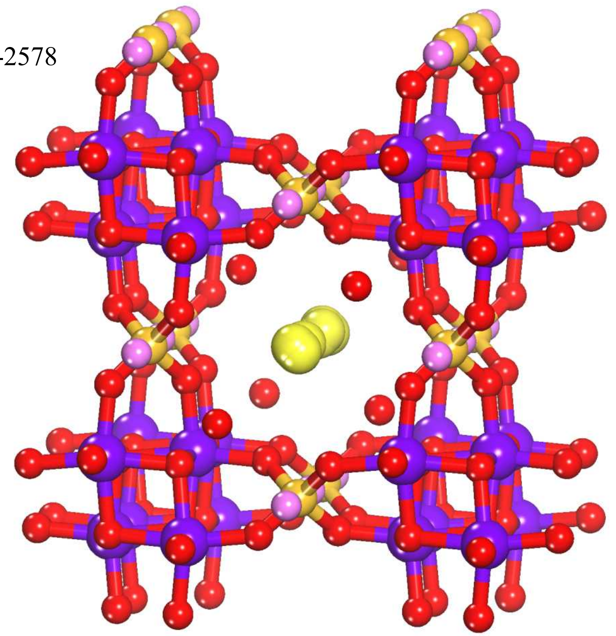


- Cooling via seawater began on Day 2
  Continued for 14 days on reactors
- Pooled seawater in buildings, pipes, basements…

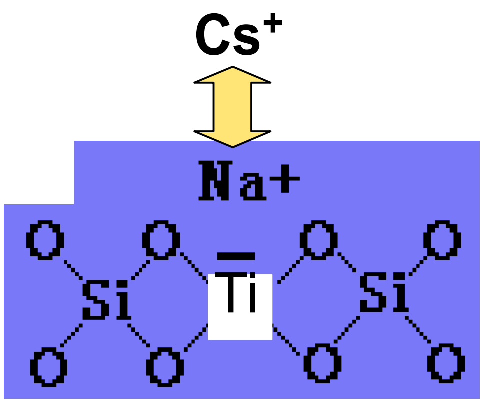
Removal of rad-Cs^+ from Pooled Seawater

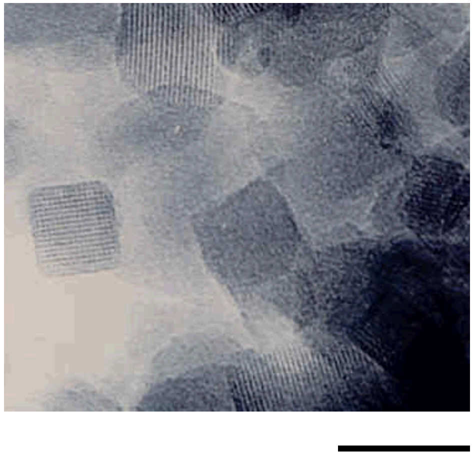
Crystalline Silicotitanates (CSTs)
Hydrothermal synthesis of a crystalline molecular sieve (Sandia, Texas A&M Univ.)
Commercialized for defense legacy waste, applied to reactor accident cleanup
With exceptional Cs^+ selectivity, and mechanical, thermal and radiological stability

Nenoff, SAND96-2578



^{137}Cs 30.7 y
^{135}Cs 2.3 x 10^6 y



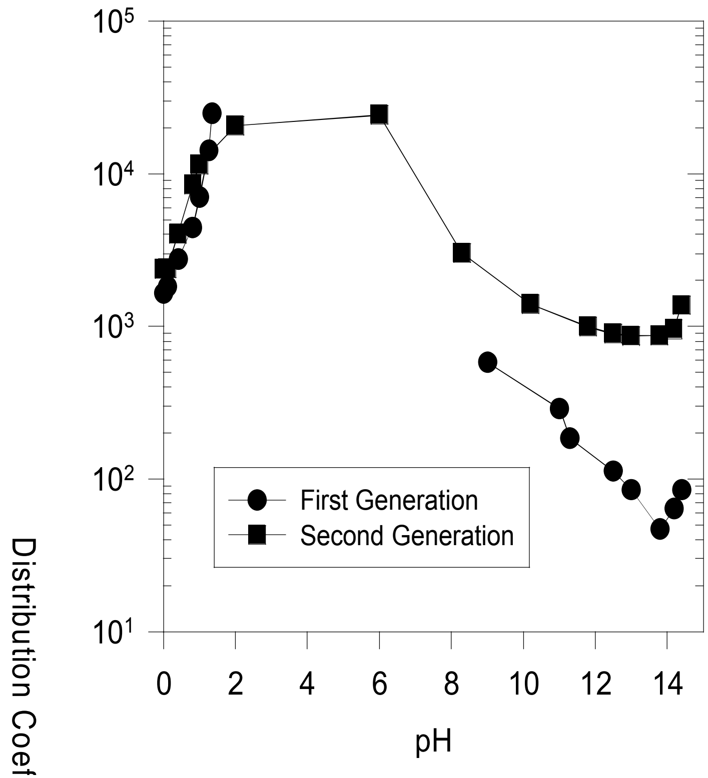


CST properties:
- Removes 1 part Cs per 100,000 parts Na
- Stable over entire pH range
- Stable in extreme environments
- 1996 R&D 100 Award Winner

Research to Development to Commercial Product

Research (1993): Sandia LDRD project – gram reactors
Development: DOE/EM – 1-5 gallon reactors
Commercialization: CRADA with UOP Corp., *IONSIV*™ *IE-910 & IE-911* (Dec 1995)
1800 lb lots produced

Sandia: Distribution Coefficient of Cs on CST



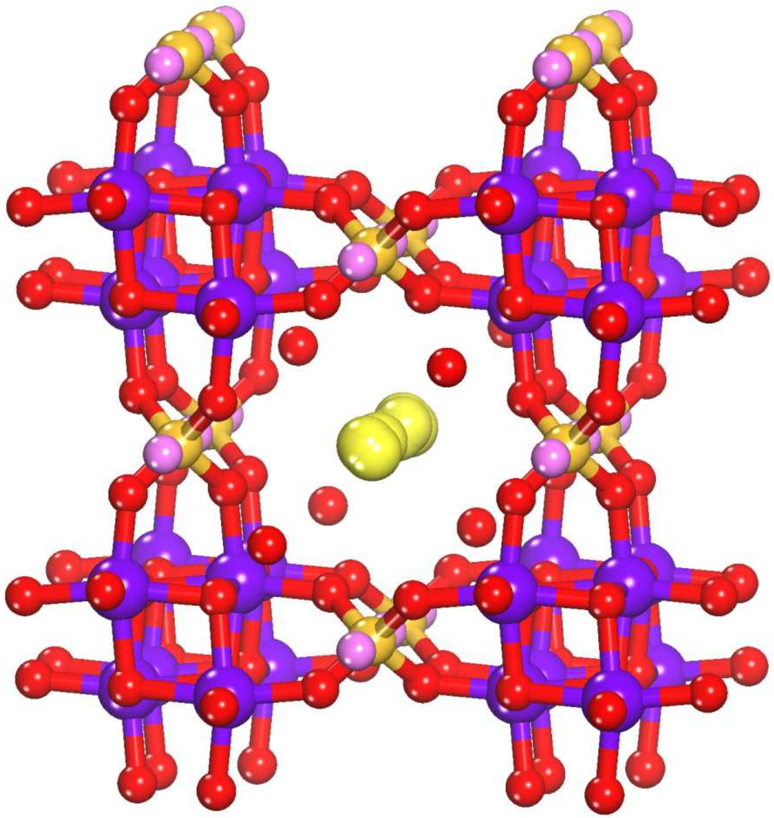
UOP IONSIV™ IE-911

SNL/TAMU US Patents:
6,479,427 (2000) and 6,110,378 (2002)

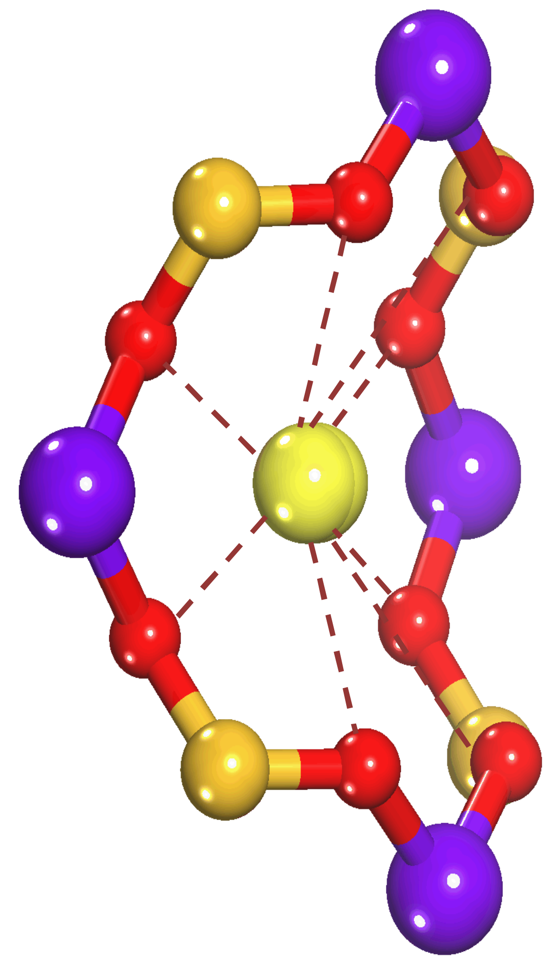
CST High Selectivity for Cs^+ over other Monovalent and Divalent cations

Selectivity is due to three materials' design elements:

- Geometric "pocket" for a perfect fit for Cs^+
- Preferential adsorption by Si/Ti/M/O for Cs^+
- Favorable cation hydration energetics



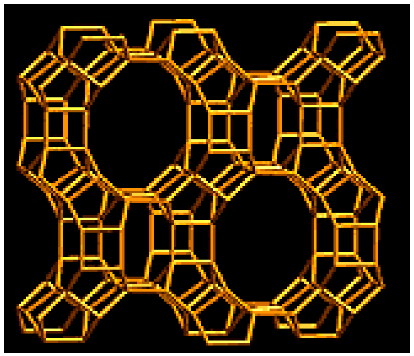
Cs^+ captured in CST cage



Cs^+ trapped in pore "pocket"

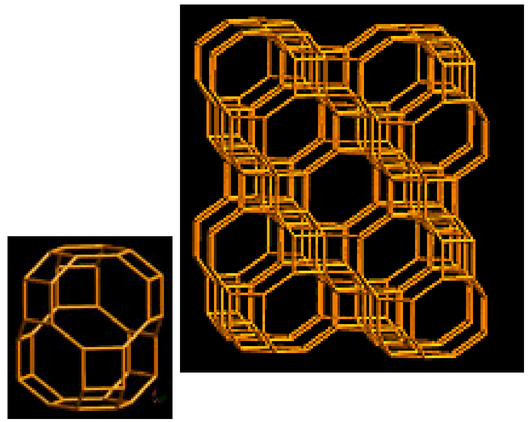
CSTs versus Available/Leading Sorption Zeolites For Cs^+ removal from Seawater at Fukushima Daiichi

Mordenite 12 MR
7.6Å pore opening



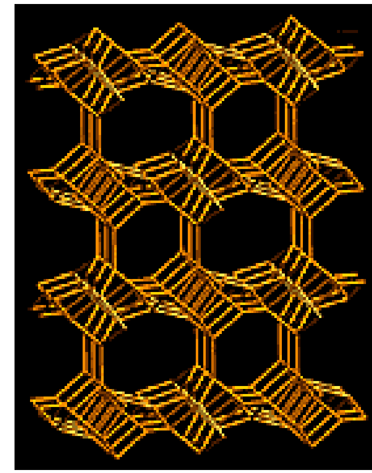
$|Na^+_8\,(H_2O)_{24}|\;[Al_8Si_{40}\,O_{96}]$

Chabazite 8MR
3.72Å pore opening



$|Ca^{2+}_6\,(H_2O)_{40}|\;[Al_{12}Si_{24}\,O_{72}]$

Clinoptilolite 10MR
7.5 x 3.1Å pore opening



$|Na^+_6\,(H_2O)_{24}|\;[Si_{30}Al_6O_{72}]$

Testing Results:

- Cs^+ removal from simulated seawater*, both "normal" and highly concentrated (9*x*) NaCl solutions
- normalized studies: particle size, solution pH (8.2), exposure time

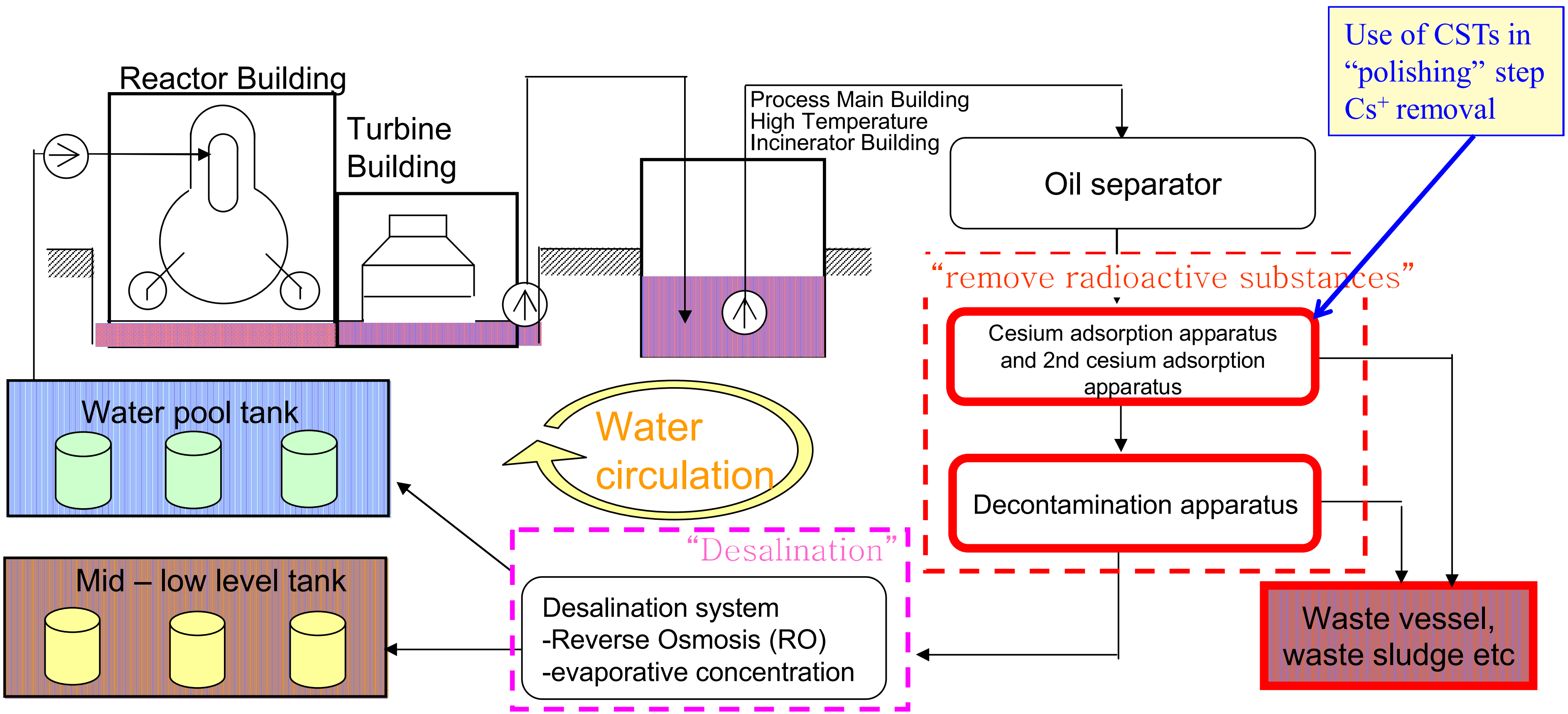
*Horne, R.A. *Marine Chemistry: The Structure of Water and the Chemistry of the Hydrosphere*; John Wiley & Sons, NJ, 1969

Acidified IE-911 (CST) > LZM MOR > Nat. (AK) MOR > IE-95 CHA >>
AW-300 MOR > St. Cloud CLI >> St. Cloud $CLI_{Manufactured}$ >> pelletized Bentonite Clay

Solvent Extraction & Ion Exchange, **2012**, *30*, 33

Water Processing at Fukushima Daiichi, provided by TEPCO

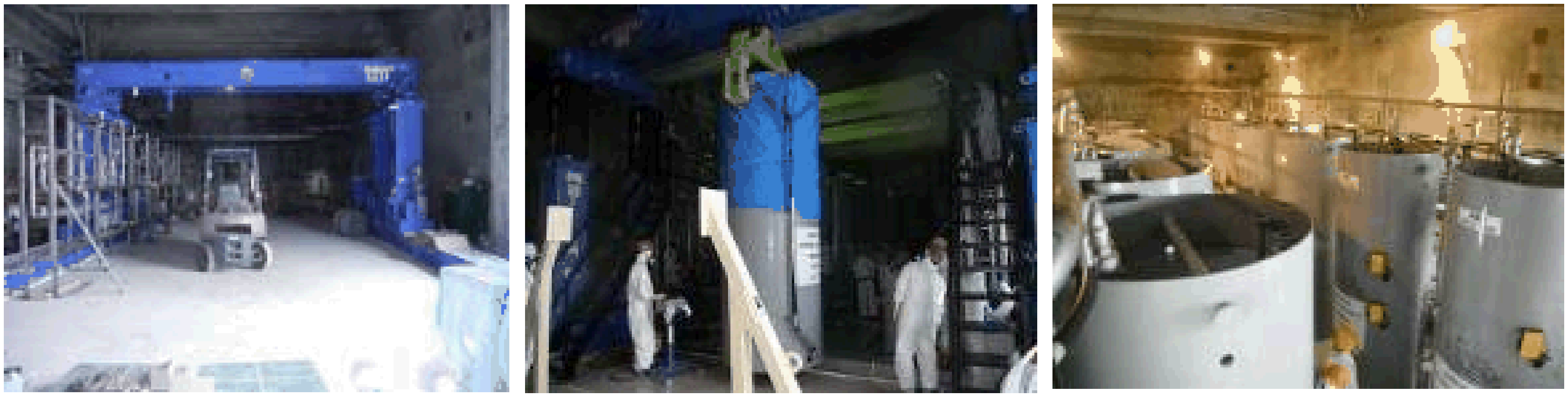
SARRY: Simplified Active Water Retrieve and Recovery System (SARRY)



SARRY developed by Toshiba, Shaw Global Services, AVANTech, IHI Corp.

SARRY PROCESS implemented at Fukushima Daiichi, provided by TEPCO

Augmentation of accumulated water processing facility (SARRY)

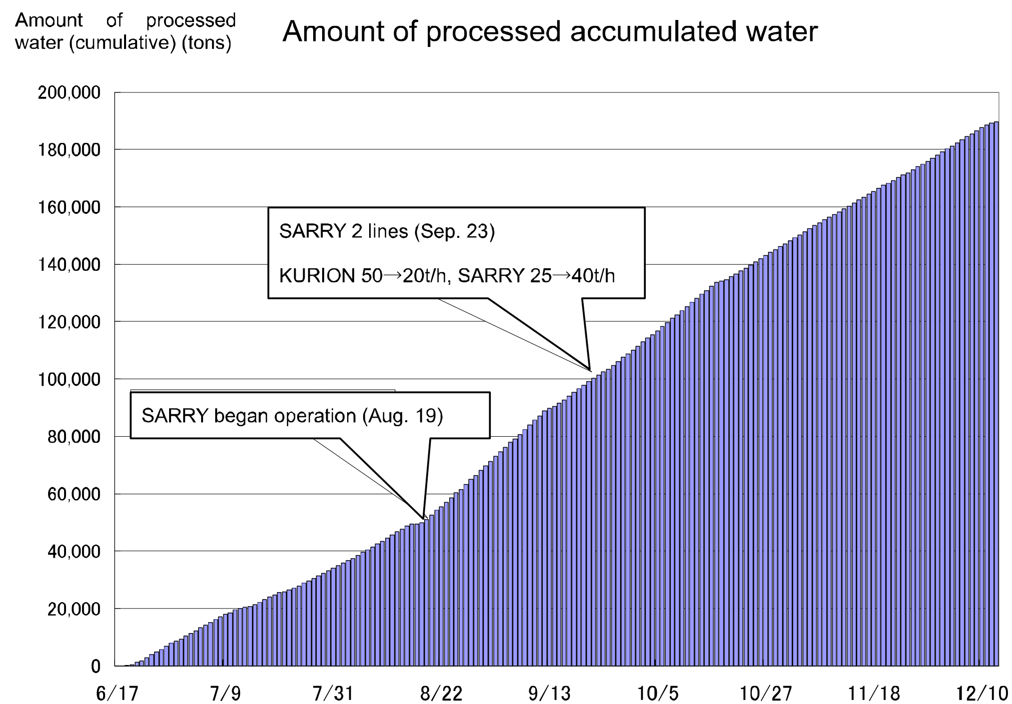


SARRY was installed August 2011, Decontamination Factors of Cs SARRY process is 5 x 10^5

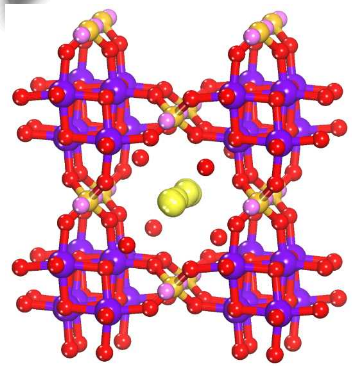
As of December 23, 2011, 6 million of 10 million gallons of Cs contaminated seawater had been cleaned with the SARRY Process.

Decon work continues.

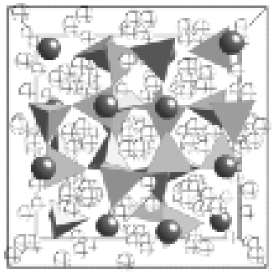
Amount of processed accumulated water



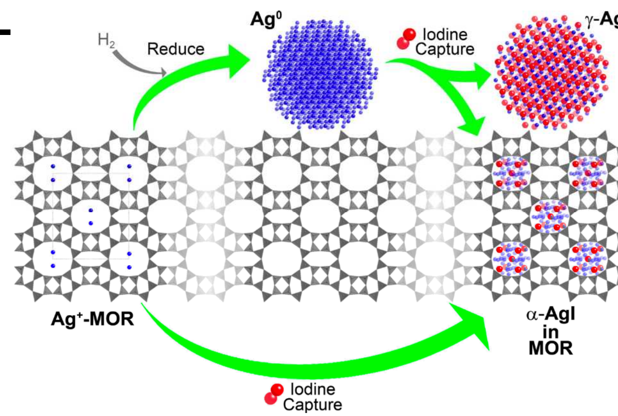
Novel Separations and Waste Forms Technologies from SNL



CST, Cs^+ removal from water to Pollucite Waste Form



R&D100 1996
JACerS, **2009**, *92*(9), 2144
JACerS, **2011**, *94*(9), 3053
Solvent Extr. & Ion Exch, **2012,** *30*, 33

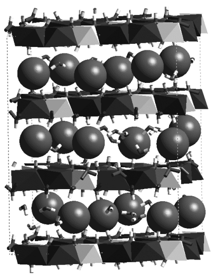


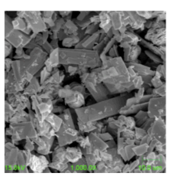
Ag-MOR
I_2(g) capture & mechanisms

JACS, **2010**, *132*(26), 8897
J Phys Chem Letters, **2011**, 2, 2742

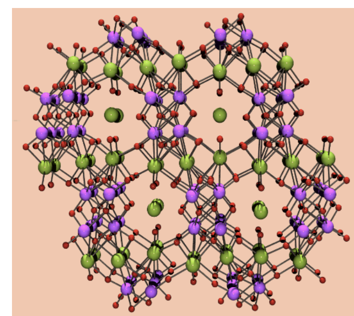
Fundamental Research to Applied to Commercial Products
Design the Separation Material To Develop the Waste Form

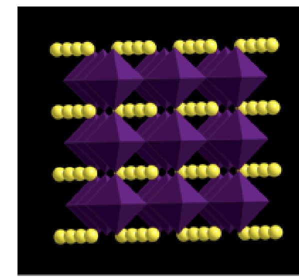
Applied Geochem, **2011**, *26*, 57



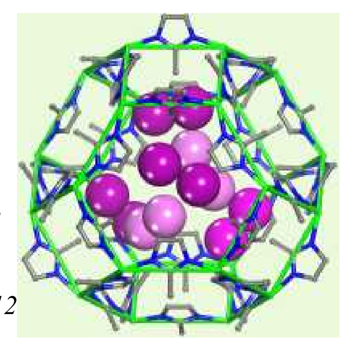


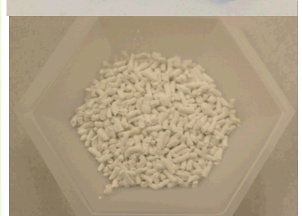
In-situ Iodine removal from water



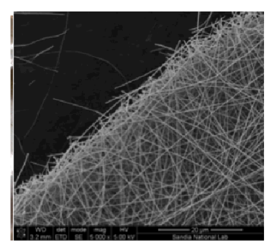


Sr^{2+} getter, 1-step to Perovksite waste form
JACS, **2002**,*124(3),* 1704

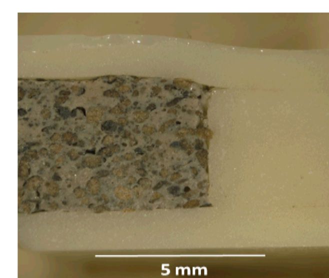




I_2/MOF, Isolation to Waste Form
JACS, **2011**,*133(32),*12398
Ind.Eng.Chem.Res, **2012**, *51*(2),614
US Patent Application, 2012



Nanoporous Nanofibers Volatile Gas Removal
US Patent Application, 2011



Universal Core-Shell Glass Waste Form Iodine & Getter
JACerS, **2011**, *94*(8), 2412

Conclusions, On-going Studies

Structure – Property Relationship

studies combining modeling, synthesis, testing

allows for a *feedback loop* in the design, tuning and optimization of materials

- The high capacity and stability of zeolites and MOFs allows for applications in
  - light weight "platforms" for tuned light emissions
  - nuclear fuel reprocessing
  - nuclear accident remediation
  - gas pre-concentrators for sensors

- Incorporation of MD simulations and GCMC modeling with Structure Analysis to study
  - competitive gas sorption from industrially relevant complex streams
  - mechanisms of sorption and transport

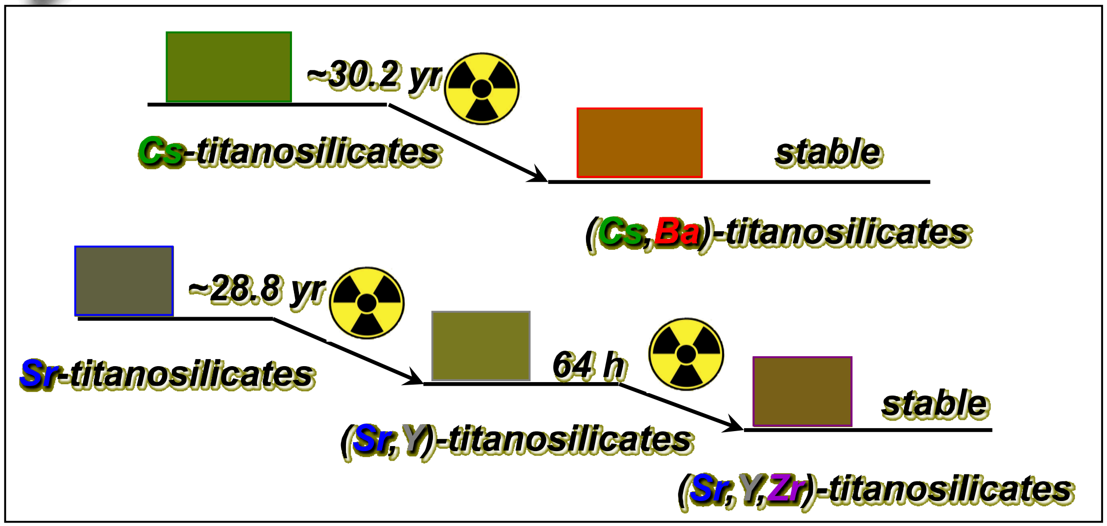
- Zeolite/ Molecular Sieve development for tuned aqueous ion & gaseous molecular selectivity:

  a combination of size selectivity, preferential surface adsorption (to pore), and tuning the geometric "pocket" for retention

- Research at a national lab enables your work to be used at the national level.

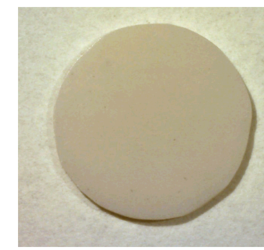
Additional Slides

CSTs Waste Form: Pollucite Ceramic Oxide



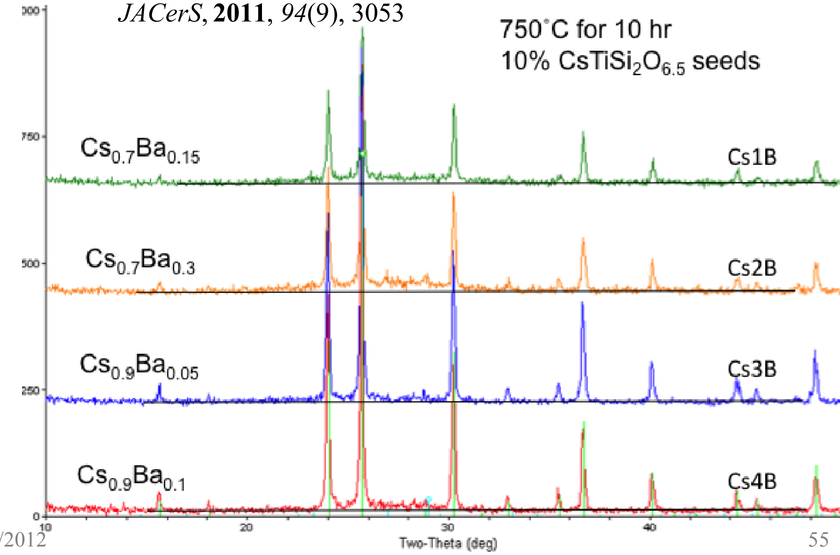
On-going basic research: into an in-situ Waste Form with framework flexibility to compensate for oxidation state changes with decay

$Cs_{0.9}Ba_{0.05}TiSi_2O_{6.5}$



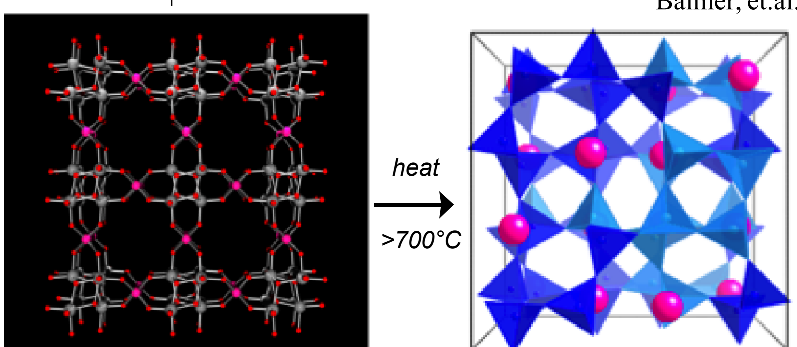
Proof of Ba incorporation

JACerS, **2009**, *92*(9), 2144
JACerS, **2009**, *92*(9), 2053
JACerS, **2011**, *94*(9), 3053



Traditionally: Incorporation into Borosilicate Glass Log
~ 5wt% loading limit, 1200°C heating temp

Balmer, et.al., 1997



CST: $CsSi_2Ti_4O_{13}$•$4H_2O$ Pollucite: $CsTiSi_2O_{6.5}$

Waste Forms: New Low Temperature Glass for Rad-occluded Zeolites and MOFs

Homogenous Glass GCM: for
AgI or AgI-MOR off-gas capture and storage

50 wt% AgI/50 wt% Glass
500°C for 3 hr

50 wt% AgI/50 wt% Glass,
500°C for 3 hr

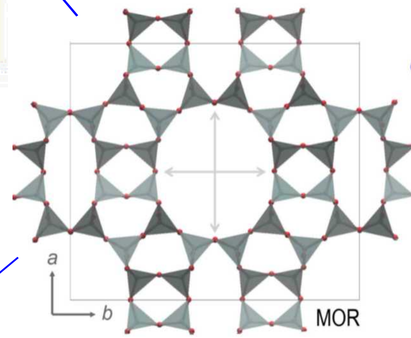
Core-Shell GCM Glass Waste Forms

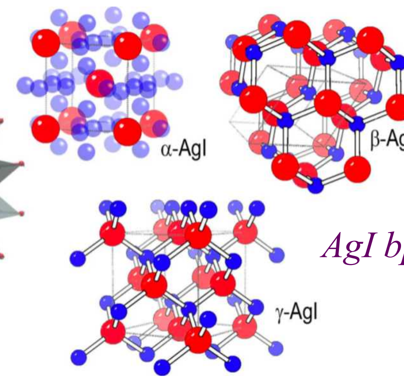
Glass shell, AgI/glass core,
75/25

Glass shell,
AgI-MOR/Ag/Glass core 80/20/5

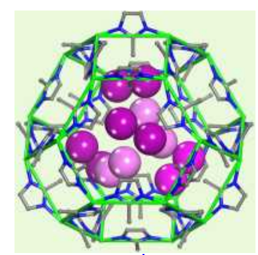
JACerS, **2011**, *94*(8), 2412

Glass Composition (2922), no HIP-ping needed:
Sintering 550°C, Mole % oxides:
32 BiO_3, 19 ZnO, 44 SiO_2, 5Al_2O_3



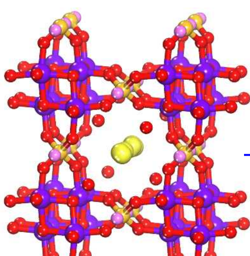


AgI bp 556°C



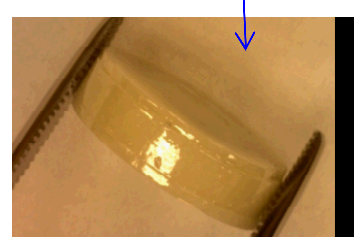
I_2/MOF, Isolation to Waste Form

JACS, **2011**, *133(32)*, 12398
Ind. Eng. Chem. Res (Invited Article) **2012**, *51*(2), *614*
US Patent Application, 2012

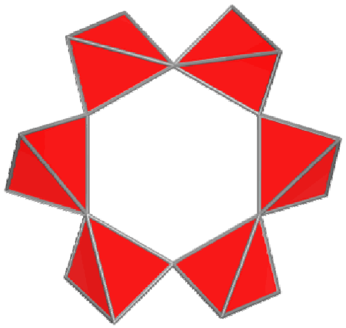


Cs-CST Low Temp Glass Waste Form, No Cs Loss in Sintering

Provisional Patent, 2012



Alternative Topological Evaluation:
(3,6) Pyrite Net



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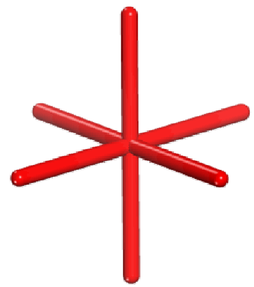
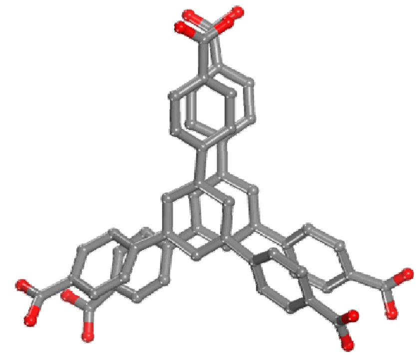


The 6-member ring corner sharing tetrahedra viewed as a 6-connected node.



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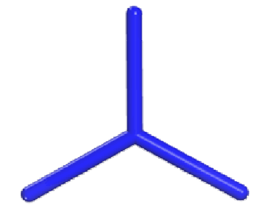
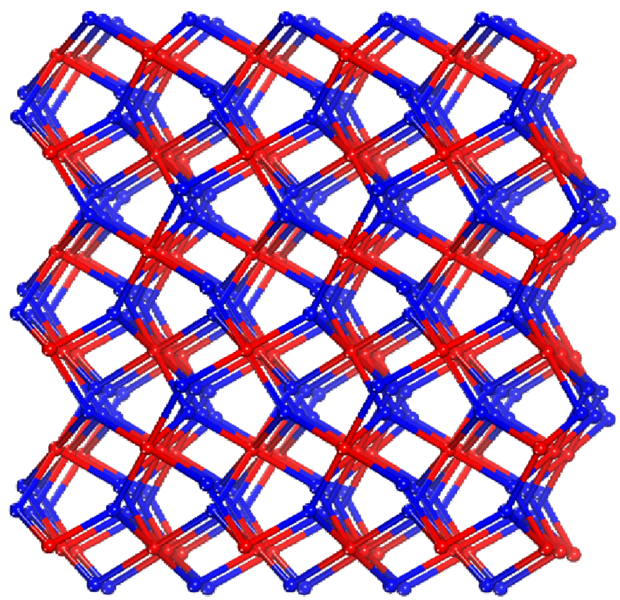


Two corrugated BTB linkers within a distinct net are simplified to a fused 3-connected point of extension.

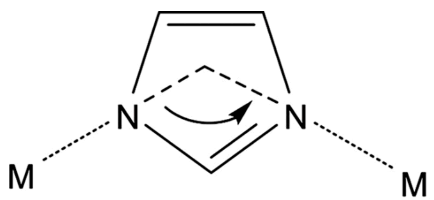


The resulting (3,6)-connected pyrite (pyr) topology.

Size Selective Separations with ZIF MOFs

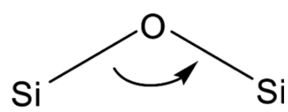
- Zeolite Structures (such as MOR) are built from $Si(Al)O_4$ tetrahedra
    linked through bridging oxygen atoms;
    >150 structures

- Possible to build MOFs with higher adsorption and selectivity by replacing zeolite linkers with transition metals and organics: Zeolitic Imidazolate Frameworks's : (ZIF MOFs)



M - IM - M

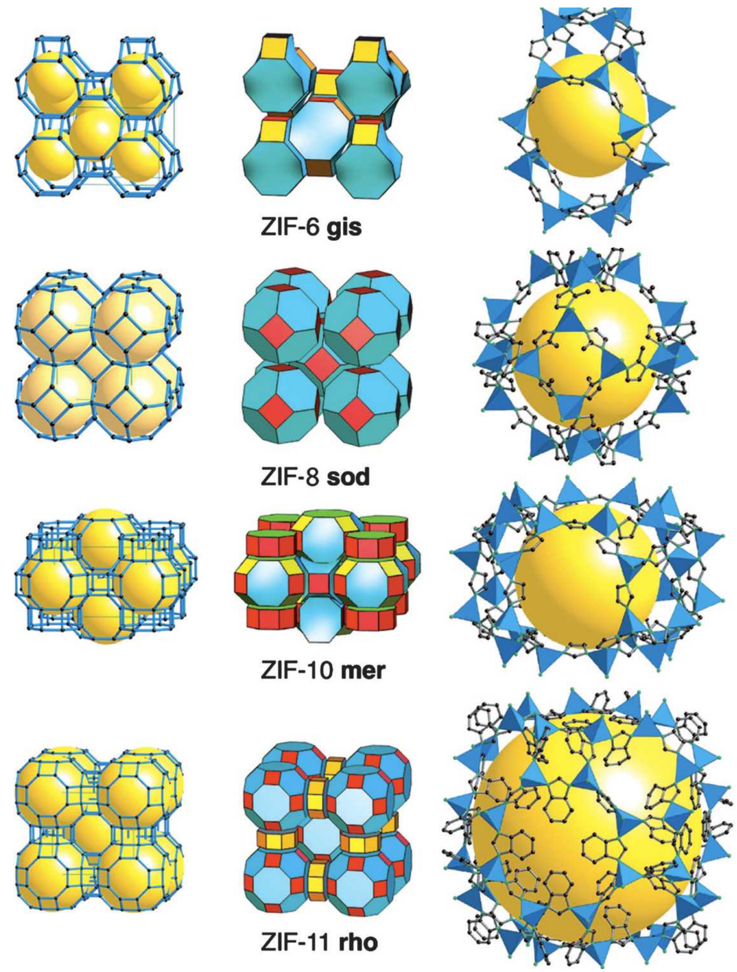
1



Si - O - Si

2

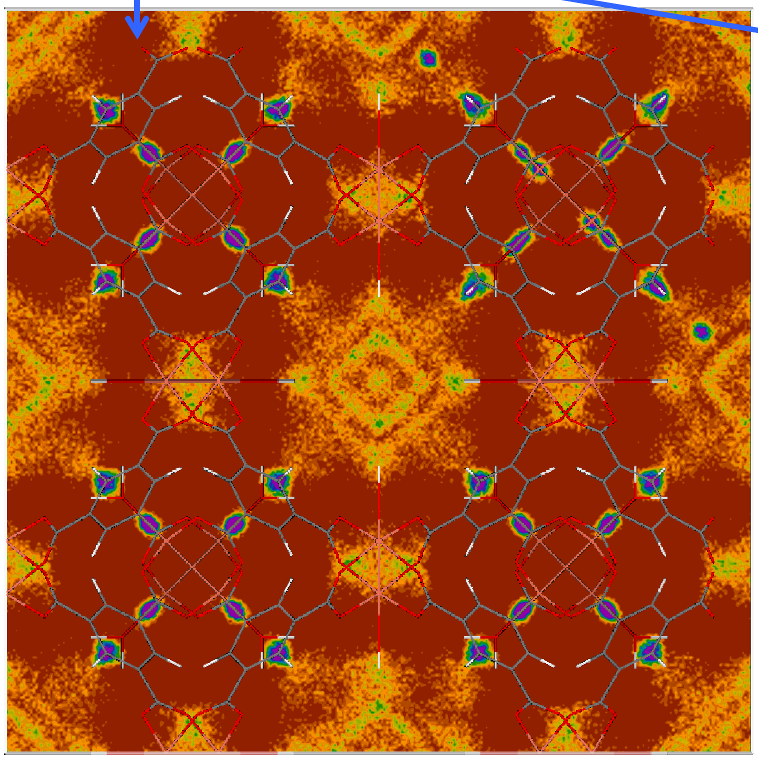
Resulting in ultra high surface areas of ≈1600 m^2/g for ZIF-8

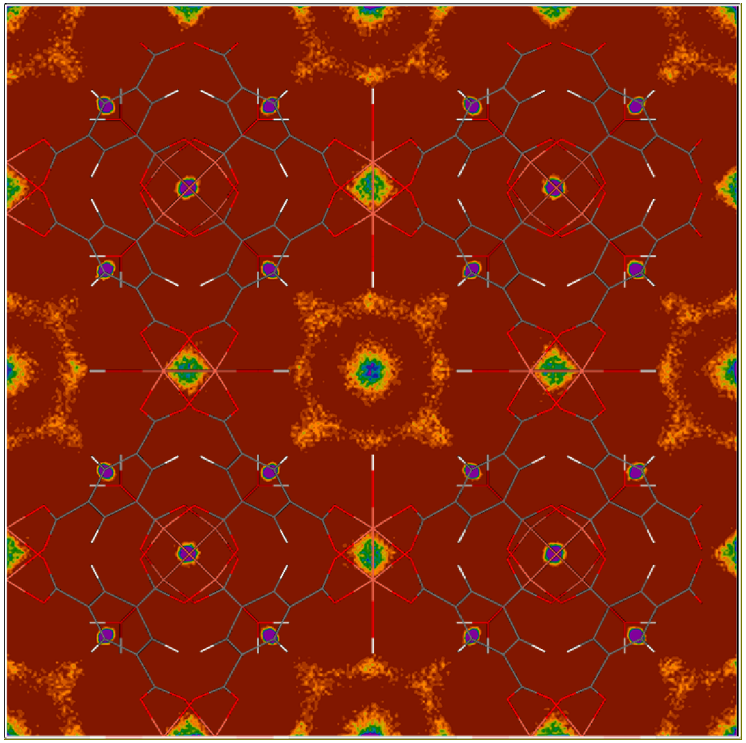


Yaghi, et al., Proc. Natl. Acad. Sci. U.S.A., **2006**, *03*, 10186

MD Simulations: 2D I_2 Density Contour Plot, Using the Explicit (diatomic) Model

MD Simulations: LAAMPS, 8 unit cell, framework atoms fixed.
Short-range van der Waals interactions, Universal Force Field (UFF) without modification
I_2: explicit and united-atom models in canonical ensemble, 298K, 10 fs timestep, steric approximations





Primary density sites are located in the tetrahedral cavities, as well as near the structural water molecules.