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U.S. DEPARTMENT OF ENERGY | Nuclear Energy

Structure-Property Relationship in Metal-Organic Frameworks for Enhanced Energy Related Applications

Dorina F. Sava

Nanoscale Science Department
Sandia National Laboratories
Albuquerque, NM

Advanced Photon Source- Argonne National Laboratory
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Acknowledgements

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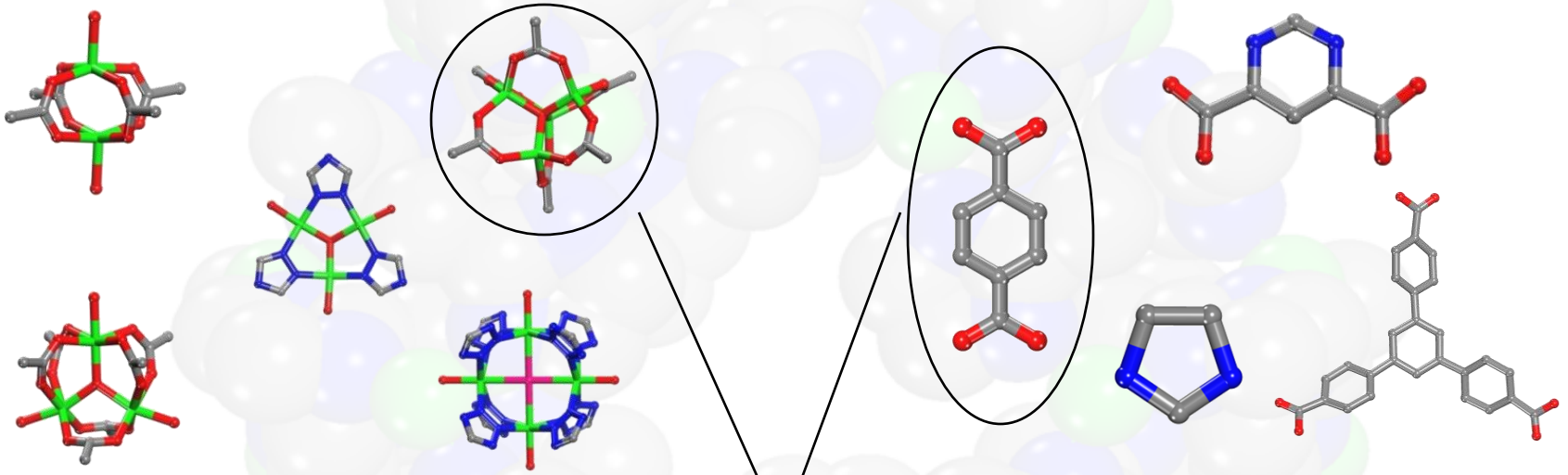
MOFs are highly crystalline materials constructed from metal nodes and organic linkers



Common metal clusters (molecular building blocks)

Organic linking units

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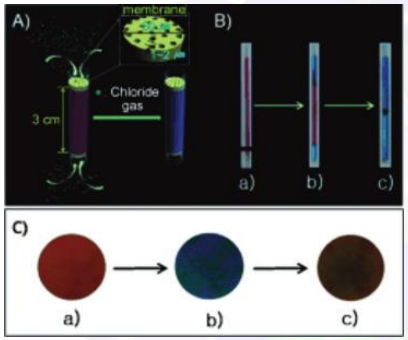
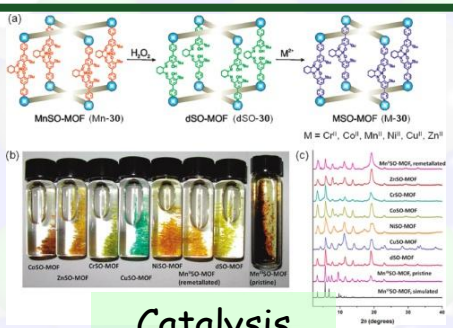
MOFs are versatile materials that span diverse applications

Chem. Rev. **2012**, *112*, 673-1268.

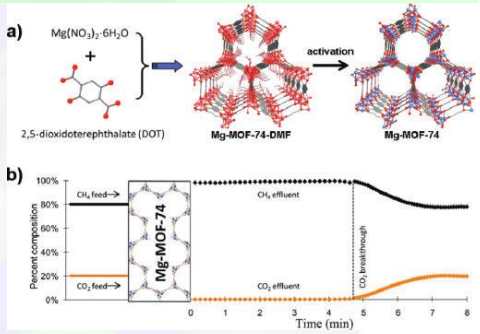
Sensors



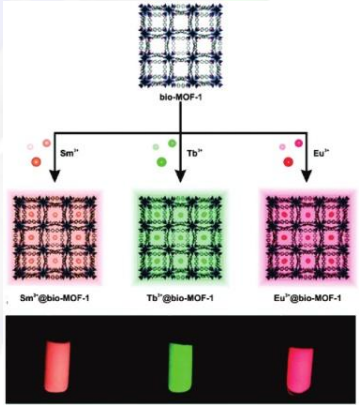


Catalysis

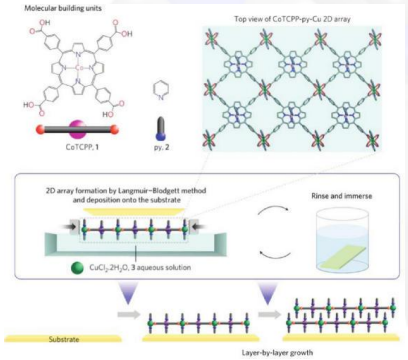
Gas storage and separations



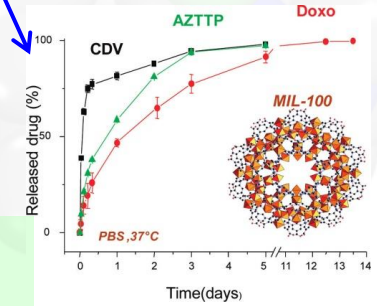
Luminescence



Membranes



Biomedicine-drug delivery



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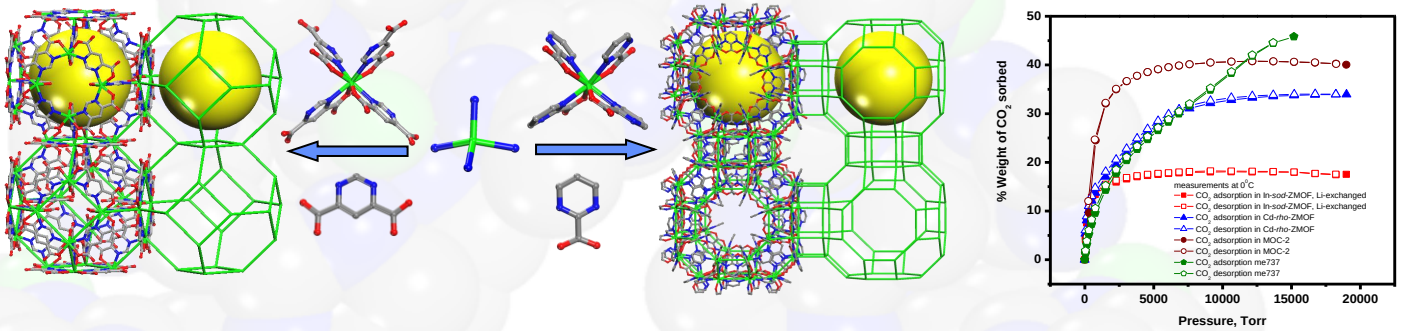
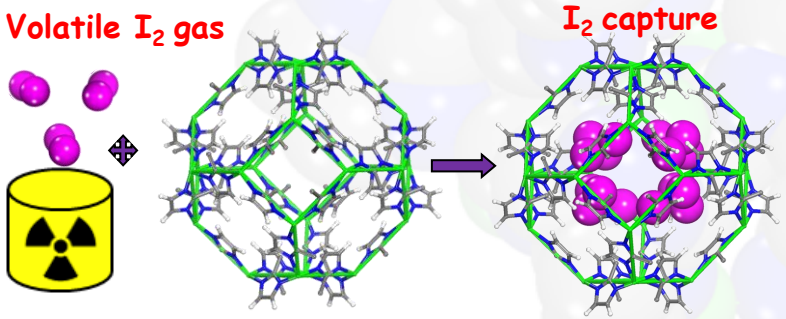
Outline

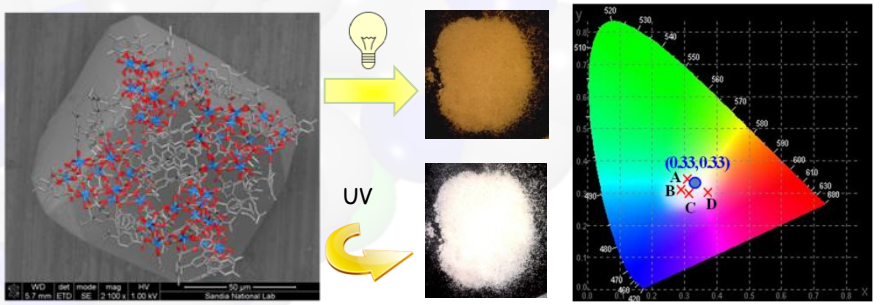
I. Design strategies for the rational construction of MOFs with zeolitic topologies



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



III. Novel MOFs with Tunable Color Properties



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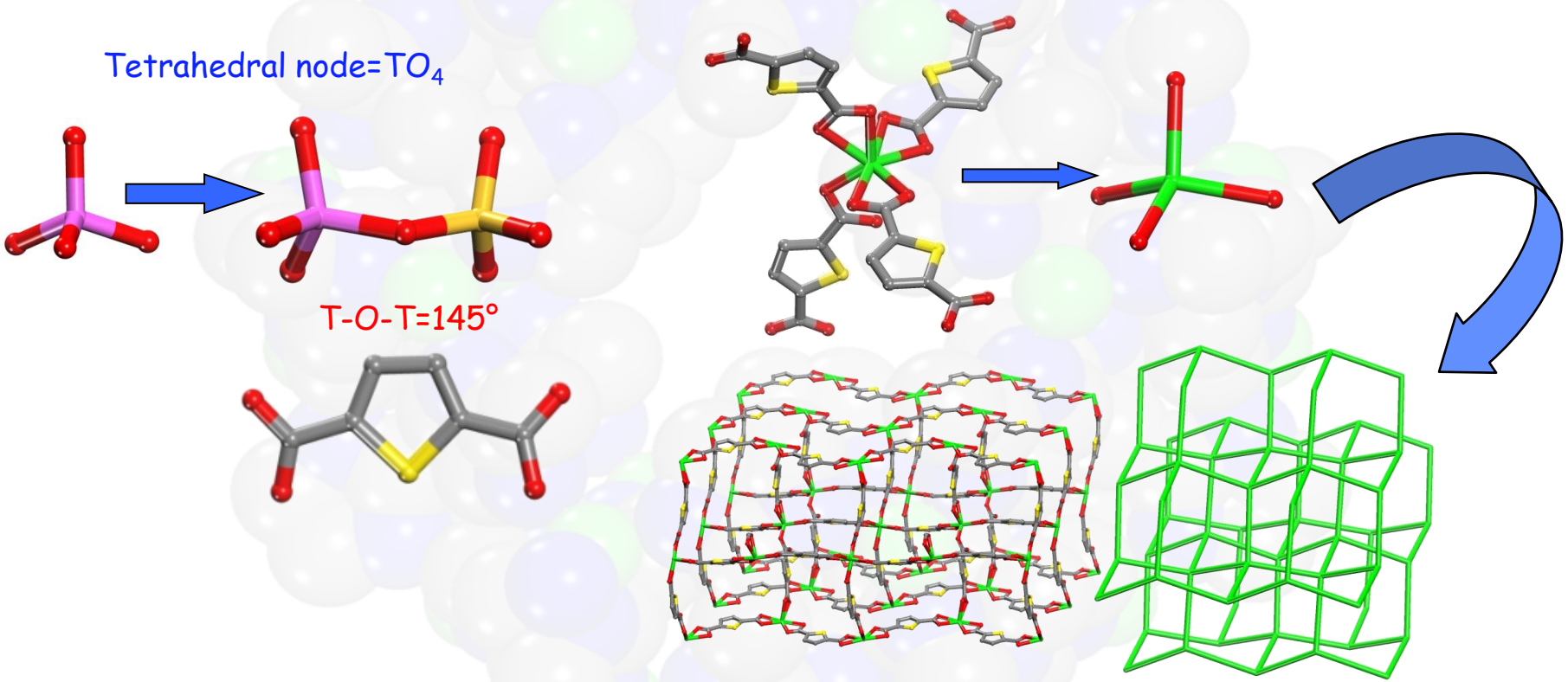
I. Design strategies for the construction of MOFs with zeolitic topologies

Top-down design and bottom-up approach for the "edge expansion" strategy for the construction of the metal-organic zeolitic analogues



MBB flexibility prevents targeted net formation – default net is preferred

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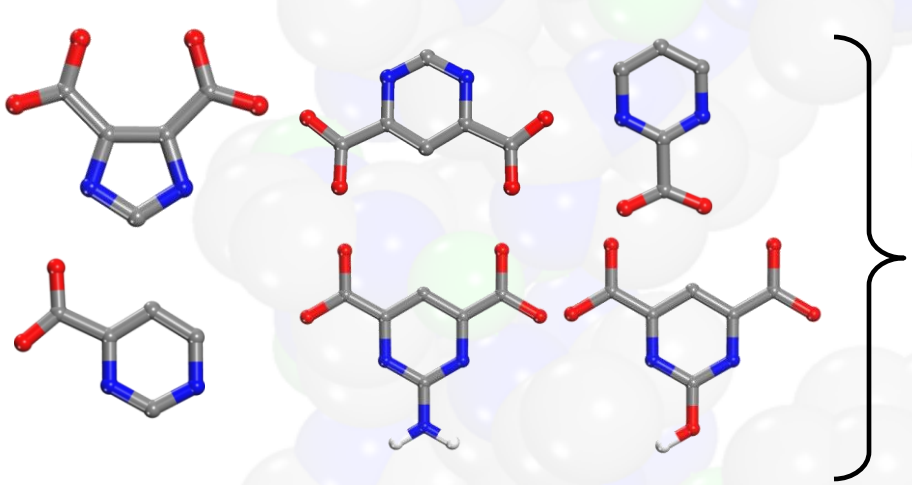
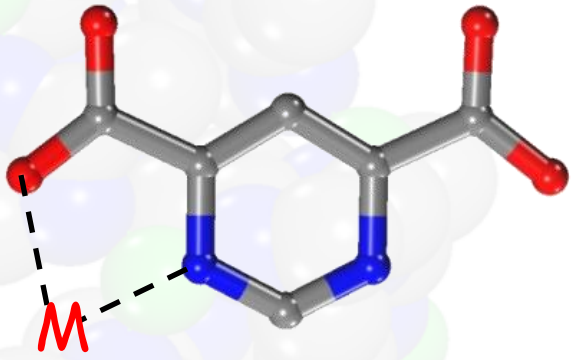
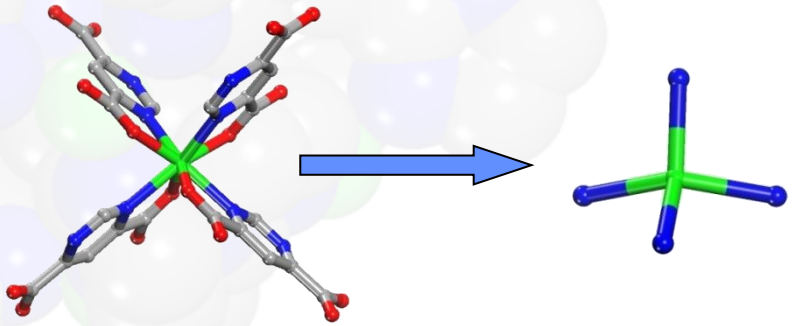
Alternative approach via *rigid* and *directional* Tetrahedral Building Blocks

The deliberate construction of porous periodic solids, utilizing the single-metal-ion-based approach





Multifunctional heterochelating ligands render *rigid* and *directional* Molecular Building Blocks



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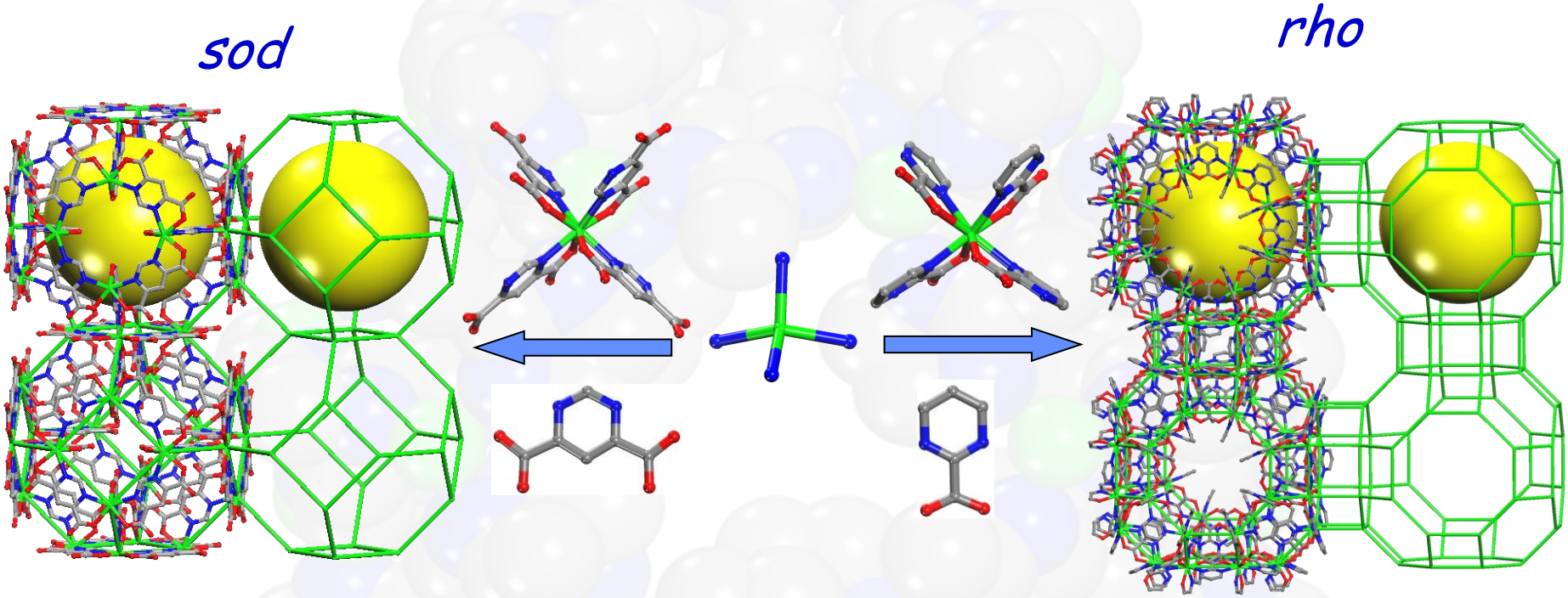
Ia. Zeolite-like Metal–Organic Frameworks from pyrimidinecarboxylate bis-chelating bridging ligands



(i) forbidden self interpenetration- design of readily accessible extra large cavities

(ii) chemical stability in water (not common in MOFs) - applications for heterogeneous catalysis, separations, and sensors

(iii) tune extra framework cations toward specific applications & removal/sequestration of toxic metal ions

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Sava, D. F. et.al *J. Am. Chem. Soc.* **2008**, *130*, 3768 – 3770.

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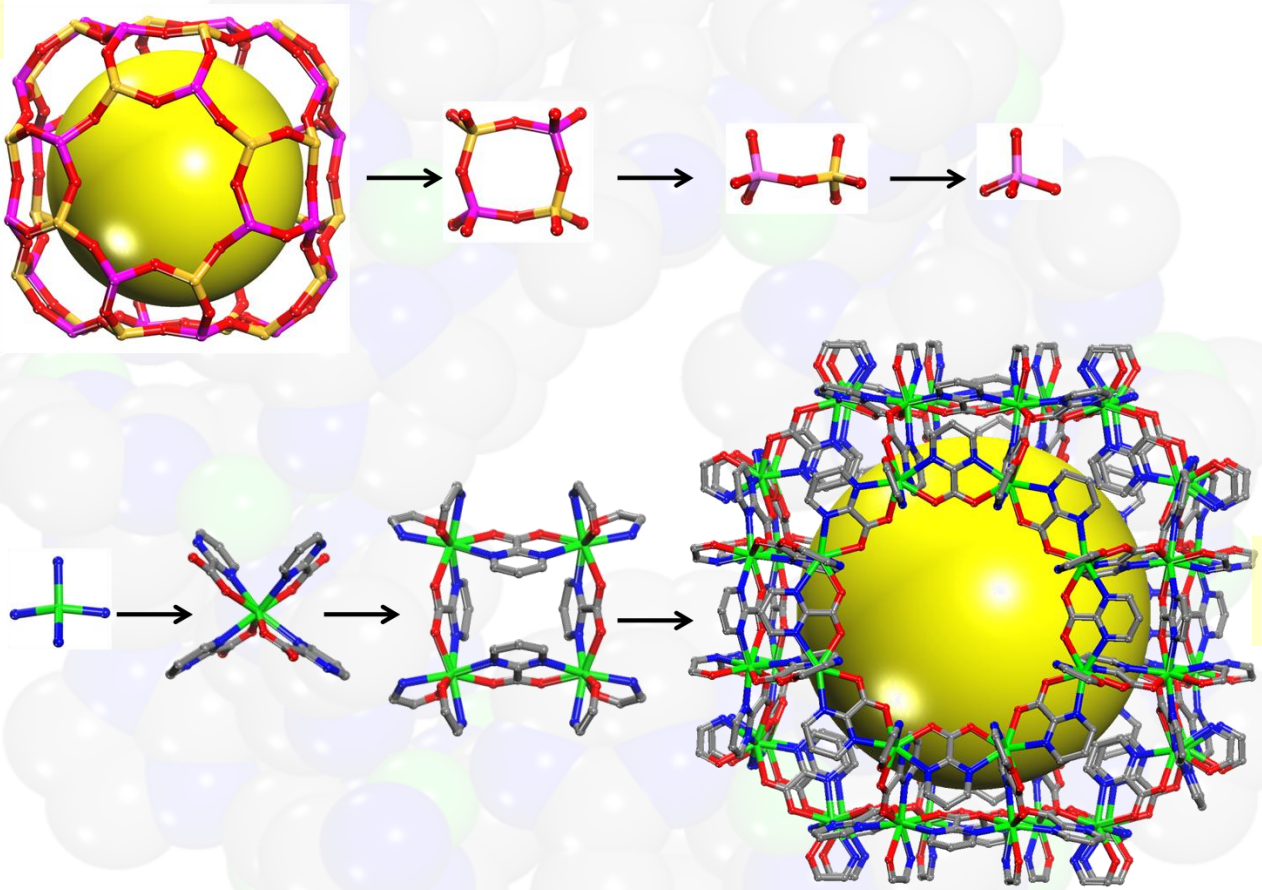
MOF zeolite *rho*: 8 times the volume and an order of magnitude higher surface area vs. inorganic RHO

Zeolite RHO



Metal-organic analogue *rho*

- The unit cell volume of the MOF *rho* framework is ~ 8 times larger than the alumino-silicate analogue- unit cell edge is doubled (3 nm vs. 1.5 nm)

- Apparent surface area: inorganic RHO ~ 100-200 m^2/g MOF *rho* ~ 1100- 1800 m^2/g

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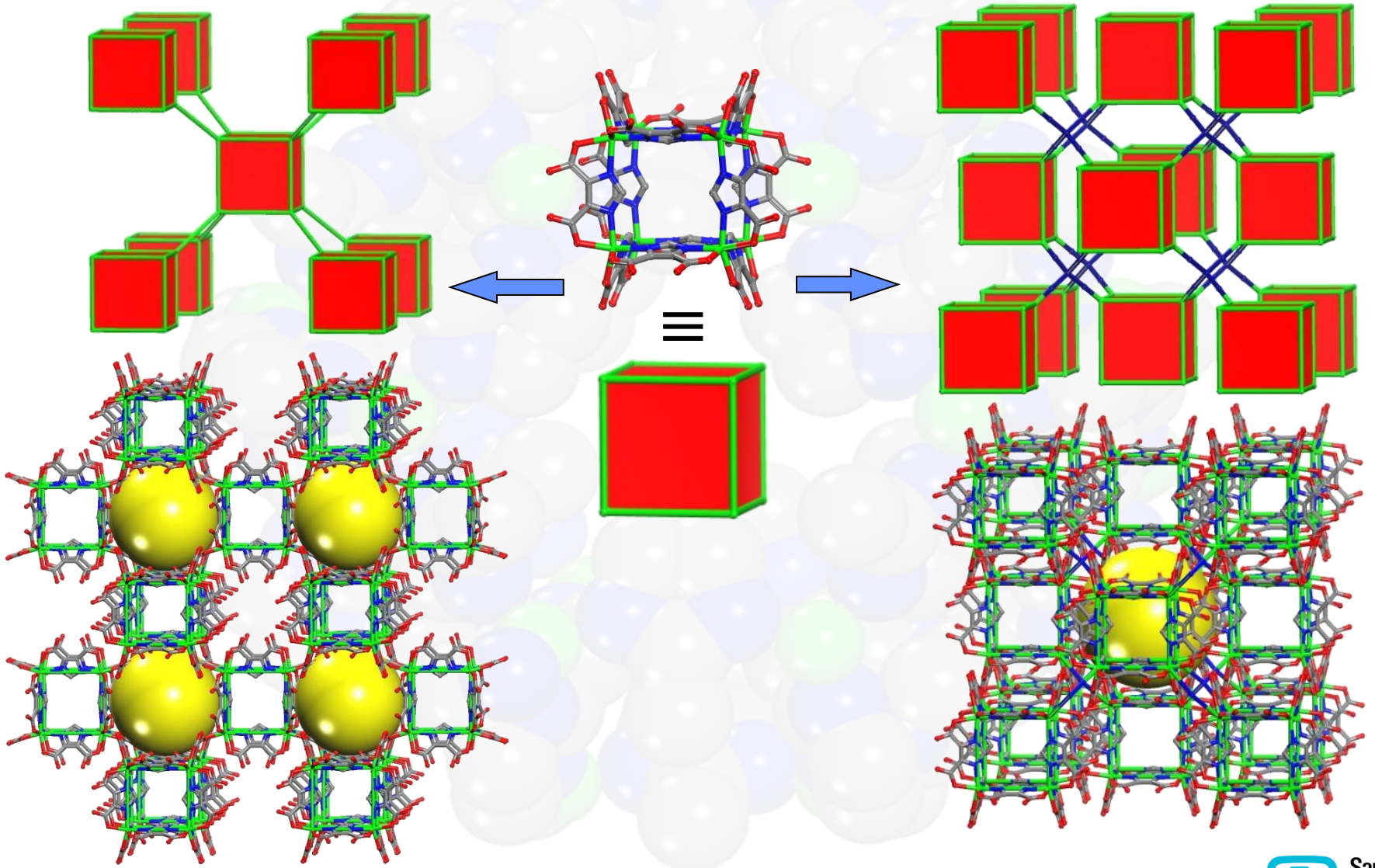
Ib. MOFs with zeolitic topologies constructed from the assembly of Metal-Organic Cubes



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Sava, D. F. et.al *J. Am. Chem. Soc.* **2009**, *131*, 10394-10396.

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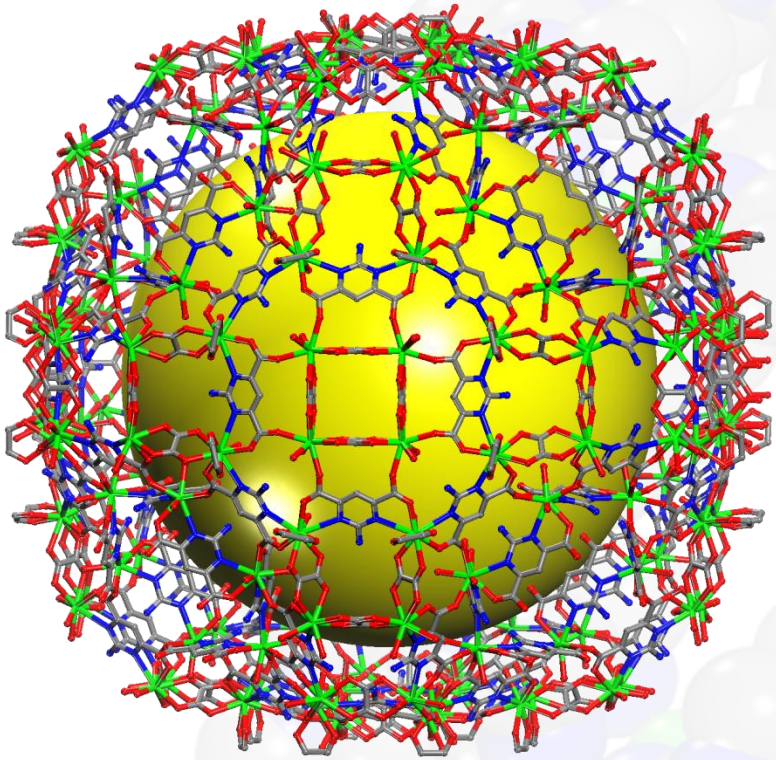
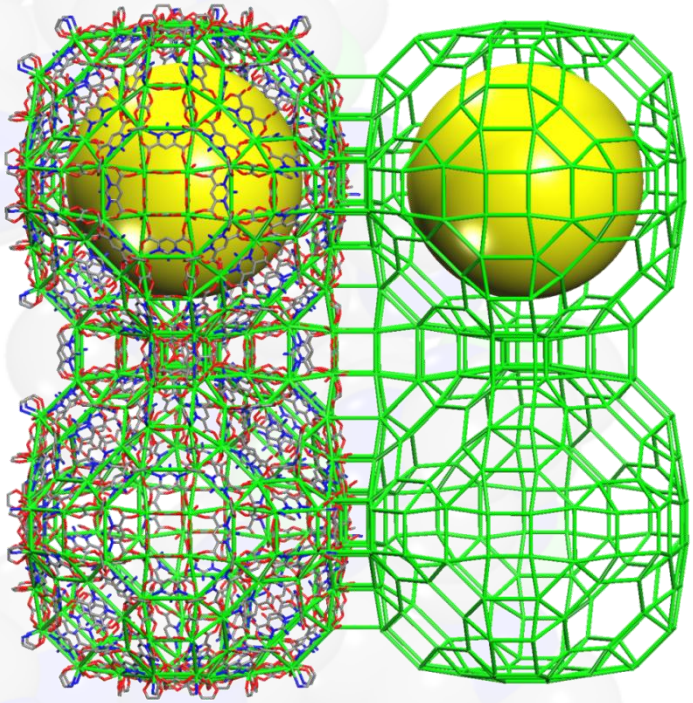
Ic. Zeolite-like MOFs with extra-large cavities



diameter of ~38Å



Material	Inner diameter	Outer diameter	Metal atoms per cage
This work	38 Å	48 Å X 53 Å	168
Mes.MOF-1	47.1 Å	59.5 Å	84
MIL-101	33.8 Å	46.7 Å	126
ZIF-100	35.6 Å	67.2 Å	264

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

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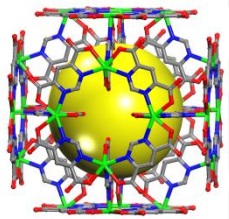
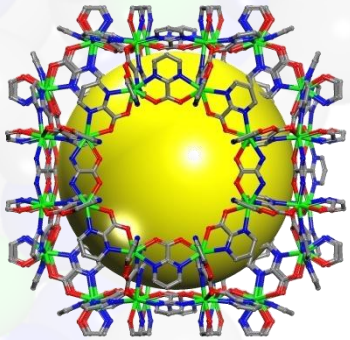
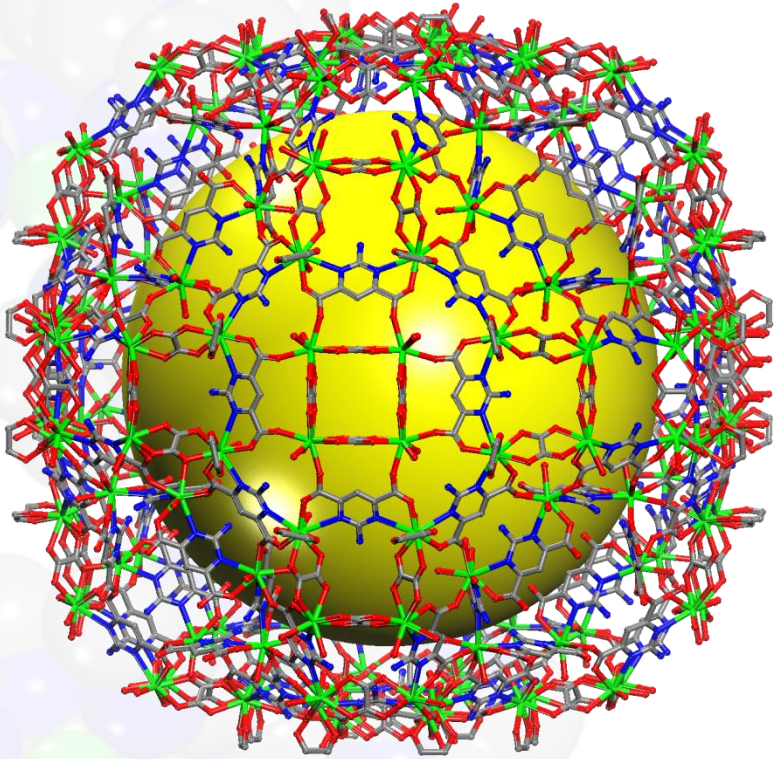
Systematic variation of the organic components leads to increased complexity



sod- diameter of ~9.6Å



rho - diameter of ~16.4 Å



diameter of ~38Å

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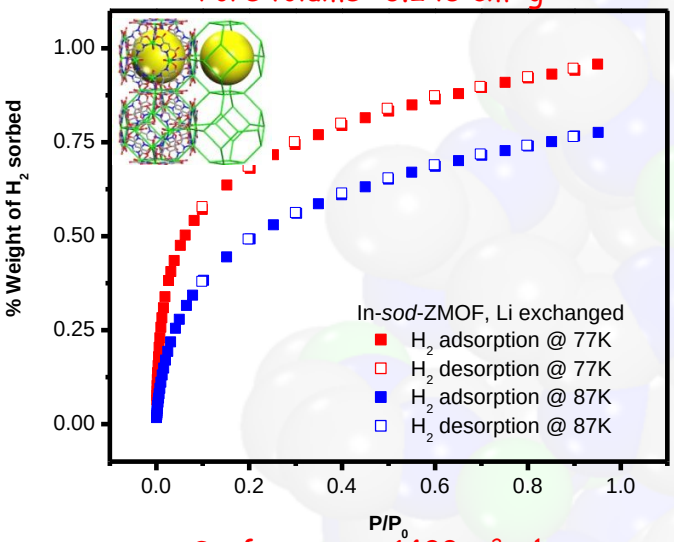
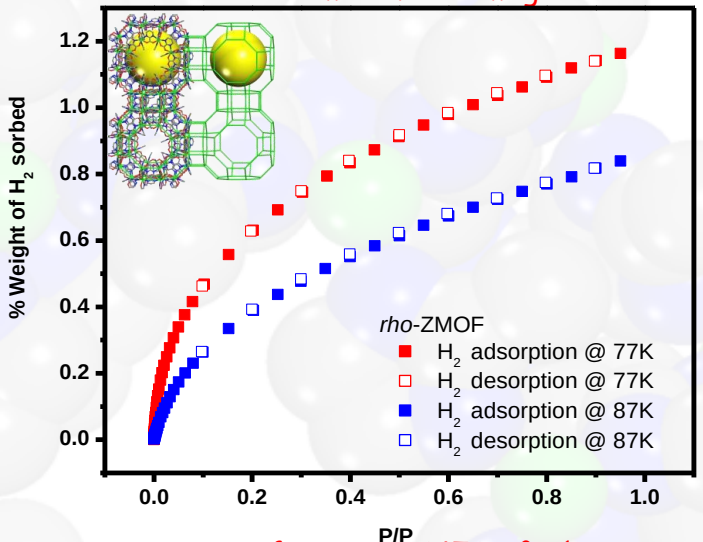
H_2 sorption isotherms

Surface area= 616 $m^2 \cdot g^{-1}$
Pore volume= 0.245 $cm^3 \cdot g^{-1}$

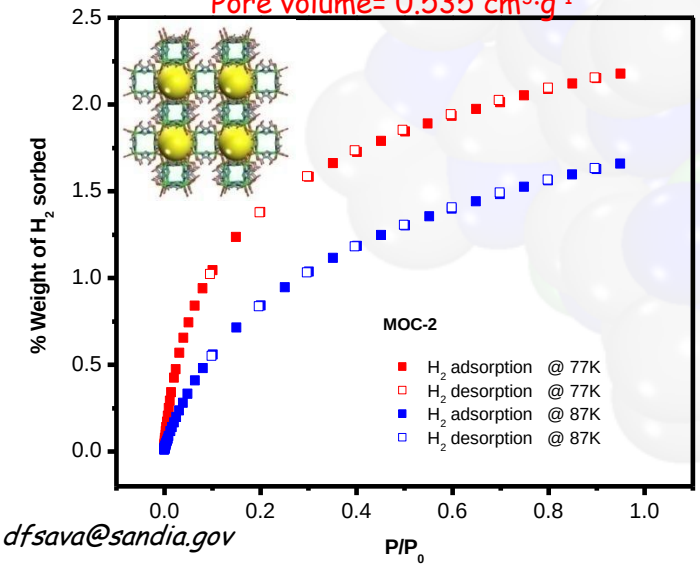


Surface area= 1168 $m^2 \cdot g^{-1}$
Pore volume= 0.474 $cm^3 \cdot g^{-1}$

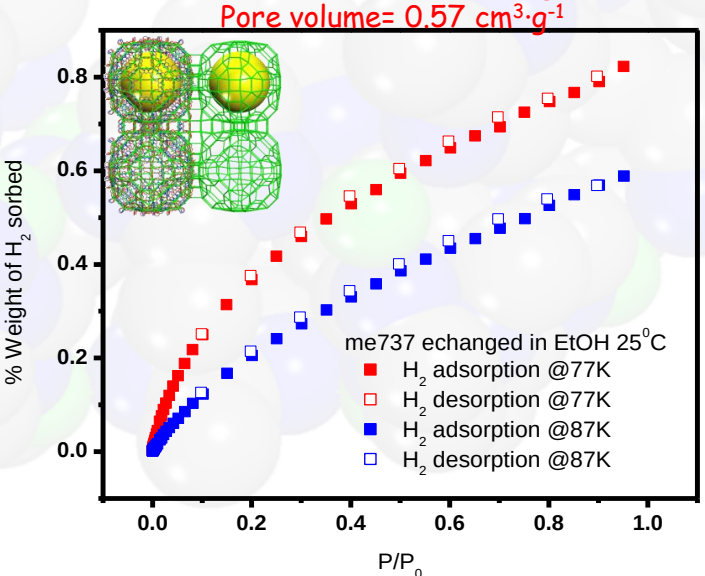


H_2 storage is dependant on surface area, pore size and pore volume, as well as on additional favorable *sites for the gas adsorption* to increase binding affinities

Surface area= 1420 $m^2 \cdot g^{-1}$
Pore volume= 0.535 $cm^3 \cdot g^{-1}$



Surface area= 1476 $m^2 \cdot g^{-1}$
Pore volume= 0.57 $cm^3 \cdot g^{-1}$



Materials with *high local charge densities* increase the binding affinities between H_2 and framework

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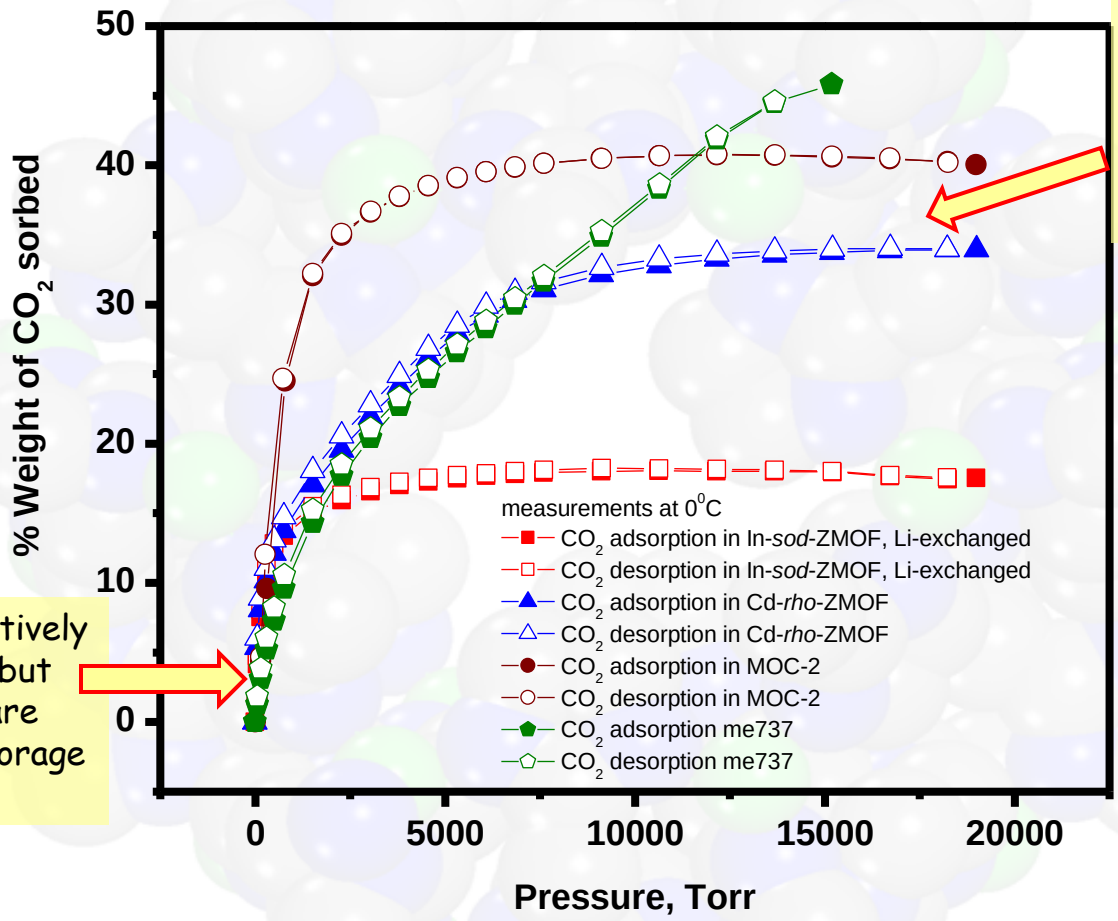
CO_2 sorption isotherms measured at 273K



Compounds with both large and extra-large cavities and high pore volumes- important for applications conducted at high pressures

Materials with relatively narrow pore sizes, but large pore volume are suitable for CO_2 storage at low pressure

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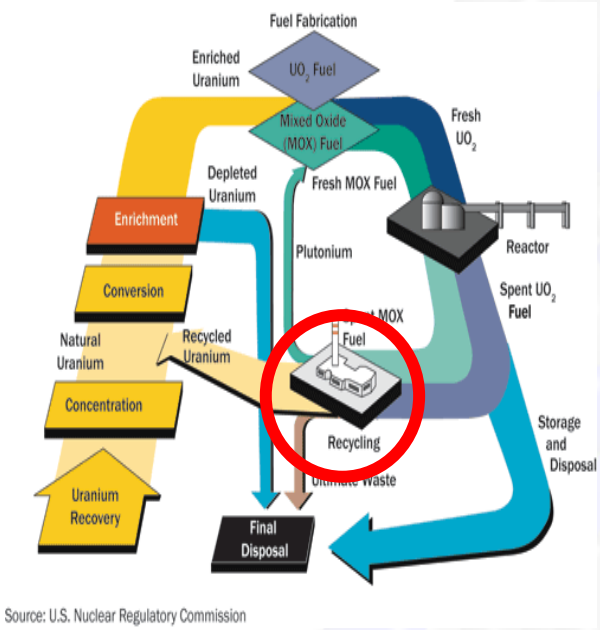
II. Capture and Storage of Volatile Fission Gas Products from Reprocessing and/or Nuclear Accidents

Nuclear Fuel Reprocessing (NE)



Source: U.S. Nuclear Regulatory Commission

Accidental Release

Fukushima Daiichi Nuclear Power Plant explosion; March 11, 2011
I^{129}, I^{131} volatile gas released (www.IAEA.org)

The importance of capturing volatile radioactive iodine (I_2) gas

- *Appropriate nuclear waste management*: a main concern for safety associated with nuclear energy
- Particularly challenging is the capture of volatile gaseous fission products from nuclear fuel reprocessing or inadvertent environmental release: ^{129}I and ^{131}I, ^{3}H, $^{14}CO_2$, and ^{85}Kr
- Unique exposure problems for radio-I_2 isotopes:
  - ^{129}I: long-lived isotope (half-life of 1.57 x 10^7 years), requiring *capture and reliable storage while it decays*
  - ^{131}I: short-lived (half-life of 8.02 days), but *requires immediate capture* as it directly affects human metabolic processes

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Judicious selection of an "ideal" candidate for I_2 sorption

Pre-requisites

- Restrictive pore apertures to impart molecular selectivity for directional diffusion of iodine (~3.35 Å)
- Large surface area and pore volume
- High *chemical*, *thermal*, and *moisture* stability

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ZIF-8: Zn(2-methylimidazole)$_2$

✓β-cages= 11.6 Å diameter,
Pore apertures ~3.4 Å

✓Surface area ZIF-8 = 1,947 $m^2\ g^{-1}$
Pore volume= 0.663 cc g^{-1}

✓Chemically stable in boiling solvents (including water), and thermally stable up to 550°C

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

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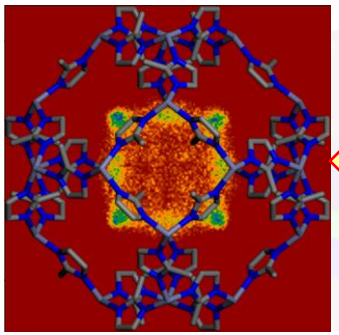
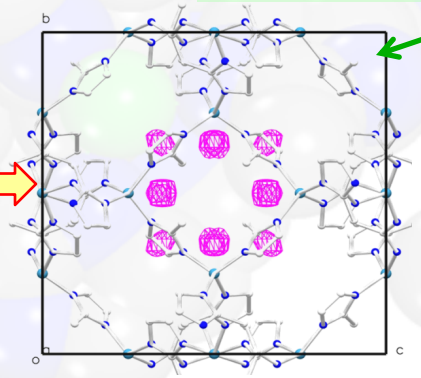
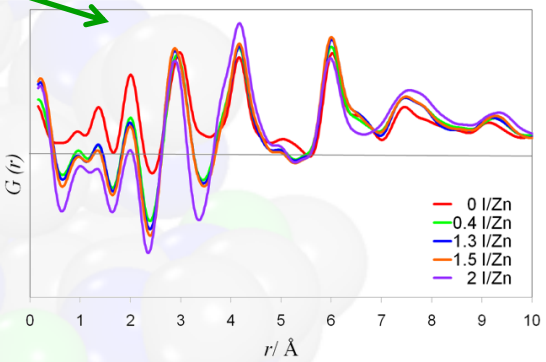
IIa. Establishing structure-function relationship: integration of experiment and modeling

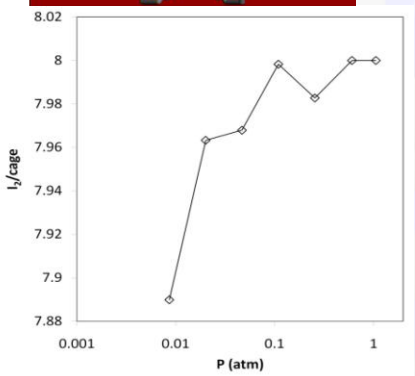
Molecular modeling

Complementary local and long-range structural probes









High-resolution synchrotron data: Difference-Fourier analysis map confirms I_2 location within cages

Pair Distribution Function analysis: histogram of all interatomic distances, independent of sample crystallinity

MD and GCMC simulations predict I_2 binding locations and maximum loading capacities

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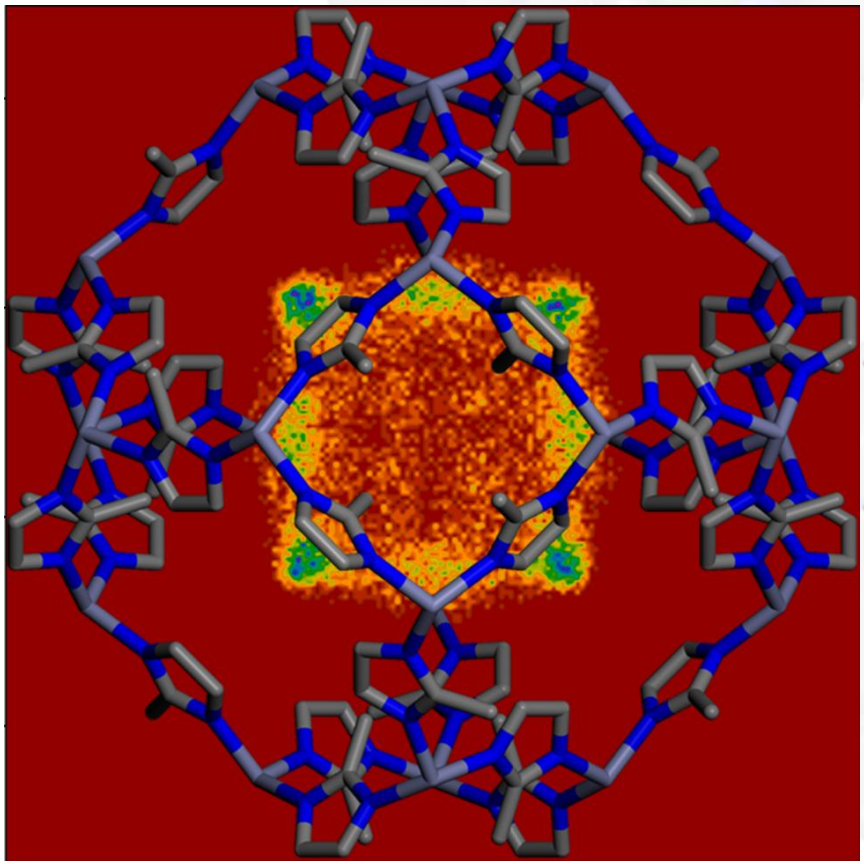
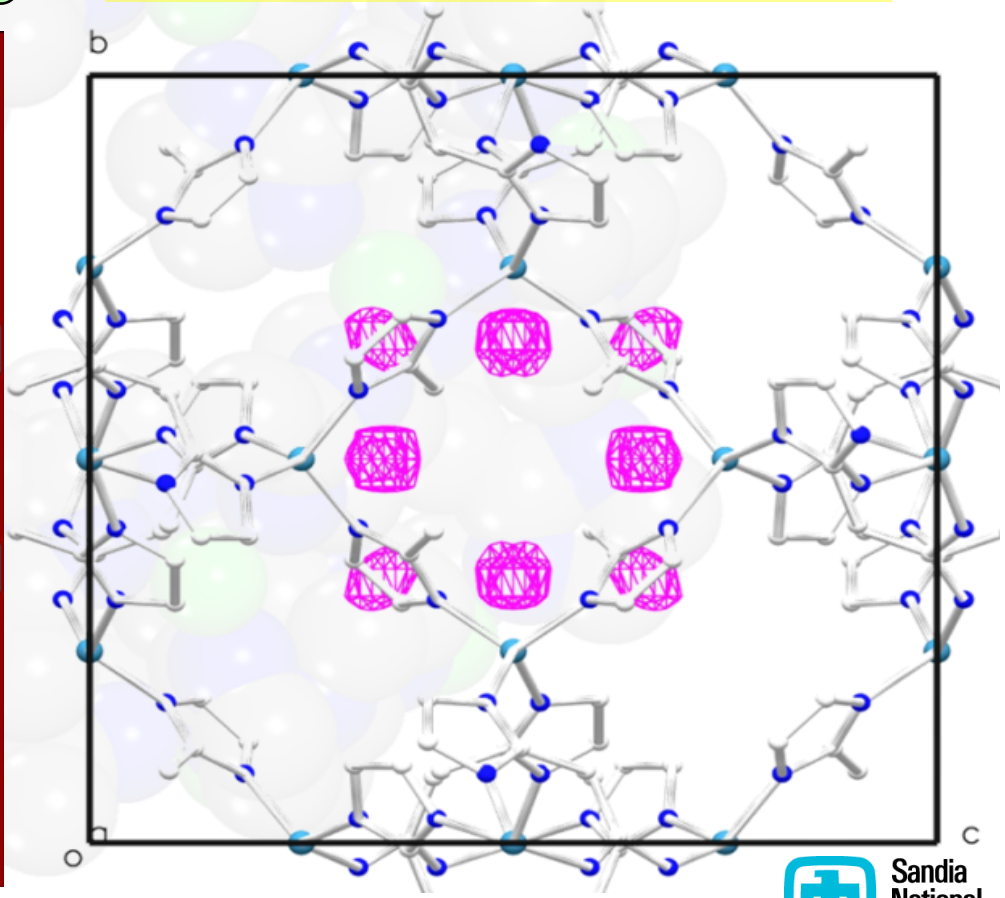
MD simulations predict I_2 location and loading capacities within ZIF-8 cage

Time-averaged atomic density plot: increased density at positions closely related to those indicated in the Bragg analysis

2 I/Zn (~6 I_2 per cage)





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Sava, D.F. et.al, *J. Am. Chem. Soc.* **2011**, *133*, 12398.

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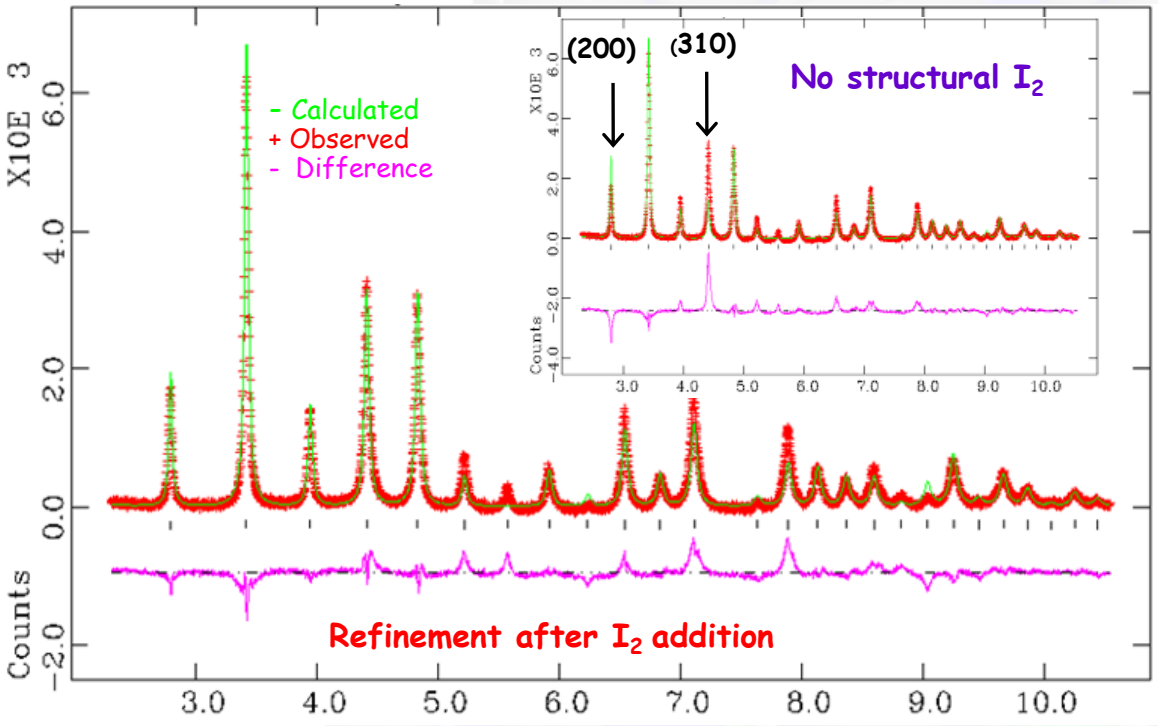
High-resolution synchrotron-based XRD



Calculated, observed and difference spectrum of 0.4 I/Zn (25 wt.% I_2) loading of I_2@ZIF-8 after I_2 inclusion in structure refinement by Rietveld analysis (inset: before I_2 inclusion).

- Sample crystallinity is maintained up to ~1.3 I/Zn (70 wt.% I_2) loadings
- Bragg reflections broaden significantly beyond this value → difficult to distinguish from the pronounced diffuse features in the "background"
- Experimental maximum capacity is reached at ~2 I/Zn (110 wt.% I_2) loadings

dfsava@sandia.gov

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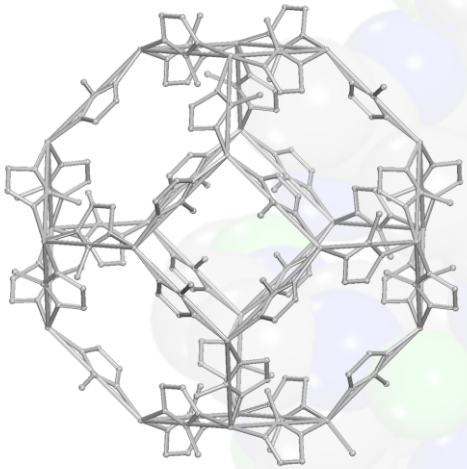
Identifying the I_2 binding locations



Activated β-cage

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Sava, D.F. et.al, *J. Am. Chem. Soc.* 2011, *133*, 12398.

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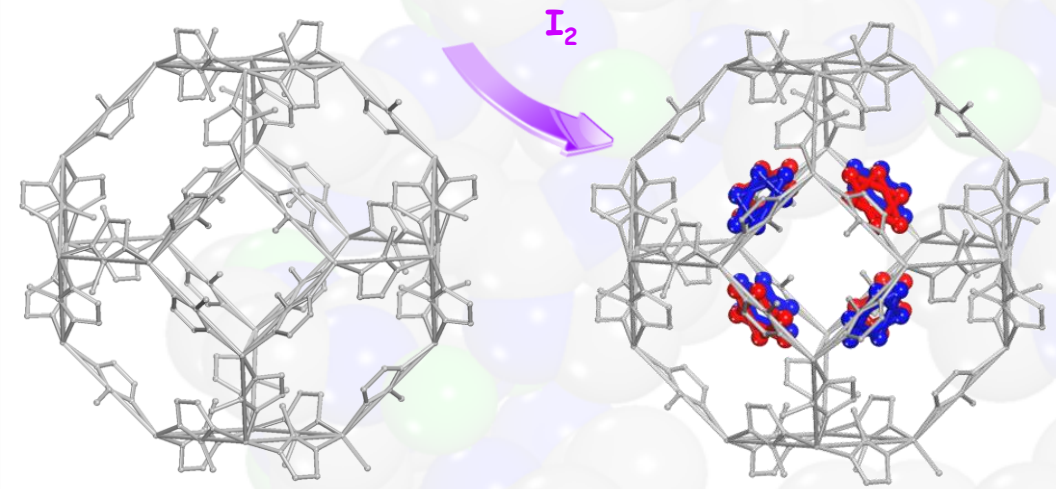
Identifying the I_2 binding locations



Activated β-cage

Dynamically disordered I_2 molecules

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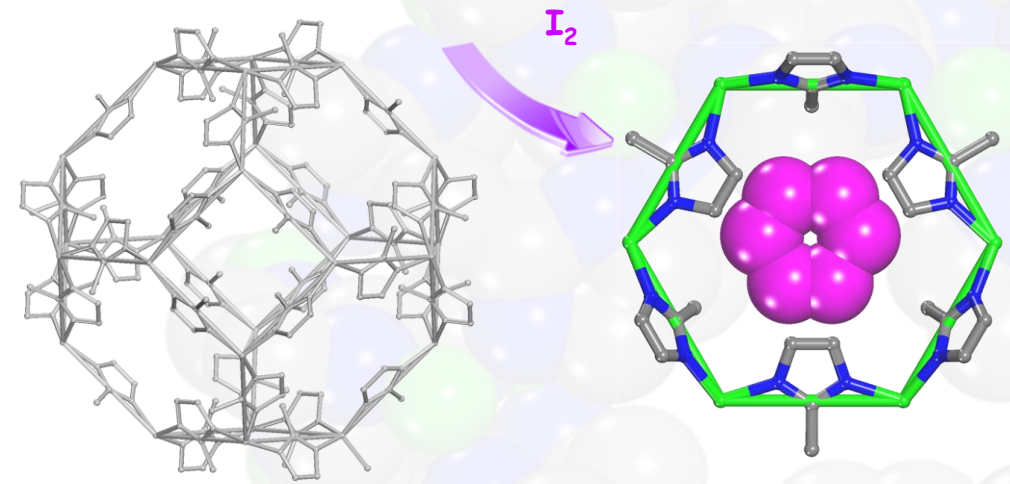
Identifying the I_2 binding locations



Activated β-cage

Dynamically disordered I_2 molecules

dfsava@sandia.gov

Sava, D.F. et.al, *J. Am. Chem. Soc.* 2011, *133*, 12398.

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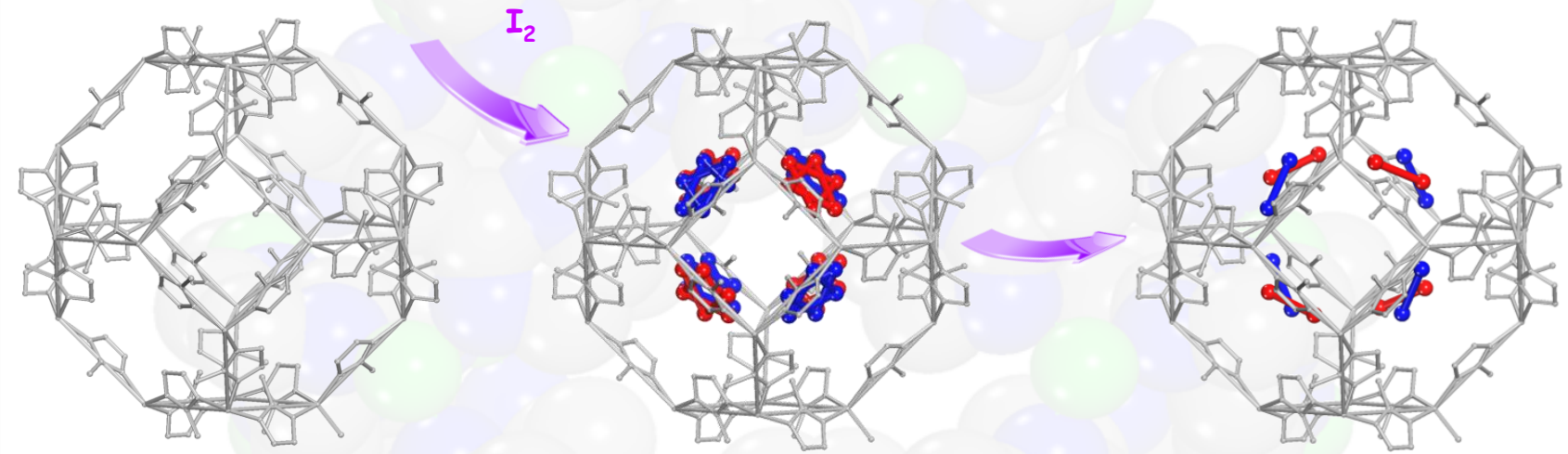
Identifying the I_2 binding locations



Activated β-cage

Dynamically disordered I_2 molecules

Refined I_2 sites: I_a (blue) and I_b (red)

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Sava, D.F. et.al, *J. Am. Chem. Soc.* **2011**, *133*, 12398.

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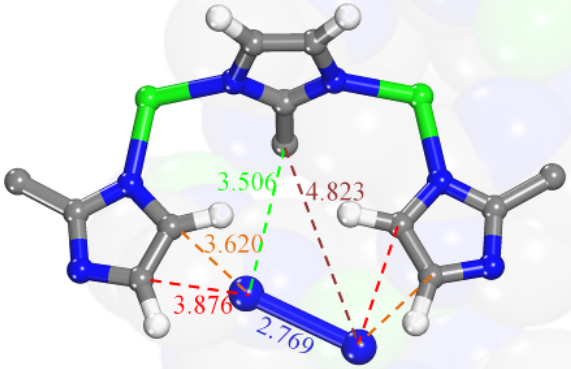
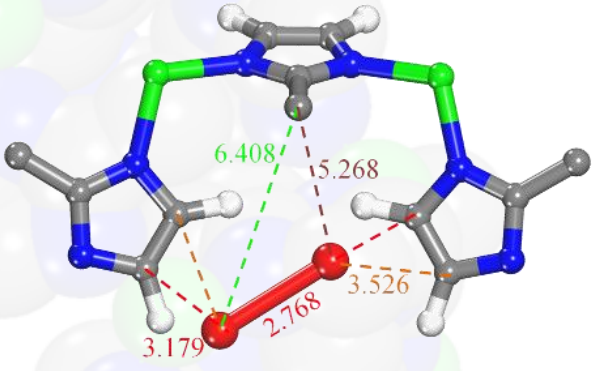
I_2 adsorption in ZIF-8 is due to favorable interactions with the 2-MeIM linker

Two distinct I_2 binding sites: I_a and I_b

I_a site



I_b site



I_2 site occupancy and I_2···MeIM close contacts in I_2@ZIF-8

I_2 site	Site occupancy		Contacts with MeIM	
	0.4 I/Zn	1.3 I/ Zn	C (CH_3)	C(H=CH)
I_a	0.28	0.88	3.506 Å; 4.823 Å	3.620 Å; 3.876 Å
I_b	0.14	0.38	5.268 Å; 6.408 Å	3.179 Å; 3.526 Å

dfsava@sandia.gov

Sava, D.F. et.al, *J. Am. Chem. Soc.* **2011**, *133*, 12398.

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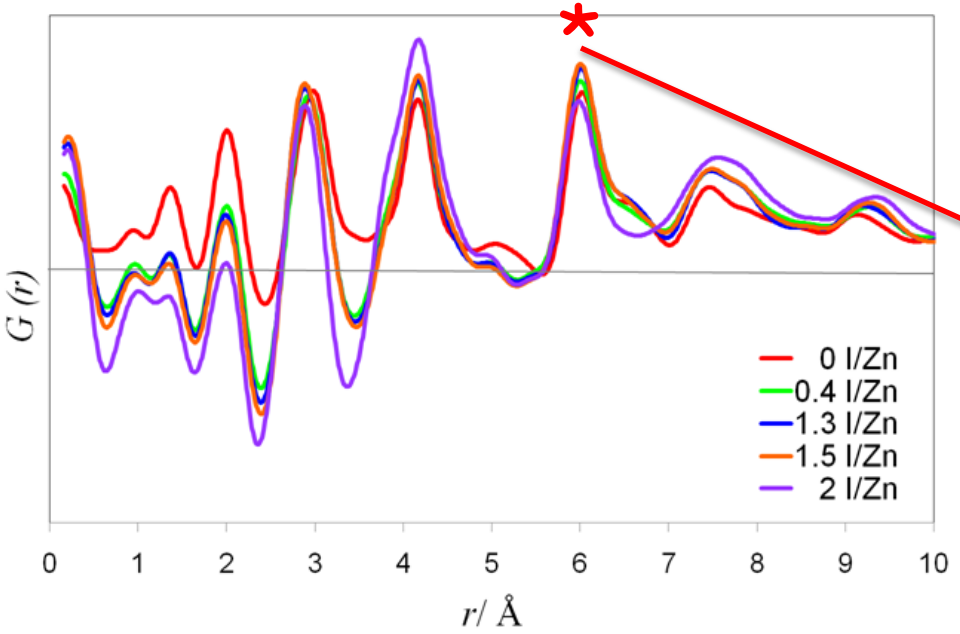
Pair Distribution Function analysis: local structure probe



Short-range order and framework connectivity are maintained at all loading levels

- The PDF method- a weighted histogram of the atomic distances, independent of sample crystallinity
- Below ~6 Å, the *MOF cage features are retained in the PDF at all I_2 loading levels*
- The persistence of the peak at ~6 Å, corresponding to the Zn-(MeIM)-Zn' distance
- >1.3 I/Zn (70wt%) lose long range structural information though individual cages maintain crystalline integrity

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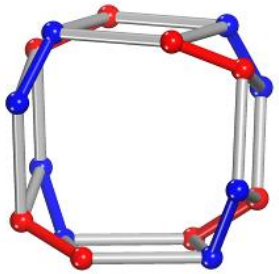
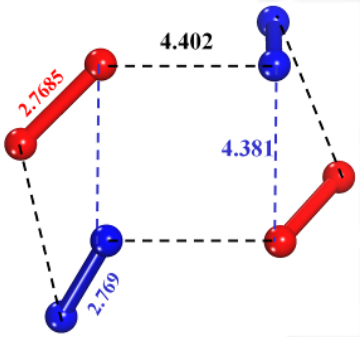
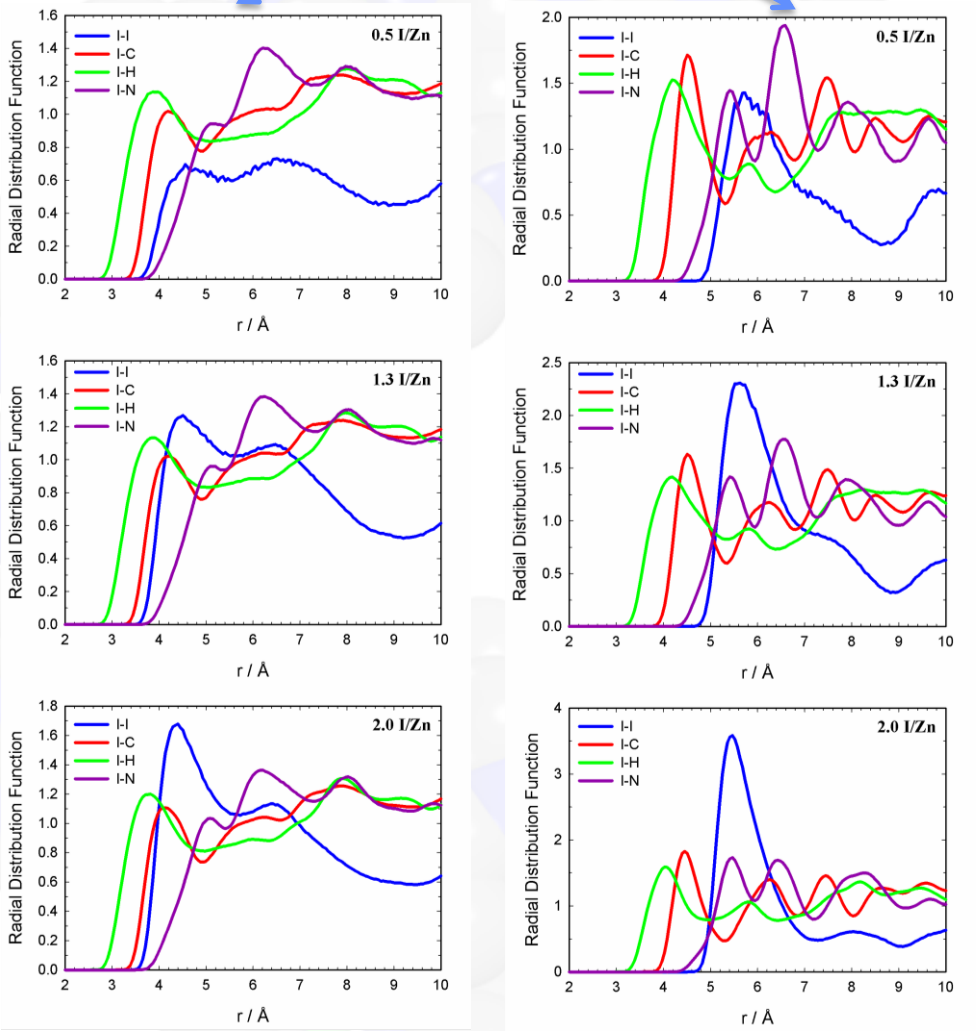
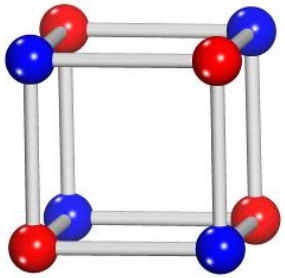
Radial Distribution Functions (RDFs) for diatomic and united-atom models

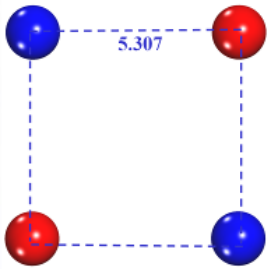




Distorted octagonal prism formed by refined I_2 molecules, and corresponding intermolecular interactions.







Cubane-like cluster derived from a united-atom model for I_2, and representative contacts for this molecular arrangement.

Good agreement between crystallography, PDF and modeling regarding nearest neighbors distances

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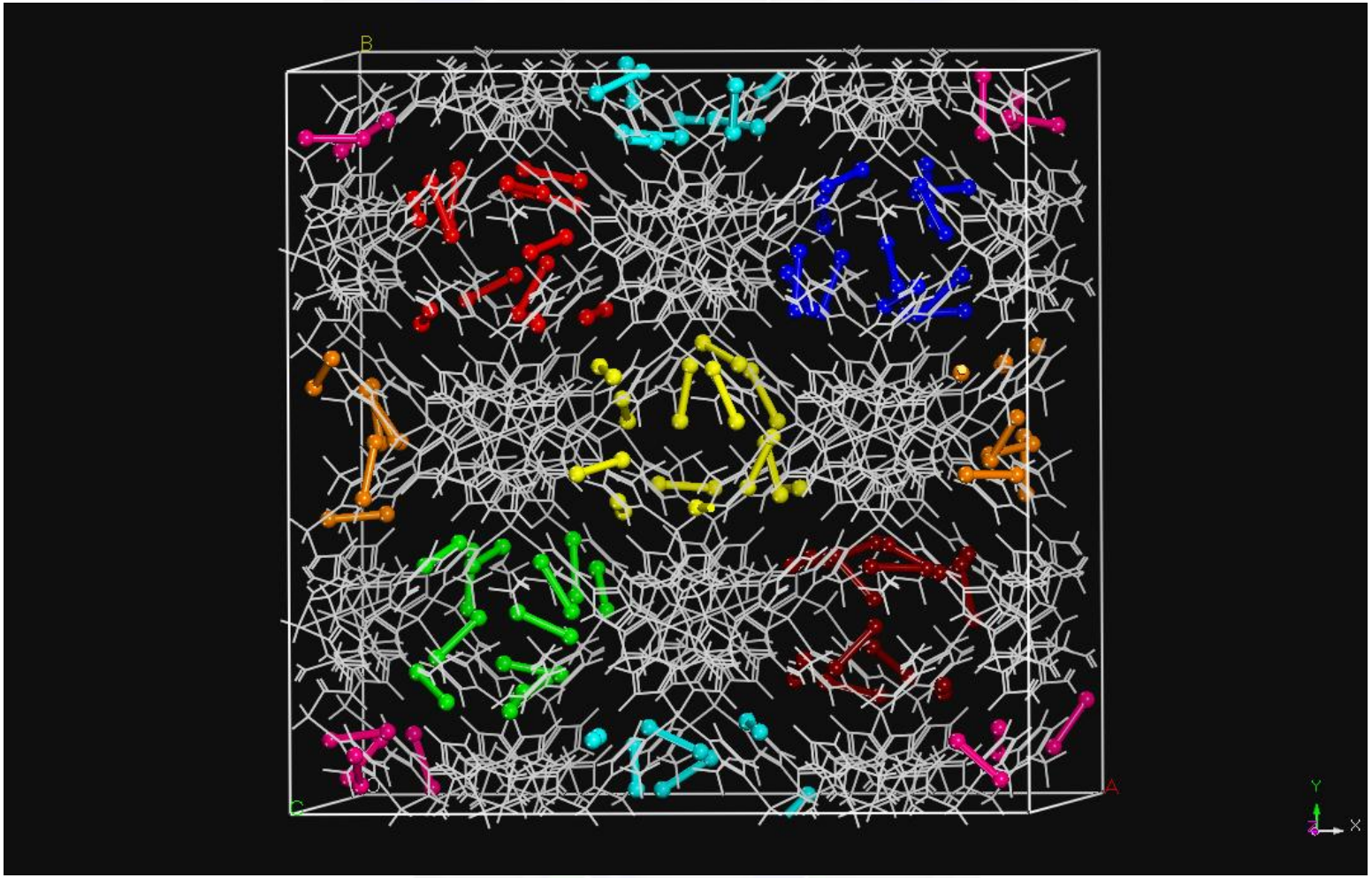
Dynamics of I_2 within cages: I_2 mobility is restricted within individual cages



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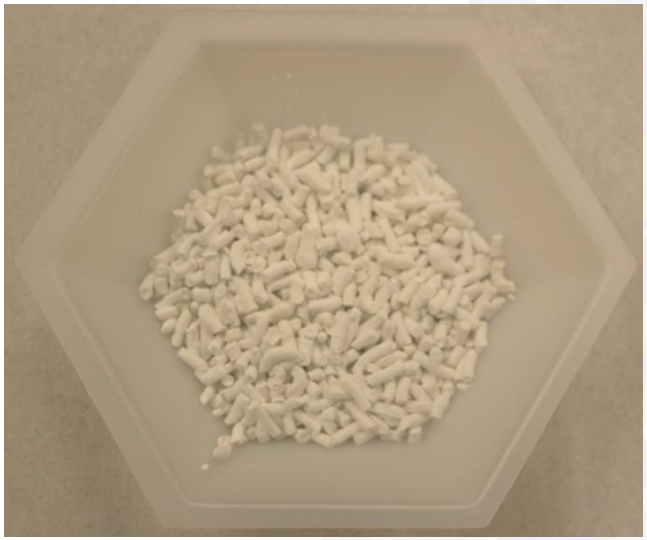
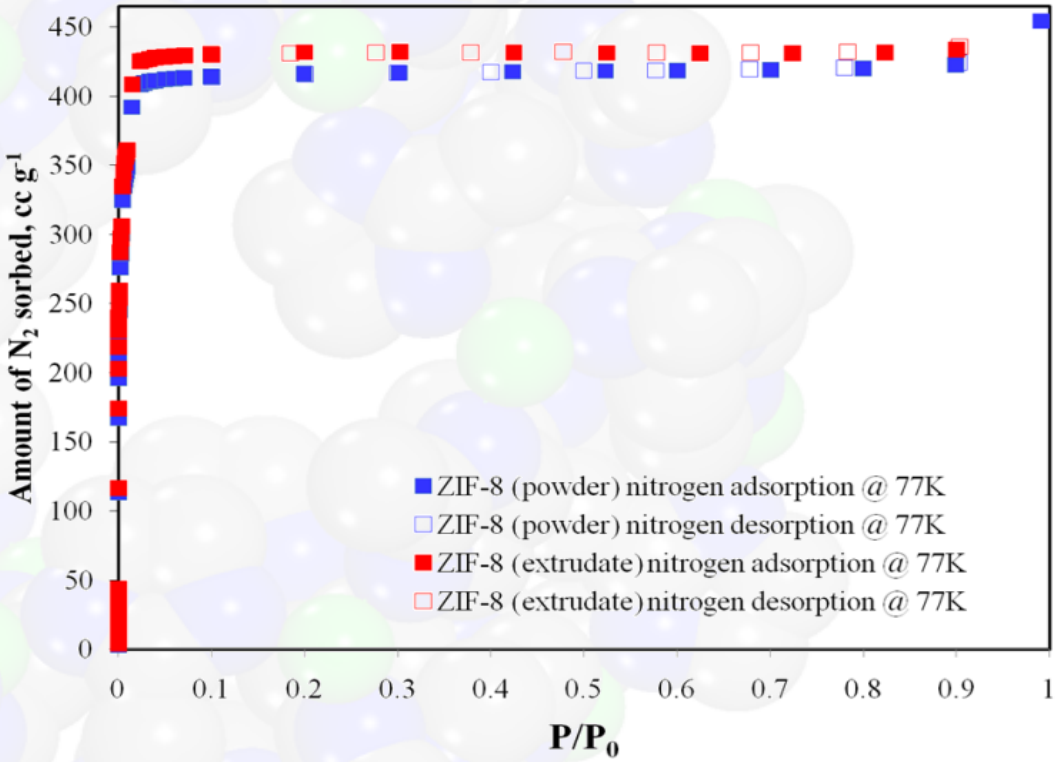
ZIF-8 binder-free extrudates: on par performance with ZIF-8 powder





I_2 loaded extrudates

Technical advance for US Patent # 11971 submitted, 04/2011

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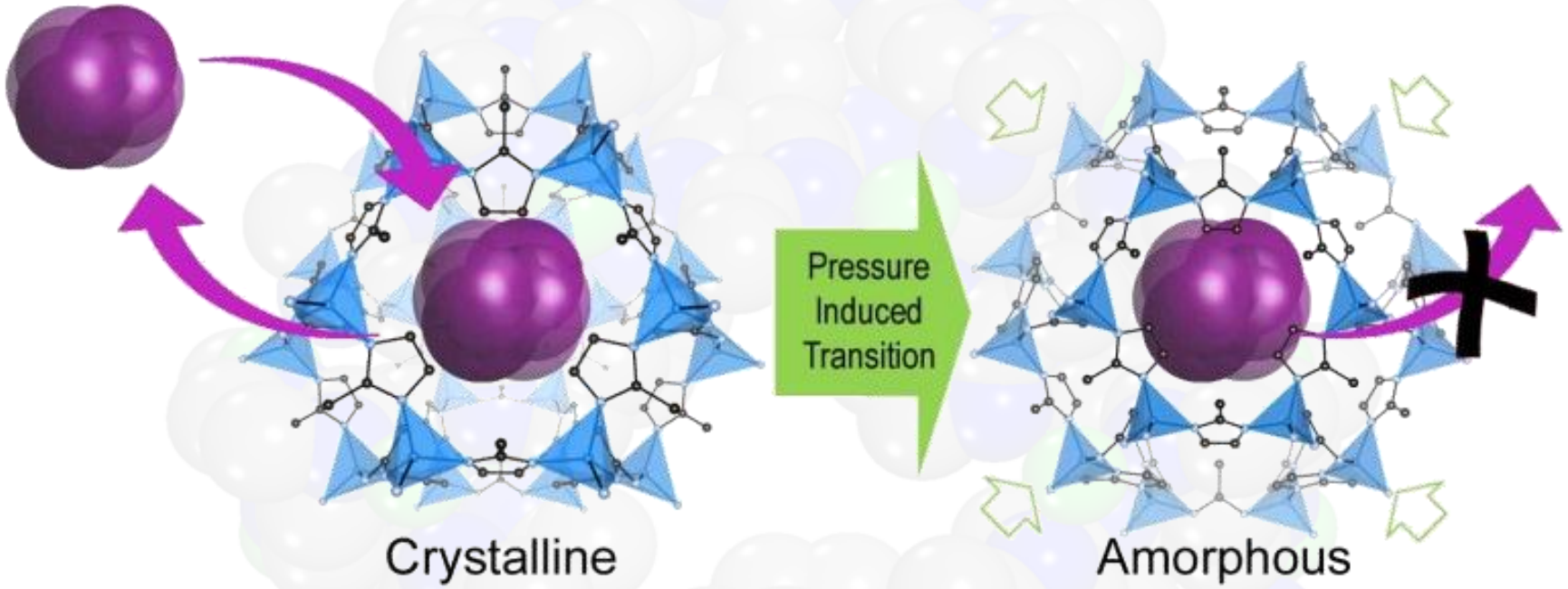
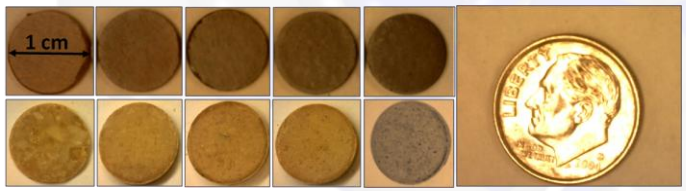
IIb. I_2@ZIF-8 pressure-induced amorphization for capture and temporary storage





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.

dfsava@sandia.gov

Chapman, K.W., Sava, D. F. et al *J. Am. Chem. Soc.* **2011**, 133 (46), 18583–18585.

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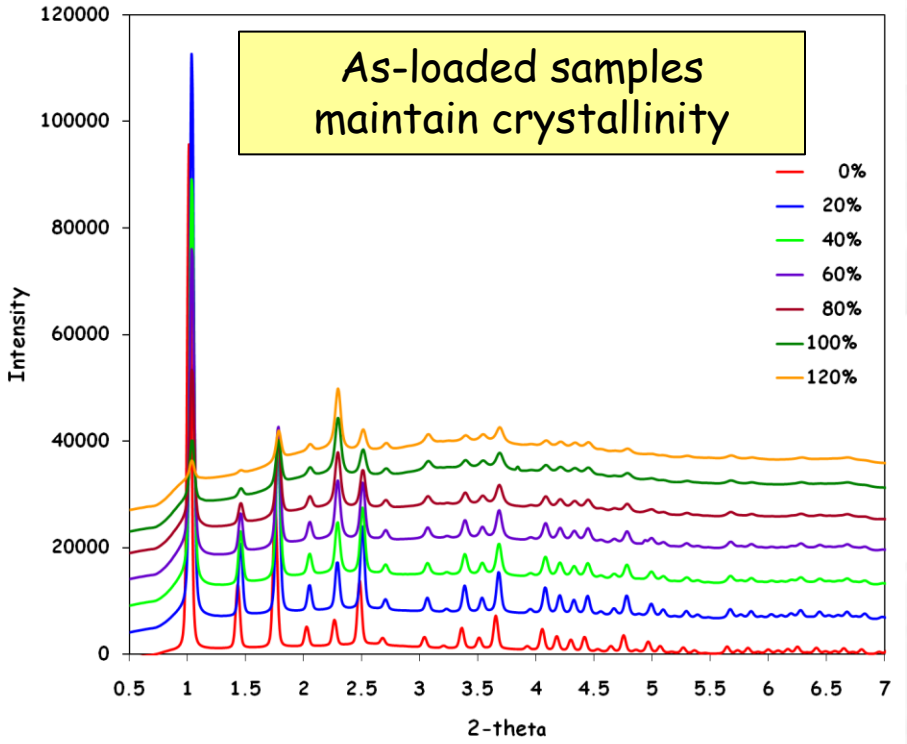
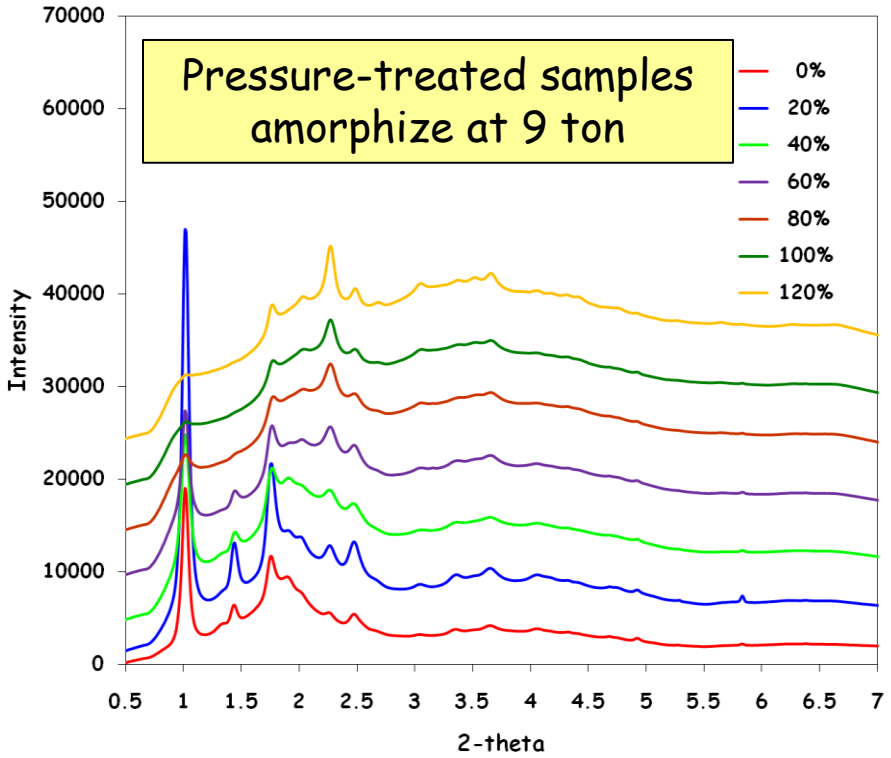
High-resolution synchrotron-based XRD on a series of incrementally loaded I_2@ZIF-8





High-resolution synchrotron-based XRD of as-loaded 20, 40, 60, 80, 100 and 120 wt% I_2@ZIF-8.

High-resolution synchrotron-based XRD of powders treated to 9 ton of 20, 40, 60, 80, 100 and 120 wt% I_2@ZIF-8.

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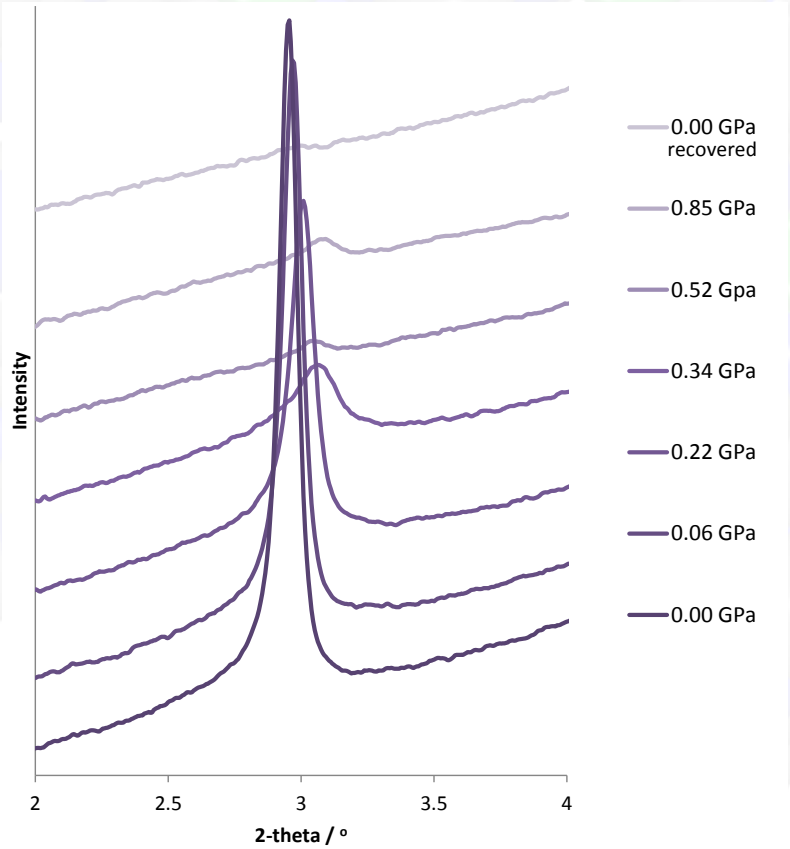
Variable pressure diffraction studies on I_2@ZIF-8

The pressure dependence of I_2-containing ZIF-8 highlighting the 110 reflection. Above 0.34 GPa, the crystalline diffraction features are largely eliminated and the framework remains amorphous upon recovery to ambient pressure.



- *In-situ* X-ray diffraction were collected at the 1-BM beamline at the APS/ANL.
- The pressure-dependent structure of ZIF-8 loaded with 40wt% I_2, was probed using synchrotron-based powder diffraction for the sample within a diamond anvil cell pressure apparatus.

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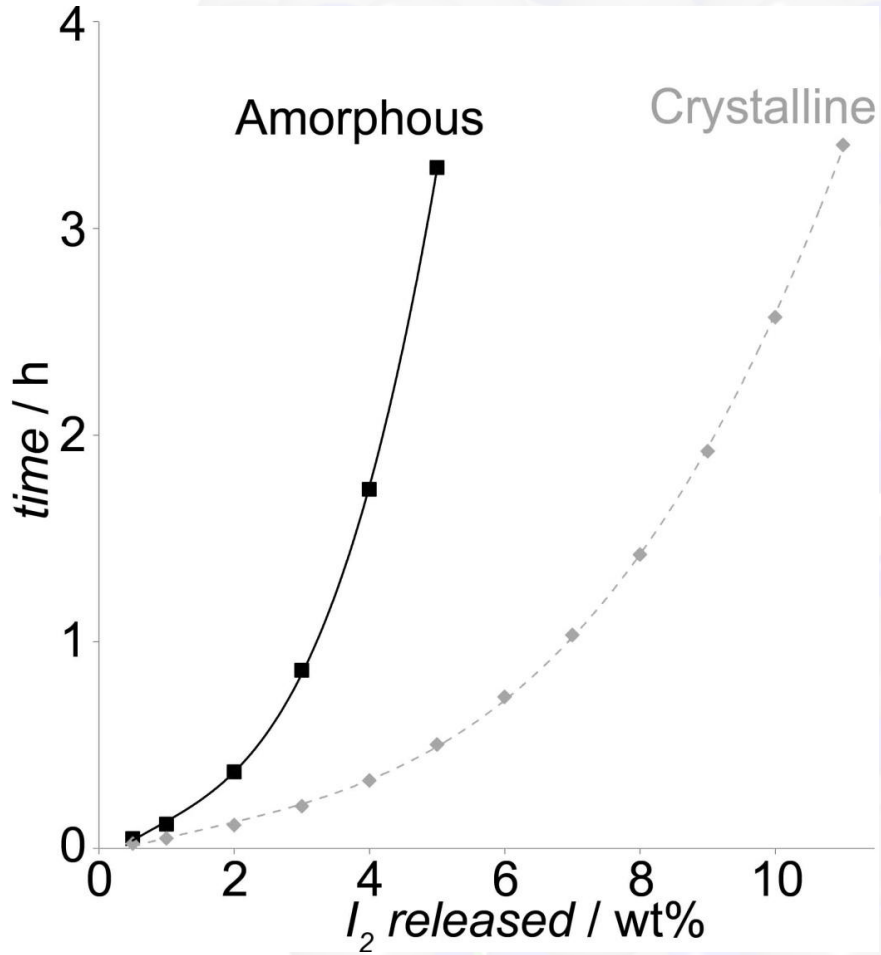
Enhanced guest retention through amorphization



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

Interim waste form: desorption kinetics are retarded in the amorphized material

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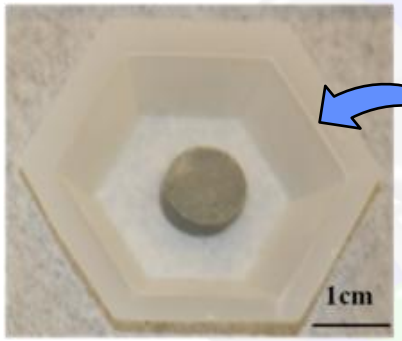
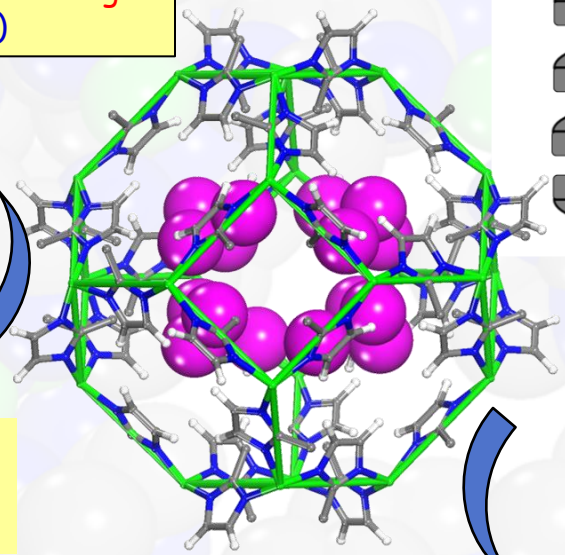
IIc. I_2@ZIF-8 successfully encapsulated in stable long-term waste forms

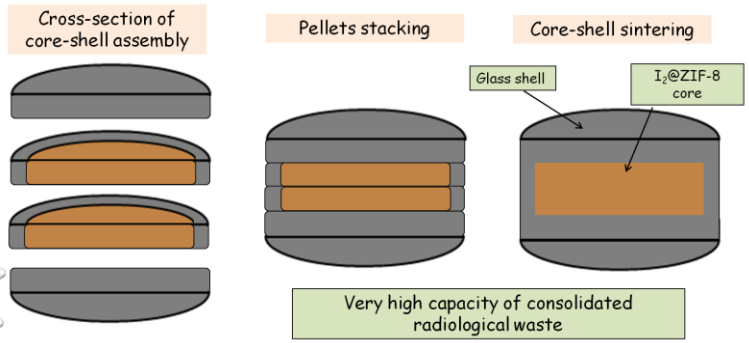
TA #SD11720, Provisional Patent 2012

Incorporation into Low Temperature Glass Composite Materials (GCM)

80 wt.% glass, 10 wt.% I_2@MOF, 10 wt% Ag
(non-optimized compositions)







GCM reveal excellent thermal & chemical stability and are appropriate for long term storage

Sava, D.F. et. al *Ind. Eng .Chem. Res*, **2012**, 51 (2), 614-620. Invited paper for the thematic Nuclear Energy special issue

Glass	ZnO		Bi_2O_3		Al_2O_3		SiO_2	
	mole %	wt. %	mole %	wt. %	mole %	wt. %	mole %	wt. %
EG 2922	14.2	7.8	20.2	63.4	7.8	5.4	57.8	23.4

Long-term core-shell waste form

The core consists of amorphized I_2@ZIF-8 pellets, and the barrier shell is made of the low-temperature sintering glass EG2922.

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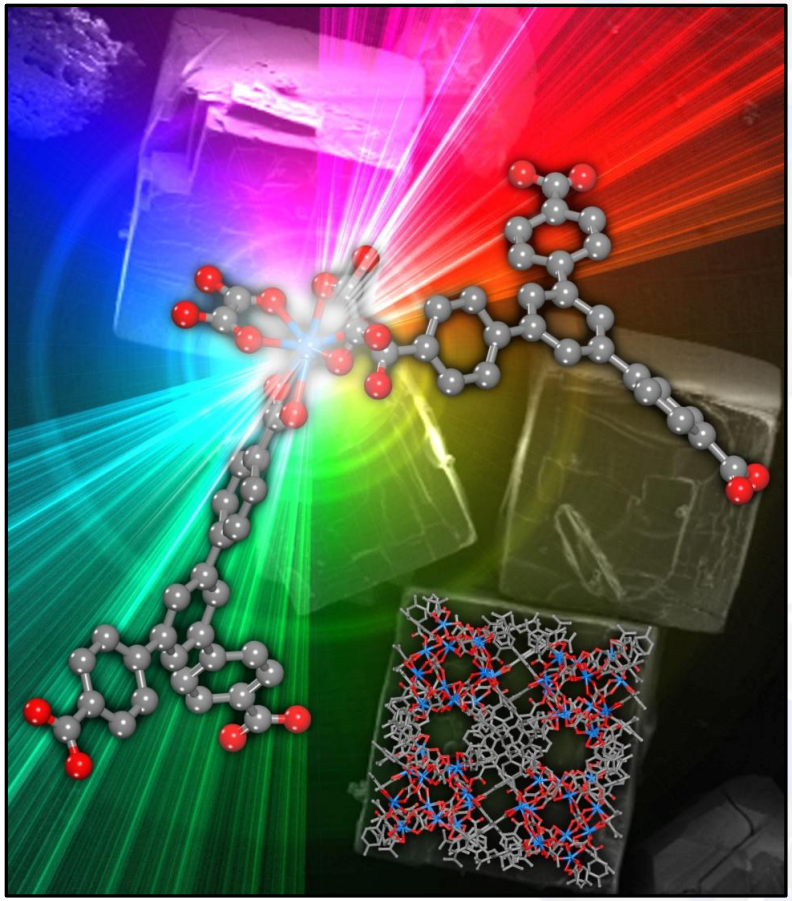
III. Novel MOFs with Tunable Color Properties



- White light from a *single phosphor* - alternatives are sought to existing color mixing approaches

- Current white LEDs for SSL: InGaN LEDs excite a yellow-emitting YAG:Ce phosphor- *cool white light made warmer* by incorporating a red-emitting phosphor

- Warm white LEDs: near-UV InGaN LEDs to excite blends of red-, green-, and blue-emitting phosphors → the additional down-conversion step (near-UV to blue) *significantly lowers the conversion efficiency of the device.*

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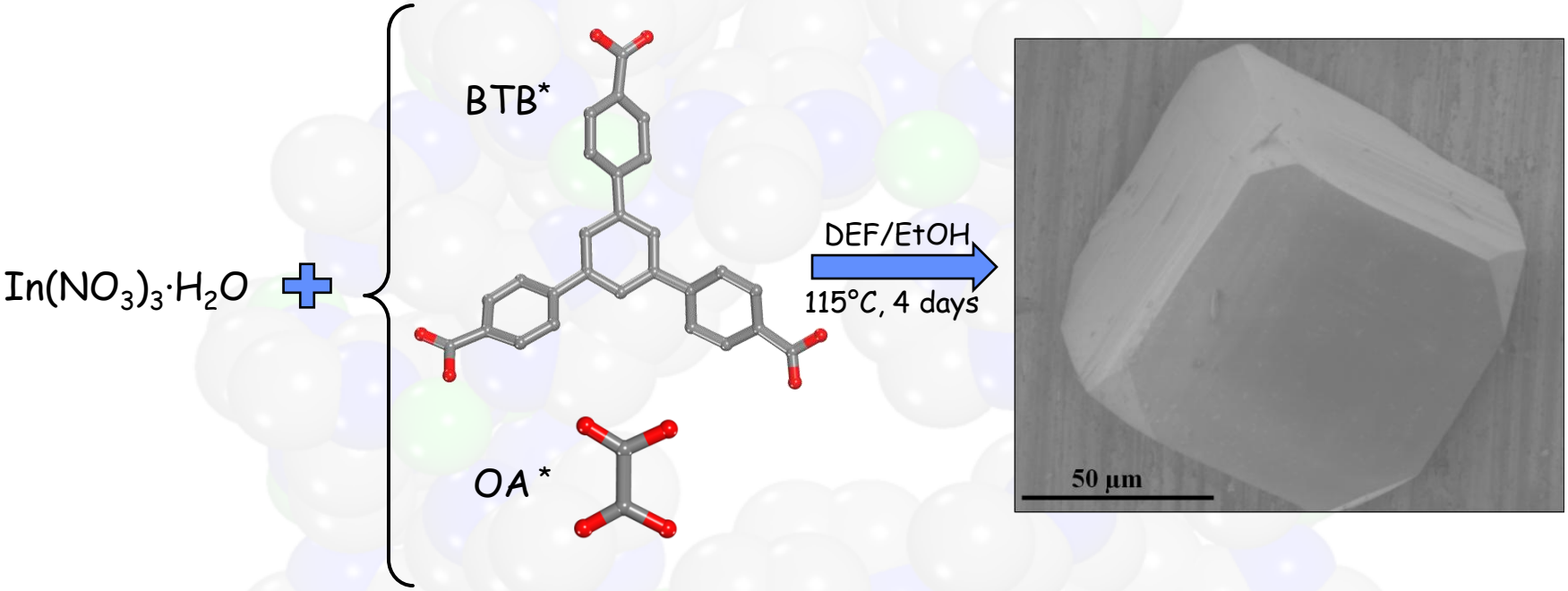
SMOF-1 (Sandia Metal-Organic Framework-1): a tunable novel In-BTB framework



✓The first In-BTB reported net

✓The first oxalic acid-BTB system explored to date

Cubic, 3-periodic

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

* BTB (4,4',4'' -benzene-1,3,5-triyl-tri-benzoic acid)
* OA (oxalic acid)

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Sava, D.F. et.al, *J. Am. Chem. Soc.* **2012**, 134 (9), 3983.

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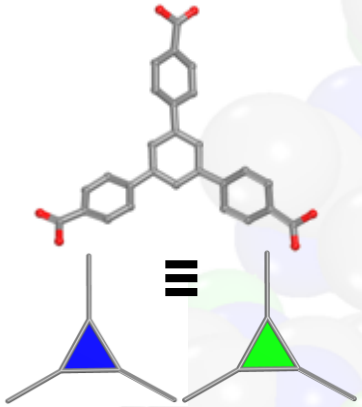
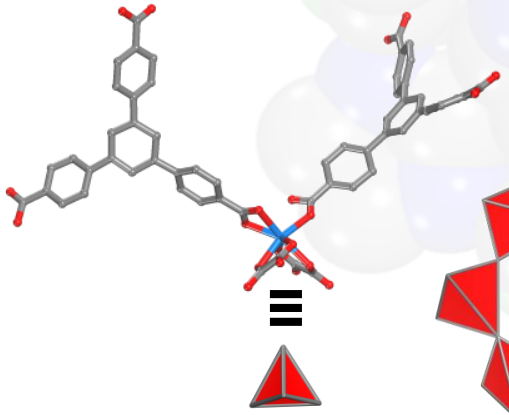
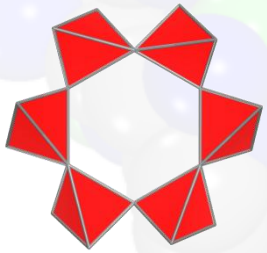
Topological evaluation: unprecedented (3,3,4) trinodal net

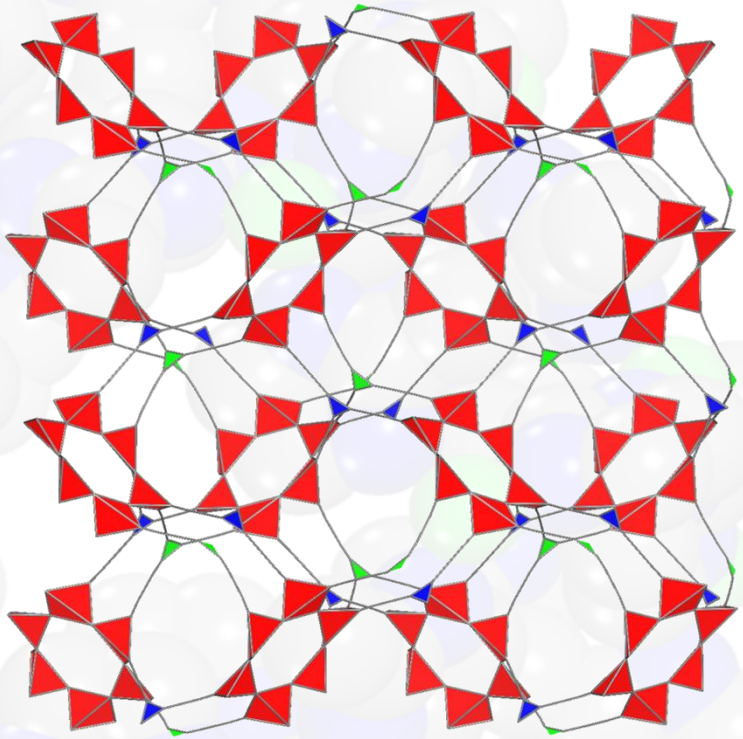


Two topologically distinct
3-connected nodes





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: $\{6^3.8^3\}3\{6^3\}2$

dfsava@sandia.gov

TOPOS Blatov, V. A. *IUCr CompComm Newsletter* **2006**, *7*, 4.

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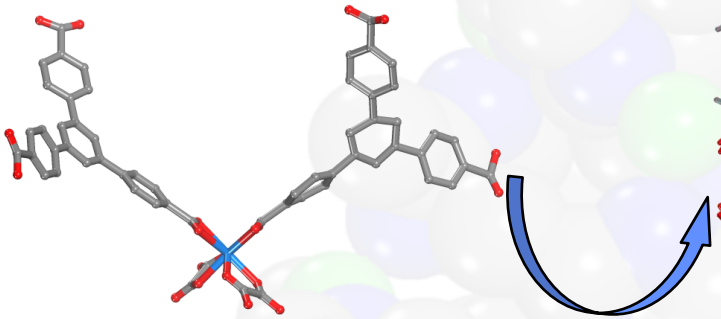
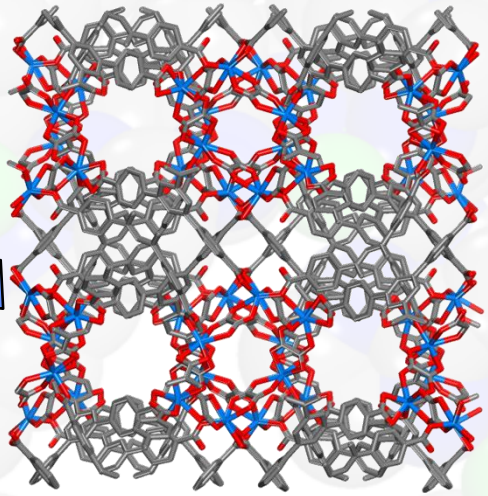
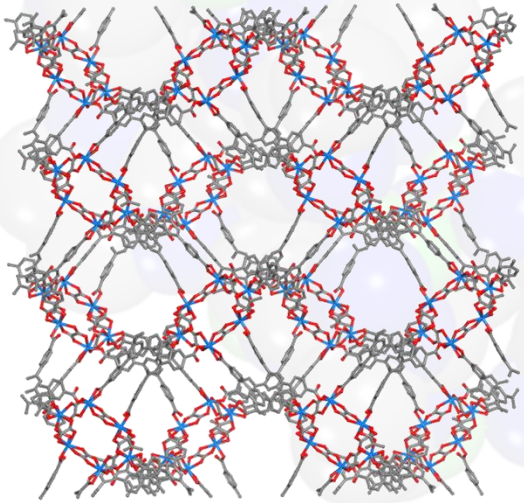
Complementary structural features direct enhanced linker interactions

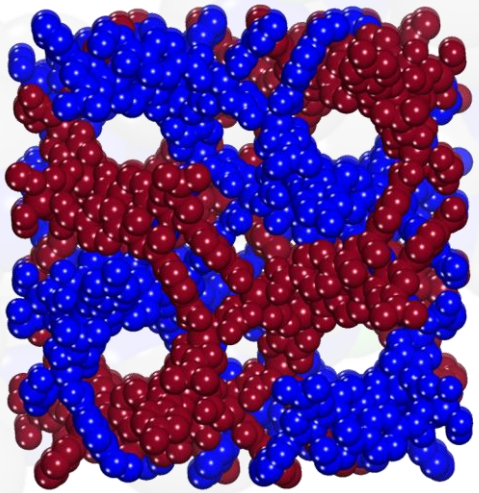




$In(BTB)_{2/3}(OA)(DEF)_{3/2}$

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





Corrugation ⟺ Interpenetration

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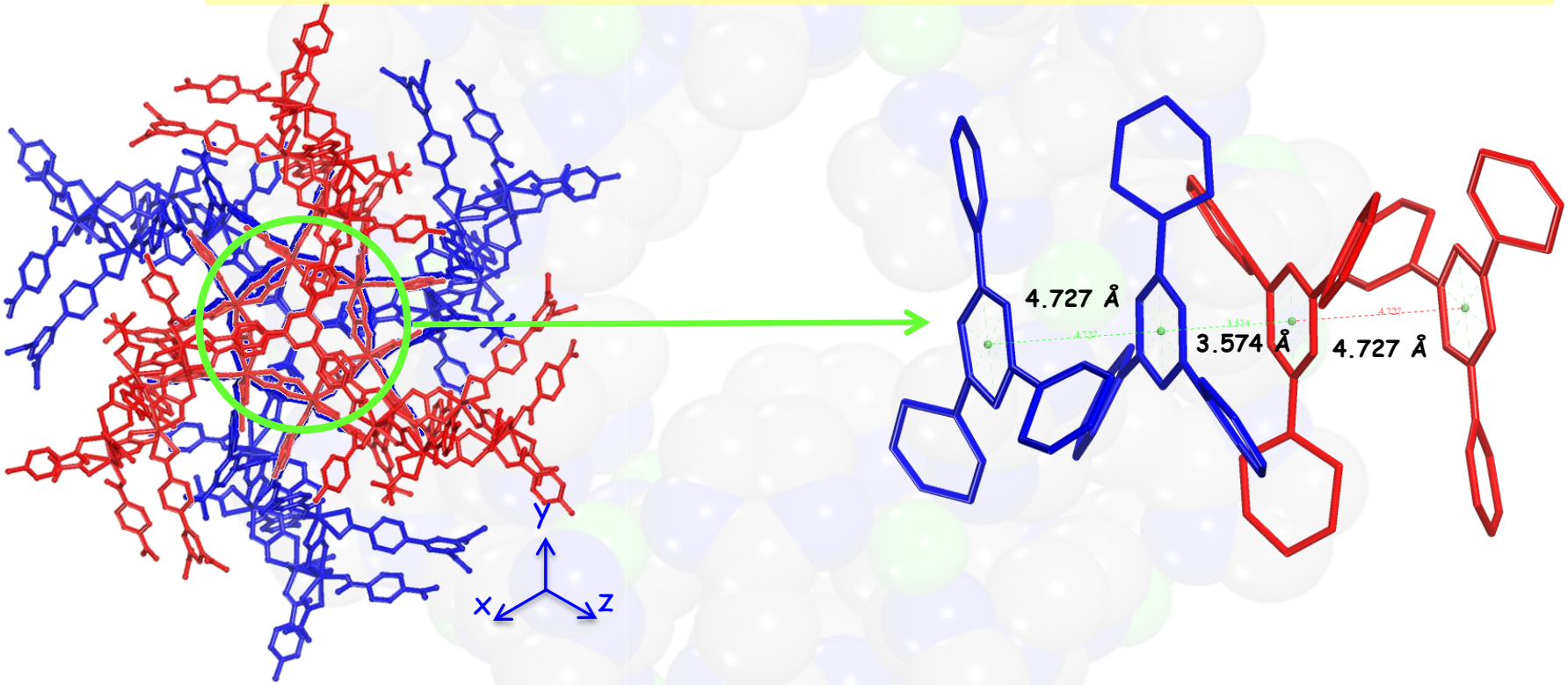
Photoluminescence originates from the unique arrangement of the conjugated aromatic rings

The structure-function relationship in SMOF-1 is driven by two complementary unique structural features: corrugation and interpenetration



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

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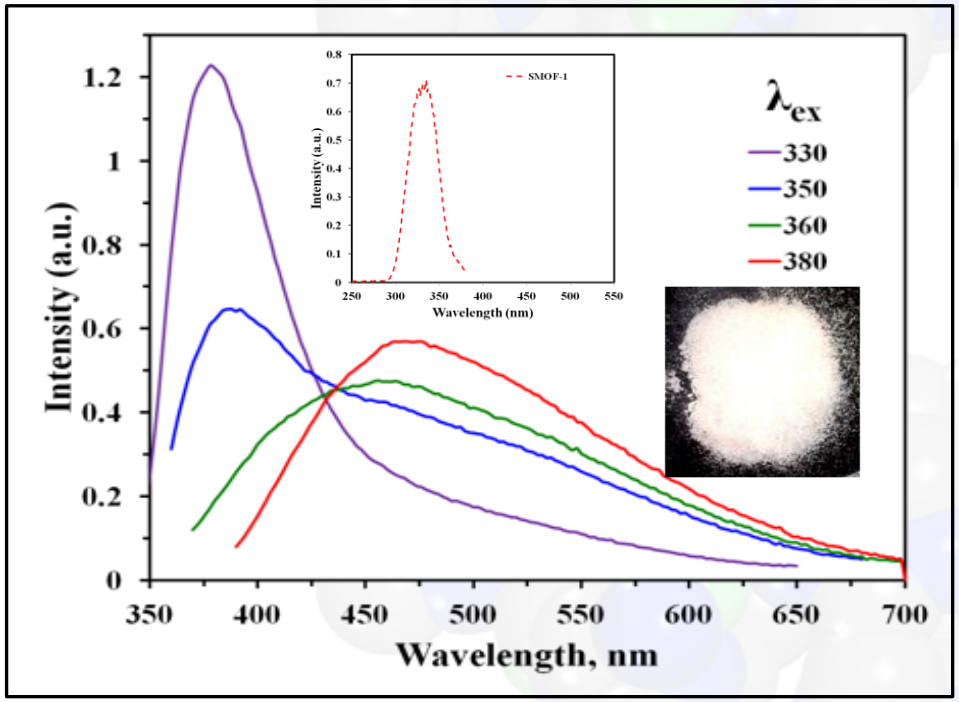
SMOF-1 framework: direct broadband white-light emitter

White-light emission in SMOF-1 is due to a combination of π---π* aromatic interactions and ligand to metal charge transfer (LMCT)



Excitation and emission spectra in SMOF-1

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/

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

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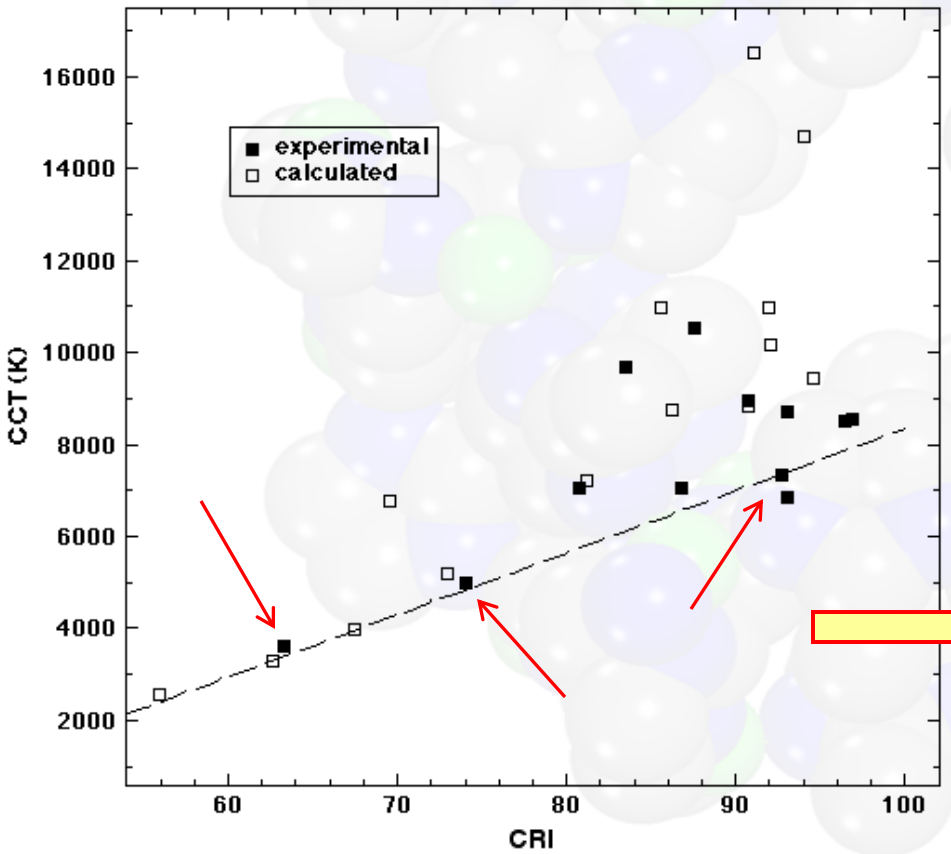
Optimized color properties via simulated spectra

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.

- 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

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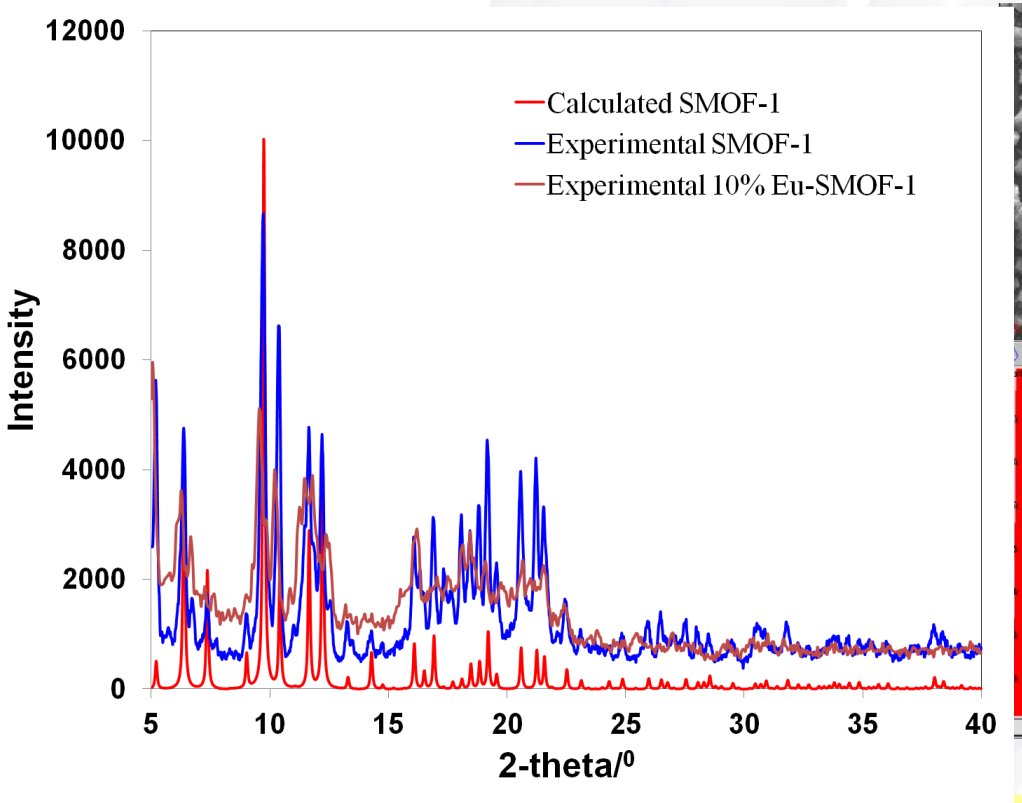
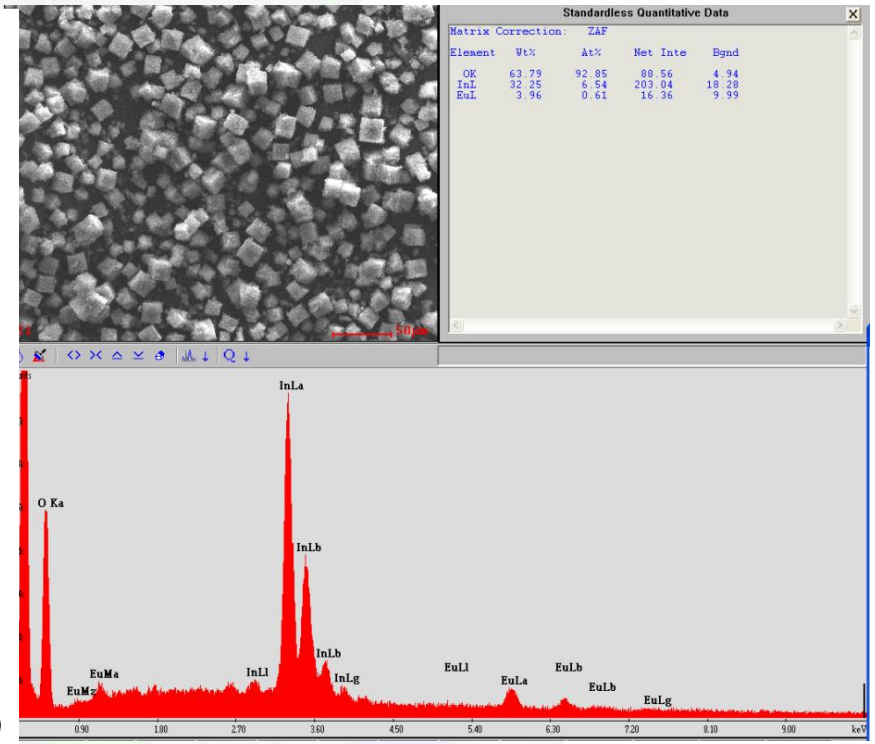
Successful in-framework Eu co-doping at 2.5, 5, and 10%



SEM-EDS



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.

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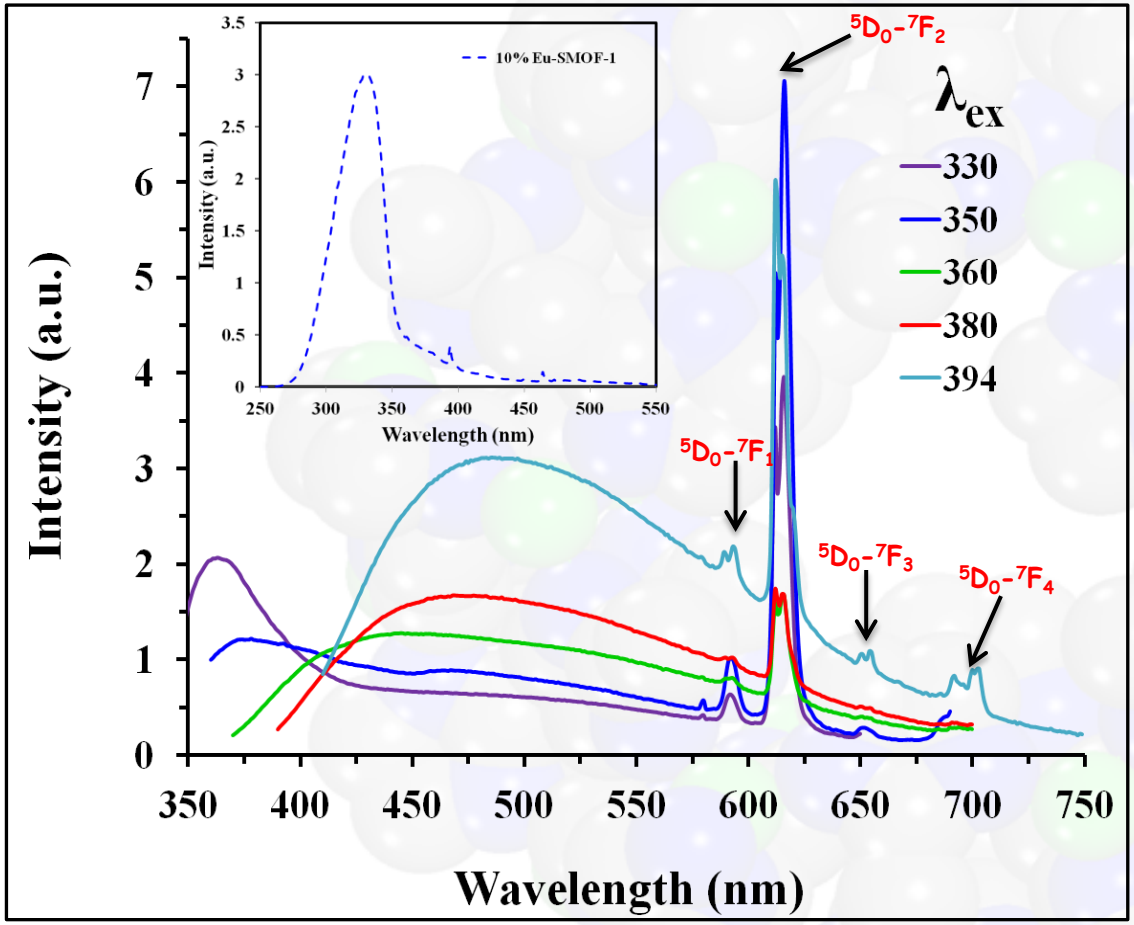
Enhanced system tunability: improved color properties with in framework 10% Eu co-doping



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

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

Absolute QY ~ 4.3% at 330nm

dfsava@sandia.gov

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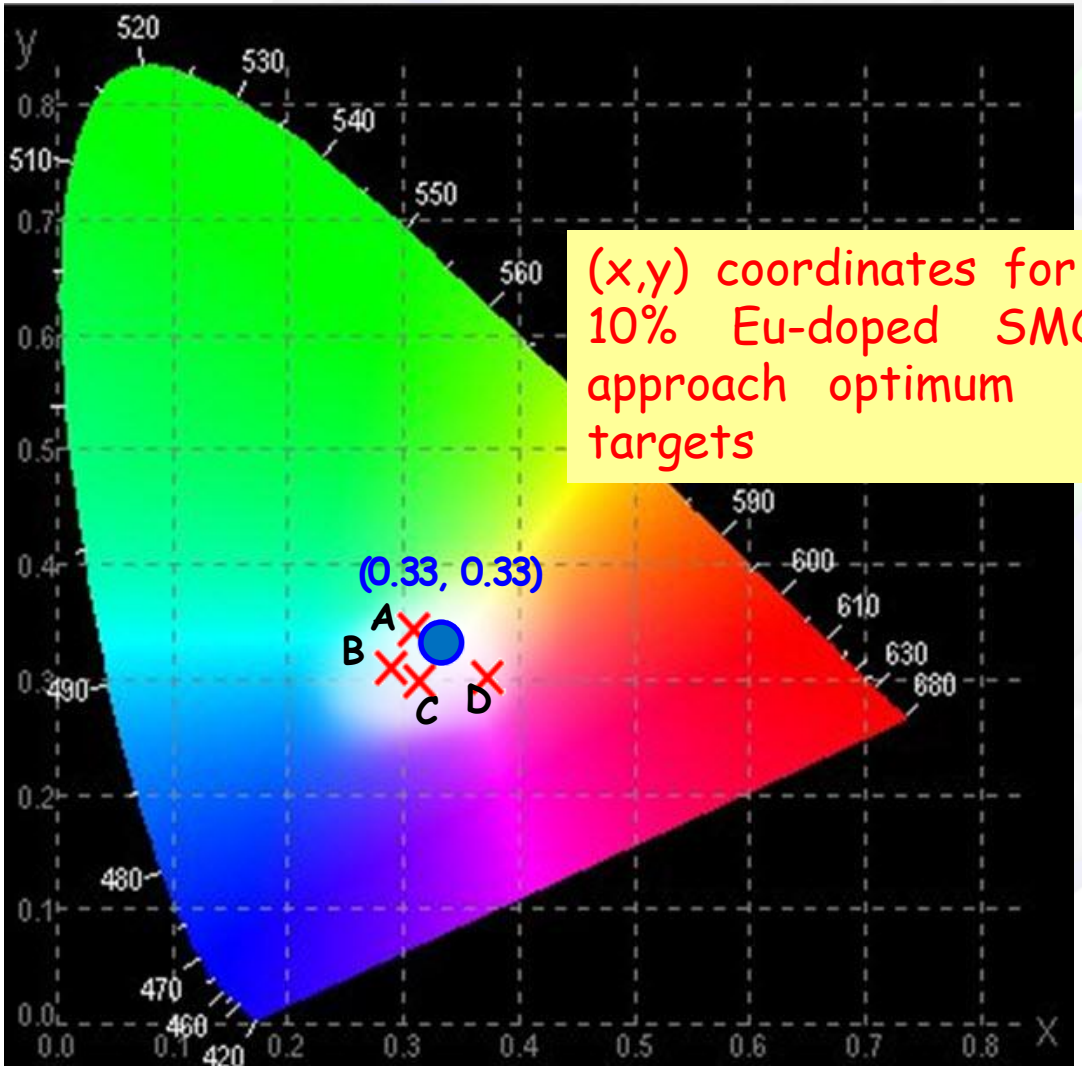
CIE* optimum white-light chromaticity coordinates: (0.33, 0.33)



(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.

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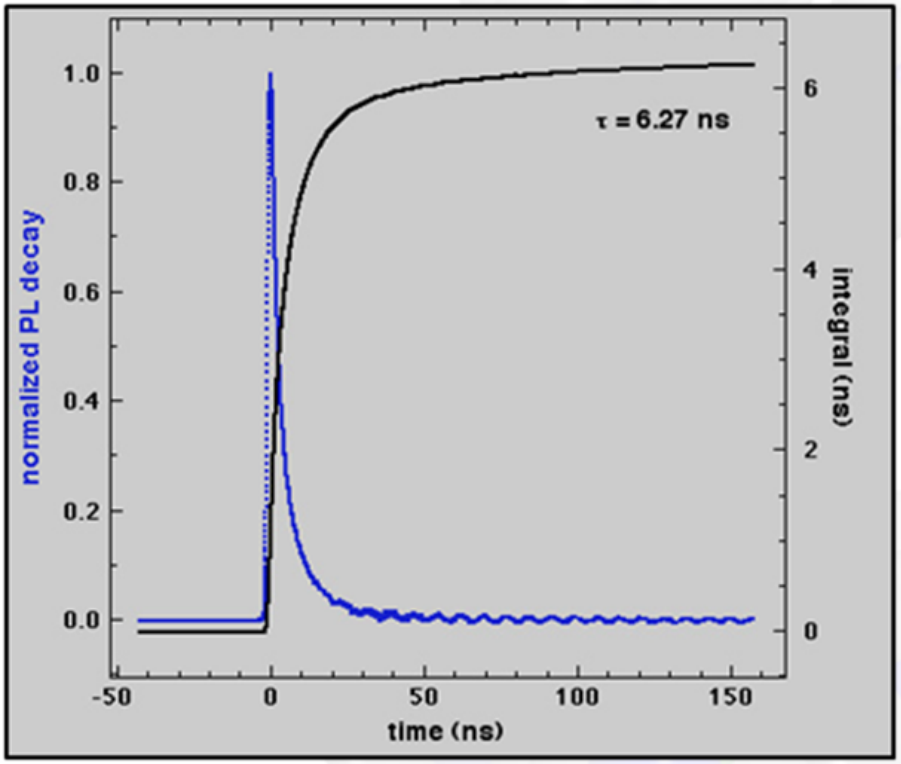
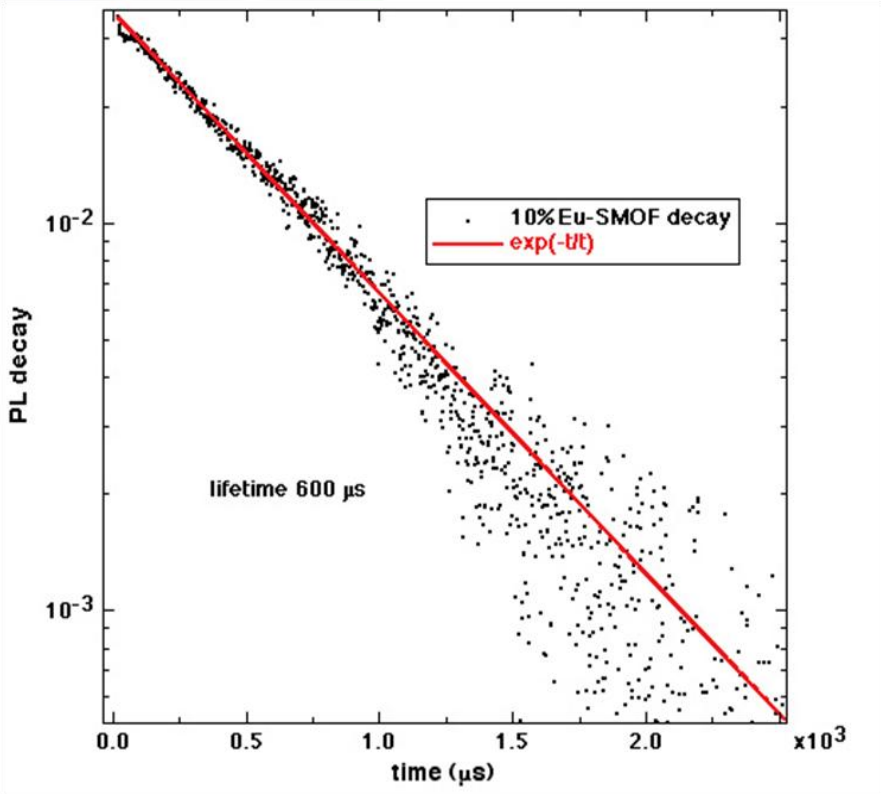
Framework tunability is reflected in the PL lifetime



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



10% doped Eu-SMOF-1 harmonic average lifetime **600 µs**

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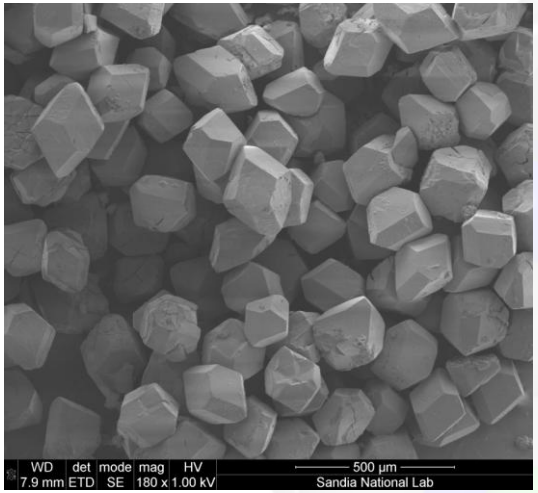
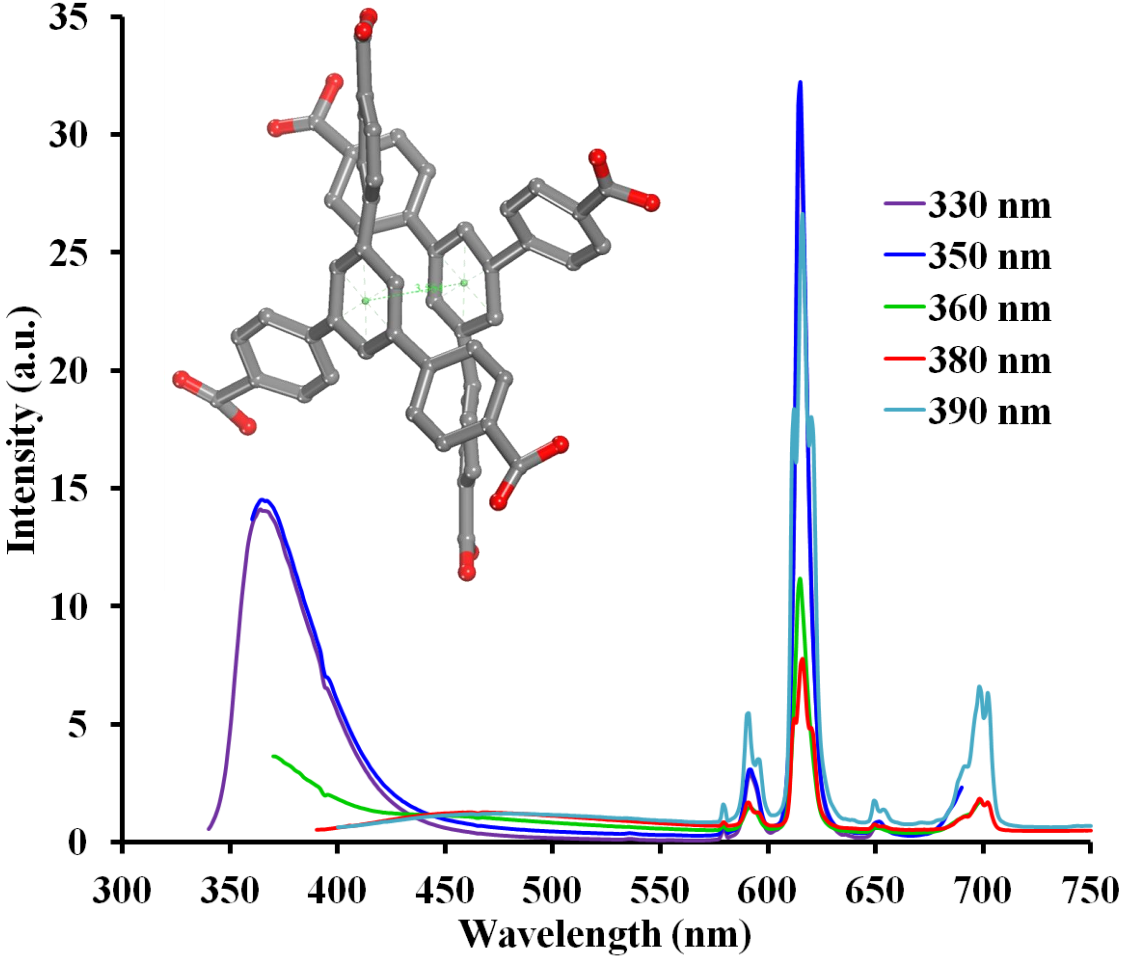
On-going studies
SMOF-2: a novel In-30% Eu- BTB framework red emitter



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 %

dfsava@sandia.gov

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

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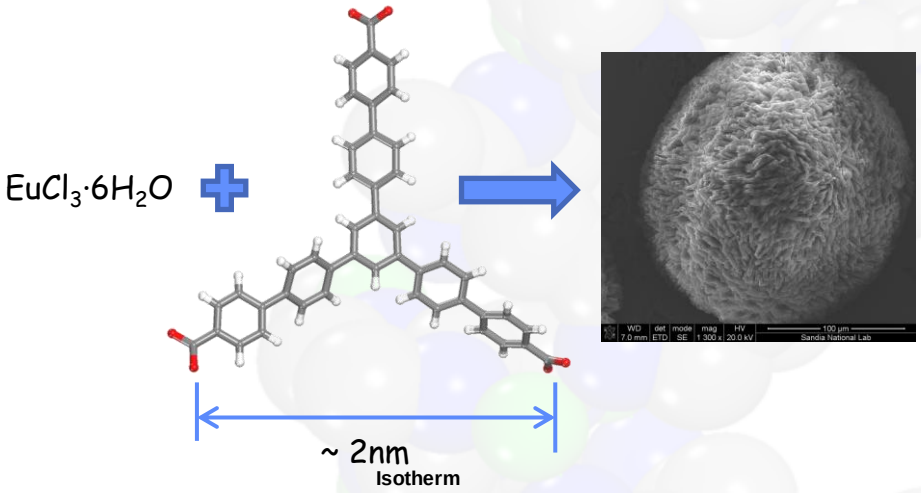
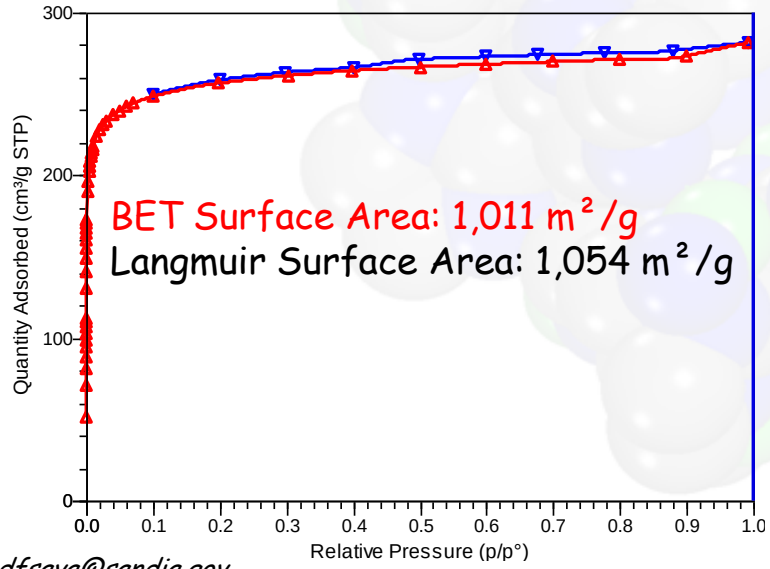
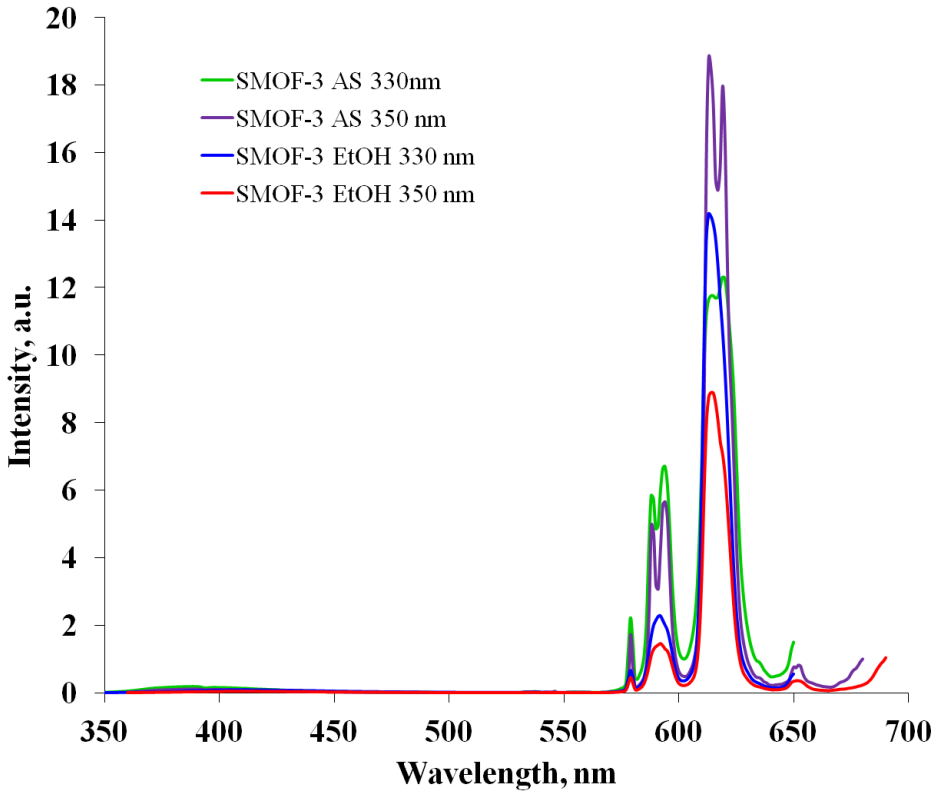
SMOF-3: a novel Eu-TCBB framework red emitter

SMOF-3:
› 115 wt% I_2 sorption ability (non-optimized)







Absolute QY ~ 21 %

dfsava@sandia.gov

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

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Summary and On-going studies

- MOFs modularity and tunability allows for a variety of energy related applications
- Introduced MOFs in nuclear waste remediation and demonstrated that ZIF-8 is an appropriate candidate for I_2 *capture and interim storage*
- I_2 is retained in ZIF-8 under amorphizing conditions providing for *consolidated secure interim storage* before incorporation into a long term waste form, ensuring non-contamination of the environment
- Developed a prototype novel MOF material featuring intrinsic broadband direct white light emission and derived a tunable platform which allows for the modifications of associated color properties
- Incorporation of MD simulations and GCMC modeling with structure analysis to study
  - competitive gas sorption from industrially relevant complex streams
  - establish binding locations, mechanisms of sorption and transport in HKUST-1 vs. ZIF-8
- On-going studies into novel MOFs , as well as pre- or post-synthesis framework functionalization for enhanced absolute quantum yields

dfsava@sandia.gov

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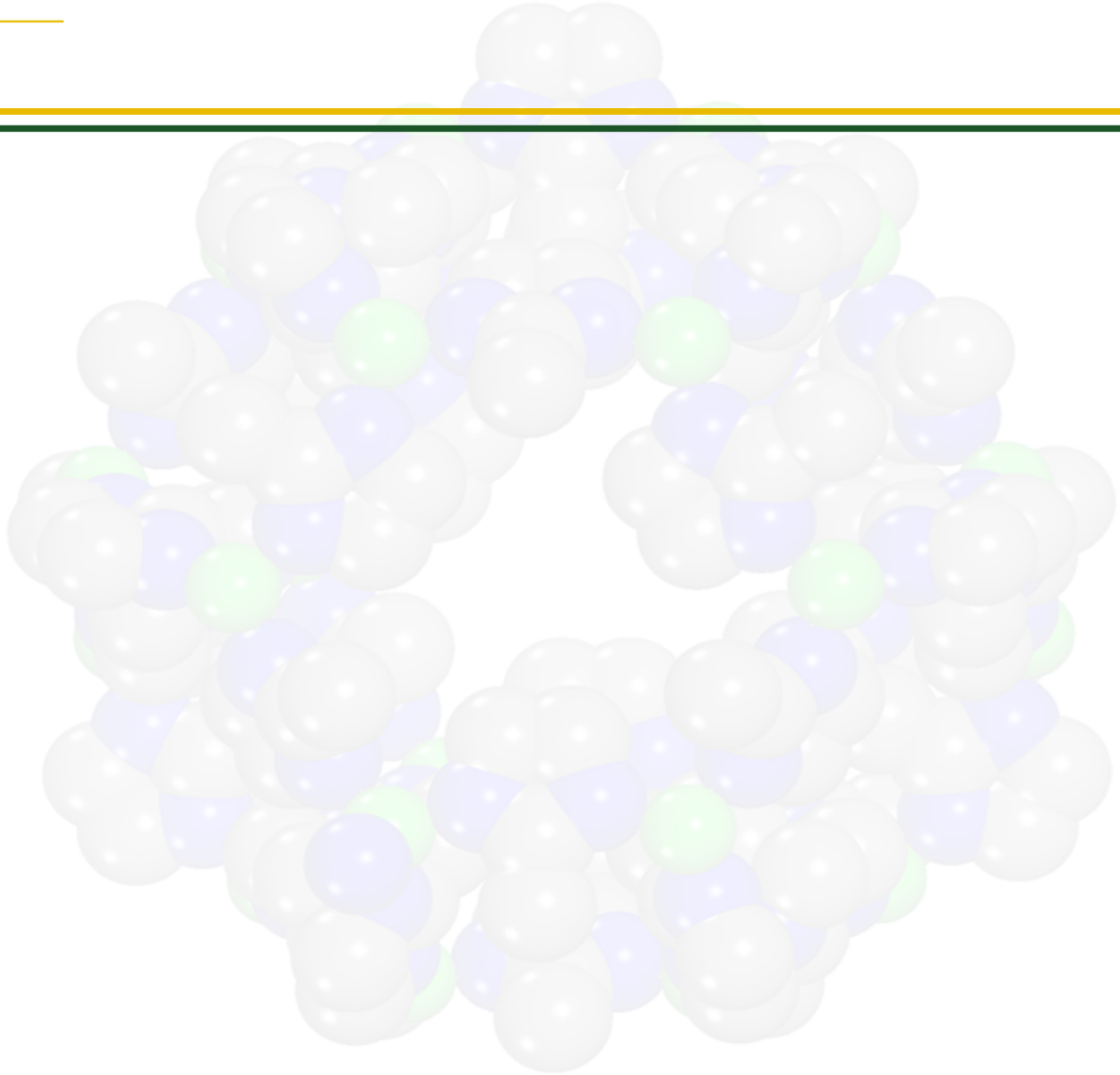

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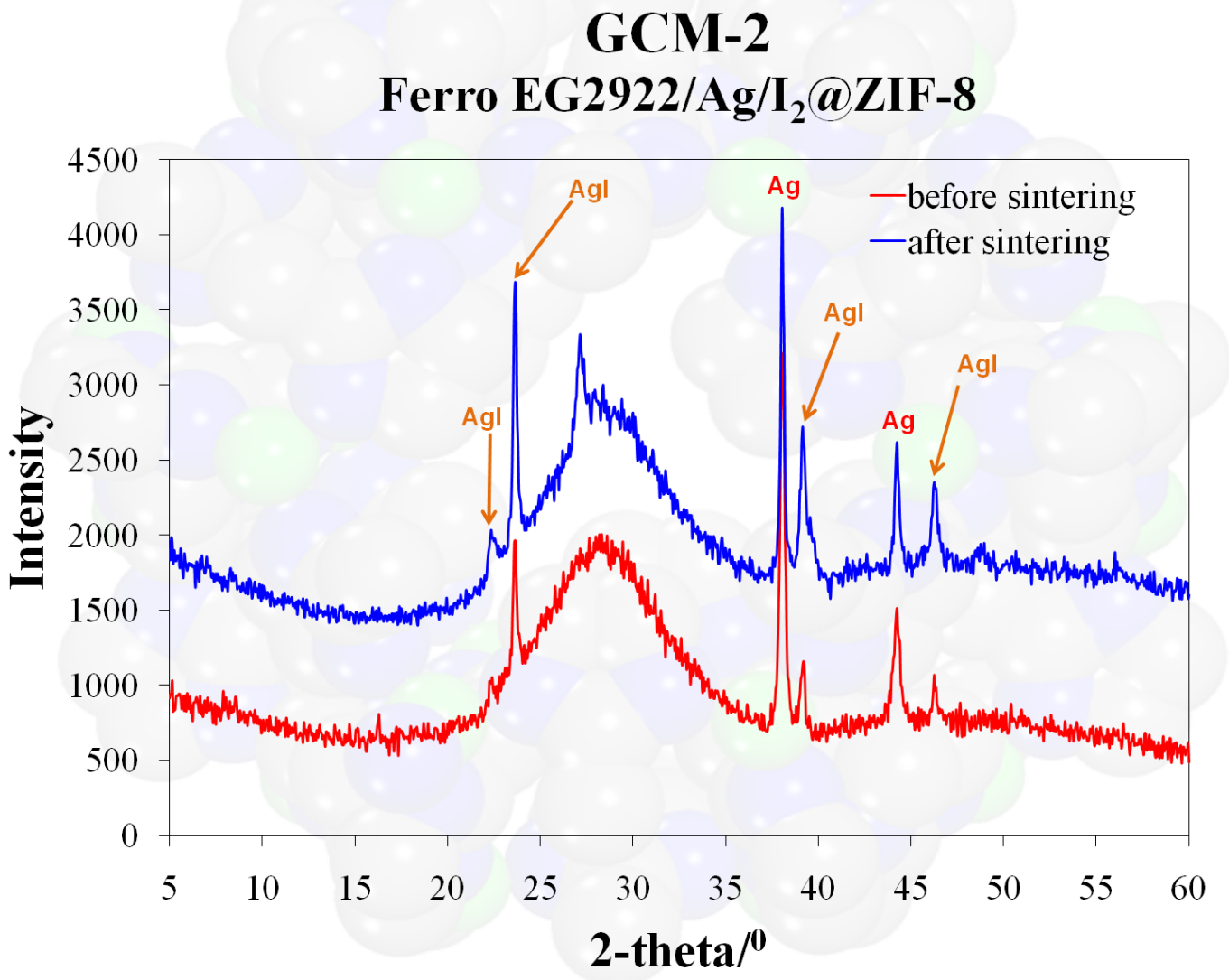
Powder X-ray diffraction pattern for GCM-2 before and after thermal treatment



D.F. Sava, dfsava@sandia.gov

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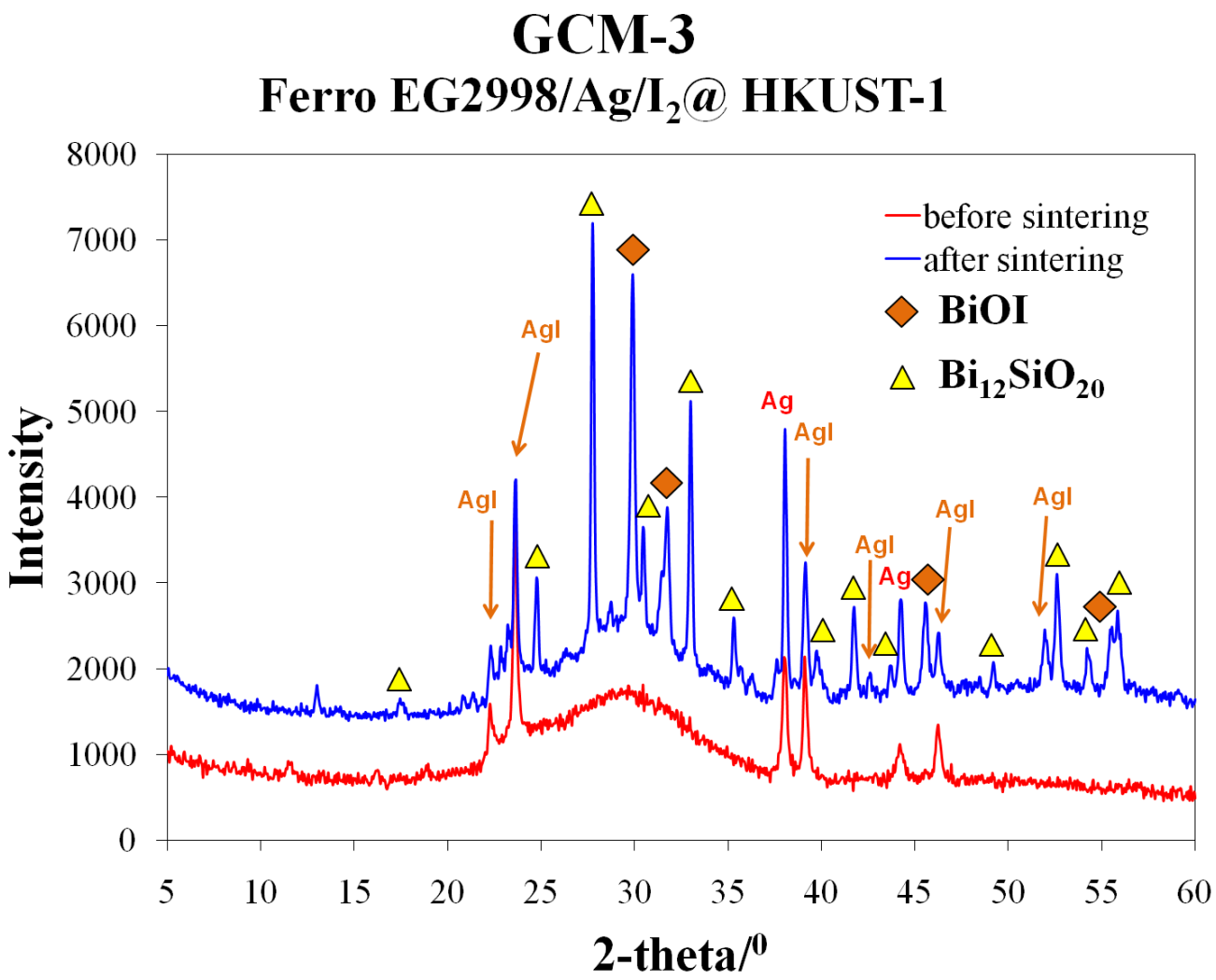
Powder X-ray diffraction pattern for GCM-3 before and after thermal treatment



D.F. Sava, dfsava@sandia.gov

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Bi-Zn oxide low-temperature sintering glasses

80 wt.% glass, 10 wt.% I_2@MOF, 10 wt% Ag (non-optimized compositions)

Glass characteristics	*EG2998	*EG2922
Composition	Bi-Zn-B	Bi-Zn-Si
Sintering temperature	500°C	525°C–550°C
Crystallinity	Crystallizing	Vitreous
Density	5.65 g cc^{-1}	5.8 g cc^{-1}

Glass	ZnO		Bi_2O_3		Al_2O_3		B_2O_3		SiO_2	
	mole %	wt. %	mole %	wt. %	mole %	wt. %	mole %	wt. %	mole %	wt. %
EG 2922	14.2	7.8	20.2	63.4	7.8	5.4			57.8	23.4
EG 2998	49.7	26.9	18.9	58.6			31.3	14.5		

D.F. Sava, dfsava@sandia.gov

*purchased from Ferro Corporation

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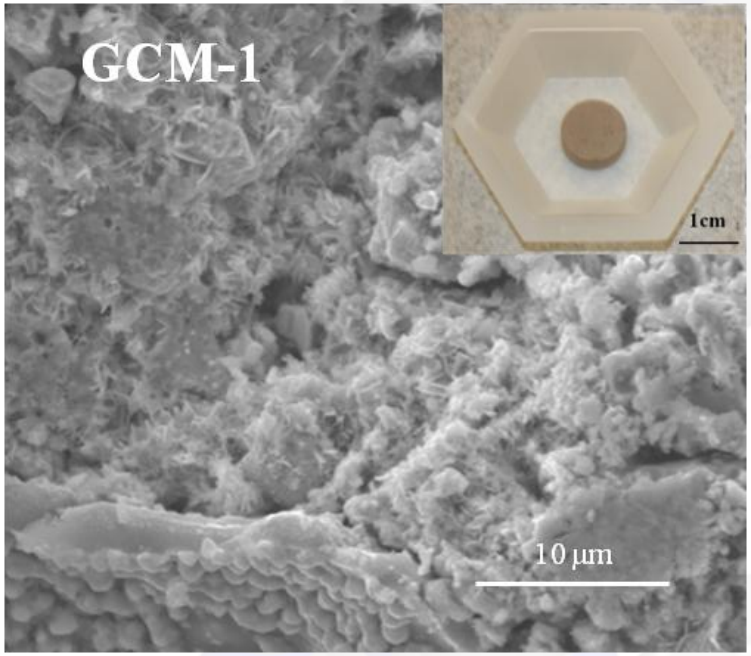
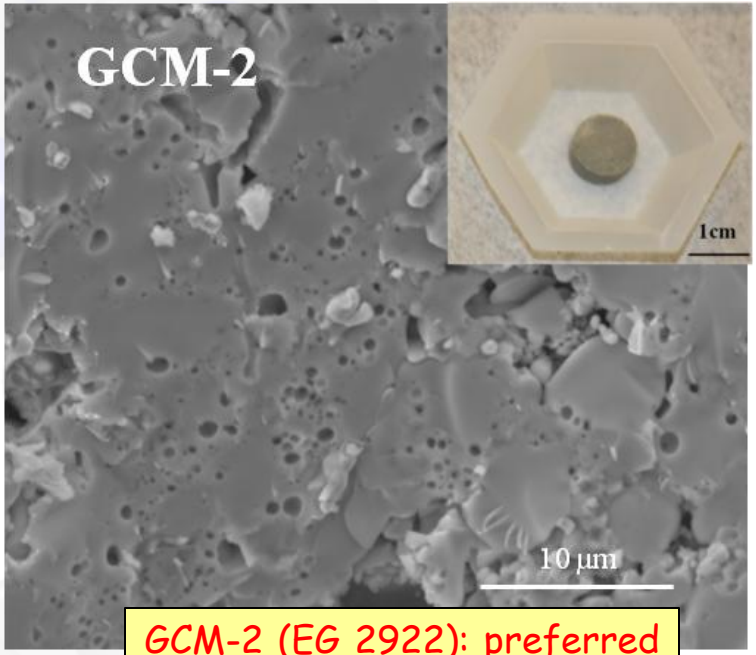
I_2@ZIF-8 successfully encapsulated in stable long-term waste forms





GCM-2 (EG 2922): preferred waste form based on higher leach durability studies

GCM reveal excellent thermal & chemical stability and are appropriate for long term storage: little to no I_2 is lost during processing or after undergoing leach durability studies

Sava, D.F. et. al *Ind. Eng .Chem. Res*, **2012**, 51 (2), 614-620.
invited paper for the thematic Nuclear Energy special issue

D.F. Sava, dfsava@sandia.gov

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Successful sintering of core-shell structures containing amorphized I_2@ZIF-8 pellets

Compact monoliths comprise high-capacity consolidated radiological waste content for extended storage (1 pellet); scale up to date: 5 pellets per shell

D.F. Sava, dfsava@sandia.gov

US provisional patent, submitted 2012
Garino, T,J. et. al *J.Am.Cer.Soc.* **2011**, *94*, 2412-2419.

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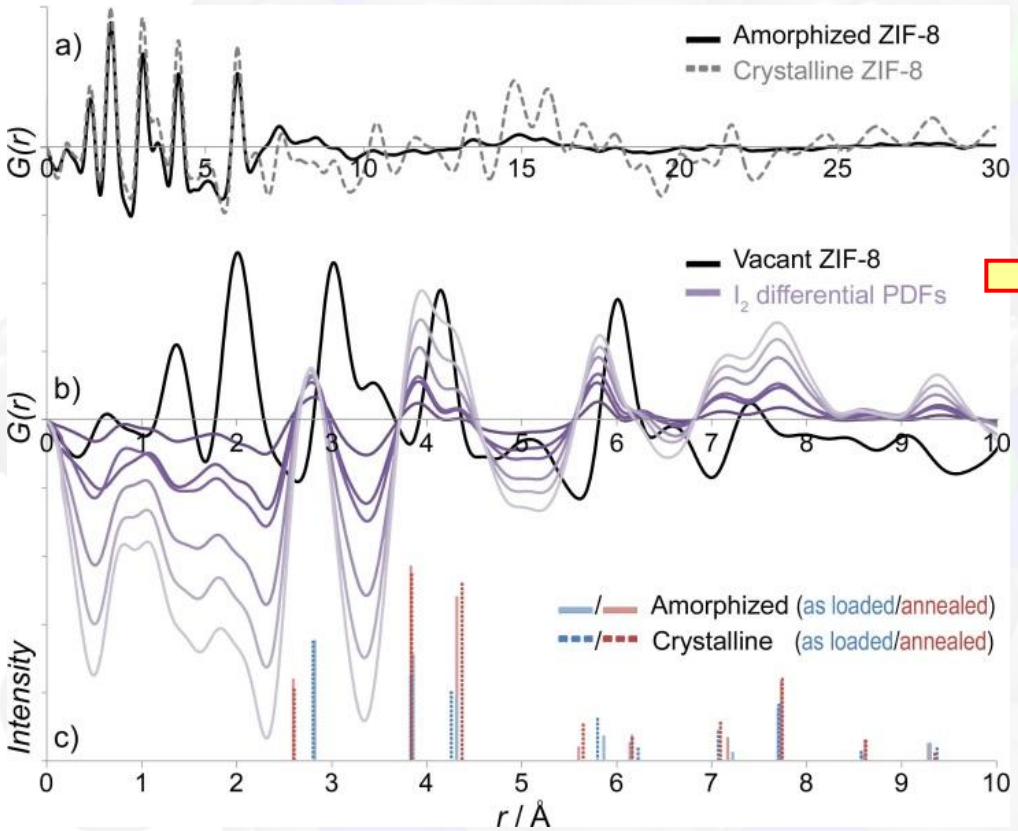
The short-range I···I and I···framework interactions remain unchanged upon amorphization



The framework retains I_2 after pressure treatment

High resolution synchrotron PDFs and differential PDFs collected at APS/ANL for the crystalline and amorphous materials

D.F. Sava, dfsava@sandia.gov

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