

Nanoscale manipulation of metal organic frameworks for tuned energy and environmental applications

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In Honor of Prof. Michael O'Keefe and Prof. Omar Yaghi

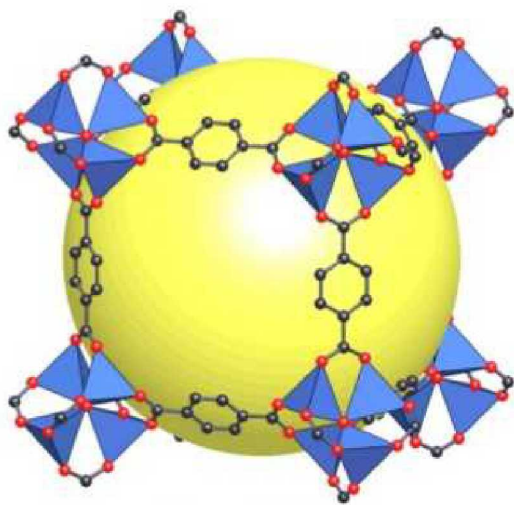
Seamless melding of designed periodic crystal structures and synthesized nanoporous periodic frameworks: (*Chem. Rev.* **2014**, *114*, 2, 1343)

establish structure-property relationships that drive new discoveries in material science & enables real-world applications

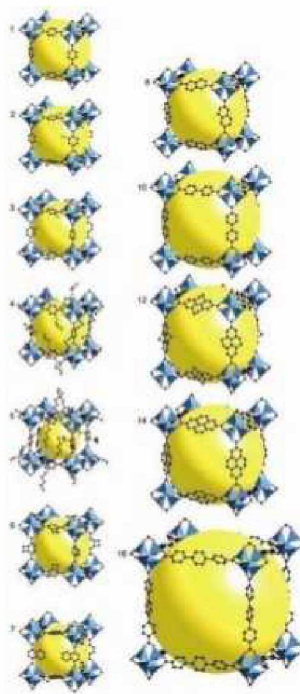
Exception team work

MOFs, COFs, ZIFs, ...

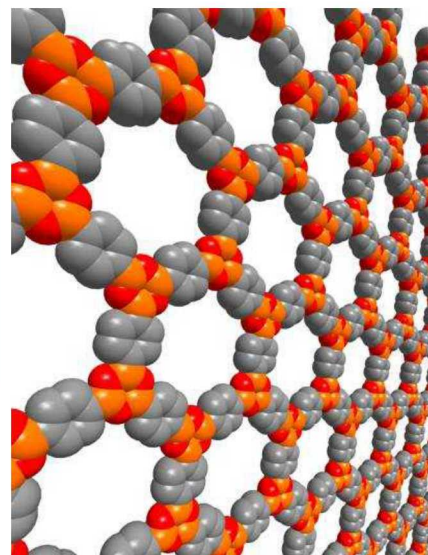
MOF-5 with exceptional surface area (3,000 m²/g), and control of its metrics and functionality



Nature 1999

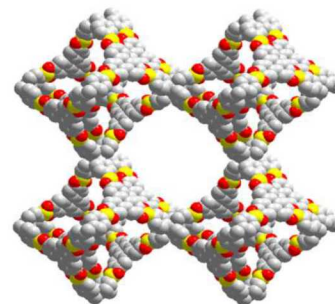


Science 2002



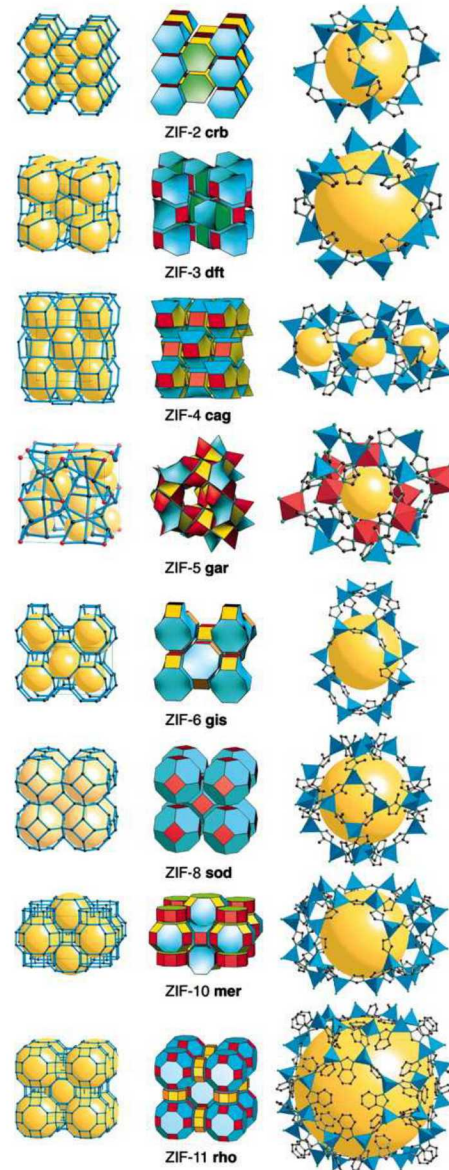
Science 2007
Acc. Chem. Res. 2015

3D COF



COF-108

PNAS 2006



ZIF-2 crb

ZIF-3 dft

ZIF-4 cag

ZIF-5 gar

ZIF-6 gis

ZIF-8 sod

ZIF-10 mer

ZIF-11 rho

In Honor of Prof. Michael O'Keefe and Prof. Omar Yaghi

Commitment to RC community, Links to complimentary Communities

Reticular Chemistry Structure Resource (RCSR)

<http://rcsr.anu.edu.au/>

RCSR

HOME ABOUT LINKS SYSTRE 3D NETS 2D NETS POL

Welcome to the
Reticular Chemistry
Structure Resource



School of Molecular Sciences,
Arizona State University



Australian
National
University
Department of Applied Mathematics,
Australian National University



NCI Vizlab,
Australian National University



College of Chemistry,
University of California, Ber

Additional hosting by

Berzelli Center EXSELENT
Stockholm University

RCSR

Search 3D Nets

HOME ABOUT LINKS SYSTRE 3D NETS

Locations: rcsr

Search Clear

Symbol ?

is

Names ?

is

Keywords ?

- ☐ bipartite
- ☐ clathrate
- ☐ polar
- ☐ quasisimple tiling
- ☐ rod net
- ☐ semiregular net
- ☐ uniform net
- ☐ weaving
- ☐ chiral
- ☐ good
- ☐ quasiregular net
- ☐ regular net
- ☐ self dual net
- ☐ simple tiling
- ☐ uniform tiling
- ☐ zeolite net

Modifiers

- ☐ include augmented (-a)
- ☐ exclude augmented (-a)
- ☐ exclude binary (-b...) and catenated (-c...)

Coordination ?

Embed Type ?

Bounds ?

density ?
td10 ?
genus ?
degrees of freedom ?
kinds of vertex ?
kinds of edge ?
kinds of face ?
kinds of tile ?
space group number ?
smallest ring ?
order ?
Dsize ?

Search Clear

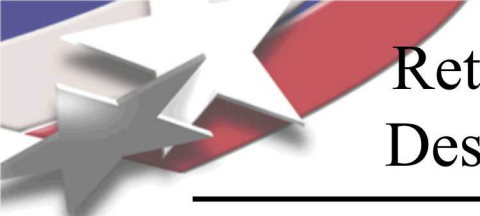
Symbols Only

Previous

Next »

Found 2910 nets matching your search, showing 1 through 12.

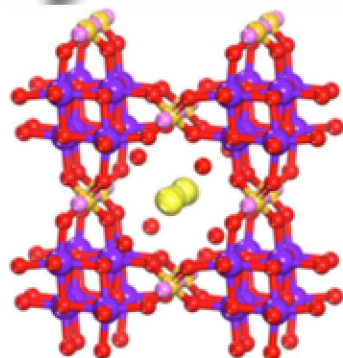
pic	symbol	embed type	space group	vertices	edges	genus
	aab	1b	Pmmm	19	32	85
	abb	1b	Pmmm	19	32	85
	abf	1b	I-4m2	3	3	5
	abr	1b	P4(2)/mcm	3	3	15
	aca	1	P6(3)/mmc	3	2	23
	aca-a	1	P6(3)/mmc	4	10	79
	acs	1b	P6(3)/mmc	1	1	5
	acs-a	1b	P6(3)/mmc	1	3	13
	acs-b	1b	P-6m2	2	1	5
	acs-f	1b	P-31c	1	3	7
	acs-g	1b	P6(3)22	1	3	7
	acs-h	1b	P-31c	1	4	19



Reticular Chemistry: Influenced from Zeolites, Designed via Modeling, Guided by Application

- Technical Focus, Nenoff Research Group:
Chemical study of confinement and reactivity of ions and molecules in micro- and nano-porous materials
 - zeolites, metal-organic frameworks (MOFs), clays and amorphous silicas
- The study of **Structure-Property Relationships** on the nanoscale enabling the informed testing of the materials for a wide range of interests. Use of synchrotron (APS/ANL) and neutron (SNS/ORNL) sources for atomic scale resolution.
- Our group spans from *basic to applied to commercialization* of novel materials.
- **Strong Interdisciplinary Teams** working in concert.
 - diverse programs require diverse teams
 - chemists, engineers, computational modelers, technoeconomic analysis/tech transfer
 - national labs, universities and industry
- **O'Keefe/Yaghi Inspired R&D discussion in three topic areas:**
 - 1) High selectivity rad ion & capture nanoporous materials
 - 2) Gas separations nanoporous materials & membranes
 - 3) Photoluminescence MOFs

R&D Area 1: Novel nanoporous materials for Rad Ion & Gas Separations and Storage



R&D100 1996

JACerS, 2009, 92(9), 2144

JACerS, 2011, 94(9), 3053

Solvent Extr. & Ion Exch, 2012, 30, 33

CST, Cs⁺ removal from water to Pollucite Waste Form

US Patents 6,479,427; 6,110,378

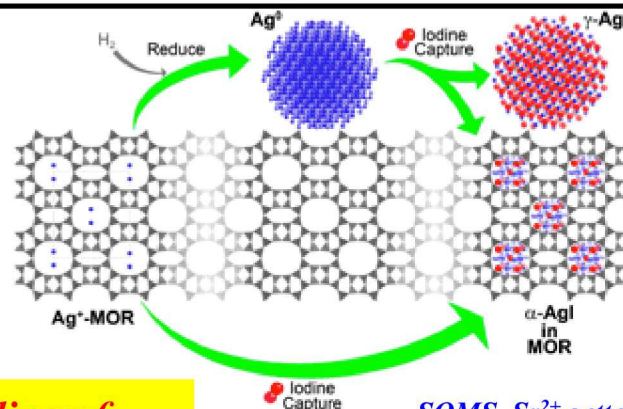
I₂/ZIF-8, Isolation to Waste Form

JACS, 2011, 133(32), 12398

US Patent filed 2012

JACS 2013, 135, 16256

Fundamental understanding of what controls ion or gas selectivity, through structure-property relationship studies



Ag-MOR

I₂(g) capture & mechanisms

JACS, 2010, 132(26), 8897

J Phys Chem Lett, 2011, 2, 2742

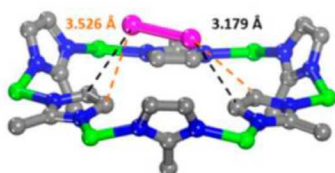
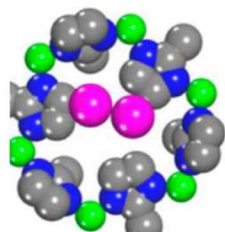
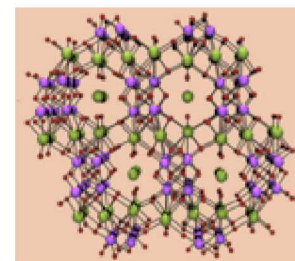
I&ECR 2017, 56(8), 2331

SOMS, Sr²⁺ getter,

1-step to Perovskite WF

JACS, 2002, 124(3), 1704

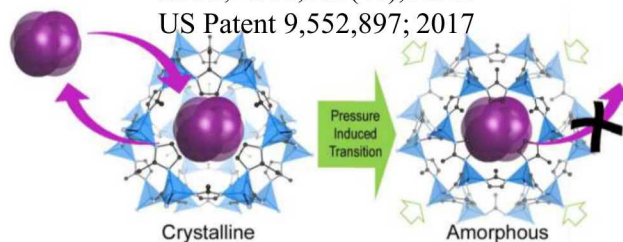
US Patent 7,122,164



MOF Amorphization for Gas Storage

JACS, 2011, 133(46), 18583

US Patent 9,552,897; 2017

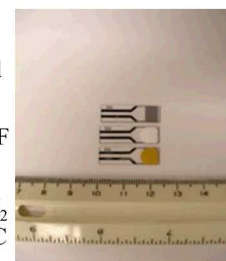


as-received

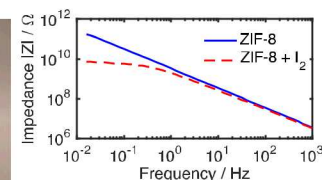
MOF

MOF + I₂

70 °C



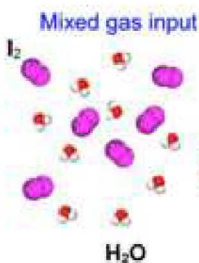
1 cm



I₂ Gas Sensor

ACS Appl. Mater.

Interfaces, 2017, 9, 44649



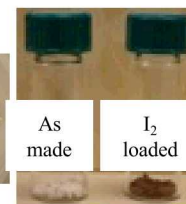
Single gas effluent

H₂O

Competitive I₂ sorption

Cu-BTC: I₂ from Humid Gas Stream

Chem. Mater. 2013, 25(13), 2591



Binder Free MOF Pelletization

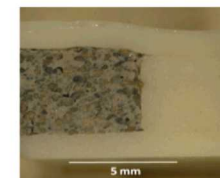
US Patent 2015

9,117,560

Universal Core-Shell Iodine Glass Waste Form & Getter

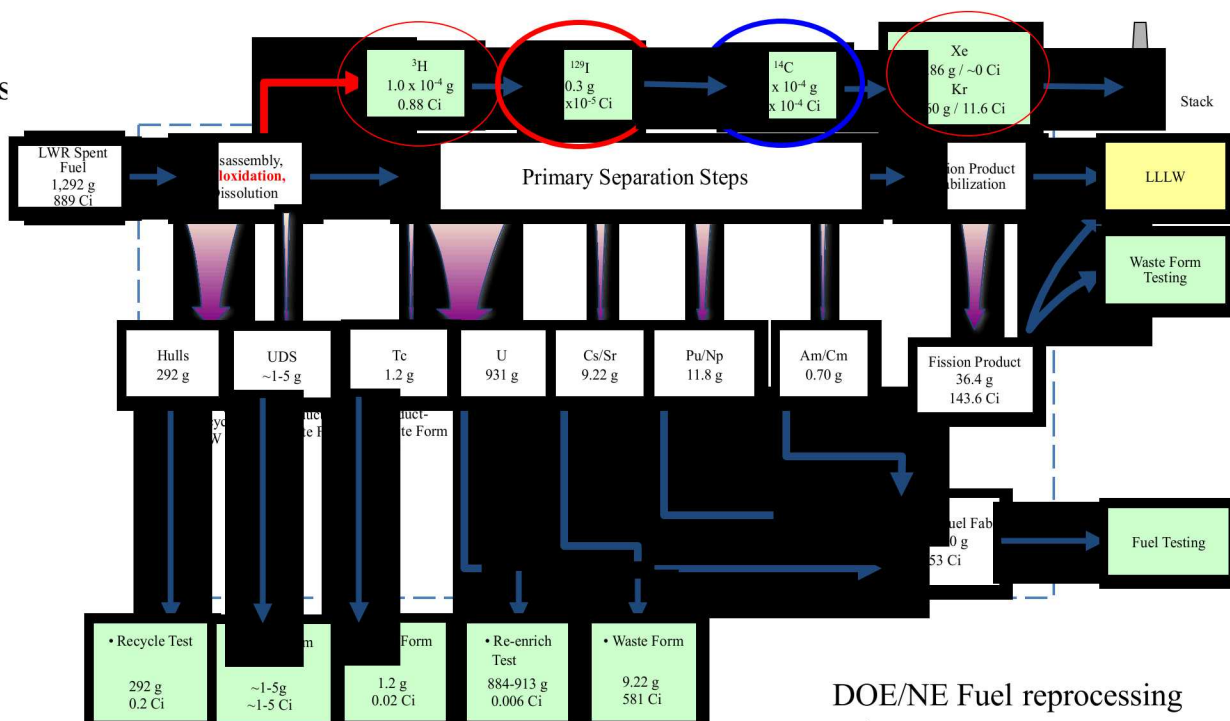
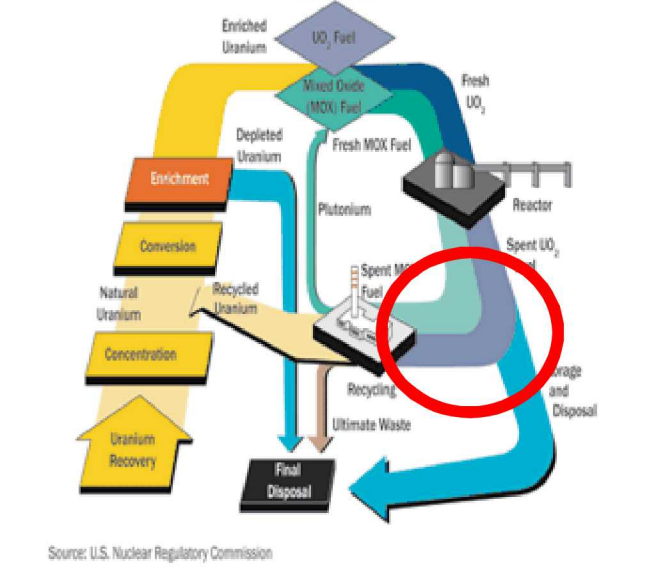
JACerS, 2011, 94(8), 2412

US Patent 8,262,950; 2012



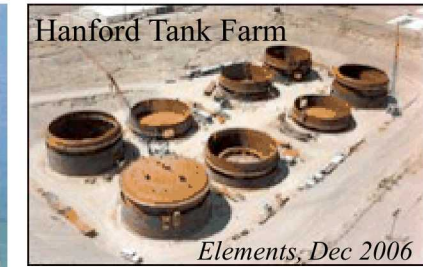
daughter

Reprocessing: capture on nonb
volatile fission products and le



Scheme, ORNL

Fukushima Daiichi
Nuclear Power
Plant explosion 2011
 I^{129} , I^{131} volatile
gas released;
 Cs^{135} , Cs^{137} & Sr^{90}
aqueous released
(www.IAEA.org)



Using the beauty and function of zeolites and molecular sieves as a starting point

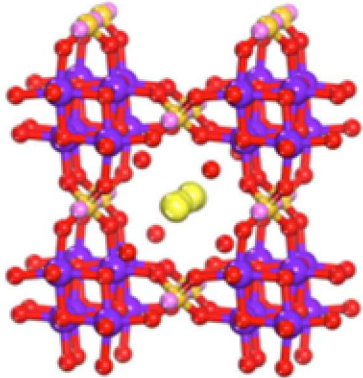
CSTs for Legacy Waste (1990s) and Fukushima (2011-2014)

Basic Research (1993): Sandia LDRD project – gram reactors

Applied Research / Development: DOE/EM – 1-5 gallon reactors

Commercialization: CRADA with UOP Corp., *IONSIV™ IE-910 & IE-911* (Dec 1995)

1800 lb lots produced



R&D100 1996

JACerS, 2009, 92(9), 2144

JACerS, 2011, 94(9), 3053

Solvent Extr. & Ion Exch., 2012, 30, 33

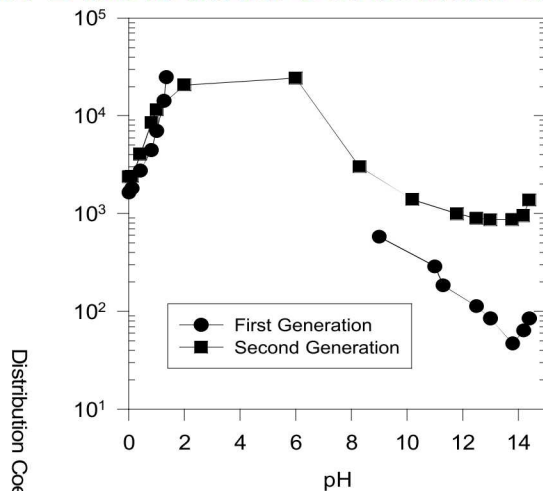
CST, Cs⁺ removal from water to Pollucite Waste Form

US Patents 6,479,427; 6,110,378

UOP IONSIV™ IE-911



Sandia: Distribution Coefficient of Cs on CST



SNL/TAMU US Patents:

6,479,427 (2000) and 6,110,378 (2002)

Fukushima Daiichi
Nuclear Power
Plant explosion 2011
 I^{129} , I^{131} volatile
gas released;
 Cs^{135} , Cs^{137} & Sr^{90}
aqueous released
(www.IAEA.org)



Fukushima Daiichi, SARRY PROCESS implemented to Selectively clean radiological Cs⁺ from Seawater

Augmentation of accumulated water processing facility (SARRY)



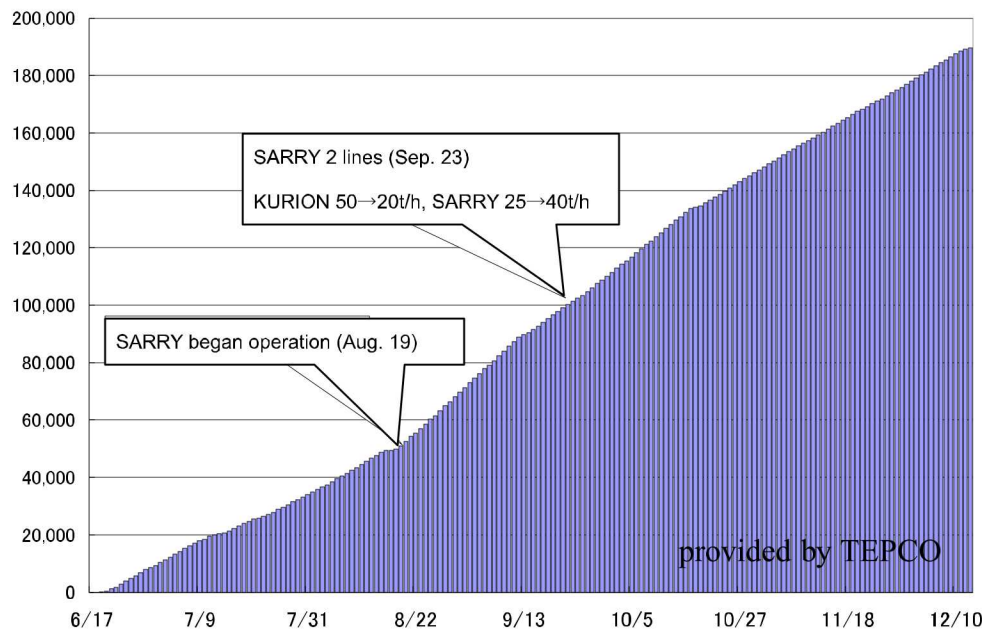
SARRY was installed August 2011,
Decontamination Factors of Cs
SARRY process is 5×10^5

As of December 2014,
160+ million gallons of
Cs contaminated seawater had been
cleaned with the SARRY Process.

August 2015 Reactor Building
Seawater decon work completed

Amount of processed
water (cumulative) (tons)

Amount of processed accumulated water

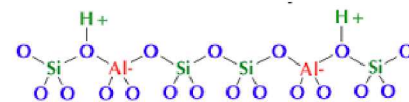
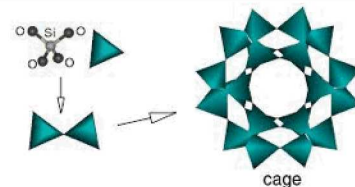


Nanoporous Gas Adsorption Materials



Higher sorption capacity
Lower Selectivity
Saturation from background gases

Activated Carbon/Charcoal > 500 m²/g

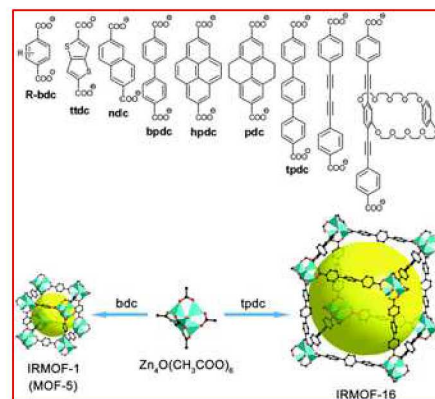
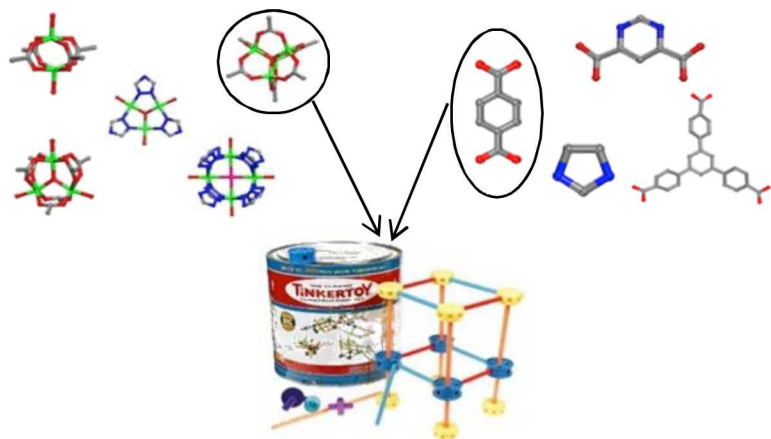


Lower Sorption
Capacity
Size & Chem
Selectivity (?)

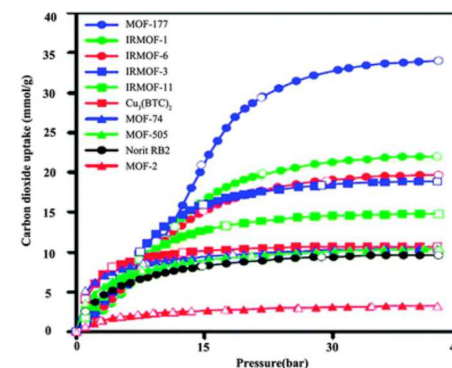


Zeolite~100 m²/g

Metal-Organic Frameworks (MOFs) >1000m²/g



Target: Extremely
High Selectivity &
High Capacity



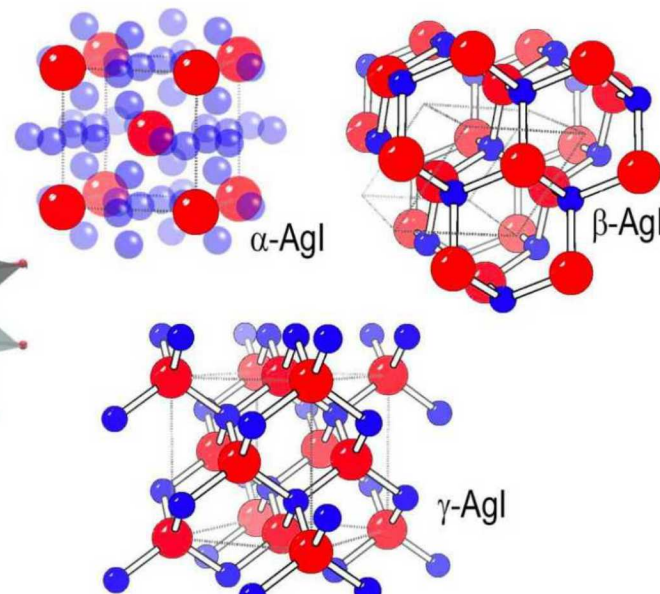
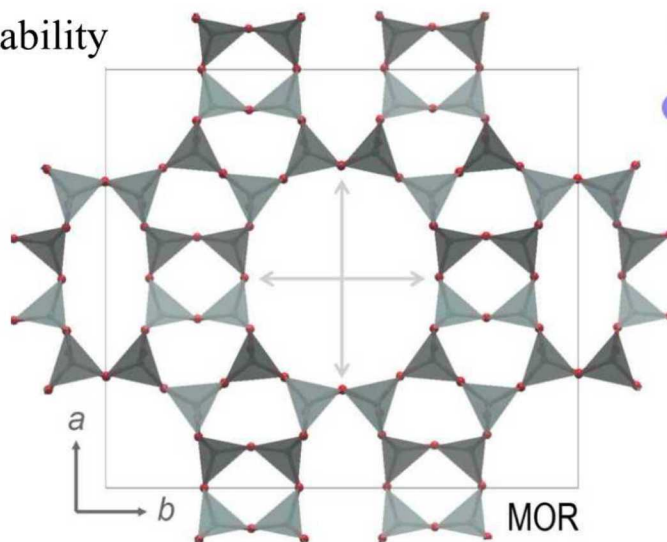
Ag-MOR zeolite, Nanoparticles for gas capture

- While I^{129} is only found in small concentrations in nuclear effluent, the effective capture and storage of iodine is critically important to public safety due to its involvement in human metabolic processes and its long half-life ($\sim 10^7$ years).
- Silver Mordenite (MOR) is a standard iodine-getter, although the iodine binding mechanism remains poorly defined. Presumably an iodide forms within the zeolite's pores
- Understanding **Structure-Property Relationship between Nanoscale and Bulk effects**
 - To optimize capture
 - Impacts processing for long term storage
 - To predict long term stability

MOR, Mordenite

$X_2Al_2Si_{10}O_{24} \cdot 7(H_2O)$

12 MR, $7.0 \times 6.5 \text{ \AA}$



PDF measurements: APS/ANL Collaboration

Does it matter which synchrotron?

Yes. Only higher energy storage rings produce significant fluxes of high energy X-rays

High energy X-rays are a unique strength of the *Advanced Photon Source* (in the western hemisphere)

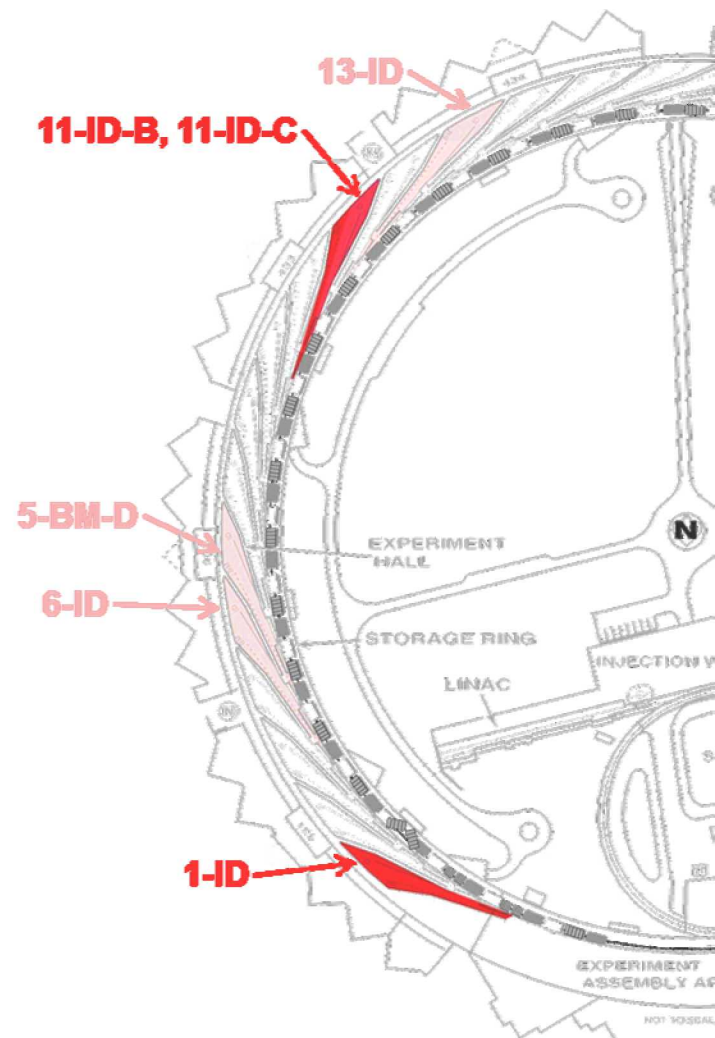
- 3 dedicated high energy beam lines
- 1 dedicated PDF beamline

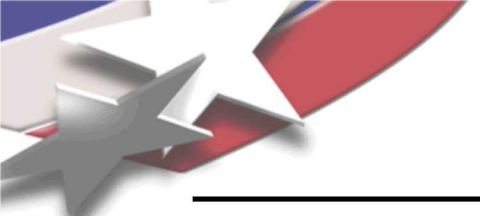
APS 11-ID-B: Dedicated PDF facility

- 58 or 90KeV high energy X-rays
- typical wavelengths = 0.1 - 0.2Å

For our experiments:

$Q > 20\text{\AA}^{-1}$; CuK_{α} to $2\Theta = 180$ results in $Q_{\text{max}} = 8\text{\AA}$





Pair Distribution Function (PDF) Analysis: *To see what is happening inside the pores*

Use of high energy synchrotron:
high energy X-rays and large area detectors key to structure resolution
of heavier elements such as *Silver*

The PDF, $G(r)$, is related to the **probability** of finding
an atom at a distance r from a reference atom.
It is the Fourier transform of the total structure factor, $S(Q)$.

$$G(r) = 4\pi r \rho_0 [g(r) - 1] = (2/\pi) \int Q [S(Q) - 1] \sin(Qr) dQ$$

probability structure factor

The structure factor, $S(Q)$, is related to coherent part of the diffraction intensity

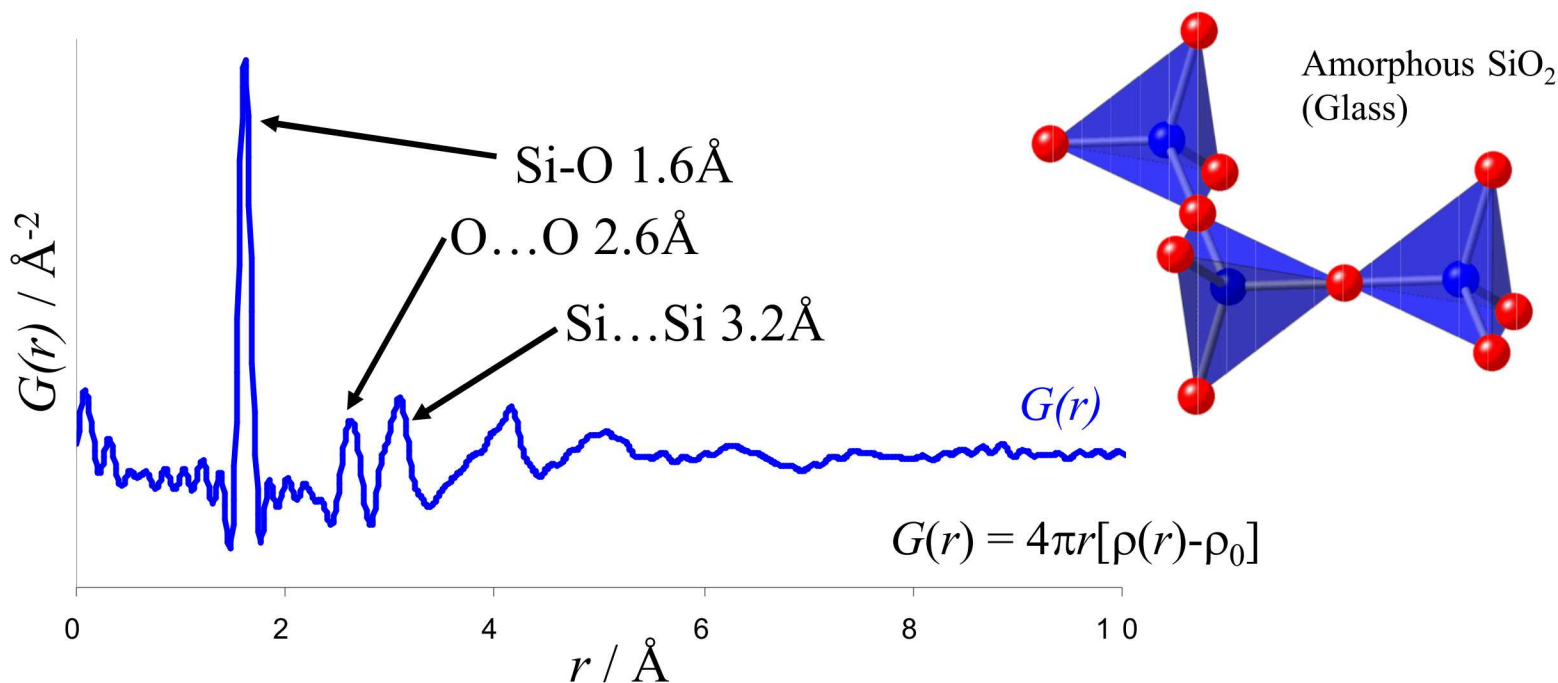
$$S(Q) = 1 + \underbrace{[I^{coh}(Q) - \sum c_i |f_i(Q)|^2]}_{\text{diffraction intensity (corrected)}} / |\sum c_i f_i(Q)|^2$$

diffraction intensity
(corrected)

Apply corrections for background, absorption, Compton & multiple scattering

PDF Provides Insight Into Short Range Structural Order

- a weighted histogram of ALL atom-atom distances



Peak position	↔	Bond length / distance
Peak area	↔	Coordination #, scattering intensity
Peak width	↔	Disorder, bond angle distribution
Peak r_{max}	↔	Particle size, coherence

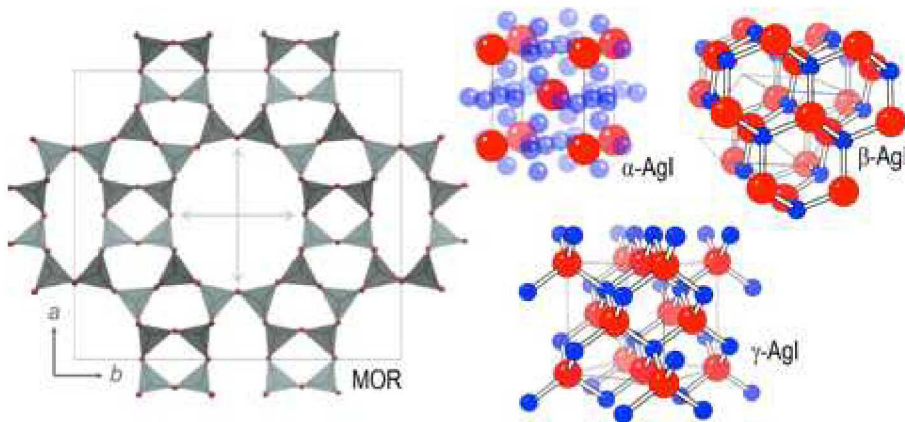
} → **Structural Modeling**

Application to Zeolites to Examine Short Range Interactions of Guests in Pores

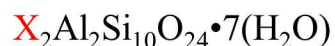
Fundamental Studies of AgI-Zeolites:

Ag-Mordenite (MOR) industry standard for I₂ capture

Mordenite Topology and AgI Polymorphs



MOR, Mordenite



12 MR, 7.0 x 6.5 Å

Idealized MOR framework: *Used for Decades*

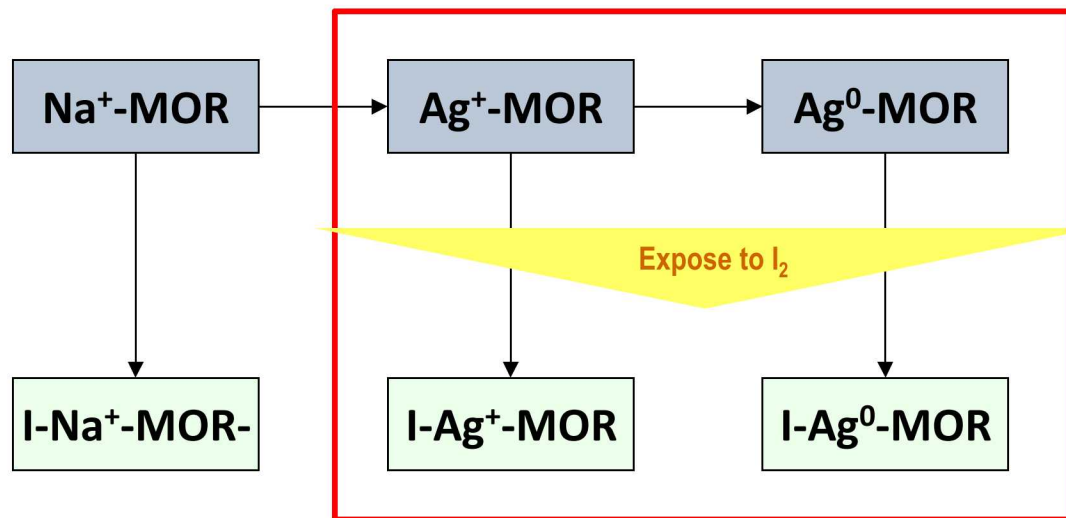
- 1D channels (12-rings, 6.5 x 7.6 Å) which contain exchangeable cations and water molecules (omitted).
- α , β , γ -AgI polymorphs (iodine-red; silver-blue)

MOR Samples from UOP: LZM5

I₂ gas exposure, saturated environment, 95°C

Ag reduction, 3% H₂ stream, 150°C

To study the capture of Iodine by either **ion exchange** or **reduced Ag-MOR**, samples were analyzed at ANL/APS by Pair Distribution Function (PDF) analysis

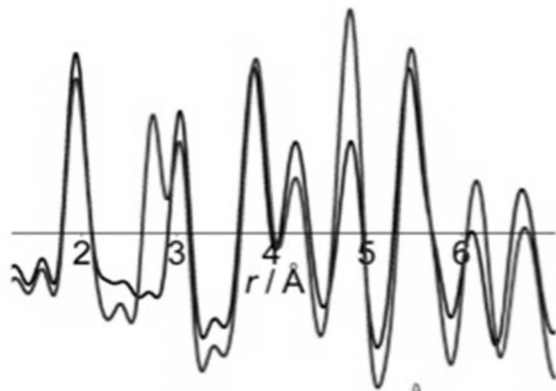


Differential-PDFs: Fundamental Study of Zeolite Framework and Occluded AgI NPs

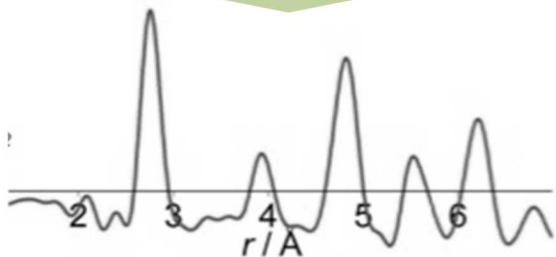
Synchrotron Pair Distribution Function Analysis (d-PDF) allows study of the AgI, minus the MOR zeolite framework (collaboration SNL & ANL/APS)

APS 11-ID-B: Dedicated PDF facility, high energy X-rays:

For our experiments: $Q > 20 \text{ \AA}^{-1}$; $\text{CuK}\alpha$ to $2\Theta = 180$ results in $Q_{\text{max}} = 8 \text{ \AA}$



$$G(r)_{\text{Ag-I-MOR}} - G(r)_{\text{Ag-MOR}}$$



Differential PDF

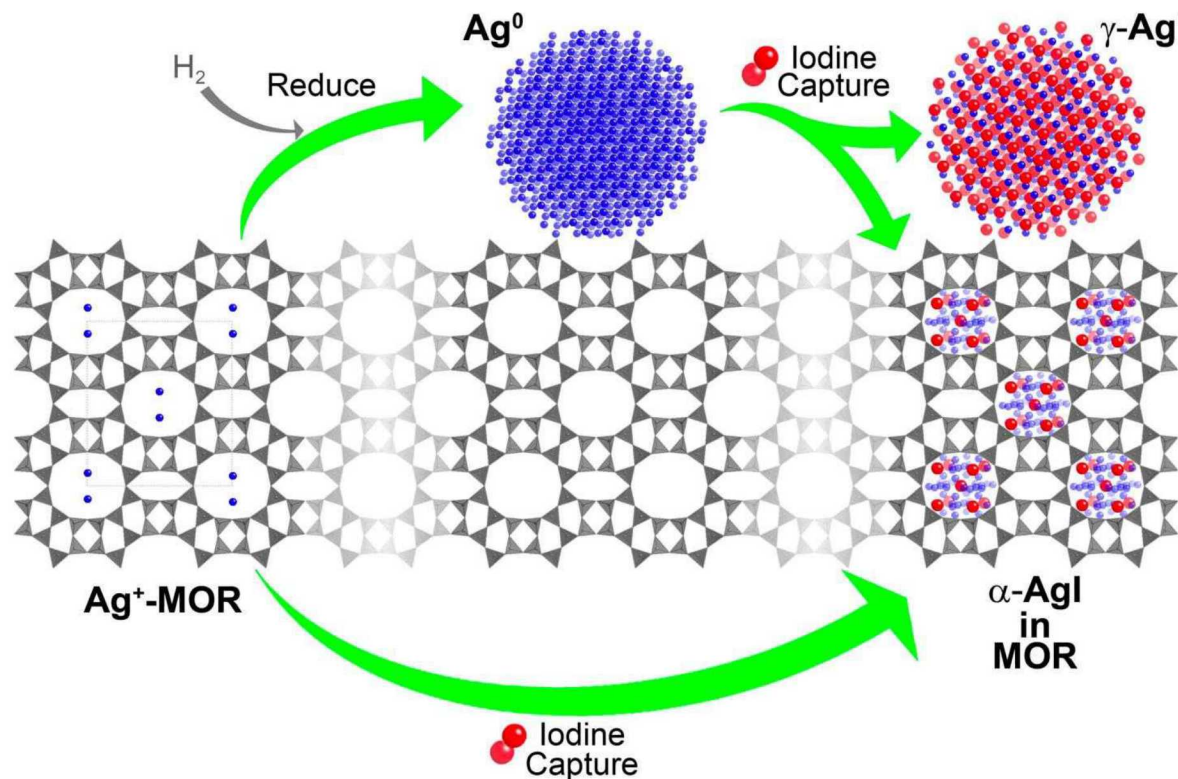
In-zeolite pore capture

	Form	r-range (Å)	R_{fit}	Phase Composition [§]			
				Ag^0	$\alpha\text{-AgI}$	$\beta\text{-AgI}$	$\gamma\text{-AgI}$
$\text{Ag}^+\text{-I}$	on MOR	2-10	27.5%	-	1	-	-
$\text{Ag}^0\text{-I}$	on MOR	2-30	18.0%	-	0.6	-	0.4
AgI (Aldrich)	bulk	2-30	13.6%	-	-	0.53	0.47
AgI ($\text{Ag}^0 + \text{I}_2$)	bulk	2-30	7.97%	0.5	-	-	0.5
Ag^0	on MOR	2-30	9.15%	1	-	-	-

[§] Ag^0 ($Fm\text{-}3m$, $a = 4.08 \text{ \AA}$); $\alpha\text{-AgI}$ ($Im\text{-}3m$, $a = 5.0 \text{ \AA}$, $r < 7 \text{ \AA}$);
 $\beta\text{-AgI}$ ($P6_3mc$, $a = 4.6 \text{ \AA}$, $c = 7.8 \text{ \AA}$, wurtzite structure);
 $\gamma\text{-AgI}$ ($F\text{-}43m$, $a = 6.5 \text{ \AA}$, zinc blende structure).

Mechanism Determined: State of the Ag determines I capture

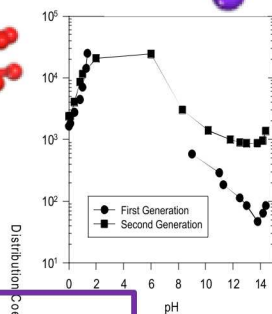
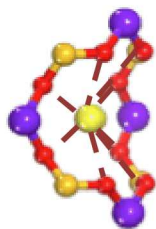
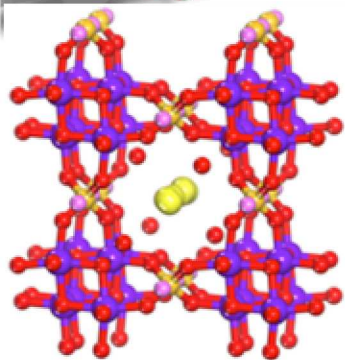
$\text{Ag}^0\text{-MOR} + \text{I}_2$ yields a mixture of $\gamma\text{-AgI}$ bulk surface nanoparticles and sub-nanometer $\alpha\text{-AgI}$.
 $\text{Ag}^+\text{-MOR} + \text{I}_2$ produces exclusively sub-nanometer $\alpha\text{-AgI}$ (“**perfect fit**”, confined in pores)



JACS, 2010, 132 (26), 8897

*Issue associated with Zeolites do include the **need for Ag** and the difficulty of working with zeolites that **selectively adsorb I₂ and Org-I**, but **not ³H₂O, and Xe***

Example 1: Nanoporous Materials Highly Selective Ion and Gas Capture



CST, Molecular Sieve:

R&D100 1996

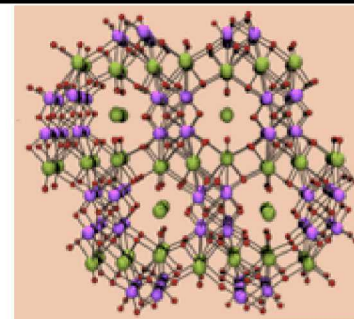
JACerS, 2009, 92(9), 2144

JACerS, 2011, 94(9), 3053

Solvent Extr. & Ion Exch, 2012, 30, 33

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SOMS Molecular Sieve,

Sr²⁺ getter,

1-step to Perovskite WF

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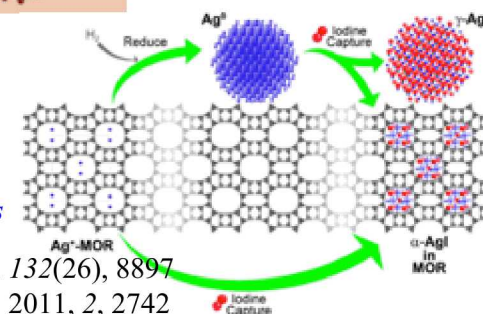
US Patent 7,122,164; 2006

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

Ag-MOR Zeolite, I₂(g) capture & mechanisms

JACS, 2010, 132(26), 8897

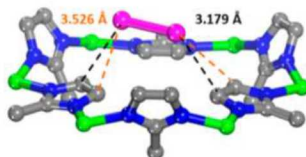
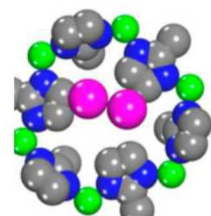
JPC Letters, 2011, 2, 2742



I₂/ZIF-8 MOF, Encapsulation to Waste Form

JACS, 2011, 133(32), 12398

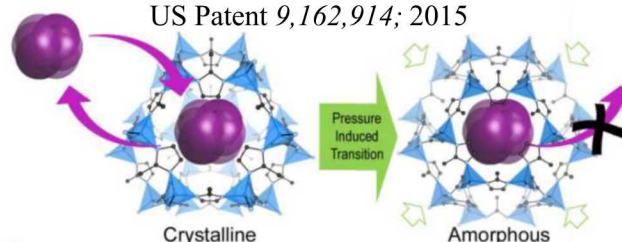
JACS 2013, 135, 16256



MOF Amorphization for Gas Storage

JACS, 2011, 133(46), 18583

US Patent 9,162,914; 2015



Correlate framework charge & pores size with Water H-bonding & Selectivity (Synthesis, INS, VASP MD sim)

JPCC, 2015, 119, 28005; JACS, 2009, 131(23),

8155; JPCC, 2008, 112, 13629; PCCP, 2008,

10, 800; JPCC, 2007, 111(35), 13212

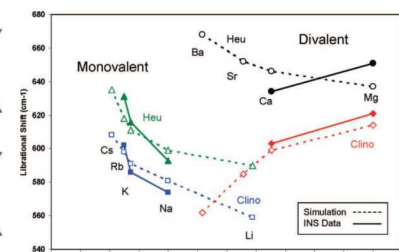
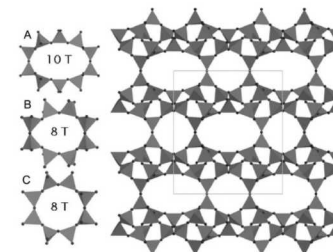
MOF Cu-BTC:

I₂ from Humid

Gas Stream

Chem. Mater. 2013,

25(13), 2591



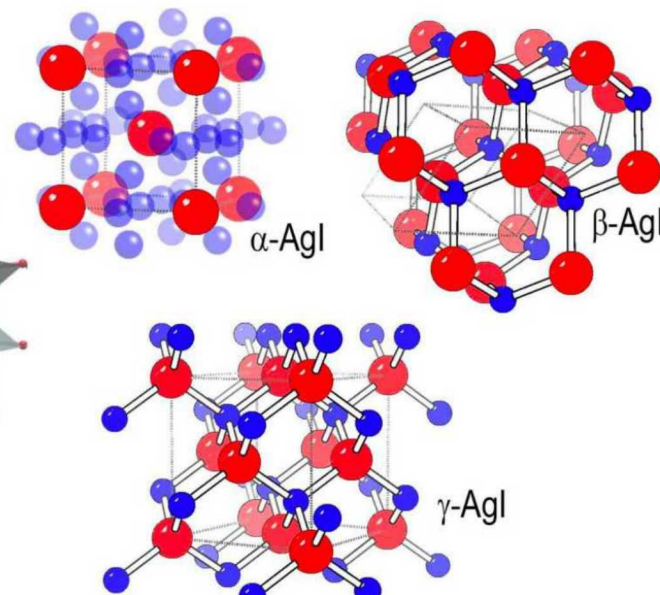
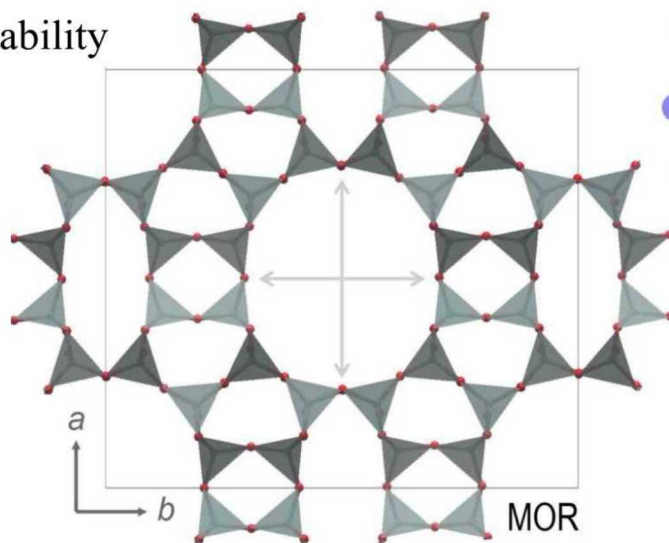
Ag-MOR zeolite, Traditional Iodine Capture Material

- While I^{129} is only found in small concentrations in nuclear effluent, the effective capture and storage of iodine is critically important to public safety due to its involvement in human metabolic processes and its long half-life ($\sim 10^7$ years).
- Silver Mordenite (MOR) is a standard iodine-getter, although the iodine binding mechanism remains poorly defined. Presumably an iodide forms within the zeolite's pores
- Understanding **Structure-Property Relationship between Nanoscale and Bulk effects**
 - To optimize capture
 - Impacts processing for long term storage
 - To predict long term stability

MOR, Mordenite

$X_2Al_2Si_{10}O_{24} \cdot 7(H_2O)$

12 MR, $7.0 \times 6.5 \text{ \AA}$



Bridging Zeolite Structural chemistry to MOFs: Zeolitic Imidizole Frameworks (ZIFs)

O'Keefe, Yaghi, et. al.
PNAS **2006**, *103*, 27, 10186



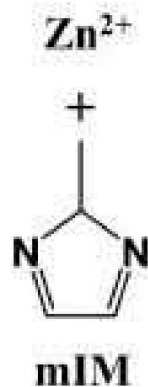
M - IM - M

1

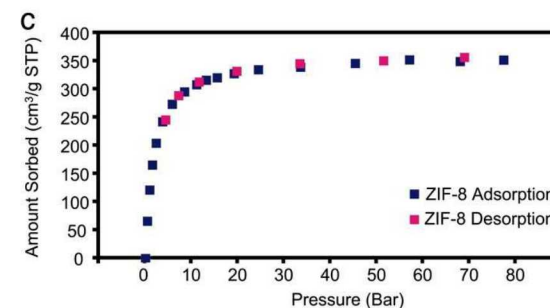
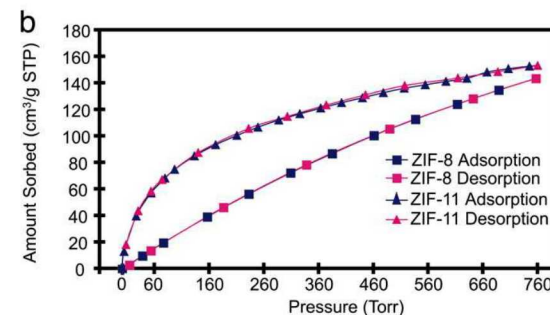
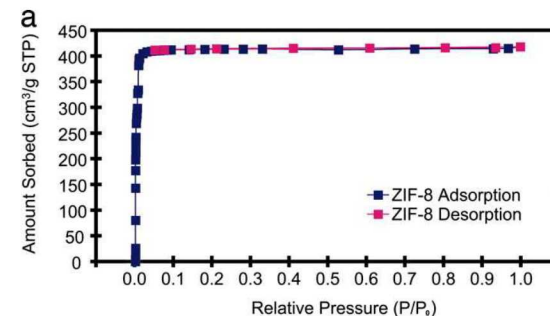
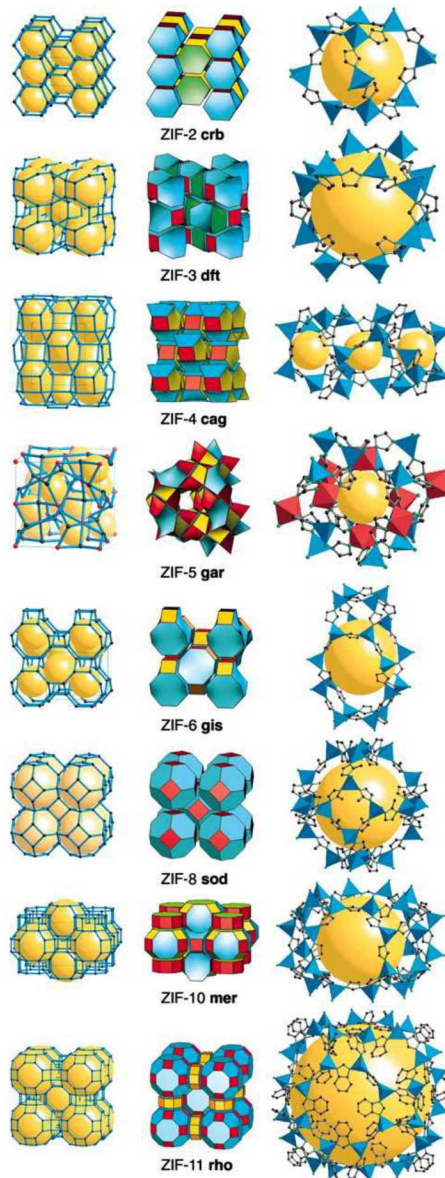


Si - O - Si

2



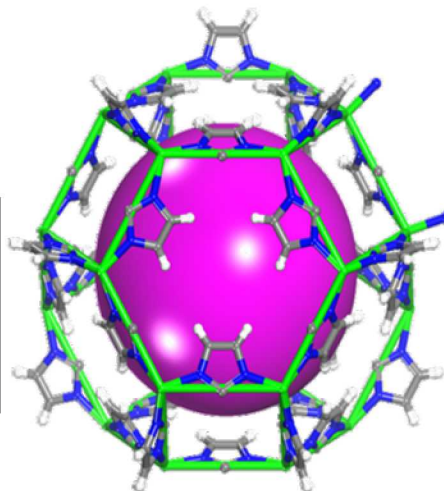
ZIF-8 (*sod*)



Judicious Selection of “Ideal” MOF Candidate

Traditionally zeolites/molecular sieves are used as baseline materials for selectivity and sorption. materials are tuned for high selectivity and high capacity.

Basolite Z1200, ZIF-8
Constricted Pore Opening ($\approx 3.4\text{\AA}$)
1100 – 1600 m^2/g
Pore Volume = 0.636 cc/g
stable in Air & H_2O



$\text{I}_2@\text{ZIF-8} \sim 125 \text{ wt.}\% \text{ I}_2$

JACS, 2011, 133(32),12398

Pre-requisites

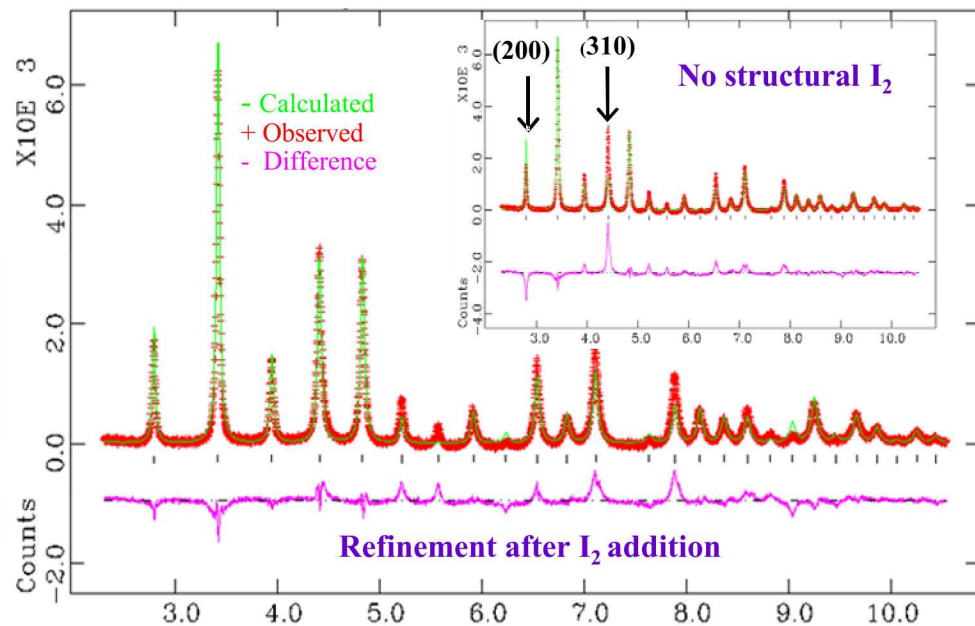
- Restrictive pore apertures to impart molecular selectivity for a directional diffusion of iodine ($\sim 3.35\text{\AA}$)
- Large surface area and pore volume
- High *chemical, thermal, and moisture* stability

ZIF-8

- ✓ The β -cages, 11.6 $\text{\AA}$ in diameter, are connected via six-member ring (6 MR) apertures of $\sim 3.4\text{\AA}$
- ✓ Surface area ZIF-8 = 1,947 $\text{m}^2 \text{ g}^{-1}$ and Pore volume= 0.663 cc g^{-1}
- ✓ Chemically stable in boiling solvents (including water), and thermally stable up to 550°C

Park, K.S. et.al *PNAS*
2006, 103, 10186.

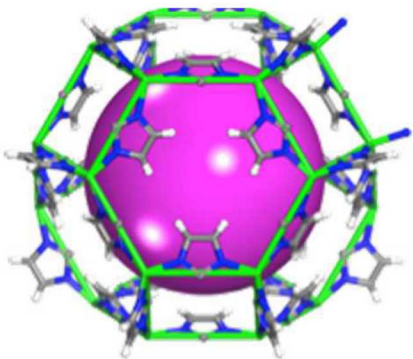
High-Resolution Synchrotron-based XRD



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

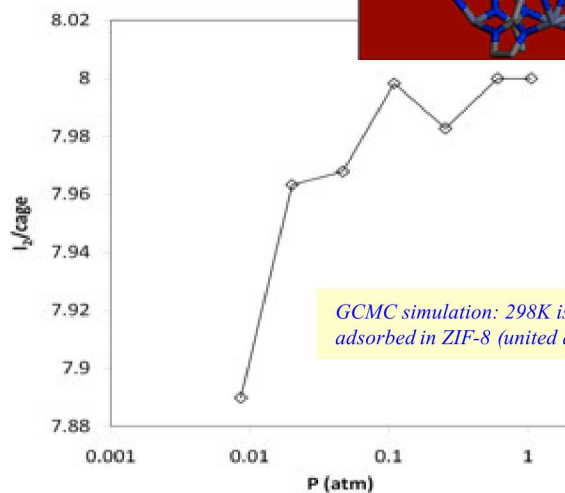
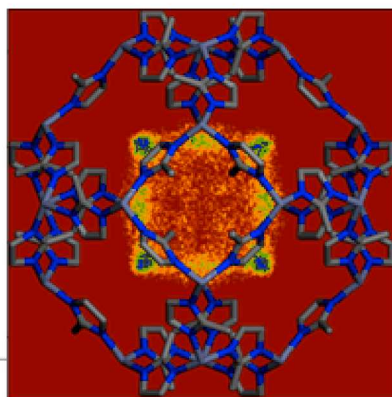
- Sample crystallinity is maintained up to ~ 1.3 I/Zn loadings
- Bragg reflections broaden significantly > 1.3 I/Zn
- difficult to distinguish from the pronounced diffuse features in the “background”
- MOF lattice contracts to accommodate increased I_2 loadings
- Not enough structural resolution obtainable from XRD

Integration of Experiment & Modeling to Identify Chemical Reasons for I₂ Sorption



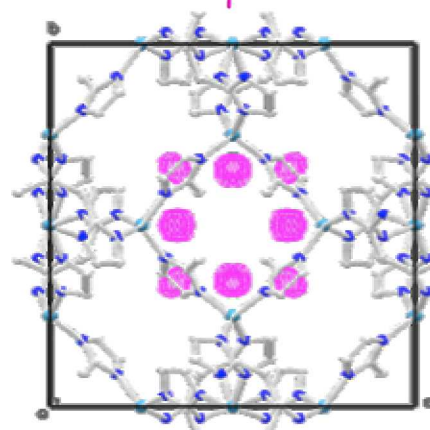
Molecular modeling

MD Simulation:
Electron density determined

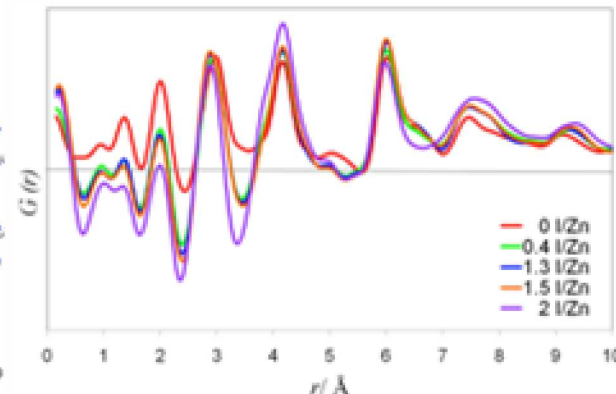


GCMC simulation: 298K isotherm of I₂ adsorbed in ZIF-8 (united atom model)

Complementary local and long-range structural probes



Difference-Fourier analysis map

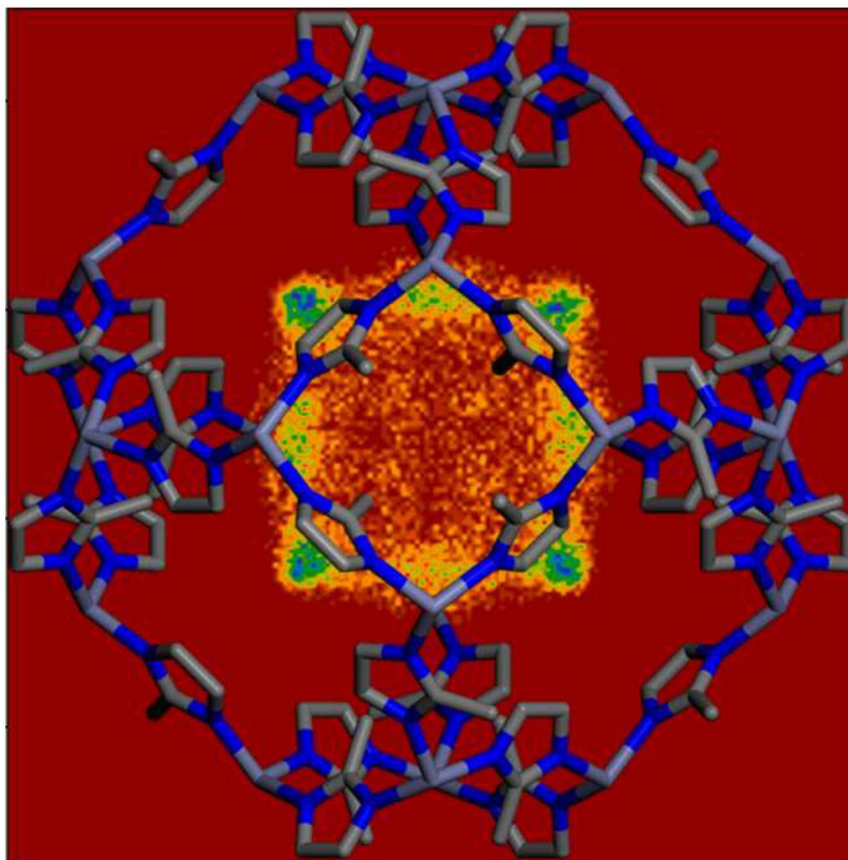


Pair Distribution Function analysis – ANL/APS synchrotron

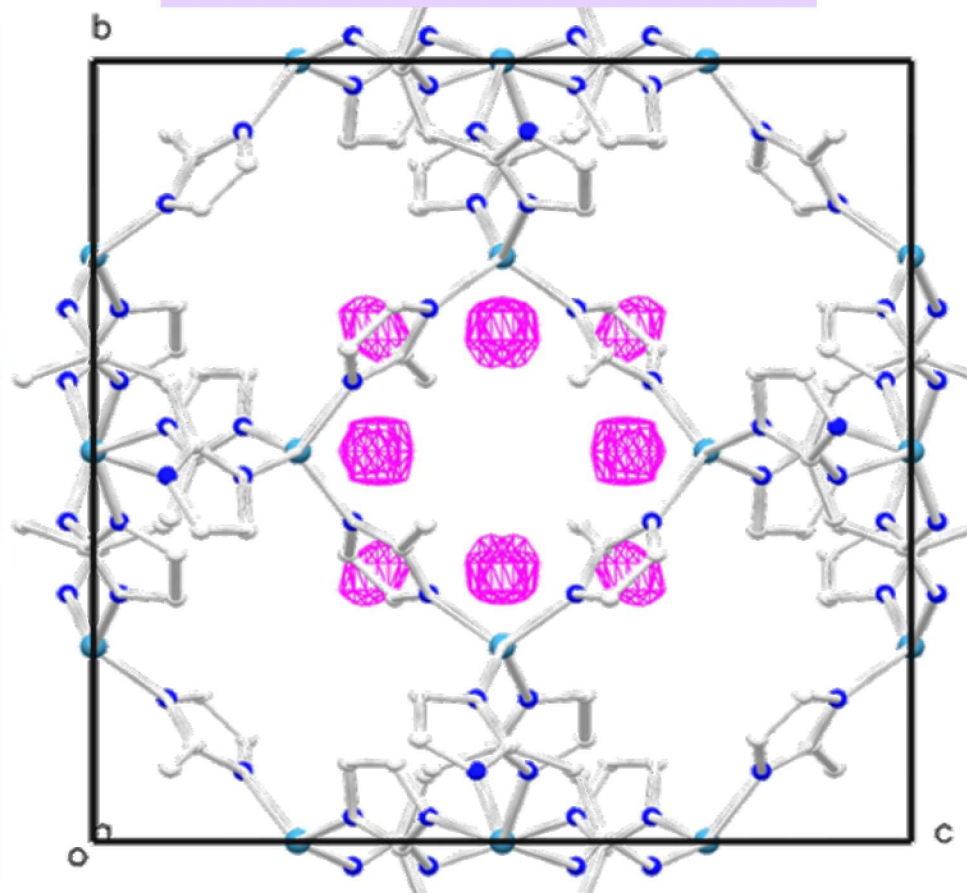
J. Amer. Chem. Soc., **2011**, 133 (32), 12398.

MD Simulations Closely Match Modeling Predictions of I₂ Electron Density

MD Simulation Analysis

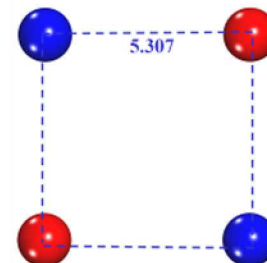
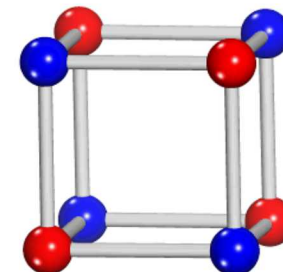
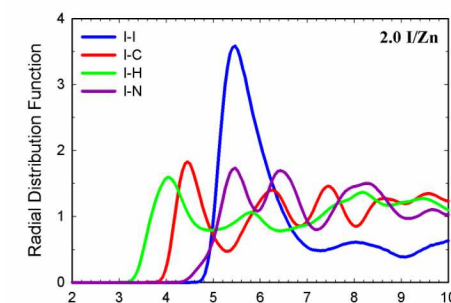
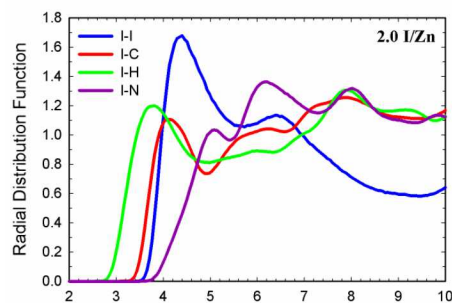
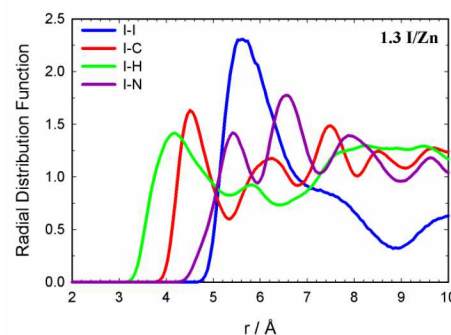
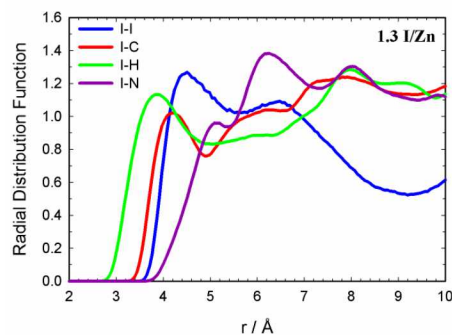
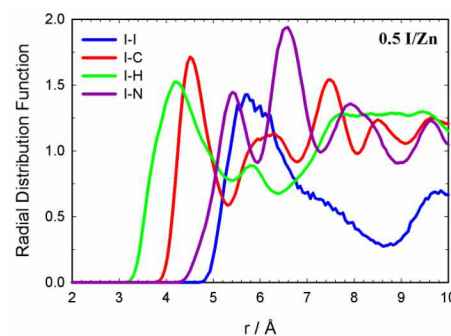
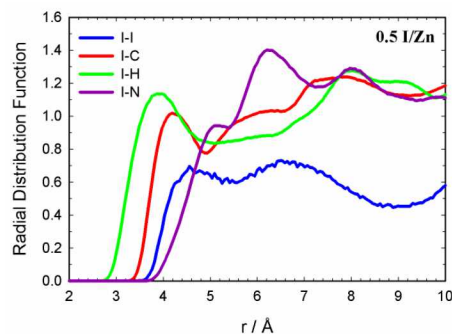
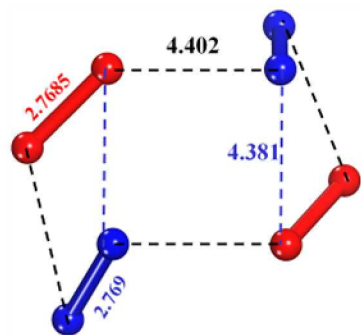
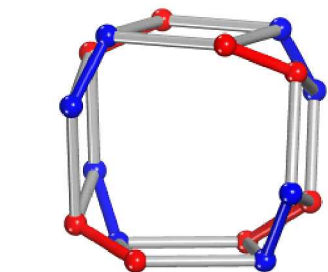


Crystallographic Data:
Difference-Fourier analysis map

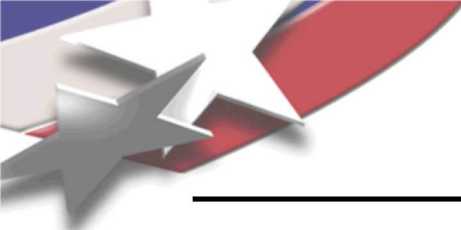


2 I/Zn (~6 I₂ per cage)

Experimental–Modeling Agreement Radial Distribution Functions (RDFs) for Diatomic and United-Atom Models

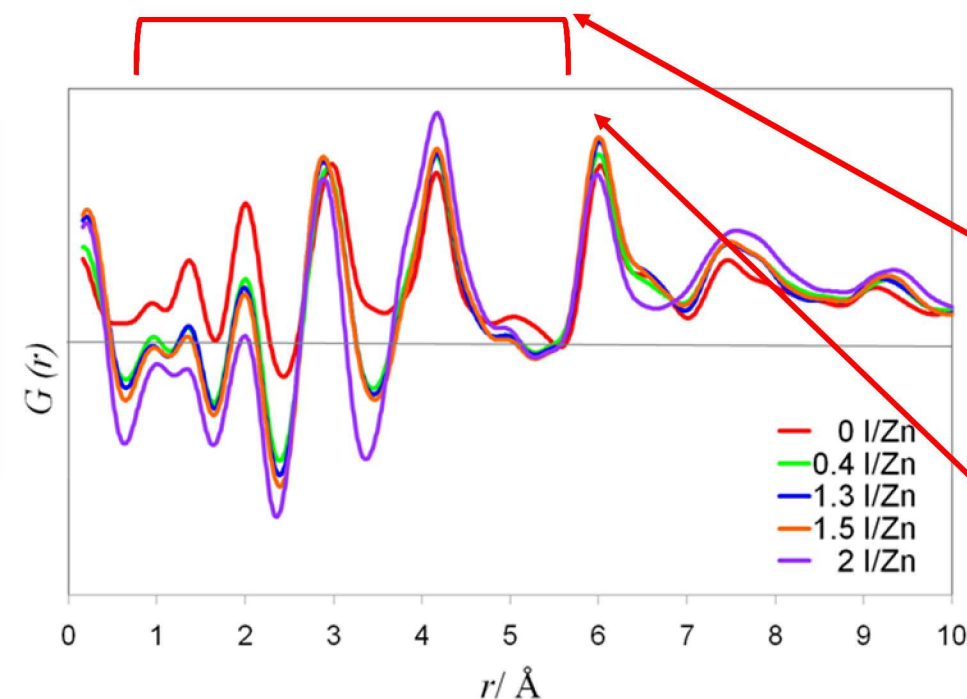


Good agreement between crystallography, PDF and modeling regarding nearest neighbors distances



d-PDF of $I_2@ZIF-8$

(acting of empty ZIF-8 from I_2 loaded ZIF-8)

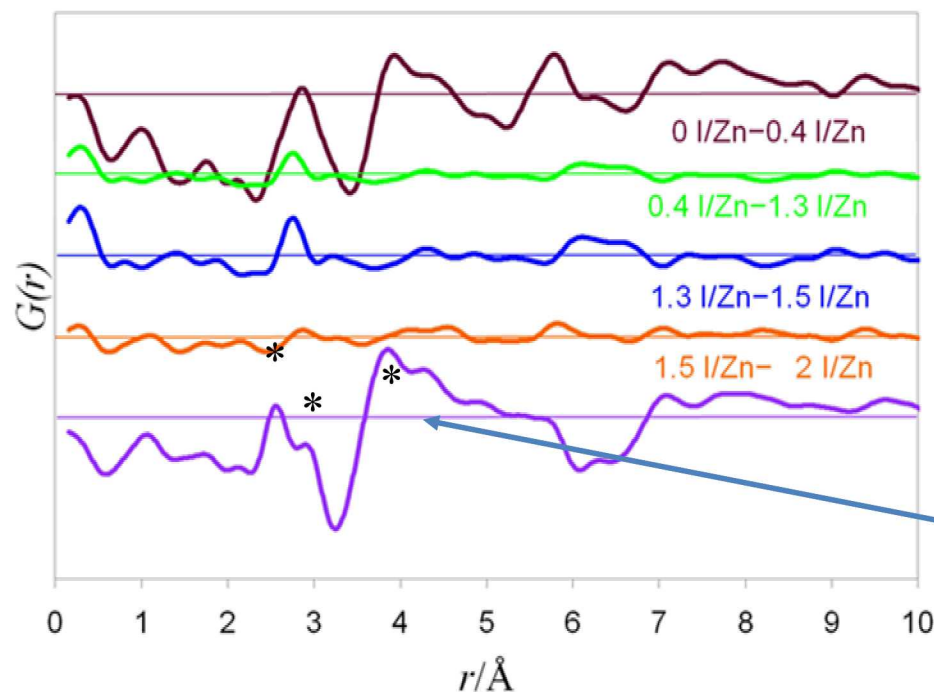
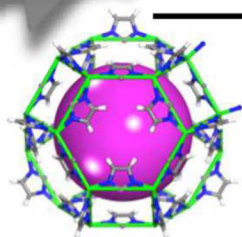


MOF cage maintained.
short-range order and framework
connectivity are maintained at all
loading levels

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

Differential PDF Analysis (d-PDF)

subtraction of framework for only I₂ information



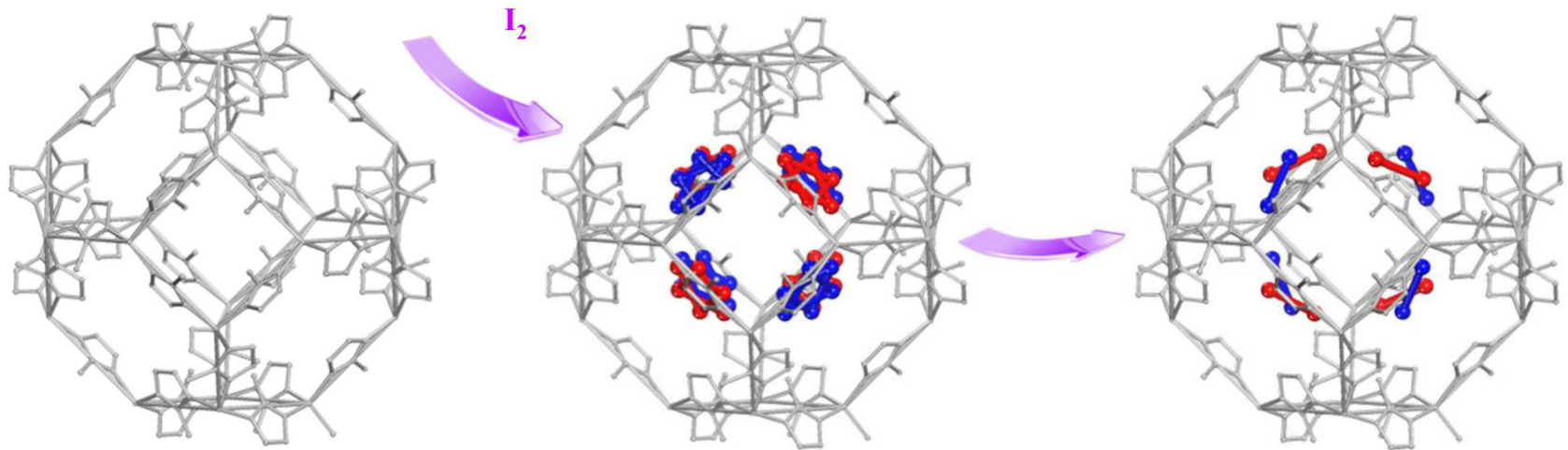
- Differential analysis applied to isolate I₂ guest molecules contributions
- Incremental I₂ loading up to 1.3 I/Zn
peaks at 2.75 Å, 3.23 Å, 4.29 Å, 4.91 Å, 5.46 Å, 6.01 Å, and 6.61 Å
- I₂ loading >1.3 I/Zn: changes observed to MOF cage structure
 - new peaks 2.56 Å, 2.94 Å, and 3.79 Å
 - intensity changes for peaks 4.29 Å, 4.91 Å, and 3.23 Å

I₂ molecule maintained.

At loadings above 1.3 I/Zn, rearrangement of I₂ molecules required inside cage

Combined Analyses: Determination of I₂ Binding Locations inside ZIF-8 Pore

Combination of d-PDF and powder XRD reveals the I₂ molecules' location



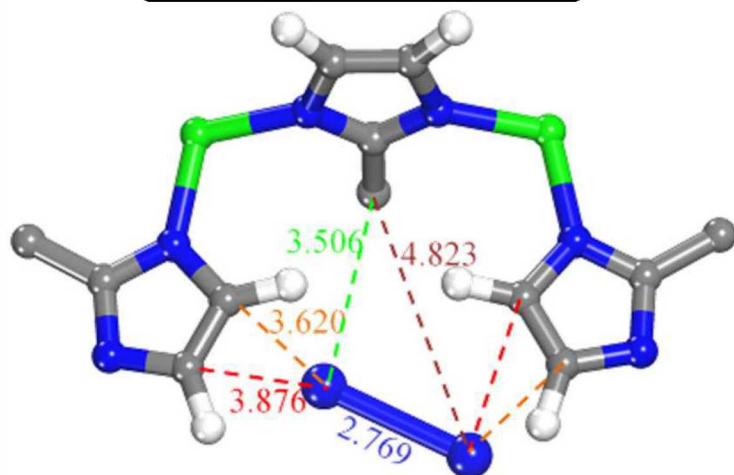
Activated β -cage

Dynamically disordered I₂
molecules

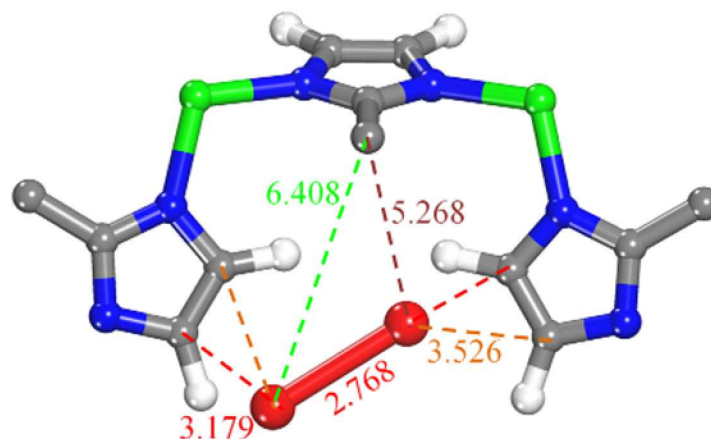
Refined I₂ sites:
I_a (blue) and I_b (red)

Two distinct I₂ binding site: I_a and I_b
 Appears site I_a has preferential binding,
 more thermodynamically stable?

I_a site



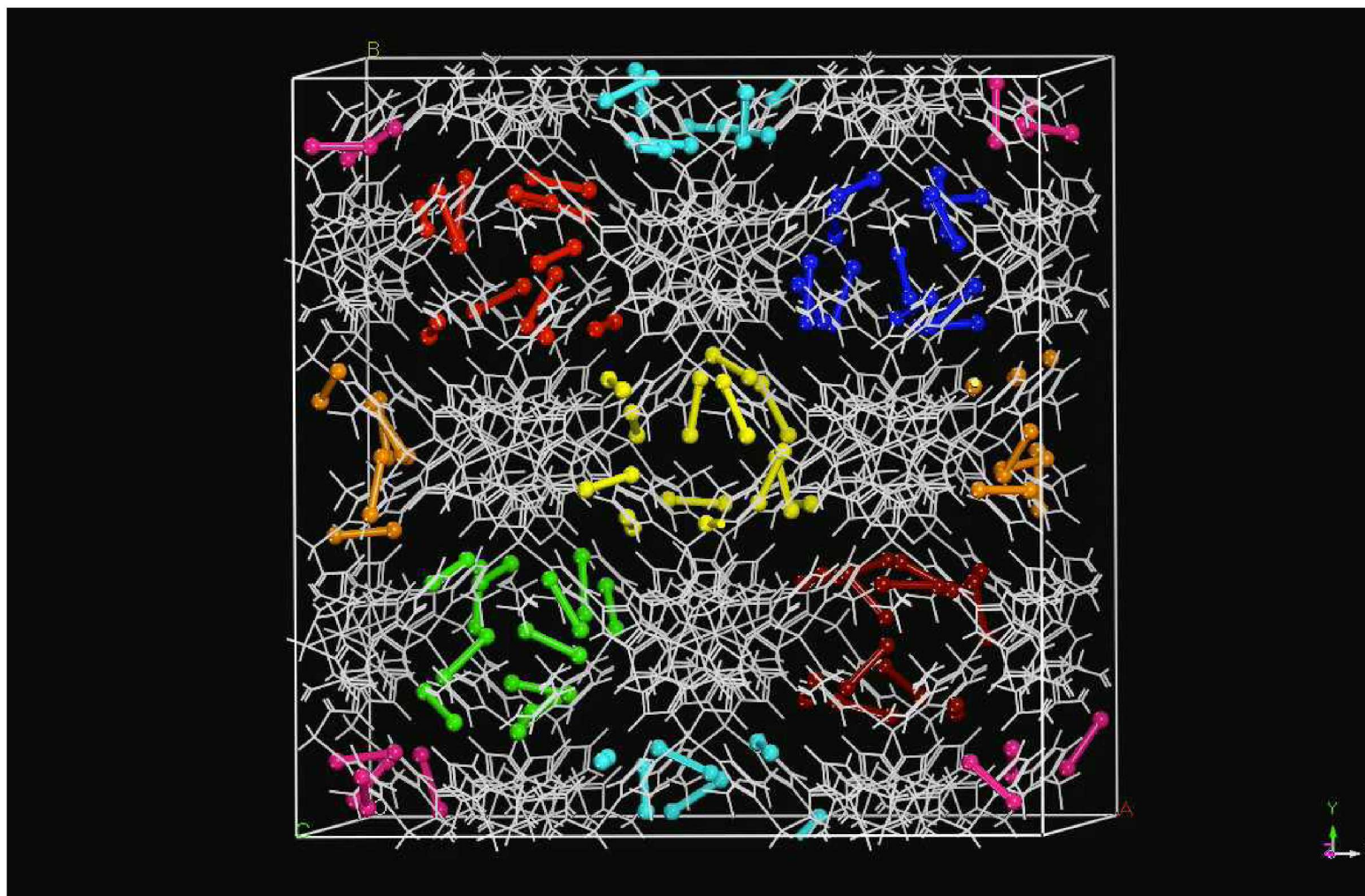
I_b site



I₂ site occupancy and I₂···MeIM close contacts in I₂@ZIF-8

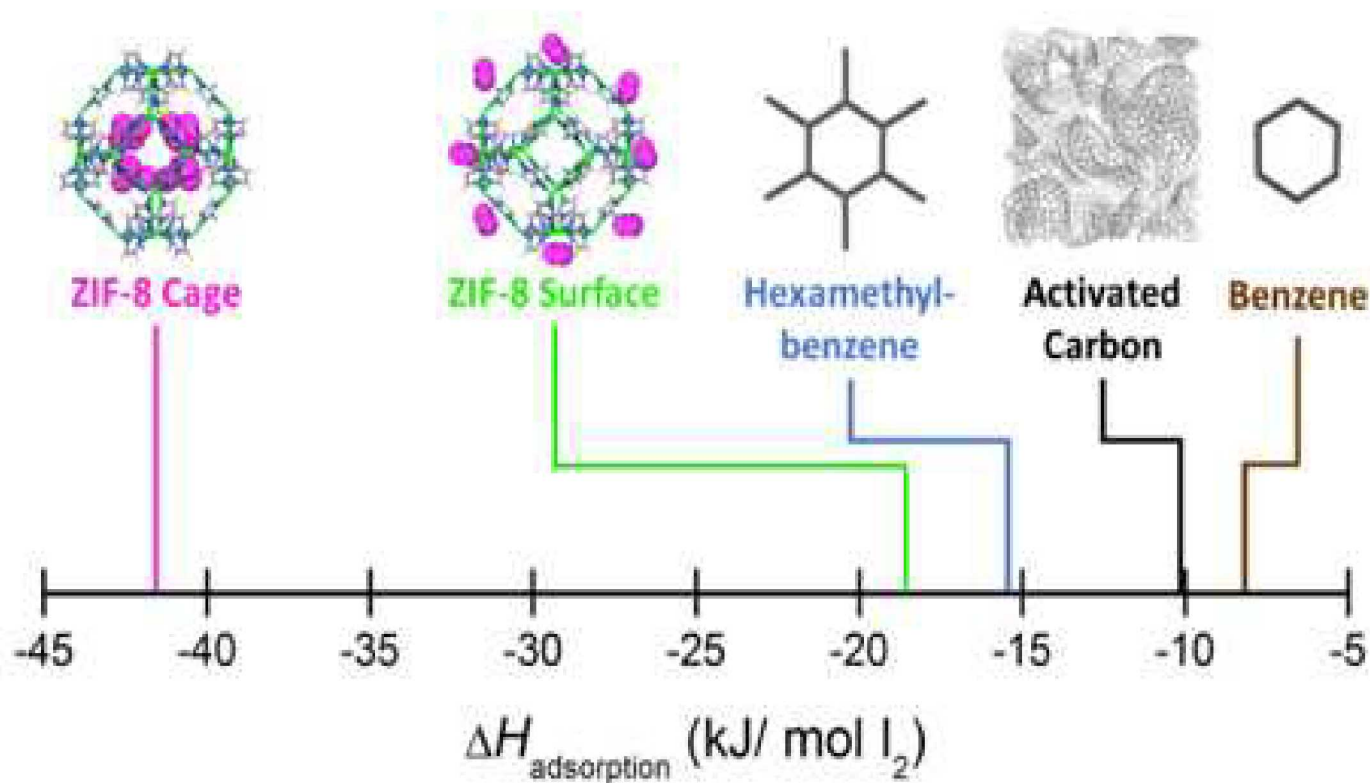
I ₂ site	Site occupancy		Contacts with MeIM	
	0.4 I/Zn	1.3 I/ Zn	C (CH ₃)	C(H=CH)
I _a	0.28	0.88	3.506 Å; 4.823 Å	3.620 Å; 3.876 Å
I _b	0.14	0.38	5.268 Å; 6.408 Å	3.179 Å; 3.526 Å

Dynamics of I_2 Within Cages: No Predicted Mobility of Gas Molecules In/Out of Individual Cages



Metal Organic Frameworks (MOFs) for fission gas adsorption: iodine (I_2)

In collaboration with J. Hughes and A. Navrotsky, UC Davis



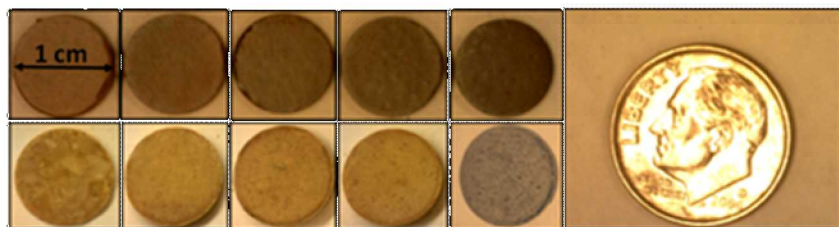
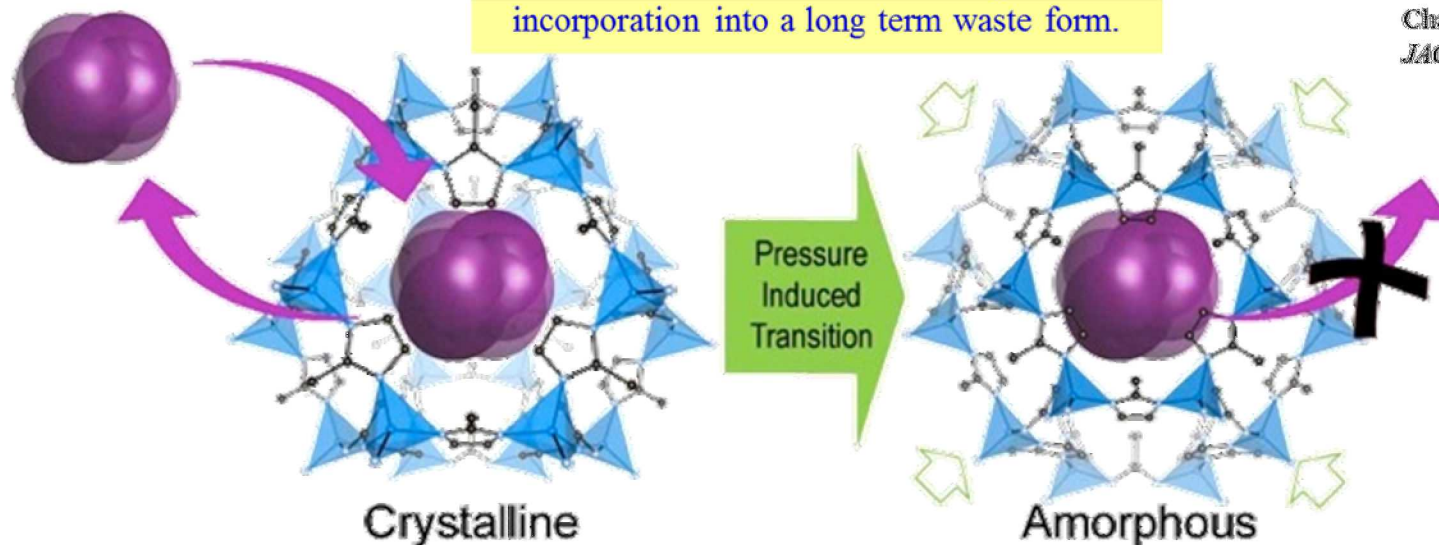
JACS, **2013**, 135(44), 16256

Ind. Eng. Chem. Res., **2017**, 56(8), 2331

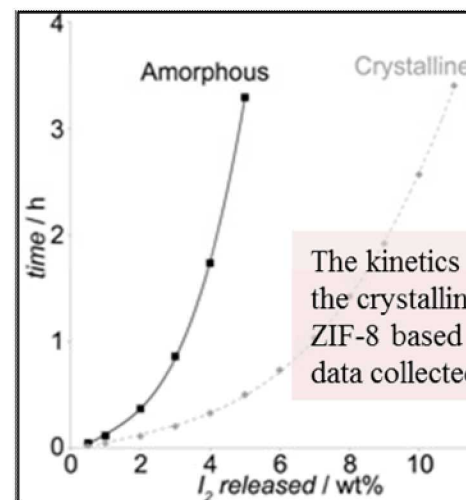
I_2 @ZIF-8 Pressure-Induced Amorphization of Trapped Gases: Enhanced Retention

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

Chapman, Nenoff, et.al.,
JACS 2011, 133(46), 18583.



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

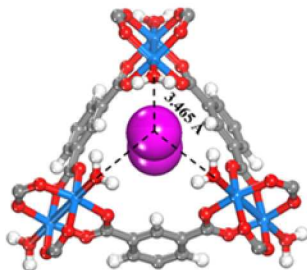
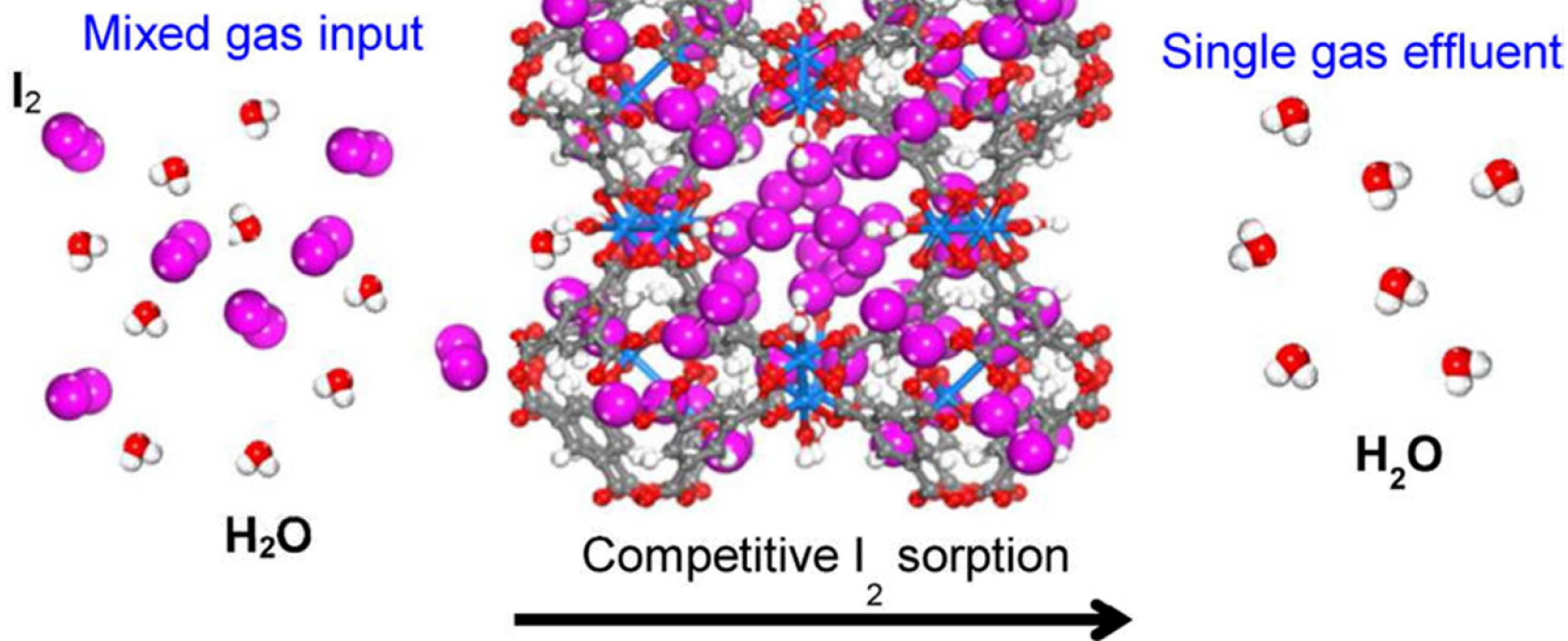


The kinetics of I_2 release from the crystalline and amorphized ZIF-8 based on isothermal TGA data collected at 200°C, 4 hours

Crystal Structure of I₂@HKUST-1, selectivity of I₂ over H₂O

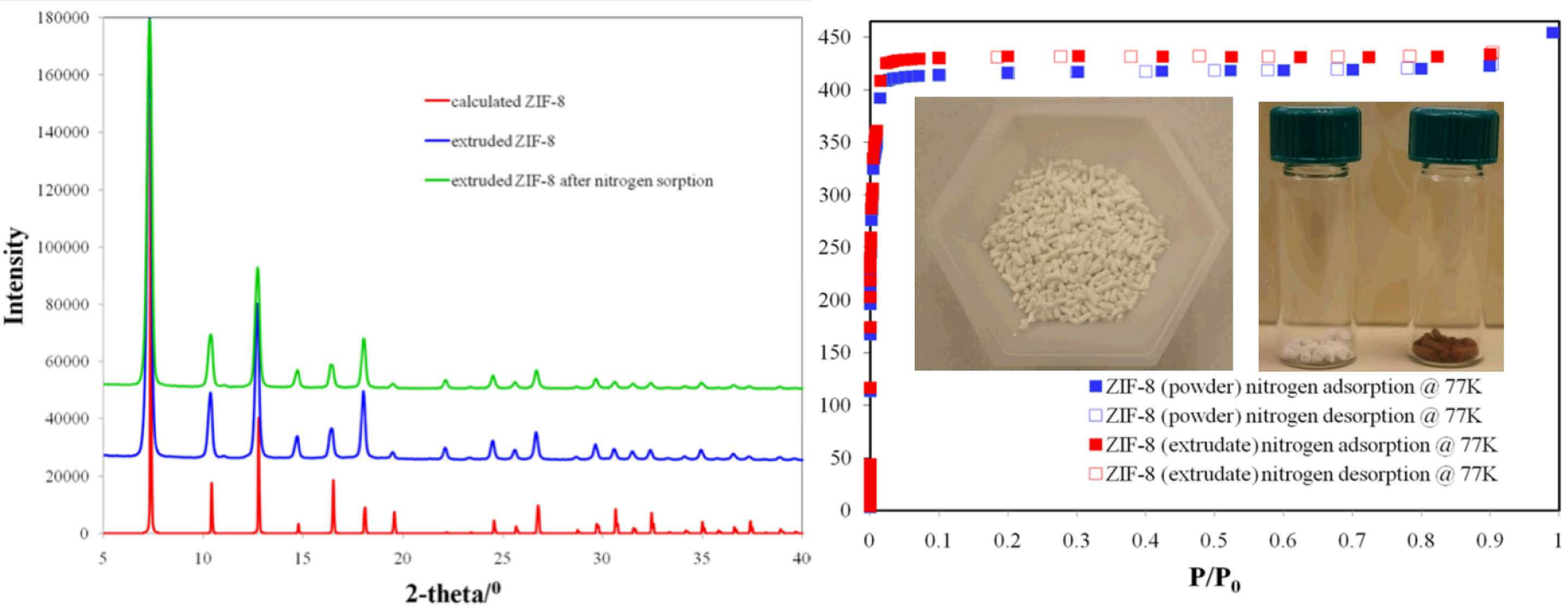
I₂/HKUST-1 3.3 I/Cu

Sava Gallis, Nenoff, et.al.,
Chem. Mater., 2013, 25 (13), 2591



Iodine – Metal center (Cu) strongly bound
High Selectivity!
Trumps hydrophilicity of MOF

Sample Pelletizing For Industrial Applications



Binder-Free, No Loss of Accessible Surface Area or Sorption Properties

Sandia GCM: “Universal” Waste Form Material

US Patent 8,262,950; Sept 2012

Homogenous Glass GCM: for
Agl 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

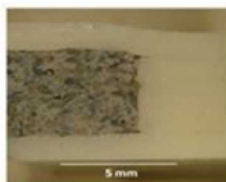
“Universal” Low Temperature Glass Waste Form
Durability studies show that SNL GCM can
successfully incorporate and store a wide variety of
“fission gas – loaded” oxide based *getters*

Core-Shell GCM Glass Waste Forms

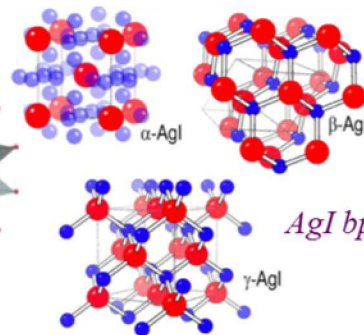
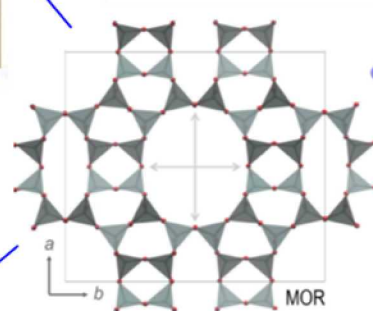


Glass shell, AgI/glass core,
75/25

JACerS, 2011, 94(8), 2412

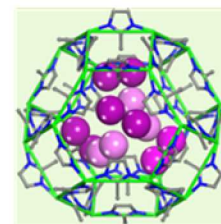
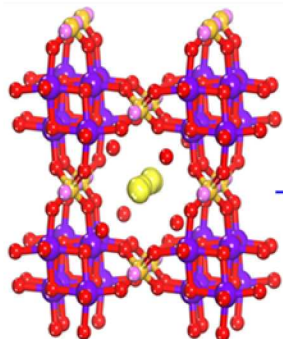


Glass shell,
AgI-MOR/Ag/Glass core 80/20/5



AgI bp 556° C

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



***I₂/MOF, Isolation
to Waste Form***

JACS, 2011, 133(32), 12398

Ind. Eng. Chem. Res (Invited Article)

2012, 51(2), 674



Irradiations stability testing of SNL Waste Forms at Sandia Gamma Irradiation Facility (GIF)



Dose rates:

-long-term exposure/low dose:

0.1 Rads/sec, with an overall dose of 2.59×10^5 Rads (2218Gy)

-short-term exposure/high dose:

800 Rads/sec, 1×10^6 Rads (10,000 Gy)

Samples tested include:

EG 2922 Glass (550°C), 87.5Glass/12.5SiO₂

80Glass/20AgI-MOR/10Ag

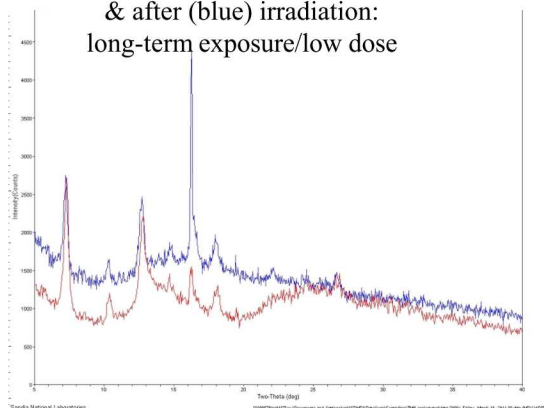
ZIF-8 (MOF), ZIF-8/I₂

HKUST-1(MOF), HKUST-1/I₂, Glass/HKUST-1/I₂

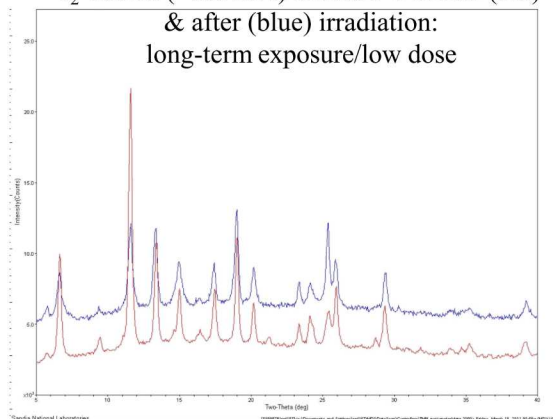
Bi-I-O

Examples of MOF irradiation studies:

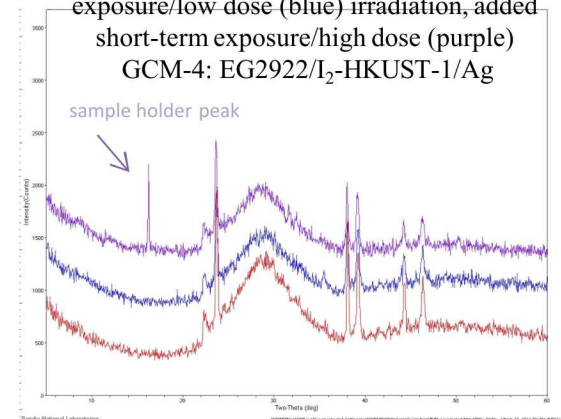
90 wt.% I₂-loaded ZIF-8 before (red)
& after (blue) irradiation:
long-term exposure/low dose



I₂-loaded (≈ 100 wt%) HKUST-1 before (red)
& after (blue) irradiation:
long-term exposure/low dose



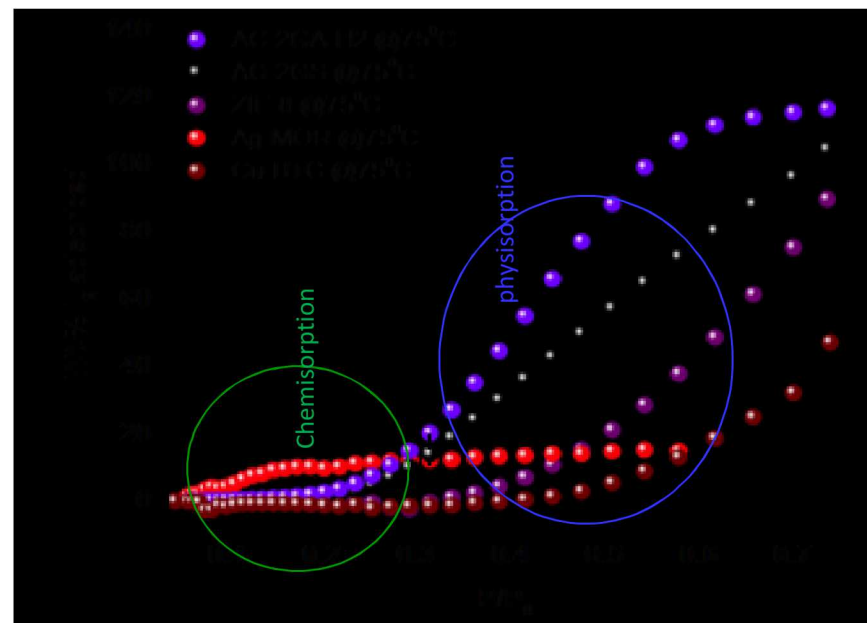
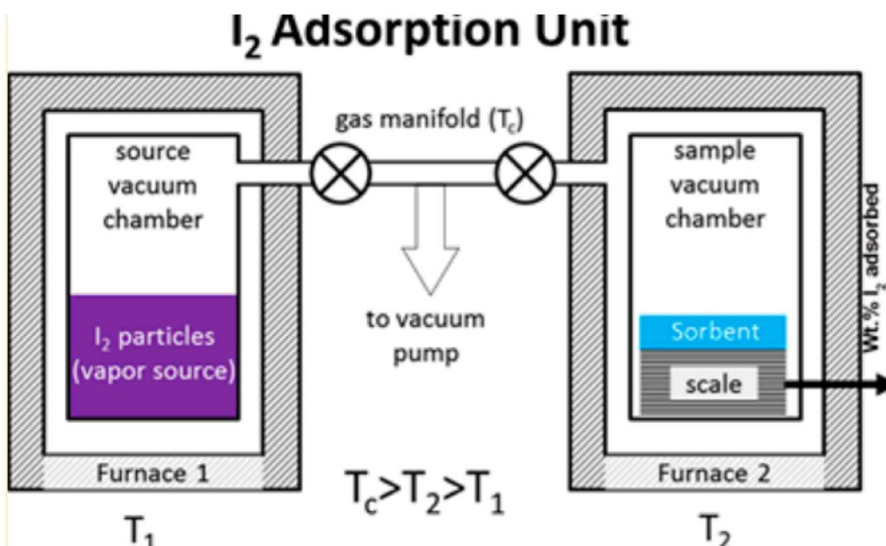
GCM-4 before (red) & after long-term
exposure/low dose (blue) irradiation, added
short-term exposure/high dose (purple)
GCM-4: EG2922/I₂-HKUST-1/Ag



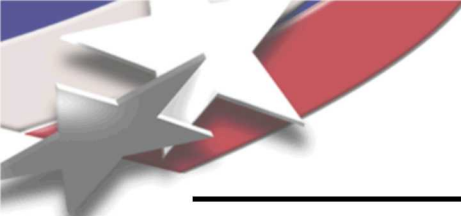
No structural changes as seen by XRD or in PCT responses of any samples. This radiological characterization is a good approximation of an adequately shielded long-term disposal environment.*

Using a combination of Modeling (GCMC) and Iodine (I_2) Adsorption Studies to compare various nanoporous phases for iodine adsorption
MOFs, Zeolites/Molecular Sieves, Activated Carbons/Charcoals

Using a combination of Modeling (GCMC) and Iodine (I_2) Adsorption Studies to compare various nanoporous phases for iodine adsorption
MOFs, Zeolites/Molecular Sieves, Activated Carbons/Charcoals



$P/P_0 < 0.3$: I_2 adsorption occurs in **small pores & **strong chemisorption interactions** with framework or extra framework**

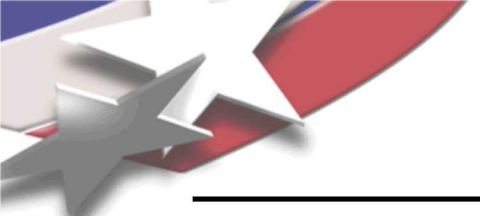


Use of High MOF selectivity to Iodine to make *Direct Electrical Readout Sensors*

Enable the safety of first responders, Real-time accident warnings

The ability to sense and identify *individual gases* from the complexity of the environment requires highly selective materials.

- Current conductivity-based devices generally fall into two categories:
 - Solid state - (oxide based) require higher temperatures ($>200^{\circ}\text{C}$) for interaction of the gas with the surface oxides; heating devices are needed.
 - Fuel cell – room temperature liquid electrolyte, easily fouled, short lifetime
- Utilization of *MOFs with impedance spectroscopy*¹ to develop novel sensing technologies
- Exceptionally high selectivity of polarizable gases of interest (eg., I_2) under ambient conditions



Iodine Sensors with High Selectivity in Environmental Conditions

Impedance spectroscopy,

polarizable molecules increase the capacitance and thereby decrease the impedance.

The selectivity of MOFs for I_2 under mild conditions paired with the **polarizability of the I_2 molecules**, enables **real-time electrical sensing (direct electrical readout)** via impedance spectroscopy.

Common air component gas molecules such as Ar, O_2 and N_2 are **not/not-highly polarizable** molecules

Modular platform:

able to test MOFs of different configurations, metal centers and charge transfer capabilities

Real-Time sensing by impedance spectroscopy (IS):

All measurements to date are simple single sine measurements.

The electrical test equipment **generates a single sine voltage wave** at a given frequency,
& **measures the returned current** in terms of its:

- **magnitude** (this relates to the impedance, $|Z|$ on the plots) and
- **phase angle** compared to the original voltage wave

In fast fourier transform (FFT), a voltage pulse is sent out.

The pulse is the FFT of 20+ frequencies.

The measurement time is limited by the lowest frequency.

High Efficient Method: can collect ~ 20 data points in nearly the same time as the 1 lowest frequency data point.

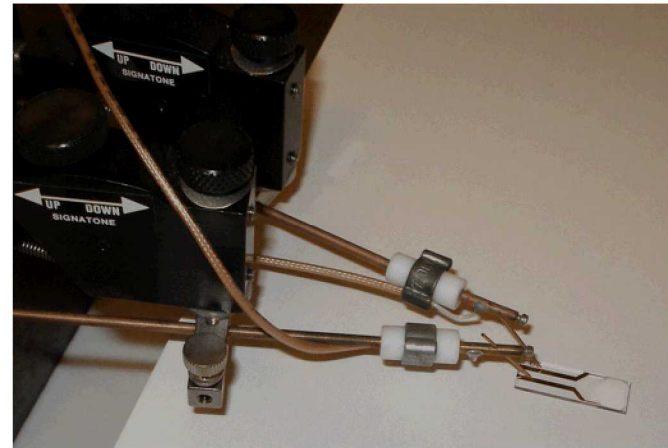
This is all contained in commercial equipment and software.

Iodine Sensors with High Selectivity in Environmental Conditions

Solartron 1296 dielectric interface in series with a Solartron 1260 frequency response analyzer.
All sensor testing in a faraday cage to minimize electrical noise.

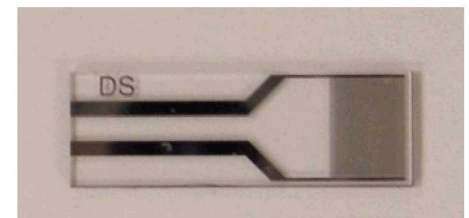


Samples are contacted with tungsten probes.



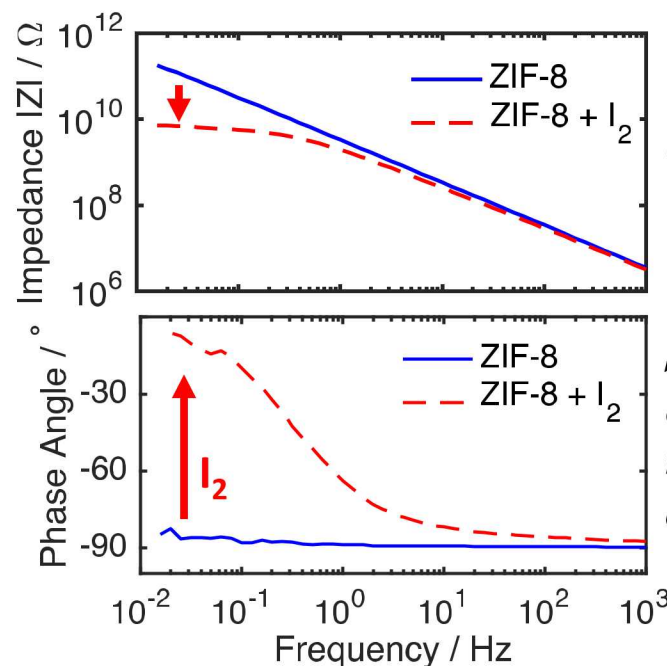
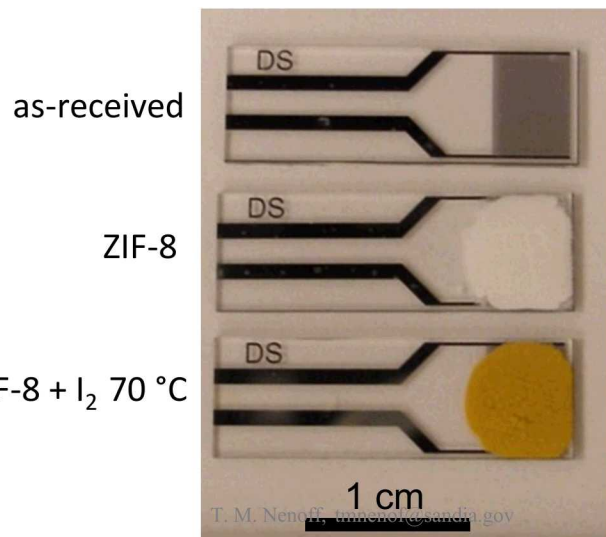
The dielectric interface allows us to **measure impedances as large as 10^{14} Ohms and frequencies 1 mHz – 1 MHz.**
Unique SNL specific: specialized high impedance, low frequency test equipment
(Common electrical test equipment has a lower input impedance than these coatings)

- Inter Digitated Electrodes (IDE's):
10 μm wide platinum lines (125 pairs), 10 μm spacing on glass substrate
- MOF film: MOF + binder
- Film: screen printed onto platinum interdigitated electrodes
- Iodine adsorption studies: in air and humidity at 25, 40, 70 $^{\circ}\text{C}$
- Test response over a broad electrical frequency response (1 MHz – 1 mHz)



1 cm

Iodine (I_2) Sensor with ZIF-8



>1 order magnitude decrease in impedance
70 °C, 30 min I_2 exposure

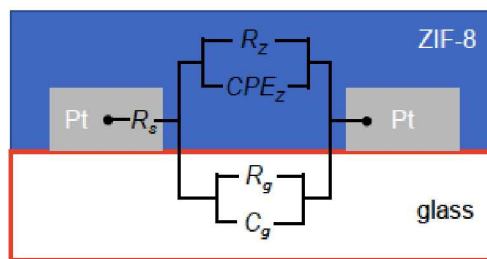
Sensor changes from ideal capacitor to nearly ideal resistor at low frequency after I_2 sorption.

Loading Temperature (°C)	"Empty MOF" Device impedance (GΩ)	" I_2 -Loaded MOF" Device impedance (GΩ)	% Change
Room temp.	171	121	-29%
40	182	20.7	-89%
70	182	7.22	-96%

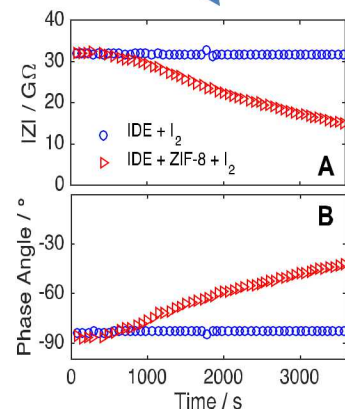
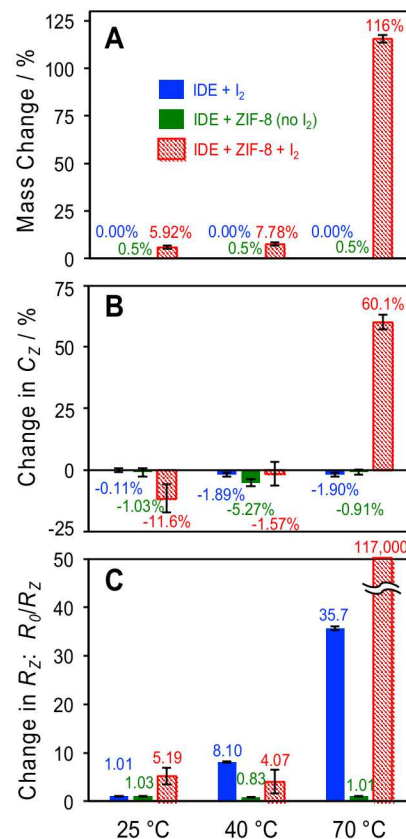
$|Z|$ recorded at 15 mHz. 10 mV AC. 0 V DC.

Effects of Temperature, Time and Competing gases

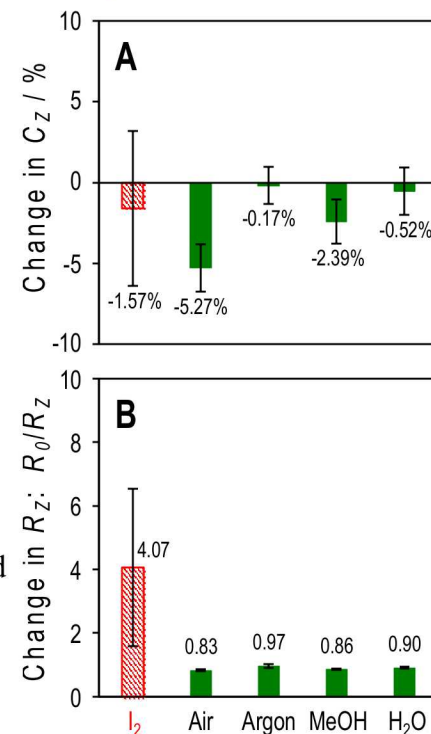
Equivalent circuit used to model impedance data



Cross sectional drawing of the sensor, (s=series, g=glass, z=ZIF-8) showing how the circuit elements R_s , R_z , CPE_z , R_g , and C_g spatially relate to the materials used.



100 mHz for uncoated & ZIF-8-coated IDEs exposed to gaseous I₂ at 25 °C.



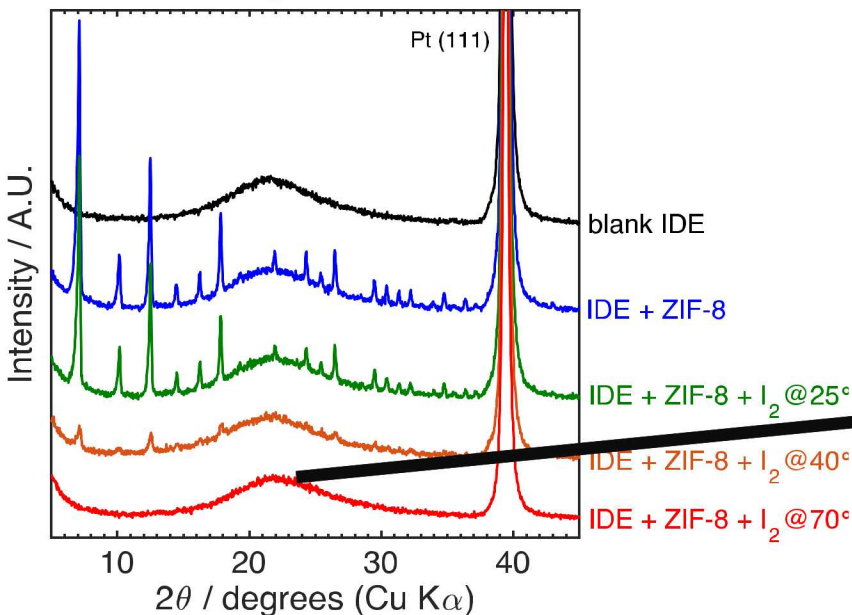
Responses evident for IDE+ I₂ gas.

However, IDE+ ZIF-8 + I₂ indicates *response plus gas selectivity*

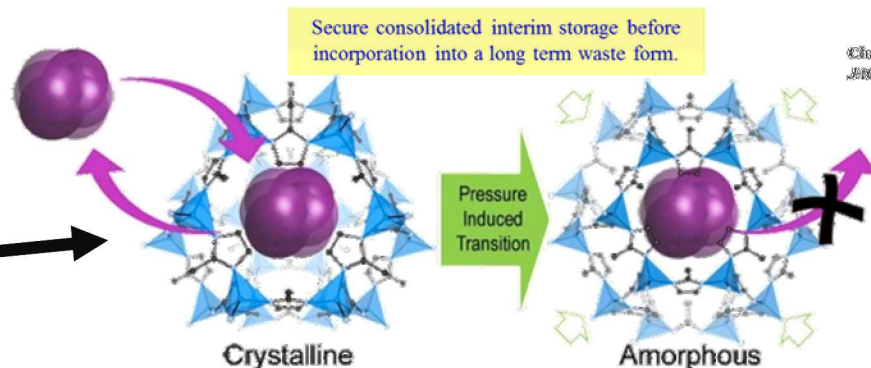
At 70°C, highest R_z >10⁵ x response

MOF/Sensor Temperature Dependence

ZIF-8@sensor



Retention of Iodine in MOF due to SHORT range crystallinity

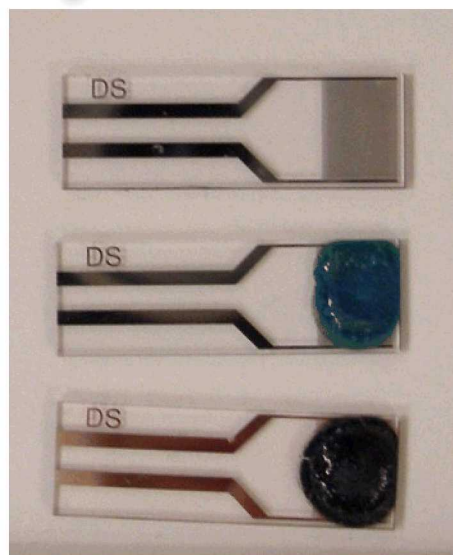


Chapman, Nenoff, et al.
ACS 2011, 13(16), 18583

Next steps:

- does framework chemistry / I_2 adsorption mechanisms translate into improved sensor
- what does an optimized sensor design look like
- sensor response to other fission gases
- sensor response to industrial gases (eg., hydrocarbons)

Iodine (I_2) Sensor with HKUST-1

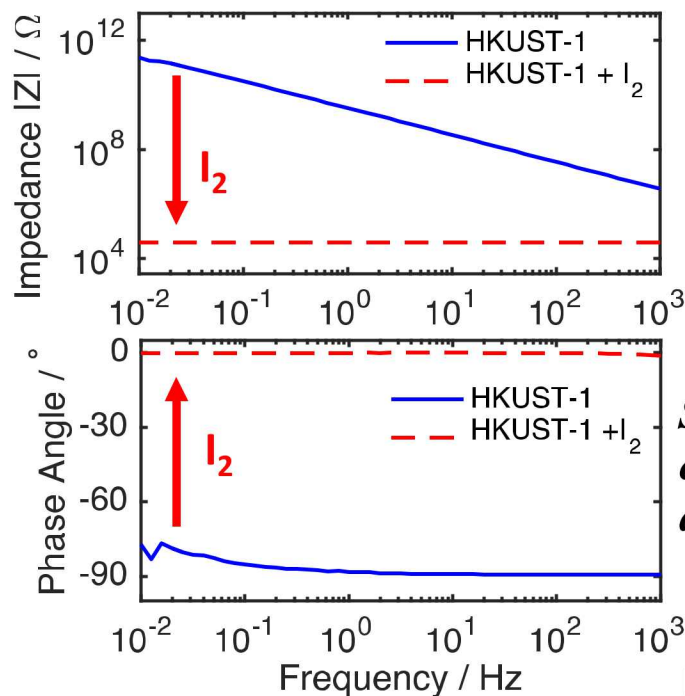


1 cm

as-received

HKUST-1 + I_2 40 °C

HKUST-1 + I_2 70 °C

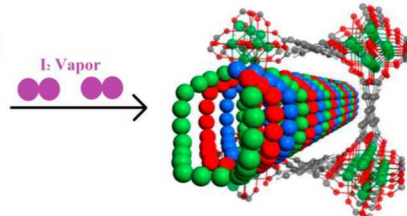
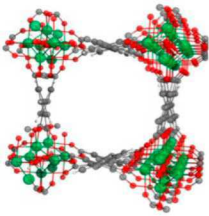


>6 order magnitude decrease in impedance
70 °C, 30 min I_2 exposure

Sensor changes from ideal capacitor to ideal resistor after I_2 sorption.

Loading Temperature (°C)	“Empty MOF” Device impedance (GΩ)	“ I_2 -Loaded MOF” Device impedance (GΩ)	% Change
Room temp.	105	21	-80%
40	106	4.73	-96%
70	99.0	38.8 kΩ	-100%

|Z| recorded at 15 mHz. 10 mV AC. 0 V DC.



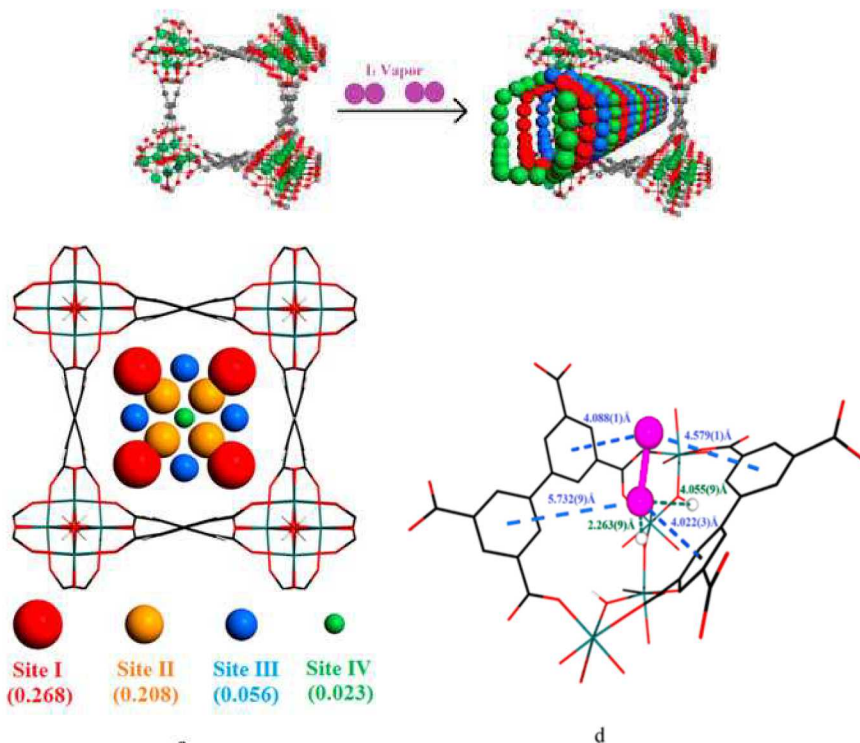
Reversible I₂ Ad/Desorption MOF Sensor: MFM-300, University of Manchester

For a reversible/re-usable sensor in the detection of iodine (eg., industrial applications) the ability to easily desorb I₂, and not need to reactivate the MOF prior to subsequent read-outs:

- Need a highly selective for I₂, yet easily regenerated MOF.
- MFM-300 requires mild (< 200°C temperature application) for I₂ desorption

Of interest to sensor development for industrial gases

JACS, 2017, 139, 16289



MFM-300 series of varying metal centers
Exhibits fully reversible I₂ uptake of 1.54g/g
Structure remains completely unperturbed
upon inclusion/removal of I₂

At high loadings, there is an self-aggregation of I₂ molecules
into a triple helical chains in the confined nanovoids,
- efficient I₂ packing
- I₂ storage density of 3.08g/cm³

Reversible/Re-Usable I₂ Sensor:

Experimental Procedure:

1. Suspend 25 mg MOF in 0.25 mL acetone (HPLC grade, 99.9%)
2. Drop cast 25 μ L onto interdigitated electrodes (IDE)
3. Dry 150 °C for 2 h at <1 mTorr.
4. Measure impedance + mass.
5. Expose to I₂ (100 mg I₂ in 100 mL) at 70 °C for 3 h.
6. Measure impedance + mass.
7. Dry at 175 °C for 8 h at <1 mTorr
8. Repeat 4-7 several times.

Step	MOF Mass / mg	Mass Gain / % of MOF
Dried	2.11 $\pm$ 0.09	(0)
I ₂ sorb1	4.59 $\pm$ 0.20	118 $\pm$ 3
Desorb1	2.18 $\pm$ 0.11	3 $\pm$ 5
I ₂ sorb2	4.48 $\pm$ 0.18	113 $\pm$ 10
Desorb2	2.21 $\pm$ 0.09	5 $\pm$ 4



IDE only

IDE + MOF

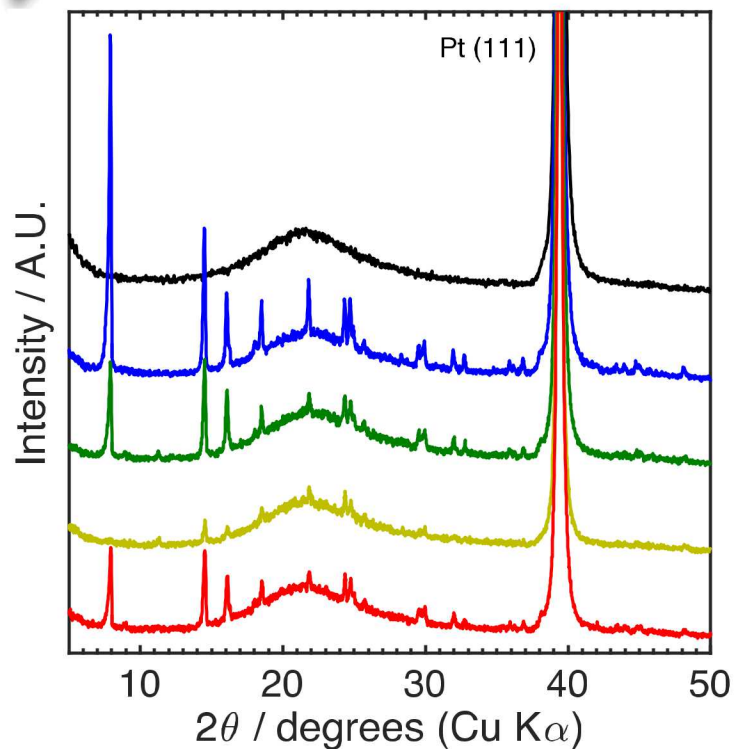
IDE + MOF + I₂

IDE + MOF
(I₂ desorbed)

Results repeated in triplicate.

Uncertainty is 1 standard deviation.

XRD Confirms Reversibility



IDE only

IDE + MOF as-cast (no heat)

IDE + MOF dried 175 °C, <1 mTorr for 8 h

IDE + MOF + I₂ 70 °C for 3 h

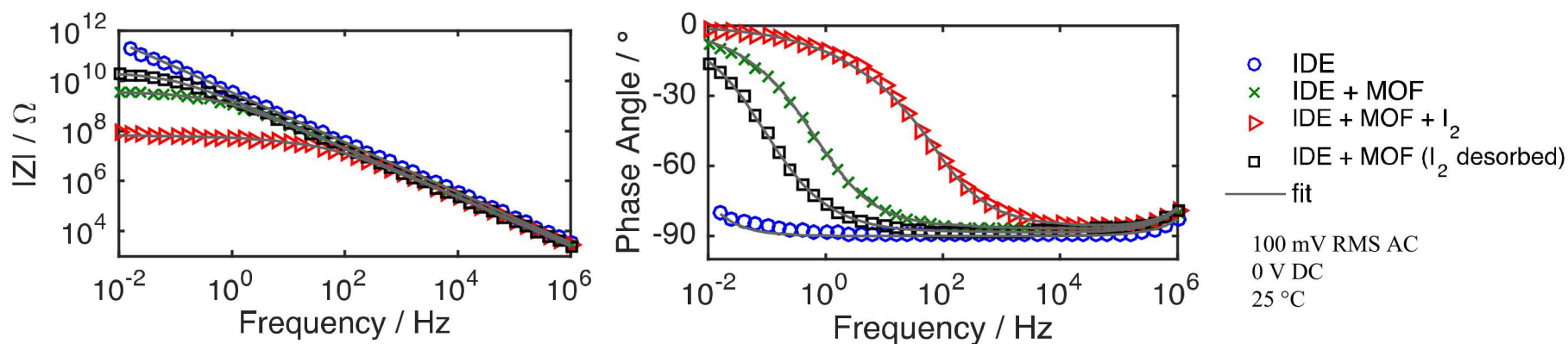
IDE + MOF I₂ desorbed 175 °C, <1 mTorr for 8 h

Peak near 8° decreases in intensity upon initial drying.

Most peaks suppressed upon I₂ sorption, but all return upon release of I₂.

Impedance Response Is Reversible

2-3 orders of magnitude decrease in MOF impedance upon I_2 sorption.



Preliminary impedance circuit analysis

Step	MOF Resistance / $G\Omega$
IDE only	$1,330 \pm 120$
MOF dried	4.15 ± 0.61
I_2 sorb1	0.118 ± 0.065
Desorb1	20.7 ± 3.8
I_2 sorb2	0.327 ± 0.023
Desorb2	129 ± 0.3

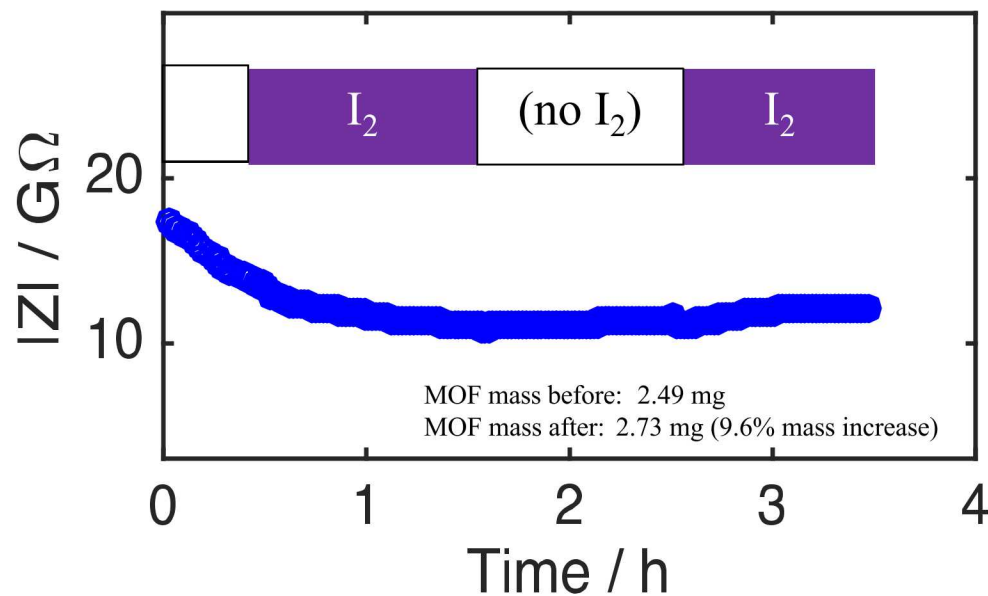
Impedance progressively increases with each desorption step. Might be due to slight change in MOF, or progressively better drying.

Results repeated in triplicate.

Uncertainty is 1 standard deviation.

Real Time Measurement at Room Temperature

- MOF dried at 175°C <1 mTorr, cooled to 25°C under vacuum, then immediately tested.
- Measured continuously at 100 mHz for 3.5 hours.
- I₂ (100mg/100 mL container) added or removed every 60 min.



No appreciable change in impedance upon I₂ exposure at room temperature over 2 h.

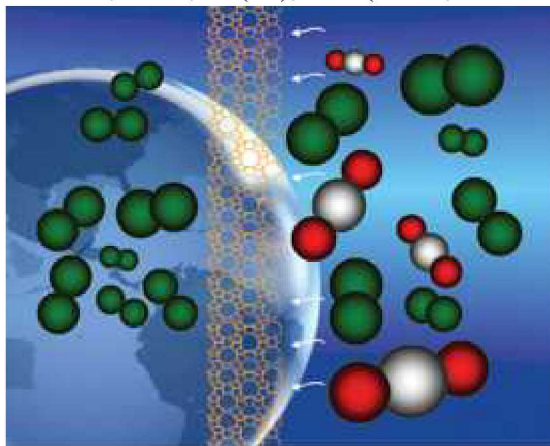
On-going: Determine correlations between metal centers and signal response,

R&D Area 3: Nanoporous Materials Membranes for Light Gas & Hydrocarbon Separations

H₂ Purification

Nature Mater., **2015**, 7, 377; *Chem. Rev.* **2007**, 107, 4078

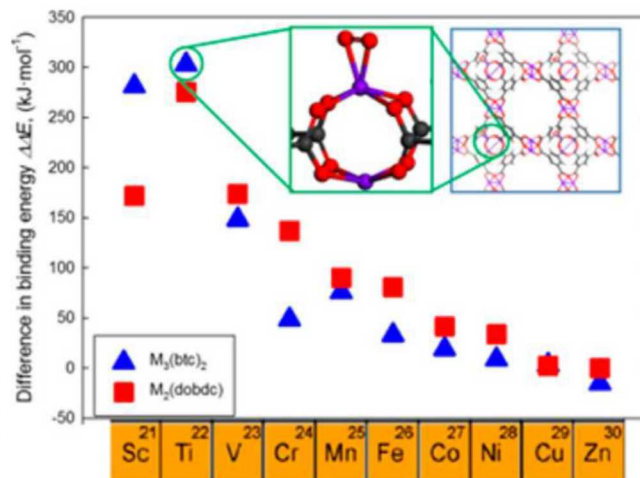
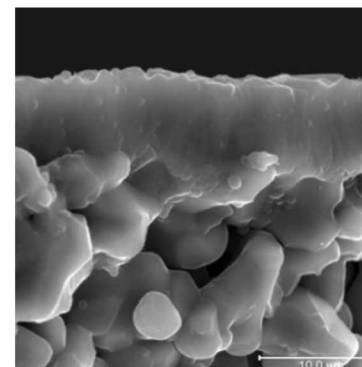
MRS Bulletin, **2006**, 31(10), 735 (cover; Editor Nenoff)



ZSM-5 Zeolite membrane for

H₂ from CO₂ separations

Micro Meso Mater., **2003**, 66, 181



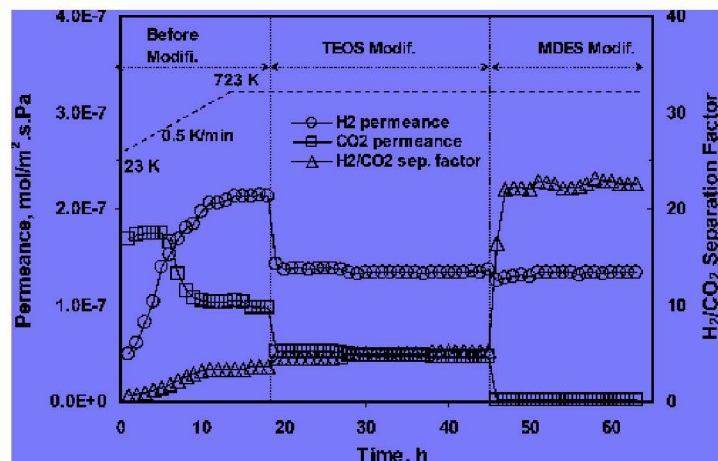
DFT/AIMD Designed Nanoporous Materials for O₂ from Air Separations for Energy Efficient Combustion

Chem. Mater. **2016**, 28(10), 3327

PCCP, **2016**, 18, 11528

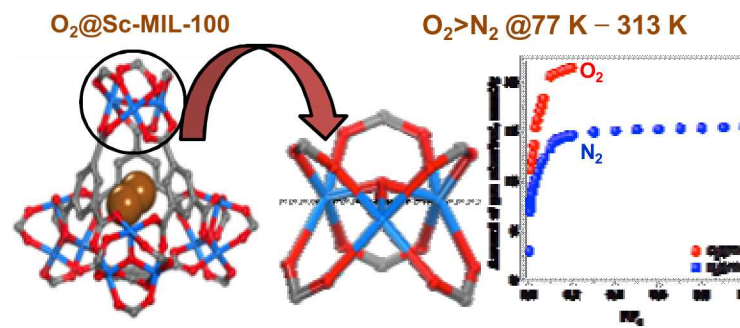
J. Phys. Chem. C, **2015**, 119, 6556

Chem. Mater. **2015**, 27(6), 2018



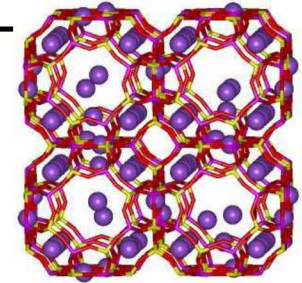
H₂ Purification from Syngas

Langmuir, **2009**, 25(9), 4848



Materials Design of an O₂ from Air Separation Material at Ambient conditions

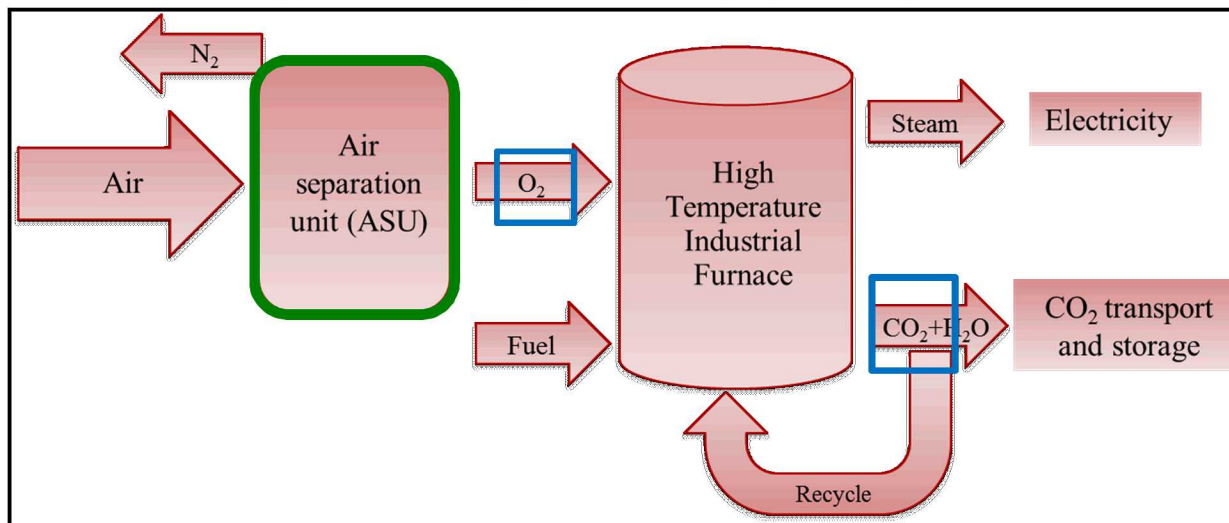
Currently Zeolite A is the preferred selectivity material
It selectively adsorbs N₂ from air, O₂ and CO₂ pass through, ~90% purity



Application Targets: 95+% purity

- Oxygen-enriched (oxy-fuel) combustion:** high temperature burning of fossil fuel in an O₂ rich atmosphere results in a flue gas composed mainly of CO₂ (for capture) & water (little or no SO_x and NO_x emissions)

Avoids need for energy and cost expenses of cryogenic separations



- On-Board Oxygen Generation (OBOGs):**
Oxygen/breathing generation devices for pilots

Design O₂ Selective Separations Materials

DFT & Experiments

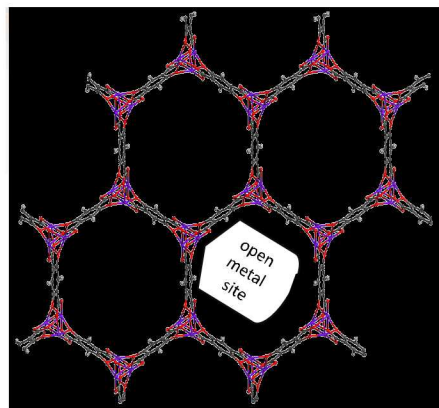
MOFs with coordinatively unsaturated metal centers are promising materials for O₂/N₂ separations

- Two prototypical MOFs from this category, Cr₂(BTC)₃¹, Fe₂(DOBDC)₂² both show preferential adsorption O₂ vs N₂
- Plane wave DFT calculations on periodic structures: [Vienna Ab initio Simulation Package \(VASP\)](#)

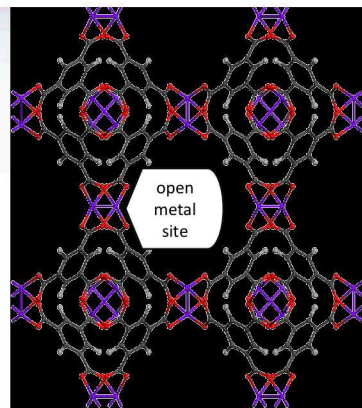
Binding geometries for side-on and bent O₂ and bent and linear geometries for N₂ were evaluated

Static binding energies for O₂ and N₂ at 0 K

- Use of [DFT to determine M-O₂ vs M-N₂ binding energies](#)



M₂(dobdc)



M₃(btc)₂

MOF metal sites = separate O₂/N₂ by differences in bonding & electronic properties

¹JACS **2010**, 132, 7856–7857

²JACS **2011**, 133, 14814–14822

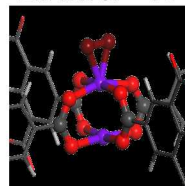
Plan wave density functional theory (DFT) calculations were performed on periodic structures of each MOF in the Vienna ab initio simulation package (**VASP**) with the Perdew-Burke-Ernzerhof (**PBE**) functional including dispersion corrections (**DFT-D2**). Geometries were optimized and **static binding energies** (ΔE_{O_2} , ΔE_{N_2}) were calculated by

$$\Delta E_{O_2} = E_{MOF+O_2} - E_{MOF} - E_{O_2}$$

The **differences in binding energies** ($\Delta \Delta E$) for oxygen and nitrogen were calculated by

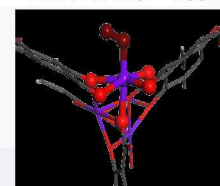
$$\Delta \Delta E = - (\Delta E_{O_2} - \Delta E_{N_2})$$

Side-on bonding
 $\angle M-X-X$ 67° - 71°



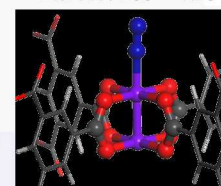
Cr₃(btc)₂(O₂)

Bent bonding
 $\angle M-X-X$ 116° - 159°



Mn₂(dobdc)(O₂)

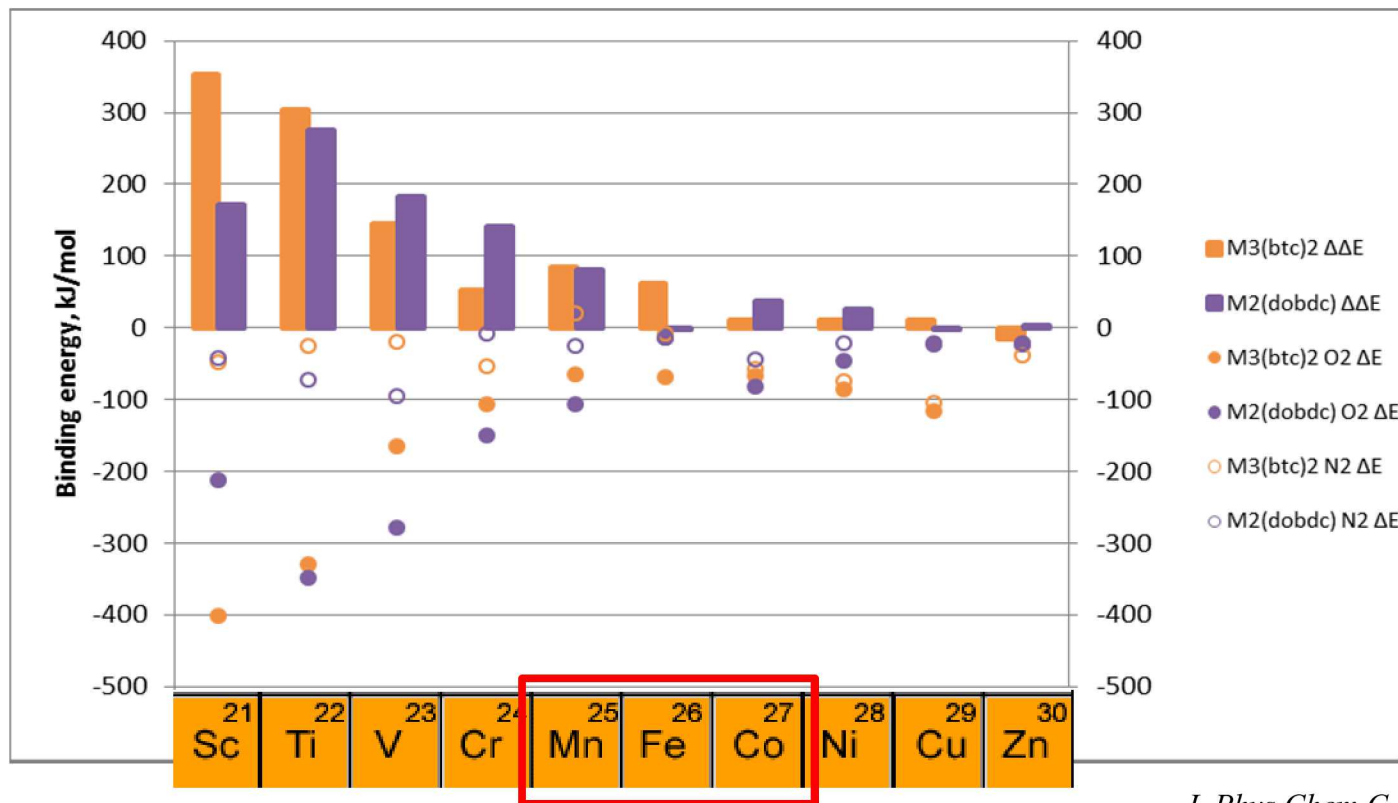
Linear bonding
 $\angle M-X-X$ 165° - 179°



Fe₃(btc)₂(N₂)

Attention Paid to Bonding Geometries

O₂ and N₂ Binding Energies Trends Across the First Row Transition Metal Series



J. Phys Chem C, **2015**, 119, 6556.

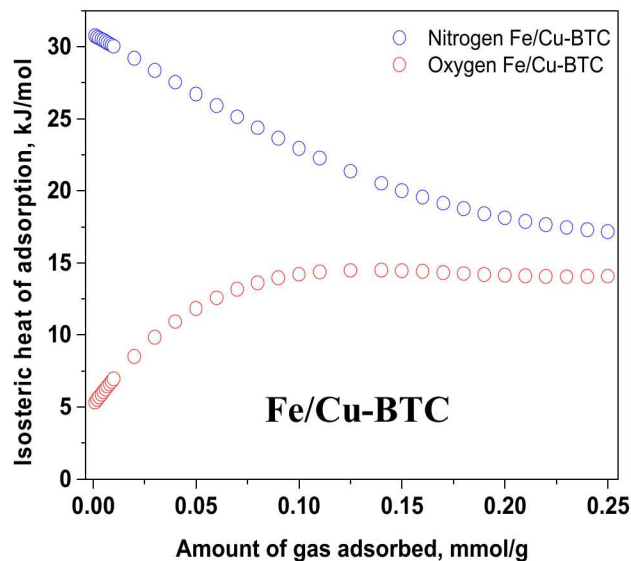
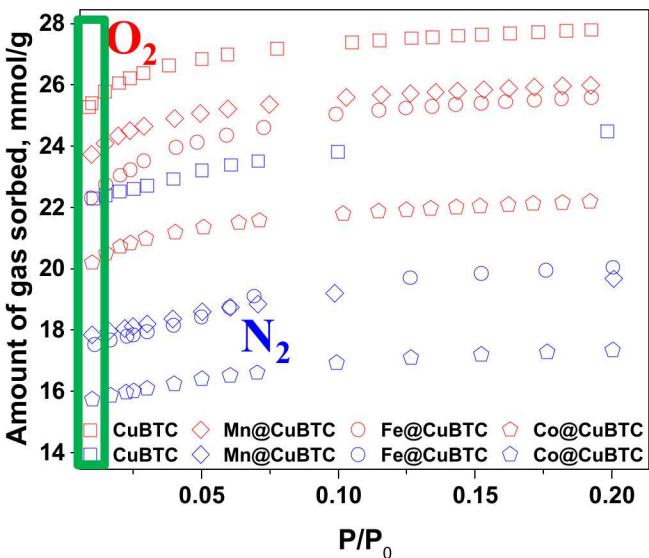
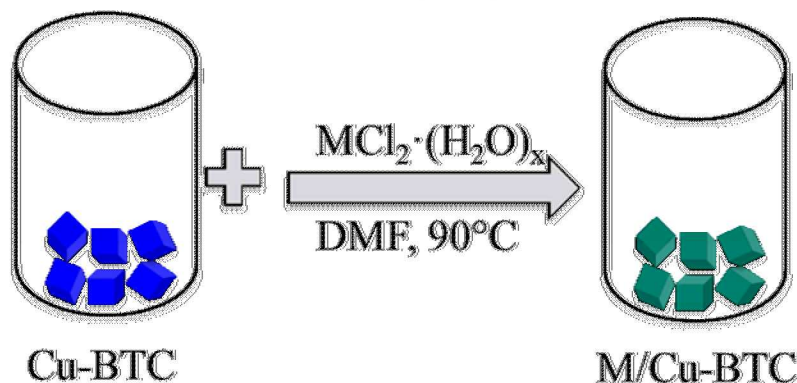
DFT predicts similar O₂ and N₂ binding to Mn, Fe, Co but with consistent stronger binding for O₂ to the metals

Postsynthetic Metal Ion Exchange to form Porous Mn-, Fe- and Co- Analogues of Cu-BTC



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

M = Mn, Fe, Co



0 K DFT binding energy:
Excellent prediction for 77K experiments,
Do not correlate as well with experimental data 273-298 K
- N₂ is preferred over O₂

Chem. Mater., **2015**, 27(6), 2018.

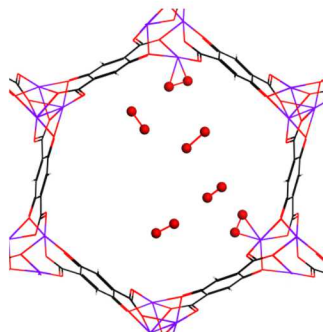
AIMD Simulations with Temperature Considerations

$M_2(\text{dobdc})$ analogs

NVT ensemble: 27.5 ps, 0.5 fs timestep
PBE density functional with dispersion correction (PBE-D2),
PAW potentials for core electrons, spin polarization

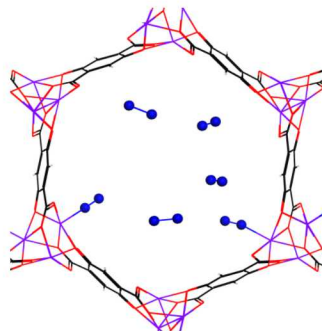
Guests

2 O₂ bound
4 O₂ unbound

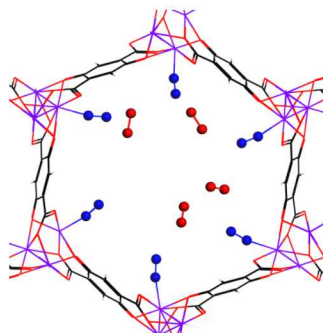


Single
component

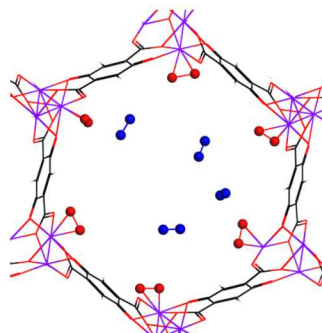
2 N₂ bound
4 N₂ unbound



Mixed gas
Competitive
binding



6 N₂ bound
4 O₂ unbound



6 O₂ bound
4 N₂ unbound

Temperatures

201 K
258 K
298 K

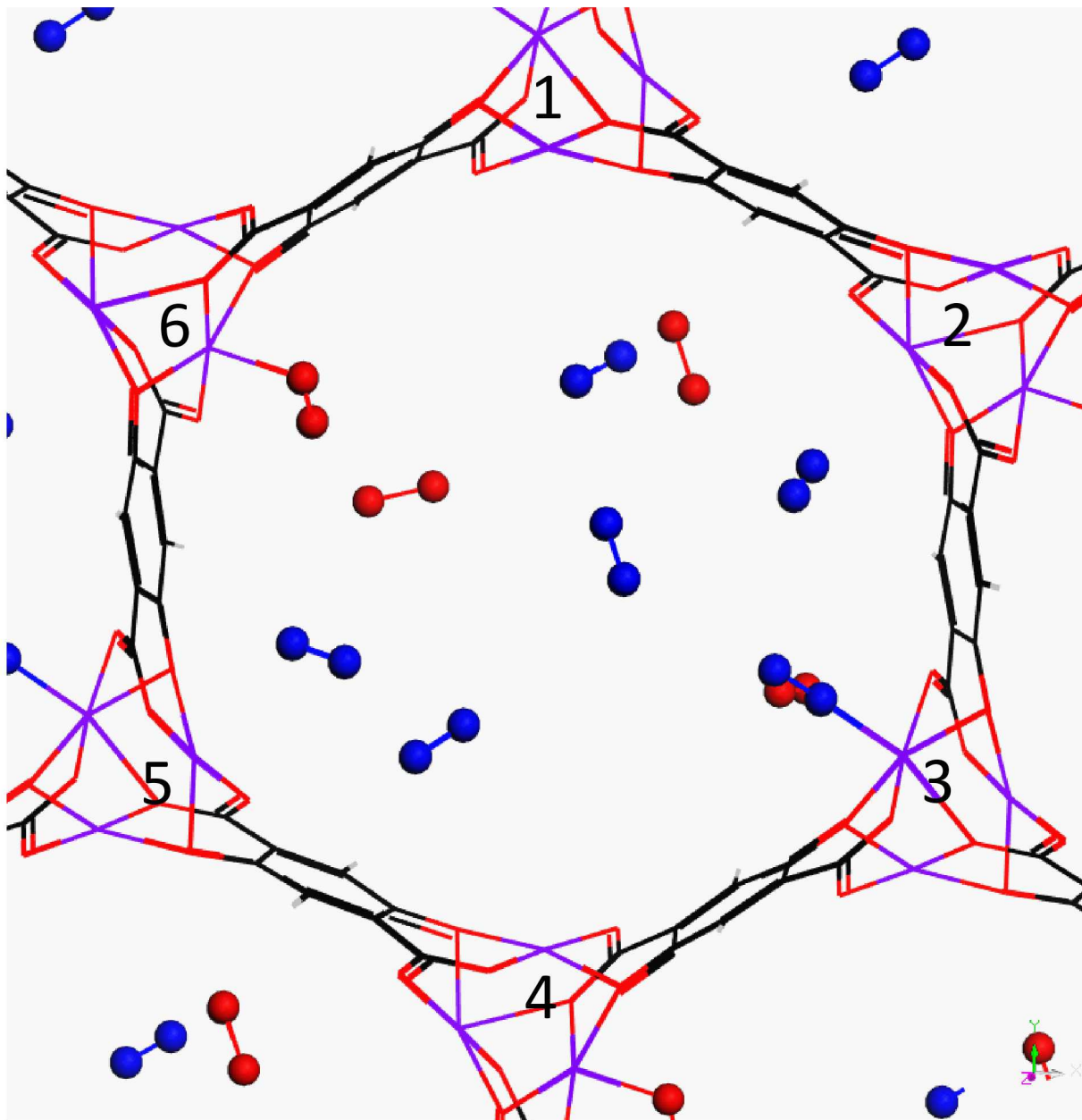
Metals

24	25	26
Cr	Mn	Fe

Red Sky Supercomputer
36 Simulations

3,800 processor-days each

<http://hpc.sandia.gov/>



$\text{Cr}_2(\text{dobdc})$

$6 \text{ N}_2 + 4 \text{ O}_2$

298 K

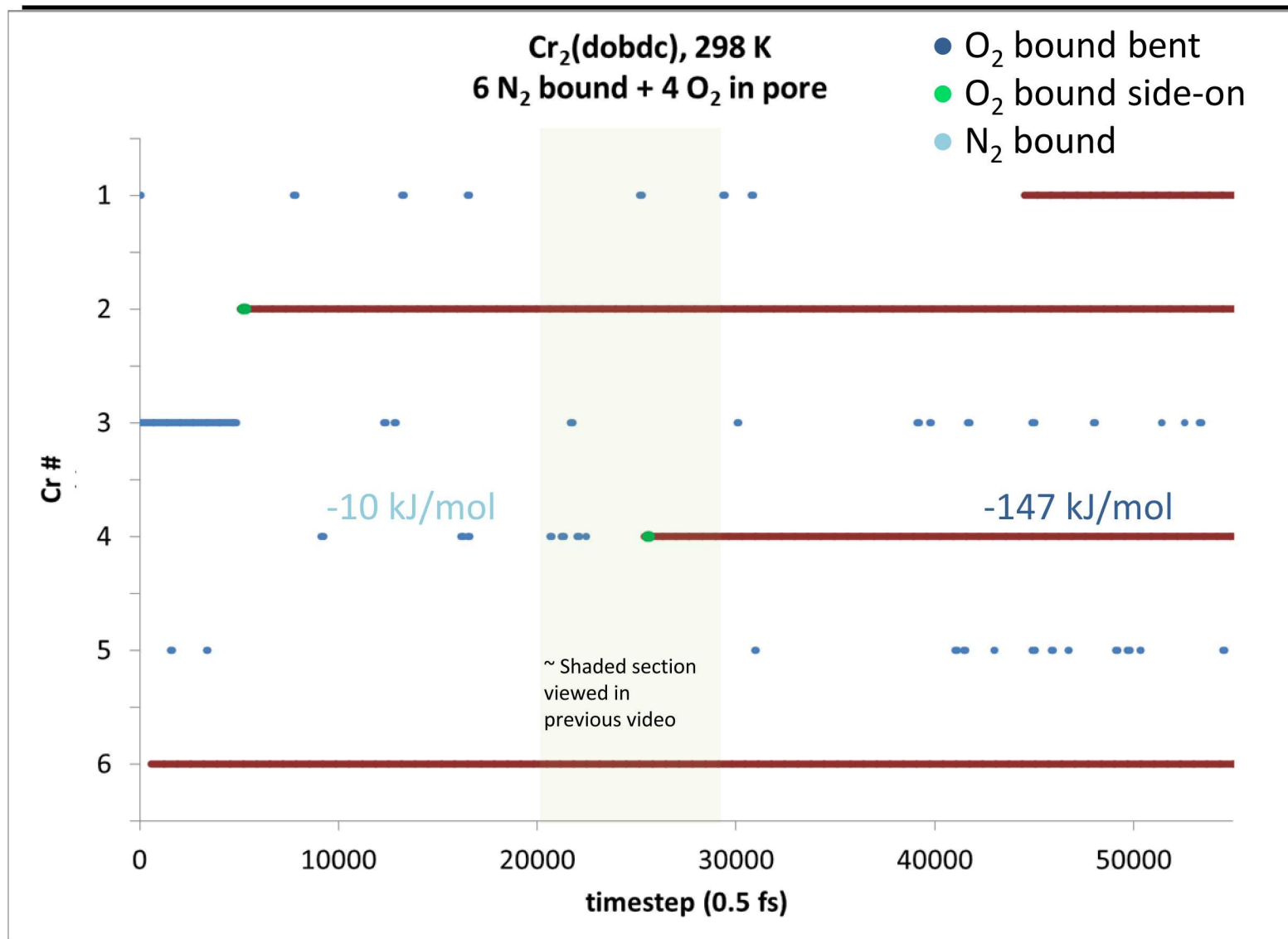
NVT

Time 2 ps – 15 ps

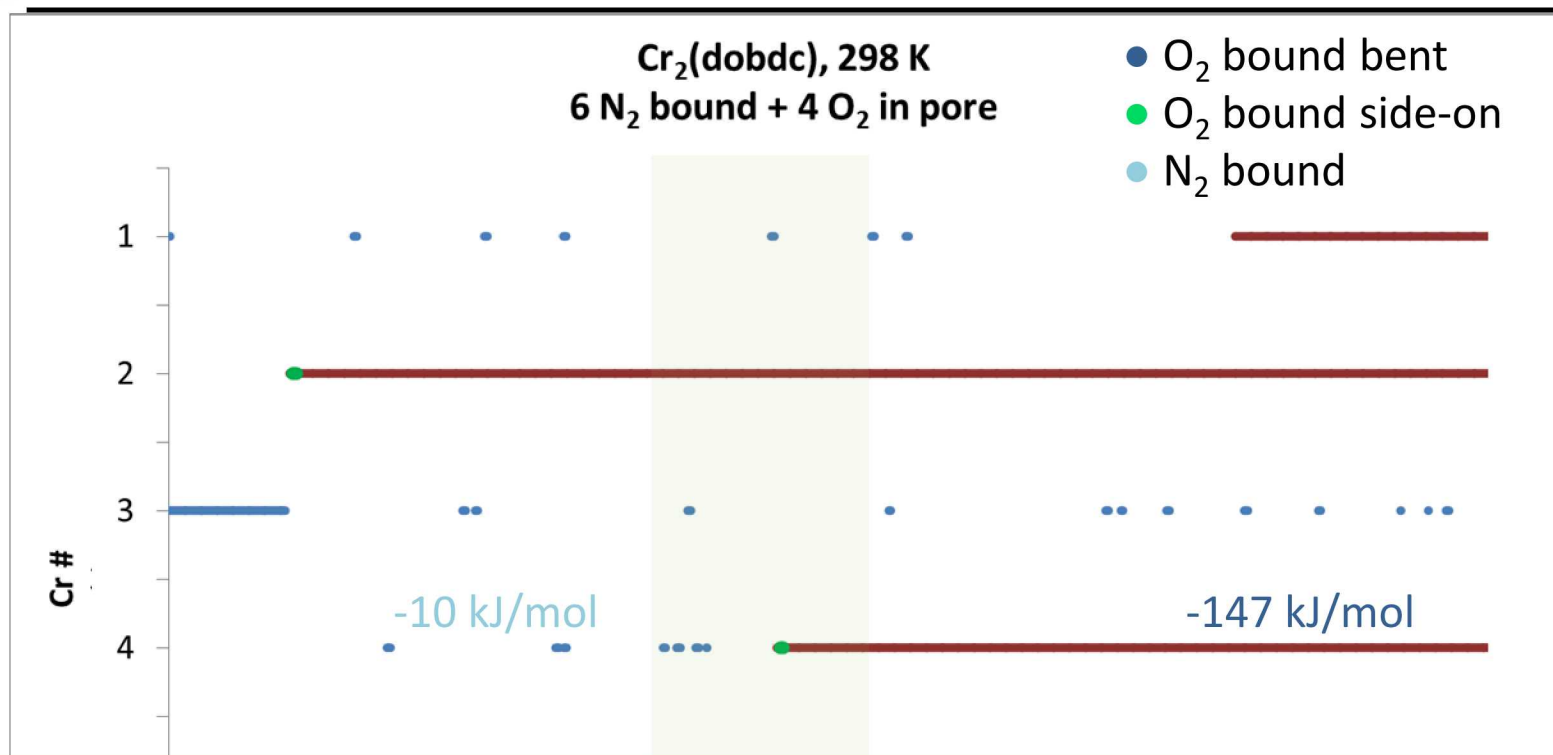
1 frame = 25 fs

- O_2 slow to bind, but once on metal center, binding holds
- N_2 rapid bind and release from metal centers
- O_2 long term binding is consistently 'bent'
- Selective for O_2

Gas Occupancy at Each Metal Site



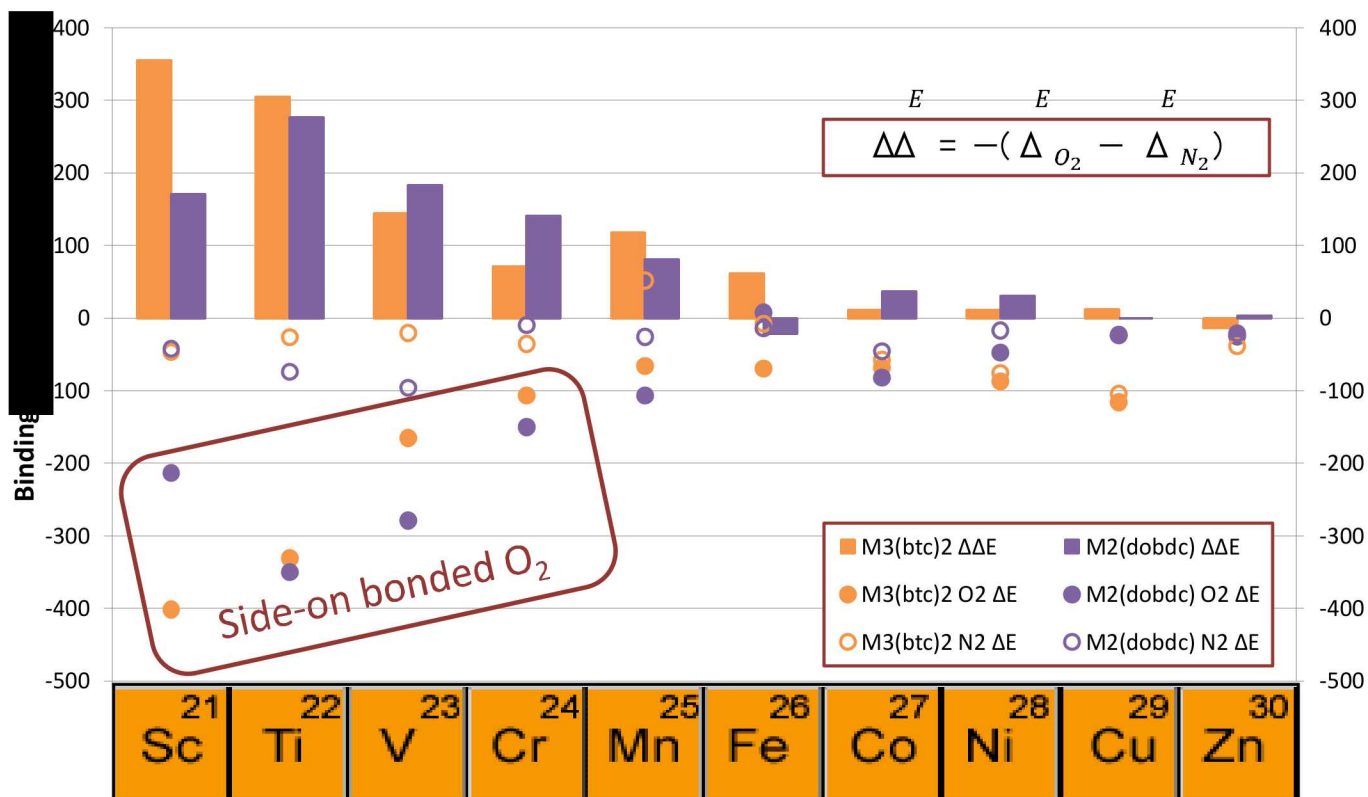
Gas Occupancy at Each Metal Site



DFT for screening: predicted *O₂ preferentially bound*
 AIMD predicted *N₂ first bound but displaced by side-on O₂*
Next Step:
follow predictions of strongly side-on bound O₂

Use of Strongest *Side-On Binding* Predictions

Binding Energy Calculated as a Function of Metal Site



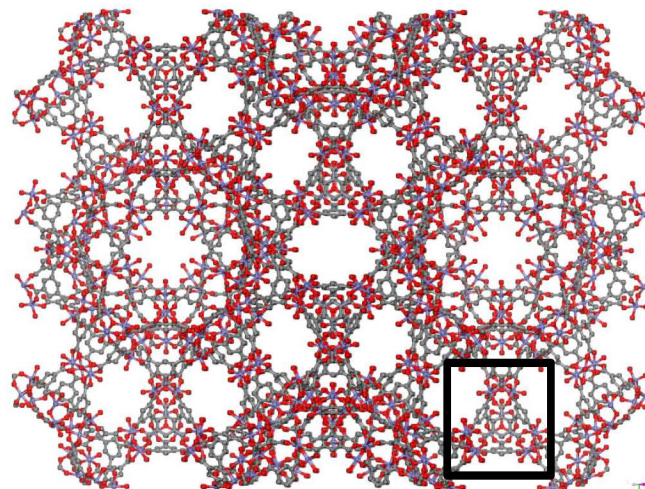
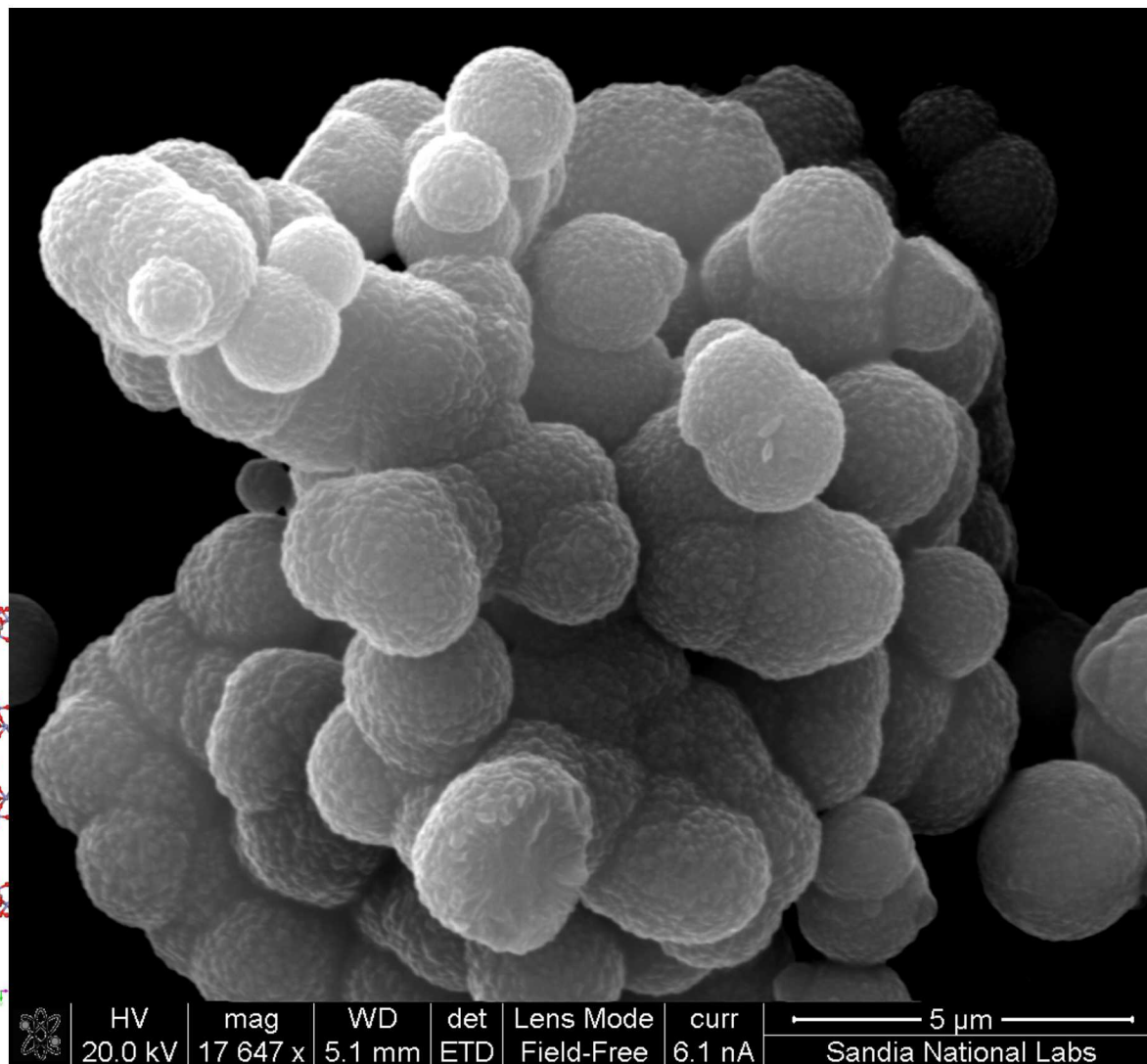
J. Phys Chem C, **2015**, 119, 6556.

MD Simulation Inspired MOF Synthesis: Sc/BTC/DMF/HCl

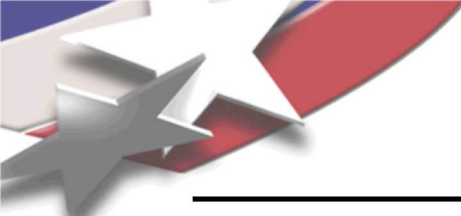
Unique synthesis:

Mixed $\text{Sc}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ and
1,3,5-benzetricarboxylic acid
in N,N'-dimethylformamide and
HCl.

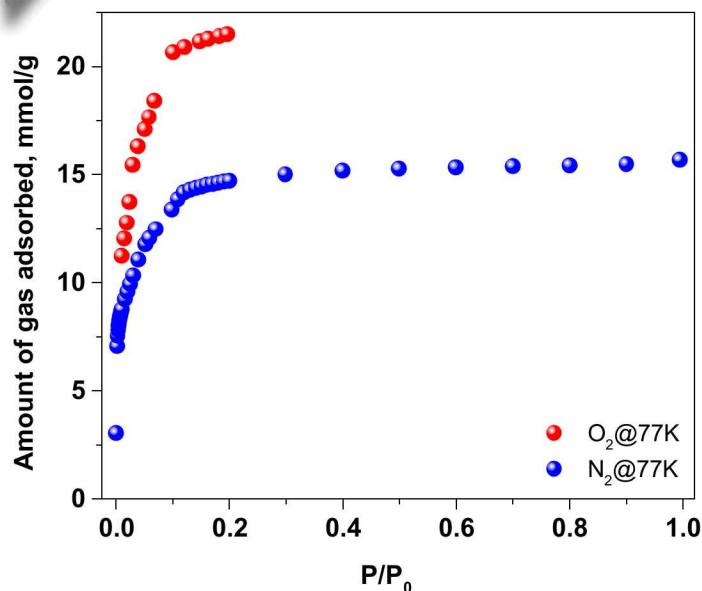
Heated to 373K overnight



Chem. Mater. **2016**, 28(10), 3327-3336



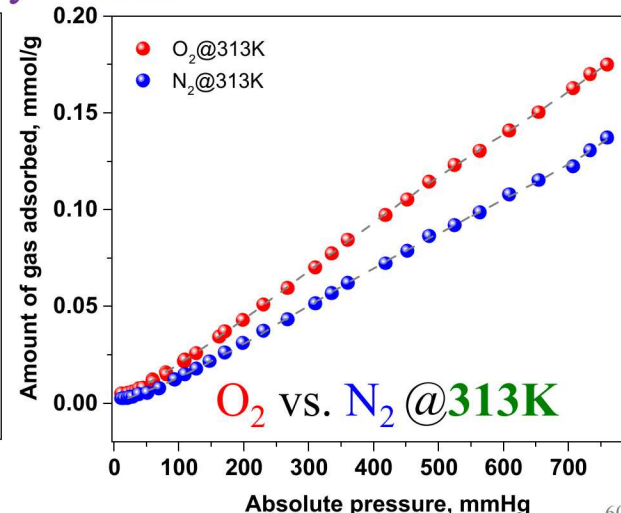
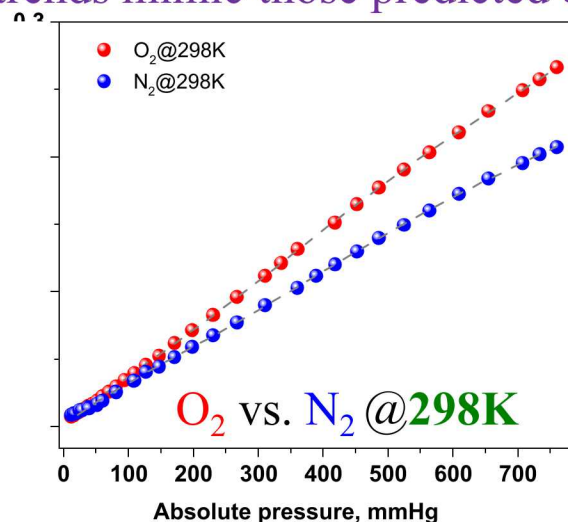
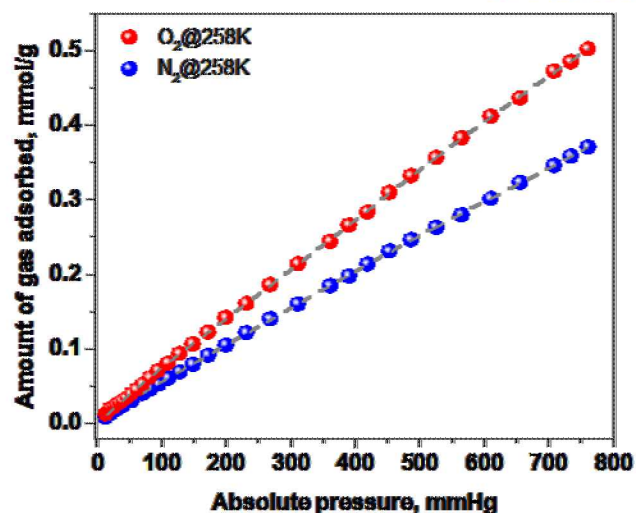
Sc-MIL-100: Metal-Center has a role at temperature



Enhanced adsorption of
 O_2 vs. N_2 at 77K

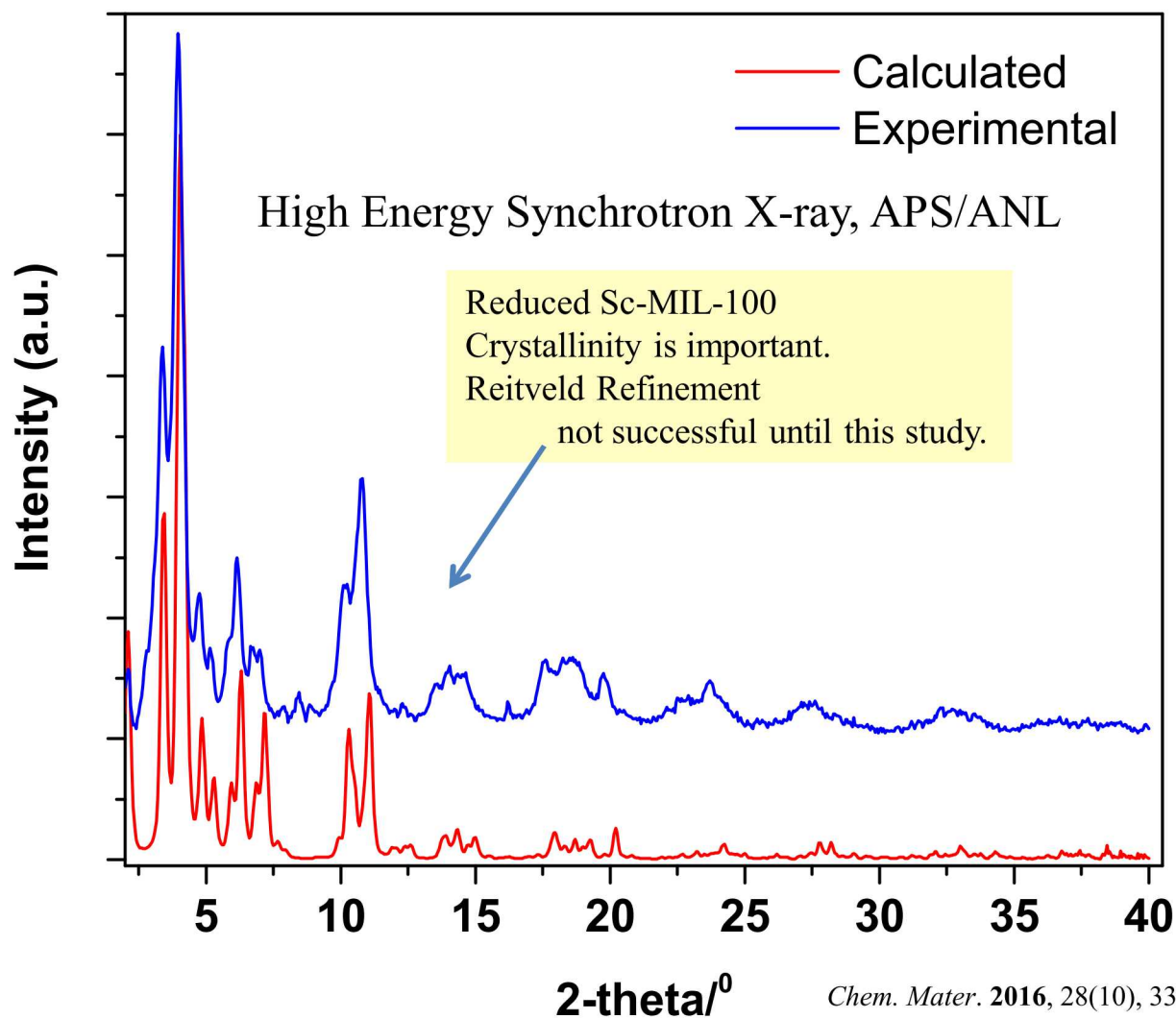
How does Sc-MIL-100 behave at more realistic operational temperatures?

Isotherm trends mimic those predicted by GCMC



Structure-Property Relationship

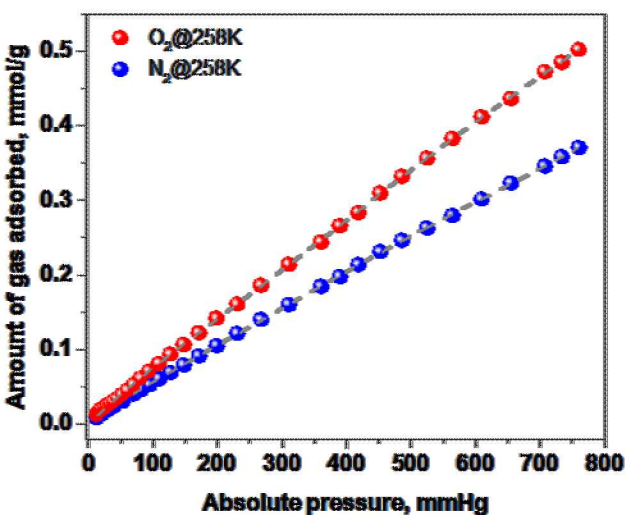
Understanding of Sc-MIL-100 O₂ Selectivity



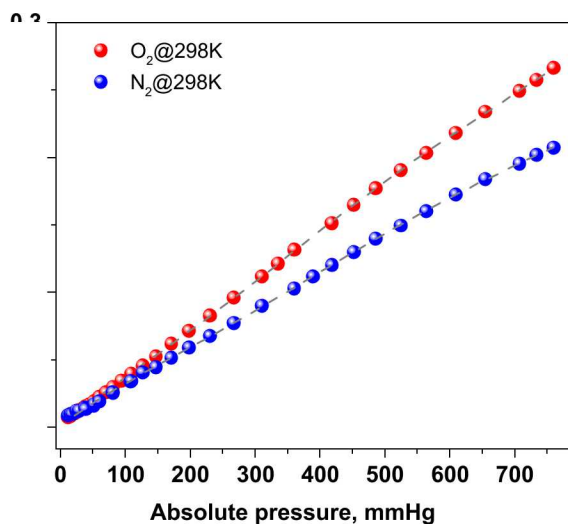
Chem. Mater. **2016**, 28(10), 3327.

Enhanced Quantity of O₂ vs N₂ Adsorbed in the Temperature Range (at least to 313K)

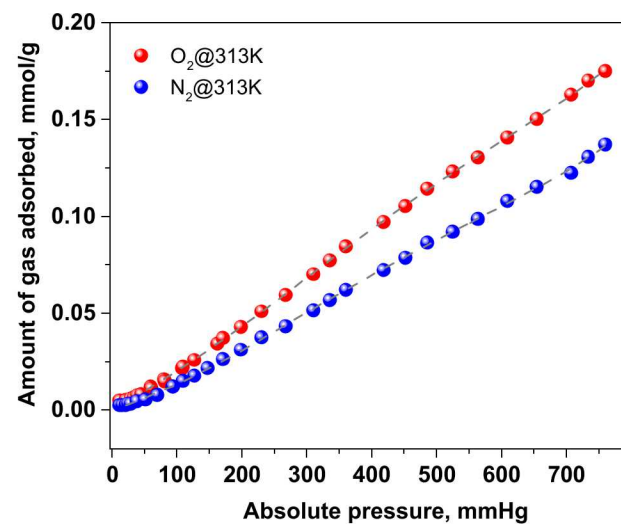
O₂ vs. N₂ @258K



O₂ vs. N₂ @298K



O₂ vs. N₂ @313K



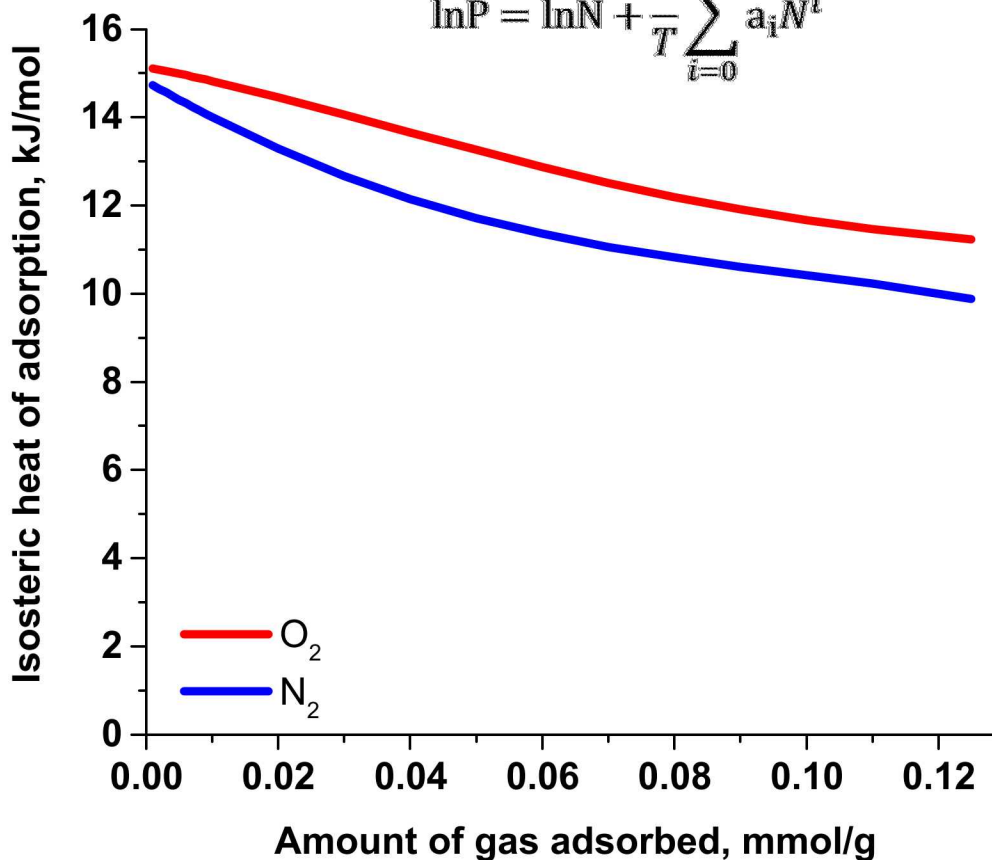
Isotherm trends mimic those predicted by GCMC

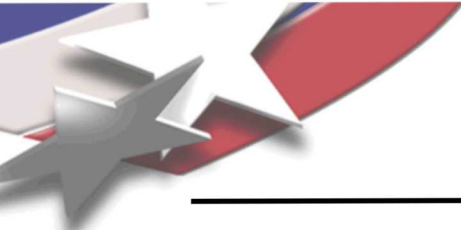
Isosteric Heat of Adsorption (kJ/mol) vs. Adsorption Energy for O₂ vs N₂

Q_{st} derived from 258K, 298K and 313 K

Independent Virial Fit HOA

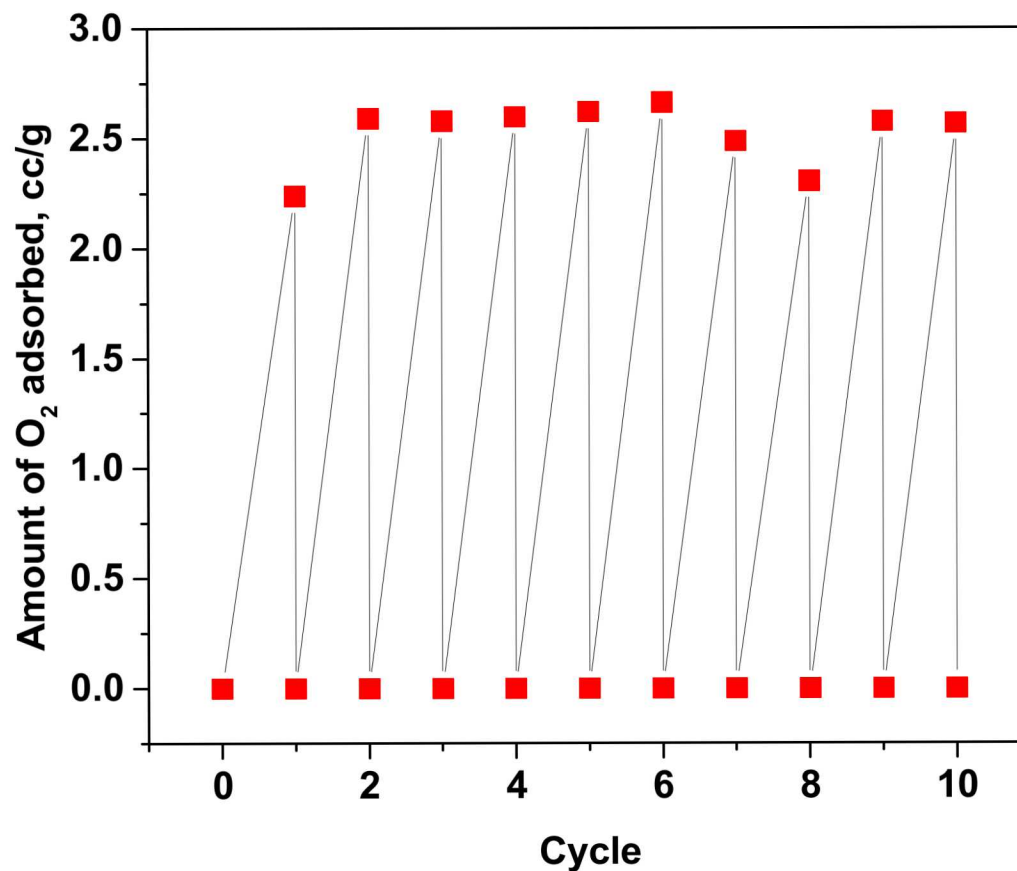
$$\ln P = \ln N + \frac{1}{T} \sum_{i=0}^m a_i N^i$$





Sc-MIL-100 Performance

O₂ adsorption & Desorption over 10 cycles, 298 K, 1 atm

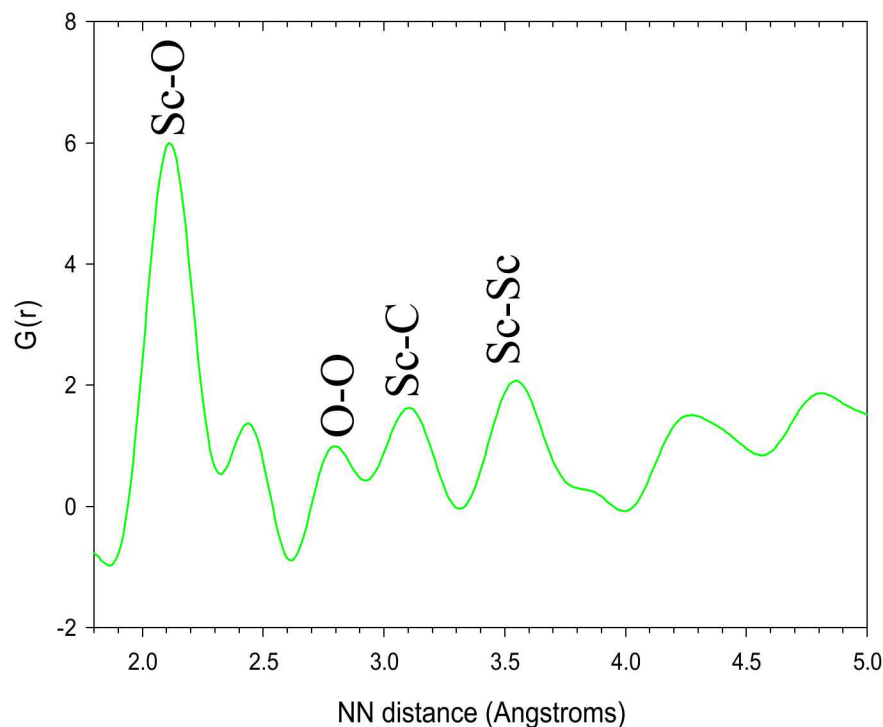


What about the structure is making Sc-MIL-100 O₂ strongly sorbing?

US provisional Patent 2019, licensed to NuMat and TDA Research 2019

Sc-MIL-100: Structure-Property relationship evaluated using Differential (d)- PDF

d-Pair Distribution Function (d-PDF)



Peaks shifted to longer distances
Consistent with larger Sc incorporation
(vs. Cr-MIL-100)

d-PDF peak analysis

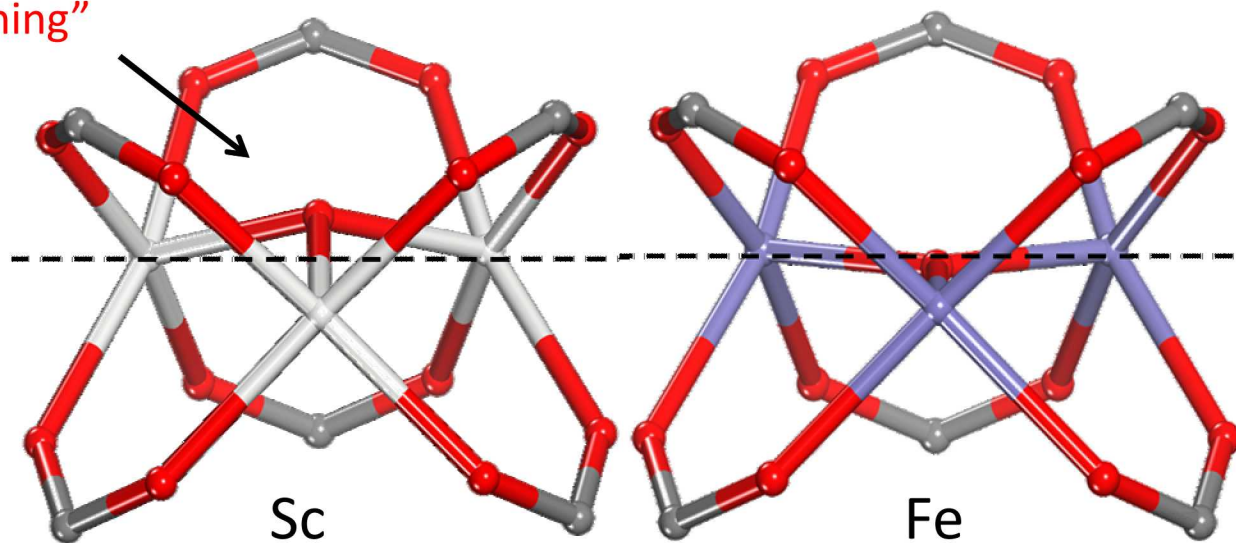
Bond	NN distance (Å)	Area	FWHM (Å)
Sc-O	2.11	1.5	0.19
O-O	2.81	0.3	0.22
Sc-C	3.08	0.8	0.26
Sc-Sc	3.53	0.5	0.24

- Oxo-centered trimers at nodes of MIL-100 framework inferred from M-O and M...M distances
- Narrow Sc-O peak = narrow Distribution of bond lengths
- Single M-O bond length (M-O(μ_3) or M-O (carboxylate)), suggests **M-O-M angle of 113°** << 120° of a planer trimer

Sc-MIL-100: Preferred O₂ sorption – Large Sc Distorts Cluster

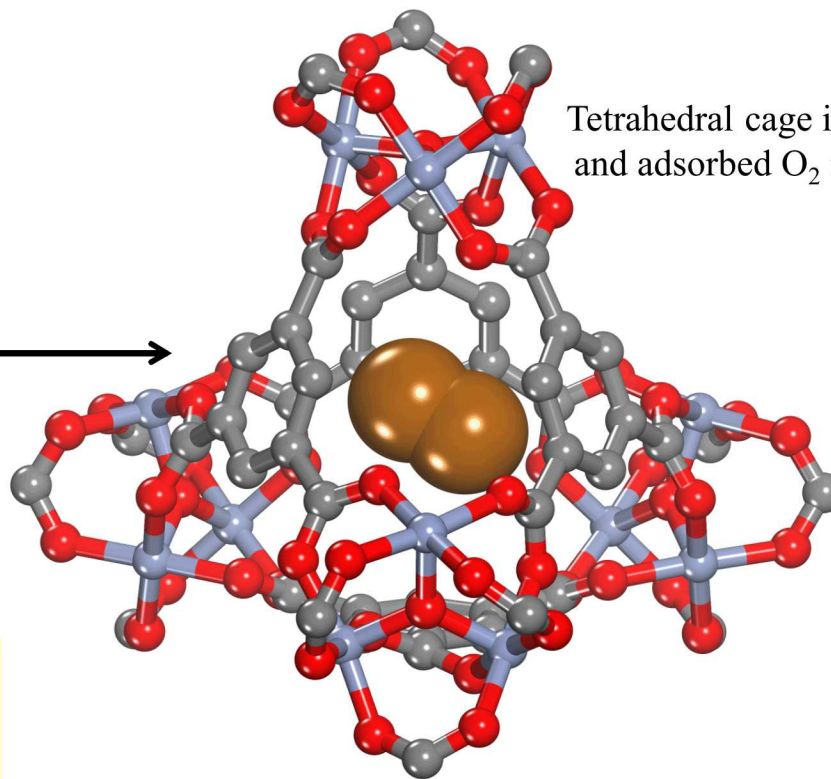
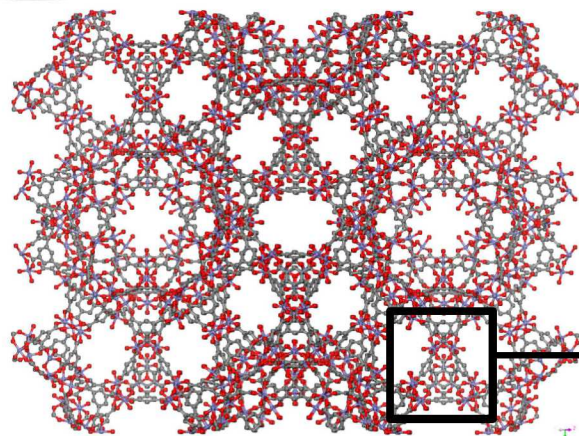
Large size of Sc atom requires **out of plane distortion** in the ozo trimer of the O(μ_3) atom. Resultant “**puckering**” of trimer and “bending” of ligand is probable route for enhanced O₂ sorption / insertion in Sc-MIL-100

“tulip opening”



Rietveld refinement unit cell for Sc-MIL-100: $a = 74.518(31) \text{ \AA}$, $R = 10.7\%$

Sc-MIL-100: Probable Sc-O binding sites



GCMC-equilibrated configurations:
Cage and pore occupancy
as determined at 298K and 1 bar

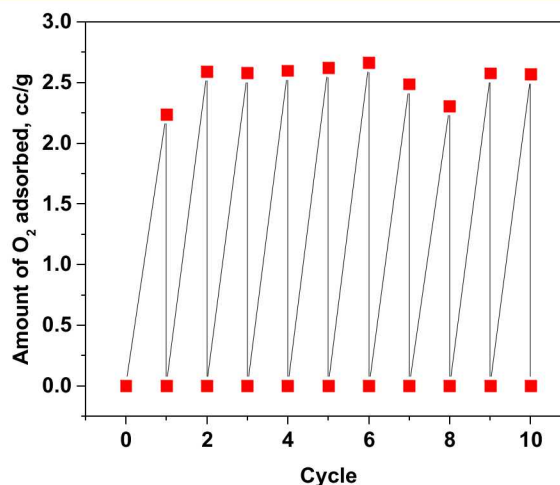
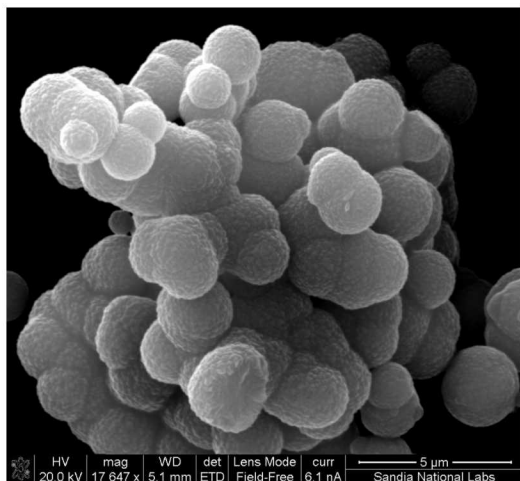
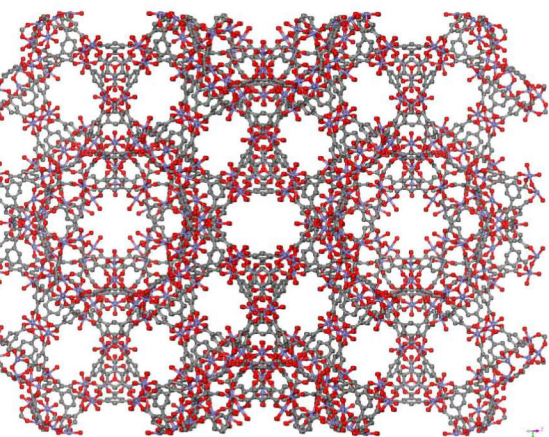
P (bar)	Gas	# in Cage	# in Pore	Total
1	N ₂	21	27	48
1	O ₂	47	20	67

2019: DOE SBIR Phase I for the Tech Transfer Air Separation

This technology has been licensed by two different US companies after a successful SBIR round of proposals Initiated by US Dept of Energy, directed funding to commercialize

Goals to scale-up the material for industrial testing, determine optimized process design and Technoeconomic analysis generated parameters

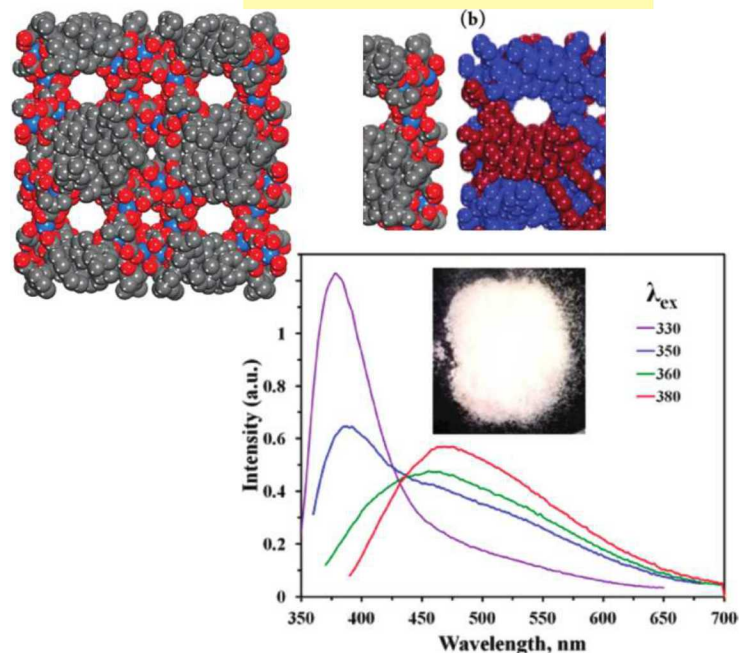
For Phase II and eventual commercial process implementation



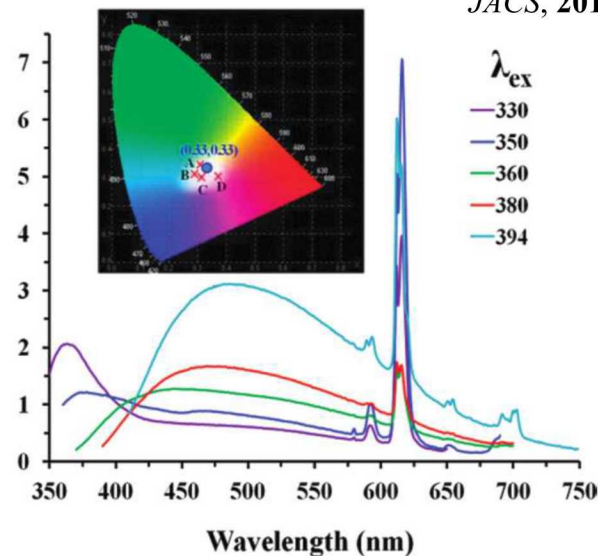
R&D Area 3: Metal-Organic Framework Materials

Photoluminescence Applications, low density, QY stability

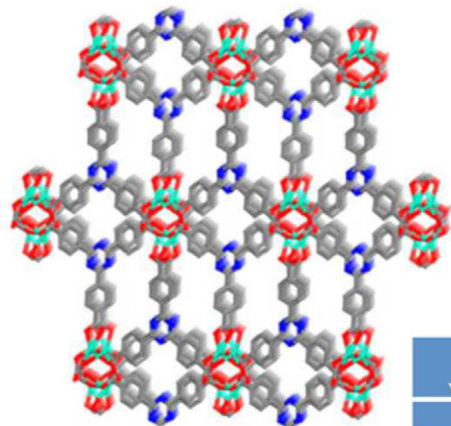
SMOF-1: white light emitter



JACS, 2012, 134, 3983

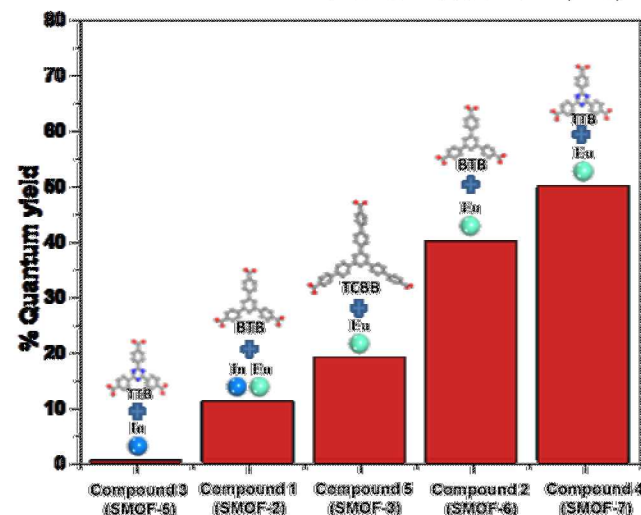


Chem. Mater. 2014, 26, 2943



SMOF-7: red light emitter,
high quantum yield with
thermal stability for OLED
applications

Excitation wavelength, nm	25°C	100°C	150°C
340	46%	50%	48%
394	22%	22.3%	19%



Example 4: Rare Earth – MOFs

PL & Acid Gas Durability

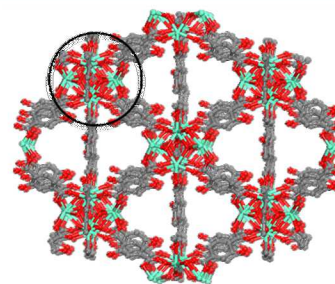
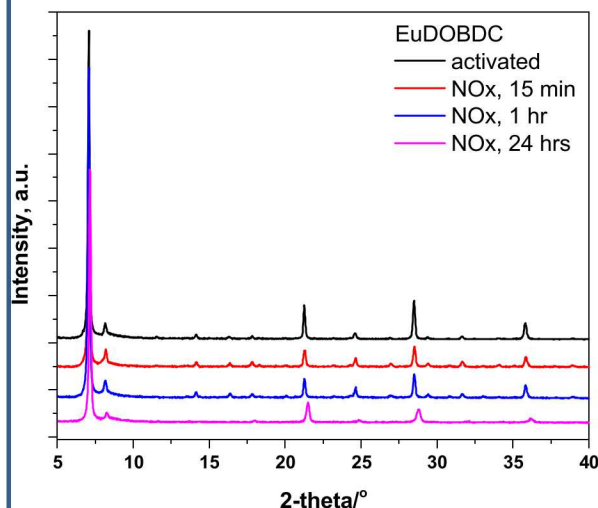
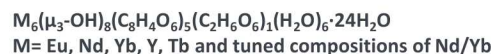
Team of modelers, synthesis and characterization of zeolites and MOFs with caustic gases

Goal: Investigate the structure-property relationship in a series of isostructural rare-earth MOF materials platform for NO_x adsorption

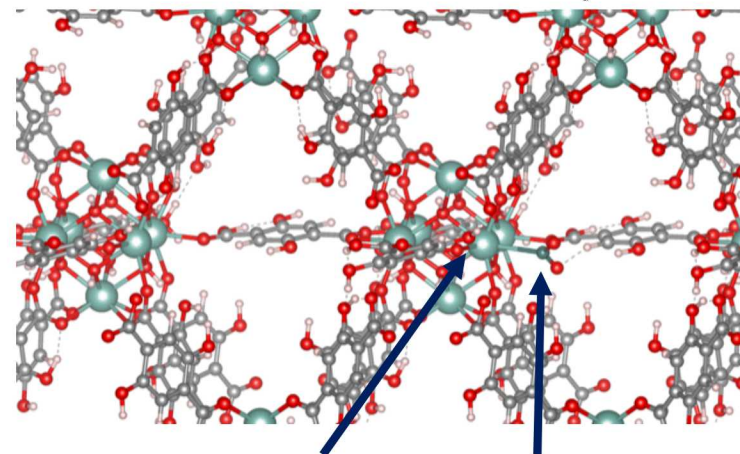
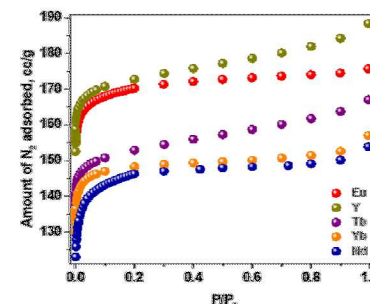
- Probe the effect of metal ion identity in the adsorption/selectivity for NO_x (Dorina Sava Gallis, Grace Vincent, UNM undergrad (SNL))
- Preliminary testing in house at SNL; Complementary modeling work for Jon Vogel (SNL postdoc)
- Team with Ryan Lively (GeorgiaTech) for mixed gas testing and Katharine Page (ORNL) for characterization

Activities/Findings

- Preliminary tests indicate that the materials remain crystalline upon NO_x exposure for 24 hrs
- XRD studies reveal noticeable peak shifts to the right in the higher two-theta region indicative of host-guest interactions
- Correlated and complimentary VASP modeling to describe MOF strength and acid gas binding energies.



ACS Appl. Mater. Inter. 2017, 9, 22268.



Y-DOBCD, Y hexanuclear cluster, NO₂ adsorbed

Rare Earth – MOFs

PL & Acid Gas Durability

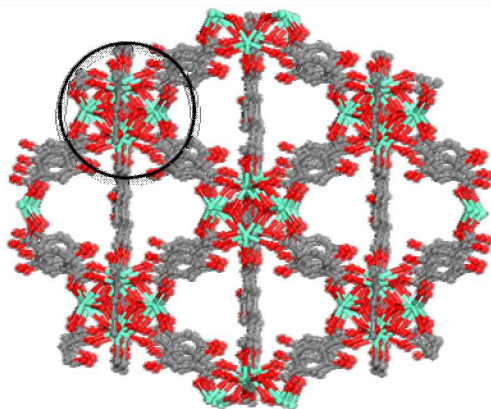
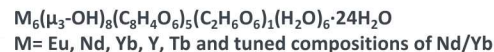
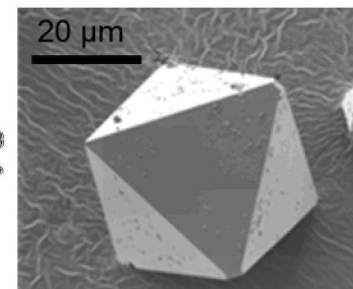
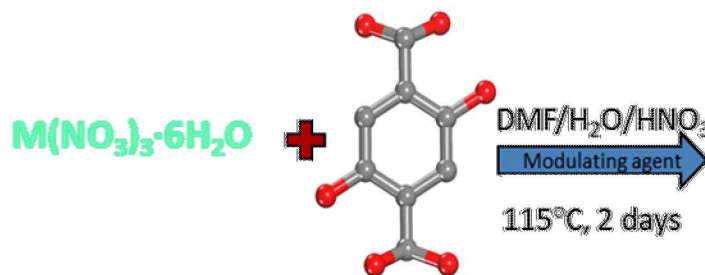
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- Correlated and complimentary VASP modeling to describe MOF strength and acid gas binding energies.
- Refs for RE-MOFs:
Dalton Trans., 2016, 45, 928
Anal.Chem, 2013, 85,22,11020
ACS Appl Mater Inter. 2017, 9, 22268



Rare Earth (RE) metals
8 Fold coordination, but unsaturated
enables energetically favorable bonding
of acid gases to metal center

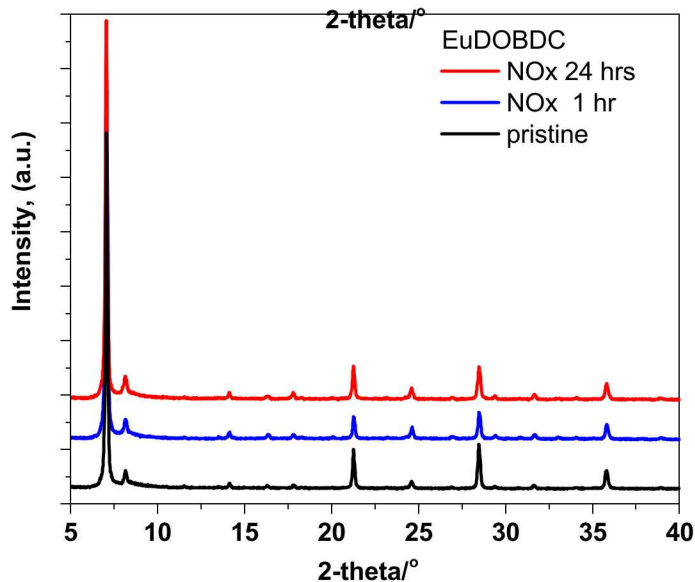
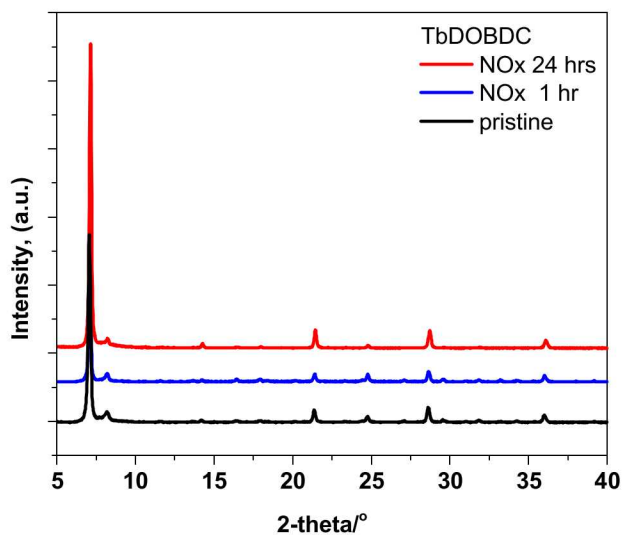
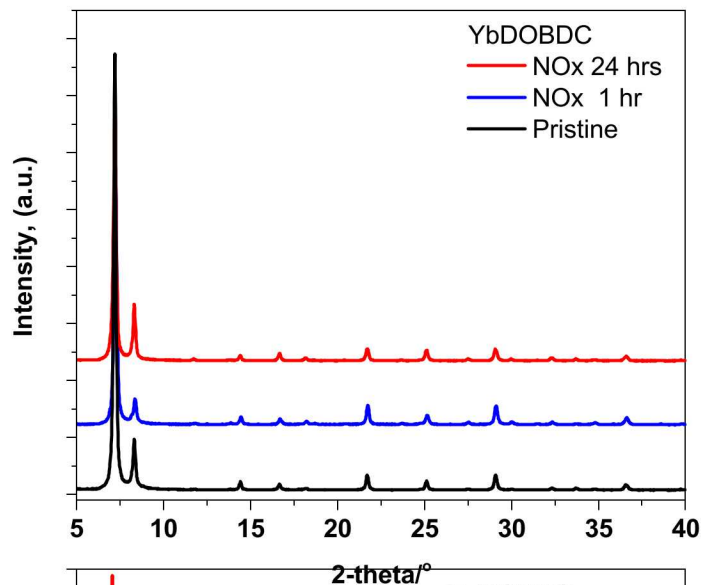
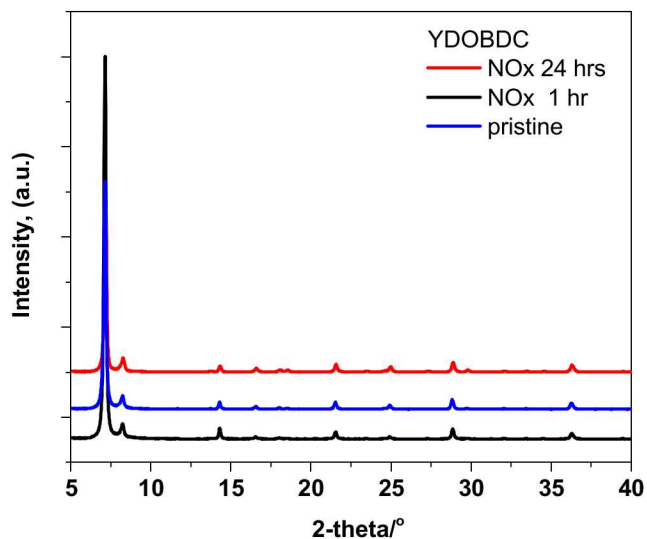
XRD pre- and post-NO_x exposure in M-DOBDC

M=Y, Yb, Tb, Eu

The NO_x was generated in an adsorption chamber at room temperature

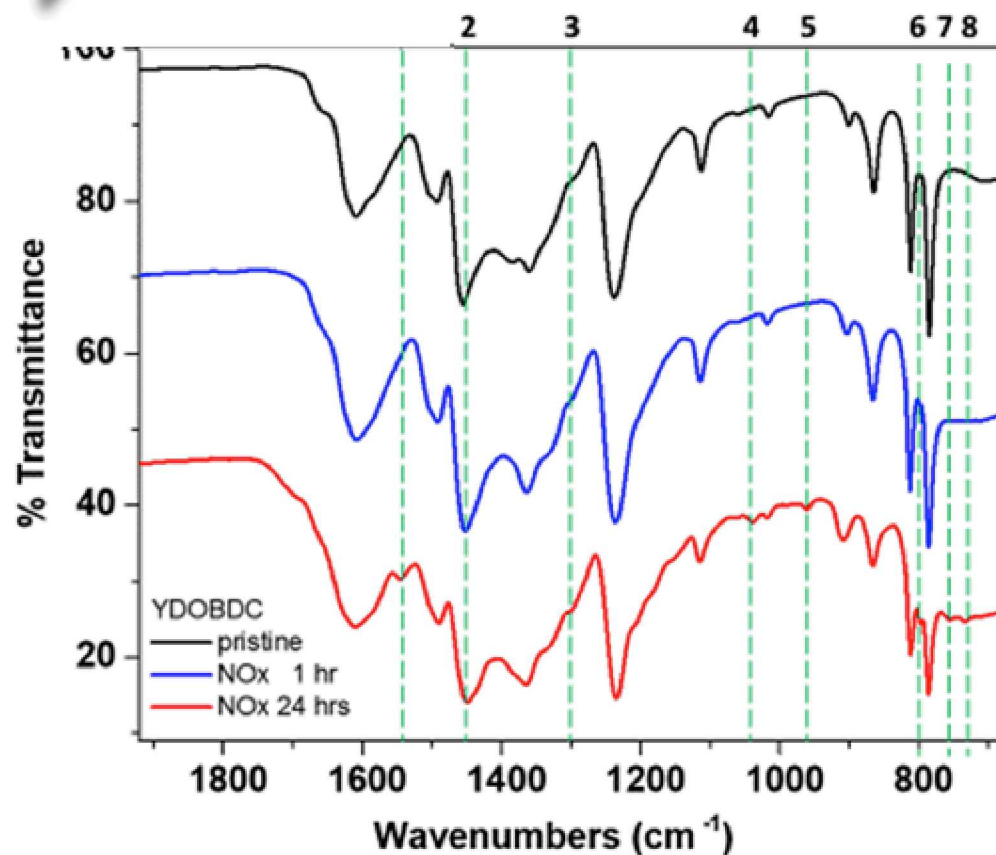
1st step: Generation of nitrous acid via acidification with H₂SO₄
 $2 \text{ NaNO}_2 + \text{H}_2\text{SO}_4 \rightarrow 2 \text{ HNO}_2 + \text{Na}_2\text{SO}_4$

2nd step: Nitrous acid decomposition
 $2 \text{ HNO}_2 \rightarrow \text{NO}_2 + \text{NO} + \text{H}_2\text{O}$



No change in XRD patterns after 24 hr exposure

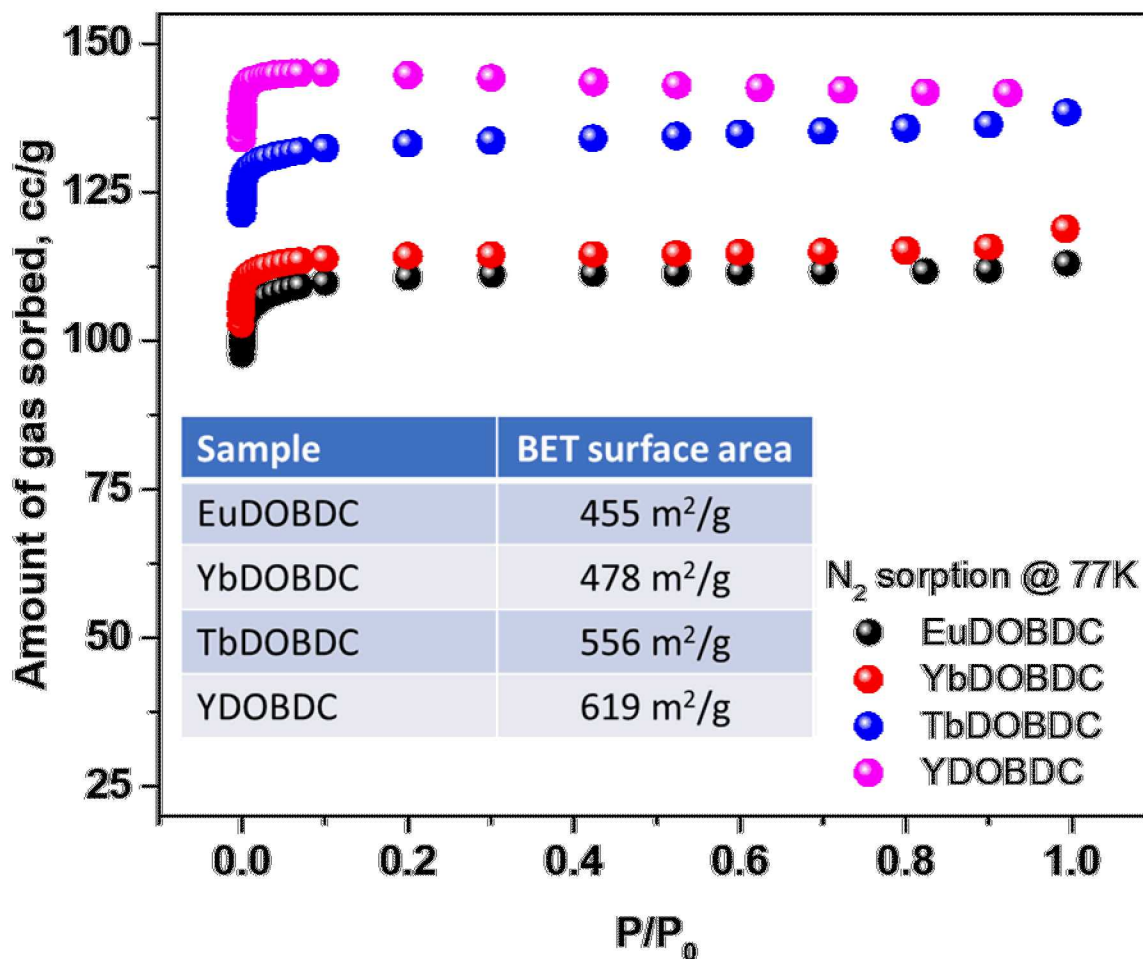
IR data showing NO_x species (new peaks, broader peaks, etc)



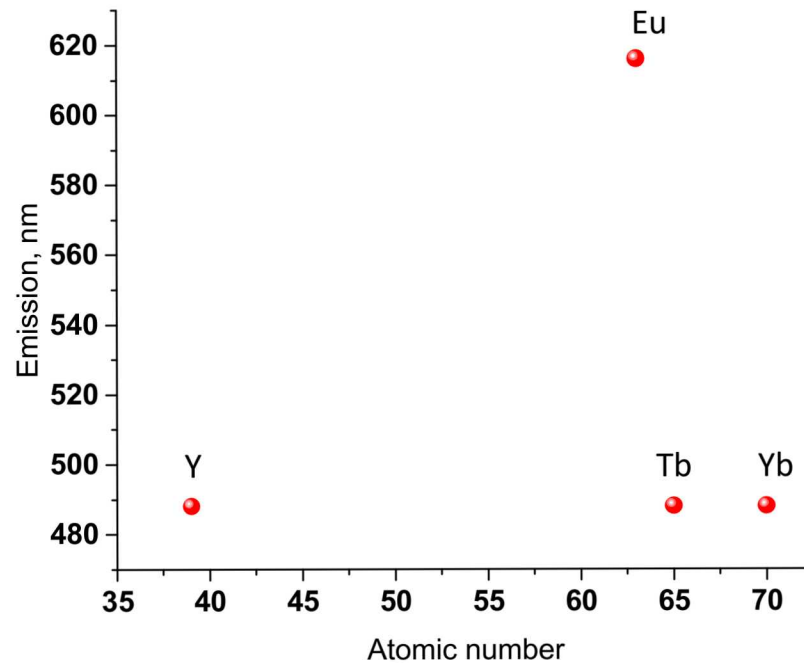
Peak number	Wavenumber (cm ⁻¹)	Peak assignment
1	1544	Asym. NO ₂ stretching
2	1489	N=O stretching
3	1297	Asym. NO ₂ stretching
4	1037	Sym. stretching NO ₂
5	959	TBD
6	796	N-O stretching
7	755	NO ₂ bending
8	732	NO ₂ bending

Peak assessments gathered from *Chem. Mater.* 2017, 29, 4227

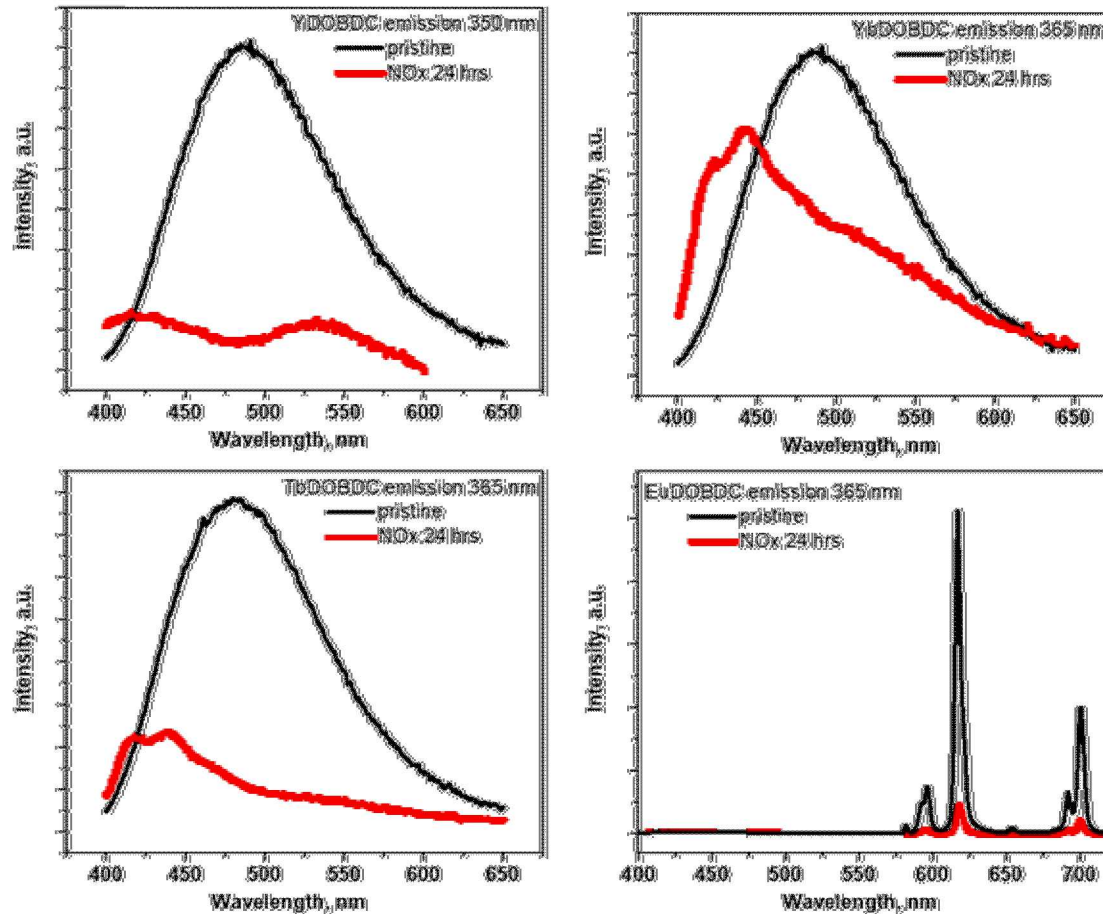
BET adsorption data confirming open porosity



Element atomic number vs. emission

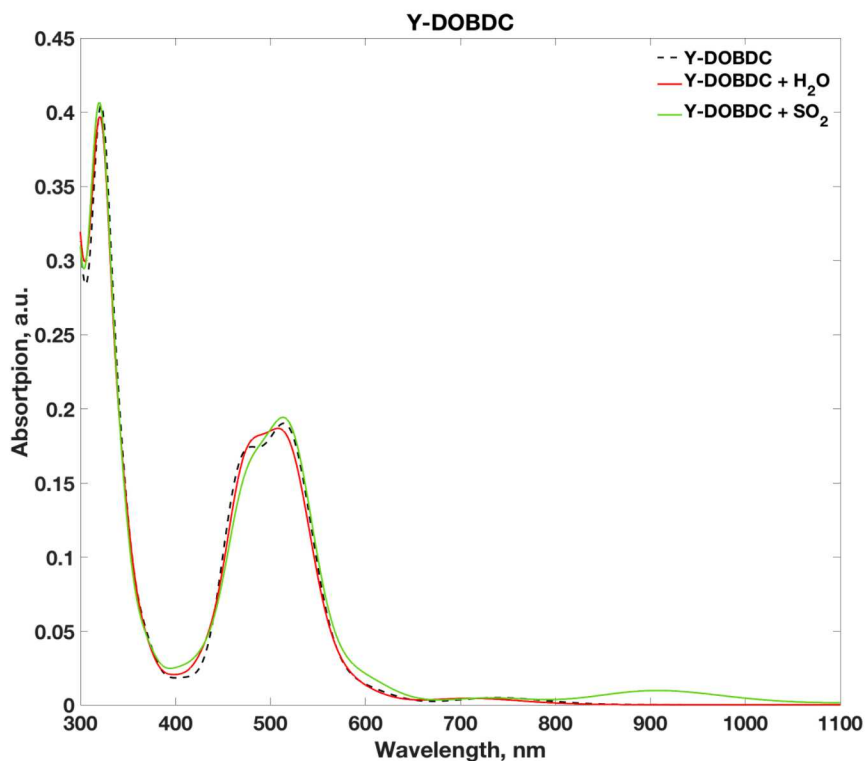


Emission data per unique metal centers, only Eu has metal emission transitions

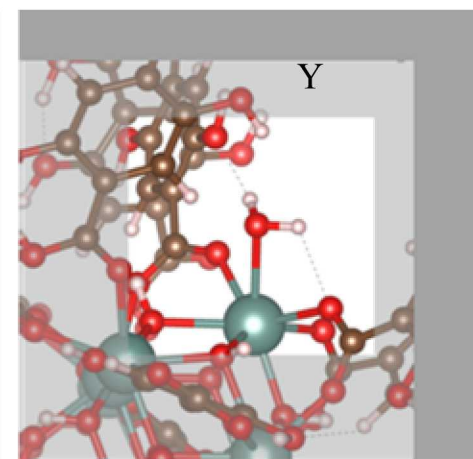
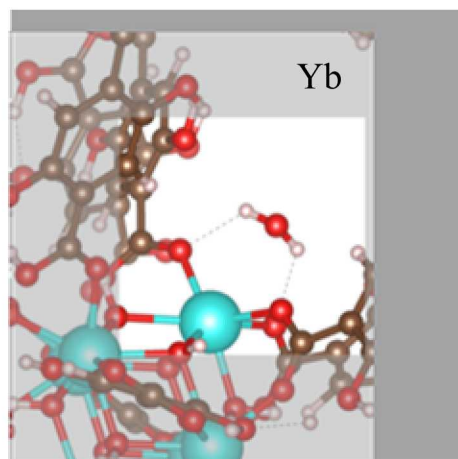
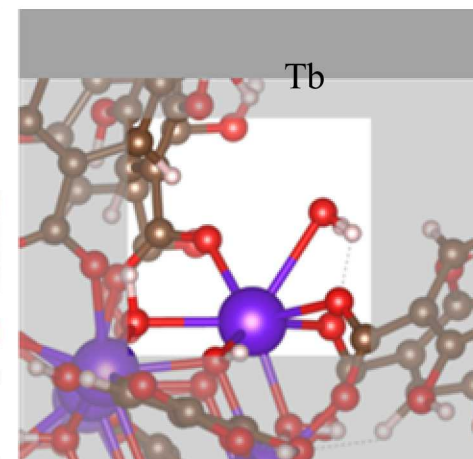
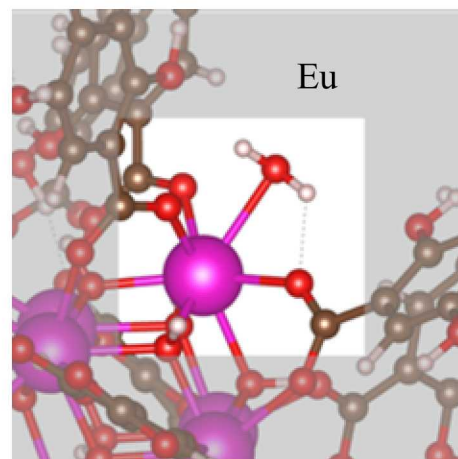


Preliminary modeled emissions for M-DOBDC with SO₂ adsorbed, with H₂O adsorbed

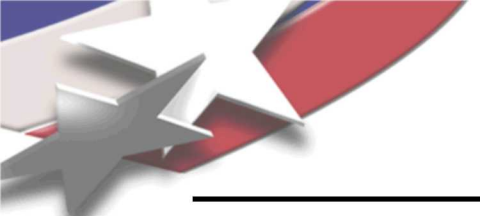
See Jon Vogel's poster



Optical emissions modeled
Pre- and post adsorption of SO₂



Ligand reorganization:
Optimized H₂O gas interactions with
metal centers



Conclusions

- Multidisciplinary teaming allows for in-depth understanding of materials structure-properties
- The collaborative use of DFT and AIMD modeling enables the materials design, and reactivity prediction, needed to understand the chemistry and reactivity inside nanopores
- STRONG collaboration of light source user facilities with materials synthesis and testing for structure-property relationship understandings.
- *We are always looking for collaborations!!*

Acknowledgements

For Projects Highlighted herein

Sandia National Labs:

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Stonybrook University:

Karena W. Chapman
Peter Chupas

Univ Idaho:

Haiyan Zhao

ORNL/SNS:

Katharine Page
Luke L. Daemon

Funding Agencies:

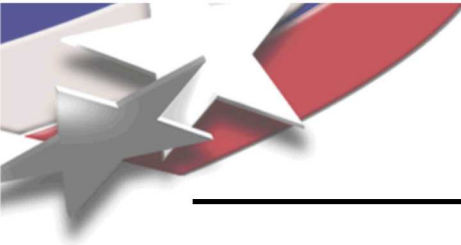
SNL LDRD
DOE/NE - Fuel Cycle
DOE/BES/EFRC- *UNCAGE-ME*
DOE/SBIR



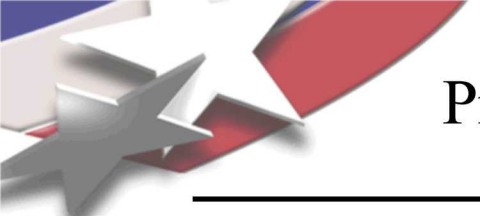
**Sandia National Labs
Albuquerque, New Mexico**

Questions? / Thank you





Extra Slides



Program Development & Management - Nenoff

- R&D portfolio divided into five general topic areas:
 - High selectivity rad ion & capture nanoporous materials
 - Supported Nanoparticles
 - Gas separations nanoporous materials & membranes
 - Photoluminescence MOFs
 - TQM oxides and chalcogenides
- Developed strong relationships at DOE, resulted in *long running* programs
 - DOE/Office of Science/EFRC *UNCAGE-ME* (PI: Krista Walton)
 - DOE/NA115 (Aging and Lifetime)
 - DOE/EERE/AMO, H₂, EM
 - DOE/Office of Nuclear Energy
- Research Group works in *TRL 1 - 9*
- PI: 2 different multiyear, multimillion \$ CRADAs
 - SNL, BP, Temec, Coors Ceramics, University Cincinnati:
Zeolite Membranes for HC isomer feedstock purification
 - SNL, Goodyear Chemicals, University Cincinnati:
Membranes for Separations of High Volume C₄/C₅/C₆ Mixtures