SAND2022-16025C

Design, Realization, Applications of Gas and Ion Separations Materials

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Matthew Christian, Matthew Hurlock, Keith J. Fritzsching, D. Jon Vogel,
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Collaboration: Co-PIs, Nenoff (Synthesis) & Rimsza (Modeling)

AVS e-talk

November 16, 2022

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Outline

- Background

I. RE-DOBDC MOFs for Humid NO_x acid gas separations
  - experiment
  - modeling (DFT, AIMD)

II. RE-DOBDC, Entire Lanthanide Series
  - reaction parameters
  - stages of crystallinity
  - kinetic driven denticity

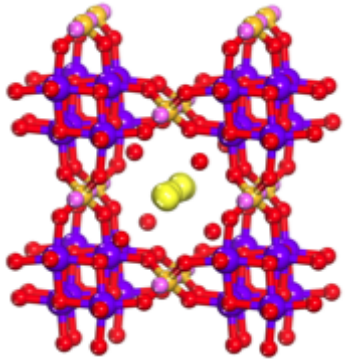
III. Fluorination of the Metal Cluster

IV. Transitioning fundamental DOBDC MOFs to Sensors (applications)

- Conclusion

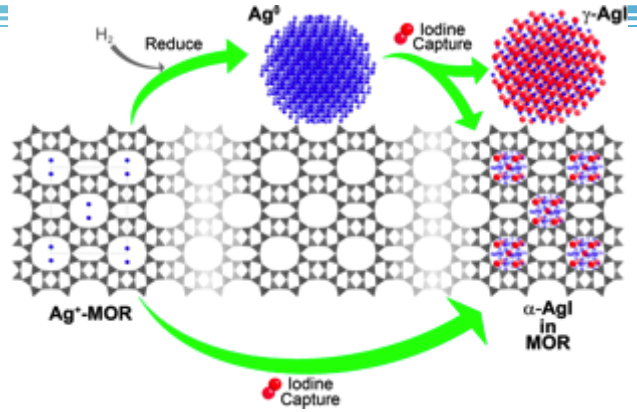
- Info about Sandia, Postdoc & Fellowship positions

Background: Nanoscale Materials for bulk scale applications



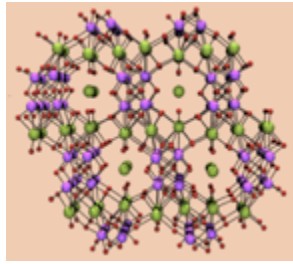
R&D100 1996
JACerS, 2009, *92(9),* 2144
JACerS, 2011, *94(9),* 3053
Solvent Extr. & Ion Exch, 2012, *30*, 33

CST, Cs^+ removal from water to Pollucite Waste Form
US Patents *6,479,427; 6,110,378*

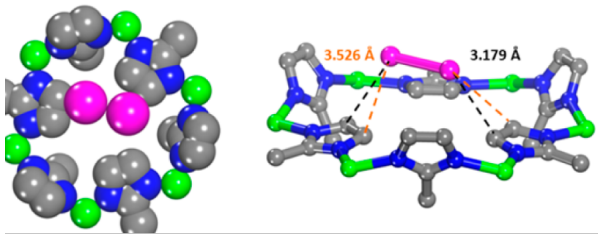


Ag-MOR I_2(g) capture & mechanisms
JACS, 2010, *132*(26), 8897
J Phys Chem Lett, 2011, *2*,2742
I&ECR 2017, *56*(8), 2331

SOMS, Sr^{2+} getter, 1-step to Perovksite WF
JACS, 2002,*124(3),* 1704
US Patent *7,122,164*

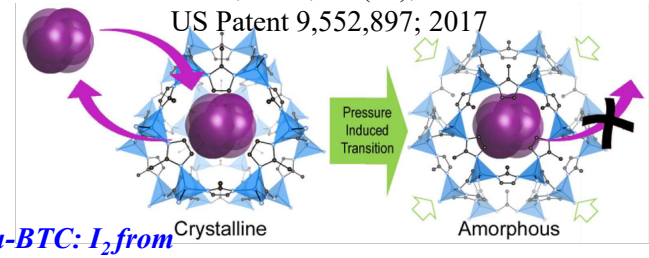


Design on the nanoscale of the Separation Material to optimize on the bulk scale

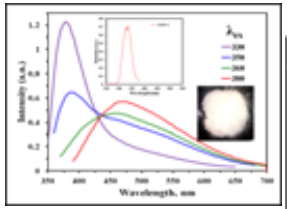


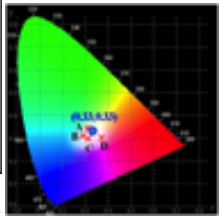
I_2/ZIF-8, Isolation to Waste Form
JACS, 2011,*133(32),*12398
US Patent filed 2012
JACS 2013, *135*, 16256

MOF Amorphization for Gas Storage
JACS, 2011,*133*(46),18583
US Patent 9,552,897; 2017

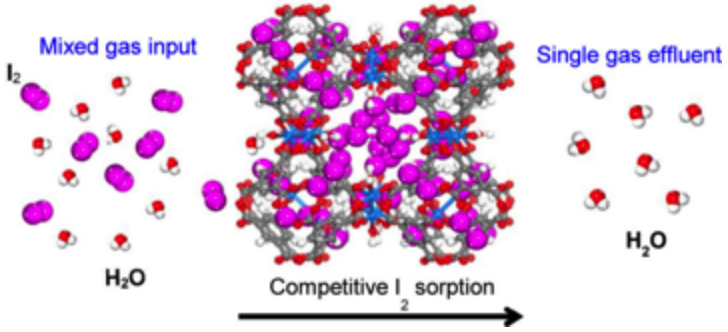


O_2 Separations with MOFs for Energy Efficient Oxyfuel Combustion
Chem. Mater. **2016**, 28(10), 3327-3336
Chemical Science **2016**, *18*, 11528
J. Phys. Chem. C, **2015**, *119*, 6556
Chem. Mater. **2015**, *27*(6), 2018

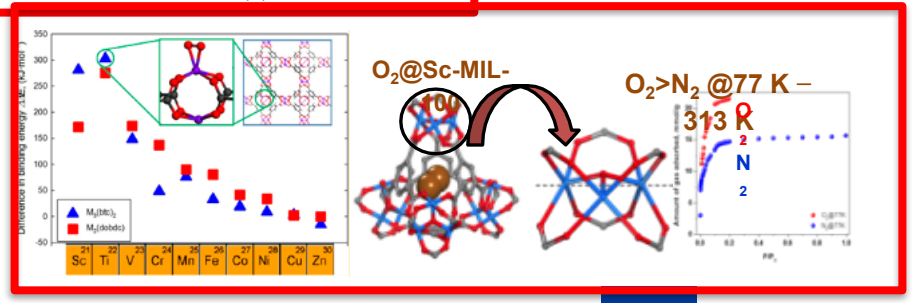




MOFs,White Light PL
JACS, 2012,*134*(9), 3983
Chem Mater, 2014, *26* (9), 2943



Cu-BTC: I_2 from Humid Gas Stream
Chem. Mater. 2013, *25*(13), 2591



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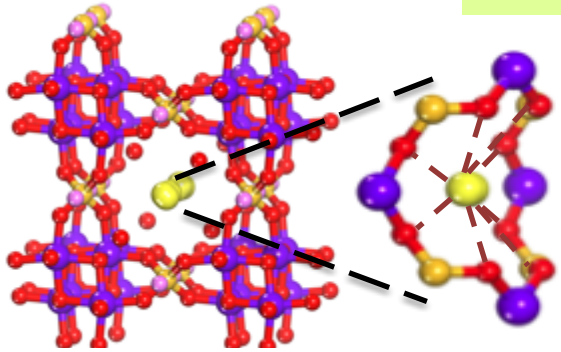
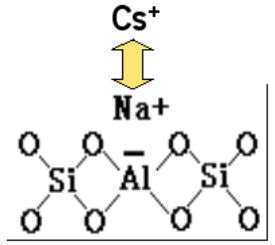
Early Career, Geo-Inspired:
CSTs for Rad Ion High Selectivity and Capture (TRL 1-9)

UNCAGE ME

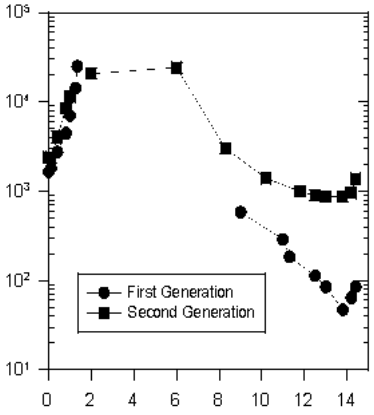
CSTs: Crystalline Silico-titanates

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





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



Sandia: Distribution Coefficient of Cs on CST

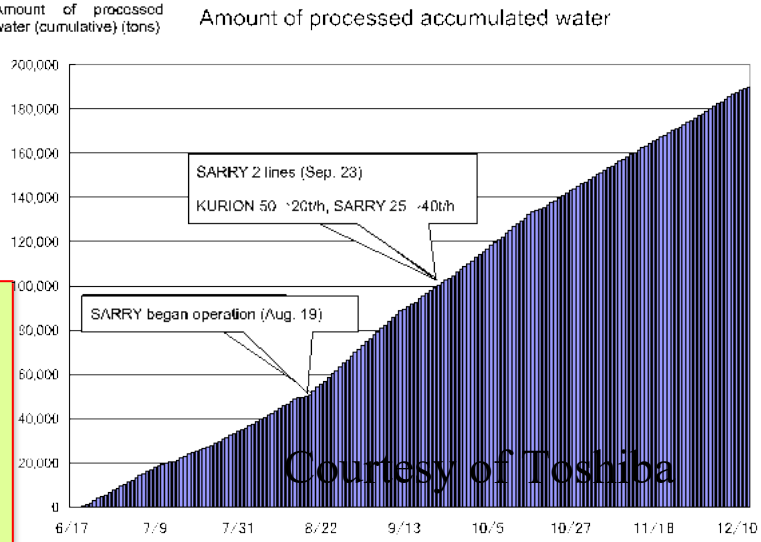
UOP IONSIV™ IE-911

Fukushima Daiichi Nuclear Power Plant Accident, March 2011
- 2011 SNL re-licensed CST IP to Honeywell UOP LLC who coordinated with Toshiba for implementation in the SARRY™ Process at Fukushima

SARRY™: Simplified Active Water Retrieve and Recovery System augmentation of Accumulated Water processing Facility

2011: UOP re-licensed CST IP, in production of 40K+ lots within 2 months of Fukushima accident

SARRY was installed August 2011, decontamination factors of Cs SARRY process is 5 x 10^5



Courtesy of Toshiba

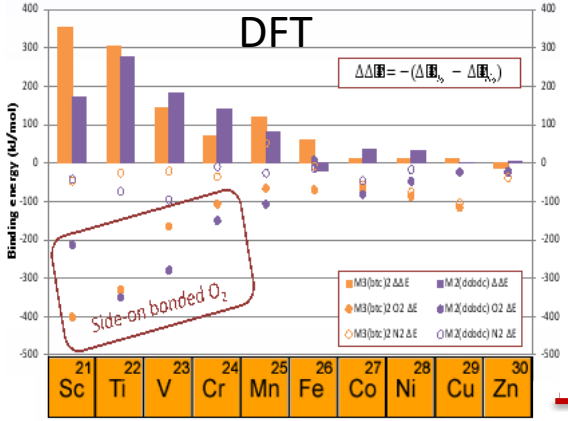
By December 2015, 160+ million gallons of Cs^+ contaminated seawater were cleaned with the *SARRY™ Process.* ***Decon work completed.***

Midcareer, Computationally Designed: MOF for Ambient O_2 Separations from Air. (TRL 1-7…)

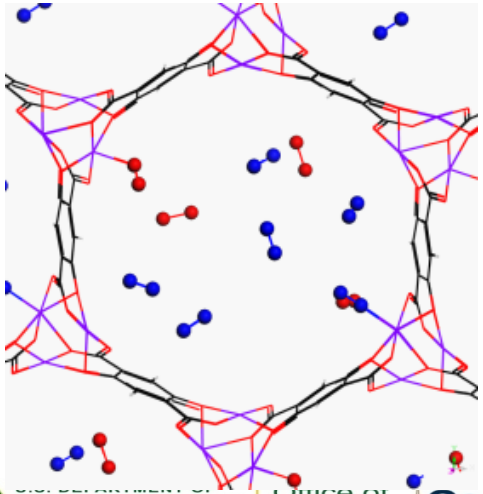
UNCAGE ME

High Performance Computing (*4000 processor hrs, 6000 processor days (Redsky, Skybridge)*) to *design* materials, *guide synthesis,* and *validated* design via *testing.*

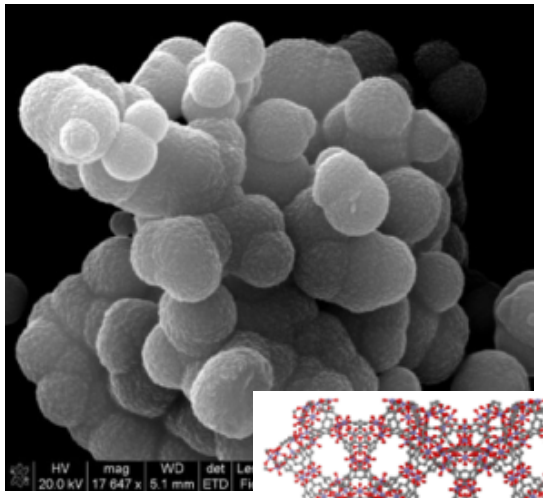
Computationally Designed Materials

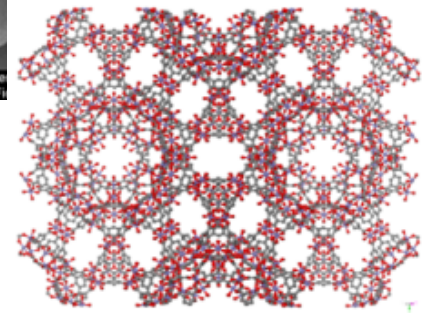


Ab initio MD



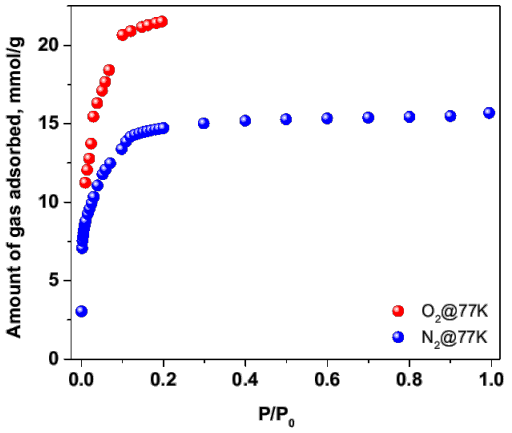
Novel Materials Synthesis

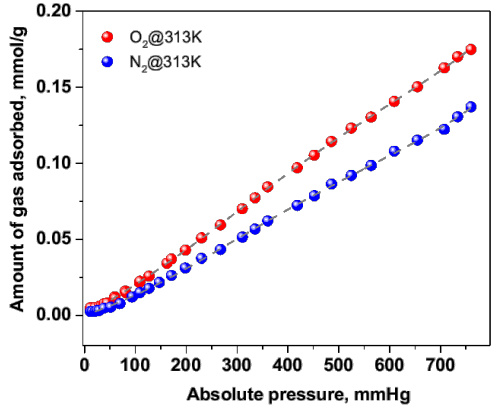




Chem. Mater. **2016**, 28(10), 3327
Chem. Mater. **2015**, 27(6), 2018

Exp Gas Testing





Industrial Scale Up To Commercialization

IP: US Patent # 10,549,261 Awarded Feb 4, 2020

DOE/SBIR Phase I FY19 (IP licensed), two industrial partners

DOE/SBIR Phase II FY21 (IP re-licensed), 1+ industrial partners

DOE/SBIR Phase IIA FY22- (IP re-licensed), 1+ industrial partners

PCCP **2016**, *18*, 11528
J. Phys Chem C, **2015**, *119*, 6556

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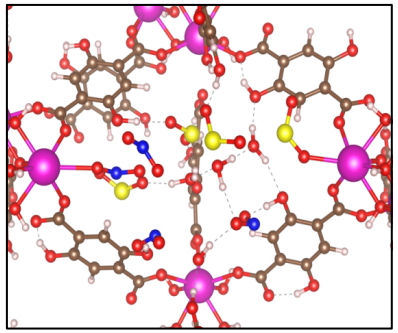
Computationally Driven, Experimentally Validated, Rapid Materials Discovery. BES/EFRC: UNCAGE-ME*

UNCAGE ME

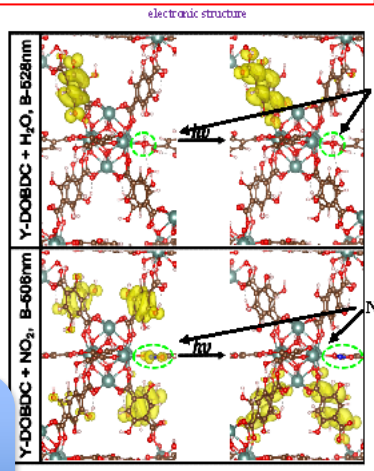
**Center for Understanding and Control of Acid Gas-Induced Evolution of Materials for Energy*

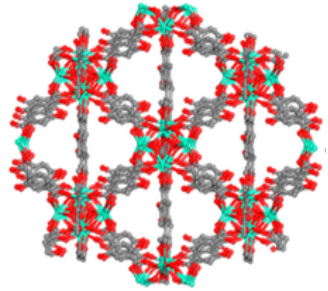
TRL 1: Design and tune adsorbents to selectively adsorb industrial caustic acid gases

Optimized Eu-DOBDC + $4H_2O$ + $4NO_2$ + $4SO_{2z}$



DFT & AIMD for mixed Gas competitive binding
PCCP, **2019**, 21, 23085
ACS AMI, **2020**, 12, 4, 4531
Angew Chemie, **2021**, *60*(20), 11514





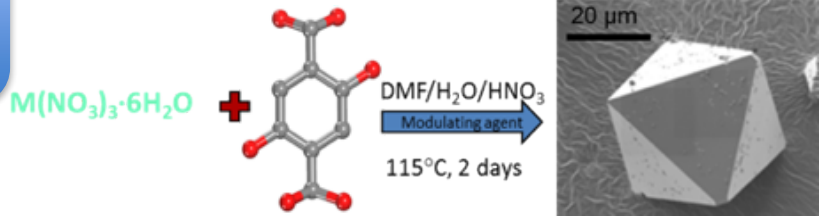
Industrial Acid Gas Adsorbents: RE-DOBDC MOFs
ACS AMI **2019**, *11, 46, 43270*
ACS AMI, **2020**, *12, 17, 19504*
ACS AMI, **2020** *12, 20, 22845*
ACS AMI, **2021**, *submitted*

Computation

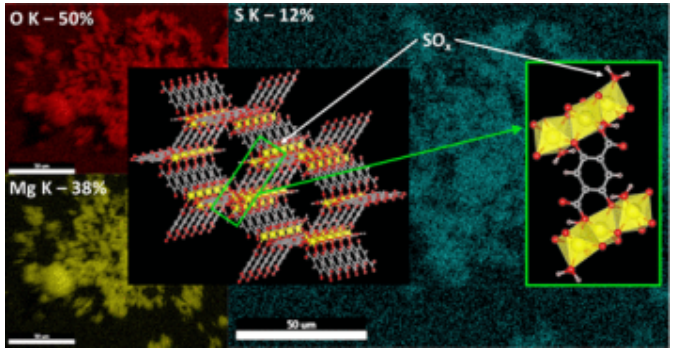
Materials Synthesis

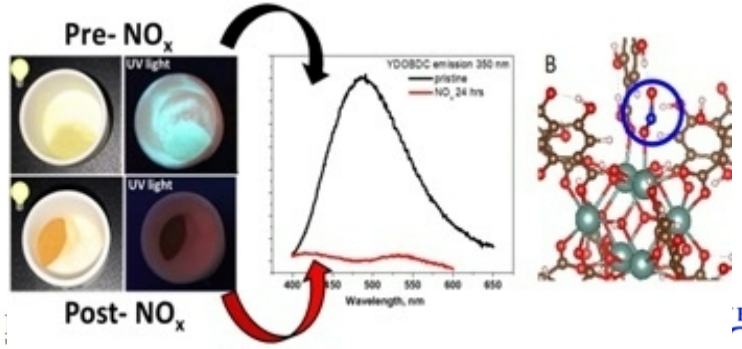
Characterization

Mixed gas adsorption Testing



Mixed H_2O + SO_x adsorption testing
ACS AMI, **2021**, 13, 7278





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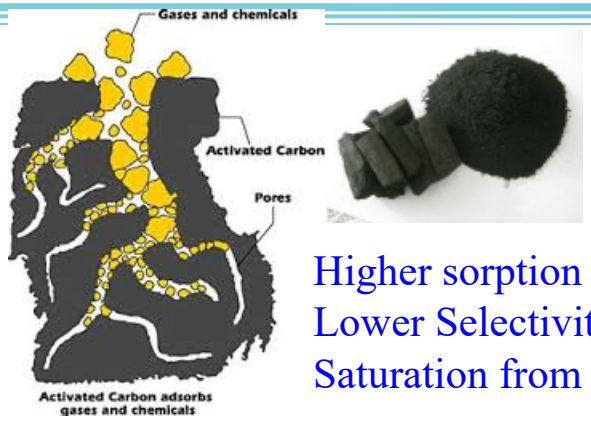
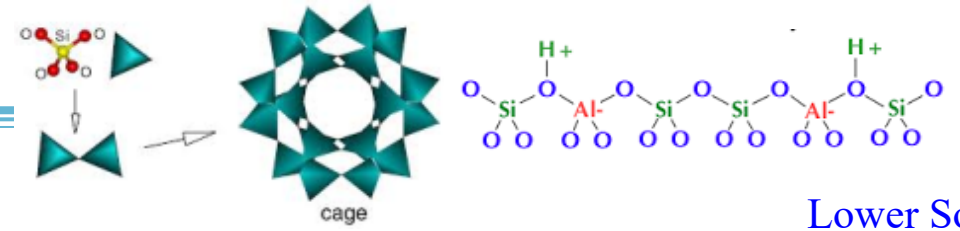
Nanoporous Gas Adsorption Materials

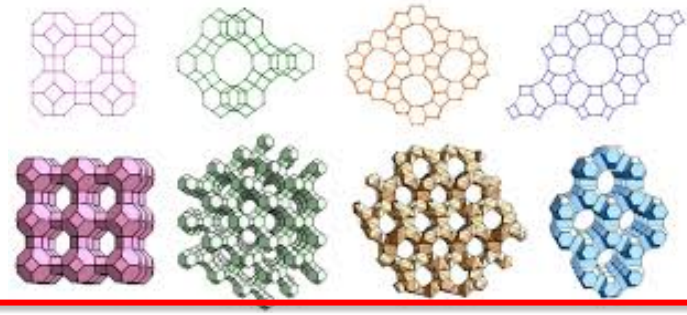
UNCAGE ME



Activated Carbon/
Charcoal > 500 m^2/g

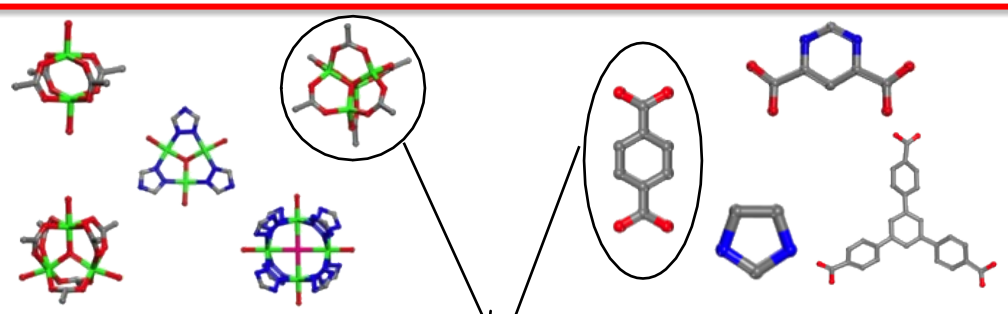
Higher sorption capacity
Lower Selectivity
Saturation from background gases





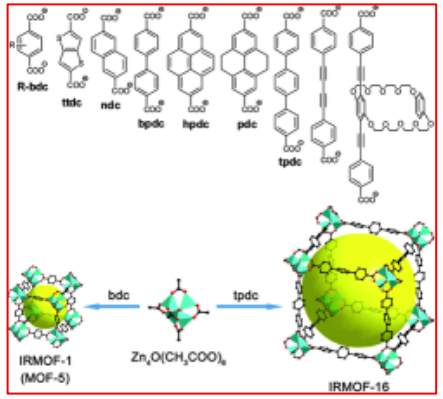
Lower Sorption
Capacity
Size & Chem
Selectivity (?)

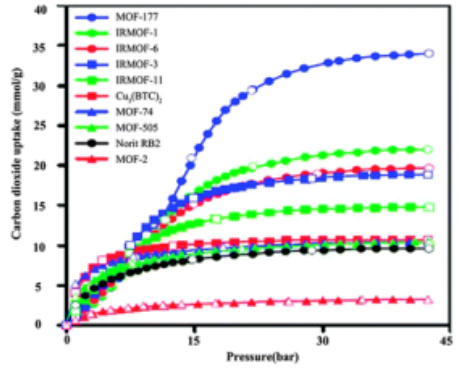
Zeolite~100 m^2/g



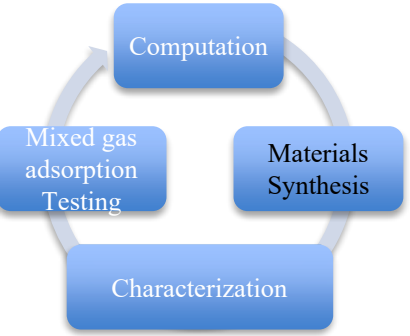
Metal-Organic Frameworks
(MOFs) >1000m^2/g

Target: Extremely
High Selectivity &
High Capacity



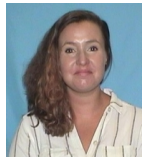


I. Rare Earth – DOBDC MOFs, Acid Gas Durability



How to design and tune adsorbents to selectively adsorb acid gases?

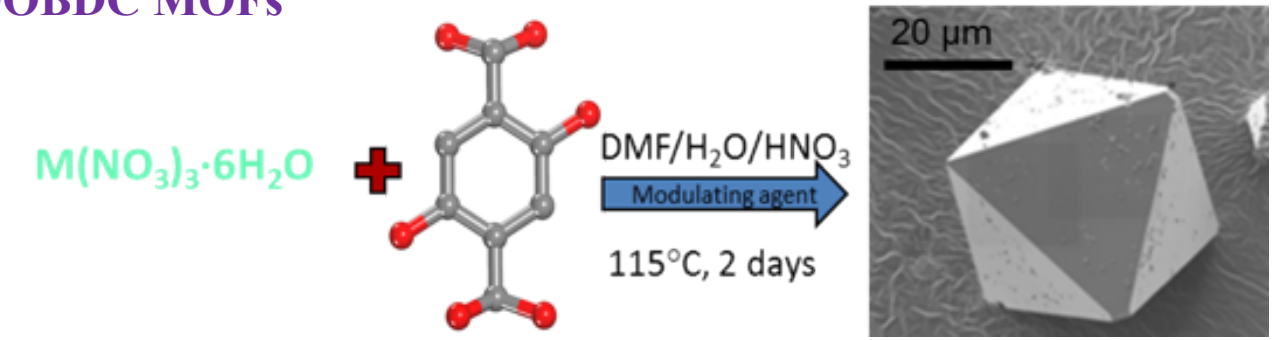

Dorina Sava Gallis


Susan Henkelis

Rare earth elements have been shown to preferentially bind to acid gases:
Optimization of binding to framework but not too strong as to be destructive

- Lanthanide oxygen-sulfur catalysts (Kay et.al, US Patent 5,213,779 (1993))
- Metal organic coordination polymers with Tb^{3+} have a strong affinity and coordination binding to H_2S (Anal. Chem, 2013, 85,22,11020)
- Europium has high selectivity for hydrogen sulfide (Dalton Trans., 2016, 45, 928)

RE-DOBDC MOFs

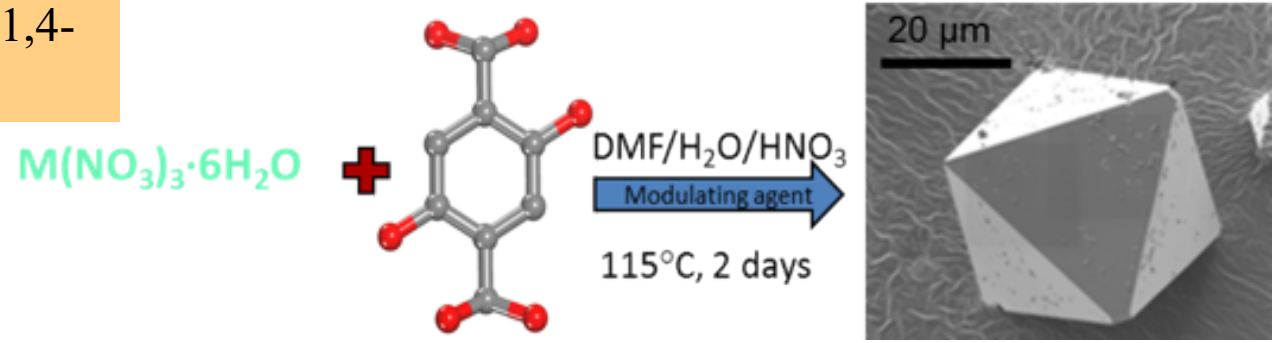


Unit Cell = $\mathbf{RE}_{12}(\mu_3\text{-OH})_{16}(C_8O_6H_4)_8(C_8O_6H_5)_4 + 12\ H_2O$
M = RE = Y, Eu, Tb, Yb
DOBDC = 2,5-dioxido-1,4-benzenedicarboxylate

Sava Gallis *et al. ACS Appl. Mater. Interfaces* ***2017,*** 9, 22268; *CrystEngComm* ***2018,*** 20, 5919; *JPPC* **2018**, 122, 47, 26889

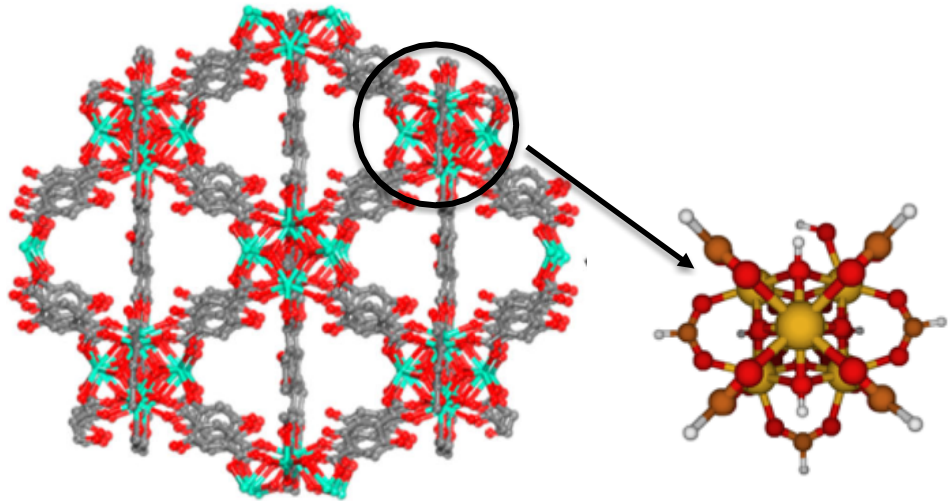
RE-DOBDC MOFs

RE = M = Y, Eu, Tb, Yb
DOBDC = 2,5-dioxido-1,4-benzenedicarboxylate



Unit Cell = $RE_{12}(\mu_3\text{-}OH)_{16}(C_8O_6H_4)_8(C_8O_6H_5)_4 + 12\ H_2O$

Single-crystal X-ray diffraction
Eu-DOBDC
Tetragonal, 3D framework *P4nc*
a= b= 15.5567 A˚
c= 21.334 A˚
α=β=γ= 90° = V= 5163.06 A^3



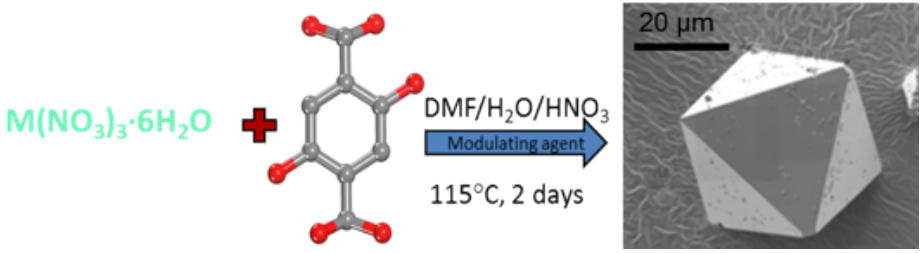
The RE-DOBDC platform is based on building block akin to prototypical Zr-hexanuclear cluster of UiO-66 yet with an unsaturated metal bond.

A combination of monodentate and bidentate linker bonding to metal center

Resultant **RE-DOBDC MOFs**
Octahedral cages of ~14Å diameter, accessible via triangular windows of ~5.5Å

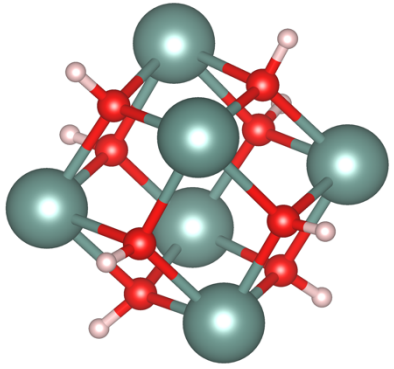
Sava Gallis *et al. ACS Appl. Mater. Interfaces* ***2017,*** 9, 22268; *CrystEngComm* ***2018,*** 20, 5919; *JPPC* **2018**, 122, 47, 26889

RE-DOBDC MOFs



- Lanthanides provide unique characteristics not found in transitions metals.
- High coordination numbers (8-9) and new optical transitions facilitated by 4f electrons.

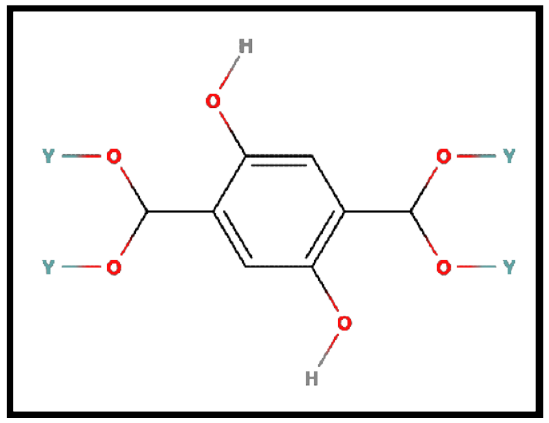
Metal Centers



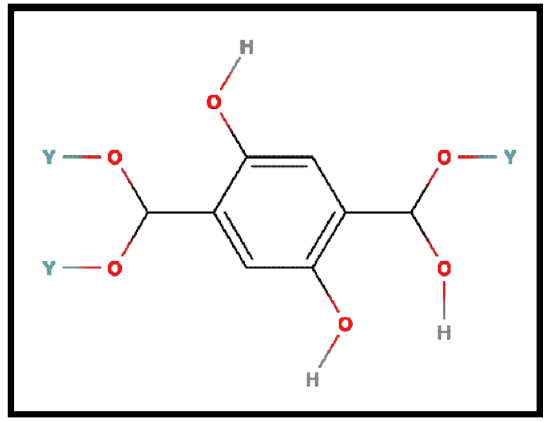
$Ln_6(\mu_3 OH)_8$

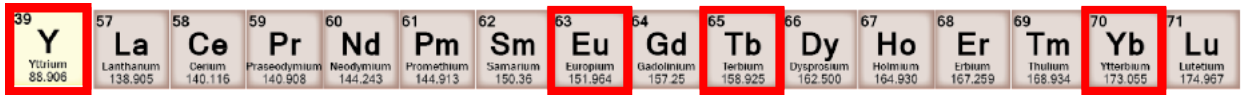
DOBDC Organic Linkers

Bidentate



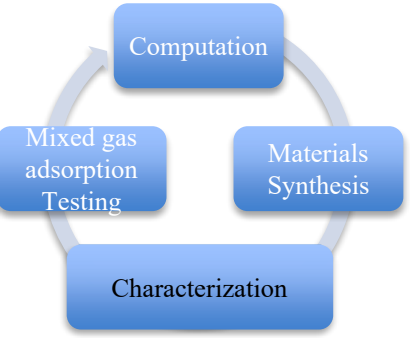
Monodentate

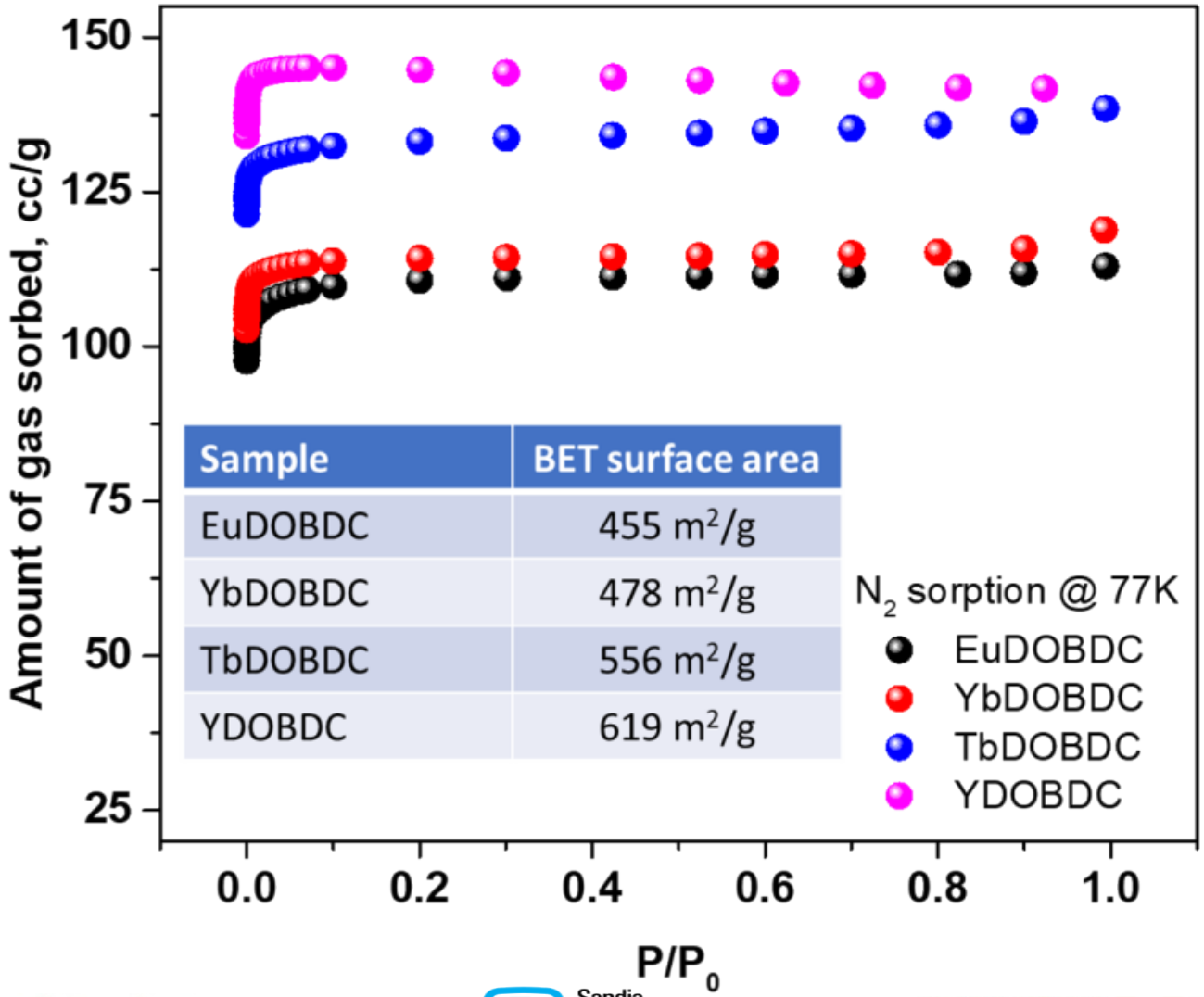




Vogel, D. J., et. al., . *PCCP* **2019**. 21, 23085-23093. Sava Gallis, D. F., et. al., *ACS Appl. Mater. Interfaces* **2019**; Sava Gallis *et al.* *ACS Appl. Mater. Interfaces* ***2017,*** 9, 22268; *CrystEngComm* ***2018,*** 20, 5919; *JPPC* **2018**, 122, 47, 26889

BET adsorption data confirming open porosity

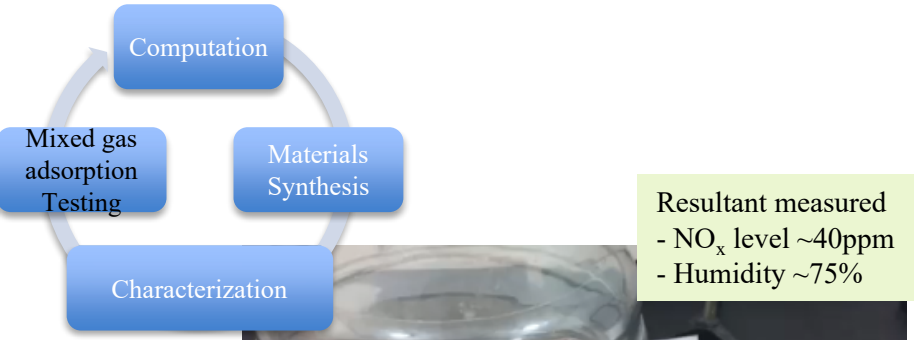




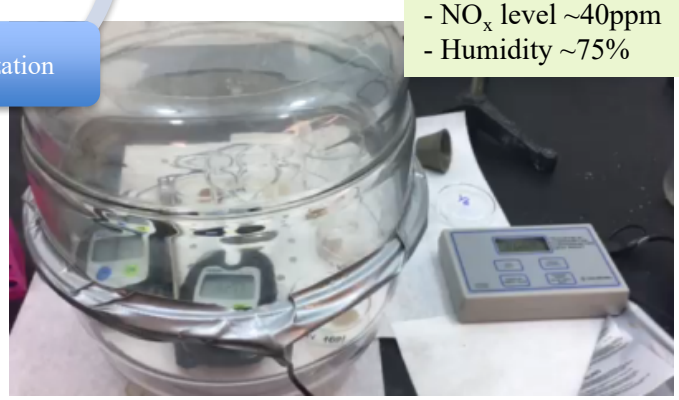
Sample	BET surface area
EuDOBDC	455 m^2/g
YbDOBDC	478 m^2/g
TbDOBDC	556 m^2/g
YDOBDC	619 m^2/g

Mixed Gas: $H_2O + NO_x$ adsorption, RE-DODC MOFs (RE = Y, Yb, Tb, Eu)

Sava Gallis, Vogel, D. J.; Vincent, G.; Rimsza, J. M.; Nenoff, T.M. , *ACS Appl. Mater. Interfaces* **2019,** *11*(46), 43270



Resultant measured
- NO_x level ~40ppm
- Humidity ~75%



NO_x is generated in an adsorption chamber at room temperature

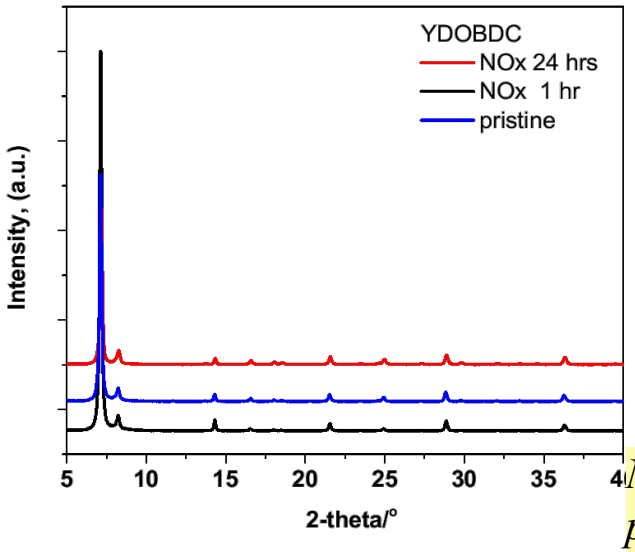
1st step: *Generation of nitrous acid via acidification with H_2SO_4*

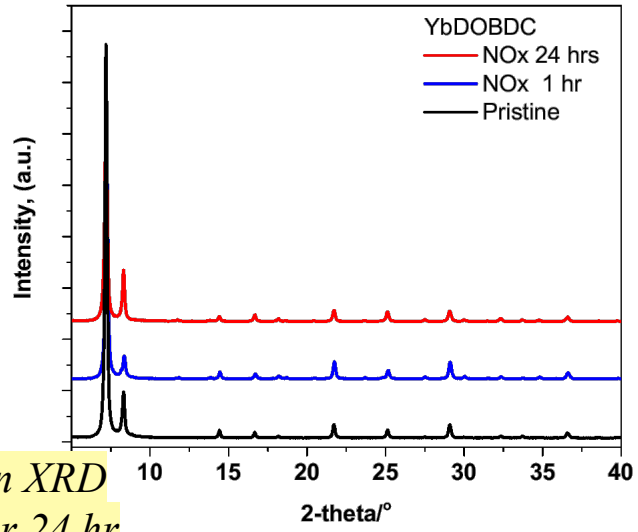
$2\ NaNO_2 + H_2SO_4 \rightarrow 2\ HNO_2 + Na_2SO_4$

2nd step: *Nitrous acid decomposition*

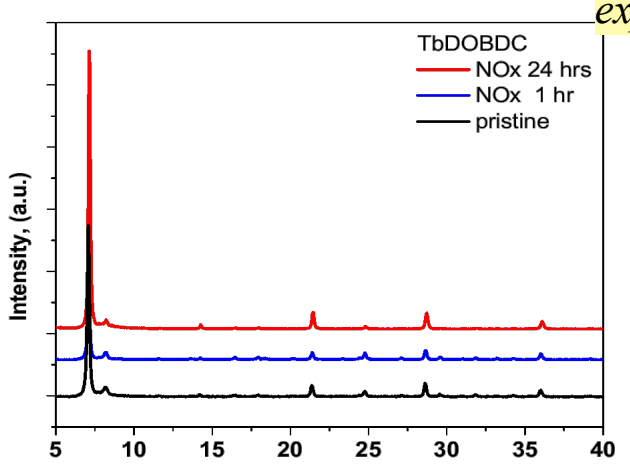
$2\ HNO_2 \rightarrow NO_2 + NO + H_2O$

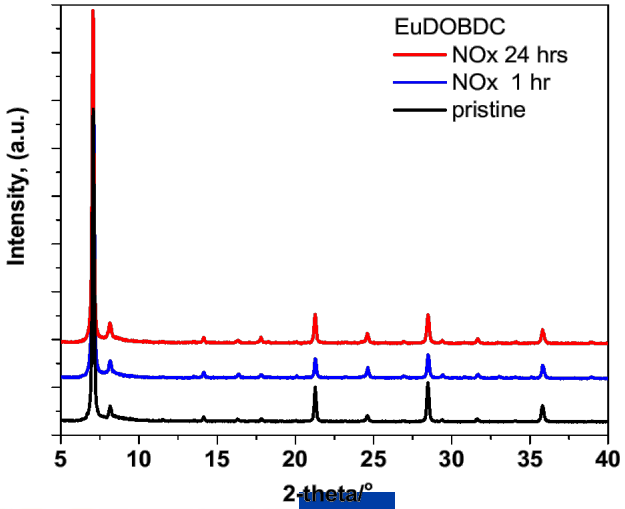
Bulk NO_x prep from UNCAGE-ME team:
Bhattacharyya, Han, Joshi, Zhu, Lively, Walton, Sholl, Nair
J. Phys. Chem. C. **2019**, *123*, 2336



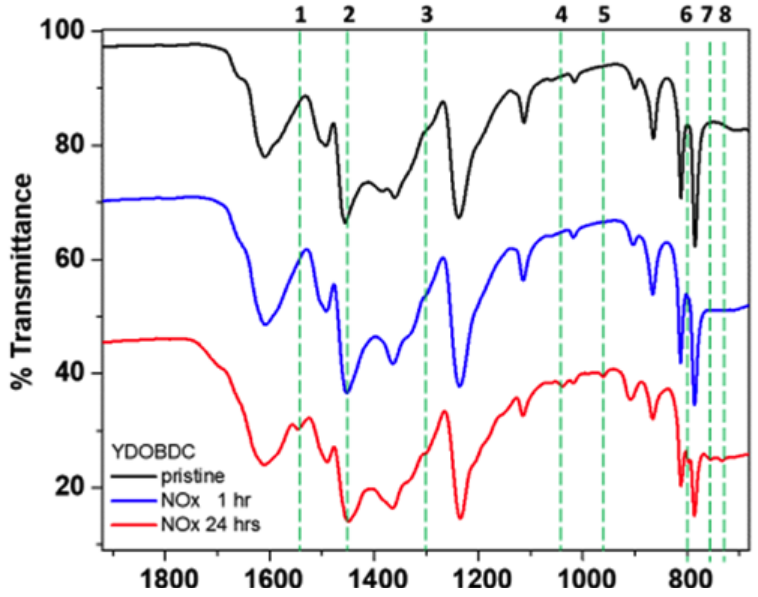


No change in XRD patterns after 24 hr exposure





Y-DOBDC: IR and thermal data showing nanopore adsorption of NO_x species

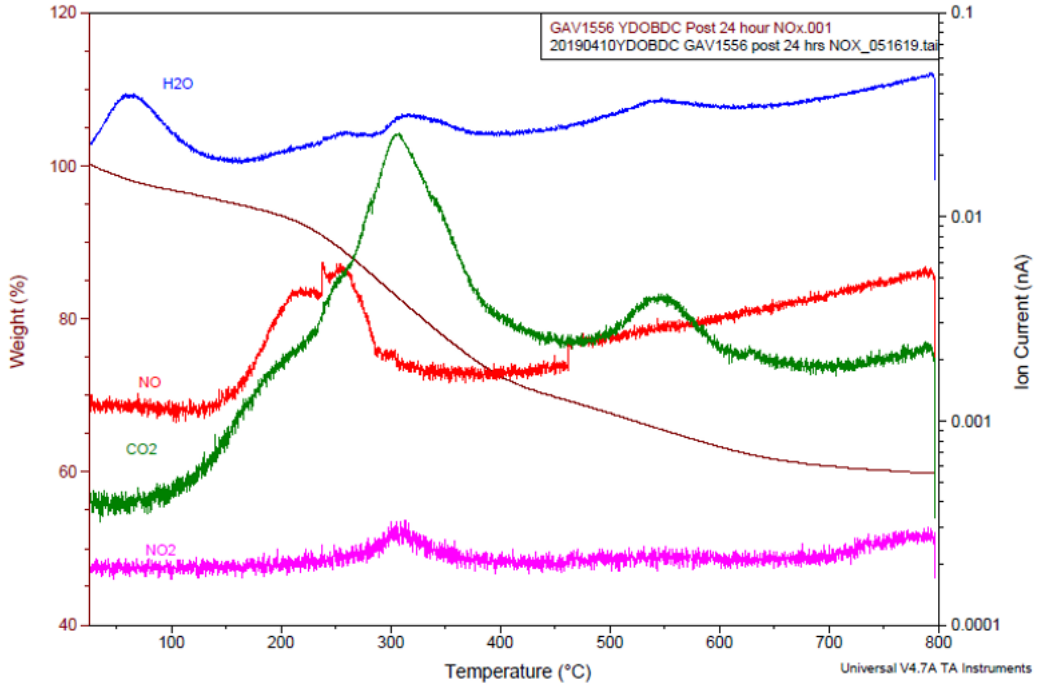


Peak number	Wavenumber (cm^{-1})	Peak assignment
1	1544	Asym. NO_2 stretch
2	1325	Sym. NO_2 stretch
3	1296	Asymmetric NO_2 stretch (R–ONO_2)
4	1206	C-O stretches of organic nitrates/nitrite
5	1177	C-O stretches of organic nitrates/nitrite
6	1038	symmetric NO_2 stretch (R–ONO_2)
7	960	aromatic C-N stretch of the nitro group
8	797	N-O stretch (R–ONO)
9	755	NO_2 deformation in R–ONO_2; N–O stretch in R–ONO
10	733	NO_2 deformation in R–ONO_2

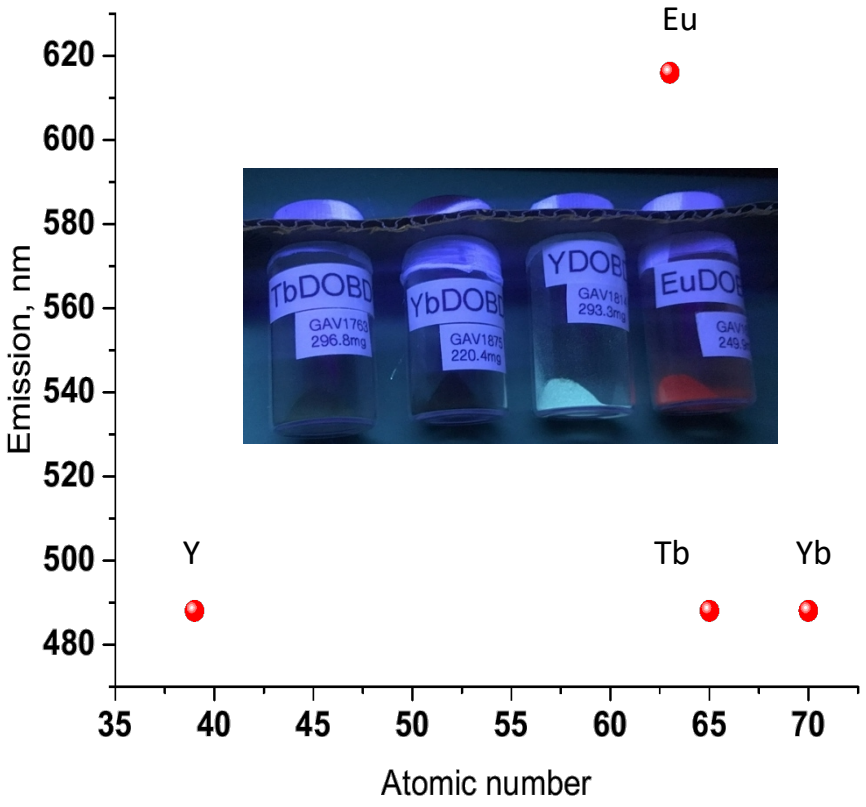
Peak assessments from
- *Chem. Mater.* **2017**, *29*, 4227
- Bhattacharyya, Han, Joshi, Zhu, Lively, Walton, Sholl, Nair
J. Phys. Chem. C. **2019**, *123*, 2336

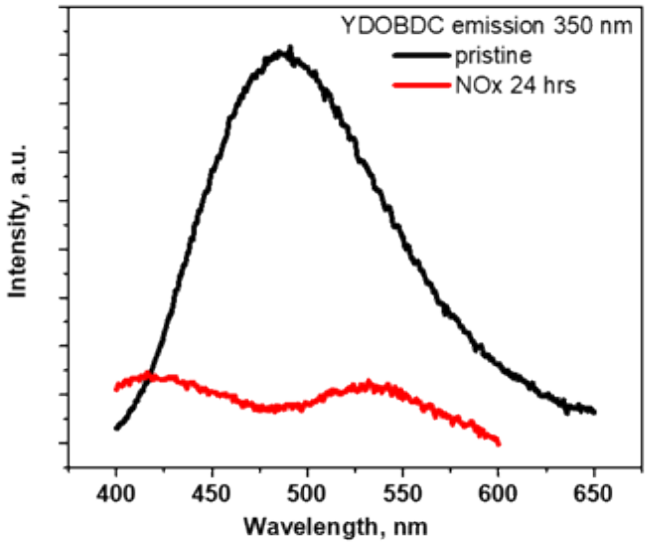
$2NO_2 \rightarrow 2NO + O_2$ @ 150°C in all plots, confidence between IR and TGA that NO_2 adsorbed

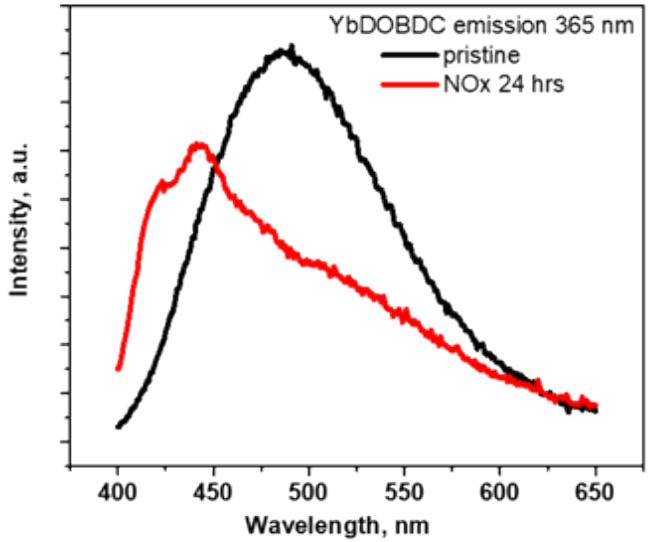
Representative IR and TGA/MS of all analogs in series

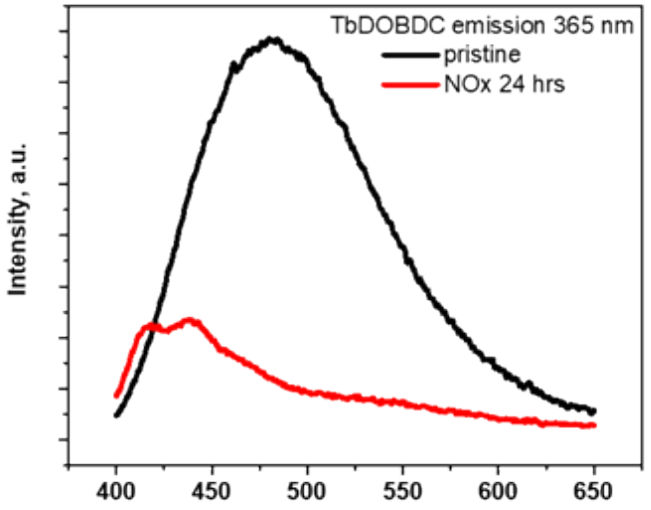


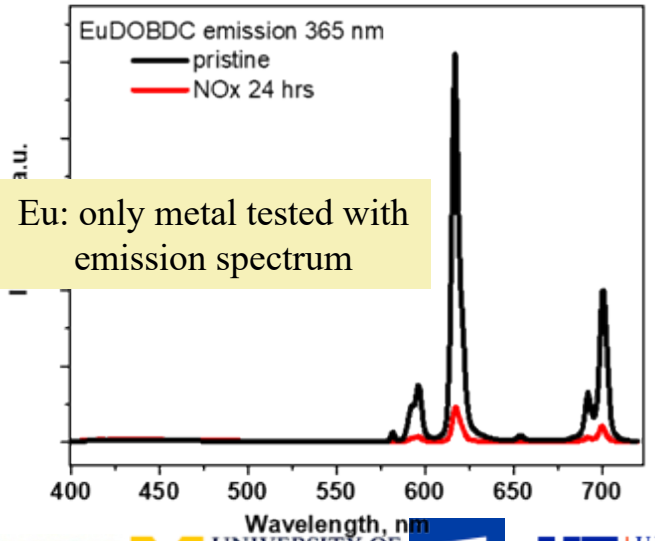
Emission data per unique metal centers, Quenching with NO_x adsorption





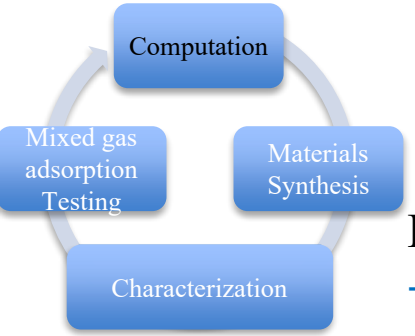






Eu: only metal tested with emission spectrum

Computational Approach: Modeling f-electron containing systems



How to efficiently simulate RE-MOFs and accurately calculate (i) the geometric and (ii) the electronic structure?

Jessica Rimsza

D. Jon Vogel

Different Methods/Corrections Tested:

- Large core potential (LCP): 4f-electrons in Ln is treated as part of the core (limited involvement in bonding and adsorption properties)
- Full valence potential: simulated 4f-electrons as valence (can be involved in bonding and adsorption)
- Hubbard corrections (1-9): used to correctly simulate band gap energies with f-electron containing molecules
- Spin restricted/unrestricted: changes if electrons must be pair (restricted) or unpaired (unrestricted)

Additional Details:
Vienna *ab initio* Simulation Package
PBEsol exchange correlation functional
DFT-D3 used for vdW interactions
Gamma point calculation

Validation of calculated binding energies

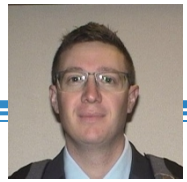
UNCAGE-ME Collaborative Studies, Univ AL, Dixon Group:
Performing higher order (e.g. coupled cluster) calculations on smaller clusters of the MOF structure,
Binding with different gas molecules,
Validation of calculated binding energies

Vogel, D.J.; Sava Gallis, D.F.; Nenoff, T.M.; Rimsza, J.M. *PCCP*, **2019**, 21, 23085-23093.

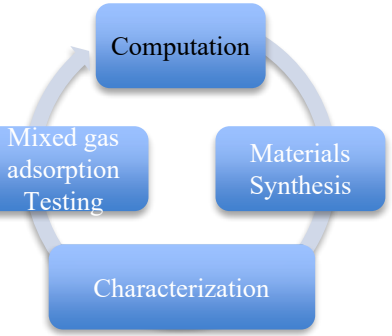
Dixon, et. al., *Comput. Theor. Chem,* **2017**, *1120*, 46

Use of DFT modeling to explain structure – property relationships of RE-DOBDC MOF

UNCAGE ME

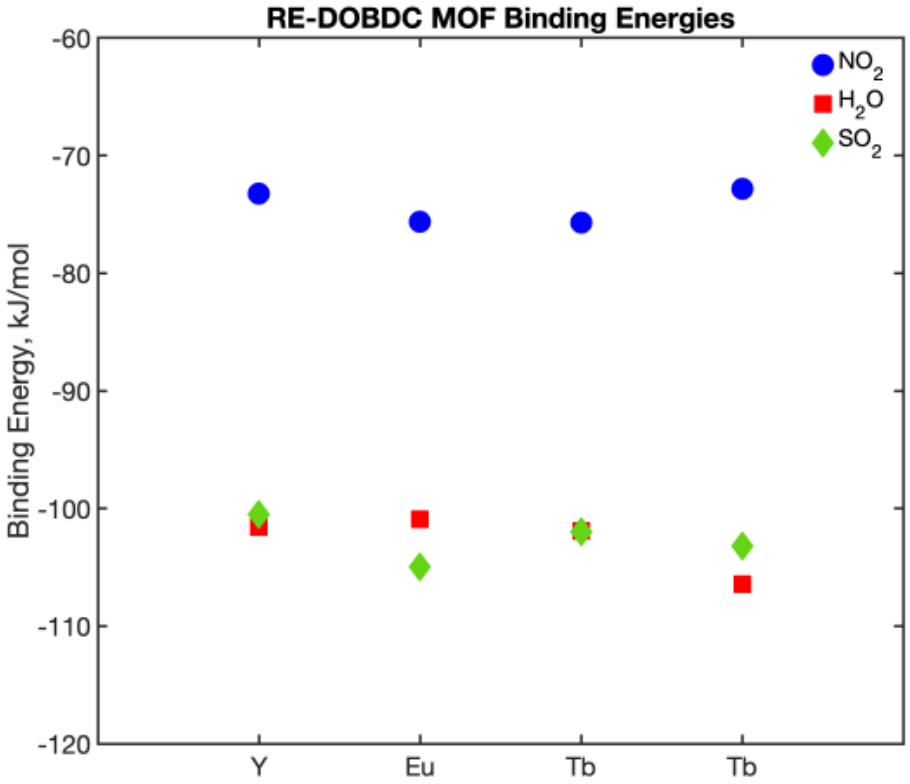

D. Jon Vogel

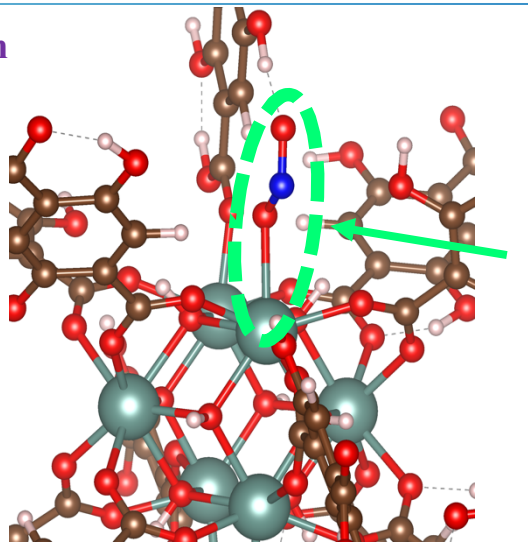

Jessica Rimsza

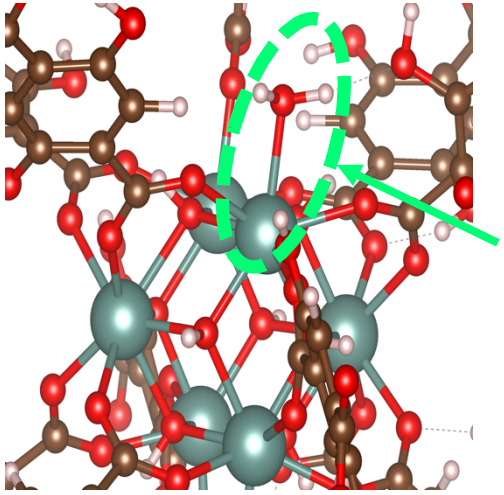


Experimental data is supported and explained by complimentary DFT modelin

- Experimental MOFs PXRD: all stable under 24hr humid NO_x exposure
- Calculated binding energies for H_2O & NO_2: unsaturated metal sites prefer H_2O







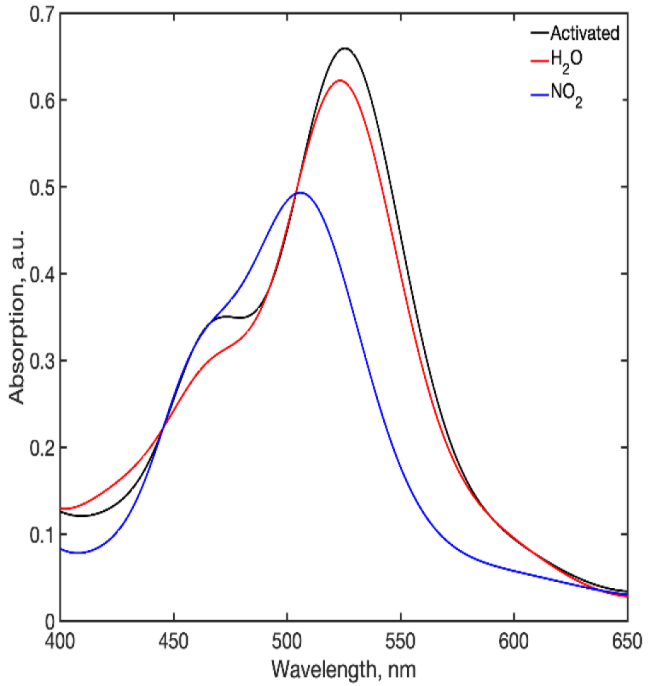
- Spin-unrestricted DFT with full 4f Valence Potential + U*
- Three different gases considered: H_2O, NO_2, SO_2 (one molecule at a time)
- Similar strong preference for H_2O and SO_2
- Different selectivity for H_2O v. NO_2
  NO_x not as strongly bound, possible preferential ad-/desorption material
- Metal center of MOF may play an added role in gas adsorption strength (eg., Tb)

Sava Gallis, Vogel, D. J.; Vincent, G.; Rimsza, J. M.; Nenoff, T.M. *ACS Appl. Mater. Interfaces* **2019,** *11*(46), 43270

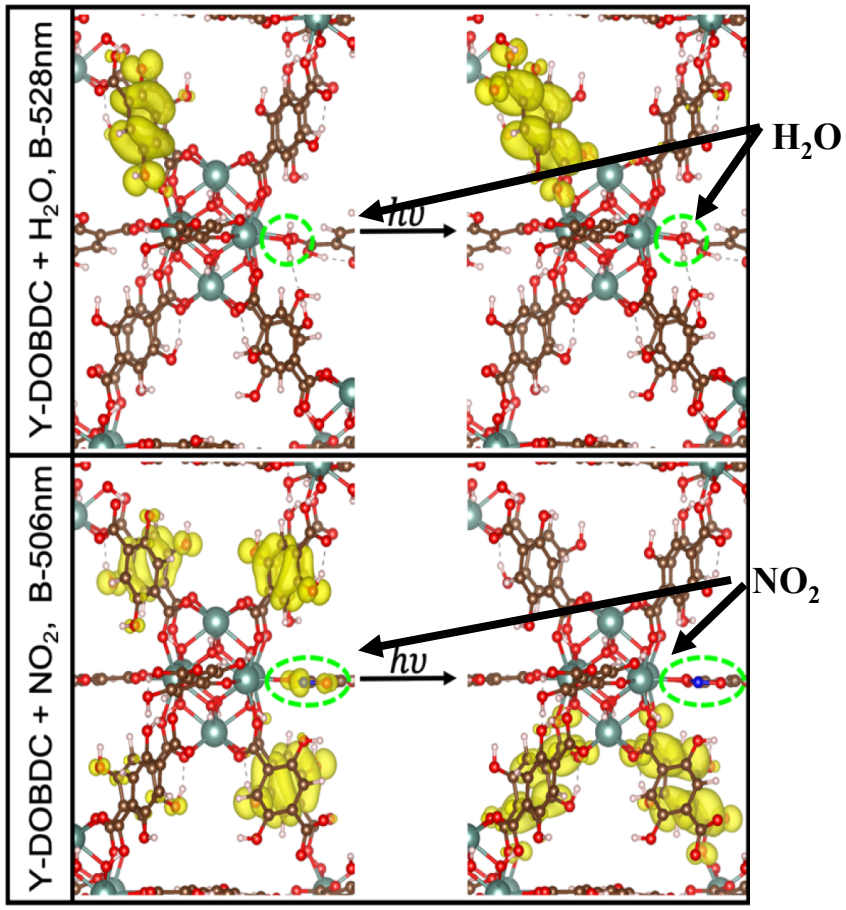
Use of DFT modeling to explain optical and electronic responses of NO_x adsorption in RE-DOBDC MOF

- Experimental FTIR characterized N-O-DOBDC linkers interactions
- Calculated: *NO_x adsorption shifts e-density from linkers to adsorbed NO_2 molecule,* reduces optical transition strength from the linkers; support exp's

optical spectra



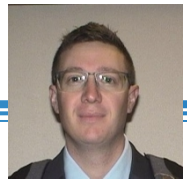
electronic structure



Sava Gallis, Vogel, D. J.; Vincent, G.; Rimsza, J. M.; Nenoff, T.M., *ACS Appl. Mater. Interfaces* **2019,** *11*(46), 43270

Competitive gas adsorption in RE-MOFs (binary gases: H_2O, NO_2)

UNCAGE ME



D. Jon Vogel

Jessica Rimsza

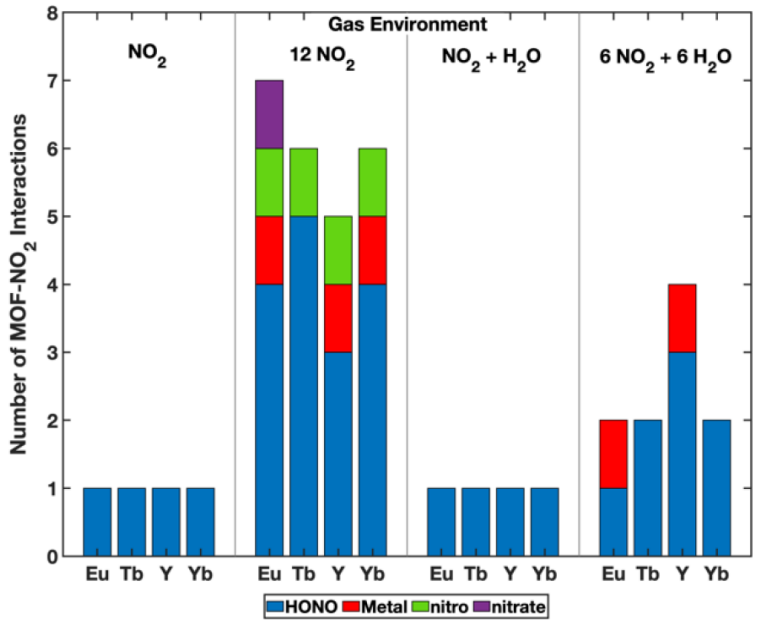
- Where and how do acid gases bind with the RE-MOF framework?
- How does competition between acid gases (NO_2, H_2O) impact adsorption ?

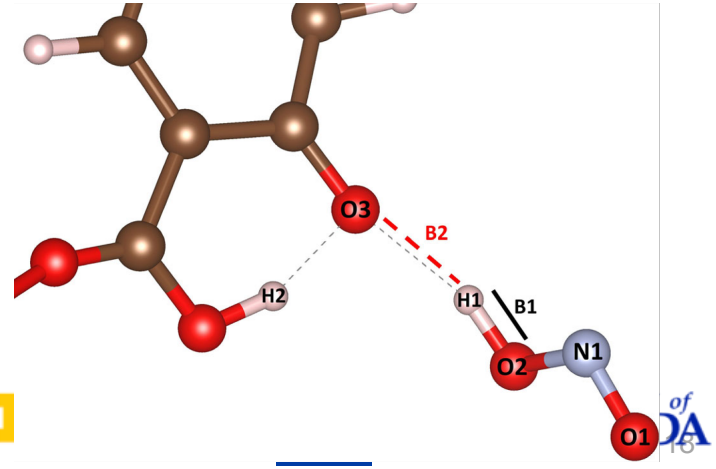
Methods

- Static and *ab initio* molecular dynamic (AIMD) periodic density functional theory (DFT) simulations – dynamically evolving DFT trajectories
- Combination of mixed gases and elevated, ambient temperatures

Results

- Competitive interactions in multicomponent gases inside MOF pores decrease adsorption
- NO_2 preferentially binds with the ligands compared with H_2O, forming secondary molecules and nitro/nitrate species





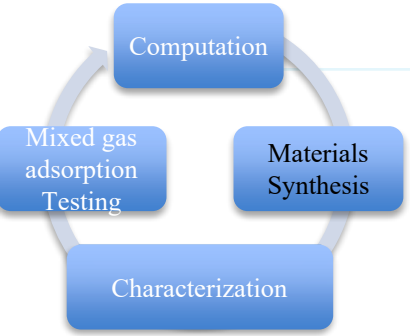
Formation of HONO via interactions of NO_2 and monodentate DOBDC linker

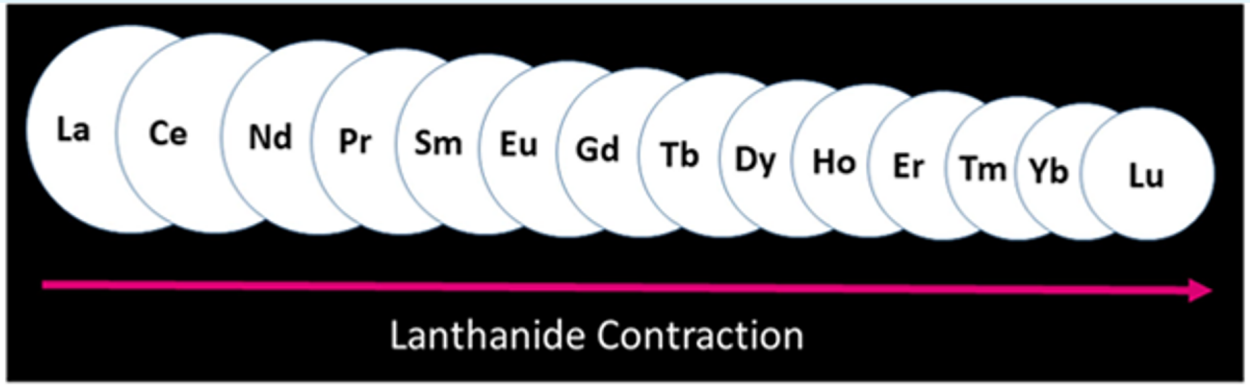
Invited: Vogel, Rimsza, Nenoff, *Angew. Chemie*. **2021**, *60*, 20, 11514.

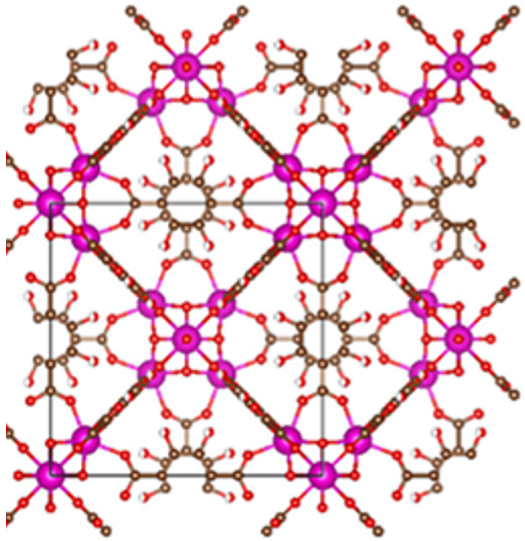
U.S. DEPARTMENT OF ENERGY | Office of Science | Georgia Institute of Technology | Oak Ridge National Laboratory | Sandia National Laboratories | The University of Alabama | Lehigh University

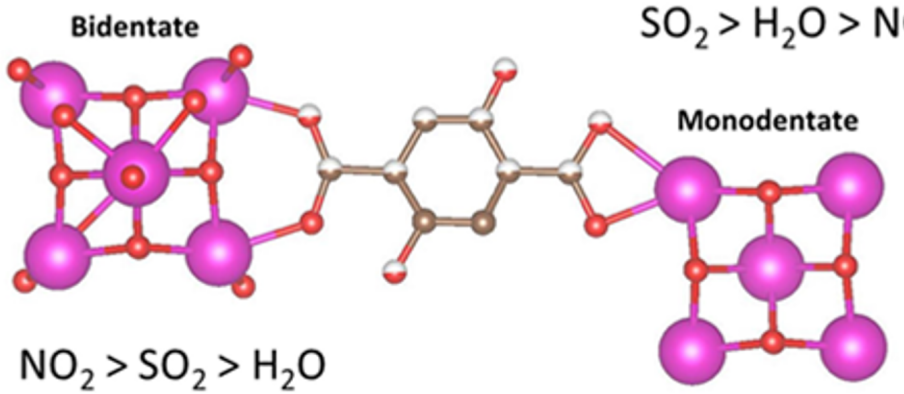
II. RE-DOBDC, Entire Lanthanide Series

Henkelis, et.al., *ACS AMI*, **2021**, *13*, 56337

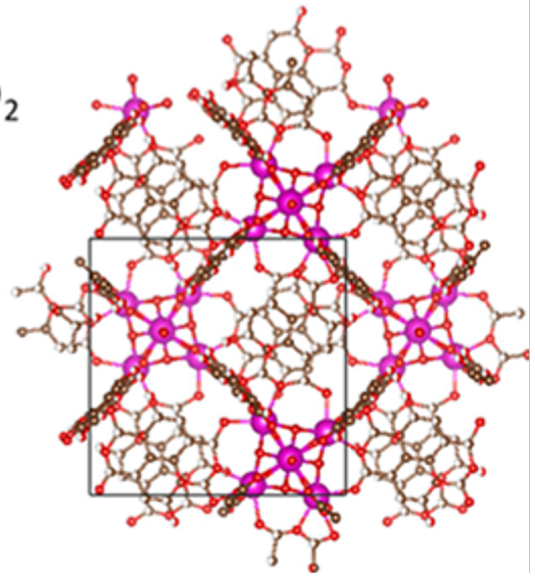


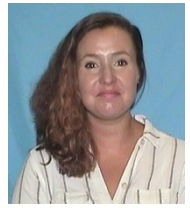






$SO_2 > H_2O > NO_2$





Susan Henkelis

D. Jon Vogel

Jessica Rimsza

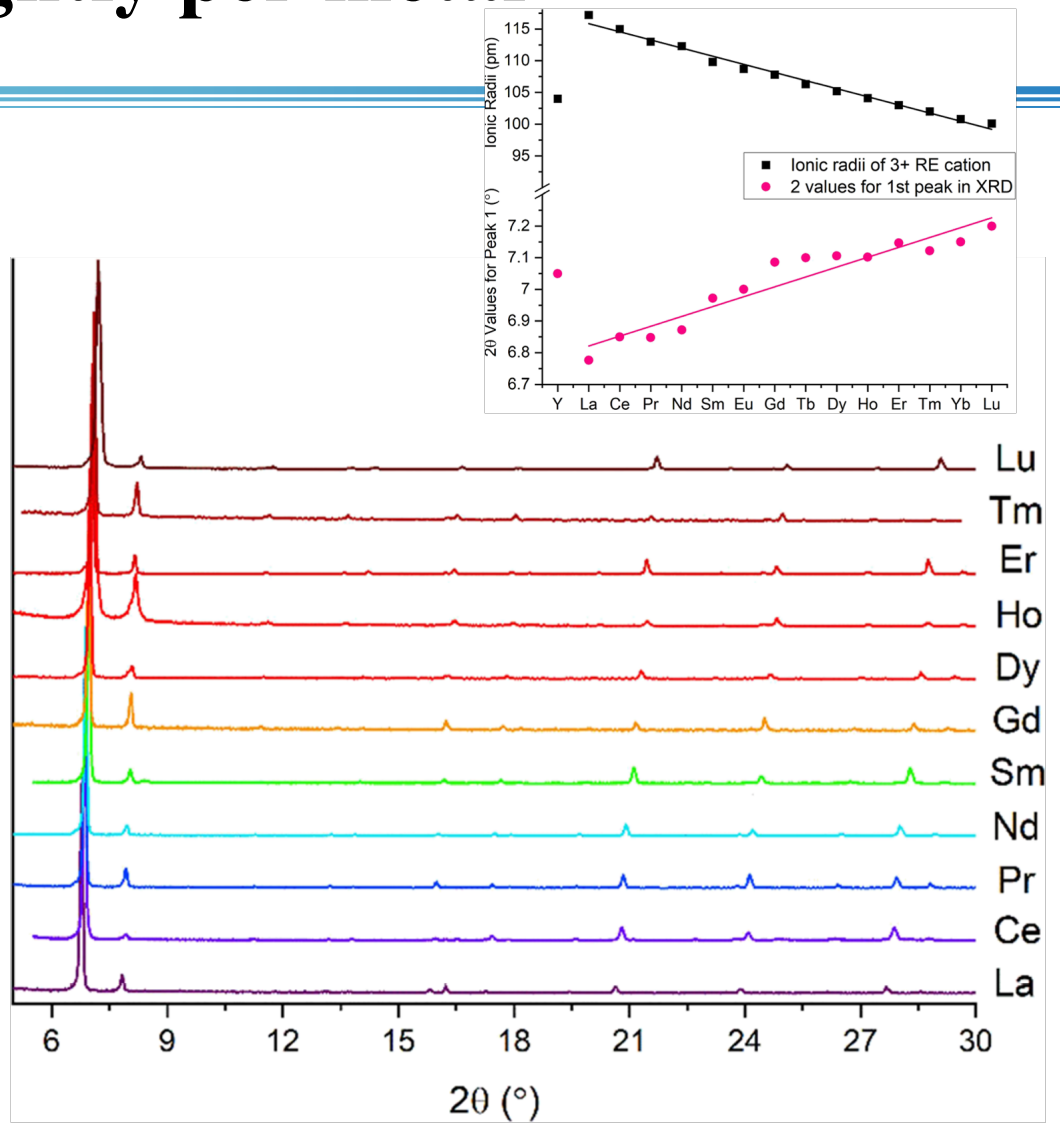
RE-DOBDC Series: Reactions vary slightly per metal

La-DOBDC example:

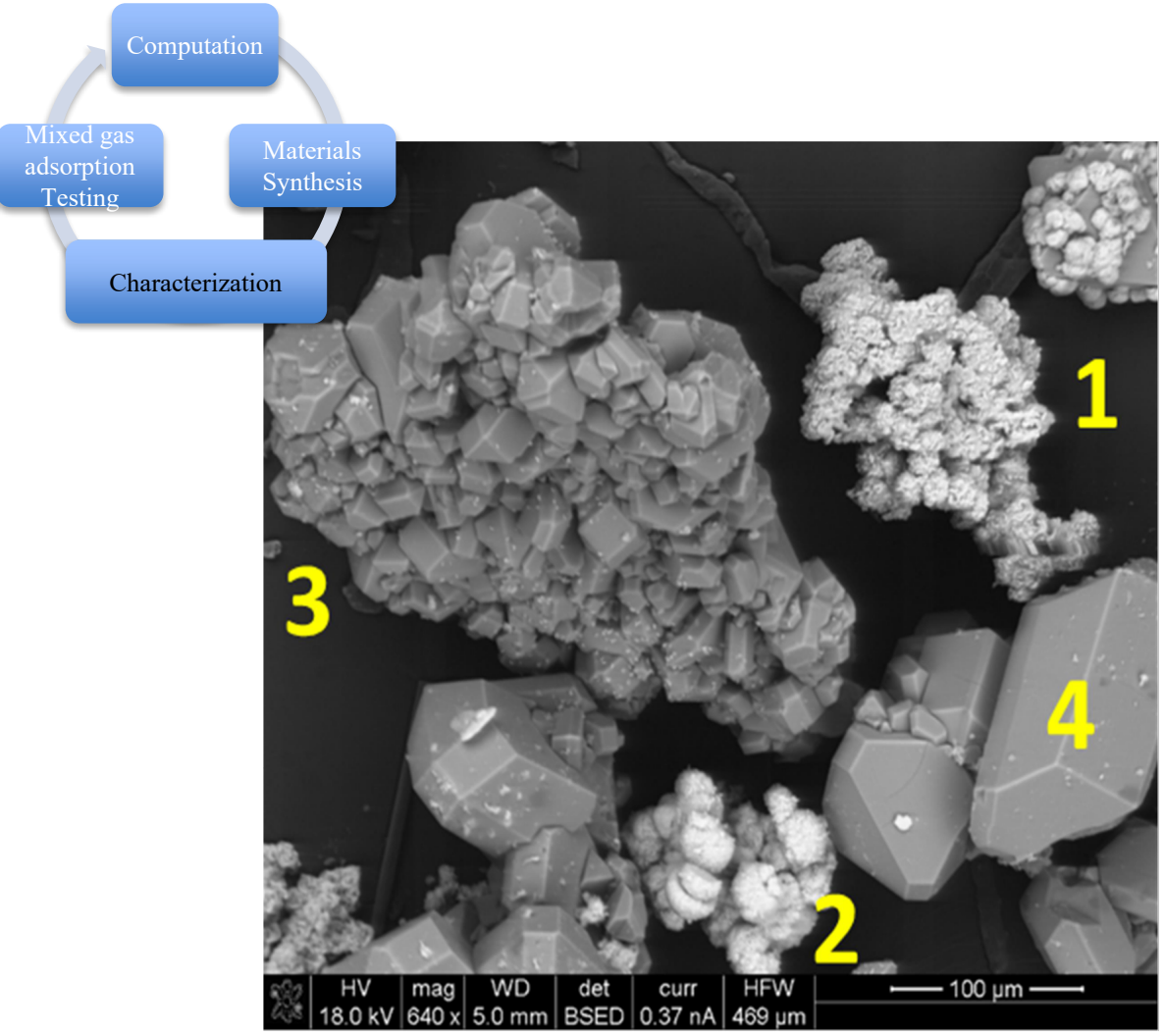
$LaCl_3 \cdot 7H_2O$ + dihydroxyterephathlic Acid + DMF
Dimethylformamide + DMF
$H_2O + HNO_3$

} 125°C, 60 hrs.

rare earth	molar ratio S:L:M	temp (°C)	days in oven
Y	1:1.32:19.84	115	3
La	1:1.46:21.86	125	3–6
Ce	1:2:21.86	125	3
Pr	1:1.46:21.86	125	6
Nd	1:1.46:21.86	125	6
Sm	1:1.46:21.86	125	3
Eu	1:1.46:21.86	115	3
Gd	1:2:21.86	125	3
Tb	1:1.46:21.86	115	3
Dy	1:1.46:21.86	125	6
Ho	1:1.58:7.98	125	3
Er	1:1.58:7.98	125	10
Tm	1:2:7.98	125	3
Yb	1:1.58:7.98	115	3
Lu	1:1.58:7.98	125	3



SEM reveals 4 stages of crystallization in these MOFs

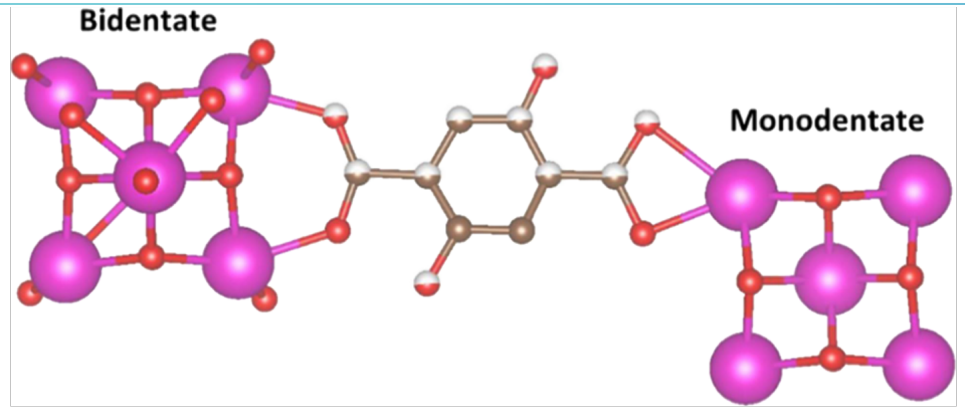


At each stage [M] decreases*,
pointing to ligand incorporation with time

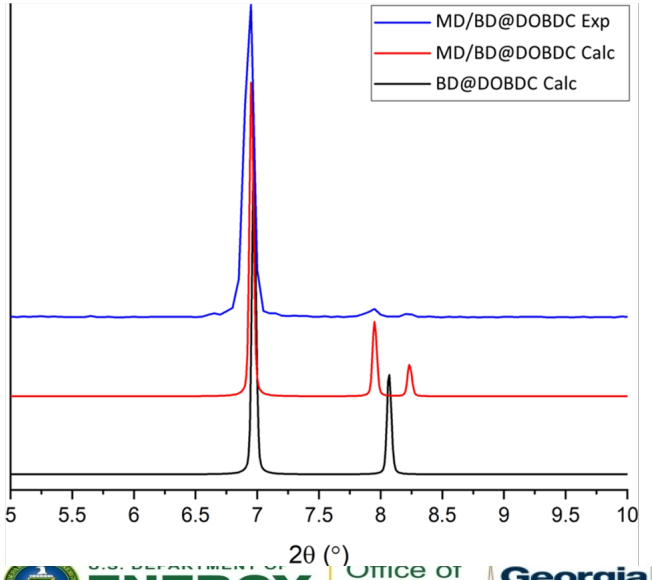
	Nd-DOBDC			Er-DOBDC	
	element	weight %	phase	element	weight %
1	Nd	91.93	nodular	Er	-
	O	8.07		O	-
2	Nd	87.56	nodular balls	Er	-
	O	12.42		O	-
3	Nd	78.10	aggregates	Er	-
	O	21.90		O	-
4	Nd	77.57	single crystal	Er	73.57
	O	22.43		O	26.43

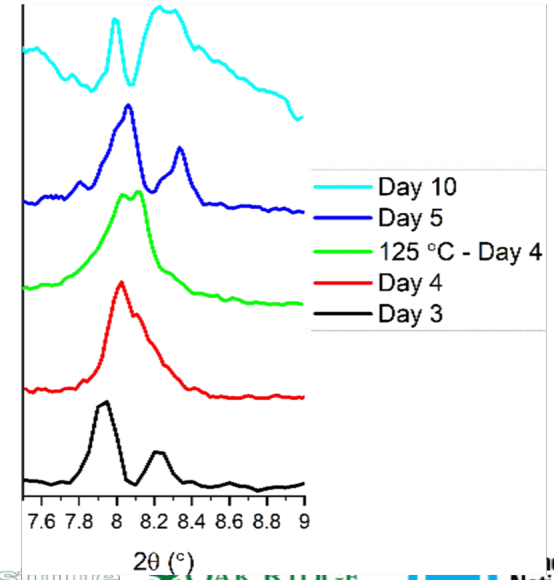
*Exception appears to be Er-DOBDC

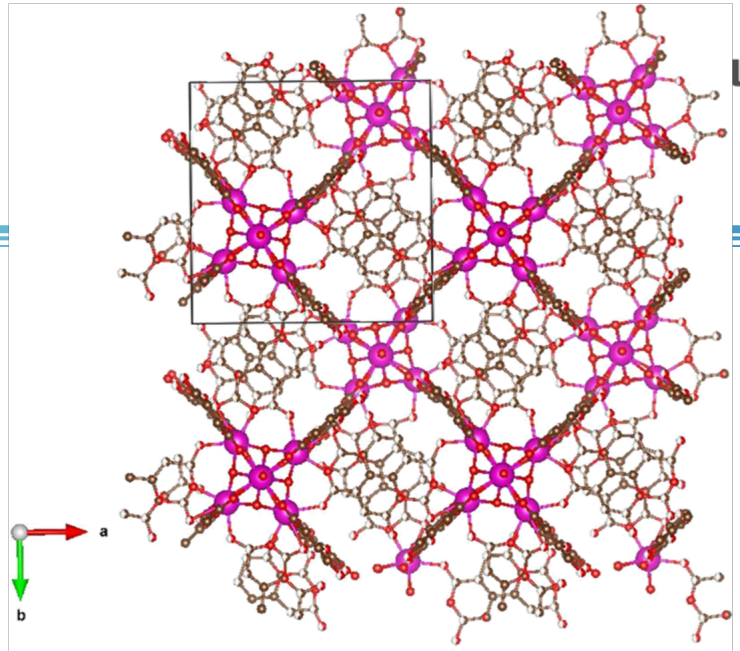
Kinetically Controlled Denticity



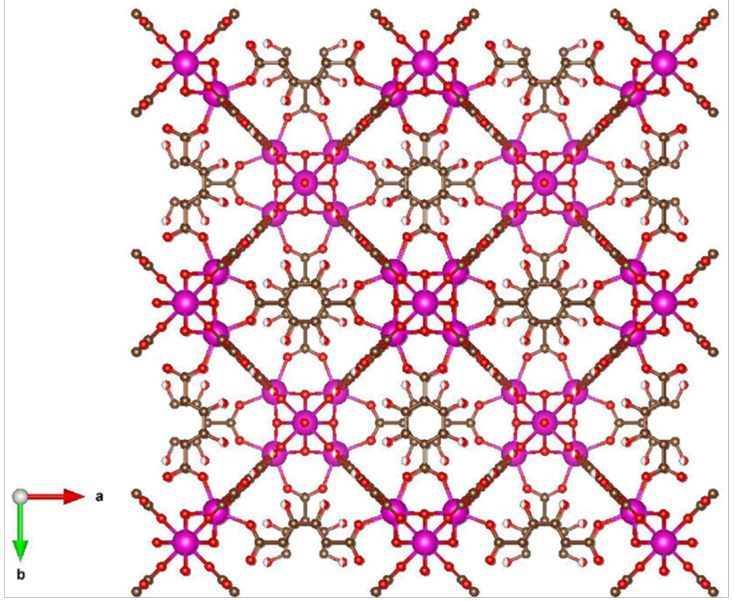
Short reaction times showed a mixture of Mono- and Bi-dentate binding of metal cluster (MD/BD-M-DOBDC)





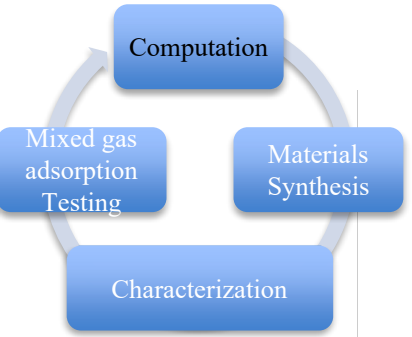


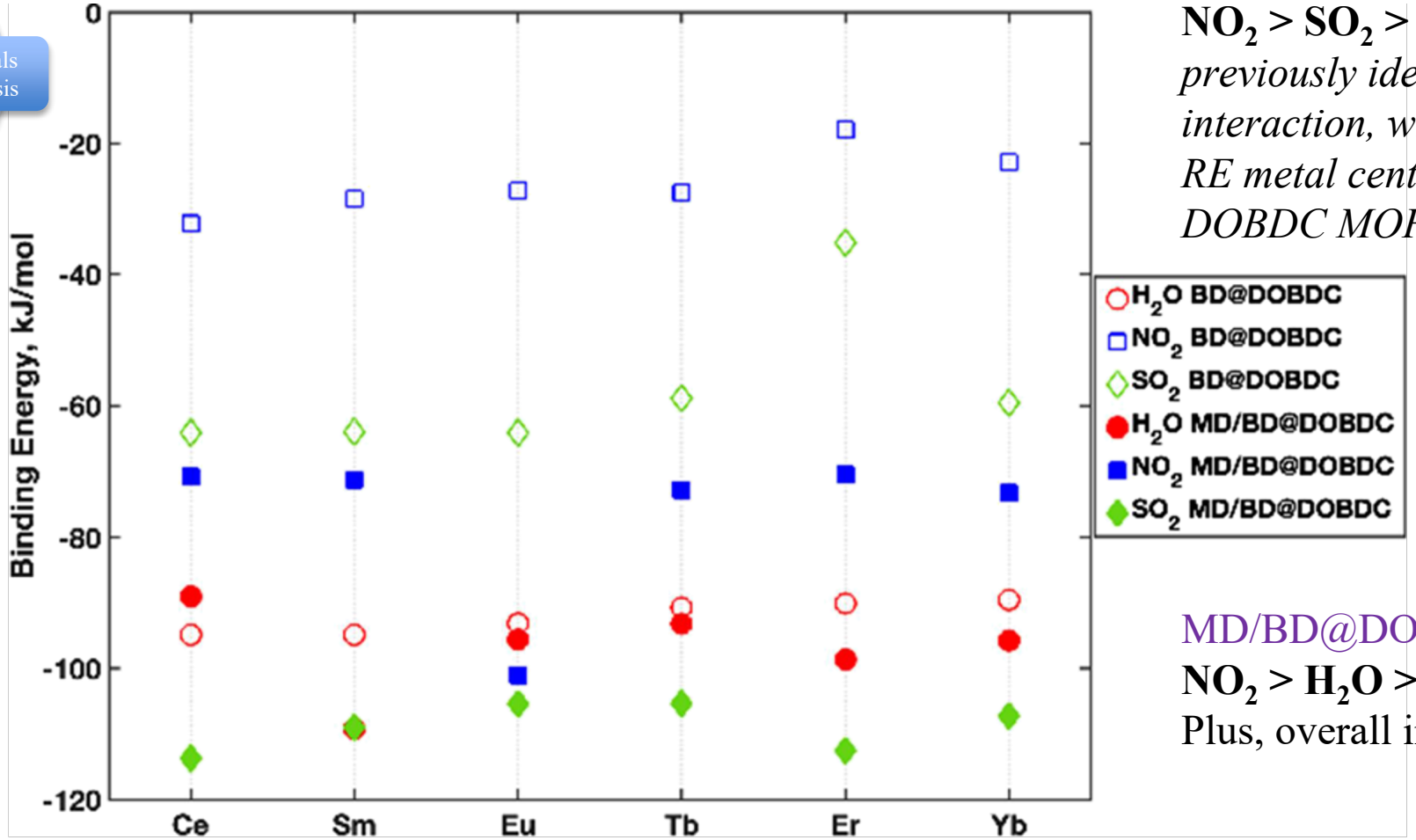
MD/BD@Eu-DOBDC



BD@Eu-DOBDC

Binding energies calculated indicating framework connectivity defines preferential gas binding





BD@DOBDC MOF:

NO_2 > SO_2 > H_2O

previously identified secondary H- bond interaction, when adsorbed to the RE metal center, does not form in the BD-DOBDC MOF phase.

MD/BD@DOBDC MOF:

NO_2 > H_2O > SO_2

Plus, overall increase in binding energies

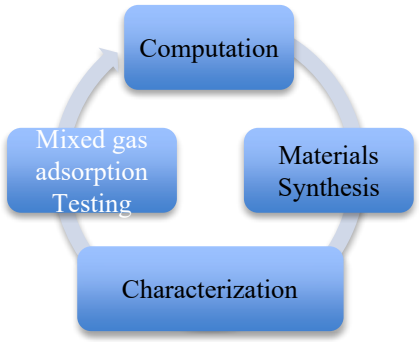
III. Enhanced Framework Stability via Cluster Fluorination

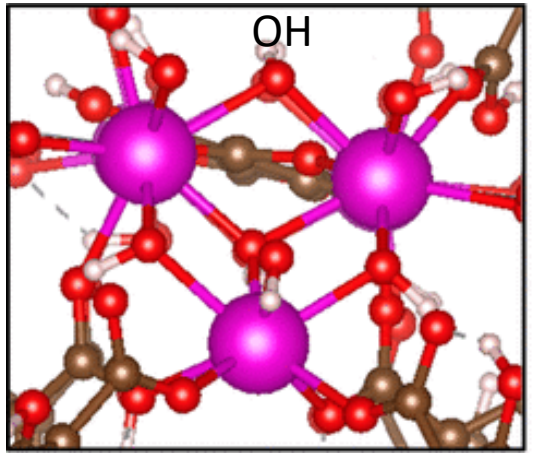
Recently, possible fluorine doping was reported in the metal clusters in Ho-DOBDC MOF (*JACS* **2021**, *143* (43), 17995)
We undertook a computational and experimental study to elucidate if fluorine incorporated into the RE-DOBDC MOFS.

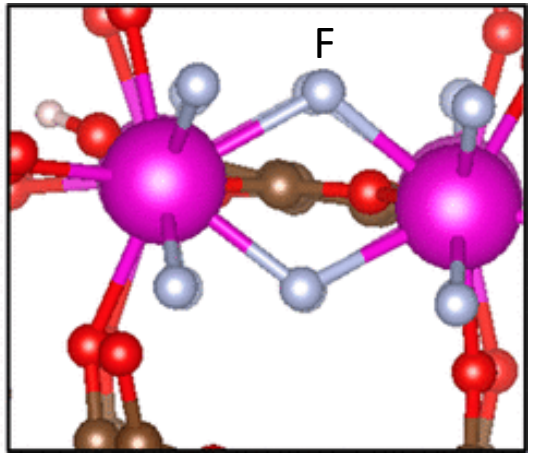
VASP DFT modeling, MOF synthesis and characterization, advanced ^{19}F NMR experiments

Completed for RE-DOBDC, RE-UiO66, RE(Eu)-TCPB MOFs

How: from the modulators used for crystallization of the MOFs in the reaction synthesis: *2-fluorobenzoic acid (2-fba)*

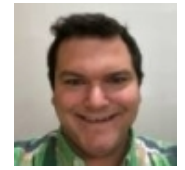






Computationally predicted fully hydroxylated RE-DOBDC MOF cluster (left) μ_3–OH and the fully fluorinated version (right) μ_3-F


Jessica Rimsza


Matt Christian

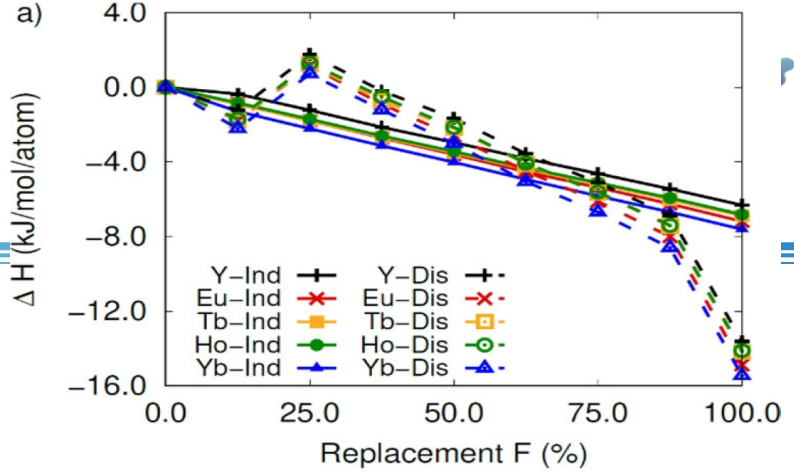

Keith Fritzsching

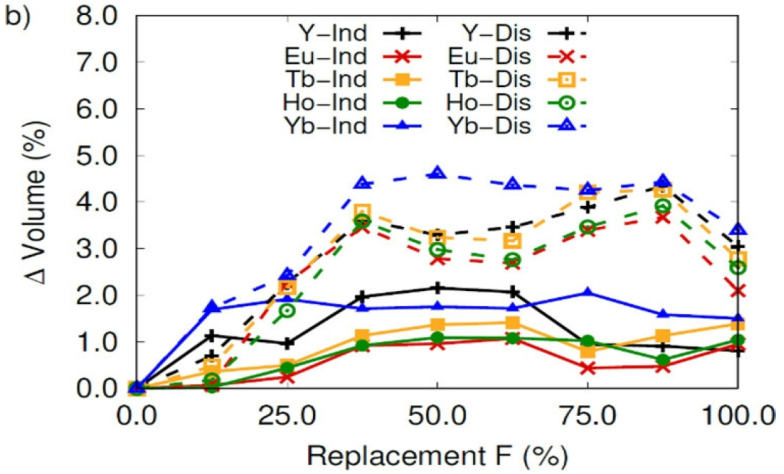
Calculated Changes of Fluorine incorporation into MOF Structures

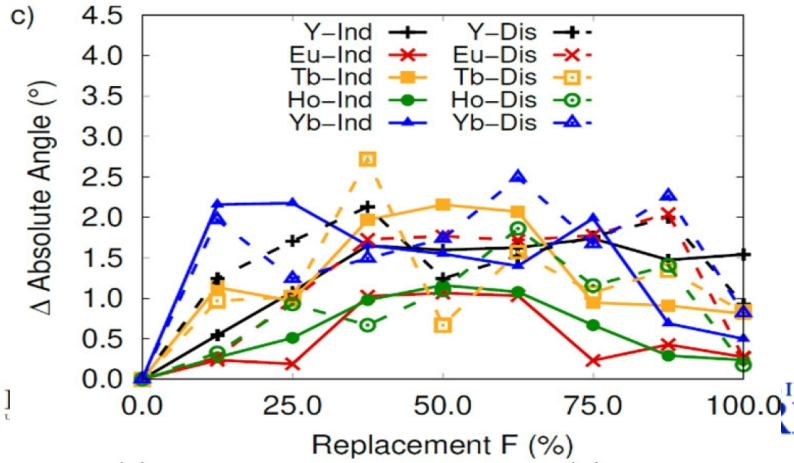
Computationally determined:
- All RE MOFs evaluated are *more stable* with the incorporation of fluorine
- Two different fluorine NMR peaks (−63 ppm, −87 ppm).

In table to right, framework topology accommodates the incorporation of F into the cluster through slide localized crystallographic changes.
(a) Change in formation enthalpy,
(b) % volume change,
(c) absolute sum in lattice angle change per RE atom

RE-DOBDC:
Solid lines, –OH replacement on single cluster in the crystal;
Dashed line, replacement on 2 metal clusters in crystal

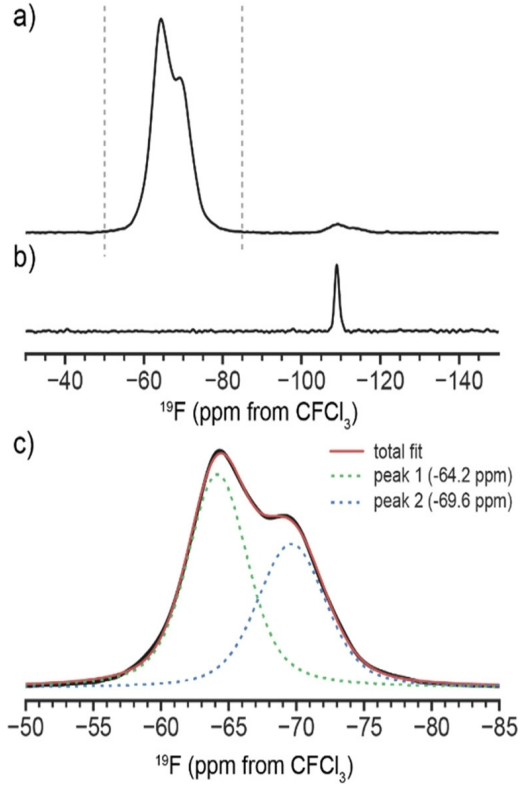




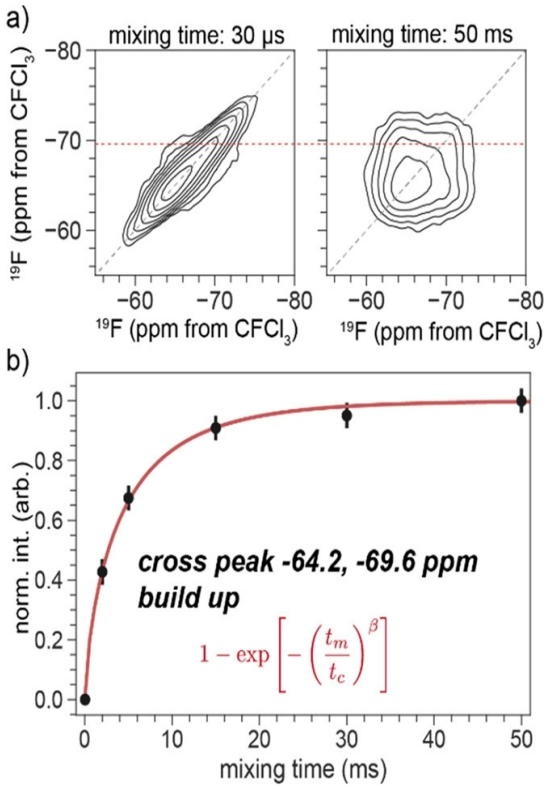


^{19}F Experiments on Y-DOBDC

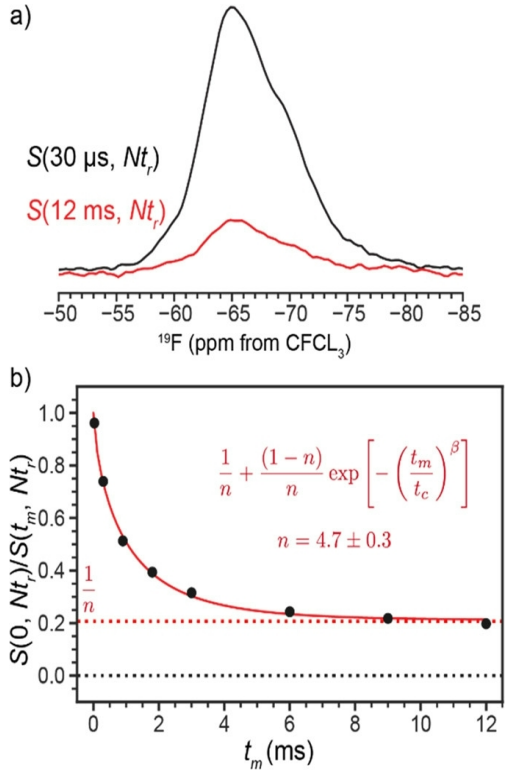
- The CODEX experiment demonstrates that >4 fluorine atoms per cluster.
- Signal decays to ~0.2 in 12 ms, corresponding to 4.7 ± 0.3 (±1σ) nearby (~5 Å) fluorine spins.
- Y-DOBDC MOF structures have 8 possible fluorine sites, data indicates a fluorination rate of > 50%



^{19}F NMR spectra



^{9}F 2D exchange NMR



^{19}F CODEX NMR

F-cluster in Y-DOBDC MOFs: no anticipated effect on Acid Gas Binding Energies and MOF Selectivities

*calculated energies, in kJ/Mol

	H_2O		NO_2		SO_2	
	OH	F	OH	F	OH	F
Y	-88	-83	-46	-58	-61	-57
Eu	-91	-89	-65	-67	-66	-61
Tb	-93	-89	-46	-66	-65	-62
Yb	-88	-81	-42	-54	-60	-59
Avg	-90 ± 3	-86 ± 4	-50 ± 10	-61 ± 6	-63 ± 3	-60 ± 2

RE-DOBDC MOFs retain the binding trend of $H_2O > SO_2 > NO_2$

Christian, M. S.; et.al., *JACS Au*, **2022**, *2*, 8, 1889

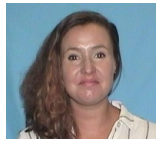
IV. Use of DOBDC – based MOFs as direct electrical readout sensors


Leo Small


Mara Schindelholz


Stephen Percival


Matthew Hurlock


Susan Henkelis

- The ability to sense and identify individual gaseous pollutants from the complexity of the environment requires highly selective materials

  Avoidance of interference from real-world air components

  - Current conductivity-based devices generally fall into two categories:
    - Solid state – (oxide based) require higher temperatures (>200°C) for interaction of the gas with the surface oxides; heating devices are needed
    - Fuel cell – room temperature liquid electrolyte, easily fouled, short lifetime
  - Electrical metal organic framework (MOF) based sensors have previously been used for direct electrical sensing of gases; however, none for NO_2 have been reported in open literature
  - By tuning the composition of MOFs, selective chemical adsorption and/or catalysis can be achieved
  - Typical sensors for this application are hard-wired or require frequent battery replacement– nanoporous MOFs allows for “near-zero” long lived sensing in a wider range of environments

Direct Electrical Readout Sensors Combined with Nanoporous Adsorption Materials

blank IDE

IDE + Ni-MOF-74

IDE + Ni-MOF-74
Exposed to 5ppm NO_2
8 h 50 °C

- Composed of **Pt interdigitated electrodes (IDEs) with a nanoporous adsorbent layer**
- Nanoporous adsorption materials chosen for **ability to selectively adsorb target** gas molecules
- Electrical readout sensor of this design:
  - Decreased power consumption
  - Ability to interrogate for specified gases selectively in real-time or as an integrating sensor for delayed/later testing
- Design of an integrated sensor:
  - Record whether any **degradation product was ever present** during the sensor's lifetime
- Integrated sensor is **useful** in cases where degradation products may:
  - Subsequently **react** with other components,
  - Gradually **leak out** of the system

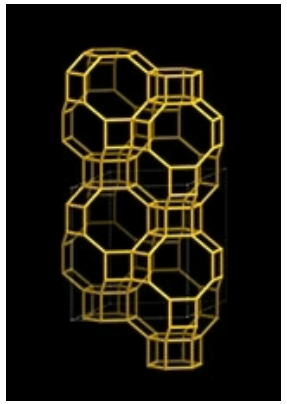
We have a wide study of sensors for various target gases:

ACS Applied Mater. Interfaces, **2017**, *9*, 44649
Micro. Meso. Mater. **2019**, *280*, 82
ACS Applied Mater. Interfaces, **2019**, *11*, 27982
Adv. Func. Mater. **2020**, *1407*, 2006598
Membranes **2021**, *11*, 176
I&ECR **2021**, *60*, 21, 7998
I&ECR, **2021**, *60*, 40, 14371
Chem. Soc. Rev. **2022**, *51*, 324

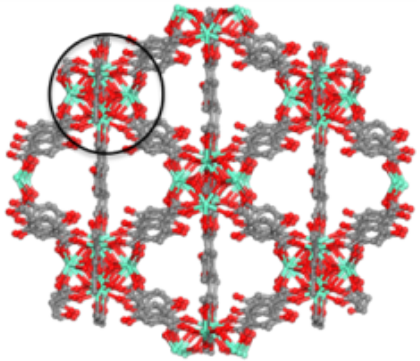
Nanoporous Materials Targeted for the Selective Adsorption of NO_x

Durable nanoporous adsorbents with selectivity for NO_x at low temperatures (near ambient)

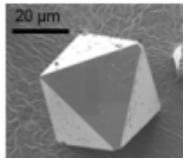
- Zeolites are aluminosilicates with high temperature durability. Specific metals give rise to NO_x selectivity
- Metal-organic frameworks (MOFs) are metal nodes with organic linkers with selectivity to NO_x designed by incorporating NO_x –friendly metals into the framework

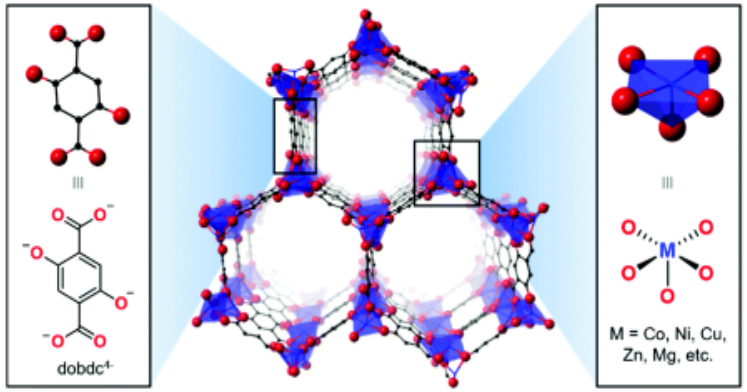


Zeolite **SSZ-13** (CHA)



Metal-organic framework **M-DOBDC** (M = Y, Yb, Eu, Tb)

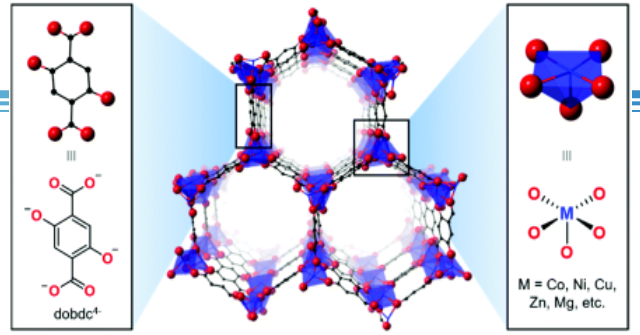




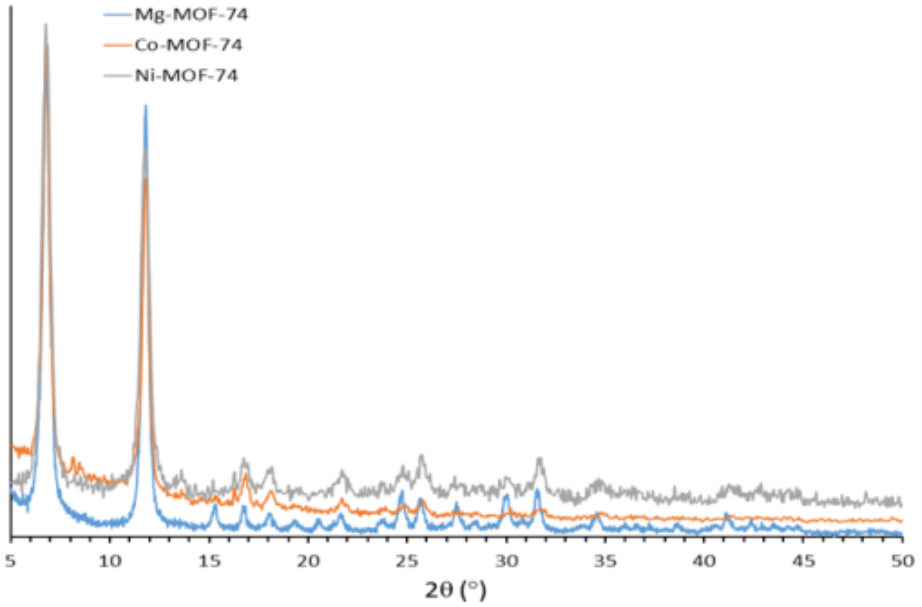
M-MOF-74 (M = Co, Mg, Ni) DOBDC ligand

Small, Schindelholz, Nenoff, *Perspective:*
"Hold on Tight: MOF-Based Irreversible Gas Sensors" *I&ECR*, **2021**, *60*, 21, 7998

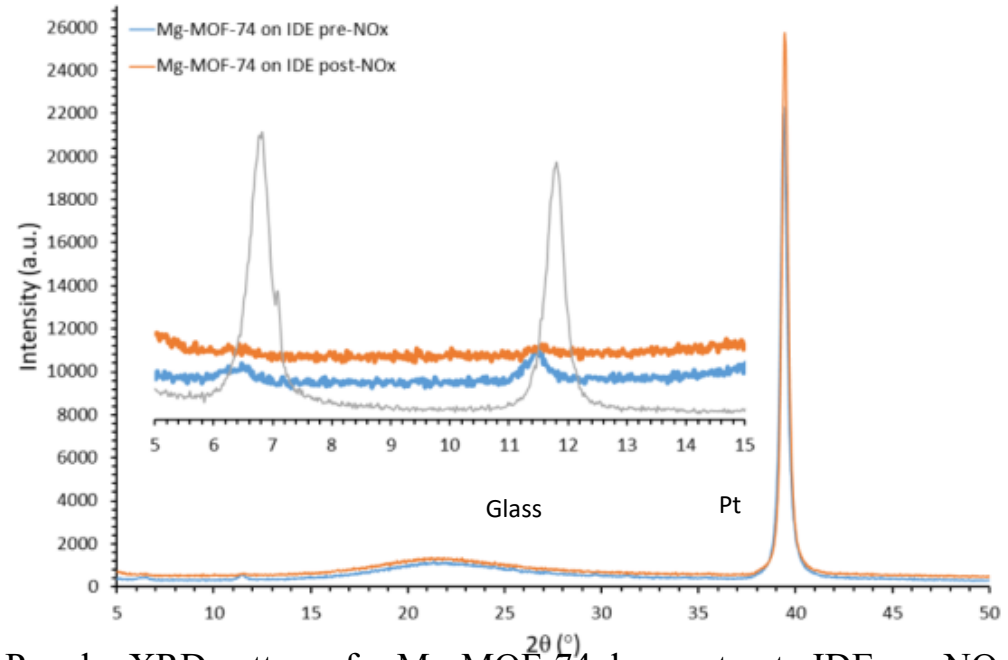
M-MOF-74-Based Sensors for the Selective Adsorption of NO_2



- M-MOF-74 (M= Co, Mg, Ni) was targeted for its selectivity to NO_2
- MOF-74 materials were synthesized and investigated as bulk materials and dropcast onto an interdigitated electrode (IDE)
- Each powder pattern highlighted two primary diffraction peaks corresponding to the MOF pore (intensities reduced for dropcast samples, with the large peak corresponding to the platinum IDE)



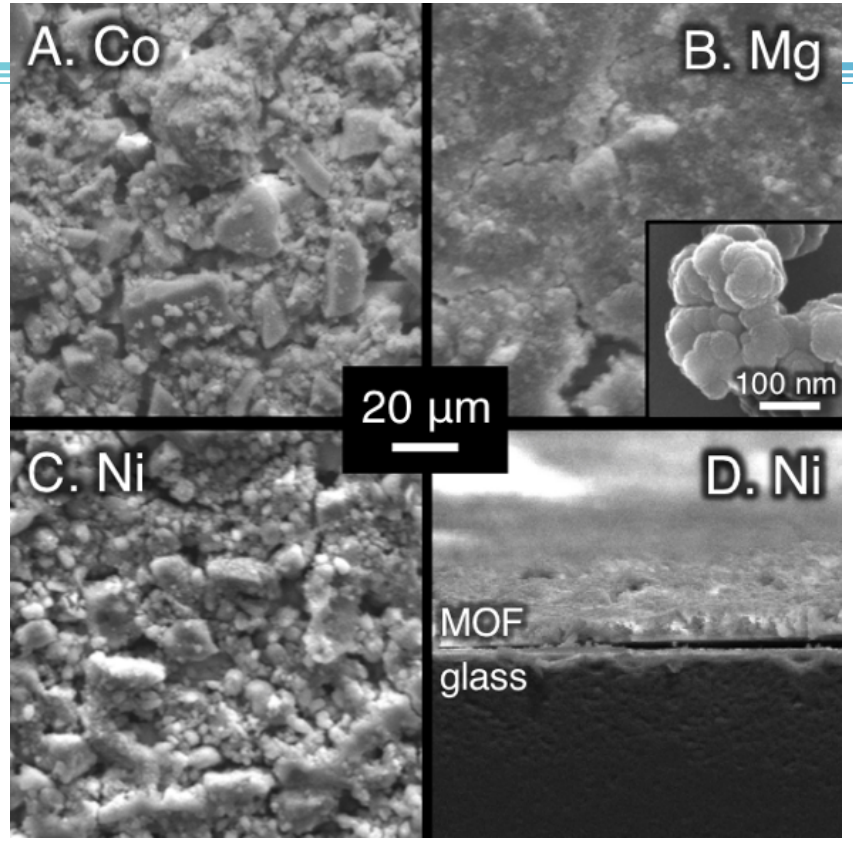
Powder XRD patterns for as-synthesized MOF-74 in the bulk phase.



Powder XRD patterns for Mg-MOF-74 dropcast onto IDE pre-NO_2 (blue) and post-NO_2 (orange). Inset: zoomed in region compared to bulk powder Mg-MOF-74.

Small et al., "Near-Zero Power MOF-Based Sensors for NO_2 Detection," *Adv. Funct. Mat.*, **2020,** *50,* 2006598

SEM Characterization of Dropcast M-MOF-74 Films

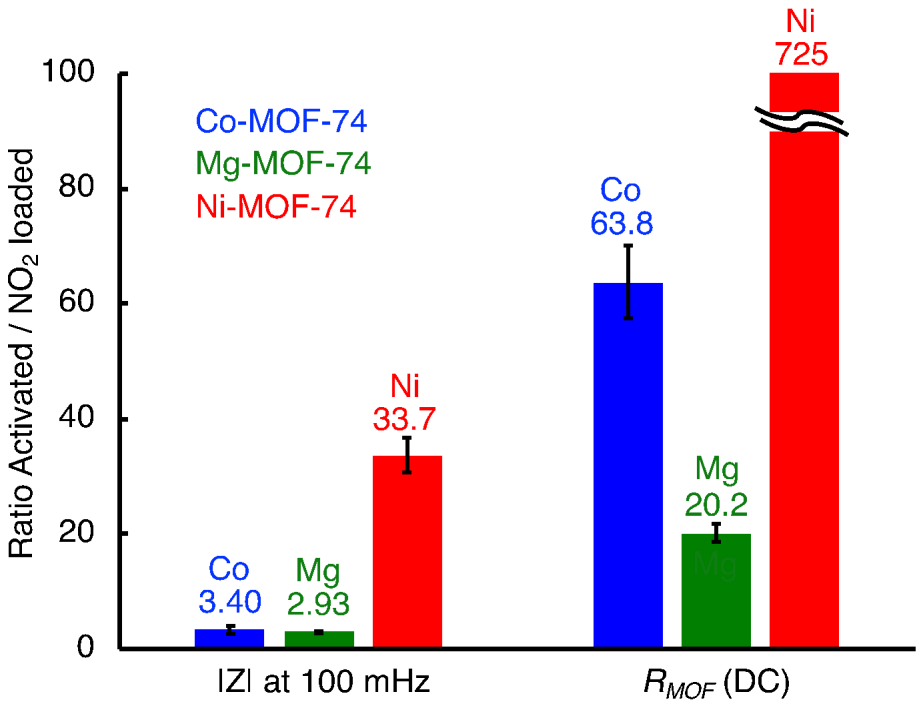


Plan-view SEM micrographs of (A) Co-MOF-74, (B) Mg-MOF-74, (C) Ni-MOF-74 powders dropcast onto IDEs. (D) Cross-sectional micrograph of Ni-MOF-74 film from (C).

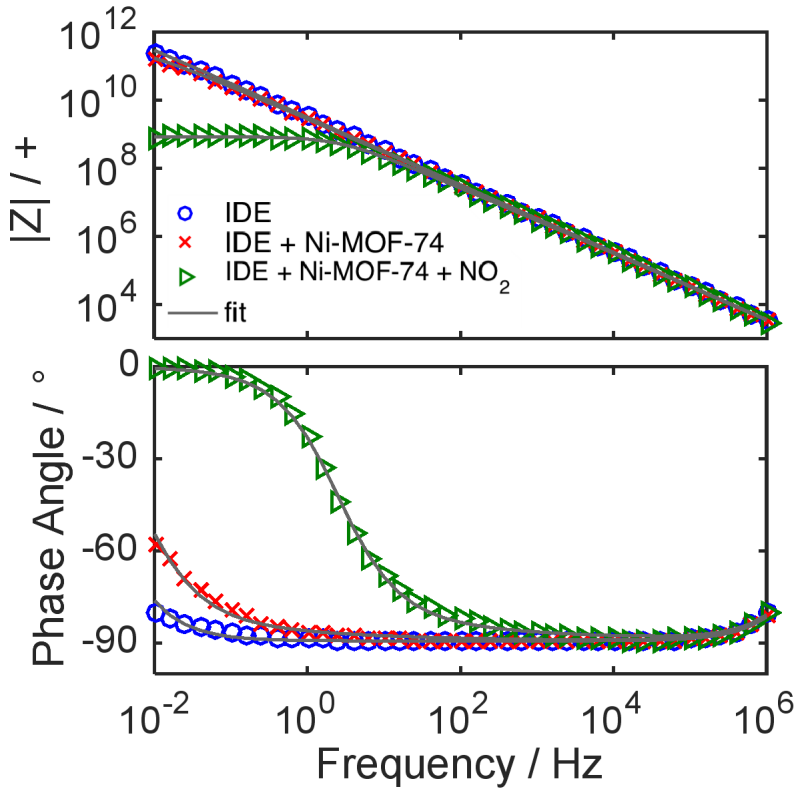
- Co- and Ni-MOF-74 contained a wide range of crystallite sizes, from 100's of µm to 100 nm
- Mg-MOF-74 crystallites were on the order of 100 nm
- Film thickness was ~ 10 µm
- *Defect-free films are not necessary*

Typical Impedance Responses of M-MOF-74-Based Sensors

Exposed M-MOF-74 (M = Co, Mg, Ni) based sensors to 5 ppm NO_2 for 8 h at 50°C.



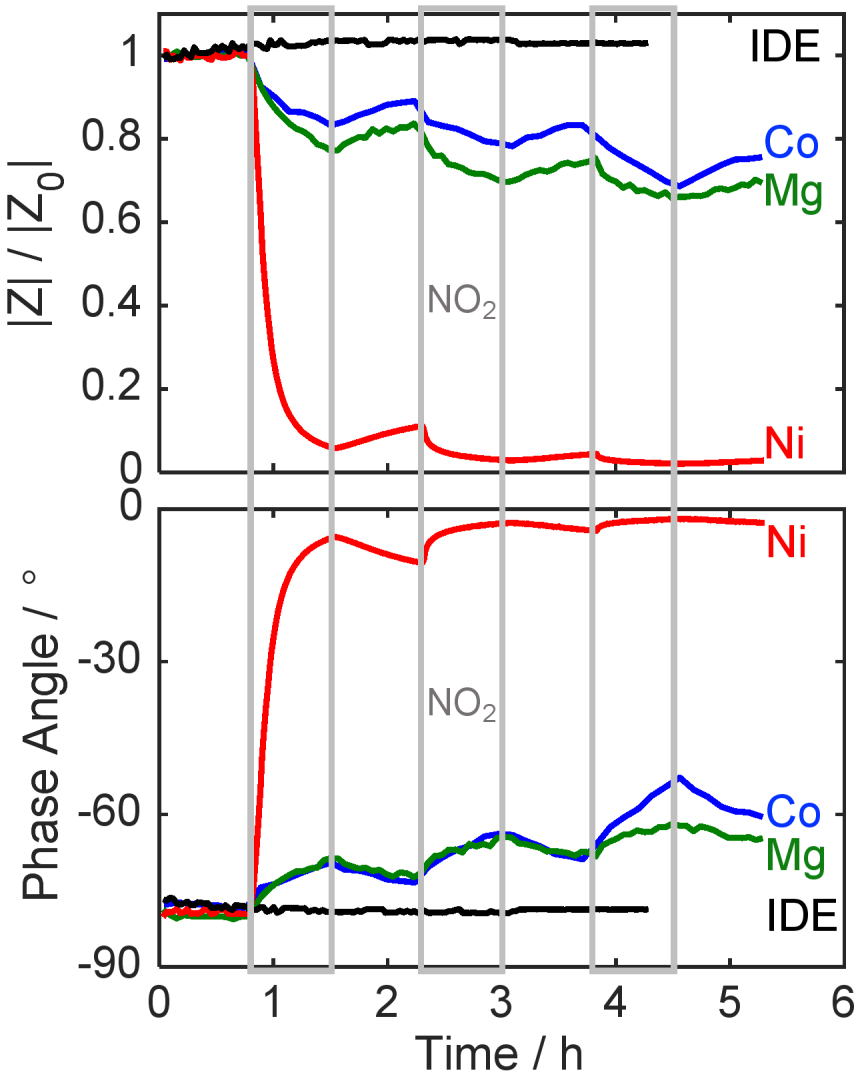
Ratio of response as-activated to NO_2-exposed for (1) impedance magnitude ($|Z_{activated}|/|Z_{NO2}|$) at 100 mHz and (2) MOF DC film resistance ($R_{activated}/R_{NO2}$).



Example impedance spectra for Ni-MOF-74-based sensor

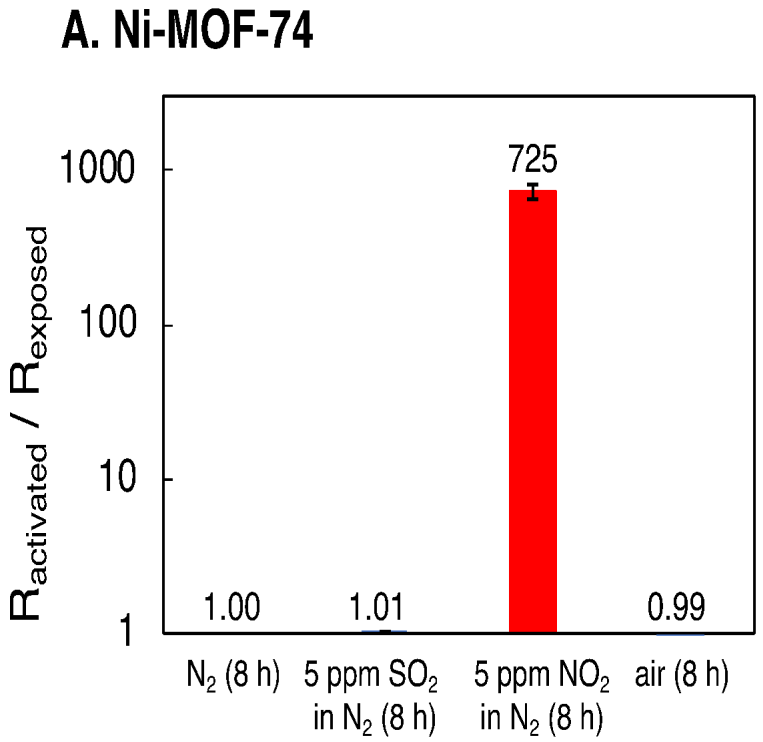
Impedance Responses as a Function of NO_2 Concentration

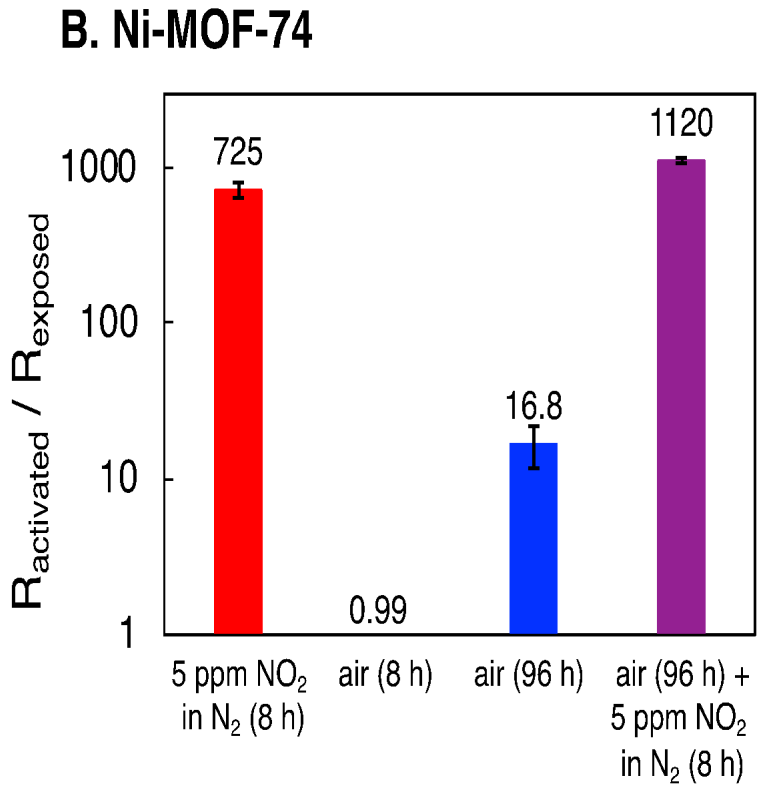
- Blank IDEs and IDEs coated in **M-MOF -74 (M= Co, Mg, Ni)** were activated and exposed to alternating 0.75 h flows of pure N_2 or N_2 containing trace NO_2, while impedance was constantly measured at 100 mHz
- Magnitude of electrical response is ordered **Ni > Co > Mg**
  - Explained by each variant's NO_2 adsorption capacity and specific chemical interaction
- Use of **Ni-MOF-74 provided the highest sensitivity to NO_2, with a 725× decrease in resistance** at 5 ppm NO_2 and a NO_2 detection limit <0.5 ppm



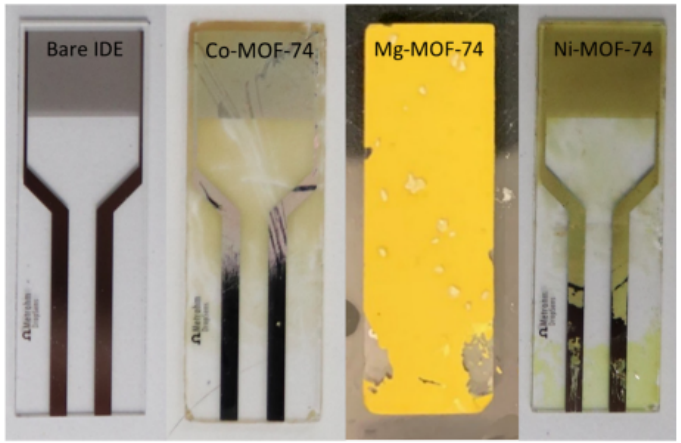
NO_2 Selectivity for a Ni-MOF-74-Based Sensor

- A Ni-MOF-74-based sensor was activated and exposed to 5 ppm SO_2 in N_2, and ambient air (25 °C, 50% RH, 400 pm CO_2) heated to 50 °C, and its response compared to previous exposures to 5 ppm NO_2 in N_2
- An extended air exposure (96 hours) followed by subsequent NO_2 exposure was also performed
- The Ni-MOF-74-based sensor demonstrated selectivity to NO_2 versus N_2, SO_2, and air.

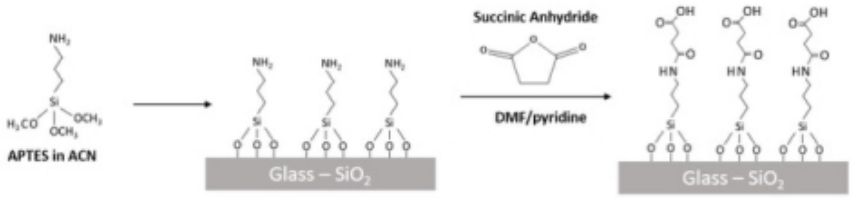




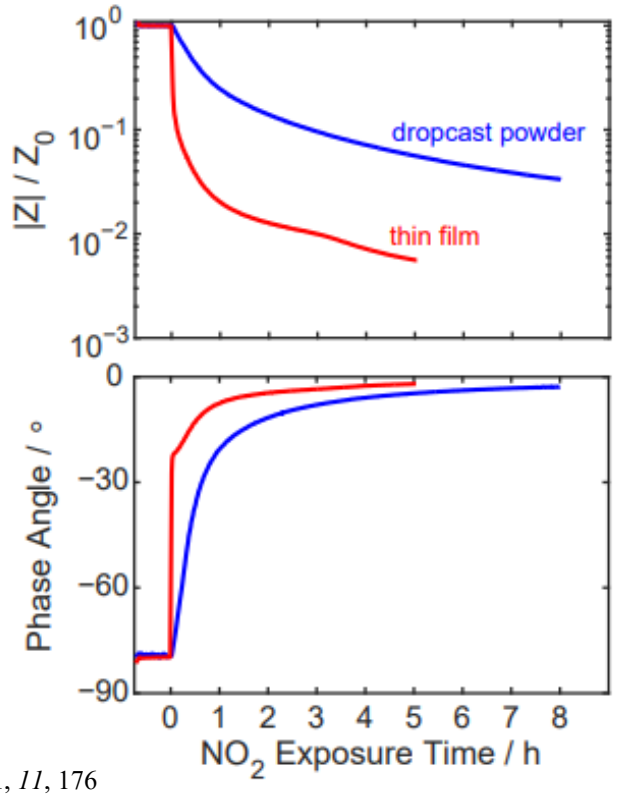
Enhanced Sensitivity of Nanoporous-Based Sensors Using MOF Thin Film Membranes



- M-MOF-74 (M=Co, Mg, Ni) MOFs synthesized as crystalline thin films on functionalized IDEs
- *Two step functionalization procedure*:
  - Reacted IDE with aminosilanes, followed by ring opening of succinic anhydride
  - Functionalization allowed for binding of metal cation and further growth of 3-D MOF



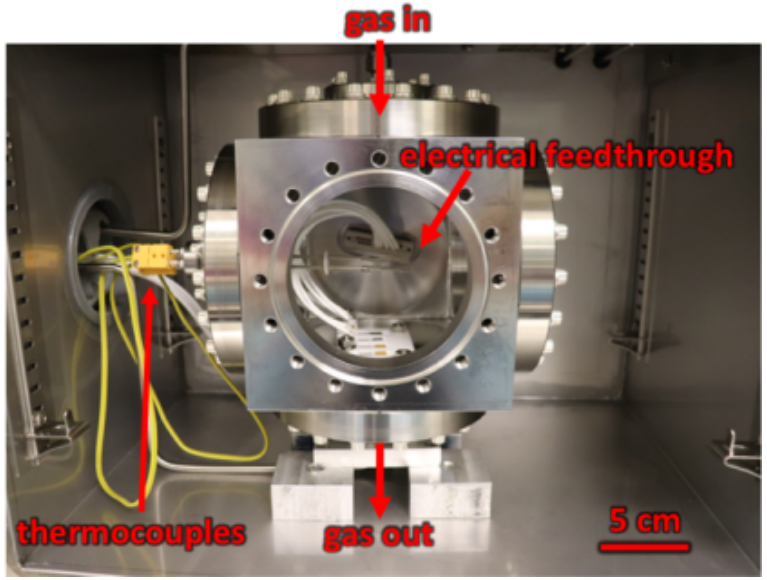
- Ni-MOF-74 boasted a continuous thin film and used in a comparison study vs. a dropcast powder
- Thin film passed a modified **ASTM D3359** test for durability
- Thin film membranes resulted in an increased response rate and larger total change in impedance

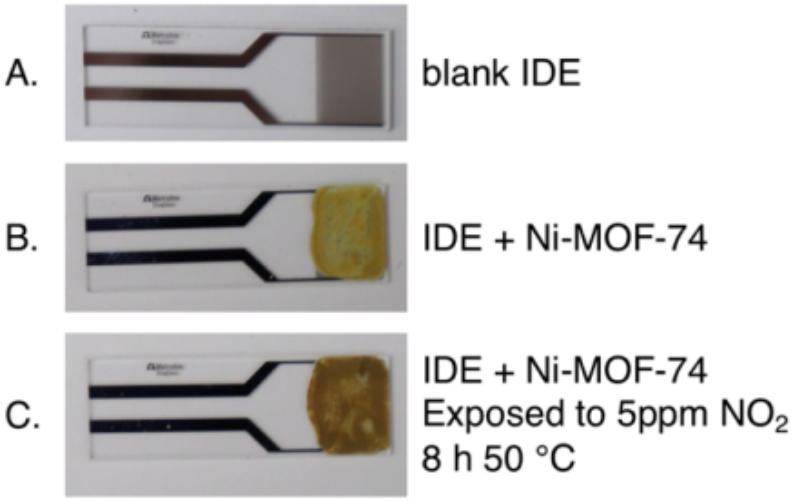


Henkelis, et al., "Continuous MOF Membrane-Based Sensors via Functionalization of Interdigitated Electrodes", INVITED: *Membranes* **2021**, *11*, 176

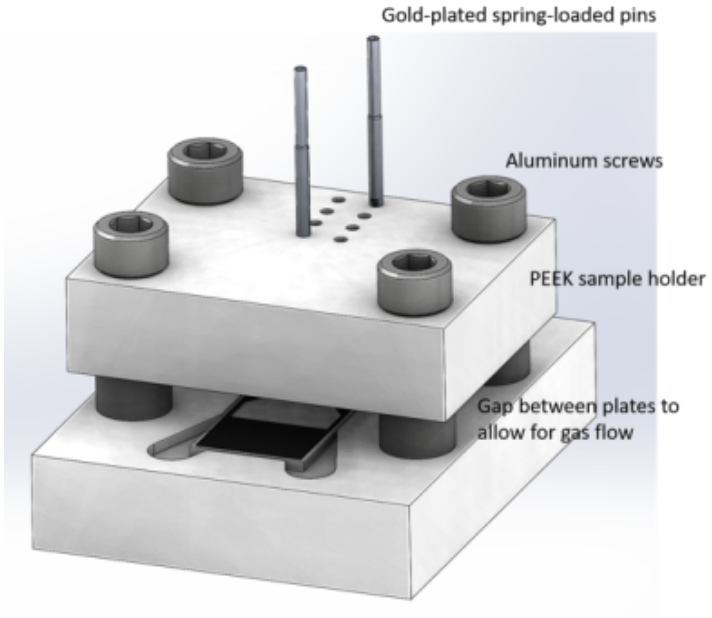
NO_x Exposure and In Situ Electrical Testing

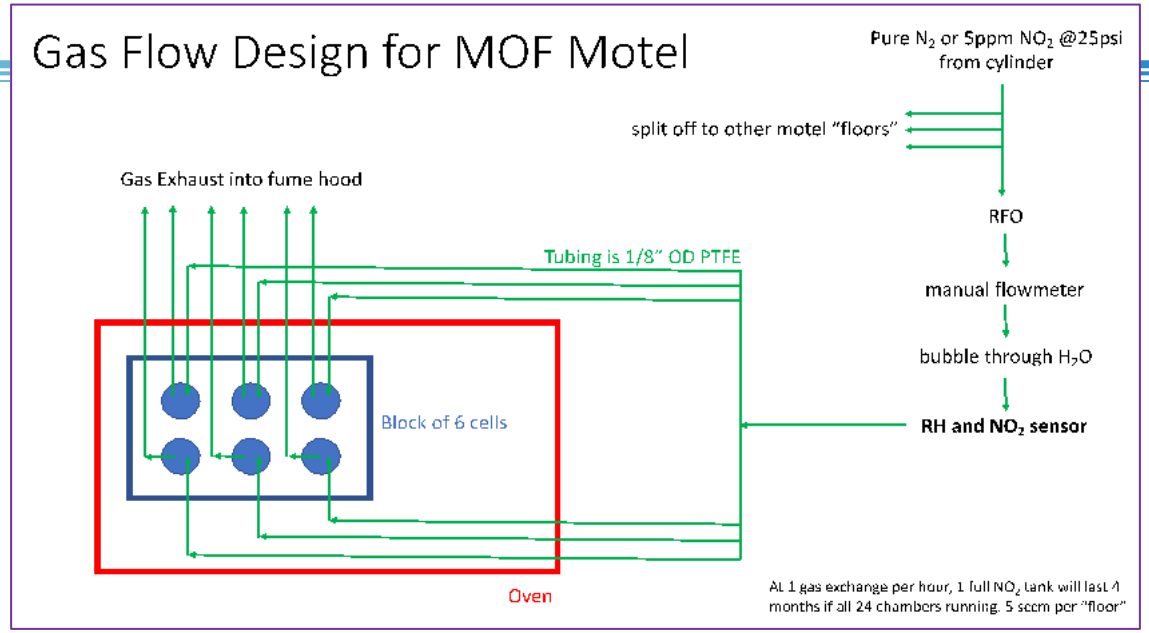
- Custom- built NO_x exposure chamber enabled Zeolite, MOF activation and subsequent in situ electrical testing under varying NO_2 concentrations without exposure to lab atmospheres
- Variable NO_2 concentrations (0.5 -5 ppm) were achieved by diluting 5 ppm NO_2 gas stream with pure UHP N_2 at 500 sccm total gas flow
- Impedance spectra recorded at 0 V DC and 100 mV (RMS) AC over 1 MHz - 10 mHz
- All electrical measurements and NO_2 exposures occurred at 50°C



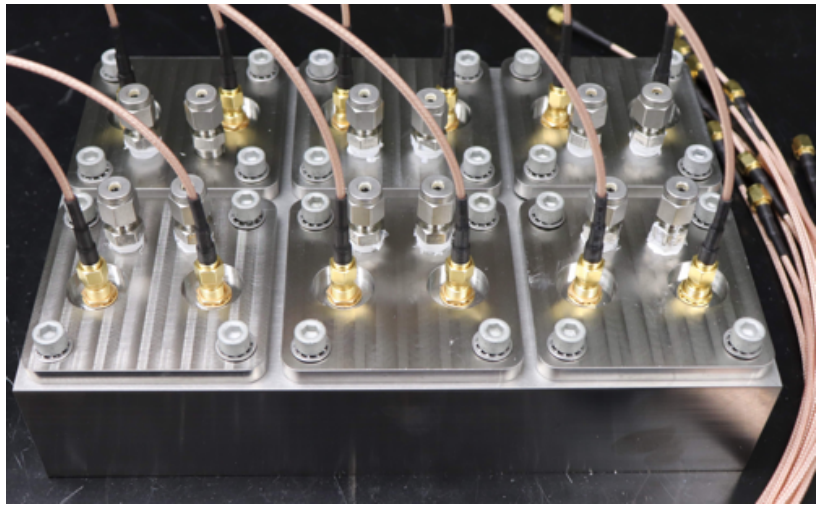


Custom Test Fixtures for Multiple & Simultaneous Long-Term Exp and Electrical Testing





- Custom designed test fixtures ('MOF Motel') for long-term exposures and in-situ electrical testing of sensors
- 24 test cells, each cell 70 mL
- Humidity/NO_x levels controlled in each chamber with constant temperature across entire test fixture



Percival, S.J., et.al., *I&ECR* **2022,** submitted.

RE-DOBDC MOF:
Conclusions, Highlights and Future Research

UNCAGE ME

We have successfully established

Structural stability of Sandia RE-DOBDC MOFs to NO_x & SO_x acid gas and humidity, RE: Y, Eu, Tb, Yb

The ability to retain the coordination geometry (cluster) across of series of rare earth elements

This control of the building block is rare in MOFs in a series

Use of modeling and experiment confirmed Fluorine incorporation into RE-DOBDC, RE-UiO66, and RE-TCPB MOFS

Use of modulator in crystallization reaction is the source, *2-fluorobenzoic acid (2-fba)*

No anticipated affects on binding preference to the metal by various acid gases, due to shielding of the F by the metals

Application use established for industrial and automotive caustic gas detectors, highly tunable and selective for gases of interest even with competing air gases

Future / On-going Research:

Accelerate Materials Discovery: Design next generation caustic gas stable adsorbents (MOFs and Zeolites) from DFT/AIMD modeling predictions with associated synthesis, characterization and testing

Transitioning into the computational design and synthesis of porous liquids and carbons for enhanced greenhouse gas selectivity

Best Team!

SNL Postdocs, Interns/students, Technologist and Young Staff*

Strong Advocate for Mentoring and Supporting Young People throughout their Careers

Postdocs


Matthew Hurlock, postdoc 1874

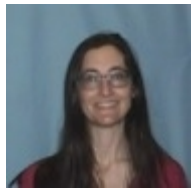

Matthew Christian Postdoc 8915

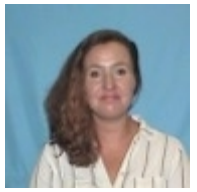

D. Jon Vogel Staff SNL1864


Dorina Sava Gallis Staff SNL 1874


Koroush Sasan Staff LLNL


Z. Mark Zhang Dept. of Interior


Summer Ferreira, Manager SNL 8812


Susan Henkelis, LTE SNL 5228

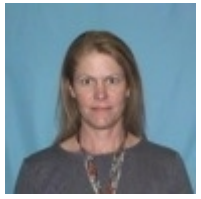

Marie Parkes, LTE SNL 8915 Consultant


Nathan Ockwig 3M Corp.


Jason Pless, Johnson Matthey


Mutlu Kartin, Staff SNL 8367, Prof. Dominican Univ


Andrea Ambrosini, Staff SNL 8923


Margaret Gordon, Manager SNL 8923


May Nyman, Staff SNL 8915 Prof. Oregon State

Postdocs, not shown
Genoveva Buelna, ACS
François Bonhomme, CNRS
Ranko Bontchev, Cabot

Interns, not shown:
Alejandra Chavez, Dow Chemical
Sarah Moore, Chevron
Sera Mirchandani, AECOM

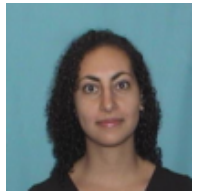
Interns


Haylie Lobeck NNSA FPM NA-192 Office of Tritium and Domestic U Enrichment

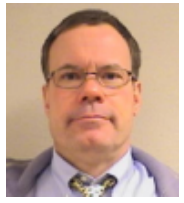

Jackie Unangst General Atomics


Melissa Teague Staff SNL1832 (On leave)


Jesse Stanchfield Intel Corp


Sylvia Hanna NNSA Graduate Research Fellow (SNL 1874) Northwestern Univ.

Technologist


David Rademacher DNTG 1874

Young Staff FY19-23*


Remi Dingreville SNL1881


Mara Schindelholz SNL 2491


Stephen Percival SNL 1816


Leo Small SNL 1874


Jessica Rimsza SNL 8915

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Acknowledgements

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This work was supported as part of the Center for Understanding and Control of Acid Gas-Induced Evolution of Materials for Energy (*UNCAGE-ME*), an Energy Frontier Research Center, funded by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES) under Award DE-SC0012577.

Sandia National Labs:
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Matt Christian (pd)
Susan Henkelis (pd)
Matthew Hurlock (pd)
Dorina Sava Gallis
Grace Vincent (undergrad)
Kennedy Block (HS intern)
Mark Rodriguez
Nichole Valdez
Dale Huber (CINT/SNL)
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Univ AL:
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Zachary Lee (grad student)

GA Tech:
Krista Walton
Ian Walton (pd)
Ryan Lively
Chunyi Li (grad student)
Stephen Dewitt (grad student)

Stonybrook University:
Karena Chapman

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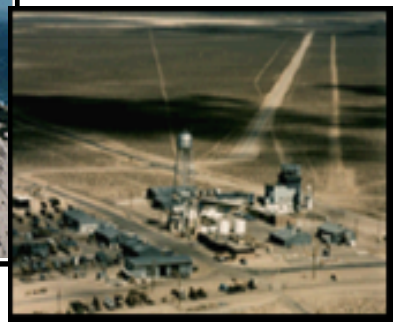
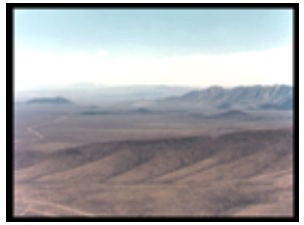


Tonopah Test
Range, Nevada



Yucca Mountain,
Nevada

WIPP,
New Mexico

Pantex, Texas

Questions? / Thank you

UNCAGE-ME
SNL Team,
Sandia Peak
(10,679'),
NM. 2019

UNCAGE-ME
SNL Team, *IZC*,
Valencia, Spain
2022

Extra Slides

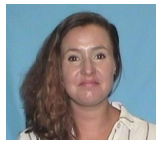
IV. Use of DOBDC – based MOFs as direct electrical readout sensors


Leo Small

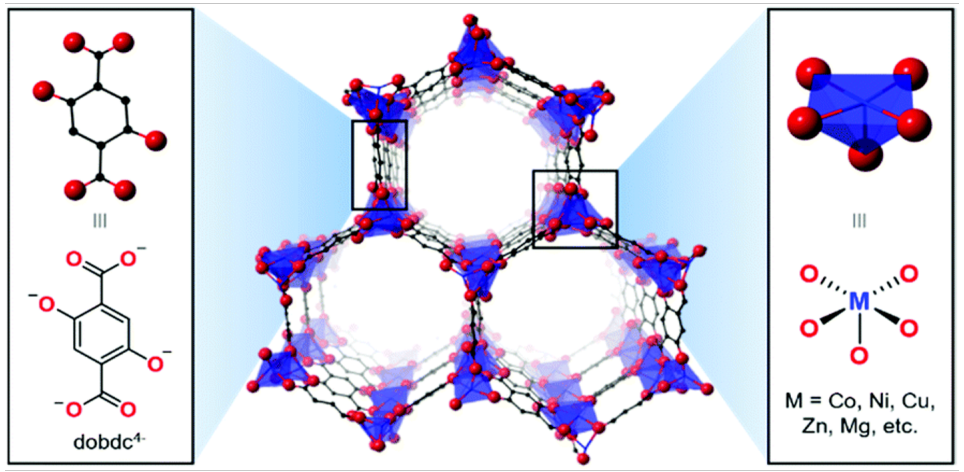

Mara Schindelholz


Stephen Percival


Matthew Hurlock

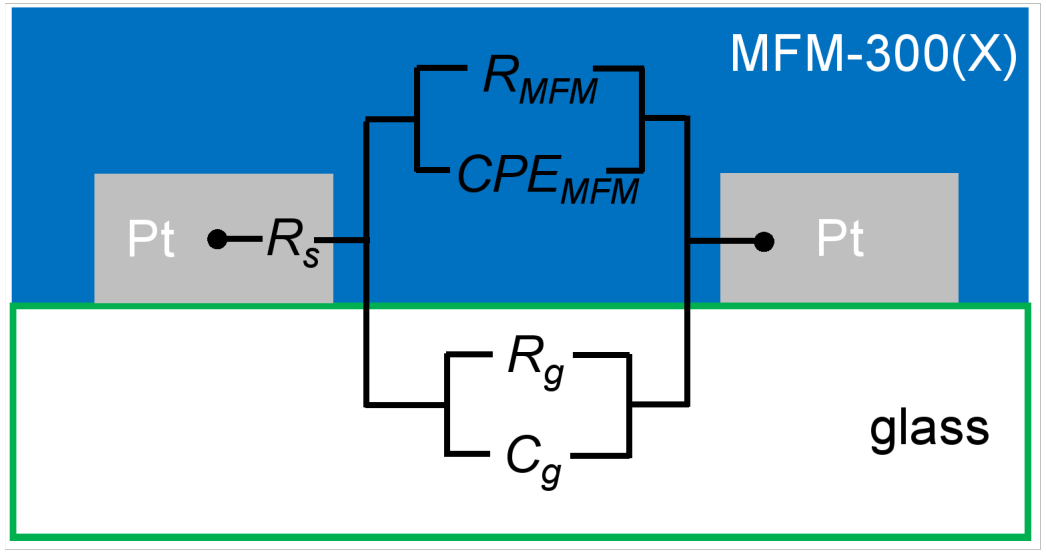

Susan Henkelis

We have successfully used DOBDC based highly tuned gas sensors, useful in complex gas streams



One example:
M-MOF-74; M = Ni, Co, Mg

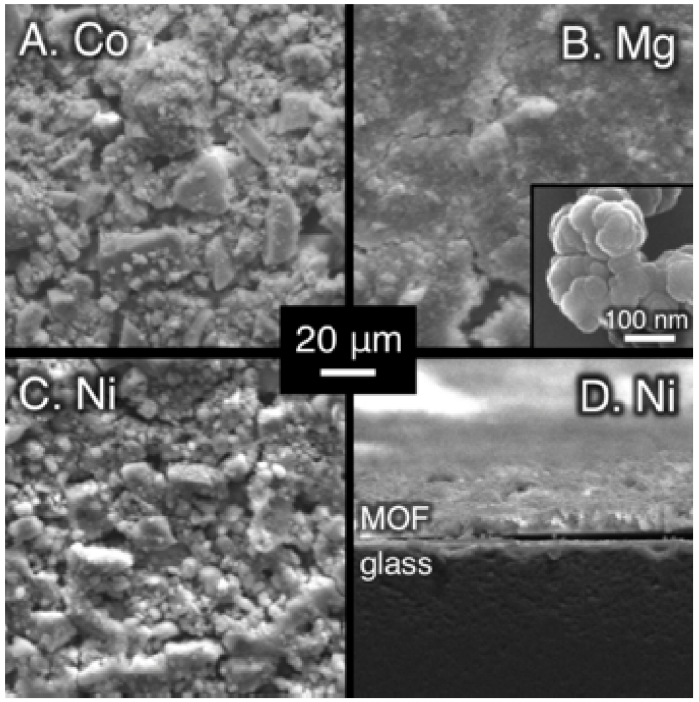
Gas binding inside the MOF and charge transfer enables the sensor response



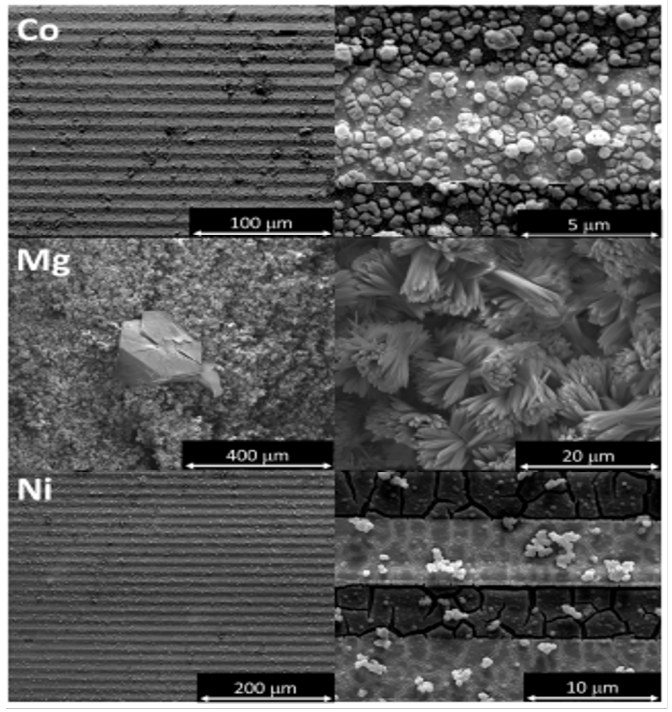
MOFs provide the selectivity to the target gas to be detected

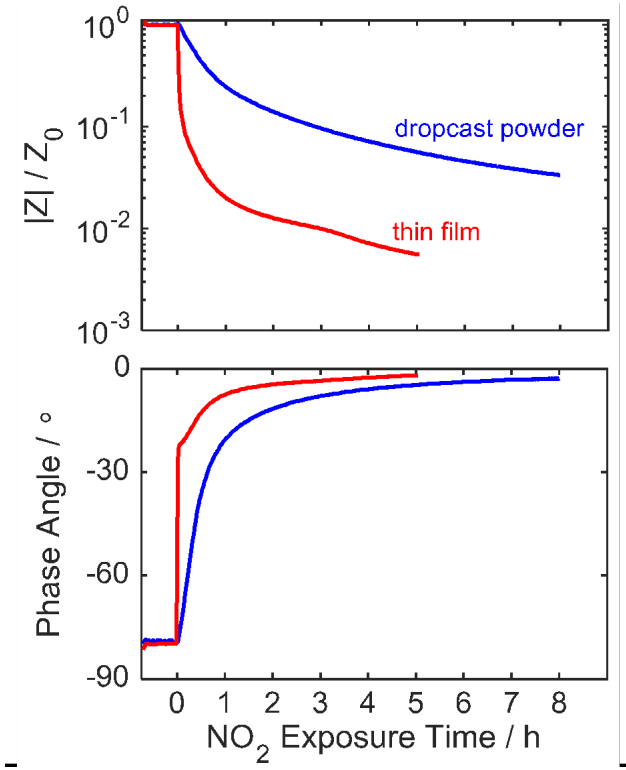
Judicious choice of MOF or Zeolite for gas of interest. Thin film fabricated on interdigitated electrode (IDE).
M-MOF-74 membranes fabricated by two methods:

(1) Dropcasting solutions



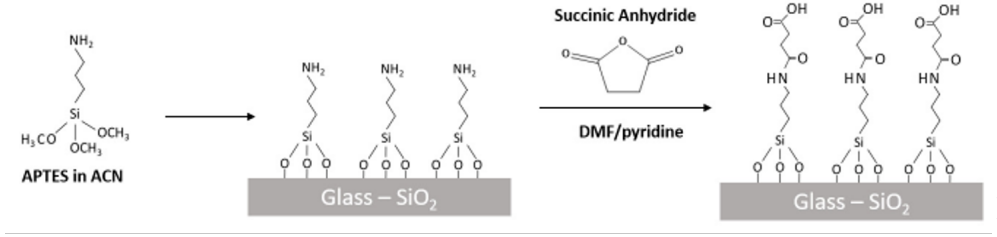
(2) Surface crystallization





MOF/IDE direct electrical Impedance response of drop cast MOF film (blue) vs. crystallized thin film (red) MOF.

Faster kinetics and response from the thinner thin film version.

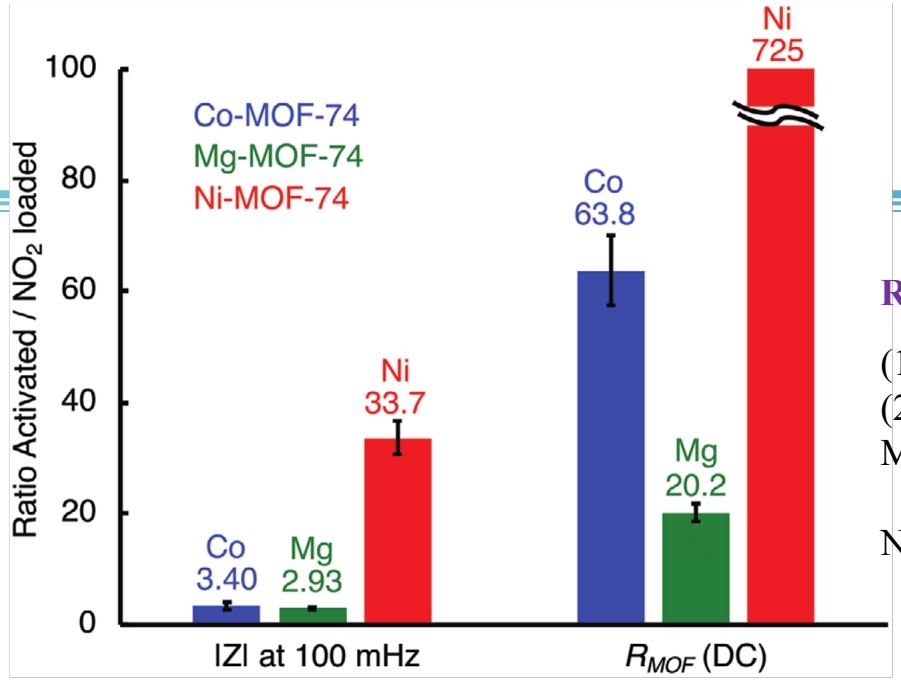


Henkelis, et.al, *Membranes*, **2021,** *11*, 176.

NO_2 Selective M-MOF based Sensor

Small, L.J.; et.al., *Adv. Func. Mater*. **2020**, *1407*, 2006598.
Henkelis, S.E., et.al., *Membranes* **2021**, *11*, 176.
Small, L.J. et.al., *I&ECR* **2021**, *60*, 21, 7998
Percival, S.J., et.al., *I&ECR* **2022,** submitted.

Small changes in MOF lead to very large electrical response changes in the sensor

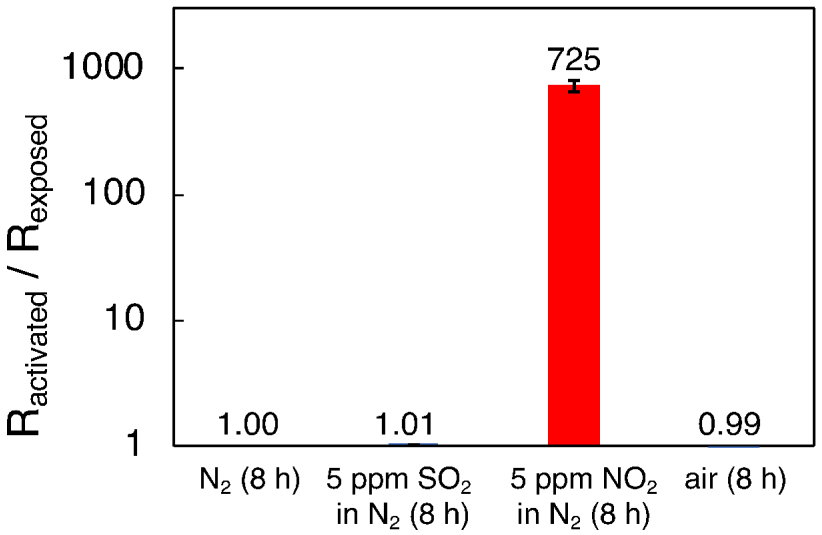


Ratio of response from activated to NO_2-exposed:

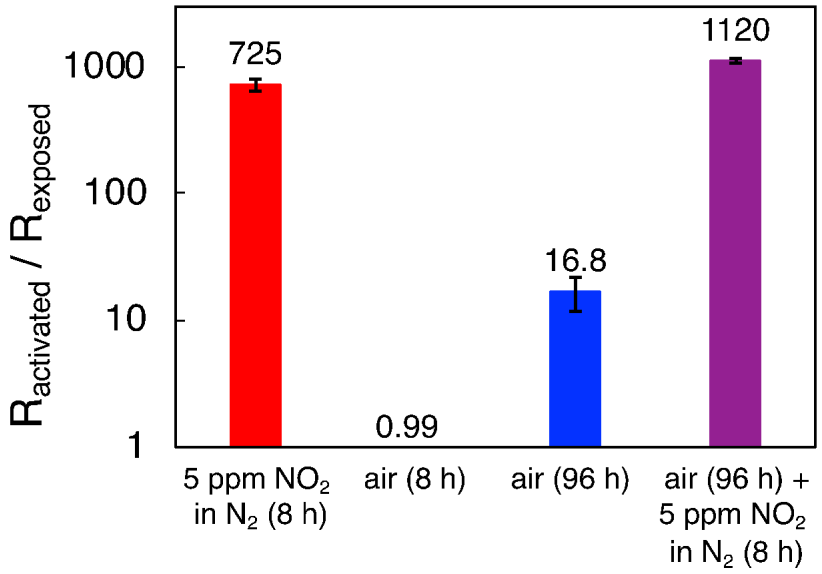
(1) impedance magnitude at 100 mHz, and
(2) MOF DC film resistance for IDEs coated with M-MOF-74 (M = Co, Mg, Ni).

NO_2 exposure was at 5 ppm NO_2 for 8h at 50 °C.

A. Ni-MOF-74



B. Ni-MOF-74



Ratio of Ni-MOF-74 resistance (R_{MOF}) when exposed to different environments at 50°C

• highly selective response towards NO_2. (A) 8 h exposures and (B) comparison of response of extended air-exposure combined with subsequent NO_2 exposure.

• "Air" is ambient atmosphere (25 °C 50% RH, 400 ppm CO_2, 21% O_2), then heated to 50 °C.

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Sandia's research focus areas are: bioscience, computing and information science, engineering science, materials science, nanodevices and microsystems, radiation effects and high energy density physics, and geosciences.

The Truman Fellowship is a three-year appointment. The salary is $111,200 plus benefits and research funding for the proposal.

The deadline is November 1 of each year and normally begins on October 1 the following year.

Requirements:
Candidates must meet the following requirements:

- Ph.D. awarded within the past three years at the time of application or completed Ph.D. requirements; with strong academic achievement and evidence of exceptional technical accomplishment, leadership, and ability to team effectively

- Candidates must be seeking their first national laboratory appointment (no previous postdoc at a national laboratory)

- Ability to obtain a DOE "Q" clearance, which requires US citizenship

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