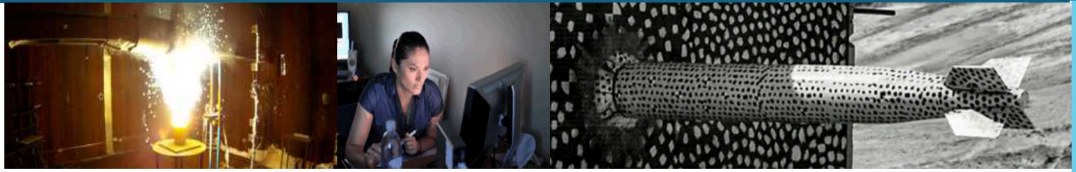
SAND2019-9844C

Acid Gas Adsorption and Structural Characterization of RE-DOBDC MOFs via Density Functional Theory



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Sandia National Laboratories, Albuquerque NM USA

ACS Fall 2019
San Diego CA USA

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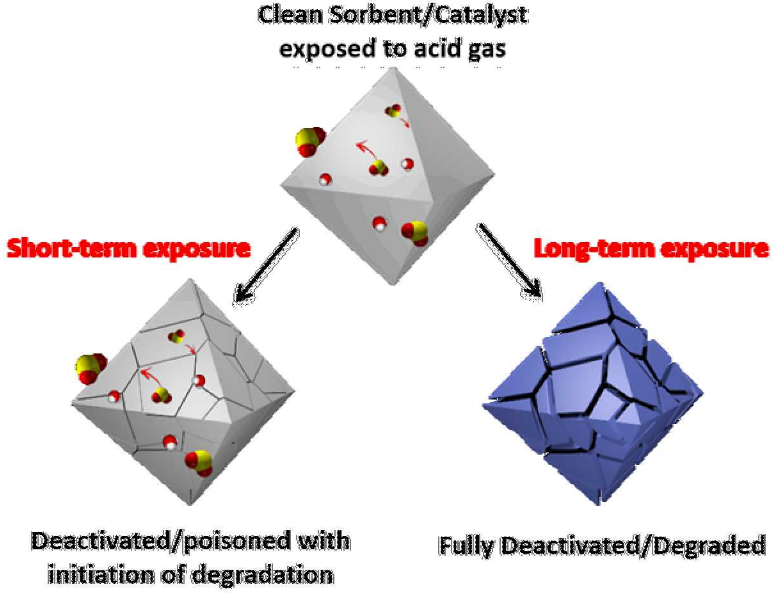
UNCAGE-ME

Mission

The mission of the Energy Frontier Research Center is to develop a deep knowledge base in the characterization, prediction, and control of acid-gas interactions with a broad class of materials to accelerate materials discovery for large-scale energy applications.



Rare Earth – MOFs, Acid Gas Durability

Rare earth elements have been shown to preferentially bind to acid gases:

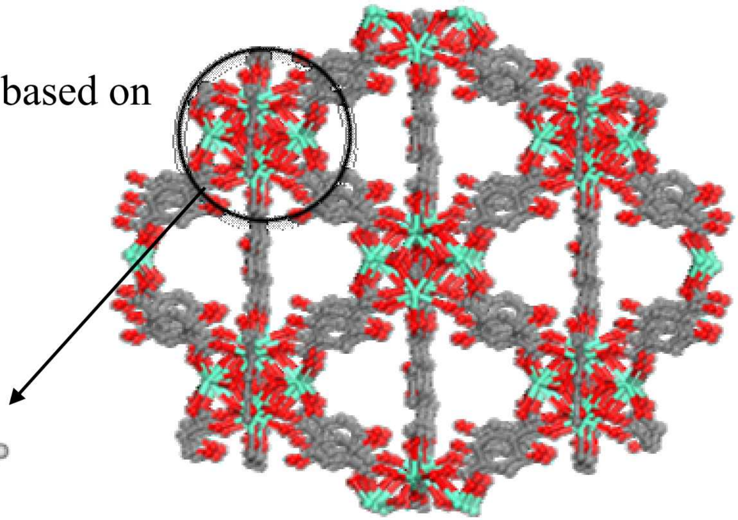
Optimization of binding to framework but not too strong as to be destructive

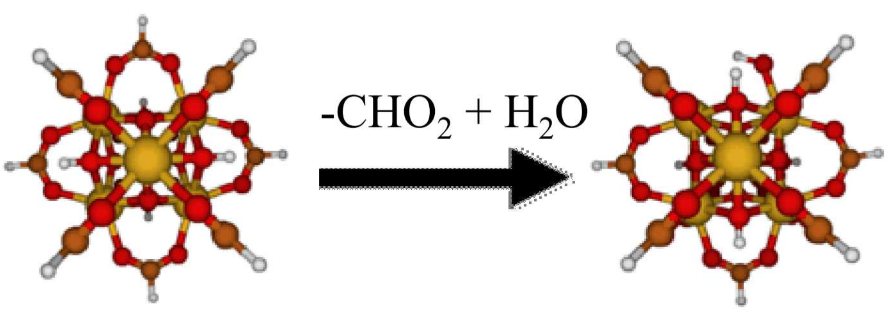
- Lanthanide oxygen-sulfur catalysts (Kay et.al, US Patent 5,213,779 (1993))
- Metal organic coordination polymers with $Tb3^{+}$ have a strong affinity and coordination binding to H_2S (Anal. Chem, 2013, 85,22,11020)
- Europium has high selectivity for hydrogen sulfide (Dalton Trans., 2016, 45, 928)

Leveraging off our group's work on RE-DOBDC: platform based on building block, akin to prototypical Zr-Hexanuclear cluster

Resultant **RE-DOBDC MOFs**

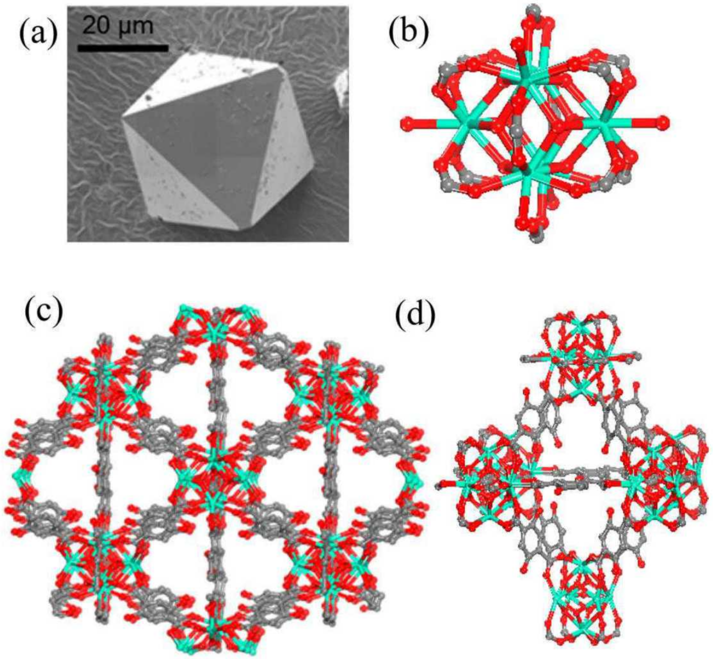
- Octahedral cages of ~14Å diameter
- Accessible via triangular windows of ~5.5Å





Sava Gallis, et.al., *J. Phys. Chem. C* **2018**,
From Zr UiO-66 structure data:
Trickett et al. *Angew. Chem. Int. Ed.* **2015**
Ling and Slater *Chem. Sci.* **2016**

Material Structure of Currently Synthesized Rare Earth MOFs



RE-DOBDC MOF

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

RE = Y, Eu, Tb, Yb

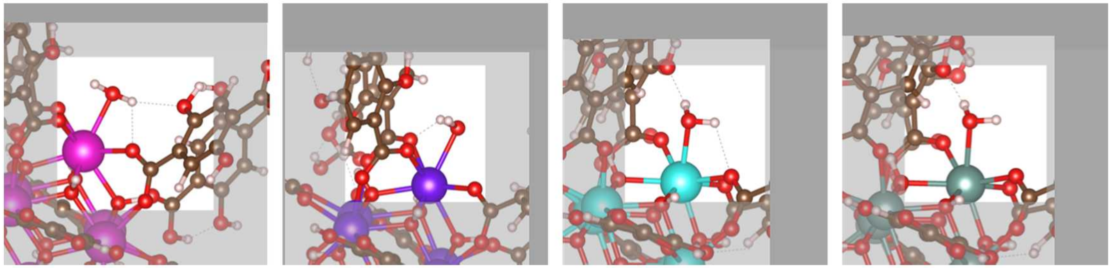
DOBDC = 2,5-dioxido-1,4-benzenedicarboxylate

Sava Gallis et al. *ACS Appl. Mater. Interfaces* ***2017***
Sava Gallis *et al. CrystEngComm* ***2018***

Why do we want to investigate Rare Earth MOFs?

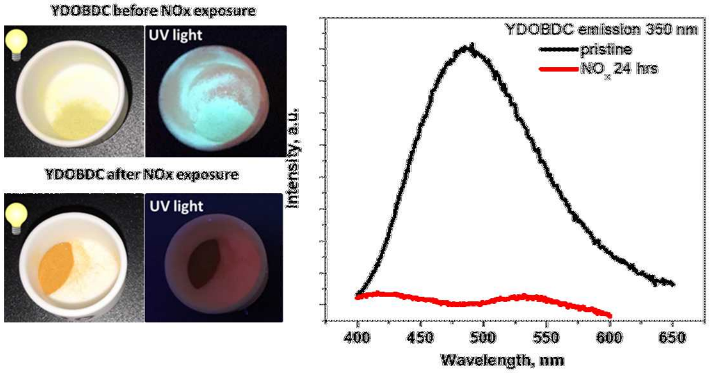
Gas Adsorption:

- Controlled coordination allowing synthesis of isostructural materials to probe metal-guest (NO_x, SO_x) energetics
- Structural advantages: formation of mesoporous RE-MOFs through ligand extensions, multiple coordination environments in one structure

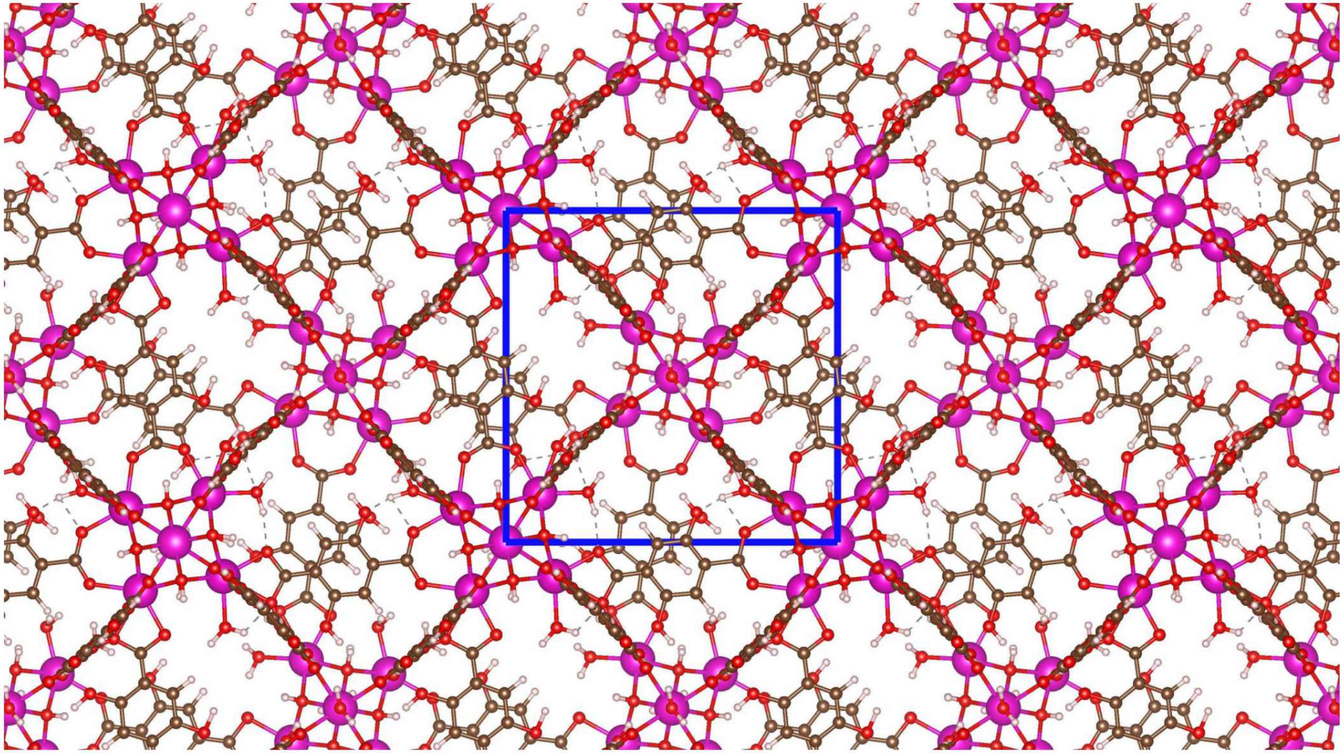


Sensing:

- Luminesce from 4f-4f and 4f-5d transitions or ligand to metal charge transfer (LMCT) or metal-ligand charge transfer (MLCT)



Computational Set-Up



Unit Cell[1] = $RE_{12}(\mu_3\text{-}OH)_{16}(C_8O_6H_4)_8(C_8O_6H_5)_4$ + 12 H_2O RE = Y, Eu, Tb, Yb

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

Geometric Structures: Spin-restricted with large core potential (LCPs)
Binding Energies: Spin unrestricted DFT with LCPs
Electronic Structure: Spin-unrestricted DFT with full 4f Valence Potential + U*

Sava Gallis *et al. ACS Appl. Mater. Interfaces* ***2017***; Harvey *et al. J. Phys. Chem. C* ***2018***

Optimized Lattice Parameters and Pair Distribution Function

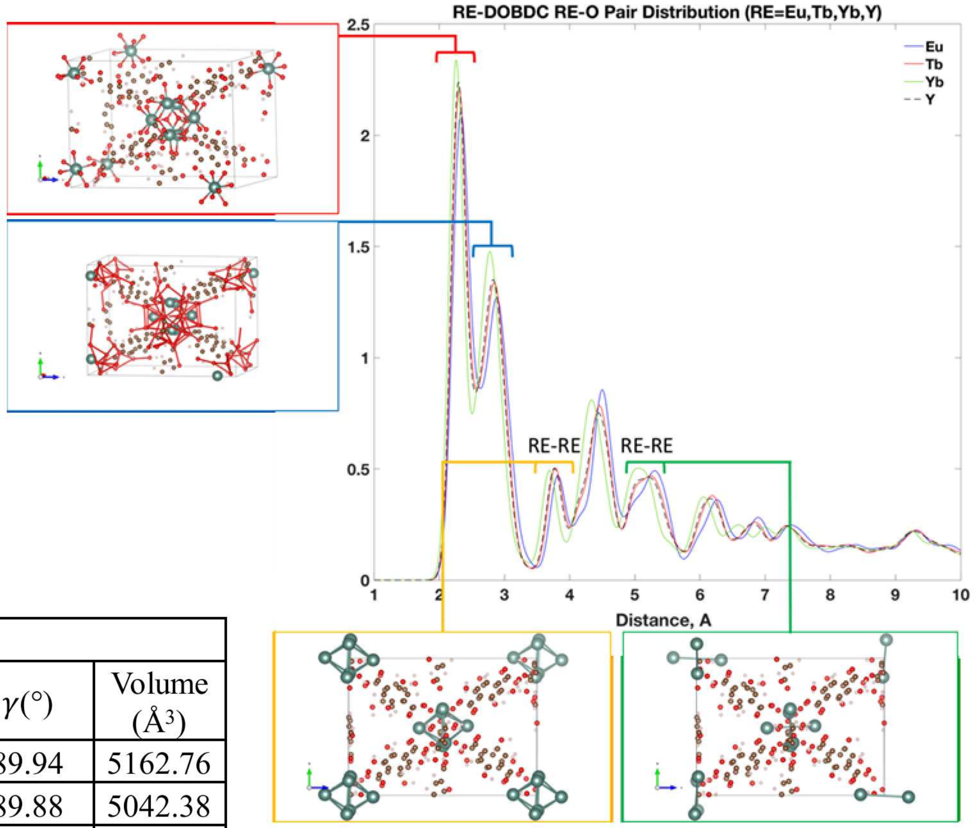
Primary Peaks of Interest are RE-O and RE-RE

Consistent peak shifts due to lanthanide contraction

Experimental peaks:

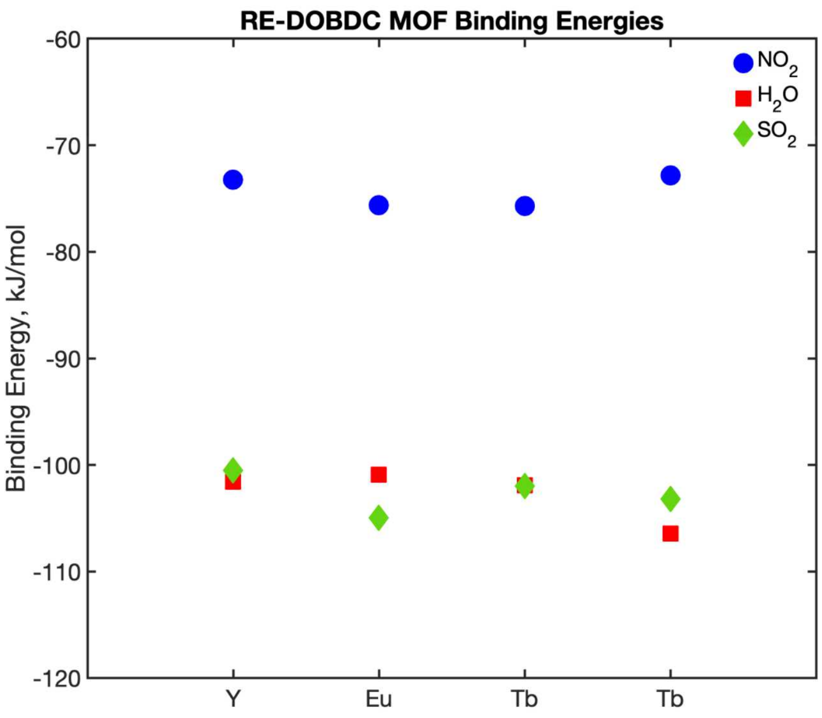
- RE-O: ~2.5 A
- RE-RE: ~4 A

Lattice parameters shift from tetragonal symmetry is due to flexible organic structures.



RE	Lattice Parameters						
	a (Å)	b (Å)	c (Å)	α(°)	β(°)	γ(°)	Volume (Å^3)
Eu	15.55	15.63	21.24	90.03	89.96	89.94	5162.76
Tb	15.44	15.46	21.12	89.97	89.92	89.88	5042.38
Yb	15.26	15.31	20.85	89.95	89.96	89.95	4870.09
Y	15.40	15.41	21.06	89.96	89.89	89.88	4997.20

Calculated Gas Adsorption Binding Energies

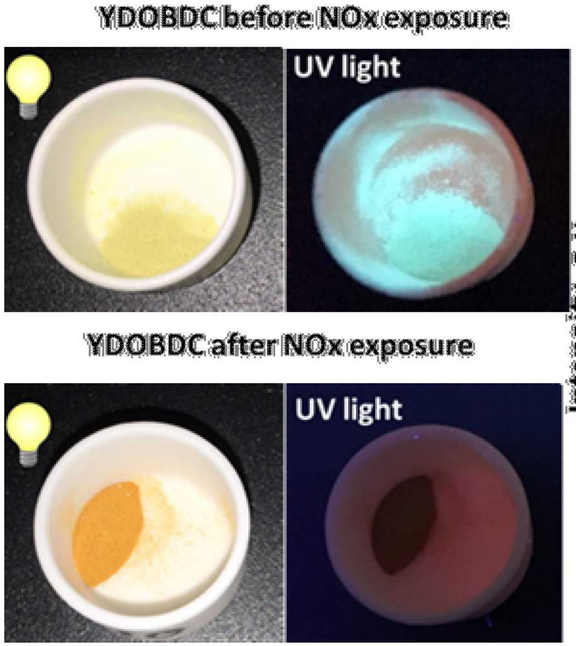


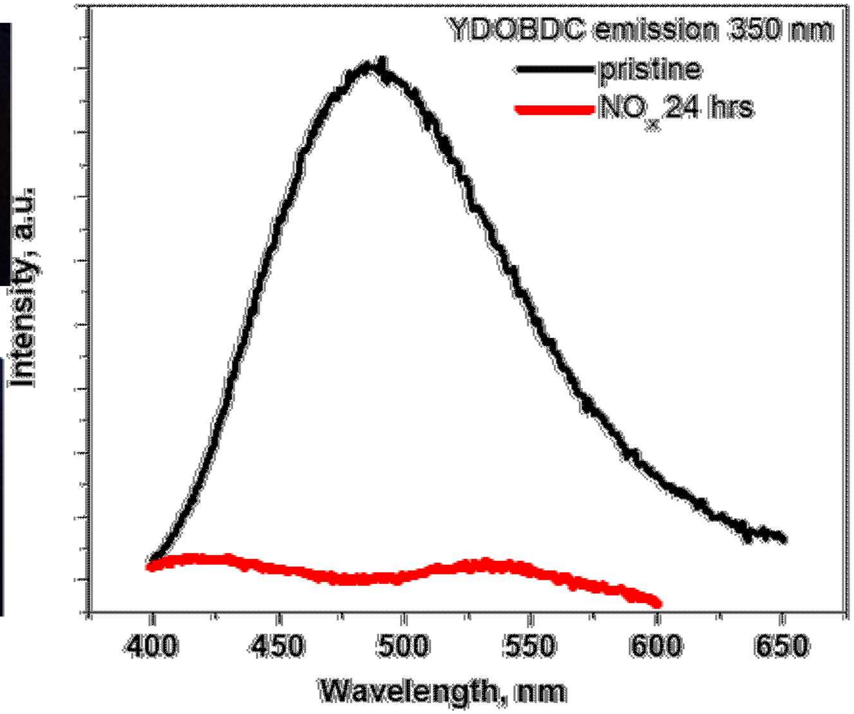
- Three different gases considered: H_2O, NO_2, SO_2 (one molecule at a time)
- Similar strong preference for H_2O and SO_2
- Different selectivity for H_2O v. NO_2
  NOx not as strongly bound, possible preferential ad-/desorption material
- Metal center of MOF may play an added role in gas adsorption strength

$$E_{Binding} = E_{MOF+Gas} - E_{MOF} - E_{Gas}$$

Gas Interaction Energy (kJ/mol)				
	Rare Earth Element			
	Y	Eu	Tb	Yb
H_2O	-101.59	-100.91	-101.90	-106.45
NO_2	-73.23	-75.64	-75.69	-72.82
SO_2	-100.50	-104.95	-101.98	-103.20

Luminescence following H_2O and NO_2 exposure

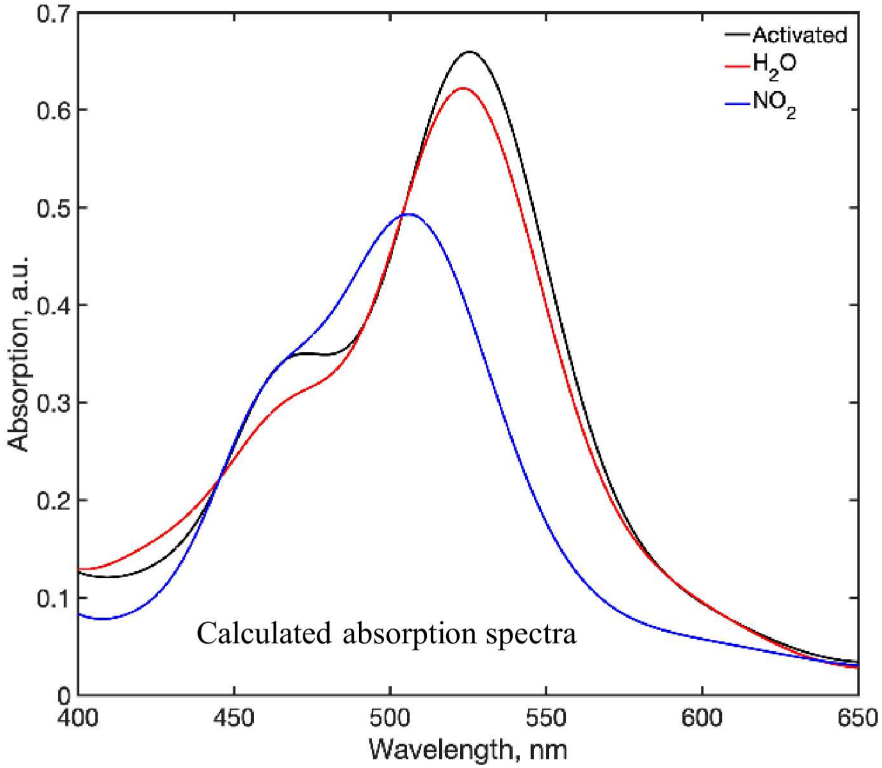




Experimental Methods:

- NO_x stream (~ 50 ppm, RH 60%) generated in an adsorption chamber at room temperature
- Gas concentration was monitored with NOx and H_2O/humidity sensors
- PL emission and excitation spectra of powder samples were collected by monitoring at the peak of the emission and scanning over UV-visible wavelengths (320-550 nm).

Adsorption of Y-DOBDC with H_2O and NO_2

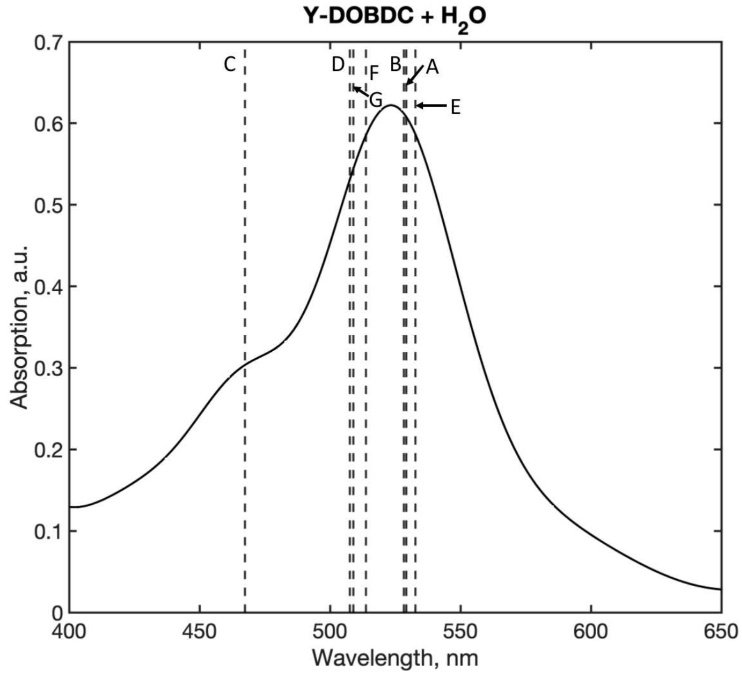


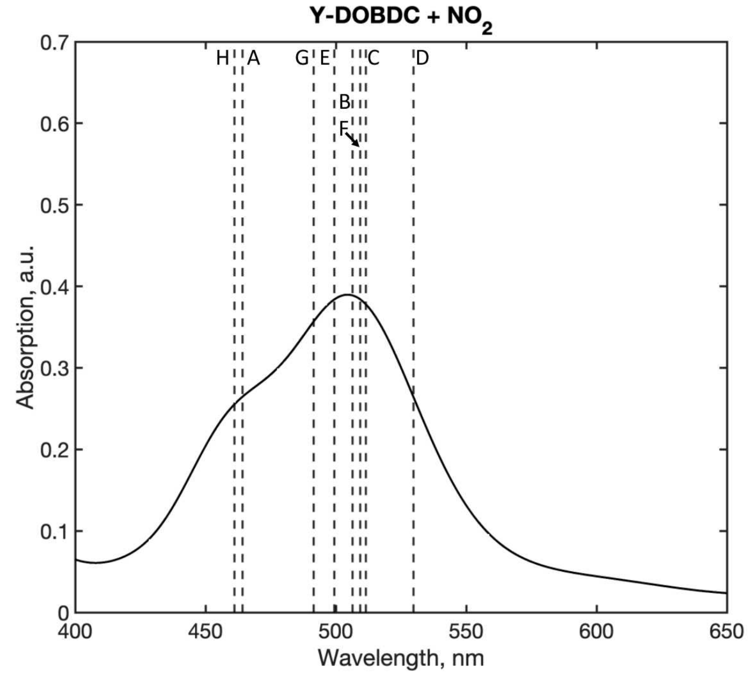
Transition Dipole: $\vec{D}_{\sigma,ij} = e \int \varphi_{\sigma,i}^{KS^*} \vec{r}\, \varphi_{\sigma,j}^{KS} d\vec{r}$

Oscillator Strength: $f_{\sigma,ij} = \left|\vec{D}_{\sigma,ij}\right|^2 \frac{4\pi m_e v_{\sigma,ij}}{3\hbar e^2}$

Absorption: $a_\sigma = \sum_{\sigma,ij} f_{\sigma,ij} \delta(\varepsilon - \Delta\varepsilon_{\sigma,ij})$

- Experimental PL spectra indicates that the primary emission energy range is between 400-650 nm -> transitions within the organic DOBDC linkers
- Calculated absorption shows good qualitative agreement for the Y-DOBDC systems, due to distribution of transitions between 400-650 nm



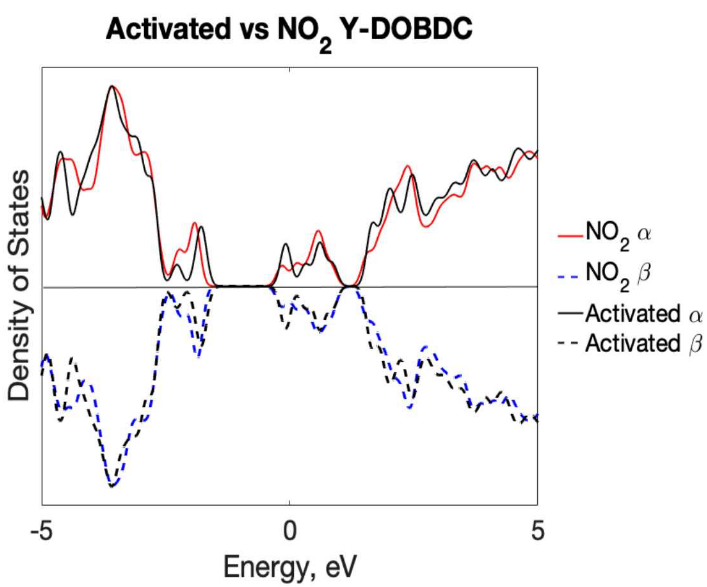


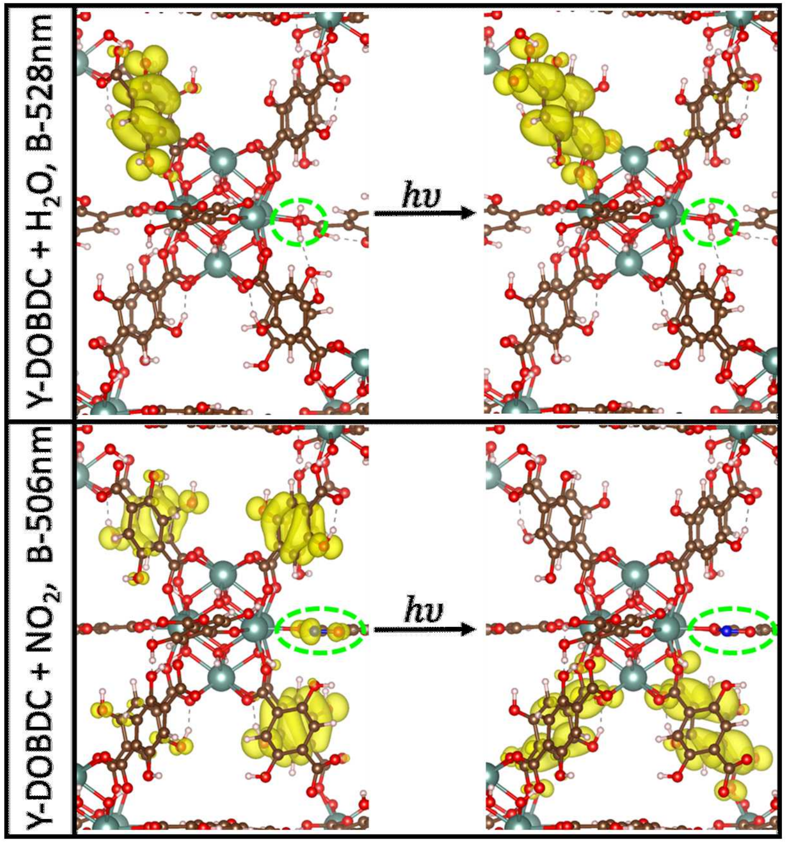
Change in adsorption with NO_2 is due to additional transitions at 460 nm

Y-DOBDC + H_2O			Y-DOBDC + NO_2		
Transition Label	f_{ij}	ω_{ij}(nm)	Transition Label	f_{ij}	ω_{ij}(nm)
A	13.93	529	A	11.22	461
B	10.06	528	B	10.69	506
C	5.98	467	C	10.23	511
D	5.29	507	D	5.48	530
E	3.80	532		5.25	304
F	3.59	513	E	4.94	499
	2.54	325	F	3.80	509
G	2.40	509	G	3.49	491
	2.22	346		3.19	299
	2.21	292	H	3.01	464

Transition States in Y-DOBDC with Adsorbed H_2O or NO_2

- Energy states from the NO_2 molecule are within the energy range of the DOBDC transition states.
- NO_2 adsorption introduces unoccupied states at the valence band edge of the Y-DOBDC system with new low energy transitions





Molecule	Primary Peak	Secondary Peak
NO_2	502 nm	461 nm
H_2O	520 nm	467 nm

Conclusions

Density functional theory calculations are used to design improved MOFs for acid gas adsorption and separation.

For RE-DOBDC (RE=Y, Eu, Tb, Yb) gas adsorption is preferential for SO_2 > H_2O > NO_2, where SO_2 and H_2O are very competitive.

Adsorption of gas molecules, provide unique electronic structures allowing new electronic relaxation pathways to exist.

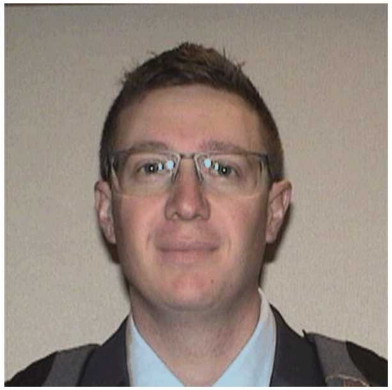
Adsorption of NO_2 in Y-DOBDC induces a reduced PL intensity.

Calculated DOS with NO_2 adsorbed show new unoccupied states in the valence band and a redistribution of state energies at the band edges.

Acknowledgements

Team Members

D. Jon Vogel



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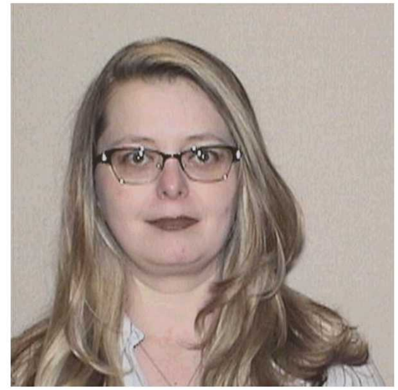

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The work was supported as part of UNCAGE-ME, an Energy Frontier Research Center Funded by the U.S. Department of Energy, Office of Science. This paper describes objective technical results and analysis. under Award #DE-SC0012577. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.