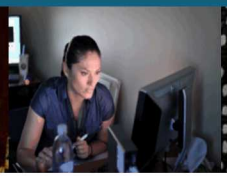
SAND2019-8359C

Rare Earth MOFs for Acid Gas Separation and Sensing



Jon Vogel

Nanomaterials: Computation, Theory, and Experiment

Telluride, CO

July 18, 2019

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.

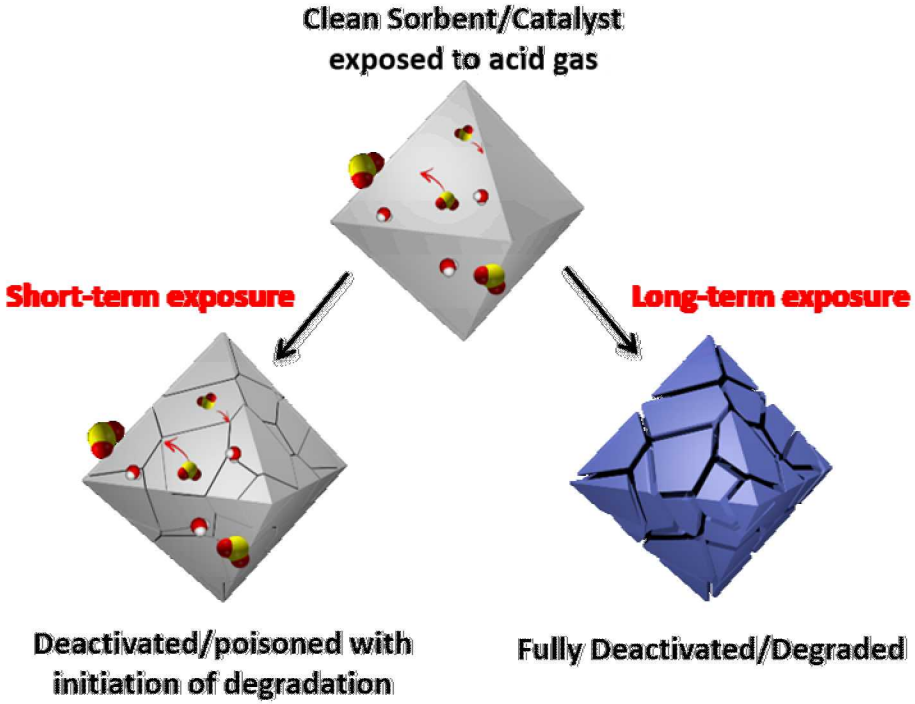
Energy Frontier Research Center: UNCAGE-ME

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.

Website: efrc.gatech.edu



Outline

Motivation

Calculating Accurate Structural Geometries

Eu-DOBDC Electronic Structure Comparisons

Applications and Physical Properties

- Organic flexibility
- Gas Adsorption

Conclusions

Applications and Desire to Design new MOFs

Highly modified materials, unlimited to creativity.

Applications in catalysis, gas separation, gas storage, sensing, gas adsorption.

Similar framework material ZIFs.

Can these materials be applied to acid gas removal and maintain their crystallinity

- Discuss efrc work on zifs – stability but only for homogeneous gas

Why do we want to investigate Rare Earth MOFs?

Rare Earth MOFs

- RE-MOFs are attractive due to related coordination geometry that can be controlled, 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
  - Electronic advantages: luminesce from 4f-4f and 4f-5d transitions or ligand to metal charge transfer (LMCT) or metal-ligand charge transfer (MLCT)

Current Work

- Structures: RE-DOBDC, RE=Eu,Tb,Yb,Y
- Applications: degradation properties of RE-DOBDC in acid gas streams (SO_2, NO_2), changing luminescence properties after acid gas adsorption
- Predict properties of un-synthesized RE-DOBDC MOFs

Previous Applications of RE-DODBC MOFs

CrystEngComm

COMMUNICATION

Biocompatible MOFs with high absolute quantum yield for bioimaging in the second near infrared window†

Check for updates

Cite this: *CrystEngComm*, 2018, 20, 5919

Received 31st May 2018,
Accepted 23rd July 2018

DOI: 10.1039/c8ce00909k

Dorina F. Sava Gallis,*[a] Kimberly S. Butler,[b] Lauren E. S. Rohwer,[c] Amber A. McBride,[b] Grace Vincent,[a] Casey V. Chong,[a] Charles J. Pearce[a] and Ting S. Luk[d]

ACS APPLIED MATERIALS & INTERFACES

Research Article

www.acsami.org

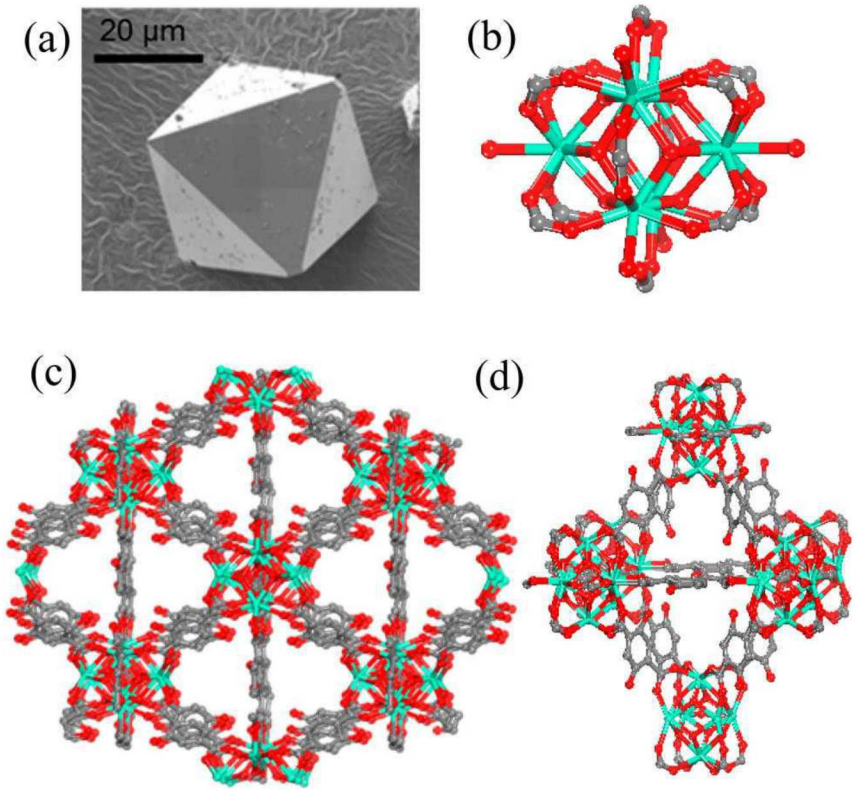
Multifunctional, Tunable Metal–Organic Framework Materials Platform for Bioimaging Applications

Dorina F. Sava Gallis,*[†] Lauren E. S. Rohwer,[§] Mark A. Rodriguez,[‡] Meghan C. Barnhart-Dailey,[⊥] Kimberly S. Butler,[#] Ting S. Luk,[∥] Jerilyn A. Timlin,[⊥] and Karena W. Chapman[▽]

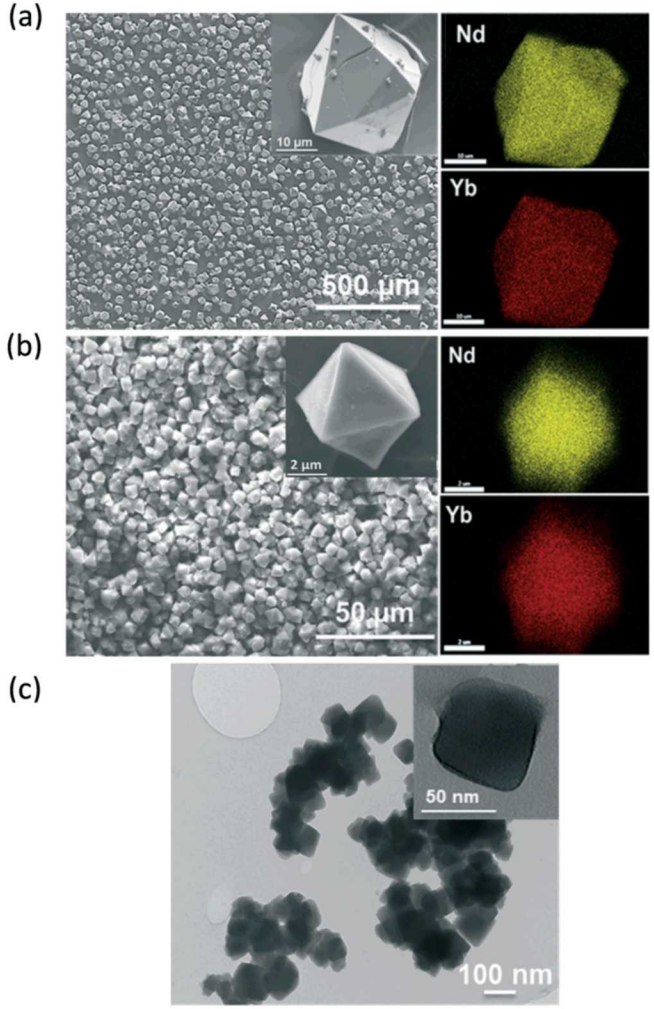
[†]Nanoscale Sciences Department, [§]Microsystems Integration Department, [‡]Materials Characterization and Performance Department, [∥]Nanostructure Physics Department, [⊥]Bioenergy and Defense Technology Department, and [#]Nanobiology Department, Sandia National Laboratories, Albuquerque, New Mexico 87185, United States

[▽]X-ray Science Division, Advanced Photon Source, X-ray Science Division, Argonne National Laboratory, Argonne, Illinois 60439, United States

Material Structure of Currently Synthesized Rare Earth MOFs



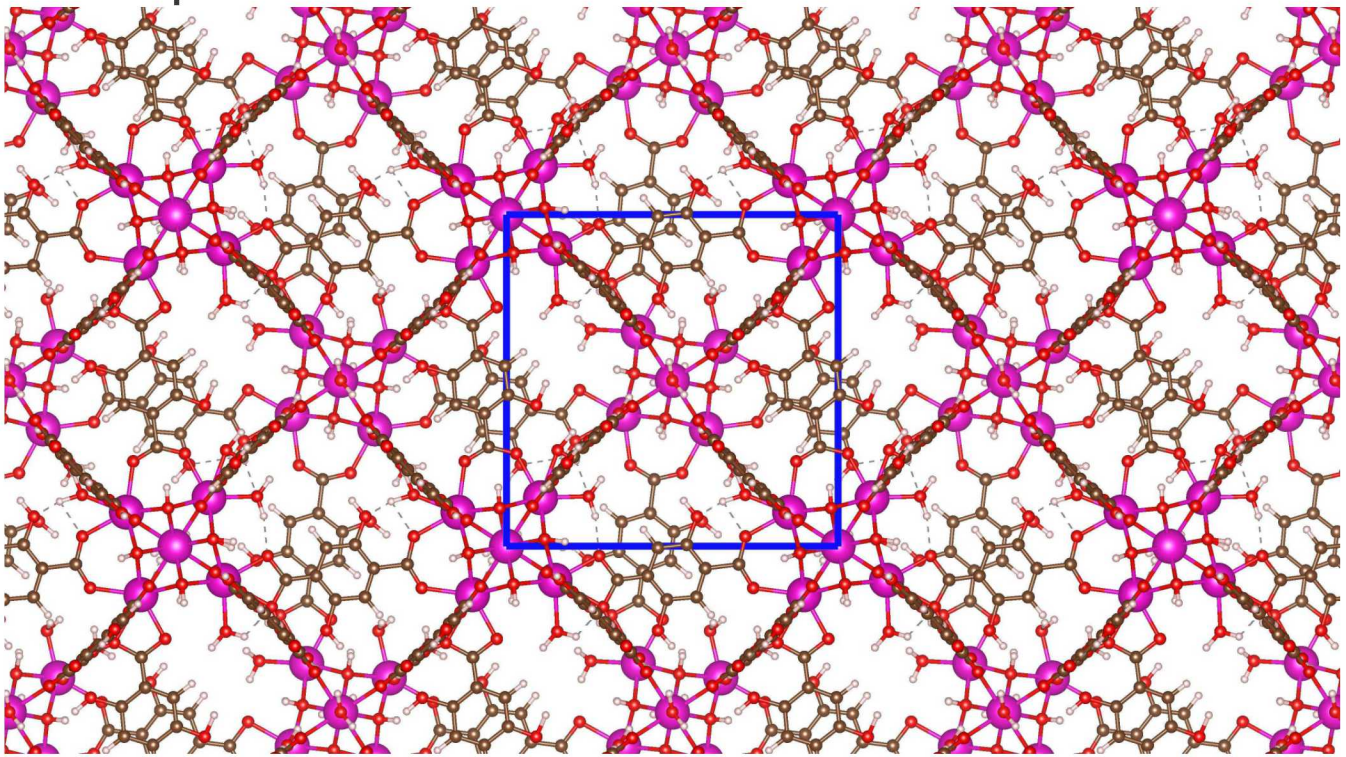
RE-DOBDC (RE=Y, Eu, Tb, Yb, Nd)
DOBDC = 2,5-dihyroxyterephthalic acid



Sava Gallis *et al. ACS Appl. Mater. Interfaces* ***2017*** *(Left)*
Sava Gallis *et al. CrystEngComm* ***2018*** *(Right)*

U.S. DEPARTMENT OF ENERGY | Office of Science | OAK RIDGE National Laboratory | THE UNIVERSITY OF ALABAMA | PENNSTATE | Washington University in St. Louis | Georgia Institute of Technology | Sandia National Laboratories | LEHIGH UNIVERSITY | WISCONSIN | UNCAGE ME

Structural Optimization Procedure



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

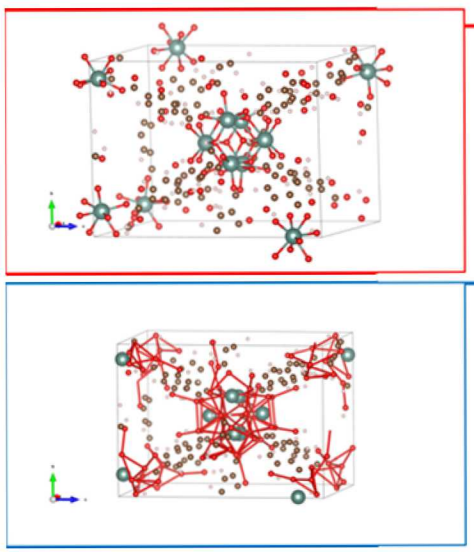
Procedure[2]:

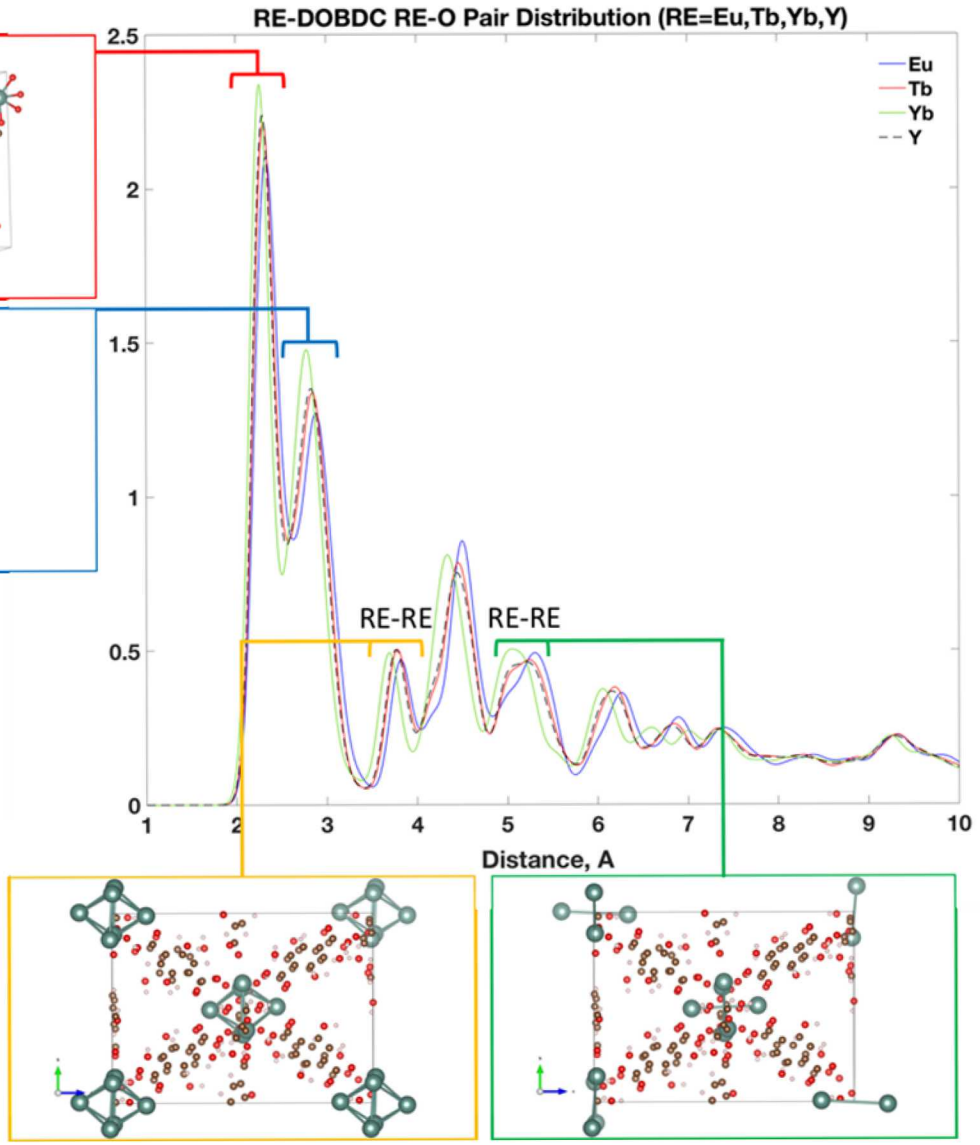
1) Optimization of atomic positions
2) Optimize atomic positions and unit cell parameters
3) Re-optimization of atomic positions

Vienna *ab initio* Simulation Package
PBEsol exchange correlation functional
DFT-D3 used for vdW interactions
Gamma point calculation
Spin-restricted with large core potential (LCPs)

[1]Sava Gallis *et al. ACS Appl. Mater. Interfaces* ***2017***; [2]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 are ~2.5 A
  RE-RE are ~4 A

[1]Sava Gallis *et al. ACS Appl. Mater. Interfaces* **2017**

U.S. DEPARTMENT OF ENERGY | Office of Science
OAK RIDGE National Laboratory
THE UNIVERSITY OF ALABAMA
PENNSTATE
Washington University in St. Louis
UNCAGE ME
Georgia Institute of Technology
Sandia National Laboratories
LEHIGH UNIVERSITY
WISCONSIN

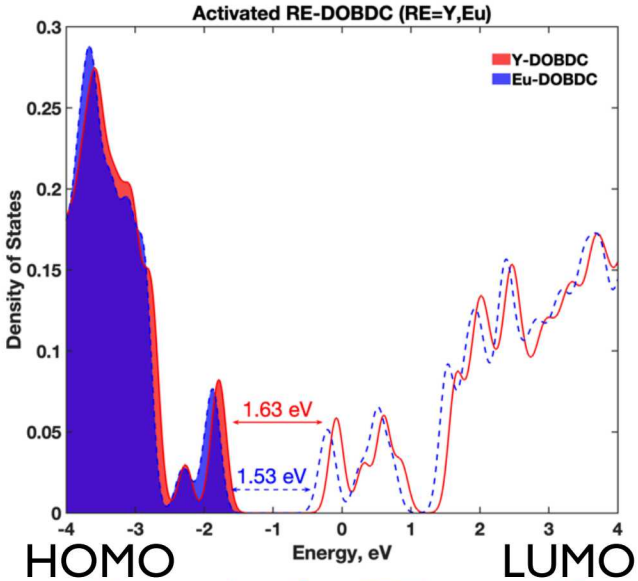
Optimized Lattice Parameters and Pair Distribution Function

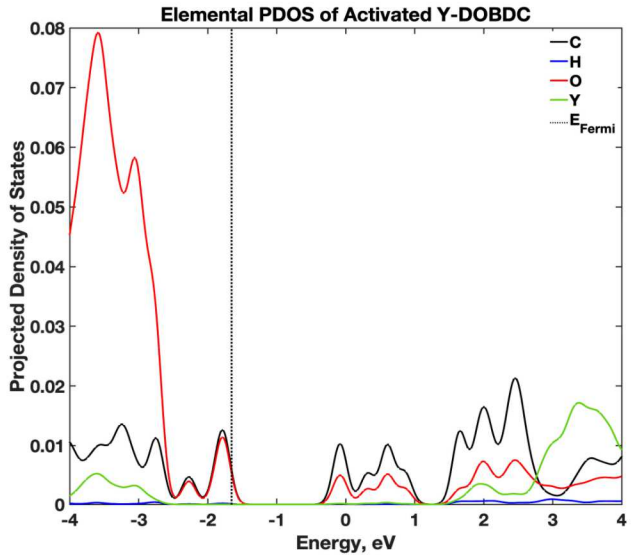
	Element	Lattice Parameters (Å)			Volume (Å^3)	Average Distance (Å) (std. dev.)		
		a	b	c		RE-RE	RE-O DOBDC	RE-O μ_3-OH
PBEsol	Yb	15.16	15.20	20.87	4804	3.74 (0.043)	2.32 (0.064)	2.28 (0.072)
	Y	15.40	15.51	21.10	5040	3.83 (0.044)	2.36 (0.061)	2.33 (0.058)
	Tb	15.47	15.57	21.17	5100	3.86 (0.039)	2.39 (0.063)	2.35 (0.056)
	Eu	15.53	15.61	21.31	5167	3.91 (0.036)	2.41 (0.067)	2.38 (0.053)
Experiment[1]	Eu	15.56	15.56	21.33	5163	3.98 (0.040)	2.40 (0.019)	2.38 (0.025)

Calculated geometry of Eu-DOBDC with large core potential match with single crystal structure.

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

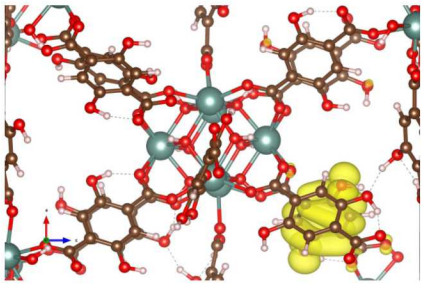
Electronic Structure of Y-DOBDC vs LCP Eu –DOBDC Baseline

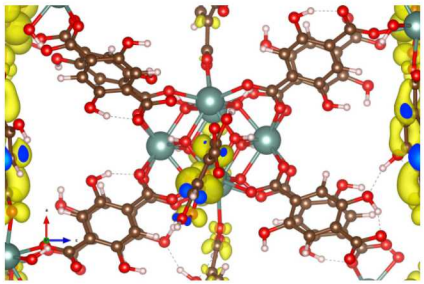




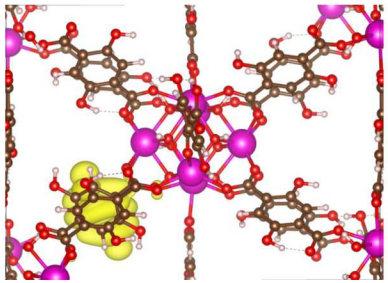
HOMO LUMO

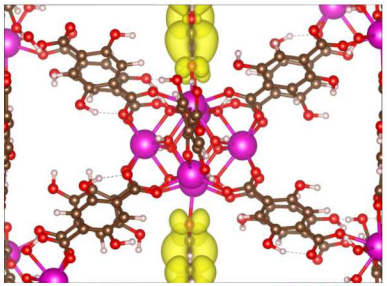
Y

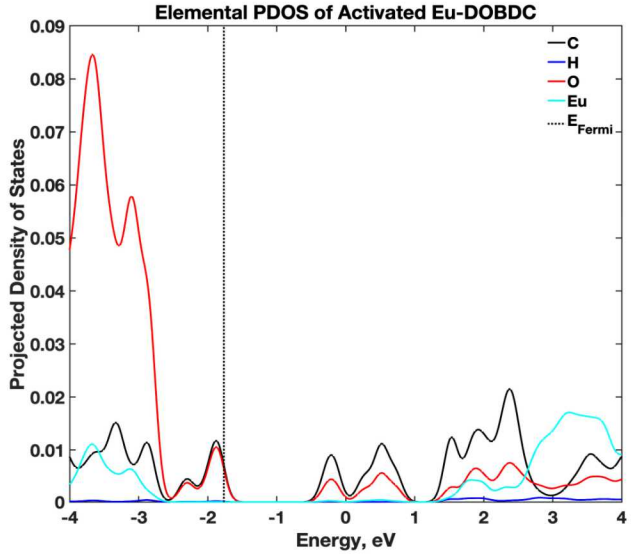




Eu

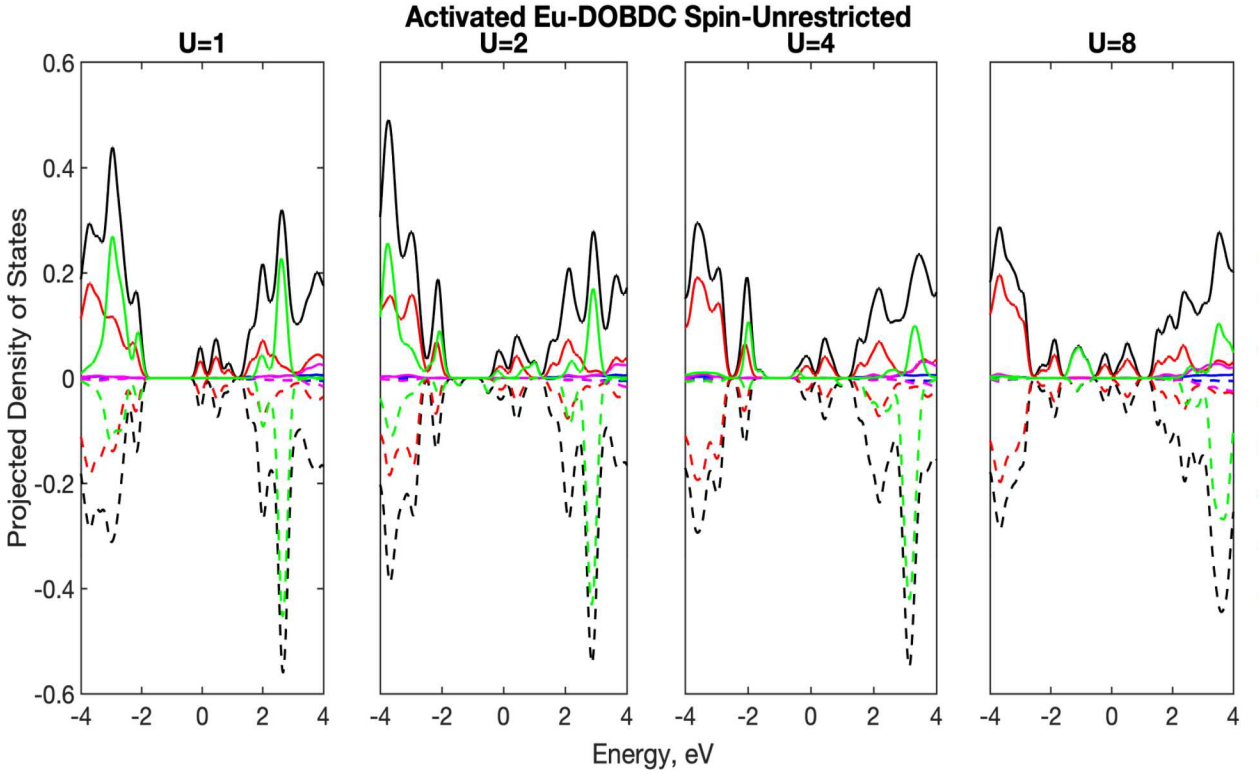




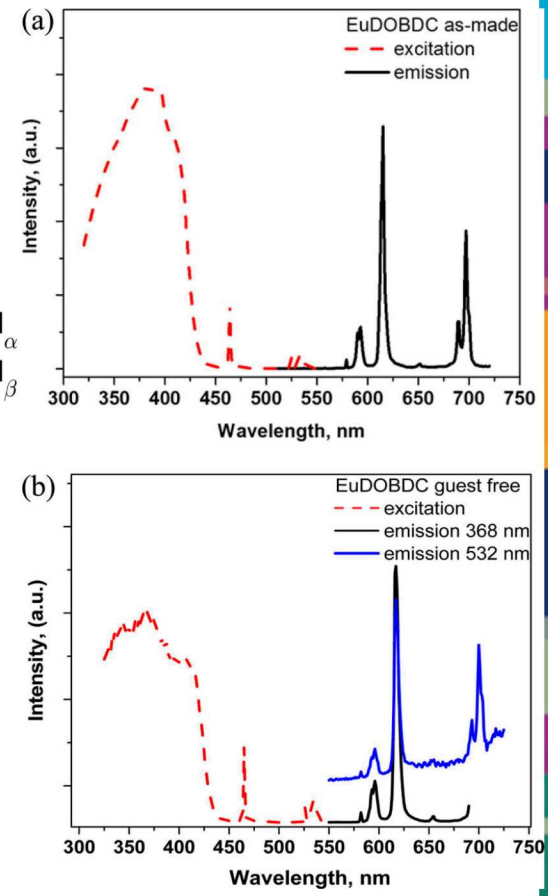


Spin-unrestricted DFT with Full 4f Valence Potential + U in Eu-DOBDC

Hubbard U	1	2	4	8
Total Energy (eV)	-1914.78	-1967.26	-1965.76	-1965.15
E_g α (eV)	2.0988	1.755	1.1797	0.4347
E_g β (eV)	1.9533	0.9206	1.7829	0.5683
Fermi Energy (eV)	-2.1582	-2.1234	-2.0421	-1.7099
Eu 4f Occupation	6.37-6.44	6.28-6.39	6.18 – 6.31	6.15-6.18
Total Magnetization	25.5196	28.2635	46.1043	35.9996



Experimental PL[1]



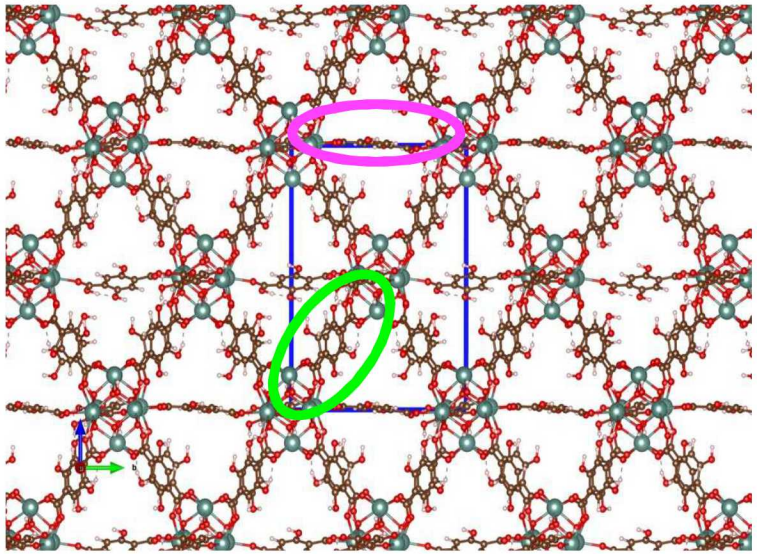
[1]Sava Gallis *et al. ACS Appl. Mater. Interfaces* ***2017***

Slide 12

VD1 Vogel, Dayton, 7/12/2019

Applications and Physical Properties

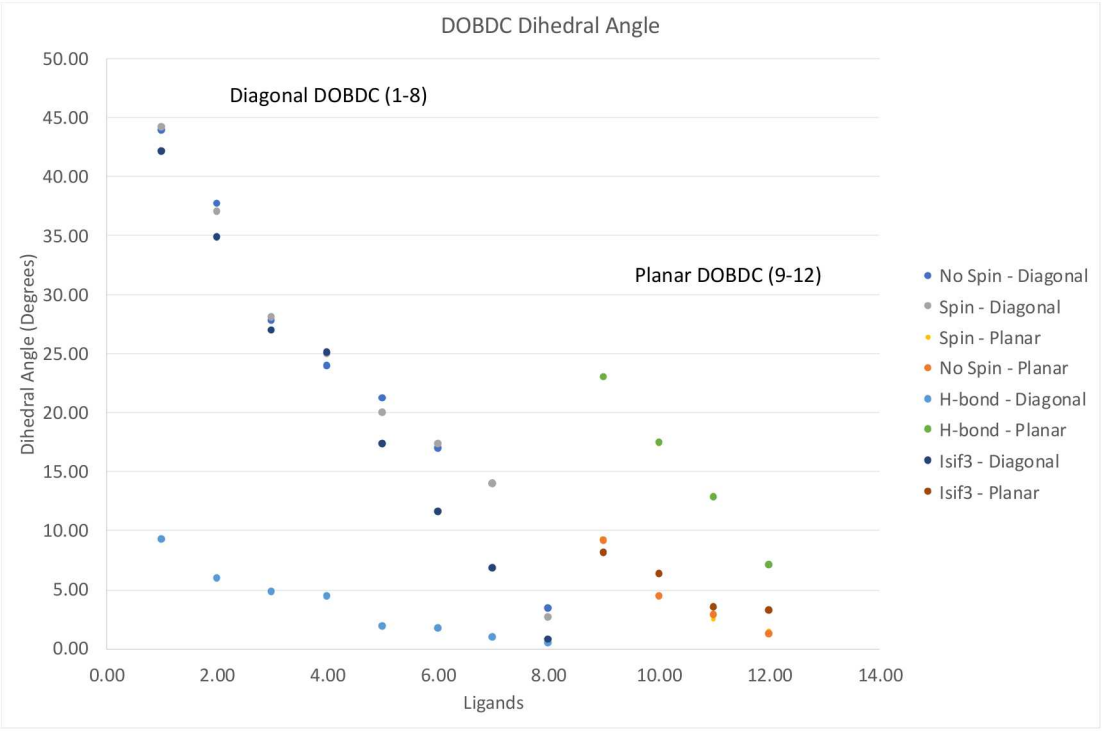
Organic Linker Flexibility



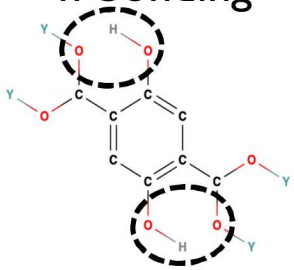
Diagonal | Planar | Unit Cell

Bidentate | Monodentate

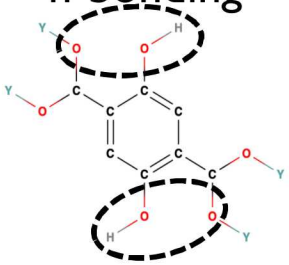
Eu-DOBDC



DOBDC max. h-bonding



DOBDC min. h-bonding

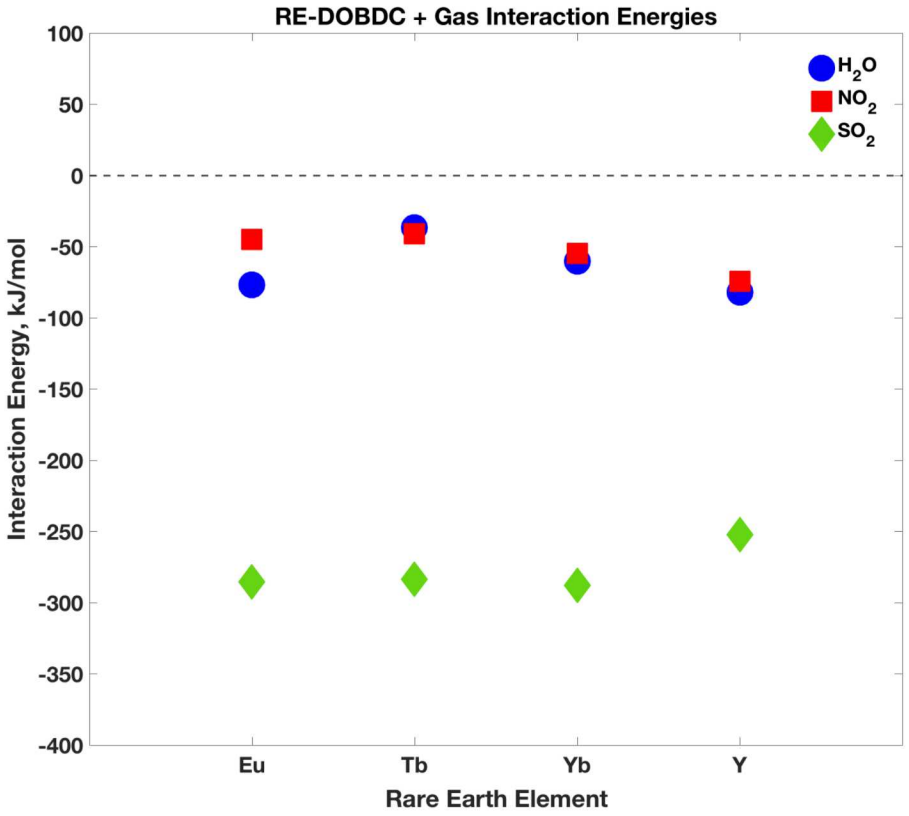


	Lattice Parameters (Å)			Volume (Å^3)	H-Bonds (No.)	Total Energy (eV)	Band Gap (eV)
	a	b	c				
Eu-DOBDC	15.57	15.49	21.10	5090	28	-1938.89	1.08
	15.02	15.06	21.61	4889	5	-1931.49	1.99
	15.56	15.32	21.25	5064	10	-1932.46	1.41
	15.50	15.49	20.83	4999	13	-1935.26	1.13
Experiment	15.56	15.56	21.33	5163			

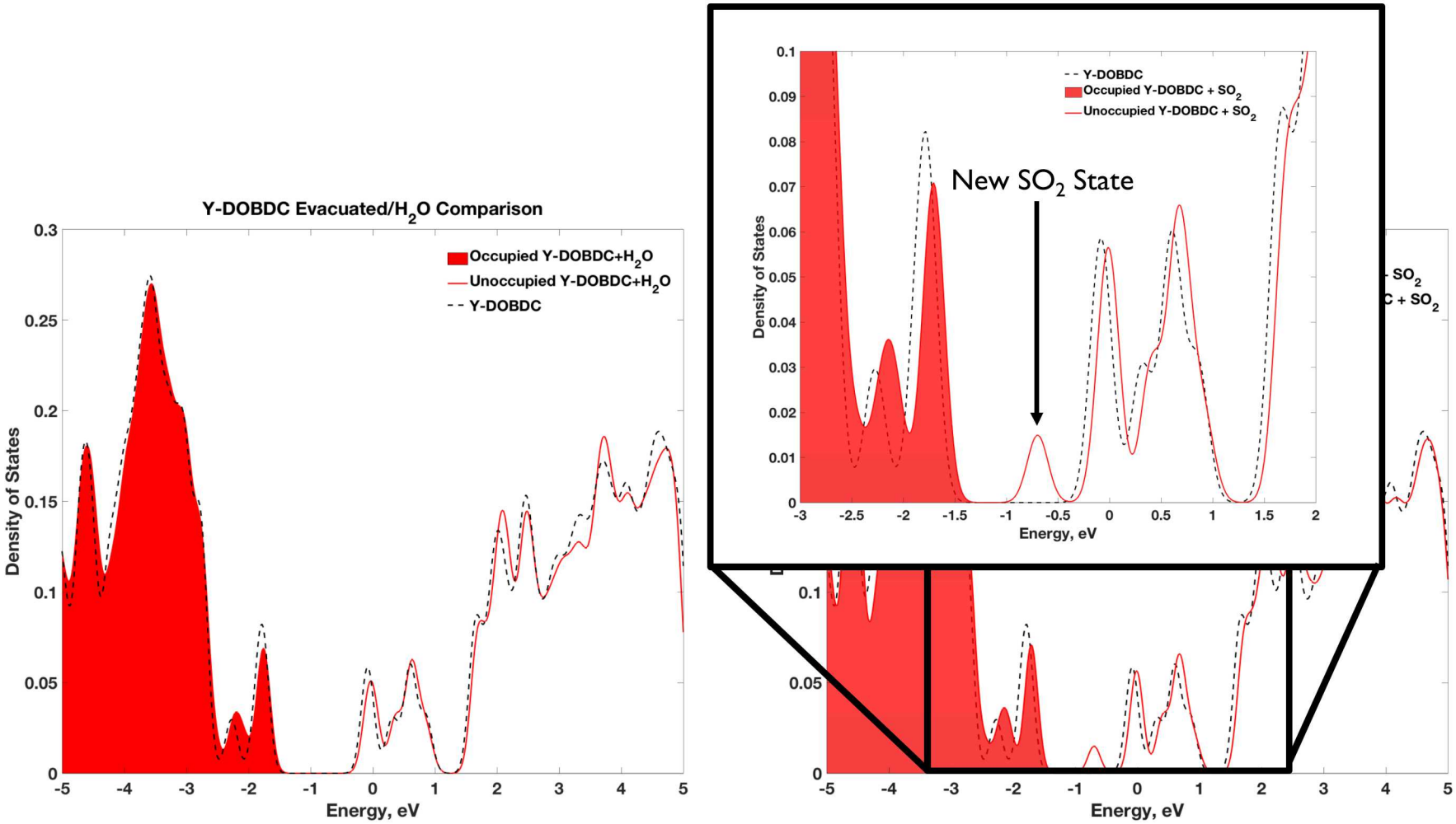
Gas Adsorption: Binding Energies

- Three different gases considered: H_2O, NO_2, SO_2 (one molecule at a time)
- Strong preference for SO_2
- Slightly different selectivity for H_2O v. NO_2 (Tb-DOBDC binds more strongly with NO_2)

Gas Interaction Energy (kJ/mol)				
Gas	Rare Earth Element			
	Eu	Tb	Yb	Y
H_2O	-76.712	-36.536	-60.167	-81.936
NO_2	-45.048	-40.812	-54.872	-74.330
SO_2	-285.461	-283.524	-287.759	-252.296

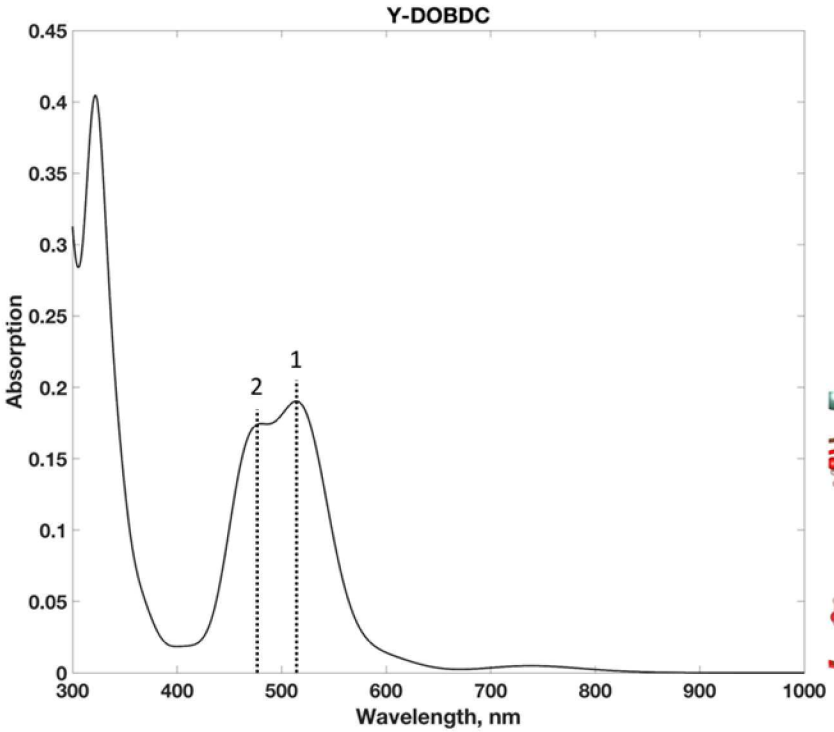


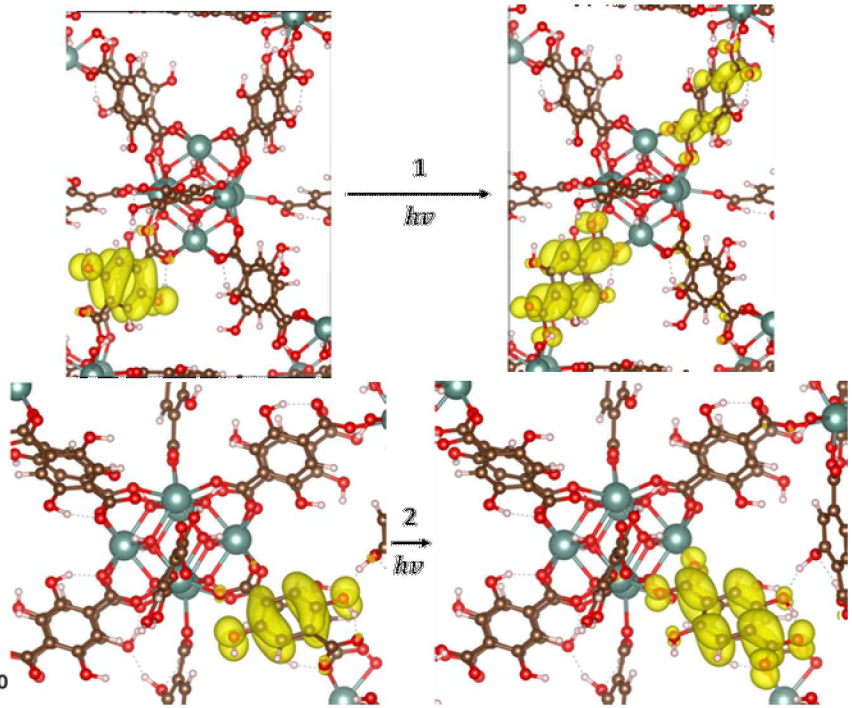
Y-DOBDC + SO_2 Density of States



Activated Y-DOBDC Absorption

Spin-restricted DFT Absorption Spectra





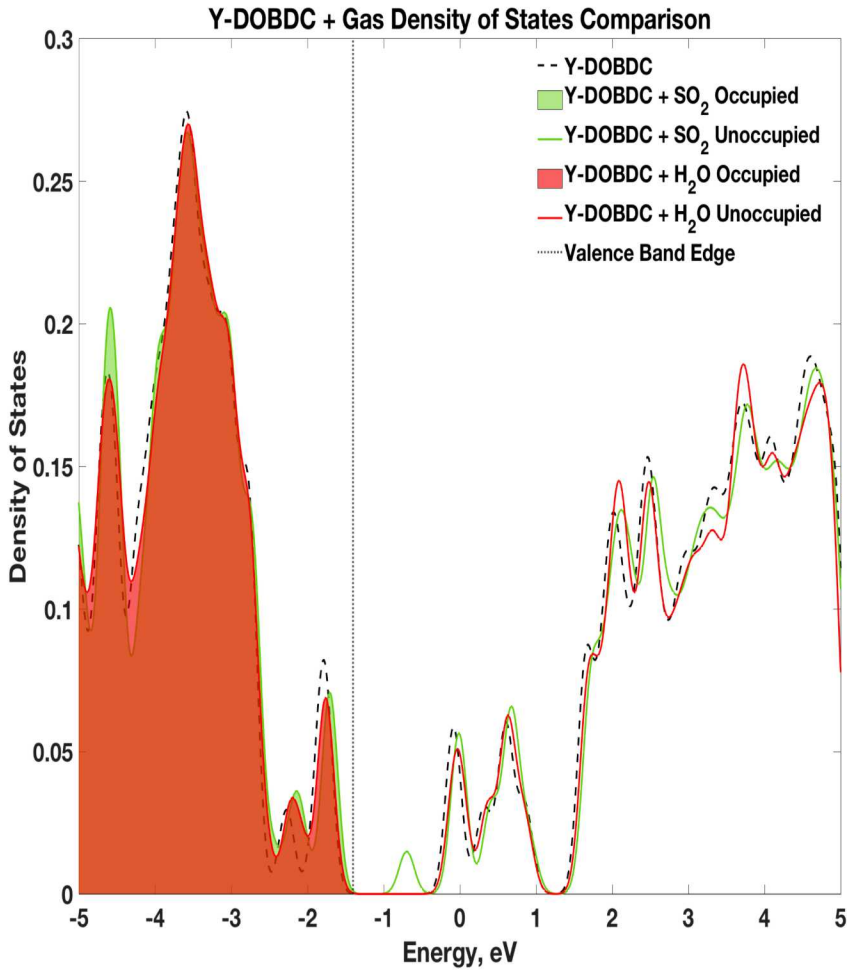
Transition Dipole: $\vec{D}_{\sigma,ij} = e \int \varphi_{\sigma,i}^{KS^*} \vec{r}\, \varphi_{\sigma,j}^{KS} d\vec{r}$

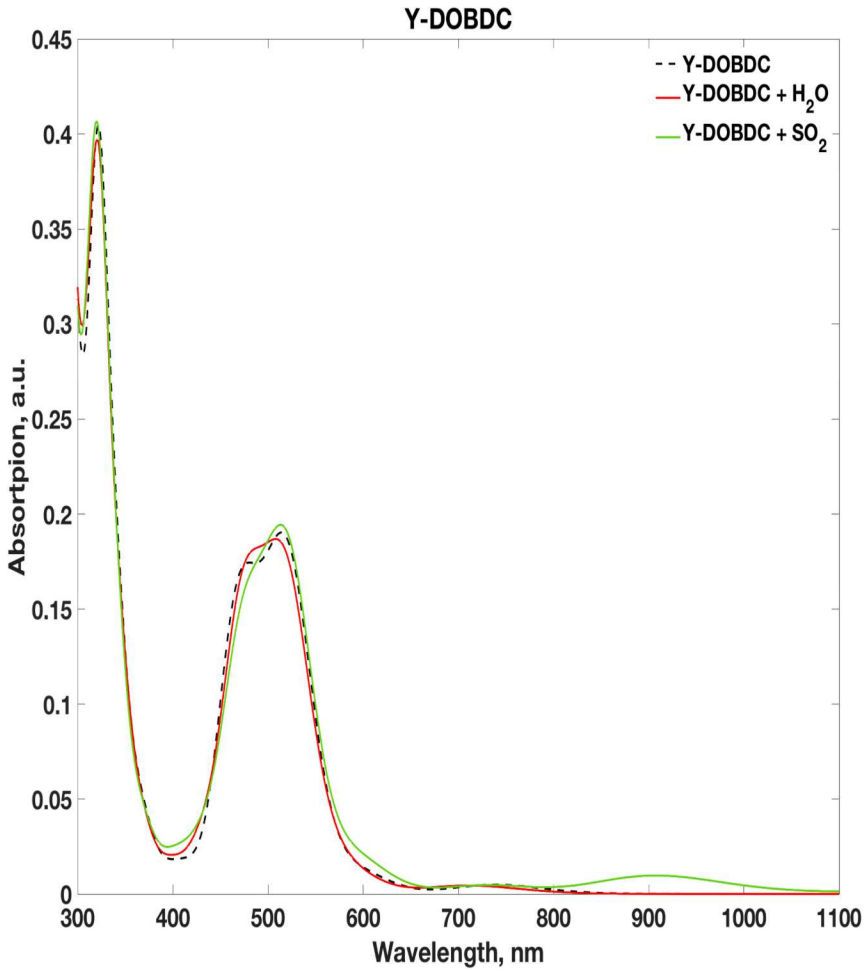
Oscillator Strength: $f_{\sigma,ij} = \left|\vec{D}_{\sigma,ij}\right|^2 \frac{4\pi m_e v_{\sigma,ij}}{3\hbar e^2}$

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

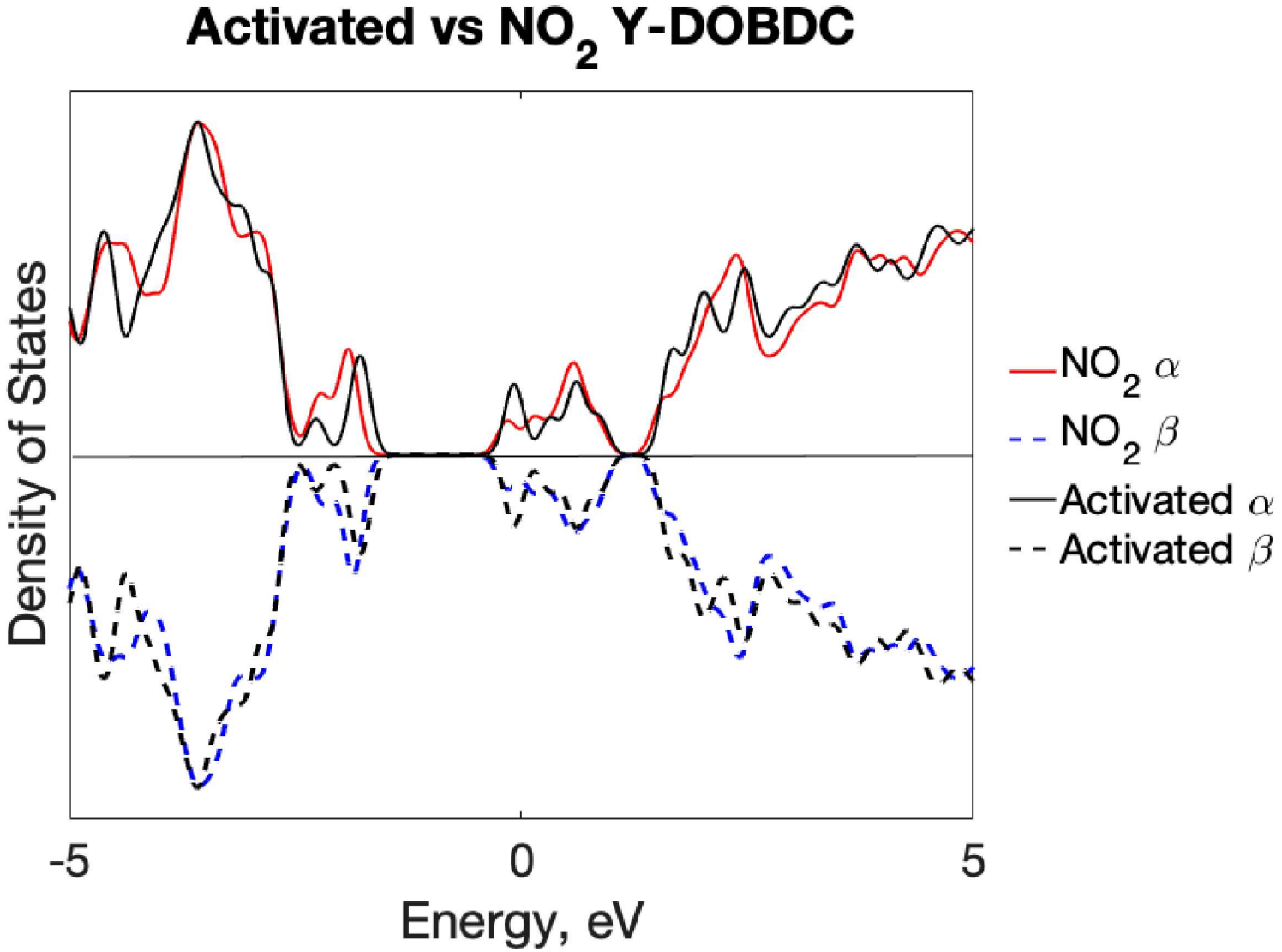
Gas Adsorption: Electronic Response in Y-DOBDC

Spin-restricted DFT DOS and Absorption Spectra

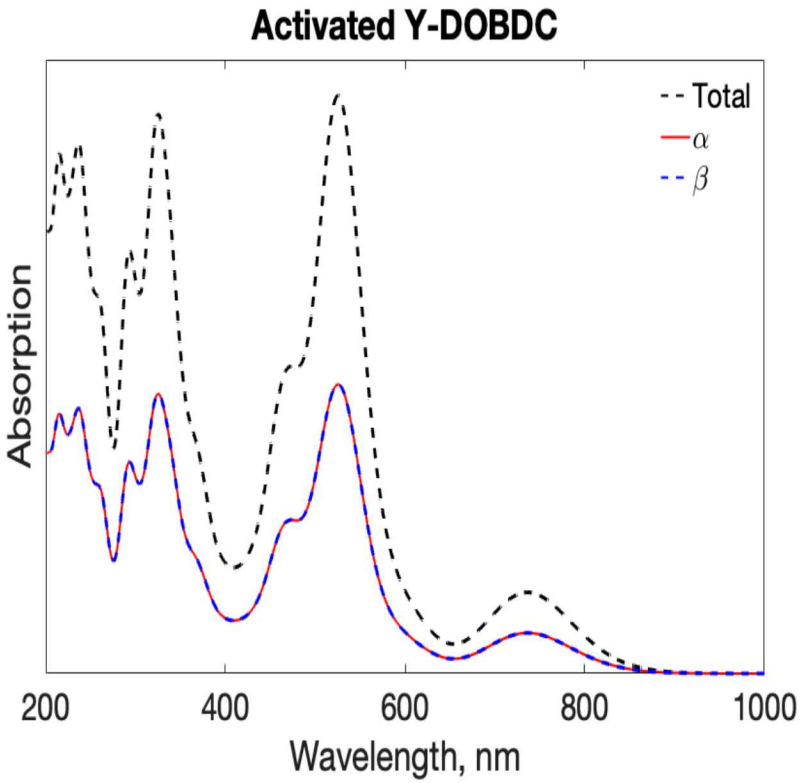


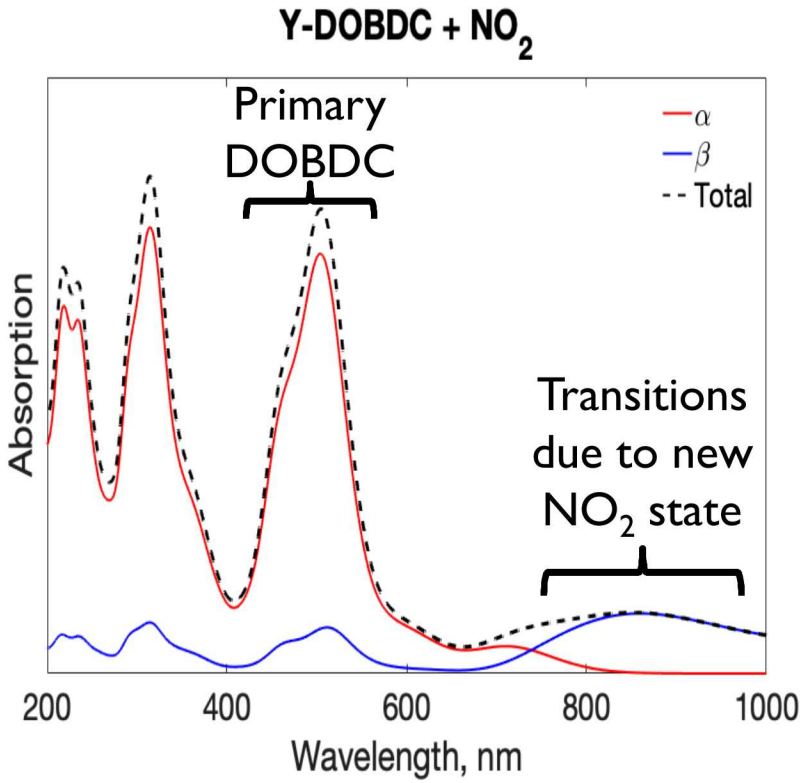


Gas Adsorption: Electronic Response in Y-DOBDC + NO_2



Gas Adsorption: Electronic Response in Y-DOBDC + NO_2

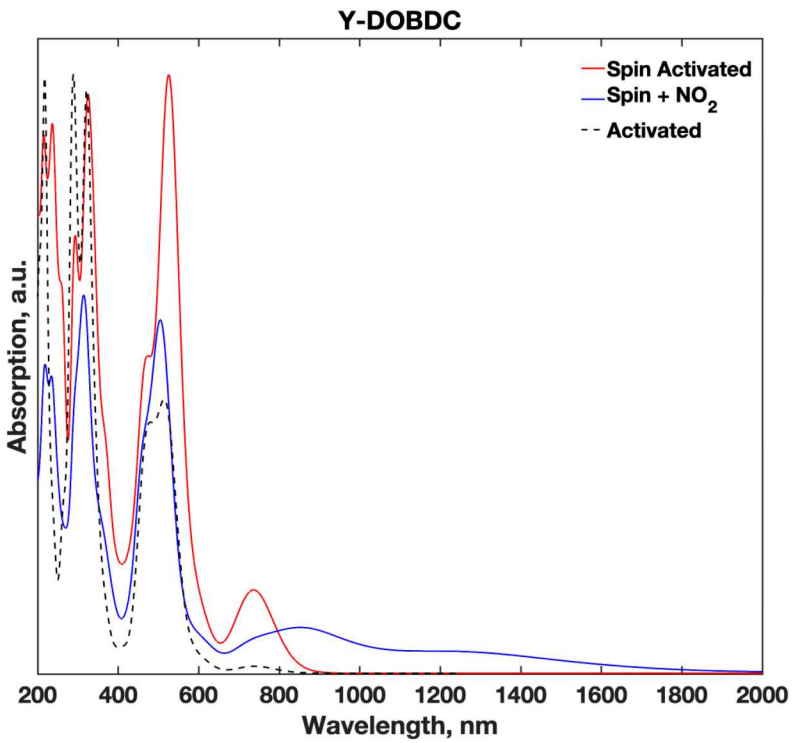




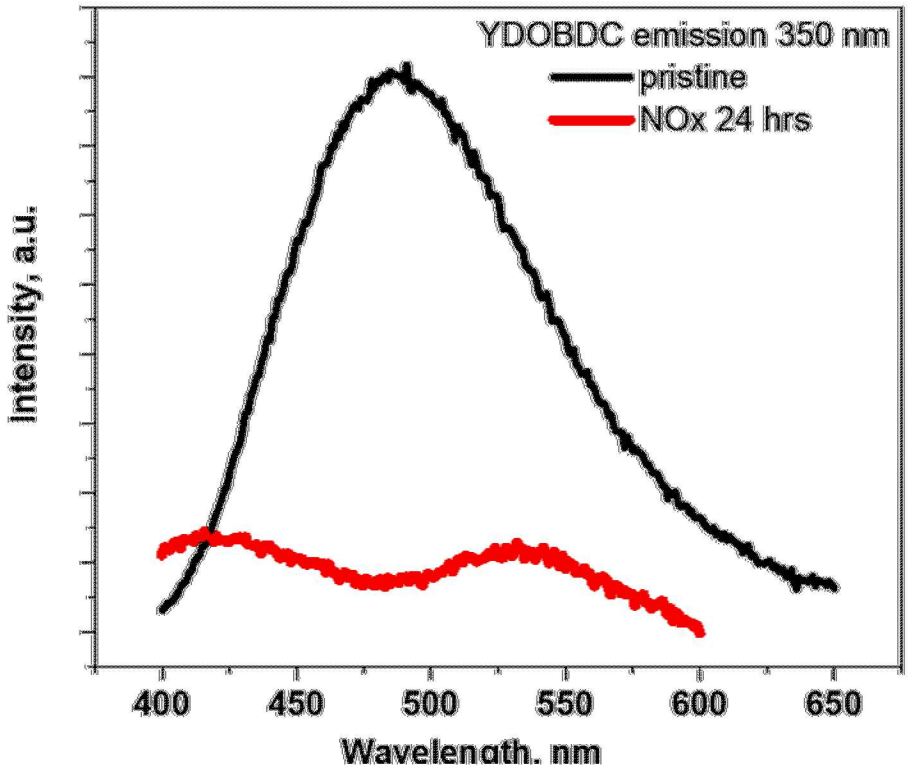
Even electron count results in identical spin up and down electronic signatures.

Gas Adsorption: Electronic Response in Y-DOBDC. NO_2 vs NOx

Computed Absorption

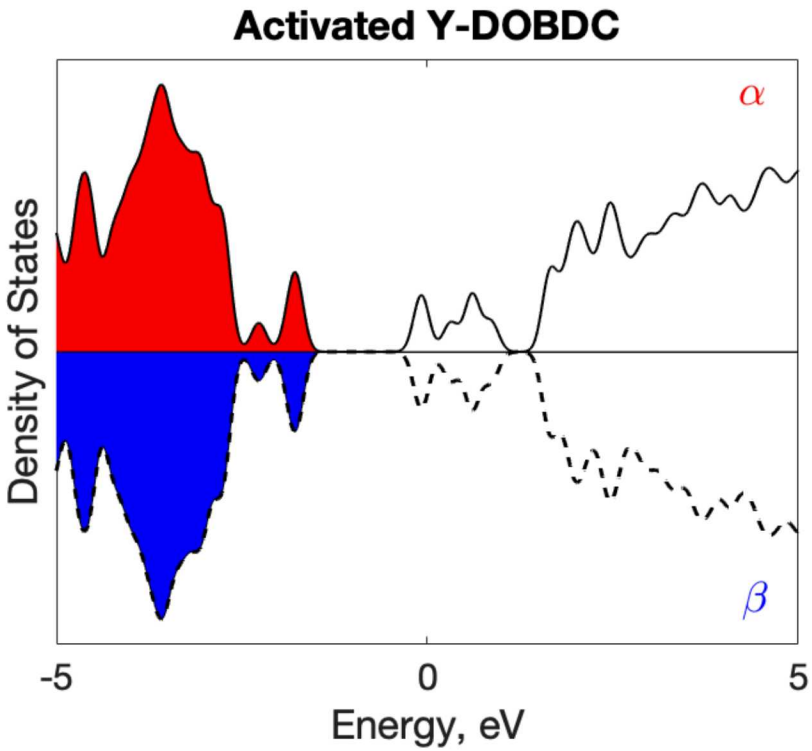


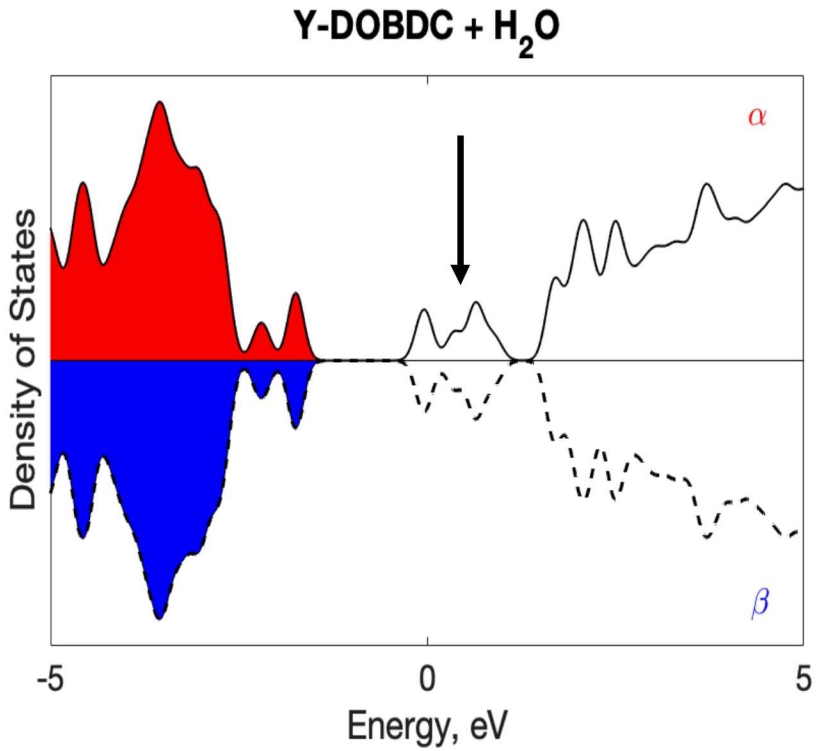
Experimental PL



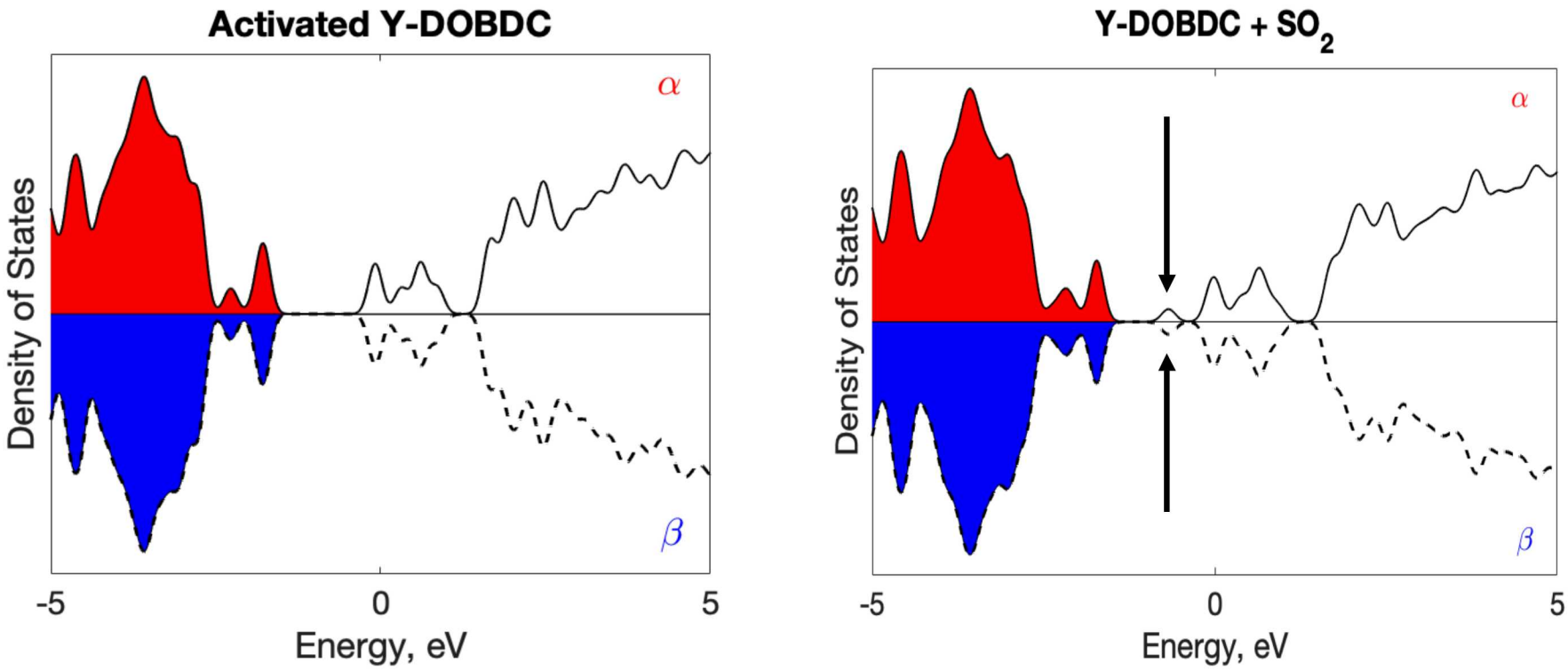
Gas Adsorption: Electronic Response in Y-DOBDC + H_2O

Minimal change in electronic structure with adsorption of H_2O.



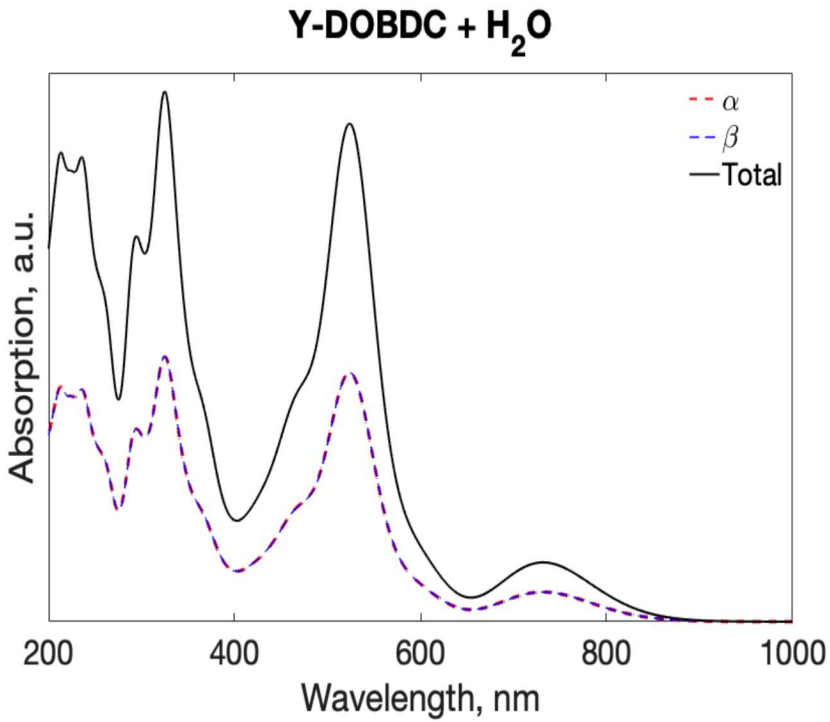


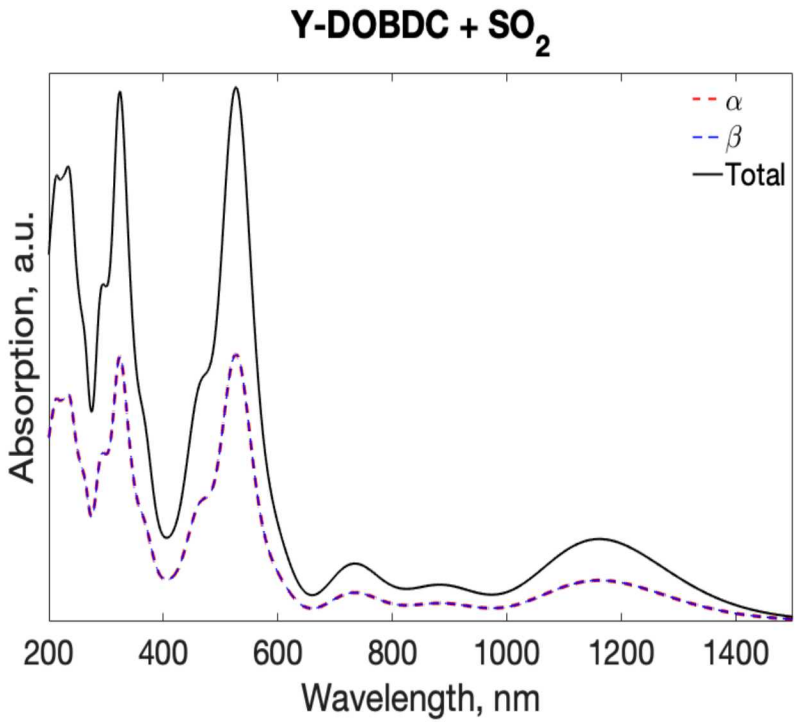
Gas Adsorption: Electronic Response in Y-DOBDC + SO_2



Spin-unrestricted confirms prediction made in spin-restricted calculation. The adsorption of an SO2 molecule at an undercoordinated metal site introduces a new state within the original band gap.

Gas Adsorption: Predicted Trends in Absorption Spectra H_2O and SO_2





Conclusions on Gas Adsorption Properties

- SO_2 has shown the strongest interaction with all current rare earth elements.
- For RE-DOBDC (RE=Y,Eu,Tb,Yb) gas adsorption is preferential for $SO_2 > H_2O > NO_2$, where H_2O and NO_2 are very competitive.
- Adsorption of gas molecules, NO_2 and SO_2, provide unique electronic structure allowing new electronic relaxation pathways to exist.
- Adsorption of NO_2 in Y-DOBDC induces a reduced PL intensity.
- Calculated DOS show new unoccupied states in the valence band and a redistribution of state energies at the band edges.

Acknowledgements

Team Members

Jessica Rimsza (PI)

SNL, Staff

Geochemistry

Tina Nenoff (PI)

SNL, Staff

Material, Physical, and Chemical Sciences

Dorina Sava Gallis

SNL, Staff

Nanoscale Sciences

Grace Vincent

UNM, Undergrad

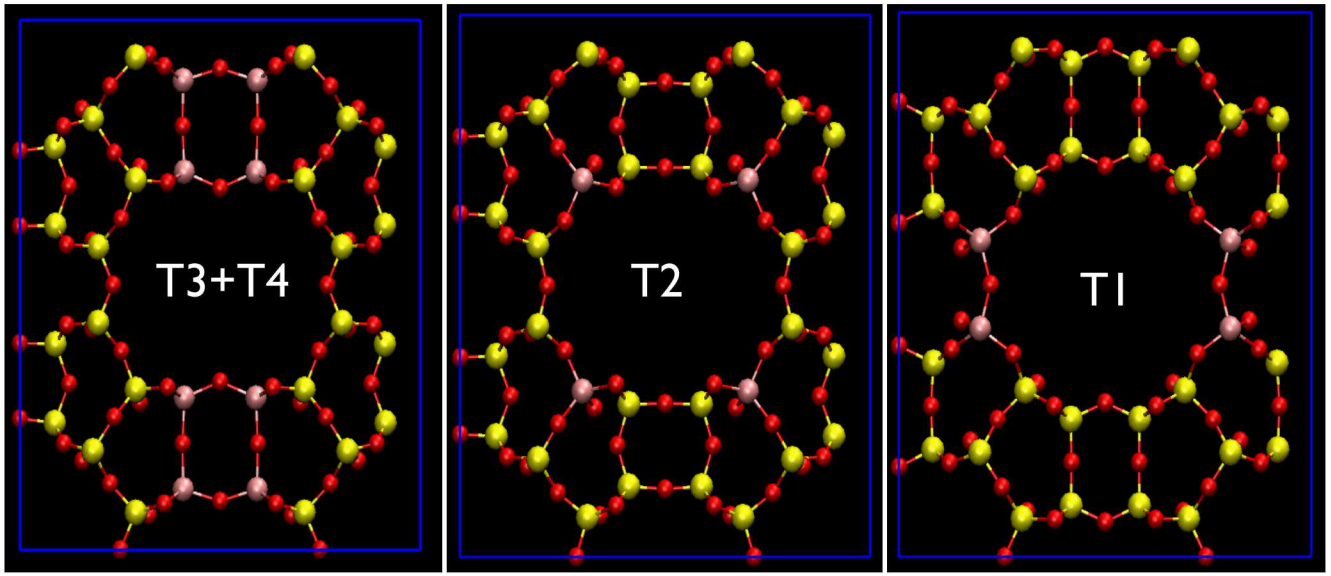
Peter Schultz (SNL), Jacob Harvey (SNL), and Jeff Greathouse (SNL).

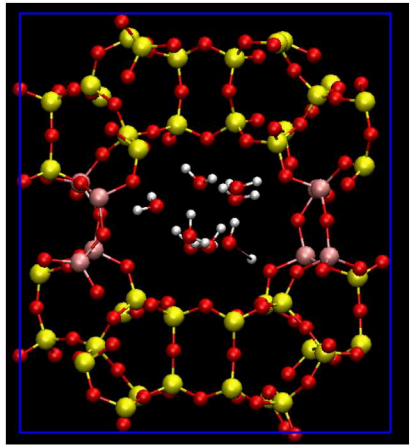
The work was supported as part of UNCAGE-ME, an Energy Frontier Research Center Funded by the U.S. Department of Energy, Office of Science. This paper describes objective technical results and analysis. under Award #DE-SC0012577. Sandia National Laboratories is a multimission laboratory managed and operated 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.

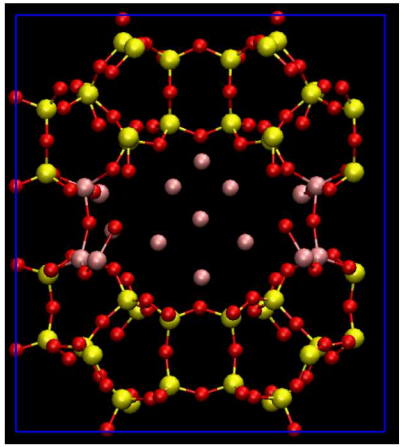
Future Zeolite Work

Structure:

- Mordenite (MOR) framework
- Si/Al ratio = 5
- Energetics of Ag+ formation in main channel and side pocket



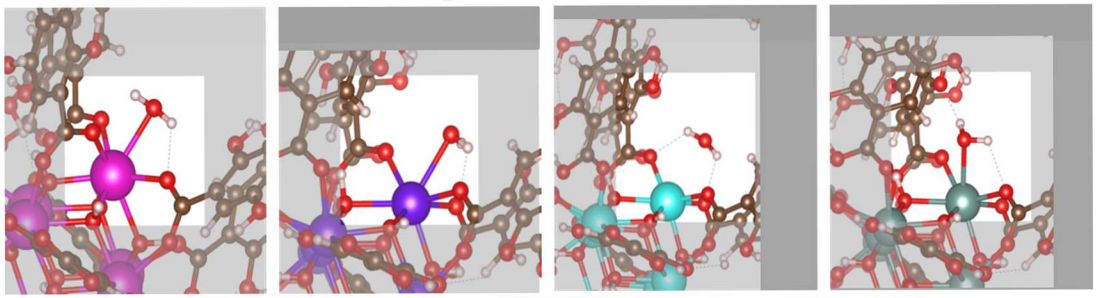


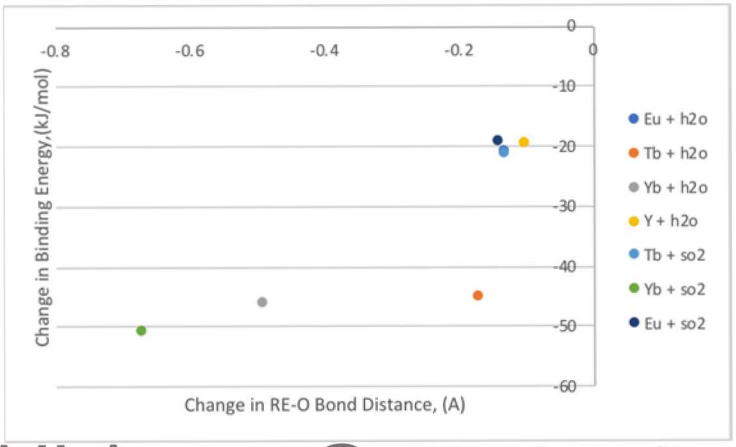


Snapshots of MOR framework structures with Al in four different tetrahedral locations (T1, T2, and T3+T4). Colors: silicon (yellow), oxygen (red), and aluminum (pink)

Gas Adsorption: Material Reorganization

Gas Only Optimization





All Atom Optimization