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Electronic and Structural Response of Rare-Earth Metal-Organic Frameworks with Acid Gases

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U.S. DEPARTMENT OF ENERGY | NNSA National Nuclear Security Administration

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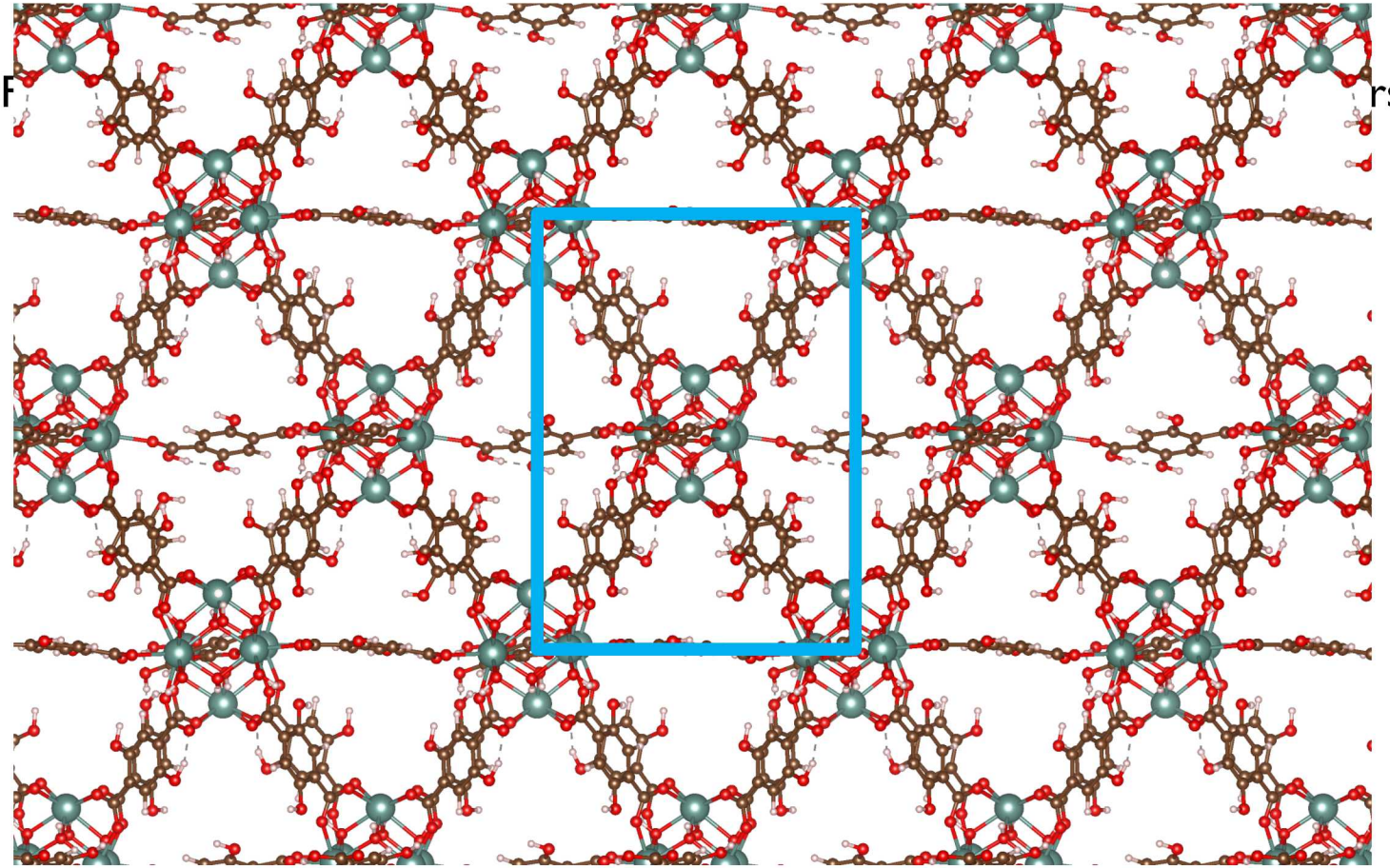
Metal-Organic Frameworks

MOF rs.



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

39	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Y	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Yttrium 88.906	Lanthanum 138.905	Cerium 140.116	Praseodymium 140.908	Neodymium 144.243	Promethium 144.913	Samarium 150.36	Europium 151.964	Gadolinium 157.25	Terbium 158.925	Dysprosium 162.500	Holmium 164.930	Erbium 167.259	Thulium 168.934	Ytterbium 173.055	Lutetium 174.967

Vogel, D. J., Sava Gallis, D. F., Nenoff, T. M., Rimsza, J. M. **2019,** *Accepted*

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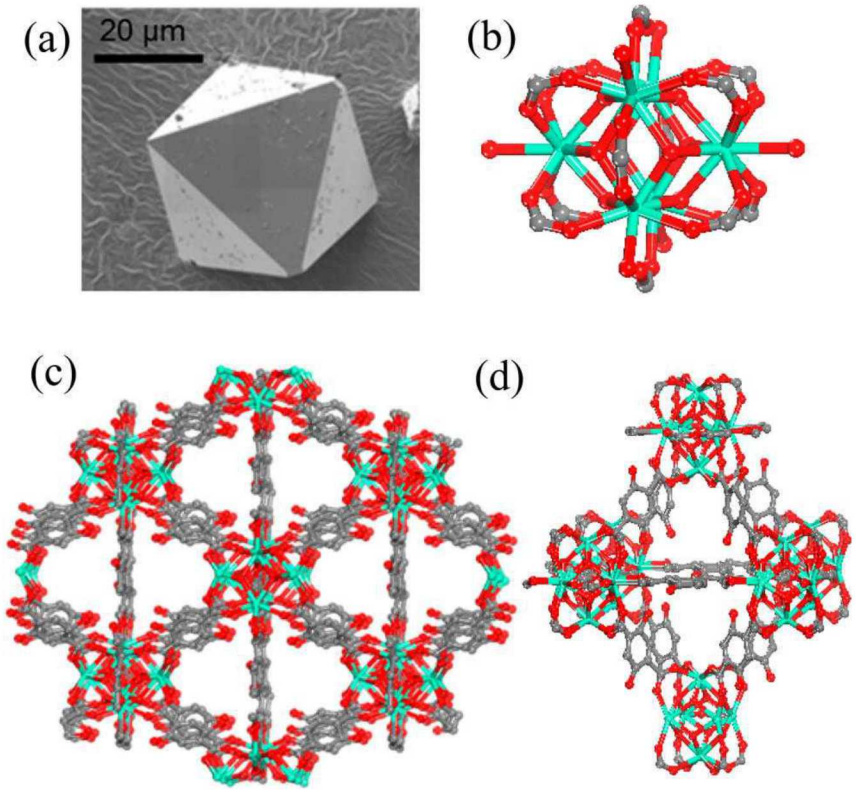
Material Structure of Currently Synthesized Rare Earth (RE) MOFs



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

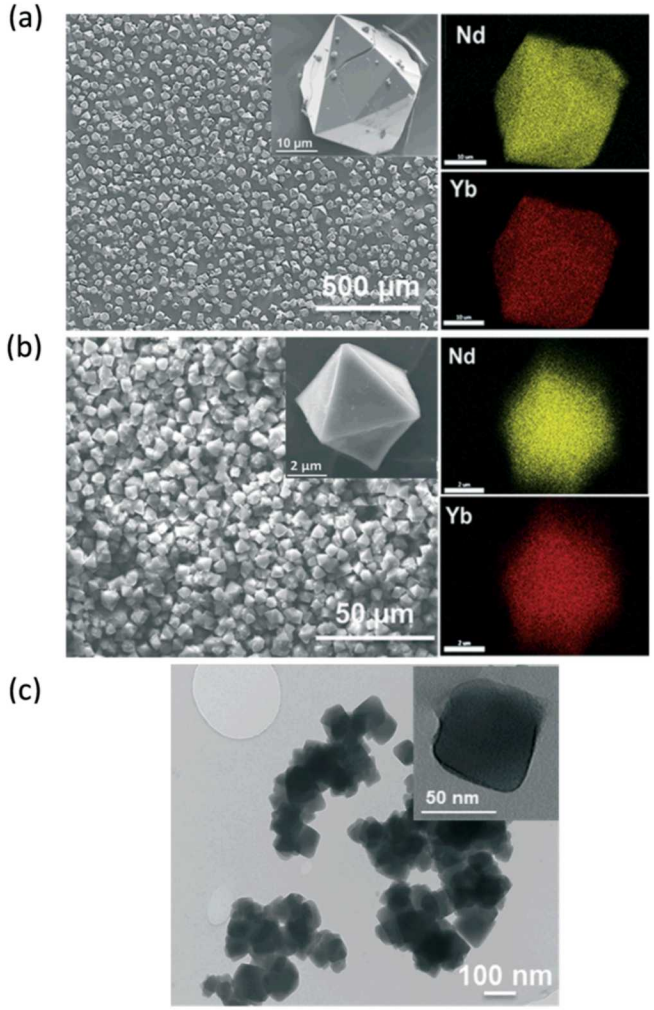


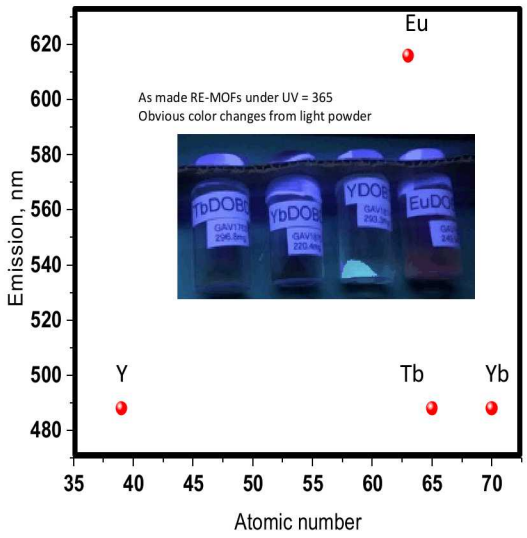
Fig. 2 SEM-EDS analyses on (a) compound **1**; (b) compound **2**; (c) TEM on compound **3**.

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

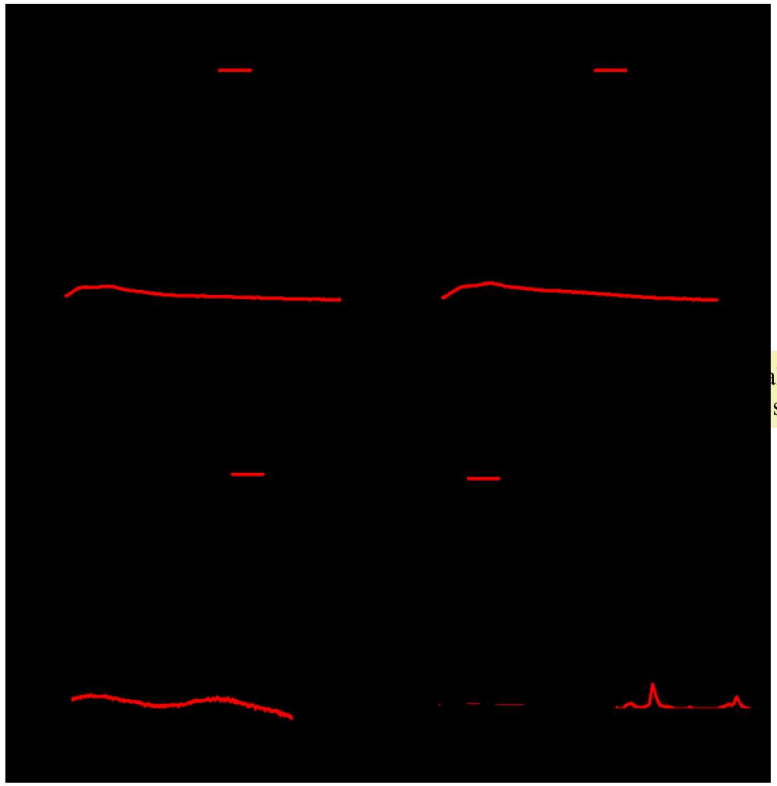
Gas Adsorption: Experimental Photoluminescence Response to NOx Exposure

UNCAGE-ME Center exemplar "Complex Mixtures":

- ***Coal-fired power plant flue gas*** (13% CO_2, 6% H_2O, ~ 4% O_2, 50 ppm CO, 420 ppm, NO_2, 420 ppm SO_2, 76% N_2)
- ***Biogas*** (65% CH_4, 32% CO_2, 2% N_2, 0.7% O_2, and 0.3% H_2S)
- ***Raw natural gas*** (CH_4, 1-5% C_2+, 1-5% H_2O, 1-10% H_2S, 1-5% N_2, 5-50% CO_2)



Sava Gallis, Nenoff, Vogel, Rimsza, Provisional US Patent, 2019



l tested with spectrum

- Quenched photoluminescence following 24 hour NOx exposure in all synthesized RE-DOBDC MOFs

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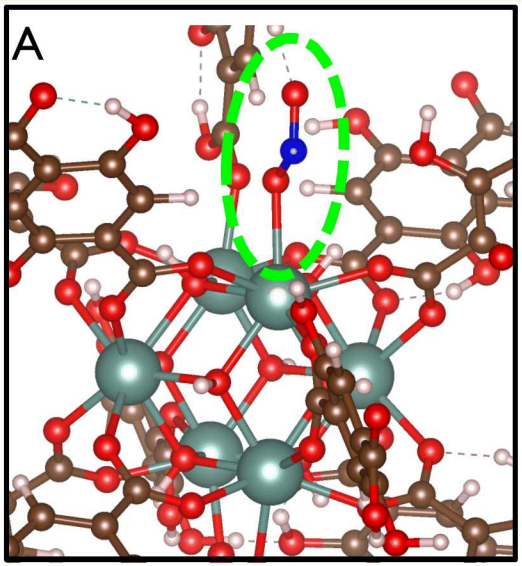
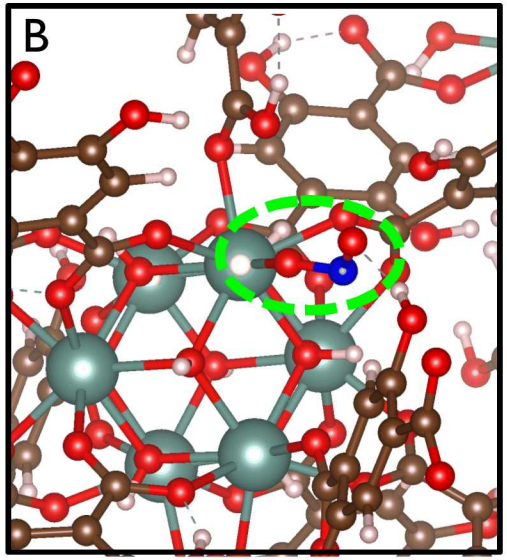
Computational Models and Methods

- Density Functional Theory as implemented in the Vienna *ab-initio* Simulation Package
- PBEsol exchange correlation functional
- DFT-D3 with Becke-Johnson Damping for dispersion corrections
- Spin-restricted and spin-unrestricted DFT
- Use **Y-DOBDC** system as example model throughout the rest of the presentation.

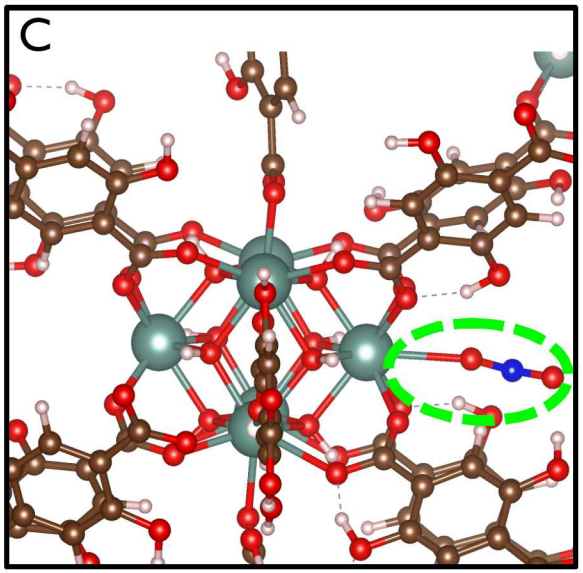
Rare Earth Metal Gas Adsorption Sites



Binding Energy: -70.27 kJ/mol



Binding Energy: -62.52 kJ/mol



Binding Energy: -21.87 kJ/mol

Element Key: Y(teal), O(red), C(brown), H(white), N(blue)

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Binding Energies of Single H_2O, NO_2, and SO_2 Gases

UNCAGE-ME Center exemplar "Complex Mixtures":

- ***Coal-fired power plant flue gas*** (13% CO_2, 6% H_2O, ~ 4% O_2, 50 ppm CO, 420 ppm, NO_2, 420 ppm SO_2, 76% N_2)
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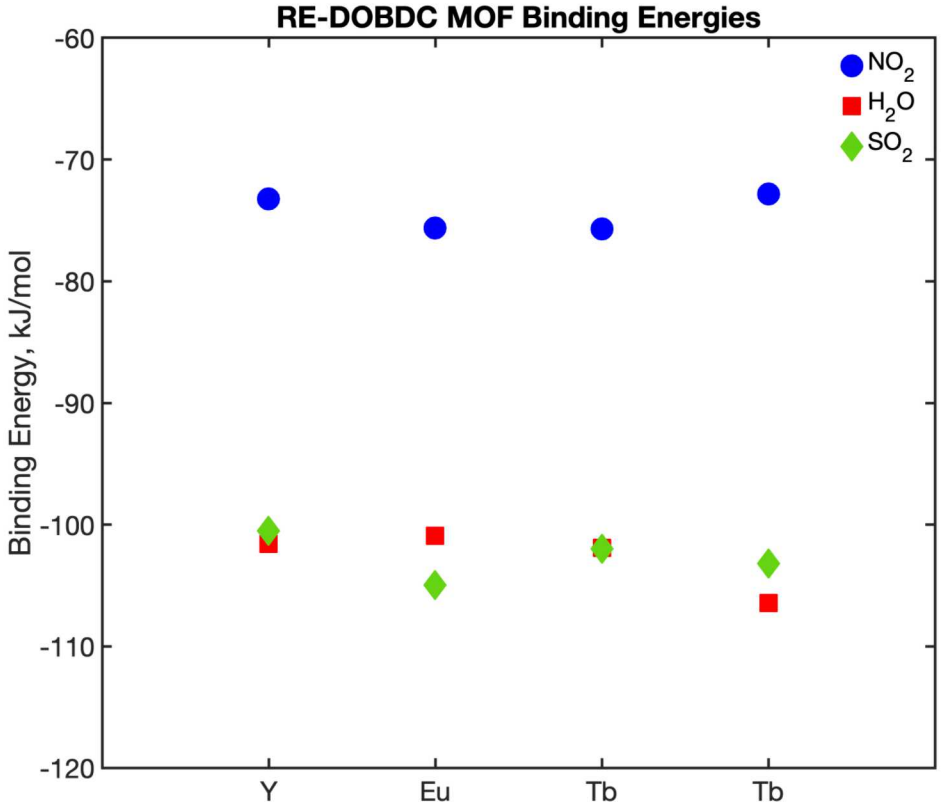
▪ Three different gases considered as a homogeneous gas: H_2O, NO_2, SO_2

Gas	Rare Earth Element Binding Energies (kJ/mol)			
	Y	Eu	Tb	Yb
H_2O	-101.59	-100.91	-101.90	-106.45
NO_2	-73.23	-75.64	-75.69	-72.18
SO_2	-100.50	-104.95	-101.98	-103.20



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

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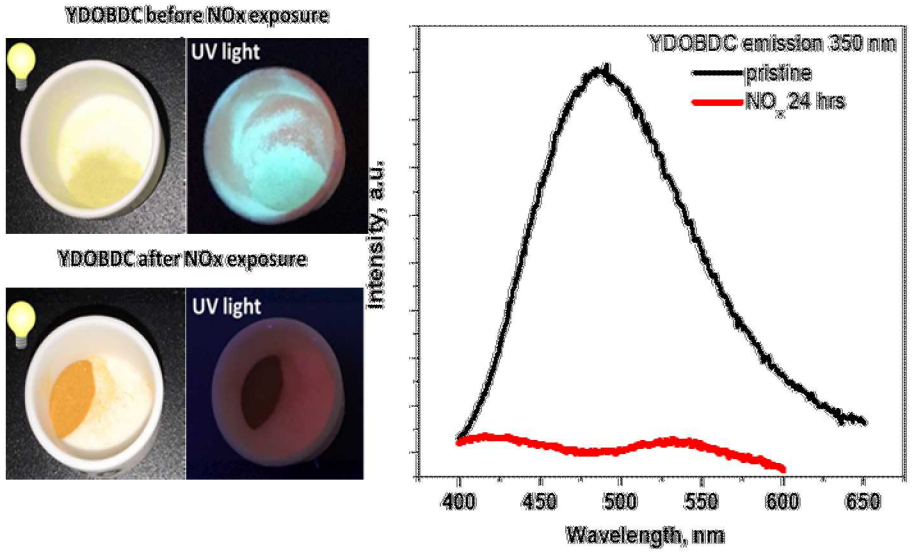
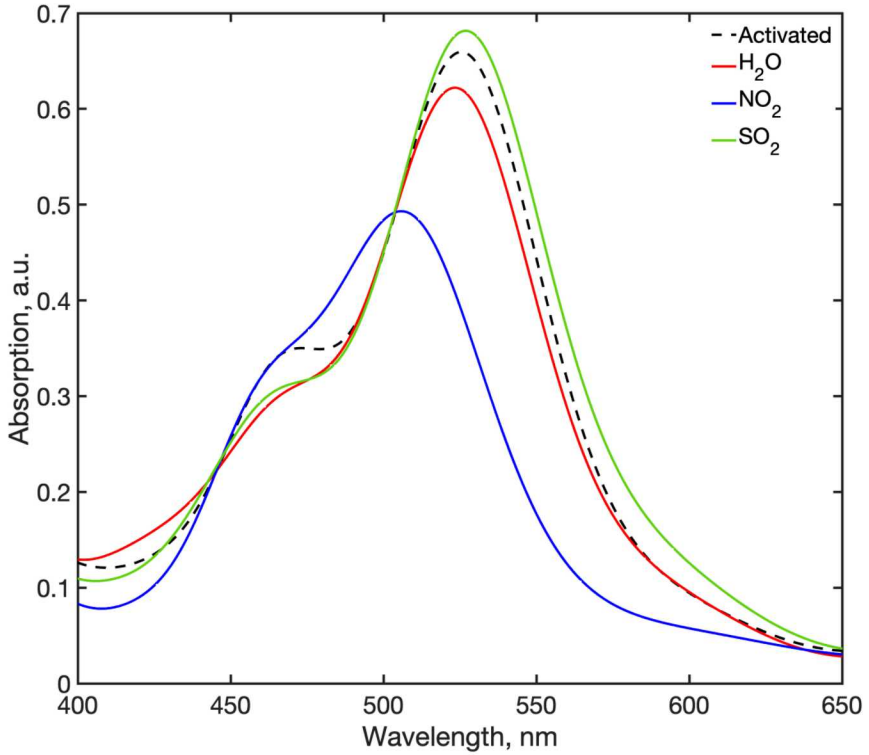
Recreating Quenched Experimental PL via DFT Calculations

Experimental Photoluminescence



Calculated Optical Absorption



- Experimental photoluminescence show quenching in RE-DOBDC MOFs after NOx exposure. (left)
- Calculated optical spectra of Y-DOBDC MOF indicates gas specific interactions for H_2O, NO_2, and SO_2, leading to unique electronic structures. (right)

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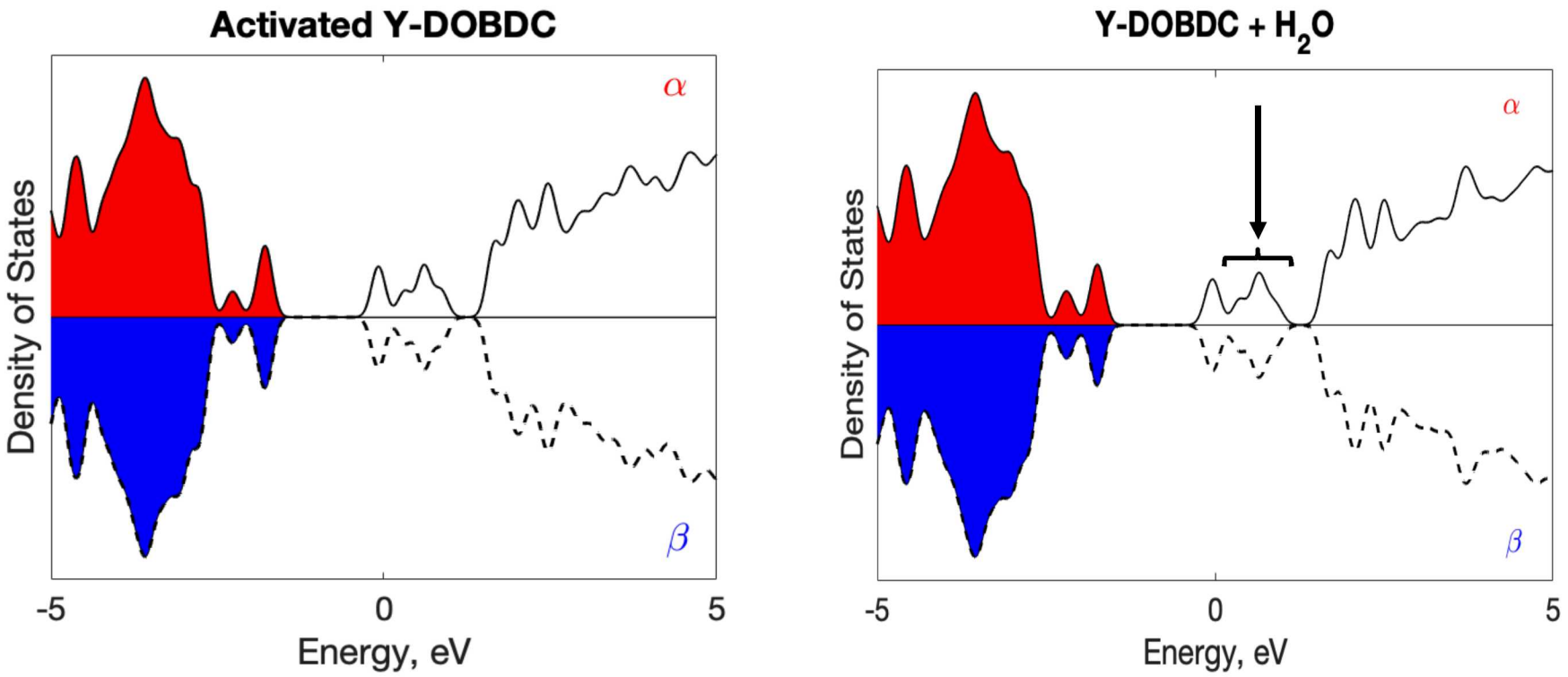
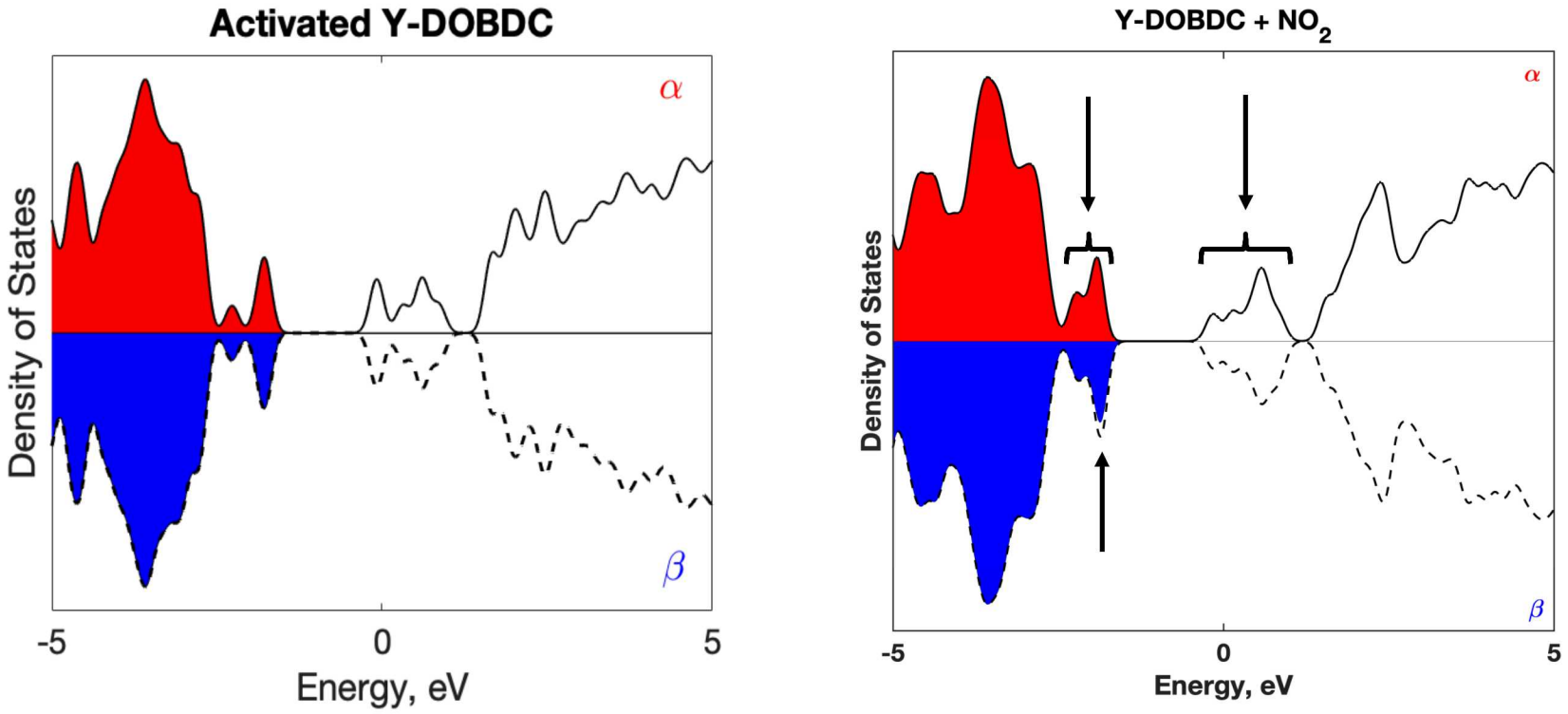
Gas Adsorption: Electronic Response in Y-DOBDC + H_2O



- Density of states provides the relative number of electronic states at a given energy value.
- Adsorption of H_2O on the RE-metal site makes minimal change to the electronic structure.

NO_2 Adsorption Modifies Electronic Structure in Optical Range



- Adsorption of NO_2 at the RE metal site creates changes in electronic structure near the band edges.
- Modification of the DOS at the band edges influences the optically active transitions.

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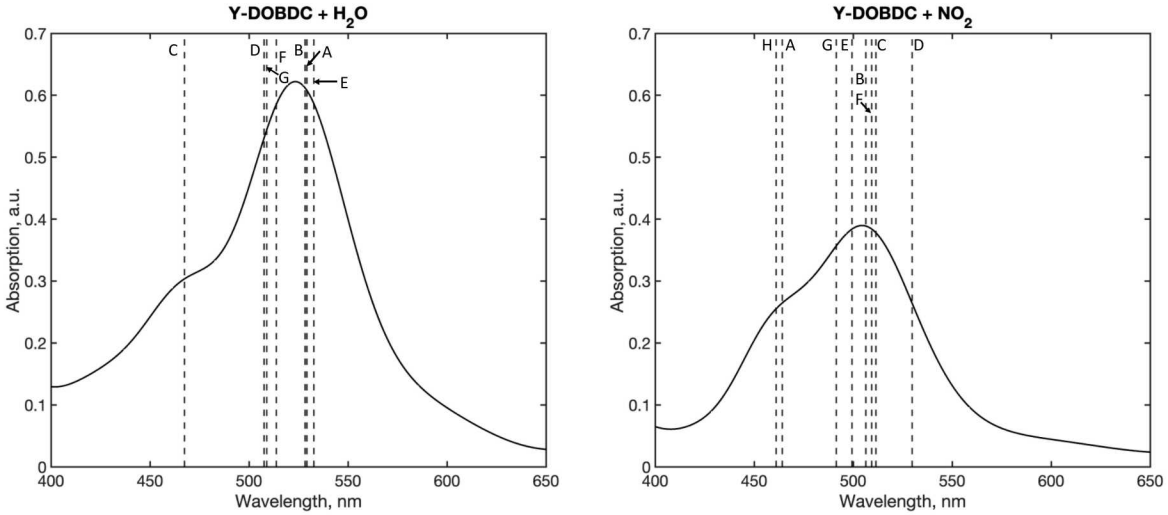
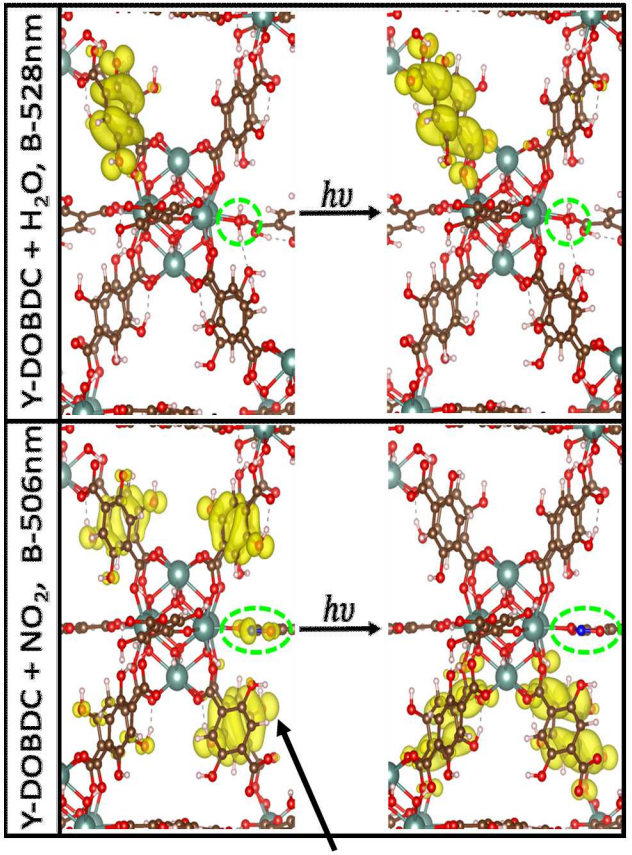
Partial Charge Densities: Indicating Active Role of NO_2 in Optical Transitions

- The strongest transitions are found in 400-650 nm range.
- Identification of orbitals for strong transitions indicate electron localization on DOBDC linkers.



Y-DOBDC + H_2O			Y-DOBDC + NO_2		
Transition label	f_{ij}	$\omega_{ij}(nm)$	Transition Label	f_{ij}	$\omega_{ij}(nm)$
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	E	4.94	499
F	3.59	513	F	3.80	509
G	2.40	509	G	3.49	491
			H	3.01	464



Partial Charge Densities (yellow isosurfaces)

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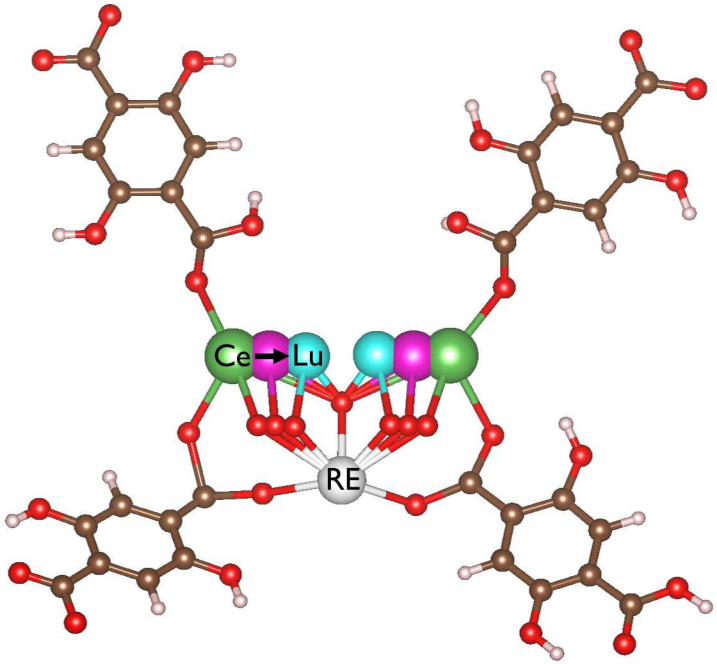
Conclusions

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

Future Directions:

- Prediction of enhanced phases of RE-MOFs for acid gas binding and optical response with new lanthanide metlas using developed calculation procedures.
- Multiple/mixed gas interaction and material response through molecular dynamics of mixed gases.



Acknowledgements

Team Members

Jessica Rimsza (PI)

SNL, Staff

Tina Nenoff (PI)

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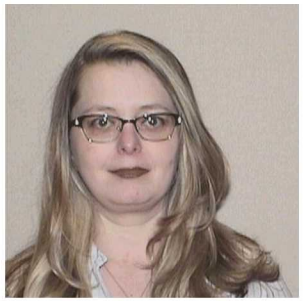

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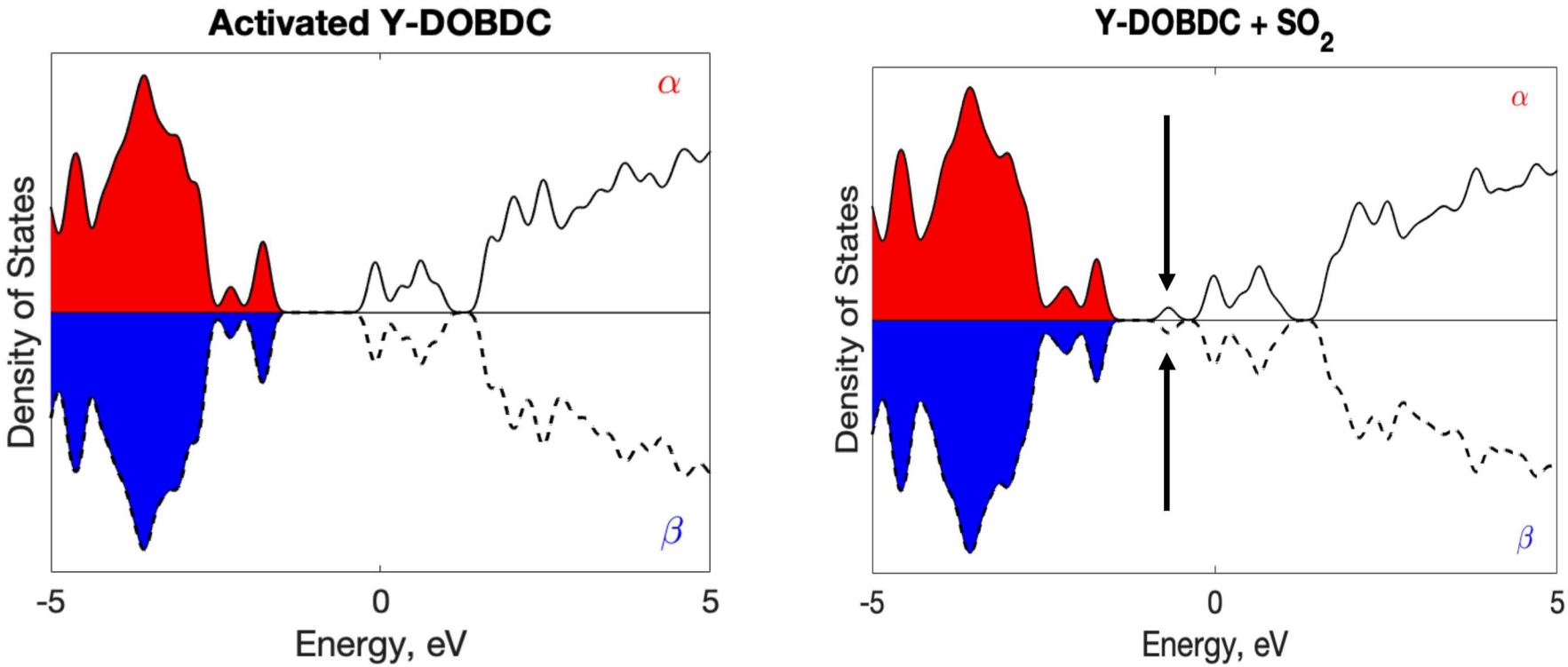
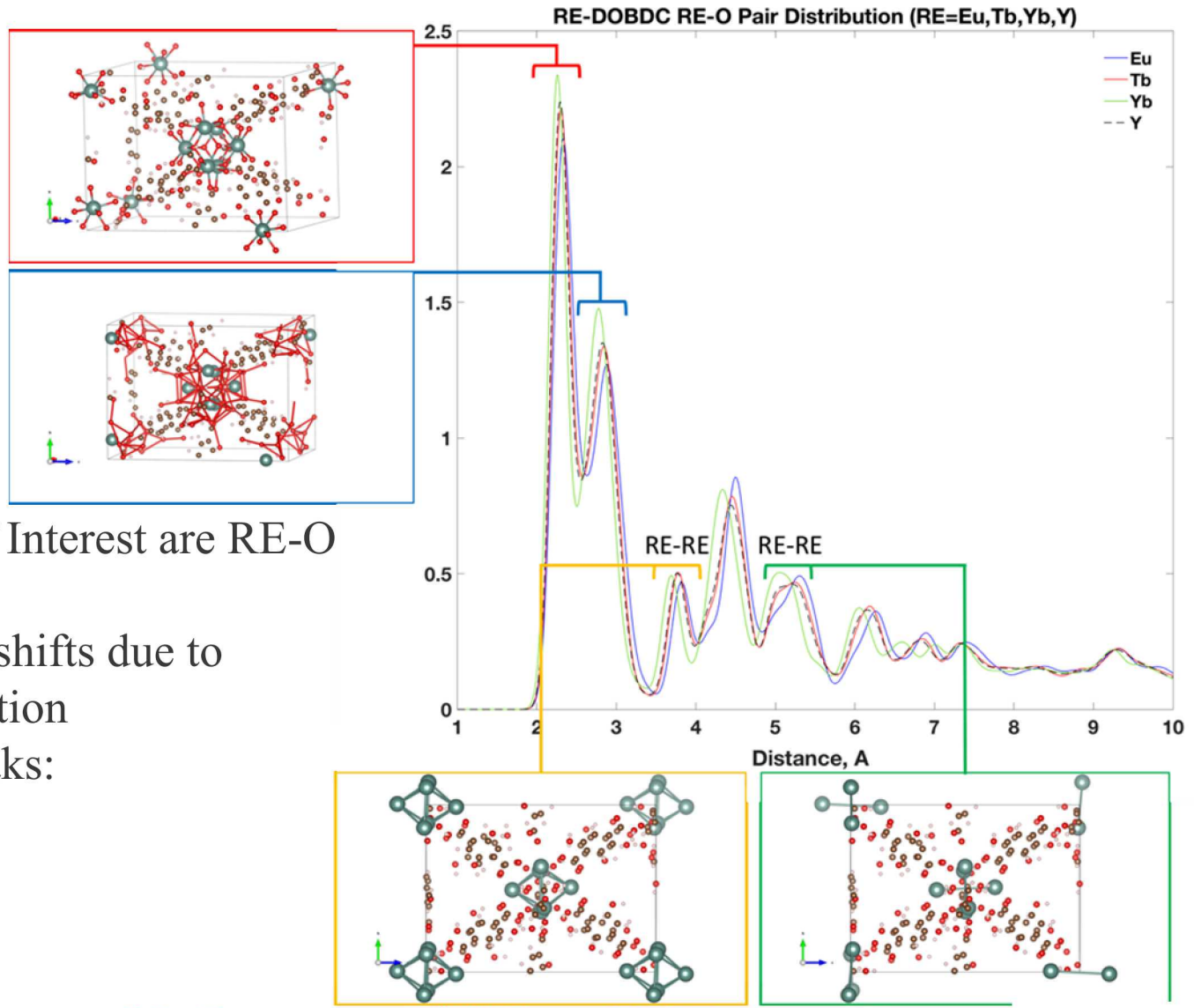
Gas Adsorption: Electronic Response in Y-DOBDC + SO_2



- Spin-unrestricted confirms prediction made in spin-restricted calculation. The adsorption of an SO_2 molecule at an undercoordinated metal site introduces a new state within the original band gap.

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

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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.

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