Structural and Optical Response of Complex Mixed Gas Dynamics in Rare Earth Metal-Organic Frameworks

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UNCAGE ME

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Introduction

A series of rare earth 2,5-dihydroxyterephthalic acid (RE-DOBDC) metal organic frameworks (MOFs) are investigated for their ability to robustly function as a separation material within harsh acid gas environments. Currently synthesized RE-MOFS, where RE=Y,Eu,Tb,Yb, have demonstrated a unique and strong optical response to the presence of NOx and have shown sustained crystallinity following 24 hr acid gas exposure. Here, density functional theory (DFT) methods are used to investigate the underlying mechanisms of interactions of acid gases within the RE-MOF frameworks at the atomistic level. Individual gas molecules are calculated to have varying binding energies and interaction types with the RE-MOF framework, indicating binding site selectivity. The results from understanding currently synthesized RE-MOFs will help to guide the design of new materials with tunable properties for gas separations and sensing.

Computational Methods

- Spin polarized ground state geometries and *ab initio* molecular dynamics calculated using Density Functional Theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP).
- Calculation parameters:
  - Plane wave basis set.
  - Projector augmented wave potentials.
  - Exchange correlation functional of Perdew-Burke-Ernzerhof designed for solids (PBEsol).
  - Van der Waals interactions included using method of Grimme (D3) with Becke-Johnson damping.
- One Electron Kohn-Sham Equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_{eff}(r)\right)\phi_i(r) = \varepsilon_i\phi_i(r)$$

- Transition Dipole Moment

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

- Transition Oscillator Strength

$$f_{\sigma,ij} = |\vec{D}_{\sigma,ij}|\frac{4\pi m_e\omega_{ij}}{3\hbar e^2}$$

- Calculated Optical Absorption

$$\alpha_\sigma(\varepsilon) = \sum_{\sigma,ij} f_{\sigma,ij}\delta(\varepsilon - \varepsilon_{\sigma,ij})$$

Conclusions

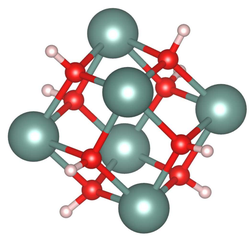
- Multiple binding sites exist at unsaturated metal sites and linker positions. Binding energies of individual gases indicate a selectivity of $SO_2 > H_2O > NO_2$.
- In humid NOx environments H_2O preferentially binds to metal sites and NOx binds to organic ligands.
- NOx exposure decreases photoluminescence in all synthesized RE-DOBDC MOFs due to interaction with DOBDC ligands.
- The percentage of intramolecular H-bonds produce a shift in the calculated optical properties of Y-DOBDC.
- *Ab initio* molecular dynamic trajectories are used to study complex acid gas mixtures in nanoconfined pore spaces.

Future Work

- Predicting new unsynthesized RE-DOBDC MOFs for acid gas separation and sensing.
- Analyzing new gas species formed via reaction due to complex gas mixtures.
- Identifying impact of nanoconfinement on gas interactions due to size of MOF pore.
- Provide large data sets, generated from *ab initio* molecular dynamic trajectories, for machine learning analysis.

Introduction to RE-DOBDC MOFs

Metal Centers

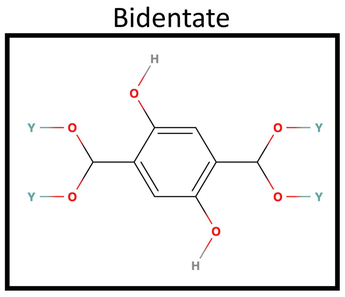


$Ln_6(\mu_3OH)_8$

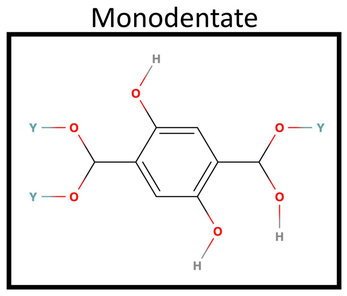
+

DOBDC Organic Linkers

Bidentate

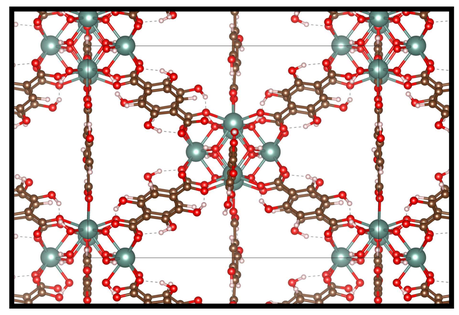


Monodentate



2,5-dihydroxyterephthalic acid

=

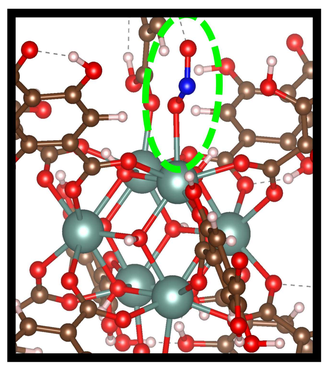


39	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Y Yttrium 88.906	La Lanthanum 138.905	Ce Cerium 140.116	Pr Praseodymium 140.908	Nd Neodymium 144.243	Pm Promethium 144.913	Sm Samarium 150.36	**Eu** Europium 151.964	Gd Gadolinium 157.25	**Tb** Terbium 158.925	Dy Dysprosium 162.500	Ho Holmium 164.930	Er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

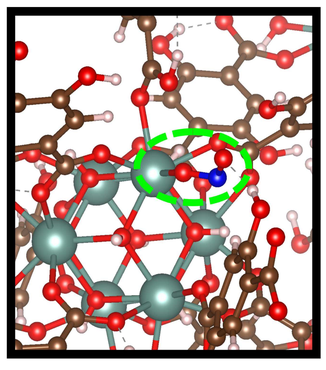
*Currently synthesized

Acid Gas Binding Energies in RE-DOBDC MOFs

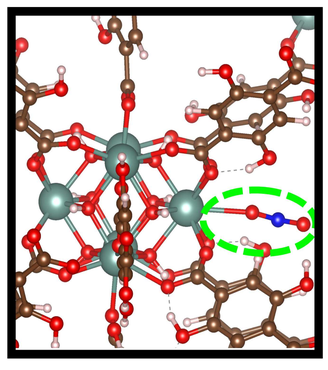
Unsaturated Metal Adsorption Sites



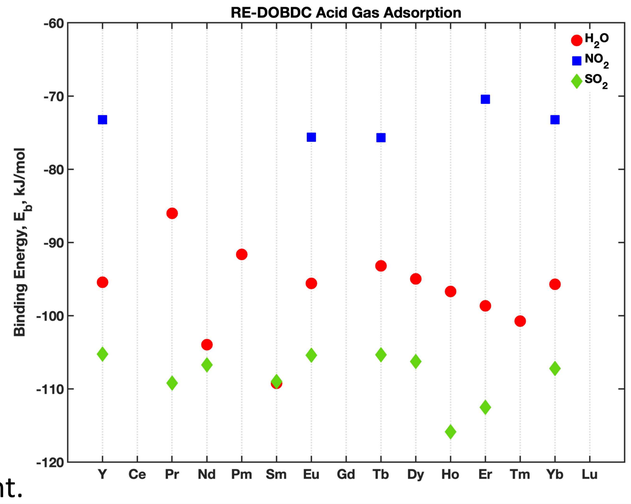
Binding Energy: -70.27 kJ/mol



Binding Energy: -62.52 kJ/mol



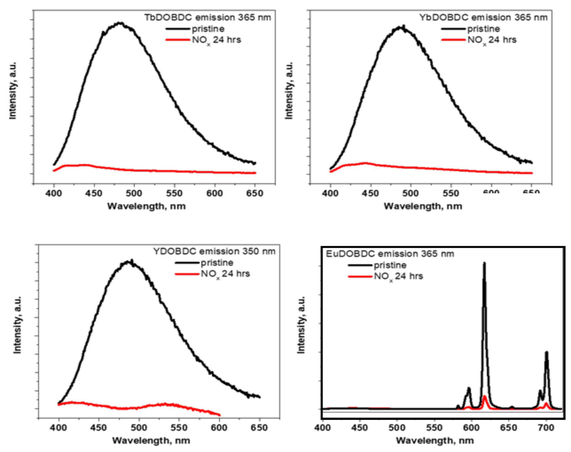
Binding Energy: -21.87 kJ/mol



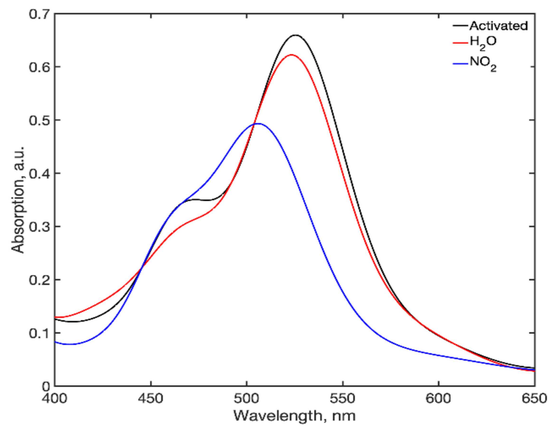
- Gas adsorption energies are dependent on metal location and local coordination environment.

RE-DOBDC Optical Response in Humid NO_x

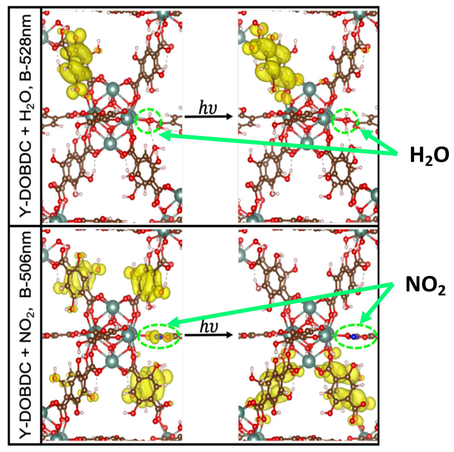
Experimental Photoluminescence



Calculated Optical Absorption



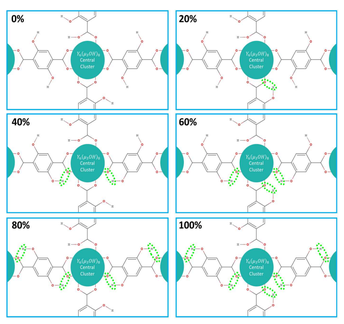
Transition Charge Densities



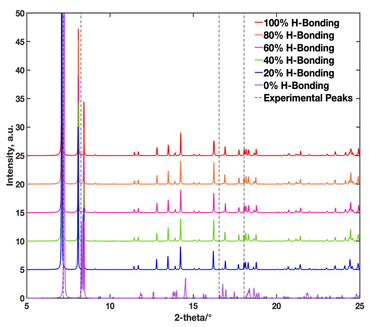
- Intrinsic RE-DOBDC MOF photoluminescence is reduced only upon exposure to NO_x.

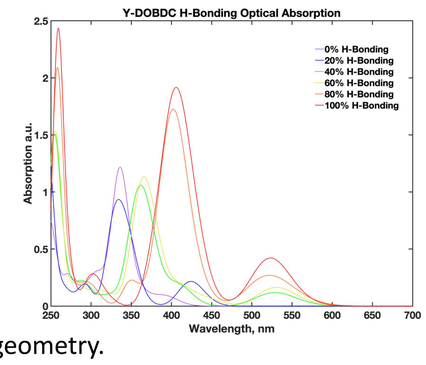
Tuning H-bonds in Y-DOBDC

H-Bond Coordination



Simulated PXRD





- H-bonding required to maintain measured geometry.
- Increased H-bonding induces red shift of primary optical absorption.

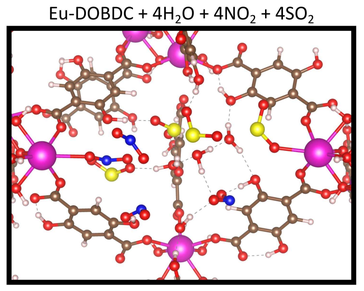
Mixed Acid Gas Dynamics

Ab initio Molecular Dynamics

RE Metal	Mixed Gas Species: 12 H_2O	12 NO_2	12 SO_2	H_2O	NO_2	SO_2	H_2O NO_2 SO_2	4 H_2O 4 NO_2 4 SO_2	6 H_2O 6 NO_2	6 H_2O 6 SO_2	6 NO_2 6 SO_2	H_2O NO_2	H_2O SO_2	NO_2 SO_2
Y														
Eu														
Tb														
Yb														

Complete | Calculating

Eu-DOBDC + 4H_2O + 4NO_2 + 4SO_2



Outcomes

- Complex Gas Interactions.
- Selectivity due to metal choice.
- New gas species formation due to pore confinement.

References

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2. Sava Gallis, D. F., Vogel, D.J., Vincent, G. A., Rimsza, J. M., Nenoff, T. M., NOx Adsorption and Optical Detection in Rare Earth Metal Organic Frameworks, *ACS Appl. Mater. Interfaces*. **2019**, 11, 43270-43277.
3. Vogel, D. J., Sava Gallis, D. F., Nenoff, T. M., Rimsza, J. M., Structure and electronic properties of rare earth DOBDC metal-organic-frameworks. *Phys. Chem. Chem. Phys.*, **2019**, 21, 23085-23093.

Acknowledgements

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