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Stabilization of Rare Earth (RE) DOBDC MOFs by Fluorine

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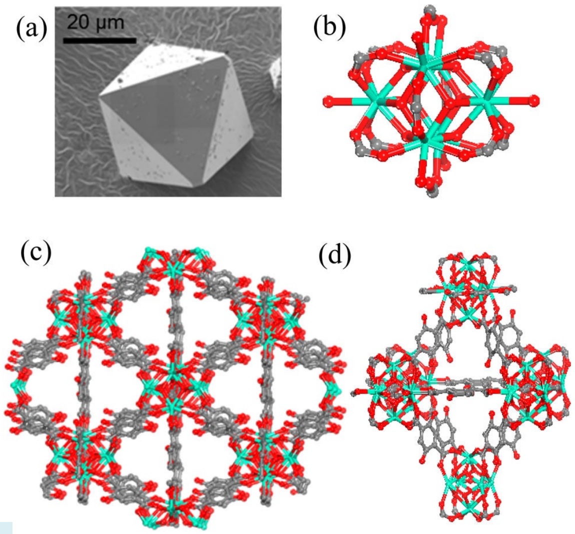
Rare-Earth (RE) MOFs Exhibit Acid Gas Binding to the Metals

- Flu gases contain concentrations of acid gases:
  - 13% CO_2, 6% H_2O, 4% O_2, 50 ppm CO, 420 ppm NO_2, 420 ppm SO_2, 76% N_2
- Rare earth elements preferentially bind acid gases in the structure:
  - Tb^{3+} strong affinity for H_2S
  - Eu has high selectivity for HS
- Previous experimental and computational work identified mechanisms of acid gas (NO_2, SO_2) adsorption in RE-DOBDC MOFs



RE-DOBDC Structure

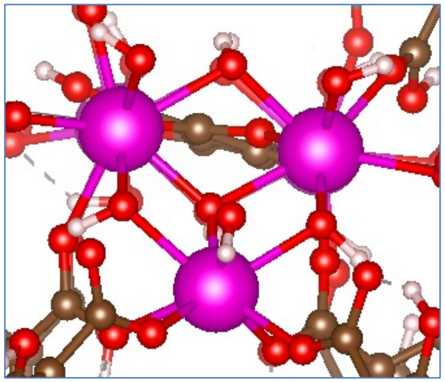
Can changes in the RE-DOBDC MOF structure be used to design new MOFs for acid gas separation?

Refs: Liu and Chen. *Anal. Chem* **85** (2013) 11020, Yip *et al. Dalton Trans* **45** (2016) 928, Sava Gallis *et al. ACS Appl. Mater. Interfaces* ***2019,*** 11, 23270, Sava Gallis *et al. ACS Appl. Mater. Interfaces* ***2017,*** 9, 22268, Sava Gallis et al. *CrystEngComm* ***2018,*** 20, 5919, Sava Gallis et al. *J. Phys. Chem. C* **2018**, 122, 47, 26889

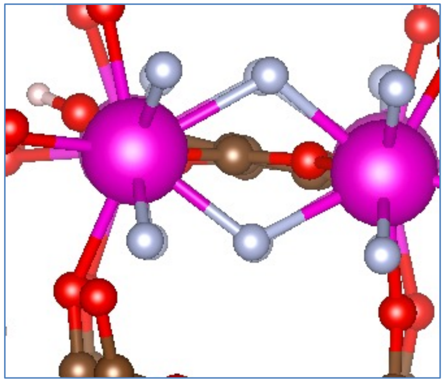
Fluorine may be Stable in the Metal Clusters in RE-DOBDC MOF

- Belief is that F is present in the metal cluster at the μ_3 position instead of OH
- “Fluoro-Bridged Clusters in Rare-Earth Metal-Organic Frameworks” were identified via XPS measurements

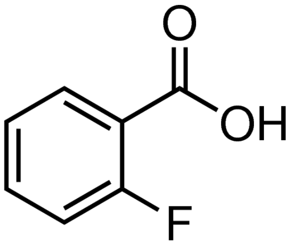
  Vincet *et al.* J. Am. Chem. Soc. **143** (2021) 17995-18000
- F would be introduced through the use of the 2-fluorobenzoic acid modulator



Original Metal Cluster



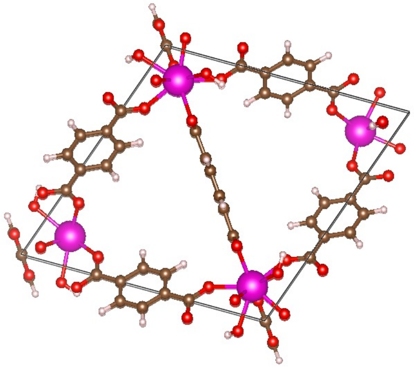
100% Fluorinated RE Cluster



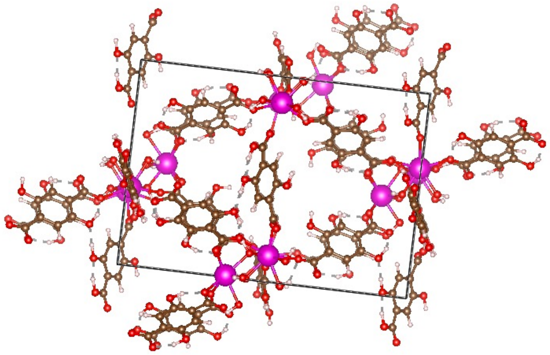
2-fba

How stable is F in the metal cluster? Does it increase stability of the entire MOF?

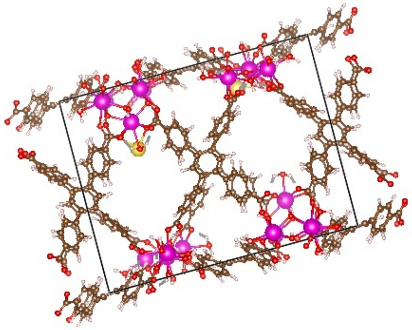
F Replacement was Investigated in Three RE-MOFs



UiO-66



RE-DOBDC



RE-TCPB

Name	UiO-66	RE-DOBDC	RE-TCPB
# OH/RE	4/1	8/2	12/2
Elements	Zr, Y, Eu, Tb, Ho, Yb	Y, Eu, Tb, Ho, Yb	Eu
F placement	Uniform	Uniform/Random	Random

F Effect on Stability Was Investigated In Three RE-DOBDC MOFs

Formation Enthalpy Calculations:

- Periodic density functional theory (DFT) simulations in VASP
- PAW-PBEsol pseudopotential
- 600 eV cut-off
- D3 dispersion correction
- $\Delta H = E_{MOF} - \sum \mu_i$, μ_i = elemental atomic potentials

Experimental Solid-State Magic Angle Spinning (MAS) NMR:

- Y-DOBDC MOFs
- Bruker 600 MHz ^{1}H, ^{19}F MAS
- Bruker 400 MHz ^{1}H/^{19}F CODEX

NMR Calculations:

- Periodic DFT in Quantum-Espresso
- Gauge-Including Projector Augmented Wave (GIPAW) method
- PBE pseudopotential and 90 Ry cut-off
- Computed δ_{iso} values are referenced to experimental value through a linear relationship:

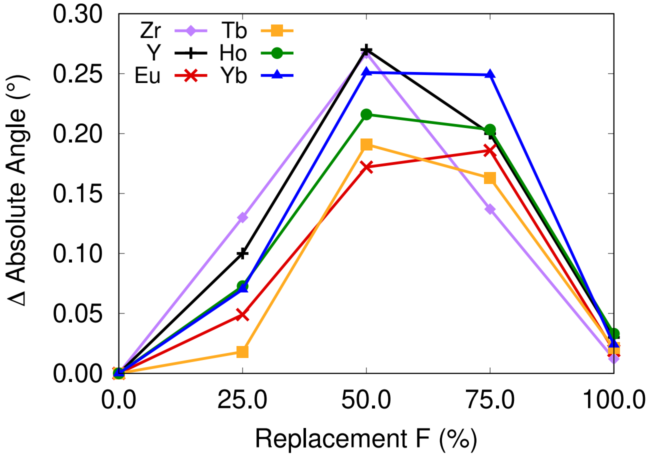
$$\delta^{exp} = \beta - \alpha\sigma^{calc}$$

- β = 89 ppm and α = -0.80 based on previous studies of crystalline fluorides and fluorinated graphene

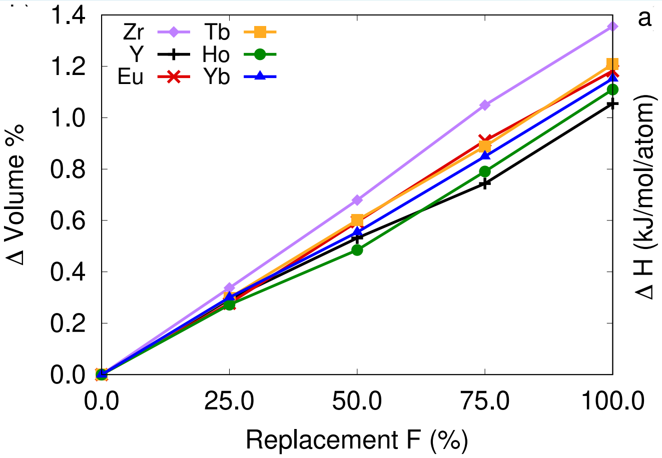
Ref: Rimsza et al. *J. Phys. Chem. C* 125.4 (2021): 2699-2712., Sadoc et al. *Phys. Chem. Chem. Phys.* 13.41 (2011): 18539-18550.

DFT Calculations and NMR Experiments are used to F Concentrations

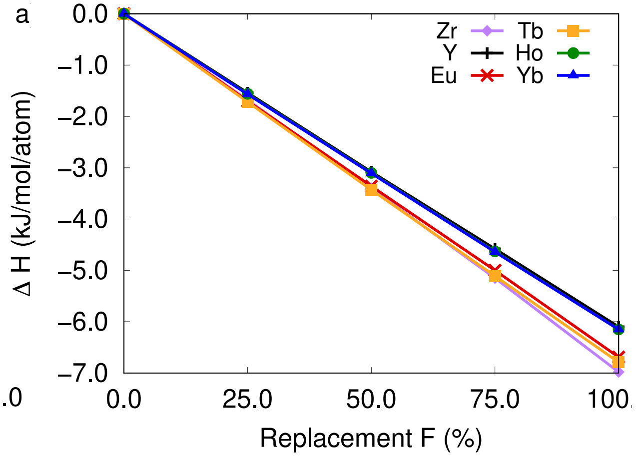
Change in Stability is Linear With F Replacement in UiO-66



- Crystal strain increases under mixed conditions



- Volume decreases with F replacement



- Formation enthalpy increases with F replacement

F Stabilizes UiO-66 Due to Formation of Stronger M-F Bonds

Georgia Institute of Technology
OAK RIDGE National Laboratory
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LEHIGH UNIVERSITY
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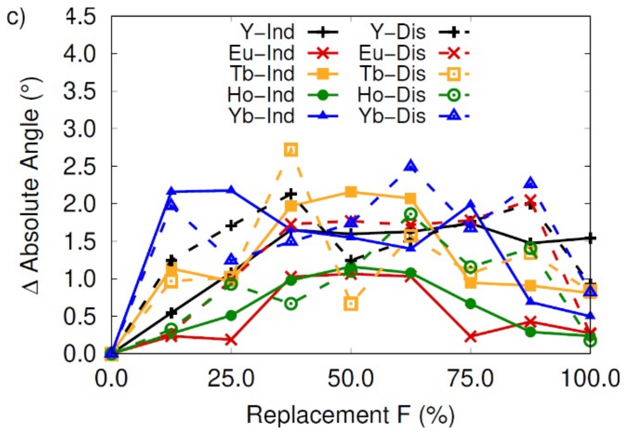
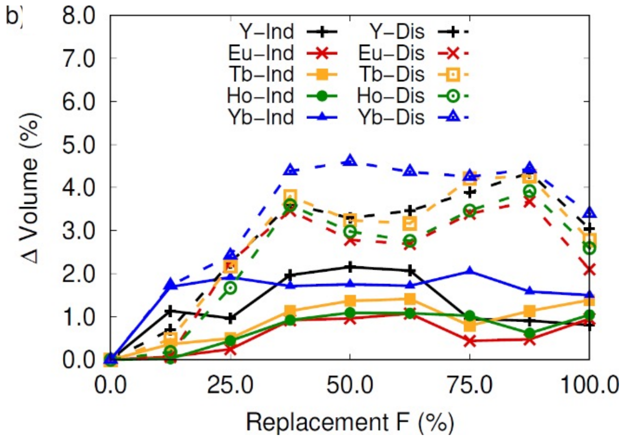
Washington University in St. Louis
WISCONSIN UNIVERSITY OF WISCONSIN-MADISON

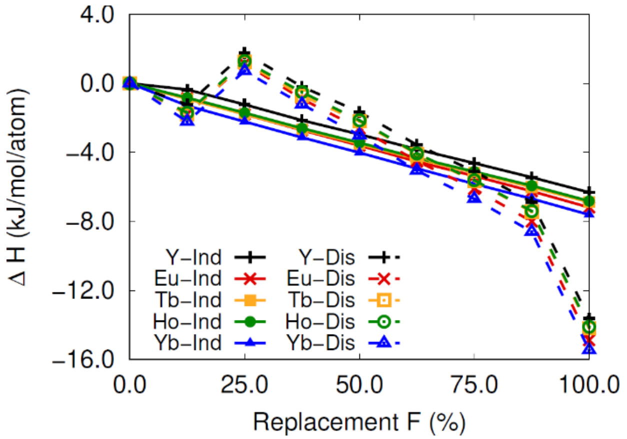
Change in Stability is Site Dependent in RE-DOBDC



- Crystal angle change is sporadic



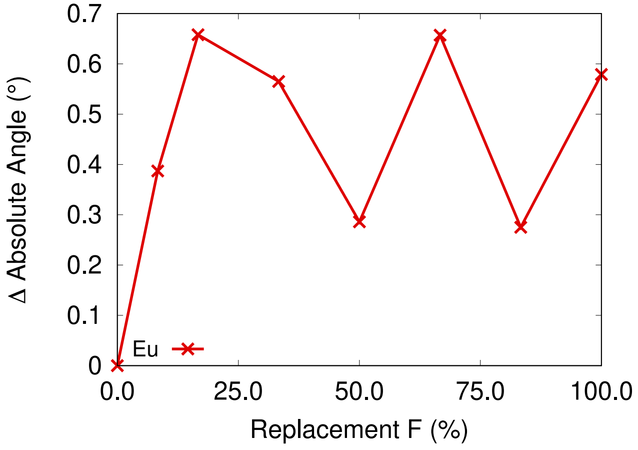
- Greater volume change when F is replaced on both metal sites



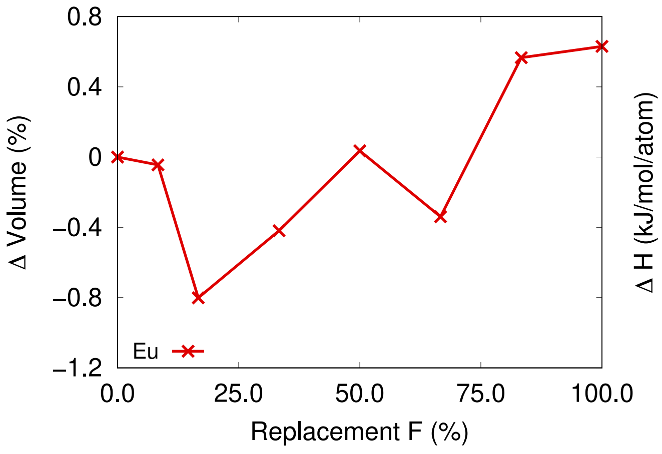
- Single-site replacement is linear
- Random-site replacement is % F dependent

F Should be Found on Two Sites in RE-DOBDC

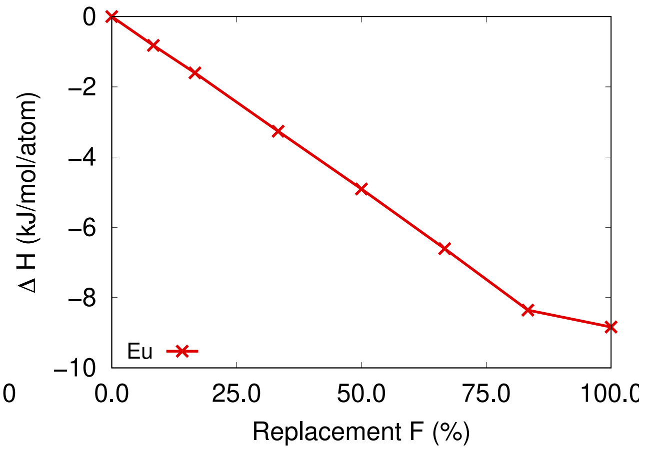
F Stabilization in RE-TCPB is Linear Despite Disorder



- Crystal angle change is sporadic



- Volume initially increases before having an overall decrease



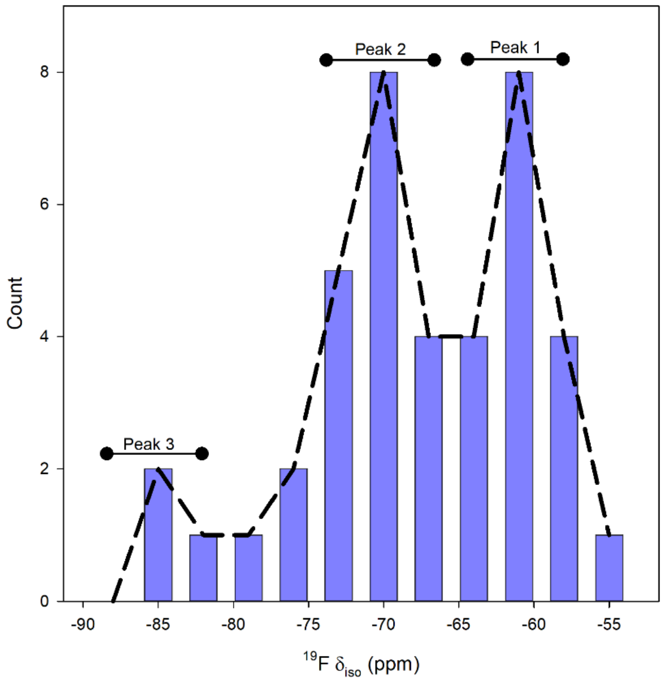
- Stabilization is linear

F Replacement Should Be Found On Multiple RE Sites

Overall, F Replacement Stabilizes DOBDC Based MOFs

- M-F bond strength is greater than M-OH bond strength
- Greater bond strength is shown by shorter bond lengths
- Smaller bond lengths result in smaller crystal cell volumes
- Smaller bond distances and cell volume increase Van der Waals interactions
- F is predicted to be located at multiple metal sites in DOBDC based MOFs

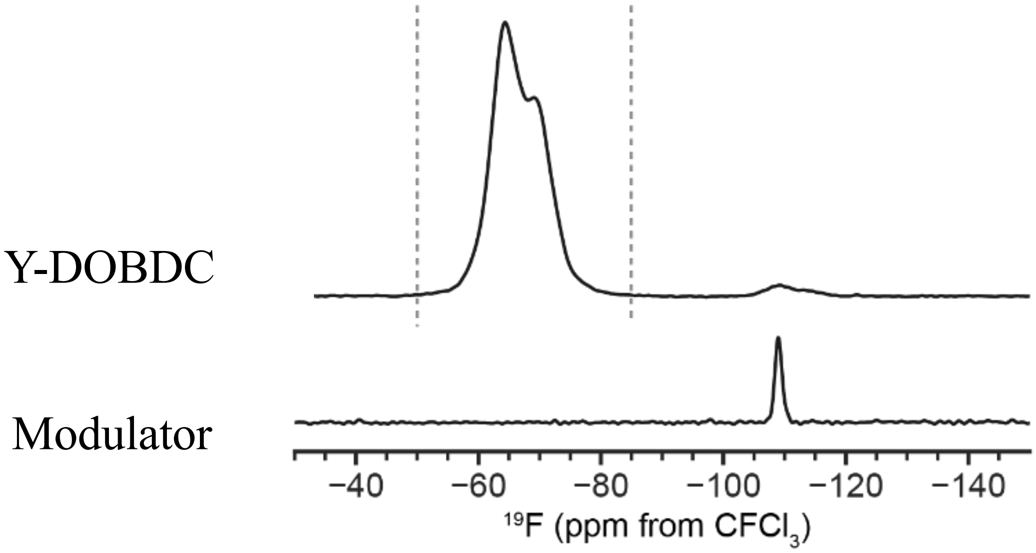
Calculated ^{19}F NMR in Y-DOBDC MOFs at Different Fluorination Levels

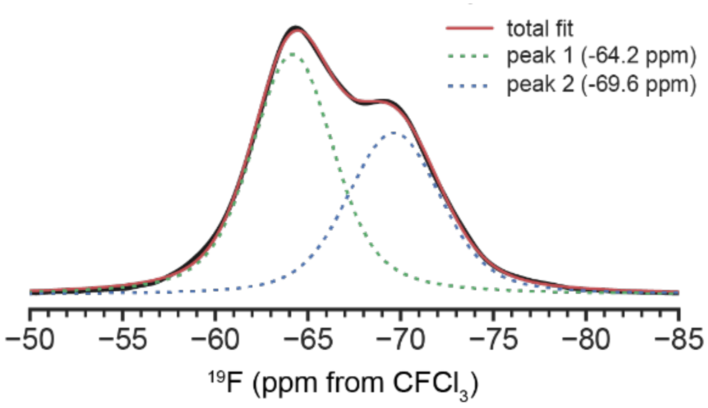


Histogram of calculated ^{19}F δ_{iso} chemical shift data for Y-DOBDC MOF structure across all fluorination levels (25%-100%)

Peak #	^{19}F δ_{iso} (ppm)	100% F	75% F	50% F	25% F
1	-63	25.0	50.0	62.5	50.0
2	-70	75.0	33.3	25.0	0.0
3	-87	0	16.6	12.5	50.0
Ratio Peak 1/Peak 2		3.0	0.67	0.4	0.0

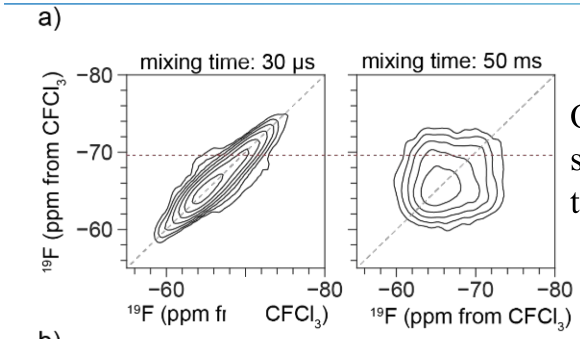
NMR Showed ^{19}F Shift at Different Location than the Modulator



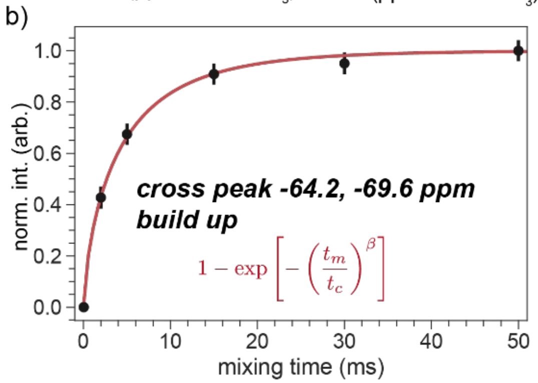


Peak Decomposition Shows Two Unique F Sites

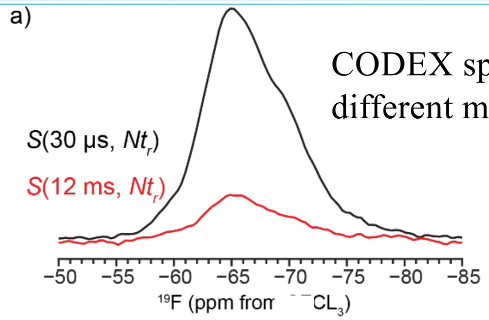
Assignment Of Two Peaks Was Corroborated with 2D NMR



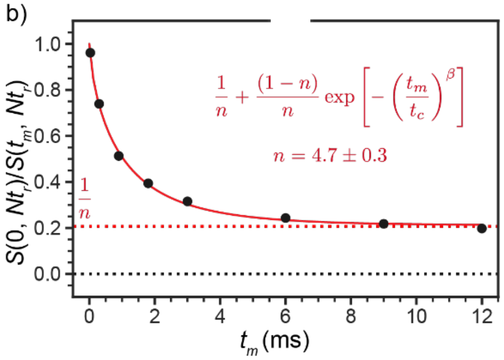
Off diagonal cross peaks show correlation between two peaks



Fast mixing time indicates close F sites



CODEX spectra at different mixing times



n is number of spins

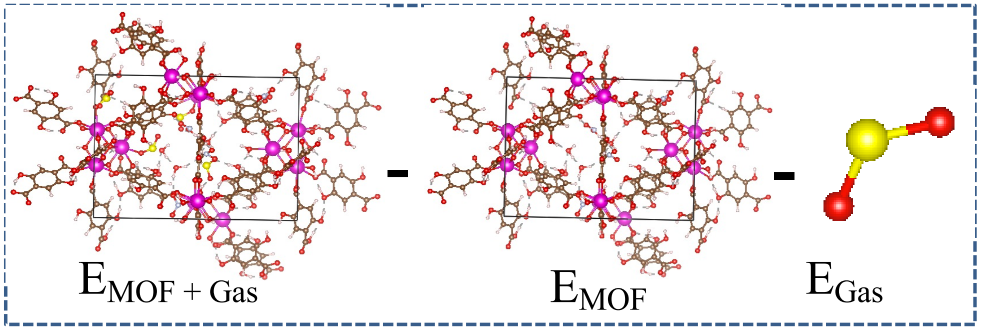
Fitted value of n ~ 4 indicates 4/8 Y-DOBDC sites are fluorinated

Peak area ratio vs mixing time

Y-DOBDC is 50% Fluorinated

Previous Modeling Studies Were On Hydroxide RE-DOBDCs

- Previous computational studies have looked at acid gas interactions in RE-DOBDC MOFs
- Electron withdrawing F and smaller volume/RE bond lengths could affect acid gas adsorption at metal site
- Adsorption energies of H_2O, NO_2 and SO_2 were calculated in 100% OH and 100% F RE-DOBDC MOFs using previous DFT methodology



Does Prescence of F in the Metal Cluster Affect Acid Gas Adsorption?

Fluorine Incorporation Does Not Change Acid Gas Adsorption

Adsorption Energies

(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

Most calculated adsorption energies are less than 5 kJ/mol

Bond Lengths

Å	H_2O		NO_2		SO_2	
	OH	F	OH	F	OH	F
Y	2.46	2.46	2.52	2.56	2.57	2.58
Eu	2.49	2.49	2.55	2.55	2.62	2.62
Tb	2.46	2.46	2.50	2.60	2.57	2.59
Yb	2.41	2.41	2.46	2.53	2.55	2.56
Avg.	2.46 ± 0.03	2.46 ± 0.03	2.51 ± 0.04	2.56 ± 0.03	2.58 ± 0.03	2.59 ± 0.03

Average bond lengths are identical for most systems

Fluorination of Metal Cluster does NOT Change Adsorption Energies

Conclusions

- DFT calculations predicted that F replacement of OH in the RE cluster of DOBDC based MOFs increase the formation enthalpy
- Calculations also predicted that F replacement would be scattered in RE-DOBDC MOFs
- NMR confirmed that F was present in the MOF and showed similarities to computed NMR spectra
- Calculated acid gas adsorption energies for fluorinated MOFs varied little from hydroxide MOFs in RE-DOBDC.

Acknowledgements

Questions?

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Article

Dramatic Enhancement of Rare-Earth Metal−Organic Framework Stability Via Metal Cluster Fluorination

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