Unique Optical and Electronic Effects of RE-DOBDC MOFs with Acid Gas Adsorption

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SAND2020-3068D

UNCAGE-ME

Georgia Tech Energy Frontier Research Center

Introduction

AIM: Design and synthesize a RE-containing MOF for the selective adsorption of NO_x and SO_x from flue streams

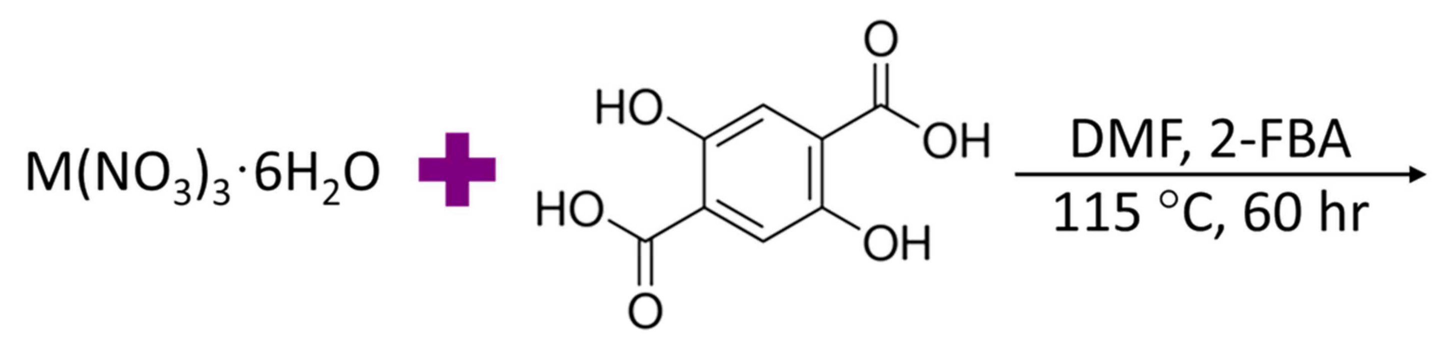
UNCAGE-ME Center exemplar "Complex Mixtures":

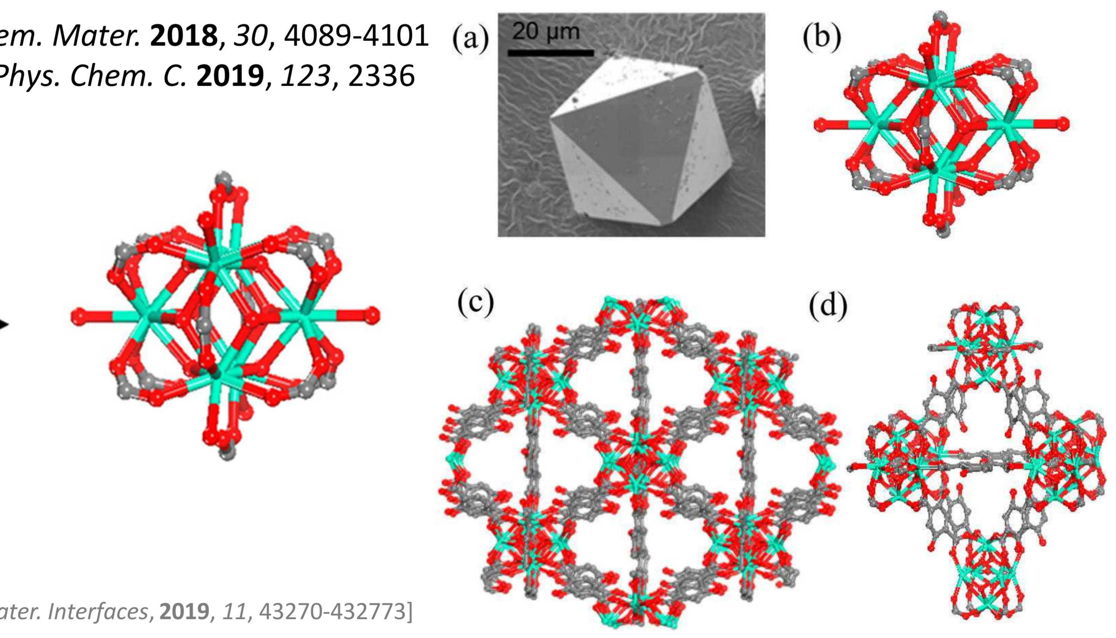
- ***Coal-fired power plant flue gas*** (13% CO_2, 6% H_2O, ~ 4% O_2, 50 ppm CO, 420 ppm NO_2, 420 ppm SO_2, 76% N_2)

- MOFs are inorganic-organic hybrid materials with extremely high surface area and the ability to form CUSs
- Rare earth (RE) elements selectively bind to acid gases (NO_x and SO_x) [1]
- RE-DOBDC (RE – Eu, Y, Tb, Yb) MOFs selectively adsorb acid gases from a humid gas stream – In collab. with GATech
- Retention of structure by PXRD after exposure to acid gases. Investigations ongoing with neutron PDF – In collab. with ORNL
- RE-DOBDC shows a reduction in paramagnetism with adsorption of NO_x – In collab. with CINT
- Fluorescence of MOF dependent on the presence of free hydroxyls

SO_x/H_2O – *Chem. Mater.* **2018**, *30*, 4089-4101

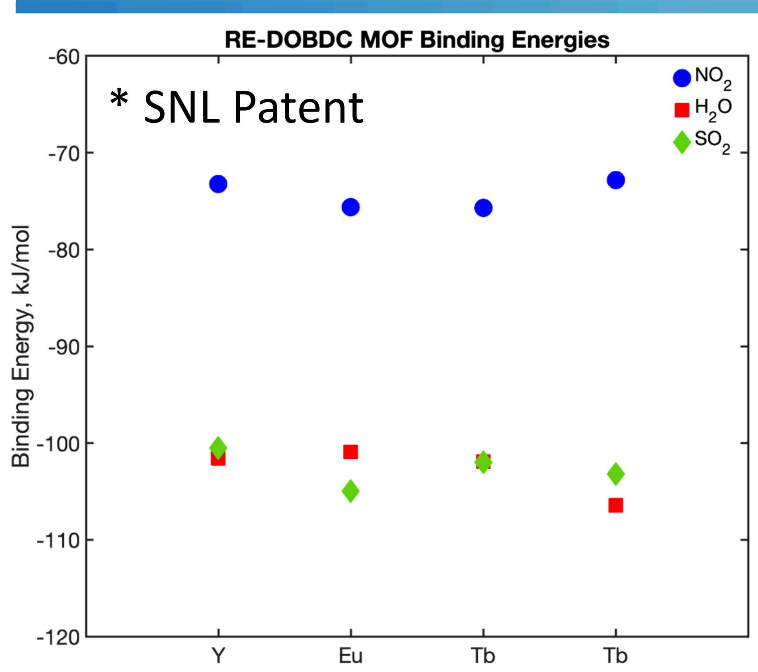
NO_x/H_2O – *J. Phys. Chem. C.* **2019**, *123*, 2336





[1] Sava Gallis *et al.*, *ACS Appl. Mater. Interfaces*, **2017**, *9*, 22268; *CrystEngComm.*, **2018**, *20*, 5919; *ACS Appl. Mater. Interfaces*, **2019**, *11*, 43270-432773]

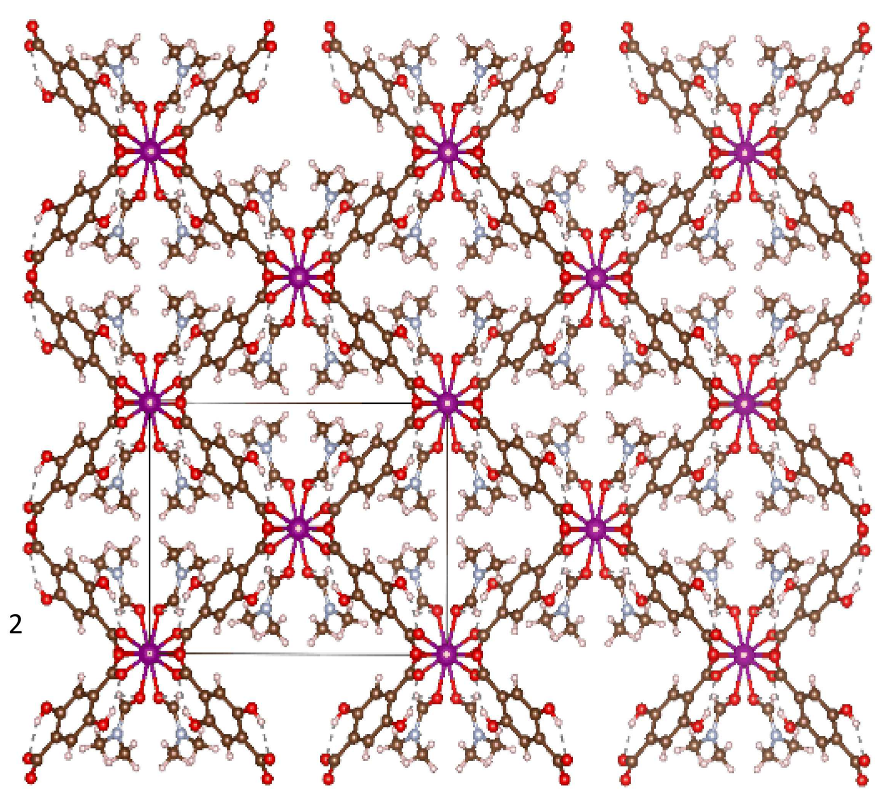
Photoluminescence

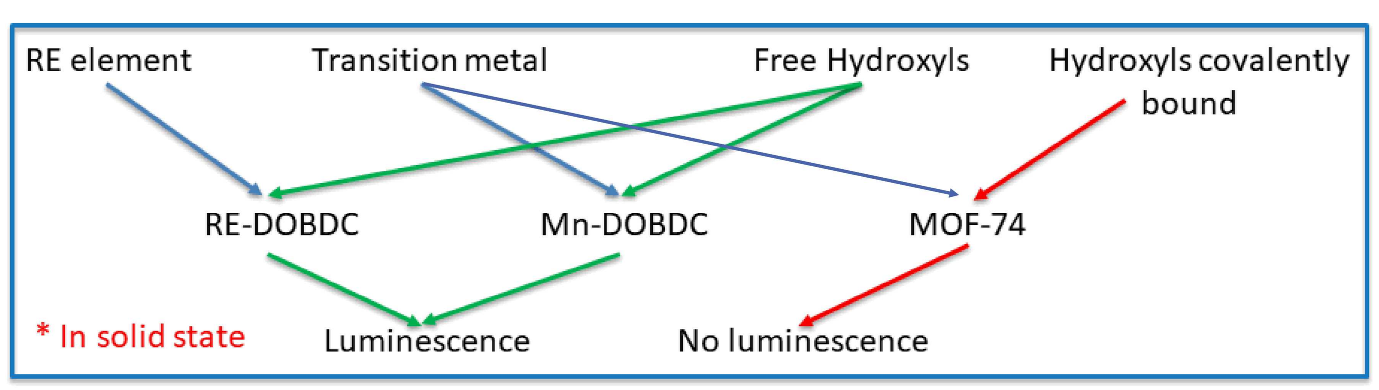


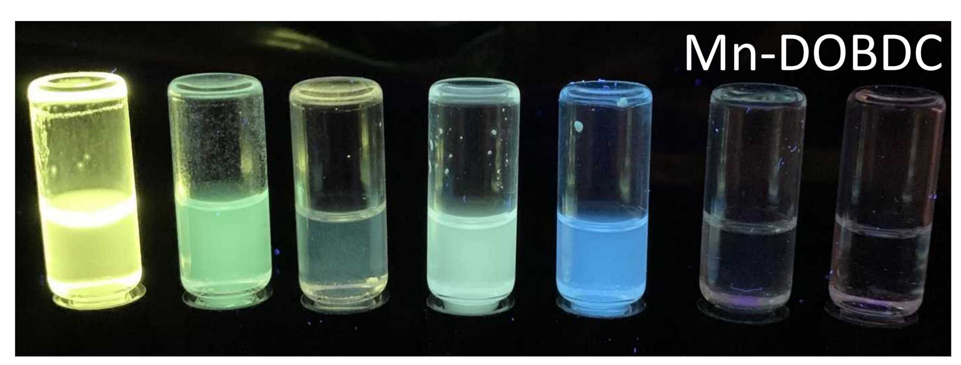
Binding energies rationalized through DFT modelling

(*** See Jon Vogel's Poster ***)

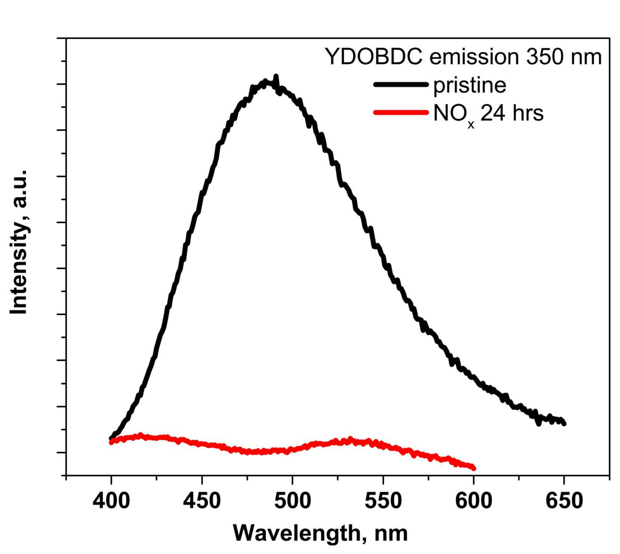
- Competitive binding to metal site between SO_x and H_2O
- NO_x : lower binding E than H_2O
- In humid NO_x, H_2O binds to the metal so NO_x only has the ability to bind to the linker
- Luminescence in MOF arises from the free linker hydroxyls
  - Corroborated by comparing with MOF-74 and Mn-DOBDC [2]







[2] Henkelis *et al.*, Tuned Luminescent Properties of DOBDC Containing MOFs: the Role of Free Hydroxyls, *ACS Appl. Mater. & Interfaces*, **2020**, *Submitted*

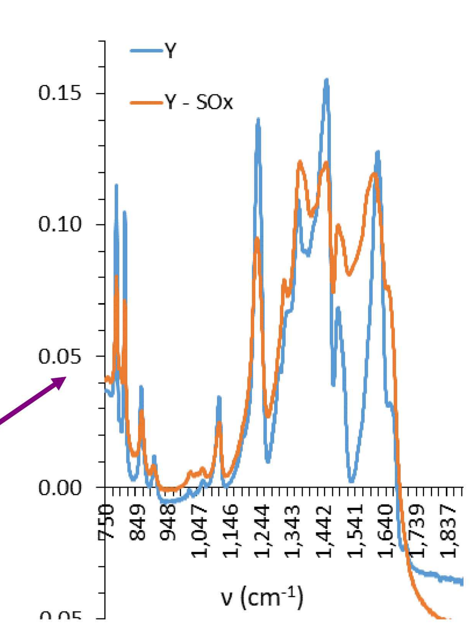


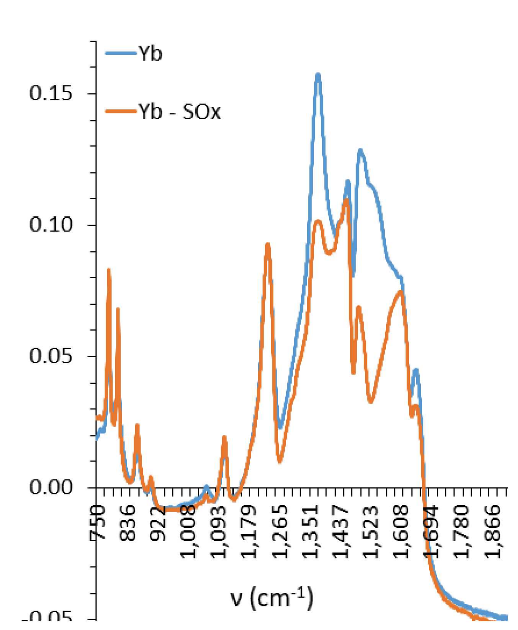
RE-DOBDC with NO_x:

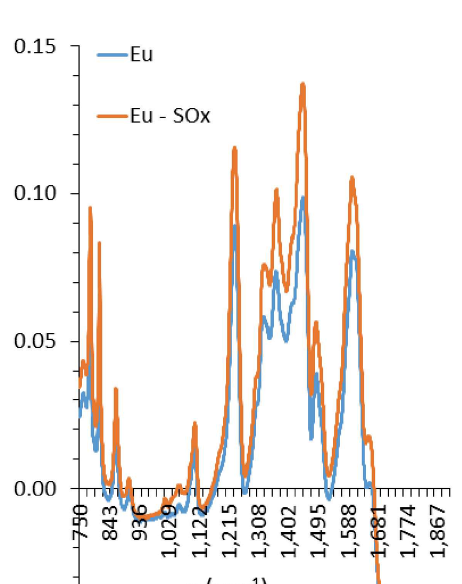
- Binds to linker hydroxyls
- Quenches photoluminescence
- No change in PXRD

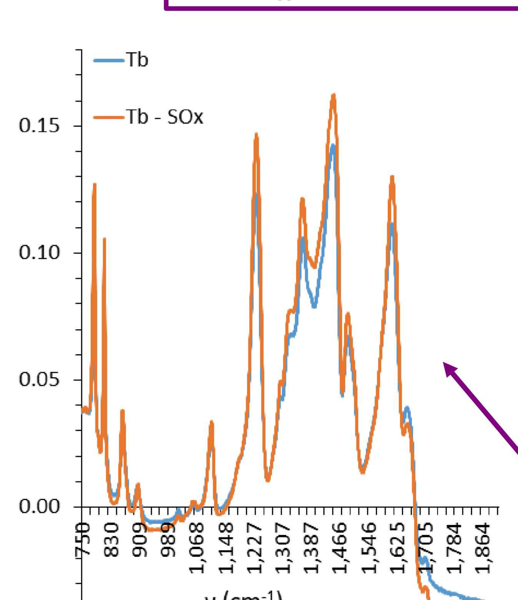
Y-DOBDC and Yb-DOBDC:

- Clear change in IR pre- and post-SO_x adsorption
- SO_x binding to metal center









RE-DOBDC with SO_x:[3]

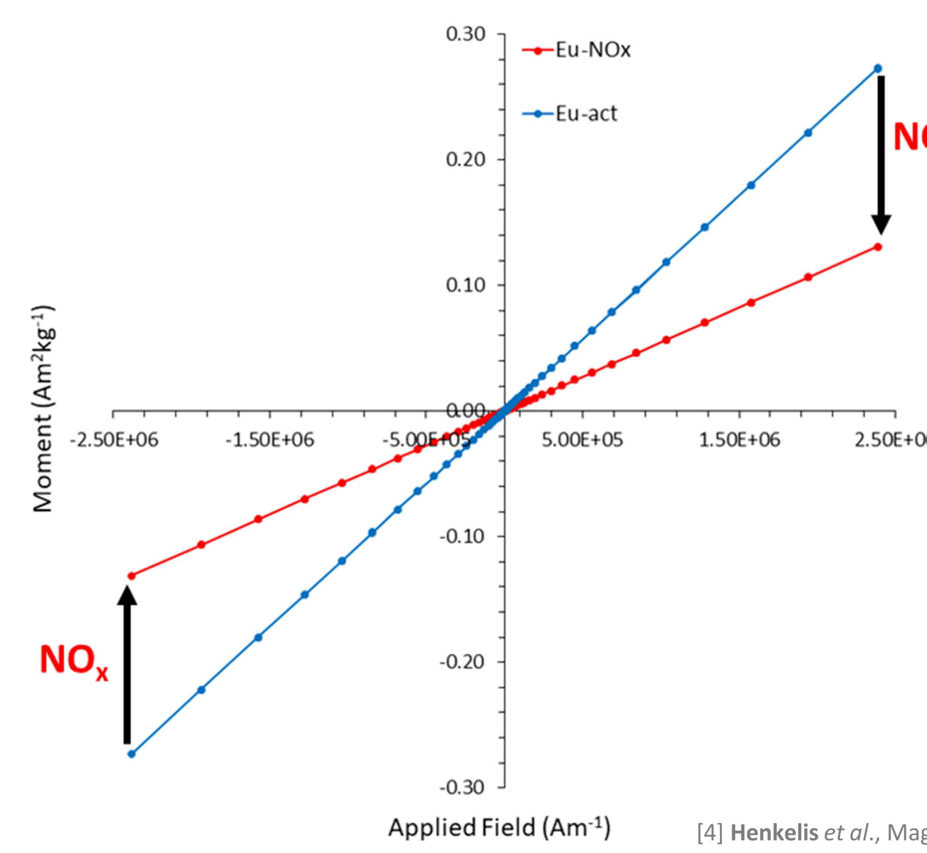
- Binds to the RE metal center
- No quenching in photoluminescence
- No change in PXRD
- Clear metal dependency: Eu and Tb vs Y and Yb

Eu-DOBDC and Tb-DOBDC:

- no change in IR
- SO_x physisorbed within pores

[3] Henkelis *et al.*, Selective adsorption of SOx from humid gas streams by DOBDC-containing MOFs, **2020**, *In Preparation*;

Magnetism

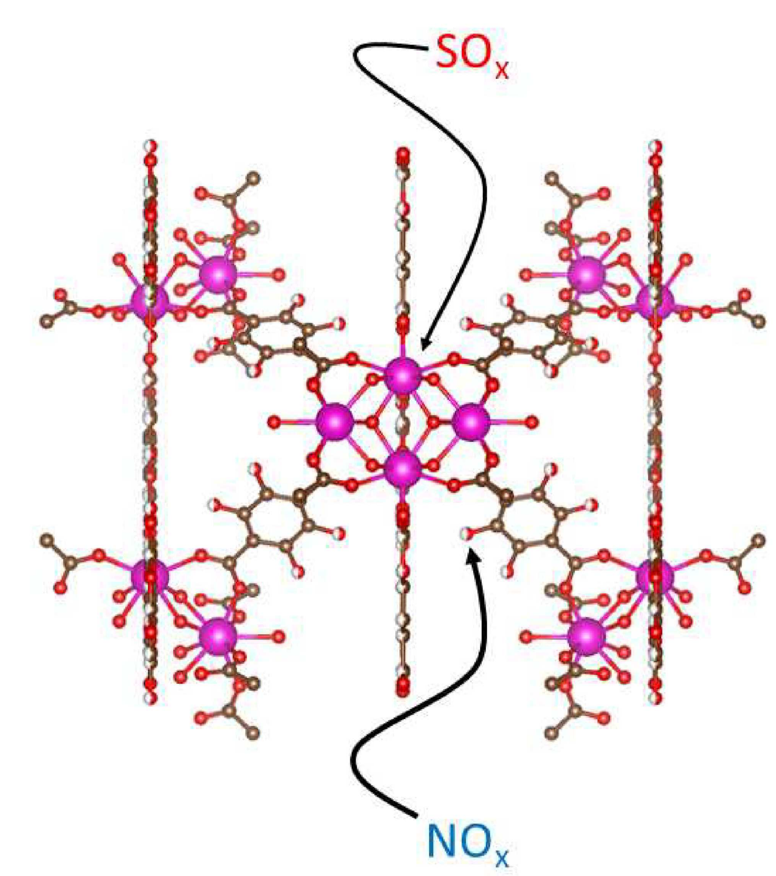


- **Magnetic moment of metal center is imparted to MOF framework**
- **NO_x is an electron withdrawing group**
- **Net result: reduction in magnetic susceptibility (χ) of overall MOF framework**
- Eu, Tb, Yb-DOBDC – paramagnetic susceptibility
- Eu > Tb > Yb   Δχ with addition of NO_x
- Charge transfer of 1 upe from: metal –> ring –> EW group ∴ reducing magnetism
- Y-DOBDC – diamagnetic; susceptibility ↓ with NO_x [4]

[4] Henkelis *et al.*, Magnetic Tunability in RE-DOBDC MOFs via NOx Acid Gas Adsorption, *ACS Appl. Mater & Interfaces*, **2020**, *Submitted*

Conclusions

- RE-DOBDC MOFs are structurally stable to humid acid gas streams – studies into the structure/property relationships are on-going
- Free linker hydroxyls = fluorescent MOF
- Quenching of photoluminescence with adsorption of NO_x – ligand binding
- No quenching with adsorption of SO_x – metal binding
- NO_x reduces overall magnetism of RE-DOBDC
- Eu & Tb-DOBDC – use as a dual optical and magnetic sensor for selectively adsorbing NO_x from mixed acid gas streams
  - Quenching of photoluminescence and large Δχ
- Y & Yb-DOBDC – use as an adsorbent for SO_x from NO_x/SO_x streams
  - S-species seen in IR
- On-going research – **Investigation into competitive NO_x/SO_x binding in DOBDC containing MOFs (RE-DOBDC, MOF-74) for selective removal of acid gases from flue streams**



Acknowledgements

This work was supported as part of UNCAGE-ME, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DE-SC0012577.

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