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Selectivity and Stability of RE-DOBDC MOFs, and their use in the Optical and Magnetic Detection of Acid Gases

UNCAGE-ME

Susan E. Henkelis†, D. J. Vogel, J. Rimsza, D. Huber, T. M. Nenoff

sehenke@sandia.gov

†*Sandia National Laboratories, Albuquerque, NM, USA*

U.S. DEPARTMENT OF ENERGY | Office of Science

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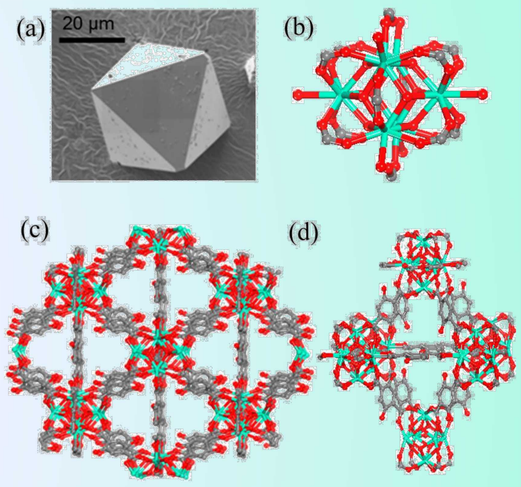
Introduction

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)

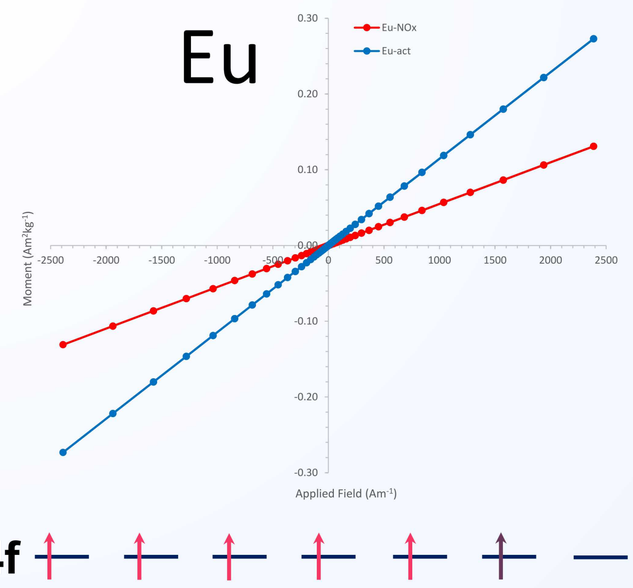


- Metal-Organic frameworks (MOFs) are inorganic-organic hybrid materials characterized by their extremely high surface area, 3D structure and ability to form coordinatively unsaturated sites
- Rare earth (RE) elements are known to selectively and preferentially bind to acid gases (NO_x and SO_x) [1]
- RE-DOBDC (RE – Eu, Y, Tb, Yb) MOFs have recently been shown to selectively adsorb acid gases from a humid gas stream whereby adsorption of NO_x produced a quenching of photoluminescence [1] and SO_x did not [2] – 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 [3] – In collab. with CINT

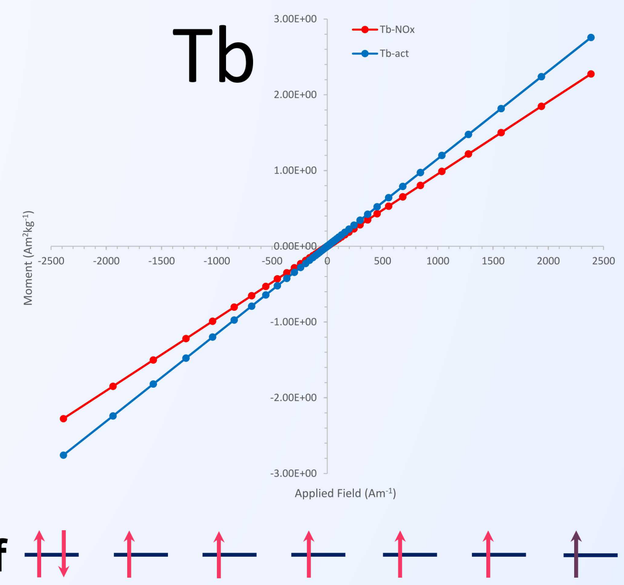
SO_x – *Chem. Mater.* **2018**, *30*, 4089-4101
NO_x – *J. Phys. Chem. C.* **2019**, *123*, 2336

[1] Sava Gallis *et al*., *ACS Appl. Mater. Interfaces*, **2017**, *9*, 22268; *CrystEngComm*., **2018**, *20*, 5919; *ACS Appl. Mater. Interfaces*, **2019**, *11*, 43270-43277; [2] **Henkelis** *et al*., Selective adsorption of SOx from humid gas streams by DOBD-containing MOFs, **2019**, *In Preparation*; [3] **Henkelis** *et al*., Selectivity and Stability of RE-DOBDC MOFs, and their use in the Optical and Magnetic Detection of Acid Gases, **2019**, *In Preparation*

Magnetic Susceptibility with NO_x



4f ↑ ↑ ↑ ↑ ↑ ↑ —



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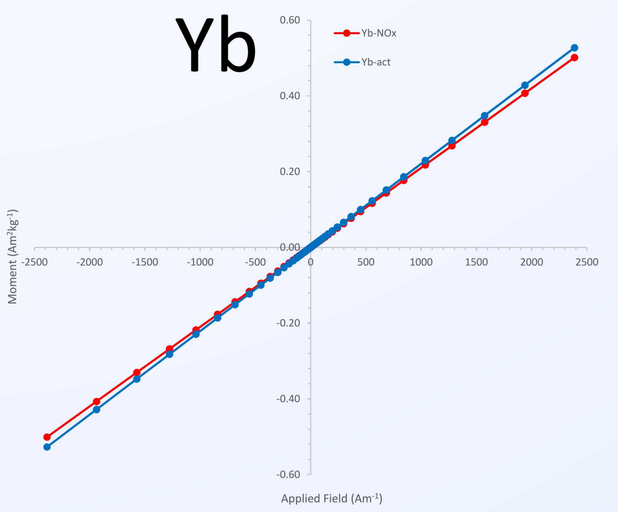

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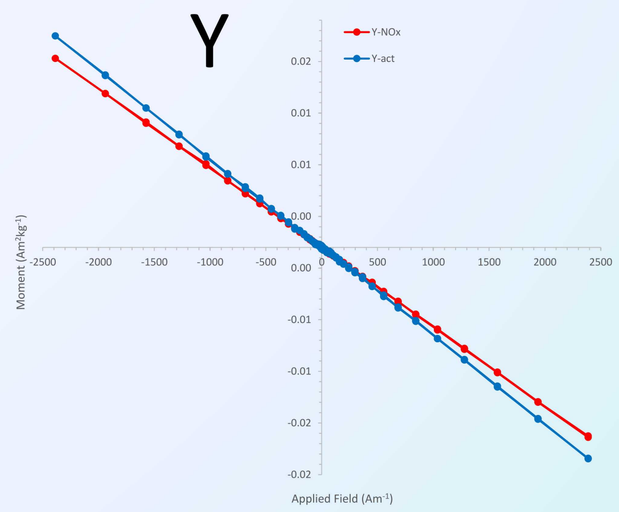


- RE-DOBDC MOFs were produced under solvothermal methods in DMF at 120 °C for 3 days
- Each MOF was activated (**blue**) and then subsequently loaded with humid NO_x (**red**)
- Each MOF was investigated upon using a VersaLab VSM as a function of metal center.

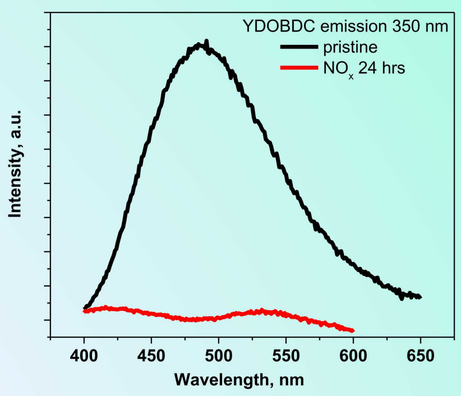
- Eu, Tb, Yb-DOBDC highlight a classic paramagnetic susceptibility with the susceptibility reduced upon addition of NO_x
- Eu > Tb > Yb $\Delta\chi$ with addition of NO_x (EW group)
- $\Delta\chi$ increases with increase in amount of unpaired electrons
- Charge transfer of 1 unpaired electron (**purple**) from: metal –> ring –> EW group ∴ reducing magnetism

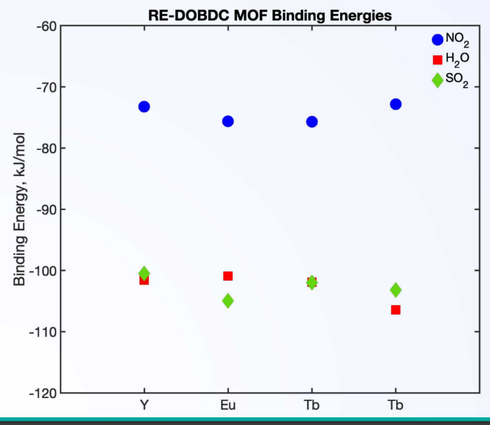
- Y-DOBDC – diamagnetic due to no f electrons, with a decrease in diamagnetic susceptibility with NO_x
- NO_x is a paramagnetic molecule and therefore reduces diamagnetism

Photoluminescence

As made RE-MOFs under UV
- Obvious color changes from visible light powder

- Competitive binding to metal site between SO_x and H_2O
- NO_x has a much lower binding energy and will bind to the linker with the H_2O binding to the metal site





- As-made samples fluoresce under UV light
- Fluorescence arises from the inker

- NO_x binds to the open hydroxyls on the linker – quenching emission
- SO_x binds to CUS metal sites – no quenching of fluorescence

Conclusions

Eu 4f ↑ ↑ ↑ ↑ ↑ ↑ — NO_2^+

- NO_x reduces overall magnetism of RE-DOBDC
  - Eu, Tb, Yb – paramagnetic susceptibility
  - Eu > Tb > Yb $\Delta\chi$ with addition of NO_x
  - Y – diamagnetic susceptibility
- Quenching of photoluminescence with adsorption of NO_x – ligand binding
- No quenching with adsorption of SO_x – metal binding

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

Away on travel – please see Jon Vogel
Or email at sehenke@sandia.gov

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