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Unique Magnetic Responses in RE-DOBDC MOFs with NO_x Adsorption

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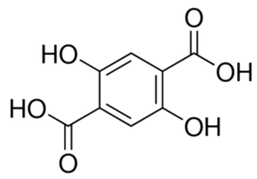
Introduction

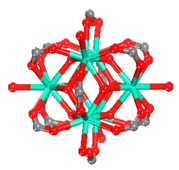
AIM: Design and synthesize a RE-containing MOF for the selective adsorption of NO_x and SO_x from flue streams

UNCAGE-ME Center exemplar "Complex Mixtures":

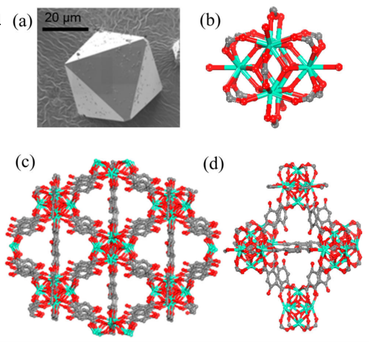
- ***Coal-fired power plant flue gas*** (13% CO_2, 6% H_2O, ~ 4% O_2, 50 ppm CO, 420 ppm NO_2, 420 ppm SO_2, 76% N_2)

- 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]
- Flue gases are produced from combustion processes and are a large environmental concern
- ***Detection and capture of toxic NO_x*** is important for emissions control of exhaust gases and human health
- RE-DOBDC shows a reduction in paramagnetism with adsorption of NO_x – In collab. with CINT
- RE-DOBDC show potential for use as a ***magnetic sensor to detect NO_x***

$M(NO_3)_3 \cdot 6H_2O$ +  DMF, 2-FBA, 115 °C, 60 hr

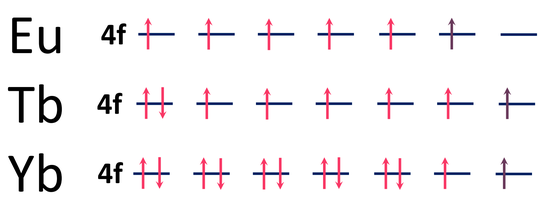


SO_x/H_2O – *Chem. Mater.* **2018**, *30*, 4089-4101
NO_x/H_2O – *J. Phys. Chem. C.* **2019**, *123*, 2336



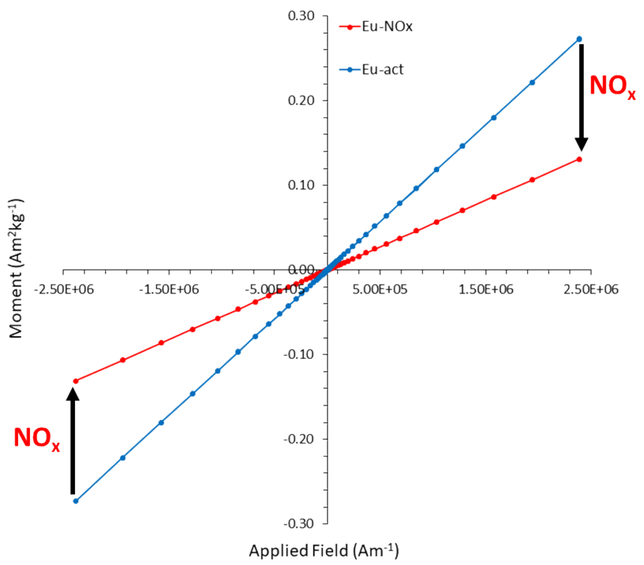
[1] Sava Gallis *et al.*, *ACS Appl. Mater. Interfaces*, **2017**, *9*, 22268; *CrystEngComm.*, **2018**, *20*, 5919; *ACS Appl. Mater. Interfaces*, **2019**, *11*, 43270-432773]

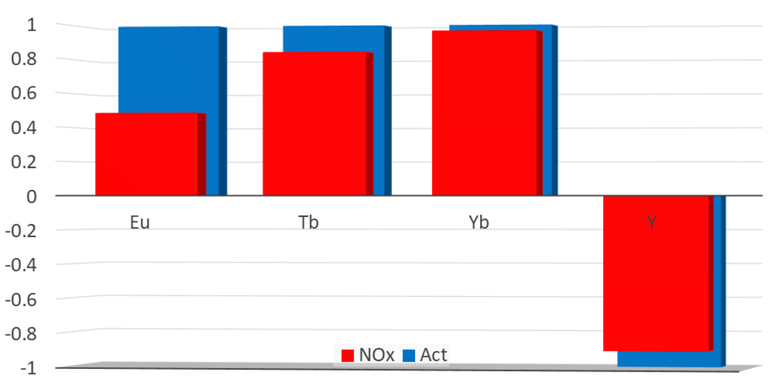
The effect of 1 unpaired f electron



- 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.

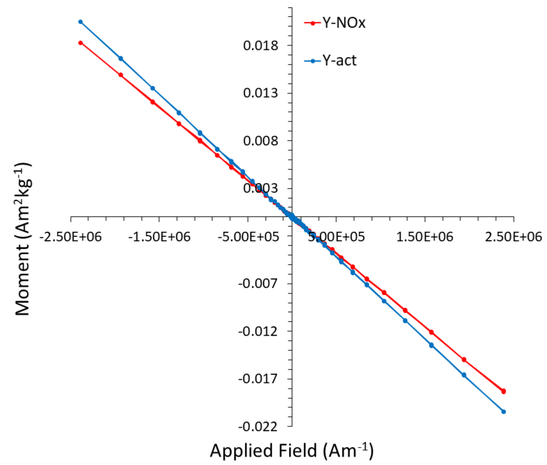
- Eu, Tb, Yb-DOBDC highlight a classic paramagnetic susceptibility with the susceptibility reduced upon addition of NO_x
- **Eu > Tb > Yb Δχ with addition of NO_x (EW group)**
- Δχ increases with increase in amount of unpaired electrons
- Charge transfer of 1 unpaired electron (**purple**) from: metal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





- Comparison of the change in magnetic susceptibility for RE-DOBDC MOFs pre- and post-NO_x exposure
- **Largest change = Eu-DOBDC**
- Positive values = paramagnetic
- Negative values = diamagnetic

Paramagnetic vs. Diamagnetic

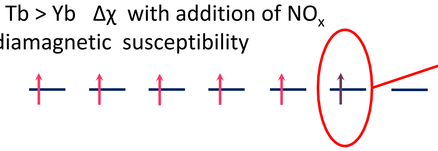


- **Y contains no f electrons**
- **Y^{3+} is paramagnetic**
- **Y donates its 1 upe to form the MOF framework**
- Y-DOBDC – diamagnetic; susceptibility ↓ with NO_x [4]

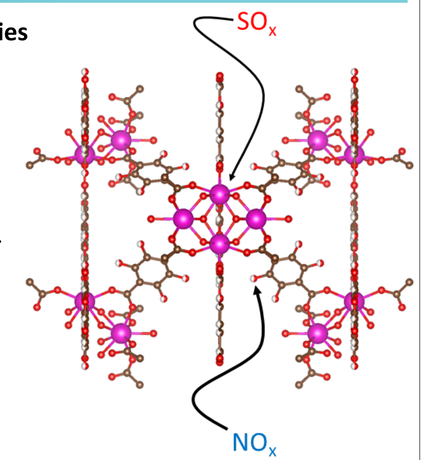
[4] **Henkelis** *et al.*, Magnetic Tunability in DOBDC MOFs via Acid Gas Adsorption, *ACS Appl. Mater. Interfaces*, **2020**, *12*, 19504-19510

Conclusions

- **RE-DOBDC MOFs are structurally stable to humid acid gas streams – studies into the structure/property relationships are on-going**
- **Potential ability for use as a magnetic sensor for NO_x**
- **Complimentary to optical and electronic sensing methods for NO_x** [1]
- NO_x reduces overall magnetism of RE-DOBDC
  - Eu, Tb, Yb – paramagnetic susceptibility
  - Eu > Tb > Yb Δχ with addition of NO_x
  - Y – diamagnetic susceptibility

Eu 4f  NO_2^+

- 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 $H_2O/NO_x/SO_x$ binding in DOBDC containing MOFs (RE-DOBDC, MOF-74) for selective removal of acid gases from flue streams

[1] Sava Gallis *et al.*, *ACS Appl. Mater. Interfaces*, **2019**, *11*, 43270-432773, **Henkelis** *et al.*, *ACS Appl. Mater. Interfaces*, **2020**, *12*, 22845-22852, Small *et al.*, *US Patent Application*, **2021**

Acknowledgements

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