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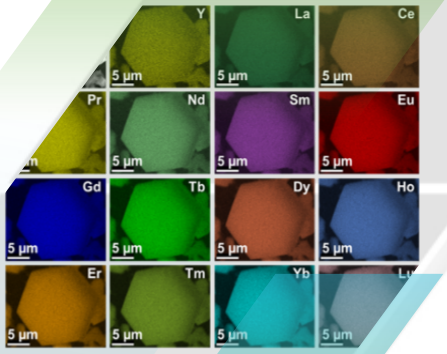
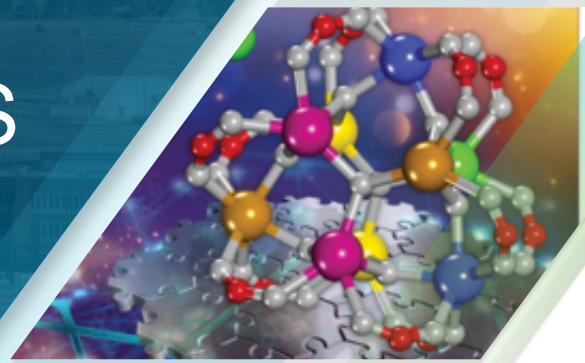
IMPACT OF HETEROGENEITY ON ELECTRONIC STRUCTURES IN HETEROMETALLIC RARE EARTH METAL-ORGANIC FRAMEWORKS

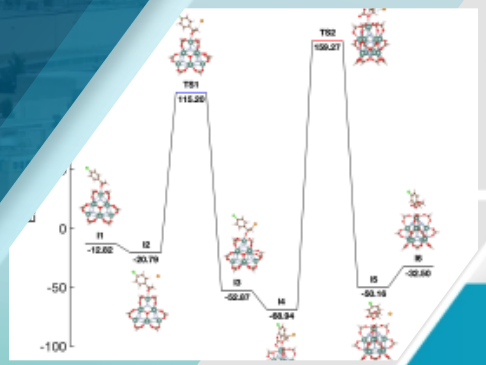
Jon Vogel

2024 Fall American Chemical Society

18 August 2024







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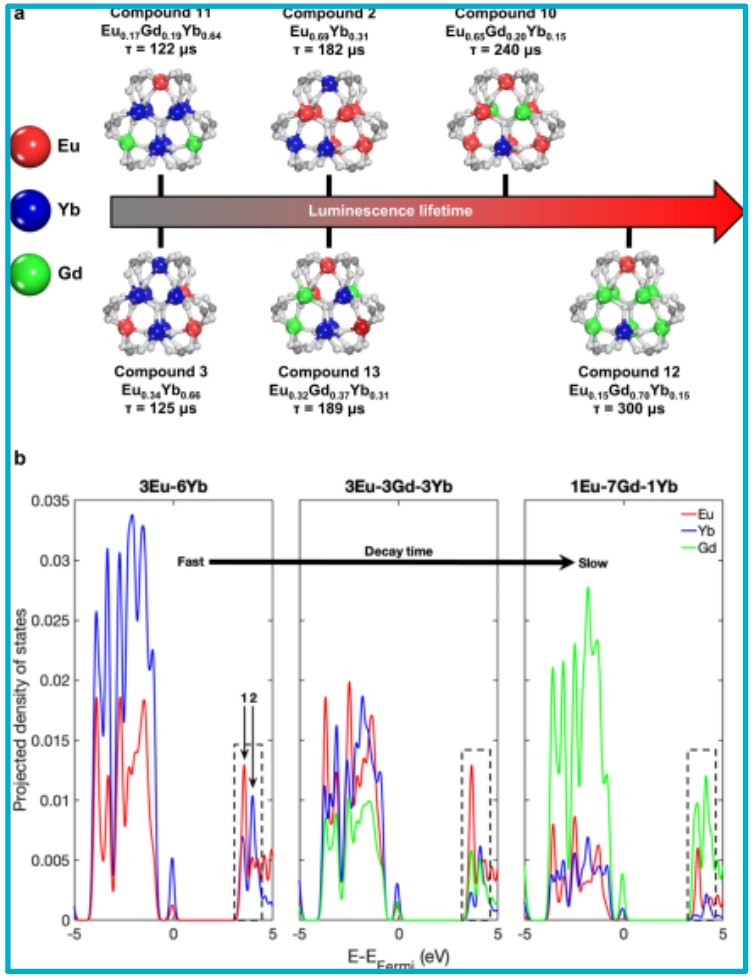
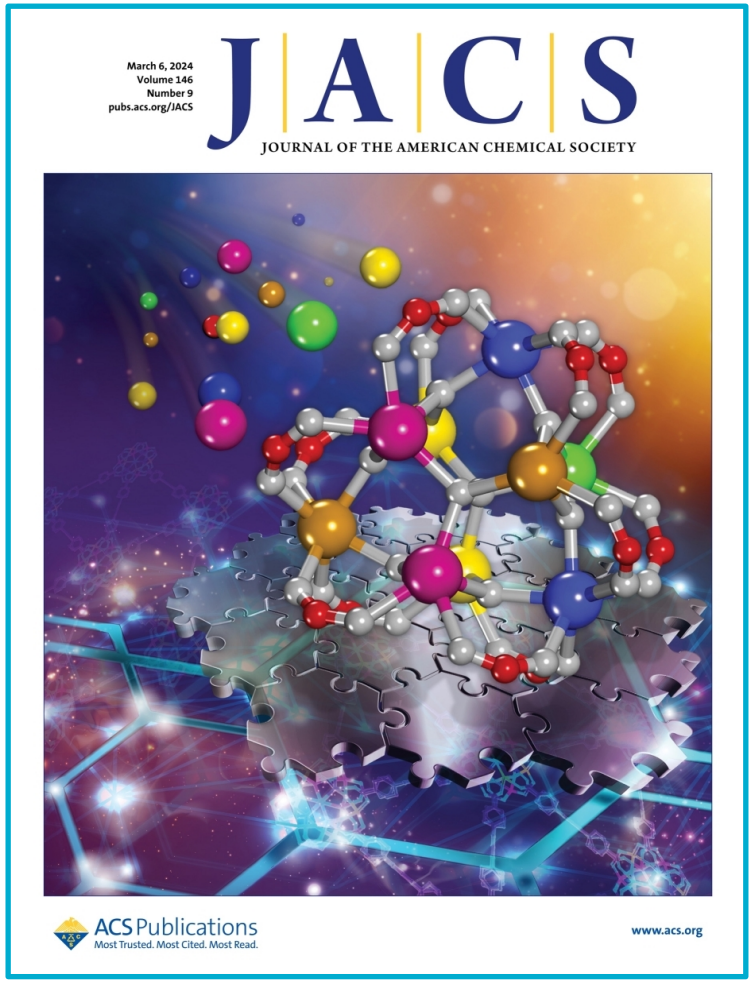
RECENT WORK TO UNDERSTAND RARE EARTH HETEROMETALLIC MOFS

Heterometallic MOFs for Directing Photoexcitation



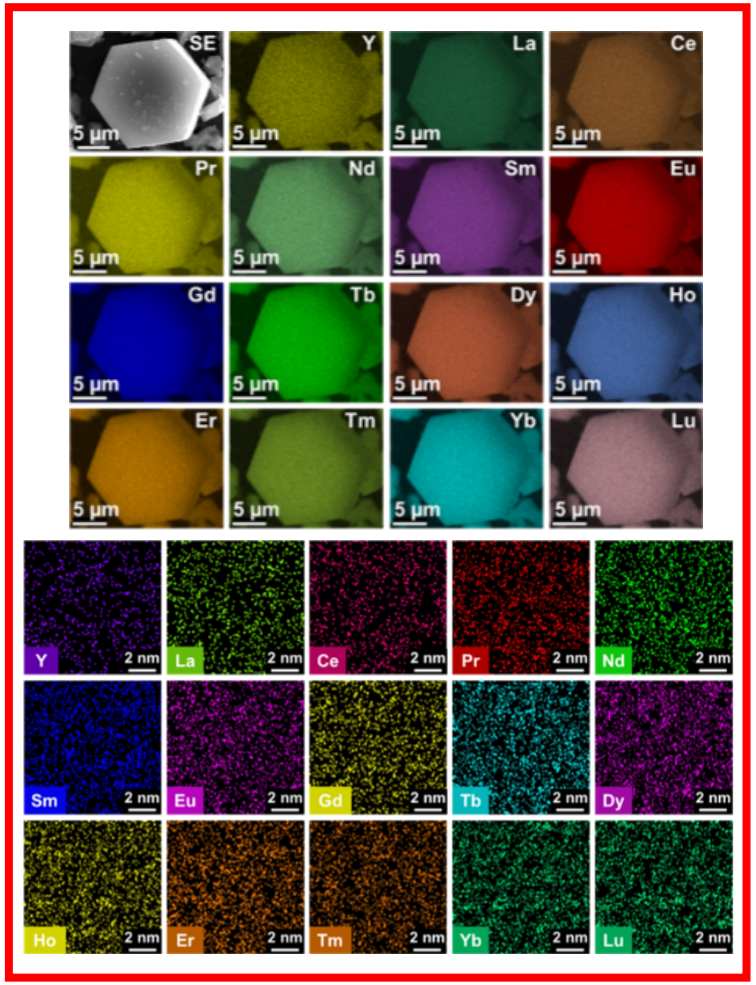
Deneff, J.I, *et al.*
Nat Commun
14, 981 (2023)

Characterization of Heterometallic MOFS



R. Eric Sikma, *et al.*
Journal of the American Chemical Society
2024 *146* (9), 5715-5734

Newly Developed High Entropy RE-MOFs

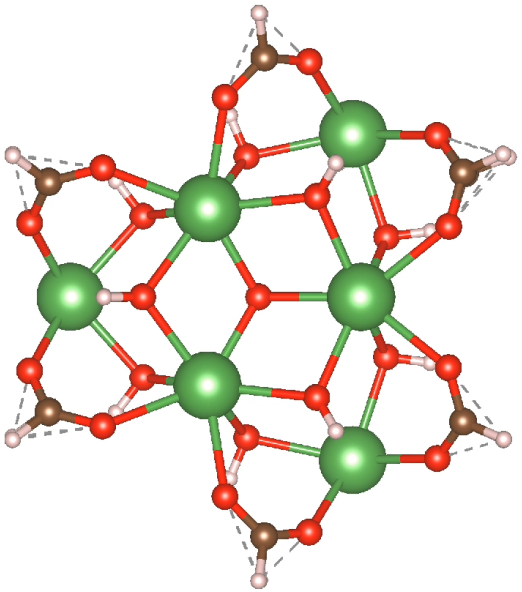


R. Eric Sikma, *et al.*
Advanced Materials
2024. *In review*

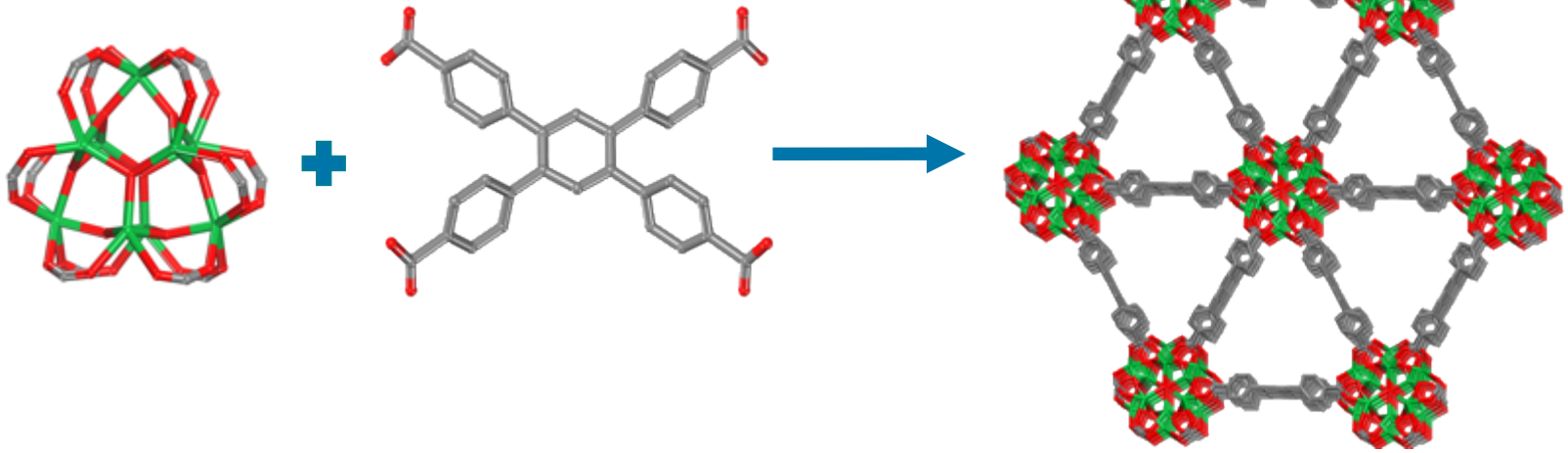
DEGREES OF FREEDOM IN MATERIALS DESIGN

Heterometallic MOFs

$[M_9(COOH)_{12}O_2(OH)_{12}]^{-1}$



Metal Node **Organic Linker** **3D MOF**



How does elemental composition drive material properties?

- MOFs are utilized in multiple applications: chemical separation and storage, imaging and sensing, drug deliver, among others.
- MOFs are generally synthesized with one metal species (homometallic).
- Heterometallic MOFs have been exemplified as candidates to harness unique features of multiple metals individual and in concerted reaction mechanisms.
- **Specifically, how can heterometallic MOFS be utilized to enhance CO_2 conversion efficiency?**

APPLYING DENSITY FUNCTIONAL THEORY (DFT) TO ATOMISTIC MODELS

- Utilize a truncated 9-metal cluster to highlight changes due to atomistic changes.
- Calculations provide electronic structure, atomic position optimization, and reaction energy barriers.
- Models focused on three homometallic composition: Y_9, Yb_9, and Eu_9 | three bimetallic compositions: Yb_5Y_4, Eu_5Y_4, Eu_5Yb_4 | one trimetallic: $Y_3Yb_3Eu_3$ | one 5M: $Y_1Eu_2Gd_2Er_2Yb_2$
- Focus on two areas of heterometallic behavior:
  1. Electronic structure state mixing at valence and conduction band edges due to composition.
  2. Catalysis reaction mechanism of CO_2 cycloaddition.

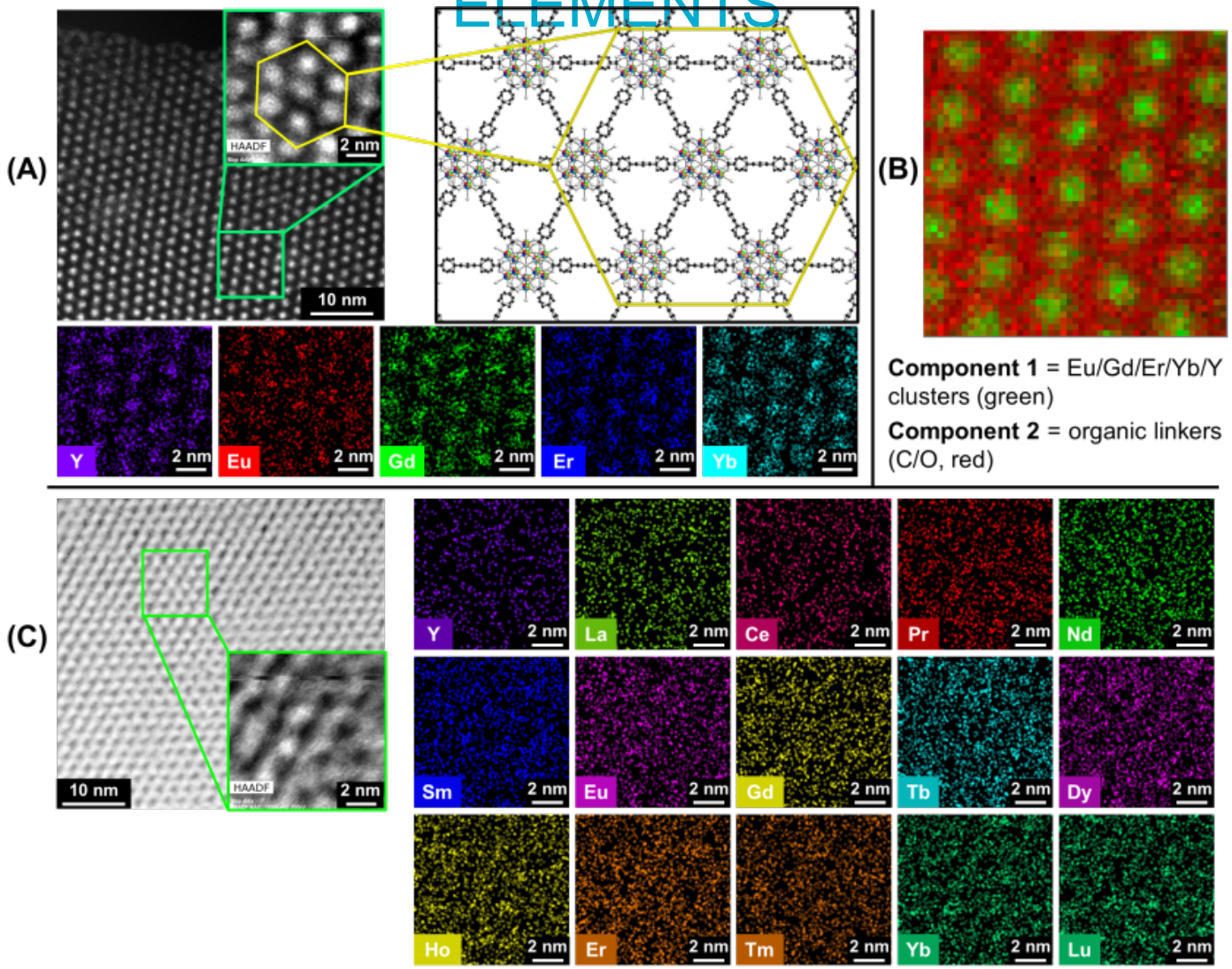
DFT Calculation Information

- Metal cluster structure: $[M_9(COOH)_{12}O_2F_{12}]^{-1}$
- TCPB ligands truncated to formates for computational speedup.
- Cluster centered in 35x35x35Å unit cell.
- Exchange correlation function: PBESol-D3
- Single Gamma Point
- Spin Polarized Calculation
- PAW Potentials

THE FIRST EXAMPLE OF A SINGLE MOF MATERIAL CONTAINING 15 RARE EARTH ELEMENTS

Ina Sava Gallis - SNL

R. Eric Sikma - SNL(PD)/Miami U.

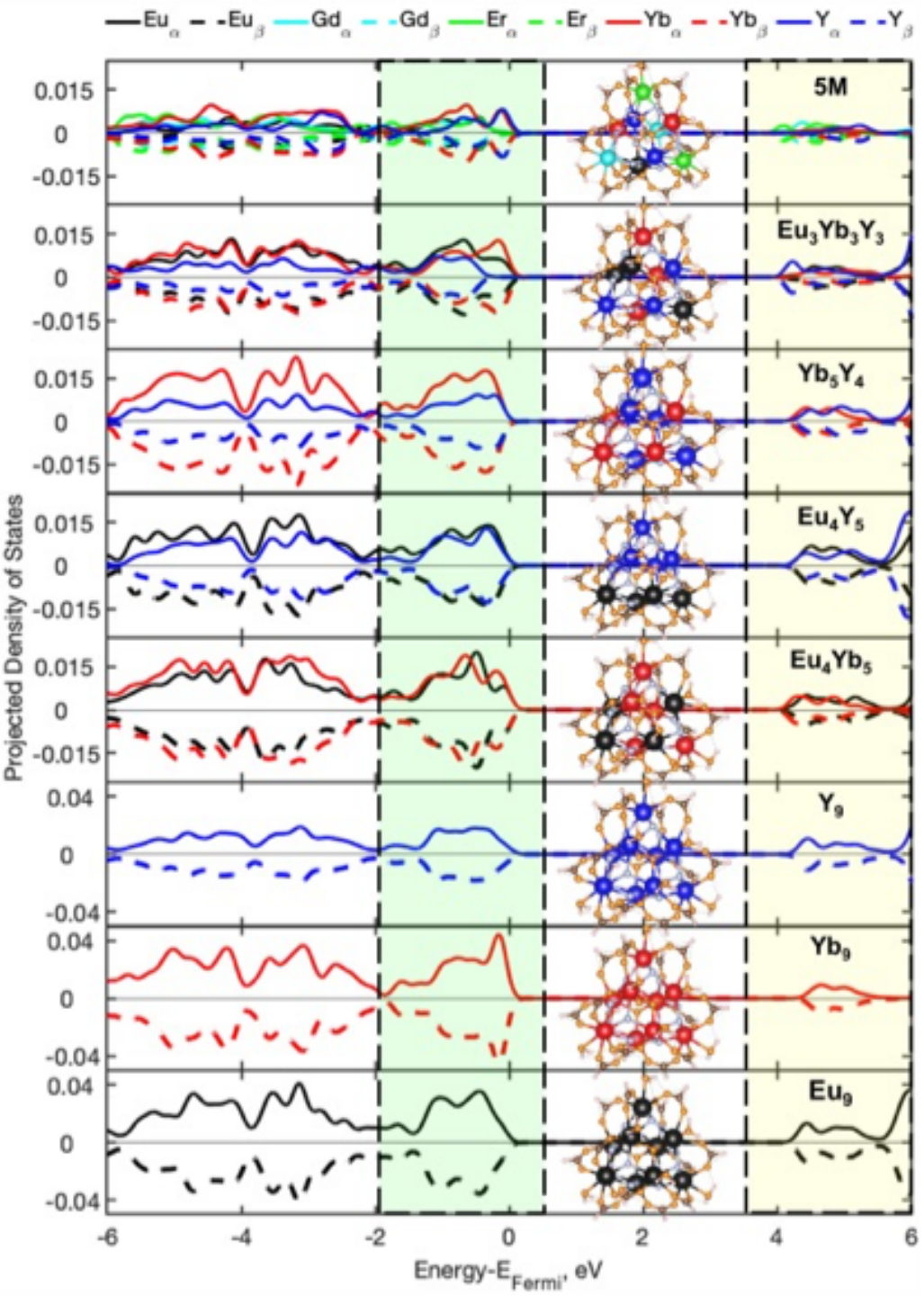


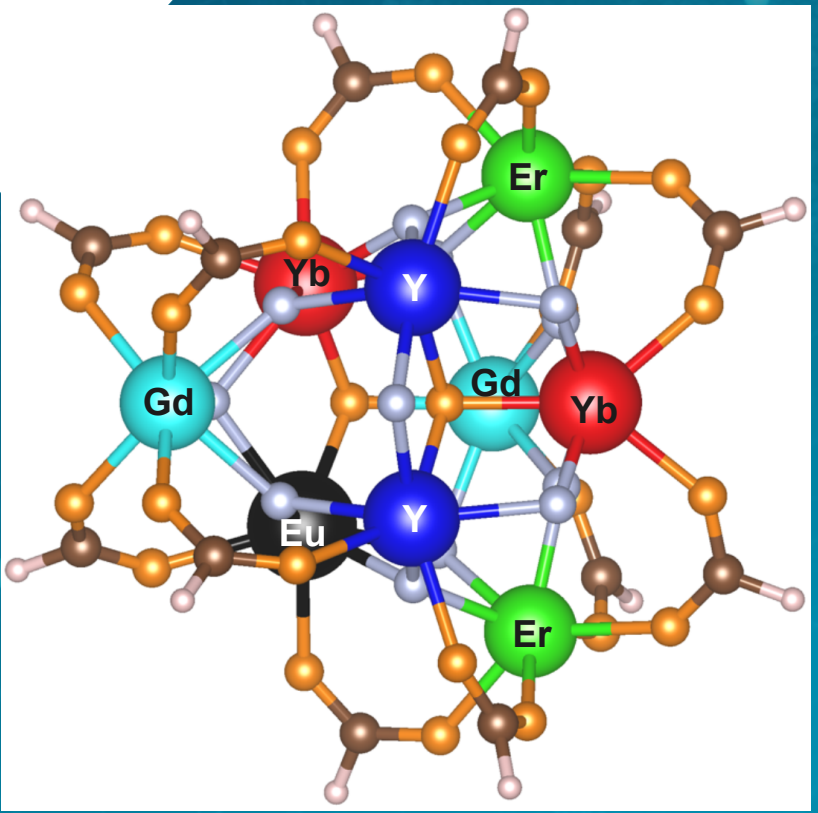
Characterization of homogeneous integration of 5 (A) and 15 (C) RE elements into single TCPB MOFs via HAADF STEM and EDX mapping.

R. Eric Sikma, et al., *Advanced Materials* **2024**. *In review*

DENSITY OF STATES SHIFTING IN HEMOFS

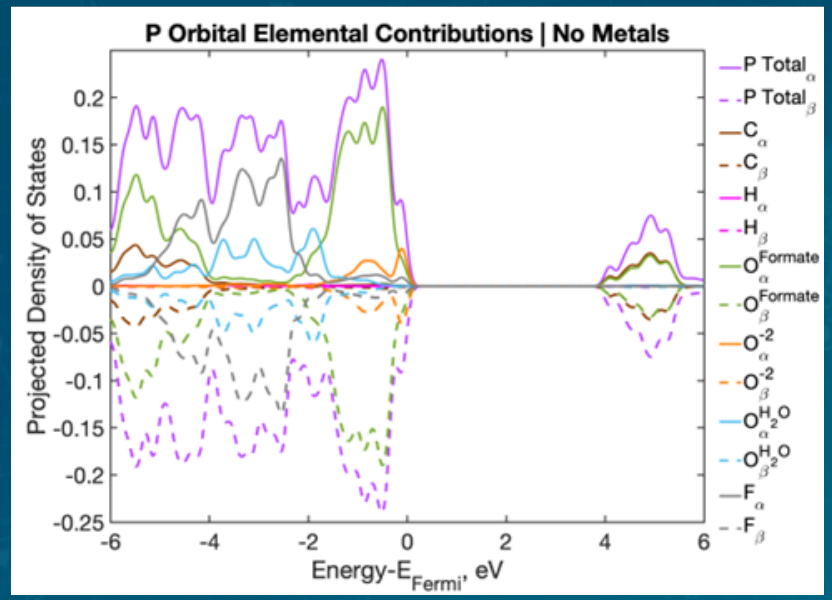
- Comparison of electronic structure for homometallic vs range of bimetallic, trimetallic, and 5M –TCPB MOFs.
- New metal combinations shift relative state contributions at the valence and conduction band edges.
- Greatest impact is on ordering of metallic contributions at the conduction band edge.

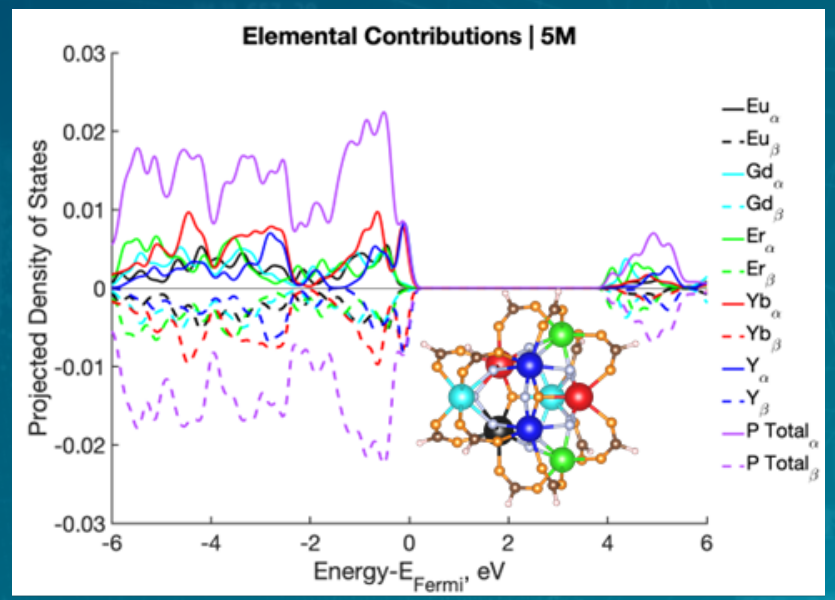


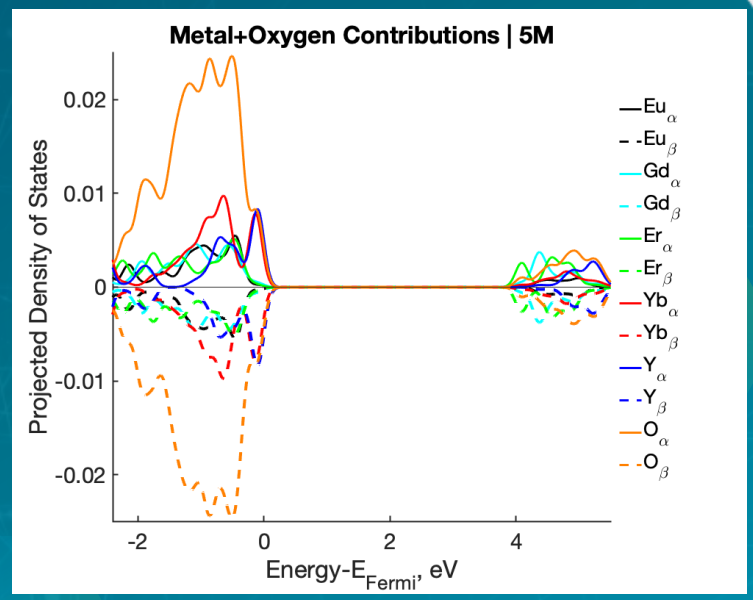


$[Y_2Eu_1Gd_2Er_2Yb_2(COOH)_{12}O_2F_{12}]^{-1}$

PREDICTING INTERACTIONS BETWEEN OXYGEN AND METALS







- Total DOS is dominated P orbitals, specifically those contributed by oxygen species and localized on formates.
- Valence band states are contributed by central $\mu_3 - O^{2-}$ species.
- Metals bonded to central $\mu_3 - O^{2-}$ species have significant population at the valance band edge.
- Photoexcitation within the materials is expected to generate excited electrons localized on organic linkers.
- Unique ordering of states at the conduction band edge indicate possible direction of relaxation mechanisms.

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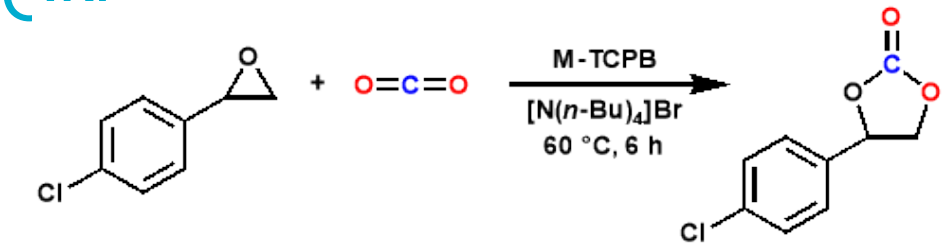
CO_2 Conversion in RE HEMOFS

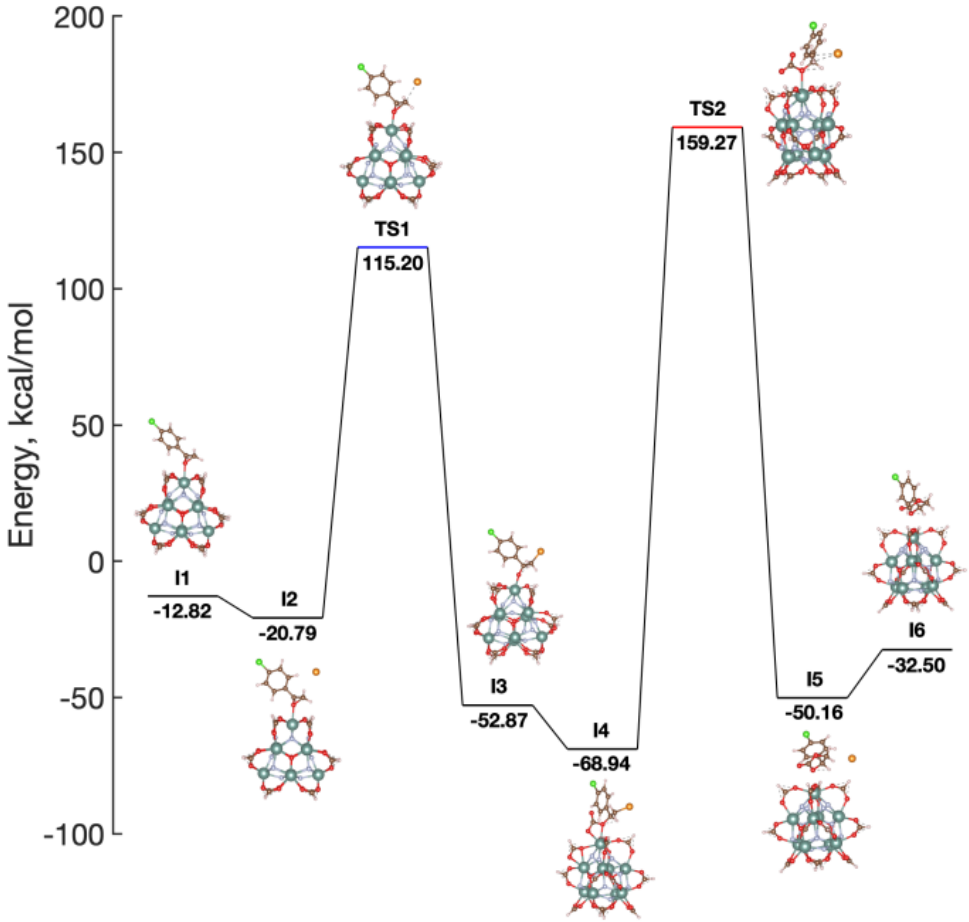
Sample	S_{BET} (m^2 g^{-1})	Time (h)	Conv. (%)[d]
Eu-TCPB[a]	1460	6	66
Yb-TCPB[a]	1380	6	72
Y-TCPB[a]	1580	6	73
Gd-TCPB[a]	1380	6	65
Er-TCPB[a]	1280	6	68
EuYbY-TCPB[a]	n.d.[c]	6	70
5M-TCPB[a]	1520	6	69
5M-TCPB[a]	1520	18	94
15M-TCPB[a]	1360	6	72
15M-TCPB[a]	1360	18	90
SiO_2/Al_2O_3 zeolite[a]	216	6	26
Y-zeolite[a]	n.d.[c]	6	32
MOF-808[a]	1680	6	57
UiO-66[a]	1390	6	56
None[b]	–	6	25
None[b]	–	18	44

a) 1.0 mmol epoxide, 0.10 eq. TBA-Br, 0.05 eq. MOF (per metal ion), heated to 60 °C for indicated time under balloon pressure CO_2
b) Identical conditions with no MOF added
c) BET surface area was not determined
d) Determined by ^1H NMR with reference to HMB internal standard

CATALYZED CO_2 CYCLOADDITION REACTION



- Y-TCPB is initially modeled due to excellent experimental performance.
- Gas phase geometry optimizations in DFT at 0K.
- Nudged elastic band calculations for transition state search between I2-I3 and I4-I5.
- Activation energies from first pass need to be further studied and optimized.



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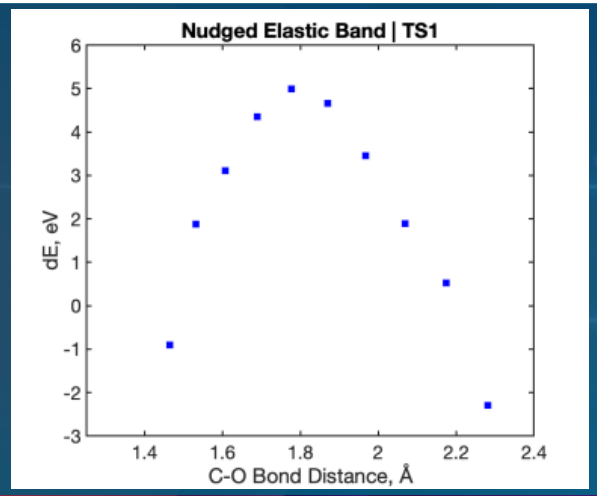
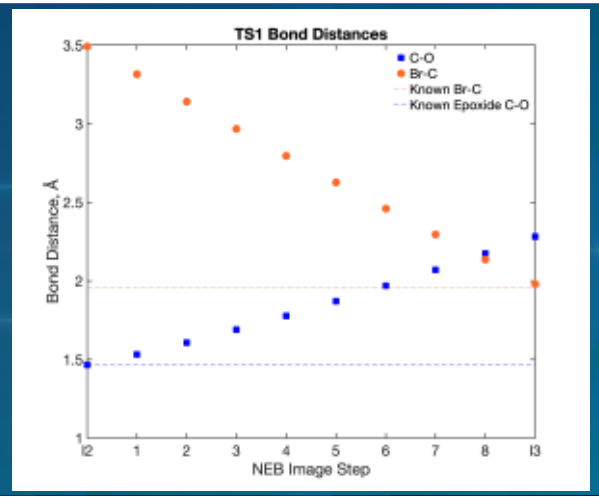
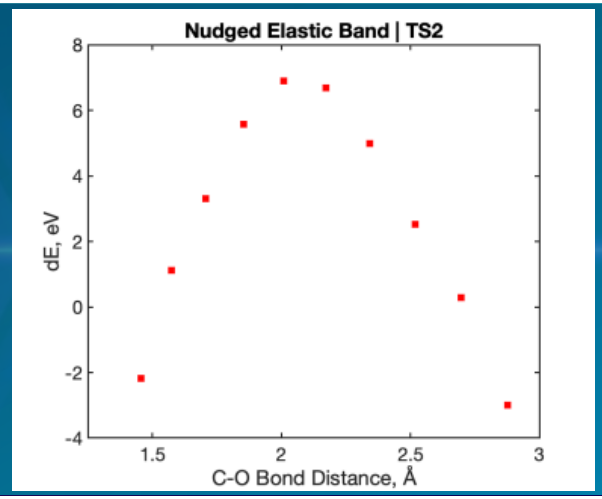
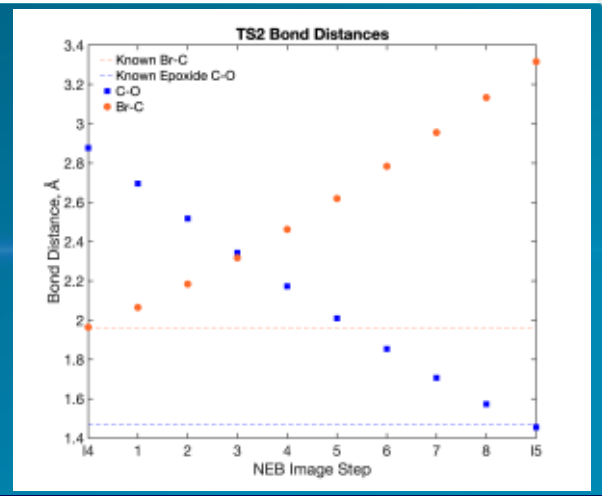
CO_2 CYCLOADDITION REACTION PATHWAY AND COORDINATE

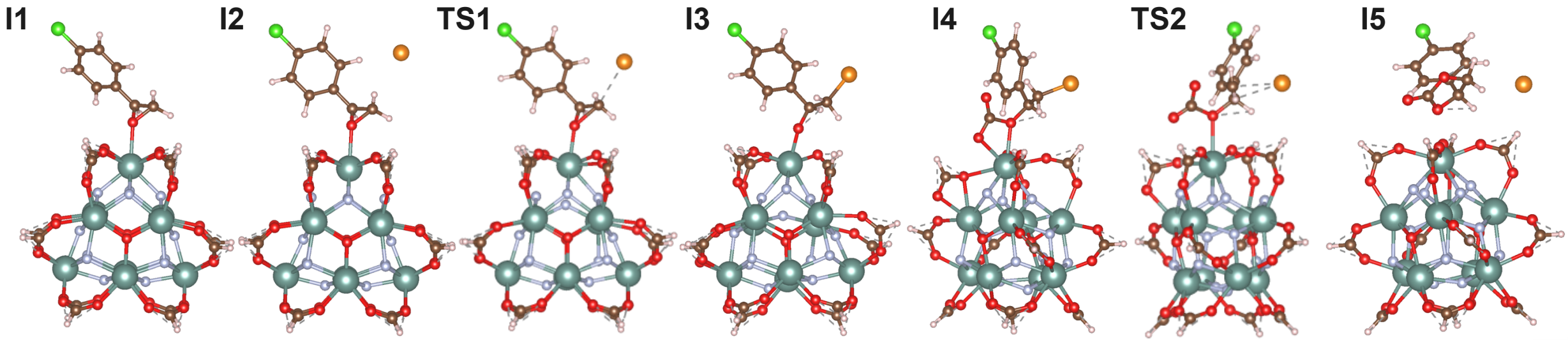








Reaction Sequence



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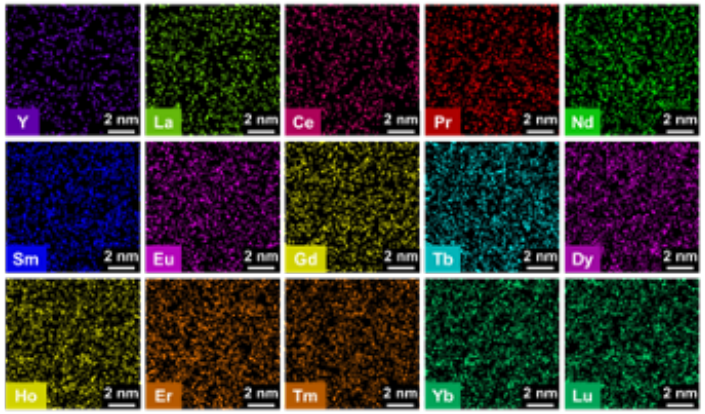
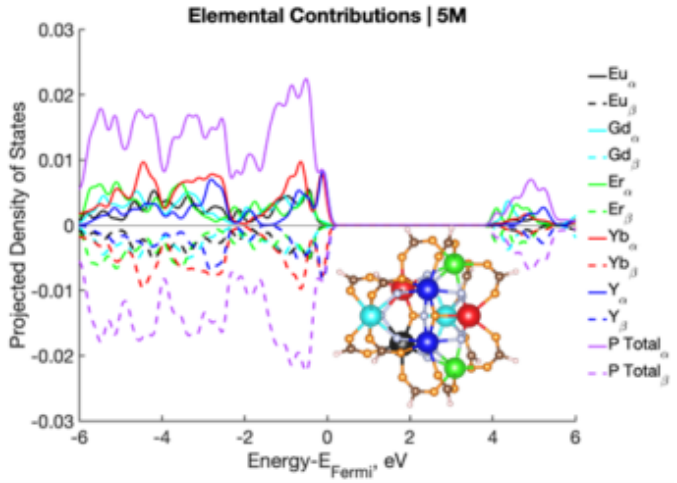
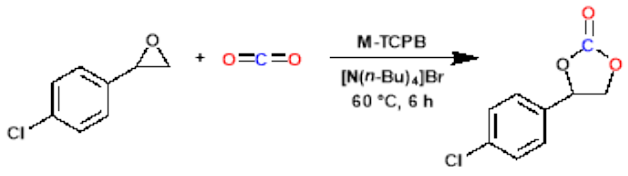
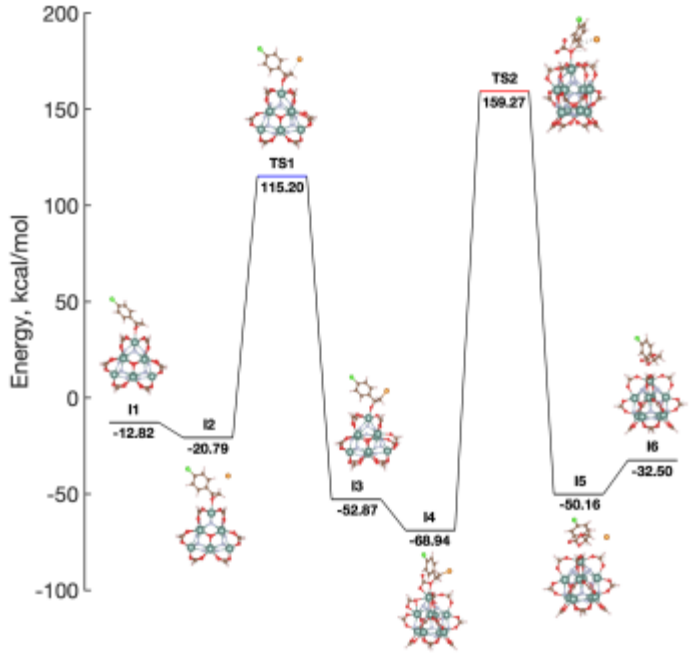
*Structure depicting removal of bromine (I6) omitted for clarity

CONCLUSIONS









- First time synthesis of a new High Entropy Metal-Organic Framework containing homogenous integration of 15 rare earth elements.
- DFT calculated electronic structures indicate particular metallic ratios modify dominant species at the band edges of the material.
- HEMOFs perform as efficient catalysts for CO_2 cycloaddition reactions.