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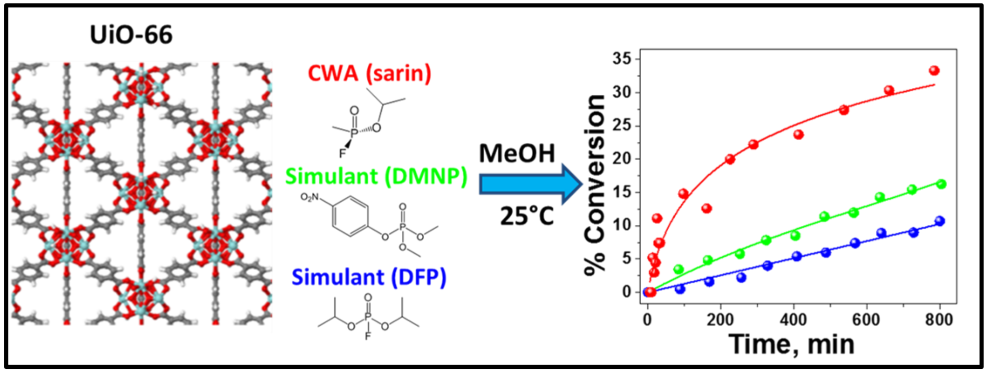

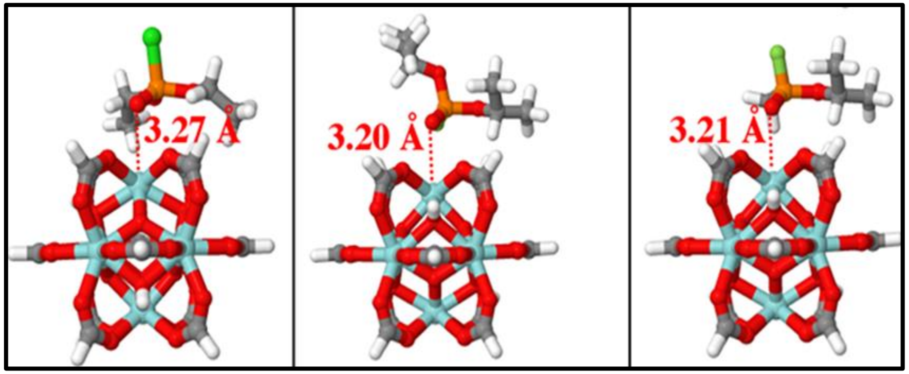

Efficient MOF-based Degradation of Organophosphates in Non-Aqueous Environments

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Jared DeCoste, Edgewood Chemical and Biological Center, Aberdeen Proving Ground, MD

2018 ACS Spring Meeting, New Orleans, LA
Catalytic & Photocatalytic Degradation of Pollutants & Chemical Threat Agents:
New Developments in Materials & in In-situ & Operando Methods
March 21, 2018

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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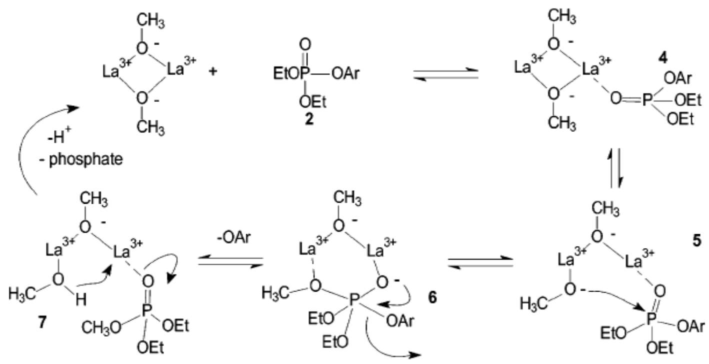
Goal: investigate chemistries to degrade organophosphorous compounds in water free environments

Methanolysis of organophosphates is accelerated by La-based catalysts

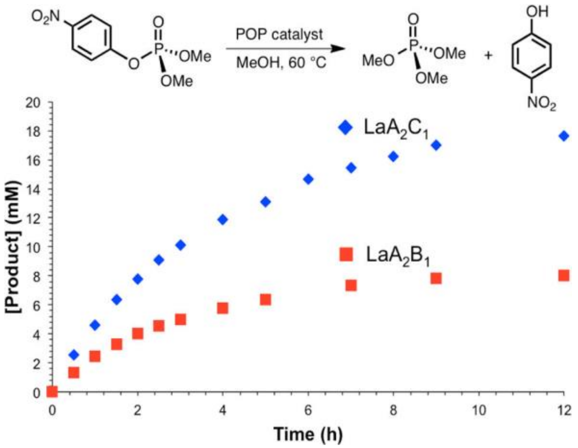
Billion-fold Acceleration of the Methanolysis of Paraoxon Promoted by La^{3+} complexes

Scheme 1 ^{a}



^{a} Methanols of solvation omitted for clarity.

La $^{3+}$ catechol-functionalized POPs show accelerated activity towards methanolysis

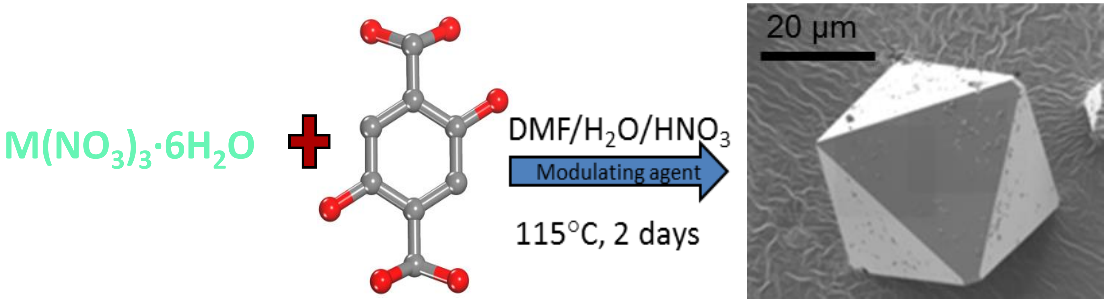


J. Am. Chem. Soc. **2003**, *125*, 7602-7607.

ACS Catal. **2013**, *3*, 1454–1459. *dfsava@sandia.gov*

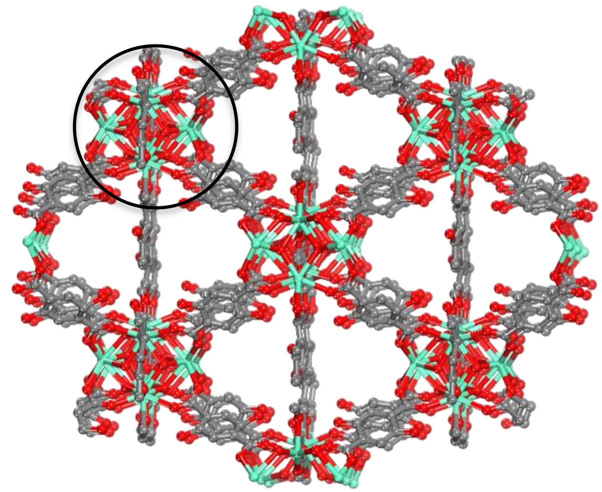
RE-DOBDC platform based on a building block akin to prototypical Zr-hexanuclear cluster

Proof-of-concept prototype structure



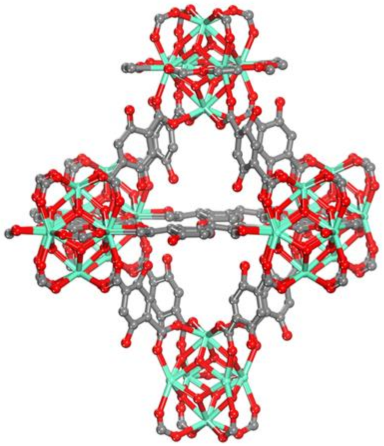
Single-crystal X-ray diffraction

Tetragonal, 3D framework
P4NC
a= b= 15.5567 Å
c= 21.334 Å
α=β=γ= 90° = V= 5163.06 Å^3



$M_6(\mu_3\text{-OH})_8(C_8H_4O_6)_5(C_2H_6O_6)_1(H_2O)_6\cdot 24\ H_2O$

M= Eu, Nd, Yb, Y, Tb



Octahedral cages of ~ 14 Å diameter, accessible via triangular windows of ~ 5.5 Å

● M
● C
● O

Sava Gallis et al., *ACS Appl.Mater.Inter.* **2017**, *9*, 22268–22277.

US Patent Application #62522006

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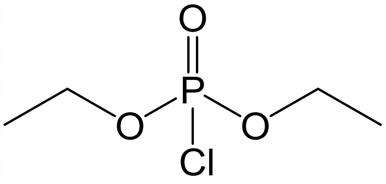
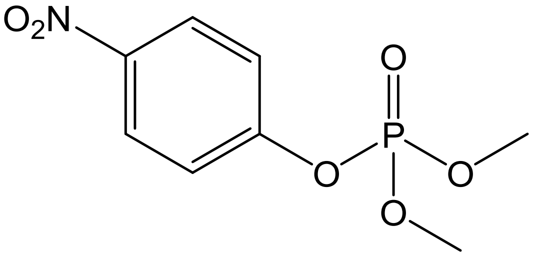
Simulants vs. CWAs: striking the balance between toxicity and reactivity

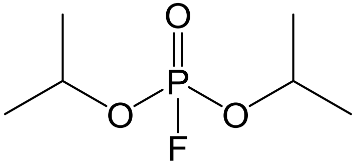
Increase in Correlation to Live Agent?



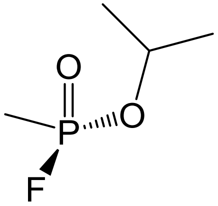
Diethyl Chlorophosphate (DECP)



Dimethyl Nitrophenylphosphate (DMNP)



Diisopropyl Fluorophosphate (DFP)



Sarin (GB)

Simulants

CWA Agent

- The molecular structure/reactivity of simulants vs. Chemical Warfare Agents (CWAs) is different
- Tests performed on CWAs are not trivial and conducted only at authorized facilities
- Simulants allow screening of materials

This study aims to *identify the most appropriate simulants* that correlate best with the methanolysis of GB

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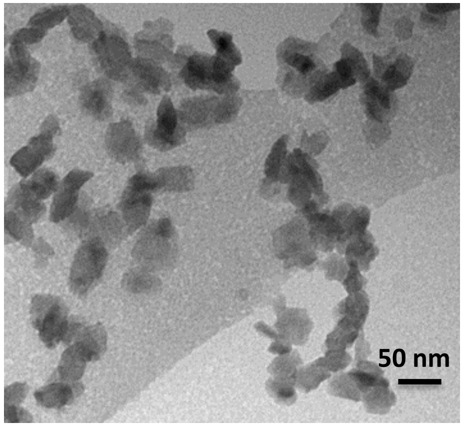
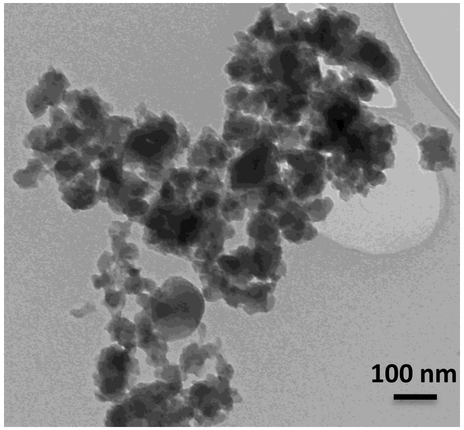
Materials downselection to probe the effect of metal site and linker functional groups

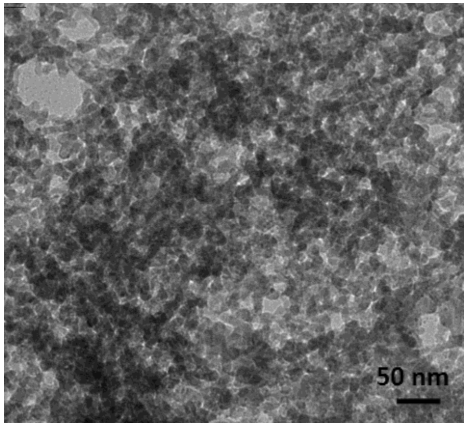
EuDOBDC



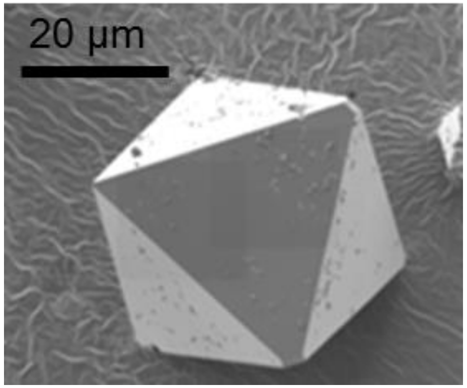
UiO-66



UiO-66-DOBDC



YDOBDC



Sample	Surface area, m^2/g
EuDOBDC UiO-66	700
UiO-66-DOBDC	550
YDOBDC	710
UiO-66	1667

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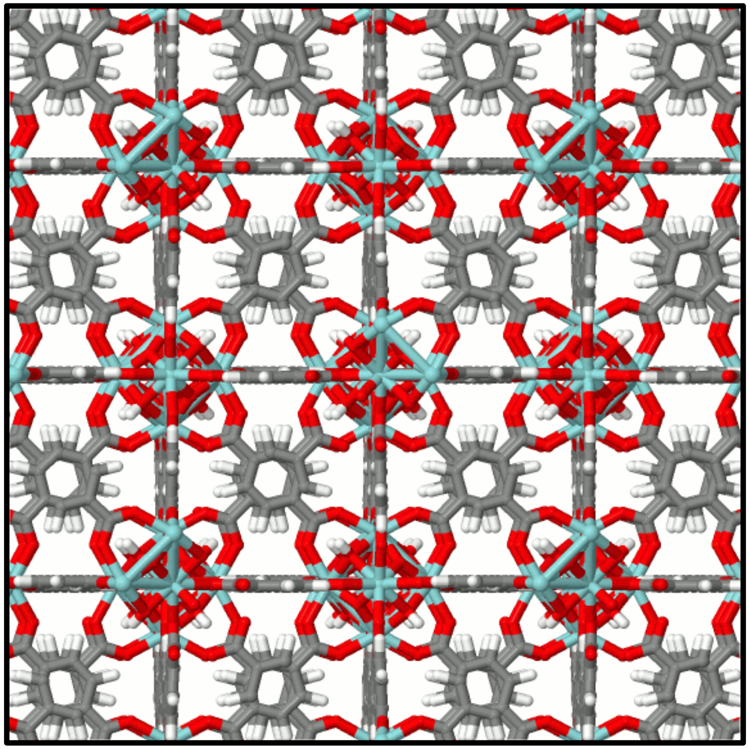
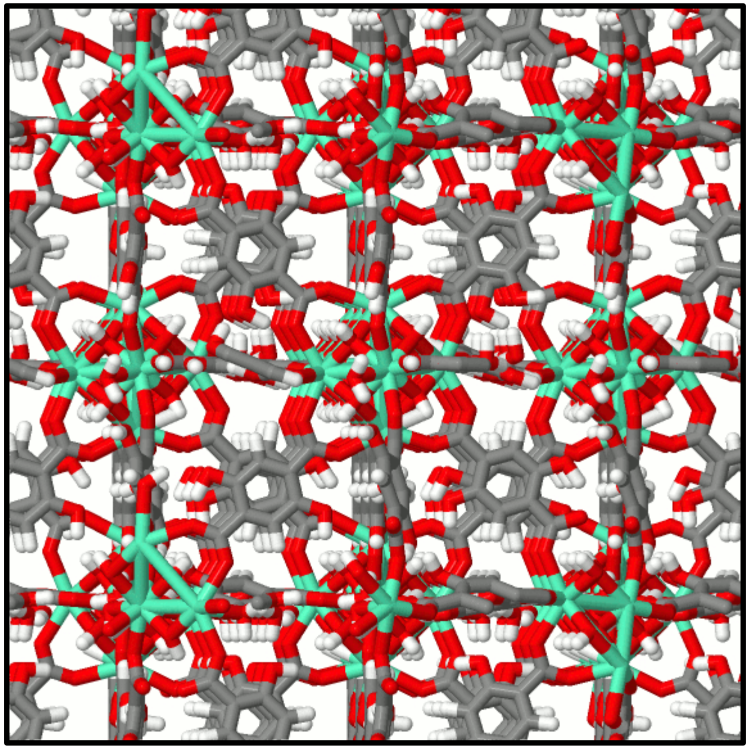
Structural characteristics in UiO-66 vs. REDOBDC

UiO-66

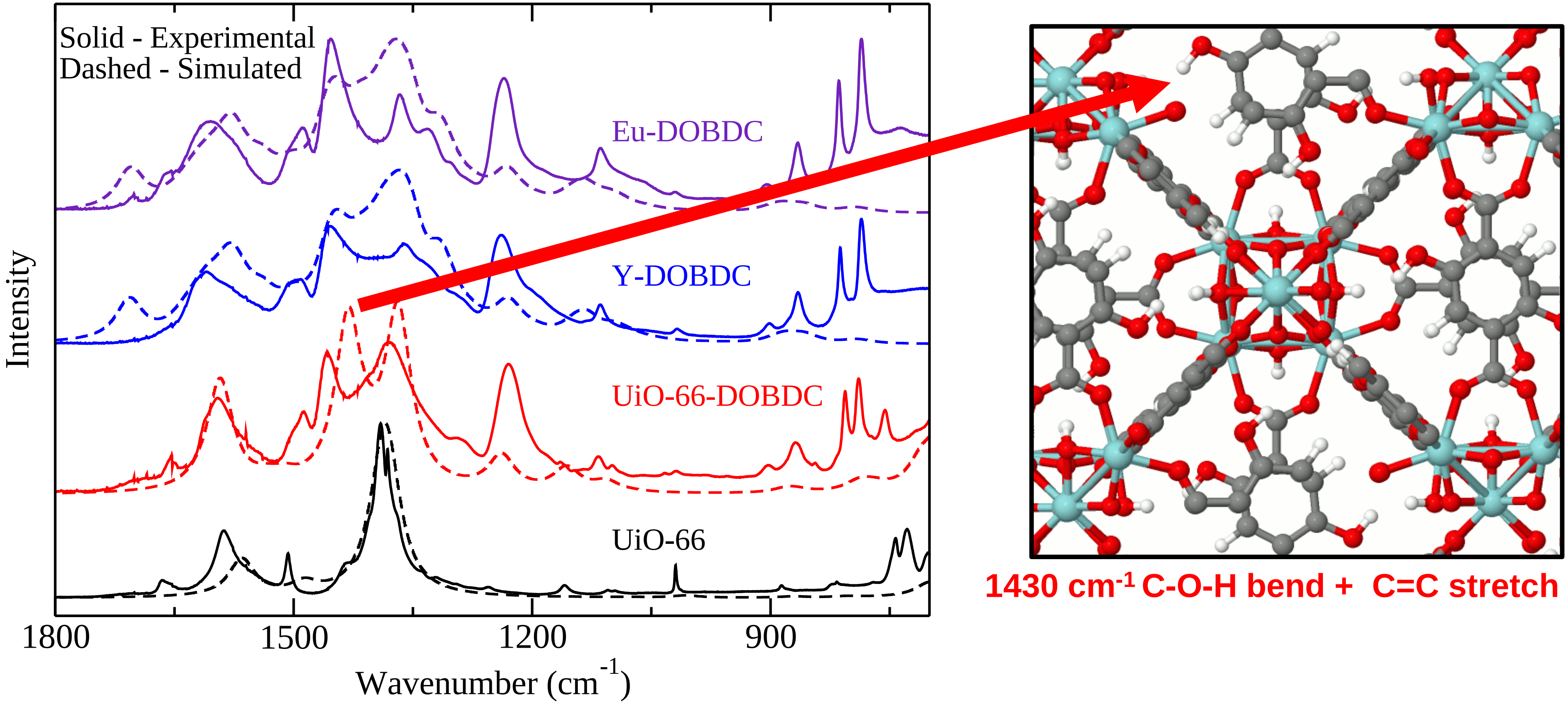


EuDOBDC



Simulated IR spectra: very good agreement with experimental results

Effect of ligand



1430 cm^{-1} C-O-H bend + C=C stretch

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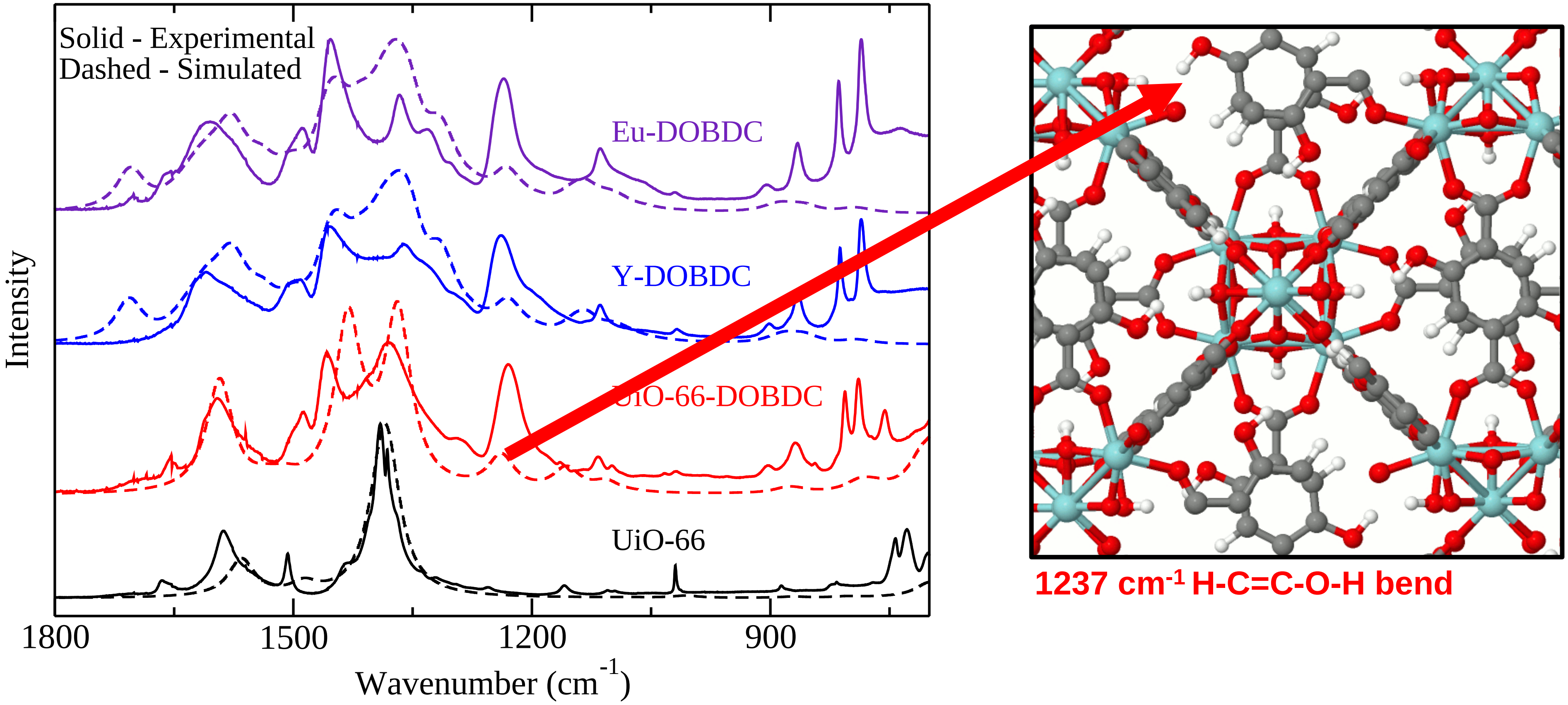
Simulated IR spectra: very good agreement with experimental results

Effect of ligand



1237 cm^{-1} H-C=C-O-H bend

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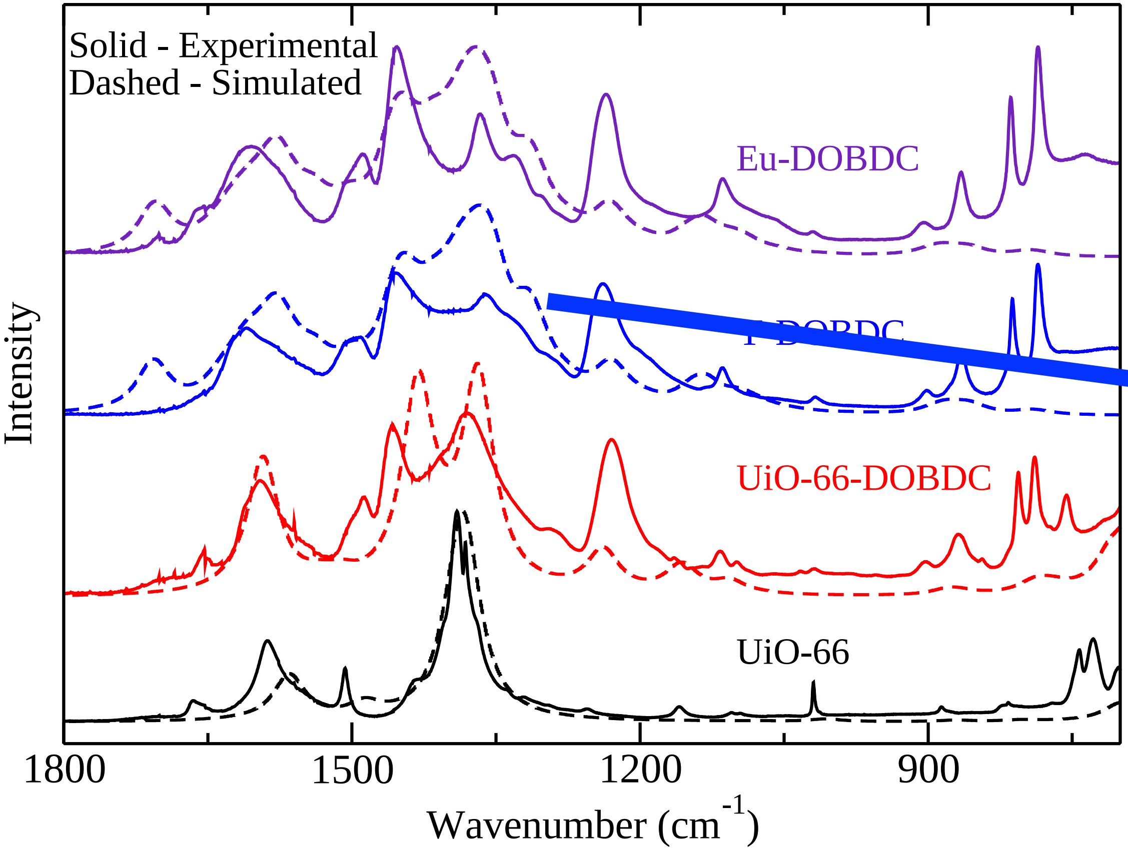
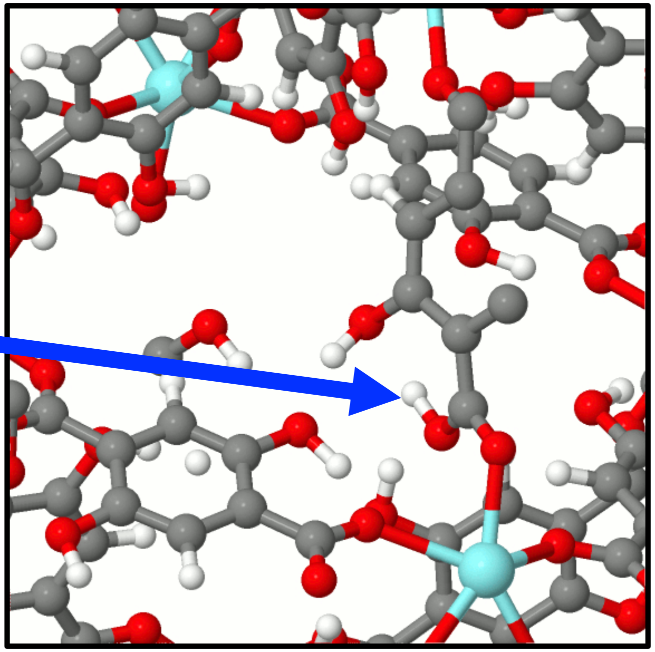
Simulated IR spectra: very good agreement with experimental results

Effect of metal





1315 cm^{-1} C-O-H bend

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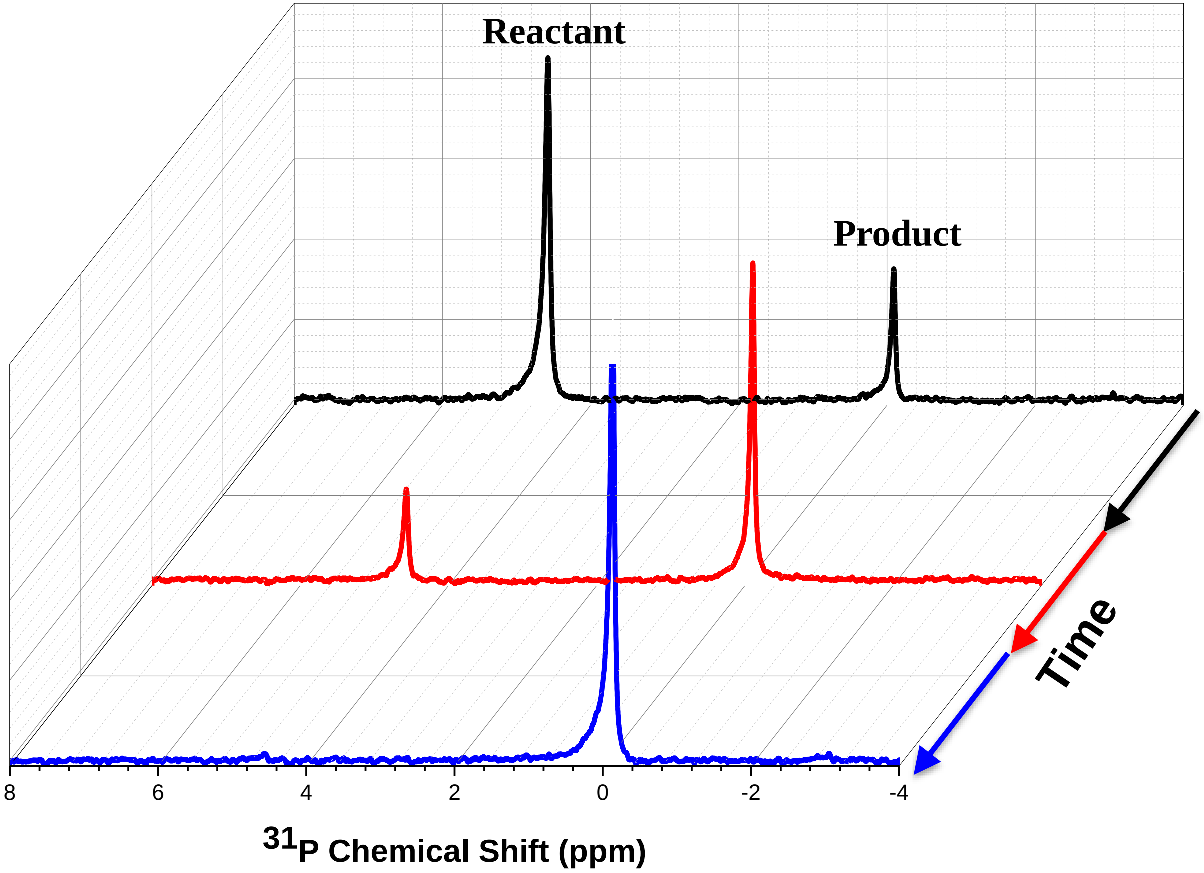
Representative ^{31}P NMR plot for DECP degradation in MeOH



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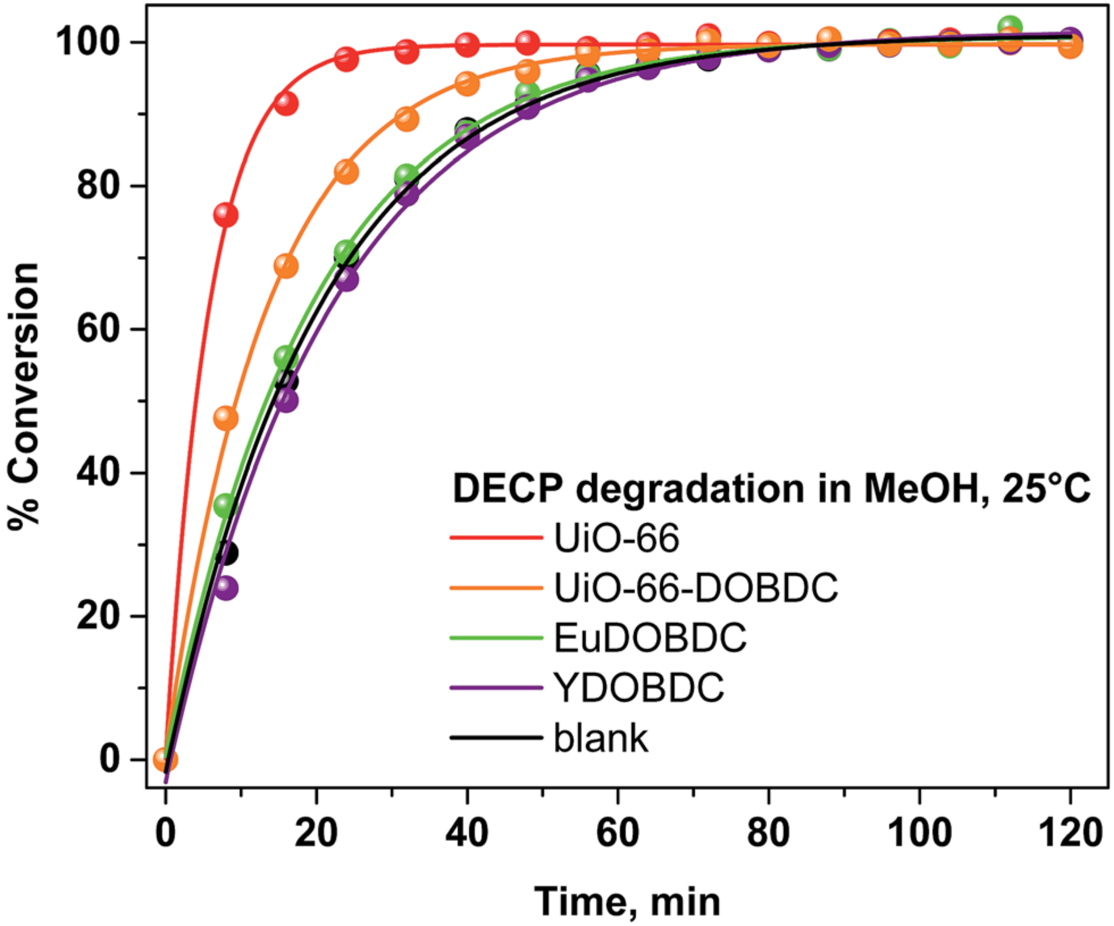
Room temperature DECP methanolysis: the highest activity is primarily dependent on the metal identity



Sample	$t_{1/2}$, min
UiO-66	5.1
UiO-66-DOBDC	8.2
EuDOBDC	11.6
YDOBDC	12.3
MeOH	12.3

Sava Gallis et al., *J. Mater. Chem. A*, **2018**, *6*, 3038–3045.

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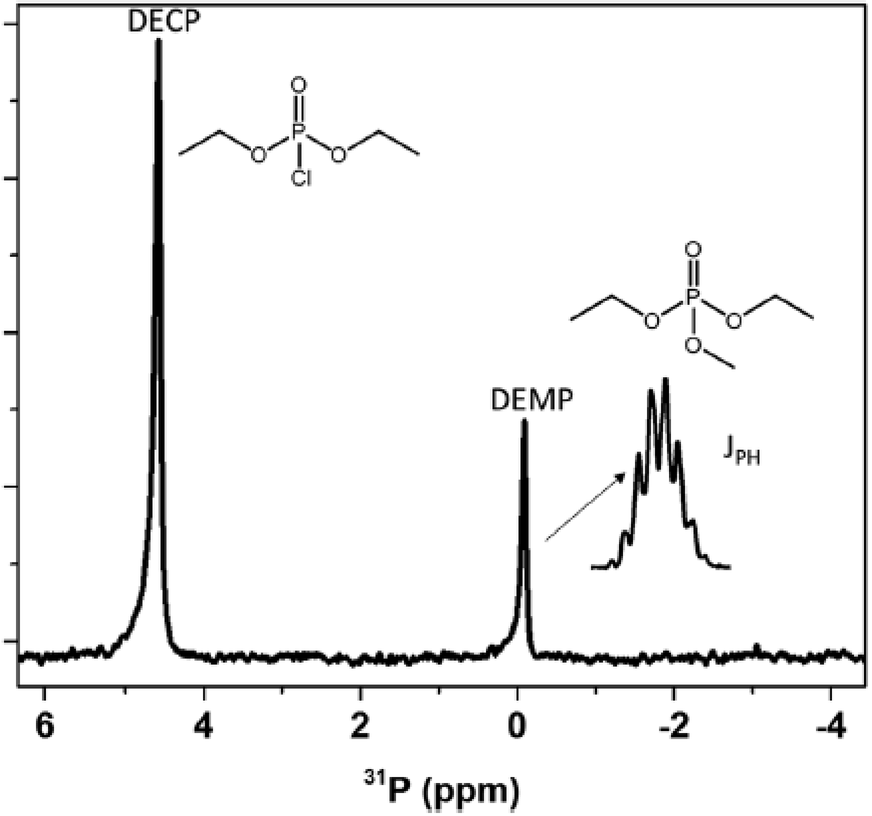
DECP methanolysis occurs via a catalytic process



- The breakdown product for DECP is diethyl methyl phosphate, DEMP, formed from the cleavage of the P–Cl bond of DECP
- DEMP product identity confirmed by ^1H-coupled ^{31}P NMR
- Octet multiplet shows seven different ^1H–^{31}P interactions, associated with the nearest H atoms in the vicinity of the P atom

Sava Gallis et al., *J. Mater. Chem. A,* **2018**, *6,* 3038–3045.

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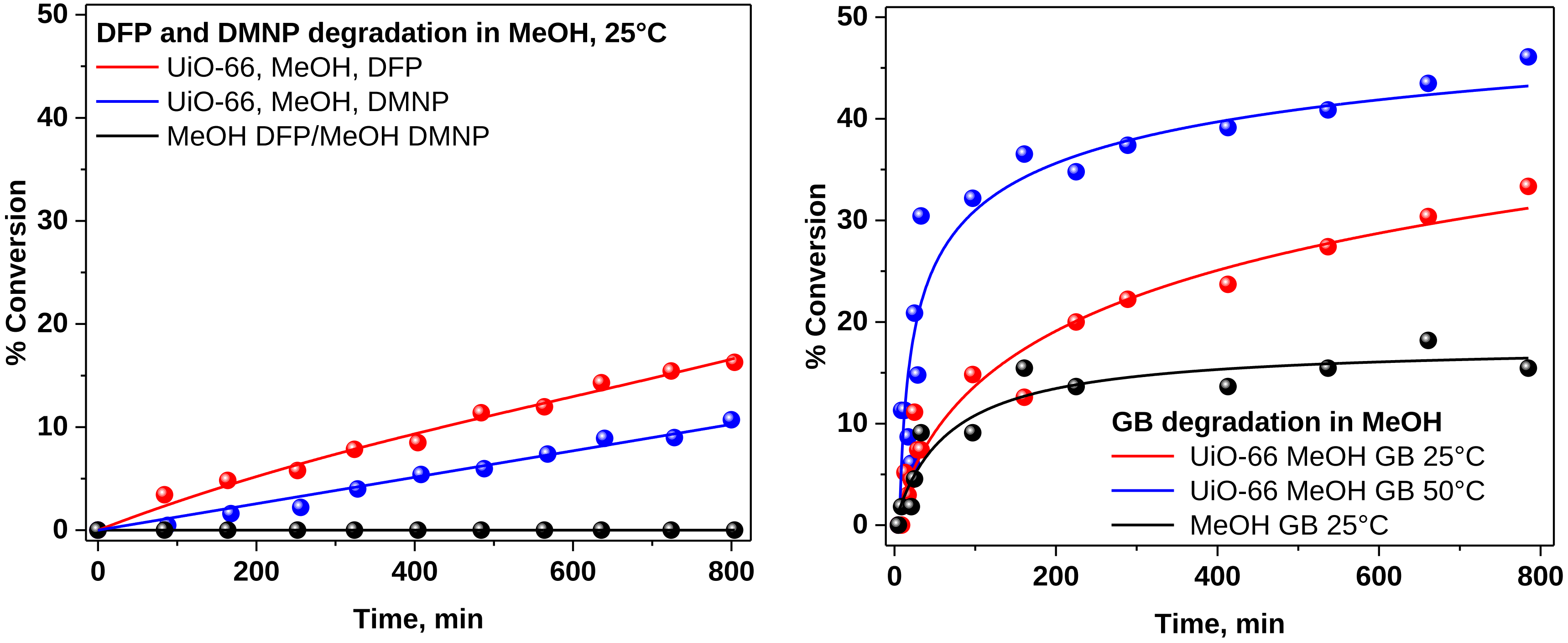
UiO-66 based degradation of DMNP, DFP and GB in MeOH is significantly slower as compared to DECP



- The reactivity of GB, DMNP and DFP runs in parallel, indicating related conversion mechanisms
- The methanolysis of GB is faster than that of both DFP and DMNP at room temperature
- DMNP and DFP are both feasible simulants to mimic the reactivity of GB

Sava Gallis et al., *J. Mater. Chem. A*, **2018**, *6*, 3038–3045.

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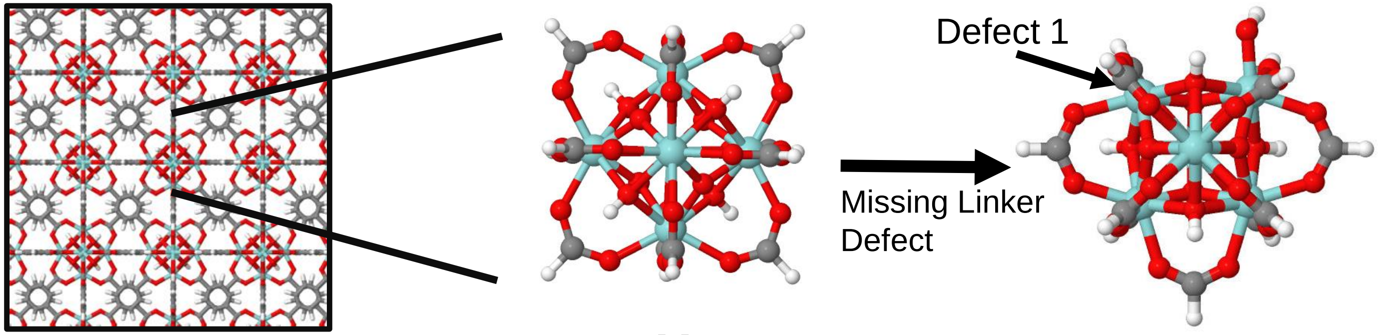
Computational Methods

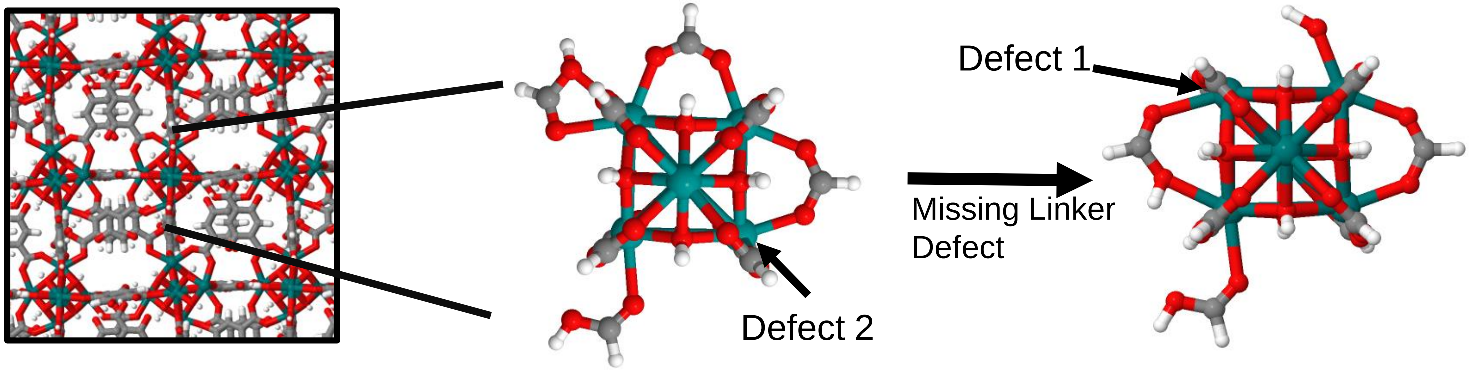
Gas Phase Cluster DFT:

- Clusters generated from VASP optimized structure
- Clusters optimized with MO6-L functional, def2-SVP basis set for all non-metal atoms and SDD ECP and psuedopotential for metal atoms
- Model ”idealized” ligands as formate ligands

Zr

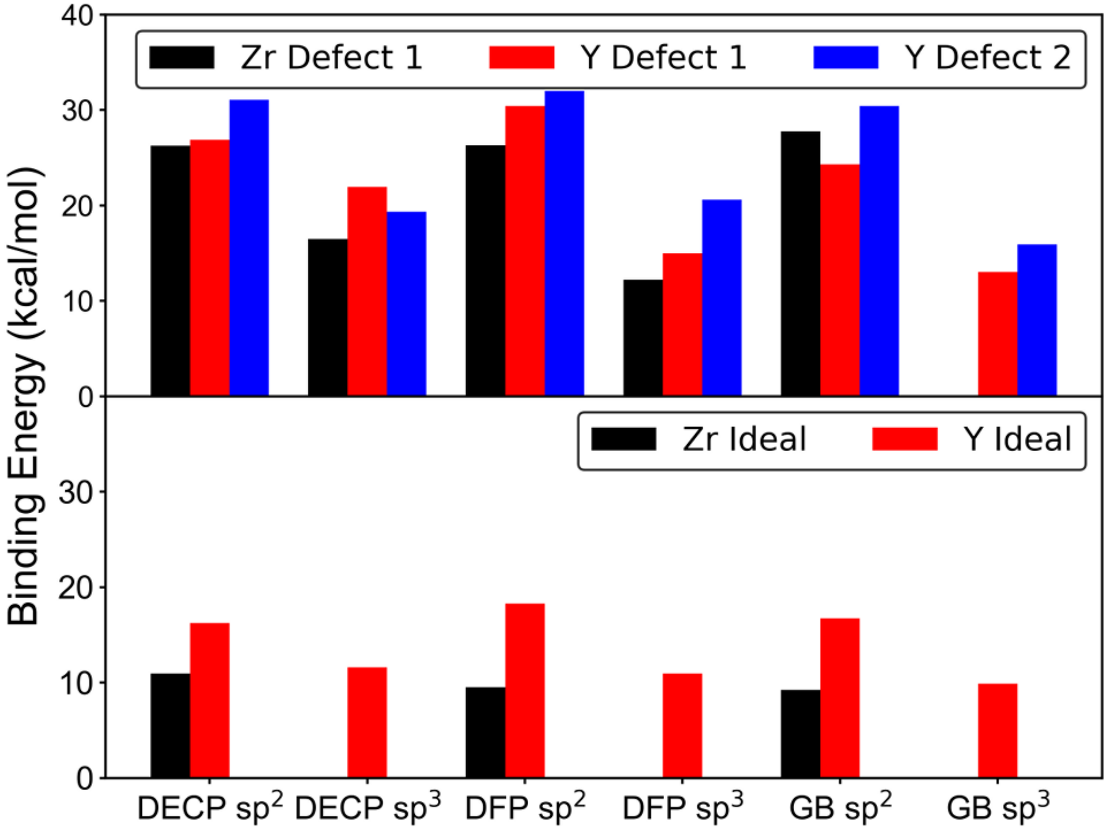


Y



Harvey, J. et al., **2018**, in preparation

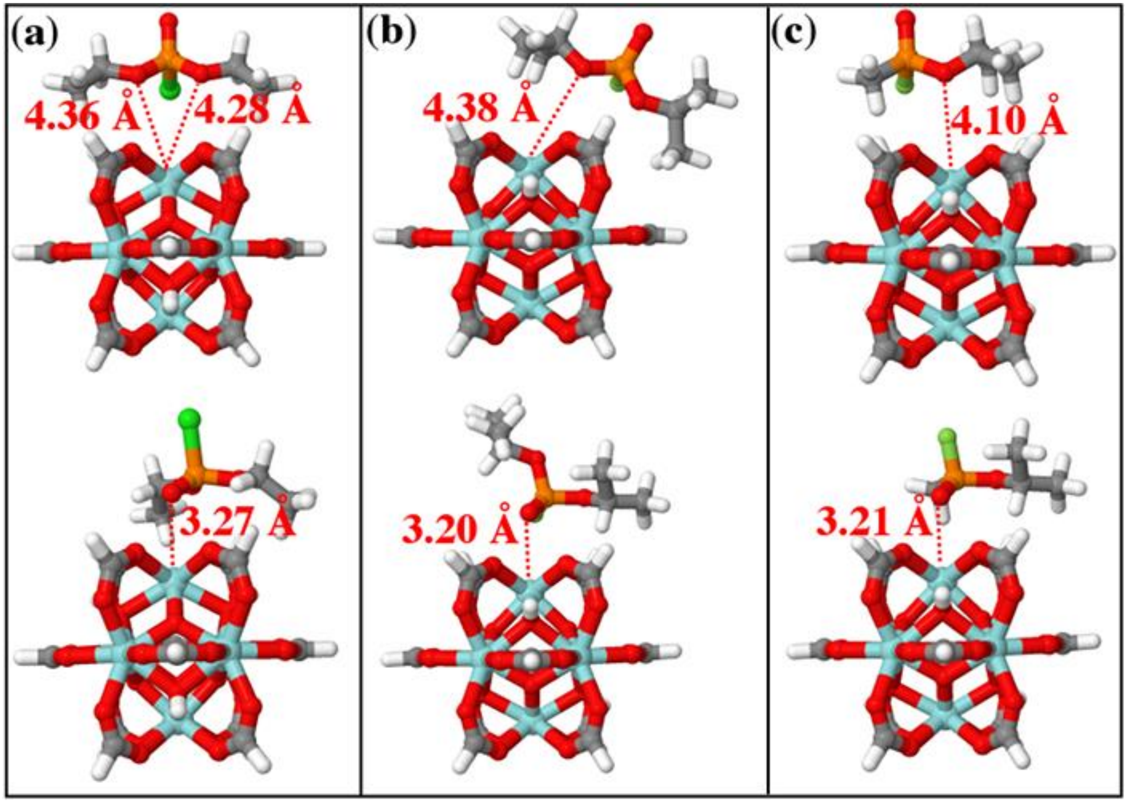
Structural defects increase the binding energy of DECP, DFP, and GB 2-fold



- Y is able to bind substrates at 8 (fully) coordinated sites more favorably than Zr, but when defects are introduced the 2 metal atoms are roughly equal
- The built-in ligand-twist defect of Y-DOBDC (defect 2) is competitive with the engineered missing linker defect (defect 1)

Harvey, J. et al., **2018**, in preparation

All substrates preferentially bind at the O(sp2) atom



O(sp3)

O(sp2)

Binding geometries on ideal Zr sites for (a) DECP, (b) DFP, and (c) GB via the O(sp^3) atom (top) and the O(sp^2) atom (bottom).

Harvey, J. et al., **2018**, in preparation

Summary

- Significant differences in the chemistry of chloro- vs. fluorophosphates
- Zr (in UiO-66 and UiO-66-DOBDC) presents a higher catalytic activity towards the methanolysis of DECP than Y and Eu DOBDC analogues
- This appears to be directly correlated with metal identity and oxidation state
- DFP and DMNP are appropriate choices to assess the reactivity of GB in MeOH.
- Ongoing studies investigate structural defects and constraints in the parameters for molecular simulations, and their combined effect on guest binding