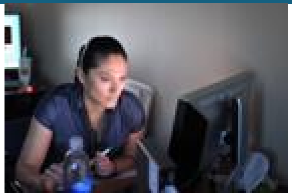
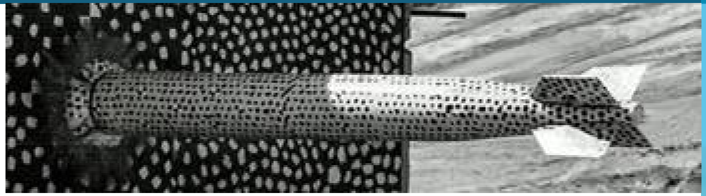
SAND2021-13236PE





Structure-Function Versatility in Metal-Organic Frameworks: Molecular Insights at the Nanoscale

UPDATED OCTOBER 2020

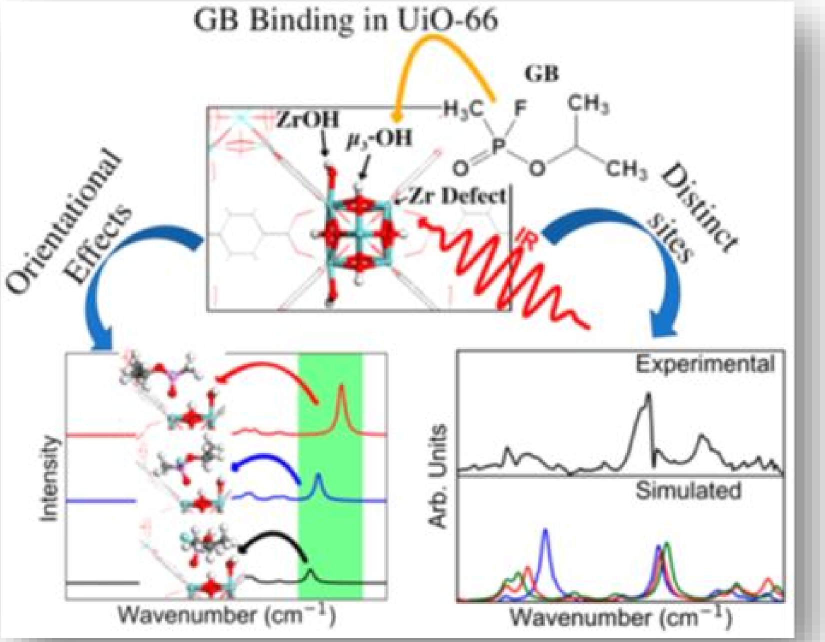
Dorina Sava Gallis, Nanoscale Sciences Department, Sandia National Laboratories

DEVCON CBC R&T Physical Chemical Phenomena Seminar

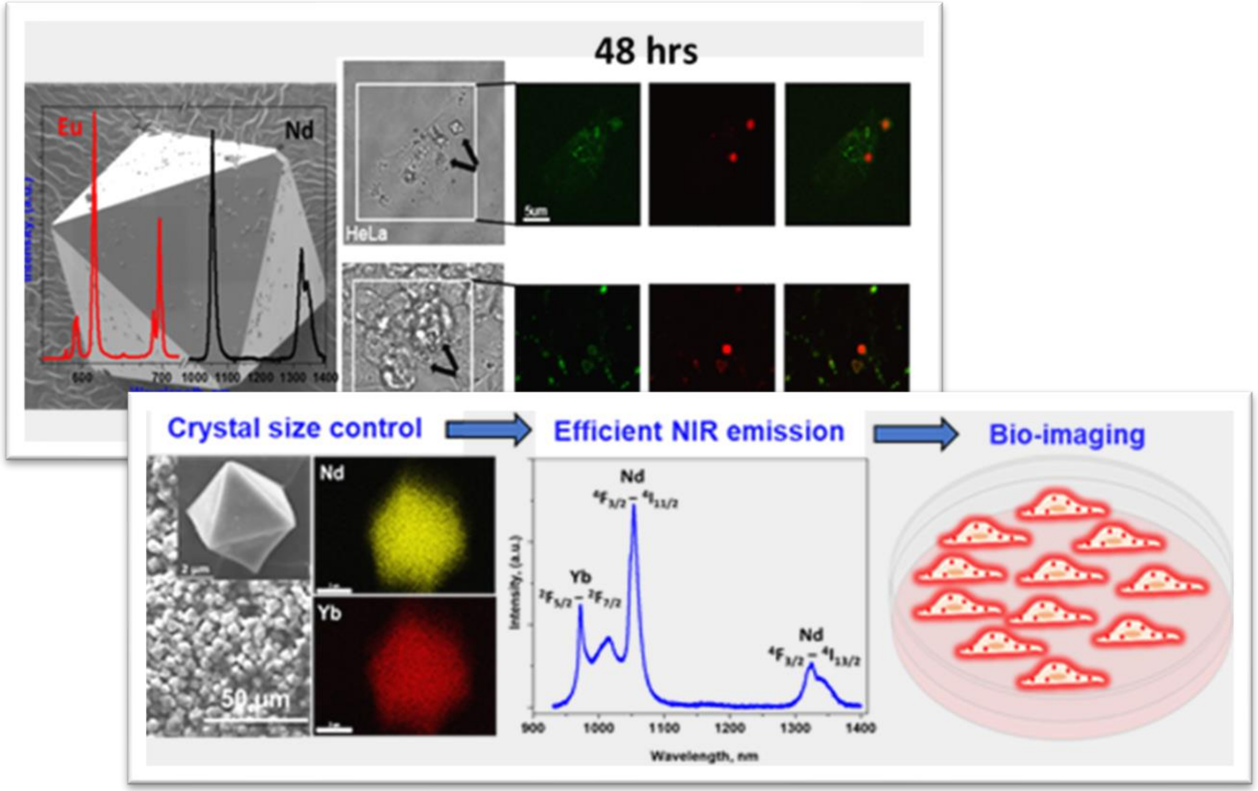
October 21, 2021

1. SNL overview

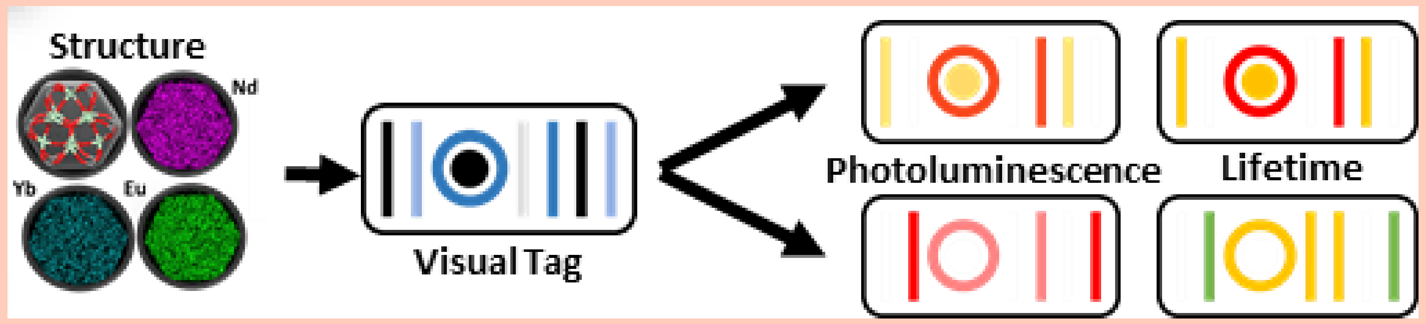
2. MOF- based degradation of organophosphorous compounds



3. MOFs for bio-related applications



4. Anti-Counterfeiting Heterometallic MOF-based Optical Tags



SANDIA HAS FACILITIES ACROSS THE NATION

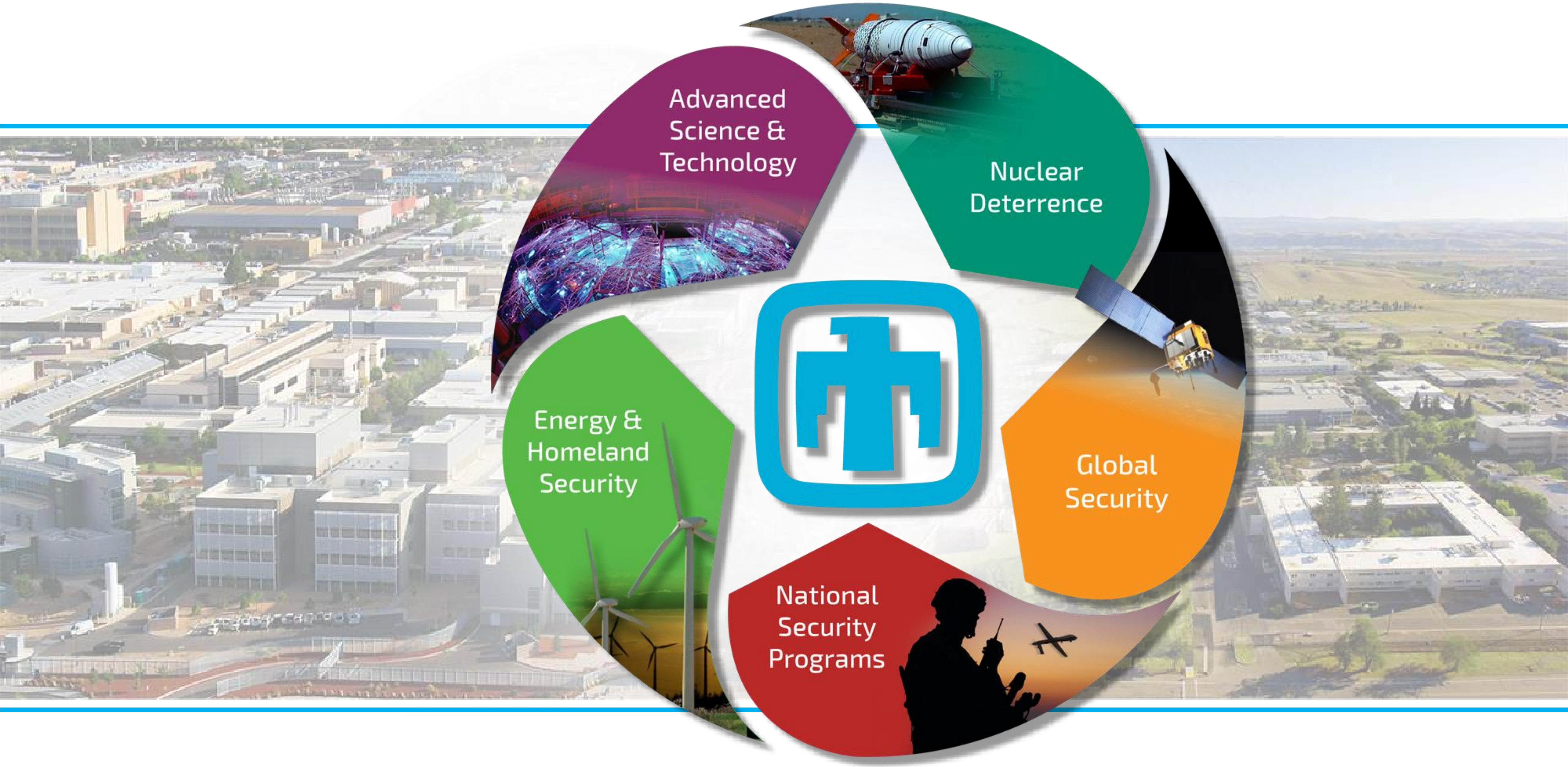
Activity locations

- Kauai, Hawaii
- Waste Isolation Pilot Plant, Carlsbad, New Mexico
- Pantex Plant, Amarillo, Texas
- Tonopah, Nevada

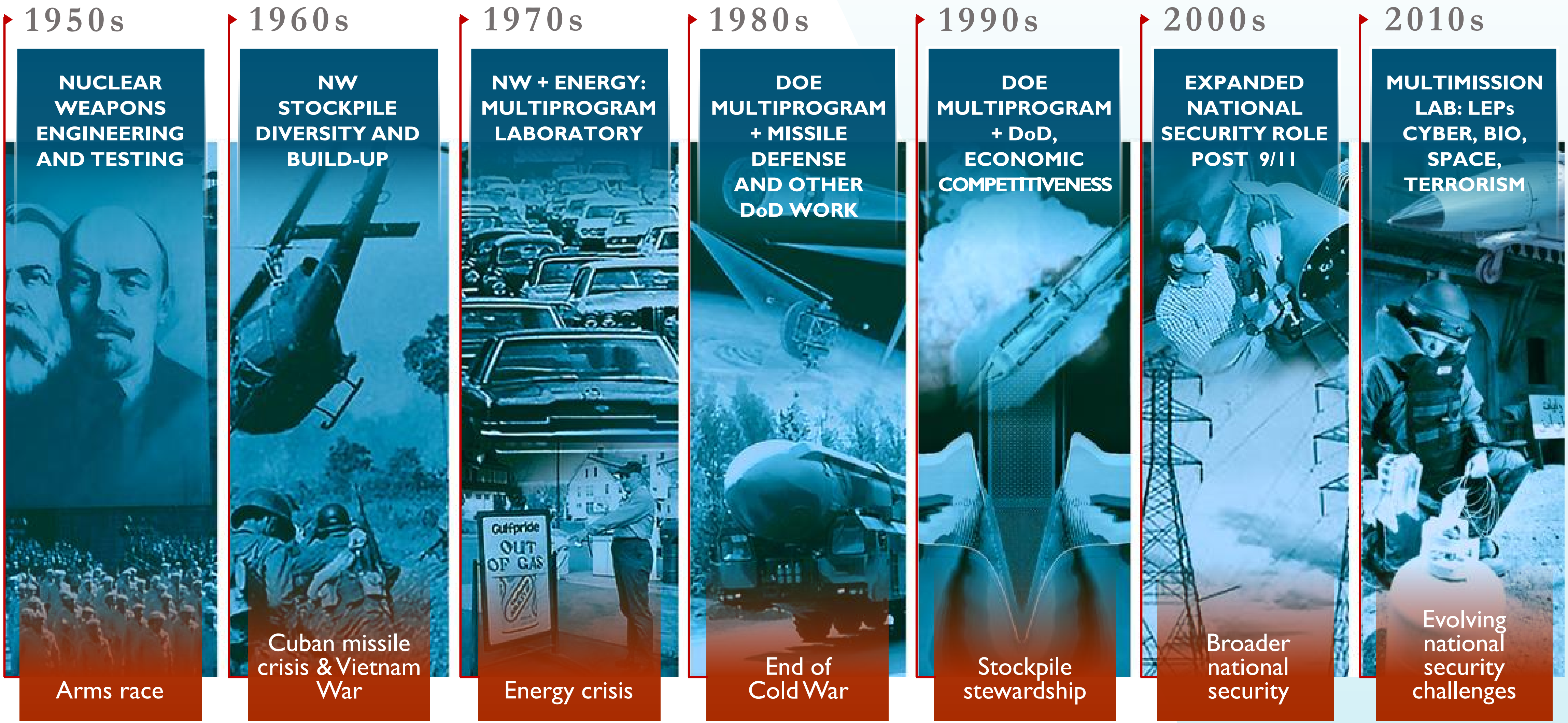
Main sites

- Albuquerque, New Mexico
- Livermore, California

SANDIA HAS FIVE MAJOR PROGRAM PORTFOLIOS

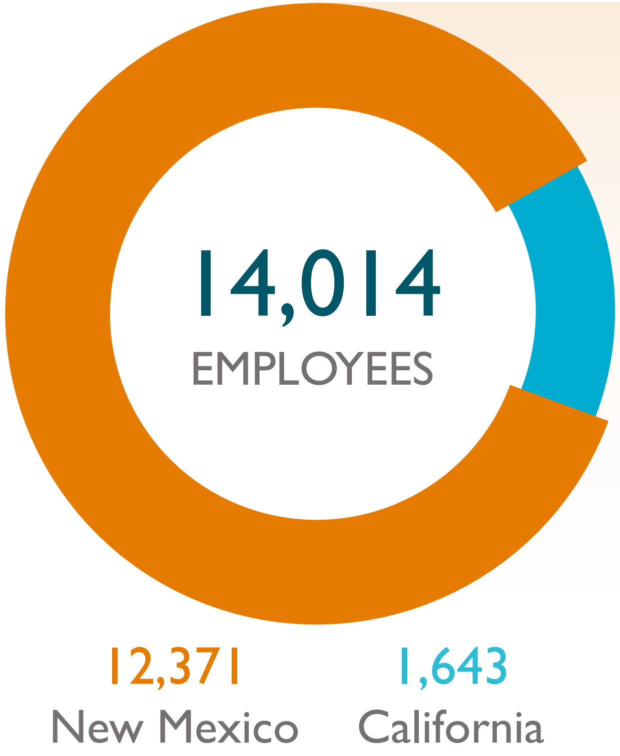


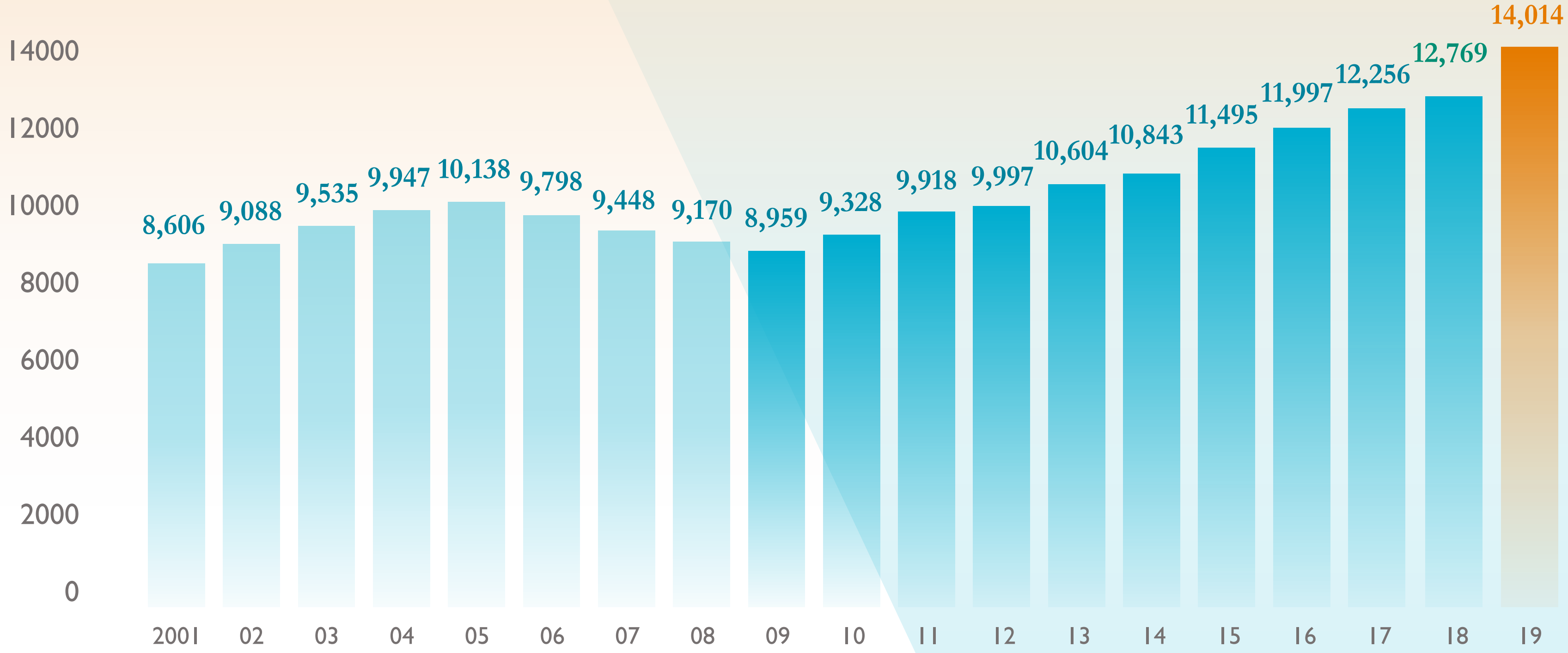
SANDIA ADDRESSES NATIONAL SECURITY CHALLENGES



SANDIA'S WORKFORCE IS GROWING

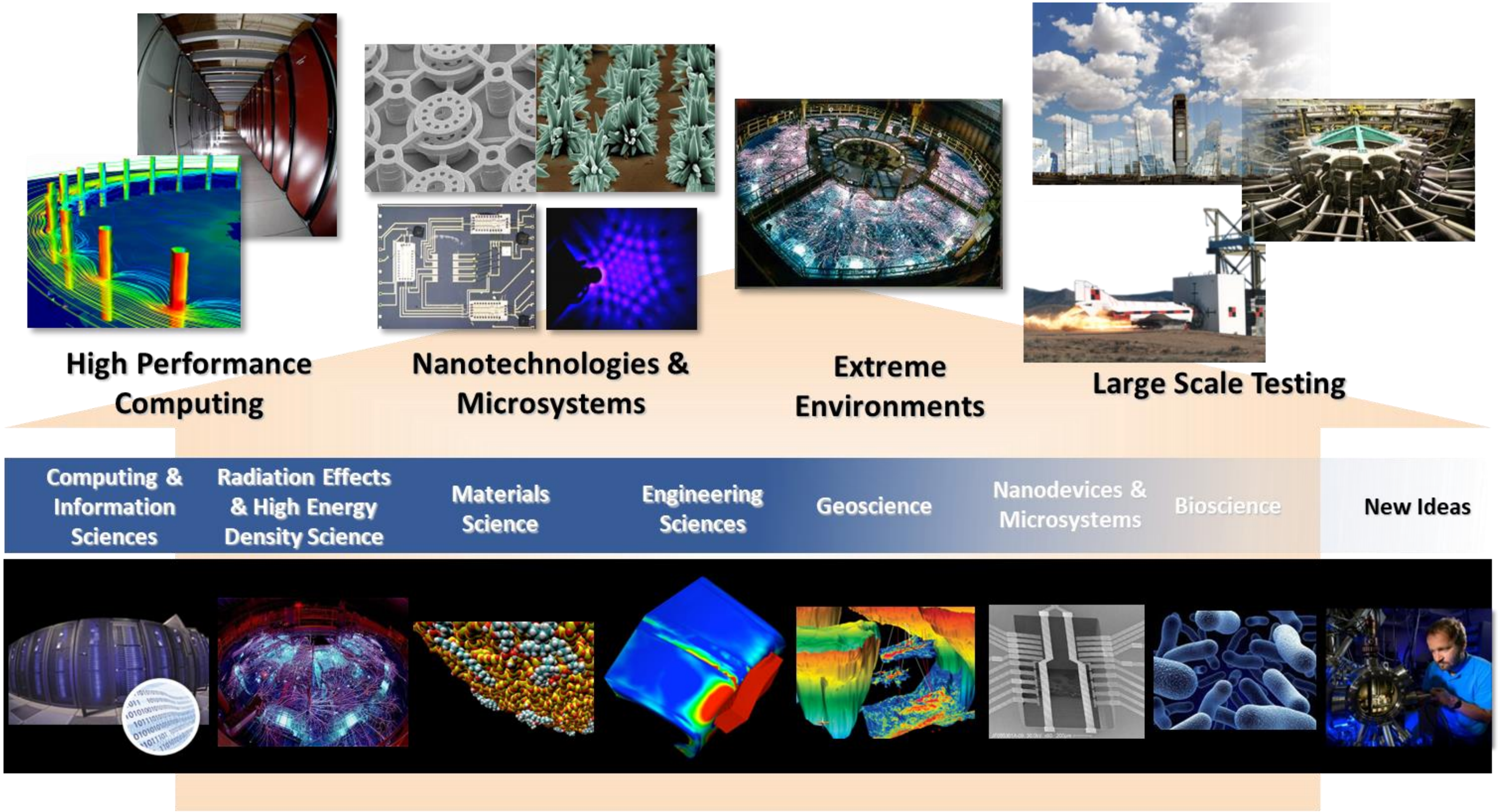
Staff has grown by over 5,000 since 2009 to meet all mission needs





RESEARCH DISCIPLINES THAT ENABLE CAPABILITIES

Strong research foundations play a differentiating role in our mission delivery

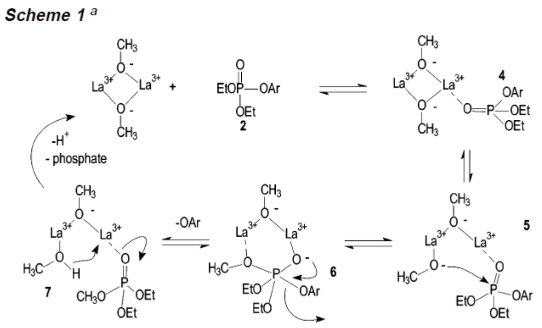


LDRD Research Foundation Disciplines

2. Investigate chemistries to degrade organophosphorous compounds in water free environments; identify suitable simulants

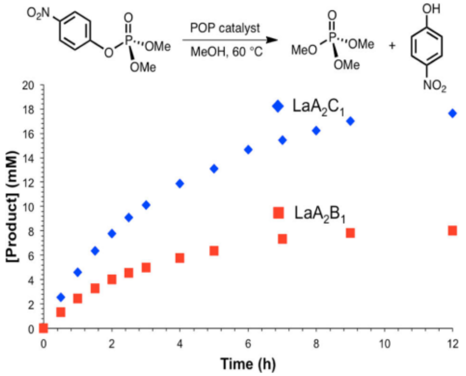
Methanolysis of organophosphates is accelerated by La-based catalysts

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



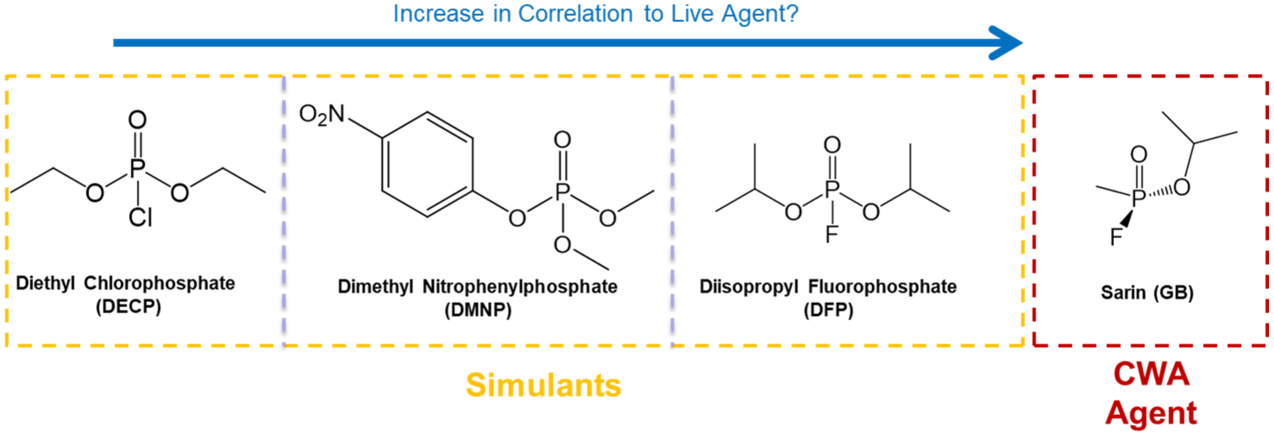
a Methanols of solvation omitted for clarity.

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

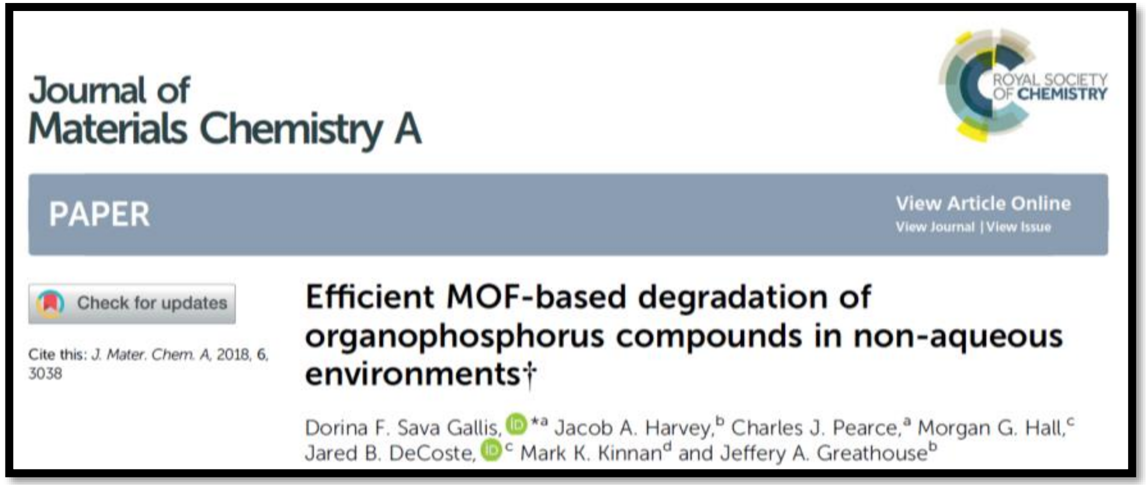


J. Am. Chem. Soc. **2003**, *125*, 7602-7607.
ACS Catal. **2013**, *3*, 1454–1459

- 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



Probing the catalytic activity of RE metals (III) vs. Zr (IV) in related MOF material systems


Journal of Materials Chemistry A

PAPER

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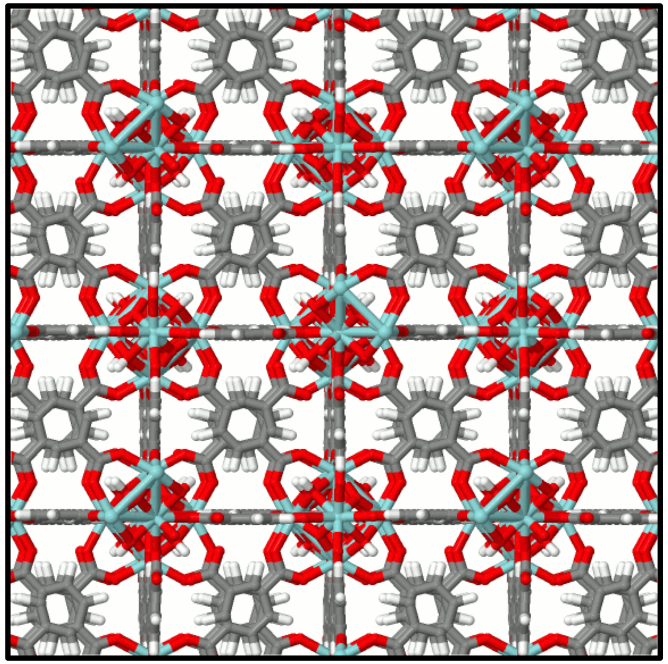
Cite this: *J. Mater. Chem. A*, 2018, 6, 3038

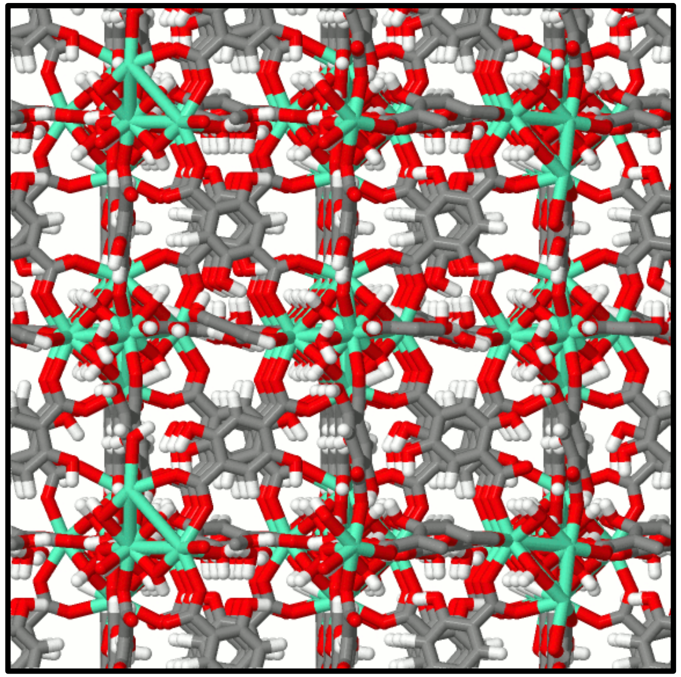
Efficient MOF-based degradation of organophosphorus compounds in non-aqueous environments†

Dorina F. Sava Gallis,*[a] Jacob A. Harvey,[b] Charles J. Pearce,[a] Morgan G. Hall,[c] Jared B. DeCoste,[c] Mark K. Kinnan[d] and Jeffery A. Greathouse[b]

Sava Gallis, D. F. et al. *Journal of Materials Chemistry A* **2018**, *6*, 3038-3045.



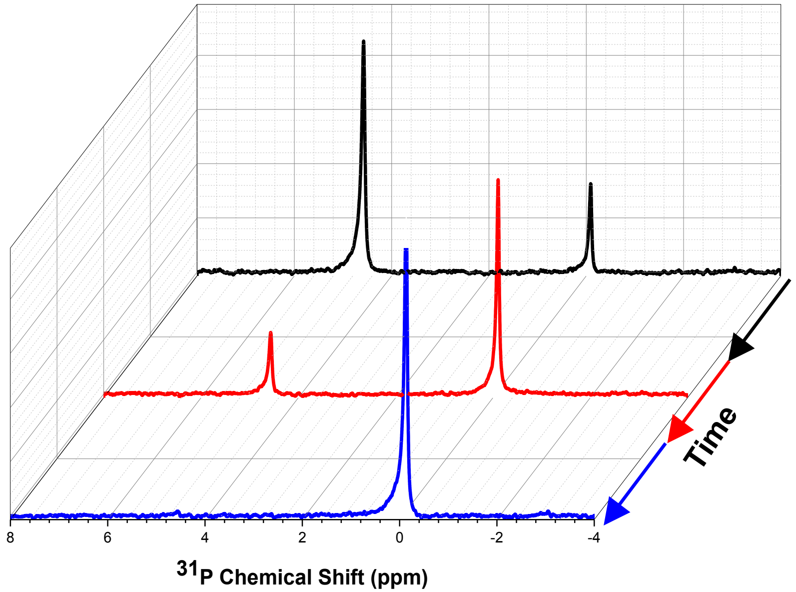
Zr-based MOF

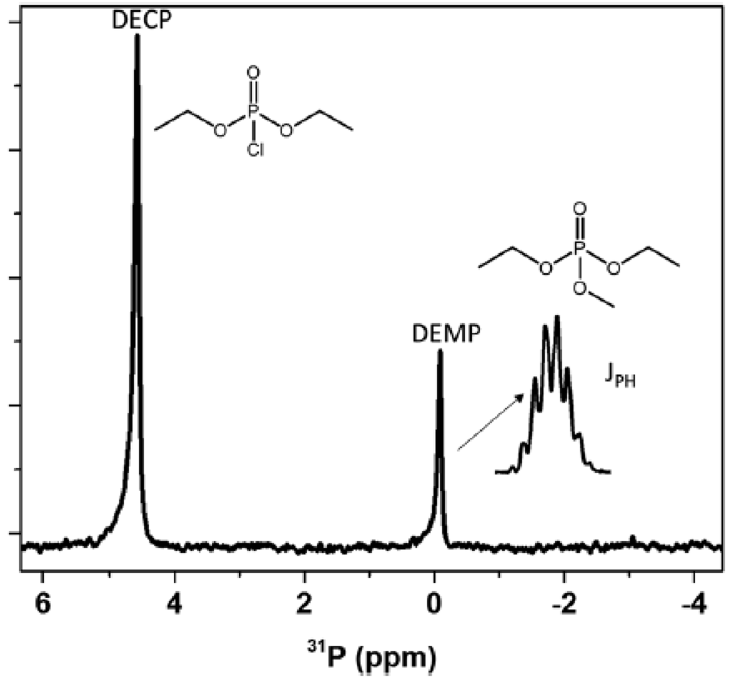


RE-based MOF

Sava Gallis, D.F. et al. ACS Appl. Mater. Interfaces **2017**, 9, 22268-22277

Catalytic degradation monitored *in situ* via NMR





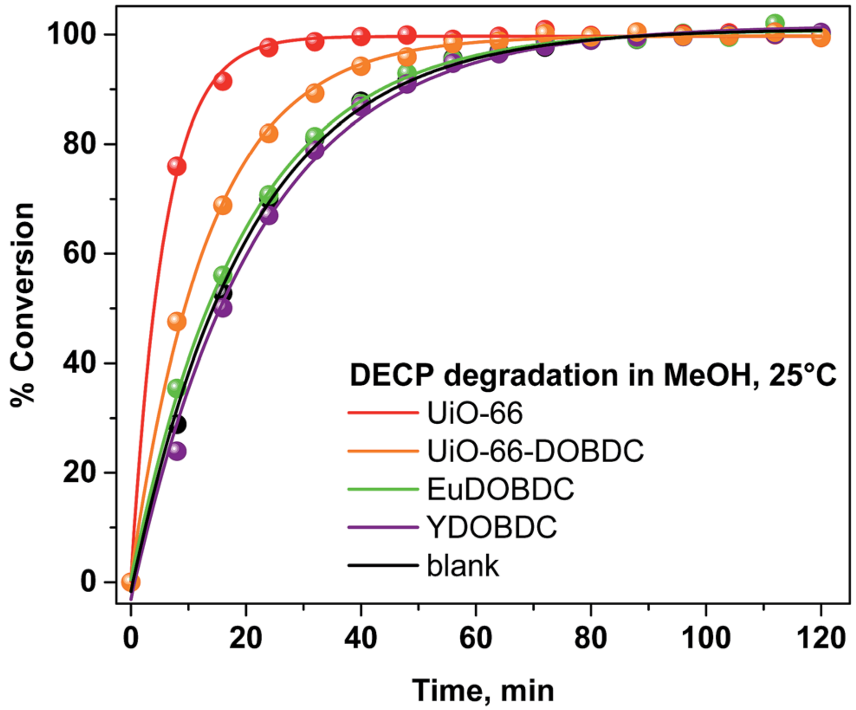
- NMR allows for quantitative and sensitive monitoring of degradation process; and unambiguous determination of the product species

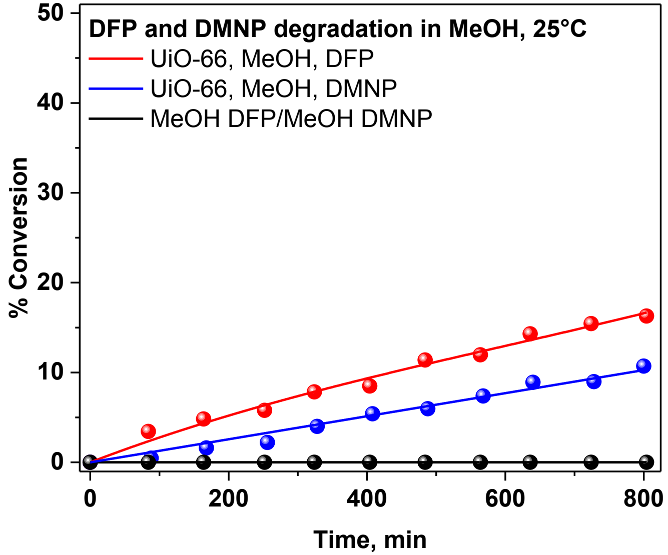
- The breakdown product for DECP is diethyl methyl phosphate, DEMP, formed from the cleavage of the P–Cl bond of DECP

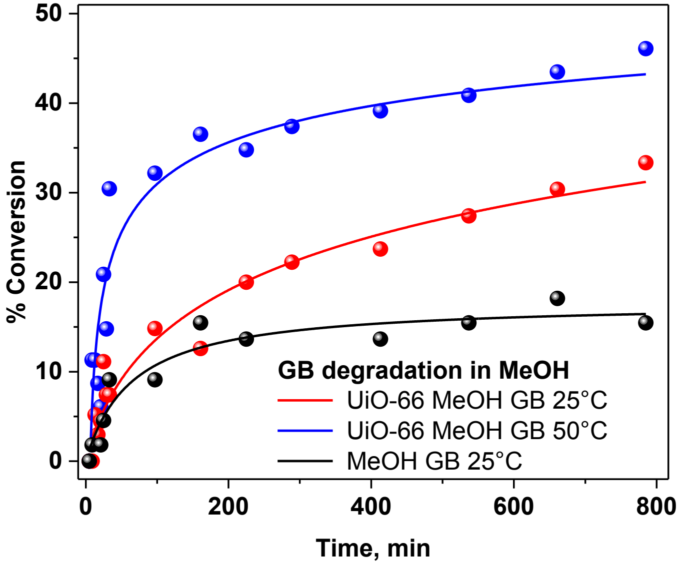
- DEMP product identity confirmed by ^{1}H-coupled ^{31}P NMR

- Octet multiplet shows seven different ^{1}H–^{31}P interactions, associated with the nearest H atoms in the vicinity of the P atom

MOF - based degradation of DECP, DMNP, DFP, and GB in MeOH







- DECP degradation significantly faster than GB; DMNP/DFP much more reliable simulants
- DMNP and DFP degradation run in parallel with GB, suggesting similar mechanisms

Can molecular modeling simulations provide additional insights regarding the degradation mechanisms?

Sava Gallis, D. F. et al. *Journal of Materials Chemistry A* **2018**, *6*, 3038-3045.

Goals: probe ***the effect of truncating the cluster*** and ***the role of defect sites*** on the binding energy of organophosphorous compounds in MOFs

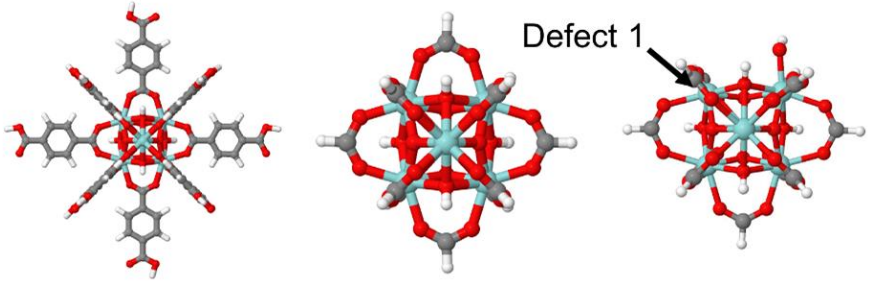
THE JOURNAL OF PHYSICAL CHEMISTRY C
Article
Cite This: J. Phys. Chem. C 2018, 122, 26889−26896
pubs.acs.org/JPCC

Defect and Linker Effects on the Binding of Organophosphorous Compounds in UiO-66 and Rare-Earth MOFs

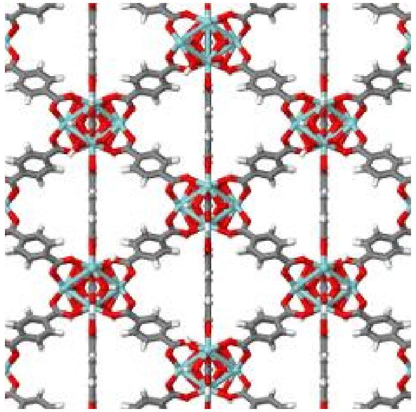
Jacob A. Harvey,[†] Jeffery A. Greathouse,[*,†] and Dorina F. Sava Gallis[*,‡]

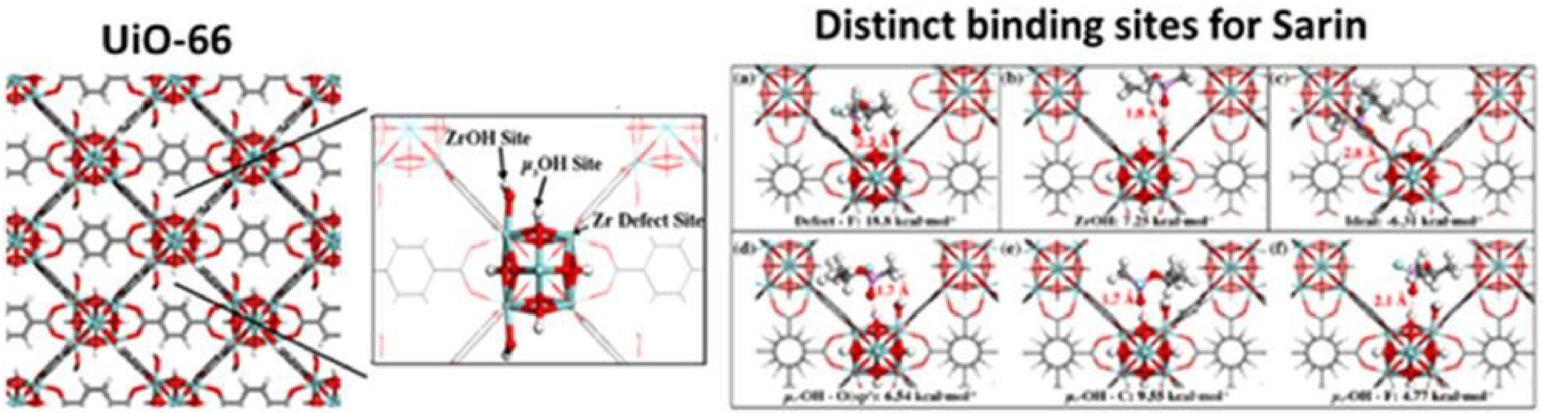
[†]Geochemistry Department and [‡]Nanoscale Sciences Department, Sandia National Laboratories, Albuquerque, New Mexico 87185, United States

Cluster Models



Periodic Models

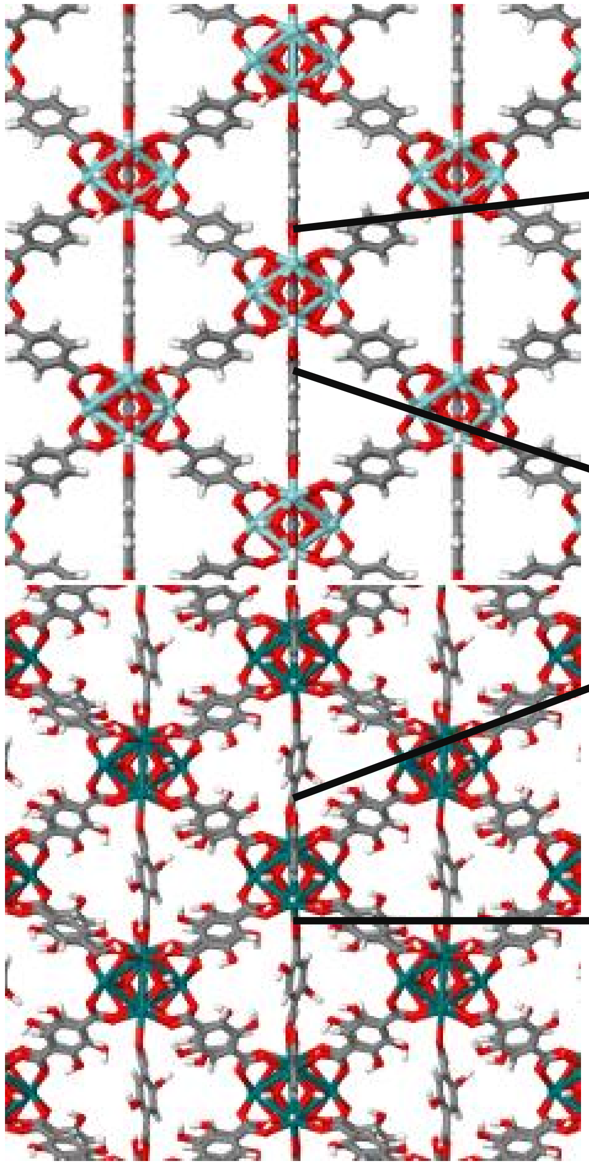


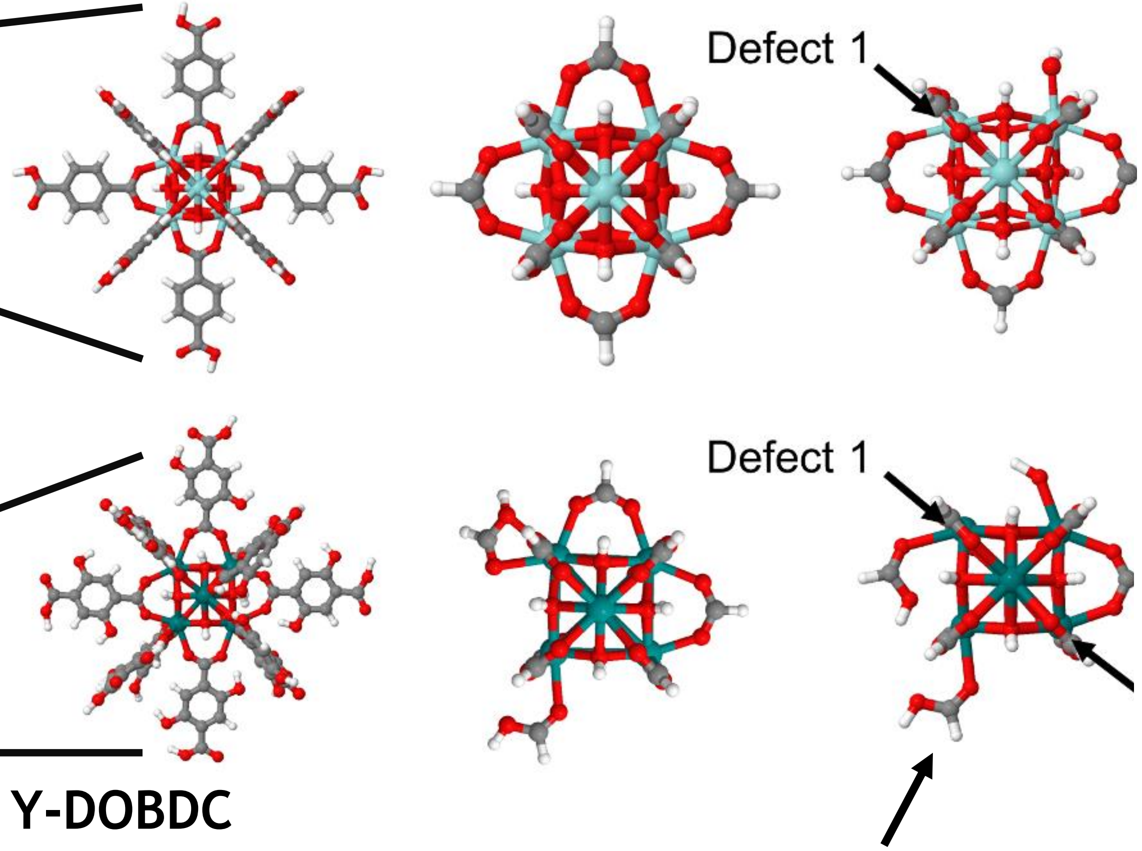


Harvey, J. A.; Greathouse, J. A.; Sava Gallis, D. F. "Defect and Linker Effects on the Binding of Organophosphorous Compounds on UiO-66 and Rare-Earth MOFs", *J. Phys. Chem. C*, **2018**, *122*, 26061-26069.

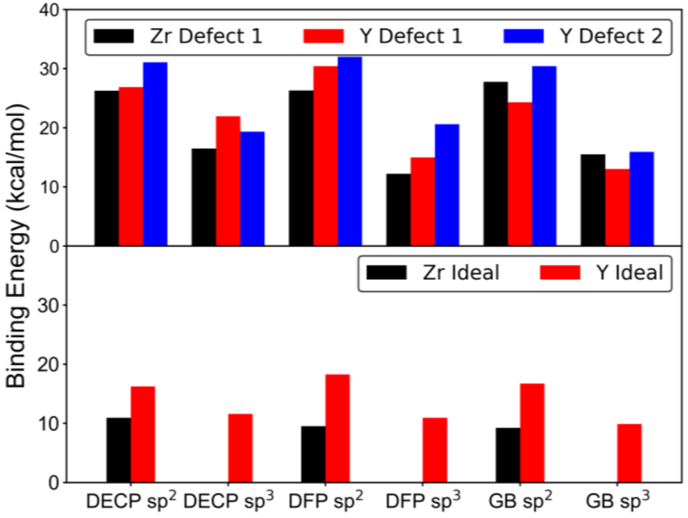
Metal, linker, and cluster model play distinct role in binding energy

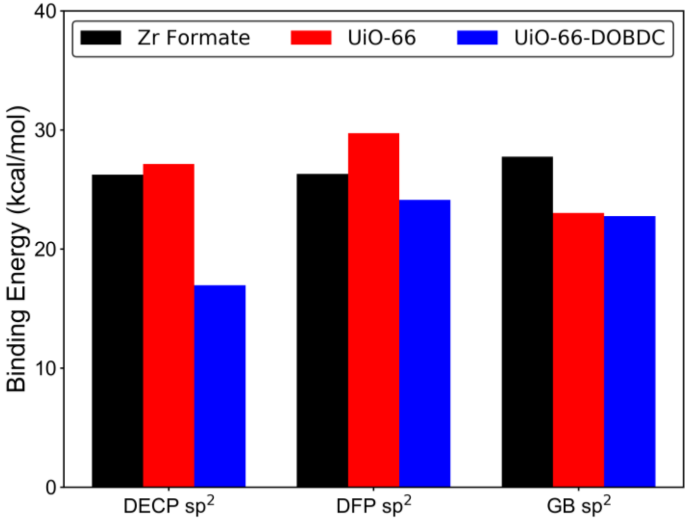
UiO-66 (Zr)
UiO-66 DOBDC (Zr)





Y-DOBDC





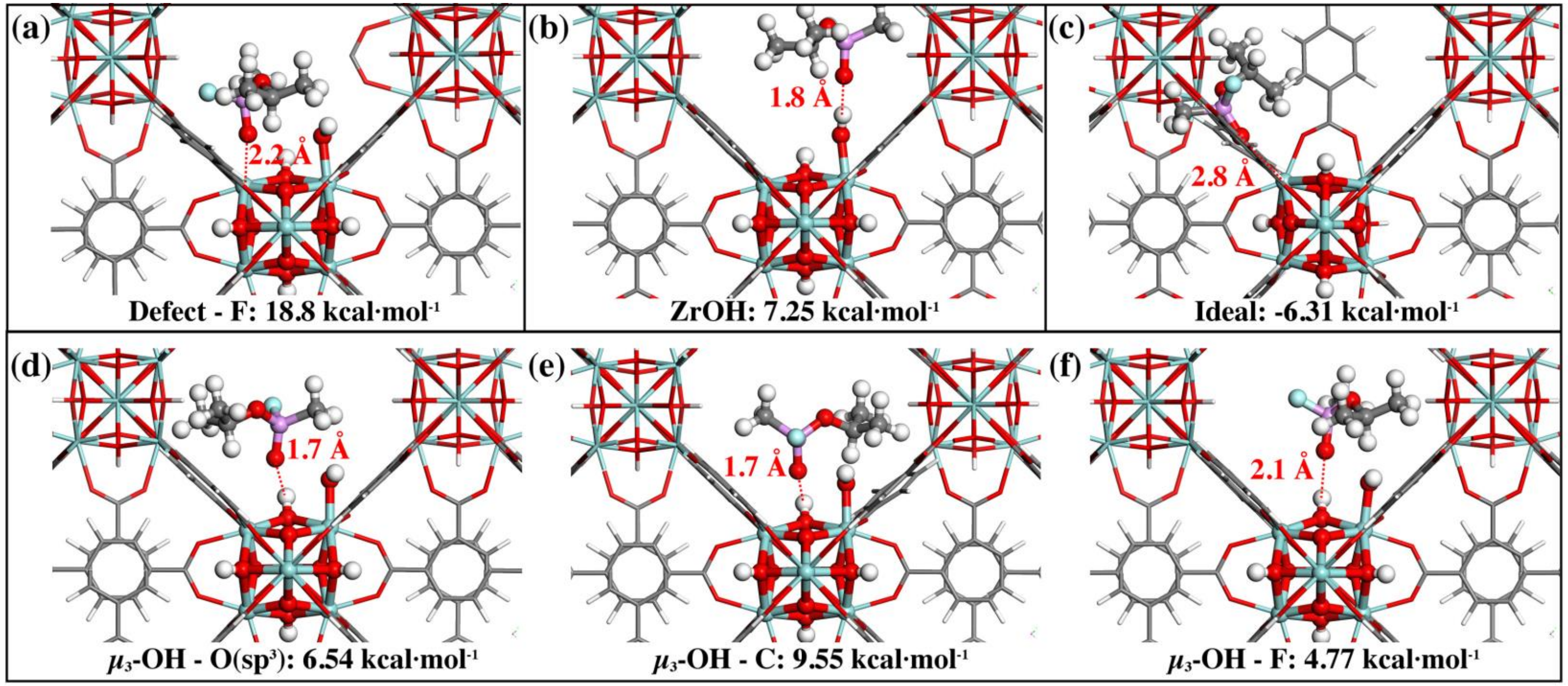
2 unique defects possible in Y-DOBDC:

- Missing linker defect identical to UiO-66 (defect 1)
- Twisted linker defect (defect 2)

Harvey, J. A.; Greathouse, J. A. **Sava Gallis, D. F.** "Defect and Linker Effects on the Binding of Organophosphorous Compounds on UiO-66 and Rare-Earth MOFs", *J. Phys. Chem. C*, **2018**, *122*, 26061-26069.

Periodic DFT approaches capture "full pore" interactions

GB binding energies and geometries via the $O(sp^2)$ site in UiO-66 periodic model

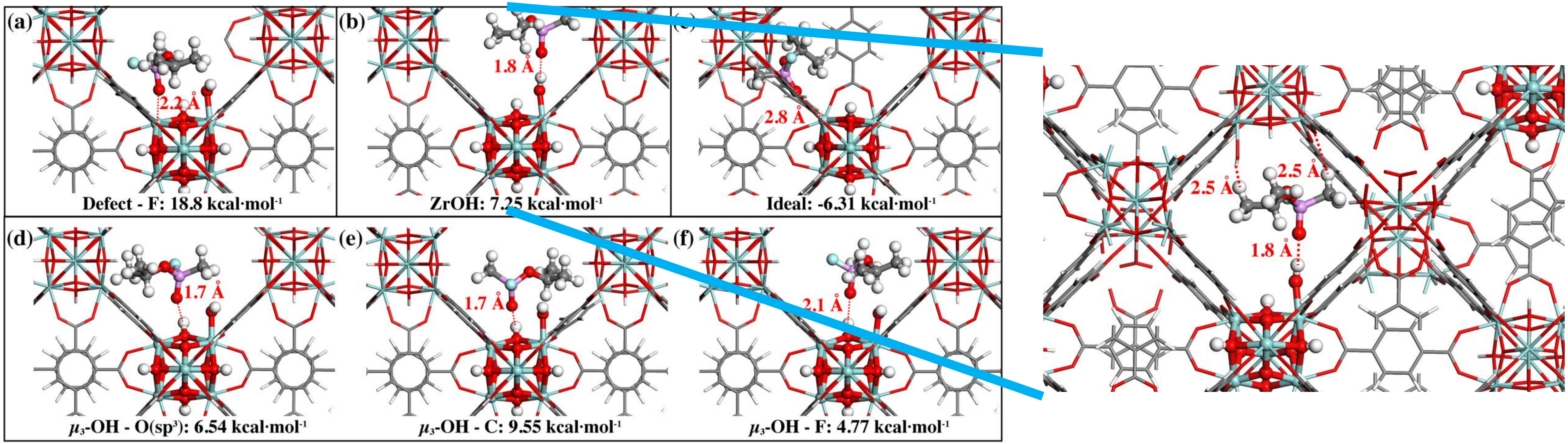


Four distinct sites are depicted:
(a) defect (under coordinated metal)
(b) ZrOH (missing linker)
(c) ideal (fully coordinated metal)
(d)-(f) μ_3-OH.

- Strong orientational effects are observed at the μ^3-OH site

Periodic DFT approaches capture "full pore" interactions

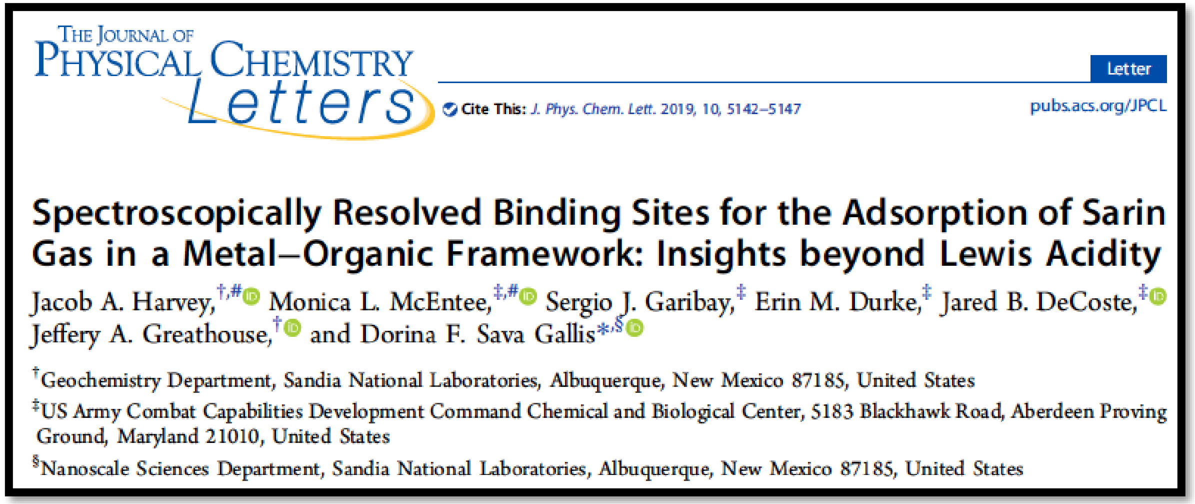
GB binding energies and geometries via the O(sp^2) site in UiO-66 periodic model



- ZrOH binding creates interactions with entire pore → Periodic systems are necessary to capture this interactio
- Wide variety of binding sites and binding energies within UiO-66; is this observable with IR spectroscopy?

Harvey, J. A.; Sava Gallis, D. F. et al., *J. Phys. Chem. C*, **2018**, *122*, 26061-26069.

Predictive Modeling- Experimental IR Spectroscopy Study to Probe GB Binding Sites

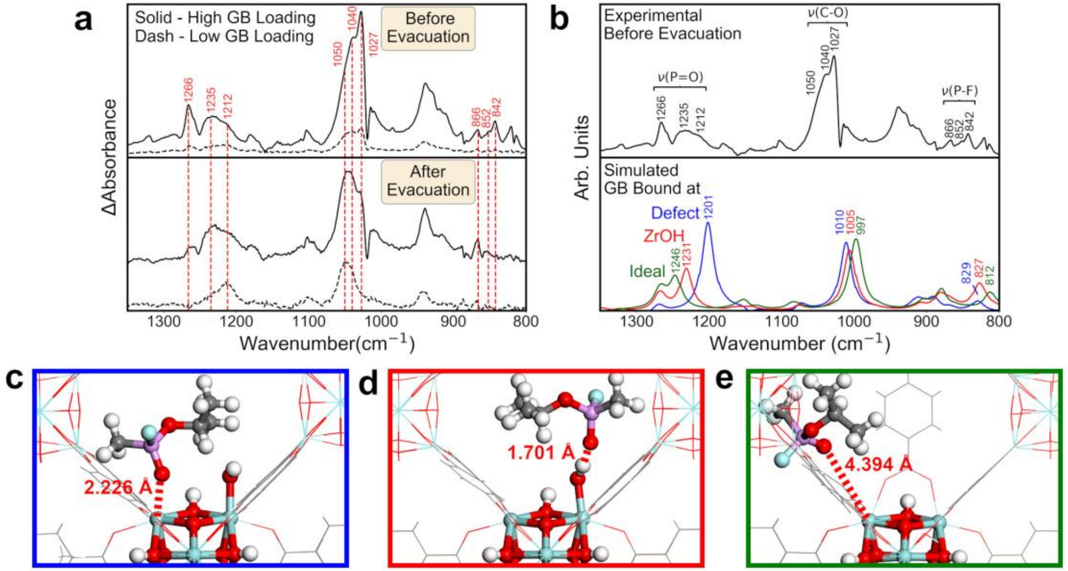


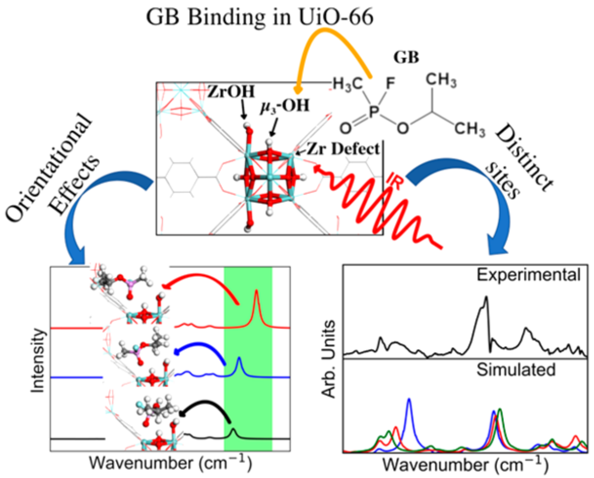
THE JOURNAL OF PHYSICAL CHEMISTRY Letters
Letter
Cite This: J. Phys. Chem. Lett. 2019, 10, 5142–5147
pubs.acs.org/JPCL

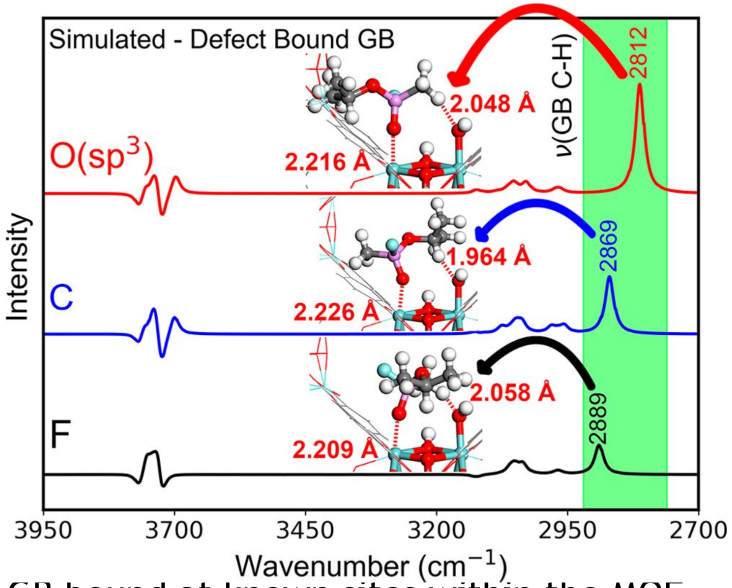
Spectroscopically Resolved Binding Sites for the Adsorption of Sarin Gas in a Metal–Organic Framework: Insights beyond Lewis Acidity

Jacob A. Harvey,[†,#] Monica L. McEntee,[‡,#] Sergio J. Garibay,[‡] Erin M. Durke,[‡] Jared B. DeCoste,[‡] Jeffery A. Greathouse,[†] and Dorina F. Sava Gallis*[,§]

[†]Geochemistry Department, Sandia National Laboratories, Albuquerque, New Mexico 87185, United States
[‡]US Army Combat Capabilities Development Command Chemical and Biological Center, 5183 Blackhawk Road, Aberdeen Proving Ground, Maryland 21010, United States
[§]Nanoscale Sciences Department, Sandia National Laboratories, Albuquerque, New Mexico 87185, United States



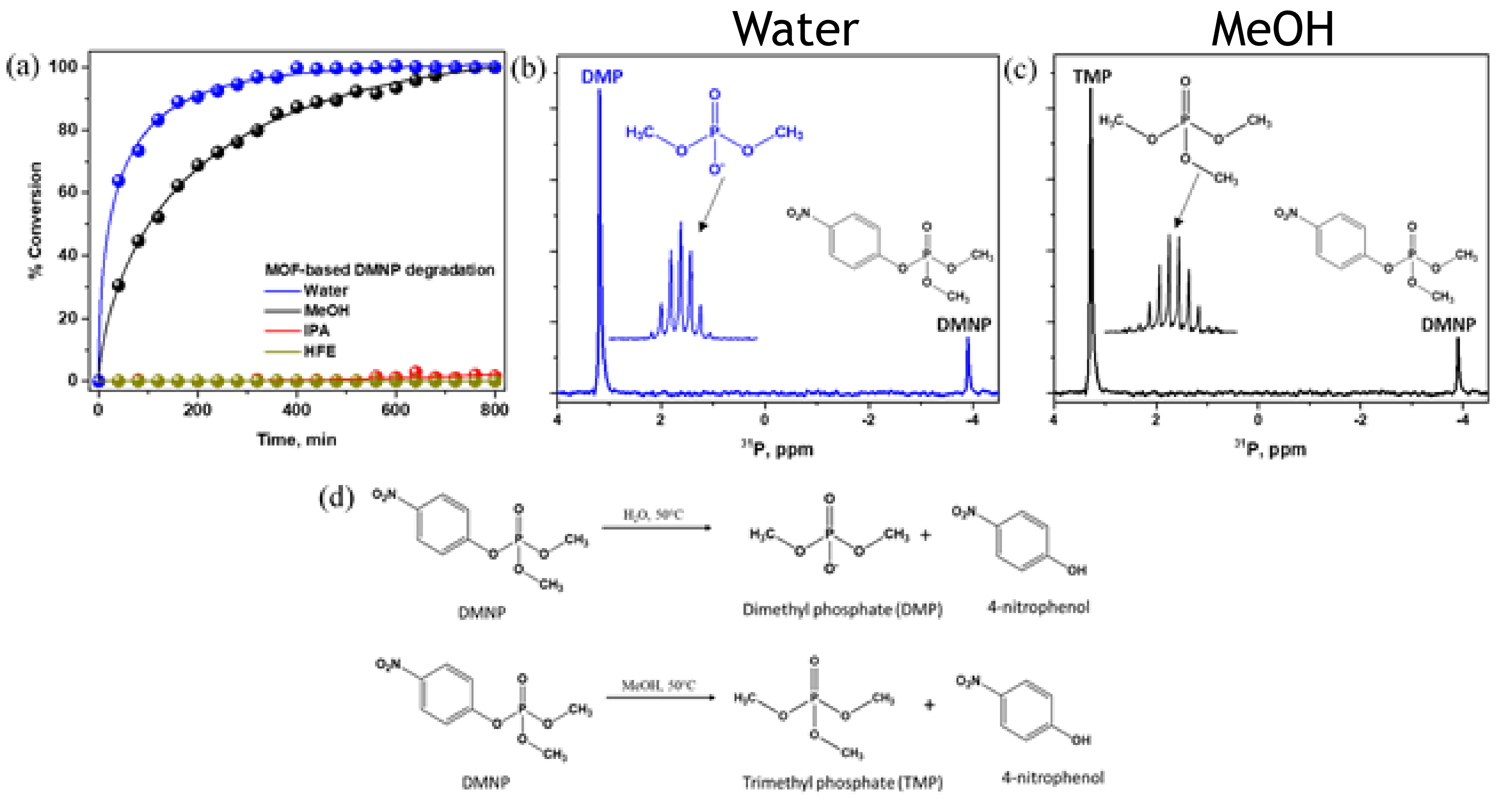


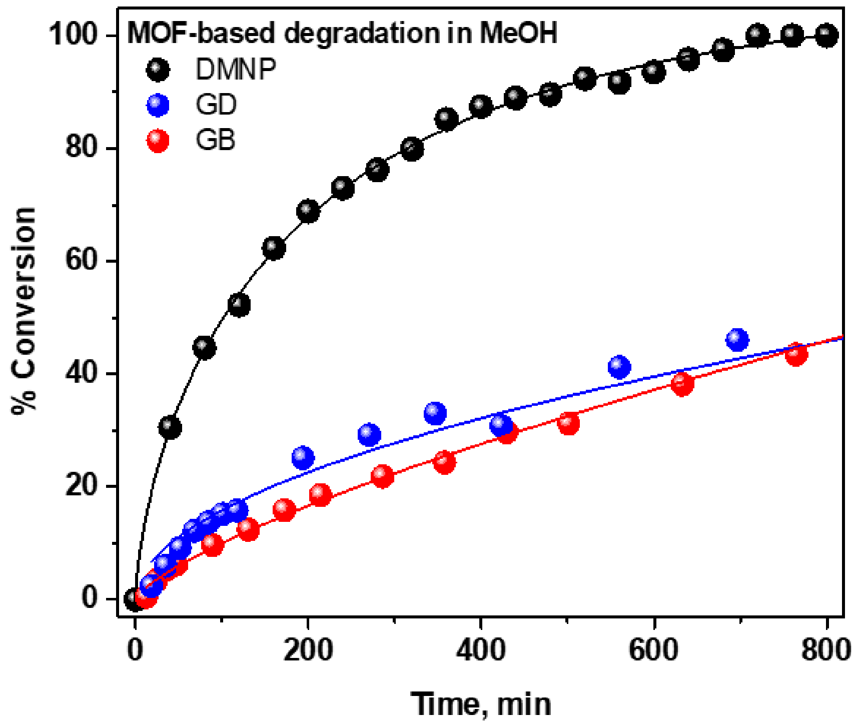


- Calculated IR spectroscopy accurately predicted the P=O stretch frequency for GB bound at known sites within the MOF

Impact: First ever direct observation of GB bound at hypothesized active site (undercoordinated metal)

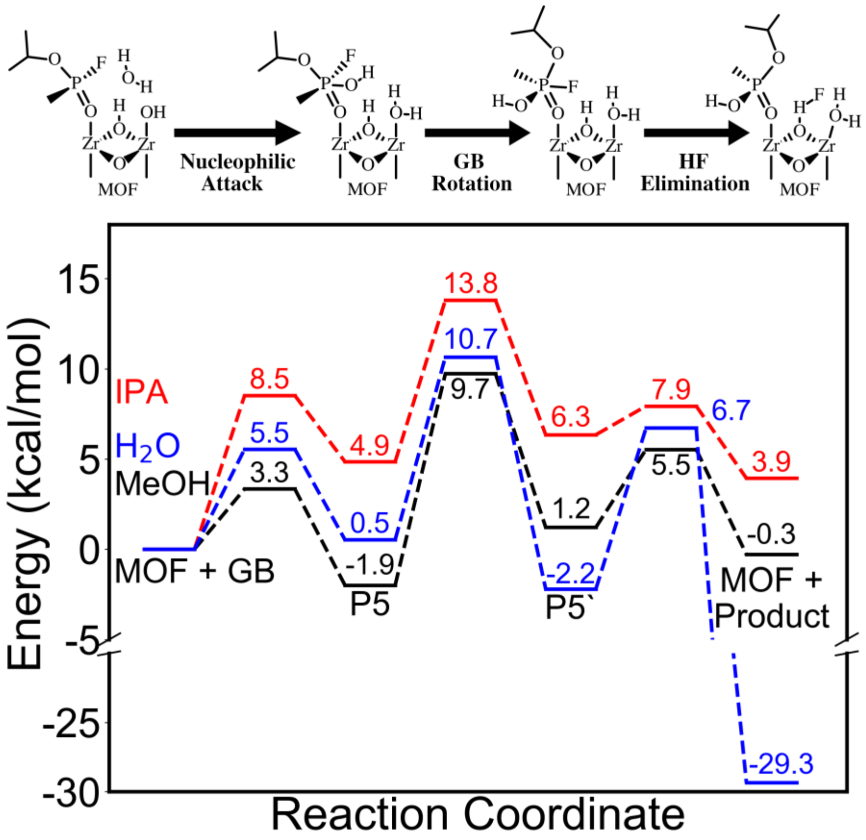
Effect of Solvent on Degradation of CWAs and Simulants





Harvey, J. A.; Pearce, Sava Gallis, D. F. et al. *Dalton Transactions* **2019,** *48* (43), 16153-16157.

Effect of Solvent on Degradation of CWAs and Simulants: Calculated Reaction Pathways Confirm the Trend Observed Experimentally

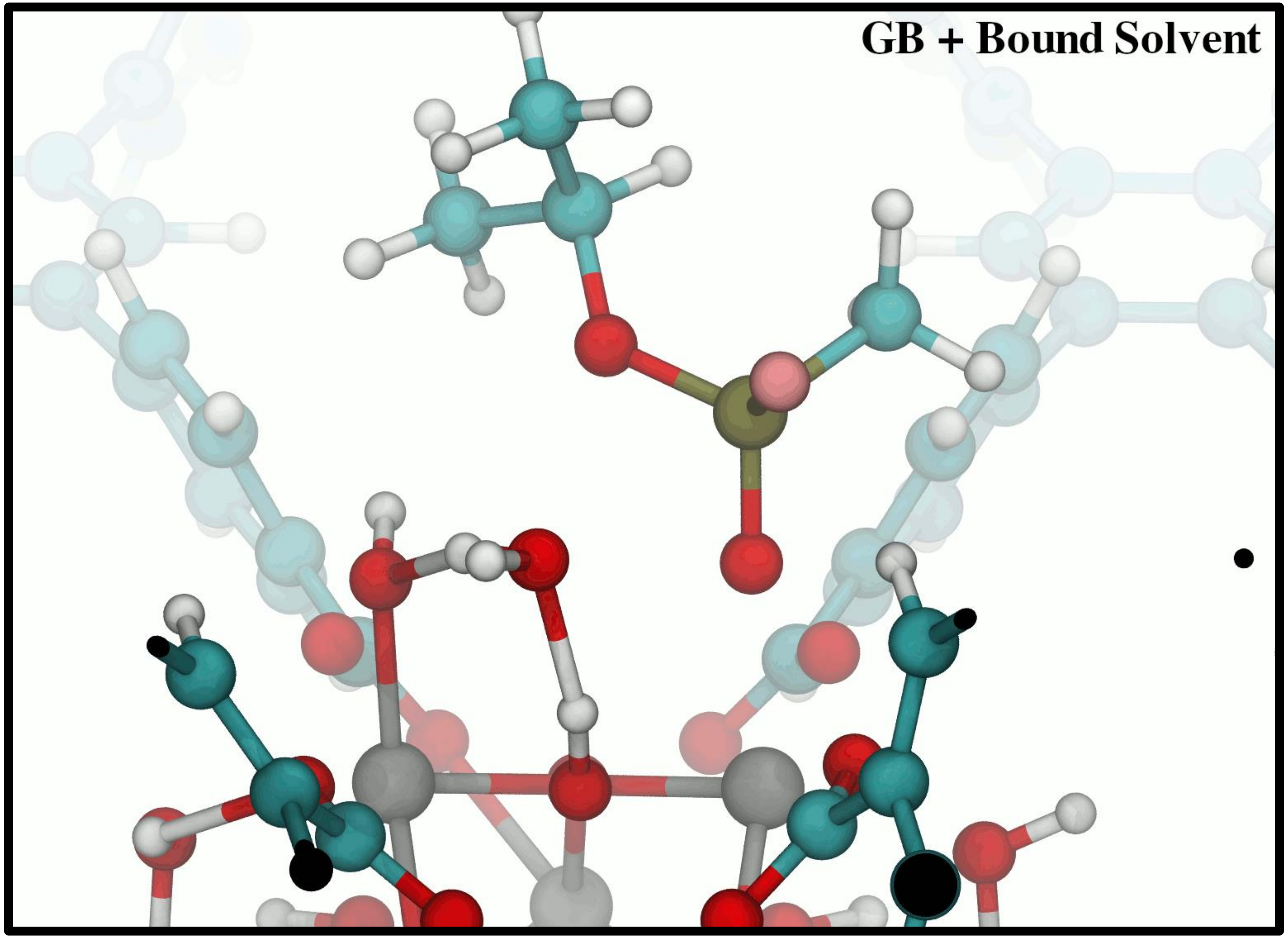


Reaction pathway energies for the degradation of GB on ZrTCPB in H_2O (blue), MeOH (black), and IPA (red). The energies shown for each transition state and intermediate are in kcal·mol^{-1} units. A 2D representation of the degradation pathway is depicted in the top image

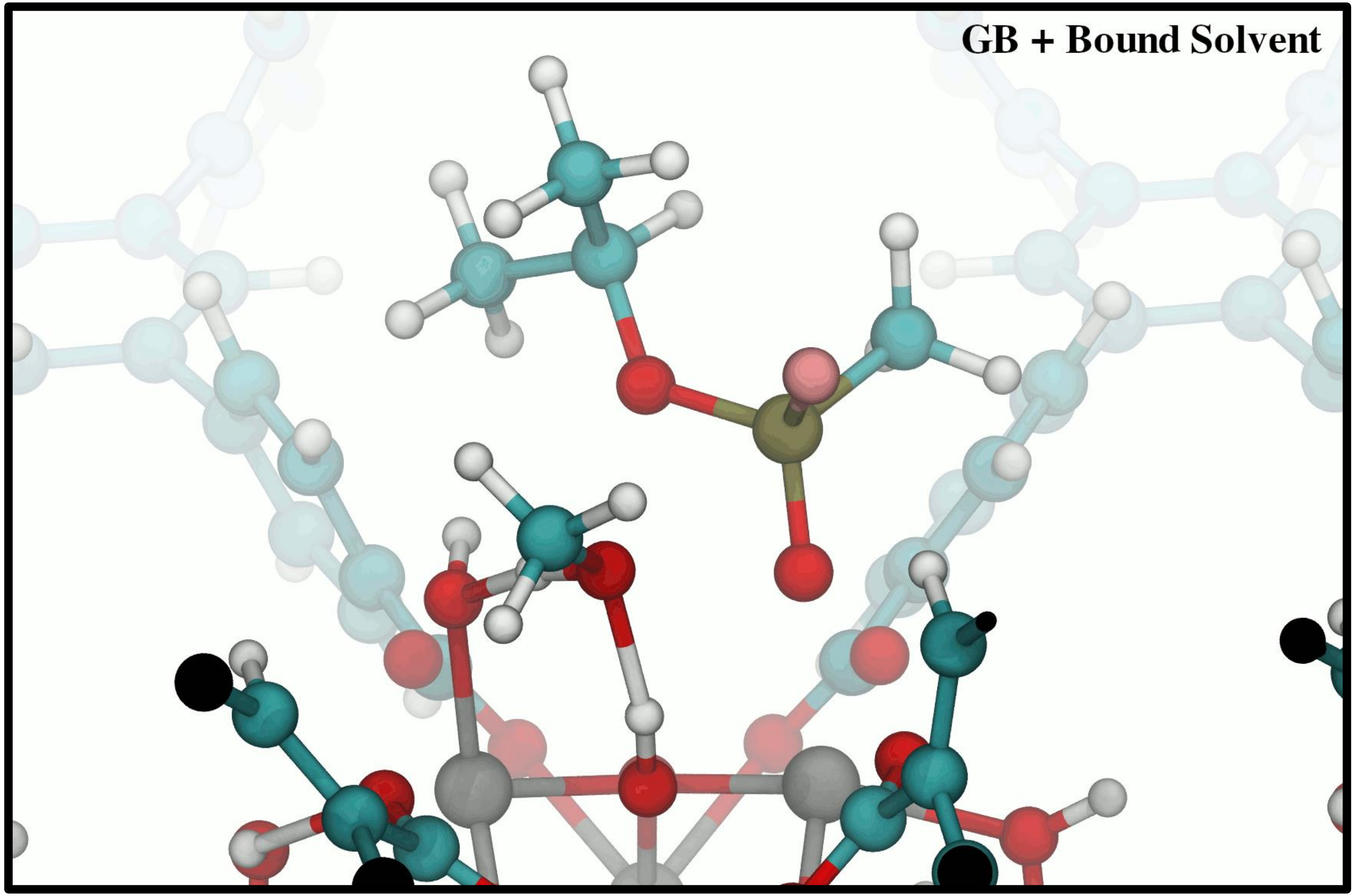
- Calculated degradation pathway accurately predicts the solvent trend observed experimentally (H_2O > MeOH > IPA)
- Provides molecular level details; *rotation of the GB molecule at the active site is rate limiting*

Impact: Previous study showed the barrier for this step was small on small truncated MOF clusters therefore most computational efforts ignore it. Our work indicates that inclusion of the entire pore geometry increases steric effects and therefore this step is critical for accurate modeling of the degradation process.

GB Degradation in H_2O

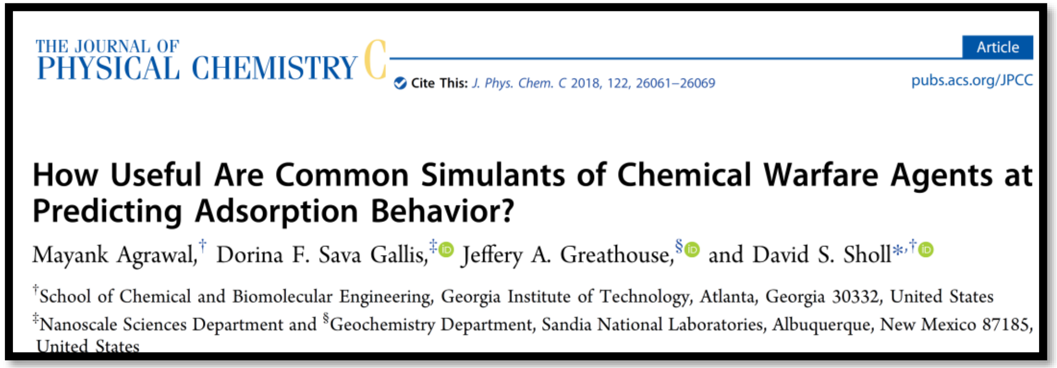


GB Degradation in MeOH



Computational screening to assess predicting the CWA adsorption by simulants

CWA/simulant adsorption properties



THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

Cite This: J. Phys. Chem. C 2018, 122, 26061−26069

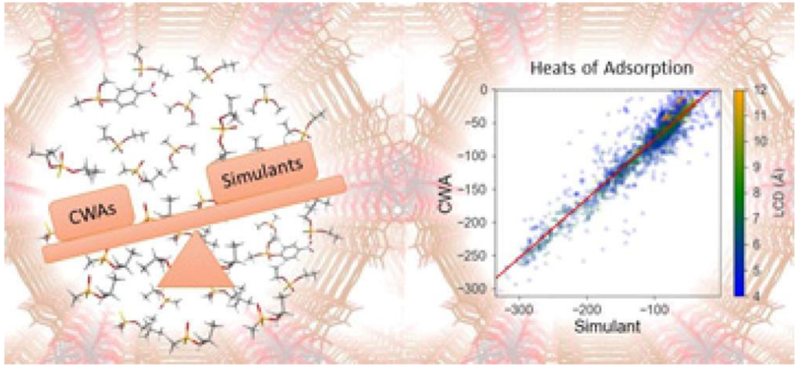
pubs.acs.org/JPCC

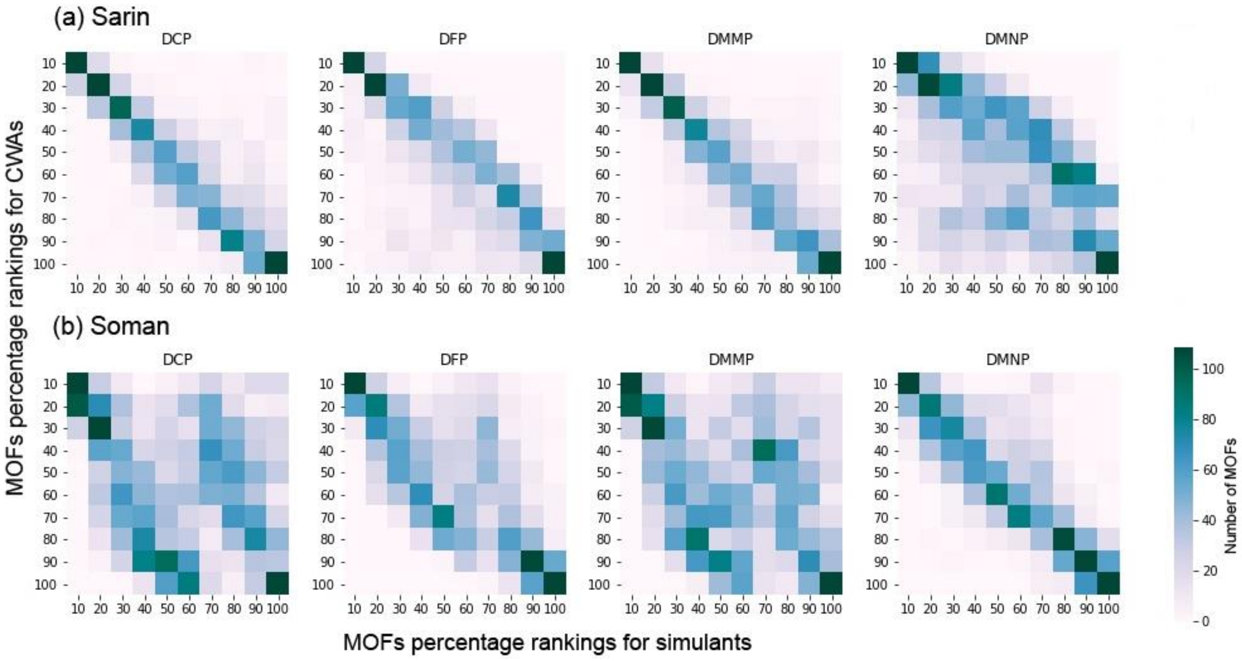
How Useful Are Common Simulants of Chemical Warfare Agents at Predicting Adsorption Behavior?

Mayank Agrawal,[†] Dorina F. Sava Gallis,[‡] Jeffery A. Greathouse,[§] and David S. Sholl*,[†]

[†]School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

[‡]Nanoscale Sciences Department and [§]Geochemistry Department, Sandia National Laboratories, Albuquerque, New Mexico 87185, United States





- DCP and DMMP are the best suited simulants to predict adsorption behavior of Sarin in nanoporous materials
- DMNP is the only simulant that is suited to predict Soman's adsorption behavior in nanoporous materials

The impact of MOF flexibility and effect of pore size in CWA diffusion and adsorption process

Computational screening of CWA selectivity in solvent-filled MOF pores

PCCP

ROYAL SOCIETY OF CHEMISTRY

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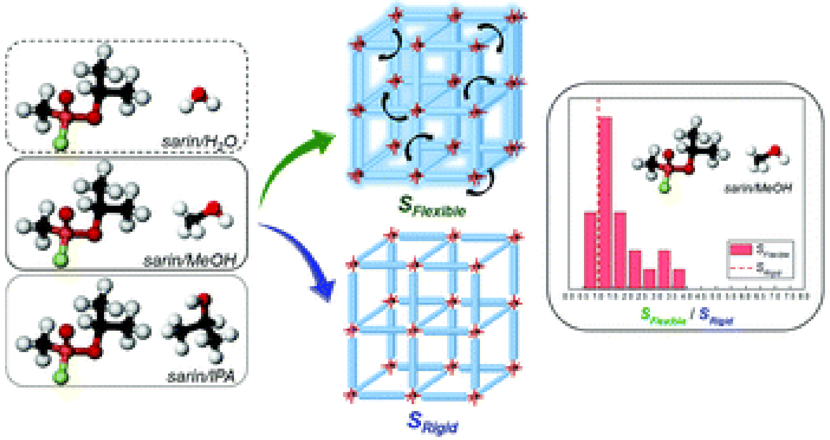
Cite this: Phys. Chem. Chem. Phys., 2020, 22, 6441

Impact of intrinsic framework flexibility for selective adsorption of sarin in non-aqueous solvents using metal–organic frameworks†

Jongwoo Park,[a] Mayank Agrawal,[a] Dorina F. Sava Gallis,[b] Jacob A. Harvey,[c] Jeffery A. Greathouse[c] and David S. Sholl*[a]



Effect of pore size on CWA diffusion

The Journal of Physical Chemistry Letters

Letter

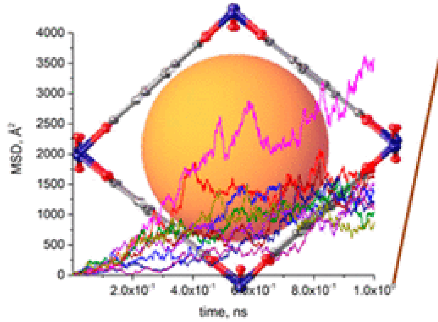
Cite This: J. Phys. Chem. Lett. 2019, 10, 7823–7830
pubs.acs.org/JPCL

Determining Diffusion Coefficients of Chemical Warfare Agents in Metal–Organic Frameworks

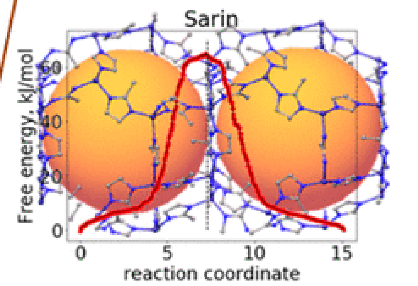
Mayank Agrawal,[†] Salah E. Boulfelfel,[†] Dorina F. Sava Gallis,[§] Jeffery A. Greathouse,[‡] and David S. Sholl*,[†]

[†]School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States
[§]Nanoscale Sciences Department, Sandia National Laboratories, Albuquerque, New Mexico 87185, United States
[‡]Geochemistry Department, Sandia National Laboratories, Albuquerque, New Mexico 87185, United States

Mean Square Displacement



dcTST using Umbrella Sampling



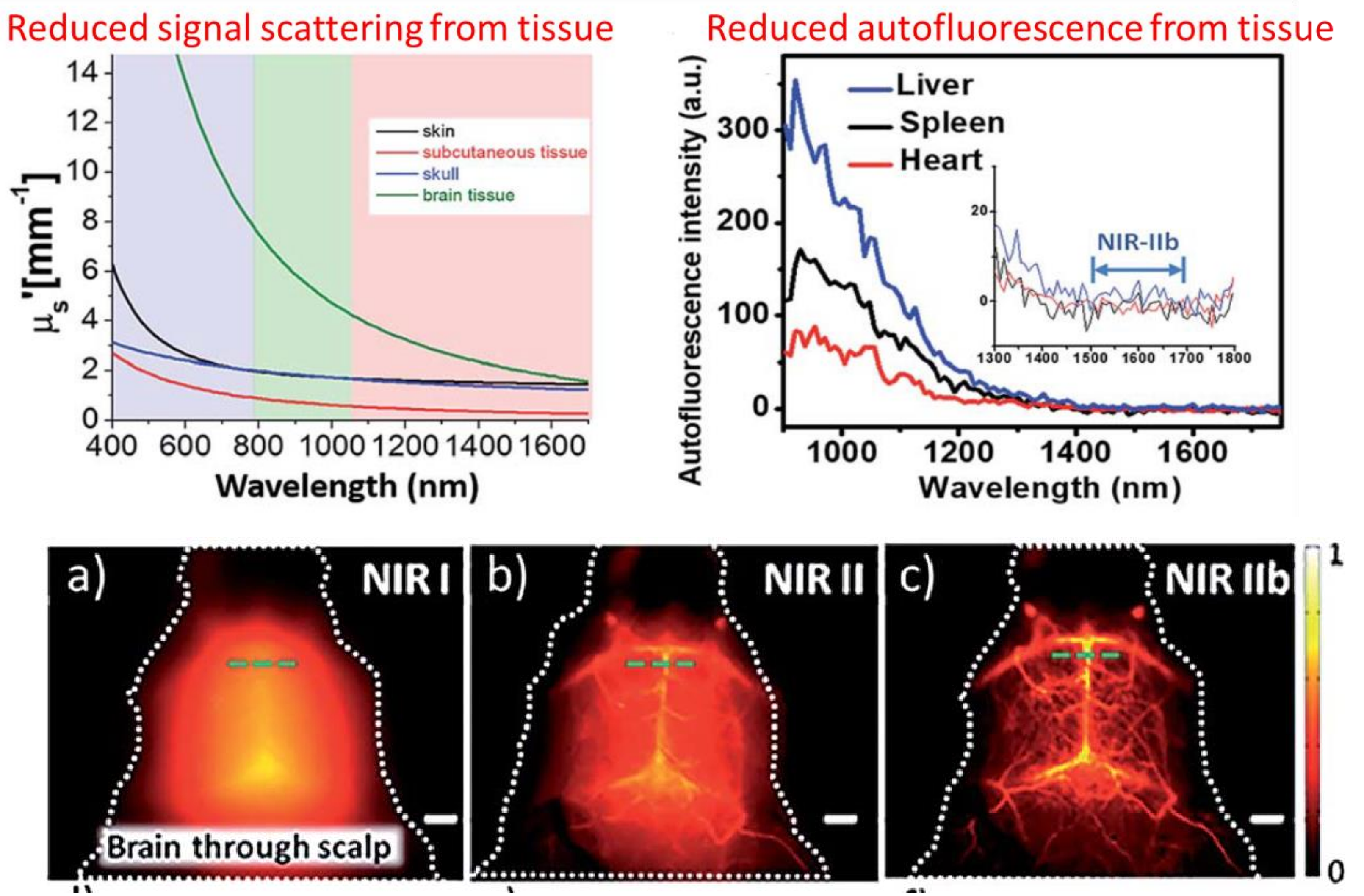
Characteristic diffusion times from MD simulations

Adsorbate	MIL-47, sec	UiO-66, hours	ZIF-8, hours	Cu-BTC, sec
Sarin	0.0003	3.1	25.5	0.025
DMMP	0.0001	8.5	28.9	0.092
DCP	0.003	5.1e4	1.6e3	28.1
DFP	0.014	1.2e5	1.2	180.2

Need to develop novel NIR fluorescent probes that match the optical window for biological tissue

- Main attributes:

1. Optical signals require no radiation for imaging
2. Optical imaging in the NIR has greatly reduced background signal
3. Further into NIR reduces signal background

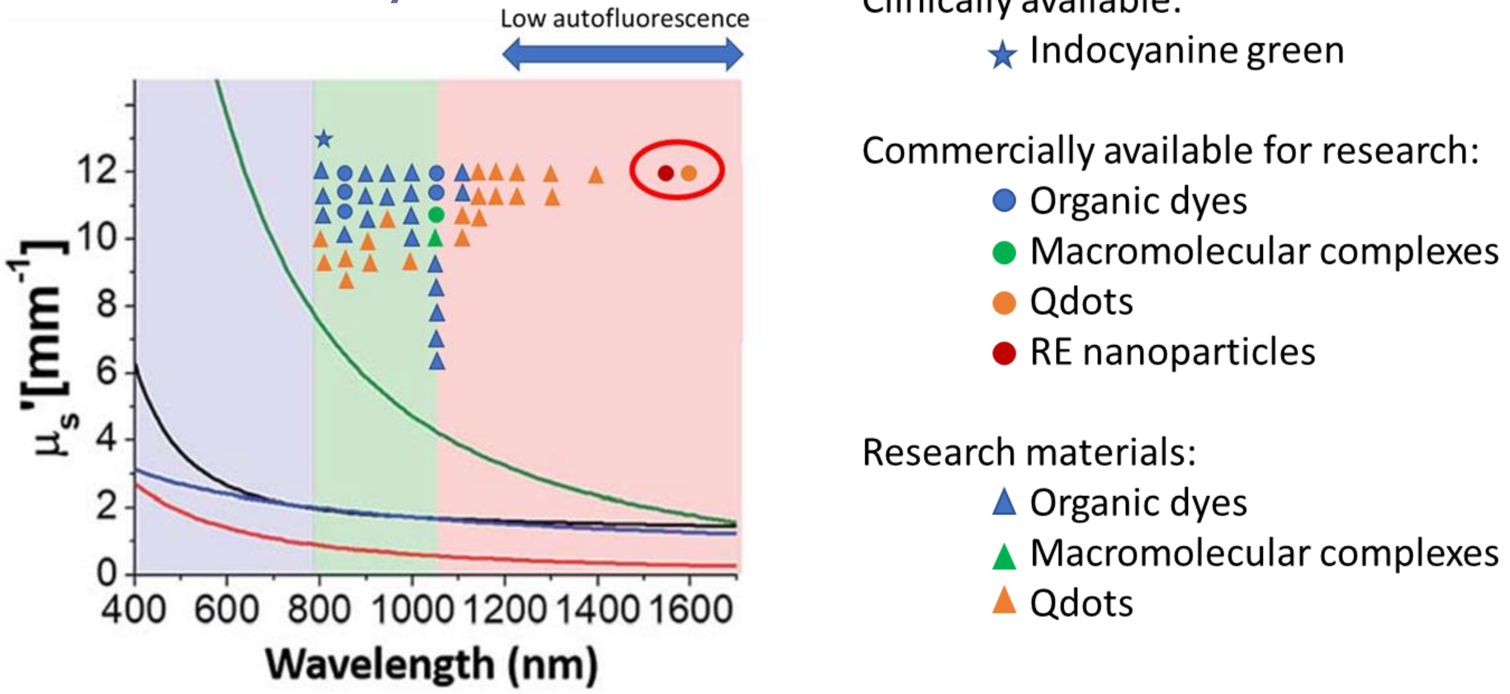


NIR I: 700-900 nm
NIR II: 1000-1700 nm
NIR IIa: 1300-1490 nm
NIR IIb: 1500-1700 nm

Near infrared (NIR) imaging has the potential to revolutionize medical (both clinical and research) imaging

Clinically and commercially available NIR systems

- Currently ***only one FDA- approved dye, for medical use*** for determining blood flow: indocyanine green (ICG)
- ICG does not interact with tissues and cannot be targeted and therefore cannot be used for diagnostic imaging beyond blood flow
- ICG and commercial molecular dyes are not active in NIR-II



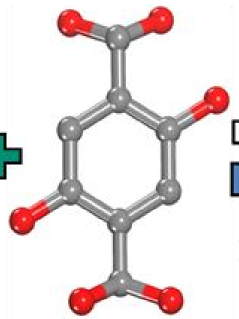
- ❖ Limitations of known NIR-emitters: broad and/or weak emissions, and short lifetimes- not appropriate for *in vivo* long-term tracking experiments
- ❖ Commercially available dyes have emission properties mainly in the first NIR window
- ❖ Very limited options for NIR window II, they have low QY (0.001 – 0.3%)
- ❖ Particles are inherently toxic and require additional steps to mitigate this disadvantage
- ❖ Formulations are proprietary and are difficult to integrate with specific platforms

NEED: highly efficient, biocompatible NIR emitting materials capable of specific, targeted interactions

Materials by design: a novel MOFs platform based on a targeted molecular building block

Proof-of-concept prototype structure

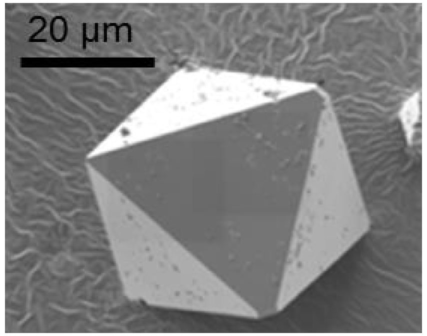
$M(NO_3)_3 \cdot 6H_2O$ +



$DMF/H_2O/HNO_3$

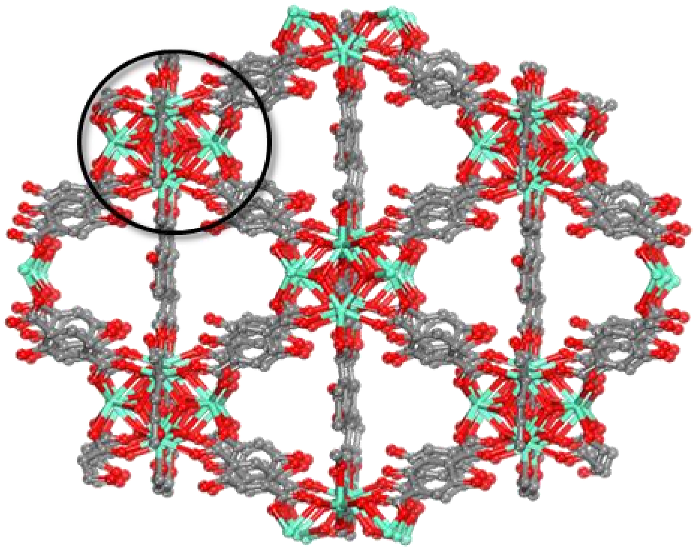
Modulating agent

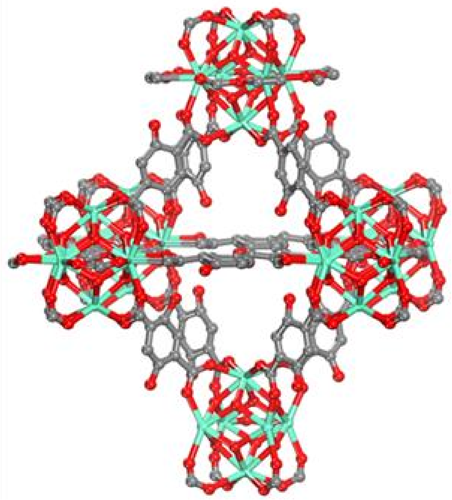
115°C, 2 days



Single-crystal X-ray diffraction

Tetragonal, 3D framework
P4NC
a= b= 15.5567 Å
c= 21.334 Å
$\alpha=\beta=\gamma=90^\circ$ = V= 5163.06 $Å^3$



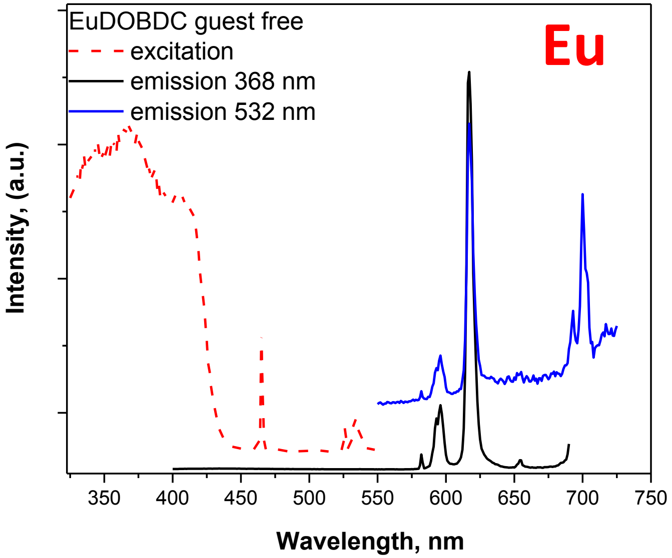


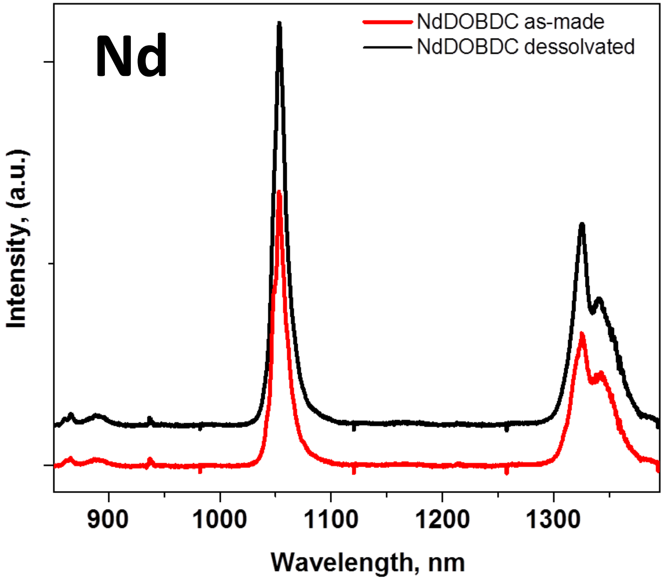
Octahedral cages of ~ 14 Å diameter, accessible via triangular windows of ~ 5.5 Å

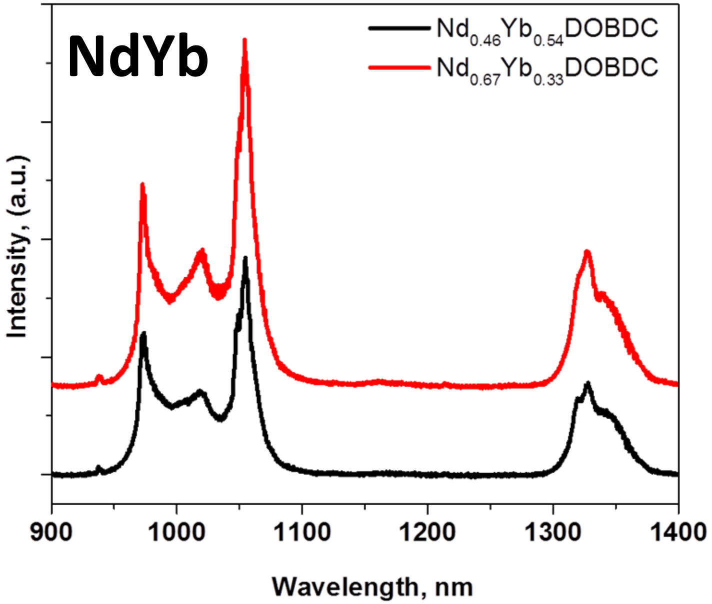
Sava Gallis et al., *ACS Appl.Mater.Inter.* **2017**, *9*, 22268–22277.

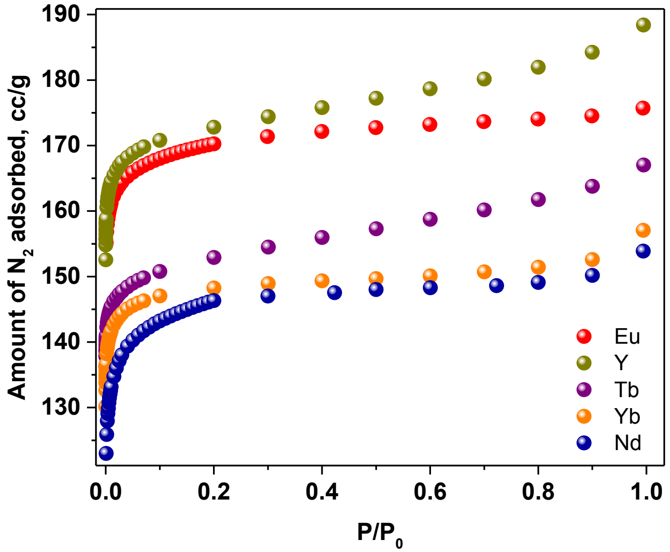
US Patent Application #62522006

Tunable emission properties: deep red to NIR spectral region 614 – 1350 nm









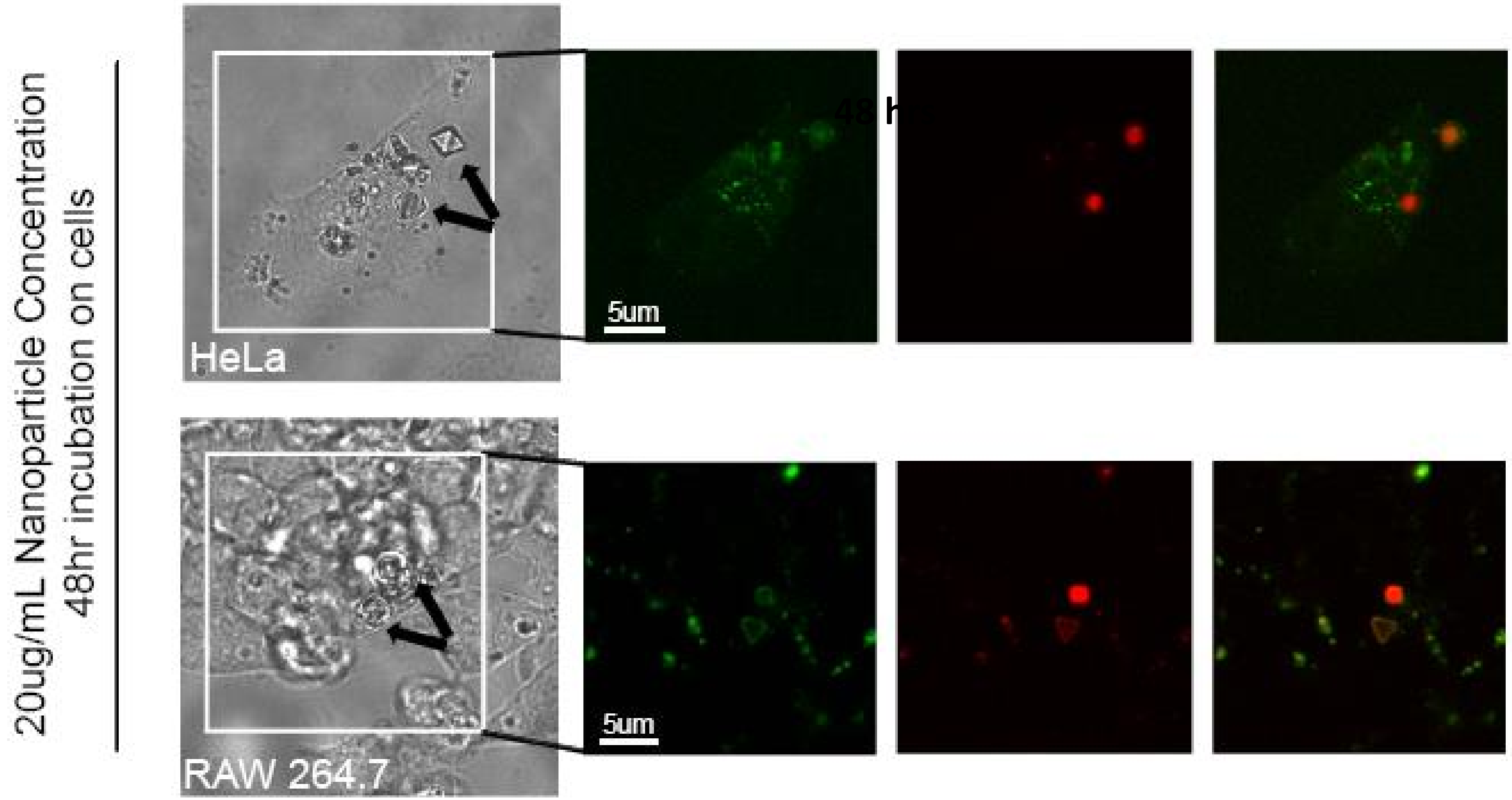
Nitrogen gas adsorption isotherms at 77K

Sample	BET SA	Langmuir SA
YbDOBDC	613 m^2/g	630 m^2/g
YDOBDC	710 m^2/g	730 m^2/g
TbDOBDC	630 m^2/g	650 m^2/g
EuDOBDC	700 m^2/g	730 m^2/g
NdDOBDC	587 m^2/g	620 m^2/g

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

Eu-NP incorporated in both type of cells after 48 hours

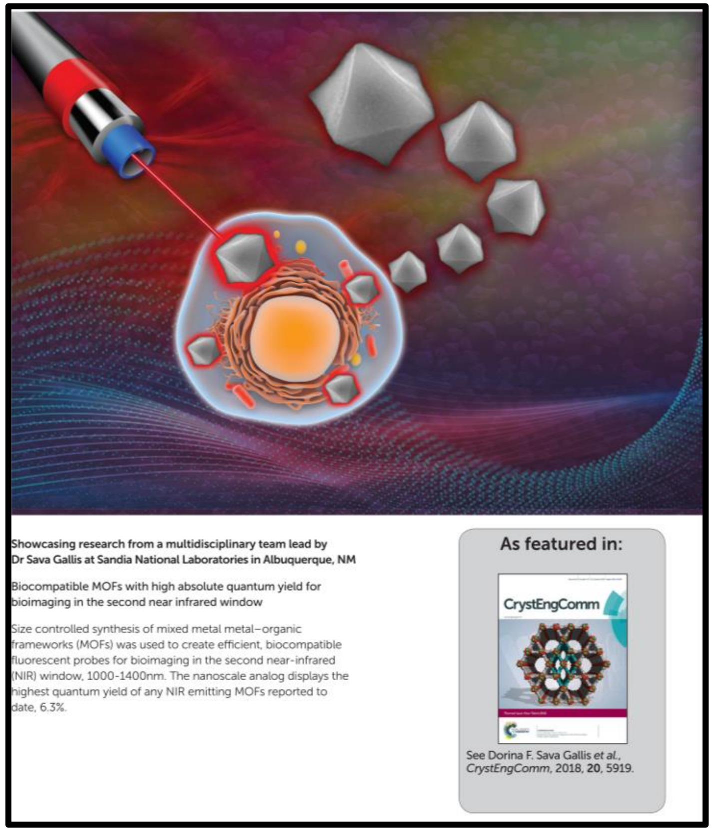
First report that documents the long-term conservation of the intrinsic emission in live cells of a fluorophore-based MOF to date

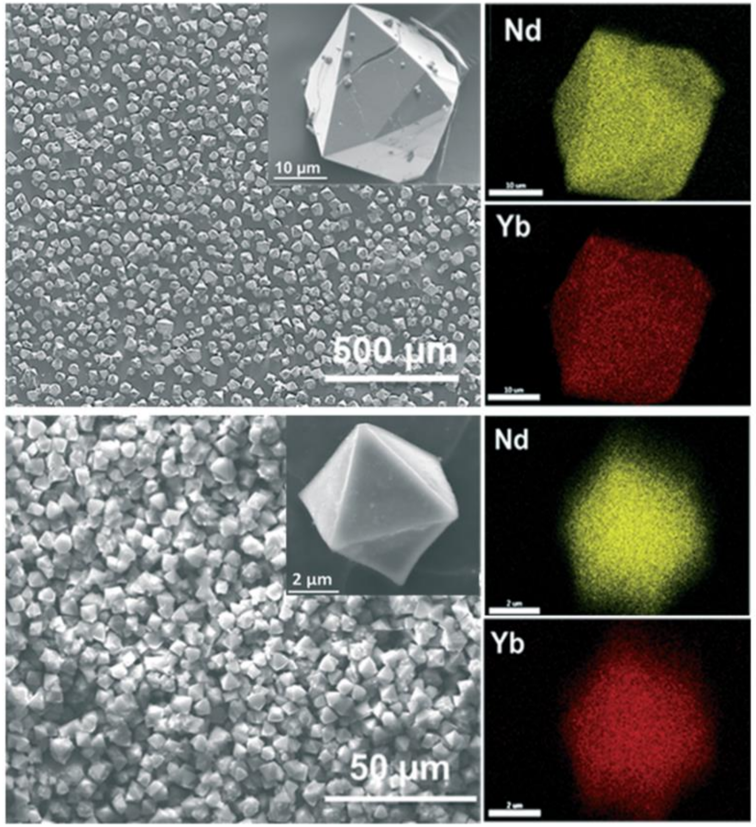


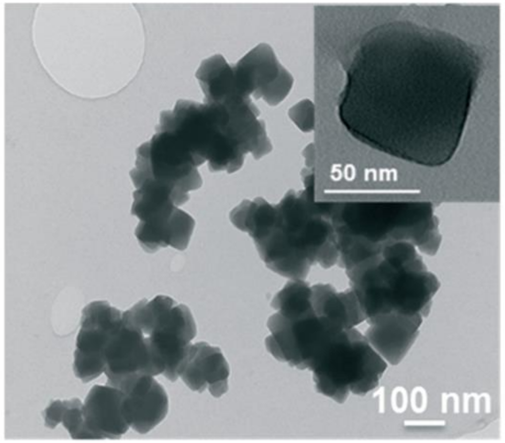
Eu-NP present in 100% of HeLa cells and 74% of RAW cells @ 48hrs incubation

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

Successful particle size fine tuning: increase in QY with particle size reduction







Solvent	$CHCl_3$	IPA	H_2O	DMF	DMSO	C_3H_6O
QY	6 %	5.4 %	4.4 %	5.2 %	6 %	6.3 %

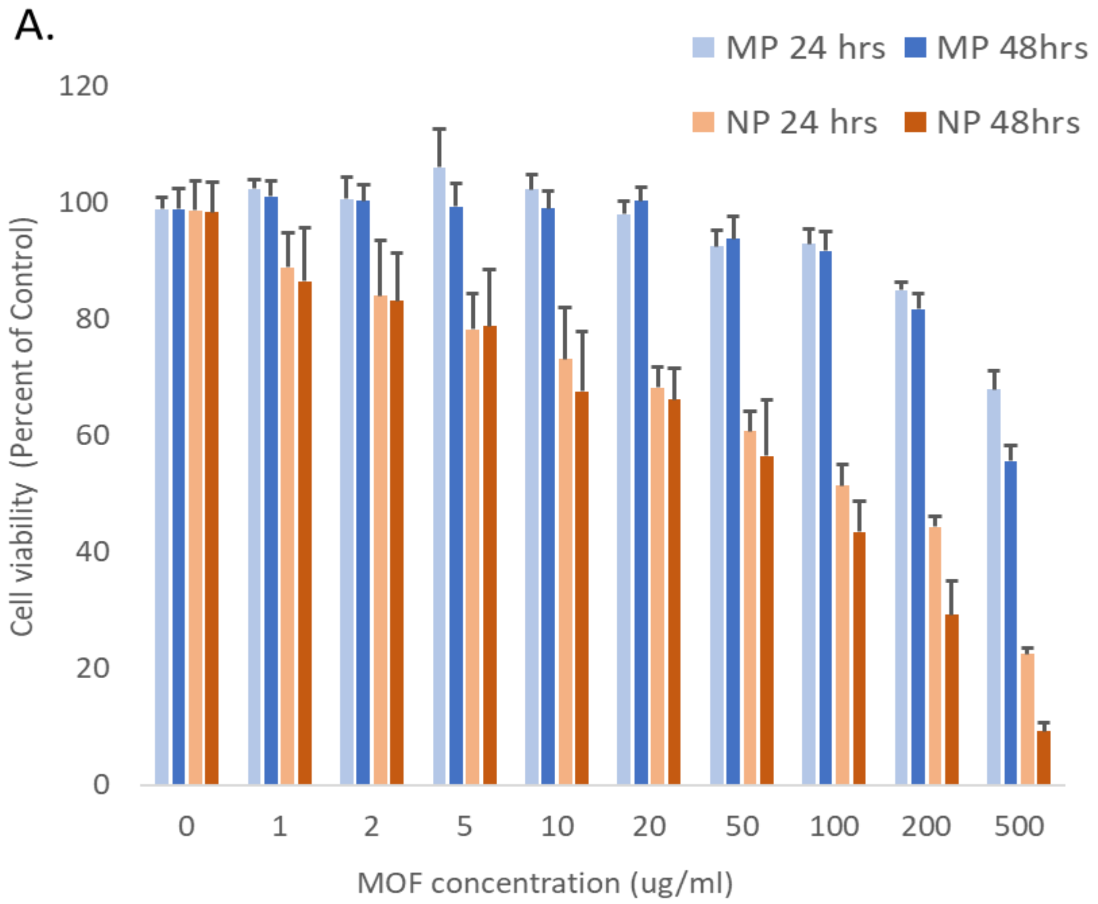
QY (30 µm) = 1.1 %
QY (5 µm) = 2 %
QY (200 nm) = 5.8 %

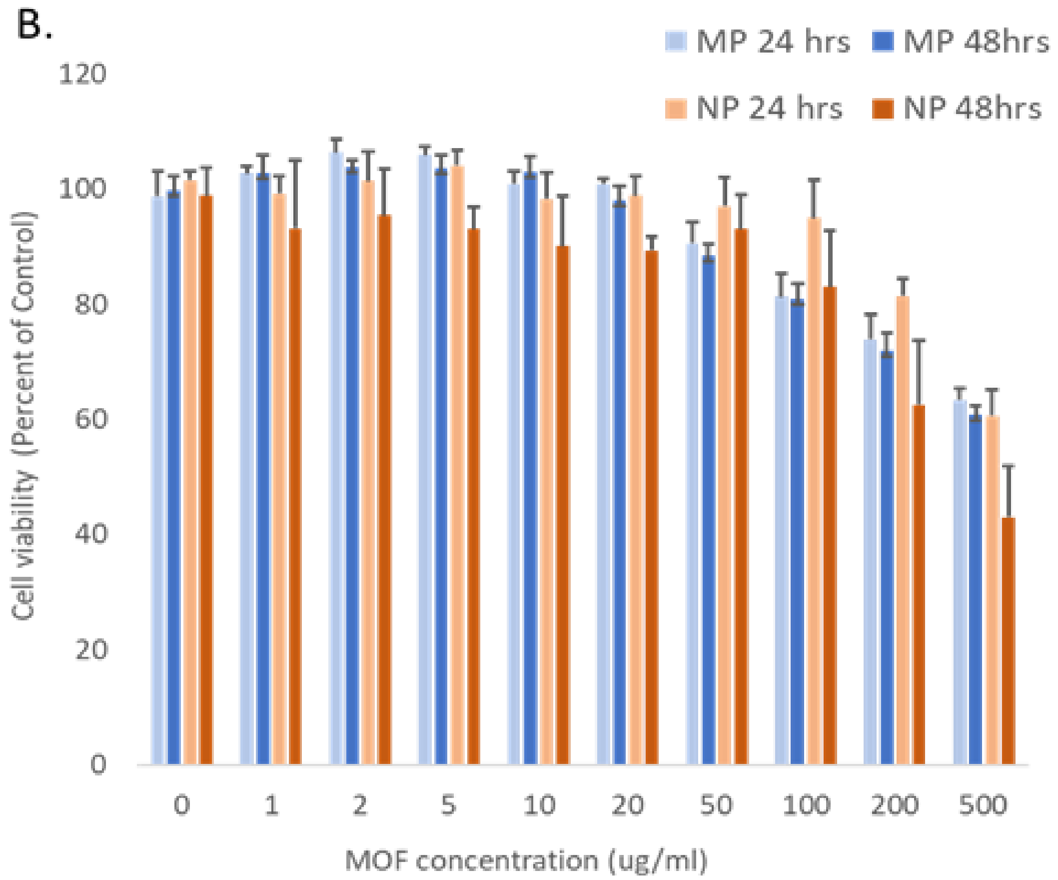
Absolute QY values exceed many times that of commercial dyes

Record high values for any NIR emitting MOFs reported to date

Sava Gallis et al. *CrystEngComm* **2018**, *20*, 5919-5924. *Invited paper for New Talent edition*

All particles display very low toxicity in both macrophage and epithelial cells





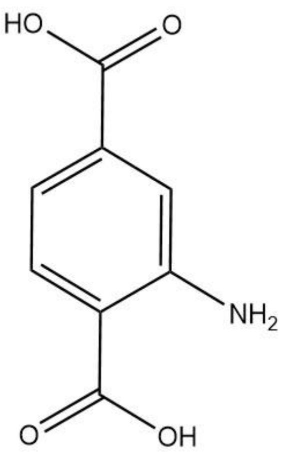
Cellular viability of (a) RAW 264.7 mouse macrophage cells and (b) A549 human lung epithelial cells after 24 hrs and 48 hrs of incubation with YbNd micron-sized MOF (MP) and nano-sized MOF (NP).

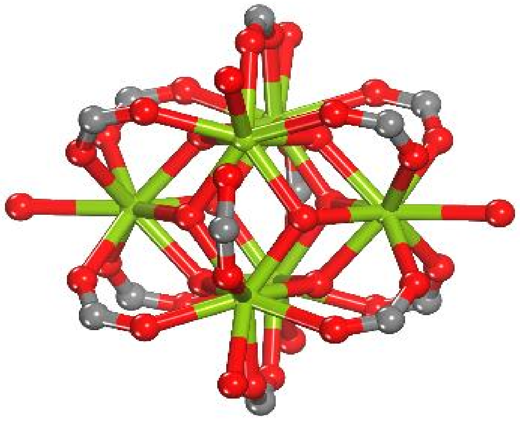
Sava Gallis et al. *CrystEngComm* **2018**, *20*, 5919-5924. *Invited paper for New Talent edition*

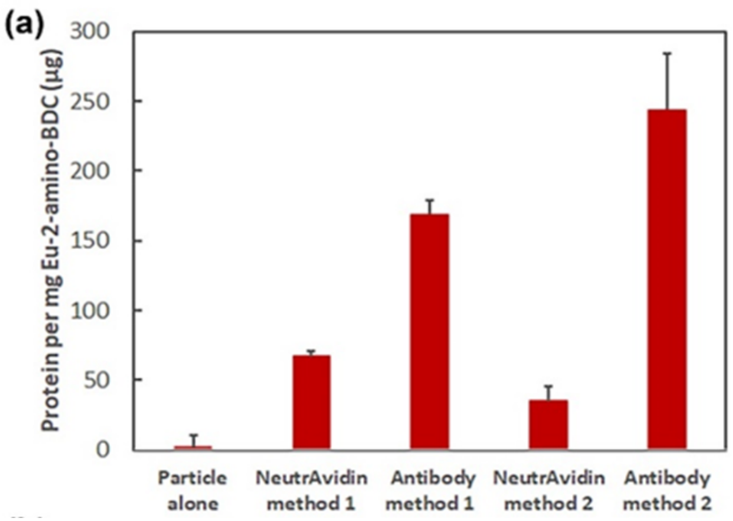
Antibody Targeted Metal-Organic Frameworks for Bio-Imaging Applications

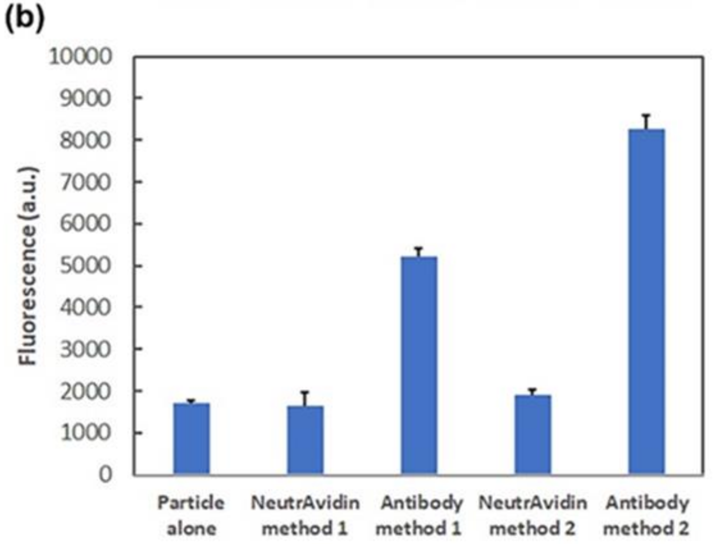
Focus: probing the availability and chemical utility of the primary amine within the organic linker for cell targeting

Confirmation of NeutrAvidin and EpCAM antibody conjugation to the Eu-2-amino-BDC particles using the carbodiimide chemistry (method 1) and thiolation chemistry (method 2).



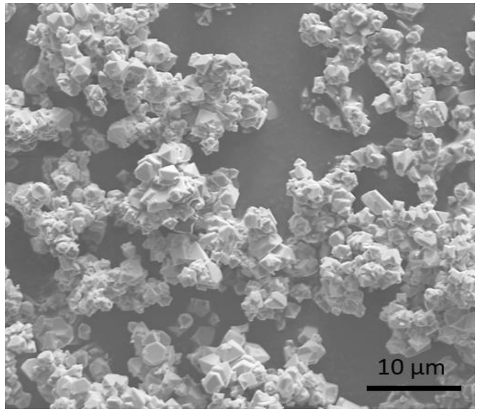


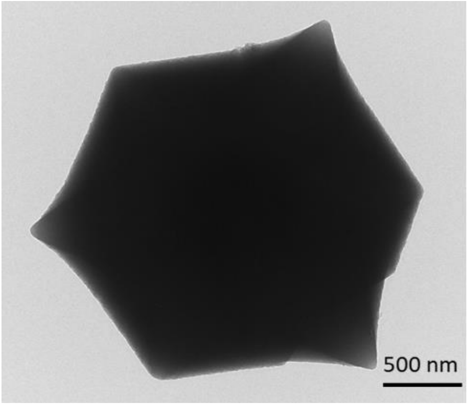




NanoOrange protein quantitation confirmed the conjugation of the NeutrAvidin protein and the EpCAM antibody to the MOF particles

Fluorescently labeled secondary antibody to the EpCAM antibody confirmed the conjugation of EpCAM antibody to the NeutrAvidin conjugated MOF particles

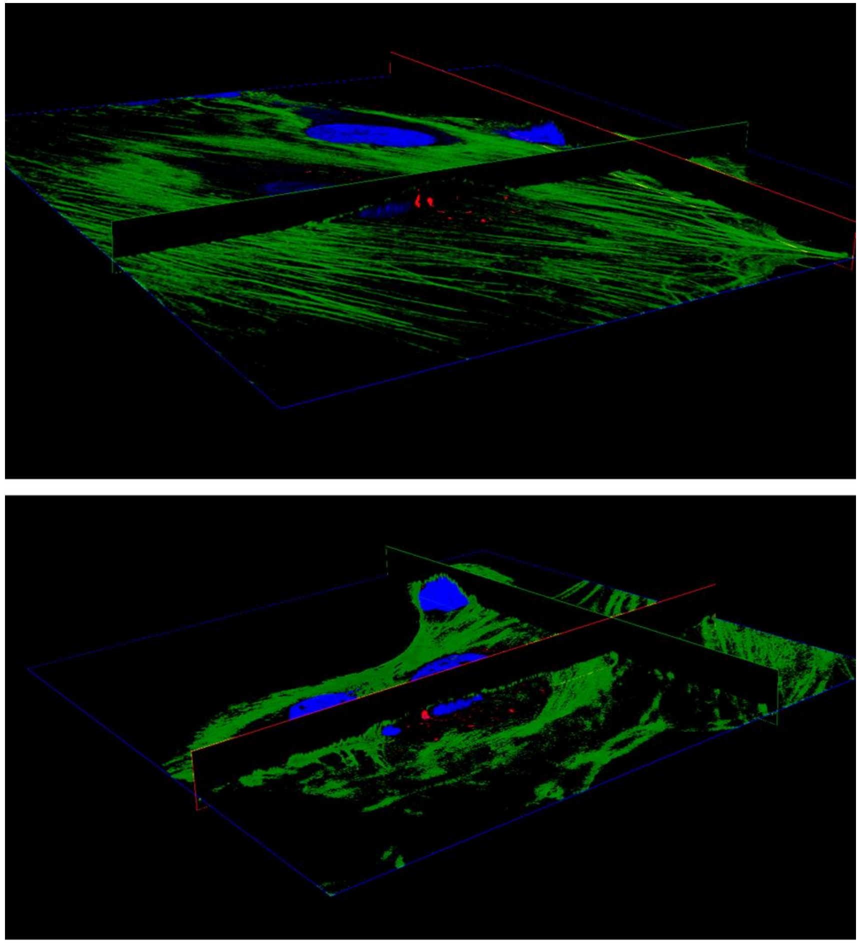




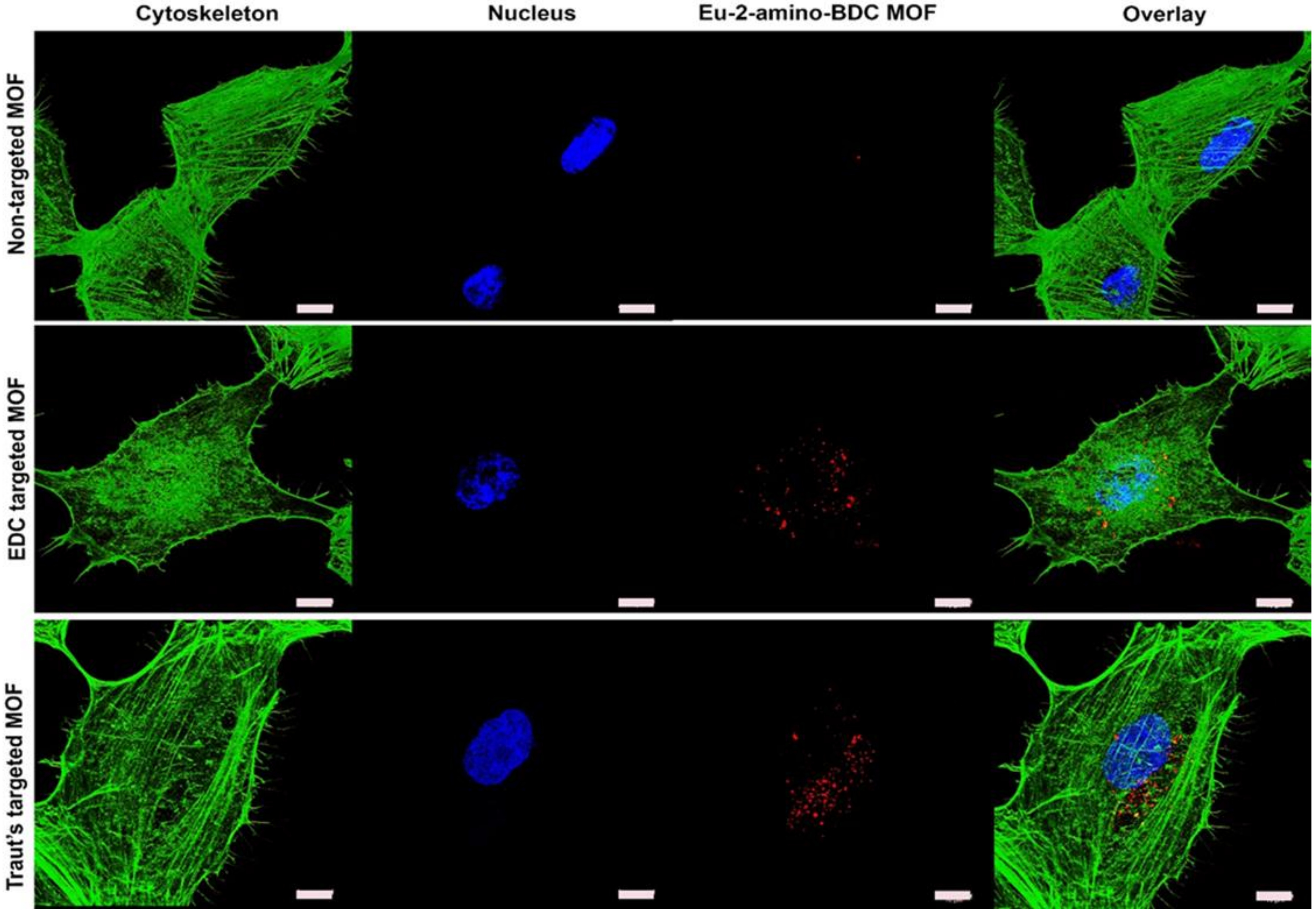
Butler, K. S.; Sava Gallis, D. F. et al. *ACS Applied Materials & Interfaces* **2020,** *12*, 31217-31224.

Antibody conjugated MOF particles show significant interaction with A549 cells regardless of conjugation methodology

3D z-stack reconstructions demonstrate internalization of EpCAM antibody targeted MOF particles into A549 cells



EpCAM antibody targeted MOF particles show significant interactions with the EpCAM bearing A549 cells, while the untargeted particles showed minimal interaction



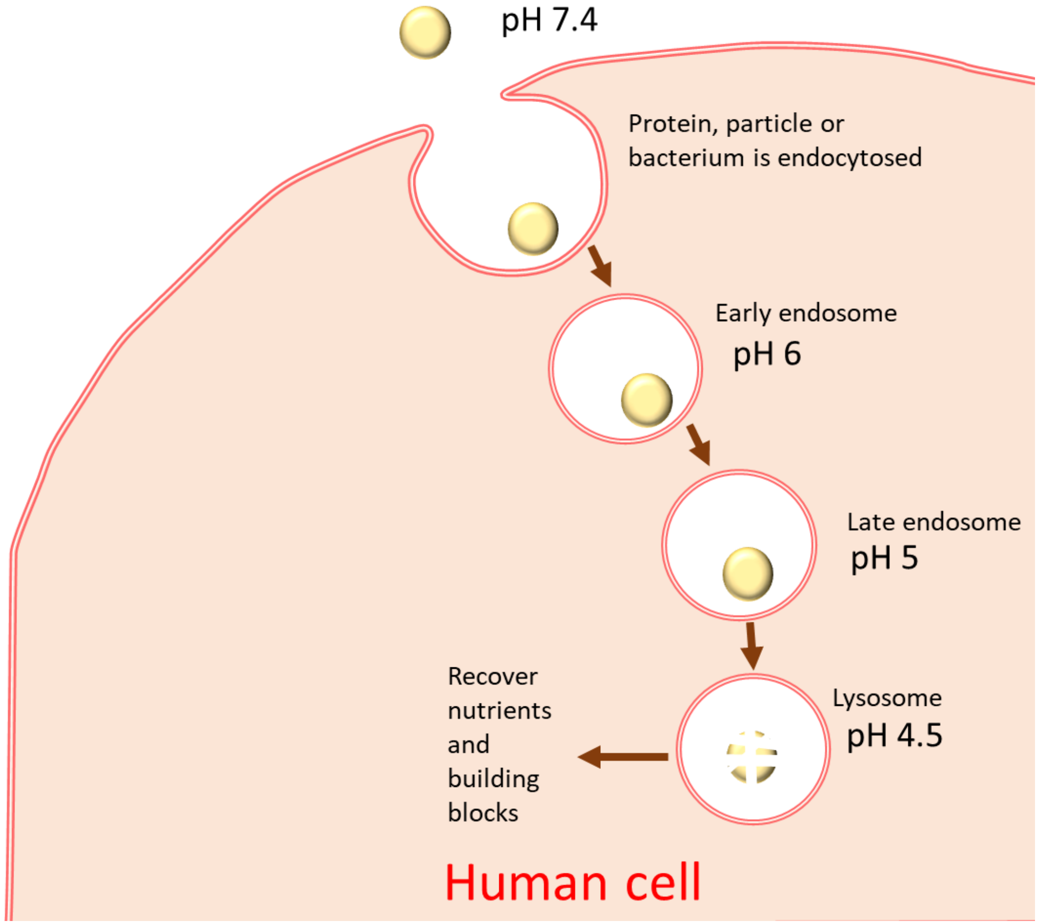
Butler, K. S.; Sava Gallis, D. F. et al. *ACS Applied Materials & Interfaces* **2020,** *12*, 31217-31224.

The endosomal/lysosomal pathway is a major hurdle for delivery of therapeutic agents

- Cells uptake from extracellular space is transported through the endosomal pathway to the lysosome

- The lysosome has a *low pH and enzymes* to destroy cargo brought in to the cell. This serves to: destroy invading bacteria and viruses & recycle old cellular components and proteins to recover nutrients and building blocks (sugars, fats, amino acids)

- The lysosome cannot discriminate helpful from harmful materials, many novel therapeutics are also digested



Many advanced therapeutics (siRNA, antimicrobial peptides and proteins, and enzymes, including Cas9) *cannot escape the endosome without aid*

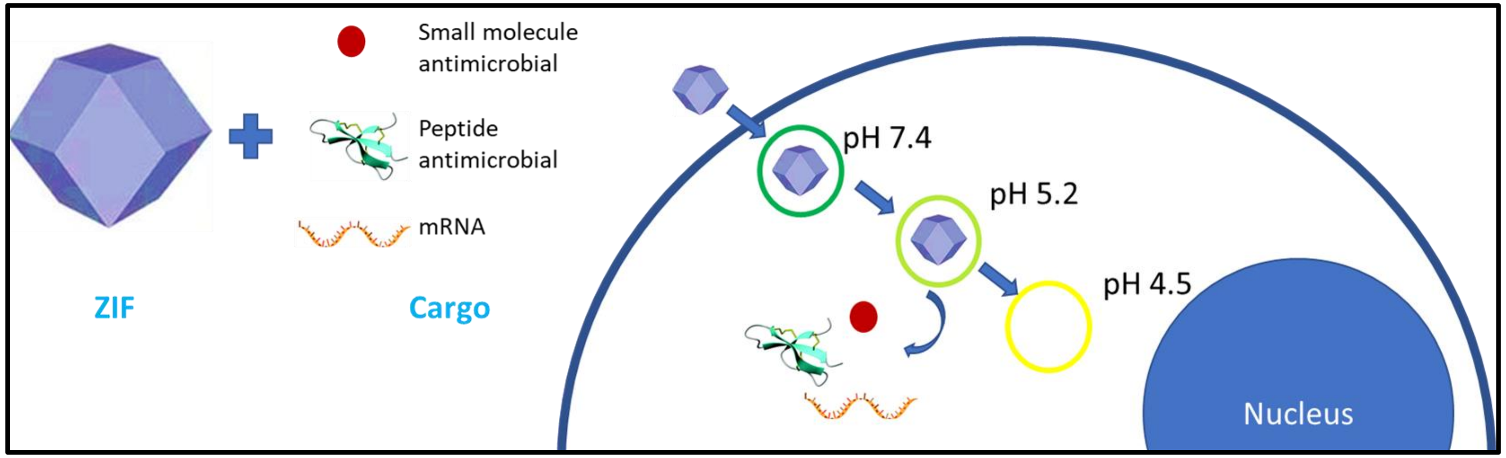
ZIFs have the potential to selectively disrupt the endosomal membrane to promote endosomal escape of cargos of interest

- ZIFs degrade at endosomal pH~ 5, releasing imidazole moieties
- Materials synthesis is straight forward
- Exceptional chemical tunability

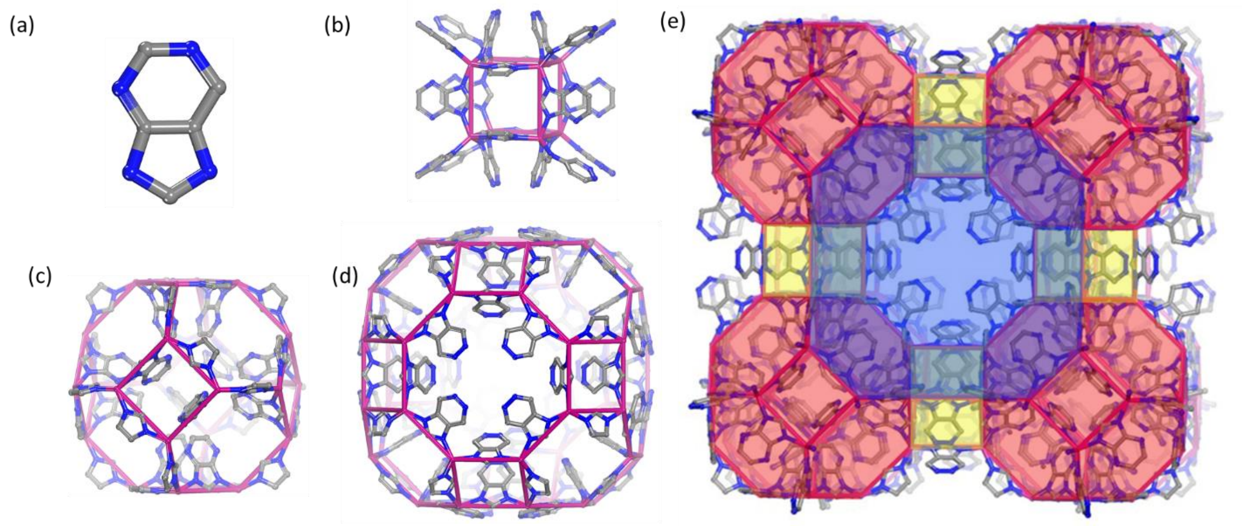
Unique built-in properties:

1. Selectively disrupt the endosomal membrane to promote *endosomal escape of cargos of interest*
2. Protect the functionality of the proposed cargos (peptide and protein- based antimicrobials)
3. Potentially signal the immune system to combat the infection by forcing the bacteria into the cytosol (mammalian cell can directly kill the bacteria)

ZIFs due to their complex nature can 'hide' linkers that can selectively disrupt the endosomes as they acidify allowing for safe release of the sensitive cargo into the target cell



Successful synthesis of purine based ZIF-20 NPs



ZIF-20

- Purine linker and zinc metal
- Large pore diameter (15.4 Å) but small pore aperture (2.8 Å) – good for holding cargo
- lta topology – not yet explored in ZIFs for nano or biological applications

Synthesis Conditions

- Conventional heating – 65 °C for 24 hours
- Microwave heating – 150 °C for 15 minutes
- Triethylamine (TEA) serves as a base in the reaction

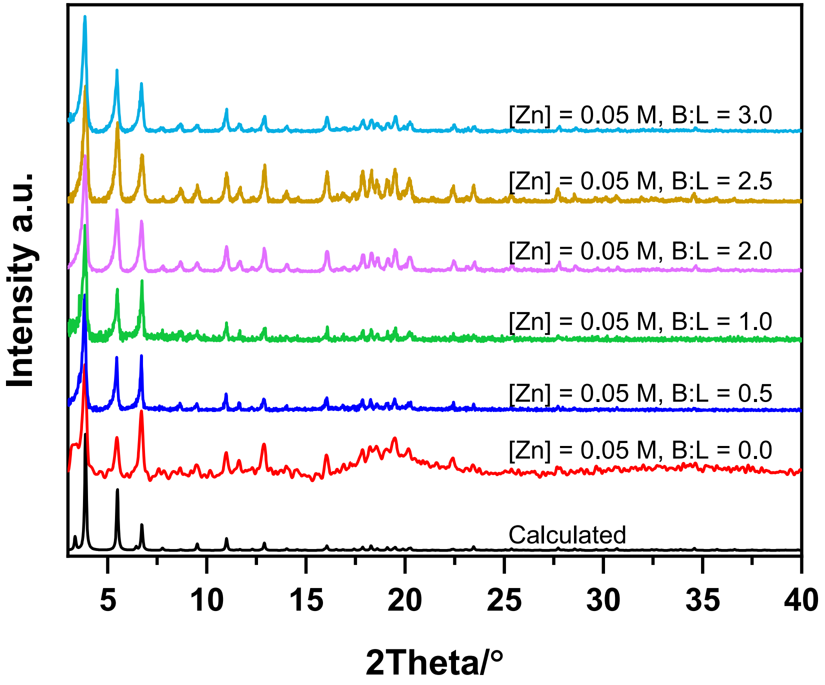
Compound	[Zn] M	TEA:Purine (B:L)
1	0.05	0
2	0.05	0.5
3	0.05	1.0
4	0.05	2.0
5	0.05	2.5
6	0.05	3.0
7	0.01	0
8	0.01	1.0

Deneff et al. *ACS Appl. Mater. Interfaces* **2021**, *13*, 23, 27295-27304

ZIF-20 particle size is directly dependent on ratio of base to imidazole

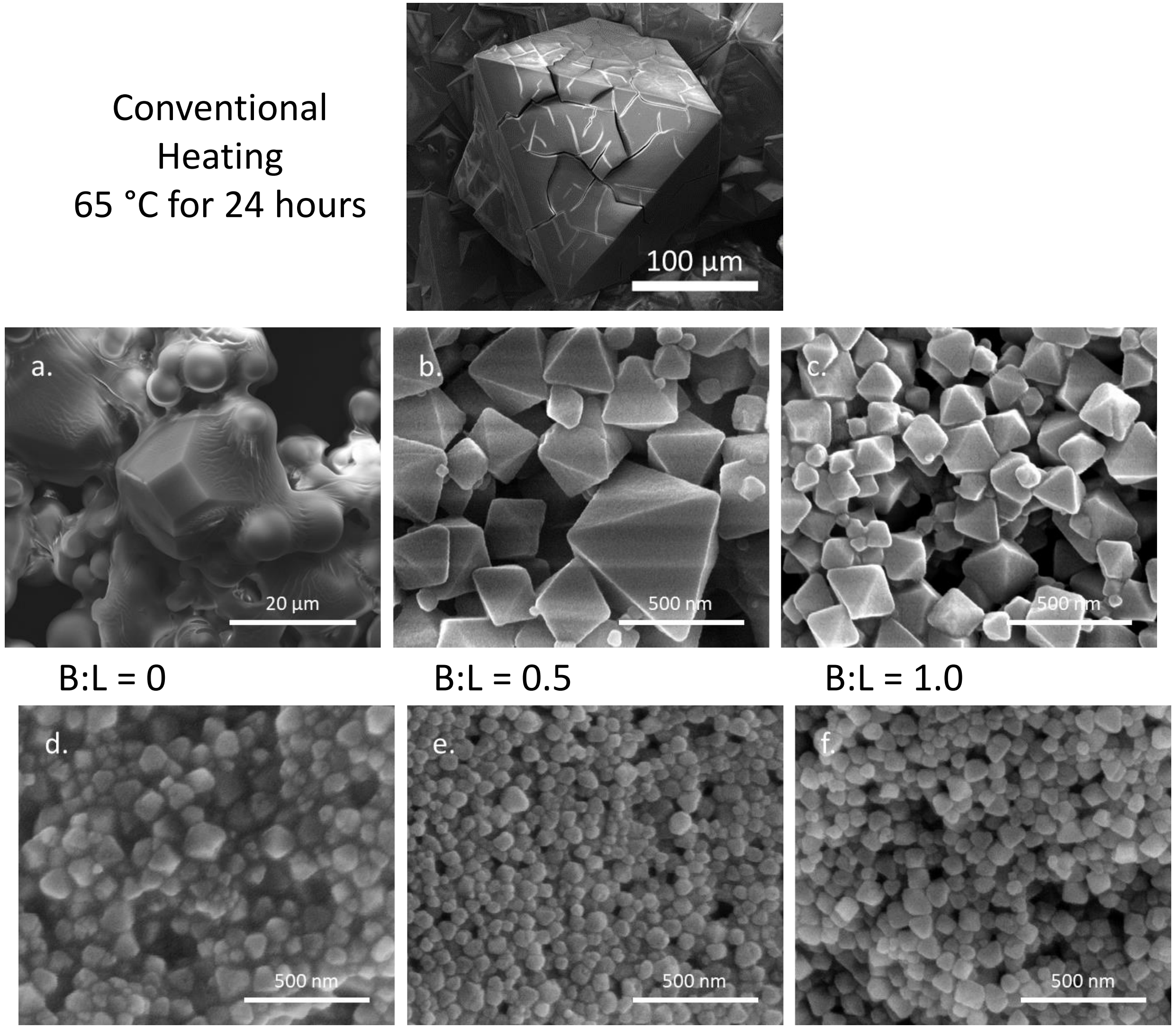
Nanoparticle synthesis is a competition between nucleation and growth rates

- Microwave heating uses higher temperatures and is more efficient – speed up reaction
- Basic additives deprotonate imidazoles in solution – encourage coordination to zinc



Conventional Heating
65 °C for 24 hours

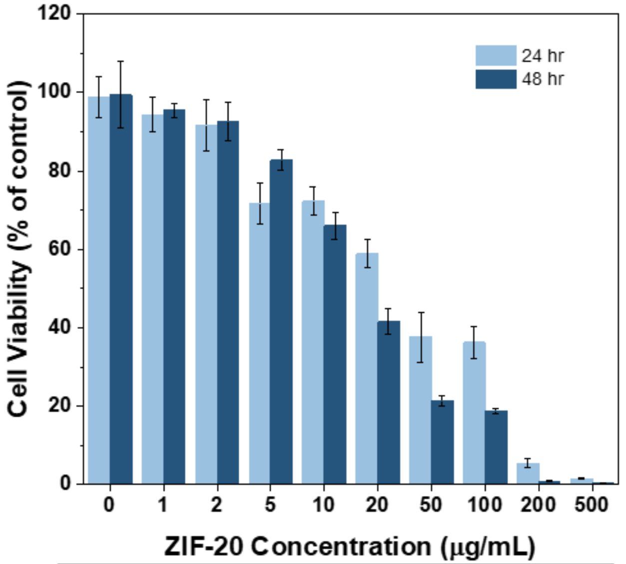
Microwave Heating
150 °C for 15 minutes

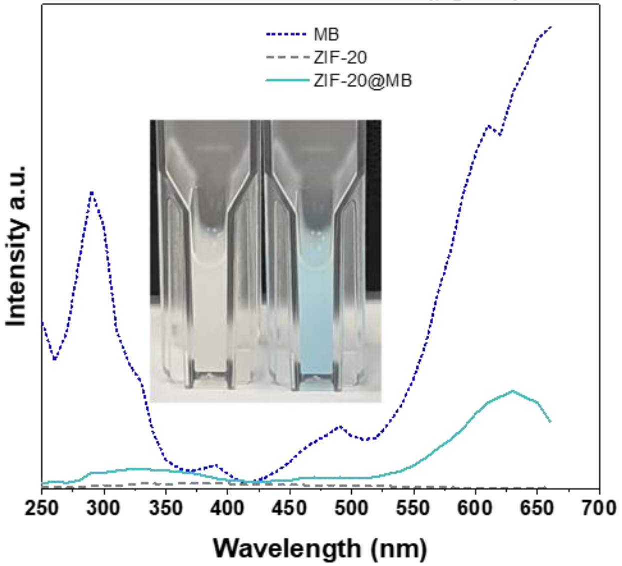


B:L = 0
B:L = 0.5
B:L = 1.0
B:L = 2.0
B:L = 2.5
B:L = 3.0

Deneff et al. *ACS Appl. Mater. Interfaces* **2021**, *13*, 23, 27295-27304

ZIF-20 successfully encapsulates and releases methylene blue, a dual imaging agent and therapeutic



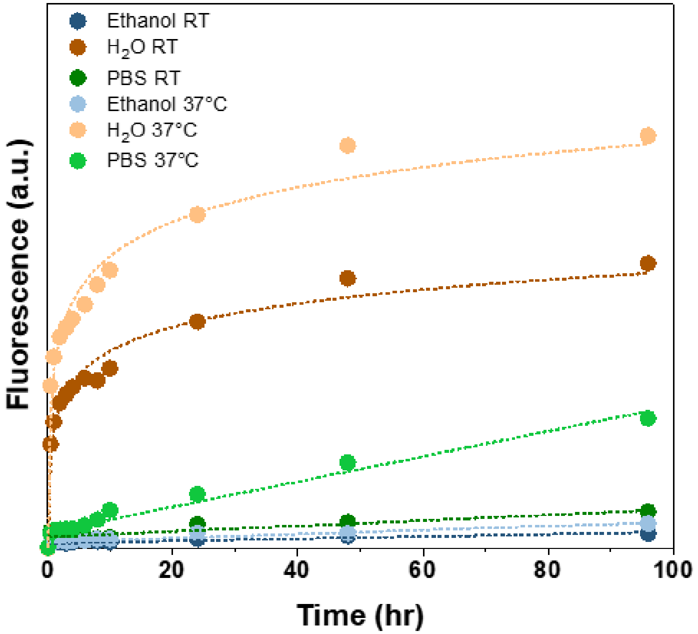


Cytotoxicity

- A549 epithelial cells
- IC_{50} concentration of 50.8 µg/mL
- Comparable to reports of prototypical ZIF-8

Encapsulation and Release

- Methylene blue model drug incorporated during synthesis
  - Imaging agent
  - Neuroprotection, malaria treatment
- Successful encapsulation detected visually and through excitation
- Negligible release in ethanol and PBS – good sign for delivery, stability in body outside lysosomes

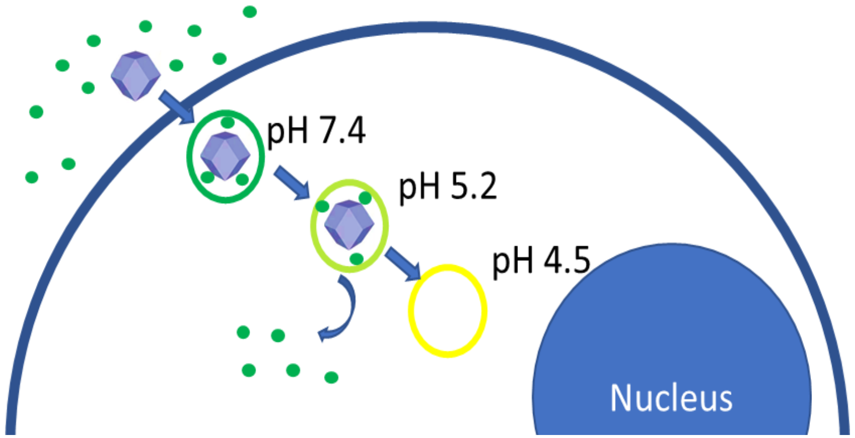


Media	Room Temperature	37°C
Ethanol	1.26%	2.16%
H_2O	25.1%	36.3%
PBS	3.19%	11.4%

Percent release after 96 hours

Deneff et al. *ACS Appl. Mater. Interfaces* **2021**, *13*, 23, 27295-27304

Development of two methods for tracking endosomal interactions

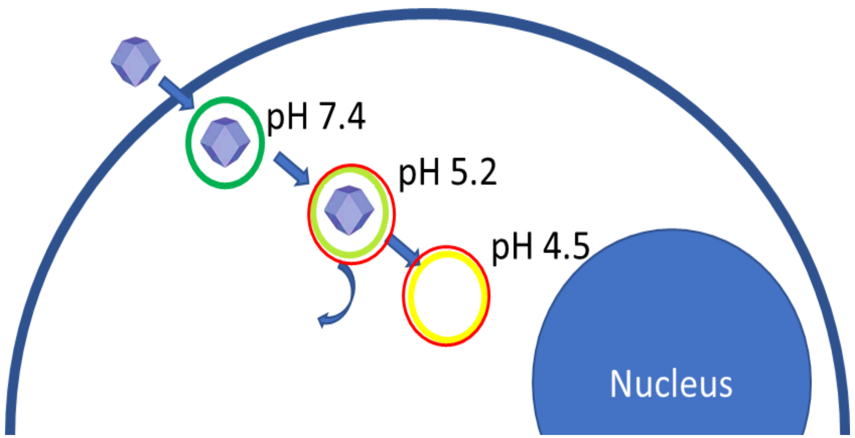


FITC-Dextran

- Added to media, taken up alongside ZIF in endosomes
- When released, the cell turns green

Drawbacks

- Dyeing whole cell prevents quantification of individual endosomes



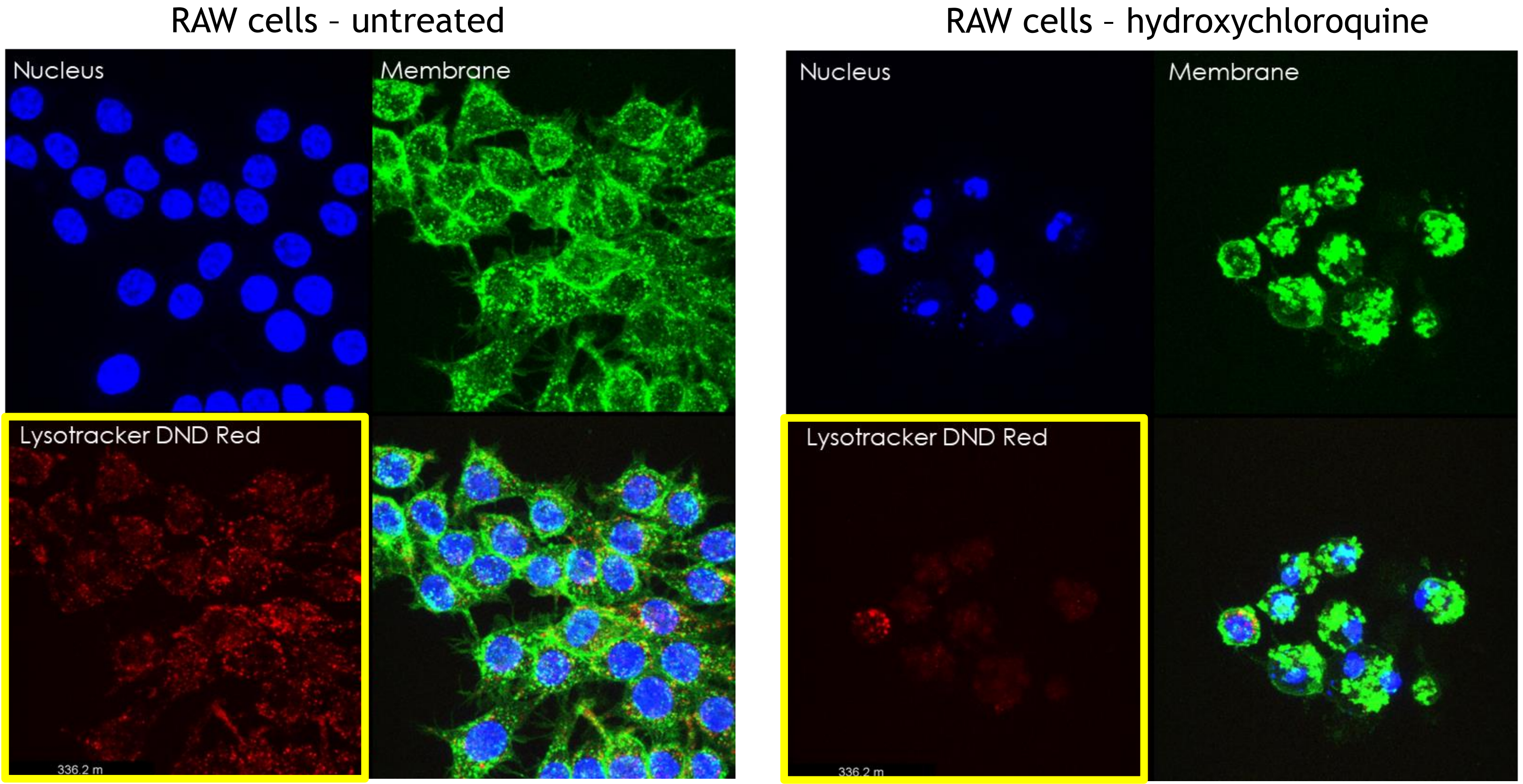
Lysotracker DND Red

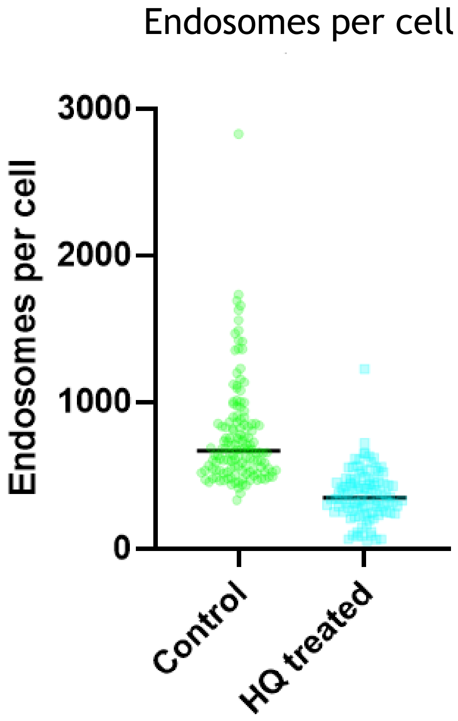
- Added to media, labels cell membrane
- Fluorescent in acid conditions (pH 6.5), labels lysosomes

Drawbacks

- Can miss early endosomes

Imaging and endosome quantification proof-of-concept using hydroxychloroquine as model molecule





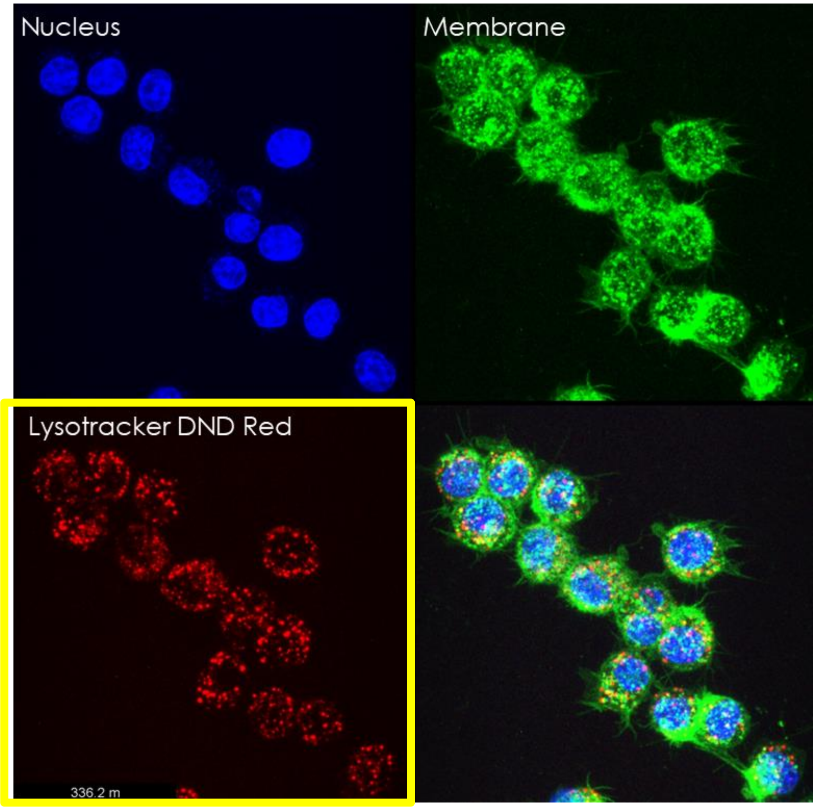
p<0.0001

Imaging Proof of Concept

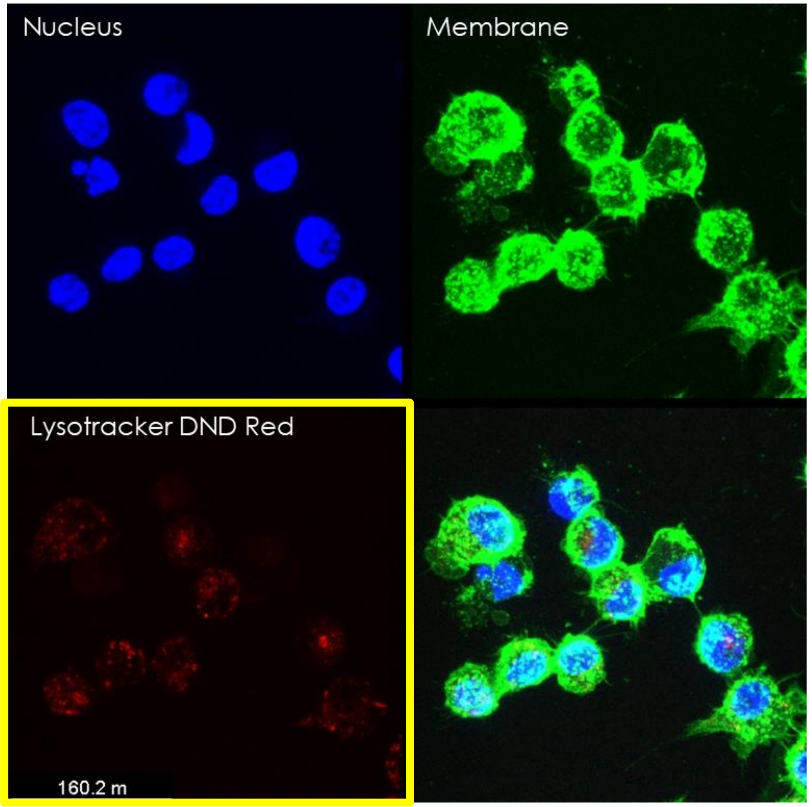
- Membrane and nuclear stain identify cells, Lysotracker shows endosomes/lysosomes
- Quantification determines the number, intensity and total endosome area per individual cell. Over 100 cells are examined per treatment
- Hydroxychloroquine significantly disrupts endosomes – approximately half the number endosomes are seen in treated cells

Using Lysotracker to determine the effect of coating ZIF-8 on endosomal disruption

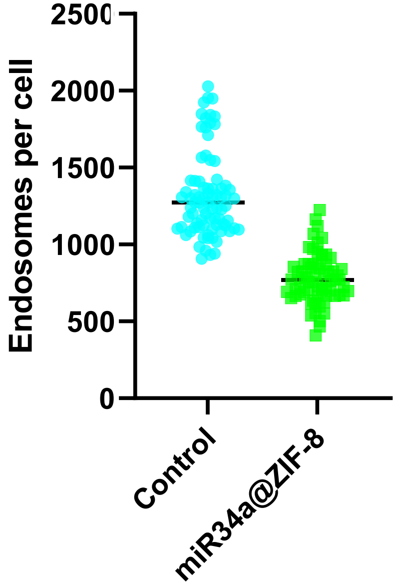
RAW cells – ZIF-8



RAW cells – miR34a@ZIF-8



Endosomes per cell



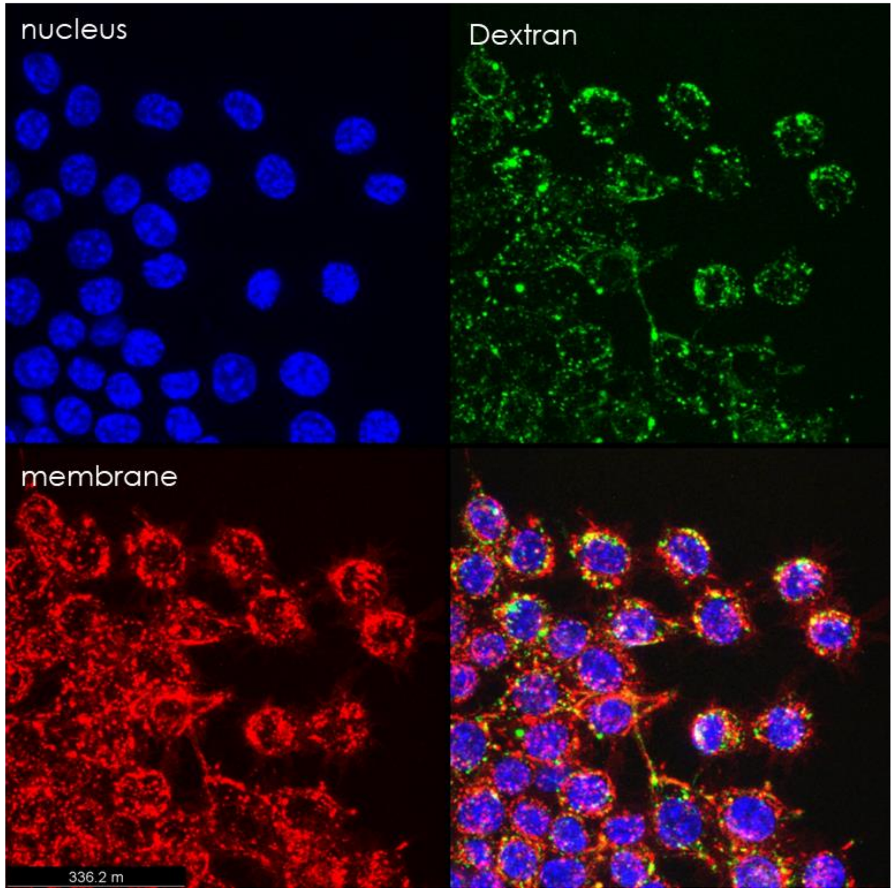
p<0.0001

ZIF-8 with and without miR34a coating

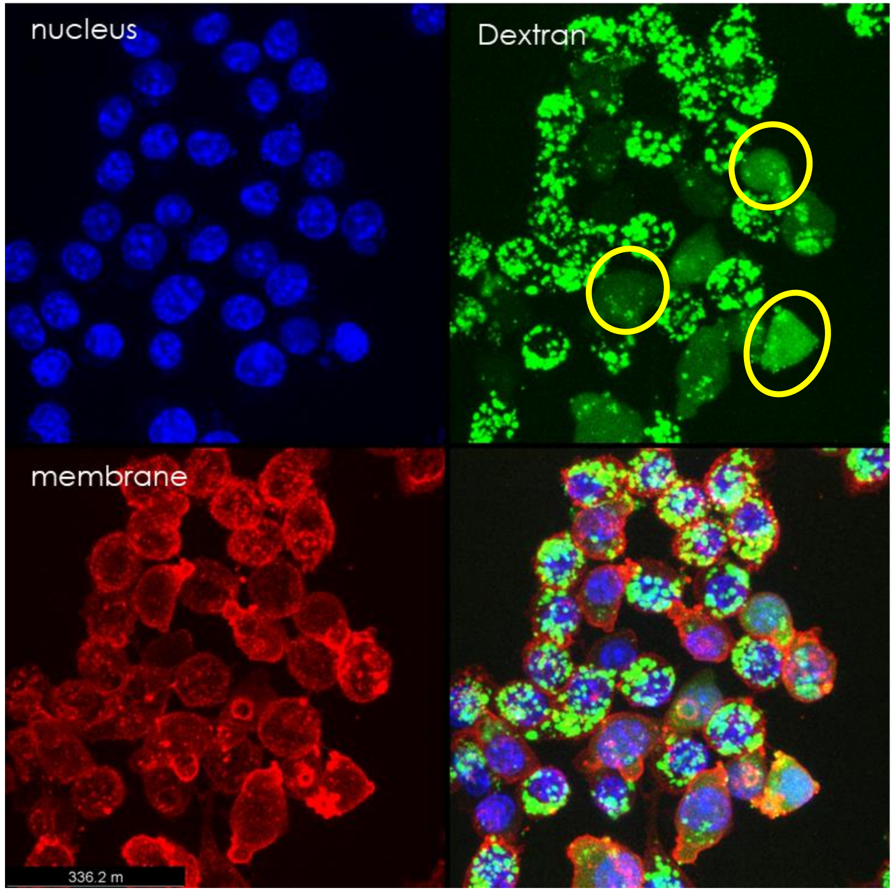
- ZIF-8 alone has no effect on endosomes, possibly due to a low level of cellular uptake
- miR34a coating has been shown to lead to endosomal uptake in the literature
- miR34a@ZIF-8 leads to a significant effect on endosomal number

Imaging proof of concept for endosomal content release with Dextran

RAW cells – untreated



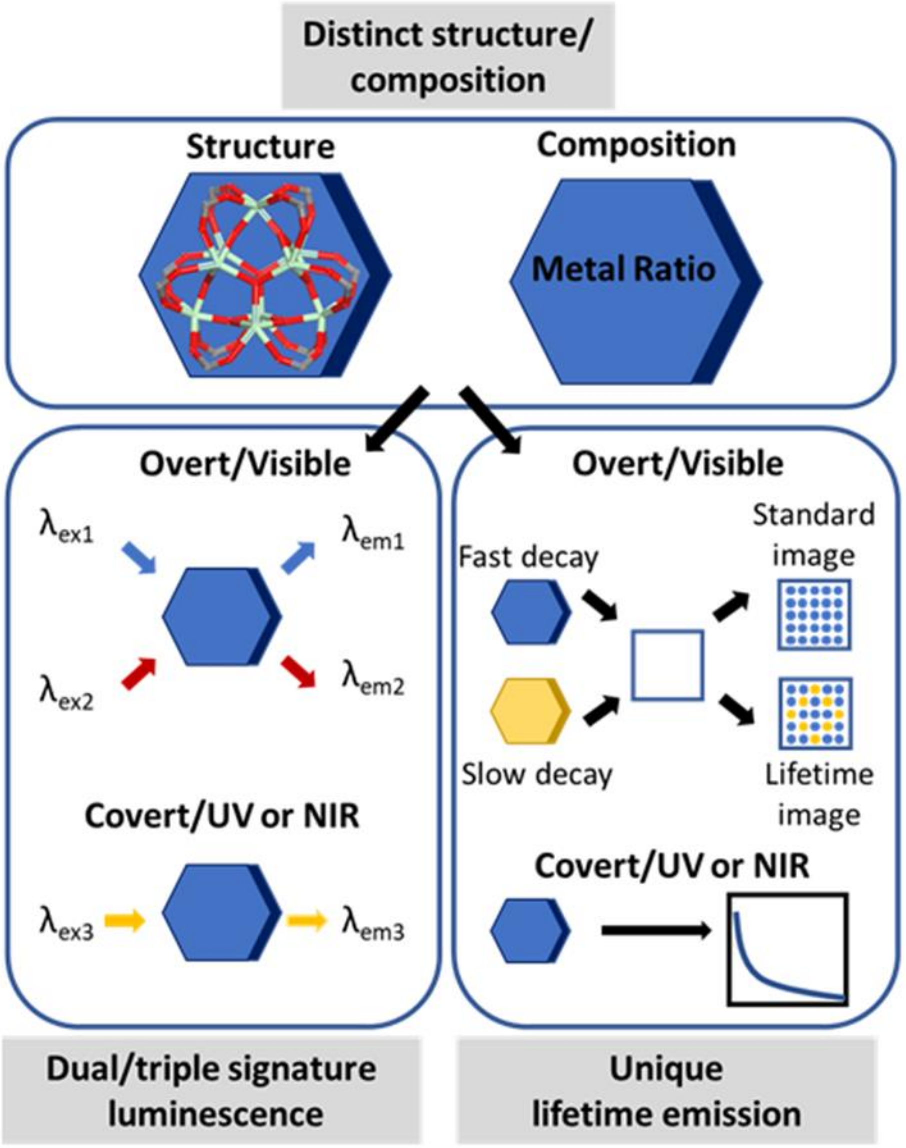
RAW cells – hydroxychloroquine



Imaging Proof of Concept

- Confirm FITC-dextran utility for endosomal tracking
- Untreated cells show punctate endosomes
- ~25% of treated cells show diffuse FITC-dextran at 8 hours due to hydroxychloroquine

4. Encoding Multilayer Complexity in Anti-Counterfeiting Heterometallic MOF-based Optical Tags



- Critical need to discover new materials that can combine unambiguous: (i) *proof-of-identity* and (ii) *sense environmental exposure/tampering* over the lifetime of the material
- Current tag fluorophore options lack the tunability to allow combined methods of encoding in a single material
- Materials design strategies to combine *multiple methods of encoding and sensing elements in a single material*

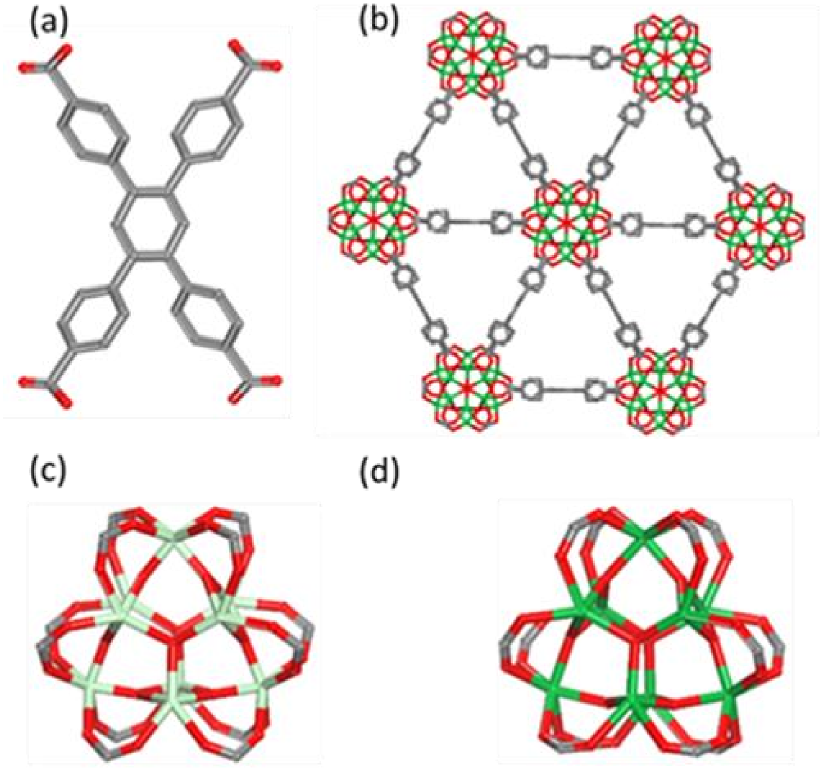
Prerequisites for the design of an ideal optical tag with complex, difficult-to-counterfeit properties:

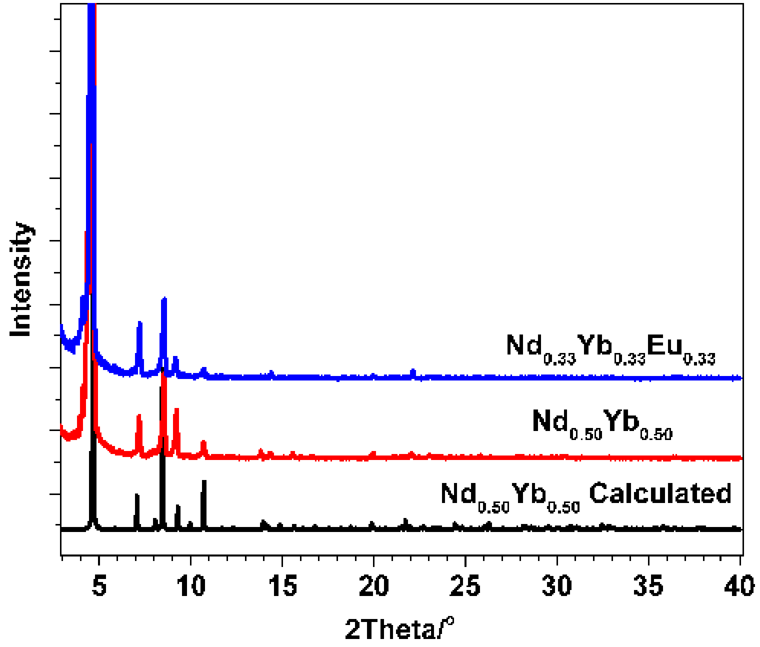
(i) combined overt and covert signatures created using tunable optical properties capable of concomitant emission in the ultraviolet (UV), visible, and/or NIR ranges;
(ii) unique fluorescence lifetime features that facilitate encoded signatures as an additional layer of complexity
(iii) distinct compositional and/or structural properties to allow orthogonal confirmation of identity

US Patent Application 63/086,419

Sava Gallis et al. *Angew. Chem. Int. Ed.* **2021**, *60*, 1203–1211.

Successful synthesis of tuned di-(NdYb) and tri-(EuNdYb) heterometallic compositions





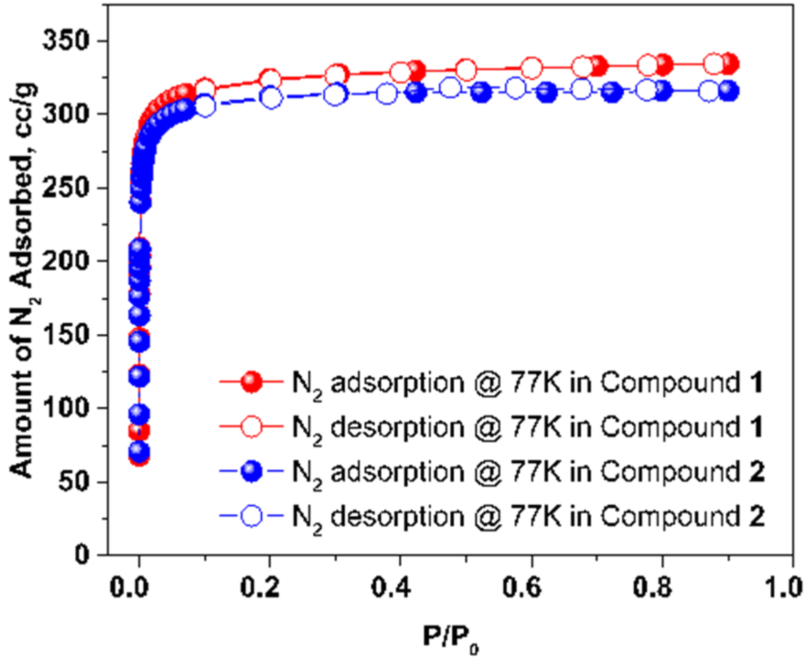
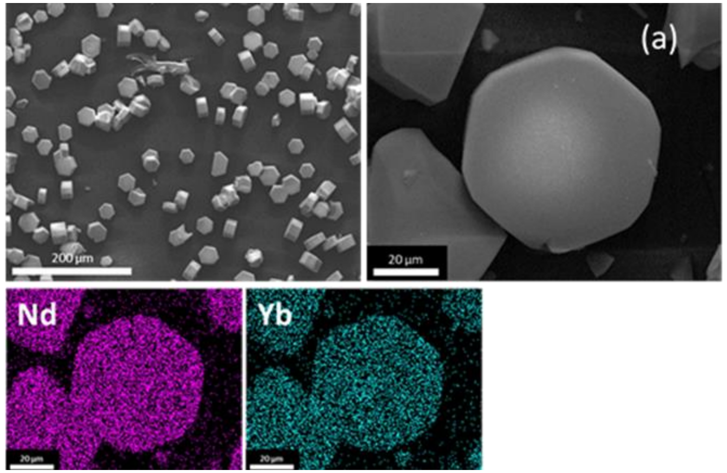
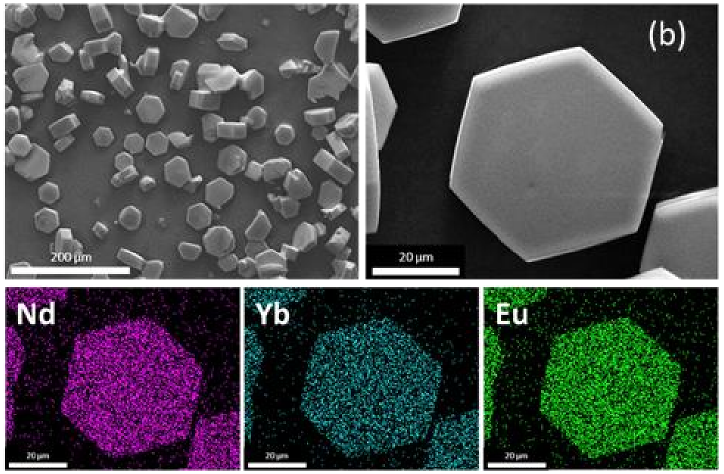


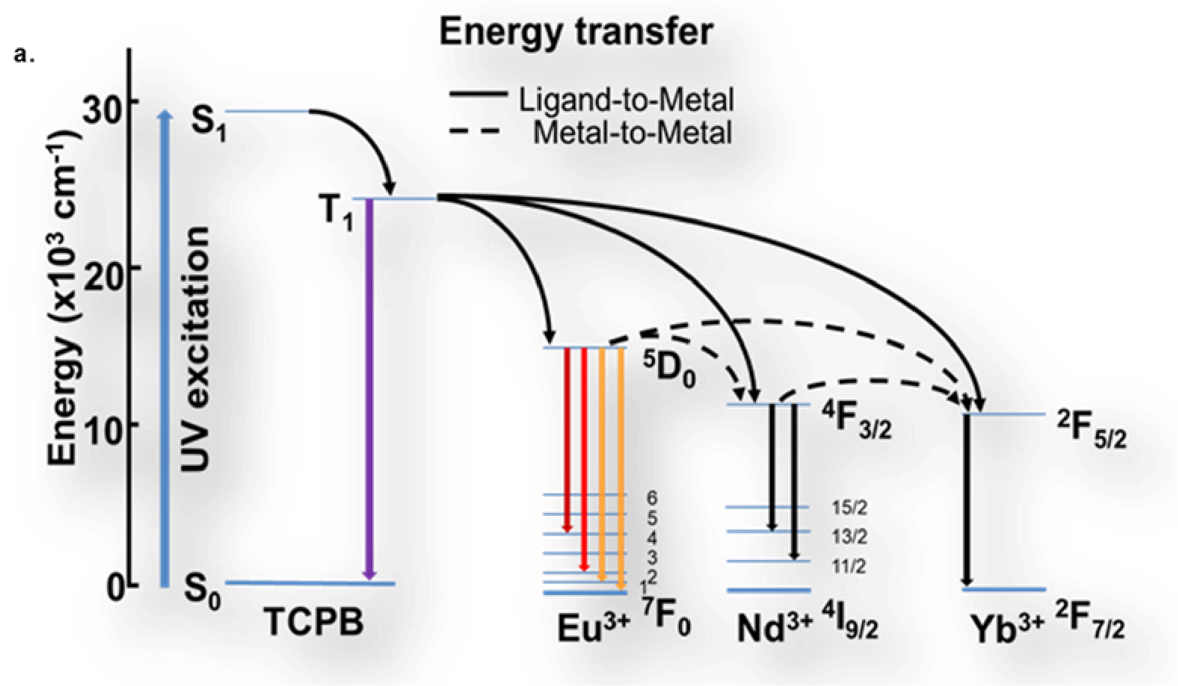
Table 1: Compound designations and compositions.

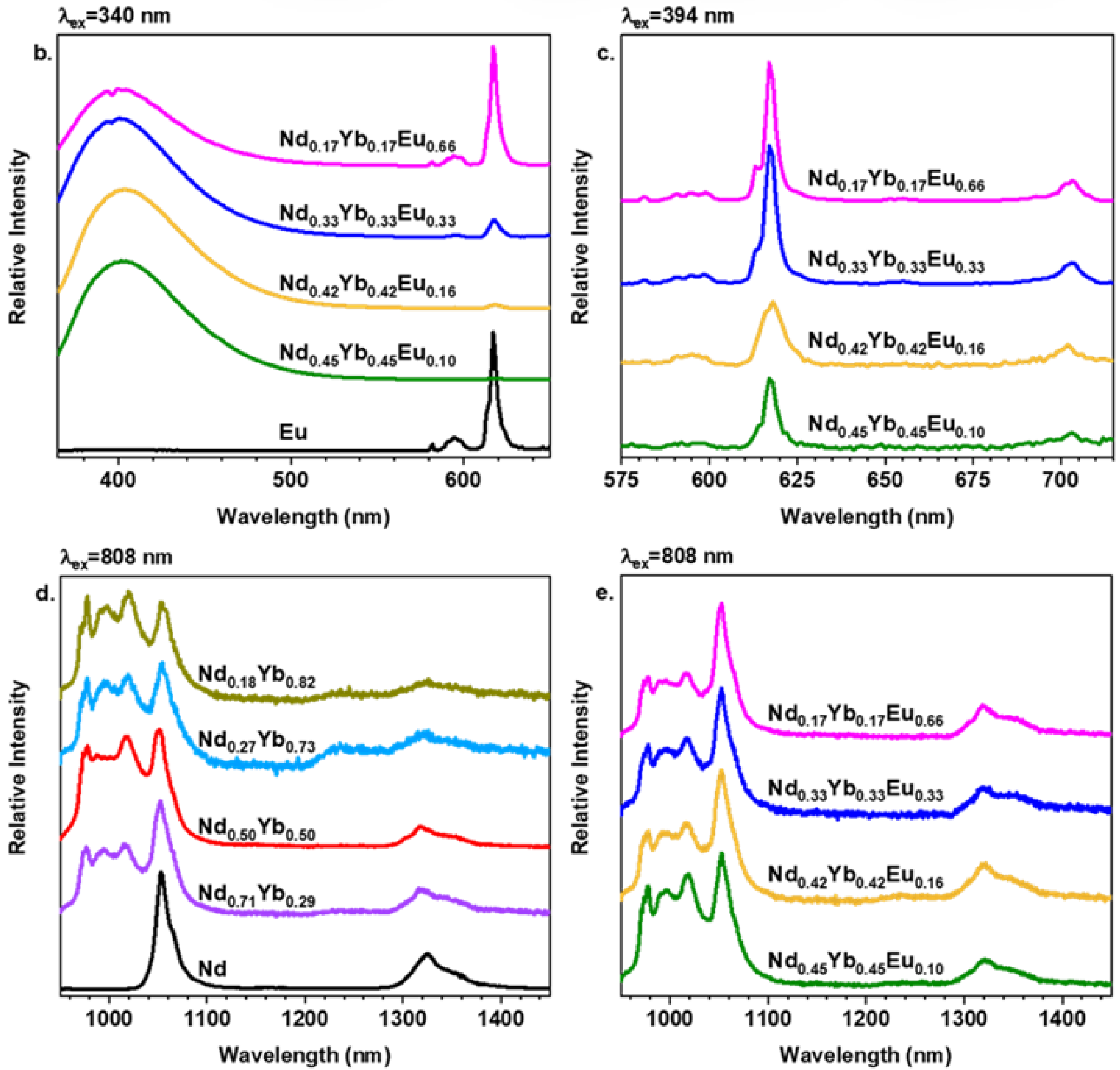
Compound	Composition	Compound	Composition
1	$Nd_{0.5}Yb_{0.5}$	7	$Nd_{0.42}Yb_{0.42}Eu_{0.16}$
2	$Nd_{0.33}Yb_{0.33}Eu_{0.33}$	8	$Nd_{0.17}Yb_{0.17}Eu_{0.66}$
3	$Nd_{0.71}Yb_{0.29}$	9	Nd
4	$Nd_{0.27}Yb_{0.73}$	10	Yb
5	$Nd_{0.18}Yb_{0.82}$	11	Eu
6	$Nd_{0.45}Yb_{0.45}Eu_{0.10}$		





Subtle compositional changes have a pronounced effect on intermetallic energy transfer, and thus, on the resulting photophysical properties





Noticeable effect of non-radiative metal-to-metal energy transfer between the long-lived Eu centers and the Nd and Yb centers and the resulting tag properties in the NIR, where Eu does not exhibit any emission features.

US Patent Application 63/086,419

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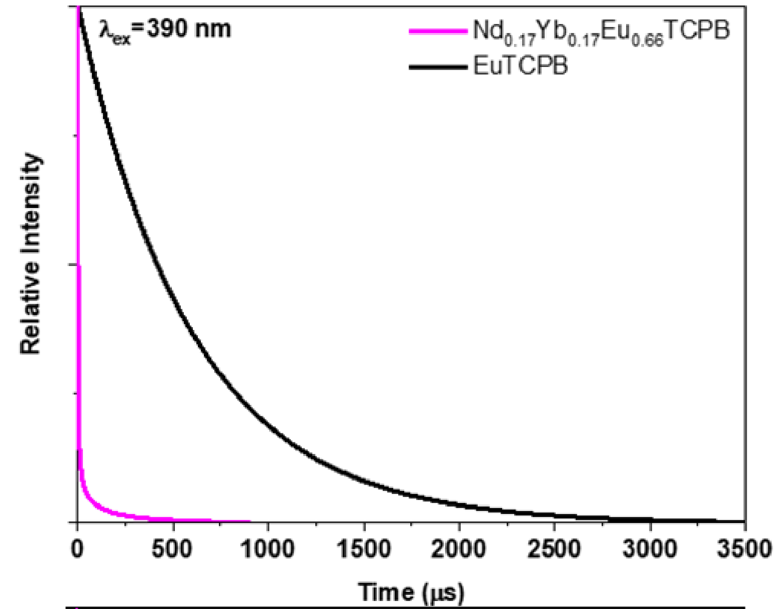
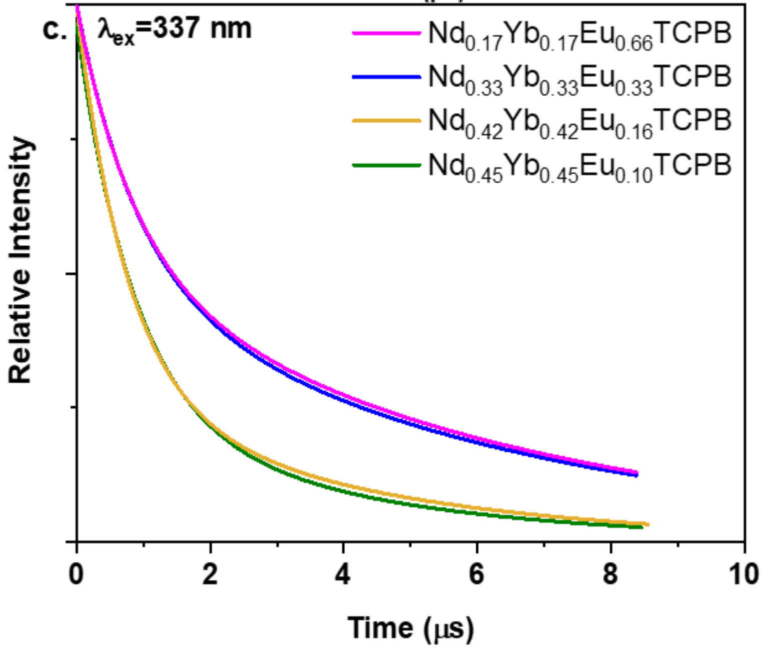
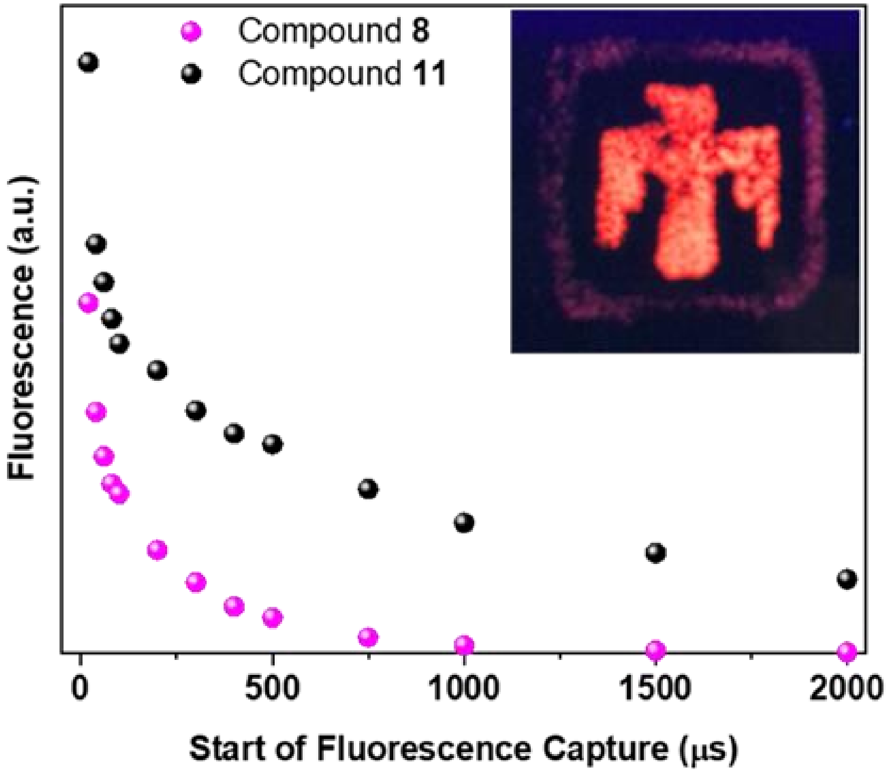
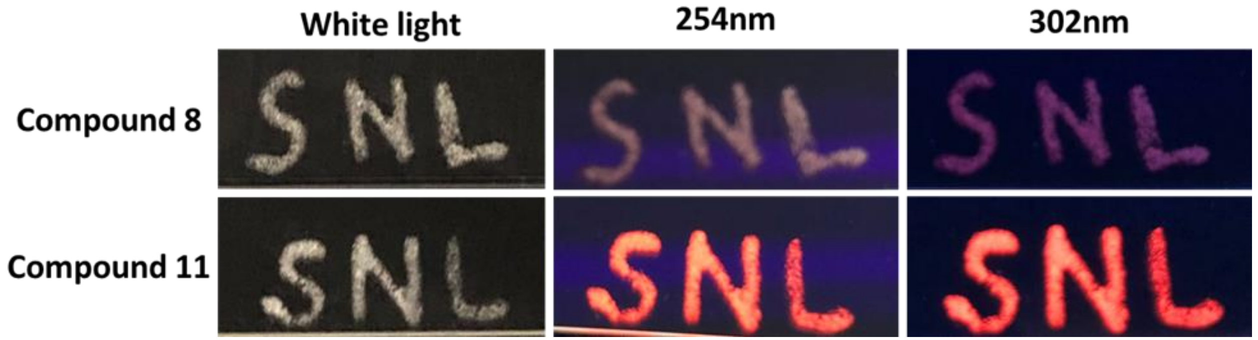
Subtle compositional changes have a pronounced effect on intermetallic energy transfer









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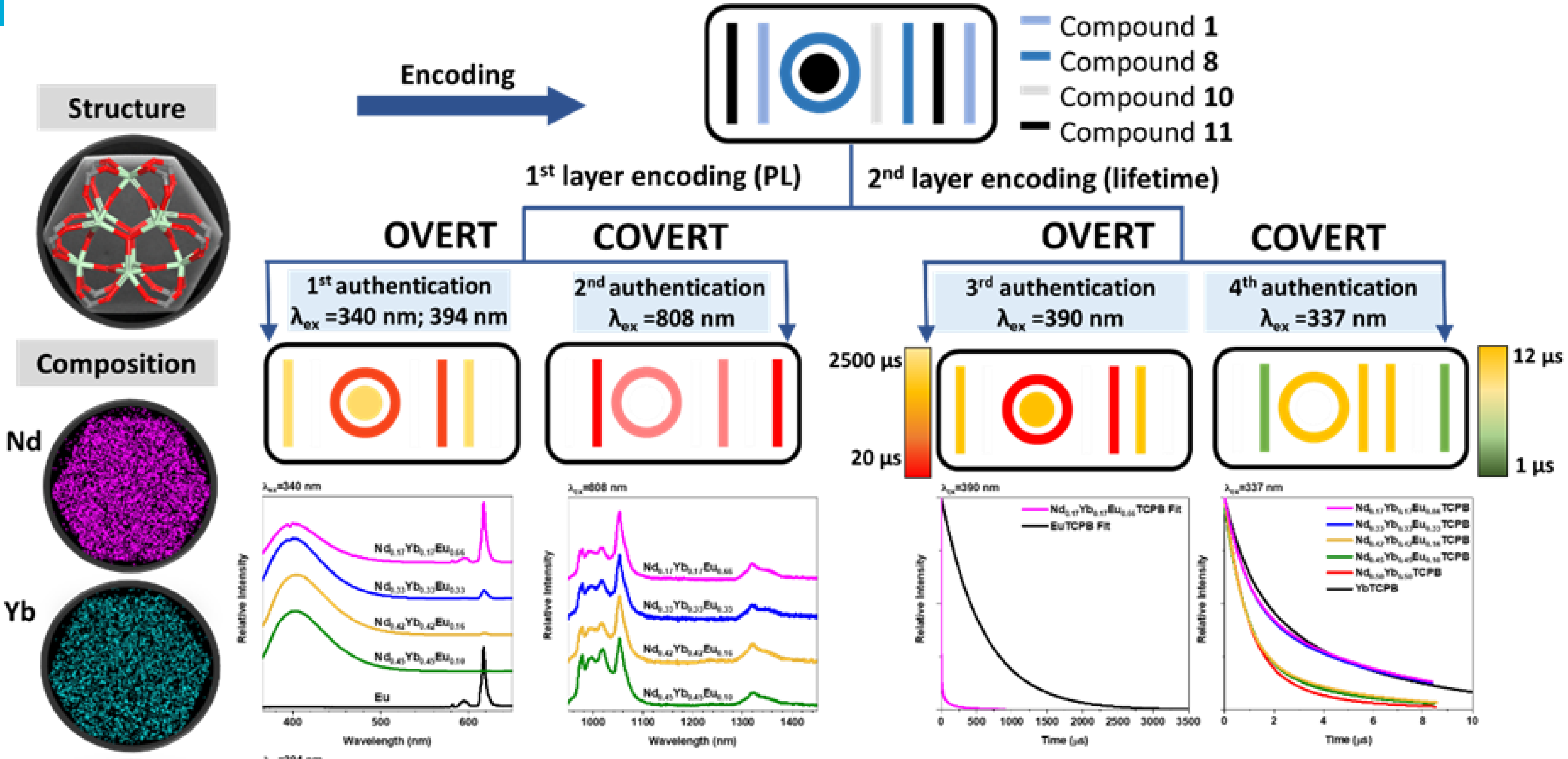
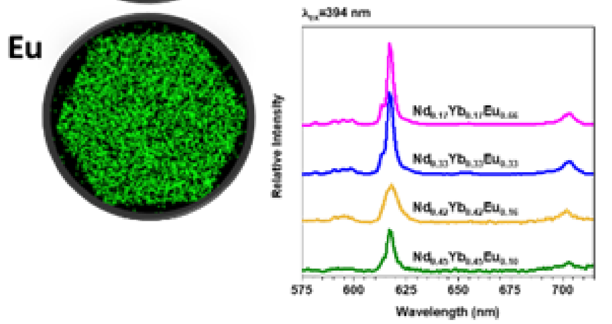
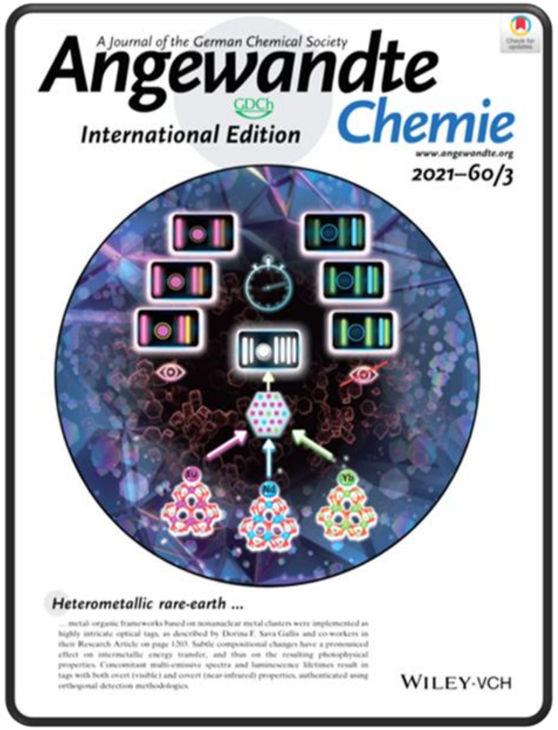
Proof-of-concept tag encoding and authentication







This design approach represents the most extensive and complex exploration of optical tag properties via combining multiple methods of encoding in a single material

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