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a. REPORT	b. ABSTRACT	c. THIS PAGE			Yangyang Liu
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RPPR Final Report

as of 18-May-2023

Agency Code: 21XD

Proposal Number: 72481SMREP

Agreement Number: W911NF-19-1-0001

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Report Date: 31-Jan-2023

Date Received: 30-Jan-2023

Final Report for Period Beginning 01-Nov-2018 and Ending 31-Oct-2022

Title: Multifunctional Metal-Organic Frameworks for Efficient Degradation of Chemical Warfare Agents: Mechanism and Synthesis

Begin Performance Period: 01-Nov-2018

End Performance Period: 31-Oct-2022

Report Term: 0-Other

Submitted By: Ph.D. Yangyang Liu

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Distribution Statement:

STEM Degrees: 14

STEM Participants: 23

Major Goals: The overarching objective of this proposed project is to understand the reaction mechanisms of catalytic degradation of toxic chemicals by a type of solid-state porous materials (metal-organic frameworks, MOFs), and ultimately realize the precise and rational design of new multifunctional materials for the desired function. Two classes of toxic chemicals of interest are sulfur-based and organophosphate-based agents, which are commonly used as simulants in the research for the deactivation of chemical warfare agents (CWAs). The mechanism studies will involve the investigation of interactions between the toxic chemicals and the surface of solid MOFs, the reaction

kinetics, diffusion, and reaction pathways. By using MOFs of varying topologies, metal nodes, pore sizes/shapes, and particle sizes, a structure-property relationship will be established for catalytic MOFs, which will guide the rational design and synthesis of multifunctional materials with better performance. As the structures of sulfur-based and organophosphate-based agents are very similar to that of sulfur mustard and nerve agents, this proposed study will offer important insight into new material discoveries for the rapid degradation of CWAs. This overarching objective can be realized with the following steps:

- 1) Investigate the mechanisms of singlet oxygen generation by solid-state materials (MOFs), including the kinetics, quantum yield, and lifetime of singlet oxygen (completed)
- 2) Determine whether the singlet oxygen generated by photoactive MOFs can diffuse out of the pores using a molecular trapping method (completed)
- 3) Obtain experimental evidence to understand the mechanism of selective photooxidation of organic sulfide, and determine if the selectivity stems from the MOF catalyst (completed)
- 4) Confirm the mechanism of acid-catalyzed hydrolysis of organophosphates by isolating the intermediates (completed)
- 5) Establish the structure-property relationship for catalytic MOFs by evaluating the effect of pore size, pore shape, functional group, metal node, and particle size (completed)
- 6) Design better-performing multifunctional materials based on the structure-property relationship and evaluate the performance of the new materials (completed)

Accomplishments: Please see the uploaded PDF document.

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Training Opportunities: Students and postdocs involved in this project were trained in organic synthesis, materials synthesis and characterizations, catalysis, data analysis, scientific writing, and presentations. The students also received training from the PI on the operation and maintenance of various instruments used for the project (e.g. PXRD, TGA, gas sorption, GC-MS, and NMR) and the interpretation of experimental data. In addition, the students also learned how to use scientific software/services (e.g. ChemDraw, Mercury, Origin, CCDC Database, and SciFinder), which are important skills for STEM research and careers.

Five undergraduate students participated in the REU program and conducted research at top PhD-granting universities, including Northwestern University, University of Wisconsin, Pennsylvania State University, and Caltech. All involved graduate students and undergraduate students have presented their research at a research symposium at Cal State LA. Three graduate students and four undergraduate students also presented poster presentations on their research at ACS national meetings. All these students received mentoring and training from the PI on how to prepare a good poster presentation. All supported students also attended department seminars with topics on chemistry and biochemistry.

The PI organized workshops to help students who are interested in applying for PhD programs in Chemistry or Materials Science & Engineering. Supported students also received one-on-one guidance on their PhD and Graduate Fellowship applications from the PI. All of the mentored students received several PhD offers from top universities, and several of them also received various Graduate Fellowships.

Results Dissemination: Results obtained from this project have been published as peer-reviewed journal articles, master's theses, and undergraduate honors theses. The PI and supported students have presented the research discoveries made under this project at various international, national, and local conferences (e.g., World Chemistry Congress & Canadian Chemistry Conference and Exhibition, American Chemical Society National Meetings, SACNAS (Advancing Chicanos/Hispanics & Native Americans in Science) Conferences) as well as research symposiums at Cal State LA.

This project recruited several summer research students from local high schools and community colleges, who also presented their summer research in the form of poster presentations and shared their discoveries with students and faculty at Cal State LA as well as local high schools and community colleges.

The PI also shared all publications that resulted from this project on her faculty website, the chemistry department website, and on social media (i.e., Twitter).

Honors and Awards: The PI, Dr. Yangyang Liu, was awarded early tenure and promotion to Associate Professor in 2021. In addition, Dr. Liu was awarded a Provost's Research Restart Award (post-COVID) at Cal State LA and two Department of Energy grants to support her research.

Juan Arriaga Gomez, a graduate student supported under this project, was awarded an Outstanding Graduate Student Award and a Vicki Kubo-Anderson Award at Cal State LA. Timothy Bennett, a graduate student who participated in this project, was awarded a Graduate Student Award at Cal State LA. He was admitted to the Chemistry PhD program at the University of Southern California. Akilah Miller, a graduate student who received support from this project, was awarded a Lloyd Ferguson Chemistry Scholarship and an NIH Bridges Master to PhD Fellowship. Akilah was admitted to the Chemistry PhD program at the University of Illinois at Urbana-Champaign and was awarded GEM Fellowship and a 3M Scholarship for her PhD studies. Anthony Castro, a graduate student who worked on this project, was awarded an NIH RISE Master to PhD Fellowship. Anthony was admitted to the Chemistry PhD program at the University of Wisconsin-Madison and was awarded a GEM Fellowship.

Several undergraduate students supported by this project were awarded scholarships, fellowships, and various awards. For example, Anna Nguyen, an undergraduate student supported by this project, was awarded the Student Award in Chemistry at Cal State LA. Anna is currently in medical school. Alisa Quon, another undergraduate student who participated in this project, was awarded the Rashad Razouk Award at Cal State LA.

Two other undergraduate students were awarded undergraduate fellowships from NIH. Several undergraduate students were admitted to PhD programs at top universities. Three other students who received partial support from this project are working in the industry as research scientists.

Protocol Activity Status:

Technology Transfer: We have been sending our samples to the U.S. Army Combat Capabilities Development Command Chemical Biological Center (DEVCOM CBC) to test our materials' capability and efficiency in degrading real chemical warfare agents, including nerve agents and mustard gas, under practical conditions.

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as of 18-May-2023

PARTICIPANTS:

Participant Type: PD/PI

Participant: Yangyang Liu

Person Months Worked: 12.00

Funding Support:

Project Contribution:

National Academy Member: N

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

Participant: Hongbin Luo

Person Months Worked: 12.00

Funding Support:

Project Contribution:

National Academy Member: N

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

Participant: Yajiao Hao

Person Months Worked: 15.00

Funding Support:

Project Contribution:

National Academy Member: N

Participant Type: Graduate Student (research assistant)

Participant: Juan Arriaga Gomez

Person Months Worked: 15.00

Funding Support:

Project Contribution:

National Academy Member: N

Participant Type: Graduate Student (research assistant)

Participant: Suki Liang

Person Months Worked: 5.00

Funding Support:

Project Contribution:

National Academy Member: N

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

Participant: Inessa Bychinskaya

Person Months Worked: 5.00

Funding Support:

Project Contribution:

National Academy Member: N

Participant Type: Graduate Student (research assistant)

Participant: Joshua Sosa

Person Months Worked: 4.00

Funding Support:

Project Contribution:

National Academy Member: N

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Participant Type: Graduate Student (research assistant)
Participant: Timothy Bennett
Person Months Worked: 4.00
Project Contribution:
National Academy Member: N
Funding Support:

Participant Type: Undergraduate Student
Participant: Brian Martinez
Person Months Worked: 1.00
Project Contribution:
National Academy Member: N
Funding Support:

Participant Type: Graduate Student (research assistant)
Participant: Akilah Miller
Person Months Worked: 2.00
Project Contribution:
National Academy Member: N
Funding Support:

Participant Type: Undergraduate Student
Participant: Matthew Tang
Person Months Worked: 6.00
Project Contribution:
National Academy Member: N
Funding Support:

Participant Type: Graduate Student (research assistant)
Participant: Matthew Tang
Person Months Worked: 4.00
Project Contribution:
National Academy Member: N
Funding Support:

Participant Type: Undergraduate Student
Participant: Nikita Mishra
Person Months Worked: 2.00
Project Contribution:
National Academy Member: N
Funding Support:

Participant Type: Undergraduate Student
Participant: Anna Nguyen
Person Months Worked: 7.00
Project Contribution:
National Academy Member: N
Funding Support:

Participant Type: Undergraduate Student
Participant: Alisa Quon

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Person Months Worked: 8.00
Project Contribution:
National Academy Member: N

Funding Support:

Participant Type: Graduate Student (research assistant)

Participant: Giovanni Munoz

Person Months Worked: 1.00

Funding Support:

Project Contribution:

National Academy Member: N

Participant Type: Graduate Student (research assistant)

Participant: Angel Arredondo

Person Months Worked: 2.00

Funding Support:

Project Contribution:

National Academy Member: N

Participant Type: Graduate Student (research assistant)

Participant: Pavithra Wijeratne

Person Months Worked: 2.00

Funding Support:

Project Contribution:

National Academy Member: N

ARTICLES:

Publication Type: Journal Article

Peer Reviewed: Y

Publication Status: 1-Published

Journal: Coordination Chemistry Review

Publication Identifier Type: DOI

Publication Identifier: <https://doi.org/10.1016/j.ccr.2020.213615>

Volume: 429

Issue:

First Page #: 213615

Date Submitted: 2/1/21 12:00AM

Date Published: 10/21/20 7:00AM

Publication Location:

Article Title: A Historical Perspective on Porphyrin-Based Metal–Organic Frameworks and Their Applications

Authors: Xuan Zhang, Megan C. Wasson, Mohsen Shayan, Ellan K. Berdichevsky, Joseph Ricardo-Noordberg, Z

Keywords: porphyrin; metal-organic frameworks; catalysis; sensing; biomedical applications

Abstract: Porphyrins are important molecules widely found in nature in the form of enzyme active sites and visible light absorption units. Recent interest in using these functional molecules as building blocks for the construction of metal-organic frameworks (MOFs) have rapidly increased due to the ease in which the locations of and the distances between the porphyrin units can be controlled in these porous crystalline materials. Porphyrin-based MOFs with atomically precise structures provide an ideal platform for the investigation of their structure-function relationships in the solid-state without compromising the accessibility to the inherent properties of the porphyrin building blocks. This review will provide a historical overview of the development and applications of porphyrin-based MOFs from early studies focused on design and structures, to recent efforts on their utilization in biomimetic catalysis, photocatalysis, electrocatalysis, sensing, and biomedical applications will be highligh

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Publication Status: 1-Published

Journal: ACS Catalysis

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Publication Identifier: <https://doi.org/10.1021/acscatal.0c04565>

Volume: 11

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Date Published: 1/14/21 8:00AM

Publication Location:

Article Title: Rapid, Biomimetic Degradation of a Nerve Agent Simulant by Incorporating Imidazole Bases into a Metal–Organic Framework

Authors: Hong-Bin Luo, Anthony Castro, Megan Wasson, Willmer Flores, Omar Farha, and Yangyang Liu

Keywords: nerve agents, metal-organic frameworks, catalysis, pure water, solid phase

Abstract: Metal-organic frameworks (MOFs) are excellent catalytic materials for the hydrolytic degradation of nerve agents and their simulants. However, most of the MOF-based hydrolysis catalysts to date are reliant on liquid water media buffered by a volatile liquid base. To overcome this practical limitation, we developed a simple and feasible strategy to synthesize MOF composites that structurally mimic phosphotriesterase's active site as well as its ligated histidine residues. By incorporating imidazole and its derivative into the pores of MOF-808, the obtained MOF composites achieved rapid degradation of a nerve agent simulant (dimethyl-4-nitrophenyl phosphate, DMNP) in pure water as well as in a humid environment without liquid base. Remarkably, one of the composites Im@MOF-808 displayed the highest catalytic activity for DMNP hydrolysis in unbuffered aqueous solutions among all reported MOF-based catalysts.

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Peer Reviewed: Y

Publication Status: 1-Published

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Volume: 125

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Publication Location: United States

Article Title: Determination of Singlet Oxygen Quantum Yield of a Porphyrinic Metal–Organic Framework

Authors: Yajiao Hao, Brandon M. Liu, Timothy F. Bennett, Charlotte G. Monsour, Matthias Selke, and Yangyang Liu

Keywords: metal-organic frameworks, singlet oxygen, quantum yield, mustard gas, heterogeneous catalysis

Abstract: Metal-organic frameworks (MOFs) have emerged as heterogeneous photosensitizers in applications ranging from photodynamic therapy to photocatalysis. However, singlet oxygen ($^1\text{O}_2$) quantum yields of MOF photosensitizers are largely unknown. Herein, we report a reliable method to quantify the $^1\text{O}_2$ quantum yield of a porphyrin MOF PCN-222/MOF-545 (free base). To accurately measure the optical density of the MOF suspensions in chloroform, a UV–vis spectrometer equipped with an integrating sphere detector was employed. However, no $^1\text{O}_2$ near-infrared luminescence signal from the excited MOF could be detected and the amount of $^1\text{O}_2$ produced by the MOF photosensitizer was quantified using a $^1\text{O}_2$ trap 9,10-dimethylantracene. Using C70 as a reference, the $^1\text{O}_2$ quantum yield of PCN-222/MOF-545 (free base) was determined to be 0.35 ± 0.02 . This method should be applicable to the determination of $^1\text{O}_2$ quantum yields of other solid-state materials.

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Journal: ACS Catalysis

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Date Submitted: 12/30/21 12:00AM

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Publication Location: United States

Article Title: Mechanism-Guided Design of Metal–Organic Framework Composites for Selective Photooxidation of a Mustard Gas Simulant under Solvent-Free Conditions

Authors: Yajiao Hao, Edgar K. Papazyan, Yong Ba, Yangyang Liu

Keywords: metal-organic frameworks, selective photooxidation, singlet oxygen, mustard gas simulant, mechanism of sulfide oxidation, solvent-free, textile composites

Abstract: Photoactive metal-organic frameworks (MOFs) and their derivatives have shown great promise for the degradation of mustard gas and its simulants (e.g., 2-chloroethyl ethyl sulfide or CEES) by selectively oxidizing these toxic organic sulfides to less toxic sulfoxide products under visible or ultraviolet (UV) light. However, these reactions must be conducted in specific solvents (e.g., methanol) to achieve satisfactory selectivity of sulfoxide, which limits the use of MOFs in protective gears. Our mechanistic study shows that during the photooxidation of CEES, the stabilization of a putative persulfoxide intermediate with hydrogen-bond donors was crucial for the formation of sulfoxide. Based on this discovery, we developed a series of MOF/ textile composites containing various hydrogen-bond donor additives for selective photooxidation of organic sulfides under solvent-free conditions. With a 3 mol % catalyst loading, our best-performing composite degraded all CEES within 15 min in oxygen

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Journal: ACS Applied Materials & Interfaces

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Date Submitted: 1/14/23 12:00AM

Date Published: 1/5/23 4:00PM

Publication Location:

Article Title: MOF–Polymer Mixed Matrix Membranes as Chemical Protective Layers for Solid-Phase Detoxification of Toxic Organophosphates

Authors: Hong-Bin Luo, Fang-Ru Lin, Zhi-Yuan Liu, Ya-Ru Kong, Karam B. Idrees, Yangyang Liu, Yang Zou, Om

Keywords: Zr-MOFs, organophosphorus nerve agents, mixed matrix membranes, catalytic detoxification, solid-state hydrolysis

Abstract: Zirconium-based metal-organic frameworks (Zr-MOFs) have been demonstrated as potent catalysts for the hydrolytic detoxification of organophosphorus nerve agents and their simulants. However, the practical implementation of these Zr-MOFs is limited by the poor processability of their powdered form and the necessity of water media buffered by a volatile liquid base in the catalytic reaction. Herein, we demonstrate the efficient solid-state hydrolysis of a nerve agent simulant (dimethyl-4-nitrophenyl phosphate, DMNP) catalyzed by Zr-MOF-based mixed matrix membranes. The mixed matrix membranes were fabricated by incorporating MOF-808 into the blending matrix of poly(vinylidene fluoride) (PVDF), poly(vinylpyrrolidone) (PVP), and imidazole (Im), in which MOF-808 provides highly active catalytic sites, the hydrophilic PVP helps to retain water for promoting the hydrolytic reaction, and Im serves as a base for catalytic site regeneration.

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CONFERENCE PAPERS:

RPPR Final Report
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Publication Type: Conference Paper or Presentation **Publication Status:** 1-Published
Conference Name: 48th World Chemistry Congress & 104th Canadian Chemistry Conference and Exhibition
Date Received: 31-Aug-2021 Conference Date: 17-Aug-2021 Date Published: 14-Aug-2021
Conference Location: Virtual
Paper Title: Optimizing Metal-Organic Frameworks for Catalysis
Authors: Yangyang Liu
Acknowledged Federal Support: Y

Publication Type: Conference Paper or Presentation **Publication Status:** 1-Published
Conference Name: American Chemical Society Meeting Fall 2022
Date Received: 14-Jan-2023 Conference Date: 23-Aug-2022 Date Published: 23-Jan-2023
Conference Location: Chicago, IL
Paper Title: Optimizing metal-organic frameworks for the removal and degradation of organic pollutants in water
Authors: Yangyang Liu
Acknowledged Federal Support: Y

DISSERTATIONS:

Publication Type: Thesis or Dissertation
Institution: California State University, Los Angeles
Date Received: 09-Sep-2019 Completion Date: 5/18/19 6:37AM
Title: Investigation of Singlet Oxygen Photosensitization of a Porphyrinic Metal-Organic Framework
Authors: Brandon Liu, Yangyang Liu, Matthias Selke
Acknowledged Federal Support: Y

Publication Type: Thesis or Dissertation
Institution: California State University, Los Angeles
Date Received: 30-Aug-2020 Completion Date: 5/13/20 1:30AM
Title: Catalytic Oxidation of Sulfur-Mustard Analogues Using Metal-Organic Frameworks
Authors: Timothy Bennett
Acknowledged Federal Support: Y

Publication Type: Thesis or Dissertation
Institution: California State University, Los Angeles
Date Received: 30-Aug-2020 Completion Date: 5/12/20 7:00AM
Title: Investigation of the Photocatalytic Properties of a Tin Doped Porphyrinic Metal-Organic Framework in the Detoxification of a Mustard Gas Simulant
Authors: Edgar Papazyan
Acknowledged Federal Support: Y

Publication Type: Thesis or Dissertation
Institution: California State University, Los Angeles
Date Received: 31-Aug-2021 Completion Date: 5/21/21 10:36PM
Title: Degradation of a Nerve Agent Simulant by Implementing Imidazole-based Structures in Metal-Organic Frameworks
Authors: Anthony Castro, Yangyang Liu
Acknowledged Federal Support: Y

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Publication Type: Thesis or Dissertation

Institution: California State University, Los Angeles

Date Received: 31-Aug-2022

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Title: The Effects of PEGylated Metal-Organic Frameworks for pH-Sensitive Drug Delivery

Authors: Suki Liang

Acknowledged Federal Support: **Y**

Publication Type: Thesis or Dissertation

Institution: California State University, Los Angeles

Date Received: 31-Aug-2022

Completion Date: 5/19/22 2:00PM

Title: Exploring the Photocatalytic Activity of Porphyrinic Metal-Organic Frameworks in the Detoxification of a Mustard Gas Simulant

Authors: Anna Nguyen

Acknowledged Federal Support: **Y**

Publication Type: Thesis or Dissertation

Institution: California State University, Los Angeles

Date Received: 14-Jan-2023

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Title: Optimization of Porphyrin-Based Metal-Organic Frameworks For Selective Oxidation of Organic Sulfides

Authors: Juan Carlos Arriaga Gomez, Yangyang Liu

Acknowledged Federal Support: **Y**

Publication Type: Thesis or Dissertation

Institution: California State University, Los Angeles

Date Received: 14-Jan-2023

Completion Date: 12/16/22 8:00AM

Title: Porphyrinic Metal-Organic Frameworks for the Photocatalytic Degradation of a Mustard Gas Simulant

Authors: Alisa Quon, Yangyang Liu

Acknowledged Federal Support: **Y**

Publication Type: Thesis or Dissertation

Institution: California State University, Los Angeles

Date Received: 14-Jan-2023

Completion Date: 12/16/22 4:00PM

Title: Porphyrinic Metal-Organic Frameworks for the Photocatalytic Degradation of a Mustard Gas Simulant

Authors: Alisa Quon, Yangyang Liu

Acknowledged Federal Support: **Y**

Partners

,

RPPR Final Report
as of 18-May-2023

I certify that the information in the report is complete and accurate:

Signature: Yangyang Liu

Signature Date: 1/30/23 8:23PM

Accomplishments/Progress:

i. Abstract

Through systematic studies, this project investigated the reaction mechanisms of catalytic degradation of toxic chemicals by a type of solid-state porous materials (metal-organic frameworks, or MOFs). By using MOFs of varying topologies, metal nodes, pore sizes/shapes, and particle sizes, structure-property relationships were established for catalytic MOFs used for the degradation of two classes of toxic chemicals, sulfur-based and organophosphate-based agents. The structures of the studied toxic chemicals highly resemble the structures of chemical warfare agents (CWAs). The mechanistic studies and structure-property relationships established in this project have guided the rational design and synthesis of multifunctional and novel materials with better performance. Ultimately, this project realized the precise and rational design of new materials that exhibited an outstanding performance for the catalytic degradation of organosulfur or organophosphates under near-practical conditions. In addition, this project also uncovered important strategies and design rules for new material discoveries and developments that promote the practical and rapid degradation of CWAs.

ii. Specific Objectives

The specific objectives of the entire proposed project are listed below, and the grant year was noted after each objective:

- 1) Investigate the mechanisms of singlet oxygen generation by solid-state materials (MOFs), including the kinetics, quantum yield and lifetime of singlet oxygen (for grant year 1, **completed**)
- 2) Determine whether the singlet oxygen generated by photoactive MOFs can diffuse out of the pores using a molecular trapping method (for grant year 1, **completed**)
- 3) Obtain experimental evidence to understand the mechanism of selective photooxidation of organic sulfide, and determine if the selectivity stems from the MOF catalyst (for grant years 1-2, **completed**)
- 4) Confirm the mechanism of acid-catalyzed hydrolysis of organophosphates by isolating the intermediates (for grant years 2-3, **completed**)
- 5) Establish the structure-property relationship for catalytic MOFs by evaluating the effect of pore size, pore shape, functional group, metal node, and particle size (for grant years 2-3; **completed**)
- 6) Design better-performing multifunctional materials based on the structure-property relationship and evaluate the performance of the new materials (for grant years 3-4; **completed**)

iii. Findings

All findings and major accomplishments are summarized under each objective.

Objective 1. Investigate the mechanisms of singlet oxygen generation by solid-state materials (MOFs), including the kinetics, quantum yield and lifetime of singlet oxygen.

The singlet oxygen ($^1\text{O}_2$) generation mechanisms, including kinetics, quantum yield (Φ_Δ), and lifetime, were investigated in a porphyrin MOF, PCN-222/MOF-545, which has been extensively studied as a photosensitizer for the production of $^1\text{O}_2$.¹⁻³ Free-base PCN-222/MOF-545 (PCN-222/MOF-545(FB)) is comprised of 6-connected $\text{Zr}_6(\mu_3\text{-OH})_8(\text{OH})_8(\text{CO}_2)_8$ metal nodes and tetrakis(4-carboxyphenyl)porphyrin (H_2TCPP) linkers, and the crystal structure of the MOF is presented in **Figure 1a**. The structure and phase purity of the obtained material were confirmed using powder X-ray diffraction (PXRD), and the successful activation of the MOF was demonstrated by nitrogen sorption experiment at 77 K. In addition, scanning electron microscope (SEM) images (**Figure 1b**) revealed the rod-shaped crystals of PCN-222/MOF-545(FB) to be 2-4 μm in length. Lastly, the UV-vis spectra of PCN-222/MOF-545(FB) showed a Soret band at 431.8 nm and four Q-bands at 521.2 nm, 556.4 nm, 594.5 nm, and 650.0 nm, respectively (**Figure 1c**). These peaks are slightly redshifted compared to those of the free ligand H_2TCPP , which has a Soret band at 414.7 nm and four Q-bands at 512.0 nm, 545.8 nm, 588.5 nm and 645.1 nm, respectively (**Figure 1c**). The redshift and broadening of the absorption bands for the MOF sample arise from the ligand-to-metal charge transfer (LMCT) (i.e., charge transfer from the TCPP ligand to the Zr_6 node in PCN-222/MOF-545(FB)).⁴⁻⁵

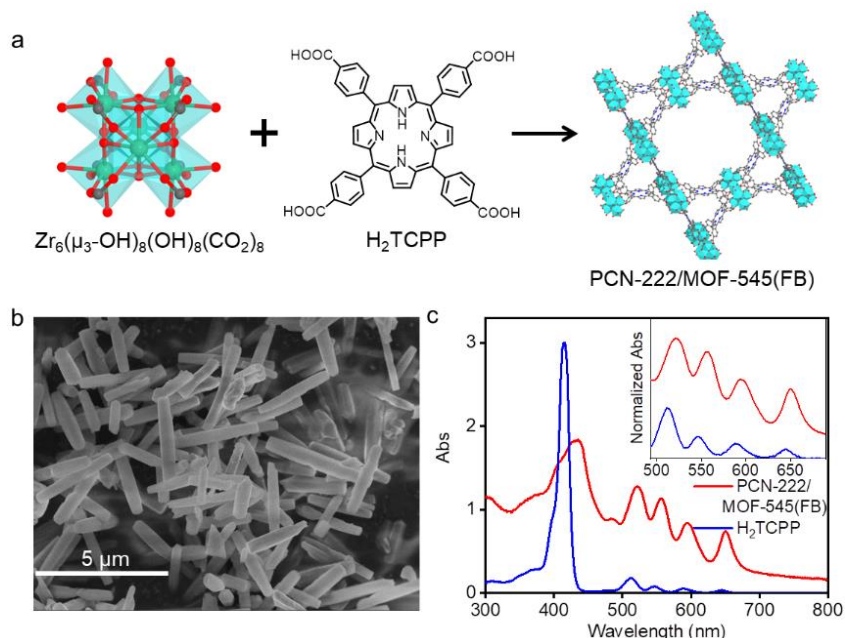


Figure 1. a) Structure of PCN-222/MOF-545(FB): $\text{Zr}_6(\mu_3\text{-OH})_8(\text{OH})_8$ metal node, H_2TCPP linker, and its three-dimensional network. b) Scanning electron microscope (SEM) image of PCN-222/MOF-545(FB), c) UV-vis spectra of H_2TCPP and PCN-222/MOF-545(FB) measured with integrating sphere accessory.

Typically, the generation of $^1\text{O}_2$ can be confirmed through direct detection of the $^1\text{O}_2$ near-infrared (NIR) luminescence (1270 nm).⁶ Despite many attempts, we were unable to detect any $^1\text{O}_2$ generated by PCN-222/MOF-545(FB) using time-resolved NIR luminescence ($\lambda_{\text{exc.}} = 532 \text{ nm}$ in chloroform). It is conceivable that the MOF framework acts as a $^1\text{O}_2$ quencher. To investigate this possibility, we added a PCN-222/MOF-545(FB) suspension to a chloroform solution of another $^1\text{O}_2$ sensitizer, namely C_{70} , and measured the lifetime (τ) of the $^1\text{O}_2$ signal before and after the addition of the MOF suspension. While the $^1\text{O}_2$ intensity at time 0 decreased upon the addition of the MOF suspension (possibly due to light scattering by the MOF), we did not observe an appreciable decrease in the lifetime compared to that of pure C_{70} solution ($\tau_{\text{C}_{70}} = 218 \mu\text{s}$, $\tau_{\text{C}_{70}+\text{PCN-222/MOF-545}} = 203 \mu\text{s}$ at $\text{OD}_{\text{PCN-222/MOF-545}, 532\text{nm}} = 0.3$), indicating that the surface of PCN-222/MOF-545(FB) does not significantly quench $^1\text{O}_2$. These results suggest that all of the $^1\text{O}_2$ molecules remain inside the pores of the MOFs. Clearly, the detection of the $^1\text{O}_2$ NIR luminescence is not a viable method for measuring the $^1\text{O}_2$ quantum yield of MOFs.

An alternative way to measure $^1\text{O}_2$ quantum yield of a photosensitizer is the chemical trapping methodology: a chemical trapping agent is oxidized by $^1\text{O}_2$, and the concentration of the oxidized product can be used to quantify the $^1\text{O}_2$ produced by a photosensitizer. A commonly used chemical trapping agent is 1,3-diphenylisobenzofuran (DPBF). However, DPBF is also known to be photosensitive and undergoes self-bleaching at high concentrations.⁷ Another notable disadvantage of DPBF is that it also reacts with radicals and other oxidants.⁸ Therefore, in our experiments, we chose 9,10-dimethylanthracene (DMA) which undergoes a [4+2] cycloaddition with $^1\text{O}_2$ resulting in the formation of 9,10-dimethyl-9,10-epidioxy-anthracene (DMA- O_2 , **Figure 2a**). Physical quenching of singlet oxygen by DMA is insignificant relative to the chemical reaction.⁹ Previous research has shown that DMA only selectively reacts with $^1\text{O}_2$ among all the ROS.¹⁰ We also found that DMA exhibited better photostability and had reduced absorptivity within the absorption region of PCN-222/MOF-545(FB) when compared to DPBF. This allows the use of a cutoff filter such that only PCN-222/MOF-545(FB) is excited during the quantum yield measurements. The chemical reaction rate constant (k_r) of DMA with $^1\text{O}_2$ is $3 \times 10^7 \text{ M}_{\text{DMA}}^{-1}\text{s}^{-1}$,⁹ and the rate of removal of $^1\text{O}_2$ by *d*-chloroform (CDCl_3) (k_d) is about $2 \times 10^3 \text{ s}^{-1}$. Therefore, as long as $[\text{DMA}] \geq 10 \text{ mmol}$, the assumption that $k_r \times [\text{DMA}] \gg k_d$ will hold, and therefore, removal of $^1\text{O}_2$ by the solvent is insignificant relative to $^1\text{O}_2$ trapping by DMA.

We then selected C_{70} ($\Phi_{\Delta} = 0.89 \pm 0.04$)¹¹ as the reference photosensitizer since it is soluble in aprotic solvents, and the absorption band of C_{70} overlaps with PCN-222/MOF-545(FB) so that irradiation within the same wavelength region can be used. Lastly, we chose CDCl_3 as the solvent due to the good solubility of the reference C_{70} and good suspendability of PCN-222/MOF-545(FB), as well as the long $^1\text{O}_2$ lifetime in CDCl_3 . The experimental setup for the $^1\text{O}_2$ quantum yield measurement of MOFs is depicted in **Figure 2b**. A suspension/solution of 50 mM DMA and PCN-222/MOF-545(FB)/ C_{70} in CDCl_3 in an NMR tube was saturated with O_2 immediately before being irradiated by a Xe lamp, and the sample was continuously purged with O_2 while being irradiated. The Xe lamp used in all the experiments was equipped with a 493 nm cutoff filter, which cuts out light below the wavelength of 493 nm, so that DMA was not irradiated. Based on the time-dependent conversion of DMA to DMA- O_2 monitored using ^1H NMR, the total irradiation

time was set to be 5 min in the experiments as an appreciable amount of DMA remained unoxidized after 5 min such that $k_r \times [\text{DMA}] \gg k_d$ still held. In order to account for the scattered light by the MOF suspension and accurately measure the light absorption by the MOF particles, a UV-vis spectrometer equipped with a barium sulfate-coated integrating sphere was utilized to obtain the absorption spectra of the samples.

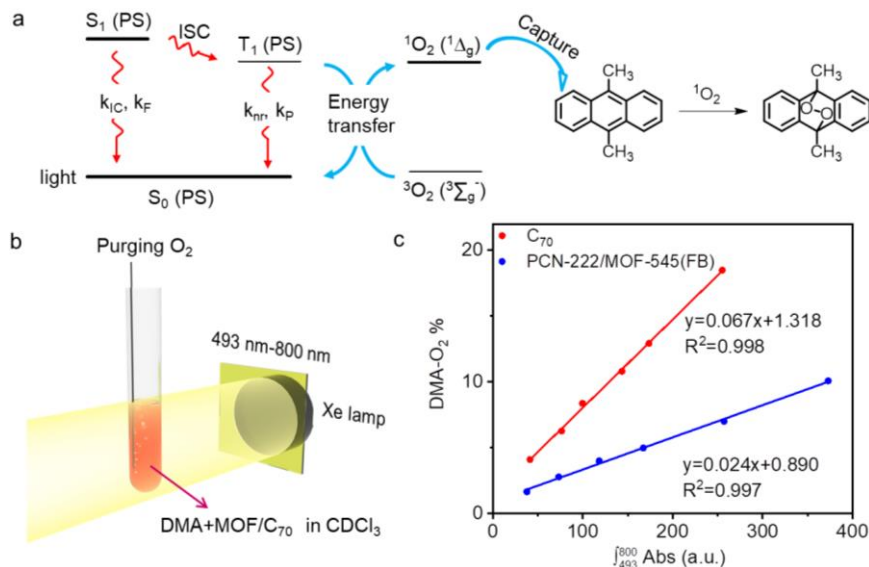


Figure 2. a) Scheme demonstrating the ¹O₂ sensitization by photosensitizers and the ¹O₂ capture by 9,10-dimethylantracene (DMA). PS: Photosensitizer, ISC: intersystem crossing. b) Schematic demonstration of the setup for the irradiation experiments: a NMR tube containing 1 mL 50 mM DMA and PCN-222/MOF-545(FB)/C₇₀ in CDCl₃ was irradiated by a Xe lamp equipped with a 493 nm cutoff filter for 5 min under O₂ purging. c) Plot of DMA conversion against the optical density (integrated area from 493 nm to 800 nm) for a series of C₇₀ (linear fitting shown as red line) and PCN-222/MOF-545(FB) (linear fitting shown as blue line) solutions/suspensions of various concentrations.

MOF suspensions and reference (C₇₀) solutions of varied concentrations were prepared and irradiated under a Xe lamp within the visible spectrum from 493 nm – 800 nm. The absorption spectra were integrated across this region for each sample, and these values were used as the integrated optical densities. The consumption of the chemical trap (DMA) was monitored by ¹H NMR, which was used to calculate the amount of ¹O₂ being generated by the MOF or by the reference under light irradiation. The amount of ¹O₂ being generated by various amounts of PCN-222/MOF-545(FB) or C₇₀ was then plotted against the sample's corresponding optical density. The slopes were obtained for the plots of both PCN-222/MOF-545(FB) and C₇₀ (**Figure 2c**).¹²⁻¹³ The ¹O₂ quantum yield of PCN-222/MOF-545(FB) was then calculated using the following equation:

$$\frac{\Phi_{\text{PCN-222/MOF-545(FB)}}}{\Phi_{\text{C}_{70}}} = \frac{\text{slope}_{\text{PCN-222/MOF-545(FB)}}}{\text{slope}_{\text{C}_{70}}} \quad [1]$$

As shown in **Figure 2c**, the observed DMA conversion vs. optical density plots for samples of varied concentration was linearly fitted with slopes of 0.024 and 0.065 for PCN-222/MOF-545(FB) and C₇₀, respectively. The ¹O₂ quantum yield of the reference,

C₇₀, was reported to be $\Phi_{\Delta} = 0.89 \pm 0.04$.¹¹ Therefore, using equation 1, the $^1\text{O}_2$ quantum yield of PCN-222/MOF-545(FB) was calculated to be $\Phi_{\Delta} = 0.35 \pm 0.02$ in CDCl_3 . It is worth noting that this number is slightly lower than the $^1\text{O}_2$ quantum yield of H₂TCPP (the free porphyrin linker of the MOF), which was previously reported as $\Phi_{\Delta} = 0.53$ by Li et al. using the aforementioned NIR luminescence method.¹⁴ Interestingly, the quantum yield of PCN-222/MOF-545(FB) we obtained is very similar to the reported quantum yield of meso-tetra(4-carboxyphenyl)porphine tetramethyl ester (TPPCOOMe) ($\Phi_{\Delta} = 0.38$),¹⁵ an esterified form of the MOF linker.

To further validate the $^1\text{O}_2$ quantum yield we obtained for PCN-222/MOF-545(FB), understand the $^1\text{O}_2$ generation kinetics as well as to illustrate the advantages of MOF-based heterogeneous photosensitizers, PCN-222/MOF-545(FB) and TPPCOOMe were used for the photooxidation of a mustard gas simulant, 2-chloroethyl ethyl sulfide (CEES). Previous studies have shown that $^1\text{O}_2$ can selectively oxidize CEES to 2-chloroethyl ethyl sulfoxide (CEESO) in protic solvents (e.g., methanol or MeOH) without forming the more toxic sulfones.^{1-2,16-20} In aprotic solvents (e.g., acetonitrile, chloroform), however, a small amount of 2-chloroethyl ethyl sulfone (CEESO₂) and ethyl vinyl sulfoxide (EVSO) were also observed (**Figure 3a**).²¹⁻²² TPPCOOMe is not very soluble in MeOH, but it readily dissolves in chloroform, which we therefore chose as the solvent for the photocatalytic studies. As such, TPPCOOMe serves as a homogeneous photosensitizer in chloroform and is compared to PCN-222/MOF-545(FB), a heterogeneous photosensitizer.

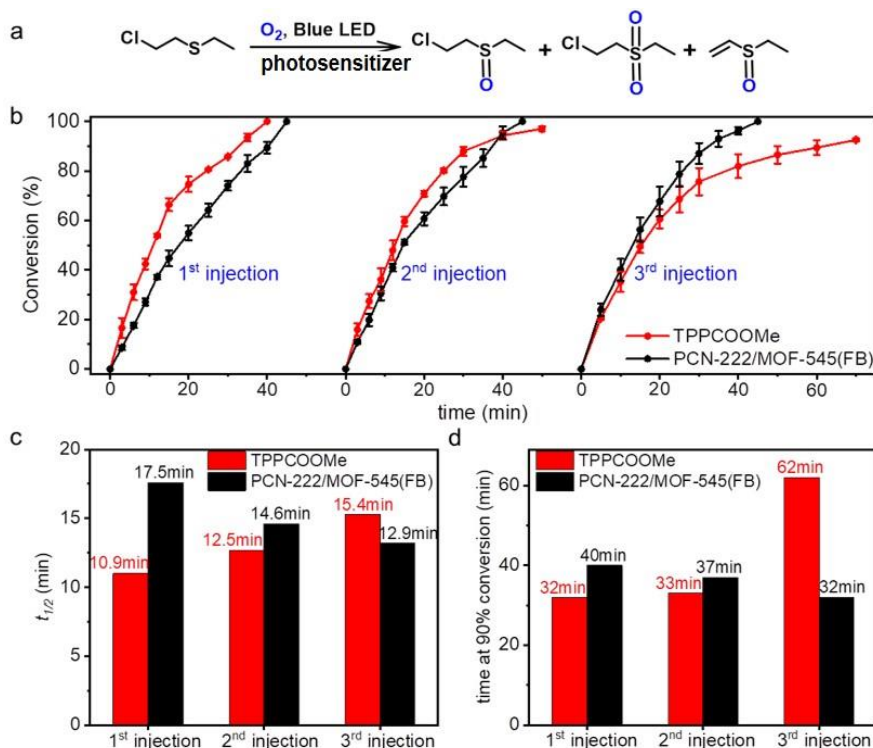


Figure 3. a) The oxidation of CEES in the presence of photosensitizer under blue LED irradiation in O_2 atmosphere. CEESO, CEESO₂, and EVSO were observed in the product when using chloroform as the solvent. b) Kinetic profiles of CEES photooxidation for three cycles in the presence of TPPCOOMe (in red) and PCN-222/MOF-545(FB) (in black). 1 mol% photosensitizer

(calculated based on porphyrin units) relative to CEES was used in each reaction. Each point is an average of three experimental runs. Error bars are one standard deviation. Comparison of c) reaction half-lives and d) time needed to reach a 90% conversion for three cycles of CEES oxidation in the presence of TPPCOOMe (in red) and PCN-222/MOF-545(FB) (in black).

In the photocatalytic experiments, equivalent amounts of PCN-222/MOF-545(FB) and TPPCOOMe (1 mol% porphyrin units relative to CEES) were first suspended or dissolved in chloroform, which was then sealed in a microwave vial and purged with O₂. The samples were then subjected to blue LED irradiation immediately after CEES was added. Gas chromatography-mass spectrometry (GC-MS) was used to monitor the reaction progress. The kinetic profiles, reaction half-lives ($t_{1/2}$) and the time needed to reach a 90% conversion for both photosensitizers are compared in Figure 3b-d. The first cycle of CEES oxidation progressed more rapidly in the presence of TPPCOOMe compared to PCN-222/MOF-545(FB). After 40 min, all CEES was oxidized by the ¹O₂ generated by TPPCOOMe with a reaction half-life of 10.9 min, whereas under the same condition, the PCN-222/MOF-545(FB)-catalyzed reaction was completed after 45 min with a half-life of 17.5 min. Given the very similar ¹O₂ quantum yields of the two photosensitizers, the faster oxidation of CEES with TPPCOOMe can be attributed to diffusion. Both TPPCOOMe and CEES are soluble in chloroform; hence the homogeneous system allows for better interaction between the generated ¹O₂ and CEES (not diffusion-controlled). On the other hand, the ¹O₂ being generated by the porphyrin linkers of the heterogeneous PCN-222/MOF-545(FB) remains in the MOF pores, and thus CEES can only be oxidized when it diffuses into the MOF pores or in close proximity to the MOF linkers (diffusion-controlled). This hypothesis was further confirmed by the closer completion times for the two reactions catalyzed by the two photosensitizers (40 min vs. 45 min; because more CEES diffused into the MOF pores over time). Furthermore, the similar but slightly longer completion time in the presence of the MOF compared to TPPCOOMe is also consistent with the measured ¹O₂ quantum yield for PCN-222/MOF-545(FB).

To evaluate the photostability and reusability of the photosensitizers, they were used for two additional cycles of CEES oxidation under blue LED irradiation, and the reaction profiles are shown in Figure 3b. The second cycle of CEES oxidation with TPPCOOMe exhibited a longer half-life than the first cycle (1st cycle: $t_{1/2}$ = 10.9 min; 2nd cycle: $t_{1/2}$ = 12.5 min), and only 97.1% of CEES was oxidized after 50 min (Figure 3bc). In contrast, the second cycle of the MOF-catalyzed reaction had a shorter half-life than the first cycle (1st cycle: $t_{1/2}$ = 17.5 min; 2nd cycle: $t_{1/2}$ = 14.6 min), and all of the CEES was reacted within 45 min (Figure 3bc). When TPPCOOMe was used for the third cycle of CEES oxidation, the reaction slowed down even further, and only 92.6% of CEES was oxidized after 70 min. Interestingly, in the third cycle, the MOF-catalyzed reaction was faster than that of the TPPCOOMe-catalyzed ($t_{1/2}(\text{MOF})$ = 12.9 min vs. $t_{1/2}(\text{TPPCOOMe})$ = 15.4 min). It is also worth noting that all three cycles of the MOF-catalyzed reactions reached 100% conversion after 45 min, whereas the TPPCOOMe-catalyzed reactions became slower after each cycle (Figure 3b-d). Essentially, the photocatalytic studies demonstrated that the homogeneous photosensitizer (i.e., TPPCOOMe) was slowly losing its efficiency over time under extended periods of irradiation, which can be a

consequence of photodegradation and/or photobleaching.²³ In contrast, the heterogeneous MOF photosensitizer exhibited excellent photostability and reusability. PCN-222/MOF-545(FB) was used for multiple cycles of photooxidation reactions under continuous irradiation with minimal loss of activity/efficiency. Furthermore, the MOF-catalyzed reactions also showed higher selectivities toward CEESO, the preferred and less toxic product. Therefore, despite a comparable quantum yield with its homogeneous counterpart (i.e., TPPCOOMe), PCN-222/MOF-545(FB) is a more robust and selective photosensitizer.

In summary, a new method was developed to measure the singlet oxygen quantum yield for a porphyrin MOF ($\Phi_{\Delta} = 0.35 \pm 0.02$ in CDCl_3). We also confirmed that MOFs are not singlet oxygen quenchers and do not affect the singlet oxygen lifetime. In addition, singlet oxygen generation kinetics were studied using the photooxidation of CEES in the presence of a porphyrin MOF. Lastly, we demonstrated that heterogeneous photosensitizers like MOFs are superior to their homogeneous counterparts for photocatalytic reactions. These findings were published in the *Journal of Physical Chemistry C* as a peer-reviewed research article (see ref 24).

Objective 2. Determine whether the singlet oxygen generated by photoactive MOFs can diffuse out of the pores using a molecular trapping method.

A series of experiments indicated that the $^1\text{O}_2$ generated by MOFs remains inside the MOF pores and that photooxidation occurs mainly inside MOF pores. The first experiment was described under **Objective 1**, in which we attempted to detect $^1\text{O}_2$ generation in PCN-222/MOF-545(FB) using time-resolved NIR luminescence. However, no $^1\text{O}_2$ NIR luminescence signal from the excited MOF could be detected. Since we confirmed that the MOF is not a $^1\text{O}_2$ quencher, this absence of $^1\text{O}_2$ NIR luminescence signal can be explained by $^1\text{O}_2$ being trapped inside the MOF pores. This explanation was further confirmed using a molecular/chemical trapping method. It is interesting to note that this is in contrast to $^1\text{O}_2$ production in zeolites, in which a fraction of the $^1\text{O}_2$ molecules does escape the zeolite cage.²⁵⁻²⁶

In the molecular/chemical trapping experiment, a $^1\text{O}_2$ trap, DMA, was mixed with MOF in chloroform, and the mixture was sonicated for 30 min to allow DMA to enter the MOF pores. The mixture was then irradiated with a halogen lamp equipped with a 493 nm cutoff filter. The cutoff filter ensured that DMA was not photosensitized, and the MOF was the only source for $^1\text{O}_2$ generation (**Figure 4a**). The UV-vis absorption spectra of DMA were collected after different irradiation periods, shown in **Figure 4b**. The decreasing intensity of the DMA absorption over time suggested that $^1\text{O}_2$ was generated by the MOF, which subsequently oxidized the DMA in the MOF pores. We also observed that with the same porphyrin loading and reaction time, the MOFs with smaller pores oxidized a small amount of DMA under the same conditions. The lower DMA conversion in MOFs with smaller pores can be attributed to a smaller amount of DMA being accommodated inside these MOF pores. These molecular trapping experiments confirmed that $^1\text{O}_2$ was generated inside MOF pores and can oxidize substrates inside MOF pores.

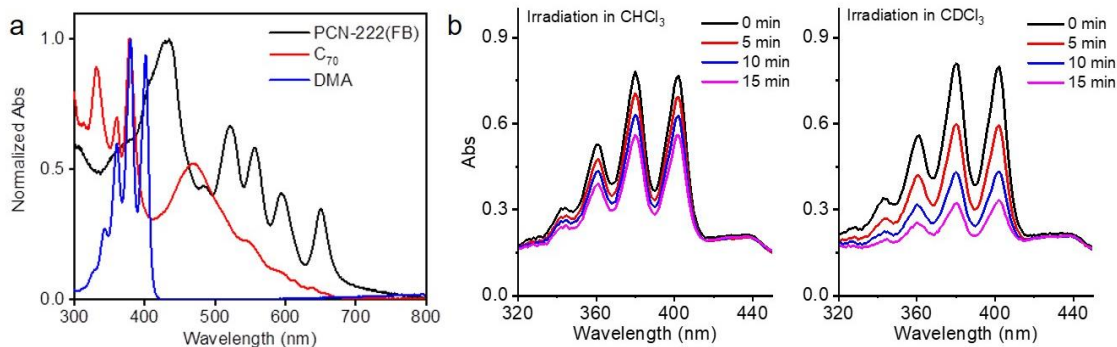


Figure 4. a) UV-vis spectra of PCN-222/MOF-545(FB), C₇₀, and DMA. b) UV-vis spectra of 0.1 mmol DMA in CHCl₃ and CDCl₃ in the presence of PCN-222/MOF-545(FB) (optical density = 21 Abs·nm) under irradiation with a halogen lamp equipped with a 493 nm cutoff filter.

To further elucidate that the photocatalytic reactions involving ¹O₂ occur inside MOF pores, we studied the photooxidation of CEES in the presence of PCN-222/MOF-545, as well as its modified counterpart. In preparation of the modified MOF, benzoic acid (BA) was introduced into the PCN-222/MOF-545 via solvent-assisted linker incorporation (SALI)²⁷ to partially block the MOF pores. The successful incorporation of BA into PCN-222/MOF-545 was confirmed using thermogravimetric analysis (TGA), N₂ isotherms, and ¹H NMR (**Figure 5a-c**). TGA of the BA-modified MOF and ¹H NMR of the digested sample indicated that approximately 3 BA molecules per Zr₆O₈ node were introduced to PCN-222/MOF-545. Due to the partially blocked pores, the BA-modified PCN-222/MOF-545 showed a smaller surface area/pore volume compared to the pristine MOF, evidenced by N₂ isotherms at 77 K (**Figure 5c**). The BA-modified PCN-222/MOF-545 (1 mol% porphyrin loading) was then used for CEES oxidation under the same condition as the pristine MOF, and their reaction profiles were compared in **Figure 5d**. As expected, CEES oxidation using BA-modified MOF was much slower than that with the pristine MOF. This observation further confirmed that the CEES oxidation indeed occurred in the MOF pores, and a larger surface area/pore volume can accommodate more substrates, enhance diffusion and thus accelerate the photocatalytic reaction.

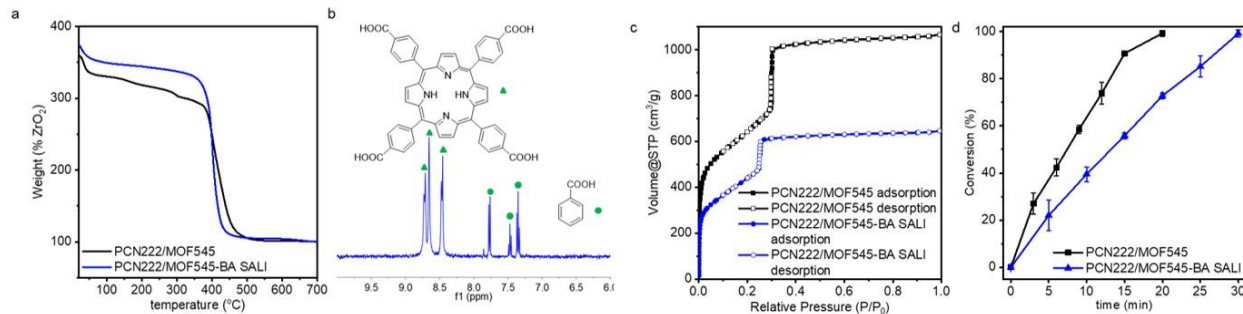


Figure 5. a) TGA curves of PCN-222/MOF-545 and BA-modified PCN-222/MOF-545 (via SALI). b) ¹H NMR spectrum of acid-digested BA-modified PCN-222/MOF545-BA in DMSO-*d*₆ (the sample was digested using D₂SO₄). c) N₂ isotherms at 77 K for PCN-222/MOF-545 and BA-modified PCN-222/MOF-545 (via SALI). d) Kinetic profiles of CEES conversion in the presence of PCN-222/MOF-545 and BA-modified PCN-222/MOF-545 (via SALI) in O₂ under blue LED irradiation (in MeCN). TGA result indicated that 2.6 BA molecules per Zr₆O₈ node were introduced

to PCN-222/MOF-545, and the ^1H NMR spectrum of the digested sample estimated that 3.2 BA molecules per Zr_6O_8 node were introduced.

In summary, the singlet oxygen NIR luminescence experiment, molecular trapping experiment, and the photooxidation of organic sulfide in a photoactive MOF all suggested that the singlet oxygen was mainly generated inside MOF pores. It is unlikely for the generated singlet oxygen to diffuse out of the pores. Therefore, photocatalytic reactions mainly occur inside MOF pores, and their reaction rate is directly affected by the pore size of MOFs. These findings were published in the *Journal of Physical Chemistry C* and *ACS Catalysis* as peer-reviewed research articles (see refs 24 and 28).

Objective 3. Obtain experimental evidence to understand the mechanism of selective photooxidation of organic sulfide, and determine if the selectivity stems from the MOF catalyst.

Zr-porphyrin MOFs with different topologies/pore sizes (**Figure 6**) were studied for their photocatalytic performance (i.e., reaction kinetics and selectivity) for the photooxidation of CEES. The sulfoxide selectivity of CEES oxidation in the presence of different MOFs was summarized in **Table 1**. Regardless of the type of MOFs used, CEES was oxidized exclusively to sulfoxides, i.e., CEESO and ethyl vinyl sulfoxide (EVSO), in MeOH without forming the toxic sulfones. This observation is consistent with previous studies.¹ In contrast, three oxidation products, including CEESO, EVSO, and CEESO₂, were formed in MeCN with a 93-94% sulfoxide selectivity for the tested MOFs. No apparent correlation was found between the MOF structure and the reaction selectivity; instead, the sulfoxide selectivity was primarily dependent on the solvent.

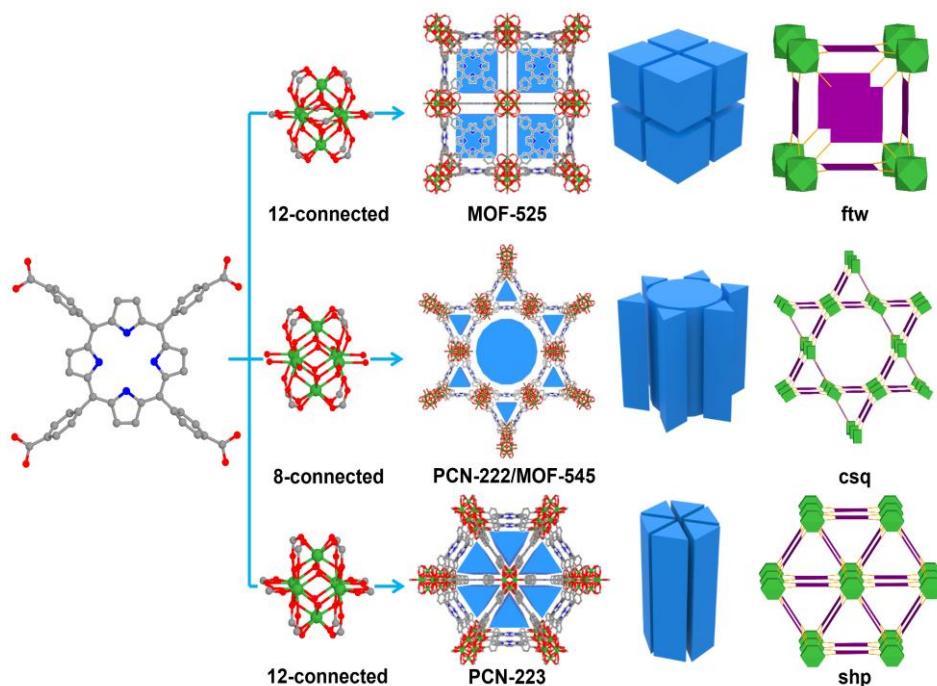


Figure 6. The tetrakis(4-carboxyphenyl)porphyrin (TCPP) linker, zirconium-oxo clusters, and crystal structures as well as topologies of MOF-525, PCN-222/MOF-545, and PCN-223.

Table 1. The surface areas and total pore volumes of studied MOFs, and half-lives and sulfoxide selectivity for CEES oxidation in different solvents.

	BET surface area (m ² /g)	Total pore volume (mL/g)	<i>t</i> _{1/2} (min) in MeCN	Sulfoxide (%) in MeCN	<i>t</i> _{1/2} (min) in MeOH	Sulfoxide (%) in MeOH
MOF-525	2660	1.52	5.4	93	6.2	100
PCN-222/ MOF-545	2200	1.58	7.4	93	9.0	100
PCN-223	1690	0.72	8.6	94	11.7	100

In the presence of a photosensitizer under light irradiation, O₂ can be converted to ROS, including ¹O₂, superoxide radical anion (•O₂[−]) and hydroxyl radical (•OH). To probe the type(s) of ROS generated by the MOFs used in our studies, we conducted electron paramagnetic resonance (EPR) spin-trapping experiments utilizing 2,2,6,6-tetramethylpiperidine (TEMP) as the ¹O₂ trap and 5,5-dimethyl-pyrroline-*N*-oxide (DMPO) as the •O₂[−]/•OH trap. In the experiment, a MOF suspension in 0.1 M trap solution (i.e., TEMP or DMPO) was first purged with O₂ and irradiated under blue LEDs for 10 min. The samples were then passed through a filter, and the filtrates were immediately analyzed on an EPR spectrometer. As shown in **Figure 7a**, a triplet 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) signal was observed on the EPR spectrum when using TEMP as the trap, indicating ¹O₂ was present in the sample. However, no EPR signals were detected when using DMPO as the trap, suggesting that •O₂[−]/•OH was not present in the solution (**Figure 7b**). When we conducted the same EPR spin-trapping experiments without MOFs or light irradiation, no EPR signals were observed, confirming that MOF photosensitization was responsible for ¹O₂ generation. Similarly, minimal CEES oxidation occurred in the absence of light, O₂, or MOF, indicating the photogenerated ¹O₂ by MOFs was responsible for CEES oxidation. The generation of ¹O₂ during CEES photooxidation was further confirmed using a ¹O₂ scavenger, 1,4-diazabicyclo[2.2.2]octane (DABCO).

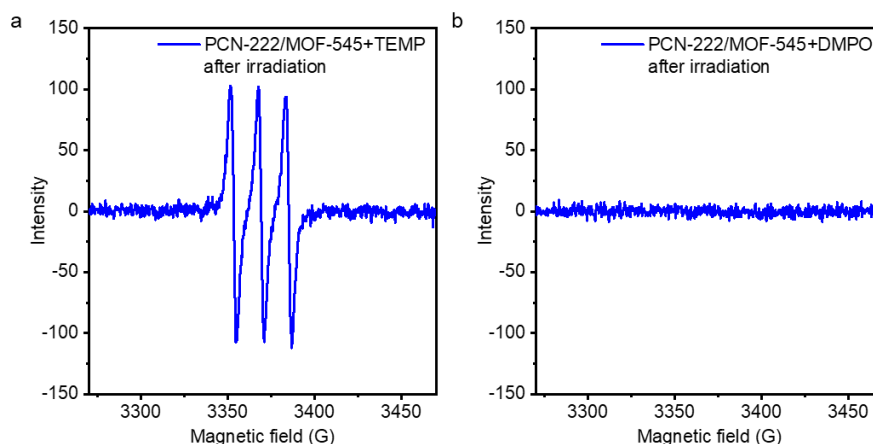
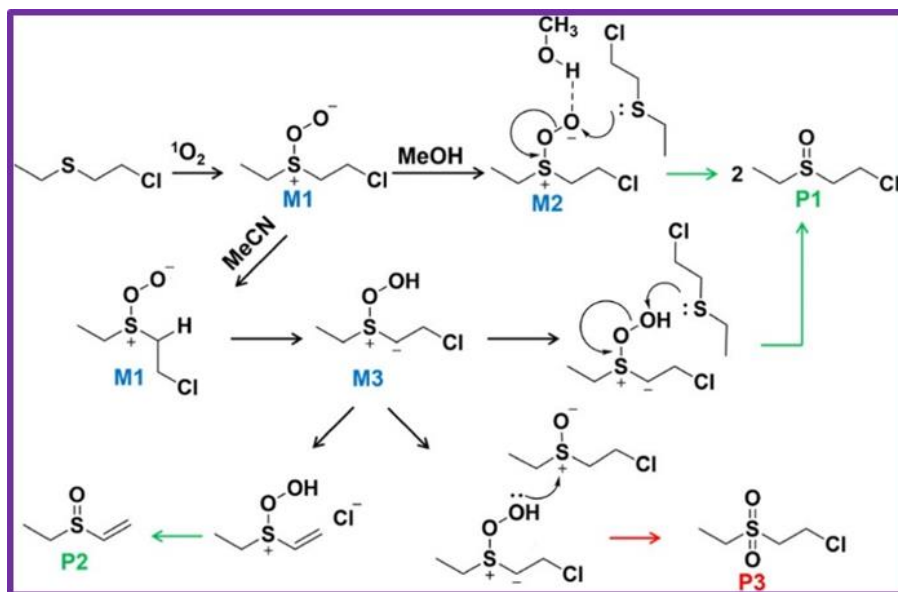


Figure 7. EPR spectra of PCN-222/MOF-545 suspensions in O₂-saturated MeCN in the presence of (a) TEMP (100 mM) and (b) DMPO (100 mM) immediately after irradiation with blue LEDs for 10min.

After confirming the responsible ROS, we next sought to understand the reaction mechanisms of CEES oxidation in different solvents. Based on prior mechanistic hypotheses²⁹⁻³⁰ and our experimental investigations, we summarized the mechanisms for CEES photooxidation, as presented in **Scheme 1**. Essentially, one CEES molecule can react with $^1\text{O}_2$ (generated by MOFs), forming a nucleophilic intermediate of persulfoxide (**M1**). **M1** can be stabilized through hydrogen bonding with protic solvents such as MeOH, affording an electrophilic intermediate (**M2**). Subsequently, electrophilic oxygen transfer occurs from **M2** to a second CEES molecule, producing two CEESO molecules (**P1**). On the other hand, aprotic solvents, such as MeCN, cannot form hydrogen bonding with **M1**, promoting β -H transfer to afford the electrophilic intermediate, **M3**. Afterward, CEESO (**P1**) was formed through the electrophilic oxygen transfer from **M3** to another CEES molecule, and EVSO (**P2**) was produced via dehydrohalogenation of **M3**. In the meantime, nucleophilic oxygen transfer can occur directly from **M3** to the sulfur in CEESO, producing CEESO₂ (**P3**).



Scheme 1. The mechanistic pathways for CEES photooxidation in methanol and acetonitrile

A series of scavenging experiments were employed to probe the intermediate structures in the outlined mechanism in **Scheme 1**. Firstly, trimethyl phosphite ($\text{P}(\text{OMe})_3$) and diphenyl sulfide (Ph_2S) were used as scavengers for the nucleophilic peroxide (**M1**) and electrophilic peroxides (**M2/3**), respectively. When $\text{P}(\text{OMe})_3$ was added to the CEES oxidation reaction with MOF photosensitizers, ^{31}P NMR spectra of the reaction mixture at 30 min suggested that $\text{P}(\text{OMe})_3$ was oxidized to trimethyl phosphate ($\text{PO}(\text{OMe})_3$), confirming the presence of **M1** (**Figure 8a**). Likewise, Ph_2S added to the CEES photooxidation was oxidized to diphenyl sulfoxide (Ph_2SO), indicating the presence of **M2/3** (**Figure 8b**). The scavenging experiments were conducted in MeOH and MeCN, which confirmed the reaction intermediates for the photooxidation of CEES in both solvents.

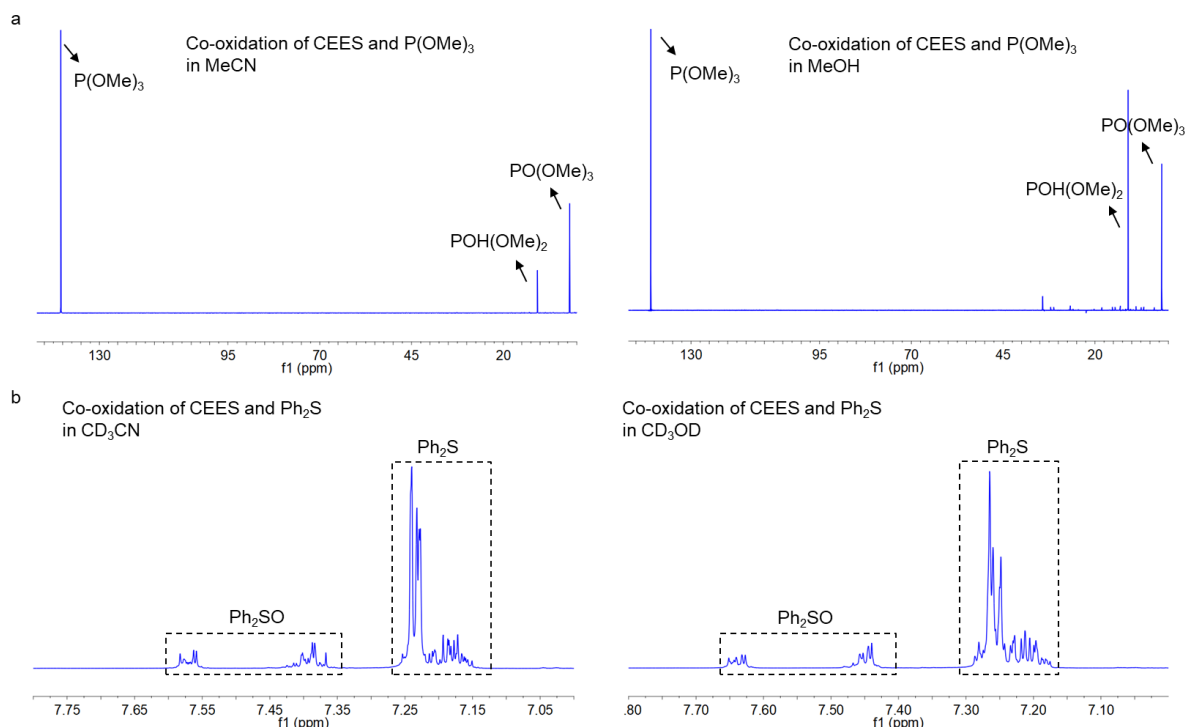


Figure 8. a) ^{31}P NMR spectra of the reaction mixture for CEES photooxidation in the presence of $\text{P}(\text{OMe})_3$ (left: in MeCN, right: in MeOH). b) ^1H NMR spectra of the reaction mixture for CEES photooxidation in the presence of Ph_2S (left: in CD_3CN , right: in CD_3OD). Reaction time: 30 min.

In summary, the mechanism of selective photooxidation of organic sulfide was investigated and established through a series of EPR and scavenger experiments. Systematic studies revealed that the selectivity of sulfide oxidation does not stem from the MOF catalyst but mainly depends on the type of solvent used in the reaction (i.e., protic vs. aprotic). Inspired by this discovery, we developed a series of MOF composite materials that exhibited remarkable sulfoxide selectivity under solvent-free conditions (discussed under **Objective 6**). These findings were published in *ACS Catalysis* as a peer-reviewed research article (see ref 28).

Objective 4. Confirm the mechanism of acid-catalyzed hydrolysis of organophosphates by isolating the intermediates.

Computational simulations suggested that during the MOF-catalyzed hydrolysis of nerve agents (or simulants), the organophosphorus substrate first forms hydrogen bonds with the node (Zr_6)-ligated water (**Figure 9a**).³¹ The substrate then binds to the Zr site by displacing a water molecule, followed by a nucleophilic attack of the hydroxyl on the organophosphorus substrate.³¹⁻³² Subsequently, the leaving group ($-\text{X}$) is eliminated from the organophosphorus substrate, and the hydrolyzed product dissociates from the Zr_6 active sites. It is worth noting that the proposed reaction mechanism for phosphotriesterase (PTE) is very similar to that of MOFs, except that the enzyme-based catalysis includes an additional step — deprotonation of the proximal conjugate acid

($\text{H}^+[\text{His}]$) and regeneration of bridging Zn–O–Zn sites (**Figure 9b**). It was proposed that the MOF active sites were regenerated upon product dissociation under basic conditions.

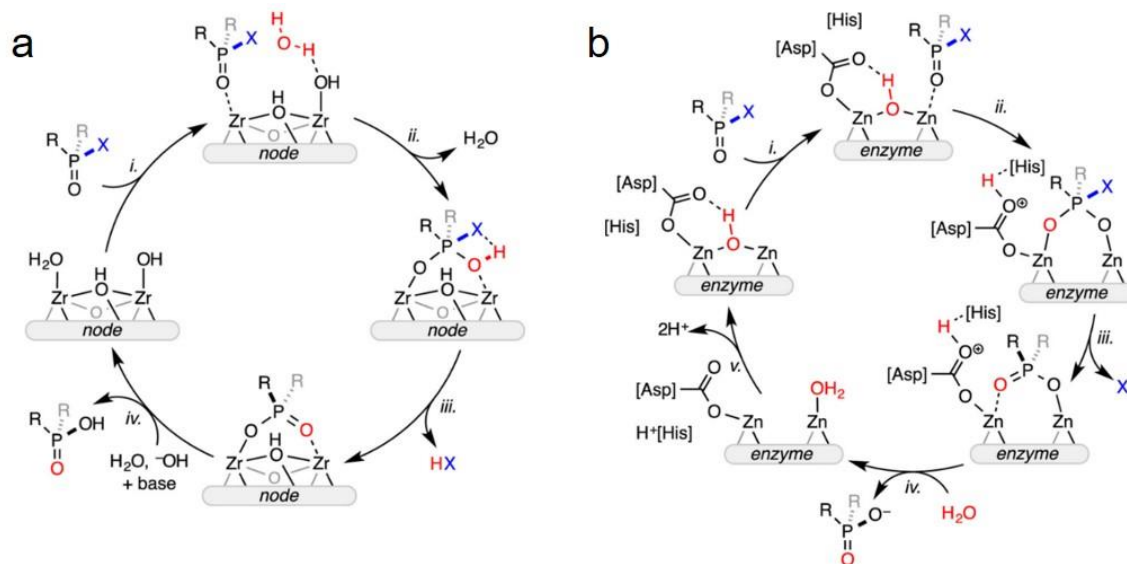


Figure 9. Proposed mechanisms for the hydrolysis of organophosphorus substrates by (a) Zr-MOFs and (b) the enzyme phosphotriesterase (PTE): (i) coordination of the organophosphorus substrate to Lewis acidic active site; (ii) nucleophilic attack of the hydroxyl on the organophosphorus substrate; (iii) elimination of the leaving group from the organophosphorus substrate; (iv) removal of the hydrolyzed product from the active site; (v) deprotonation of the proximal conjugate acid and regeneration of bridging Zn–O–Zn moiety (PTE only). [Asp] = aspartic acid; [His] = histidine; $-\text{OH}/\text{H}_2\text{O}$ involved in the nucleophilic attack of organophosphorus molecule is highlighted in red; leaving group on the organophosphorus molecule highlighted in blue.³¹

Due to the short lifetime of the intermediates in the reaction pathways, we were unable to isolate and detect the reaction intermediates. However, a series of experiments were conducted to confirm that the hydrolysis of organophosphorus undergoes a similar mechanism as that in PTE. More importantly, new bio-inspired materials were designed based on the above mechanistic information. Several Zr-MOFs displayed high activity for the hydrolysis of different types of nerve agents/simulants with half-lives of only a few minutes or even seconds.³¹ Among them, MOF-808 containing 6-connected $\text{Zr}_6\text{O}_4(\text{OH})_4$ clusters and benzene tricarboxylate linkers achieved almost instantaneous hydrolysis of nerve agent GD and VX ($t_{1/2} < 1 \text{ min}$)³³ and a simulant dimethyl-4-nitrophenyl phosphate (DMNP, $t_{1/2} < 30 \text{ s}$) in aqueous alkaline solutions.³⁴ It is worth noting that most studies investigated the MOF-catalyzed nerve agent/simulant degradation in bulk water buffered by *N*-ethylmorpholine (NEM). The NEM serves as an essential base to regulate the pH and regenerate the active Zr sites in MOFs during catalysis.^{31,35-36} While this approach holds promise for the catalytic detoxification of nerve agent stockpiles, it is not ideal for use in personal protective equipment given the high volatility of NEM and the large volume of water required in these reactions.

In nature, the PTE enzyme from soil bacteria is highly efficient in catalyzing the hydrolysis of organophosphorus compounds. The active site of PTE contains a hydroxide-

bridged binuclear Zn(II) center ligated to residues of histidine, aspartate, and lysine (**Figure 10a**). The binuclear metal centers facilitated the activation of the organophosphate for nucleophilic attack; the ligated aspartate carboxylate and histidine imidazole are also crucial in the enzymatic hydrolysis mechanism.³⁷ Specifically, these ligated groups serve as proximate bases in the catalytic cycle, promoting proton transfer and the regeneration of the active binuclear Zn centers of PTE. In essence, the binuclear Zn center and the surrounding ligands work collaboratively, enabling the extraordinary catalytic activities of PTE. The high cost and poor stability of PTE, however, have limited their practical application in nerve agent detoxification. On the other hand, Zr-MOFs are very robust solid-state materials that retain their structures and activities under various conditions (e.g., different pH, temperature and humidity). In Zr-MOFs, the Zr₆ cluster resembles the structure of the Zn₂ center in PTE with a Zn^{II}-OH-Zn^{II} active site and is considered responsible for the MOF's catalytic activity in the hydrolysis of phosphoester bonds. By incorporating imidazole derivatives (which mimic the histidine residue in PTE) into Zr-MOFs, we can create MOF composites that are structurally reminiscent of the PTE active sites as well as their surrounding ligands (**Figure 10b**). This bioinspired design will likely lead to new catalysts with extraordinary activities for nerve agent detoxifications.

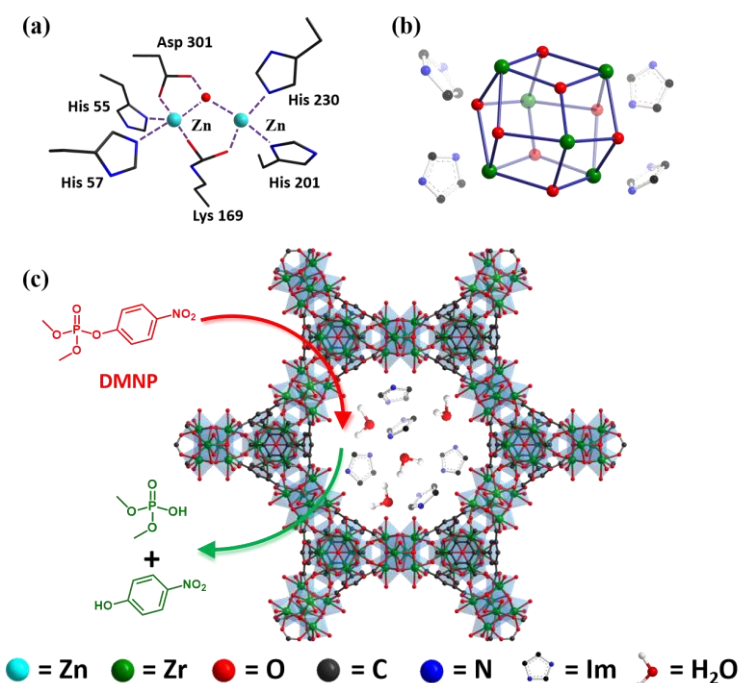


Figure 10. (a) Binuclear metal active site of phosphotriesterase (PTE). (b) the PTE-mimicking active sites in Im@MOF-808, containing Lewis acidic sites and imidazole bases. (c) Schematic illustration of the catalytic hydrolysis of DMNP by Im@MOF-808.

To test our hypothesis, imidazole (Im) and 2-Methylimidazole (MeIm) were encapsulated into the pores of MOF-808, affording two MOF composites Im@MOF-808 and MeIm@MOF-808, respectively. These MOF composite catalysts displayed high catalytic activity toward the hydrolysis of a nerve agent simulant, DMNP, in an unbuffered

aqueous solution (**Figure 10c**). To the best of our knowledge, Im@MOF-808 exhibited the highest catalytic activity among all MOF-based materials toward DMNP hydrolysis in pure water (unbuffered) and displayed a half-life of shorter than 30 s (**Figure 11a**). Notably, Im@MOF-808 can also rapidly hydrolyze DMNP in the solid phase under high humidity conditions (without bulk water or external bases; **Figure 11b**), and this advancement serves as a key step toward the practical implementation of MOF-based CWA detoxification catalysts.

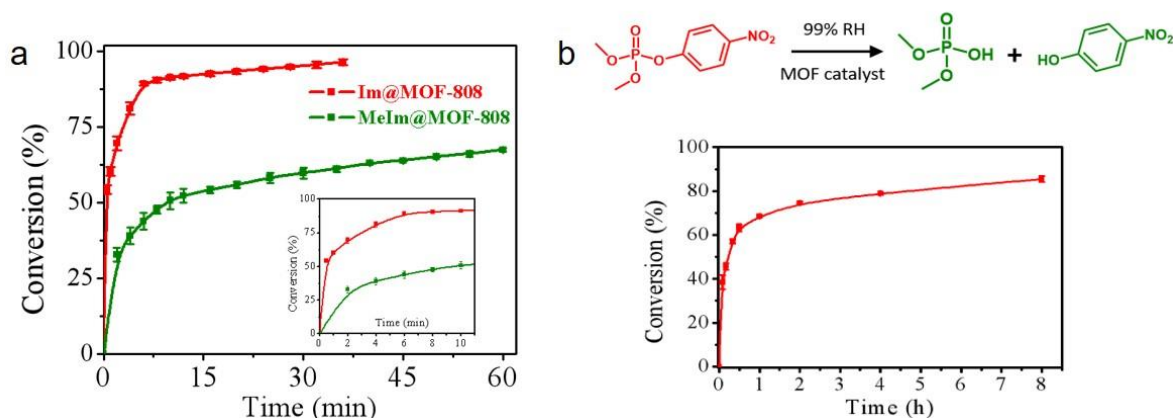


Figure 11. a) Hydrolysis profiles of DMNP catalyzed by Im@MOF-808 and Melm@MOF-808 with 6 mol% catalyst loading (relative to dimethyl-4-nitrophenyl phosphate, DMNP) in pure water (inset figure shows the magnified hydrolysis during the first 10 min).

In summary, the catalytic mechanism of organophosphate hydrolysis was probed by introducing a histidine mimic (i.e., imidazole) into a Zr-MOF containing Lewis acid catalytic sites (MOF-808). The composite exhibited enhanced catalytic efficiency toward the hydrolysis of organophosphates without needing an external buffer or bulk water. These experiments confirmed that the hydrolysis of organophosphates in MOFs undergoes similar mechanisms as those in PTE. These findings were published in *ACS Catalysis* as a peer-reviewed research article (see ref 38).

Objective 5. Establish the structure-property relationship for catalytic MOFs by evaluating the effect of pore size, pore shape, functional group, metal node, and particle size.

We selected three Zr-porphyrin MOFs, MOF-525, PCN-222/MOF-545, and PCN-223, to study how metal node connectivity, pore size/shape, and MOF topology affect their photocatalytic performance for CEES oxidation. As shown in **Figure 6**, the three MOFs are all constructed from Zr₆-oxo clusters and TCPP linkers, featuring different topologies and pore shapes/sizes. MOF-525 has an **ftw** topology and cubic-shaped pores with TCPP linkers on the six faces and the 12-connected Zr₆O₈ clusters on the eight corners. Assembled in a **csq** topology, PCN-222/MOF-545 has a Kagome-like structure with a one-dimensional (1-D) channel surrounded by six triangular channels that are interconnected by TCPP linkers and 8-connected Zr₆O₈ clusters. PCN-223 crystallizes in an **shp** topology featuring six 1-D triangular channels stacked into a hexagonal prism

shape. It is important to note that the Zr_6O_8 clusters in MOF-525 and PCN-223 are both 12-connected but with different site symmetry, thereby giving rise to different framework topologies.³⁹⁻⁴⁰

The structures and phase purity of all three MOFs were validated using PXRD. N_2 isotherm measurements at 77 K probed the MOFs' surface areas and pore sizes, confirming their full activation. As shown in **Figure 12a**, MOF-525 and PCN-223 exhibited type I isotherms indicating their microporous structures with pore diameters estimated to be 23 Å and 13 Å, respectively. The type IV isotherm of PCN-222/MOF-545 suggested its mesoporous structure, and its pore diameters were calculated to be 18 Å (triangular channels) and 36 Å (hexagonal channels) (**Figure 12b**). The Brunauer–Emmett–Teller (BET) surface areas and pore volumes of the MOFs analyzed based on their N_2 isotherms are similar to previously reported,^{3,39-40} as summarized in **Table 1**. In addition, the shapes of the MOF crystals observed under an SEM were consistent with their crystal symmetry – MOF-525 were cubic crystals, whereas PCN-222/MOF-545 and PCN-223 were rod-shaped crystals (**Figure 13**). The SEM images also showed that the MOFs featured a particle size of 1-3 μm . Finally, the absorption spectra of the MOF suspensions were collected on a UV-vis spectrometer equipped with an integrating sphere, and the three MOFs exhibited similar absorption bands and intensities (**Figure 12c**). The Soret band and Q-bands of the MOFs were slightly redshifted and broadened compared to the free TCPP linker, which can be attributed to LMCT.⁴⁻⁵

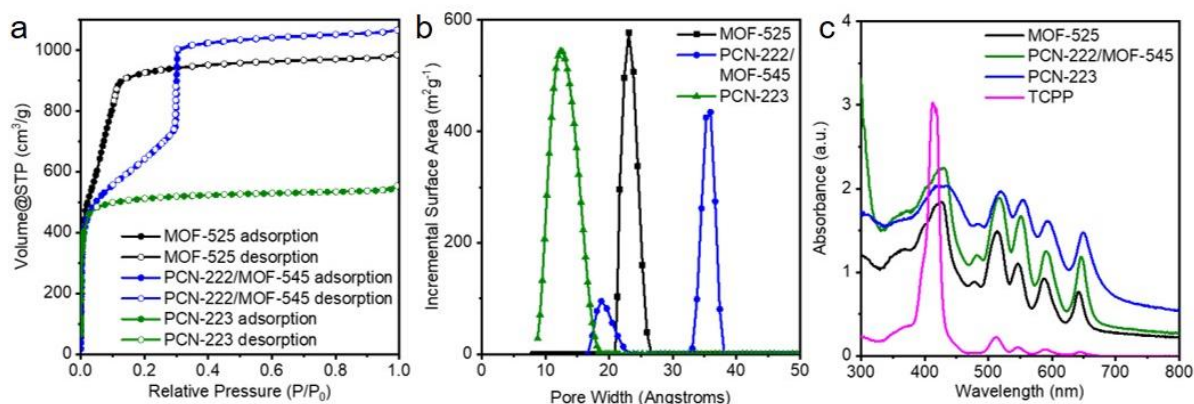


Figure 12. a) N_2 adsorption-desorption isotherms at 77 K and (b) DFT pore size distributions (PSD) calculated based on the N_2 adsorption data for MOF-525 (in black), PCN-222/MOF-545 (in blue), and PCN-223 (in green). (c) UV-Vis spectra of TCPP solution and MOF suspensions in MeCN measured using a UV-vis spectrometer equipped with an integrating sphere.

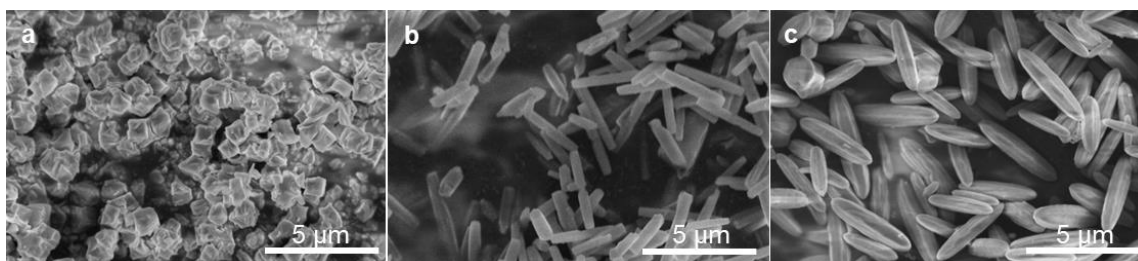


Figure 13. SEM images of (a) MOF-525, (b) PCN-222/MOF-545 and (c) PCN-223.

We first carried out the photooxidation of CEES in O₂ under blue LED irradiations utilizing the synthesized MOFs as photosensitizers. All the reactions were performed in the presence of 1 mol% photosensitizer loading (based on the porphyrin units in MOFs) and in two different solvents, including a protic solvent MeOH and an aprotic solvent MeCN. CEES conversion was monitored using GC-MS, and the reaction profiles and half-lives ($t_{1/2}$) for three MOFs are presented in **Figure 14** and **Table 1**. In both MeOH and MeCN, the reaction half-lives of three MOFs exhibited the trend of MOF-525 < PCN-222/MOF-545 < PCN-223. CEES oxidation rates for three MOFs exhibited a good correlation with the MOFs' BET surface area and pore volume. This correlation suggests that the CEES photooxidation occurs inside the MOF pores, consistent with observations in our previous work.²⁴ Using BA-modified MOFs (details discussed under **Objective 2**), we confirmed that with the same amount of catalytic sites (porphyrins), MOFs with larger surface areas/pore volumes could accommodate more reaction substrate (CEES) and enhance the diffusion of substrates/products, leading to faster CEES oxidation. We also studied PCN-222/MOF-545 of different particle sizes for CEES oxidation, and the reaction rate did not vary significantly.

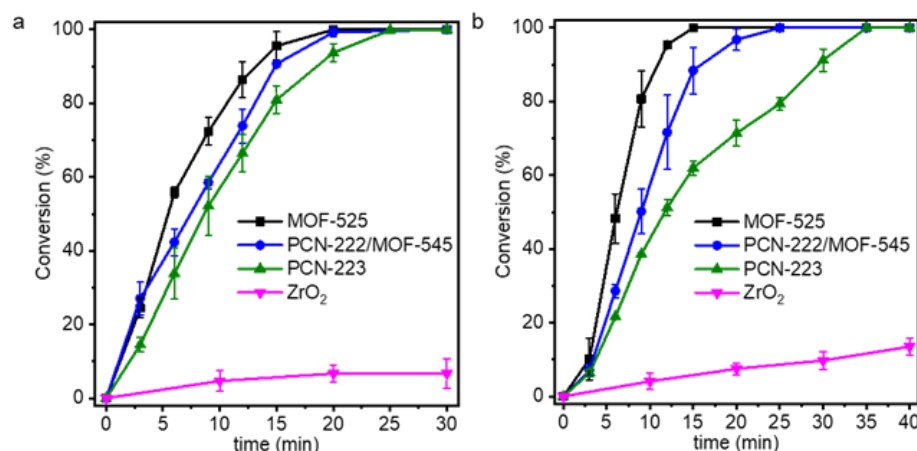


Figure 14. Kinetic profile of CEES conversion in the presence of MOF-525, PCN-222/MOF-545, PCN-223, and ZrO₂ in O₂ under blue LED irradiation in (a) MeCN and (b) MeOH (1 mol% MOFs and 2 mol% ZrO₂ were used for all experiments).

In addition, we investigated how metal nodes and metal-ligand combinations of MOFs affect their efficiency and selectivity for the photooxidation of CEES. For this purpose, porphyrin MOFs (PMOFs) with different metal clusters, including Al³⁺, Ti³⁺, In³⁺, and Y³⁺, were synthesized, and their crystal structures and metal nodes are shown in **Figure 15**. These MOFs were studied for the photooxidation of CEES using a 0.5 mol% catalyst loading under blue LED irradiations. The reaction profiles, selectivity, and half-lives of CEES oxidation in the presence of different MOFs are shown in **Figure 16**. In general, the reactions conducted in MeOH had higher selectivity and faster rates compared to those in MeCN, consistent with previous publications. The half-lives of the screened MOFs exhibited the following trend In-PMOF < DGIST-1 < NUPF-2Y < Al-PMOF. The half-lives ranged from 2.27 min (In-PMOF) to 4.87 min (Al-PMOF), while DIGIST-1 and NUPF-2Y showed similar reaction rates to In-PMOF, as shown in **Figure 16d**.

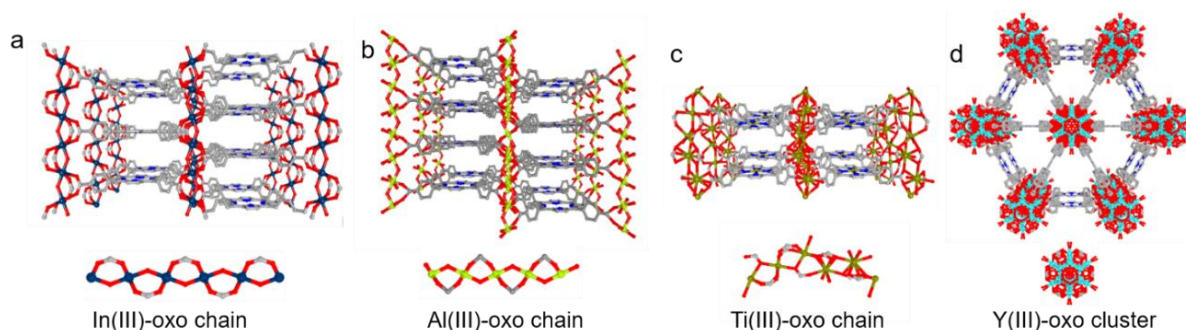


Figure 15. Porphyrin MOFs with varying metal chains/clusters.

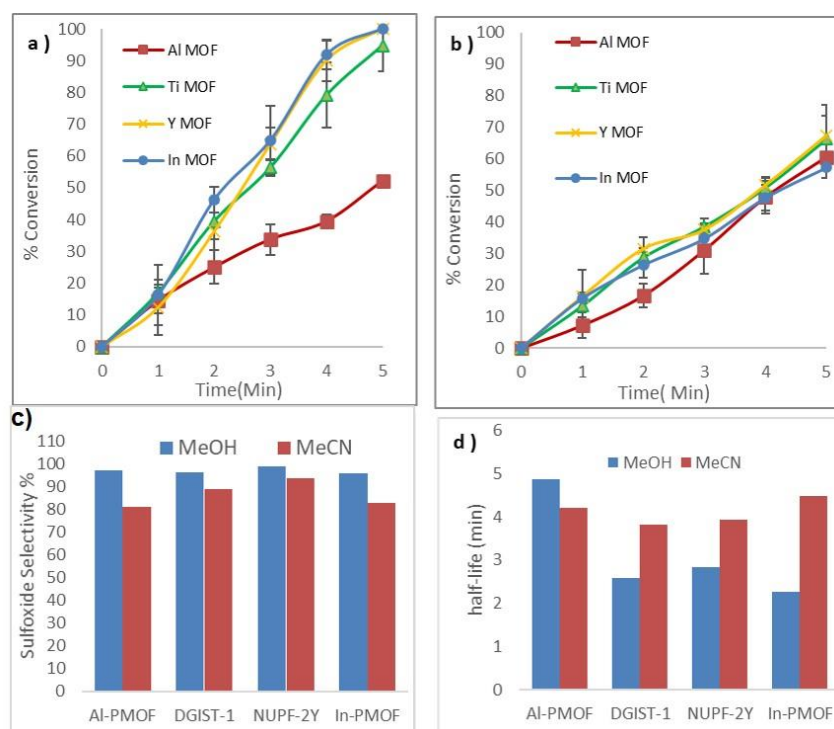


Figure 16. Kinetic profiles of CEES photooxidation conversion in the presence of Al-PMOF, DGIST-1, In-PMOF-bs-th, and NUPF-2Y in (a) MeOH and (b) MeCN. (c) sulfoxide selectivity of and (d) half-lives.

The catalysis results in **Figure 16** showed that porphyrin MOFs with heavy metal nodes, such as In and Y, had faster reaction rates for CEES oxidation, indicating enhanced $^1\text{O}_2$ generation in these MOFs. Similar observations were previously reported for metalated porphyrins.⁴¹⁻⁴² It was determined that the *d*-orbitals of heavier metals had better overlap with porphyrin MOFs, enhancing intersystem crossing (ISC) and increasing $^1\text{O}_2$ generation. This would explain the trend observed in our study, in which Al-PMOF showed the slowest reaction rate due to its light metal node. Another factor to consider is the topology of the PMOFs: Al-PMOF, DGIST-1, and In-PMOF have an **ftw** topology, while NUPF-2Y has an **shp** topology. NUPF-2Y structure is denser and possesses three times more porphyrin molecules per unit volume than the other structures.⁴³ As shown in Figure 16, the activity of NUPF-2Y lies between DGIST-1 and Al-PMOF, but its half-life is very similar to those of In-PMOF and DGIST-1. In terms of sulfoxide selectivity, NUPF-

2Y had the highest selectivity of 99%, and In-PMOF exhibited the lowest at 96%. The reaction profiles in MeCN were very similar to those in MeOH, with half-lives ranging from 3.83-4.49 min (**Figure 16bd**). Selectivity of all PMOFs decreased in MeCN, but NUPF-2Y maintained a high selectivity of 94%, followed by DGIST-1(89%), In-PMOF (83%), and Al-PMOF (81%) (**Figure 16c**).

Furthermore, the porphyrin linker of PCN-222/MOF-545 was functionalized with various metal ions to study their effect on CEES oxidation. Metallating porphyrins was reported to affect the singlet oxygen quantum yield. For example, the singlet oxygen quantum yield of tetraphenylporphyrin (TPP) was reported as 0.55, but metallating the same porphyrin with copper resulted in a low quantum yield of 0.03.⁴⁴ Other studies have suggested Sn TCPP has many properties that make it a promising photosensitizer.⁴⁵ Therefore, we sought to synthesize and study four metalloporphyrin MOFs for their efficiency and selectivity for CEES oxidation. Instead of free base TCPP, the porphyrin linkers in these MOFs were metallated with tin (Sn), indium (In), manganese (Mn), and copper (Cu). The MOF structures were confirmed using PXRD, and the metallation of the porphyrin linkers was confirmed using UV-vis absorption spectra (**Figure 17ab**).

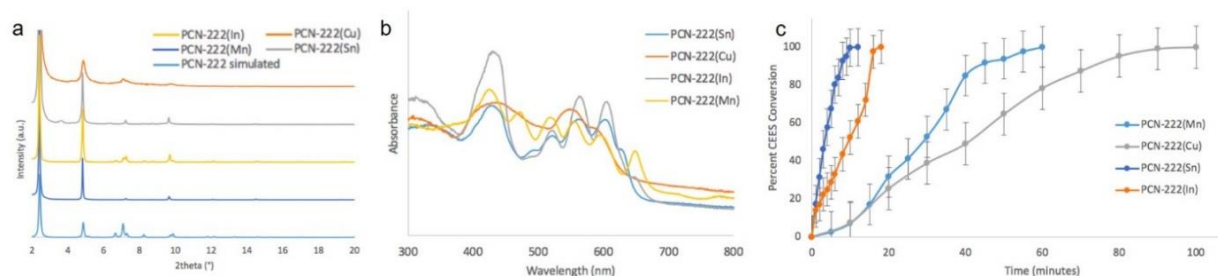


Figure 17. a) PXRD of PCN-222/MOF-545 containing linkers functionalized with various metal ions. b) The UV-vis absorption spectra of PCN-222/MOF-545(M) suspensions obtained using an integrating sphere accessory. c) the photooxidation conversion profile for CEES in the presence of PCN-222/MOF-545 containing various metallated porphyrin linkers.

Photocatalytic runs were performed for each of the porphyrins and porphyrinic MOFs. **Figure 17c** shows the CEES conversion over time using each MOF catalyst in MeOH. From these data, we calculated the half-lives of CEES to be 3.4, 9.5, 28.8, and 40.3 min for PCN-222/MOF-545(M) (M = Sn, In, Mn, Cu), respectively. Remarkably, PCN-222/MOF-545(Sn) and PCN-222/MOF-545(In) exhibited significantly shorter CEES conversion half-lives compared to the non-metallated porphyrin MOF, which suggests that doping the porphyrin ligands with these metals can increase the efficiency of the CEES oxidation.¹ The faster CEES oxidation can be attributed to the higher rate of ISC in PCN-222/MOF-545(Sn) and PCN-222/MOF-545(In) compared to PCN-222/MOF-545(FB). ISC is a spin-forbidden, non-radiative transition from an excited singlet state to an excited triplet state. Higher rates of ISC are associated with enhanced ¹O₂ generation and, thus, faster rates of CEES oxidation. Our catalysis results also suggested that MOFs with In- and Sn-porphyrin linkers had faster rates of ISC than those with Mn- and Cu-porphyrin linkers, which is consistent with previously reported heavy metal effects.⁴¹⁻⁴²

In summary, MOFs with higher surface areas/pore volumes can increase photocatalytic activity for CEES degradation, but the selectivity was primarily dependent

on the solvent. The pore size/shape or particle size of the MOFs, on the other hand, had minimal effect on the reaction rate or selectivity of CEES oxidation. Both functional groups and metal nodes of MOFs showed influences on the reaction rate, which can be attributed to the enhanced intersystem crossing and increasing singlet oxygen generation in MOFs with heavy metals. Part of the results was published as a peer-review journal article in *ACS Catalysis* (see ref. 28). Some of the results are unpublished, and two manuscripts are in preparation for submission to peer-reviewed journals.

Objective 6. Design better-performing multifunctional materials based on the structure-property relationship and evaluate the performance of the new materials.

Based on the structure-property relationship established under **Objective 1-5**, we have designed and developed better-performing MOF catalysts for the degradation of organophosphates (nerve agent simulant) and organic sulfide (mustard gas simulant), as discussed below.

Mechanism-Guided Design of MOF Composites for Solvent-Free Sulfide Oxidation. The established mechanism in **Scheme 1** revealed that introducing hydrogen-bond donors can stabilize the persulfoxide intermediate (**M1**), leading to improved sulfoxide selectivity. Following this important discovery, we rationally designed a series of MOF/textile composites containing various hydrogen-bond donor additives to achieve selective CEES oxidation under solvent-free conditions. We selected MOF-525 to prepare the composites, given its higher CEES degradation rate in organic solvents compared to the other two MOFs. The MOF/additive/textile composites were prepared using a facile dip-coating method. In brief, a 2 cm × 2 cm cloth was submerged in a suspension mixture of 12 mg MOF-525 and varying amounts of additive in MeOH before drying at 60 °C (in a convection oven) for 0.5 hours to remove the organic solvent. This process was repeated three times until the cotton adsorbed all the suspension mixture and completely dried in the oven. The textile composite was then cut into four 1 cm × 1 cm pieces for further characterizations and photocatalytic studies. Several hydrogen-bond donor additives, including benzoic acid (BA), 1,3,5-benzene tricarboxylic acid (BTC), 4-fluorobenzoic acid (FBA), 4-methylbenzoic acid (MeBA), and citric acid (CA), were used in the fabrication of different composites. SEM images and energy-dispersive X-ray spectroscopy (EDS) elemental mapping of the MOF/BA/textile composites indicated that the MOF particles uniformly adhered to the surface of the cotton fibers (**Figures 18a-c**). In addition, PXRD patterns of the MOF/additive/textile composites demonstrated the well-maintained crystallinity of MOF-525 and confirmed the presence of additive molecules (**Figure 18d**). ¹H NMR spectra of the digested composites were used to determine the additive/MOF ratios in the samples.

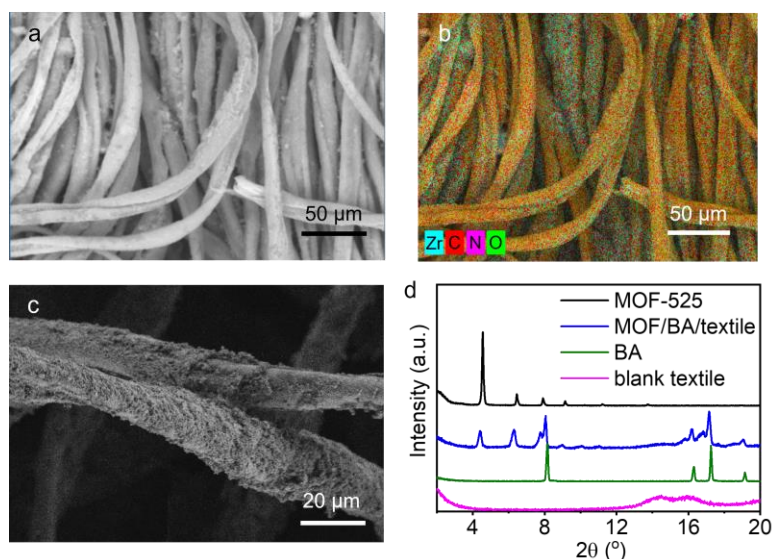


Figure 18. a) Scanning electron microscope (SEM) image and b) energy-dispersive X-ray spectroscopy (EDS) elemental mapping of Zr, C, N, O on the MOF/BA/textile composite. c) SEM image of individual fibers in the MOF/BA/textile composite. (d) Powder X-ray diffraction patterns of MOF-525 (in black), MOF/BA/textile (in blue), benzoic acid (in green), and blank textile (in magenta).

The MOF/textile composites with various hydrogen-bond donor additives were then studied for their capability of degrading CEES under solvent-free conditions. In the experimental setup, 1 × 1 cm MOF/additive/textile (3 mol% porphyrin units relative to CEES) was placed in a quartz tube attached to a balloon filled with O₂ or air, which was then irradiated with blue LEDs for different periods of time. After irradiation, an organic solvent (CH₂Cl₂ or CDCl₃) was added to extract the reaction mixture from the textile composites. The extracted samples were then analyzed using GC-MS and ¹H NMR to determine the conversion and selectivity of the CEES oxidation. Remarkably, compared to the MOF powders, the rationally designed MOF/textile composites with various additives all exhibited significantly higher selectivity toward the sulfoxide (the less toxic product) under solvent-free conditions (**Figure 19**).

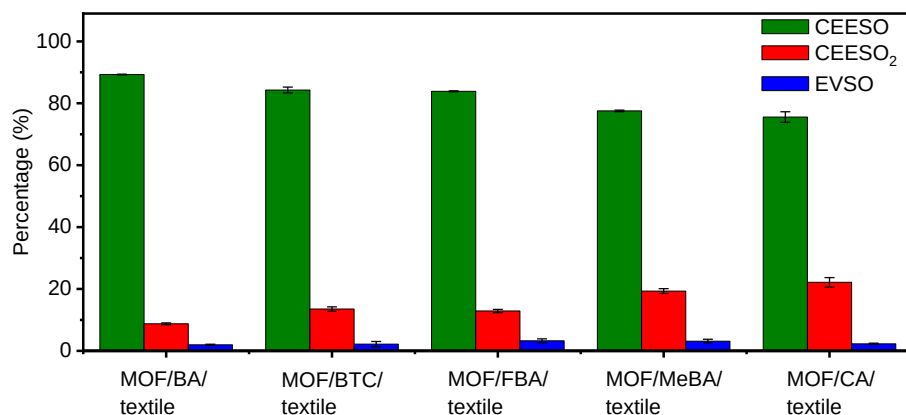


Figure 19. Percentages of CEESO, CEESO₂, and EVSO produced from CEES photooxidation (at 100% conversion) in the presence of MOF-525/additive/textile composites containing various additives in O₂ under blue LED irradiations.

While MOF-525 powders only had a sulfoxide selectivity of 52-58%, the reactions catalyzed by various MOF/additive/textile composites showed a selectivity of 75-91% in O₂ and 69-92% in air, respectively (**Figure 20ab**). In particular, the best-performing MOF/BA/textile composite exhibited a sulfoxide selectivity of 92% in air. Among our tested materials, MOF/BA/textile also showed the fastest CEES degradation in both O₂ and air, featuring reaction half-lives ($t_{1/2}$) of 4.4 min in O₂ and 9.9 min in air, respectively (**Figure 20cd**). It is also worth noting that MOF/textile composites with additives are significantly faster in degrading CEES than the MOF powders or MOF/textile without the additives, as shown in **Figure 20cd**. These results demonstrated that we rationally designed better-performing catalysts for the selective photooxidation of CEES through systematic and mechanistic studies.

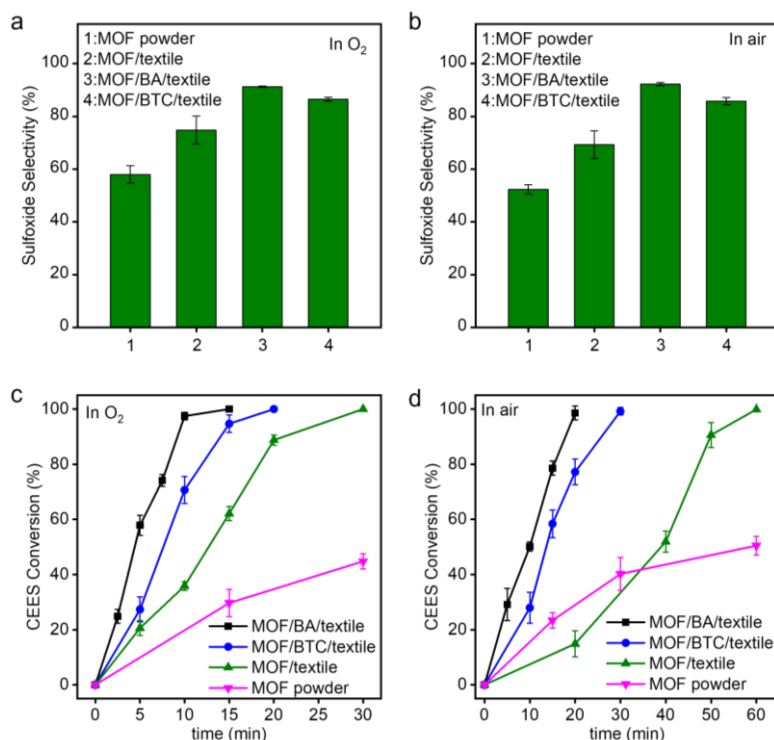


Figure 20. Sulfoxide selectivity for solvent-free photooxidation of CEES in the presence of MOF powder, MOF/textile, MOF/BA/textile, and MOF/BTC/textile in (a) O₂ and (b) air atmosphere, and their kinetic profiles of CEES conversion in (c) O₂ and (d) air atmosphere. The sulfoxide selectivity for all materials was determined when CEES reached 100% conversion.

The Practicality of the MOF/BA/textile Composite. To further demonstrate the practicality of the designed materials, we selected the best-performing composite, MOF/BA/textile, for solvent-free CEES degradation in air under simulated sunlight (**Figure 21a**). With a 3 mol% catalyst loading, all of the added CEES was degraded within 30 min ($t_{1/2}$ = 17.6 min) while maintaining a sulfoxide selectivity of 95% (**Figure 21bc**). In contrast, the CEES oxidation catalyzed by MOF-525 powders under the same condition only reached a CEES conversion of 13% after 30 min, with a sulfoxide selectivity of 70% for the final products. To confirm that both the MOF and the additive (BA) are essential for the highly efficient and selective CEES oxidation, we also tested textile composites without the MOF or BA. As shown in **Figure 21b**, no CEES degradation was observed

after 30 min for the blank textile (without MOF and BA) and the textile modified with only BA (i.e., BA/textile). Since the textile can provide some hydrogen bonding interactions (through hydroxyl groups in cotton cellulose) with the persulfoxide intermediates, the textile composite containing only the MOF but no BA, namely MOF/textile, exhibited slightly higher selectivity than the MOF powders (75% vs. 70%). Nevertheless, due to the additional hydrogen-bond donors that BA provided, the CEES photooxidation in the presence of MOF/BA/textile was much faster and more selective than that catalyzed by MOF/textile (**Figure 21b**). Through these experiments, we demonstrated that, with the rationally designed MOF/BA/textile composite, solvent-free photooxidation of CEES could be achieved with high efficiency and selectivity utilizing sunlight and air under ambient temperature.

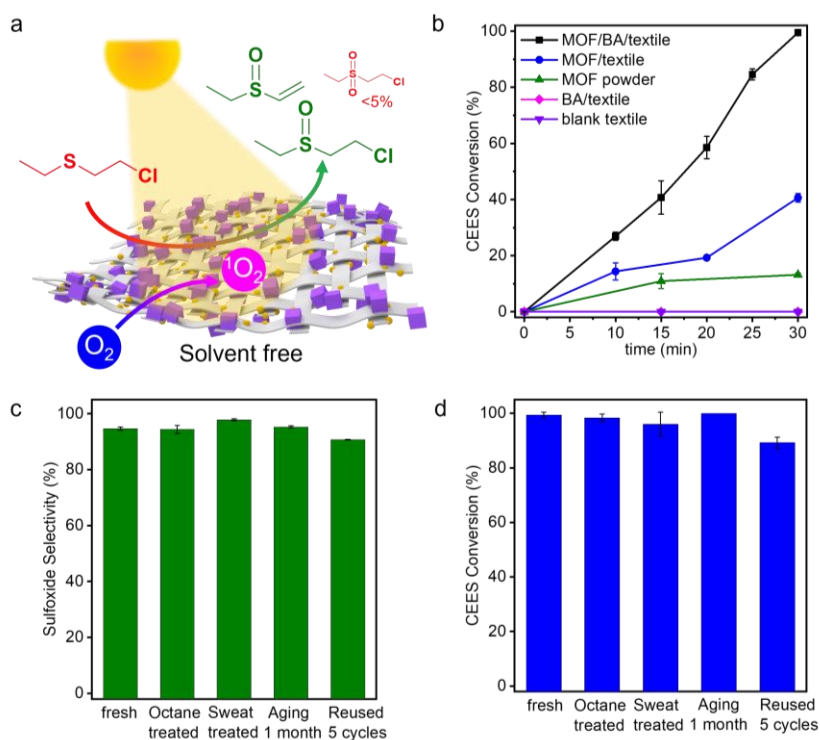


Figure 21. (a) Demonstration of selective photooxidation of CEES in the presence of MOF/additive/textile under solvent-free conditions utilizing sunlight and air. (b) Kinetic profiles of CEES conversion in the presence of MOF/BA/textile, MOF/textile, MOF powder, BA/textile, and blank textile under solvent-free conditions utilizing simulated sunlight and air. (c) The sulfoxide selectivity and (d) catalytic efficiency (reaction time: 30 min) of MOF/BA/textile after stability and reusability tests. The sulfoxide selectivity for all materials was determined when CEES reached 100% conversion.

We then investigated the long-term stability and practicality of MOF/BA/textile by storing the composites under 50% RH and ambient temperature for one month. As presented in **Figure 21cd**, the composite aged for one month fully converted CEES within 30 min while maintaining a sulfoxide selectivity of 95% (with a 3 mol% porphyrin loading). The PXRD of the aged composites also indicated that the MOF crystallinity was retained after one month. In addition, MOF/BA/textile exhibited excellent reusability and resistance to environmental contaminants. In the fifth reuse cycle, the composites still converted

90% of the CEES with a 90% sulfoxide selectivity after 30 min (**Figures 21cd**). After octane or artificial sweat treatment, the MOF/BA/textile composite achieved a 96-98% CEES conversion after 30 min with a 94-98% sulfoxide selectivity (**Figure 21cd**). Interestingly, the sweat-treated composites showed a sulfoxide selectivity of 98%, which is higher than that of the fresh composite under the same condition (95%). This increase in selectivity could be attributed to the additional hydrogen-bond donors (i.e., water) in the artificial sweat, which further stabilized the persulfoxide intermediate during the photooxidation of CEES. Furthermore, PXRD patterns and SEM images of MOF/BA/textile after catalysis also confirmed the excellent stability of the composite. It is important to note that the extraordinary performance of MOF/BA/textile for CEES photooxidation under near-practical conditions (i.e., utilizing sunlight and air without organic solvents) is comparable with previously reported materials that required organic solvents, pure oxygen, and LED irradiations.

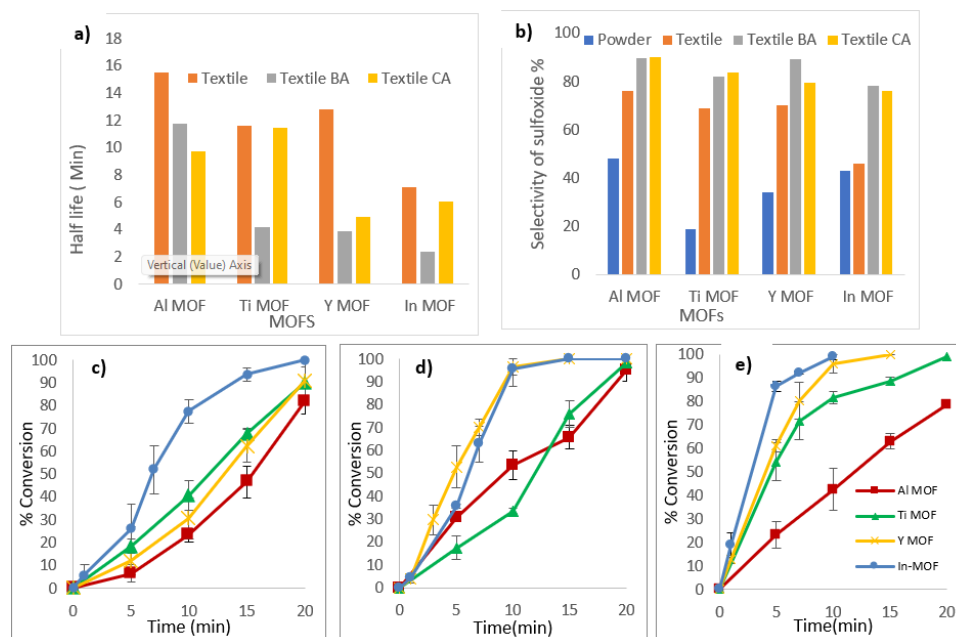


Figure 22. (a) Half-lives, and (b) sulfoxide selectivity of solvent-free CEES oxidation in the presence of MOF powders, MOF/textile, MOF/BA/textile, and MOF/CA/textile. Kinetic profiles of CEES conversion in the presence of (c) PMOF/textile, (d) MOF/CA/textile, and (e) MOF/BA/textile.

Porphyrim MOFs with Different Metal Nodes for Enhanced Sulfide Oxidation. In addition to Zr-porphyrin MOFs, we also studied porphyrin MOFs with other metals for CEES degradation under solvent-free conditions; results are summarized in **Figure 22a-b**. A general trend observed in all the textile composites was that In-MOF always had the lowest selectivity and shortest half-live. This behavior can be correlated to pore volume/diameter since In-MOF has the largest pores among all the MOFs studied, increasing diffusions of substrates and products in and out of the MOF. Overall, textile composites with benzoic acid additives were the best-performing among the tested derivatives. Particularly, NUPF-2Y textile with benzoic acid additive is the best candidate for solution-free sulfide photooxidation since it has the best balance between reaction efficiency and selectivity, with a half-life of 3.91 min and a selectivity of 89.3%, which is

competitive among materials of its kind. The NUPF-2Y textile with citric acid was the second best performing, with a half-life of 4.92 min and selectivity of 80%. The In-PMOF textile composites were the most efficient, with the In-PMOF/BA/Textile having the smaller half-life of 2.41 minutes but were outperformed by all the other MOFs in selectivity.

MOF-Polymer Matrix Membranes as Chemical Protective Layers for Solid-Phase Detoxification of Toxic Organophosphates. We prepared Zr-MOF/polymer composites by fabricating them into mixed matrix membranes. MOF-808 was selected as a model Zr-MOF in our design due to its exceptional catalytic activity for organophosphate hydrolysis. The mixed matrix membranes were fabricated by incorporating MOF-808 sub-microcrystals into the blending matrix of poly(vinylidene fluoride) (PVDF), poly(vinylpyrrolidone) (PVP) and imidazole (Im) (**Figure 23**). With this design, we anticipated that the resultant membranes would inherit the characteristic properties of each individual component – the outstanding mechanical strength of PVDF will lend the membrane with excellent robustness, the hydrophilic polymer PVP can improve water adsorption/retention of the membranes, and Im serves as an effective base to regulate the pH and regenerate the active sites of Zr-MOFs. Remarkably, our rationally designed membranes showed high catalytic activity for the solid-state hydrolysis of DMNP under high humidity, suggesting their promising application as protective layers against nerve agents.

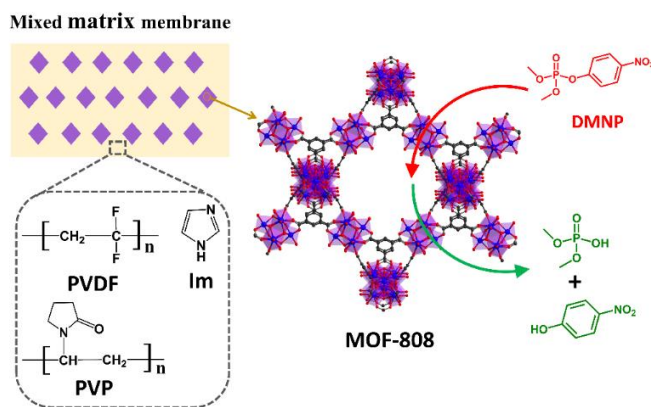


Figure 23. Schematic illustration of the mixed matrix membrane composition used for DMNP detoxification.

The mixed matrix membranes were fabricated by integrating MOF-808 sub-microcrystals into the blending matrix of PVDF, PVP, and Im. As indicated by the optical photographs in **Figure 24a**, the membranes showed reduced transparency with increasing MOF-808 content ranging from 0 to 40%. The PXRD patterns of MOF-808@PP-X (X = 20, 30, and 40%) were compared to the as-synthesized MOF-808, as shown in **Figure 24b**. In comparison with the pure PVDF/PVP membrane, MOF-808@PP-X (X = 20, 30, and 40%) showed all the characteristic peaks of MOF-808, suggesting that the structural integrity of MOF-808 was maintained after its incorporation into the supporting matrix. The TGA data indicated that the membranes were thermally stable up to 410 K. In addition, the stress-strain curves of membranes were measured to evaluate the mechanical properties of the membranes. The composite membranes of

MOF-808@PP- X ($X = 20, 30$, and 40%) showed increased elongation relative to the pristine PVDF/PVP membrane, indicating that the incorporated MOF-808 sub-microcrystals may serve as a cross-linking agent in the composite membranes. Moreover, the composite membranes can recover from folding and twisting, exhibiting excellent flexibility.

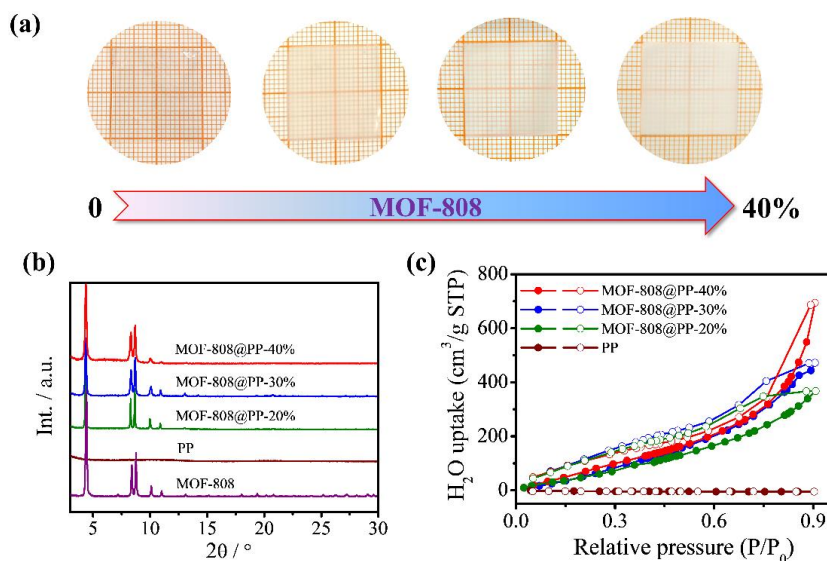


Figure 24. (a) Optical photographs, (b) PXRD patterns, and (c) water adsorption/desorption isotherms of the pure PVDF/PVP membrane and the mixed matrix membranes of MOF-808@PP- X ($X = 20, 30$, and 40%).

Since water is an essential reactant involved in the catalytic hydrolysis of organophosphorus nerve agents, the water-adsorption capacity of the synthesized membranes was studied. As depicted in **Figure 24c**, the pure PVDF/PVP membrane showed negligible water adsorption. In contrast, after the incorporation of MOF-808 sub-microcrystals, the membranes exhibited a significant improvement in water-adsorption capacity, and their water adsorption capability improved with the increasing content of MOF-808. MOF-808@PP-40%, with the highest MOF-808 content, displayed the highest water adsorption capacity among the series of membranes. Essentially, the remarkable water-adsorption capacity of the mixed matrix membranes can be attributed to the incorporation of MOF-808, an excellent water adsorbent featuring high porosity and surface area.⁴⁶⁻⁴⁷

To evaluate the capability of the mixed matrix membranes as chemical protective layers against nerve agents, we studied the hydrolysis of a nerve agent simulant, DMNP, catalyzed by the membranes in the solid phase under high humidity (98% RH) (**Figure 25a**). As shown in **Figure 25b**, upon the addition of the colorless liquid DMNP, the membrane of MOF-808@PP-40% showed a rapid color change from pale white to yellow, owing to the generation of the nontoxic hydrolysis product, dimethyl phosphate (DMP). This rapid color change indicated the fast degradation of DMNP by the membranes. To further understand the reaction kinetics, DMNP hydrolysis on the membranes was monitored using ³¹P NMR spectroscopy (**Figure 25c**), and the conversion was calculated

by comparing the integrated ^{31}P peak of the substrate DMNP (-5 ppm) with that of the nontoxic product DMP (0.5 ppm). As expected, MOF-808@PP-40%, with the highest MOF-808 content, exhibited the highest catalytic activity toward the hydrolysis of DMNP, achieving 46% and 69% conversions after 2 and 20 min, respectively. Moreover, the hydrolysis profile of DMNP catalyzed by MOF-808@PP-40% presented a short half-life ($t_{1/2}$) of 5 min (**Figure 25d**), featuring it as one of the most efficient MOF/polymer composite catalysts for DMNP hydrolysis.⁴⁷⁻⁴⁹ Additionally, the membrane of MOF-808@PP-40% showed an air permeability of $6.792 \times 10^{-3} \text{ L cm}^{-2} \text{ S}^{-1}$, indicating air can pass through the membranes for their practical application as protective layers.

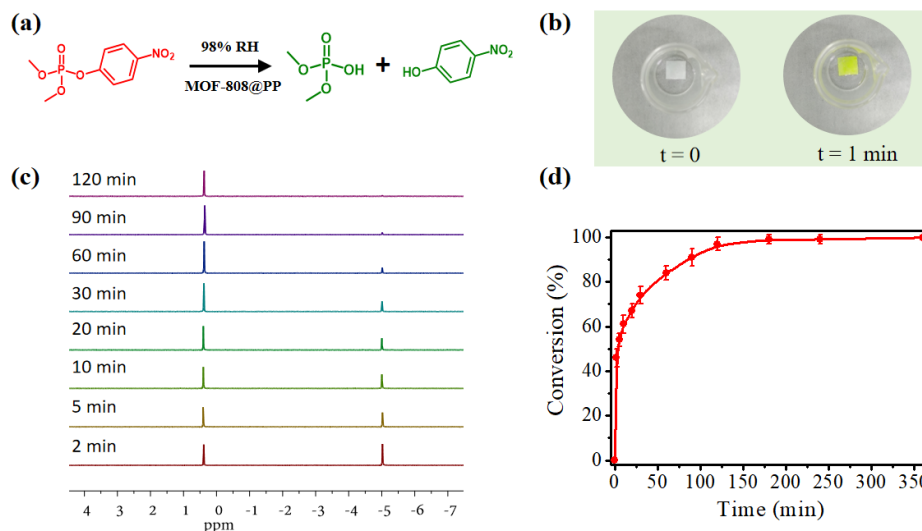


Figure 25. (a) Solid-phase hydrolysis of DMNP catalyzed by MOF-808@PP-X ($X = 20, 30$, and 40%) under a highly humid ($98\% \text{ RH}$) environment. (b) Optical photographs showing the rapid color change of MOF-808@PP-40% membrane (size: $1.0 \text{ cm} \times 1.0 \text{ cm}$) under $98\% \text{ RH}$, resulting from the degradation of DMNP. (c) Representative ^{31}P NMR spectra and (d) conversion profile of DMNP hydrolysis catalyzed by MOF-808@PP-40% under $98\% \text{ RH}$.

To date, Zr-MOFs/polymer composites that can achieve efficient solid-state hydrolysis of nerve agents/simulants have been rarely reported.^{47-48,50} The few reported examples employed dip-coating methods to deposit MOFs/polymers on fibers, which may lead to poor mechanical stabilities of the composites because of the weak adhesion between the Zr-MOFs and fibers. Notably, the mixed matrix membranes we developed in this work showed not only high catalytic activity for the solid-state hydrolysis of a nerve agent simulant but also good mechanical properties, rendering them great candidates for practical applications as protective layers against CWAs.

In summary, guided by our mechanistic studies and structure-property relationships for catalytic MOFs, we rationally designed and developed a variety of new MOF catalysts and composite materials that showed remarkable performance for the catalytic degradation of toxic chemicals, including organosulfur and organophosphate compounds. The methods, mechanisms, strategies, and new materials discovered under this project are expected to provide insight into the development of effective and efficient protective materials against chemical warfare agents.

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