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RPPR Final Report
as of 06-Jun-2022

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Final Report for Period Beginning 01-Aug-2019 and Ending 31-Jul-2020
Title: Towards Design Rules for the Synthesis of Functional Metal-Organic Frameworks in Aqueous Media at Ambient Temperature for Targeted Applications
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Phone: (847) 467-4934
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STEM Degrees: 1
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Major Goals: Major goals of this program are:
1- Understanding the design rules needed to access hydrochemically stable MOFs with various functionalities and topologies
2- Developing synthesis procedures to access these highly stable MOFs in aqueous media at room temperature
3- Investigating the effect of modulators with different pKa, steric hindrance and chemical functionality on the synthesis of MOFs in water
4- Developing methods (including designing alternative linkers) to increase the solubility of the linkers that are used for desired MOFs
5- Developing methods to access desired topologies using pre-made secondary building blocks of MOFs
6- Developing synthesis procedures to access phosphonate based robust MOFs

Accomplishments: Study 1: Water-Based Synthesis of a Stable Iron-Based Metal–Organic Framework for Capturing Toxic Gases.
In work project, we developed a facile, inexpensive, and scalable water-based synthesis of a stable iron-based MOF—Fe-soc-MOF, also known as PCN-250-Fe and Fe-MIL-127, constructed from iron trinuclear clusters and tetratopic ligands. Fe-soc-MOF was synthesized in water and acetic acid mixture solution. Gram-scale synthesis showed similar crystallinity to those of synthesized from milligram scales as well as those obtained from using hazardous, flammable solvent, dimethylformamide which shows the possibility of the further scaling the method developed here.
The capture of toxic gases such as sulfur dioxide (SO2) and ammonia (NH3) can mitigate widespread air pollution. In this work, we utilized a stable iron-based MOF for the effective capture of SO2 and NH3. This MOF demonstrated a high uptake of SO2 and NH3, rendering it a promising candidate for flue-gas desulfurization and NH3 capture. The SO2 and NH3 adsorption isotherms demonstrate a high capacity of Fe-soc-MOF; this MOF uptakes ∼14.7 mmol g-1 of NH3 and ∼11.7 mmol g-1 of SO2 at 1 bar and 298 K, respectively.

Study 2: Aqueous Synthesis of MOF-808: A zirconium-based MOF shows promise for DoD related applications
Here, we focused on MOF-808 due to the relatively low cost of the organic linker and promising adsorption capacity and catalytic activity of CWAs.
Six kinds of MOF-808 (MOF-808-FA, MOF-808-AA, MOF-808-TFA, MOF-808-OH, NH2-MOF-808-TFA, and NH2-MOF-808-OH) with different pore environments were successfully designed and synthesized in aqueous solutions. Traditionally, as-synthesized MOFs will be soaked in organic solvents to exchange the guest molecule from DMF to low boiling point solvents. This method usually produces large amount of organic solvents waste and thus

increases the overall cost and waste. While traditional MOF-808 with the formic acid capped node shows major decrease in its porosity, MOF-808-TFA developed here maintained the full porosity, while MOF-808-AA showed a minor decrease. This phenomena can be explained by the different pore environments of different MOF-808 since TFA is the most hydrophobic one, which can protect the Zr-node by preventing water cluster formation. For the MOF-808-FA, MOF-808-AA, and MOF-808-OH, water had to be exchanged with solvent to maintain the porosities. To insist on the cheap and green synthetic concept, we used ethanol which is the greenest organic solvent to activate the samples. Instead of long-time soaking, we found only a three-time quick wash with ethanol is enough to fully transfer the guest molecules from water to ethanol. Thus, the activation of MOF-808 samples only costs several times of wash by water and a quick wash by a very small amount of ethanol.

Intrigued by these results, we investigated the water cyclability using single point isotherms to establish the stability of these frameworks. We postulated that MOF-808-TFA would be perform well since it can maintain the porosity after direct activation from water. As proved by the water isotherms, the MOF-808-TFA showed nearly identical capacity for multiple cycles while MOF-808-OH showed nearly 30% decrease after the first cycle.

Study 3: Benign Integration of a Zn-Azolate Metal–Organic Framework onto Textile Fiber

In the earlier years of the program, we have demonstrated the synthesis of carboxylate (a hard Lewis base) and Zr4+, Fe3+ (hard Lewis acids) based MOFs which resulted in the chemically robust MOFs. Later, we developed stable MOFs based on soft Lewis bases (i.e azolates) and soft Lewis acids (i.e. Zn2+, Co2+). This shows the structure of an archetypal metal-azolate MOF, MFU-4. This MOF presents high chemical and thermal stability. We herein report a benign procedure to synthesize a Zn-azolate metal–organic framework (MOF), MFU-4, for NH3 capture. The surface area and morphology of MFU-4 obtained in alcohol solvents at room temperature is consistent with that of traditionally synthesized MFU-4 in N,N-dimethylformamide at 140 °C. In addition to its large NH3 uptake capacity at 1 bar (17.7 mmol/g), MFU-4 shows outstanding performance in capturing NH3 at low concentration (10.8 mmol/g at 0.05 bar). Furthermore, the mild synthetic conditions implemented make it facile to immobilize MFU-4 onto cotton textile fiber. Enhanced NH3 capture ability of the MFU-4/fiber composite was also attributed to the well-exposed MOF particles.

Study 4: Benign Synthesis and Modification of a Large Pore and High Surface Area Zn–Azolate Metal–Organic Framework

After we have shown that MFU-4 can be synthesized under mild conditions, we turned our interest into other Zn-azolate based MOF systems since MFU-4's ultra small micropores makes it challenging to use it for DoD related catalytic applications such as hydrolysis of organophosphorous chemicals. MFU-4l, an isoreticular expansion of MFU-4 (MFU denoting metal–organic framework Ulm University), is constructed from [Zn5Cl4]6+ building units and BTDD2–. Commonly used synthetic procedures for MFU-4l require the use of toxic, flammable solvents s uch as DMF at high temperatures, which lead to environmental, safety, and economic concerns. Therefore, we elected to develop a more mild synthetic method to yield the MFU-4l framework. Here, MFU-4l powder can be obtained in EtOH at 60 °C with triethylamine (TEA) as a modulator. The PXRD pattern of EtOH-synthesized MFU-4l matched well with the simulated pattern. Moreover, the N2 adsorption capacity (at 77 K) and DFT pore size distribution of MFU-4l-EtOH featured as 900 cm2/g and ～15 Å, respectively, in good agreement with that synthesized in DMF. The yielded MFU-4l-EtOH has smaller particles, which increased its catalytic activity in solid phase degradation of DMNP at 70% RH is twice as much as that of MFU-4l-DMF. Besides, the hydrolysis of DMNP was continued even under a low humidity (RH = 30%).

Study 5: Phosphonate-Based Metal–Organic Frameworks Synthesized in Aqueous Media

In addition to carboxylate and azolate based frameworks, we have also studied the phosphonate based ligands to build MOFs in water. Here, we also utilized a very affordable industrial chemical, glyphosate, as a starting material. Importantly, glyphosate solidifies as N,N′-diphosphono-methyl-2,5-piperazinedione (dpmp) at high temperatures where dpmp is a robust building block due to the cyclic central ring.

We report the aqueous synthesis of two new phosphonate-based MOFs comprising glyphosate linkers, [Mg(dpmp)]·2H2O (Mg-NU-225) and [Fe(dpmp)]·2H2O (Fe-NU-225), (dpmp = N,N′-diphosphonomethyl-2,5-piperazinedione). Single crystals grown from the reaction of metal fine powder or a metal salt and glyphosate in aqueous solution. Using one-pot synthesis conditions at pH 3.0, we obtained crystalline materials in high yields. The colorless diamond shaped plate-like crystals of Mg-NU-225 and Fe-NU-225 were obtained after 2 days. Single crystal X-ray diffraction measurements revealed that both frameworks display a two-dimensional layered structure with a cyclic ring ligand which forms in situ from the condensation of two glyphosate molecules.

Training Opportunities: Two postdoctoral fellow and one graduate students were trained on this project. They gained knowledge on the design and synthesis of crystalline porous materials, as well as they learned their basic and advanced characterizations such as porosity, crystal diffraction, scanning electron microscopy, transmission electron microscopy. Due to COVID, there were not many opportunities for in person conferences.

RPPR Final Report
as of 06-Jun-2022

Results Dissemination: The work under this program has resulted in the following publications and presentations.

Publications:

Chen, Z.; Wang, X.; Cao, R.; Idrees, K. B.; Liu, X.; Wasson, M. C.; Farha, O. K.,
Water-Based Synthesis of a Stable Iron-Based Metal–Organic Framework for Capturing Toxic Gases. ACS Mater Lett 2020, 1129-1134.

Wasson, M.C.; Otake, K.; Gong, X.; Strathman, A.R.; Islamoglu, T.; Gianneschi, N.C.; Farha, O.K. Modulation of crystal growth and structure within cerium-based metal–organic frameworks
CrystEngComm., 2020, 22, pp. 8182-8188.

Cao, R.; Mian, M.R.; Liu, X.; Chen, Z.; Wasson, M.C.; Wang, X.; Idrees, K.B.; Ma, K.; Sun, Q.; Li, J.-R.; Islamoglu, T.; Farha, O.K. Benign Synthesis and Modification of a Zn–Azolate Metal–Organic Framework for Enhanced Ammonia Uptake and Catalytic Hydrolysis of an Organophosphorus Chemical ACS Mater. Lett. 2021, 3, pp. 1363-1368.

Afrin, U.; Mian, M.R.; Otake, K.; Drout, R.J.; Redfern, L.R.; Horike, S.; Islamoglu, T.; Farha, O.K. Proton Conductivity via Trapped Water in Phosphonate-Based Metal–Organic Frameworks Synthesized in Aqueous Media Inorg. Chem, 2021, 60, pp. 1086-1091.

Zhou, X.; Gong, X.; Cao, W.; Forman, C.J.; Oktawiec, J.; D'Alba, L.; Sun, H.; Thompson, M.; Hu, Z.; Kapoor, U.; McCallum, N.C.; Malliakas, C.D.; Farha, O.K.; Jayaraman, A.; Shawkey, M.D.; Gianneschi, N.C. Anisotropic Synthetic Allomelanin Materials via Solid State Polymerization of Self?Assembled 1,8?Dihydroxynaphthalene Dimers Angew. Chem. Int. Ed., 2021, 60, pp. 17464-17471

Ran, C.; Chen, Z.; Chen, Y.; Idrees, K.B.; Hanna, S.L.; Wang, X.; Goetjen, T.A.; Sun, Q.; Islamoglu, T.; Farha, O.K. Benign Integration of a Zn-Azolate Metal?Organic Framework onto Textile Fiber for Ammonia Capture ACS Appl. Mater. Interfaces, 2020, 12, pp. 47747-47753.

Gong, X.; Gnanasekaran, K.; Ma, K.; Forman, C. J.; Wang, X.; Su, S.; Farha, O.K.; Gianneschi, N. C. Rapid Generation of Metal–Organic Framework Phase Diagrams by High-Throughput Transmission Electron Microscopy J. Am. Chem. Soc., 2022, 144, pp. 6674-6680.

Liu, X.; Kirlikovali, K.O.; Chen, Z.; Ma, K.; Idrees, K.B.; Cao, R.; Zhang, X.; Islamoglu, T.; Liu, Y.; Farha, O.K. Small Molecules, Big Effects: Tuning Adsorption and Catalytic Properties of Metal–Organic Frameworks Chem. Mater., 2021, 33, pp. 1444-1454.

Ma, K.; Idrees, K. B.; Son, F. A.; Maldonado, R.; Wasson, M. C.; Zhang, X.; Wang, X.; Shehayeb, E.; Merhi, A.; Kaafarani, B. R.; Islamoglu, T.; Xin, J. H.; Farha, O. K Fiber Composites of Metal–Organic Frameworks. Chem Mater 2020, 32, 17, 7120–7140.

Zhang, K.; Kirlikovali, K. O.; Suh, J. M.; Choi, J.-W.; Jang, H. W.; Varma, R. S.; Farha, O. K.; Shokouhimehr, M. Recent Advances in Rechargeable Aluminum-Ion Batteries and Considerations for Their Future Progress. ACS Appl Energ Mater 2020, 3 (7), 6019.

Song, H. I.; Bae, J.; Lee, E. J.; Kirlikovali, K. O.; Farha, O. K.; Jeong, N. C. Vibrational Paddlewheel Cu–Cu Node in Metal–Organic Frameworks: Probe of Nonradiative Relaxation. The Journal of Physical Chemistry C 2020, 124 (24), 13187.

Zhang, K.; Kirlikovali, K. O.; Varma, R. S.; Jin, Z.; Jang, H. W.; Farha, O. K.; Shokouhimehr, M. Covalent Organic Frameworks: Emerging Organic Solid Materials for Energy and Electrochemical Applications. ACS Applied Materials & Interfaces 2020, 12 (25), 27821.

Tajik, S.; Beitollahi, H.; Nejad, F. G.; Kirlikovali, K. O.; Le, Q. V.; Jang, H. W.; Varma, R. S.; Farha, O. K.; Shokouhimehr, M. Recent Electrochemical Applications of Metal-Organic Framework-Based Materials. Cryst Growth Des 2020, 20, 10, 7034–7064.

Zhang, K.; Kirlikovali, K. O.; Le, Q. V.; Jin, Z.; Varma, R. S.; Jang, H. W.; Farha, O. K.; Shokouhimehr, M. Extended Metal–Organic Frameworks on Diverse Supports as Electrode Nanomaterials for Electrochemical Energy Storage. ACS Appl Nano Mater 2020, 3 (5), 3964.

Zhang, K.; Lee, T. H.; Noh, H.; Farha, O. K.; Jang, H. W.; Choi, J.-W.; Shokouhimehr, M. Tailorable Topologies for Selectively Controlling Crystals of Expanded Prussian Blue Analogues. Cryst Growth Des 2019, 19 (12), 7385.

Insights into the Structure and Dynamics of Metal–Organic Frameworks via Transmission Electron Microscopy Gong, X.; Gnanasekaran, K.; Chen, Z.; Robison, L.; Wasson, M.C.; Bentz, K.C.; Cohen, S.M.; Farha, O.K.; Gianneschi, N.C. J. Am. Chem. Soc. 2020, 142, pp. 17224-17235.

Reticular Chemistry for Highly Porous Metal–Organic Frameworks: The Chemistry and Applications Chen, Z.; Kirlikovali, K.O.; Li, P.; Farha, O.K.; Acc. Chem. Res., 2022, 55, 4, 579–591.

Are you using the right probe molecules for assessing the textural properties of metal–organic frameworks? Islamoglu, T.; Idrees, K.B.; Son, F.A.; Chen, Z.; Lee, S.-J.; Li, P.; Farha, O.K. J. Mater. Chem. A, 2022, 10, pp. 157-173.

A historical perspective on porphyrin-based metal–organic frameworks and their applications
Zhang, X.; Wasson, M.C.; Shayan, M.; Berdichevsky, E.K.; Ricardo-Noordberg, J.; Singh, Z.; Papazyan, E.K.; Castro, A.J.; Marino, P.; Ajoyan, Z.; Chen, Z.; Islamoglu, T.; Howarth, A.J.; Liu, Y.; Majewski, M.B.; Katz, M.J.; Mondloch, J.E.; Farha, O.K.; Coord. Chem. Rev., 2021, 429, 213615.

The State of the Field: From Inception to Commercialization of Metal–Organic Frameworks
Chen, Z.; Wasson, M.C.; Drout, R.J.; Robison, L.; Idrees, K.B.; Knapp, J.G.; Son, F.A.; Zhang, X.; Hierse, W.; Kühn, C.; Marx, S.; Hernandez, B.; Farha, O.K.; Faraday Discuss.; 2020, 225, 9-69.

Talks:

- “Smart and Programmable Sponges for protection From Bench to Market,” Tulane University, New Orleans, Louisiana, November 8, 2021. Virtual. Invite
- “Smart and Programmable Sponges for protection From Bench to Market,” Chemistry Department’s Graduate Student-Invited Seminar, Colorado School of Mines, October 15th, 2021. Invite
- “Smart, Crystalline, and Programmable Sponges for protection From Bench to Market,” 2021 AAFM-UCLA International Conference on Advances in Functional Materials, August 18-20th, 2021. Virtual. Award Talk
- “Smart and Programmable Sponges for protection From Bench to Market,” Solid-State Science & Research, June 10-11, 2021. Virtual. Plenary
- “Programmable and Smart Sponges for Protection,” Clemson University, Clemson, South Carolina, November 5, 2020. Virtual. Invite
- “Programmable and Smart Sponges for Protection,” Royal Society of Chemistry Porous Materials Group Online Webinar, November 3, 2020. Virtual. Invite
- “New Challenges Require New Materials: Smart and Programmable Sponges,” Northwestern University Materials Research Science and Engineering Center, Northwestern University, Evanston, Illinois, July 7, 2020. via zoom. Invite
- “Smart and Programmable Sponges from Design and Synthesis to Implementation,” Micromeritics, July 7, 2020. webinar. Invite
- “Design & Synthesis of Crystalline Smart Programmable Sponges,” Energy Frontier Research Centers - MUSE, University of Utah, Salt Lake City, Utah, June 24, 2020. via zoom. Invite
- “Programmable Smart Sponges,” Crystal Engineering and Emerging Materials
- Workshop of Ontario and Quebec (CEMWOQ), May 30-31, 2020. via zoom. Opening Talk
- “Programmable Smart Sponges,” University of Houston, Houston, Texsas, April 28, 2020. via zoom. Invite
- “Programmable Smart Sponges,” Molecular and Materials for Solar Fuel, Pittcon, Chicago, March 5, 2020. Invite
- “Programmable Smart Sponges,” University of Washington, Seattle, Washington, February 25, 2020. Invite
- “Programmable Smart Sponges,” ACS Chicago Section, Chicago, Illinois, February 22, 2020. Invite
- “Programmable Smart Sponges,” University of Texas, Dallas, Texas, February 8, 2020. Invite
- “Programmable Smart Sponges,” University of Kuwait, Kuwait, February 3, 2020. Invite
- “Design & Synthesis of Crystalline Smart Programmable Sponges,” Advanced Membrane Workshop, University

of Pennsylvania, Phalidelphia, Pennsylvania, December 16-18, 2019. Invite

Honors and Awards: Awards:

- “Top 100 World's Most Highly-Cited Chemists, Farha is #35” (Research.com, 2022)
- “Highly Cited Researchers in Chemistry” (Clarivate Analytics, 2021)
- Inaugural recipients of the American Association for Advances in Functional Materials (AAAFM)-Stoddart award (UCLA, 2021)
- 2021 Barrer Lectureship (Pennsylvania State University, 2021)
- “Highly Cited Researchers in Chemistry” (Clarivate Analytics, 2020)
- Elected as Fellow of the Academy of Arab Scientists, 2020
- 2020 ACS ENFL Emerging Researcher Award, 2020
- Appointed to the Dow Chemical Company Research Professorship in Chemistry, 2020
- Elected as Foreign Fellow of the European Academy of Sciences (EurASc), 2020
- Kuwait Prize – Applied Sciences (Kuwait Foundation for the Advancment of Science, 2019
- “Highly Cited Researchers in Chemistry” (Clarivate Analytics, 2019)
- JSCC International Award for Creative Work (Japan Society of Coordination Chemistry, 2019)

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PARTICIPANTS:

Participant Type: PD/PI
Participant: Omar K Farha
Person Months Worked: 1.00 **Funding Support:**
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National Academy Member: N

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Zhijie Chen
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Xuan Zhang
Person Months Worked: 5.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Staff Scientist (doctoral level)
Participant: Timur Islamoglu
Person Months Worked: 12.00 **Funding Support:**
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Participant Type: Graduate Student (research assistant)

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ARTICLES:

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Article Title: Water-Based Synthesis of a Stable Iron-Based Metal–Organic Framework for Capturing Toxic Gases
Authors: Zhijie Chen, Xingjie Wang, Ran Cao, Karam B. Idrees, Xinyao Liu, Megan C. Wasson, Omar K. Farha
Keywords: metal-organic frameworks
Abstract: The capture of toxic gases such as sulfur dioxide (SO2) and ammonia (NH3) can mitigate widespread air pollution. An emerging class of adsorbents known as metal–organic frameworks (MOFs) offer high porosity and tunability to capture targeted analytes. However, challenges remain in the development of safe, environmentally friendly, and inexpensive MOF syntheses. In this work, we utilized a stable iron-based MOF–Fe-soc-MOF—also known as PCN-250-Fe and Fe-MIL-127—for the effective capture of SO2 and NH3. This MOF demonstrated a high uptake of SO2 and NH3, rendering it a promising candidate for flue-gas desulfurization and NH3 capture. To accommodate the potential large-scale implementation of Fe-soc-MOF as an adsorbent, we developed a facile, inexpensive, and scalable water-based synthesis for this material.
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Article Title: Fiber Composites of Metal–Organic Frameworks
Authors: Kaikai Ma, Karam B. Idrees, Florencia A. Son, Rodrigo Maldonado, Megan C. Wasson, Xuan Zhang, Xi
Keywords: metal-organic frameworks
Abstract: The high chemical and structural diversity of metal–organic frameworks (MOFs), which are porous crystalline materials, has attracted significant academic and industrial interest. However, the poor processability of MOF powders limits their full potential in practical applications. Toward this end, MOF-based composite materials increase the framework robustness and subsequent utility. Among these hybrid materials, MOF composites prepared on commercially available textile fibers offer the high flexibility needed for important applications—such as heterogeneous catalysis, chemical sensing, pollutant removal, and drug release—while maintaining the functional properties of MOFs. The ability to further tailor these composites' shapes for incorporation into industrial equipment increases their potential in applications such as adsorption devices and protective gears. In this Review, we summarize recently reported MOF/fiber fabrication methods and applications. Our discussion on the advancemen
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Article Title: Recent Advances in Rechargeable Aluminum-Ion Batteries and Considerations for Their Future Progress
Authors: Kaiqiang Zhang, Kent O. Kirlikovali, Jun Min Suh, Ji-Won Choi, Ho Won Jang, Rajender S. Varma, Oma
Keywords: aluminum-ion battery electrode material high performance electrolyte rechargeable
Abstract: Owing to their high theoretical capacity and reliable operational safety, nonaqueous rechargeable aluminum batteries (RABs) have emerged as a promising class of battery materials and been intensively studied in recent years; however, a lack of suitable, high-performing positive electrode materials, along with the need for air-sensitive and expensive ionic liquid electrolytes, has significantly hindered the practical use of RABs in large-scale applications. Therefore, we sought to carefully analyze positive electrode materials and the associated electrolytes that have been reported in these battery systems in order to stimulate the design of the next generation of high-performance and low-cost RABs. In this review, we have summarized the electrode materials that have been used in both nonaqueous and aqueous RAB systems and provided a rational classification based on the types of materials used and their respective structures.
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Article Title: Vibrational Paddlewheel Cu–Cu Node in Metal–Organic Frameworks: Probe of Nonradiative Relaxation
Authors: Hye In Song, Jinhee Bae, Eun Ji Lee, Kent O. Kirlikovali, Omar K. Farha, Nak Cheon Jeong
Keywords: metal-organic frameworks
Abstract: Nonradiative relaxation, a ubiquitous phenomenon in natural and artificial molecules and materials, has been extensively studied in contemporary chemistry. In this report, we show the nonradiative relaxation of Cu(II)-based paddlewheel metal–organic frameworks (MOFs), HKUST-1 and Cu-MOF-2, with Raman measurements. Irradiation of the Cu-based MOF crystals by a 532 nm laser with the minimum power of 1.5–8.0 mW results in the dissociation of the axially ligated solvent molecules at the paddlewheel Cu(II) sites. Dissociation arises by the accumulated thermal energy formed by nonradiative relaxation, and the minimum power necessary is dependent on both the type of MOF and the Lewis basic solvent molecule that is coordinated to the metal node. We demonstrate that the minimum power is associated with an equilibrium between the accumulation and dissipation of thermal energy and also that thermal dissipation is dependent on the coordination strength, molecular interaction energy, and kinetic.
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Article Title: Covalent Organic Frameworks: Emerging Organic Solid Materials for Energy and Electrochemical Applications
Authors: Kaiqiang Zhang, Kent O. Kirlikovali, Rajender S. Varma, Zhong Jin, Ho Won Jang, Omar K. Farha, Moh
Keywords: covalent organic frameworks structural design and synthesis electrochemical applications energy conversion and storage porous crystalline materials
Abstract: Covalent organic frameworks (COFs), materials constructed from organic building blocks joined by robust covalent bonds, have emerged as attractive materials in the context of electrochemical applications because of their high, intrinsic porosities and crystalline frameworks, as well as their ability to be tuned across two- and three-dimensions by the judicious selection of building blocks. Because of the recent and rapid development of this field, we have summarized COFs employed for electrochemical applications, such as batteries and capacitors, water splitting, solar cells, and sensors, with an emphasis on the structural design and resulting performance of the targeted electrochemical system. Overall, we anticipate this review will stimulate the design and synthesis of the next generation of COFs for use in electrochemical applications and beyond.
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Authors: Somayeh Tajik, Hadi Beitollahi, Fariba Garkani Nejad, Kent O. Kirlikovali, Quyet Van Le, Ho Won Jang,
Keywords: metal-organic frameworks
Abstract: Metal–organic frameworks (MOFs), a versatile class of porous materials that exhibit high specific surface areas, controllable structures, and tunable pores, have been identified as a promising platform in the field of electrochemistry in recent years, and researchers have now designed MOFs specific to electrochemical applications. In this review, we describe the recent uses of MOFs and their composites for use in electrochemical sensing, electrocatalysis, and electrochemical energy storage devices (e.g., batteries and supercapacitors), followed by an overview of the remaining challenges and viewpoints for MOF-based materials for these applications.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

RPPR Final Report
as of 06-Jun-2022

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Volume: 3 Issue: 5 First Page #: 3964
Date Submitted: 5/25/22 12:00AM Date Published: 4/1/20 5:00AM
Publication Location:
Article Title: Extended Metal–Organic Frameworks on Diverse Supports as Electrode Nanomaterials for Electrochemical Energy Storage
Authors: Kaiqiang Zhang, Kent O. Kirlikovali, Quyet Van Le, Zhong Jin, Rajender S. Varma, Ho Won Jang, Omar
Keywords: metal?organic framework bridging and connecting high-performance conductivity electrochemical energy storage nanomaterial
Abstract: The incorporation of renewable and sustainable energy sources in electric grids has been acknowledged as a potential strategy to solve the ever-growing environmental issues that result from the use of fossil fuels. In order to realize the full potential of these systems, advanced electrochemical energy storage devices must be developed. Recently, researchers have turned their attention toward obtaining high-performance electrode nanomaterials in order to develop these next-generation electrochemical systems. Metal–organic frameworks (MOFs), well-known for their relatively straightforward fabrication methods, high nanoscale porosities, robust nanostructures, and intrinsic crystallinities, have emerged as a class of nanomaterials potentially capable of meeting the stringent demands for these systems...
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Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.cgd.9b01309
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Date Submitted: 5/25/22 12:00AM Date Published: 10/1/19 5:00AM
Publication Location:
Article Title: Tailorable Topologies for Selectively Controlling Crystals of Expanded Prussian Blue Analogues
Authors: Kaiqiang Zhang, Tae Hyung Lee, Hyunho Noh, Omar K. Farha, Ho Won Jang, Ji-Won Choi, Mohammac
Keywords: metal-organic frameworks
Abstract: Chemical manipulations of Prussian blues and Prussian blue analogues (PBAs) beyond first-row transition-metal cations have remained quite preliminary to this day. The presented report demonstrates the feasibility of using different types of cations, including general transition-metal ions, p region elements in the periodic table, lanthanide elements, and overlooked cations such as Al3+ and Mo3+ to build unique PBAs. A systematic study of the different types of PBAs is provided in terms of physical and chemical features by means of transition electron microscopy, X-ray photoelectron spectroscopy, and X-ray absorption near-edge structure. Diverse PBAs can be synthesized with different morphologies. The [Ni(CN)4]2−-based PBAs mainly exhibited layered products owing to their 4-fold-coordinated anions. The 6-fold-coordinated anion-based PBAs displayed cubic or distorted cubic crystal structures following the same method of ion arrangements with conventional [Fe (CN)6]2-/3−-based PBAs..
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Volume: 22 Issue: 47 First Page #: 8182
Date Submitted: 5/25/22 12:00AM Date Published:
Publication Location:
Article Title: Modulation of crystal growth and structure within cerium-based metal–organic frameworks
Authors: Megan C. Wasson, Ken-ichi Otake, Xinyi Gong, Annabella R. Strathman, Timur Islamoglu, Nathan C. G
Keywords: metal-organic frameworks
Abstract: The intriguing catalytic properties of cerium-based materials have motivated the development of Ce-based metal–organic frameworks (MOFs). However, the controlled crystallization of Ce MOFs remains nascent due to complications with the high reduction potential of Ce4+ species. Modulators offer a route in other well-studied coordination networks to slow down crystallization processes to allow for corrective, uniform crystal growth. Herein, we report an investigation of modulator identity and concentration on the synthesis of a Ce-UiO-type MOF with 2,6-naphthalenedicarboxylic acid (NDC) as a linker. At low concentrations using both benzoic acid and trifluoroacetic acid, we observed a mononuclear Ce3+ MOF (NU-350) through single-crystal X-ray diffraction studies. Higher modulator concentrations yielded pure-phase Ce-UiO-NDC, with uniform particle sizes observed with utilizing benzoic acid as a modulator. Moreover, we demonstrated the transferability of this synthesis through the pure...
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Volume: 12 Issue: 42 First Page #: 47747
Date Submitted: 5/25/22 12:00AM Date Published: 10/1/20 5:00AM
Publication Location:
Article Title: Benign Integration of a Zn-Azolate Metal–Organic Framework onto Textile Fiber for Ammonia Capture
Authors: Ran Cao, Zhijie Chen, Yongwei Chen, Karam B. Idrees, Sylvia L. Hanna, Xingjie Wang, Timothy A. Goe
Keywords: benign synthesis MOF/fiber composite NH3 capture azolate MOF
Abstract: Ammonia (NH3) exposure has a serious impact on human health because of its toxic and corrosive nature. Therefore, efficient personal protective equipment (PPE) such as masks is necessary to eliminate and mitigate NH3 exposure risks. Because economically and environmentally viable conditions are of interest for large-scale manufacture of PPE, we herein report a benign procedure to synthesize a Zn-azolate metal–organic framework (MOF), MFU-4, for NH3 capture. The surface area and morphology of MFU-4 obtained in alcohol solvents at room temperature is consistent with that of traditionally synthesized MFU-4 in N,N-dimethylformamide at 140 °C. In addition to its large NH3 uptake capacity at 1 bar (17.7 mmol/g), MFU-4 shows outstanding performance in capturing NH3 at low concentration (10.8 mmol/g at 0.05 bar). Furthermore, the mild synthetic conditions implemented make it facile to immobilize MFU-4 onto cotton textile fiber. Enhanced NH3 capture ability of the MFU-4/fiber composite was...
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Volume: 60 Issue: 2 First Page #: 1086
Date Submitted: 5/25/22 12:00AM Date Published: 1/1/21 6:00AM
Publication Location:
Article Title: Proton Conductivity via Trapped Water in Phosphonate-Based Metal–Organic Frameworks Synthesized in Aqueous Media
Authors: Unjila Afrin, Mohammad Rasel Mian, Ken-ichi Otake, Riki J. Drout, Louis R. Redfern, Satoshi Horike, Tir
Keywords: metal-organic frameworks
Abstract: Metal–organic frameworks (MOFs) are promising candidates for proton-conducting applications. Herein, we report the aqueous synthesis of two new phosphonate-based MOFs comprising glyphosate linkers, [Mg(dpmp)]·2H2O (Mg-NU-225) and [Fe(dpmp)]·2H2O (Fe-NU-225), (dpmp = N,N?-diphosphonomethyl-2,5-piperazinedione), and explore their proton conductivities. Single crystal X-ray diffraction measurements revealed that both frameworks display a two-dimensional layered structure with a cyclic ring ligand which forms in situ from the condensation of two glyphosate molecules. Under humid conditions and over a wide temperature range, water molecules are trapped between adjacent layers and facilitate rapid proton conduction. Mg-NU-225 and Fe-NU-225 recorded proton conductivities of 1.5 × 10–5 and 1.7 × 10–5 S cm–1, respectively, along the plane direction and 1.6 × 10–3 and 9.1 × 10–5 S cm–1 perpendicular to the plane direction at 55 °C and 95% relative humidity, as confirmed by two-contact probe ...
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Angewandte Chemie International Edition
Publication Identifier Type: DOI Publication Identifier: 10.1002/anie.202103447
Volume: 60 Issue: 32 First Page #: 17464
Date Submitted: 5/25/22 12:00AM Date Published: 6/1/21 5:00AM
Publication Location:
Article Title: Anisotropic Synthetic Allomelanin Materials via Solid?State Polymerization of Self?Assembled 1,8?Dihydroxynaphthalene Dimers
Authors: Xuhao Zhou, Xinyi Gong, Wei Cao, Christopher J. Forman, Julia Oktawiec, Liliana D'Alba, Hao Sun, Ma
Keywords: metal-organic frameworks
Abstract: A new method to achieve synthetic melanin materials with various well-defined architectures, ranging from spheres to anisotropic sheets and ellipsoidal platelets, is described. The specific shapes are obtained through pre-organizing the building blocks of melanins, followed by solid-state oxidative polymerization to render polymeric materials without changing the overall morphology.
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Publication Identifier Type: DOI Publication Identifier: 10.1021/jacs.2c01095
Volume: 144 Issue: 15 First Page #: 6674
Date Submitted: 5/25/22 12:00AM Date Published: 4/1/22 5:00AM
Publication Location:
Article Title: Rapid Generation of Metal–Organic Framework Phase Diagrams by High-Throughput Transmission Electron Microscopy
Authors: Xinyi Gong, Karthikeyan Gnanasekaran, Kaikai Ma, Christopher J. Forman, Xingjie Wang, Shengyi Su,
Keywords: metal-organic frameworks
Abstract: Metal–organic frameworks (MOFs) constructed from Zr6 nodes and tetratopic carboxylate linkers display high structural diversity and complexity in which various crystal topologies can result from identical building units. To determine correlations between MOF topologies and experimental parameters, such as solvent choice or modulator identity and concentration, we demonstrate the rapid generation of phase diagrams for Zr6-MOFs with 1,4-dibromo-2,3,5,6-tetrakis(4-carboxyphenyl)benzene linkers under a variety of conditions. We have developed a full set of methods for high-throughput transmission electron microscopy (TEM), including automated sample preparation and data acquisition, to accelerate MOF characterization. The use of acetic acid as a modulator yields amorphous, NU-906, NU-600, and mixed-phase structures depending on the ratio of N,N-dimethylformamide to N,N-diethylformamide solvent and the quantity of the modulator. Notably, the use of formic acid as a modulator enables...
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Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.chemmater.0c04675
Volume: 33 Issue: 4 First Page #: 1444
Date Submitted: 5/25/22 12:00AM Date Published: 2/1/21 6:00AM
Publication Location:
Article Title: Small Molecules, Big Effects: Tuning Adsorption and Catalytic Properties of Metal–Organic Frameworks
Authors: Xinyao Liu, Kent O. Kirlikovali, Zhijie Chen, Kaikai Ma, Karam B. Idrees, Ran Cao, Xuan Zhang, Timur I
Keywords: metal-organic frameworks
Abstract: Metal–organic frameworks (MOFs) have emerged as a highly tunable class of porous materials, and in particular, zirconium-based MOFs (Zr-MOFs) have demonstrated the potential to address challenges in a variety of practical applications due to their excellent chemical and thermal stabilities. However, Zr-MOFs are typically synthesized using flammable and toxic organic solvents. An effective, green, scalable route to obtain high-quality Zr-MOFs has yet to be developed as these procedures typically yield Zr-MOFs with relatively lower crystallinities and porosities than those obtained via the former route. Herein, we report the aqueous synthesis of MOF-808, a versatile Zr-MOF, that yields products with high crystallinities and porosities that are comparable to those of solvothermally synthesized MOF-808. We demonstrate that modifying the carboxylic acid-based modulator used in this hydrothermal procedure enables the straightforward tuning of the pore environment in MOF-808.
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Volume: 142 Issue: 41 First Page #: 17224
Date Submitted: 5/25/22 12:00AM Date Published: 9/1/20 5:00AM
Publication Location:
Article Title: Insights into the Structure and Dynamics of Metal–Organic Frameworks via Transmission Electron Microscopy
Authors: Xinyi Gong, Karthikeyan Gnanasekaran, Zhijie Chen, Lee Robison, Megan C. Wasson, Kyle C. Bentz, S
Keywords: metal-organic frameworks
Abstract: Metal–organic frameworks (MOFs) are hybrid materials composed of metal ions and organic linkers featuring high porosity, crystallinity, and chemical tunability at multiple length scales. A recent advancement in transmission electron microscopy (TEM) and its direct application to MOF structure–property relationships have changed how we consider rational MOF design and development. Herein, we provide a perspective on TEM studies of MOFs and highlight the utilization of state-of-the-art TEM technologies to explore dynamic MOF processes and host–guest interactions. Additionally, we provide thoughts on what the future holds for TEM in the study of MOFs.
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Volume: 55 Issue: 4 First Page #: 579
Date Submitted: 5/25/22 12:00AM Date Published: 2/1/22 6:00AM
Publication Location:
Article Title: Reticular Chemistry for Highly Porous Metal–Organic Frameworks: The Chemistry and Applications
Authors: Zhijie Chen, Kent O. Kirlikovali, Peng Li, Omar K. Farha
Keywords: metal-organic frameworks
Abstract: we provide an overview of potential applications of these highly porous MOFs, including water capture, catalysis, methane storage, hydrogen storage, and the separation of organic dyes and biological macromolecules. We hope that this Account may serve as a blueprint and stimulate researchers to develop the next generation of highly porous materials for energy- and environment-related applications and beyond.
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Publication Identifier Type: DOI Publication Identifier: 10.1039/D1TA08021K
Volume: 10 Issue: 1 First Page #: 157
Date Submitted: 5/25/22 12:00AM Date Published:
Publication Location:
Article Title: Are you using the right probe molecules for assessing the textural properties of metal–organic frameworks?
Authors: Timur Islamoglu, Karam B. Idrees, Florencia A. Son, Zhijie Chen, Seung-Joon Lee, Peng Li, Omar K. Fa
Keywords: metal-organic frameworks
Abstract: Textural properties—such as the surface area, pore size distribution, and pore volume—are at the forefront of characterization for porous materials. Therefore, it is essential to accurately and reproducibly report a material's textural properties as they could ultimately dictate its applicability. This work aims to provide insightful and comprehensive studies of textural properties for a set of metal–organic frameworks (MOFs), a class of porous materials, using various gases to equip researchers in the field with a helpful guide and reference. We selected a series of nine MOFs with different surface areas, pore sizes, shapes, and chemical environments to represent a wide range of materials. We probed the textural properties of these MOFs using traditional and distinctive gases: N_2, Kr and O_2 at 77 K, Ar at 87 K, and CO_2 at 195 and 273 K.
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Volume: 429 Issue: First Page #: 213615
Date Submitted: 5/25/22 12:00AM Date Published: 2/1/21 6:00AM
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: PorphyrinMetal–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 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.
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Journal: Faraday Discussions
Publication Identifier Type: DOI Publication Identifier: 10.1039/D0FD00103A
Volume: 225 Issue: First Page #: 9
Date Submitted: 5/25/22 12:00AM Date Published:
Publication Location:
Article Title: The state of the field: from inception to commercialization of metal–organic frameworks
Authors: Zhijie Chen, Megan C. Wasson, Riki J. Drout, Lee Robison, Karam B. Idrees, Julia G. Knapp, Florencia
Keywords: metal-organic frameworks
Abstract: As chemists and materials scientists, it is our duty to synthesize and utilize materials for a multitude of applications that promote the development of society and the well-being of its citizens. Since the inception of metal–organic frameworks (MOFs), researchers have proposed a variety of design strategies to rationally synthesize new MOF materials, studied their porosity and gas sorption performances, and integrated MOFs onto supports and into devices. Efforts have explored the relevance of MOFs for applications including, but not limited to, heterogeneous catalysis, guest delivery, water capture, destruction of nerve agents, gas storage, and separation. Recently, several start-up companies have undertaken MOF commercialization within industrial sectors. Herein, we provide a brief overview of the state of the MOF field from their design and synthesis to their potential applications, and finally, to their commercialization.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

Partners

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I certify that the information in the report is complete and accurate:
Signature: Omar Farha
Signature Date: 5/25/22 7:33PM

Project Title: Towards Design Rules for the Synthesis of Functional Metal-Organic Frameworks in Aqueous Media at Ambient Temperature for Targeted Applications
Award Number: W911NF1910340
Type: Final Report
Date: May 25, 2022

Technical point of contact & PI: Omar K. Farha
Ph.: 847-467-4934
E-mail: o-farha@ northwestern.edu
Department of Chemistry, Northwestern University, Evanston, IL 60208

Personnel supported by the grant:

Start – 8/30/20:

Omar Farha, PI, 0.25 AY person-months charged, and 0.25 AY person-months cost shared
Zhijie Chen, Postdoctoral Fellow, 2.8 person-months
Xuan Zhang, Postdoctoral Fellow, 1.8 person-months
Timur Islamoglu, Research Associate, 3.75 person-months

8/30/20 – 8/1/21:
Omar Farha – 0.33 AY (and 0.25 cost shared summer, which will be the case for this period as well)
Zhijie Chen – 1.2 calendar months
Xinyi Gong – 4.5 calendar months
Timur Islamoglu – 5.34 calendar months
Xuan Zhang – 3 calendar months

8/1/21 – 7/31/22:

Omar Farha – 0.18 academic months
Zhijie Chen – 1.2 calendar months
Timur Islamoglu – 4.5 calendar months
Xinyi Gong – 6 calendar months

Abstract: The objective of this effort is to develop protocols for the synthesis of chemically stable MOFs in aqueous environment and room temperature. Here, we developped synthetic protocols of Zr-MOFs to multitopic (i.e. beyond ditopic) organic linkers and demonstrated improved hydrolytic stability of the MOFs obtained via the procedure developed here.

Progress Report:

Key findings under this program, we;

1- Developed synthesis protocols for accessing highly stable iron, zirconium, zinc and magnesium based MOF with multitopic linkers with various coordinating groups including carboxylate, azolate and phosphonate in aqueous solutions and demonstrated the gram scale synthesis of selected MOFs

2- Investigated the effect of the modulator coordinated to the node on the stability of MOF-808

3- Demonstrated the stability of MOF-808-TFA after multicycle water adsorption/desorption isotherms which is important for water harvesting applications

4- Demonstrated the high uptake capacity of the iron based MOF for SO_2 and NH_3 gases with high chemical stability

5- Demonstrated high ammonia uptake and catalytic activity with Zn-azolate MOFs

Major goals of this program are:

1- Understanding the design rules needed to access hydrochemically stable MOFs with various functionalities and topologies

2- Developing synthesis procedures to access these highly stable MOFs in aqueous media at room temperature

3- Investigating the effect of modulators with different pK_a, steric hindrance and chemical functionality on the synthesis of MOFs in water

4- Developing methods (including designing alternative linkers) to increase the solubility of the linkers that are used for desired MOFs

5- Developing methods to access desired topologies using pre-made secondary building blocks of MOFs

6- Developing synthesis procedures to access phosphonate based robust MOFs

Study 1: Water-Based Synthesis of a Stable Iron-Based Metal–Organic Framework for Capturing Toxic Gases.

In work project, we developed a facile, inexpensive, and scalable water-based synthesis of a stable iron-based MOF—Fe-**soc**-MOF, also known as PCN-250-Fe and Fe-MIL-127, constructed from iron trinuclear clusters and 3,3′,5,5′-azobenzenetetracarboxylate ($ABTC^{4-}$) ligands (**Figure 1**). Fe-soc-MOF was synthesized in water and acetic acid mixture solution. The powder X-ray diffraction (PXRD) patterns and scanning electron microscopy (SEM) images

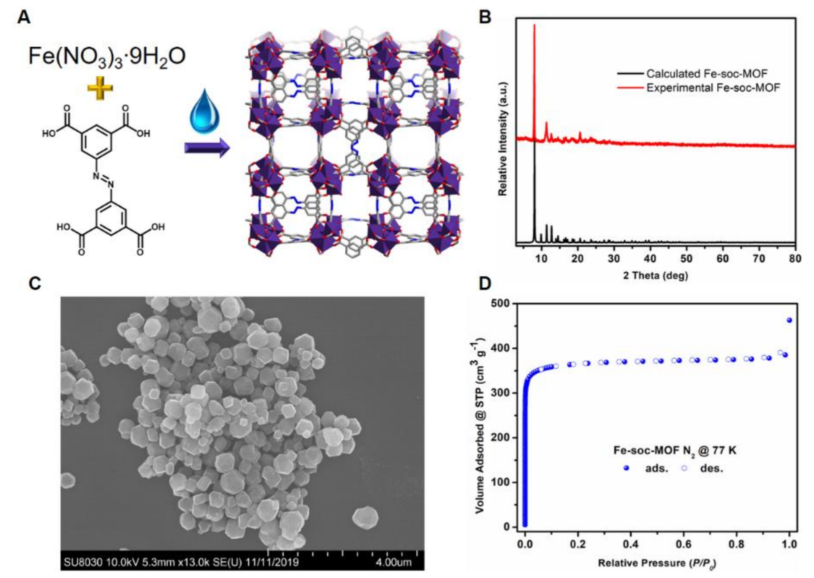

Figure 1. (A) The schematic representation of water-based synthesis of Fe-**soc**-MOF. (B) experimental and calculated PXRD patterns, (C) a SEM image, and (D) N_2 adsorption-desorption isotherms of Fe-**soc**-MOF.

support the phase purity of the materials synthesized. The N_2 adsorption isotherm of this MOF reveals the apparent Brunauer–Emmett–Teller (BET) area of 1470 m^2 g^{-1} and the experimental total pore volume of 0.58 cm^3 g^{-1} at $P/P_0 = 0.9$. Gram-scale synthesis showed similar crystallinity to those of synthesized from milligram scales as well as those obtained from using hazardous, flammable solvent, dimethylformamide which shows the possibility of the further scaling the method developed here.

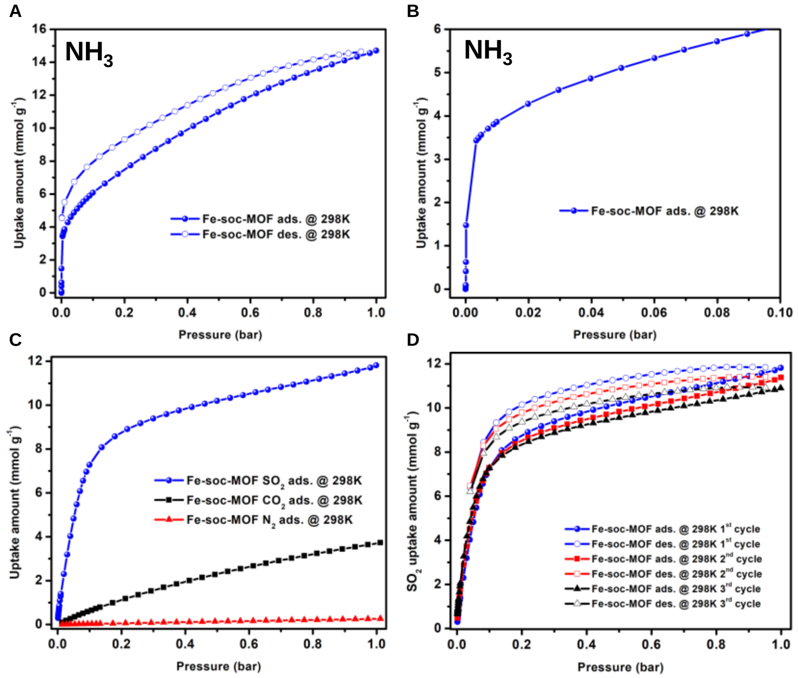

Figure 2. (A) NH_3 adsorption-desorption isotherms of Fe-**soc**-MOF at 298 K. (B) Zoomed-in view of low-pressure range of NH_3 adsorption isotherm for clarity. (C) Low-pressure adsorption isotherms of SO_2, CO_2 and N_2 for Fe-**soc**-MOF at 298 K. A PXRD pattern of Fe-**soc**-MOF after SO_2 sorption test. (D) Three cycles of SO_2 sorption isotherms of Fe-**soc**-MOF at 298 K (room temperature regeneration under vacuum for 3 hours).

The capture of toxic gases such as sulfur dioxide (SO_2) and ammonia (NH_3) can mitigate widespread air pollution. An emerging class of adsorbents known as metal–organic frameworks (MOFs) offer high porosity and tunability to capture targeted analytes. However, challenges remain in the development of safe, environmentally friendly, and inexpensive MOF syntheses. In this work, we utilized a stable iron-based MOF—Fe-**soc**-MOF—for the effective capture of SO_2 and NH_3. This MOF demonstrated a high uptake of SO_2 and NH_3, rendering it a promising candidate for flue-gas desulfurization and NH_3 capture (**Figure 2**). The SO_2 and NH_3 adsorption isotherms demonstrate a high capacity of Fe-**soc**-MOF; this MOF uptakes ~14.7 mmol g^{-1} of NH_3 and ~11.7 mmol g^{-1} of SO_2 at 1 bar and 298 K, respectively. Furthermore, the MOF's preferred adsorption of SO_2 over CO_2 and N_2 suggests Fe-**soc**-MOF as a promising candidate adsorbent for flue-gas desulfurization.

Study 2: Aqueous Synthesis of MOF-808: A zirconium-based MOF shows promise for DoD related applications

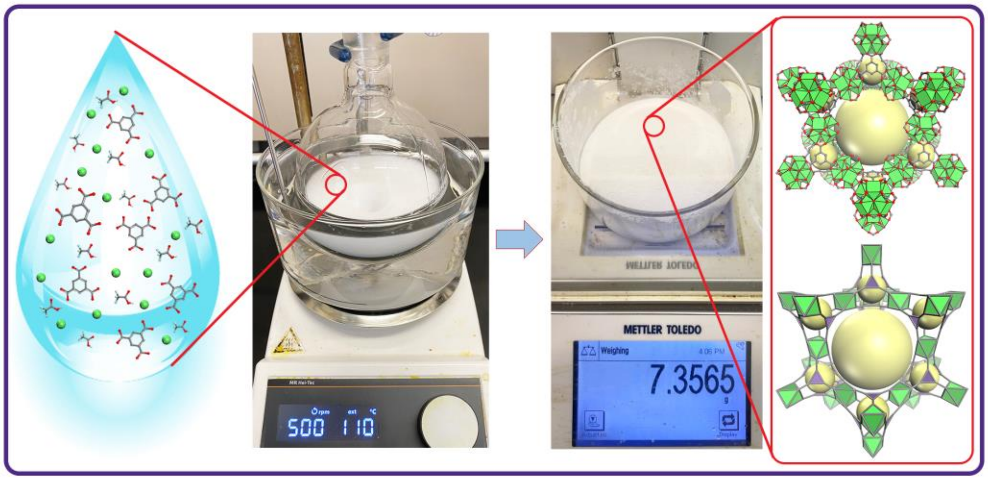

Figure 3. The schematic illustration of water-phase synthesis of MOF-808. More than 7 grams of samples can be obtained in a 150 mL reaction in one day.

The development of a safe, green, and low-cost synthesis of zirconium MOFs has been of great interest due to promising performance of this class of MOFs on many applications. To this end, we focused on MOF-808 (**Figure 3**) due to the relatively low cost of the organic linker and promising adsorption capacity and catalytic activity of CWAs.

Since organic monoacids, such as formic acid (FA), acetic acid (AA), trifluoroacetic acid (TFA) can slow down the precipitation of MOF formation and can lead highly crystalline MOF material, we applied this strategy to access highly crystalline MOF-808 particles. In many cases, the synthesis of Zr-MOFs using different modulators can lead to the formation of different polymorph. However, with the combination of Zr_6-node and BTC linker, *spn* topology is the only network that can be obtained. This exclusive structural guidance enabled us to explore different modulators. With the reaction of $ZrOCl_2·8H_2O$ and 1,3,5-benzene tricarbocylic acid (H_3BTC) in water with different modulators, MOF-808 was successfully synthesized. The PXRD patterns (**Figure 4**) agreed well with the simulated pattern.

Generally, the modulators role is to slow down the coordination between the organic linker and metal (Zr^{4+}) which can lead to slower crystallization and increase in crystallinity during the solvothermal reaction. It is worth mentioning that the low amount of acid present in the solution can also result in gelation due to early precipitation. Therefore, the synthesis in water and formic acid mixture (volume ratio: 1/1) resulted in MOF-808 with gel-like impurities and a relatively lower BET area compared to the usual MOF-808. So, we added a small portion of

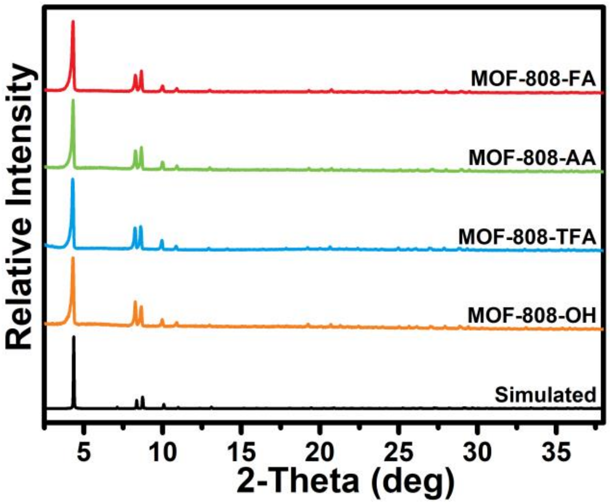

Figure 4. The PXRD patterns of Synthesized MOF-808 and simulated one.

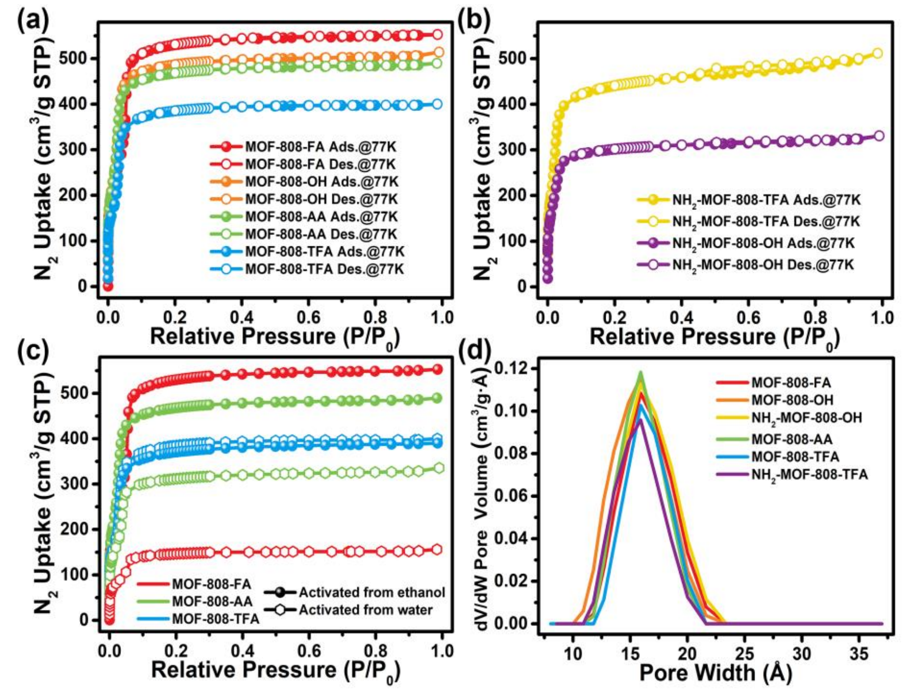

Figure 5. The N2 isotherms of (a) MOF-808s with different attached molecules on the Zr-nodes; (b) NH2-MOF-808s with TFA and OH on the Zr-nodes; (c) different MOF-808s which were activated from ethanol and water. (d) The pore size distributions of different MOF-808s.

concentrated HCl (2 vol%) to adjust the acidity. As a result, the synthesized MOF-808 in the presence of HCl showed high purity and identical BET area, and pore volume (**Figure 5**) to that synthesized in DMF. The same strategy was also used when synthesizing the MOF-808 by using acetic acid as the modulator. But in the case of trifluoroacetic acid, the optimum reaction condition is water and TFA mixture with a volume ratio of 10:5 and without any HCl. The difference between optimum condition for FA, AA, and TFA can be attributed to the different pKa values of these modulators. The pKa of TFA is 0.23, which is much lower than that of FA (3.74) and AA (4.74). Importantly, the synthesis conditions can be scaled-up to yield multi-gram MOF-808. The yields of conditions using FA, AA, and TFA are about 28, 30, and 49 g·L^{-1}·day^{-1}, respectively. These methods allowed us to prepare the MOF-808 in an eco-friendly, low-cost, and high efficient way (**Figure 3**).

During the formation of Zr-MOFs in the presence of modulators, the Zr^{4+} ions will usually be chelated by modulators to form the Zr$_6$-clusters. Then, the modulator will be replaced by organic ligands to construct the final frameworks. When the structural carboxylate on the Zr node

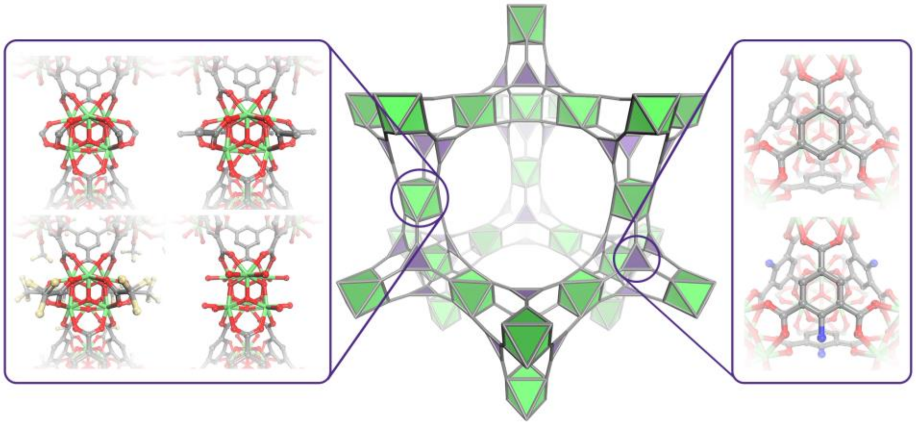

Figure 6. The structural illustration of MOF-808s with different attached molecules on the Zr-nodes and different organic ligands.

is lower than 12, the residual modulators stay on the Zr-node. In the structure of MOF-808, Zr-nodes have 6-structural carboxylate from the linkers while the remaining sites can be occupied by the modulators. We synthesized different MOF-808-modulator materials where FA, AA, or TFA attached to the Zr-node, named MOF-808-FA, MOF-808-AA, and MOF-808-TFA (**Figure 4 and 5**). According to the ^{1}H-NMR , the residue connected sites on the node of MOF-808 were occupied with modulators. Moreover, the attached modulators can be replaced by -OH/H_2O pair ligands. The MOF-808-OH was obtained by immersing the MOF-808-modulator samples in 1M HCl aqueous solution at 90 °C for 12h. Proved by ^{1}H-NMR data, the modulators were nearly completely removed.

In addition to the diversifying the Zr-nodes of MOF-808, we also functionalized the ligand of MOF-808. By mixing 2-aminobenzene-1,3,5-tricarboxylic aid (NH_2-BTC) with H_3BTC in the reaction system, NH_2-MOF-808-TFA was successfully synthesized. PXRD patterns proved that the synthesized amino-MOFs has an identical structure to that of MOF-808 (**Figure 4**). ^{1}H-NMR data showed that the molecular ratio of BTC and NH_2-BTC is 1/1.5. Moreover, the attached modulator can be also removed by the same procedure mentioned above to acquire NH_2-MOF-808-OH.

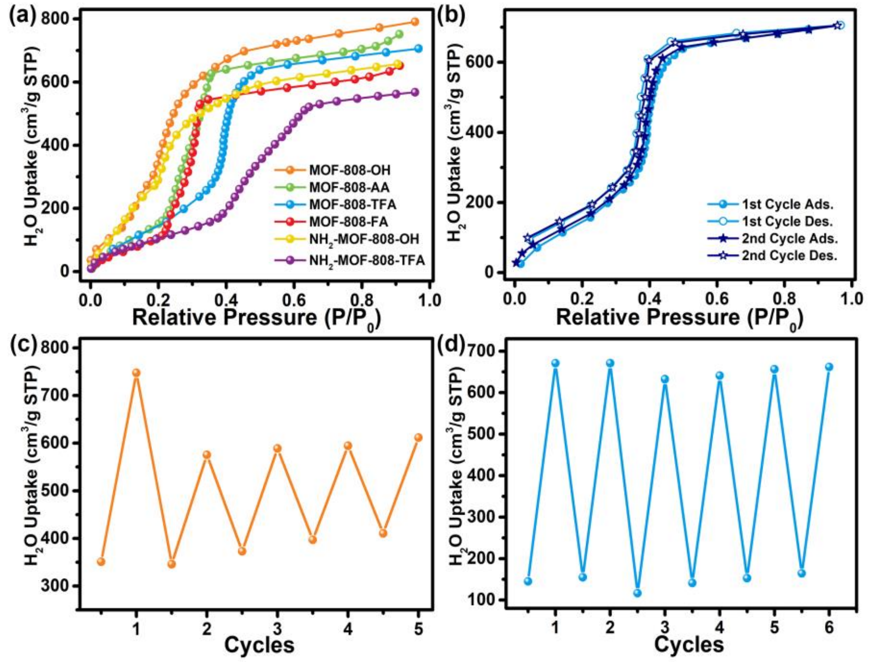

Figure 7. (a) The water adsorption curve of different MOF-808 samples. (b) Water isotherms of MOF-808-TFA with two cycles. (c) The cycle test of MOF-808-OH. (d) The cycle test of MOF-808-TFA.

Six kinds of MOF-808 (MOF-808-FA, MOF-808-AA, MOF-808-TFA, MOF-808-OH, NH_2-MOF-808-TFA, and NH_2-MOF-808-OH) with different pore environments were successfully designed and synthesized in aqueous solutions. Typically, to access the full porosity of a MOF, the activation (solvent removal) usually plays an important role. Traditionally, as-synthesized MOFs will be soaked in organic solvents to exchange the guest molecule from DMF to low boiling point solvents. This method usually produces large amount of organic solvents waste and thus increases the overall cost and waste. While traditional MOF-808 with the formic acid capped node shows major decrease in its porosity, MOF-808-TFA developed here maintained the full porosity, while MOF-808-AA showed a minor decrease (**Figure 5c**). This phenomena can be explained by the different pore environments of different MOF-808 since TFA is the most hydrophobic one, which can protect the Zr-node by preventing water cluster formation. For the MOF-808-FA, MOF-808-AA, and MOF-808-OH, water had to be exchanged with solvent to maintain the porosities. To insist on the cheap and green synthetic concept, we used ethanol which is the greenest organic solvent to activate the samples. Instead of long-time soaking, we found only a three-time quick wash with ethanol is enough to fully transfer the guest molecules from water to ethanol. Thus, the activation of MOF-808 samples only costs several times of wash by water and a quick wash by a very small amount of ethanol.

The pore environments of different MOF-808 samples was also show cased by water isotherms. As shown in **Figure 7a**, MOF-808 with different modulators and ligands showed different shapes of isotherms and condensation pressures. Since the modulators are directly the pointed into the pore of MOF-808, the hydrophilicity of the attached molecules on the Zr-nodes effects the hydrophilicity of the frameworks. Among all samples, the -OH/H_2O capped nodes are the most hydrophilic molecules, as a result, the MOF-808-OH showed the lowest condensation pressure. Meanwhile, the amount of captured water before condensation of MOF-808-OH is also the highest. On the other hand, the MOF-808-TFA has the highest condensation pressure confirming its hydrophobicity. In comparison, the MOF-808-FA and MOF-808-AA showed similar condensation points, which suggested similar hydrophilicity. For the NH_2-MOF-808, the amine group had minimal effect on the hydrophilicity of the frameworks since it resides on the same plane of BTC linker, thus not pointing into the pore.. So, we postulated that the influence of amine groups was diminished by its location in the structure.

Intrigued by these results, we investigated the water cyclability using single point isotherms to establish the stability of these frameworks. We postulated that MOF-808-TFA would be perform well since it can maintain the porosity after direct activation from water. As proved by the water isotherms (**Figure 7b**), the MOF-808-TFA showed nearly identical capacity for multiple cycles while MOF-808-OH showed nearly 30% decrease after the first cycle (**Figure 7c**).

Study 3: Benign Integration of a Zn-Azolate Metal–Organic Framework onto Textile Fiber

In the earlier years of the program, we have demonstrated the synthesis of carboxylate (a hard Lewis base) and Zr^{4+}, Fe^{3+} (hard Lewis acids) based MOFs which resulted in the chemically robust MOFs. Later, we developed stable MOFs based on soft Lewis bases (i.e azolates) and soft Lewis acids (i.e. Zn^{2+}, Co^{2+}). **Figure 8** shows the structure of an archetypal metal-azolate MOF, MFU-4. This MOF presents high chemical and thermal stability. We herein report a benign procedure to synthesize a Zn-azolate metal–organic framework (MOF), MFU-4, for NH_3 capture. The surface area and morphology of MFU-4 obtained in alcohol solvents at room temperature is consistent with that of traditionally synthesized MFU-4 in N,N-dimethylformamide at 140 °C. In addition to its large NH3 uptake capacity at 1 bar (17.7 mmol/g), MFU-4 shows outstanding performance in

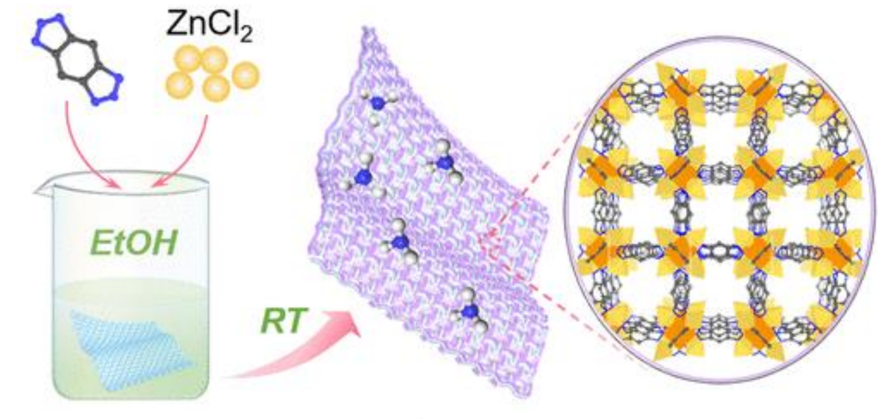

Figure 8. Schematic representation of MFU-4 synthesis and its incorporation on textile fibers.

capturing NH3 at low concentration (10.8 mmol/g at 0.05 bar). Furthermore, the mild synthetic conditions implemented make it facile to immobilize MFU-4 onto cotton textile fiber. Enhanced NH_3 capture ability of the MFU-4/fiber composite was also attributed to the well-exposed MOF particles. The benign synthetic MFU-4 procedure, high NH3 uptake, and easy integration onto fiber pave the way toward implementation of similar materials in PPE.

Study 4: Benign Synthesis and Modification of a Large Pore and High Surface Area Zn–Azolate Metal–Organic Framework

After we have shown that MFU-4 can be synthesized under mild conditions, we turned our interest into other Zn-azolate based MOF systems since MFU-4's ultra small micropores makes it challenging to use it for DoD related catalytic applications such as hydrolysis of organophosphorous chemicals. MFU-4l, an isoreticular expansion of MFU-4 (MFU denoting metal–organic framework Ulm University), is constructed from $[Zn_5Cl_4]^{6+}$ building units and $BTDD^{2-}$ (H_2BTDD = bis(1*H*-1,2,3-triazolo[4,5-*b*],[4′,5′-*i*])dibenzo-[1,4]-dioxin) ligands (**Figure 9a**). Commonly used synthetic procedures for MFU-4l require the use of toxic, flammable solvents such as DMF at high temperatures, which lead to environmental, safety, and economic concerns. Therefore, we elected to develop a more mild synthetic method to yield the MFU-4l framework. Here, MFU-4l powder can be obtained in EtOH at 60 °C with triethylamine (TEA) as a modulator. As shown in **Figure 9b**, the PXRD pattern of EtOH-synthesized MFU-4l matched well with the simulated pattern. Moreover, the N_2 adsorption capacity (at 77 K) and DFT pore size distribution of MFU-4l-EtOH featured as 900 cm^2/g and ~15 Å, respectively, in good agreement with that synthesized in DMF (**Figure 9c**). The yielded MFU-4l-EtOH has smaller particles, which increased its catalytic activity in solid phase degradation of DMNP at 70% RH is twice as much as that of MFU-4l-DMF. Besides, the hydrolysis of DMNP was continued even under a low humidity (RH = 30%). After treating MFU-4l with base, the obtained MFU-4l-(OH) exhibited a steep NH_3 uptake at 0.1 bar. In contrast, the sharp NH_3 uptake of MFU-4l occurred at 0.22 bar. The increased low-pressure affinity is attributed to the high affinity between –OH ligands and NH_3, indicated through the *in situ* NH_3 FT-IR spectra of MFU-4l and MFU-4l-(OH). With the impressive performance in degrading DMNP and high NH_3 uptake at low pressure, MFU-4l, and MFU-4l-(OH) are promising materials for a myriad of personal protective equipment applications while offering mild synthetic conditions.

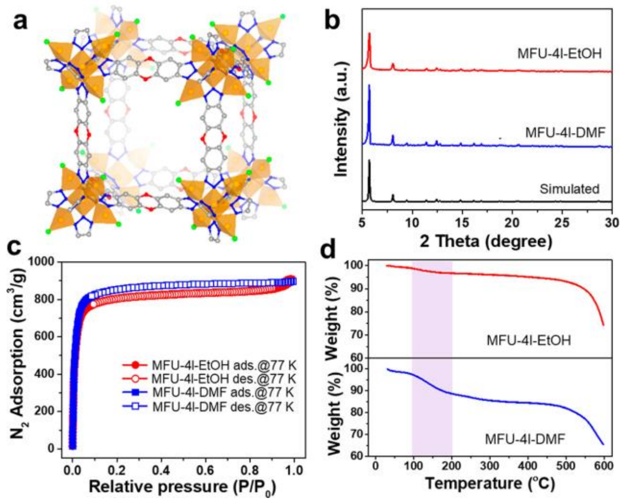

Figure 9. Structure and characterization of MFU-4l. (a) Structural illustration of MFU-4l. Zn, yellow; C, gray; N, blue; O, red; Cl, green. (b) PXRD patterns, (c) N_2 adsorption/desorption isotherms, and (d) TGA of MFU-4l synthesized in EtOH and DMF, respectively.

Study 5: Phosphonate-Based Metal–Organic Frameworks Synthesized in Aqueous Media

In addition to carboxylate and azolate based frameworks, we have also studied the phosphonate based ligands to build MOFs in water. Here, we also utilized a very affordable industrial chemical, glyphosate, as a starting material. Importantly, glyphosate solidifies as N,N′-diphosphono-methyl-2,5-piperazinedione (dpmp) at high temperatures where dpmp is a robust building block due to the cyclic central ring. Therefore, we undertook a proof-of-concept study to demonstrate the assembly of MOFs where building units are first formed in situ from glyphosate.

We report the aqueous synthesis of two new phosphonate-based MOFs comprising glyphosate linkers, [Mg(dpmp)]·2H2O (Mg-NU-225) and [Fe(dpmp)]·2H2O (Fe-NU-225), (dpmp = N,N′-diphosphonomethyl-2,5-piperazinedione)(**Figure 10**). Single crystals grown from the reaction of metal fine powder or a metal salt and glyphosate in aqueous solution. Using one-pot synthesis conditions at pH 3.0, we obtained crystalline materials in high yields. The colorless diamond shaped plate-like crystals of Mg-NU-225 and Fe-NU-225 were obtained after 2 days.

Single crystal X-ray diffraction measurements revealed that both frameworks display a two-dimensional layered structure with a cyclic ring ligand which forms in situ from the condensation of two glyphosate molecules (**Figure 10b**). Under humid conditions and over a wide temperature range, water molecules are trapped between adjacent layers and facilitate rapid proton conduction. Mg-NU-225 and Fe-NU-225 recorded proton conductivities of 1.5×10^{-5} and 1.7×10^{-5} S cm^{-1}, respectively, along the plane direction and 1.6×10^{-3} and 9.1×10^{-5} S cm^{-1} perpendicular to the plane direction at 55 °C and 95% relative humidity, as confirmed by two-contact probe impedance methods. The mechanism of proton transport was found to be that of the Grotthuss model from the low activation energy for proton hopping.

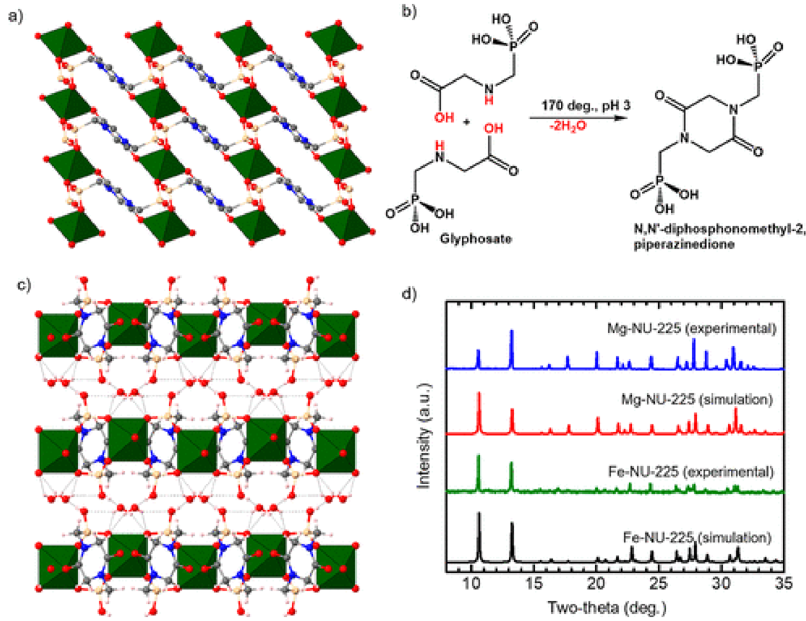

Figure 10. (a) Two-dimensional layered structure of Mg-NU-225 and Fe-NU-225 as viewed from top. (b) Schematic representation of the formation of the cyclic ring of *N*,*N*′-diphosphonomethyl-2,5-piperazinedione (dpmp) from two glyphosate molecules at elevated temperature and pH 3.0. (c) (d) PXRD patterns of Fe-NU-225 (simulated, black; as-synthesized, green) and Mg-NU-225 (red, simulated; as-synthesized, blue).

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Awards:

- "Top 100 World's Most Highly-Cited Chemists, Farha is #35" (Research.com, **2022**)
- "Highly Cited Researchers in Chemistry" (Clarivate Analytics, **2021**)
- Inaugural recipients of the American Association for Advances in Functional Materials (AAAFM)-Stoddart award (UCLA, **2021**)
- 2021 Barrer Lectureship (Pennsylvania State University, **2021**)
- "Highly Cited Researchers in Chemistry" (Clarivate Analytics, **2020**)
- Elected as Fellow of the Academy of Arab Scientists, **2020**
- 2020 ACS ENFL Emerging Researcher Award, **2020**
- Appointed to the Dow Chemical Company Research Professorship in Chemistry, **2020**
- Elected as Foreign Fellow of the European Academy of Sciences (EurASc), **2020**
- Kuwait Prize – Applied Sciences (Kuwait Foundation for the Advancment of Science, **2019**
- "Highly Cited Researchers in Chemistry" (Clarivate Analytics, **2019**)
- JSCC International Award for Creative Work (Japan Society of Coordination Chemistry, **2019**)

Talks:

- "Smart and Programmable Sponges for protection From Bench to Market," Tulane University, New Orleans, Louisiana, November 8, **2021**. *Virtual.* Invite
- "Smart and Programmable Sponges for protection From Bench to Market," *Chemistry Department's Graduate Student-Invited Seminar*, Colorado School of Mines, October 15th, **2021**. Invite
- "Smart, Crystalline, and Programmable Sponges for protection From Bench to Market," 2021 AAFM-UCLA International Conference on Advances in Functional Materials, August 18-20th, **2021**. *Virtual.* Award Talk
- "Smart and Programmable Sponges for protection From Bench to Market," Solid-State Science & Research, June 10-11, **2021**. *Virtual.* Plenary
- "Programmable and Smart Sponges for Protection," Clemson University, Clemson, South Carolina, November 5, **2020**. *Virtual.* Invite
- "Programmable and Smart Sponges for Protection," *Royal Society of Chemistry Porous Materials Group Online Webinar*, November 3, **2020**. *Virtual.* Invite
- "New Challenges Require New Materials: Smart and Programmable Sponges," Northwestern University Materials Research Science and Engineering Center, Northwestern University, Evanston, Illinois, July 7, **2020**. *via zoom.* Invite
- "Smart and Programmable Sponges from Design and Synthesis to Implementation," Micromeritics, July 7, **2020**. *webinar.* Invite
- "Design & Synthesis of Crystalline Smart Programmable Sponges," Energy Frontier Research Centers - MUSE, University of Utah, Salt Lake City, Utah, June 24, **2020**. *via zoom.* Invite
- "Programmable Smart Sponges," Crystal Engineering and Emerging Materials

- Workshop of Ontario and Quebec (CEMWOQ), May 30-31, **2020**. *via zoom.* Opening Talk
- "Programmable Smart Sponges," University of Houston, Houston, Texsas, April 28, **2020**. *via zoom.* Invite
- "Programmable Smart Sponges," *Molecular and Materials for Solar Fuel*, Pittcon, Chicago, March 5, **2020**. Invite
- "Programmable Smart Sponges," University of Washington, Seattle, Washington, February 25, **2020**. Invite
- "Programmable Smart Sponges," ACS Chicago Section, Chicago, Illinois, February 22, **2020**. Invite
- "Programmable Smart Sponges," University of Texas, Dallas, Texas, February 8, **2020**. Invite
- "Programmable Smart Sponges," University of Kuwait, Kuwait, February 3, **2020**. Invite
- "Design & Synthesis of Crystalline Smart Programmable Sponges," Advanced Membrane Workshop, University of Pennsylvania, Phalidelphia, Pennsylvania, December 16-18, **2019**. Invite