REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
13-03-2023	Final Report	1-Sep-2018 - 31-Jul-2022

4. TITLE AND SUBTITLE
Final Report: Dynamics of Nanoscale Self-Assembled Porous Materials

5a. CONTRACT NUMBER
W911NF-18-1-0359

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611102

6. AUTHORS

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
University of California - San Diego
Office of Contract & Grant Adm
9500 Gilman drive, MC 0934
La Jolla, CA 92093 -0934

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
72967-SM.9

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Francesco Paesani
UU	UU	UU	UU		19b. TELEPHONE NUMBER 858-822-3383

RPPR Final Report
as of 24-May-2023

Agency Code: 21XD

Proposal Number: 72967SM **Agreement Number: W911NF-18-1-0359**
INVESTIGATOR(S):

Name: Francesco Paesani
Email: fpaesani@ucsd.edu
Phone Number: 8588223383
Principal: Y

Organization: **University of California - San Diego**
Address: Office of Contract & Grant Adm, La Jolla, CA 920930934
Country: USA
DUNS Number: 804355790 EIN: 956006144

Report Date: 31-Oct-2022 Date Received: 13-Mar-2023
Final Report for Period Beginning 01-Sep-2018 and Ending 31-Jul-2022
Title: Dynamics of Nanoscale Self-Assembled Porous Materials
Begin Performance Period: 01-Sep-2018 **End Performance Period:** 31-Jul-2022
Report Term: 0-Other

Submitted By: Francesco Paesani Email: fpaesani@ucsd.edu
Phone: (858) 822-3383

Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 0 **STEM Participants:** 5

Major Goals: 1) To observe and theoretically model the formation of MOFs. The kinetics, and hence mechanistic details, of MOF formation are presently not well understood. It is not known whether identical, similar, or completely different mechanisms are engaged in the synthesis of different MOFs. Using in situ TEM and newly developed approaches for initiating reactions in the TEM using a precision robotic picoliter dispensing technology, we will map the kinetic landscape for the growth of several canonical MOFs. In situ TEM provides the ability to monitor these processes on the nanoscale in real time.
2) To observe and develop theoretical models for the expansion of MOFs by postsynthetic exchange (PSE). Several studies have shown that organic linkers in MOFs can undergo exchange with longer ligands via a postsynthetic exchange (PSE) process. However, little is known about how this PSE process occurs and what, if any, strains, dynamics, or intermediates occur in the MOF lattice during these processes. These exchange processes can ultimately produce crystalline materials with cell/lattice constants many times larger than the parent material. In this objective in situ TEM will be used to examine extended linker PSE in a model MOF system to gain deep insight into the details of this unusual solid-state process.
3) To observe and develop theoretical models for the formation and morphology of polyMOFs. Our team has pioneered the development of a new class of polymer-MOF hybrid material termed ‘polyMOFs’. polyMOFs are porous solids that recapitulate the framework structure of MOFs but are formed from polymeric ligands rather than from discrete small molecule organic linkers. The resulting polyMOF materials share a topological relationship with MOFs (e.g. near-identical X-ray diffraction patterns) but are completely distinct morphologically. Unlike MOFs, which generally form microcrystalline solids, polyMOFs exhibit a wide range of distinctive morphologies including clusters, films, and fractal-like habits.

Accomplishments: See attached report.

Training Opportunities: Throughout this program, students and researchers have had numerous training opportunities. Participants have received training in a wide range of techniques, including chemical synthesis, spectroscopic methods, X-ray diffraction, TEM imaging, and the like. Researchers have also received thorough training in laboratory safety and research ethics. Formal class instruction, such as courses on powder X-ray diffraction, have been included as part of the training for some researchers. Participants have attended workshops and meetings, including those organized by the ARO, the MOF2018 conference, EuroMOF2019 and regional and national American Chemical Society meetings. Professional development and networking opportunities have been made available to trainees on this award. Several trainees have been recognized with honors and awards, including numerous poster and presentation awards from symposia, department and society accolades, an sponsored fellowships (NDSEG, ARCS, etc.).

Results Dissemination: Eight published manuscripts in top journals and additional manuscripts, as well as dozens of conference/symposia abstracts, talks, and presentations.

Honors and Awards: Trainee Dr. Kyle Bentz was the recipient of a Cottrell Fellowship from the Research Corporation for Scientific Advancement (RCSA).

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Prantik Mondal
Person Months Worked: 11.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Grant Domecus
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

ARTICLES:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of the American Chemical Society
Publication Identifier Type: DOI Publication Identifier: 10.1021/jacs.9b01789
Volume: 141 Issue: 15 First Page #: 6146
Date Submitted: 5/19/19 12:00AM Date Published: 3/1/19 4:00PM
Publication Location:
Article Title: Interrogating Kinetic versus Thermodynamic Topologies of Metal–Organic Frameworks via Combined Transmission Electron Microscopy and X-ray Diffraction Analysis
Authors: Xinyi Gong, Hyunho Noh, Nathan C. Gianneschi, Omar K. Farha
Keywords: MOFs, TEM, crystallization
Abstract: Synthetic protocols that preferentially result in metal–organic framework (MOF) crystallization of one topology over another remain an elusive, empirical process. This is primarily because of a lack of fundamental insights into MOF crystal growth and the effect of various experimental parameters on the resulting topologies. In this Communication, we demonstrate the temperature–topology relationship of MOFs constructed from hexanuclear oxozirconium cluster nodes and tetrakis(4-carboxylphenyl)porphyrin linkers via a combined transmission electron microscopy and powder X-ray diffraction study. Synthesis at room temperature led to a mixed phase consisting of 12-connected (assuming no defects) MOF-525 and 6-connected PCN-224, possessing ftw and she topologies, respectively. When the temperature was raised to 145 °C, 8-connected PCN-222 (csq topology) was found, with a possible concurrence of another 8-connected NU-902 (scu topology) and 12-connected PCN-223 (shp topology)...
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

RPPR Final Report
as of 24-May-2023

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of the American Chemical Society
Publication Identifier Type: DOI Publication Identifier: 10.1021/jacs.9b04586
Volume: 141 Issue: 26 First Page #: 10177
Date Submitted: 8/28/19 12:00AM Date Published: 6/1/19 4:00AM
Publication Location:
Article Title: Elucidating the Growth of Metal–Organic Nanotubes Combining Isoreticular Synthesis with Liquid-Cell Transmission Electron Microscopy
Authors: Kristina M. Vailonis, Karthikeyan Gnanasekaran, Xian B. Powers, Nathan C. Gianneschi, David M. Jenk
Keywords: nanotubes, TEM, crystal growth
Abstract: Metal–organic nanotubes (MONTs) are tunable porous 1D materials that are envisioned to be complementary to carbon nanotubes for anisotropic applications. To date, characterization of MONTs relies on single crystal X-ray diffraction (SCXRD) to determine structure and composition. This requires crystals on the micrometer regime, effectively rendering bulk 3D materials. By tracking the growth of a MONT as a function of time with liquid-cell transmission electron microscopy (LCTEM), TEM, and SCXRD, it was possible to ascertain that the material in the bulk phase matches the nanomaterial in terms of molecular structure. This result allowed for the first measurements of finite bundles of MONTs on the nanometer scale. By employing in situ LCTEM, a time course of the formation of small bundles of MONTs could be acquired which provided mechanistic information on MONT formation which is of utility in reaction optimization and applications development.
Distribution Statement: 2-Distribution Limited to U.S. Government agencies only; report contains proprietary info
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Chemical Science
Publication Identifier Type: DOI Publication Identifier: 10.1039/D0SC03651J
Volume: 11 Issue: First Page #: 10523
Date Submitted: 8/17/21 12:00AM Date Published:
Publication Location:
Article Title: Inside polyMOFs: Layered Structures in Polymer-Based Metal-Organic Frameworks
Authors: Kyle C. Bentz, Karthikeyan Gnanasekaran, Jake B. Bailey, Sergio Ayala Jr., F. Akif Tezcan, Nathan C. (
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.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

RPPR Final Report
as of 24-May-2023

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of the American Chemical Society
Publication Identifier Type: DOI Publication Identifier: 10.1021/jacs.0c08773
Volume: 142 Issue: 41 First Page #: 17224
Date Submitted: 8/17/21 12:00AM Date Published: 9/1/20 7:00AM
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: TEM, MOFs
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.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: ACS Nano
Publication Identifier Type: DOI Publication Identifier: 10.1021/acsnano.0c03209
Volume: 14 Issue: 7 First Page #: 8735
Date Submitted: 8/17/21 12:00AM Date Published: 6/1/20 7:00AM
Publication Location:
Article Title: Monitoring of the Seeding and Growth of Silver Metal–Organic Nanotubes by Liquid-Cell Transmission Electron Microscopy
Authors: Karthikeyan Gnanasekaran, Kristina M. Vailonis, David M. Jenkins, Nathan C. Gianneschi
Keywords: MONT, TEM, self-assembly
Abstract: Metal-organic nanotubes (MONTs) are highly ordered one-dimensional crystalline porous frameworks. Despite being nanomaterials, virtually all studies of MONTs rely on characterization of the bulk crystalline material (micron-sized) by single-crystal X-ray diffraction. For MONTs to achieve their raison d'être as tunable one-dimensional nanomaterials, individual tubes or small finite bundles of tubes must be synthesized and characterized. Therefore, to directly observe their formation under a variety of reaction conditions in solution, we employ liquid-cell transmission electron microscopy (LCTEM), which allows the early stages of MONT assembly to be monitored in real time. Notably, changing the metal-to-ligand ratio alters the local concentrations of reactant monomers, resulting in multiple nucleation and growth pathways and diverse morphologies at the nanoscale. These various initial seeds grow to form the same nanocrystalline needle phase.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

RPPR Final Report
as of 24-May-2023

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of the American Chemical Society
Publication Identifier Type: DOI Publication Identifier: 10.1021/jacs.0c11266
Volume: 143 Issue: 3 First Page #: 1503
Date Submitted: 8/17/21 12:00AM Date Published: 1/1/21 8:00AM
Publication Location:
Article Title: Transient Catenation in a Zirconium-Based Metal–Organic Framework and Its Effect on Mechanical Stability and Sorption Properties
Authors: Lee Robison, Xinyi Gong, Austin M. Evans, Florencia A. Son, Xingjie Wang, Louis R. Redfern, Megan C
Keywords: TEM, MOF
Abstract: Interpenetration of two or more sublattices is common among many metal?organic frameworks (MOFs). Herein, we study the evolution of one zirconium cluster-based, 3,8-connected MOF from its non-interpenetrated (NU-1200) to interpenetrated (STA-26) isomer. We observe this transient catenation process indirectly using ensemble methods, such as nitrogen porosimetry and X-ray diffraction, and directly, using high-resolution transmission electron microscopy. We developed a post-processing script, which automatically rasters a small region-of-interest across an image, extracts the Fourier transform of that sub-image, and then assigns the dominant interpenetration within that region based on the relative intensity ratios of the FFT (Figure 7). This method allows us to spatially resolve the interpenetration of entire crystallites across a series of images.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of the American Chemical Society
Publication Identifier Type: DOI Publication Identifier: 10.1021/jacs.0c00542
Volume: 142 Issue: 10 First Page #: 4609
Date Submitted: 8/17/21 12:00AM Date Published: 2/1/20 8:00AM
Publication Location:
Article Title: Phase Transitions in Metal–Organic Frameworks Directly Monitored through In Situ Variable Temperature Liquid-Cell Transmission Electron Microscopy and In Situ X-ray Diffraction
Authors: Jiafei Lyu, Xinyi Gong, Seung-Joon Lee, Karthikeyan Gnanasekaran, Xuan Zhang, Megan C. Wasson, X
Keywords: TEM, MOF, phase transition
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.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

RPPR Final Report
as of 24-May-2023

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of the American Chemical Society
Publication Identifier Type: DOI Publication Identifier: 10.1021/jacs.7b10453
Volume: 140 Issue: 4 First Page #: 1348
Date Submitted: 8/17/21 12:00AM Date Published: 1/1/18 8:00AM
Publication Location:
Article Title: Transmission Electron Microscopy Reveals Deposition of Metal Oxide Coatings onto Metal–Organic Frameworks
Authors: Michael S. Denny, Lucas R. Parent, Joseph P. Patterson, Santosh Kumar Meena, Huy Pham, Patricia A
Keywords: MOF, TEM, PSE
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.

Acknowledged Federal Support: **Y**

Partners

,

I certify that the information in the report is complete and accurate:
Signature: Francesco Paesani
Signature Date: 3/13/23 11:50AM

Grants Agreement Award#: W911NF-18-1-0359

Final Progress Report for the period of September 1, 2018 and ending August 31, 2021
(***No-cost Extension final period of performance July 31, 2022***)

The Chemistry of Metal-Organic Frameworks Captured by STEM Elemental Analysis and Gas Phase in situ ETEM

RDRL-ROS-I Proposal Number: 72967-CH

Submitted to,
Army Research Office

By,
The University of California, San Diego

Principle Investigator:
Francesco Paesani, Dept. Chemistry & Biochemistry, U.C. San Diego
Tel: (858)-822-3383, E-mail: fpaesani@ucsd.edu

Co-PI:
Nathan C. Gianneschi, Chemistry (Northwestern U.),
nathan.gianneschi@northwestern.edu

August 31, 2021

Abstract

Metal-organic frameworks (MOFs) are self-assembled networks of inorganic nodes (metal ions or metal ion clusters often referred to as secondary building units, SBUs) bridged by multitopic organic ligands (i.e. linkers). MOFs are highly porous materials and are highly tunable by pre- or post-synthetic methods. MOFs have attracted great attention as materials for gas storage, separation, catalysis, and other uses. To date, there have been few studies on MOF formation, partly due to difficulties in analyzing the formation of the particles as they assemble and precipitate from solution, leaving a large gap in the understanding of mechanisms underlying the formation of these important materials such as how to precisely control and tune the porosity or final morphology. It is of course, precisely these properties of the materials that make them important and interesting. However, the precise mechanisms that govern MOF formation and their resulting structures are largely unknown.

The goal of this research program is to gain a deep mechanistic understanding of the dynamics and assembly of porous, self-assembled materials, with a focus on metal-organic frameworks (MOFs). The primary analytical tool in this program will be a variety of transmission electron microscopy (TEM) techniques including environmental (ETEM), in situ liquid cell (LCTEM), analytical TEM such as electron energy loss spectroscopy, energy dispersive spectroscopy, and other related methods that allow for the study of these materials in real time and in the presence of gases or liquids. It should be noted that these TEM methods themselves are highly innovative and cutting-edge, such that the methods developed and used in this program will enable the study of other porous materials, such as covalent-organic frameworks (COFs) and porous aromatic frameworks (PAFs). The data obtained in these experiments will be performed in parallel with theoretical modeling using both atomistic and coarse-grained (CG) molecular dynamics (MD) simulations to identify the structure of the materials, determine molecular driving forces, and elucidate underlying molecular mechanisms. Such studies will give unparalleled information about the fundamental mechanisms of formation, and the behavior of individual particles, information that can be used toward the development of specifically optimized functional MOFs.

Objectives

1) To observe and theoretically model the formation of MOFs. The kinetics, and hence mechanistic details, of MOF formation are presently not well understood. It is not known whether identical, similar, or completely different mechanisms are engaged in the synthesis of different MOFs. Using in situ TEM and newly developed approaches for initiating reactions in the TEM using a precision robotic picoliter dispensing technology, we will map the kinetic landscape for the growth of several canonical MOFs. In situ TEM provides the ability to monitor these processes on the nanoscale in real time.

2) To observe and develop theoretical models for the expansion of MOFs by postsynthetic exchange (PSE). Several studies have shown that organic linkers in MOFs can undergo exchange with longer ligands via a postsynthetic exchange (PSE) process. However, little is known about how this PSE process occurs and what, if any, strains, dynamics, or intermediates occur in the MOF lattice during these processes. These exchange processes can ultimately produce crystalline materials with cell/lattice constants many times larger than the parent material. In this objective in situ TEM will be used to examine extended linker PSE in a model MOF system to gain deep insight into the details of this unusual solid-state process.

3) To observe and develop theoretical models for the formation and morphology of polyMOFs. Our team has pioneered the development of a new class of polymer-MOF hybrid material termed 'polyMOFs'. polyMOFs are porous solids that recapitulate the framework structure of MOFs but are formed from polymeric ligands rather than from discrete small molecule organic linkers. The resulting polyMOF materials share a topological relationship with MOFs (e.g. near-identical X-ray diffraction patterns) but are completely distinct morphologically. Unlike MOFs, which generally form microcrystalline solids, polyMOFs exhibit a wide range of distinctive morphologies including clusters, films, and fractal-like habits.

Training

Throughout this program, students and researchers have had numerous training opportunities. Participants have received training in a wide range of techniques, including chemical synthesis, spectroscopic methods, X-ray diffraction, TEM imaging, and the like. Researchers have also received thorough training in laboratory safety and research ethics. Formal class instruction, such as courses on powder X-ray diffraction, have been included as part of the training for some researchers. Participants have attended workshops and meetings, including those organized by the ARO, the MOF2018 conference, EuroMOF2019 and regional and national American Chemical Society meetings. Professional development and networking opportunities have been made available to trainees on this award. Several trainees have been recognized with honors and awards, including numerous poster and presentation awards from symposia, department and society accolades, an sponsored fellowships (NDSEG, ARCS, etc.).

Results Published Under Funding from Award

1. Insights into the Structure and Dynamics of Metal–Organic Frameworks via Transmission Electron Microscopy

Published Citation: Xinyi Gong, Karthikeyan Gnanasekaran, Zhijie Chen, Lee Robison, Megan C. Wasson, Kyle C. Bentz, Seth M. Cohen, Omar K. Farha, and Nathan C. Gianneschi, "Insights into the Structure and Dynamics of Metal–Organic Frameworks via Transmission Electron Microscopy" *J. Am. Chem. Soc*. **2020**, *142*, 17224-17235.

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.

Summary: This review article prepared by our team highlighted our advancements and those by other research teams in the use of TEM in examining MOFs and MOF-related materials. Many of the accomplishments from this continuing award were highlighted, as well as future goals and challenges in the field (Figure 1).

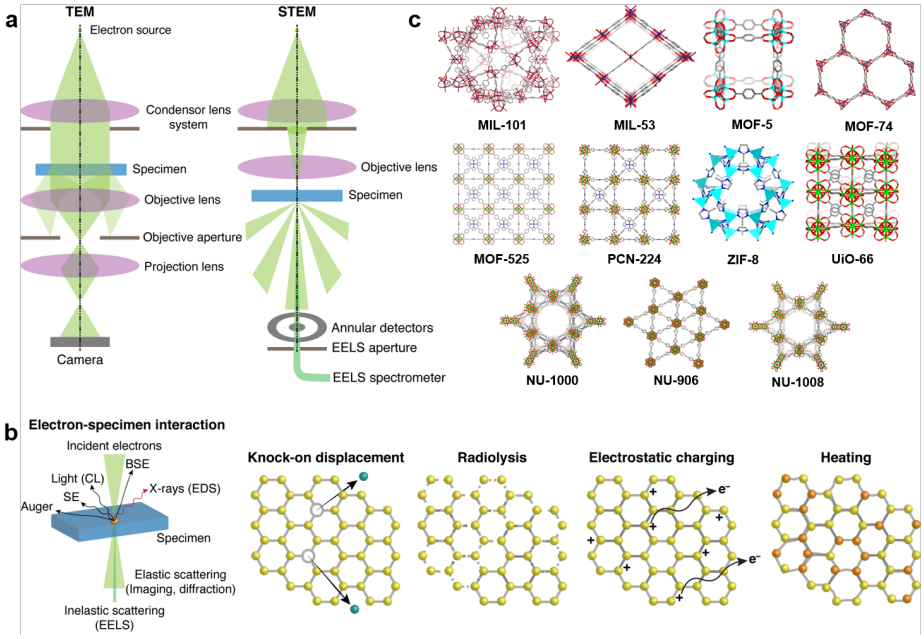

Figure 1. (a) Schematic illustration of electron beam path in TEM and STEM modes. (b) Electron-specimen interaction and beam damages. EELS, EDS, CL, SE, and BSE refer to electron energy loss spectroscopy, energy dispersive X-ray spectroscopy, cathodo-luminescence, secondary electron, and back scattering electron, respectively. (c) MOF crystal structures discussed in this perspec-tive. Atom color scheme: Zr, green; Cr, purple; Zn, turquoise; Mg, blue gray; C, grey; O, red; N, blue; Br, yellow, Pt, plum. H atoms are omitted for clarity.

2. Looking Inside polyMOFs: Revealing the Structural Interior of Polymer-Based Metal-Organic Frameworks

Published Citation: Kyle C. Bentz, Karthikeyan Gnanasekaran, Jake B. Bailey, Sergio Ayala Jr., F. Akif Tezcan, Nathan C. Gianneschi, and Seth M. Cohen, "Inside polyMOFs: Layered Structures in Polymer-Based Metal-Organic Frameworks" *Chem. Sci.,* **2020**, *11*, 10523-10528.

Abstract: In this report, we explore the internal structural features of polyMOFs consisting of equal mass ratios of metal-coordinating poly(benzenedicarboxylic acid) blocks and non-coordinating poly(ethylene glycol) (PEG) blocks. The studies reveal alternating lamellae of metal-rich, crystalline regions and metal-deficient non-crystalline polymer, which span the length of hundreds of nanometers. Polymers consisting of random PEG blocks, PEG end-blocks, or non-coordinating poly(cyclooctadiene) (COD) show similar alternation of metal-rich and metal-deficient regions, indicating a universal self-assembly mechanism. A variety of techniques were employed to interrogate the internal structure of the polyMOFs, including transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and small-angle synchrotron X-ray scattering (SAXS). Independent of the copolymer architecture or composition, the internal structure of the polyMOF crystals showed similar lamellar self-assembly at single-nanometer length scales.

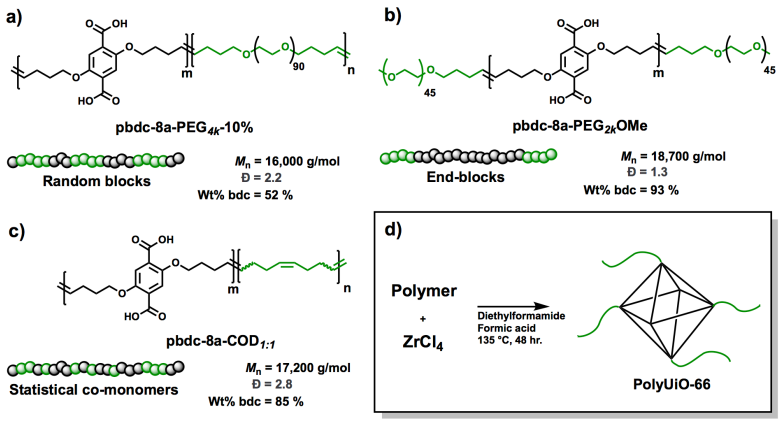

Figure 2. Schematic representation of polymers used in this study with names, molecular weights, dispersities, and weight percent of ligand block pbdc-8a. a) Random block polymer, b) end-blocks, and c) statistical copolymers. d) Synthesis conditions for conversion of copolymer ligands to polyUiO-66.

Summary: In this study, polyMOFs constructed from polymers containing poly(benzenedicarboxylic acid) with both non-coordinating blocks located in the interior, termini, and containing statistical copolymers (Figure 2) were studied by advanced imaging methods. A universal feature is observed in these materials wherein alternating lamellae of crystalline, metal-rich and non-crystalline metal-deficient domains are formed (Figure 3). The PEG and polyCOD chains are excluded from the crystalline domains because the polyMOF pore interior is unable to accommodate non-metal coordinated polymer. We hypothesize that lamellae are the preferred morphology due to the polyMOF structure, which prefers to form highly faceted morphologies. In general, the bulk crystal morphologies in the PEG-containing systems are highly faceted, and correspondingly, the interior morphology of the self-assembled lamellae display the lowest degree of

curvature. In contrast, the polyCOD system displays bulk morphologies that are the most spherical and thus the corresponding lamellae have the highest degree of curvature among the systems examined in this study. Furthermore, there appears to be a general preference in these specific systems for lamellae thickness on the single nanometer length scale (Figure 3), likely due to the roughly similar overall molecular weight of the polymers used to construct the polyMOFs. It is likely that higher molecular weight non-coordinating blocks would lead to correspondingly larger distances between layers. However, the polymer architecture plays an important role in the organization of the lamellae. These results contrast with thin films of polyUiO-66 from homo-pbdc-8a (single-block polymer) that, unlike all of the copolymer systems, no self-assembled lamellae are observed.

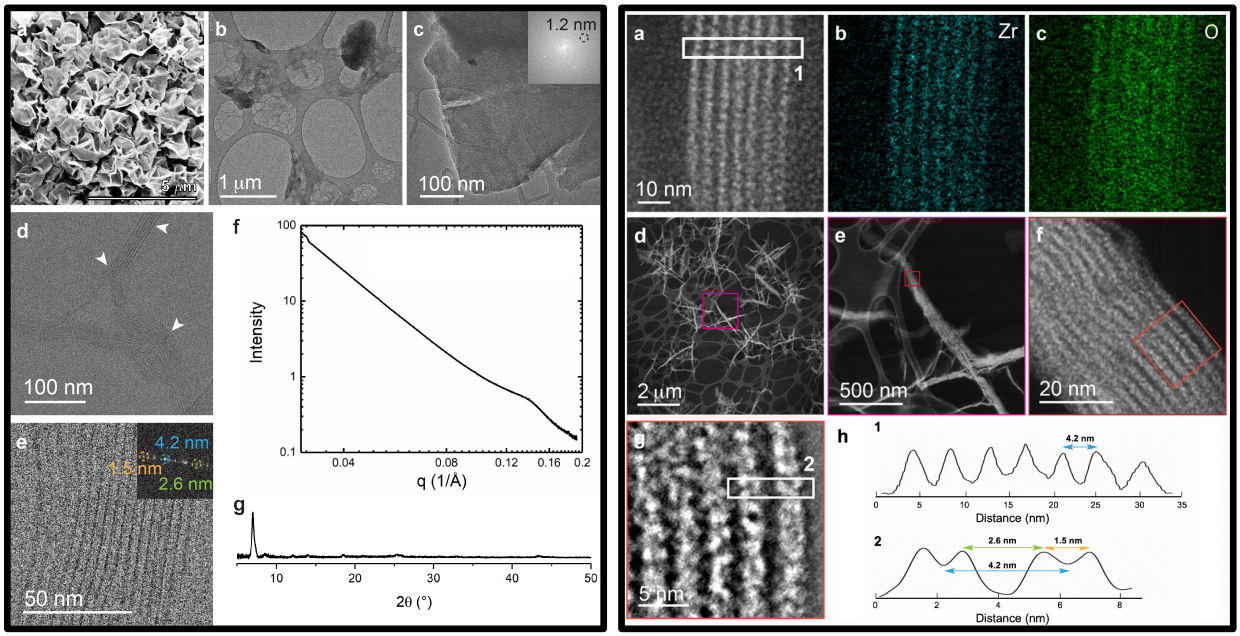

Figure 3. ***Left Panel:*** Morphological analysis of polyUiO-66 derived from pbdc-8a-PEG: a) SEM of bulk crystals; b, c) TEM of bulk crystals. Inset shows the spacing corresponds to UiO-66 crystals; d, e) TEM of ultramicrotomed section revealing the layered morphology of polyUiO-66 (white arrows in (d) denote layered assemblies); f) SAXS scattering profile of the bulk crystals showing a spacing at 4.5 nm; g) PXRD powder pattern of the bulk material shows the spacing of UiO-66 at 1.2 nm.
Right Panel: Elemental mapping and HAADF-STEM of layered assembly of polyUiO-66 derived from pbdc-8a-PEG. a) HAADF-STEM of polyUiO-66 derived from pbdc-8a-PEG; b, c) Zirconium and oxygen mapping of layered assembly illustrates the assembly of individual UiO-66 moieties forming layered architecture; d-h) HAADF-STEM of layered assemblies in polyUiO-66 from pbdc-8a-PEG and the corresponding line profiles from boxes denoted (1) and (2) in (a) and (g).

3. In Situ Monitoring of the Seeding and Growth of Silver Metal−Organic Nanotubes by Liquid-Cell Transmission Electron Microscopy

Published Citation: Karthikeyan Gnanasekaran, Kristina M. Vailonis, David M. Jenkins, Nathan C. Gianneschi, "In Situ Monitoring of the Seeding and Growth of Silver Metal-Organic Nanotubes by Liquid-Cell Transmission Electron Microscopy" *ACS Nano,* **2020**, *14*, 8735-8743.

Abstract: Metal-organic nanotubes (MONTs) are highly ordered one-dimensional crystalline porous frameworks. Despite being nanomaterials, virtually all studies of MONTs rely on characterization of the bulk crystalline material (micron-sized) by single-crystal X-ray diffraction. For MONTs to achieve their raison d'être as tunable one-dimensional nanomaterials, individual tubes or small finite bundles of tubes must be synthesized and characterized. Therefore, to directly observe their formation under a variety of reaction conditions in solution, we employ liquid-cell transmission electron microscopy (LCTEM), which allows the early stages of MONT assembly to be monitored in real time. Notably, changing the metal-to-ligand ratio alters the local concentrations of reactant monomers, resulting in multiple nucleation and growth pathways and diverse morphologies at the nanoscale. These various initial seeds grow to form the same nanocrystalline needle phase. This approach of employing LCTEM to study these nanomaterials is analogous to monitoring typical homogeneous solution phase reactions by NMR for controlled nanomaterial formation.

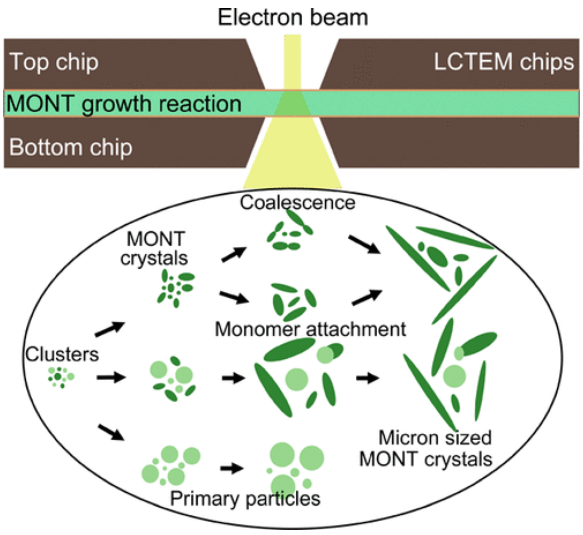

Figure 4. Schematic representation of multiple growth pathways of MONT crystals observed in situ within the liquid-cell.

Summary: Continuing the previous report on MONT growth within the liquid-cell, in this study, we have shown multiple growth pathways exist for MONT formation from silver nitrate and ditriazole ligand (L1) using liquid-cell TEM (Figure 4). We demonstrated that differences in pathways can be visualized, and kinetics can be measured using LCTEM by studying the reaction across metal to ligand ratios ($AgNO_3$:L1). Local concentrations of reactants, precursor ions, and amorphous clusters can dictate the formation of thermodynamically stable MONT crystals and/or kinetically driven assembly within the same reaction medium. We observed that at low concentrations of $AgNO_3$ surface energy minimization is attained by the aggregation and short-range clustering of precursor ions that form primary particles immediately (Figure 5). As the supersaturation increases, anisotropic MONT bundles are formed by heterogeneous nucleation from the primary particles (Figure 5). Excess $AgNO_3$ (6:1 ratio) results in coalescence and oriented attachment of ensemble particles to generate bundled fibers formed as MONT crystals (Figure 5). This growth mechanism of coalescence is not generally observed with MOFs and may be characteristic of these one-

dimensional materials. In this reaction mixture, MONT bundles also form by classical pathways, which include continuous transformation of the supersaturated solution into crystalline MONTs. More broadly, the ability to monitor reactions that yield solid crystalline materials in real time is critical, and we demonstrated that LCTEM is a viable reaction development tool for these crystalline porous one-dimensional materials. We believe that studying nanomaterials by LCTEM will become a central tool in reaction development and design.

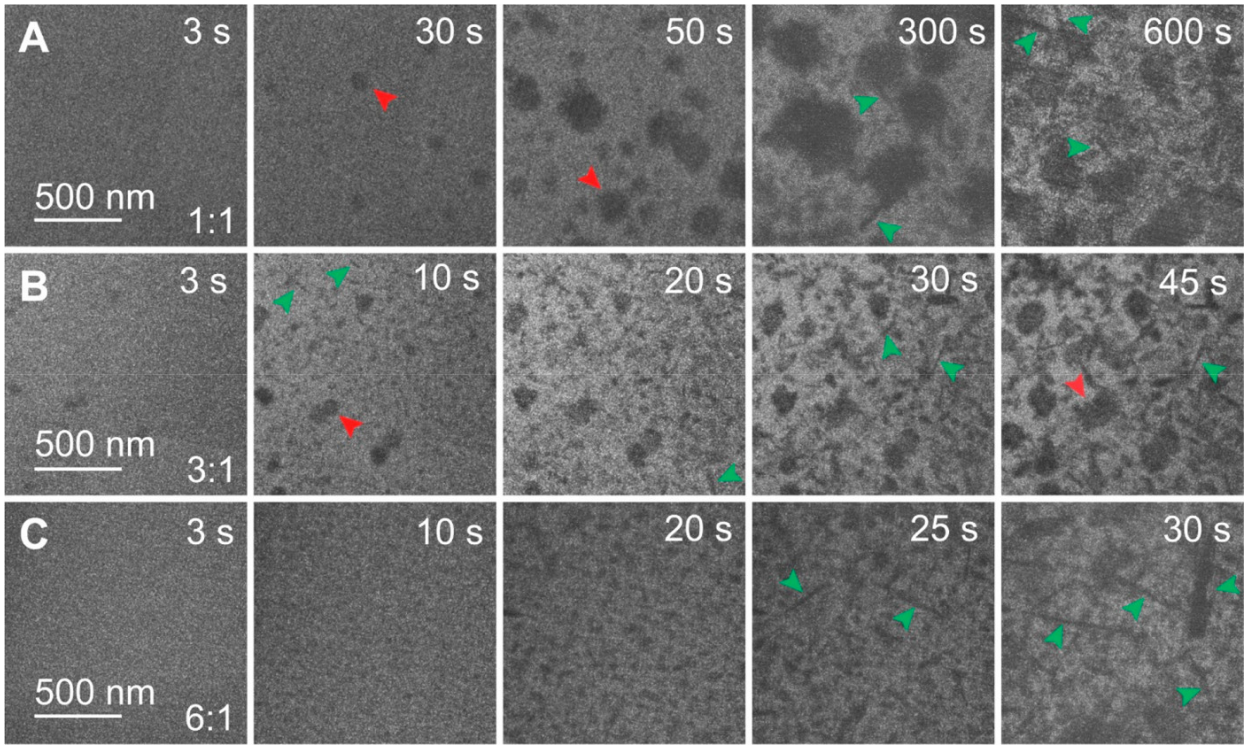

Figure 5. LCTEM snapshots of growth of MONT bundles at various reaction conditions acquired with an electron flux of 0.36 $e^{-}Å^{-2}s^{-1}$. Varying ratios of AgNO3 in DI water and L1 in NMP were flowed into the liquid cell separately at a rate of 1 μL min^{-1} and allowed to mix in the cell, followed by heating at 85 °C. Red arrows represent the primary particles, and green arrows represent the nanotubes. (A) 1:1 ratio of AgNO3:L1, (B) 3:1 ratio of AgNO3:L1, (C) 6:1 ratio of AgNO3:L1.

4. Elucidating the Growth of Metal−Organic Nanotubes Combining Isoreticular Synthesis with Liquid-Cell Transmission Electron Microscopy

Published Citation: Kristina M. Vailonis, Karthikeyan Gnanasekaran, Xian B. Powers,† Nathan C. Gianneschi, David M. Jenkins, "Elucidating the Growth of Metal−Organic Nanotubes Combining Isoreticular Synthesis with Liquid-Cell Transmission Electron Microscopy" *J. Am. Chem. Soc*. **2019**, *141*, 10177-10182.

Abstract: Metal−organic nanotubes (MONTs) are tunable porous 1D materials that are envisioned to be complementary to carbon nanotubes for anisotropic applications. To date, characterization of MONTs relies on single crystal X-ray diffraction (SCXRD) to determine structure and composition. This requires crystals on the micrometer regime, effectively rendering bulk 3D materials. By tracking the growth of a MONT as a function of time with liquid-cell transmission electron microscopy (LCTEM), TEM, and SCXRD, it was possible to ascertain that the material in the bulk phase matches the nanomaterial in terms of molecular structure. This result allowed for the first measurements of finite bundles of MONTs on the nanometer scale. By employing in situ LCTEM, a time course of the formation of small bundles of MONTs could be acquired which provided mechanistic information on MONT formation which is of utility in reaction optimization and applications development.

Summary: In this study, we have tracked the growth of finite bundles of MONTs in real time by LCTEM without electron beam damage or influence to the structures formed (Figure 6A-6B). The same MONT material captured over a time course measured in seconds by LCTEM could be examined by conventional single crystal X-ray diffraction, with many days required to grow a sufficiently large crystal. Two microscopy techniques were critical to matching the nanomaterial to the bulk MONT. First, the SAED measurements gave diffraction spots that were consistent with the measured distances between heavy atoms (Cu or Br) that was found in the single crystal X-ray analysis of the MONT. Second, the EDS measurements from TEM imagining confirmed the same elemental composition found in the bulk material (Figure 6C-6F). Our analysis shows anisotropic MONT growth is a thermodynamically driven surface-specific monomer−monomer attachment process (Figure 6G). We anticipate that reaction development of this kind, conducted in tandem with liquid phase TEM experiments, will accelerate the discovery of new MONT materials.

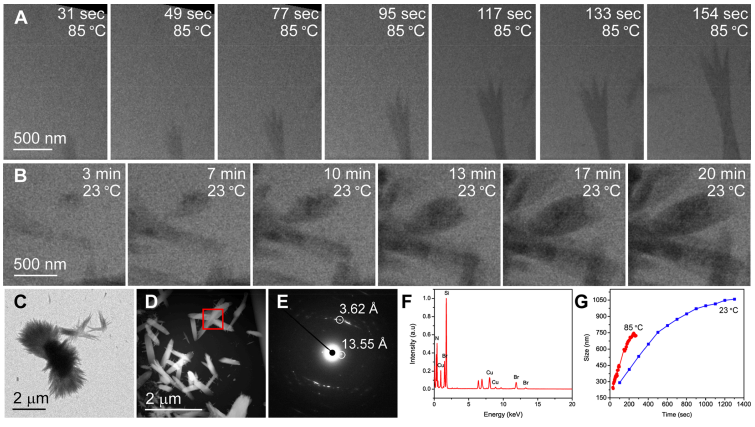

Figure 6. (A, B) Snapshots of growth of MONT acquired by LCTEM. (C, D) Fully grown MONT in LCTEM environment acquired during post-mortem analysis. (E) SAED of MONT grown in LCTEM. (F) EDS spectrum of MONT grown in LCTEM. (G) Size of MONT plotted as a function of time.

5. Transient Catenation in a Zirconium-Based Metal−Organic Framework and Its Effect on Mechanical Stability and Sorption Properties

Published Citation: Lee Robison, Xinyi Gong, Austin M. Evans, Florencia A. Son, Xingjie Wang, Louis R. Redfern, Megan C. Wasson, Zoha H. Syed, Zhijie Chen, Karam B. Idrees, Timur Islamoglu, Massimiliano Delferro, William R. Dichtel, François-Xavier Coudert, Nathan C. Gianneschi, Omar K. Farha, "Transient Catenation in a Zirconium-Based Metal−Organic Framework and Its Effect on Mechanical Stability and Sorption Properties" *J. Am. Chem. Soc*. **2021**, *143*, 1503-1512.

Abstract: Interpenetration of two or more sublattices is common among many metal−organic frameworks (MOFs). Herein, we study the evolution of one zirconium cluster-based, 3,8-connected MOF from its non-interpenetrated (NU-1200) to interpenetrated (STA-26) isomer. We observe this transient catenation process indirectly using ensemble methods, such as nitrogen porosimetry and X-ray diffraction, and directly, using high-resolution transmission electron microscopy. We developed a post-processing script, which automatically rasters a small region-of-interest across an image, extracts the Fourier transform of that sub-image, and then assigns the dominant interpenetration within that region based on the relative intensity ratios of the FFT (Figure 7). This method allows us to spatially resolve the interpenetration of entire crystallites across a series of images. The approach detailed here will serve as a template for other researchers to monitor the interpenetration of their MOF samples at the bulk and single-particle limits.

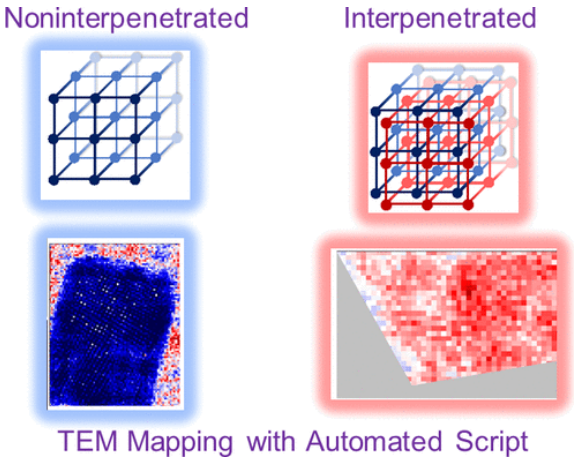

Figure 7. Illustration of non-interpenetrated and interpenetrated MOFs and their corresponding intensity distribution measured by TEM.

Summary: In this study, we have investigated the interpenetration of the zirconium cluster-based mesoporous NU-1200 MOF to the chemically identical microporous STA-26 MOF at the bulk and single-particle limits. Using bulk methods, one may propose that we have obtained partially interpenetrated crystallites. However, we find that our TEM measurements better describe our system as statistical mixtures of crystallites with integral values of interpenetration, rather than fractionally occupied phases (Figure 8). This suggests that interpenetration, once initialized occurs rapidly. Experimental and computational evaluation of the mechanical properties for each framework revealed that the interpenetrated phase is more mechanically robust and thermodynamically stable than its non-interpenetrated counterpart. Future studies should aim to explore mechanistic processes and physical characteristics related to interpenetrated MOFs more broadly, which we suspect will be an important area of study for the commercial deployment of these materials.

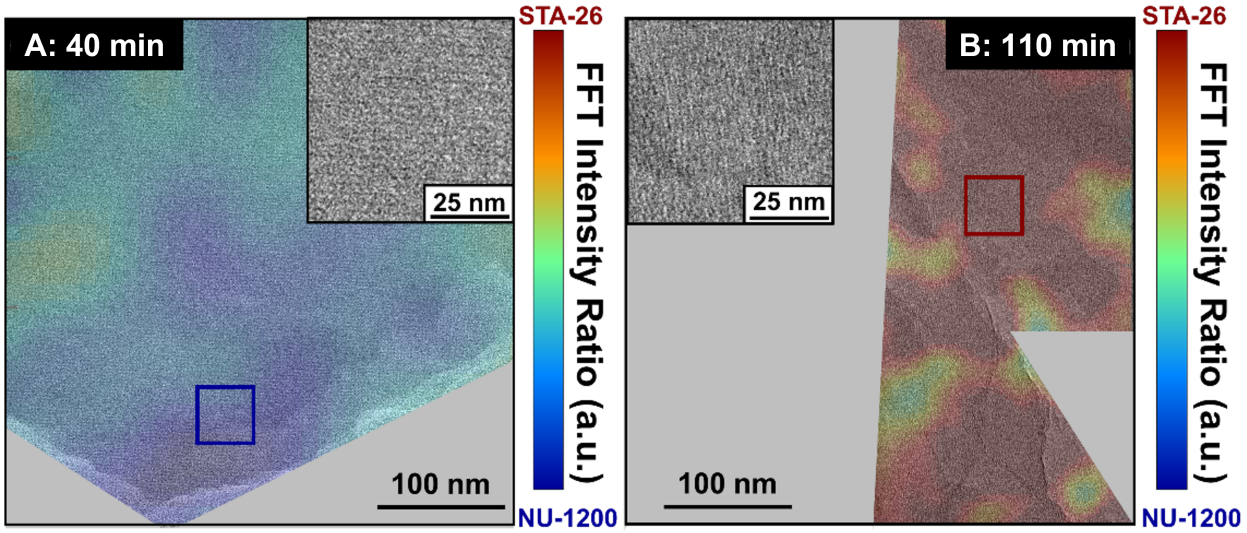

Figure 8. (A) TEM obtained after 40 min of reaction revealing a predominant non-interpenetrated structure. Lattice-resolution image of the blue boxed region in A, showing a NU-1200 structure. (B) TEM obtained after 110 min of reaction revealing a predominant interpenetrated structure. Lattice-resolution image of the red boxed region in B, showing an STA-26 structure. Grey regions indicate void space, lacey carbon substrate, or damaged crystallites.

6. Phase Transitions in Metal−Organic Frameworks Directly Monitored through In Situ Variable Temperature Liquid-Cell Transmission Electron Microscopy and In Situ X-ray Diffraction

Published Citation: Jiafei Lyu, Xinyi Gong, Seung-Joon Lee, Karthikeyan Gnanasekaran, Xuan Zhang, Megan C. Wasson, Xingjie Wang, Peng Bai, Xianghai Guo, Nathan C. Gianneschi, Omar K. Farha, "Phase Transitions in Metal−Organic Frameworks Directly Monitored through In Situ Variable Temperature Liquid-Cell Transmission Electron Microscopy and In Situ X-ray Diffraction" *J. Am. Chem. Soc*. **2020**, *142*, 4609-4615.

Abstract: Zr_6-based metal−organic frameworks (MOFs) with tetratopic organic linkers have been extensively investigated owing to their versatile structural tunability. While diverse topologies and polymorphism in the resulting MOFs are often encountered with tetratopic linkers and Zr_6 nodes, reports on phase transitions within these systems are rare. Thus, we have a limited understanding of polymorph transformations, hindering the rational development of pure phase materials. In this study, a phase transition from a microporous MOF, scu-NU-906, to a mesoporous MOF, csq-NU-1008, (Figure 9) was discovered and monitored through in situ variable temperature liquid-cell transmission electron microscopy (VT-LCTEM), high-resolution transmission electron microscopy (HRTEM), and in situ variable temperature powder X-ray diffraction (VT-PXRD). It was found that the microporous-to-mesoporous transformation in the presence of formic acid occurs via a concomitant dissolution−reprecipitation process.

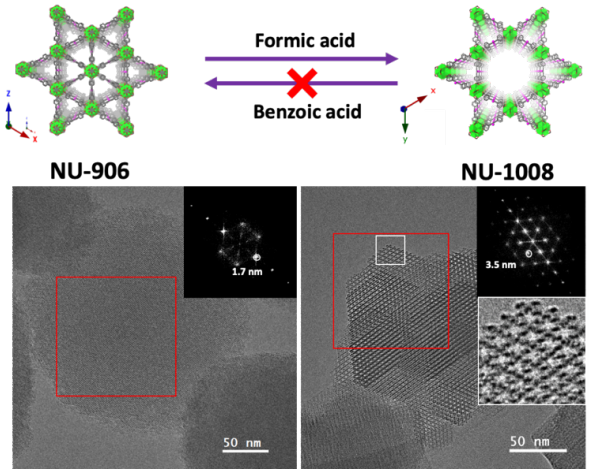

Figure 9. Schematic representation of the phase transition between NU-906 and NU-1008; and TEM images of NU-906 and NU-1008.

Summary: This study provides a correlation between MOF topologies and experimental parameters through the synthesis of two phase-pure MOFs with different topologies built from identical building units yet different modulators. A phase transition from the bulk, pure phase scu-NU-906 yielded new phase csq-NU-1008, characterized through PXRD and nitrogen isotherms. Moreover, a combination of in situ characterization techniques, VT-PXRD, HRTEM and VT-LCTEM, investigated the mechanism of the dynamic MOF phase transition. These methodologies suggested that the phase transition from scu-NU-906 to csq-NU-1008 occurs through a dissolution-reprecipitation mechanism (Figure 10). Future work will focus on methods to improve spatiotemporal resolution of VT-LCTEM, ultimately providing more detailed mechanistic studies on dynamic processes of beam-sensitive materials. We anticipate, and propose that the combination of these techniques will be broadly applicable, providing mechanistic insights of dynamic processes within crystalline materials generally.

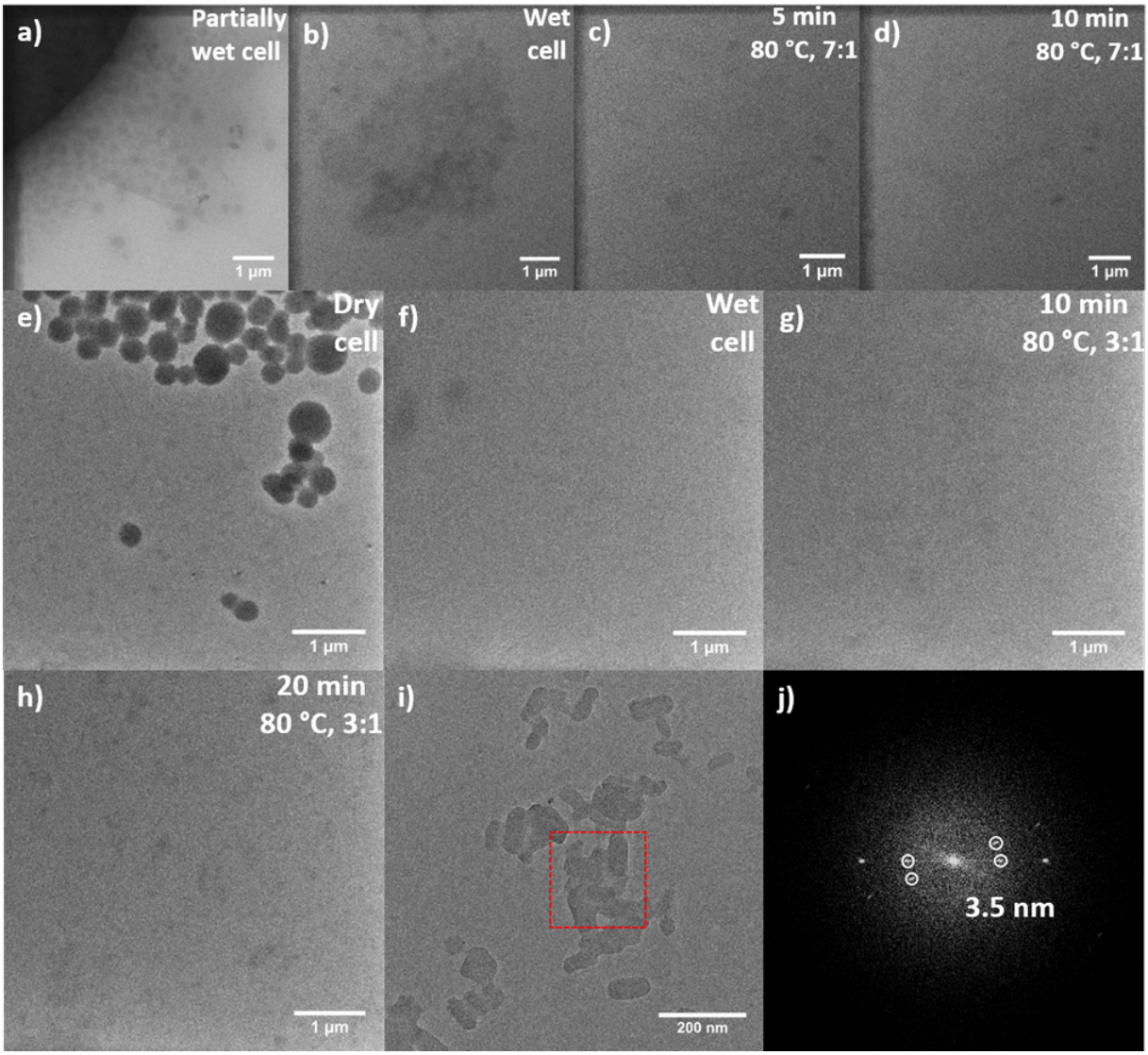

Figure 10. (a-d) LCTEM images revealing the dissolution of NU-906 particles with DMF : formic acid = 7:1 at 80 °C: (a) partially wet cell and wet cell (b) right before heated to 80 °C, (c) after 5 min at 80 °C, and (d) after 10 min at 80 °C. (e-j) LCTEM images revealing the formation of NU-1008 particles with DMF : formic acid = 3:1 at 80 °C: (e) dry cell and wet cell (f) right before heated to 80 °C, (g) after 10 min at 80 °C, and (h) after 20 min at 80 °C, (i) rod-shape NU-1008 particles grown in liquid cell acquired during post-mortem analysis, and (j) FFT of the image inside the red square of (i).

7. Interrogating Kinetic versus Thermodynamic Topologies of Metal−Organic Frameworks via Combined Transmission Electron Microscopy and X-ray Diffraction Analysis

Published Citation: Xinyi Gong, Hyunho Noh, Nathan C. Gianneschi, Omar K. Farha, "Interrogating Kinetic versus Thermodynamic Topologies of Metal−Organic Frameworks via Combined Transmission Electron Microscopy and X-ray Diffraction Analysis" *J. Am. Chem. Soc*. **2019**, *141*, 6146-6151.

Abstract: Synthetic protocols that preferentially result in metal−organic framework (MOF) crystallization of one topology over another remain an elusive, empirical process. This is primarily because of a lack of fundamental insights into MOF crystal growth and the effect of various experimental parameters on the resulting topologies. We demonstrate the temperature−topology relationship of MOFs constructed from hexanuclear oxozirconium cluster nodes and tetrakis(4-carboxylphenyl)porphyrin linkers via a combined transmission electron microscopy and powder X-ray diffraction study. Synthesis at room temperature led to a mixed phase consisting of 12-connected MOF-525 and 6-connected PCN-224, possessing ftw and she topologies, respectively. When the temperature was raised to 145 °C, 8-connected PCN-222 (csq topology) was found, with a possible concurrence of another 8-connected NU-902 (scu topology) and 12-connected PCN-223 (shp topology), in addition to MOF-525 and PCN-224. With an increase in reaction time at 145 °C, a change in product distribution was observed where PCN-222 remained the major crystal phase after 7 days, while the contribution from MOF-525 and PCN-224 decreased. These data suggest that MOF-525 and PCN- 224 are the kinetic products while PCN-222 is the thermodynamic product.

Summary: In a porphyrinic MOF-based system, dynamic crystal phase change from MOF-525 and PCN-224 to PCN-222 was observed with increasing temperature. The csq-net topology, compared to ftw or she topologies, requires a larger torsion angle of the four benzoates to the central porphyrin. By modifying organic linkers with Pt, linker arrangements can be distinguished between MOF-525 and PCN-224, commonly invisible next to a more electron-dense metal nodes under an electron microscope (Figure 11). We propose these approaches for achieving a more comprehensive and fundamental understanding of the correlation between experi-mental parameters and MOF topologies, ultimately assisting in the facile development of MOF synthetic protocols yielding the desired topology without laborious screening of reaction conditions.

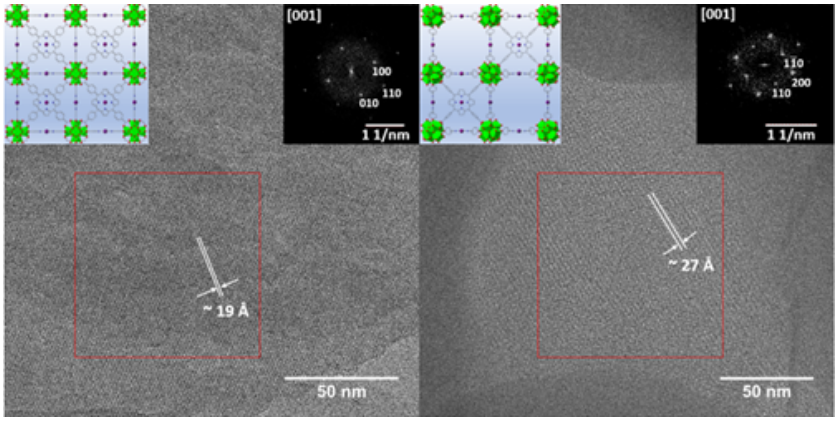

Figure 11. HRTEM images of MOF-525(Pt) and PCN-224(Pt) with their crystal structures

8. Transmission Electron Microscopy Reveals Deposition of Metal Oxide Coatings onto Metal−Organic Frameworks

Published Citation: Michael S. Denny, Jr., Lucas R. Parent, Joseph P. Patterson, Santosh Kumar Meena, Huy Pham, Patricia Abellan, Quentin M. Ramasse, Francesco Paesani, Nathan C. Gianneschi, and Seth M. Cohen, "Transmission Electron Microscopy Reveals Deposition of Metal Oxide Coatings onto Metal−Organic Frameworks" *J. Am. Chem. Soc*. **2018**, *140*, 1348-1357.

Abstract: Postsynthetic strategies for modifying metal-organic frameworks (MOFs) have proven to be an incredibly powerful approach for expanding the scope and functionality of these materials. Previously, we reported on the postsynthetic exchange (PSE) of metal ions and ligands in the University of Oslo (UiO) series of MOFs. Detailed characterization by several analytical methods, most notably inductively coupled plasma mass spectrometry (ICP-MS) and transmission electron microscopy (TEM) reveal that metal ion deposition on the surface of these MOFs occurs in the form of nanoscale metal oxides, rather than yielding exchanged metal sites within the MOFs, as was previously reported. By contrast, these combined analytical methods do confirm that ligand-based PSE can occur in these MOFs. These findings provide new insight into the postsynthetic manipulation of MOF materials, highlight the importance of rigorously characterizing these materials to correctly assign their composition and structure, and provide a new route to making hybrid solids with a MOF@metal oxide architecture.

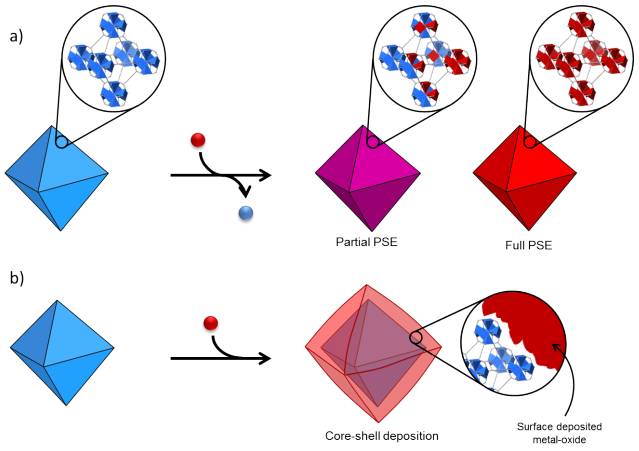

Figure 12. a) The presumed mechanism of postsynthetic exchange (PSE) is a process of displacement of Zr^{4+} ions in the MOF SBU with exogenous metal ions from solution. PSE may consist of partial or full replacement of the native Zr^{4+} ions (blue) with the exogenous metals (red). b) The metal oxide deposition process described here following the addition of exogenous Ti^{4+} and Hf^{4+} occurs at the surface of UiO-66 particles, giving a core-shell, MOF@metal oxide, structure.

Summary: To improve our fundamental understanding of PSE exchange processes and the utility of PSE reactions, this study examined metal-based PSE processes in UiO-66(Zr) MOFs with both Ti^{4+} and Hf^{4+} (**Figure 12**). High-resolution transmission electron microscopy (TEM), scanning (S)TEM with energy dispersive X-ray spectroscopy (STEM-EDX), and electron energy loss spectroscopy (STEM-EELS) were used to generate high resolution maps of the exchanged samples. Curiously, these analyses revealed that a wholly different phenomenon was occurring in the PSE processing of these materials. The resulting MOFs were not exchanging Zr^{4+} at the SBUs (**Figure 12a**), but rather having metal oxides deposited as nanoscale coatings on the MOF surfaces (**Figure 12b**). This finding was consistent with and related to a recent report describing grafting of Ti^{4+} to the

SBU of UiO-66(Zr). The use of high-resolution, analytical STEM revealed that what was originally proposed as PSE, based on other, standard analytical methods and alternative techniques, was actually a metal oxide deposition process masquerading as PSE. This discovery of nanoscale HfO_2 and TiO_2 coatings on UiO-66(Zr) (**Figure 13**), as well as ZrO_2 coatings on UiO-66(Hf), suggests that analysis by STEM spectroscopy should be adopted as a more common protocol for MOF systems, especially those that appear to display metal-based PSE. This study is another example of how our collaborative team is advancing state-of-the-art methods and characterization of self-assembled materials and gaining insight not accessible by conventional characterization methods.

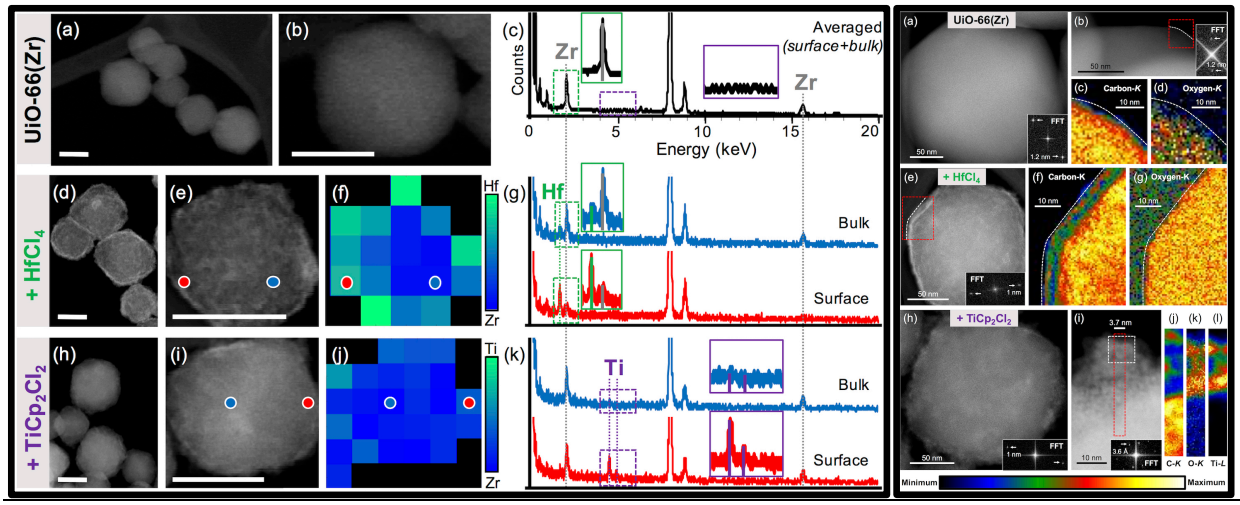

Figure 13. ***Left Panel:*** TEM-EDX characterization for UiO-66(Zr), UiO-66(Zr)+$HfCl_4$, or UiO-66(Zr)+$TiCp_2Cl_2$. All scale bars are 50 nm. STEM images of low- (a, d, h) and high-magnification (b, e, i) are shown for each sample. STEM-EDX spectra are provided (c, g, k). (f) STEM-EDX Hf:Zr atomic ratio map for UiO-66(Zr)+$HfCl_4$ in panel (e). (g) STEM-EDX spectra for UiO-66(Zr)+$HfCl_4$ from the surface (red) and interior (blue) regions (the red and blue dots in panels (e, f) indicate where these spectra where acquired). (j) STEM-EDX Hf:Ti atomic ratio map for UiO-66(Zr)+$TiCp_2Cl_2$ in panel (i). (k) STEM-EDX spectra for UiO-66(Zr)+$TiCp_2Cl_2$ from the surface (red) and interior (blue) regions (the red and blue dots in panels (i, j) indicate where these spectra where acquired).
Right Panel: STEM-EELS characterization of: (a-d) UiO-66(Zr), (e-g) UiO-66(Zr)+$HfCl_4$, or (h-l) UiO-66(Zr)+$TiCp_2Cl_2$. (a, e, h) HAADF STEM images, where insets of the Fast Fourier Transform (FFT) of each image show in the interior of the particles (111) or (002) fringes of UiO-66(Zr) observed at ~1.2 and 1 nm, respectively. Only for UiO-66(Zr) do these lattice fringes extend to the particle surface. (c, d) STEM-EELS spectral maps of Carbon-*K* and Oxygen-*K* for a region of the UiO-66(Zr) sample marked by the red box in panel (b). (f, g) STEM-EELS spectral maps of Carbon-*K* and Oxygen-*K* for a region of the UiO-66(Zr)+$HfCl_4$ sample marked by the red box in panel (e). (j-l) STEM-EELS spectral maps of Carbon-K, Oxygen-*K*, and Titanium-*L*2,3 for a region of the UiO-66(Zr)+$TiCp_2Cl_2$ sample marked by the red box in panel (i). Color bar at the bottom indicates the EELS mapping of relative signal intensity.

Summary and Future Work

With 8 published manuscripts in top journals and additional manuscripts in preparation, we have met most of the objectives proposed above during this award period and we hope the sponsors are satisfied with our results. This collaborative effort combining synthesis, microscopy, and theory funded over the last three years has proven fruitful with impactful results that have opened the eyes of the community to a lot of unknowns about MOFs and related materials. With this in mind, we seek to develop several new ideas while finishing remaining objectives upon renewal of this award. Our future work aims to focus on developing a fundamental understanding of the synthesis of MOFs at room temperature, aqueous conditions, as well as diving in further into the analysis of novel MOF-polymer hybrid materials (self-assembled MOF monolayers and polyMOFs). MOF-polymer composites have been explored from a synthetic perspective by the MOF community over the last half decade, but there remains a lack of fundamental understanding of the compatibility of MOFs and polymers that could lead to the design of high targeted and functional materials.