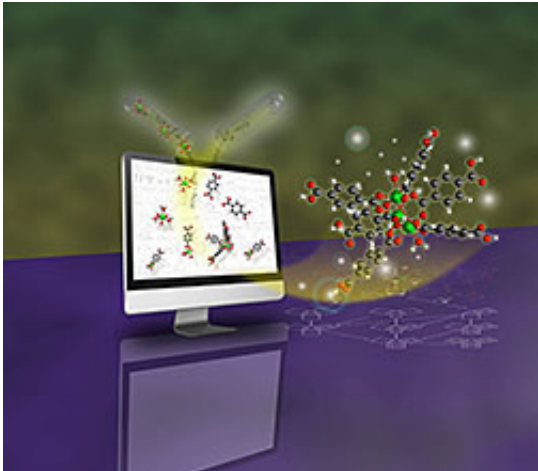


# Mapping the march to methodical materials

November 11 2014, by Kristin Manke

---



Scientists showed the fundamental reactions that occur when synthesizing the building blocks of a metal-organic framework.

Selective and reactive, metal-organic frameworks or MOFs could replace inefficient materials in batteries, catalysts, solid-state heat pumps, and other products where gas separation and storage are vital. While scientists knew how to synthesize MOFs, they didn't know the details of the reactive steps that occurred during assembly of the framework. Now, a trio of scientists at DOE's Pacific Northwest National Laboratory (PNNL) determined the individual reactions and the energy needed at each step to form the basic unit of a popular MOF, MIL-101.

The team took a computation- and simulation-based approach that

allowed them to delve into the intricacies of the reaction sequence that creates the short-lived intermediate molecules that form the MOF building blocks. Understanding those steps is vital to eventually being able to synthesize the materials by the boxcar, not the test tube.

"If you want control over a process, you need to know what's going on and when; in other words, you need to know the mechanism," said Dr. Vassiliki-Alexandra Glezakou, a computational chemist at PNNL and the corresponding author on the study, which appears in *Chemistry of Materials*.

## **The power of MOFs**

Successfully tailoring MOFs could lead to catalysts that quickly produce fuels, chemicals, and other products with less waste and requiring less energy. They could lead to batteries that let electric cars travel greater distances between charges. They could revolutionize technologies as diverse as sensors and building chillers. To do so, the MOFs designed in laboratories must be made on an industrial scale at low cost. The study, funded by DOE's Office of Fossil Energy, describes how MOF's building blocks are formed. Knowing the fundamental steps gives scientists insights into the speed, energy, and efficiency of MOF nucleation.

"To get smarter about how to scale up synthesis of MOFs so that they can be deployed in commercial products, we need a much better understanding of the basics of the self-assembly process than we have today," said Dr. B. Peter McGrail, a Laboratory Fellow at PNNL who is leading several projects developing MOFs for gas separations and building/residential cooling.

## **Starting with the basic blocks**

To understand how a MOF is formed, the team began by looking at the basic building block, known as a secondary building unit or SBU. The SBU contains metal [atoms](#) and linkers or strands of carbon-based molecules. Connect SBUs together, create a MOF.

"Forming the SBUs is the rate-limiting step in creating different MOFs," said Dr. David Cantu, a chemical engineer who worked on this study as part of his postdoctoral fellowship at PNNL. "The faster you can make SBUs, the faster you can make a MOF."

Using resources at EMSL, the National Energy Research Scientific Computing Center, and PNNL Institutional Computing, the team examined the reactivity of the material's basic components. "We looked at these initial reactions using computational chemistry to examine very specific scenarios that give us proof of what's happening and let us know how to influence the outcomes," said Glezakou.

The team worked with MIL-101, a [chromium](#)-based MOF, because of the availability of experimental data. The MIL-101 SBU has a single oxygen atom, surrounded by a triad of chromium ions and wrapped up by six carboxylic linker molecules. The reactions were not quite what the team expected. They discovered a very specific order in which the chromium ions and organic linkers are combined.

Initially, each of the three chromium atoms connects to a single linker molecule. Then, two of the chromium-linker sets combine. This is the most energy-intensive step along the most efficient path. Next, the two-metal linker unit and a third chromium-linker unit merge together. Water molecules constantly vie for a place close to the chromium atoms, blocking access to the metal. Working around the water molecules takes energy, but becomes easier as the unit grows. Finally, the other three linker molecules attach.

"In some ways, this study was a lot like writing," said Cantu. "We started with a blank page. We knew the introduction and the conclusion, but not what happened in between. We figured out what happened in between."

## Researchers look at the bigger picture

Next, the team is looking to scale up their research to determine the steps involved in stacking up the basic units to form MOFs. "We saw how the SBU is formed," said Cantu. "Now, we want to see how the whole material is formed."

**More information:** "Formation Mechanism of the Secondary Building Unit in a Chromium Terephthalate Metal–Organic Framework." *Chem. Mater.*, Article ASAP [DOI: 10.1021/cm5027859](https://doi.org/10.1021/cm5027859)

Provided by Oak Ridge National Laboratory

Citation: Mapping the march to methodical materials (2014, November 11) retrieved 18 April 2024 from <https://phys.org/news/2014-11-methodical-materials.html>

This document is subject to copyright. Apart from any fair dealing for the purpose of private study or research, no part may be reproduced without the written permission. The content is provided for information purposes only.