



properties, pressure, etc.” In his opinion, the group has done a nice job of expanding the electrochemical research community’s characterization toolbox by integrating a handful of these relevant measurement parameters with their recently developed “electrochemical high-speed AFM.” The utility of the new tool to track the nanoscopic structure of electrochemically active material as a function of both time and electrochemical

potential is well conveyed in their article, as well as the video provided in the supplemental material. Larson is curious to see the future work that follows.

The researchers are excited about various future investigations for this technique. Other positive electrode materials such as lithium iron phosphate and lithium nickel manganese cobalt oxide will be studied, particularly over larger voltage windows where they have been known to

undergo morphological changes. Another interesting possibility is to study negative electrode materials like graphite and silicon, which are known to show side reactions and volume expansion. Such *in situ* imaging studies will finally allow researchers to verify degradation predictions of physics-based battery models, especially at faster rates relevant to next-generation batteries.

Aashutosh Mistry

Trigonal prismatic cage molecule enables new type of 3D covalent organic framework

Porous crystalline solids are made up of molecules connected in a network such that there is a high degree of porosity. Think of tinker toys: large, complex node molecules are coordinated to smaller linking molecules, forming two- or three-dimensional (3D) arrays. The chemistry of these molecules allows materials to be rationally designed with specific—even dynamic—structures and functionalities. Covalent organic frameworks (COFs) are a type of porous crystalline solid that, to date, have mostly been realized as stacks of two-dimensional layers. In an article published in a recent issue of the *Journal of the American Chemical Society* (doi:10.1021/jacs.0c07732), researchers at the University of Liverpool, UK, describe their work synthesizing a new dynamic organic cage-based 3D COF.

COFs are a cousin of the more well-studied metal–organic frameworks (MOFs),

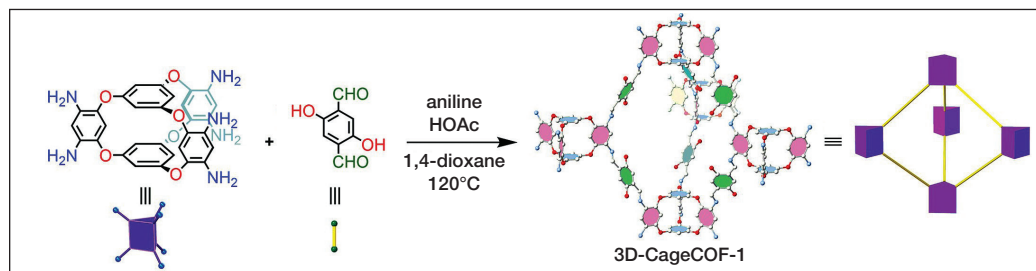
which have a wealth of 3D structures. Researcher Marc Little talks about starting with that family resemblance: “Our approach took inspiration from the three-dimensional secondary building blocks that have been used to synthesize MOFs and enabled the synthesis of topologically diverse MOF nets.” Specifically, molecules with trigonal prismatic coordination greatly expanded the variety of 3D MOF structures, so the researchers worked to design a similar molecule for COFs. They named their bespoke molecule Cage-6-NH₂ for the pendant amine group at each of the triangular prism’s six vertices and the empty cage at its center. Paired with the linear linking molecule 2,5-dihydroxyterephthalaldehyde (DHTPA), Cage-6-NH₂ resulted in 3D-CageCOF-1, the first example of a 3D COF with a topology, a designation which describes a hexagonal arrangement of linked triangular prisms.

The unique porosity and chemistry of COFs and MOFs allow them to accommodate guest molecules for a variety of purposes. But, according to Little, 3D-CageCOF-1 did this in a surprising

way: “Qiang Zhu, a PhD student working on the project, found that by loading the pores with different solvents, including dimethylformamide, the COF structure changed.” Another PhD student, Xue Wang, built computer models to study the structure of 3D-CageCOF-1. “Using a combination of powder x-ray diffraction and our structural models, we were able to determine that the COF structure expanded to accommodate the solvent molecules in the pores,” Little says. Moreover, this change was reversible. 3D-CageCOF-1 returned to its small-pore phase when the guest molecule was removed via thermal treatment. “Although three-dimensional COFs and MOFs are known to exhibit reversible dynamic behavior, we were surprised to find that our COF switched from a small-pore structure to a large-pore structure as we filled the pores with solvent,” Little says.

With potential for applications in sensing, capture, and catalysis, COFs and their MOF cousins make for a rich and exciting field of research. The Liverpool team is hopeful that further research will build on this work, using the researchers’ approach to synthesize more diverse COF topologies and enable new functionalities. With the trigonal prismatic cage molecule, and its pendant amine groups, 3D-CageCOF-1 takes a big step toward achieving that goal.

Antonio Cruz



Scheme for the synthesis of 3D-CageCOF-1 from Cage-6-NH₂ and 2,5-dihydroxyterephthalaldehyde, which can be topologically represented as a triangular prism and a linear strut, respectively. Model atom colors: C, white; N, blue; O, red. H atoms are omitted for clarity. Credit: American Chemical Society.