It’s an Interesting MOF, but Is It Stable?

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The mechanical stability of metal-organic framework (MOF) structures is key to their functionality. In this issue of Matter, Moghadam et al. use high-throughput simulations and machine learning to derive structure-mechanical properties and predict bulk moduli of MOFs from a few physical parameters.

Interest in metal-organic frameworks (MOFs) has grown tremendously since the term was coined almost 25 years ago.1 MOFs are interesting for their diverse chemistry, the beauty of their crystal structures, and their potential technological applications, which range from gas storage and chemical separations to catalysis and photocatalysis to drug delivery and medical applications.2 In many of these applications, the mechanical stability of the material is an important factor. For example, mechanical strength is important in pelletizing MOF powders into larger, shaped particles that are required in industrial gas separation. Despite its importance, there are relatively few studies on MOF stability in the open literature, and a general understanding of how MOF topology, the length of the organic linkers, and the coordination geometry of the building blocks affect the mechanical stability of the resulting MOF is not available. As MOFs move toward commercialization, this lack of understanding becomes an increasingly important knowledge gap.

In this issue of Matter, Moghadam et al.3 present an interactive “map” of the structure-mechanical landscape of MOFs. To derive general relationships that should apply to a diverse set of MOFs, they turned to high-throughput molecular simulations and analyzed 3,385 MOFs containing 41 network topologies. For each MOF, they calculated the bulk, shear, and Young’s moduli using classical molecular mechanics. Then, to understand how the mechanical properties are related to the structural properties (linker length, gravimetric surface area, pore-limiting diameter, etc.), they developed an interactive visualization tool. The web-based tool is publicly available and allows the user to analyze the results interactively with 15 structural and mechanical features in 5D plots. Using this tool, Moghadam et al. could answer questions such as whether linker length or the coordination number and topology is a more important factor in determining the mechanical stability. The results indicate that extension of the organic linkers induces bigger reductions in stability for network topologies with high coordination numbers such as fcu and fkw.

Moghadam et al.3 also used their large dataset to train and validate an artificial neural network (ANN) to predict the bulk modulus from four MOF structural descriptors: the density, gravimetric surface area, largest cavity diameter, and void fraction. Adding the topology as a fifth descriptor dramatically improved the accuracy of the ANN, indicating that topological features are essential in accurately predicting the bulk modulus. The ANN can be used to rapidly estimate the bulk modulus for existing or new MOFs from five readily obtained descriptors, making it a valuable tool for the MOF community.

To complement the molecular mechanics calculations (zero Kelvin results), Moghadam et al. examined a small number of materials at finite temperatures and pressures using molecular dynamics simulations with an ab initio-derived force field. The results indicate that the bulk moduli from the high-throughput calculations (zero Kelvin and simple force field) are representative of the critical pressure these materials can withstand at more typical operating conditions. It should be noted that the study focuses on mechanical stability and does not address whether a structure can withstand moisture, which can lead to degradation of some MOFs.

Developing our understanding of the hydrothermal stability of MOFs remains an open challenge.

Beyond its contribution to the development of mechanically stable MOFs, this paper illustrates some encouraging trends that have the potential to vastly accelerate research in the coming years. First, the 11 authors come from six different institutions and three countries. Rather than viewing each other as “competitors,” the authors have come together to solve an important problem, each research group bringing different expertise to the project. Second, the project both uses and creates open-source computational tools, including a database of MOFs,4 molecular modeling software,5 the ANN, and the web-based

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DECLARATION OF INTERESTS

R.Q.S. has a commercial interest in the company NuMat Technologies, which is seeking to commercialize metal-organic frameworks.

1. Velasco-Hogan et al.1, they are not only material science. As cleverly discovered by that are the latest and greatest in biomaterial science. As cleverly discovered by Velasco-Hogan et al.1, they are not only razor-sharp, hard, and stiff, but they are completely transparent when wet, that is, their index of refraction must exactly match that of seawater, and they do not scatter light at all. Why bother? Because if they scattered light, when illuminated by bioluminescent light either from the dragonfish itself or by prey bioluminescence, the prey would discover the fero-cious teeth and quickly swim away to save themselves. Thus, besides their structure and mechanical properties, the dragonfish teeth must have sophisticated optical behavior, as cleverly discovered and shown by Velasco-Hogan et al.1

Transparent teeth are not per se unique; they exist in other animals too, e.g., the radula teeth of the red abalone (Figure 1A), but in abalone teeth transparency is accidental, not functional, since the mouth radula is located under the shell and under the animal’s soft body, where nobody can see it during the animal’s life. In dragonfish teeth, instead, the function of transparent teeth is clear. Pun intended.

So, dragonfish teeth are transparent, and useful so. But how is transparency achieved? The first-discovery paper by Velasco-Hogan et al.1 addresses this point by presenting transmittance and reflectance data, and scattering calculations based on simplified assumptions, which hint at the possible role of nanocrystal size. Extremely informative density and refractive index measurements, however, remain to be done. So does the full characterization of the teeth surface: the enamel-like layer. One of the open questions is: How does a mineralized material match the density and refractive index of

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