



## Algorithmic Exploration of “Building-Block” Chemistry

Christopher E. Wilmer

In the last decade a wealth of novel materials has been synthesized through what has come to be called “modular” or “building-block” chemistry. This new approach leverages the self-assembly of rigid molecular building blocks that only connect in very specific orientations and stoichiometries. The resulting assemblies are constrained into discrete geometries (e.g., polyhedra, tubes, spheres) or crystalline structures (e.g., metal-organic frameworks (MOFs)).

A remarkable feature of building-block chemistry is that the products are typically monodisperse, and their geometry and composition can be predicted *a priori*. Due to this predictability and the abundance of known building blocks (drawn from the vast organic chemistry literature), the field of MOF chemistry alone has reported thousands of novel structures in the past few years. While these numerous reports showcase the success of the building-block approach, they also belie the underlying combinatorial difficulty of finding the best material for a given application. Clearly, trying to find the optimal material for a specific application by experimental trial-and-error of millions of possible MOFs is impractical and inefficient at best.

In my doctoral research at Northwestern University I developed algorithms that systematically enumerate all of the *hypothetical* MOFs that could be made from a given library of building blocks. Over 150,000 novel MOF structures were screened in a high throughput manner via molecular simulations. The scope of this computational screening effort was without precedent in the MOF field [1]. For each MOF I obtained a range of material properties such as surface area, pore volume, pore size distribution, powder x-ray diffraction pattern, and gas adsorption. In addition to rapidly identifying MOFs that had higher gas storage performance than any previously known materials, I illuminated hitherto unidentified structure-property relationships that could only have been recognized by taking a global view of MOF structures.

Working with synthetic chemists, we synthesized some of the highest performing MOFs predicted by my algorithms, and their measured gas adsorption agreed well with the simulations. Furthermore, by making our database of MOFs publicly available online, this research has already made a measurable, global impact in both academic and industrial labs, as well as stimulated significant commercial interest (>\$1 million in venture capital). This disruptive approach to exploring the space of MOFs will significantly accelerate the discovery of better materials for applications such as hydrogen and natural gas storage.

[1] C.E. Wilmer, M. Leaf, C.Y. Lee, O.K. Farha, B.G. Hauser, J.T. Hupp, and R.Q. Snurr, “Large-scale screening of hypothetical metal-organic frameworks for methane storage,” *Nature Chemistry* (2012), 4, 83-89.