COMMENT

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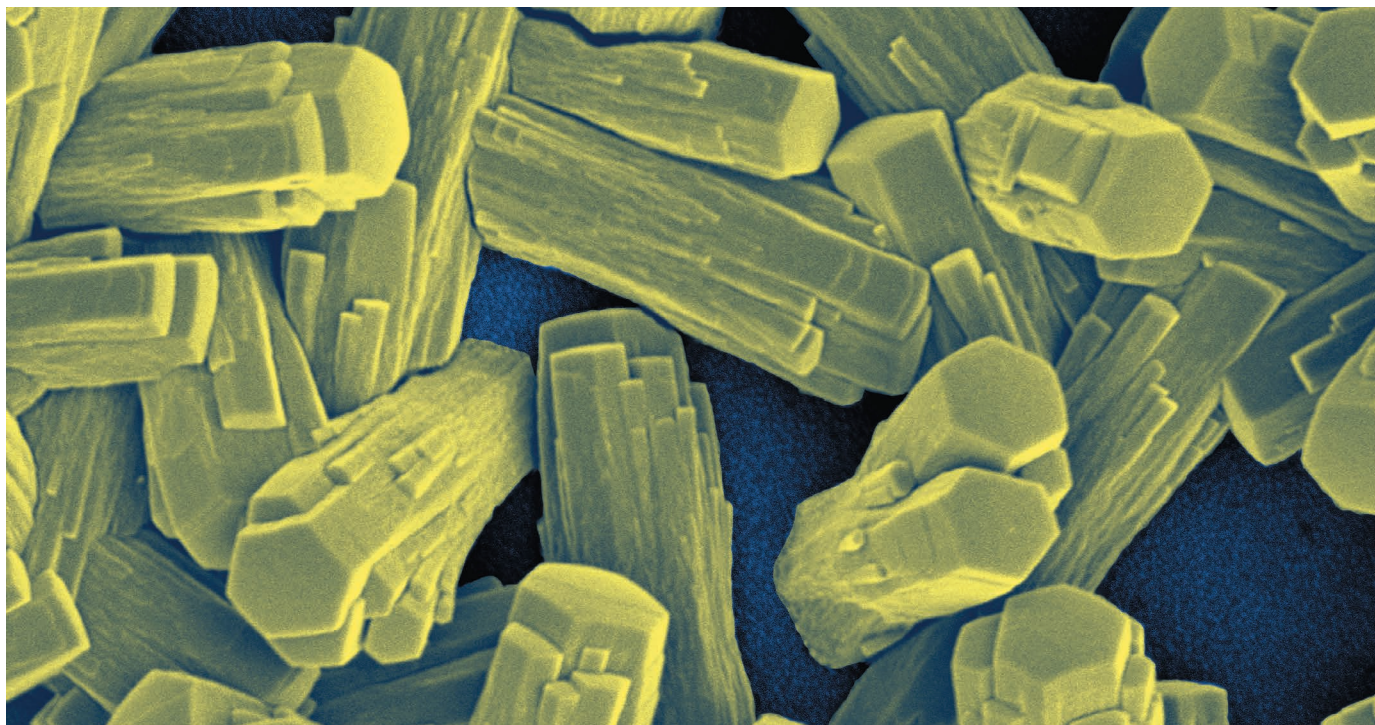
Porous zirconium-based metal–organic frameworks could be used for gas storage and separation, energy conversion and catalysis.

Experimentalists and theorists need to talk

Chemists should thrash out discrepancies in modelling, synthesizing and applying porous materials, urge **Aaron W. Peters**, **Ashlee J. Howarth** and **Omar K. Farha**.

Porous materials are widely used for storing and separating gases and to catalyse reactions. A class of these materials called metal–organic frameworks (MOFs) is ushering in fresh uses[1]. These materials consist of metal ions or clusters linked through organic bridges. There are potentially millions of ways to arrange the elements within them.

This very variety poses a challenge. Choosing the right MOF for a task is daunting for even the most seasoned chemist. Computational screening can help to whittle down the range of optimal MOFs within weeks, rather than the years it might take a legion of graduate students. But computational chemistry must be grounded by experimental evidence. This necessitates partnerships between research groups with expertise in each. For example, our group collaborates with computational experts to solve various problems ranging from gas separation to catalysis.

When experimental evidence does not support theoretical predictions, or vice versa, frustrations can seed and grow. The easiest way to rationalize conflicting results is to blame a collaborator. If heated debates at recent conferences are anything to go by, such frictions between theorists and experimenters are slowing progress in MOF-related research. Both camps can be blind to the strengths of the other and the benefits each would gain by working across the divide.

In the hope of moving past this rocky patch, we illustrate some areas where tension can build, and offer examples of successful marriages between experimental and theoretical chemistries. By ▶

learning to understand one another better, researchers can develop close collaborations that provide insights that could not be achieved from either route alone.

THEORETICAL LEADS

MOF structures can be fine-tuned to sift out specific atoms or compounds by size. Such physical attributes are best scanned *in silico*. For example, a MOF was found last year with pores just large enough to hold a xenon atom (around 4 ångströms diameter), allowing it to separate the element from krypton and other radioactive components of spent nuclear fuel. It was spotted in a database containing 100,000 possible structures because of a predicted affinity for Xe roughly 16 times greater than for Kr (ref. 2). Experimental tests confirmed this, validating the computational method.

Chemical properties such as reactivity are harder to predict. But modelling can yield explanatory and practical insights. *In silico* investigations can be useful in situations where experiments are too dangerous to conduct, such as those involving agents used in chemical weapons. Standard lab practice here is to work with safer equivalent chemicals to predict how the toxic agents might behave in certain situations. But, in practice, the agents and their simulants often differ substantially. Models frequently predict the chemical behaviour of the nerve agents better.

Modelling can also help to minimize researchers' exposure to toxic by-products made during reactions. For example, a MOF with Zr_6 nodes degrades the nerve agents VX (O-ethyl S-diisopropylaminoethyl methylphosphonothiolate) and GD (O-pinacolyl methylphosphonofluoridate). It is important that the MOF node cleaves one bond (P–S) rather than another (P–O) to avoid producing a toxic chemical[3]. Calculations based on 'density functional theory', which explore the stabilities of various chemicals produced during a reaction, identified this MOF as a potential catalyst without researchers having to perform many hazardous lab tests[4].

MOF catalysis is another area in which computational guidance is accelerating discovery. Modelling is drastically reducing the time and resources needed to synthesize, characterize and screen, for example, iron-based MOFs that mimic the behaviour of enzymes and promote reactions such as the conversion of ethane to ethanol[5].

REAL-WORLD CHALLENGES

That said, simple computational calculations often fail to explain or predict observed phenomena. In fact, subtleties

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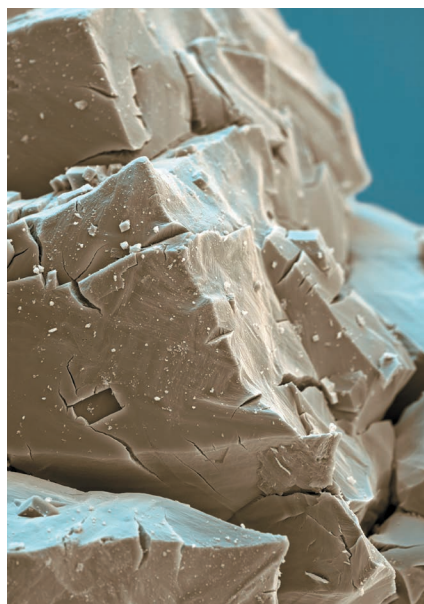
The properties of metal–organic frameworks can be predicted by *in silico* modelling.

and imperfections can contribute to many MOF properties, which is only revealed by experiments. For example, defects are the source of the catalytic activity in the iron-based MOFs used to produce ethanol[6].

MOF structures are also dynamic — exhibiting kaleidoscopic properties under varying conditions. A benzyl ring might rotate, or organic-chain links flex and stretch. Apertures collapse or expand and allow molecules to enter that would otherwise be too large to fit. Such 'breathing' and 'gating' may make it easier, or harder, than expected for a synthesized MOF to adsorb a chemical. For example, dynamic structural changes enhance the capability of a flexible MOF to act as a methane-storage adsorbent[7].

Unfortunately, most computer models still assume that MOFs are rigid. Each type of imperfection, as well as the application the material is being used for, needs to be modelled using a different approach. This complicates computational screening greatly and means that models cannot truly capture the properties of a real material or predict its properties accurately[8].

Of course, experiments have shortcomings too. The difficulties of performing them can lead theoretical and experimental researchers alike to latch on to one-off results as the 'truth', when MOF properties vary. It takes weeks or months of careful optimization to grow crystals that are large and regular enough to have their structures probed through X-ray crystallography. Yet the crystal data that took so long to collect reveal the structure only at that particular time. The X-ray scans are taken at low temperature and under nitrogen — unrealistic conditions for practical applications.

BETTER COLLABORATION

MOF chemists of all stripes need to talk to one another more. They should experience life on the other side of the collaboration to understand the limitations of each technique and gain perspective on how to solve discrepancies. Theorists who spend a week or two in the lab to synthesize or characterize a material will improve their understanding of how each chemical or physical observation is made. Planting an experimentalist in front of the Gaussian software that is used to optimize a structure may allow them to better understand the calculations being made.

Research areas at the interface of theory and experiment should be the focus of such collaboration — they are most likely to yield advances. For example, in gas storage and separations, theorists could identify promising materials for experimenters to follow up speedily. Difficult problems still abound, for example, in room-temperature hydrogen storage or dinitrogen activation for separation of nitrogen and methane or for ammonia synthesis. Similarly, identifying — computationally— intermediate compounds in catalytic reactions would improve next-generation catalysts[9].

Experimenters should characterize their MOF materials as much as possible under conditions that are relevant for applications. This will help theorists to refine their models to serve experimentalists better. New models will need experimental tests to validate them.

Both sides will need to be patient. As our computational collaborators are quick to remind us, "we can model anything, but we cannot model everything." ∎

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