

Three Future Directions for Metal–Organic Frameworks



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It has been twenty-eight years since the first metal–organic framework (MOF) was crystallized using transition metal ions (Co^{2+}) and negatively charged organic linkers [trimesate = $1,3,5\text{-C}_6\text{H}_3(\text{COO})_3^{3-}$]. This was followed by proof of permanent porosity in MOF-2 and ultrahigh porosity in MOF-5. These contributions opened the door to what has become one of the largest fields of chemistry, MOF chemistry, where it is now common practice for a researcher to imagine a structure and identify the molecular building blocks which could be linked into that structure. Overcoming the crystallization challenge by designing the appropriate conditions for the crystallization of MOFs was a dream come true for chemists, especially since it allowed for definitive characterization of MOFs using X-ray and more recently electron diffraction techniques. The strong metal-charged linker bonds holding MOFs together ensured architectural and chemical robustness, thereby giving rise to postsynthetic modifications of MOFs without loss of their permanent porosity and crystallinity. In essence a MOF is an extremely large molecule, which can be treated with chemical reactions as one would with a molecule in solution, except the MOF “molecule” encompasses space within which matter can be further controlled and transformed. The vast number of possible MOF structures and the flexibility of modifying them coupled with their many applications in climate, environment, energy, water, and health support the fact that this chemistry is vast. What is the future of MOFs and how do we harness the power and full potential of this new chemistry?

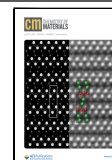
We contend that at least part of the future of MOFs will involve developments in three directions.

First, multivariable MOFs: MOFs are intrinsically chemical in nature and accordingly the concepts and techniques of molecular chemistry will continue to be of interest in the study of MOFs. The best way to appreciate this aspect in a MOF is through the “eye of the molecule”: imagine a molecule passing through the pores and observing events taking place inside the MOFs. Such events include binding of substrates (e.g., carbon dioxide and water) to framework atoms, reacting substrates on catalytic metal or organic sites which are integral to the frameworks, growing polymers within or from the pores to improve the processability of MOFs, and so on. In addition to these “bread and butter” type pursuits and the resulting useful chemistry, an important opportunity emerges from the recognition that the interior of the MOF is a highly heterogeneous environment especially when chemistry is taking place within the pores. For example, a reaction carried out within the MOF (postsynthesis), let us say involving an organic functionality bound to the backbone, creates a heterogeneous spatial arrangement (multivariate) of the

reacted and unreacted functionalities. In a multistep post-synthetic modification of a MOF, this heterogeneity is exponentially increased with the number of functionalities and therein lies the question and opportunity: what spatial arrangement is underlying this heterogeneity and could it be used to create new chemistry. Preliminary evidence shows that such multivariable MOFs outperform their “pure, homogeneous” analogues in affecting programmed drug release, highly selective separations, and catalysis akin to those carried out by enzymes. Almost every aspect of MOF chemistry yields multivariable and therefore opportunities to describe, study, and decipher multivariate MOFs, and the spatial sequences underlying such systems will continue to become important for applications and for growing the basic science of the field. Could such sequences be designed, without losing their multivariate nature, and could their chemistry be controlled?

Second, the emerging MOF innovation cycle: MOFs have allowed us to develop a cycle of innovation in which molecules are linked into frameworks, engineered in a form factor, and integrated into devices, which demonstrate impact on society. Such an innovation cycle requires knowledge of chemistry and engineering to ensure the full functioning of the MOF and the device, for example, in capturing carbon dioxide or water harvesting from air. Once the MOF is integrated into the device to be maximally exposed to incoming guests, consideration of air flow, heat, and mass transfer become paramount for achieving the highest efficiency under real world operating conditions. In such an innovation cycle a close link is created between the MOF and the device performance, which can be optimized well because of the designability of the MOF and the correlation between molecular based behavior and device performance. This was recently illustrated in water harvesting using a MOF in which two carbon atoms were added to a linker to produce a MOF with larger pore volume delivering 50% more water than the state-of-the-art MOF. Such close connection between the molecular design and performance can also allow for lower desorption temperature and harvesting water at low humidity. The elements of the MOF innovation cycle, being entirely implemented in a

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chemistry laboratory, also provide for better, more current, and more relevant education of our researchers.

Third, digital reticular chemistry: Computational chemistry has emerged as an integral component of modern chemistry with the advances of digital computing. Its significance in reticular chemistry lies in its ability to determine structures at the molecular level and forecast novel structures that exhibit enhanced capabilities across various applications. In this field, a wide array of computational methodologies is employed, encompassing electronic structure calculations predominantly employing density functional theory (DFT), as well as classical molecular dynamics (MD) and Monte Carlo (MC) simulations. These methodologies enable researchers to investigate and determine energy landscapes, charge transport, adsorption and gas separation, guest–host interactions, thermodynamic properties, etc.

It is indeed crucial to integrate computational calculations with experimental information and data science techniques to accelerate the discovery process in MOF chemistry. However, it is equally important to recognize the limitations of these computational approaches. The reliability and accuracy of computer simulations heavily rely on the chosen method and model. Therefore, it is essential to establish physically motivated models that appropriately represent the system under study.

For example, when performing electronic structure calculations on a catalyst supported on a MOF node, a decision needs to be made regarding its representation either as a single atom catalyst or a nanoparticle. This choice may not always be informed by experimental data. Additionally, the catalyst structure might undergo changes along the reaction pathway. In the case of metal-based catalysis, it is not uncommon for the nuclearity and spin state of the metal to vary during the reaction. These factors should be considered when designing computational models to accurately capture the catalytic processes.

Similarly, in MD and MC simulations, the presence of a guest molecule can lead to structural changes in the MOF framework. It is crucial to account for these changes in the simulations or, at the very least, be aware that the model system used may not perfectly represent the real system. In such cases, focusing on trends resulting from minor structural modifications may be more insightful than attempting to predict absolute values of specific properties.

By acknowledging these limitations and utilizing computational methods in conjunction with experimental data, researchers can gain valuable insights into MOF chemistry, identify trends, and make informed predictions. This interdisciplinary approach, combining theory, experiment, and data science, can significantly enhance the discovery and development of MOF materials with tailored properties and functionalities.

The integration of AI into computational chemistry has the potential to revolutionize the field, not only in reticular chemistry but also in the wider chemistry. However, it is essential to acknowledge that AI operates within the chemical space in which it is trained and does not reliably extrapolate beyond that space. Humans must still make critical decisions on when to introduce drastic changes in the exploration process, guided by their domain knowledge and expertise. An important aspect that will shape the future of AI in computational chemistry is the reproducibility of computations and AI-generated results. Researchers must strive to make their

data and algorithms fully available to the scientific community, ensuring transparency and facilitating the verification and validation of computational findings. By leveraging the power of AI and embracing a culture of reproducibility, the integration of computation and AI in reticular chemistry and chemistry at large can lead to transformative advancements, accelerating discovery, optimizing performance, and fostering collaborations within the scientific community.

Imagine being able to use Learning Language Models (LLMs) such as GPT-4 to mine information reliably and tabulate for example the reaction conditions under which MOFs could be made and crystallized or using machine learning algorithms to predict new MOF and correlate their structures with specific properties and applications. Imagine being able to tabulate the information on all the calculations ever performed on MOFs and compute, with the aid of ChatGPT, at different scales, the microscopic as well as the macroscopic properties of the MOF innovation cycle. We believe that the fast-emerging field of AI for science will have a revolutionary impact on chemistry and that reticular chemistry is ideally suited, because of its modularity and definition, to exemplify the power of AI in automating the MOF innovation cycle in its entirety. This is being facilitated by LLMs to provide easy entry for researchers into this vast and yet untapped reticular potential. Let us face it, chemistry needs to catch up with the times and it needs to become more sustainable and impactful on society. For the first time, we have an opportunity to use AI to be more relevant and more widely sought after as scientists. As chemistry is about the study of change so should we have the ability to change as chemists. It is a matter of survival rather than convenience. Reticular chemistry is an arena ripe for this change which we're delighted to say is just beginning to show its impact.

Indeed, the advancements in computations and AI have the potential to democratize the field of reticular chemistry and make it more accessible to researchers worldwide. With the aid of computational tools, apps, AI, and LLMs, researchers can model and simulate reticular systems more easily and efficiently. These technological advancements enable researchers to explore and analyze MOFs, covalent organic frameworks, and other reticular structures regardless of their geographical location. The availability of computational tools, AI algorithms, and LLMs allows for the creation of a networked community where information can be shared, collaborations can be fostered, and knowledge can be collectively built. The accessibility of reticular chemistry through computations and AI empowers researchers to contribute to the field irrespective of their resources or physical proximity to specialized facilities. This inclusivity can lead to diverse perspectives, faster knowledge dissemination, and accelerated progress in reticular chemistry research.

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Notes

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