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Frontiers in Modeling Metal–Organic Frameworks

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During the past two decades, metal–organic frameworks (MOFs) have evolved towards one of the most intriguing materials of current science. The main reason for the growing attention these materials receive is their inherent hybrid nature, as they are composed of both inorganic and organic fragments. The combination of these fragments into many different structures and topologies gives rise to an almost unlimited number of existing and hypothetical MOFs.

Besides the large versatility in obtainable MOF structures, these materials also often possess a stable and largely crystalline structure with a high to ultra-high porosity while retaining sufficient stability. This has allowed MOFs to be proposed for a vast variety of applications, ranging from gas storage and separation, to heterogeneous catalysis and mechanical and chemical sensing, and to (opto)electronic devices. Recently, the discovery and engineering of inherent defects and structural disorder has paved the way towards other unique applications. Furthermore, many MOFs show very fascinating stimuli-responsive properties, which may be exploited for beneficial purposes.

Because of the large number of hypothetical MOF structures, an experimental characterization and screening of new candidates for state-of-the-art applications has become unfeasible. Therefore, one must rely more and more on computational techniques to predict the properties of MOFs before their actual synthesis and allow for an application-oriented design of new materials (see **Figure 1**). This special issue therefore gathers several articles, a communication, an essay, and a review that look at the frontiers of modeling MOFs from first principles to coarse-graining techniques.

Due to MOFs' hybrid nature, the modeling of these materials requires simulation approaches that are on the crossroads of molecular and solid-state modeling. Atomistic simulations are an active area, and there is therefore a crucial need to rely on accurate force fields not only to describe the flexibility of this class of materials but also to predict their properties for a range of applications. The challenge of designing and parametrizing adequate atomic force fields is reviewed by D. Dubbeldamm et al. (1900135) along with an outlook on new developments, such the "open force field initiative" and machine learning. The development of efficient computational toolboxes is presented by B. Space and co-workers (1900113), who describe a simulation software package to capture the adsorption and diffusion properties of guests in MOFs using polarizable force fields. A. Martin-Calvo et al. (1900112) report the development of force field parameters for the MOF MAF-6 to further predict its co-adsorption performances for a series of mixtures including aliphatic alcohols and benzene.

Along with atomistic simulations, quantum mechanical calculations play an important role in the actual modeling of MOFs. This special issue contains two exemplary case studies. A. Erba and co-workers (1900093) use a fully ab initio quasi-harmonic lattice dynamics approach to predict the mechanical stability and thermophysical properties of MOF-5 considered as a protoypic MOF. J. L. Mancuso and C. H. Hendon (1900126) explore the role of Ti(IV) to modulate the electronic structure of MOFs and induce a photoactive response of the materials.

A continuous effort has been deployed over the past few years to devise high-throughput screening approaches to scan MOF databases containing more than 80 000 materials. This strategy aims to assist the experimentalists with the identification of existing MOFs or refined versions with optimal performances for mainly adsorption and catalysis applications. To this end, F.-X. Coudert (1900131) comments on the increasingly relevant role of materials databases in the current community of computational scientists with some emphasis on the peculiar status of MOF databases. S. Keskin and co-workers (1900109) report an illustration of a systematic study of MOFs as fillers in mixed matrix membranes for flue gas separation.

Furthermore, to further advance the field, one needs computational techniques that extend simulations to longer time scales and larger length scales than typically encountered in today's simulations. This is the purpose of the work carried out by J. Keupp and R. Schmid (1900117), in which they stimulate the thermal- and pressure-induced structural transformations in DMOF-1 crystallites by means of molecular dynamics (MD) simulations using a flexible force field for the host framework. Similarly, R. Semino and co-workers (1900116) tackle the challenge of modeling complex MOF/polymer interfaces and composites using MD. Another related article is reported by A. Ozgur Yazaydin et al. (1900120) who developed a non-equilibrium MD approach to predict the perm-selectivity of different gas mixtures in a ZIF-membrane.

Finally, modeling the flexibility in MOFs can be tackled by alternative strategies. L. Vanduyfhuys et al. (1900124) and P. Melix et al. (1900098) present two approaches, a semi-analytical

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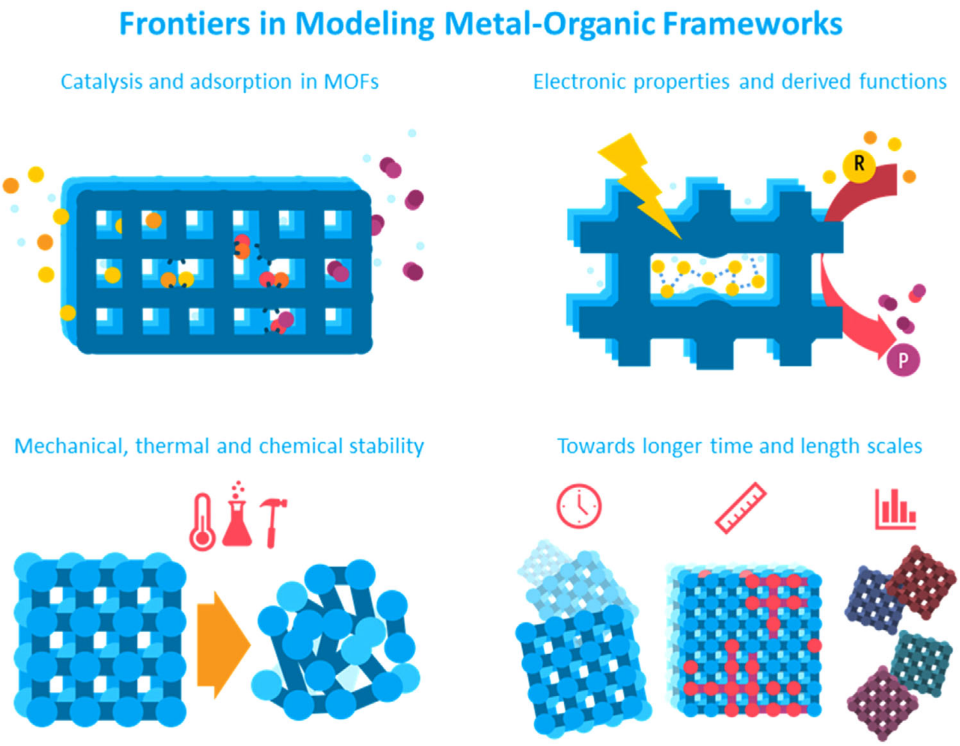

Figure 1. The frontiers in modeling metal–organic frameworks cover different fields of applications, different length and time scale simulations, and different level of theory from first principles to coarse-graining techniques.

mean-field model and ligand field molecular mechanics, to capture the guest-induced breathing behavior of flexible MIL-53 and DUT-8 MOFs respectively.

This special issue clearly emphasizes how theoretical methodologies with different levels of complexity may give be a relevant contribution to the understanding of structure–property relationships in MOFs. Yet it is also clear that modeling MOFs is a very challenging field and that a synergy between theoreticians and experimentalists is of the utmost importance to further advance. We believe this special issue offers a glance at the current frontiers in the modeling of MOFs and sheds some lights beyond them to see and/or foresee what is next.

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