Metal–Organic Frameworks and Covalent Organic Frameworks: Emerging Advances and Applications

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n the last two decades, new classes of porous materials have captured the imagination of scientists and engineers. Metal–organic frameworks (MOFs), originally discovered in the 1990s, are now among the most important and popular materials in an array of fields, being widely explored in studies of both fundamental and applied nature. MOFs are a class of crystalline organic–inorganic hybrid materials formed by the self-assembly of metal ions or clusters as nodes and organic linkers as connectors. In many cases MOFs are porous, offering regular porosity in the micropore and mesopore range. More recently, covalent organic frameworks (COFs) have emerged as related porous materials that are also being widely researched. COFs are a class of materials that form two- or three-dimensional structures through reactions between organic precursors resulting in covalent bonds to afford porous organic materials. In this JACS Au Virtual Issue, we collect an array of recently published papers that feature MOFs and COFs.

Over 90,000 MOFs have been reported to date, with over 500,000 MOF structures predicted, providing a seemingly unlimited number of MOF structures for study and application. Despite the abundance of known MOFs, the self-assembly mechanisms of MOF synthesis are still being elucidated. Giri, Singh, and co-workers employed time-resolved X-ray scattering and a microkinetic model to probe such pathways, and they proposed autocatalysis and oriented attachment as mechanisms for nucleation and growth of the MOF UiO-66 (DOI: 10.1021/jacsau.1c00494). The authors describe the factors impacting secondary building unit formation, the induction time, as well as MOF crystal growth. Myriad combinations of metals and ligands have been explored to date, taking both screening/exploratory paths and purpose driven, targeted syntheses. As an example of a targeted synthesis, Wang et al. report the synthesis of 3D MOFs built from metal clusters known to be effective components in energetic materials (DOI: 10.1021/jacsau.1c00334). Specifically, they created MOFs from silver clusters and energetic ligands to produce an open cationic framework, ZZU-363, with a short ignition delay time, high volumetric energy density, and high specific impulse, making this new structure a potentially useful propellant.

One of the key application areas for MOFs is in chemical separations. For decades, researchers have utilized the porous, crystalline nature of MOFs to perform molecular separations by exploiting the sorption and diffusion properties of the materials. Feng and co-workers utilized two layered indium-based MOFs to concentrate Cs+ ions from mixed ionic waste streams (DOI: 10.1021/jacsau.1c00533). Given the importance of 137Cs separations, more efficient ways of separating such ions from aqueous ion mixtures are highly sought after. The authors demonstrate the chosen MOFs to exhibit fast kinetics, high sorption capacities, and an interesting single crystal to single crystal structural transformation during Cs sorption. MOFs are also widely applicable to gas separations, and a trio of recent papers describe their use in specific CO2 separation challenges. Jones and co-workers used MIL-101(Cr) MOFs loaded with molecular and oligomeric amines for CO2 extraction from air at cold temperatures, such as those found in polar regions of the earth (DOI: 10.1021/jacsau.1c00414). They found that the nature of the amine, the free pore space remaining within the MOF, and the adsorption temperature all impacted the performance of the materials. Whereas Jones and co-workers studied MOF powders, two recent papers reported the creation of crystalline MOFs within polymer fibers. Koh et al. reported a procedure for spinning poly(etherimide) fibers containing MgO nanoparticles, which were subsequently transformed into crystalline Mg2(dobpdc) MOFs loaded with amines (DOI: 10.1021/jacsau.1c00068). This approach overcomes the difficulty associated with directly spinning polymer fibers that contain some MOFs, and the obtained fibers showed promising CO2 separation performance from simulated flue gas and simulated air. Subsequently, Weston, Lively, Koros, and co-workers were able to directly spin polymeric fibers from poly(ether sulfone) solutions containing the same MOF, Mg6(dobpdc) (DOI: 10.1021/jacsau.2c00029). These fibers were shown to exhibit characteristic kinetic and thermodynamic features of the parent MOF when the MOF pores were loaded with specific amines, demonstrating a robust composite fiber synthesis pathway. Several of the examples above incorporated guests into the pores of MOFs to enable specific chemical properties targeting a key application. Ostubo, Kitagawa, and co-workers incorporated proton dimethylammonium (HDMA⁺) cations within the pores of a Pt dimer-based MOF (DOI: 10.1021/jacsau.1c00388). This proton cation acted as a switch for superprotonic conduction, where the change in the relative

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position of the HDMA\textsuperscript{+} in the pores upon hydration enabled a 10\textsuperscript{5}-fold increase in proton conduction. The authors also demonstrated anisotropy of proton conductivity within the crystals. Liu, Zhang, and co-workers produced a Perspective on stimuli-responsive proton conduction in MOF structures (DOI: 10.1021/jacsau.1c00516). They delved into the switchability of proton conduction in MOF structures, the role and location of water in the pores, which plays a large role in proton conduction, investigation and elucidation of proton conducting pathways, as well as potential applications.

In silico design of MOFs and COFs is now widely researched, with numerous application targets in mind. Deng et al. described a methodology for computationally screening M-N-O structures for COFs capable of catalysis of the oxygen evolution reaction (DOI: 10.1021/jacsau.1c00258). Focusing on 3D transition metals, the authors used DFT and machine learning techniques to identify an effective Ni-COF with performance comparable to the best COFs prepared to date for this reaction. Tailored MOFs are also effective in electrochemical systems. Wang et al. prepared amine-functionalized MIL-101(Fe) MOFs on porous nickel foam supports, which were subsequently functionalized with follicle-stimulating hormone (FSH) antibody. This composite electrode functioned as an effective immunosensor for the recognition of FSH electrochemically (DOI: 10.1021/jacsau.1c00371). Molecular recognition studies using tailored MOFs were also reported by Khashab et al. (DOI: 10.1021/jacsau.1c00516). They produced biocompatible frameworks with well-defined porous channels dubbed KBM-1 and KBM-2 from adenine and unnatural amino acids coordinated with Zn\textsuperscript{2+} cations. These structures have an accessible Watson–Crick ADE face that allows for hydrogen bonding, enabling loading with single stranded DNA (ssDNA). The loading and unloading of ssDNA were explored under various conditions. The authors imagine applicability of such structures in sensing, stabilization, or delivery of genetic material. An additional way of targeting biologically relevant molecular recognition is via incorporation of proteins into MOF hosts. Liang, Huang, and co-workers explored the immobilization of two enzymes of varying size (lipase and insulin) on the mesoporous MOF PCN-333(Al) (DOI: 10.1021/jacsau.1c00226). Solid state NMR spectroscopy revealed changes in the structures of the proteins as well as the MOFs after protein immobilization, with key interactions hypothesized to occur between open Al sites in the MOF and free amines in the protein.

MOFs, containing isolated metal centers or clusters, offer connections to many other types of materials or macromolecules. Metalloproteins are important species in biology, and artificial metalloproteins are increasingly investigated for applications in catalysis, molecular recognition, and related fields. Borovik and co-workers’ recent Perspective on artificial metalloproteins delves into this rapidly evolving field (DOI: 10.1021/jacsau.2c00102). In heterogeneous catalysis, the subfield of single atom catalysts (SACs) has recently emerged, whereby catalyst designers seek to synthesize materials with isolated, single metal atoms on support surfaces in various catalytic chemistries. MOF materials are sometimes used as precursors for such SACs, owing to their structures that often inherently isolate the metal centers from each other. Speck, Choi, Cherevko, and co-workers explore SACs for electrochemical energy conversion in their Perspective (DOI: 10.1021/jacsau.1c00121). Yang et al. further explore single atom catalysis in their Perspective from the viewpoint of computation and theory (DOI: 10.1021/jacsau.1c00384). They identify three fields for further SAC development, (i) practical, large-scale synthesis of SACs, (ii) understanding their performance in practical devices like fuel cells and electrolyzers, and (iii) understanding and mitigating catalyst deactivation. Finally, the general understanding of catalysts under working conditions and the elucidation of structures and reaction pathways in working catalysts via operando techniques remains a global focus of research in catalysis. Zhao, Gong, and co-workers describe in their Perspective on catalysis dynamics probed by operando methods some of the latest advances in this field (DOI: 10.1021/jacsau.1c00355).

We hope you find something of interest in this collection of recent papers on MOFs and COFs that have appeared in JACS Au. ACS Publications publishes a large number of papers in this subject area every year across multiple journals, and JACS Au is pleased to feature this first collection of such papers appearing in our new journal.

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Complete contact information is available at: https://pubs.acs.org/10.1021/jacsau.2c00376

Notes
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