

Packing Metal–Organic Frameworks into an Opal Structure

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MOFs with an ordered opal structure were synthesized using the template method in a confined space, generating mesopores in addition to the intrinsic micropores.

Opal, the popular gemstone, from the Latin *opalus*, meaning “to see a change in color,” reflects different colors when viewed from different directions. This optical effect is due to the diffraction and reflection of light within the ordered packing of silica spheres at the nanometer scale within the mineral. Artificial materials mimicking the opal structure not only give appealing colors but also offer unique optical, mechanical, and other physical properties. In this issue of *ACS Central Science*, Shen and coauthors draw inspiration from the opal structure to synthesize metal–organic frameworks (MOFs) using a 3D-ordered template replicating a silica opal via a confined space strategy,¹ and the resulting MOF crystal monolith shows excellent catalytic performance in the Knoevenagel reaction.

The crystalline nature of MOFs lays out orderly arranged pores decorated by metal clusters and organic functional groups, thus providing a plethora of chemical environments for interaction with guest molecules.^{2–4} These porous crystals usually exhibit micropores smaller than 2 nm. Expanding the pore size into the mesopore regime (2–50 nm) favors the diffusion of guest molecules in and out of the MOF and allows for the inclusion of larger molecules such as inorganic particles, DNA, and proteins.^{5–8} As well as the bottom-up synthesis of mesoporous MOFs through linker extension and topological design, it is also possible to generate mesopores in MOF crystals using templates.⁹

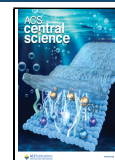
The template method has three general challenges: (1) regulation of the MOF precursor in the template, (2) uniform crystallization, and (3) maintenance of the MOF structure during the template removal process. In their work, Shen and coauthors used a low-temperature and

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vacuum-assisted method to precisely control the infiltration of the precursor into the template, thus achieving its regulation (Figure 1).¹ The subsequent crystallization process was also carried out at a relatively low temperature. This allows for the gradual conversion from the precursor to the MOF, leading to the uniform confinement of MOF crystals on-site. Finally, the template was gently removed by organic solvent without causing structural deformation to the MOFs. In this way, the above three challenges were overcome simultaneously, revealing a new strategy to pack MOF crystals into opal structures, and therefore generating mesopores within the monolith.

The confined growth of MOFs in a template is sensitive to the concentration of the precursor. By allowing a sufficient level of precursor to infiltrate into the template, Shen and coauthors constructed an MOF monolith with a long-range and highly ordered opal structure. In contrast, an insufficient concentration of precursor resulted in smaller MOF particles, and although the MOF crystals were packed in an ordered arrangement due to the confinement of the template, the particles were isolated from each other. This indicates that, during the conversion process, the precursor can move between the pores if the pores are not fully filled

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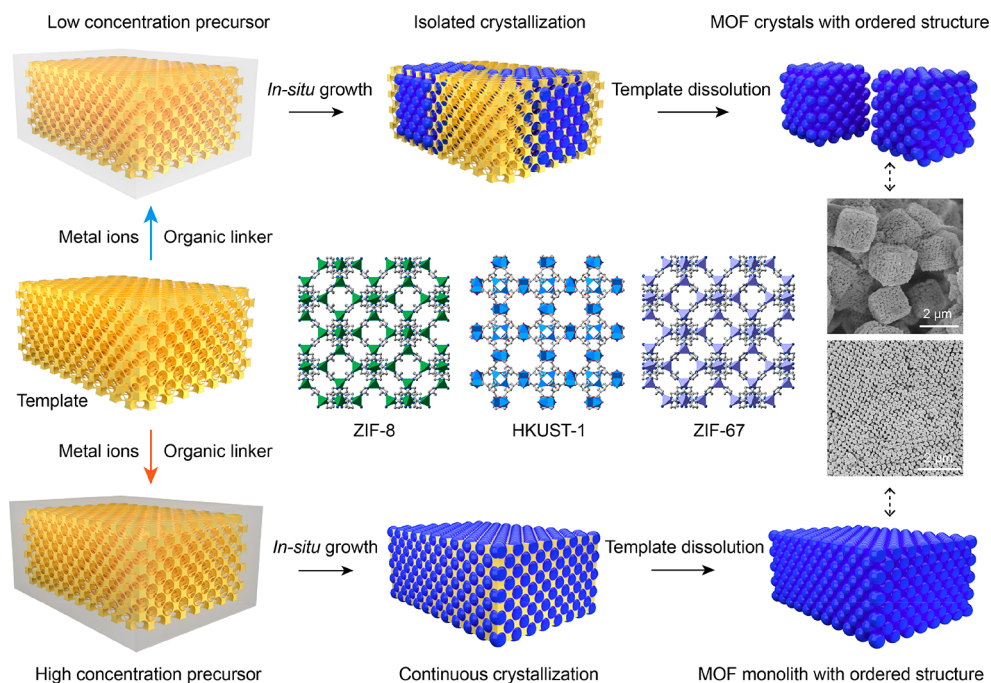


Figure 1. Schematic of the synthetic procedures for constructing MOFs with an opal structure. SEM images are reproduced with permission from ref 1. Copyright 2022 The Authors. Published by American Chemical Society.

and, therefore, will aggregate into domains to form particles instead of a monolith. This trend was observed in the formation of three MOFs, ZIF-8, ZIF-67, and HKUST-1, demonstrating the generality of this method.

This work sheds light on a new way to achieve orderly arranged mesopores in MOFs. Beyond the structural design and compositional control of MOFs, morphology engineering becomes an inevitable step toward the industrial application of this fascinating class of porous crystals, where the substance's momentum, diffusion, and energy exchange are critical. The ordered pore space favors the precise inclusion of biomolecules or inorganic nanoparticles, leading to excellent biological and catalytic performances.^{6,7} However, mesoporous MOFs are scarce, and creating ordered mesopores in microporous MOFs may be a potential way to extend their availability. This combined with the alignment of biomolecules and inorganic nanoparticles in the mesopores is

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likely to provide new material bases for the development of biological and catalytic applications.

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