Assembling A Synthetic Toolbox for Hierarchical Metal-Organic Frameworks

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Introduction

Sequence-defined nucleic acids and proteins with internal monomer sequences and arrangement are vital components in the living world, as a result of billions of years of molecular evolution. These natural hierarchical systems have inspired researchers to develop artificial hierarchical materials that can mimic similar functions such as replication, recognition, and information storage. My graduate research focuses on the development of synthetic strategies for the construction of metal-organic frameworks (MOFs) with hierarchical porosities, architectures and compositions. Specifically, we explore (A) the design and synthesis of hierarchical porous MOFs with multi-scale porosities within one framework, (B) the fabrication of hierarchical superstructures with mesoscopic architectures, and (C) the preparation of multicomponent MOFs with hierarchical compositions. These progresses are expected to offer inspiration for the development of the next generation of smart MOF materials with controllable heterogeneity and tailorability architectures.

A. Hierarchical Porosities

Most MOFs exhibit microporosity, which impedes the diffusion of large molecules. We reported a strategy, linker thermolysis, to create mesopores in a series of microporous MOFs controllably. Thermolable MOFs decompose at ~350°C, while Thermostable MOFs decompose at ~480°C. Linker Thermolysis, combining stepwise linker dissociation and installation, brings new opportunities into the preparation of high-crystalline zirconium-organic frameworks.

B. Hierarchical Architectures

The hierarchical assembly process requires careful control over MOF nucleation, orientational growth and stability consideration. We recently discovered unprecedented assembly cases wherein hierarchical MOF-74 architectures can be assembled. These superstructures contain precisely defined modules that execute specific tasks in sequence.

C. Hierarchical Compositions

The hierarchical compositions in MOFs are related to the arrangement of varying components within selected domains in one MOF lattice at multiple length scales. In organic synthesis, the concept of modularity has been widely utilized to promote the synthesis of diverse natural products. We further demonstrate that the conceptual scope of modular total synthesis can be further expanded from organic molecules into framework materials.

References


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