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abstract

As an emerging class of porous crystalline solids, metal-organic frameworks (MOFs) have enjoyed an almost unparalleled rapid growth in the last two decades owing to their intriguing properties and vast application potential. This remarkable success was built upon the establishment of cluster science, organic chemistry, and X-ray crystallography. Initially topological analysis and symmetry guided rational design of MOFs have propelled the development of the MOF field. The participation of synthetic chemists with advanced organic preparation skills has played an important role in ligand design and synthesis as well as post-synthetic modification.

Although most of the MOF chemists are engaged in teaching inorganic chemistry, the cluster science aspect of MOF research has remained mostly dormant. MOF synthetic work has relied almost exclusively on the “one-pot” approach. In the last few years, attentions have been refocused on coordination chemistry, especially the labile nature of the metal-carboxylate bonds. Using existing coordination assemblies, including metal-organic polyhedron (MOPs) and MOFs, as templates, through bridging ligand substitution, new MOPs and MOFs that are otherwise difficult or impossible to obtain are now readily accessible. The key is to systematically analyze the kinetics of ligand substitution reactions and apply kinetic control in the preparation of MOFs.

For high-valent MOFs, the kinetic inertness of the metal-carboxylate bonds is a double-edged sword: The MOFs are difficult to make but they are generally exceptionally stable. This has posed a synthetic challenge for the preparation of high-valent MOFs.

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(abstract cont'd.)

Through judicious kinetic control, we have developed the following synthetic methods: (1) Kinetically tuned dimensional augmentation (KTDA), in which a robust cluster with terminal carboxylate groups has been extended to 3D frameworks by systematically tuning the kinetics of the synthetic procedure; (2) Post-synthetic metathesis and oxidation (PSMO) and post-synthetic reduction, metathesis and oxidation (PSRMO), where redox chemistry has been applied to tune the kinetics of bridging ligand substitution; and (3) Sequential linker installation (SLI), through which up to three different linkers can be installed sequentially to obtain mixed linker MOFs with ordered structure by applying kinetic adjustments.

biosketch

Hong-Cai “Joe” Zhou obtained his Ph.D. in 2000 from Texas A&M University under the supervision of F. A. Cotton. After a postdoctoral stint at Harvard University with R. H. Holm, he joined the faculty of Miami University, Oxford in 2002. He rose to the rank of full professor in Texas A&M University in 2008 and was promoted to Davidson Professor of Science in 2014 and Robert A. Welch Foundation Chair in 2015. His research focuses on the discovery of synthetic methods to obtain robust framework materials with unique catalytic activities or desirable properties for clean-energy-related applications, taking advantage of the confinement effect in a microscopic or mesoscopic cavity.