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FRAMEWORK MATERIALS AS SINGLE-SITE SOLID CATALYSTS FOR ASYMMETRIC REACTIONS

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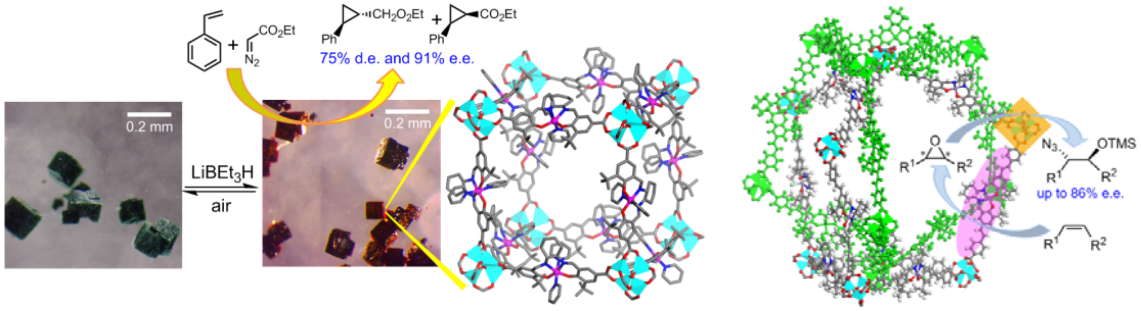
The chemistry of framework materials has received much recent attention owing to the ability to fine-tune their properties at the molecular level. In the past 15 years, we have explored the rational design of functional solids based on coordination polymers (as known as metal-organic frameworks, MOFs) for applications in nonlinear optics,[1] biomedical imaging and drug delivery,[2] and light-harvesting.[3] In this lecture, I would like to discuss our recent success in the design and synthesis of catalytically active chiral porous MOFs by connecting metal nodes with bridging ligands that have orthogonal functionalities.[4] We have developed two complementary approaches to synthesize chiral MOFs. In the first approach, the primary functional groups are linked by metal-connecting units to form porous MOFs whereas the orthogonal secondary chiral groups can then be used to generate asymmetric catalytic sites via coordination to a secondary metal center.[5] In the second approach, the primary functional groups are used to generate robust transition metal precatalysts which are then linked by the metal nodes to form porous MOFs via the secondary functional groups.[6] These synthetic approaches have led to a wide range of single-site solid catalysts for asymmetric organic transformations, including reduction of ketones and aldehydes, epoxidation, cyclopropanation, and tandem epoxidation/epoxide ring-opening reactions. We have also observed the dependence of catalytic activities and selectivities on the MOF channel size, as a result of different substrate diffusion rates through the open channels. We believe that chiral porous MOFs represent a novel class of recyclable and reusable solid asymmetric catalysts as a result of their unprecedentedly high catalyst loadings, truly single-site nature, and straightforward structural characterization by X-ray crystallography.



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