Metal-Organic Frameworks (MOFs) prepared by self-assembly of metal ions and organic ligands have attracted much attention because of their wide applications in gas storage, molecular recognition, and catalysis. The characteristic features of MOFs are highly regular channel structures, controllable channel sizes approximating molecular dimensions, and designable surface functionality. Use of their regulated and tunable channels for a field of polymerization can allow multi-level controls of the resulting polymer structures. In addition, construction of nanocomposites between MOFs and polymers will provide unprecedented material platforms to accomplish many nanoscale functions.

Controlled radical polymerization of vinyl monomers can be attained in MOF nanochannels, showing many remarkable effects of pore size, shape, and functionality on the structures and alignment of the resulting polymers. For example, stereo- and regioregularity of polymers could be systematically changed depending on the pore structure. Controlled uniaxial alignment of vinyl polymer chains was achieved by host-guest cross-polymerization. A variety of polymerization reactions can be also catalyzed in functionalized MOFs. For example, MOFs with specific basic sites accelerated stereo- and monomer-selective polymerization of substituted acetylenes. Oxidative polymerizations of pyrrole within 2D and 3D MOFs containing redox-active sites gave polypyrroles whose orientations were directly related to the original host templates. Use of MOFs as removable templates was a promising method for the preparation of morphological polymer particles as well as the mixing of immiscible polymer pairs at the molecular level.

Polymers confined in nanochannels of MOFs have distinctly different properties to those in the bulk state because of the formation of specific polymer assemblies and conformations. For example, incorporation of poly(ethylene glycol) (PEG) into MOFs enabled observation of thermal transitions of only a few chain assemblies. Confinement of photoconductive polymers, such as poly(vinyl carbazole) and polysilane in one-dimensional channels of MOFs led to increase in their conductivity because of the specific conformational changes. Fluorescent oligomers accommodated in a flexible MOF showed conformational variations concurrently with the host structural change during gas adsorption, which is a key for fluorescent detection of gases. We also developed new autonomous chemical motors by integrating MOFs and self-assembling peptides.