Novel synthesis, activation, and transformation strategies for the preparation of covalent organic framework powder, foams, and films

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Covalent organic frameworks (COFs) are an emerging class of organic, crystalline polymers. They have recently received significant attention for various applications including catalysis, energy storage, and remediation. However, developing materials for these applications requires addressing many fundamental challenges in COF synthesis, activation, and transformation. In this presentation, we present novel strategies for synthesis that increase crystallinity, new catalysts for the rapid synthesis of COFs under ambient conditions, activation approaches that preserve the porosity even for fragile COFs, and transformation approaches that enable the conversion of linear polymers to COFs. First, we focus on COF synthesis and show that benzaldehyde modulators compete with multi-functional aldehyde monomers to slow down the imine-COF polymerization and growth chemistry, and thus improve their crystallinity. We also demonstrate that transition metal nitrates can rapidly produce COFs under ambient conditions. These catalysts produce crystalline COFs within 10 minutes at room temperature and could catalyze a wide range of COF targets varying in linker chemistry, linker lengths and substituents. In the second part, we demonstrate that the use of an ultralow surface tension solvent perfluorohexane enables rapid, simple and effective activation of COFs with reduced pore collapse. This approach avoids the use of supercritical CO₂, which is not widely accessible. Finally, we demonstrate a novel route to the synthesis of COFs through the transformation of linear polymers using reversible chemistries. Specifically, triformylphloroglucinol (TPG) first reacts through dynamic chemistry to replace linkers in the linear polymers and then undergoes irreversible tautomerism to produce ketone linkages. Additionally, we will present processing of COFs and characterization of mechanical properties. Altogether, these studies significantly advance synthetic control over COFs and processing approaches critical to the development and implementation of COFs for applications.

