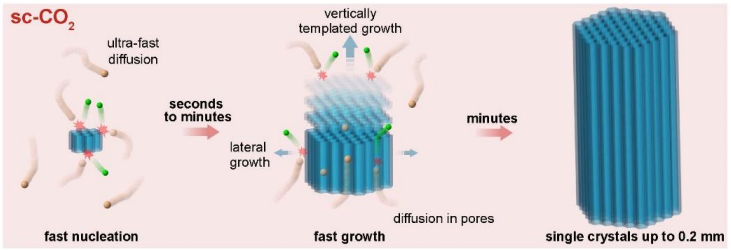
Ultra-fast supercritically-solvothermal polymerization for large-sized single-crystalline covalent organic frameworks

([1]*State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, Shanghai 200433, China.*) ○Dacheng Wei[1]

Keywords: covalent organic framework; single crystal; supercritical fluid; solvothermal polymerization

Crystalline polymer materials, e.g., hyper-crosslinked polystyrene, conjugate microporous polymers and covalent organic frameworks are used for catalyst carrier, organic electronic device and molecular sieve. Their properties and applications are highly dependent on their crystallinity. An efficient polymerization strategy for the rapid preparation of highly or single-crystalline materials is beneficial to not only structure-property studies but also practical applications. However, polymerization usually leads to the formation of amorphous or poorly crystalline products with small grain sizes. It has been a challenging task to efficiently and precisely assemble organic molecules into a single crystal through polymerization.

To address this issue, we developed a supercritically-solvothermal method that uses supercritical carbon dioxide (sc-CO2) as the reaction medium for polymerization. sc-CO2 accelerates crystal growth due to its high diffusivity and low viscosity compared with traditional organic solvents. Six covalent organic frameworks with different topologies, linkages and crystal structures are synthesized by this method. Sub-mm-sized single crystals are synthesized within 1~5 min, including 6 covalent organic frameworks with different topologies, linkages or crystal structures. The crystal growth rate reaches 40 μm min−1, at least 6,000 times faster than state-of-the-art results of other ultra-fast polymerization technologies. The as-synthesized products feature polarized photoluminescence and second harmonic generation, indicating their high-quality single-crystal nature. This method holds advantages such as rapid growth rate, high productivity, easy accessibility, industrial compatibility and environmental friendliness.



1) Peng, L. et al. *Nat. Commun*. **2021,** *12,* 5077: 2) Peng, L. et al. *Chem. Mater*. **2022,** *34,* 2886-2895.