Mechanochemistry-Accessed MOF Polymorphism Revealed by an Integrated 3DED/DFT-Assisted Rietveld Analysis

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Metal–organic frameworks (MOFs) are among the most versatile classes of porous materials and are widely investigated for applications in gas storage and separation, catalysis, sensing, and molecular recognition [1]. Their transformative impact on chemistry and materials science has recently been recognized by the 2025 Nobel Prize in Chemistry [2]. While MOFs are traditionally synthesized under solvothermal conditions, mechanochemistry is emerging as a rapid and sustainable alternative that enables solvent-minimized synthesis. In addition, mechanochemical methods can unlock reaction pathways that are inaccessible or inefficient under conventional solution-based conditions [3]. However, mechanochemical reactions typically yield products as microcrystalline powders, preventing the use of conventional single-crystal X-ray diffraction and placing powder-based structural methods at the center of characterization.

Although mechanochemical synthesis has been widely reported for homoleptic MOFs, heteroleptic pillared frameworks have only recently been explored. Here we report the synthesis of the Zn-based pillared-layer MOF PUM198-m, a polymorphic [4-5] form selectively produced under mechanochemical conditions. As the material is obtained exclusively as a microcrystalline powder, its structure was elucidated through a state-of-the-art integrated workflow combining three-dimensional electron diffraction (3DED), Plane-Wave DFT optimization, and Rietveld refinement against high-resolution powder X-ray diffraction data. This integrated multi-technique strategy represents a novel and powerful approach for solving the structures of flexible MOFs accessible only as microcrystalline powders, overcoming the intrinsic limitations of conventional crystallographic methods. This study demonstrates how advanced powder diffraction approaches enable the structural characterization of mechanochemically derived MOF polymorphs, expanding the structural landscape accessible to functional porous materials.

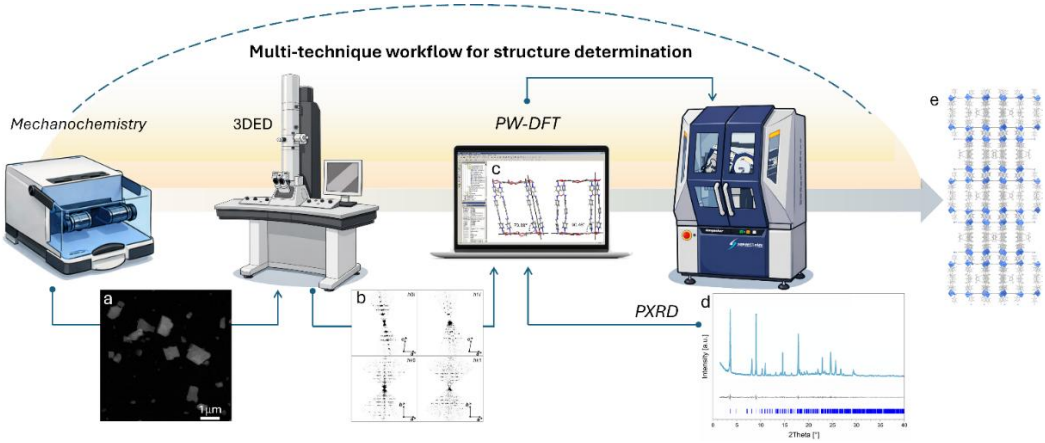


Figure 1. Schematic workflow followed for the structural elucidation of **PUM198-m**.

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