Mechanochemistry is emerging as a promising environmental-friendly strategy for the preparation of new organic and metal-organic materials in the form of molecular crystals, salts, cocrystals as well as polymeric and framework structures.

This approach drastically reduces the use of solvents and excess reagents in the synthetic process and potentially allows to achieve high conversion while minimizing energy consumption and chemical waste. Moreover, mechanochemical synthesis can allow the formation of products, polymorphs and topologies different from what is obtained with solution methods.

The structural characterization of such new materials is typically complicated by the small crystallite size and multiple twinning induced by the grinding process and the nucleation in almost solvent-free conditions. Conventional single-crystal XRD is therefore not applicable in such cases and also powder methods are extremely challenging, especially in case of large unit cells, low symmetry, severe peak broadening and, not least, because of the difficulty of obtaining pure phases.

In this contribution we will show how the most recent developments in electron crystallography allow successful indexing and structure solution of new mechanochemically synthesized organic and metal-organic materials with different dimensionalities, and even porous structures, overcoming their typical beam sensitivity. In particular, a 1D coordination polymer based on Zn and pyridinedicarboxylate could be expanded by the incorporation of pyridine-based polytopic ligands in the mechanochemical synthesis, obtaining higher dimensional topologies and porous structures. A challenge for electron diffraction is the localization and identification of guest molecules, aiming to a complete characterization of the sorption-desorption properties of these promising framework materials.