

Structural elucidation of mechanochemically synthesized reticular materials: the key role of 3D Electron Diffraction

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In recent years, mechanochemistry has emerged as alternative approach for the synthesis of novel organic and metal-organic materials such as molecular crystals, salts, cocrystals and polymeric structures. This method allows the formation of products, polymorphs and topologies different from those obtained in solution. Despite its advantages, a major challenge in mechanochemical synthesis relies on the structural characterisation of the resulting products, due to the presence of nanometric crystals which are not suitable for conventional single-crystal X-ray diffraction (sc-XRD). Furthermore, the structure solution based on powder diffraction methods can be extremely difficult to apply in the case of large unit cells, low symmetry and polyphasic systems. In the last decade, 3D electron diffraction (3D ED) has emerged in the field of nanosized materials as valuable characterisation technique (Figure 1a). [1] This technique, based on single-crystal diffraction protocols, allows the structure determination of materials that would normally fail in sc-XRD studies, spanning from zeolites, metal-organic frameworks (MOFs), supramolecular organic frameworks (SOFs), covalent organic frameworks (COFs), active pharmaceutical ingredients (APIs), and proteins. [1 - 3]. In this contribution, we present a combined approach based on mechanochemistry and 3D ED analysis for the synthesis and structural characterisation of new reticular compounds [4-7]. In particular, we show/demonstrate how the 3D ED technique can be directly applied on as-synthesized mechanochemical products, spanning from zinc(II) and 2,6-pyridine dicarboxylic acid coordination polymers (CPs) [4], to tetrahedral pyridyl-based SOFs [5] and MOFs based on copper(II) and phenolic ligands. [6] In particular, we report the mechanochemical synthesis of a series of highly interpenetrated MOF featuring a dynamical behaviour, obtained by combining a TPPM (tetra-4-(4-pyridil)phenylmethane) linker with Cu(II) paddle wheels (CPW). In these materials, the framework functionalization plays a crucial role in the affinity towards specific fluorinated pollutants (Figure 1b). [7] The discussion highlights how 3D ED and X-ray powder diffraction data provide complementary structural information, bridging the gap between single isolated crystal to the bulk material characterization.

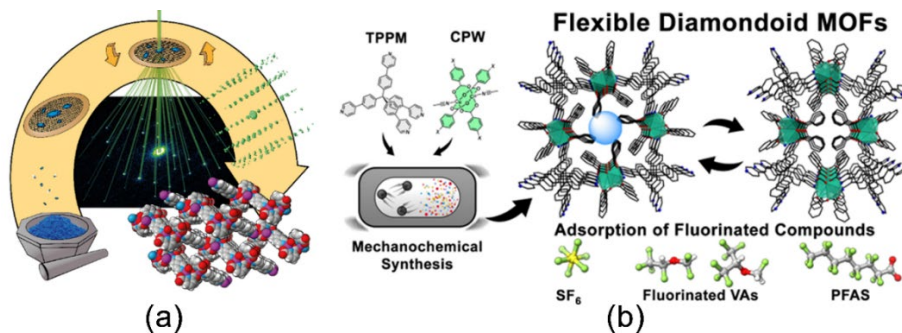


Figure 8. (a) Schematic view of the combined use of mechanochemistry and 3D electron crystallography. (b) Scheme of the synthetic process, dynamic behavior, and applications of TPPM-based MOFs.

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