Poster

A novel family of hexanuclear macromolecular complexes obtained under ball-milling conditions.

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Mechanochemical synthesis is emerging as one of the most interesting routes to obtain crystalline materials. As of today, it is abundantly clear that this method can often replace solution-based approaches thanks to its minimal to no solvent use and generally mild conditions. At the same time mechanochemical strategies, due to being relatively unexplored, can often lead to reaction products unobtainable through more conventional means. For these reasons, IUPAC listed mechanochemistry as one of the "Ten Chemical Innovations That Will Change Our World" [1].

In this contribution, we present the mechanochemical synthesis of a novel family of Zn (II) hexanuclear tetrahedral complexes in which nicotinamide and a variety of benzoic acid derivatives act as monodentate ligands, while acetate anions bridge different metal atoms in 24-membered metal-organic rings, forming small, inaccessible cavities at their center (**Figure 1, c**) [2].

This peculiar secondary building unit (SBU) can additionally self-assemble into rhombohedral (*R-3*) columnar entities by means of hydrogen and halogen bonds.

We demonstrate the reproducibility, scalability, and flexibility of this synthetic approach by means of powder and single-crystal X-Ray diffraction. Important parallels between the stability of the experimental structures and those of different zinc based SBUs are also drawn [3].

Overall, we clearly demonstrate how phases usually inaccessible through traditional solution-based approaches can be rationally obtained in quantitative yields thanks to mechanochemistry. Of note, this work highlights cutting-edge strategies to reliably obtain an extremely uncommon SBU the nontoxic, widely employed zinc metal can form, which should be taken into account when designing novel porous coordination polymers and other functional materials. [4]

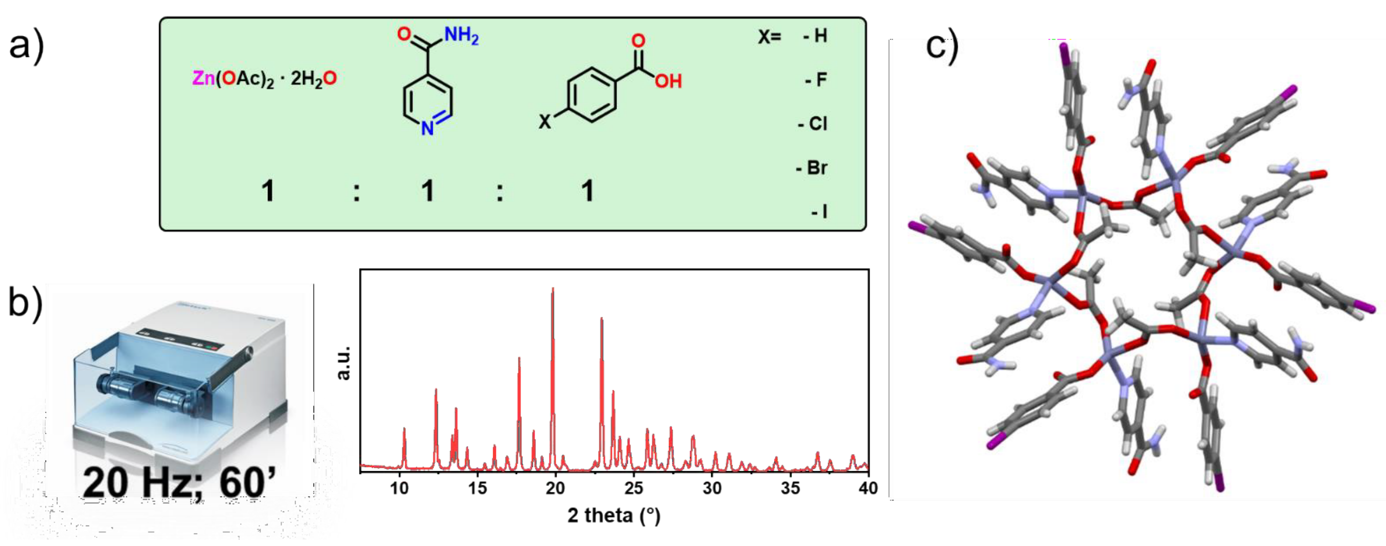

Figure 1. *a)* Schematic representation of the tectons employed in this study, highlighting their stoichiometric ratios. *b) Left*, ball-milling conditions employed in this work; *right* a representative PXRD pattern obtained from the ball-milling experiments. *c)* Secondary building unit of the 24-membered metal-organic ring in stick representation.

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