

Discovery of new polymorphs of metal organic frameworks *via* mechanochemical screening

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Zeolitic Imidazolate Frameworks (ZIFs) are a class of MOFs built from tetrahedral metal centers and imidazolate linkers. These materials can adopt many zeolitic and nonzeolitic topologies, and their many potential applications such as separations, gas capture, and catalysis, are all highly dependent on their solid form.[1] For example, the archetypal ZIF representative zinc imidazolate (ZnIm_2), is known to exist in at least 18 topologies[2], which commonly appear concomitantly. Furthermore, ZIFs are often quite flexible so many of these topologies can appear in multiple distinct crystallographic forms, often depending on the incorporated guests. Mechanochemistry has recently emerged as an excellent method for preparing MOFs, as it is fast, quantitative in yield, independent of solubility and creates little waste.[3] Importantly, it can be effectively applied to ZIF syntheses, and the ZIF solid form outcome can be controlled by using different additives, such as liquids or salts.[4]

We here demonstrate the use of commercially available liquid templates as structure-directing agents in the mechanochemical synthesis of new solid forms of zinc imidazolate (ZnIm_2). We show that multiple ZnIm_2 forms can be prepared using LAG screening, including new forms of the **crb** topology, and can often interconvert. Furthermore, we use previously validated periodic DFT modeling[5] to explain the observed synthetic results, and in some cases predict the outcomes of screening.

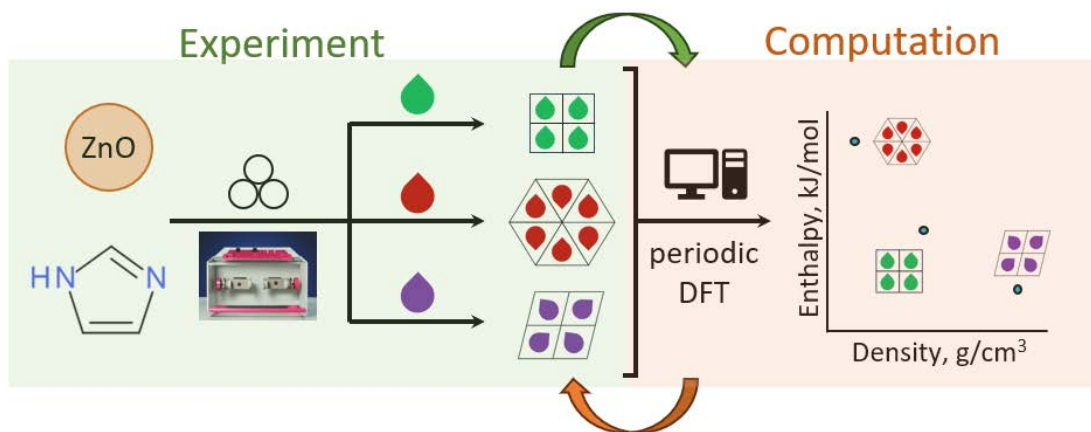


Figure 1. Schematic representation of the dependence of form outcome of the mechanochemical synthesis of ZnIm_2 on liquid additives, and the interplay of computation and experiment.

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