Thermo-mechanochemistry towards new MOF-74 derivatives

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Metal-organic frameworks are porous materials build from organic linkers and a secondary building unit–metals or metal clusters. Their great modularity of structure and nature of pores makes them attractive for a wide range of applications.[1] One of the most thoroughly investigated families of MOFs are MOF-74 materials, composed of divalent metal ions and 2,5-dihydroxyterephthalic acid or 4,6-dihydroxyisophthalic acid linkers in a 2:1 ratio.[2,3] They are characterized by a hexagonal honeycomb structure and a high density of unsaturated metal centers in a 1D oxometallic chain along the *c*-crystallographic axis, and exibit exeptional properties including high surface area, tunable porosity, thermal stability, and magnetic behaviour.[4] MOF-74 materials can be precisely tailored by varying the metal center and/or organic ligand which enables fine-tuning of structural features and properties, therefore expanding their application potential.[5] Although solvothermal synthesis is still the conventional method for MOF preparation, these materials can be synthesized significantly faster and more efficiently via mechanochemical methods. It allows reduced reagent consumption, higher yields, minimal use of solvents, and substantial savings in energy and time.

Herein, we present a thermo-mechanochemical approach[5] for a rapid, controllable, and efficient synthesis of expanded MOF-74 materials employing 4,4′-dihydroxy-[1,1′-biphenyl]-3,3′-dicarboxylic acid as linker. Furthermore, a two-step synthesis enabled the preparation of a coordination polymer intermediate with 1:1 metal to ligand stoichiometric composition[6], which was then used as a precursor for the synthesis of unique bimetallic MOF-74 analogues with precise metal ratio and positioning. These materials are characterized by powder X-ray diffraction, thermogravimetric analysis, IR and Raman spectroscopy, and their formation can be observed employing in situ monitoring of the thermo-mechanochemical reaction by synchrotron X-ray diffraction.

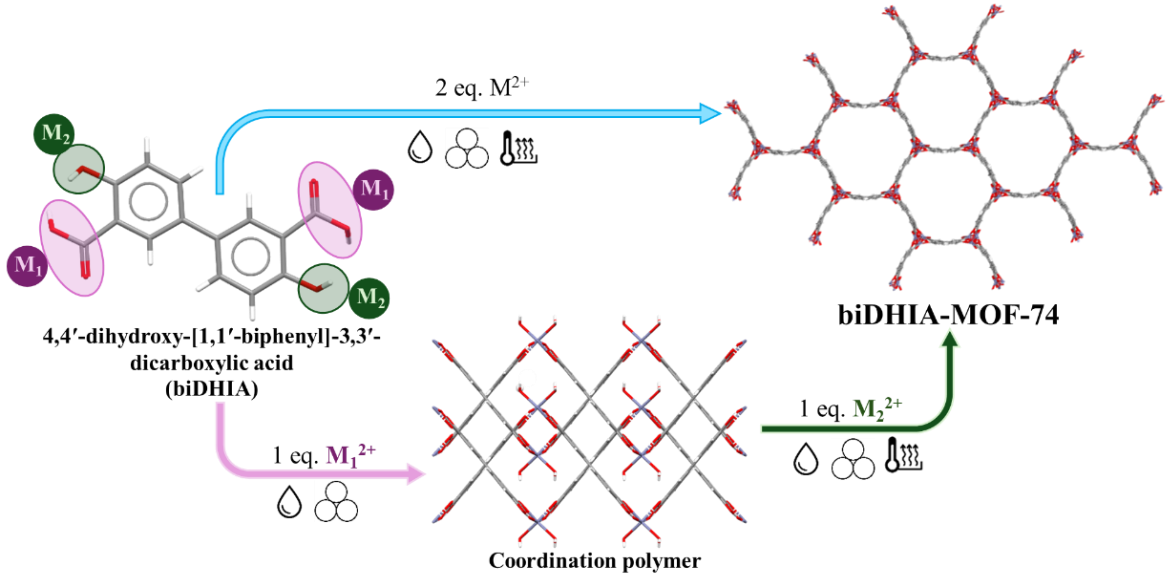


Figure 1. *Two paths for the synthesis of an expanded MOF-74 derivative.*

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