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# From non-conductive MOF to proton-conducting metal-HOFs: a new class of reversible transformations induced by solvent-free mechanochemistry†

Magdalena Lupa-Myszkowska, <sup>ab</sup> Marcin Oszajca <sup>a</sup> and Dariusz Matoga <sup>\*a</sup>

Proton-conducting materials play an important role as solid electrolytes in electrochemical devices for energy storage and conversion, including proton exchange membrane fuel cells. Metal-organic frameworks (MOFs), covalent-organic frameworks (COFs) and more recently hydrogen-bonded organic frameworks (HOFs) have emerged as useful crystalline platforms for proton transport that provide high conductivity and enable insight into conduction pathways. Here, we present two new HOFs with high conductivity, reaching  $2 \times 10^{-2} \text{ S cm}^{-1}$  at 60 °C and 75% relative humidity, obtained in reactions that represent a new class of reversible transformations of solids. The reactions are induced by solvent-free mechanochemistry and involve breaking of coordination linkages in a MOF and formation of extended hydrogen-bonded networks of metal-HOFs (MHOFs). This unprecedented class of MOF-to-MHOF transformations has been demonstrated using a non-conductive MOF (JUK-1) and formamidineium or methylammonium thiocyanates as solid reactants. Structural details of the solid-state reactions are revealed by powder X-ray diffraction and Rietveld refinements for the MHOF products. None of the attempts using conventional methods were successful in obtaining the MHOFs, emphasizing a unique role of mechanochemical stimuli in the reactivity of supramolecular polymer solids, including crystalline MOFs and HOFs. The reversible nature of non-covalent interactions in such materials may be utilized for the development of healable polymer systems.

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## Introduction

Hydrogen-bonded organic frameworks (HOFs) represent a novel class of crystalline, functional porous structures that self-assemble through intermolecular hydrogen-bonding interactions from a multitude of organic building blocks or metal-organic building blocks,<sup>1,2</sup> the latter case leading to a subclass of metal hydrogen-bonded organic frameworks (MHOFs).<sup>3</sup> Whereas a number of H-bonding motifs were successfully used for constructing porous HOFs,<sup>4</sup> the nature of relatively weak, reversible and flexible hydrogen bonds often entails the presence of polymorphs, which complicates synthesis, characterization and reproducibility.<sup>5-7</sup> Despite these challenges, however, well-defined HOFs were recently demonstrated in

a variety of applications,<sup>8</sup> such as gas adsorption,<sup>9-11</sup> sensing,<sup>12-16</sup> catalysis,<sup>17-20</sup> biomedicine,<sup>21,22</sup> and proton conduction.<sup>23-27</sup> Proton-conducting materials are of tremendous importance for renewable energy technologies, including fuel cells and proton exchange membrane-based devices. The inherent well-defined H-bonded networks, porosity, and tunability of HOFs make them excellent solid-state candidates for efficient water-mediated high superprotonic conduction.<sup>28,29</sup> In other related open framework materials such as metal-organic frameworks (MOFs) and covalent organic frameworks (COFs), in addition to proper backbone functionalization, high proton conductivity has been achieved by introducing pore-filling Brønsted acid centres (molecules or ions), but examples of such HOFs remain uncommon.<sup>29-35</sup>

Chemical reactions induced by mechanical force, have emerged as a promising and sustainable method for developing new materials.<sup>36-43</sup> This new approach in synthetic chemistry has shown tremendous potential in revolutionizing traditional synthesis methods with energy-efficient, simple, low-temperature, and highly economical processes.<sup>44-51</sup> Mechanochemical reactions can be performed in solvent-free conditions, decreasing environmental impact and providing access to unique reaction pathways that are often inaccessible by

<sup>a</sup>Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Kraków, Poland. E-mail: [dariusz.matoga@uj.edu.pl](mailto:dariusz.matoga@uj.edu.pl)

<sup>b</sup>Doctoral School of Exact and Natural Sciences, Jagiellonian University, ul. prof. S. Łojasiewicza 11, 30-348 Kraków, Poland

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conventional methods.<sup>30,34,35,52,53</sup> In particular, future perspectives of mechanochemistry in the synthesis and fine-tuning of functional HOFs, including proton-conducting ones, are also promising.<sup>54</sup> Additionally, mechanochemistry offers the capability to access elusive polymorphs and increase the reproducibility of HOFs production, responding to one of the crucial challenges facing the field.<sup>7</sup>

In this work, we provide an accessible strategy for post-synthetic conversion of a metal-organic framework (MOF) into metal hydrogen-bonded organic frameworks (MHOFs) with the simultaneous introduction of proton conduction by solvent-free mechanochemistry. We demonstrate that grinding the layered metal-organic framework JUK-1 ( $\{[\text{Mn}_2(\text{ina})_4(\text{H}_2\text{O})_2] \cdot 2\text{EtOH}\}_n$ )<sup>55</sup> with methylammonium (MA) or formamidinium (FA)

thiocyanate leads to the formation of highly proton-conducting metal hydrogen-bonded organic frameworks. In comparison with our previous research covering the inter-MOF transformation from JUK-1 to JUK-2 that contains ammonium (AM) cations ( $\{(\text{AM})_2[\text{Mn}(\text{ina})_2(\text{NCS})_2]\}_n \cdot x\text{H}_2\text{O}$ ),<sup>30,52</sup> the mechanochemical reactions carried out in this work lead to the cleavage of coordination bonds between  $\text{COO}^-$  and manganese, and the stabilization of the resulting framework by hydrogen bonding. The crystal structures of the MHOFs, determined by applying Rietveld refinement, as well as proton conductive properties of the MHOFs, elucidated by electrochemical impedance spectroscopy (EIS), are compared and discussed. A postsynthetic modification using ionic compounds demonstrates for the first time the capability to obtain metal hydrogen-bonded organic



**Fig. 1** Solid-state reaction of JUK-1 with  $\text{CH}(\text{NH}_2)_2\text{SCN}$  (FASCN) or  $\text{CH}_3\text{NH}_3\text{SCN}$  (MASCN): (a) general reaction scheme for the mechanochemical synthesis of Mn-HOFs. IR spectra in the 2150–1300  $\text{cm}^{-1}$  range with characteristic wavenumbers in  $\text{cm}^{-1}$  are given for comparison – top. Structural details of molecular rearrangement inside the coordination region, cations omitted for clarity (H atoms omitted, Mn – purple, O – red, N – blue, S – yellow, C – grey) – bottom. (b) FT-IR spectra of Mn-HOFs with characteristic band shift of the strong  $\nu(\text{CN})$  band. Numbers indicate wavenumbers (in  $\text{cm}^{-1}$ ) of the CN stretches. (c) PXRD patterns of mixtures after grinding JUK-1 with various amounts of MASCN; 1 : 1, 1 : 2 (Mn-HOF-MA) and 1 : 3 (given as JUK-1 to MASCN stoichiometric ratio), characteristic reflections of MASCN are labeled with "\*".



frameworks from a metal-organic framework by mechanochemical approach. Reverse incorporations of metal ions into suspensions of HOF solids that led to the formation of MOFs or 1D coordination polymers have been recently reported in the literature.<sup>56,57</sup>

## Results and discussion

### Postsynthetic modification and physicochemical characterization

Postsynthetic modifications of a layered JUK-1 with methylammonium (MA) or formamidinium (FA) thiocyanates were performed, resulting in two HOFs with coordinated NCS<sup>-</sup> ligands and extra-framework cations as proton carriers: (MA)<sub>2</sub>[Mn(ina)<sub>2</sub>(NCS)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] and (FA)<sub>2</sub>[Mn(ina)<sub>2</sub>(NCS)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], denoted Mn-HOF-MA and Mn-HOF-FA, respectively. Both syntheses involved fast solvent-free grinding of JUK-1 with an appropriate thiocyanate salt (see the ESI for details<sup>†</sup>). The formation of new crystalline Mn-HOFs phases can be detected by powder X-ray diffraction (PXRD) and infrared (IR) spectroscopy. For both reactions, stoichiometry (1 : 2; metal : thiocyanate ratio) and the evidence of thiocyanate coordination are provided by IR band shift of the strong  $\nu(\text{CN})$  band from 2059 for the initial FASCN to 2098 cm<sup>-1</sup> (Mn-HOF-FA), whereas for Mn-HOF-MA the band at 2045 cm<sup>-1</sup> (for the initial MASCN) shifts to 2078 cm<sup>-1</sup> (Fig. 1 and S2–S9, ESI<sup>†</sup>). The reactions carried out at higher stoichiometries of thiocyanate salts result in mixtures of uncoordinated thiocyanates and Mn-HOFs (observable by the appearance of extra X-ray reflections of MASCN/FASCN or extra  $\nu(\text{CN})$  IR bands). On the other hand, the use of lower stoichiometric ratios leads to mixtures of unreacted JUK-1 and Mn-HOFs due to a deficiency of salts.

For verification of potential Mn-HOFs formation in solution, JUK-1 was immersed in saturated solutions of FASCN or MASCN in ethanol – the IR measurements showed the absence of CN bands (see the ESI for details, Fig. S10<sup>†</sup>). Additionally, the *de novo* synthetic trials to obtain Mn-HOFs were also performed (see the ESI for details, Fig. S11 and S12<sup>†</sup>). None of these attempts succeeded in obtaining modified frameworks, confirming the necessity of mechanochemical grinding. Significantly, the solid-state modifications are fully reversible, with both Mn-HOF-FA and Mn-HOF-MA returning to JUK-1 after immersion in ethanol (see the ESI for details, Fig. S13<sup>†</sup>).

### Structural details of solid-state reactions

Using X-ray diffraction on polycrystalline samples followed by the Rietveld refinement allowed the structural elucidation of Mn-HOF-MA and Mn-HOF-FA (Fig. S15 and S16, ESI<sup>†</sup>). The solid-state reaction of JUK-1 with appropriate thiocyanate salts includes the coordination of two thiocyanates and two labile aqua ligands per one manganese centre (with accompanying conversion of dinuclear Mn<sub>2</sub> to mononuclear Mn nodes) as well as the breaking of coordination bonds of the COO<sup>-</sup> ions with manganese, and stabilization of the resulting discrete complexes *via* hydrogen bonding (Fig. 1 and 2). Considering the formation of Mn-HOF-MA, a comparable, yet significantly



Fig. 2 Structural transformation between JUK-1 and Mn-HOFs. (a) PXRD patterns for JUK-1 and Mn-HOFs, compared with related JUK-2. (b) Stacked coordination bilayers in the initial JUK-1 (top), and the resulting: stacked hydrogen-bonded layers in Mn-HOF-MA (middle) and 3D hydrogen-bonded network in Mn-HOF-FA (bottom), all packing views along the *c* axes. The layers in JUK-1 and Mn-HOF-MA are stabilized by interlayer hydrogen bonds.

different situation occurred in our previous work when NH<sub>4</sub>SCN was used instead of MASCN and a new coordination polymer (JUK-2) was formed. Here, in contrast, as a result of 2D MOF to 3D MHOF structural transformation (Fig. S20, ESI<sup>†</sup>), isonicotinates are no longer coordination linkers and together







