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Simple, scalable mechanochemical synthesis of metal-organic frameworks using liquid-assisted resonant acoustic mixing (LA-RAM)

Liquid-assisted resonant acoustic mixing (LA-RAM) is introduced as a rapid, readily scalable methodology for the mechanochemical synthesis of metal-organic frameworks (MOFs). The LA-RAM approach avoids using milling media required by other kinds of mechanochemical syntheses, and its versatility is illustrated in the synthesis of 2- and 3-dimensional MOFs of Zn(II), Co(II) and Cu(II), including a mixed-linker material. The LA-RAM approach allowed the synthesis of ZIF-L frameworks, previously never obtained in a mechanochemical environment, which was used to demonstrate straightforward scale-up from milligrams to at least 25 grams.

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# Simple, scalable mechanosynthesis of metal–organic frameworks using liquid-assisted resonant acoustic mixing (LA-RAM)†

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We present a rapid and readily scalable methodology for the mechanosynthesis of diverse metal–organic frameworks (MOFs) in the absence of milling media typically required for other types of mechanochemical syntheses. We demonstrate the use of liquid-assisted resonant acoustic mixing (LA-RAM) methodology for the synthesis of three- and two-dimensional MOFs based on Zn(II), Co(II) and Cu(II), including a mixed ligand system. Importantly, the LA-RAM approach also allowed the synthesis of the ZIF-L framework that has never been previously obtained in a mechanochemical environment, as well as its Co(II) analogue. Straightforward scale-up from milligrams to at least 25 grams is demonstrated using the metastable framework ZIF-L as the model.

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## Introduction

Mechanochemical synthesis,<sup>1</sup> conducted by milling, grinding or shearing, has over the past decade been deployed in a wide range of processes, from the synthesis of pharmaceutically active ingredients<sup>2</sup> and cocrystals,<sup>3</sup> to metal–organic frameworks (MOFs)<sup>4</sup> and nanoparticle materials.<sup>5</sup> Rapid, room-temperature reactions in a solvent-free or solvent-limited mechanochemical environment are not only highly attractive in the context of Green Chemistry, but also provide access to new materials, reactions and reaction selectivity that is difficult to achieve in conventional solution-based syntheses.<sup>6,7</sup> Typically, mechanochemical reactions on the laboratory or manufacturing scale are conducted by using ball milling<sup>8</sup> or twin screw extrusion.<sup>9</sup> While these approaches rely on the grinding or shear forces created by the grinding media or rotating screws in the equipment, recent reports have begun investigating mechanochemical reactivity without such components, *e.g.* by ultrasonic<sup>10</sup> or acoustic<sup>11</sup> frequency sample agitation (Fig. 1a and b). These two nascent methodologies are highly promising as, in principle, they offer a route for considerable simplification of sample preparation and scaling up. However, they have so far been applied exclusively to cocrystal formation.<sup>12</sup>



Fig. 1 Herein employed LabRam resonant acoustic mixer: (a) exterior and (b) interior shown during operation. Schematic illustration of herein developed MOF syntheses using RAM: (c) ZIF-8, mixed-ligand SOD-Zn(MeIm)(EtIm) and ZIF-L (Zn and Co variants) and (d) copper-based HKUST-1.

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As the next step in developing cleaner, simpler and readily scalable synthetic methodologies that do not use bulk solvents, we now demonstrate the application of resonant acoustic mixing (RAM)<sup>11,12</sup> for the assembly of MOFs. This proof-of-principle study shows how the versatility of RAM can be enhanced by a small amount of a liquid additive, in a process analogous to liquid-assisted grinding (LAG)<sup>13</sup> previously used to advance the efficiency and scope of ball milling mechanochemistry, to enable the synthesis of two- (2-D) and three-dimensional (3-D) MOFs without bulk solvent or any grinding media. This liquid-assisted resonant acoustic mixing (LA-RAM) methodology is demonstrated for simple, rapid synthesis of imidazolate and carboxylate MOFs based on Zn(II) or Cu(II), including a mixed-ligand system, as well as commercially-relevant frameworks ZIF-8 and HKUST-1 (Fig. 1c and d). Importantly, LA-RAM also enabled a simple, rapid route for making the metastable 2-D layered MOF material ZIF-L<sup>13,14</sup> and its Co(II) analogue, neither of which have previously been obtained *via* mechanochemistry. Using ZIF-L as a model, the scale-up of LA-RAM synthesis of MOFs from hundreds of milligrams to at least 25 grams is demonstrated.

All described RAM reactions were done using a Resodyn LabRAM II system (Fig. 1a and b),<sup>15</sup> operating in auto-resonance

mode of 60 Hz. In most cases, the reaction mixtures were contained in 8 mL plastic vials, at 200–300 mg scale. Scale-up reactions were conducted on the scale from *ca.* 1.5 grams (for ZIF-8, SOD-Zn(MeIm)(EtIm) materials) to 25 grams (for ZIF-L) of product. Products were characterized by powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), Fourier-transform infrared attenuated total reflectance (FTIR-ATR) spectroscopy, N<sub>2</sub> sorption analysis, solution- and solid-state nuclear magnetic resonance (NMR) spectroscopy, and scanning electron microscopy (SEM). Further details of synthetic procedures and instrumental techniques are given in the ESI.†

## Results and discussion

As a first attempt of RAM-based MOF mechanosynthesis, we investigated the reaction of ZnO and 2-methylimidazole (HMeIm) to form the popular sodalite (SOD) topology Zn(MeIm)<sub>2</sub> framework (ZIF-8, MAF-4).<sup>16–18</sup> The principal parameters expected to affect a chemical reaction in a resonant acoustic mixer are time and the acceleration experienced by the sample. The acceleration is expressed in *g* units ( $g = 9.81 \text{ m s}^{-2}$ ) and is varied by changing the amplitude of acoustic agitation. It



Fig. 2 Comparison of selected: (a) PXRD patterns and (b) TGA thermograms for ZIF-8 materials obtained by LA-RAM for 60 minutes in the presence of MeOH (liquid-to-solid ratio  $\eta \approx 0.3 \mu\text{L mg}^{-1}$ ) and  $\text{NH}_4\text{NO}_3$  (5 mol% with respect to Zn) at different *g* acceleration values. The TGA measurements are reported for samples after washing and activation. The PXRD patterns of products obtained using accelerations of 30g and 45g reveal the presence of ZIF-L impurity, highlighted by '\*'. (c) PXRD pattern for ZIF-L obtained by LA-RAM with water as the additive, compared to the simulated patterns for the reported crystal structure (CSD code IWOZOL) and (d) image of a 25 gram sample of ZIF-L obtained by LAG, compared to a one cent Canadian coin.







Fig. 3 (a) PXRD pattern of SOD-Zn(EtIm)(MeIm) prepared by LA-RAM with  $\text{CH}_3\text{CN}$  (1 hour, 95g,  $\eta \approx 0.3 \mu\text{L mg}^{-1}$ ) compared to a simulated pattern for isostructural ZIF-8 (CSD code VELVOY); (b) solid-state  $^{13}\text{C}$ -NMR spectra for SOD-Zn(EtIm)(MeIm) (blue) and ZIF-8 (black) samples obtained by LA-RAM, after washing and evacuation (for solid-state  $^{15}\text{N}$  NMR spectra see ESI $^\dagger$ ); (c)  $^1\text{H}$  NMR spectrum for SOD-Zn(EtIm)(MeIm) after dissolution in DCl and DMSO- $d_6$ , illustrating the 1 : 1 ratio of MeIm $^-$  and EtIm $^-$  ligands (for relative signal integrations, see ESI $^\dagger$ ); (d) nitrogen desorption and adsorption curves for a washed and evacuated sample of SOD-Zn(EtIm)(MeIm) prepared by LA-RAM on  $\approx 1.2$  gram (5 mmol) scale.

linker was kept at 1 : 2.1, respectively, and the stoichiometric ratio of HMeIm : HEtIm was varied between 0.15 : 1.95 and 0.35 : 1.75. Analysis of products by PXRD revealed the formation of separate phases (see ESI $^\dagger$ ) with SOD- and RHO-topology (CSD code MECWOH).

The described investigation of reactivity of ZnO and HMeIm at lower  $g$ -values revealed the formation of small amounts of a crystalline phase other than ZIF-8 (Fig. 2a). Comparison of X-ray reflections suggests the unexpected product is ZIF-L (see ESI $^\dagger$ ), a layered 2-D Zn(MeIm) $_2$  framework containing additional neutral HMeIm ligands (CSD code IWOZOL).<sup>13,14,24</sup> The observation of ZIF-L was particularly intriguing as this phase has not yet been observed in any reports on mechanochemical or solvent-free synthesis of ZIF-8, and has been significantly less explored compared to ZIF-8. Consequently, we explored the possibility of using RAM for targeted synthesis of ZIF-L. The observation of this phase under conditions of low acceleration guided us towards exploring milder RAM conditions, and using reactive metal precursors commonly used in solution synthesis: acetates or nitrates. While zinc acetate dihydrate Zn(OAc) $_2 \cdot 2\text{H}_2\text{O}$  was found to lead to very low conversions even in presence of a liquid (water), zinc nitrate hexahydrate Zn(NO $_3$ ) $_2 \cdot 6\text{H}_2\text{O}$  was much more reactive (see ESI $^\dagger$ ). Analysis of a reaction mixture resulting from LA-RAM (acceleration of 30g,

30 minutes in presence of water) of Zn(NO $_3$ ) $_2 \cdot 6\text{H}_2\text{O}$  and HMeIm in a stoichiometric ratio of 1 : 3.5, corresponding to the composition of ZIF-L, confirmed the formation of ZIF-L in a mixture with ZIF-8 (see ESI $^\dagger$ ). In order to optimize the reaction towards complete conversion to ZIF-L, the ratio of Zn precursor to HMeIm was increased. Complete conversion into ZIF-L was achieved at a Zn : HMeIm stoichiometric ratio of 1 : 8 (Fig. 2c), as evidenced by PXRD analysis, and TGA of the material after washing with water to remove excess HMeIm (see ESI $^\dagger$ ). The product was obtained, after washing and drying, in 86% isolated yield. Identical reaction conditions were also readily applicable for the synthesis of the Co(II) version of ZIF-L,<sup>25</sup> by using Co(NO $_3$ ) $_2 \cdot 6\text{H}_2\text{O}$  as a metal precursor (see ESI $^\dagger$ ), providing the target material in 90% isolated yield after washing and drying. As ZIF-L is a very recently reported form of zinc 2-methylimidazolate<sup>26</sup> we also considered it as a suitable target for RAM reaction scale-up, which proved to be straightforward, enabling one-pot syntheses of at least 25 grams of ZIF-L (Fig. 2d). To the best of our knowledge, this represents the first report of a bulk, multi-gram scale, as well as mechanochemical, synthesis of ZIF-L. Importantly, we were not able to obtain ZIF-L under identical conditions using ball milling, which yielded an as yet unidentified product (see ESI $^\dagger$ ). As ZIF-L is known to thermally transform to ZIF-8,<sup>27</sup> its bulk synthesis



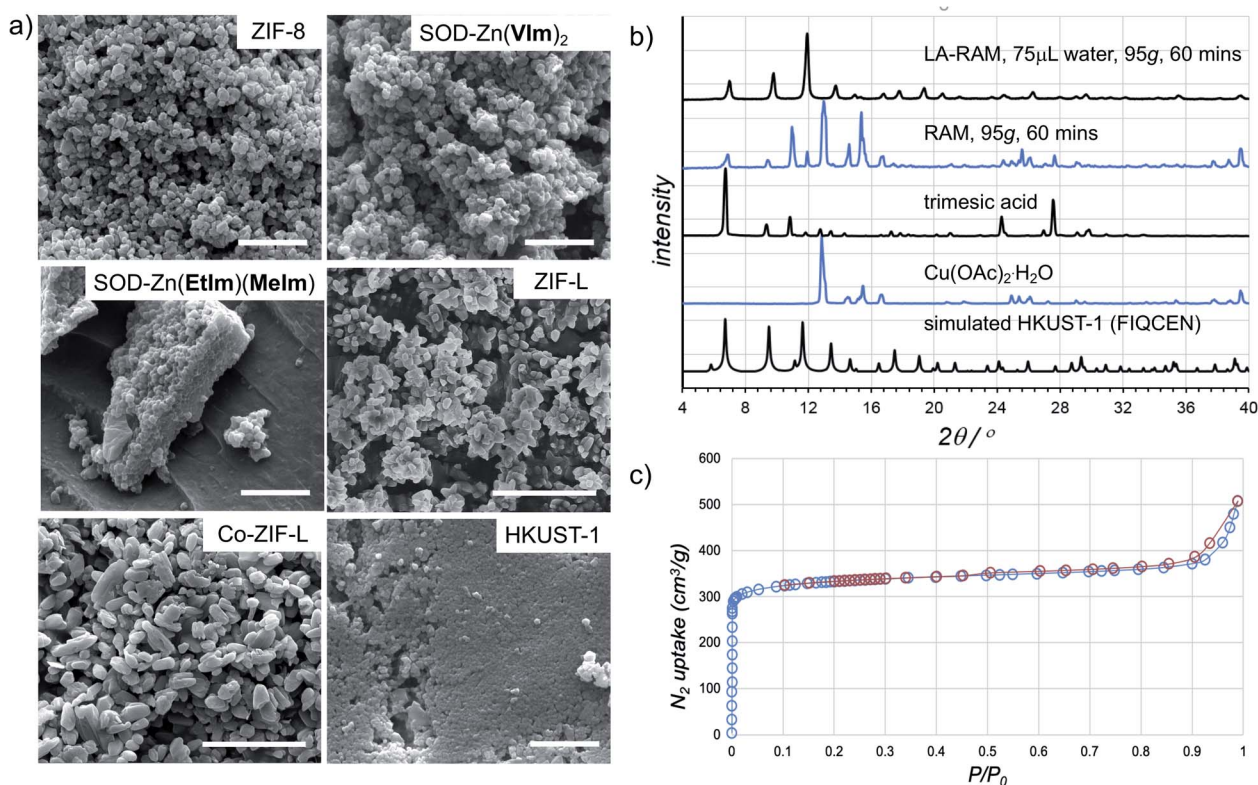


Fig. 4 (a) Example SEM images for samples of herein prepared MOFs (in each case, the bar corresponds to 1  $\mu\text{m}$ ). (b) Comparison of the PXRD patterns for HKUST-1 prepared by LA-RAM with water (1 hour, 95g) to the neat reaction mixture, and the patterns of reactants and a simulated one for the MOF structure (CSD code FIQCEN). PXRD patterns for other LA-RAM experiments are given in the ESI† (c) Nitrogen desorption and adsorption curves for HKUST-1 prepared by LA-RAM with water, after washing and evacuation.

further demonstrates the absence of significant thermal effects in LA-RAM synthesis.

The morphology of LA-RAM products was also studied by SEM, revealing hexagonal nanocrystalline particles of 50–200 nm size for  $\text{Zn}(\text{MeIm})_2$  and  $\text{Zn}(\text{VIm})_2$ , and leaf-like particles with sizes ranging from 30–900 nm for ZIF-L (Fig. 4a).

In order to evaluate the applicability of RAM to other types of MOFs, we also explored the synthesis of the popular Cu(II) trimesate framework material HKUST-1 (Fig. 1d), based on copper(II) paddlewheel nodes.<sup>28,29</sup> The mechanochemical synthesis of HKUST-1 by ball milling was previously reported by several groups, most often using copper(II) acetate monohydrate  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  and trimesic acid as starting materials.<sup>30,31</sup> Resonant acoustic mixing of a neat mixture of these reactants, in the stoichiometric ratio of 3 : 2 led to no reaction according to PXRD analysis. However, LA-RAM in the presence of diverse liquid additives produced HKUST-1, as evidenced by product PXRD patterns which in all cases exhibited Bragg reflections consistent with those of the MOF (CSD code FIQCEN).<sup>28</sup> In most cases, the PXRD pattern also exhibited additional X-ray reflections (see ESI†), indicative of impurities or side products. We believe that these, so far not identified phases, could result from the liquid additive coordinating to the metal center and/or templating a different type of framework structure.<sup>32</sup> Indeed, we have recently shown that choice of milling additive can have a strong effect on mechanochemical LAG synthesis of

zirconium MOFs due to coordination properties of the liquid.<sup>33</sup> Nevertheless, using water as the liquid additive led to the formation of HKUST-1 as the only product, as evidenced by PXRD and TGA (Fig. 4b, also see ESI†). The HKUST-1 made by RAM (95g, 1 hour,  $\eta = 0.15 \mu\text{L mg}^{-1}$ ) was obtained, after washing and evacuation, in 88% isolated yield. The material exhibited a surface area of  $1310 \text{ m}^2 \text{ g}^{-1}$  (Fig. 4c), consistent with previously reported values (see ESI†).<sup>29,30</sup>

## Conclusions

The use of resonant acoustic mixing as a simple, rapid and readily scalable methodology for synthesizing metal–organic frameworks of different levels of complexity, including two- and three-dimensional networks, has been demonstrated. This methodology is based on high-frequency acoustic agitation, does not use bulk solvent, and in contrast to other mechanochemical routes for MOF synthesis it does not require any milling or grinding media, enabling simple and straightforward scaling-up of batch synthesis from hundreds of milligrams to at least tens of grams, while still permitting the use of a metal oxide as a starting material. Importantly, the herein explored model systems demonstrate the ability to use acoustic mixing not only for making conventional, well-explored MOF materials such as ZIF-8 or HKUST-1, but also more complex mixed-ligand microporous solids, as well as the metastable<sup>27</sup> layered material



ZIF-L, that has previously never been reported by mechano-synthesis. We believe that the ability to form the ZIF-L product might be associated to LA-RAM being a milder mechano-chemical methodology, in which mechanical activation takes place by direct contact of reactant particles rather than through impact and abrasion by external milling media that are used in other types of mechanochemistry. Importantly, in each of these cases LA-RAM methodology appears to be superior to ball milling, which provided poorer control of product composition in the synthesis of a mixed-ligand MOF, and also did not yield ZIF-L. Further uses of LA-RAM as a general and easily scalable route to other types of functional materials, and the ability to use liquid additives and catalysts to enhance reactions in an acoustically-agitated solid-state environment, are currently being explored.

## Conflicts of interest

There are no conflicts to declare.

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