Title: Simple, scalable mechanosynthesis of metal organic frameworks using liquid-assisted resonant acoustic mixing (LA-RAM)

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Abstract: We present a methodology for the rapid and readily scalable mechanochemical synthesis 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 never previously obtained in a solventless 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.

Main text: Mechanochemical synthesis,1 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 ingredients2 and cocrystals,3 to metal organic frameworks (MOFs)4 and nanoparticle materials.5 Rapid, room-temperature reactions in a solvent-free or solvent-limited mechanochemical environment are 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.6,7 Whereas mechanochemical reactions in the laboratory or chemical manufacturing are typically conducted using ball milling8 or twin screw extrusion,9 approaches that rely on the use of grinding or extrusion media, recent reports have begun investigating approaches to mechanochemical reactivity without such components, by ultrasonic10 or acoustic11 frequency sample agitation (Figure 1a,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.12

As the next step in developing cleaner, simpler and readily scalable solvent-free synthetic methodologies, we now demonstrate the application of resonant acoustic mixing (RAM)11,12 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)13 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. Herein, we present liquid-assisted resonant acoustic mixing (LA-RAM) methodology that enables simple 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 (Figure 1c,d). Importantly, LA-RAM also enabled a simple, rapid route for making the metastable 2-D layered MOF material ZIF-L13,14 and its Co(II) analogue, neither of which have
previously been obtained via mechanochemistry. Using ZIF-L as a model, we demonstrate that LA-RAM synthesis of MOFs can be easily scaled from hundreds of milligrams to at least 25 grams.

Figure 1. Herein employed LabRam resonant acoustic mixer: a) exterior and b) interior. Schematic illustration of herein developed MOF syntheses using RAM: c) ZIF-8, mixed-ligand SOD-Zn(Melm)(EtIm) and ZIF-L obtained with HMelm as the ligand precursor and d) HKUST-1 obtained with trimesic acid as a ligand precursor.

All described RAM reactions were done using a Resodyn LabRAM II system (Figure 1a,b),\textsuperscript{15} 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 using starting materials in the range of 1.5 to >80 grams. Products were characterized by powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), Fourier-transform infrared attenuated total reflectance (FTIR-ATR) spectroscopy, N\textsubscript{2} sorption analysis, nuclear magnetic resonance (NMR) spectroscopy, and scanning electron microscopy (SEM).

As our first entry into RAM-based MOF mechanosynthesis, we investigated the reaction of ZnO and 2-methylimidazole (HMelm), known to quantitatively yield the popular sodalite (SOD) topology framework, Zn(Melm)\textsubscript{2} framework (ZIF-8, MAF-4)\textsuperscript{16} by either ion- and liquid-assisted grinding\textsuperscript{17} (ILAG, milling with a liquid additive and a catalytic salt) or reaction in supercritical CO\textsubscript{2}.\textsuperscript{18}

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 m/s\textsuperscript{2}) and is varied by changing the amplitude of acoustic agitation. It was previously observed that higher g values lead to improved mixing and reactivity in cocystal synthesis.\textsuperscript{ref\textsubscript{5}} The maximum achievable acceleration in the herein used Resodyn acoustic mixer was 95 g. Agitation of a neat mixture of ZnO and HMelm in a 1:2.1 stoichiometric ratio (5 mol\% excess of HMelm) at 95 g led to no reaction after 60 minutes, as evidenced by the PXRD pattern of the reaction.
mixture exhibiting only Bragg reflections of solid reactants (Figure 2a). Similarly, RAM at 95 g in the presence of a small amount of MeOH (75 μL, corresponding to the liquid-to-solid ratio $\eta = 0.30 \mu$L/mg, see ESI) led to only to trace amounts of ZIF-8 after an hour. The poor reactivity of ZnO and HMeIm mixtures upon RAM at 95 g is very different from that observed in ball milling, where both neat milling and LAG easily lead to incomplete but significant formation of ZIF-8.\(^{20}\) The reaction outcome did not change significantly even when the RAM process was performed in the presence of additional milling media, in the form of 10 zirconia (ZrO\(_2\)) balls of 3 mm diameter (see ESI).

Next, we explored RAM with MeOH ($\eta = 0.30 \mu$L mg\(^{-1}\)), but this time in the presence of a catalytic amount of NH\(_4\)NO\(_3\) (5 mol% with respect to Zn), mimicking the ILAG conditions\(^{17}\) previously shown to enable quantitative synthesis of ZIF-8 from ZnO by ball milling. Under these conditions, liquid-assisted RAM (LA-RAM) for 1 hour at 95 g led to complete transformation of ZnO to ZIF-8, without the need for any milling media, as evidenced by PXRD and TGA of the product after washing with MeOH and evacuation (Figures 2a,b). The sample temperature was measured before and immediately after mixing, revealing only a 0.7 °C temperature increase over 60 minutes, indicating that the reactivity is most likely driven by improved contact and mixing, rather than bulk heating effects. The LA-RAM synthesis of ZIF-8 was also readily accomplished using acetone, ethanol (EtOH), acetonitrile (CH\(_3\)CN) or N,N-dimethylformamide (DMF) as liquid additives. The conversion to ZIF-8 was also not significantly affected by varying the amount of liquid phase, with complete disappearance of ZnO observed upon LA-RAM in the presence of either 100 μL, 75 μL or even 50 μL of MeOH (see ESI).

![Figure 2](image_url)

**Figure 2.** Comparison of selected: a) PXRD patterns and b) TGA thermograms for ZIF-8 materials obtained by RAM for 60 minutes in the presence of MeOH (liquid-to-solid ratio $\eta = 0.3 \mu$L/mg) and NH\(_4\)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 30 g and 45 g reveal the presence of a 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.

After establishing conditions for production of ZIF-8 at 95 g, we explored reactivity under milder conditions at 15, 30, 45, 60 and 75 g (Figure 2a). As confirmed by PXRD and TGA (Figure 2b), quantitative conversion of ZnO to ZIF-8 as the sole product was observed at 60 g and 75 g, with lower acceleration giving only partial transformation of ZnO after one-hour of RAM, presumably due to poorer mixing.

After optimizing reaction composition and RAM acceleration, we next focused on the reaction time. Analysis of the reaction mixture containing ZnO, HMeIm, and catalytic amounts of MeOH and NH₄NO₃ after RAM treatment at 95 g for different time periods revealed almost complete disappearance of ZnO after 5 minutes. However, LA-RAM for 15 minutes or more always provided complete conversion to ZIF-8 (Figures 2a,b). The resulting product, after washing with MeOH and evacuation provided a Brunauer-Emmet-Teller (BET) surface area of 1,200 m²/g (Table 1, also see ESI). Importantly, the reaction was also readily scaled at least 5-fold, providing access to gram quantities of ZIF-8 within only 60 minutes (see ESI).

The ease and simplicity with which ZIF-8 was obtained through LA-RAM in the presence of a salt catalyst led us to investigate other ligand systems. Using the same optimized conditions identified for ZIF-8 synthesis, the analogous SOD-topology framework based on 2-vinylimidazole (HViIm, Figure 1a) was obtained in quantitative conversion (see ESI), as evidenced by PXRD, and TGA. Nitrogen sorption evaluation of SOD-Zn(ViIm)₂ gave a BET surface area of 1,110 m²/g, comparable to previous reports (see ESI).

Table 1. Measured BET surface areas and typical particle sizes (by SEM) for selected samples of microporous MOFs prepared using LA-RAM, after washing and evacuation.

| MOF                   | BET area (m²/g) | particle size (nm) |
|-----------------------|-----------------|--------------------|
| Zn(MeIm)₂ᵃᵇ           | 1200            | 50-200             |
| Zn(ViIm)₂ᵃᵇ           | 1110            | 50-300             |
| Zn(EtIm)(MeIm)ᵃᶜ       | 1140            | 40-90              |
| HKUST-1ᵃᵈ             | 1310            | 40-90              |

ᵃ all samples prepared at 95 g; ᵇ using MeOH as liquid additive; ᵇ using CH₃CN as liquid additive; ᵅ using water as liquid additive.

The LA-RAM methodology was readily applied for the synthesis of a mixed-ligand ZIF system, by RAM of ZnO in the presence of a 1:1 stoichiometric mixture of 2-methyl (HMeIm) and 2-ethylimidazole (HEtIm, Figure 1). After one-hour of RAM at 95 g, PXRD analysis of the reaction mixture revealed complete disappearance of ZnO, and the formation of a product isostructural to ZIF-8 (Figure 3a). As Zn(EtIm)₂ framework is known to adopt qtz-, ANA- and RHO-topologies, this result indicates the formation of a mixed-ligand SOD-Zn(EtIm)(MeIm) framework. This was confirmed by TGA in air, as well as by solid-state NMR analysis of the washed and evacuated material, which clearly revealed the presence of both MeIm and EtIm ligands in the solid state (see ESI). The composition of the material was additionally confirmed by washing extensively with MeOH to remove any potentially unreacted imidazoles, followed by dissolution in D₂O acidified with DCl. After further dilution with d₆-DMSO, ¹H NMR
spectroscopy (Figure 3d, see also ESI) confirmed the 1:1 stoichiometric ratio of $\text{MeIm}^-$ and $\text{EtIm}^-$ ligands in the material. Importantly, performing the reaction of a 1:1:1 mixture of $\text{ZnO}$, $\text{HMeIm}$ and $\text{HEtIm}$ under otherwise identical conditions, but by ball milling, gave a SOD-topology product which, after washing and dissolution in acid, contained the two ligands in the respective stoichiometric ratio 60:40. This preliminary result suggests that LA-RAM provides for more efficient mixing than ball milling.

Figure 3. a) PXRD pattern of SOD-Zn(EtIm)(MeIm) prepared by RAM with water (1 hour, 95 g) compared to a simulated MOF (CSD code VELVOY) Solution. b) Nitrogen desorption and adsorption curves for SOD-Zn(EtIm)(MeIm) prepared by LA-RAM. c) Solid state $^{13}$C-NMR of ZIF-8 (black) and SOD-Zn(EtIm)(MeIm) (blue) products of RAM after washing and evacuation. The aliphatic carbons exhibit various possible of Zn-environments. d) $^1$H NMR spectrum of the SOD-Zn(EtIm)(MeIm) framework after dissolution in DCl, illustrating the 1:1 ratio of $\text{MeIm}^-$ and $\text{EtIm}^-$ ligands.

The synthesis of mixed-ligand SOD-Zn(MeIm)(EtIm) was also readily scaled five-fold (total amount of product ca. 1.2 grams), giving a phase-pure product based on PXRD analysis, with a TGA residue of 34.0% (compared to theoretically calculated 33.7%, see ESI) and BET surface area of 1140 m$^2$/g (Figure 3b). Next, we screened the reactivity of a broader range of mixtures involving $\text{ZnO}$, $\text{HEtIm}$ and $\text{HMeIm}$. The overall stoichiometric ratio of $\text{ZnO}$ to total imidazole-based linker was kept at 1:2.1, respectively, and the stoichiometric ratio of $\text{HMeIm}$:$\text{HEtIm}$ 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) with SOD- and RHO-topology (CSD code MECWOH).

The described investigation of reactivity of $\text{ZnO}$ and $\text{HMeIm}$ at lower $g$-values revealed the formation of small amounts of a crystalline phase other than ZIF-8 (Figure 2a). Comparison of X-ray reflections suggests the unexpected product is ZIF-L (see ESI), a layered 2-D Zn(MeIm)$_2$ framework containing additional neutral $\text{HMeIm}$ ligands (CSD code IWOZOL). 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)\(_2\)·2H\(_2\)O was found to lead to very low conversions even in presence of a liquid (water), zinc nitrate hexahydrate Zn(NO\(_3\))\(_2\)·6H\(_2\)O was much more reactive (see ESI). Analysis of a reaction mixture resulting from LA-RAM (acceleration of 30 g, 30 minutes in presence of water) of Zn(NO\(_3\))\(_2\)·6H\(_2\)O and HMelm 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). In order to optimize the reaction towards complete conversion to ZIF-L, the ratio of Zn precursor to HMelm was increased. Complete conversion into ZIF-L was achieved at a Zn:HMelm stoichiometric ratio of 1:8 (Figure 2c), as evidenced by PXRD analysis, and TGA of the material after washing with water to remove excess HMelm (see ESI). Identical reaction conditions were also readily applicable for the synthesis of the Co(II) version of ZIF-L,\(^{25}\) by using Co(NO\(_3\))\(_2\)·6H\(_2\)O as a metal precursor (see ESI). As ZIF-L is a very recently reported form of zinc 2-methylimidazolate\(^{26}\) 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 (Figure 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 a so far not identified product (see ESI). As ZIF-L is known to thermally transform to ZIF-8,\(^{27}\) its bulk synthesis 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 Zn(Melm)\(_2\) and Zn(VIm)\(_2\), and leaf-like particles with sizes ranging from 30-900 nm for ZIF-L (Figure 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 (Figure 1d), based on copper(II) paddlewheel nodes.\(^{28,29}\) The mechanochemical synthesis of HKUST-1 by ball milling was previously reported by several groups, most often using copper(II) acetate monohydrate Cu(OAc)\(_2\)·H\(_2\)O and trimesic acid as starting materials.\(^{30,31}\) 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, Figure 4b).\(^{28}\) In most cases, the PXRD pattern also exhibited additional X-ray reflections (see ESI), indicative of impurities or side products. However, using water as the liquid additive led to the formation of HKUST-1 as the only product, as evidenced by PXRD and TGA (Figure 3c, also see ESI). The HKUST-1 made by RAM (95 g, 1 hour, \(\eta = 0.15 \mu\)L/mg) exhibited a surface area of 1,310 m\(^2\)/g (Figure 4c), consistent with previously reported values (see ESI).\(^{29,30}\)
In summary, we demonstrated resonant acoustic mixing as a simple, rapid and readily scalable solvent-free methodology for synthesizing metal-organic frameworks of different levels of complexity, including two- and three-dimensional networks. This methodology is based on high-frequency mechanical agitation, 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 layered material ZIF-L, that has previously never been reported by 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. We are currently exploring further uses of LA-RAM as a general and easily scalable route to other types of functional solids.

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Conflicts of Interest
None.
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