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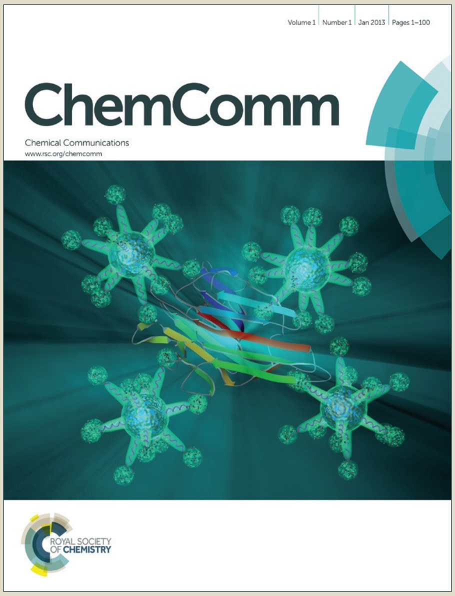

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DOI: 10.1039/C5CC09146B

Journal Name

COMMUNICATION

Mechanochemical and Solvent-free Assembly of Zirconium-Based Metal-organic Frameworks

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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We develop the first mechanochemical and solvent-free routes for zirconium metal-organic frameworks, making the frameworks UiO-66 and UiO-66-NH$_2$ accessible on gram scale without strong acids, high temperatures or excess reactants. The frameworks form either by milling, or spontaneously self-assemble by simply exposing solid mixtures of reactants to organic vapour. Generated frameworks exhibit high porosity and catalytic activity in hydrolysis of model nerve agents, on par with solvothermally generated counterparts.

Metal-organic frameworks (MOFs)[1] are one of the most active areas of materials science, with proof-of-concept applications in gas storage and separation,[2,3] catalysis,[4] chemical defense,[5] sensing,[6] light harvesting[7] and more. Growing impact of MOFs is reflected by their recent commercialisation, which made a small number of MOFs based on Mg, Al, Fe, Cu and Zn commercially available on laboratory research scale.[8] However, chemical stability to strong acids or bases, and retention of microporosity upon extended exposure to different atmospheres remain central problems for most MOFs, including those currently being manufactured commercially.[9]

MOFs based on carboxylate linkers and 12-coordinate cationic $Zr_6O_4(OH)_4^{12+}$ clusters (Figure 1),[10] exemplified by terephthalate-based UiO-66[11] and derivatives, have great potential as catalysts,[12] given a high concentration of well-dispersed metal-based nodes, exceptional aqueous stability over a range of pH values, high surface areas, and tunable chemical structures.[13] Despite continuous efforts and improvements,[14] however, syntheses of UiO-66 and analogues remain encumbered by challenging procedures involving aggressive reagents.[11a,15] So far, the most reliable syntheses of UiO-66 and related MOFs rely on hydrochloric acid in hot organic solvents, achieving reproducibility at expense of structural defects.[16] Thus, the exploitation and potential commercialisation of excellent materials properties of UiO-66 and analogues remain hindered by adverse synthesis.

Mechanochemistry, *i.e.* reactivity induced or sustained by mechanical force,[17] has been recently introduced as an alternative to conventional MOF syntheses.[18] Mechanochemical techniques, such as liquid-assisted grinding (LAG)[19] can enable the synthesis of MOFs[20] without bulk solvents, aggressive conditions and/or corrosive reagents frequently employed in solution syntheses.[21] Importantly, varying the liquid additive (given as *η*, ratio of liquid volume to weight of reactants[22]) in LAG provides a unique opportunity to optimise and direct mechanochemical reactions without large modifications in the milling procedures. Recent applications of LAG enabled the synthesis of MOFs from poorly soluble metal oxides and discovery of novel phases.[23]

We now describe the first implementation of mechanochemistry and solvent-free 'accelerated aging' (AA)[24] for the synthesis of zirconium-based MOFs, providing new, surprisingly simple routes to gram amounts of UiO-66 and its amino- analogue UiO-66-NH$_2$[11,25] without using bulk solvents, aggressive reagents or high temperatures.

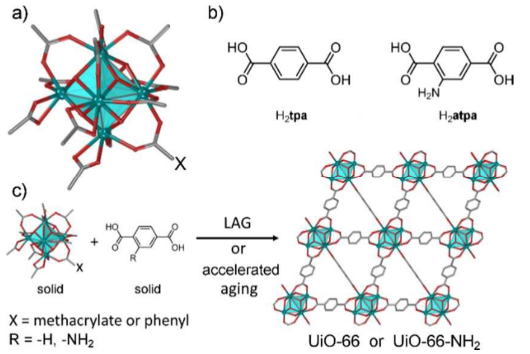

Figure 1. (a) A carboxylate-capped $Zr_6O_4(OH)_4^{12+}$ cluster; (b) terephthalic and 2-aminoterephthalic acids; (c) herein developed syntheses of UiO-type MOFs.

Principal requirement for the synthesis of UiO-66 and related MOFs is the formation of $Zr_6O_4(OH)_4$ nodes. We considered a mechanochemical strategy similar to that recently used for

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Electronic Supplementary Information (ESI) available: Selected PXRD, FTIR-ATR, BET, TGA, SEM and DLS data. See DOI: 10.1039/x0xx00000x

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IRMOFs,[26] *i.e.* reaction of a pre-assembled benzoate cluster $Zr_6O_4(OH)_4(C_6H_5CO_2)_{12}$ (**1**) with terephthalic acid (H_2**tpa**, Figure 1). Precursor **1** was readily obtained from zirconium propoxide, $Zr(OPr)_4$, (see ESI).[27] Dry milling of **1** and H_2**tpa** in correct stoichiometric ratio 1:6 did not lead to a chemical reaction, according to powder X-ray diffraction (PXRD) analysis of the reaction mixture after 90 min milling. Switching to LAG (η=0.66 µL/g[22]) with *N*,*N*-dimethylformamide (DMF) gave a new product exhibiting a broad PXRD feature consistent with the (111) reflection of UiO-66 (Figure 2a-f, also see ESI). Product formation was accompanied by complete disappearance of reactant X-ray reflections.

PXRD analysis suggests successful exchange of benzoate ligands on **1**, leading to UiO-66 of poor crystallinity. Alternative precursor based on methacrylic acid, $Zr_6O_4(OH)_4(C_2H_3CO_2)_{12}$ (**2**),[28,14c] was used as well, without much improvement. At this point, we turned to varying the milling liquid. Switching from DMF to methanol (MeOH) led to little improvement in crystallinity of product from **1** (Figure 2g). However, LAG of **2** and H_2**tpa** with MeOH (η=0.66 µL/mg[22]) gave a product whose PXRD pattern exhibited sharp, well-defined reflections, with positions consistent with UiO-66 structure (Figure 2h). Washing was performed with MeOH only, allowing for the first time complete exclusion of HCl and DMF from the synthesis of a UiO-type MOF. Using a Spex 8000 mill, synthesis of UiO-66 by MeOH LAG was accomplished on 3 g scale in 75 min (Figures 2i, S1, S2). BET surface area for the product, calculated from the N_2 sorption isotherm at 77 K, was 1020 m^2 g^{-1} (Table 1, Figure 3).[29] Next, we targeted UiO-66-NH_2, based on 2-aminoterephtalic acid (H_2**atpa**),[25] recently established as an excellent catalyst for hydrolytic degradation of nerve agent simulants.[30] Based on optimised mechanosynthesis of UiO-66, we milled **2** and H_2**atpa** in presence of MeOH. After 90 min, PXRD revealed formation of UiO-66-NH_2, isostructural to UiO-66. Using a Spex 8000 mill, mechanosynthesis of UiO-66-NH_2 was performed on 1.5 g scale in 45 min (Figures 2j, S1-S3). Based on a N_2 isotherm at 77 K, BET surface of UiO-66-NH_2 after washing and activation was 945 m^2 g^{-1} (Table 1, Figure 3a), consistent with literature.[11e,16a,25,31]

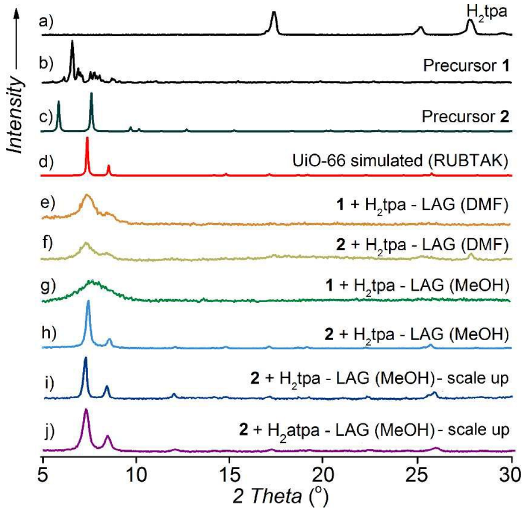

Figure 2. PXRD patterns for LAG syntheses of UiO-66 and UiO-66-NH_2: a) H_2**tpa**; b) precursor **1**; c) precursor **2**; d) simulated for UiO-66 (CSD RUBTAK); e) LAG of **1** and H_2**tpa** with DMF; f) LAG of **2** and H_2**tpa** with DMF; g) LAG of **1** and H_2**tpa** with MeOH; h) LAG of **2** and H_2**tpa** with MeOH; i) UiO-66 made on 3 gram scale by LAG of **2** and H_2**tpa** with MeOH; j) UiO-66-NH_2 made on 1.5 gram scale by LAG of **2** and H_2**atpa** with MeOH.

Table 1. BET surface areas for mechanochemically made zirconium MOFs.[a,b]

MOF	Precursor	BET surface area (m^2 g^{-1})
UiO-66[29]	**2**	1020
UiO-66-NH_2	**1**	925
UiO-66-NH_2	**2**	945
UiO-66[29]	$Zr(OPr)_4$[c]	890

a) Details of activation are given in SI; b) all reactions were done by LAG, using MeOH as the milling liquid; c) one-pot synthesis from $Zr(OPr)_4$, acrylic acid and H_2**tpa** with MeOH as the grinding liquid.

UiO-66-NH_2 was also accessible by LAG from **1**, giving a BET surface area of 925 m^2 g^{-1} (Table 1, Figure S4). Synthesis of UiO-66-NH_2 involved only MeOH as the milling and washing liquid, again eliminating the need for DMF. Finally, we attempted a one-pot synthesis of UiO-66 directly from commercial zirconium propoxide, methacrylic acid and stoichiometric H_2**tpa**. After 90 min, one-pot milling in the presence of MeOH gave UiO-66 of high surface area (Table 1, Figures 3a, S5), providing the first one-step route to UiO-66 from zirconium propoxide, an attractive replacement for $ZrCl_4$ and $ZrOCl_2$.

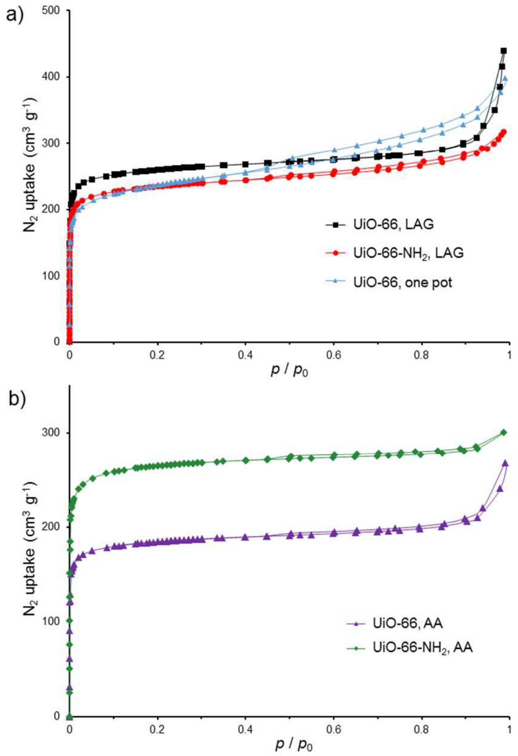

Figure 3. BET isotherms (N_2, 77 K) for: (a) UiO-66 and UiO-66-NH_2 from optimised LAG syntheses using MeOH, and UiO-66 made by one-pot reaction from $Zr(OPr)_4$; (b) UiO-66 and UiO-66-NH_2 from AA in MeOH vapour at 45 °C.

We next explored AA, an operationally simple technique that can achieve solvent-free, low-energy synthesis of metal-organic materials[24] by exposing a physical mixture of reactants to mild temperature and suitable atmosphere. AA was

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previously applied to make salts, cocrystals, metal oxalate MOFs, zeolitic imidazolate frameworks and, recently, HKUST-1.[24] Short grinding (<1 min in agate mortar) of a physical mixture of **2** with H_2**tpa** or H_2**atpa**, followed by exposure to MeOH vapor at 45 °C led to spontaneous assembly of UiO-66 and UiO-66-NH_2, respectively (see ESI). Throughout aging, samples remained solid and products were highly crystalline, as evidenced by PXRD which revealed complete disappearance of reactants after 3 days (UiO-66-NH_2) and 1 week (UiO-66) (Figures S6,S7). MOFs, synthesised at >1 g scale, exhibited high BET areas after activation (Table 2, Figure 3b).

With the materials in hand, we examined catalytic activity of UiO-66-NH_2 made by LAG and by AA. Both samples show high hydrolysis activity: 2.5 min and 2 min for an initial half-life for degradation of the nerve agent simulant dimethyl 4-nitrophenyl phosphate (DMNP, Figure 4), respectively. Catalytic activity of UiO-66-NH_2 made by AA is comparable to that of solvothermally prepared material ($t_{1/2}$=1min);[30] the difference in half-life is attributed to a difference in particle size. For mechanochemically made UiO-66-NH_2, average particle size was found to be below 100 nm by dynamic light scattering (DLS) in water (Figure S8). Slower reaction kinetics ($t_{1/2}$=2.5min) compared to those for UiO-66-NH_2 made by AA are likely due to rapid aggregation and precipitation of nanoparticles during the catalytic reaction. UiO-66 made by LAG or AA also exhibited high catalytic activity similar to that of solvothermal.[5a] Samples of UiO-66 and UiO-66-NH_2 were characterised by scanning electron microscopy (SEM, see ESI) before and after evaluating catalytic activity. Overall, the catalysis and porosity measurements show that zirconium MOFs made by LAG or AA have properties comparable to solvothermally made materials.

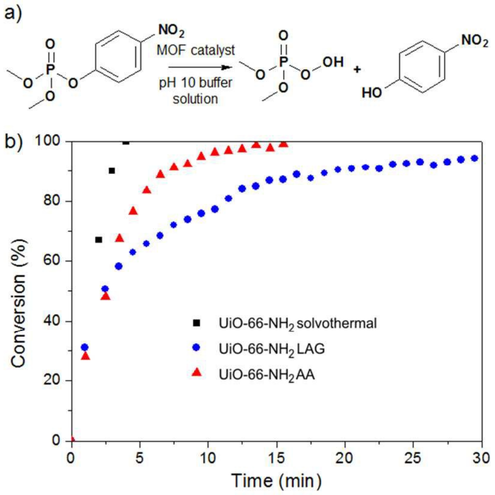

Figure 4. Hydrolysis of nerve agent simulant DMNP: a) reaction; b) hydrolysis profiles in presence of UiO-66-NH_2 made solvothermally (black), by LAG (blue) and AA (red).

Table 2. BET surface areas for MOFs made by accelerated aging in MeOH vapor[a]

MOF	Precursor	BET surface area (m^2 g^{-1})
UiO-66[29]	**2**	730
UiO-66-NH_2	**2**	1050
UiO-66-NH_2	**1**	915

a) Details of activation procedure are given in the SI.

Conclusions

We demonstrated that non-conventional synthetic approaches of mechanochemistry and accelerated aging enable a surprising simplification of procedures for making zirconium-based MOFs. Frameworks UiO-66 and UiO-66-NH_2, noted for their outstanding stability and catalytic activity, can now be synthesised on gram scale by a simple, rapid and room-temperature milling procedure which also allows using zirconium propoxide as a starting material.

Surprisingly, gram amounts of the microporous MOFs are obtainable by spontaneous assembly of the organic linker with a readily accessible carboxylate-capped zirconium cluster, simply by exposing a physical mixture of reactants to organic vapour. Herein presented techniques offer a route to highly porous, catalytically active UiO-frameworks under conditions resembling mild processes of small molecule self-assembly, contrasting the conventional approaches that require acidic reagents (HCl, $ZrCl_4$, $ZrOCl_2$) under solvothermal conditions. These results have the potential to not only improve the wide accessibility of UiO-type MOFs but also to change the way microporous MOFs are synthesised in general.

Acknowledgments

We acknowledge NSERC Discovery Grant for funding. KU is supported by the European Commission and the Croatian Ministry of Science, Education and Sports from the Marie Curie FP7-PEOPLE-2011-COFUND program NEWFELPRO, Grant Agreement No. 62. OKF and JTH acknowledge funding by the Army Research Office (project no. W911NF-13-1-0229). We acknowledge Tim Osborne-Jones (Spex SamplePrep LLC) for providing access to a Spex 8000 mill.

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