Electronic Supplementary Material for CrystEngComm

Supplementary Material

Mechanochemical conversion of a metal oxide into coordination polymers and porous frameworks using liquid-assisted grinding (LAG)

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Experimental

Mechanochemical experiments

For the construction of coordination polymers of **1**, 50 μL of a liquid was added to a mixture of 80 mg (1 mmol) of ZnO and 116 mg (1 mmol) of **fa**. The mixture was then ground in a stainless steel jar, using two stainless steel balls of 7 mm diameter, for 30 min in a Retsch MM200 mill operating at 30 Hz. After grinding the solid product was left to stand in air for approximately 30 minutes, before being stored in a closed vial.

The synthesis of **1**·$4H_2O$ required grinding for 45 minutes, otherwise a product would contain impurities of **1**·$5H_2O$. The temperature of the reaction mixture immediately after grinding never exceeded 33 ^oC.

For MOF synthesis, the reaction mixture also contained 78 mg (0.5 mmol) of **bipy** or 90 mg (0.5 mmol) of **bpe**, and the volume of added liquid was 100 μL. Grinding was performed as described above, but for a shorter period of 20 minutes. After grinding, the obtained products were dried in air for approximately 15 minutes and then kept in a desiccator over P_2O_5. If left in air for over 2 days, the samples readily lost their entire content of DMF (adsorbed on surface, as well as included in the porous structure).

Powder X-ray Diffraction

PXRD data was collected on a laboratory Philips X'Pert Pro diffractometer, equipped with an X'celerator RTMS detector, using Ni-filtered CuKα radiation, using a flat plate configuration. Data stuitable for structure.solution and refinement were collected in the angular range 5-60^o over a period of 55 minutes.

NMR Specotroscopy

All ^1H NMR spectra were collected using acidic D_2O as the solvent, on a Bruker 400 MHz spectrometer and interpreted using Bruker TopSpin software. The samples were dissolved in 0.75 mL of D_2O by the addition on 200 μL of 36% solution of DCl in D2O, followed by heating.

Scanning electron microscopy (SEM)

Samples of MOFs **2** and **3** prepared by LAG with DMF were imaged using a JEOL 5800LV instrument. No attempt was made to disperse the sample particles before imaging, to avoid post-synthetic modifications to particle shape.However, a thin platinum coating was applied to reduce the effects of sample charging. As a result of this technique, the samples that were imaged probably contained very little or no included DMF solvent.

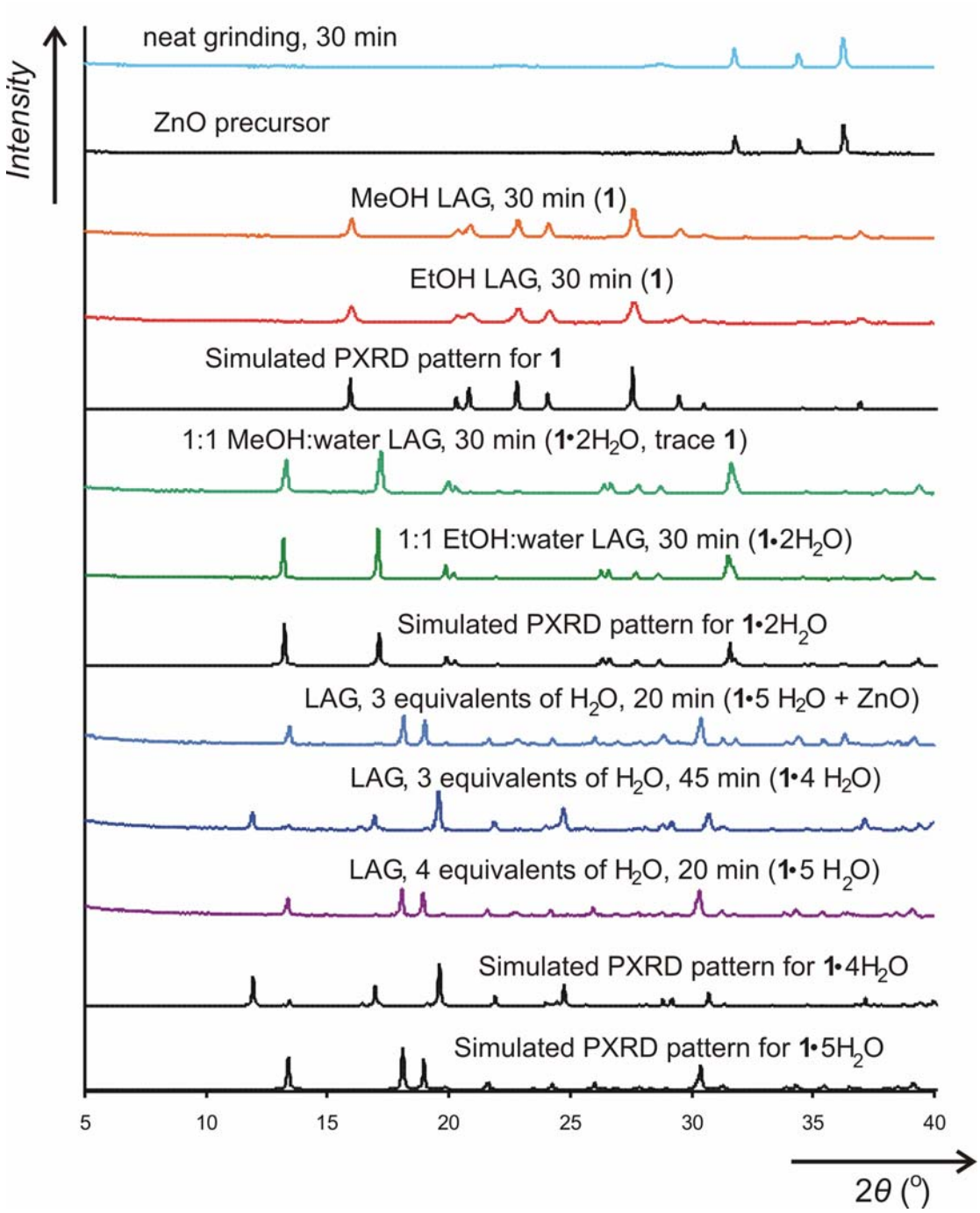

Figure S1. PXRD patterns for the mechanochemical reactions of ZnO and fumaric acid to yield **1**, **1**·2H_2O, **1**·4H_2O and **1**·5 H_2O. The reaction conditions and assignment of products are indicated for each pattern. Simulated patterns are shown in black.

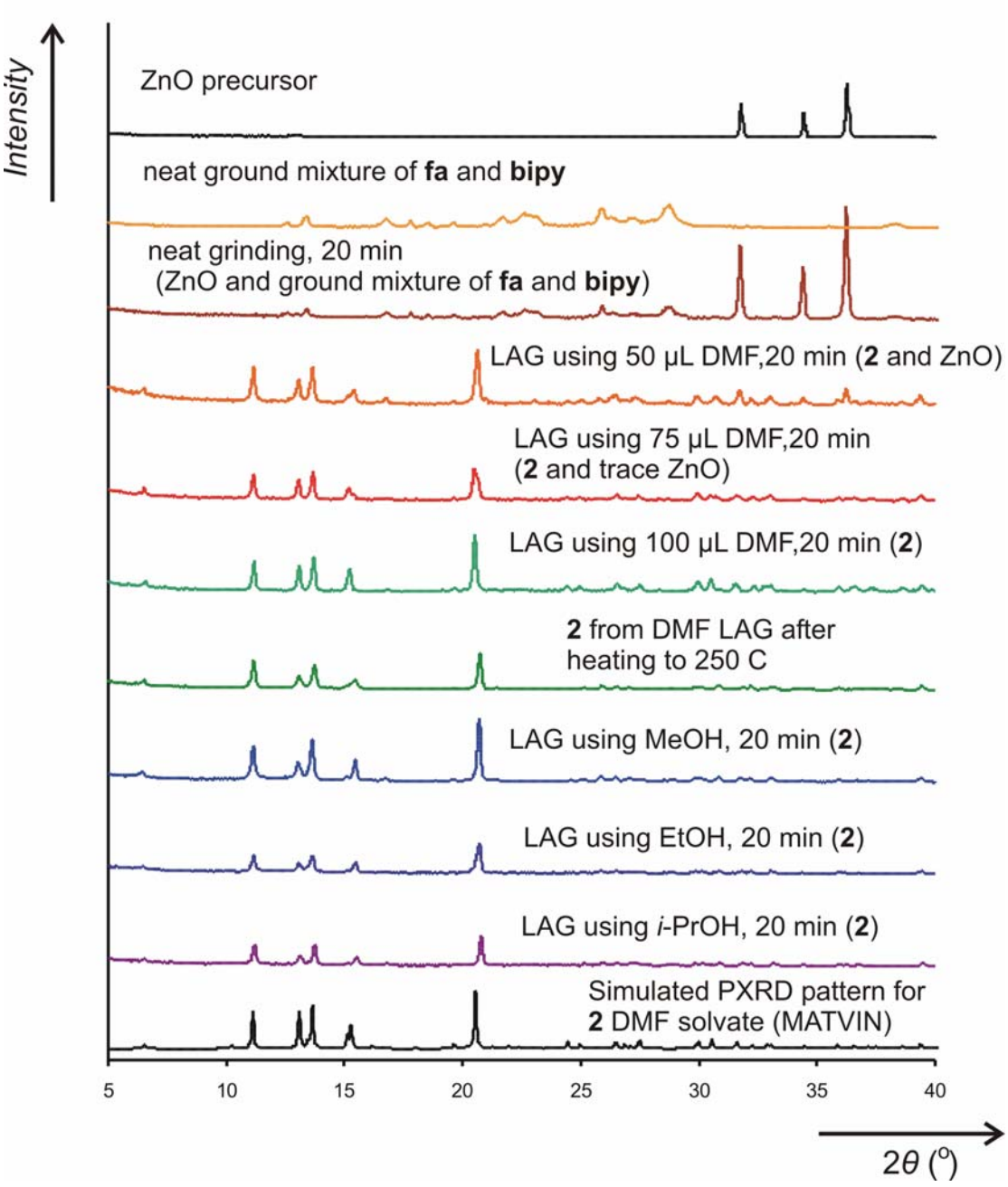

Figure S2. PXRD patterns for the mechanochemical construction of **2**. The reaction conditions and assignment of products are indicated for each pattern. Simulated patterns are shown in black.

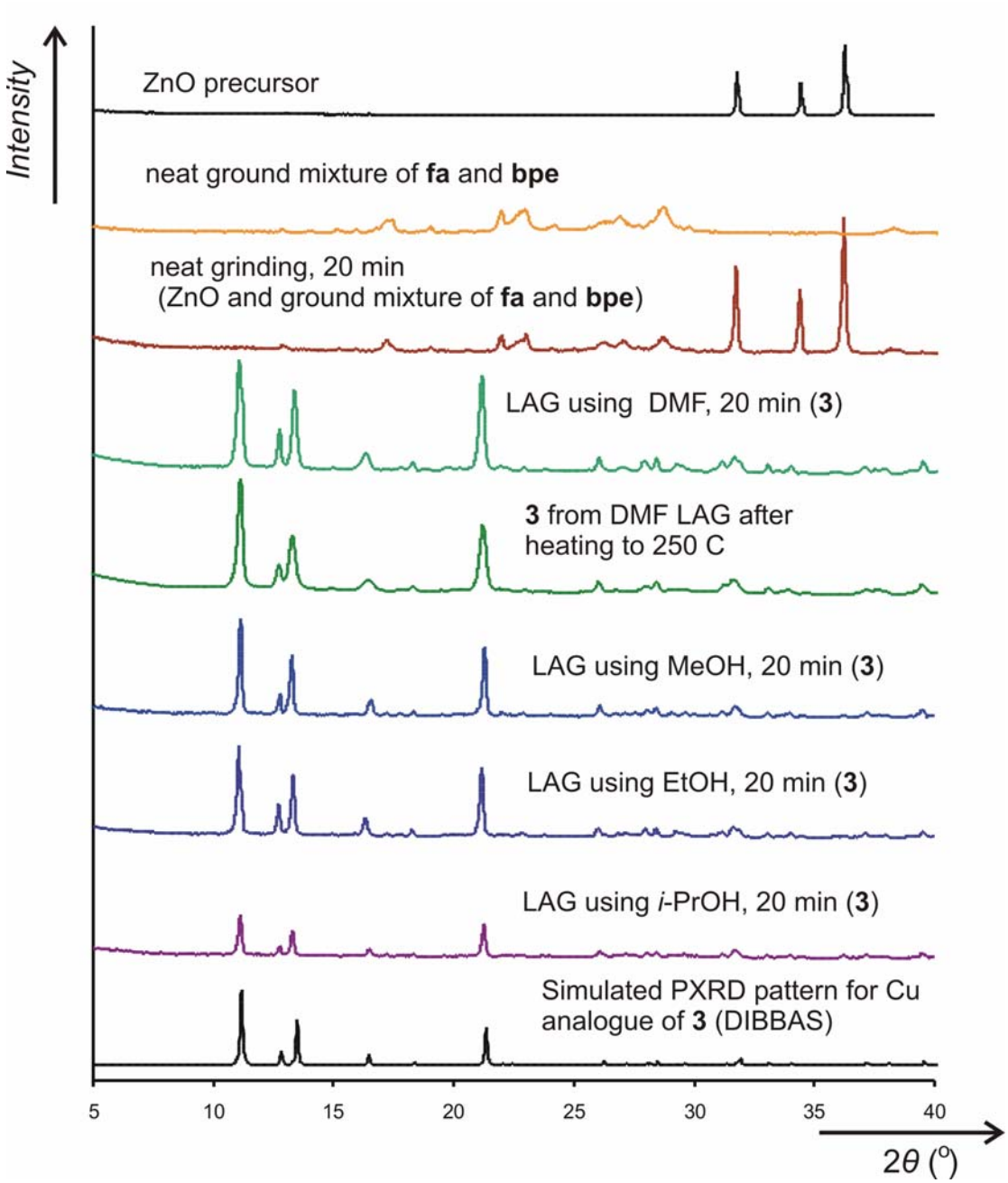

Figure S3. PXRD patterns for the mechanochemical construction of **3**. The reaction conditions and assignment of products are indicated for each pattern. Simulated patterns are shown in black.

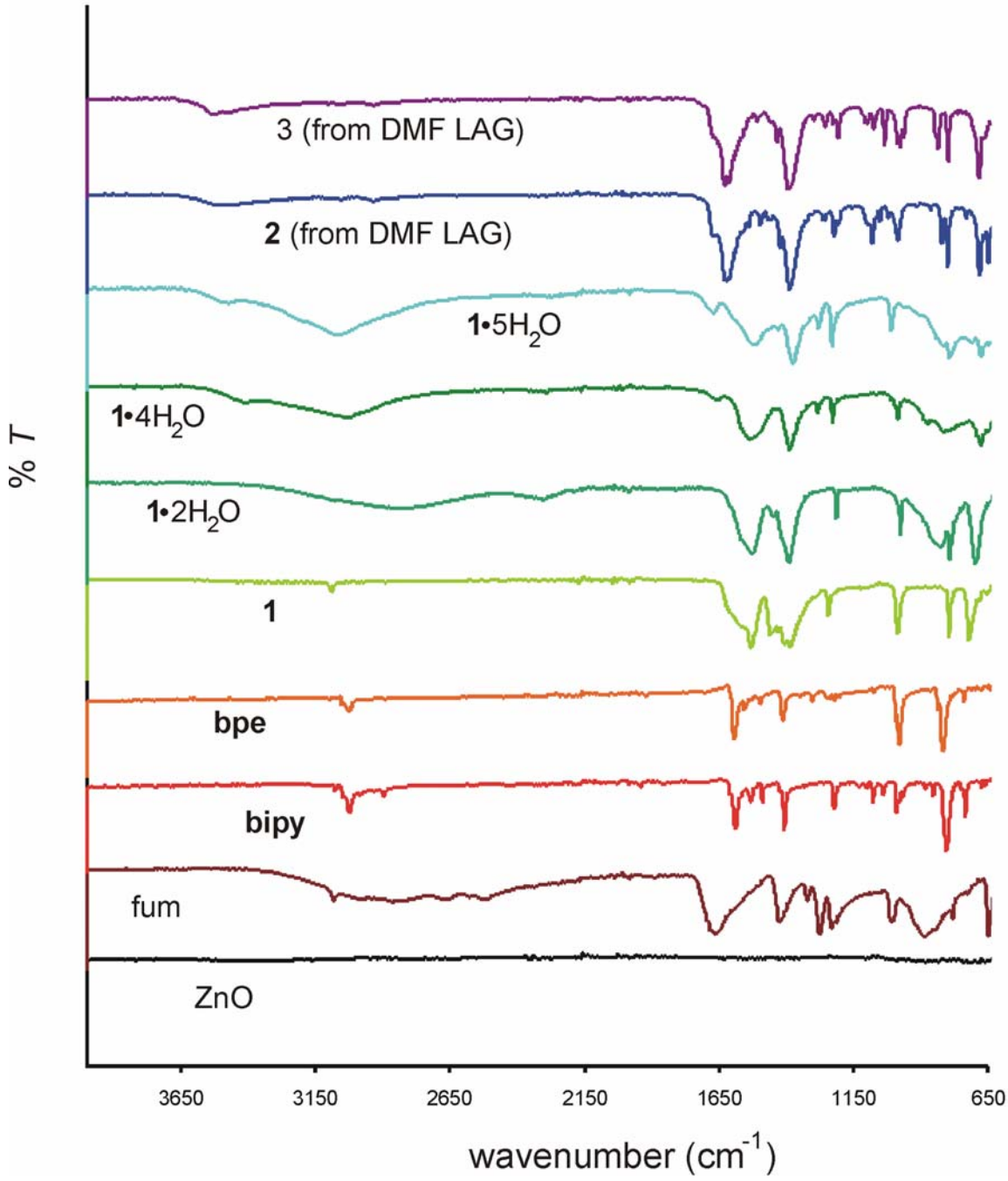

Figure S4. FT-IR spectra for the reactants and product of mechanochemical LAG reactions. From bottom to top: ZnO, **fum**, **bipy**, **bpe**, **1**, **1**·2H_2O, **1**·4H_2O, **1**·5H_2O, **2** (via LAG with DMF), **3** (via LAG with DMF).

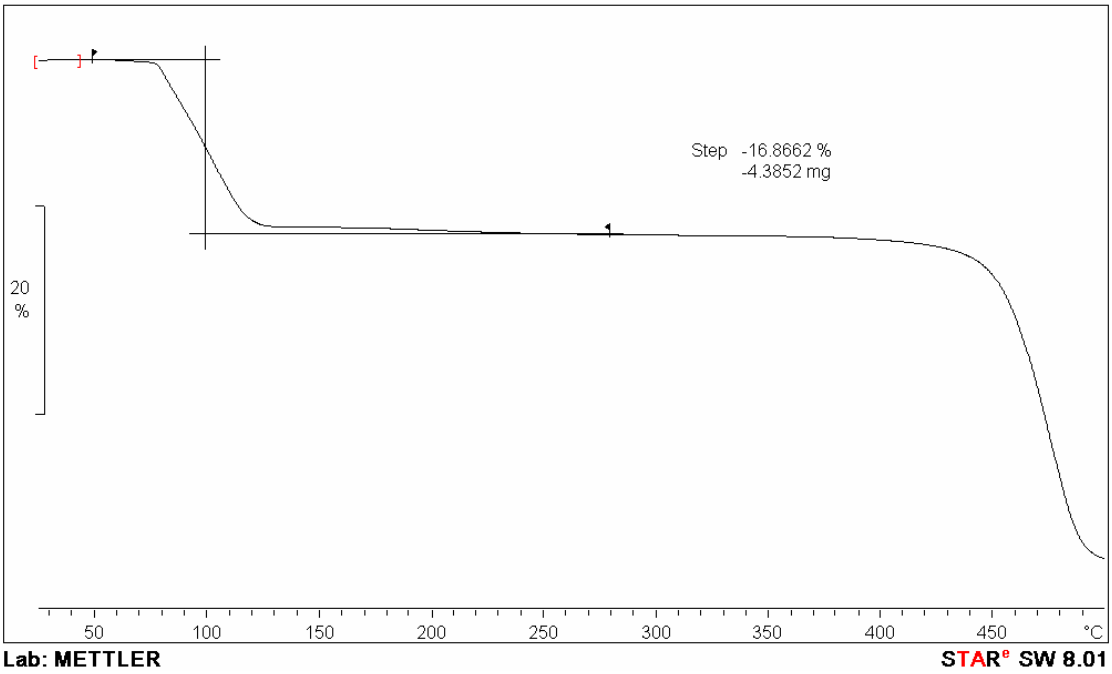

Figure S5. TGA curve for **1**·2H_2O. Experimentally determined water content is 16.86%, corresponding to the content expected for **1**·2H_2O of 16.86%.

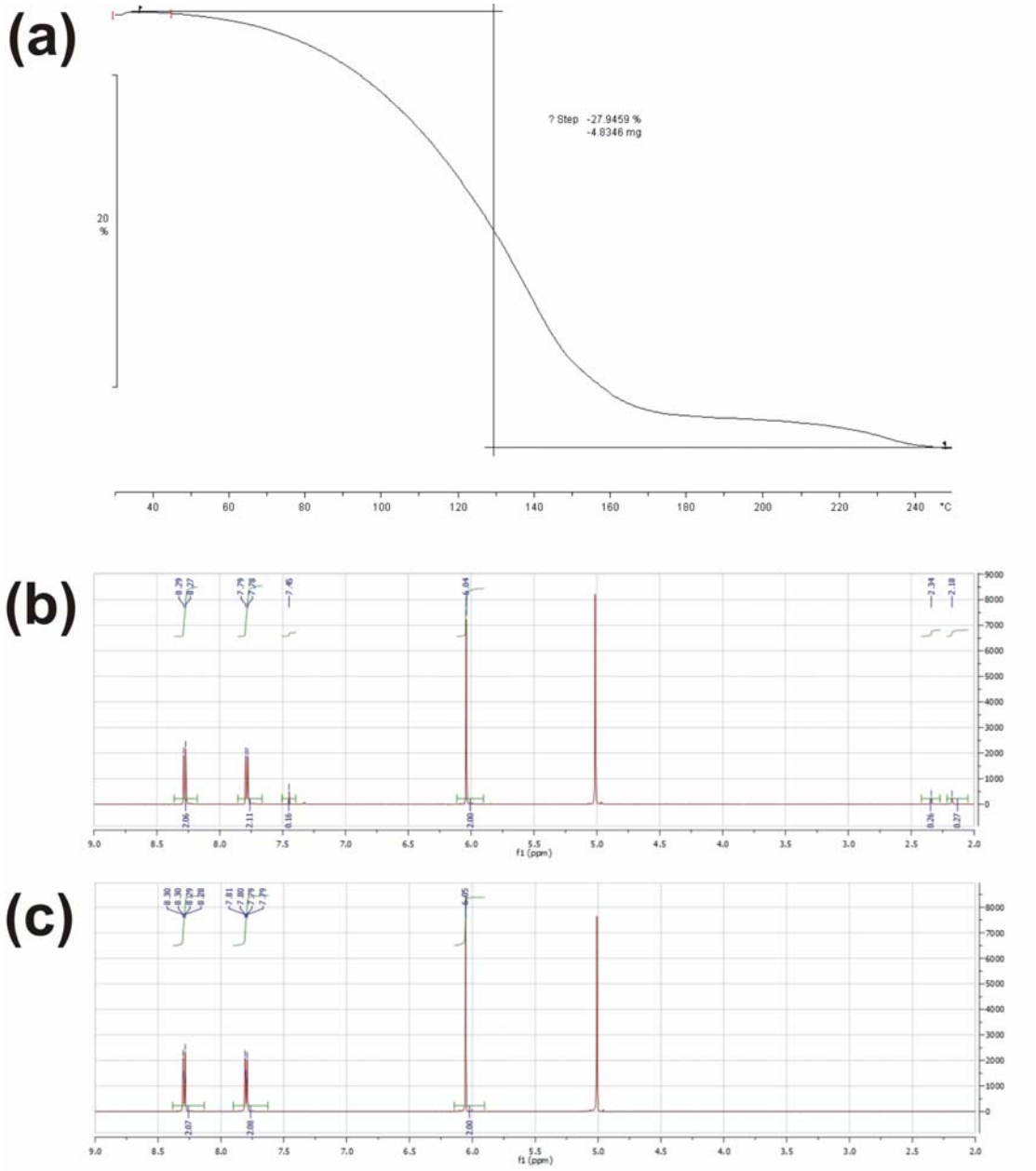

Figure S6. (a) TGA curve; (b) and (c) ^{1}H NMR spectra before and after heating to 250 ^{o}C, respectively, for **2** made by DMF LAG. The NMR spectra demonstrate the absence of DMF in the product after heating.

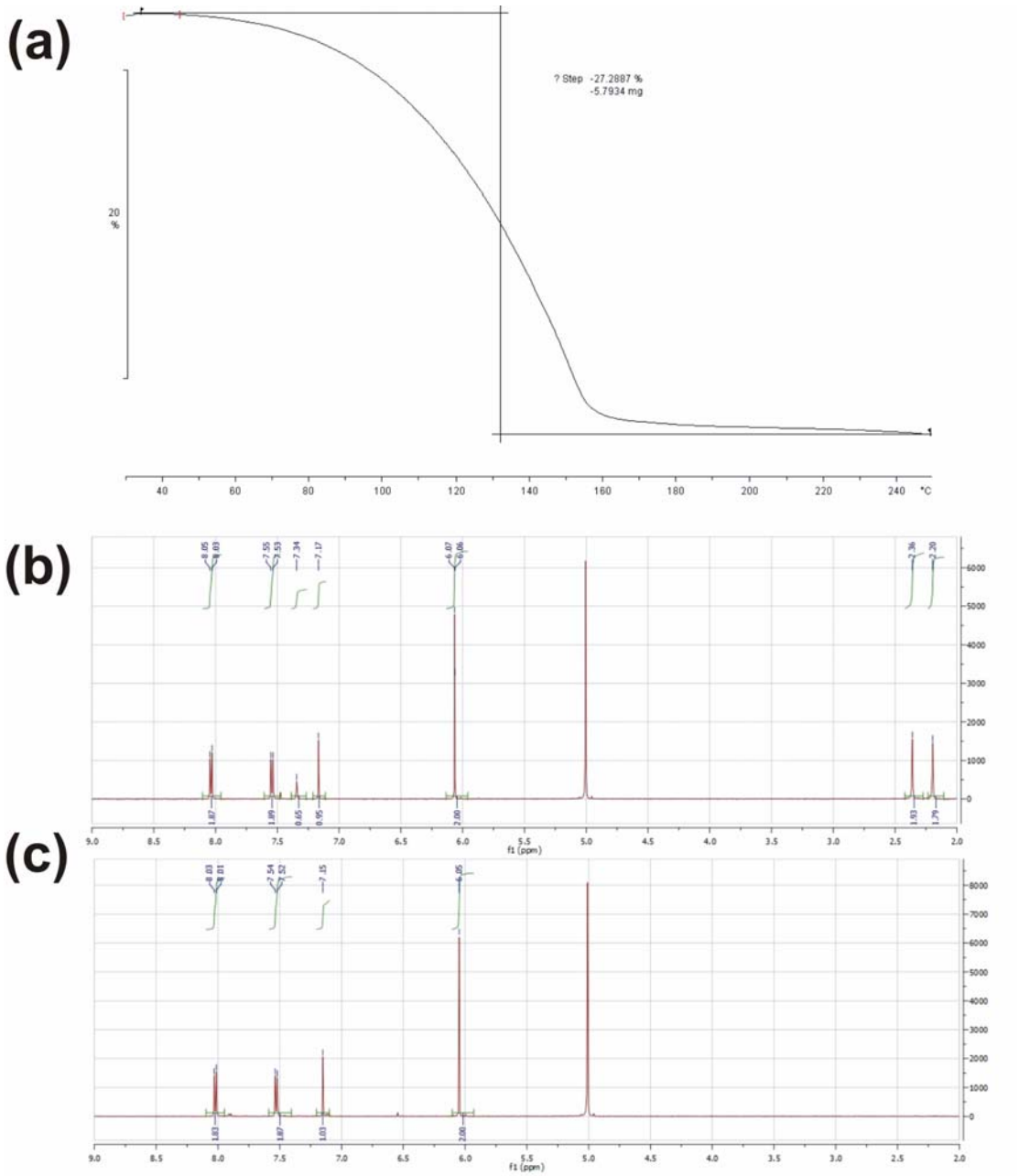

Figure S7. (a) TGA curve; (b) and (c) ^{1}H NMR spectra before and after heating to 250 ^{o}C, respectively, for **3** made by DMF LAG. The NMR spectra demonstrate the absence of DMF in the product after heating.

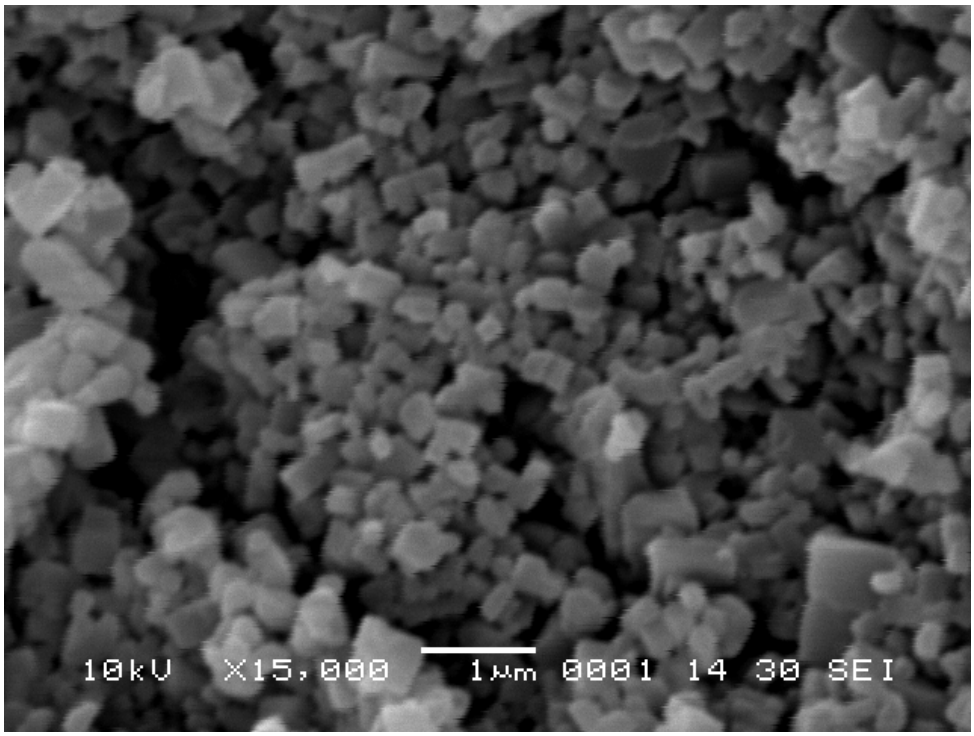

Figure S8. SEM image of **2** from DMF LAG.

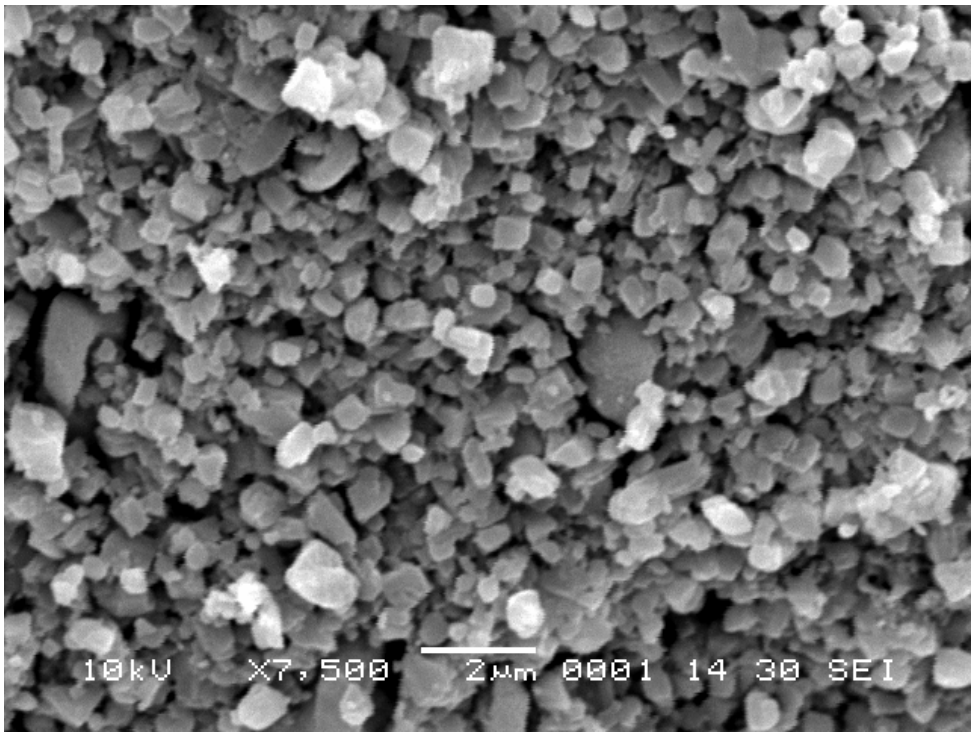

Figure S9. SEM image of **3** from DMF LAG.