Synthesis and post-synthetic modification of UiO-67 type metal-organic frameworks by mechanochemistry

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A B S T R A C T

Herein, we report the synthesis of zirconium metal-organic frameworks by a mechanochemical route. The frameworks are obtained by the coordination of a zirconium cluster with the biphenyldicarboxylic acid linker to obtain **UiO-67** or with the iso-structural 2,2′-bipyridine-5,5′-dicarboxylic acid to access to a functional MOF (**UiO-67-bpy**). In a second mechanochemical reaction, it has been possible to coordinate by post-synthetic modification a copper salt on each bipyridine site (**UiO-67-bpy-Cu**). Both materials exhibit crystallinity and porosity (up to 750 m^2/g) showing the possibility to get access to elaborated materials in a cleaner way than the classical solvothermal route in DMF.

1. Introduction

Hybrid materials, combining switchable organic and robust inorganic moieties, are nowadays becoming more and more popular [1]. In this family, metal-organic frameworks (MOFs), which are nanoporous crystalline materials, are recognized for their versatile properties that go along with their high structural diversity [2]. They find numerous applications in drug delivery, [3] gas storage, [4] catalysis, [5] metal extraction, [6] etc. In particular, artificial photosynthesis has gained a lot of attention since MOF's structure can contain a photosensitizer and a catalytic center due to the presence of a coordination site on the structural linker [7]. Because of their high stability under light excitation or photocatalytic conditions, Zr and Ti MOFs are among the best candidates in this domain. Their syntheses often require harsh conditions and long reaction times, in toxic solvent such as DMF [8]. In addition, side-products arising from the metal source hydrolysis ($ZrCl_4$, $TiCl_4$...) are often obtained in these conditions [9]. To circumvent such issues, mechanochemistry by using ball-mills could become an excellent alternative to the classical solvothermal conditions. This method can also allow the synthesis of MOFs in a cleaner and larger production; two needs that are mandatory in order to

be introduced into the industry and a larger market. Indeed, working under solvent-free or solvent-less conditions, with an excellent agitation, allows to react efficiently highly concentrated mixtures, thus enhancing reaction rates. Moreover, since few quantities of solvent are used, substrate hydrolysis that occurs during MOF synthesis can be limited in ball-mills. Applications of ball-milling in various domains can be found in literature [10] but it is at an early stage of development when it is applied to the synthesis of MOFs [11]. In 2015, the group of Friščić demonstrated that it was highly convenient to synthesize UiO-66 or UiO-66-NH_2, zirconium MOFs featuring terephtalic acid or 2-aminoterephtalic acid as organic ligands, respectively, using mechanochemistry as activation technique [12]. After less than 3 h of milling at 30 Hz, MOFs with PXRD (powder X-ray diffraction) patterns and BET (Brunauer, Emmett and Teller) areas consistent with literature were obtained. Another interesting material from the same family of MOFs is the UiO-67, [13] which essentially is an analogue of the UiO-66 with bigger pores and surface area due to the increase of the length of the ligand 4,4′-biphenyldicarboxylic acid (BPDC) instead of the terephtalic acid but preserving the same morphology. In literature, synthesis of UiO-67 generally involves zirconium precursors such as $ZrCl_4$ or $Zr(On-Pr)_4$, but recently, alternative routes involving the use of a pre-assembled clusters revealed promising [14].

Following our interest in the mechanochemistry involving organometallics species, [15–18] two Zr-based MOFs, the **UiO-67** MOF
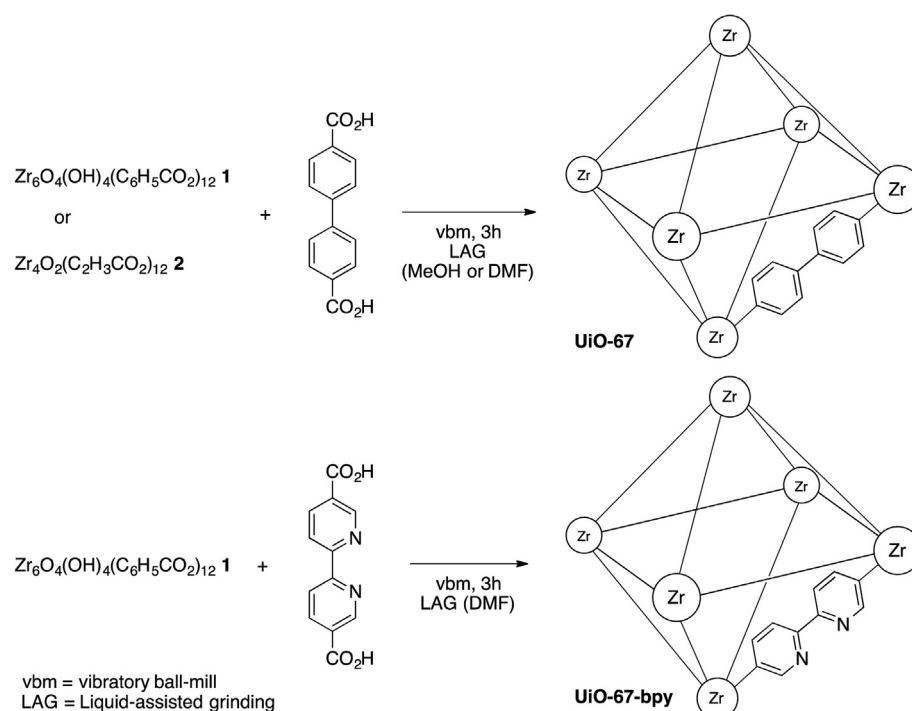
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and its bipyridine analogue (**UiO-67-bpy**) were synthesized by ball-milling in this work. This material was later modified by PSM (Post-Synthetic Modification) with Cu to obtain efficiently more complex MOF by mechanochemistry instead of using the classical solvothermal conditions.

2. Results and discussion

Benzoate and methacrylate clusters **1** $Zr_6O_4(OH)_4(C_6H_5CO_2)_{12}$ and **2** $Zr_4O_2(C_2H_3CO_2)_{12}$ were prepared as previously described in literature. Zirconium sources were then ball-milled, using a Retsch

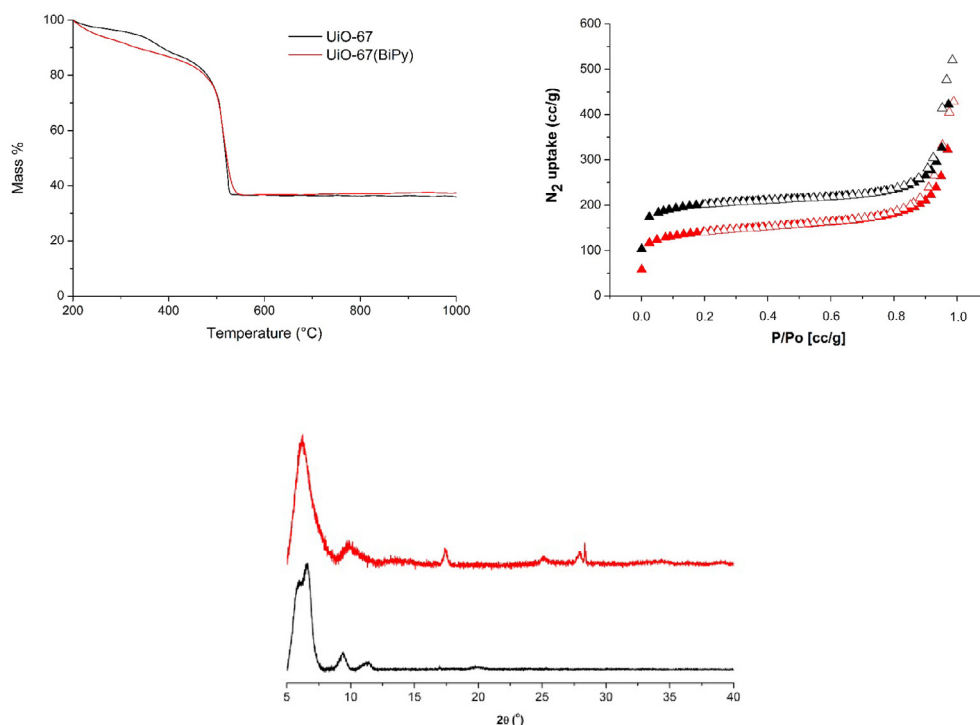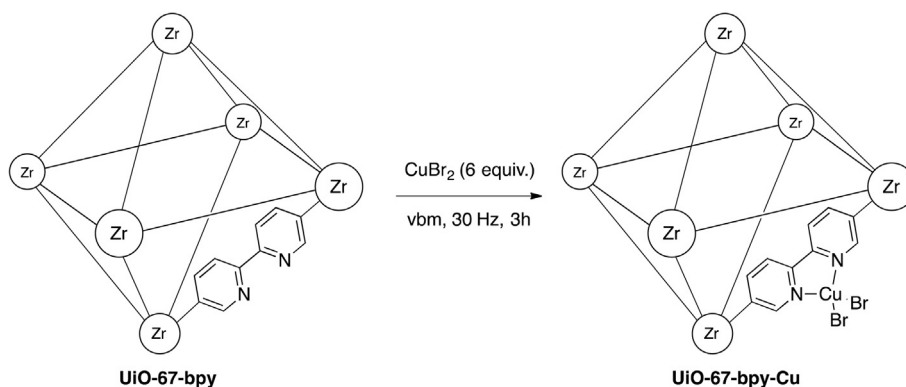**Scheme 1.** Mechanochemical synthesis of UiO-67 and UiO-67-bpy.

Fig. 1. (top) Thermogravimetric analyses and Nitrogen sorption (bottom) PXRD analyses of UiO-67 (black) and UiO-67-bpy (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

MM400 vibratory ball-mill (vbm), in the presence of BPDC in Teflon jars with a 12 mm diameter zirconium oxide ball, at a frequency of 30 Hz, for 3 h (Scheme 1).

Reactions were performed under liquid-assisted grinding [19] using a small amount of methanol or DMF ($\eta = 0.67 \ \mu L.mg^{-1}$). Insoluble materials were recovered after milling, washed with DMF and then MeOH to remove unreacted substrates. The best results, in terms of purity of the material, were obtained using cluster **1** as substrate and DMF as grinding assistant. A similar protocol was used, starting from cluster **1**, for the synthesis of **UiO-67-bpy**, featuring 2,2′-bipyridine-5,5′-dicarboxylic acid as organic ligand. **UiO-67** and **UiO-67-bpy** were then analysed by nitrogen sorption (BET), thermogravimetric analyses and Powder X-ray

diffraction (PXRD) (Fig. 1) and values were compared with those observed for the MOFs obtained by a classical solvothermal route.

Through TGA results, it was possible to determine the thermal stability, the ratio between the organic and the inorganic fractions as well as the purity of the two different MOFs. The results for the two MOFs are quite similar due to the equivalent molecular weight of both ligand and to an equal thermal stability of the MOF. They exhibit a first mass loss before 450 °C corresponding to the attached solvents (water and DMF molecules) and a total decomposition at 515 °C of the organic part to form the Zirconium Oxide. The results are consistent with the formation of materials with the UiO phase ($Zr_6L_6(OH)_4(H_2O)_4$) and the formation of ZrO_2 (obs. 36.5%, calcd 34.5%).

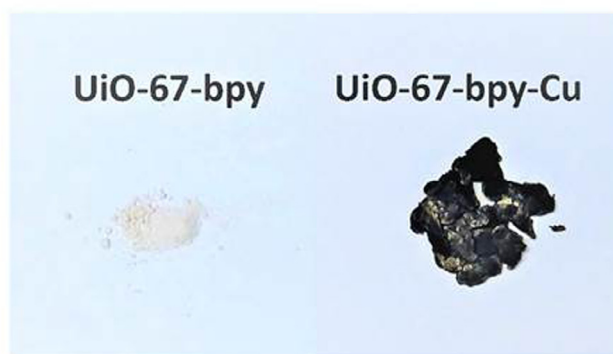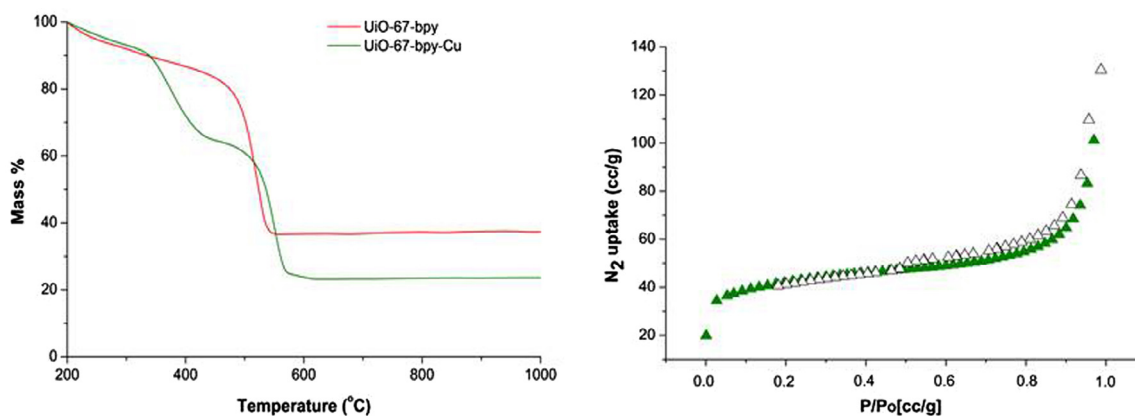**Scheme 2.** Mechanochemical and post-synthetic modification of UiO-67-bpy.

Fig. 2. (top) Thermogravimetric analyses of UiO-67-bpy compared to UiO-67-bpy-Cu and Nitrogen sorption of UiO-67-bpy-Cu (bottom) Images of UiO-67-bpy and UiO-67-bpy-Cu.

Permanent porosity of MOFs was determined after the removal of residual solvent molecules under vacuum pump at 100 °C for 24 h. Nitrogen sorption at 77 K showed type I isotherms for both materials proving that the MOFs have a microporous structure with a BET surface area of 750 m^2/g and 650 m^2/g for **UiO-67** and **UiO-67-bpy**, respectively. The observed surface areas are lower than those expected for the synthesis of these MOFs by solvothermal syntheses (3000 m^2/g). This is mainly due to the low crystallinity of these materials. PXRD analyses have confirmed the formation and maintenance of the UiO phase. Matching low angle and broad peaks below 15° indicate small crystalline structure for this UiO. This is due to reaction conditions in the ball-mill that allow the formation of the MOFs but, because of the friction, the crystallinity is not as high as in a solvothermal route [20].

Finally, a post-synthetic modification of **UiO-67-bpy** to coordinate copper(II) bromide was realized by solvent-free mechanochemistry (Scheme 2). The formed complex was already demonstrated to oxidize efficiently olefins into epoxides [21]. ICP-AES of the digested MOF (in a piranha solution, see SI) has revealed a complete coordination of the bpy ligand sites of the MOF with copper (ratio L:Cu = 1:1) to conduct to a functional MOF with the formula $Zr_6L_6(OH)_4(H_2O)_4(CuBr_2)_6$. TGA profile of **UiO-67-bpy-Cu** was quite different of **UiO-67-bpy** but confirms this formula. In this case, a first mass loss was observed from 200 to 430 °C corresponding to strongly attached solvent molecules into the framework and a decomposition of the organic moiety at 520 °C conducting to the formation of the inorganic ZrO_2 and CuO in the expected proportion (obs. 39%, calcd 35%). Nitrogen sorption experiment is in accordance with the coordination of the metals and conduct to the reduction of the surface area compared to **UiO-67-bpy** (155 m^2/g instead of 650 m^2/g before coordination). Indeed, incorporation of copper(II) bromide on each bipyridine site of **UiO-67-bpy** would significantly fill in the pores of the material and thus reduce its ability to adsorb nitrogen Fig. 2.

3. Conclusion

We present here for the first time the synthesis of **UiO-67** and an iso-structural **UiO-67-bpy** by mechanochemistry. The materials were obtained in short reaction time, with a high purity confirmed by TGA analysis. The porosity of the materials was confirmed by nitrogen sorption. We also demonstrated that post-synthetic modification of **UiO-67-bpy** was possible under solvent-free ball-milling, giving access to a copper-functionalized material with high purity.

Acknowledgements

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