

Synthesis of 2D Cu(II) and Zn(II) trifluoroacetate based Metal-Organic Frameworks using supercritical CO₂

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ABSTRACT

Recently, we have demonstrated that supercritical CO₂ can be used for the preparation of MOFs, where micro and mesoporous can be prepared obtaining activated porous materials in one step [1-5]. In this work, we show the precipitation of 2D metal-organic frameworks based in the combination of Cu(II) and Zn(II) trifluoroacetate transition metals, and bidentate pyridine derivatives also using supercritical CO₂ as solvent. However, in some cases, due to the low solubility of the trifluoroacetate metal, the reaction was too slow and incomplete in neat supercritical CO₂ (scCO₂). To overcome this problem, two improved strategies were followed. In the first one, it was used ethanol as co-solvent, and in the second, the use of *tert*-butylpyridine (*t*-bpy) as auxiliary ligand was employed to overcome this lack of solubility. All materials were characterized by elemental analysis, ATR-FTIR and powder X-Ray diffraction. Powder XRD analysis allowed to ascertain the success of the reaction for the combinations that yields previously described compound ([Zn(tfa)₂(bpe)₂]_∞).

INTRODUCTION

Metal-organic frameworks (MOFs) are a class of crystalline materials produced by the coordination of transition-metal cation complexes with multidentate organic linkers, forming extended frameworks that often are highly porous [1]. Over the past decade, coordination polymers MOFs have emerged as enabling materials for a wide variety of sustainable technologies, having a large fraction of their potential applications in the direction of roles of green materials, such as gas separation and gas storage [2], leading to their recent commercialization in a natural gas car prototype [3]. The development of valuable MOFs is dependent on the availability of synthetic and manufacturing procedures mindful of environmental impact. However, developed synthetic methods for MOFs are based on the use of large amounts of organic solvents, such as in the solvothermal method, as well as other not so polluting methods such as electrochemical, or mechanochemical approaches among others [4]. scCO₂ is a poor solvent for high-molecular weight and polar molecules, which, in principle, would rule out many possibilities in MOFs synthesis. However, an effective way to solve this problem is to create mixtures of scCO₂ with other solvents that own the capacity of solubilizing both polar and apolar building units needed for MOFs synthesis. One example is the use of

combinations of scCO₂ and organic solvents (e.g., dimethylformamide), known as expanded switchable solvents [5]. In the recent past, the use of neat scCO₂ in the field of MOFs has been mainly limited to post-synthesis activation by cleansing entrapped undesired by-products or solvents to obtain ultra-high surface area MOFs [6]. However, a generic method for the crystallization of MOFs in scCO₂ is being developed in our research group, which focuses on the synthesis of one- (1D) [7], two- (2D) [8] and three-dimensional (3D) [9] MOFs.

In this work we aim to study two different approaches that can be used to crystallize MOFs in scCO₂, using additives in scCO₂. Thus as a model, we used the reaction of a metal trifluoroacetate (M(tfa)₂) complex, that has very low or null solubility in scCO₂, with a bidentate pyridine linker highly soluble in scCO₂ [10]. To increase the solubility of the metal precursor, the use of either ethanol as a co-solvent or *tert*-butylpyridine (*t*-bpy) as auxiliary ligand for the metal complex is assayed [11].

MATERIALS AND METHODS

Materials

The structures of the used reagents and additives are schematized in Fig. 1 a). Copper(II) trifluoroacetate hydrate (Cu(tfa)₂), zinc(II) trifluoroacetate hydrate (Zn(tfa)₂), 4,4'-dipyridine (bpy), 1,2-bis(4-pyridyl)ethylene (bpe), 1,3-bis(4-pyridyl)propane (bpp), *tert*-butylpyridine (*t*-bpy) were of commercial grade and used as received (Sigma Aldrich). Ethanol (EtOH) was purchased from Panreac. Compressed CO₂ (99.95 v%) was supplied by Carbueros Metálicos S.A. (Spain).

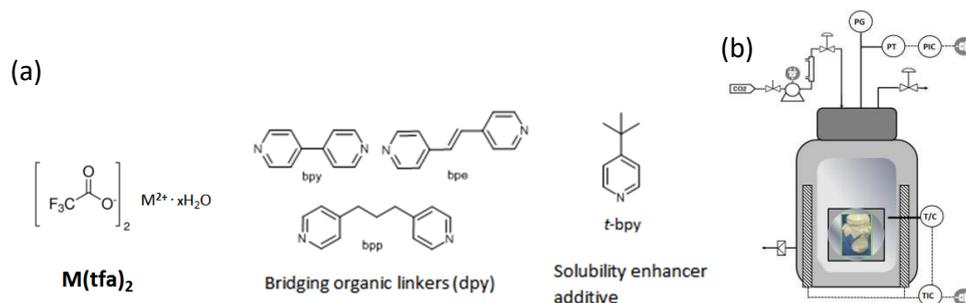


Fig 1. a) Structures of the used reagents and additives. b) Schematic representation of the high pressure equipment used in the MOFs crystallization experiments.

Methods

MOFs preparation in scCO₂ was carried out in a high pressure 100 mL Thar Design autoclave, equipped with two opposite sapphire windows (Fig. 1 (b)). In each experiment, the autoclave was charged with *ca.* 200 mg of M(tfa)₂ and a weighted amount of each studied dipyridin (dpy), calculated slightly in excess of the quantity needed to achieve the molar ratio 1:2 for M^{II}:dpy. The reagents were added into a 10 mL Pyrex vial together with a small magnetic stir bar. The vial was capped with filter paper. The reactor was sealed at ambient temperature and filled with liquid CO₂ at 6 MPa, while stirring at 500 rpm. In the standard protocol, the system was then heated at 333 K using resistances and the pressure was increased up to 20 MPa with a syringe pump (Teledyne Isco 260D). These working conditions were maintained for a period of 3 h. Finally, the system was depressurized to atmospheric pressure and cooled to room temperature. Three different methods were used to obtain the desired end-product, which are described following.

Method A. 2 mL of EtOH was added as a co-solvent to the Pyrex vial together with the MOF reagents.

Method B. A metal complex intermediate containing the *t*-bpy unit, with formula $M(tfa)_2(t-bpy)_x$, was previously prepared by reacting $M(tfa)_2$ with an excess of liquid *t*-bpy. In the MOF synthesis experiments, the intermediate was added to the Pyrex vial instead of the corresponding $M(tfa)_2$ hydrate together with the pyridine reagent.

Method C. The *t*-bpy was added to the Pyrex vial as a free ligand, together with the MOF building blocks ($M(tfa)_2$ hydrate and pyridine reagent) thus avoiding the necessity of synthesizing the intermediate. Different ratios of $M^{II}:t$ -bpy were experimentally tested (Table 1).

Characterization

Prepared samples were structurally characterized by X-ray diffraction (XRD) on a Siemens D-5000 diffractometer with Cu K_α radiation, in the 2θ range of 5 - 30° . Samples chemical composition was assessed by elemental analysis (EA) carried out using a Flash EA2000 Thermo Fisher Scientific analyser. Morphological features were examined by scanning electron microscopy (SEM) with a Quanta Fei 200 microscope.

RESULTS

Method A: Reactions performed by adding a co-solvent.

To overcome the solubility problems in $scCO_2$ associated with the metal complexes, 2 ml of ethanol was added as a co-solvent to the reactor. The addition of EtOH not only rises de polarity of the solvent mixture, but also increases substantially the solubility of hydrated coordination compounds like the reagent $M(tfa)_2 \cdot xH_2O$ used in this work, by breaking the hydrogen bonds established between metal complex molecules [12]. Following the standard protocol, the formation of the targeted $[Zn(tfa)_2(bpe)_2]_\infty$ and $[Zn(tfa)_2(bpy)_2]_\infty$ coordination polymers was achieved (Figs. 2a(C), b(B) respectively), although $[Zn(tfa)_2(bpy)_2]_\infty$ was obtained as a contaminated phase. The stoichiometry was calculated in based of the elemental analysis obtained from pure phases.

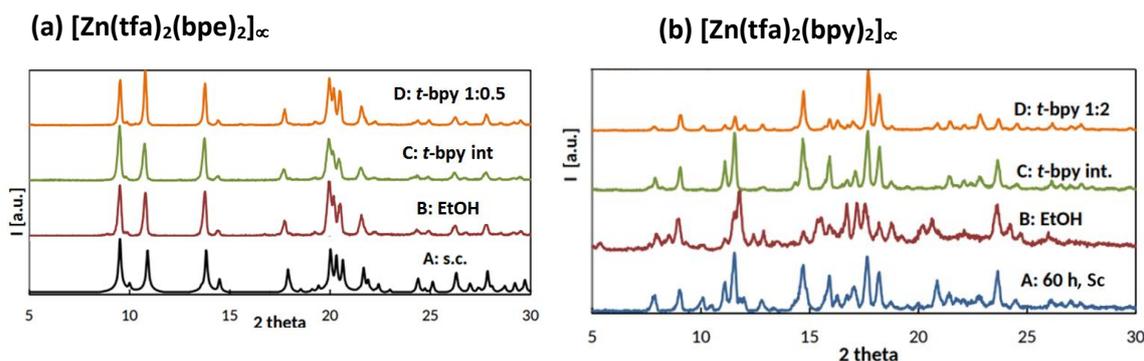


Fig 2. Powder XRD patterns obtained for the precipitated Zn MOFs: (a) $[Zn(tfa)_2(bpe)_2]_\infty$; **A**: simulated from single crystal reported data [20]; **B**: with EtOH; **C** using the $Zn(tfa)_2(t-bpy)_{2.3}$ intermediate; **D** adding free *t*-bpy in a 1:0.5 molar ratio; and (b) $[Zn(tfa)_2(bpy)_2]_\infty$, synthesized in; **A**: in $scCO_2$, in 60 h, **B**: with EtOH, **C**: using the $Zn(tfa)_2(t-bpy)_{2.3}$ intermediate; and **D**: adding free *t*-bpy in a 1:2 molar ratio.

$[Zn(tfa)_2(bpe)_2]_\infty$, has a known structure, [13] and data presented gave an excellent match between reported and our obtained XRD data Figs. 2a(A).

Method B: Reactions performed by using a precursor of $M(tfa)_2(t-bpy)_x$.

In a previous work [11] we showed how *t*-bpy, having the bulky apolar *tert*-butyl group interacts favorably with CO_2 molecules increasing the solubility of insoluble compounds.

Based on this findings, in this work *t*-bpy ligand was added to the reaction media as a part of a solid precursor in the form of $M(tfa)_2(t-bpy)_x$ previously prepared. An intermediate of the type $Zn(tfa)_2(t-bpy)_{2.3}$, was first synthesized and further reacted in $scCO_2$ with either bpe or bpy. XRD characterization showed that using this method, pure phases of $[Zn(tfa)_2(bpe)_2]_\infty$ and $[Zn(tfa)_2(bpy)_2]_\infty$ could be straightforwardly crystallized in neat $scCO_2$ in runs of only 3 h (Fig. 2a(C) and 2b(C), respectively).

The effectiveness of this approach was also examined for similar reactions involving Cu^{II} , for which the intermediate $Cu(tfa)_2(t-bpy)_{2.5}$ (Fig. 3(B)) was synthesized. In this case, when using the bpp linker, the EA indicated that a coordination polymer of stoichiometry $[Cu(tfa)_2(bpp)_2]_\infty$ was obtained, as in the case of the Zn^{II} complex.

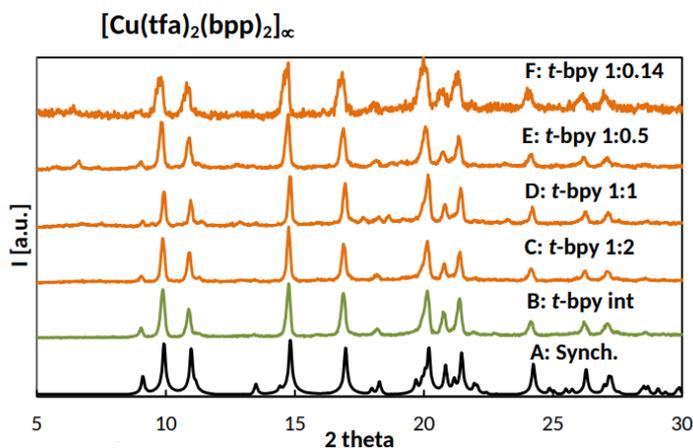


Fig. 3. Powder XRD patterns obtained for the precipitated MOFs $[Cu(tfa)_2(bpp)_2]_\infty$. (A) simulated from synchrotron elucidated structure (SI), and synthesized in $scCO_2$: (B) using the $Cu(tfa)_2(t-bpy)_{2.5}$ intermediate, and adding free *t*-bpy in $M^{II}:t$ -bpy molar ratios of C 1:2, D 1:1, E 1:0.5 and F 1:0.14.

Method C: Reactions performed by addition of *t*-bpy directly added to the reactor.

In the previous method, a common observation in all the experiments is that the auxiliary ligand *t*-bpy was never incorporated to the final coordination polymer. On the contrary, it was released to the supercritical phase once its substitution by the dpy linker was effective. Based on this finding, we introduced *t*-bpy directly to the reactor to allow this secondary ligand to thermodynamically compete *in situ* with the dpy for the metal positions. Moreover, it was observed experimentally that the amount of added secondary ligand can be reduced considerably, in some cases even 50 times, and still getting the crystalline expected end product. In this protocol, the process of MOF crystallization is envisioned as starting with the formation of an intermediate of the type $M(tfa)_2(t-bpy)_x$ by the favored reaction of $M(tfa)_2$ with solubilized *t*-bpy. Then, the soluble intermediate can react with solubilized dpy linker forming the thermodynamically stable coordination polymer, which precipitates. The released *t*-bpy ligand turns out to the solution and can react over with remaining $M(tfa)_2$ molecules, thus having a catalyst-like behavior. The process is schematized in Fig. 4.

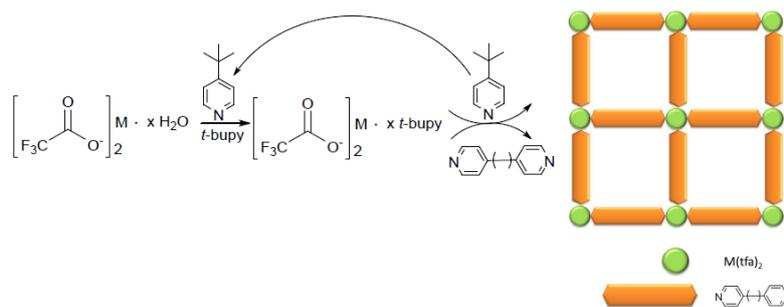


Fig. 4. Schematic representation of the pathway used for $[M(tfa)_2(dpy)_2]_\infty$ synthesis following Method C, showing the recirculation of the *t*-bpy towards $M(tfa)_2$.

Table 1 displays the $M^{II}:t$ -bpy molar ratios studied in the different experiments, ranging from 1:2 to 1:0.15. For systems involving either Zn^{II} or Cu^{II} and free *t*-bpy in molar ratios from 1:2 to 1:0.5, the recorded XRD patterns, in general, revealed the precipitation of the expected phase after only 3 h of reaction time (Fig. 2a(D) and b(C) for Zn^{II} and Fig. 3(C,D,E) for Cu^{II}). An exception to this rule was the MOF $[Zn(tfa)_2(bpy)_2]_\infty$, which could not be obtained pure at molar ratios lower than 1:2. For Cu^{II} compounds, the linker concentration was further lowered to 1:0.14 molar ratio.

Table 1: Experimental conditions and reagents molar ratios used in the different experiments.

Metal	Linker	Additive	t [h]	$M^{II}:t$ -bpy added molar ratio		
Zn(II)	bpe	EtOH	3	1:0		
		<i>t</i> -bpy(int) ^(a)	3	1:2.5		
		<i>t</i> -bpy ^(b)	3		1:0.5	
	bpy	EtOH	3	1:0		
		<i>t</i> -bpy(int) ^(a)	3	1:2.5		
		<i>t</i> -bpy ^(b)	3		1:0.5	1:0.14
Cu(II)	bpp	<i>t</i> -bpy(int) ^(a)	3	1:2.5		
		<i>t</i> -bpy ^(b)	3	1:2	1:1	1:0.5

^a added as intermediate $M(tfa)_2(t-bpy)_{2.5}$

^b added as a liquid

The influence on the morphology of the addition of *t*-bpy and its concentration was studied in the precipitated pure compounds.

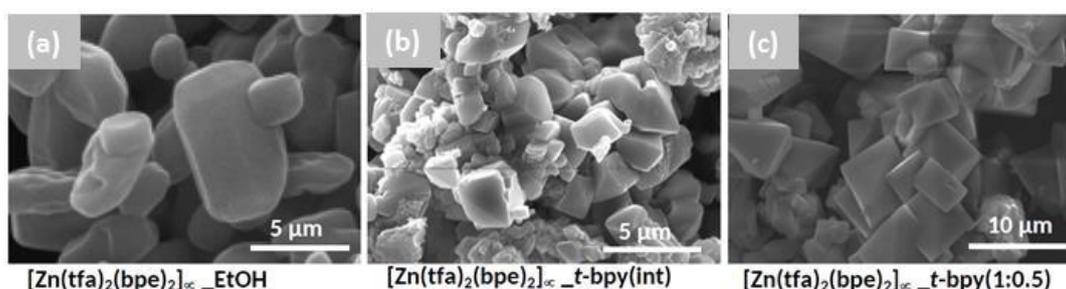


Fig. 5. SEM micrographs of the $[Zn(tfa)_2(bpe)_2]_\infty$ precipitated samples described in Table 1: (a, in neat $scCO_2$, (b) with EtOH, and (c) with *t*-bpy solid intermediate, and (d) with added free *t*-bpy.

For $[Zn(tfa)_2(bpe)_2]_\infty$, polyhedral micrometric crystals were obtained by using the ethanol as co-solvent (Fig. 5 (a)), the intermediate (Fig. 5 (b)), and by adding free *t*-bpy in the relatively high molar ratio of 1:0.5 (Fig. 5(c)). Comparing the three micrographs, it

can be observed that crystals using *t*-bpy in either way were better shaped than those obtained with EtOH co-solvent. Crystals obtained using Method C (Fig. 5c) were better crystallized than those obtained following Method B (Fig. 5a), likely due to slower crystal growth kinetics occurring in the former.

The SEM analysis was extended to the precipitated $[\text{Cu}(\text{tfa})_2(\text{bpp})_2]_\infty$. In a reaction media involving a relatively high concentration of *t*-bpy, i.e., the one with the intermediate $[\text{Cu}(\text{tfa})_2(\text{t-bpy})_{2.5}]$ and those with $\text{Cu}^{\text{II}}:\text{t-bpy}$ molar ratios of 1:1, small particles of 1 to 3 μm were precipitated (Fig. 6a-c). On the contrary, significantly larger crystals, higher than 5 μm , were obtained in reactions involving low concentrations of the auxiliary ligand, e.g., $\text{M}^{\text{II}}:\text{t-bpy}$ molar ratios of 1:0.5 and 1:0.14 (Fig. 6d,e).

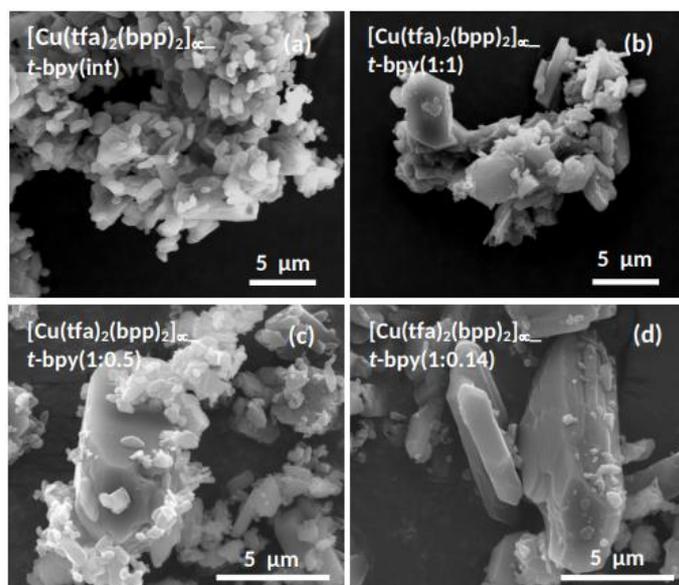


Fig. 6. SEM micrographs of the different precipitated samples of $[\text{Cu}(\text{tfa})_2(\text{bpp})_2]_\infty$ MOF in the presence of *t*-bpy added as: (a) intermediate, or free in $\text{Cu}^{\text{II}}:\text{t-bpy}$ molar ratios of (b) 1:1, (c) 1:0.5, and (d) 1:0.14.

CONCLUSION

This work demonstrates the efficiency of the alternative procedure using an intermediate involving *t*-bpy as auxiliary ligand. The *t*-bpy forms and adduct with the metal complex, highly increasing its solubility. Further, the synthesis of the solid intermediate can be avoided by adding small amounts of free *t*-bpy ligand to the reaction media, thus upgrading the synthetic protocol by reducing the number of reaction steps needed to achieve the objective. The process has been tested in 2D MOFs involving Zn^{II} or Cu^{II} trifluoroacetate and several linear bipyridines. Modulation of the solubility and thus, of the coordination equilibrium, arises from the introduced auxiliary ligand, competing with MOF's bridging linkers for coordination to the metal ions. The auxiliary ligand lack of further binding sites, thus hindering additional assembly of the crystal network in this direction and inducing some control over the MOF crystal size and shape.

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