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Exploring a novel preparation method of 1D metal organic frameworks based on supercritical CO_2

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The preparation of copper(II) one-dimensional MOFs using an eco-efficient method is here reported. This method is based exclusively on using supercritical CO_2 as a solvent, without the addition of any other additive or co-solvent. Neutral acetylacetonate copper complexes and two linear linkers, the bidentate 4,4'-bipyridine and 4,4'-trimethylenedipyridine molecules, were reacted under compressed CO_2 at 60 ºC and 20 MPa for periods of 4 or 24 h. The successfulness in the synthesis of the different studied 1D-MOFs was related to reagents solubility in supercritical CO_2. The reaction yield of the synthesized coordination polymers *via* the supercritical route was close to 100 %, since both reactants were almost completely depleted in the performed experiments.

Introduction

Metal organic frameworks (MOFs) are comprised of metal and multidentate organic units, linked together to form an infinite array through an extended covalent or coordinative interaction.[1] MOFs are a special type of crystalline hybrid materials broadly studied, since they have an enormous potential of forming one (1D), two (2D) and three dimensional (3D) architectures. Specific features, such as the metal used, the size and structure of the ligands or the steric hindrance, would induce a large variety of properties in the designed MOFs, going from inertness to very responsive products.

The unlimited collection of feasible structures is described for a large range of applications in the areas of molecular electronics, magnetism, chemical sensing, catalysis and gas adsorption, among others.[2] 2D and 3D-MOFs are often synthesized with large surface areas, in the order of several hundred to several thousand square meters per gram, which have generated massive attention as candidate materials for gas adsorption, separation and storage. Conversely, the unusual properties of coordination metal complexes with 1D polymeric structures confer them uses as molecular ferromagnets, superconducting polymers, linear optical materials or ferroelectric compounds.[3] Moreover, the high metal content in MOFs, their high thermal and mechanical stability, together with their insolubility in water and common organic solvents, make them excellent candidates for heterogeneous catalysts processes, highlighting in this application the use of some copper(II)-based MOFs with Lewis acid sites for the transformation of organic molecules.[4,5]

The synthesis method plays an important role in defining the final MOF composition and structure. Most MOFs are synthesized by the solvothermal route under autogenous pressure and above the boiling point of the used organic solvent.[6,7] Some prominent MOFs have also been obtained at room temperature by mixing the starting reagents previously dissolved in an adequate medium.[8] Solvents are often incorporated in the synthesized MOFs, acting as space-filling molecules and defining the final product structure. Regarding more environmentally friendly solvent techniques, microwave assisted, electrochemical and sonochemical approaches have been developed.[9,10] Mechanochemistry, also considered as a green chemistry approach, produces MOFs just by grinding an organic linker with a metal containing precursor. Although it is considered as a solid-state process, the use of small quantities of solvent is often included in the protocol to enhance the yield, or to control the nature of the final product.[11]

The main goal of this work was the development of an effective and eco-friendly procedure for the synthesis of 1D-MOFs by using exclusively supercritical carbon dioxide ($scCO_2$) as a solvent. Aside from the very limited reports addressing the kinetics of the formation of copper(II) coordination complexes in $scCO_2$,[12] to date the use of this solvent in the field of MOFs processing was limited to post-synthesis activation by cleansing of entrapped undesirable by-products or solvents.[13,14] Copper(II) metal complexes and linear ligands, in particular the bidentate 4,4'-bipyridine and 4,4'-trimethylenedipyridine,[15] were chosen for analysis. Physicochemical and textural properties of prepared samples were measured and compared against those prepared by a conventional solvent method.

Experimental

Materials

Neutral copper(II) building blocks: $Cu(hfacac)_2$ (copper hexafluoroacetylacetonate), $Cu(tfacac)_2$ (copper trifluoroacetylacetonate) and $Cu(acac)_2$ (copper acetylacetonate) were chosen as the metal complexes (Fig. 1). 4,4'-bipyridine (bpy) and 4,4'-trimethylenedipyridine (tpy) were used in the synthesis as ligands (Fig. 1). For the conventional synthesis protocol, dichloromethane (DCM) was used as a solvent. Reagents and liquid solvents were all purchased from Sigma Aldrich and used without further purification. In the supercritical procedure, the used compressed CO_2, (99.995 %) was supplied by Carburos Metálicos S.A., Air Products Group (Spain).

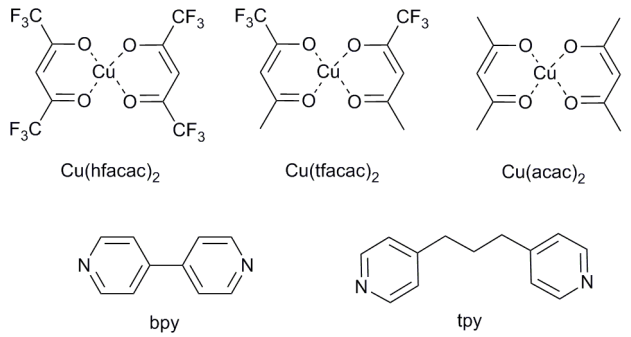

Fig. 1. Structures of the used reagents: metal complexes ($Cu(hfacac)_2$, $Cu(tfacac)_2$, and $Cu(acac)_2$) and organic linkers (bpy and tpy).

Synthetic procedures

Supercritical method. Samples preparation under $scCO_2$ was carried out in a 100 mL batch high pressure reactor (TharDesign) described elsewhere.[16] The autoclave was charged with *ca.* 150-200 mg of a copper(II) complex and, predominantly, an equimolar amount of ligand (Table 1). The physical contact between the two reagents was avoided by placing them inside of the autoclave in two separate Pyrex vials. The autoclave was electrically heated with resistances and pressurized with a syringe pump (Teledyne Isco Model 260D). Supercritical experiments were carried out at the standard conditions of 20 MPa and 60 ºC during a reaction time of 4 h, which was increased to 24 h when necessary. Experiments were performed without using stir bars for agitation to prevent any mechanochemistry effects. However, for the $Cu(acac)_2$ metal complex, with the lowest solubility in $scCO_2$, gentle stirring was applied to the vial containing the metal with the aim of increasing the process kinetics. In a separated test, performed under ambient conditions and in the absent of CO_2, it was confirmed that the used agitation did not cause any mechanochemical effect. At the end of each experiment, the system was slowly depressurized and allowed to cool to room temperature.

Conventional method. For comparative reasons, a conventional liquid approach was investigated to synthesize the products not previously reported in the literature. In this procedure, the metal complex and the ligand were dissolved separately in DCM and then mixed in a 1:1 metal:ligand molar ratio at room temperature. The resulting precipitate was filtered and further dried at 45 ºC in an air oven.

Characterization

The products were obtained as green crystalline powders, which made possible their study by powder X-ray diffraction (XRD, with a Siemens D5000) using the Cu Kα incident radiation. The diffraction patterns were recorded from 2θ = 5 to 50º with a step scan of 0.02º counting for 1 s at each step. For the products in which the crystal structure was known, the XRD powder patterns were analyzed by Le Bail method.[17] The background was described by an interpolation of fixed (not refined) points and peak profile by a pseudo-Voigt function. The zero-error, cell parameters, profile parameters and peak asymmetry were refined. Moreover, the crystal structure of one of these products, $[Cu(hfacac)_2bpy]_n$, could be determined after collecting synchrotron powder X-ray diffraction data in the MSPD Beamline of ALBA Synchrotron using the microstrip MYTHEN-II detector (λ = 0.61978 Å). The powder pattern was indexed using DICVOL04[18] and further refinement of cell parameters, space group identification and intensity extraction was performed with DAJUST software[19]. Extracted intensities were used in the direct-space strategy TALP[20] to solve the crystal structure using the previously reported structure[21] of $[Cu(tfacac)_2bpy]_n$ as starting model to generate the geometrical restraints. A Rietveld refinement of the obtained solution gave the final crystal structure of the compound. Crystallographic data, refinement details, Hirshfeld surface with d_{norm} as mapped property (Fig. S1) and CIF file are included in the supplementary information.

The weight percentage or organic atoms in the obtained samples was estimated by elemental analysis of C, H and N by using a Flash EA2000 Thermo Fisher Scientific analyzer. The textural properties were determined by N_2 adsorption at 77 K applying the BET method, using an ASAP 2000 Micromeritics INC. Samples were first degassed at 60 ºC for 24 h. Morphological features were examined by scanning electron microscopy (SEM) with a Hitachi S570 apparatus.

Results and discussion

Taking into account the common solvating properties of $scCO_2$, neutral copper(II) acetylacetonates complexes with different degree of fluorination were chosen as building blocks (Fig. 1). These compounds have a significant solubility in this supercritical fluid, which is determined by the fluoride content and categorized as: $Cu(acac)_2 < Cu(tfacac)_2 < Cu(hfacac)_2$.[22] Under working experimental conditions, organic linkers were totally soluble in $scCO_2$. For the metal complexes, solubility values, reported at 40 ºC and 10-30 MPa, are in the order of 0.7-2.3 10^{-5}, 2.9-5.9 10^{-4} and 6.1-7.4 10^{-4} mole fraction for $Cu(acac)_2$, $Cu(tfacac)_2$ and $Cu(hfacac)_2$, respectively.[23]

Reaction yield in the described supercritical procedure was very high, since both reactants were mostly depleted in the performed experiments. Moreover, the post-reaction steps of solvent elimination by filtration and drying, which are necessary to obtain a pure product following the conventional solvent procedure, were eliminated from the supercritical synthesis protocol. Indeed, the compressed CO_2 is eliminated as a gas during depressurization. This fact not only increases process yield, but also reduces considerably the processing time for each experimental batch.

As a part of an ongoing work, the nine possible reactions between bipyridyl ligands and copper(II) acetylacetonate derivatives shown in Fig. 1 are being surveyed under $scCO_2$ conditions. Nevertheless, in this article only data corresponding to four selected combinations are presented (Table 1), corresponding to the three studied metal complexes $Cu(hfacac)_2$, $Cu(tfacac)_2$ and $Cu(acac)_2$ reacted with 4,4'-bipyridine, and the $Cu(hfacac)_2$ reagent combined with 4,4'-trimethylenedipyridine. The chosen species were either previously described in the literature or could be clearly characterized in regard to the stoichiometry. The reaction between $Cu(tfacac)_2$ or $Cu(acac)_2$ with 4,4'-trimethylenedipyridine in $scCO_2$ have also been tested. However, complex product mixtures difficult

to characterize were obtained. The experimental conditions required to obtain pure products are currently under investigation.

Table 1. Prepared samples following the supercritical procedure, indicating the added metal:ligand (m:L) mole ratio and reaction time, as well as the measured m:L ratio in the end product.

Sample	Added m:L ratio	Reaction time [h]	Product m:L ratio
$[Cu(hfacac)_2tpy]_n$-sc	1:1	4	1:1
$[Cu(hfacac)_2bpy]_n$-sc	1:1	4	1:1
$[\{Cu(tfacac)_2\}_xbpy]_y$-sc	1:1	4	mixture
$[Cu(tfacac)_2bpy]_n$-sc	1:2	24	1:1
$[Cu(acac)_2bpy]_n$ & reagents	1:1	24	mixture
$[Cu(acac)_2bpy]_n$-sc	1:1	4 (stirring)	1:1

The measured weight percentages of C, H and N in each prepared sample are given in the Table 2, together with the theoretically calculated values.

Table 2. Theoretically calculated and experimentally measured C, H and N weight percentages for the synthesized samples either by the supercritical or conventional route in $scCO_2$ or DCM, respectively.

Sample	Atom	Theor. [%]	$scCO_2$ [%]	DCM [%]
$[Cu(hfacac)_2tpy]_n$	C	40.87	40.91	41.17
	H	2.39	2.37	2.60
	N	4.14	4.02	4.01
$[Cu(hfacac)_2bpy]_n$	C	37.90	38.03	-
	H	1.59	1.62	-
	N	4.43	4.59	-
$[Cu(tfacac)_2bpy]_n$	C	45.68	45.54	46.04
	H	3.07	3.18	3.15
	N	5.32	5.20	5.13
$[Cu(acac)_2bpy]_n$	C	57.48	56.15	-
	H	5.31	5.32	-
	N	6.70	6.20	-

The textural properties of selected synthesized products were studied by low temperature N_2 adsorption isotherms. In accordance with results obtained by other authors, the crystallized 1D-MOFs exhibited very low BET surface area, in the range of 5-10 m^2g^{-1},[24,25] in comparison to 3D-MOFs reported in the literature with surface areas as high as 7000 m^2g^{-1}.[26] The average pore diameter was between 5 and 10 nm, while the pore volume was in the order of 0.01 cm^3g^{-1}. Based on the IUPAC classification, these results indicate mesoporous solids. According to the small values of pore volume and surface area, these values are ascribed to adsorption only in the external surface of the precipitated crystals. As a consequence those materials should not be considered for adsorption applications. However, 1D-MOFs find uses in other important technological applications, such as heterogeneous catalysis, magnetic devices, linear optics and so on.[3-5]

$[Cu(hfacac)_2ligand]_n$ coordination polymers. The high solubility in $scCO_2$ of the fully fluorinated $Cu(hfacac)_2$ complex (*ca.* 6.5 10^{-4} mole fraction under working conditions[23]) facilitated the straightforward preparation of 1:1 coordination polymers by reaction with any of the two bipyridyl ligands studied in this work (Table 1). From them, only the $[Cu(hfacac)_2(tpy)]_n$ product has been found described in the literature, prepared as a single crystal from a DCM solution.[27,28] This structure is described as octahedral coordinated copper(II) centres linked by the 4,4'-trimethylene-dipyridine ligand adopting a cis-trans geometry.[28]

Elemental analysis of the synthesized $[Cu(hfacac)_2tpy]_n$-sc sample (Table 2) was coincident with the theoretically calculated value for the equimolar polymer structure. The crystallographic data of sample $[Cu(hfacac)_2tpy)]_n$ in ref. 27 [*Pc* space group and a=7.9502(5) Å, b=9.6866(6) Å, c=18.5732(10) Å, β=95.8090(10) º] was used as the starting point for Le Bail refinement (Fig. 2 and S2). Found refined lattice parameters were a=7.978(3) Å, b=9.678(2) Å, c=18.607(4) Å, and β=95.56(4) º, which fairly coincided with those reported in the mentioned reference [$\Delta a/a$=0.003, $\Delta b/b$=-0.001, $\Delta c/c$=0.002, and $\Delta\beta/(\beta-90)$=0.04]. In addition, just a few low intense peaks did not correspond to $[Cu(hfacac)_2(tpy)]_n$ phase, thus proving that only a very small percentage of impurities appears beside this compound, as suggested by elemental analysis.

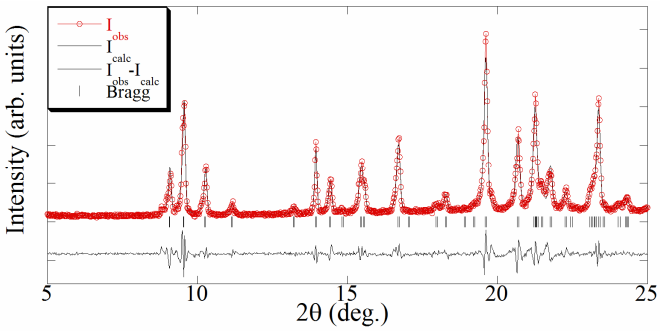

Fig. 2. Final Le Bail whole pattern decomposition plot for the $[Cu(hfacac)_2tpy]_n$-sc sample.

The supercritically precipitated product adopted the form of platelet-like microcrystals with a submicrometric thickness, as observed in the morphological analysis of this sample performed by SEM (Fig. 3).

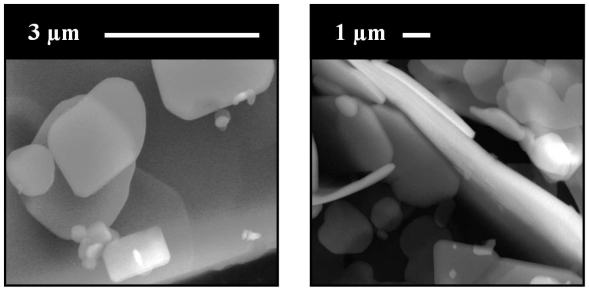

Fig. 3. SEM micrographs of the supercritically precipitated $[Cu(hfacac)_2tpy]_n$-sc polymer at two different magnifications.

Contrarily to the $[Cu(hfacac)_2tpy]_n$ product, the structure of the $[Cu(hfacac)_2bpy]_n$ polymer have not been found described in the literature. For this material, the supercritically synthesized sample was compared with the equivalent material obtained by the conventional procedure. The diffraction patterns of analogous compounds obtained using both synthesis routes are compared in Fig. 4. Similar diffraction angles were measured for DCM and $scCO_2$ prepared materials. Though a slight divergence related to the relative intensities of recorded peaks was observed, it was attributed to the texture and the distribution of the crystallographic preferred orientations in the polycrystalline samples. Further, elemental analysis also supported the finding that the $Cu(hfacac)_2$ metal complex combined in an equimolar ratio with 4,4'-bipyridine. Similar results were obtained for the conventionally precipitated polymer (Table 2).

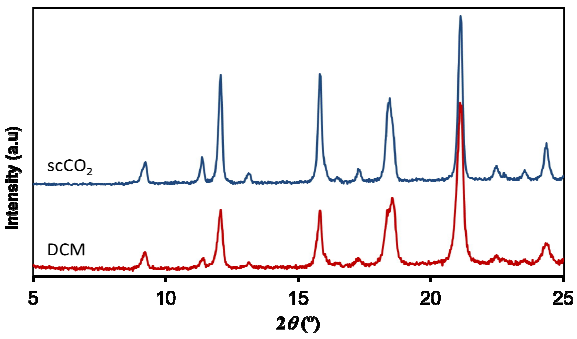

Fig. 4. XRD patterns of $[Cu(hfacac)_2bpy]_n$, prepared using $scCO_2$ and compared to DCM synthesized equivalent material.

The crystal structure of $[Cu(hfacac)_2bpy]_n$ has been solved from synchrotron powder diffraction data. The compound crystallizes in the tetragonal $P4_12_12$ space group [lattice parameters are a=b=7.882(2) Å, c=38.0767(7) Å, vol=2369.3(1) Å^3] and no other crystalline phases (impurities) are present in the pattern. The main feature of the structure is the Cu-bpy chain that gives rise to the 1D-MOF propagation (Fig. 5). The propagation of the chain is along two directions, [1 1 0] and [1 -1 0], due to the 4_1 screw axis that changes the relative orientation of the chain along c. There is no relevant intermolecular interaction between chains. Rietveld plot with observed, calculated and difference profile is shown in Figure 6.

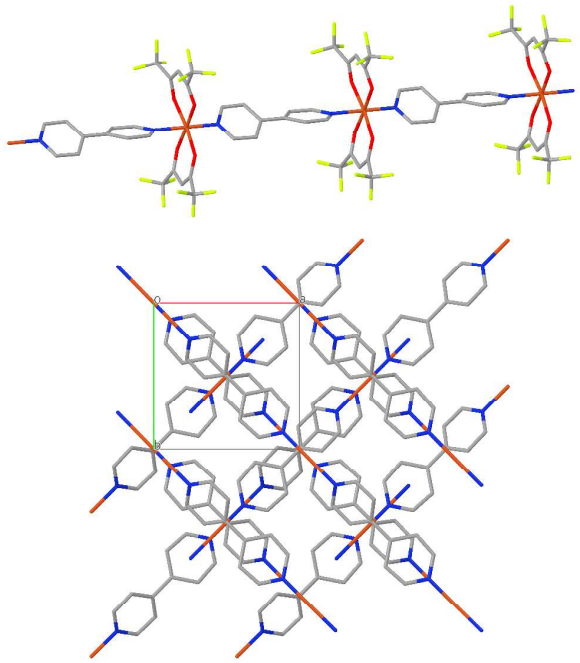

Fig. 5. (top) Polymeric chains in the crystal structure of $[Cu(hfacac)_2bpy]_n$ (H-atoms omitted) and (bottom) propagation of the chains along the [110] and [1-10] directions. The hfacac ligand has been omitted for clarity.

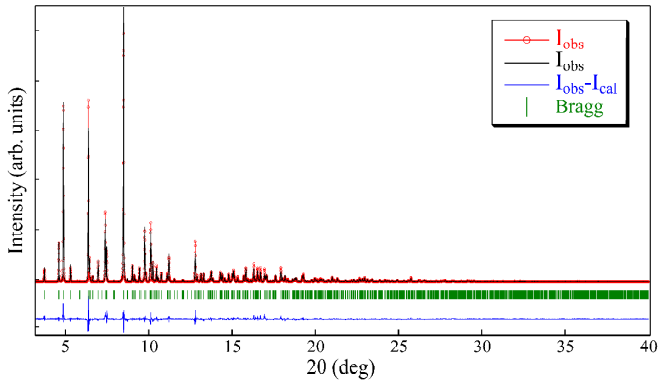

Fig. 6. Rietveld plot with observed, calculated and difference profile for $[Cu(hfacac)_2bpy]_n$ material

$[Cu(tfacac)_2bpy]_n$ coordination polymer. In comparison to the other two copper(II) complexes used in this work, the copper salt $Cu(tfacac)_2$ presents an intermediate solubility in $scCO_2$ (*ca.* 4.0 10^{-4} mole fraction under working conditions[23]). This metal complex was reacted in a 1:1 molar ratio with the 4,4'-bipyridine ligand under the $scCO_2$ standard conditions previously used to form the $Cu(hfacac)_2$:ligand materials (Table 1). As a result, a mixture of two products was obtained, identified as the expected $[Cu(tfacac)_2bpy]_n$ coordination polymer and a second compound, whose exact nature is currently under study. To precipitate solely the equimolar coordination polymer, it was necessary to increase the relative amount of 4,4'-bipyridine to a 1:2 metal:ligand molar ratio, and to use a long reaction time of 24 h (Table 1). Under these experimental conditions, the elemental analysis showed that the equimolar polymer, represented by sample $[Cu(tfacac)_2bpy]_n$-sc, was exclusively obtained (Table 2). The close match in the 1:1 stoichiometry indicated a high degree of purity for the supercritically synthesized polymer, which could be easily attained due to the high solubility of 4,4'-bipyridine in $scCO_2$. The added excess of ligand was eliminated during depressurization without the need of a further cleaning step. The 1D polymer $[Cu(tfacac)_2bpy]_n$ has been described in the literature, synthesized by either mechanochemistry[29] or liquid phase.[21] Thus, for sample $[Cu(tfacac)_2bpy)]_n$-sc the crystallographic information obtained from ref. 21 [*P nnm* space group and a=8.3790(10) Å, b=8.3790(10) Å, and c=15.832(4) Å] was used as the starting point for Le Bail fitting of the XRD pattern (Fig. 7 and S3). Lattice parameters found [a=8.405(4) Å, b=8.405(4) Å, and c=15.842(8) Å] were in good agreement with the reported ones ($\Delta a/a$=0.003, $\Delta b/b$=0.003, and $\Delta c/c$=0.001). Alongside of the diffraction peaks corresponding to this phase, only small additional peaks were observed, which evidenced again that impurities were present only in a very small percentage.

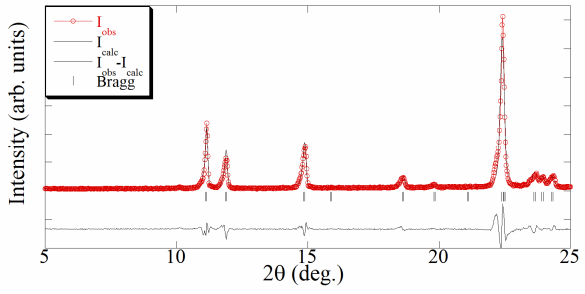

Fig. 7. Final Le Bail whole pattern decomposition plot of $[Cu(tfacac)_2bpy]_n$-sc sample

$[Cu(acac)_2bpy]_n$ coordination polymer. The complex $Cu(acac)_2$ has the lowest solubility in $scCO_2$ (*ca.* 1.5 10^{-5} mole fraction under working conditions[23]) of the three studied metal complexes, which would reduce the driving force for the metal to react with the ligand. This product was mixed with 4,4'-bipyridine and allowed to react under the standard supercritical reaction conditions for 24 h. Even with this prolonged reaction time, the recovered product was a mixture of $[Cu(acac)_2bpy]_n$ and residual reagents, indicating very slow reaction kinetics. For this product, the reaction rate in $scCO_2$ was enhanced by smooth agitation of the vial containing the metal complex. In this case, the complete reaction of the precursors occurred and the elemental analysis suggested that an equimolar polymer was obtained (Table 2). It has been described in the literature that $[Cu(acac)_2bpy]_n$ can be produced by refluxing an equimolar ratio of the reagents in chloroform for a long period of time,[30] while the mechanochemical approach needed an excess of ligand.[29]

Le Bail method for $[Cu(acac)_2bpy]_n$-sc (Fig. 8 and S4) was applied in this sample starting with the crystallographic information provided in ref. 30 [$P2_1/n$ space group and a=11.2162(3) Å, b=14.3523(7) Å, c=11.9411(7) Å, and β= 92.987(4) º]. The fitting procedure rendered the following cell parameters: a=11.366(3) Å, b=14.583(4) Å, c=12.051(4) Å, and β=94.19(4) º, which presented a discrepancy with reported values [$\Delta a/a$=0.01, $\Delta b/b$=-0.02, $\Delta c/c$=0.001, and $\Delta\beta/(\beta-90)$=0.4] slightly larger than in the other compounds presented in this work. To further ensure that the synthesized compound corresponded to $[Cu(acac)_2bpy]_n$ coordination polymer, a Rietveld refinement of the measured pattern was performed by keeping the structure in ref. 30 fixed (Fig. S5). The refinement rendered good agreement parameters (R_B=11 %, and χ^2=5.2), which confirmed that the phase formed was very similar to that reported in the literature. Only tiny diffraction peaks remained not reproduced by both procedures (Le Bail and Rietveld), indicating a small presence of impurities besides the main phase. This small amount of impurities accounts for the discordance between experimental and theoretical values observed in the elemental analysis for this sample (Table 2).

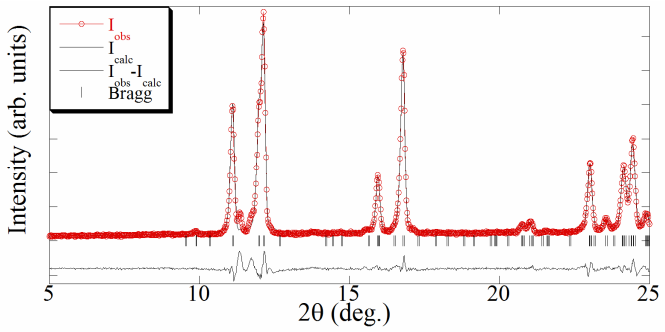

Fig. 8. Final Le Bail whole pattern decomposition plot of $[Cu(acac)_2bpy]_n$-sc sample.

Conclusions

The results obtained from the reaction between the studied copper(II) metal complexes and two different bipyridyl organic ligands carried out in $scCO_2$ have demonstrated that this method can be used to prepared 1D-MOFs held together by axial Cu–N bonds, giving place to highly crystalline products. The influence in the formation of the desired product of the metal complex concentration could be assessed by selecting three metal reagents with different solubility values in $scCO_2$. Indeed, 1D coordination polymers were easily formed by using the highly $scCO_2$ soluble metal complex $Cu(hfacac)_2$, which readily reacted with the two bipyridyl ligands studied in this work to give equimolar products. A characteristic advantage of using $scCO_2$ as the solvent to synthesize 1D-MOFs is related to the CO_2 greener properties in comparison with most organic solvents. Moreover, it is also remarkable the lack or reactivity of this solvent with most of the reagents, including the N atom in the bipyridyl ligands. In this respect, we expect that this work establishes a solid foundation to continue the research into the synthesis with $scCO_2$ of more complex 2D and 3D-MOFs structures.

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Notes and references

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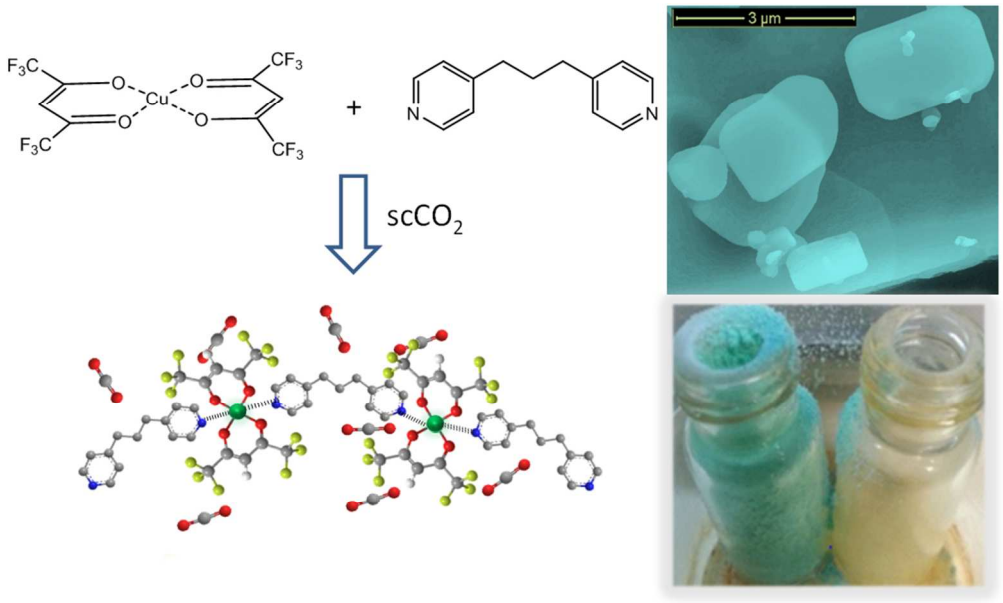

Graphical Abstract
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