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Synthesis of curcuminoid-MOFs: Comparison between supercritical CO_2 and solvothermal methods

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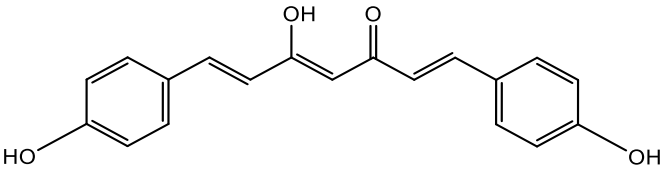
ABSTRACT
Metal organic frameworks (MOFs) are promising hybrid materials for multiple applications (gas storing, catalysis, nanodevices etc.). In the literature, solvothermal methods are used for obtaining the vast majority of MOFs, but they are slow, not environmentally friendly and sometimes post-synthetic activation is necessary. The alternative propose here is the use of supercritical CO_2 ($scCO_2$) as the solvent. Several MOFs, involving Zn as a metal center, bisdemethoxycurcumin as a linker and, in some cases, bipyridines as co-ligands have been synthesized using the supercritical and the solvothermal methods. The obtained results prove the potential of this relatively new approach for the synthesis of these MOFs, although more studies are still necessary.

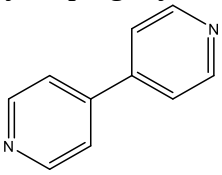
INTRODUCTION
Metal organic frameworks (MOFs) are crystalline polymeric materials formed by the union of metal ions or metal cluster and organic linkers. They are promising materials for multiple applications like gas adsorption, catalysis, biomedical applications or electronic devices, because of their interesting properties [1]. There are multiple methods to obtain MOFs but the most common one is the solvothermal synthesis. In this approach the solution with the inorganic salt and the organic linker is heated at a temperature above the boiling point of the solvent. The process permits the growth of the network and the precipitation of the MOF crystals [2]. Despite of the huge quantity of MOFs obtaining whit these techniques, there are also some drawbacks, e.g. long time runs, high quantity of hazard organic solvents and need of extensive cleaning and drying. In our research group, a methodology with supercritical CO_2 ($scCO_2$), that can avoid all of this problems, is being developed and the synthesis of different MOFs have been obtained [3][4]. The $scCO_2$ is highly used as green solvent due to their special properties of non flammability, negligible toxicity, stability and low critical temperature and relatively low critical pressure [5]. In the MOFs field, the scCO2 is widely used for the post-synthetic activation of these porous materials producing a remarkable increase of their surface areas, but the supercritical synthesis has not really been explored [6].
The crystallization of different hybrid MOFs, involving Zn as a metal center and bisdemethoxycurcumin (BDMC) as organic linkers has been carried out by using the solvothermal and the supercritical methods. The bisthemethoxycurcumin (Figure 1) is one of the natural curcuminoids extracted from the rhizomes of the plant C*urcuma Longa* and it is widely used as spice and in the traditional medicine. It is an interesting molecule because of their high conjugation and the possibility of binding metals in the b-diketone and the phenolic rings [7].



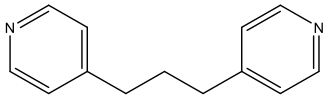
(1E,6E)-1,7-Bis(4-hydroxyphenyl)hepta-1,6-diene-3,5-dione

Figure 1. Structure and IUPAC name of the enol form of the bisthemethoxycurcumin.

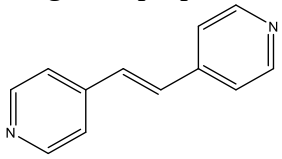
Furthermore, the used of co-ligands has been studied using the bipyridine linkers present in the Figure 2. According whit the literature, the use of additional bipyridine organic ligands modified the characteristic of the MOFs, increasing the dimensionality and rigidity helping crystallization, changing the pore size or altering their properties [8][9].



4,4′-Bipyridine
(bpy)



1,3-Bis(4-pyridyl)propane
(bpp)



1,2-Bis(4-pyridyl)ethylene
(bpe)

Figure 2. Structure and IUPAC name of the bipyridine ligands

The proposed future applications for these new MOFs are its use as active part of transistors, but more characterizations and optimizations should be done to reach this aim. There are already some positive results for MOFs achieved in this field [10].

MATERIALS AND METHODS

Materials

The metal precursors used, Zinc acetate dihydrate ($Zn(OAc)_2.2H_2O$) and Zinc acetylacetonate dehydrate ($Zn(acac)_2.2H_2O$) and the co-ligands (4,4′-Bipyridine, 1,2-Bis(4-pyridyl)ethylene and 1,3-Bis(4-pyridyl)propane), were provided by Sigma Aldrich and the BDMC was synthetized using the Pabon method [11]. The reactants necessary for this synthesis (acetyl acetonate, boric acid, 4-hidroxybenzaldehide, tributilborate and n-butylamine) were supplied by abcr GmbH and the compressed CO2 by Carburos Metálicos S.A. The ethyl acetate for the curcuminoid synthesis was purchased in CARLO ERBA Reagents S.A.S. and the ethanol for the MOF synthesis in Panreac Química SLU.

Methods

$ScCO_2$ method

The $scCO_2$ synthesis was carried out in high-pressure equipment formed by the CO_2 bottle, a pump, a pressure and temperature controller and a stainless-steel reactor of 100 mL volume (Thar process). In a 10 ml pyrex vial, 150 mg of BDMC, the corresponding amount of $Zn(acac)_2$ or $Zn(OAc)_2$ (ratio 1:1) are added. In the experiments whit a co-ligand the correspondent bipyridine ligand was also incorporated obtaining a ratio of 1:1:1. Then, 2ml of Absolut ethanol as a co-solvent and a small magnetic stir bar were

added, the vial was capped with filter paper and placed within the reactor. The system was heated to 60ºC or 40ºC and pressurized to 150 bars and maintained at these conditions during 72h under stirring (150 rpm). After the reaction time and the slow depressurization the product is obtained as a crystalline powder completely dry inside of the vial.

Solvothermal method

The solvothermal synthesis method was adapted from one previously described in the literature for the synthesis of a curcumin-MOF[12]. In a 10 ml pressure resistant pyrex vial with a hermetic tap, 30 mg of BDMC, the corresponding amount of $Zn(acac)_2$ or $Zn(OAc)_2$ (ratio 1:1) are added. In the experiments whit a co-ligand the correspondent bipyridine ligand was also incorporated obtaining a ratio of 1:1:1. Then they are solubilized in 2 ml of Absolut ethanol and placed during few seconds in an ultrasonic bath. Finnally, the vial is placed in an oven at 80ºC during 72h, obtaining the MOF crystals in the walls and the bottom of the vial. Before the obtaining of the crystals, they are cleaned whit fresh ethanol and dried.

Characterization

The products were characterized using different techniques. The crystallinity has been studied using powder X-ray diffraction (XRD), with a Siemens D5000. The structure of some products was elucidated by single crystal XRD in the Alba Synchrotron. For the crystals without the size or the quality need for this technique, elemental analysis was used to qualitatively elucidate the molecular formulas. The weight percentage of C, H, and N was measured in a Flash EA2000 Thermo Fisher Scientific analyzer. Surface area was determined by N2 adsorption at 77 K using an ASAP 2000 Micromeritics instrument and the BET equation. Samples were previously outgassed under reduced pressure at 60 ºC for 24 h. The Morphological characteristics were studied using scanning electron microscopes (SEM, Quanta FEI 200).

RESULTS

The summary of the reactions carried out in the solvothermal method is presented in Table 1, and for $scCO_2$ in Table 2.

Tabla 1. Solvothermal experiments

Ligand	Co-ligand	Metal salt	Solvent	Temperature (ºC)	Time (h)
BDMC	-	$Zn(OAc)_2$	Ethanol	80	72
BDMC	-	$Zn(acac)_2$	Ethanol	80	72
BDMC	bpy	$Zn(OAc)_2$	Ethanol	80	72
BDMC	bpy	$Zn(acac)_2$	Ethanol	80	72
BDMC	bpp	$Zn(OAc)_2$	Ethanol	80	72
BDMC	bpp	$Zn(acac)_2$	Ethanol	80	72
BDMC	bpe	$Zn(OAc)_2$	Ethanol	80	72
BDMC	bpe	$Zn(acac)_2$	Ethanol	80	72

Tabla 2.Supercritical CO_2 experiments

Ligand	Co-ligand	Metal salt	Solvent	Temperature (ºC)	Time (h)	Pressure (bar)
BDMC	-	$Zn(OAc)_2$	Ethanol	60	72	150
BDMC	-	$Zn(acac)_2$	Ethanol	60	72	150
BDMC	bpy	$Zn(OAc)_2$	Ethanol	60	72	150
BDMC	bpy	$Zn(acac)_2$	Ethanol	60	72	150
BDMC	bpp	$Zn(OAc)_2$	Ethanol	60	72	150
BDMC	bpp	$Zn(acac)_2$	Ethanol	60	72	150
BDMC	bpp	$Zn(acac)_2$	Ethanol	40	72	150
BDMC	bpe	$Zn(OAc)_2$	Ethanol	60	72	150
BDMC	bpe	$Zn(acac)_2$	Ethanol	60	72	150

The product of the solvothermal reaction between $Zn(OAc)_2$ and the BDMC is crystalline, as shown by the XRD profile (Figure 3). However, the product of the same reaction but using as metal salt $Zn(acac)_2$ is a precipitate and in the $scCO_2$ an amorphous materials is produced with both salts.

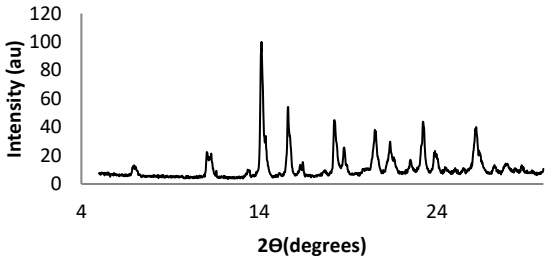


Figure 3. XRD patter of the estructure obtaining in the solvothermal reaction between $Zn(Oac)_2$, and BDMC

The use of the bpy and bpp and $Zn(OAc)_2$ in the solvothermal method, allows the obtaining of crystals whit enough quality to be resolved in the synchrotron. The structures (Figures 4 and 5) have the formula $Zn_2(BDMC)_4(Bpy).H_2O$. EtOH and $Zn_4(BDMC)_4(prBipy)_2$. 2EtOH.

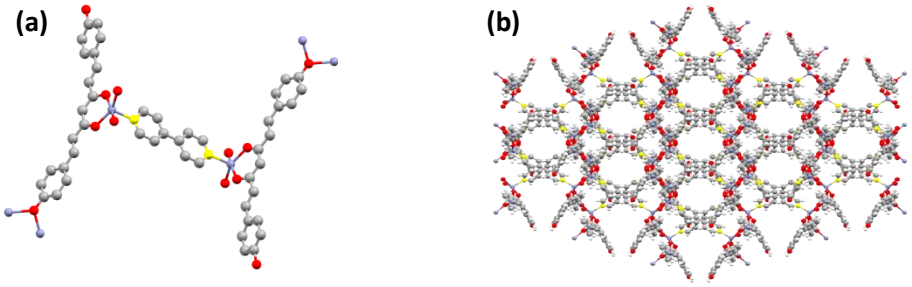


Figure 4. (a) Structure of the MOF $Zn_2(BDMC)_4(Bpy)$, and (b)Extended structure of the MOF $Zn_2(BDMC)_4(Bpy)$.

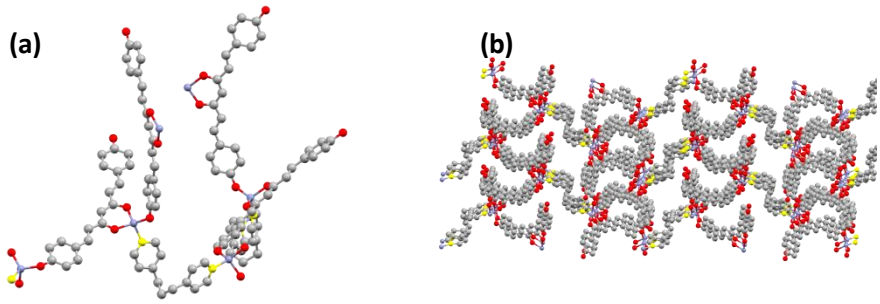


Figure 5. (a) Structure of the MOF $Zn_4(BDMC)_4(prBipy)_2$, and (b)Extended structure of the MOF $Zn_4(BDMC)_4(prBipy)_2$.

In the case of the bpe with the same metal salt, the product cannot be resolved, but the XRD indicated high crystallinity (Figure 6).

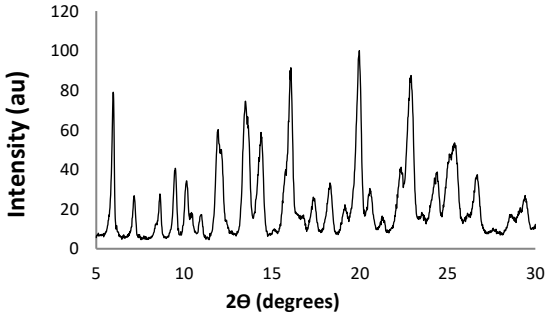


Figure 6. XRD patter of the estructure obtaining in the solvothermal reaction between $Zn(Oac)_2$, BDMC and bpe.

The use of $Zn(acac)_2$ produce a precipitate, except in the reaction whit bpe, where crystals whit the same XRD patter as the ones resolved are obtained. The used of co-ligands in the supercritical approach results in an improvement of the crystallinity. In the reactions whit bpy and bpe whit $Zn(acac)_2$ at 60ºC and at 40ºC in the case of the bpp a crystalline powder is obtained as the XRD patters prove (Figure 7). The reaction whit the bpp at 60ºC produced an amorphous powder, possibly due the proximity between the work temperature and the boiling point of the molecule. All the products obtained are crystalline powders and their size make impossible their resolution in the synchrotron.

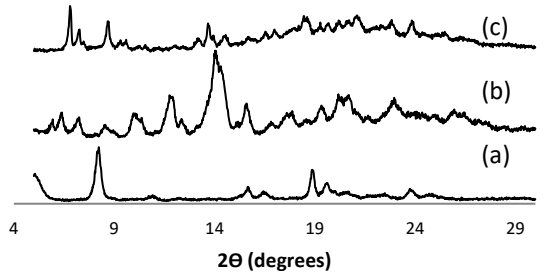


Figure 7. (a) XRD patter of the estructure obtaining in the $scCO_2$ reaction between $Zn(OAc)_2$, BDMC and bpy, **(b)** XRD patter of the estructure obtaining in the $scCO_2$ reaction between $Zn(OAc)_2$, BDMC and bpp at 40ºC, and **(c)** XRD patter of the estructure obtaining in the $scCO_2$ reaction between $Zn(OAc)_2$, BDMC and bpe.

The products obtained in the supercritical reactions whit $Zn(OAc)_2$ are in general less crystalline than whit the other metal salt, possibly because of the lower solubility of the acetate in $scCO_2$. The SEM pictures of the solvothermal and the $scCO_2$ products are presented in Figure 8. Observing the scale, the size of the crystals obtained in the solvothermal method is bigger than in the $scCO_2$. Moreover, in the solvothermal samples different individual blocks depending of the co-ligand are observed and in some cases (b and c), this blocks form bigger spherical structures (spherulites).

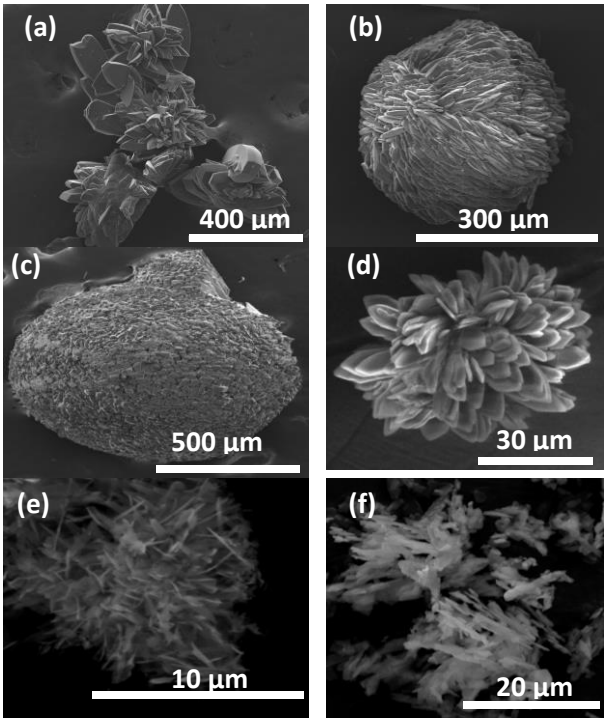


Figure 9. SEM images of the crystalline estructures obtaining in the solvothermal (a,b, c and d) and the scCO2 reactions (e and f): (a) BDMC and $Zn(OAc)_2$, (b) BDMC, $Zn(OAc)_2$ and bpy, (c) BDMC, $Zn(OAc)_2$ and bpe, (d) BDMC, $Zn(OAc)_2$ and bpp, (e) BDMC, $Zn(acac)_2$ and bpy, and (f) BDMC, $Zn(acac)_2$ and bpe.

In all the experiments in which a co-ligand is used, the XRDs were compared whit those of blanks whitout the BDMC in order to verify if both organic linkers are participating in the reaction.

Bases on the results of N_2 adsorption, all the structures obtained had a really low surface area, although the theorical calculations of the resolved structures disagree. For this reason, different post-synthetical activations are being done in order to improve this surface area values.

CONCLUSIONS

In this work, several new MOF structures combining the natural organic molecule bisthemethoxycurcumin and metal salts of Zn have been obtaining. The benefits of the use of co-ligands, specifically bipyridines, have been tested, proving their ability to promote the formation of crystalline products. The synthesis was performed using both solvothermal and supercritical methods, obtaining new structures. In addition, some of the structures of the solvothermal synthesis have the quality necessary to be resolved in the synchrotron. Regarding of the $scCO_2$ samples, extended characterization is taking place. Simultaneously, the process is being optimize to obtain large well-crystallized crystals. Finally, having as objective their use as active part of transistor, some parameters

necessary for this aim are being measured, such as the conductivity, the activation-energy, the band-gap and the charge-mobility.

ACKNOWLEDGEMENTS

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