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Optimization of the synthesis of UiO-66(Zr) in ionic liquids.

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ABSTRACT

In order to rationalize the production of porous Metal-Organic Frameworks (MOFs) in ionic liquids (ILs) as main solvent, we selected the archetype UiO-66(Zr) to analyze its precipitation in four commercial candidates of ILs commonly used in the literature. We did the choice to investigate the reactivity of two hydrophobic salts, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Emim][NTf₂]) and 1-Butyl-3-methylimidazolium hexafluorophosphate [Bumim][PF₆], as well as two other salts considered as hydrophilic, ([Omim][Cl]) and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([Emim][TFO]). Whereas the synthesis in hydrophilic ILs gave rise to the crystallization of pure UiO-66(Zr), the solvo-thermal reaction (120°C) performed in hydrophobic salts did not lead to the same results. In the case of [Bumim][PF₆], we noted the precipitation of zirconium phosphate $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, while the synthesis in [Emim][NTf₂] favored the formation of distinct zirconium terephthalate called hcp UiO-66. These different phases have been characterized by powder X-ray diffraction, BET, IR and SEM.

KEYWORDS

Metal-Organic Framework, UiO-66(Zr), hcp UiO-66, ionic liquid.

1. INTRODUCTION

In the family of hybrid porous Metal-Organic Frameworks (MOFs), the UiO-66 series appears today as one of the most studied members, attracting the academic and the industrial worlds.[1] Many characteristics and properties explain such an interest. The original UiO-66 produced with zirconium (**Fig. 1**), combines a very good stability and porosity, opening a wide range of applications.[2] UiO-66 is also the first member of a new class of materials, using tetravalent metal involved in a hexameric polyoxo-hydroxo cluster $\text{Zr}_6\text{O}_4(\text{OH})_4$ associated to poly-

carboxylic organic ligands, giving rise to the design of several dozen of new porous architectures.[2] This versatility is also extendable to other heavy metals like hafnium,[3] lanthanides (Eu^{3+} , [4, 5] Ce^{4+} [6, 7]) or actinides (Th^{4+} , [8] U^{4+} , [9] Np^{4+} [10]) incorporated in the hexanuclear node and opens new perspectives in the crystal chemistry of these elements.

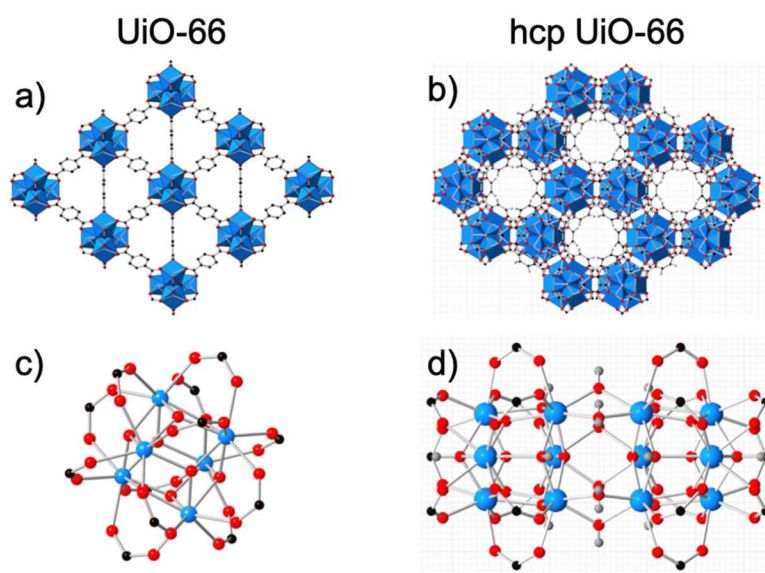


Fig. 1. Representation of the UiO-66 (a) and hcp UiO-66 (b) structures, constructed from the $\{\text{Zr}_6\}$ (c) and the $\{\text{Zr}_{12}\}$ (d) poly-oxo/hydroxo clusters, respectively.

Whereas the synthesis of UiO-66-type MOFs is well established in the literature, whether for the production of large crystals[11] or large scale production,[12] the use of a controversial classical solvent, i.e. N,N-dimethylformamide (DMF), is usually pointed out. Indeed, this popular organic molecule is suspected to cause liver damage and possible carcinogenesis.[13]

Efforts were already made in order to develop greener synthesis of UiO-66(Zr), as well as other analogous Zr-based MOFs.[14, 15] The relative low solubility of terephthalic acid (H_2bdc) in water limits its efficiency for the complexation of zirconium in this solvent and required some adjustments. Therefore, the usual synthesis of UiO-66(Zr) was adapted in water by using functionalized ligands (i.e. amino-terephthalate, benzene tricarboxylate, etc.. [16-18]) as well as the utilization of modulator agents (i.e. acetic acid, formic acid, benzoic acid) under

hydrothermal conditions,[19, 20] in order to increase the solubilization of the organic precursor in the aqueous solvent and the crystallization of the porous framework. Continuous-flow spray-drying[21] or mechanochemistry[22] are other powerful aqueous methods able to generate a large amount of powdered UiO-66(Zr) samples.

The use of ionic liquids (hereafter denoted ILs) can be also an alternative route to substitute dangerous organic solvent and to reduce the toxic impact of MOF in the synthesis process. The attractiveness of ILs is mainly explained by a very low vapor pressure, very good stability, an infinite library of compositions and the possibility to optimize chemical processes (extraction,[23] synthesis, catalysis,[24] dissolution,[25] ...). The literature reports many examples of MOFs synthesized in ILs and the resulting open-frameworks can be divided in two groups.[26, 27] In the first one, the structure exhibits a net charge which is counterbalanced by ionic fragments from the IL incorporated into the pore system. This approach appears very promising for the production of new structural topologies. The second group is less represented in the literature and is related to the generation of neutral framework. In this case IL has a unique role of solvent. Among the prototypical MOFs, only a few are synthesizable in ILs. For example, Yang *et al.* reported the electrochemical crystallization of MOF-5 in 1-butyl-3-methylimidazol.[28]. More recently, Sang *et al.* also proposed the production of UiO-66(Zr) in 1-octyl-3-methylimidazolium chloride ([Omim]Cl).[29] This result appeared very promising since this Zr-based MOF solid precipitate is well crystallized at room temperature in a quick kinetic reaction, in less than one hour.

Recently, the group of Hartman[30] developed the synthesis of a new zirconium MOF-type terephthalates, utilizing di-(tributyl-ethoxymethyl-phosphonium) terephthalate ([PBuMEE]2[BDC]), a terephthalate-based IL as organic linker precursor. Typically, the synthetic procedure used the combination of this IL with an aqueous solution in the presence zirconium tetrachloride and a monocarboxylic acid (i.e. acetic acid, formic acid, benzoic acid)

as modulator agent (benzoic acid, formic acid, acetic acid). After a 24h ionothermal treatment at 100°C, this reactants mixture generated a new structural version of UiO-66(Zr) topology, called hcp UiO-66 (hcp stands for hexagonal closed packed) (Fig. 2). This novel open structure is composed of a dodecanuclear oxo-hydroxo cluster $[\text{Zr}_{12}\text{O}_8(\text{OH})_{14}]$ (instead of hexanuclear brick $[\text{Zr}_6\text{O}_4(\text{OH})_4]$ in UiO-66), linked to each other through terephthalate ligands, in order to build a hexanuclear arrangement of porous channels. Very recently, hcp UiO-66 was also synthesized from a mixture of hafnium tetrachloride and tetrafluoroterephthalic acid dissolved in hydrated DMF.[31]

In order to rationalize the production of UiO-66(Zr) in ILs, we investigated its precipitation in four commercial ILs, commonly used in the literature. For that purpose, we selected two hydrophobic salts, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Emim][NTf₂]) and 1-Butyl-3-methylimidazolium hexafluorophosphate [Bumim][PF₆], as well as two other salts considered as hydrophilic, ([Omim][Cl]) and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([Emim][TFO]). We first attempted to reproduce the crystallization of UiO-66(Zr) at room temperature, but were unsuccessful. We therefore pursued our investigations at 120°C under ionothermal conditions. This study reports the influence of using such hydrophobic or hydrophilic ILs on the preparation of UiO-66(Zr) for two sets of reaction temperature, either at room temperature or 120°C. The resulting powdered solids were characterized by X-ray diffraction, scanning electron microscope (SEM), infrared spectroscopy and BET.

2. EXPERIMENTAL

2.1. Materials and instrumentation

All the chemicals were obtained from commercial sources and used without further purification. [Emim][TFO]), [Bumim][PF₆] and [Emim][NTf₂] were purchased from Solvionic and [Omim][Cl] from Sigma Aldrich. Water content of ILs was determined by Karl-Fisher titration and summarized in supplementary information (**Table S1**). Zirconium tetrachloride (ZrCl₄, >99.5%), zirconyl chloride octahydrate (ZrOCl₂·8H₂O, 98%), terephthalic acid (H₂bdc, 98%) and acetic acid (CH₃COOH, 99.7%) were purchased from Sigma Aldrich.

The powder X-ray diffraction (PXRD) patterns of the different compounds were scanned at RT by using a Bruker D8 Advance A25 diffractometer with Bragg-Brentano geometry (θ - 2θ mode), ranging from 3 to 50° (2θ), a step length of 0.02° (2θ) and a counting time of 0.5 s/step. The D8 system was equipped with a LynxEye detector with CuK α radiation.

N₂ adsorption isotherms were recorded at liquid nitrogen temperature using a Micromeritics ASAP2020 apparatus. Specific surface area were calculated in the P/P₀ range: 0.015–0.15 using the BET method. Before sorption measurements, the sample was outgassed at 150°C under primary vacuum (5 Pa) at high temperature for 15 h.

IR spectra were measured on a Perkin–Elmer Spectrum Two spectrometer that was equipped with a diamond attenuated total reflectance (ATR) accessory between 4000 and 400 cm⁻¹.

2.2. Synthesis of Zr-based MOF at room temperature.

The samples were typically prepared in a 12 mL glass-vial, loaded with 19 mg of ZrCl₄ (0.08 mmol) or 26 mg of ZrOCl₂·8H₂O (0.08 mmol), 2 mL of ionic liquid and 600 μ L of glacial acetic acid (10.5 mmol). It is then magnetically stirred at room temperature for 1 hour at room temperature. The resulting white solid is separated by centrifugation, soaked in methanol (2 x 4 ml during 4h) and dried at 50°C. This protocol reproduces the synthetic procedure reported by Sang et al.[29]

2.3. Synthesis of Zr-based MOF at 120°C.

The samples were prepared in a 2 ml glass-vial charged with 80 mg of ZrCl_4 (0.034 mmol), 57 mg of H_2bdc (0.34 mmol), and 2 ml of ionic liquid. For some syntheses, the addition of deionized (10, 100 or 1000 μL water) and/or acetic acid (420 μL , 7.3 mmol) was also carried out to improve the crystallinity of the final solids. After the ionothermal treatment at 120°C for 24 hours, the resulting white powdered solid is centrifugated and washed with dichloromethane (5 ml) to eliminate the ionic liquid and dried at 50°C. After PXRD analysis, optimized syntheses are further washed at room temperature with methanol (10 ml, 1h), then with DMF (10 ml, 4h), and finally rinsed with acetone (5 ml) in order to remove unreacted terephthalic acid.

1. RESULTS AND DISCUSSION

1. Synthesis of Zr-UiO-66 type MOF at room temperature in ILs

Based on the publication from Sang *et al.*, [29], we initiated our study by testing different synthesis batches at room temperature. Therefore, a first series of experiments were realized from a mixture of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and terephthalic acid in the different ILs containing acetic acid as modulator, at room temperature. After mixing for 24h, white fine powders were observed in [Omim][Cl] and [Bumim][PF₆]. XRD analyzes (**Fig. S1**) indicate a very badly product in the case of [Omim][Cl] with a broad Bragg peak with very low intensity in the range 7-9° (2θ) associated to UiO-66, but showing an amorphous phase. In contrast, with [Bumim][PF₆], it clearly appears well-crystallized compounds by PXRD analyses, which reflect the occurrence of unreacted terephthalic acid and an unidentified phase with Bragg peaks located at $d = 8.98$, 4.59, 3.83 Å ($2\theta = 9.8$, 19.3, 23.2°). The crystallization of UiO-66 starts to be visible when working with [Emim][TFO] and is improved in [Emim][NTf₂].

A second series of experiments was carried out with the addition of a small amount of water (100 μL) in order to promote efficiently the hydrolysis of Zr(IV) or in order to examine the

influence of the zirconium precursor by replacing $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (previously reported by Sang et al.) [29] by ZrCl_4 . When adding water, the X-ray diffraction analyses (**Fig. S2**) showed either powder diagrams of typical amorphous phase with hydrophobic ILs ([Bumim][PF₆] or [Emim][NTf₂]), or only crystallized terephthalic acid with hydrophilic ILs ([Omim][Cl] or [Emim][TFO]). When using ZrCl_4 (without any addition of water, **Fig. S3**), amorphous phases are observed for the hydrophobic ILs [Omim][Cl] or [Emim][TFO]), but crystallized terephthalic acid appears with hydrophilic ILs ([Omim][Cl] or [Emim][TFO]). Once again, our present synthetic conditions did not allow for the formation of UiO-66(Zr). These results are quite surprising since Sang et al. [29] reported the quick precipitation of well crystallized UiO-66 in [Omim][Cl] from the reaction of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ with terephthalic acid by the means of acetic acid as modulator, and in less than 1h at room temperature. Therefore, it was not possible to reproduce the results of Sang in our conditions (same concentrations of reagents but adapted to a volume of 2 ml of ILs).

2. Synthesis of Zr-based MOF at 120°C in hydrophobic ILs

Afterward, all the experiments were repeated at 120°C for a heating time of 24h, which are typical conditions for the synthesis of Zr-based MOFs from a mixture of ZrCl_4 precursor and acetic acid. [1, 12]

First attempts were carried out by using the hydrophobic ionic liquid [Emim][NTf₂], without acetic acid. The white powdered precipitate obtained from H₂O-free [Emim][NTf₂] contains a mixture of UiO-66 and hcp-UiO-66 together with a large amount of terephthalic acid as clearly shows the X-ray diffraction diagram (**Fig. 2**). Indeed, the SEM image (**Fig. S9**) indicates the existence of some octahedrally-shaped crystals (maximal size 1 μm) attributed to the UiO-66(Zr) phase, together with larger elongated particles (3-6 μm), which could correspond to the crystallized terephthalic acid. Whereas the addition of water up to 100 μL (5.56 mmol) does

not modify the nature of the phases in the final mixture, the synthesis using 1000 μL (55.6 mmol) of H_2O results in the formation of badly crystallized compounds, with Bragg peaks related to those of hcp UiO-66, and low intense signals assigned to terephthalic acid. The addition of acetic acid modulator to the mixture (involving the addition of 1000 μL (55.6 mmol) of H_2O) allows to improve drastically the crystallinity of the final product, which contains a majority of hcp UiO-66 and traces of UiO-66, with tiny Bragg signals for terephthalic acid (**Fig. 2**). In this case, the SEM examination shows the occurrence of some UiO-66 crystals (2 μm size) adopting the typical octahedral shape, embedded in a gangue of smaller crystalline particles ($< 1 \mu\text{m}$), which could be assigned to the hcp UiO-66 (**Fig. S9**). These particles of hcp UiO-66 are better defined from a crystallization in terephthalate based IL $[\text{PBU}\text{MEE}]_2[\text{BDC}]$ and can be described as large flat plate with a diameter of 300 nm.[30]

It is noted that the addition of acetic acid (without any water) still give rise to crystallized terephthalic acid, but additional Bragg peaks in the range $d = 8.8\text{-}9.8 \text{ \AA}$ ($2\theta = 9\text{-}10^\circ$) are visible, and associated to $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CH}_3\text{COO})_{12} \cdot 8.5 \text{ H}_2\text{O}$ (pdf file: 031-1916).[32] This molecular species is analogous to the hexanuclear cluster encountered in UiO-66 structure, where the acetate ligands are substituted by terephthalate groups. This results indicates that hexameric brick can be generated from $[\text{Bumim}][\text{PF}_6]$ and stabilized by the soluble acetic acid.

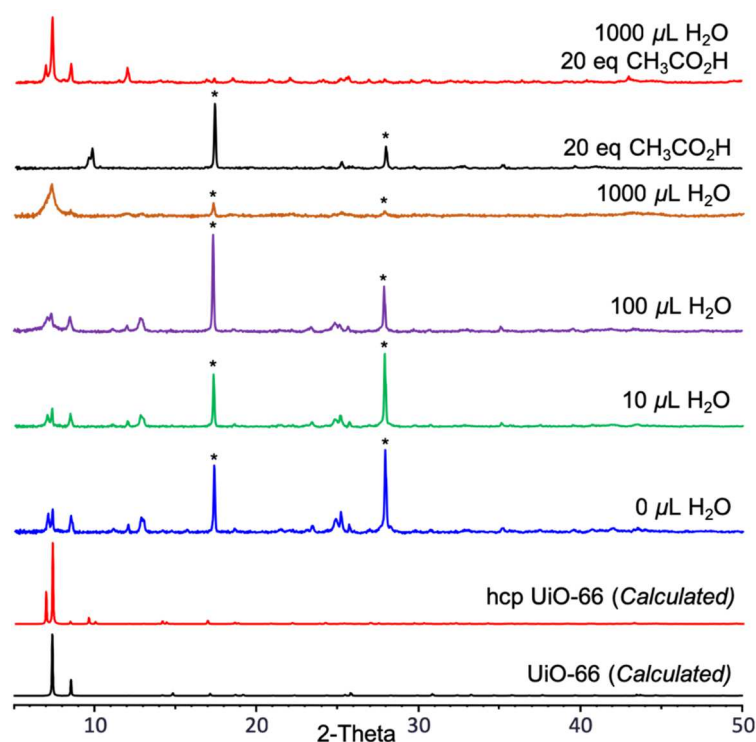


Fig. 2. Powder X-ray diffraction patterns of the resulting powders obtained from [Emim][NTf₂]. The main peaks of crystallized H₂bdc are marked by asterisks. For clarity, the solid obtained from the addition of 1000 μ L of H₂O and acetic acid was treated by DMF in order to remove traces of crystallized H₂bdc. Copper wavelength radiation.

With the second hydrophobic ionic liquid tested in our study [Bumim][PF₆], similar results are observed. Within the water amount range of 0-100 μ L, the main resulting powdered product is crystallized terephthalic acid (**Fig. 3**). The mixture with high concentration of water (1000 μ L of H₂O in 2 ml of IL) generates the formation of a distinct crystallized compound, with Bragg peaks related to $d = 7.6, 4.4, 3.6, 3.5 \text{ \AA}$ ($2\theta = 11.7, 20.0, 24.9, 25.2^\circ$), related to a known hydrated zirconium phosphate Zr(HPO₄)₂·H₂O (pdf file: 34-0127) (**Fig. S5a**). The crystallinity of this last compound is slightly improved when acetic acid (20 molar eq.) is added to the mixture. The hydrolysis of PF₆⁻ anions from ionic liquid was already mentioned in the literature for the discovery of new uranium phosphate materials for instance.[33]

This chemical process is therefore at the origin of the phosphate anions which are more complexing than the carboxylate one, toward zirconium cations, and thus producing the stable zirconium phosphate. We also noticed that the addition of acetic acid without water, also induce the occurrence of crystallized terephthalic acid, as we observed with low water content (0-100 μL).

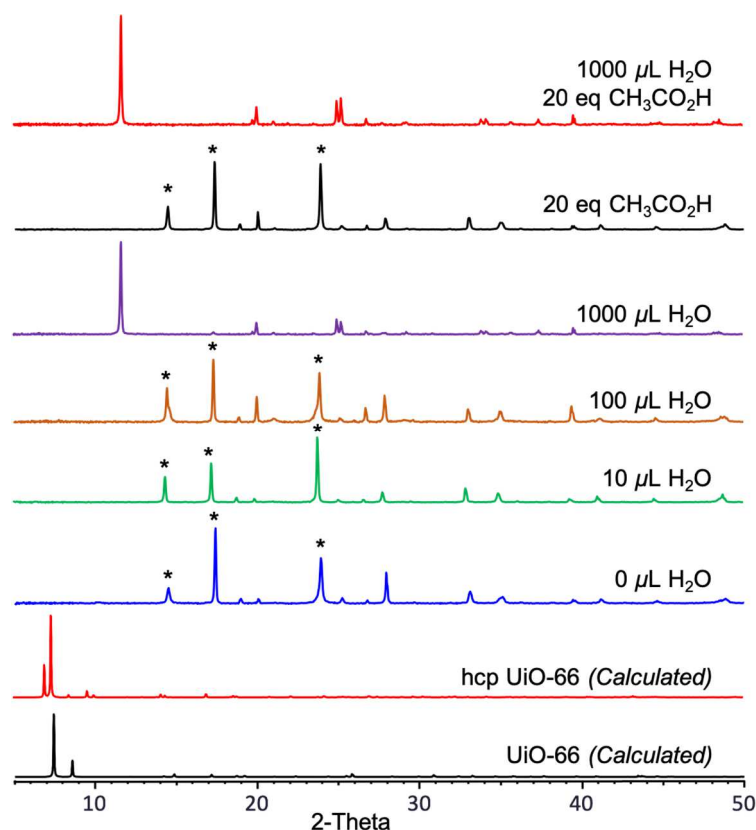


Fig. 3. Powder X-ray diffraction patterns of the resulting samples obtained from [Bumim][PF₆], after heating a mixture of ZrCl₄ and terephthalic acid at 120°C for 24h. The influence of addition of water and/or acetic acid is shown. The main peaks of crystallized H₂bdc are marked by asterisks. Copper wavelength radiation.

3. Synthesis of Zr-MOF in hydrophilic ILs at 120°C.

The production of UiO-66 from the mixture of ZrCl_4 and terephthalic acid, is more favourable in hydrophilic ILs ([Omim][Cl] or [Emim][TFO]), since the different X-ray diffraction patterns only reveals the precipitation of this Zr-based MOF phase. For [Omim][Cl], the crystalline quality of UiO-66 is very low from dried or hydrated chemical system (up to 1000 μL of H_2O in 2 ml of IL), with the observation of a low intense and broad peak in the range $6\text{--}9^\circ$ (2θ) (**Fig. 4**). The addition of acetic acid (20 molar eq.) improves significantly the quality of the solids, with the appearance of the typical Bragg peaks doublets at $12.2, 10.5$ and $7.2, 8.4^\circ$ (2θ), which is assigned to the UiO-66 topology. Higher intense Bragg peaks are observed when adding both acetic acid (20 molar eq.) an 1 mL of H_2O , reflecting improved crystallinity for the UiO-66(Zr), after heating time of 24h at 120°C . SEM analysis (**Fig. S10**) confirms this point, with undefined aggregates of particles with low water content and nice discrete crystals of 1 μm size.

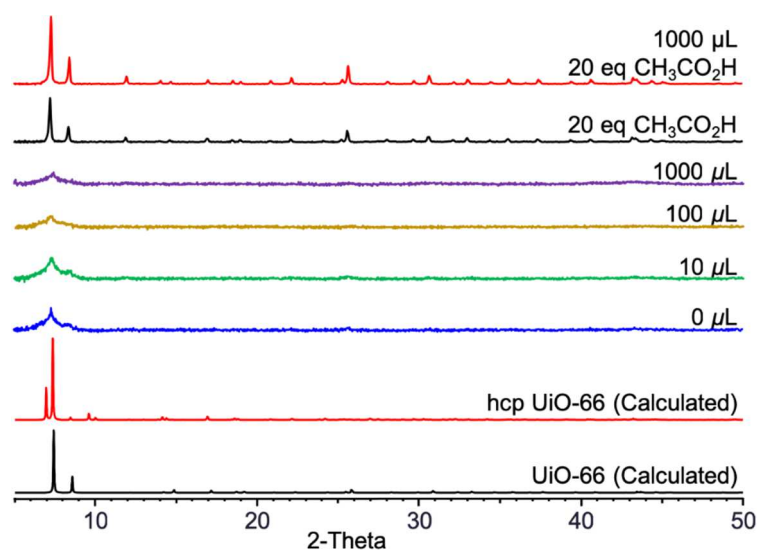


Fig. 4. Powder X-ray diffraction patterns of the resulting samples obtained from synthesis batches carried out in [Omim][Cl] solvent for 24h at 120°C , from a mixture of ZrCl_4 and terephthalic acid. Copper wavelength radiation.

The same strategy was extended to the use of [Emim][TFO]. The evolution of the powder X-ray diffraction patterns (**Fig. S4**) clearly shows the formation of the UiO-66(Zr), but the

crystallinity of the resulting MOF compounds is much better as reveals the higher Bragg peaks intensity, in comparison with those obtained with the ionic liquid [Omim][Cl]. However, the addition of water (up to 1000 μL of H_2O in 2 ml of IL) reduces drastically the crystallinity. The same trend is observed when adding acetic acid (20 molar eq.). To the best of our knowledge, the effect of water concentration in DMF as well as other solvent was never examined for UiO-66(Zr) production. However, a similar study was already mentioned for the synthesis of the uranium-based UiO-66, concluding that excess of water favours the precipitation of uranium oxide and limits the reactivity of terephthalic acid.[34] Due to the chemical analogy between U^{4+} and Zr^{4+} , we suppose the appearance of amorphous ZrO_2 will also reduce the porosity of the final sample, as observed hereafter.

Nevertheless, a better crystalline product of UiO-66 is obtained with the addition of acetic acid together with 1000 μL of H_2O . Due to the very small size of crystallites ($< 1\mu\text{m}$), SEM images does not allow to observe the typical octahedral morphology of UiO-66 crystal and the influence of additional molecules (**Fig. S11**). When acetic acid is added to dry [Emim][TFO], the crystalline quality of UiO-66 is comparable to that obtained with dry or hydrated [Omim][Cl]. As before, the best solid quality is reached from the conditions mixing water, acetic acid and [Omim][Cl].

The powdered samples of UiO-66(Zr), exhibiting the best crystallinity from synthesis batches in hydrophilic ILs [Emim][TFO] and [Omim][Cl] mixed with H_2O and acetic acid, were activated (see experimental section) in order to quantify their porosity. The BET specific surface area are 1155 m^2/g and 1421 m^2/g for the samples coming from the synthesis in [Emim][TFO] and [Omim][Cl], respectively (**Fig. 5**). These values are in accordance with those commonly reported for UiO-66(Zr),[1, 35] but we noticed a specific surface area difference of around 19% between these two samples, indicating that the [Omim][Cl] route gives rise to a better crystallization for UiO-66(Zr). This point has been also indicated when regarding the

quality of the powder X-ray Diffraction patterns, with higher Bragg peaks intensities for the [Omim][Cl] sample (**Fig. 4**).

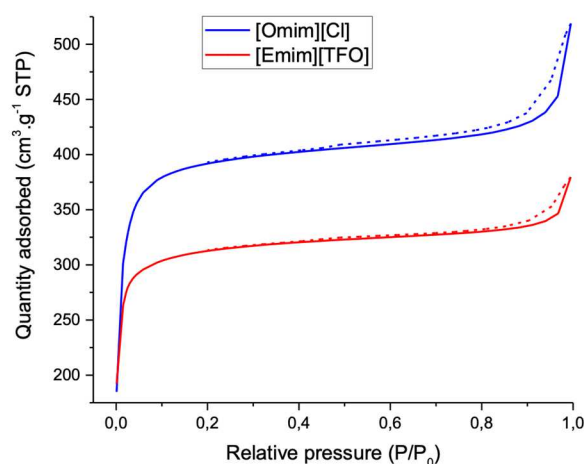


Fig. 5: Isotherm curves of adsorption (solid) and desorption (dashed) of nitrogen (77K) of UiO-66(Zr) synthesized in [Omim][Cl] (blue) and [Emim][TFO] (red).

The BET surface area has also been collected from samples in [Emim][TFO] prepared with different water contents (**Fig. S8**). These corresponding values follow the evolution of the crystallinity reported by X-ray diffraction analysis. A relatively nice PXRD diagram was observed with no additional water (228 cm³/g of N₂ adsorbed at $P/P_0 = 0.5$). When adding water, the Bragg peaks become broader and less intense, together with decreasing quantity of N₂ adsorbed (at $P/P_0 = 0.5$) equal to 152, 144 and 113 cm³/g for water content of 10, 100 and 1000 μ L, respectively.

The two optimized UiO-66 powdered samples produced in [Omim][Cl] and [Emim][TFO] solvents by addition of acetic acid and water, were analysed by infrared spectroscopy after their chemical activation followed by a thermal treatment at 150°C under secondary vacuum.

The two IR spectra are very similar and do not show the presence of IL into the pores or at the surface of the crystallites (**Fig. S6 and S7**). For both compounds, the typical large band centred at 3300 cm⁻¹ are assigned to water trapped within the pores of adsorbed at the surface of the

crystallites. The vibrations ranging from 1650 to 1560 cm^{-1} correspond to OCO asymmetric stretching. The first peak at 1650 cm^{-1} is characteristic of a dehydroxylated version of UiO-66(Zr),[36] transformation occurring during the thermal treatment at 150°C. The bands between 1507 and 1300 cm^{-1} are attributed to benzene ring. Below 800 cm^{-1} , the different peaks are mainly associated to the zirconium cluster (Zr-O and O-H vibrations).

3.4. Influence of the nature of ILs for the synthesis of UiO-66(Zr)-like MOFs

The set of experiments emphasized important trends about the synthesis of Zr-based MOF in ionic liquids. Although [Emim][NTf₂] is considered as hydrophobic, the mutual solubilities of water and this IL[37] makes possible the controlled hydrolysis of tervalent zirconium, the formation of Zr-based cluster $\text{Zr}_6\text{O}_4(\text{OH})_4$ or $[\text{Zr}_{12}\text{O}_8(\text{OH})_{14}]$, and their stabilization by terephthalate ligand in MOFs. However, the effect of water is more negative for [Bumim][PF₆] since this molecule induces the hydrolysis of $[\text{PF}_6]^-$ anion.

[Emim][NTf₂] was the only one IL studied, showing a mixture of UiO-66 and UiO-66 hcp. This last phase can be presented as a ligand-deficient analogue of the common UiO-66 structure ($\text{Zr}/\text{bdc} = 1/1$ for UiO-66 whereas it is 1/0.75 For hcp UiO-66).[38] The existence of this structure could be explain by the coordinating ability of $[\text{NTf}_2]^-$ anion[39] which limits the reactivity between zirconium and terephthalate ligands.

The synthesis of pure UiO-66 is favoured in the hydrophylic [Omim][Cl] and [Emim][TFO]. Indeed, these ILs were stable in the presence of water and are good solvent for the solubilisation of organic molecules.[40] The better crystallinity of UiO-66 obtained in [Omim][Cl] is assigned to the occurrence of a long alkyl chain in this IL and the associated viscosity, slowing down the crystallization process. Furthermore, these hydrophilic ILs are well adapted for porous materials, since they are well soluble in polar solvent and facilitate the activation process.

CONCLUSION

In this study, we have experimentally investigated the synthesis of zirconium terephthalate MOFs in different commercially available ILs. The first series of experiments was performed at room temperature. In these conditions, the syntheses carried out in [Omim][Cl], [Emim][NTf₂] and [Emim][TFO], allows the precipitation of amorphous UiO-66(Zr) compound. At higher temperature (120°C), the investigations in neat [Emim][NTf₂] or in the presence of water, allows the production of UiO-66 as well as its ligand deficient analogue called hcp-UiO-66. The same attempt performed in the other hydrophobic IL [Bumim][PF₆], causes the decomposition of the [PF₆]⁻ anion, and generate zirconium phosphate, Zr(HPO₄)₂·H₂O and

Hydrophilic ILs that we tested appear as more favourable for the production of standard UiO-66, since this solid is obtained pure in ([Omim][Cl]) and [Emim][TFO] solvents, but with the addition of a controlled amount of water and acetic acid. In the pure hydrophilic ILs we tested, it was not possible to generate a well crystallized UiO-66(Zr) developing porosity comparable to those observed from syntheses effectuated in DMF.

We also highlighted the tendency of hcp-UiO-66 to crystallized in a IL ([Emim][NTf₂]) limiting the disponibility of terephthalate ligand. This observation is in agreement with the structural organization of hcp-UiO-66 structure which contains less terephthalate ligands that the common UIO-66 version.

From this systematic study, we can conclude that the commercial hydrophilic ILs we used are more adapted to the synthesis of well crystallized UiO-66(Zr) structure. However this approach requires the addition of mineralizer (i.e. acetic acid) as well as water for the hydrolysis of

zirconium. This method of synthesis could be also extended to the production of new UiO-66-like compounds, using other ligands or others cations.

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