Synthesis of Ordered Microporous/Macroporous MOF-808 through Modulator-Induced Defect-Formation, and Surfactant Self-Assembly Strategies

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ABSTRACT

Ordered materials with interconnected porosity allow the diffusion of molecules within their inner porous structure to access the active sites located in the microporous core. As a follow-up of our work on engineering of MOF-808, in this contribution, we study the synthesis of defective MOF-808 using two different strategies: the use of modulators and the surfactant-assisted synthesis to
obtain materials with ordered and interconnected pores. The results of the study indicated that (i) modulators agents led to formation of microporous/mesoporous MOFs through the formation of missing linker defects and (ii) the self-assembly of CTAB surfactant produced ordered microporous/macroporous network which enhanced crystallinity. However, the surface properties of the materials seem to be unaffected by the use of surfactants during synthesis. These results contribute to the development of ordered materials with a broad range of pore size distributions and give rise to new opportunities to extend the applications of MOF-808.
1. Introduction

Metal Organic Frameworks (MOFs) are most often synthesized from assembling metallic clusters, called inorganic nodes or secondary building units, and organic molecules called organic struts or simply linkers, in solution by a solvothermal method [1]. In the case of MOF-808, the metallic cluster is Zr$_6$O$_4$(OH)$_4$(-CO$_2$)$_6$, the linker is trimesic acid, commonly denoted H$_3$BTC, and the solvent is typically N,N-dimethylformamide (DMF) [2]. MOF-808 was first synthesized by Furukawa et al. [3] from ZrOCl$_2$·8H$_2$O, and H$_3$BTC dissolved in a 50-50 vol. % mixture of DMF and formic acid submitted to a solvothermal stage at 100 °C for seven days. Formic acid, as well as other carboxylic acids, is a ligand that seems to play the role of a modulator for the rate of crystal growth [4]. The synthesis performed by Furukawa et al. [3] yielded octahedral crystals of the cubic system and Space group $Fd-3m$ whose structure was represented by the formula Zr$_6$O$_4$(OH)$_4$(BTC)$_2$(HCOO)$_6$ and whose empirical formula, from monocystal, XRD data, was found to be C$_{24}$H$_6$O$_{44.35}$Zr$_6$. The pore diameter of MOF-808, also calculated from XRD data, was estimated to be 1.84 nm, and the authors reported an apparent surface area, from the BET method [3], of 2060 m$^2$/g. We highlight these properties because they are crucial for the application of MOFs in adsorption and catalysis. Afterwards, Liang et al. [5] analyzed the effect of the concentrations of ZrCl$_4$ -another zirconium precursor-, H$_3$BTC, DMF, of the carbon chain length of the modulator: formic -C1-, acetic -C2-, propionic -C3-, iso-butyric -C4-, and benzoic -aromatic C6- acid, and of the temperature of the solvothermal stage on the synthesis of MOF-808. The authors found that formic, acetic, and propionic acid formed isostructural MOF-808 materials, whereas iso-butyric and benzoic acid failed to produce a MOF. Based on a previous report by Schaate et al. [6], these authors postulated that the C1, C2, and C3 monocarboxylates acted not only as modulators for crystal growth but that they were also able to
partially replace the H$_3$BTC organic linker in the structure of MOF-808. Owing to the later, the porosity of the materials increased with the length of the carbon chain of the acids. They reported a quasi-linear increase in the apparent BET surface areas of the materials with the reduction of the carbon chain length: namely, 2330 m$^2$/g (C1) > 1606 m$^2$/g (C2) > 1408 m$^2$/g (C3), whereas, the average pore size diameters, estimated via a Non-Local Density Functional Theory calculation routine assuming a carbon slit-pore model, showed differences that are rather within the margin of error for this type of calculations; average pore diameters equal to ~0.152 nm for formic acid, ~0.146 nm for acetic acid, and ~0.142 nm for propionic acid. In addition, the XRD patterns and their further Le Bail analysis, for estimating the structural parameters of the crystallites, did not produce results hinting at significant structural changes that may modify the microporosity of the materials. In general, these authors modified the original synthesis method of Yaghi’s group [3] and instead of producing single crystals of MOF-808, they synthesized parent crystalline powders of the latter MOF using a shorter time, 24 h, but a higher temperature, 135 °C, during the solvothermal stage of the synthesis. Afterward, the group of Yaghi focused on post-synthetically modifying MOF-808 to produce a superacidic sulfated material that was applied as a catalyst for diverse reactions requiring strong BrØnsted acid moieties as active sites [7]. Following the success of such an application, the same research group aimed at making a molecular level characterization of the BrØnsted acid moieties [8]. These works have encouraged other researchers to produce distinct variations of MOF-808 for applications in catalysis [9-11], adsorption [12-14], and sensing [15].

We have focused our efforts on understanding how specific parameters of the synthesis of MOF-808 influence its physicochemical properties; particularly, its porosity, thermal stability, and surface chemistry. We first tried to understand how the nature of the zirconium precursor
may influence these properties [16]. We employed zirconium chloride -ZrCl₄-, zirconyl chloride -ZrOCl₂·8H₂O-, and zirconyl nitrate -ZrO(NO₃)₂·xH₂O- as zirconium precursors, a ~60/40 vol.% mixture of N,N-dimethylformamide/acetic acid and a solvothermal treatment at 120 °C for 24 h.

Our synthesis protocol was based on the one reported by Liang et al. [5] and, as they, we produced crystalline powders of MOF-808 instead of the single crystals reported by Yaghi’s group [3]. The use of zirconium chloride yielded the finest MOF-808 powders with the highest crystallinity and the most developed porous network. The porous network of our materials was composed of two families of micropores with average pore diameters very similar to those found by Liang et al. [5] and one family of mesopores whose average pore size was modified by the nature of the zirconium precursor. These mesopores seem to be making the amorphous part of the materials. To explain these results, we hypothesized that the structural water of the zirconium precursors plays a role during the crystallization of MOF-808 hence acting as a structure-directing agent.

Conversely, the surface chemistry of the materials was not modified by the zirconium precursors, and this explained why, despite the changes in crystallinity, the thermal stability of these MOFs did not change. The surface of the MOFs was mainly composed of uncoordinated carboxylates, uncoordinated zirconium oxo-clusters, and free carboxylates. Also, nitrogen species from the N,N-dimethylformamide solvent were found at the surface. Afterward, we investigated the effect of the concentration of acetic acid on the physicochemical properties of MOF-808 [17]. For this, we used zirconyl chloride as a metallic precursor and made the solvothermal treatment at 108°C for 24 h. We obtained crystalline powders of MOF-808 with micropores and mesopores again. We found that increasing the concentration of acetic acid led to a higher degree of crystallinity of MOF-808. In addition, the porosity of the materials was more
developed when augmenting the concentration of acetic acid. Namely, a larger number of wider mesopores were formed after increasing the concentration of acetic acid. We also found that the mesopores are connected to the largest family of micropores of MOF-808, and, in agreement with our previous work [16], the mesoporosity belongs to the amorphous part of the material. As Liang et al. [5] did before, we found that these changes can be explained considering that the modulator, acetic acid, replaces the organic linker, H$_3$BTC, in the structure of MOF-808. Such modifications did not affect the thermal stability of MOF-808 because their surface chemistry remained mostly unaltered as compared to what we found when using different zirconium precursors. In the same paper, we also analyzed the effect of applying a post-synthetic modification procedure to MOF-808 with sulfuric acid. Though the conditions for this experiment were adapted from the work of the group of Yaghi [7], we found that sulfuric acid reacted with both the organic and inorganic moieties of MOF-808. Therefore, our materials were both sulfonated and sulfated at the benefit of their thermal stability but the cost of their crystallinity and porosity. This was not the case for the single crystals of MOF-808 synthesized by Yaghi et al. [7]. In general, the materials that we synthesized are defective [18].

Defective MOFs are the focus of intensive research because defects promote chemical reactivity, selective adsorption, and electronic conductivity [18, 19]. Among Zr-MOFs, the so-called UiO-66 has been postulated as a model for the analysis of the introduction of defects in Zr-MOFs [20]. In the case of MOF-808, a sparing number of examples of defective materials of this type can be found in the literature [11, 21]. Therefore, our research efforts are justified by the need to systematically understand how to control the nature and distribution of these defects, i.e., its defect engineering.
For this contribution, we continue to investigate the defect engineering of MOF-808 by a de novo synthetic strategy [18]. We wanted to know how to synthesize a MOF-808 with an ordered and interconnected porous network composed by the micropores of its crystallites and the external mesopores or macropores and what are the consequences on the physicochemical properties of the synthesized MOFs after implementing strategies towards such a goal. We approached the problem following a strategy that first involved revisiting the role of the chain length of the carboxylic acid modulator on the modulator-induced defect formation for MOF-808 and then analyzed the consequences of adding a surfactant, hexadecyltrimethylammonium bromide -CTAB-, during the synthesis of a selected MOF-808. The main findings of the work were: (i) modulator agents led to the formation of microporous/mesoporous MOFs in which the average mesopores size diameters are not linearly related to the modulator chain length, (ii) the addition of the surfactant produced ordered porous networks with enhanced crystallinity and intercrystalline voids, and (iii) the surface chemistry of synthesized materials seems to be unaffected by the use of surfactant during synthesis.
2. Results and Discussion

2.1. Influence of the chain length of the modulator on the physicochemical properties of MOF-808

The thermograms for the as-synthesized MOFs ZrBTC-F, ZrBTC-A, and ZrBTC-P MOFs are shown in Figure 1, and one of the things that they tell us is that decreasing the length of the carbon chain of the modulator leads to more developed pore structures with larger surface areas, see Section 2.1. of the Supporting Information. Accordingly, an analysis of the recorded argon adsorption-desorption isotherms and χ-plots of ZrBTC-F, ZrBTC-A, and ZrBTC-P, Figure 2, following IUPAC’s classification [22], shows that the porous structure of the synthesized materials comprises micropores and mesopores.

![Figure 1. Thermogravimetric analysis (TGA) in an air atmosphere of synthesized MOFs.](image)

**Figure 1.** Thermogravimetric analysis (TGA) in an air atmosphere of synthesized MOFs.
Figure 2. Ar adsorption/desorption isotherms of (a) ZrBTC-F (b) ZrBTC-A and, (c) ZrBTC-P, in all range of the linear P/Po. $\chi$-method adsorption/desorption isotherms of the same materials (d) ZrBTC-F, (e) ZrBTC-A, and (f) ZrBTC-P.

The $\chi$-surface areas of the materials decreased with increasing the length of the carbon chain of the modulators, Table 1. Comparatively, the $\chi$-surface areas of the MOF synthesized with formic acid were ca. 18 and 20% larger than those estimated for the MOFs synthesized with acetic and propionic acid, respectively. According to our calculations, these differences in surface area are due to a more considerable development of the micropore surface of the materials when using formic acid as the modulator, Table 1. It is pertinent to recall that the $\chi$-method for assessing
porosity allows differentiating the surface areas related to the different families of pores that the material may possess [23].

Table 1. Summary of the textural properties calculated by the $\chi$ method of the ZrBTC-F, ZrBTC-A, ZrBTC-P, ZrBTC-AE1, and ZrBTC-AE2 materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Microporous Range</th>
<th>Mesoporous Range</th>
<th>Total $\chi$ surface area m$^2$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Surface 1</td>
<td>Surface 2</td>
<td>Total</td>
</tr>
<tr>
<td>ZrBTC-F</td>
<td>$\chi$ surface area m$^2$/g</td>
<td>Rsq</td>
<td>$\chi$ surface area m$^2$/g</td>
</tr>
<tr>
<td>ZrBTC-A</td>
<td>840</td>
<td>0.99</td>
<td>91</td>
</tr>
<tr>
<td>ZrBTC-P</td>
<td>727</td>
<td>0.99</td>
<td>19</td>
</tr>
<tr>
<td>ZrBTC-AE1</td>
<td>646</td>
<td>0.99</td>
<td>18</td>
</tr>
<tr>
<td>ZrBTC-AE2</td>
<td>753</td>
<td>1.00</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>701</td>
<td>1.00</td>
<td>42</td>
</tr>
</tbody>
</table>

Regarding the characteristics of the pore structure of the materials, we performed NLDFT and BJH calculations to derive their pore size distributions, as presented in Figure 3; this figure also shows the corresponding cumulative pore volume plots as a function of the pore diameters. In general, our calculations reflect the existence of at least three families of pores; two families associated with micropores and one associated with mesopores. The main families of micropores had average diameters of 0.6 and 1.6 nm regardless of the modulator. The presence of these two families of micropores agrees with the characteristics of MOF-808 crystals [3], in which its framework is formed through tetrahedral cages with the smallest pore distribution and also, they share vertices forming an adamantane cage with internal pores related to the second microporous size distribution.
Figure 3. Cumulative pore volume and pore-size distribution of (a) ZrBTC-F (b) ZrBTC-A, and (c) ZrBTC-P. The microporous range is determined using a pore adsorption NLDFT cylindrical model (Ar on oxides at 87 K) and the mesoporous range by the BJH desorption method, respectively.

The pore size distributions for the mesopores did not follow a straightforward relationship with the chain length of the modulator. Indeed, while propionic acid led to the narrowest distribution of mesopore diameters with the lowest average pore diameter, 7.5 nm, formic acid produced mesopores with the second lower average pore diameter, 18.3 nm, and acetic acid produced the broadest distribution of mesopores centered at 27.2 nm plus pores in the size range for macroporous materials. For mesopores, the features of the hysteresis loop of the isotherms reflect the tortuosity of the network of pores [24-26]. Notably, our results suggest that using formic and propionic acid produces Zr-MOFs with a disordered and tortuous mesopore network that has cavities interconnected by narrow necks [22]. Conversely, the use of acetic acid as the modulator produced a relatively more ordered mesopore network combining opener pores with partially blocked mesopores [27].

To summarize, the length of the carbon chain of the modulator has a specific impact on the mesoporous structure of MOF-808 type materials without compromising their microporosity. Remarkably, the total surface area follows a straightforward positive correlation with the length of the carbon chain, which is specifically associated with an increase in the surface area.
associated with the microporous structure of MOF-808. Such a trend may be associated with a modification of the crystallization stage of the synthesis.

X-Ray diffractograms recorded for samples of ZrBTC-F, ZrBTC-A, and ZrBTC-P are shown in Figure 4. The featured patterns match those reported for MOF-808 [3] and, at first sight, do not differ from what has already been reported in the literature. However, structure refinement calculations (Section 2.3. of the Supporting Information) indicated a positive correlation between the length of the carbon chain of the modulator, the cell parameters, and the volume of the crystallites of the synthesized MOFs. Therefore, the use of a modulator with a larger carbon chain length produces larger MOF-808 crystallites that, in turn, will reduce the total microporous surface area, Table 1.

**Figure 4.** Experimental PXRD data of synthesized MOFs.

On the other hand, we find worth mentioning that the mesoporosity of the synthesized materials is related to the presence of an amorphous phase whose mechanism of formation is still to be established. In a previous work, we have proposed that the monocarboxylic acid used as modulator coordinates to the metal cluster and contributed to the formation of missing linker defects. The pore size, as well as the order of the mesoporous distributions, depends on the concentration of the modulator [17]. Regardless of the mechanism of the formation of the
amorphous phase, it seems clear that it is a product of missing linker defects. In our case, the results of the dissolution-1H-NMR experiments. Figures 5, S3, and S4 evidenced that monocarboxylates remained coordinated to the zirconium nodes before and after the activation stage of the synthesis process. Besides, we found evidence of the presence of formate groups typically produced by the hydrolysis of DMF solvent under the conditions of the synthesis of MOFs [28]. We estimated the relative concentration of modulator coordinated to the zirconium nodes, \( R_{m/Zr} \), before and after activation (Section 2.2. of the Supporting Information). Besides finding a positive correlation between this parameter and the length of the carbon chain of the modulator, we also determined that acetic acid led to a slightly larger relative concentration of modulator coordinated to the zirconium nodes. In principle, such a difference may be considered to be insignificant, \( R_{m/Zr} = 2.13 \) for ZrBTC-A as compared to 2.03 for ZrBTC-P, but we found that the ZrBTC-A lost the largest quantity of mass in TGA experiments, (Section 2.1. of the Supporting Information), and also that ZrBTC-A had the largest mesopores of all of the materials. Therefore, we think that such evidences might be correlated. We do not know the reason for such a trend, but we speculate that some of the acetates formed during the synthesis of the ZrBTC-A MOF did not bind to the zirconium nodes and instead formed organic clusters.
Figure 5. Dissolution/1H NMR spectra obtained on the MOF synthesized using formic acid as modulator before (ZrBTC-F-as) and after (ZrBTC-F-ac) the activation process.

The chemical analysis of the surface of the MOFs synthesized with the different modulators gives further insight into their defective nature. In this sense, the relative concentration of the elements and the components found on the surface of the synthesized materials are displayed in Table 2. Besides carbon, oxygen, and zirconium, traces of nitrogen and chlorine were detected and quantified. The presence of nitrogen gives further support to our hypothesis on the deposition of residua from the hydrolysis of the DMF solvent [28], while residual chlorine is due to the counter-ion of the zirconium precursor.

Table 2. C 1s, O 1s, Zr 3d, S 2p, and N 1s peaks contributions concentration for ZrBTC-F, ZrBTC-A, ZrBTC-P, ZrBTC-AE1, and ZrBTC-AE2 MOFs. The species are coded as C-Ar: Carbon belonging to an aromatic ring, Ar-(C-O)-Zr, C-NH$_3$: Carbon from the carboxylic acid group linked to the Zr cluster, Ar-Carboxy: carbon belonging to the carboxylic acid group of H$_3$BTC, Aliph-Carboxy: Carbon from the carboxylic acid group linked to an aliphatic chain, Zr-O: oxygen linked to Zr in the organic cluster, R-(C=O)-OH: oxygen belonging to a carboxylic acid functional group, C-O-Zr: oxygen belonging to the C-O-Zr bonds, Zr-O: zirconium belonging to the inorganic cluster and, Zr-O-C: zirconium coordinated to an organic group through oxygen.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relative Molar %</th>
<th>ZrBTC-F</th>
<th>ZrBTC-A</th>
<th>ZrBTC-P</th>
<th>ZrBTC-AE1</th>
<th>ZrBTC-AE2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C 1s</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-Ar</td>
<td>22.51</td>
<td>21.29</td>
<td>21.12</td>
<td>22.38</td>
<td>19.96</td>
<td></td>
</tr>
<tr>
<td>Ar-(C-O)-Zr, C-NH$_3$</td>
<td>2.77</td>
<td>3.36</td>
<td>3.72</td>
<td>4.54</td>
<td>3.16</td>
<td></td>
</tr>
<tr>
<td>Ar-Carboxy</td>
<td>11.29</td>
<td>8.06</td>
<td>7.21</td>
<td>7.41</td>
<td>8.95</td>
<td></td>
</tr>
<tr>
<td>Aliph-Carboxy</td>
<td>12.5</td>
<td>12.22</td>
<td>12.96</td>
<td>11.95</td>
<td>13.87</td>
<td></td>
</tr>
</tbody>
</table>
By calculating empirical formulas for the surface of the synthesized MOFs, Table 2, one finds that the surface of the MOFs synthesized herein is deficient in both oxygen and zirconium as compared to the crystalline core composition of MOF-808 [3]. In other words, the surface of our MOFs is enriched by carbonaceous species. To complement the chemical analysis of the synthesized MOFs, we performed a decomposition of the high-resolution spectra of the C 1s, O 1s, Zr 3d, N 1s, and Cl 2s core levels of ZrBTC-F, ZrBTC-A, and ZrBTC-P following the methodology that we developed in previous works [16, 17]. The chemical species considered for this procedure are illustrated in Figure 6, and the results of quantifying these chemical species are shown in Table 3. According to results, the surface of the materials synthesized using acetic and propionic acid as modulators is enriched by uncoordinated carboxylates. Meanwhile, the molar ratios that refer to the proportion between the carbon atoms of the aromatic ring of H$_3$BTC...
and those of the carboxylate functional groups in H$_3$BTC and the inorganic bonds of the zirconium oxo- clusters of the materials were very close to those expected for crystalline MOF-808 [3].
Figure 6. C 1s, O 1s, Zr 3d, N 1s, and Cl 2s peaks decomposition recorded in XPS analysis of (a,b,c,d,e) ZrBTC-F, (f,g,h,I,j) ZrBTC-A, and (k,l,m,n,o) ZrBTC-P, respectively. The C-(C,H) component at 284.8 eV was taken as a reference for the binding energy calibration.

Table 3. Species molar ratios of ZrBTC-A, ZrBTC-AE1, and ZrBTC-AE2 materials.

<table>
<thead>
<tr>
<th>Species molar ratios</th>
<th>Sample</th>
<th>ZrBTC-F</th>
<th>ZrBTC-A</th>
<th>ZrBTC-P</th>
<th>ZrBTC-AE1</th>
<th>ZrBTC-AE2</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-Ar/Ar-Carboxy</td>
<td>1.60</td>
<td>1.87</td>
<td>1.93</td>
<td>1.65</td>
<td>1.86</td>
<td></td>
</tr>
<tr>
<td>&quot;Free&quot;-[Carboxy/CarbOxy]</td>
<td>0.84</td>
<td>0.63</td>
<td>0.65</td>
<td>0.70</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>Coordinated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ar-(C-O)-Zr]/[Ar-(C-O)-Zr]</td>
<td>0.52</td>
<td>0.93</td>
<td>0.90</td>
<td>0.47</td>
<td>0.91</td>
<td></td>
</tr>
<tr>
<td>[Ar-(C-O)-Zr]/[Ar-(C-O)-Zr, C-NH₃]</td>
<td>0.60</td>
<td>0.96</td>
<td>1.03</td>
<td>0.88</td>
<td>0.92</td>
<td></td>
</tr>
<tr>
<td>[Ar-(C-O)-Zr]/[Ar-(C-O)-Zr]</td>
<td>1.16</td>
<td>1.04</td>
<td>1.14</td>
<td>1.87</td>
<td>1.01</td>
<td></td>
</tr>
<tr>
<td>Inorganic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr-O/Zr-O</td>
<td>0.31</td>
<td>0.32</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
<td></td>
</tr>
</tbody>
</table>

In summary, our investigation indicates that, regardless of the length of the carbon chain of the modulator, defective MOF-808 is synthesized under the conditions employed in this work. More defective MOF-808 materials are formed when using acetic acid as a modulator. This modulator promotes the formation of larger MOF-808 crystallites compared to missing linker moieties of uncoordinated formates and propionates. Yang et al. [29] also studied the effect on the mesoporosity of the three mentioned modulators on the synthesis of micro/mesoporous UiO-66 materials. They found that the trend in the decrease of acidity formic acid > acetic acid > propionic acid is related to the progressive decrease of the mesopore size distributions of the synthesized materials. This same trend is followed by the materials synthesized herein using formic and propionic acid, but this is not the case for acetic acid modulation.
To continue our research, we chose ZrBTC-A as a model for investigating how the addition of a surfactant during the synthesis of the material may modify its physicochemical properties. The reason for choosing this material was that it exhibited the most ordered and largest mesopores. We present our results below.

2.2. Influence of the addition of a surfactant on the physicochemical properties of MOF-808

In the second part of this work, we added cetyltrimethylammonium bromide as the surfactant during the synthesis of ZrBTC-A. In general, the addition of this surfactant modified the porous structure of the material. On the one hand, the surface area increased when adding 3.34 mmol of cetyltrimethylammonium bromide, ZrBTC-AE1, see Table 1. The increase in surface area was also evidenced in the thermogram of ZrBTC-AE1. Doubling the concentration of cetyltrimethylammonium bromide to 6.67 mmol, ZrBTC-AE2 did not increase the surface area further, and instead, the synthesized material showed the same surface area of ZrBTC-A. It can be noticed that the microporous surface of ZrBTC-AE2 was the one that mainly increased by ca. 6%.

On the other hand, the addition of the surfactant modified the hysteresis loop of the MOF, Figure 7. Namely, the type H5 hysteresis loop of the parent ZrBTC-A material evolved into a type H1 hysteresis loop with a sharp rise in the adsorption branch near saturation. This type of hysteresis loop is ascribed to materials with an ordered mesoporous structure consisting of uniform cylindrical inter-crystalline voids [27, 30, 31]. The calculated pore size distributions for ZrBTC-AE1 and ZrBTC-AE2 are shown in Figure 8. These calculations showed that the addition of CTAB did not alter the microporous structure of the materials, but instead, it expanded the mesopores of ZrBTC-A, turning them into macropores, i.e., pores whose average diameter is
larger than 50 nm [22]. Particularly, ZrBTC-AE1, whose concentration of CTAB was lower, showed larger macropores than ZrBTC-AE2.

**Figure 7.** $\chi$-method adsorption/desorption isotherms of the materials (a) ZrBTC-AE1 and (b) ZrBTC-AE2.

**Figure 8.** Cumulative pore volume and pore-size distribution of (a,c) ZrBTC-AE1, and (b,d) ZrBTC-AE2. The microporous range is determined using a pore adsorption NLDFT cylindrical model (Ar on oxides at 87 K) and the mesoporous-macroporous range by BJH desorption method, respectively.
In general, though we plotted the curves for the cumulative pore volume of ZrBTC-AE1 and ZrBTC-AE2, we will refrain from analyzing these results since a saturation of their porous network was not reached during the analyzes as it was evidenced by the fact that the recorded isotherms did not reach a plateau in the high relative pressure region. This behavior suggested that ZrBTC-AE1 and ZrBTC-AE2 had an open macroporous structure. We decided to enquire about the connectivity of the porous network of the synthesized MOFs. For this purpose, we performed a post-synthetic modification of ZrBTC-AE1 and ZrBTC-AE2 with sulfuric acid following the procedure reported in our previous work [17]. We may recall that this procedure served to demonstrate that the ultramicropores of defective MOF-808 were disconnected from the rest of their porous network. According to Figure 9, in the case of ZrBTC-AE1 and ZrBTC-AE2, we found that the treatment with sulfuric acid caused a general decrease in the micro and macropore pore volumes of the materials.

![Figure 9](image)

**Figure 9.** Cumulative pore volume (solid symbols) and pore-size distribution (open symbols) of (a,c) ZrBTC-AE1, and (b,d) ZrBTC-AE2, before (squares), and after (circles) sulfation process. The microporous range is determined using a pore adsorption NLDFT cylindrical model (Ar on oxides at 87 K) and the mesoporous range by the BJH desorption method, respectively.
We interpret this trend as a hint of the existence of an interconnectivity pattern between the different pore families of Zr-MOFs synthesized by a surfactant-assisted method. We propose that during this kind of synthesis, the carboxylic acid groups of BTC linker probably act as a counteranion that promotes the assembly between the crystallizing material and the cationic head group of CTAB. The ionic interaction between oppositely charged groups has been previously reported in the context of the synthesis of zeolites [32]. We illustrate our proposal in Scheme 1. In it, the carboxylates of BTC interact with the cationic head group of the micelles formed by CTAB. After adding the solution of ZrCl$_4$, the formed zirconium oxo-clusters and the BTC$^{3-}$ anions begin to crystallize around the external surface of the CTAB micelles. After removing CTAB, the resulting defective MOF-808 is arrayed around ordered macroporous channels in the inter-crystalline voids. To support the above proposal, we demonstrate, see Sections 1.2. and 2.4. of the Supplementary Information, that the concentration of CTAB in the DMF/acetic acid mixture used during the synthesis of the materials is higher than the critical micelle concentration of the system. Under such conditions, it is predicted that surfactants form spherical aggregates that end up making worm-like structures [33, 34].

**Scheme 1.** Representation of the possible mechanism of CTAB template synthesis of hierarchical MOF-808.
Furthermore, it has been shown that CTAB can self-assembly into aggregates of different morphologies above a threshold concentration and depending on the particularities of a given system [35]. Also, results from FTIR analyses for ZrBTC-AE1 and ZrBTC-AE2, Figure 10, showed that CTAB reacted neither with the organic ligand nor with the zirconium-oxo clusters to form other crystals. Instead, the FTIR spectra for ZrBTC-AE1 and ZrBTC-AE2 exhibited the usual bands ascribed to carboxylate MOFs, see Section 2.5. of the Supporting Information, and were similar to the spectrum of ZrBTC-A.

![Infrared spectra of synthesized ZrBTC-A, ZrBTC-AE1, and ZrBTC-AE2.](image)

Figure 10. Infrared spectra of synthesized ZrBTC-A, ZrBTC-AE1, and ZrBTC-AE2.

As commented earlier, CTAB promoted the uniformity of the structure of defective MOF-808. In this sense, the SEM images for ZrBTC-A, Figures 11a and 11c, showed larger ill-defined particles as compared to the well-defined particles of ZrBTC-AE2 (Figures 11b and 11d). Furthermore, TEM images offered insight into the local structure of the crystalline phase; Figures 11e, 11g, and 11f, 11h, for ZrBTC-A and ZrBTC-AE2, respectively. For the latter, the images show a structure formed by dense nanoparticles randomly stacked together with inter-crystalline voids [36, 37]. Diffractograms recorded for samples of ZrBTC-AE1 and ZrBTC-AE2 are displayed in Figure 4. The recorded patterns show that using CTAB as a surfactant enhanced the crystallinity of the parent ZrBTC-A.
Figure 11. SEM and TEM images of the hierarchical porous (a,c,e,f) ZrBTC-A, and (b,d,f,h) ZrBTC-AE2

Moreover, the increase in the concentration of the surfactant further increased crystallinity. The interested reader can consult the Supplementary Information, Section 2.3, for details. Our results differ from what has been presented in previous works. Indeed, other research groups [38-40] found that adding a surfactant during the synthesis of MOFs leads either to partial amorphization or to the collapse of their structure. We hypothesize that the crystallinity enhancement in our work can be due to the separate preparation of the modulator and the
zirconium precursor and the organic ligand and the surfactant solutions. Under such conditions, both the zirconium-oxo clusters and the self-assembled CTAB micelles form before mixing, leading to the formation of ordered structures.

Finally, we found that the addition of CTAB did not have a marked impact on the surface chemistry of the materials. The decomposition of the C 1s, O 1s, Zr 3d, N 1s, and Cl 2s peaks of ZrBTC-AE1, and ZrBTC-AE2 recorded in XPS are shown in Figure 12, and the results for the quantification of the identified surface chemical species is shown in Table 3. We did not find marked differences between the results for ZrBTC-A, ZrBTC-AE1, and ZrBTC-AE2.
Figure 12. C 1s, O 1s, Zr 3d, N 1s, and Cl 2s peaks decomposition recorded in XPS analysis of (a,b,c,d,e) ZrBTC-AE1, and (f,g,h,i,j) ZrBTC-AE2, respectively. The C-(C,H) component at 284.8 eV was taken as reference for the binding energy calibration.

Further evidence showing that the addition of the CTAB surfactant during the synthesis of defective MOF-808 does not modify its surface chemistry was found by ToF-SIMS, Figures 13 and S12. Indeed, the data collected from both the positive and negative ion spectra for both ZrBTC-A and ZrBTC-AE2 were very similar and consisted on strong, ZrO$^+$, (ZrO$_2$)$_3$H$^+$, (ZrO$_2$)$_3$H$^+$, (ZrO$_2$)OH$^-$, (ZrO$_2$)$_2$(OH)$_2$H$^+$, and (ZrO$_2$)$_3$OH signals along with weaker signals due to ZrO$_2$H$^+$, Zr$_2$O$_3^{3+}$, and (ZrO$_2$)$_2$H$^+$, ZrO$_2^-$, and (ZrO$_2$)$_3$OH$^-$ and similar signals of high m/z ratios coming from the fragmentation of the metal-organic clusters. The sole difference found between ZrBTC-A and ZrBTC-AE2 was that the latter contains some residual bromine; Figure S13 compares the negative ion spectra recorded in the range from 78.7 to 79 m/z for these two samples. The concentration of this residue was below the limit of detection of the XPS technique mentioned earlier. Therefore, we conclude that the surface chemistry of the defective MOF-808 remains unaltered after adding a surfactant during the synthesis.

In summary, the addition of CTAB during the synthesis of the acetic acid modulated MOF-808 enhanced both its porosity and crystallinity without significantly altering its molecular structure and surface chemistry.
Figure 13. Spectra of the surface (a) Positive (b) Negative Secondary Ion Polarity of ZrBTC-A MOF.
3. CONCLUSIONS

This work elucidates the effect of defect engineering through the modulator and surfactant approaches on the physicochemical and surface properties of the defective microporous/macroporous MOF-808 series. Results showed that the use of different modulators during synthesis led to the formation of materials with different amounts of missing linker defects and pore size distributions. Notably, the acetic acid attached to the zirconium oxo-cluster was found to be inferior compared to the materials synthesized with formic and propionic acid as modulators. This correlates with the formation of a microporous/mesoporous material with a larger mesopore size distribution compared to the others. On the other hand, the addition of surfactant allowed the synthesis of ordered and crystalline microporous/macroporous materials. The addition of CTAB did not seem to alter the surface chemical composition compared to the material synthesized with no surfactant. Thus, the MOF-808 series exhibited a defective structure at the surface with adjustable pore size distribution by the application of the defect engineering approach for a wide range of applications.

4. Experimental Section

4.1. Materials. MOFs were synthesized with the following reagents. Zirconium precursor: zirconium chloride, ZrCl$_4$ (98%), from Merck. The organic ligand, Benzene-1,3,5-tricarboxylic acid (H$_3$BTC, 95%), and the surfactant hexadecyltrimethylammonium bromide, CTAB (>98%) were obtained from Sigma-Aldrich. The solvent N, N-dimethylformamide (99.8%), the modulators: formic acid (98 -100%), acetic acid (99.8%) and propionic acid (99%) and the
washing solvents: acetone (99.8%) and methanol (99.9%) were all purchased from Merck.
Reactants were used as received.

4.2. **Synthesis of the materials.** Zirconium MOFs were synthesized using a solvothermal method based on a modification of the synthesis reported by Liang et al. [9]. Typically, 9.99 mmol of zirconium chloride was put in a 250 mL screw-capped glass jar reactor. Then, 98 equivalents (related to the zirconium precursor) of modulator agent (formic, acetic or propionic acid) and 80 mL of DMF were introduced in the reactor, and the solution was stirred. After 20 min, 3.34 mmol of H$_3$BTC and the required amount of CTAB (0, 3.34 or 6.67 mmol) [41] were dissolved in 120 mL of DMF and added dropwise to the solution containing the dissolved zirconium precursor. The mixture was stirred for an additional 15 min and later sonicated for 30 min. The resulting mixture was distributed among twenty 50 mL screw-capped glass jar reactors and remained at 25°C for 24 h and after that at 120°C for an additional 24 h. After cooling down to room temperature, the contents of the reactors were combined, and the as-synthesized MOFs were recovered by filtration and washed twice with DMF, twice with water, and twice with acetone. The resulting powder was dried at 120°C for 12 h. An activation procedure was performed overnight at 120°C under a vacuum pressure of 0.06 mbar. The materials synthesized using formic, acetic, and propionic acid as modulators were named as ZrBTC-F, ZrBTC-A, and ZrBTC-P, respectively. Furthermore, the materials synthesized by adding the CTAB surfactant were named as ZrBTC-AER (R = the CTAB: H$_3$BTC molar ratio = 1 or 2). Under the above conditions, the yields for the syntheses were 38.2 ± 10.9, 54.6 ± 1.34, 42.8 ± 3.07, 55.1 ± 1.18, and 75.6 ± 5.25 % for ZrBTC-F, ZrBTC-A, ZrBTC-P, ZrBTC-AE1, and ZrBTC-AE2, respectively. These yields are based on the overall weight of the ligand and of the metallic salt [42].
4.3. **Assessment of the physicochemical properties of ZrBTC MOFs.** The thermal stability, morphology porous structure, crystallinity, molecular structure, and surface chemistry of the materials were assessed. Thermal stability was studied by recording thermal gravimetric analysis profiles. Tests were performed in a Discovery 5500 TA instrument. Samples were heated to 900 °C at a rate of 5°C/min under an air (Linde, 4.7, 99.997% purity) flow of 25 mL/min. Morphology was studied by recording scanning electron microscopy images in a Quanta FEG 650 equipment. The acceleration voltage was set to 2.5 kV through an everhart Thornley detector (secondary electrons detector). Samples were prepared by spreading them on a carbon tape in a Quorum 150ES equipment. Also, transmission electron microscopy images were recorded with a Philips CM200 microscope operating at 200 kV and equipped with an Energy-dispersive X-ray spectrometer. The porosity and surface of the materials were evaluated after recording Ar adsorption-desorption isotherms at 87 K using a 3Flex (Micromeritics) apparatus. The relative pressure range went from 1.82×10-5 to 0.995, with equilibrium intervals of 10 s. Isotherms for the materials were recorded twice in independent experiments. Before measurements, the materials were degassed at a temperature of 120°C under vacuum for 12 h. Surface area calculations were performed using the methods based on the $\chi$ theory [23]. For some selected materials that were post-synthetically modified, pore connectivity was tested according to our previous work [7]. The test consists on performing a sulfation procedure, which is like the one proposed by Jiang et al. [7] followed by an assessment of porosity by Ar physisorption. For sulfation, 50 mg of the synthesized material is treated with 50 mL of 0.05 M sulfuric acid (2.5 mmol) for 24 h. The supernatant liquid is then solvent exchanged with 50 mL of water for three days changing the water once a day. Afterward, the liquid is quickly exchange with 50 mL of acetone, and the recovered solid is immersed in 50 mL of chloroform for three days. During this
time, chloroform was exchanged once per day. The crystalline structure of the materials was assessed by recording X-ray diffraction patterns with a Bruker AXS D8 Advance DaVinci geometry instrument equipped with monochromatized Cu Kα radiation (λ = 1.5418 Å). This instrument was operated at 40 kV and 40 mA. Diffraction patterns were recorded in the 2θ value range from 3.0 to 50.0° (with a step time of 0.6 s). For gaining further insight into the molecular structure of the materials, we wanted to identify and quantify the concentration of the modulators coordinated to the zirconium node. This was made by dissolution/H NMR spectroscopy. For this purpose, MOFs are digested in a deuterated medium [43]. During the experiment, hydroxide ions digest the organic part of the MOF, i.e., the organic linker, the modulator, and the solvent that may still be trap inside the pores of the materials. The digested product can thence be analyzed by Nuclear Magnetic Resonance (NMR) spectroscopy, while the inorganic component, namely ZrO2, of the material precipitates. Further details for this experiment are included in Section 1.1 of the Supporting information. Liquid 1H NMR spectra were recorded on a Bruker Ultrashield 400 MHz (Avance III, 400) using a relaxation delay (D1) of 20 s and 64 scans [43]. The identification of functional groups of the as-synthesized and modified MOFs was performed by Infrared spectroscopy on a Thermo Scientific Nicolet iS50 FT-IR spectrometer. The surface chemistry of the materials was analyzed by X-ray photoelectron spectroscopy. Analyses were performed in the XPS/ISS/UPS-A.Centeno surface characterization platform (SPECS). The platform is provided with a PHOIBOS 150 2D-DLD energy analyzer package. A monochromatized Al Kα X-ray source (Focus 500) operated at 100 W was employed. The pressure in the analysis chamber was approximately 1×10−7 Pa. The angle between the normal to the sample surface and the direction of photoelectrons collection was about 54°. Samples were mounted on carbon conductive tape over metallic sample holders for analysis. Surface charge
compensation was controlled with a flood gun (FG 15/40-PS FG500 device) operated at 58 μA and 1.0 eV. Spectra were collected in the Fixed Analyzer Transmission mode. The spot area for analyses was 3.5×1.0 mm². The pass energy of the hemispherical analyzer was set at 100 eV for general spectra and to 15 eV for high-resolution spectra. The energy step for the acquisition was set to 0.050 eV. General spectra were recorded first for all samples followed by high-resolution spectra. The C 1s peak was recorded both at the beginning and the end of the measurements for checking the evolution of surface charge during the analyses. High-resolution spectra were recorded following elements identification in the general spectra and according to samples chemistry and history. Data analysis was performed with the CasaXPS program (Casa Software Ltd) using the SPECS Prodigy library for R.S.F. values. A U 3 Tougaard baseline [44] was employed for background modeling together with a Lorentzian line shape, LA(1.53,243) in CasaXPS, for peak decomposition. The peak decomposition for the quantification of surface chemical species was performed according to our previous works [16, 17]. For the C 1s peak, the following chemical species, ordered from lower to higher binding energies (BEs), were considered: (i) Carbon belonging to an aromatic ring, labeled as C-Ar. Under the analysis conditions employed herein, this component is indistinguishable from the peak from the C-(C,H) species from aliphatic hydrocarbons. In consequence, a single component centered at 284.8 eV [45] was assumed for both species. This component was employed as a reference for correcting the BE scale of the spectra [45]. (ii) Carbon from the carboxylic acid group linked to the Zr cluster labeled as Ar-(C-O)-Zr, [286.14, 286.54] eV. (iii) Carbon belonging to the carboxylic acid group of H₃BTC, labeled as Ar-Carboxy. Based on literature references [45, 46], Ar-Carboxy was fixed at 288.0 eV. (iv) Carbon from the carboxylic acid group linked to an aliphatic chain labeled as Aliph-Carboxy and fixed at 289.0 eV [46]. An additional peak corresponding to
the $\pi - \pi^*$ from the aromatic ring was considered for peak decomposition [47], [290.6, 291.0] eV. For this component, the R.S.F. was set to 0 for quantification. The same FWHM was considered for all carbon species and the $\pi - \pi^*$ transition peak. For the O 1s peak, three species were considered. The first was oxygen linked to Zr in the inorganic cluster, labeled O-Zr, [530.5, 531.2] eV. The second was oxygen belonging to a carboxylic acid functional group, [531.9, 532.4] eV. In the O 1s peak, this component, labeled as R-(C=O)-OH, cannot be further decomposed into carboxylates linked to an aromatic or aliphatic chain [45]. The third oxygen component, [533.8, 534.2] eV, was ascribed to oxygen belonging to the Zr-O-C bonds in the MOF. This proposal is coherent with the BE shifts expected when comparing the parent carbon components described before, in the sense that if the corresponding carbon is more oxidized, the oxygen must be more reduced. No constraints were imposed during peak decomposition except for assuming the same FWHM for all components. Finally, for the Zr 3d peak, two species were considered. The first was Zr coordinated to an organic group through oxygen, labeled Zr-O-C, the Zr 3d$_{5/2}$ peak = [181.6, 182.5] eV, and the second Zr belonging to inorganic clusters, the Zr 3d$_{5/2}$ peak = [182.0, 183.0], labeled Zr-O. The above BE assignation was also made considering the relative BE shifts expected from the corresponding oxygen and carbon components. The following constraints were imposed during peak decomposition: a) the area of the Zr 3d$_{3/2}$ core level is equal to two-thirds of the area of the Zr 3d$_{5/2}$; core level, and, b) a separation of 2.37 eV between both core levels was assumed [48]. Besides, four components corresponding to overlapping loss features from the Zr 3d core levels of each assigned species were considered for peak decomposition but not accounted for in quantification; i.e., R.S.F. fixed to 0. Additional insights into the surface chemistry were gained by performing a series of time-of-flight secondary ion mass spectrometry analyses. Spectra were recorded using an IONTOF TOF.SIMS
5 instrument in both positive and negative ion secondary ion polarity applying Bi$^{3+}$ primary ions with 30 keV and a pulsed primary ion beam current of 0.3 pA. The analysis area varied from 66 x 66 µm$^2$ to 141 x 141 µm$^2$ over which the Bi$^{3+}$ beam was rastered. The resulting primary ion dose density was below $3.4 \times 10^{12}$ cm$^{-2}$ for all measurements so that the corresponding spectra mainly contain chemical information on the sample surface. In order to stabilize the surface potential, charge compensation by low energy (20eV) electron flooding was used.

**Supporting Information**

TGA and FTIR results, Dissolution/ H NMR Spectroscopy, Spectrophotometric Determination of the CMC of CTAB, Le Bail profile fittings and data of synthesized materials, and chemical surface composition through XPS and ToF-SIMS.

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REFERENCES


Ordered micro/macroporous MOF-808 materials with tunable porosity and similar chemical surface composition were synthesized through the modulator-induced defect-formation and surfactant self-assembly strategies.