Combined study of structural properties on metal-organic frameworks with same topology but different linkers or metal

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Abstract. The recently discovered UiO-66/67/68 class of isostructural metalorganic frameworks (MOFs) [2008 J. Am. Chem. Soc. 130 13850] has attracted great interest because of its remarkable stability at high temperatures, high pressures and in presence of different solvents acids and bases [2011 Chem. Mater. 23 1700]. UiO-66 is obtained connecting Zr6O4(OH)4 inorganic cornerstones with 1,4-benzene-dicarboxylate (BDC) linkers, while for the isostructural UiO-67, the longer 4,4′-biphenyl-dicarboxylate (BPDC) is used as linker [2012 Phys. Chem. Chem. Phys. 14 1614]. Hf-UiO-66 is built with the same linker of UiO-66 but, in this case, Hf6O4(OH)4 blocks substitute the Zr6O4(OH)4 ones [2012, Phys. Rev. B 86 125429]. In all cases isostructural cubic MOFs are obtained. Here we report a systematic EXAFS investigation of UiO-66 and UiO-67 (at Zr K-edge) and of Hf-UiO-66 (at Hf L3-edge) before and after the removal of solvent in their pores, needed to make the channel volume available. The study reveals that, for the three systems, the perfect M6O4(OH)4 (M = Zr or Hf) octahedron forming the cornerstones of the as prepared material undergoes a remarkable local rearrangement into a distorted M6O6 octahedron, with the loss of two water molecules under the desolvation process. Notwithstanding the high crystallinity of the materials, this rearrangement, moving M atoms from 8-fold to 7-fold coordination and distorting the M-M distance of the octahedron side by more than 0.2 Å, escape XRPD detection (because not ordered on the long range scale) but is clearly observed by EXAFS owing to its local sensitivity.

1. Introduction

Metal-Organic Frameworks (MOFs) have received much attention in the past decade and a huge number of new materials with a wide range of different compositions and properties have been reported.[1, 2] The most sought after MOF materials are those with internal open-pore systems exhibiting some of the main properties of the traditional porous materials, zeotype and mesoporous materials. The highest specific surface area materials are now found within MOFs[3] that, being constructed directly from simple organic molecules (acting as linkers or spacers) and metal centers (acting as connecting corner units), allow to tailor their chemical composition and physico-chemical properties to a large extent towards any given application. Although the industrial application of MOFs is still limited to few cases,[4] these materials being three-dimensional polymers of alternating metal/metal cluster and organic units have already shown potentialities in: (i) gas storage,[5, 6] (ii) gas separation and purification,[7] liquid phase separation,[8] (iii) drug delivery,[9] (iv) catalysis,[10] (v)
molecular sensors,

(vi) contrast agents for tomography imaging inside living tissues; and (vii) interim radioactive waste scavenging.

In the past we have widely documented the relevance in combining XRPD and EXAFS to disclose the structure of such complex materials, exhibiting unit cells as large as several thousand of Å³. Here we present a compared EXAFS study of the metal center edges on three isostructural MOFs: UiO-66, UiO-67 and Hf-Uio-66.

2. Experiment and Methods

2.1. Materials

MOFs materials have been synthesized at the inGAP centre of the Oslo University. For details on the synthesis of the different materials the reader should refer to the following papers: UiO-66, UiO-67 and Hf-Uio-66. Desolvation of UiO-66 and UiO-67 has been done inside a cell suitable for in situ EXAFS data collection, heating the sample at 300 °C (5 °C/min) and keeping the sample at 300 °C for 30 min; data collection has then been done at room temperature. Hf-Uio-66 was desolvated inside a 1 mm capillary heated in situ under inert flow directly on the X-ray beam with a heater gun up to 300 °C; data collection has been done at 300 °C.

2.2. EXAFS data collection and analysis.

In all cases XAFS data collection has been performed in transmission mode on ESRF beamlines. For UiO-66 Zr K-edge data collection has been performed at BM29 beamline, while for UiO-67 and Hf-Uio-66 we have used BM01B beamline at Zr K- and Hf L3-edges, respectively.

The extraction of the χ(k) function was performed using the Athena code. For each sample, three consecutive EXAFS spectra were collected and corresponding χ(k) functions were averaged before data analysis. EXAFS data analysis was performed using the Arthemis software. Phase and amplitudes for all single scattering (SS) and multiple scattering (MS) paths were calculated by FEFF6 code, according to the strategy outlined elsewhere.

2.3. Theoretical methods.

The theoretical investigation of UiO-66 and UiO-67 MOF (in its hydroxylated and dehydroxylated structures) was carried out with periodic density functional theory (DFT) calculations employing the hybrid B3LYP functional as implemented in the CRYSTAL program as described elsewhere.

3. Results and Discussion

The recently discovered UiO-66/67/68 class of isostructural MOFs has attracted great interest because of its remarkable stability at high temperatures, high pressures and in presence of different solvents, acids and bases. UiO-66 is built up connecting Zr₆O₆(OH)₄ inorganic cornerstones with 1,4-benzene-dicarboxylate (BDC) linker; while for the isostructural UiO-67 is formed using as linker the longer 4,4′ biphenyl-dicarboxylate (BPDC) (Figure 1a). Hf-Uio-66 is obtained keeping the UiO-66 linker (BDC) and substituting the Zr₆O₆(OH)₄ cornerstones (inset in Figure 1e). XRPD data testify the quality of the synthesis, see Figure 1b,e. Due to the rigidity of the framework several isostructural UiO MOFs have been prepared and tested for stability and gas adsorption capacity. Kandiah et al. studied the thermal and chemical stabilities of isostructural UiO-66-X (X= NH₂, Br and NO₂) and observed the lower stability of this analogue with respect to parent UiO-66. Conversely, as documented by the thermogravimetry studies (reported in Figure 1c,f), UiO-67 and Hf-Uio-66 show thermal and chemical stability similar to the one of UiO-66 and they exhibit the expected surface area, as determined by low temperature volumetric N₂ adsorption isotherms (Figure 1d,g). Such a high stability is related to the fact that each Zr- (Hf-) octahedron is 12-fold connected to adjacent octahedra. This connectivity is very common for metals, resulting in the highly packed fcc structure, but it is still almost unique in MOF topologies.
Figure 1. Part (a): Comparison of the dimension of linker and overall structure, for the isostructural UiO-66 and UiO-67 MOFs. Part (b): Comparison of the XRPD patterns (\(\lambda=1.540\ \text{Å}\)) for UiO-66 and UiO-67 materials as prepared (orange and cyan lines) and activated at 300 °C (red and blue lines). The patterns in the 10-40° 2\(\theta\) region are amplified by a factor 4. Patterns related to UiO-66 are vertically translated for clarity. Part (c): TGA curves of UiO-66 and UiO-67 samples, red and blue lines respectively. In both cases, the heating ramp was of 5°C/min in \(\text{N}_2\) flow (100ml/min). Part (d): volumetric \(\text{N}_2\) adsorption isotherms recorded at 77 K on UiO-66 (red squares) and UiO-67 (blue circles). Empty and filled scatters refer to the adsorption and desorption branches. Part (e): XRPD pattern (\(\lambda=1.540\ \text{Å}\)) of Hf-UiO-66 (green) and Zr-UiO-66 (red) in their solvated forms (as prepared). The inset reports the Hf-UiO-66 structure. Part (f) TGA curve of Hf-UiO-66, it shows the weight loss relative to the initial mass (green curve). The weight loss for Zr-UiO-66 (orange curve) is also reported as a reference. Since Hf is 41% heavier than Zr, the Zr-UiO-66 shows both higher initial and breakdown losses. Part (g): volumetric \(\text{N}_2\) adsorption/desorption isotherm for Hf-UiO-66 recorded at 77 K.

All MOFs were synthesized in presence of a solvent that has to be removed to make the large pore volume available for any practical applications. The desolvation process left almost unchanged the XRPD patterns of such materials (Figure 1b), besides a gain of intensity of the basal reflections (due to the removal of the electron density inside the pores\([17, 33, 34]\)), all peaks remains in almost the same 2\(\theta\) position with small intensity changes. Conversely, a huge modification of the EXAFS spectra is obtained in all cases, see Figure 2.

In the three hydroxylated materials, the structure determined from the Rietveld refinement of the XRPD corresponding patterns resulted in a straightforward interpretation of the complex EXAFS signals, see first three columns in Table 1. The dramatic modification undergone by the EXAFS spectrum upon dehydroxylation (see Figure 2) makes the data analysis not so straightforward. In the case of UiO-66 (see Figure 2b, but similar effects are observed also in the two other cases) the changes are basically explained in terms of three main effects: (i) small contraction of the first M-O shell accompanied by a small decrease in coordination (erosion of the shoulder around 1.9 Å); (ii) relevant
distortion of the second shell contribution showing a maximum that moves from 3.17 Å to 2.91 Å, with a shoulder at 3.41 Å, thus reflecting an important splitting of the R_{M1} distances of the octahedron sides; (iii) the almost complete disappearance of the weak contribution around 4.7 Å, due to the M-M SS signal of the octahedron diagonal (R_{M2}). For the three systems, differently to the hydroxylated cases, the 3D model obtained from the Rietveld refinement of XRPD data in the highly symmetric Fm-3m space group was inadequate to simulate the experimental datum. The origin of this failure was, obviously due to the inability of the model to account for two different R_{M1} and R_{M2} distances. For both UiO-66\[^{[30]}\] and UiO-67\[^{[25]}\] cases, the failure of the XRPD model was overcome by using the optimized geometry obtained by ab initio periodic calculations.

![Figure 2](https://example.com/figure2.png)

Figure 2. k- (top panels) and R-space (bottom panels) EXAFS data collected on UiO-66, UiO-67 and Hf-UiO-66, parts (a,b), (c,d) and (e,f), respectively. Both as prepared (hydroxylated) and desolvated (dehydroxylated) forms of the three different isostructural MOFs have been measured. With the exception of desolvated Hf-UiO-66 sample (collected at 573 K), all the remaining spectra were collected at 300 K.

The inorganic cornerstones of the as synthesized materials are perfect M_{6}(OH)_{4}O_{4} octahedron (see model in Figure 3b), with 6 equivalent M at the vertex, 12 equivalent M-M1 sides and 3 equivalent and M-M2 diagonals. Upon desolvation 2 structural water molecules are lost per cornerstone unit (Figure 3a), that evolves from M_{6}(OH)_{4}O_{4} to M_{6}O_{6}\[^{[13, 25, 30]}\]. The new M_{6}O_{6} octahedron is compressed (2 opposite vertexes approaching, see model in Figure 3c) resulting in the shortening of 8 of the 12 edges, and the elongation of the other 4 edges. To take into account this variation we simulated the EXAFS contribution with two independently parameterized paths fixing for the degeneration a ratio of 1/3 and 2/3 with respect to the case of the single contribution. For the three systems, this combined XRPF, EXADS and DFT approach allowed a full interpretation of the EXAFS data in both hydroxylated and dehydroxylated forms.\[^{[13, 25, 30]}\]

4. Conclusions

EXAFS spectroscopy allows to detect the evolution from M_{6}(OH)_{4}O_{4} to M_{6}O_{6} (M = Zr or Hf) of the inorganic cornerstones of UiO-66, UiO-67 and Hf-UiO-66 MOFs occurring in the desolation process, that escaped XRPD detection. On Zr-UiO-66 and Zr-UiO-67, periodic calculations performed with CRYSTAL code\[^{[31]}\] at DFT level of theory support EXAFS data.
as input a model optimized by the corresponding XRPD patterns. The EXAFS refinement of the dehydroxylated materials was obtained using diagonals $R_{M1ax}$ of the M066, UiO-67 and Hf-UiO-66. Parameters without error bars were not optimized. The EXAFS refinement of the dehydroxylated materials was obtained using as input a model optimized by ab initio calculations. With this approach the coordination number (N) of each contribution is fixed by the model stoichiometry. Refinement of the experimental amplitude is done by optimizing the overall amplitude factor $S_0^2$ only. The fitting of the higher shells was possible only adopting the axial compressed model of the M6O6 octahedron represented in Figure 3c where the twelve sides $R_{M1}$ are split into eight short prismatic distances ($R_{M1}$, $N=8/12$) and four long planar ones ($R_{M2b}$, $N=4/12$) and where the three diagonals $R_{M2}$ are split into a short axial diagonal and $R_{M2a}$, involving two M atoms out of six; $N=1/3$) and two long planar diagonals ($R_{M2b}$ involving four M atoms out of six; $N=2/3$): Figure 3c.

Table 1. Summary of the EXAFS refinement obtained on the hydroxylated and dehydroxylated forms of UiO-66, UiO-67 and Hf-UiO-66. Parameters without error bars were not optimized. The EXAFS refinement of the hydroxylated materials was obtained using as input the optimized structure from Rietveld refinement of the corresponding XRPD patterns. The EXAFS refinement of the dehydroxylated materials was obtained using as input a model optimized by ab initio calculations. With this approach the coordination number (N) of each contribution is fixed by the model stoichiometry. Refinement of the experimental amplitude is done by optimizing the overall amplitude factor $S_0^2$ only. The fitting of the higher shells was possible only adopting the axial compressed model of the M6O6 octahedron represented in Figure 3c where the twelve sides $R_{M1}$ are split into eight short prismatic distances ($R_{M1}$, $N=8/12$) and four long planar ones ($R_{M2b}$, $N=4/12$) and where the three diagonals $R_{M2}$ are split into a short axial diagonal and $R_{M2a}$, involving two M atoms out of six; $N=1/3$) and two long planar diagonals ($R_{M2b}$ involving four M atoms out of six; $N=2/3$): Figure 3c.
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