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ARTICLE TYPE

Acid-functionalized UiO-66(Zr) MOFs and their evolution after intra-framework cross-linking: structural features and sorption properties.

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10 Abstract

The functionalization of metal-organic frameworks (MOFs) with free carboxylic groups is naturally difficult due to their potential coordination with metal ions. The impact of functionalizing the archetypical metal organic framework UiO-66(Zr) with free pending carboxylic groups was thus studied by a multi-technique approach. First, an environmentally-friendly water synthesis route was developed to produce UiO-66(Zr)-(COOH)_x (x = 1, 2) and their kinetics of crystallization was followed by *in situ* energy dispersive X-ray diffraction. In a second step, their structural features were studied by temperature-dependent X-ray diffractometry and further characterized by density functional theory calculations and solid-state nuclear magnetic resonance spectroscopy. Their gas sorption properties, acidity and conductivity features were respectively assessed by gas isotherms and calorimetry, infrared spectroscopy and complex impedance spectroscopy. These data show the noticeable influence of the acidic groups introduced. Finally, it was shown that the thermal treatment of such solids leads to an intra-framework cross-linking associated with the formation of anhydride bridges, as evidenced by FTIR and solid-state NMR, and modelled by DFT simulations. These species have a strong impact on the acidity, but a limited effect on gas sorption properties at room temperature. The reversibility of the carboxylic acids to anhydrides transformation was also assessed.

Introduction

Unlike many other porous materials, metal organic frameworks (MOFs) can easily be functionalized following different strategies. One convenient approach to fine-tune their properties consists in using substituted organic ligand. This is an efficient way to directly tune the stability, the physicochemical properties, the catalytic or the sorption-related properties of the material¹⁻⁷. Alternatively, substituted linkers also introduce potential for subsequent post-synthetic modifications (PSM)⁸. Among the huge number of functional groups which can be introduced, truly acidic functions, such as sulfonic⁹⁻¹² or carboxylic^{2, 12-16} groups, are of broad interest. They can be advantageously used to perform acid catalysis, as shown when sulfonic groups were incorporated into MIL-53 and MIL-101^{9, 11, 17} (MIL stands for Materials of the Institute Lavoisier), to tune the sorption

selectivity for different mixtures, such as favoring the adsorption of CO₂¹⁸⁻²⁰, or even to enhance the proton conductivity²¹, as recently highlighted in the case of MIL-53 functionalized solids²². On the other hand, carboxylic groups can also be used as reactive groups for PSM, *e.g.* through the formation of amide bonds⁸. Alternatively, carboxylic functional groups may allow the intra-framework cross-linking of the ligands through the formation of anhydride bridges upon dehydration, as observed in the case of MIL-53(Al)-(COOH)¹⁴. If cross-linking is indeed known to improve some properties of materials such as with organic polymers, it is also of interest to determine to what extent it may also induce alternative properties in MOFs²³⁻²⁴. However, MOFs bearing free sulfonic or carboxylic groups remain rather scarce.^{9-14, 25} This can be easily explained by the fact that such functions are prone to complex metal cations in the reaction medium to afford new structure types. One way to circumvent this problem relies on post-synthetic modifications⁸.

^{11, 20, 26}; however, this route requires MOFs that are stable to the post-synthetic conditions while a total and homogeneous modification is not assured. Direct synthesis is also possible if the chosen inorganic secondary building unit (SBU) is robust enough ⁵ to direct the formation of the structure. The Zr₆ unit present in the Zr terephthalate UiO-66(Zr) ²⁷, has proven quite stable and offers potential as such an SBU; in fact, a wide range of polar/non-polar functional groups has already been introduced in analogous structures utilizing this same SBU, ^{3, 10, 12, 28-32} whilst maintaining ¹⁰ in most cases the significant thermal and/or chemical stability of the parent structure. ^{27, 31, 33-39} Though the non-functionalized UiO-66(Zr) shows promising adsorption and catalytic properties ⁴⁰⁻⁴⁴, experimental and computational investigations reveal that the UiO-66(Zr)-(COOH) material presents a higher CO₂/CH₄ ¹⁵ selectivity ^{12, 19}. This trend is even more pronounced when a second acidic function was substituted on the organic linker, the resultant UiO-66(Zr)-(COOH)₂ outperforming the pristine material for the selective capture of CO₂ from different mixtures whilst maintaining a good water stability ^{32, 45}.

²⁰ We report here on the in-depth study of the synthesis, structural and sorption properties and thermal behaviour of UiO-66 solids functionalized with carboxylic acid substituents. Especially, whilst most Zr-based MOFs are prepared in toxic solvents (mostly N,N'-dimethylformamide, DMF), a more ²⁵ environmentally-friendly water synthesis route was developed. In order to get a deeper insight into the formation mechanism and to anticipate future possible upscaling, their crystallization kinetics were also studied by time-resolved, energy-dispersive X-ray diffraction (EDXRD). Using a multi-technique approach, ³⁰ combining temperature dependent XRD, thermogravimetric analysis (TGA) together with solid-state nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR) spectroscopy and density functional theory (DFT) calculations, we also evidenced that such solids experience, upon heating, a ³⁵ reversible cross-linking of the ligands ²³⁻²⁴ through the formation of anhydride bridges within the pores. The effect of such a phenomenon on the porosity, acidity and conductivity of the resulting solids was then assessed by adsorption measurements, FTIR and Complex Impedance Spectroscopy (CIS), respectively.

Experimental section

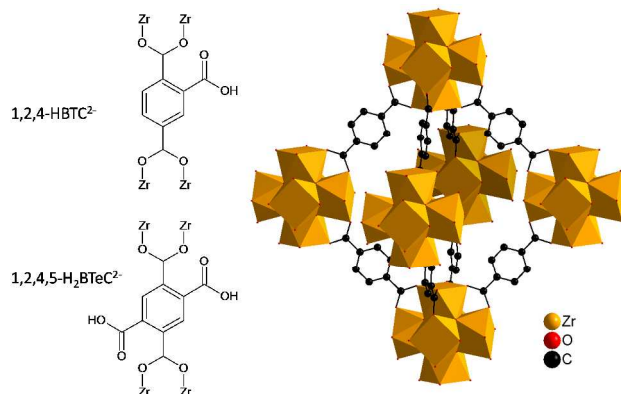
Synthesis

⁴⁵ High Throughput (HT) Synthesis

The HT screening was performed using a stainless steel multiclave reactor block with 24 cavities containing Teflon lined vessels of 2 mL developed by Stock ⁴⁶. This reactor was used to study the influence of two different parameters on the formation ⁵⁰ of crystallized phases, namely the pH and ligand to cation ratio. The proper amount of ligand (either 1,2,4-benzenetricarboxylic acid (H₃BTC) or 1,2,4,5-benzenetetracarboxylic acid (H₄BTeC), (Scheme 1) was first introduced in the reactor, followed by the H₂O/HCl (37%) mixture (volume = 1 mL) and finally ZrCl₄ (see ⁵⁵ Supplementary Information Table S1). The reaction mixtures were stirred for 5 min, and the sealed multiclave was placed in an

oven at 100 °C for 72 hours. After cooling to room temperature, the reaction vessels were filtered, dried in air, and directly examined by HT powder X-ray diffraction (PXRD).

Scheme 1. Left : polycarboxylate ligands used in the present study; Right: view of the parent structure, UiO-66 (octahedral cage).



⁶⁵ Optimized synthesis

Both solids (UiO-66(Zr)-(COOH) and UiO-66(Zr)-(COOH)₂) were synthesized following the same procedure using a 50 mL round-bottom flask route (see Supplementary Information, Table S2).

⁷⁰ In a round-bottom flask equipped with reflux condenser and magnetic stirrer, 1.1 g (5 mmol) of H₃BTC (Aldrich, > 97 %) or 1.3 g (5 mmol) of H₄BTeC (Aldrich, > 97 %) and 1.2 g (5 mmol) of ZrCl₄ (Aldrich, 98 %) were dispersed in 25 mL of distilled water (1.4 mol) at room temperature under stirring and then ⁷⁵ heated under reflux under air for 24 hours. The resulting white gel was filtered off and washed with distilled water at room temperature. The solid was then dispersed in distilled water (~10 mL per 1 g of product) and heated under reflux for 16 hours. The solid was then recovered by filtration, washed with water and ⁸⁰ dried at 30 °C under vacuum yielding ~ 2 g of white powder.

In situ crystallization studies

The crystallization studies were performed in borosilicate Schott DURAN® culture tubes of 12 mm diameter and 100 mm length ⁸⁵ sealed with screw caps. A reaction volume of around 2 mL and a zirconium concentration of 0.2 M were used (see Supplementary Information, Table S3 for details). The starting reagents (ZrCl₄ and either H₃BTC or H₄BTeC) were dispersed in distilled water, and the clear solutions were heated at the desired reaction ⁹⁰ temperature (temperature range: 100°C-150°C) using a conventional oven; the temperature was electronically controlled to ± 2 K (set up developed by Bensch *et coll.* ⁴⁷). Reaction mixtures were rapidly stirred during data collection to ensure that solid material remains in the X-ray beam during the whole ⁹⁵ measurement.

High throughput X-ray powder diffraction data were collected with a Bruker D8-Advance diffractometer using a CuK_α radiation (λ = 1.54059 Å). The diffractometer is equipped with a ¹⁰⁰ x,y sample stage allowing the automatic analysis of the 24

samples issued from the HT synthesis.

Powder X-ray diffraction data (PXRD) were recorded using a conventional high resolution (θ - 2θ) Siemens D5000 diffractometer at the Cu $K\alpha$ radiation ($\lambda = 1.54059 \text{ \AA}$). DICVOL06⁴⁸ was used for pattern indexing; the cell refinements were carried out by a structureless whole pattern profile refinement using the FULLPROF software and its graphical interface WINPLOTR.⁴⁹

X-ray thermodiffraction was performed with Siemens D-5000 diffractometer in the θ - θ mode using Co $K\alpha$ radiation ($\lambda = 1.79 \text{ \AA}$) and equipped with in an Anton-Paar chamber. Measurements were performed between 20 and 400°C with a 10°C step and at 500°C.

EDXRD

Product formation was studied by *in situ* EDXRD on the Beamline F3 of the HASYLAB facility (DESY, Hamburg, Germany). This beamline receives white synchrotron radiation with energy 13.5-65 keV and the incident X-ray beam is collimated at $20 \times 20 \text{ mm}^2$. Scattered X-rays were detected using a liquid nitrogen cooled solid-state germanium detector positioned at around 2.92° and data accumulated in 30, 60 or 120 s intervals. From collected EDXRD spectra, the extent of crystallization (α) was extracted by integration of the most intense diffraction peak, namely the (111) Bragg peak for both UiO-66(Zr)-(COOH) and UiO-66(Zr)-(COOH)₂ solids. All integrated intensities were normalized by the zirconium fluorescence to take into account the drop of the beam as a function of time and scaled from zero at the beginning of the reaction to unity at the end. These Bragg peak integrations were performed using the software "calf3" (software offered and available for free at beamline F3, private copy by A. Rothkirch/DESY). The crystallization time t_f corresponds to the time when no increase of peak intensity is observed, characterized by the presence of a plateau on the crystallization curve. The induction period t_0 is the time required to detect any crystallinity (normalized peak intensity $> 5 \%$).

TGA

TGA curves were performed on a STA6000 simultaneous thermal analyzer from Perkin-Elmer, under O₂ atmosphere ($20 \text{ mL}\cdot\text{min}^{-1}$) between room temperature and 600°C with a heating rate of $2^\circ\text{C}\cdot\text{min}^{-1}$.

N₂ sorption measurements (-196°C)

Experiments were performed on a Micromeritics ASAP-2010 apparatus using nitrogen as the probe gas. The UiO-66(Zr)-(COOH)_x solids (50-100 mg) were outgassed at various temperatures ranging from 30 to 200°C under vacuum for 12 to 24 hours prior to measurement.

IR spectroscopy

Solid samples were usually analyzed as self-supported wafers (ca.

15 mg). In some cases, the solid was deposited on a silicon wafer after dilution in ethanol. The mixture was then dried in air. The wafers were finally placed in an IR quartz cell equipped with KBr windows. The cell was connected to a vacuum line for evacuation, calcinations and introduction of known doses of vapours (H₂O, CD₃CN). The compounds were activated in vacuum from room temperature (R.T.; ca. 20°C) to 300°C, with a dwell of 30 minutes at each temperature chosen (one spectrum every 50°C). Transmission spectra were recorded in the 500 – 5600 cm^{-1} range at 4 cm^{-1} resolution on a Nicolet Nexus spectrometer equipped with an extended KBr beam splitting device and a mercury cadmium telluride (MCT) cryo-detector. The spectra were normalized for a 10 mg pellet.

The stability of the anhydrides was tested by leaving the sample, after heating at 200°C, under 9.3 mbar H₂O for several hours at R.T. For acidity measurements, 26.7 mbar CD₃CN were introduced at R.T. on the solid after heating at various temperatures.

Solid-state NMR

The ¹³C cross-polarization under magic-angle spinning (CP-MAS) NMR spectra were recorded on an Avance Bruker 500 NMR spectrometer ($B_0 = 11.7 \text{ T}$, corresponding to Larmor frequencies of 500.1 and 125.7 MHz for ¹H and ¹³C, respectively). The samples were packed on 4 mm outer diameter rotors, and spun at 10 kHz. The initial ¹H 90° pulse length was 3 μs , the contact time 5 ms, and radiofrequency (RF) fields of 60 and 50 kHz were applied on ¹H and ¹³C, respectively, during the polarization transfer. ¹H step small-phase incremental alternation (SPINAL-64)⁵⁰ decoupling was applied during the signal acquisition ($\sim 70 \text{ kHz}$ RF field). The recycle delay was 3 s, and about 1000 transients were accumulated for each sample. The ¹³C chemical shifts were referenced to TMS. The spectra were analyzed using the DMfit software⁵¹. To study the anhydride formation, the solids were packed in a rotor, put in an oven under 5 mbar vacuum for an hour in temperatures ranging from 25 to 150°C. After heating, the rotors were rapidly closed to avoid contact with air and moisture. The NMR measurements were then done at room temperature. It must be noted that the results arising from these experiments could not be used directly for quantitative information, as the ¹³C NMR spectra were recorded with a CPMAS sequence for sensitivity purpose.

Modelling of the structures

The structure of the UiO-66(Zr)-(COOH)₂ was previously successfully modelled using a ligand replacement strategy applied to the crystal structure of the parent UiO-66(Zr) followed by a geometry optimization protocol combining force-field based and quantum calculations where both cell parameters and atomic positions were allowed to fully relax³². Starting with this crystal structure, the model of the anhydride form was further constructed by connecting two neighbouring carboxylate groups via the deletion of one -OH group from one ligand and one hydrogen atom from the other. The so-obtained model was then geometry optimized by the same computational strategy mentioned above (see Supplementary Information for more details).

The theoretical accessible surface area and pore volume for each structure were further calculated using the geometric⁵² and thermodynamic⁵³ methods respectively (see Supplementary Information). The calculations of the ¹³C isotropic chemical shifts were performed with the CASTEP density-functional-theory (DFT)-based code. The projector augmented waves (PAW)⁵⁴ and gauge included projector augmented waves (GIPAW)⁵⁵ algorithms were considered. The Perdew-Burke-Ernzerhof (PBE) functional⁵⁶ was used in the generalized gradient approximation (GGA) for the exchange correlation energy and the core-valence interactions were described by ultrasoft pseudopotentials⁵⁷.

Gas adsorption and calorimetry

To follow the influence of outgassing temperature on the gas uptakes in the adsorption isotherms, a recently developed ‘high throughput’ adsorption apparatus with six adsorption stations was used⁵⁸. Here, samples from the same batch were placed into different adsorption stations and outgassed under vacuum to 30, 50, 75, 100, 150 and 200°C respectively. The adsorption of methane and carbon dioxide was then performed at 30°C and up to 30 bar.

The adsorption energies were obtained for samples outgassed under vacuum to 30°C and 150°C for nitrogen, methane, carbon monoxide and carbon dioxide. These enthalpies were measured experimentally at 30°C and up to 40 bar using a Tian-Calvet type microcalorimeter coupled with an in-house manometric gas dosing system⁵⁹. This apparatus allows the simultaneous measurement of the adsorption isotherm and the corresponding differential enthalpies. Gas is introduced into the system using a step-by-step method and each dose is allowed to stabilize in a reference volume before being brought into contact with the adsorbent, located in the microcalorimeter. The introduction of the adsorbate to the sample is accompanied by an exothermic thermal signal, measured by the thermopiles of the microcalorimeter. The peak in the calorimetric signal is integrated over time to give the total energy released during that adsorption step.

Conductivity measurements

The proton conductivity was measured by ac impedance spectroscopy, using a Novocontrol dielectric alpha analyzer, in the 10²-10⁴ Hz frequency range. The conductivity of the solids was derived from the dc plateau deduced from the plot of the ac conductivity with respect to the frequency. Measurements were performed at 25°C, using the Quatro Novocontrol system, via nitrogen flux. To avoid the use of mechanical constraint, conductivity experiments were not carried out on pellets prepared from compressed powder. Rather, we employed a specific cell similar to the one generally used for liquids. About 100 mg of the powder sample was poured on the lower electrode of the cell, and then very gently pressed by the upper metallic electrode. The activated solids were hydrated by maintaining the cell into contact with a water saturated atmosphere for 24 hours at room temperature. The cell was then transferred into the cryostat of the impedance meter and the solid was *in situ* treated at 25°C under dried nitrogen, for 30 min, before conductivity measurements.

Results and Discussion

1- Synthesis and in-situ crystallization studies

1.1 High throughput and kinetic study

Zr carboxylates-based MOFs are traditionally obtained via solvothermal conditions from a solution of ZrCl₄ (or ZrOCl₂.xH₂O) and polycarboxylic acids in a polar solvent (DMF, N,N'-diethylformamide (DEF) or dimethylacetamide (DMA)), sometimes in the presence of acidic modulators (*e.g.* hydrochloric or monocarboxylic acids) to achieve a good crystallinity^{44, 60-63}. So far, only minor amounts of water (coming from the reactants or additives) were introduced in the reaction mixtures, acting more as a reactant or a modulator rather than a solvent. Nevertheless, as the Zr₆ units are robust and able to be formed in water,⁶⁴⁻⁶⁵ UiO-66(Zr) type solids are likely to be synthesized in pure water, providing that the organic linker is soluble enough (*e.g.* 2-nitroterephthalic acid⁶⁶). Indeed, using polar terephthalic derivatives (*i.e.* 1,2,4-benzenetricarboxylic acid and 1,2,4,5-benzenetetracarboxylic acid) and ZrCl₄ in water under hydrothermal conditions, we were able to produce UiO-66 derivatives (UiO-66(Zr)-COOH and UiO-66(Zr)-(COOH)₂, respectively), as confirmed by PXRD analysis (see Supplementary Information, Figures S1-S2).

In a first step, a high-throughput (HT) methodology⁴⁶ was employed to study the influence of two experimental parameters, namely the ligand to metal ratio (L : M) and the HCl content on the reaction product, while the temperature was kept constant (100°C). Both parameters were indeed found to notably affect the crystallinity of UiO-66 derivatives prepared in DMF^{61, 66}. The results are summarized in Figure 1.

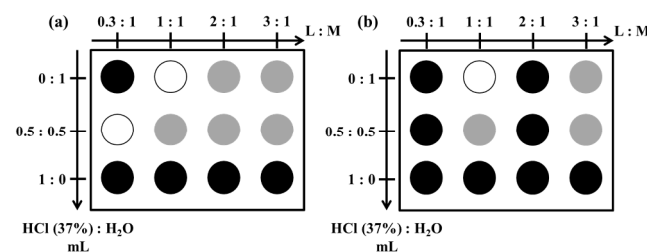


Figure 1. HT investigation of the influence of L : M ratio and HCl (37 wt% or 12 M) : H₂O ratio on the product formation in the system (a) ZrCl₄/BTC and (b) ZrCl₄/BTeC. Experiments were carried out in a closed vessel at 100°C for 72 hours. Black: Amorphous solid or recrystallized ligand; grey: poorly-crystallized UiO-66 type solid; white: well-crystallized UiO-66 type solid.

For any experimental conditions, only UiO-66 type materials were observed (see as an example Figure 2), confirming the robustness of this structure type even in the presence of additional complexing functional groups. While the L : M ratio seemed to have a minor effect on the crystallinity, addition of large excess of HCl prevented from the formation of the solid, the extreme acidity probably limiting the deprotonation of the linker.

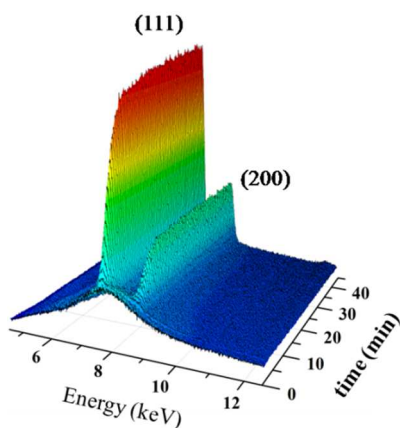


Figure 2. Time-resolved in situ EDXRD data of the hydrothermal synthesis of UiO-66(Zr)-(COOH) solid synthesized at 150 °C with 7.5 eq. HCl/Zr. The two main Bragg peaks (111) and (200) are shown.

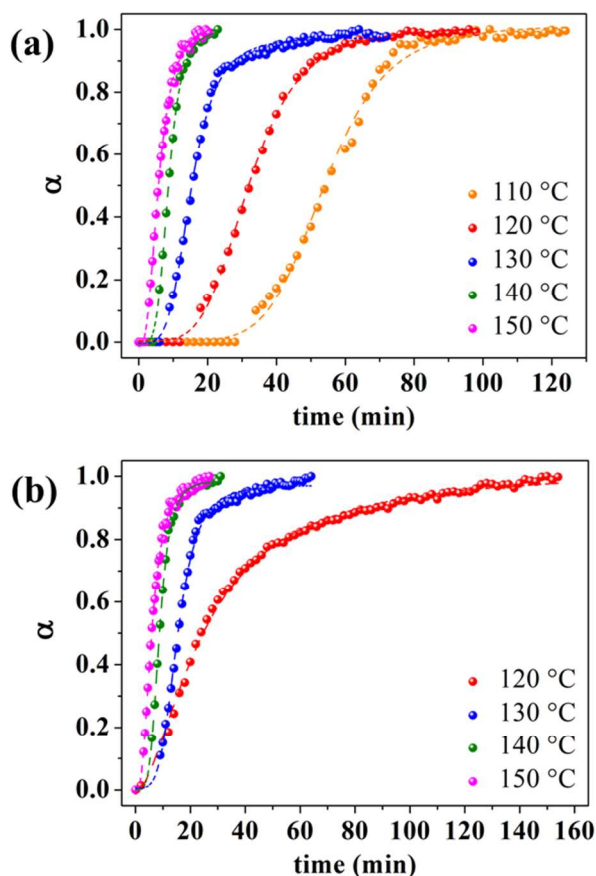


Figure 3. Plots of the extent of crystallization (α) against time obtained by integration of the (111) Bragg peak of the (a) UiO-66(Zr)-(COOH) and (b) UiO-66(Zr)-(COOH)₂ synthesized at different temperatures using ZrCl₄ in the presence of 7.5 HCl/Zr. Crystallization curves were fitted using sigmoidal functions for clarity.

The crystallization kinetics of both UiO-66(Zr)-(COOH) and UiO-66(Zr)-(COOH)₂ were further investigated by means of time-resolved EDXRD. For the sake of comparison, the experimental conditions (HCl/Zr ratio) previously used for the

studies of UiO-66(Zr) derivatives were kept^{61, 66}. The crystallization reactions were carried out from 110 to 150 °C to not only observe the temperature effect but also to assess the characteristic parameters of the reactions (*e.g.* activation energy). As an example, the results of the crystallization process at 150 °C for UiO-66(Zr)-(COOH) is shown in Figure 2. Figure 3 shows the normalized crystallization curves produced for both compounds by the integration of the (111) Bragg peaks at different temperatures.

First, whatever the ligand (H₃BTC or H₄BTeC) and the temperature (110, 120, 130, 140, 150 °C) considered, no intermediate crystalline phase was observed prior to the formation of UiO-66, once again confirming the robustness of such a structure type. At 110 °C, the reactions are completed within a few hours, whereas higher temperatures (>130 °C) led to very short crystallization times t_f , shorter than 30 minutes (see Supplementary Information, Table S5), as already observed for UiO-66 analogues prepared in DMF.^{61, 66} If one takes into account the full shape of the crystallization curve, a striking difference emerges between UiO-66(Zr)-(COOH)₂ and UiO-66(Zr)-(COOH). Whilst for the first one, the crystallization starts as soon as the solution is heated, for the second one a first step of induction, with no crystallization, is observed (Figure 3 and Figure S5). This induction time t_0 (see Supplementary Information, Table S5) decreases with increasing temperature. The reason of such a discrepancy remains unclear, and seems to have no direct connection with solubility issues, H₃BTC being more soluble than H₄BTeC in water.⁶⁷

In order to extract the kinetic information from the EDXRD data, the crystallization curves were fitted using two models. The first one is the Avrami-Erofe'ev equation (1), which relates the extent of crystallization α to the reaction time t and the induction time t_0 (equation 1), allowing the extraction of the Avrami exponent n_{SH} and the rate constant k_{SH} ⁶⁸⁻⁶⁹. The second one is the Gualtieri model (2)⁷⁰, which considers nucleation and growth as distinct processes, where a ($= 1/k_n$) and b are constants related to the nucleation, while k_g and n are the rate constant of the crystal growth and the dimension of the growth ($n = 3$ for a cubic symmetry), respectively.

$$\alpha = 1 - \exp(-k_{SH}(t-t_0)^{n_{SH}}) \quad (1)$$

$$\alpha = \frac{1}{1 + \exp^{-(t-a)/b}} [1 - \exp^{-(k_g t)^n}] \quad (2)$$

Concerning the first model, plotting $\ln(-\ln(1-\alpha))$ versus $\ln(t-t_0)$ (see Supplementary Information, Figure S6 for the Sharp-Hancock⁷¹ linearization) leads to two linear regions with different slopes. This observation could indicate that two dominating mechanisms are taking place during the crystallization, as already reported for few other solids (including MOFs).⁷²⁻⁷⁴ Thus, this non-unique linearity precludes the extraction of meaningful n_{SH} values. Using the Gualtieri model equation (2), we extracted both the nucleation (k_n) and growth (k_g) rates (see Supplementary Information, Table S6). In all cases, $k_g > k_n$ indicates that the nucleation process is rate-limiting, as already observed for the non-functionalized UiO-66 solid⁶¹. Finally, for both materials and processes (nucleation and growth), the activation energies (E_a) were extracted (see Supplementary

Information, Figure S9) using the Arrhenius equation (3).

$$k = A \exp(-E_a/RT) \quad (3)$$

These values are summarized in Table 1. Although it is not obvious to relate these data to physico-chemical parameters, one can note that these values are on the whole similar to those measured for other MOF systems, belonging or not to the UiO-66 series^{61, 66, 74-75}.

Table 1. Activation energy of UiO-66(Zr)-(COOH) and UiO-66(Zr)-(COOH)₂ deduced from Arrhenius plots.

Solid	E _a (kJ.mol ⁻¹)	E _a (kJ.mol ⁻¹)
UiO-66(Zr)-(COOH)	86(3)	49(12)
UiO-66(Zr)-(COOH) ₂	85(6)	56(24)

From these experiments, it was obvious that both UiO-66(Zr)-(COOH) and UiO-66(Zr)-(COOH)₂ could be prepared under reflux conditions (T = 100°C) in a reasonable time (~1 day). Using a round-bottom flask in a room-pressure setup, their synthesis procedures were optimised, to finally produce both UiO-66(Zr)-(COOH) and UiO-66(Zr)-(COOH)₂, well-crystallized under reflux in water in only 24 h (see experimental section for details). These final experimental conditions (water, 100°C) appear 'greener' and cheaper than the one initially reported by Biswas *et al.*¹² for the preparation of UiO-66(Zr)-(COOH) (DMF, 150°C) and moreover, are easily scalable, as recently exemplified by the preparation of UiO-66(Zr)-(COOH)₂ at the 40 g scale.³²

1.2. Thermal analysis

The thermal behaviour of the title solids was first analyzed by thermogravimetric analyses as shown in Figure S3. Both solids present a similar behaviour with a first marked weight loss below 100°C, attributed to the free water departure, followed by a slightly decreasing plateau between 100 and 300°C and, finally, another pronounced weight loss at higher temperature (> 300°C) associated to the full degradation of the linker. Weight losses matched with the chemical formula Zr₆O₄(OH)₄(O₂C-C₆H₃-CO₂-CO₂H)₆.x H₂O (x ~ 14) and Zr₆O₄(OH)₄(O₂C-C₆H₂-CO₂-CO₂H)₆.x H₂O (x ~ 17) for UiO-66(Zr)-(COOH) and UiO-66(Zr)-(COOH)₂, respectively. Nevertheless, one cannot fully exclude a slight sub-stoichiometry of the ligands, as already detected for UiO-66(Zr)^{41, 76}. Chemical analysis (see Supplementary Information, Table S4) indeed suggests this might

be the case for UiO-66(Zr)-(COOH).

Temperature dependent PXRD patterns are shown in Figure 4 and evidence that both structures remain intact up to 200 and 250 °C for UiO-66(Zr)-(COOH) and UiO-66(Zr)-(COOH)₂, respectively. Such temperatures are significantly lower than the ones observed for other UiO-66 type solids. Although this may indicate a degradation of the solids, the TGA did not show any significant weight loss in this temperature range. Alternatively, a loss of long-distance order without any chemical degradation could induce such changes of the PXRD patterns. In order to shed light onto this peculiar behaviour, temperature dependent spectroscopic studies were performed, whose results are detailed in the next section.

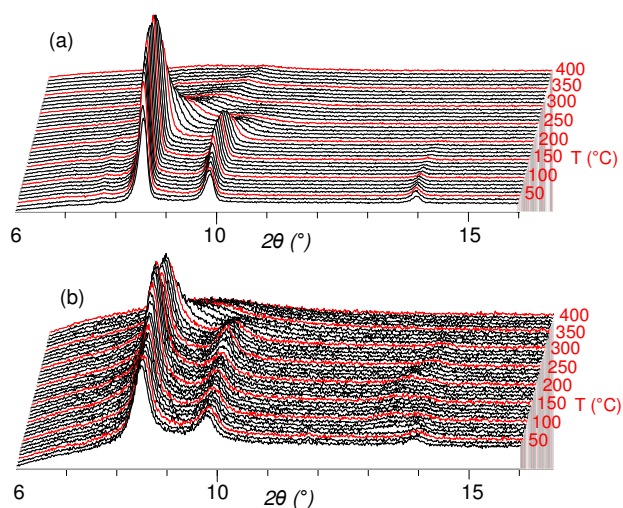


Figure 4. X-ray thermodiffractometry under air ($\lambda_{Co} \sim 1.79 \text{ \AA}$) of (a) UiO-66(Zr)-(COOH) and (b) UiO-66(Zr)-(COOH)₂. Each red line corresponds to a 50°C stage.

2. Development of cross-linking species

2.1 Formation of anhydrides upon heating

The thermal behaviour of the title solids was studied by FTIR under vacuum. The characteristic peaks obtained during the heating treatment of the UiO-66(Zr)-(COOH) are described below. Very similar results were obtained for UiO-66(Zr)-(COOH)₂.

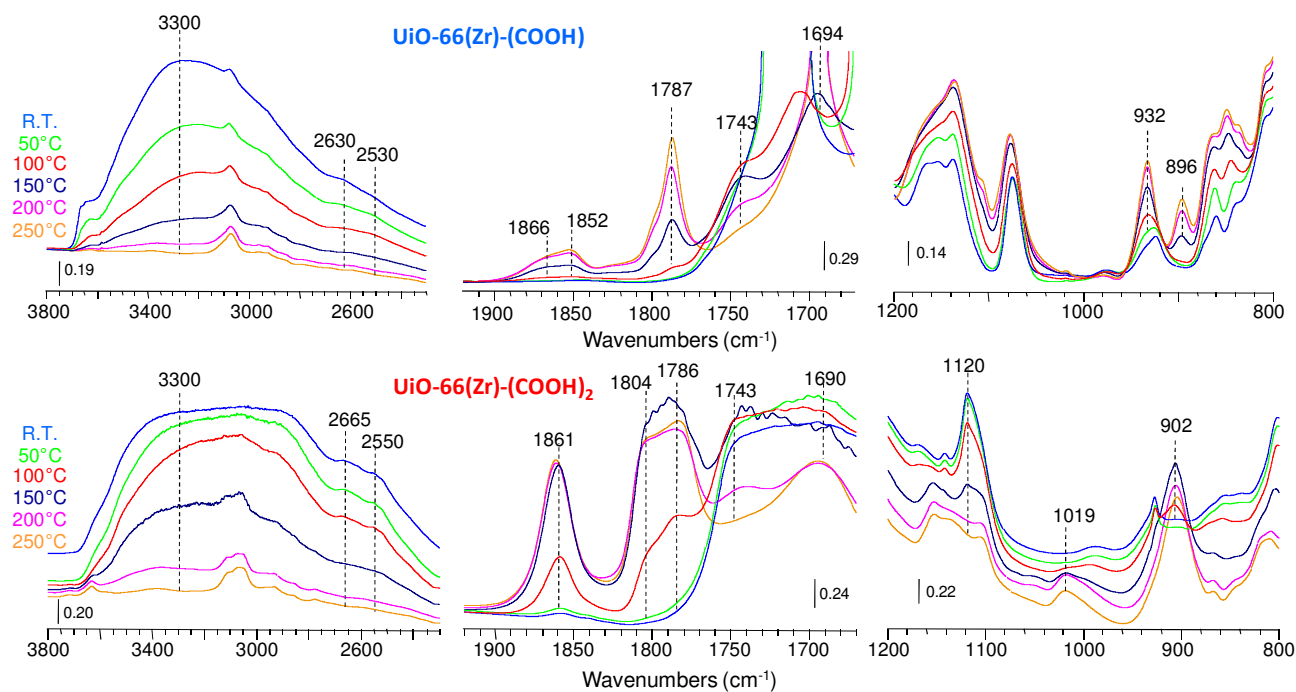


Figure 5. FTIR spectra upon heat treatment of UiO-66(Zr)-(COOH) (top) and UiO-66(Zr)-(COOH)₂ (bottom).

FTIR spectra of the solids (Figure 5) show the usual bands for MOF carboxylates, notably bands around 1600-1400 cm⁻¹ due to -COO groups linked to the metal centres⁴¹. The FTIR spectrum of the as-synthesized UiO-66(Zr)-(COOH) under vacuum shows a broad band around 1712 cm⁻¹. This band is characteristic of a free carboxylic group, *i.e.* carboxylic side-group of the ligand or unreacted ligand molecules. This band first sharply decreases upon mild heating and, around 100°C, splits into two bands at 1690 and 1743 cm⁻¹. Comparable splits are observed in the case of acid hydrates.⁷⁷ The position of the band at 1690 cm⁻¹ is in agreement with the carboxylic side-group assignment. The band at 1743 cm⁻¹ decreases upon heating and completely disappears around 250°C. This might be due to perturbed $\nu(\text{C}=\text{O})$ vibration. On the contrary, above 100°C, new bands are observed at 1787, 1797 (shoulder), 1852 and 1866 cm⁻¹ and also at 896 and 932 cm⁻¹. These bands are characteristic of strained anhydride species,^{14, 78} and develop when the temperature increases. It may be noteworthy to mention that these bands develop at much lower temperature than on MIL-53(Al)-(COOH)¹⁴. These species persist upon cooling to room temperature under vacuum. Similar bands were observed with UiO-66(Zr)-(COOH)₂, except for slight changes in position or relative band intensities of the anhydride bands: bands were indeed observed at 1786, 1804 and 1861 cm⁻¹ and at 902 and 1019 cm⁻¹.

For both solids, a broad band is observed in the OH region, at around 3300 cm⁻¹, indicating large perturbations by H-bonding as usually observed for the OH groups of carboxylic acids. Interactions with adsorbed water may also participate in the broadening of this band. This band is accompanied by others at around 2640 and 2540 cm⁻¹, which are characteristic of strong hydrogen bonds between facing carboxylic acid groups.⁷⁷ These bands decrease upon heating and disappear at around 250°C at the same time as the one at 1743 cm⁻¹. At this stage, the

anhydride bands did not increase anymore. It is thus likely that the proximity of adjacent COOH groups first gives rise to O-H...O hydrogen bonds which vanish when anhydride bridges appear.

The development of anhydride species has been quantified on both UiO-66(Zr)-(COOH)_x materials. Their amount sharply increases above 50°C and then reaches a plateau around 200°C (Figure 6). Noteworthy, the amount of anhydrides on UiO-66(Zr)-(COOH)₂ is *ca.* 3.5 times larger than on UiO-66(Zr)-(COOH). This might be in agreement with the simple probability of finding two carboxylic groups in front of each other across the pore. This should be four times larger on UiO-66(Zr)-(COOH)₂ than on UiO-66(Zr)-(COOH). This suggests that anhydrides are formed as long as the free carboxylic groups are in close proximity.

The evolution of the anhydrides formation can be compared with the decreasing intensity of bands due to the carboxylic acids. Figure 6b shows, as expected, that for both solids, the development of the anhydrides was accompanied by a decrease of the bands due to carboxylic groups. However, these two parameters cannot be quantitatively and directly correlated due to i) band shifts in these regions and ii) the fact that only a part of the carboxylic groups are initially interacting with a second carboxylic group and can thus further dehydrate.

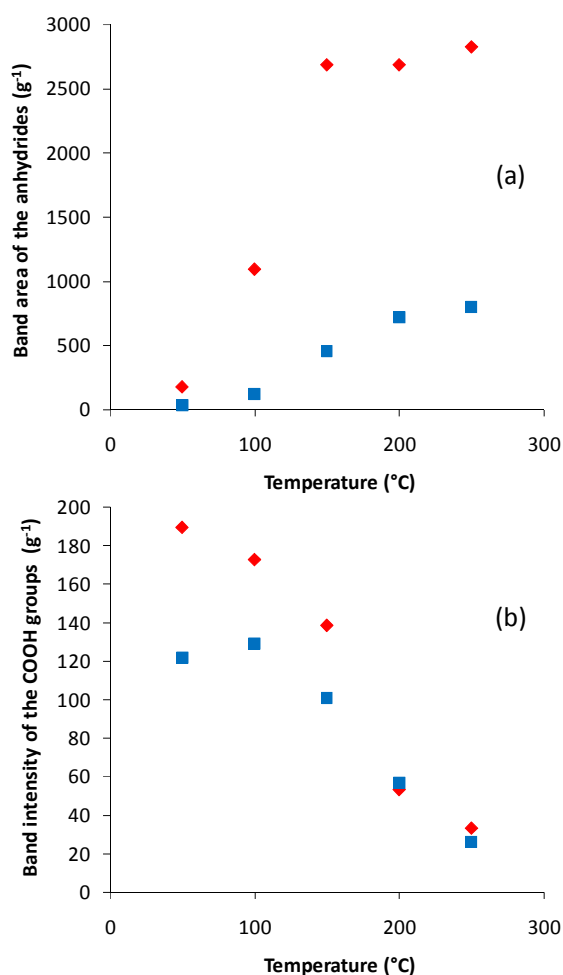


Figure 6. Comparison of the amount of species observed by FTIR on UiO-66(Zr)-(COOH) (■) and UiO-66(Zr)-(COOH)₂ (◆): (a) Anhydrides (band at ca. 1860 cm⁻¹) and (b) COOH groups (band at 1743 cm⁻¹).

The development of the anhydride bands has been compared to the evolution of the bands related to hydroxyl groups. No clear correlation can be observed between the anhydride bands and the band at ~3300 cm⁻¹. By contrast, Figure 7 shows that for both solids, the amount of anhydrides formed is directly correlated to the decrease of the amount of hydroxyl groups involved in short hydrogen-bonds (bands around 2640 and 2540 cm⁻¹). This indicates that only carboxylic groups in close interaction will be able to yield anhydride species. In addition, it is noteworthy that both curves are parallel to each other. This implies that, in this pore configuration, the unavoidable presence of some carboxylic groups close to each other is the only factor that will influence the final formation of anhydrides upon heating.

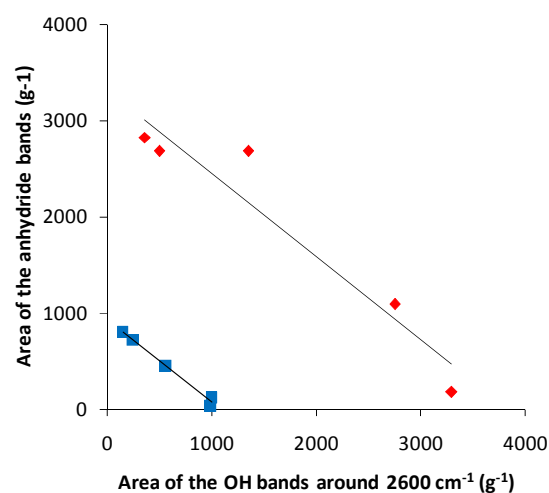


Figure 7. Role of the strongly hydrogen-bonded OHs on the formation of anhydrides in UiO-66(Zr)-(COOH) (■) and UiO-66(Zr)-(COOH)₂ (◆).

The ¹³C CPMAS NMR spectra of UiO-66(Zr)-(COOH)₂ and UiO-66(Zr)-(COOH) after activation at various temperatures are shown in Figure 8. After activation at 25°C, both spectra contain two sets of peaks: a first set located in the 170-180 ppm range, which corresponds to the carboxyl carbon atoms and a second set in the 110-140 ppm range, which corresponds to the quaternary and C-H carbon atoms of the HBTC²⁻ and H₂BTeC²⁻ linkers. Based on the line intensity and DFT-calculations of the ¹³C isotropic chemical shifts, the ¹³C NMR resonances have previously been assigned to the various carbon atoms in UiO-66(Zr)-(COOH)₂.³² In particular, the line at lower chemical shift (170 ppm) was assigned to the C-O-Zr carbon atom, whilst the line at higher chemical shift (176 ppm) corresponded to the 'free' carboxyl function from the BTeC linker. A similar line assignment can be made in UiO-66(Zr)-COOH (see Figure 8).

In both solids, a peak appears around 166 ppm upon heating. This chemical shift is close to the one reported for the formation of anhydride in MIL-53-(COOH)₂,¹⁴ in agreement with the formation of anhydride bridges by condensation of two neighbouring free carboxyl groups.

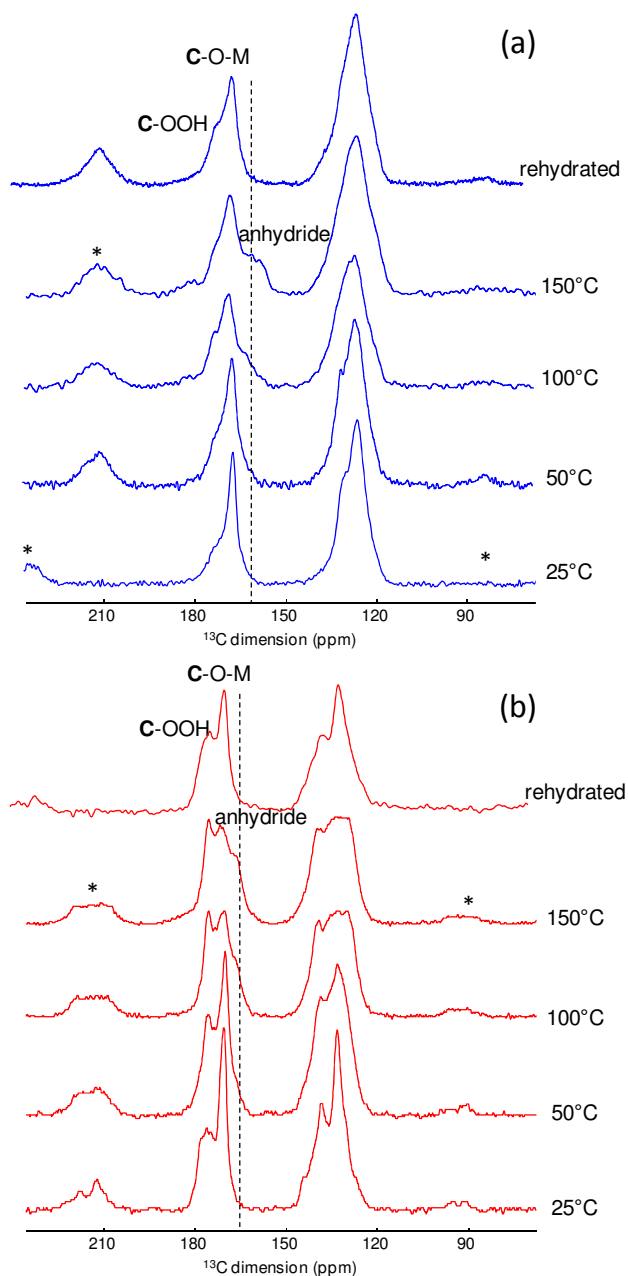


Figure 8. ^{13}C CPMAS NMR spectra of UiO-66(Zr)-(COOH) (a) and UiO-66(Zr)-(COOH)₂ (b) recorded on the sample previously heated at temperatures in the range 25–150°C. On top are shown the spectra of the rehydrated solids. Stars indicate spinning sidebands. The dash lines are merely a guide for the eye.

NMR analyses indeed confirm the presence of a large amount of anhydride species, which cannot be explained solely by defective

10 sites (such as intra-molecular ligand dehydration), but more likely by cross-linking anhydrides between two ligands. In order to estimate the geometric feasibility of such cross-linked anhydride species and to confirm NMR assignments, DFT calculations were achieved to propose a plausible structure model of the anhydride structure as the quality of the PXRD pattern prevented any accurate structure determination from diffraction analysis. A model was built starting from the previously modelled structure of UiO-66(Zr)-(COOH)₂³². The latter was built-up in a cubic unit-cell with the F23 space group, in agreement with the experimental data (see Supplementary Information). In the construction of the anhydride form, 32 hydrogen atoms and 16 oxygen atoms (corresponding to 16 H₂O molecules) are removed (*per* unit-cell), leading to a structure containing 16 –COOH groups (that is, 8 H₂BTEC²⁻ organic linkers) and 16 –COOCO groups *per* unit cell. The so-obtained structure was further DFT geometry optimized with a full relaxation of both atomic positions and cell parameters, leading finally to an orthorhombic (but close to cubic) unit-cell. The geometric features of the optimized anhydride structure are compared with the ones previously reported for the modelled UiO-66(Zr)-(COOH)₂ in Table 2.

A fragment of such a structure is presented Figure 9. It shows that the formation of anhydride bridges between neighbouring ligands (angle ligand 1 - Zr₆ - ligand 2 = 60°) is geometrically feasible without any drastic structural distortion.

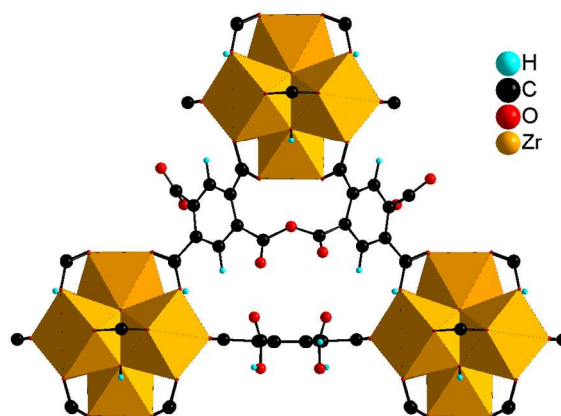


Figure 9. Simulated structure of the anhydride form of UiO-66(Zr)-(COOH)₂: view of an anhydride bridge formed between two adjacent ligands. This figure also highlights the reduction of the size and rigidification of the triangular pore windows upon dehydration.

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ARTICLE TYPE

Table 2. Structural features of the UiO-66(Zr)-(COOH)_x and the anhydride form of UiO-66(Zr)-(COOH)₂.

Materials	Experimental		Theoretical			
	Possible space group	Lattice param. (Å)	Space group	Lattice param. (Å)	V_{pore} (cm ³ /g)	a_{acc} (m ² /g)
UiO-66(Zr)-(COOH) ^a	F23	20.758(1)	P1	20.8039	0.31	551
UiO-66(Zr)-(COOH) ₂ ^b	F23	20.731(5)	F23	20.9674	0.26	428
Anhydride form	not determined		F222	a = 20.9725 b = 20.8143 c = 20.8758	0.29	464

a: Theoretical data from ¹⁹b: Theoretical data from ³².

5 The above NMR assignments were confirmed by further DFT calculations performed on the anhydride structure. The calculated isotropic ¹³C shifts indeed agree very well with the experimental values as summarized in Table 3, similarly to what has been previously obtained for UiO-66(Zr)-(COOH)₂. We further checked that such a correlation was not generated by chance considering for each form of UiO-66(Zr) a structure that was not preliminarily optimized and for which the calculations of the isotropic ¹³C shifts were repeated. One observes in Figure S10 that the correlation between experimental and simulated ¹³C shifts is of much less quality than the one obtained based on the optimized structure. These findings, combined with our previous studies on a series of functionalized UiO-66(Zr) ⁷⁹, not only allowed us to provide a further validation of the predicted crystal structures for this anhydride form but also for the UiO-66(Zr)-(COOH)₂ solid.

Table 3. Experimental $\delta_{iso,exp}$ (ppm) and DFT-calculated $\delta_{iso,calc}$ (ppm) ¹³C isotropic chemical shifts of UiO-66(Zr)-(COOH)₂ and of the anhydride form (in bold) and corresponding assignment. As Lines 1 and 2 have very close chemical shifts, the assignments of these two lines could be exchanged.

Line	$\delta_{iso,exp}$ (± 1)	$\delta_{iso,calc}$	Assignment
1	134	133.8	C _{quat.}
	135	136.0	
2	135	134.1	CH
	139	142.1	
3	139	141.7	C-COOH
	139	140.9	
4	171	171.3	C-O-Zr
	171	171.4	
5	176	174.4	C-OOH
	168	168.6	
6	168	168.6	C-O-C

2.2 Influence of the anhydrides on gas sorption properties

30 As shown above in Figure 6, increasing the activation temperature of these solids favours the formation of anhydride species. To follow this effect on the accessible surface area and pore volume, nitrogen adsorption at -196°C was carried out on the solids after outgassing to different temperatures. The resulting BET (Brunauer-Emmett-Teller) surface areas and pore volumes are given in Figure 10 and Table S7 which can be compared with the theoretical results, extracted from the simulated structures, in Table 2.

35 First, as expected,¹⁹ the presence of bulky COOH groups, induced a decrease in the BET area compared to the parent UiO-66(Zr). The experimental BET areas are slightly higher than the values calculated theoretically in this study (Table 2). On the whole, UiO-66(Zr)-(COOH) shows a lower surface area and UiO-66(Zr)-(COOH)₂ a higher surface area than the values reported by Biswas *et al.* ^{12, 31}.

40 As shown in Table 2, the theoretical approach suggests that hardly any change in the accessible surface area and pore volume can be expected on formation of anhydride species in the two UiO-66(Zr)-(COOH)_x structures. The variation of the experimental BET area as a function of the activation temperature is plotted in Figure 10a. Similar variations were obtained for the pore volumes (Supplementary Information, Table S7). It can be seen that for both UiO-66(Zr)-(COOH)_x at low temperature (<70°C), increasing the temperature of activation leads to a slight increase in BET areas and pore volumes. At higher temperature (especially >130°C), the effect is opposite with a higher activation temperature leading to lower sorption capacities. Below 200°C, neither XRD, nor TGA nor infrared spectroscopy gave any indication of sample degradation which would explain

the porosity decrease. This decrease must then be attributed to other factors. As shown earlier, the amount of anhydride becomes significant at these temperatures. However, from modelling data, the presence of anhydride is expected to modify only slightly the surface area and pore volume (see the anhydride form in Table 2). Nevertheless, such theoretical calculations only take into account the availability of the pore space, and not its accessibility. At low temperature, when motions are more limited, the formation of anhydride bridges between facing ligands may both decrease the size of the pore apertures (triangular windows) and rigidify the framework (rotation of the phenyl rings no longer possible); both effects may prevent the efficient adsorption of nitrogen at low temperature (-196°C) and hence decrease the total sorption capacity, as experimentally observed.

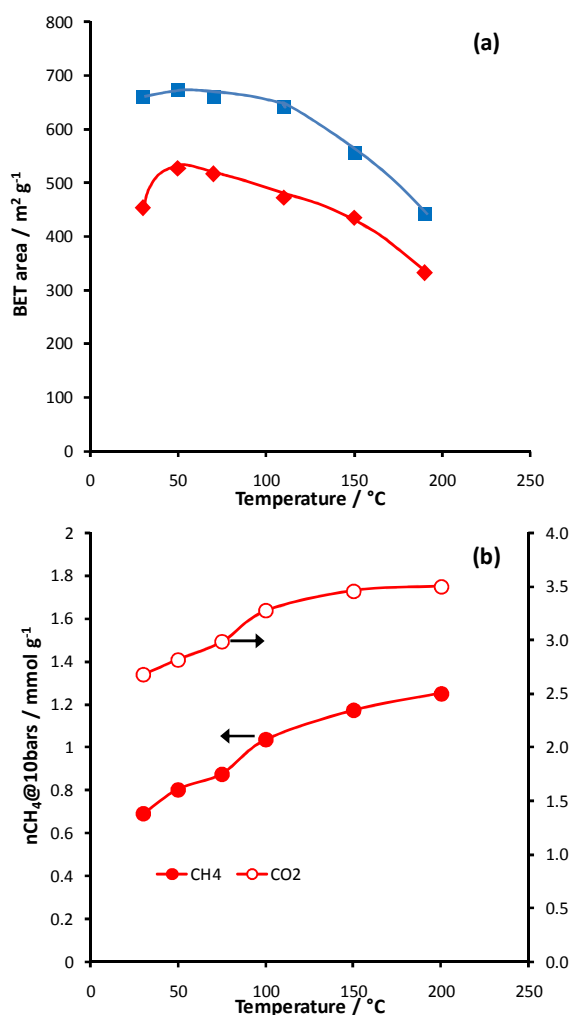


Figure 10. Effect of outgassing on the adsorption properties. (a) Variation of BET area for on UiO-66(Zr)-(COOH) (■; blue) and UiO-66(Zr)-(COOH)₂ (◆; red) from nitrogen sorption at -196°C, and (b) variation of amounts of CO₂ (○) and CH₄ (●) adsorbed at 10 bars at 30°C for the UiO-66(Zr)-(COOH)₂ solid.

The effect of outgassing temperature and thus anhydride formation has also been studied with respect to the adsorption properties of gases at 30°C. The uptakes at 10 bar for methane and carbon dioxide adsorbed on UiO-66(Zr)-(COOH)₂ are shown as a function of the activation temperature in Figure 10b (adsorption isotherms are given in Figure S12). In contrast to the variations of surface area measured at -196°C (Figure 10a), at 30°C the amount of gases adsorbed at 10 bar increases with increasing activation temperature.

To gain a deeper insight into the influence of the presence of anhydrides, calorimetry experiments were carried out at 30°C with the UiO-66(Zr)-(COOH)₂ solid after outgassing to 30°C and 150°C. The results obtained with methane and carbon dioxide are given in Figure 11, the results with N₂ and CO are provided in the Supplementary Information, Figure S13.

For both methane and carbon dioxide (the same holds true for nitrogen and carbon monoxide, see Supplementary Information) the difference in activation temperature has no effect on the adsorption enthalpies, associated with little changes in pore size or shape. In the case of CO₂ only, a slight increase in overall enthalpies of adsorption is observed with increased coverage on the solid outgassed at 150°C while its initial enthalpy does not change.

All these results indicate that the presence of anhydride species does not induce any detrimental effect on the gas uptakes at 30°C, with no significant change of enthalpy values. Furthermore, this confirms that the loss of capacity, observed with nitrogen at -196°C after activation above 100°C, is not related to the degradation of the framework. Nevertheless, the differences obtained on the anhydride form between the gas adsorption at -196°C and 30°C are not fully understood; they could rather be tentatively explained by the higher thermal motion and hence the flexibility and the accessibility of the windows at higher temperatures. Gas adsorption in the anhydride form would thus be favoured only when the temperature is high enough to allow sufficient flexibility at the pore windows. One may then suggest that, at such temperature, a cooperative motion of the atoms at the pore mouth might be induced by the anhydride linkages, leading to higher capacities than without such linkages.

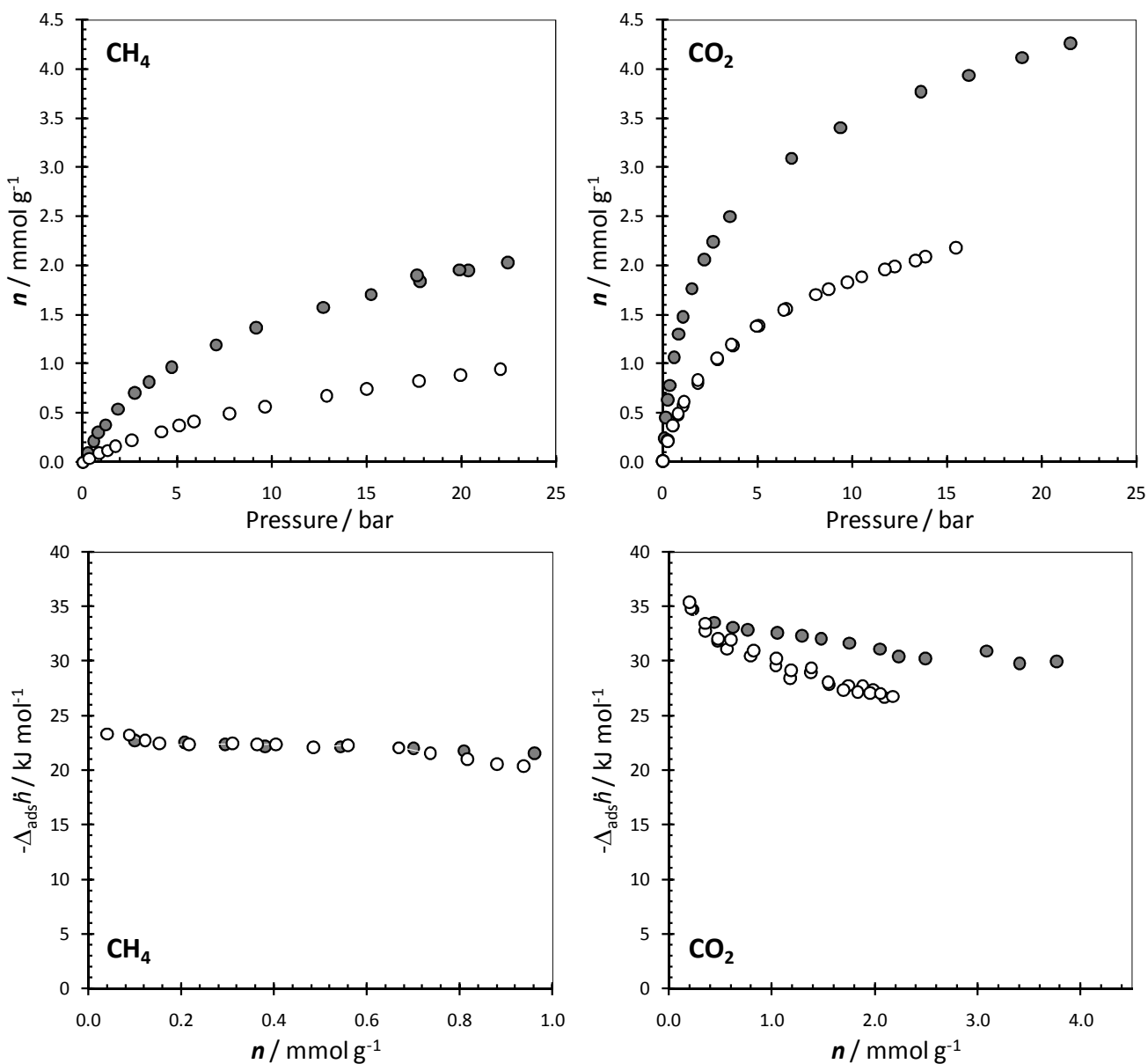


Figure 11. Isotherms (upper curves) and adsorption enthalpies (lower curves) obtained at 30°C with CH₄ (left) and CO₂ (right) for UiO-66(Zr)-(COOH)₂ outgassed to 30°C (○) and 150°C (●).

2.3 Reversibility of the anhydrides formation

The dissociation of the anhydrides upon contact with water vapour was evidenced by different techniques. The PXRD patterns of the as-synthesized solids and after treatment at 180°C and re-exposure to water were found to be almost identical (see Supplementary Information, Figure S4). Similarly, the ¹³C CPMAS NMR spectra of both rehydrated solids are almost identical to those of the as-synthesized compounds, indicating that the process of formation of anhydrides is mostly reversible (Figure 8).

IR spectroscopy showed that, after heating at 200°C for 3 hours, anhydrides were formed as described above. Upon contact with water vapour, the anhydride IR bands were shifted to lower wavenumbers (1849 and 1781 cm⁻¹ for the main bands of UiO-66(Zr)-(COOH) and 1857 and 1782 cm⁻¹ for UiO-66(Zr)-

(COOH)₂). The -COOH band in the presence of water was also shifted to 1708 cm⁻¹ on UiO-66(Zr)-(COOH). Unfortunately, the very intense bands of the carboxylates tend to overwhelm this band on UiO-66(Zr)-(COOH)₂. Therefore a band at 1120 cm⁻¹ was used instead to evaluate carboxylic groups on this solid (specific experiments showed that the band at 1120 cm⁻¹ on UiO-66(Zr)-(COOH)₂ evolved similarly to the bands at 1740 cm⁻¹).

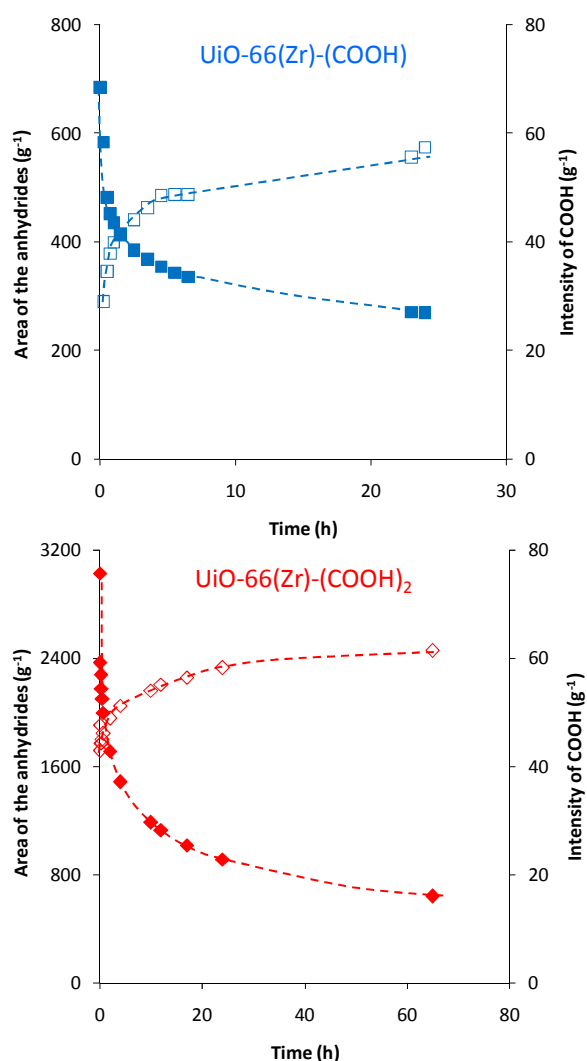


Figure 12. Hydrolysis of the anhydrides on UiO-66(Zr)-(COOH) (top) and UiO-66(Zr)-(COOH)₂ (bottom). Evolution of the amount of anhydrides (solid symbols; area of the band at ca. 1860 cm⁻¹) and COOH groups (hollow symbols; intensity of the band). [Note that for UiO-66(Zr)-(COOH), the COOH groups were estimated from the band at 1708 cm⁻¹ while for UiO-66(Zr)-(COOH)₂ the intensity of the band at 1125 cm⁻¹ was used instead]

The band areas of anhydrides progressively decreased with contact time. Figure 12 shows that both solids lose half of their anhydrides content in less than 5 h. After a long exposure of both solids to water (>20 h), ca. 40% of the anhydrides persisted on UiO-66(Zr)-(COOH) and ca. 20% on UiO-66(Zr)-(COOH)₂. Meanwhile, bands due to carboxylic groups were partly restored. This clearly supports the reversible formation of a large part of the anhydrides under the studied conditions. Moreover, the hydrolysis process appears independent of the type of functionalized solid.

3. Properties of the materials

3.1 Acidity

Acidity was evaluated by the adsorption of acetonitrile (CD₃CN) followed by FTIR (Figure 13). On the solids evacuated at 50°C,

three ν(CN) vibration bands are observed at 2304, 2275 and 2262 cm⁻¹ which can be attributed respectively to Lewis acid sites, Brønsted acid sites and physisorbed CD₃CN⁸⁰. Lewis acid sites were also observed on the pristine UiO-66(Zr) by CO⁴⁰ or CD₃CN⁴⁴ adsorption. These bands appear associated to the dehydroxylation process of the inorganic cluster. However, although similar bands can be detected on the unmodified UiO-66(Zr) and on the UiO-66(Zr)-(COOH)_x solids, differences are observed in the spectra.

After evacuation at 50°C, Lewis acid sites appear on the carboxylic modified solids at slightly higher wavenumber (2304 cm⁻¹) than on pure UiO-66(Zr) (2299 cm⁻¹) indicating a higher acid strength. However it shifts to 2299 cm⁻¹ when the solid is activated at higher temperatures.

After evacuation at 50°C, the band at 2275 cm⁻¹ is only observed as a shoulder on UiO-66(Zr). This band is nevertheless much more intense with UiO-66(Zr)-(COOH) and even more prominent with UiO-66(Zr)-(COOH)₂, indicating a higher relative amount of Brønsted acid sites on the latter. Increasing the activation temperature did not change the position of this band but it disappeared progressively.

Brønsted acid sites observed after evacuation at mild temperature can originate from the μ₃-OH groups of the inorganic cluster. In the hydroxyl region on UiO-66(Zr), one can indeed observe on the difference spectrum (subtracted with the spectrum of the solid before adsorption), a negative band at 3672 cm⁻¹ and a large perturbed positive band at 3460 cm⁻¹, which shifts to 3417 cm⁻¹ when the physisorbed CD₃CN was removed. This shift, larger than the Δν(OH)=180 cm⁻¹ shift and expected for weakly H-bonded acetonitrile⁸⁰, confirms that OH groups can act as Brønsted acid sites and give rise to the band at 2275 cm⁻¹ on UiO-66(Zr). These μ₃-OH groups are also expected on UiO-66(Zr)-(COOH)_x and thus probably also contribute to the Brønsted acid sites detected by acetonitrile. However, several features indicate substantial differences between UiO-66(Zr) and the UiO-66(Zr)-(COOH)_x materials. First, the band intensity at 2275 cm⁻¹ is higher on the UiO-66(Zr)-(COOH)_x while a modification of the ligand is not expected to modify the inorganic cornerstone.

Second, the perturbation of the hydroxyl groups by CD₃CN is also different on the three solids. On UiO-66(Zr)-(COOH), the difference spectrum shows a main negative band at 3640 cm⁻¹ and a positive band at 3233 cm⁻¹. This much larger shift (Δν(OH)=410 cm⁻¹) is indicative of a higher overall acid strength and implies that the carboxylic groups also induce Brønsted acidity, stronger than the acidity of the pristine UiO-66(Zr). After evacuation at 100°C, the shift is more important (Δν(OH)=460 cm⁻¹). This higher strength is however not sufficient to be clearly evidenced by an additional shift of the ν(CN) band. It is therefore likely that the Brønsted acid sites detected are partly induced by the inorganic hydroxyls and partly by the organic carboxylic groups. On UiO-66(Zr)-(COOH)₂, the main negative band is observed at 3529 cm⁻¹ but a positive band is not observed. On the contrary, the solid evacuated at 50°C shows a broad negative band of low intensity around 3100 cm⁻¹. The expected positive band due to perturbed μ₃-OH may be present but it is obscured by a larger negative band. Combination bands due to carboxylates are indeed expected in this region, which complicates the analysis. After activation at 100 and 150°C, a positive broad band

centred at 3100 cm^{-1} is finally obtained, while the formation of anhydrides has already suppressed the bonds between adjacent carboxylic groups. Bonds, likely the H-bonds between adjacent carboxylic groups, are thus probably displaced by CD_3CN . This band is at slightly lower wavenumber than for UiO-66(Zr)-(COOH) , suggesting that this solid is more acidic.

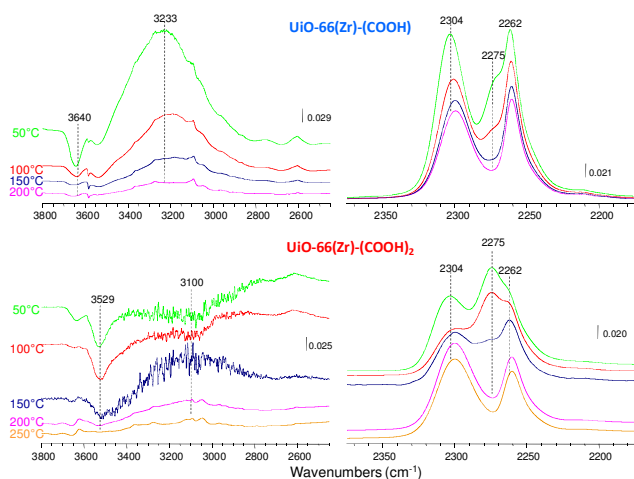


Figure 13. FTIR spectra of UiO-66(Zr)-(COOH) (top) and $\text{UiO-66(Zr)-(COOH)}_2$ (bottom) after adsorption of CD_3CN on solids heated at various temperatures. (The spectra shown are obtained after subtraction of the spectrum recorded before adsorption)

Overall the band attributed to acetonitrile coordinated with Brønsted acid sites at 2275 cm^{-1} decreased on all the samples after evacuation of the solids at higher temperature (Figure 14a). On UiO-66(Zr)-(COOH) and $\text{UiO-66(Zr)-(COOH)}_2$, Brønsted acid sites vanished in a similar manner. This decrease is consistent with both the dehydroxylation process and the fact that the number of carboxylic groups decreases upon heat treatment due to their transformation into anhydrides. The anhydride formation is thus detrimental to the overall amount of Brønsted acid sites.

Lewis acid sites detected by CD_3CN (Figure 14b) evolved differently on UiO-66(Zr)-(COOH) and $\text{UiO-66(Zr)-(COOH)}_2$ but do not increase with the activation temperature as observed on UiO-66(Zr) . This might indicate that dehydroxylation at low temperature is partially perturbed on the $\text{UiO-66(Zr)-(COOH)}_x$ solids, especially on $\text{UiO-66(Zr)-(COOH)}_2$ on which Lewis sites only increased above 150°C . However, after activation at 200°C , the concentration of Lewis acid sites was within the same range, around $300\text{ }\mu\text{mol/g}$, very close to the values measured on unmodified UiO-66(Zr) or $\text{UiO-66(Zr)-(NH}_2)$.

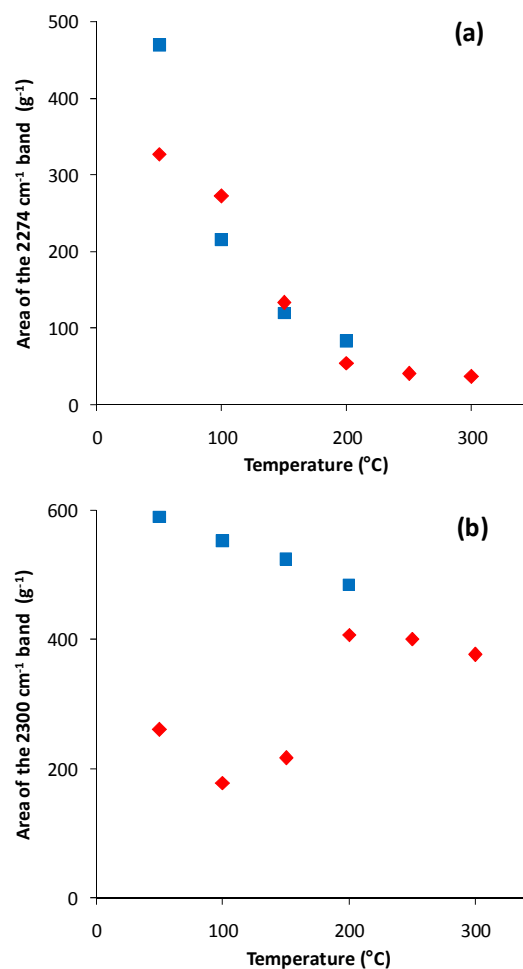


Figure 14. Amount of Brønsted (a) and Lewis (b) acid sites detected by CD_3CN after heating at various temperatures of UiO-66(Zr)-(COOH) (■, blue) and $\text{UiO-66(Zr)-(COOH)}_2$ (◆, red).

3.2 Conductivity

The values of the proton conductivity (σ_{dc}) of the hydrated UiO-66(Zr)-(COOH) and $\text{UiO-66(Zr)-(COOH)}_2$ solids are listed in Table 4 together with those of the hydrated UiO-66(Zr) and UiO-66(Zr)-NH_2 for comparison. The so-obtained values are much lower than those reported so far for the best proton conductor MOFs⁸¹. The samples can be classified as follows: $\sigma_{\text{dc}}(\text{UiO-66(Zr)-(COOH)}_2) > \sigma_{\text{dc}}(\text{UiO-66(Zr)-(COOH)}) > \sigma_{\text{dc}}(\text{UiO-66(Zr)}) > \sigma_{\text{dc}}(\text{UiO-66(Zr)-NH}_2)$. A good correlation is observed between the increase of the proton conductivity and the expected acidity of the functional group, as previously reported for substituted MIL-53(M)s ($\text{M}=\text{Fe}$ or Al)²², which makes the most acidic $\text{UiO-66(Zr)-(COOH)}_2$ associated with the highest conductivity. In the substituted UiO-66(Zr) series, the proton carriers are expected to originate from $\mu_3\text{-OH}$ groups constituting the metallic clusters and/or the functional groups linked to the organic ligands of the MOF. Considering that the number of the $\mu_3\text{-OH}$ groups is similar in the whole set of the modified UiO-66(Zr)s and that their acidity is neglected compared to the one exhibited by the protons of the functional groups²², one concludes that the conductivity sequence is mainly governed by the Brønsted acidity of the substituted functional groups on the

ligands. Both absolute values and trend agree very well with those previously reported for the analogous functionalized MIL-53(M)s (M=Fe or Al)²². This suggests that both types of materials are characterized by a similar ordered array of the water molecules, which ensures the pathway for the proton propagation⁸²⁻⁸³. Finally, we also studied the conductivity properties of the UiO-66(Zr)-(COOH) and UiO-66(Zr)-(COOH)₂ solids *in situ* treated at 150°C under nitrogen flow for 4 hours. No dc conductivity was detected in the temperature range studied [20-150]°C, although in absence of water a signal should appear, as the characteristic distances between the functions bearing the proton carriers ~2.9 Å (see DFT optimized structures of UiO-66(Zr)-(COOH) and UiO-66(Zr)-(COOH)₂) are expected to make possible the propagation of the protons. The absence of dc conductivity is indeed consistent with the loss of acidic protons which occurs concomitantly to the formation of anhydride bridges.

Table 4. dc conductivity values of UiO-66(Zr)s and MIL-53(M)s, recorded at 25°C in the hydrated state.

	σ_{dc} (S.cm ⁻¹)	
	MIL-53(M)s ²²	UiO-66(Zr)s
Non modified	2.10 ⁻⁸	8.10 ⁻⁹
-NH ₂	2.10 ⁻⁹	3.10 ⁻⁹
-(COOH)	-	9.10 ⁻⁷
-(COOH) ₂	2.10 ⁻⁶	5.10 ⁻⁶

Conclusion

The impact of free pending carboxylic side-groups on MOF structures has been tested in the case of UiO-66(Zr)'s. UiO-66(Zr)-(COOH) and UiO-66(Zr)-(COOH)₂ have been synthesized directly from trimellitic and pyromellitic acids using an environmentally-friendly water-based synthesis route. After a detailed high throughput and kinetic study of their crystallization process, the robustness of their synthesis was established, allowing their efficient up-scaling. The introduction of free carboxylic acid groups on the organic linker induced modifications of the pristine UiO-66(Zr), which, for both solids, led to an enhanced Brønsted acidity and proton conductivity, due to the sufficient mobility of the acidic protons of the free carboxylic groups. These acid groups also have the ability to act as intra-framework cross-linking centres via the formation of anhydride species across the pores without neither structure degradation nor decrease of their gas sorption properties at ambient temperature. However, dehydration of the functional carboxylic groups led to a detrimental effect on the acidity and conductivity. Nonetheless, carboxylic groups could easily and reversibly be restored upon contact with water vapour. These features confirm on the whole that functionalisation of MOFs with free carboxylic acid groups is thus an efficient and versatile method for several types of applications.

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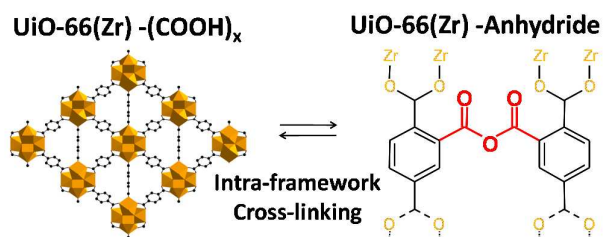
Notes and references

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- † Electronic Supplementary Information (ESI) available: Details of the synthesis conditions, PXRD, TGA, extended kinetic data of the crystallization, complete description of the modelling methodology, correlation NMR-modelling, additional gas adsorption data, notably CO and N₂ adsorption at 30°C. See DOI: 10.1039/b000000x/
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Table of Content illustration



Metal Organic Framework UiO-66 functionalized with carboxylic acid side-groups demonstrates intraframework cross-linking by the formation of anhydride species