

Electronic Supplementary Information for:

A zirconium methacrylate oxocluster as precursor for the low-temperature synthesis of porous zirconium (IV) dicarboxylates

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Experimental

A) Synthesis

Zirconium methacrylate oxocluster, synthesised as previously reported¹, *trans,trans* – muconic acid and DMF, molar ratio 1:30:1485, were mixed at room temperature under continuous stirring. The reactants were placed in a Teflon lined steel autoclave, and heated at 150°C over a range of various times (from 1h to several days). The reaction yielded a crystalline white powder, with small traces of a yellow impurity, typically observed in reactions of short time and also at room temperature. This impurity was easily removed by suspension in DMF for a short period of time (approximately 5 minutes). The DMF was removed by filtration and the product was dried at 100°C.

Muconic acid (mmol)	Zr6 cluster (mmol)	DMF volume (mL)	Synthesis Temperature (°C)	Synthesis time (h)
0,22	0,059	3	150	24
0,43	0,059	3	150	24
0,86	0,059	3	150	24
0,43	0,059	4	150	24
0,86	0,059	4	150	24
0,43	0,059	4	150	24
0,86	0,059	4	150	24
0,86	0,059	4	150	24
0,43	0,029	4	150	24
0,43	0,029	4	150	24
1,73	0,118	4	150	24
0,86	0,059	8	150	24
0,43	0,059	4	150	96
1,06	0,059	4	150	96
2,59	0,176	5	150	24
0,09	0,006	4	150	24
1,06	0,035	4	150	1 night
1,06	0,035	4	150	24h
1,06	0,035	4	150	48h
1,06	0,035	4	150	72h
1,06	0,035	4	150	96h
1,06	0,035	4	150	120h
1,06	0,035	4	RT	1 night
1,06	0,035	4	150	135h
1,06	0,035	4	150	144h
1,06	0,035	4	RT	1 night
1,06	0,035	4	RT	24h
1,06	0,035	4	RT	48h
1,06	0,035	4	RT	72h
1,06	0,035	4	RT	96h

1,06	0,035	4	150	2h
1,06	0,035	4	150	3h
1,06	0,035	4	150	5h30
1,06	0,035	4	150	7h
1,06	0,035	4	150	8h
1,06	0,035	4	150	9h
1,06	0,035	4	150	10h
1,06	0,035	4	150	11h
1,06	0,035	4	RT	48h
1,06	0,035	4	RT	72h
1,06	0,035	4	RT	2h
1,06	0,035	4	RT	3h
1,06	0,035	4	RT	4h
1,06	0,035	4	RT	5h
1,06	0,035	4	RT	6h
1,06	0,035	4	RT	1h
1,06	0,035	4	RT	2h
1,06	0,035	4	RT	3h
1,06	0,035	4	RT	4h
1,06	0,035	4	RT	5h
1,06	0,035	4	RT	1 night
1,06	0,035	4	RT	24h
1,06	0,035	4	RT	1h
1,06	0,035	4	RT	2h
1,06	0,035	4	RT	3h
1,06	0,035	4	RT	4h
1,06	0,035	4	RT	5h
1,06	0,035	4	RT	6h
1,06	0,035	4	RT	7h
1,06	0,035	4	RT	8h
1,06	0,035	4	RT	9h
1,06	0,035	4	RT	1h
1,06	0,035	4	RT	2h
1,06	0,035	4	RT	3h
1,06	0,035	4	RT	4h
1,06	0,035	4	RT	5h
1,06	0,035	4	RT	6h
1,06	0,035	4	RT	7h
1,06	0,035	4	RT	24
1,06	0,035	4	RT	1 night
1,06	0,035	4	150	1 night
1,06	0,035	4	150	1 night
1,06	0,035	4	150	1 night
1,06	0,035	4	150	1 night
1,06	0,035	4	RT	1 night
1,06	0,035	4	RT	1 night
1,06	0,035	4	RT	1 night

Table S1. Synthesis conditions used to synthesis the Zirconium Muconate MOF.

Attempts to synthesize this material using different metallic precursors (eg. $ZrCl_4$, $ZrSO_4$, Zr isopropoxyde) resulted in the formation of very poorly crystalline materials.

Muconic acid (mmol)	ZrCl₄ (mmol)	DMF volume (mL)	H₂O volume (mL)	Synthesis Temperature (°C)	Synthesis time (h)
0,25	0,25	4	-	200	48
0,25	0,25	4	-	150	96
0,25	0,25	4	-	150	18
0,25	0,30	4	-	150	48
0,13	0,25	4	-	150	96
0,13	0,22	4	-	150	18
0,13	0,42	4	-	150	48
1,06	0,43	4	-	150	72
0,23	0,23	26,2	-	120	24
0,23	0,23	26,2	4	120	24

Muconic acid (mmol)	Zr isopropoxide (mmol)	DMF volume (mL)	Synthesis Temperature (°C)	Synthesis time (h)
0,77	0,50	4	150	18
0,75	0,50	4	150	72
0,75	0,50	4	200	96

Muconic acid (mmol)	ZrSO₄ (mmol)	DMF volume (mL)	Synthesis Temperature (°C)	Synthesis time (h)
1,50	1,00	4	150	72
1,50	1,00	4	150	24
1,50	1,00	4	150	15
1,50	1,00	4	200	72
1,50	1,00	4	200	18

Table S2-3-4. Synthesis conditions used to synthesis the Zirconium Muconate MOF, all products were amorphous under these conditions.

Table S5 : Crystal data and structure refinement parameters for **Zr muconate**.

Formula	Zr₆O₄(OH)₄[O₂C-C₄H₄-CO₂]₆.xH₂O
Chemical formula	Zr ₂₄ O ₁₂₈ C ₁₄₄ H ₁₁₂
Molar weight (g.mol ⁻¹) (dry)	6133.9
Calculated density (g.cm ⁻³) (dry)	1.13
Crystal system	Cubic
Space group	F m -3 m (n°225)
<i>a</i> (Å)	20.818(1)
<i>V</i> (Å ³)	9022.6(7)
<i>Z</i>	1
Figures of merit <i>M</i> ₂₅ / <i>F</i> ₂₅	20/20 (0.0070, 103)
Instrument	Bruker D5000
Radiation <i>λ</i> (Å)	1.540598 1.544390
Temperature (K)	293
2 <i>θ</i> range (°)	4-60
Step (°)	0.02
N. reflections	90
N. independent atoms	6 (dried phase) or 10 (hydrated)
N. intensity parameters	17
N. profile parameters	8
N. soft distance/angle constraints	13/12
<i>R</i> _p	8.8 %
<i>R</i> _{WP}	11.5 %
<i>R</i> _{Bragg}	8.9 %
Isotropic thermal factor (Å ²)	4.5
Profile function	Pseudo-Voigt
Background	Experimental (points)
N. of asymmetry parameters	2
Preferred orientation vector	None

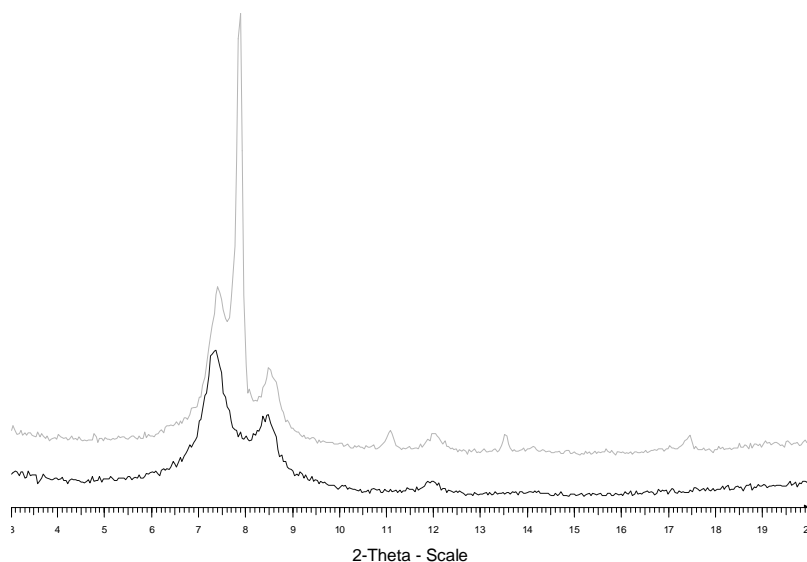


Fig. S1. XRD pattern for the Zirconium Muconate phase synthesized at room temperature (grey). Please note the presence of an organic impurity (see intense peak at 2-theta close to 7.8°) which is totally soluble in DMF. In black, the X-ray powder diffraction pattern of the same solid but soaked one hour under stirring at room temperature in DMF (black).

The Zr terephthalate (UiO-66) was synthesized using the same synthetic route (see table S6) as the one chosen for the muconate sample (Zr₆ oxocluster route). Despite a strong increase in the Bragg peaks width due to the presence of nanoparticles, x-ray powder diffraction shows (figure S2) that this solid is isostructural as the previously reported UiO-66 sample made using solvothermal conditions.²

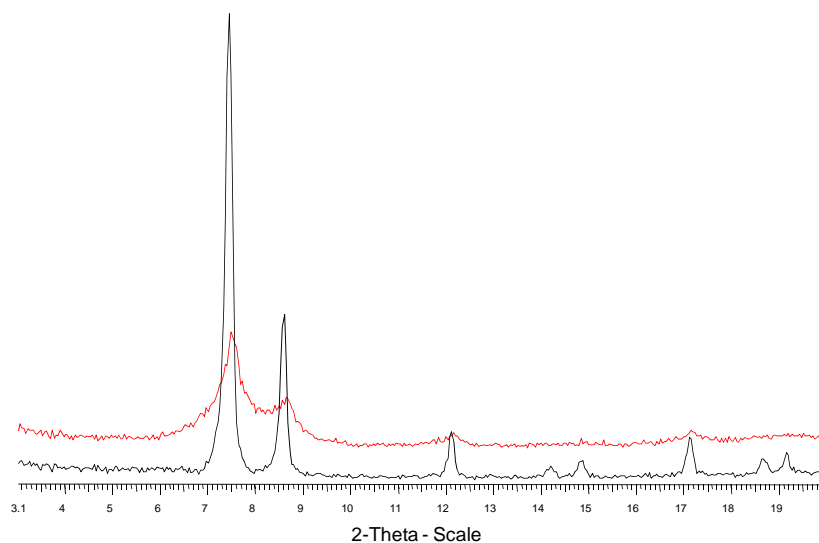


Fig. S2. XRD patterns for the UiO-66 solid synthesized from ZrCl₄ salt (black), or using the Zr₆ methacrylate oxocluster (red) ($\lambda_{Cu}=1.5406\text{\AA}$).

Terephthalic acid (mmol)	Zr ₆ cluster (mmol)	DMF volume (mL)	Synthesis Temperature (°C)	Synthesis time (h)
0,35	0,590	4	100	24

Table S6. Synthesis conditions used for the synthesis of the UiO-66 terephthalate solid starting from the Zr₆ oxocluster.

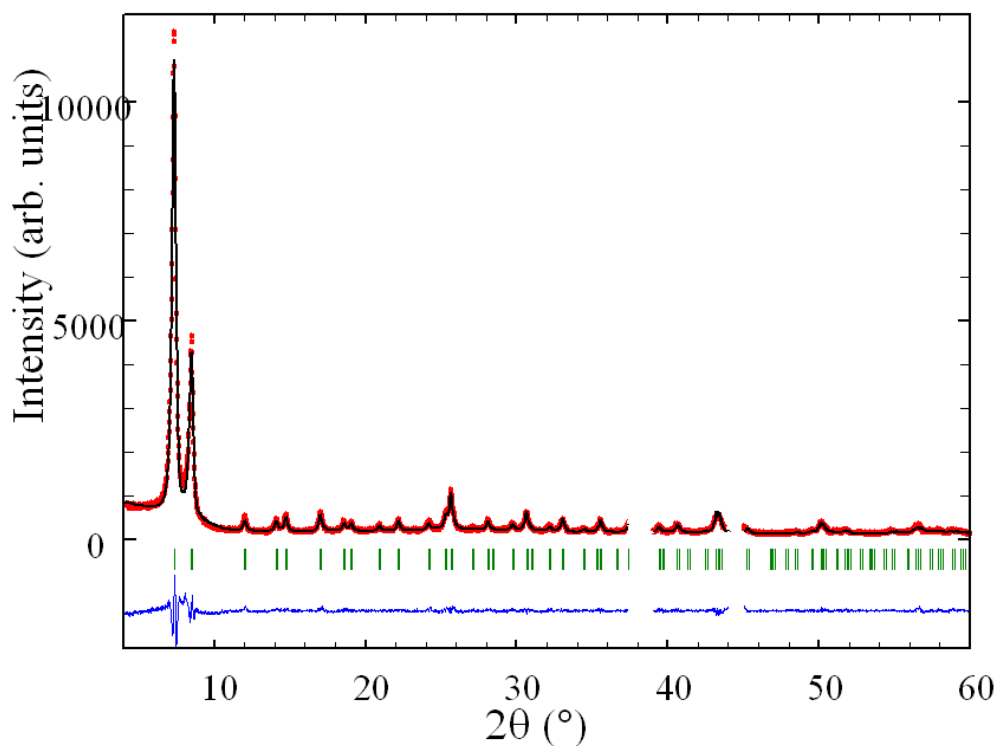


Figure S3 : final Rietveld plot of the Zr muconate solid ($\lambda_{Cu}=1.5406\text{\AA}$).

B) X-Ray Thermodiffraction measurements.

The title sample was dispersed in ethanol on a platinum plate at room temperature. Experiment was performed using a D5000 Bruker thermodiffractometer equipped with a temperature chamber.

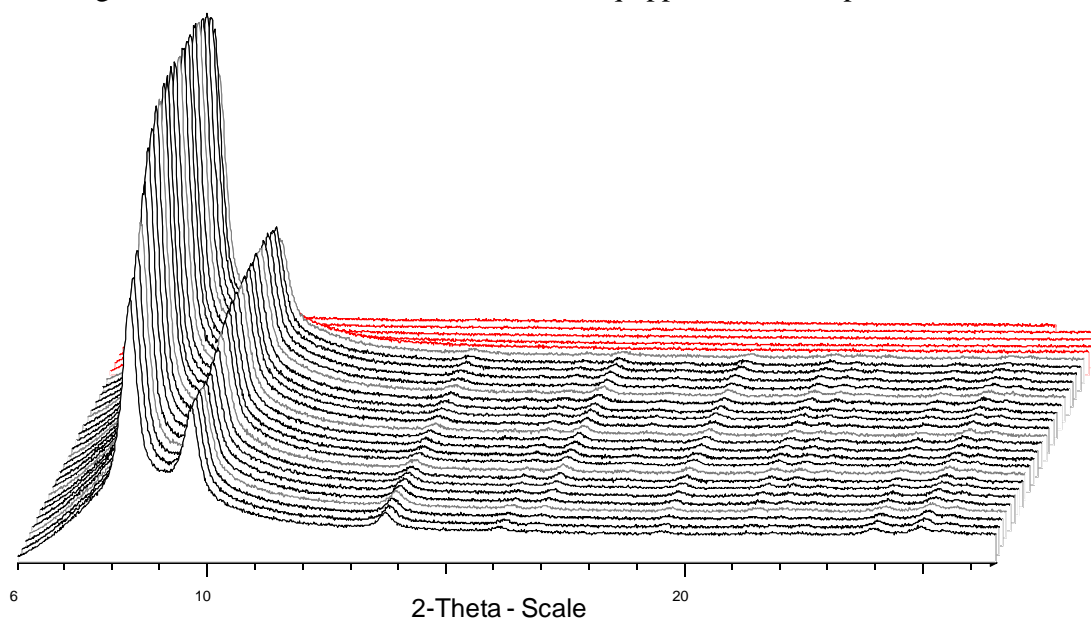


Fig. S4. X-Ray thermodiffractiongram of the Zirconium Muconate under air atmosphere ($\lambda_{Co}=1.7906\text{\AA}$). Data was collected every 50°C with red colour standing for the degradation product at higher temperatures.

C) Thermal analysis

Thermogravimetric analysis on the Zr Muconate (as-synthesized) shows a significant weight-loss over three different steps (figure S5). The first weight-loss, between room temperature and 80°C can be attributed to the loss of adsorbed water. The second step between 100°C and 150°C can be attributed to the loss of DMF from within the pores of the material.

The third step, above 250°C, is owing to the thermal degradation of the material, with a loss of the organic part (exp. 46.9%, calc. 44.7%). The remaining mass (exp. 33.95%, calc. 39.1%) is attributed to ZrO₂. This temperature is in agreement with the thermal behavior deduced from the x-ray thermodiffraction experiment.

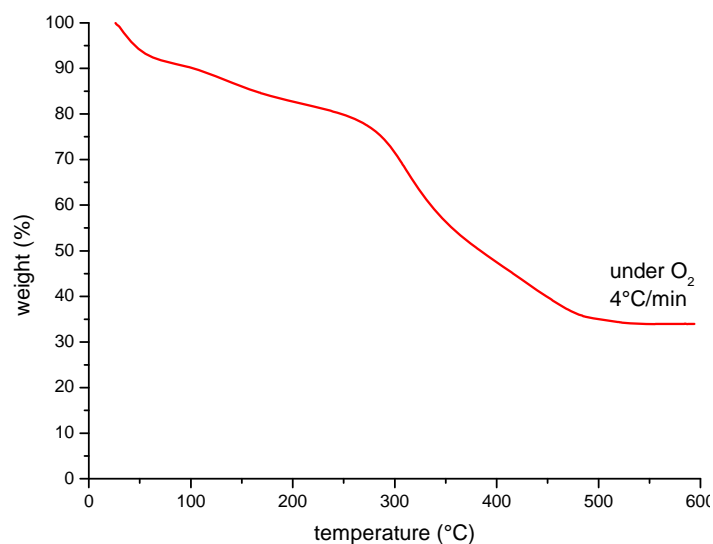


Fig. S5. TGA of the Zirconium Muconate under air atmosphere (heating rate of 4°C/minute).

D) Porosimetry

Zirconium Muconate

The BET surface area is calculated to be 705 m²g⁻¹, this not as large as expected, thought to be due to the difficulties to remove the DMF without degradation of the sample.

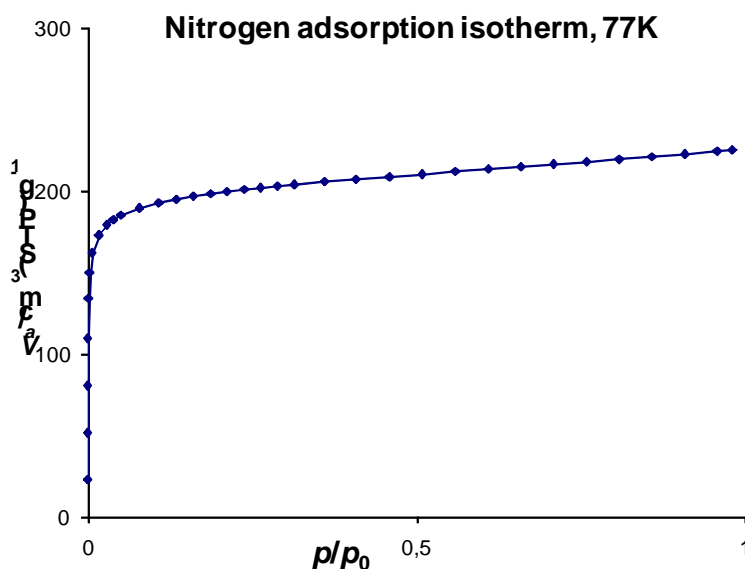


Fig. S6. Nitrogen adsorption isotherm on the Zirconium muconate, at 77K (P₀=1atm.).

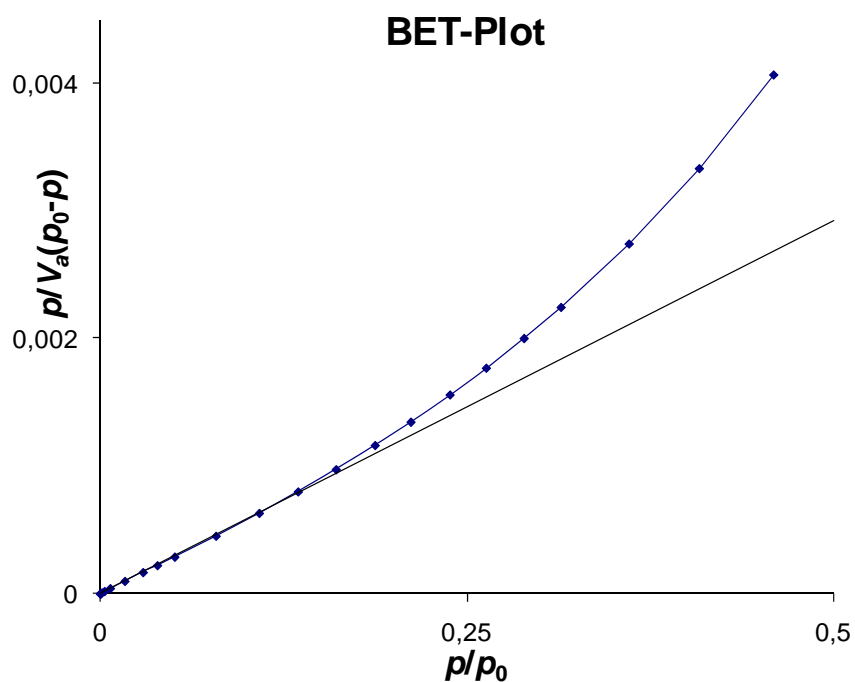


Fig. S7. BET plot for the nitrogen adsorption isotherm on the Zirconium muconate, at 77K.

Starting point	1	
End point	17	
Slope	0,0061845	
Intercept	-8,6315E-06	
Correlation coefficient	0,9991	
V_m	161,92	[cm ³ (STP) g ⁻¹]
$a_{s,BET}$	704,76	[m ² g ⁻¹]
C	-715,5	
Total pore volume ($p/p_0=0.981$)	0,3481	[cm ³ g ⁻¹]
Average pore diameter	1,9758	[nm]

Table. S7. BET calculations for the nitrogen adsorption isotherm on the Zirconium muconate, at 77K.

Zirconium terephthalate (UiO-66)

The BET surface area is calculated to be $904 \text{ m}^2\text{g}^{-1}$, this not as large as expected, thought to be due to the difficulties to remove the DMF without degradation of the sample.

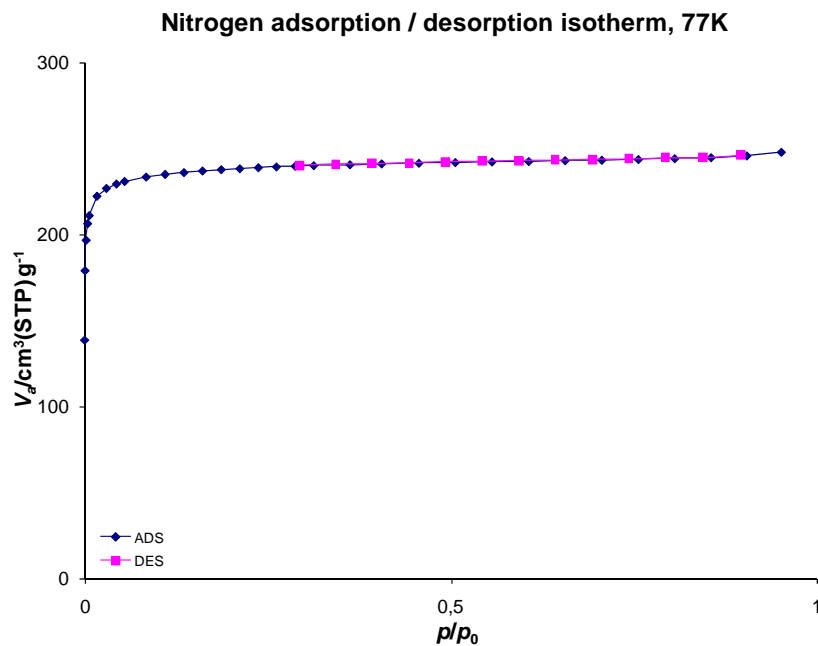


Fig. S8. Nitrogen adsorption isotherm on the Zirconium terephthalate, at 77K.

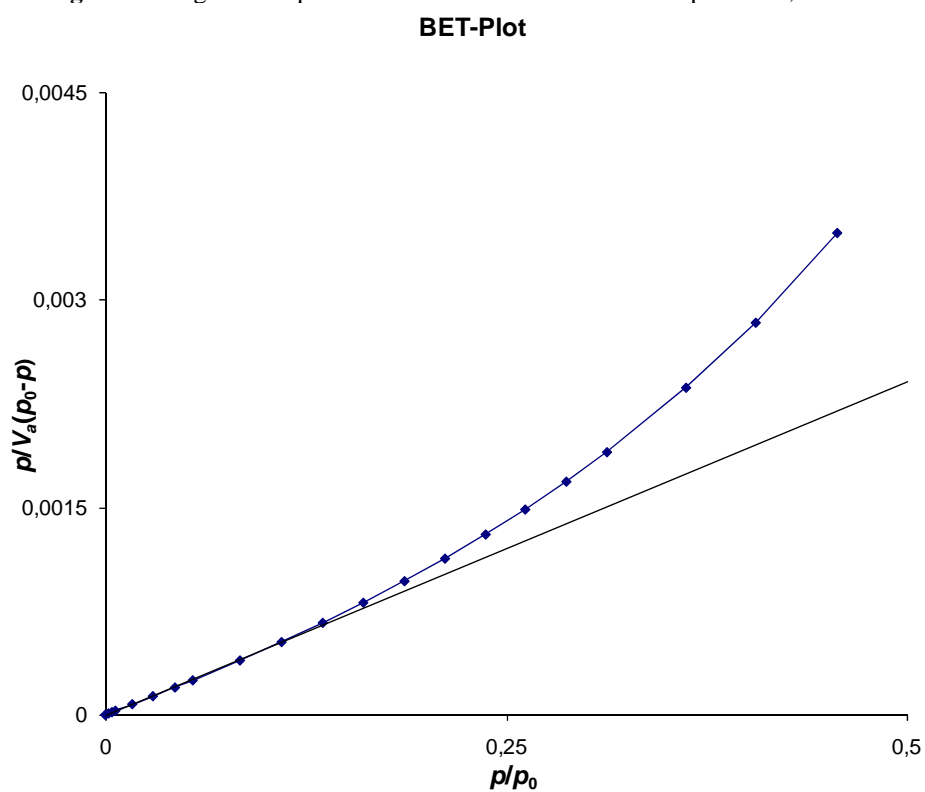


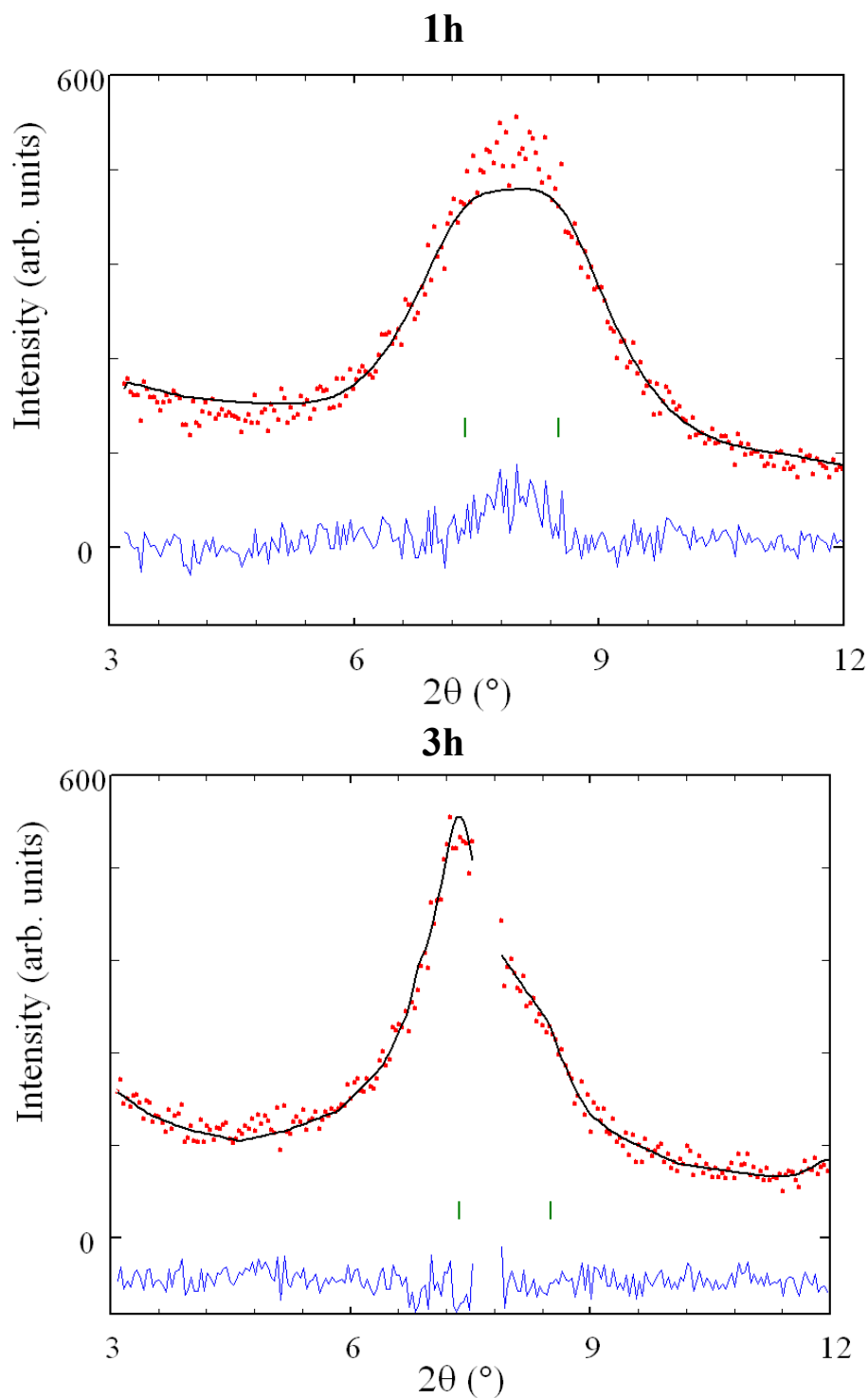
Fig. S9. BET plot for the nitrogen adsorption isotherm on the Zirconium terephthalate, at 77K.

Starting point	1	
End point	17	
Slope	0,0048157	
Intercept	-2,6208E-06	
Correlation coefficient	0,9996	
V _m	207,77	[cm ³ (STP) g ⁻¹]
a _{s,BET}	904,3	[m ² g ⁻¹]
C	-1836,5	
Total pore volume ($p/p_0=0.952$)	0,3832	[cm ³ g ⁻¹]
Average pore diameter	1,695	[nm]

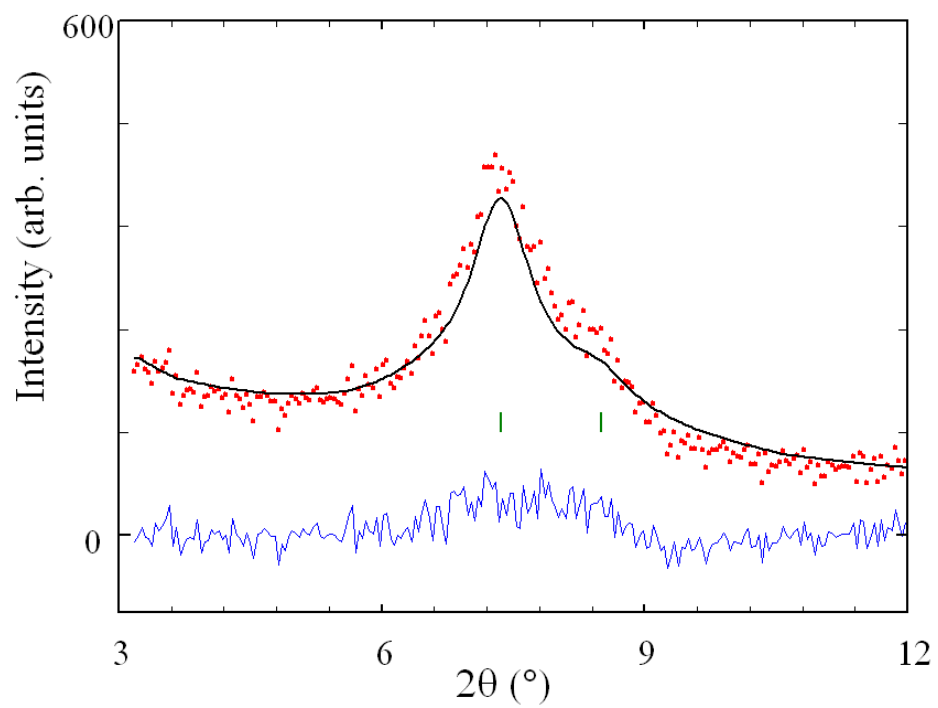
Table S8. BET calculations for the nitrogen adsorption isotherm on the Zirconium terephthalate, at 77K.

E) Particle size determination from XRPD analysis.

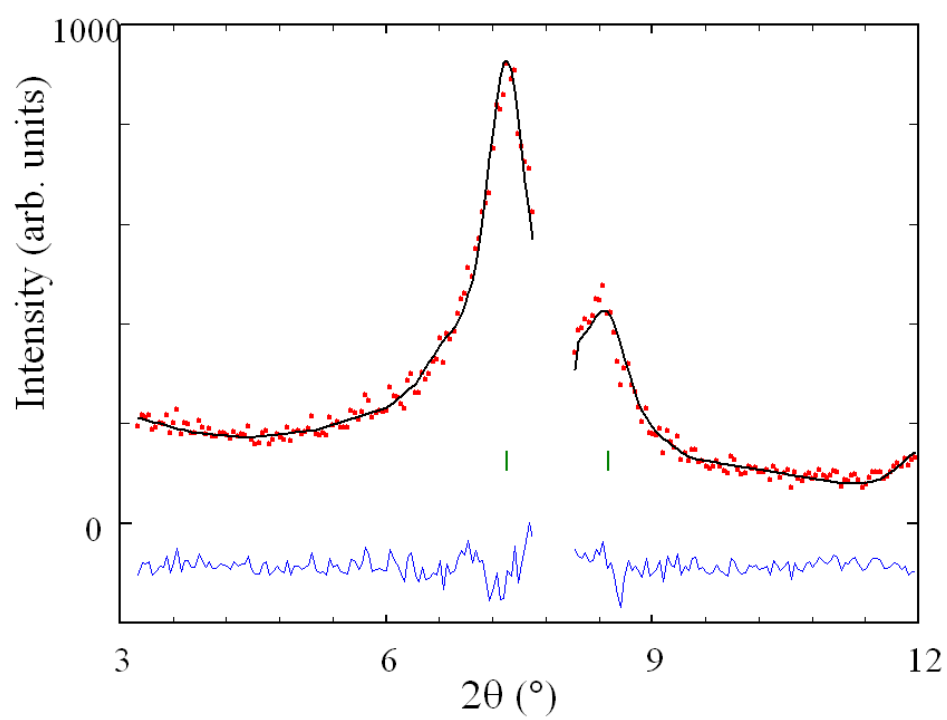
The particle size of each sample was estimated using the Debye-Scherrer equation. The following tables contain the FWHM (Full Width at Half Mid-height) and the particle size for the synthesis at 150°C & the room temperature, and also for the best UiO-66 sample obtained under conventional solvothermal synthesis. Due to presence of an unknown organic crystalline impurity which is soluble in DMF, which forms at low temperature, angular domains from 7.6° to 8.0° and from 10.9° to 11.5° have been excluded on some of the patterns. The cell parameter was kept constant (equal to 20.82Å) using only the first two Bragg peaks during the pattern matching due to the low quality of the XRPD data particularly at short synthesis times.



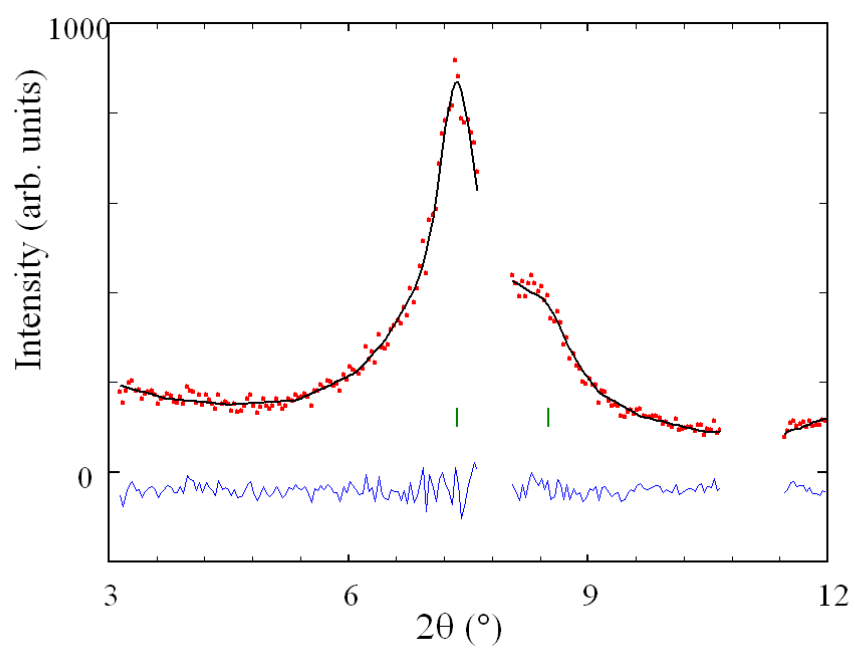
4h



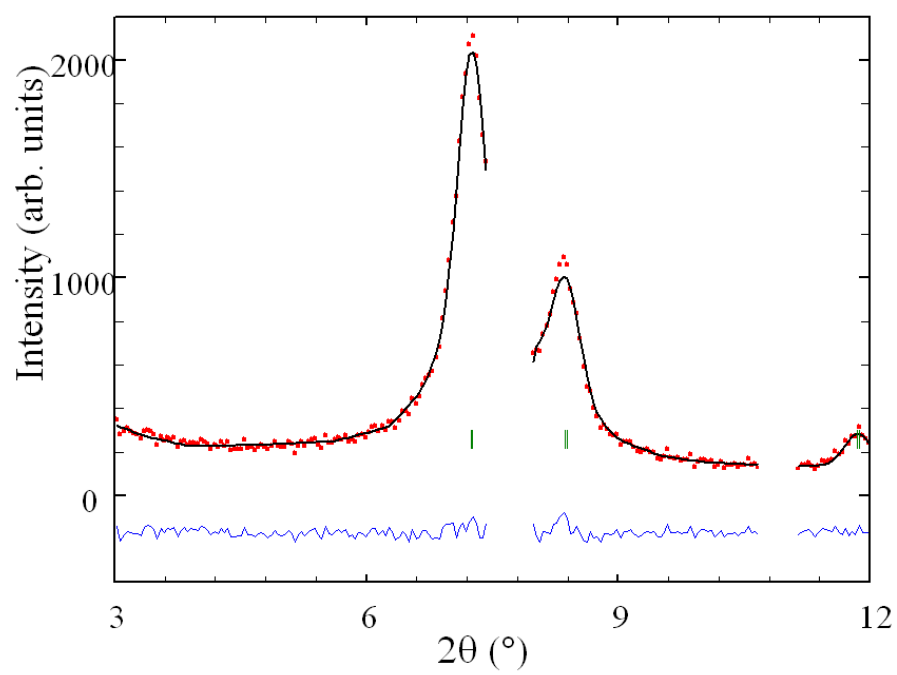
5h

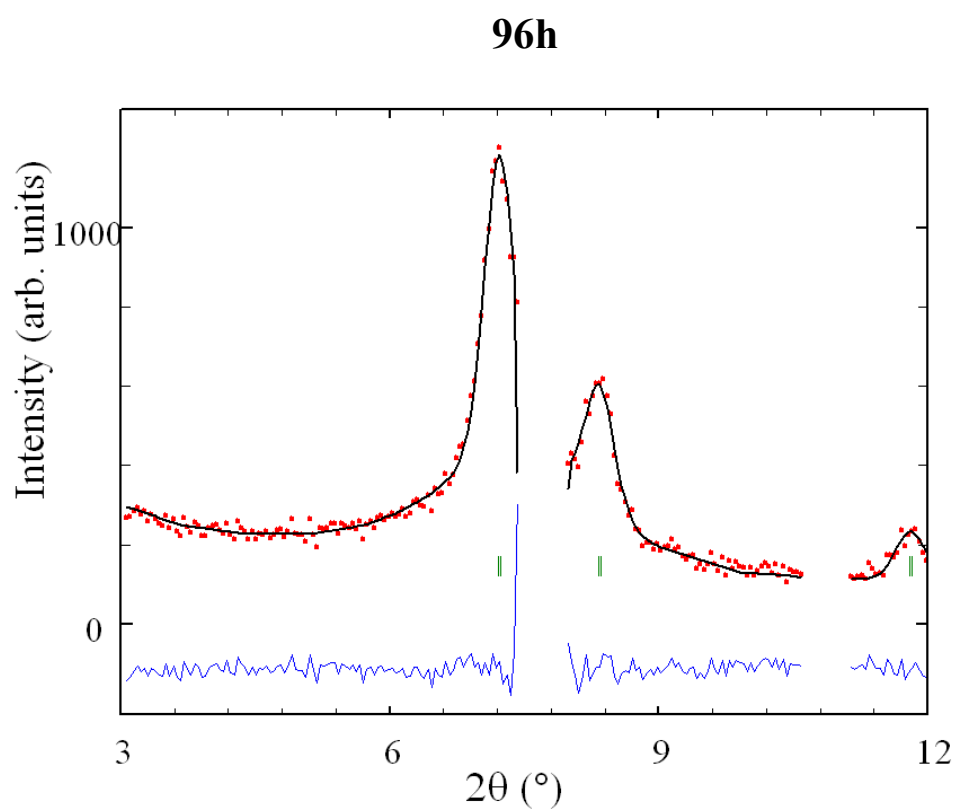
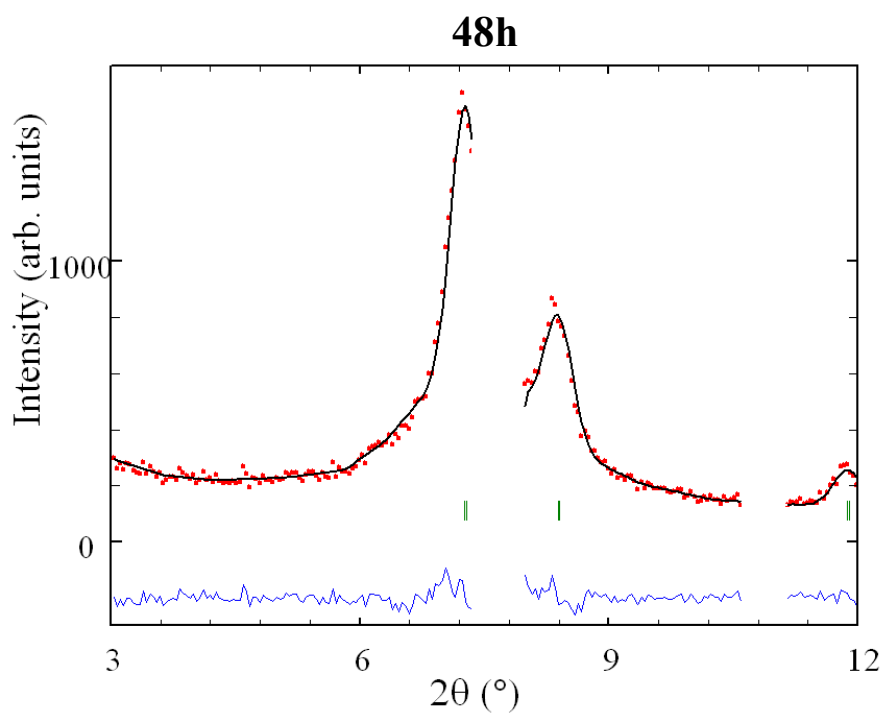


6h

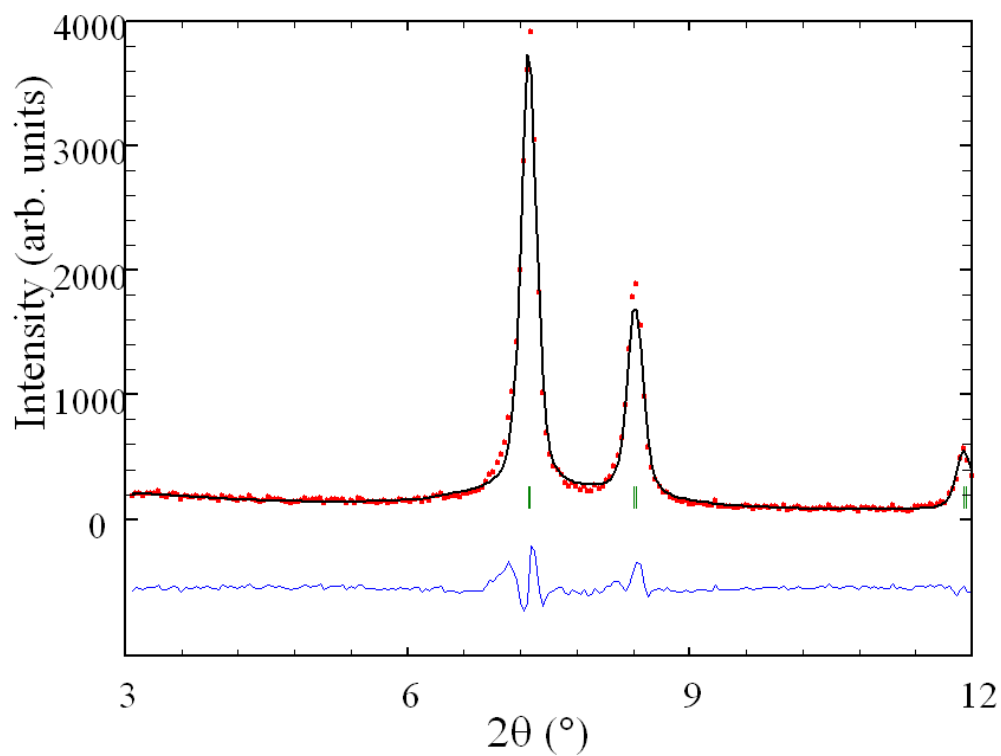


24h



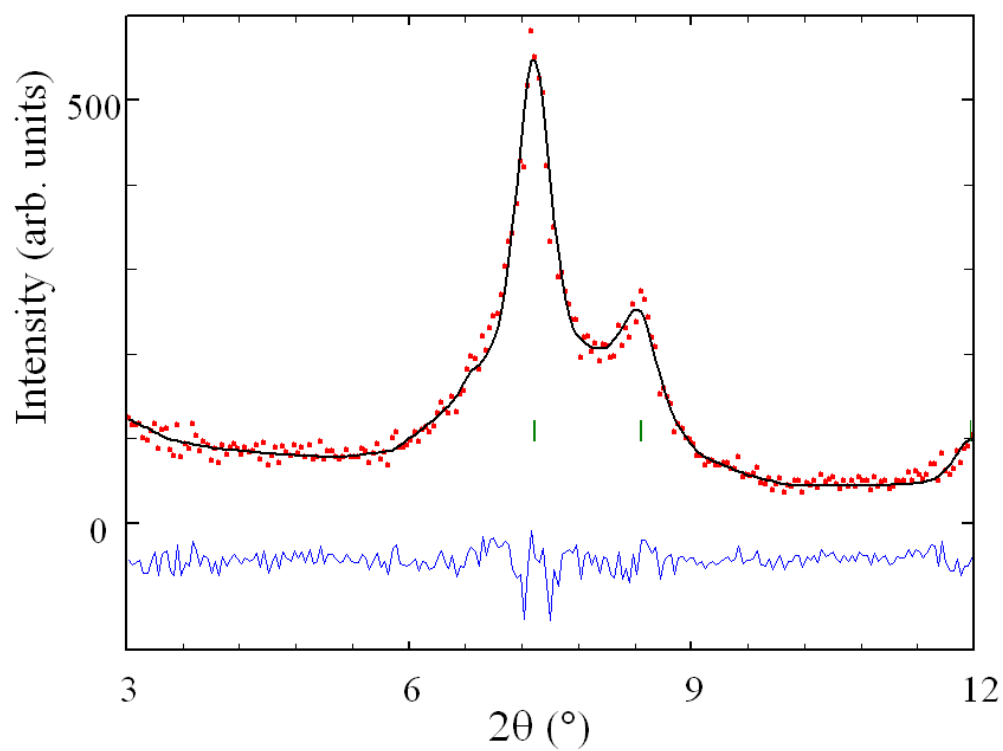


1night@150°C



Time (h)	Particle size (Å)
1	44(5)
3	85(6)
4	124(7)
5	136(7)
6	155(10)
24	192(10)
48	195(10)
96	196(10)
1 night@150°C	399(20)

UiO-66, 24h@100°C



Particle size : 187(10) Å

F) EXAFS analysis.

The EXAFS measurements were performed at beamline X1 of the Hamburger Synchrotronstrahlungslabor (HASYLAB) at DESY (Hamburg, Germany). They were performed at the Zr K-edge (17998.0 eV) using a Si(311) double crystal monochromator. The synchrotron beam current at HASYLAB (positron energy 4.45 GeV) was between 80–140 mA. All the experiments were carried out under ambient conditions at 25°C. The tilt of the second monochromator crystal was set to 40 % harmonic rejection at beamline X1. Energy resolution was estimated to be about 5 eV for the Zr-K edge. All the spectra were collected in transmission mode with ion chambers, which were filled with argon. The energy calibration of the transmission experiments was performed with the corresponding zirconium metal foil. The samples were pressed into pellets with BN with individual concentrations in order to achieve an edge jump of approximately 1.5.

Two EXAFS scans of 30 minutes each were averaged. During the whole measurement time no obvious changes could be detected in the EXAFS spectra, suggesting that no structural changes took place.

Data evaluation started with background absorption removal from the experimental absorption spectrum by subtracting a Victoreen-type polynomial.³ To determine the smooth part of the spectrum, corrected for pre-edge absorption, a piecewise polynomial was used. It was adjusted in such a way that the low-R components of the resulting Fourier transform were minimal. After division of the background-subtracted spectrum by its smooth part, the photon energy was converted to photoelectron wave numbers k . The resulting $\chi(k)$ -function was weighted with k^3 and Fourier transformed using a Hanning window function.

Adjustment of the common theoretical EXAFS expression

$$\chi(k) = \sum_j \frac{N_j}{kr_j^2} S_0^2(k) F_j(k) e^{-2k^2\sigma_j^2} e^{-2r_j/\lambda} \sin[2kr_j + \delta_j(k)]$$
 according to the curved wave formalism

of the EXCURV98 program with XALPHA phase and amplitude functions.⁴ The mean free path of the scattered electrons was calculated from the imaginary part of the potential (VPI set to -4.00 eV).

Since XALPHA phases and amplitudes were used, an amplitude reduction factor S_0^2 was necessary to account for inelastic processes.⁵ It was experimentally determined by fitting the experimental spectrum of the crystalline Zr_6 cluster with coordination numbers fixed to the crystallographic values. The obtained value of 0.68 was used for all samples in the data evaluation. An inner potential correction E_f was introduced when fitting experimental data with theoretical models that accounts for an overall phase shift between the experimental and calculated spectra.

The quality of fit is given in terms of the R-factor according to

$$R = \sum_i \frac{k^3 |\chi^{\text{exp}}(k_i) - \chi^{\text{theo}}(k_i)|}{k^3 |\chi^{\text{exp}}(k_i)|} \cdot 100\% .^6$$

The samples which were investigated by XAS (X-ray Absorption Spectroscopy) are the pure crystalline cluster and the muconate-based MOF.

The XANES (X-ray Absorption Near Edge Structure) spectra are shown in figure S10. The missing splitting of the white-line (first resonance after the edge jump) is indicative of an oxygen coordinate larger than six,⁷ as expected for a Zr_6 -cluster.

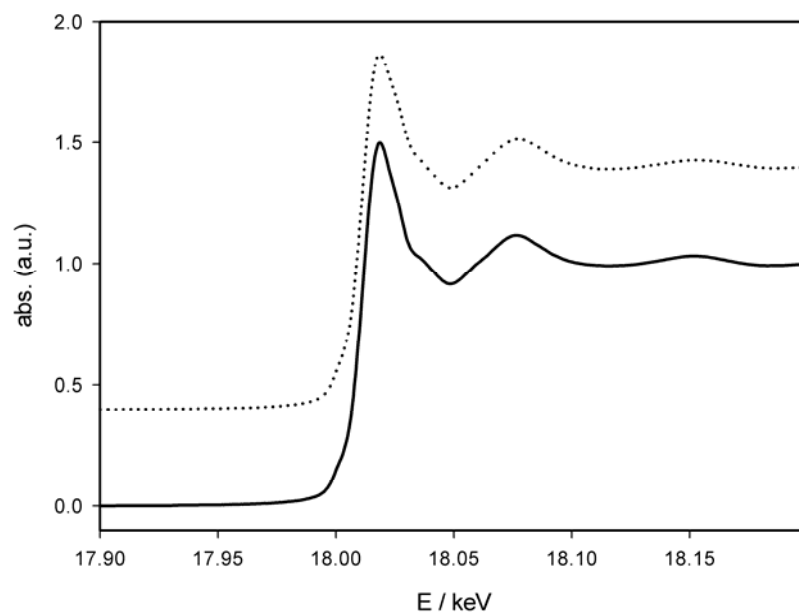


Fig. S10. XANES spectra of the crystalline Zr₆ cluster (solid line), and muconate-based MOF (dotted line). The spectra were shifted on the ordinate for clarity.

In figure S11, the EXAFS (Extended X-ray Absorption Fine Structure) spectra of the investigated samples are shown. It can be seen that the spectra of the muconate-based solid is closely related to the Zr₆ reference. Due to this close relation, the applied method for obtaining structural parameters of the MOF, is justified: the coordination numbers of the oxygen and zirconium shells during the fitting of the experimental spectra with theoretical models were set to the values of the reference compound and hold fix in order to reduce the number of adjusted parameters.

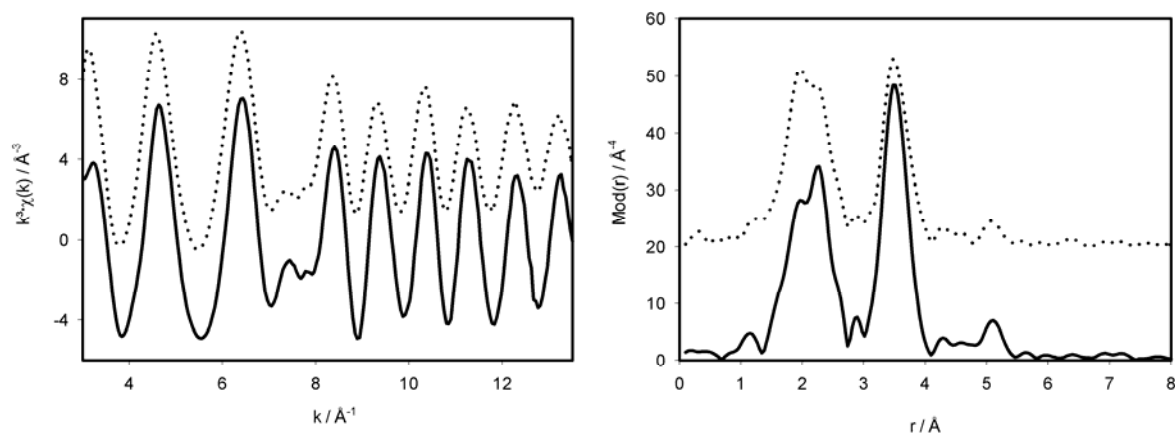


Fig. S11. The k³χ(k) spectra (left) and their corresponding Fourier transformed function (right) of the crystalline Zr₆ - reference (solid line) and of the muconate-based MOF (dotted line). Spectra were shifted on the ordinate for clarity.

Sample	Abs-Bs	N(Bs)	R / Å	σ / Å	E _f / eV	R-factor
Crystalline Zr ₆	Zr-O	2	2.07			
	Zr-O	6	2.21			
	Zr-Zr	4	3.51			
Crystalline Zr ₆	Zr-O	2	2.11 ± 0.02	0.045 ± 0.005	3.62	27.99

	Zr-O	6	2.26 ± 0.02	0.092 ± 0.009		
	Zr-Zr	4	3.52 ± 0.04	0.067 ± 0.013		
Muconate-based MOF	Zr-O	2	2.12 ± 0.02	0.050 ± 0.005	0.28	32.24
	Zr-O	6	2.27 ± 0.02	0.077 ± 0.008		
	Zr-Zr	4	3.54 ± 0.04	0.081 ± 0.016		

Table S9. Structural parameters for the investigated samples as obtained by adjustment of theoretical models to the experimental spectra. The XRD-values of crystalline Zr₆ are also given.

The results of the data analysis are given in table S9. The muconate-based MOF exhibits similar distances in comparison to the crystalline Zr₆-cluster within the error bar. The increased value of the Zr-Zr shell is the reason for the reduced intensity of this signal in the Fourier transformed functions of the muconic cluster.

Considering the XANES and EXAFS data, it can be clearly stated, that the structure of the Zr₆ cluster is conserved in the muconic cluster.

References

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