

Supporting information for

Controlling the Synthesis of Metal-Organic Framework UiO-67 by Tuning its Kinetic Driving Force

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1 Methods and instrument information

1.1 Powder X-ray diffraction

Samples were prepared using ~20 mg of the sample on a glass plate XRD sample holder by spreading it evenly and covering with transparent plastic film. The plastic film gives a small signal in the PXRD patterns observed at 2θ = ~22 ° and 34 ° as broad peaks. PXRD patterns (Cu Kα radiation, λ = 1.5418

Å, 2θ range = 2-50 °, time scale = 1, resulting in a d-spacing to 1.82 Å) were collected in reflectance Bragg-Brentano geometry with a Bruker D8 Discovery diffractometer equipped with a focusing Ge-monochromator and a Bruker LYNXEYE detector.

1.2 Thermogravimetric analysis (TGA)

TGA analysis was performed on a Netzsch STA 449 F3-Jupiter instrument, by flowing a mixture of 5 mL/min O₂ and 20 mL/min of N₂ and using a ramp rate of 5 °C/min. ~20 mg of the sample was weighed and transferred into an Al₂O₃ sample holder and the data was collected for the temperature range of 30 °C to 800 °C.

1.3 ¹H NMR Spectroscopy

Samples were prepared by weighing 20 mg of the dry sample in a centrifuging tube and adding 1 mL of 1M NaOH (in D₂O). The tubes were shaken properly to get a homogeneous suspension and kept overnight for digestion. After centrifuging the digested suspension for 15 min, 600 µL solution was pipetted to an NMR tube. This hydroxide-based procedure dissolves only the organic portion of the MOF (linker, modulator, solvent etc.), while the inorganic content is converted into mixed oxides/hydroxides of Zr that settle at the bottom of the NMR tube and do not influence the spectra. Liquid ¹H NMR spectra were obtained with a Bruker AVII 400 NMR Spectrometer (400 MHz). The relaxation delay (d1) was set to 20 seconds with 64 scans.

1.4 Scanning Electron Microscopy (SEM)

SEM images were taken on a Hitachi SU8230 Field Emission Scanning Electron Microscope (FE-SEM).

1.5 Nitrogen Sorption Measurements at 77 K

Nitrogen sorption were performed with a BelSorp mini II instrument. In each measurement, ~40 mg of the sample was weighed into a 9.001 cm³ glass cell and pretreated at 80 °C for 30 min and 200 °C for 60 minutes, under vacuum.

1.6 Vibrational characterization

Attenuated total reflectance spectra (ATR-IR) were collected with a Bruker Vertex 70 instrument, equipped with a liquid nitrogen-cooled MCT detector and a Bruker Platinum ATR accessory with diamond crystal. Before measurements, the samples were dried overnight at 200 °C in order to remove most of the solvent (DMF) and moisture. *In-situ* DRIFT-IR spectra, have been collected on the same instrument this time equipped with a Harrick Praying Mantis cell, monitoring the activation of the MOFs and interaction with CD₃CN used as probe molecule. Samples activation was performed with 10 ml/min of He flow, from RT to 300 °C with a ramp rate of 5 °C/min and kept at 300 °C for 180 min. Successively the samples were cooled at 120 °C in inert and CD₃CN vapors started to be dosed in a 10 ml/min He flow. This precaution was adopted in order to avoid samples re-hydration below 100 °C, which can interfere in the interaction between the samples and the probe molecule. Then the temperature was further lowered to 70 °C in the presence of CD₃CN vapors till the spectra stopped changing upon the CD₃CN flux. The relative stabilities of the adsorbed species were monitored during a 10 ml/min He flow overnight.

1.7 Karl Fischer titrations

Karl Fischer titrations were performed on a Schott Titroline KF titrator, using volumetric one-component HYDRANAL™ - Composite 5 titrant. The instrument was calibrated against commercial HYDRANAL™ - Water Standard 10.0. Approximately 20 mg sample sizes of DMF was dissolved in conditioned methanol (VWR, HPLC grade)."

2 Chemicals

2,2'-bipyridine-5,5'-dicarboxylic acid (H₂bpydc) was synthesized as described in the following section 3.1. 4,4'-biphenyldicarboxylic acid was bought from Fox-Chemicals whereas zirconium(IV) chloride ($\geq 99.5\%$), benzoic acid ($\geq 99.5\%$) and N,N-Dimethylformamide ($\geq 99.8\%$) were bought from Merck. All the chemicals were used as it is, without further purification.

3 Synthesis procedures for linker and MOFs

3.1 Synthesis of 2,2'-bipyridine-5,5'-dicarboxylic acid (H₂bpydc) linker

In a 25 ml beaker glass, 6.0 g HNO₃ (aq) (65 %) was slowly added to 9.0 mL deionized water to obtain 26 wt.% HNO₃. 1.50 g 5,5'-dimethyl-2,2'-bipyridine was added and quickly dissolved in the acid. The solution was transferred to a 25 ml Teflon-lined autoclave which was heated to 160 °C and kept at that temperature for 16 hours. The autoclave was allowed to slowly cool to room temperature before opening. A crystalline, weakly yellow powder was isolated by filtration and then washed 5 times with approximately 50 ml portions of water. The filtrate was cooled to 0 °C and carefully brought to pH 7 by addition of saturated NaHCO₃ solution, at which a weakly yellow precipitate was formed. This solid was isolated by filtration and washed in the same manner as above. ¹H-NMR confirmed the two solids were both pure H₂bpydc. The yield was 1.74 g (92 %). Crystals of H₂bpydc suitable for single crystal XRD were obtained directly from the autoclave. A complete data set was acquired on a Bruker D8 Venture equipped with a Photon 100 detector and using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Data reduction was performed with the Bruker Apex3 Suite,¹ the structure was solved with ShelxT,² and refined with ShelXL.³ Olex2 was used as user interface.⁴ The crystallographic data for this compound has been reported in CCDC 1541993.

3.2 General approach to synthesize UiO-67

UiO-67 was synthesized via a simple one-pot reaction in DMF at 130 °C, using benzoic acid and water as additives. Zirconium chloride was added to the mixture of 0.46 mL distilled water (3 eq) and DMF at room temperature on a stirring plate. This solution was heated and benzoic acid was added, waited until completely dissolved and then added the linker. The solution was transferred to a round bottom flask and heated at 130 °C, overnight with stirring under reflux. A white powder was obtained which was filtered and washed with hot DMF and acetone, followed by drying at 150 °C, overnight. Details about the precise amounts can be found in the following sections.

3.2.1 Synthesis of UiO-67-bpy_{0.1}

UiO-67-bpy_{0.1} was synthesized in DMF at 130 °C, using benzoic acid and water as additives, similarly as described in the general approach. 2 g of Zirconium chloride (1 eq) was added to the mixture of 0.46 mL distilled water (3 eq) and 33.2 mL DMF (50 eq) at room temperature on a stirring plate. This solution was heated and 1.869 g bpdc linker (0.9 eq) and 0.209 g of bpy linker (0.1 eq) was added, together. The solution was transferred to a round bottomed flask and heated at 130 °C, overnight with stirring under reflux. Thus obtained slight yellow coloured powder was filtered and washed with hot DMF and acetone, followed by drying at 150 °C, overnight.

4 Preliminary screening

The preliminary screening was done such that the parameters given in Table S 1 are varied, as described below. The synthesis of the MOF was done at Zr:DMF as 1:300. These sample were subjected to inspect thermal stability. The thermal stability tests were done by heating the samples at 450 °C for 2 hours and recording the XRD.

Table S 1 Synthesis parameters for the initial high-throughput synthesis.

Synthesis parameter	Parameter value
Solvent amount (DMF:Zr) (molar eq w.r.t.to Zr moles)	300, 100, 50, 35, 20
Modulator type	Benzoic acid, acetic acid
Modulator amount (molar eq w.r.t.to Zr moles)	0, 3, 6, 9, 12, 15
Additives	HCl, H ₂ O
Temperature (°C)	120, 130, 140

4.1 Procedure

503 μ L of water (3 eq) was added to a beaker containing 216 mL of DMF (300 eq) and a magnet. 2.167 g of zirconium chloride was added at room temperature and the solution was heated to 110 °C, under stirring. The solution was transferred to 12 beakers (18 mL each) labelled 0 Ac, 3 Ac, 6 Ac, 9 Ac, 12 Ac, 15 Ac, 0 BA, 3 BA, 6 BA, 9 BA, 12 BA and 15 BA, where Ac and BA stands for acetic acid and benzoic acid, respectively. Acetic acid and benzoic acid was added to the 12 beakers according to Table S 2, followed by 0.188 g of bpdc. The solution of each beaker was divided into three test tubes (6 mL each) and closed loosely with a teflon cap. Thus obtained three group of 12 test tubes called set W was kept at 120 °C, 130 °C and 140 °C, overnight. The white solid was collected by centrifugation and washed with acetone and dried overnight at 150 °C. The above procedure was repeated to obtain Set H by adding 658 μ L of hydrochloric acid (3 eq) instead of water.

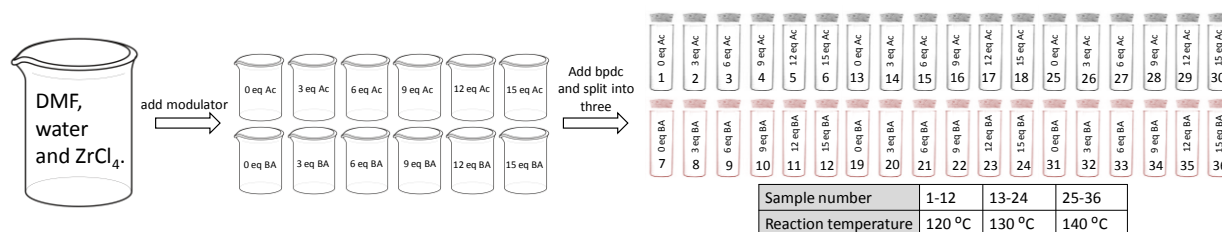


Figure S 1 Schematic representation of the formation of 36 reactions of set W. Similarly, set H was made by adding HCl instead of water giving rise to another 36 samples.

Table S 2 Amount of modulator used to make set W and set H.

Entry	Modulator	Amount of modulator to be added					
		0 eq	3 eq	6 eq	9 eq	12 eq	15 eq
1	Ac (μ L)	-	133	266	399	532	665
2	BA (g)	-	0.284	0.568	0.862	1.136	1.420

4.2 Preliminary screening results

In 2013, Farha et al.⁵ extensively explored the utility of hydrochloric acid in the synthesis of UiO-66 and extended the results to UiO-67 and UiO-type MOFs. They demonstrate that hydrochloric acid enhances the solubility of ZrCl₄ in DMF and speeds up the product formation, regardless of reaction time and reaction temperature (60 °C to 120 °C) and propose either HCl neutralizes the basic impurities like amines in DMF and/or it assists in zirconium cluster formation before the linker attaches. We began with two sets of 36 trial reactions to synthesize UiO-67 (Section S4.1.) by varying i) Additive- water and HCl (35 %) ii) Reaction temperature (120 °C /130 °C /140 °C), iii) Modulator (acetic acid and benzoic acid) and iv) Amount of modulator (0 to 15 equivalent, in the interval of 3). The amount of solvent (DMF: 300 eq) and linker (H₂bpdc: 1 eq) were kept fixed. Each of this set was called set H and set W which contains 3 eq of HCl and water, respectively. Each set was divided into three subsets (12 samples each) according to the temperatures they were synthesized i.e. 120 °C, 130 °C and 140 °C. Further, the uncommon factors within the subsets were the modulator (acetic acid or benzoic acid) and the amount of modulator (0 to 15 eq), as described in section S4.1. Powder X-ray diffraction pattern were taken

for set H and set W, presented in Figure S 2 and Figure S 3 and the crystallite size was estimated by refining the diffractograms using TOPAS rietveldt refinement against an ideal UiO-67 structure (Table S 3 and Figure S 4). Firstly, set W shows sharp high intensity peaks as compared to set H, which correlates with the estimated particle size. High intensity sharp peaks of XRD are attributed to bigger and distinctive particles. Set W has particles in the range of 10 to 370 nm whereas the particles in set H are upto 100 nm only. Although modulators facilitate the crystal formation by slowing down the rate of formation of particles, strong acids have the tendency to protonate the linker which acts as a barrier in particle formation.⁶

4.3 Thermal stability tests

Set W and set H were heated for 2 hours at 450 °C and recorder XRD to check their thermal stability (Figure S 2 and Figure S 3). The material has been highly affected by heating at high temperature and most of the sample lose crystallinity as seen by the loss of peaks in XRD. PXRD refinement for for the samples which sustained crystallinity and their crystal size regularity decrease (Table S 3). The set W now have the crystal size in the range of 10 to 270 nm and set H has particles mostly upto 20 nm with the exception of two sample having 90 and 100 nm size. In our results addition of HCl did not give any better result and in addition, UiO-67 made in the presence of 3 eq water has better resistivity for thermal treatment. This suggests that water plays a crucial role in the particle formation whereas HCl has a poor modulating affect which is in good agreement with other reports.⁷⁻⁹ Secondly, XRD of the set W synthesized at 130 °C (sample 13-24), showed to be most resistant to the thermal treatment suggesting that 130 °C is a suitable reaction temperature. It is interesting to note that sample 1, 7, 13, 19, 25, 31 in both the sets (set W and set H) are synthesized identically as they have no modulator in them, but still the XRD is not identical which highlights that without the use of modulators, reproducibility of synthesis of UiO MOFs is challenging.⁷ These preliminary results narrows our work and for simplicity, we chose one sample as a starting criteria i.e. 9 eq benzoic acid, 3 eq water and 300 eq DMF at 130 °C.

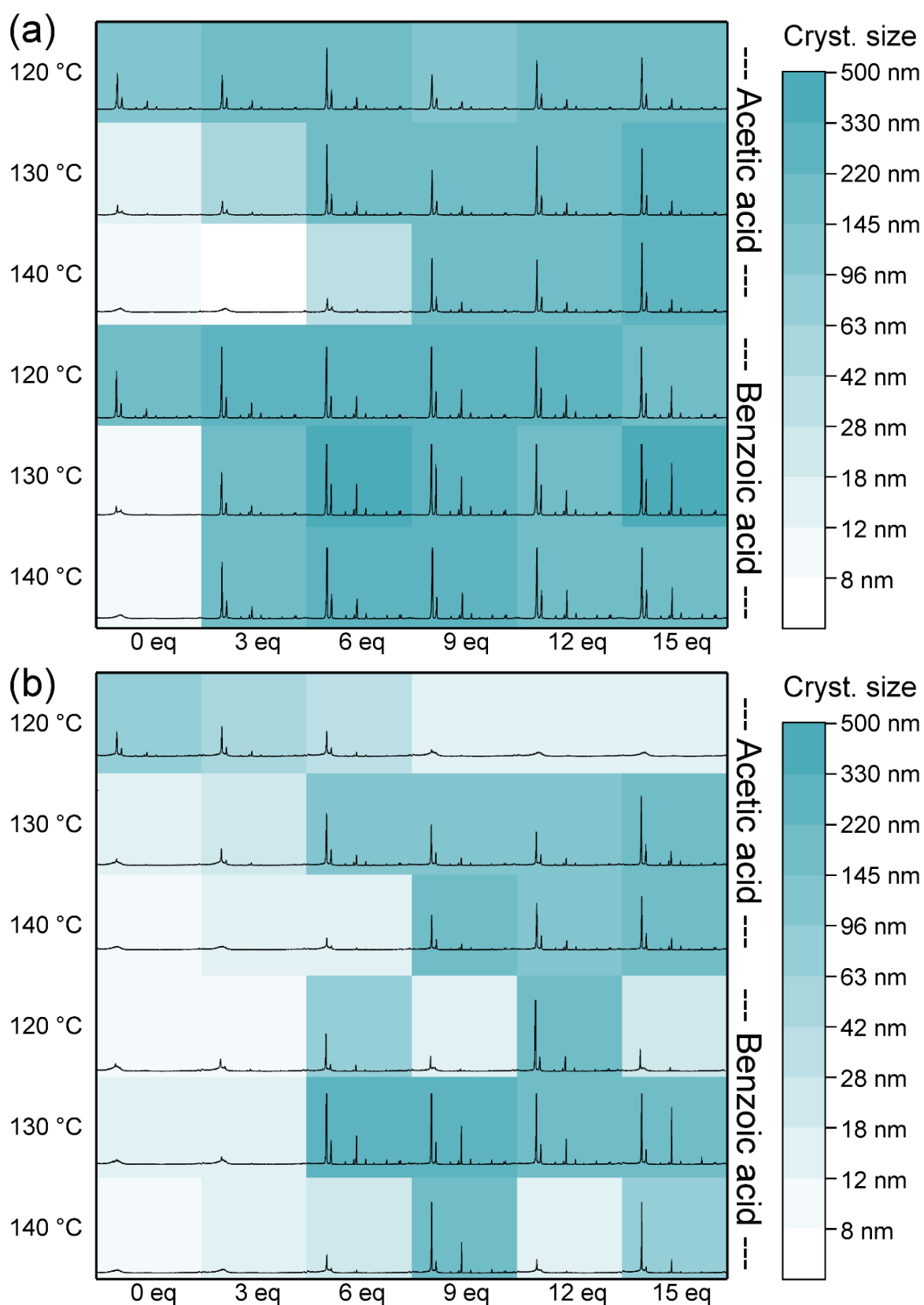


Figure S 2 PXRD patterns of set W (using water as an additive as opposed to HCl). Samples 1-12 were synthesized at 120 °C, 12-24 at 130 °C and 25-36 at 140 °C. The variation in background colour indicates the estimated particle size. (a) shows patterns of the UiO-67 as synthesized. (b) shows patterns of the same samples after a thermal stability tests were the samples were kept for 2 hours in air at 450 °C.

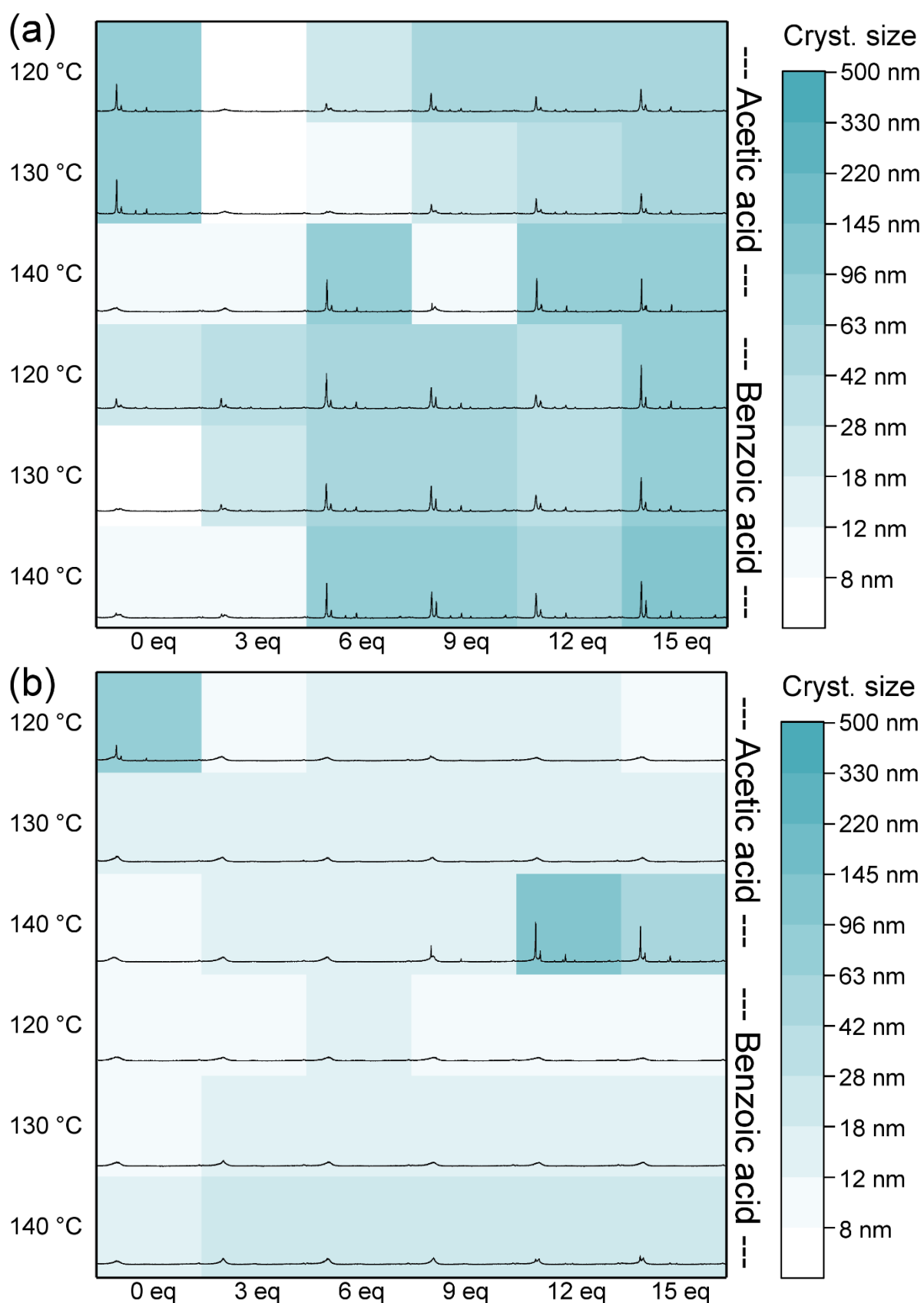


Figure S 3 PXRD patterns of set H (using HCl as an additive as opposed to water). Samples 1-12 were synthesized at 120 °C, 12-24 at 130 °C and 25-36 at 140 °C. The variation in background colour indicates the estimated particle size. (a) shows patterns of the UiO-67 as synthesized. (b) shows patterns of the same samples after a thermal stability test where the samples were kept for 2 hours in air at 450 °C.

Table S 3 Estimated particle size of UiO-67 synthesized with water and HCl as additive and thermally tested at 450 °C for 2 hours.

Number	UiO-67 with water as additive (Figure S 2a) (nm)	UiO-67 with water as additive, thermally tested at 450 °C for 2 hours (Figure S 2b) (nm)	UiO-67 with HCl as additive (Figure S 3a) (nm)	UiO-67 with HCl as additive, thermally tested at 450 °C for 2 hours (Figure S 3b) (nm)
1	101	82	74	89
2	152	54	7	11
3	177	38	25	14
4	110	13	43	14
5	155	14	44	13
6	145	13	46	10
7	152	12	27	9
8	221	10	34	11
9	267	73	49	13
10	243	13	55	11
11	230	147	35	11
12	211	22	89	10
13	16	17	80	15
14	59	22	7	14
15	163	125	8	18
16	174	101	25	18
17	212	119	39	15
18	253	161	52	15
19	8	13	7	12
20	158	15	24	18
21	371	265	57	14
22	282	255	60	15
23	196	191	35	15
24	371	203	72	15
25	10	12	10	9
26	7	13	8	15
27	34	14	73	14
28	169	154	8	18
29	184	144	75	100
30	219	192	91	53
31	10	12	8	15
32	178	13	8	21
33	229	24	92	19
34	232	179	68	23
35	216	16	56	20
36	189	64	96	20

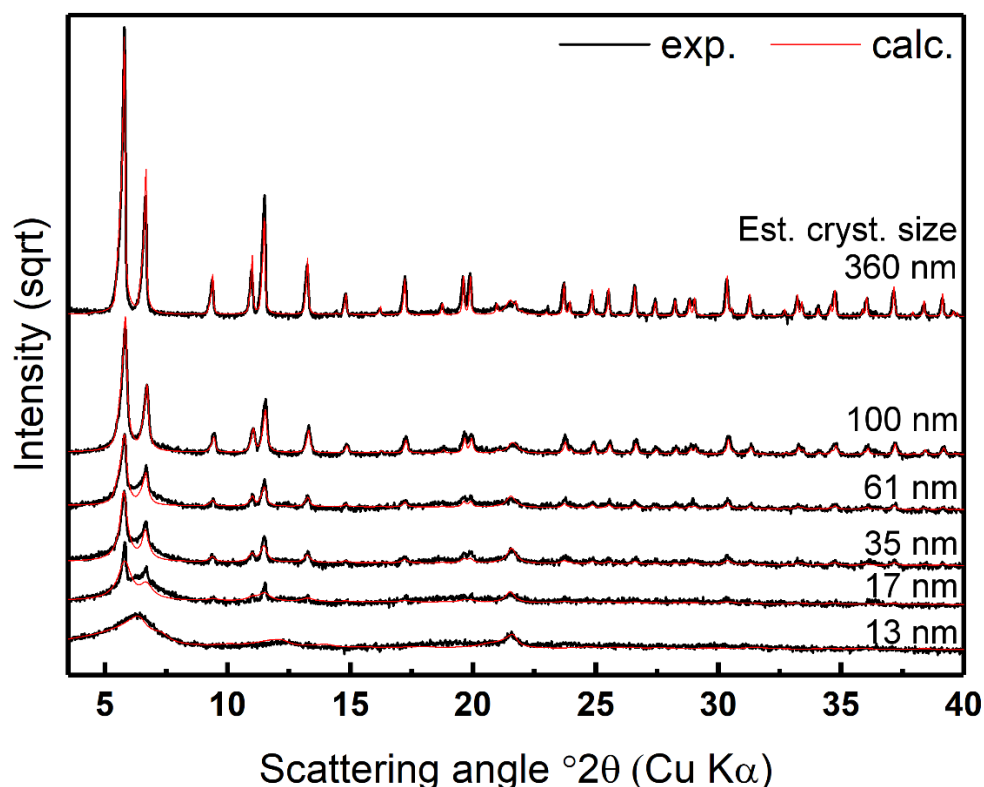


Figure S 4 Examples of estimated sizes from PXRD refinement. Note that the y-scale shows the square root of the diffraction signal to better accommodate the low and high intensity portions of the patterns in the same figure. Acquired patterns are shown in bold black lines, and the best fits are shown as thin red lines.

5 Screening for Zr:DMF:BA

5.1 Screening of Zr:DMF ratio

This was done by preparing a set of 5 experiments where amount of DMF was screened with 20, 35, 50, 100 and 300 eq and other parameters as constant; Zr: 1 eq, bpdcc: 1 eq, water: 3 eq, benzoic acid: 9 eq at 130 °C.

Table S 4 Amount of reagents used in the screening of Zr: DMF.

Entry	ZrCl ₄ (g)	Bpdcc (g)	H ₂ O (mL)	Benzoic acid (g)	DMF (mL)
1	2	2.078	0.46	9.4	13.3
2	2	2.078	0.46	9.4	23.3
3	2	2.078	0.46	9.4	33.3
4	2	2.078	0.46	9.4	66.5
5	2	2.078	0.46	9.4	199.4

5.2 Screening of amount of benzoic acid for concentrated synthesis

This was done by preparing a set of 6 experiments where benzoic acid was screened using 0 eq, 3 eq, 6 eq, 9 eq, 12 eq and 15 eq with other parameters as constant; Zr: 1 eq, bpdcc: 1 eq, water: 3 eq and DMF: 50 eq at 130 °C. They were labelled as C-x_{BA} where x ranges from 0 to 15 depending on amount of benzoic acid used in the preparation of the sample and C stands for concentrated synthesis.

Table S 5 Amount of reagents used in the screening of amount of benzoic acid for 50 eq DMF (concentrated synthesis).

Entry	Label	ZrCl ₄ (g)	Bpdc (g)	H ₂ O (mL)	Benzoic acid (g)	DMF (mL)
1	C-0 _{BA}	2	2.078	0.46	0	33.3
2	C-3 _{BA}	2	2.078	0.46	3.14	33.3
3	C-6 _{BA}	2	2.078	0.46	6.29	33.3
4	C-9 _{BA}	2	2.078	0.46	9.43	33.3
5	C-12 _{BA}	2	2.078	0.46	12.08	33.3
6	C-15 _{BA}	2	2.078	0.46	15.72	33.3

5.3 Screening of amount of benzoic acid for dilute synthesis

This was done by preparing a set of 7 experiments where benzoic acid was screened using 0 eq, 3 eq, 6 eq, 9 eq, 12 eq, 15 eq and 18 eq with other parameters as constant; Zr: 1 eq, bpdc: 1 eq, water: 3 eq and DMF: 300 eq at 130 °C. They were labelled as D-x_{BA} where x ranges from 0 to 18 depending on amount of benzoic acid used in the preparation of the sample and D stands for dilute synthesis.

Table S 6 Amount of reagents used in the screening of amount of benzoic acid for 300 eq DMF (diluted synthesis).

Entry	Label	ZrCl ₄ (g)	Bpdc (g)	H ₂ O (mL)	Benzoic acid (g)	DMF (mL)
1	D-0 _{BA}	2	2.078	0.46	0	33.3
2	D-3 _{BA}	2	2.078	0.46	3.14	33.3
3	D-6 _{BA}	2	2.078	0.46	6.29	33.3
4	D-9 _{BA}	2	2.078	0.46	9.43	33.3
5	D-12 _{BA}	2	2.078	0.46	12.08	33.3
6	D-15 _{BA}	2	2.078	0.46	15.72	33.3
7	D-18 _{BA}	2	2.078	0.46	18.87	33.3

6 Screening of the Zr:DMF ratio

In the generally reported synthesis procedure (1:300 ratio for Zr:DMF), H₂bpdc completely dissolves shortly after addition, before the precipitation of a white solid occurs when MOF particles are formed. Previous work in our group suggests that solubility of H₂bpdc with respect to DMF is approximately 1:150-200 at synthesis temperature, but this lacks a systematic detailed study. It is dependent on temperature and the presence of water and modulator. In this screening, UiO-67 synthesis was attempted using the following Zr: DMF ratio; 1: 20, 1:35, 1:50, 1:100 and 1:300. A white solid was obtained in all syntheses and washed with 10 times excess hot DMF (~ 140 °C) and acetone (room temperature) and dried overnight at 150 °C. Note that the optimization of the washing was not the subject of interest in this work. Interestingly, PXRD patterns of the obtained materials revealed that it is possible to synthesize UiO-67 with as low as 1: 50 ratio with respect to H₂bpdc and Zr but below that, no MOF formation was observed (Figure S 5). The PXRD pattern of the white solid obtained from the syntheses with 1:35 and 1:20 matches the pattern of pure H₂bpdc linker.

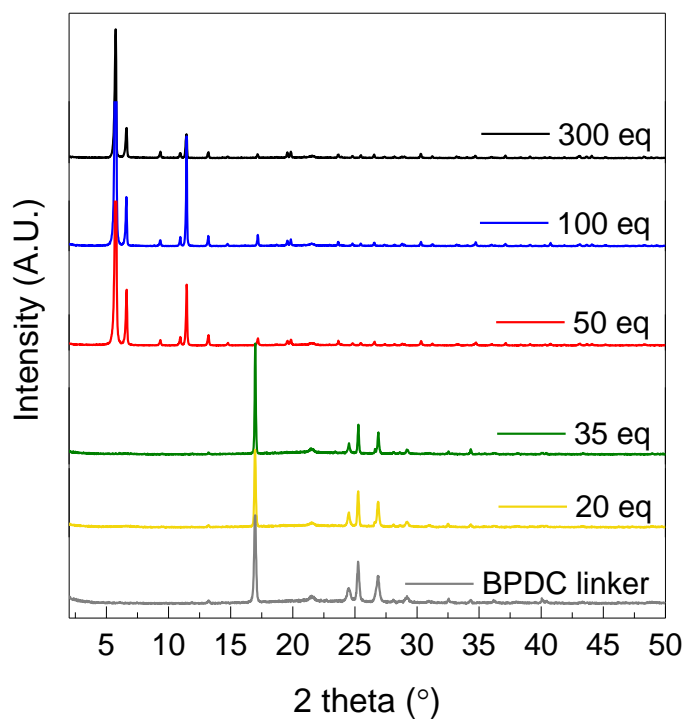


Figure S 5 XRD of the UiO-67 made with different concentrations of DMF.

7 Particle size determination by peak fitting in TOPAS

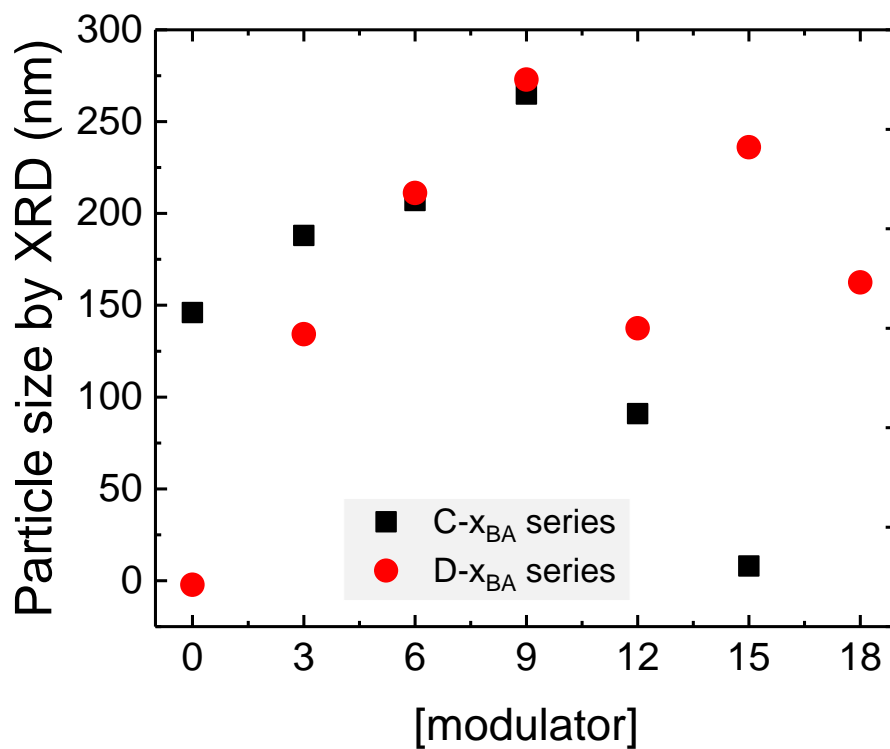
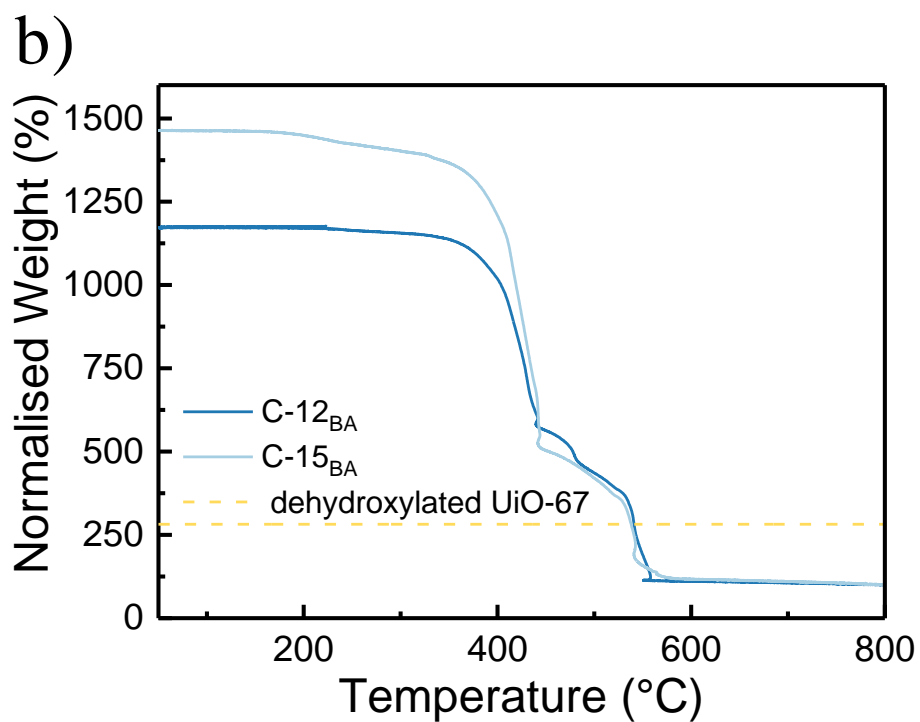
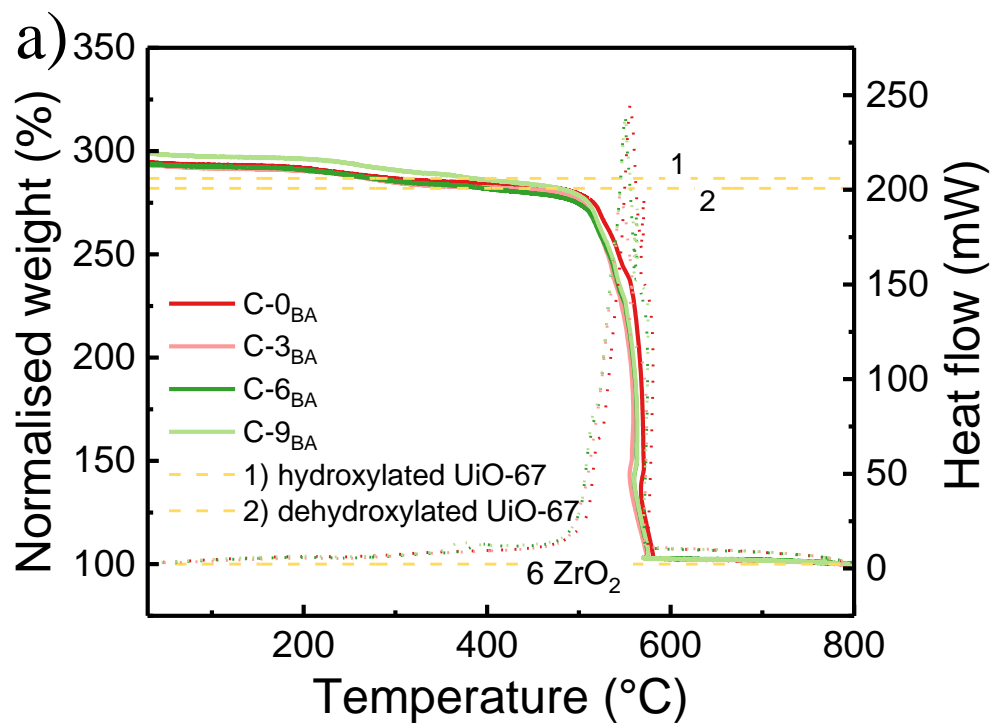


Figure S 6 Peak fitting in TOPAS to determine particle size for C-x_{BA} and D-x_{BA}.

8 TGA-DSC data



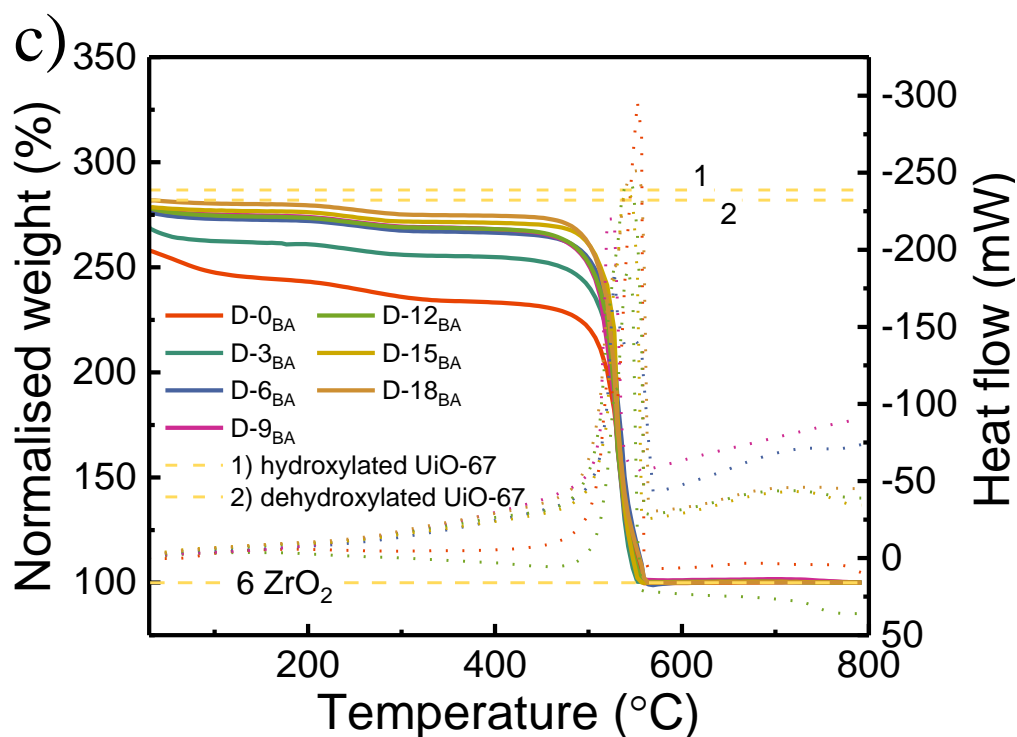


Figure S 7 TGA and DSC signals of a) C- x_{BA} ($x=0$ to 9), b) C- x_{BA} ($x=12$ to 15) and c) D- x_{BA} ($x=0$ to 18).

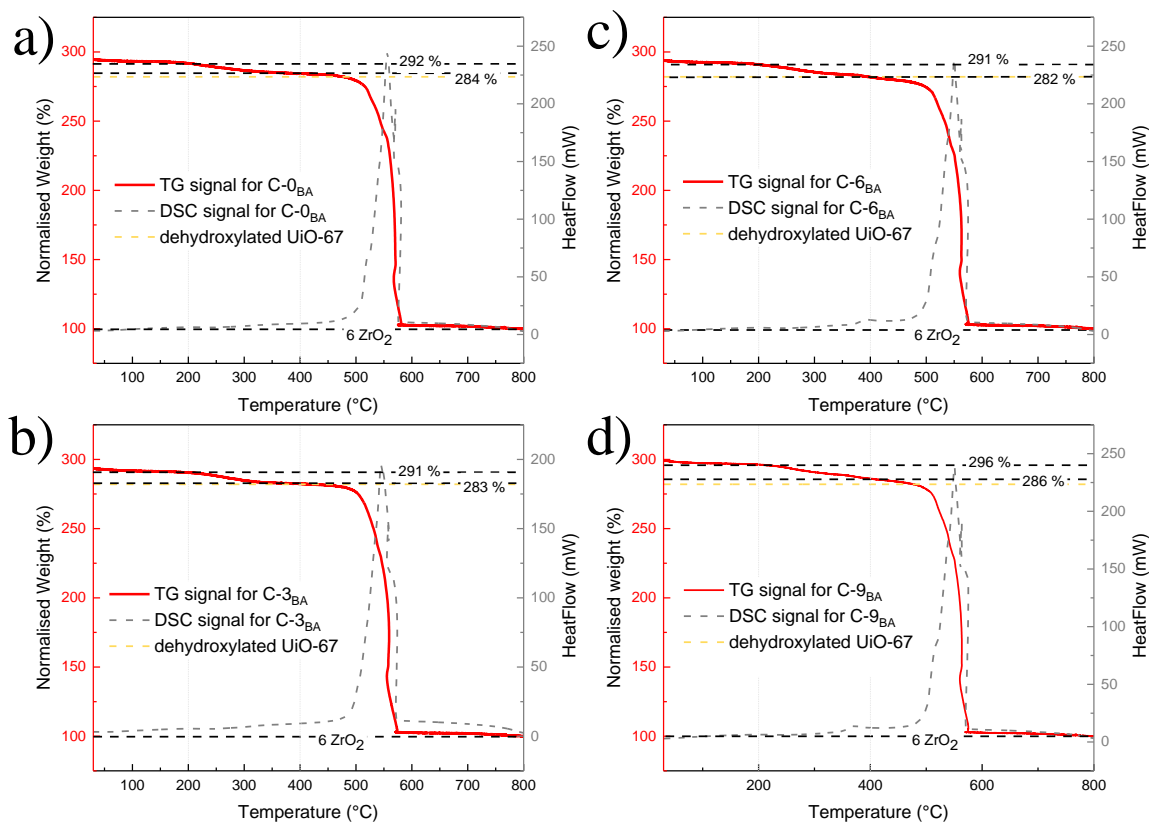


Figure S 8 TGA-DSC signal of a) C- 0_{BA} , b) C- 3_{BA} , c) C- 6_{BA} and d) C- 9_{BA} .

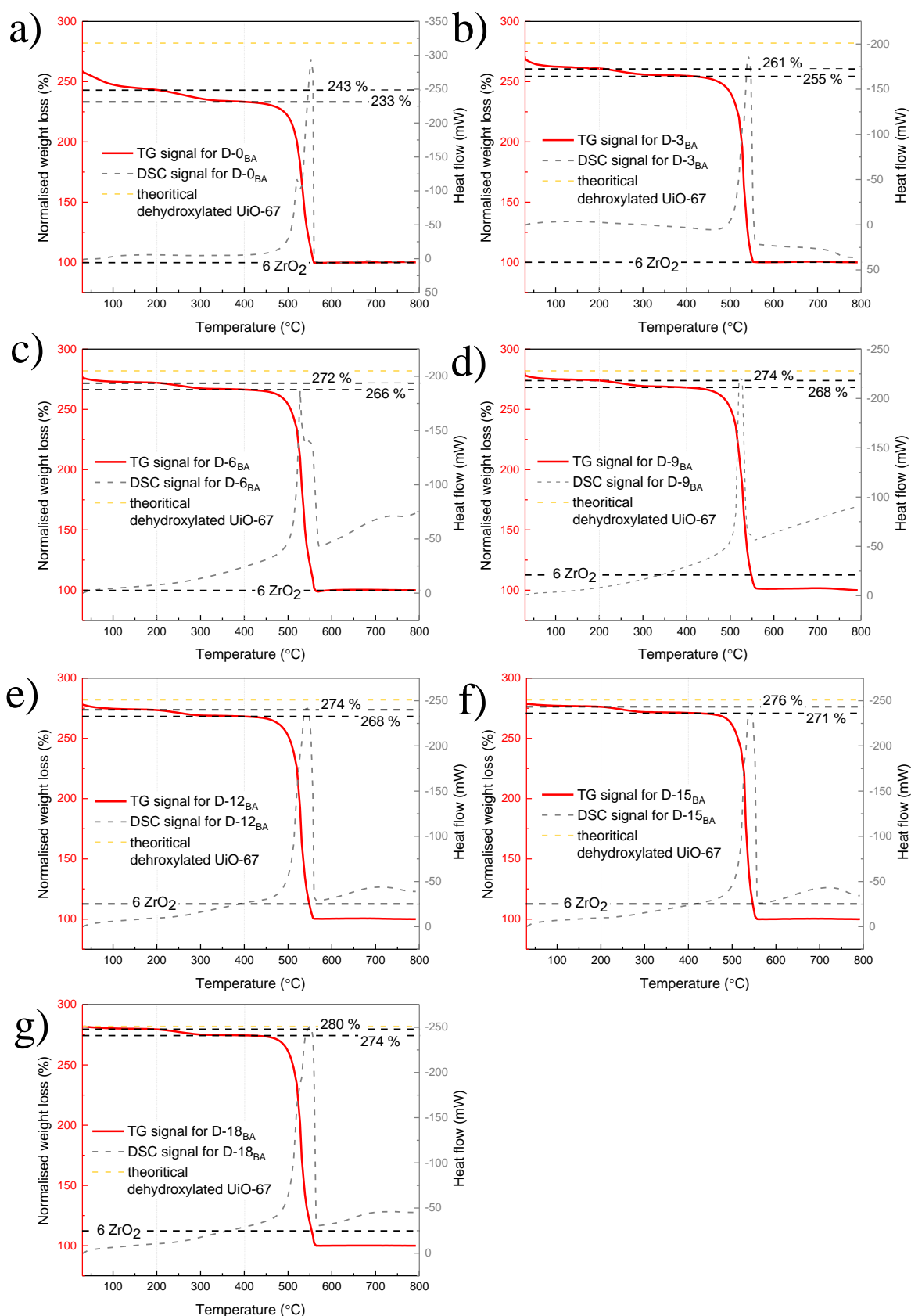


Figure S 9 TGA-DSC signal of xBA-D series; a) D-0_{BA}, b) D-3_{BA}, c) D-6_{BA}, d) D-9_{BA}, e) D-12_{BA}, f) D-15_{BA} and g) D-18_{BA}.

9 ^1H NMR data

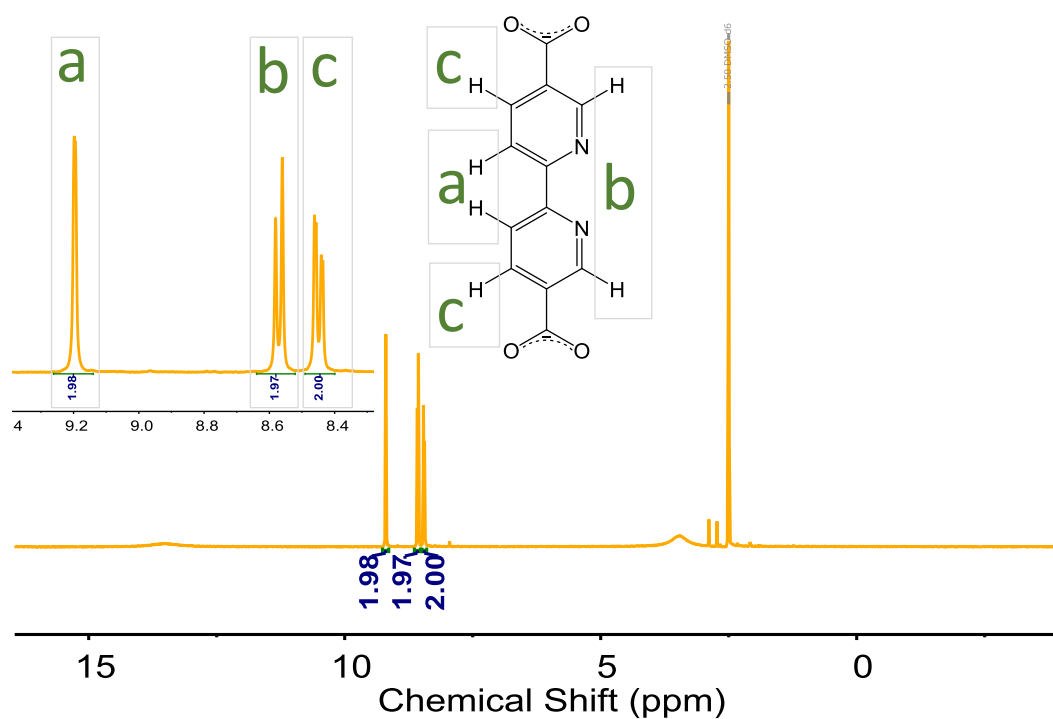
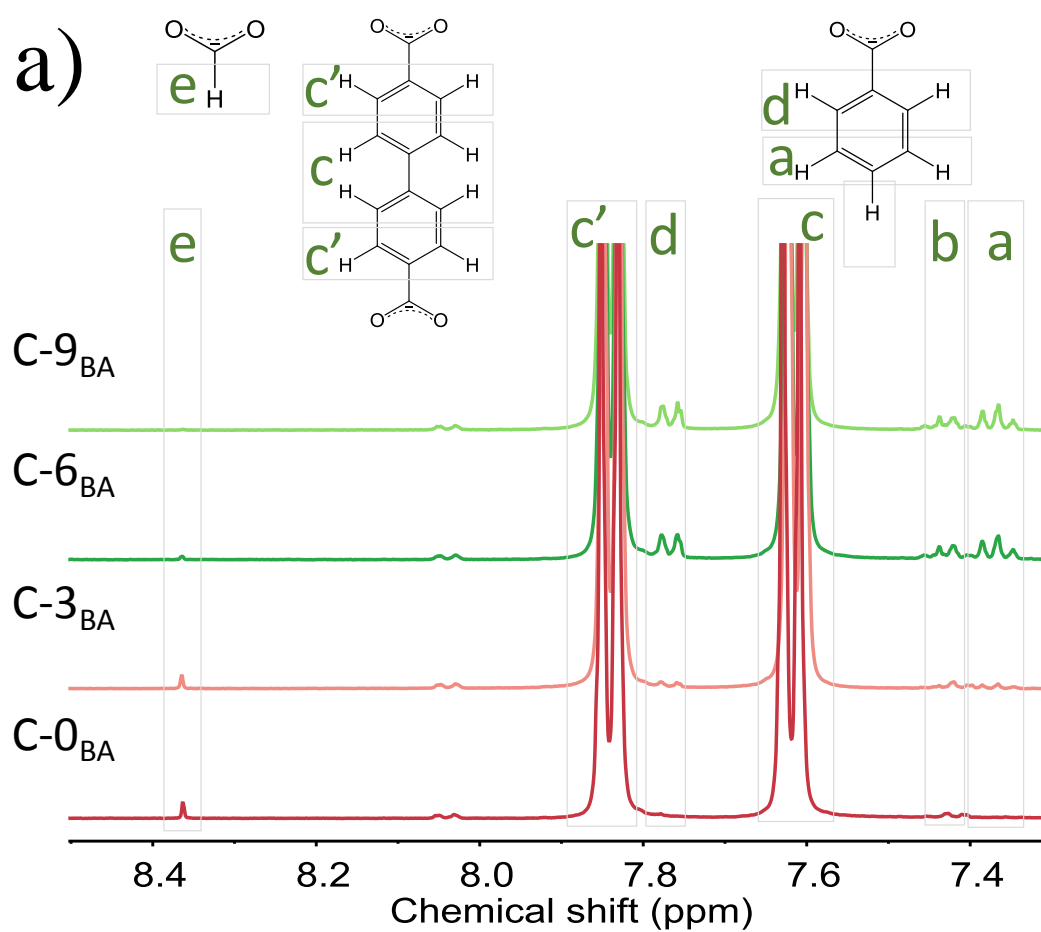


Figure S 10 ^1H NMR of 2,2'-bipyridine-5,5'-dicarboxylic acid (H_2bpydc) linker



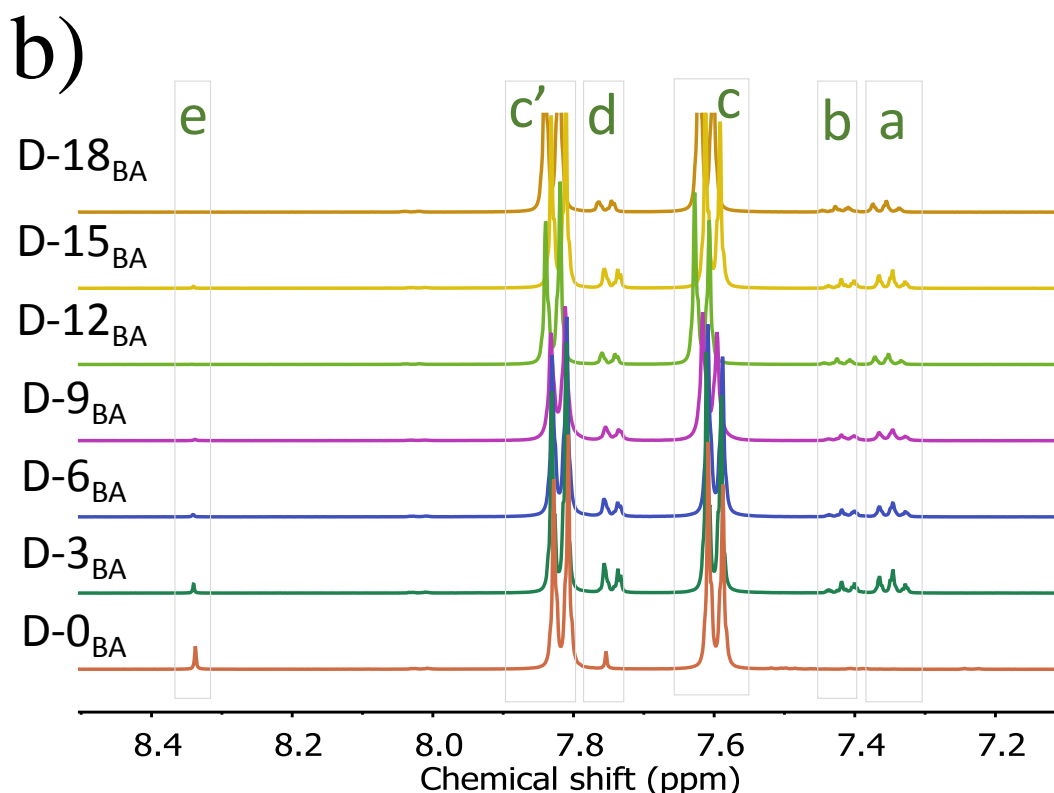


Figure S 11 ^1H NMR data for a) C- x_{BA} series and b) D- x_{BA} series.

10 Calculations for the missing linker defects

Herein, we have used two methods to calculate the degree of linker incorporation in the synthesized MOF samples. Both methods assume that the amount of cluster vacancy defects is negligible, as we do not observe any signs of forbidden low-angle reflections in PXRD, nor any mesoporosity from adsorption isotherms associated with such defects. Both methods also assume that the residue at 800 °C is pure ZrO_2 .

Method 1: From TGA-DSC in this and previous studies, it has been found that incorporated benzoate decomposes at a slightly lower temperature than the linker, at 350-400 °C. Assuming negligible linker loss in the same temperature range, the amount of linkers per Zr is calculated directly by comparing the mass of the MOF before and after linker combustion. 400 °C was chosen as this shows negligible mass loss in the time scale of the experiment according to our static thermal stability tests (Figure S 18).

Molar mass of dehydroxylated UiO-67 ($\text{Zr}_6\text{O}_6(\text{bpdc})_6$) = 2084.57 g/mol

Molar mass of hydroxylated UiO-67 ($\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bpdc})_6$) = 2120.59 g/mol

Molar mass of 6 formula units of ZrO_2 = 739.308 g/mol

This implies that in case of dehydroxylated UiO-67, 2084.57 g/mol is higher than 6 moles of ZrO_2 with the factor of 2.819. So the TGA plateau ideally should be at 281.9 % = ~282%

On the other hand, in case of hydroxylated UiO-67, 2120.59 g/mol is higher than 6 moles of ZrO_2 with the factor of 2.868. So the TGA plateau ideally should be at 286.8 %.

The difference between the ideal plateau of hydroxylated UiO-67 and dehydroxylated UiO-67 can thus be calculated by subtracting both the values i.e. 4.8 %, assuming that only two water molecules per cluster are lost and no BA or bpdc linkers are affected.

Method 2: The sample is heated in air at 200 °C for 24 hours to remove residual solvent, digested in NaOD and the organic components are quantified with ¹H-NMR. The composition (a mixture of bpdc²⁻, benzoate and formate) is then scaled to the relative mass of the organic constituents of the MOF using the mass value of the sample at 200 °C from TGA measurements.

10.1 Method 1

The ideal composition of UiO-67 after the dehydration of the cluster is Zr₆O₆(bpdc)₆, but in the presence of missing linkers it is Zr₆O₆(bpdc)_x. Assuming all benzoate and formate is decomposed.

$$\frac{n_{linker}}{n_{6 ZrO_2}} = \frac{Wt_{400\text{ }^{\circ}\text{C}} * Mm_{ZrO_2} - Mm_{clusters}}{Mm_{linker}}$$

Table S 7 Calculation for number of linkers coordinated to Zr₆ cluster in C-x_{BA} series, by TG-DSC.

Entry	MOF	<i>W</i> _{exp. plat.} (%)	bpdc ²⁻ :Zr
1	C-0 _{BA}	284	1.017
2	C-3 _{BA}	282	1.005
3	C-6 _{BA}	283	0.999
4	C-9 _{BA}	286	1.019

Table S 8 Calculation for number of linkers coordinated to Zr₆ cluster in D-x_{BA} series, by TG-DSC.

Entry	MOF	<i>W</i> _{exp. plat.} (%)	bpdc ²⁻ :Zr
1	D-0 _{BA}	233	0.755
2	D-3 _{BA}	255	0.822
3	D-6 _{BA}	266	0.884
4	D-9 _{BA}	268	0.893
5	D-12 _{BA}	268	0.9
6	D-15 _{BA}	271	0.902
7	D-18 _{BA}	274	0.935

10.2 Method 2

The ideal composition of UiO-67 at 200 °C is Zr₆O₄(OH)₄(bpdc)₆, but in the presence of missing linkers it is Zr₆O₄(OH)₄(bpdc)_x(BA)_y(FA)_z. The ratios of x:y:z is determined by ¹H NMR, and thus the average molar mass of the organic components (Mm_{organics}) can be found.

$$Mm_{organics} = C_{bpdc^{2-}} * Mm_{bpdc^{2-}} + C_{BA} * Mm_{BA} + C_{FA} * Mm_{FA}$$

Where the sum of concentrations equals 1. The weight of the sample at 200 °C relative to the weight of ZrO₂ after complete combustion corresponds to the mass of the clusters and the mass of the organic components:

$$Wt_{200\text{ }^{\circ}\text{C}} = \frac{m_{clusters} + m_{organics}}{m_{ZrO_2}}$$

The number of organic components per cluster can thus be found by inserting $m_A = Mm_A * n_A$:

$$Wt_{200\text{ }^{\circ}\text{C}} = \frac{Mm_{clusters} * n_{clusters} + Mm_{organics} * n_{organics}}{Mm_{6\text{ }ZrO_2} * n_{6\text{ }ZrO_2}}$$

Rearrangement of the expression, and inserting $n_{clusters} = n_{6\text{ }ZrO_2}$ gives the amount of organics relative to Zr:

$$\frac{n_{organics}}{n_{6\text{ }ZrO_2}} = \frac{Wt_{200\text{ }^{\circ}\text{C}} * Mm_{6\text{ }ZrO_2} - Mm_{clusters}}{Mm_{organics}}$$

Inserting the relative concentration of each of the organic components and the relative sample mass at 200 °C from TGA, the number of linkers, BA and FA per cluster can be found:

$$\frac{n_{bpdC^{2-}}}{n_{6\text{ }ZrO_2}} = \frac{n_{organics}}{n_{6\text{ }ZrO_2}} * C_{bpdC^{2-}}$$

The values are given in Table S 9 and Table S 10 below.

Table S 9 Calculation for linker deficiency per Zr_6 cluster in C- x_{BA} series, by a combination of ^1H NMR and TGA.

Entry	MOF	Wt % _{200 °C}	bpdC ²⁻ :Zr	BA:Zr	FA:Zr
1	C-0 _{BA}	292	1.023	0	0.020
2	C-3 _{BA}	291	1.010	0.018	0.013
3	C-6 _{BA}	291	0.992	0.058	0.002
4	C-9 _{BA}	296	1.016	0.062	<0.001

Table S 10 Calculation for linker deficiency per Zr_6 cluster in C- x_{BA} series, by a combination of ^1H NMR and TGA.

Entry	MOF	Wt % _{200 °C}	bpdC ²⁻ :Zr	BA:Zr	FA:Zr
1	D-0 _{BA}	243	0.760	0	0.078
2	D-3 _{BA}	261	0.781	0.160	0.031
3	D-6 _{BA}	272	0.850	0.142	0.013
4	D-9 _{BA}	274	0.856	0.151	0.011
5	D-12 _{BA}	274	0.871	0.123	0.003
6	D-15 _{BA}	276	0.859	0.165	0.012
7	D-18 _{BA}	280	0.910	0.110	0

11 Nitrogen adsorption isotherms

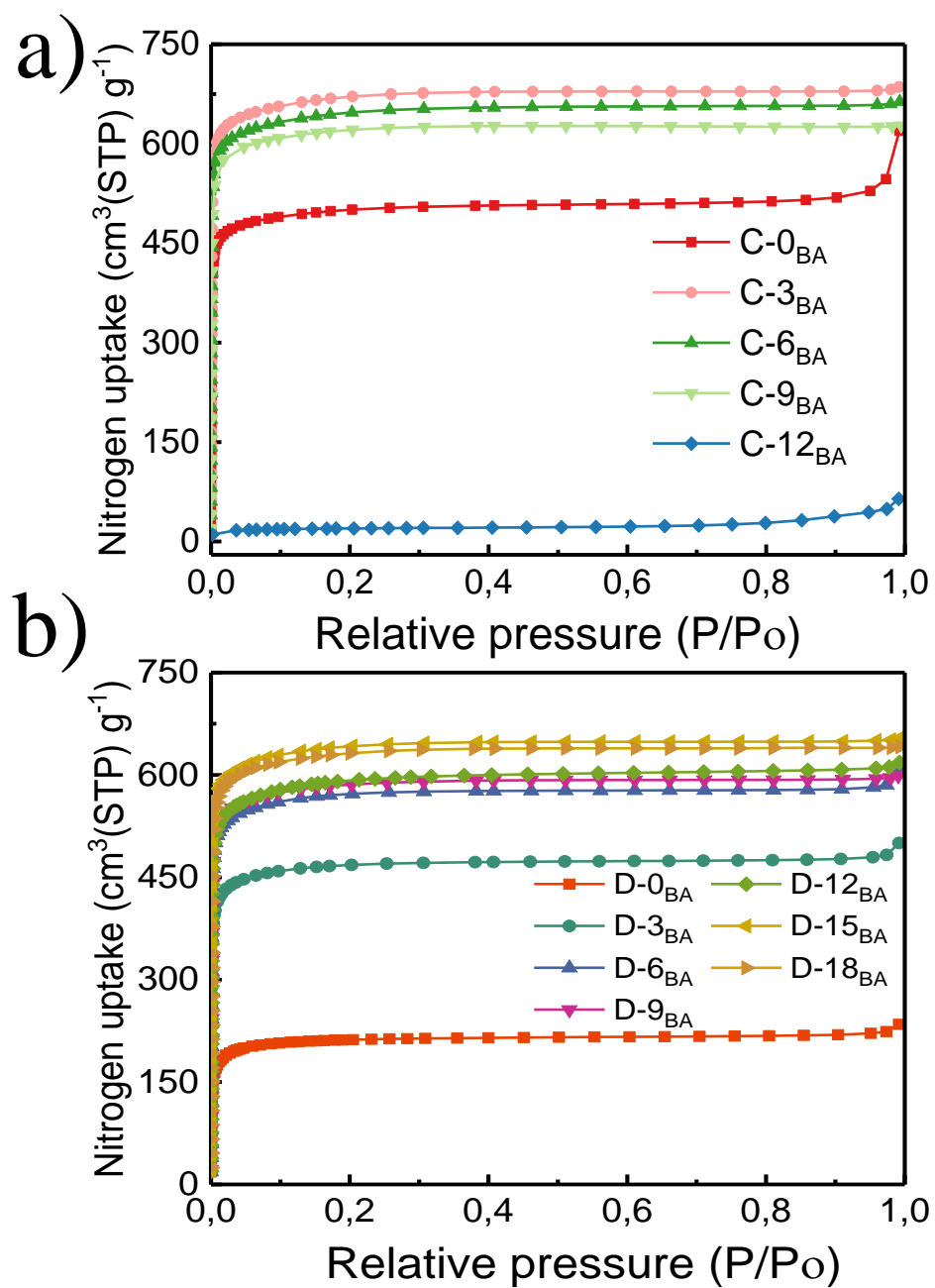


Figure S 12 Nitrogen isotherms at 77 K for a) C- x_{BA} series and b) D- x_{BA} series.

Table S 11 Surface area and pore volume data for C- x_{BA} and D- x_{BA} series (calculated from nitrogen adsorption isotherms)

Entry	BA concentration (eq)	xBA-C series		xBA-D series	
		Surface area [m ² g ⁻¹]	Pore volume [cm ³ g ⁻¹]	Surface area [m ² g ⁻¹]	Pore volume [cm ³ g ⁻¹]
1	0	2043	469	542	193
2	3	2734	628	1888	434
3	6	2632	605	2320	533
4	9	2549	585	2387	548
5	12	74	17	2374	545
6	15	-	-	2614	601
7	18	-	-	2562	589

12 SEM images

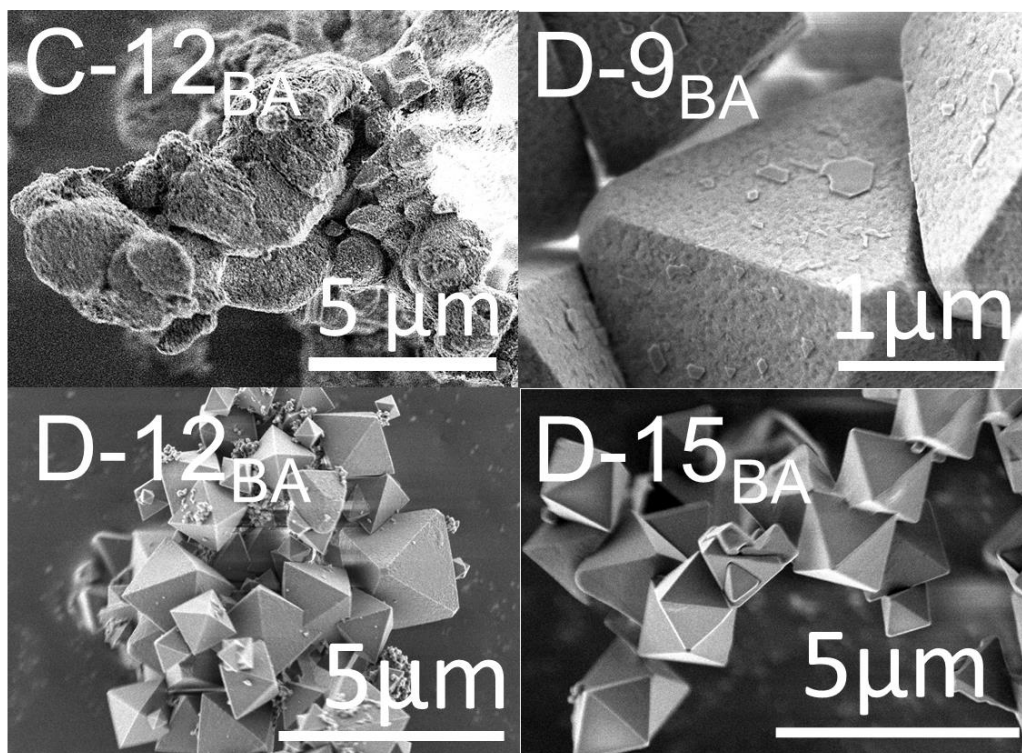


Figure S 13 SEM micrograph for C-12_{BA}, D-9_{BA}, D-12_{BA} and D-15_{BA}.

13 Yields

Table S 12 Yield in percentage (with respect to Zr) for the synthesized samples.

Entry	Sample label	Yield (%)	Sample label	Yield (%)
1	C-0 _{BA}	92	D-0 _{BA}	73
2	C-3 _{BA}	86	D-3 _{BA}	89
3	C-6 _{BA}	92	D-6 _{BA}	92
4	C-9 _{BA}	86	D-9 _{BA}	96
5	C-12 _{BA}	25	D-12 _{BA}	86
6	C-15 _{BA}	22	D-15 _{BA}	92
7	-		D-18 _{BA}	95

14 IR data

14.1 ATR

Figure S 14 illustrates ATR-IR spectra for selected samples of C-x_{BA} and D-x_{BA} (Part a and Part b, respectively). The spectra collected on the samples prepared with concentrated synthesis (C-3_{BA}, C-6_{BA} and C-9_{BA}) and that with diluted synthesis (D-3_{BA}, D-12_{BA} and D-18_{BA}) are very similar. Major bands are: i) a sharp peak at 680 cm⁻¹, ascribed to Zr-μ₃-OH; ii) a very strong maximum at around 1400 cm⁻¹, due to the symmetric ν(O-C-O) stretching mode; iii) maxima around 1500–1550 cm⁻¹, due to the asymmetric ν(O-C-O) stretching mode of the carboxylates; iv) a complex band around 1600 cm⁻¹, due to ν(C-C) stretching modes in the aromatic rings; v) broad, complex and weak components around 1700–1730 cm⁻¹ due to ν(C=O) of benzoic acid (coordinated to Zr or entrapped in the pores after the synthesis) or that of amide of DMF¹⁰⁻¹². A weaker counterpart at 1240 cm⁻¹, due to ν(C-O) is also expected. Between the two series of spectra, we observe that the signals of both species (ν(C=O) and ν(C-O)) are more evident in the spectra reported in Figure S14b), especially in case of D-18_{BA}. The ATR spectra obtained for C-0_{BA} and D-0_{BA} shows some differences. Particularly, C-0_{BA} shows clearly some extra bands (highlighted with dotted lines) whereas D-0_{BA} mostly shows broader bands with a different intensity ratio.

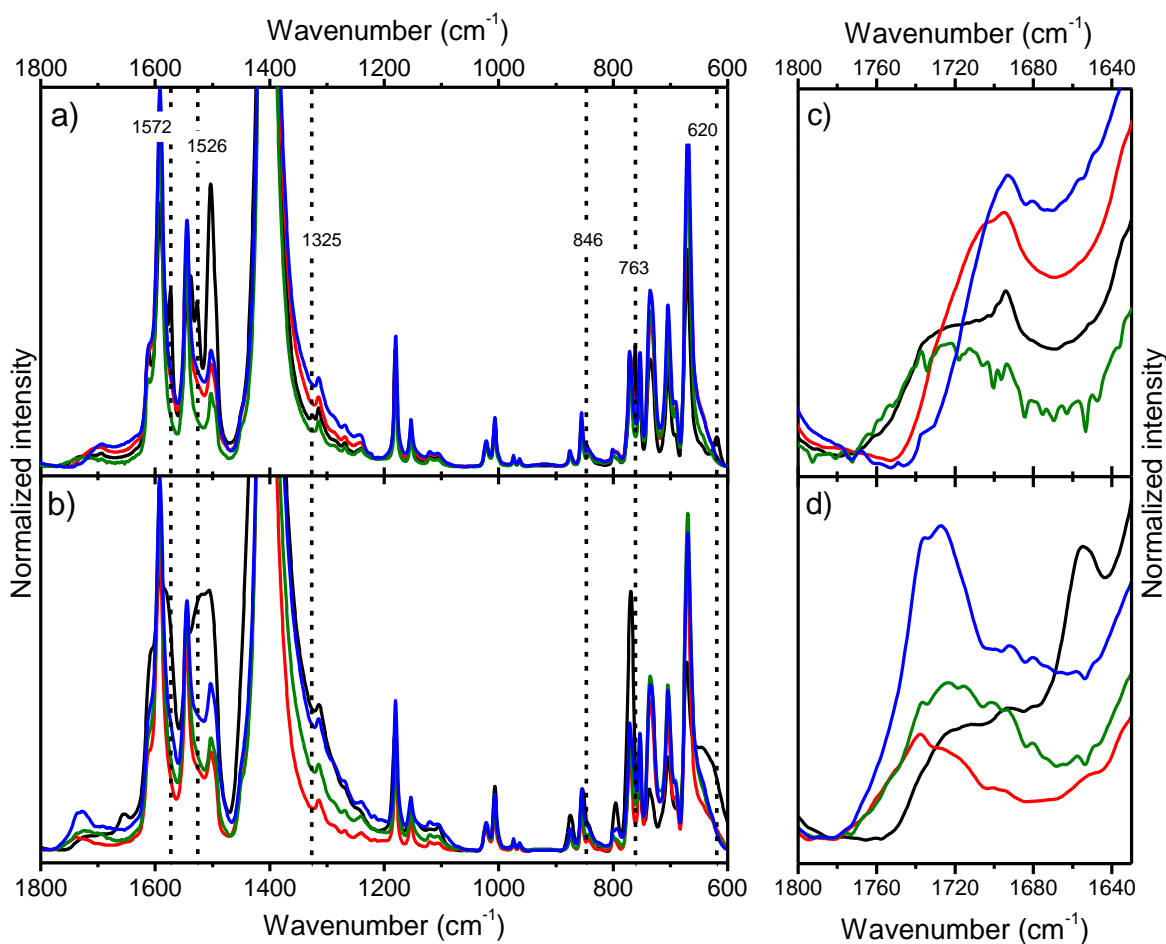


Figure S 14 Part a) and c): ATR spectra of UiO-67 MOFs prepared with concentrated synthesis, using 0 eq (black curve), 3 eq (red curve), 6 eq (green curve) and 9 eq (blue curve) of benzoic acid as modulator. Dotted lines help in the identification of the extra signal for the sample synthesized without modulator. Part b) and d): ATR spectra of UiO-67 MOFs prepared with diluted synthesis, using 0 eq (black curve), 3 eq (red curve), 12 eq (green curve) and 18 eq (blue curve) of benzoic acid as modulator.

14.2 DRIFT spectroscopy with CD_3CN as probe molecule

Figure S15 Figure S 15a), b) illustrates the spectra for samples C-0_{BA} and C-3_{BA}, while Figure S16a), b) and c) reports the data for the samples D-0_{BA}, D-3_{BA} and D-18_{BA}. Main figures report the spectra collected after activation in the same color used in Figure S14 (black C-0_{BA} and D-0_{BA}; red C-3_{BA} and D-3_{BA}; blue D-18_{BA}); curves from dark to light gray, illustrate the effect of progressive desorption of CD_3CN from the samples. The activation procedure performed before the dosage of the probe (He flux from RT to 300 °C with a ramp rate of 5 °C/min and kept at 300 °C for 180 min) was able to completely remove the solvent but preserved the $\mu_3\text{-OH}$ groups formed at the Zr_6 clusters, as testified by the presence of the sharp band at 3676 cm^{-1} . Upon interaction with CD_3CN , the bands associated to the OH groups were eroded and shifted at lower frequencies (centered at 3350 cm^{-1}).¹³ As counterpart, in the $\nu(\text{CN})$ region (see the insets of Figure S15 and Figure S16), blue shifted, new components around 2276 cm^{-1} , are observed.¹⁴ In the same spectral range, the absence of relevant bands around 2300 cm^{-1} , exclude the abundance of accessible Lewis sites (e.g. uncoordinated Zr sites). The only sample that shows a clear component at 2300 cm^{-1} , is the D-0_{BA} material (Figure S16a), inset). On the basis of what evaluated by TGA and by ^1H NMR, we know that also the sample D-3_{BA} should be highly defective. The fact that we do not appreciate a clear component at 2300 cm^{-1} , implies that the Zr species in that

sample are not present as highly uncoordinated Lewis site, able to perturb the CN group, but are most probably capped by OH groups.

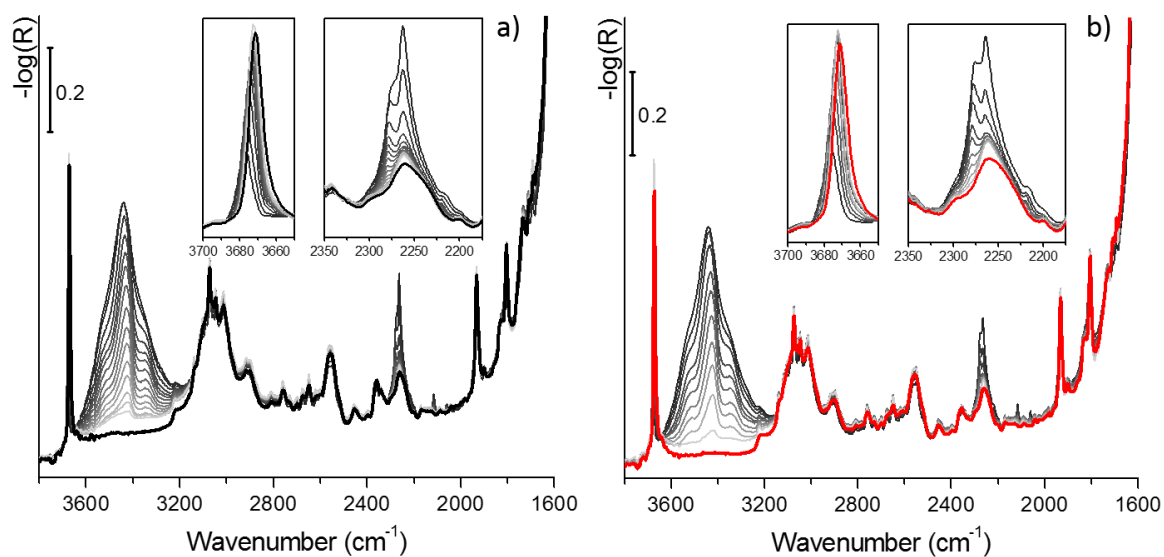


Figure S 15 DRIFT spectra of samples C-0_{BA} (part a) and C-3_{BA} (part b). Black curve represent the sample C-0_{BA} prior to CD₃CN dosing, the same for the sample C-3_{BA} (red curve). Curves from dark to light grey represent the progressive desorption of CD₃CN from the adsorption sites on the samples. Insets show a magnification of the $\nu(\text{Zr-OH})$ region (3700-3650 cm^{-1}) and of the $\nu(\text{C}\equiv\text{N})$ region (2350-2175 cm^{-1}).

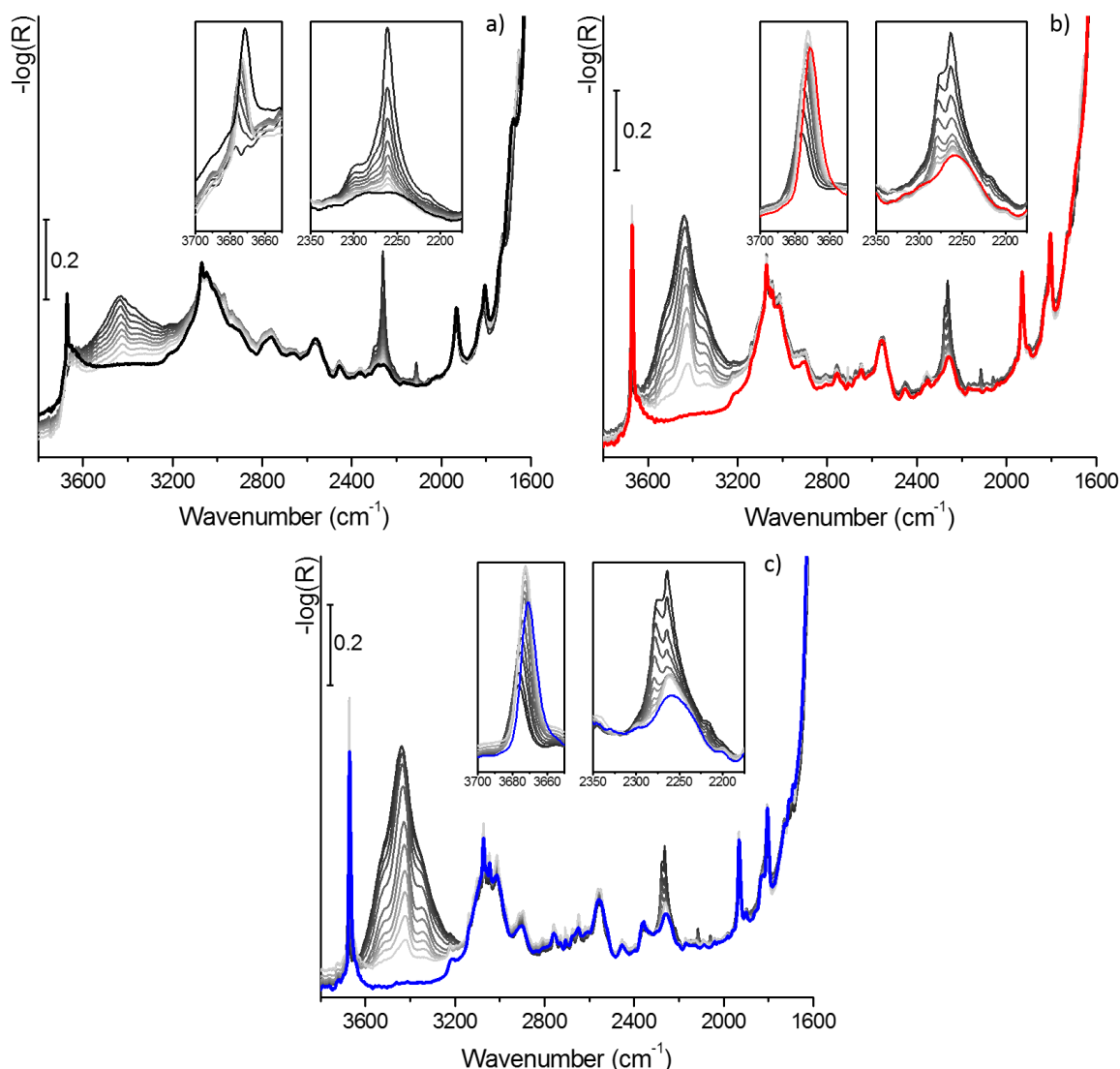


Figure S 16 DRIFT spectra of samples a) D-0_{BA}, b) D-3_{BA} and c) D-18_{BA}. Black curve represent the sample 0-D prior to CD₃CN dosing, the same for the sample D-3_{BA} (red curve) and D-18_{BA} (blue curve). Curves from dark to light grey represent the progressive desorption of CD₃CN from the adsorption sites on the samples. Insets show a magnification of the $\nu(\text{Zr-OH})$ region (3700-3650 cm^{-1}) and of the $\nu(\text{C}\equiv\text{N})$ region (2350-2175 cm^{-1}).

15 Thermal stability test on C-3_{BA}

Thermal stability test were performed to check the applicability of this material. C-3_{BA} was calcined at 300 °C, 350 °C, 375 °C and 400 °C in air for 24 hours, and labelled as C-3_{BA}@300 °C, C-3_{BA}@350 °C, C-3_{BA}@375 °C and C-3_{BA}@400 °C, respectively. PXRD patterns and nitrogen adsorption isotherms were acquired for the calcined samples (Figure S 17). The PXRD patterns show that the MOF structure is intact in all the calcined samples, but C-3_{BA}@400 °C displays less intense peaks (Figure S 17a). The nitrogen adsorption isotherms shows that of C-3_{BA}@300 °C and C-3_{BA}@350 °C are comparably porous with surface area of 2459 $\text{m}^2 \text{g}^{-1}$ and 2458 $\text{m}^2 \text{g}^{-1}$ respectively (Figure S 17 b) and Table S13). It is interesting to see that these samples shows only a 10 % decrease in surface area with respect to C-3_{BA}. However, C-3_{BA}@375 °C shows a 14 % decrease in the surface area, showing that heating C-3_{BA} at 375 °C affects the MOF to a greater magnitude. On the other hand, C-3_{BA}@400 °C is affected to the greatest magnitude and the surface area is seen to be decreased by 51 %, which reveals that the MOF is highly damaged. To further investigate the thermal stability, we performed static TGA measurements

for 12 h at the respective temperatures (Figure S 18). The TGA curve for C-3_{BA}@300 °C and C-3_{BA}@350 °C overlaps with the TGA curve for C-3_{BA} which shows that C-3_{BA} can withstand a temperature up to 350 °C without losing any species from the framework by the effect of heat. As we move to higher temperatures we see a weight loss during calcinations, indicating damage to the framework. The TGA results are in good agreement with the XRD and nitrogen adsorption isotherm results which suggested that calcination of C-3_{BA} at 375 °C, affects it to some extent and at 400 °C, affects largely by diminishing its porosity to half. These thermal tests show that C-3_{BA} can withstand temperature upto 350 °C for 24 h in air.

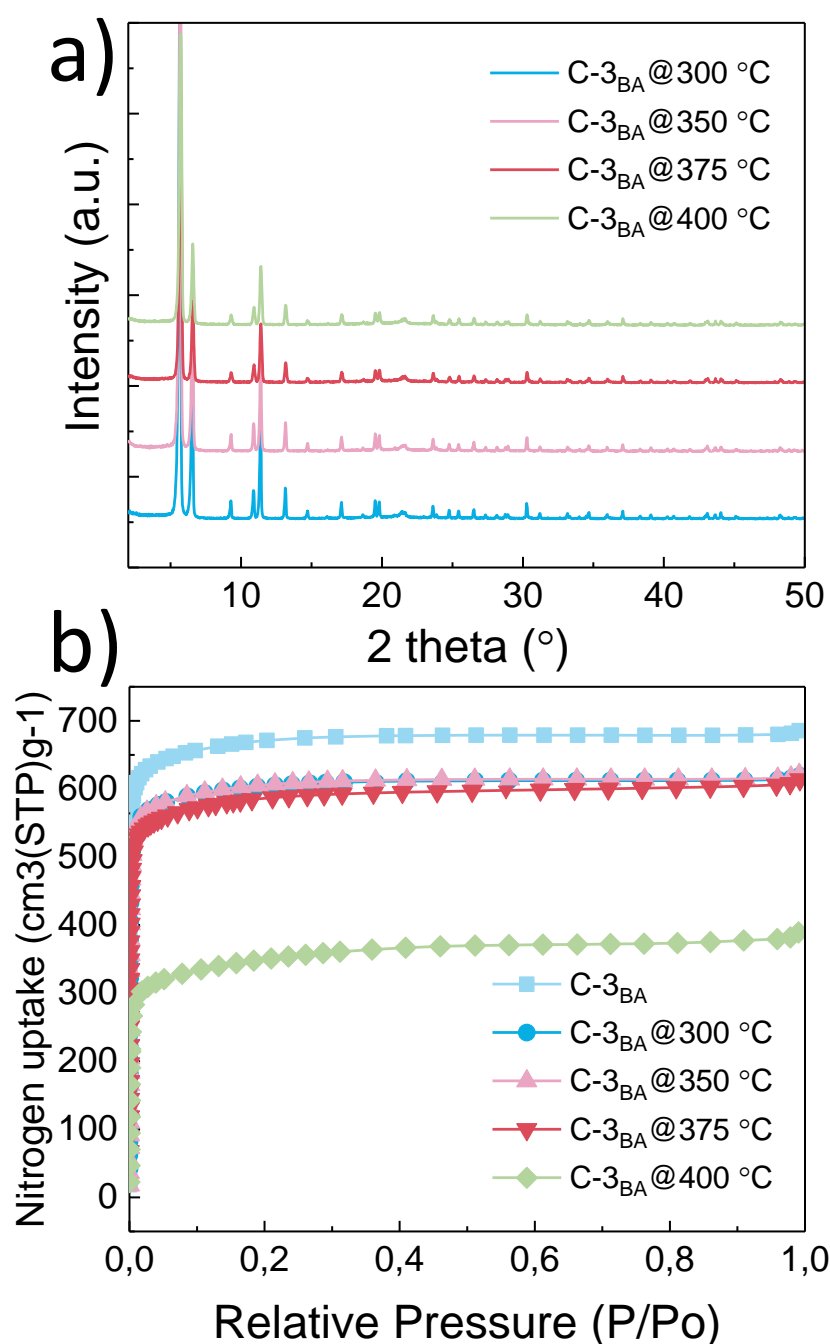


Figure S 17 a) PXRD and b) N₂ adsorption isotherm at 77 K of C-3_{BA} after calcination at 300 °C, 350 °C and 400 °C for 24 hours in air.

Table S 13 Surface area and pore volume of C-3_{BA} after heating at 300 °C, 350 °C, 375 °C and 400 °C for 24 hours in air.

Entry	MOF (heated for 24 h)	Surface area [m ² g ⁻¹]	Pore volume [cm ³ (STP) g ⁻¹]
1	C-3 _{BA} @300 °C	2459	565
2	C-3 _{BA} @350 °C	2458	565
3	C-3 _{BA} @375 °C	2351	540
4	C-3 _{BA} @400 °C	1341	308

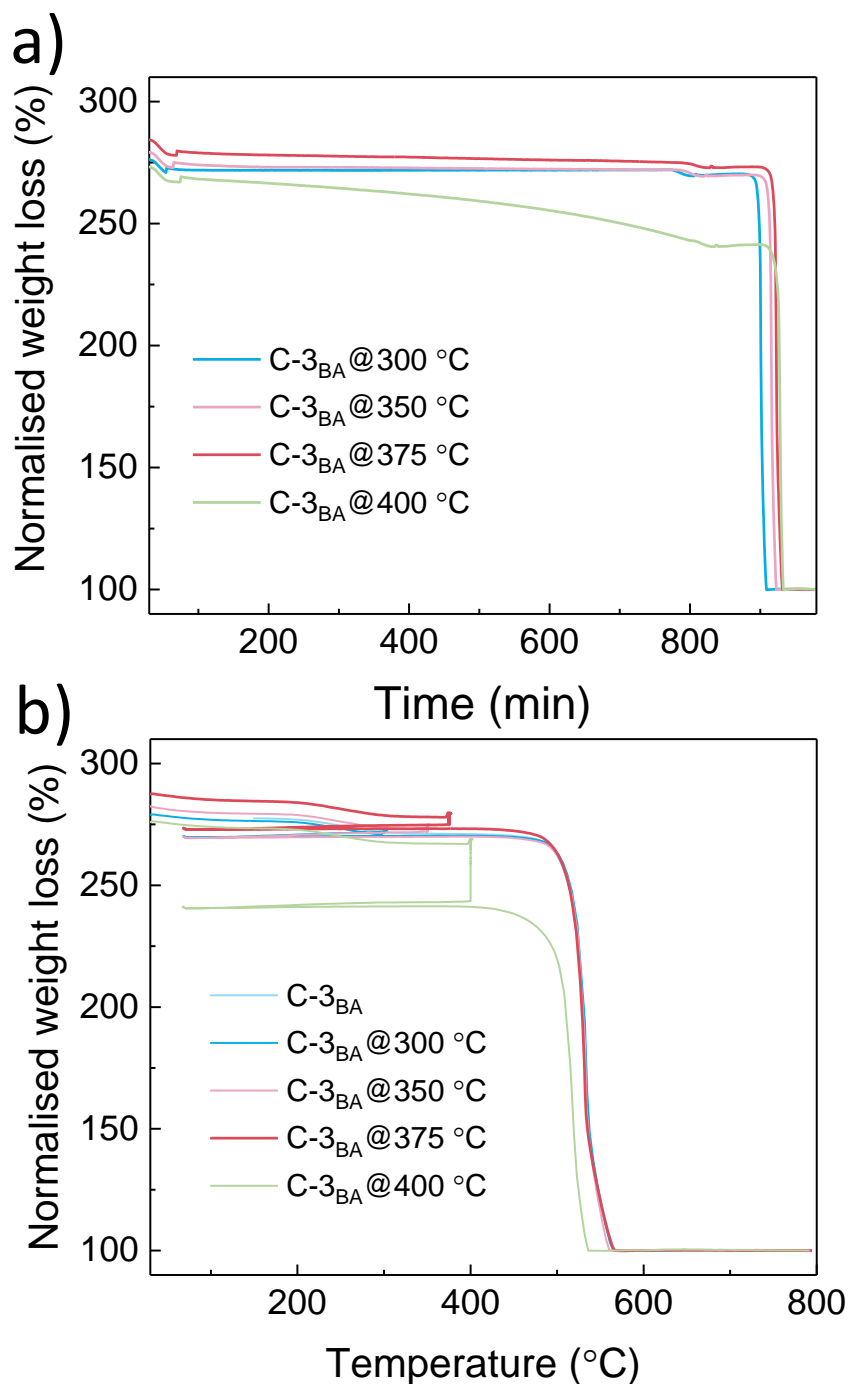


Figure S 18 TGA curves for the thermally heated C-3_{BA} where a) is Normalised weight loss vs Time and b) Normalised weight loss vs Temperature

16 Continuous sampling of C-3_{BA} synthesis

To verify that linker concentration in the synthesis liquor is kept constant by the presence of its corresponding solid throughout MOF crystal formation, we performed a synthesis using the **C-3_{BA}** protocol, sampling the suspension 25 times during the first 12 hours of the synthesis. The solid fraction of each sample was isolated by filtration and PXRD patterns were acquired. We did not perform any washing beyond filtering off the synthesis liquor, as this would have affected the residual linker. However, it also affects the pattern of the MOF, which appears to be poorly crystalline due to pore filling. We observed a gradual decrease in the diffraction pattern of H₂bpdc_(s), until it disappeared after around 11 hours. It can be assumed that the solution is saturated by H₂bpdc in this period, due to the continuous agitation of the mixture. Simultaneously, the most intense diffraction peaks from UiO-67 ([1 1 1] and [2 0 0]) appeared as separate peaks already after 45 minutes of reaction, and the reaction was mainly complete after 12 hrs (Figure S 19).

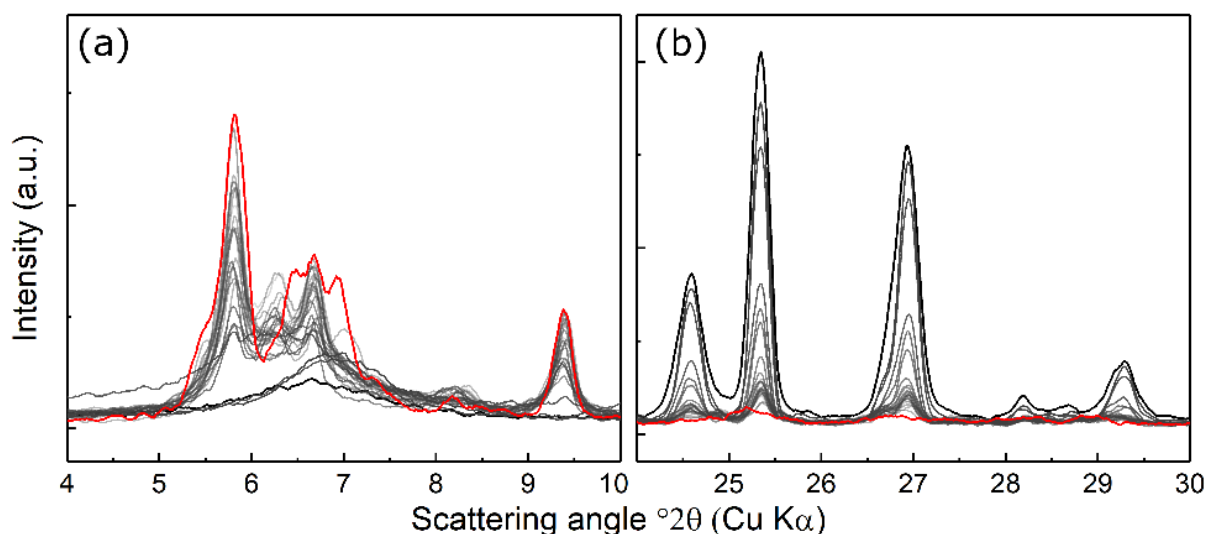


Figure S 19 Superimposed PXRD patterns (regions of interest) of samples taken at ~20 minute intervals from a synthesis of **C-3_{BA}**. The black line is at the start of the reaction, whereas the red line is the final (unwashed) product. Intermediate stages are shown in grey notes (gradually lighter as time progresses). (a) shows the growth of the (1 1 1), (2 0 0), (2 2 0) and merged (3 1 1) and (2 2 2) peaks of UiO-67. (b) shows the gradual disappearance of the most intense peaks of the linker in its solid, crystalline phase.

17 Time course study to monitor the composition of D-9_{BA} synthesis

UiO-67 was synthesized using the general synthesis approach described in section S3.2, using 2 g of Zirconium tetrachloride (1 eq), 0.46 mL water (3 eq), 200 mL of DMF (300 eq), 9.433 g of benzoic acid (9 eq) and 2.077 g of bpdc linker. After the addition of linker (considered 0 minute), 20 mL of the reaction mixtures were collected at an interval of 4 hours after the start of precipitation i.e. at 0.5 h. Thus the samples were collected at 0.5 h, 4.5 h, 8.5 h, 12.5 h, 16.5 h, 20.5 h and after the end of reaction at 24 h. These samples were filtered and washed with hot DMF and acetone, followed by drying at 150 °C, overnight. Three identical reactions were carried out to obtain sample for 0.5 h from reaction 1; 4.5 h, 8.5 h and 12.5 h from reaction 2 and 16.5 h and 20.5 h from reaction 3. The samples were characterized by SEM, ¹H-NMR and TGA.

The formation of UiO-67 is favoured as the time proceeds and 70 % of the product is formed in 8.5 hours (Figure S20a). After 8.5 h, probably the exchange of modulator and linker takes place with the

slight increase in the yield. After 24 hours, the reaction reaches maximum with almost 100 % yield. To be noted that the discrepancies here can be resulted from the errors caused due to 1) the uncertainty of collection of homogeneous sample from the reaction slurry and 2) these results are from three different reactions even if he aimed to make them identical. Furthermore, the composition of the samples were observed by digesting the samples and collecting NMR spectra. It reveals that the benzoic acid concentration increases as the reaction time proceeds (Figures S20b and S23). The amount of formic acid in the beginning of the reaction is about 7 % but as the reaction proceeds, formic acid decreases and remains constant for about 1 %. Moreover, the SEM images shows the formation of octahedral crystals at 4.5 hour and not much change in the topology of the material after 4.5 hour (Figure S21). Interestingly the TGA isotherms for these samples do not show major differences (Figure S22). At 0.5 hour the MOF is highly defected and as the time proceeds, the mass of the MOF is closer to the theoretically expected mass of UiO-67. This supports that while modulator and solvent are present in excess (implying that their concentration changes little during MOF crystal growth), the linker is optimally present in stoichiometric ratio to Zr. Hence, its concentration decreases with MOF crystal growth, leading to increase of modulator-covered defect formation with time.

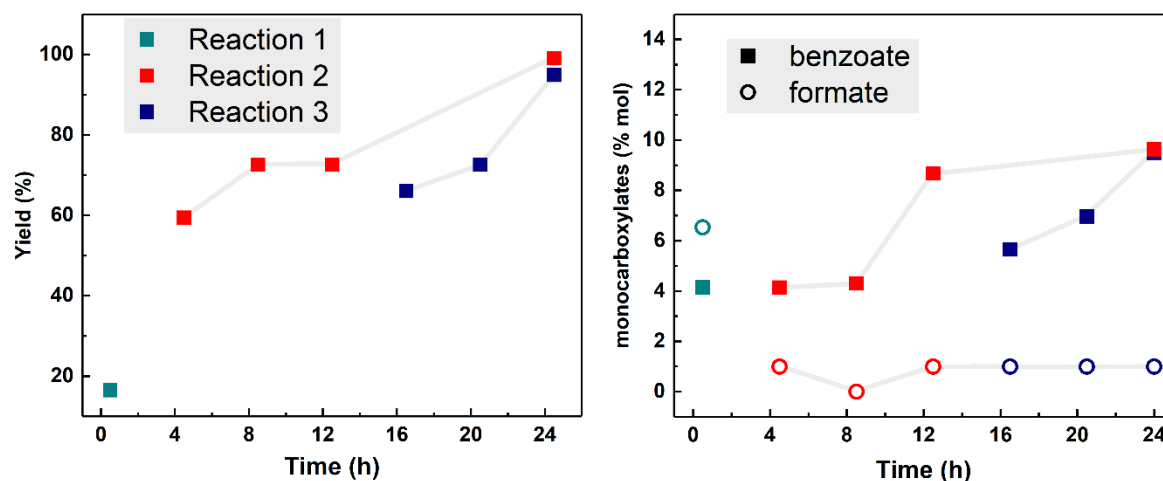


Figure S 20 a) yield for the samples extracted at various intervals and b) their composition, determined by $^1\text{H-NMR}$.

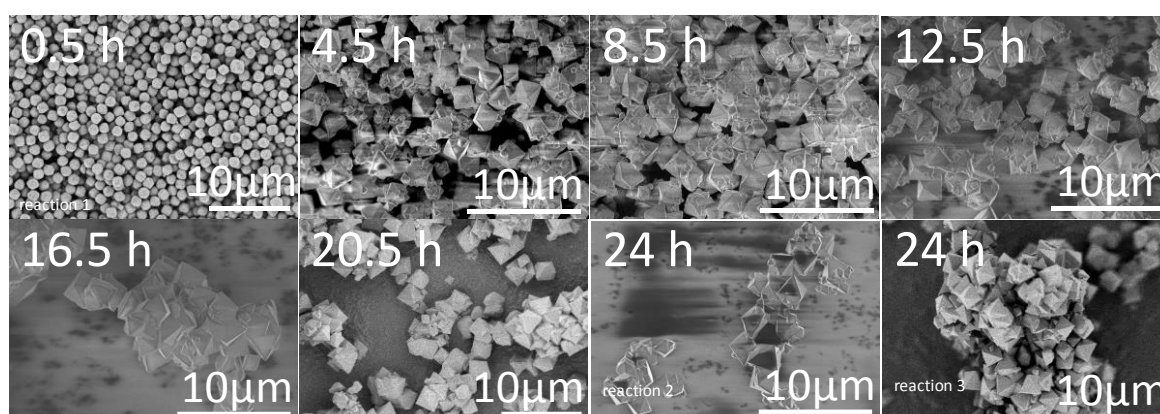


Figure S 21 SEM images of time course for the synthesis of UiO-67.

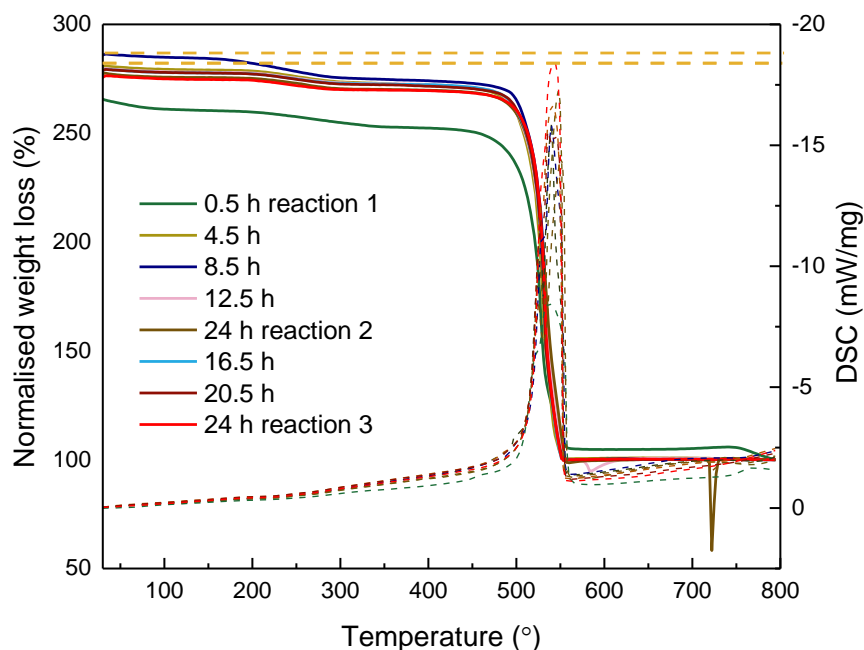


Figure S 22 TGA isotherms on the samples from time course study

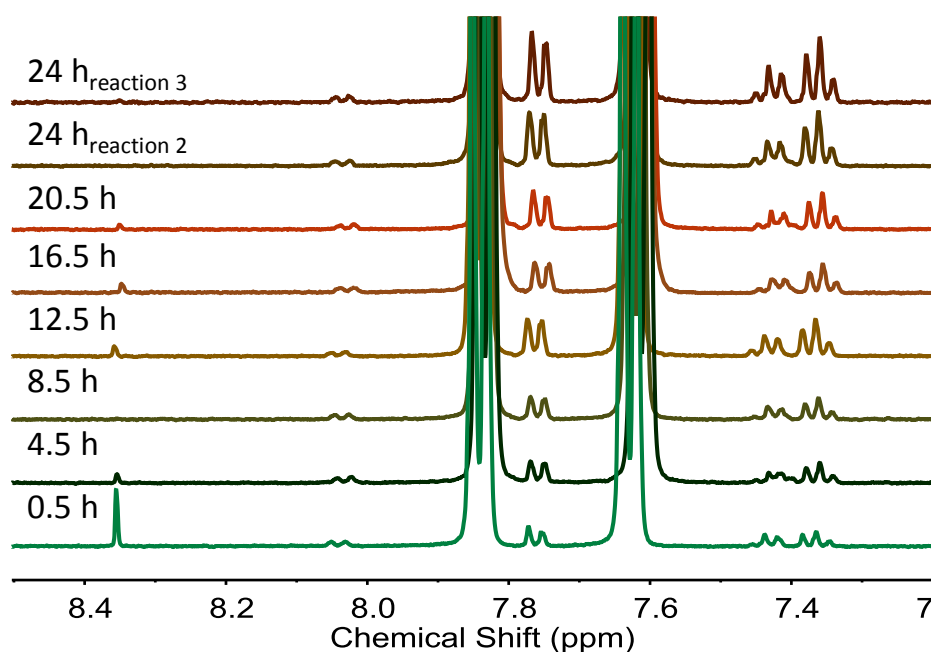


Figure S 23 NMR spectra of the samples from time course study of D-9BA

18 Synthesis and characterization of UiO-67-bpy_{0.1}

Applicability of the concentrated synthesis method on the mixed linker UiO-67 type MOF-Synthesis of UiO-67-bpy_{0.1}. UiO-67-bpy_{0.1} was synthesized using 10 % bpy linker and 90 % bpdc linker in the presence of 3 eq BA, 3 eq H₂O and 50 eq DMF. The synthesis was carried out similarly to the synthesis of C-3_{BA}. **Feil! Fant ikke referansekinden.** shows the PXRD of UiO-67-bpy_{0.1}, where the diffractogram is identical to the UiO-67 diffractogram (Figure 24a). This suggests that the UiO-67 formation is successful and the bpy linker did not interfere in the synthesis of the MOF. Also, this suggests that the

concentrated synthesis method can be applicable in the formation of the mixed linker UiO-67-bpy_{0.1}. Further, to check the quality of the synthesized UiO-67-bpy_{0.1}, it was characterized with TGA, ¹H NMR, BET and SEM (Figures 24b-26). Calculation of defects were done using TGA and ¹H NMR data.

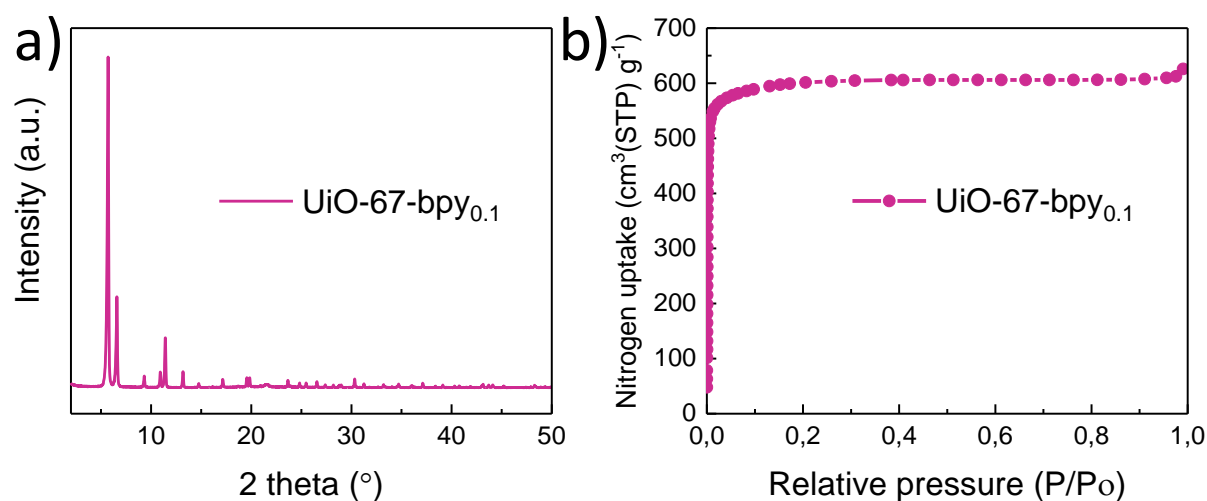


Figure S 24 a) PXRD and b) Nitrogen isotherm for UiO-67-bpy_{0.1}

18.1 Defect determination by TGA and ¹H NMR

The defects in UiO-67-bpy_{0.1} were determined in the same way as for UiO-67.

Entry	MOF	Wt % _{200 °C}	bpdC ²⁻ :Zr	bpydc ²⁻ :Zr	BA:Zr	FA:Zr	Wt % _{400 °C}	linker:Zr
1.	UiO-67-bpy _{0.1}	294	0.910	0.110	0.021	0.016	284	1.018

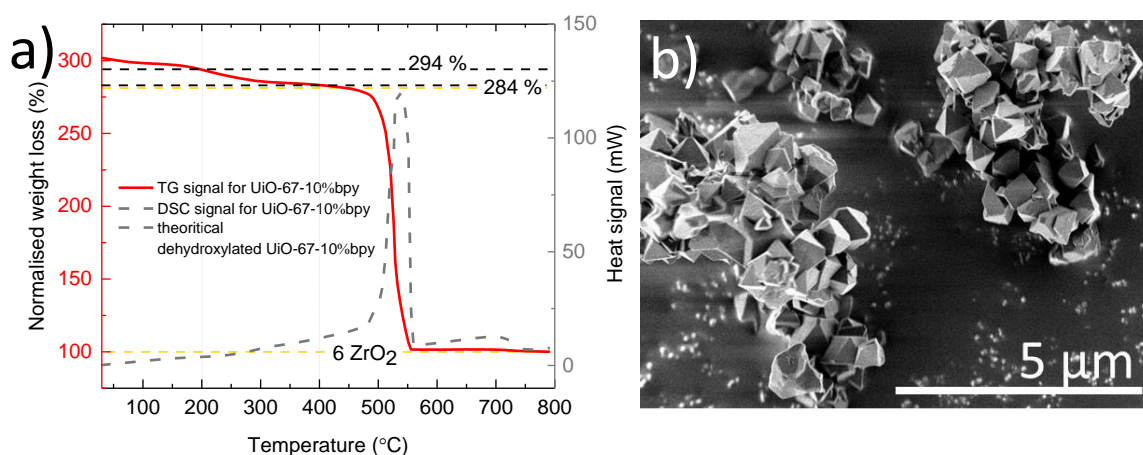


Figure S 25 a) TGA-DSC signal and b) SEM image for UiO-67-bpy_{0.1}

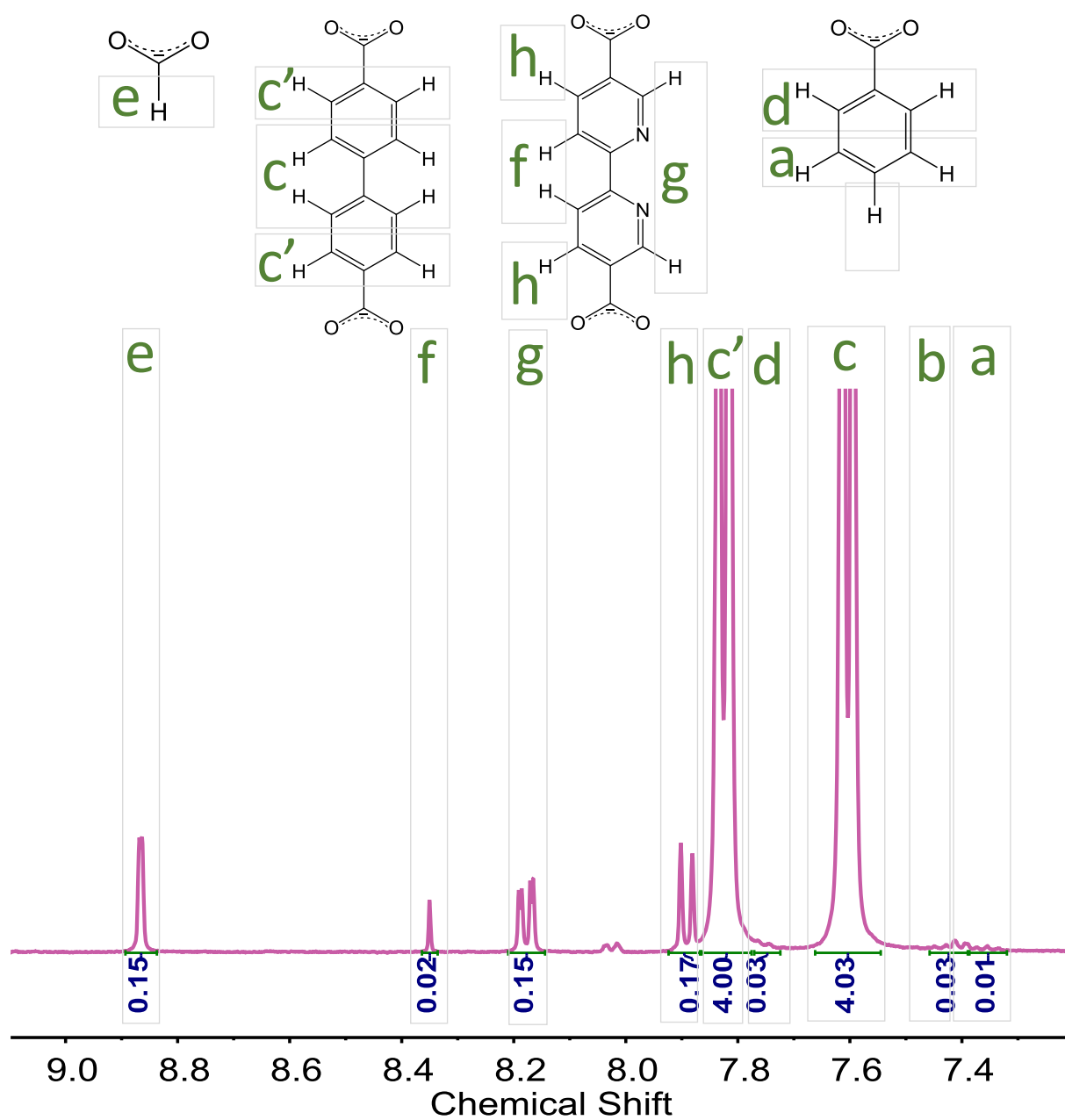


Figure S 26 ^1H NMR for UiO-67-bpy_{0.1}

19 References

1. AXS, B. *Bruker AXS: APEX2, SAINT, SADABS.*, Madison, Wisconsin, USA, 2014.
2. Sheldrick, G., SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallogr. Sect. A* **2015**, *71* (1), 3-8.
3. Sheldrick, G., Crystal structure refinement with SHELXL. *Acta Crystallogr. Sect. C* **2015**, *71* (1), 3-8.
4. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42* (2), 339-341.
5. Katz, M. J.; Brown, Z. J.; Colon, Y. J.; Siu, P. W.; Scheidt, K. A.; Snurr, R. Q.; Hupp, J. T.; Farha, O. K., A facile synthesis of UiO-66, UiO-67 and their derivatives. *Chem. Commun.* **2013**, *49* (82), 9449-9451.
6. Ragon, F.; Horcajada, P.; Chevreau, H.; Hwang, Y. K.; Lee, U. H.; Miller, S. R.; Devic, T.; Chang, J.-S.; Serre, C., In Situ Energy-Dispersive X-ray Diffraction for the Synthesis Optimization and Scale-up of the Porous Zirconium Terephthalate UiO-66. *Inorg. Chem.* **2014**, *53* (5), 2491-2500.
7. Schaate, A.; Roy, P.; Godt, A.; Lippke, J.; Waltz, F.; Wiebcke, M.; Behrens, P., Modulated Synthesis of Zr - Based Metal - Organic Frameworks: From Nano to Single Crystals. *Chem. Eur. J.* **2011**, *17* (24), 6643-6651.
8. Gutov, O. V.; Hevia, M. G.; Escudero-Adán, E. C.; Shafir, A., Metal-Organic Framework (MOF) Defects under Control: Insights into the Missing Linker Sites and Their Implication in the Reactivity of Zirconium-Based Frameworks. *Inorg. Chem.* **2015**, *54* (17), 8396-8400.
9. Marshall, R. J.; Hobday, C. L.; Murphie, C. F.; Griffin, S. L.; Morrison, C. A.; Moggach, S. A.; Forgan, R. S., Amino acids as highly efficient modulators for single crystals of zirconium and hafnium metal-organic frameworks. *J. Mater. Chem. A* **2016**, *4* (18), 6955-6963.
10. Atzori, C.; Shearer, G. C.; Maschio, L.; Civalleri, B.; Bonino, F.; Lamberti, C.; Svelle, S.; Lillerud, K. P.; Bordiga, S., Effect of Benzoic Acid as a Modulator in the Structure of UiO-66: An Experimental and Computational Study. *J. Phys. Chem. C* **2017**, *121* (17), 9312-9324.
11. Chavan, S.; Vitillo, J. G.; Gianolio, D.; Zavorotynska, O.; Civalleri, B.; Jakobsen, S.; Nilsen, M. H.; Valenzano, L.; Lamberti, C.; Lillerud, K. P.; Bordiga, S., H₂ storage in isostructural UiO-67 and UiO-66 MOFs. *Phys. Chem. Chem. Phys.* **2012**, *14* (5), 1614-1626.
12. Valenzano, L.; Civalleri, B.; Chavan, S.; Bordiga, S.; Nilsen, M. H.; Jakobsen, S.; Lillerud, K. P.; Lamberti, C., Disclosing the Complex Structure of UiO-66 Metal Organic Framework: A Synergic Combination of Experiment and Theory. *Chem. Mat.* **2011**, *23* (7), 1700-1718.
13. Morterra, C.; Cerrato, G.; Novarino, E.; Mentrut, M. P., On the adsorption of acetonitrile on pure and sulfated tetragonal zirconia (t-ZrO₂). *Langmuir* **2003**, *19* (14), 5708-5721.
14. Plessers, E.; Fu, G. X.; Tan, C. Y. X.; De Vos, D. E.; Roeyffers, M. B. J., Zr-Based MOF-808 as Meerwein-Ponndorf-Verley Reduction Catalyst for Challenging Carbonyl Compounds. *Catalysts* **2016**, *6* (7), 104.