

The University of Nottingham

**Group IV metal clusters as discrete building blocks for the
synthesis of metal-organic frameworks**

A thesis submitted for the degree of Master of Science (by research) at the
University of Nottingham

By

Alexandre Ollier de Marichard, BSc (Hons)

Declaration

Unless specific references are made to other sources, the work presented in this thesis is the original work of the author. It has not been submitted, in either part or full, for any other degree.

Alexandre Ollier de Marichard

Abstract

This thesis shows my investigations into the formation of metal-organic frameworks from discrete group IV metal clusters. To that end, three clusters were synthesised, namely Zr_6 benzoate, Zr_6 methacrylate and Ti_6 aminobenzoate. Novel clusters were synthesised, but poor crystallinity meant that they could not be fully characterised, and therefore were not suitable for further reactions.

Using these three clusters, MOFs were synthesised. In typical MOF reactions starting from a metal salt and a linker, metal-oxo clusters are formed through self-assembly. Starting from pre-synthesised clusters has the potential to lead to milder synthetic conditions, and offer control over the nature and topology of the framework. The conditions needed for the formation of crystalline MOFs from clusters were investigated through systematic modifications of the reaction conditions. Changes in reaction temperatures and times, molar ratios and concentrations led to little change in the crystallinity of the obtained products. Modulation led to a significant change in crystallinity and particle sizes. This suggested that the modulation mechanism in MOFs is more complex than the common understanding, and that “self-modulating” properties of discrete clusters were not the main mechanism. It was also established that modulation is dependent on the clusters’ metal and associated ligand.

Finally, using a mixture of two different metal clusters, the synthesis of mixed-cluster MOFs was attempted. While these attempts did not produce the desired products, it helped to emphasize the issues associated with them, as well as the possible conditions needed for successful synthesis.

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Table of contents

Declaration.....	I
Abstract.....	II
Acknowledgments	III
Table of contents	IV
Abbreviations	VII

Chapter 1: Introduction

1.1. Metal-organic frameworks	1
1.2. Synthesis of zirconium-based MOFs.....	2
1.3. Mixed-metal MOFs	3
1.4. Metal clusters.....	5
1.4.1. Self-assembly of metal clusters in MOFs	5
1.4.2. Discrete group IV metal clusters	6
1.4.3. Clusters as starting materials for the synthesis of MOFs	12
1.5. Research objectives	17

Chapter 2: Clusters syntheses

2.1. Results.....	19
2.1.1. Zr benzoate cluster, $Zr_6O_4(OH)_4(OBz)_{12}(OPr)$	19
2.1.2. Zr methacrylate cluster, $Zr_6O_4(OH)_4(OMc)_{12}$	21
2.1.3. Zr aminobenzoate cluster, $Zr_6O_4(OH)_4(ABZ)_{12}$	26
2.1.4. Zr 2,2-dimethylbutyrate cluster, $Zr_6O_4(OH)_4(BTA)_{12}$	30
2.1.5. Ti aminobenzoate cluster, $Ti_6O_6(O^iPr)_6(ABZ)_6$	31
2.1.6. Ti benzoate cluster, $Ti_6O_6(O^iPr)_6(OBz)_6$	35
2.2. Discussion.....	37
2.2.1. Effects of the cation	37
2.2.2. Phase purity.....	38
2.2.3. Characterisation of novel structures.....	39

Chapter 3: MOF syntheses

3.1. Results	41
3.1.1. Using the Zr_6 benzoate cluster as starting material	41
3.1.1.1. Varying the linker	41
3.1.1.2. Phases comparison	47
3.1.1.3. Decreased concentration	48
3.1.1.4. Concentration series	49
3.1.1.5. Molar ratio series	50
3.1.1.6. Modulated syntheses	51
3.1.2. Using the Zr_6 methacrylate cluster as starting material	56
3.1.3. Using the Ti_6 aminobenzoate cluster as starting material	60
3.1.4. Mixed-cluster MOF reactions	61
3.2. Discussion	68
3.2.1. Unmodulated reactions	69
3.2.2. Modulated reactions	70
3.2.3. Mixed cluster reactions	72

Chapter 4: Conclusion and future work

4.1. Conclusion	73
4.2. Future work	74

Chapter 5: Experimental

5.1. Characterization techniques	77
5.1.1. Powder X-ray diffraction	77
5.1.2. Nuclear magnetic resonance	78
5.1.3. Solid-state UV-vis spectroscopy	78
5.1.4. Scanning electron microscopy	79
5.1.5. Energy dispersive X-rays	79
5.2. Syntheses of metal clusters	79
5.2.1. Zr benzoate cluster, $Zr_6O_4(OH)_4(OBz)_{12}$	79
5.2.2. Zr methacrylate cluster, $Zr_6O_4(OH)_4(OMc)_{12}$	79

5.2.3. <i>Zr₁₂ acetate cluster, Zr₁₂O₈(OH)₈(OAc)₂₄</i>	80
5.2.4. <i>Ti aminobenzoate cluster, Ti₆O₆(OⁱPr)₆(ABZ)₆</i>	80
5.3. MOF syntheses	80
5.3.1. <i>Zr₆ benzoate cluster as starting material</i>	80
5.3.1.1. <i>Varying linker</i>	80
5.3.1.2. <i>Decreased concentration</i>	81
5.3.1.3. <i>Concentration series</i>	81
5.3.1.4. <i>Molar ratios</i>	82
5.3.1.5. <i>Modulated syntheses</i>	82
5.3.1.5.1. <i>Acetic acid as modulator</i>	82
5.3.1.5.2. <i>Varying equivalents of acetic acid</i>	83
5.3.1.5.3. <i>Varying equivalents of benzoic acid</i>	84
5.3.1.5.4. <i>Screen of different modulators</i>	85
5.3.1.5.5. <i>Modulated reaction of Zr₁₂ acetate</i>	85
5.3.2. <i>Zr₆ methacrylate cluster as starting material</i>	86
5.3.2.1. <i>Unmodulated reaction with trans,trans-muconic acid</i>	86
5.3.2.2. <i>Modulated reactions</i>	86
5.3.3. <i>Ti₆ aminobenzoate cluster as starting material</i>	87
5.3.3.1. <i>Unmodulated reaction with trans,trans-muconic acid</i>	87
5.3.4. <i>Mixed cluster MOF reactions</i>	87
References	89

Abbreviations

ABZ	Aminobenzoate
BET	Brunauer – Emmett – Teller
BPDC	Biphenyl dicarboxylic acid
BTA	Butyrate
BuOH	Butanol
DGIST	Daegu Gyeongbuk Institute of Science and Technology
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
EDX	Energy dispersive X-rays
FIR	Fujian Institute Research
HKUST	Hong Kong University of Science and Technology
IPA	Isopropyl alcohol
LAG	Liquid-assisted grinding
MOF	Metal-organic framework
NMR	Nuclear magnetic resonance
NU	Northwestern University
OAc	Acetate
OBz	Benzoate
OMc	Methacrylate
O ⁿ Pr	Propionate
O ⁿ Bu	Butanoate
PCN	Porous Coordination Network
nPrOH	Propan-1-ol
PXRD	Powder X-ray diffraction
SCXRD	Single-crystal X-ray diffraction
SEM	Scanning electron microscopy
UiO	University of Oslo
Wt%	Weight percentage

Chapter 1: Introduction

1.1. Metal-organic frameworks

Metal-organic frameworks (MOFs) are a class of hybrid inorganic-organic compounds that have an extended crystalline framework composed of metal clusters, known as nodes, and multitopic organic ligands, known as linkers (figure 1). These compounds are readily synthesised using solvothermal methods, where the reaction mixture is heated above the solvent's boiling point in a sealed vessel, which leads to self-assembly to form node-linker bonds. The term metal-organic Framework was first used by O. M. Yaghi¹, where the first example of a solvothermally synthesised MOF was presented. The structure was composed of copper nodes bonded to 4,4'-bipyridine and exhibited zeolitic properties such as high porosity, surface area and catalytic activity. The high porosity of MOFs was reported in 1998² and the field has since been extensively researched due to the near infinite possibilities of combinations of different metals and organic linkers, allowing for tailorable properties and pore sizes³. Furthermore, the possibility to post-synthetically functionalise MOFs^{3,4}, without disrupting the extended crystal framework, leads to further possibilities in the discovery of novel structures.

The applications of MOFs are varied and include gas separation⁵ and storage⁶, drug delivery⁷ and catalysis⁸.

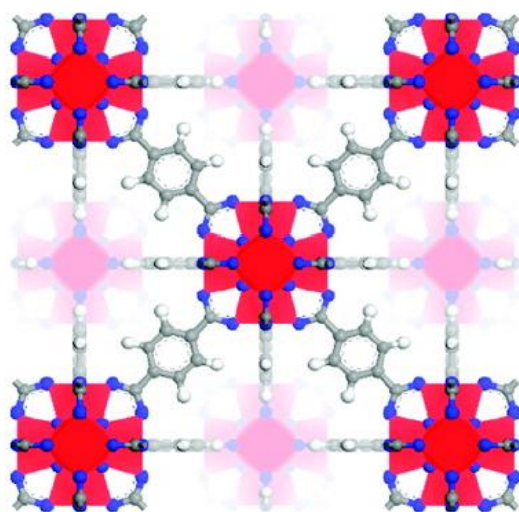


Figure 1. Structure of UiO-66⁹. Figure adapted from Ref 9.

1.2. Synthesis of zirconium-based MOFs

From the large number of MOF structures registered in the Cambridge Structure Database (over 100,000 as of March 2021), it is apparent that MOFs can be easily synthesised. Although traditionally solvothermal methods are used, many other methods have been developed¹⁰, such as grinding¹¹, room temperature mixing¹² and microwave-assisted synthesis¹³.

MOFs form through self-assembly of molecular building blocks into extended frameworks¹⁴, in this case the combination of a metal source and organic linker in solvent. However, this methodology comes with its set of issues, especially in zirconium-based MOFs: the high charge density of Zr (IV) polarises the Zr-O carboxylate linker bond and slows down ligand exchange reactions¹⁵. A prerequisite for highly crystalline MOF formation is the association/dissociation of metal-ligand bond during self-assembly, therefore slow ligand exchange leads to poorly crystalline materials.

Modulated synthesis was developed as a method to produce large phase-pure crystals of MOF materials, and to control properties such as pore sizes and crystallinity. Modulated synthesis involves the introduction of a monotopic organic compound with similar chemical functionality as the linker in the reaction mixture as a capping agent (modulator), thus hindering rapid reaction between self-assembled metal clusters and the organic linkers¹⁶. This competitive reaction leads to more crystalline materials as it modulates nucleation rate and growth of the framework¹⁷. Tsuruoka *et al.*¹⁶ were the first to explore the idea of modulated MOF synthesis, based on a method for metal or semiconductor nanoparticle synthesis^{18,19} and preliminary work conducted by Fischer *et al.*²⁰ This study investigated the effect of acetic acid in the reaction mixture on the synthesis of $\{\text{Cu}_2(\text{ndc})_2(\text{dabco})\}_n$ (ndc = 1,4-naphthalene dicarboxylate; dabco = 1,4-diazabicyclo[2.2.2]octane), a copper-based MOF with a ditopic carboxylate linker. The structure of this is shown in figure 2. The addition of varying concentrations of the modulator led to higher crystallinity within the framework compared to unmodulated synthesis, as shown in figure 3. As concentration is increased, the particle size and crystallinity increase.

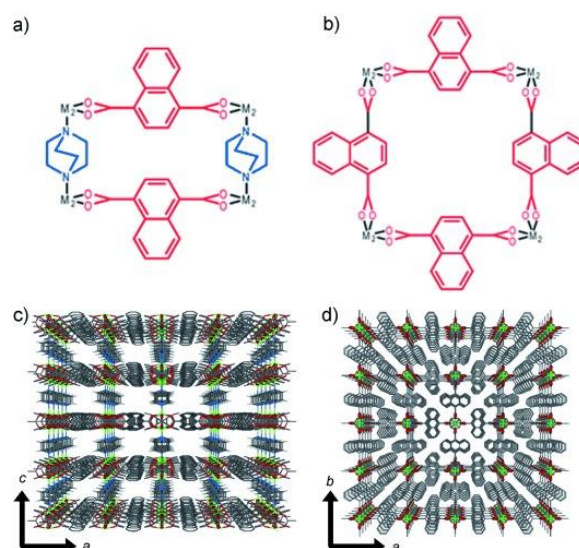


Figure 2. (a) Chemical structure of $\{Cu_2(ndc)_2(dabco)\}_n$ at the (100) surface and (b) the (001) surface. (c) Crystal structure along the b axis and (d) the c axis¹⁶. Figure adapted from Ref 16.

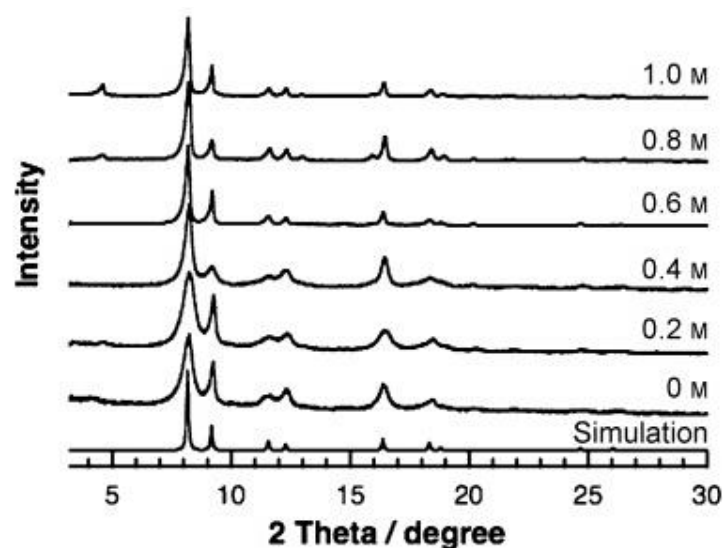


Figure 3. PXRD patterns showing the improvement in crystallinity as concentration of acetic acid is increased¹⁶. This is shown by the sharpening of the peaks. Figure adapted from Ref 16.

1.3. Mixed-metal MOFs

MOFs with multiple metals incorporated into the framework present opportunities in multifunctionalities. The presence of multiple metal centres is advantageous in many of the applications of MOFs^{21,22}, most notably in the field of heterogeneous catalysis where the metal centres present distinct catalytic activities.

Mixed-metal MOFs can be obtained by using a mixture of two metal precursors in the reaction mixture^{23,24} or post-synthetic modification²⁵. The main challenge is the control over the distribution of the metal cations in the framework. Yeung *et al.* have investigated the cation distribution inhomogeneity in mixed-metal MOFs^{26,27}. In their first study²⁷, they prepared mixed-metal Cd-Zn ZIF-8, following $\text{Zn}_{1-x}\text{Cd}_x$, with Cd composition ranging from 0 to 1, increasing in evenly-spaced 0.1 increments. They found considerable variability in the nominal and actual compositions. Using PXRD, it was determined that this indeed formed continuous isostructural structures, rather than a segregated mixture of Zn-ZIF-8 and Cd-ZIF-8. In a second study²⁶, they expanded on their previous research on mixed-metal ZIF-8, maintaining the variations in metal compositions, as well as adding a temperature variable. Two-phase refinements of high-resolution synchrotron diffraction data using the Pawley method showed the existence of Zn-rich and Cd-rich domains, which manifested as nanoparticles made up of a Cd core and a Zn outer shell, the compositions and structures of which were dependent on temperature and metal composition.

The metal cations must be carefully selected to allow cooperative reaction to provide control over the distribution and to prevent the formation of a framework based on a single metal²⁸. Serre *et al.* presented a one-pot synthesis of MIL-53(Cr/Fe)²⁹. Cr^{3+} is fairly unreactive, so the formation of MIL-53(Cr) requires high temperature (150 °C) for 4 days. On the other hand, MIL-53(Fe) is commonly formed from highly reactive Fe^{3+} chloride and only requires 1 day reaction time at 150 °C. MIL-53(Fe) can also be formed from less reactive Fe^0 and water under microwave conditions. For the synthesis of the mixed-metal MIL-53(Cr/Fe), a mixture of Cr^{3+} and Fe^0 cations was used. The selection of Fe^0 allowed to slow down the reaction and provide more control over the reactivity of the metal cations. Later on, the same research group provided a method to provide a higher degree of control in the distribution of metal cations based on the secondary building unit approach³⁰.

The post-synthetic exchange method usually involves the soaking of mono-metallic MOFs in a metal ion solution for several days. While effective, this technique provides poor control over the degree of metal exchange. Lah *et al.* showed that this was dependent on the choice of solvent, concentration and reaction time³¹. Dinca and Brozek developed a method to introduce redox-active di- and trivalent transition metals (Ti^{3+} , $\text{V}^{2+/3+}$, $\text{Cr}^{2+/3+}$, Mn^{2+} , and Fe^{2+}) into Cr- and

Fe-MOF-5, by soaking the MOF-5 crystals into concentrated DMF solutions of the corresponding metal salts³². This was the first example of a MOF containing V^{2+} cations.

These mixed-metal MOFs offer important potential in the field of heterogeneous catalysis. By varying the metal centres, the regio-, chemo- and stereo-selectivity can be tailored. Studies have shown that mixed-metal MOFs exhibit higher catalytic activity, especially in oxidation reactions. One such example is MOF-74 (Cu/Co) which was used in the oxidation of styrene towards benzaldehyde, styrene oxide and phenylacetaldehyde³³. While the monometallic MOF-74(Cu) showed poor catalytic activity (0.6% conversion) with 100% selectivity to benzaldehyde, incorporating Co^{2+} centres into the MOF-74(Cu) framework showed improvements to the conversion styrene to benzaldehyde, styrene oxide and phenylacetaldehyde. Mixed-metal MOFs also show an increase in gas adsorption and separation compared to their monometallic counterparts^{34,35}.

1.4. Metal clusters

1.4.1. Self-assembly of metal clusters in MOFs

Despite the high volume of MOFs being discovered, the discovery of new stable metal cluster building block is an uncommon occurrence. Some common examples are the $Cu_2(OH)_2(CO_2)_4$ cluster from HKUST-1³⁶ (figure 4), the $Zn_4O(CO_2)_6$ cluster from MOF-5³⁷ and the $Zr_6O_4(OH)_4(COO)_{12}$ building block from UiO-66⁹. The high stability of MOF frameworks is attributed to the inorganic building block and the strength of the bonding between the metal clusters and the organic linker.

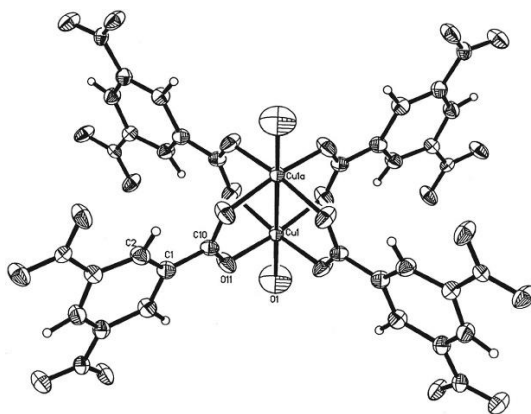


Figure 4. Representation of the $\text{Cu}_2(\text{OH})_2(\text{CO}_2)_4$ cluster from HKUST-1³⁶. Figure adapted from Ref 25.

The metal node of UiO-66 is formed by a 12-coordinated Zr_6 metal cluster. It is a key factor in the exceptional stability of the framework⁹. The cluster consists of a $\text{Zr}_6\text{O}_4(\text{OH})_4$ inner core, formed by a Zr_6 octahedron where each triangular face is alternatively bridged by an $\mu_3\text{-O}$ or an $\mu_3\text{-OH}$ group, where μ_3 indicates that the groups are bridging between three metal centres. Each edge of the octahedron is bridged by carboxylates from the linker, to give a $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{RCOO})_{12}$ metal cluster, where (RCOO) is a carboxylate (figure 5).

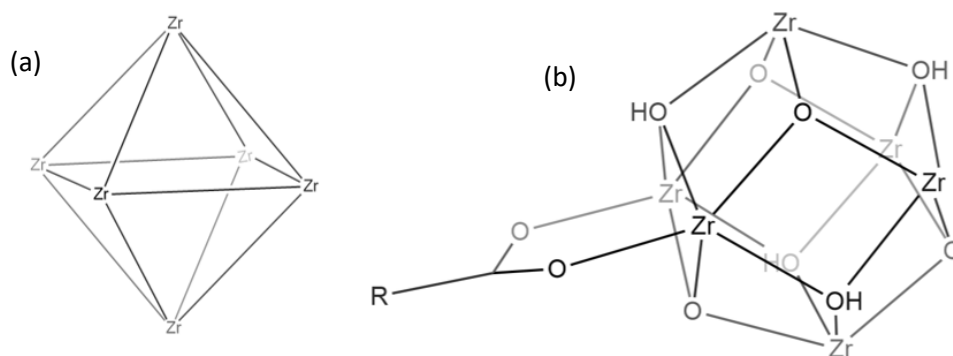


Figure 5. Representations of (a) the Zr_6 octahedron and (b) of the overall cluster found in UiO-66.

1.4.2. Discrete group IV metal clusters

The metal clusters found in MOFs were first synthesised as discrete molecules. For example, there are many Zr_6 clusters that preceded the discovery of UiO-66, for example Zr_6 methacrylate, $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{OMc})_{12}$ ($\text{OMc} = \text{CH}_2=\text{CH}(\text{CH}_3)\text{COO}$)³⁸ and Zr_6 benzoate,

$\text{Zr}_6\text{O}_4(\text{OH})_4(\text{OBz})_{12}$ ($\text{OBz} = (\text{C}_6\text{H}_5)\text{COO}$). The monocarboxylate is readily exchangeable without compromising structural integrity of the core. Other Zr cluster types exist with different nuclearity, such as Zr_4 , Zr_8 and Zr_{12} , where two Zr_6 clusters combine through a condensation reaction to give a bridging $(\text{Zr}_6)_2$ cluster³⁹ (figure 6).

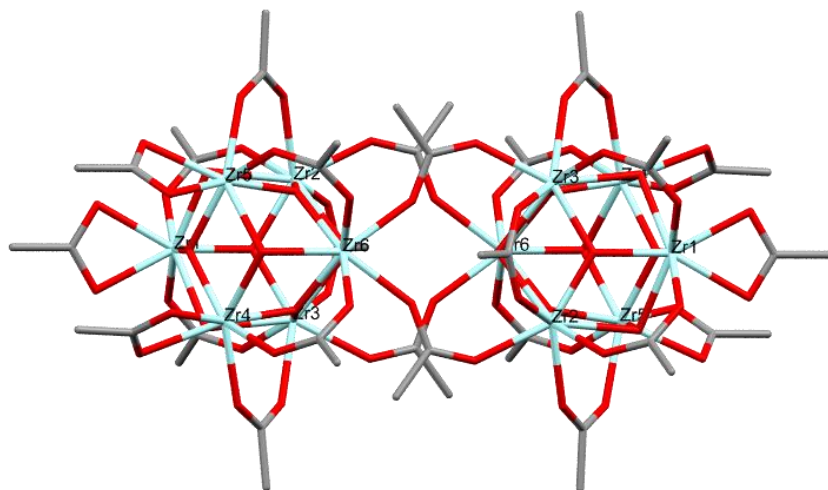


Figure 6. Structure of $(\text{Zr}_6 \text{ acetate})_2$ cluster. Here two Zr_6 clusters are joined through acetate molecules.⁴⁰ H atoms are omitted for clarity. Colour key: Zr, blue; C, grey; O, red.

The Zr_6 benzoate cluster, $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{OBz})_{12}(\text{OPr})$, can be synthesised by refluxing Zr butoxide and benzoic acid in $n\text{PrOH}$ for 24 hours. Unlike the Zr_6 nodes found in UiO-66, the discrete pre-synthesised clusters vary slightly in structure. The Zr nodes formed in the self-assembly of UiO-66 consist of the $\text{Zr}_6\text{O}_4(\text{OH})_4$ inner core, and 12 carboxylate molecules, bridging between two zirconium atoms, where each O atom of the carboxylate is bonded to a Zr atom. While the structure of the synthesised Zr_6 cluster retains the inner core, only eight of the benzoate ligands are bridging, while two of the remaining three are chelating, where both O atoms are bonded to the same Zr atom. The last benzoate ligand is converted to a monodentate ligand and leaves a vacant coordination site where a propanol ligand is bonded⁴¹ (figure 7).

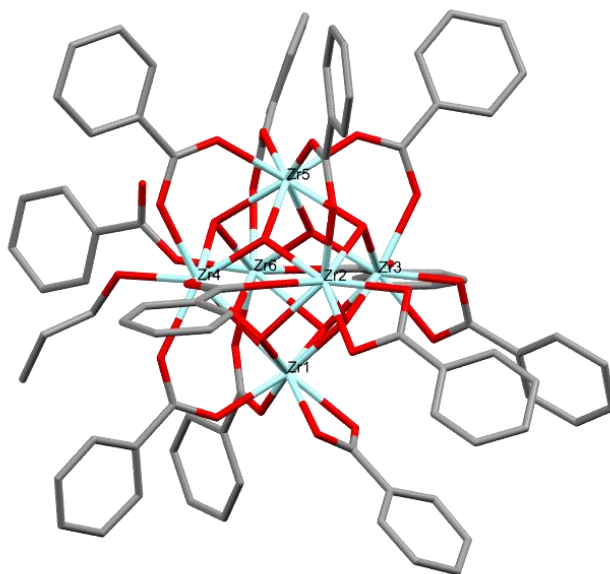


Figure 7. Structure of Zr_6 benzoate cluster, $Zr_6O_4(OH)_4(OBz)_{12}(OPr)$. H atoms omitted for clarity. Colour key: Zr, blue; C, grey; O, red.

The Zr_6 methacrylate cluster, $Zr_6O_4(OH)_4(OMc)_{12}$, was discovered in 1996, by reacting $Zr(O^iPr)_4$ with an excess of methacrylic acid.⁴² Like the Zr benzoate cluster, the $Zr_6O_4(OH)_4$ core is retained and nine of the methacrylate ligands are bridging while the remaining three are chelating, with both O atoms bonded to the same Zr atom. The original paper presents two zirconium methacrylate clusters, with their structure being determined only by the molar ratios of starting material. When using a four-fold excess of methacrylic acid, the Zr_6 methacrylate cluster (figure 8), $Zr_6O_4(OH)_4(OMc)_{12}$, is obtained, whereas using a fifteen-fold excess leads to a Zr_4 cluster (figure 9), $Zr_4O_2(OMc)_{12}$.

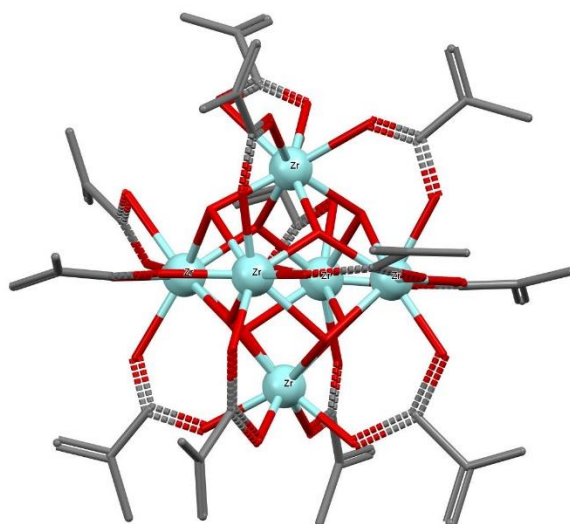


Figure 8. Structure of Zr_6 methacrylate cluster. H atoms omitted for clarity. Colour key: Zr, blue; C, grey; O, red.

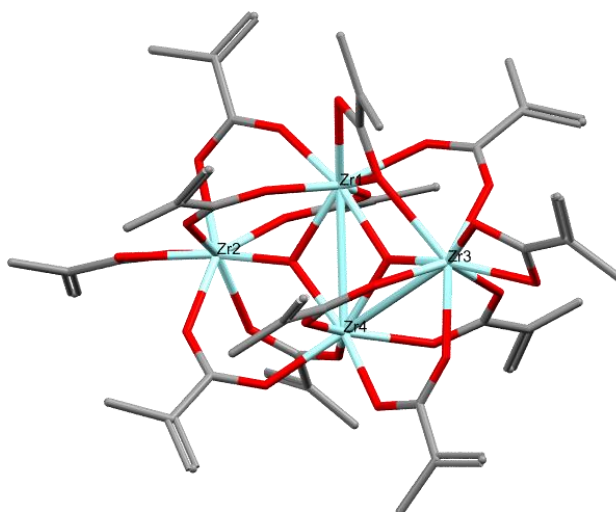


Figure 9. Structure of Zr_4 methacrylate cluster. H atoms omitted for clarity. Colour key: Zr, blue; C, grey; O, red.

Zr_{12} clusters are made up of two Zr_6 subunits, with their inner core ($\text{Zr}_6\text{O}_4(\text{OH})_4$) being the same as the previous clusters. Zr_6 clusters capped by either water or hydroxyl ligands can rearrange to form a $(\text{Zr}_6)_2$ cluster connected through hydroxyl groups. Alternatively, non-coordinating oxygen atoms of a carboxylate-capped cluster can replace a terminal ligand of another cluster, thus rearranging to a carboxylate-bridged $(\text{Zr}_6)_2$ cluster (figure 10). These have

been obtained with multiple carboxylates including acetate, acrylate, propanoate and methacrylate^{39,43}.

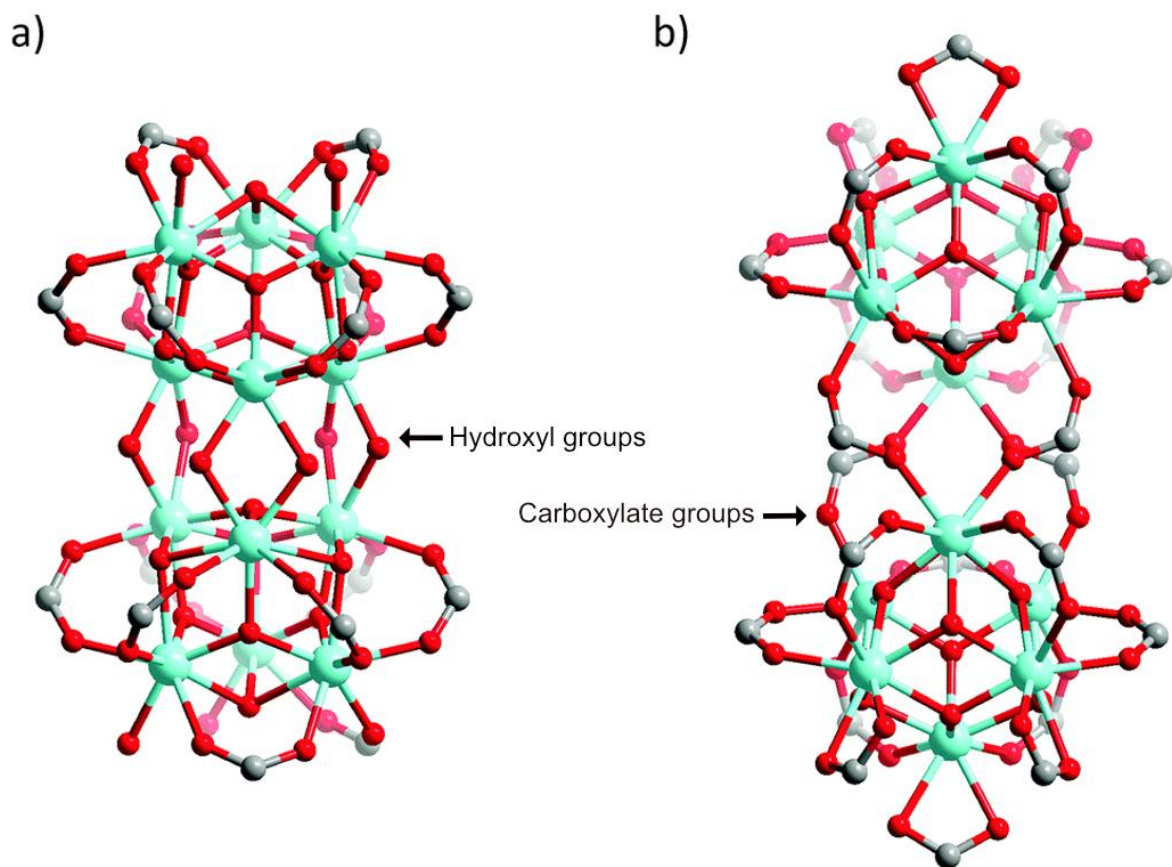


Figure 10. Zr_{12} clusters formed from two Zr_6 subunits bridged by (a) hydroxyl groups and (b) carboxylate groups⁴⁰. Colour key: Zr, blue; C, grey; O, red. Figure adapted from Ref 29.

The Zr_{12} acetate cluster, $Zr_{12}O_8(OH)_8(OAc)_{24}$ ($OAc = CH_3CO_2$), is composed of two Zr_6 acetate subunits connected by four bridging acetate ligands. Out of the remaining acetate ligands, seven are bridging between two Zr atoms and three are bonded to a single Zr atom where both O atoms are chelating in each of the Zr_6 octahedra (figure 11).

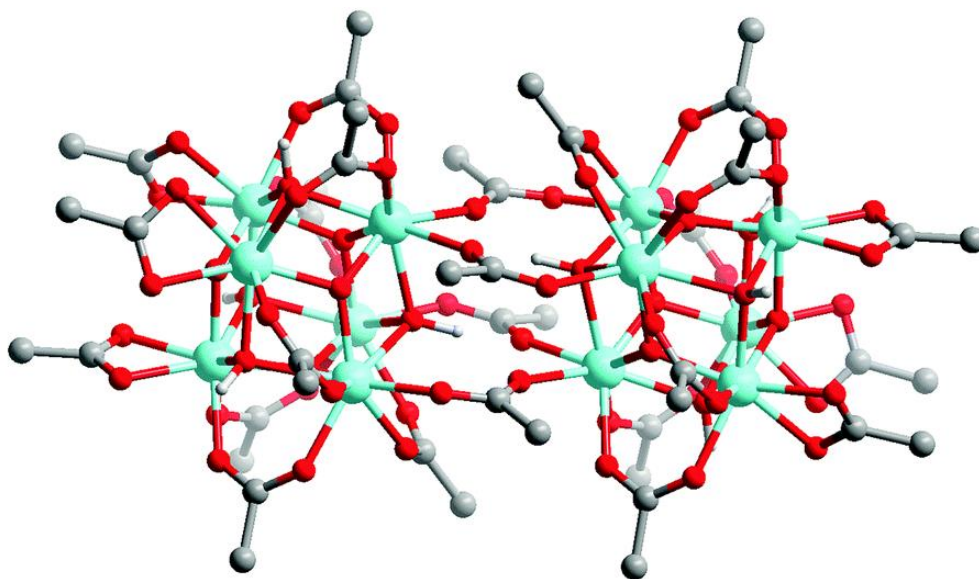


Figure 11. Structure of the Zr_{12} acetate cluster⁴⁰. Colour key: Zr, blue; C, grey; O, red. Figure adapted from ref 29.

Titanium clusters are also readily attainable. The Ti_6 inner core, $Ti_6O_6(O^iPr)_6$, differs from the Zr_6 inner core, $Zr_6O_4(OH)_4$, and leads to clusters with formula $Ti_6O_6(O^iPr)_6(RCOO)_6$, where (RCOO) is a carboxylate. Some examples include Ti_6 aminobenzoate⁴⁴, $Ti_6O_6(O^iPr)_6(ABZ)_6$, and Ti_6 butyrate⁴⁵, $Ti_6O_6(O^iPr)_6(BTA)_6$.

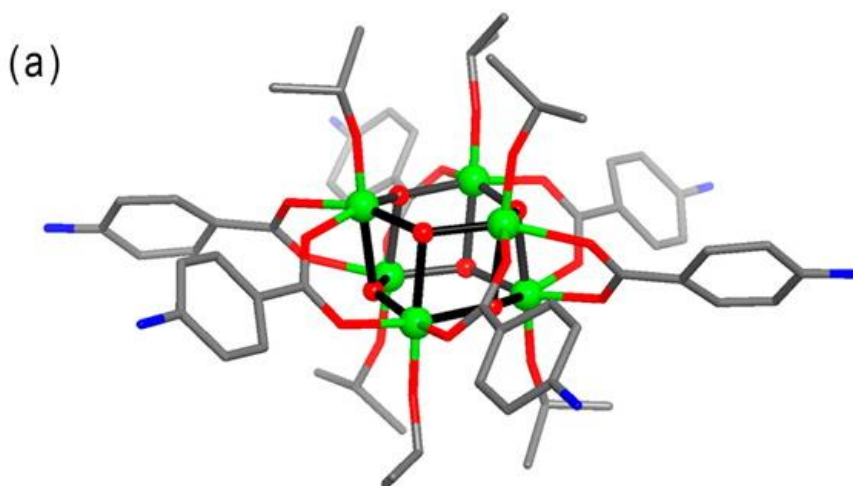


Figure 12. Ti_6 aminobenzoate cluster. H atoms omitted for clarity⁴⁴. Colour key: Ti, green; C, grey; O, red; N, blue. Figure adapted from Ref 33.

While the focus of this project was on zirconium and titanium clusters, hafnium clusters can also be synthesised. Hafnium-oxo clusters are much rarer than both zirconium and

titanium clusters. To my knowledge the only Hf₆ cluster that has been successfully synthesised is a Hf₆ methacrylate⁴⁶ (figure 13). Similarly to the formation of the Zr₆ methacrylate cluster, the Hf analogue is obtained when a 90% solution of Hf(OBu)₄ in BuOH is reacted with 7.5 equivalents of methacrylic acid. The formula of the cluster is Hf₆O₄(OH)₄(OMc)₁₂(BuOH). The Hf cluster is iso-structural to its Zr analogue. The only difference is that one of the bridging methacrylate ligands is converted into a chelating one, leaving a vacant site for the coordination of a butanol molecule.

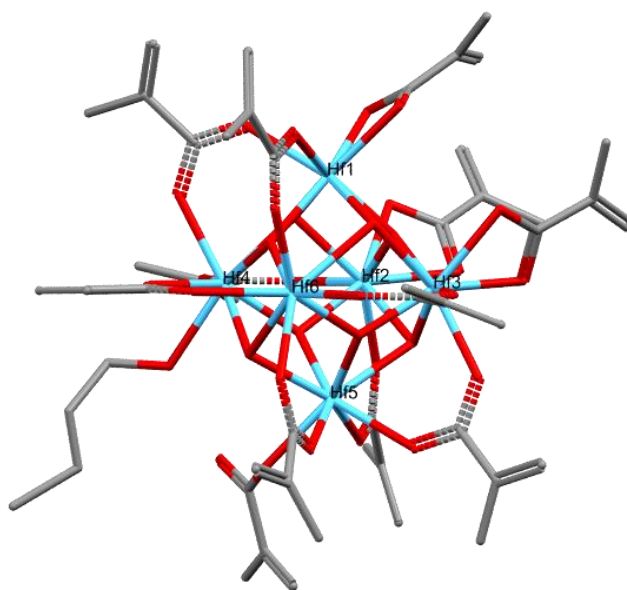


Figure 13. Structure of the Hf₆ methacrylate cluster. H atoms omitted for clarity. Colour key: Hf, blue; C, grey; O, red.

1.4.3. Clusters as starting materials for the synthesis of MOFs

Because of their structural stability and unvarying nature, pre-formed metal clusters have been used as precursors in MOF reactions, rather than simply using a metal salt. Early work focused on copper dimers⁴⁷ and iron trimers⁴⁸. This technique of using “self-modulating” clusters presents many advantages such as the possibility of milder conditions (lower temperature, greener solvents, etc.) and control of the nature and topology of the framework.

Férey *et al.* were the first to use a Zr₆ cluster for the synthesis of MOFs to successfully produce a framework with UiO-66 topology⁴⁹. Whereas previous syntheses of UiO-66 had used solvothermal conditions (dimethylformamide (DMF), 120 °C) beginning from a mixture of

ZrCl₄ and terephthalic acid, their study replaced the metal salt with a Zr₆ methacrylate cluster precursor, Zr₆O₄(OH)₄(OMc)₁₂, and used both terephthalic acid and *trans,trans*-muconic acid individually as the organic linkers (figures 14 and 15).

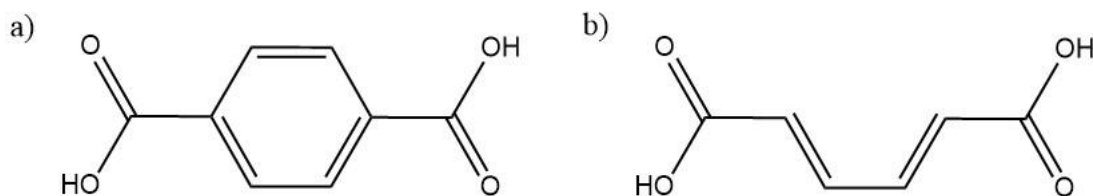


Figure 14. Structure of (a) terephthalic acid and (b) *trans,trans*-muconic acid.

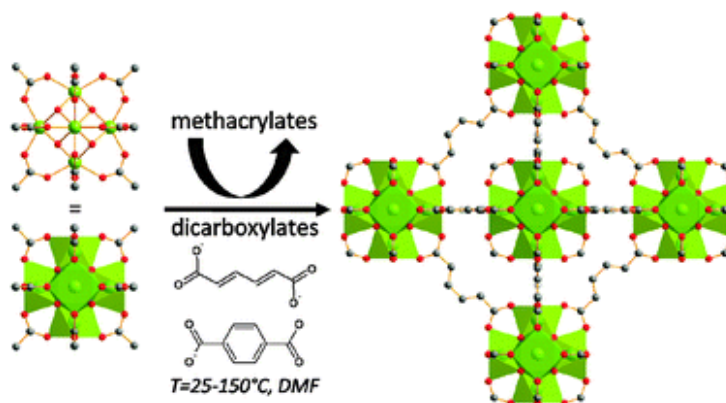


Figure 15. General scheme of synthetic conditions of UiO-66 using Zr₆ methacrylate precursor⁴⁹. Figure adapted from Ref 38.

Using terephthalic acid as the linker, the framework was found to have lower crystallinity than when using ZrCl₄ but diffraction peaks matched those of UiO-66 (figures 16 and 17), and the BET surface area was found to be similar⁴⁹. Brunauer-Emmett-Teller (BET) surface area analysis is a technique that can be used to measure the surface area of MOFs, with varying pore sizes and surface areas, through adsorption of gases.

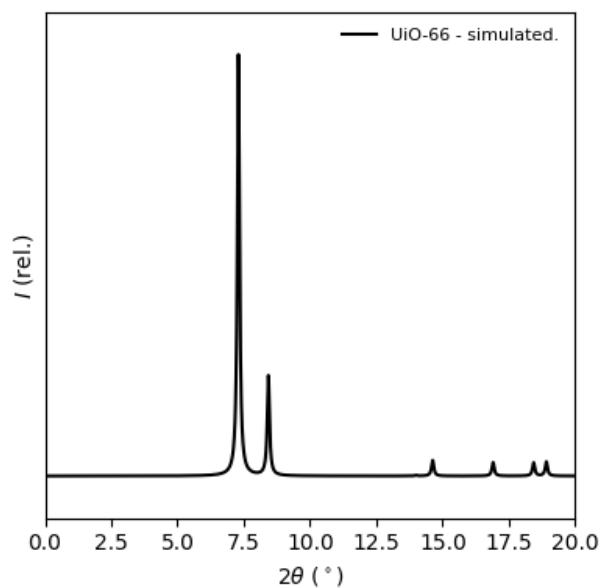


Figure 16. Simulated PXRD pattern of UiO-66 ($\lambda = 1.5406 \text{ \AA}$) showing characteristic peaks at $2\theta = 7.26^\circ$ and $2\theta = 8.43^\circ$.

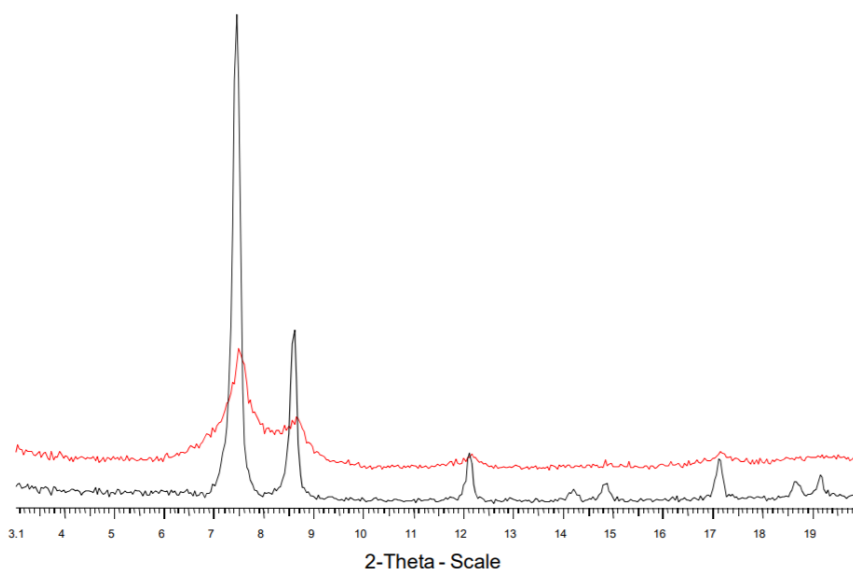


Figure 17. PXRD pattern of UiO-66 ($\lambda = 1.5406 \text{ \AA}$) formed from ZrCl_4 (black) and Zr_6 methacrylate cluster (red)⁴⁹. Figure adapted from SI of Ref 38.

In contrast, when using *trans,trans*-muconic acid, no crystalline product was formed when using ZrCl_4 as precursor, no matter what temperature or reaction time are used. However, using the cluster as starting material, UiO-66 readily formed regardless of the stoichiometry, concentration, temperature or reaction time (figure 18).

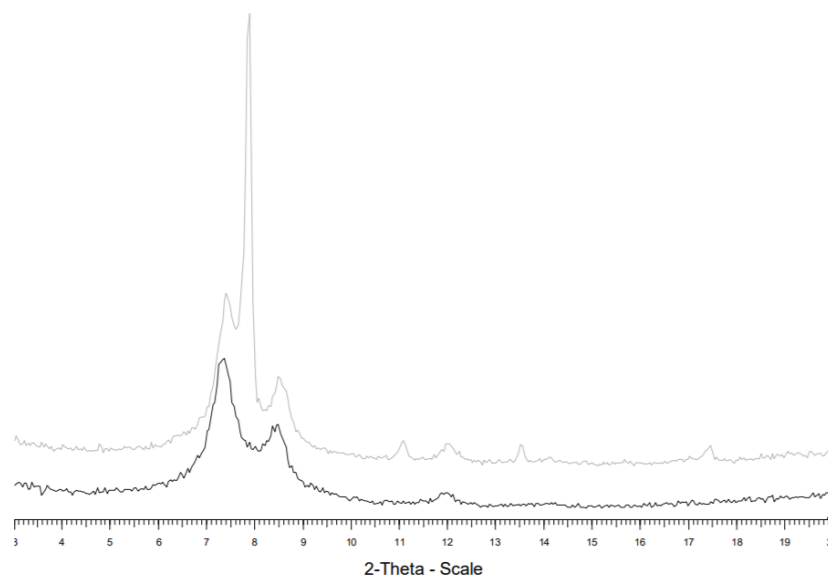


Figure 18. PXRD pattern of UiO-66 ($\lambda = 1.5406 \text{ \AA}$) formed from *trans,trans*-muconic acid and Zr_6 methacrylate with organic impurity at $2\theta = 7.8^\circ$ (grey) and after washing with DMF (black)⁴⁹. Figure adapted from SI of Ref 38.

Other methods have been employed to synthesise MOFs using Zr-oxo clusters. Frišćić *et al.* were the first to report a mechanochemical and solvent-free route to UiO-66 and UiO-66-NH₂, using both Zr_6 methacrylate, $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{OMc})_{12}$, and Zr_6 benzoate, $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{OBz})_{12}$, clusters as starting materials⁵⁰. The reactions were performed under liquid-assisted grinding (LAG) using small amounts of DMF or methanol, and used terephthalic acid and aminoterephthalic acid as the linker for UiO-67 and UiO-67-bpy respectively (figure 19).

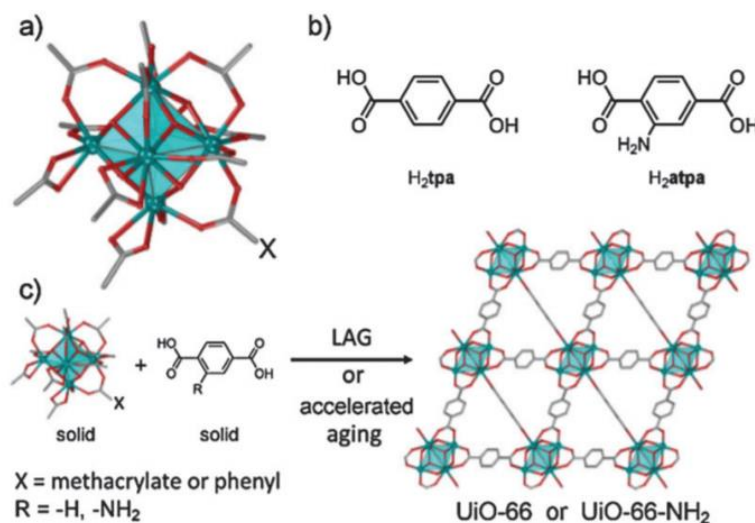


Figure 19. (a) Structure of carboxylate-capped Zr_6 clusters, (b) structures of terephthalic acid and amino terephthalic acid and (c) LAG syntheses of UiO-66 and UiO-NH₂⁵⁰. Figure adapted from Ref 39.

Dry-milling of their starting materials, the Zr_6 clusters and terephthalic acid, did not lead to chemical reaction with either of the clusters. However, using DMF in LAG reactions led to broad peaks consistent with the reflections of UiO-66, suggesting the successful formation of UiO-66 with poor crystallinity (figure 20e and 20f).

Using methanol as the milling liquid showed little improvement for the reaction with the benzoate cluster (figure 20g). However, using the methacrylate cluster, crystallinity was widely improved leading to sharp, well-defined peaks consistent with those of UiO-66 (figure 20h). At the time, this was the first example of the formation of UiO-66 without using DMF or HCl.

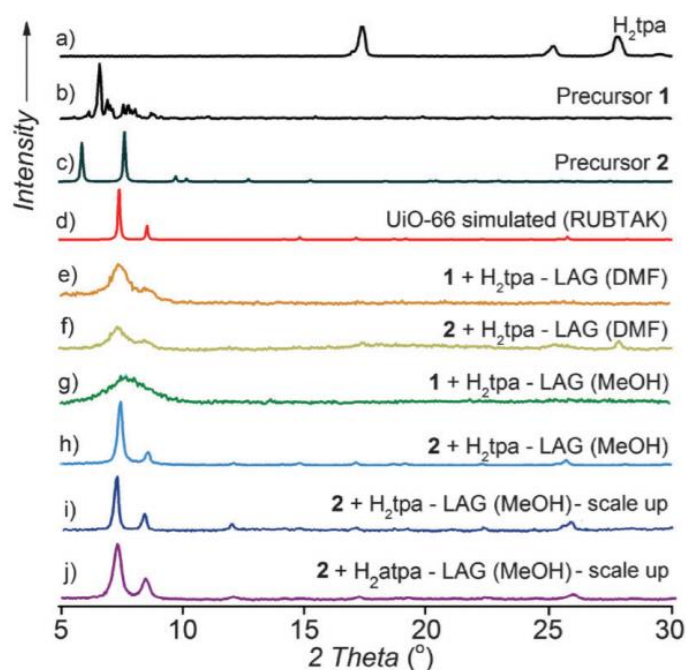


Figure 20. PXRD patterns of (a) terephthalic acid, (b) Zr_6 benzoate cluster, (c) Zr_6 methacrylate cluster, (d) simulated UiO-66, (e) LAG of Zr_6 benzoate cluster and terephthalic acid with DMF, (f) Zr_6 methacrylate and terephthalic acid with DMF, (g) LAG of Zr_6 benzoate cluster and terephthalic acid with methanol, (h) LAG of Zr_6 methacrylate cluster and terephthalic acid with methanol, (i) scaled-up reaction of Zr_6 methacrylate cluster and terephthalic acid with methanol and (j) scaled-up reaction of Zr_6 methacrylate cluster and aminoterephthalic acid with methanol⁵⁰. Figure adapted from Ref. 39.

Finally, Noh *et al.* successfully synthesised NU-901 at room temperature using a Zr_6 benzoate cluster, $Zr_6O_4(OH)_4(OBz)_{12}$, as starting material and acetic acid as a modulator⁵¹. Compared to the usual method for the preparation of NU-901, $\{Zr_6(\mu_3-O)_4(\mu_3-OH)_4(H_2O)_4(OH)_4(H_4TBAPy)\}_n$ (H_4TBAPy = 1,3,6,8-tetrakis-(*p*-benzoate)-pyrene), which requires the reaction to be performed at 120 °C⁵², their method is considered much “greener” and demonstrates the possibility for more sustainable synthetic conditions using clusters instead of traditional metal salts.

Titanium MOFs are very challenging to synthesise as single crystals⁵³ due to charge density and poor ligand exchange reactions. Because of this, there are only a handful of Ti-carboxylate MOFs that have been characterised by single-crystal X-ray diffraction, namely FIR-125 – FIR-127⁵³, Ti₃-BPDC⁵⁴, PCN-22⁵⁵, NTU-9⁵⁶ and DGIST-1⁴⁵. Zhou *et al.*⁵⁵ were the first to synthesise single-crystals of a Ti-MOF, PCN-22, using a Ti₆ aminobenzoate cluster. They concluded that using clusters as precursors not only slowed down the crystallisation process, but also diminished the hydrolysis of the Ti⁴⁺ ions which would lead to the formation of TiO₂. The field of Ti-MOFs is underdeveloped and this paper was a breakthrough to access highly-crystalline Ti-MOFs and has enabled increasing development of Ti-MOFs since its publication in 2015.

Pre-synthesised clusters are potentially a powerful route for the synthesis of new MOFs. They are very close in structure to clusters found in MOFs and therefore negate the need for in-situ self-assembly of the clusters. They can be considered to have “self-modulating” properties and the use of monocarboxylate modulators may no longer be needed as one of their roles is to block metal coordination site during the self-assembly process⁵⁷. Studies also show that using clusters can lead to formation of frameworks with certain linkers that were previously unattainable by using ZrCl₄ as precursor⁴⁹. They can also be used to obtain crystalline Ti-MOFs, a difficult procedure using simple Ti salts or alkoxides. Clusters have the potential of leading to new synthetic routes for more sustainable syntheses of MOFs and new structures.

1.5. Research objectives

The aim of this project was to use pre-synthesised group IV metal clusters to make MOFs, and to investigate the factors that affect crystallinity and formation of extended frameworks. While conditions for the formation of MOFs can be quite harsh, using high-temperatures and strong acids as modulators, clusters have the potential to require milder, “greener” conditions. While the formation of MOFs from pre-synthesised clusters has been previously established^{47–51,55}, no extensive studies on how specific factors, such as temperature, reaction time, molar ratios, etc., affected the formation of crystalline products have been done. The research presented in this thesis shows these systematic investigations towards a better understanding of the

mechanisms of MOFs formation from clusters and the role of various conditions in the synthetic environment.

Understanding and idealising synthetic conditions was important, as another target was to attempt to synthesise mixed-cluster MOFs, where there are two types of clusters in the framework with each a different metal, in this case zirconium and titanium, as opposed to mixed-metal MOFs²⁸, where multiple metals are contained within the same cluster. This could lead to a new class of MOFs with potentially very interesting properties. Mixed-metal MOFs show promising opportunities in the fields of heterogeneous catalysis and gas adsorption and separation^{21,22,33-35}. However, the main issue with these is the lack of control over the distribution and ratios of the metal centres^{26,27}. Mixed-cluster MOFs could potentially provide more control over these issues.

The incorporation of Ti into Zr-UiO-66 has been studied⁵⁸⁻⁶⁰. There are two hypothesis on the integration of Ti into the framework: either through metal exchange in the clusters, or by grafting onto the surface of a linker vacancy site. Metal exchange attempts were made, but the results were inconclusive in regards to the nature of the exchange^{59,61}. Further studies⁶² showed that the integration of Ti into the Zr-UiO-66 framework was through grafting of the linker vacancy sites rather than through metal exchange. A mixture of pre-synthesised Zr and Ti clusters could potentially lead to a true mixed-metal Zr/Ti framework rather than Ti-grafted Zr-UiO-66.

Chapter 2: Clusters syntheses

This section discusses the clusters that have been successfully synthesised, as well as the challenges faced when trying to form novel clusters.

As mentioned in the introduction, modulators can be used in MOF reactions starting from metal salts to slow down reactions between the self-assembling clusters and the linkers. These modulators usually have similar functionalities as the linker, so one might choose benzoic acid when using terephthalic acid as the linker for example. Because the MOF reactions that were later explored used terephthalic acid and its derivatives as the linkers, the ABZ and OBz clusters were of great interest as they most closely resemble the self-assembled clusters formed in modulated reactions.

One of the aims of the project was to try to synthesise zirconium and titanium mixed-cluster MOFs, so the focus was on trying to make clusters with the same carboxylates. While the benzoate and aminobenzoate clusters are known for zirconium and titanium respectively, the synthesis of the same carboxylate-capped cluster for both metals proved to be challenging, mainly due to issues with characterisation due to low crystallinity of the products.

Here I highlight the successful syntheses of Zr_6 benzoate and methacrylate and Ti_6 aminobenzoate clusters, as well as the attempts to synthesise new clusters.

2.1. Results

2.1.1. Zr benzoate cluster, $Zr_6O_4(OH)_4(OBz)_{12}(OPr)$

Initial attempts to synthesise the Zr_6 benzoate cluster were successful using a procedure adapted from the literature⁵¹. Zr butoxide and benzoic acid in a 1:25 molar ratio were refluxed in nPrOH for 24 hours. The formation of the correct phase of the cluster was confirmed by PXRD (figure 21). The presence of small diffraction peaks between $Q = 1.3 \text{ \AA}^{-1}$ and $Q = 2.3 \text{ \AA}^{-1}$ indicated that small amounts of benzoic acid were still present in the sample.

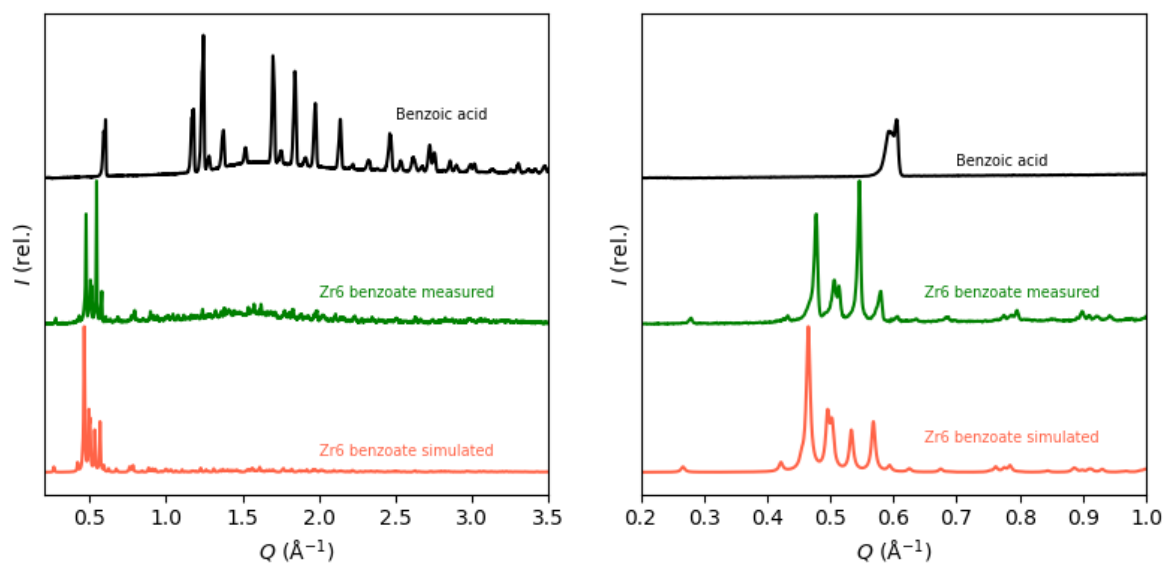


Figure 21. Calculated PXRD pattern of Zr benzoate cluster acid (orange), and the measured patterns of Zr₆ benzoate cluster (green) and benzoic acid (black). The figure on the right is a zoom in between $Q = 0.2 \text{ \AA}^{-1}$ and $1.0 \text{ \AA}^{-1}$.

To try to remove the benzoic acid, washes were then done on the samples with $3 \times 6 \text{ mL}$ of nPrOH. This, however, led to a different, less crystalline polymorph of the cluster (figure 22), and so no washes were done on further batches of the cluster.

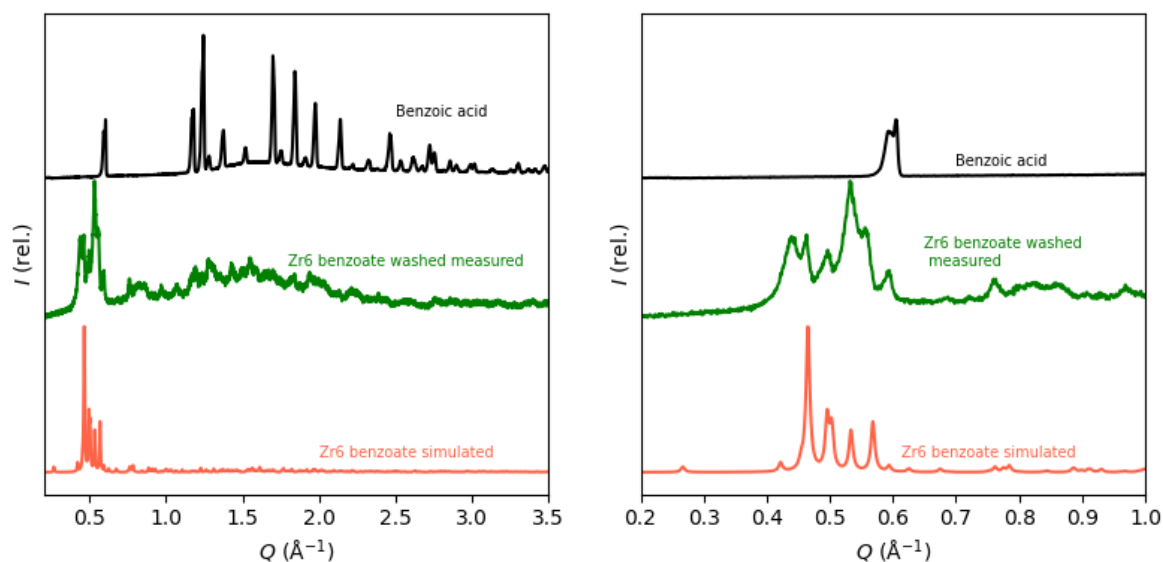


Figure 22. Calculated PXRD pattern of Zr benzoate cluster (orange) and measured patterns of Zr₆ benzoate cluster after washing with nPrOH (green) and of benzoic acid (black). The figure on the right is a zoom in between $Q = 0.2 \text{ \AA}^{-1}$ and $1.0 \text{ \AA}^{-1}$.

Room temperature synthesis was explored as an alternative route to the cluster, to try to avoid the need for higher temperatures. All variables were kept the same as the reflux reaction but instead, the reaction mixture was stirred at room temperature for 24 hours. Similarly to the reflux reaction, white precipitate formed. PXRD indicated the room temperature synthesis was less crystalline than the reflux one, and also contained more benzoic acid (figure 23).

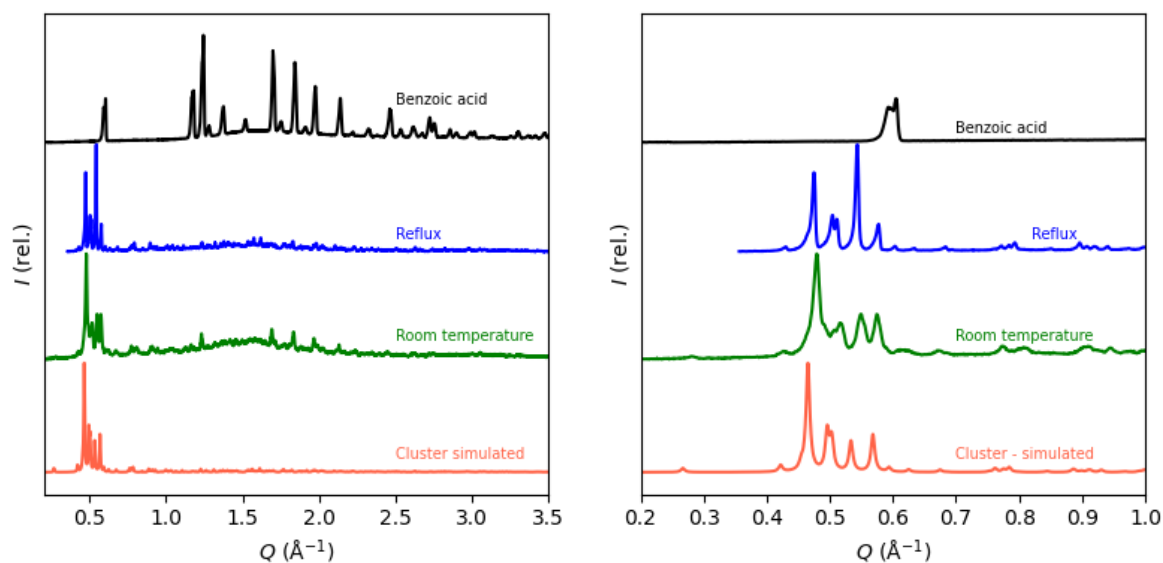


Figure 23. Calculated PXRD pattern of Zr benzoate cluster (orange), and the measured patterns of the room temperature synthesis of Zr_6 benzoate cluster (green), the reflux synthesis of Zr_6 benzoate cluster (blue) and benzoic acid (black). The figure on the right is a zoom in between $Q = 0.2 \text{ \AA}^{-1}$ and $1.0 \text{ \AA}^{-1}$.

2.1.2. Zr methacrylate cluster, $Zr_6O_4(OH)_4(OMc)_{12}$

The method for the Zr_6 cluster was adapted from literature⁴², however this was not done in argon atmosphere like in the paper as neither the starting materials or the product are particularly air-sensitive, and Zr propoxide, $Zr(O^iPr)_4$, was substituted with Zr butoxide, $Zr(O^iBu)_4$, in BuOH. Unlike in the paper, crystals started forming after a week rather than a day, and gave big colourless needles (figure 24).

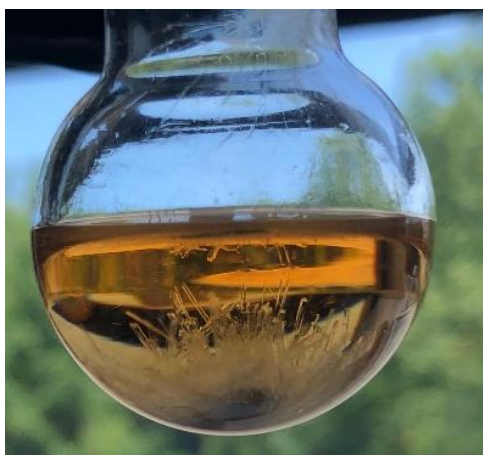


Figure 24. Needles of Zr_6 methacrylate cluster.

A unit cell check was done on some single-crystals of the cluster, which showed that it had successfully formed a Zr_6 methacrylate cluster, however, the quality of the data was not sufficient to fully characterise what had been made. The needles were ground and analysed by PXRD (figure 25). This showed that the product was not very crystalline, and that the phase did not correspond to the simulated Zr_6 methacrylate cluster pattern for the known structure. It is possible that the drying of the grinding of the samples had led to a phase change. The synthesis of the cluster was repeated to try to get a more crystalline and phase-pure product.

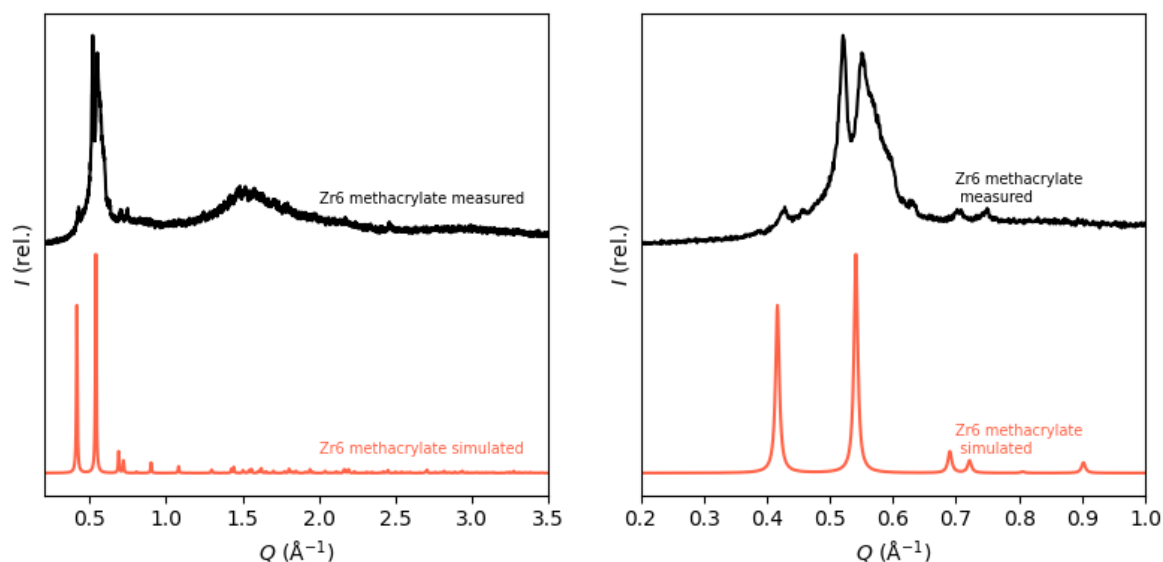


Figure 25. Calculated PXRD pattern of the Zr_6 methacrylate cluster (orange) and the measured pattern of the attempted synthesis (black). The figure on the right is a zoom in between $Q = 0.2 \text{ \AA}^{-1}$ and $1.0 \text{ \AA}^{-1}$.

The PXRD analysis of the second attempt at synthesising the cluster showed that the product was more crystalline but that it was still not phase pure (figure 26).

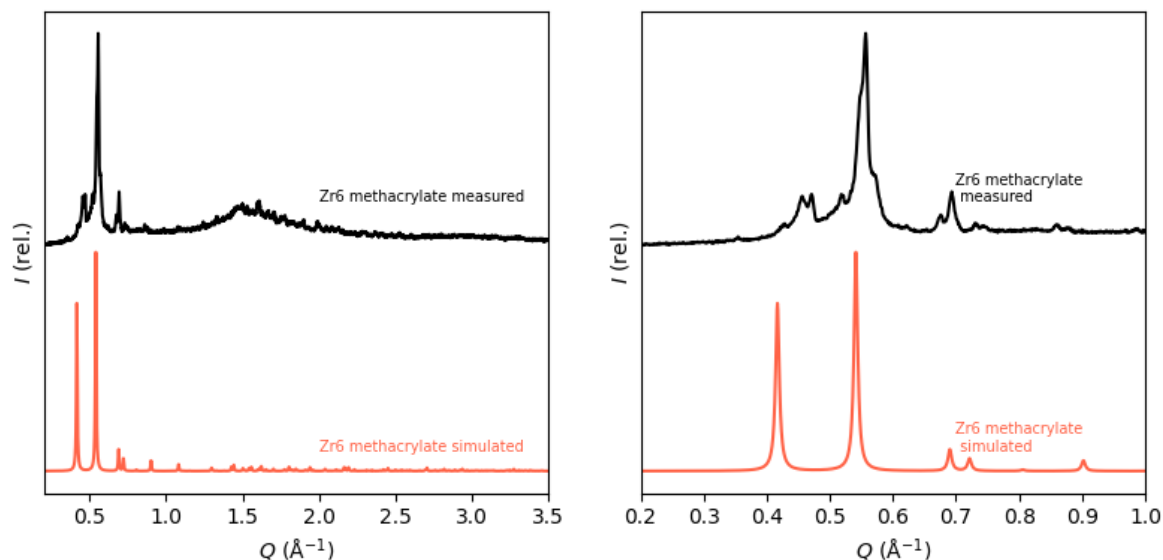


Figure 26. Calculated PXRD pattern of the Zr_6 methacrylate cluster (orange) and the measured pattern of the second attempted synthesis (black). The figure on the right is a zoom in between $Q = 0.2 \text{ \AA}^{-1}$ and $1.0 \text{ \AA}^{-1}$.

To try to determine the phase of the cluster, this measured set of data was compared to the calculated patterns for other possible Zr methacrylate clusters (figure 31). All these are variations of the $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{OMc})_{12}$ cluster and their formation largely depend on the molar ratio of Zr (O^iBu)₄ to methacrylic acid in the reaction conditions. The Zr_6 cluster that was trying to be synthesised (figure 27), $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{OMc})_{12}$, is obtained when a four-fold excess of methacrylic acid is used. A Zr_4 methacrylate cluster (figure 28), $\text{Zr}_4\text{O}_2(\text{OMc})_{12}$, is obtained when using a 15-fold excess of methacrylic acid⁴². Two other Zr_6 clusters can be obtained by using different ratios. The cluster $\text{Zr}_6\text{O}_2(\text{OBu})_{10}(\text{OMc})_{10}$ (figure 29) is obtained when 1.6 molar equivalents of methacrylic acid is used⁶³. The low molar ratio leads to low substitution of the butoxide groups with methacrylate ligands, hence the formation of this cluster. The final cluster, $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{OMc})_{12}(\text{OPr})$ (figure 30) is obtained when 9 equivalents of acid are used⁴¹. The cluster is different from the desired cluster as one of the bridging methacrylate ligands is converted to a monodentate one. The vacant coordination site is occupied by a propanol molecule.

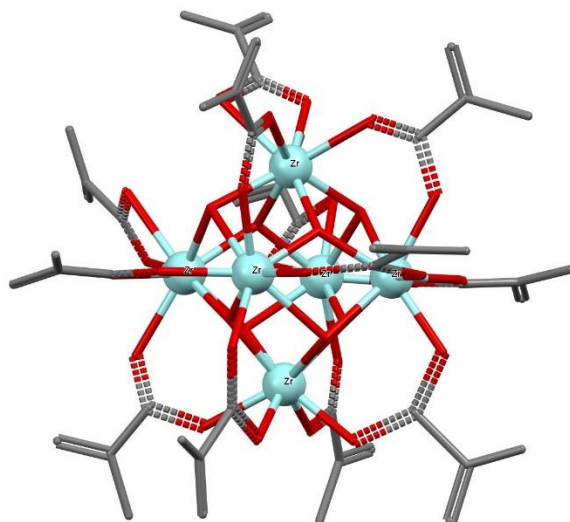


Figure 27. Structure of $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{OMc})_{12}$ cluster. H atoms omitted for clarity. Colour key: Zr, blue; C, grey; O, red.

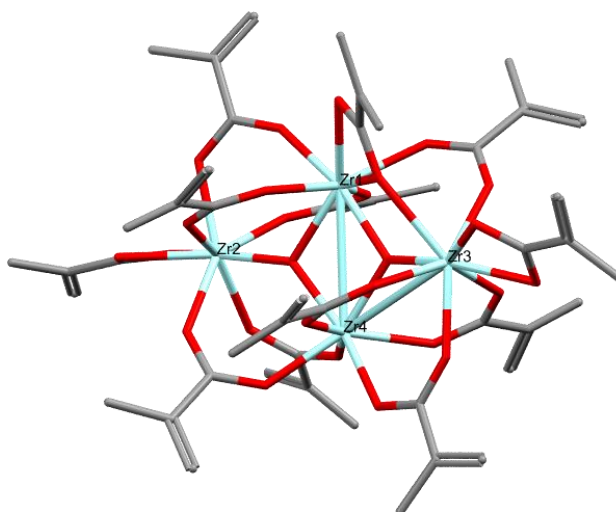


Figure 28. Structure of $\text{Zr}_4\text{O}_2(\text{OMc})_{12}$ cluster. H atoms omitted for clarity. Colour key: Zr, blue; C, grey; O, red.

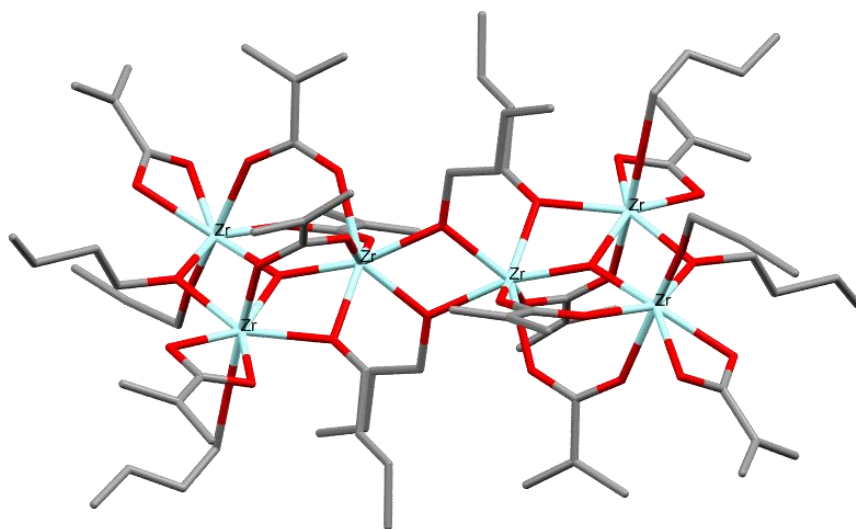


Figure 29. Structure of $\text{Zr}_6\text{O}(\text{OBu})_{10}(\text{OMc})_{10}$ cluster. H atoms omitted for clarity. Colour key: Zr, blue; C, grey; O, red.

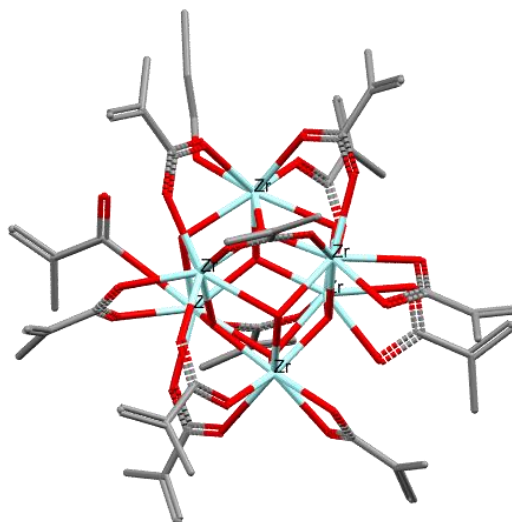


Figure 30. Structure of $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{OMc})_{12}(\text{PrOH})$ cluster. Hydrogen-bonded methacrylic acid molecules and H atoms omitted for clarity. Colour key: Zr, blue; C, grey; O, red.

From figure 31, the PXRD patterns indicate a mix of phases of Zr_6 methacrylate clusters. Although the sample was not phase pure it was determined that it was suitable to be used in MOF reactions as they are all variations of Zr_6 methacrylate clusters.

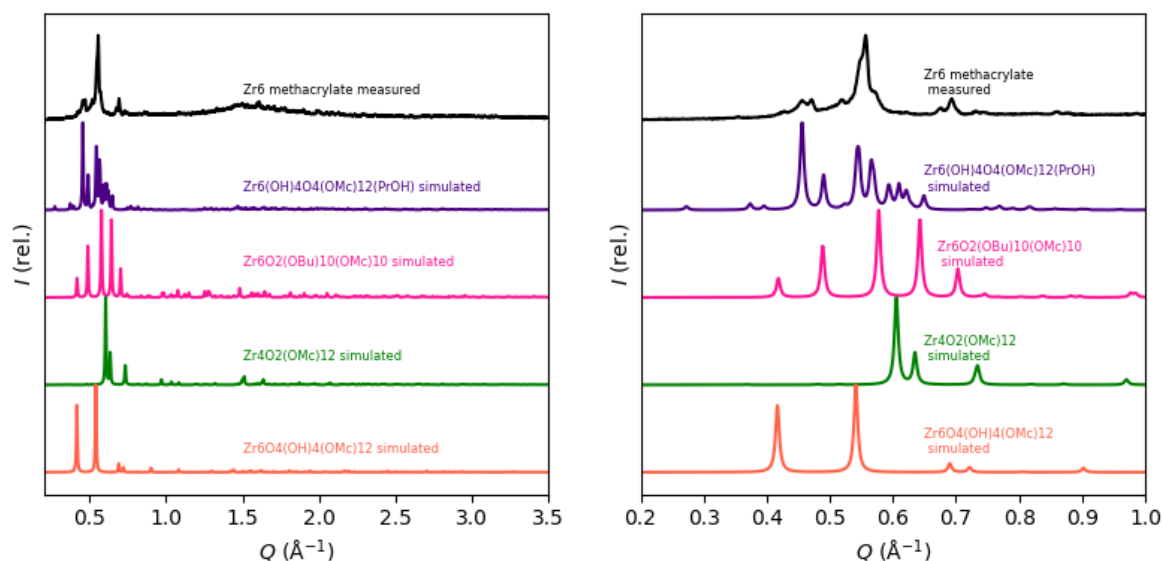


Figure 31. Simulated PXRD patterns of the $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{OMc})_{12}$ cluster (orange), $\text{Zr}_4\text{O}_2(\text{OMc})_{12}$ (green), $\text{Zr}_6\text{O}_2(\text{OBu})_{10}(\text{OMc})_{10}$ (pink), $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{OMc})_{12}(\text{PrOH})$ (purple) and the measured pattern of the synthesised cluster (black). The figure on the right is a zoom in between $Q = 0.2 \text{ \AA}^{-1}$ and $1.0 \text{ \AA}^{-1}$.

2.1.3. Zr aminobenzoate cluster, $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{ABZ})_{12}$

To synthesise the Zr_6 aminobenzoate cluster, $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{ABZ})_{12}$, I used conditions adapted from the synthesis of the Ti_6 aminobenzoate⁴⁴ cluster, namely the solvothermal reaction of Ti isopropoxide and benzoic acid in isopropanol. Ti isopropoxide was exchanged for Zr propoxide for the Zr cluster. The metal to 4-aminobenzoic acid molar ratio was changed slightly in the reaction. For the Ti cluster a 1:2 molar ratio of Ti:4-aminobenzoic acid is used as opposed to a four-fold excess of 4-aminobenzoic acid in the Zr cluster. In the Zr cluster, $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{ABZ})_{12}$, the Zr to benzoate ratio is double than that of the Ti cluster, and therefore a four-fold excess of 4-aminobenzoic acid was used in the synthetic conditions to compensate for this. Another difference is that Ti isopropoxide is a liquid, but Zr propoxide is a solid. Using these condition, the reaction gave an off-yellow powder, which was washed with IPA and analysed by PXRD (figure 32). This showed that the product formed was poorly crystalline. The peak found at low angles indicates a fairly big structure. As the cluster is unknown, single crystals would have to be grown in order for the structure to be fully solved via single-crystal X-ray diffraction. While attempts were made to recrystallise the product, none were successful. The reaction was also attempted with Zr butoxide solution but yielded no product.

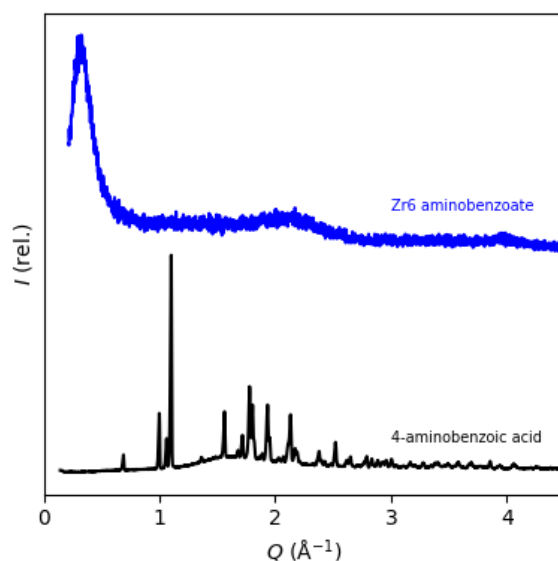


Figure 32. Measured PXRD patterns of 4-aminobenzoic acid (black) and of the attempted solvothermal synthesis of Zr_6 benzoate cluster (blue).

Based on the successful synthesis of the Zr_6 benzoate cluster, multiple attempts were made to synthesise the aminobenzoate cluster via reflux. The first attempt maintained the 1:4 molar ratio of Zr butoxide solution to aminobenzoic acid and was done in IPA. PXRD shows that the product is more crystalline than the solvothermal reaction but was very contaminated with 4-aminobenzoic acid (figure 33).

The next attempt used a higher molar ratio, 1:25, to mirror the one in the Zr_6 benzoate cluster synthesis. The PXRD pattern looked very similar to that of 4-aminobenzoic acid, although a new small peak can be seen at $Q = 0.6 \text{ \AA}^{-1}$. This meant that the sample was mostly the starting material, with very small amounts of products in.

For the final attempt, the solvent was changed to nPrOH, again to mirror the synthetic condition of the synthesis of the benzoate cluster. This showed some promising results with a new sharp peak at $Q = 0.51 \text{ \AA}^{-1}$.

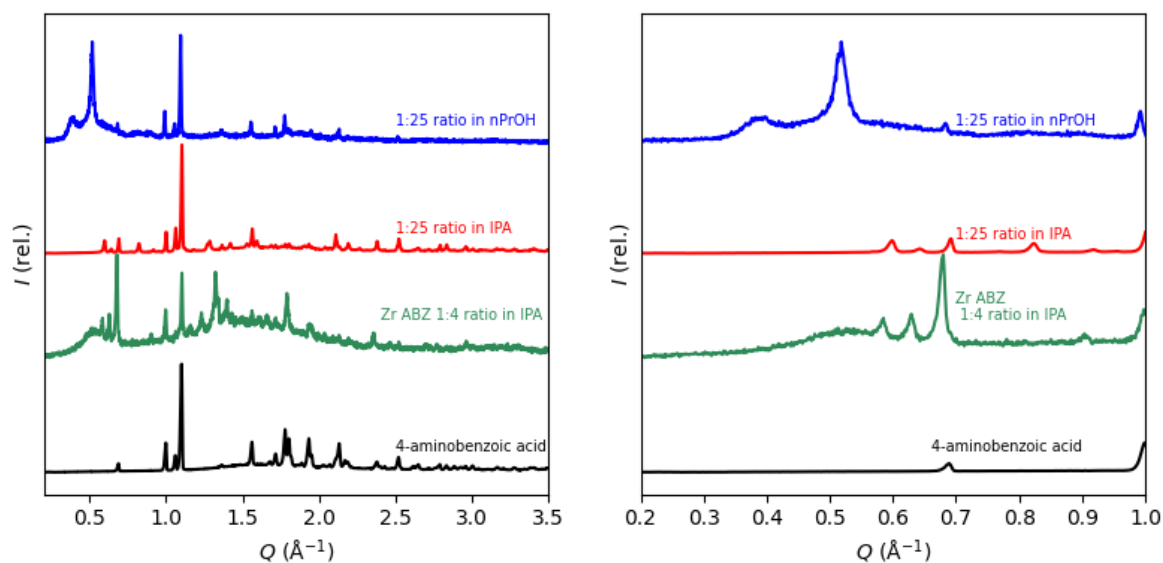


Figure 33. Measured PXRD patterns of 4-aminobenzoic acid (black), the attempted reflux syntheses of Zr_6 aminobenzoate cluster with 1:4 molar ratio in IPA (green), with 1:25 molar ratio of benzoic acid in IPA (red) and with 1:25 molar ratio in *n*PrOH (blue). The figure on the right is a zoom in between $Q = 0.2 \text{ \AA}^{-1}$ and $1.0 \text{ \AA}^{-1}$.

Unfortunately, since the cluster is unknown, no PXRD pattern can be simulated to confirm formation of the cluster.

^1H NMR of the cluster was done in DMSO-d_6 (figure 34). There are three compound peaks in the spectrum. There are doublets at 7.61 ppm, with integration of 2.00, and 6.53 ppm, with integration of 1.99. These can be attributed to aromatic hydrogens labelled **B** and **C** respectively. The last compound peak is at 5.80 ppm and corresponds to the H atoms of the amino group labelled **D**. It has integration of 1.18 which is much lower than the expected 2, however this is justified by the exchangeable nature of these H atoms. There are a few impurities: the triplet at 3.78 ppm (isopropanol), singlet at 2.09 ppm (acetone, most likely from the NMR tube still containing traces of acetone after washing), singlet at 1.24 ppm (hexane solvent trace impurity) and doublet at 1.04 ppm (isopropanol).

The low intensity of the “compound” peaks indicates that these are most likely due to some starting material present in the sample. These clusters are very insoluble in most solvents, but 4-aminobenzoic acid is fairly soluble in a variety of solvents. While the cluster seemed to dissolve when preparing the sample for analysis, the yellow powder precipitated out after a few minutes in the NMR tube. This was also attempted with other readily-available

deuterated solvents including acetone, dichloromethane, chloroform, methanol and toluene, to no success.

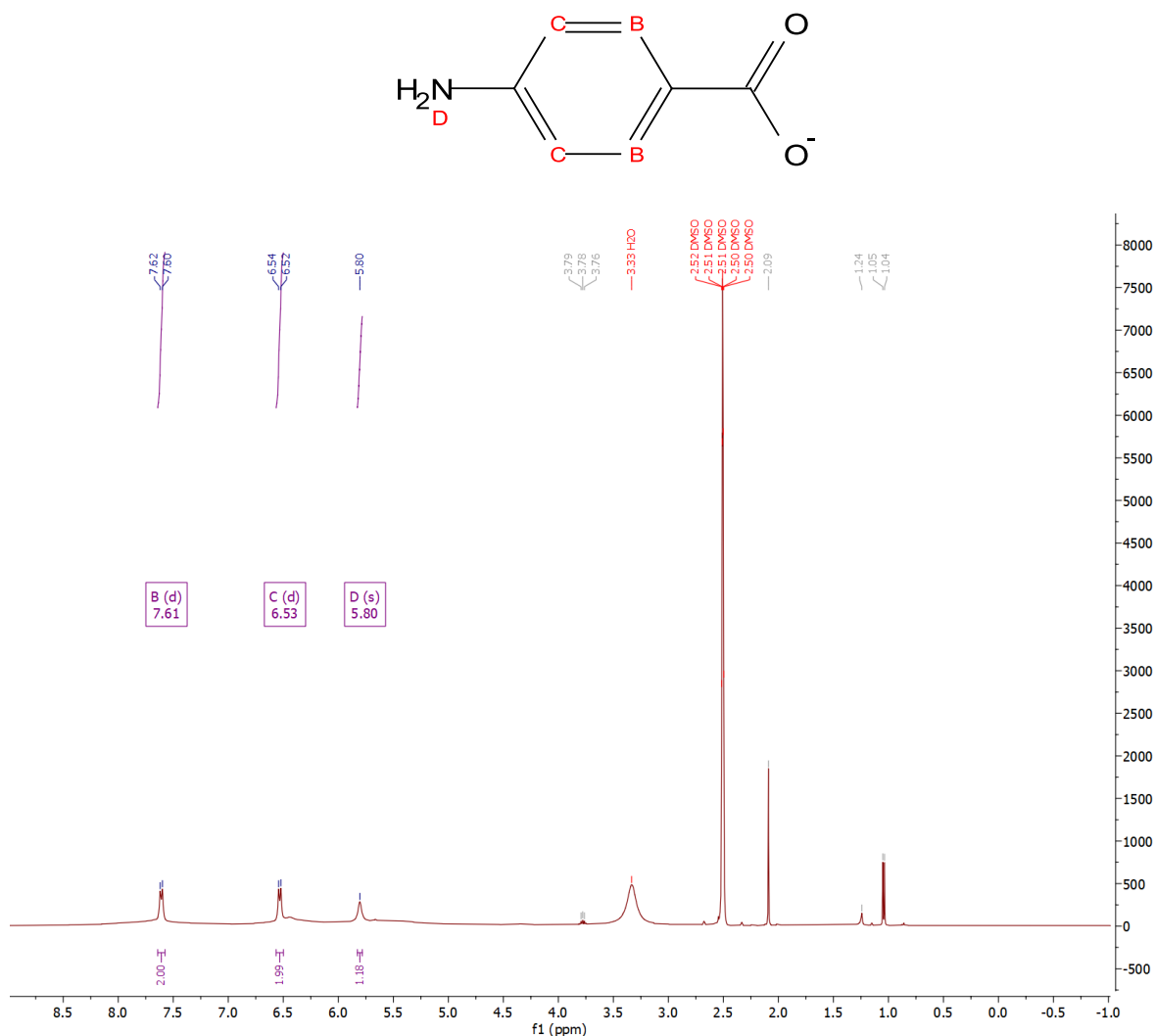


Figure 34. ¹H NMR spectrum of Zr aminobenzoate cluster in DMSO-*d*₆.

Mass spectrometry was also tried as a characterisation technique, but, similarly to NMR, proved to be challenging due to solubility issues. The lack of evidence of full characterisation of the cluster led to the decision that it was not suitable for MOF reactions.

2.1.4. Zr 2,2-dimethylbutyrate cluster, $Zr_6O_4(OH)_4(BTA)_{12}$

Multiple different methods were tried to synthesise a 2,2-dimethyl butyrate substituted Zr_6 cluster. As a starting point, a method to synthesise a similar Ti-based cluster was followed⁴⁵. The cluster $Ti_6O_6(O^iPr)_6(BTA)_6$ (BTA = butyrate) is synthesised through the solvothermal reaction of $Ti(O^iPr)_4$, 3,3-dimethyl butyric acid and $Mn(NO_3)_2$ in IPA. In the case of the Ti cluster, $Mn(NO_3)_2$ is not incorporated into the core but facilitates the formation of the cluster, and no product is formed in its absence. The same conditions were followed for the Zr-analogue, replacing $Ti(O^iPr)_4$ for $Zr(O^iPr)_4$ and trying reactions with and without $Mn(NO_3)_2$. The reactions were ran for 1 day at 80 °C. Similarly to the Ti reaction, no product was obtained in the absence of $Mn(NO_3)_2$ but a brown powder was obtained for the reaction with it. The colour was most likely due to Mn being present in the sample, either because of small amounts of the starting material still being present or because the cluster formed was bimetallic, however this theory was not investigated further as the Ti reaction does not form a bimetallic cluster. The powder was analysed by PXRD (figure 35) and compared to the PXRD pattern of the Ti cluster, as the Zr-analogue is unknown. This showed that the product formed was fairly crystalline with two peaks at $Q = 0.51 \text{ \AA}^{-1}$ and $Q = 0.55 \text{ \AA}^{-1}$. The peak at $Q = 0.55 \text{ \AA}^{-1}$ can also be found in the calculated pattern of the Ti butyrate cluster.

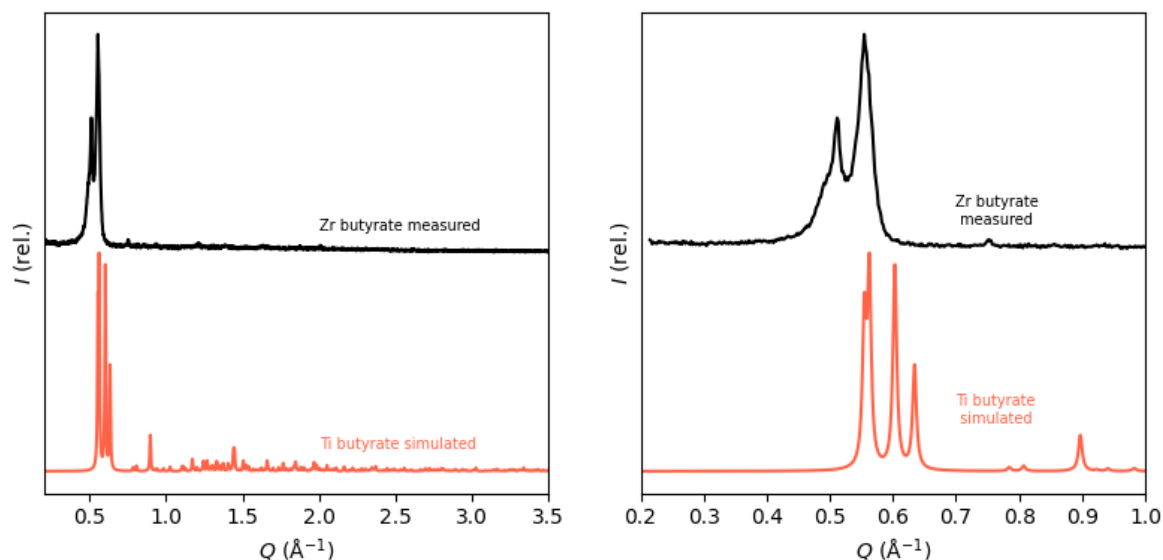


Figure 35. Calculated PXRD pattern of the Ti butyrate cluster (orange) and the attempted synthesis of Zr butyrate cluster. The figure on the right is a zoom in between $Q = 0.2 \text{ \AA}^{-1}$ and $1.0 \text{ \AA}^{-1}$.

Similarly to the attempted synthesis of a Zr aminobenzoate cluster, further characterisation of the product was very difficult as it was insoluble in readily-available deuterated solvents for ^1H NMR, and no single-crystals were obtained for SCXRD.

2.1.5. *Ti aminobenzoate cluster, $\text{Ti}_6\text{O}_6(\text{O}^i\text{Pr})_6(\text{ABZ})_6$*

Titanium-oxo clusters are different to zirconium-oxo clusters. In Zr_6 clusters, the Zr atoms have an octahedral arrangement within the inner core (figure 36) where each triangular face is bridged by alternating $\mu_3\text{-O}$ and $\mu_3\text{-OH}$ groups, and 12 carboxylate ligands are either bridging or chelating the Zr atoms.

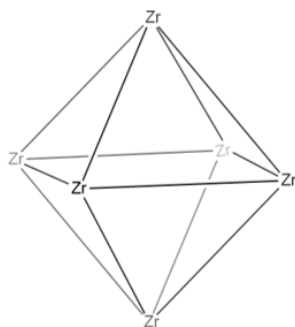


Figure 36. Representation of the Zr_6 cluster inner core, with the six Zr atoms in an octahedral arrangement.

In contrast, Ti_6 clusters adopt a hexagonal prism geometry (figure 37). Each vertex of the prism core is alternating between a Ti atom and a $\mu_3\text{-O}$ atom. The core is then supported by six carboxylate ligands, in this case 4-aminobenzoate, along the horizontal axis, and six isopropoxide anions along the vertical axis to complete the octahedral sphere of the titanium atoms (figure 38).

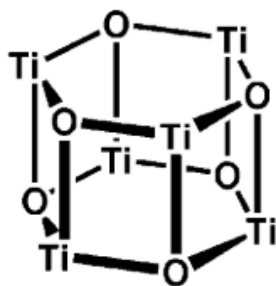


Figure 37. Representation of the hexagonal prism geometry of Ti-oxo clusters⁴⁴. Figure adapted from Ref 26.

The titanium aminobenzoate cluster (figure 38), $\text{Ti}_6\text{O}_6(\text{O}^i\text{Pr})_6(\text{ABZ})_6$, was synthesised by solvothermal reaction of $\text{Ti}(\text{O}^i\text{Pr})_4$ and 4-aminobenzoic acid in IPA⁴⁴. After 24 hours at 100 °C, bright orange crystals are formed. PXRD of the crystals confirmed that they were phase pure (figure 39).

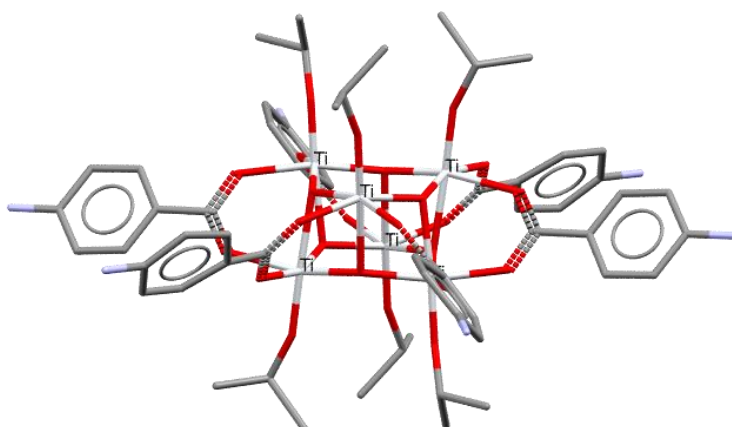


Figure 38. Structure of $\text{Ti}_6\text{O}_6(\text{O}^i\text{Pr})_6(\text{ABZ})_6$ cluster. H atoms omitted for clarity. Colour key: Ti, white; C, grey; O, red; N, purple.

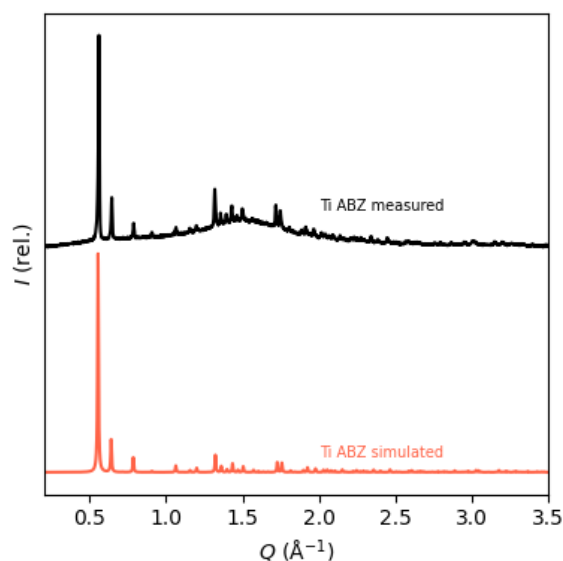


Figure 39. Calculated PXRD pattern of the Ti ABZ cluster (orange) and the measured pattern (black).

^1H NMR can also be used to determine the successful synthesis of the cluster (figure 40). The peaks seen correspond to the H atoms of the carboxylates and those of the isopropoxide molecules of the inner core.

^1H NMR was done in DMSO-d_6 . The doublets at 7.66 ppm and 6.54 ppm correspond to the H atoms found in the benzene ring of 4-aminobenzoate labelled as **B** and **C** respectively. They have integration of 2.00 (**B**) and 2.05 (**C**) which is in accordance with the expected structure. The next compound peak is a singlet found at 5.92 ppm and is attributed the two amino H atoms labelled **D**. The peak has integration of 1.42, which is lower than the expected 2. The heptet found at 5.09 ppm corresponds to the H atom **E** in the isopropoxide anion, and with integration of 0.94 is in accordance with the structure. The final compound peak is a doublet at 1.43 ppm attributed to the two methyl groups' H atoms of the isopropoxide anions labelled **F**, and has integration of 5.54, which again is in accordance with the expected structure. The peaks at 2.51 ppm are attributed to the solvent, and the one at 3.33 ppm to water.

A few trace impurities are also observed: doublet at 4.35 ppm (ethanol), multiplet at 3.77 ppm (isopropanol), singlet at 2.09 ppm (acetone) and doublet at 1.05 ppm (isopropanol).

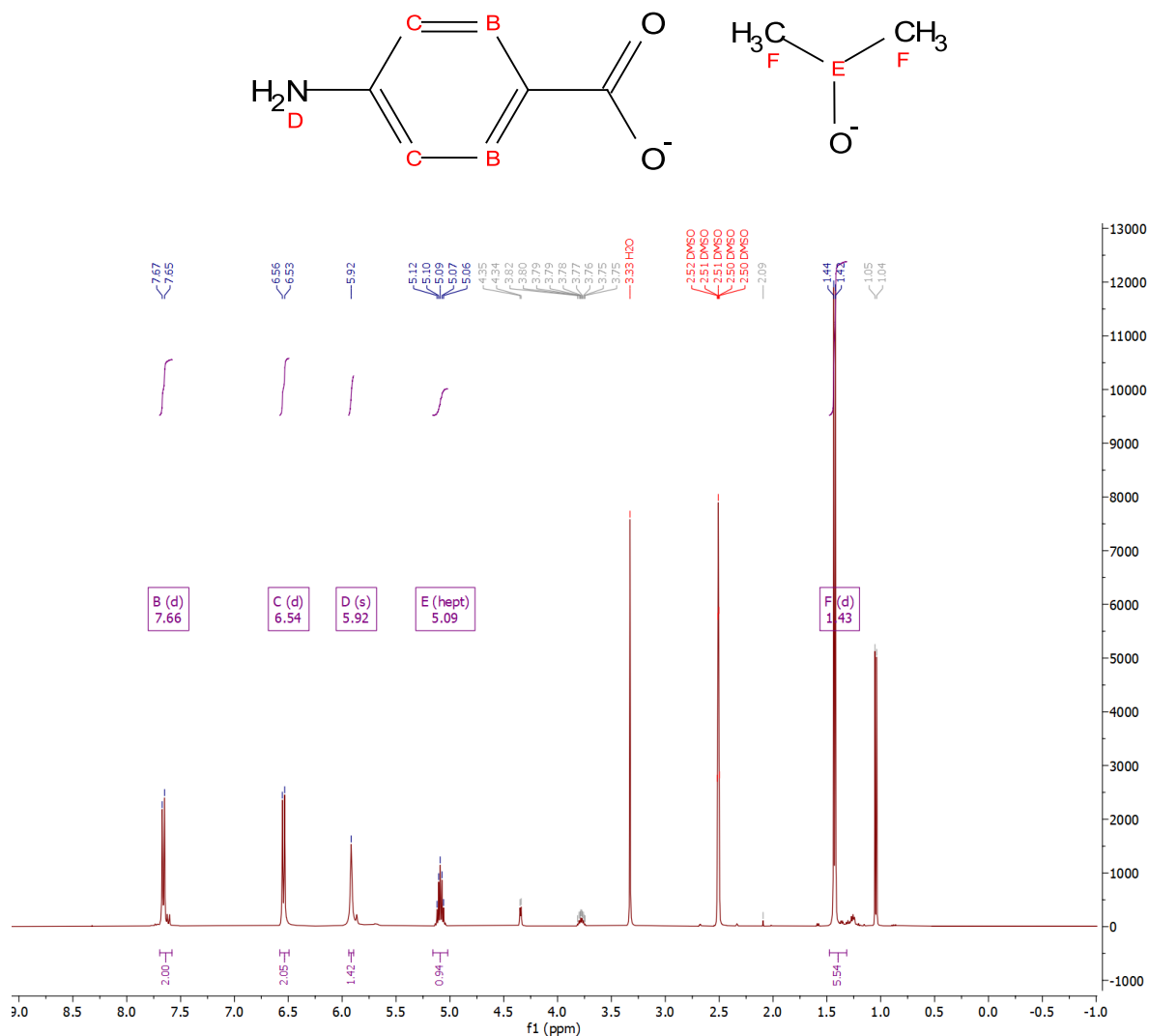


Figure 40. ^1H NMR spectrum of Ti_6 aminobenzoate cluster in $\text{DMSO}-d_6$.

In the NMR spectrum of 4-aminobenzoic acid, the H atom of the hydroxyl group is observed at 11.94 ppm (figure 41). This peak is absent from the spectrum of the Ti aminobenzoate cluster.

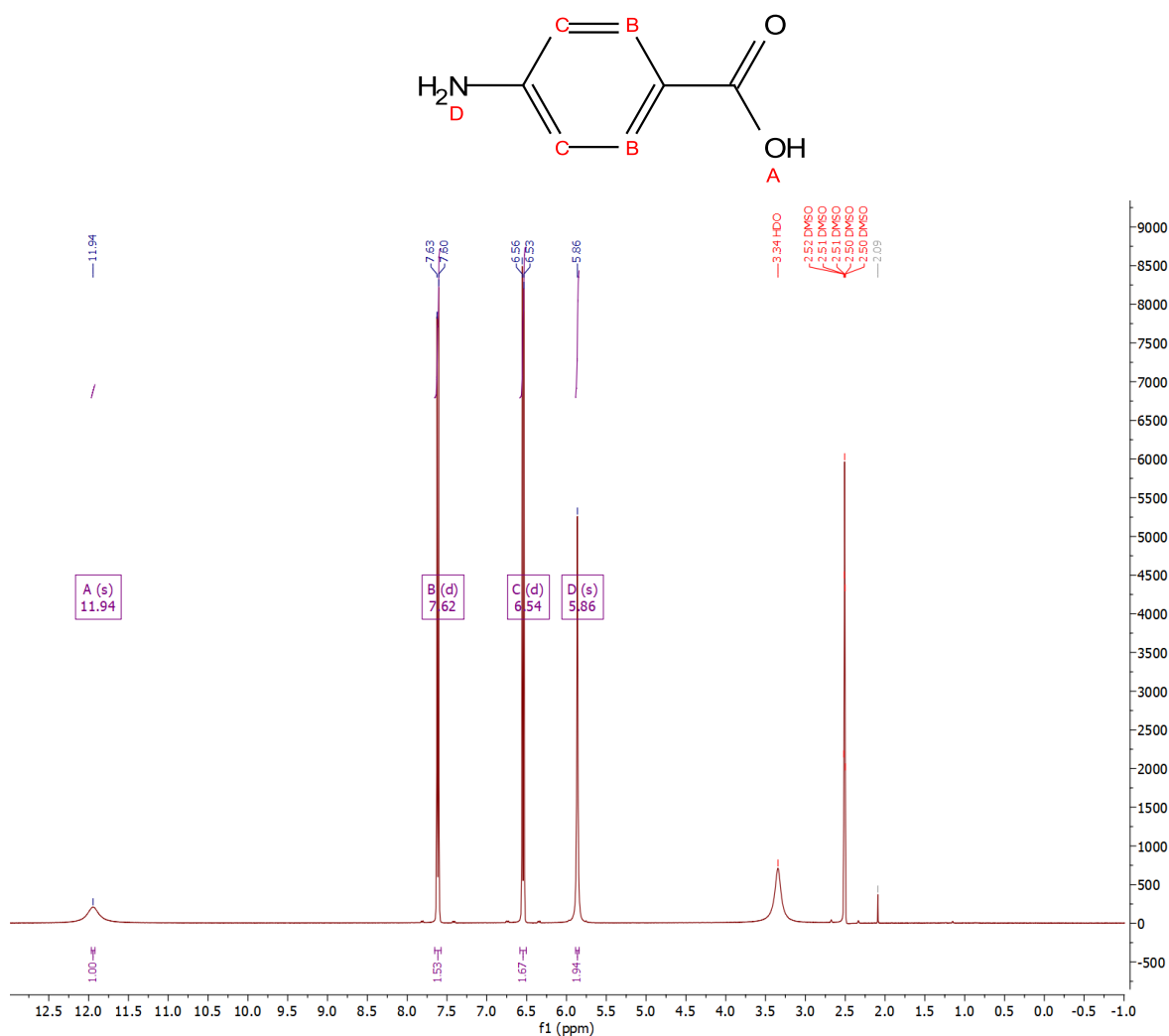


Figure 41. ^1H NMR spectrum of 4-aminobenzoic acid in $\text{DMSO}-d_6$.

2.1.6. *Ti* benzoate cluster, $\text{Ti}_6\text{O}_6(\text{O}^i\text{Pr})_6(\text{OBz})_6$

Following the method for the Ti_6 aminobenzoate cluster, the synthesis of the benzoate cluster was attempted. Benzoic acid and $\text{Ti}(\text{O}^i\text{Pr})_4$ in IPA were heated to 100 °C in a sealed pressure vessel for 24h, after which a white precipitate formed. PXRD showed that the product was fairly crystalline with two new peaks appearing at $Q = 0.51 \text{ \AA}^{-1}$ and $Q = 0.54 \text{ \AA}^{-1}$ (figure 42). The presence of small diffraction peaks between $Q = 1.0 \text{ \AA}^{-1}$ and $Q = 2.0 \text{ \AA}^{-1}$ indicates the presence of small amounts of benzoic acid.

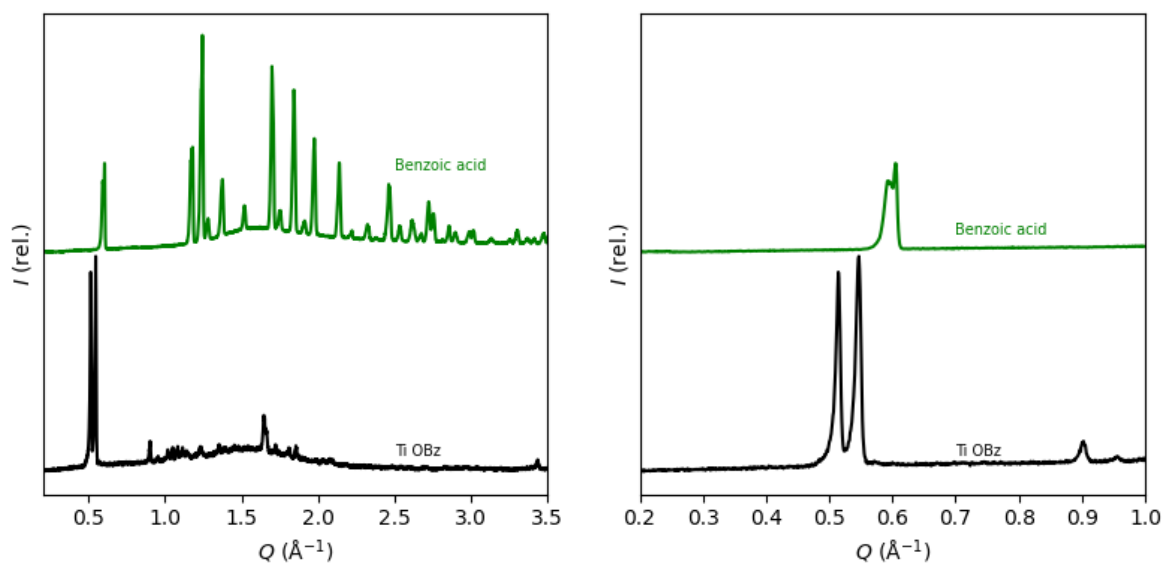


Figure 42. Measured PXRD patterns of Ti OBz cluster (black) and benzoic acid (green). The figure on the right is a zoom in between $Q = 0.2 \text{ \AA}^{-1}$ and $1.0 \text{ \AA}^{-1}$.

While ^1H NMR was very useful in the characterisation of the Ti aminobenzoate, proton NMR of the Ti benzoate cluster was not as valuable (figure 43). There are two doublets at 7.95 ppm and 7.52 ppm, which are typical for aromatic H atoms, and with integration of 2.00 and 1.93 respectively seems to agree with the structure of benzoic acid. However, the minuscule intensity of both these doublets (around 10 each) indicates that it most likely is just some of the starting material left over in the sample. All the other peaks are just trace impurities and some water as well as the solvent. Just like with the attempted characterisation of the Zr aminobenzoate cluster, the Ti benzoate cluster precipitated out minutes after the samples were prepared. To try to counter this, other solvents were tried to no success.

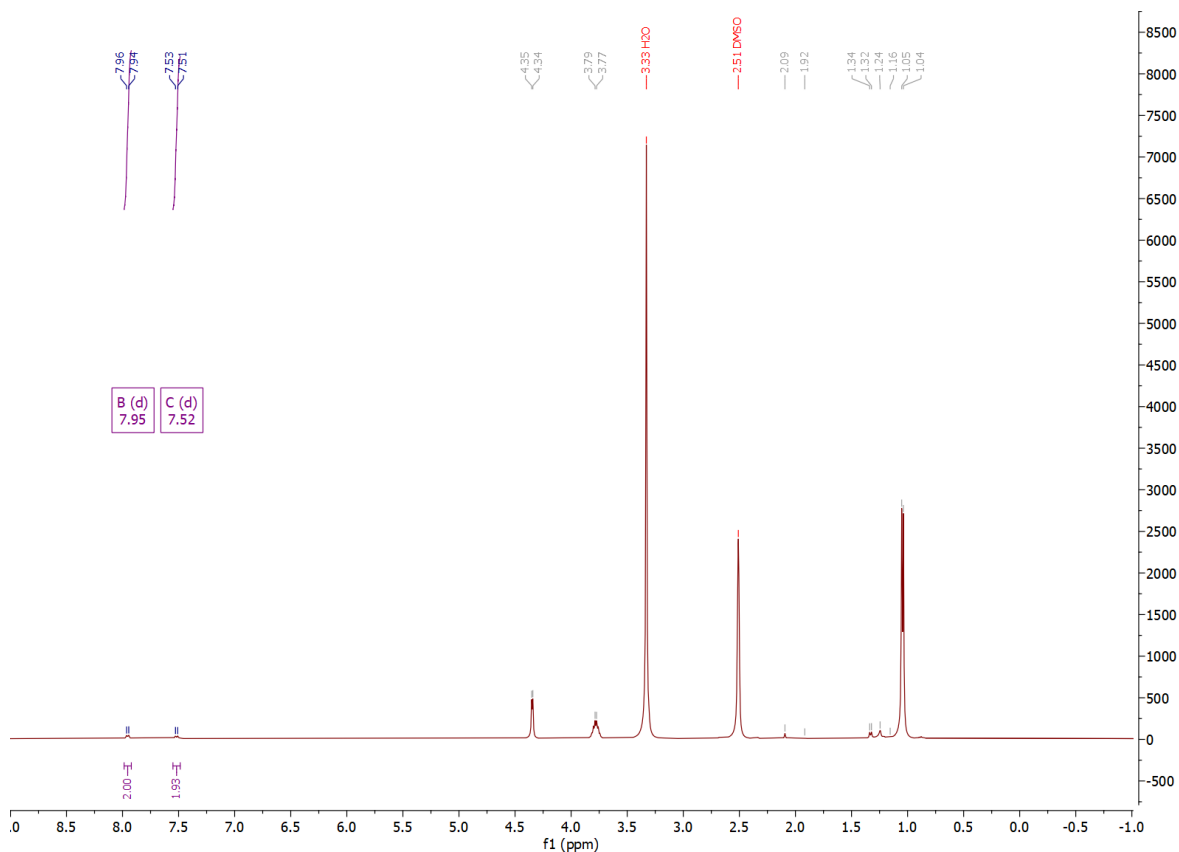


Figure 43. ^1H NMR of the Ti_6 benzoate in $\text{DMSO}-d_6$.

2.2. Discussion

The principal aims were to synthesise phase-pure and impurity-free metal clusters and to use them in MOF reactions. To that end, three clusters were successfully synthesised: Zr_6 benzoate, Zr_6 methacrylate and Ti_6 aminobenzoate. While attempts were made to synthesise novel clusters, issues with the characterisation of the products meant they were not suitable for use in further reactions.

2.2.1. Effects of the cation

In general, Ti clusters require harsher conditions to form. The Ti ABZ cluster⁴⁴ requires solvothermal conditions in isopropanol at 100 °C, which is higher than the boiling point of IPA (82.5 °C). Another example is the Ti butyrate cluster which requires both solvothermal conditions and the addition of $\text{Mn}(\text{NO}_3)_2$ to form the cluster⁴⁵. While the role of the manganese is unknown, the cluster does not form without it.

In contrast, Zr clusters form more readily. The Zr OBz cluster can be synthesised by refluxing at 80 °C⁵¹ or at room temperature by simply stirring the reactants although the product is slightly less pure than the reflux method. The methacrylate cluster is synthesised by mixing the starting materials without any solvent and crystallises over a few days⁴².

As mentioned before, group IV metals readily form strong bonds with carboxylates and alkoxides. This is true for zirconium and especially titanium which forms even stronger bonds^{64,65}. The relative strengths of these may be the cause for harsher conditions for the Ti clusters.

2.2.2. Phase purity

It was generally challenging to achieve phase-pure syntheses of these clusters despite previous reports in the literature, especially for the Zr clusters. In the case of the Zr OBz cluster, simple washing with nPrOH led to a phase change. While the starting materials are soluble in the solvent, not washing the product will still lead to small amounts of starting material in the sample. However, phase purity is a priority over traces of starting material.

SCXRD of the Zr OMc cluster showed that it had the correct unit cell for the expected Zr₆ cluster. However, PXRD showed that there was a mixture of phases. This change could be due to a few things, namely grinding or drying of the single crystals.

The Ti ABZ cluster did not have similar issues. It was washed extensively with IPA and ground for analysis and still stayed phase pure.

The presence of impurities in the samples was an issue with the Zr OBz cluster, where the most common impurity was benzoic acid. In most cases, washing the samples with solvent is sufficient to remove impurities, however as mentioned above, washing this particular cluster with nPrOH led to a phase change. Comparing the PXRD patterns of the room temperature and reflux syntheses of the zirconium benzoate cluster, the reflux reaction leads to a more crystalline product with less impurities. The increased temperature likely increases the conversion of the starting materials into the cluster, leaving less unreacted benzoic acid in the reaction mixture. Impurities were not an issue with the zirconium methacrylate or the titanium aminobenzoate cluster.

2.2.3. Characterisation of novel clusters

PXRD was the most used characterisation technique for the synthesis of the known clusters. Because they were fully characterised by SCXRD, the PXRD patterns could be simulated and compared to the measured ones. In the attempts to synthesise novel clusters, no single crystals were obtained for full characterisation. Conditions for the synthesis of single crystals take a long time to establish. While there were multiple attempts at recrystallisation, the low solubility of these clusters in most readily-available solvents hinders this process. This low solubility led to difficulties in other analytic techniques, including NMR and mass spectrometry.

Mass spectrometry analysis of metal-oxo clusters, such as polyoxometalates, has been a valuable method to determine cluster sizes⁶⁶. One of the challenges I faced, however, was the high number of stable isotopes of the metal species in the clusters. Zirconium has 5 stable isotopes (⁹⁰Zr, 51.45%; ⁹¹Zr, 11.22%; ⁹²Zr, 17.15%; ⁹⁴Zr, 17.38%; ⁹⁶Zr, 2.80%)⁶⁷. Because of this, high-resolution mass spectrometry would be required. Another issue was the low solubility of the clusters, which would make the selection of an inappropriate solvent difficult. As a result, although mass spectrometry was attempted it proved unsuccessful, even in identifying compounds known to be phase pure from PXRD measurements, and so was not pursued further.

IR spectroscopy was also considered, however, the spectra of the clusters would quite likely resemble that of the starting materials, besides a shift in the $\nu(\text{OH})$ bands⁶⁸, and would have to be paired with computational studies to be viable.

High resolution transmission electron microscopy (HR-TEM) could potentially be a powerful tool to solve the structures of novel structures, but is a challenging technique, especially in the field of MOFs. Typical conditions used in HR-TEM can lead to amorphization of MOF materials, and therefore the resolution of the data acquired is not dependent on the resolving power of the microscope, but rather the electron-beam stability of the material⁶⁹.

X-ray pair distribution function (XPDF) could also be very valuable to characterise the novel clusters. XPDF measurements can acquire structural information of non-crystalline materials, and is particularly sensitive to Zr and Ti due to their high electron densities. In MOFs, it has

been used to analyse their clusters and precursors⁷⁰, as well as understand the interactions between clusters and coordinating molecules⁷¹. Firth *et al.* showed that XPDF can be used to differentiate between closely-related Hf clusters⁷². This technique could be used to characterise the Zr clusters in this thesis, as Hf and Zr are chemically similar.

Chapter 3: MOF syntheses

The synthesised clusters were subsequently used for the synthesis of MOFs. Specifically, I wanted to explore how these clusters formed different MOFs, and how different variables affected the products.

The following parameters were chosen to explore the variable synthetic conditions: cluster and linker structures, reactant concentrations, reactant molar ratios and use of modulators. This helped us highlight some of the issues encountered that are discussed in this section.

These systematic investigations were done firstly with the Zr_6 benzoate cluster as it was the most phase-pure of the two Zr clusters. Ti MOFs are famously hard to form and therefore the Ti ABZ cluster could not be used for these initial sets of reactions. Zr MOFs are easier to synthesise, so starting with Zr clusters would allow to investigate and understand the parameters required for the formation of crystalline MOFs as a case study. These series of experiments allowed me to determine what the ideal conditions were to form crystalline UiO-66 from clusters and these conditions could be used on different clusters including the Zr_6 methacrylate and the Ti_6 aminobenzoate clusters.

The formation of Zr MOFs have been extensively studied. One such example is the formation of UiO-66 which uses terephthalic acid and $ZrCl_4$ as starting materials⁹. Their results are used throughout this report as a point of reference as similar linkers are being used. Furthermore, Zr_6 oxide clusters form through self-assembly in reactions starting with $ZrCl_4$, so using pre-formed clusters as starting material should yield similar results.

3.1. Results

3.1.1. Using the Zr_6 benzoate cluster as starting material

3.1.1.1. Varying the linker

To determine what linker to use in these reactions, a systematic series was set up by using three different linkers: terephthalic acid, aminoterephthalic acid and *trans,trans*-muconic acid

(figure 44). MOF reactions using terephthalic and aminoterephthalic acid have been extensively studied in reactions involving metal salts and therefore results from other studies would give us a good point of reference when analysing data. *Trans,trans*-muconic acid was chosen as it is a precursor for both terephthalic and aminoterephthalic acids, and it would be interesting to compare all three. Furthermore, *trans,trans*-muconic acid can be used as starting material in a variety of reactions, including polymerisation, esterification and cyclisation reactions⁷³, and could lead to post-synthetic modifications of the frameworks due to its alkene moiety⁷⁴. While the synthesis of UiO-66 has been previously performed using pre-formed clusters and these linkers by Friščić *et al.*⁵⁰, their studies focused on liquid-assisted milling (LAG) and how using different milling liquids affected crystallinity. In the context of this thesis, I wanted to explore other synthetic conditions. Reactions between the Zr benzoate cluster and terephthalic, aminoterephthalic and *trans,trans*-muconic acids were done to understand how the choice of linker might affect the formation of product, and so that a linker could be chosen for further experimentation.

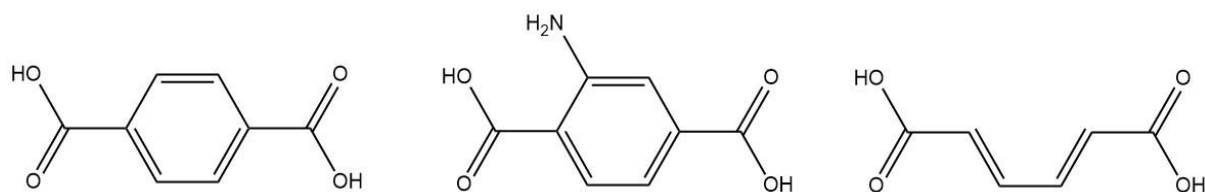


Figure 44. Structure of terephthalic acid (left), aminoterephthalic acid (middle) and *trans,trans*-muconic acid (right).

In the formation of UiO-66, each metal cluster is connected to six linkers, and each linker is connected to two clusters, giving an overall cluster to linker stoichiometry of 1:6. In the initial reactions, a two-fold stoichiometric excess of linker was used to give a 1:12 cluster to linker molar ratio in the reaction mixtures. The reactions were carried out in DMF as solvent for 1 and 3 days at room temperature, 50 °C and 100 °C. Both the cluster and linker were dissolved in 1 mL DMF, and the metal cluster was added dropwise to the linker. After reaction, the precipitates were centrifuged and left to dry. PXRD was used to characterise these materials as it can be used to determine crystallinity and phase purity.

The plots below (figures 45-47) show the results from the reactions of Zr benzoate cluster and the three linkers, as well as the calculated pattern of fcu UiO-66⁹ and the measured patterns of the cluster starting material and the three linkers. This was done to identify whether starting material was still present in the product. The bottom plots show the region between $Q = 0.1 \text{ \AA}^{-1}$ and $Q = 1.0 \text{ \AA}^{-1}$ as face-centred cubic (fcu) UiO-66 has two characteristic peaks at $Q = 0.52 \text{ \AA}^{-1}$ and $Q = 0.60 \text{ \AA}^{-1}$.

The reaction with terephthalic acid has signs of formation of frameworks (figure 45). After a reaction time of 1 day, only the 100 °C reaction seems to be starting to form a framework. For the other two reaction temperatures, the PXRD data indicates that only linker is present. However, after 3 days, all three reactions have broad peaks between $Q = 0.4 \text{ \AA}^{-1}$ and $Q = 0.7 \text{ \AA}^{-1}$, which indicates the formation of framework. All samples show signs of starting material still being present in the product.

The reactions with aminoterephthalic acid show very similar results (figure 46). They differ in that a framework starts forming after 1 day at 50 °C for the reaction with the amino linker. Again, there are signs of starting materials still being present in the product.

Using *trans,trans*-muconic acid as the linker leads to more crystalline products, with clear peaks indicating the formation of UiO-66, especially in the reaction at 100 °C (figure 47). However, at room temperature and 50 °C other peaks are present that are not found in the simulated PXRD pattern of fcu UiO-66, indicating the presence of other phases.

From this initial set of reactions, *trans,trans*-muconic acid was chosen as the favoured linker as it showed the most promising results, with clear peaks indicating the formation of UiO-66. Washes with DMF were then done on the samples to remove starting material, followed by acetone to try to help dry the product.

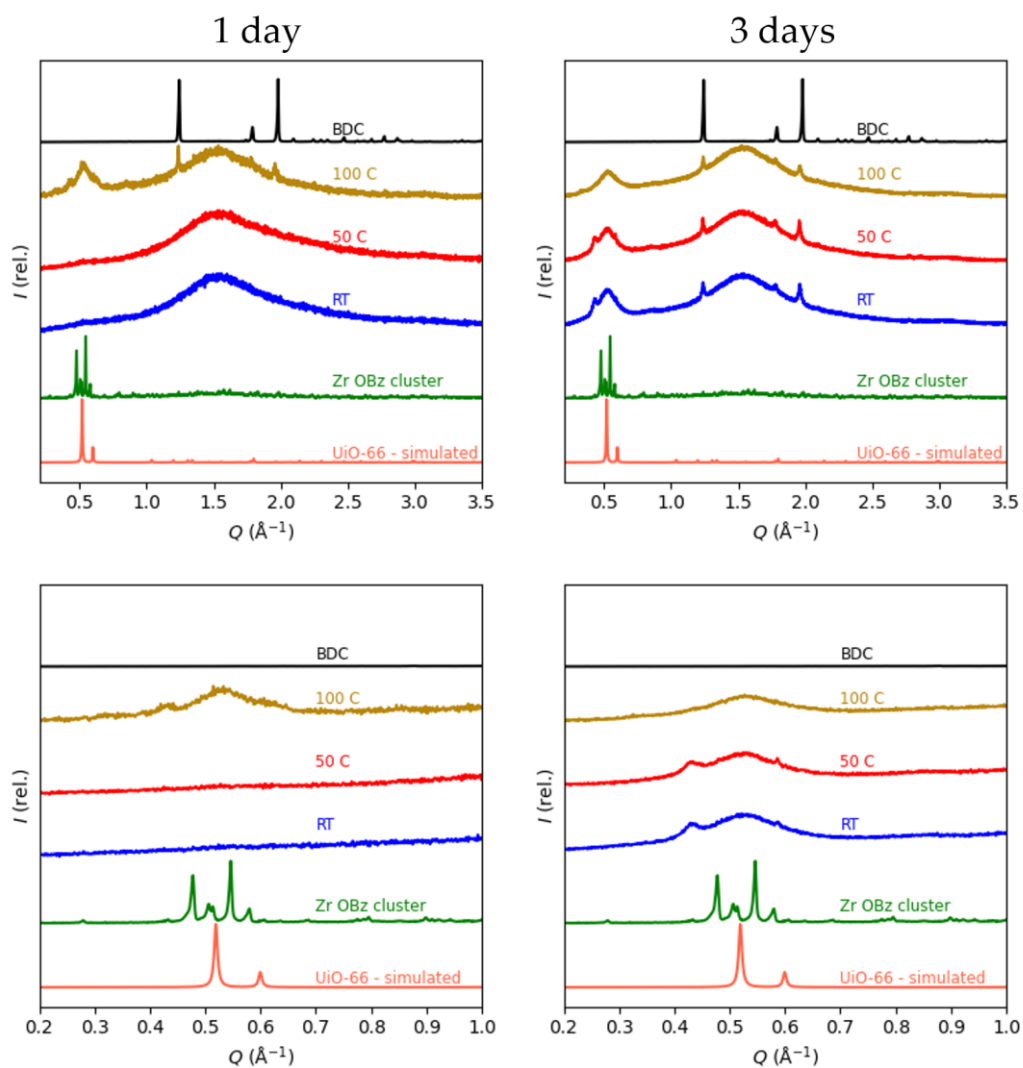


Figure 45. Simulated PXRD pattern of fcu UiO-66 (orange) and measured patterns of Zr_6 benzoate cluster starting material (green), the reaction of Zr OBz cluster with terephthalic acid at room temperature (blue), at 50 °C (red), at 100 °C (gold) and the measured pattern of terephthalic acid (black). The PXRD patterns were measured after reaction times of 1 day (left) and 3 days (right). The figures on the bottom are zoomed in between $Q = 0.2 \text{ \AA}^{-1}$ and $Q = 1.0 \text{ \AA}^{-1}$.

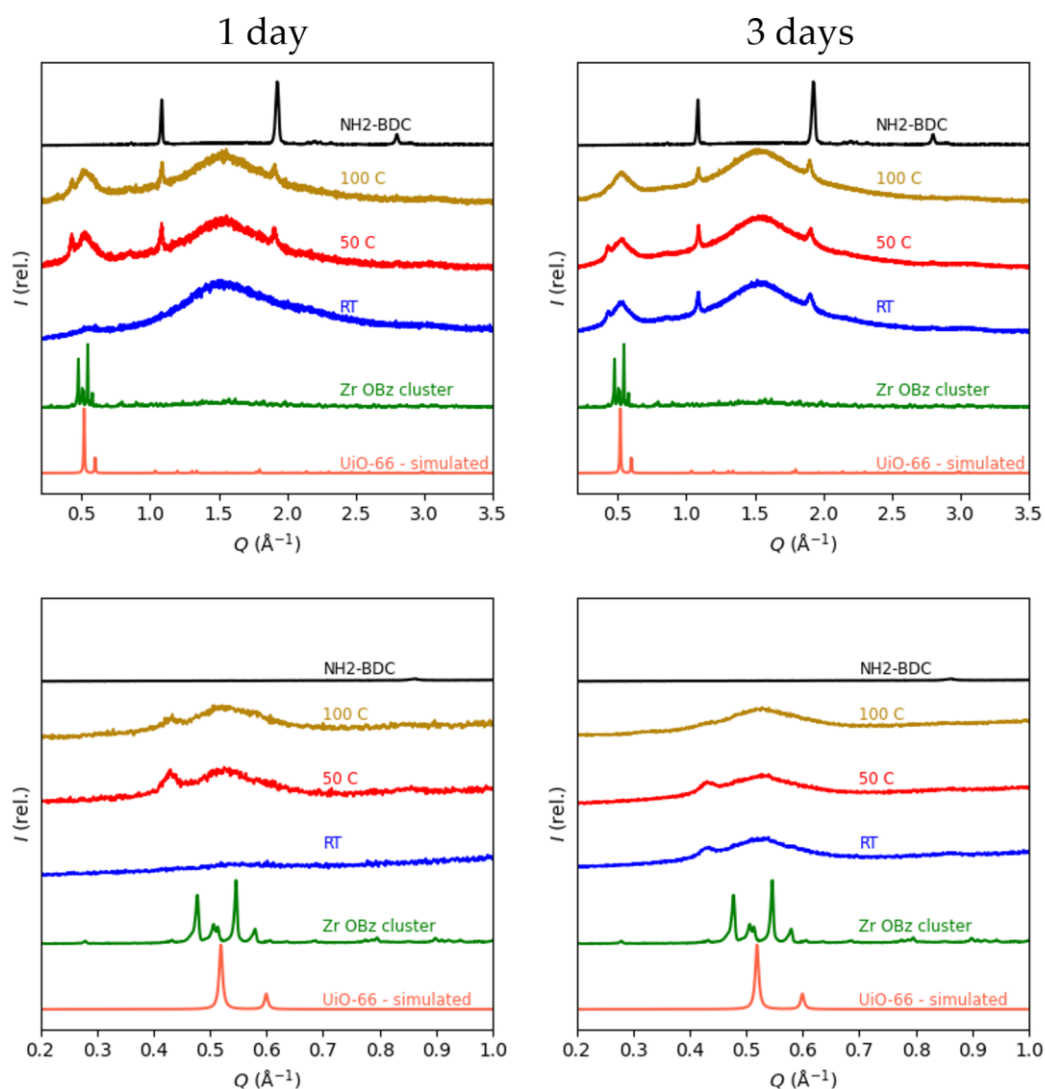


Figure 46. Simulated PXRD pattern of fcu UiO-66 (orange) and measured patterns of Zr₆ benzoate cluster starting material (green), the reaction of Zr OBz cluster with aminoterephthalic acid at room temperature (blue), at 50 °C (red), at 100 °C (gold) and the measured pattern of terephthalic acid (black). The PXRD patterns were measured after reaction times of 1 day (left) and 3 days (right). The figures on the bottom are zoomed in between $Q = 0.2 \text{ \AA}^{-1}$ and $Q = 1.0 \text{ \AA}^{-1}$.

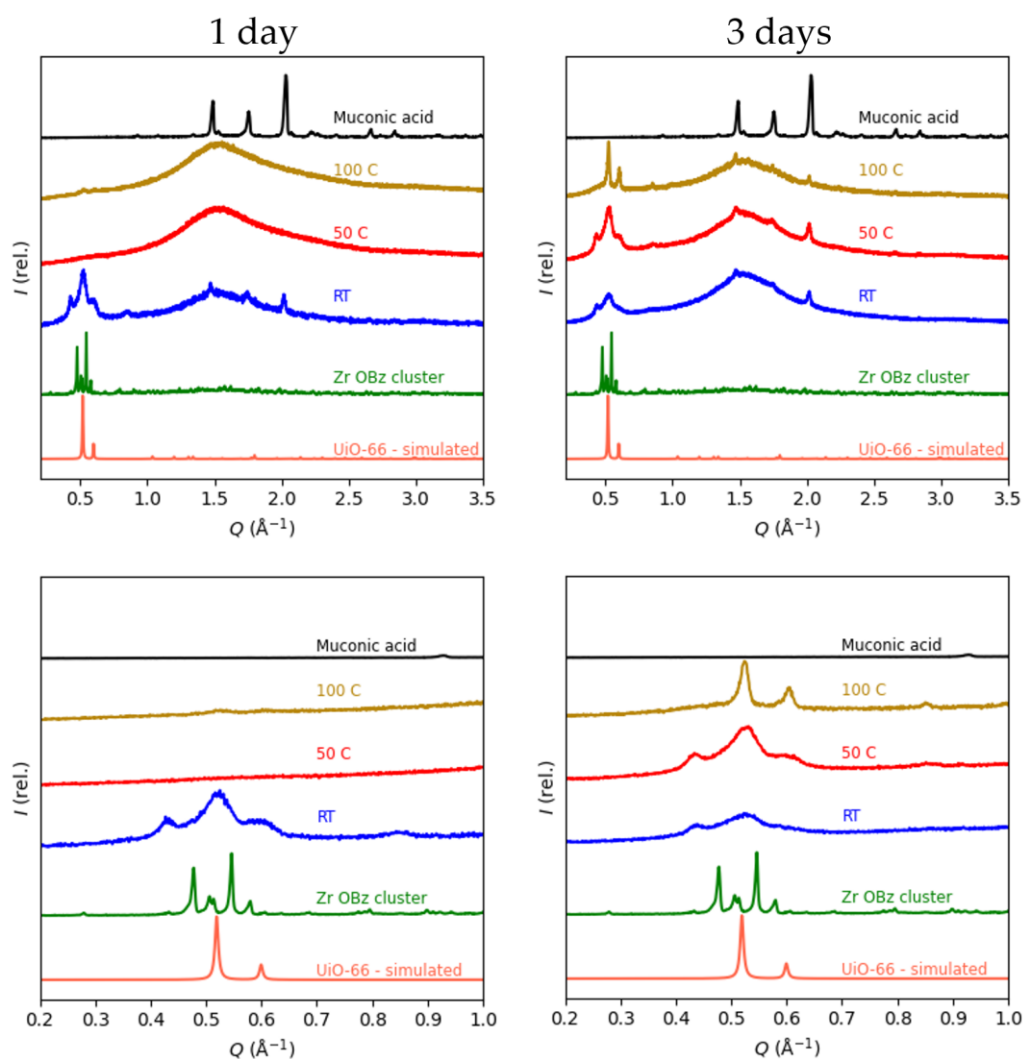


Figure 47. Simulated PXRD pattern of *fcu* UiO-66 (orange) and measured patterns of Zr_6 benzoate cluster starting material (green), the reaction of Zr OBz cluster with *trans,trans*-muonic acid at room temperature (blue), at 50 °C (red), at 100 °C (gold) and the measured pattern of terephthalic acid (black). The PXRD patterns were measured after reaction times of 1 day (left) and 3 days (right). The figures on the bottom are zoomed in between $Q = 0.2 \text{ \AA}^{-1}$ and $Q = 1.0 \text{ \AA}^{-1}$.

After washing the samples of the reaction of the Zr OBz cluster with *trans,trans*-muonic acid with $3 \times 6 \text{ mL}$ DMF, all starting material was removed from the samples. Unlike with the reactions performed at room temperature and 50 °C, washing the reaction that was performed at 100 °C unexpectedly leads to loss of crystallinity. Washing with $1 \times 6 \text{ mL}$ acetone and subsequent drying at room temperature leads to loss of crystallinity in all three cases (figure 48).

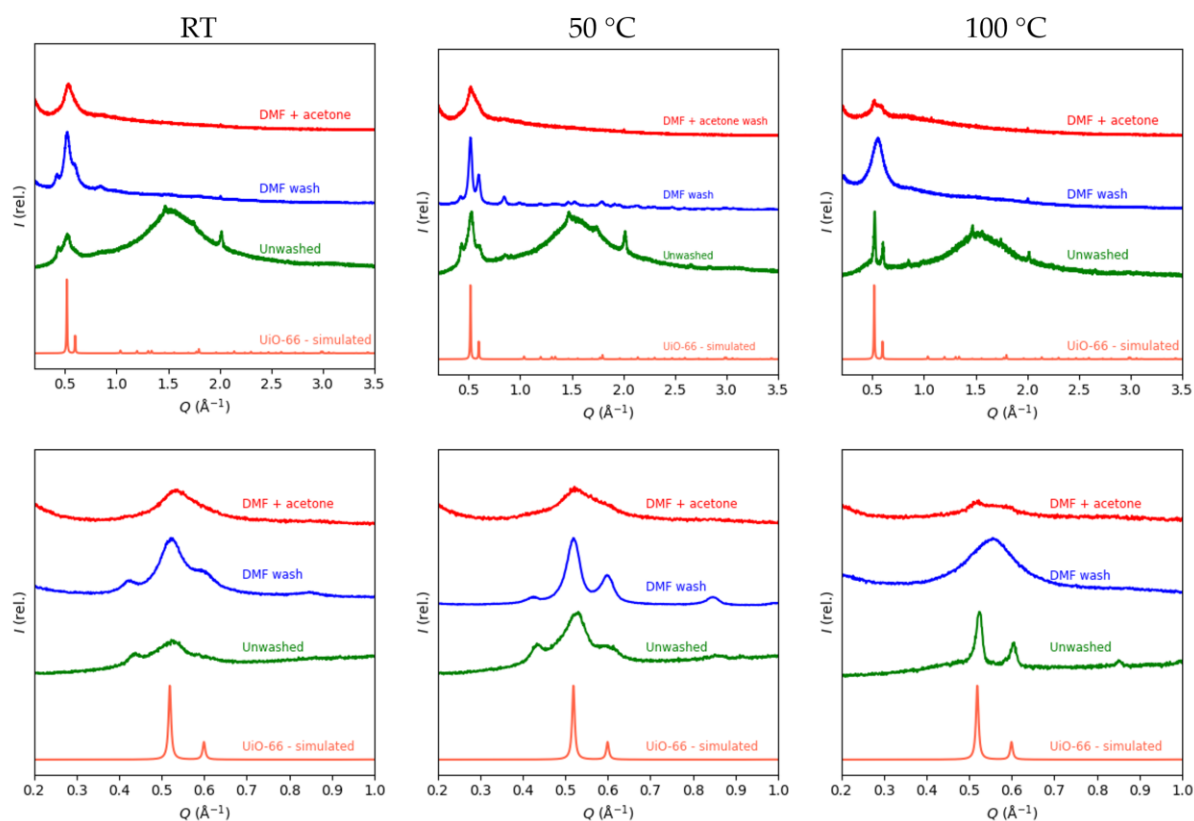


Figure 48. Simulated PXRD pattern of fcu UiO-66 (orange) and measured patterns of the reaction of the Zr₆ benzoate cluster and *trans,trans*-muconic acid after 3 days (green), followed by washes with DMF (blue) and with an additional washing with acetone (red). This was done for the reactions at room temperature (left), 50 °C (middle) and 100 °C (right). The figures on the bottom are zoomed in between $Q = 0.2 \text{ \AA}^{-1}$ and $Q = 1.0 \text{ \AA}^{-1}$.

3.1.1.2. Phases comparison

From the washed series of reactions of Zr₆ benzoate cluster and *trans,trans*-muconic acid, there were indications that different phases of UiO-66 were present in the reactions done at room temperature and 50 °C. The peak present at $Q = 0.42 \text{ \AA}^{-1}$ is not seen in the PXRD pattern of fcu UiO-66. The data were therefore plotted against other phases: hexagonal close packed (hcp)⁷⁵, hexagonal (hex)⁷⁶ and a cluster and linker defective phase (reo)⁷⁷.

For room temperature and 50 °C, both peaks that are characteristic to fcu UiO-66 are observed (figure 49). The extra peak at $Q = 0.42 \text{ \AA}^{-1}$ in the samples can also be found in the simulated pattern of reo UiO-66, although the peak at $Q = 0.30 \text{ \AA}^{-1}$ in the simulated pattern is missing from the samples. This indicates that there is a mixture of phases with low degrees of crystallinity, most likely fcu and reo for reactions at room temperature and 50 °C. At 100 °C,

product is fcu phase pure. Note that data for the 100 °C reaction is from the unwashed product as washing resulted in loss of crystallinity.

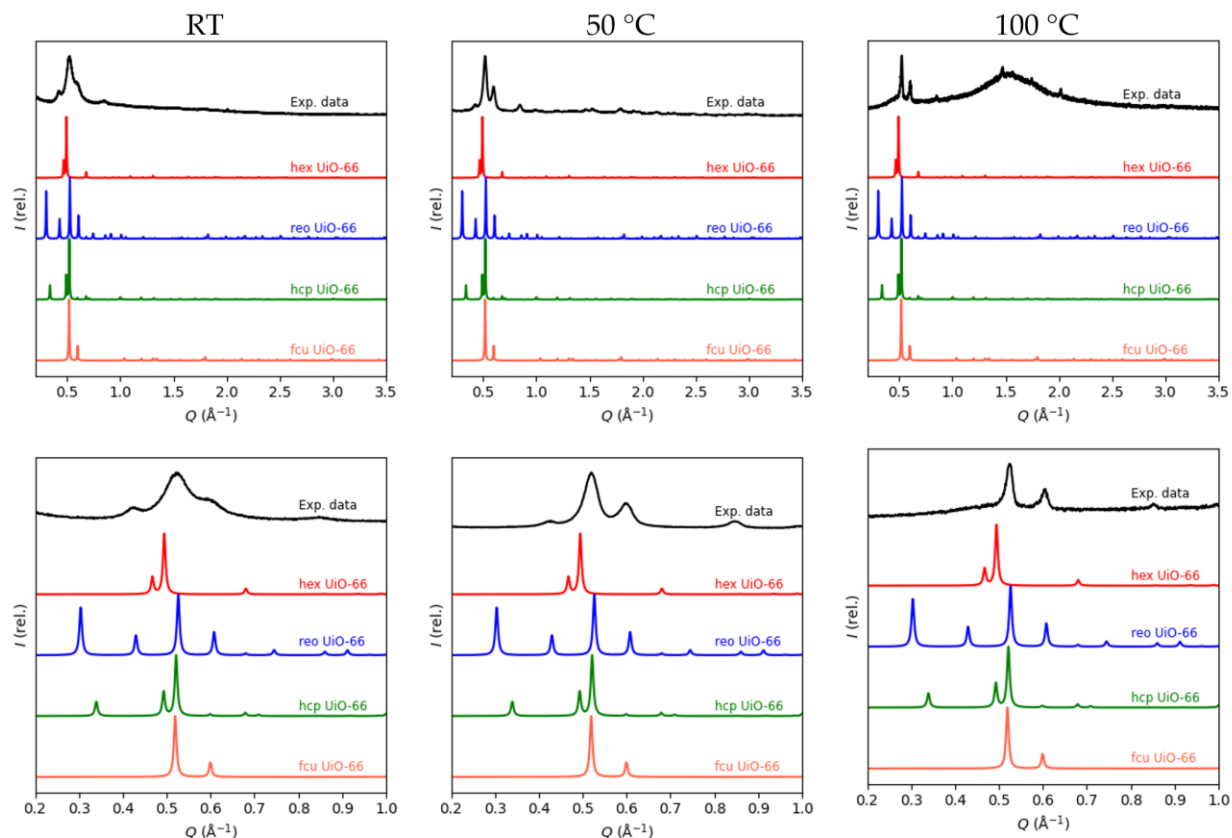


Figure 49. Simulated PXRD patterns of fcu UiO-66⁹ (orange), hcp UiO-66⁷⁵ (green), reo UiO-66⁷⁷ (blue), hex UiO-66⁷⁶ (red) and the measured pattern of the reaction of the Zr₆benzoate cluster with *trans,trans*-muconic acid. This was done for the reactions at room temperature (left), 50 °C (middle) and 100 °C (right). The figures on the bottom are zoomed in between $Q = 0.2 \text{ \AA}^{-1}$ and $Q = 1.0 \text{ \AA}^{-1}$.

3.1.1.3. Decreased concentration

When running the initial series of MOF reactions, the cluster was dissolved in 1 mL of DMF which did not completely dissolve and gave a cloudy suspension. This was particularly a problem as stock solutions were made up for that initial series and that undoubtedly led to uneven distribution of starting material in the reactions. To counter this, in the following series

of reactions, the concentration was decreased, where the cluster was dissolved in 5 mL DMF to give a solution rather than a suspension. All other variables were kept the same.

No solid product was obtained for 100 °C. For the other two, there are indications of formation of framework in the PXRD patterns, however it is poorly crystalline (figure 50). Temperature and reaction time have no impact on product formation or crystallinity, but concentration must be a key factor as the previous series which used a higher concentration led to crystalline material. Note that the broad feature at $Q = \sim 1.6 \text{ \AA}^{-1}$ seen in a few PXRD patterns is likely due to traces of linker.

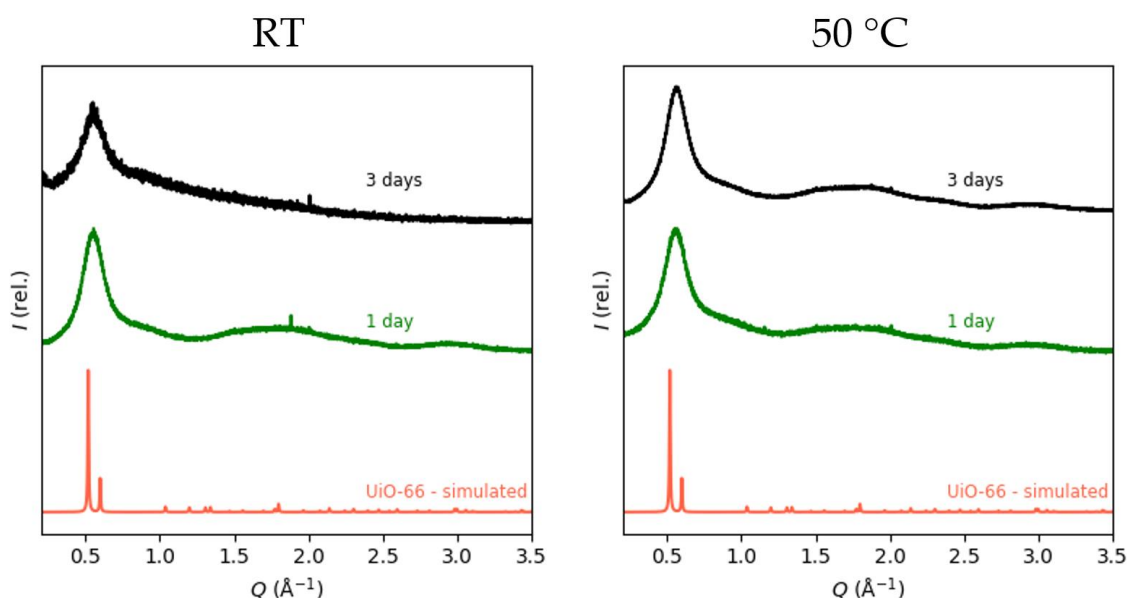


Figure 50. Calculated PXRD pattern of UiO-66 (orange), and measured patterns of the reactions after 1 day (green) and after 3 days (black).

3.1.1.4. Concentration series

To investigate the effect of concentrations on formation of product, a systematic series of varying concentrations of cluster was performed. Similarly to the previous experiments, the cluster was dissolved in DMF but the amount was varied from 1 mL to 5 mL, in 1 mL increments to give concentrations: 27.7 mg/mL, 13.8 mg/mL, 9.2 mg/mL, 6.9 mg/mL and 5.5 mg/mL. These were added dropwise to the linker in 1 mL DMF. These reactions were ran for

3 days at both room temperature and 50 °C. On addition of the metal to the linker, the most highly concentrated reaction started reacting almost immediately, forming a gel-like solid, whereas the other four took longer to start forming precipitate.

From the PXRD data, temperature seems to have no effect on product formation or crystallinity, nor does concentration (figure 51). The PXRD data contradicts findings from previous reactions as crystalline product had been obtained when using 1 mL of DMF to dissolve the cluster (27.7 mg/mL). All variables were kept the same for both the reactions apart from the batch of the Zr benzoate cluster used so it was hypothesised that the first batch which had given crystalline material contained small amounts of benzoic acid, essentially acting as a modulator in the reaction. This could have been investigated further by performing reactions at lower concentrations in the presence of benzoic acid, however this was not done.

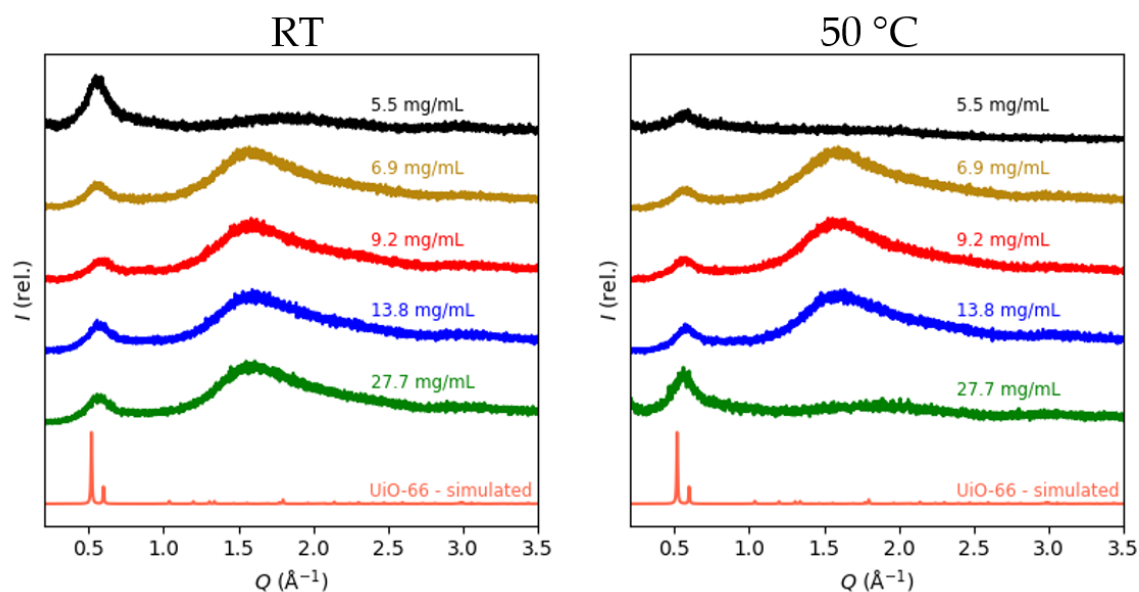


Figure 51. Calculated PXRD pattern of UiO-66 (orange), and the measured patterns of the reactions with cluster concentration in DMF of 27.7 mg/mL (green), 13.8 mg/mL (blue), 9.2 mg/mL (red), 6.9 mg/mL (gold) and 5.5 mg/mL (black).

3.1.1.5. Molar ratios series

Another variable that was explored was varying the molar ratios of cluster to linker. Most previous reactions used a 1:12 molar ratio, so in these reactions 1:24 and 1:36 molar ratios were

used. This was simply done by increasing the amount of *trans,trans*-muconic acid in the reaction solutions. These reactions were ran for 3 days at both room temperature and 50 °C. All formed a gel-like product a few minutes after addition of the metal to the linker, with no changes in characteristics throughout the rest of the experiment. All products were analysed using PXRD. From figure 52, the increased molar ratios seem to have no impact on crystallinity or formation of product.

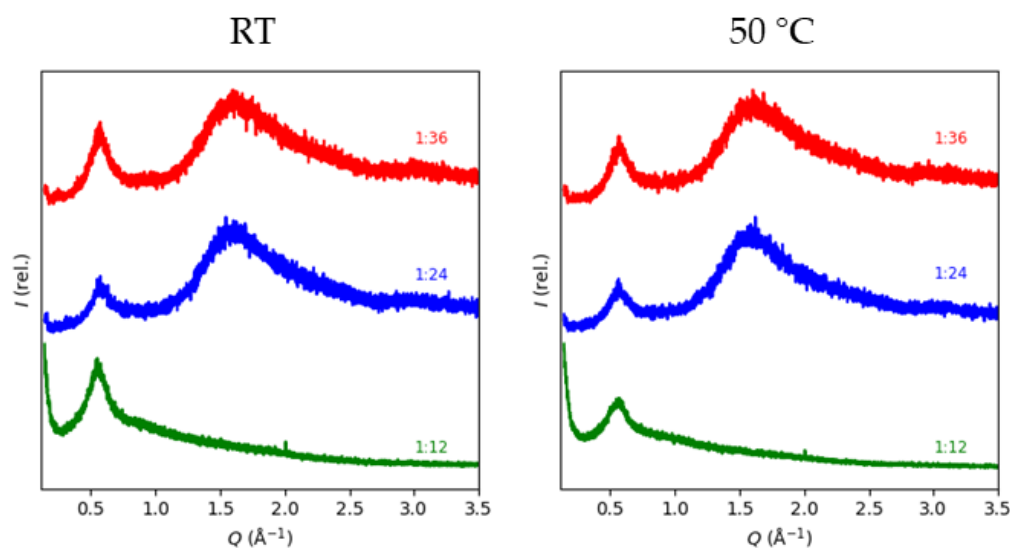


Figure 52. Measured PXRD patterns of the reactions with 1:12 ratio of cluster to linker (green), 1:24 ratio (blue) and 1:36 ratio (red).

3.1.1.6. Modulated syntheses

Modulated synthesis is commonly used in the synthesis of MOFs. Modulators are carboxylic acids used to slow down linker exchange reactions, leading to more crystalline products. From the previous reactions, it was clear that linker exchange reactions were happening quickly, as gels started forming within minutes of the start of the experiments. To try to slow these down, modulated synthesis was explored to try and obtain more crystalline products.

The Zr OBz cluster (27.7 mg) was dissolved in a solution of 1 mL of DMF and 538 molar equivalents of the chosen modulator with respect to the cluster. This high equivalence of modulator was chosen as this is the same as a method from literature where UiO-66 is formed from metal-oxo clusters⁵¹. All other variables were unchanged. Table 1 shows the acids used

and their pKa's. The reactions with propanoic, butyric and acetic acids all led to crystalline product with peaks in the PXRD patterns confirming the successful synthesis of fcu UiO-66, with the two peaks at $Q = 0.52 \text{ \AA}^{-1}$ and $Q = 0.6 \text{ \AA}^{-1}$ matching the ones in the simulated pattern (figure 53). All three acids have similar pKa values (4.88 - 4.75).

The reactions using benzoic, formic and dichloroacetic acids led to clear solutions. The lack of precipitate could be due to the lower pKa of these acids, slowing down or even stopping ligand exchange reactions. Heating theses reactions may increase the rate at which the linker-cluster bond form to give crystalline product, but this was not investigated due to lack of time.

Modulator	pKa
Propanoic acid	4.88
Butyric acid	4.82
Acetic acid	4.75
Benzoic acid	4.20
Formic acid	3.74
Dichloroacetic acid	1.26

Table 1. pKa's of carboxylic acids used as modulators.

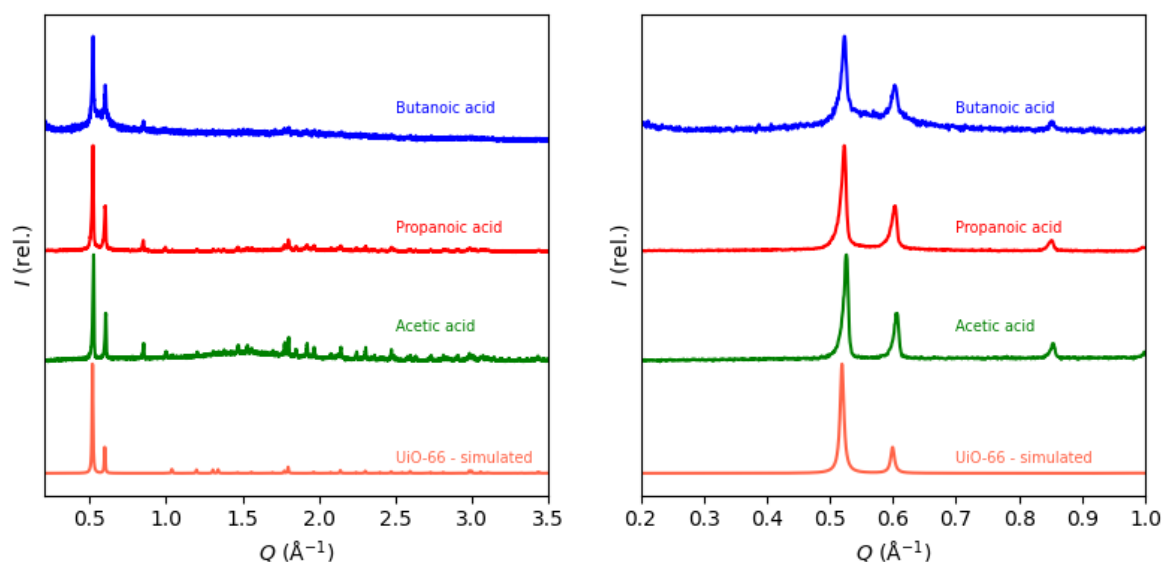


Figure 53. Simulated PXRD pattern of UiO-66 (orange) and measured patterns for the reactions using acetic acid (green), propanoic acid (red) and butanoic acid (blue) as modulators. No solid products were obtained for the reactions using benzoic, dichloroacetic and formic acids as modulators. The figure on the right is a zoom in between $Q = 0.2 \text{ \AA}^{-1}$ and $1.0 \text{ \AA}^{-1}$.

From this set, acetic acid was chosen as the modulator for further reactions as it formed crystalline product and because it is commonly used as a modulator in MOF reactions.

SEM images were taken of the powder of the reaction using acetic acid as modulator (figure 54). UiO-66 has well-defined sharp octahedral shape in SEM images⁷⁸, and the particles are about 500 nm in length. The SEM images of the modulated synthesis of UiO-66 from the Zr_6 OBz cluster shows that the particles are much smaller than expected, about 100 nm across. Some particles vaguely resemble an octahedron, but the edges are not as sharp as the usual images of UiO-66.

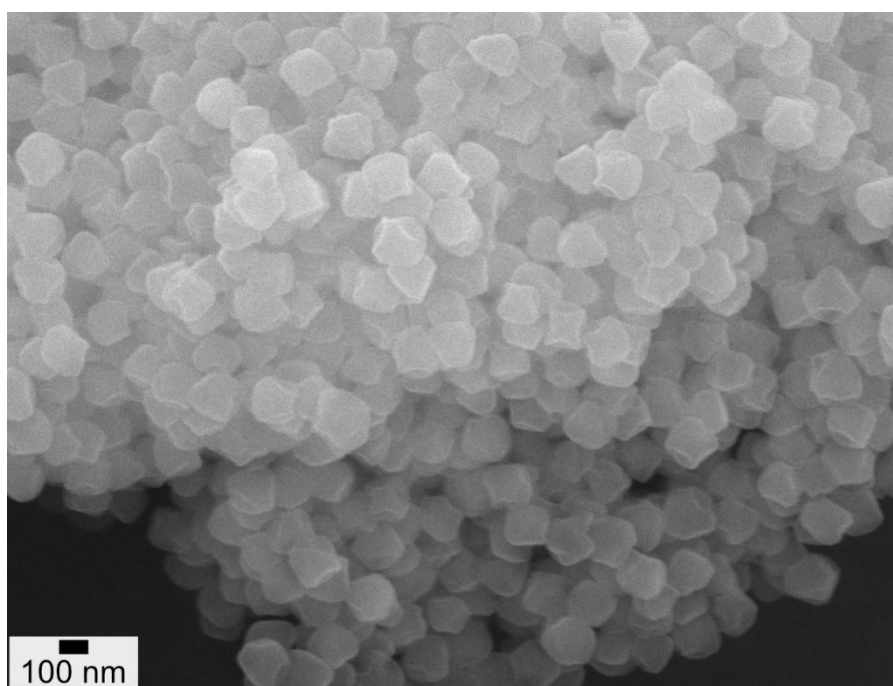


Figure 54. SEM image of modulated synthesis of UiO-66 from Zr_6 OBz cluster.

In this reaction system a significant excess of modulator (538 molar equivalents with respect to cluster) is used. Most reactions using $ZrCl_4$ use much smaller equivalents, so more experiments with varying molar ratios of acetic acid were done to try and establish if such a high molar ratio had to be used in order to obtain crystalline products. The cluster was dissolved in a solution of 1 mL DMF and varying amounts of acetic acid molar equivalents with respect to the cluster: 10, 20, 30, 40, 50, 100, 250. All reactions formed gels except for the reaction with 250 equivalents that formed a clear solution. The gels formed more slowly as

the equivalents of acetic acid were increased. From figure 55, none of the reactions show improved crystallinity compared to the unmodulated synthesis

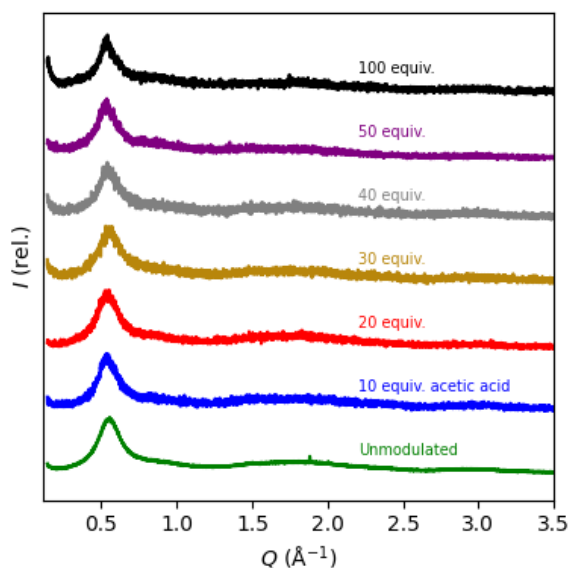


Figure 55. Measured PXRD patterns of the unmodulated reaction of Zr OBz cluster with *trans,trans*-muconic acid (green), the reaction using 10 equivalents of acetic acid (blue), 20 equiv. (red), 30 equiv. (gold), 40 equiv. (grey), 50 equiv. (purple) and 100 equiv. (black).

The reaction not working with 250 equivalents of acetic acid was quite puzzling. With the reaction with 100 equivalents forming a gel and the one with 538 equivalents forming white precipitate, the 250 equivalents reaction was expected to form some solid product. While all variables were kept the same including methods and using the same batch of cluster between all modulated reactions, there must have been some other factor that affected the lack of solid product from this reaction.

Another systematic series using benzoic acid was done to investigate whether it can act as modulator. It was hypothesised earlier that small amounts of benzoic acid found in a batch of Zr benzoate cluster might lead to crystalline product, whereas a purer batch would not.

This series was similar to the one done with acetic acid, where 10, 20, 30, 40, 50, 100 and 250 molar equivalents of benzoic acid were dissolved in 1 mL of DMF, and this solution was then used to dissolve the cluster in. No product was obtained for 100 and 250 equivalents. PXRD indicated no increase in crystallinity from the unmodulated reaction (figure 56).

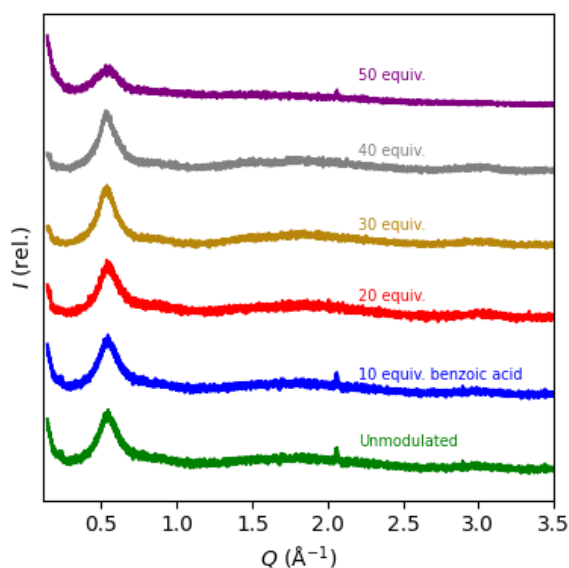


Figure 56. PXRD patterns of the unmodulated reaction of Zr OBz cluster with *trans,trans*-muconic acid (green), the reaction using 10 equivalents of benzoic acid (blue), 20 equiv. (red), 30 equiv. (gold), 40 equiv. (purple) and 50 equiv. (black).

One of the hypothesis as to why the reaction using acetic acid was successful was that the Zr benzoate cluster was rearranging to a $(\text{Zr}_6)_2$ cluster.

The Zr_{12} acetate cluster can be synthesised as a discrete molecule. It is made up of two Zr_6 acetate sub-units that are bonded through bridging acetate molecules. To investigate whether the Zr_6 cluster was rearranging, MOF reactions were done with the Zr_{12} acetate cluster as starting material. This was done modulated with acetic acid (538 molar equivalents with respect to cluster) and unmodulated. The conditions were kept the same as reactions with the Zr_6 cluster, apart from the molar amount of the cluster which was halved as to maintain the metal to linker ratio. Both reactions formed white precipitate after 1 day. PXRD analysis of the reactions showed that neither of the reactions had formed UiO-66 with these conditions, and that the starting cluster had come out of solution (figure 57).

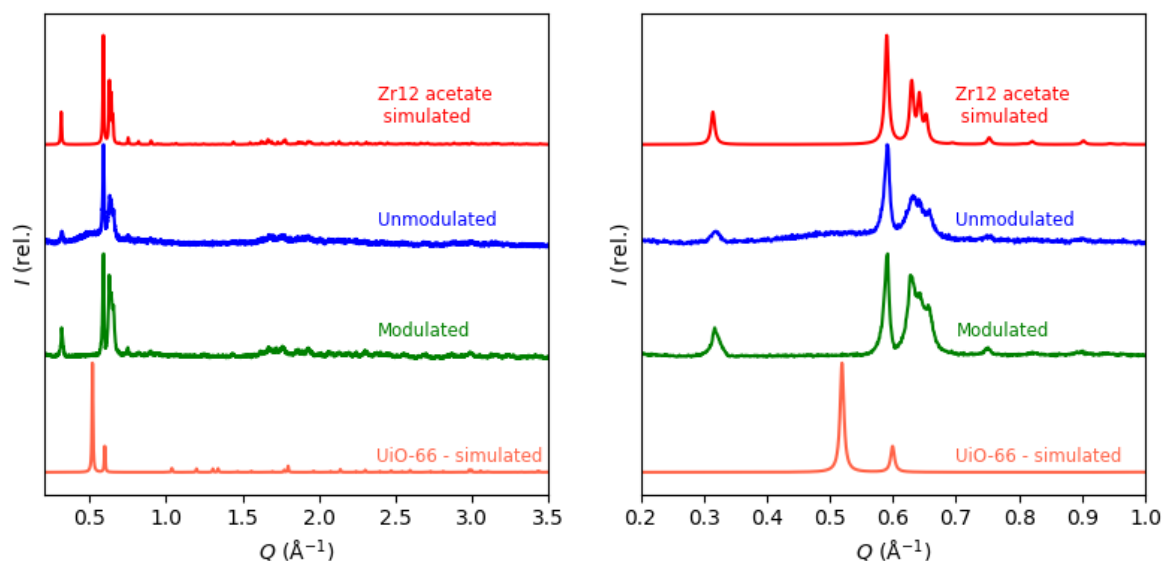


Figure 57. Simulated PXRD patterns of UiO-66 (orange) and Zr_{12} acetate cluster (green), and measured patterns for modulated reaction of Zr_{12} acetate cluster with *trans,trans*-muconic acid (green) and unmodulated reaction (blue). The figure on the right is a zoom in between $Q = 0.2 \text{ \AA}^{-1}$ and $1.0 \text{ \AA}^{-1}$.

This seemed to disprove the hypothesis that the Zr_6 cluster was rearranging to an acetate-bridged Zr_{12} cluster. Furthermore, studies have shown that the solvothermal reaction of the Zr_{12} acetate cluster with a ditopic linker, such as the one used in this reaction, leads to the breaking of the bridging acetate ligands between the two subunits, leading to the formation of UiO-66⁴⁰.

3.1.2. Using the Zr_6 methacrylate cluster as starting material

From the initial experiments with the benzoate cluster, *trans,trans*-muconic acid was chosen as the preferred linker for the subsequent reactions, as it led to more crystalline product. Therefore, using *trans,trans*-muconic acid, a series with the methacrylate cluster was done to investigate whether temperature and reaction time had an impact on crystallinity in an unmodulated reaction. PXRD patterns of the products show that temperature has no impact on crystallinity (figure 58). There is a broad peak between $Q = 1.0 \text{ \AA}^{-1}$ and $Q = 2.5 \text{ \AA}^{-1}$ in the plots after a reaction time of 1 day which is no longer present after 3 days. The peak at around $Q = 0.6 \text{ \AA}^{-1}$ shows the formation of framework, however it is poorly crystalline and the width

of the peak indicates small particle sizes. Thorough washing of the products with DMF ensures that this peak is not due to starting material being present in the samples.

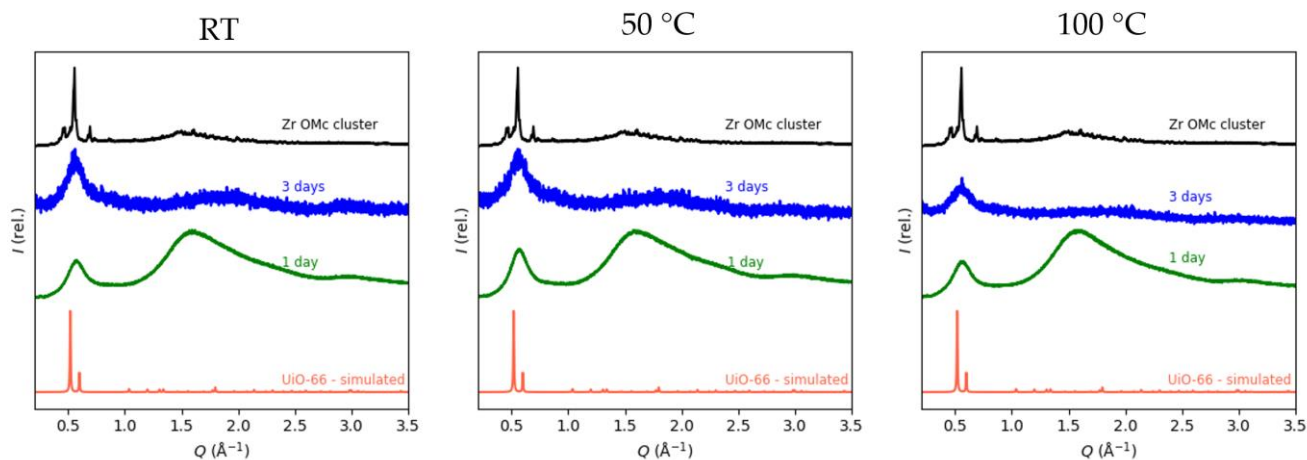


Figure 58. Simulated PXRD pattern of UiO-66 (orange) and measured patterns of the reaction of Zr OMc cluster and muconic acid after 1 day (green), after 3 days (blue) and Zr OMc cluster (black) for the reactions at room temperature (left), 50 °C (middle) and 100 °C (right).

The PXRD analysis of the modulated reaction of Zr OMc cluster and *trans,trans*-muconic acid using acetic acid clearly leads to formation of UiO-66, with two peaks at $Q = 0.52 \text{ \AA}^{-1}$ and $Q = 0.6 \text{ \AA}^{-1}$ matching those of the simulated pattern (figure 59). There are also traces of *trans,trans*-muconic acid present, despite washing the product with DMF. It is not as crystalline as the modulated reaction of the Zr_6 benzoate cluster with *trans,trans*-muconic acid.

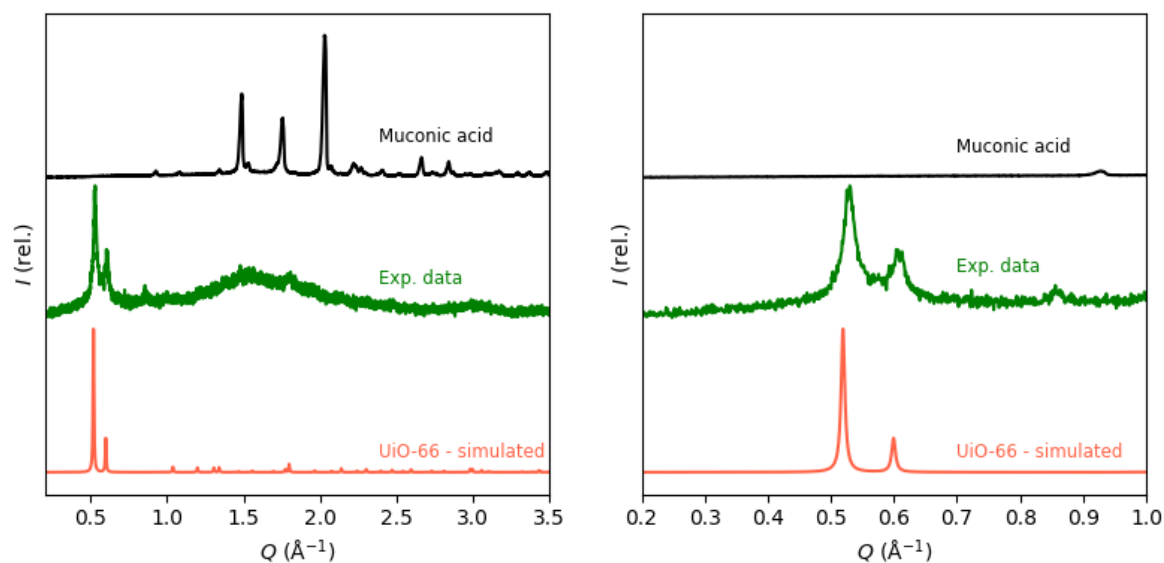


Figure 59. Simulated PXRD pattern of UiO-66 (orange) and measured pattern of the reaction of Zr OMc cluster with *trans,trans*-muconic acid using acetic acid as a modulator (green) and of *trans,trans*-muconic acid (black). The figure on the right is a zoom in between $Q = 0.2 \text{ \AA}^{-1}$ and $1.0 \text{ \AA}^{-1}$.

Formic, methacrylic and dichloroacetic acids were all also tried as modulators with no solid product formed. Similarly to the Zr OBz cluster, this could be due to the lower pK_a 's of these as compared to acetic acid.

The SEM images of the modulated synthesis of UiO-66 using the methacrylate cluster (figure 60) shows that the particles measure about 100 nm across, which is similar to the benzoate cluster. The edges are a bit less well-defined compared to the other cluster.

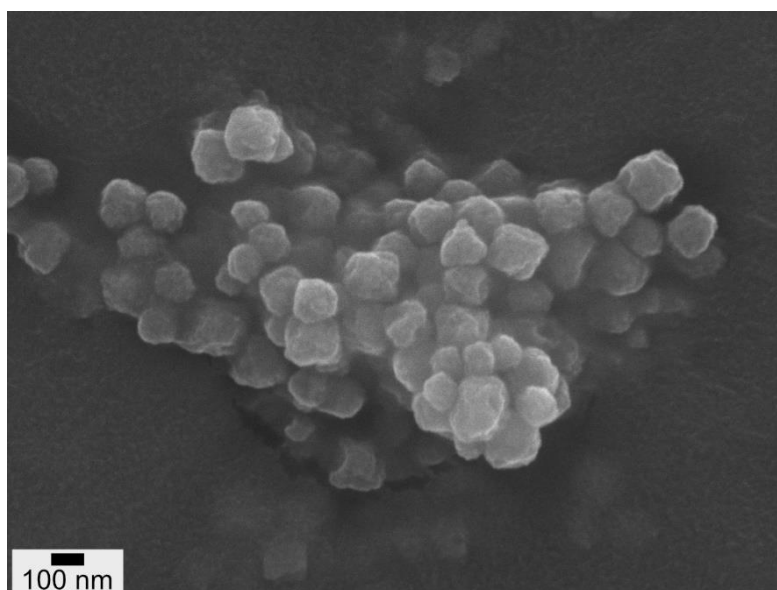


Figure 60. SEM images of the modulated synthesis of UiO-66 using Zr_6 OMc cluster.

Comparing the products from the two zirconium clusters, UiO-66 formed from the Zr OBz cluster is more crystalline than with the Zr OMc cluster (figure 61). The lower crystallinity of product from the methacrylate cluster is likely due to the mixture of phases in the methacrylate cluster starting material leading to side reactions.

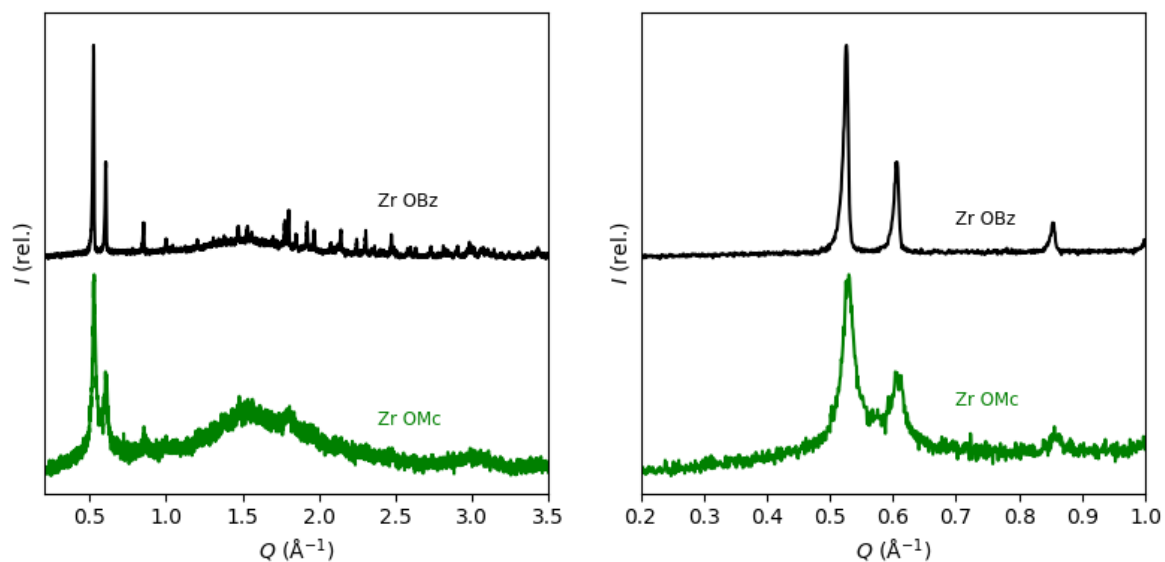


Figure 61. Measured PXRD patterns from the reactions of *trans,trans*-muconic acid with Zr OMc cluster (green) or Zr OBz cluster (black). The figure on the right is a zoom in between $Q = 0.2 \text{ \AA}^{-1}$ and $1.0 \text{ \AA}^{-1}$.

3.1.3. Using the Ti_6 ABZ cluster as starting material

To use as a point of comparison, the reaction of the Ti_6 aminobenzoate cluster with *trans,trans*-muconic acid was investigated, both modulated and unmodulated. MOF reactions involving titanium are known for being quite difficult, and usually require harsher conditions such as stronger acids, high temperatures or different solvents. This is due to the high polarisation of the Ti-linker carboxylate bonds, hindering ligand association-dissociation. Just like with the other clusters, the unmodulated reaction of Ti ABZ with *trans,trans*-muconic acid was done with a 1:12 cluster to linker ratio, and three different temperatures (RT, 50 °C and 100 °C) were used as well as two different reaction times (1 or 3 days). While Ti-MOFs are harder to synthesise, these relatively mild conditions were used so that the results could be compared to the same conditions applied to the Zr-MOFs. PXRD shows that no product is formed for all reactions (figure 62). The broad peak between $Q = 1.5 \text{ \AA}^{-1}$ and $Q = 2.0 \text{ \AA}^{-1}$ visible in the pattern after the one day reactions is most likely due to linker.

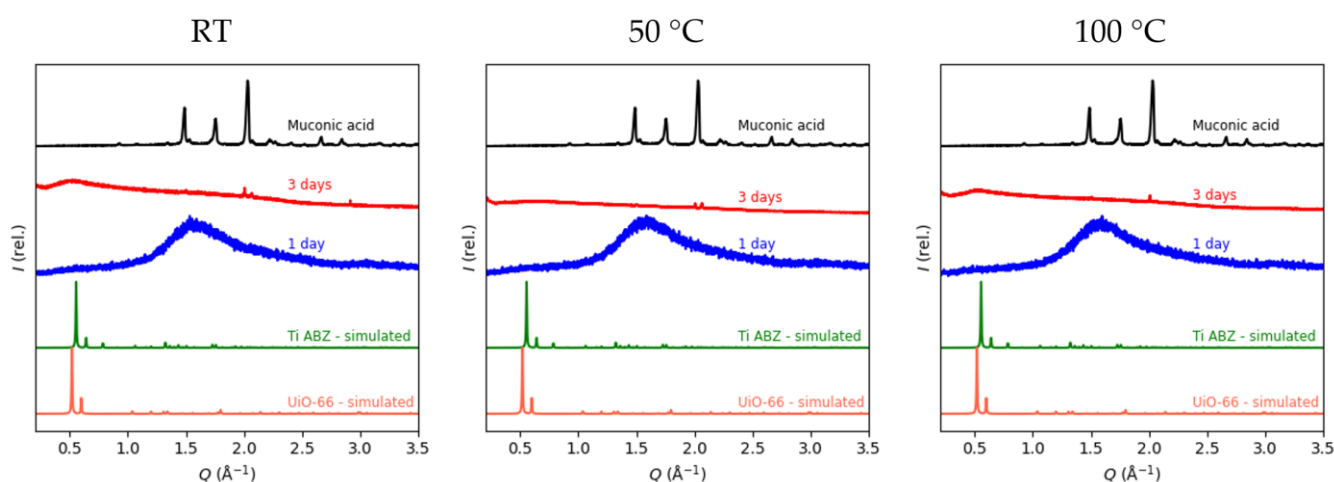


Figure 62. Simulated PXRD patterns of UiO-66 (orange) and Ti ABZ cluster (green) and measured patterns of the reaction of Ti ABZ cluster and *trans,trans*-muconic acid after 1 day (blue), after 3 days (red) and *trans,trans*-muconic acid (black) for the reactions at room temperature (left), 50 °C (middle) and 100 °C (right).

Multiple different acids were tried as modulators, including acetic acid which had worked with the Zr cluster reactions, with no solid product formed.

3.1.4. Mixed-cluster MOF reactions

One of the targets of this project was to synthesise mixed-cluster MOFs. There are multiple examples of mixed-metal cluster MOFs in the literature, where different metals are found within the same cluster²⁸. However, there is, to my knowledge, no example of a MOF with two distinct clusters with different metals. As seen previously, MOFs based on zirconium clusters readily form when modulated using acetic acid, whereas titanium MOFs do not. By incrementally increasing the molar amount of Ti ABZ cluster in both modulated and unmodulated reactions of Zr OBz cluster with *trans,trans*-muconic acid, the idea was that the forming Zr-based MOF may act as a template for the titanium cluster to be integrated into the framework. To do this, the molar amount of cluster was kept the same as the reactions that had previously worked (0.013 mmol in 1 mL of DMF). Starting with a pure Zr OBz cluster reaction, the molar percentage of the Ti ABZ cluster was increased in 10% increments, all the way to 90% of the Ti cluster.

For the unmodulated reactions, gel-like precipitates started forming rapidly after adding the clusters to the linker, but the gels formed more slowly as the percentage of Ti clusters was increased. Product was obtained for all reactions. However, PXRD shows that all samples produced amorphous products (figure 63).

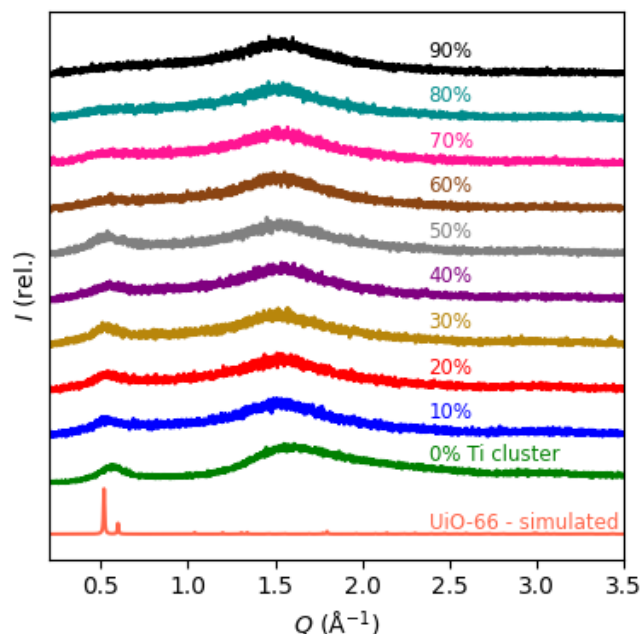


Figure 63. PXRD patterns of simulated UiO-66 (orange), and measured patterns of the unmodulated reactions with 0% Ti cluster (green), 10% (blue), 20% (red), 30% (gold), 40% (purple), 50% (grey), 60% (brown) 70% (pink), 80% (cyan) and 90% (black).

For the modulated reactions, white precipitate was formed for all reactions up to 70% of the titanium cluster. However, yield decreased as the percentage of the Ti cluster was increased, hinting that the reactions had not worked as intended. PXRD shows that samples with up to 40% Ti cluster in the reaction mixture are crystalline for the exception of 20% which seems anomalous in that there was an unexpected peak broadening in the PXRD pattern (figure 64). The peaks correspond to those in the simulated pattern of UiO-66. However, crystallinity decreases as the percentage of Ti is increased, marked by the broadening of the peaks in the patterns.

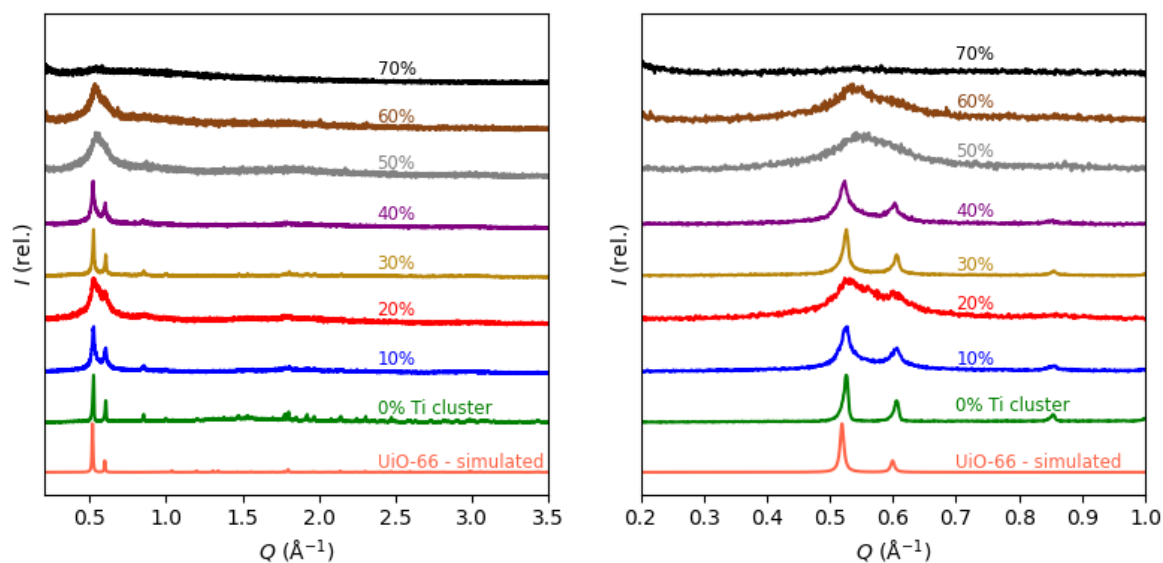


Figure 64. PXRD patterns of simulated UiO-66 (orange), and measured patterns of the modulated reactions with 0% Ti cluster (green), 10% (blue), 20% (red), 30% (gold), 40% (purple), 50% (grey), 60% (brown) and 70% (black). The figure on the right is a zoom in between $Q = 0.2 \text{ \AA}^{-1}$ and $1.0 \text{ \AA}^{-1}$.

Studies have shown that Ti-doping of Zr-UiO-66 led to no new peaks associated with the titanium centres compared to pure Zr-UiO-66, but there was a decrease in peak intensities and the peak at $Q = 0.6 \text{ \AA}^{-1}$ shifted to higher values⁷⁹. These are not observed in my data. As mentioned in the research objectives, the integration of Ti into the Zr-UiO-66 is controversial, and occurs through grafting of Ti onto linker vacancy sites rather than through metal exchange⁶². This introduces unhomogeneous distribution of Ti centres throughout the framework, due to high defect concentrations⁸⁰.

MIL-125 is the Ti analogue of UiO-66⁸¹. The PXRD pattern of MIL-125 is shown in figure 65, and differs from the pattern of UiO-66. If the integration of the Ti cluster would have been successful, we would expect changes in the PXRD patterns, particularly the lattice parameters, with new peaks appearing that correspond to MIL-125. However, this is not the case.

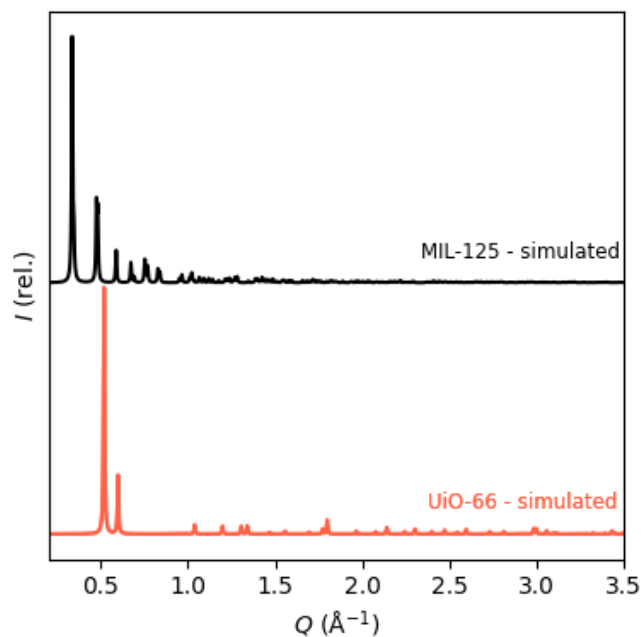


Figure 65. Simulated PXRD patterns of UiO-66 (orange) and MIL-125 (black).

SEM images were taken of the reactions with up to 40% of the Ti cluster (figure 66). Samples above this percentage were not imaged as they showed poor crystallinity in their PXRD patterns. The particles look similar in the shape and size to the Zr benzoate reaction.

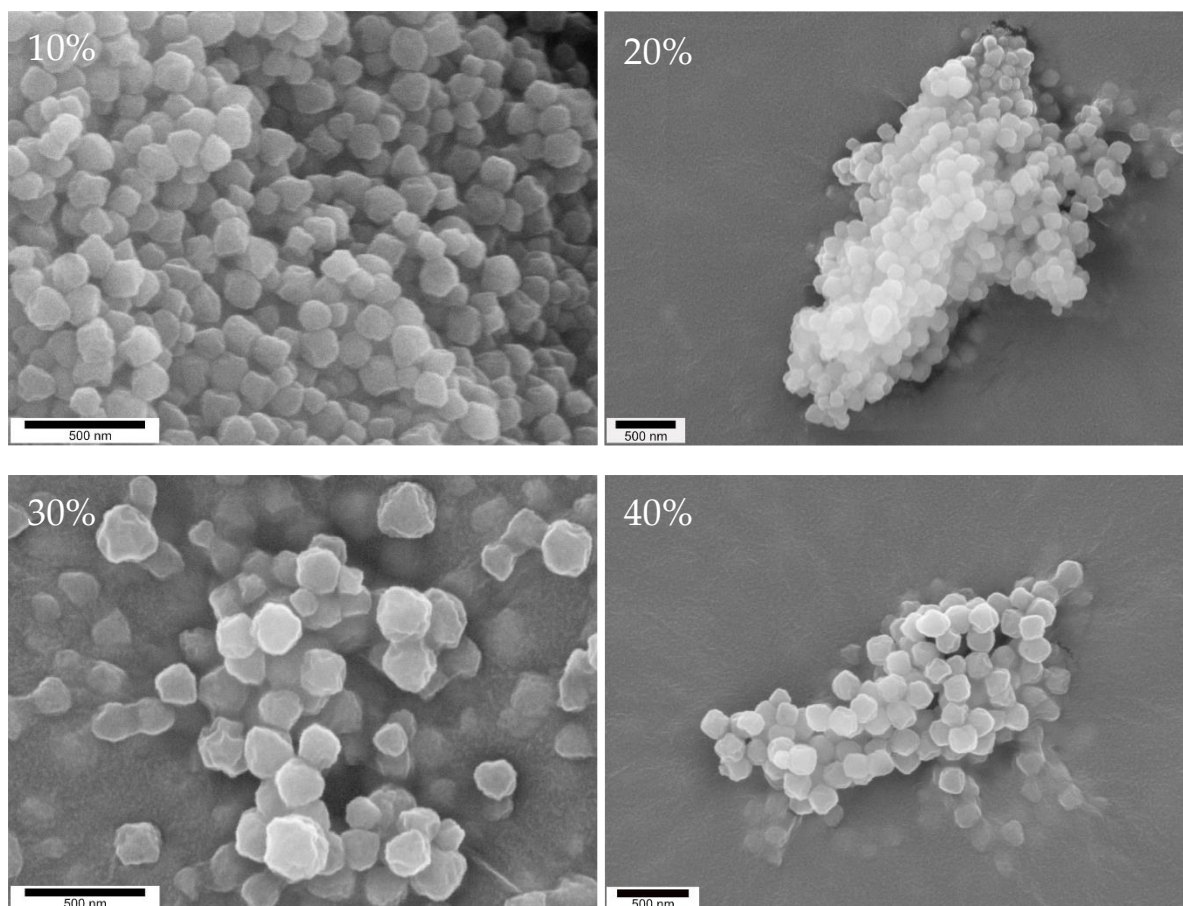


Figure 66. SEM images of the modulated mixed cluster reactions with 10% Ti ABZ cluster, 20%, 30% and 40%.

Energy-dispersive X-ray spectroscopy (EDX) experiments were also done on the samples above (figure 67). This can be used to determine the chemical composition of samples, and relies on the excitation and ejection of an inner-shell electron by an incident electron beam. The atom then relaxes and loses energy by ejecting an outer-shell electron, leading to the emission of X-rays. The energy of the X-ray photon is specific to each element and can therefore be used to determine the chemical composition of samples.

The EDX spectra show that the abundance of Zr, Ti, C and O atoms as a weight percentage (figure 67). The samples with 10% and 20% Ti cluster contain 0.1 wt% Ti, and the samples with 30% and 40% contain 0.2 wt% Ti. Compared to the weight percentages of Zr atoms, this is very low and indicates that the Ti atoms present are from starting material present in the samples. Note that wt% of carbon is very high as the samples are set on carbon tabs.

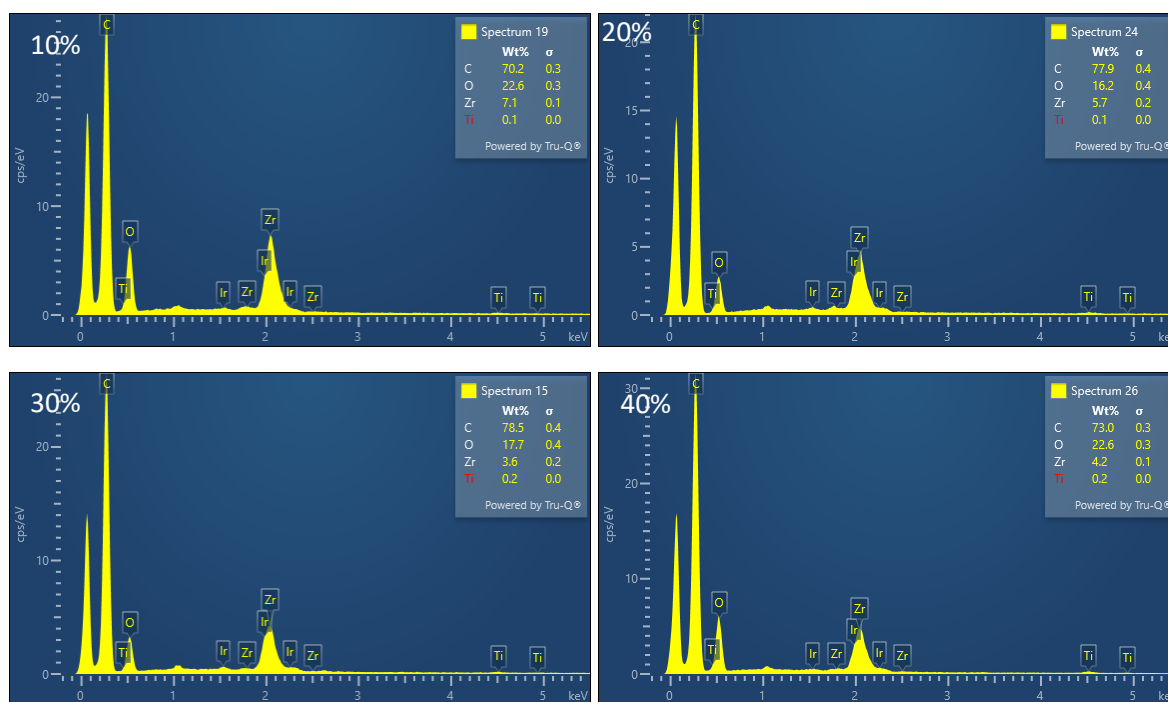


Figure 67. EDX spectra of the modulated mixed cluster reactions with 10% Ti ABZ cluster, 20%, 30% and 40%.

EDX mapping was done on the 30% Ti sample. Mapping shows the position of the detected atoms on a SEM image. Figure 68 shows the SEM image chosen for the mapping, and the corresponding maps for carbon K α 1,2, oxygen K α 1, zirconium L α 1 and titanium K α 1 emissions. The C map shows carbon atoms throughout since the sample was set on carbon tabs. The O map shows the outline of the SEM image, and the Zr map also shows a clear outline of the image. The Ti map shows little titanium atoms that are randomly scattered with no outline of the shape. This confirms that the small wt% of titanium in the previous EDX spectra are due to starting material in the samples.

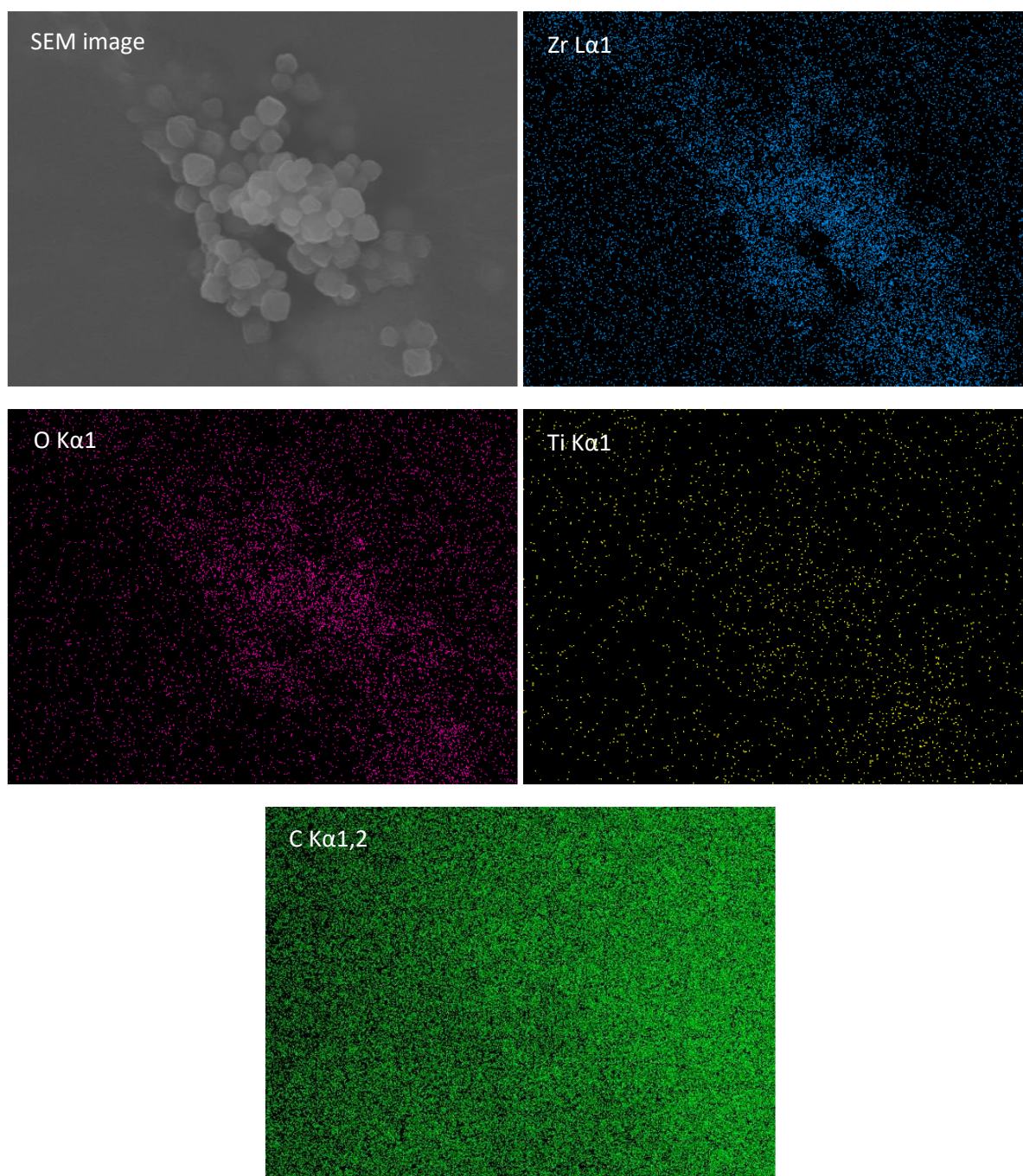


Figure 68. SEM image used for EDX mapping and EDX maps showing Zr L α , O K α 1, Ti K α 1 and C K α 1,2 emissions.

Finally, solid-state UV-vis was done on the mixed-cluster reactions. The absorptions seen in the spectra would most likely be due to ligand to metal charge transfer for the metal – O bonds from the cluster cores (bridging O and OH groups in the Zr cluster, and bridging O and chelating OⁱPr in the Ti cluster), so integration of the Ti cluster within the framework could be determined by comparing the spectra of the clusters starting material and of the products.

From figure 69, the Ti ABZ cluster has two peaks in its UV-vis spectrum at $\lambda = 400$ nm and $\lambda = 250$ nm. The Zr OBz cluster has one sharp peak at $\lambda = 275$ nm. The spectra of the mixed cluster reactions all have one peak at $\lambda = 275$ nm, and all look similar to the Zr OBz cluster, indicating that no Ti clusters are present in the samples.

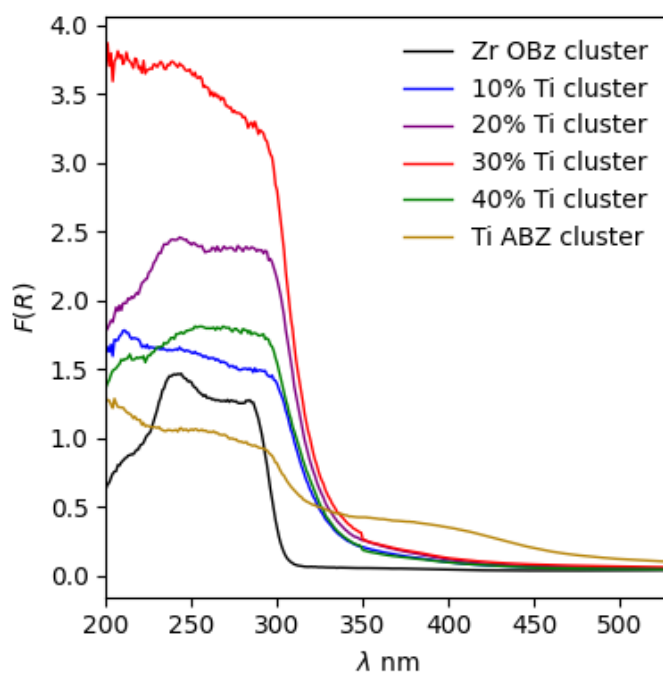


Figure 69. UV-vis spectra of Zr OBz cluster (black), reactions with 10% Ti ABZ cluster (blue), 20% (purple), 30% (red), 40% (green) and Ti ABZ cluster (gold).

3.2. Discussion

My original motivation for using pre-made clusters as starting materials for MOF reactions was that they can be considered “self-modulating”. In a typical MOF reaction starting from a metal salt, a modulator is used to help lead to more crystalline products. The conventional understanding is that main role of the modulator is to occupy metal coordination sites while the metal clusters form through self-assembly and leads to more crystalline materials as it regulates the rate of linker association-dissociation, allowing for better crystalline ordering. Pre-made clusters with carboxylates are closely related to these pre-MOF clusters formed in the self-assembly process and therefore should present an advantage over an unmodulated reaction of metal salt and linker. The results obtained from my MOF syntheses from discrete

clusters suggest that the role of modulators is more complex than simply coordinating to the metal and regulating the rate of linker exchange.

3.2.1. Unmodulated reactions

Starting with unmodulated reactions, systematic series of MOF syntheses were done to try and establish the conditions needed for the formation of crystalline material. Three linkers were chosen as a starting point: terephthalic acid, aminoterephthalic acid and *trans,trans*-muconic acid. The first two were chosen as they have been extensively studied in MOF systems. *Trans,trans*-muconic acid is a precursor to both terephthalic acid and aminoterephthalic acids, and can be used as starting material in a variety of reactions, including polymerisation, esterification and cyclisation reactions⁷³. Furthermore, its alkene moiety could allow for post-synthetic modification⁷⁴ of the framework.

From this initial set of experiments, *trans,trans*-muconic acid showed the most promising results, with clear indications of formation of UiO-66 in the PXRD patterns, and was therefore chosen for further experiments.

Table 2 shows the linkers and their associated pKa's and solubility in water at room temperature. Polarity of these could have been useful to show trends, however, the data is not easily accessible. No trend can be seen in the pKa values to explain the increase in crystallinity in the reaction with *trans,trans*-muconic acid, however, it is the most soluble in water.

Linker	pKa	Solubility in water (25 °C)
Aminoterephthalic acid	3.95	Slightly soluble
<i>Trans,trans</i> -muconic acid	3.87	Soluble
Terephthalic acid	3.51	Poorly soluble

Table 2. Linkers and their associated pKa's and solubility in water.

Férey *et al.* investigated the formation of UiO-66 with *trans,trans*-muconic acid and the phase-pure Zr methacrylate cluster and demonstrated that it can be easily synthesised showing the

two distinct peaks found in the PXRD pattern of UiO-66, with the crystallinity of the product being proportional to reaction time⁴⁹. Comparing their results to mine, all unmodulated reactions with the Zr methacrylate led to a wide broad peak regardless of temperature or reaction time. This is most likely due to the mixture of different phases found in the Zr methacrylate cluster starting material.

Similarly to the reactions with the Zr methacrylate cluster, PXRD analysis of the reactions starting with the Zr benzoate cluster showed a wide broad peak. Unlike the methacrylate cluster, the benzoate cluster was phase-pure. This highlighted that the clusters' ligands can influence the formation of crystalline material.

Different variables, including reaction time, temperature and reactant molar ratios and concentrations, were then varied to investigate how these affected the formation of crystalline UiO-66 starting with the Zr benzoate cluster and *trans,trans*-muconic acid. In most of these reactions, gels formed rapidly after addition of the cluster to the linker. Reaction times of 1 and 3 days were explored but, in most cases, 1 day reaction time was sufficient for complete precipitation, and neither did longer reaction time improve crystallinity. Only the initial unmodulated reaction of the Zr benzoate cluster and *trans,trans*-muconic acid showed an increase in crystallinity after 3 days compared to 1 day. Temperatures ranging from room temperature to 100 °C were used, but higher temperature only benefitted few reactions, e.g. the initial scans of linkers with the Zr benzoate cluster. Starting from the first set of reactions the concentrations were lowered and molar ratios of metal to linker were varied to no effect on crystallinity or formation of product.

3.2.2. Modulated reactions

An initial screening of different organic monocarboxylic acids was done in the reaction of the Zr benzoate cluster with *trans,trans*-muconic acid. The acids used were formic, acetic, propionic acid, butanoic, benzoic and dichloroacetic acid. Table 3 show the modulators and their associated pKa values and solubility in water at room temperature. Like with the linkers, polarity data is not easily accessible.

Solid products were obtained from acetic, propionic and butanoic acids. Two trends can be made from this: all three have similar high pKa value, and they are all aliphatic acids. This might suggest that acids with lower pKa values more strongly interact with the clusters, completely hindering linker exchange reactions or that modulators with different organic functionalities such as aromatic or chlorinated aliphatic acids might lead to different reactions. Shearer *et al.* demonstrated that modulators with higher acidity do indeed bind more strongly to the clusters, inducing cluster defects⁸². Morris *et al.* also investigated the effect of acetic, formic, difluoroacetic and trifluoroacetic acids on the stability and particle size of UiO-66⁸³. They showed that these are directly influenced by the concentration and acidity of the modulator. They also showed that the use of higher concentrations of modulator with lower pKa values led to no product, which is similar to the results showed in this thesis.

Modulator	pKa	Solubility in water (25 °C)
Propanoic acid	4.88	Miscible
Butanoic acid	4.82	Miscible
Acetic acid	4.75	Miscible
Benzoic acid	4.20	Poorly soluble
Formic acid	3.74	Miscible
Dichloroacetic acid	1.26	Miscible

Table 3. Modulators and their associated pKa's and solubility in water.

Benzoic acid is commonly used as a modulator in the synthesis of UiO-66 starting with ZrCl₄ and terephthalic acid. Behrens *et al.* showed that, even in small molar equivalents, benzoic acid increases crystallinity and particle size¹⁷. The use of acetic acid displayed similar results. They also showed that using a different linker (biphenyl dicarboxylic acid) required modified conditions to form crystalline material. This highlights that conditions required for modulated reactions are dependent on starting materials, and reinforces the complexities of the modulation mechanism.

In typical modulated reactions, high temperatures are required, however with clusters these can be done at room temperature. From all previous reactions, the conditions leading to

crystalline material were established as: 1:12:538 molar ratios of cluster:linker:modulator using acetic acid, with DMF as solvent for 24 hours at room temperature. These conditions were applied to the Zr OMc and Ti ABZ clusters. Titanium MOFs are famously difficult to form, and while this set of conditions worked for the Zr OMc cluster, the titanium cluster formed no solid product. Even though they are both group IV metals, this shows how different their chemistries are.

3.2.3. *Mixed cluster reactions*

Mixed-metal MOFs, where a mixture of metals is found in the clusters, can be synthesised by using specific mixtures of metal precursors in a reaction mixture²⁴. This method provides low control over the distribution of each metal within the framework. The use of discrete clusters made from different metals as starting material for MOF syntheses would provide better control over the distribution of each metal throughout the framework as it would counter the random arranging of the metals when the clusters formed through self-assembly. Furthermore, MOFs with separate clusters with two different metals, as opposed to a mix of metal within the same clusters, has yet to be made. These mixed-cluster MOFs could be synthesised by tuning conditions when using two types of discrete clusters in the reaction mixture.

Attempts to synthesise mixed-cluster MOFs with the conditions that had worked with the Zr OBz cluster were unsuccessful in this project. The hypothesis was that, by using a mixture of the Zr OBz cluster and Ti ABZ cluster, the forming Zr-UiO-66 would act as a template for the integration of Ti clusters into the framework.

While mixed-clusters MOFs might be possible, the conditions for the formation of the individual single-cluster MOFs would have to be the same for both clusters before attempting mixed-cluster MOFs. This might also just lead to the individual MOFs to form in the same reaction mixture. The intricacies of this problem is shadowed by the complexity of the chemistry group IV metals, and will require further experimentation to develop.

Chapter 4: Conclusion and future work

4.1. Conclusion

The aim of this project was to synthesise group IV metal clusters, specifically Zr and Ti clusters to use in reactions to form metal-organic frameworks.

To that end, three clusters were synthesised, namely Zr₆ benzoate, Zr₆ methacrylate and Ti₆ aminobenzoate. Novel clusters were synthesised, but difficulties were encountered with characterisation due to poor crystallinity.

MOF reactions were first undertaken with the Zr₆ benzoate cluster. This was chosen as it was the most phase-pure of the Zr clusters. To find the ideal conditions, multiple variables were changed to investigate how they affected formation of product and crystallinity. Starting with unmodulated reactions, three different linkers were chosen: terephthalic acid, aminoterephthalic acid and *trans,trans*-muconic acid. *Trans,trans*-muconic acid was chosen as it produced the more crystalline products. Gels started forming rapidly after mixing of the reactants suggesting that product was forming rapidly and that longer reaction times were not necessary. Reaction times of 1 and 3 days were explored, but longer reaction time only benefitted one reaction, namely the initial unmodulated reaction of the Zr benzoate cluster with *trans,trans*-muconic acid in DMF which showed improvement in crystallinity after 3 days compared to 1 day. Using a range of temperatures from room temperature (RT) to 100 °C, it was established that temperatures above RT only benefitted few reactions, e.g. the initial scans of terephthalic, amino terephthalic and *trans,trans*-muconic acid with the Zr benzoate cluster in DMF. Experiments where the molar ratios of metal to linker were changed (1:12, 1:24 and 1:36 metal to linker ratio), and the concentrations of cluster were lowered (27.7 mg/mL – 5.54 mg/mL in DMF) showed no improvement to the products.

Different organic acids were explored to investigate modulated synthesis conditions. It was determined that aliphatic acids with higher pK_a values (4.75 – 4.88) worked best as modulators and acetic acid was chosen for further reactions. Experiments were done to determine the required amounts of modulator and showed that a high molar ratio had to be used (1:538 with respect to cluster). These conditions were applied to other clusters. These were 1:12:538 molar ratio of cluster:linker:modulator, DMF as solvent and reaction at room

temperature for 24 hours, and were used for the Zr₆ methacrylate and Ti₆ aminobenzoate clusters. The reactions with the zirconium methacrylate cluster yielded similar results to the zirconium benzoate reactions. Unsurprisingly, the titanium aminobenzoate cluster reactions did not lead to the formation of a MOF. The results from these reactions suggested that the “self-modulating” properties of discrete clusters are not the main concept at play, and that in general the modulation mechanism is more complex than the common understanding. Acidity effects are also essential, and work together with coordinating effects to provide the full modulation mechanism.

Finally, MOF reactions were tried with a mixture of titanium and zirconium clusters. This was done to try to obtain a MOF with separate distinct clusters. By keeping the total molar amount of cluster constant, the percentage of the Ti ABZ cluster was incrementally increased, from 10% to 100% Ti cluster, while keeping the other conditions the same as the previously established ones. These mixed-cluster MOFs were characterised by different techniques, namely PXRD, solid-state UV-Vis and EDX. Unfortunately, no Ti clusters were detected in the MOFs.

4.2. Future work

Optimisation of the synthetic conditions of the Zr aminobenzoate and Ti benzoate would be beneficial for mixed-cluster reactions. The main issue was phase-purity. If single crystals could be obtained, full characterisation could be done using SCXRD. While attempts were made to recrystallise the poorly crystalline products using a single-solvent process, other recrystallisation techniques, such as slow evaporation, slow diffusion or layering, could lead to phase-pure crystals. A more thorough solvent solubility scan would be beneficial. By understanding these clusters’ solubilities, improvements could be made to their synthetic and recrystallization conditions, as well as potentially providing a route to solution-based analytical techniques such as NMR and mass spectrometry.

Synthetic conditions should also be improved to obtain phase-pure Zr methacrylate cluster. In the paper showing the first synthesis of the cluster, the reaction is done under Ar atmosphere. In my research, this was considered unnecessary as none of the starting materials

seemed air-sensitive. Trying this again under N₂ or Ar atmosphere could be beneficial and it would be interesting to see if it leads to phase-pure product.

The Zr benzoate and the Ti aminobenzoate clusters used in the mixed-cluster reactions in this project are closely related, but ideally clusters with the same carboxylate ligand should be used.

Clusters with different functionalities could be interesting to investigate. While alkenes, arenes and anilines were studied in the form of the Zr methacrylate, Zr benzoate and Ti aminobenzoate respectively, different functional groups would lead to some interesting reactivities that could be exploited in MOF reactions.

While the main focus of this project was on titanium and zirconium clusters, the Hf₆ methacrylate cluster can be synthesised. This cluster is very close in structure to the zirconium cluster and it would be interesting to explore how simply changing the metal affects the reactivity of the cluster, especially in MOF reactions. Subsequently, this would require improvements in the synthesis of the Zr methacrylate cluster to produce phase-pure material.

Having a wider range of different metal clusters with varying ligands would help develop our understanding of both ligand and metal effects in MOF syntheses through systematic investigations of variables, similarly to those done with the zirconium benzoate cluster.

Using HCl as a modulator would help understand the acidity and coordination effects in modulated synthesis. Because it is non-coordinating and concentration can be varied, HCl makes for an ideal acid to investigate both these effects.

While a lot of variables were explored for the Zr OBz cluster, the same systematic exploration should be done with Ti ABZ cluster. Modulation is a key variable in the formation of crystalline MOFs from clusters, so a more thorough systematic screen of different modulators and molar equivalents would be beneficial to the understanding of the chemistry of Ti-MOFs from clusters. It is clear from my results that titanium clusters have very different chemistry than zirconium clusters so variables other than modulation should be explored as they might produce different results to the reactions with the zirconium clusters.

Finding conditions that allow the formation of MOFs from Ti clusters would not only be beneficial for the field of Ti-MOFs but also help towards the understanding of the conditions needed for mixed-cluster MOFs.

Chapter 5: Experimental

5.1. Characterisation techniques

5.1.1. Powder X-ray diffraction

Powder X-ray diffraction (PXRD) was the most used characterisation technique throughout this project. It is a very powerful tool in the field of crystalline materials, as it can be used to determine phase purity, crystallinity, lattice parameters and structure. When X-rays are scattered from a material, the difference in angle between the incoming and outgoing beam is measured in 2θ . The positions of the peaks are given by Bragg's equation:

$$\lambda = 2d \sin \theta$$

where λ is the wavelength of the X-ray beam (which is constant in most diffractometers), d is the spacing between the planes of the lattice and θ is half the angle of the diffracted beam.

This equation is used to calculate at what angles constructive interference occurs for a set of parallel planes. Therefore, a family of planes only give sharp peaks at specific values of 2θ .

Throughout this report, PXRD patterns are plotted in Q ($\text{\AA}^{-1}$). The main advantage of Q -spacing is that it shows real space and can therefore be used to calculate the distances in the repeat structures. Another advantage is that it can be used to standardise data from different radiation sources: for example, neutron and X-ray diffractions techniques, with different wavelengths, will show the same peaks but at different values of 2θ , as this is a function of wavelength.

Q is given by:

$$Q = \frac{2\pi}{d}$$

The width of peaks can be used to determine particle size and therefore crystallinity of the material. This is given by Scherrer's equation:

$$\beta = \frac{K\lambda}{\tau \cos \theta}$$

where β is the peak broadening at half intensity after subtracting instrument widening, K is a dimensionless shape factor, λ is the X-ray wavelength, τ is the mean size of the material and θ is half of the diffracted angle.

In short, this equation says the size of the crystallite is inversely proportional to the width of the measured peak. Because crystals are defined as long-range highly-ordered materials, a small particle size/wide peak indicates poor crystallinity.

All PXRD measurements were collected using a Malvern PANalytical Xpert MPD operating in Bragg-Brentano geometry equipped with PIXcel area detector and a sealed tube Cu source operating at 40 kV and 40 mA. A Johansson focussing beam monochromator selected pure $K\alpha_1$ radiation which was then passed through 0.04 rad Soller slits to reduce axial beam divergence. Programmable divergence slits and programmable anti-scatter slits were used in automatic mode to match the prepared sample length. A fixed mask matching the prepared sample width and a fixed 1° anti-scatter slit were used in the incident beam path.

Data was collected with a step size of 0.013° in continuous mode and variable scan speeds depending on the sample size and scattering power. Repeated scans were measured and merged after inspection to ensure no sample degradation had occurred. The sample holder was spun with a duration per spin of 2 seconds.

5.1.2. Nuclear magnetic resonance

NMR measurements were done on a Bruker AV400 with atma probe, Bruker AV(III)400 with atma probe and Bruker AV(III)400HD with Nitrogen-cooled cryoprobe.

5.1.3. Solid-state UV-vis spectroscopy

Solid-state UV-vis absorbance measurements were done on a UV-VIS NIR Agilent Cary Spectrometer.

5.1.4. Scanning electron microscopy

SEM images were taken using a JEOL 7100F field emission gun scanning electron microscope. Samples were prepared on a 10mm aluminium sample holder with an adhesive carbon tab and coated with 8 nm layer of Iridium using a QUORUM QISOT ES coater. Imaging was conducted at a working distance of 10 mm and an electron accelerating potential of 15 kV.

5.1.5. Energy dispersive X-rays

Qualitative chemical microanalysis measurements were done using an Oxford Instruments XMax 80 solid state detector using the Aztec software.

5.2. Syntheses of metal clusters

5.2.1. Zr_6 benzoate cluster, $Zr_6O_4(OH)_4(OBz)_{12}(OPr)$

Procedure adapted from literature⁵¹. Benzoic acid (16000 mg, 131 mmol) in nPrOH (50 mL) was sonicated for 20 mins to give a clear solution. Zr butoxide solution 80 wt% in 1-butanol (2.5 mL, 5.45 mmol) was then added to the stirred clear solution of benzoic acid. Upon addition, white precipitate started forming, but the solution became clear again after a few minutes of heating. The solution was heated under reflux at 95 °C overnight to give a white precipitate. This was then filtered on a Büchner funnel and dried in an oven at 50 °C for 2 hours.

5.2.2. Zr_6 methacrylate cluster, $Zr_6O_4(OH)_4(OMc)_{12}$

Zr butoxide solution 80 wt% in 1-butanol (3.0 mL, 6.4 mmol) was added while stirring to methacrylic acid (2.55 mL, 29.76 mmol). The solution was stirred for 30 minutes after which it was set aside. After 7 days, large needles formed and were separated using a Büchner funnel and washed with butanol.

5.2.3. Zr_{12} acetate cluster, $Zr_{12}O_8(OH)_8(OAc)_{24}$

Procedure adapted from literature⁴⁰. This cluster was synthesised by a colleague. $ZrOCl_2 \cdot 8H_2O$ (1.16 g, 3.59 mmol) in 1.8 mL DMF was stirred until completely dissolved. Acetic acid (7.95 mL, 139 mmol) was added, and the reaction mixture was stirred for 10 minutes. The solution was added to a sealed pressure vial and placed in an oven at 100 °C for one day, after which white crystals formed. The crystals were separated using a Büchner funnel and washed with a 1:1 mixture of acetic acid and DMF.

5.2.4. Ti_6 aminobenzoate cluster, $Ti_6O_6(O^iPr)_6(ABZ)_6$

Procedure adapted from literature⁴⁴. To a solution of 4-aminobenzoic acid (460 mg, 3.35 mmol) in isopropanol (5 mL) was added Ti isopropoxide (0.5 mL, 1.69 mmol). After addition of the metal, the solution went from slightly yellow to bright orange. The solution was then placed in a sealed pressure tube and put in an oven set to 100 °C for 24h to form bright orange needles. These were separated using a Büchner funnel and washed with isopropanol.

5.3. MOF reactions

5.3.1. Zr_6 benzoate cluster as starting material

5.3.1.1. Varying the linker

Zr_6 benzoate cluster (27.7 mg, 0.013 mmol) was dissolved in 1 mL DMF, and was added dropwise to the linker (0.156 mmol of terephthalic acid, aminoterephthalic acid or *trans,trans*-muconic acid) (table 4) dissolved in 1 mL of DMF. The reactions were ran at room temperature, 50 °C and 100 °C for 1 and 3 days, to form gel-like precipitates. The precipitates were isolated by centrifugation, washed 3 times with 6 mL of DMF and left to dry on a watch glass in a fumehood for 24 hours.

Linker	Amount / mg
Terephthalic acid	25.9
Aminoterephthalic acid	28.2
<i>Trans,trans</i> -muconic acid	22.2

Table 4. Amounts of terephthalic, aminoterephthalic and *trans,trans*-muconic acids.

5.3.1.2. Decreased concentration

Zr₆ benzoate cluster (27.7 mg, 0.013 mmol) was dissolved in 5 mL of DMF, and was added dropwise to *trans,trans*-muconic acid (22.2 mg, 0.156 mmol) dissolved in 1 mL of DMF. The reactions were ran at room temperature and 50 °C for 1 and 3 days, to form gel-like precipitates. The precipitates were isolated by centrifugation, washed 3 times with 6 mL of DMF and left to dry on a watch glass in a fumehood for 24 hours.

5.3.1.3. Concentration series

Zr₆ benzoate cluster (27.7 mg, 0.013 mmol) was dissolved in various amounts of DMF (1 mL – 5 mL, in 1 mL increments), and was added dropwise to *trans,trans*-muconic acid (22.2 mg, 0.156 mmol) dissolved in 1 mL of DMF. The reactions were ran at room temperature and 50 °C for 3 days, to form a gel-like precipitates. These were isolated by centrifugation, washed 3 times with 6 mL of DMF and left to dry on a watch glass in a fumehood for 24 hours.

5.3.1.4. Molar ratios series

Zr₆ benzoate cluster (27.7 mg, 0.013 mmol) was dissolved in 1 mL DMF, and was added dropwise to various amounts of *trans,trans*-muconic acid dissolved in 1 mL DMF, to give metal:linker molar ratios equal to 1:24 and 1:36 (table 5). The reactions were ran at room temperature and 50 °C for 3 days, to form gel-like precipitates. The precipitates were isolated by centrifugation, washed 3 times with 6 mL of DMF and left to dry on a watch glass in a fumehood for 24 hours.

Metal : linker molar ratio	Amount of linker / mg	Amount of linker / mmol
1:24	44.37	0.312
1:36	66.55	0.468

Table 5. Molar ratios of cluster to *trans,trans*-muconic acid and the corresponding amounts in the reaction mixtures.

5.3.1.5. Modulated syntheses

5.3.1.5.1. Acetic acid as modulator

Zr₆ benzoate cluster (27.7 mg, 0.013 mmol) was dissolved in 1 mL of a solution of 0.4 mL acetic acid and 0.7 mL DMF. This solution was added dropwise to a solution of *trans,trans*-muconic acid (22.2 mg, 0.156 mmol) dissolved in 1 mL of DMF. The reaction mixture was stirred for 5 minutes and then set aside for 1 day, giving a white precipitate. The precipitate was isolated by centrifugation, washed with 6 mL DMF and left to dry on a watch glass in a fumehood for 24 hours.

5.3.1.5.2. Varying equivalents of acetic acid

Zr₆ benzoate cluster (27.7 mg, 0.013 mmol) was dissolved in a solution of 1 mL DMF and various equivalents of acetic acid (table 6), and was added dropwise to *trans,trans*-muconic acid (22.2 mg, 0.156 mmol) dissolved in 1 mL of DMF. The reaction mixtures were stirred briefly and set aside for 1 day at room temperature. Gel-like precipitates formed for all reactions up to 100 molar equivalents. The precipitates were isolated by centrifugation, washed with 6 mL of DMF and left to dry on a watch glass in a fumehood for 24 hours.

Equivalents of acetic acid with respect to cluster	Amount of acetic acid / μ L	Amount of acetic acid / mmol
10	7.4	0.13
20	14.9	0.26
30	22.3	0.39
40	29.7	0.54
50	37.2	0.67
100	74.4	1.30
250	185.9	3.25

Table 6. Equivalents of acetic acid with respect to cluster and corresponding amounts in the reaction mixtures.

5.3.1.5.3. Varying equivalents of benzoic acid

Zr₆ benzoate cluster (27.7 mg, 0.013 mmol) was dissolved in a solution of 1 mL DMF and various equivalents of benzoic acid (table 7), and was added dropwise to *trans,trans*-muconic acid (22.2 mg, 0.156 mmol) dissolved in 1 mL of DMF. The reaction mixtures were stirred briefly and set aside for 1 day at room temperature. Gel-like precipitates formed for all reactions up to 50 molar equivalents. The precipitates were isolated by centrifugation, washed with 6 mL of DMF and left to dry on a watch glass in a fumehood for 24 hours.

Equivalents of benzoic acid with respect to cluster	Amount of benzoic acid / mg	Amount of acetic acid / mmol
10	15.8	0.13
20	31.7	0.26
30	47.6	0.39
40	63.5	0.54
50	79.4	0.67
100	158.8	1.30
250	369.9	3.25

Table 7. Equivalents of benzoic acid with respect to cluster and corresponding amounts in the reaction mixtures.

5.3.1.5.4. Screening of different modulators

Zr₆ benzoate cluster (27.7 mg, 0.013 mmol) was dissolved in a solution of 1 mL DMF and 538 equivalents of various acids (table 8), and was added dropwise to *trans,trans*-muconic acid (22.2 mg, 0.156 mmol) dissolved in 1 mL of DMF. The reaction mixtures were stirred briefly and set aside for 1 day at room temperature. Only the reactions with propanoic and butyric acids formed precipitates. The precipitates were isolated by centrifugation, washed with 6 mL of DMF and left to dry on a watch glass in a fumehood for 24 hours.

Modulator	Amounts
Propanoic acid	523 μ L
Butyric acid	646 μ L
Benzoic acid	842 mg
Formic acid	260 μ L
Dichloroacetic acid	570 μ L

Table 8. Modulators in the reaction of Zr OBz cluster with *trans,trans*-muconic acid and their amounts in the reactions.

5.3.1.5.5. Modulated reaction of Zr₁₂ acetate cluster

Zr₁₂ acetate cluster (18.0 mg, 0.0065 mmol) was dissolved in 1 mL DMF, and was added dropwise to *trans,trans*-muconic acid (22.2 mg, 0.156 mmol) dissolved in 1 mL of DMF. Another reaction was set up where the cluster was dissolved in a solution of 1 mL of DMF and 0.4 mL of acetic acid and added to the same amount of linker. Both reactions were set

aside for 1 day after which white precipitates formed. The precipitates were isolated by centrifugation, washed with 6 mL of DMF and left to dry on a watch glass in a fumehood for 24 hours.

5.3.2. *Zr₆ methacrylate cluster as starting material*

5.3.2.1. *Unmodulated reaction with trans,trans-muconic acid*

Zr₆ methacrylate cluster (22.1 mg, 0.013 mmol) was dissolved in 1 mL DMF, and was added dropwise to *trans,trans*-muconic acid (22.2 mg, 0.156 mmol) dissolved in 1 mL of DMF. The reactions were ran at room temperature, 50 °C and 100 °C for 1 and 3 days, to form gel-like precipitates. The precipitates were isolated by centrifugation, washed with 6 mL of DMF and left to dry on a watch glass in a fumehood for 24 hours.

5.3.2.2. *Modulated reaction*

Zr₆ methacrylate cluster (22.1 mg, 0.013 mmol) was dissolved in a solution of 1 mL of DMF and 538 molar equivalents of modulator with respect to cluster (table 9), and was added dropwise to *trans,trans*-muconic acid (22.2 mg, 0.156 mmol) dissolved in 1 mL of DMF. The solutions were stirred for 5 minutes and set aside for 1 day. Only the reaction with acetic acid formed solid product. The white precipitate was isolated by centrifugation, washed with 6 mL DMF and left to dry on a watch glass in a fumehood for 24 hours.

Modulator	Amounts / μL
Acetic acid	400
Methacrylic acid	580
Formic acid	260
Dichloroacetic acid	570

Table 9. Modulators in the reaction of Zr OBz cluster with *trans,trans*-muconic acid and their amounts in the reactions.

5.3.3. *Ti₆* aminobenzoate cluster as starting material

5.3.3.1. Unmodulated reaction with *trans,trans*-muconic acid

Ti aminobenzoate cluster (20.2 mg, 0.013 mmol) was dissolved in 1 mL DMF, and was added dropwise to *trans,trans*-muconic acid (22.2 mg, 0.156 mmol) dissolved in 1 mL of DMF. The reactions were ran at room temperature, 50 °C and 100 °C for 1 and 3 days, to form gel-like precipitates. The precipitates were isolated by centrifugation, washed with 6 mL of DMF and left to dry on a watch glass in a fumehood for 24 hours.

5.3.4. Mixed cluster MOF reactions

0.013 mmol of a mixture of Zr OBz cluster and Ti ABZ were dissolved in 1 mL DMF. Starting from a pure Zr OBz mixture, the percentage of the Ti cluster was increased in 10% increments, all the way to a 90% Ti cluster reaction (table 10). The cluster solutions were added dropwise to as solution of *trans,trans*-muconic acid (22.2 mg, 0.156 mmol) in 1 mL DMF. The reactions mixtures were set aside for one day. Gel-like products formed for all reactions, and these were

isolated by centrifugation, washed with 6 mL of DMF and left to dry on a watch glass in a fumehood for 24 hours.

A repeat of this series was done using acetic acid as modulator. The clusters mixtures were dissolved in a solution of 1 mL of DMF and 0.4 mL of acetic acid and the rest of the procedure was the same as the unmodulated reaction. However, this produces white precipitates for all reactions up to 70% Ti cluster.

Molar percentage of Ti ABZ cluster	Amount of Ti ABZ cluster / mmol	Amount of Ti ABZ cluster / mg	Amount of Zr OBz cluster / mmol	Amount of Zr OBz cluster / mg
0%	0	0	0.013	27.7
10%	0.0013	2.02	0.0117	24.9
20%	0.0026	4.04	0.0104	22.2
30%	0.0039	6.06	0.0091	19.4
40%	0.0052	8.08	0.0078	16.6
50%	0.0065	10.10	0.0065	13.9
60%	0.0078	12.12	0.0052	11.1
70%	0.0091	14.14	0.0039	8.3
80%	0.0104	16.16	0.0026	5.5
90%	0.0117	20.20	0.0013	2.8

Table 10. Amounts of Ti and Zr cluster in the mixed cluster MOF reactions.

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