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# Polyhedral oligomeric silsesquioxane based precursors as linkers for porous materials



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Submitted in partial fulfilment of the requirements for the degree of

Master of Philosophy

in Chemistry

12th October 2016

This thesis is dedicated to the memory of my beloved father Without whom, this entire experience would not have been possible I extend you my sincerest gratitude for the blessing that you have been For when we leave this world, the love we impart extends beyond this life

#### Abstract

Within this thesis, the organic synthesis and characterisation of various polyhedral oligomeric silsesquioxane (POSS) based compounds has been explored. The target POSS based compounds studied have been chosen because of their eight functionalised organic corners which house the ability to be modified and designed by a variety of organic reactions. Following this, their characteristic stable inorganic core and well defined three dimensional structure determined them to be suitable monomers for the synthesis of ordered frameworks with potential porosity. The first series of reactions involved the synthesis of octaphenylsilsesquioxane (OPS) and discusses the successful functionalisation to produce octa(iodophenyl)silsesquioxane (I<sub>8</sub>OPS), in addition to subsequent functionalisation attempts to produce a carboxylic acid derivative of I<sub>8</sub>OPS. Interestingly, this series was found to be highly selective for functionalisation in the para position of the phenyl ring, reinforcing the symmetrical nature of the molecule. An additional reaction series aimed to synthesise an imidazole derivative of an alkyl-POSS compound, following the successful synthesis of octakis(3-chloropropyl)silsesquioxane, through two procedures. Within this thesis, a different direction of study was explored, involving the synthesis of various metal organic frameworks and zeolitic imidazolate frameworks through variations in the experimental conditions and procedures. A systematic approach was also explored, where it was determined that a high number of ligands and metal combinations could be investigated simultaneously. This resulted in the synthesis of various metal organic frameworks from both powder and single crystal X-Ray Diffraction (XRD). From these findings, appropriate synthetic approaches for the eventual synthesis of a POSS based framework were identified.

#### Acknowledgements

Firstly, I would like to thank my exceptional mother for her tireless support during all of my endeavours throughout my life. You have been my rock, support system and biggest believer, for that I will always be thankful. Secondly, I would like to thank my loved ones for their continued compassion, kindness, and exceptional abilities to keep me sane during this entire experience. I hope that one day I can do the same for you. I would also like to thank every single educator that I have ever had the fortune of being influenced by, you imparted the gift of knowledge and inspired me to pursue my greatest ambitions. Lastly, I would like to thank my supervisors Dr. Katherine Haxton and Dr. Richard Jones. Your guidance and support in this process has been invaluable and I will always be grateful for this experience.

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Chapter 1: An Introduction to POSS and Porous Materials

#### 1.1 Silsesquioxanes: An Introduction and Basic Structures

The chemistry around silsesquioxanes has been developed substantially over the past 20 years; what was once a small research field has evolved into a readily expanding area which combines materials chemistry with organic synthesis. These materials are classed as 'hybrid' molecules, having both inorganic and organic properties making them ideal for use as an intermediate material of ceramics and organics [1, 2]. The term silsesquioxane describes molecules with the formula [RSiO<sub>1.5</sub>]<sub>n</sub> and originates from the combination of the words *siloxane*, compounds of silicon and oxygen, and *sesqui*, the Latin word indicating one and a half [3]. This class of compounds incorporates a wide variety of structures, all of which share a general formula and a common property of containing a rigid Si-O-Si linked constituent, although their properties can vary substantially [4]. Structural examples can be seen in Figure 1.1.



**Figure 1.1**: The chemical names and structures of different types of silicon and oxygen bound compounds, were R represents an organic substituent and POSS: **p**olyhedral **o**ligomeric **s**il**s**esquioxane [1].

A wide range of different structures of silsesquioxanes have been characterised. Structures included within the definition of a silsesquioxane range from random polymeric structures (a) and ladder sequences (b) to partially formed cages (d) and the highly structured cube moieties (c), seen in Figure 1.2 [5, 6].



Cube Structure (c)

Partial Cage Structure (d)

Figure 1.2: Different types of characterised silsesquioxane compounds [2].

Structures based around the formula of  $[RSiO_{1.5}]_n$ , where n = 6, 8, 10, 12 etc, are deemed to be a more ordered species and fall under the category of cage structures [7]. The stable inorganic Si-O-Si core of a silsesquioxane molecule provides a rigid centre for a highly ordered nanoscale building block, where diversities in structures originate from the value of 'n' and the identity of 'R' in the molecular formula. The value of 'n' will dictate the shape of the cage structure, where an increasing number leads to an increasing cage size. Structures are labelled according to their 'n' value which depicts how many silicon atoms are in each individual cage [8], examples of structures where n = 8, 10 and 12 can be seen in Figure 1.3.



**Figure 1.3**: The simplified structures of the most widely researched silsesquioxane molecules (n = 8, 10, 12);  $T_8$  (octa-) molecules adopt the cubic structure with 6 square faces,  $T_{10}$  (deca-) molecules have five distorted square faces and two distorted pentagonal faces and  $T_{12}$  (dodeca-) have four distorted pentagonal faces and three distorted square faces [2, 9].

It is interesting to note that  $T_4$  structures are less common and more difficult to synthesise due to their strained structure. As silsesquioxanes preferentially form a larger cage structure, the  $T_4$  synthesis has to be directed by large R groups, such as *t*-Bu or *i*-Pr, which stabilise the strained core. With an increasing core size, molecules start to become more sought-after;  $T_6$  molecules are more common than  $T_4$ , although they still exhibit a strained structure, and  $T_{10}$  are more readily synthesised compared to  $T_6$  [10]. It should also be noted that all of these structures are not synthesised as readily as  $T_8$  structures. As an individual research area, there is an abundance of literature based entirely on  $T_8$ structures and their functionalised compounds. The respective ease of synthesis makes them more readily available [9].

In silsesquioxanes,  $[RSiO_{1.5}]_n$ , there are three Si-O bonds per each sp<sup>3</sup> hybridised silicon molecule and one Si-R bond which is connected to an organic substituent [2]. When n = 8, these types of silsesquioxanes are known as cubic polyhedral oligomeric silsesquioxanes

(POSS), acquire the  $T_8$  structure, and are thought of as fully condensed species [11]. The  $T_8$  molecules have eight arms which extend out from each corner of the cube, Figure 1.4. These are of equal distance away from each other due to the symmetrical ordering of the central cage unit, each having an average diameter of 1 nm [7, 12]. The equal distance of the arms and the regularity of the cage make these ideal units which can be assembled nanometer by nanometer to tailor the dimensions of precise building blocks [11].



**Figure 1.4**: A cubic silsesquioxane molecule,  $T_8$ , (where n = 8) with its superior properties highlighted [7].

#### 1.2 A Brief History

In 1875 Ladenburg discovered phenylsiliconic acid. This was also identified by Khotinski and Seregenkov in 1908, however the precise chemical formula and structure remained ambiguous [13, 14]. In 1914, the Meads & Kipping research group thought to clarify the chemical formula and proposed it to be PhSiO<sub>2</sub>H [15]. In 1915 it was concluded by the same group that phenylsiliconic acid did not have a definitive formula and was in fact a mixture of condensation products from phenyltrichlorosilane. The products proved to be significantly more complex than originally thought and brought about the idea of silicon and oxygen atoms being linked in an alternate short chain, essentially theorising the existence of the random polymeric chain, as shown in Figure 1.2 (a) [16].

The real advancement was seen in 1946 by Scott who reported the first fully condensed methyl-substituted silsesquioxane with the formula  $[(CH_3)SiO_{1.5}]_n$ , where n was an unknown number. The T<sub>8</sub> shape of this structure was determined by Barry and co-workers in 1955 by single crystal X-ray diffraction (XRD) [17, 18]. The first synthesis of the fully condensed cubic structure of octaphenyl-silsesquioxane was published by Brown and co-workers in 1964, [19 - 21].

#### 1.3 The Synthesis of T<sub>8</sub> Compounds

Trifunctionalised silanes (RSiX<sub>3</sub>, where X = Cl, OCH<sub>3</sub>, OCH<sub>2</sub>CH<sub>3</sub> and R = CH<sub>3</sub>, phenyl, vinyl, etc) are starting materials for the synthesis of POSS molecules [4]. From the monomeric tri-functional precursor, new Si-O-Si bonds are made through base or acid catalysed hydrolytic condensation reactions; the assembled cage contains eight functionalised corners, each with the organic substituent R [22, 23]. The proposed mechanism for this synthesis can be seen in Figure 1.5.

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**Figure 1.5**: The proposed mechanism for the synthesis of various silsesquioxane molecules, starting with the hydrolysis of a trifunctionalised silane followed by repeating condensation steps [3, 10]. i: Stir at room temperature, ii: addition of benzyltrimethyl-ammonium hydroxide (BzTMAOH), reflux.

The process begins with the hydrolysis of the tri-functional silane to form the triol (RSi(OH)<sub>3</sub>). This is then followed by the addition of the catalyst benzyltrimethylammonium hydroxide (BzTMAOH) which initiates repeating steps of intermolecular condensation reactions where RSi(OH)<sub>3</sub> groups conjoin in turn, with each subsequent step producing one more siloxane in the group. At this point, where four silanes have conjoined to form a square like structure, intermolecular rearrangement occurs and the formation of random structures, ladder chains, partial cages, corner capped moieties or fully condensed structures can be seen [11, 23]. The preferential formation of these structures is

dependant on a variety of synthetic factors: reaction time, pH, reactant concentrations, water content and rate of addition, which have been studied to identify which details give preferential formation of which structure [25]. All of the POSS reagents have been documented as being highly soluble in common organic solvents such as THF, hexane, toluene and chloroform, meaning that the majority of the synthetic process avoids the need for expensive and non commercially available solvents [26, 27].

The functional groups on each corner of the inorganic centre can be modified which will alter the properties of the whole molecule [1]. As the inorganic core is stable in itself, it is the variation of the organic moieties (R) which dictate the solution and solid state chemical properties of the molecule [28]. There are two distinct types of initial synthesis which produce two distinct types of products; incompletely condensed cages, containing a silanol group, and fully condensed cages containing eight R groups, as shown in Figure 1.5 [2, 29, 30].

#### 1.4 Mono-functionalised POSS Molecules

Mono-functionalised silsesquioxanes are less common than the octa-functionalised alternative but have their own unique features nonetheless. They have the formula of  $(R)_7(R')Si_8O_{12}$ , where one corner of the cage is distinct upon synthesis, a reactive site (R') compared to the rest which remain inert (R). These structures originate from the incompletely condensed partial cage structure seen in Figure 1.5; the trichlorosilanes are reacted through hydrolytic condensation to give a mixture of partial cages. Treating the desired corner exposed cage with a trichlorosilane with a different R group (R') results in a corner capped cubic silsesquioxane, Figure 1.6 [29]. This provides silsesquioxanes that are appropriate for certain types of polymer chemistry. They can be incorporated into linear polymer systems due to the singularly reactive corner which allows the grafting onto

polymers from this one site, as opposed to cross linked structures which would be achieved as a result of an octafunctionalised silsesquioxane [27]. Blanco and coworkers synthesised various structures which contained seven cyclopentyl groups (R), cyclopentane was selected for its good compatibility with polymeric matrices and high thermal stability, whilst the mono-functionalised group contained various substituted phenyl derivatives [33].



**Figure 1.6**: The process of corner capping an incompletely condensed cube to synthesise a mono-functional T<sub>8</sub> monomer [27, 29].

#### 1.5 Octa-functionalised POSS Molecules, T<sub>8</sub>

Octa-functionalised silsesquioxanes originate from fully condensed cubes and the nature of the corner constituents are known to vary immensely. The possible diversity seen within these molecules expands with the functionalisation of these corner moieties. These organic 'R' extremities can include: phenyl, alkyl, allyl, vinyl, amino terminated and hydride [6, 25, 29, 33, 34]. The resulting T<sub>8</sub> molecules are then suitable for further functionalisation via organic reactions, producing a range of useful materials. For example; vinyl-POSS is well known as a dendrimer core, whereas allyl and alkyl derivatives are used in copolymerisation reactions [4, 35].

#### 1.6.1 T<sub>8</sub> Molecules as a Polymer Monomer

Mono-functionalised  $T_8$  cubes, through the process of corner capping, provide POSS molecules that can be incorporated into polymers [1]. However, the process of corner capping can be argued to not be 'functionalising' the  $T_8$  cube, rather synthesising a completely condensed  $T_8$  structure which has seven unreactive arms and one reactive arm before any subsequent reactions. Corner capping involves a one pot synthesis, where the open cornered silsesquioxane is synthesised without the need for separation from the reaction mixture and the reactive trichlorosilane (R'SiCl<sub>3</sub>) is added thereafter [27]. Functionalisation of the cube is seen when the molecule is grafted onto the polymer via the reactive site, as seen in Figure 1.7 [36]. It should be noted that, while the R groups remain unreactive in the polymer synthesis, subtle changes in the nature of the R groups can alter the global property of the resulting polymer, for example, a significant increase in polymer solubility has been seen from a pentyl R chain to a hexyl [26, 37].



Monofunctional POSS monomer

POSS as a pendant arm in a polymer

**Figure 1.7**: How a  $T_8$  molecule can be incorporated into a polymeric system, with a cube used to represent the Si<sub>8</sub>O<sub>12</sub> for simplicity [38].

#### 1.6.2 Functionalisation of Phenyl Substituted T<sub>8</sub> Molecules

The functionalisation of octaphenylsilsesquioxane (OPS) is a well studied area of silsesquioxane chemistry, specifically for the synthesis of nanoscale building blocks with definitive sizes [11]. For functionalised OPS, high yields are required to produce products with specific substitution patterns [39]. Figure 1.8 depicts various routes for synthesising OPS.



**Figure 1.8**: Various synthetic routes for OPS, including halogenation, nitration, acetylation and sulfonation, where 'X' denotes the remainder of the silsesquioxane cube. [10, 11, 39 - 43]

#### 1.6.2.1 The Nitration of OPS

The nitration of OPS requires nitric acid, either fuming or in the presence of a different acid, and can give various derivatives through subsequent functionalisation. In 2007, Hong-Ji and Meng nitrated OPS to give octa-(2,4-dinitrophenyl)silsesquioxane, a disubstituted compound that they have then used as a new pore generating material in polyalkoxy-silsesquioxane films. The substitution pattern for this molecule was confirmed by proton NMR, validating a selective route for the di-substituted compound with a relatively high yield of 81.7% [44].

The synthesis of octa(aminophenyl)silsesquioxane (OAPS) from octa(nitrophenyl)silsesquioxane (ONPS) is a well documented procedure published in 2001 by Laine and coworkers, an improved version of a previous procedure [45]. OPS is treated with fuming nitric acid to form ONPS in a 90% yield, followed by a mild hydrogen transfer reduction using formic acid, triethylamine and a palladium over carbon catalyst to give the final OAPS product in an 82% yield [42].



Figure 1.9: The nitration of OPS to yield ONPS and subsequently OAPS [40, 41].

This two step synthesis yielded an important compound that has undergone many more reactions. Zhang and coworkers reduced the time period for the production of ONPS to avoid double nitration of the phenyl ring, which was thought to have been observed previously, whilst also altering the reducing agent to hydrazine dihydrate, achieving a comparable yield of 86% and therefore improving upon the original synthesis [41].

#### 1.6.2.2 The Halogenation of OPS

The halogenation of OPS produced various forms of  $Br_xOPS$  and  $I_xOPS$  from well known aromatic halogenation reactions. The position (ortho-, meta- or para- with respect to the  $T_8$ cage) and the extent of substitution on the phenyl ring (mono-, di-, or tri-substituted) are desired to be controlled throughout the course of the reaction. A general observation for the mono substitution of the phenyl ring is that the meta position is preferential for an electron-withdrawing substituent and for an electron-donating substituent the ortho or para position is favoured [46].

The synthesis of octa(bromophenyl)silsesquioxane is carried out in an inert atmosphere, where bromine is added drop-wise to a solution of OPS in dichloromethane then allowed to stir at 60°C for 7 days [43, 47]. This synthesis gave a product that was mono-substituted and favoured the ortho position, as 85% of the product was ortho substituted and 15% para substituted. In addition to this,  $Si_8O_{12}Br_{16}$  was synthesised from FeBr<sub>3</sub> instead of bromine, with substitution seen in the ortho and meta position of the phenyl ring.  $Si_8O_{12}Br_{24}$  was also synthesised as a result of a 2.5 fold increase of the molar ratio of bromine used for the synthesis of  $Si_8O_{12}Br_8$ . This is a revised theory from Laine and coworkers who previously found that only 5.3 out of the 8 phenyl rings were actually bromo substituted with a pattern of 70 : 20 : 10 (para : meta : ortho) for the same reaction and similar conditions [48]. This original paper introduced the idea of bromination and provided a synthesis that has since been tailored to give an ideal route for a monosubstituted bromophenylsilsesquioxane molecule in the ortho position.

A more recent publication has seen a detailed investigation into the substitution pattern of the phenyl ring. It poses the question as to why the ortho position is favoured over the less sterically hindered para position. It suggests that the bromine molecule is hydrogen

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bonded to the ortho hydrogen of the phenyl group and an electronic interaction stabilises the transition state, resulting in selective bromination for the ortho position [46].

In a similar manner to bromination, the iodination of OPS is also a well studied synthesis and similar mechanisms and outcomes have been predicted [46]. In 2008 Laine & coworkers published the first directive synthesis for the para-substituted iodinated OPS molecule, I<sub>8</sub>OPS. The procedure describes how OPS was treated with iodine monochloride (ICI) in DCM for 24 hours at - 40°C, where the recrystallisation of the crude product is said to give ≥93% para selectivity in a 35% yield. Improvements on the paraselectivity have been made in more recent publications, providing a nano building block that has minimal defects upon the incorporation into subsequent procedures, notably coupling reactions that include Heck, Sonogashira and Suzuki reactions [39].



Figure 1.10: Thermal ellipsoid plot of *p*-I<sub>8</sub>OPS with H-atoms omitted [39].

#### 1.6.3 Derivatives of Octavinylsilsesquioxane

POSS compounds with functional groups based on a hydrocarbon chain, such as alkanes and alkenes, have attracted popularity due to an array of hydrocarbon organic reactions available. Alkenyl (-CH=CH<sub>2</sub>) POSS compounds, octavinylsilsesquioxane (OVS), can be transformed into a variety of different functionalised molecules through alkene addition, alkene metathesis, AIBN radical polymerisation and Heck reactions [10, 49 - 51]. These are reported in Table 1.1 and show routes of functionalisation for OVS.

Reaction	Starting Materials	Resulting R Group	Reference
Alkene Metathesis	OVS + CH <sub>2</sub> =CH(CH <sub>2</sub> ) <sub>3</sub> Br + [Ru]	-CH=CH(CH <sub>2</sub> ) <sub>3</sub> Br	52
	$OVS + CH_2 = CHPh + [Mo]$	-CH=CHPh	52
Addition Reaction	OVS + H <sub>2</sub> + Pd/C	-Et	53
	OVS + HBr + (BzO) <sub>2</sub>	-(CH <sub>2</sub> ) <sub>2</sub> Br	54
	OVS + Benzene + AlCl₃	-(CH <sub>2</sub> ) <sub>2</sub> Ph	56
	OVS + HPEt <sub>2</sub> + AIBN	-(CH <sub>2</sub> ) <sub>2</sub> PEt <sub>2</sub>	56

**Table 1.1**: Various reactions of vinyl POSS, adapted from reference 9. Note: [Ru] = Grubbs catalyst, [Mo] = Schronk's catalyst, BzO = C<sub>6</sub>H<sub>5</sub>CO, and AIBN = azobisisobutyronitrile [52 - 56].

Alkyl (-CH<sub>3</sub>, -H, etc) T<sub>8</sub> compounds, synthesised from simple trifunctionalised silanes (MeSiX<sub>3</sub>, HSiX<sub>3</sub>, etc), are also examples of hydrocarbon POSS molecules. These are ideal precursors for highly ordered monomers and commonly undergo substitution reactions [10]. Octakis(3-chloropropyl)POSS (T<sub>8</sub>(CH<sub>2</sub>)<sub>3</sub>Cl), being a larger molecule than T<sub>8</sub>H<sub>8</sub> and T<sub>8</sub>Me<sub>8</sub>, is a well known precursor for a high number of intricate T<sub>8</sub> structures and was originally synthesised through a 5 week acid hydrolysis [57]. A two part synthesis was published by Marciniec & coworkers in which (chloromethyl)triethoxysilane was hydrolysed under acidic conditions, followed by a condensation step upon the addition of the di-*n*-butyltin dilaurate catalyst, Figure 1.11. The whole procedure spanned 4 days and

showed a significant improvement upon the original synthesis with regard to time of reaction whilst maintaining a comparable yield of 35% [58]. While this procedure is still popular for the synthesis of octakis(3-chloropropyl)POSS, a more recent method has been published in which a 90% yield has been obtained. In this synthesis a solution of dry methanol, concentrated HCI and (chloromethyl)triethoxysilane is stirred at 40°C for a period of two weeks [59]. This recent synthesis compromises between the two other procedures with regard to synthetic time and provides a procedure with a significantly improved yield. Octakis(3-chloropropyl)POSS is a rigid unit that can act as a precursor for many reactions with its eight functional chloro groups that extend from each corner.



Figure 1.11: The two step synthesis of octakis(3-chloropropyl)POSS that spans the course of 4 days [58]

#### 1.7 Applications of POSS

All of these materials offer a unique interface between organic and inorganic chemistry, where the nature of silsesquioxanes can affect the properties of the material. This is not only due to the sum of the organic and inorganic components, but because of the interfacial interactions that are also present [2]. Another outstanding feature is molecular shape; they are an easily accessible material which can offer perfect cubic symmetry [30]. These combined properties result in a material which can be used as a nano building block with heightened thermal and chemical properties from the modification of the organic 'R' groups [60].

POSS-based polymers have potential to be used in the biomedical sector, specifically for cardiovascular diseases and imaging. Polymers have been designed to be used as components for an artificial capillary bed enhanced by evenly distributed POSS monomers along the polymer. This increases the polymers stability as a medical device by preventing bulk accumulation of the polymer [61]. POSS based compounds have also been used as contrast agents for magnetic resonance imaging (MRI). An aqueous solution of a POSS core dendrimer with Gd<sup>3+</sup> ions has been successfully used as a highly sensitive contrast agent. This material expands from amino-POSS and this class of compounds are biocompatible due to their high water solubility and stability under biological conditions [1].

POSS molecules can also enhance the thermal and mechanical properties of materials, with thermogravimetric analysis showing an increase in thermal stability of polymer matrices which contain POSS fillers respective to those without [1].

Halogenated OPS molecules have potential as building blocks and enhancing materials. For example, the mono-substituted version of octa(bromophenyl)silsesquioxane has been noted as serving as a high dielectric due to its high electron density. Additionally, the mono, di, and tri substituted bromophenylsilsesquioxane have potential as a nano building block with either 8, 16, or 24 functional groups on the phenyl ring, depending on the substitution pattern [42].

In addition to those previously mentioned, there are many areas in which POSS has been applied as an advanced material (see references [1] and [7] for an enhanced review), for example; heterogeneous catalyst models [62 - 64], supported homogeneous catalyst models [65, 66], homogenous catalytic systems [67], molecular optics and electrical systems [68, 69], other biomedical applications including potential drug delivery systems [69, 70], varnishes [71], and inks [72].

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#### 1.8 An Introduction to Porous Materials

Porous materials, known as 'inclusion compounds' in earlier texts, belong to a family called supramolecular compounds; a term associated with large structures assembled from smaller molecules [73]. Porous materials are thought of as one species forming a host in which a different species resides, where the properties of the whole complex are separate and distinct from the properties of the individual components, a description based on the characteristics of zeolites and their ability to accommodate small molecules [74]. Various examples of porous materials can be seen in Figure 1.12.



**Figure 1.12**: Schematic representations of various porous materials. (a): zeolite; MFI [75], (b) metal organic framework; MOF-74 [76] and (c): covalent organic framework COF-5 [77], each depicting the framework structure and channels.

A porous structure consists of a three dimensional framework in which individual molecules bond to create channels, pores and cavities within the structure [78]. It is the shape, volume, size and distribution regularity of these pores and channels which directly affect the properties of the material and its ability to perform a desired function [79]. It is the size of the pores which determine whether the structure is microporous ( $\leq 2$  nm), mesoporous (2 - 50 nm) or macroporous (> 50 nm), each variation having different properties and potential applications, see Figure 1.13 [80]. Porous materials are also

known to have high surface areas and it is thought that the higher the surface area, the more desirable the material due to heightened properties regarding adsorption and performance ability [79].



Figure 1.13: A scheme showing various porous materials and their classification [81 - 87]

Porous materials can be organic, inorganic or a hybrid of both. A common organic porous material is activated carbon. It has a claim for the highest surface area of an unordered structure, resulting in a high adsorption capacity [88]. Porous silicon is also widely researched; the size of the pores and the framework structure are of high interest with regard to their influence on the optical and electronic properties of the resulting material [80]. Inorganic porous materials, such as zeolites, have a highly ordered structure, a vast catalogue of research, and are a major product used in industry due to their high performance ability [89]. Metal organic frameworks (MOFs) are another well known type of porous frameworks and are based on the connection of organic linkers with metal centres and truly define a hybrid material. There are many different types of MOFs with a wide number of combinations of metal with organic linker, many of which offer unprecedentedly high porosity [90]. Within the category of MOFs there are subsets which include metal-

carboxylate frameworks and zeolitic imidazolate frameworks (ZIFs), each showing porosity and unique features [91]. Other types of materials, such as covalent organic frameworks (COFs), have been synthesised to show various levels of porosity [77]. These materials highlight a sample of many frameworks that offer great potential with regard to their possible applications due to their individually unique features and their porous nature.

Many research areas have been influenced and developed by the emergence of porous materials, including; catalysis, ion exchange, molecular separation, adsorbents; resulting in technological, medical and scientific advancements. The many different types of porous materials and their potential applications make it easy to see why this field is expanding so rapidly [79, 92].

#### 1.8.1 Zeolites

The three dimensional structure of zeolites consists of [SiO<sub>4</sub>]<sup>4-</sup> or [AlO<sub>4</sub>]<sup>5-</sup> tetrahedra [93], a representation of which can be seen in Figure 1.14. These tetrahedra are assembled so that the oxygen atom at each tetrahedral corner is shared with that in a neighbouring tetrahedron, see Figure 1.15. The sharing of these corners creates an infinite lattice made of identical building blocks [93] and it is the way in which these tetrahedra are arranged that determines how zeolites are classified [94]. The degree of freedom within the angle between the corner linked tetrahedra is important as it allows the formation of the great variety of zeolite framework structures with minimal thermodynamic penalty [94]



**Figure 1.14**: (a): A ball and stick representation of [SiO<sub>4</sub>] or [AlO<sub>4</sub>]<sup>-</sup> tetrahedra, coloured atoms represent oxygen and the grey atom represents Si or Al, and (b): the geometric structure of the tetrahedron with atoms omitted for clarity [93].



**Figure 1.15**: Two corner linked tetrahedra; the X-O bond length (1.60Å to 1.64Å) and X-O-X bond angle (X = Si or Al), which ranges 130° and 180°, will define the orientation of the tetrahedra relative to one another and ultimately determine the overall structure and classification of the zeolite [94].

Zeolites are known for their porosity and the potential arrangements of the tetrahedron units make over 200 different types of zeolite frameworks, each with a different arrangement of channels and voids. The frameworks have strict uniform pore diameters and pore widths [95]. These pores are usually occupied by other smaller molecules. This is because the net formulae for a tetrahedron unit are SiO<sub>2</sub> and AlO<sub>2</sub>, therefore, there is one negative charge at each tetrahedron in a framework with Al as its centre. Other small cations compensate for these negative charges within the framework and reside within channels, voids and intersections upon crystallisation, where small water molecules may also reside within channels [95, 96].

The usual synthesis of zeolites occurs in alkaline media under hydrothermal conditions, from silicate or aluminosilicate gels, where temperatures range between 60 °C and 200 °C [97, 98]. Parts of this original synthesis have come under criticism from green chemists due to its use of organic templates, high pressures and low efficiency [99]. The increasing popularity of green chemistry has seen suggestions for alternatives ways to overcome these problematic areas, for example; the use of recyclable, cheaper or non toxic organic templates [98, 99]; organotemplate free zeolite synthesis [100]; ionic liquids as solvents to remove the safety concerns associated with high pressure synthesis [101] and increasing the efficiency of the procedure by using microwave synthesis, saving time and energy [102]. The crystalline nature of zeolites allows detailed structural analysis through X-ray fluorescence (XRF). Other methods of analysis of zeolites include neutron and electron diffraction studies, high resolution electron microscopy, Fourier Transform Infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR), specifically magic angle spinning NMR (MAS-NMR) [93].

In 1954 the first commercially available zeolites, types A(LTA), X(FAU) and Y(FAU), were synthesised for applications that utilised their hydrophilic nature; refrigerant desiccants

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and the drying and sweetening of natural gas. These synthetic zeolites differ from the natural zeolites that had previously been at the centre of early zeolite studies [103]. One of the main synthetic zeolite in commercial use is Linde Type-A (LTA) and is noted for its exceptional ion exchange capacity, sorption and catalytic activity due to its low silica content [104]. Like all ordered structures, the regularity of the zeolitic framework is due to the assembly of larger structural units known as the secondary building units (SBU's). For LTA, the SBU's are double four member rings (D<sub>4</sub>R) which consist of double rings with four tetrahedral atoms in the ring and can be seen in Figure 1.16 [105]. LTA is made of these D<sub>4</sub>R secondary building units which are connected through oxygen bridges [106].



**Figure 1.16**: The D<sub>4</sub>R secondary building unit and the framework structure of zeolite type A, LTA, [107].

Zeolites are given a three letter name according to IUPAC guidelines, consisting of different types of SBU's that are joined in different ways. Each has a unique unit cell and space group and exhibit different types of symmetry. This class of materials has been highly important to the development of porous materials and continues to expand.

#### 1.8.2 Metal Organic Frameworks

Metal organic frameworks (MOFs) are known as coordination polymers, an older term first used in 1964 by J. C. Bailar [108] to describe extended polymeric structures made of ligands and metals. The early development of MOFs is owed to the interest in coordination polymers. The development was application driven because of their properties as inorganic materials to withstand thermal and oxidative stress [109]. In more recent times, their potential as a hybrid materials has been observed as the material is able to take advantages of the properties of both organic and inorganic materials that comprises it [89].

For a material to be a MOF it should display the following attributes: strong bonding providing a robust structure, linkers that can be modified by organic reactions and a geometrically well defined structure [110]. MOFs are essentially a molecular scaffold; a porous structure consisting of rigid organic linkers which are joined to inorganic metal centres that act as joints [110]. The voids within the structure, and their chemical environment, are a result of the length and functionalities of the organic units and the way in which they coordinate to the metal centres [110]. The different combinations of organic linkers and metal centres can produce many different types of frameworks. Organic linkers coordinate to the metal centres through the donation of lone pairs from either an oxygen or nitrogen atom. It is with these two atoms that major types of metal organic frameworks are established. Carboxylic acid species, examples of which can be seen in Figure 1.17, are often at the basis of a metal-carboxylate framework and establish a rigid structure based on metal-oxygen bonds [111]. Whereas, linkers which contain C-N bonds, Figure 1.18, can coordinate to the metal through the nitrogen atom and are known as Ndonor based ligands. For example, imidazole based molecules form the subclass of MOFs called zeolitic imidazolate frameworks (ZIFs) and donate through their nitrogen atom [109].

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**Figure 1.17**: Examples of rigid carboxylate ligands used in the synthesis of various MOFs, (a): 1,4-benzenedicarboxylate (BDC), (b): 1,3,5-benzenetricarboxylate (BTC), (c): 1,3,5-Tri(4-carboxyphenyl)benzene and (d): 1,3,5,7-adamantanetetracarboxylate (ATC) [111].



**Figure 1.18**: N-donor ligands used in MOF synthesis, (a): 4,4'-bipyridine (4,4'-bipy), (b): 2,4,6-(tri-4-pyridinyl)-1,3,5-triazine (TPT) and (c):1,2-bis(4-pyridyl)ethane (bpa) [111, 112].

MOFs and ZIFs are usually synthesised under solvothermal conditions. This involves a 'one pot' method that directly mixes the organic ligand and metal ion precursors in a certain solvent system at temperatures less than 300°C [113]. Various factors have to be controlled during the procedure as they have the ability to directly affect the resulting framework, these include: pH of the solution, changes in concentration, the polarity of the

solvent and temperature [110]. This method usually yields crystals that are suitable for XRD for structural analysis. Other recent methods of synthesising MOFs have been developed that avoid the use of high temperatures and have shown promise in synthesising MOF-5, MOF-74, MOF-177 and other porous frameworks at room temperature [113]. This method, and other traditional solvothermal synthesis, describe how the addition of a base, usually triethylamine and in some cases NaOH, causes deprotonation of the organic linker and leads to the precipitation of the MOF crystal. When this is done slowly by diffusion, single crystal mixtures are seen and when done rapidly, in the form of an aliquot, microcrystalline powders are obtained [114, 115].

Hundreds of MOFs have been synthesised, however only a small percentage of these exhibit permanent porosity. Permanent porosity is established when the guest molecules residing within the pores of a material are removed without the collapse or rearrangement of the whole framework [110, 114]. This feature was first seen in MOF-5, Figure 1.19, the most popular MOF to date, which exhibits low densities, high accessible surface area, high thermal stabilities and a simple synthetic procedure [116]. MOF-5 is made of a zinc oxide cluster and BDC complex which form the SBU of the structure [117]. These SBU's have the ability to impact the pore size and porosity of the resulting frameworks. For example, the use of a longer linker, Figure 1.17 (c) compared to (b), would produce a net with larger void spaces that are proportional to the length of the linker. The use of a larger linker however poses its own problems as they are associated with interpenetration within the framework which ultimately reduces porosity [114].




**Figure 1.19 (a)**: MOF-5 unit cell structure, eight ZnO<sub>4</sub> tetrahedra (blue) that are joined by twelve BDC linkers (black and red). **(b)**: A cluster of eight unit cells. **(c)**: Ball and stick representation of the unit cells to depict the primitive cubic net topology. The large yellow cavity has a diameter of 12 Å with a pore opening of 8 Å [116, 118].

Applications of MOFs that involve gas separation, purification and storage fall under the category of solid phase gas storage. The enhancement of the study of MOFs has arisen from these original applicational findings. These materials are required to have high porosity as this maximises the uptake of molecules in the continuous networks, minimising the wasted space in a given volume [109]. MOF-5, along with other structures, offers permanent porosity and sorption isotherm studies of these materials have shown exceptionally high capacities to store gas molecules, specifically hydrogen, nitrogen, argon, carbon dioxide and methane [111, 119]. Gas isotherm studies measure the MOF for its attainment of permanent porosity after the removal of guests which reside within the

pores after synthesis [110]. Studies have shown type I isotherms for MOF-177, MOF-2, MOF-3 and MOF-5, along with many others, which indicate permanent porosity within the structure [120, 121]. These studies show that these microporous structures are resilient to the reversible physisorption of small molecules along with the attainment of the surface area of the materials. These studies have found structures with some exceptional qualities, for example; the nitrogen isotherm study of MOF-177, Figure 1.20, has shown one of the largest Langmuir surface area calculated of any reported material, with values of 4,500 m<sup>2</sup> g<sup>-1</sup> [88, 110].



**Figure 1.20**: The crystal structure of MOF-177, with Zn(O)<sub>4</sub> clusters connected through BTB organic linkers [121].

The ability to functionalise the organic linkers is an advantage with regard to gas sorption qualities, a study has shown a significant increase in CO<sub>2</sub> adsorption upon the addition of an amine group to the BDC linker [122]. An additional quality of an organic linker is its ability to be chiral. If the chiral nature of an organic linker could be harnessed and incorporated into a framework it could deliver an enantiomerically pure porous structure.

This structure could therefore be able to be selective and separate compounds base on their enantiomeric structure [111].

MOFs also show potential to be used in biomedical applications, where specific pore size and delivery methods are required. Larger MOFs of the isoreticular series MOF-74 have shown promise in their ability to encapsulate myoglobin in its hexagonal channels [110]. Other studies have shown that the MIL family of MOFs are capable of the storage and controlled release of biologically important molecules due to their enhanced stability, large pores and high porosity. This has created a strategy for the delivery of contrast agents and anticancer drug delivery by the post synthetic modification of MIL-101 [90]. It should be noted that there is a significant lack of toxological studies of MOFs, with the need for high biocompatibility for any *in vivo* studies [123].

MOFs have been utilised in sensing, electronic and photophysical applications. When a MOF is used as a sensor, the electrochemical, optical and magnetic properties of the material are altered due to the host and guests interactions [110]. The binding of a guest to an internal cavity can change the electronic structure and result in emission charges depending on the nature of the guest and the framework, from here, frameworks can be designed to be selective of which guests they adsorb and detect [109]. Two dimensional MOF based materials have also been developed that are electronically conductive and display bulk conductivity throughout the framework, with Cu<sub>3</sub>(hexaiminotriphenylene)<sub>2</sub> having a bulk conductivity of 0.2 S cm<sup>-1</sup> [124].

All of these applications illustrate why the field of MOFs is expanding so rapidly. The ability to tailor a structure so intricately to fit a specific application is advantageous over many other current porous materials. With a relatively simple synthesis and many other desirable properties, there is no difficulty in seeing why MOFs have developed so quickly as a field of research.

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# 1.8.3 Zeolitic Imidazolate Frameworks (ZIFs)

With increasing research into MOFs, an apparent lack of frameworks that show a zeolite framework topology has been observed. With zeolites showing structural advantages, as seen with their huge commercial success based on their porosity, it is clear to see why it is desirable to create a metal organic framework that can adopt a zeolitic topology and harness the properties that the structure of a zeolite can give. Additionally, a MOF with a zeolite topology could essentially be tailored based on the size of the organic linkers while also containing metal centres [107, 125].

MOFs with imidazolate (Im), deprotonated imidazole, as the organic linker and divalent metal cations (usually Zn<sup>2+</sup>) create structures that can have a zeolite type framework or new topologies [126]. The structure consists of the tetrahedral Si or Al centre atom as a transition metal and the bridging oxygen units as imidazolate linkers. This type of framework resembles a zeolite topology because of the resulting imidazolate—metal—imidazolate bond angle of 145°, seen in Figure 1.21, and tetrahedral networks [125, 127].



**Figure 1.21**: A diagram of the 145° angle of the M-Im-M bond seen in ZIFs and the Si-O-Si bond seen in zeolites [125].

In 2008, a series of experiments were conducted by Yaghi and coworkers to investigate various different imidazolate linkers (Figure 1.22) with metals. Their results showed the synthesis of 25 different ZIF crystals, 16 of which were previously unseen compositions of linker and metal, in addition to the discovery of 5 new structural topologies that were previously unobserved in zeolites. A selection of these synthesised structures also displayed exceptionally high selectivity for the uptake of  $CO_2$  [126].



**Figure 1.22**: Various imidazolate linkers used by Yaghi and coworkers in their breakthrough investigation into the synthesis of ZIFs [126].

Many ZIFs show zeolite type A (LTA) topology, making an interesting comparison between the properties of aluminosilicates and MOFs that have the same structural design. ZIF-20 was originally discovered by the high-throughput methods of Yaghi and coworkers and displays an LTA topology, Figure 1.23 [126]. It consists of tetrahedrally bound Zn(II) atoms linked through the N atoms of the imidazole ring of a purine molecule. Studies of ZIF-20 have shown that, when incorporated into a polymeric system, an increase in performance to separate an equimolar mixture of  $O_2/N_2$  is observed [128], displaying one of the many potential applications of this porous material.



**Figure 1.23**: ZIF-20 with the crystal structure of the LTA topology of zeolite type A (left) and the local environment of the Zn(II) metal centres that are coordinated to a purine molecule [128].

### 1.9 POSS Based Porous Materials

Although the area of porous materials as a whole has increased in development, there is a noteworthy lack of examples of highly functionalised molecules that are used as building blocks. It is theorised that a molecule with a high degree of functionality would give rise to a highly ordered network, albeit not without defects [129]. The synthesis of a porous material based on POSS structures, specifically  $T_8$ , is a concept that focusses on the ability to accurately tailor the organic functional groups to create molecules with a specific size and therefore pores with specific dimensions. This idea overcomes the disadvantage that is seen with zeolites in that there is a significant lack of ability to tailor the pore size, possibly due to a lack of understanding of their formation mechanism [130]. One of the fundamental properties of POSS is its rigid and periodical structure, making it suitable as a 3D building block. POSS molecules have a distinct resemblance to the SBU's seen within zeolites, most notably LTA and ACO nets found in zeolitic structures containing D<sub>4</sub>R units [131]. This idea has been explored to create hybrid porous materials with frameworks similar to zeolites that are based on POSS precursors [50].

The molecular building block, *para*-iodo-octaphenylsilsesquioxane (I<sub>8</sub>OPS), has been the subject of a small number of studies concerning the cross linking of silsesquioxane structures to create a hybrid porous framework. JUC-Z1 is a covalently linked microporous framework that is prepared from a Yamamono-type Ullmann cross-coupling reaction of the I<sub>8</sub>OPS monomer. The structure is described as siloxane cubes being linearly linked through covalent bonds to biphenyl molecules [132]. The XRD pattern of this compound has two clearly distributed peaks at 14.9 and 21.8 Å. These are analogous to the peaks seen at 11.6 and 20.0 Å for a framework that has an LTA topology and JUC-Z1 is thought of as affording an LTA-type net, Figure 1.24 [133]. Another structure that consists of the I<sub>8</sub>OPS monomer as an SBU is PAF-12, a micro-mesoporous hybrid material. PAF-12 is synthesised through a Suzuki cross-coupling reaction of I<sub>8</sub>OPS and 1,4-phenyldiboronic acid to linearly link siloxane units through bonds to phenyl molecules, similarly to that seen in JUC-Z1 [134]. This resulting framework was predicted to share either an LTA or ACO topology due to the linking of D<sub>4</sub>R units. XRD studies showed that PAF-12 does in fact have an LTA topology [133].



**Figure 1.24**: The building process of the Ullman cross-linked JUC-Z1 structure, with the possibility to afford the LTA or ATO net [133].

JUC-Z1 and PAF-12 show many similarities with regard to structural topology and have shown stability under high temperatures, with JUC-Z1 stable up to 397°C and PAF-12 stable to 500°C [132, 134]. Both materials show high porosity and surface areas. These factors facilitated the ability to adsorb organic vapours, PAF-12 even displayed adsorption of gases at low pressures, giving these types of hybrid porous molecules a great potential for applications associated with gas adsorption [133].

A series of reactions have investigated the effect of the substitution pattern of I<sub>8</sub>OPS on the structural framework of a resulting hybrid porous polymer (HPP), Figure 1.25. Within this series, octavinylsilsesquioxane (OVS) was reacted via Heck coupling with a nonspecific mixture of nona- and octa-substituted IOPS. HPP-1 was obtained with a > 99% octa-substituted I<sub>8</sub>OPS and HPP-2 was obtained with 93% para selectivity. Results showed that both structures displayed high surface areas, porosity and the ability to adsorb CO<sub>2</sub>. HPP-2, consisting of the more ordered monomer I<sub>8</sub>OPS, displayed a more ordered structure, with less deformities and a higher CO<sub>2</sub> adsorption capacity. These results suggest that the use of an asymmetrical monomer, with a nonspecific substitution pattern, as a nano building block would give a structure with less effective application abilities due to its less ordered framework, as seen in HPP-1 [51].



**Figure 1.25**: The linking of the siloxane units in the hybrid porous polymers, where HPP-1 is made of a non-specifically iodo-substituted siloxane monomer and HPP-2 is made of the para-substituted iodo compound [51].

OVS has also been the subject of other attempts to produce hybrid porous frameworks. A series of nanoporous hybrid polymers were synthesised from the Heck coupled reaction of OVS and various aromatic bromide monomers. These polymers displayed various heightened properties including porosity, adsorption behaviour and luminescent features. It has been suggested that these polymers have the potential to detect picric acid along with addition luminescent properties [135].

The AIBN initiated radical polymerisation of OVS in THF has produced an additional series of hybrid porous materials. It suggests that the reactant concentration plays a significant role in determining the porosity of the resulting material. With careful choice of reactant concentration, materials with high porosities have been synthesised that are thought to display the highest adsorption of hydrogen for any POSS based porous material reported so far [50]. A Friedel-Crafts reaction of varying molar ratios of OVS and benzene has seen the synthesis of another series of hybrid porous polymers, all of which were highly porous, with relatively high surface areas, and more thermally stable when compared to other POSS based porous materials and MOFs. It has been noted with these polymers, likewise to all other porous frameworks that have been synthesised based on POSS monomers, that they have significant potential in the adsorption of gases [136].

The simple OPS monomer has also been incorporated into a series of hybrid porous networks via a Friedel-Crafts reaction (POPS-1) and a Scholl coupling reaction (POPS-2). Both of these networks show a micro and mesoporous structure, with high surface areas and thermal stabilities. The researchers highlight how the D<sub>4</sub>R structure remains completely intact throughout the acidic synthesis and how the POSS based networks are well suited as candidates for the storage and capture of H<sub>2</sub> and CO<sub>2</sub> [137].

In addition to POSS based molecules being used as monomers to construct a porous framework, an instance has occurred where aminopropylisooctyl polyhedral oligomeric silsesquioxane (O-POSS) has been used to make the external surface of a porous MOF hydrophobic. The study aimed to increase stability of the porous material against humidity, a common issue that is faced with many MOFs as water has the ability to penetrate the pores and destroy the structure by replacing coordinated ligands or via hydrolysis. The study suggested that the resulting O-POSS Cu<sub>3</sub>(BTC)<sub>2</sub> framework would be an ideal candidate for the storage and separation of gases that are in especially humid environments and provided a different approach to incorporate POSS based molecules within porous materials, Figure 1.26 [138].



**Figure 1.26**: The surface modification of the MOF Cu<sub>3</sub>(BTC)<sub>2</sub> with O-POSS to enhance the hydrophobicity of the material and increase the resiliency to water damage of the framework [138].

Porous structures that are based on POSS molecules house the potential of being new and exciting materials. These structures can harvest the thermal and chemical stability that is associated with the siloxane molecule in addition to its ability to exist as a tailorable SBU. This is due to its rigid inner core and extended arms that can be functionalised. With the early studies of these novel structures, the idea of a building unit that can be designed for a specific function is established. This could possibly create an innovative area of designing structures within the field of porous materials.

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Chapter 2: The Synthesis of Various POSS Molecules

# 2.1 Background and Aims

Silsesquioxane molecules have been used as molecular building blocks and incorporated into various porous organic frameworks, for example PAF-12 and JUC-Z1 [1, 2]. However, few researchers have suggested the idea of utilising the robustness, thermal stability, ability to functionalise and nanoscale size of silsesquioxanes in attempts to synthesise a metal organic framework with potential porosity [3 - 6].

The synthetic strategies of creating porous organic frameworks are such that monomers must satisfy two criteria; reactive groups must be present for further bonding, and the geometries of the monomers must match with regular structures [7]. With these criteria in consideration, it would seem that a silsesquioxane molecule, with terminal carboxylic acid or imidazole groups, would have the ability to be an ideal linker for a porous framework; it possesses the qualities of functional groups that are able to coordinate to metal centres and the cubic nature of a  $T_8$  molecule can create LTA and ACO type nets [8].



**Figure 2.1**: The building of an ACO and LTA net and the subsequent framework structure from the  $D_4R$  SBU that is seen in  $T_8$  molecules [8].

To create a framework joined through eight terminal groups, a silsesquioxane molecule would have to be modified in such a way that each silicon corner would contain a functional group that could participate in bonding to a metal centre. The eight sites that would be present and the various metals that they could coordinate to could provide many different structural frameworks, each with the potential ability to create an extended network with possible porosity. The porosity of the resulting material could be tailored by specific functionalisations of a POSS molecule, as seen with derivatives of octa-(aminophenyl)silsesquioxane. This could include adjusting the length of the of the pendant arms, therefore altering the size of the monomer [9].

This chapter will focus on the synthetic efforts to produce two different silsesquioxane molecules, each with the potential to link to metal centres; octa(carboxyphenyl)-silsesquioxane (OCS), Figure 2.2, and N-propylimidazolyIPOSS (ImPOSS), Figure 2.5.



**Figure 2.2**: Octacarboxyphenylsilsesquioxane (OCS), a potential linker for a metal organic framework containing eight pendant arms, each with a terminal carboxylic acid group.

The synthesis of OCS has been attempted through two distinct pathways. The first synthetic pathway aimed to modify the phenyl rings which reside on the corners of octaphenylsilsesquioxane (OPS), through a series of reactions, Figure 2.3.



**Figure 2.3**: The synthetic pathway for the synthesis of OCS through the modification of OPS. i; (a) H<sub>2</sub>O, RT, (b) benzyltrimethylammonium hydroxide, toluene, 126°C. ii: ICl, I<sub>2</sub>, DCM, - 40°C. iii: (a) n-BuLi, THF, - 78°C (b) CO<sub>2</sub>, RT.

The first functionalisation reaction, after the initial synthesis of OPS, is the iodination of the phenyl ring in the para position, a reaction procedure established by Laine and coworkers [10]. This reaction has been reported with a high yield and a high selectivity for iodination in the para position; a vital quality for a potential building block. If this initial functionalisation reaction was unable to specify the position in which the iodine group would result, or if all eight corners would not react, it would form an unsymmetrical molecule. It is expected that a higher level of symmetry within a starting molecule would impart the highest level of order in future assemblies as a perfectly symmetrical nano building block would reduce the chance of deformities, suggesting that an unsymmetrical molecule would be inadequate for building a highly ordered structure [11]. If all of the eight

corners cannot contribute to the structure of the framework this would result in a defected crystal structure or worse, the inability to form an ordered network [4].

The next reaction is the carboxylation in the para-position of the phenyl ring to produce OCS. This involves the lithiation of I<sub>8</sub>OPS, using n-BuLi in THF, followed by the carboxylation through the addition of CO<sub>2</sub>. This route has been reported by Pescarmona and coworkers with the characterisation of the compound through FTIR, NMR, MALDI-TOF, TGA and elemental analysis [12]. It is noted that the compound is highly stable under acidic conditions in addition to having a high solubility in a range of common solvents, perhaps due to the increased polarity and potential for hydrogen bonding through the carboxylic acid groups. The paper also discusses the idea of combining silsesquioxane chemistry with metal organic frameworks, a central concept explored in this chapter.

The second synthetic pathway that will be discussed is the designing of a specific trifunctionalised silane molecule to create a precisely functionalised POSS cube. This route would see each corner of the siloxane cube designed before the actual formation of the T<sub>8</sub> structure, ensuring that each corner is already partly functionalised upon synthesis of the POSS cube. This method would preclude the concerns associated with the minority of pendant arms that may remain unfunctionalised, which would have the potential to introduce defects into any porous material it may be incorporated into.

A similar concept has been implemented in an alternative synthesis of a completely parasubstitued octa(bromophenyl)silsesquioxane molecule. This synthesis displayed an improvement when compared to the conventional synthesis of brominating OPS [13]. The substitution selectivity for the position of the bromine on the phenyl ring and the extent of bromination was improved; all 8 phenyl rings were brominated in contrast to the previous 5.3 per molecule. This method saw the synthesis of a T<sub>4</sub> molecule in the form of a sodium salt, [4-BrC<sub>6</sub>H<sub>4</sub>Si(O)ONa]<sub>4</sub>, from 4-bromophenyltriethoxysilane [14]. This molecule then

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underwent a condensation reaction to yield the silanol form and similarly to the typical OPS synthesis, upon addition of benzyltrimethyl ammonium hydroxide a T<sub>8</sub> structure was produced. This molecule was deemed to be octa(4-bromobenzene)-silsesquioxane, with high selectivity for substitution in the para-position and a 58% yield [15, 16].

One of the attempted pathways discussed in this chapter, Figure 2.4, incorporates these concepts and aims to synthesise a functionalised trichlorosilane molecule with the hopes of ultimately synthesising a  $T_8$  molecule with specifically designed corners.



**Figure 2.4**: The proposed synthetic pathway for the synthesis of OCS. i: *p*-toluenesulfonic acid, ethylene glycol, toluene, 190°C. ii: Mg, I<sub>2</sub> crystal, THF, 70°C. iii: SiCl<sub>4</sub>, THF, RT. iv: (a)  $H_2O$ , RT (b) benzyltrimethylammonium hydroxide, toluene, 126°C.

The synthesis of ImPOSS, Figure 2.5, will also be investigated. Similar to the way in which a carboxylate linker is able to make a framework structure, a POSS cube with terminal imidazole groups could be a linker in a zeolitic imidazolate framework (ZIF) type structure. The synthesis of ImPOSS has been reported by Zhang and coworkers and is prepared from octakis(3-chloropropylsilsesquioxane) (CIPOSS) [17], various synthetic procedures for which have been discussed in the previous chapter.



**Figure 2.5**: N-propylimidazolyIPOSS (ImPOSS), a potential linker for a zeolitic imidazolate framework type structure containing eight pendant arms with terminal imidazole groups.

In addition to CIPOSS being an appropriate precursor for more complex molecules [18, 19], it, and similar imidazole POSS molecules, have been incorporated as a building block for the preparation of amphiphilic mesoporous cationic liquids and frameworks through polymerisation reactions. These POSS derived materials have demonstrated hetero-geneous catalytic activity, selectivity, and the ability to be reused [20]. These findings

support the idea that POSS molecules can be integrated as building blocks for the synthesis of stable and functional porous materials.

The imidazole functionalised POSS molecule, ImPOSS, has been synthesised at room temperature through the nucleophilic substitution of CIPOSS and an imidazole molecule. Proceeding from this, ImPOSS and Nafion were both used to synthesise a polymer electrolyte hybrid membrane. This material displayed enhanced thermal properties due to the strong Coulombic interactions between the sulfonate groups of Nafion and the imidazole groups of ImPOSS. It was also suggested that the POSS groups reinforced the polymeric membranes [17]. Following this, researchers have combined Nafion with other types of silicon based molecules, including sulfonated POSS and imidazole functionalised silica, to synthesise hybrid membranes with heightened thermochemical properties and enhanced conductivity [21, 22].

Interestingly, a silsesquioxane molecule with terminal dipyridylamine (DPA) groups has been synthesised from CIPOSS [23]. The research team present novel results where the two nitrogen atoms on each corner of the silsesquioxane molecule coordinates to molybdenum (II) groups, presenting further examples of organometallic coordination within silsesquioxane chemistry. This complex is also thought to be a potential heterogeneous catalyst, however no consideration of porous frameworks is discussed.

# 2.2 The Modification of OPS to Create a Carboxylic Acid POSS Derivative

### 2.2.1 The Synthesis of OPS

This section will discuss the attempted synthesis of OCS, beginning with the synthesis of OPS. The general reaction pathway can be seen in Figure 2.3. The synthesis of OPS was attempted through two similar methods. Both followed an early published synthesis by Brown and coworkers in 1964 with subtle variations [24].

The first attempt began with the hydrolysis of phenyltrichlorosilane in toluene and deionised water. The original synthesis [24] uses benzene, a known hazardous solvent. A more modern approach replaces benzene with toluene, alleviating the safety concerns associated with the carcinogenic nature of benzene while remaining an effective solvent for the reaction. To ensure that the yield of OPS is high, all phenyltrichlorosilane molecules must undergo hydrolysis to become phenylsilanetriol, meaning that the hydrolysis step must be sufficiently long. Brown and coworkers do not specify an appropriate amount of time for this step, however stirring at room temperature for a period of 20 minutes was deemed appropriate for the first attempt. Following this was a series of separation steps; the aqueous layer of the reaction mixture was washed with toluene, this toluene phase was then combined with the original toluene layer, the organic phase was then washed with deionised water. This separation sequence ensures that all PhSi(OH)<sub>3</sub> molecules remain in the organic phase for the next step.

The next step was the addition of a catalyst which initiated the formation of the  $T_8$  structure. A common catalyst for this step is benzyltrimethylammonium hydroxide (BzTMAOH), but tetra-n-butylammonium fluoride is also known as an effective alternative, where both can be seen in Figure 2.6 [25]. All synthesis attempts used BzTMAOH and

once added, the reaction mixture was refluxed for 24 hours at 126°C. Heating was stopped and the reaction was stirred at room temperature for a period of 4 days. Within this period, a white precipitate formed. The reflux was then reapplied for 24 hours, as stated in the original literature procedure [24], until finally being removed, where the solid was filtered and washed with toluene.



**Figure 2.6**: The common catalyst benzyltrimethylammonium hydroxide (BzTMAOH) that is used in the synthesis of OPS and tetra-n-butylammonium fluoride (TBAF) that is known to be used as an alternative catalyst.

The first attempt gave 2.37 g of white powder with a yield of 17.5%. This low value of this yield was noted when compared to other published values, which were reported in the range of 80%. The collected filtrate was left in the fume hood to allow the precipitation of further silsesquioxane products, as demonstrated by Brown and coworkers [24].

Analysis of the product of the first attempt began with <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, which can be seen in section A.1. The <sup>1</sup>H NMR spectrum showed various peaks within the aromatic region, attributed to the hydrogen atoms on each Ph group. Upon initial inspection, the region appears to have a large number of different peaks which makes the specific assignment of these peaks more complex. The proton peaks of the solvent for this reaction, toluene, also appear within the aromatic region of the spectrum, with an additional singlet expected at 2.36 ppm [26].

A mixture of multiplets can be seen within the aromatic region, 7.35 ppm and 7.70 ppm, that prove difficult to assign to individual aromatic hydrogen atoms due to overlapping. However, a peak is observed at 7.76 ppm that can be assigned as a double doublet, shown in Figure 2.7. This peak can be assigned to the hydrogens at the ortho position on the phenyl ring in reference to the siloxane cube. These protons will both be in the same environment and will couple to the two adjacent protons at the meta position of the ring in the form of a doublet with a large coupling constant of 8.0 Hz. The second doublet signal arrises from coupling to the proton in the para position of the ring and will also take the form of a doublet. This coupling is weaker and has a smaller coupling constant of 1.4 Hz.



Figure 2.7: <sup>1</sup>H NMR spectrum, in the region of 7.65 - 7.90 ppm, of OPS.

The remaining aromatic section of the spectrum proved to be complex and assigning any specific regions to hydrogens remains difficult due to a significant presence of peak overlapping. The spectrum does however have a region of multiplicity, 7.34 - 7.48 ppm, where these peaks would be found. No specific splitting patterns can be identified and the integrations are not as accurate as they would be if the only protons influencing the aromatic region were the three remaining hydrogens on the phenyl ring. It could be

theorised that peaks from toluene may be residing in this area and therefore causing overlap of peaks and altering the expected multiplicity and integration patterns. There is however a significant lack of reported <sup>1</sup>H NMR data for OPS, those of which describe an ambiguous region between 7.2 ppm and 7.8 ppm [27]. The experimental obtained results can therefore be argued to be in accordance with that of published data.

For the T<sub>8</sub> precursor, PhSi(OH)<sub>3</sub>, there is an expected proton peak at 5.53 ppm which corresponds to the OH proton peaks [28]. If this peak was present in the NMR spectrum it would suggest that the structure is not fully a condensed system. As there is no peak at 5.35 ppm it can be thought that the system does contain a fully condensed Si-O-Si system with no remaining OH protons. However, it could also be possible that the precursor may be present as the OH group could undergo a proton exchange with the deuterated solvent to form PhSi(OD)<sub>3</sub>, as this would not be seen on the proton spectrum either.

As the assigned doublet of doublets for the ortho-hydrogens is seen further downfield, away from the ambiguous multiplet region, it could be thought that the electron withdrawing nature of the fully condensed siloxane cube could alter their proton shifts as they reside closest to the cage system [29]. This has made identifying these peaks more straightforward when compared to the others and supports the notion of the product containing a fully condensed siloxane system.

The <sup>13</sup>C spectrum for this product showed 4 peaks at 127.9, 128.3, 129.1, and 134.2 ppm, all of which correlate to peaks from aromatic carbons. The phenyl rings on an OPS molecule have 4 carbon environments, therefore the four peaks that are observed can be assigned to these carbons. Similarly, the electron withdrawing effect of the siloxane cube that was observed for the proton spectrum can be expected to be seen for carbon atoms in the closest proximity to the cage system, and therefore appear further downfield than to those further away.

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The IR spectrum of this product can be seen in section A.1. Three peaks which correspond to a siloxane system can be seen; a strong broad peak at 1094 cm<sup>-1</sup>, assigned to the Si-O-Si stretching vibration of a T<sub>8</sub> cage, a sharp peak at 1026 cm<sup>-1</sup> which is associated with the Si-O-Si intercage stretching vibration and a sharp peak at 738 cm<sup>-1</sup> for a Si-O vibration. In addition to these, there were a number of peaks that are associated with the aromatic phenyl rings; 3052 cm<sup>-1</sup>, 1592 cm<sup>-1</sup>, and 698 cm<sup>-1</sup> which correspond to a C-H stretching vibration, C=C stretching vibration and C-H out of plane deformation of the phenyl ring respectively [30, 31]. The absence of any OH peaks in the IR spectrum indicates that there are no silanol molecules, PhSi(OH)<sub>3</sub>, or open S-OH corners in the product and therefore a fully condensed cage is present.

A repeat attempt of the synthesis of OPS with the same procedure gave a yield of 42.7%, higher than achieved on the initial synthetic attempt. Analysis of IR, <sup>1</sup>H and <sup>13</sup>C NMR spectral data showed equivalent peaks to the previously reported OPS product.

A third attempt of the synthesis of OPS saw a slight variation in procedure; the length of the hydrolysis stage was increased and the second reflux was not included. Instead, the product was collected after 4 days of stirring and a yield of 75.0% of OPS was seen, as confirmed by obtained spectra, compound **1**. The higher yield for this attempt may be attributed to a more thorough hydrolysis and extraction step. This step would have ensured that the reaction mixture contained a higher amount of the silanol intermediate, PhSi(OH)<sub>3</sub>, and therefore gave a higher final yield. Alternatively, the second reflux in the previous attempts could have caused other types of silanol molecules to precipitate from the reaction solution. This would therefore lower the yield of OPS that was observed in the first and second attempts.

## 2.2.2 The Synthesis of I<sub>8</sub>OPS

The following reaction in the series was the synthesis of  $I_8$ OPS. This molecule has been implemented as a precursor for the synthesis of two novel porous structures that are derived from POSS molecules; JUC-Z1 and PAF-12. Although this molecule will be used as a precursor for OCS it is interesting to note that, through cross coupling reactions and aromatic linkers, it has directly made porous materials [1, 2, 32, 33]. This gives a stable basis for the synthesis of other porous structures from a molecule derived from  $I_8$ OPS.

For this procedure, as the iodination of OPS must occur at - 40 °C for an extended period of time, a cooling refrigerant system was implemented. The reaction followed a procedure published in 2008 by Laine and coworkers [10]. It began with dissolving OPS in dichloromethane. This was then added through a pressure equalised dropping funnel to a stirring solution of ICI dissolved in DCM under N<sub>2</sub>. To ensure that there were no remnants of OPS in the dropping funnel, it was subsequently washed with DCM. This was then stirred for 24 hours at - 40°C.

Following this period, the reaction was allowed to stir for a further 24 hours while warming to room temperature over the first 2 hours. Sodium metabisulphite was added to quench the reaction. The organic layer was then collected and washed three times with deionised water. The solution was then dried over anhydrous magnesium sulphate, filtered and dried to yield a white solid. This was redissolved in THF and then precipitated from cold methanol. Collection of the precipitate via vacuum filtration gave a product in the form of a white powder with a 12.4% yield (1.165 g). The proton NMR of this crude product showed two distinct regions, one at 7.44 ppm and the other at 7.76 ppm, with equal integrations. The crude product was recrystallised from hot ethyl acetate to yield colourless crystals with an overall yield of 9.5% (0.8902 g), compound **2**. The published values for the yield of  $I_8OPS$  are 90% for the crude product, which is reduced to 30% upon recrystallisation [10].

The experimental percentage yield values obtained are comparably lower. This may be attributed to a loss of product within the organic work up stage or perhaps the methanol precipitation step, if the methanol was not cooled enough.

NMR analysis of this compound showed peaks that are expected of I<sub>8</sub>OPS, as published by Laine and coworkers. The <sup>1</sup>H NMR spectrum of the recrystallised compound showed two doublets at 7.74 ppm and 7.39 ppm, both with the same relative integration. This NMR pattern can be seen in Figure 2.8 and is indicative of a para-substituted phenyl ring, confirming the position selectivity of this iodination reaction. The <sup>13</sup>C NMR spectrum displayed four peaks at 137.2, 135.5, 134.1 and 128.1 ppm in the aromatic region of the spectrum, indicative of four carbon environments, which is also expected with a parasubstituted phenyl ring.



**Figure 2.8**: <sup>1</sup>H NMR spectrum for I<sub>8</sub>OPS in the aromatic chemical shift region of 7 - 8 ppm.

The <sup>29</sup>Si NMR spectrum of I<sub>8</sub>OPS can be seen in Figure 2.9, where a peak at - 78.23 ppm can be clearly seen, which is in accordance with published data [10]. This peak corresponds to a silicon atom of OPS which is in an environment of a  $T_8$  system, indicating the formation of the octahedral molecule, confirming that the synthesis was

successful. The broad peak within the range of - 100 and - 120 ppm can be attributed to background signal from the glass NMR tube [34]



**Figure 2.9**: <sup>29</sup>Si NMR of I<sub>8</sub>OPS, where a clear peak at - 78.23 ppm can be seen, indicative of a  $T_8$  system where a silicon atom is surrounded by a phenyl ring and 3 oxygen atoms.

The results of the IR spectrum are in accordance with published data for I<sub>8</sub>OPS [10], with weak C-H peaks at 2991 cm<sup>-1</sup>, strong C=C peaks at 1573 and 1477 cm<sup>-1</sup>, strong Si-O peaks at 1078 and 1002 cm<sup>-1</sup>, and strong C-H peaks at 802 and 739 cm<sup>-1</sup>.

From the spectra obtained for this compound, it can be concluded that I<sub>8</sub>OPS has been synthesised and is suitable for the next reaction in the series.

## 2.2.3 The Attempted Synthesis of OCS

The synthesis of a carboxylic acid functionalised POSS cube from I<sub>8</sub>OPS followed a procedure outlined by Pescarmona and coworkers, the schematic of which can be seen in Figure 2.10 [12].



**Figure 2.10**: The attempted synthetic pathway for the carboxylation of I<sub>8</sub>OPS. i: BuLi, THF, - 78°C. ii: CO<sub>2</sub>, THF, RT. iii: MeOH, H<sub>2</sub>O, 2M HCl, RT.

The experimental set-up for this procedure included an inlet vessel for the  $N_2$  gas to keep an inert atmosphere and to keep a consistent flow of CO<sub>2</sub> gas, a reagent in this procedure. Both passing through a drying column before entering the reaction, ensuring that all gases were dry before commencing the moisture sensitive organo-lithium reaction [35]. Additionally, anhydrous THF was purchased and all glassware was thoroughly dried in a glassware oven before being flushed with  $N_2$ . The initial attempt began with the slow addition of n-BuLi to a stirring solution of dry THF and  $I_8OPS$  at - 78°C under N<sub>2</sub>. This was then left to lithiate for 5 hours, upon which an off-white colour precipitate was observed, thought to be the compound lithiated in the para position of the phenyl ring, a theory proposed in the literature procedure. Following this, the reaction was warmed to room temperature and  $CO_2$  was allowed to flow through.

After a period of time, a sudden drop in pressure from the CO<sub>2</sub> gas cylinder inlet caused the oil from the outlet bubbler to be pulled back into the reaction flask. Various attempts to separate the oil from the product, through aqueous and basic work ups, proved unsuccessful and the product could not be salvaged.

For the second attempt, an empty drechsel bottle was included between the parafin oil filled outlet bubbler and the reaction vessel to ensure that any back flow of parafin oil would reside in the empty bubbler and not reach the reaction vessel. In addition to this, the flow of CO<sub>2</sub> was increased. The procedure saw the formation of the lithiated precipitate prior to CO<sub>2</sub> addition which then flowed for a period of 2.5 hours. The reaction was then quenched with methanol, water, and 2M HCl to give a cloudy solution. The solvent was then evaporated under reduced pressure to a volume of approximately 5 mL, which was filtered to yield a clear gel. This was washed with DCM and water, then redissolved in THF. The final step was supposed to result in precipitation of the product from the drop-wise addition of water to the THF solution. However, this was not achieved and the THF solution was left in the freezer to initiate precipitation.

After 48 hours, the solution was removed, allowed to warm to room temperature, and the remaining solvent was removed under reduced pressure to give a colourless oil. Analysis of the oil through <sup>1</sup>H NMR showed various amounts of impurities, with no clear identification of the two aromatic regions for the para-substituted phenyl ring that would be expected upon a successful carboxylation reaction. <sup>29</sup>Si NMR also gave no identifiable
peaks, suggesting that the silsesquioxane compound was not isolated. The IR spectrum of the oil that was obtained lacked a prominent and broad Si-O-Si region, expected at approximately 1026 cm<sup>-1</sup>. This, in addition to the <sup>29</sup>Si data, suggests that the product obtained was not a silsesquioxane molecule.

As the yellow coloured precipitate was observed during the lithiation step, as expected from the literature procedure, it can be deduced that a problem was encountered within the proceeding carboxylation and work up step, which introduced water to the reaction. The unsuccessful carboxylation step could be due to an insufficient amount of  $CO_2$  supplied for the reaction, making the formation of the carboxylic acid not feasible, or possible faults within the experimental set up which could allow water into the moisture sensitive reaction. Either of these possibilities would result in the lithium in the para position on the benzene ring being exchanged for a proton, forming the starting material of OPS. As this method was ineffective at obtaining the desired product, It may be beneficial in future work to consider possible alterations to the experimental setup and procedure to allow the synthesis and isolation of the OCS product.

### 2.3 The Synthesis of OCS Through the Condensation of a Trichlorosilane

Figure 2.4 shows the synthetic pathway which aimed to produce OCS through an alternative pathway of that discussed in Section 2.2. The objective was to synthesise a POSS cube where each silicon corner is functionalised prior to the synthesis of the  $T_8$  molecule. This idea focusses on the synthesis of a specifically designed trifunctionalised silane molecule that can create a POSS cube with a high level of functionality.

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The synthesis of 2-(4-bromophenyl)-1,3-dioxolane, the first step in this pathway, followed the procedure published by Han and coworkers [36]. The reaction began with a solution of 4-bromobenzaldehyde and *p*-toluenesulfonic acid in toluene. Ethylene glycol was added and the solution was refluxed under Dean-Stark conditions for 9 hours at 150°C. As the reaction is reversible, azotropically removing the byproduct of water, using a Dean-Sark trap, ensured that the reaction equilibrium resides towards the dioxolane product. The solution was cooled and then washed with a saturated Na<sub>2</sub>CO<sub>3</sub> solution. This was followed by an extraction with ethyl acetate and removal of the solvent under reduced pressure. The product was dried over MgSO<sub>4</sub> to give a 79.5% yield of a yellow oil, compound **3**.

The <sup>1</sup>H NMR of this product showed two doublets at 7.52 ppm and 7.36 ppm, both with an integration of 2H, corresponding to two aromatic proton environments. A singlet with an integration of 1H was seen at 5.78 ppm and corresponds to the dioxolane proton in position 2, highlighted in red in Figure 2.12. Lastly, a multiplet with an integration of 4H was observed at 4.08 ppm and corresponds to two dioxolane CH<sub>2</sub> groups in positions 4 and 5. In addition to these, peaks were also seen at 7.74 ppm and 9.98 ppm corresponding to peaks from one of the starting materials, 4-bromobenzaldehyde, in accordance to published data [37]. An additional singlet peak at 3.73 ppm was also seen and corresponds to the CH<sub>2</sub> groups on the other starting reagent, ethylene glycol [26]. The presence of these starting materials indicate that the reaction has not fully gone to completion, perhaps justifying the yield of 75.5%.

When a peak representing a proton environment with an integration of 1 from the product, 5.78 ppm, was compared to a peak with a relatively equivalent integration from the precursor 4-bromobenzaldehyde, 9.98 ppm, a ratio of 1 : 0.15 was seen, Figure 2.12. This indicates that, while the product has been synthesised, starting material still remains. To investigate this, and the effect that the length of reflux has on the equilibrium reaction, the refluxing time was increased from 4.5 hours to 5.5 hours and then to 9 hours on three

different synthesis attempts. It can be seen that with an increasing reflux time, the amount of remaining starting material decreases. Figure 2.12 (a) and (b) show that when the reflux is increased by a period of an hour, there is around three times less starting material when compared to the product. Figure 2.12 (c) shows that an undetectable amount of starting material remains upon a reflux of 9 hours, suggesting that a period of reflux of 9 hours is ideal.



**Figure 2.11**: <sup>1</sup>H NMR of three different synthesis attempt of 2-(4-bromophenyl)-1,3dioxolane, all of which have different reflux times, a: 4.5 hours, b: 5.5 hours, and c: 9.0

hours. The spectra focuses on the region of 5.0 - 10.5 ppm and highlights the difference in relative integrations of starting material and product. Two clear doublets can also be seen at 7.36 and 7.52 ppm and correlate to the aromatic protons of the dioxolane



Figure 2.12: 2-(4-bromophenyl)-1,3-dioxolane with carbons 1 - 6 labelled for identification.

The <sup>13</sup>C NMR of for the product refluxed at 9 hours showed peaks at 65.33 (6), 103.04 (5), 123.26 (1), 128.20 (3), 131.52 (2) and 136.99 ppm (4), labelled in Figure 2.12, all of which are in accordance with published data for 2-(4-bromophenyl)-1,3-dioxolane [38]. Additional weaker peaks were seen for products from the 4.5 hour and 5.5 hour reflux from the precursor, 4-bromobenzaldehyde [37], supporting the idea that a longer reflux reduces the amount of residual starting material, producing a more pure product of 2-(4-bromophenyl)-1,3-dioxolane which can then be incorporated into the next step of the series.

The next step in this pathway was the synthesis of the Grignard reagent, 4-(1,3dioxolane-2-yl)-phenyl magnesium bromide, which would be used as a precursor for the synthesis of a functionalised trichlorosilane. This reaction involved the refluxing of 2-(4bromophenyl)-1,3-dioxolane with magnesium and a single iodine crystal under N<sub>2</sub> in anhydrous THF. Due to the moisture sensitivity of Grignard reagents, it is essential that the reaction was completed under as dry conditions as possible and therefore glassware was dried thoroughly in a glassware oven and flushed with N<sub>2</sub> before use in addition to the inert atmosphere that was used. After a refluxing period of 24 hours, a dark solution was observed, suggesting the formation of the Grignard reagent [39]. This was then transferred via syringe to a flask containing SiCl<sub>4</sub> dissolved in toluene with the aim to synthesise the phenyl-dioxolane functionalised trichlorosilane, Figure 2.4 (iii). This solution was then allowed to stir at room temperature for a period of 94 hours.

At this point, a small sample was taken for NMR analysis where the colour had changed from black to dark orange. The analysis of the <sup>1</sup>H spectrum showed two doublets at 7.44 ppm and 7.30 ppm, each integrating for 2H, suggesting the presence of the para-substituted phenyl ring. In addition to these peaks, a singlet was observed at 6.43 ppm, with an integration of 1H, perhaps corresponding to the dioxolane proton as highlighted in red in Figure 2.12. The dioxolane mulitplet, expected at 4.10 ppm, is observed, however the integrations are not completely accurate. Solvent peaks from toluene were seen in between 7.20 - 7.08 ppm. Residual peaks associated with 4-bromobenzaldehyde were also seen at 9.87 ppm and 7.61 ppm. At this point in the reaction it can be thought that the product remains in the dixolane form, however small amounts of 4-bromobenzaldehyde are present which suggests that minor amounts of dioxolane molecules have been deprotected.

As trichlorosilane molecules are known precursors for the formation of a  $T_8$  POSS molecule, the synthesis of the functionalised cube was conducted in a similar manner in which OPS is synthesised. This began with the hydrolysis of all CI sites on a trichlorosilane molecule, where deionised water was added to the solution of toluene and the functionalised trichlorosilane, as seen in Figure 2.13. The solution was stirred for 20 minutes and worked up similarly to the method seen for OPS. This was followed by the addition of a catalyst, BzTMAOH, which would initiate the formation of the T<sub>8</sub> cube. This was then refluxed for a period of 24 hours, giving a dark brown solution. As the T<sub>8</sub> POSS

cube is the least soluble, it is usually seen first in the form of a precipitate. As no precipitate had formed after 48 hours of stirring at room temperature, the flask and its contents were frozen to initiate the precipitation of the functionalised POSS cube, if it had in fact formed.



**Figure 2.13**: The hydrolysis of the dioxolane functionalised trichlorosilane to produce a potential precursor for the formation of a silsesquioxane cube with eight dioxolane terminated corners.

After two weeks, the solution was inspected and no precipitate had developed. Following this, the period of freezing was extended. After a period of 8 months, with regular inspection, the toluene solution remained a clear orange colour without precipitate, suggesting that the T<sub>8</sub> structure had not formed, or at least in the form of a precipitate. The solution was then removed and allowed to adjust to room temperature before the removal of the solvent under reduced pressure. This gave an orange oil, which solidified after 3 days at room temperature in a fumehood. Any remaining toluene in the sample was removed under high vacuum.

The <sup>1</sup>H NMR spectrum for this product showed a singlet at 9.98 ppm, with an integration of <sup>1</sup>H, and a double doublet at 7.73 ppm, with an integration of 4H. The double doublet splitting pattern is indicative of an aromatic ring substituted in positions 1 and 4, much like that expected of all the aromatic intermediates in this reaction series. The singlet at 9.98 ppm indicates that the dioxolane protecting group is no longer present, having reverted to

the aldehyde starting material. As the experimental procedure for the synthesis of the Grignard reagent was replicated from a successful literature method [40], the problematic areas of the series are within either the addition of  $SiCl_4$  or with the  $T_8$  synthetic conditions.

The procedure for the synthesis of the  $T_8$  molecule involved the addition of the base catalyst BzTMAOH. It has been found that bases are in fact capable of facilitating the deprotection of dioxolane molecules [41]. This would mean that the addition of BzTMAOH within the base catalysed hydrolysis step, Figure 2.4 (iv), would actually deprotect the dioxolane and revert the molecule back to the aldehyde, making the protecting system ineffective and therefore resulting in the unsuccessful reaction observed.

This situation could be rectified if the base catalysed hydrolysis step, Figure 2.4 (iv), produced the POSS cube already deprotected in the form of the aldehyde, thus eliminating step (v) in Figure 2.4. However, as the Si NMR spectrum of this compound showed a lack of peak at -78 ppm or -67 ppm, which usually indicate a  $T_8$  system, it can be inferred that the reaction was unsuccessful in producing a POSS cube.

The IR spectrum is also in agreement with the unsuccessful formation of the POSS cube due to the lack of a Si-O-Si broad region at 1026 cm<sup>-1</sup>. There is however, a sharp peak at 1680 cm<sup>-1</sup> indicating the presence of the C=O group of the aldehyde. The lack of C-O-C bending peak at around 724 cm<sup>-1</sup>, which would indicate the presence of a dioxolane group [42], also indicates that the product had reverted back to the aldehyde starting material. A peak is observed at 686 cm<sup>-1</sup> which may indicate the presence of a C-Br bond, suggesting that the product obtained was in fact the staring material 4-bromobenzaldehyde.

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#### 2.4 The Synthesis of a POSS Based ZIF Component

The synthesis of an imidazole terminated POSS molecule, ImPOSS, began with the initial synthesis of CIPOSS. This was attempted through two different procedures based on the scheme seen in Figure 2.14, where the most notable difference seen between the procedures is the reaction duration and the use of a catalyst.



**Figure 2.14**: The synthetic pathway for the general synthesis of CI-POSS, where two different synthetic attempts were made. For the first attempt i: MeOH, conc HCI, RT, 48 hours, ii: di-n-butyltin dilaurate, RT, 48 hours. For the second attempt, steps occur in a tandem fashion, where i & ii: MeOH, conc HCI, 40°C, 2 weeks.

The first synthetic procedure was based on the 4 day literature procedure, published by Marciniec and coworkers, where (3-chloropropyl)trimethoxysilane was added slowly to a solution of dry methanol and concentrated HCI [43]. This was left to stir at room temperature for a period of 48 hours when a catalyst, di-n-butyltin dilaurate, was added. This solution was left to stir for a further 48 hours, after which small amounts of a white crystalline product had formed. This was collected via vacuum filtration to give CIPOSS in a 1.42% yield, compound **4**. This yield was extremely low with respect to the literature values reported at 35%. Despite the low yield of this reaction, the product collected was crystalline and the <sup>1</sup>H NMR spectrum displayed the peaks expected for CIPOSS, in accordance with reported data; a triplet at 0.81 ppm, a quintet at 1.88pm, and a triplet at 3.54 ppm, all with equal integrations. The <sup>13</sup>C spectrum also displayed the expected peaks for CIPOSS with three peaks at 9.37, 26.28, and 47.02 ppm, representing the three

different carbon environments on the propyl chain. The  $^{29}$ Si spectrum provided confirmation that the T<sub>8</sub> cube had formed, despite the low yield, as a peak was observed at - 67.08 ppm which is in accordance with the published data for CIPOSS [43].

Additional attempts of this synthesis produced amorphous gel-like solids, where no crystalline precipitate was observed throughout the reaction. The physical nature of the amorphous gel like solid indicated that a random polymeric mixture of siloxane compounds may have been produced and the attempts were deemed unsuccessful [44 - 45]. Despite the first successful synthesis, low yields or amorphous gels were seen for any subsequent reactions and, thus for the successful synthesis of ImPOSS, other higher yielding methods were explored.

The second procedure for the synthesis of CIPOSS followed a more recent synthesis published by Chen, Zhou and coworkers in 2015 which avoided the use of a catalyst [46]. This saw a solution of dry methanol, concentrated HCI and (3-chloropropyl)trimethoxy silane stirred at 40 °C for a period of 2 weeks. After 2 days, a white precipitate could be seen which gradually increased in amount throughout the duration of the reaction. The precipitate was collected to give CIPOSS in a 39% yield, compound **5**, a significant increase upon the previous synthetic endeavour. Analysis of the NMR spectra, shown in Figure 2.15, determined that CIPOSS had been produced, with <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si all in accordance with published data. A peak at 2.18 ppm in the <sup>1</sup>H spectrum can be attributed to acetone impurities from incomplete drying of the NMR tube.



**Figure 2.15**: The <sup>1</sup>H (i), <sup>29</sup>Si (ii), and <sup>13</sup>C (iii) NMR spectral data for CIPOSS, achieved from the synthetic route established in 2015 by Chen, Zhou and coworkers. All spectra show the desired peaks for CIPOSS, where residual solvent peaks from CDCl<sub>3</sub> and acetone can be seen in (i) and background noise from the glass NMR tube can be seen in (ii).

In addition to NMR data, FTIR data also confirmed the successful synthesis with peaks observed at 2981 - 2854 cm<sup>-1</sup> and 1454 - 1242 cm<sup>-1</sup>, indicative of alkyl C-H vibrations, and others at 1192 - 932 cm<sup>-1</sup> and 527 cm<sup>-1</sup>, indicating the presence of a siloxane system.

Due to the increased amount of product, XRD data was obtained and the crystal structure was compared to that of published data, Figure 2.16.



**Figure 2.16 (above):** The powder XRD spectrum for CIPOSS between the region of 5-50°, as predicted from the single crystal data published by Marciniec and coworkers [44]. **(Below)**: The obtained powder XRD spectrum for CIPOSS, where definite similarities can be seen between the experimental and the published spectra.

The next reaction in the series, the synthesis of ImPOSS, was published by Zhang and coworkers and can be seen in Figure 2.17 [17]. It began with a solution of imidazole and NaOH in water. The water was removed under reduced pressure at 100°C to give an off-

white solid upon cooling. This was then redissolved in anhydrous acetonitrile, where CIPOSS was added drop-wise. This solution was stirred at room temperature for a period of 48 hours. The solution was then filtered and the filtrate was collected. The solvent was removed from the filtrate under reduced pressure to give an off white solid upon standing. This solid was subject to NMR analysis, though it proved to be sparingly soluble in both CDCl<sub>3</sub> and DMSO.



**Figure 2.17**: The synthetic pathway for the synthesis of ImPOSS. i: H<sub>2</sub>O, NaOH, 100°C. ii: CH<sub>3</sub>CN, RT.

Analysis of the compound through <sup>1</sup>H NMR spectroscopy showed the peaks expected for a POSS cube with terminal propyl chain groups, however the relative integrations of these peaks and chemical shifts were not all in accordance with that of published data for the desired product. Peaks were observed at 0.78, 1.87 and 3.55 ppm, all of which with equal integrations, which correspond to the three CH<sub>2</sub> groups on the propyl chain. These peaks are expected for both the product and the starting material, CIPOSS, however, the chemical shifts do not accurately correlate to those published for ImPOSS which are expected at 0.44, 1.67, 3.43, 6.96 and 7.60 ppm [17]. As the chemical shift values observed for the product are in agreement with those published for CIPOSS, and those experimentally obtained in Figure 2.15 (i), it can therefore be assured that ImPOSS has not been successfully synthesised. Interestingly, additional peaks can also be seen at 7.18 ppm, with an integration of 2H, and 7.69 ppm, with an integration of 1H relative to each other, however these do not match to those of the CH<sub>2</sub> peaks. From published values, it can be thought that these chemical shifts and integrations correspond to an imidazole molecule [47]. This addition information suggests that imidazole and CIPOSS exist both in the collected material as the necessary integrations for ImPOSS are not observed, whereas those for CIPOSS are. It may therefore have been beneficial to consider a potential separation step for the crude material to determine if this was in fact the case.

The published procedure for this reaction does not state any difficulties in the substitution of the CI group on the propyl chain for the imidazole molecule. As repeat attempts gave similar results, the troublesome reaction could be attributed to the step involving anhydrous THF. If the imidazole and NaOH solution was not completely dehydrated, water could be introduced to the proceeding step. Additionally, if the step was not completely anhydrous, for example leaks in the flask around the septum and balloon area or the THF became contaminated before use, then the reaction would be unsuccessful due to the possibility of the reaction between the primary halogenoalkane and water. Therefore, for a potentially successful synthesis of ImPOSS, it must be of upmost importance that the anhydrous step is free from any moisture and that the preceding NaOH step is successful.

#### 2.5 Conclusions

The synthesis of OCS was attempted through two methods; one functionalising OPS in the para position of the phenyl ring, the other designing a functionalised trichlorosilane to produce a POSS cube.

The first method saw the successful synthesis of p-I<sub>8</sub>OPS from OPS, following a procedure highlighted for its selectivity of the position of substitution, directing subsequent functionalisation symmetrically outwards from the corners of the POSS cube [10]. The next reaction saw the lithiation of p-I<sub>8</sub>OPS, deemed to be moderately successful. The following carboxylation attempt of this moisture sensitive intermediate were however unsuccessful. It is thought that the problematic area resides within either the carboxylation following the lithiation or within the work-up procedure, where other solvent systems could be explored to precipitate OCS in a more prominent way. As the carboxylate groups on OCS have the ability to form hydrogen bonds, it may be important to explore the use of non-polar solvents.

The second method centred around the idea that the corners could be functionalised before the formation of the silsesquioxane centre. This saw the synthesis of 2-(4-bromophenyl)-1,3-dioxolane [37], where optimum conditions to achieve the purest and highest yield of product were determined. The following reaction synthesised a Grignard reagent as a precursor for a functionalised trichlorosilane molecule. A dark solution was observed 24 hours into the Grignard reaction, suggesting positive results [40]. The solution was then reacted with SiCl<sub>4</sub> with the intention of synthesising a phenyl dioxolane functionalised trichlorosilane. This molecule was then reacted similarly to that of well known OPS procedures. NMR analysis of the final product indicated that the dioxolane was no longer present and that the compound had reverted to 4-bromo-benzaldehyde, confirmed by <sup>29</sup>Si NMR and FTIR, showing the absence of a silsesquioxane system. The

POSS cube synthetic procedure may have deprotected the dioxolane due to the addition of BZTMAOH, a basic catalyst. This would facilitate the deprotection under the harsher experimental circumstances required to produce the  $T_8$  cube. It may be beneficial to consider alternative methods that do not inadvertently enable the deprotection of the dioxolane without producing the  $T_8$  cube.

The synthesis of ImPOSS was attempted from CIPOSS [17], employing two similar procedures to synthesise CIPOSS, both giving the desired product in varying yields. The 4 day procedure involving the catalyst di-n-butyltin dilaurate gave CIPOSS in a 1.42% yield. An alternative synthesis, involving a stirring solution at 40°C for two weeks, gave CIPOSS in a 39% yield [46]. The synthesis of ImPOSS was then attempted, the synthetic procedure was however deemed unsuccessful, with NMR spectra showing the starting materials; CIPOSS and imidazole. The faults can be identified within the moisture sensitive step seen in Figure 2.17 (ii). Future attempts would see alternative methods of maintaining a water free atmosphere. It has also been theorised that all reactants, specifically imidazole, should be purchased new before the attempted reaction or purified before use to ensure that the sodium exchange step in Figure 2.17 (i) is successful.

Various organic pathways which aim to synthesise hybrid linkers have been presented. Although the synthetic methods were unsuccessful at obtaining the final product, various perspectives of silsesquioxane chemistry have been explored and improvements in the methods have been identified which can be employed in future work. If OCS and ImPOSS could be obtained in a crystalline form suitable for XRD analysis, more detailed structural information could be obtained. Following this, the desired functionalised POSS molecules would be suitable monomers for subsequent reaction, attempting to incorporate the silsesquioxane molecules, as octadentate linkers, in either a metal organic framework or a zeolitic imidazolate framework.

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#### 2.6 References

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Chapter 3: An Investigation Into the Synthesis of Various MOFs and ZIFs

### 3.1 Background and Aims

The synthesis of various extended frameworks, particularly the porous materials of MOFs and ZIFs, have been achieved through a wide range of experimental approaches. It should be noted that there is no absolute way in which the synthesis of porous materials must be investigated, rather that different approaches have produced a range of materials. Some researchers decide to investigate through a 'trial and error' approach though a systematic design process [1], some focus upon modification of existing procedures [2] and newer strategies are beginning to adopt an 'out of the box' approach where structures are modified post-crystallisation [3, 4].

The strategies are usually in accordance with three main criteria, as outlined by Yaghi and coworkers [5]. Firstly, the organic linkers must have the appropriate attributes which facilitate the assembly of the skeleton of the structure, that is the ability to coordinate more than once to metal centres. Secondly, the synthesis must be adaptable for derivatives of the original building block, which is arguably where the idea of modification and systematic design originates. Thirdly, products that are synthesised must be crystalline to facilitate XRD characterisation.

It has become apparent that procedures have become slightly standardised to include the same basic reactants; a metal salt to create the metal centre, an organic molecule capable of forming metal-organic bonds, solvent molecules to facilitate the reaction and potentially act as a coordinating molecule, and a base to deprotonate the organic linker and initiate the formation of metal-organic bonds [6 - 8].

A common approach to systematically investigate various linkers, metals, and solvents to produce porous materials is to decide on an existing motif or skeleton upon which the new frameworks will be based. Many have digressed from the structure of MOF-5, one of the few known MOFs to show permanent porosity and exist as an isoreticular series, e.g. IRMOF-1 [9, 10]. Experimental conditions are then established to determine how potential structures can be efficiently synthesised; these new procedures are commonly based on the conditions used in the original synthesis. As the nature of most MOFs and ZIFs causes them to be insoluble, it is necessary that their assembly is achieved in a single step procedure [5]. The conditions of this single step procedure must sustain a balance between being mild enough to maintain the functionality and structure of the linker but reactive enough to facilitate the creation of metal-organic bonds [11]. Typically, the synthesis of MOFs and ZIFs has been achieved through the self assembly of structures as a result of thermodynamic conditions [12]. However, one reason to use such high temperatures is to facilitate the deprotonation of the organic linker with a weaker base [13], where more recent procedures have conditions which include the use of a stronger base and need not be dependant upon the temperature of the reaction [14]. This simple experimental change shows how the 'standard' procedures for synthesising these materials are changing and expanding with ongoing research. Many other synthetic factors influence the resulting structure of MOFs and ZIFs, their porosities, and any resulting functionalities they may posses.

Considering all of the previously mentioned ideas, the aim of the work reported in this chapter was to investigate the synthetic conditions used for the production of various different types of frameworks and how to approach the synthesis of new materials, relative to future POSS focussed endeavours. A select few conditions have been implemented as continuous themes to investigate. For example, zinc, in the form of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, has been chosen as a key metal to investigate due to its success in synthesising variety of materials including MOF-5, ZIF-8, and MOF-177 [15 - 17]. Other factors including; room

temperature vs heated synthesis, solvent systems, various metal salts, carboxylic and imidazole linkers, and reaction lengths will also be investigated with the hopes of determining ideal experimental conditions for the eventual synthesis of frameworks which incorporate metal centres and molecules derived from POSS. In addition to determining ideal experimental conditions, this chapter will also explore how a wide range of linkers and metals can be investigated simultaneously, through a systematic approach, in the hopes of establishing a general procedure in which POSS based linkers can be incorporated.

### 3.2 The Synthesis of MOF-5

The synthesis of MOF-5 followed a procedure reported by Fang and coworkers suggesting that, by varying certain experimental properties, the interpenetration of the resulting MOF-5 structure can be altered. These variations in experimental properties include the grinding of samples prior to analysis, the grinding duration, period of drying, reaction length, temperature, water content, and molar ratios of reactants and solvents [18]. With this in consideration, this small series of experiments was aimed at investigating the effect that differing the quantities of water in the synthetic procedure had upon the interpenetration of the product structure, according to powder XRD spectra.

The synthesis began with dissolving benzene-1,4-dicarboxylic acid, H<sub>2</sub>BDC, and  $Zn(NO_3)_{2}$ ·6H<sub>2</sub>O in anhydrous DMF as a standard solution. This standard solution was used to make five samples in polyethene bottles where a varying amount of deionised water, 0 - 200 µl, was added to each, Table 3.1. These were then heated in the oven at 120°C for 48 hours, at which point colourless crystals were collected, washed with anhydrous DMF and returned to the oven for a further 24 hours to dry. The samples were examined through powder XRD analysis. A further sample was prepared which followed

the published procedure, with regard to the amount of water added, to produce the typical interpenetrated MOF-5 material.

Compound Number	Amount of water / µl	Percentage yield / %
A1	0	80.67
A2	50	79.68
A3	100	81.29
A4	150	70.32
A5	200	84.58
A (Reference)	180	71.72

**Table 3.1**: The percentage yields of all synthesised MOF-5 samples based on the initial amount of  $Zn(NO_3)_2$  used and equation 1. The compound numbers are assigned according to the varying amounts of water added.

$$Zn(NO_3)_2 \cdot 6H_2O + XH_2O + 3H_2BDC \rightarrow ZnO_4(BDC)_3 + YH_2O + 8HNO_3$$
(1)

From Table 3.1, it can be noted that the percentage yields remain relatively constant and within the range of 70 - 85% for all compounds. The powder XRD pattern for these compounds can be seen in Figure 3.1, where the relative intensities of certain peaks can indicate certain properties of the material. For this material, there are two values that can be obtained from the peaks within the pattern; the intensity ratio of the peak at  $9.7^{\circ}$  to  $6.8^{\circ}$  the R<sub>1</sub> value and the intensity ratio of the peak at  $13.8^{\circ}$  to  $6.8^{\circ}$  the R<sub>2</sub> value. The lower the R<sub>1</sub> value, the more porous the resulting material is and the higher the surface area [19, 20]. In addition to this, a high R<sub>2</sub> value indicates the higher the interpenetration of the material, which is especially the case when the value of R<sub>1</sub> is low [18].

The synthesis from which this procedure is adapted states that the optimal reaction temperature is  $120^{\circ}$ C, and that a lower temperature would produce an unknown species and higher would increase the R<sub>1</sub> value. It also describes an ideal reaction length of 30 - 48 hours, where outside of these times an increased R<sub>1</sub> value would be observed and

therefore reduce the porosity and surface area of the material. Therefore, as previously stated, these reaction conditions were implemented and followed to ensure that only the amount of water added would affect the resulting material. It is notable that the addition of water in the synthetic procedure is necessary to achieve an interpenetrated structure, and that the amount of which will affect the peak observed at 20.6°. This trend can be observed within Figure 3.1, as the peak at 20.6° can be seen to increase in intensity from samples A1 to A5, which also have increasing amounts of water.



Figure 3.1: The powder XRD pattern of samples A - A5 containing varying amount of water.

It can be seen that compound A4 displays a profile with broad peaks, indicating low crystallinity within the sample where determining  $R_1$  and  $R_2$  values becomes non-viable.

Compound	Value at 6.8°	Value at 9.7°	Value at 13.8°	R <sub>1</sub>	R <sub>2</sub>
Α	26.3	34.0	22.2	1.29	0.84
A1	25.9	112.8	37.0	4.35	1.42
A2	24.3	108.3	38.1	4.44	1.56
A3	31.2	18.2	31.9	0.58	1.02
A5	1.6	99.9	72.5	62.43	45.31

**Table 3.2**: The 2 $\theta$  values observed at 6.8°, 9.7°, and 13.8° for all compounds, excluding A4, and their respective R<sub>1</sub> and R<sub>2</sub> values.

As a value of  $R_1$  that is lower than 1, observed by a peak with a higher intensity at 6.8° than 9.7°, indicates a material with a higher surface area, it can be deemed that compound A3, followed by compound A, has the highest theoretical surface area of all the samples and can be seen in Table 3.2. These compounds contain 100 µl and 180 µl of water respectively. Compounds A1, A2 and A5 can be thought to have the lowest surface area of all the samples due to the high than 1  $R_1$  values. With this being said, a higher than 1  $R_1$  value can also be attributed to a sample which has been incompletely dried, which may explain the discrepancies seen within the amount of water added and  $R_1$  values observed.

As mentioned, the  $R_2$  value obtained can be an indication of the interpenetration within the structure, although  $N_2$  adsorption analysis and thermogravimetric analysis (TGA) would be required to confirm this. The peak at 13.8° corresponds to the reflections observed from the (400) plane within a cubic MOF-5 structure, where a non-interpenetrated structure has a low intensity. As the (400) planes are half of the (200) planes, a high intensity of the 13.8 peak is though to correspond to an increased amount of interpenetration within the structure. From Figure 3.1, compound A5 is the only synthesised samples which has an  $R_2$  value much greater than 1, suggesting that the structure is highly interpenetrated and may also be incompletely dried.

The original paper that reported the amount of water and the resulting interpenetration of the material found that the optimum amount of water to be added was 180  $\mu$ l, where lower amounts would result in an unknown phase and greater would result in impurities [18]. Compound A3, with 100  $\mu$ l of water, displayed low R<sub>1</sub> and high R<sub>2</sub> values and is predicted to have the highest surface area of all of the synthesised products. Compound A5, with 200 µl of water added, displayed exceptionally high R values and is predicted to have the lowest surface area of all synthesised products, possibly due to containing higher amount of impurities from the higher amounts of water added. Compounds A1 and A2 both have a broad pattern which does not correspond to the predicted MOF-5 spectra, perhaps in agreement with the theory that low amounts of water produces an unknown phase. As compound A3, with 100 µl of water, produced the best match to that of MOF-5, it suggests that this investigation was unable to replicate that of the original paper which reported this data, but has shown the synthesis of crystalline material that contains lower amounts of water than thought necessary. Nonetheless, an interesting exploration route has been identified which can be employed with other synthetic procedures to investigate the effect of experimental details, which may not just be limited to the organic linker and metal, on resulting structures.

# 3.3 The Room Temperature Synthesis of a Crystalline Material with a Tridentate Ligand

The following reaction was aimed at investigating the room temperature synthesis of a MOF and can be seen in Figure 3.2. The reaction involves a tridentate organic linker, 1,3,5-benzenetricarboxylic acid (H<sub>3</sub>BTC), combined with Zn(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O in ethanol. The procedure published by Yaghi and coworkers, from which this synthesis is adapted, discusses a previous attempt of the synthesis in which a two dimensional framework is achieved from the use of pyridine as the deprotonating agent [21]. It is suggested that this

base is not able to fully deprotonate the organic linker, thus producing a two dimensional network. Therefore, to produce a three dimensional extended network, the stronger base of triethylamine should be implemented.



**Figure 3.2**: The reaction scheme for the room temperature synthesis of a MOF from H<sub>3</sub>BTC and zinc nitrate hexahydrate.

The reaction began with dissolving the metal salt and H<sub>3</sub>BTC, with a ratio of 1 : 2, in ethanol inside a vial which was then placed into a larger vessel containing triethylamine. The whole system was sealed and allowed to stand at room temperature for a period of 7 days. Upon the sealing of the system, a white precipitate had developed almost instantly at the interface of the surface of ethanol and the air. This suggests that the reaction began fairly quickly upon exposure to the base. After 7 days, the white solid was collected and washed with ethanol and dried at room temperature for XRD analysis. The product collected was given the name B1 and was in a form of a fine white powder.

The powder XRD pattern of B1 can be seen in Figure 3.3 where a reasonably high amount of background noise and perhaps spectral overlay are present. It is clear that the sample contains a crystalline material, however the obtained pattern does not coincide with that published for  $Zn_2(BTC)(NO_3) \cdot (H_2O)(C_2H_5OH)_5$ . The published diffraction pattern for this MOF has peaks at 8°, 10.5°, and 13.5° attributed to the (011), (111), and (102) *hkl* planes respectively. It can be seen that this pattern does not contain these specific initial reflections, suggesting that a different structure has been synthesised. There are however peaks within the spectrum which suggest that ZnO is present, observed at 32°, 35°, and

36° [22]. The remaining overlapping peaks within the pattern could be a result of the organic ligand, BTC.



Figure 3.3: Powder XRD pattern of B1; a material synthesised at room temperature,

consisting of an aromatic tridentate organic linker and zinc metal centres.

The FT-IR spectrum of this product can be seen in Figure 3.4 and displays the peaks expected for this MOF. Peaks at 1435 cm<sup>-1</sup> and 1572 cm<sup>-1</sup> are seen for the asymmetric and symmetric vibration of the deprotonated BTC organic linker, with C-H peaks observed at 2950 cm<sup>-1</sup>. The C=O peak of BTC is also seen at 1631 cm<sup>-1</sup>. The lack of peaks between 1730 and 1690 cm<sup>-1</sup> indicates a deprotonated BTC molecule, confirming that the addition of triethylamine has facilitated this complete deprotonation. The strong peak at 1361 cm<sup>-1</sup> confirms the presence of a nitrate group. In addition to these, the peaks at 3400 cm<sup>-1</sup> and 1046 cm<sup>-1</sup> indicate the presence of water and ethanol solvent molecules respectively.



**Figure 3.4**: FT-IR spectrum of B1, where peaks from the deprotonated organic linker can be found at, 2950, 1572 and 1435 cm<sup>-1</sup>, in addition to signals from solvent molecules.

Although the XRD pattern for B1 does not indicate that the desired MOF was synthesised, the FT-IR spectrum suggests that triethylamine was successful in deprotonating the organic linker, which was a main objective for this section. It also suggests the presence of the correct solvent molecules and ligands associated with this structure, with a high likeness to the published data. It has been demonstrated that a room temperature synthesis may be applicable to future work so long as the deprotonating agent is sufficient. This can be supported by other studies that have used trialkyamine bases as deprotonating agents in a room temperature synthesis. For example the synthesis of ZIF-8 and ZIF-67, frameworks which contain Zn and Co metal centres respectively and 2methylimidazole, have been synthesised in a similar method [23]. For this particular synthesis however, larger crystals would be required to confirm the specific structure through single crystal XRD, confirming the validity of a room temperature synthesis.

### 3.4 A Systematic Approach for the Heated Synthesis of MOFs and ZIFs

The reactions involved in this experimental series comprise an investigation into the various combinations of ligands, both carboxylate and imidazole based, and metal salts. To ensure consistency, the separate reaction procedures for imidazole based linkers and carboxylate linkers will not be altered. Instead, three different organic molecules for each of the two types of organic linkers will be investigated, with six linkers in total. The ratios of metal to ligands, solvent systems, reaction temperatures and lengths remained constant.

The carboxylate synthesis involved a total of 15 samples, where each linker in Figure 3.5 was combined with each of six metal salts, Table 5.1, where quantities can be found in Section 5.11. Each compound was labelled as a product of the 'C' synthetic procedure, with a specific number. The solvent system was pure DMF with 180  $\mu$ l of water. The samples were heated at 90°C for 48 hours, where after 24 hours crystals had developed for the majority of samples. The solutions were filtered, washed with DMF, and allowed to dry in a fume hood for a further 24 hours.



**Figure 3.5**: The carboxylate linkers investigated in this reaction series; i) benzene-1,4dicarboxylic acid, H<sub>2</sub>BDC, ii) benzene-1,3,5-tricarboxylic, H<sub>3</sub>BTC, and iii) benzene-1,2,4,5tetracarboxylic acid.

All samples, C1 - C15, were prepared and submitted for XRD analysis. All obtained spectra displayed no long range order and it was determined that the samples were of an amorphous nature. It is interesting to note that even though sample C6 was collected as a crystalline material no specific XRD pattern with long range order was obtained, indicating that the material was not of an ordered nature. As no other samples displayed such long range order, the majority of which were not of a crystalline material nature but powdered, it can be concluded that this specific systematic approach was unsuccessful at producing ordered frameworks.

The imidazole synthesis was adapted from the previously mentioned carboxylate series. Each imidazole linker, seen in Figure 3.6, was combined with each metal salt shown in Table 5.1 to give a total of 15 samples. The solvent system involved pure DMF and sodium formate was added to each sample. The samples were then heated at 90°C for a period of 24 hours, after which they were removed. The solutions were then filtered, washed with DMF, and allowed to dry in a fume hood for a further 24 hours.



**Figure 3.6**: The imidazole based linkers investigated in this reaction series i) imidazole, ii) 2-methylimidazole and iii) 4-methylimidazole

Unfortunately, all imidazole samples were collected in low yields, with many samples unable to be collected in crystalline forms and for others, no product had formed. For this reason, XRD analysis was not applicable and no patterns were collected.

Future attempts at synthesising ZIFs and MOFs through a heated process would require a different experimental procedure, perhaps involving an alternative solvent system,

deprotonating agent, reaction length and temperature. For these two particular series, a systematic approach was ineffective at producing framework structures, highlighting the importance of a more individually tailored experimental procedure with regard to imidazole or carboxylate linker and metal.

# 3.5 A Systematic Approach for the Room Temperature Synthesis of MOFs

The final reaction series that was investigated was comparable to the metal-carboxylate reactions discussed in Section 3.4 with regard to the metals and linkers used. This series differed however due to the room temperature synthesis and solvent system involved. The carboxylate linkers involved are depicted in Figure 3.5 and the 5 metal salts can be found in Table 5.1.

This series of experiments was adapted from a room temperature synthesis similar to that published by Yaghi and coworkers for the synthesis of MOF-199 [13]. The procedure involved a carboxylate linker to metal ratio of 1:2 in a solvent system containing ethanol, DMF and water in equal ratios. To this solution, triethylamine was added and the resulting solutions were allowed to stand at room temperature for 72 hours.

After a period of 72 hours, two of the samples had developed crystals, both of which involved the organic linker of benzene-1,2,4,5-tetracarboxylic acid. Unfortunately, the other thirteen remaining samples did not develop product suitable for XRD analysis. The products obtained are listed in Table 3.3.

Linker		Metal	Description	Compound Number
HO HO HO O O O O O O HO	Zinc	Colourless rhomboid crystals	D1	
	OH.	Cobalt	Pink small crystals Purple-red crystals	D2



The crystals obtained for D1 were colourless and those that were suitable for single crystal XRD analysis were of a rhomboid shape. The crystal data for this structure can be seen in Table 3.4, where it was found that the sample was of a triclinic crystal system and had a space group of *P*1. This obtained crystal data was in accordance with that of a previously published crystal structure, containing the same linker and metal, which was obtained from a different room temperature procedure [24].

Crystal Data			
Chemical formula	C <sub>10</sub> H <sub>18</sub> O <sub>14</sub> Zn <sub>2</sub>		
Mr	492.98 g mol <sup>-1</sup>		
Crystal System	Triclinic		
Space Group	<i>P</i> 1		
Unit Cell Dimensions	a = 6.8418 (3) Å	b = 7.9869 (3) Å	c = 16.6414 (7) Å
	α = 101.968 (2) °	$\beta=92.335$ (2) $^{\circ}$	γ = 93.111 (2) °
Volume	887.03 (6) Å <sup>3</sup>		
Z	2		
Calculated Density	1.846 g cm <sup>-3</sup>		
Adsorption Coefficient	2.774 mm <sup>-1</sup>		
Temperature	100 K		

 Table 3.4: The crystal data obtained for compound D1; colourless rhomboid shaped crystals.

The crystal structure for D1 was obtained, the unit cell of which is displayed in Figure 3.7. It can be seen that the unit is asymmetric, where two different Zn metal centres are joined by a water molecule which acts as a bridging molecule. Carboxylate groups, belonging to two distinct benzene-1,2,4,5-tetracarboxylic acid molecules, also act as bridging molecules between the two Zn centres. These carboxylate groups join to the next Zn centre in the structure through the carboxylate group in the relative para position, leaving the carboxylate groups in positions 2 and 5 of benzene-1,2,4,5-tetracarboxylic acid uncoordinated. It is interesting to note that both of the oxygen atoms on the carboxylate group are coordinated to a Zn centre, where one bridges to both centres and the other coordinates to only one. The metal centres display a distorted octahedral geometry, where water molecules supplement the remaining coordination spaces after joining to the organic ligand.



**Figure 3.7**: A perspective view of the unit cell structure of D1, viewed along the b\* axis. The two independent zinc atoms can be seen (purple) to be coordinated to the organic ligand, through the oxygen (red) atoms on the carboxylic acid group, the carbon (grey) and hydrogen (white) atoms can also be seen. Coordinated water molecules can also be seen.

In addition to the single unit cell, the 3:3:3 structure along the b axis can be seen in Figure 3.8. This whole structure is thought to be mono-dimensional with a close network of hydrogen bonding which supports the crystal packing, however, the strength of this network is thought to depend upon the amine used in the synthesis [24].



**Figure 3.8:** The 3:3:3 crystal structure of D1 viewed along the b axis, showing the alternative linking of organic linkers and two zinc metal centres, where the unit cell is indicated.

The experimental procedure for the synthesis of D1 differed to that of the published procedure by Rotondo and coworkers who initially reported this crystal structure. For example, the published procedure uses melamine whereas the stronger base of triethylamine was used in the experimental procedure. This suggests that a weaker base would still be appropriate for a room temperature synthesis. However, during the experimental procedure, crystals had developed and were collected after 3 days; this was quicker than during the published procedure which took 5 days. This suggests that the stronger base of triethylamine decreased the length of the reaction. The solvent systems used also differed, however both were water based. The ligand : metal ratio used in the experimental procedure was 1 : 2, whereas the published procedure used a 1 : 1 ratio, this suggests that the metal could have been used in a lower ratio without causing alteration to the crystal structure. However, regardless of variances in experimental

procedures, both resulted in the same crystal structure from a simple water based synthesis which was independent of extreme hydrothermal conditions.

During single crystal analysis of D1, through a crystal structure database search, another structure, identified and published by Fabelo and coworkers, was found to have a very similar nature [25]. This structure contained the same ligand of benzene-1,2,4,5tetracarboxylic acid and a different metal centre in cobalt. It was found that this crystal data was indeed very similar to that of D1, adopting a triclinic crystal system and a space group of P1. In addition to this, the arrangement of ligand, metal and water molecules in the unit cell appeared to be identical to D1 and resembled that seen in Figure 3.7, where the purple octahedral atoms were cobalt instead of zinc. For sample D2, two types of crystals had been produced in the same reaction vessel; purple-red crystals and smaller crystals of a light pink colour. Both of the crystals, consisting of benzene-1,2,4,5tetracarboxylic acid and a cobalt metal centre, were unsuitable for single crystal analysis with regard to shape and clarity. However, the light pink crystals were suitable for powder XRD analysis and were separated and prepared, the profile of which can be seen in Figure 3.9. The material is of a crystalline nature from the clear reflections that can be seen. However, this powder diffraction pattern does not correlate to the predicted powder pattern obtained from the crystal structure that was published by Fabelo & coworkers. It can therefore be concluded that D2 is not the structure identified by Fabelo which also resembles D1.

### pXRD of Compound D2



Figure 3.9: The powder XRD pattern of the light pink crystals of compound D2.

Unfortunately, the darker purple-red crystals were in such low yield that they could not be collected for powder XRD analysis. To obtain the full crystal data for D2, larger single crystals that were of a higher quality would have to be grown.

### 3.6 Conclusions

The investigation was designed to investigate the reaction conditions associated with the synthesis of various frameworks, and the synthetic strategies used to potentially produce new structures. This work supports the eventual aim of this entire thesis; to synthesise a framework that contains a POSS derived linker.

The first part of this Chapter, Section 3.2, investigated the effect that varying the amounts of water in the synthetic procedure had upon the resulting crystal structure, analysed
through the discrepancies seen within the reported XRD patterns. It was clear that, while keeping other experimental conditions consistent, differing amounts of water resulted in different crystal structures. The compounds synthesised with low amounts of water resulted in unknown phases. One synthesised compound had low crystallinity, as evidenced by a broader XRD profile while another showed similar results to those published for the study carried out by Fang and co-workers [18]. This series of experiments investigated one of many experimental factors that could be varied to result in differences within the crystal structures. This idea could be applied to future POSS based investigations, where other factors could be explored; reaction duration, temperature, solvent system, pH, drying period and reactant ratios.

Section 3.3 reports a short investigation into the room temperature synthesis of a MOF using a tridentate organic linker and metal salt. It was determined, through powder XRD and FT-IR analysis, that room temperature procedures were viable when they included a strong enough base to act as a deprotonating agent. This suggests that, while solvothermal techniques would be used initially to synthesise any POSS based frameworks, room temperature synthesis could also be appropriate and would be dependent on the stability of the linker with a strong base.

The final part of this Chapter, Sections 3.4 and 3.5, investigated various synthetic procedures for the synthesis of new frameworks and are reported. Organic linkers and metal salts were combined in three different procedures to produce a wide array of potential products. Amongst the total of 45 samples that were attempted to be synthesised, two distinct compounds, D1 and D2, were obtained through a room temperature synthesis. Compound D1, containing benzene-1,2,4,5-tetracarboxylic acid and zinc metal centres, was analysed through single crystal XRD. The resulting crystal structure was obtained and identified as that of a previously published crystal structure [24]. This compound was originally synthesised at room temperature, and though specific

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experimental details varied, the procedures had analogous details. The other compound synthesised, D2, was analysed through powder XRD as the crystals were not applicable to obtain single crystal data. This compound was found to be of a crystalline nature, however further in-depth structural analysis is required to determine its exact nature.

The systematic approaches of Sections 3.4 and 3.5 have shown that, through the combination of various metal salts and organic linkers, an array of potential frameworks can be investigated over a short period of time. This systematic approach could be applied to POSS based molecules in the initial search for any potential frameworks that they may synthesise through either a solvothermal procedure or room temperature investigation. Following this, experimental optimisation could then be achieved through the variation of specific experimental factors, as investigated in Sections 3.2 and 3.3, including water content, solvent systems, the nature of the deprotonating agent and the temperature.

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#### Chapter 4: Final Conclusions

The field of materials science, more specifically porous frameworks, is rapidly expanding. This can be attributed to the vast amount of possible structures which have an abundance of potential applications from their inherent diversities. There is however a prominent lack of research around POSS based compounds, their abilities to form ordered framework structures, their potential applications and the heightened properties that they may posses. However, a limited number of compounds have currently been investigated, which describe how POSS molecules show great potential as hybrid compounds that can impart their heightened chemical properties upon materials that they comprise.

This thesis has focussed around the idea that POSS compounds, when functionalised appropriately, could be potential MOF or ZIF linkers. From this idea, the synthesis of two framework appropriate POSS compounds has been attempted. This thesis has discussed the synthetic attempts of these compounds, OCS and ImPOSS, with promise shown in the synthesis of both. These compounds were chosen because of their ability to bond to metal centres through either the terminal carboxylate or imidazolate groups.

The synthesis of OCS was attempted through two distinct methods, the first involving the modification of OPS, the second involving the synthesis of a functionalised trichlorosilane molecule. The first reaction series saw the successful synthesis of both OPS and I<sub>8</sub>OPS. However, the eventual synthesis of OCS was deemed unsuccessful. This was not a completely futile synthetic attempt however; faults within the procedure were identified and appropriate improvements were theorised. These involve investigations into the use of alternative solvents systems in which OCS may be insoluble, and therefore precipitate from, and other slight modifications of the experimental procedure.

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The second reaction series saw an extensive scheme beginning with the synthesis of 2-(4-bromophenyl)-1,3-dioxolane. Following this, through a Grignard reaction then addition of SiCl<sub>4</sub>, a functionalised trichlorosilane molecule was attempted to be synthesised, ready to be involved in the synthesis of a  $T_8$  molecule. This followed a general procedure for the synthesis of OPS, however the harsh reaction conditions did not produce the expected product and the starting materials were recovered. Therefore, for any future attempts at the synthesis of OCS, it may be more beneficial to focus upon the first method which involves the modification of OPS.

The synthesis of ImPOSS was attempted, beginning with the synthesis of CIPOSS. This series showed promise, indicated by the successful synthesis of CIPOSS. The structure of which was confirmed by NMR, IR and XRD analysis, which were in agreement with that of published data. The synthesis of ImPOSS was however challenging due to the water sensitive nature of the reagents within the procedure. It has been suggested that any future attempts focus upon the maintenance of a water free environment.

In addition to these specific POSS compounds, future work could involve the organic synthesis of other types of POSS molecules which may vary in terminal corner groups. So long as the ability to join to metal centres through multiple sites on the molecule is retained, the possible variations in appropriate POSS molecules becomes immense.

The synthetic procedure for various MOFs was also explored in this thesis. A variety of factors were investigated, where their effect on resulting structures was of high importance. While the attempts were mostly for reference and for applications to further studies of POSS molecules, it is important to note that water content, reaction temperature, choice of ligand and metal, solvent system and reactant ratios all had a significant influence upon the resulting structures. Studies similar to these can be incorporated to any future investigations of the potentially octa-dentate ligand. These

could be implemented to help to refine and optimise the synthesis to gain the appropriate reaction conditions for POSS-based MOFs.

In addition to this MOF based study, a systematic approach for the combination of various linkers and metals was also investigated. This approach, through 3 different methods, combined 6 linkers with 5 metals to give a product range of 45 possible materials. While only two products were found to be of crystalline nature, the scope of investigation remained vast with regard to possible combinations, aided by a short investigation time. Again, this could be applicable to future work to investigate various POSS molecules with numerous metal centres. This approach could establish successful combinations of POSS linkers with metals which could then be optimised by the variations in experimental procedures, as also briefly investigated.

To conclude, the procedures described in Chapter 2 offer various approaches to the synthesis of framework appropriate POSS compounds. In addition to this study, Chapter 3 also discussed strategies for the optimisation of the synthetic procedures for MOFs and ZIFs and identified possible approaches for the synthesis of new porous frameworks. The first initial stages of combining POSS molecules with the vast sector of materials chemistry has been developed through the designing of framework structures with potential porosity. With this, a truly hybrid notion has been touched upon, marking a pathway for similar future endeavours.

#### 5.1 Characterisation

<sup>1</sup>H and <sup>13</sup>C NMR spectra were collected on both a Bruker Avance 300 MHz and 400 MHz spectrophotometer using CDCl<sub>3</sub> or DMSO as solvent. <sup>29</sup>Si NMR spectra were collected on a Bruker Avance 400 MHz spectrophotometer using CDCl<sub>3</sub>, DMSO or D<sub>2</sub>O as solvent. FTIR spectra were recorded on a Thermo Nicolet Diamond ATR spectrophotometer. Powder x-ray diffraction spectra were obtained using a Bruker D8 Advance X-Ray Diffractometer operating with a CuKα source. Single crystal data was obtained using a Bruker eco D8 Quest single crystal diffractometer.

#### 5.2 The Synthesis of Octaphenylsilsesquioxane (OPS) [1]



Phenyltrichlorosilane (8 mL, 21.6 g, 50 mmol) was dissolved in toluene (100 mL), shaken with deionised water (50 mL) and stirred for 20 minutes. The aqueous layer was removed and extracted with toluene (2 x 30 mL). All toluene layers were combined and washed with deionised water (30 mL). 40% methanolic benzyltrimethylammonium hydroxide (3.32 mL)

was added and the mixture was heated to reflux for 24 hours. The heat was removed and the solution was stirred for 4 days at room temperature as a white precipitate formed. The solution was then filtered to give 4.9670 g (4.80 mmol, 75.0%) of octaphenyl-silsesquioxane (compound **1**), as a white crystalline solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 7.76 (d, 2H, Ar-H, J = 6.0 Hz), 7.35 - 7.57 (m, 3H, Ar-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 127.9 (3°, Ar), 128.2 (3°, Ar), 129.1 (3°, Ar), 134.2 (4°, Ar). IR ( $\nu$  / cm<sup>-1</sup>): 3053 - 2996 (C-H, w), 1591 (C=C, m), 1430 (C=C, m), 1121 - 1048 (Si-O, s), 996 (Si-O, s), 736 (C-H, s), 694 (C-H, s).



lodine monochloride in DCM (25.5 mL, 1.0 M, 0.0255 mol), under the flow of nitrogen, was cooled to - 40 °C with an ethylene glycol, ethanol and dry ice bath. A refrigerant system maintained the temperature at - 40 °C throughout the course of the reaction. Octaphenyl-silsesquioxane (2.3691 g, 4.59 mmol) was dissolved in dry DCM (30 mL) and added drowse (4 mL/min) to the 3 neck flask through a pressurised dropping funnel. As HCI was produced it was flushed from the system with flowing N<sub>2</sub>. The reaction was stirred at - 40 °C for 24 hours and then allowed to return to room temperature over the following 24 hours. A sodium metabisulphite solution (25 mL, 1.0M) was added to quench the reaction and the solution went from dark red to yellow upon neutralisation. The organic layer was collected and washed with deionised water (4 x 50 mL) gradually changing from yellow to colourless after each separation. The organic layer was dried over anhydrous magnesium sulphate, filtered and the solvent evaporated to give a white solid. This was then dissolved into THF (25 mL) and precipitated into cold methanol (100 mL). The precipitate was collected under vacuum filtration and 1.1646 g (12.4 %) of a white solid was obtained

(compound **2**). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 7.64 - 7.66 (d, 2H, Ar-H, J = 6.0 Hz), 7.30 - 7.35 (d, 2H, Ar-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 128.1 (4°, Ar), 134.1 (3°, Ar), 135.6 (3°, Ar), 137.2 (4°, Ar). IR ( $\nu$  / cm<sup>-1</sup>): 3024 - 2991 (C-H, w), 1573 (C=C, m), 1477 (C=C, m), 1078- 1002 (Si-O, s), 987 (Si-O, s), 802 (C-H, s), 739 (C-H, s).

#### 5.4 The Attempted Synthesis of Octa(carboxyphenyl)silsesquioxane



Anhydrous THF (40 mL) was added to a flask containing octaiodophenylsilsesquioxane (0.47 g, 0.24 mmol) under N<sub>2</sub>. The system was then cooled to - 80 °C using a methanol and liquid N<sub>2</sub> bath. <sup>n</sup>BuLi (3.5 mL, 1.6 M in hexane) was added drop wise to the stirring solution and thus was allowed to stir for 4 hours, after which time, the formation of a faint yellow precipitate was seen. The system was warmed to room temperature.  $CO_2$  and N<sub>2</sub> were then allowed to flow through the solution simultaneously for 5 minutes where upon the N<sub>2</sub> flow was stopped and  $CO_2$  flow continued for 2.5 hours. To quench the reaction, methanol (5 mL), water (10 mL), and HCI (2M, 3.5 mL) were added to give a cloudy

solution. The solvents were removed under reduced pressure to a volume of approximately 5 mL. This acidic solution was filtered to give a colourless gel. This was washed with DCM (4 x 5 mL) and then water (4 x 5mL). The gel was then redissolved in THF, where water was then added drop-wise to initiate precipitation. Following a filtration, no solid was collected and the filtrate was sealed and frozen to initiate precipitation. After 3 days, no precipitation had formed and the solvent was removed under reduced pressure to yield a colourless oil, NMR and FT-IR analysis of which showed a failure to isolate the desired product with a mixture of impurities observed.

#### 5.5 The Synthesis of 2-(4-bromophenyl)-1,3-dioxolane



4-bromobenzaldehyde (3 g, 16.2 mmol) and *p*-toluenesulfonic acid (50 mg, 0.290 mmol) were dissolved in toluene (50 mL). Ethylene glycol (1.5 mL, 0.0268 mol) was added and the solution was refluxed under Dean-Stark conditions at 150 °C for 9 hours to azeotropically remove water. The resulting solution was cooled to room temperature and washed with a saturated solution of Na<sub>2</sub>CO<sub>3</sub> (2 x 30 mL). The aqueous phase was extracted with ethyl acetate (3 x 30 mL), combined with the previous organic phase and dried over magnesium sulphate. The solution was filtered and the solvent was removed under a high pressure vacuum to give 2.966 g (12.9 mmol, 79.5%) of 2-(4-bromophenyl)-1,3-dioxolane (compound **3**). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm:) 7.51 - 7.53 (d, 2H, Ar-**H**, J = 6.0 Hz), 7.35 - 7.38 (d, 2H, Ar-**H**, J = 9 Hz), 5.78 (s, 1H, -OPhCHO-), 4.00 - 4.14 (m,

4H, RO-CH<sub>2</sub>CH<sub>2</sub>-OR). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm:) 65.3 (2°, RO-CH<sub>2</sub>CH<sub>2</sub>-OR), 103.0 (3°, OPhCHO), 123.3 (4°, Ar), 128.3 (3°, Ar), 131.5 (3°, Ar), 137.0 (4°, Ar).

# 5.6 Attempted Synthesis of a T<sub>8</sub> cube from 2-(4-bromophenyl)-1,3dioxolane

2-(4-bromophenyl)-1,3-dioxolane (2.0260 g, 8.844 mmol), magnesium (0.4299 g, 17.6 mmol) and a single iodine crystal were dissolved in dry THF (30 mL) and refluxed under  $N_2$  for 24 hours to give a black solution. The mixture was transferred by syringe into a separate flask containing SiCl<sub>4</sub> (1.0152 ml, 8.844 mmol) dissolved in toluene (30 mL). The solution was left to stir at room temperature for 96 hours to give a transparent orange solution. Deionised water (25 mL) was added and the solution was stirred for 30 minutes. yielding a light precipitate. The aqueous layer was separated and washed with 3 x 20 mL of toluene. All organic phases of toluene were then combined to give a dark orange solution. Methanolic benzyltrimethylammonium hydroxide (40%, 0.5 mL) was added to the toluene mixture to give a yellow solution. The mixture was heated to reflux for 24 hours to yield a dark brown solution which was allowed to stir at room temperature for 48 hours. After this period the flask and contents were frozen to initiate precipitation. After an 8 month period the flask was allowed to warm to room temperature and the solvent was removed under reduced pressure to yield an orange-brown oil which solidified after 3 days at room temperature. NMR analysis determined the product to be the initial starting material of 4-bromobenzaldehyde.

(CIPOSS)



This synthesis was attempted through two different procedures.

**Procedure 1 [3]**: To methanol (150 mL) and concentrated HCl (5 mL), (3-chloropropyl)trimethoxy silane (13.7 mL, 0.075 mol) was added over a period of 10 minutes with stirring. The solution was allowed to stir at room temperature for 48 hours, at which point di-n-butyltindilaurate (0.15 g, 141 μL) was added. The solution was allowed to stir for a further 48 hours, at which point a white crystalline product had formed. This was collected through vacuum filtration to give 0.1368 g (1.42 %) of octakis(3-chloropropyl)silsesquioxane (compound 4). <sup>1</sup>H NMR (ppm): 3.54 (t, 2H, ClCH<sub>2</sub>), 1.88 (qui, 2H, CH<sub>2</sub>), 0.81 (t, 2H, SiCH<sub>2</sub>). <sup>13</sup>C NMR (ppm): 9.37 (2°, SiCH<sub>2</sub>), 28.28 (2°, CH<sub>2</sub>), 47.02 (1°, ClCH<sub>2</sub>). <sup>29</sup>Si NMR (ppm): -67.08 (s, Si-O-Si). IR (ν / cm<sup>-1</sup>): 2953 (C-H, w), 1456 - 1269 (C-H, w), 1187 - 1074 (Si-O, s), 995 (Si-O, s), 764 (C-H, m), 688 (C-H, s) 527 (Si-O, m).

**Procedure 2 [4]**: To a solution of anhydrous methanol (350 mL) and concentrated HCI (15 mL), (3-chloropropyl)trimethoxy silane (20 mL, 0.109 mol) was slowly added. The flask was sealed and allowed to stir at 40°C for a period of 2 weeks. A white crystalline

precipitate had developed after 48 hours of stirring. The precipitate was then collected to give 5.5335 g of octakis(3-chloropropylsilses-quioxane) in a 39.0% yield (compound **5**). <sup>1</sup>H NMR (ppm): 3.54 (t, 2H, ClCH<sub>2</sub>), 1.88 (t, 2H, CH<sub>2</sub>), 0.81 (t, 2H, SiCH<sub>2</sub>). <sup>13</sup>C NMR (ppm): 9.32 (2°, SiCH<sub>2</sub>), 28.23 (2°, CH<sub>2</sub>), 46.98 (2°, ClCH<sub>2</sub>). <sup>29</sup>Si NMR (ppm): -67.08 (s, Si-O-Si). IR (*v* / cm<sup>-1</sup>): 2998 (C-H, w), 1440 - 1237 (C-H, w), 1145 - 999 (Si-O, s), 993 (Si-O, s), 742 (C-H, m), 688 (C-H, s) 527 (Si-O, m).

#### 5.8 The Attempted Synthesis of N-propylimidzaolyIPOSS (ImPOSS)



NaOH (0.32 g, 8.0 mmol) and imidazole (0.54 g, 8.0 mmol) were dissolved in deionised water (20 mL). The solvent was removed under reduced pressure at 100°C to give a pale yellow powder. This was redissolved in anhydrous acetonitrile (30 mL). To this solution, Cl-POSS (1.00 g, 0.96 mmol) dissolved in anhydrous acetonitrile (20 mL) was added dropwise. The colourless solution was sealed and allowed to stir at room temperature for 48 hours. The solvent was removed under reduced pressure to give a colourless oil, yielding 0.9974 g of a white-yellow solid upon standing for an hour. NMR analysis determined the product to be CIPOSS and imidazole and the synthesis therefore unsuccessful.

#### 5.9 The Synthesis of the Interpenetrated MOF-5

Benzene-1,4-dicarboxylic acid (0.1843 g, 1.11 mmol) was dissolved in anhydrous DMF (10 mL). Zinc nitrate hexahydrate (0.4399 g, 1.48 mmol) was also dissolved in anhydrous DMF (10 mL). These two solutions were combined and stirred for 10 minutes. This was repeated a total of 6 times and to each was added various amounts of deionised water (0 - 200  $\mu$ l). Solutions were heated in polyethene bottles for 48 hours at 120 °C. Samples were removed from the oven and allowed to cool to room temperature. Each was filtered and dried with DMF (10 mL) to give colourless crystals which were then returned to the oven to dry at 120 °C for 24 hours. The crystals collected varied from 0.2357 - 0.2834 g (70.32 - 84.58%) and were analysed via powder XRD (compounds **A - A5**). IR ( $\nu$  / cm<sup>-1</sup>): 3600-3200 (O-H, b), 1604 (C=O, s), 1425 (C=C, m), 750 (C-H, s).

#### 5.10 The Synthesis of a MOF From a Tridentate Ligand and Zinc Salt

Zinc nitrate hexahydrate (0.3 g, 10 mmol) and benzene-1,3,5-tricarboxylic acid (0.105 g, 0.5 mmol) were dissolved in ethanol (10 mL) in a 28 mL vial. This vial was placed into a larger vessel with the lid off. Triethylamine (2 mL) was added to the larger vessel, the system was sealed and the triethylamine was allowed to diffuse through the ethanol solute at room temperature. A white solid precipitate formed on the surface of the ethanol-air interface upon the sealing of the system. After 7 days, the solid was collected through vacuum filtration, washed with ethanol (4 x 10 mL), and allowed to dry at room temperature for 24 hours. A white powder was collected with a mass of 0.3965 g (97.9 %) (compound **B1**). IR ( $\nu$  / cm<sup>-1</sup>): 3400 (O-H, b), 2980 (C-H, w), 1631 (C=O, s), 1572 (C=C, m), 1435 (C=C, m), 1361 (N-O, s), 1046 (C-O, m).

#### 5.11 The Heated Synthesis of Various MOFs and ZIFs

A series of carboxylate organic linkers were each dissolved in DMF (10 mL); benzene-1,4dicarboxylic acid (0.1661 g, 1 mmol), benzene-1,3,5-tricarboxylic acid (0.2105 g, 1 mmol), and benzene-1,2,4,5-tetracarboxylic acid (0.2542 g, 1 mmol). A separate series of metal salts, Table 5.1, were each dissolved in DMF (10 mL).

Metal Salt	Formula
Zinc nitrate hexahydrate	Zn(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O
Calcium nitrate tetrahydrate	Ca(NO <sub>3</sub> ) <sub>2</sub> · 4H <sub>2</sub> O
Cobalt nitrate hexahydrate	Co(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O
Nickel nitrate hexahydrate	Ni(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O
Copper nitrate hemi(pentahydrate)	Cu(NO <sub>3</sub> ) <sub>2</sub> · 2.5H <sub>2</sub> O

Table 5.1: The hydrated metal salts investigated in experiments 5.11 and 5.12.

Each carboxylate solution was combined with each metal salt solution in a polyethene bottle, giving a total of 15 different combinations of ligand and metal. 180  $\mu$ l of deionised water was then added to each mixture which were mixed for 5 minutes before being sealed and then heated at 90 °C for 48 hours. Crystals had developed after 24 hours. Once removed, crystals were filtered, washed with DMF, and allowed to dry at room temperature for 48 hours. Tables 5.2 - 5.4 show the yield, product description and compound number for all 15 combinations of carboxylate ligands and linkers.

Linker	Metal	Product Yield by Mass	Description	Compound Number
НО 🏑 О	Zinc	53.1%	white powder	C1
	Calcium	50.7%	white powder	C2
	Cobalt	78.8%	purple powder	C3
	Nickel	43.5%	light green powder	C4
о≁он	Copper	28.3%	blue powder	C5

Table 5.2: The product information for samples containing the bidentate linker H<sub>2</sub>BDC.

Linker	Metal	Product Yield by Mass	Description	Compound Number
HOFO	Zinc	46.4%	colourless small crystals	C6
	Calcium	7.4%	white powder	C7
О ОН	Cobalt	77.0%	purple powder	C8
	Nickel	71.6%	light green powder	C9
	Copper	82.7%	blue powder	C10

Table 5.3: The product information for samples containing the tridentate linker H<sub>3</sub>BTC.

Linker	Metal	Product Yield by Mass	Description	Compound Number
0 0	Zinc	66.3%	white powder	C11
но	Calcium	18.9%	white powder	C12
но он	Cobalt	75.7%	purple powder	C13
Щ ~ Д	Nickel	65.3%	light green powder	C14
0 0	Copper	64.3%	green powder	C15

**Table 5.4**: The product information for samples containing the linker benzene-1,2,4,5-tetracarboxylic acid.

This procedure was repeated for a series of imidazole molecule, where each linker was dissolved in DMF (10 mL); imidazole (0.2859 g, 4.2 mmol), 2-methylimidazole (0.3449 g, 4.2 mmol) and 4-methylimidazole (0.3449 g, 4.2 mmol). A separate series of metal salts, Table 5.1, were each dissolved in DMF (10 mL). Each imidazole solution was combined with each metal salt solution in a polyethylene bottle, totalling 15 samples. To each of these samples, sodium formate (0.14 g, 2 mmol) was added. These samples were then heated at 90°C for 24 hours. The solutions were then removed, filtered, and washed with DMF and allowed to dry at room temperature for 24 hours. The information for the products collected from this synthesis can be seen in Table 5.5, where all other combinations did not result in any product.

Linker	Metal	Product Yield by Mass	Description	Compound Number
Imidazole	Zinc	17.9%	white powder	C16
	Cobalt	23.3%	dark purple powder	C17
	Copper	28.5%	navy blue powder	C18
2-methyl	Zinc	16.1%	white powder	C19
Imidazole	Nickel	12.3%	green powder	C20
	Copper	15.8%	brown powder	C21
4-methyl	Zinc	22.4%	white powder	C22
imidazole	Copper	32.7%	brown powder	C23

**Table 5.5:** The product information for the imidazole synthesis of experiment 5.11.

#### 5.12 The Room Temperature Synthesis of Various Carboxylate MOFs

A series of carboxylate organic linkers were each dissolved in a 1:1:1 solvent system of water, ethanol and DMF (9 mL); benzene-1,4-dicarboxylic acid (0.1661 g, 1 mmol), benzene-1,3,5-tricarboxylic acid (0.2105 g, 1 mmol), and benzene-1,2,4,5-tetracarboxylic acid (0.2542 g, 1 mmol). A separate series of metal salts, Table 5.1, were each dissolved in the same solvent system (9 mL). Each carboxylate solution was combined with each metal salt solution in a polyethene bottle, giving a total of 15 different combinations of ligand and metal. 0.5 mL of triethylamine was then added to each bottle which were then mixed, sealed and left for 72 hours at room temperature. Upon addition of triethylamine, most solutions had formed a cloudy precipitate which began to separate upon standing. Solutions were then filtered and dried to give either single crystals, a micro crystalline powder, or, in some cases no product was collected. The successful metal and ligand combinations and obtained product information can be seen in Table 5.6.

Linker	Metal	Description	Compound Number			
но Но Он	Zinc	Colourless rhomboid crystals	D1			
но П ОН	Cobalt	Pink small crystals Purple-red crystals	D2			

Table 5.6: The product information for the synthesised compounds from experiment 5.12.

#### 5.13 References

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Appendix

# A.1 Octaphenylsilsesquioxane (OPS)































## A.4.2 CIPOSS <sup>13</sup>C NMR in CDCl<sub>3</sub>









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A clear colourless rhomboid plate-like specimen of  $C_{10}H_{18}O_{14}Zn_2$ , with approximate dimensions of 0.080 mm x 0.280 mm x 0.280 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

¥	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	
Temperature/	F	-	-	-	-	-	-	F	-	-	F	F	-	F	F	-	-	-	-	-	-	-	-	-	F	-	-	
Current/mA	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	
Voltage/kV	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	
Vavelength/Å	0.71076	0.71076	0.71076	0.71076	0.71076	0.71076	0.71076	0.71076	0.71076	0.71076	0.71076	0.71076	0.71076	0.71076	0.71076	0.71076	0.71076	0.71076	0.71076	0.71076	0.71076	0.71076	0.71076	0.71076	0.71076	0.71076	0.71076	
Time/s	8	8	8	8	8	8	8	8	8	8	8	8	8	8	-	-	-	-	-	-	-	-	-	-	-	-	-	
Frames	107	107	107	107	107	108	108	108	107	107	108	108	107	107	56	56	56	56	56	56	56	56	56	56	56	56	56	
Width/°	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	
×ر»	54.74	54.74	54.74	54.74	54.74	54.74	54.76	54.74	54.74	54.74	54.74	54.74	54.74	54.74	54.74	54.74	54.74	54.74	54.74	54.74	54.76	54.74	54.74	54.74	54.74	54.74	54.74	
¢/°	45	06-	-180	90	0	270	-29.18	90	102	-54	180	0	0	-156	45	06-	-180	90	0	270	-29.18	06	102	-54	180	0	0	
w/°	-136.94	-136.94	-136.94	-136.94	-136.94	-183.67	-237.01	-183.67	-197.92	-197.92	-183.67	-183.67	-197.92	-197.92	-136.94	-136.94	-136.94	-136.94	-136.94	-183.67	-237.01	-183.67	-197.92	-197.92	-183.67	-183.67	-197.92	
20/°	35.81	35.81	35.81	35.81	35.81	-10.17	-63.51	-10.17	-25.17	-25.17	-10.17	-10.17	-25.17	-25.17	35.81	35.81	35.81	35.81	35.81	-10.17	-63.51	-10.17	-25.17	-25.17	-10.17	-10.17	-25.17	
dx/mm	38.662	38.662	38.662	38.662	38.662	38.662	38.662	38.662	38.662	38.662	38.662	38.662	38.662	38.662	38.662	38.662	38.662	38.662	38.662	38.662	38.662	38.662	38.662	38.662	38.662	38.662	38.662	
Axis	Omega																											

Table A.5.1: Data collection details for D1

A total of 2287 frames were collected. The total exposure time was 3.56 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 54355 reflections to a maximum  $\theta$  angle of 33.23° (0.65 Å resolution), of which 6794 were independent (average redundancy 8.000, completeness = 99.6%, R<sub>int</sub> = 3.79%, R<sub>sig</sub> = 2.23%) and 6126 (90.17%) were greater than  $2\sigma(F^2)$ .

Unit cell The final cell constants of  $\underline{a} = 6.8418(3)$  Å,  $\underline{b} = 7.9869(3)$  Å,  $\underline{c} = 16.6414(7)$  Å,  $a = 101.968(2)^{\circ}$ ,  $\beta = 92.335(2)^{\circ}$ ,  $\gamma = 93.111(2)^{\circ}$ , volume = 887.03(6) Å<sup>3</sup>, are based upon the refinement of the XYZ-centroids of 9794 reflections above 20  $\sigma(I)$  with 5.011° < 2 $\theta$  < 66.36°. Scaling Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.733.

The final anisotropic full-matrix least-squares refinement on F<sup>2</sup> with 325 variables converged at R1 = 2.33%, for the observed data and wR2 = 5.63% for all data. The goodness-of-fit was 1.046. The largest peak in the final difference electron density synthesis was 0.628 e<sup>-</sup>/Å<sup>3</sup> and the largest hole was -0.816 e<sup>-</sup>/Å<sup>3</sup> with an RMS deviation of 0.103 e<sup>-</sup>/Å<sup>3</sup>. On the basis of the final model, the calculated density was 1.846 g/cm<sup>3</sup> and F(000), 500 e<sup>-</sup>.

## Table A.5.2: Sample and crystal structure for D1

Chemical formula	$C_{10}H_{18}O_{14}Zn_2$				
Mr	492.98 g mol <sup>-1</sup>				
Crystal System	Triclinic				
Space Group	<i>P</i> 1				
Unit Cell Dimensions	a = 6.8418 (3) Å	b = 7.9869 (3) Å	c = 16.6414 (7) Å		
	$\alpha = 101.968$ (2) °	$\beta$ = 92.335 (2) °	$\gamma=93.111$ (2) $^{\circ}$		
Volume	887.03 (6) Å <sup>3</sup>				
Z	2				
Calculated Density	1.846 g cm <sup>-3</sup>				
Adsorption Coefficient	2.774 mm <sup>-1</sup>				
Temperature	100 K				

Table A.5.3: Data collection and structure refinement for D1

Theta range for data collection	2.61 to 33.23						
Index ranges	-10<=h<	<=10, -12<=k<=12, -25<=l<=26					
Reflections collected	543						
Independent reflections	6795 [R(int) = 0.0379]						
Coverage of independent reflections	99.60%						
Absorption correction	Multi-scan						
Refinement method	Full-matrix least-squares on F <sup>2</sup>						
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)						
Function minimized	$\Sigma w(F_0^2 - F_c^2)^2$						
Data / restraints / parameters		6795 / 0 / 325					
Goodness-of-fit on F <sup>2</sup>		1.046					
$\Delta \sigma_{max}$		0.001					
Final B indices	6126 data; I>2σ(I)	R1 = 0.0233, wR2 = 0.0541					
	all data	R1 = 0.0285, wR2 = 0.0563					
Weighting achomo	$w=1/[\sigma^2(F_0^2)+(0.0251P)^2+0.6788P]$						
	where $P=(F_0^2+2F_c^2)/3$						
Largest diff. peak and hole	0.628 and -0.816 eA						
R.M.S. deviation from mean	0.103 eÅ						
Table A.5.4: Atomic coordinates and equivalent isotropic atomic displacement parameters

for D1

Table A.5.5: Bond lengths (Å) for D1

Zn01-O004	2.0417(9)	Zn01-O006	2.0488(9)
Zn01-O007	2.0534(9)	Zn01-000I	2.0556(9)
Zn01-O00A	2.1384(9)	Zn01-O008	2.2508(9)
Zn02-O00E	1.9909(9)	Zn02-O003	2.0133(8)
Zn02-000G	2.0440(10)	Zn02-O00D	2.0889(9)
Zn02-O008	2.1544(9)	Zn02-O00A	2.4357(9)
Zn02-C00S	2.5953(11)	O003-C00J	1.2734(13)
O004-H7	0.81(3)	O004-H14	0.82(3)
0005-C00L	1.2647(14)	O006-C00J	1.2435(14)
О007-Н8	0.84(3)	О007-Н9	0.81(2)
O008-H4	0.85(2)	O008-H11	0.85(3)
0009-C00N	1.2508(14)	000A-C00S	1.2656(13)
O00B-H10	0.84(2)	O00B-H16	0.74(3)
000C-C00L	1.2562(14)	000D-C00S	1.2688(14)
O00E-H3	0.78(2)	O00E-H6	0.75(3)
000F-C00N	1.2644(14)	000G-H5	0.81(2)
O00G-H18	0.83(3)	O00H-H15	0.82(3)
O00H-H17	0.82(3)	O00I-H12	0.79(3)
O00I-H13	0.85(3)	C00J-C00M	1.5025(15)
C00K-C00Q	1.3936(15)	C00K-C00M	1.3997(15)
C00K-C00N	1.5090(16)	C00L-C00P	1.5125(15)
C00M-C00Q	1.3946(15)	C00O-C00P	1.3900(15)
C00O-C00R	1.3986(15)	C00O-H2	0.93(2)
C00P-C00R	1.3995(15)	C00Q-C00K	1.3936(15)
C00Q-H1	0.962(18)	C00R-C00P	1.3995(15)
C00R-C00S	1.4908(15)		

	x/a	y/b	z/c	U(eq)
Zn01	0.30157(2)	0.90928(2)	0.31198(2)	0.00497(3)
Zn02	0.23499(2)	0.52835(2)	0.18966(2)	0.00495(3)
O003	0.30849(13)	0.67774(11)	0.11049(5)	0.00727(15)
O004	0.18920(14)	0.90122(12)	0.42301(6)	0.00895(16)
O005	0.20334(13)	0.15428(11)	0.56448(5)	0.00799(15)
O006	0.41889(14)	0.91598(11)	0.20128(5)	0.00860(15)
O007	0.54009(14)	0.05741(12)	0.37149(6)	0.00965(16)
O008	0.05443(13)	0.72585(11)	0.24846(5)	0.00586(14)
O009	0.81185(14)	0.80341(11)	0.13364(6)	0.00983(16)
<b>O00A</b>	0.43191(13)	0.67203(11)	0.31227(5)	0.00685(15)
O00B	0.71134(14)	0.48303(12)	0.05311(6)	0.00941(16)
000C	0.15726(13)	0.40415(11)	0.64857(5)	0.00847(15)
000D	0.23798(13)	0.43668(11)	0.29847(5)	0.00704(15)
000E	0.03226(15)	0.37643(12)	0.11590(6)	0.01195(17)
000F	0.91809(15)	0.07740(12)	0.15260(6)	0.01348(18)
000G	0.45320(15)	0.36877(13)	0.15343(6)	0.01141(17)
O00H	0.31233(15)	0.72146(12)	0.72254(6)	0.01181(17)
000I	0.12844(14)	0.10320(12)	0.29552(6)	0.01078(16)
C00J	0.39083(16)	0.82845(14)	0.13028(7)	0.00524(18)
C00K	0.64476(16)	0.97800(14)	0.05836(7)	0.00459(17)
COOL	0.23910(16)	0.31393(14)	0.59006(7)	0.00563(18)
COOM	0.45236(16)	0.91121(14)	0.06126(7)	0.00453(17)
C00N	0.80294(17)	0.95056(14)	0.11933(7)	0.00590(18)
C00O	0.31698(17)	0.42939(15)	0.46629(7)	0.00627(18)
C00P	0.37962(16)	0.40619(14)	0.54351(7)	0.00541(18)
C00Q	0.30932(16)	0.93307(14)	0.00283(7)	0.00538(18)
C00R	0.43613(16)	0.52295(14)	0.42270(7)	0.00510(18)
COOS	0.36391(16)	0.54636(14)	0.34025(7)	0.00517(18)

## Table A.5.6: Bond angles (°) for D1

O004-Zn01-O006	178.99(4)	O006-C00J-C00M	116.85(10)	O00A-Zn02-C00S	28.92(3)
O006-Zn01-O007	89.68(4)	C00Q-C00K-C00M	119.37(10)	Zn01-O004-H7	116.2(18)
O006-Zn01-O00I	88.81(4)	C00M-C00K-C00N	120.64(10)	H7-O004-H14	103.(2)
O004-Zn01-O00A	89.63(4)	O00C-C00L-C00P	117.10(10)	Zn01-O007-H8	114.0(16)
O007-Zn01-O00A	94.17(4)	C00Q-C00M-C00K	119.89(10)	H8-O007-H9	106.(2)
O004-Zn01-O008	89.81(3)	C00K-C00M-C00J	121.50(10)	Zn02-O008-H4	111.6(16)
O007-Zn01-O008	174.77(4)	0009-C00N-C00K	117.79(10)	Zn02-O008-H11	111.5(16)
O00A-Zn01-O008	80.61(3)	C00P-C00O-C00R	120.53(10)	H4-O008-H11	108.(2)
O00E-Zn02-O00G	93.06(4)	C00R-C00O-H2	118.7(12)	C00S-O00A-Zn02	82.56(7)
O00E-Zn02-O00D	104.54(4)	C00O-C00P-C00L	118.11(10)	H10-O00B-H16	110.(2)
O00G-Zn02-O00D	87.18(4)	C00M-C00Q-C00K	120.73(10)	Zn02-O00E-H3	121.1(17)
O003-Zn02-O008	88.53(3)	C00K-C00Q-H1	120.1(11)	H3-O00E-H6	108.(2)
O00D-Zn02-O008	87.61(3)	C00O-C00R-C00S	119.15(10)	Zn02-O00G-H18	113.3(18)
O003-Zn02-O00A	100.82(3)	O00A-C00S-O00D	121.14(10)	H15-O00H-H17	103.(2)
O00D-Zn02-O00A	57.79(3)	000D-C00S-C00R	118.99(10)	Zn01-O00I-H13	112.1(17)
O00E-Zn02-C00S	133.43(4)	O00D-C00S-Zn02	52.80(6)	O006-C00J-O003	126.08(10)
O00G-Zn02-C00S	87.61(4)	O004-Zn01-O007	89.70(4)	O003-C00J-C00M	117.02(10)
O008-Zn02-C00S	82.13(3)	O004-Zn01-O00I	92.06(4)	C00Q-C00K-C00N	119.97(10)
C00J-O003-Zn02	125.46(8)	O007-Zn01-O00I	98.42(4)	O00C-C00L-O005	124.70(10)
Zn01-O004-H14	114.3(18)	O006-Zn01-O00A	89.63(3)	O005-C00L-C00P	118.05(10)
C00J-O006-Zn01	134.53(8)	O00I-Zn01-O00A	167.30(4)	C00Q-C00M-C00J	118.41(10)
Zn01-O007-H9	112.6(16)	O006-Zn01-O008	90.74(3)	O009-C00N-O00F	124.15(11)
Zn02-O008-Zn01	96.55(3)	O00I-Zn01-O008	86.81(4)	000F-C00N-C00K	118.06(10)
Zn01-O008-H4	110.3(16)	O00E-Zn02-O003	96.91(4)	C00P-C00O-H2	120.7(12)
Zn01-O008-H11	118.8(16)	O003-Zn02-O00G	92.00(4)	C00O-C00P-C00R	119.32(10)
C00S-O00A-Zn01	127.76(7)	O003-Zn02-O00D	158.55(4)	C00R-C00P-C00L	122.46(10)
Zn01-O00A-Zn02	91.69(3)	O00E-Zn02-O008	99.70(4)	C00M-C00Q-H1	119.2(11)
C00S-O00D-Zn02	98.27(7)	O00G-Zn02-O008	167.07(4)	C00O-C00R-C00P	120.15(10)
Zn02-O00E-H6	120.8(19)	O00E-Zn02-O00A	161.65(4)	C00P-C00R-C00S	120.70(10)
Zn02-O00G-H5	115.9(17)	000G-Zn02-000A	91.03(4)	000A-C00S-C00R	119.85(10)
H5-O00G-H18	110.(2)	O008-Zn02-O00A	76.19(3)	O00A-C00S-Zn02	68.53(6)
Zn01-O00I-H12	116.9(18)	0003-Zn02-C00S	129.63(4)	C00R-C00S-Zn02	169.86(8)
H12-O00I-H13	107.(2)	O00D-Zn02-C00S	28.93(3)		

	U 11	U 22	U 33	U <sub>23</sub>	U <sub>13</sub>	U <sub>12</sub>
Zn01	0.00663(6)	0.00454(6)	0.00389(6)	0.00130(4)	0.00053(4)	-0.00008(4)
Zn02	0.00653(6)	0.00477(6)	0.00390(6)	0.00196(4)	0.00007(4)	-0.00045(4)
O003	0.0107(4)	0.0055(3)	0.0058(3)	0.0021(3)	0.0011(3)	-0.0021(3)
0004	0.0086(4)	0.0111(4)	0.0061(4)	-0.0003(3)	0.0021(3)	-0.0019(3)
O005	0.0083(4)	0.0065(3)	0.0087(4)	0.0011(3)	0.0010(3)	-0.0024(3)
O006	0.0129(4)	0.0087(4)	0.0037(3)	0.0010(3)	0.0012(3)	-0.0029(3)
0007	0.0098(4)	0.0090(4)	0.0100(4)	0.0027(3)	-0.0019(3)	-0.0015(3)
0008	0.0054(3)	0.0077(3)	0.0054(3)	0.0032(3)	0.0008(3)	0.0003(3)
O009	0.0131(4)	0.0056(3)	0.0108(4)	0.0030(3)	-0.0052(3)	0.0003(3)
O00A	0.0077(4)	0.0073(3)	0.0071(4)	0.0044(3)	0.0015(3)	0.0012(3)
O00B	0.0134(4)	0.0070(4)	0.0073(4)	0.0002(3)	-0.0002(3)	0.0006(3)
O00C	0.0091(4)	0.0078(4)	0.0085(4)	0.0014(3)	0.0038(3)	-0.0003(3)
000D	0.0081(4)	0.0075(3)	0.0053(3)	0.0015(3)	-0.0013(3)	-0.0010(3)
O00E	0.0132(4)	0.0071(4)	0.0153(4)	0.0045(3)	-0.0075(3)	-0.0036(3)
000F	0.0138(4)	0.0095(4)	0.0173(5)	0.0068(3)	-0.0100(3)	-0.0059(3)
000G	0.0123(4)	0.0134(4)	0.0101(4)	0.0047(3)	0.0027(3)	0.0046(3)
000H	0.0128(4)	0.0088(4)	0.0133(4)	0.0009(3)	0.0011(3)	0.0001(3)
0001	0.0130(4)	0.0065(4)	0.0127(4)	0.0024(3)	-0.0033(3)	0.0001(3)
C00J	0.0044(4)	0.0067(4)	0.0053(4)	0.0029(3)	0.0001(3)	0.0004(3)
СООК	0.0052(4)	0.0047(4)	0.0041(4)	0.0015(3)	-0.0005(3)	0.0000(3)
COOL	0.0049(4)	0.0074(4)	0.0051(4)	0.0032(3)	-0.0008(3)	-0.0010(3)
С00М	0.0061(4)	0.0045(4)	0.0034(4)	0.0019(3)	0.0004(3)	-0.0004(3)
C00N	0.0061(4)	0.0076(4)	0.0043(4)	0.0020(3)	-0.0006(3)	0.0002(4)
C00O	0.0056(4)	0.0083(4)	0.0051(4)	0.0024(4)	-0.0005(3)	-0.0014(4)
C00P	0.0055(4)	0.0061(4)	0.0049(4)	0.0021(3)	0.0010(3)	-0.0005(3)
C00Q	0.0056(4)	0.0058(4)	0.0052(4)	0.0023(3)	0.0000(3)	-0.0002(3)
COOR	0.0058(4)	0.0061(4)	0.0039(4)	0.0021(3)	0.0004(3)	0.0004(3)
COOS	0.0051(4)	0.0063(4)	0.0045(4)	0.0016(3)	0.0010(3)	0.0015(3)

Table A.5.7: Anisotropic atomic displacement parameters (Å2) for D1

 Table A.5.8: Hydrogen atomic coordinates and isotropic atomic displacement parameters

(Ų) for D1

	x/a	y/b	z/c	U(eq)
H1	0.177(3)	0.890(2)	0.0064(11)	0.008(4)
H2	0.194(3)	0.383(2)	0.4426(12)	0.014(5)
Н3	-0.061(3)	0.414(3)	0.0990(14)	0.025(6)
H4	-0.016(4)	0.692(3)	0.2837(15)	0.030(6)
Н5	0.516(3)	0.339(3)	0.1900(15)	0.026(6)
Н6	0.003(4)	0.289(3)	0.1228(15)	0.029(6)
H7	0.218(4)	0.983(3)	0.4598(16)	0.033(6)
H8	0.628(4)	1.001(3)	0.3881(15)	0.031(6)
Н9	0.593(3)	1.116(3)	0.3429(15)	0.027(6)
H10	-0.294(3)	0.446(3)	0.0017(15)	0.025(5)
H11	-0.021(3)	0.758(3)	0.2138(15)	0.029(6)
H12	0.180(3)	1.197(3)	0.3030(15)	0.030(6)
H13	0.070(4)	1.083(3)	0.2481(16)	0.033(6)
H14	0.069(4)	0.894(3)	0.4222(16)	0.036(7)
H15	0.248(4)	0.633(4)	0.7004(17)	0.039(7)
H16	-0.275(4)	0.578(3)	0.0625(16)	0.033(6)
H17	0.235(4)	0.774(3)	0.7535(16)	0.041(7)
H18	0.529(4)	0.405(3)	0.1227(17)	0.039(7)