Novel PMOs:
Studies in Periodic
Mesoporous Organosilicas

by

Wesley Whitnall

A thesis submitted in conformity of the requirements for the degree of Doctor of Philosophy
Graduate Department of Chemistry
University of Toronto

Copyright by Wesley Whitnall 2008
Abstract

Novel PMOs: Studies in Periodic Mesoporous Organosilicas

Wesley Whitnall, Doctor of Philosophy
Department of Chemistry, University of Toronto
2008

The field of mesoporous materials has been expanding rapidly in recent years, and has come to include a wide variety of different types of materials from organic to inorganic, as well as hybrid materials that encompass both worlds. The following account explores one type of mesoporous materials, specifically those consisting of silica with an attached organic group that have come to be known as periodic mesoporous organosilicas (PMOs). Much of the work here involves incorporating new types of organic groups into a mesoporous framework for the purpose of adding a useful functionality, either chemical or physical, to the material. Firstly it is shown that a borazine moiety can be successfully incorporated into a mesoporous material with a very high loading. It was further shown that once incorporated into the material many of the borazine moieties are available for further chemical reactions with acids and transition metals. Next, a new class of materials termed hybrid periodic mesoporous organosilicas (HPMOs) was developed that was able to circumvent many of the problems associated with PMO self-assembly. Now, using very simple techniques, virtually any type of silsesquioxane can be incorporated into a PMO, and the organic
group can be specifically at the surface of the pores, thereby maximizing its accessibility. And finally, a PMO is made that incorporates buckyballs, and it is shown that, given the right synthetic conditions, the buckyballs are homogeneously distributed throughout the material.
Acknowledgements

There are many people that I would like to thank for their help over the course of my work in this field. Firstly, I would like to thank Dr. Masakatsu Kuroki with whom I was able to work as an undergraduate in the Ozin labs. He provided me with my first introduction to the world of PMOs for which I am grateful. Next I would like to thank Dr. Tewodros “Teddy” Asefa, one of the first pioneers in PMO research whom I worked alongside in my first few years as a graduate student, and from whom I gained much insight into the field. I would also like to acknowledge the post-doctoral fellows that I have worked with over the years, namely Dr. Kai Landskron, William Hunks and Corrina Frietag, as well as fellow graduate students Benjamin Hatton, and Rebecca Voss, and undergraduate Jon Zhu. There are also the numerous post-doctoral fellows, graduate students, and undergraduate students who have come and gone from the Ozin labs over my years here. In particular I would like to single out Ludovico Cademartiri with whom I worked very closely on the C_{60}PMO project presented herein.

The people outside of the Ozin group that deserve my thanks are Dr. Hiltrud Grondey and Dr. Tim Burrows for their assistance with the solid-state and solution NMR respectively, Dr. Srebi Petrov for the PXRD patterns, and Dr. Neil Coombs for his work with the SEM, and STEM, without whom these projects could not have succeeded.
Mostly I would like to thank my supervisor Geoff Ozin, who was a constant source of inspiration, and capable of providing a seemingly endless supply of new and interesting ideas.
# Table of Contents

Abstract .......................................................................................................................... ii
Acknowledgements ........................................................................................................ iv
Table of Contents .......................................................................................................... vi
List of Abbreviations ..................................................................................................... ix
List of Schemes ............................................................................................................. x
List of Figures ................................................................................................................ xii
1. Introduction ............................................................................................................. 1
   1.1. Mesoporous Silicas ......................................................................................... 1
       1.1.1. MCM41 and Related Materials ................................................................. 1
       1.1.2. Modification of Mesoporous Silicas ....................................................... 3
   1.2. Periodic Mesoporous Organosilicas (PMOs) ................................................. 5
       1.2.1. Discovery of PMOs ................................................................................ 5
       1.2.2. Current Work ........................................................................................ 9
   1.3. Instrumentation and Analysis ....................................................................... 11
       1.3.1. PXRD .................................................................................................... 11
       1.3.2. Solid State NMR .................................................................................. 14
       1.3.3. Nitrogen Adsorption Isotherms ............................................................... 18
       1.3.4. SEM and STEM .................................................................................... 22
   1.4. References ....................................................................................................... 26
2. Borazine PMOs .......................................................................................................... 36
   2.1. Introduction ..................................................................................................... 36
   2.2. Results and Discussion .................................................................................. 38
       2.2.1. Precursor Synthesis ............................................................................. 38
       2.2.2. Material Synthesis ............................................................................... 39
       2.2.3. Effect of Catalyst ................................................................................. 42
       2.2.4. Reactivity of Material ........................................................................... 46
   2.3. Conclusions .................................................................................................... 48
   2.4. Experimental ................................................................................................. 48
2.4.1. Materials and Reagents ........................................................................ 48
2.4.2. N,N,N-trimethyl-B,B,B-trichloroborazine ........................................... 48
2.4.3. N,N,N-trimethyl-B,B,B-tris(triethoxysilylmethyl)borazine ................. 49
2.4.4. Self-Assembly in Acid Conditions (BN-PMOa) ................................. 50
2.4.5. Self-Assembly in Basic Conditions (BN-PMOb) ............................... 50
2.4.6. Reaction with Acid .......................................................................... 51
2.4.7. Characterization ............................................................................ 51
2.5. References .......................................................................................... 53

3. HPMOs .................................................................................................... 57
3.1. Introduction .......................................................................................... 57
3.2. Results and Discussion ......................................................................... 60
  3.2.1. Material Formation ......................................................................... 60
  3.2.2. Monolayer Orientation ................................................................... 63
  3.2.3. Monolayer Coverage ..................................................................... 68
  3.2.4. Pore Size Control .......................................................................... 69
  3.2.5. Reactivity .................................................................................... 73
3.3. Conclusions ......................................................................................... 75
3.4. Experimental ........................................................................................ 76
  3.4.1. Materials and Reagents ................................................................ 76
  3.4.2. Mesoporous Silica Synthesis ......................................................... 76
  3.4.3. Synthesis of Ethene PMO .............................................................. 77
  3.4.4. Synthesis of HPMOs .................................................................... 77
  3.4.5. Hydroboration of Ethene HPMO-1 and Ethene PMOs ...................... 78
  3.4.6. Hydrolysis of Residual Ethoxy Groups ........................................... 78
  3.4.7. Characterization ........................................................................... 78
3.5. References .......................................................................................... 79

4. C\textsubscript{60} PMOs .................................................................................... 84
4.1. Introduction ......................................................................................... 84
4.2. Results and Discussion ........................................................................ 87
  4.2.1. Self Assembly of Pure Precursor .................................................... 87
  4.2.2. Effect of Catalyst .......................................................................... 88
4.2.3. Reactivity of Material ........................................................................... 103
4.3. Conclusions ......................................................................................... 105
4.4. Experimental ....................................................................................... 105
  4.4.1. Materials and Reagents ............................................................... 105
  4.4.2. Synthesis of C\textsubscript{60} PMO Precursor 1 ............................... 106
  4.4.3. Synthesis of C\textsubscript{60}B50 ............................................................. 106
  4.4.4. Synthesis of C\textsubscript{60}A50 ............................................................. 107
  4.4.5. Reaction with Osmium Tetroxide ................................................. 107
  4.4.6. Characterization ........................................................................... 108
4.5. References.......................................................................................... 109

5. Conclusions and Future Work ............................................................... 113
  5.1. Conclusions ....................................................................................... 113
  5.2. Borazine PMO Future Work ............................................................... 115
  5.3. HPMO Future Work ........................................................................... 117
  5.4. C\textsubscript{60} PMO Future Work ............................................................. 118
  5.5. The Future of PMOs ........................................................................... 120
  5.6. References ........................................................................................ 125
List of Abbreviations

BTE - 1, 2-bistriethoxysilylethene
BTEA - 1, 2-bistriethoxysilylethane
BTH - 1, 6-bistriethoxysilylhexane
BTM - bistriethoxysilylmethane
BTPA - N, N-bis(triethoxysilylpropyl)amine
CP-MAS - cross-polarized magic angle spinning
CTAB - cetyltrimethylammoniumbromide
EDX - energy dispersive X-ray spectroscopy
FTIR - Fourier transform infrared
HPMO - hybrid periodic mesoporous organosilica
HPMO-1 - hybrid periodic mesoporous organosilica type 1
HPMO-2 - hybrid periodic mesoporous organosilica type 2
IR - infrared
MAS - magic angle spinning
NMR - nuclear magnetic resonance
P123 - (polyethyleneoxide)$_{20}$-block-(polypropyleneoxide)$_{80}$-block-(polyethyleneoxide)$_{20}$
PMO - periodic mesoporous organosilica
PMS - periodic mesoporous silica
PXRD - powder X-ray diffraction
SEM - scanning electron microscopy
STEM - scanning transmission electron microscopy
TEOS - tetraethylorthosilicate
THF - tetrahydrofuran
List of Schemes

Scheme 1.1. Method for the self-assembly of mesoporous silicas ..................... 2

Scheme 1.2. The generation of monochromatic X-rays via the impact of a high voltage electron on a metal atom ......................................................... 12

Scheme 1.3. Schematic showing Bragg diffraction of X-rays from an arbitrary crystal plane .............................................................................. 13

Scheme 1.4. A sample of crystal planes that will diffract X-rays in a 2D-hexagonal system ................................................................................ 14

Scheme 1.5. Schematic of the nature, and approximate location of the T and Q sites found in the $^{29}$Si MAS NMR of organosilicas. ......................... 18

Scheme 1.6. Hypothetical layering of gas molecules on specific sites of a solid substrate .................................................................................. 21

Scheme 1.7. Schematic illustrating a simplified model of an STEM, including the location of the various detectors .............................................. 23

Scheme 1.8. Electrons passing through a 2D hexagonal material. When the electrons pass through the [0,1] face many are able to penetrate through the entire material, making the pores visible in STEM (left). When the electrons pass through the [0,1] face the majority cannot penetrate through the material, and thus the material will appear dense in STEM. .................................................................................. 25

Scheme 2.1. Synthesis of the borazine based PMO precursor 1. .................... 39

Scheme 3.1. Possible binding motifs of silsesquioxanes in PMS or PMO host materials. ......................................................................................... 65

Scheme 4.1. The self-assembly of $C_{60}$ modified with 3-aminopropyltriethoxysilane to make a $C_{60}$PMO. ...................................................... 87
Scheme 4.2. Synthesis of the C\textsubscript{60}-PMO precursor. .................................................. 88
List of Figures

Figure 2.1. PXRD patterns of BN-PMOa (a) and BN-PMOb (b)...........................40

Figure 2.2. Nitrogen adsorption isotherms (top) and pore size distributions (bottom) for BN-PMOa (a) and BN-PMOb (b). ..............................................41

Figure 2.3. $^{29}$Si MAS NMR spectra of BN-PMOa (a) and BN-PMOb (b). .........43

Figure 2.4. $^{13}$C CP-MAS NMR spectra of BN-PMOa (a) and BN-PMOb (b).....44

Figure 2.5. $^{11}$B MAS-NMR spectra of BN-PMOa (a) and BN-PMOb (b).........45

Figure 2.6. FTIR spectra of BN-PMOa that has been surfactant extracted (a), then treated with a solution of HCl in diethyl ether (b), and finally treated with sodium borohydride (c). .........................................................47

Figure 3.1. $^{13}$C CP-MAS NMR of a PMS material after the addition of a single layer of BTE before base treatment (a), and after base treatment (b) (* indicates spinning sidebands). .........................................................61

Figure 3.2. $^{29}$Si MAS NMR of a PMS before treatment with a silsesquioxane (a), and after treatment with BTE silsesquioxane (b). .................................63

Figure 3.3. $^{29}$Si MAS NMR of a PMS material to which a layer of 2,5-bis(triethoxysilyl)-p-xylene was added. ..........................................................65

Figure 3.4. $^{29}$Si MAS NMR of a PMS that has been treated with 1,2-bis(triethoxysilyl)ethane (a), and a PMS that has been treated with 1,2-bis(triethoxysilyl)ethene (b). The arrows indicate the position of the $T_0$ site for each of the samples. It should be noted that the 1,2-bis(triethoxysilyl)ethene silsesquioxane that was used is a mixture of approximately 20 % of the cis isomer and 80 % of the trans isomer, and that binding through both ends should be favorable for the cis
isomer. If only the trans isomer were used then it is likely that the $T_0$ signal would be more intense.

**Figure 3.5.** PXRD patterns of PMS treated with: $\text{N,N-bis(triethoxysilylpropyl)amine (BTPA)}$ (a); $\text{bis(triethoxysilyl)methane (BTM)}$ (b); $\text{1,6-bis(triethoxysilyl)hexane (BTH)}$ (c); and refluxed in toluene in the absence of a silsesquioxane (d).

**Figure 3.6.** Nitrogen sorption isotherms (top) and pore size distributions (bottom) of a PMS from which the polymer template has been removed (a), and the PMS after the addition of one (b), two (c) and three (d) layers of BTEA.

**Figure 3.7.** These are TEM images of an HPMO after three treatments with BTEA (the scale bar on the top image represents 60 nm, and on the bottom image represents 30 nm).

**Figure 3.8.** $^{13}$C CP-MAS NMR of a PMS to which a layer of 1,2-bis(triethoxysilyl)ethene has been added (a); the same material after treatment with $\text{BH}_3\text{.THF}$ (b); and then after treatment with a dilute $\text{NH}_4\text{OH}$ solution (c).

**Figure 4.1.** PXRD patterns of $\text{C}_{60}\text{B50}$ (a); $\text{C}_{60}\text{B33}$ (b); $\text{C}_{60}\text{B21}$ (c); $\text{C}_{60}\text{B14}$ (d); and $\text{C}_{60}\text{B09}$ (e). All materials give the appearance of being well-ordered.

**Figure 4.2.** $^{13}$C CP-MAS NMR spectra of $\text{C}_{60}\text{B50}$ (a), and $\text{C}_{60}\text{B33}$ (b). The signal from the $\text{C}_{60}$ can be clearly seen at 143ppm and the signals from the aminopropyl linker can be seen at 44ppm, 25ppm and 19ppm.

**Figure 4.3.** $^{29}$Si MAS NMR spectra of $\text{C}_{60}\text{B50}$ (a), and $\text{C}_{60}\text{B33}$ (b). It can be clearly seen that the intensity of the $Q$ signals (-50 to –75ppm) is proportional to the amount of the $\text{C}_{60}$ precursor that was used during self-assembly.
Figure 4.4. STEM micrographs of C60B50 in which the hexagonally ordered mesopores can be clearly observed (a), and where the length of the channels can be seen (b). The scale bar represents 50nm.

Figure 4.5. Nitrogen adsorption isotherms (top) and pore size distributions (bottom) for C60B50 (a), C60B33 (b), and C60B14 (c). The pore size distributions were calculated from the adsorption branch of the isotherm, and are offset for clarity.

Figure 4.6. PXRD patterns of C60A50 (a); C60A33 (b); C60A21 (c); and C60A14 (d). Only C60A21 and C60A14 give the appearance of being mesoscopically ordered.

Figure 4.7. SEM (left) and STEM (right) micrographs of C60A21 (a), and C60A14 (b). Although both materials appear to be porous, C60A21 appears to be quite disordered, while C60A14 appears to be very well-ordered. The scale bar represents 500nm.

Figure 4.8. Nitrogen adsorption isotherms (top) and pore size distributions (bottom) for C60A21 (a) and C60A14 (b). The pore size distributions were calculated from the adsorption branch of the isotherm.

Figure 4.9. EDX line scan of C60A14. STEM of the analyzed area (a); intensity of the Si Kα1 signal along the line (b); and the intensity of the Os Lβ1 signal along the line (c).
Chapter 1

Introduction

1.1. Mesoporous Silicas

1.1.1. MCM 41 and Related Materials

The industrial impact of porous materials increased greatly once the chemical properties of the class of materials known as zeolites were elucidated. Zeolites are highly porous alumino-silicate frameworks that have well ordered pores in the size range of 2-15 Å. Zeolites are made through a self-assembly process in which a small molecule, which is usually a cation such as a quaternary amine, is used as a template around which a silica network is crystallized. By changing the size and shape of the cation, as well as the synthesis conditions, the nature of the resulting pore structure can be controlled.

It was believed that by choosing a suitable supramolecular template the pore size of zeolites could be increased to the nanometer scale. By using surfactant templates well-ordered mesoporous silica materials were first reported by Mobil Corporation in 1991, and many groups around the world began working rapidly in this field. Soon, using this basic methodology, many mesoporous silicas were made with a wide variety of pore sizes and morphologies.

Using cationic surfactants, with reasonably short alkyl chains, such as cetyltrimethyl ammonium bromide (CTAB) as one example, materials with a pore size of approximately 30 Å are produced. By replacing the cationic head group with a larger non-ionic group such as an oligoethylene oxide, the size of the
surfactant micelles can be increased yielding materials with pore sizes in the range of 50-60 Å. Even larger surfactants like polyethyleneoxide-polypropyleneoxide-polyethyleneoxide triblock copolymers can give materials with pore sizes of 70 Å and higher. Hydrophobic swelling agents like mesitylene have even been used to push the pore sizes up to as much as 300 Å.

A simplified mechanism by which these mesoporous silicas are formed is shown in Scheme 1.1. Put simply, a silica source, frequently TEOS or sodium silicate, is mixed together with the surfactant template and a suitable catalyst, most frequently a simple acid or base. The silica will form and then condense around the surfactant micelles, yielding a solid product from which the surfactant can be extracted or burned out to give the final porous material.

**Scheme 1.1.** Method for the self-assembly of mesoporous silicas
A lot of work has also been devoted to the control of the final morphology of the materials. When at first the mesoporous silicas were synthesized as powders, but now, through the careful control of factors like pH, surfactant concentration, and even stirring rate, they are now commonly made as thin films, thick films, freestanding films, monoliths, and even micron sized spheres, fibers and gyroids, as well as other shapes. The pore structure of the material can also be controlled through the appropriate selection of surfactant type and concentration, and can produce disordered wormhole structures, two-dimensional hexagonal, and cubic pore geometries. This work has been covered in several reviews.1-7

Despite the fact that these materials form well ordered structures that are capable of diffracting X-rays they are not crystalline like their zeolite counterparts. The walls of the silica pores are effectively an amorphous glass despite the ordering of the pores. One of the main consequences of this is that the mesoporous silicas lack the chemical reactivity zeolites.

1.1.2. Modification of Mesoporous Silicas

Although they do not share the reactivity of zeolites, mesoporous silicas are nonetheless interesting materials, having well ordered pore structures despite their lack of crystallinity, and they have enormous surface areas that are very desirable for separation and catalysis applications. Many groups then made efforts to change the reactivity of mesoporous silicas through the addition of organic groups. There were two main ways in which this was accomplished.
The first was to add a suitable silsesquioxane of the general formula \((\text{RO})_3\text{SiR'}\) to the TEOS or other silica source during the self-assembly process, and the second is to graft an organic group onto the surface of a pre-formed mesoporous silica.

The first examples of the co-assembly method of incorporating organic groups into a mesoporous silica were seen in the mid-1990s.\(^8\)\(^-\)\(^10\) Using this process it is possible to incorporate chemically useful functionalities, from simple acids and bases, which are useful in catalysis, to thiols, which are useful for removing heavy metals from solution. This process is not limited to only small molecules. Some very large compounds such as cyclams, cyclodextrins, and calixarenes have been successfully incorporated, and have been shown to be chemically accessible. Interestingly, when the co-condensation occurs, the majority of the organic groups appear to be present on the surface of the pores, while relatively few are buried within the siliceous walls. It has also been demonstrated that using a co-condensation process along with unique surfactants the shape of the final particle can be controlled. Using a chiral, anoinic surfactant, along with a quartenary aminopropylsilane, Che was able to synthesize helical, hexagonal rods.\(^11\) Although not enantiomerically pure, it still remains an impressive feat. There are however some limitations to this process. Since this is a co-condensation the relative concentrations of the inorganic silica and the organosilica become important, since it is the organic group that is providing functionality to the material. Typically the organosilica is limited to a relative concentration of around 25%. Higher concentrations are possible, but
much of the structural order, surface area and porosity will be sacrificed in doing so.

The second method involved functionalizing preformed mesoporous silica with a silsesquioxane of the general formula \((\text{RO})_3\text{Si}R'\). The silsesquioxane is able to react with the silanol groups on the surface of the pore walls and thus become chemically attached to the material. This grafting procedure allowed for a wide variety of organic groups to be successfully incorporated into mesoporous silicas, including amine,\(^{12-18}\) acids,\(^{14, 17}\) thiols,\(^{12, 16, 19}\) and a host of other compounds.\(^{20-25}\) The only real limitations on the organic group were that they are physically able to fit inside the pores. As a result several devices were made that could function as sensors, catalysts, and controlled release devices.

1.2. **Periodic Mesoporous Organosilicas (PMOs).**

1.2.1. **Discovery of PMOs.**

In 1999 a class of materials called periodic mesoporous organosilicas (PMOs) was simultaneously, and independently discovered by three research groups.\(^{26-28}\) The revolutionary aspect of these materials was that the organic groups were not an ancillary part of the mesoporous structure, but were instead an integral part of the material. Briefly, an appropriate silsesquioxane precursor of the general formula \([(\text{RO})_3\text{Si}]_n\text{R}'\) where \(n\geq2\), can be condensed and self assembled around an amphiphilic surfactant\(^{26-34}\) or micellar triblock copolymer\(^{35-41}\) to produce a mesoporous material in the same way as the inorganic silicas discussed above. The main difference between PMO and the modified silicas discussed above is
that in PMOs the organic group is guaranteed to be homogeneously distributed throughout the material, and the loading of the organic group is very high relative to the materials were the organic component were co-assemble with another silica source.

At the time of their discovery, the organic groups that were incorporated into PMOs were fairly simple, generally consisting of short alkanes or alkenes. Despite their simplicity, some interesting chemistry has been done with these materials. For example, the bridging group simplest PMO, consisting of Si-CH$_2$-Si, has been shown to undergo a thermally induced transition from a bridging Si-CH$_2$-Si to a terminal Si-CH$_3$ group. It has also been shown that the alkene on Si-CH=CH-Si PMOs is at least partially chemically accessible, and can be brominated. Since this time a variety of other bridging groups have been incorporated into PMOs, including the aromatic compounds like benzene, biphenyl, toluene, xylene, biphenylethers, and biphenylthioethers as the bridging groups, as well as a few small dendrimers, and the cyclic trimer (SiCH$_2$)$_3$, as well as a variety of other compounds.

It was with the use of aromatic bridging groups that is was possible to produce a degree of order within the pore walls of the material, which are usually amorphous. By careful selection the synthesis conditions it was possible to have benzene molecules undergo $\pi$-$\pi$ stacking during self-assembly, and maintain this ordered structure in the final material. This phenomenon has since been extended to a few other aromatic bridging groups.
The potential advantages of PMOs over modified silicas are several. The most obvious is that the concentration of the organic group within the PMO is much higher than is possible in the modified silicas. Additionally, the concentration can be easily tailored to any degree desired by co-polymerizing the organic containing compound with another silica source during the self-assembly process in the desired ratio.

At first it may seem that the use of PMOs will make it possible to incorporate any type of organic group into the walls of a mesoporous material in any desired concentration, allowing for a simple method of fine tuning both the physical and chemical properties of the material. Unfortunately, the reality of the situation is not that simple. There are some strict limitations as to the types of organic groups that can be used. At the time of their discovery, the only types of organic molecules that were used were quite small and rather simple, and while this is quite useful for the proof of concept, it does not allow for the modification of the chemistry in the materials, which is one of the primary justifications for the synthesis of PMOs. The limitations on the types of organic groups that can be used appear to be related to their flexibility, and solubility. With regards to flexibility, the more rigid the bridging organic group, the more likely it is that the precursor will be able to self-assemble. For example, when the bridging group is either a methylene or ethylene group the self-assembly proceeds to give very well ordered materials. However, if the alkyl chain is extended by one more carbon atom to a propyl group, then the resultant material is simply an amorphous gel. The failure of the propyl precursor to self-assemble is presumed
to be a result of its flexibility as opposed to its size, because it is found that larger precursors can self-assemble, provided that they are sufficiently rigid. For example, if benzene is used as the bridging organic group the resultant materials are very well ordered, despite the fact that the benzene is considerably larger than the propyl group. There have also been reported some very large precursors that can self-assemble, all of which are quite rigid.

These limitations on the types of precursors that can be used make incorporating useful organic groups into the materials quite difficult. Most commercially available precursors are quite long and flexible, making them unsuitable for use in PMOs, which means that the precursors must be synthesized from scratch. The most efficient method of creating new silicon-carbon bonds to make new precursors is through the hydrosilylation of olefins. However, this invariably produces precursors that are quite flexible and difficult to self-assemble. In order to avoid this flexibility it is necessary to use less efficient synthetic methods, such as Grignard, or organolithium reactions with alkoxyisilanes or chlorosilanes.

A common method of circumventing these problems is to dilute the PMO precursor with another silica source, usually TEOS, in a method analogous to the modification of mesoporous silica that was discussed above. This has produced a variety of materials with exploitable functionalities. For example, diamines have been used to coordinate Cu$^{2+}$ ions in a reversible fashion.\textsuperscript{50,51} If the Cu$^{2+}$ is added during the self-assembly process it acts a molecular imprint, greatly increasing the affinity of the final material for the ions.\textsuperscript{51} The introduction of
cyclams into the mesostructure has also been achieved, and they have been shown to bind a variety of metal ions.\textsuperscript{52-54} Other groups have added tetrasulphides,\textsuperscript{55} which have an enormous capacity for binding Hg\textsuperscript{2+} ions despite the low relative concentration of the tetrasulphide. Electrically active dyes have been incorporated.\textsuperscript{56, 57} A variety of chiral ligands have been incorporated,\textsuperscript{58} as well as a large, chiral, transition metal catalyst.\textsuperscript{59}

1.2.2. Current Work

In this work a variety of aspects of PMO chemistry will be examined. In Chapter 2 a novel bridging group containing a borazine moiety is incorporated into a mesoporous framework. Because the borazine PMO precursor was specifically designed to be as short and rigid as possible it was possible for self-assembly to occur without having to dilute the precursor with any other silica source, allowing for the highest possible concentration of borazine within the sample. The effect of the self-assembly conditions on the final material are also examined, and it is shown that the material is particularly sensitive to basic conditions and will undergo significant degradation if self-assembled in a basic medium. However, the borazine PMO is shown to be stable in acidic conditions, which is the opposite of what is observed for many other PMO precursors which generally tend to be acid sensitive, while being stable to base. The chemical reactivity of the borazine PMO is also tested by reacting it with hydrochloric acid.

Unfortunately, not all PMO precursors can be self-assembled in the same manner as the borazine PMO, and the potential pitfalls of diluting the desired
precursor with another silica source were outlined above. In Chapter 2 a new class of materials will be introduced that allows virtually any type of PMO precursor to be incorporated into a mesoporous material, regardless of its size or flexibility, while avoiding any issues with phase separation, or inaccessible functional groups. This class of compounds is called Hybrid Periodic Mesoporous Organosilicas (HPMOs). The concept behind HPMOs is very simple. The surface silanol groups of a pre-existing large pore (>50Å pore diameter) PMS or PMO framework can react with the alkoxyisilyl groups of a PMO precursor, thereby covalently bonding the precursor to the surface of the pore wall. The resulting HPMO will have the desired functionality located solely at the surface of the pores, making them readily accessible, while simultaneously avoiding the potential for phase separation, presenting significant advantages over the other methods of self-assembling difficult precursors. This method also allows multi-layers of PMO precursors to be built up on the pore walls, allowing for the fine tuning of the final pore size of the material through pore size reduction, and also its chemical properties.

Finally, in Chapter 4 a new PMO that contains a $C_{60}$ moiety is discussed. This is potentially quite valuable due to the many interesting chemical, electrical and optical properties that $C_{60}$ exhibits. The precursor that is used to synthesize this PMO is very large and has very flexible aminoalkane groups linking the $C_{60}$ to the silica, which required it to be diluted with TEOS in order to have it self assemble. Because of this it is necessary to look at how the self-assembly process occurs in order to ensure that no phase separation occurs, and that the
C\textsubscript{60} is homogeneously distributed throughout the material. In this study it is shown that phase separation can and does occur under some conditions, while under other conditions it can be avoided. We also examine the difficulty in determining whether or not this has occurred.

1.3. Instrumentation and Analysis

1.3.1. Powder X-Ray Diffraction

In depth explanations of X-ray diffraction can be found in a variety of texts\textsuperscript{60-62}, and only the basics will be presented here. To get useful information from X-ray diffraction it is necessary to have a source of monochromatic X-rays. Firing a beam of high-voltage electrons at a source metal will cause an electron in the K shell of the metal atom to be ejected, as shown in Scheme 1.2. When an electron in a higher shell drops down to fill this vacancy, an X-ray is emitted. Since the energies of the orbitals involved in this process are insensitive to the chemical environment, the frequencies of the emitted X-rays will depend only on the metal that is used as the source, and will be characteristic of that metal.
Scheme 1.2. The generation of monochromatic X-rays via the impact of a high voltage electron on a metal atom

When they impact an atom in the solid the X-rays are scattered in all directions. Most of these X-rays will interfere destructively with each other, so in most directions very low X-ray intensity will be observed. However, in certain directions the scattered X-rays will be perfectly in phase with each other, thus producing a strong signal. This constructive interference occurs when Bragg’s law is satisfied.

\[ n\lambda = 2d \sin \theta \]

A diagram illustrating the origin of Bragg’s law is shown in Scheme 1.3. For diffraction to occur it is not necessary for the scattering atoms to be aligned one above the other. What is required is that planes in which the atoms lie are the appropriate distance apart to satisfy Bragg’s law.
Scheme 1.3. Schematic showing Bragg diffraction of X-rays from an arbitrary crystal plane.

X-ray diffraction from mesoporous materials occurs in effectively the same way as it does from crystalline materials, however, the X-rays are not scattered from single points from within a lattice but rather they are scattered from lines within the material. It is necessary to keep this in mind when determining from which planes X-rays will be diffracted from, and which ones will be forbidden. Some of the diffraction planes for a two-dimensional hexagonally ordered mesoporous material are shown in Scheme 1.4.
Scheme 1.4. A sample of crystal planes that will diffract X-rays in a 2D-hexagonal system.

1.3.2. Solid-State Nuclear Magnetic Resonance

In depth explanations of NMR spectroscopy can be found in a variety of texts, and only the basics will be presented here. Depending on their atomic composition, specific isotopes of a variety of elements will exhibit a magnetic moment. When placed in an external magnetic field these magnetic moments will align themselves either parallel or anti-parallel to the external field, creating two distinct energy levels. The energy difference between these two levels is given by:

\[ E = \frac{\gamma \hbar H}{2\pi} m \]

These energy differences are usually in the radio-frequency range. Since the surrounding chemical environment consists of moving electrons, they will create
local magnetic fields, and as such the magnetic field experienced by a given
nuclei will be the sum of the external and local fields. In this way the energy
difference between the two states is dependant on the chemical environment of
the nuclei in question. Since radio waves that match the energy difference
between the two states can be absorbed this provides a means of detecting
different atoms. If the magnetic field is kept constant, and the compound is
swept with a range of radio waves, the frequencies that are absorbed can be
determined. Alternatively, the radio frequency can be kept constant and a range
of external magnetic fields can be swept through, and information can be
garnered from the field intensities at which absorption occurs. These two
methods are known as continuous wave spectroscopy and are indeed how early
NMR machines function.

Modern spectrometers use a technique known as Fourier transform
spectroscopy, and it theory is significantly different than that of the continuous
wave method. When the magnetic moment of a nucleus aligns itself either with
or against the external magnetic field, they are not static, but rather they oscillate
at a specific frequency that is known as the Larmor frequency \( \omega_0 \).

\[
\omega_0 = \frac{\gamma H_0}{2\pi}
\]

When a broad-spectrum radio frequency pulse is applied to the sample the
magnetic moment is tipped to lie in the xy plane. This results in an oscillating
magnetic field in the xy plane that can be monitored. After being tipped the
magnetic moment will eventually realign itself with the external magnetic field and
the signal in the xy plane will diminish. This is known as free induction decay
(FID). The signal observed can then be converted into the standard spectrum through a mathematical treatment (Fourier transform).

When looking at the NMR in the solid state, there are a few complications that arise that are not present in solution phase spectroscopy, the most notable of which is the directionality of the bonds around a nucleus. In the solution phase the molecules generally tumble and spin very rapidly, and as such any impacts from directional bonding will be averaged out on the NMR time scale. However, in the solid state this averaging cannot occur since the molecules will be locked in position. The result is a wide range of signals that correspond to the different orientation of the molecule in the solid. The breadth of these signals can vary widely, and can potentially be as wide as several hundred ppm. This problem can be partially resolved by spinning the sample during data acquisition. By rapidly spinning the sample at the so called “magic angle” of $54.1^\circ$ relative to the external field the x, y, and z axis will be interchanged and the same type of local field averaging that occurs in solution can be obtained, causing a drastic reduction in the line widths. This spinning gives rise to a phenomenon known as spinning side bands. These are signals that are spaced at regular intervals around the main band, and their relative intensities mirror the intensity of the signal that result when the sample is held stationary. The spacing of these bands is dependant on the frequency of the spinning relative to the external magnetic field. If the sample can be spun fast enough, then the spinning side bands can be completely removed.
When analyzing silicas, and organosilicas, the $^{29}$Si MAS NMR provides a lot of information about the degree of condensation in the material, as well as what ratio of silica to organosilica is present in a sample in the case of a mixed system. It can also be used to determine the extent of Si-C cleavage that has occurred during self-assembly. In a silica gel or mesoporous silica, each silicon atom will give a characteristic signal that is dependant on the degree of cross-linking that has occurred at that atom. Scheme 1.5. illustrates the most frequently observed signals and the connectivity that each signal results from. It should be noted that the absolute position of the T signals are dependent on the nature of the organic group that the silicon is attached to, but their relative positions will always be similar. In a single pulse experiment that has a sufficiently long delay between each pulse, the intensity of the observed signal will be directly proportional to the number of silicon atoms in that environment.
**Scheme 1.5.** Schematic of the nature, and approximate location of the T and Q sites found in the $^{29}$Si MAS NMR of organosilicas. This spectrum was simulated using an NMR peak fitting program.

1.3.3. Nitrogen Adsorption Isotherms

Detailed theory of nitrogen adsorption can be found elsewhere.\textsuperscript{65-68} Physisorption, which is used to determine the porosity of a sample, occurs
whenever a gas comes into physical contact with the surface of a solid substrate. The Van der Waals forces between the gas and substrate can result in the formation of a layer of condensed gas forming on the solid surface. The strength of the solid gas interaction is given by the following equation:

\[ U(r) = \frac{b}{r^{12}} - \frac{C}{r^6} \]

Where \( b \) is an empirical constant, \( C \) is a constant that is related to the polarizabilities of the two atoms in question, and \( r \) is the distance between the two atoms.

The most frequently used method of extracting the surface area of a material from the nitrogen adsorption isotherm was developed by Brunauer, Emmett, and Teller in 1938. Their method adopts a rather simplified view of how a gas interacts with the surface of a solid, but despite this simplification it is able to provide an accurate measurement in most situations. They assume that the solid surface contains a number of well-defined binding sites to which the gas molecules can adhere when they collide with the surface. Since the adsorption of the gas is an equilibrium process it is necessary to consider both the rate of gas adsorption onto the surface, and the rate of gas desorption off of the surface. The rate of adsorption is given by the equation:

\[ n_1 = \frac{N}{(2\pi MRT)^{1/2}} p a_1 \theta_0 \]

Where \( p \) is the pressure of the gas, \( a_1 \) is the probability that any given gas molecule will adhere to the solid surface when it collides with it, \( \theta_0 \) is the fraction
of the solid surface that is not covered in a layer of the gas. The rate of desorption is given by the equation:

\[ n_{-1} = z_m \theta_1 \nu_1 e^{\frac{-E_1}{RT}} \]

Where \( z_m \) is the monolayer capacity of the solid surface, \( \theta_1 \) is the fraction of the surface that is covered by the adsorbate, \( \nu_1 \) is the vibrational frequency of the adsorbate in a direction perpendicular to the surface, and \( E_1 \) is the binding energy between the gas and the surface. At equilibrium \( n_1 = n_{-1} \) giving:

\[ K p a_1 \theta_0 = z_m \theta_1 \nu_1 e^{\frac{-E_1}{RT}} \]

Once gas begins binding to the substrate, multilayers can begin to grow, such that the structure of the surface will resemble what is shown in Scheme 1.6. To simplify the following equations the assumption is made that each molecule of adsorbate only interacts with the one directly above and below it, and does not interact with any molecules that are in the same layer as it. At equilibrium, for any given layer \( i \) will give:

\[ K p a_i \theta_{i-1} = z_m \theta_i \nu_i e^{\frac{-E_i}{RT}} \]

Where \( z_m \theta_i \) gives the number of adsorbate molecules in layer \( i \) that do not have another molecule above them. Thus the total number of molecules adsorbed on the surface is:

\[ n = \sum_{i=1}^{i} z_m i \theta_i \]

Two further assumptions are made that allow every layer of adsorbate beyond the first to be treated identically, namely that the binding energy of each layer beyond the first is identical (ie. \( E_i = E_{i+1} \) when \( i \geq 2 \)), and that the
evaporation/condensation constants for every layer beyond the first are identical (ie. \( \nu_i/a_i = \nu_{i+1}/a_{i+1} \) when \( i \geq 2 \)). Through much mathematical manipulation, which can be found elsewhere, the final form of the BET equation is arrived at:

\[
\frac{p}{x(p_0 - p)} = \frac{1}{x_m c} + \frac{c - 1}{x_m c} \frac{p}{p_0}
\]

where \( c = \frac{a_2 V_2}{a_1 V_1} e^{(\nu_1 - \nu_2)/\nu_1} \)

The value \( c \) is a constant that depends on the strength of the interaction between the material and the gas. This equation gives the form of a straight line. The values of \( x \) and \( p \) are obtained from the isotherm, \( p_0 \) and \( c \) are both constants, which allows the value of \( x_m \) to be determined. However it should be noted that most isotherms will begin to deviate from a straight line when \( p/p_0 > 0.35 \), and thus only the low pressure points can be used for surface area determination.

**Scheme 1.6.** Hypothetical layering of gas molecules on specific sites of a solid substrate.

Apart from the surface area of the porous material it is also important to know the pore sizes and their distribution. The most commonly used method for mesoporous materials, and the method that will be used thought this text, is the
BJH method developed by Barret, Joyner, and Hallenda in 1951.\textsuperscript{70} Their method uses a modification of the Kelvin equation for the condensation of a gas inside a capillary, taking into account the volume of the pores that empty at a given pressure, as well as the amount of gas that evaporates from the surface of the material at that pressure.

\[
\ln\left(\frac{p}{p_o}\right) = -\frac{2V\gamma}{rRT}\cos\phi
\]

Where \(p\) is the vapour pressure, \(p_o\) is the saturation vapour pressure, \(r\) is the pore radius, \(R\) is the gas constant, \(T\) is the temperature, \(V\) is the molar volume, \(\gamma\) is the surface tension, and \(\phi\) is the contact angle between the liquid and the substrate. By using this equation and examining the pressures at which the adsorbed volume of gas changes, then the range of pore radii that were emptied or filled in that pressure range can be determined.

1.3.4. SEM and STEM

Detailed information on the theory of SEM and STEM can be found elsewhere.\textsuperscript{71-73} SEM and STEM both work through a very similar process. Briefly, a tightly focused electron beam is directed towards a sample and then scanned through the x, and y coordinates, similar to the way an electron beam is scanned over the pixels of a cathode ray tube. The difference in the two techniques lies primarily in the placement of the detectors. A schematic showing the basic set up for both SEM and STEM is shown in Scheme 1.7.
**Scheme 1.7.** Schematic illustrating a simplified model of an STEM, including the location of the various detectors.

SEM relies on the detection of secondary electrons that are emitted from a sample after the impact of an electron from the primary beam. The electron from the primary beam has sufficient energy to knock an electron out of the valence shell of an atom that it impacts with. This electron will have a much lower energy than those in the primary beam, and they will be emitted in all directions. Because of the lower energy of the secondary electrons they will not be able to penetrate any significant depth of material, and as a result the information garnered from the SEM primarily gives information about the surface of the
material. The secondary electron detector is typically placed above the sample, off to one side. The placement of the detector in this position is what provides the shadows and depth that are seen in the micrographs. If the secondary electrons are required to pass through another portion of the sample on their way to the detector, they will be absorbed or scattered, resulting in a dark spot, or shadow. However if the path for the secondary electron to the detector is clear a large number of electrons will be counted, resulting in a bright spot.

STEM differs in that the detector is placed directly behind the sample. Whereas SEM detects emitted electrons, the STEM detects electrons from the primary beam that have passed through the sample without being absorbed or scattered. This allows it to give information about the interior of the sample, but also limits the use of this technique to relatively thin samples. When examining mesoporous materials, as well as a wide variety of other sample types, the orientation of the sample will have an impact on the structure that can be observed. For example, in the case of a hexagonal mesoporous material, when the beam passes through the [1,0,0] face of the material, it will appear to be dense, as the majority of the electrons will be absorbed or scattered, while if the beam passes through the [0,1,0] face, the quantity of material that it must pass through is significantly less, so the structure can be observed as shown in Scheme 1.8.
Scheme 1.8. Electrons passing through a 2D hexagonal material. When the electrons pass through the [0,1] face many are able to penetrate through the entire material, making the pores visible in STEM (left). When the electrons pass through the [0,1] face the majority cannot penetrate through the material, and thus the material will appear dense in STEM.

Another issue that must be considered with mesoporous materials, and those that contain organic components in particular, is their beam sensitivity. If a single area of the material is focused on for too long then the material will begin to decompose and the collapse of the mesostructure can be observed. This is one area in which STEM provides an advantage over TEM. The scanning nature of the STEM gives the material a lower dosage of electrons per unit time, thereby slowing the rate at which the mesostructure collapses.
References


Chapter 2

Borazine PMO

Abstract: Here we report the synthesis of a periodic mesoporous organosilica (PMO) containing a borazine moiety. The nature of the material proves to be heavily dependent on the synthesis conditions, specifically, the materials prove to be sensitive to basic conditions, while being quite stable in acidic conditions which is contrary to what is observed in most PMO materials. The reactivity of the materials is also examined, and it is shown that they will take up simple acids in a reversible reaction.

2.1. Introduction:

Many of the early investigations into the chemistry of borazine were focused on elucidating its electronic structure in an attempt to determine if it truly was an inorganic analogue of benzene, and numerous groups have reported theoretical calculations in this regard.\textsuperscript{1-3} Despite its resemblance to benzene, borazine shows significantly different chemical reactivity. Unlike benzene, borazine is capable of acting as both a Lewis acid and base, allowing it to react with a variety of different compounds, including simple acids\textsuperscript{4} and amines.\textsuperscript{5, 6} Studies have shown that it is capable of reversibly coordinating up to three equivalents of simple acids, such as hydrochloric, or hydrobromic acid.\textsuperscript{4} Reaction with a diamine can even substitute out entire sections of the ring creating new heterocyclic compounds.\textsuperscript{5} Several transition metal complexes containing borazine have been synthesized,\textsuperscript{7-13} and again it shows even more deviance from the behavior of benzene, at least in terms of its conformation. Rather than
remaining planar, as benzene does, the borazine will buckle into a chair conformation with the nitrogen atoms directed towards the metal.\textsuperscript{8}

In recent years, borazine has been finding its way into more high-tech applications. Some of the most promising work has been in the development of high temperature ceramics. Using either molecular or polymeric borazine derivatives as easily processed, single-source precursors, a variety of ceramics with novel elemental compositions have been produced.\textsuperscript{14-21} The use of single-source precursors for these materials is very desirable since it allows the mole ratio of the various elements to be strictly controlled and increases the likelihood that there will be a homogeneous distribution of the elements throughout the material. In particular, borazine derivatives have found use in the development of Si-C-B-N and Si-C-B-N-O\textsuperscript{22} ceramics, which have garnered much attention in the last decade due to their high thermal stability, in many cases being able to survive temperatures of 1600°C and higher.

Interest in borazine, and aminoboranes has also developed in the field of hydrogen storage for use in fuel cells.\textsuperscript{23} Ammonia borane complexes have one of the highest known hydrogen storage values per unit of mass making them potentially useful for on-board storage in hydrogen-powered vehicles. Borazine and related materials are often the major byproducts of these reactions making it necessary to understand borazine chemistry in order to make the transformations easily reversible, so that they can be industrially viable.\textsuperscript{24, 25}

For these applications it is desirable to be able to control the morphology of the borazine containing material, and for some applications, of which hydrogen
storage is a prime example, it would be useful if the material were highly porous to allow the free flow of gases both into and out of the material. Previous attempts to accomplish this have included adsorbing ammonia borane. The current work describes a method by which a borazine moiety can be incorporated into mesoporous silica. The atomic composition of our materials is suitable for transformation into a mesoporous ceramic and clearly it has potential as a hydrogen storage container. The self-assembly of our precursor is heavily dependant on the conditions used, specifically whether an acid or a base was used as a catalyst. The differences in the resultant materials are examined in detail. We also examine the chemical reactivity of the borazine PMO.

2.2. Results and Discussion

2.2.1. Precursor synthesis.

There are a number of methods that could be used to bind a borazine moiety between hydrolysable silicon atoms. However many of these options are not viable for the synthesis of a single-source PMO. For example, Seyferth\textsuperscript{26} and Cowley\textsuperscript{27} independently reported the formation of Si-B bonds around the borazine, however these bonds are not stable enough to survive the conditions required for the self-assembly process.\textsuperscript{26, 27} Organic linkers could be incorporated through the hydrosilylation of either vinyl or allyl groups around the borazine, but this would result in a large and flexible molecule which would be unlikely to self assemble unless diluted with another silica source such as TEOS. We designed a PMO precursor in which there is a carbon atom connecting the
silicon atom to the borazine ring, making the molecule compact, and as rigid as possible, thereby maximizing its chance of self-assembling.

The precursor for the borazine PMO was synthesized according to the method shown in Scheme 2.1. B,B,B-trichloro-N,N,N-trimethylborazine was synthesized from methylammonium chloride and boron trichloride according to methods reported in literature. This was then used in a Grignard reaction with triethoxysilylmethychloride that gives the desired compound in a reasonable yield.

**Scheme 2.1.** Synthesis of the borazine based PMO precursor 1.

2.2.2. Material synthesis

The borazine precursor was self-assembled using standard procedures in both acidic and basic conditions. In brief, under acidic conditions the borazine precursor 1 was stirred into an aqueous solution of cetylpyridinium chloride and hydrochloric acid to give the compound BN-PMOa, while under basic conditions 1 was stirred into an aqueous solution of cetyltrimethyammonium bromide and
ammonium hydroxide to give the compound BN-PMOb. The PXRD spectra of these materials are shown in Figure 2.1. Both BN-PMOa and BN-PMOb exhibit diffraction peaks in the region of 1.5° 2θ and 2.1° 2θ respectively, which is indicative of meso scale order in the materials.

![PXRD patterns of BN-PMOa (a) and BN-PMOb (b).](image)

**Figure 2.1.** PXRD patterns of BN-PMOa (a) and BN-PMOb (b).

The nitrogen adsorption isotherms shown in Figure 2.2 confirm the porosity of the materials. Both BN-PMOa and BN-PMOb show Type IV isotherms, indicating mesoporosity in the samples. However, BN-PMOb shows a bimodal pore size distribution, with some of its pores being approximately 25Å in diameter, while the rest are much larger, in the range of 80-250Å in diameter. This indicates that in BN-PMOa the vast majority of the pores result from the surfactant template, while in BN-PMOb although approximately half of the total pore volume of the
material resulted from the surfactant template, a significant portion was not templated and is present as a disordered xerogel.

![Graphs showing nitrogen adsorption isotherms and pore size distributions for BN-PMOa and BN-PMOb.](image)

**Figure 2.2.** Nitrogen adsorption isotherms (top) and pore size distributions (bottom) for BN-PMOa (a) and BN-PMOb (b).
2.2.3. Effect of catalyst

Despite the fact that both the acid and base catalyzed materials are well ordered with similar pore sizes, there are some significant differences in the structure of the materials. The main differences are observed when comparing the NMR spectra of the compounds. Figure 2.3 shows the $^{29}$Si MAS NMR of the BN-PMOa and BN-PMOb samples. It can easily be seen that when an acid is used as the catalyst only T sites can be observed, indicating that little to no Si-C bond cleavage occurs during the self-assembly process. In contrast when a base is used as the catalyst a significant amount of Q signals are observed, indicating that approximately 50% of the Si-C bonds were broken during the self-assembly process.
Figure 2.3. $^{29}$Si MAS NMR spectra of BN-PMOa (a) and BN-PMOb (b).

The degradation of the precursor during the self-assembly process could help to explain the differences in the pore structure of the two materials, and justify why BN-PMOb has such a broad pore size distribution. This degradation can also be seen in the $^{13}$C CP-MAS NMR in Figure 2.4. In BN-PMOa two signals can be observed. One is centered on 11 ppm corresponding to the Si-CH$_2$-B linkages, while the other is centered on –6 ppm corresponding to the N-CH$_3$. In BN-PMOb the signal at 9 ppm is greatly reduced in intensity, and a new band
emerges at 3 ppm, which is a result of the aforementioned Si-C bond cleavage. Similarly, the $^{11}$B MAS-NMR shows the degradation of BN-PMOb. In the spectrum of BN-PMOa a single peak, along with its spinning side bands, is observed centered on –5 ppm, corresponding to the one type of B in the material. In the spectrum of BN-PMOb, this peak is significantly broadened and is less well defined due to the presence of B-CH$_3$ moieties, however the overlapping peaks are too close together to be able to assign specific frequencies to each group.

![Figure 2.4. $^{13}$C CP-MAS NMR spectra of BN-PMOa (a) and BN-PMOb (b).](image)
The observed sensitivity to basic conditions can be attributed to the location of the Lewis acidic boron atom. Ordinarily, Si-C bonds are electron rich, and susceptible to protonation, which explains why Si-C bond cleavage is frequently observed in acidic conditions. However, in this case the Lewis acid pulls electrons from the Si-C bond causing it to be electron deficient, enabling hydroxide to attack the corresponding Si atom. The boron stabilizes the carbanion that results until it can become protonated.
2.2.4. Reactivity of the material.

One of the major interests in PMO materials is the ability to tune the chemical reactivity of the material for a specific purpose. Changing the organic groups that are used in the material can do this. However, even if the desired organic groups can be included their reactivity is not trivial. The steric constraints imposed by the surrounding material invariably cause many of the organic groups to be inaccessible to chemical reagents. And indeed studies have shown that only around 20% of the organic groups in a typical PMO are chemically accessible.

It is already known that borazine and its derivatives can react with simple acids, as has been shown in several publications. Usually the reaction is monitored by IR spectroscopy. The N-H bands at around 3200 cm\(^{-1}\), and the B-X bands at around 1000 cm\(^{-1}\) are most commonly looked at. In the borazine PMO materials it is not feasible to use these particular bands as an analysis point due to the overlapping bands from the silica network. However the B-N mode at 1638 cm\(^{-1}\) is isolated and can be readily analyzed.

To determine the reactivity of the material a small sample of the BN-PMOa was stirred in a 2 M solution of HCl in diethyl ether. To remove the added HCl the PMO was then treated with NaBH\(_4\) in THF. The IR spectrum of the material was recorded before and after each step, the results of which are shown in Figure 2.6.
Figure 2.6. FTIR spectra of BN-PMOa that has been surfactant extracted (a), then treated with a solution of HCl in diethyl ether (b), and finally treated with sodium borohydride (c).

Of primary note is that the B-N band at 1638 cm\(^{-1}\) is present in all three spectra indicating that only a portion of the borazine moieties undergo reaction,
which is consistent with what is known about the reactivity of PMOs. After the HCl has been added a new peak can be seen at 1706 cm\(^{-1}\). Following treatment with NaBH\(_4\) it can be seen that this peak is effectively removed completely, indicating that the reaction with the borazine is reversible.

2.3. Conclusion:

In summary, well-ordered PMOs containing a borazine moiety were synthesized in both acidic and basic conditions. The materials were shown to be sensitive to basic conditions, with significant Si-C bond cleavage occurring in the base catalyzed sample, while showing good tolerance to acidic conditions. Furthermore, the borazine moieties were shown to be chemically accessible, being able to reversibly bind HCl.

2.4. Experimental.

2.4.1. Materials and reagents

All chemicals were commercially obtained and used as received. Methylamine hydrochloride, boron trichloride, (triethoxysilyl)methylchloride, sodium borohydride, and the HCl solution in diethylether were obtained from Aldrich. All the solvents were obtained from BDH.

2.4.2. Synthesis of N,N,N-trimethyl-B,B,B-trichloroborazine

N,N,N-trimethyl-B,B,B-trichloroborazine was synthesized according to literature procedure. In brief, 5.4 g (80 mmol) of methylamine hydrochloride was
stirred in 50 ml of xylenes, and was heated to reflux. A reflux condenser was fitted to flask and was set to a temperature of –10 °C. The methylamine hydrochloride was only sparingly soluble in the solvent and did not dissolve completely. Then 125 ml of a 1.0 M boron trichloride solution in p-xylene was added very slowly over an 18-hour period. At this time all solids in the flask had dissolved completely. After the addition of boron trichloride was complete the solution was refluxed for a further three hours. The temperature of the condenser was then increased to 5 °C and the solution was refluxed for a further two hours to remove any unreacted boron trichloride, as well as any traces of hydrochloric acid. The solvent was removed via rotary evaporation to yield a gray solid. The solid was sublimed under vacuum to yield a white solid.

2.4.3. Synthesis of N,N,N-trimethyl-B,B,B-tris(triethoxysilylmethyl)borazine

Under a nitrogen atmosphere 0.5 g (2.21 mmol) of N,N,N-trimethyl-B,B,B-trichloroborazine was dissolved in 100 ml of THF. To this was added 0.54 g (22.1 mmol) of magnesium turnings that had been crushed with a mortar and pestle, as well as a small crystal of iodine. The mixture was stirred until the colour of the solution had faded to a pale yellow. A solution of 1.65 g of (triethoxysilyl)methylchloride in 20 ml of THF was then added drop wise over two hours and the mixture was then stirred at room temperature for 18 h. 100 ml of hexanes was added to the solution and the precipitate, as well as the excess magnesium was filtered off. The solvent was removed via rotary evaporation, a
second portion of 100 ml of hexanes was added, the precipitate filtered off, and
the solvent removed again which yielded clear colourless oil.

2.4.4. Self-assembly in acidic conditions (BN-PMOa)

A solution of 0.19 g of cetylpyridinium chloride, 0.58 g of HCl, and 7.7 g of
water. To this was added 0.61 g of N,N,N-trimethyl-B,B,B-
tris(triethoxysilylmethyl)borazine. After five minutes of stirring a white precipitate
was observed to form. This mixture was stirred at room temperature for a total of
6 hours, and was then aged without stirring at 80 °C for a further 24 h. The white
precipitate was isolated via vacuum filtration and was subsequently washed with
copious amounts of water. The surfactant was removed by solvent extraction,
which involved stirring the powder in a mixture of 150 ml methanol and 10 ml 2M
HCl for 12 h and then isolating the solid via vacuum filtration. This process was
repeated at least three times. The powder was then dried in an 80 °C oven.

2.4.5. Self-assembly in basic conditions (BN-PMOb)

A solution was made of 0.39 g of CTAB, 6.02 g of a 29% ammonium
hydroxide solution, and 16.4 g of water. To this was added 0.80 g of N,N,N-
trimethyl-B,B,B-tris(triethoxysilylmethyl)borazine. A white precipitate rapidly
formed. The mixture was stirred at room temperature for one hour, and was then
aged without stirring at 80 °C for a further 24 h. The white precipitate was
isolated via vacuum filtration and was subsequently washed with copious
amounts of water. The surfactant was removed by solvent extraction, which
involved stirring the powder in a mixture of 300 ml of methanol and 10 ml of 1.0 M hydrochloric acid.

2.4.6. Reaction with Acid

A small quantity of BN-PMOa (0.05 g) was stirred into 10 mL of a 2.0 M hydrochloric acid solution in diethyl ether for 6 h. The powder was then isolated via vacuum filtration and allowed to dry at room temperature for 2 h before its IR spectrum was recorded. The sample was then suspended in 10 mL THF and treated with sodium borohydride (0.1 g). This mixture was stirred at room temperature for 6 h. Excess sodium borohydride was neutralized by the addition of methanol (1.0 mL) before the powder was isolated via vacuum filtration dried at 80 °C for 2 h, and then its IR spectra was recorded again.

2.4.7. Characterization

The $^{13}$C solid-state cross-polarized magic-angle spinning nuclear magnetic resonance (CP-MAS NMR) spectra and the $^{29}$Si magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra were obtained using a Bruker DSX 200 spectrometer with samples packed into a zirconia rotor spinning at 5 kHz. The $^{13}$C CP-MAS NMR was run using a 5 sec recycle delay, 5 msec contact time, and a $\pi/2$ pulse width of 4.5 $\mu$sec. The $^{29}$Si MAS NMR spectra was run using a 10 sec recycle delay, and a $\pi/6$ pulse width of 5 $\mu$sec. The PXRD was measured with a Siemens D5000 diffractometer using high power Ni filtered Cu-K$_{\alpha}$ radiation with a $\lambda = 1.54178$ Å source operating at 50 kV/35mA. Nitrogen adsorption
isotherms were measured on a Quantachrome AS1C-VP2 with a bath temperature of 77 K. Pore size distributions were calculated using the BJH method from the adsorption branch of the isotherm.
2.5. References


Chapter 3

Hybrid Periodic Mesoporous Organosilicas (HPMOs)

Reproduced with permission from Adv. Funct. Mater., 15(10), 1696, 2005
Copyright 2005 Wiley-VCH

Abstract: In this study we report the synthesis of a new class of materials called hybrid periodic mesoporous organosilicas (HPMO). By coupling a silsesquioxane precursor through at least two chemical linkages to the mesopore walls of a pre-existing periodic mesoporous silica (PMS) or periodic mesoporous organosilica (PMO) many of the problems of a conventional PMO material can be avoided while ensuring efficient use of the bridging organic functional groups of the silsesquioxane. We demonstrate this concept for PMS by anchoring various silsesquioxanes such as ethene and ethane silsesquioxanes to the mesopore walls of the PMS. The addition of anchored silsesquioxane monolayers and multi-layers to the mesopore walls also allows for the strict control of the diameter of the mesopore as well as the mesopore wall thickness in the final HPMO material. Additionally it is shown that having the silsesquioxane located solely on the surface of the mesopores in HPMOs gives increased chemical accessibility of the organic bridge-bonded moiety when compared with their PMO counterparts containing the bridge-bonded organic both on the surface and within the pore walls.

3.1. Introduction

It would be desirable to be able to use any type of silsesquioxane that has the general formula \([(RO)_{3-n}Si]_nR'\), where \(n \geq 2\), in the self-assembly process outlined in Chapter 1.1.1. (Scheme 1.1.) to make a well ordered PMO. Unfortunately, few silsesquioxanes are able to self-assemble in this fashion and those that do, generally lack a desirable functionality that can be exploited. Reasons for this deficiency include hydrolytic Si-C bond cleavage,\(^1\) competitive intramolecular cyclization\(^2\).\(^3\) and insolubility of the silsesquioxane precursor, as well as
instability of the PMO framework due to excessive flexibility of the bridging organic group. Even though several elaborate organosilane precursors have been synthesized that show interesting properties ranging from heavy metal chelation\(^4\text{–}^9\) to catalysis,\(^10\) most of these cannot self-assemble on their own. It is, therefore, necessary to dilute them with another silica source like tetraethyl orthosilicate (TEOS) in order to get them to form a well-ordered mesostructure, a method that can lead to uncertainties concerning precursor phase separation and the nature of the distribution of the organic groups in the framework of the material, as has been discussed in Chapter 1.2.1. This also severely limits the concentration of the organic groups within the material, and risks having many of the already dilute organic groups being inaccessible.

The reactivity of some types of PMO’s has been tested previously. In most cases they have been shown to be able to bind metal cations,\(^4\text{–}^9\) which while a useful property, does not fully exploit the reactivity of the materials. Enantioselective transition metal catalysts have also been incorporated into PMOs,\(^10\) and while they are shown to retain much of their activity, they sacrifice their selectivity. Other studies have tried to make use of the functional organic groups by transforming them into other functional species after the material has been synthesized, such as the hydroboration of an alkene.\(^11\) Although successful to a certain extent, only terminally bound vinyl groups were reactive, whereas the bridging alkenes were not, suggesting a limit to the functionality of the material due to steric and/or electronic constraints of bridge-bonded framework organics directly self-assembled from silsesquioxane precursors into PMOs. The limits on
the reactivity of organic groups within a PMO is likely in a large part due to the location of the organic groups within the material. Only the groups located at the pore surface will be able to undergo any type of reaction, since the rest will be buried within the dense siliceous bulk of the material, and there is no guarantee that those groups that are at the surface will be in a suitable geometry for a reaction to take place. Indeed, studies have been done that suggest that a mere 20% of the organic groups within a PMO are actually able to react at all.

The current work describes a universal method by which bridge-bonded organic functional groups can be added in a controlled and reproducible fashion to the pore surface of either a pre-assembled periodic mesoporous silica (PMS) or periodic mesoporous organosilica (PMO) framework. The organic groups form an integral part of a silsesquioxane precursor of the kind \([(RO)_3Si]_nR'\) where \(n \geq 2\), with very few restrictions on the types of silsesquioxane precursors that can be used. The method described in this chapter, exemplified by the case \(n=2\), ensures that the largest possible fraction of organic functional groups is chemically accessible on the pore surface and not buried within the pore walls of the mesoporous material. It also works well for silsesquioxane precursors that are unable to self-assemble into PMOs because of the aforementioned constraints. This new class of mesoporous organic-inorganic nanocomposite is referred to as hybrid periodic mesoporous organosilica (HPMO). The HPMOs can be further subdivided into two categories depending on the type of framework to which the silsesquioxane is added, in the case where a PMS framework is used a HPMO-1 is formed whereas if a PMO framework is used a
HPMO-2 is formed. This study will focus solely on the synthesis, characterization and chemical reactivity of the HPMO-1 class of compounds.

3.2. Results and Discussion

3.2.1. Synthesis of materials.

The synthesis of large pore PMS and PMO materials was carried out using triblock copolymer templates as previously reported.\textsuperscript{12-18} The triblock copolymer template was then removed from the PMS and PMO hosts using solvent extraction methods to yield the respective template-free materials. A variety of $[(RO)_3Si]_2R'$ were then reacted with the residual silanol groups of the PMS to chemically anchor them via Si-O-Si linkages to the walls of the mesopores by refluxing the $[(RO)_3Si]_2R'$ with the template extracted PMS (giving an HPMO-1) host materials in a toluene suspension for 96 hrs.

The $^{13}$C CP-MAS NMR and $^{29}$Si MAS NMR of the HPMOs clearly show that the silsesquioxane precursors have been successfully attached to the PMS and PMO host materials. Figure 3.1 shows the $^{13}$C CP-MAS NMR of an ethene HPMO-1 resulting from treating a PMS with 1,2-bis(triethoxysilyl)ethene (BTE). The emergence of the ethene carbon peaks can be seen clearly at 145 ppm after the treatment. The additional peaks at 57 ppm and 17 ppm, corresponding to $-OCH_2-$ and $-CH_3$ groups respectively, can be attributed to incomplete hydrolysis of the ethoxysilyl groups of the silsesquioxane. These ethoxy groups are to be expected since the anchoring of the silsesquioxanes is conducted in a dry environment and they react solely with the silanol groups in the pore walls of the
PMS. By further treating the powder in dilute NH₄OH, hydrolysis is completed and the ethoxysilyl peaks are removed.

![Figure 3.1](image_url)

**Figure 3.1.** $^{13}$C CP-MAS NMR of a PMS material after the addition of a single layer of BTE before base treatment (a), and after base treatment (b) (* indicates spinning sidebands).

The $^{29}$Si MAS NMR further supports the formation of the HPMO materials. Figure 3.2 shows the emergence of new T peaks in the region between -53 and -83 ppm, which correspond to organosilane silicon species. If the BTE were physisorbed on the surface of the PMS, rather than being chemically bound, then the new T sites would only correspond to T0 sites which are centered around -60 ppm. However, the T1, T2 and T3 sites from -61 ppm to -83 ppm predominate, indicating that chemical anchoring is in fact achieved. There are also changes in
the ratio and intensities of the Q sites. After treatment with BTE the number of Q2 sites decreases while the number of Q3 and Q4 sites increase. This could be caused by either the reaction of the BTE with the surface silanol groups, or by further condensation of silanol groups to silyl ethers, via the loss of water, within the PMS framework as a result of the heat applied while refluxing during the HPMO synthesis. Both of these reactions will result in the loss of Si-OH groups and the formation of Si-O-Si linkages, which is what the change in the intensity of the Q signals indicates in the $^{29}$Si MAS NMR.
3.2.2. Monolayer Orientation

There are several possible binding motifs that can occur when the bridging silsesquioxanes bind to the wall of a PMS, and these are illustrated in Scheme 3.1. Namely, the silsesquioxane can bind to the wall through both available silicon atoms, which is quite likely when the silsesquioxane is flexible, or it bind to the
wall through only a single silicon atom, which is more likely when the silsesquioxane is rigid and bulky, or a mixture of these motifs could be present. The orientation of the silsesquioxanes can be determined by $^{29}$Si MAS NMR as shown in Figure 3.3. Using the rigid and sterically bulky precursor 2,5-bis(triethoxysilyl)-p-xylene to form an HPMO-1, the $^{29}$Si MAS NMR shows a strong signal at -61 ppm corresponding to the T0 [(RO)$_3$SiR$'$-] signal prior to the basic post-treatment. This signal indicates a silicon atom that is not linked to any other silicon atoms, and is thus located in the pore void, rather than attached to the pore wall as shown in Scheme 3.1. After deconvoluting the T region of the spectrum it was found that the T0 signal at –60.9 ppm accounted for 47 % of the total T signal. The T1 [(SiO)(RO)$_2$Si-R$'$-] signal at –65.3 ppm, the T2 [(SiO)$_2$(RO)Si-R$'$-] signal at –69.8 ppm, and the T3 [(SiO)$_3$Si-R$'$-] signal at –74.0 ppm represented 15 %, 25 %, and 13 % of the signal respectively. This indicates that 2,5-bis(triethoxysilyl)-p-xylene exclusively binds to the PMS through only one of its two Si atoms.
Scheme 3.1. Possible binding motifs of silsesquioxanes in PMS or PMO host materials.

Figure 3.3. $^{29}$Si MAS NMR of a PMS material to which a layer of 2,5-bis(triethoxysilyl)-p-xylene was added.

The orientation of the silsesquioxane guest depends on its flexibility as can been seen in Figure 3.4. Flexible guests such as 1,2-bis(triethoxysilyl)ethane
(BTEA) (Figure 3.4(a)) are able to bond to the framework via both silicon atoms as evidenced by the very low intensity of the T0 signal, whereas the similarly sized but more rigid guest BTE (Figure 3.4(b)) exhibits a mixture of both singly and doubly bound configurations on the framework as evidenced by the moderate intensity of the T0 signal. Thus, through judicious choice of the silsesquioxane it is possible to predictably control the orientation of the organic group within the pore of the HPMO, creating an advantage over a PMS which has been modified with trialkoxysilanes of the type (RO)₃SiR', in which the organic group is always directed into the pore void.
Figure 3.4. $^{29}$Si MAS NMR of a PMS that has been treated with 1,2-bis(triethoxysilyl)ethane (a), and a PMS that has been treated with 1,2-bis(triethoxysilyl)ethene (b). The arrows indicate the position of the $T_0$ site for each of the samples. It should be noted that the 1,2-bis(triethoxysilyl)ethene silsesquioxane that was used is a mixture of approximately 20 % of the cis isomer and 80 % of the trans isomer, and that binding through both ends should be favorable for the cis isomer. If only the trans isomer were used then it is likely that the $T_0$ signal would be more intense.
Powder X-ray diffraction (PXRD) shows that the structural integrity of the HPMO material is retained during this [(RO)$_3$Si)$_2$R' surface treatment, as the d-spacing and peak intensity remain virtually unchanged for both the treated and untreated samples as shown in Figure 3.5, which is reasonable for monolayer anchoring of silsesquioxane on pore surfaces.

![PXRD patterns of PMS treated with: N,N-bis(triethoxysilylpropyl)amine (BTPA) (a); bis(triethoxysilyl)methane (BTM) (b); 1,6-bis(triethoxysilyl)hexane (BTH) (c); and refluxed in toluene in the absence of a silsesquioxane (d).](image)

**Figure 3.5.** PXRD patterns of PMS treated with: N,N-bis(triethoxysilylpropyl)amine (BTPA) (a); bis(triethoxysilyl)methane (BTM) (b); 1,6-bis(triethoxysilyl)hexane (BTH) (c); and refluxed in toluene in the absence of a silsesquioxane (d).

### 3.2.3. Monolayer Coverage

An important issue with this work is the degree to which the pore surfaces are covered with the silsesquioxane. This can be estimated by calculating the
relative amount of the silsesquioxane in the HPMO from the integrations of the T region of the $^{29}$Si MAS-NMR, estimating the cross sectional area of the bound silsesquioxane, and then comparing this to the surface area of the mesoporous silica as calculated by BET measurements. The surface area of the mesoporous silica that was used in these experiments was 353 m$^2$/g, which is typical for the methods used. Estimating the cross sectional area of BTEA to be 22 Å$^2$, that of BTE to be 28 Å$^2$, and that of 2,5-bis(triethoxysilyl)-p-xylene to be 50 Å$^2$ then these silsesquioxanes can be estimated to cover 95%, 83%, and 85% of the surface respectively. This indicates that the surfaces of the pores are covered extensively with the silsesquioxanes. The degree of coverage is only approximate because the cross sectional area of the silsesquioxanes can vary greatly depending not only on their orientation, but also on the number of ethoxy groups that were not hydrolyzed, since it is the ethoxy groups that provide the majority of the steric bulk for the silsesquioxanes used here. It should also be noted that the estimated cross sectional area of BTE is larger than that for BTEA because there are a larger number of T$_0$ and T$_1$ sites in the $^{29}$Si MAS NMR for BTE (Figure 3.4) indicating that there are a larger number of ethoxy groups still attached, thereby increasing the steric bulk of this silsesquioxane.

3.2.4. Pore Size Control.

The fact that the addition of the silsesquioxanes to the PMS and PMO materials occurs only through reaction with the available silanol groups, means that even in the presence of a large excess of the silsesquioxane, only a
monolayer can be added to the surface of the pore during a single reaction. By cleaving the residual ethoxy groups in a basic solution, a new set of accessible silanols is created, which allows multilayers of the silsesquioxanes to be added in a sequential fashion, providing for very fine control over the pore size of the final material. Figure 3.6 shows how the pore volume, as well as the pore size distribution, decreases as successive layers of BTE are added to a PMS. It can be clearly seen that the isotherms monotonically shift to lower pressures as successive layers are added. By looking at the pore size distributions calculated from the adsorption branches of these isotherms it can be seen that the decrease in pore size is approximately 4.5Å per layer, which suggests that the silsesquioxanes are adding as a monolayer, supported by PXRD results. The fact that the pore size distributions remain quite narrow suggests that the coverage of the silsesquioxanes on the pore surfaces is more or less complete and uniform, giving further support to the degree of coverage that was calculated above. It is unlikely that the addition of trialkoxysilanes of the type \((RO)_3SiR'\) to a PMS \(^{19-26}\) will be able to show this level of pore size control due to the fact that the number of silanol groups available to react, will be quite small after the addition of each layer. It should be noted however that with the addition of each successive silsesquioxane layer each layer beneath it is effectively buried and expected to be less accessible.
Figure 3.6. Nitrogen sorption isotherms (top) and pore size distributions (bottom) of a PMS from which the polymer template has been removed (a), and the PMS after the addition of one (b), two (c) and three (d) layers of BTEA.

TEM studies confirm that the added silsesquioxane binds to the pore walls in a smooth and uniform fashion. Figure 3.7 shows TEM images of a PMS above that had undergone three treatments with BTEA. It can clearly be seen that even
after multiple treatments the pores still have a uniform diameter, indicating a uniform addition of the BTEA to the pore walls. Additionally, if the pores had been blocked by aggregates of BTEA the contrast from these aggregates would have been observable in the TEM. The fact that these aggregates could not be observed indicates that the channels are clear.

Figure 3.7. These are TEM images of an HPMO after three treatments with BTEA (the scale bar on the top image represents 60 nm, and on the bottom image represents 30 nm).
3.2.5. Reactivity.

One of the chief advantages of placing the organic groups solely on the pore walls of the materials is that they should be more chemically accessible than organic groups that are buried within the walls of a traditional PMO. A number of groups have previously reported incorporating functional groups such as diamines\textsuperscript{7,9} and cyclams\textsuperscript{4-6} into PMO materials and have found them to be able to bind a variety of cations, showing that the pores of the material can be penetrated, at least by small cations. However, most reactions require the use of larger reagents than simple ions that may not be able to penetrate dense walls.

To test whether the HPMO’s are more reactive than the traditional PMOs we chose a simple hydroboration reaction of an alkene. An HPMO-1 was made by treating a PMS with 1,2-bis(triethoxysilyl)ethene, while the analogous PMO was made from the same precursor. After extracting the surfactant from the PMO both materials were treated with a BH\textsubscript{3}.THF adduct. The $^{13}$C NMR analysis of the HPMO in Figure 3.8 shows the appearance of two new broad signals at 7 ppm and 12 ppm corresponding to the alkyl carbons of the hydroborated product. The peaks centered around 65 ppm and 26 ppm in Figure 3.8(b), correspond to ethoxy groups that were not hydrolysed when the hydroboration reaction was quenched with water. The hydrolysis of these residual ethoxy groups can be completed by treating the sample with a dilute aqueous ammonia solution as evidenced by the absence of these peaks in Figure 3.8(c). The fact that the alkene signal at 143 ppm still partly remains after the hydroboration, shows that the reaction does not go to completion in 24h. However, the small relative
intensity of the peak at 143 ppm when compared to the peaks at 7 ppm and 12 ppm indicates that the majority of the alkene reacted to give the hydroborated product.

Figure 3.8. $^{13}$C CP-MAS NMR of a PMS to which a layer of 1,2-bis(triethoxysilyl)ethene has been added (a); the same material after treatment with BH$_3$.THF (b); and then after treatment with a dilute NH$_4$OH solution (c).
When a conventional PMO is treated with BH$_3$.THF under the same conditions, the $^{13}$C NMR spectra shows little to no new signal around 10 ppm, suggesting that the hydroboration of this material occurs only to a very small extent. This lack of reaction of the conventional PMO is also supported by earlier work that showed that a bridging ethene group contained within a pore wall will not react with BH$_3$.THF at a fast rate. This is to be expected since in a HPMO the olefin is located solely on the pore wall with relatively low number of siloxane bonds where there is relatively little steric hindrance, making reaction with the borane quite facile. In a traditional PMO the borane must penetrate into the pore walls before it can react. Additionally, in a traditional PMO the alkene groups on the surface of the pores may have an unfavorable orientation for the reaction to occur, or they may be more rigidly bound with siloxane bonds and therefore be less sterically and chemically accessible than the alkenes in an HPMO.

### 3.3. Conclusions

In summary, a synthetic strategy has been described that leads to a new class of organic-inorganic nanocomposites, that we refer to as hybrid periodic mesoporous organosilicas (HPMOs), in which silsesquioxanes bearing one or more bridging organic functional groups are bound to the pore walls of a periodic (or aperiodic) mesoporous silica (HPMO-1) or organosilica (HPMO-2) material. The approach of chemically anchoring silsesquioxanes to the pore surface of a pre-existing mesoporous silica or organosilica material to create a HPMO effectively overcomes a number of existing problems with PMOs, such as those
associated with silsesquioxane Si-C cleavage, intramolecular cyclization and insolubility, over flexible bridging groups, and inaccessible bridge-bonded organic groups buried within the pore walls and/or organized in an unfavorable geometry on the surface of the pore wall. Furthermore the method allows the control of pore size, wall thickness and surface and physical properties of organic functionalized mesoporous materials. The ability to be able to generate bridge-bonded organic functional groups on the pore surface of a PMS (or PMO) bodes well for the use of HPMOs in catalysis, separation, sensor, microelectronic and controlled chemical delivery applications.

3.4. Experimental Section

3.4.1. Materials and Reagents.

All chemicals were commercially obtained and used as received. Tetraethyl orthosilicate (TEOS), borane-tetrahydrofuran (BH₃·THF), HCl, NaCl, 1,2-bis(triethoxysilyl)ethane (BTEA), and Pluronics P123 (Polyethyleneoxide-block-polypropyleneoxide-block-polyetheleneoxide) were all obtained from Aldrich. 1,2-Bis(triethoxysilyl)ethene (BTE), 1,6-bis(triethoxysilyl)hexane, bis(triethoxysilyl)methane (BTM), and N,N-bis(triethoxysilylpropyl)amine (BTPA) silsesquioxane precursors were obtained from Gelest. All the solvents were obtained from BDH.

3.4.2. Synthesis of PMS.

In a typical synthesis 8.4 g P123 was dissolved in a solution of 208.8 g of 2N HCl, 69.6 g of water and 24.4 g of NaCl. Once the P123 had dissolved
completely, 14.2 g TEOS was added. The mixture was stirred for 24 hrs at room temperature, followed by aging without stirring at 80 °C for 24 hours. A white solid was isolated via vacuum filtration and was washed thoroughly with water and acetone. The P123 was then removed by solvent extraction in which 3.0 g of the resulting powder was stirred in 400 mL of a 1:1 mixture of acetone and ether for at least 12 hrs, then filtered and redispersed and stirred in 400 mL of a 1:1 mixture of acetone and water for at least 12 hours before being isolated. This extraction was repeated four times to yield a porous white material.

3.4.3. Synthesis of ethene PMO.

The ethene PMO was synthesized analogously to the PMS material. Typically, 1.4 g P123 was dissolved in a solution of 35.6 g of 2N HCl, 11.9 g of water and 4.2 g of NaCl. Once the P123 had dissolved completely 2.0 g of 1,2-bis(triethoxysilyl)ethene was added. The mixture was stirred for 24 h at room temperature, followed by aging without stirring at 80 °C for 24 h. A white powder was then isolated from which the P123 was removed as above.

3.4.4. Synthesis of HPMOs.

In a typical synthesis 0.5 g of PMS was suspended in 25 mL of toluene. This mixture was then stirred for approximately 30 min. until a fine suspension was produced. To this mixture was added 1.8 mmol of BTEA, BTE, BTM, or BTPA (0.6 g in the case of BTEA). This mixture was then refluxed for 96 h before the white solid was filtered off and washed exhaustively with toluene to remove any
residual silsesquioxane. HPMOs using other silsesquioxanes were prepared analogously.

3.4.5. Hydroboration of ethene HPMO-1 and ethene PMO.

Under a nitrogen atmosphere, 0.15 g of either the ethene HPMO-1 or ethene PMO was stirred in 25 mL THF until a fine suspension was produced. Then 10 mL of 1 M BH$_3$.THF was added drop-wise over a 5 min period. This mixture was stirred for 24 h before the excess borane was neutralized by the addition of 5 mL of water, and the white powder was filtered off, washed with THF and left to dry under ambient conditions.

3.4.6. Hydrolysis of residual ethoxy groups.

To remove any residual ethoxy groups from a HPMO, 0.5 g of the HPMO powder was suspended in 15 mL water along with 2 drops of a 35% NH$_4$OH solution. The mixture was stirred for 3 h before the powder was filtered off and washed with water and acetone.

3.4.7. Characterization.

The $^{13}$C solid-state cross-polarized magic-angle spinning nuclear magnetic resonance (CP-MAS NMR) spectra in Figure 3.1, and Figure 3.8(a) and the $^{29}$Si magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra were obtained using a Bruker DSX 400 spectrometer with samples packed into a zirconia rotor spinning at 5 kHz. The $^{13}$C CP-MAS NMR was run using a 3 sec
recycle delay, 4 msec contact time, $\pi/2$ pulse width of 4 $\mu$sec. The $^{29}$Si MAS NMR was run using a 15 sec recycle delay, and a $\pi/6$ pulse width of 5 $\mu$sec. The $^{13}$C CP-MAS NMR spectra in Figures 3.8(b) and 3.8(c), and the $^{29}$Si MAS NMR spectra in Figure 3.2 and Figure 3.4 were obtained using a Bruker DSX 200 spectrometer with samples packed into a zirconia rotor spinning at 6.5 kHz. The $^{13}$C CP-MAS NMR was run using a 5 sec recycle delay, 5 msec contact time, and a $\pi/2$ pulse width of 4.5 $\mu$sec. The $^{29}$Si MAS NMR spectra was run using a 10 sec recycle delay, and a $\pi/6$ pulse width of 5 $\mu$sec. The PXRD was measured with a Siemens D5000 diffractometer using high power Ni filtered Cu-K$_\alpha$ radiation with a $\lambda = 1.54178$ Å source operating at 50 kV/35mA. Nitrogen adsorption isotherms were measured on a Quantachrome AS1C-VP2 with a bath temperature of 77 K. Pore size distributions were calculated using the BJH method from the adsorption branch of the isotherm. TEM images were measured on a Hitachi HD-2000 STEM with an accelerating voltage of 200 kV and a 30 mA current.
3.5. References


Chapter 4

C₆₀-PMO: Periodic Mesoporous Buckyballsilica

Abstract: Here we report the first documented synthesis of a periodic mesoporous organosilica (PMO), that contains a multiply bonded C₆₀ moiety integrated into the silica channel walls of the material, dubbed C₆₀-PMO. This is accomplished through the acid catalyzed co-assembly, of C₆₀(NHCH₂CH₂CH₂Si(OEt)₃)x and tetraethylorthosilicate (TEOS) with a polyethyleneoxide-polypropyleneoxide-polyethyleneoxide triblock copolymer template. The percentage of C₆₀ in the final material was estimated to be a minimum of 63 vol%, but potentially as high as 91 vol%. The effects of the synthesis conditions on the mesostructure of the resulting materials are examined. In particular, we demonstrate that the C₆₀ is uniformly distributed throughout the entire sample by the use of energy dispersive X-ray fluorescence (EDX) analysis and an OsO₄ label directly bonded to the C₆₀.

4.1. Introduction

The fullerenes, and especially the C₆₀, will always remain a milestone of chemical research not only because of the academic interest of discovering the first new phase of carbon since diamond and graphite,¹ but also because it represented a truly archetypical nanoscopic building block: spherical, perfectly monodisperse, surface tailorable²-¹⁴ and with unique functionalities.

It is with this concept in mind that we entertained the idea of using C₆₀ as a structural building block for the self-assembly of a new class of mesoporous materials. Larger and larger building blocks are being used successfully for the
templated self-assembly of mesoporous materials, so that many fundamental questions arise on how a building block behaves in templated self-assembly when its size starts to be comparable with that of the template. In a previous report, we demonstrated how a large carbosilane precursor of dendritic nature could be self-assembled into a mesoporous material.\textsuperscript{15} The success was attributed to the flexibility of the dendrimer and to the large number of reactive alkoxysilane groups on the surface of the dendrimer, which together would facilitate the formation of a stable network and the first periodic mesoporous dendrisilica, called PMD. In this chapter, we demonstrate for the first time that a large, C\textsubscript{60} precursor functionalized with surface alkoxysilane groups can be self-assembled successfully, when the appropriate conditions are provided to provide a new class of materials, which we call C\textsubscript{60}-PMO, periodic mesoporous buckyballsilica, in which bridge-bonded C\textsubscript{60} is homogeneously integrated into the siliceous pore walls.

Numerous groups have incorporated C\textsubscript{60} into periodic mesoporous silica (PMS) materials using a variety of methods. The first example of this was done in 1997 by Gu et al, in which they used vapor transport to deposit C\textsubscript{60} in MCM-41 powder, and conducted photoluminescence studies of resulting host-guest inclusion materials.\textsuperscript{16} More recently, Garcia and Bourdeland have reported incorporating C\textsubscript{60} into periodic mesoporous silica, PMS, as well as a variety of zeolites, also via vapor transport, in order to study the second order non-linear optical properties of the host-guest inclusion materials.\textsuperscript{17} Alternatively, C\textsubscript{60} has been deposited into PMS through toluene solutions, which was first done with MCM-48 powders by
Govinderaj, but has since been utilized by several groups, and applied not only to powders but also to films and monoliths. Lin and Mou have found that modifying the PMS to contain surface anchored amine groups enhances the binding of the C\textsubscript{60} to the channel walls, allowing for C\textsubscript{60} concentrations as high as 6.7 wt\%. Mokaya has even been able to add the C\textsubscript{60} during the self-assembly process, yielding a PMS in which the C\textsubscript{60} moieties are located within the pores of the material.

C\textsubscript{60} modified to have pendant hydrolysable alkoxyisilane groups have been incorporated into amorphous silica gels by a few groups. Gunji accomplished this through a platinum catalyzed hydrosilylation of C\textsubscript{60} followed by the co-condensation of the precursor with TEOS. The resultant monoliths contained a Si:C\textsubscript{60} mole ratio in the range of 500-2000, in which the C\textsubscript{60} moieties were homogeneously distributed throughout the material, a feat which could not be accomplished through the use of unmodified C\textsubscript{60}. Similarly, Tang used a hydroamination reaction to create a similar material, in which he was able to make transparent glasses with C\textsubscript{60} concentrations ranging from 0.02 to 0.55 wt\%.

The current work describes the template-directed self-assembly of C\textsubscript{60} functionalized with 3-aminopropyltriethoxysilane surface groups to create the first example of a C\textsubscript{60}-PMO. Rather than including C\textsubscript{60} into the pore spaces of a PMS material to form a host-guest inclusion compound (pea-pod), instead the C\textsubscript{60} groups are formed into an integral part of the pore walls (pod-pea), as shown in Scheme 4.1. This allows for an easily controllable quantity of C\textsubscript{60} to be
incorporated into the pore walls of the material while leaving the pore system open and accessible, with the added advantage of keeping the C\textsubscript{60} groups immobile, thereby preventing intrapore migration and the formation of C\textsubscript{60} clusters.\textsuperscript{18, 24}

Scheme 4.1. The self-assembly of C\textsubscript{60} modified with 3-aminopropyltriethoxysilane to make a C\textsubscript{60}PMO.

4.2. Results and Discussion


The precursor that we used to synthesize a PMO containing a C\textsubscript{60} moiety as an integral portion of the siliceous pore wall, was made in an analogous method to that reported by Tang.\textsuperscript{22} In brief, C\textsubscript{60} was reacted with a large excess of a suitable amine, in this case 3-aminopropyltriethoxysilane, as shown in Scheme 4.2. It can be seen that the resultant precursor is large, and the aminopropyl groups connecting the silicon atoms to the C\textsubscript{60} are quite flexible. Both of these factors decrease the likelihood that this precursor will be able to undergo template-directed self-assembly in its pure form.\textsuperscript{25} A variety of methods were
therefore explored in attempts to self-assemble this precursor into a well-ordered C$_{60}$-PMO. The chosen self-assembly conditions are known to work for a variety of reported materials. Briefly, the surfactant cetyltrimethyl ammonium bromide (CTAB) in conjunction with ammonium hydroxide as a catalyst; the surfactant cetylpyridinium chloride (CPyCl) was used in conjunction with hydrochloric acid as a catalyst; and finally the tri-block copolymer surfactant P123 was used in conjunction with hydrochloric acid as a catalyst. In all cases amorphous gels were formed which showed no peaks in their PXRD patterns, which is usually indicative of a material that lacks long-range-ordered mesoporosity. This suggested that it would be necessary to dilute the C$_{60}$ with another silica source in the self-assembly process in order to obtain a well-ordered material. TEOS was chosen as this source since it would not add any additional organic groups to the material, which allowed for easier characterization.

**Scheme 4.2.** Synthesis of the C$_{60}$-PMO precursor.

\[ \text{Si(OEt)}_3 \text{NH}_2 \xrightarrow{\text{(EtO)}_3\text{Si}} \text{(EtO)}_3\text{Si} \text{Si(OEt)}_3 \]

### 4.2.2. Effect of Catalyst.

It is well known that the addition of another silica source (usually TEOS, but other PMO precursors have been used as well) can be used to assist the self-
assembly of large or otherwise difficult to assemble precursors, and there are many examples of this method in the literature. The addition silica increases the amount of connectivity in the pore wall, granting it additional strength and stability. The dilution of a PMO with another silica source lowers the concentration of the organic group in the final material but it is frequently necessary for self-assembly to occur. We performed these dilutions with the \( \text{C}_{60} \) precursor 1 and once again attempted the self-assembly process using CTAB as the surfactant with ammonium hydroxide as the catalyst, as well as with P123 as the surfactant with hydrochloric acid as the catalyst. These different methods of self-assembly produced very different results and will be discussed separately below.

A variety of dilutions were made for each set of self-assembly conditions. The \( \text{C}_{60} \) dilutions, as well as the self-assembly conditions for the ammonium hydroxide catalyzed materials are shown in Table 4.1. The PXRD patterns of the resultant materials are shown in Figure 4.1. It can readily be seen that all of these materials appear to be well-ordered and show periodicity in the mesoscale range as evidenced by the reasonably sharp and intense peaks in the region around 2.2\(^{\circ}\) 2\(\theta\). This type of result generally indicates a well-ordered material, which will usually contain uniform mesopores of around 30Å in diameter. However, the PXRD alone is not sufficient to prove that the material has this structure, and as will be shown below, this result was in fact a false positive, in which the bulk of the material is disordered and effectively non-porous.
Table 4.1. Synthesis conditions for base catalyzed C$_{60}$-PMOs

<table>
<thead>
<tr>
<th>Sample</th>
<th>C60</th>
<th>TEOS</th>
<th>H$_2$O</th>
<th>NH$_4$OH</th>
<th>CTAB</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{60}$B50</td>
<td>0.35g</td>
<td>0.35g</td>
<td>15.1g</td>
<td>2.86g</td>
<td>0.31g</td>
</tr>
<tr>
<td>C$_{60}$B33</td>
<td>0.23g</td>
<td>0.47g</td>
<td>15.1g</td>
<td>2.86g</td>
<td>0.31g</td>
</tr>
<tr>
<td>C$_{60}$B21</td>
<td>0.15g</td>
<td>0.55g</td>
<td>15.1g</td>
<td>2.86g</td>
<td>0.31g</td>
</tr>
<tr>
<td>C$_{60}$B14</td>
<td>0.09g</td>
<td>0.61g</td>
<td>15.1g</td>
<td>2.86g</td>
<td>0.31g</td>
</tr>
<tr>
<td>C$_{60}$B09</td>
<td>0.06g</td>
<td>0.64g</td>
<td>15.1g</td>
<td>2.86g</td>
<td>0.31g</td>
</tr>
</tbody>
</table>

Figure 4.1. PXRD patterns of C$_{60}$B50 (a); C$_{60}$B33 (b); C$_{60}$B21 (c); C$_{60}$B14 (d); and C$_{60}$B09 (e). All materials give the appearance of being well-ordered.

The presence of the C$_{60}$ in these materials could be seen visually from the red-brown color that they exhibit, and this was confirmed by NMR spectroscopy. In the $^{13}$C CP-MAS NMR for C$_{60}$B50 and C$_{60}$B33, shown in Figure 4.2, peaks can clearly be seen at 145 ppm that corresponds to the C$_{60}$ itself, as well as peaks at 42 ppm, 22 ppm, and 19 ppm that correspond to the aminopropyl connecting...
arms, which indicates that the C\textsubscript{60} precursor was in fact incorporated into the material. This incorporation can also be seen in the $^{29}$Si MAS NMR in Figure 4.3. The T sites are clearly visible in the range of –48 ppm to –78 ppm and their intensity relative to the Q sites, seen in the range of –87 ppm to –122 ppm, scales with the quantity of the C\textsubscript{60} precursor that was added during the self assembly process exactly as expected.
Figure 4.2. $^{13}$C CP-MAS NMR spectra of $C_{60}$B50 (a), and $C_{60}$B33 (b). The signal from the $C_{60}$ can be clearly seen at 143ppm and the signals from the aminopropyl linker can be seen at 44ppm, 25ppm and 19ppm.
Figure 4.3. $^{29}$Si MAS NMR spectra of $C_{60}B50$ (a), and $C_{60}B33$ (b). It can be clearly seen that the intensity of the Q signals (-50 to -75ppm) is proportional to the amount of the $C_{60}$ precursor that was used during self-assembly.

The fact that portions of the material are indeed mesoporous and well-ordered, can be directly observed in the STEM micrographs of the samples. Figure 4.4 shows STEM micrographs for $C_{60}B50$. Figure 4.4a clearly shows the two-dimensional hexagonal structure, and in Figures 4.4b shows the channels running through portions of the material, which is typical for the type and concentration of the surfactant that was used. However, it is the microscopy of
these samples that gives the first indications that these materials do not exhibit
the desired order throughout the material. Although the few areas that are
shown do exhibit a very well-ordered structure, they are not representative of the
majority of the sample. The majority of the sample that was observed in the
STEM gave the appearance of being dense and non-porous.

Figure 4.4. STEM micrographs of C$_{60}$B$_{50}$ in which the hexagonally ordered
mesopores can be clearly observed (a), and where the length of the channels
can be seen (b). The scale bar represents 50nm.
This lack of porosity in the samples is confirmed by the nitrogen adsorption isotherms of the materials that are shown in Figure 4.5. $\text{C}_{60}\text{B50}$ and $\text{C}_{60}\text{B33}$, both of which contain significant quantities of the $\text{C}_{60}$ precursor show Type II isotherms that indicate a lack of mesoporosity in the materials, which is consistent with the STEM images of the samples. The isotherm of $\text{C}_{60}\text{B21}$ is Type IV indicating a significant amount of mesoporosity. It also shows a narrow pore size distribution, suggesting that the pores are of uniform size. However this does not prove that the $\text{C}_{60}$ moieties are incorporated into the ordered portion of the sample.
Figure 4.5. Nitrogen adsorption isotherms (top) and pore size distributions (bottom) for C_{60}B50 (a), C_{60}B33 (b), and C_{60}B14 (c). The pore size distributions were calculated from the adsorption branch of the isotherm, and are offset for clarity.

The structure in these materials results from a phase separation of the TEOS and the C_{60} precursor during the self-assembly process. This phase separation
can be observed visually. When all of the precursor materials were combined, it was observed that the deep red C$_{60}$ precursor did not dissolve in the synthesis solution. After several minutes of stirring a white precipitate formed, which was a result of the TEOS condensing into silica without incorporating any of the C$_{60}$ precursor. After extensive stirring and aging, the sparingly soluble C$_{60}$ precursor condensed and dispersed throughout the solution giving the illusion of a homogeneous distribution. The materials that result from this phase separation consists of portions of well-ordered mesoporous silica, which are devoid of any C$_{60}$ moieties, and other portions that are rich in C$_{60}$ but lack an ordered mesostructure. This would account for why all samples showed a diffraction peak in the PXRD, but only the samples in which the C$_{60}$ precursor was heavily diluted with TEOS, such as C$_{60}$B21, showed a significant amount of mesoporosity.

If an acid catalyst is used instead of base, the situation changes dramatically. In acidic conditions the amine functionalities on the C$_{60}$ become protonated, greatly increasing the compounds solubility in water and the stability of the co-assembly. In contrast to when a base was used as the catalyst for self-assembly, when an acid was used no phase separation was visually observed. The C$_{60}$ precursor readily dissolved in the acidic solution along with the TEOS, giving a homogeneous brown synthesis mixture. In a similar manner as when using the base catalyst a series of materials were synthesized, having varying quantities of the C$_{60}$ precursor, the compositions of which are shown in Table 4.2. The PXRD patterns of these materials are shown in Figure 4.6. In C$_{60}$A50 and
C₆₀A33 it can be seen that when high concentrations of the C₆₀ precursor are used there appears to be little or no meso-scale ordering in the materials, which is consistent with what is known for other large PMO precursor molecules that need to be diluted with another silica source in order to self-assemble. As the concentration of the C₆₀ precursor is decreased, as in C₆₀A21 and C₆₀A14, the ordering of the material improves significantly, as would be expected.

Table 4.2. Experimental conditions for the acid catalyzed synthesis of C₆₀-PMOs

<table>
<thead>
<tr>
<th>Sample</th>
<th>C₆₀</th>
<th>TEOS</th>
<th>H₂O</th>
<th>HCl</th>
<th>NaCl</th>
<th>P123</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆₀A50</td>
<td>0.35g</td>
<td>0.35g</td>
<td>13.56g</td>
<td>0.8g</td>
<td>1.2g</td>
<td>0.41g</td>
</tr>
<tr>
<td>C₆₀A33</td>
<td>0.23g</td>
<td>0.47g</td>
<td>13.56g</td>
<td>0.8g</td>
<td>1.2g</td>
<td>0.41g</td>
</tr>
<tr>
<td>C₆₀A21</td>
<td>0.15g</td>
<td>0.55g</td>
<td>13.56g</td>
<td>0.8g</td>
<td>1.2g</td>
<td>0.41g</td>
</tr>
<tr>
<td>C₆₀A14</td>
<td>0.09g</td>
<td>0.61g</td>
<td>13.56g</td>
<td>0.8g</td>
<td>1.2g</td>
<td>0.41g</td>
</tr>
</tbody>
</table>

Figure 4.6. PXRD patterns of C₆₀A50 (a); C₆₀A33 (b); C₆₀A21 (c); and C₆₀A14 (d). Only C₆₀A21 and C₆₀A14 give the appearance of being mesoscopically ordered.
Figure 4.7 shows the STEM images of $C_{60}A21$ and $C_{60}A14$. The mesopore system in both samples can be clearly seen. In $C_{60}A21$ the pore system gives the appearance of being irregular and not completely ordered, which is consistent with the low intensity of the peak seen in the PXRD in Figure 4.6. $C_{60}A14$ on the other hand shows a very well-ordered pore system in its STEM image, which is consistent with the higher intensity narrower peak in its PXRD. In contrast to the $C_{60}BXX$ series of materials discussed above, the images of the pore systems shown in Figure 4.7 are absolutely representative of the majority of the samples.

It is useful to know what volume fraction of the materials consist of the anchored $C_{60}$. Considering we know the weight percentage of the unhydrolyzed precursors, we can estimate the volume percentage in the solid hydrolyzed phase by multiplying the mole fraction of the precursors by their molecular volume (in the hydrolyzed form) and then normalizing to 100. The molecular volume in the hydrolyzed form of the $C_{60}$ precursor was estimated in two limiting cases: with the amine ligands fully extended and the amine ligands fully contracted. In these two cases the diameter of the $C_{60}$ precursor varies from 1.07 nm to 1.9 nm. Given the flexibility of the propyl chain we can expect the real average value to lie in between. In this framework, the volume percentage of $C_{60}$ in $C_{60}A21$ and $C_{60}A14$ can be estimated to be 63-91 vol% and 51-86 vol% respectively, showing that even though the mole fraction of the $C_{60}$ in the materials is quite low, it still makes up the bulk of the volume. These values of course do not consider the natural microporosity of the glassy solid and the
decrease in the C₆₀’s rigidity due to functionalization, both of which would be very hard to take into account. Nonetheless this should serve as a viable assumption for the time being.

![SEM and STEM micrographs](image)

**Figure 4.7.** SEM (left) and STEM (right) micrographs of C₆₀A21 (a), and C₆₀A14 (b). Although both materials appear to be porous, C₆₀A21 appears to be quite disordered, while C₆₀A14 appears to be very well-ordered. The scale bar represents 500nm.

The nitrogen adsorption isotherms of C₆₀A21 and C₆₀A14 are shown in Figure 4.8, and their characteristic Type IV isotherms indicate mesoporosity in the samples. A summary of the adsorption data for C₆₀A21 and C₆₀A14 is shown in Table 4.3. The total pore volume of 0.33 cc/g and 0.40 cc/g respectively, indicate that the majority of the samples are in fact porous, because if the materials consisted primarily of bulk, non-porous regions, with isolated pockets of mesopores the pore volume would have been much lower. The fact that C₆₀A21
has a broader pore size distribution than C$_{60}$A14 is consistent with the lower degree of order in this sample as was observed in the STEM images and PXRD patterns discussed above. The use of a triblock co-polymer surfactant in the self-assembly of PMOs and mesoporous silicas creates materials that not only have a large pore diameter, but also thick pore walls when compared to similar materials made using smaller ionic surfactants. The thick pore walls in C$_{60}$A21 and C$_{60}$A14 may aid in the self-assembly of the C$_{60}$ precursor by providing sufficient space for the rather large molecule to fit. The thickness of the pore walls of the materials was estimated as being the difference between the d-spacing from the PXRD, and the pore diameter calculated from the adsorption branch of the nitrogen adsorption isotherms. The wall thickness of both C$_{60}$A21 and C$_{60}$A14, being 3.9 nm and 3.7 nm respectively, is sufficient to have 2-3 C$_{60}$ groups across, even if the aminopropyl ligands are fully extended. For C$_{60}$A50 and C$_{60}$A33, both of which contained high concentrations of C$_{60}$, neither showed a diffraction peak in the PXRD and mesopores were not observed in the nitrogen adsorption. In these cases both samples show Type II isotherms, which is indicative of materials that lack mesoporosity, which is exactly what would be expected based on the PXRD.
Figure 4.8. Nitrogen adsorption isotherms (top) and pore size distributions (bottom) for $C_{60}A21$ (a) and $C_{60}A14$ (b). The pore size distributions were calculated from the adsorption branch of the isotherm.
Table 4.3. Nitrogen adsorption and PXRD data for C\textsubscript{60}A21 and C\textsubscript{60}A14.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C\textsubscript{60}A21</th>
<th>C\textsubscript{60}A14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area</td>
<td>242 m\textsuperscript{2}/g</td>
<td>244 m\textsuperscript{2}/g</td>
</tr>
<tr>
<td>Pore volume</td>
<td>0.33 cc/g</td>
<td>0.40 cc/g</td>
</tr>
<tr>
<td>Pore diameter</td>
<td>5.8 nm</td>
<td>6.2 nm</td>
</tr>
<tr>
<td>d-spacing</td>
<td>9.7 nm</td>
<td>9.9 nm</td>
</tr>
<tr>
<td>Wall thickness</td>
<td>3.9 nm</td>
<td>3.7 nm</td>
</tr>
</tbody>
</table>

4.2.3. Reactivity of Material.

Since the base synthesis results indicate that the C\textsubscript{60} precursor can in fact phase separate during the self-assembly process it is necessary to verify that in C\textsubscript{60}A21 and C\textsubscript{60}A14 the C\textsubscript{60} molecules are indeed uniformly spread throughout the mesostructured channel wall network of the material and not simply located in an amorphous block of the material. One of the best ways to do this is through EDX analysis of the channel wall STEM images, but before this can be done it is necessary to chemically label the C\textsubscript{60} molecules with a heavy atom to aid in the observation. Osmium tetroxide was chosen as an ideal label since its reaction with double bonds in C\textsubscript{60} to give C\textsubscript{60}-OsO\textsubscript{4} adducts has been previously reported in the literature\textsuperscript{2, 3, 33, 34} and its peaks in the EDX spectra will be easily distinguishable from the carbon, silicon and oxygen peaks that will also be present.

The results of the EDX for OsO\textsubscript{4}-labeled C\textsubscript{60}A21 and C\textsubscript{60}A14 can be seen in Figure 4.9. The elemental line trace for osmium closely matches the line shape seen for silicon, which indicates that it is evenly distributed throughout the channel walls of the material. If these EDX results are compared to a blank, which was simply a periodic mesoporous silica that was treated with osmium...
tetroxide in the same manner it can be seen that there is virtually no trace of osmium in the EDX spectra, indicating that the signals observed for OsO₄ labeled C₆₀A21 and C₆₀A14 are a result of the osmium tetroxide reacting with the C₆₀ bonded in the silica pore walls and not simply adhering to the silica surface.

**Figure 4.9.** EDX line scan of C₆₀A14. STEM of the analyzed area (a); intensity of the Si Kα₁ signal along the line (b); and the intensity of the Os Lβ₁ signal along the line (c).
4.3. Conclusions

In summary, we have synthesized the first example of a C$_{60}$-PMO material that contains as much as 70 vol% of a C$_{60}$ moiety integrated into the silica pore walls of the material, and have demonstrated a portion of these C$_{60}$ groups are chemically accessible through selective reaction of C$_{60}$ with osmium tetroxide. Furthermore, we have examined how the synthesis conditions affect the mesostructure of the material; specifically establishing that it is necessary to run the self-assembly under acid catalyzed conditions in order to obtain a well-ordered material in which the C$_{60}$ moieties are uniformly distributed in the pore walls of the material. Studies of the chemical and physical properties of periodic mesoporous buckyball silica C$_{60}$-PMO will constitute the subject of future work. In this work is contained a further step towards the development and understanding of hierarchical mesoporous materials. Even larger building blocks with more complex function and morphology need to be used to further investigate the limits of these self-assembly routes in terms of structure and function.

4.4. Experimental Section

4.4.1. Materials and Reagents

All chemicals were commercially obtained and used without further purification. The C$_{60}$ (99%+) was obtained from MER Corporation. The aminopropyltriethoxysilane and osmium tetroxide were obtained from Aldrich. All solvents were obtained from BDH.
4.4.2. Synthesis of $C_{60}$ PMO Precursor 1:

The $C_{60}$ precursor $C_{60}(NHCH_2CH_2CH_2Si(OEt)_3)_xH_x$ was prepared according to literature procedure with slight modifications to the purification. In a typical synthesis, 0.25 g of $C_{60}$ was stirred in 50 ml of triethoxysilylpropylamine for at least 14 days. After this time the mixture had turned from dark gray to a deep red. Excess triethoxysilylpropylamine was removed via distillation to give viscous oil. Following this, 100 ml of chloroform was added and the solution was filtered. Removal of the solvent via rotary evaporation yielded a deep red solid.

4.4.3. Synthesis of $C_{60}B_{50}$:

The $C_{60}$ precursor (0.35 g) was stirred with TEOS (0.35 g) until a homogeneous paste was formed. A solution of water (15.1 g), ammonium hydroxide (2.86 g), and CTAB (0.31 g) was then stirred into this mixture. The mixture was stirred at room temperature for 1 h, and was then aged without stirring at 80 °C for 24 h. The resultant powder was isolated via vacuum filtration, washed with copious amounts of water, and then dried at 80 °C. The surfactant was removed via solvent extraction, which involved stirring the powder in a solution of 400 ml of methanol and 10 ml of 2 M hydrochloric acid for 12 hours. The powder was then isolated via vacuum filtration. This process was repeated at least three times. The materials $C_{60}B_{33}$, $C_{60}B_{21}$, $C_{60}B_{14}$, and $C_{60}B_{09}$ were made analogously.
4.4.4. Synthesis of C$_{60}$A50:

The C$_{60}$ precursor (0.35 g) was stirred with TEOS (0.35 g) until a homogeneous paste was formed. A solution of water (13.56 g), hydrochloric acid (0.8 g), sodium chloride (1.2 g), and P123 (0.41 g) was then stirred into this mixture. The mixture was stirred at room temperature for 24 h, and was then aged without stirring at 80 °C for 24 h. The resultant powder was isolated via vacuum filtration, washed with copious amounts of water, and then dried at 80 °C. The surfactant was removed via solvent extraction, which involved stirring the powder in a solution of 200 ml of acetone and 200 ml of diethyl ether for 12 h. The powder was then isolated via vacuum filtration. This process was repeated at least three times. The materials C$_{60}$A33, C$_{60}$A21, and C$_{60}$A14 were made analogously.

4.4.5. Reaction with Osmium Tetroxide

A solution was made of osmium tetroxide (5 mg), tert-butanol (10 ml), and tert-butyl peroxide (0.5 ml). To this solution was added tetramethylethylene diamine (0.5 g) followed by C$_{60}$A23 (50 mg). The mixture was stirred at room temperature for 24 h. The powder was then isolated via vacuum filtration, washed with tert-butanol, and then resuspended in tert-butanol. After stirring for a further 6 h the powder was isolated via vacuum filtration, and dried at 80 °C.
4.4.6. Characterization

The $^{13}$C solid-state cross-polarized magic-angle spinning nuclear magnetic resonance (CP-MAS NMR) spectra and the $^{29}$Si magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra were obtained using a Bruker DSX 200 spectrometer with samples packed into a zirconia rotor spinning at 5 kHz. The $^{13}$C CP-MAS NMR was run using a 5 sec recycle delay, 5 msec contact time, and a $\pi/2$ pulse width of 4.5 $\mu$sec. The $^{29}$Si MAS NMR spectra was run using a 10 sec recycle delay, and a $\pi/6$ pulse width of 5 $\mu$sec. The PXRD was measured with a Siemens D5000 diffractometer using high power Ni filtered Cu-K$_{\alpha}$ radiation with a $\lambda$ = 1.54178 Å source operating at 50 kV/35mA. Nitrogen adsorption isotherms were measured on a Quantachrome AS1C-VP2 with a bath temperature of 77 K. Pore size distributions were calculated using the BJH method from the adsorption branch of the isotherm. TEM images were measured on a Hitachi HD-2000 STEM with an accelerating voltage of 200 kV and a 30 mA current.
4.5. References.


Chapter 5

Conclusions and Future Work

5.1. Conclusions

In this work a variety of aspects of PMO chemistry have been explored. Notably, the restrictions on the types of PMO precursors that can be used have been discovered, and methods of circumventing these shortcomings have been developed. The greatest limitation on the type of precursor that can be used to synthesize a PMO appears to be the flexibility of the precursor. The potential reasons for this are several. The condensation kinetics could be unfavorable due to a competing intramolecular cyclization,\footnote{1} \footnote{2} or the material may just lack the rigidity needed to maintain an ordered structure. The size of the precursor also appears to influence the self-assembly process, but to a lesser degree since quite large molecules have been successfully incorporated into PMOs. Now that this information is known it will allow researchers to plan ahead what methods will be necessary to create the desired materials, thereby avoiding trial and error studies that are very time intensive. They will even be able to determine beforehand the likelihood of their experiments success. This will allow for much faster progress in the effort to make PMOs commercially viable, or at least chemically useful.

Specifically, it has been shown that well-ordered PMOs containing a borazine moiety can be synthesized in both acidic and basic conditions, although it is very
sensitive to the conditions used. Importantly, it was also shown that the borazine moieties are chemically accessible, being able to reversibly bind HCl. The synthesis of this material represents a departure from strictly using organic elements to control the physical and chemical properties of mesoporous silicas, but instead introduces novel inorganic elements that perform a similar function.

The HPMOs represent a new class of mesoporous silicas in which the location of the organic moieties is strictly controlled. This control allows for the circumvention of many of the problems traditionally associated with the formation of a PMO. Precursors that would not normally self-assemble due to problems like silsesquioxane Si-C cleavage, intramolecular cyclization, insolubility, and overly flexible bridging groups can now be readily incorporated into well-ordered materials. Also, none of the bridge-bonded organic groups will be buried within the bulk of the pore walls, thereby maximizing the fraction of the organic group that is available for future reactions. And finally, the use of HPMOs allows for an unprecedented level of pore size control, allowing the pore diameters of a PMS of PMO to be systematically reduced with angstrom level precision.

The development of the C_{60} PMO advanced the field of mesoporous silicas in several respects. Firstly, and most obviously, it showed that a C_{60} moiety could be incorporated into the pore wall of a mesoporous material. Having the C_{60} located in the bulk of the pore wall allows the pores to remain open and accessible to other reagents. It also ensures that there will be no migration of the C_{60} through the pores once the material has been made, and will prevent the formation of clusters. Although incorporating C_{60} into mesoporous silica has
been accomplished previously, in all instances the $C_{60}$ was added into the pore void, leaving the materials with the aforementioned shortcomings. Secondly, this work revealed some of the potential pitfalls that can arise when a PMO precursor is co-assembled with another silica source. Specifically, it was revealed that the phase separation of the PMO precursor and the additional silica source can, and in some situations does, occur. This is very important because when the concentration of the PMO precursor is relatively low, in the 1-20% range, much of the data, such as PXRD, NMR and nitrogen adsorption isotherms, is unable to distinguish between a homogeneous material and one that has phase separated.

### 5.2. Borazine PMO Future Work

The future of the borazine PMO lies in exploiting its chemical reactivity. As mentioned in Chapter 2, borazines and their derivatives are strong candidates for use in hydrogen full cells, due to their high capacity per unit of weight. If the ammonia borane/borazine cycle does in fact become a viable method of reversibly storing hydrogen gas, then a system will be needed that will allow the hydrogen to easily flow into and out of the substrate, for which the highly porous PMO materials would be ideal. For a system such as this great care will need to be taken in designing an appropriate precursor, as the one used in this case may not prove to be ideal. For example the borazine precursor used in this work had the hydrolysable silicon atom attached to the boron atom through a short alkyl linker. The silicon could also have been bound to the nitrogen atoms through a similar linker, or potentially through both the boron and nitrogen atoms in a six-
point attachment. This last scenario with the six-point attachment will likely be required in order to maximize the hydrogen storage capacity, and reversibility of the material. In the ideal case, it would be desirable to have the PMO capable of storing six molecules of hydrogen per molecule of borazine. If the silicon atoms were linked solely to the boron atoms, then in its fully reduced state it would be possible for the ammonia to dissociate and leech out of the material, and vice versa if there were only silicon atoms attached to the nitrogen atoms. This would severely limit the number of cycles that the material could go through before losing capacity.

Another aspect of borazine PMOs that would be interesting to explore is its reaction with transition metals. It may be possible to modify a borazine PMO with a variety of transition metals through either gas phase or solution phase reactions. It could also be possible to pre-form the borazine-metal complex prior to the self-assembly of the PMO, which would guarantee the maximum loading of the metal within the material. This would require that the borazine-metal complex be quite stable to survive the acidic, aqueous conditions that are required for self-assembly. An alternate and perhaps simpler approach would be to use the borazine-transition metal precursor in the synthesis of an HPMO. This would allow a much larger fraction of the borazine to be chemically accessible, and the synthesis conditions would be milder, using a neutral anhydrous environment, which would increase the likelihood that a preformed borazine-metal complex would survive the synthesis. The three point attachment of the borazine precursor would also prove advantageous since if they all bind to the pore wall
this would direct the face of the borazine towards the void which would be ideal for future chemical reactions.

5.3. HPMO Future Work

The HPMO class of materials developed in Chapter 3 is perhaps the most promising from an industrial chemistry perspective. The fact that the PMS scaffolds are very inexpensive and easy to prepare in a variety of morphologies makes them a very useful starting point. As well, very efficient use is made of the generally more expensive PMO precursors that are added to the surface of the pore walls, allowing a very large fraction of them to be chemically accessible within the final material. What remains to be tested is the efficiency with which this process can be applied to other morphologies of PMS, such as films and monoliths. In powders, which have a very large external surface area, and a large number of pore mouths per unit volume, it is very easy for materials to penetrate throughout the entire material. With films however, the pores generally run parallel to the substrate, only having openings at the very edges of the films. Thus in order to get a high degree of coverage, it is possible that the PMO precursor may have to navigate through several centimeters of pores to reach the center of the film. It is also quite possible, due to defects and twisting pores, that large areas of the films may be completely enclosed and inaccessible which would lead to inhomogeneous coverage. This could be partially solved by changing the morphology of the film. For example, a film in which the pores exhibit a cubic geometry will be much easier to make into an HPMO than one in
which the pores exhibit a hexagonal geometry since any material within the pore structure will have more degrees of freedom, and the likelihood of certain areas of the film being self-contained will be greatly diminished. Also hexagonal PMS film with the channels oriented orthogonally to the substrate would be ideal for making an HPMO.

5.4. C\textsubscript{60} PMO Future Work

The C\textsubscript{60} PMO, discussed in Chapter 4 has many potential uses in devices. The C\textsubscript{60} molecule has a variety of properties that make it useful in optical and electrical devices. For instance, pristine C\textsubscript{60} is known to exhibit third-order nonlinear optical properties. The C\textsubscript{60} can also be reversibly reduced, making it an electron carrier, allowing for electron conduction to occur in what would otherwise be an insulating material. The optical properties of C\textsubscript{60} have been shown to change depending on what molecules are coordinated to it, making it potentially useful as an optical sensor. For sensing applications, having a highly porous material is ideal since it would allow for gases and liquids to have rapid access to a large portion of the material, allowing for high sensitivity and fast switching times. The first step that would be required for many of these applications would be to make the C\textsubscript{60} PMO in the form of a thin film. Changing the morphology of the C\textsubscript{60} PMO from a powder to a film is not trivial, but based on the experiences with the powder it is quite feasible. The main issue to be concerned with would be the solubility of the C\textsubscript{60} precursor in the casting solution, which is typically an alcohol, with ethanol and propanol being the most commonly
used. The lower polarity of the alcohol relative to water should increase the solubility of the C_{60} precursor, making formation of the film facile. Additionally, all reported synthesis of PMO and PMS thin films are done under acidic conditions, most frequently using hydrochloric acid as the catalyst, which has already proven to be successful, as well as necessary, for the formation of PMO powders.

An interesting expansion of the C_{60} PMOs discussed here would be to move from C_{60} to the larger and more complicated fullerenes such as C_{70}, C_{80}, all the way up to single walled carbon nanotubes of varying length. The anisotropy in these systems, particularly with the carbon nanotubes, could force the precursors to adopt specific geometries in the final material. For example, in a two dimensional hexagonal system, which is a common geometry for PMO and PMS materials, a carbon nanotube, if sufficiently long, would likely be forced to align parallel to the direction of the channels. This type of orientation would have some interesting corollaries in that the PMO would exhibit anisotropic electrical conductivity, where charge transport along and orthogonally to the channel direction would be different. The incorporation of a carbon nanotube could also have some interesting effects on the nature of the topological defects within the PMO. Regardless of their morphology, whether powders, films, or monoliths, PMOs contain topological defects in their pore structure. The pores, although they may be straight over significant distances, will invariably twist and turn in defect regions of the material. With the relatively small and roughly spherical precursors that are currently used in PMO synthesis this is not much of an issue as they can easily accommodate this curvy structure. However, the situation
changes significantly when a relatively rigid, rod shaped precursor like a carbon nanotube is used. The presence of the carbon nanotube could make the twisting and turning of the pores more difficult thereby reducing the number of topological defects, resulting in a material whose pores run in only a single direction throughout the entire material. It is also possible that the carbon nanotubes will selectively exclude themselves from the portions of the material in which the radius of curvature is too small, and become more concentrated in the straight areas of the material.

### 5.5. The Future of PMOs

The next step for the PMO class of materials will be to transform them from being merely novel and interesting materials into materials that are functional and industrially useful, whether that is for high-tech or low-tech applications. Several attempts are already being made in this regard. There are reports of materials with tetrasulphide bridging groups that have enormous capacities for adsorbing mercury contaminant, capacities that exceed most of the commercially available products on the market.³ Another aspect in which PMOs in their various forms could find industrial application is as use as a catalyst support, and there are already a few of examples where this is the case,⁴ or where the PMO could act as the catalyst itself. Using PMOs in their available forms, either a pure PMO, a PMO co-assembled with another silica source, or an HPMO, as supports for transition metal catalysts is very desirable due to their enormous surface areas, and easy accessibility of the pores, which would allow for a high loading of the
catalyst per unit weight, and a high throughput of either gaseous or dissolved reagents. In the cases where it is desirable it would also make the recovery of the catalyst very easy since it is attached to a solid support that could easily be removed from solution through filtration. The problem of the catalyst leaching from the material would also be minimized due to the covalent nature of the bonding in the materials as well as the multiple binding sites. The idea of PMOs as catalyst supports is not without its problems however. The porous nature of the material, which provides many benefits, can also be the source of potential problems. With many catalysts, the substrate is required to approach the transition metal very closely at very specific geometries. Having the catalyst as an interior part of a solid support can cause significant steric restrictions on the various substrate molecules, potentially reducing the turnover rate, as well as the selectivity of the catalyst, as has already been shown in some reports.\textsuperscript{4} Using an HPMO instead of a traditional PMO could circumvent much of this problem. Having the catalyst located solely at the surface of the pore walls would greatly increase the accessibility of the catalyst. It is also possible that the confined nature of the pores may have some beneficial effects on any catalysis that is occurring. For example, in an olefin polymerization it is possible that branching of the chains will be limited since there would be insufficient space for the branched polymer to be present in the confines of the pore. The pore confines could also serve as a molecular weight limiter, with the polymer growing until the pores are full.
Another, as yet unexplored aspect of catalysis within a PMO could result from the molecular imprinting of the surface of the pore walls. Molecular imprinting within a PMO has already been shown to be possible when a diamine was co-assembled in the presence of Cu$^{2+}$ ions and the final material was shown to have a significantly higher affinity for Cu$^{2+}$ than a material of the same composition assembled in the absence of any metal ions.$^5$ This simple idea could be readily expanded to include more complicated geometries, analogous to those found within enzymes. This could potentially be as simple as co-assembling multiple precursors with a variety of different functionalities, such as amines and acids, in the presence of a transition state analogue. Methods can also be imagined that would force the molecular imprint to be located at the surface of the walls. In either case this could add much utility to the PMO materials.

PMO materials are not only interesting for their chemical properties, but also their physical properties. One of the major limiting factors in the further miniaturization of microelectronics is the substrate to which the microelectronics is applied. As the circuits get closer together their capacitance increases significantly, slowing down the switching speed. Applying the circuits to a material with a very low dielectric constant can reduce this capacitance. The PMOs are ideal for this since they are highly porous. Since air has a dielectric constant of one, the lowest possible, a material that consists primarily of air will also have a very low dielectric constant. For these applications, PMOs have an advantage over PMSs in that they can be made hydrophobic, thereby excluding water, allowing them to keep their low dielectric constant, even in humid
conditions. There are some problems with using PMOs as electronic supports however. The porous nature of the material not only decreases its dielectric constant but also makes it quite fragile, and thus unable to withstand the processing procedures that are required. What it necessary now is to increase the durability of PMO films, while retaining their porosity. There are several means through which this could be accomplished. One is to simply increase the wall thickness of the material, which would add strength, but would also decrease the relative porosity. Other methods would involve increasing the cross-linking density in the material, which could be done by having the silica condense further, increasing the number of T3 sites relative to the T1 and T2 sites. The organic groups also have the potential to be cross-linked. If this idea of increasing the cross-linking density of the material is taken to its conclusion, then it can be imagined that the pore walls of the PMOs could be made fully crystalline, thereby being analogous to zeolites. This would not only maximize the structural strength of the PMO, but it would most likely alter the chemical properties of the material as well.

There is also the possibility of using PMOs as the stationary phase in chromatography. Their small pores, with very narrow distributions make them ideally suited for this application. The adjustable surface properties of PMOs would allow for the formation of specialized columns that could be specifically designed for certain tasks, by controlling for example the hydrophobicity or hydrogen bonding capabilities of PMO. The only drawback for this would be that most chromatography systems require good control over the particle size and
shape. However, recent advances are making strides in this area, allowing PMOs to be made in the form of spherical particles with narrow size distributions, which is exactly what chromatography would require.⁶

This just scratches the surface of what can potentially be done with PMOs. Beyond this PMOs could be incorporated into a variety of hierarchical structures. Multilayer films could be made in which alternating organic groups are in each successive layer, or a PMO could be layered with another completely unrelated material, which could be either porous or non-porous. The mesoporosity of PMOs could also be combined with the macroporosity of other types of structures. For example, if PMOs are made to form spherical particles, these particles could then be self-assembled to form a colloidal crystal. Alternately, a pre-existing colloidal crystal could be infiltrated with a PMO precursor solution to give the corresponding inverse colloidal crystal. In either case this would introduce a variety of interesting optical properties that could then be exploited. At any rate it is clear that there is still much work that can be done in this relatively young field of chemistry. There are still many interesting scientific questions to be answered, as well as commercial opportunities to be explored, and as such work in this field is likely to continue for many years to come.
5.6. References:


