### Chiral Nematic Mesoporous Organosilica Materials Templated with Cellulose

### Nanocrystals

by

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### Abstract

The synthesis and characterization of new mesoporous organosilica materials with twisted porous networks and defined nanostructures was explored. Spindle-shaped cellulose nanocrystals (CNCs) with nanoscale dimensions can be isolated through the acid-catalyzed hydrolysis of wood pulp. These CNCs behave as chiral nematic lyotropic liquid crystals and are advantageous for the soft-templating of mesoporous materials as they can produce helically arranged pores. As such, CNCs show promise as inexpensive and renewable precursors for the development of nanomaterials.

In this thesis, CNCs were used to template chiral nematic mesoporous organosilica (CNMO) materials through the co-condensation of bridged alkoxysilanes,  $R(Si(OR')_3)_2$ , with aqueous CNC suspensions. Removal of the CNCs produced free-standing organosilica films that have interconnected pore structures and long-range chiral order imparted by the CNC template. Organic functionality was introduced as an integral component of the organosilica structure by varying the alkoxysilane precursors. The syntheses of alkylene-bridged (C<sub>1</sub>-C<sub>6</sub>), aromatic-bridged, ethenylene-bridged, and sulfur-containing CNMO films are reported. It was determined that phase separation between the alkoxysilanes and CNC suspension could be minimized by using mixed solvent systems of water and DMF during self-assembly. The new CNMO films display tunable photonic properties resulting from the repeating helical structure as well as thermal stabilities and pore connectivity that depend on the organic linker used.

The combination of chirality and mesoporosity in these organosilica films suggests applications in hard templating, chiral catalysis, and sensing. CNMO films were investigated as support materials by functionalizing them with spiropyran molecules for sensing or manganese salphen complexes for catalysis. Spiropyran-bound CNMO films were used for photopatterning and behaved as reversible divalent metals sensors. Heterogeneous manganese salphen/CNMO films displayed similar catalytic conversion to the homogeneous catalyst, however, a small enantiomeric excess (5%) was observed suggesting that the chiral environment of the films may affect catalysis. Finally, metal ferrites [MFe<sub>2</sub>O<sub>4</sub> (M = Ni, Cu, Zn, Co)] with chiral nematic nanostructures were prepared through hard templating with chiral nematic mesoporous silica. These materials beautifully replicated the three-dimensional structure of the CNCs liquid crystalline phase and their crystallinity and pore sizes were controlled by altering the calcination temperatures.

### Lay Summary

Biopolymers are long strings of molecules naturally produced in living organisms. The most abundant biopolymer, cellulose, is a major component of plants and shows significant promise as an inexpensive and renewable starting material for applications in nanomaterial science. Bulk cellulose can be converted into cellulose nanocrystals (CNCs), which are spindles of cellulose with dimensions in the nanoscale. Remarkably, these CNCs spontaneously organize into spiral structures in water and in dried films. By constructing other materials around the CNCs while they organize, composite materials can be created with helically organized CNCs embedded inside. Removing the CNCs creates porous solids with nanometre-sized helical holes. These solid materials have fascinating optical properties when the helical structure repeats with distances matching the wavelengths of visible light. In this thesis, we demonstrate that using CNCs as a template, various materials can be produced with tunable nanostructured features and have applications for both sensing and catalysis.

### Preface

Work in this thesis was carried out under the guidance of my supervisor Prof. Mark MacLachlan. Dr. Wadood Hamad from FPInnovations, Vancouver, Canada, was a collaborator for all research chapters (Chapter 2-5) and provided us with the suspensions of cellulose nanocrystals. Mass spectra, elemental analyses, and X-ray photoelectron spectra were performed in the UBC Mircoanalyitcal Facility at the Department of Chemistry, UBC, and the Interfacial Analysis & Reactivity Lab at UBC. Solid-state NMR experiments were performed by Alan Manning and Prof. Carl Michal in the Department of Physics and Astronomy, UBC. Helium ion microscopy was performed by Jijin Yang, Carl Zeiss Microscopy, Thornwood, New York.

Chapter 1: A portion of this Chapter has been previously published as: G.R. Meseck, A.S Terpstra, M.J. MacLachlan, *Curr. Opin. Colloid Interface Sci.* **2017**, *29*, 9. I co-authored this review with Prof. Mark MacLachlan and Dr. Georg Meseck. I wrote the sections on liquid crystal templating with cellulose derivatives and collagen.

Chapter 2: Portions of this Chapter have been previously published as: (1) A.S. Terpstra, K.E. Shopsowitz, C.F. Gregory, A.P. Manning, C.A. Michal, W.Y. Hamad, J. Yang, M.J. MacLachlan, *Chem. Commun.* **2013**, *49*, 1645. (2) A.P. Manning, M. Giese, A.S. Terpstra, M.J. MacLachlan, W.Y. Hamad, R.Y. Dong, C.A. Michal, *Magn. Reson. Chem.* **2014**, *52*, 532. (3) A.S. Terpstra, L.P. Arnett, A.P. Manning, C.A. Michal, W.Y. Hamad, M.J. MacLachlan. Manuscript submitted. I was the principle author for (1) and (3) and co-edited it with Prof. Mark MacLachlan and Dr. Wadood Hamad. I synthesized the CNMO films used for water diffusion measurements reported in (2). Alan Manning performed the solid-state NMR spectra and water diffusion experiments

reported in Chapter 2. Loryn Arnett synthesized and helped characterize the **Hex-CNMO-DMF** and the **Biphenyl(20)-CNMO** films. I preformed all other experiments and analyses reported in Chapter 2.

Chapter 3: A version of Chapter 3 has been previously published as: A.S. Terpstra, W.Y. Hamad, M.J. MacLachlan, *Adv. Funct. Mater.* **2017**, *27*, 1703346. I was the principle author for this work and co-edited it with Prof. Mark MacLachlan and Dr. Wadood Hamad. I carried out experiments reported in Chapter 3.

Chapter 4: The work presented in this chapter was carried out under the guidance of Prof. Mark MacLachlan and Prof. Pascal Van der Voort, University of Ghent, Ghent, Belgium. Dr. Asamanjoy Bhunia, University of Ghent, synthesized the salphen catalyst and Dr. Dolores Esquivel, University of Ghent, performed and analyzed the XRF, GC, and HPLC data for the catalytic reactions. Chris Walters ran SEM images for the **4**-(**60**)-**CNMO** and **5**-(**60**)-**CNMO** films. I preformed all other experiments reported in Chapter 4.

Chapter 5: Portions of this Chapter have been previously published as: G.R. Meseck, A.S Terpstra, A.J. Marenco, S. Trudel, W.Y. Hamad, M.J. MacLachlan, *J. Mater. Chem. C*, **2016**, 4, 11382. I co-authored this work with Dr. Georg Meseck and co-edited it with Prof. Mark MacLachlan, Dr. Georg Meseck, Prof. Simon Trudel, and Dr. Wadood Hamad. Armando Marenco performed the SQUID measurements. Georg Meseck synthesized and characterized the cobalt ferrite materials. I performed all of the other experiments reported in Chapter 5.

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# List of Symbols and Abbreviations

λ	wavelength
$\lambda_{max}$	wavelength with maximum intensity
$M_r$	saturation remanence
$M_{ m s}$	saturation magnetization
n	refractive index
navg	average refractive index
Р	helical pitch
$T_{\mathrm{B}}$	blocking temperature
$\mu_0 H_c$	coercivity
AIBN	azobisisobutyronitrile
ATMS	3-aminopropyltrimethoxysilane
ATR	attenuated total reflectance
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
BTESB	1,4-bis(triethoxysilyl)benzene
BTESEthylene	1,2-bis(triethoxysilyl)ethene
BTESM	bis(triethoxysilyl)methane
BTMSA	9,10-bis(trimethoxysilyl)anthracene
BTMSBP	4,4-bis(trimethoxysilyl)biphenyl
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BTMSH	1,6-bis(trimethoxysilyl)hexane

BTMSPe	1,5-bis(trimethoxysilyl)pentane
BTMSPr	1,3-bis(trimethoxysilyl)propane
BTMSU	N,N'-Bis(3-trimethoxysilylpropyl)urea
CD	circular dichroism
CNC	cellulose nanocrystal
CN-LC	chiral nematic liquid crystal
CNMC	chiral nematic mesoporous carbon
CNMO	chiral nematic mesoporous organosilica
CNMS	chiral nematic mesoporous silica
CP/MAS	cross-polarization/magic angle spinning
DI	de-ionized
DMPA	2,2-dimethoxy-2-phenylacetophenone
DMF	dimethylformaldehyde
DNA	deoxyribonucleic acid
EDC	1-ethyl-3-(3-dimethylaminopropyl)carbodiimide
EDX	energy dispersive X-ray spectroscopy
EIMS	electron ionization mass spectroscopy
EISA	evaporation induced self-assembly
FID	flame ionization detection
FT-IR	Fourier transform infrared
GC	gas chromatography
HPLC	high-performance liquid chromatography
IR	infrared

LC	liquid crystal
LH	left-handed
m-CPBA	meta-chloroperoxybenzoic acid
MC	merocyanine
МСМ	Mobil composition of matter
МО	mesoporous organosilica
MS	mass spectroscopy
MUF	melamine-urea-formaldehyde
nd	not detected
NIR	near infrared
NMO	methylmorpholine-N-oxide
NMR	nuclear magnetic resonance
NP	nanoparticle
PF	phenol-formaldehyde
РМО	periodic mesoporous organosilica
РОМ	polarized optical microscopy
PXRD	powder X-ray diffraction
PyNO	pyridine-N-oxide
QD	quantum dot
RH	right-handed
SA	BET surface area
SEM	scanning electron microscopy
SP	spiropyran

TBDS	tert-butyl(chloro)diphenylsilane
TEM	transmission electron microscopy
TEOS	tetraethyl orthosilicate
TGA	thermal gravimetric analysis
THF	tetrahydrofuran
TMOS	tetramethyl orthosilicate
TON	turnover number
UF	urea-formaldehyde
UV-Vis	ultraviolet-visible
XPS	X-ray photoelectron spectroscopy
XRF	X-ray fluorescence spectrometry

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### **Chapter 1: Introduction**

### **1.1 Nanomaterials**

#### 1.1.1 Overview

Nanomaterials are defined as materials with spatial dimensions between 1-100 nm - afraction of the width of a single strand of spider silk. Consequently, these materials display properties that can differ significantly from their bulk properties and have the potential to revolutionize health care, transportation, building materials and other critical areas of our lives.<sup>[1]</sup> Some of these unique features include high surface areas when compared to bulk materials, controllable shapes and structures, novel optical properties, and improved mechanical properties.<sup>[2–4]</sup> For example, silver nanomaterials have improved antibacterial properties over bulk silver and are used in consumer and medical products.<sup>[5]</sup> Biological nanofibers are another example and have been shown to enhance the thermal stability and mechanical properties of plastics.<sup>[6]</sup> Nanostructures and nanomaterials are being utilized in solar cells.<sup>[7,8]</sup> sensors.<sup>[9,10]</sup> batteries.<sup>[11,12]</sup> and many other technologies ranging from fundamental research to commercial applications.<sup>[13]</sup> Recent advancements in the field of nanoscience have been driven by the development of instrumentation that allows for the manipulation of features on the nanoscale and control of their properties. The following sections are a brief overview of key concepts of nanomaterials as they relate to the overall scope of this thesis.

#### 1.1.2 Synthesis of nanomaterials

The controlled synthesis of nanostructured materials is important for developing new nanotechnologies. Scientists have developed many methods to control the composition, surface chemistry, and hierarchical structure of nanomaterials. The synthetic approaches to creating nanomaterials can be classified into two broader categories: top-down fabrication or bottom-up synthesis.<sup>[14,15]</sup>

Using a top-down approach, researchers can transform bulk materials into a nanostructured form. This approach uses methods, such as ball milling and etching using lithography, to produce patterned nanostructures that can be externally controlled. The semiconductor industry uses top-down methods to fabricate many of the microelectronic chips used in computer devices.<sup>[16]</sup> Alternatively, a bottom-up approach, such as self-assembly, starts with atoms or molecules that can organize into nanostructures. These methods rely on specific interactions between the atoms or molecules to drive the assembly of ordered structures. Although there are advantages and disadvantages to both approaches, self-assembly is emerging as a cost-effective and powerful tool to produce new materials with controlled three-dimensional morphologies and narrow size distributions.<sup>[14]</sup>

#### **1.1.3** Nanofabrication by self-assembly

Self-assembly is a process by which discrete molecules in initially disordered systems are spontaneously formed into well-ordered structures.<sup>[17]</sup> Self-assembly can be seen throughout nature and is responsible for the creation of many hierarchical structures. Complex biological structures, such as lipid bilayers, proteins, and nucleic acids, are formed almost exclusively through self-assembly. Hierarchical structures arise when individual building blocks organize

themselves into 'first order' assemblies, which can further organize to form complex structures over multiple length scales. For example, collagen proteins are made up of polypeptide chains that can self-assemble to form ordered secondary structures (e.g.,  $\alpha$ -helices and  $\beta$ -sheets) that further fold into 3D proteins. Collagen can also have a higher ordered hierarchical structure resulting from the self-assembly of collagen monomers (~2 nm in diameter) into macromolecular fibers with diameters greater than 100 nm.<sup>[18,19]</sup> Such self-assemblies in nature typically occur in the liquid phase under biological temperatures, pressure, and pH, and can be manipulated by local environments within the organism.

Synthetic self-assembly systems arose from the observation of natural systems as well as from key work done by Langmuir and Blodgett in 1935 and Bigelow and coworkers in 1946.<sup>[20,21]</sup> Langmuir and Blodgett observed the arrangement of amphiphilic molecules on liquid and solid surfaces. Bigelow *et al.* observed the formation of well-ordered monolayers of long chain alkylamines on the surface of platinum foil. Both reports are illustrations of molecular self-assembly, which is generally considered to be driven by reversible interactions between molecules such as hydrogen bonding, electrostatic interactions, and van der Waals forces.<sup>[17]</sup> While in the absence of external influences self-assembly of these building blocks is entropically-driven, self-assembly can also occur at larger scales and can be influenced by capillary, colloidal, electric, and magnetic forces.<sup>[22]</sup>

The structure of a self-assembled system is dependent on the specific size, shape, and surface properties of the building blocks. One of the goals in developing self-assembly approaches for nanofabrication is precisely controlling the synthesis of the building blocks so that they have specific dimensions and surface properties (e.g., charge, functionality). This allows for chemical control over the system and can promote the self-assembly of more complex structures over

multiple length scales. Self-assembly is extensively used in the synthesis of porous materials, such as metal organic frameworks formed from the self-assembly of metal ions with ligands, and mesoporous materials formed from the spontaneous ordering of liquid crystals.<sup>[17,23–25]</sup>

#### **1.1.4** Biological nanomaterials

Recent developments in instrumentation that allows for the rapid visualization of nanoscale structures are leading to the discovery that many biological systems contain nanostructures. The formation of these organized nanostructures are often responsible for the unique physical properties found in nature and can be essential for the function of these biological systems.<sup>[26]</sup> By investigating designs in nature, scientists can begin to engineer new materials with advanced properties.

Spider silk is one of the most well-known biopolymers and outperforms the mechanical properties of many synthetic materials. It has been demonstrated that spider silk can exceed the strength of steel of the same weight.<sup>[27,28]</sup> Spider silk is a fibrous protein that forms a self-assembled composite nanomaterial with a hierarchical structure. This hierarchical structure is composed mainly of proteins that are held together by hydrogen bonds and electrostatic interactions (Figure 1-1a).<sup>[29]</sup> To date, spider silk remains an excellent model for understanding and mimicking natural self-assembly and designing high tensile strength fibers. Other fibrous proteins and polymers, such as collagen in bones, elastin in connective tissues, and cellulose in plant materials also rely on hierarchical nanostructures to impart unique mechanical properties.<sup>[18,30,31]</sup>

Biological nanomaterials can also display remarkable properties when interacting with surfaces, water, and light. One example is a gecko's ability to stick to most surfaces, which is exclusively because of the shape and size of nanofilaments on the gecko's feet (Figure 1-1b).<sup>[26]</sup>

These nanofilaments are designed to have extremely high surface area and can maximize van der Waals interactions between the gecko's feet and the surface they are in contact with. Another well investigated example is the origin of colours in peacock feathers. Peacock feathers have been shown to physically manipulate light based on periodic nanostructures. The brilliant iridescent colours are due to a 2D periodic array of melanin rods causing thin-film interference (Figure 1-1c).<sup>[26]</sup>



**Figure 1-1.** (a) The hierarchical structure of spider silk (Reproduced from reference 32 with permission, copyright 2010 Nature Publishing Group).<sup>[32]</sup> The nanostructure of (b) a gecko's foot and (c) a peacock feather (inset scale bar = 2  $\mu$ m and 1  $\mu$ m, respectively) (Reproduced and adapted from reference 26 with permission from Elsevier).<sup>[26]</sup>
More recently, researchers have discovered that plants can use self-assembled nanostructure to produced brilliant colours.<sup>[33,34]</sup> In 2012, Vignolini *et al.* reported that the fruit of the plant *Pollia condensata* displayed an intense blue colour that persisted for years (Figure 1-2). Transmission electron microscopy (TEM) images of cross-sections of this fruit shows a helical nanostructure consisting of twisting cellulose microfibrils. Bragg reflection of this periodic helicoidal stacking gives rise to a reflection of circularly polarized light that matches the helical pitch of the stack structure. Both the peacock feathers and the *Pollia condensata* plant display structural colour that, in contrast to pigments or dyes, arises from the physical interaction of light with the biological nanostructures. While pigments and dyes fade over time, some structural colouration can persist for hundreds of years, long after the death of the organism.<sup>[33]</sup>



**Figure 1-2.** (a) A single dried fruit from *Pollia condensata*. (b) TEM of the cellulose microfibrils that constitute the thick cell wall. The red lines highlight the twisting of the microfibrils. (c) 3D representation of the cellulose microfibril assembly (Reproduced and adapted from reference 33, copyright 2012 PNAS).<sup>[33]</sup>

## **1.2 Mesoporous Materials**

### 1.2.1 Overview

Mesoporous materials are defined as materials with pore sizes of 2-50 nm in diameter.<sup>[35]</sup> This pore size provides an excellent combination of high surface areas and molecular diffusion. Mesoporous materials can be composed of a wide variety of chemical compositions including silica,<sup>[36]</sup> alumina,<sup>[37]</sup> carbon,<sup>[38]</sup> and transition metal oxides.<sup>[39]</sup> A tremendous amount of research has been conducted on the development of porous materials. The ability to control pore size, pore network morphology, and surface chemistry is critical for optimizing mesoporous materials for specific applications. Consider porous aluminosilicate framework materials, which are synthesized using a cation that functions as a template.<sup>[40]</sup> By changing the size of the cationic template, it is possible to control the size of the pore network within the material and therefore the reactivity of the material.

Small molecules and ions are appropriate to synthesize porous materials with pores up to ~2 nm in diameter. However, accessing materials with larger pores requires a supramolecular approach where the template is larger than a single molecule or small ion. Significant research into the development of mesoporous materials has occurred during the last 30 years as they are attractive for diverse applications including catalysis, chromatography, drug delivery, biosensing, and environment remediation.<sup>[41–43]</sup> The following sections will focus on the approach of using liquid crystal templating to synthesize mesoporous materials.

## **1.2.2** Soft templating

## **1.2.2.1** Introduction to liquid crystals

Liquid crystals (LCs) are a state of matter between a solid (crystalline) and an isotropic liquid (a liquid that is uniform in all directions). Although LCs appear to share many of the physical attributes to liquids, they also have varying degrees of orientational and positional ordering (Figure 1-3).<sup>[44]</sup> There are two general categories that can be used to describe LCs: thermotropic and lyotropic. A pure substance that has a liquid crystalline behavior dependent on temperature is known as a thermotropic LC. Thermotropic LCs form solids at low temperatures and form isotropic liquids at high temperature due to thermal motion disrupting intermolecular interactions. Temperature-dependent LCs are commonly used for their optical properties in applications, such as displays.<sup>[45]</sup> Lyotropic LCs consist of molecules or particles in solvent that display LC phase transitions depending on concentration, temperature, and other factors. The most well-known lyotropic LCs are amphiphilic molecules that self-assemble into micelles. Above a critical concentration in water, amphiphilic surfactants self-assemble so that their hydrophilic heads face towards the water molecules and their hydrophobic tails interact with each other. LC properties are not restricted to low molecular weight molecules and can also occur in high molecular weight systems like polymers and colloidal particles.<sup>[46,47]</sup>

The formation of self-assembled LC structures is driven by specific intermolecular interactions, such as hydrogen bonding and ionic interactions.<sup>[45]</sup> The specific LC phases are dependent on the shape of the "molecular building blocks". The two most common types of liquid crystalline phases are nematic and smectic. Nematic LCs have only orientational ordering whereas smectic LCs have positional and orientational ordering (Figure 1-3). At high concentrations, LCs can organize to form higher ordered polygonal or lamellar LC phases.<sup>[48]</sup>



**Figure 1-3.** A comparison between isotropic liquids (left) and a nematic (middle) or a smectic (right) liquid crystal phase.

## **1.2.2.2** Chiral nematic phase

The nematic phase is the simplest of the liquid crystalline phases. In this phase, LCs align along their molecular axis and have long-range orientational ordering but no positional ordering.<sup>[44]</sup> The average direction of the molecular axis of the LCs in a nematic liquid crystalline phase is called the nematic director. When chirality is introduced into a nematic system, intermolecular forces between the LCs cause the molecular axis between layers to be at slight angle to each other. This leads to the formation of an intrinsic helical structure where the director in each layer is slightly twisted with respect to the layers above and below it, giving a long-range chiral order (Figure 1-4). This type of liquid crystalline phase is referred to as a chiral nematic liquid crystal (CN-LC) or a cholesteric phase and can occur for both thermotropic and lyotropic LCs. Notably, many chiral biomolecules have been observed to behave as lyotropic CN-LCs. These include cellulose derivatives, DNA, chitin, collagen fibers and rod-shaped viruses.<sup>[49]</sup>

An important characteristic of the CN-LC phase is the distance it takes for the nematic director to complete one full rotation  $(360^\circ)$  about the helical structure. This distance known as the

chiral pitch (*P*) and its axis runs perpendicular to the plane of the nematic director. The angle that the director changes between layers determines the length of the pitch. The orientation or direction that the director rotates depends on the chirality of the LCs. CN-LCs can have a left-handed (LH) or right-handed (RH) helical axis.

CN-LCs typically display unique optical properties. The chiral ordering of the anisotropic LCs results in periodic changes in the refractive index and causes these systems to behave as one-dimensional photonic crystals (periodic nanostructures with an alternating refractive index along one direction) (Figure 1-4). These alternating layers of different refractive indices selectively reflected light from the material based on Bragg's diffraction. The handedness of light reflected from the materials matches the handedness of the chiral nematic structure and can be detected by ultraviolet-visible (UV-Vis) spectroscopy and circular dichroism (CD) spectroscopy.



Figure 1-4. Representation of a CN-LC phase.

## **1.2.2.3** Liquid crystal templating

In 1992, Kresge and co-workers described a new way to synthesize mesoporous silica materials with well-organized, periodic pore structures.<sup>[36]</sup> This discovery was a breakthrough for materials chemistry scientists as it greatly improved upon the disordered porous materials that were being synthesized at the time. Kresge *et al.* found that quaternary ammonium surfactants mixed into water formed micelles that could further self-assemble into a lyotropic liquid crystalline phase comprising of a hexagonal arrangement of cylindrical micelles. Silica could be condensed around the cylindrical arranged micelles in a sol-gel reaction followed by removal of the quaternary ammonium surfactant to form mesoporous silica materials, known as MCM-41 and MCM-48, with 2-D and 3-D well-ordered hexagonally packed pores. This procedure is now known as liquid crystal templating.

Liquid crystal templating is a versatile approach to produce mesoporous materials. During LC templating, surfactant micelles are used as structure directing agents to template inorganic precursors (Figure 1-5). The inorganic precursors condense around the organic LC to form composite materials composed of both the inorganic precursors and the LCs. "True" LC templating uses lyotropic LCs that pre-organize into a LC phase independent of the inorganic precursors. This ensures more predictable morphologies of the subsequent materials and control over long-range ordering.<sup>[50]</sup> However, LC templating can also occur through cooperative self-assembly with the inorganic precursor. In cooperative self-assembly, the inorganic species can interact with the template and strongly influence self-assembly of the LC, but the resulting materials are typically less ordered and have less predictable structures.<sup>[36,51]</sup>

After formation of the composite materials, mesoporous materials are synthesized by removal of the LCs through incineration at high temperatures (known as calcination) or by liquid extraction. The overall porous structures of the mesoporous materials are determined by the selfassembly of surfactants into lyotropic LC phases (Figure 1-5). Since the original experiment by Kresge and co-workers in 1992,<sup>[36]</sup> the types of surfactants used for LC templating have expanded to a wide variety of templates, such as block-copolymers,<sup>[52]</sup> biological polymers,<sup>[49]</sup> and charged surfactants of varying sizes and shapes.<sup>[53]</sup> Altering the type and concentration of the template allows the pore structure, organizational pattern and pore sizes to be specifically tailored.



Figure 1-5. The synthesis of ordered mesoporous materials by true liquid crystal templating.

In the late 1990s, Brinker and Ozin developed a protocol to form mesoporous thin film materials with periodic organized nanostructures by LC templating combined with a process known as evaporation-induced self-assembly (EISA).<sup>[54–56]</sup> In EISA, both inorganic precursors and LCs are mixed together into a homogeneous solution and allowed to dry freely in air. The progressive increase in surfactant concentration drives self-assembly of the inorganic precursors and surfactant micelles to further organize into liquid crystalline mesophases. It is important to balance the polymerization of the inorganic precursors with the formation of the LC mesophase to ensure a well-ordered mesoporous material can be formed.

#### **1.2.3 Hard templating**

Hard templating (otherwise referred to as nanocasting) has emerged as a powerful alternative to soft templating as a means to develop nanostructured materials. Hard templating was first reported by Ryoo and co-workers in 1999, who synthesized mesoporous carbon with an ordered structure by converting sucrose into carbon inside a mesoporous silica template.<sup>[57]</sup> Once the silica template was removed, the three-dimensional porous network in their mesoporous carbon material closely replicated the original mesoporous silica structure.

Creating novel structured materials using a hard templating approach requires three major steps.<sup>[58]</sup> First, the ordered mesoporous template materials are synthesized, typically using a LC templating approach. Second, the target precursors are infiltrated into the pores and channels of mesoporous templates and converted into a solid. Finally, after solidification is achieved within the pores, the parent template material is selectively removed (Figure 1-6). The resulting material has an ordered structure that replicates the shape of the mesoporous template. This approach is particularly advantageous for precursors that are not compatible with certain soft templating methods. The incompatibility could arise from the precursor condensing too quickly, disrupting the self-assembly of the LC, or being unable to mix in a given solvent.<sup>[58]</sup> By using silica as a hard template, a wide range of nanostructured materials have been obtained including mesoporous carbons,<sup>[57]</sup> metal nanowires,<sup>[59]</sup> and mesoporous metal oxides.<sup>[60]</sup> Two of the major challenges when using a hard templating approach are selectively removing the mesoporous template without affecting the casted material and obtaining sufficient infiltration of the precursors into the pores of the template to maintain the structure after the template is removed.<sup>[58]</sup>



Figure 1-6. The synthesis of ordered mesoporous materials by hard templating.

## 1.2.4 Mesoporous silica

Mesoporous silicas are inorganic materials synthesized by the polycondensation of silica species in the presence of a structural templating agent.<sup>[17]</sup> As described above, the first well-ordered mesoporous silica materials were reported by Mobil Oil Research and Development scientists in 1992 who used a cationic surfactant as a LC template and alkoxy silane precursors.<sup>[36]</sup> Alkoxy silanes, such as tetramethyl orthosilicate (TMOS) and tetraethyl orthosilicate (TEOS), form silica networks in mild aqueous conditions through a sol-gel process. During this process, the molecular alkoxy silane precursors condense together to form a colloidal suspension (*sol*) that further aggregates and condenses to form integrated networks (*gel*).<sup>[61]</sup> Sol-gel processing to form silicate materials is highly versatile and can be carried out using a wide variety of different precursors and reaction conditions (e.g., temperature, concentration, and solvent mixtures).<sup>[61]</sup> The rate of the reaction is influenced by a several parameters including the kind of precursors used, the type of solvent, and the ratio of precursor to water, and is typically catalyzed by an acid or a base. To synthesize mesoporous silica materials by liquid crystal templating, composite inorganic-organic materials are first created when the alkoxy silane precursors hydrolyze and condense

around the surfactant into a solid silica network. The organic template is removed by calcination or solvent extraction yielding a pure silica framework with ordered pore structures.

Mesoporous silica is one of the most investigated materials in inorganic chemistry due to its chemical and physical stability, and tunable surface chemistry.<sup>[61]</sup> The incorporation of organic groups into silica networks is attractive due to the number of organic molecules that could be integrated into the stable silica network. Organic-functionalized mesoporous silica can be tailored for specific applications, whether it be controlling the polarity of the pore surface or introducing sites for catalysis or sensing.<sup>[62]</sup> Surfaces of mesoporous silica can be easily modified through free silanol groups that readily react with trialkoxyorganosilanes. This type of functionalization is known as grafting, or post-synthetic modification, and can be used to modify the inner porous network of mesoporous silica materials. Mesoporous silica can also be modified with organic groups through co-condensation.<sup>[62]</sup> In this method, TMOS or TEOS are mixed together with trialkoxyorganosilanes and structure-directing templates during self-assembly in a one-pot synthesis. Co-condensation generally has a more homogeneous distribution of the organic group and avoids the pore blocking that can sometimes occur using post-synthetic modification. However, using co-condensation can decrease the order of the porous network and care must be taken so that the organic functionality is not destroyed during template removal. Organicfunctionalized mesoporous silica has attracted increasing interest for applications including catalysis,<sup>[41,63]</sup> metal scavenging,<sup>[64]</sup> chromatography,<sup>[65]</sup> and biomedical applications.<sup>[66]</sup>

#### 1.2.5 Mesoporous organosilica

In 1999, three research groups independently reported the incorporation of organic groups into the 3-D network of mesoporous silica materials.<sup>[24,67,68]</sup> These syntheses followed a similar LC templating approach for the production of mesoporous silica but employed simple bridged dipodal alkoxysilane precursors, (R'O)<sub>3</sub>Si-R-Si(OR')<sub>3</sub>, in place of Si(OR)<sub>4</sub> precursors. Sol-gel processing of the (R'O)<sub>3</sub>Si-R-Si(OR')<sub>3</sub> precursors around a structure-directing template resulted in the formation of mesoporous materials that had organic functionality integrated directly into the backbone of the ordered porous structure (Figure 1-7). These materials are referred to as periodic mesoporous organosilicas (PMOs). In contrast to organic-functionalized mesoporous silica made from post-synthetic modification or co-condensation, the direct incorporation allows the organic group to be homogeneously distributed throughout the pore walls. Well-defined PMOs can be synthesized with many different structures (e.g., hexagonal, cubic, lamellar, wormlike) and pore sizes by varying the type of templating agent, the organic functionality, and the reaction conditions.



**Figure 1-7.** Synthesis of a PMO from bridged alkoxysilane precursors (Reproduced from reference 53 with permission from the Royal Society of Chemistry).<sup>[53]</sup>

The first reported PMO materials were synthesized using small organic functional groups (e.g., R= methylene (-CH<sub>2</sub>-), ethylene (-CH<sub>2</sub>CH<sub>2</sub>-), and ethenylene (-CH=CH-)).<sup>[24,67,68]</sup> PMO 16

materials that are prepared from 100% organic-bridged precursors are significantly influenced by the bridging organic moiety due to the dense packing of organic species within the framework. The addition of organic functional moieties "R" into mesoporous silica produced unique properties including hydrothermal stability, improved mechanical properties, and chemical reactivity of the material. The organic bridging group can also influence that structure and surface properties of the porous network. For example, unlike the amorphous silica network commonly found in mesoporous silicas, hexagonal PMOs synthesized with bridging phenylene groups have highly crystalline pore walls as confirmed by powder X-ray diffraction (PXRD).<sup>[69]</sup> These phenylenebridged PMO materials have alternating hydrophobic phenylene groups and hydrophilic silica layers. It has been shown that direct sulfonation of the phenylene moieties creates PMO materials with promising catalytic applications<sup>[69,70]</sup> while spherical particles of phenylene-bridged PMOs could be used for high-performance liquid chromatography.<sup>[71]</sup> More recently, the introduction of other aromatic bridging groups, such as anthracene and naphthalene, have produced materials with interesting and controllable optical properties, such as efficient white light phosphors.<sup>[53,72]</sup> Another interesting application for the modified surface properties of PMOs is the ability of ethylene-bridged PMOs to help with the refolding of certain proteins. It has been demonstrated that the periodic pores in these PMOs can entrap denatured proteins and the hydrophobic ethylene moiety and charged silanols in the framework can interact with different parts of protein and control the protein's release.<sup>[73]</sup>

More complex organic moieties have also been introduced into PMOs to tailor these materials for specific applications. Urea-functionalized PMOs have been shown to selectively absorb metals, such as Co<sup>2+</sup>, from aqueous solutions and have potential application in environmental remediation.<sup>[74,75]</sup> PMOs containing azobenzene bridging groups exhibit photoinduced reversible changes in the porosity of the materials as a result of the change in the molecular dimensions of azobenzene from the *trans* to *cis* configurations.<sup>[76]</sup> PMOs functionalized with diimines have a strong affinity for metal cations and have potential applications as sensing materials.<sup>[77]</sup> The introduction of chiral centers in PMO materials is also very attractive when developing novel organosilica materials. PMOs functionalized with vanadyl salen complexes have been used as solid supports for catalytic reactions,<sup>[78]</sup> and spherical particles of PMOs functionalized with chiral *trans*-(1*R*, 2*R*)-diaminocyclohexane have been used for chiral chromatography and chiral separations.<sup>[79]</sup>

Since their discovery 18 years ago, PMOs have been synthesized with a vast library of different (R'O)<sub>3</sub>Si-R-Si(OR')<sub>3</sub> precursors and have offered new paths for the development of fluorescent systems,<sup>[72]</sup> sensors,<sup>[77]</sup> and solid-state catalysts.<sup>[78]</sup> However, there are limitations to the synthesis of PMOs. In the case of larger and more complex organic bridging groups, it is often not possible to form highly porous or ordered materials using 100% loading of the organic-bridged precursors. Often it is necessary to dilute the desired organic moiety with another simpler silica precursor, such as TMOS, TEOS, or bis(trimethoxysilyl)ethane.<sup>[80]</sup> Through the condensation of two or more bridged organosilane precursors, multi-functional PMOs can be obtained.

## **1.3 Cellulose Nanocrystals**

#### 1.3.1 Overview

Transforming renewable biomass into value-added materials is a rapidly growing industry. Low cost lignocellulosic biomass is of particular interest for the production of functional materials.<sup>[81]</sup> Lignocellulose is the primary building block in plant tissues. Due to its natural abundance, lignocellulose is one of the most universally used materials with a worldwide production estimated to be around 10<sup>12</sup> metric tons annually.<sup>[81,82]</sup> Lignocellulosic biomass consists of three major biopolymers: (i) cellulose (a linear D-glucose polymer), (ii) hemicellulose (a branched complex carbohydrate heteropolymer), and (iii) lignin (a complex three-dimensional phenolic polymer) (Figure 1-8). Lignocellulosic biomass is extracted from a wide variety of feedstocks including agriculture resides, food wastes and forestry.<sup>[82]</sup> Its chemical composition can be vastly different depending on the source of the biomass. For example, wood is a cellular biocomposite that is comprised of approximately ~40-55% by weight of cellulose, 25-40% by weight of hemicellulose, and 20-35% by weight of lignin.<sup>[82,83]</sup> The unique hierarchical structure of these biopolymers within wood leads to the unique strength and high-performance properties of different species of trees.

Each of the biopolymers present in lignocellulose can be chemically or catalytically converted into fuels, chemicals or reactive intermediates. Lignin and hemicellulose are primarily being researched as biofuels for alternative energy or in biorefineries where they can be converted to higher value chemicals.<sup>[83,84]</sup> Cellulose, in particular cellulose nanocrystals, has applications in biocomposites and as a reinforcement material.<sup>[49,85]</sup> The major obstacle for using lignocellulose as a renewable starting material to synthesizing novel value-added products is the separation of these biopolymers from each other. The complex hierarchical structure and compositional factors of plant cell walls cause them to be resistant to degradation but can hinder the fractioning of these components. The following sections will focus on the isolation, physical properties and applications of cellulose biopolymers with emphasis on cellulose nanocrystals.



**Figure 1-8.** The three major biopolymers in lignocellulosic biomass; (i) cellulose, (ii) hemicellulose, and (iii) lignin and their applications.

## **1.3.2** Introduction to cellulose

Cellulose is one of the most abundant biopolymers found in nature. It is a linear polymer of D-glucose units linked through  $\beta$ -1,4-glycosidic bonds (Figure 1-9). Cellulose is the major structural component of plants and can be commonly isolated from the cell walls of plants and algae.<sup>[86]</sup> In addition, cellulose can be found in certain species of bacteria, fungi, and marine animals.<sup>[87]</sup> Its unique combination of mechanical support, crystallinity, abundance, and biocompatibility presents promising applications for cellulose in the field of materials chemistry.

During the biosynthesis of cellulose, van der Waals interactions and intermolecular hydrogen bonding between hydroxyl groups promote the formation of stacked planar cellulose chains (Figure 1-9).<sup>[30]</sup> These chains are composed of crystalline and amorphous regions that form 3-5 nm long fibrils which can aggregate into larger microfibers. There are several methods to isolate naturally derived cellulose microfibers from the other lignocellulose components.<sup>[82]</sup> The first major method uses mild acid hydrolysis to dissolve hemicellulose followed by subsequent bleaching to remove soluble polysaccharides and residual phenolic molecules.<sup>[88]</sup> The second major method is through an alkaline hydrolysis and oxidative extraction treatment, usually 2-4 v/v % NaOH at elevated temperatures. The isolated cellulose microfibers are typically 2-20 nm in diameter and up to tens of microns long.<sup>[88]</sup>

Cellulose materials are widely used in the pulp and paper industry for paper and cardstock but can also be found in textiles. Recently, cellulose has been investigated as an additive in composite materials, in medical applications, and as a templating agent.<sup>[89–91]</sup> Cellulose with dimensions in the nanoscale is of particular interest in the emerging field of templating using naturally derived LCs.



Figure 1-9. The chemical structure of cellulose polymers and possible intra- and intermolecular hydrogen-bonding.

## **1.3.3** Preparation of cellulose nanocrystals

Cellulose microfibers contain highly crystalline regions of cellulose I, a parallel arrangement of cellulose chains held together by hydrogen bonding. These closely packed crystalline regions are separated by amorphous regions. The first synthesis of colloidal cellulose particles with nanoscale dimensions was reported by Ränby in 1951.<sup>[92]</sup> Ränby and co-workers developed a method to isolate the crystalline regions of cellulose microfibers. They found that the low density amorphous regions are more susceptible to acid hydrolysis than the crystalline domains. Therefore, exposing the cellulose microfibers to mild acidic conditions selectively degrades the amorphous regions in the microfibers, thereby yielding rod-shaped cellulose nanocrystals (CNCs) (Figure 1-10). Isolated CNCs have dimensions between 50 to 2000 nm in length and can vary depending on the biological source from which they are extracted.<sup>[86]</sup> For

example, CNCs extracted from wood have diameters of 5 to 10 nm and are 100 to 200 nm long whereas CNCs extracted from algae have lengths of 1000 to 2000 nm.

The dimensions and properties of the CNC rods also depend on the hydrolysis conditions, such as the type of acid, acid concentration, temperature of reaction, and duration of treatment. CNCs are often prepared using sulfuric acid-catalyzed hydrolysis because the sulfuric acid partially converts hydroxyl groups on the surface of the CNC rods into sulfate esters. The introduction of these negative sulfate surface groups helps stabilize the colloidal suspensions of CNCs through electrostatic repulsion. Other acids can also be used for hydrolysis to produce CNCs but result in neutral particles that are much harder to disperse.<sup>[93]</sup> After acid hydrolysis, the CNC suspensions are typically purified by centrifugation and dialysis to remove by-products and excess acid.



**Figure 1-10.** (a) The synthesis of CNCs by acid hydrolysis. (b) Negatively stained TEM image of CNCs (Reproduced with permission from reference 94, copyright 2008 American Chemical Society).<sup>[94]</sup>

## 1.3.4 Chiral nematic self-assembly of cellulose nanocrystals

The lyotropic liquid crystalline phase of cellulose derivatives in water was first reported in 1976 by Werbowyj and Gray for hydroxypropyl cellulose (HPC).<sup>[95]</sup> HPC has been used in an array of organic templating approaches, yielding composite materials, such as HPC/polyacrylic acid.<sup>[96,97]</sup> Other cellulose derivatives (e.g., ethyl cellulose) have also been observed to form lyotropic and thermotropic liquid crystalline phases in water and other solvents.<sup>[98]</sup> However, most cellulose derivatives require high critical concentrations (40-70 wt.%) to form liquid crystalline phases which results in slow self-assembly and low solubility of any precursors added to the suspension.

The lyotropic liquid crystalline phase of CNCs was first reported in 1959 by Marchessault *et al.*,<sup>[99]</sup> however, the chiral nematic phase was not reported until 1992.<sup>[100]</sup> Gray and co-workers found that a colloidal CNC suspension could form a chiral nematic phase at much lower concentrations (~3-6 wt.%) than what was seen for the previously mentioned cellulose derivatives. Below a critical concentration, CNC suspensions are isotropic and can be stabilized by anionic sulfate surface groups. As the concentration of the CNC suspension is increased, an ordered chiral nematic phase is formed that is in equilibrium with the isotropic phase. The ordered phase appears as droplets of anisotropic phase LCs dispersed in the isotropic phase, otherwise known as tactoids.<sup>[101,102]</sup> These short-range ordered tactoids are the intermediate state between the isotropic phase and the long-range anisotropic structure.<sup>[102]</sup> At high enough concentrations, the isotropic phase, the rod-shaped LC CNCs align along their long molecular axis. In the simplest case, this alignment would lead to a nematic phase with long-range orientational ordering. However, the CNC rods introduce chirality into the nematic system causing an helical twist

perpendicular to the long axis of the CNCs.<sup>[104]</sup> CNCs contain three levels of chirality: (1) asymmetric carbons in the D-glucose units at the molecular level; (2) a twisted morphology of the individual CNC rods; and (3) the chiral nematic ordering of the LC. Although the exact mechanism for the chiral nematic ordering of CNCs is still under debate, it has been proposed that a screw-like morphology of the CNC rods and/or the surface charges on the CNC rods gives rise to the chiral interactions.<sup>[105]</sup> In the case of CN-LC phase of CNCs, only left-handed chiral nematic structures have been observed (Figure 1-11d-e).



**Figure 1-11.** (a–c) Cartoon depictions of tactoids and their transformations as the solvent evaporates from the CNC suspension. (d, e) Cross-sectional SEM images of a CNC tactoid captured in a polyacrylamide hydrogel (scale bars = 30  $\mu$ m and 40  $\mu$ m respectively). (Reproduced from reference 103 copyright 2016 Nature Publishing Group).<sup>[103]</sup>

Pure CNC films are obtained through EISA where the chiral nematic structure of the CNC rods is retained.<sup>[106]</sup> These solid chiral nematic films have optical properties due to the long-range periodic chiral nematic ordering imparted by the CNC LC template. The helical ordering of the chiral nematic director within the CNCs causes periodic changes in the refractive index of resulting films, leading them to selectively reflect light of a certain wavelength. The relationship between wavelength reflected by a chiral nematic structure ( $\lambda_{max}$ ) for incident light normal to the surface, refractive index ( $n_{avg}$ ), and helical pitch (P) can be described by the following equation:<sup>[107]</sup>

$$\lambda_{\max} = n_{avg} P \sin\theta \tag{1}$$

Bragg diffraction of the periodic chiral nanostructure gives rise to a reflection of circularly polarized light. Only light with circular polarization that matches the handedness of the helical structure is reflected. Since CNCs only form a LH chiral nematic structure, LH circularly polarized light is reflected from the CNC films while RH circularly polarized light is transmitted through the films (Figure 1-12). When the helical pitch of the CNC films is on the order of microns, the films reflect light that can range from the UV to near-IR wavelengths.



**Figure 1-12.** (a) Photograph of a CNC film dried by EISA. (b) A depiction of CN-LCs. Discrete layers are shown to illustrate the orientation of the nematic director corresponding to the rotation of the helical pitch (Reproduced and adapted with permission from reference 91, copyright 2010 Nature Publishing Group).<sup>[91]</sup>

The relationship between the chiral nematic helical pitch (*P*) and the properties of individual CNCs depend on their aspect ratio, surface charge and molecular structure.<sup>[93,108]</sup> Other factors that affect the chiral nematic phase formation include ionic strength, the nature of the counterions, acid hydrolysis condition of the CNCs, and the CNC suspension evaporation conditions.<sup>[93,109,110]</sup> A variety of methods have been developed to control the final helical pitch and therefore the optical properties of the dried CNC films. These include the addition of salt into the CNC suspension to decrease the pitch, ultrasonication of the suspension prior to drying to increase the pitch, or altering drying times by adjusting humidity and temperature.<sup>[91,111–113]</sup> Control of the self-assembly and nanostructures of CNC films is important for future applications of these materials.

## **1.4** Cellulose Nanomaterials by Liquid Crystal Templating

### 1.4.1 Overview

Current research in nanotechnology has focused on measuring the properties of materials, such as quantum dots and carbon nanotubes, on the nanoscale. Biological materials (e.g., wood and plant materials) have received less attention despite their many advantages including sustainability and the ability to self-assemble.<sup>[81]</sup> Many natural substances, such as collagen and cellulose, are known to form LCs with hierarchical assemblies that span multiple length scales.<sup>[46,49,100]</sup> These substances present exciting opportunities to develop novel materials using LC templating.<sup>[114]</sup> Cellulose nanocrystals are of particular interest in LC templating due to their abundance and biocompatibility. The following sections will highlight some of the exciting work that has been done on synthesizing porous materials using cellulose nanocrystal templates.

## **1.4.2** Silica materials templated with CNCs

The first example of CNC templating was reported by Mann and co-workers in 2003.<sup>[115]</sup> They combined an aqueous suspension of CNCs with a solution of pre-hydrolyzed TMOS. Upon evaporation of the suspension, the CNC rods formed a LC template and produced birefringent silica composite materials. However, no long-range chiral nematic ordering was observed in their materials.

In 2010, the MacLachlan group reported the synthesis of free-standing chiral nematic mesoporous silica (CNMS) films with long-range chiral nematic ordering imparted by a CNC template.<sup>[91]</sup> These materials were synthesized by the hydrolysis and condensation of the alkoxysilane precursors (TMOS or TEOS) in an aqueous suspension of CNCs. EISA was performed on the composite suspension causing the CNCs to self-assemble into an ordered chiral

nematic structure while the silica condensed around the CNC rods (Figure 1-13a). The resulting CNC/silica composite films displayed iridescent colours with positive ellipticity measured by CD spectroscopy. This LH CD signal matched the wavelength of reflected light measured by UV-Vis spectroscopy, indicating that the films exclusively reflected LH circularly polarized light. By changing the silica to CNC ratio, Shopsowitz *et al.* synthesized composite CNC/silica material with tunable helical pitches and films that reflect wavelengths of light ranging from ultraviolet to infrared.

The CNC templates were removed from the composite materials by calcination at 540 °C under air or acid hydrolysis yielding pure silica films.<sup>[91,116]</sup> The resulting free-standing mesoporous silica films displayed intense iridescence, and reflected LH circularly polarized light that was blue-shifted with respect to the composite films. The films had high surface areas ranging from 300 - 800 m<sup>2</sup>/g, pore volumes of 0.25 to 0.60 cm<sup>3</sup>/g, and pore sizes of 3 to 5 nm. Retention of the chiral nematic structure imparted by the CNC template was confirmed by scanning electron microscopy (SEM) (Figure 1-13b, c). The resulting silica films had a chiral nematic organization of pores with a long-range periodic structure that was several hundred nanometers long. This periodic nanostructure was visible throughout the thickness of the films and the counter clockwise twist of the mesopores was consistent with the LH chiral nematic structure of CNCs. These films were the first example of a new family of functional photonic materials based on silica chemistry and CNCs.



**Figure 1-13.** Chiral nematic CNC-derived materials. (a) Synthesis of CNMS. (b) Photograph of CNMS (left) and chiral nematic mesoporous organosilica (CNMO) (right). (c) SEM image of a CNMS film (Reproduced from reference 49 with permission from Elsevier).<sup>[49]</sup>

In 2012, Shopsowitz *et. al.*, extended the procedure to synthesize CNMS films to chiral nematic mesoporous ethylene-bridged organosilica films using bis(trimethoxysilyl)ethane (BTMSE) as the silane precursor.<sup>[116]</sup> The CNC template was removed using 6 M sulfuric acid to prevent the degradation of the organic spacers. Nitrogen adsorption measurements of chiral nematic mesoporous organosilica (CNMO) films displayed high surface areas of 400 to 740 m<sup>2</sup>/g, pore volumes of  $0.6 - 1.0 \text{ cm}^3$ /g, and pore diameters of 7-9 nm. The incorporation of ethylene bridging groups into the pore structure improved the mechanical properties of the films when compared to the CNMS films.

#### **1.4.3** Applications of chiral nematic mesoporous silica

The chiral nematic mesoporous (organo)silica films have promising applications including as sensors, as chiral separation materials, and as chiral support materials. One important feature of CNMS and CNMO films is their optical properties resulting from the long-range chiral nematic nanostructure of the porous network. The MacLachlan group demonstrated that introducing guest molecules into the porous network, such as different solvent molecules or aqueous sucrose solutions, could alter the iridescent colour of the films.<sup>[91,117]</sup> It was found that when the refractive indices between the solvent in the pores and silica were closely matched (e.g. n = 1.33 for H<sub>2</sub>O and n = 1.46 for SiO<sub>2</sub>), the reflectance colour was quenched and the films appeared translucent (Figure 1-14a). Additionally, by monitoring the CD signal of the films, it was possible to incorporate analytes into the films and allow for the determination of the analyte's concentration in water. Thermotropic LCs, 4-cyano-4'-octylbiphenyl (8CB) or phloroglucinol derivatives, were also incorporated into the CNMS and CNMO films. Changes in temperature altered the alignment of the guest LC molecules and caused a change in their refractive index. This allowed the photonic properties of the films to be controlled through an external stimuli.<sup>[118,119]</sup> The response of the optical properties of the chiral nematic silica films to guest molecules offers a new route to create sensors based on CNC LC templated materials.

CNMS materials can also be used for enantioselective separation, as solid supports and as hard templates. In 2014, Zhang *et al.* tested the separation of a variety of achiral and chiral molecules using a CNMS-coated capillary column in high-resolution gas chromatography (GC).<sup>[120]</sup> The CNMS-coated capillary column showed good selectivity for the separation of linear alkanes and aromatic hydrocarbons as well as reasonable enantioselectivity for chiral compounds like 2-amino-1-butanol, isoleucine, and serine. In 2011 and 2014, Qi *et al.* and Kelly *et al.*,

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respectively, used CNMS as a support material to synthesize CNMS films doped with silver, gold, or platinum nanoparticles (NPs).<sup>[121,122]</sup> The NP/CNMS composites were synthesized by either co-assembly (NP precursors were introduced to the CNC and silica suspension prior to EISA) or post-synthetic modification (NP precursors were introduced after the CNMS was synthesized). In 2014, Nguyen *et al.* co-assembled CdS quantum dots (QDs) with a CNC and silica suspension to synthesis CdS QD doped CNMS films.<sup>[123]</sup> The resulting composite material showed iridescence from the long-range chiral nematic nanostructure and luminescence of the QDs with lifetimes of 1.75 ns (Figure 1-14b). These composites may have promise as chiral supports for sensing applications. Finally, Shopsowitz *et al.* demonstrated that chiral nematic titania films could be obtained through hard templating with CNMS.<sup>[124]</sup> Titania/silica composites were synthesized by loading a TiCl4 solution into CNMS films. The composite films were annealed, calcined and the silica template was removed using sodium hydroxide. The resulting chiral nematic mesoporous anatase titania films reflected LH circularly polarized light and displayed a long-range chiral nematic nanostructure when analyzed by SEM (Figure 1-14c).



**Figure 1-14.** (a) Photograph of a CNMS film infiltrated with water (Reproduced from reference 91 with permission from Nature Publishing Group).<sup>[91]</sup> (b) Photograph of the CdS/silica/CNC composites (Reproduced from reference 123 with permission from John Wiley and Sons).<sup>[123]</sup> (c) Photograph of hard templated chiral nematic titanium dioxide films viewed under a LH circular polarizing filter (Reproduced from reference 124 with permission from John Wiley and Sons).<sup>[124]</sup>

#### **1.4.4** Organic materials templated with CNCs

CNCs have also been used as a LC template to transfer chirality into polymeric and organic materials. Chiral nematic mesoporous carbon (CNMC) materials were first reported by Shopsowitz *et al.* in 2011.<sup>[125]</sup> To obtain the CNMC films, CNC/silica composite films were first synthesized by EISA then heated under an inert nitrogen atmosphere at 900 °C to form carbon/silica composites. The silica was then removed using sodium hydroxide to produce mesoporous carbon materials that retained the chiral nematic structure from the CNCs. The porosity of the films was controlled by the amount of silica precursor used in the original CNC/silica composites and ranged from microporous to mesoporous with surface areas of 570 - 1460 m<sup>2</sup>/g.

Tatsumi *et al.* reported the first hydrogel material templated with CNCs.<sup>[126]</sup> They demonstrated that an anisotropic poly(2-hydroxyethylmethacrylate)/CNC composite displayed long-range chiral nematic ordering as observed by SEM. In 2013, Kelly *et al.* synthesized a series of composite hydrogel/CNC materials from polymer precursors including methacrylate derivatives, acrylamide derivatives, and acrylic acid. Each monomer was mixed into an aqueous CNC suspension containing a cross-linker and a photoinitiator. Once the CNC suspension formed an anisotropic phase, films were irradiated with UV light to initialize polymerization and form hydrogel materials. These hydrogels reflected visible light due to the long-range chiral nematic ordering of the CNCs.

One of the key features of hydrogels is their ability to swell (change volume) in response to external stimuli. The hydrogel/CNC composite materials displayed reversible swelling in response to stimuli including pH and solvent polarities.<sup>[127]</sup> As the hydrogel/CNC composites swelled, the helical pitch of the CNCs incorporated into the hydrogel expands resulting in a redshift of the reflected wavelength. Changes in the optical properties of the hydrogel/CNC composites make these materials promising for sensing applications. Additionally, the degree of polymerization of the hydrogel directly effects the swelling of the hydrogel. Introducing a photomask during irradiation with UV light creates less cross-linked regions in the hydrogels that swell faster. As such, Kelly *et al.* created photopatterned hydrogels where the pattern was only observable after the introduction of solvent to the hydrogel (Figure 1-15a).



**Figure 1-15.** Organic composite materials templated with CNCs. (a) CNC/hydrogel composite materials swollen in water to reveal a photomasked pattern (inset shows the dry hydrogel).<sup>[127]</sup> (b) Irreversible patterning of MUF/CNC films by compression (inset shows the film prior to compression).<sup>[128]</sup> (c) PF films swelling in water/ethanol mixtures.<sup>[129]</sup> (d) Mesoporous cellulose films soaked in ethanol/water at different ratios.<sup>[130]</sup> (Reproduced from reference 49 with permission from Elsevier).

The MacLachlan group also reported the synthesis of resin/CNC composite materials and resin mesoporous materials by mixing water-soluble phenol-formaldehyde (PF), melamine-urea-formaldehyde (MUF), or urea-formaldehyde (UF) precursors with CNCs followed by EISA.<sup>[128,129,131]</sup> The composite materials were thermally cured to enhance cross-linking of the organic polymer and the CNCs were selectively removed using sodium hydroxide followed by supercritical drying with CO<sub>2</sub>. The resulting mesoporous resins retained the chiral nematic structure imparted by the CNCs and reflected light in the visible range.

Similar to the hydrogel/CNC composite materials, the resin materials were tested for their response to external stimuli, such as pressure and solvents, to investigate their applications as sensors. The MUF/CNC composite films were highly compressible, therefore, the helical pitch of the CNCs was altered by applying pressure to the material. Compression of the films caused a blue-shift in the reflected wavelength that was reversible at room temperature. However, upon heating of the films to 100 °C after compression, the films permanently held the newly compressed helical pitch (Figure 1-15b). The mesoporous PF resin films displayed swelling comparable to the hydrogel/CNC composites where PF films treated with acid swelled less than untreated PF films, and PF films treated with formaldehyde swelled more than the untreated films. Therefore, the reflected wavelengths from PF films exposed to water/ethanol mixtures was dependent on both the solvent composition and the treatment of the films after synthesis (Figure 1-15c).<sup>[129]</sup> These photonic resin films have potential applications in optical displays and as security tags.

Finally, a mesoporous cellulose material composed entirely of CNCs was developed by Giese *et al.* and Schlesinger *et al.*,<sup>[130,132]</sup> using CNCs as a LC template. CNC rods were co-condensed with either urea formaldehyde (UF) or TMOS forming CNC/UF or CNC/silica composite materials. The UF polymer or silica matrix was removed through an alkaline treatment resulting in a novel mesoporous cellulose film with long range chiral nematic ordering and surface areas of  $250 - 310 \text{ m}^2/\text{g}$  (Figure 1-15d). Interestingly, the synthesis of the mesoporous cellulose materials resulted in cleavage of the sulfate ester groups on the CNC rods and greatly improved the stability of the films in polar solvents. These mesoporous cellulose materials swell rapidly in water displaying up to 400 nm red-shifts in the reflected wavelength.

## **1.5** Goals and Scope of the Thesis

The goal of this thesis is the development and application of new mesoporous materials with long-range chiral nematic ordering imparted by the self-assembly of CNCs. Many examples of applications for chiral nematic composite materials and chiral nematic mesoporous materials synthesized from liquid crystal templating with CNCs have been described above. The use of biological liquid crystals for the liquid crystal templating of novel materials is a rapidly growing field of research. Their unique structural properties allow researchers to capture and utilize the complex hierarchical structures found in nature. Additionally, their natural abundance and biocompatibility make them easier to scale up to industrial quantities. Cellulose nanocrystals are advantageous to use as liquid crystal templates due to their nanometer dimensions and lyotropic liquid crystalline behavior. Although there are many materials that have been used to template mesoporous materials with ordered pore structures, cellulose nanocrystals impart a unique longrange chiral nematic ordering to the porous network. The development of chiral nematic mesoporous organosilica materials is particularly interesting due to the chemical and physical stability of mesoporous silica. Additionally, these materials can be easily tuned because of a wide range of potential precursors.

In this thesis, I have prepared and characterized mesoporous chiral nematic materials with high surface areas and long-range chiral nematic structures, and analyzed their potential applications. All chiral nematic materials presented have been synthesized by either directly or indirectly templating with CNCs. In Chapter 2, I discuss my efforts to synthesize and characterize a library of chiral nematic mesoporous organosilica (CNMO) films using different organosilica precursors. I describe the challenges in extending the original CNMS synthesis to hydrophobic precursors and use both aqueous suspensions of CNCs as well as CNCs suspended in organic 37 solvents for templating. In Chapter 3, I report the post-functionalization of mesoporous organosilica films with photoresponsive spiropyran molecules in order to develop free-standing photoresponsive materials. In Chapter 4, I expanded the synthesis of CNMOs to ethenylene- and sulfur- functionalized films and test the application of the chiral films as a solid support to form heterogeneous salphen catalysts. In Chapter 5, I report the hard templating of mesoporous ferrite materials from CNMS films and investigate the magnetic properties of the materials. Finally, Chapter 6 states conclusions based on my findings and proposes future directions to this work.

# Chapter 2: Chiral Nematic Mesoporous Organosilicas Films with Alkylene and Aromatic Spacers<sup>\*</sup>

## 2.1 Introduction

Liquid crystal templating has emerged as a powerful tool for the synthesis of mesoporous materials. In 1992, Kresge and coworkers revolutionized the field of mesoporous materials when they used liquid crystals (LCs) to template mesoporous silica materials.<sup>[36]</sup> The self-assembly of the LC surfactants into a liquid crystalline phase imparted periodic ordering into their surfactant-silica composite, forming materials with ordered pore structures (e.g., MCM-41). Composite surfactant-silica materials are routinely prepared via a sol-gel method where alkoxysilane precursors are hydrolyzed and condensed to produce a solid silica network around the LC template.<sup>[61]</sup> Subsequent removal of the surfactant by either combustion or solvent extraction creates mesoporous materials with ordered pore structures. The organization of the pores is determined by the liquid crystalline phase and chemical structure of the surfactant. Therefore, it is possible to fabricate mesoporous materials with a range of different symmetries and pore sizes.<sup>[36,52]</sup> Since the original experiments by Kresge *et al.*,<sup>[36]</sup> various templates, such as small molecules (both ionic and non-ionic),<sup>[133]</sup> biological polymers,<sup>[49]</sup> and colloidal particles,<sup>[134]</sup> have been used to prepare mesoporous silicas with specific pore sizes and symmetries.

<sup>\*</sup> Portions of this chapter have been previously published as: (1) A.S. Terpstra, K.E. Shopsowitz, C.F. Gregory, A P. Manning, C.A. Michal, W.Y. Hamad, J. Yang, M.J. MacLachlan, *Chem. Commun.* 2013, 49, 1645. (2) A.P. Manning, M. Giese, A.S. Terpstra, M.J. MacLachlan, W.Y. Hamad, R.Y. Dong, C.A. Michal, *Magn. Reson. Chem.* 2014, 52, 532. (3) A.S. Terpstra, L.P. Arnett, A.P. Manning, C.A. Michal, W.Y. Hamad, M.J. MacLachlan. Manuscript submitted.

The addition of organic functionality into mesoporous silica can produce unique properties including molecular organization, hydrothermal stability, mechanical strength, and chemical reactivity.<sup>[69,135,136]</sup> In 1999, three research groups independently reported the incorporation of organic groups into mesoporous silica by using (R'O)<sub>3</sub>Si-R-Si(OR')<sub>3</sub> precursors for sol-gel condensation.<sup>[24,67,68]</sup> It proved possible to construct periodic mesoporous organosilica (PMO) materials with organic groups directly integrated into the walls of the mesoporous structure. Solgel processing of silicate materials can be carried out under a variety of reaction conditions (e.g., variable pH, temperature, concentration, precursor type and solvent mixtures).<sup>[61]</sup> As such, PMOs have been synthesized with diverse organic components and have offered new routes for developing materials in the fields of chromatography,<sup>[71]</sup> sensing,<sup>[77,137]</sup> solid-state catalysis,<sup>[41,63,78]</sup> and biomedicine.<sup>[138]</sup> Incorporating chirality into mesoporous silica is particularly attractive when developing novel functional organosilica materials for catalysis and separation applications. Chirality has been achieved through the introduction of chiral silvlated precursors during the self-assembly process or can be introduced by templating with chiral molecules to produce chiral mesoporous organosilica materials with twisted helical structures.<sup>[139–142]</sup>

Chiral nematic liquid crystal (CN-LC) templating of novel materials is a process inspired by nature. Biological materials often contain complex hierarchical nanostructures that display unique properties, ranging from improved tensile strength, to the physical manipulation of light based on the periodic arrangement of nanostructures.<sup>[26,33]</sup> Cellulose nanocrystals (CNCs) obtained from renewable biomass are remarkable materials that have impressive mechanical properties, arising from their high crystallinity and large aspect ratios.<sup>[86,92,93]</sup> Highly crystalline regions of cellulose microfibers can be isolated from plants through sulfuric acid-catalyzed hydrolysis to produce CNCs. The first isolation of colloidal CNCs with nanoscale dimensions was reported by Ränby in 1951.<sup>[92]</sup> Remarkably, CNCs form a chiral nematic liquid crystalline phase in water. This order can be retained upon drying to give coloured, iridescent films.<sup>[106]</sup> The CNCs arrange into a Bouligand structure, where the crystallites themselves are aligned in layers, but each layer is twisted in relation to the other layers with a characteristic helical pitch, *P*. This repeating helicoidal nanostructure leads to diffraction of circularly polarized light.<sup>[107]</sup>

In 2010, Shopsowitz *et al.* discovered that mesoporous silica films with chiral nematic nanostructures could be prepared using CNCs as a LC template.<sup>[91]</sup> When Si(OR)<sub>4</sub> is condensed with aqueous suspensions of CNCs, the resulting composite CNC/silica film contains a solid silica network with a chiral nematic organization of CNCs embedded within. CNCs can be removed from the composite materials using calcination or acid hydrolysis, leaving behind iridescent mesoporous silica films with a long-range chiral nematic porous network. The first chiral nematic mesoporous organosilicas (CNMOs) were prepared in 2012 by the MacLachlan group.<sup>[116]</sup> Bis(trimethoxysilyl)ethane (BTMSE), (RO)<sub>3</sub>Si-CH<sub>2</sub>CH<sub>2</sub>-Si(OR)<sub>3</sub>, was condensed in the presence of an aqueous suspension of CNCs followed by acid hydrolysis of the cellulose to give ethylene-bridged organosilica films (Et-CNMO).<sup>[116]</sup> In this method, 6 M sulfuric acid was used to remove the CNC template to prevent the degradation of the organic spacers that would occur if thermal methods of extracting the CNCs were used. By incorporating organic spacers into the pore structure, the ethylene-bridged CNMO films showed improved flexibility when compared to the CNMS films.

In this Chapter, I examined the extension of the synthesis of ethylene-bridged CNMO films to other alkylene and aromatic organic spacers in an effort to modify the properties of the CNMO and to investigate the limits of the self-assembly process. The first part of this Chapter focuses on the incorporation of alkylene-bridged organosilanes including methylene, propylene, butylene,
pentylene, and hexylene precursors. I report the synthesis and characterization of a family of alkylene-bridged CNMO films and discuss how long of an alkylene spacer can be incorporated and still maintain the chiral nematic structure. In the second part of this Chapter, I investigate the introduction of aromatic bridging groups into CNC suspensions and report the synthesis and characterization of aromatic CNMO films. Incorporating new organic groups as integral components of the cross-linked structure of these mesoporous organosilica films can change the chemical environment within the pores, modify the material properties, and open the door to the development of new tunable materials that could find use in optical sensing devices and enantioselective separation.

## 2.2 Experimental

## 2.2.1 Materials

All solvents and reagents including 1,2-bis(trimethoxysilyl)ethane (BTMSE, Sigma Aldrich), bis(triethoxysilyl)methane (BTESM, Gelest). 1,3-bis(trimethoxysilyl)propane (BTMSPr, JSI Silicone Co.), 1,4-bis(trimethoxysilyl)butane (BTMSBu, JSI Silicone Co.), 1,5-bis(trimethoxysilyl)pentane (BTMSPe, JSI Silicone Co.), 1,6-bis(trimethoxysilyl)hexane (BTMSH, JSI Silicone Co.), N,N'-bis(3-trimethoxysilylpropyl)urea, (BTMSPU, Gelest), 1,1,3,3,5,5-hexaethoxy-1,3,5-trisilacyclohexane (Gelest), 1,4-bis(triethoxysilyl)benzene (BTESB, Gelest). 9,10-bis(trimethoxysilyl)anthracene (BTMSA, JSI Silicone Co.), and 4.4bis(trimethoxysilyl)biphenyl (BTMSBP, JSI Silicone Co.) were purchased and used without further purification.

## 2.2.2 Characterization

Solid-state nuclear magnetic resonance (NMR) spectra were collected on a 400 MHz Varian Unity Inova equipped with a Varian/Chemagnetics 4 mm T3 MAS probe. <sup>13</sup>C cross-polarization/magic angle spin (CP/MAS) experiments (3000-7000 scans) used glycine as a reference. Samples were spun at a rate of 5 or 7 kHz. A contact time of 1.5 ms and recycle delay of 2 s was applied. N<sub>2</sub> adsorption-desorption isotherms were performed using a Micromeritics ASAP 2020 at 77 K. Samples were degassed under vacuum at 120-150 °C prior to analysis. The specific surface areas of the samples studied were calculated using the standard Brunauer-Emmett-Teller (BET) method with relative pressures from 0.04 to 0.2. Total pore volumes were estimated from the amount of N<sub>2</sub> adsorbed at a relative pressure of 0.99. Barrett-Joyner-Halenda (BJH) pore size distributions were calculated from the adsorption branch of the isotherms. Thermogravimetric analysis (TGA) was performed on a PerkinElmer Pyris 6 thermogravimetric analyzer and samples were heated under air from 30 °C to 800 °C at 5 °C/min. Infrared (IR) spectra were obtained with a Nicolet 6700 FTIR spectrometer equipped with a Smart Orbit diamond attenuated total reflectance (ATR). The photoluminescence spectra were recorded on a Photon Technology International QuantaMaster spectrofluorometer. Raman spectra were collected on a 785 nm fiber coupled Olympus BX-51 microscope at 60 s exposure time. Elemental analysis (EA) was carried out by UBC Microanalytical Services. Powder X-ray diffraction (PXRD) spectra were collected using a D8 Advanced X-ray diffractometer.

Ultraviolet-visible/near-IR (UV-vis/NIR) spectroscopy was conducted on a Cary 5000 UV-Vis/NIR spectrophotometer and circular dichroism (CD) spectroscopy was performed using a JASCO J-815 spectropolarimeter. Spectra were collected by mounting the films in a solid-state holder so that the surfaces of the films were perpendicular to the beam path. It is important to note that due to the large CD signal generated by these materials, small pieces of film were used to avoid saturating the detector. Additionally, samples with signals above 850 nm could not be detected due to a limitation of the CD detector.

## 2.2.3 Microscopy

Scanning electron microscopy (SEM) images were collected on a Hitachi S4700 electron microscope. Samples were prepared by breaking the films into small pieces and attaching them to aluminum stubs using double-sided adhesive tape. Samples were sputter-coated with 5 nm of gold. Helium ion microscopy (HIM) was performed on a Zeiss Orion Plus Helium Microscope. Images were taken without sputter-coating at an accelerating voltage of 31 kV.

# 2.2.4 Diffusion measurements

Diffusion of absorbed water molecules was measured for the organosilica films in two perpendicular directions, designated longitudinal and transverse. The samples and NMR pulse sequence followed a previously reported procedure.<sup>[143]</sup> In short, dry films (~ 5 mg) were mounted in a 5 mm NMR tube either pressed flat between plastic spacers parallel to the gradient for measurements in the longitudinal direction, or sandwiched between strips cut from slide covers perpendicular to the gradient for measurements in the transverse direction. Water (~25 mg) was added to completely saturate the pore network of the films. Samples were cooled and NMR spectra were collected at -3.5 °C on a Varian Unity Inova 400 MHz (9.4 T) spectrometer with a Varian Pulsed Field Gradient (PFG) probe delivering a 50 G/cm maximum Z gradient.

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## 2.2.5 Preparation of cellulose nanocrystals (CNCs)

Aqueous suspension of cellulose nanocrystals (CNCs) were prepared by FPInnovations according to literature.<sup>[91]</sup> Generally, softwood pulp was milled and passed through a 0.5-mm screen in a Wiley mill to ensure uniform particle sizes. The milled pulp was hydrolyzed using sulfuric acid (8.75 mL / 1 g pulp, 64 wt.%) at 45 °C and vigorously stirred for 25 min to extract cellulose. The cellulose suspension was diluted with de-ionized (DI) water, allowed to settle, then the clear top layer was decanted and the remaining layer was centrifuged. The supernatant was decanted and the resulting thick white suspension was washed DI water ( $\times$  3). The thick white suspension obtained after the last centrifugation step was placed inside dialysis membrane tubes (12,000-14,000 molecular weight cut-off) and dialyzed against DI water for 1-4 days until the pH of the water became constant. The suspensions from the membrane tubes was dispersed by ultrasound treatment in a Fisher Sonic Dismembrator (Fisher Scientific) for 10 minutes at 60% power. The final CNC suspensions were diluted with DI water to concentrations between 2-4 wt.% and pH of 2-3. Previous work showed that the CNC nanocrystals were approximately 8-10 nm in diameter and 100-200 nm in length.<sup>[144]</sup> Sulfate ester groups on the surface of the CNC rods (calculated to be ~1 sulfate group per 20 glucose units as determined by combustion analysis) stabilizes the colloidal suspension of the CNC.<sup>[91,144]</sup>

Neutral CNC suspensions were also obtained from FPInnovations and contain sodium counterions on the sulfate group of the CNC rods. Neutral suspensions were acidified using a cation exchange resin 50W-x12 50-100 mesh (Bio-rad laboratories, 0.5 g / 1 g CNC). In short, the resin was stirred with 1 M HCl (10 mL / 1 g resin) for 15 min. The solution was decanted and the resin was washed with DI water until neutral. The resin was added to the CNC suspension, stirred for 30 min then the suspension was filtered to remove the resin. The acidity of the CNC suspension

is due to the  $H^+$  associated with the surface sulfate groups and is important for the hydrolysis of silica precursors. The suspensions were stored at 5 °C for the period of 1-2 years.

## 2.2.6 Preparation of CNC/organosilica composite films

The CNC/organosilica films were prepared using the following general procedure:<sup>[116]</sup> Ethanol was added to the aqueous CNC suspension up to a final concentration of 33-50% v/v ethanol in water. The organosilica precursors were added dropwise to the CNC suspension while the sample was stirring. Alkylene-bridged, anthracene-bridged and biphenylene-bridged samples were made from a ratio of 0.57 mmol precursor / 150 mg CNCs. Phenylene-bridged samples were made from ratios of 0.48-0.75 mmol precursors / 150 mg CNCs. Stirring of the mixtures was continued at  $22 \pm 3$  °C until the suspensions appeared homogeneous (typically 2-4 h). The CNC/organosilica precursor mixtures were transferred to polystyrene Petri dishes (5 cm in diameter) and left to dry under ambient conditions. The volume added to each Petri dish was varied to ensure that 175 mg of CNCs was placed in each dish for consistent film thickness. The specific conditions for samples of organosilica films synthesized in this Chapter using 3.5 wt.% CNC suspensions with pH of 2.4 and conductivity of 1.5 mS/cm are listed below.

**Me-Comp.** BTESM (469  $\mu$ L, 1.34 mmol) was added dropwise to an ethanol/aqueous CNC suspension (15 mL, 33% v/v), stirred for 2 h and dried in a Petri dish (7.5 mL/dish) under ambient conditions overnight.

**Pent-Comp, Hex-Comp,** and **Urea-Comp.** BTMSPr (345  $\mu$ L, 1.34 mmol), BTMSH (431  $\mu$ L, 1.34 mmol) or BTMSPU (467 mg, 1.34 mmol), respectively, was added dropwise to an

ethanol/aqueous CNC suspension (20 mL, 50% v/v), stirred for 2 h and dried in a Petri dish (10 mL / dish) under ambient conditions overnight.

**Prop/Et-Comp, But/Et-Comp** and **Pent(50)/Et-Comp.** BTMSPr (288  $\mu$ L, 1.0 mmol), BTMSBu (305  $\mu$ L, 1.0 mmol) or BTMSPe (320  $\mu$ L, 1.0 mmol), respectively, and BTMSE (253  $\mu$ L, 1.0 mmol), was added dropwise to an ethanol/aqueous CNC suspension (30 mL, 50% v/v), stirred for 2 h and dried in a Petri dish (10 mL / dish) under ambient conditions overnight.

**Pent/Et-Comp, Hex/Et-Comp** and **Urea/Et-Comp.** BTMSPe (128  $\mu$ L, 0.4 mmol), BTMSH (129  $\mu$ L, 0.4 mmol) or BTMSPU (154 mg, 0.4 mmol), respectively, and BTMSE (253  $\mu$ L, 0.94 mmol), was added dropwise to an ethanol/aqueous CNC suspension (20 mL, 50% v/v) stirred for 2 h and dried in a Petri dish (10 mL / dish) under ambient conditions overnight.

**CycMeth-Comp.** 1,1,3,3,5,5-Hexaethoxy-1,3,5-trisilacyclohexane (272  $\mu$ L, 0.69 mmol) was added dropwise to an ethanol/aqueous CNC suspension (10 mL, 50% v/v) stirred for 6-8 h and dried in a Petri dish (10 mL / dish) under ambient conditions overnight.

**Bz-Comp and Bz/Et-Comp.** BTESB (513  $\mu$ L, 1.34 mmol) or BTESB (159  $\mu$ L, 0.4 mmol) and BTMSE (253  $\mu$ L, 0.94 mmol) was added dropwise to the freshly sonicated suspension of ethanol/aqueous CNC suspension (20 mL, 50% v/v), stirred for 3-4 h and dried in a Petri dish (10 mL / dish) under ambient conditions overnight.

Anth-Comp, Biphenyl-Comp. BTMSA (25 mg, 0.06 mmol) or BTMSBP (24 mg, 0.06 mmol),

respectively, and BTMSE (321  $\mu$ L, 1.27 mmol), was added dropwise to the freshly sonicated suspension of ethanol/aqueous CNC suspension (20 mL, 50% v/v) stirred for 4 h and dried in a Petri dish (10 mL / dish) under ambient conditions overnight.

**Et-Comp-DMF** and **Hex-Comp-DMF**. These organosilica composite materials were synthesized under similar conditions as **Et-Comp** and **Hex-Comp** films except *N*,*N*-dimethylformamide (DMF) was added to the aqueous CNC suspension up to a concentration of 30-70% v/v and the films were dried in a 5 cm diameter glass Petri dish treated with dichlorodimethylsilane for approximately two weeks. Unlike the alkylene-bridged CNMO films listed above, these films were made using 0.67 mmol precursor / 150 mg CNCs and compared to **Et-CNMO** made using this ratio of precursor to CNC.

**Biphenyl(20)-Comp**. This organosilica composite material was synthesized under similar conditions as **Biphenyl-Comp** films except DMF and acetone were added to the aqueous CNC suspension. The ratio of DMF to acetone to aqueous CNC was 1:1.2:1, respectively. The films were dried in a 5 cm diameter glass Petri dish treated with dichlorodimethylsilane for approximately two weeks.

## 2.2.7 Preparation of mesoporous organosilica

Removal of CNCs from the composite materials was accomplished using acid hydrolysis to create CNMO films. Two different acid treatments were employed; the alkylene-bridged CNMO films used sulfuric acid hydrolysis and the aromatic-bridged CNMO films used hydrochloric acid. Me-CNMO, Et-CNMO, Et-CNMO-DMF, Prop-MO, Prop/Et-CNMO, But/Et-CNMO, Pent/Et-MO, Pent/Et-CNMO, Hex-MO, Hex/Et-CNMO, Hex-CNMO, Urea-MO, Urea/Et-CNMO and CycMeth-CNMO. The composite films (~150-200 mg) were placed in 300 mL of 6 M sulfuric acid and heated to 100 °C for 18 h (this was done without stirring in order to avoid breaking the films). The films were filtered, washed with 1 L of water, and alternately washed with a room-temperature solution of piranha (20 mL 30%  $H_2O_2/100$  mL  $H_2SO_4$ ) and water until they appeared colourless. The films were then rinsed with 2 L of water and allowed to air-dry.

**Bz-CNMO**, **Bz/Et-CNMO**, **Anth-CNMO**, **Biphenyl-CNMO**, **Biphenyl(20)-CNMO** and **Et-CNMO-HCI**. The CNC/organosilica composite films were treated in 10-12 M HCl and heated to 100 °C for 24-48 h. After filtration, 100 mg of films were placed in 20 mL of 30% hydrogen peroxide solution with 5 mg of silver nitrate and heated to 70-80 °C until the films appeared colourless (typically 2-3 h). The films were filtered and heated to 70 °C in distilled water for 18 h before the final filtration and air-drying steps.

## 2.3 **Results and Discussion**

CNC LC templating of organosilica precursors was used to create a library of alkylenebridged and aromatic-bridged CNMO films. Chiral nematic CNC/organosilica composite materials and CNMO films were prepared by evaporation-induced self-assembly (EISA) according to the general procedure seen in Scheme 2-1. The initial concentration of the CNC suspension (typically between 2-4 wt.%) is below the critical concentration for the formation of an anisotropic phase. However, as the mixture evaporates, the concentration is increased and an ordered chiral nematic phase is formed. Organosilane precursors were condensed around the CNC rods to create an organosilica network with embedded chiral nematic ordered CNCs. The following sections discuss the incorporation of different organosilica precursors and how this general scheme was tailored to accommodate these new organic moieties.



Scheme 2-1. Synthesis of CNMO films.

# 2.3.1 Alkylene-bridged CNMO films

# 2.3.1.1 Preparation of alkylene-bridged CNMO films

Ethylene-bridged mesoporous organosilica materials prepared from either bis(trimethoxysilyl)ethane (BTMSE) or bis(triethoxysilyl)ethane (BTESE) are the most reported PMOs in literature.<sup>[136]</sup> Ethylene-bridged PMOs have been synthesized with a range of different

morphologies, including hexagonal symmetries<sup>[67]</sup> cubic symmetries,<sup>[145]</sup> and 3D worm-holelike<sup>[68]</sup>, by varying the templating agent or sol-gel reaction conditions. The type of organosilanes used for co-condensation can also greatly impact the shape and properties of the resulting materials. For example, long alkylene spacers provide hydrophobic character to mesoporous organosilica films that could affect the water adsorption or mechanical stability of these materials.<sup>[146]</sup>

Although alkylene precursors have been used to synthesize organosilica materials (aerogels and xerogels),<sup>[147,148]</sup> reports of the synthesis of  $C_{1,3+}$  alkylene-bridged PMOs by liquid crystal templating are less common. The first reported synthesis of methylene-bridged PMOs was by Asefa *et al.* in 2000.<sup>[149]</sup> Longer chain PMOs, such as alkylene spacers containing urea functionalities or hexylene spacers, were not reported until the mid-2000s to early 2010s.<sup>[75,150–152]</sup> Researchers have found that it is often difficult to synthesize highly ordered PMOs containing long alkylene moieties. The lack of rigidity of these precursors can result in deformations in symmetry or complete loss of porosity (after removal of the template), and cyclization of the silane precursors can affect the sol-gel condensation.<sup>[153–155]</sup> Additionally, an inappropriate hydrophobic/hydrophilic balance between the templating agent and the organosilanes, as well as solubility limitations, can restrict the type of organic groups that can be incorporated into PMOs.<sup>[154]</sup>

Despite these limitations, we were interested in using suspensions of CNCs to template novel alkylene-bridged mesoporous organosilica materials with chiral nematic porous networks. A library of CNC/organosilica composite films with  $C_1$ - $C_6$  bridging groups was prepared using the alkylene organosilica precursors shown in Figure 2-1 to investigate the limits of the CNC LC templating approach to synthesizing ordered mesoporous organosilicas.



Figure 2-1. Alkylene organosilica precursors used to create CNC/organosilica composite materials and CNMO films.

Producing homogeneous films containing both CNCs and organosilica depends on the solubility of the silane precursor in suspensions of CNCs, the rate of hydrolysis and condensation of the silane, and self-assembly of the CNC LC template. The fine balance between these variables determines whether a silica network is able to form around the ordered LC mesophase. Reactivity of different silane precursors plays a significant role in determining the conditions used to produce organically functionalized ordered materials. As reported by Shopsowitz *et al.*,<sup>[116]</sup> organosilica precursors are initially immiscible in aqueous suspensions of CNCs but become more miscible with stirring over time; presumably as they are hydrolyzed. Additionally, triethoxysilyl precursors are less miscible in aqueous CNC suspensions than trimethoxysilyl precursors due to their slower rates of hydrolysis. In order to create a library of different CNMO films, we first focused on developing a procedure that could be easily tailored to account for the different miscibility of these precursors in a CNC suspension.

We found that all precursors reported in Figure 2-1 with longer spacers than ethylene required a different set of conditions to produce homogeneous mixtures with CNCs than the conditions previously used to prepare chiral nematic ethylene films.<sup>[116]</sup> The organosilica precursors were initially immiscible when added to isotropic suspensions of CNCs (3.5 wt.% in

water, pH 2.5). Unlike the BTMSE precursor that becomes miscible after several minutes of stirring, all other alkylene precursors attempted remained immiscible or only partially miscible even after several hours of stirring. The methylene-bridged precursor was only commercially available as a bis(triethoxysilyl) compound and has a lower rate of hydrolysis than that of the trimethoxysilanes as well as decreased water solubility. The longer bis(trimethoxysilyl)alkylene precursors have lower solubility than the BTMSE in aqueous CNC suspensions. To compensate for their low solubility, CNC suspensions were mixed with ethanol prior to the addition of the organosilica precursors. Self-assembly of the CNC template was able to tolerate a large amount of ethanol and still form a chiral nematic liquid crystal upon EISA. We found that the solubility of these precursors was significantly improved by the addition of ethanol (30-50% v/v) to the CNC suspension.

CNC/organosilica composite materials synthesized from CNC suspensions with ethanol were prepared with the precursors listed in Figure 2-1. BTESM, BTMSPr, BTMSH and BTMSPU composite films are denoted as **Me-Comp**, **Prop-Comp**, **Hex-Comp** and **Urea-Comp**, respectively. CNCs were removed from the organosilica composite materials through acid hydrolysis by heating the films to 100 °C in 6 M sulfuric acid followed by a brief rinse with a H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub> solution. Removal of CNCs was carried out for representative samples of all composite films, each containing 0.57 mmol of precursor / 150 mg CNCs. Organosilica films obtained after removal of CNCs are denoted **Me-CNMO**, **Prop-MO**, **Hex-MO**, and **Urea-MO**. The films designated "CNMO" formed chiral nematic nanostructures, whereas those with only an "MO" designation showed no evidence of chiral nematic ordering.

Of the four organosilica materials listed above, only the **Me-CNMO** films appeared to retain the chiral nematic structure imparted by the CNC template. The **Prop-MO**, **Hex-MO**, and

**Urea-MO** samples all formed cloudy films or powders that did not display any reflectance signal when observed by UV-Vis spectroscopy or CD spectroscopy, even at low loading of the precursors into the CNC suspension. The silyl precursors that were unable to form chiral nematic nanostructured materials at 100% loading were instead diluted with BTMSE in different ratios until chiral nematic composite materials were successfully synthesized. We found that the propylene-bridged and butylene-bridged precursors require a 1:1 precursor:BTMSE dilution in ethanol/water (50% v/v) CNC suspensions to form organosilica materials with long-range chiral nematic porous networks. These materials are denoted **Prop/Et-Comp** and **But/Et-Comp**.

Removal of CNC from the films made from 1:1 pentylene:BTMSE precursors, denoted **Pent-MO**, resulted in a material with no observable reflectance signal. We found that the pentylene, hexylene, and propylurea-bridged precursors require approx. 3:7 precursor:BTMSE dilution in ethanol/water (50% v/v) CNC suspensions to form organosilica materials with long-range chiral nematic porous networks. These materials are denoted **Pent/Et-Comp**, **Hex/Et-Comp** and **Urea/Et-Comp**, respectively. Removal of CNCs was carried out for representative samples of the composite films using acid hydrolysis to obtain alkylene-bridged mesoporous organosilica films, denoted as **Prop/Et-CNMO**, **But/Et-CNMO**, **Pent/Et-CNMO**, **Hex/Et-CNMO** and **Urea/Et-CNMO**.

# 2.3.1.2 Structural properties of the alkylene-bridged mesoporous organosilica films templated with CNCs

Retention of the chiral nematic ordering imparted by the CNC LC template can be easily observed by scanning electron microscopy (SEM) (Figure 2-2). The chiral nematic alignment of the CNC rods during EISA creates a 1-D long-range periodic structure where the helical axis is orientated perpendicular to the surface of the films. Within the chiral nematic mesoporous organosilica materials, the pores are arranged in periodic layers that perfectly replicate the morphology of the chiral nematic self-assembled CNC template. These layers are observed throughout the thickness of the films (Figure 2-2a, b). Each periodic layer observed by SEM corresponds to a 180° rotation of the chiral nematic director - half of the helical pitch. The rotation of the chiral nematic director within the films is shown by the green rods in Figure 2-2c. The chiral nematic nanostructure can be clearly seen in the Me-CNMO, Et-CNMO, Prop/Et-CNMO, But/Et-CNMO, Pent/Et-CNMO, Hex/Et-CNMO, and Urea/Et-CNMO films. The organosilica rods form an interconnected silica network with pores that twist in a counter-clockwise direction, consistent with the left-handed (LH) chiral nematic structure of CNCs. This creates a worm-hole like helical porous network where the pores are oriented in the direction of the CNC liquid crystal director. The films have helical pitches from ~600–1000 nm in length and can reflect wavelengths of light from visible to near infrared, depending on the combination of organosilica precursors used during synthesis.



**Figure 2-2.** SEM images of CNMO films. (a) Cross-sectional image of a **Me-CNMO** film and (b) a **But/Et-CNMO** film (scale bar =  $20 \ \mu\text{m}$ ). (c) Edge view of a **Me-CNMO** film (scale bar =  $1 \ \mu\text{m}$ ) with the green rods highlighting the helical pitch. (d) Top view of a **Prop/Et-CNMO** film (scale bar =  $20 \ \mu\text{m}$ ). (e) Edge view of a **But/Et-CNMO** film (scale bar =  $20 \ \mu\text{m}$ ). (f) Top view of a **Pent/Et-CNMO** film (scale bar =  $10 \ \mu\text{m}$ ) (g) Edge view of a **Hex/Et-CNMO** film (scale bar =  $500 \ \text{nm}$ ). (h) Edge view of a **Urea/Et-CNMO** film (scale bar =  $2 \ \mu\text{m}$ ).

The nanostructure of the **Prop-MO**, **Hex-MO**, **Urea-MO** and **Pent-MO** materials were also analyzed by SEM. These materials look vastly different than the ordered CNMO materials seen in Figure 2-2. SEM images of these films reveal highly disordered species or films that are composed of globular nanoparticles packed together (Figure 2-3), consistent with the lack of chiral

nematic order in these materials. The hydrophobicity of the organosilica precursors plays an important role in the self-assembly of CNCs. Precursors that are too hydrophobic do not properly condense around the suspended CNC rods and disrupt the self-assembly of CNCs. It was observed that as the length of the alkylene-bridged organosilanes increases, the amount of dilution with BTMSE needed to retain the chiral nematic nanostructure also increases to compensate for solubility limitations. Additionally, the long, flexible spacers may not be sufficiently rigid on their own, causing the nanostructure and porous network to collapse after removal of the CNCs. In the case of the pure propylurea-bridged films (Figure 2-3e, f), disruption of the CNC self-assembly was most likely a result of both hydrophobicity and hydrogen bonding from the urea functional group interfering with normal packing of the CNC rods.



**Figure 2-3.** SEM images of mesoporous organosilica (MO) films without chiral nematic ordering. **Hex-MO** at (a) low and (b) high magnification (scale bar = 50  $\mu$ m and 500 nm, respectively). (c) Edge view of **Prop-MO** (scale bar = 5  $\mu$ m) (d) Top view of **Pent-MO** (scale bar = 20  $\mu$ m) (e) Top view of **Urea-MO** (scale bar = 20  $\mu$ m). (f) **Urea-MO** at high magnification (scale bar = 1  $\mu$ m).

### 2.3.1.3 Selective removal of CNCs from alkylene-bridged/CNC composite films

Solid-state <sup>13</sup>C CP/MAS (cross-polarization/magic angle spinning) NMR spectroscopy was carried out for select organosilica samples before and after acid hydrolysis to investigate the removal of CNCs from the composite materials and confirm the retention of the alkylene spacer. The <sup>13</sup>C NMR spectrum of the proplyurea-bridged/CNC composite films (Urea-Comp) shows peaks corresponding to both the cellulose derivatives and the alkylene bridging group (Figure 2-4a). Peaks between 60-120 ppm in the composite sample are assigned to cellulose, whereas peaks at 160, 42, 23, and 9 ppm correspond to the carbonyl of the urea moiety and the three alkyl carbons. <sup>13</sup>C NMR spectrum of the propylurea-bridged organosilica materials after acid hydrolysis shows the complete removal of CNCs. The spectrum for the Urea-MO films has 4 remaining peaks at 160, 42, 23 and 9 ppm corresponding to carbons in the propylurea spacer whereas the spectrum for the Urea/Et-CNMO films has 5 peaks at 160, 42, 23, 9 and 5 ppm corresponding to the propylurea and ethylene spacers (Figure 2-4a, note that the peak at 9 ppm overlaps with the ethylene carbons at 5 ppm and is seen as a shoulder in the spectrum). This demonstrates that acid hydrolysis can selectively remove cellulose from the composite films while retaining functional alkylene-bridged spacers.

<sup>13</sup>C NMR spectra of CNMO films synthesized from the shortest bridging group (**Me-CNMO**) and the longest bridging group (**Hex/Et-CNMO**) were also measured. **Me-CNMO** films after template removal show a singular peak at 0 ppm corresponding to the methylene carbon whereas the **Hex/Et-CNMO** films show three peaks at 32, 23 and 13 ppm for the hexylene spacer and a peak at 5 ppm for the ethylene spacer (Figure 2-4b). All spectra of the CNMO films confirm complete removal of CNCs and retention of the organic bridge. Although we did not measure the <sup>29</sup>Si NMR spectrum of the samples to look for Si-C cleavage, it is known that in the case of other

organosilicas (e.g., **Et-CNMO**), the acid hydrolysis conditions used for removing cellulose does not affect the Si-C bonds.<sup>[116]</sup>



**Figure 2-4.** Solid-state <sup>13</sup>C NMR spectra for the (a) composite CNC/propylurea-bridged organosilica films (top), **Urea-MO** (middle) and **Urea/Et-CNMO** (bottom). (b) **Me-CNMO** (top) and **Hex/Et-CNMO** (bottom) after removal of the CNCs.

Composite and mesoporous alkylene-bridged organosilica films were analyzed by TGA to confirm the removal of the CNC template and investigate the thermal stability of the CNMO films. Since the films are very hygroscopic, samples were degassed prior to analysis, however, some weight loss attributed to adsorbed water is still observed. As seen in Figure 2-5a, the composite CNC/organosilica films show a significant weight loss (~70-80 wt.%) due to the decomposition of both the CNC template and the alkylene bridging group. CNCs within the composite organosilica material start to decompose around ~250 °C, which closely matches the decomposition for CNCs reported for ethylene-bridged/CNC composite materials.<sup>[116]</sup> Interestingly, TGA of the composite films containing propylurea derivatives are thermally stable up to 375 °C (Figure 2-5b). This indicates that the propylurea bridging groups enhance the stability of the CNCs, and they can

withstand temperatures 100-150 °C higher than the alkylene-bridged composite materials. This increase in thermal stability is likely caused by hydrogen bonding between the CNCs and the urea functional groups.

After removal of the template, the mesoporous organosilica materials show significantly smaller weight losses of 10-25 wt.%. Larger weight losses are observed for the longer spacers, consistent with the larger proportion of organic groups in the materials and closely resembling the %C and %H determined by elemental analysis (EA) (Table 2-1). The C<sub>1</sub>-C<sub>6</sub> alkylene-bridged CNMO films have similar thermal stabilities and are stable up to ~350-400 °C (Figure 2-5c). Additionally, the organosilica materials that do not have observable chiral nanostructures by SEM, such as the **Prop-MO** and **Urea-MO** samples, show retention of a small amount of CNCs after acid hydrolysis. The collapse or incomplete formation of the pore network within these films enables trapping of CNCs. (Figure 2-5b, d).



**Figure 2-5.** TGA of alkylene-bridged organosilica films. (a) Hexylene-bridged composite and organosilica derivatives. (b) Propylurea-bridged composite and organosilica derivatives. (c) Methylene, propylene, butylene, and pentylene CNMO films. (d) Non-chiral **Prop-MO** and **Pent-MO** materials.

		0	
Sample	%N	%C	%H
Me-CNMO	nd	7.47	3.40
Prop/Et-CNMO	nd	18.97	4.23
But/Et-CNMO	nd	19.47	4.76
Pent/Et-CNMO	nd	16.68	5.06
Hex/Et-CNMO	nd	19.41	4.76
Urea/Et-CNMO	3.91	20.48	4.34
Prop-MO	nd	14.05	5.21
Pent-MO	nd	19.33	5.41
Hex-MO	nd	35.72	6.46
Urea-MO	8.69	26.46	5.56

Table 2-1. Elemental analysis of the alkylene-bridged CNMO and MO films

\*nd = not detected

FTIR spectra and Raman spectra of the CNMO films were obtained after CNC removal (Figure 2-6). In the FTIR spectra, Si-O bonding modes are the most intense peaks and have characteristic absorption bands at 1020 cm<sup>-1</sup> and 800 cm<sup>-1</sup>. Water adsorbed onto the surface of the films can also be observed with peaks at 3330 cm<sup>-1</sup> (OH-stretch) and 1640 cm<sup>-1</sup>. The alkylene spacers of the organosilica materials show absorption bands assigned to Si-C stretching vibrations  $(670 \text{ cm}^{-1} \text{ and } 765 \text{ cm}^{-1})$  as well as CH<sub>2</sub> deformations (1450-1400 cm<sup>-1</sup> and 1270 cm<sup>-1</sup>).<sup>[156]</sup> The incorporation of longer alkylene spacers into the CNMO films can be observed by the increase in absorption 2950-2850 cm<sup>-1</sup> (CH<sub>2</sub> stretch) from the Me-CNMO films to the Hex/Et-CNMO films. Additionally, both the composite and mesoporous organosilica films containing the propylurea bridging group show peaks at 1635 cm<sup>-1</sup> (amide I) and 1550 cm<sup>-1</sup> (amide II) that can be assigned to urea (Figure 2-6g, h).<sup>[75]</sup> This supports the <sup>13</sup>C NMR data confirming the retention of the urea functional group after acid hydrolysis. The amide I band is sensitive to hydrogen bonding and its large range of frequencies (ca. 100 cm<sup>-1</sup>) in both the composite and mesoporous organosilica materials may suggest the presence of hydrogen-bonding between the carbonyls and the CNC template or silanol groups within the films.<sup>[75]</sup>



**Figure 2-6.** IR spectra of the CNMO films displaying characteristic absorption bands from C-H, Si-O, and Si-C. (a) **Me-CNMO**, (b) **Et-CNMO**, (c) **Prop/Et-CNMO**, (d) **But/Et-CNMO**, (e) **Pent/Et-CNMO**, (f) **Hex/Et-CNMO**, and (g, h) propylurea-bridged derivatives, as labelled.

Raman spectra of the organosilica films are consistent with the FTIR spectra. Since the organosilica films are quite thin (40-60  $\mu$ m), the signal-to-noise ratio is low. However, some broad peaks within the spectra can be observed. The ethylene-bridged mesoporous organosilica films show

peaks at 517, 1290 and 1430 cm<sup>-1</sup>, which are attributed to the Si–C and CH<sub>2</sub> bonds of the organic spacer as well as CH<sub>2</sub> stretching modes visible around 2950-2850 cm<sup>-1.[157–159]</sup> In comparison, the peaks associated with CH<sub>2</sub> bends in pure hexylene-bridged organosilica films are shifted and appear as 3 peaks at 1330, 1425, and 1450 cm<sup>-1</sup> (Figure 2-7). Although dilution of the longer spacers with shorter precursors (such as BTMSE) helps maintain the nanostructure of the CNMO films, using mixed organosilane systems can sometimes cause heterogeneous distributions of the silanes within the films. Raman spectroscopy of the **Hex/Et-CNMO** films was performed at several different spots to assess the homogeneity of these films. The representative spectrum of the **Hex/Et-CNMO** films shows peaks associated with both the ethylene and hexylene bridging groups. Five different Raman spectra were taken on a single **Hex/Et-CNMO** film and each displayed the same mixture of peaks associated with ethylene and hexylene spacers, indicating that the silanes are most likely homogeneously distributed throughout the material.



**Figure 2-7.** Raman spectra of ethylene-bridged (black), hexylene-bridged (red) and **Hex/Et-CNMO** films (green) (zoomed in to highlight the C-H peaks).

## 2.3.1.4 Optical properties of the alkylene-bridged CNMO films

Liquid crystal templating of organosilanes with CNCs in an ethanol/water mixture followed by acid hydrolysis produced free-standing organosilica films with dimensions of several centimeters. The films displayed vibrant iridescent colours that are easily observed by the naked eye (Figure 2-8). It has been previously reported by Shopsowitz *et al.* in 2010<sup>[91]</sup> that the strong selective reflection of light from the silica films templated with CNCs is characteristic of the chiral nematic nanostructure imparted by the self-assembled CNCs. The wavelength of maximum reflected light from the chiral structure ( $\lambda_{max}$ ) is given by  $\lambda_{max} = n_{avg}P\sin\theta$ , where  $n_{avg}$  is the average refractive index of the material, *P* is the pitch of the chiral nematic order, and  $\theta$  is the angle of incidence measured from the plane of the film.<sup>[107]</sup>



**Figure 2-8.** (a) Photograph of CNMO films as labeled. Photograph of the CNMO films taken at a (b) normal incidence and (c) oblique incidence.

Iridescence was measured by UV-Vis spectroscopy for the composite and mesoporous chiral nematic organosilica films. Strong reflection of visible light was seen, confirming the preservation of the chiral nematic structure in both the composite and the CNMO materials. Similar to the ethylene-bridged and pure silica chiral nematic mesoporous materials,<sup>[91,116]</sup> the reflected light of the CNMO films is blue-shifted relative to the corresponding composite films by 400-500 nm (Table 2-2). This blue shift results from the combination of a decrease in average refractive index that occurs when the CNCs are removed as well as a contraction in the helical pitch.

Table 2-2. Summary of the UV-Vis spectra for the alkylene composite and CNMO films					
Organosilica bridging	$\lambda_{\max}(nm)$	$\lambda_{\max}(nm)$			
Group	Composite films	Mesoporous films			
Methylene	1139	665			
Ethylene (Et)	1177	745			
50 Propylene/ 50 Et	1268	762			
50 Butylene/ 50 Et	1279	789			
30 Pentylene/ 70 Et	1233	745			
30 Hexylene/ 70 Et	1257	754			
30 Propylurea/ 70 Et	1470	640			

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The UV-Vis spectra of the CNMO films display a slight red shift in the reflection peak upon increasing the length of the alkylene bridging group from  $C_1$  to  $C_4$  (Figure 2-9). In contrast, introducing the propylurea functional spacer causes a blue shift in the reflection peak of the mesoporous films when compared to the Et-CNMO films (Figure 2-9). These shifts result from changes to the helical pitch caused by individual precursors, a difference in the average refractive index or a combination of both factors. CD spectra of the films also show strong signals with positive ellipticity at wavelengths that closely match the reflectance peaks, indicating that the films selectively reflect LH circularly polarized light as a result of their nanostructures (Figure 2-9).



**Figure 2-9.** (a) Optical characterization by UV-Vis (top line) and CD spectroscopy (bottom line) for the **Urea/Et-CNMO**. (b) UV-Vis spectra of the alkylene-bridged CNMO films. (c) CD spectra of the alkylene-bridged CNMO films.

## 2.3.1.5 Mesoporosity of alkylene-bridged CNMO films

Porosity of the organosilica films was investigated using nitrogen adsorption-desorption, and are summarized in Table 2-3. Specific surface areas of the CNMO films were calculated using the BET method and pore size distributions were calculated using a BJH model from the adsorption branch of the isotherm.

Sample	BET Surface Area	Pore volume	<b>BJH Pore Diameter</b>
	$(m^2/g)$	$(cm^3/g)$	(nm)
CNMO			
Me-CNMO	520	0.54	5
<b>Et-CNMO</b>	590	0.87	7
Prop/Et-CNMO	600	1.25	14
<b>But/Et-CNMO</b>	470	1.18	13
Pent/Et-CNMO	400	1.20	13
Hex/Et-CNMO	470	0.76	9
Urea/Et-CNMO	420	0.45	4.5
MO			
Prop-MO	210	0.45	5-30
Pent-MO	320	1.02	10, 30
Hex-MO	130	0.51	5, 30
Urea-MO	3	0.002	1

**Table 2-3.** Nitrogen adsorption data of the alkylene-bridged organosilica materials.

\*CNMO (chiral nematic mesoporous organosilica); MO (mesoporous organosilica).

The organosilica samples display type IV isotherms with hysteresis curves that are characteristic of mesoporous materials (Figure 2-10). The BET surface areas of the CNMO materials ranged from 400-600 m<sup>2</sup>/g with pore volumes of 0.45-1.25 cm<sup>3</sup>/g. The BJH pore size analysis of the CNMO films show that the films have a broad distribution of pores (~2-20 nm) with average pore sizes ranging from 5-15 nm. The average pore sizes are similar to the width of the CNC template.<sup>[144]</sup> Although there is no clear trend between surface area or pore volume and length of the alkylene bridging group, nitrogen adsorption measurements demonstrated that the CNMO films synthesized from longer alkylene spacers generally have larger pores and lower surface areas. The small pore sizes observed in the **Urea/Et-CNMO** films and the large decrease in the helical pitch between the composite and mesoporous films (as shown by a large blue shift in the reflectance peak) indicate that these films significantly contract during acid hydrolysis. We postulate that the composite material containing the propylurea spacer may be less interconnected and more susceptible to shrinkage or, that hydrogen bonding between the urea functional group and silanols favor contraction of the material.

As the hydrophobicity of the precursor increases, phase separation between the precursor and template can occur causing a significant reduction in surface area. This can be observed in the

**Prop-MO, Hex-MO** and **Pent-MO** materials, which have the lowest surface areas and very broad pore size distributions extending from 2 to 50 nm (Table 2-3, Figure 2-11). Bimodal pore size distributions observed for the non-chiral 'MO' films indicate that although some of the CNC rods are acting to template mesoporosity, phase separation and aggregation is also occurring between the CNCs and organosilica precursors. Urea-MO shows no surface area or mesoporosity; we postulate that hydrogen bonding of the urea group to the CNCs at high loadings interfered with normal CNC self-assembly and any potential pores collapsed during CNC removal.

The use of multi-organic bridging silanes over typical single bridged silanes offers an alternative approach to incorporating more organic functional groups directly into the silica network.<sup>[160]</sup> Multi-organic bridged mesoporous organosilica films were also synthesized from 100% of the 1,1,3,3,5,5-hexaethoxy-1,3,5-trisilacyclohexane precursors (interconnected ((RO)<sub>2</sub>SiCH<sub>2</sub>)<sub>3</sub> rings), denoted **CycMeth-CNMO**. These films have similar properties to the **Me-CNMO** films and retained the chiral nematic structure and mesoporosity after removal of CNC template (see Appendix A, Figure A-1 for SEM, UV-Vis, IR and N<sub>2</sub> isotherm). The **CycMeth-CNMO** films have a surface area of 740 m<sup>2</sup>/g, a pore volume of 1.18 cm<sup>3</sup>/g and an average pore size of 9 nm.



**Figure 2-10.** Nitrogen adsorption data for the CNMO films; (a) **Me-CNMO**, (b) **Prop/Et-CNMO**, (c) **But/Et-CNMO**, (d) **Pent/Et-CNMO**, (e) **Hex/Et-CNMO**, and (f) **Urea/Et-CNMO** (inset: BJH pore size distributions).



**Figure 2-11.** Nitrogen adsorption data of the MO samples; (a) **Prop-MO**, (b) **Hex-MO**, (c) **Pent-MO** and (d) **Urea-MO** (inset: BJH pore size distributions).

## 2.3.1.6 Qualitative flexibility of organosilica films

Stress-strain curves have previously shown that ethylene-bridged organosilica films have improved mechanical properties over the pure silica films.<sup>[116]</sup> However, obtaining data from stress-strain curves was difficult as CNMO materials are brittle and defects in the films caused large variation in the fracture point. We qualitatively noted the responses of the new organosilica films to stress upon drying. Mesoporous organosilica thin films prepared by sol-gel methods develop large internal tensile stresses during the drying process due to film shrinkage, causing them to crack and curl.<sup>[56]</sup> While drying, all composite films cracked into smaller pieces but remained flat. After removal of the CNCs, samples containing long, flexible alkylene bridging groups curled (Figure 2-12), and the amount of curling of the samples increased as the length of the bridging group increased. Films synthesized from the longest linker (**Urea/Et-CNMO**) curled the most, wrapping around itself 1-2 times. Flexibility was also qualitatively tested by flattening the curled films using tweezers. It was found that the **Hex/Et-CNMO** films could be uncurled without damaging them and they showed similar flexibility to the previously reported **Et-CNMO** films.



Figure 2-12. (a) Side view photograph of the CNMO films; (from left to right; Me-CNMO, Et-CNMO, Prop/Et-CNMO, But/Et-CNMO, Pent/Et-CNMO, Hex/Et-CNMO, and Urea/Et-CNMO). (b) Uncurling and curling of the Hex/Et-CNMO films.

## 2.3.1.7 Preparation of 100% Hex-CNMO films from DMF/water CNC suspensions

As described above, we found that the incorporation of hydrophobic organosilica precursors into aqueous suspensions of CNCs is limited due to low solubility of the precursors. The ability to use a liquid crystal templating approach to make CNMO films composed entirely of hydrophobic precursors could expand the potential uses of these materials. For example, mesoporous organosilica materials with hydrophobic bridging groups in the silica network could make optimal hosts for hydrophobic guests, allowing these materials to be used for storage and sensing of hydrophobic analytes.<sup>[161]</sup> Work by Cheung *et al.* in 2013 showed that neutralized CNCs can be suspended in polar organic solvents such as DMF without impacting the chiral nematic self-assembly of the mesogens.<sup>[162]</sup> By altering the solvent composition of CNC suspensions with organic solvents, we postulated that CNCs could template hydrophobic organosilica precursors with minimal effect on their self-assembly and produce novel mesoporous materials with desirable properties.

To investigate the impact of DMF on the evaporation-induced self-assembly of CNCs with organosilyl precursors, ethylene-bridged organosilica composite films were synthesized using the same procedure as the synthesis of **Et-CNMO** films, but DMF was added to the aqueous CNC suspension (50% v/v or 1:1 DMF:CNC suspension) prior to adding the organosilica precursors. The composite film obtained after solvent drying displayed an iridescent colour consistent with the previously reported alkylene-bridged CNMO films indicating that the DMF/water solvent mixture did not disrupt the chiral nematic organization of the CNC mesogens. These materials are denoted **Et-Comp-DMF**. After removal of the CNCs by acid hydrolysis, chiral nematic mesoporous ethylene films synthesized using the DMF/water CNC suspension (**Et-CNMO-DMF**) were analyzed by SEM, CD spectroscopy and N<sub>2</sub> adsorption, and compared to ethylene films synthesized from aqueous CNCs (**Et-CNMO**) to investigate the effect of DMF on the formation of the organosilica films (Figure 2-13).



**Figure 2-13.** (a) SEM image of **Et-CNMO-DMF** (scale bar = 1  $\mu$ m). (b) CD spectrum of **Et-CNMO-DMF**. (c) Nitrogen adsorption and (d) pore size distributions of **Et-CNMO** (black trace) and **Et-CNMO-DMF** films (blue trace).

SEM images of the **Et-CNMO-DMF** films confirmed the retention of the long-range chiral nematic nanostructure imparted by the CNC template. A periodic layered nanostructure can be observed throughout the thickness of the films (Figure 2-13a). The ethylene-bridged organosilica films synthesized from DMF/water CNC suspensions were slightly cloudy, which reduced the transmission of light through the films and made it difficult to observe reflected light by UV-Vis spectroscopy. However, CD spectra of the films show a strong positive signal with  $\lambda_{max} = 430$  nm, indicating that the materials selectively reflect LH circularly-polarized light (Figure 2-13b). The

light reflected from these materials is significantly blue-shifted in comparison to **Et-CNMO** films that reflect light at  $\lambda_{max} = 650$  nm (Figure 2-9). The major difference between the **Et-CNMO-DMF** and **Et-CNMO** films is the drying times (~2 weeks versus 1 day, respectively). Longer drying times appear to decrease the helical pitch of the films causing a blue-shift in the light reflected, whereas shorter drying times (allowing EISA to occur within a well-ventilated environment) result in films with longer helical pitches and a red-shifted  $\lambda_{max}$ . This trend is consistent with the observations of other researchers that the drying times affect the pitch of CNC films.<sup>[108,111]</sup> Finally, porosity of these two ethylene-bridged organosilica films were compared and are summarized in Table 2-4. The **Et-CNMO-DMF** films show a type IV isotherm and have similar surface areas, pore volumes and average pore sizes when compared to the Et-CNMO films. (Figure 2-13c, d). The SEM, CD and N<sub>2</sub> isotherms all indicate that the addition of DMF into an aqueous acidified CNC suspension allows for the self-assembly of CNCs into a chiral nematic mesophase concomitant with the condensation of the organosilica precursor during EISA. Other organic solvents, such as acetone and THF, were also investigated as additives, but they did not result in high quality films with chiral nematic order.

	1 1 2 adsorption data 10		
Sample	BET Surface Area	Pore Volume	BJH Avg. Pore Diameter
	$(m^2/g)$	$(cm^{3}/g)$	(nm)
<b>Et-CNMO-DMF</b>	480	0.95	8
<b>Et-CNMO</b> *	510	0.98	7

Table 2-4. Summary of N<sub>2</sub> adsorption data for Eth-CNMO-DMF compared to Et-CNMO.

\* Note: **Et-CNMO** reported here was synthesized with a different batch of CNCs than the ethylene CNMO films reported in Table 2-3. However, these films were made with the same batch of CNCs used to synthesis of **Et-CNMO-DMF** and **Hex-CNMO DMF**.

Liquid crystal templating of organosilica materials using a CNC suspension containing 50% v/v DMF to water was extended to the bis(trimethoxysilyl)hexylene precursor (BTMSH). As observed with the **Hex-MO** materials, BTMSH failed to form CNMO composite films when 75

combined alone with aqueous dispersions of CNCs. However, using DMF as an additive prevented phase separation between the CNCs and the BTMSH. Composite hexylene-bridged organosilica films (**Hex-Comp-DMF**) displayed strong iridescent colours indicating that the long hydrophobic organosilica precursor integrated into the self-assembled CNC structure without disrupting the CNC self-assembly. Selective removal of the template by acid hydrolysis with 6 M H<sub>2</sub>SO<sub>4</sub> produced free-standing mesoporous hexylene-bridged films, denoted **Hex-CNMO**.

Removal of the CNC template was investigated by solid-state <sup>13</sup>C CP/MAS NMR spectroscopy. The **Hex-CNMO** spectrum shows only three peaks at 32, 23, and 13 ppm, confirming that the CNC template was successful removed and the hexylene spacer was retained (Figure 2-14b). These peaks match closely those seen in the <sup>13</sup>C NMR for **Hex/Et-CNMO** films (Figure 2-4). SEM images of cross-sections of **Hex-CNMO** films clearly show well-ordered periodic layers characteristic of the chiral nematic nanostructure and LH twisting organosilica rods that perfectly matches the LC behavior of the CNC template (Figure 2-14c, d). CD spectroscopy of these films (Figure 2-14) shows a signal at 450 nm with positive ellipticity, indicating that the materials selectively reflect LH circularly polarized light. The SEM and CD spectroscopic data clearly show that by using this modified CNMO synthesis, we are able to form organosilica films with long alkylene spacers that retain the chiral nanostructure after removal of the template. It is worth noting that SEM images of the surface of the film showed the presence of some small crystals of organosilica precursor (see Appendix A, Figure A-2), which may be the cause of the slight cloudiness observed in the films.



**Figure 2-14.** (a) CD spectrum of **Hex-CNMO**. (b) Solid state <sup>13</sup>C CP/MAS NMR spectrum of **Hex-CNMO** films after the removal of CNCs. SEM images of the **Hex-CNMO** film at (c) low and (d) high magnification (scale bar = 5  $\mu$ m and 500 nm, respectively).

 $N_2$  isotherms of the **Hex-CNMO** films displayed a type IV isotherm with hysteresis, indicative of the presence of mesopores (Figure 2-15a). The **Hex-CNMO** films have a surface area of 350 m<sup>2</sup>/g and a pore volume of 0.67 cm<sup>3</sup>/g. Although the surface area and pore volume are lower than the ethylene-bridged and **Hex/Et-CNMO** films, it is a significant improvement over the 100% hexylene sample that was synthesized from purely aqueous CNCs (**Hex-MO**). Additionally, the **Hex-CNMO** films display no bimodal pore distribution, which was seen for the **Hex-MO** films due to phase separation. The average pore size of the films was 7 nm and closely matched pore sizes of the **Et-CNMO** and **Et-CNMO-DMF** films, and the width of the CNC template.


**Figure 2-15.** (a) N<sub>2</sub> adsorption isotherm and BJH pore size distribution (inset) for **Hex-CNMO**. (b) TGA of **Hex-Comp-DMF** (green) and **Hex-CNMO** (black) and (c) IR spectrum for the **Hex-CNMO**.

TGA of the hexylene-bridged composite and mesoporous organosilica films were analyzed to investigate template removal and thermal stability (Figure 2-15b). Similar to the films reported above in Section 2.3.1.3, total mass losses of ~70-80 wt.% starting at approximately 250-275 °C in **Hex-Comp-DMF** corresponds to the decomposition of the CNC template. The **Hex-CNMO** films obtained after removal of the CNC template are stable to 350 °C and show a total mass loss of ~35-40 wt.%, closely resembling the %C and %H determined by EA (Appendix, Table A-1). The **Hex-CNMO** films have similar thermal stability to the **Et-CNMO** and **Hex/Et-CNMO** films.

Notably, the mass loss measured in the TGA of **Hex-CNMO** is greater than that of the **Hex/Eth-CNMO** films (~25 wt.% loss), consistent with the **Hex-CNMO** having a larger proportion of organic groups in the material. IR spectra of the **Hex-CNMO** films show characteristic peaks at 1020 cm<sup>-1</sup> and 800 cm<sup>-1</sup> (Si-O), 2900 cm<sup>-1</sup> (CH<sub>2</sub> stretch), 3330 cm<sup>-1</sup> (OH stretch) and 1450-1400 cm<sup>-1</sup> (CH<sub>2</sub> bend) indicating retention of the alkyl bridging groups (Figure 2-15c).

CNMO materials containing long hexylene-bridged spacers were successfully prepared by CNC templating with a mixture of DMF and water. To test whether the proportion of DMF impacted the formation of the porous nanostructure within the films, hexylene-bridged organosilicas were synthesized following the same procedure as **Hex-CNMO** but with 30% and 70% v/v DMF added to the CNC suspension, denoted **Hex-CNMO-DMF(30)** and **Hex-CNMO-DMF(70)**, respectively. The average BJH pore size of the hexylene-bridged CNMO films was consistent regardless of the proportion of DMF used (Table 2-5). However, the surface area and pore volume could be controlled depending on the ratio of DMF used, with an increase in the surface area and pore volume being observed as the % v/v of DMF increases from 30 to 70. Increasing the concentration of DMF further would likely enhance solubility of the hydrophobic precursor and therefore increase surface areas of the material.

v/v DMF	BET Surface Area (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)	BJH Avg. Pore Diameter
30	310	0.55	7
50	350	0.67	7
70	380	0.75	7

Table 2-5. Summary of  $N_2$  adsorption data for the Hex-CNMO-DMF(30), Hex-CNMO, and Hex-CNMO-DMF(70).

#### **2.3.1.8** Surface properties and pore structure of the organosilica films

The organization of the hydrophobic bridging groups within the CNMO films and the effects of the alkylene-bridge on the surface properties of the organosilica were characterized by the following three methods: (1) their response to the addition of a water droplet; (2) the rate of diffusion of absorbed water; and (3) their BET *C* constants determined from gas sorption data. To obtain a qualitative picture of the change in hydrophobicity resulting from the incorporation of long alkylene spacers, a 3  $\mu$ L drop of water was placed onto a sample of **Et-CNMO** and **Hex-CNMO** and monitored over a period of 2 min (Figure 2-16). After 0.5 s, the droplet of water placed onto a film of **Et-CNMO** was absorbed into the pores, rendering the sample transparent in the area occupied by the water. This loss of iridescence is due to a close match between the refractive indices of water and silica.<sup>[91]</sup> In contrast, it takes 5 s for water droplet to be absorbed into the **Hex-CNMO** films. As the average pore size of the two samples is nearly the same, the results support enhanced hydrophobicity for the **Hex-CNMO** films compared to **Et-CNMO**. It is important to note, however, that the larger total surface area of **Et-CNMO** may also be a minor contributor to the difference in behavior.

BET *C* constants are related to the adsorption energy or the affinity of the material to an adsorbate.<sup>[163]</sup> Although rigorous interpretation of the *C* constant is limited due to the approximate nature of the BET model, lower *C* constant values in a material generally correlate to lower average surface energy. Previous research has shown that BET *C* constants can be used to qualitatively provide information about the polarity of the external and porous surfaces of silica materials.<sup>[164–166]</sup> For mesoporous SBA-15 silica, the dimensionless *C* constant is typically between 100-150, indicating the high energy, polar surfaces of surface silanol groups.<sup>[166]</sup> The *C* constant of the **Et-CNMO** films was  $90 \pm 10$  (average measurement of 5 different samples of ethylene-bridged films).

The films containing mixed systems of the longer alkylene-bridged and ethylene-bridged precursors (**Prop/Et-CNMO** to the **Hex-Et-CNMO**) displayed lower *C* constants, with values ranging from ~ 65–80. The 100% hexylene films (**Hex-CNMO**) had the lowest *C* constant with an average value of  $54 \pm 6$  (average measurement of 4 different samples of hexylene-bridged films). The low *C* constant of the **Hex-CNMO** films is comparable to silica materials that has been post-functionalized with alkylsilanes to produce hydrophobic surfaces.<sup>[166]</sup>

The rate of diffusion of absorbed water was also measured for the Hex-CNMO films and compared to the rate of diffusion of absorbed water for pure chiral nematic silica films (CNMS) and Et-CNMO films. Using pulsed field gradient (PFG) NMR diffusion measurements, the effective diffusion coefficient of absorbed water can be measured in both the longitudinal direction  $(D_{eff}^{long})$  and transverse directions  $(D_{eff}^{tran})$  of the films, relative to the bulk self-diffusion coefficient of water molecules  $(D_o)$ .<sup>[143]</sup> In the longitudinal direction (the direction of the chiral nematic axis), water molecules diffuse through periodic layers within the porous network that results from the removal of the CNC template (Figure 2-16c). This direction is perpendicular to the director of the CNC template and therefore, perpendicular to the pore axes. Alternatively, in the transverse direction, water molecules diffuse across the films in the plane of the CNC director. It was observed that absorbed water is able to diffuse in both the longitudinal and transverse directions which is consistent with the view that the porous network has a worm-hole like structure (Figure 2-16d). The diffusion rates of the CNMS (SA: 680 m<sup>2</sup>/g, pore size: 4 nm) in the longitudinal and transverse direction was lower than both the Et-CNMO (SA: 590 m<sup>2</sup>/g, pore size: 7 nm) and Hex-CNMO (SA: 350 m<sup>2</sup>/g, pore size: 7 nm). The rate of diffusion of absorbed water in the CNMO films depends on the average pore size of the films, where the smaller pore sizes have more barriers for intra-pore transport and smaller rates of diffusion.<sup>[143]</sup> In all three films, rates of 81

diffusion in the longitudinal direction differ from rate in the transverse direction. Both the **CNMS** and **Et-CNMO** films have effective diffusion coefficients in the longitudinal direction that are half the magnitude of the transverse direction  $(D_{eff}^{long} = \frac{1}{2} D_{eff}^{tran})$ . This means that although the porous network is interconnected in a three-dimensional woven structure, there are more connections or less constriction between the pores in the transverse direction. In comparison, the **Hex-CNMO** films have an effective diffusion coefficient in the longitudinal direction that is one third of the magnitude of the transverse direction  $(D_{eff}^{long} = \frac{1}{3} D_{eff}^{tran})$ . Considering that the pore sizes measured for the **Hex-CNMO** films are similar, this suggests that the connectivity between the main pores in the hexylene-bridged film may be fewer or more constricted.



**Figure 2-16.** Evolution of a 3  $\mu$ L droplet of distilled water over 5 s when placed on (a) **Et-CNMO** and (b) **Hex-CNMO** films. (c) Representation of the direction of the longitudinal (gradient is parallel to the films surface) and transverse (gradient is perpendicular to the films surface) measurements. (d) Pulsed-field gradient diffusion measurements on **Hex-CNMO** films at -3.5 °C. The effective diffusion coefficients have been scaled by the self-diffusion coefficient for supercooled bulk water at the same temperature,  $D_0=1.0 \times 10^{-9}$  m<sup>2</sup>/s.

#### 2.3.2 Aromatic-bridged CNMO films

#### 2.3.2.1 Preparation of CNMO films with phenylene, biphenylene and anthracene

### bridging groups

Aromatic functionalized mesoporous organosilica materials have been widely studied as the rigid structures of the precursors allow the porous network to be maintained after removal of the template. The first phenylene-bridged mesoporous organosilica was reported by Ozin *et al.* in 1999.<sup>[167]</sup> Since then, phenylene-bridged PMOs have been synthesized with highly crystalline pore walls<sup>[69,168]</sup> and employed in catalysis<sup>[70]</sup> and chromatography<sup>[71]</sup> applications. Other aromatic spacers, such as thiophene,<sup>[167,169]</sup> methyl and vinylbenzene,<sup>[170,171]</sup> biphenylene,<sup>[168]</sup> and anthracene,<sup>[172]</sup> have also been used to synthesize PMO materials that have potential applications in the field of optical materials.

Given the interest in aromatic functionalized periodic mesoporous organosilica, we set out to synthesize aromatic-bridged organosilica films from the precursors reported in Figure 2-17. Similar to the alkylene spacers described in Section 2.3.1, it was difficult to obtain homogeneous mixtures of aqueous CNC suspensions and aromatic organosilica precursors. It was once again possible to improve the solubility through ethanol addition and sonication of the CNC suspension prior to addition of the alkoxy precursors.



Figure 2-17. Aromatic organosilica precursors used to create CNC/organosilica composite materials and CNMO films.

Of the precursors listed in Figure 2-17, only BTESB was able to form CNC/organosilica chiral nematic films at 100% loading, denoted as **Bz-Comp**. Phenylene-bridged/CNC composite films were formed over a wide range precursor:CNC ratios (0.38-0.75 mmol / 150 mg of CNC), but were brittle and difficult to work with; therefore, 3:7 BTESB:BTMSE films were also made and are denoted as **Bz/Et-Comp**. It was found that the BTMSBP and BTMSA precursors were too hydrophobic to form homogeneous mixtures with the aqueous CNC suspensions even after the

addition of ethanol, instead forming large crystals that were visible both on top of and throughout the composite films. These aromatic precursors were diluted with BTMSE to different ratios until chiral nematic composite materials were created. It was found that a 5:95 ratio of BTMSBP or BTMSA to BTMSE was needed to obtain homogeneous films with chiral structures. These films are denoted as **Biphenyl-Comp** and **Anth-Comp**, respectively. Removal of the CNCs was carried out for samples of the composite films containing 0.57 mmol of precursor / 150 mg CNCs and are denoted **Bz-CNMO**, **Bz/Et-CNMO**, **Biphenyl-CNMO** and **Anth-CNMO**.

We initially used sulfuric acid to remove CNCs from the **Bz-Comp** films, as previously described above for the alkylene CNMO films and **Et-CNMO** films.<sup>[116]</sup> However, unlike the alkylene CNMO films that appear completely colourless when wet, a yellow colouration in the phenylene-bridged films was observed, and the colour persisted even after treatment with piranha solution. Previous studies have reported that sulfonation of the benzene moieties in phenylene-bridged PMOs occurs following the addition of sulfuric acid.<sup>[1173]</sup> We postulated that this may be responsible for the colouration of the films, as sulfuric acid was used to hydrolyze the CNCs. Therefore, it was necessary to develop a new method for extracting CNC from the films containing the new aromatic organosilica precursors. In this alternative procedure, acid hydrolysis using 10-12 M HCl followed by a silver-activated hydrogen peroxide wash for 24 to 48 h was employed. Aqueous hydrochloric acid solutions are commonly used for the acid hydrolysis of biomass and have been successfully utilized in the synthesis of other porous silica materials templated with cellulose derivatives.<sup>[82,174]</sup>

Samples of ethylene-bridged CNMO films were prepared using both sulfuric acid hydrolysis (**Et-CNMO**) and hydrochloric acid hydrolysis (**Et-CNMO-HCl**). Nitrogen adsorption-desorption isotherms and UV-Vis spectra of the **Et-CNMO** and **Et-CNMO-HCl** were compared.

The pore sizes, pore volumes and chiral nematic pitches of the samples are almost identical, indicating that changing the acid used during hydrolysis did not significantly influence the porosity, organic spacer or long-range chiral structure of the samples (Figure 2-18), a summary of the  $N_2$  isotherms data can be seen in Appendix A, Table A-2 and Figure A-3).



**Figure 2-18.** (a) BJH pore size distribution of ethylene-bridged organosilica samples using 6 M sulfuric acid for **Et-CNMO** (black) and 12 M HCl for **Et-CNMO-HCl** (blue). (b) UV-Vis spectra for the **Et-CNMO** (black) and **Et-CNMO-HCl** films (blue).

# 2.3.2.2 Selective removal of the CNC template from aromatic-bridged/CNC composite

films

Solid-state <sup>13</sup>C CP/MAS NMR spectroscopy was carried out for the 100% loaded phenylene-bridged composite and mesoporous organosilica materials. The <sup>13</sup>C NMR spectrum of the composite sample shows cellulose peaks at 60-120 ppm and a single peak at 130 ppm corresponding to phenylene carbons (Figure 2-19a). After acid hydrolysis, only a single peak was observed, confirming the removal of the CNCs and retention of the phenylene moieties. Although we did not measure the <sup>29</sup>Si NMR spectrum of the samples to look for Si-C cleavage, previously

reported **Et-CNMO** showed no cleavage after acid hydrolysis.<sup>[116]</sup> Additionally, the comparison between **Et-CNMO** and **Et-CNMO-HCl** films showed that the acid conditions did not affect the organosilica films.

TGA analysis of the aromatic/CNC composite materials demonstrate a characteristic weight loss starting at 200-250 °C due to the decomposition of the CNC rods and a total mass loss of ~70-80%, which is consistent with the TGA data for the alkylene-bridged films reported in Section 2.3.1.3. After removal of the CNC template, the mass losses observed decreased to 15-35% and closely resemble the %C and %H determined by EA (Appendix A, Table A-3). The **Bz/Et-CNMO**, **Biphenyl-CNMO** and **Anth-CNMO** films, composed of both their respective spacer and ethylene bridging groups, have similar thermal stabilities as the alkylene CNMOs (300-400 °C). However, the pure phenylene CNMO films are stable to 400-450 °C, which is similar to other reported phenylene PMOs.<sup>[136]</sup> IR spectra of all the aromatic-bridged films show characteristic peaks at 1020 cm<sup>-1</sup> (Si-O), 800 cm<sup>-1</sup> (Si-O), 3330 cm<sup>-1</sup> (OH stretch) and 1640 cm<sup>-1</sup> (water). While the **Biphenyl-CNMO** and **Anth-CNMO** films have spectra similar to the ethylene-bridged films, the **Bz-CNMO** and **Bz/Et-CNMO** have additional peaks at 1630 cm<sup>-1</sup>, and 1380 cm<sup>-1</sup> that can be assigned to C=C and aromatic C-H bonds (see Appendix A, Figure A-4).<sup>[171,175]</sup>



**Figure 2-19.** (a) Photograph of the **Bz-CNMO** films observed at an oblique angle of incidence. (b) Solid state <sup>13</sup>C CP/MAS NMR spectra of **Bz-Comp** and **Bz-CNMO** films (SS = spinning side band). (c) TGA of phenylene-bridged composite and CNMO films. (d) TGA of anthracene and biphenylene-bridged composite and CNMO films.

# 2.3.2.3 Optical and structural properties of the aromatic-bridged CNMO films

All aromatic-bridged CNMO films display LH reflection peaks in the composite materials and CNMO films, confirming the chiral nematic ordering had been retained after CNC removal (Table 2-6, Figure 2-20). Similar to the alkylene organosilica films, the reflected wavelength is blue-shifted compared to the composite films by 200–500 nm. Comparison of the blue shifts of the aromatic and alkylene films synthesized using the same organosilica precursor to CNC ratio indicates that composite films with longer helical pitches (~1200-1500 nm) undergo more contraction upon CNC removal than those with shorter helical pitches (~600-800 nm). The significantly smaller helical pitches observed in both the 5% loaded anthracene and biphenylene films compared to the ethylene films is likely due to the presence of trace salt leftover after the synthesis of the organosilica precursors. The introduction of salt into self-assembled CNCs has been reported to mask the electrostatic interactions of the CNC rods, increase the twisting angle  $\theta$ , thereby reducing the pitch value.<sup>[110,176]</sup> The **Anth-CNMO** and **Biphenyl-CNMO** films also display absorption at 300-400 nm and 260 nm, respectively, corresponding to the introduction of anthracene and biphenylene into the films (Figure 2-20b). However, the Anth-CNMO showed a decrease in intensity of the anthracene absorption after CNC removal that could indicate a small loss of bridging groups during acid hydrolysis.

Table 2-6. Summary of the UV-Vis spectra for the aromatic composite and CNMO films					
Organosilica bridging	$\lambda_{\max}(nm)$	$\lambda_{\max}(nm)$			
group	Composite films	Mesoporous films			
Phenylene	1310	780			
30 Phenylene/ 70 Et	1510	1000			
5 Biphenylene/ 95 Et	500	380			
5 Anthracene/ 95 Et	830	600			

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CD spectra of the films show strong positive signals with positions that corresponded to the reflectance peak, confirming the selective reflection of LH circularly polarized light due to the long-range chiral nematic nanostructure (Figure 2-20c, note that due to limitations in the CD spectrometer, the  $\lambda_{max}$  of the **Bz/Et-CNMO** films were too red-shifted to be observed). A small peak at 700 nm is observed in the **Biphenyl-CNMO** films that is likely caused by inhomogeneous drying rates or phase separation of the two organosilica precursors. Since chiral PMOs have potential applications as heterogeneous asymmetric catalysts and optically active materials, we investigated whether this chiral nanostructure would induce a chiral signal in the aromatic spacers. Unfortunately, no signals from the aromatic groups were observed in the CD spectra. Due to the disordered structure of the pores, the local environment of the bridging groups within the pores does not appear to be influenced by the overall chiral structures.

Fluorescence spectroscopy was carried out to verify to retention of the aromatic bridging groups for the **Biphenyl-CNMO** and **Anth-CNMO** films (Figure 2-20d). Fluorescence due to the incorporation of biphenylene and anthracene chromophores into the stable organosilica framework was observed. The fluorescence bands of the **Biphenyl-CNMO** films are shifted to longer wavelengths and broadened compared to a diluted solution of the pure precursor ( $\lambda \sim 310$  nm) reported by Inagaki and co-workers.<sup>[172,177]</sup> This emission behavior is consistent with that of both crystalline and amorphous biphenylene-bridged PMO thin films that have previously reported, which also showed a broadening and red-shift due to interaction among bridging aromatic biphenyl groups.<sup>[172,177]</sup> This suggests that the biphenylene precursors may preferentially condense near each other in the CNMO films. Similar to previous observations for anthracene PMOs diluted with TMOS,<sup>[178]</sup> dilution of the anthracene-bridged spacer in CNMO films with BTMSE resulted in a slight broadening and red shift of the fluorescence band but dilution suppressed the interaction between the anthracene groups (emission of anthracene precursors is  $\lambda \sim 410$  nm<sup>[172]</sup>).



**Figure 2-20.** Optical characterization of the organosilica films by (a, b) UV-Vis spectroscopy (as labelled) and (c) CD spectroscopy of **Bz-CNMO**, **Anth-CNMO** and **Biphenyl-CNMO** films. (d) Emission spectra for **Biphenyl-CNMO** ( $\lambda_{ex}$  275 nm) and **Anth-CNMO** ( $\lambda_{ex}$  350 nm).

SEM images of the organosilica samples containing aromatic groups show the periodic organization that is characteristic of chiral nematic organosilica films synthesized by CNCs (Figure 2-21). The long-range chiral nematic nanostructure can be clearly seen throughout the thickness for all films, with the organosilica rods rotating in a LH chiral structure. PXRD was performed on 100% loaded **Bz-CNMO** films and compared to the ethylene-bridged CNMO films synthesized by HCl acid hydrolysis (Figure 2-22). One broad peak centered at 23° 2θ is observed

for the **Et-CNMO-HCl**, characteristic of amorphous silica. For the **Bz-CNMO** films, two broad peaks are observed at ~11° 20 and ~22° 20 indicating a small degree of ordering that is not present in ethylene-bridged organosilica films. In both samples, the peaks corresponding to cellulose nanocrystals (~15° 20 and 23° 20<sup>[91]</sup>) are also missing, further confirming the removal of the CNC template. However, the broad appearance of the **Bz-CNMO** peaks and the absence of a third smaller peak at ~35° 20 indicates that these films are significantly less crystalline than the phenylene-bridged mesoporous organosilica reported in the literature.<sup>[69]</sup> This supports our findings that, although the films contain long-range ordering, the local environment of the pores is disordered. Additionally, it has been found that most phenylene PMOs prepared under acidic conditions do not have highly crystalline pore walls.<sup>[136]</sup>



**Figure 2-21.** SEM images of organosilica films with different aromatic spacers; (a) **Bz-CNMO** (scale bar = 1  $\mu$ m), (b) **Bz/Et-CNMO** film (scale bar = 5  $\mu$ m), (c) **Anth-CNMO** film (scale bar = 1  $\mu$ m), and (d) **Biphenyl-CNMO** film (scale bar = 4  $\mu$ m).



#### 2.3.2.4 Mesoporosity of aromatic-bridged CNMO films

The porosity of the aromatic organosilica films was investigated using nitrogen adsorption-desorption Figure 2-23 and is summarized in Table 2-7. All samples in this series show type IV isotherms with hysteresis, which is associated with mesoporosity. The high surface areas of the **Bz-CNMO** and **Bz/Et-CNMO** are due to the increased carbon content reducing the material density. The Anth-CNMO and Biphenyl-CNMO show similar surface areas to Et-CNMO as they contain 95% ethylene-bridged precursor. However, the larger pore volumes and pore sizes observed in the Anth-CNMO (1.62 cm<sup>3</sup>/g, 9 nm) and Biphenyl-CNMO (1.63 cm<sup>3</sup>/g, 11 nm) films when compared to the **Et-CNMO-HCl** films (0.89  $\text{cm}^3/\text{g}$ , 7.5 nm) may be due to a reduction in the contraction of the porous network after acid hydrolysis as observed by UV-Vis spectroscopy. Pore sizes are consistent with the sizes observed for the alkylene-bridged CNMO films with a broad distribution from ~5-20 nm and average pore sizes ranging from 5-15 nm. The 100% loaded phenylene-bridged samples have the smallest pore diameter. **Bz-CNMO** of varying ratios from (0.48-0.75 mmol of precursor) were also prepared. All Bz-CNMO samples have surfaces areas between 740–840 m<sup>2</sup>/g, pore volumes of 0.7 - 1.1 cm<sup>3</sup>/g and pore sizes of 2–8 nm. Increasing the ratio of the phenylene alkoxysilane precursors to CNC resulted in films with increased surface area, pore volume and pore sizes.

<b>Table 2-7.</b> Nurogen adsorption data of the aromatic organostica times					
Sample*	BET Surface Area	Pore volume	<b>BJH Pore Diameter</b>		
	$(m^2/g)$	$(cm^3/g)$	(nm)		
Bz-CNMO	740	0.72	7		
<b>Bz/Et-CNMO</b>	680	1.07	9		
Anth-CNMO	580	1.62	9		
<b>Biphenyl-CNMO</b>	620	1.63	11		

**Table 2-7.** Nitrogen adsorption data of the aromatic organosilica films

\* Table compares films prepared using 0.57 mmol of precursor / 150 mg CNCs.



Figure 2-23. Nitrogen adsorption isotherms of the aromatic CNMO films; (a) Bz-CNMO, (b) Bz/Et-CNMO, (c) Biphenyl-CNMO, and (d) Anth-CNMO. (inset: BJH pore size distributions).

#### 2.3.2.5 Helium ion microscopy of Bz-CNMO and Et-CNMO films

The SEM of these organosilica materials indicates that they have long-range periodicity but disordered porous networks (e.g., worm-hole structures) that make it difficult to obtain meaningful information about the order from X-ray diffraction. Furthermore, since these materials are good insulators, sputter-coating of the sample with metals is required for SEM imaging, which modifies the surface of the material and conceals subtle surface features. Therefore, the samples were analyzed with helium ion microscopy (HIM).<sup>[179]</sup> Helium ion microscopy (HIM) is a new technique that uses charged helium ions in the place of electrons for imaging.<sup>[180]</sup> The small de Broglie wavelength of the helium ion and the very high source brightness available in these instruments lead to enhanced resolution when compared to SEM. As well, the technique is more surface sensitive than SEM and thus gives more detailed topological information. HIM has proven effective for imaging nanostructured materials, including gold-decorated nickel spheres, carbon nanotubes, and semiconductor structures.<sup>[181]</sup>

HIM micrographs of the Bz-CNMO and Et-CNMO films revealed fascinating structural details that had not been observed in the previous SEM images and enabled the pore structures of the organosilica materials to be compared. HIM images of **Bz-CNMO** reveal a worm-hole like porous structure. As seen in Figure 2-24a, these materials have a well-ordered long-range structure imparted by the CNC template that matches the periodic ordering seen in the SEM images. Images taken at higher magnification showed that the organosilica rods are interconnected and form pores where individual CNC rods have been removed from the silica network. The chiral nematic axis is oriented vertically in the plane of the image and the organosilica rods rotate perpendicularly to the plane of the image, exposing the anisotropy of the pore structure. Regions in the Bz-CNMO images where the organosilica rods are oriented along the x-axis of the image do not appear very porous since we are looking perpendicular to the pore channels. However, the high-resolution images do show that pores have a high degree of disorder which could not be resolved by electron microscopy. In comparison, high magnification HIM images of the Et-CNMO films reveal that the organosilica rods create a more ordered, woven-like, porous structure in this material and the chiral nematic twisting of the pore channels that is generated by the removal of CNCs can be clearly observed. Although both films display the long-range chiral nematic nanostructure, by introducing different organic moieties into the CNMO films we were able to change the connectivity and shape of the porous structure.

HIM images can also be used to measure the size of the pores, which can then be compared to the size data obtained from nitrogen adsorption-desorption isotherms. Measurements of the pores throughout the high magnification images give an average diameter of  $8.4 \pm 2.1$  nm for the **Et-CNMO** films, which corresponds quite closely to the value determined by N<sub>2</sub> adsorption (7 nm) and  $4.9 \pm 1.4$  nm for the **Bz-CNMO** films, which agrees quite closely with the value extracted from gas sorption analysis (ca. 5 nm, see Appendix A- Figure A-5 for the 0.48 mmol of precursor/ 150 mg CNC **Bz-CNMO** films were used for HIM).



**Figure 2-24.** HIM images of (a) **Bz-CNMO** films and (b) **Et-CNMO** films at 3 different length scales. (Larger images of the higher magnification of **Bz-CNMO** can be found in Appendix A)

#### 2.3.2.6 Preparation of biphenylene-CNMO films from DMF/water CNC suspensions

Using the previously obtained knowledge that the addition of DMF to aqueous CNC suspensions enabled the preparation of long alkylene-bridged CNMO films, we applied this method to increase the loading of the biphenylene and anthracene spacers. CNC/organosilica samples prepared using 100% loading of BTMSA and BTMSBP were initially synthesized using both 50% and 70% v/v DMF into aqueous CNC suspensions. However, in each sample the organosilica precursors precipitated out of solution resulting in cloudy films and no iridescence was observed. Dilution of the anthracene and biphenylene precursors with varying amounts of BTMSE was also attempted using the DMF/water CNC suspensions but this did not improve the loading of these precursors beyond 5%. Therefore, a new solvent mixture of DMF, acetone and water was employed to help improve the solubility of these aromatic precursors in the CNC suspension. By using a DMF, acetone and aqueous CNC suspension at a ratio of 1:1.2:1, respectively, homogeneous films containing 20% BTMSBP diluted with 80% BTMSE films could be obtained (denoted **Biphenyl(20)-Comp**). Removal of the CNC template was carried out by acid hydrolysis using 12 M HCl and a wash with H<sub>2</sub>O<sub>2</sub> and AgNO<sub>3</sub> to produce CNMO films denoted Biphenyl(20)-CNMO.

**Biphenyl(20)-CNMO** films were characterized by N<sub>2</sub> adsorption, SEM, CD, and TGA confirming the successful removal of the CNC template and retention of the organic bridge. Characteristics were very similar to those of the **Biphenyl-CNMO**, with some notable differences. The **Biphenyl(20)-CNMO** films have a higher thermal stability (400 °C) and mass loss (25%) than the **Biphenyl-CNMO**, consistent with the larger proportion of aromatic spacers (Figure 2-25). This mass loss closely resembles the %C and %H determined by EA (see Appendix A, Table A-3). Additionally, the CD spectrum of the **Biphenyl(20)-CNMO** does not display the additional peak

at 700 nm suggesting that these films are more homogeneous than the biphenylene films synthesized from ethanol/water CNC suspensions. The **Biphenyl(20)-CNMO films** have a surface area of 690 m<sup>2</sup>/g, a pore volume of 1.04 cm<sup>3</sup>/g and an average pore size of 8 nm. Increasing of the loading of the biphenylene spacer from 5% (**Biphenyl-CNMO:** 620 m<sup>2</sup>/g, 1.63 cm<sup>3</sup>/g, 11 nm) to 20% increases the surface area of the films, associated with the increase in carbon content, but decreases both the pore volume and pore size. Incorporating more aromatic spacers in the CNMO films appears to introduce more microporosity into the sample. For example, the **Bz-CNMO** and **Bz/Et-CNMO** films have micropore volumes of 0.05 cm<sup>3</sup>/g and 0.03 cm<sup>3</sup>/g, respectively, and the 20% and 5% loaded biphenylene films have micropore volumes of 0.05 cm<sup>3</sup>/g and 0.05 cm<sup>3</sup>/g and 0.02 cm<sup>3</sup>/g, respectively.



**Figure 2-25.** Characterization of **Biphenyl(20)-CNMO** films by (a) SEM (scale bar = 1  $\mu$ m), (b) TGA, (c) CD, and (d) N<sub>2</sub> adsorption (inset: BJH pore size distributions).

# 2.4 Conclusions

CNCs have been used as a liquid crystal template to synthesize C<sub>1</sub> to C<sub>6</sub> alkylene-bridged mesoporous organosilica films and aromatic bridging groups as an integral component of the porous structure. Removal of the CNC template by acid hydrolysis using either 6 M H<sub>2</sub>SO<sub>4</sub> or 12 M HCl did not disrupt the organosilica framework and resulted in mesoporous, free-standing organosilica films that retain a long-range chiral nematic ordering of the porous network imparted by the CNCs. These films reflect LH circularly polarized light with tunable wavelengths that are 101 dependent on the type of spacer employed. The chiral nematic composite materials and mesoporous organosilica films are stable to 200-250 °C and >300 °C in air, respectively. Interestingly, the propylurea-bridged composite materials enhanced the stability of the CNCs and gave thermal stability 100-150 °C higher than the alkylene-bridged composite materials. It was found that increasing the hydrophobicity of the bridging groups in the organosilica was difficult due to phase separation of the organosilica precursor from the aqueous CNC suspension. This was solved through two methods: combining the long alkylene-bridge precursors with shorter precursors, or by using a mixed solvent system of water and DMF to prepare the films. Integrating different organic spacers into the CNMO films impacted the shape of porous structure as well as the mechanical and chemical properties of the organosilica films. In this Chapter, a new method to synthesize CNMO films that can be tailored to different precursors was developed. This method opens the door to creating new mesoporous organosilica films with targeted properties that could be used for sensing, chromatography, and gas separation applications.

# Chapter 3: Photopatterning of Free-standing Chiral Nematic Mesoporous Organosilica Films<sup>†</sup>

# 3.1 Introduction

Stimuli-responsive materials (sometimes referred to as 'smart materials') are capable of a reversible chemical or conformational transformation in response to an external stimulus. There are numerous external stimuli that have been reported to induce these changes including temperature, pH, humidity, light, and mechanical force.<sup>[182,183]</sup> Stimuli-responsive materials can have a wide range of applications, such as optically rewritable data storage,<sup>[182,184]</sup> smart windows, ophthalmic lenses, and sensors.<sup>[185,186]</sup> Using hybrid organic-inorganic materials for the development of stimuli-responsive materials is of particular interest for applications involving tunable optical devices or sensors.<sup>[187]</sup> By integrating responsive organic components into porous inorganic materials, one can take advantage of the solid-state properties imparted by the porous network within the inorganic host (e.g., controlled analyte diffusion, large surface areas, or size exclusion properties) to tailor the function of these hybrid 'smart' materials.<sup>[188,189]</sup>

Photochromic materials are extensively investigated stimuli-responsive materials that display reversible light induced transformations at the molecular structure or nanostructure level. Many molecular structures, including diarylethenes,<sup>[190]</sup> spiropyrans,<sup>[191]</sup> and azobenzenes,<sup>[192]</sup> have been investigated for the synthesis of stimuli-responsive materials. Spiropyrans are one of the oldest and most studied family of photochromic molecules.<sup>[193–195]</sup> Spiropyrans exist in two

<sup>&</sup>lt;sup>†</sup> Portions of this chapter have been previously published as: A.S. Terpstra, W.Y. Hamad, M.J. MacLachlan, *Adv. Funct. Mater.* **2017**, *27*, 1703346.

thermodynamically stable states where each form has a different  $\lambda_{max}$ . They undergo reversible isomerization between their open polar merocyanine form (MC) and closed hydrophobic spiropyran (SP) form (Scheme 3-1). This rearrangement can be induced by light (photochromism) or by heat (thermochromism). When the colourless SP form is exposed to ultraviolet light, the C(sp<sup>3</sup>)-O bond in the SP form is cleaved, causing the ring to open and produce the more conjugated purple MC form. Visible irradiation of the MC form reverses the transformation and returns the complex to the SP form.<sup>[191]</sup>



Scheme 3-1. Photoisomerization of a spiropyran molecule between the SP (colourless) and MC (purple) forms and photographs of the solutions of SP and MC forms.

Previously, photochromic molecules have been incorporated onto inorganic materials, such as silica substrates,<sup>[195,196]</sup> silica particles,<sup>[197]</sup> and porous silicates,<sup>[193,198]</sup> for applications ranging from drug delivery to chromatography. Mesoporous (organo)silica materials are advantageous as solid supports for organic molecules due to their high surface area, tunable pore diameters, and readily-modified surface chemistry.<sup>[24,67,68]</sup> Wirnsberger *et al.* and Malfatti *et al.* incorporated spiropyran molecules into silica materials that were then deposited onto glass substrates and showed reversible photochromic properties.<sup>[199,200]</sup> Raboin *et al.* combined spirooxazines within

the solid support. However, they did not demonstrate continued reversibility or patterning of the photochromic dyes in their material.<sup>[201]</sup> Unfortunately, it is often difficult to obtain mesoporous organosilica materials as large, freestanding films that could be used for applications like sensing. However, the MacLachlan group previously reported a method to create freestanding chiral nematic mesoporous organosilica (CNMO) films by condensing organosilica precursors with cellulose nanocrystals (CNCs).<sup>[116]</sup> Subsequent removal of the CNCs yields freestanding mesoporous films with a long-range chiral nematic nanostructure. We identified that these freestanding films of CNMO are ideal candidates for the incorporation of photoresponsive molecules to create new photoswitchable materials.

There are two general approaches to functionalized mesoporous (organo)silica materials. The previous chapter described the modification of mesoporous organosilica films through one-pot or co-condensation synthesis, where the desired organic functional group is incorporated into the condensable precursors and is homogeneously integrated into the resulting organosilica material.<sup>[24,36]</sup> The second approach to functionalizing silica materials is through post-synthetic methods or grafting. During post-synthetic modification, the desired functional groups are introduced after the mesoporous silica has been formed by ionically or chemically interacting the functional group with the silanol groups on the surface of the silica.<sup>[202]</sup> Post-synthetic modifications allow for specific parts of the mesoporous silica surface to be modified (e.g., surface or pore channels). Additionally, this method allows for the introduction of functional groups that are incompatible with liquid crystal templating of the mesoporous silica or are not stable to the conditions use for template removal.

Using a post-synthetic method, I found that the interconnected pores of the CNMO films could be functionalized with a mixture of hydrophobic and amine-containing organosilanes.

Photochromic spiropyran could then be tethered to the CNMO films to create mesoporous organosilica films with spiropyran molecules integrated throughout the pore network. In this Chapter, I report the synthesis and characterization of new hybrid freestanding films that show intense MC absorption after irradiation and undergo reversible photopatterning. These hybrid organic-inorganic materials are promising for the development of photochromic displays, sensors with reversible binding, and patternable security features.

#### **3.2 Experimental**

#### 3.2.1 Materials

All solvents and reagents including 1,2-bis(trimethoxysilyl)ethane (BTMSE), tert-butyl(chloro)diphenylsilane (TBDS), 3-aminopropyltrimethoxysilane (ATMS), and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) were purchased from Sigma Aldrich and used without further purification. Aqueous suspensions of CNCs were obtained from FPInnovations.

#### 3.2.2 Characterization

Ultraviolet-visible/near-IR (UV-Vis/NIR) spectroscopy was conducted on a Cary 5000 UV-Vis/NIR spectrophotometer and circular dichroism (CD) experiments were performed using a JASCO J-815 spectropolarimeter. Spectra were collected by mounting free-standing films in a solid-state holder so that the surfaces of the films were perpendicular to the beam path. N<sub>2</sub> adsorption studies were performed using a Micromeritics ASAP 2020 at 77 K. All samples were degassed under vacuum at 120-150 °C immediately prior to analysis. The specific surface areas of the samples studied were calculated using the standard BET method in the range of relative 106 pressures from 0.04 to 0.2. The total pore volumes were estimated from the amount adsorbed at a relative pressure of 0.99. BJH pore size distributions were all calculated from the adsorption branch of the isotherm. Thermogravimetric analysis (TGA) was performed on a PerkinElmer Pyris 6 thermogravimetric analyzer and samples were heated under air from 30 °C to 800 °C at 5 °C/min. Nuclear magnetic resonance (NMR) was performed on a Bruker 300 MHz spectrometer. Mass spectrometry (MS) was conducted on a Kratos MS-50. Infrared spectroscopy (IR) was performed on a Nicolet 6700 FTIR spectrometer equipped with a Smart Orbit diamond attenuated total reflectance (ATR). The <sup>13</sup>C cross-polarization/magic angle spin (CP/MAS) SS-NMR spectrum (7000 scans) was collected on a 400 MHz Varian Unity Inova equipped with a Varian/Chemagnetics 4 mm T3 MAS probe using used glycine as a reference. Samples were spun at a rate of 5 kHz with a contact time of 1.5 ms and a recycle delay of 2 s.

# 3.2.3 Microscopy

Scanning electron microscopy (SEM) images were collected on a Hitachi S4700 electron microscope. Samples were prepared by breaking the film into small pieces and attaching them to aluminum stubs using double-sided adhesive tape. Samples were sputter-coated with 5 nm of gold or platinum/palladium (80/20).

#### **3.2.4** Synthesis of spiropyran

**Synthesis of 1'-(β-carboxyethyl)-3',3'-dimethyl-6-nitrospiro(indoline-2',2[2H-1]benzopyran (1).** The spiropyran derivative **1** was prepared as described in literature.<sup>[43,203]</sup> A mixture of 2,3,3-trimethylindolenine (0.69 mL, 4.3 mmol) and 3-bromopropionic acid (0.66 g, 4.3 mmol) was dissolved in dry toluene (20 mL) and heated under nitrogen at 100 °C for 12 h. The 107 product was extracted from toluene using 100 mL of distilled water, washed with chloroform (50 mL x 4) and dried. The remaining solid was dissolved in ethanol (18 mL) and combined with 5-nitrosalicylaldehyde (0.80 g, 4.8 mmol) and piperidine (0.52 mL, 5.3 mmol). The mixture was heated at reflux for 5 h then cooled in an ice bath, filtered, and washed with cold ethanol. The resulting precipitate was recrystallized from hot ethanol and dried to yield **1** (640 mg, 1.7 mmol, 40%). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  1.07 (s, 3H), 1.20 (s, 3H), 2.45-2.57 (m, 2H), 3.34-3.40 (m, 2H), 5.99 - 8.2 (aromatic, 9H). EIMS *m/z*: calculated for C<sub>21</sub>H<sub>20</sub>O<sub>5</sub>N<sub>2</sub>, 380; found: 380. NMR data was consistent with literature.<sup>[43]</sup>

#### 3.2.5 Synthesis of spiropyran-functionalized CNMO films

Synthesis of Et-CNMO films. Et-CNMO films were prepared according to literature and as described in Chapter 2.<sup>[116]</sup> In short, BTMSE (506  $\mu$ L, 2.01 mmol) was added dropwise to the CNC suspension (3.5 wt.%, 15 ml, pH = 2.5) and stirred until homogeneous (~2 h). The composite mixture was transferred to polystyrene Petri dishes and left to dry under ambient conditions. The CNCs were removed from the resulting composite material by acid hydrolysis, using 6 M H<sub>2</sub>SO<sub>4</sub> (300 mL acid / 200 mg of films) followed by a piranha wash (1:5 30% H<sub>2</sub>O<sub>2</sub>:conc.H<sub>2</sub>SO<sub>4</sub>) to obtain chiral nematic mesoporous ethylene-bridged organosilica films. These films are denoted **Et-CNMO**.

Several different batches of **Et-CNMO** films were used during the synthesis and characterization of the spiropyran-functionalized CNMO films and two different batches of aqueous CNC suspensions were used throughout this chapter (3.5 wt.%, pH = 2.4 and 4.1 wt.%, pH = 2.5). All of the films synthesized used the same ratio of CNCs to organosilica precursor, 0.57 mmol BTMSE:150 mg CNCs. Individual batches of ethylene-bridged organosilica films had

slightly different chiral nematic pitches resulting from day-to-day changes in humidity and temperature affecting the drying times as well as the different CNC batches used. These pitch differences are observable when analyzing the films by UV-Vis spectroscopy as the films reflected different wavelength of light. To the best of our knowledge, the different chiral pitches of the films did not affect the functionalization of the organosilica films.

**Post-synthetic functionalization of CNMO films.** The **Et-CNMO** films (55 mg) were heated under vacuum at 100 °C overnight. Films were placed in dry toluene (20 mL) and *tert*-butyl(chloro)diphenylsilane (TBDS) (320  $\mu$ L of 1 M in methylene chloride, 0.32 mmol) and stirred at 100 °C for 12 h. After the reaction, films were filtered, washed with methylene chloride (3 × 10 mL), acetone (10 mL), methylene chloride (2 × 10 mL), and dried under vacuum at 100 °C for 3 h. This procedure was repeated for a solution of 3-aminopropyltrimethoxysilane (ATMS) (16  $\mu$ L, 0.09 mmol) in dry toluene (15 mL). Dried TBDS/ATMS-functionalized films (50 mg) were placed in a solution of ethanol (20 mL) containing 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) (35 mg, 0.23 mmol) and compound **1** (5.0 mg, 0.01 mmol) at room temperature in the dark for 24 h. After the reaction, films were washed with ethanol overnight to obtain spiropyran-functionalized Et-CNMO films denoted (**SP-Et-CNMO**).

#### **3.2.6** Synthesis of non-porous SP-Et-Films.

The non-porous freestanding ethylene-bridged organosilica films (**Et-films**) were synthesized using similar reaction conditions to the **Et-CNMO** films but without the addition of the template material (CNCs). BTMSE (270 uL, 1.06 mmol) was mixed with water (5 mL), ethanol (1 mL), and hydrochloric acid (0.5 M, 50  $\mu$ L) to promote condensation of the silane and

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stirred for 3 h. The reaction mixture was dried in a 5 cm diameter polystyrene Petri dish overnight to form solid silica films without porosity or chiral nematic structure. Post-functionalization of non-porous **Et-films** with **TBDS**, **ATMS** then **1** to form **SP-Et-films** followed the exact procedure as the **SP-Et-CNMO** films mentioned above.

#### 3.2.7 Control 1: Et-CNMO and TBDS-Et-CNMO films reacted with 1 and EDC

A solution of ethanol (20 mL) containing EDC (35 mg, 0.23 mmol) and compound **1** (5.0 mg, 0.01 mmol) was stirred until a homogeneous mixture was obtained. Samples of **Et-CNMO** films (10 mg) and **TBDS-Et-CNMO** films (10 mg) were transferred into vials containing a homogeneous solution of compound **1** and EDC (4 mL) and allowed to react at room temperature in the dark for 24 h. Films were washed with ethanol overnight to remove any physically adsorbed spiropyran on **Et-CNMO** and **TBDS-Et-CNMO** films and characterized by UV-Vis.

#### 3.2.8 Control 2: TBDS/ATMS-Et-CNMO films reacted with 1 but without EDC

A solution of ethanol (4 mL) containing **1** (1 mg, 0.002 mmol) was stirred until a homogeneous mixture was obtained. A sample of **TBDS/ATMS-Et-CNMO** films (10 mg) was transferred into a vail containing the homogeneous solution of compound **1** and allowed to react at room temperature in the dark for 24 h. Films were washed with ethanol overnight. A subset of these films as well as **SP-Et-CNMO** films were washed with sodium hydroxide (0.7 M, 20 mL) followed by DI water until the films returned to a neutral pH, then they were analyzed by UV-Vis spectroscopy.

#### 3.2.9 Metal Complexation of SP-Et-CNMO/MC-Et-CNMO

For sensing experiments, the samples of **SP-Et-CNMO** films were irradiated with an 8 W 365 nm light in the solid state for 7 min to obtain purple films (denoted **MC-Et-CNMO**). The **MC-Et-CNMO** films (5 mg) were submerged into a metal salt solution (2 mM  $M^{2+}$  in 10 mL ethanol) for 2 min then dried. Chloride salts of each metal were used. To decomplex the metal, the films were irradiated in ethanol (20 mL) for 10 min with visible LED light.

#### **3.3 Results and Discussion**

#### 3.3.1 Preparation of spiropyran-functionalized CNMO films

Liquid crystal templating and evaporation induced self-assembly (EISA) of CNC rods was used to synthesize ethylene-bridged organosilica/CNC films from 1,2-bis(trimethoxysilyl)ethane to form composite materials with a long-range chiral nanostructure. After removal of the CNCs, the resulting mesoporous ethylene-bridged organosilica films (**Et-CNMO**) are approximately 50 - 60  $\mu$ m thick, have BET surface areas of ~500 m<sup>2</sup>/g and BJH pore diameters of ~7 nm. As mentioned in Chapter 2, the CNMO films are iridescent owing to the chiral nematic nanostructure that is imparted by the CNC template. Because of the left-handed (LH) helical structure in these materials, LH circularly polarized light is selectively reflected from the films and the materials show an intense signal when analyzed by UV-Vis and CD spectroscopy. As the wavelength of light reflected from the films is sensitive to the refractive index of components within the pores, the  $\lambda_{max}$  can serve as a way to monitor the functionalization of the porous network and incorporation of molecules in the pores.

The photochromic spiropyran (1) was used for the synthesis of CNMO/spiropyran hybrid materials as it is a well-studied photochromic substance. Scheme 3-2 shows the synthesis of the 111

carboxylic acid-functionalized spiropyran molecule **1** and the post-synthetic modification of the CNMO films. Grafting of 3-aminopropyltrimethoxysilane (ATMS) incorporated amine sites onto the surface of the films that could react with compound **1** using a coupling reagent, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC), to form an amide bond and immobilize **1** into the porous network of the CNMO films.



Scheme 3-2. Synthesis of spiropyran-functionalized ethylene CNMO films (SP-Et-CNMO).

The photochromic properties of immobilized spiropyran molecules are sensitive to the surface properties of the host material and steric constraints.<sup>[196,204]</sup> When first attempting to form CNMO/spiropyran hybrid materials, the CNMO films were only functionalized with ATMS and **1** resulted in films that displayed a constant red colouration and no photochromic properties despite long exposure times to UV or white light. Previous research has shown that photoisomerization of

spiropyran is hampered at high concentration because of intermolecular interactions between spiropyran molecules. Additionally, the polar silica environment stabilizes the charged MC form allowing hydrogen bonding to occur between the oxygen of the MC and the silanol surface that can quench the photochromic response.<sup>[205,206]</sup> This can be overcome by capping OH groups on the surface of the (organo)silica and reducing the polarity of the silica films through the addition of tert-butyl(chloro)diphenylsilane (TBDS).<sup>[196,207,208]</sup> TBDS grafted onto the silica also helps reduce the surface coverage of ATMS and the bound spiropyran, thus reducing intermolecular interactions that stabilize the MC form. Therefore, the CNMO films were first functionalized with TBDS by placing the films into a pre-mixed solution of TBDS at 100 °C for 12 h followed by a pre-mixed solution of ATMS at 100 °C for 12 h, creating organosilica films modified with TBDS and ATMS groups, denoted TBDS-Et-CNMO and TBDS/ATMS-Et-CNMO, respectively. The **TBDS/ATMS-Et-CNMO** films were then soaked in a pre-mixed solution containing 1 and EDC in the dark and at room temperature for 24 h to form the spiropyran-functionalized CNMO films, denoted **SP-Et-CNMO**. Unreacted spiropyran was removed from the films by thoroughly washing the films in ethanol overnight.

# **3.3.2** Chiral nematic optical and structural properties of spiropyran-functionalized organosilica films

The functionalization of the CNMO films and the immobilization of the spiropyran into the films were characterized by UV-Vis, CD, and IR spectroscopy as well as nitrogen adsorptiondesorption isotherms and SEM (Figure 3-1 and Figure 3-2). As seen in Figure 3-1a, the UV-Vis spectra show a red-shift in the wavelength reflected by the chiral nematic nanostructure of the films as a result of the surface functionalization, which increases the average refractive index ( $n_{avg}$ )
of the material. A CD spectrum of the **SP-Et-CNMO** films confirms the retention of the LH chiral structure with a positive signal matching the reflection peak seen in the UV-Vis spectrum. Previous analyses of spiropyran derivatives have reported the maximum absorbance of the SP form to be between 300-380 nm and the maximum absorbance for the MC form is typically between 500-600 nm.<sup>[191,209]</sup> Due to the presence of TBDS in the pores, the pores have a hydrophobic environment and the SP form of the spiropyran molecules in the CNMO films are more stable under ambient conditions. When observing the **SP-Et-CNMO** films by CD, no induced chirality was observed for the spiropyran component (Figure 3-1a). This is consistent with previous observations made in Chapter 2 for the aromatic-bridged CNMO films and from the MacLachlan Group for conducting polymers,<sup>[210]</sup> molecules,<sup>[118]</sup> and other species<sup>[211]</sup> inside CNMS or CNMO, where no induced CD signal for the guest molecules is observed.



**Figure 3-1.** (a) UV-Vis (top), CD (bottom) and (b) TGA of the **Et-CNMO** (black), **TBDS-Et-CNMO** (blue), **TBDS/ATMS-Et-CNMO** (green) and **SP-Et-CNMO** (red) films. IR spectra (c) full trace and (d) zoomed-in region with arrows indicating the amide and aryl nitro vibrations for films as labeled.

Post-synthetic modification of the CNMO films was monitored by TGA (Figure 3-1b). To ensure that weight losses between the samples were comparable, the films were degassed at 110 °C overnight prior to analysis and the spectra were normalized to the weight at 150 °C to account for the different losses of water in the films. As seen in Figure 3-1b and described in Chapter 2, the **Et-CNMO** films display a typical weight loss of around 15% and the organic bridging group embedded into the chiral nematic mesoporous organosilica framework is stable to over 300 °C. The overall weight loss of the films increases with each progressive step in the modification procedure. The **SP-Et-CNMO** modified films show an overall weight loss of 30% and the organic components of the hybrid material are stable until 250 °C. The earlier decomposition of the organic groups within the **SP-Et-CNMO** films and the increase in overall weight loss is due to the incorporation of ATMS, TBDS, and spiropyran into the films. A comparison between the **TBDS/ATMS-Et-CNMO** films and **SP-Et-CNMO** films shows ~1 wt.% of compound **1** (0.03 mmol/g) was present in the **SP-Et-CNMO** material. Additionally, although the **SP-Et-CNMO** films are functionalized with TBDS to create a hydrophobic environment within the pore network, the films still contained about 2% water (full trace for **SP-Et-CNMO** films can be seen in Appendix B, Figure B-1).

IR spectra of the **SP-Et-CNMO**, the photo-switched **SP-Et-CNMO** (denoted **MC-Et-CNMO**), **TBDS/ATMS-Et-CNMO**, and **Et-CNMO** films were compared. As seen in Figure 3-1c, all four spectra show absorption peaks characteristic of organosilica materials with bands at 1020 cm<sup>-1</sup> (Si-O bonds), as well as broad peaks at 1640 cm<sup>-1</sup> and 3600 cm<sup>-1</sup> (O-H stretch).<sup>[212]</sup> Additionally, CH<sub>2</sub> vibrations of the ethylene bridging spacer were observed at 2950-2850 cm<sup>-1</sup>, 1410 cm<sup>-1</sup> and 1270 cm<sup>-1</sup>. Since these organosilica films have strong FTIR absorbance related to the silica support, it is often difficult to observe IR signatures of grafted functional groups. However, the introduction of the TBDS, ATMS and spiropyran can be observed by an increase in intensity for the C-H stretching vibrations at 2950-2850 cm<sup>-1</sup> and new peaks at 3000-3050 cm<sup>-1</sup> that are assigned to the aromatic C-H bonds. As noted by the arrows in Figure 3-1d, the appearance of a small absorption band at 1625 cm<sup>-1</sup> in the IR spectrum of the **SP-Et-CNMO** films corresponds to the presence of an amide functional group indicating that EDC coupling between the amine on the **TBDS/ATMS-Et-CNMO** and the carboxylic acid of the spiropyran molecule occurred. Additionally, the appearance of new peaks at 1515 cm<sup>-1</sup> and 1340

cm<sup>-1</sup> in both the **SP-Et-CNMO** and **MC-Et-CNMO** films corresponds to stretching vibrations of the aryl nitro functional group and provides further evidence that spiropyran has been incorporated in the mesoporous organosilica films to produce hybrid organic-inorganic materials. The **SP-Et-CNMO** films were also analyzed by <sup>13</sup>C CP/MAS NMR (Figure B-2, Appendix B). The <sup>13</sup>C NMR spectrum shows a large peak at 4 ppm that corresponds to the carbons in the ethylene bridging group. Additional peaks are observed at 43, 22, and 10 ppm corresponding to the addition of ATMS and 26 ppm corresponding to the t-butyl group of TBDS.<sup>[213,214]</sup> However, the large percentage of the ethylene bridge carbons in comparison to the spiropyran carbons and a broad bump from 100-200 ppm due to background from the rotor makes it difficult to assign peaks associated with spiropyran. A small peak is observed at 165 ppm that suggests the presence of the amide linkage resulting from the immobilization of spiropyran onto the films.

The hierarchical nanostructure of the mesoporous organosilica materials was imaged by SEM (Figure 3-2c, d). At fractures in the **Et-CNMO** films, a long-range periodic LH chiral nanostructure was observed throughout the thickness of the films imparted by the CNC template. No disruption of the nanostructure was observed after post-synthetic modification and **SP-Et-CNMO** films show the same long-range chiral structure. However, a few clusters of condensed silanes are observable on the surface of the **SP-Et-CNMO** films after grafting. These clusters can occur when silane precursors condense in solution with themselves and are deposited on the silica surface.<sup>[215]</sup> The pore size distribution and surface area of representative samples of the functionalized **TBDS/ATMS-Et-CNMO** films were probed by nitrogen adsorption-desorption isotherms and compared to the **Et-CNMO** (Figure 3-2a,b). **TBDS/ATMS-Et-CMNO** films had a BET surface area of 370 m<sup>2</sup>/g and a BJH pore diameter of ~6-7 nm whereas **Et-CNMO** films had a BET surface area of 490 m<sup>2</sup>/g and a BJH pore diameter of ~7-8 nm. Grafting of ATMS and

TBDS resulted in a decrease in both the surface area and pore size of the CNMO films indicating that these silanes are being incorporated into the porous network. However, some of this reduction may be due to blockage of the pores by aggregated ATMS and TBDS. Overall, the IR spectra, UV-Vis spectra, SEM images and N<sub>2</sub> isotherms illustrate that we were able to successful functionalize CNMO with spiropyran molecules and retain the morphology and porosity of the organosilica films.



**Figure 3-2.** (a) Nitrogen adsorption-desorption isotherms and (b) BJH pore diameters as labeled. SEM images of (c) **Et-CNMO** (scale bar = 1  $\mu$ m) and (d) **SP-Et-CNMO** (scale bar = 1  $\mu$ m) reveal the well-ordered chiral nematic structure.

#### 3.3.3 Photochromic properties of SP-Et-CNMO films

UV-Vis spectroscopy was used to analyze the photochromic properties of compound 1 embedded in the CNMO films. The SP-Et-CNMO films under ambient light are composed mainly of the colourless SP form. Fast colour transitions were observed when the films were irradiated for different lengths of time using an 8 W 365 nm Hitachi black light. As seen in Figure 3-3a, the absorbance maximum of the MC form in the solid-state SP-Et-CNMO films is 548 nm. A rapid increase in the UV-Vis signal at this wavelength was observed for the first minute after exposure to UV-light corresponding to the transformation of the SP form into the ring open MC form. The maximum conversion of SP to MC is reached after ~18 min of irradiation forming free-standing films with an intense purple colour. Decolourization or thermal fading of the MC absorbance is caused by closure of the pyran ring. A slow conversion from MC back to the SP form for the SP-**Et-CNMO** films occurs in the dark over a period of 150 minutes (Figure 3-3b). This thermal bleaching is well fitted to an exponential decay curve similar to previously reported spiropyranfunctionalized mesoporous silica hybrid materials (Figure 3-3c).<sup>[199,201]</sup> When embedded into the inorganic CNMO support, the local hydrophobic environment of the films and lower surface density of spiropyran favours a fast, reversible photochromic response in the immobilized spiropyran molecules.<sup>[201]</sup>

Irradiation of the CNMO films with UV light results in a photostationary state that contains both open MC and closed SP forms. In previous spiropyran/silica materials, reports have indicated that only ~10% of the molecules are activated by UV light.<sup>[208]</sup> Therefore, the concentration of the MC form in the CNMO films after irradiation with UV light was estimated using a modified Beer-Lambert law formula (A = 1000ɛct), where t is the film thickness (cm).<sup>[216,217]</sup> The difference in absorption between the films before and after irradiation was approximately 0.4 at 548 nm (Figure

3-3c). The molar absorptivity of compound **1** in ethanol after a 7 min irradiation with UV light was determined to be  $\varepsilon_{548} \sim 7000 \text{ M}^{-1} \text{ cm}^{-1}$  and was used as  $\varepsilon$  for this estimation, although, the solid state molar absorptivity would give a more accurate calculation. Overall, it was determined that the CNMO films with ~400 m<sup>2</sup>/g of surface area contain approximately 1-20 µmol/cm<sup>3</sup> of open MC form after irradiation with UV light.



**Figure 3-3.** (a) UV-Vis spectrum of **SP-Et-CNMO** films showing the transmission at 548 nm after photo-irradiation at 365 nm for different lengths of time. Insert: Full scan after 0, 1, 2, 7, and 15 mins of irradiation. (b) UV-Vis spectrum showing the relaxation of irradiated **MC-Et-CNMO** films (irradiated with 365 mn light for 18 mins) to **SP-Et-CNMO** in ambient light over 150 mins. (c) Variation of the absorbance at 548 nm as a function of time for the conversion of MC to SP and exponential decay fit.

# **3.3.4** Investigating the coating of spiropyran into the interconnected pore network of the CNMO films

One concern when post-functionalizing silica material is that the desired functional groups will only coat the outer surface of the material and will not fully integrate into the porous structure. In order to investigate whether the spiropyran had been integrated into the interconnected porous network of the CNMO films, the absorption of **SP-Et-CNMO** films upon irradiation with UV-light was compared to that of spiropyran bound to non-porous ethylene-bridged organosilica films (**SP-Et-films**).

To create the **SP-Et-films**, non-porous freestanding ethylene-bridged organosilica films (**Et-films**) were synthesized in similar conditions to the **Et-CNMO** films but without the addition of a LC template material. In short, BTMSE was mixed into an acidified mixture of ethanol and water, allowed to condense in solution and dried in Petri dishes to produce organosilica films. The non-porous ethylene films were then post-functionalized with **TBDS**, **ATMS**, and compound **1** using the same conditions as the **Et-CNMO** films to form non-porous **SP-Et-films**. Similar to the **SP-Et-CNMO** films, the **SP-Et-films** in ambient light displayed mainly the colourless SP form. Films were irradiated using an 8 W 365 nm light, resulting in a rapid increase in the UV-Vis signal at 548 nm corresponding to the presence of the MC form. **SP-Et films** were irradiated for 7 minutes and compared to the **SP-Et-CNMO** films irradiated for the same amount of time.

As seen in Figure 3-4, the **SP-Et-CNMO** films showed significantly more absorption from the MC molecules (~20-30x) after irradiation with UV-light than the **SP-Et-films**. Spiropyranfunctionalized glass substrates<sup>[196]</sup> or the free-standing nonporous **SP-Et-films**, which can only support monolayer functionalization, results in low absorption from the spiropyran or merocyanine moieties. However, the highly porous and interconnected nanostructure of the CNMO films allows for the incorporation of spiropyran molecules throughout the porous network resulting in a higher absorption signal compared to the non-porous **SP-Et-films**. This increased absorption signal is necessary for using CNMO as hybrid materials for applications, such as sensing and photopatterning.



**Figure 3-4.** UV-Vis characterization of the mesoporous **SP-Et-CNMO** films before (black trace) and after irradiation of the films with an 8 W 365 nm light for 7 min (red trace) and the non-porous **SP-Et-films** before (green trace) and after irradiation of the films with an 8 W 365 nm light for 7 min (blue trace).

# 3.3.5 Post-synthetic functionalization of spiropyran onto the surface of CNMO analyzed

## for chemisorption versus physisorption.

Two control experiments were performed to investigate the binding of compound **1** onto the surface of the CNMO films and determine whether the spiropyran was chemically bound or physically adsorbed onto the silica. As both the amino-functionalized silane and the EDC coupling agent are needed to form a chemical bond between the surface of the films and the spiropyran, we explored the effect of omitting either of these during the incorporation of spiropyran into CNMO films. The two experiments are described in detail in the following subsections.

#### **3.3.5.1** Removing ATMS from the synthesis of SP-Et-CNMO films

In the first set of control experiments, CNMO films that did not contain aminopropyltrimethoxysilane were exposed to a solution containing compound **1** and EDC. Without the amine sites functionalized onto the films, compound **1** should be unable to chemically attach to the silica surface and any spiropyran left in the films would be a result of physical adsorption of the molecules into the pores. Following the same procedure used to synthesize the **SP-Et-CNMO** films; **Et-CNMO** films and **TBDS-Et-CNMO** films were placed into solutions containing ethanol, EDC, and compound **1** at room temperature in the dark. After 24 h, the films were removed from the solution and washed thoroughly in ethanol overnight. As the MC form on the silica films have a distinct absorption maximum that could be easily observed, UV-Vis spectroscopy can be used to investigate the concentration of compound **1** in the films.

As seen in Figure 3-5, UV-Vis spectra of both the **Et-CNMO** films and **TBDS-Et-CNMO** films that were exposed to compound **1** and EDC show no absorption of MC ( $\lambda_{max} = 548$  nm) after irradiation of the films with 365 nm light for 7 mins. This indicates that unreacted spiropyran was successfully removed from the CNMO films following the ethanol wash. Additionally, this data implies that ATMS is essential component to incorporate compound **1** into the films. The reflectance peaks seen at 425 nm and 555 nm, for the **Et-CNMO** and **TBDS-Et-CNMO** films respectively, are a result of the chiral nematic reflection.



**Figure 3-5.** UV-Vis spectra of the (a) **Et-CNMO** films and (b) **TBDS-Et-CNMO** films after exposure to a spiropyran/EDC solution overnight. Spectra were taken before (black traces) and after irradiation of the films with an 8 W 365 nm light for 7 min (red traces).

# 3.3.5.2 Removing EDC from the synthesis of SP-Et-CNMO films

In the second set of control experiments, films grafted with both TBDS and ATMS were placed into a solution of compound 1 using the same procedure used to synthesize **SP-Et-CNMO** but the amide coupling reagent, EDC, was not added to the reaction. As seen in Figure 3-6a, the UV-Vis spectrum of the **TBDS/ATMS-Et-CNMO** films after irradiation of the films shows an absorption signal at 548 nm. This indicates the presence of physically adsorbed compound 1 onto the surface of the amino-functionalized films that remains even after washing with ethanol. Previous work on aminopropyl-functionalized silica materials has shown that the amine group can be used to chemically attach desired functionality on the surface of silica but it can also interact ionically or through intermolecular interactions. These intermolecular interactions between the amine site on silica and a host molecule have been observed for metals, fluorescent dyes, polysaccharides, and even DNA stands.<sup>[215,218,219]</sup> Since physical adsorption of spiropyran was only seen after grafting ATMS onto the films, we hypothesized that ionic or hydrogen bonding interactions were occurring between the carboxylic acid on the spiropyran and the amine on silica surface.

In order to remove this unreacted spiropyran from the surface of the films, **TBDS/ATMS-Et-CNMO** films containing physically adsorbed spiropyran were washed with sodium hydroxide followed by several washes with distilled water until the washing has a neutral pH. UV-Vis spectra of **TBDS/ATMS-Et-CNMO** films after the base wash show no absorption signal at 548 nm upon irradiation, demonstrating that any spiropyran that had been adsorbed to the surface of the films was removed.

Finally, a sample of the **SP-Et-CNMO** films (synthesized using the coupling agent) was washed with sodium hydroxide using the same conditions as previously mentioned in order to remove any spiropyran that was not chemically bound to the organosilica films. As seen in Figure 3-6b, an absorption signal for MC is observed for an irradiated sample of **SP-Et-CNMO** films after washing the sample with base (blue and green traces). We postulate that the retention of this signal after washing the films with base is likely due to the MC form of compound **1** that is chemically bonded (through an amide linkage) to the surface of the CNMO films. However, a decrease in the MC absorbance is observed after this base wash resulting from the removal of unbound spiropyran. Overall, we conclude that about half of the spiropyran molecules are chemically bonding to the surface of the films and about half are immobilized through ionic or hydrogen bonding interactions.



**Figure 3-6.** (a) UV-Vis characterization of **TBDS/ATMS-Et-CMNO** films reacted with a solution of **1** without EDC. The black trace displays the non-irradiated films and red trace displays irradiated films prior to base wash whereas the blue trace is non-irradiated films and green trace is irradiated films after a sodium hydroxide wash. (b) UV-Vis characterization of **SP-Et-CNMO** films before (black trace is non-irradiated films and red trace is irradiated films) and after a sodium hydroxide wash (b) UV-Vis characterization of **SP-Et-CNMO** films before (black trace is non-irradiated films and red trace is irradiated films).

#### 3.3.6 Photopatterning of SP-Et-CNMO films

The free-standing nature of the CNMO films allows the photochromic properties of the CNMO/spiropyran hybrid materials to be controlled using a photomask during UV irradiation. The fine features of a photomask can be transferred to the organosilica materials and retained after the mask has been removed. Photopatterned **SP-Et-CNMO** films were created by placing a cellulose acetate film containing the characters "UBC" printed in black ink on top of a **SP-Et-CNMO** film. The films were irradiated with ultraviolet light (365 nm) for 2 min (Figure 3-7). When the photomask was removed, only sections of the films exposed to the UV light were converted from the SP to the purple MC form and the characters are visible on the surface of the film. The photopattern was successfully erased by exposing the purple film to white LED light for 10 min or allowing the films to thermally bleach over time, regenerating the colourless film. The interconnected pore structure within the CNMO films allows a consistent coverage of porous

network with the immobilized spiropyran molecules creating films that can be using for photopatterning.



**Figure 3-7.** Photographs of the writable/erasable nature of the freestanding mesoporous organosilica films through UV irradiation and exposure to white LED light.

As illustrated in Figure 3-8, the photoisomerization of the films is reversible, switching from the SP form to the MC form by irradiating with UV (365 nm, 8 W, 10 mins) then reverting to the SP form using white LED light (10 mins). However, fatigue of photochromic molecules is often observed and caused by photodegradation of the dyes under UV-irradiation.<sup>[220]</sup> In the CNMO/spiropyran hybrid materials, some photodegradation of the spiropyran molecules is observed after repeated cycles. This photodegradation was similar to other reported silica/spiropyran materials.<sup>[196]</sup> In the future, the amount of photodegradation of the photochromic CNMO films could be reduced by using less intense UV and white lights, or by filtering the white light to only excite the MC form at the  $\lambda_{max}$ .



**Figure 3-8.** Repeated cycling for the photoisomerization of spiropyran-immobilized on CNMO films monitored by absorbance of the MC form at 548 nm.

# 3.3.7 Application of SP-Et-CNMO as a reversible metal sensor

Reversible sensors that can switch between passive and active states can offer advantages over typically organic indicator dyes immobilized onto support materials, which have limitations such as non-reversible binding, leaching of dyes, and blockage of the binding sites over time.<sup>[221]</sup> Spiropyran-functionalized composite materials are of interest for metal detection and purification as a reversible metal ion-binding site is formed in opened MC form through the negatively charged oxygen species.<sup>[193,194,222]</sup> The large absorption band and high surface area of the freestanding **SP-Et-CNMO** films allow for detection of metals that can create a visible colour changes upon binding to spiropyran in the films.

Four divalent metal ions (Zn(II), Sn(II), Ni(II), Cu(II)) were examined to test the application of **SP-Et-CNMO** films as reversible metal sensors. These metal ions were chosen as they have been previously shown to cause a characteristic blue shift in the  $\lambda_{max}$  of the MC absorbance in SP polymeric systems that was dependent on the metal introduced to the system as well as the host material.<sup>[222,223]</sup> **MC-Et-CNMO** films were exposed to 2 mM ethanol solutions

containing one of the metal ions, dried and their colourimetric responses were observed by UV-Vis. As seen in Figure 3-9a and b, complexation with the different metal ions causes the MC absorbance signal to decrease accompanied by a blue shift in the maximum absorption wavelength. Blue shifts of the MC-M<sup>2+</sup> complexes range from ~5 nm for the Ni<sup>2+</sup> and Cu<sup>2+</sup> ions, ~30 nm for the Zn<sup>2+</sup> ion and ~90 nm for the Sn<sup>2+</sup> ion. For the larger blue shifts, a noticeable change in appearance of the CNMO films is observed with the films complexed with Zn<sup>2+</sup> appearing an pinkorange colour and the films complexed with Sn<sup>2+</sup> appearing a slightly yellow-orange colour similar to the non-irradiated **SP-Et-CNMO** films (Figure 3-9c). No significant changes in the wavelength of light reflected from the films due to the chiral structure observed after complexation with metal ions. This indicates that the metals had a negligible influence on the refractive index of the CNMO film.

The metal ions were dissociated from the MC molecules by exposing the films to white LED light while were they were immersed in an ethanol solution, thus transforming the films back to their ring-closed inactive SP form. As seen by the blue dotted line in Figure 3-9a, the films could be irradiated again with UV light to form the ring-opened MC form free of the metal ions. The reversible binding of metal ions resulted in visible colour changes, making these chiral nematic mesoporous organosilica films good candidates for use as metal sensors.



**Figure 3-9.** UV-Vis spectra demonstrating the reversible binding of M<sup>2+</sup> in the **SP-Et-CNMO** films. (a) Irradiated **MC-Et-CNMO** films (blue line) bind Zn(II) (pink line). The metal is completely removed using white light and ethanol to return the original MC absorbance (dotted line). (b) Blue shifts of MC absorbance for Sn(II), Ni(II) and Cu(II) in the **MC-Et CNMO** films. (c) Photograph of free standing CMNO films with observable colour changes upon complexation of metal ions.

# 3.4 Conclusions

In this Chapter, I have demonstrated that chiral nematic mesoporous organosilica (CNMO) films can be functionalized with TBDS, ATMS, and spiropyran to create free-standing photochromic films that can be used for reversible photopatterning. The unique interconnected pore structure of the films imparted by the CNC template facilitates functionalization of the material. As a result, the materials show an intense absorption by UV-Vis spectroscopy from the 130

tethered spiropyran molecules and rapid colour changes when irradiated with UV or white light. The hydrophobic environment of the pores is essential for the photochromic properties observed in these mesoporous organosilica films. The spiropyran-bound CNMO films behave as reversible sensors of divalent metals where binding of the metals to the spiropyran molecules results in visible colour changes. Treatment of these films with ethanol and white light can remove the metals, regenerating the metal-free film. This proof-of-concept demonstrates that small molecules or ions can diffuse through the porous network of the CNMO films and interact with the surface functionality of the silica matrix. Therefore, chiral nematic mesoporous (organo)silica films have potential to be used as mesoporous solid supports and could have applications for the development of new photochromic displays, security features materials or as sensors.

# Chapter 4: Ethene and Sulfur Functionalized CNMO Films and their Applications as Heterogeneous Catalysts

# 4.1 Introduction

The incorporation of functional groups into the framework of periodic mesoporous organosilica (PMO) materials is essential to create novel materials that can be tailored for specific applications. Although functionality is typically introduced through either the condensation of bridged organosilanes [(R'O)<sub>3</sub>Si-R-Si(OR')<sub>3</sub>] or the post-synthetic modification of the PMO surface, direct modification to the organic bridging group that is embedded within the silica network is also possible. To date, many functional organic moieties, such as chiral groups, metal binding ligands, and nitrogen- or sulfur- containing bridges, have been incorporated into PMOs using these modification procedures.<sup>[136]</sup> Of these organic groups, sulfur-containing PMOs have been extensively studied for applications in metal binding and catalysis.<sup>[136]</sup> The introduction of thiol groups to the PMOs provides a handle through which the material can be modified further. For example, the thiol groups can be oxidized to form sulfonic acids creating acidic sites that are distributed within the porous networks of the PMO materials.<sup>[224,225]</sup> Unsaturated hydrocarbon bridging groups, such as an ethenylene-bridge or phenylene-bridge, have also been used to produce unique, functionalized PMOs.<sup>[24,68,168,226]</sup> These unsaturated functionalities have been used to modify the backbone of the organosilica network within the PMOs and can undergo chemical modification through reactions including sulfonation, bromination, thiol-ene reactions, ozonolysis, or Diels-Alder reactions.<sup>[24,68,227-229]</sup>

Functionalized PMOs have found uses in many fields, but one of their main applications is as catalytic supports. PMOs have high surface areas, tunable pore diameters and readilymodifiable surfaces, coupled with a high chemical and thermal stability, making them ideal supports for heterogeneous catalysts.<sup>[61,62]</sup> Two types of catalysts that are commonly incorporated into PMOs are Bronsted acids (i.e. sulfonic groups) and metal complexes with unique organic ligands (i.e. salens or salphens, which are chelating ligands consisting of phenol and aryl-imine groups).<sup>[136]</sup> Sulfonic acid groups can be used for a range of acid-catalyzed reactions including acetylation, esterification and hydrolysis.<sup>[224,225,230–232]</sup> Metal complexes containing salen or salphen ligands are a versatile family of Schiff-base metallic complexes that are used for oxidative reactions such as epoxidations.<sup>[233,234]</sup> Heterogeneous catalytic materials synthesized from PMOs not only offer advantages in terms of catalyst recovery, but the catalytic performance can be enhanced by tailoring the surface properties (hydrophobicity/hydrophilicity), the mesostructure and the organic bridge of the PMO.<sup>[224,230]</sup>

The discovery of chiral nematic mesoporous organosilica (CNMO), synthesized by the condensation of bridging organosilica precursors with cellulose nanocrystals (CNCs), introduced a new family of mesoporous organosilica materials with a unique three-dimensional chiral nematic pore structure.<sup>[116]</sup> The unusual pore structure of the CNMO film could lead to interesting properties and applications that may vary from current PMO materials. In this Chapter, I explore the extension of the synthesis of CNMO films to ethylene-bridging, thioether-bridging, and thiol-containing precursors by both co-condensation and direct modification of the organic bridging group. Additionally, I investigate the incorporation of Mn-salphen complexes into functionalized CNMO films to produce heterogeneous catalysts where the catalyst is integrated into the chiral porous networks of the CNMO films.

# 4.2 Experimental

#### 4.2.1 Materials

All solvents and reagents including 1,2-bis(trimethoxysilyl)ethane (BTMSE), triethoxyvinylsilane, trimethoxyvinylsilane, Grubb's generation 1 catalyst, 2,2-dimethoxy-2-phenylacetophenone (DMPA), azobisisobutyronitrile (AIBN), thioacetic acid, and (3-mercaptopropyl)trimethoxysilane were purchased from Sigma Aldrich and used without further purification.

For the heterogeneous catalysis, meta-chloroperoxybenzoic acid (*m*-CPBA), N-methylmorpholine-N-oxide (NMO), sodium hypochlorite, and pyridine-N-oxide (PyNO) were purchased from Sigma Aldrich and used without further purification. The MnCl(Salphen) catalyst was provided by Dr. Asamanjoy Bhunia at the University of Ghent, Belgium and synthesized according to literature (See Appendix C).

# 4.2.2 Characterization

N<sub>2</sub> adsorption studies were performed using a Micromeritics ASAP 2020 at 77 K. All samples were degassed under vacuum at 120-150 °C immediately prior to analysis. The specific surface of the samples areas studied were calculated using the standard Brunauer-Emmett-Teller (BET) method with relative pressures from 0.04 to 0.2. Total pore volumes were estimated from the amount of N<sub>2</sub> adsorbed at a relative pressure of 0.99. Barrett-Joyner-Halenda (BJH) pore size distributions were calculated from the adsorption branch of the isotherms. Thermogravimetric analysis (TGA) was performed on a PerkinElmer Pyris 6 thermogravimetric analyzer and samples were heated under air from 40 °C to 800 °C at 10 °C /min. Infrared (IR) spectra were obtained with a Nicolet 6700 FTIR spectrometer equipped with a Smart 134

Orbit diamond attenuated total reflectance (ATR). Solid-state nuclear magnetic resonance (NMR) spectra were collected on a 400 MHz Varian Unity Inova equipped with a Varian/Chemagnetics 4 mm T3 MAS probe. <sup>13</sup>C cross-polarization/magic angle spin (CP/MAS) experiments (100 MHz, 3000-7000 scans) used glycine as a reference. Samples were spun at a rate of 5 or 7 kHz. A contact time of 1.5 ms and recycle delay of 2 s was applied. Elemental analysis (EA) was carried out by UBC Microanalytical Services. Solution NMR spectroscopy was performed on a Bruker 400 MHz spectrometer. X-ray fluorescence spectrometry (XRF) measurements were performed by using a Rigaku NexCG, Energy Dispersive XRF instrument. An ultra-fast gas chromatography (GC) with flame ionization detection (FID) and a 5% diphenyl/95% polydimethylsiloxane column (10 m x 0.10 mm ID) was employed to calculate the conversion of the reaction. X-ray photoelectron spectroscopy (XPS) was performed on a Leybold MAX200 spectrometer using an aluminum Ka X-ray source (Al K $\alpha$  = 1486.6 eV) and operating at a base pressure of 1 × 10<sup>-9</sup> Torr. The highresolution scan was acquired with a pass energy of 48 eV. XPS data were fit with a mixed Gaussian Lorentzian shape using Origin analysis software and Shirley functions were used to remove the background prior to curve fitting. Scanning electron microscopy (SEM) images were collected on a Hitachi S4700 electron microscope. Samples were prepared by breaking the films into small pieces and attaching them to aluminum stubs using double-sided adhesive tape. Samples were sputter-coated with 5 nm of platinum/palladium (80/20) or gold.

Ultraviolet-visible/near-IR (UV-vis/NIR) spectroscopy was conducted on a Cary 5000 UV-Vis/NIR spectrophotometer and circular dichroism (CD) spectroscopy was performed using a JASCO J-815 spectropolarimeter. Spectra were collected by mounting free-standing films in a solid-state holder so that the surfaces of the films were perpendicular to the beam path.

# 4.2.3 Silane precursor synthesis

**1,2-(***E***)-Bis(triethoxysilyl)ethylene (BTESEthylene).** 1,2-(*E*)-Bis(triethoxysilyl)ethylene was synthesized according to literature.<sup>[235]</sup> In short, triethoxyvinylsilane (43 mL, 0.210 mol) was mixed with Grubb's generation 1 catalyst (54 mg, 0.061 mmol) under an inert atmosphere and stirred at 22 °C  $\pm$  3 for 1 h. The mixture was heated to 160 °C, allowed to stir for an additional 3 h then cooled to 90 °C. The silane was purified by two sequential distillations under vacuum at two different temperatures. Distillation at 90 °C removed unreacted triethoxyvinylsilane starting material, then distillation at 160 °C yielded pure 1,2-(*E*)-bis(triethoxysilyl)ethylene as a clear liquid (19.9 mL, 0.054 mol, 88%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.19-1.25 (m, 18H), 3.80-3.90 (m, 12H), 6.67 (s, 2H) ppm. NMR data were consistent with those previously reported.<sup>[235]</sup>

1-(Acetylthio)-1,2-bis(triethoxysilyl)ethane (2) and 1-thio-1,2-bis(triethoxysilyl)ethane (3). Precursors 2 and 3 were synthesized according to literature.<sup>[236]</sup> The photoinitiator DMPA (20 mg, 0.078 mmol) was added to a solution of BTESEthylene (1.0 mL, 2.7 mmol) and thioacetic acid (0.25 mL, 3.5 mmol, 1.3 eq) then sonicated until the DMPA dissolved. N<sub>2</sub> was bubbled through the mixture for 10 min to displace oxygen. The mixture was placed in a Metalight Classic UV irradiation chamber fitted with twelve 360 nm UV-lamps and was irradiated for 2 h forming compound 2. Compound 2 was used without further purification for the synthesis of compound 3. A solution containing 2 was placed in an ice bath and excess propylamine (~2 mL, 0.02 mol) was slowly added. The unreacted propylamine and propylacetamide were removed by rotary evaporation and flash chromatography yielding 3 as a clear liquid and ~5% impurity of N-propylacetamide. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.96 (dd, 1H), 1.20-1.30 (m, 18H), 1.36 (dd, 1H), 136 2.02 (d, 1H), 2.23-2.31 (m, 1H), 3.83-3.95 (m, 12H) ppm. NMR data were consistent with those previously reported.<sup>[236]</sup>

## 3,3,10,10-Tetramethoxy-2,11-dioxa-6-thia-3,10-disiladodecane (4)

Compound **4** was synthesized based on a modified procedure of **3** and previously reported literature.<sup>[237]</sup> The photoinitiator DMPA (15 mg, 0.059 mmol) was added to a solution of trimethoxyvinylsilane (1.0 mL, 6.5 mmol) and (3-mercaptopropyl)trimethoxysilane (1.2 mL, 6.5 mmol). N<sub>2</sub> was bubbled through the mixture for 2-3 min to displace oxygen. The mixture was placed in a Metalight Classic UV irradiation chamber fitted with twelve 360 nm UV-lamps and was irradiated for 2 h. Distillation at 90 °C under vacuum removed unreacted trimethoxyvinylsilane starting material yielding >95% pure **4** as a clear liquid (2.1 g, 6.1 mmol, 95%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.50-0.63 (m, 2H), 0.95-1.15 (m, 2H), 1.68-1.77 (br. m, 2H), 2.53-2.62 (t, 2H), 2.63-2.68 (m, 2H), 3.50-3.70 (m, 18H) ppm. NMR data were consistent with those previously reported.<sup>[237]</sup>

#### 3,3,9,9-Tetramethoxy-2,10-dioxa-6-thia-3,9-disilaundecane (5)

Compound **5** was synthesized based on a modified procedure of **3**. The photoinitiator DMPA (80 mg, 0.312 mmol) was added to a solution of trimethoxyvinylsilane (4.0 ml, 0.026 mol) and sonicated for 10 min under an inert atmosphere. Thioacetic acid (1.9 ml, 0.026 mol) was added and the mixture was degassed by bubbling N<sub>2</sub> through the solution for 10 min to displace oxygen. The mixture was placed in a Metalight Classic UV irradiation chamber fitted with twelve 360 nm UV-lamps and was irradiated for 2.5 h. The solution was placed in an ice bath and excess propylamine (~4 mL, 0.04 mol) was slowly added and allowed to react for 2 h. The unreacted

propylamine was removed by rotary evaporator. A degassed solution of DMPA (80 mg, 0.312 mmol) and trimethoxyvinylsilane (4.0 ml, 0.026 mol) was added to the reaction mixture and placed back in the UV irradiation chamber for 3.5 h. Distillation at 110 °C removed unreacted reagents yielding **5** as a dark yellow liquid at 90% purity (1.4 g, 4.3 mmol, 16%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.88-1.03 (m, 4H), 2.71-2.86 (m, 4H), 3.50-3.70 (m, 18H) ppm.

## 4.2.4 Synthesis of CNMO films

All films were synthesized using the modified procedure described in Chapter 2. Ethanol was added to the aqueous CNC suspension up to a final concentration of 50% v/v ethanol in water. The organosilica precursors (0.57 mmol precursor / 150 mg CNCs) were added dropwise to the CNC suspension (4.1% wt.%, pH of 2.5) and stirred at room temperature ( $22 \pm 3$  °C) until the suspensions appeared homogeneous (typically 4-7 h). The CNC/organosilica precursor mixtures were transferred to polystyrene Petri dishes (5 cm in diameter), ensuring that 175 mg of CNCs was placed in each dish, and left to dry under ambient conditions. The CNCs were removed from the resulting composite material by acid hydrolysis, using 6 M H<sub>2</sub>SO<sub>4</sub> followed by a wash with a solution of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> (1:5).

#### (3-Mercaptopropyl)trimethoxysilane functionalized CNMO films (Mer-CNMO).

Ethylene-bridged CNMO (**Et-CNMO**) films were prepared according to literature and as described in Chapter 2.<sup>[116]</sup> The **Et-CNMO** films (80 mg) were heated under vacuum at 100 °C overnight. Films were placed in a pre-mixed solution of dry toluene (20 mL) and (3-mercaptopropyl)trimethoxysilane (210  $\mu$ L, 1.13 mmol) and stirred at 110 °C for 16 h. After the

reaction, films were filtered, washed with methylene chloride (10 mL  $\times$  3), acetone (10 mL), and methylene chloride (10 mL  $\times$  2) and then dried under vacuum at 100 °C for 3 h.

#### 4.2.5 Post-functionalization of the organic bridge in the CNMO films

# 4.2.5.1 Bromination of Ethene-CNMO

A gravimetric analysis of the bromination of the **Ethene-CNMO** films was prepared according to literature.<sup>[238]</sup> Films were heated to 120 °C under vacuum for 12 h prior to analysis. **Ethene-CNMO** films (28 mg) were placed in a pre-weighed flask under argon. The PMOs were treated with bromine vapor at 35 °C for 3 h. Physisorbed bromine was removed under vacuum at 120 °C for 24 h and the brominated **Ethene-CNMO** films were weighed to calculate the Br content.

#### 4.2.5.2 Thiol-ene reaction of Ethene-CNMO with thioacetic acid

A thiol-ene reaction of **Ethene-CNMO** films was modified from the synthesis of organosilica precursor **3**.<sup>[236]</sup> **Ethene-CNMO** films (30 mg) were heated to 110 °C under vacuum for 2 h prior to the reaction. For the thermal reaction, a solution containing excess thioacetic acid (1.0 mL) and AIBN (0.10 g, 0.61 mmol) in dry THF (5 mL) was freeze-pump-thawed to remove oxygen, added to the degassed films and heated to 60 °C for 12 h. For the UV reaction, a solution containing excess thioacetic acid (1.0 mL), dichloromethane (7 mL), and DMPA (40 mg, 0.16 mmol) was freeze-pump-thawed to remove oxygen, added to the degassed films and placed into the UV reactor containing twelve 360 nm UV-lamps for 2 h. After the reactions, films were washed in acetone (4  $\times$  20 mL).

#### 4.2.5.3 Synthesis of achiral heterogeneous Mn(III) salphen catalyst

SH-CNMO or Mer-CNMO films were dried at 110 °C under vacuum overnight. The films (60 mg) were added to a flask containing the MnCl(salphen) complex (64 mg, 0.1 mmol), chloroform (30 mL), and AIBN (58 mg) that was previously degassed by three freeze-pump-thaw cycles. The mixture was heated to 50 °C for 10 h.<sup>[239]</sup> The brown Mn-films were collected by filtration and washed in chloroform for 6 h (~50 mL  $\times$  2) in an effort to remove physisorbed MnCl(salphen) complex from the pores.

## 4.2.6 Asymmetric epoxidation of dihydronaphthalene

A solution of dichloromethane (4 mL) containing 1,2-dihydronaphthalene (20  $\mu$ L, 0.15 mmol), N-methylmorpholine N-oxide (90 mg, 0.76 mmol), the heterogeneous catalyst (0.006 mmol Mn active sites), and decane (20  $\mu$ L), employed as an internal standard, was mixed. Meta-chloroperoxybenzoic acid (52 mg, 0.3 mmol) was added into the mixture in three equal portions and allowed to react for 45–120 min.<sup>[240]</sup> The films were filtered off and the filtrate was analyzed by GC and HPLC to determine the conversion and selectivity, respectively. The films were washed with dichloromethane (~50 mL), dried at 50 °C overnight under vacuum and reused for the next run with the same conditions.

# 4.3 **Results and Discussion**

# 4.3.1 Ethenylene-bridged CNMO films "Ethene-CNMO" and thiol CNMO films

The most common unsaturated hydrocarbon moiety used to synthesize PMO material is the ethenylene-bridging group. Ethenylene-bridged PMOs, otherwise referred to as "Ethene-PMOs", were first synthesized in 1999.<sup>[24,68]</sup> The incorporation of double bonds as 140 integral parts of the organosilica framework allows for subsequent modification to the organosilica materials. An array of reactions have been performed to modify the double bonds within PMOs including bromination, epoxidation, ozonolysis, Friedel-crafts or Diels-Alder reactions.<sup>[24,68,136,227–229,235]</sup> Given the interest in Ethene-PMO materials, we sought to expand the synthesis of CNMO films to include ethene precursors (BTESEthylene) in an effort to produce ethene organosilicas with a chiral nematic porous network. CNMO materials were synthesized from commercially available bis(triethoxysilyl)ethene that contains 80% of the *trans* isomer and 20% of the *cis* isomer. An ethanol/water (50% v/v) mixture of the CNC suspension (as described in Chapter 2) was used to account for the decreased water solubility of the bis(triethoxysilyl) compound. CNC/organosilica composite materials were synthesized from CNC suspensions (4.1 wt.%, pH = 2.5) using 0.57 mmol of precursor / 150 mg CNCs and denoted **Ethene-Comp**. CNCs were removed from the composite materials through acid hydrolysis by heating the films to 100 °C in 6 M sulfuric acid followed by a rinse with a H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub> solution and denoted **Ethene-CNMO**.

Removal of the CNC template was investigated by solid-state <sup>13</sup>C CP/MAS NMR spectroscopy. The **Ethene-CNMO** spectrum shows one peak at 146 ppm, corresponding to the C=C double bond, and no peaks related to cellulose, 80-120 ppm, confirming the complete removal of the CNC template (Figure 4-1a). A CD spectrum of the **Ethene-CNMO** confirms the presence of a LH chiral nematic nanostructure and shows positive ellipticity at  $\lambda_{max} = 550$  nm due to the selective reflectance of LH circularly polarized light (Figure 4-1b). This well-ordered helical nanostructure can be clearly seen in the SEM images of cross-sections of the **Ethene-CNMO** films that show a characteristic replica of the LC behavior of the CNC template (Figure 4-1c). The high magnification SEM image of the films clearly shows a 180° rotation of the organosilica rods within the materials (Figure 4-1d).



**Figure 4-1.** (a) <sup>13</sup>C CP/MAS solid-state NMR spectrum of **Ethene-CNMO** films after the removal of CNCs where the \* represents spinning side bands. (Note that a first order phase correction was applied to the sample causing the non-linear baseline). (b) CD spectrum of **Ethene-CNMO** films. Edge view SEM images of the **Ethene-CNMO** at (c) low magnification (scale =  $3 \mu m$ ) and (d) high magnification of a one-half rotation of the chiral pitch (scale =  $1 \mu m$ ).

The composite and mesoporous ethenylene-bridged organosilica films were analyzed by TGA and IR spectroscopy to confirm the removal of the CNC template and investigate the thermal stability of the films. Similar to the alkylene-bridged films reported in Chapter 2, samples were degassed prior to analysis. As seen in Figure 4-2a, the composite CNC/organosilica films show a weight loss of ~70 wt.% starting at 200 °C due to the decomposition of both the CNC template and the ethenylene bridging group. After removal of the template, the **Ethene-CNMO** films show a smaller weight loss of ~15 wt.% that resembles the %C and %H determined by elemental analysis 142

(EA) (Table 4-1). IR spectra of the **Ethene-Comp** and **Ethene-CNMO** films were obtained and compared to an IR spectrum of **Et-CNMO** films (Figure 4-2b-c). All spectra show intense peaks at 1020 cm<sup>-1</sup> and 800 cm<sup>-1</sup> (Si-O) and adsorbed water at 1640 cm<sup>-1</sup>. The **Ethene-Comp** shows characteristic peaks for cellulose at 1500 - 1150 cm<sup>-1</sup> (C-O and CH<sub>2</sub>), and 2850 cm<sup>-1</sup> (C-H stretch) (Figure 4-2c). As seen in Figure 4-2d (full scan) and Figure 4-2e (highlighted region), upon removal of CNCs, the **Ethene-CNMO** films display absorption bands at 2980, 1430 and 1300 cm<sup>-1</sup> that can be assigned to C-H vibrations and a small peak at 1580 cm<sup>-1</sup> that can be assigned to the C=C double bond. These peaks are not present in the **Et-CNMO** materials that show CH<sub>2</sub> deformations at 1410 cm<sup>-1</sup> and 1270 cm<sup>-1</sup>.<sup>[24,156,235]</sup> Mesoporosity of the **Ethene-CNMO** sample was determined by N<sub>2</sub> adsorption-desorption isotherms. The films displayed a type IV isotherm with hysteresis indicating mesoporosity and have a surface area of 530 m<sup>2</sup>/g, a pore volume of 1.28 cm<sup>3</sup>/g and an average pore size of 12 nm (Figure 4-2e).



**Figure 4-2.** (a) TGA of **Ethene-Comp** (green) and **Ethene-CNMO** films (black). IR spectrum for the (b) **Ethene-Comp**, (c) **Ethene-CNMO** (black) and **Et-CNMO** (blue). (d) Zoomed-in region of the IR spectra in part (c) with arrows indicating the  $CH_2$  and C=C vibrations of the ethenylene-bridged CNMO. (e) N<sub>2</sub> adsorption-desorption isotherm and BJH pore size distribution (inset) for **Ethene-CNMO**.

The chemical accessibility of the ethenylene-bridging group within the CNMO materials was investigated by bromination. The addition of bromine across C=C double bonds in ethene-PMOs materials has been studied since 1999 and can be performed using either gaseous bromine or bromine dissolved in chlorinated solvents.<sup>[24,68,227,241]</sup> An in-depth analysis and characterization of the bromination process has been described in the literature.<sup>[238]</sup> The accessibility of the surface ethenylene-bridging group in the CNMO films was investigated by means of gravimetric analysis. The Ethene-CNMO films were treated with bromine vapor at 35 °C and allowed to react for 3 h. This reaction time was based on previous research that reported a 95% conversion for the bromination of Ethene-PMOs within the first 2 min when utilizing gaseous bromine and completion of the reaction after ~2 h.<sup>[238,241]</sup> Chemical accessibility of the double bonds within the ethenylene-bridged CNMO films was determined to be 0.9 mmol/g. As suggested by elemental analysis, this corresponds to approximately 15% of the total ethenylene bridging groups that are accessible for modification. Bromination of Ethene-CNMO also resulted in decreased surface area (350 m<sup>2</sup>/g), pore volume (0.88 cm<sup>3</sup>/g) and average pore size (10.5 nm) of the films.

The post-synthetic modification of the **Ethene-CNMO** films using thiol-ene chemistry was also examined as a method for producing sulfur-functionalized CNMO materials. The thiol–ene radical reaction involves the addition of a thiol group across an alkene group with regioselectivity and high yields. Utilizing thiol-ene reactions as a pathway to modify PMOs has recently been investigated as a means to modify the surface of silica for applications in chromatography and catalysis.<sup>[242–244]</sup> We sought to test the modification of CNMO films using thiol-ene chemistry by adding thioacetic acid into the materials and using a radical initiator generated by either UV light or thermal conditions, as seen in Scheme 4-1.



Scheme 4-1. Post-modification of the Ethene-CNMO films with thioacetic acid.

The resulting materials, denoted **Thioester-CNMO**, were analyzed by elemental analysis. Thioester-CNMO films synthesized in thermal conditions and in UV light show similar increases in the amount of sulfur present in the films of ~2 wt.% (Table 4-1). This corresponds to the introduction of approximately 0.5 mmol/g of thioester groups into the Ethene-CNMO materials indicating that not all of the accessible double bonds reacted with the thioacetic acid. Overall, only 65% of the accessible double bonds reacted or ~10% of the total double bonds within the material.

I a	<b>ble 4-1.</b> Elemental analysis o	f Etnene-CN	MO and	I hioester-UNMU
	Sample	%C	%H	% S
	Ethene-CNMO	15.70	2.51	
	Thioester-CNMO (heat)	14.69	2.07	1.96
	Thioester-CNMO (UV)	14.46	2.10	1.76

As the thermal reaction produced films with the largest amount of functionalization of thioester groups, further analysis was only performed on these films. IR spectra of the films taken after the thiol-ene reaction shows new peaks at 2900-2850 cm<sup>-1</sup> (C-H stretch), 1370 cm<sup>-1</sup> (CH<sub>2</sub> bend) and 1710 cm<sup>-1</sup> (C=O) confirming the presence of thioester groups (Figure 4-3a, b). Additionally, a small shoulder at 1270 cm<sup>-1</sup> is observed indicating that the double bond reacted to form a functionalized ethylene-bridging group. The ethenylene C=C double bond absorption band 146

at 1580 cm<sup>-1</sup> is still observed as only ~10% of the double bonds reacted. N<sub>2</sub> isotherms and CD spectroscopy confirmed that the mesoporosity and the chiral nanostructure are retained after modification of the films. The **Thioester-CNMO** materials showed a slight decrease in both the surface area (500 m<sup>2</sup>/g) and pore size (11 nm) when compared to the **Ethene-CNMO** films (Figure 4-3c-d). The CD spectrum displayed an intense positive ellipticity with a  $\lambda_{max}$  = 425 nm consistent with the reflection of LH circularly polarized light (Figure 4-3e). Interestingly, unlike post-synthetic grafting, which typically causes a red-shift in the  $\lambda_{max}$  of the CNMO materials, post-synthetic modification of the organic bridging group caused a blue shift in the  $\lambda_{max}$  of the **Thioester-CNMO** material. This change in  $\lambda_{max}$  may be due to a contraction in the helical pitch of the materials as a result of modifying the backbone of the silica network. Overall, we were able to modify the **Ethene-CNMO** materials using thiol-ene chemistry to produce sulfur-functionalized materials that maintain the porosity and chiral nematic nanostructure of the CNMO films.



**Figure 4-3.** (a) IR spectrum for the **Thioester-CNMO**. (b) Zoomed-in region of the IR spectrum in Part (a) with black arrows indicate the new  $CH_2$  vibrations and a red dashed arrow indicating the C=O peak. (c) N<sub>2</sub> isotherm and (d) BJH pore size distribution for **Thioester-CNMO** (red) compared to the **Ethene-CNMO** (black). (e) CD spectrum for **Thioester-CNMO**.

In order to increase the amount of sulfur functionalization loaded into the mesoporous organosilica materials, thiol-containing CNMO films were directly synthesized through the cocondensation of 1-thio-1,2-bis(triethoxysilyl)ethane (**3**) with bis(trimethoxysilyl)ethane (BTMSE) (Scheme 4-2). Precursor **3** was synthesized by a photoinitiated radical thiol-ene reaction between 1,2-(E)-bis(triethoxysilyl)ethene and thioacetic acid in the presence of DMPA.<sup>[236]</sup>



Scheme 4-2. Synthesis of precursor 3 from 1,2-(*E*)-bis(triethoxysilyl)ethylene

CNMO materials were synthesized from precursor **3** using an ethanol/water (50% v/v) suspension of CNCs suspension using 20-30% **3** diluted with BTMSE and denoted **SH-CNMO**. Originally, the droplets of SH-precursor were difficult to disperse into the CNC suspension and tended to stay clustered together. In order to obtain homogeneous films, **3** needed to be diluted with ethanol (~0.5 mL) prior to the addition of the precursor into the CNC suspension and long stirring times were need for this mixture (4-7 h). Additionally, I attempted to synthesize films from precursor **2** and formed chiral nematic composite materials at 100% loading (see Appendix C, Figure C-1); however, removal of CNC from these films resulted in powders.

Solid-state <sup>13</sup>C CP/MAS NMR spectroscopy, TGA, EA and IR spectroscopy were carried out for the **SH-CNMO** films. The <sup>13</sup>C NMR spectrum of the sample shows no cellulose peaks at 149
60-120 ppm indicating removal of the CNC template (Figure 4-4a). A single peak at 4 ppm and a shoulder around 14-15 ppm are assigned to the ethylene bridging group and the thiol-ethylene bridging group, respectively.<sup>[236]</sup> The small peak at 46 ppm is due to the oxidation of the thiol groups to sulfonic acids as a result of the addition of hydrogen peroxide to the films during CNC removal.<sup>[225,245]</sup> It has previously been shown that in SH-PMO materials synthesized from the same thiol precursor **3**, exposure of the material to a solution of 30 wt.% hydrogen peroxide for 3 h resulted in 66% of the thiol groups being oxidized to sulfonic acid. X-ray photoelectron spectra (XPS) of the **SH-CNMO** films show two peaks around 169 eV and 164 eV indicating the presence of both oxidized sulfur and thiol groups, respectively. During the removal of CNCs from the composite materials, ~60-70% of the thiols are oxidized into sulfonic acid groups (Figure 4-4b). Although other CNC removal methods were attempted (ionic liquids and sodium hydroxide washes), only the acid hydrolysis removal method was able to successfully remove CNCs from the **SH-CNMO** films.



**Figure 4-4.** (a) <sup>13</sup>C CP/MAS solid-state NMR spectrum of **SH-CNMO** films compared to **Et-CNMO** films. (b) XPS of the S 2p for **SH-CNMO** films (experimental data (dotted) and fitted curves (solid)).

The organic content for the **SH-CNMO** films was measured by EA and determined to be ~13% C, ~4% H and ~5% S. TGA analysis of the films show a large mass loss of the **SH-Comp** materials (~70%) consistent with the loss of CNCs and a smaller mass loss of the **SH-CNMO** materials (~15%) consistent with the loss of the organic bridge. (Figure 4-5a). The **SH-CNMO** films display a similar thermal stability as both the **Et-CNMO** and **Ethene-CNMO** materials (~300-350 °C). IR spectra of the **SH-Comp** and **SH-CNMO** materials display peaks associated with Si-O (1020, 800 cm<sup>-1</sup>), O-H (3300 cm<sup>-1</sup>) and CH<sub>2</sub> (2950-2850, 1410-1270 cm<sup>-1</sup>) vibrations (Figure 4-5b, c). However, neither the composite nor the mesoporous materials show S-H stretching signals corresponding to the thiol groups; these peaks are typically very weak in silica materials due to hydrogen bonding to the silica network.<sup>[246]</sup>



Figure 4-5. (a) TGA data of SH-CNMO, (b) IR spectrum of SH-Comp and (c) IR spectrum of SH-CNMO.

Retention of the porosity and chiral nematic nanostructure was confirmed by SEM, CD and N<sub>2</sub> isotherms (Figure 4-6). SEM images of the **SH-CNMO** material display a long-range periodic nanostructure. A CD spectrum of the films shows positive ellipticity at  $\lambda_{max} = 525$  nm due to the selective reflectance of LH circularly polarized light. As determined by N<sub>2</sub> isotherm data, the **SH-CNMO** materials have a surface area of 500 m<sup>2</sup>/g, a pore volume of 1.23 cm<sup>3</sup>/g, and a pore size of 11 nm. Overall, sulfur-functionalized CNMOs could be synthesized using both cocondensation or post-synthetic modification methods. The co-condensation of precursor **3** resulted in bifunctional nanostructured CNMO films that contain both acidic groups (SO<sub>3</sub>H) and thiol groups (SH). These materials could have potential applications as heavy metal absorbents or as solid-catalytic support material for acid-catalyzed reactions.



**Figure 4-6.** Characterization of the **SH-CNMO** films. (a) N<sub>2</sub> isotherm and BJH pore size distribution (inset), (b) CD spectrum, and (c, d) SEM images (scale bar = 5  $\mu$ m and 1  $\mu$ m, respectively).

#### 4.3.2 Thioether-bridged CNMO films

Another interesting class of functional PMOs are materials that contain sulfur bridging groups in the backbone of the silica network. The two most common thioether bridging groups incorporated into PMOs are disulfide and tetrasulfide bridges.<sup>[247,248]</sup> In 2013, Wang *et al.* used thiol-ene chemistry to synthesize a bridging alkoxysilanes, which contained one bridging sulfur atom. This compound was prepared by reacting (3-mercaptopropyl)trimethoxysilane with trimethoxyvinylsilane and was then employed to produce highly porous aerogels.<sup>[237,249]</sup> Similar to the long flexible alkylene precursors reported in Chapter 2, it is often difficult to synthesize PMOs from these thioether functionalities due to their flexibility. Therefore, dilution of these precursors with TEOS or TMOS is required. In this section, I describe the synthesis of sulfur-containing bridging precursors using thiol-ene chemistry, as shown in Scheme 4-3, and then use them to prepare the corresponding composite and mesoporous organosilica films. It is important to note that precursor **4** is >95% pure after synthesis but precursor **5** was only 90% pure, containing trace amounts of both N-propylacetamide and 2-mercaptoethyltrimethoxysilane as detected by NMR. Both precursors were used to produce CNMO materials without further purification.



Scheme 4-3. Synthesis of the thioether precursors 4 and 5 by thiol-ene chemistry.

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CNMO materials were synthesized from precursors **4** and **5** using an ethanol/water (50% v/v) CNC suspension and after formation of the composite films, the CNCs were removed through acid hydrolysis to yield the desired CNMOs. The maximum loading of **4** and **5** into the CNC suspension was examined by UV-Vis spectroscopy, CD spectroscopy and SEM (Figure 4-7). Similar to the hexylene-bridged materials reported in Chapter 2, the composite films synthesized with 100% loading of precursor **4** did not display a reflectance signal; this indicated that the chiral nematic structure of the LC template was disrupted. The loading of **4** was reduced to 60%, 50% and 30% by diluting with BTMSE in an attempt to produce films that maintain the chiral nematic structure of the CNC rods and are denoted **4-(60)-CNMO**, **4-(50)-CNMO**, **4-(30)-CNMO**, respectively. For all 3 precursor loadings, the reflection of light is observed using UV-Vis spectroscopy for both the composite and mesoporous materials (Figure 4-7a), indicating that the chiral nematic structure of the CNC template has been retained.

The composite and mesoporous films of precursor **5** were synthesized at 100% and 60% loading, denoted **5-(100)-CNMO** and **5-(60)-CNMO**, respectively. There materials display signals for reflected light when analyzed by UV-Vis spectroscopy (Figure 4-7b) indicating the retention of the chiral nematic phase of the CNC template. Although no clear trend was observed for changes in  $\lambda_{max}$  between the films prepared from **4** or **5**, generally high thioester precursor loading resulted in lower  $\lambda_{max}$ . SEM images and CD spectra were taken for **4-(60)-CNMO** and **5-(60)-CNMO** as representative samples and show that the films reflect LH circularly polarized light and have a long-range chiral nanostructure throughout the thickness of the films (Figure 4-7). However, the CD spectrum of the **4-(60)-CNMO** films shows a broad reflection peak indicating inconsistencies in the length of the chiral pitch of this sample. This could result from uneven loading of the precursor in the films or alterations to the bridging groups during CNC removal.

Elemental analysis of **4-(60)-CNMO** shows these films contain ~21% C, ~4% H, ~9% S confirming the retention of sulfur after CNC removal. It was found that both precursors **4** and **5** were able to form CNMO materials at higher loadings than the similar length alkylene precursors reported in Chapter 2 (**Hex-CNMO** at 30% loading and **Pent-CNMO** at 30% loading) using ethanol/water CNC suspensions due to an increased compatibility of the precursor with the CNC suspensions.



**Figure 4-7.** UV-Vis spectra of the composite and mesoporous organosilica materials synthesized from (a) **4** as labeled and (b) **5** as labeled. CD spectra of (c) **4-(60)-CNMO** and (d) **5-(60)-CNMO**. (e, f) SEM images of **4-(60)-CNMO** (scale bar = 3  $\mu$ m and 1  $\mu$ m, respectively). (g, h) SEM images of **5-(60)-CNMO** (scale bar = 3  $\mu$ m and 1  $\mu$ m, respectively).

Solid-state <sup>13</sup>C CP/MAS NMR spectroscopy and TGA were performed to investigate the removal of the CNC template and retention of the thioether-bridging group (Figure 4-8). The  $^{13}$ C NMR spectra of the representative samples, 4-(50)-Comp and 5-(60)-Comp, show peaks at 60-120 ppm that are assigned to the CNC template. 5-(60)-Comp shows additional peaks at 25 ppm and 17 ppm assigned to the Si-CH<sub>2</sub>-CH<sub>2</sub>-S-CH<sub>2</sub>-CH<sub>2</sub>-Si carbons and a peak at 4 ppm assigned to the ethylene bridge. 4-(50)-Comp shows peaks from 35-10 ppm assigned to the carbons in precursor 5 as well as a peak at 4 ppm assigned to the ethylene bridge. However, similar to the SH-CNMO films, treatment of the films with hydrogen peroxide during CNC removal causes large peaks at ~51-48 ppm to be observed in both 4-(50)-CNMO and 5-(60)-CNMO samples, indicating the cleavage of the thioether bond and oxidation of the thiol to sulfonic acid groups.<sup>[245,250]</sup> Additionally, peaks between 170-130 ppm are observed in the 4-(50)-Comp potentially due to incomplete removal of the hydrolyzed byproducts of the CNC template or breaking of precursor 4 in the films. TGA analysis of the films show typical losses in mass of ~70% for the composite materials, ~15-40% for the CNMO films with larger mass losses for the films with higher loadings of 4 or 5 and thermal stabilities of 300-400 °C (Appendix Figure C-2).



**Figure 4-8.** <sup>13</sup>C CP/MAS solid-state NMR spectrum of (a) **4-(50)-Comp** (green) and **5-(50)-CNMO** (black) and (b) **5-(60)-Comp** (green) and **5-(60)-CNMO** (black).

Nitrogen adsorption-desorption isotherms of the 4-CNMO and 5-CNMO films show type IV isotherms with hysteresis curves for every sample (Figure 4-9, Table 4-2). The BET surface areas of the CNMO materials ranged from 200-500 m<sup>2</sup>/g with pore volumes of 0.22-0.8 cm<sup>3</sup>/g. The BJH pore size analysis of these CNMO films show a broad distribution of pores (~2-15 nm) with average pore sizes ranging from 6-8 nm, smaller than what was previously observed from the alkylene CNMO materials (5-15 nm). Nitrogen adsorption measurements demonstrated that increasing the loading of the sulfur-bridging spacers resulted in lower surface areas, pore volumes and pore diameters, likely due to cleavage of the organic bridge and the oxidation of the sulfur. However, no bimodal pore size distributions in the mesoporous range were observed for these materials. This indicates that the decreases were not a result of phase separation between the CNCs and organosilica precursors, as had previously been seen in the alkylene-bridged CNMO materials. FTIR spectra of the CNMO films were obtained after CNC removal (Appendix C, Figure C-2) and showed characteristic absorption at 1020 cm<sup>-1</sup> and 800 cm<sup>-1</sup> (Si-O), 3330 cm<sup>-1</sup> (OH stretch), 1640 cm<sup>-1</sup> (water), 1450-1400 cm<sup>-1</sup> and 1270 cm<sup>-1</sup> (CH<sub>2</sub> deformations).<sup>[156]</sup> Unfortunately, due to the intense signals of the silica matrix and hydrogen bonding, it is difficult to observe and confirm peaks associated with C-S, S-H or sulfonic acid. Although CNMO films with thioether linkages were not successfully synthesized, controlling the synthesis of the CNMO films allowed for the creation of new chiral films containing acidic groups (SO<sub>3</sub>H) with controllable mesoporosity and retention of the long-range chiral nematic nanostructure.

Sample	BET	Pore volume	BJH Pore	$\lambda_{max}$ (nm)	$\lambda_{max}$ (nm)
Su	rface Area	$(cm^3/g)$	Diameter	Composite	CNMO
	$(m^2/g)$		(nm)	Films	Films
4-(30)-CNMO	410	0.80	8	731	534
4-(50)-CNMO	370	0.52	6	725	466
4-(60)-CNMO	240	0.38	6	760	500
5-(60)-CNMO	480	0.80	8	730	537
5-(100)-CNMO	180	0.22	6	590	320

Table 4-2. Nitrogen adsorption data of the 4-CNMO and 5-CNMO films



**Figure 4-9.** (a)  $N_2$  adsorption isotherm and (b) BJH pore size distribution for CNMO films synthesized from precursor **4**. (c)  $N_2$  adsorption isotherm and (d) BJH pore size distribution for CNMO films synthesized from precursor **5**.

#### **4.3.3** CNMO films as heterogeneous catalysts

A preliminary study into the application of the CNMO films as supports for heterogenous catalysis was pursued. Inorganic solids, such as silica, zeolites, mesoporous solids, carbon materials or metal organic frameworks, have been widely used as heterogeneous catalyst supports due to their enhanced chemical and thermal stability.<sup>[240,251]</sup> Many factors can influence the catalytic behavior of the PMO supports including pore structure, pore size, hydrophobicity, and accessibility.

We sought to incorporate Mn-salphen complexes into the chiral nematic porous network of CNMO materials and create a new type of heterogeneous catalyst. Salen and salphen ligands are a versatile family of tetradentate ligands obtained from the condensation of diamine and salicylaldehyde precursors.<sup>[233,234]</sup> Metal-derived salen/salphen complexes have been proven to be effective catalysts for the epoxidation of functionalized olefins.<sup>[252]</sup> Although the chiral manganese Jacobson-type salen complex is the most widely studied catalyst, achiral complexes with phenylene-bridged salen ligands or "salphens" are interesting due to their  $\pi$ -conjugated ligand system and rigid geometry.<sup>[252,253]</sup> Recent developments into Mn(III)salphen complexes have focused on tethering these catalysis to various supports for improved catalyst stability and recyclability when performing oxidative reactions.<sup>[254,255]</sup> We hypothesized that tethering of Mnsalphen complexes into the CNMO films could yield useful heterogenous catalysts whose selectivity may be affected by the unusual pore structure of CNMOs.

Specific functionalization of both the catalytic complex and the CNMO support films was required to form the desired heterogenous catalysts. An achiral salphen catalyst, MnCl(salphen), was synthesized containing a double bond that could be covalently bound to thiol modified CNMO films. Two CNMO materials were investigated as catalytic supports, mercaptopropylfunctionalized CNMO films (**Mer-CNMO**) and CNMO films with a thiol/sulfonic acid functionalized organic bridge (**SH-CNMO**). The catalytic properties of the inorganic/organic hybrid organosilica films were tested as well as the retention of the chiral nanostructure and porosity of the CNMO.

#### 4.3.3.1 Mer-CNMO with MnCl(salphen) catalyst

The catalytic performance of CNMO films as a heterogeneous catalytic support was first tested on ethylene-bridged CNMO films that had been post-synthetically modified with 3-mercaptopropyltrimethoxysilane, denoted **Mer-CNMO**. Though the previous sections describe new routes to obtaining sulfur-functionalized CNMO films, the post-synthetic modification using 3-mercaptopropyltrimethoxysilane was chosen as the resulting films have the largest quantity of accessible thiol groups. The %C, %S, and %H was determined by EA and shows that the Mer-CNMO films contain ~6% S, ~20% C and ~4% H. The increase of carbon content and the appearance of sulfur compared to the Et-CNMO films (~14% C, ~3% H) indicates the successful introduction of thiol sites onto the surface of the CNMO films. This is corroborated by TGA that shows the Mer-CNMO have a larger weight loss than the Et-CNMO films, displaying stability until 300 °C and an overall mass loss of ~30% (Et-CNMO, ~15%). The achiral MnCl(salphen) catalyst was introduced into the thiol functionalized CNMO materials through a thiol-ene reaction, Scheme 4-4.<sup>[250]</sup> Loading of the Mn-catalyst into the porous network was confirmed by XRF and shows 0.30 mmol/g loading of Mn was achieved after addition of the catalyst. It should be noted that after binding of the catalyst, the films were heated in chloroform at reflux for 6 h twice in an attempt to remove unbound catalyst. However, a control experiment was performed where the Mncatalyst was introduced to Et-CNMO films using similar conditions to the Mer-CNMO films.

The **Et-CNMO** films still contained the Mn-catalyst after the washing steps, indicating that by using these conditions the CNMO films likely contain catalyst both immobilized onto the pore walls and physically adsorbed into the films.



Scheme 4-4. Loading of the MnCl(salphen) into the Mer-CNMO films and photographs of the films before and after introduction of the catalysis.

The catalytic performance of the achiral Mn complex within the CNMO support material was evaluated by performing an epoxidation of 1,2-dihydronaphthalene as a model substrate (Scheme 4-5). Although several oxidants have been reported for the asymmetric oxidation of unfunctionalized olefins, the most common are *m*-CPBA/NMO and NaClO/PyNO.<sup>[256,257]</sup> NaClO and PyNO were initially used as oxidant and axial ligand, respectively, to test the catalytic activity of heterogeneous Mn-salphen/CNMO materials. However, the Mn-salphen/CNMO films were not stable under the strongly basic conditions and the films tended to break down in solution. Therefore, the catalytic tests were carried out with *m*-CPBA as an oxidant and NMO as an axial

ligand, which has been shown to be an effective oxidant for the asymmetric epoxidation of olefins catalyzed by Mn(III) salen complexes in both homogeneous<sup>[258]</sup> and heterogeneous systems.<sup>[259,260]</sup>



Scheme 4-5. Epoxidation of 1,2-dihydronaphthalene using the homogeneous Mn-salphen catalyst or the heterogeneous CNMO/Mn-salphen catalysts.

First, the catalyst performance of the homogeneous Mn-salphen catalyst was determined by reacting 1,2-dihydronaphthalene with ~3 mol% of catalyst. After 2 h, the homogeneous catalyst reached 48% conversion when the *m*-CPBA/NMO oxidant system was employed with a turnover number (TON) of 12 (TON = mmol of product / mmol of Mn active sites). This was compared to the heterogeneous catalyst, **Salphen-Mer-CNMO** films, using the same catalyst loading. The **Salphen-Mer-CNMO** film showed a similar conversion rate of 42% after 2 h with a TON of 10. However, upon repetition of this experiment using a new batch of **Salphen-Mer-CNMO** films with slightly smaller pore sizes (~ 1 nm smaller, see Appendix C- Figure C-3), the conversion rate after the 2 h reaction dropped to 37%. Similar to previously reported PMO materials, fine tuning of the pore size and surface area affects the performance of heterogeneous catalysts.<sup>[250]</sup> Nevertheless, this data demonstrated that the films are able to be used as heterogeneous catalysts, where optimization of the system could result in improved conversion rates. Unfortunately, the long-range chiral nematic structure of the **Mer-CNMO** films did not induce any enantioselectivity from the achiral salphen catalyst.

SEM images and CD spectra were taken of the Mer-CNMO films, the heterogeneous CNMO support material (Salphen-Mer-CNMO), and CNMO support material after the 163

epoxidation of dihydronaphthalene (**Epox-Mer-CNMO**) to confirm that the chiral nanostructure was retained during the catalytic reaction. SEM images show that the organosilica films before and after the epoxidation reaction have a long-range periodic organization that is characteristic of the chiral nematic organosilica films synthesized from CNC templating (Figure 4-10). The chiral nematic nanostructure can be clearly seen throughout the thickness of the films. Several images were taken for each sample and no loss of the nanostructure was observed in these films.



**Figure 4-10**. SEM images. **Mer-CNMO** films at (a) low magnification (scale bar = 5  $\mu$ m) and (b) high magnification (scale bar = 1  $\mu$ m). **Salphen-Mer-CNMO** film at (c) low magnification (scale bar = 10  $\mu$ m) and (d) high magnification (scale bar = 2  $\mu$ m). **Epox-Mer-CNMO** film at (e) low magnification (scale bar = 3  $\mu$ m) and (f) high magnification (scale bar = 1  $\mu$ m).

**Mer-CNMO** films and heterogeneous catalyst supports were also characterized by  $N_2$ adsorption-desorption isotherms, IR spectroscopy and CD spectroscopy (Figure 4-11). Each material displayed a type IV isotherm with hysteresis indicative of mesoporosity. Binding of the catalyst resulted in a small decrease in the surface area, pore volume and pore size of the CNMO material indicating that some of the catalyst can be found in the porous network of the CNMO films (Table 4-3). After the epoxidation reaction, a small increase in pore volume was observed that could be due to the loss of physically absorbed catalyst from the CNMO support material. CD spectra of representative samples show strong signals with positive ellipticity indicating that the films selectively reflect LH circularly polarized light and further confirm the retention of the nanostructure after addition of the catalyst to the films and after the epoxidation reaction. Although similar  $\lambda_{max}$  were observed, the  $\lambda_{max}$  of each sample varied by ~50 nm making it difficult to compare changes in  $\lambda_{max}$  during the reaction (Appendix C, Figure C-4). IR spectra were taken of the Salphen-Mer-CNMO and Epox-Mer-CNMO films and compared to the Mer-CNMO films. Salphen-Mer-CNMO films show new absorptions at 1600 cm<sup>-1</sup> (C=C) and 1530 cm<sup>-1</sup> (H-C=N) illustrating incorporation of catalyst into the films.<sup>[250]</sup> The **Epox-Mer-CNMO** films show similar absorption bands, however, no peak at 1530 cm<sup>-1</sup> is observed that may further indicate the loss of physically absorbed catalyst after the reaction.

Sample	BET Surface Area	Pore volume	<b>BJH Pore Diameter</b>		
	$(m^2/g)$	$(cm^3/g)$	(nm)		
Mer-CNMO	290	0.47	7		
Salphen-Mer-CNMO	280	0.40	6		
Epox-Mer-CNMO	280	0.44	6		

**Table 4-3.** Nitrogen adsorption-desorption measurements of mercaptopropyl-functionalized

 CNMO support materials



**Figure 4-11.** Characterization for **Mer-CNMO** (black), **Salphen-Mer-CNMO** (red) and **Epox-Mer-CNMO** (blue); (a) N<sub>2</sub> adsorption-desorption isotherm, (b) BJH pore size distribution, (c) CD spectra, and (d) IR spectra (inset: highlighted region with arrows indicating the C=C and H-C=N absorption bands).

#### 4.3.3.2 SH-CNMO with achiral salphen catalyst

The use of CNMO films as a heterogeneous catalyst support was also tested on **SH-CNMO** films. The sulfur content of the **SH-CNMO** films (~5% S as determined by element analysis) was similar to **Mer-CNMO** films, therefore, the same reaction conditions were used to load catalyst into the films (Scheme 4-4). (Although, as mentioned in Section 4.3.1, this sulfur content is from

both thiols and sulfonic acid groups in the films). Loading of the Mn-catalyst into the porous network was confirmed by XRF and shows 0.33 mmol/g of Mn was achieved after addition of the catalyst.

SEM images, IR spectra, CD spectra and  $N_2$  isotherms of the heterogeneous CNMO support material (**Salphen-SH-CNMO**) and CNMO support material after the epoxidation of 1,2-dihydronaphthalene (**Epox-SH-CNMO**) were taken to investigate the retention of the chiral nematic nanostructure and binding of the catalyst. Several SEM images were taken and show no significant changes in the periodic organization of the films after the catalytic reaction (Figure 4-12).



**Figure 4-12**. SEM images. **Salphen-SH-CNMO** films at (a) low magnification (scale bar =  $3 \mu m$ ) and (c) high magnification (scale bar =  $2 \mu m$ ). **Epox-SH-CNMO film** at (c) low magnification (scale bar =  $10 \mu m$ ) and (d) high magnification (scale bar =  $2 \mu m$ ).

N<sub>2</sub> adsorption-desorption isotherms of each material displayed a type IV isotherm with hysteresis indicative of the mesoporous samples (Figure 4-13a, b and summarized in Table 4-4). Binding of the catalyst resulted in a large decrease in both the surface area, pore volume and pore size of the CNMO material indicating the inclusion of catalyst into the porous network of the CNMO films. Similar to the Mer-CNMO films, the films before and after the catalytic reaction showed little change, supporting that the overall organization of the films is retained. CD spectra of the films show strong signals with positive ellipticity from the reflection of LH circularly polarized light further confirming the retention of the nanostructure after catalysis (Figure 4-13c). IR spectra were taken of the Salphen-SH-CNMO and Epox-SH-CNMO films and show changes similar to the Mer-CNMO series, with absorption at 1600 cm<sup>-1</sup> and 1530 cm<sup>-1</sup> for the Salphen-SH-CNMO films. The presence of the reagent/products from the epoxidation reaction within the **Epox-SH-CNMO** films was also observed (Figure 4-13d).

Table 4-4. Nitrogen adsorption data of the SH-CNMO support material					
Sample	BET Surface Area	Pore volume	BJH Pore Diameter		
	$(m^2/g)$	$(cm^3/g)$	(nm)		
SH-CNMO	500	1.23	11		
Salphen-SH-CNMO	330	0.78	10		
Epox-SH-CNMO	320	0.80	10		



**Figure 4-13.** Characterization for **SH-CNMO** (black), **Salphen-SH-CNMO** (red) and **Epox-SH-CNMO** (blue); (a)  $N_2$  adsorption-desorption isotherm, (b) BJH pore size distribution, (c) CD spectra, and (d) IR spectra (inset: highlighted region with arrows indicating the C=C and H-C=N absorption bands).

The catalytic performance of the **Salphen-SH-CNMO** was also tested using a 45 min reaction time. The heterogeneous Mn-catalyst/SH-CNMO films yielded a conversion of 46% for the epoxidation of dihydronaphthalene and a TON of 11, which was comparable to the homogeneous catalyst (conversion 48%, TON of 12). The recyclability of the **Salphen-SH-CNMO** catalyst was tested by washing the films with dichloromethane and reusing them for another two catalytic cycles (Figure 4-14). During the second run, the catalytic activity remained the same. After the third run, the conversion rate dropped slightly due to the leaching of Mn. This 169

was confirmed by XRF, which showed that after three cycles the Mn-loading had decreased from 0.33 mmol/g to 0.15 mmol/g. Interestingly, this catalytic activity was accompanied by a modest enantiomeric excess (5% e.e.) that remained constant during all three successive catalytic cycles and was completely absent in both the homogeneous phase reaction and the **Mer-CNMO** films. This induced enantioselectivity is comparable to previously reported systems that use a chiral cavity as the unique source of enantioselectivity. For example, Rothenberg *et al.* reported chiral modified metal-organic composites, cinchonidine@Pd, that catalyze the asymmetric hydrogenation of acetophenone by hydrogen transfer with isopropanol and gave enantiomeric excesses of 5%.<sup>[261]</sup> Pt nanoparticles loaded onto chiral MCM-41 containing channels with local chiral characteristics have also been shown to exhibit 1.4% e.e. when used as catalyst for the asymmetric hydrogenation of dimethyl itaconate compared to achiral MCM-41 that exhibited no selectivity.<sup>[262]</sup>



**Figure 4-14.** Catalytic performance (conversion (%) (blue) and e.e. (%) (green)) of the **Salphen-SH-CNMO** films for the epoxidation of 1,2-dihydronaphthalene compared to homogeneous achiral MnCl(salphen) catalyst for the same reaction conditions.

The enantioselectivity observed in the **SH-CNMO** films could have arisen due to a number of different factors. The first important factor is the long-range chiral nematic nanostructure of the CNMO films. The nanostructure within the films could be providing a local chiral environment for either the catalyst or the reactant as it binds to the catalyst. This induced chirality is similar to the cavity of an enzyme where the active site is achiral but is surrounded by a chiral environment, or the heterogenous systems by Rothenberg et al. and Yang et al. (Figure 4-15).<sup>[261,262]</sup> However, since the pore size and surface areas of the Mer-CNMO and SH-CNMO films are different, it is difficult to conclude if attachment of the catalyst through the organic bridging group as opposed to the surface-functionalized thiol group plays a significant role in the catalytic performance. Another interesting possibility is that some of the Mn-salphen catalyst is coordinating to the surface of the CNMO films through the sulfonic groups.<sup>[263,264]</sup> Coordination between the catalyst and the sulfonic acid groups may result in the catalyst being closer to the pore walls and potentially more affected by the chiral structure. A second important factor to consider is the racemic mixture of the SH-silane precursor used to synthesized the SH-CNMO films. It is possible that one enantiomer may preferentially bind to the CNCs and thus be enriched in the outer portion of the pore walls (Figure 4-15).

The last factor that could be influencing this enantioselectivity is the innate chirality of the CNC rods. In addition to the long-range chiral nematic nanostructure, individual CNCs contain chirality at the molecular level attributed to asymmetric carbon atoms in the D-glucose subunits and a chiral twisted morphology within each rod (Figure 4-15). It is possible that the chiral surface of the CNC rods, either through the glucose components or the screw-like morphology of the rods, is imprinted onto the surface of the silica and causes the catalysts to experience a chiral surface. More detailed investigation into the mechanism behind this enantioselectivity is required before

any conclusions can be made. Overall, this analysis shows that the CNMO have potential applications in heterogeneous catalysis. By modifying the binding of the catalysts to the silica surface as well as the pore sizes, pore volumes and surface areas of the material, it may be possible to create asymmetric heterogeneous catalysts.



**Figure 4-15.** Representation of the potential sources of enantioselectivity from the Salphen/SH-CNMO heterogeneous catalysts.

## 4.4 Conclusion

The synthesis of functionalized CNMO films using CNCs as a liquid crystal template was extended to ethenylene-bridging and thioether-bridging precursors. Although both types of functionalities were incorporated into composite organosilica/CNC materials and produced mesoporous organosilica material with ordered periodic structure, the thioether bridging groups were not sufficiently stable during CNC removal and cleavage of the bridging group occurred. Sulfur-containing CNMO materials were also synthesized using both the condensation of SH organosilica precursors and the post-synthetic modification of the ethylene bridging group using thiol-ene reactions. The size of the mesopores, the surface areas and the reflected wavelength due to the chiral nematic pitch of the materials were easily tailored by altering the loading of the precursors.

Two sulfur-functionalized CNMO films were examined as heterogeneous supports for a Mn-salphen catalyst using the epoxidation of dihydronaphthalene as a model substrate. Both CNMO films displayed similar conversion rates to the homogeneous Mn-salphen catalyst, however, the **SH-CNMO** films also displayed 5% enantiomeric excess that remained consistent over three cycles of the films. Although these are promising results for the application of CNMO as heterogeneous catalysts, further investigations into the source of this enantioselectivity is required. Apart from catalysis, these materials could be investigated for other applications since thiol groups are known to coordinate many different metals, which could lead to chiral metal nanoparticles or absorbents for heavy metals.

# Chapter 5: Hard Templating of Chiral Nematic Mesoporous Ferrites<sup>‡</sup>

# 5.1 Introduction

Ferrite nanoparticles (NPs) of the type MFe<sub>2</sub>O<sub>4</sub> (M = Co, Ni, Mn, Cu, Zn, *etc.*) are one of the most studied nanomaterials and have been extensively investigated for applications in Fenton catalysis,<sup>[265]</sup> gas sensing,<sup>[266]</sup> lithium ion batteries,<sup>[267]</sup> and as microwave absorbers.<sup>[268,269]</sup> Different combinations of metal cations within the ferrite NPs allows for tunability of the physical properties of these materials.<sup>[270]</sup> In particular, vast efforts have focused on the preparation and characterization of ferrites with improved magnetic properties.<sup>[270,271]</sup> Although precipitation reactions are commonly used to synthesize ferrite NPs,<sup>[272,273]</sup> such materials typically lack mesoporosity or hierarchical structures. The assembly of these NPs into hierarchical structures could lead to materials with new properties arising from the organization of the individual NP building blocks.

Hard templating is an effective method for the construction of materials with highly ordered structures. It is often used for materials that are not accessible through soft templating methods and has been applied to the synthesis of many metal oxides.<sup>[58,274]</sup> Mesoporous silicas, such as SBA-15 (hexagonal pore structure) and KIT-6 (three-dimensional cubic pore structure), are commonly employed as hard templates.<sup>[275,276]</sup> For example, the linear pore structure of SBA-15 has been used to template zinc ferrite and cobalt ferrite nanowires.<sup>[277,278]</sup> The branched

<sup>&</sup>lt;sup>‡</sup> Portions of this chapter have been previously published as: G.R. Meseck, A.S Terpstra, A.J. Marenco, S. Trudel, W.Y. Hamad, M.J. MacLachlan, *J. Mater. Chem. C*, **2016**, 4, 11382.

mesoporous network of KIT-6 has been used to template a variety of ferrites, such as copper ferrite,<sup>[265]</sup> cobalt ferrite,<sup>[279]</sup> and nickel ferrite materials.<sup>[268]</sup> Interestingly, the surface area, crystallite size and nanostructure of these ferrite materials have been demonstrated to influence their magnetic behavior.<sup>[279]</sup> Haffer *et al.* found that an increase in surface to volume ratio of cobalt ferrite disturbs the magnetic ordering and changes the magnetic moments compared to the respective bulk materials. Since structural order can modify the magnetic properties<sup>[280]</sup> and gives rise to effects such as anisotropic magnetic coupling between particles,<sup>[281]</sup> distortion of the magnetic ordering,<sup>[279]</sup> and dipolar interactions,<sup>[282]</sup> hard templating is an exciting tool to make magnetic materials with unique physical properties.

The discovery of chiral nematic mesoporous silica (CNMS) prepared from the liquid crystal templating of cellulose nanocrystals (CNCs) has added a unique three-dimensional pore structure to the family of mesoporous silicas.<sup>[91,179]</sup> The self-assembly of the CNC rods into a chiral nematic liquid crystal imparts a helically-arranged porous network into the resulting silica material. Using CNMS as a hard template could allow for the synthesis of novel materials with long-range chiral nanostructure. This hard-templating approach is particularly advantageous for precursors that disrupt the self-assembly of the CNC template. To date, CNMS films have been successfully employed for the hard templating of titanium dioxide<sup>[124]</sup> and Prussian blue analogues.<sup>[211]</sup> In this Chapter, I report the synthesis and characterization of chiral nematic nanostructured ferrite and iron oxide materials using CNMS as a hard template. The structural features of the silica template are retained in the resulting mesoporous metal oxide materials. In addition, we investigated the magnetic properties of these hierarchical nanostructured materials.

## 5.2 Experimental

#### 5.2.1 Materials

All solvents and reagents including, iron(III) nitrate nonahydrate (Fisher Scientific), copper(II) nitrate hemi(pentahydrate) (Fisher Scientific), nickel(II) nitrate hexahydrate (Sigma Aldrich), cobalt(II) nitrate hexahydrate (Sigma Aldrich), zinc(II) nitrate hexahydrate (Sigma Aldrich), manganese(II) nitrate hydrate (STREM Chemicals), and tetramethyl orthosilicate (TMOS, Acros) were used without further purification. Aqueous solutions of CNCs (4.1 wt.%, pH 2.5) with (195  $\pm$  93) nm in length and (15  $\pm$  8) nm in width (determined by TEM) were supplied from FPInnovations.

#### 5.2.2 Characterization

Nitrogen sorption studies were performed using a Micromeritics ASAP 2020 at 77 K. All samples were degassed under vacuum at 120-150 °C immediately prior to analysis. The specific surface of the samples studied calculated areas were using the standard Brunauer-Emmett-Teller (BET) method with relative pressures from 0.04 to 0.2. Total pore volumes were estimated from the amount of N<sub>2</sub> adsorbed at a relative pressure of 0.99. Barrett-Joyner-Halenda (BJH) pore size distributions were calculated from the adsorption branch of the isotherms. Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 Advance diffractometer using  $CuK_{\alpha}$  as the X-ray source and a NaI scintillation detector. Crystallite sizes were determined from the integral breadth of non-overlapping peaks using the EVA software package (Bruker). Energy dispersive X-ray (EDX) spectroscopy of the samples were taken by finely grinding the metal oxides and mounting the resulting powder on an aluminum sample holder using an adhesive carbon tab. The EDX spectra were acquired on a Hitachi S-2600N at an 176

acceleration voltage of U = 16 kV and fitted using the Quartz Imaging Systems XOne software package before calculating the concentrations from the K<sub>a</sub> lines.

#### 5.2.3 Magnetometry

Superconducting quantum interference device (SQUID) magnetometry measurements were performed using a Quantum Design MPMS XL-7S system. Nanoparticles were loaded into a gelatin capsule, sealed with Kapton tape, and inserted in a diamagnetic clear plastic straw. Thin-film measurements were performed with the sample loaded in a longitudinal or transverse fashion with respect to the applied external magnetic field. For longitudinal measurements, films were secured to a quartz rod with GE 7031 varnish diluted in a 1:1 ratio with isopropyl alcohol. For transverse measurements, films were sandwiched between two plastic straw cutouts and sealed with GE varnish. This "puck" was then loaded into a diamagnetic clear plastic straw held in place by plastic straw adapters.

Isothermal magnetization as a function of magnetic field strength measurements were carried out at 300 K by cycling the applied field between 4 and -4 T. Zero-field-cooled (ZFC) and field-cooled (FC) magnetization measurements were carried out by cooling samples to 1.9 K in the absence (ZFC) or presence (FC) of an applied magnetic field of 10 mT, and measuring the magnetization under a field of 10 mT upon warming the sample. M(H) measurements to a maximum magnetic field strength of 7 T were carried out to obtain M<sub>s</sub>.

#### 5.2.4 Preparation of chiral nematic mesoporous silica (CNMS)

CNMS was prepared according to a modified literature procedure.<sup>[91]</sup> TMOS was added dropwise to a stirring CNC suspension (4.1 wt.%) using a ratio of 1.69 mmol TMOS / 150 mg of

CNC. Stirring of the mixtures was continued at  $22 \pm 3$  °C until the suspensions appeared homogeneous (~2 h). The CNC/TMOS mixture was transferred to polystyrene Petri dishes (20 mL / 9 cm dish) and left to dry under ambient conditions. The CNC/silica composite films were placed in 6 M H<sub>2</sub>SO<sub>4</sub> (~250 mg / 500-750 mL) and heated to 100 °C for 18 h. After cooling to room temperature and filtering, the films were washed with water (~1 L), and alternately washed with a 22 °C ± 3 solution of piranha solution (20 mL 30% H<sub>2</sub>O<sub>2</sub> / 100 mL conc. H<sub>2</sub>SO<sub>4</sub>) and water until they appeared colourless. The films were then washed with water (2 L) and allowed to dry in air.

#### 5.2.5 Hard templating of the ferrites/metal oxides

CNMS films (200 mg) were passed through a sieve with a 30 µm mesh size to obtain ground silica flakes. The ground CNMS flakes were placed into the bottom of a polypropylene beaker that was propped up on angle ( $30^\circ \pm 10^\circ$ ) so that the flakes were in a small mound. Freshly prepared pre-mixed solutions of the respective metal nitrate (0.27 mmol, 333 µL in ethanol) and iron nitrate (0.53 mmol, 666 µL in ethanol) were added dropwise onto the silica. After 2 h at 22 ± 3 °C, the beaker was heated to 100 °C for 4 h to evaporate the remaining solvent. The resulting composite material was heated to 200 °C under air for 3 h at a ramp of 1 °C min<sup>-1</sup> to decompose the nitrate precursor. The addition of the pre-mixed solution containing the respective nitrate precursors and their subsequent decomposite samples were then calcinated at temperatures of 400 °C, 600 °C, or 800 °C for 4 h ( $\Delta T = 2.5$  °C min<sup>-1</sup>) and the silica matrix was etched by immersing the sample in sodium hydroxide solution (2 M, 15 mL) for 5 h. The material was gently washed by exchanging the solution repeatedly with DI water (4 × 20 mL) using a pipette, followed by ethanol (4 × 15 mL) and were left to dry in air.

### 5.3 **Results and Discussion**

#### 5.3.1 Synthesis of mesoporous silica films and the hard templating of metal oxides

Early attempts to produce chiral nematic metal oxides by soft templating metal nitrate salts with aqueous suspensions of CNCs produced composite films where the chiral nematic self-assembly of the CNC rods was disrupted and no long-range chiral nematic ordering was observed. Therefore, in order to create novel metal oxide materials with long-range chiral nematic porous structures, we sought to develop a standard hard-templating approach that could be employed for a variety of metal nitrate precursors. To date, many chiral nematic mesoporous materials have been synthesized that could be used as hard templates (e.g. (organo)silica, carbon, mesoporous cellulose). Of these materials, chiral nematic mesoporous silica (CNMS) films were chosen as they can be synthesized with controllable porosities and have thermal stability up to the temperatures (~400-900 °C) needed for calcination of the metal nitrate precursors.

When preparing structured titanium dioxide films using a hard-templating approach, Shopsowitz *et al.* showed that CNMS films containing larger mesopores (~7 nm vs. ~2 nm) allowed for more efficient diffusion of titanium precursors into the CNMS template. This resulted in a larger loading of precursors into the template and a better replication of the long-range chiral nematic nanostructure.<sup>[124]</sup> Therefore, I prepared CNMS films containing large average pore sizes by condensing TMOS with an aqueous suspension of CNCs using a ratio of 1.69 mmol TMOS / 150 mg of CNC.<sup>[91]</sup> Removal of the CNCs through acid hydrolysis yielded mesoporous silica films that were approximately 160-180 µm thick and reflected LH circularly polarized light ( $\lambda_{max} = 850$ nm) due to the long-range chiral nematic structure imparted by the CNC template. To help optimize the infiltration of precursors in the porous structure, the CNMS films were passed through a sieve with a 30 µm mesh size and small silica flakes were obtained. Scanning electron microscopy 179 (SEM) images and a nitrogen adsorption-desorption isotherm of the CNMS flakes show that they retain the interconnected long-range chiral nematic nanostructure, have average pore diameters between 16-19 nm, and surface areas of  $\sim 300 \text{ m}^2/\text{g}$  (Figure 5-1).



**Figure 5-1.** SEM images of a cross-section of the CNMS flakes used as a hard template (scale bars = (a) 1 mm and (b) 1  $\mu$ m). (c) Nitrogen sorption isotherm and (d) BJH pore size distribution for the CNMS flakes.

Metal oxide replicas from five different metal nitrate precursors were synthesized using these large pore CNMS flakes as a hard template. This procedure employed a solvent-based method from the literature and is summarized in Scheme 5-1.<sup>[283]</sup> Briefly, solutions containing 2:1  $Fe(NO_3)_3$  to the respective divalent metal nitrate precursors (M(NO\_3)\_2, M = Mn, Co, Ni, Cu, and Zn) in ethanol were added onto the crushed CNMS films and the solution was evaporated, allowing the precursors to infiltrate into the porous network of the films. The resulting metal nitrate-silica composite materials were annealed at 200 °C to decompose the precursors within the films.

Ground CNMS flakes





#### **CNMS/Metal Oxide Composite**



Scheme 5-1. Synthesis of CNMS/metal oxide materials.

In order to consistently replicate the continuous three-dimensional chiral nematic structure of the silica template it is critical that the metal nitrate precursors are sufficiently loaded into the porous network of the CNMS prior to removal of the template. Replication of the chiral nanostructure within the metal oxide materials was analyzed after 1-3 precursor infiltration cycles. While the bulk of the CNMS/metal oxide composite material was directly used for next infiltration cycle, after each loading cycle a small fraction of the composite material was soaked in 2 M NaOH<sub>(aq)</sub> to remove the silica template. SEM images of the resulting porous metal oxide materials were compared and the replication of the chiral nematic structure was analyzed. After 1 infiltration cycle of the metal nitrate precursors into the CNMS films, regions of the resulting porous metal oxide materials contained chiral nematic nanostructures (see Figure 5-2a for the nickel ferrite sample after 1 loading cycle). However, the chiral nematic structure within the material was more disordered than the silica template and regions with no hierarchical nanostructures were often observed. It was found that increasing the number of loading cycles promoted retention of the chiral nematic nanostructure after removal of the silica (see Appendix D, Figure D-1 for SEM images of nickel ferrites from 1-3 loading cycles).



**Figure 5-2.** SEM images of (a) porous nickel ferrite after a single loading cycle (scale bar = 5  $\mu$ m) and (b) composite CNMS/nickel ferrite after three loading cycles (scale bar = 3  $\mu$ m). (c) Nitrogen adsorption-desorption isotherm data showing a decrease in the total pore volume of the zinc, copper, nickel, cobalt and manganese ferrites/silica composites after each infiltration cycle.

The reduction of the total pore volume within the composite materials compared to the silica template was also analyzed using nitrogen adsorption-desorption isotherms after each loading step. For all 5 metal nitrate precursors used in this Chapter, increasing the number of loading cycles resulted in a decrease in both the surface areas and pore volumes of the composite materials. After 3 loading cycles, the accessible pore volume of the CNMS flakes was reduced by 63-75% (Figure 5-2b, c). Overall, by analyzing the nitrogen isotherms and SEM images, it was

observed that 3 loading cycles of the metal nitrate precursors (~70% of the total pore volume) was sufficient to replicate the nanostructure of the CNMS flakes without promoting significant growth of ferrite material outside the template.

#### 5.3.2 Optimization of crystallinity and porosity

Once the impregnation method used to load the metal nitrate precursors into the CNMS template was optimized, we were interested in investigating the effect of the calcination temperature on the crystallinity and mesoporosity of the oxide materials. Therefore, the metal ferrite/silica composite materials were calcined at increasing temperatures ( $T_{calc} = 600$  and 800 °C), followed by etching the silica matrix in 2 M NaOH<sub>(aq)</sub> similar to a previously reported method and as shown in Scheme 5-2.<sup>[125]</sup> The etching step was performed at room temperature to minimize the risk of altering the chiral nematic nanostructure of the ferrite material. Removal of silica was confirmed using energy dispersive X-ray (EDX) spectroscopy for three representative samples; nickel, copper and cobalt ferrite calcined at 600 °C. After etching with NaOH, the remaining chiral nematic mesoporous ferrites had ~1-2 wt.% residual Si content compared to the ~16 wt.% of Si in the composite materials. This residual Si content is comparable to previously reported CNMS hard templating approaches.<sup>[124]</sup>







 $MFe_2O_4$ ; M = Ni, Cu, Zn, Co

Scheme 5-2. Synthesis of chiral nematic mesoporous ferrite materials.

Powder X-ray diffraction (PXRD) patterns were analyzed for the resulting mesoporous materials after removal of the silica template. As seen in Figure 5-3a-d, the PXRD traces confirm the synthesis of nickel ferrite, copper ferrite, zinc ferrite and cobalt ferrite materials with patterns that matched well to the expected crystal structures for spinel shaped ferrite nanoparticles. Trace impurities were observed in the copper ferrite PXRD pattern (hematite (Fe<sub>2</sub>O<sub>3</sub>) and copper oxide (CuO)) and in the zinc ferrite PXRD pattern (zinc oxide), likely due to phase separation between the iron and copper or zinc precursors, respectively. For each of the ferrite materials with M = Ni, Cu, Zn, and Co, the PXRD data showed an increase in crystallinity with increasing calcination temperature. This change in crystallinity due to calcination temperature is similar to what has been previously reported for other ferrite nanomaterials.<sup>[278]</sup> The crystallite sizes of the ferrite materials were estimated by applying the Scherrer equation to the PXRD data and are summarized in Table 5-1.<sup>[284]</sup> A clear trend is observed that shows an increase in the average crystallite sizes from  $\sim 6 - 10$  nm to  $\sim 8 - 14$  nm for calcination temperatures of 600 and 800 °C, respectively. In addition, the cobalt ferrite/silica composite was also calcined at 400 °C and displayed low crystallinity after removal of the silica template. Since the crystallinity of this sample was very low, the 400 °C calcination temperature was not further investigated for the nickel, copper or zinc ferrite materials.

Nitrogen adsorption-desorption measurements were also performed on the ferrite samples and are summarized in Table 5-1. The replica ferrite materials all display mesoporosity with average pore sizes ranging from ~20-30 nm, which are larger than that of the silica template (16-19 nm). The ferrite replicas also have BET surface areas ranging from ~50-150 m<sup>2</sup>/g and pore volumes ranging from 0.5-0.8 cm<sup>3</sup>/g. It was observed that increasing the calcination temperature (or increasing the crystallite size within the material) generally resulted in an increase in the pore size and a decrease in the surface area of the ferrites. These results are comparable with previously reported mesoporous ferrite materials synthesized using a mesoporous silica hard template (SA: ~100-160 m<sup>2</sup>/g and crystallite sizes of 10-20 nm).<sup>[279]</sup>

PXRD patterns of the mesoporous materials synthesized using manganese and iron nitrate precursors were also analyzed (Figure 5-3e). A PXRD pattern of this material calcined at 600 °C showed the sample was composed predominantly of hematite as well as FeMnO<sub>3</sub> and MnFe<sub>2</sub>O<sub>4</sub>. Increasing the calcination temperature to 800 °C resulted in materials contained only crystalline hematite indicating that the manganese precursor mixture was not compatible with the synthetic conditions reported in this Chapter. However, the iron oxide material obtained had comparable crystal sizes, surfaces areas and pore sizes to the ferrite materials.

-	Sample	T <sub>calc</sub> (°C)	Crystallite Size (nm)	BET Surface Area (m <sup>2</sup> /g)	BJH Avg. Pore Diameter (nm)	Pore Volume (cm <sup>3</sup> /g)
	Nickel ferrite,	600	6.8	140	24	0.85
	NiFe <sub>2</sub> O <sub>4</sub>	800	8.2	110	26	0.73
	Copper ferrite,	600	8.2	110	27	0.81
	CuFe <sub>2</sub> O <sub>4</sub>	800	9.7	60	29	0.41
	Zinc ferrite,	600	11.3	90	24	0.54
	ZnFe <sub>2</sub> O <sub>4</sub>	800	13.0	75	34	0.69
	Calcult formits	400	6.4	122	19	0.60
	Coball lerrite,	600	8.6	76	28	0.53
	C0FC2O4	800	10.6	52	33	0.44
	Iron Oxide,	600	22.4	64	35	0.58
	Fe <sub>2</sub> O <sub>3</sub>	800	19.4	117	26	0.83

**Table 5-1.** Crystallinity and mesoporosity of the chiral nematic mesoporous ferrite and iron oxide materials.

Note: Initial CNMS flakes have surface areas of  $\sim 300 \text{ m}^2/\text{g}$ , average pore diameters of 16-19 nm and pore volumes of  $\sim 1.2 \text{ cm}^3/\text{g}$ .


**Figure 5-3.** PXRD data of the chiral nematic ferrite and oxide materials with the most prominent lattice planes indexed and calcination temperature as labeled. (a) Nickel ferrite, (b) copper ferrite with (104) identifying trace hematite and (111) identifying trace copper oxide, (c) zinc ferrite with (101) identifying trace zinc oxide, (d) cobalt ferrite and (e) iron oxide (hematite). Data was matched to PDF cards: 01-076-6119, 00-034-0425, 01-070-6393, 00-022-1086 and 00-033-0664, respectively.

#### 5.3.3 Chiral nematic nanostructure of the ferrite replicas

I was particularly interested in observing if the long-range chiral nematic structure of the CNMS template could be imparted into the crystalline ferrite materials. Therefore, SEM images of the hard-templated ferrites were obtained and compared to the morphology of the CNMS films as seen in Figure 5-1. Figure 5-4 for the  $T_{calc} = 600$  °C samples and Figure 5-5 for the  $T_{calc} = 800$  °C samples demonstrate that the chiral nematic liquid crystalline phase of the cellulose nanocrystals was beautifully replicated in all ferrite samples at all calcination temperatures. The long-range repeating nanostructure can be clearly seen through-out the thickness of the ferrite material (parallel to the surface of the ferrite particles), and perfectly matches the morphology of the silica template. The ferrite crystals twist in a counter-clockwise direction, consistent with the left-handed chiral nematic structure of CNCs. In addition, SEM images of the iron oxide material also displayed a long-range repeating chiral nematic nanostructure that matches the silica template (Figure 5-6). Although structural differences induced by the calcination are difficult to distinguish using SEM, the ferrite materials calcined at 600 °C appear slightly more ordered than the materials calcined at 800 °C. Since increasing the calcination temperature is associated with an increase in both the pore size and crystallite sizes of the material, it may be difficult for the larger crystallites to grow while maintaining the chiral nanostructure. Overall, by infiltrating metal nitrate precursors into CNMS flakes with large pore sizes, chiral nematic mesoporous ferrite materials (MFe<sub>2</sub>O<sub>4</sub>, M = Ni, Cu, Zn, Co) were synthesized with controlled crystallinity and mesoporosity.



**Figure 5-4.** SEM images of chiral nematic mesoporous ferrites calcined at T = 600 °C (after removal of the silica template). (a, b) Nickel ferrite with an illustration of the helical pitch (green), (c, d) copper ferrite, (e, f) zinc ferrite, and (g, h) cobalt ferrite. Scale bar = (a, c, e, g) 1 µm and (b, d, f, h) 5 µm.



**Figure 5-5.** SEM images of chiral nematic mesoporous ferrites calcined at T = 800 °C (after removal of the silica template). (a, b) Nickel ferrite (c, d) copper ferrite, (e, f) zinc ferrite, and (g, h) cobalt ferrite. Scale bar = (a, c, e, g) 1 µm and (b, d, f, h) 5 µm.



**Figure 5-6.** SEM images of chiral nematic mesoporous iron oxide calcined at T = 800 °C (after removal of the silica template). Scale bar = (a) 1 µm and (b) 5 µm.

#### 5.3.4 Magnetic measurements of the chiral nematic copper, nickel and cobalt ferrites

The inherent magnetic properties of the copper, nickel and cobalt ferrite NPs were studied using superconducting quantum interference device (SQUID) magnetometry. The overall magnetic moment of a ferrite NP consists of a single magnetic domain that can rotate with respect to the crystalline structure.<sup>[270]</sup> By applying a sufficiently large magnetic field to the ferrite samples, the magnetic moments within the material align in the direction of the applied field. The maximum value of magnetization achieved by the sample in the applied magnetic field is referred to as the saturation magnetization ( $M_s$ ). The magnitude of the magnetic field applied in the negative direction that is needed to bring the magnetization of the ferrites back to zero is referred to as coercivity ( $\mu_0 H_c$ ) and measures the resistance of a magnetic material to changes in magnetization. All SQUID measurements were performed at the University of Calgary by Prof. Simon Trudel and Armando Marenco.

Magnetization reversal loops (M(H)) for the powdered ferrite materials in fields of 4 or 7 T were used to measure the saturation magnetization and the coercivity of the ferrite materials. As

seen in Figure 5-7 and summarized in Table 5-2, the cobalt ferrite material shows the highest saturation magnetization followed by the nickel ferrite then the copper ferrite materials. Calcination at higher temperatures resulted in ferrite materials with higher saturation magnetization. For example, the copper ferrite materials calcined at 600 and 800 °C have  $M_s$  of 11.9 emu g<sup>-1</sup> and 18.3 emu g<sup>-1</sup>, respectively. Generally, the higher calcination temperatures also created materials with increased coercivity and remanence ratios  $(M_r/M_s)$ , where  $M_r$  is the magnetization left behind after an external magnetic field was applied). It was observed that for all calcination temperatures used in this Chapter, the chiral nematic mesoporous ferrites demonstrate soft-ferromagnet characteristics at room temperature and can be easily magnetized and demagnetized in an external electric field (as shown in Figure 5-8a). Though the ferrite materials have a chiral nematic nanostructure, the measurements were performed on the crushed ferrite samples, therefore, the materials displayed similar magnetic properties to previously reported NPs. For example, CoFe<sub>2</sub>O<sub>4</sub> NPs have been reported with  $M_s$  values of 58.4 emu g<sup>-1</sup> for ~12 nm NPs,<sup>[285]</sup> and 55.8 emu g<sup>-1</sup> for 49.5 nm NPs,<sup>[272]</sup> synthesized by co-precipitation as well as a value of 46.2 emu g<sup>-1</sup> for hard-templated CoFe<sub>2</sub>O<sub>4</sub> with a crystallite size of 9 nm.<sup>[279]</sup>

Field-cooled and zero-field-cooled (FC-ZFC) M(T) curves were recorded to analyze the blocking temperature ( $T_B$ ) of the NPs, which is designated from the peak in the ZFC measurements (Figure 5-8b). Above the  $T_B$ , thermal energy rapidly randomizes the direction of the domain and anhysteretic M(H) loops are observed. Below the  $T_B$ , the orientation of the magnetic domain is fixed with respect to the crystal axes and hysteresis is observed in M(H) measurements. The  $T_B$ s of ferrite samples ranged from ~150 to >400 K and increased with increasing crystallite sizes and increased calcination temperatures.

Chiral nematic mesoporous	$T_{calc}$	<i>M</i> <sub>s</sub> @ 7 T	<i>M</i> <sub>s</sub> @ 4 T	$M_{ m r}/M_{ m s}$	$\mu_0 H_c (\mathrm{mT})$	T(V)	$K_{\rm eff}$
ferrites	(°C)	(emu g <sup>-1</sup> )	(emu g <sup>-1</sup> )	$(\mu_0 H_{\rm max} = 4 {\rm T})$	$(\mu_0 H_{\text{max}} = 4 \text{ T})$	$I_{\rm B}$ (K)	(kJ m <sup>-3</sup> )
Cobalt ferrite, CoFe <sub>2</sub> O <sub>4</sub>	400	13.6	11.2	0.02	1.73	241	606
	600	40.7	37.9	0.10	10.6	> 400	> 415
	800	54.3	52.0	0.17	33.1	> 400	> 221
Nickel ferrite, NiFe <sub>2</sub> O <sub>4</sub>	600	20.1	17.9	0.006	1.00	151	317
	800	26.4	23.7	0.009	0.86	166	189
Copper ferrite, CuFe <sub>2</sub> O <sub>4</sub>	600	13.1	11.7	0.02	1.91	176	210
	800	19.3	18.3	0.16	19.9	> 400	> 289

Table 5-2. Magnetic properties of the chiral nematic mesoporous ferrites.



**Figure 5-7.** (a) M(H) at 300 K for chiral nematic mesoporous ferrites to a maximum magnetic field of 7 T to determine  $M_S$ .



**Figure 5-8.** SQUID magnetic measurements for the copper ferrite samples. (a) Magnetization reversal loops at 300 K (insert: zoomed-in area near the origin). (b) ZFC-FC measurements ( $\mu_0 H = 10 \text{ mT}$ ) (open symbols: ZFC; solid symbols: FC).

Millimeter-sized cobalt ferrite/silica composites and cobalt ferrite films were also synthesized and their inherent magnetic properties were studied using SQUID magnetometry. The millimeter-sized films were prepared following the same procedure as the ferrite materials described above except the CNMS films were not passed through a sieve. This allowed us to analyze the magnetic properties of the chiral nematic layers aligned along (longitudinal) or perpendicular (transverse) to the applied magnetic field. As shown in Figure 5-9, the millimeter-sized ferrite and composite films show very weak magnetic anisotropy. Higher coercive fields in the M(H) reversal loops and higher susceptibility in the FC/ZFC curves were observed for the longitudinal orientation. This orientational effect is most pronounced in cobalt ferrite/silica composites calcined at 600 °C. However, etching of the silica template lowered the anisotropy observed in the M(H) loops of the mesoporous ferrite films.



**Figure 5-9.** (a) Photographs of CoFe<sub>2</sub>O<sub>4</sub>/silica composite films (scale bar = 10 mm). (b) Illustration of transverse and longitudinal alignment of the films for SQUID magnetometry. Orientation-dependent measurements for the cobalt ferrite/silica composite sample calcined at 600 °C. (c) Magnetization reversal loops at 5K and 300 K (insert: zoomed-in area near the origin). (d) ZFC-FC measurements ( $\mu_0 H = 10 \text{ mT}$ ) (open symbols: ZFC; solid symbols: FC).

Overall, the magnetic properties of the chiral nematic mesoporous ferrite materials match well with the results observed from the PXRD data. The larger crystallite sizes and improved crystallinity of the ferrite materials resulting from higher calcination would be expected to yield materials with higher  $T_{\rm B}$  and  $M_s$ . Further experiments are necessary to understand the origin of the weak magnetic anisotropy observed in the silica/ferrite composite films. This anisotropy could be due to an alignment of the ferrite NPs resulting from the chiral nanostructure, or the presence of dipolar interactions between NPs<sup>[286,287]</sup> that can align the moment of several NPs into a preferred orientation.

# 5.4 Conclusions

Chiral nematic mesoporous silica (CNMS) templated from cellulose nanocrystals was used as a hard template to produce structured mesoporous metal oxide materials. The synthetic approach development in this Chapter was used to create four chiral nematic mesoporous ferrite materials ( $MFe_2O_4$ , M = Zn, Cu, Ni and Co) where the organization of the ferrite NPs perfectly replicate the chiral nematic structure that can be found in the liquid crystalline phase of CNCs. By altering the calcination temperature of the ferrite/silica composite samples, the crystallinity, mesoporosity and magnetic properties of the resulting mesoporous ferrites materials could be tuned. Calcination of the ferrites at increasing temperatures leads to improved crystallinity and higher saturation magnetization. A weak magnetic anisotropy was also observed when the chiral nematic ferrite films were aligned longitudinal or transverse to the magnetic field. This makes these ferrite materials promising candidates to study structure-related magnetic effects at the nanoscale. Magnetic materials with such a hierarchical nanostructure may show novel cooperative magnetic effects or may find use for selective absorbance of circularly polarized microwaves.

# **Chapter 6: Conclusions and Future Directions**

### 6.1 Conclusions

Inorganic mesoporous materials are attractive for diverse applications, such as enantioselective separations and catalysis, owing to their defined pore sizes and tunable nanostructures. Since the first report of liquid crystal templating by Kresge and coworkers in 1992,<sup>[36]</sup> researchers have used surfactant templates to impart periodic ordering into a range of composite and mesoporous materials. By altering the type of liquid crystal surfactants and the inorganic precursors, it is possible to synthesize materials with diverse symmetries and pore sizes, as well as unique physical properties.<sup>[36,52]</sup> In particular, chiral surfactants are advantageous when synthesizing organosilica materials as they create novel mesoporous materials with unique twisted pore structure.<sup>[142]</sup>

Colloidal cellulose nanocrystals (CNCs) obtained from sulfuric-acid catalyzed hydrolysis of cellulose microfibers are extraordinary materials. Originally isolated by Ränby in 1951,<sup>[92]</sup> CNCs can be synthesized with nanoscale dimensions and have impressive mechanical properties.<sup>[93]</sup> Remarkably, CNCs can self-assemble to form a chiral nematic liquid crystalline phase where the CNC spindles align in layers that twist with a characteristic helical pitch. This liquid crystalline phase can be captured by evaporation induced self-assembly to produce free-standing iridescent films.<sup>[106]</sup> Over the past decade, researchers have taken advantage of the repeating helicoidal structure of CNCs to synthesize new chiral nematic materials and study their properties and potential applications.<sup>[104,108,288,289]</sup> Recently, the MacLachlan group discovered that films of mesoporous silica and ethylene-bridged organosilica with chiral nematic structure could

be prepared using CNCs as a liquid crystal template.<sup>[91,116]</sup> Sol-gel condensation of Si(OR)<sub>4</sub> with aqueous suspensions of CNCs resulted in composite films containing chiral nematic assembled CNCs. Removal of the CNCs created films of iridescent mesoporous silica with a chiral nematic porous network. These mesoporous (organo)silica materials have been shown to be of interest as hard templates and for refractive index-based sensors.<sup>[116]</sup> The aim of this thesis has been to explore the synthesis of novel mesoporous materials templated from the self-assembly of CNCs and investigate the chemical compositions and physical properties of the resulting materials. I have developed methods that allow for the chiral nematic structure of the CNCs to be imparted into mesoporous films with a range of chemical compositions.

In Chapter 2, I extended the synthesis of chiral nematic mesoporous organosilica (CNMO) films to a library of organic spacers, modified the physical properties of the CNMO films and investigated the limits of the self-assembly process. By evaporation induced self-assembly, free-standing organosilica/CNC composite and mesoporous organosilica materials were obtained. The new organic bridging groups were incorporated into the organosilica as integral components of the cross-linked structures. The wavelengths of light reflected from the nanostructures within the films and thermal stability of the films can be tailored depending on the type of bridging group employed. The organic bridge was also found to impact the pore structure as well as mechanical and chemical properties of the organosilica films. However, I found that the type of bridging groups used to synthesize CNMO films was limited due to phase separation of the organosilica precursor from the aqueous CNC suspension. To resolve the phase separation problem, mixed solvent system of water and DMF were employed to prepare the films. By controlling solvent composition conditions during CNC self-assembly, I demonstrated that hydrophobic organosilica precursors could be introduced into CNC suspensions to create films with high surface areas and

controllable pore structures. The results of this study will be useful for developing new chiral nematic mesoporous films, which could open the door for new tunable materials for optical sensing devices and enantioselective separation.

In Chapter 3, I investigated an application of the CNMO materials as solid supports for photochromic molecules. CNMO films were post-functionalized with a mixture of hydrophobic silanes and spiropyran compounds to create free-standing photochromic films, which can be used for reversible photopatterning and metal sensing. The interconnected pore structure of the films enabled the material to be functionalized with photochromic molecules. As a result, I was able to obtain hybrid organic-inorganic materials that showed intense absorption spectra from the tethered spiropyran. Rapid colour changes were observed due to reversible isomerization between the merocyanine and spiropyran forms when irradiating the films with UV or white light. The films also behaved as reversible sensors where binding of a metal to the spiropyran resulted in visible colour changes and the metal-free spiropyran could be regenerated by treating the films with ethanol and white light. This proof-of-concept work may help in the development of new photochromic displays, security features and patterns.

Even with my success to form a library of alkylene-bridged and aromatic-bridged CNMOs, the synthetic approach developed in Chapter 2 is still limited in the types of organic precursors that can be introduced. In Chapter 4, I discussed my efforts to synthesize and characterize ethenylene-bridging and sulfur-containing CNMO materials. The introduction of thiol groups into CNMO materials was of particular interest as sulfur-containing periodic mesoporous organosilica (PMOs) have been extensively studied for applications in metal binding and catalysis.<sup>[136]</sup> I was able to synthesize composite materials from ethenylene, thioether and thiol organosilica precursors through co-condensation methods with aqueous CNC suspensions, and produced mesoporous organosilica materials with ordered periodic structure. Similar to the films synthesized in Chapter 2, the type of organic bridge altered the size of the mesopores, surface areas and reflected wavelength of the resulting CNMO materials. However, the thiol organosilica and thioether bridging groups were not entirely stable to the oxidative conditions used during the removal of CNCs, which resulted in partial oxidation of the thiol group or complete cleavage of the bridging group, respectively.

I also explored the application of these films as heterogeneous supports for Mn-salphen catalysts. Sulfur-functionalized CNMO films were post-synthetically modifed with Mn-salphen and their catalytic performance was examined using the epoxidation of dihydronaphthalene. The CNMO films displayed similar conversion rates to the homogeneous Mn-salphen catalyst. Additionally, the films synthesized using 1-thio-1,2-bis(triethoxysilyl)-ethane displayed a modest enantiomeric excess of 5% that remained consistent over three cycles of the films. This induced enantioselectivity is comparable to previously reported systems that use a chiral cavity as the unique source of enantioselectivity.<sup>[261,262]</sup> Although further investigations are required, we propose that this enantioselectivity could be due to the chiral environment of the CNMO support material or the CNC spindles. These are promising preliminary results for the application of CNMO as heterogeneous catalysts.

Finally, in Chapter 5, I used the chiral nematic mesoporous silica films as a hard template to prepare the first chiral nematic nanostructured magnetic metal ferrites. The ferrite materials,  $MFe_2O_4$  (M = Ni, Cu, Zn, Co), were obtained by repeatedly filling the pores of the mesoporous silica template with solutions of the respective metal nitrate precursors followed by thermal treatment. Calcination of the composite materials and removal of the silica matrix yielded mesoporous ferrites that perfectly replicated the chiral nematic liquid crystalline phase of CNCs. The crystallinity, mesoporosity, surface areas and saturation magnetization of the ferrites could be controlled by altering the calcination temperature. Additionally, weak magnetic anisotropy was observed when the chiral nematic layers were aligned transverse or longitudinal to the magnetic field. These new materials may provide insight into magnetically anisotropic materials with hierarchical chiral structures.

### 6.2 Future Directions

The MacLachlan group has been working to explore the liquid crystal self-assembly of CNCs and its applications as a soft-template that can impart chiral nematic order into novel mesoporous materials. The focus of this thesis was on the development of synthetic procedures to expand and optimize the chiral nematic mesoporous organosilica materials and to begin exploring their potential applications as hard templates and supports.

The materials reported in Chapter 2 and Chapter 4 have provided a framework for the future development of CNMO films with controllable reflected wavelengths and physical properties. Also, they have outlined the limitation of the self-assembly process of CNCs when combined with organosilica precursors. However, there are still opportunities to further investigate the synthesis of CNMOs to create methodology that is more compatible with functional organic bridging groups (i.e. azobenzenes or catalysts directly integrated into the cross-linked structure). It would also be interesting to further investigate the applications of the chiral nanostructured mesoporous organosilicas reported. The propylurea-functionalized CNMO films synthesized in Chapter 2 are of interest as urea-functionalized PMOs are known to have been used in environmental applications, such as remediation of heavy metals in water.<sup>[75]</sup> Another area of future work could be investigating the thermally induced metamorphosis of the alkylene films to produce CNMOs 200

with unique chemical or physical properties. Thermal decomposition the alkylene bridge in the CNMO films could increase the porosity of the material while retaining the chiral nanostructure. This increase in porosity may prove useful when using these materials as hard templates.

The materials reported in Chapter 3 provide a starting point from which the incorporation and future application of the CNMO films as supports for photochromic molecules can be studied. Investigations into the sensitivity and selectivity of metal detection, as well as using aqueous systems is of interest as it would facilitate the real-world application of the materials. Additionally, the effect of both pore size and surface area on the photochromic abilities of the spiropyran/silica composites could be investigated. Furthermore, it would also be interesting to introduce photochromic molecules into the organic bridge of the CNMO materials as a method to control the pore size or reflected wavelength of the films.

In Chapter 4, I reported the first efforts of applying the CNMO films as heterogeneous catalytic supports. Although modest enantioselectivity was observed, detailed investigation into the source of the enantiomeric excess is required. Comparisons between the CNMO and non-chiral organosilicas (i.e. SH-precursor made with disordered or hexagonally arranged pores) as well as detailed analysis on the effect that pore size has on the catalytic conversion and enantioselectivity may help explain these results. I also reported the synthesis of sulfur-bridged CNMO films. Although the desired thioether-bridged CNMO films were not obtained, the synthesis of CNMO films containing acidic groups (SO<sub>3</sub>H) has promise for the continued exploration of the films as heterogeneous supports. Sulfonic acid functionalized PMOs have attracted interest as acid catalysts due to their high surface areas, hydrothermal stability and accessibility of the acid site, and are known to catalyze many reactions including acetylation, esterification and hydrolysis.<sup>[224,230,232]</sup> The sulfur-functionalized CNMO materials could also be investigated for

applications that coordinate metals to the thiol group, which could lead to the production of chiral metal nanoparticles. We are also beginning to investigate the ethenylene-bridged CNMO films as a potential handle for the post-synthetic modification of the CNMO films with functional groups that would not be compatible with the CNC soft-templating procedure. These modifications could include the introduction of aromatic groups, such as anthracene or tetrazine derivatives, through Diels-Alder reactions, or larger functionalized organic molecules, such as peptides, through thiol-ene reactions.

The solvent-based method developed in Chapter 5 was used to successfully synthesize five different chiral nematic mesoporous metal oxide materials. This chapter focused mainly on optimizing the synthetic methodology, therefore, there is significant work that can still be done on the potential application of these materials, such as targeted drug delivery, catalysis, and in microwave circuit design. There are also many opportunities to expand this method to other novel materials. The synthesis of chiral nematic mesoporous aluminum oxides or aluminum-supported metal oxide materials from aluminum nitrate precursors could produce materials with welldeveloped mesoporosity, large pore diameters and crystalline pore walls. These types of materials are known to be catalytically active and have high CO<sub>2</sub> adsorption capacities.<sup>[290,291]</sup> However, a challenge with this synthesis would be the selective removal of the silica template from the crystalline aluminum oxide. The reduction of metal salts (e.g. ammonium tetrachloroplatinate) into the chiral nematic silica materials could also produce mesoporous noble metals with chiral nematic nanostructures.<sup>[292]</sup> Nanostructured mesoporous noble metals are an emerging class of cutting-edge catalysts due to their abundant active sites, highly accessible surfaces and unique chemical and physical properties that can be different from the bulk materials.

The hard-templating of  $C_{60}$  into chiral nematic mesoporous silicas materials is also interesting for the development of mesoporous poly- $C_{60}$  films with an interconnected porous network imparted by the mesoporous organosilica template.<sup>[293]</sup> We have begun to investigate efficient methods to load  $C_{60}$  into the silica through solvent-based methods or vacuum assisted loading. Similar to the ferrite materials reported in Chapter 5, sufficient loading of the precursors is needed to retain the chiral nematic nanostructure after removal of the silica. Optimizing the polymerization of  $C_{60}$  in the solid state and subsequent removal of the silica template could create a poly- $C_{60}$  type material with a unique three-dimensional interconnected structure, which may be beneficial for making efficient solar cells when combined with p-type materials.

Finally, exciting research into understanding the liquid crystal self-assembly of the CNCs is still being explored. Researchers have been investigating the effect of solvents, applied magnetic fields, and drying times on the self-assembly of the CNCs. Since the nanoscale dimensions of isolated CNC rods can vary depending on the biological source, it would be interesting to explore other sources of CNCs and their potential uses as liquid crystal templates.

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# Appendices

### Appendix A Additional characterization for Chapter 2



### A.1 Alkylene-bridged CNMO films

Figure A-1. Characterization for CycMeth-CNMO films. (a)  $N_2$  isotherm, (b) UV-Vis, (c) IR and (d) SEM (scale bar = 2  $\mu$ m).



Figure A-2. SEM image of Hex-CNMO with the repeating chiral nematic nanostructure but containing deposited organosilica crystals (scale bar =  $10 \ \mu m$ ).

Table A-1. Elementa	l analysis of the Hex	-CNMO films
Sample	%C	%H
Hex-CNMO	30.75	5.90
Hex-CNMO	30.75	5.90

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# A.2 Aromatic-bridged CNMO films



**Figure A-3.** N<sub>2</sub> adsorption isotherms for ethylene-bridged organosilica samples with different acid hydrolysis procedures. **Et-CNMO** (black) and **Et-CNMO-HCl** (blue).

<b>Table A-2.</b> N <sub>2</sub> adsorption data for eurylene-bridged organosinca mins					
Sample	BET Surface Area	Pore Volume	<b>BJH Pore Diameter</b>		
	$(m^2/g)$	$(cm^{3}/g)$	(nm)		
Et-CNMO	590	0.87	7.5		
Et-CNMO-HCl	650	0.89	7.5		

Table A-2. N<sub>2</sub> adsorption data for ethylene-bridged organosilica films

Table A-3. Elemental analysis of the aromatic functionalized CNMO films

Sample	%C	%H
Bz-CNMO	31.57	3.63
<b>Bz/Et-CNMO</b>	22.81	3.46
Anth-CNMO	15.73	3.63
<b>Biphenyl-CNMO</b>	16.48	3.76
Biphenyl(20)-CNMO	24.23	3.50



Figure A-4. IR spectra for (a) Bz-CNMO, (b) Bz/Et-CNMO, (c) Biphenyl-CNMO, and (d) Anth-CNMO.



Figure A-5.  $N_2$  adsorption data for phenylene-bridged organosilica samples made from 0.48 mmol precursors / 150 mg of CNC.



Figure A-6. Expanded of the HIM image for Bz-CNMO films at 1.00 µm.

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Figure A-7. Expanded of the HIM image for Bz-CNMO films at 500 nm.

Appendix B Additional characterization for Chapter 3



**B.1** Additional characterization of the SP-Et-CNMO films





Figure B-2. <sup>13</sup>C CP/MAS solid-state NMR spectrum of SP-Et-CNMO films.
## Appendix C Additional characterization for Chapter 4

## C.1 Synthesis of the achiral MnCl(salphen) complex

(2-Aminophenyl)((3,5-di-*tert*-butyl-2-hydroxyphenyl)methylene)-amine (phensal(tBu)H<sub>3</sub>), 3-*tert*-butyl-2-hydroxy-5-(4'-vinylphenyl)benzaldehyde and the MnCl(salphen) complex were prepared according to the procedures reported in the literature.<sup>[294,295]</sup> Phensal(tBu)H<sub>3</sub> (0.033 g, 0.102 mmol), 3-*tert*-butyl-2-hydroxy-5-(4'-vinylphenyl)benzaldehyde (0.028 g, 0.1 mmol), MnCl<sub>2</sub>·4H<sub>2</sub>O (0.020 g, 0.101 mmol) were dissolved in methanol/acetonitrile (10 mL/6 mL) mixture. Triethylamine (35  $\mu$ L) was added and the resulting solution was stirred for 6 h. The solution was then filtered and left undisturbed. Within a few days, the crystals had formed and were collected, washed with pentane, and dried in a vacuum. Yield: (48 mg, 0.075 mmol, 75%). ESI-MS: [M<sup>+</sup>-Cl], m/z = 639.4 (calc.: m/z = 639.3). UV-vis: 253, 306, 358, 478 nm. IR (ATR): 3009 (w), 2951 (m), 2909 (w) 2868 (w), 2351 (w), 1599 (m), 1577 (m), 1529 (s), 1514 (w), 1494 (w), 1463 (m), 1425 (s), 1393 (s), 1357 (s), 1315 (s), 1270 (w), 1258 (w), 1247 (s), 1197 (w), 1181 (s), 1133 (w), 1072 (w), 1048 (w), 1027 (w), 989 (m), 955 (w), 931 (w), 902 (s), 868 (m), 840 (s), 820 (m), 780 (s), 744 (s), 718 (w) cm<sup>-1</sup>.

## C.2 Additional characterization for sulfur functionalized CNMO films



Figure C-1. CD spectrum of a composite film synthesized from precursor 2.



**Figure C-2.** (a) TGA of **5-(60)-Comp** (dashed) and **5-(60)-CNMO** (solid). (b) TGA of **4-CNMO** as labeled. IR spectra for the (c) **5-(60)-Comp** (red) and **5-(60)-CNMO** (black), (d) **4-(30)-Comp** (red) and **4-(30)-CNMO** (black), (e) **4-(50)-CNMO** and (f) **4-(60)-CNMO**.



**Figure C-3.** (a) N<sub>2</sub> isotherms and (b) BJH pore size distributions for two batches of **Mer-CNMO** films used as heterogeneous catalytic supports.



**Figure C-4.** CD spectra demonstrating the variations of  $\lambda_{max}$  in the CNMO samples used for catalysis (a) **Salphen-Mer-CNMO**, (b) **Epox-Mer-CNMO**, (c) **Salphen-SH-CNMO**, and (d) **Epox-SH-CNMO**. Samples varied by ~50 nm making it difficult to compare difference in the  $\lambda_{max}$  between these samples as different pieces of films were used for the CD measurements.



Appendix D Additional characterization for Chapter 5

**Figure D-1.** SEM images of the nickel ferrite material calcined at 200 °C (after removal of the silica template) using (a, b) 1 loading cycle, (c, d) 2 loading cycles, or (e, f) 3 loading cycles. Scale bar = (a, e) 500 nm, (c, f) 1  $\mu$ m, and (b, d) 5  $\mu$ m.