

DESIGN AND SYNTHESIS OF FERROELECTRIC LIQUID CRYSTALS:

- 1) Studies on the de Vries Phase, and
 - 2) Bent-core Achiral Ferroelectrics
-

by

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2) BENT-CORE ACHIRAL FERROELECTRICS

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The final copy of this thesis has been examined by the signatories, and we
find that both the content and the form meet acceptable presentation standards
of scholarly work in the above mentioned discipline.

Abstract

Gong, Tao (Ph.D., Chemistry)

DESIGN AND SYNTHESIS OF FERROELECTRIC LIQUID CRYSTALS:

- 1) Studies on the de Vries phases, and
- 2) Bent-core achiral ferroelectrics

Thesis directed by Professor David M. Walba

Two separate projects in the field of ferroelectric liquid crystals are described, in which target molecules are synthesized to fulfill specific goals: obtaining a better understanding of de Vries liquid crystal behaviors through synthesis of new mesogens; and design, synthesis and characterization of novel polar achiral phases of bent-core liquid crystals.

de Vries liquid crystals are famous for their minimal layer shrinkage on transition from the SmA into the SmC phase. Since such layer shrinkage causes problems for photonics applications such as LCDs, de Vries materials have considerable potential in the display industry. In the de Vries project, work aimed at developing an improved understanding of the de Vries phase by design and synthesis of new compounds possessing de Vries characters. Thus, by incorporating a carbosilane tail, which is expected to suppress out of layer fluctuations in the smectics, into the formally "anti-de Vries" liquid crystal W317, de Vries phases were obtained as evidenced by the "diagnostic" double peak profile in the polarization reversal current. This property, along with other characterization techniques such as differential scanning calorimetry (DSC), X-ray scattering, and polarized light microscopy (PLM), provide insight into the molecular packing in de Vries phases. In

addition, a family of binary smectic mixtures of de Vries/anti-de Vries materials was studied to exam the “cone model” of de Vries phases.

The polar phases of achiral bent core liquid crystals have been a topic of intense investigation since their discovery in 1997. In this project, a family of "one-tail" bent core liquid crystals with polar group on one side of the aromatic core, and a carbosilane tail on the other, were synthesized and studied by means of DSC, X-ray, PLM, and other techniques. A novel structure designed to test a popular model for formation of the SmAP_F phase refuted the model, as hoped, and provided a new material with very high polarization, and showing "ideal" electrostatic V-shaped electro-optic switching. Such behavior could be potentially applied in devices exhibiting optical latching (no or little power required to maintain a gray level). Furthermore, another novel low temperature phase, denoted as the SmX phase since the structure is not understood, was discovered in one of the family. This SmX phase seems to be similar to the B4 helical nanofilament phase.

This thesis is dedicated to my parents and my wife, Wei,

for their never ending love and support!

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Chapter 1. Introduction

1.1 Liquid Crystals and Liquid Crystal Phases

Liquid Crystals (LCs), which were first discovered by Friedrich Reinitzer in 1888, are anisotropic liquids possessing the fluidity of true liquids, as well as varying degrees of long range orientational order normally associated with crystalline solids.¹ LC phases are also called mesophases and LC molecules are also called mesogens.

For many LC phases, including the thermotropic smectic and columnar phases, and lyotropic phases, a key unique feature is immiscibility of different parts of the molecules. Typical LC molecules of this kind will contain two or more groups with limited compatibility, so that each group prefers to interact with corresponding groups on adjacent molecules rather than with the incompatible groups.

Lyotropic LCs often occurs when parts of the LC mesogens are immiscible in a solvent. This is most common when the solvent is water and the mesogens are amphiphilic (e.g., biological membranes).² A lyotropic LC mesogen usually consists of one or more long, nonpolar alkyl tails, immiscible with water, and an ionic, hydrophilic polar head group. In the lyotropic phases, solvent molecules fill the space around oriented domains of mesogen molecules. In lyotropic systems, changing concentration of the mesogens does give changes in the preferred phase (e.g., lamellar, cubic, etc.)

Thermotropic LCs, on the other hand, can be neat fluids or miscible mixtures of mesogens exhibiting one or more anisotropic liquid phases between the melting point and

the temperature at which they become orientationally isotropic; such temperature is called the clearing point due to the milky, translucent appearance of LC phases, and the transparent appearance of isotropic organic melts. In general, thermotropic LC mesogens can be divided into three classes according to their shapes: discotic, calamitic and bent-core. As illustrated in figure 1.1, discotic (or disc-shaped) mesogens can self-assemble into columns of discs, forming columnar phases; calamitic (or rod-shaped) mesogens can form layered or lamellar phases (smectics); and bent-core mesogens can form smectic and columnar phases.³ In all of these cases, the mesogens contain relatively rigid cores and relatively flexible tails while the bent-core mesogens possess a chevron-shaped rigid core.⁴ The work described herein will focus on LC phases obtained from calamitic and bent-core mesogens.

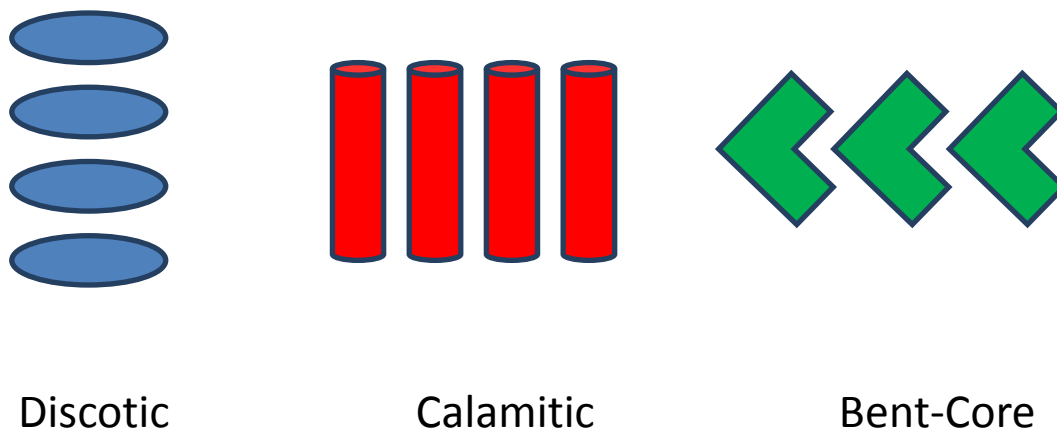


Figure 1.1: Three common molecular shapes for thermotropic LC molecules are discotic, calamitic, and bent-core.

1.2 Calamitic Liquid Crystals

Most calamitic mesogens exhibit more than one LC phase, a phenomenon known as polymorphism. The phase observed is temperature dependent and generally occurs

reproducibly with heating or cooling. Some LC phases only exist in a super-cooled state below the melting point, and are termed monotropic; these phases are kinetically stable but will eventually crystallize or transition to another, more thermodynamically stable LC phase. LC phases observed upon heating above the melting point are termed enantiotropic, and are thermodynamically stable. Of the many known LC phases, there are three common and well-studied phases: Nematic (N), Smectic A (SmA) and Smectic C (SmC), as illustrated in figure 1.2.

The nematic phase is the least ordered, and unique in that there is no long range positional order, there being only long range orientational order. This phase is thus not driven by immiscibility of parts of the mesogens. Typically, the nematic phase is the first mesophase observed upon cooling from the clearing point. In the nematic phase, the average molecular long axis (the director, denoted $\mathbf{n}$) orients along a macroscopic axis (the macroscopic director, also denoted $\mathbf{n}$) and is usually more or less parallel to the long axis of the molecules, depending upon the degree of order.

Upon further cooling, the mesogens will often spontaneously assemble into layers, producing a smectic phase. Smectic phases possess not only the long range orientational order similar to the nematic phases, but also long range positional order in one dimension.

In the SmA phase, the molecules form layers where the molecular long axis is parallel to the layer normal ($\mathbf{Z}$). Since the director ($\mathbf{n}$) is defined by the long axis of the molecules, it is parallel to $\mathbf{Z}$, in the SmA phase.

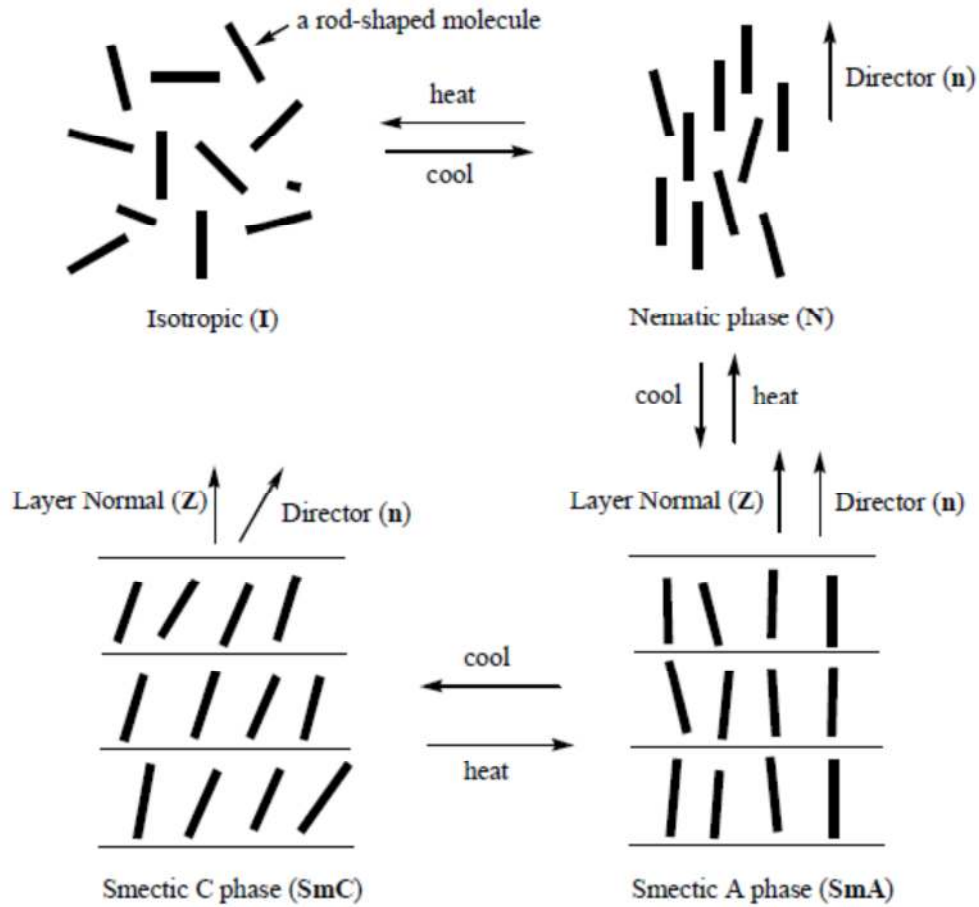


Figure 1.2: Three common calamitic LC phases are nematic, smectic A, and smectic C, listed in order of descending temperature. The individual molecules have average alignment along the director (n), and if layers exist they have a layer normal (Z).

In the SmC phase, molecules are more ordered, assembling into layers, as in the SmA, and in addition tilting uniformly from the layer normal. The angle between Z and n is defined as the tilt angle θ . The tilt angle θ usually increases with decreasing temperature until it saturates at some characteristic value. The tilt plane is defined as the plane including the layer normal and the director.

1.3 Ferroelectric Liquid Crystals and de Vries Smectic Liquid Crystals

1.3.1. Symmetry, Chirality and Ferroelectric Liquid Crystals

The study of ferroelectric liquid crystals (FLCs) has grown rapidly during the past 30 years, since the invention of surface stabilized ferroelectric liquid crystal (SSFLC) devices by Clark and Lagerwall in 1980.⁵ Ferroelectricity, which was first discovered by Valasek in inorganic solids in 1920, is a property of certain materials in which they possess a spontaneous electric polarization that can be reversed by the application of an external electric field.⁶ In order to have such spontaneous polarization, the material must possess certain symmetry. There are 32 different crystal symmetries, denoted as point groups. If a crystal has a structure which does not possess the inversion symmetry, the crystal would exhibit piezo-electricity (except O). Piezo-electric crystals exhibit induced electric dipoles (polarization) under a mechanical stress, and the piezo-electric materials include 20 of the crystal point groups, 10 of which are also pyro-electric. The pyro-electric crystals may possess polarization even in the absence of external fields like mechanical stress or an electric field (i.e. pyro-electric crystals possess spontaneous polarization) [see Table 1.1]. This polarization can be temperature dependent, hence the name. Crystals classified with one of the 10 pyro-electric point groups are able to become ferroelectric, a phase where the spontaneous polarization switches its direction by application of external electric fields. Ferroelectrics are said to possess polar symmetry, and can be chiral (C_n symmetry in the Schoenflies nomenclature) or achiral (Schoenflies C_{nv}).

Point group (32)									
Piezo-electric					Center-symmetric				
Pyro-electric									
C_1 (1)	C_s (m)				C_i ($\bar{1}$)				
C_2 (2)	C_{2v} (mm2)			D_2 (222)	C_{2h} (2/m)	D_{2h} (mmm)			
C_3 (3)	C_{3v} (3m)			D_3 (32)	C_{3i} ($\bar{3}$)	D_{3d} ($\bar{3}m$)			
C_4 (4)	C_{4v} (4mm)	S_4 ($\bar{4}$)	D_{2d} ($\bar{4}2m$)	D_4 (422)	C_{4h} (4/m)	D_{4h} (4/mmm)			
C_6 (6)	C_{6v} (6mm)	C_{3h} ($\bar{6}$)	D_{3h} ($\bar{6}m2$)	D_6 (622)	C_{6h} (6/m)	D_{6h} (6/mmm)			
		T (23)	T_d ($\bar{4}3m$)		T_h (m3)	O_h (m3m)			
						O (432)			

Table 1.1: 32 point groups and electric properties allowed in these point groups.

The existence and consequences of polar order in organic molecules makes organic ferroelectric materials possible in principle. For practical and scientific reasons, the possibility of spontaneous polar order in liquid phases is a fascinating prospect. However, isotropic organic materials (normal liquids) are not ferroelectric, since they possess isotropic point group symmetry (K_h), in which case individual dipole moments from organic molecules cancel themselves out macroscopically. Liquid crystals, on the other hand, are anisotropic, which makes them a candidate for ferroelectricity in fluid phases.

If we consider the point group symmetries of LC phases, they are obviously different from the point group symmetries of crystals since the average nuclear positions are invariant in crystals. However, it is natural to consider the symmetry of a fluid as the group of symmetry operation that leaves the phase unchanged on the time average. Therefore, the nematic and SmA phases of calamitic LCs can be classified as possessing

$D_{\infty h}$ point group of symmetry, and the SmC phase of calamitic LCs can be classified as possessing C_{2h} point group of symmetry. Neither of these, however, fit into the pyro-electric point groups.

To obtain an LC phase with piezo- or pyro-electric properties, the system must possess polar symmetry. Meyer first realized that the situation could be achieved by introducing chirality in a tilted smectic.⁷ At the time of Meyer's insight, chiral liquid crystals were well-known. Indeed, the first liquid crystals studied by Reinitzer were chiral natural products (esters of cholesterol), and therefore enantiomerically pure. Such chiral LCs, composed of non-racemic molecules, form chiral nematic (N^*) and chiral smectic (SmA^* and SmC^*) phases. These phases do not possess inversion symmetry, and more importantly, the SmC^* phase, with C_2 symmetry, is pyro-electric. In their famous paper of 1975, Meyer and coworkers demonstrated the existence of a spontaneous polarization in a SmC^* LC mesogen.

However, in bulk SmC^* LC phases, molecular chirality causes the tilt direction precess slightly from layer to layer; the tilt directions of molecules forming a helical structure as shown in figure 1.3, and the spontaneous polarization is cancelled out macroscopically just as in isotropic liquids. To observe bulk spontaneous polarization, the helix must be unwound. Furthermore, to observe the simplest true ferroelectric behavior, the system must exhibit bistable polarization switching with hysteresis in the polarization current response to applied fields.

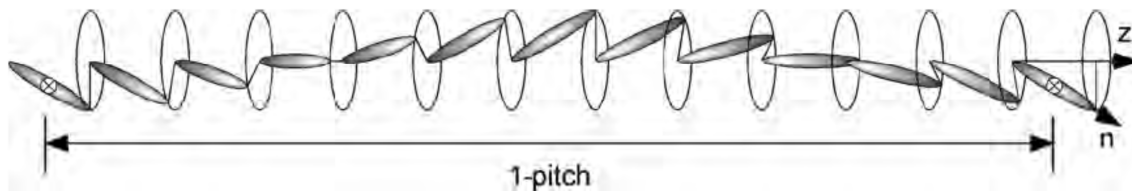


Figure 1.3: SmC* phase helical superstructure of a calamitic liquid crystal.

Clark and Lagerwall proposed a way to suppress the helix, and to achieve bistability and hysteresis with the demonstration of the surface-stabilized ferroelectric liquid crystal (SSFLC) arrangement.⁵ In a thin cell in which smectic layers align more or less perpendicular to the substrates, and the director prefers to orient more or less parallel to the substrates, the helix is constrained when the cell gap that is less than about two times the helical pitch. Interaction forces between the liquid crystal and the bounding plates unwind the intrinsic helix, and provide bistability. Ferroelectric domains in which spontaneous polarization is in opposite directions are observed in such cells and the polarization switches by application of an external electric field with magnitude greater than a characteristic threshold value dependent upon the details of the cell surface treatments and the LC material.

1.3.2. Antiferroelectric Liquid Crystals

It is less known that, although possessing fewer applications, there are in fact more antiferroelectric materials than ferroelectric materials in crystals.⁸ So it would be interesting to look at the corresponding antiferroelectric analogs in smectic LC phases. In the ferroelectric SmC* phase, molecules tilt in the same direction from layer to layer (ignoring the small precession angle in the bulk) and hence in an SSFLC cell the directions of spontaneous polarization from layer to layer orient uniformly as expected. If

the molecular tilt directions (and the tilt planes) alternate from layer to layer with a near 180° dihedral, the antiferroelectric SmC_A^* phase is obtained, and the directions of the spontaneous polarization also alternate from layer to layer. Such a phase possesses non-polar symmetry, and the layer polarizations cancel for pairs of layers. Chandani *et al.* first reported such materials, and showed that with an external electric field above a threshold value, the spontaneous polarization in each layer would align along the field to produce field induced SmC^* phases, as illustrated in figure 1.4.⁹

Initially, antiferroelectric LC materials received less attention than ferroelectric LC materials. But due to the details of driving LC cells (specially the requirement that the integrated electric field over a relatively short time must be zero, i.e. no net DC field should be applied to the LC), antiferroelectric LCs did become a subject of intense study for applications in the information display field. Even more recently, orthoconic antiferroelectric LCs have been found extremely useful in principle: when the tilt directions in adjacent layers are made perpendicular to each other (i.e. $\pm 45^\circ$ tilt), the material becomes negatively uniaxial which means a perfect dark state can be achieved.¹⁰ Another interesting fact about antiferroelectric calamitic LCs is that the kinds of molecular structures that provide such phases is much more limited than for the SmC^* phases. Techniques for creations of new SmC_A^* phases forms an important aspect of the research described herein.

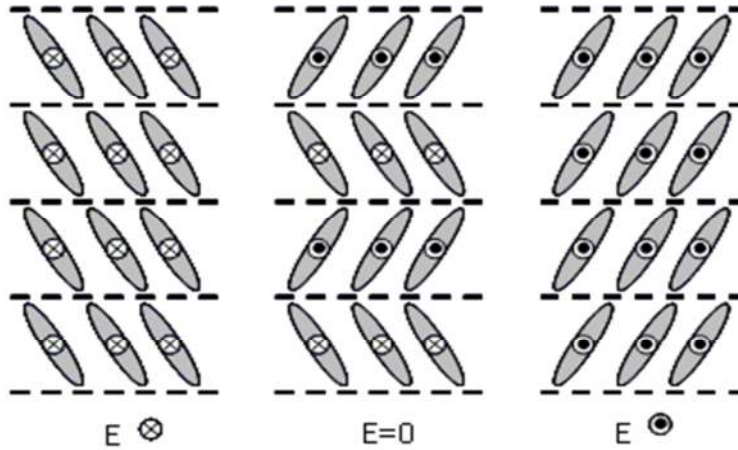


Figure 1.4: Side views of SmC_A^* LC in a surface stabilized cell. With an external electric field, the material exhibits induced SmC^* behavior.¹¹

1.3.3. de Vries Smectic Liquid Crystals

The great application potential of both ferroelectric and antiferroelectric LCs has especially been demonstrated in flat-panel displays, which are now dominated by nematic LCs. In nematic LCs, the lack of positional order makes them easy to incorporate in various device geometries without forming defects. However, nematic LCs are relatively slow, with response times of about 10-20 ms. Ferroelectric and Antiferroelectric Smectic LCs, on the other hand, are 100-1000 times faster and therefore are very attractive for the most demanding applications in this area.

Although it looks very promising, there have been many serious problems in the application of those materials due to the fact that the smectic layers normally shrink and form a variety of defects at the tilting transition from the SmA^* phase to the $\text{SmC}^*/\text{SmC}_A^*$ phase as shown in figure 1.5.¹² In the SmA^* phase, molecules are translationally anchored along the surface. At the transition, molecules tend to tilt and the smectic layers tend to shrink. However, molecules at the surface preserve their anchoring

and the only possibility compatible with both the surface anchoring and the $\text{SmC}^*/\text{SmC}_A^*$ structure is that the layers buckle into the chevron geometry from the bookshelf geometry in the SmA^* phase.

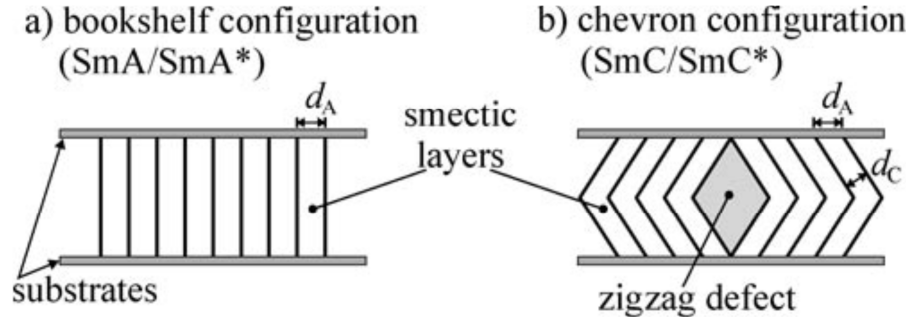


Figure 1.5: As a result of smectic layer shrinkage, a SmA sample confined between two glass substrates in the bookshelf configuration (a) transforms from the bookshelf configuration (b) when entering the SmC phase.¹²

Chevrons pointing in opposite directions are separated from each other by striking defects called zigzag lines, an example of which is shown in figure 1.6. The formation of chevrons and zigzag defects severely degrades the quality of any electro-optic device based on ferroelectric and antiferroelectric LC materials. So it is natural to think that one possible solution to this problem is to find materials without substantial layer shrinkage at the tilt phase transition.

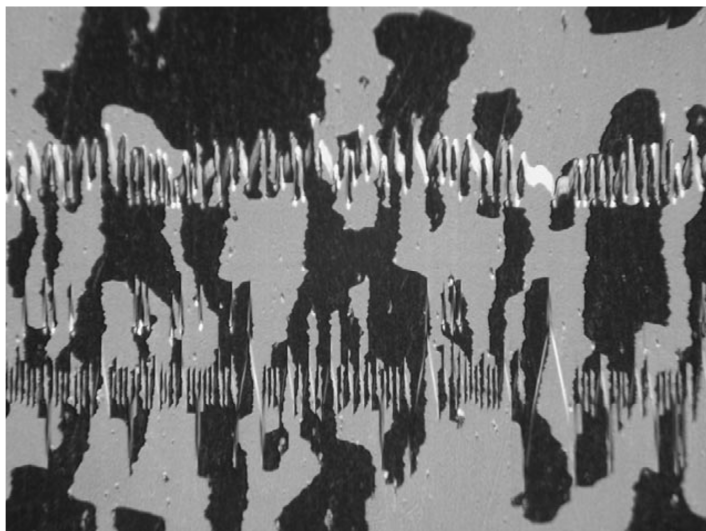


Figure 1.6: Example of zigzag defects in the SmC phase seen in the polarizing microscope.¹²

Interestingly, long before people started to think about the possibility of using ferroelectric and antiferroelectric LCs in display, materials with virtually no layer shrinkage at the SmA-SmC transition have been found and de Vries was among the first to propose a possible model for such material: mesogens in the SmA phase have a tilted molecular orientation and random azimuthal distribution and the SmA-SmC transition is described as an ordering of azimuthal distribution that results in zero layer shrinkage.^{12, 13} Such materials didn't attract much attention until they became a clear solution to make ferroelectric and antiferroelectric LC devices and lots of effort were put in this research field since. However, despite many models proposed by de Vries and other people, the structure of de Vries smectic liquid crystals has yet to be fully elucidated.¹⁴

1.4 Bent-core Liquid Crystals

1.4.1 Bent-core Liquid Crystals

Unlike calamitic LCs, bent-core LCs, also known as “banana-shaped” LCs (see figure 1.1 and figure 1.7), possess a bent-shaped rigid core which was first synthesized in 1903 by Vorlander.¹⁵ However, at that time the LC phases of such mesogens were not paid much attention. 90 years later, bent-core mesogens were again independently synthesized by Niori *et al.* and they also reported electro-optic switching behavior in one of bent-core LC phases (B2 phase) which started to attract people’s interest.¹⁶

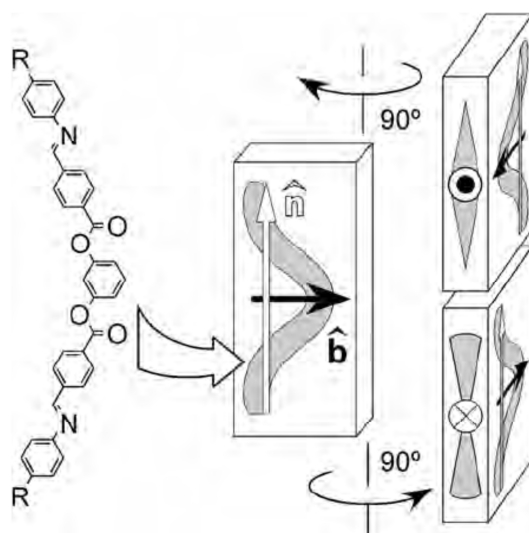


Figure 1.7: One of conventional chemical structure of bent-core mesogens P-n-(O)-PIMB (left) and symbolic representation of the bent-core molecules (right). White arrow in right figure represents molecular long axis, $\hat{n}$, black arrows represent bent director $\hat{b}$.

Because of the bent shape of the core, the mesogen doesn’t possess C_∞ symmetry as in the calamitic LC along the molecular long axis, and such mesogens are capable of producing unique phases that calamitic LCs do not form. In the relatively short history of bent-core LCs, there are many bent-core LC phases have been discovered and people started to name them B_i (B_1 to B_7) at first.¹⁷ Later on, as detailed structures of new phases was gradually investigated, people realized that there were a lot of bent-core LC phases having similar but slightly different structures and start to name those phases the same

way as names used in calamitic LC phases, for example, SmA or SmC, with additional characters and suffixes. In this thesis, both names will be used. Among many bent-core LC phases, our group is particularly interested in B₂, B₄ and their related phases.

1.4.2 B₂ Phase

As illustrated in figure 1.7, bent-core mesogens possess C_{2v} point group symmetry and such molecular structures are considered pyro-electric (see Table 1.1) and should lead to the spontaneous polarization along bent director **b**. Based on that principle, whereas molecular chirality allows for a macroscopic spontaneous polarization and results in ferroelectric or antiferroelectric polar structures in tilted smectic phases in calamitic mesogens, we can also obtain ferroelectric and antiferroelectric LCs from achiral bent-core mesogens. Many achiral bent-core mesogens with C_{2v} symmetry (some of them are asymmetric, as we will see in this thesis, but the local symmetry of a smectic layer can be regarded as C_{2v}, since the head and the tail are equivalent in the layer) effectively results in a polar packing of bent molecules within a given layer if molecules do not rotate freely around their long axis. Niori *et al.* first observed the ferroelectric-like switching current in B₂ phase and attributed such behavior to the close packing of molecules in a smectic layer.¹⁶ Later on, B₂ phase was investigated in more details by Link *et al.* and now is a general term for simple SmCP structures in which four possible variations exist: SmC_AP_F, SmC_SP_F, SmC_AP_A, SmC_SP_A as illustrated in figure 1.8, the subscript S and A is used to denote synclinic and anticlinic; the subscript F and A is used to denote ferroelectric and antiferroelectric.^{4, 18, 19} Among those four structures, two are conglomerates of enantiomers.

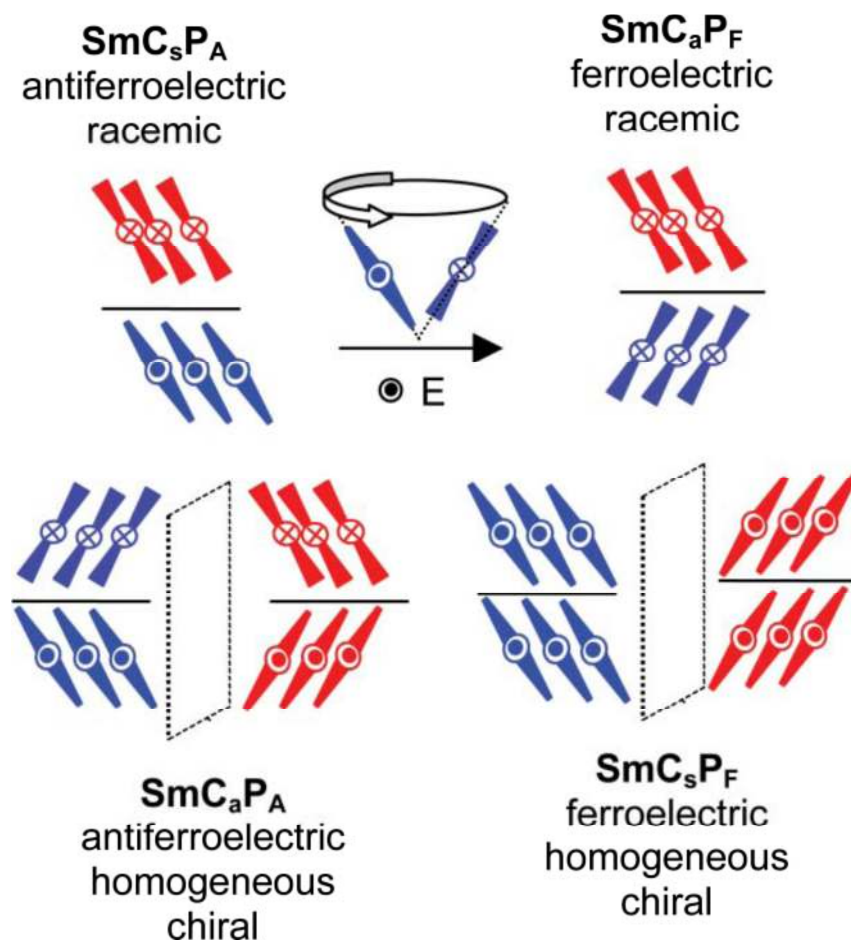


Figure 1.8: Four structures of B_2 phase (SmCP phase). In two of them (SmC_aP_A and SmC_sP_F) the layer chirality (indicated by blue and red) is identical in adjacent layers. In other two (SmC_sP_A and SmC_aP_F) the layer chirality changes from layer to layer which corresponds to macroscopic racemic structures. In addition, the switching on the cone is shown in the middle.⁴

1.5 Experimental Techniques

Several techniques were used in this thesis to characterize LCs and LC phases. In addition to common techniques used to characterize organic molecules such as proton and carbon nuclear magnetic resonance spectrometry (1H -NMR and ^{13}C -NMR), mass spectrometry and elemental analysis, there are also techniques to characterize the bulk phase behavior of the LCs rather than individual molecular properties.

Optical observations of LC phases were carried out through a polarized light microscope (PLM) (Zeiss, Germany) equipped with a hot stage (Instec, US). The

function of PLM is as follows: when the regular, unpolarized light passes through the polarizer, polarized light will be generated. This polarized light is split into ordinary and extraordinary rays when passing through the sample and recombine to pass through the second crossed polarizer (usually named the analyzer). If the sample is isotropic, the light does not pass through the analyzer and thus the sample appears black under PLM. If the sample is anisotropic (i.e. LCs), it would have different refractive indices in different direction, a condition known as birefringence. Since the ordinary and extraordinary rays travel at different speeds, the two will be out of phase when they recombine and as a result, the ray will become elliptically polarized and capable of passing through the analyzer. That's the reason why LCs always shows a lot of different colors under PLM. Also, by adding the hot stage to the PLM, we could study the phase behaviors of LCs under different temperatures.

In most of the PLM experiments in this thesis, as shown in figure 1.9, LCs were sandwiched between two pieces of glass that were coated with a thin layer of indium tin oxide (ITO), a transparent conductive electrode so that the electro-optic behavior of LCs could be measured, and sometimes an alignment layer such as polyimide, nylon or Teflon. LC cells with both planar (LC molecules parallel to the substrate) and homeotropic (LC molecules perpendicular to the substrate) alignments were used.

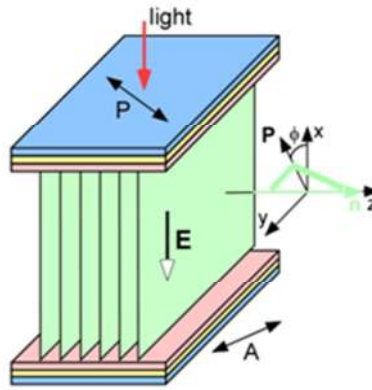


Figure 1.9: An example of a LC cell in PLM, showing bent-core LCs with bookshelf smectic layers (green) in a cell with ITO electrodes (yellow) and planar alignment layers (pink) between crossed polarizer and analyzer.

Electro-optical behavior was studied using LC cells of 2-10 μm thickness with ITO conductive electrodes and proper alignment layers. In the cell, switching of the FLC molecules in response to a reversal of applied field causes a current that can easily be measured. If the area of the electrode is known, then the integration of this polarization reversal current peak and division by the electrode area gives a measure of the magnitude of polarization, which has units of charge/unit area (figure 1.10).

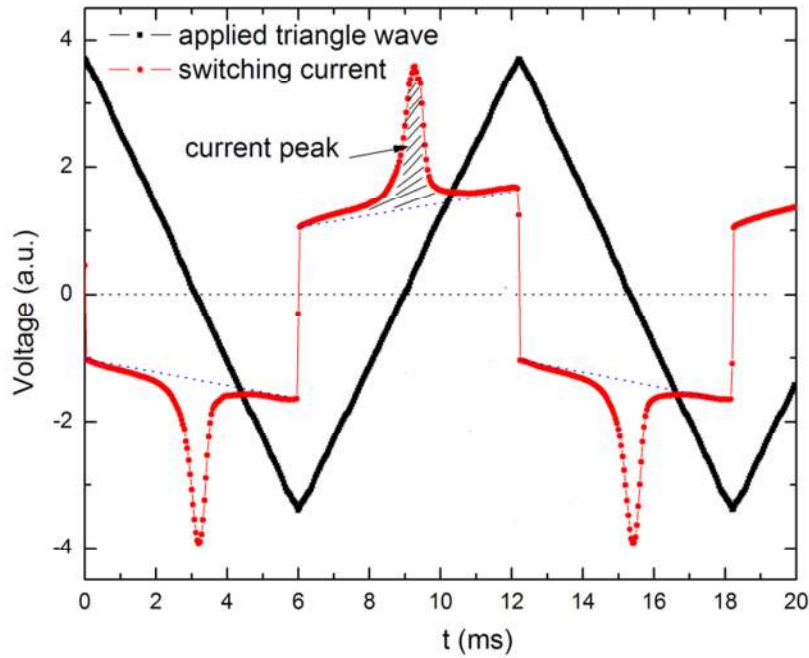


Figure 1.10: An example of the measurement of the polarization (shadowed area) in FLCs.

Differential scanning calorimetry (DSC) is a thermoanalytical technique for detecting LC phase transitions with high accuracy. Both the sample and the reference are sealed in a small aluminum pan, placed in a chamber and heated at a controlled rate. When the sample undergoes a phase transition, more or less heat will need to flow to it than the reference to maintain both at the same temperature and the difference in energy required is plotted with respect to temperature to produce a DSC curve with multiple peaks, which are corresponding to certain phase transitions. There are two different types of phase transitions on DSC curves. First order phase transitions show a big peak, corresponding to a large enthalpy change and second order phase transitions, on the other hand, are based on very small enthalpy change and therefore show a very small peak (i.e. the SmA to SmAP_F transition in bent-core LC W623) as illustrated in figure 1.11.

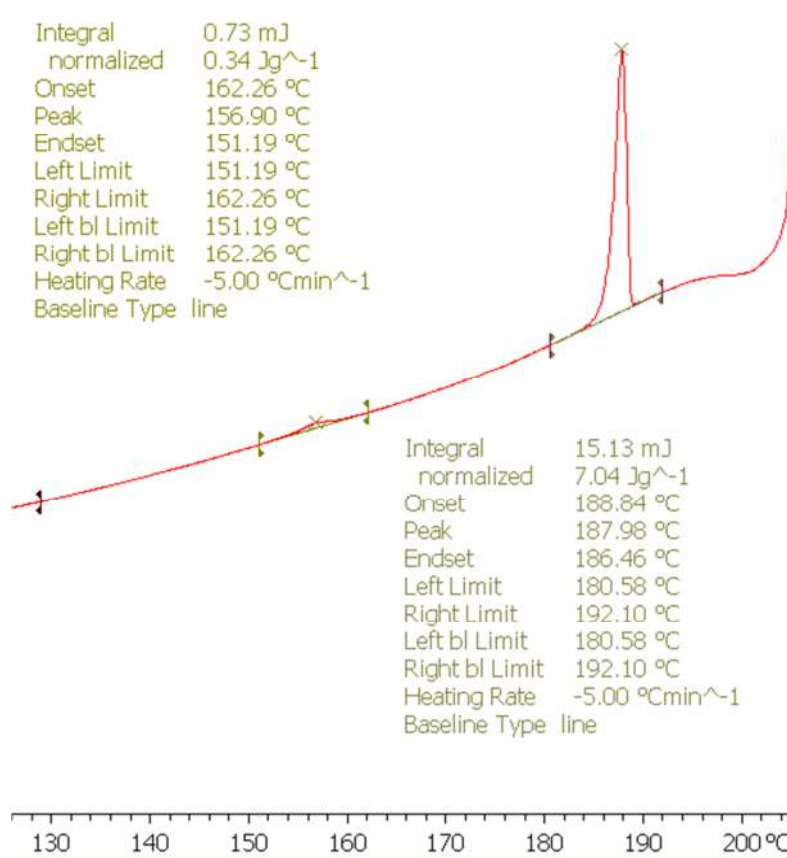


Figure 1.11: DSC curve of W623 on cooling, showing a first order transition from isotropic to SmA and a second order transition from SmA to SmAP_F.

The x-ray diffraction (XRD) experiment is another very useful technique to measure the properties of LCs. In general, powder XRD experiments can be used to measure the periodicity in bulk LCs. For SmC* and SmAP_F materials which will be studied in the following chapters, that periodicity is often times the layer spacing of the smectic layers and that not only gives the information of phase transition but also the LC molecular behavior at the phase transition. In addition, resonant XRD experiments were carried out to explore the subtle information in between the layers.²⁰ In this thesis, XRD experiments were carried out at the National Synchrotron Light Source at Brookhaven and at the University of Colorado at Boulder.

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Chapter 2. Studies on the de Vries Phase

2.1 Introduction

As discussed in chapter 1, although ferroelectric and antiferroelectric smectic LCs are very promising as faster alternative to nematic LCs in applications such as flat-panel displays, there have been many serious problems. Mainly, these involve two issues: 1) Obtaining “clean molecular alignment”, meaning the liquid crystal exists as a stable monodomain free of visible defects; and 2) the need for net DC balance in driving the liquid crystal pixels.

Focusing on the former problem, alignment in FLCs is difficult due to the fact that the smectic layers shrink, forming various defects at the tilting transition from the SmA* phase to the SmC*/SmC_A* phase (figure 1.5).¹ In this chapter a possible solution to this problem is discussed. The issue of DC balanced drive is addressed in Chapter 3 of this thesis.

With regard to problems caused by layer shrinkage with tilt, this issue also affects another highly promising FLC electro-optic mode: the electroclinic effect; First described by Meyer and Garoff,² involves an induced tilt in SmA* materials upon application of an applied field, with the tilt occurring in a plane normal to the field as illustrated in figure 2.1. These materials are also promising candidates for display application and there are a lot of such materials possessing quite a large maximum induced tilt angle. Unfortunately, like SmC materials, tilt-induced layer shrinkage occurs, causing defects in the smectic layer. A strong temperature dependence of the electroclinic coefficient, χ (defined as tilt

per unit applied field), approaching the SmC* phase on cooling, is also highly problematical. So materials which do not exhibit layer shrinkage within the SmC* and/or SmA* tilt would be highly desirable.

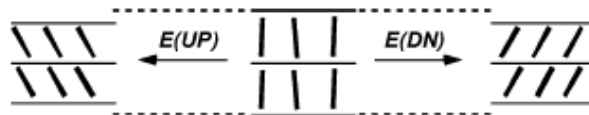


Figure 2.1: electroclinic effect of SmA* LCs under applied field.

One possible solution was suggested by Adriaan de Vries in 1977.³ de Vries first described materials showing a novel type of SmA-SmC transition with small layer shrinkage. These materials are, as a class, now termed as de Vries Smectics. In one model, in the de Vries SmA phase, molecules are tilted with respect to the layer normal, but the tilt direction is random on a small length scale, giving an average orientation parallel to the layer normal, as illustrated in figure 2.2. The molecules can be thought of as being constrained to lie on a cone, where the cone's vertex angle remains constant but the molecule can lie on any path from the top of the cone to the base.

In the presence of an electric field, or at the SmA-SmC transition, the tilt becomes “biased” towards one side of the cone coherently, leading to the observed optical tilt, but without nominal layer shrinkage. In principle, by exploiting de Vries SmA* LC materials, the problem of smectic layer shrinkage could be largely overcome. Moreover, the discovery of materials with a large value of χ make de Vries Smectics highly promising in display applications.

Other de Vries materials' properties include increase in birefringence for increasing optical tilt; lack of a nematic phases; “shallow” chevrons; electrostatic V-shaped

switching for materials with high polarization; optically bistable electro-optic switching and bookshelf alignment in SSFLC cells for materials with low polarization; and a large value of the surface electroclinic effect.⁴ While de Vries materials are sometimes lacking in one or more of these characteristics, de Vries materials often possess many of them. However, until recently it was unknown how to achieve de Vries Smectic LCs in a directed way and why these materials have such unique properties.

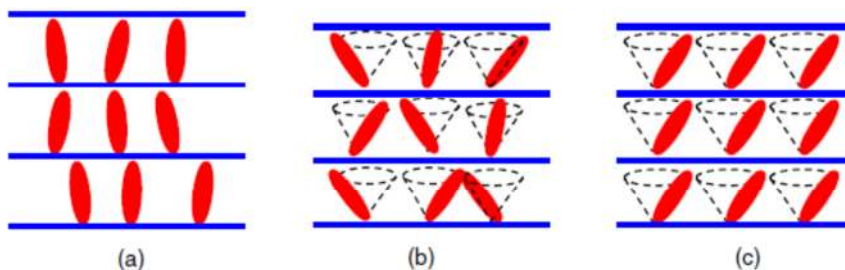


Figure 2.2: Schematic representation of molecular arrangement in (a) conventional SmA, (b) de Vries SmA, and (c) SmC.⁵

2.2 Goals and Prior Work

Our group has proposed a hypothesis of achieving de Vries materials. Just like anticlinic antiferroelectric LCs, in order to obtain such a phase without a large entropy cost, the typical out-of-layer fluctuations occurring in nominal synclinic smectic LCs must be suppressed by the mesogen structure.⁶ This suppression of out-of-layer fluctuations by the mesogen structure also suggests an explanation for the observed lack of nematic phase in both anticlinic antiferroelectrics and de Vries smectics, since the nematic-smectic phase transition involves such fluctuations. And it is known that incorporating heteroatoms or changing the conformation of the tail could result in such suppression.

Based on this strategy, several years ago, Lixing Wang in our group synthesized one interesting LC material, **W530**, with a perfluorocarbon tail at one end and an O-2-methylalkoxy tail at the other (figure 2.3).⁷ While the reason this combination of structural elements produces de Vries phases is a current topic of great interest in the community, one simple mode holds that two factors are involved: 1) The fluorocarbon essentially nano-phase separates with a high degree of order, thereby suppressing out of layer fluctuations; and 2) The alkoxy tail exists in the phase in conformations where the alkyl chain is on average more orthogonal to the director than usual – i.e. the hydrocarbon tail orients parallel to the layer interface, thereby also suppressing out of layer fluctuations. Whatever the reasons, **W530** shows a de Vries SmA phase over a wide temperature range (figure 2.4 (a)) and also shows an interesting double peak profile in the polarization reversal current, as shown in figure 2.4 (b), which is normally observed in antiferroelectric LC materials. On ramping an applied triangular electric field from the positive maximum, an electric field-induced SmC* first relaxes to the non-polar SmA* phase (the thermodynamic phase for antiferroelectric LCs), producing one current peak. Passing through zero applied field and increasing the negative applied field, when the FLC switching threshold is reached, switching to the SmC* with polarization reversal produces the second current peak. The occurrence of two peaks in one “ramp” of the applied field with **W530** led us to believe that some version of anticlinic layer interfaces might be involved in the structure of de Vries LCs. Prasad *et al.* also reported similar results in de Vries LCs with siloxane tails.⁸

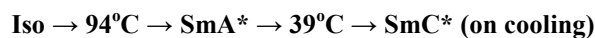


Figure 1 consists of two plots, (a) and (b), showing the thermal behavior of P(VAc-co-VAcO).

Plot (a) shows the d-spacing (Å) versus Temperature (°C). The d-spacing increases from approximately 31.0 Å at 30°C to a plateau of about 33.8 Å between 60°C and 75°C, and then decreases to about 33.5 Å at 90°C. The plot includes data for Cooling (solid line with circles), Heating (dotted line with circles), and Cooling (dashed line with squares). A shaded gray region highlights the temperature range from approximately 35°C to 45°C.

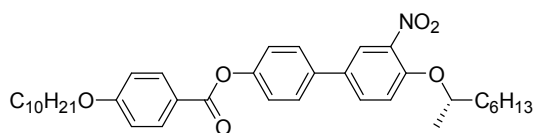
Plot (b) shows the variant intensity versus Temperature (°C). The variant intensity is zero for temperatures below 35°C and above 85°C. It shows a positive peak of about 0.5 at 50°C and a negative peak of about -0.6 at 75°C. The plot includes data for Cooling (solid line with circles), Heating (dotted line with circles), and Cooling (dashed line with squares). A shaded gray region highlights the temperature range from approximately 35°C to 45°C.

In another approach to developing and understanding de Vries phase, two other interesting LC materials produced by our group, **W317** and **W415**(structures, phase, and transition temperatures give below), which possess very similar structures, as illustrated in figure 2.5, are under investigation.⁹⁻¹²

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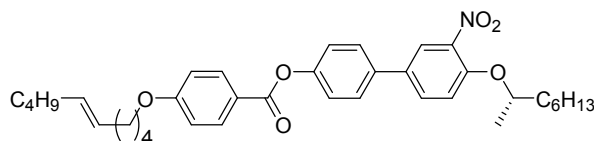
In addition, **W317** also exhibits a relatively large χ , which is remarkably temperature independent over a wide SmA* temperature range. This phenomenon is also very rare.¹¹

Interestingly, a very small modification of the **W317** structure; removing two hydrogens from the n-decyl tail to produce a trans double bond, to give **W415**, provides a material with de Vries character with a relatively small SmA* temperature range.¹² Because of their similarity in structure, those two materials are believed to be miscible and should provide very interesting mixtures with promising properties, ideally de Vries SmA LC phases with temperature independent χ . In addition, the properties of the mixtures could provide useful information to help explore the origin of de Vries Smectic LC behavior. It would also be interesting to replace the hydrocarbon tail in **W317** with some other tails expected to show nano phase-segregation and to suppress out of layer fluctuations to see whether or not such changes would generate new de Vries Smectics.



W317

Iso $\rightarrow$ 76°C $\rightarrow$ SmA* $\rightarrow$ 23°C $\rightarrow$ SmB $\rightarrow$ -7°C $\rightarrow$ X (on cooling)



W415

Iso $\rightarrow$ 34°C $\rightarrow$ SmA* $\rightarrow$ 26°C $\rightarrow$ SmC* $\rightarrow$ 0°C $\rightarrow$ X (on cooling)

Figure 2.5: Molecular structures of W317, W415 and their phase sequence on cooling.

2.3 Design and Synthesis

As first accomplished in our group by Blanca Ross, the synthesis of **W317** is quite straightforward, as illustrated in figure 2.6.¹² Selective mononitration of biphenyl-4,4'-diol gave a mixture of the desired mono-nitro-biphenol **1**, along with dinitrated product, after chromatography of the crude product. This mixture was carried forward without further purification. Mitsunobu coupling of R-2-octanol with nitrophenol **1** gave the desired nitrophenol ether **2**.¹³ Commercially available 4-Decyloxy benzoic acid was then used to couple with nitrophenol ether **2** under DCC coupling condition to yield compound **3**, **W317**, as final product.

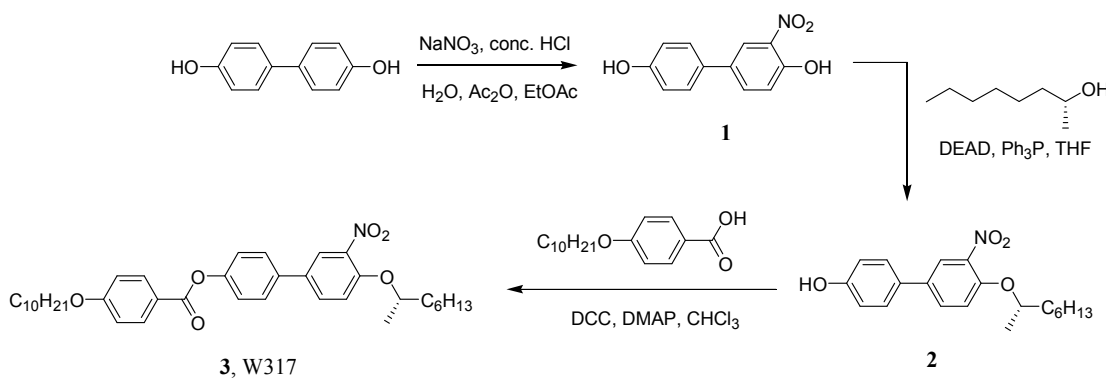


Figure 2.6: Synthesis of **W317**.

Synthesis of **W599**, a **W317** analog possessing the tricarbosilane tail (also an analog of an interesting de Vries material TSIKN65, produced by chemists working in the Naval Research labs following leads from our group, and that of Coles in the UK) was accomplished as indicated in figure 2.7 in order to provide additional de Vries type materials.¹⁴

Thus, the mixture of mono and di nitrated biphenol **1** were used to couple with R-2-pentanol under Mitsunobu coupling conditions to give the desired nitrophenol ether **4**. Meantime, the tricarbosilane tail **6** can be synthesized based on nucleophilic substitution. Commercially available Chloromethyltrimethylsilane can be successfully converted to the corresponding Grignard reagent and attack the chloro(chloromethyl)dimethylsilane under a substitution pathway to form chloro dicarbosilane **5** with excellent yield. A similar reaction to convert chloro dicarbosilane **5** to the Grignard reagent followed by coupling with chlorodimethylsilane would generate the desired tricarbosilane tail **6**. Hydrosilylation was then carried out between the tricarbosilane tail **6** and the alkene **7**, which can be easily generated under Williamson-ether conditions with 6-Bromo-1-hexene and Benzyl 4-hydroxybenzoate, to achieve compound **8**. Compound **8** was then deprotected using catalytic hydrogenation to afford the carboxylic acid **9**, which was directly coupled with nitrophenol ether **4** under DCC coupling condition to provide **W599 (10)**.

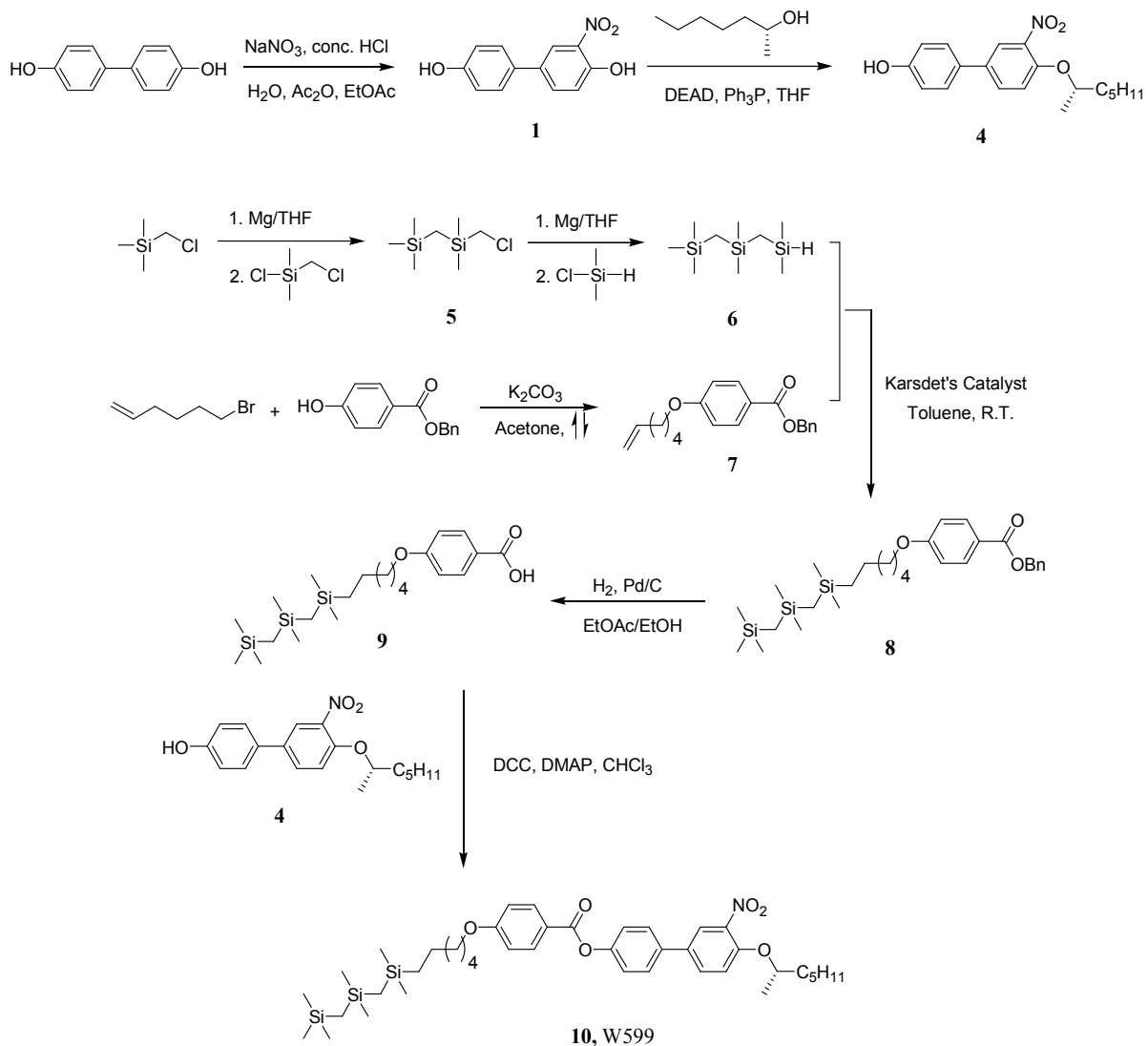


Figure 2.7: Synthesis of W599.

Gratifyingly, **W599** is indeed a de Vries SmA* LC material with very interesting properties (details will be discussed in later chapter).

In work aimed directly at testing the “anticlinicity” model for de Vries behavior, a sulfur-containing mesogen was prepared. The rationale for this is as follows. Conventional X-ray scattering can only probe relative clinicity of the smectic layers indirectly, and there is no expected X-ray signature of the proposed disordered anticlinic

model for the de Vries phases. In order to support or refute this model, new technique such as resonant x-ray scattering can be used, as has been demonstrated for several exotic smectic subphases existing in some antiferroelectrics.¹⁵

Resonant X-ray requires one of several possible heavy atoms, including sulfur, in the molecule, so a sulfur atom was introduced into the new de Vries LC material **W599**. Two synthetic methods were attempted. First, Lawesson's reagent was used to directly convert **W599** to its thiocarbonyl analog compound **11**, as shown in figure 2.8.¹⁶

Unfortunately, this pathway didn't work out well for **W599** as only starting materials were recovered. Synthesis of the thioester analog of **W599**, **W649**, was then attempted as sketched in figure 2.9. The strategy was to introduce the sulfur via a Newman-Kwart rearrangement (NKR) as an efficient method for conversion of phenols to thiophenols by the thermally activated rearrangement of an O-thiocarbamate to the corresponding S-thiocarbamate.¹⁷⁻¹⁹ The O-thiocarbamate **12** was synthesized by treating nitrophenol ether **4** with dimethylcarbamoyl chloride using sodium hydride as base.^{20, 21} The O-thiocarbamate **12** was then dissolved in diphenyl ether and heated to reflux until the completion of the rearrangement to S-thiocarbamate **13**, which was monitored by TLC. Then, S-thiocarbamate **13** was converted to thiolphenol **14** after hydrolysis with potassium hydroxide in methanol with good yield. Finally, carboxylic acid **9** was used to couple with thiolphenol **14** under DCC coupling conditions to afford **W649 (15)**.

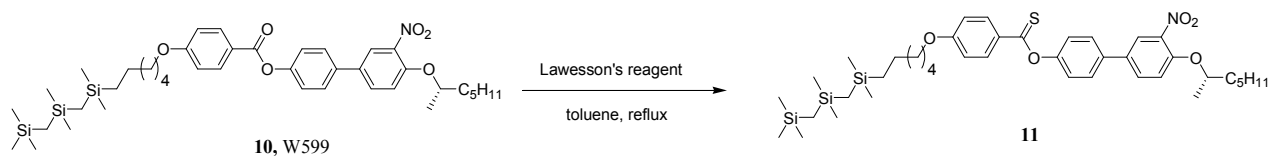


Figure 2.8: Intended synthesis of compound 11, thiocarbonyl analog of W599.

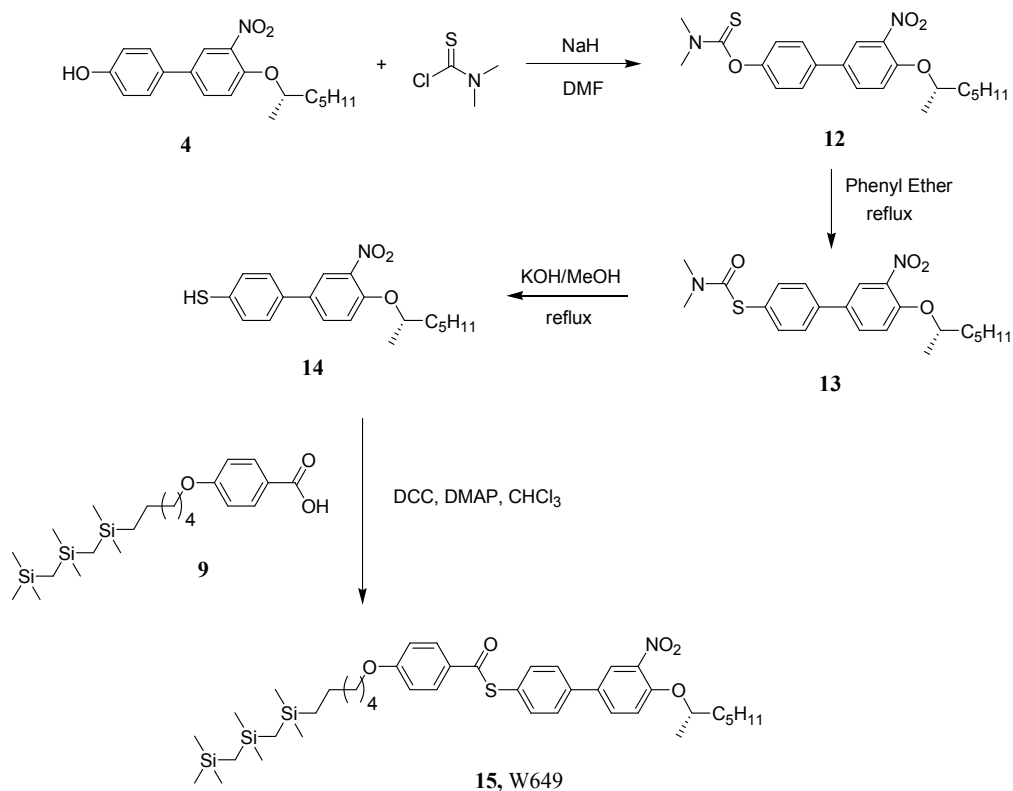


Figure 2.9: Synthesis of W649, a thioester analog of W599.

2.4 Results and Discussion

2.4.1 W599 and W649

W599 was designed to explore the possibility that a terminal tricarbosilane grouping on the unbranched (achiral) alkoxy tail would suppress out of layer fluctuations and provide a de Vries phase. Compare to tails like tricarbosiloxane mentioned above, the tricarbosilane tail has advantages such as better chemical stability, particularly in the

presence of traces of water, relative to the siloxanes. Based upon this, it is expected that this class of tails (the alkyl-tricarbosilanes) could be used in the display industry.²²

W599 was identified to have the following phase sequence on cooling based on the analysis by differential scanning calorimetry (DSC): Iso $\rightarrow$ 39°C $\rightarrow$ SmA* $\rightarrow$ 23°C $\rightarrow$ SmC*, as shown in figure 2.10. Although there clearly is a peak corresponding to the SmA*-SmC* transition, it is much weaker compare to the Iso-SmA* transition and was considered “weakly first order”. Such a transition is quite normal in the de Vries SmA to SmC transitions. In addition, the room temperature range of the SmA* phase made this molecule a promising candidate as a material for studying the de Vries phases, and also as a lead for future applications.

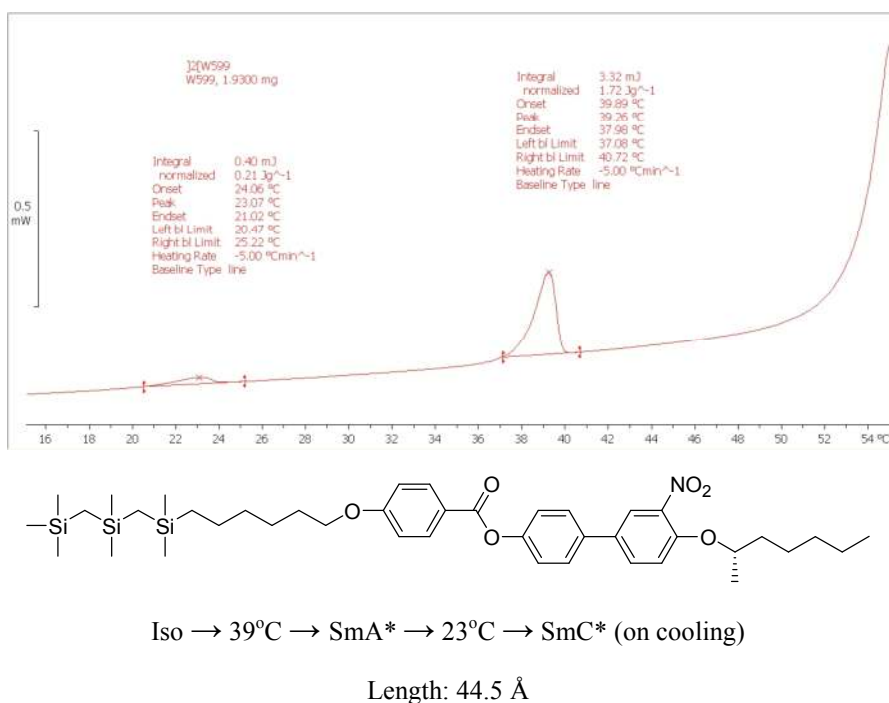


Figure 2.10: Molecular structure, molecular length and DSC of W599 on cooling.

In order to confirm the de Vries nature of **W599** on cooling, synchrotron X-ray data was collected on an un-oriented (“powder”) sample, giving the layer spacing as a function of temperature as shown in figure 2.11 (this work was performed by Dr. Chenhui Zhu and Mr. Yongqiang Shen in Professor Clark’s group, at the National Synchrotron Light Source – NSLS – at Brookhaven). It is clear that when the LC transitions from the SmA* phase to the SmC* phase, the maximum layer shrinkage was less than 1%; this alone demonstrates strong de Vries character for **W599**, assuming the optical tilt of the material in the SmC* phase is not small. Of course weak layer shrinkage is expected if the optical tilt angle is small, as will be discussed in more details below.

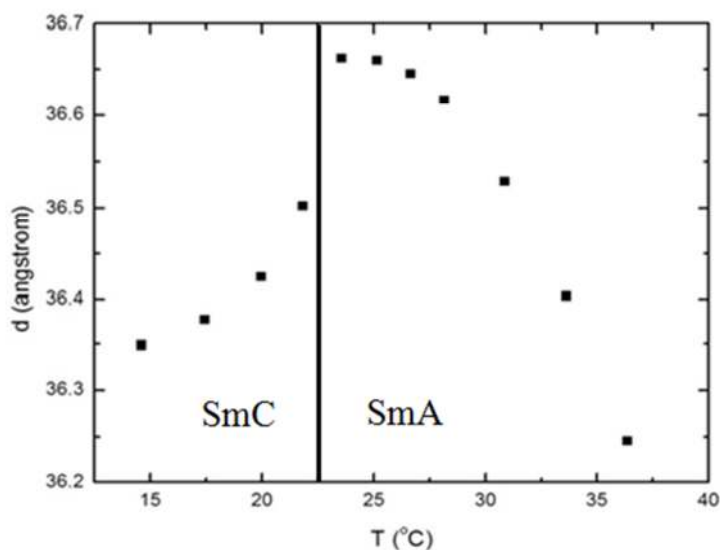


Figure 2.11: Synchrotron x-ray measurement of layer spacing, d , of W599 on cooling.

In the de Vries scenario for the SmA-SmC transition, the increasing director tilt comes through a gradual azimuthal biasing towards a certain inclination direction (the tilt direction) of the molecular director. This model was referred to as the “asymmetric

diffuse cone” (ADC) model.^{3,23} The observed optical tilt angle for **W599** at the “bottom” (lowest temperature) of the SmC* range is 35°. The X-ray tilt calculated from the observed layer shrinkage, however, is only 7° at the same temperature. This simply proved that the small layer shrinkage during the transition was not due to the fact of small tilt from the SmA* phase to the SmC* phase and thus confirmed **W599** is indeed a de Vries SmA* material with the cone angle around 35°

Recent analysis of the ADC model has shown that, in the case of chiral smectics, the birefringence Δn strongly increases with tilt angle ψ and that the SmA* electroclinic effect and spontaneous polarizations are unusually large.^{24, 25} This behavior can be explained by a simple Langevin model.^{26, 27}

Electroclinic effect and birefringence measurements under external electric field were performed on **W599**, giving the results are shown in figure 2.12. In the SmA* phase, the electroclinic tilt angle ψ increases significantly with decreasing temperature. The tilt angle increases with electric field and reaches a saturation value at a threshold electric field. The threshold field decreases with temperature and the electroclinic coefficient χ became larger approaching the SmA*-SmC* transition. Accompanying the induced electroclinic tilt, the birefringence Δn increases as well. In the SmA* phase, when there is no applied field, the molecules orient randomly around the tilt cone, at least at length scales considerably smaller than the wavelength of visible light. However, when an electric field is applied, the disorder decreases as the director is biased on the cone to give net polarization normal to the tilt plane. When this happens, the molecules are, on average, more ordered, providing an increase in Δn . As the sample approaches the

transition to the SmC* phase, the birefringence becomes larger and saturates more quickly.

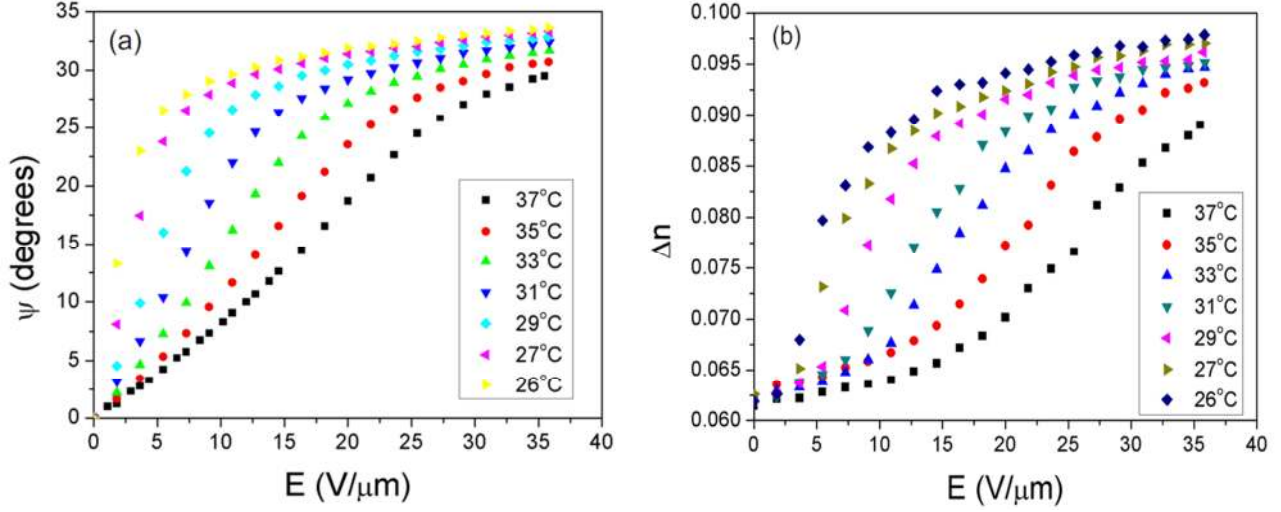


Figure 2.12: Electroclinic tilt angle ψ (a) and birefringence Δn (b) as a function of applied external electric field in a 2.7 μm cell of W599.

Using the Langevin equation along with the ADC model, the spontaneous polarization P of W599 can be calculated from the electroclinic tilt angle ψ and birefringence Δn .²⁸ The experimental results were compared to the calculated results and shown in figure 2.13. The quantitative fitting of polarization using the Langevin model matches the direct experimental measurements in the SmA* phase of **W599**. All these data suggest that **W599** is a classic de Vries smectic LC, behaving in a manner consistent with the ADC model.

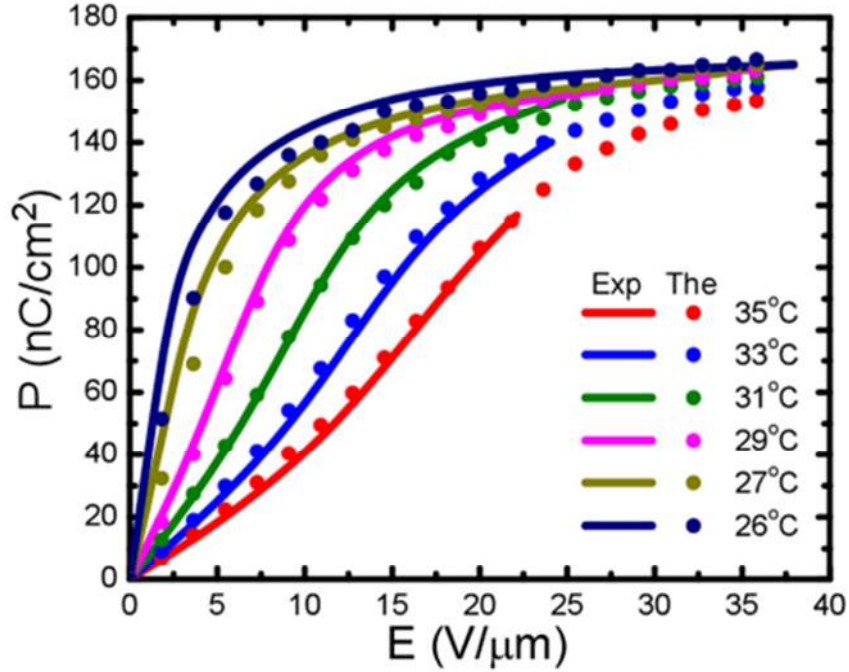


Figure 2.13: Experimental results and theoretical values of spontaneous polarization P of W599 under different temperatures.

Meanwhile, the polarization reversal current was also characterized for **W599**. As shown in figure 2.14 and figure 2.15, the response of **W599** to applied fields also has the double peak profile, similar to that of **W530**. Thus, in the SmA* phase, at high temperature, as shown in figure 2.14 (b), there is no clear polarization current peak. As the temperature decreases, when close to the SmA-SmC transition, the current response exhibits a clear double peak profile. After the sample enters the SmC* phase, the current response exhibits a single peak profile, which is characteristic of a ferroelectric response. In general, the double peak profile is seen in antiferroelectric LCs which possess anticlinic layer interface.²⁹ Glaser *et al.* in the Boulder group, and Prasad *et al.*, suggested that de Vries LCs possess small domains with anticlinic molecular packing in adjacent layers in the SmA* phase. To account for the de Vries character, adjacent domains can be considered to be weakly correlated in the usual de Vries fashion.⁸ To

verify this hypothesis, resonant x-ray scattering were used to investigate the newly synthesized heavy atom containing de Vries LC **W649** in order to probe for superlattice periodicities (a characteristic of antclinic order).^{15, 20}

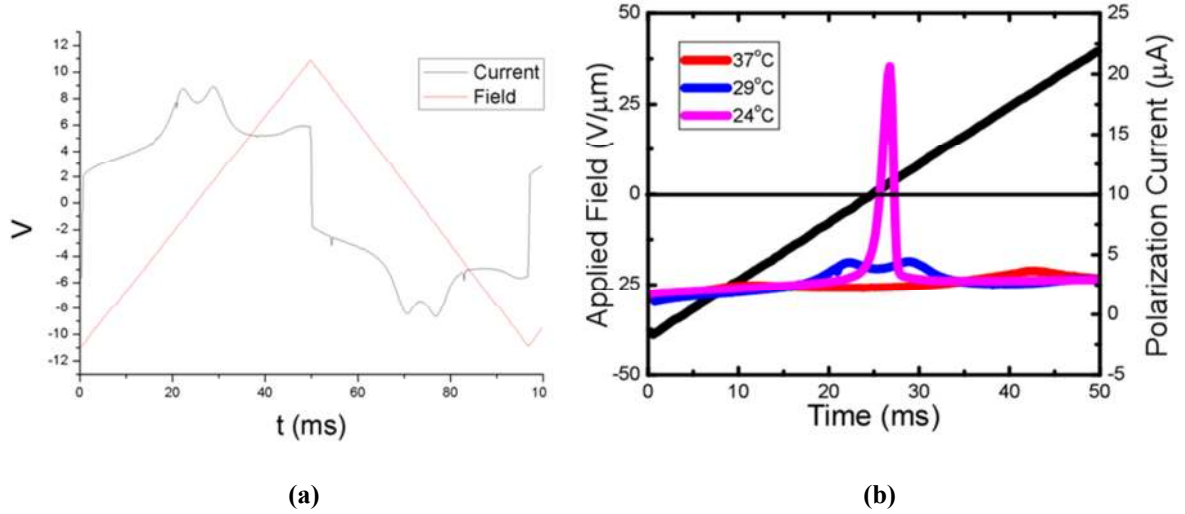


Figure 2.14: Polarization reversal current curve of W599 under triangle waveform electric field at (a) 29°C in a 2.7 μm cell and (b) at 3 different temperatures in a 2.7 μm cell, indicating 3 different currents.

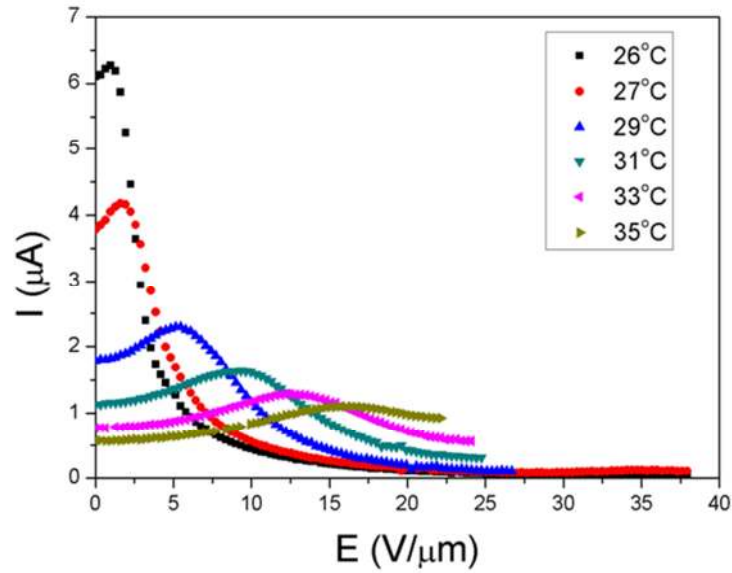


Figure 2.15: Half polarization reversal current curve of W599 under triangle waveform electric field at different temperatures in a 2.7 μm cell.

The phase sequence as well as synchrotron x-ray measurements taken on **W649** are shown in figure 2.16. Although **W649** only possesses a three degree temperature window of the SmA* phase, it is clear that the material indeed has de Vries character by layer spacing and comparison of optical tilt with x-ray tilt. From the SmA* phase to the SmC* phase, the layers only shrink by less than 1%. The optical tilt angle θ_{opt} by polarized light microscopy is 26° at the “bottom” of the SmC* temperature range and the x-ray tilt angle θ_{xray} can be calculated as 6° . These data clearly shows that **W649** is also de Vries.

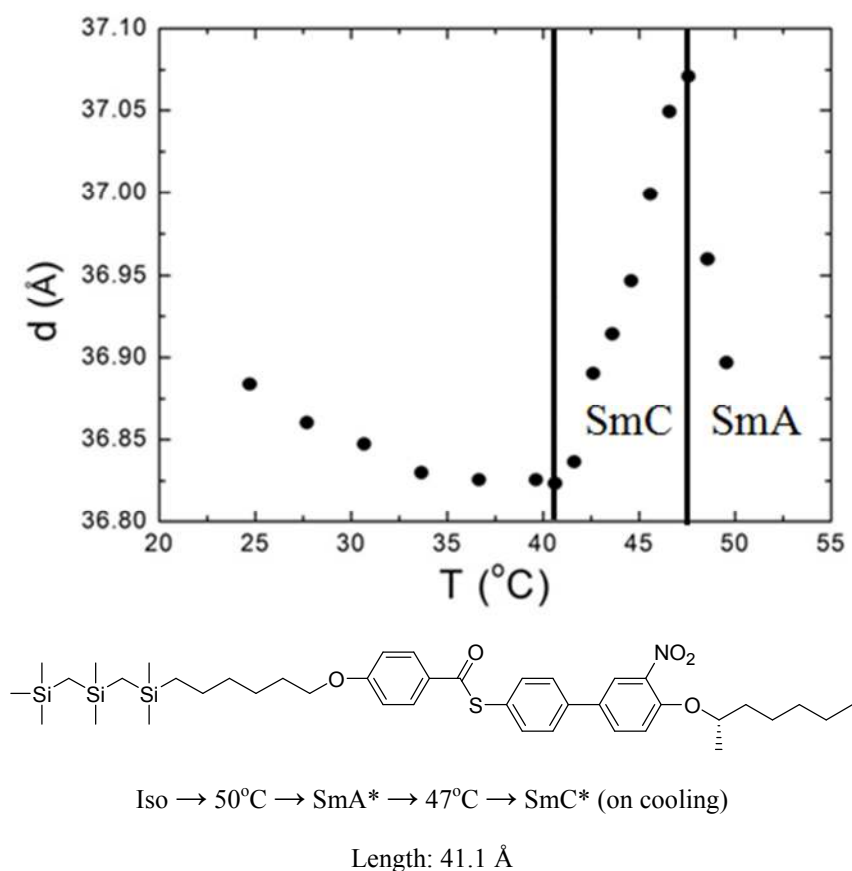


Figure 2.16: Molecular structure, molecular length and layer spacing of W649 on cooling.

Interestingly, **W649** does not show the double peak profile in the polarization current response to an applied triangular electric field. The polarization reversal current of **W649**

was quite flat in the SmA* phase as in the high temperature range of the SmA* phase of **W599**. It is proposed that is due to the relatively small SmA* phase temperature window of **W649**, or to a very small spontaneous polarization, although **W649** does switch upon application of an external electric field.

This issue was resolved for the purposes of the resonant X-ray experiment by formulation of mixtures of **W599** and **W649**, which showed a broader SmA* phase temperature window and clear double peaks in polarization reversal current. Since the resonant X-ray experiment does not require a neat sample of “labeled” material, the mixture provided a good sample for resonant x-ray scattering.

In the event, no resonant satellite peaks were observed for **W599/W649** mixtures, or in other-sulfur containing de Vries LCs.²⁸ Based on these results, one can conclude with a high degree of confidence that there is no anticlinic molecular packing in adjacent layers of these de Vries smectics. Thus, a new model is required to explain de Vries phases. Development of such a model is in progress in the Glaser and Clark labs.

2.4.2 Formulation and study of mixtures of W317 and W415

As discussed earlier, **W317** is a rare anti-de Vries smectic LC material while **W415** is considered a de Vries smectic; the only difference between these two LCs in their molecular structures is the presence of a double bond in the achiral tail of **W415**, while the **W317** achiral tail is saturated.⁹⁻¹² In an effort to understand how a system transforms from “de Vries” to “anti-de Vries” behavior, especially with regard to the electroclinic effect, a series of **W317/W415** mixtures were formulated. Figure 2.17 shows their layer spacing (by X-ray scattering) vs. temperature. It should be pointed out that although

W317 has strong electroclinic effect, it doesn't have a SmC* phase. Therefore, when an external electric field was applied to samples in the SmA* phase, the **W317** molecules tilt in the plane with layer shrinkage close to $\cos(\text{tilt angle})$ (figure 2.1) which is different from classic de Vries SmA* materials, tilting on the cone, with bias towards one side. The mixtures show a SmA* to SmC* transition if the concentration of **W415** is greater than 8%. When the concentration of **W317** increases, the layer spacing of the mixtures becomes larger but the layer also shrinks less. The SmA* to SmC* phase transition temperature first increases and then decreases with increasing **W317** concentration.

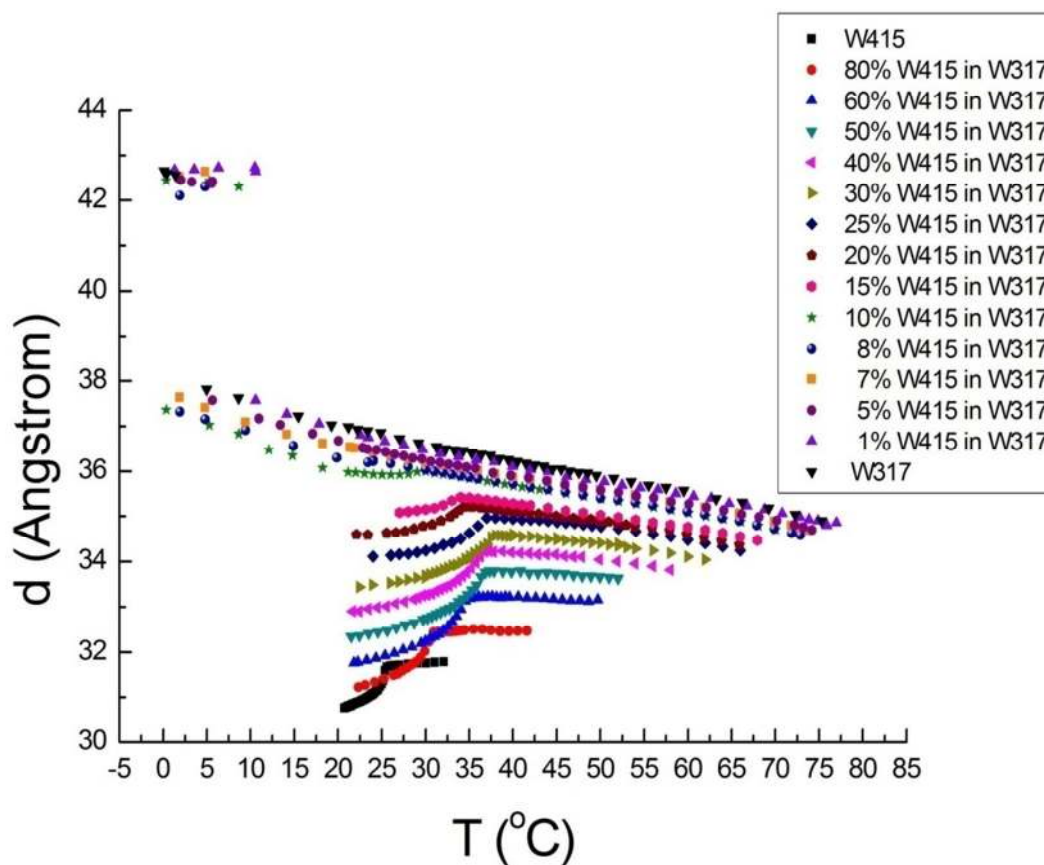


Figure 2.17: Layer spacing of mixtures of W317/W415, measured by x-ray scattering using the rotating anode X-ray diffraction setup operated by the Liquid Crystal Materials Research Center.

Detailed layer spacing and tilt angle data for mixtures of **W317/W415** are shown in figure 2.18. It is clear that with increasing concentration of **W317**, the layer spacing of the mixture increases but the calculated tilt angle in the SmA* phase (determined from the fully extended molecular length and the X-ray layer spacing) decreases. Since **W415** is considered de Vries, by using the ADC model, the tilt angle should be the same as the cone angle. When the concentration of **W415** decreases, the de Vries character of the mixture decreases as well, and as a result, the cone becomes smaller and the cone angle decreases, causing the layer spacing to increase. On the other hand, from both graphs, when **W415** clearly shows a weak first order transition, which is common for de Vries Smectic LCs, the mixture of 15% **W415** in **W317** is second order, which is common for normal Smectic LCs.

To investigate more details of the mixtures, high-resolution synchrotron X-ray experiments on pure **W415** and on four mixtures which have 80%, 60%, 50% and 40% **W415** were performed giving the results shown in figure 2.19. The layer thickness was measured while cooling very slowly, showing that the SmA* to the SmC* transitions in pure **W415** and in the 80% **W415** mixture are weakly first-order, but the other mixtures show second-order phase transitions. These data suggest that by decreasing the concentration of **W415**, the mixtures showed a smooth transition from de Vries Smectic behavior to anti-de Vries Smectic behavior.

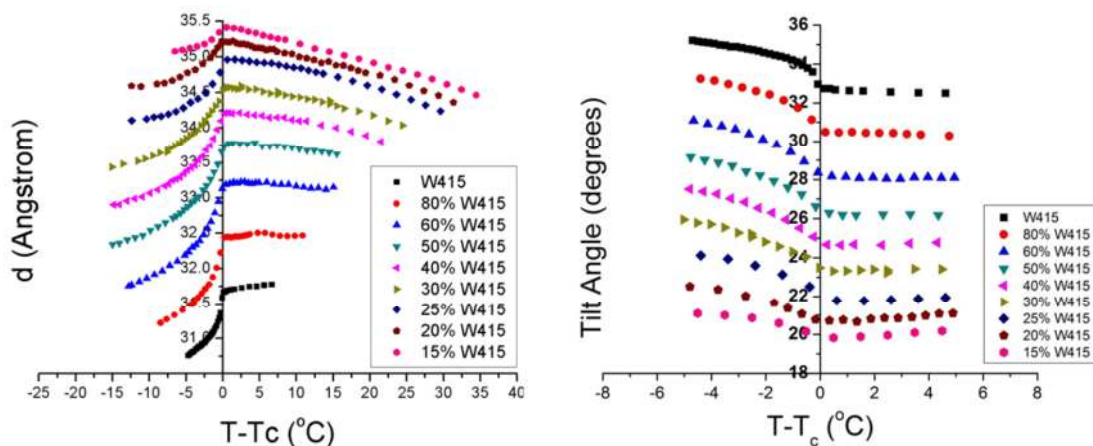


Figure 2.18: Layer spacing (left) and tilt angle (right) during the SmA* to the SmC* transition for mixtures of W317 and W415.

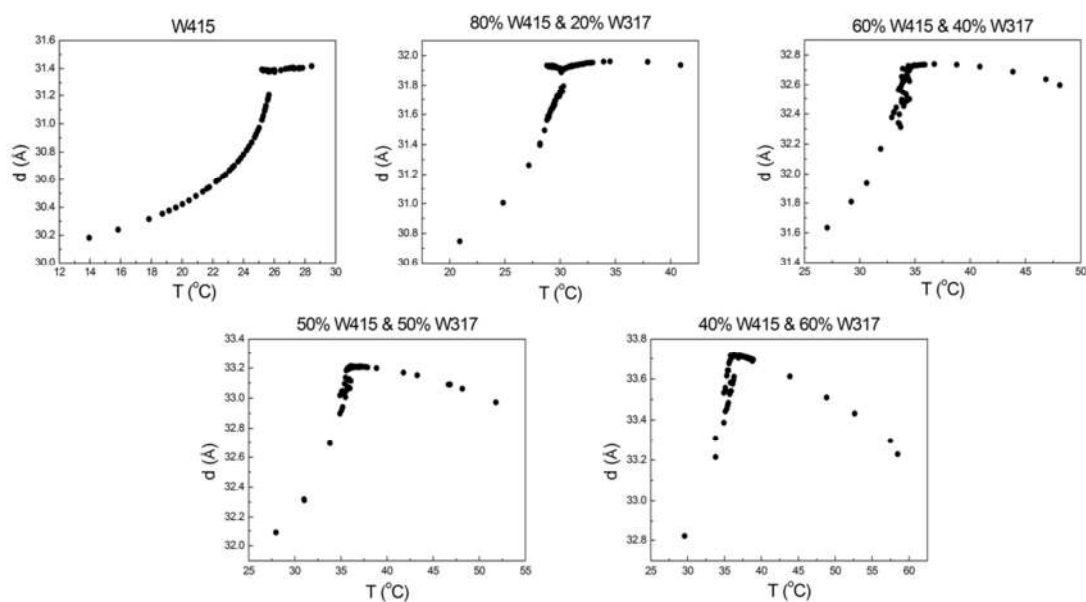


Figure 2.19: Synchrotron x-ray measurement of layer spacing of mixtures of W317/W415 at Brookhaven National Lab.

Both **W415** and **W317** show a large electroclinic effect.^{9, 12} For mixtures of **W317/W415**, the electroclinic tilt as a function of field was measured, and the results are shown in figure 2.20. For pure **W415**, and in mixtures with 80%, 60%, 40% and 25% **W415**, the saturation electroclinic tilt angle is close to the cone angle calculated from the

X-ray results (figure 2.18). However, for mixtures with 15% and 10% **W415**, the saturation tilt angle is much bigger than the calculated cone angle, which means the ADC model does not apply to these mixtures. Also, with low concentrations of **W415**, these mixtures were considered more anti-de Vries/**W317** like. But, unlike for **W317**, the mixtures still possess the SmC* phase. To explain the behavior of all the mixtures, the following model was proposed.

For mixtures with high **W415** concentration, the LC molecules are tilted on a cone in the SmA* phase, and the cone angle is larger than the saturation electroclinic tilt angle of **W317**, therefore there is no further tilt under the external electric field – the observed rotation of the optic axis is due to a biasing of the orientational distribution of the director on the cone.

When the concentration of **W415** decreases, the cone as well as the cone angle becomes smaller, and when the concentration of **W415** in the mixture reaches 15%, the cone angle is smaller than the electroclinic tilt angle of **W317** and the molecules of the mixture would have further tilt under external electric field. So the overall tilt angle of the mixture would be the cone angle and the electroclinic tilt angle combined, thus causing the saturated tilt angle to be even bigger than the higher concentration **W415** mixture as shown in figure 2.20. On the other hand, because of the existence of the smaller cone in those mixtures the SmA* phase, they still exhibit the SmC* phase and the small layer shrinkage during the transition is due to the small cone angle. When the concentration of **W415** is lower than 8%, the mixture exhibits anti-de Vries behavior as pure **W317**. The fact that mixtures with low concentration of **W415** behave similarly to **W317**, but possess a SmC* phase, refutes the hypothesis that lack of a tilted smectic under the SmA* phase

of **W317** is responsible for its unusual properties, i.e. a large electroclinic coefficient but no de Vries character.

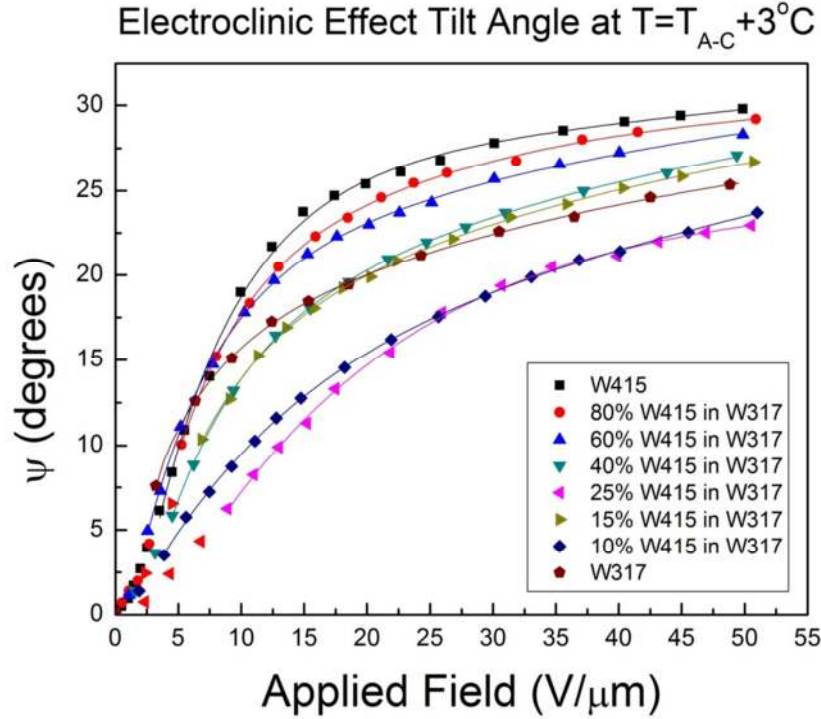


Figure 2.20: Electroclinic tilt angle of mixtures of W317/W415 at 3 degrees above the SmA* to the SmC* transition.

Polarization reversal current measurements were also performed for **W317/W415** mixtures as well as pure **W317** and **W415** at different temperatures, and the results are shown in figures 2.21 and 2.22. As a typical “de Vries” type material, **W415** showed the double peak per field ramp in the polarization current response in the SmA* phase and a single peak polarization current response in the SmC* phase. As an “anti-de Vries” type material, **W317** showed a single sharp peak response in the SmA* phase. The 80% **W415** and 60% **W415** mixtures also showed double peak response. However, when the percentage of **W415** is less than 60% in the mixture, a single peak response was observed.

These data suggested that although mixtures such as 50% **W317/W415** behave like de Vries Smectic LCs because of their small layer shrinkage at the SmA* to the SmC* transition and large electroclinic effect in the SmA* phase, their molecular packing in the bulk LC is more like that of a normal SmC LC. This property might be the key to the relationship between the normal SmA phases, and de Vries SmA phases. More detailed experiments are undergoing to better define this relationship.

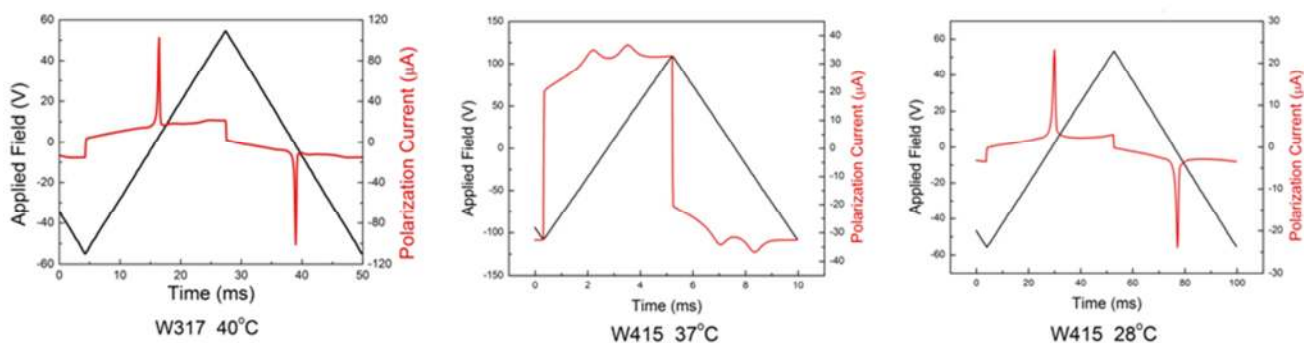


Figure 2.21: Polarization reversal current for W317 (during the SmA* phase) and W415 (during the SmA* phase in the middle and during the SmC* phase on the right).

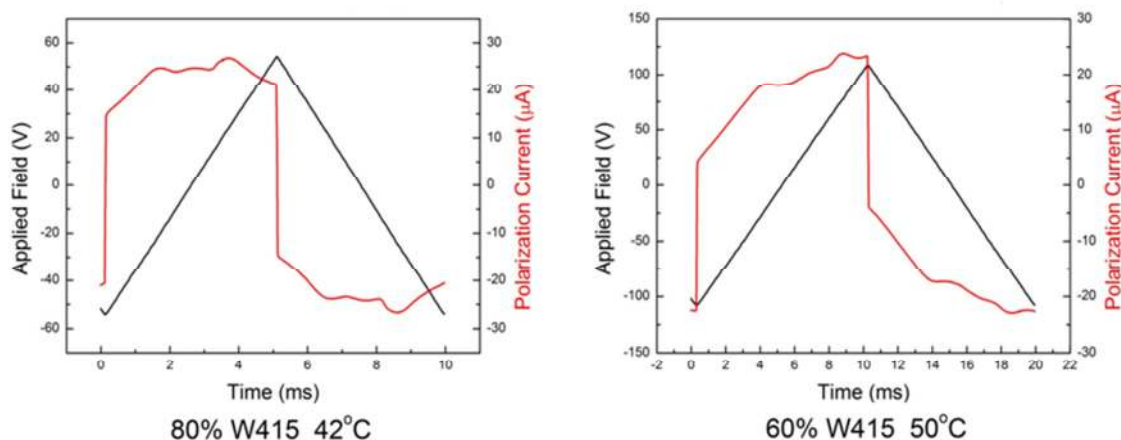
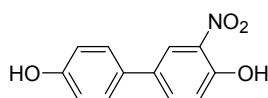


Figure 2.22: Polarization reversal current for W317/W415 mixtures during the SmA* phase.

2.5 Experimental Procedures

General Methods: Commercially available reagents were used as purchased without further purification unless otherwise noted. THF was purified by distillation from sodium/benzophenone ketyl under an argon atmosphere prior to use. All non aqueous reactions were performed in oven-dried glassware under an atmosphere of dry argon unless otherwise noted. All aqueous solutions used for reaction work up were saturated unless otherwise noted. All flash chromatography was performed with silica gel (40-63 microns, 230-400 mesh) purchased from Silicycle. Analytical thin-layer chromatography (TLC) was performed on Silica G TLC plates w/ UV with a thickness of 200 μ m, purchased from Sorbent Technologies. Compounds were visualized with shortwave UV, or by staining with I₂, p-anisaldehyde, or vanillin. If either of the latter two stains were used, the plate was heated to visualize spots. New compounds in the synthetic route were routinely characterized by NMR spectroscopy. ¹H and ¹³C NMR spectra were recorded using a Varian Unity INOVA-500, a Bruker AM-400 spectrometer, or a Bruker 300 UltraShield. ¹H NMR spectra are reported in parts per million (δ) relative to residual solvent peaks (7.24 for CDCl₃ or otherwise noted). ¹³C NMR spectra are reported in parts per million (δ) relative to residual solvent peaks (77.23 for CDCl₃ or otherwise noted). For the mesogenic materials, phase transition temperatures were determined by differential scanning calorimetry using a Mettler Toledo DSC823e. Liquid crystal phases were determined by polarized light microscopy using a Nikon-HCS400 microscope with an Instec STC200 temperature-controlled stage. The magnitude of the spontaneous polarization P_s was measured by integrating the polarization reversal current while switching the sample with a triangular waveform electric field. X-ray experiments were temperature controlled with an Instec STC200 hot stage, and data were collected using a

point detector mounted on a Huber four-circle goniometer at either of the following: Synchrotron radiation at beamline X10A of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, or Cu K(R) radiation from a Rigaku UltraX-18 rotating anode generator, operated by the Liquid Crystal Materials Research Center, University of Colorado-Boulder.

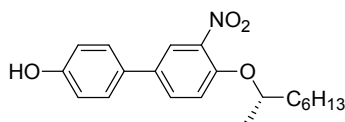


1

3-Nitro-biphenyl-4,4'-diol (1)

Biphenyl-4,4'-diol (10.0 g, 53.7 mmol) was dissolved in 500 mL of ethyl acetate. To the resulting solution was added NaNO₃ (5.0 g, 58.8 mmol) in 100 mL of H₂O solution. Acetic anhydride (0.5 mL) was then added. To this solution was added concentrated HCl (20.3 mL) dropwise. The two-phase reaction mixture was allowed to stir at room temperature for 2 h. Then, the layers were separated, and the aqueous layer was further extracted with ethyl acetate (3 x 200 mL). The combined organic layers were dried over anhydrous MgSO₄, filtered, and then concentrated at reduced pressure to give black oil. Purification of this crude product by flash chromatography (9:1 hexane:EtOAc) gave a mixture of 3-nitro-biphenyl-4,4'-diol, **1**, and 3,3'-dinitro-biphenyl-4,4'-diol (88% and 12%, respectively, based upon ¹H NMR analysis) as a dark orange solid (9.5 g, 40.2 mmol, 74.9 %). This material was used in the subsequent reaction without further purification. ¹H NMR (CDCl₃, 500 MHz): δ 10.53 (s, 1H), 8.23 (d, 1H, J = 2.5 Hz), 7.75

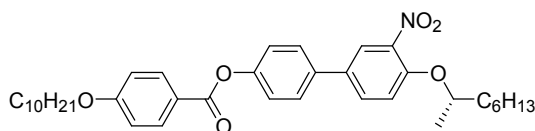
(dd, 1H, J = 8.5, 2.5 Hz), 7.40 (m, 2H), 7.19 (d, 1H, J = 8.5 Hz), 6.90 (m, 2H), 4.79 (s, 1H).



2

(S)-4'-(1-Methyl-heptyloxy)-3'-nitro-biphenyl-4-ol (**2**)

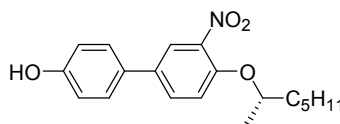
Diethylazodicarboxylate (DEAD) (1.68 mL, 1.85 g, 10.67 mmol) was added via syringe with stirring and under argon to a solution of a mixture of 3-nitro-biphenyl-4,4'-diol and dinitro-diol (1.88 g total, containing 1.27 g, 5.50 mmol of 3-nitro-biphenyl-4,4'-diol in admixture with dinitro-diol) prepared as described above, 2-(R)-octanol (1.59 mL, 1.30 g, 10.01 mmol), and triphenyl phosphine (TPP) (2.74 g, 10.45 mmol) in 70 mL of dry THF. The reaction mixture was allowed to stir for 12 h at room temperature and was then concentrated by reduced pressure to give an orange oil which was directly subjected to purification by flash chromatography (19:1 hexane:EtOAc) to provide (S)-4'-(1-Methyl-heptyloxy)-3'-nitro-biphenyl-4-ol, **2**, (1.65 g, 4.80 mmol, 87.3% based on mononitrodiol) as an orange oil. ¹H NMR (CDCl₃, 500 MHz): δ 7.92 (d, 1H, J = 2.5 Hz), 7.62 (dd, 1H, J = 8.5, 2.5 Hz), 7.40 (m, 2H), 7.08 (d, 1H, J = 8.5 Hz), 6.89 (m, 2H), 4.96 (s, 1H), 4.50 (m, 1H), 1.79-1.27 (m, 13H), 0.86 (t, 3H, J = 7 Hz).



3, W317

4-Decyloxy-benzoic acid 4'-(1-methyl-heptyloxy)-3'-nitro-biphenyl-4-yl ester (**3, W317**)

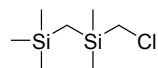
A mixture of (S)-4'-(1-Methyl-heptyloxy)-3'-nitro-biphenyl-4-ol, **2**, (1.38 g, 4.02 mmol), 4-Decyloxy benzoic acid (1.34 g, 4.81 mmol) and 4-dimethylaminopyridine (DMAP) (25 mg, 0.21 mmol) in 50 mL CH₂Cl₂ was stirred for 10 minutes. To this mixture, dicyclohexylcarbodiimide (DCC) (1.26 g, 6.10 mmol) in 9 mL of CH₂Cl₂ was added and the reaction mixture was continued to stir for 12 h at room temperature. The precipitated dicyclohexylurea was filtered off and washed with excess CH₂Cl₂. The solvent of the filtrate was removed and the crude product was purified by flash chromatography (CHCl₃) to yield 4-Decyloxy-benzoic acid 4'-(1-methyl-heptyloxy)-3'-nitro-biphenyl-4-yl ester, **3, (W317)** (2.04 g, 3.37 mmol, 83.8%) as a yellowish solid. ¹H NMR (CDCl₃, 500 MHz): δ 8.14 (m, 2H), 7.98 (d, 1H, J = 2.5 Hz), 7.68 (dd, 1H, J = 9, 2.5 Hz), 7.57 (m, 2H), 7.27 (m, 2H), 7.11 (d, 1H, J = 9 Hz), 6.96 (m, 2H), 4.52 (m, 1H), 4.03 (t, 2H, J = 6.5 Hz), 1.80-1.28 (m, 29H), 0.87 (t, 3H, J = 6 Hz), 0.87 (t, 3H, J = 6 Hz).



4

(S)-4'-(1-Methyl-hexyloxy)-3'-nitro-biphenyl-4-ol (**4**)

Diethylazodicarboxylate (DEAD) (1.35 mL, 1.49 g, 8.57 mmol) was added via syringe with stirring and under argon to a solution of a mixture of 3-nitro-biphenyl-4,4'-diol and dinitro-diol (1.50 g total, containing 1.29 g, 5.58 mmol of 3-nitro-biphenyl-4,4'-diol in admixture with dinitro-diol) prepared as described above, 2-(R)-heptanol (1.00 g, 8.61 mmol), and triphenyl phosphine (TPP) (2.35 g, 8.96 mmol) in 50 mL of dry THF. The reaction mixture was allowed to stir for 12 h at room temperature and was then concentrated by reduced pressure to give an orange oil which was directly subjected to purification by flash chromatography (9:1 hexane:EtOAc) to provide (S)-4'-(1-Methyl-hexyloxy)-3'-nitro-biphenyl-4-ol, **4**, (1.66 g, 5.04 mmol, 90.3% based on mono-nitrodiol) as an orange oil. ¹H NMR (CDCl₃, 500 MHz): δ 7.92 (d, 1H, J = 2.5 Hz), 7.61 (dd, 1H, J = 8.5, 2.5 Hz), 7.41 (m, 2H), 7.08 (d, 1H, J = 8.5 Hz), 6.89 (m, 2H), 4.83 (s, 1H), 4.50 (m, 1H), 1.83-1.26 (m, 14H).

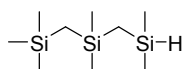


5

(Chloromethyl-dimethyl-silanyl)-trimethylsilanyl methane (**5**)

A solution of chloromethyltrimethylsilane (9.56 g, 78 mmol) in 30 mL of anhydrous THF was added 1-2 ml to a suspension of oven-dried magnesium turnings (2.08 g, 86 mmol) in 50 mL of anhydrous THF, few drops of dibromoethane under an argon atmosphere. Continued stirring until the reaction started, the remaining solution of chloromethyltrimethylsilane was slowly added dropwise at a rate that just maintains a gentle reflux. After the addition was complete, the resultant reaction mixture continued at reflux for an additional 2 hours. To this mixture at room temperature, 30 mL of the

anhydrous THF solution of chloromethyldimethyl chlorosilane (10.3 mL, 11.13 g, 78 mmol) was slowly added dropwise over 30 min. The resultant reaction mixture was then refluxed for additional 20 hours. To this cold solution, added 100mL of water and extracted the aqueous phase with hexane (3 x 100 mL). The combined hexane extracts dried over MgSO₄. After the removal of solvent carefully, the crude product was distilled (186°C at 760 mm of Hg) to afford (Chloromethyl-dimethyl-silanyl)-trimethylsilanyl methane, (chloro oligo-silane), **5**, (12.5 g, 64 mmol, 82.1%) as colorless oil: ¹H NMR (CDCl₃, 500 MHz): δ 2.76 (s, 2H), 0.148 (s, 6H), 0.056 (S, 9H), -0.133 (S, 2H).

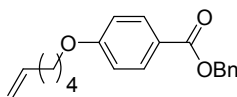


6

(Dimethylsilanylmethyl-dimethyl-silanyl)-trimethyl-silanyl methane (**6**)

The Grignard reagent of (Chloromethyl-dimethyl-silanyl)-trimethylsilanyl methane was prepared from (Chloromethyl-dimethyl-silanyl)-trimethylsilanyl methane, **5**, (10.31 g, 53 mmol), Mg (1.42 g, 58 mmol), 1-2 drops of 1,2-dibromoethane in 100 mL of anhydrous THF, similarly as in the previous step. To this mixture, 20 mL of the THF solution of chlorodimethylsilane (5.01 g, 53 mmol) was added slowly at 0°C over 30 min. The resultant reaction mixture was then stirred at room temperature for additional 20 hours under argon. At room temperature 100 mL of water and 100 mL of hexanes were added. The aqueous phase separated was then extracted with hexanes (2 x 100 mL). The liquid crude product obtained was purified by distillation (80-82°C at 12 mm of Hg) to afford (Dimethylsilanylmethyl-dimethyl-silanyl)-trimethyl-silanyl methane,

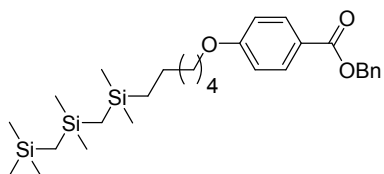
(tricarbosilane), **6**, (9.9 g, 45 mmol, 84.9%) as colorless oil: ^1H NMR (CDCl_3 , 500 MHz): δ 3.996 (m, 1H), 0.134-0.072 (m, 6H), 0.059-0.046 (m, 15H), -0.197 (m, 4H).



7

4-Hex-5-enyloxy-benzoic acid benzyl ester (**7**)

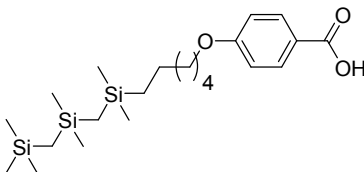
6-Bromo-1-hexene (0.36 mL, 0.44 g, 2.70 mmol) was added via syringe with stirring and under argon to a solution of a mixture of Benzyl 4-Hydroxybenzoate (0.64 g, 2.80 mmol) and Potassium Carbonate (1.11g, 8.03 mmol) in 20 mL acetone. The reaction mixture was allowed to heat to reflux for 2 days. Then, the solvent was removed by reduced pressure, and 50 mL diethyl ether was added to the residue. The insoluble material was filtered off and the filtrate was washed with 10% NaOH (3 x 25 mL) and saturated NaCl (3 x 25 mL), dried over anhydrous MgSO_4 , filtered and then concentrated at reduced pressure. The crude product was subjected to purification by flash chromatography (9:1 hexane:EtOAc) to provide 4-Hex-5-enyloxy-benzoic acid benzyl ester, **7**, (0.82 g, 2.64 mmol, 97.8%) as a white solid. ^1H NMR (CDCl_3 , 500 MHz): δ 8.00 (m, 2H), 7.43 (m, 2H), 7.38 (m, 2H), 7.35 (m, 1H), 6.88 (m, 2H), 5.80 (m, 1H), 5.32 (s, 2H), 5.01 (m, 1H), 4.98 (m, 1H), 3.99 (t, 2H, $J = 6.5$ Hz), 2.11 (m, 2H), 1.79 (m, 2H), 1.55 (m, 2H)



8

Tricarbosilane-hexyloxy-benzoic acid benzyl ester (8)

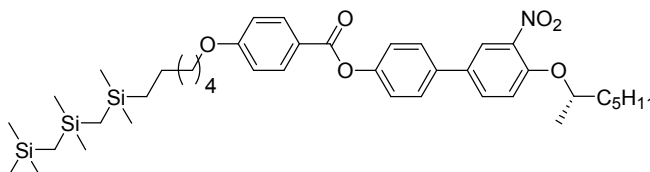
4-Hex-5-enyloxy-benzoic acid benzyl ester, **7**, (0.67 g, 2.16 mmol) was dissolved in 9 mL anhydrous toluene under an argon atmosphere. To this solution, tricarbosilane, **6** (0.68 g, 3.13 mmol) and a few drops of Karstedt's catalyst (platinum-divinyltetramethylsiloxane complex in xylene) were added. The flask was covered with aluminum-foil and the reaction mixture was allowed to stir at room temperature for 3 days until the reaction completed, which was determined by TLC. The solvent was evaporated and the black residue obtained was purified by flash chromatography (3:2 hexane:CH₂Cl₂) to give Tricarbosilane-hexyloxy-benzoic acid benzyl ester, **8**, (0.73 g, 1.38 mmol, 63.9%) as colorless oil. ¹H NMR (CDCl₃, 500 MHz): δ 8.00 (m, 2H), 7.43 (m, 2H), 7.38 (m, 2H), 7.35 (m, 1H), 6.88 (m, 2H), 5.32 (s, 2H), 3.98 (t, 2H, J = 6.5 Hz), 1.77 (p, 2H, J = 7.5 Hz), 1.48-1.25 (m, 6H), 0.47 (m, 2H), 0.00 (m, 21H), -0.29 (m, 4H). ¹³C NMR (CDCl₃, 100 MHz): δ 166.2, 163.1, 136.3, 131.7, 128.5, 128.1, 128.1, 122.2, 114.1, 68.2, 66.3, 33.3, 29.0, 25.7, 23.9, 18.0, 5.8, 4.0, 2.5, 1.6, -0.5



9

Tricarbosilane-hexyloxy-benzoic acid (8)

Tricarbosilane-hexyloxy-benzoic acid benzyl ester, **8**, (0.73 g, 1.38 mmol) was dissolved in 30 mL EtOH/EtOAc (1:1) and 10% Pd/C catalyst (0.08 g) was added. The resultant solution was stirred at room temperature in an atmosphere of hydrogen till the required quantity of hydrogen was absorbed. This mixture was filtered through Celite and the solvent was removed under reduced pressure to yield Tricarbosilane-hexyloxy-benzoic acid, **9**, as a white solid (0.54 g, 1.23 mmol, 89.1%) which was directly used for the subsequent reaction. ¹H NMR (CDCl₃, 500 MHz): δ 8.02 (m, 2H), 6.91 (m, 2H), 4.00 (t, 2H, J = 7.0 Hz), 1.78 (p, 2H, J = 7.5 Hz), 1.48-1.25 (m, 6H), 0.47 (m, 2H), 0.00 (m, 21H), -0.29 (m, 4H). ¹³C NMR (CDCl₃, 100 MHz): δ 171.5, 163.7, 132.3, 121.3, 114.2, 68.3, 33.3, 29.0, 25.7, 23.9, 18.0, 5.8, 4.0, 2.5, 1.5, -0.5. MS: Calculated for C₂₂H₄₂O₃Si₃, ([M-H]⁺) requires: 437.2369, found: 437.2360.

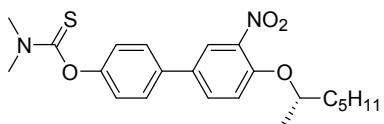


10, W599

Tricarbosilane-hexyloxy-benzoic acid (S)-4'-(1-Methyl-hexyloxy)-3'-nitro-biphenyl-4-yl ester (**10, W599**)

A mixture of Tricarbosilane-hexyloxy-benzoic acid, **9**, (1.43 g, 3.26 mmol), (S)-4'-(1-Methyl-hexyloxy)-3'-nitro-biphenyl-4-ol, **4**, (1.00 g, 3.04 mmol) and 4-dimethylaminopyridine (DMAP) (50 mg, 0.41 mmol) in 100 mL dry CH₂Cl₂ was stirred for 10 minutes. To this mixture, dicyclohexylcarbodiimide (DCC) (0.70 g, 3.39 mmol) in 10 mL of dry CH₂Cl₂ was added and the reaction mixture was continued to stir for 10 h at room temperature under argon atmosphere. The precipitated dicyclohexylurea was

filtered off and washed with excess dichloromethane. The solvent of the filtrate was removed and the crude product obtained was purified by flash chromatography (19:1 hexane:EtOAc) to yield Tricarbosilane-hexyloxy-benzoic acid (S)-4'-(1-Methyl-hexyloxy)-3'-nitro-biphenyl-4-yl ester, **10**, (**W599**) (1.92 g, 2.56 mmol, 84.2%) as a light green glue. ^1H NMR (CDCl_3 , 500 MHz): δ 8.14 (m, 2H), 7.98 (d, 1H, $J = 2.5$ Hz), 7.68 (dd, 1H, $J = 9.0, 2.5$ Hz), 7.57 (m, 2H), 7.27 (m, 2H), 7.11 (d, 1H, $J = 9.0$ Hz), 6.97 (m, 2H), 4.53 (h, 1H, $J = 6.0$ Hz), 4.03 (t, 2H, $J = 6.5$ Hz), 1.81 (m, 3H), 1.63 (m, 1H), 1.52-1.22 (m, 15H), 0.88 (t, 3H, $J = 7.0$ Hz), 0.49 (m, 2H), 0.02 (m, 21H), -0.28 (m, 4H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 164.9, 163.6, 150.8, 150.8, 141.0, 136.1, 132.5, 132.3, 131.9, 127.7, 123.8, 122.4, 121.3, 116.1, 114.3, 76.5, 68.3, 36.2, 33.3, 31.6, 29.0, 25.7, 25.0, 23.9, 22.5, 19.6, 18.0, 14.0, 5.7, 4.0, 2.5, 1.5, -0.5. MS: Calculated for $\text{C}_{41}\text{H}_{63}\text{NO}_6\text{Si}_3$, ($[\text{M}-\text{H}]^+$) requires: 750.1956, found: 750.4036.

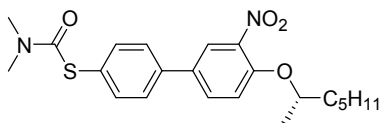


12

*Dimethyl-thiocarbamic acid O-[4'-(1-methyl-hexyloxy)-3'-nitro-biphenyl-4-yl] ester (**12**)*

(S)-4'-(1-Methyl-hexyloxy)-3'-nitro-biphenyl-4-ol, **4**, (0.45 g, 1.37 mmol) was dissolved in 10 mL DMF and added dropwise to a solution of sodium hydride (60% moistened with oil, 0.15 g, 3.75 mmol) in 5 mL DMF at 0 °C under argon. The ice bath was taken away and the mixture stirred for 30 min at room temperature. Then dimethyl carbamoyl chloride (0.46 g, 3.75 mmol) was added and it was stirred for 2 h at 80 °C and 15 h at room temperature. The reaction mixture was then quenched with 100 mL H_2O and

extracted with diethyl ether (3 x 75 mL). The combined organic phases were washed with 5% aqueous HCl (3 x 50 mL) and saturated NaCl (3 x 50 mL), dried over anhydrous MgSO₄, filtered and then concentrated at reduced pressure. The crude product was subjected to purification by flash chromatography (2:1 CH₂Cl₂: hexane) to provide Dimethyl-thiocarbamic acid O-[4'-(1-methyl-hexyloxy)-3'-nitro-biphenyl-4-yl] ester, **12**, (0.43 g, 1.03 mmol, 75.2%) as light yellow oil. ¹H NMR (CDCl₃, 500 MHz): δ 7.98 (d, 1H, J = 2.5 Hz), 7.67 (dd, 1H, J = 8.5, 2.5 Hz), 7.53 (m, 2H), 7.15-7.09 (m, 3H), 4.52 (m, 1H), 3.46 (s, 3H), 3.36 (s, 3H), 1.80-1.25 (m, 11H), 0.88 (t, 3H, J = 7.5 Hz).

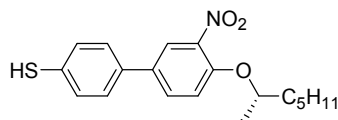


13

Dimethyl-thiocarbamic acid S-[4'-(1-methyl-hexyloxy)-3'-nitro-biphenyl-4-yl] ester (**13**)

Dimethyl-thiocarbamic acid O-[4'-(1-methyl-hexyloxy)-3'-nitro-biphenyl-4-yl] ester, **12**, (0.47 g, 1.03 mmol) and 5 mL phenyl ether were placed in a 25 mL pearl flask charged with stir bar and argon. The reaction mixture was heated to reflux (259 °C) for 1.5 h. The reaction mixture was then cooled to room temperature and concentrated by reduced pressure to give a black residue which was directly subjected to purification by flash chromatography (4:1 hexane: EtOAc) to provide Dimethyl-thiocarbamic acid S-[4'-(1-methyl-hexyloxy)-3'-nitro-biphenyl-4-yl] ester, **13**, (0.37 g, 0.89 mmol, 86.4%) as yellowish oil. ¹H NMR (CDCl₃, 500 MHz): δ 7.98 (d, 1H, J = 2.5 Hz), 7.68 (dd, 1H, J =

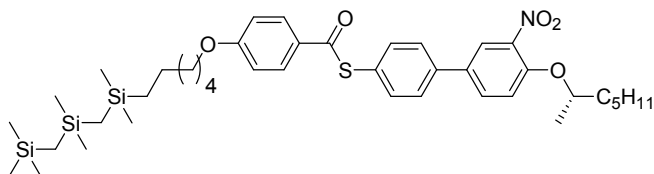
8.5, 2.5 Hz), 7.56-7.52 (m, 4H), 7.11 (d, 1H, J = 8.5 Hz), 4.52 (m, 1H), 3.10 (s, 3H), 3.02 (s, 3H), 1.83-1.24 (m, 11H), 0.87 (t, 3H, J = 7.5 Hz).



14

4'-(1-Methyl-hexyloxy)-3'-nitro-biphenyl-4-thiol (**14**)

A solution of the Dimethyl-thiocarbamic acid S-[4'-(1-methyl-hexyloxy)-3'-nitro-biphenyl-4-yl] ester, **13**, (0.36 g, 0.86 mmol) in 50 mL MeOH was charged with argon. Then KOH (0.32 g, 5.70 mmol) was added and the reaction mixture was heated to 80 °C for 2.5 h. The reaction mixture was then cooled at ice bath and quenched with 10 mL 1 M aqueous HCl and it was extracted with CH₂Cl₂ (3 x 25 mL). The combined organic phases were washed with H₂O (3 x 50 mL) and saturated NaCl (3 x 50 mL), dried over anhydrous MgSO₄, filtered and then concentrated at reduced pressure. The crude product was subjected to purification by flash chromatography (4:1 hexane: EtOAc) to provide 4'-(1-Methyl-hexyloxy)-3'-nitro-biphenyl-4-thiol, **14**, (0.23 g, 0.67 mmol, 77.9%) as yellowish oil. ¹H NMR (CDCl₃, 500 MHz): δ 7.94 (d, 1H, J = 2.5 Hz), 7.64 (dd, 1H, J = 8.5, 2.5 Hz), 7.39 (m, 2H), 7.32 (m, 2H), 7.09 (d, 1H, J = 8.5 Hz), 4.52 (m, 1H), 3.49 (s, 1H), 1.78-1.23 (m, 11H), 0.87 (t, 3H, J = 7.5 Hz).



15, W649

Tricarbosilane-hexyloxy-thiobenzoic acid S-4'-(1-methyl-hexyloxy)-3'-nitro-biphenyl-4-yl ester (15, W649)

A mixture of Tricarbosilane-hexyloxy-benzoic acid, **9**, (0.12 g, 0.27 mmol), 4'-(1-Methyl-hexyloxy)-3'-nitro-biphenyl-4-thiol, **14**, (0.09 g, 0.26 mmol) and catalytic amount of 4-dimethylaminopyridine (DMAP) in 10 mL dry CHCl_3 was stirred for 10 minutes. To this mixture, dicyclohexylcarbodiimide (DCC) (0.06 g, 0.29 mmol) in 1 mL of dry CHCl_3 was added and the reaction mixture was continued to stir for 10 h at room temperature under argon atmosphere. The precipitated dicyclohexylurea was filtered off and washed with excess CHCl_3 . The solvent of the filtrate was removed and the crude product obtained was purified by flash chromatography (19:1 hexane:EtOAc) to yield Tricarbosilane-hexyloxy-thiobenzoic acid (S)-4'-(1-Methyl-hexyloxy)-3'-nitro-biphenyl-4-yl ester, **15**, (**W649**) (0.15 g, 0.20 mmol, 76.9%) as light yellowish oil. ^1H NMR (CDCl_3 , 500 MHz): δ 8.02 (d, 1H, $J = 2.5$ Hz), 7.98 (m, 2H), 7.72 (dd, 1H, $J = 9.0, 2.5$ Hz), 7.60 (m, 2H), 7.57 (m, 2H), 7.12 (d, 1H, $J = 9.0$ Hz), 6.94 (m, 2H), 4.54 (h, 1H, $J = 6.0$ Hz), 4.02 (t, 2H, $J = 6.5$ Hz), 1.82 (m, 3H), 1.64 (m, 1H), 1.53-1.23 (m, 15H), 0.88 (t, 3H, $J = 7.0$ Hz), 0.47 (m, 2H), 0.00 (m, 21H), -0.29 (m, 4H). MS: Calculated for $\text{C}_{22}\text{H}_{42}\text{O}_3\text{Si}_3$, $([\text{M}-\text{H}]^+)$ requires: 766.2651, found: 766.3831.

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Chapter 3. Bent-core Achiral Ferroelectrics

3.1 Introduction

Since the rediscovery of bent-core LCs about 15 years ago, they have attracted a lot of interests because of their unique and interesting behavior, which is quite different from that of calamitic LCs.¹⁻³ Among the many bent-core LC phases, the SmCP phases (B_2 phases), which are tilted polar phases, have been investigated in most details, and they show many interesting properties. For example, in the B_2 phases the layer structure is chiral, even though the molecules themselves are achiral.⁴ Furthermore, two of the B_2 phases are macroscopically chiral, forming a fluid conglomerate. However, non-tilted orthogonal phases, SmAP phases, which are also fundamentally important and interesting, are much less common in the literature.^{5, 6}

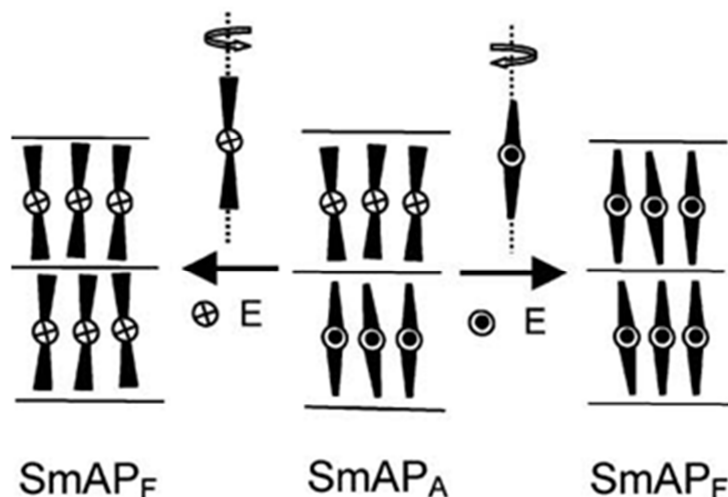


Figure 3.1: Schematic representation of polar switching in between the SmAP_A phase and the SmAP_F phase in which the polarization reversal takes place by a rotation of the molecules around the long axis.²

In principle, there should be two possible non-tilted SmAP phases, SmAP_A and SmAP_F as illustrated in Figure 3.1, while there are four tilted polar phases differing not only in polar directions from layer to layer, but also on tilt directions of bent-core molecules in adjacent layers. These are the SmC_{AP}_F, SmC_SP_F, SmC_{AP}_A, SmC_SP_A (see figure 1.8).² In general, bent-core LCs favor self-assembly into a tilted polar (SmCP) layer structure. One model explaining this tendency is as follows.

Smectic LC phases represent a system of fluid core and tail sublayers that are nano-phase segregated. In the case of bent-core LCs, this segregation is particularly strong compare to that of typical calamitic LCs, due to their biaxial shape, molecular bend and relatively long polarizable aromatic cores. These features tend to reduce out-of-layer fluctuations, stratifying the layers and keeping like-molecular parts next to one another, a generally suboptimal situation. For example, steric bumps on neighboring molecules tend to be next to each other and compete for the same free volume, or like charges on neighboring molecules repel. Generally this can be improved by a coherent tilt of the cones, giving molecular subcomponents a route to seek lower entropic and enthalpic free energy interactions with more complementary subcomponents on neighboring molecules. If such specific interactions are weakened, as in the case of short rod-shaped calamitic LCs with strong out-of-layer fluctuations, then untilted layers generally result.

Furthermore, for bent-core molecules the steric shape also promotes polar ordering, as filling space is more efficient and lower entropy overall if the bent-cores are on average oriented with the molecular bend in the same direction. Thus the core structure plays a key role in establishing the tilt and polar ordering.⁷

Another key energy ingredient in the layer of bent-core LCs is the entropic pressure of melted tails. In smectic bent-core LC phases, those melted tails prefer an area/molecule relatively large compared to that of cores.⁸ Tails are thus compressed and can increase their entropy by increasing their in-plane area. Since tilt increases the area/molecule, the entropy of tails generally favors tilt, suggesting that manipulation of tails may also have a key role in generating SmAP phases.

On the other hand, in SmCP phases, as illustrated in figure 1.8, the polar smectic layers can organize into two distinguishable structures depending on the direction of the polar order in adjacent layers. Either the polar direction can be parallel and thus become ferroelectric ($\text{SmC}_\text{AP}_\text{F}$ and $\text{SmC}_\text{S}_\text{P}_\text{F}$) or antiparallel and thus become antiferroelectric ($\text{SmC}_\text{AP}_\text{A}$ and $\text{SmC}_\text{S}_\text{P}_\text{A}$). The ferroelectric state represents a macroscopic polar structure whereas the antiferroelectric structure is macroscopically nonpolar. For bent-core molecules the antiferroelectric state is thought to be enhanced stabilized by the possibility of out-of-layer fluctuations due to synclinic layer interfaces, i.e., alkyl chains are aligned parallel at layer interfaces, which is favorable for these fluctuations. These out-of-layer fluctuations are hindered in the ferroelectric state, which represents an arrangement with anticlinic layer interfaces. Therefore, in most polar smectic phases, both SmAP and SmCP phases, of bent-core LCs the ground state is antiferroelectric. Up to now, for non-tilted orthogonal polar phases, there are only a few bent-core LCs showing the SmAP_A phase, and SmAP_F phases could only be seen under the influence of an electric field, relaxing back to the SmAP_A ground state after removal of the field.^{5, 6}

Meanwhile, the search for new methods of processing and displaying information has emphasized the importance of development and characterization of novel electro-optic

materials.⁸ Fast electro-optical switching has been a hot topic in this area, and further developments in the field could benefit from a better understanding of high polarization materials that allow controllable switching between different optical states.¹⁰ In the future, these materials may fill even greater needs for high speed switching in fiber optic applications.¹¹ In addition to their technological importance, some high polarization LCs have a rich phase sequence in a fairly narrow temperature window. Up to now, some SmCP bent-core LCs show quite high spontaneous polarization. It would be interesting and potentially useful to find a general approach for developing high spontaneous polarization LCs.

3.2 Goals and Prior Work

In order to generate the SmAP_F phase, both core and tail structures should be manipulated in a way distinct from the traditional SmCP materials. Several years ago, R. A. Reddy and B. K. Sadashiva developed a methodology by synthesizing asymmetric mesogens possessing only one tail, as exemplified by the cyanophenyl ester **1**, with all ester linkages between aromatic rings oriented in the same direction along the molecular axis.^{12, 13} Reddy and Sadashiva purposefully designed the core so that the dipolar interactions between two neighboring molecules favor an antiparallel configuration in principle and therefore a “partial bilayer” structure in the smectic layers could be achieved as shown in figure 3.2. The term “partial bilayer” applies when the layer spacing is larger than the molecular length, but less than twice the molecular length. Indeed, these bent-core LCs show a smectic layer spacing that is considerably larger than the molecular length, though less than twice the molecular length.¹³ In addition, by installing only one tail instead of two, the resulting factor of two reduction in tail volume

provides more in-plane space for the tails, reducing their entropic pressure, as illustrated in figure 3.3, and promoting orthogonal SmAP phases. The overall result of these two design features (one tail, and the same orientation of the carbonyloxy linkage groups) is an approach routinely giving both polar ordering and untilted (SmAP) layers, with antiferroelectric ordering of adjacent layers.

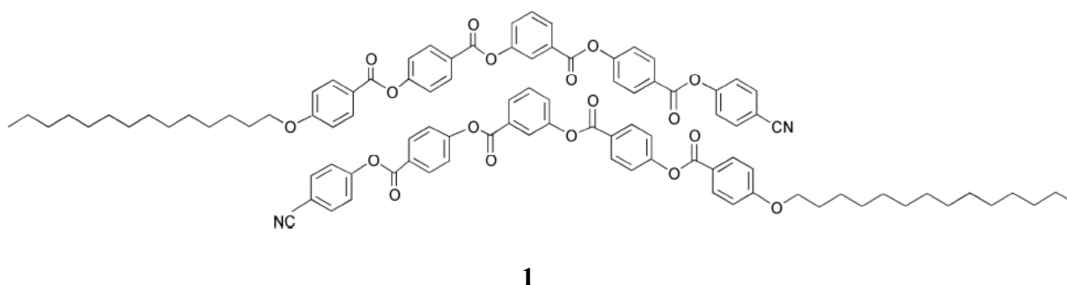


Figure 3.2: Chemical structure of cyanophenyl ester **1**, first reported by Sadashiva *et al.*, and the proposed antiparallel configuration of a pair of molecules showing the complete overlap of aromatic cores.¹³

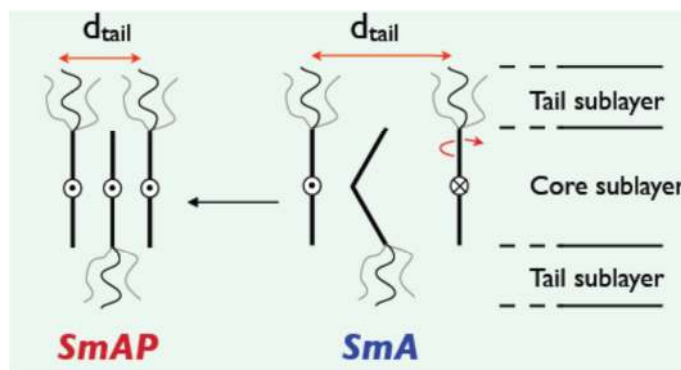


Figure 3.3: Reducing the number of tails from two to one per molecule creates more space for the tails, promoting orthogonal SmAP phases.

In order to induce a ferroelectric structure, creating the SmAP_F phase from the SmAP materials, we view the SmAP bent-core LC smectic layers as a system of layer interfaces. For the case of SmC* calamitic and SmAP_A bent-core mesogens, layer interfaces between classic LC tails (i.e. alkyl tails or alkoxy tails) are synclinal, which is favored by

out-of-layer fluctuations. Therefore, modification of the molecular structure of the tails to enable the formation of anticlinic layer interfaces by suppression of out-of-layer fluctuations is expected to provide the target SmAP_F phase in bent-core LCs, as sketched in figure 3.4. There are several reliable approaches for providing anticlinic layer interfaces in the literature.

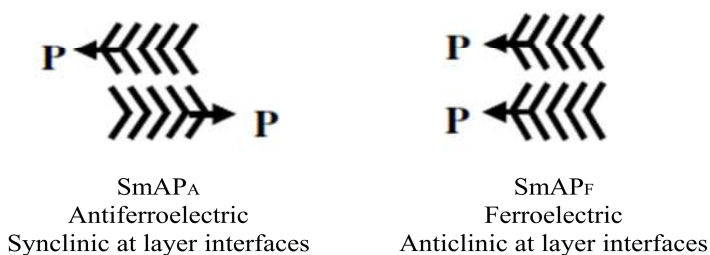


Figure 3.4: Schematic layer structures of the SmAP_A phase and the SmAP_F phase, showing the average molecular polar axis P . The SmAP_A phase is stabilized by synclinal ordering of molecular tails at layer interfaces.

One of these is incorporation of the MHPOBC tail (methylheptyloxycarbonyl tail), which successfully produced the first classic calamitic antiferroelectric LCs as well as the first ferroelectric SmCP bent-core LCs (SmC_8P_F).^{14, 15} The hypothesis is that the MHPOBC tail suppresses out-of-layer fluctuations at the layer interface because of its conformational behavior (the alkyl group on the chiral tail prefers on average to orient perpendicular to the core – more or less parallel to the layer interfaces), allowing normally entropically disfavored anticlinic layer interfaces to form.¹⁶ However, this approach failed in the asymmetric bent-core LC system by only yielding materials lacking mesophases.⁷

Based on the same principle, some other tails, including oligo-siloxane-terminated alkyl tails, trans-alkene alkyl tails, as seen in **W415**, and perfluorinated alkyl tails are also capable of showing properties resulting from suppression of out-of-layer fluctuations, and in some cases forming anticlinic layer and resulting in antiferroelectric calamitic LCs.¹⁷⁻¹⁹ R. A. Reddy in our group developed the tricarbosilane fragment **2** for this use, which in principle should behave similarly to the oligo-siloxane tail, yet possess enhanced chemical stability. (see figure 3.5).⁷

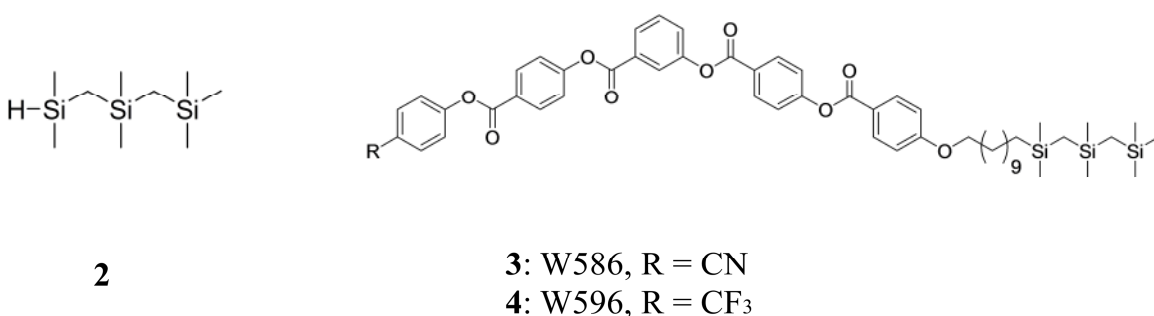


Figure 3.5: Chemical structures of tricarbosilane tail 2, SmAP_F LCs W586 and W596.

Based on the designed core and tail manipulation, our group successfully synthesized the first examples of SmAP_F bent-core LCs - **W586** and **W596** - as shown in figure 3.5.⁷ Various experiments, including X-ray, electro-optical, DSC measurements, and depolarized reflected light microscopy on thin freely suspended films, were performed to prove that **W586** and **W596** are indeed showing SmAP_F phases. For example, as shown in figure 3.6, under PLM, the random planar samples of **W586** exhibited focal conic textures, and showed a strong increase of effective birefringence with applied electric field of either sign normal to the plates, but no accompanying SmC-like optic axis rotation about the applied field direction, a behavior consistent with the SmAP_F phase.⁷

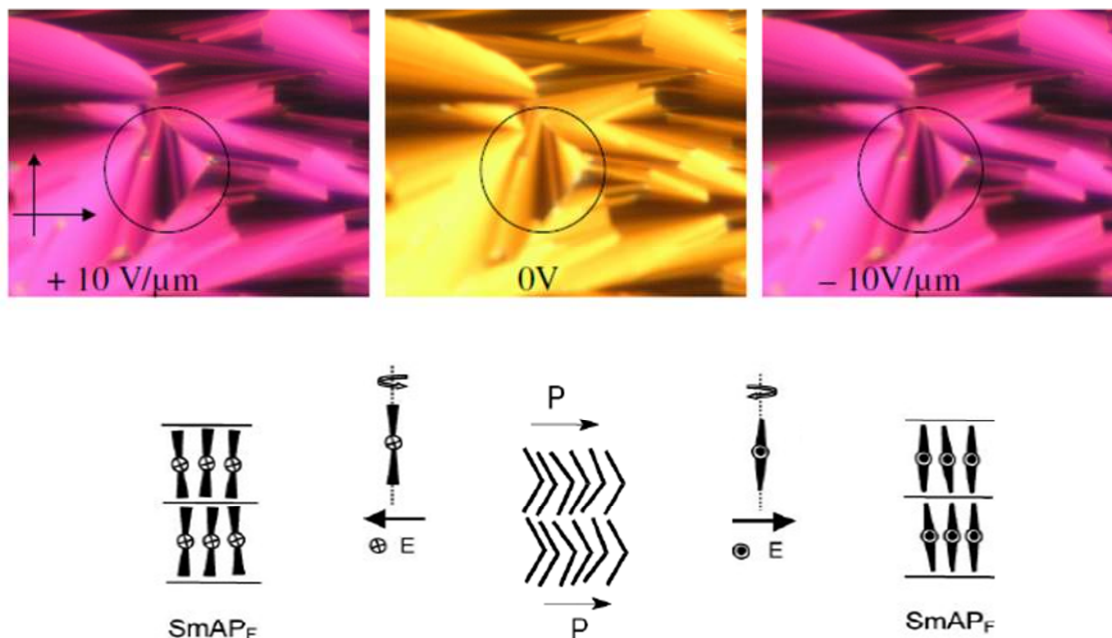


Figure 3.6: Nylon alignment layers on glass give random planar focal conics of W586 with the layers normal to the plates. At zero field the bent-core plane director is nearly parallel to the glass plates, exhibiting smaller apparent birefringence, while under applied electric field ($\pm 10\text{V}/\mu\text{m}$) the bent-core plane director is nearly perpendicular to the glass plates, exhibiting larger apparent birefringence.⁷

Based on these prior results, the current project involved manipulating both the core and the tail of the new asymmetric bent-core LC system to create a number of analogs of **W586** and **W596**. These bent-core LCs were examined by PLM, XRD and other techniques to determine their phase sequence and spontaneous polarization value, as well as electro-optical properties. A series of bent-core molecules with different orientations of ester linkages in the core were synthesized to test the hypothesis of the “dipole dimer” model proposed by B. K. Sadashiva *et al.* as well as to achieve high polarization SmAP_F materials.¹³ **W586** analogue with a very tight 60 degree bent-core angle was also prepared in order to achieve high spontaneous polarization in the LC phase.²¹ In addition, replacement of the terminal cyano or trifluoromethyl group with the tricarbosilane alkyl tail in the current system was also tested to obtain SmC_{APF} bent-core LCs which, to the

best of our knowledge, has only been reported previously in one special system possessing alkoxy tails with a methyl branch on the second to last carbon of the tail. The prototype material in this class has been given the name **KYOBOW** in our group.²²

3.3 Design and synthesis

In previous work from the Walba labs by Reddy, **W586** and **W596** were synthesized via a linear route, starting from the left side of each molecule and adding the aromatic rings one by one in each reaction step.^{7, 13} To create a family of similar bent-core molecules, a more efficient synthesis route needed to be developed. Therefore, a convergent synthetic route was pursued. In this thesis, most desired bent-core molecules were synthesized via the new convergent route, but using chemistry similar to that used for synthesis of **W586** and **W596**. In developing the new approach, **W586**-type structures were considered as deriving from coupling of three different components, as sketched in figure 3.7, using appropriate protecting groups and reaction conditions. Manipulating one or two of those three components would then yield a variety of different bent-core molecules, with structures allowing testing of the “dipole dimer” hypothesis, and perhaps yielding increased ferroelectric polarization in the SmAP_F phase.

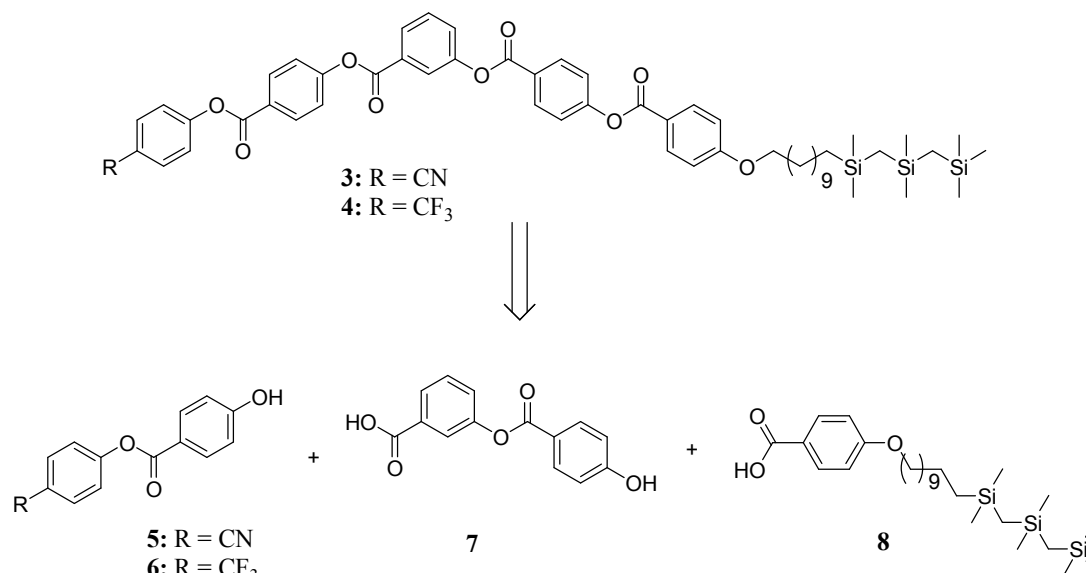


Figure 3.7: Retro synthesis of compound 3, W586, and 4, W596.

As illustrated in figure 3.8, the “left wing” component **5**, 4-Hydroxy-benzoic acid 4'-cyano-phenyl ester, can be prepared from compound **9**, 4-Benzyloxy-benzoic acid 4'-cyano-phenyl ester, by catalytic hydrogenation. It should be pointed out that this reaction needed to be monitored carefully since hydrogen gas with palladium catalyst can easily reduce the cyano group as well. Compound **9** can be readily synthesized in high yield using DCC (dicyclohexylcarbodiimide) coupling conditions from 4-cyanophenol and 4-Benzloxy-benzoic acid, both of which are commercially available. It should be noted that EDCI [1-ethyl-3-(3-dimethylaminopropyl) carbodiimide] was occasionally used in the coupling reaction instead of DCC, but the reaction conditions and outcomes are very similar. Synthesis of compound **6** can be achieved using the same route from the appropriate starting materials.

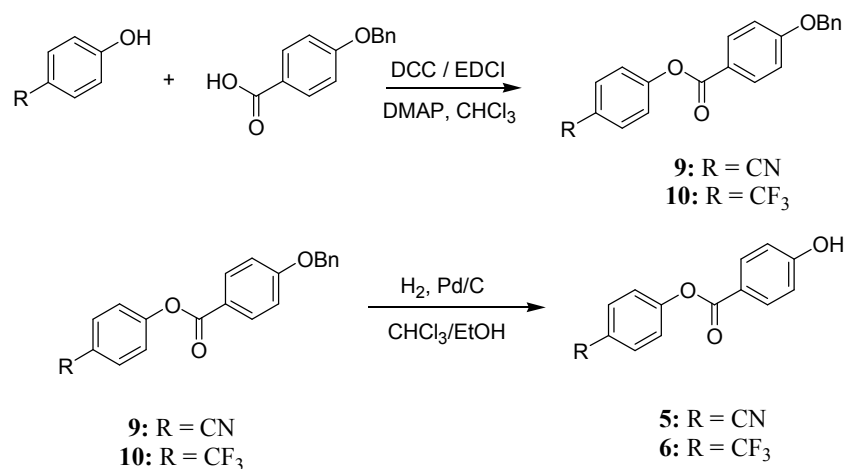


Figure 3.8: Synthesis of compound 5 and 6.

Compound **7** (figure 3.7) is the precursor of the “middle” fragment of the bent core, and contains both a phenol group and carboxylic acid group as coupling components in the retro synthesis of **W586** and **W596**. However, depending on the order of coupling left and right-wing components to compound **7**, one of these two functional groups need to be protected. In the **W586** and **W596** syntheses, the phenolic hydroxyl was protected as a benzyl ester to yield compound **12**, Isophthalic acid mono-(4-benzyloxy-phenyl) ester, and the unprotected carboxylic acid group was coupled with components **5** or **6** (see figure 3.9).

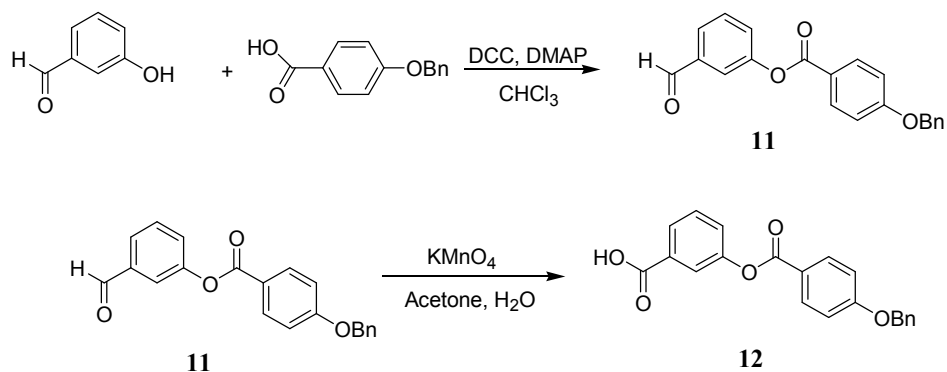


Figure 3.9: Synthesis of compound 12.

To get compound **12**, commercially available 4-Benzloxy-benzoic acid and 3-Hydroxy-benzaldehyde were used first under DCC coupling conditions to afford compound **11**, 4-Benzyloxy-benzoic acid 3-formyl-phenyl ester, in good yield. Then compound **11** was oxidized with KMnO_4 to give compound **12**, which was then coupled in the next step with compound **5** or **6** under DCC coupling conditions to yield compound **13** or **14**, respectively. In the following step, either molecule's benzyl group was deprotected by catalytic hydrogenation to give compound **15** or **16**, respectively, as the core of **W586** or **W596** as shown in figure 3.10.

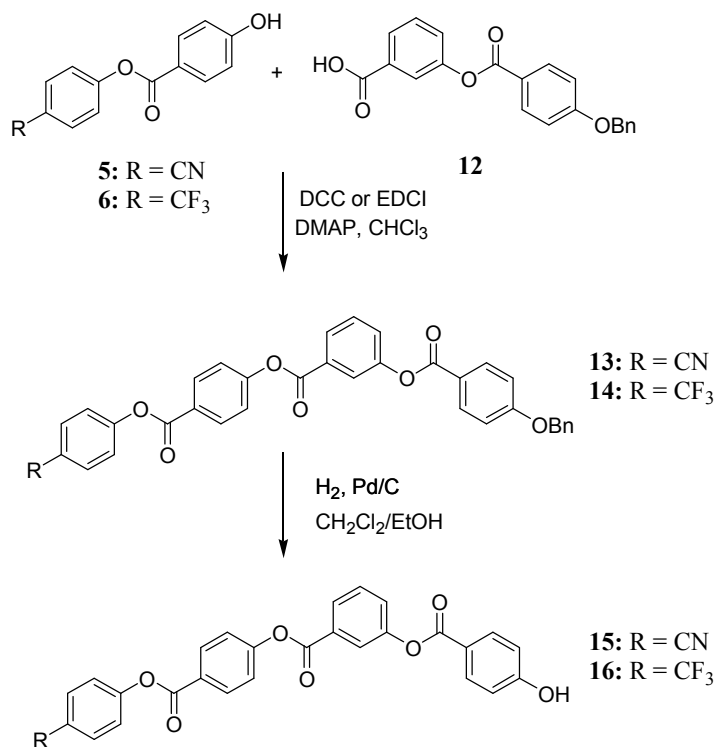


Figure 3.10: Synthesis of compound **15** and **16**.

To get the “right wing” of **W586** and **W596**, the tricarbosilane tail **2** was first synthesized under the same reaction condition as described in chapter 2. Then, tricarbosilane **2** was installed onto the bent cores by hydrosilation with Karstedt’s catalyst

(platinum-divinyltetramethyl-siloxane complex in xylene) to the terminal alkene group of benzyl ester **17**, as shown in figure 3.7. Alkene-ester **17**, in turn, is easily obtained from commercially available starting materials under Williamson-ether synthesis conditions (figure 3.7). The hydrosilation is not regioselective, but isomers could be easily separated using column chromatography to give desired tricarbosilane-ester **18**. After that, removing benzyl ester protecting group under catalytic hydrogenation conditions gives the “right wing” compound **19**, which can be used to couple, with compound **15** or **16** to form **W586** or **W596**, respectively, under DCC coupling conditions (see figure 3.11).

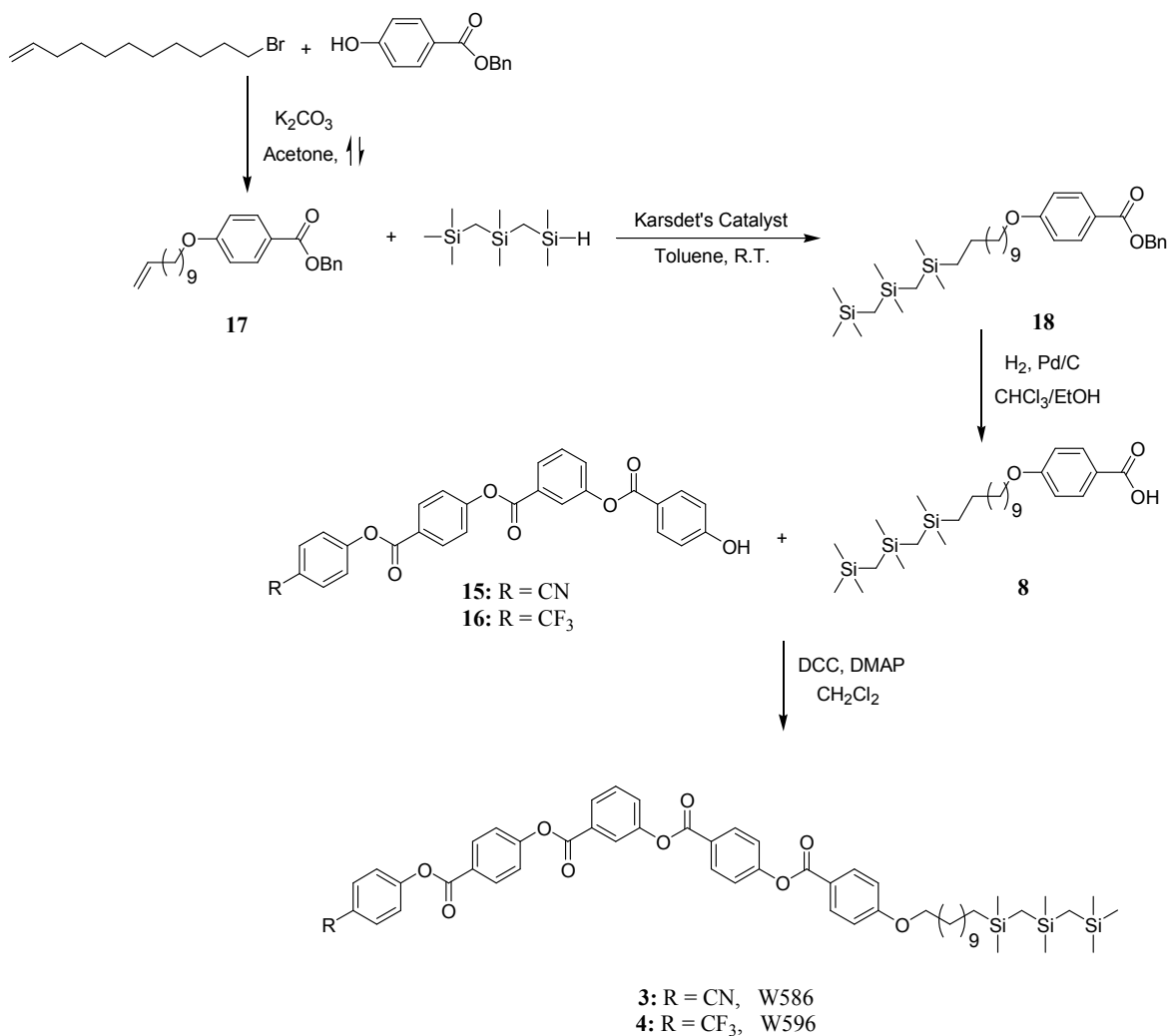


Figure 3.11: Synthesis of W586 and W596.

Both **W586** and **W596** were successfully synthesized using this approach, which provides a general synthetic strategy for making similar bent-core molecules.

The experimental X-ray data showed that **W586** has a layer spacing of 61.5 Å, which is about 9.5 Å longer than the calculated fully extended molecular length L , 52 Å, suggesting that the compound may adopt the intercalated “partial bilayer” structure as has been proposed for asymmetric SmAP bent-core LCs.^{7, 13} Figure 3.12 shows a schematic representation of a polar packing of molecular “dipole dimer” pairs within the layer, and a ferroelectric ordering with partial interdigitation between adjacent layers for these single-tail bent-cores. However, although the dipole moments of each ester linkage groups as well as the terminal cyano group were purposefully designed to align in the same direction as the molecular long axis, the electron dispersion among aromatic cores is more complicated than the “dipole dimer” model suggests, and it would be interesting to see how molecular structural changes – basically “flipping” carbonyloxy groups, affects the properties of the bent-core molecules.²³ Such “flipping” could increase the horizontal dipole, as shown in figure 3.12, at the molecular level, and could translate to higher spontaneous polarization in the SmAP_F phase, but would break the continuity of carbonyloxy dipoles, in principle negating the ability of the molecules to form “dipole dimers”, and also the formation of the desired high polarization SmAP_F phases.

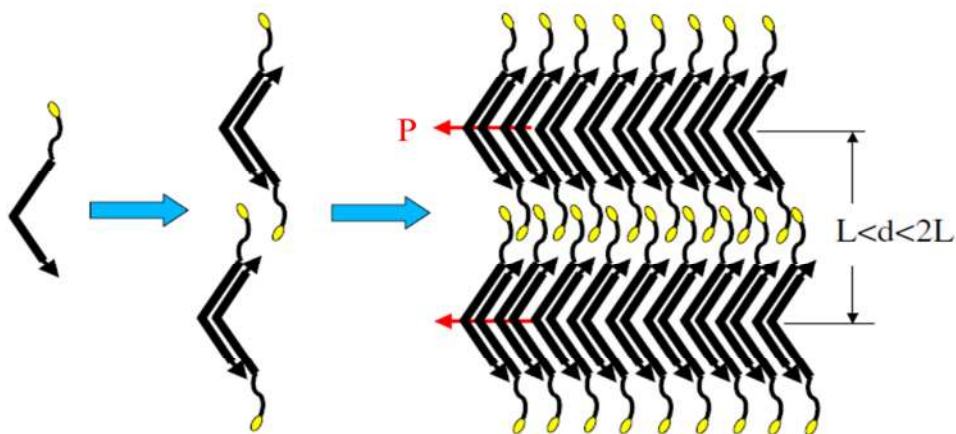


Figure 3.12: Hypothesis of molecular organization in the SmAP_F phase of W586. Spontaneous dipole P points in the same direction from layer to layer. In each layer, half the molecules point upwards and the other half point downwards to form the “dipole dimer”s, while keeping the core and tail separated.

To test the “dipole dimer” model in this way, and to obtain new SmAP_F mesogens, several new bent-core molecules were synthesized by flipping either the ester linkage (or both) in the “right wing” of **W586** and **W596**. The new molecules were synthesized by using the same synthetic strategy as described above, but using different components. As shown in figure 3.13, **W623** (or **W628**) can be synthesized using same components **5** (or **6**) and **8**, as used for **W586** (or **W596**), along with a slightly different middle core component **20** under similar reaction conditions.

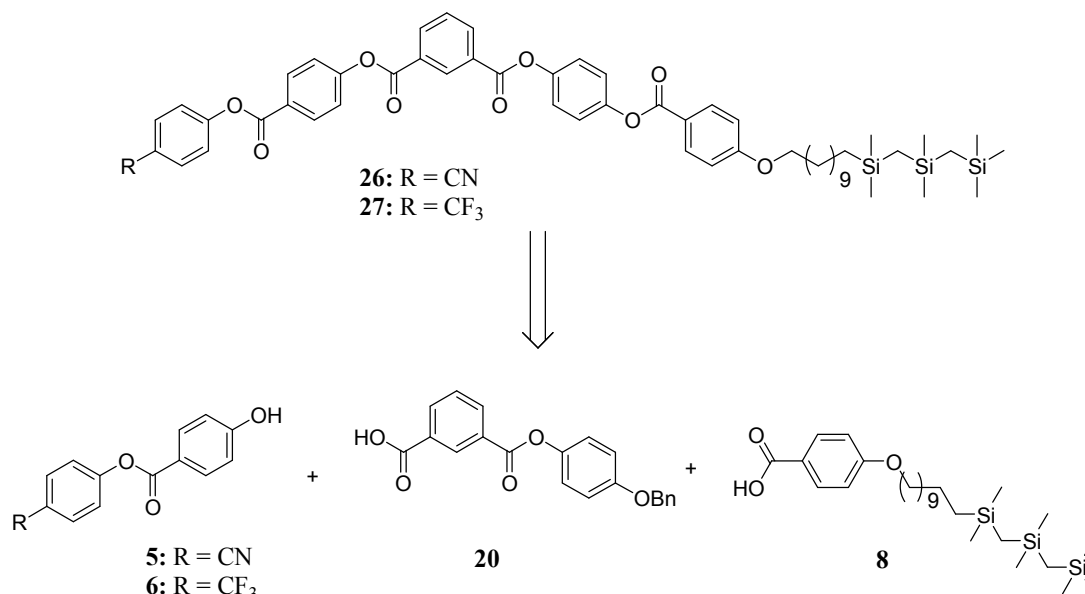


Figure 3.13: Retro synthesis of compound 26, W623 and 27, W628.

Initial coupling between acid **20** and phenol **5** (or **6**) worked as expected. However, the product **22** (or **23**) was highly insoluble in either CH₂Cl₂ or CHCl₃, typical solvents for DCC coupling, and precipitated out with the byproduct dicyclohexylurea. Therefore, acid **20** was converted to the acid chloride (**21**) in order to get pure esters **22** (or **23**) in a reaction which doesn't produce any insoluble byproducts (see figure 3.14 and figure 3.15).

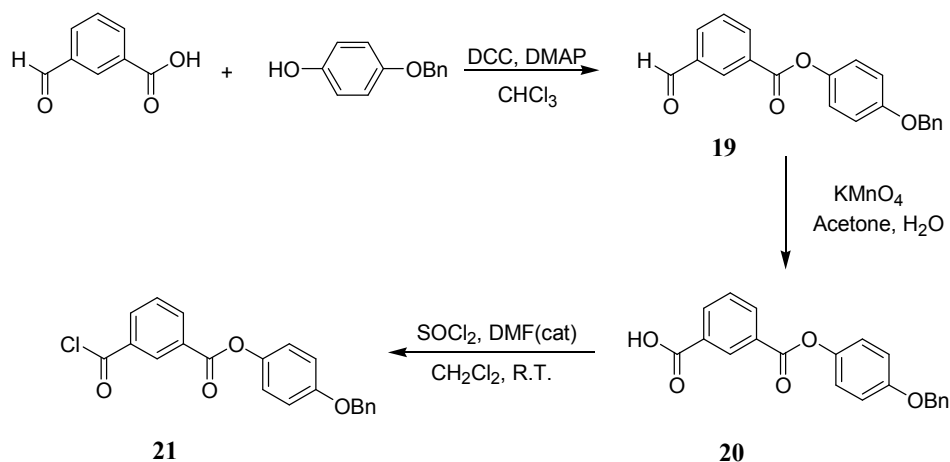


Figure 3.14: Synthesis of compound 20 and 21.

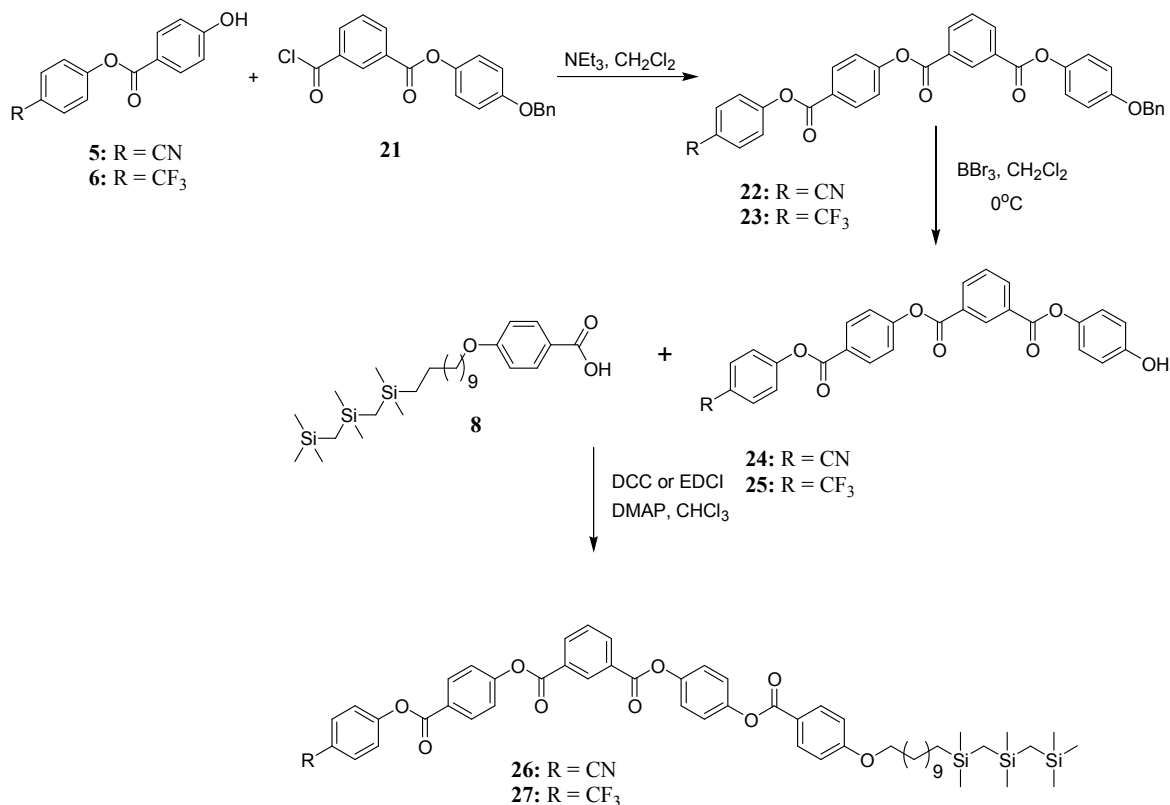


Figure 3.15: Synthesis of compound 26, W623, and 27, W628.

After successfully achieving synthesis of clean benzyl ethers **22** and **23**, the phenol groups in either molecule were readily deprotected to produce phenols **24** and **25** for the final coupling reaction. It should be noted that for compound **22**, using catalytic hydrogenation to remove the benzyl group took a relatively long time (about 1 day) and this was problematic since the cyano group was also reduced. To avoid the undesired reduction, another method was needed to remove benzyl group in compound **22** or similar molecules. In this regard, boron tribromide (BBr₃) was used to deprotect the benzyl group in such systems, to give clean product in high yield.²⁴ After BBr₃ debenzilation to obtain phenols **24** and **25**, these were used to couple with acid **8** to

obtain the desired bent-core molecule **26**, (**W623**) and **27** (**W628**) using carbodiimide promoted esterification as shown in figure 3.15.

To change the dipole moment of the other ester linkage in the “right wing” of **W586** and **W596**, the same synthetic strategy was initially tried, based on different synthetic components as shown in figure 3.16. However, after successfully coupling phenol **5** (or **6**) and mono-protected diacid **29**, the diester’s benzyl protecting group could not be cleanly removed by either catalytic hydrogenation or BBr_3 debenzylation.

Therefore, an alternative strategy for assembling bent-core targets **30**, **W631** and **31**, **W632** was developed, as indicated in figure 3.17. The chemistry used here is similar to that described above.

Flipping both ester linkages in the “right wing” of **W586** to get compound **44**, **W635**, was also achieved under a slightly different but successful synthesis as show in figure 3.18. Such bent-core molecules are expected to possess the largest possible spontaneous polarization for this series of isomers, since all of the carbonyloxy dipoles, projected onto the polar axis, on average should orient in the same direction, and also parallel to the projection of the $-\text{CN}$ or $-\text{CF}_3$ dipoles. This argument is highly oversimplified, but is nevertheless appealing.

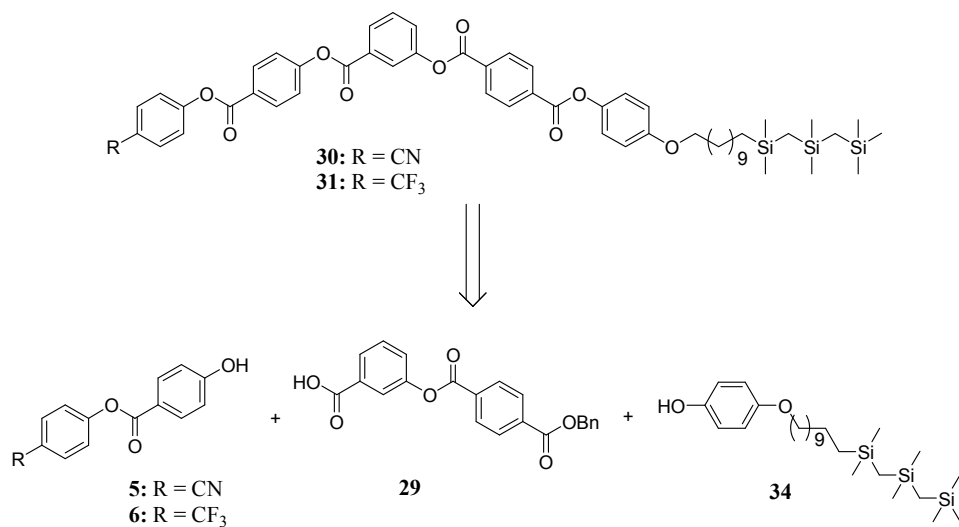


Figure 3.16: Retro synthesis of compound 30, W631 and 31, W632.

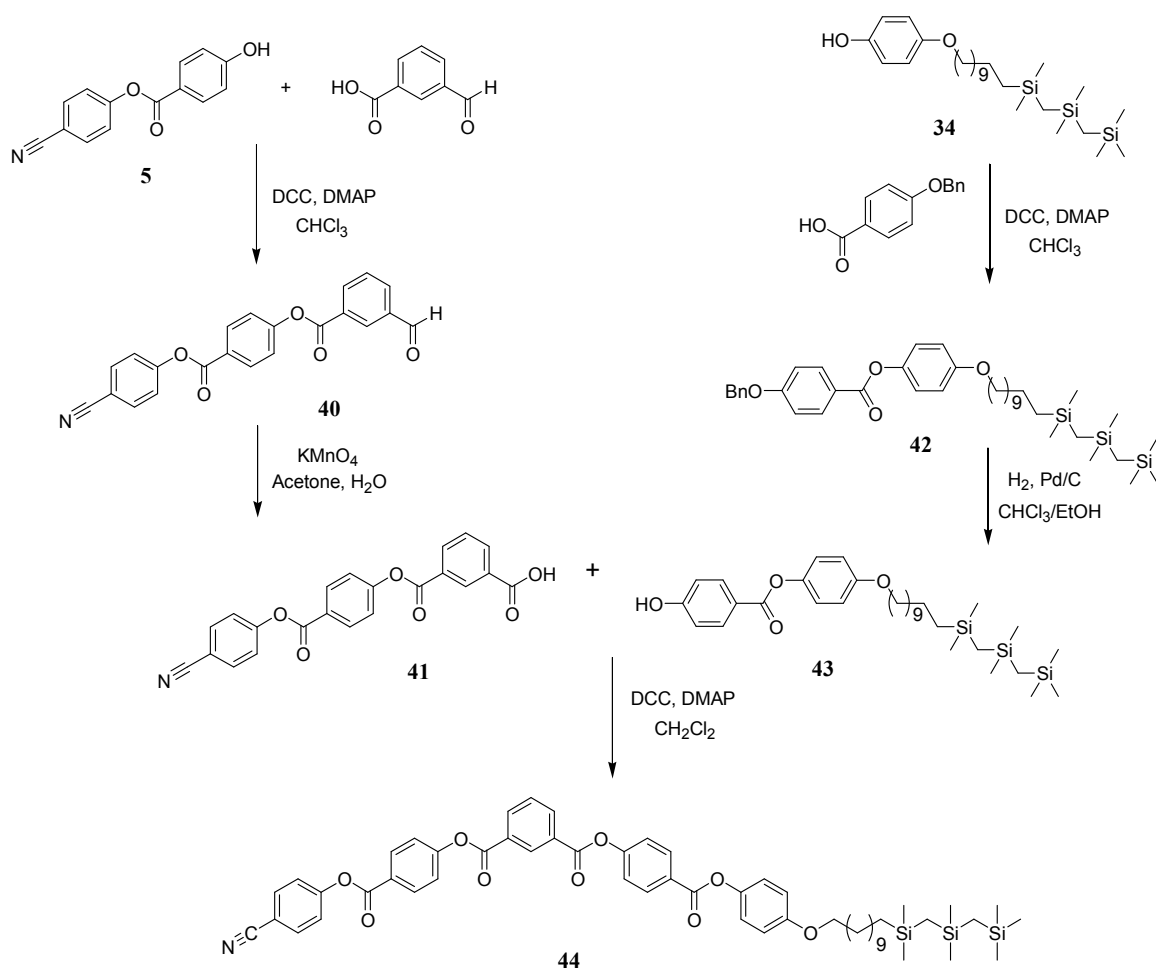


Figure 3.18: Synthesis of compound 44, W635.

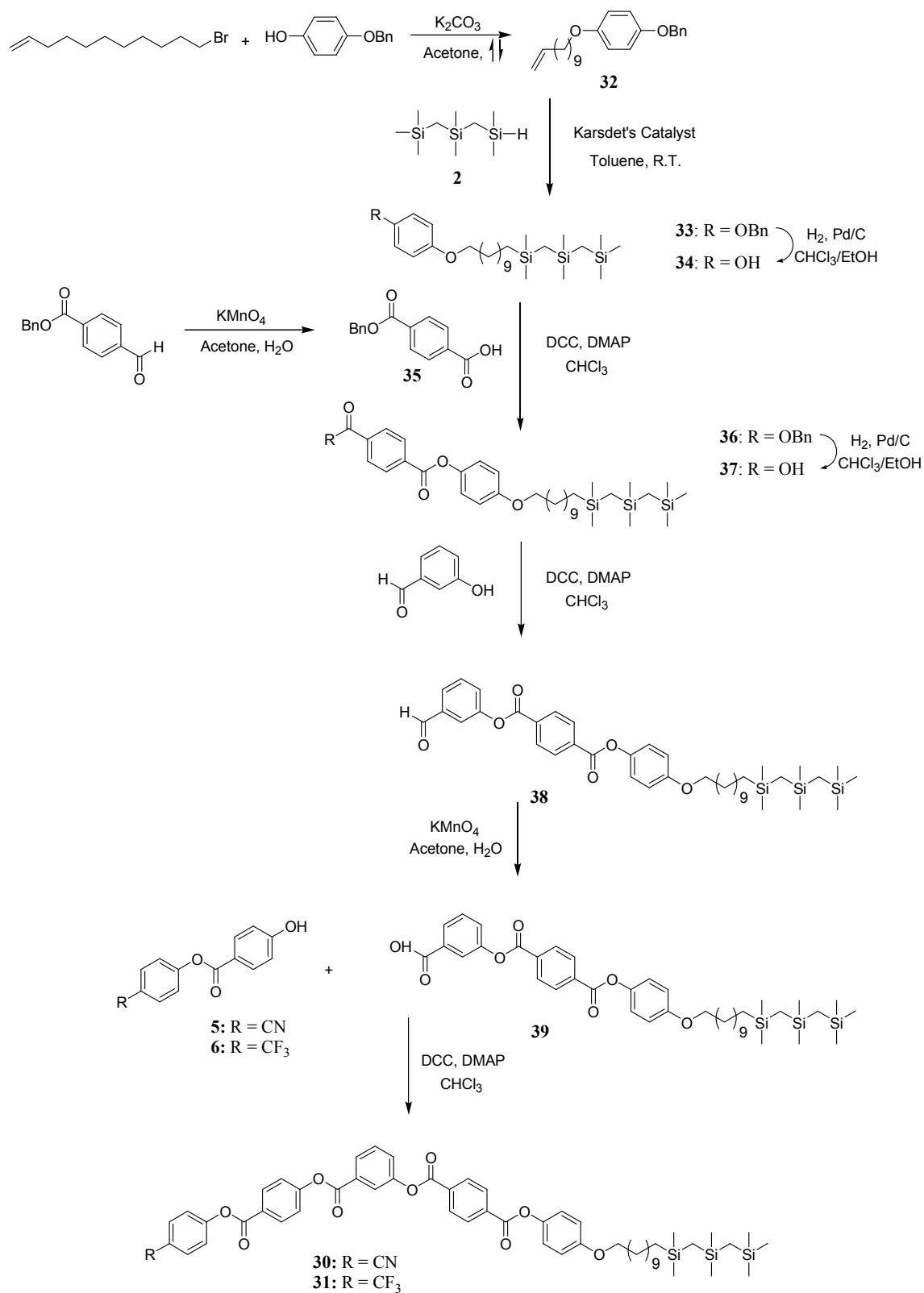
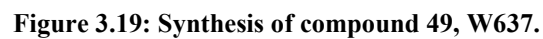


Figure 3.17: Synthesis of compound 30, W631 and 31, W632.

To get a smaller angle between the two wings or the bent-core, which is expected to dramatically increase the polarization in the SmAP_F, a different core component, 2-Hydroxy-benzaldehyde, was used to couple with similar “left wing” and “right wing” components as used above.

As indicated in figure 3.19, the synthetic route was similar to the routes previously described, and the synthesis was successfully carried out to yield compound **49**, **W637**.



Double tricarbosilane tail symmetric bent-core molecules were also synthesized in order to pursue the $\text{SmC}_\text{AP}_\text{F}$ bent-core LC phase. Such bent-core molecules were successfully obtained using either resorcinol (benzene-1,3-diol) or Isophthalic acid with corresponding “wing” components, which were both synthesized earlier (see figure 3.20 and figure 3.21).

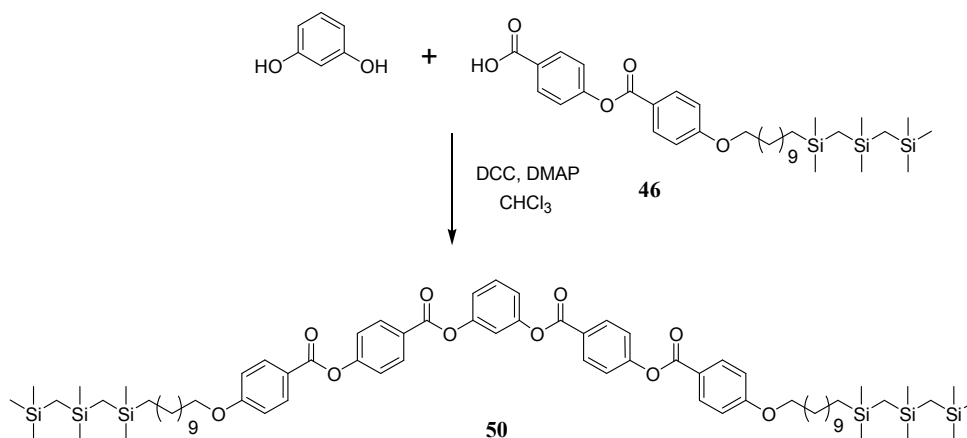


Figure 3.20: Synthesis of compound 50, W634.

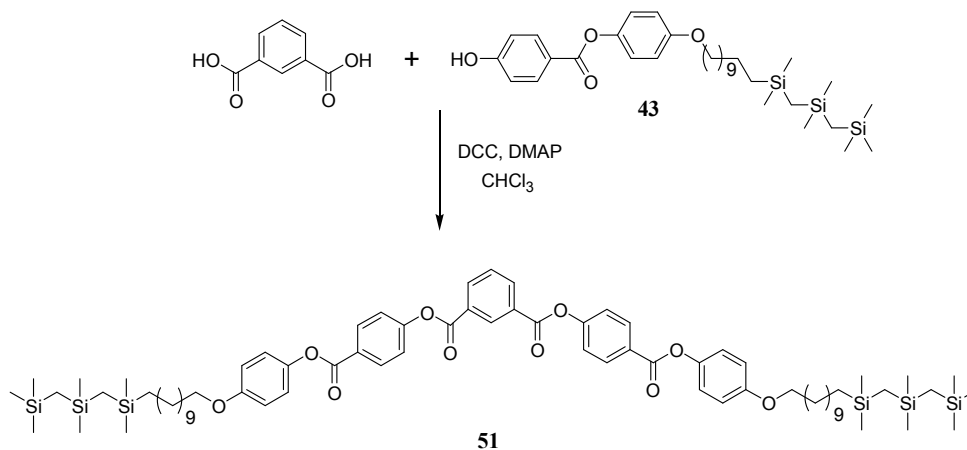


Figure 3.21: Synthesis of compound 51, W638.

3.4 Results and Discussions

Overall, ten bent-core molecules were successfully synthesized by new routes. Eight of these compounds are previously unreported. Trivial names and phase transition data are presented in table 3.1 below.

Name	Phase Transitions on Cooling (°C)
W586 ⁷	Iso $\rightarrow$ 155 $\rightarrow$ SmA $\rightarrow$ 136 $\rightarrow$ SmAP _F $\rightarrow$ 80 $\rightarrow$ X
W596 ²⁰	Iso $\rightarrow$ 162 $\rightarrow$ SmAP _F $\rightarrow$ 127 $\rightarrow$ SmAP _F $\rightarrow$ 104 $\rightarrow$ X
W623	Iso $\rightarrow$ 195 $\rightarrow$ SmA $\rightarrow$ 165 $\rightarrow$ SmAP _F $\rightarrow$ 135 $\rightarrow$ SmX
W628	Iso $\rightarrow$ 200 $\rightarrow$ SmAP _F $\rightarrow$ 175 $\rightarrow$ X
W631	Iso $\rightarrow$ 165 $\rightarrow$ SmA $\rightarrow$ 125 $\rightarrow$ SmAP _F $\rightarrow$ 120 $\rightarrow$ X
W632	Iso $\rightarrow$ 170 $\rightarrow$ SmA $\rightarrow$ 152 $\rightarrow$ SmAP _F $\rightarrow$ 145 $\rightarrow$ X
W634	Iso $\rightarrow$ 102 $\rightarrow$ X
W635	Iso $\rightarrow$ 180 $\rightarrow$ SmAP _F $\rightarrow$ 175 $\rightarrow$ SmC _A P _F $\rightarrow$ 170 $\rightarrow$ X
W637	Iso $\rightarrow$ 170 $\rightarrow$ X
W638	Iso $\rightarrow$ 96 $\rightarrow$ X

Table 3.1: Names and phase transitions of the ten bent-core molecules synthesized. All data obtained are from PLM.

3.4.1 W623

This bent-core molecule was the first among the family of new materials to be synthesized, and it was designed to serve two purposes: 1) by switching one ester linkage dipole moment direction (flipping the carbonyloxy group) in the “right wing” of the core,

we would expect either different mesogenic behavior based on the “dipole dimer” model, or mesogenic behavior similar to **W586**, which would refute the model; and 2) If we could observe the SmAP_F phase, we would expect a large spontaneous polarization because of the presumably larger projection of the total ester dipole along the bow axis of the molecule (the polar axis).

W623 was identified to have the following phase sequence on cooling: Iso $\rightarrow$ 195°C $\rightarrow$ SmA $\rightarrow$ 165°C $\rightarrow$ SmAP_F $\rightarrow$ 135°C $\rightarrow$ SmX. Several experiments were carried out to determine the phase sequence and the phase behavior. As shown in figure 3.22, on cooling, the DSC curve of **W623** clearly showed two big peaks representing first order transitions, which were later identified as the Isotropic to SmA and the SmAP_F to SmX transitions. There was another very small peak indicating a second order or weakly first order transition, which was believed to be the SmA to SmAP_F transition. The SmA to SmAP_F transition of W586 behaved similarly in the DSC.

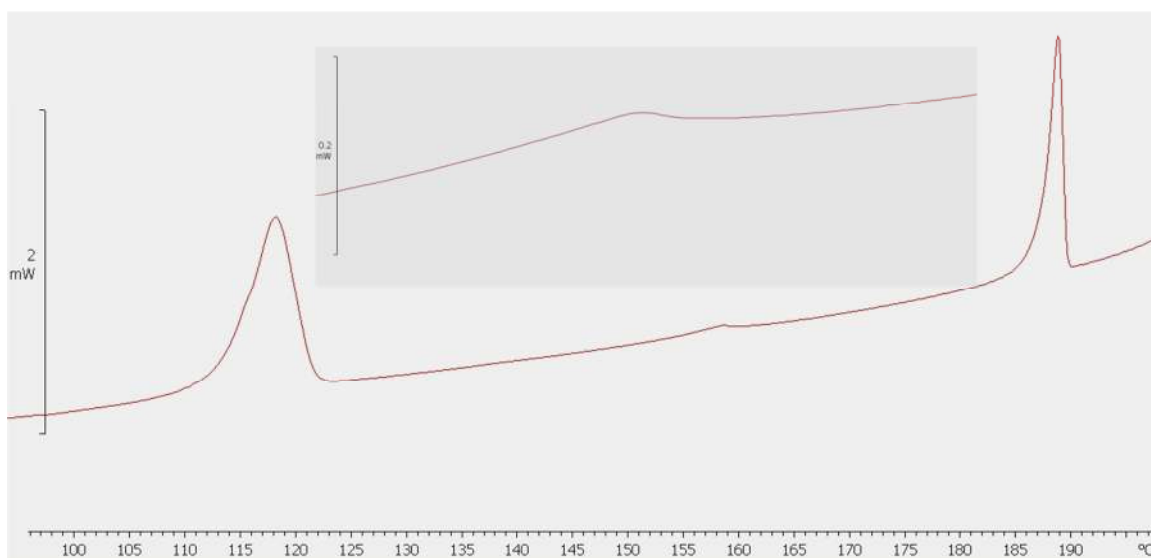


Figure 3.22: DSC of W623 on cooling. The inset is a close look at the SmA-SmAPF transition.

In order to confirm the phase transitions suggested by DSC, an X-ray diffraction study was accomplished on **W623** by Yongqiang Shen in the Clark group. The first order transitions can be easily identified by a discontinuous jump in layer spacing, d , or equivalently the Bragg peak position, q . Figure 3.23 shows the variation of layer spacing d versus temperature during LC phase transition on cooling and the variation of peak position q versus temperature for the whole phase sequence on cooling. The phase transition temperature obtained from X-ray was slightly different from the phase transition temperature obtained from DSC and PLM which is common for most LCs. The distinct changes can be clearly observed at 205°C and 145°C from layer spacing d and peak position q and they represent first order transitions. Additionally, we can see a continuous change from 185°C to 180°C representing the second order transition from possibly the SmA to SmAP_F phase transition, which agrees well with the tiny enthalpy peak from DSC. The layer spacing of this compound in the LC phases is about 63.5 Å, which is 11.5 Å longer than the fully extended molecular length L , 52 Å. This suggests that **W623** also adopts the same intercalated structure proposed for **W586** and clearly implies that the asymmetric bent-core molecules do not have to possess opposite dipole to adopt the intercalated structure. Another interesting fact observed from the X-ray experiments was that at the first order transition of **W623** starting at 145°C, it went from one sharp peak to four separate peaks, as illustrated in figure 3.24, which is quite different from the result of its analog **W586**, which enters the crystal phase after the SmAP_F phase. Similar behavior was observed in the B4 phase of **NOBOW** and this particular “mystery” phase will be discussed later in this chapter.²⁷

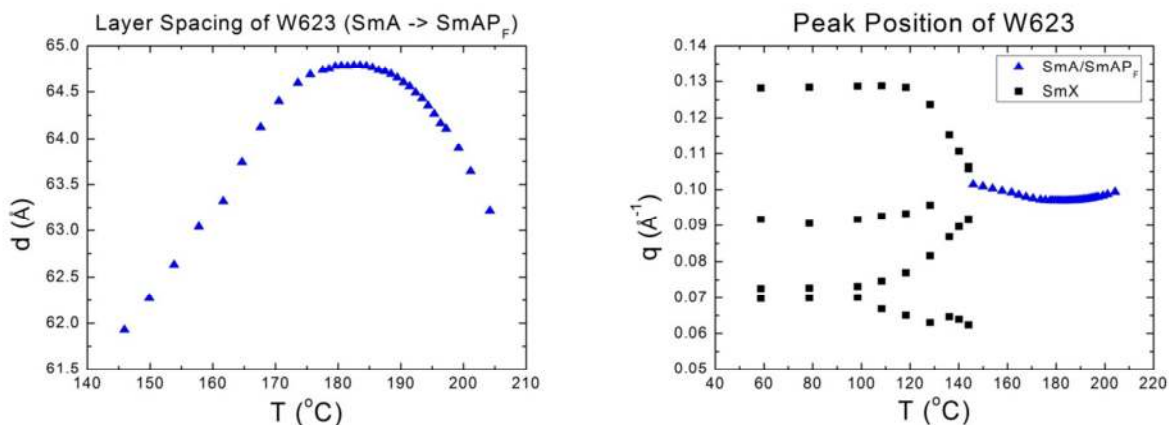


Figure 3.23: X-ray measurements of layer spacing, d , and peak position, q , as a function of T on cooling for W623.

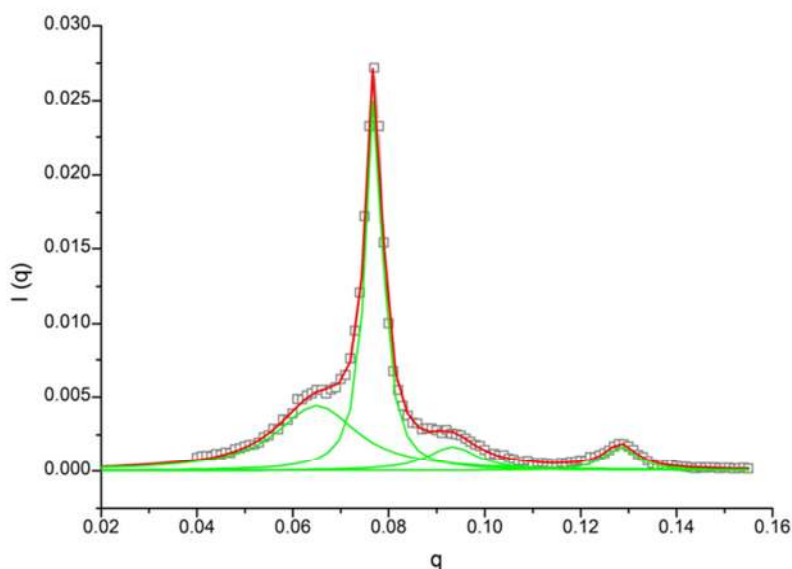


Figure 3.24: X-ray measurement of W623 at 118°C, obtained at Brookhaven National Laboratory.

Then, the optical textures of samples of **W623** were studied using two different preparation methods under PLM: homeotropic cells (using clean glass plates, yielding homeotropic alignment) and random planar cells (using polyimide films on ITO plates, yielding random planar focal conic textures with the smectic layers locally normal to the plates). (See figure 3.25)

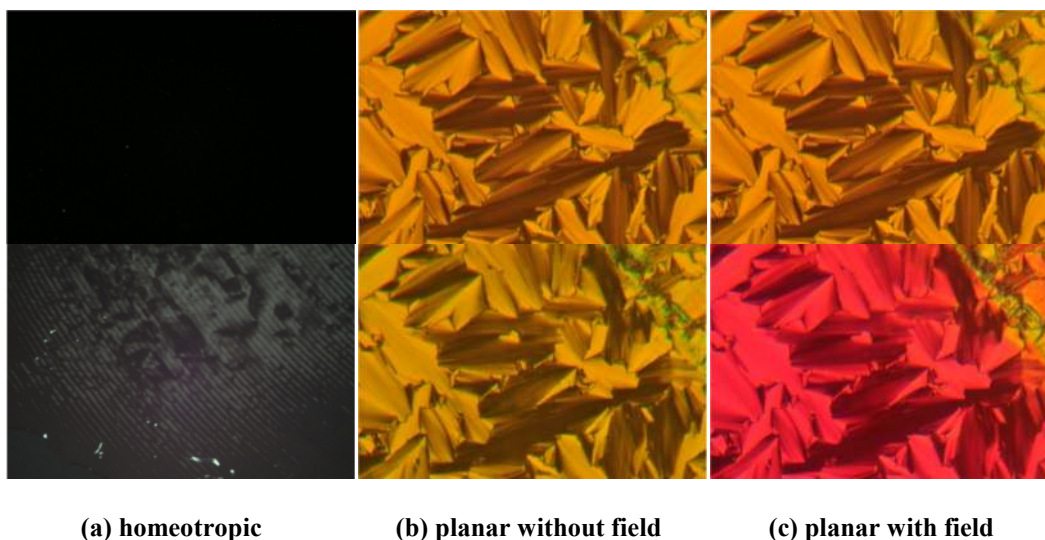


Figure 3.25: Optical textures of W623 between treated glass plates between crossed polarizer and analyzer, top row is the images at high temperature SmA phase (185°C) and bottom row is the images at low temperature SmAP_F phase (145°C): (a) clean glass preparation with layers parallel to the plates, molecules normal to the plates, (b) polyimide films on glass give random planar focal conics with the layers normal to the plates at zero field, and (c) polyimide films on glass give random planar focal conics with the layers normal to the plates at 10V/μm external field.

The high temperature phase identified as SmA phase gives excellent extinction between crossed polarizer and analyzer in the homeotropic cell (figure 3.25(a), top), evidence for an optically uniaxial normal to the layers and plates. On the other hand, upon cooling to the low temperature phase, a distinct Schlieren texture of in-layer birefringence appeared (figure 3.25(a), bottom), characterized by smooth brush patterns indicative of slowly varying optical anisotropy and thus in-layer orientational ordering of the molecular bow-planes. Additionally, a remarkable quasi-periodic pattern of stripes appeared, each of which marks the termination of a single smectic layer accommodating the spatial variation of the gap between the glass plates. The appearance of these stripes is analogous to that found in homeotropic samples of rod-like molecules as one passes through the SmA to SmC transition.^{25, 26} Those PLM images showed that **W623** samples are uniaxial in the high temperature SmA phase, and locally biaxial ordering with an

optic axis normal to the layers and increasing in-plane birefringence Δn with decreasing temperature in the low temperature phase.

The random planar samples exhibited focal conic textures, which showed a strong increase of effective birefringence with applied electric field normal to the plates, indicating such low temperature phase is ferroelectric, but no accompanying SmC-like optic axis rotation about the applied field direction in the low temperature phase (figure 3.25(c)). This observation along with the homeotropic Schlieren texture indicates that one optical dielectric tensor principal axis is along the layer normal and suggests the low temperature phase is SmAP_F.

The birefringence of **W623** was measured in the SmA and SmAP_F phases with and without applied external electric field as shown in figure 3.26. There are three different refractive indices either along the molecular long axis, n_z , or molecular bow axis (polar axis), n_p , or n_o which is perpendicular to both n_z and n_p . When **W623** in the high temperature SmA phase, because of the random distribution of the molecular bow axis, birefringence Δn equals $n_z - (n_o + n_p)/2$. Since the SmA to SmAP_F phase transition is second order, when the temperature approaches the transition, the molecular bow axis distribution becomes more ordered and birefringence Δn equals $n_z - n_{\text{eff}}$. n_{eff} is smaller than $(n_p + n_o)/2$ and becomes smaller with decreasing temperature, therefore the birefringence of **W623** increases with decreasing temperature in the SmA phase. After **W623** entered the SmAP_F phase, however, the molecular bow axis distribution became even more ordered towards aligning along the polar axis and the n_{eff} becomes bigger approaching n_p , indicating a reduced fluctuation, therefore the birefringence of **W623** decreased with decreasing temperature in the SmAP_F phase.

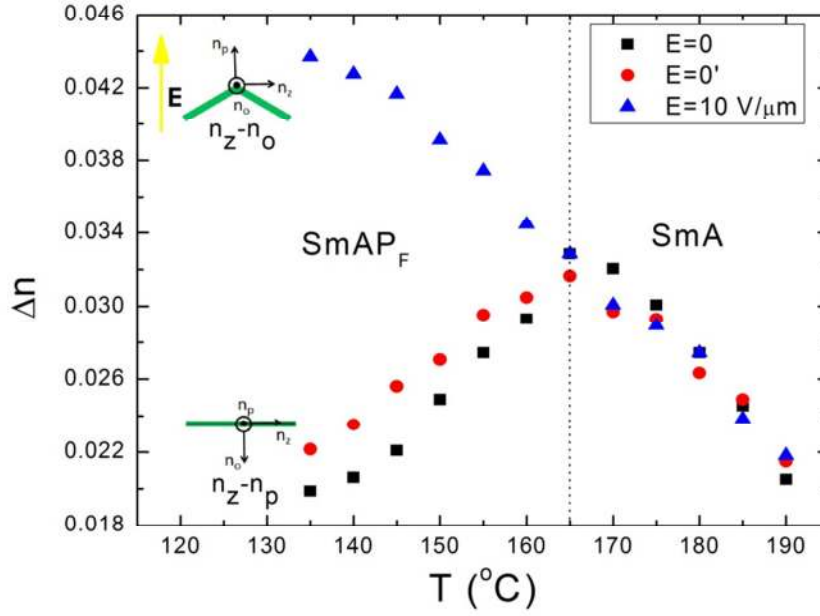


Figure 3.26: Birefringence of W623 in a 9 μm polyimide planar-aligned cell measured using a Berek compensator with normally incident white light and schematic representation of three different refractive indices in SmAP_F phase. The black dots represent the birefringence of the virgin state.

Electro-optic measurements of **W623** were also carried out, with the results shown in figure 3.27. This material showed one particularly interesting behavior: the polarization current in the analog switching regime is constant, i.e., capacitive, with the liquid crystal block polarization acting as a short circuit. To the best of our knowledge, this kind of behavior had never been observed before, and to better understand such behavior, it is useful to briefly describe the concept of “electrostatic V-shaped switching”.

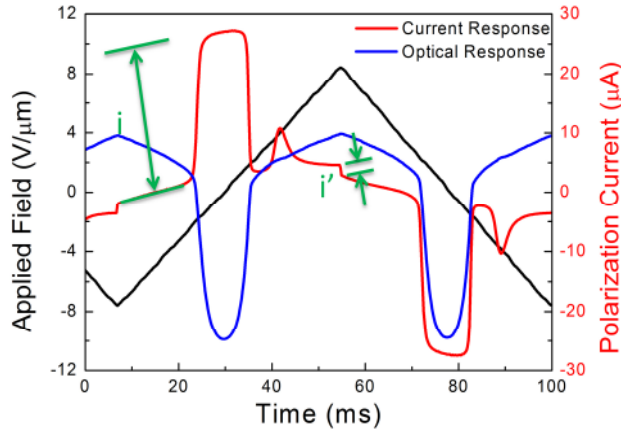


Figure 3.27: Electro-optic response of W623 at $T=158^{\circ}\text{C}$ in a $4.8\text{ }\mu\text{m}$ thick cell with ITO electrodes and rubbed polyimide alignment layers observed with crossed polarizers at 45° to the layer normal.

In crystal ferroelectrics, the macroscopic polarization density $\mathbf{P}$ is stabilized to a set of discrete orientations by the underlying lattice, and ferroelectricity heralded by field-induced switching of $\mathbf{P}$ between these stable states. The electrical current accompanying field-induced polarization reversal then comes from the motion of domain boundaries. In fluid LCs having macroscopic polarization, such as in the chiral SmC phase or the SmCP_F phases, orientational constraints are absent in the bulk, leading to the possibility of continuous field-induced reorientation of $\mathbf{P}$, manifest as hysteresis-free, “analog” or “thresholdless” field-induced reorientation of the director.^{28, 29} In high polarization materials, such analog reorientation approaches a particularly simple limit, sketched in figure 3.28(b), in which the liquid crystal polarization $\mathbf{P}(\mathbf{r})$ is rendered spatially uniform by the electrostatic polarization charge interaction, constraining it to reorient as a homogeneous “block”, with uniform orientation ϕ . For a static voltage V applied to such a cell, such reorientation will proceed until the electric field in the liquid crystal, E_{LC} , is reduced to zero.^{30, 31} This condition obtains when $\mathbf{P}$ reorients to make the polarization

charge density on the LC surfaces, $\sigma_P = P \cos \phi$, where ϕ is the angle between $\mathbf{P}(\mathbf{x})$ and the surface normal, $\mathbf{x}$, exactly equal and opposite to the electrode charge density. The cell voltage V is then given by $V = \sigma_P / c$, where c is the interfacial capacitance per unit area, leading to analog, voltage-controlled reorientation of $P(\phi)$ given simply by $\phi(V) = \cos^{-1}(cV/P)$. Measurements of the optic axis reorientation in chiral SmC LCs and of the optical biaxial birefringence of bent-core SmC_AP_F confirm this model for quasistatic voltages.^{31, 32}

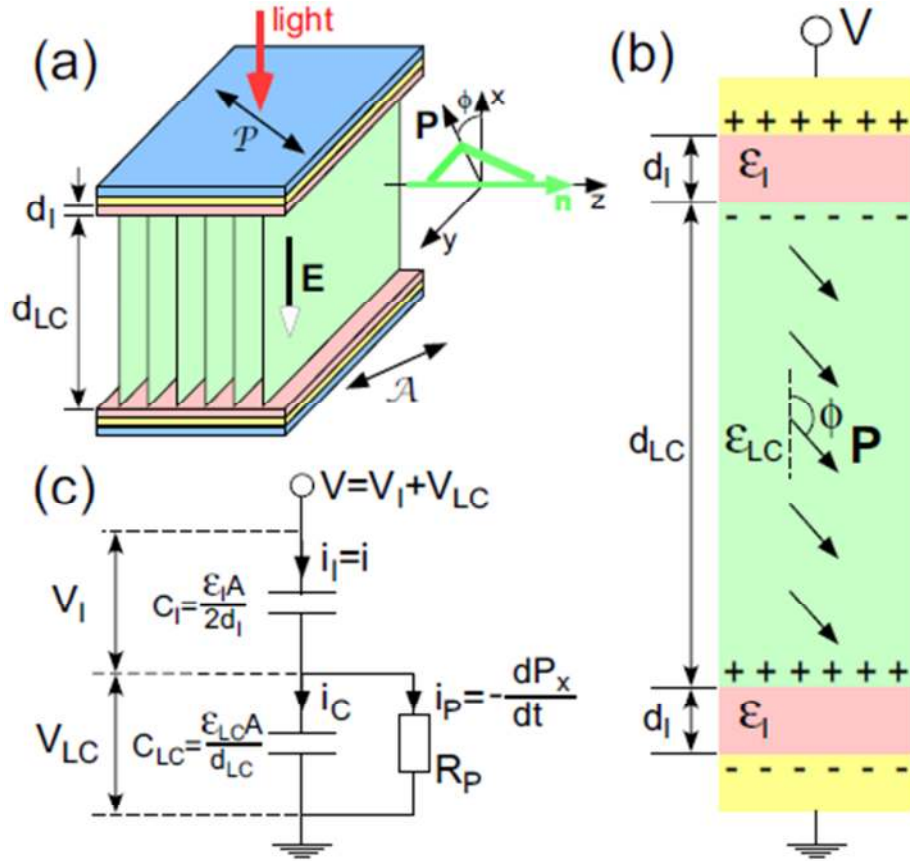


Figure 3.28: Block polarization reorientation in a fluid polar liquid crystal. (a) Electro-optic geometry, showing a bent-core molecule in the SmAP_F phase in a bookshelf cell with ITO electrodes (yellow) and rubbed polyimide insulating layers (pink). (b) Illustration of the model of electrostatically-controlled block polarization reorientation. (c) Equivalent circuit of the cell.

With application of time varying voltage, the reorientation of $\mathbf{P}$ in a liquid crystal generates a measurable polarization current, which provides information about the dynamics of the block polarization reorientation process, governed by a balance of electrostatic and viscous torques.³²⁻³⁴ In our SmAP_F material **W623**, it exhibits nearly ideal block polarization field-induced reorientation that such polarization reorients as a homogeneous block, with the continuously reorienting polarization field behaving electrically as a resistor.

The experimental cell geometry is sketched in figure 3.28(a). The LC is a smectic monodomain with planar alignment, i.e., with the LC in a gap of thickness d_{LC} between glass cell plates coated first with ITO electrodes of area A on the interior plate surfaces and then with insulating alignment layers of dielectric constant ϵ_I and thickness d_I , with the layers normal to the plates. The molecular long axes are normal to the layers and so the director $\mathbf{n}$ is parallel to the cell plates. The polarization is perpendicular to the director, enabling field-induced reorientation around the molecular long axis by an electric field generated by applying a voltage on the electrodes. The two insulating layers are electrically equivalent to a capacitor of capacitance $C_I = \epsilon_I A / 2d_I$, as indicated in the cell sketch figure 3.28(b) and equivalent circuit of figure 3.28(c). In absence of polarization reorientation, the LC layer is also insulating and is electrically equivalent to a capacitor of capacitance $C_{LC} = \epsilon_{LC} A / d_{LC}$, where ϵ_{LC} is the LC dielectric constant and d_{LC} is the LC layer thickness. With voltage V applied to the electrodes, the voltage across the insulating and LC layers will be V_I and V_{LC} respectively, with $V = V_I + V_{LC}$, and the current through the cell will be $i = i_I = i_{LC} = i_C + i_P$, where i_C and i_P are respectively the capacitive and polarization components of current in the LC. Under dynamic driving conditions, the

electric field within the liquid crystal $\mathbf{E}_{LC}$ is in general non-zero, resulting in a torque on $\mathbf{P}(\phi)$, which is balanced by the viscous torque due to orientational viscosity γ damping reorientation of $\mathbf{P}$ as follows:³⁵

$$\gamma \frac{d\phi}{dt} = P \frac{V_{LC}}{d_{LC}} \sin \phi . \quad (1)$$

The resulting LC polarization current is $i_P = A(-dP_z/dt) = -Ad(P \cos \phi)/dt = AP \sin \phi (d\phi/dt)$.

Eliminating $d\phi/dt$ from this expression gives

$$i_P = \frac{AV_{LC}P^2 \sin^2 \phi}{\gamma d_{LC}} = \frac{AV_{LC}(P^2 - P_z^2 \cos^2 \phi)}{\gamma d_{LC}} = \frac{V_{LC}}{R_P(\phi)} , \quad (2)$$

where $R_P(\phi) = \gamma d_{LC}/A(P^2 - P_z^2(\phi)) = \gamma d_{LC}/A(P^2 - P^2 \cos^2 \phi)$ is the effective resistance of the LC due to the field-driven reorientation of $\mathbf{P}$. $R_P(\phi)$ is smallest for $P_z(\phi) = 0$ ($\phi = \pi/2$), where the electrical torque $\mathbf{T}_E = \mathbf{P} \times \mathbf{E}_{LC}$ has the largest magnitude. This minimum value, $R_{Pmin} = \gamma d_{LC}/AP^2 = 106 \, \Omega$ for W623 in the cells used ($d_{LC} = 4.8 \, \mu\text{m}$, $A = 25 \, \text{mm}^2$, $\gamma = 0.04 \, \text{kg}/(\text{s}\cdot\text{m})$, and $P = 850 \, \text{nC}/\text{cm}^2$). Therefore, the effective minimum bulk resistivity of the LC during polarization reversal is $\rho_{Pmin} = AR_{Pmin}/d_{LC} = 5.5 \times 10^4 \, \Omega\cdot\text{cm}$, which is in the semiconducting range. That is, because of the large value of P , the effective resistivity is much smaller than the LC resistivity in absence of reorientation ($\rho_{LC} \sim 10^{12} \, \Omega\cdot\text{cm}$). If, during field application, $\mathbf{P}$ approaches its limiting $+\mathbf{x}$ or $-\mathbf{x}$ orientations, then $P_z^2(\phi)$ approaches P^2 and $R_P(\phi)$ grows, actually diverging to infinity in these limits ($\phi = 0$ or π).

The key experimental probe of R_P is the nature of the current accompanying the analog reorientation of $\mathbf{P}$, and specifically the flat-topped step in the cell current $i(t)$ found in response to a triangle wave $V(t)$, shown in figure 3.27 and 3.29(a). We believe that such plateau in the current is a universal signature in block polarization reorientation that

should be expected for fluid smectic cells with substantial polarization ($P \approx 300 \text{ nC/cm}^2$) and insulating layers on the electrodes, and can be simply understood in the case of W623.

For a typical cell, $C_{LC} \sim 1 \text{ nF}$, $C_I \sim 10 \text{ nF}$, the minimum $\tau_{LCmin} = R_{pmin}C_{LC}$ is on the order of 10^{-7} sec and $\tau_{Imin} = R_{pmin}C_I \sim 10^{-8} \text{ sec}$. Such very short RC constants imply that the polarization current will short out the liquid crystal capacitance C_{LC} for typical millisecond to microsecond LC reorientation dynamics, the cell appearing electrically as C_I in series with R_p . As a result, if the time in an AC cycle for which $\mathbf{P}$ rotates from $\phi = 0$ to $\phi = \pi$ is large compared to τ_{LC} , then the cell impedance is dominated by C_I and the cell appears to be capacitive with $Z_{cell} \approx (j\omega C_I)^{-1}$. However, as ϕ approaches $\phi = 0$ or $\phi = \pi$, P_z quickly saturates and R_p diverges to infinity, switching Z_{cell} to $Z_{cellsat} = (j\omega C_I)^{-1} + (j\omega C_{LC})^{-1} \approx (j\omega C_{LC})^{-1}$. Since in the typical case τ_{LCmin} is very small, this crossover from large to small R_p behavior occurs very near the limiting orientations $\phi = 0$ to $\phi = \pi$, so that for nearly the entire range $0 \lesssim \phi \lesssim \pi$ where there is polarization reorientation, the cell impedance is $Z_{cellp} = (j\omega C_I)^{-1}$, predicting a ratio $Z_{cellp}/Z_{cellsat} \approx C_{LC}/C_I$ of the cell impedances without and with saturation. The corresponding current step has height in $i(t)$ from $C_{LC}(dV/dt)$ for $|V| > V_{sat}$ to $C_I(dV/dt)$ for $|V| < V_{sat}$, and width in $V(t)$ of $2|V_{sat}|$. As R_p switches from $R_p \sim 0$ to $R_p \sim \infty$, V_{LC} changes from $V_{LC} \sim 0$ to $V_{LC} \sim V(t) \pm V_{sat}$, so that ion conduction only becomes significant when $|V| > V_{sat}$.

In our experiments, the cell is placed between crossed polarizers and illuminated at normal incidence by a He-Ne laser beam with wavelength $\lambda = 632 \text{ nm}$. The transmitted intensity is given by $I = I_0 \sin^2(2\psi) \sin^2(\pi \Delta n d / \lambda)$, where ψ is the angle between the analyzer and the optic axis of the liquid crystal, and d is the cell thickness. In high

polarization chiral SmC materials, the optic axis orientation is coupled to the direction of P and changes with applied field, giving contrast in optical transmission as the director moves on the tilt cone. In the SmAP_F case, the molecular long axis remains along the layer normal z as P reorients. The phase is, however, strongly biaxial, with n_p larger than n_o , so that in the geometry of figure 3.28(a), the effective birefringence Δn changes from $\Delta n = n_z - n_p$, when there is no applied field and P is parallel to the glass, to $\Delta n = n_z - n_o$, at high applied electric field where P is aligned normal to the glass. Field-induced modulation of the birefringence is responsible for variation in the optical transmission. At low temperature ($T = 135^\circ\text{C}$), the effective birefringence of **W623** changes substantially with applied field from $\Delta n(E = 0) = 0.02$ to $\Delta n(E = 10 \text{ V}/\mu\text{m}) = 0.045$ (see figure 3.26).

The current and optical response when the SmAP_F cell is driven by a 10 Hz triangular voltage is shown in figure 3.27 and figure 3.29(a). When the applied voltage $|V| < V_{\text{sat}}$, P rotates between $\phi = 0$ and $\phi = \pi$ and the transmission curve is V-shaped due to the analog change in birefringence. As analyzed above, in this regime, the polarization effectively short circuits the LC and the current is constant, the current response curve showing an at-topped peak with magnitude $I \approx C_I |dV/dt|$. When the sign of the slope of the applied voltage changes, the current response jumps by an amount $I' = (2C_I C_{LC} / (C_I + C_{LC})) |dV/dt|$. The spontaneous polarization of the SmAP_F phase increases on cooling as a result of reduced thermal fluctuations in the orientation angle ϕ , reaching a maximum value of 850 nC/cm² just above the transition to the SmX phase (see figure 3.29(c)). Since $V_{\text{sat}} = 2d_I P / \epsilon_L$, the larger the polarization, the higher the voltage required to achieve saturation and the broader the flat current peak, as illustrated in figure 3.29(b). The height of the polarization current peak does not change. The saturation voltages V_{sat} were measured at

different temperatures and from figure 3.29(c), it could be seen that V_{sat} is proportional to polarization, as predicted. A fit of the data indicates that $d_I/\epsilon_I = 0.00850 \text{ V}/(\text{nC}/\text{cm}^2)$. The current peaks circled in figure 3.29(a) and (b) that occur shortly after $|V|$ exceeds V_{sat} , immediately following the polarization current peaks, are due to ion transport in the LC. Since $E_{\text{LC}} \approx 0$ for $|V| < V_{\text{sat}}$, there is no ion current in the low voltage, analog regime.

Since the LC cell is capacitive during polarization reorientation, the height of the flat peak increases with increasing driving frequency, as illustrated in figure 3.29(d), resulting in a “sharp” peak usually seen for FLCs. The saturation voltage V_{sat} is, however, independent of frequency at a given temperature. To explore the relationship between I , I' and $|dV/dt|$, the current response at fixed temperature was measured while applying a triangular voltage with constant amplitude ($V_{\text{max}} = 38.47 \text{ V}$) and variable frequency to the cell. As shown in figure 3.29(e), I and I' depend linearly on f as expected, with slopes of $2.26 \text{ } \mu\text{A}/\text{Hz}$ and $0.12 \text{ } \mu\text{A}/\text{Hz}$ respectively. Since $|dV/dt| = 4V_{\text{max}}f$, we have $4V_{\text{max}}C_I = 2.26 \text{ } \mu\text{A}/\text{Hz}$ and $4V_{\text{max}}(2C_IC_{\text{LC}}/(C_I + C_{\text{LC}})) = 0.12 \text{ } \mu\text{A}/\text{Hz}$, which can be used to solve to find $C_I = 14.69 \text{ nF}$ and $C_{\text{LC}} = 0.40 \text{ nF}$. Since $C_I = \epsilon_I A/2d_I$ and $C_{\text{LC}} = \epsilon_{\text{LC}} A/d_{\text{LC}}$, taking $\epsilon_I = 3.5\epsilon_0$ (for polyimide), $d_{\text{LC}} = 4.8 \text{ } \mu\text{m}$, and $A = 25 \text{ mm}^2$, we obtain $d_I = 26.4 \text{ nm}$ and $\epsilon_{\text{LC}} = 8.7\epsilon_0$. We may also compute $d_I/\epsilon_I = 0.00851 \text{ V}/(\text{nC}/\text{cm}^2)$, which agrees well with the value obtained above from the slope of the saturation voltage versus polarization curve.

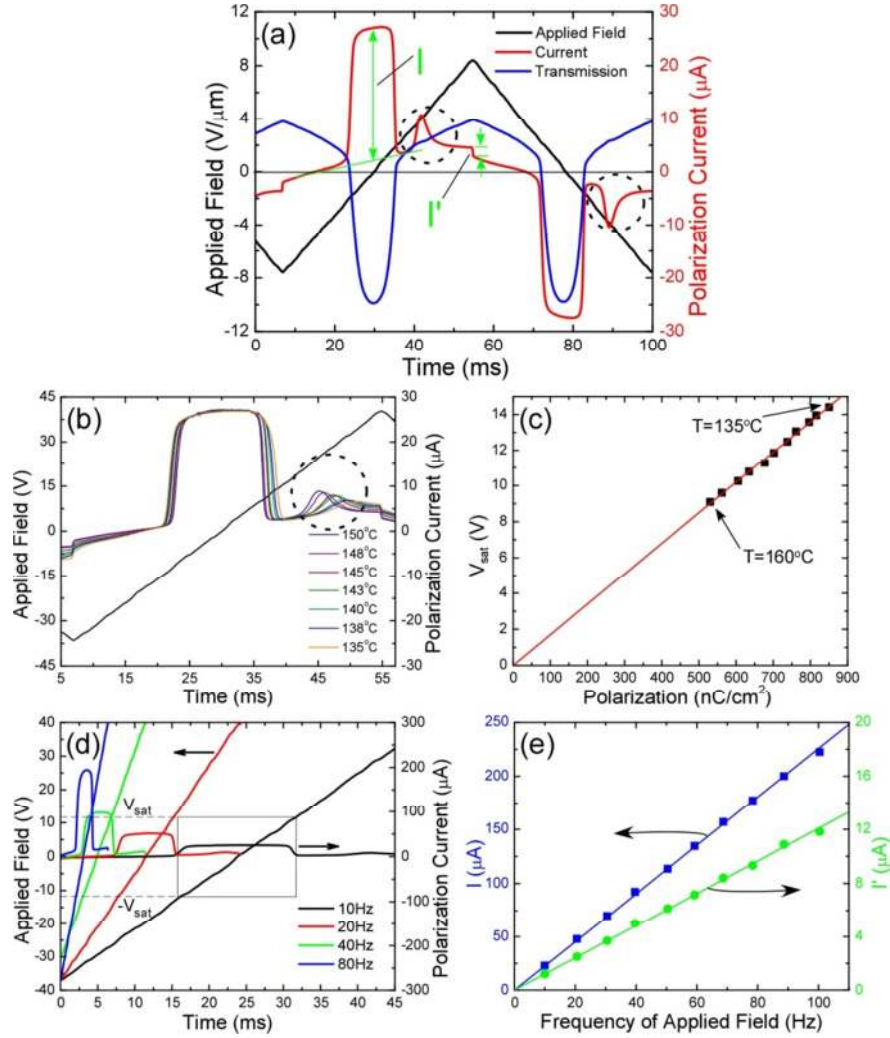


Figure 3.29: Experimental measurements of electro-optic and current response of W623. (a) Electro-optic response of W623 at $T=158^{\circ}\text{C}$ in a $4.8\ \mu\text{m}$ thick cell with ITO electrodes and rubbed polyimide alignment layers, observed with crossed polarizers oriented at 45° to the layer normal. **(b)** Polarization current at different temperatures when a triangular voltage is applied to the cell. The dashed circles in (a) and (b) mark the current peaks due to ions. **(c)** Saturation applied voltage measured as a function of spontaneous polarization. **(d)** Polarization current vs. time for triangular applied voltages with different driving frequencies ($T=145^{\circ}\text{C}$). In each case the current switches on when $|V|$ falls below V_{sat} , as illustrated by the box constructed for the 10 Hz data. **(e)** I and I' measured as a function of the driving frequency of the applied triangular voltage ($T=145^{\circ}\text{C}$).

To better understand the dynamics of the block polarization reorientation in a time-varying electric field, we find the general solution for the polarization orientation ϕ , the current through the cell i and the electric field in the liquid crystal E_{LC} . Referring to the equivalent circuit shown in figure 3.28(c), and using $i_1 = C_1 dV_1/dt$, $i_c = C_{\text{LC}} dV_{\text{LC}}/dt$, $i = i_1$

$= i_{LC} = i_C + i_P$, and Eqs. (1) and (2), we may derive the following expressions for ϕ , i and E_{LC} in the analog regime, when $|V| < V_{sat}$:

$$\frac{d\Phi}{dt} = \frac{1}{\tau_0} \left(\frac{V}{V_{sat}} + \cos \Phi \right) \sin \Phi \quad (3)$$

$$i = C_I \frac{dV}{dt} - C_I \frac{\gamma d_{LC}}{P} \frac{d\left(\frac{1}{\sin \Phi} \frac{d\Phi}{dt}\right)}{dt} \quad (4)$$

$$E_{LC} = \frac{\gamma}{P \sin \Phi} \frac{d\Phi}{dt} \quad (5)$$

Here $V_{sat} = 2d_I P / \epsilon_l$ is the saturation voltage and $\tau_0 = (1 + C_{LC}/C_I) \gamma d_{LC} / P V_{sat}$ is the time constant for director orientation around $V = 0$ (where $\phi = \pi/2$). When $|V| > V_{sat}$, ϕ is aligned along $\phi = 0$ or $\phi = \pi$, $d\phi/dt = 0$, and the current from the reorientation of the spontaneous polarization vanishes, yielding:

$$i' = \frac{C_I C_{LC}}{C_I + C_{LC}} \frac{dV}{dt} \quad (6)$$

$$E_{LC}' = \frac{C_I}{(C_I + C_{LC})} \frac{(V \pm V_{sat})}{d_{LC}} \quad (7)$$

Numerical solutions of Eqs. (3) to (7) are presented in figure 3.30. Using the cell parameters above and assuming $P = 850 \text{ nC/cm}^2$, we have $V_{sat} = 14.7 \text{ V}$ and $\tau_0 = 1.6 \times 10^{-6} \text{ s}$. A 10 Hz triangular voltage with $V_{max} = 2V_{sat}$ is applied to the model cell, as shown in figure 3.30(a). The reorientation of the polarization field between $\phi = 0$ and $\phi = \pi$ when $|V| < V_{sat}$ is shown in figure 3.30(b). Because the time constant $\tau_0 \propto P^{-2}$ and P is large, τ_0 is small compared with the period of the 10 Hz triangle wave, thus ϕ reaches its steady position very quickly. Since $\gamma d_{LC} / P \approx 2.3 \times 10^{-5} \text{ V} \cdot \text{S} \ll 1 \text{ V} \cdot \text{S}$, the second term in Eq. (4) is very small compared to the first so that $i \approx C_I (dV/dt)$. In other words, the cell looks

capacitive in this regime, as though only the insulating layers were present, and the polarization current associated with block polarization reorientation is constant. Because the saturation voltage V_{sat} and P is large, the magnitude of V_{sat} is also large. Consequently, we see a broad flat-topped peak in the i versus time curve as shown in figure 3.30(c). If a static voltage $|V| < V_{\text{sat}}$ is applied to the cell, the block polarization reorientation screens the electric field in the liquid crystal E_{LC} completely. However, if the applied voltage varies in time, E_{LC} is small but non-zero ($\sim 10^{-4}$ V/ μm). As shown in figure 3.30(d), once reorientation of $\mathbf{P}$ ceases (when $|V| > V_{\text{sat}}$), E_{LC} increases linearly with voltage as $E_{\text{LC}} \approx (V \pm V_{\text{sat}})/d_{\text{LC}}$, inducing ion flow in the real LC cell, striking evidence that $E_{\text{LC}} \approx 0$ for $|V| < V_{\text{sat}}$.

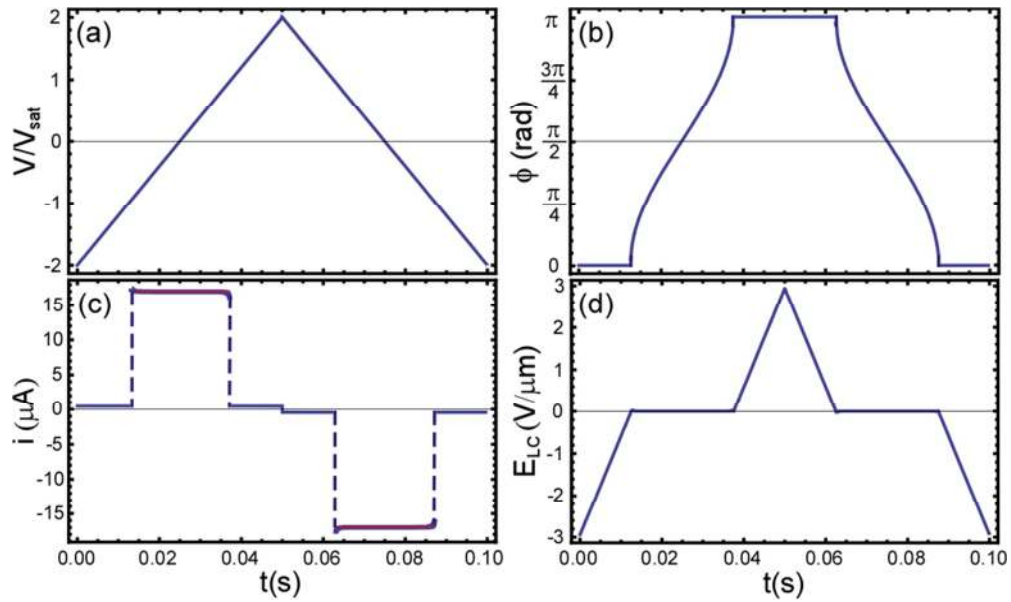


Figure 3.30: Simulated electrical response of a SmAP_F liquid crystal cell driven by a 10 Hz triangular voltage with $V_{\text{max}} = 2V_{\text{sat}}$. The cell parameters are given in the text. (a) Applied voltage. (b) Polarization orientation. (c) Polarization current. The blue curve is calculated using Eqs. (4) and (6), while the red lines show an approximation, $i = C_I(dV/dt)$, valid in the analog region, obtained by neglecting the second term in Eq. (4). (d) Electric field in the liquid crystal. In the analog regime, the internal field (blue curve) is small but non-zero for finite frequencies. Once reorientation stops ($\phi = 0$ or π), the internal field increases linearly.

If the insulating layers have low resistance leakage, the absence of the electric field in the LC layer when $|V| < V_{\text{sat}}$ leads to an electro-optic response to direct current (DC) or quasistatic applied voltage that is free of ion screening effects over long times. This is demonstrated in figure 3.31, where we compare the **W623** cell transmission using a 50 Hz triangle wave applied voltage to that obtained after applying DC voltages for one hour. The transmission for each DC voltage matches the dynamic response at that voltage and shows little change over time. Overall, the block reorientation of the director of **W623** enables a simple mode of analog control of birefringence and can potentially be used in “optical latching”.

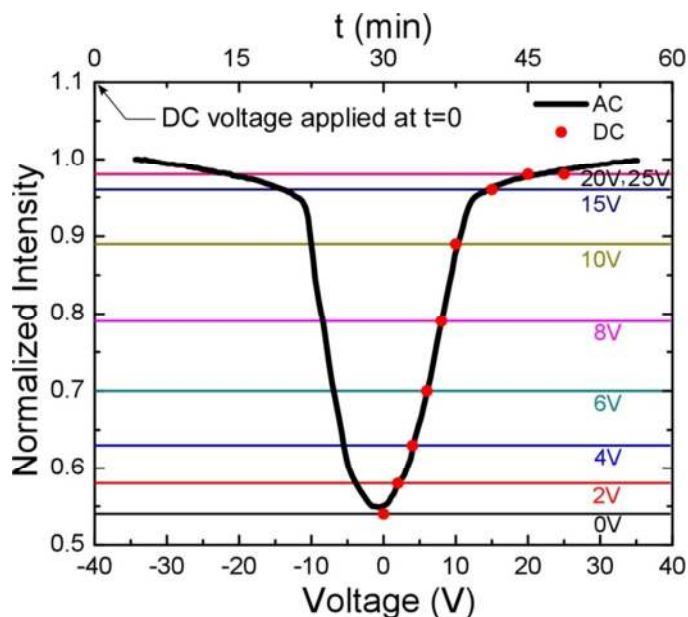


Figure 3.31: Optical transmission of W623 under AC (50 Hz triangular voltage) and DC control at $T = 145^{\circ}\text{C}$ in a $4.8\ \mu\text{m}$ thick cell. The transmitted light intensity remains the same for 1 hour at different applied DC voltages.

As mentioned earlier, **W623** possess a “mystery” phase below the SmAP_F phase on cooling and was labeled as “SmX”. As shown in figure 3.32, in the SmX phase there appear stripes but the overall texture of the LC does not change. Such behavior is

commonly seen at the SmA phase transition to the more ordered smectic phases like SmB, SmC and SmE for calamitic LCs.³⁶ However, the LC didn't respond to the external field which ruled out the possibility of SmC_{APF} phase at low temperature. The small and wide angle X-ray data of **W623** (see figure 3.24 and figure 3.33) showed similar pattern to that of B4 bent-core LCs which leaded us to believe the SmX phase could be an ordered nanofilament phase.^{27, 37}

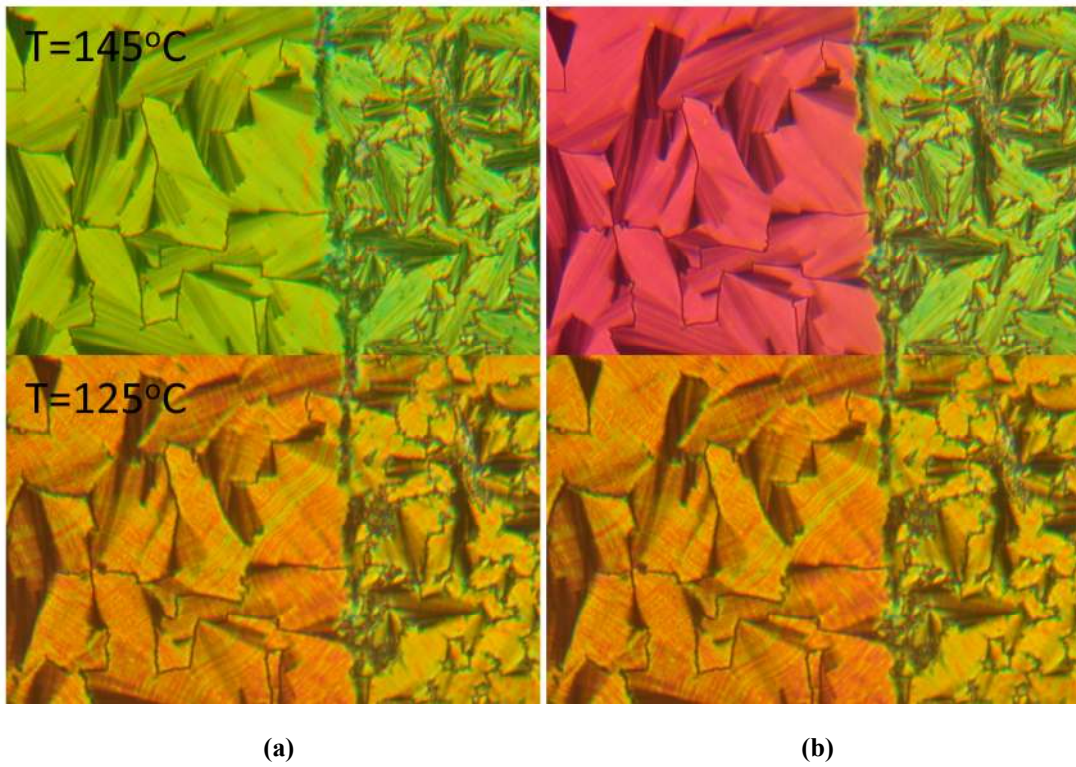


Figure 3.32: Optical textures of W623 between treated glass plates between crossed polarizer and analyzer, top row is the images at SmAP_F phase (145°C) and bottom row is the images at SmX phase (125°C); (a) without external field (b) with 10V/μm external field.

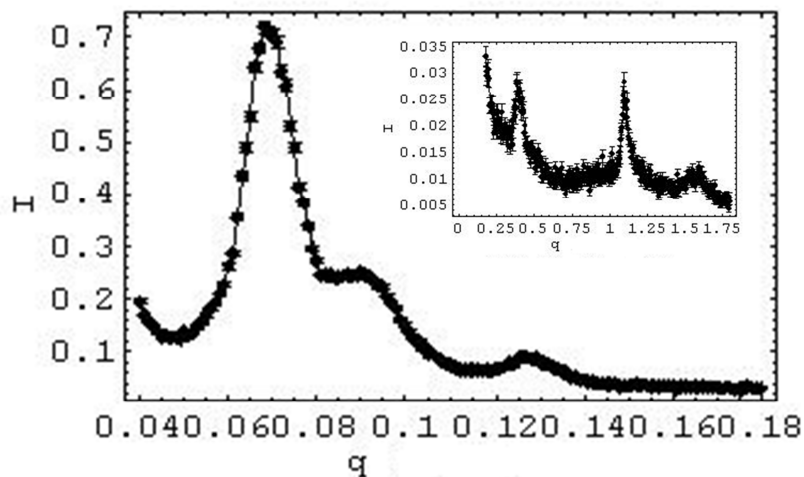


Figure 3.33: Small and wide angle X-ray measurements of W623 at 99°C, obtained at CU.

Freeze-fracture transmission electron microscopy (FFTEM) was used to probe the structure of **W623** at different temperatures and results are shown in figure 3.34 and figure 3.35. At 160°C (just entering the SmAP_F phase) and 140°C (SmAP_F phase), only one periodicity was observed which corresponds to smectic layer structure. However, at 100°C (SmX phase), FFTEM images not only are clearly showing at least two different types of periodicity, but fiber-like features are also observed.

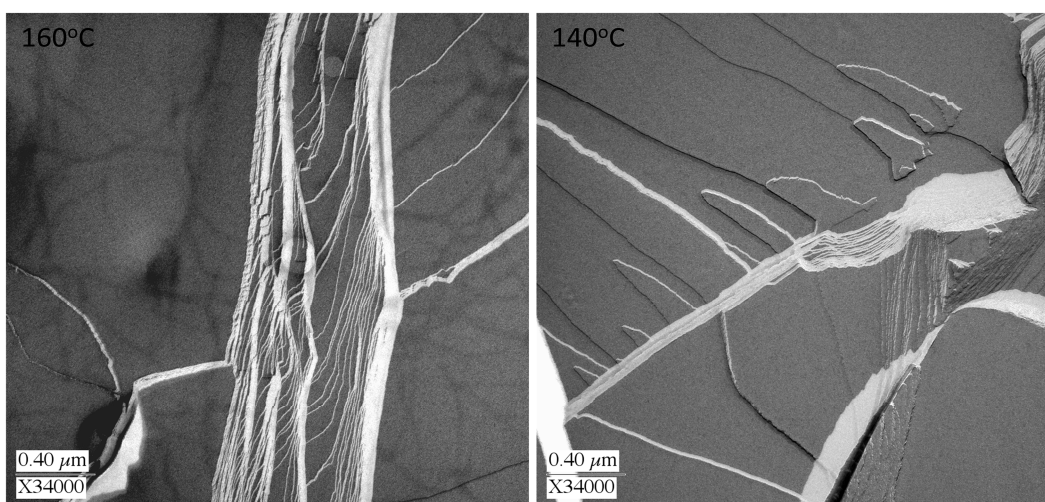


Figure 3.34: FFTEM images of W623 at 160°C and 140°C respectively, showing layer steps.

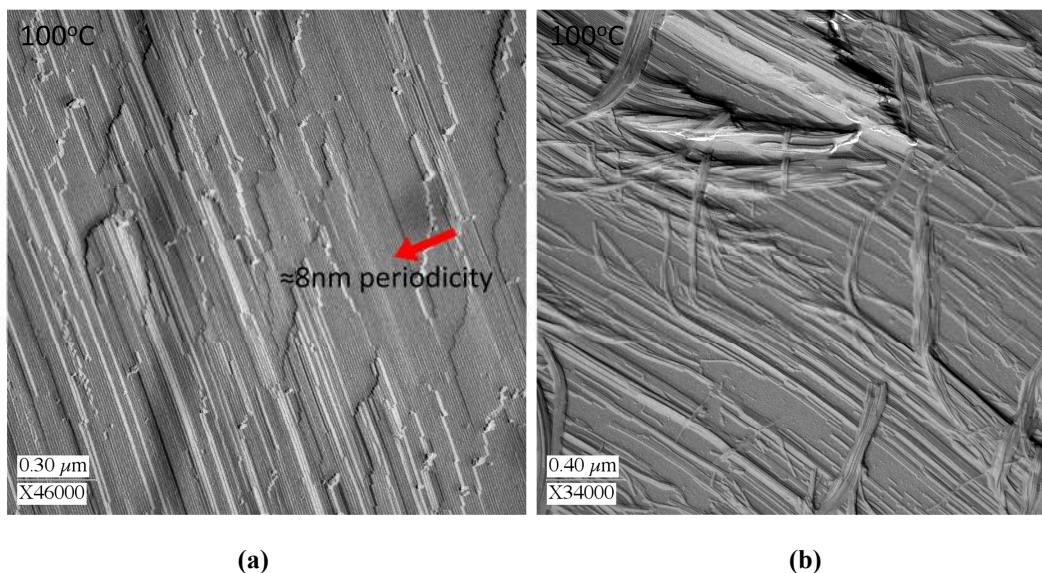


Figure 3.35: FFTEM images of W623 at 100°C, showing (a) two different types of periodicity, one of which is about 8nm, corresponding to one of 4 peaks observed, and (b) characteristic of fibers.

When LCs enters lower temperature phases, sometimes the higher temperature phase could be “trapped” and remains at lower temperature in neat sample. To better understand the SmX phase of **W623**, mixtures of 4-cyano-4'-octylbiphenyl (**8CB**) and **W623** were prepared and studied by both PLM and FFTEM. **8CB** is a calamitic LC which possesses the phase sequence as follows: Iso $\rightarrow$ 40.5°C $\rightarrow$ N $\rightarrow$ 33.5°C $\rightarrow$ SmA $\rightarrow$ 21.5°C $\rightarrow$ X.³⁸ It is immiscible with bent-core molecules and serves as an “isotropic solvent” so that **W623** can grow in separate small domains. As illustrated in figure 3.36, under PLM, at high temperature SmA phase, **W623** shows a focal conic texture; When **W623** enters the SmX phase, it starts to grow as rods. X-ray data of different mixtures of **8CB/W623** shows multiple peaks which means SmX phase does indeed exist which is proved by FFTEM images.

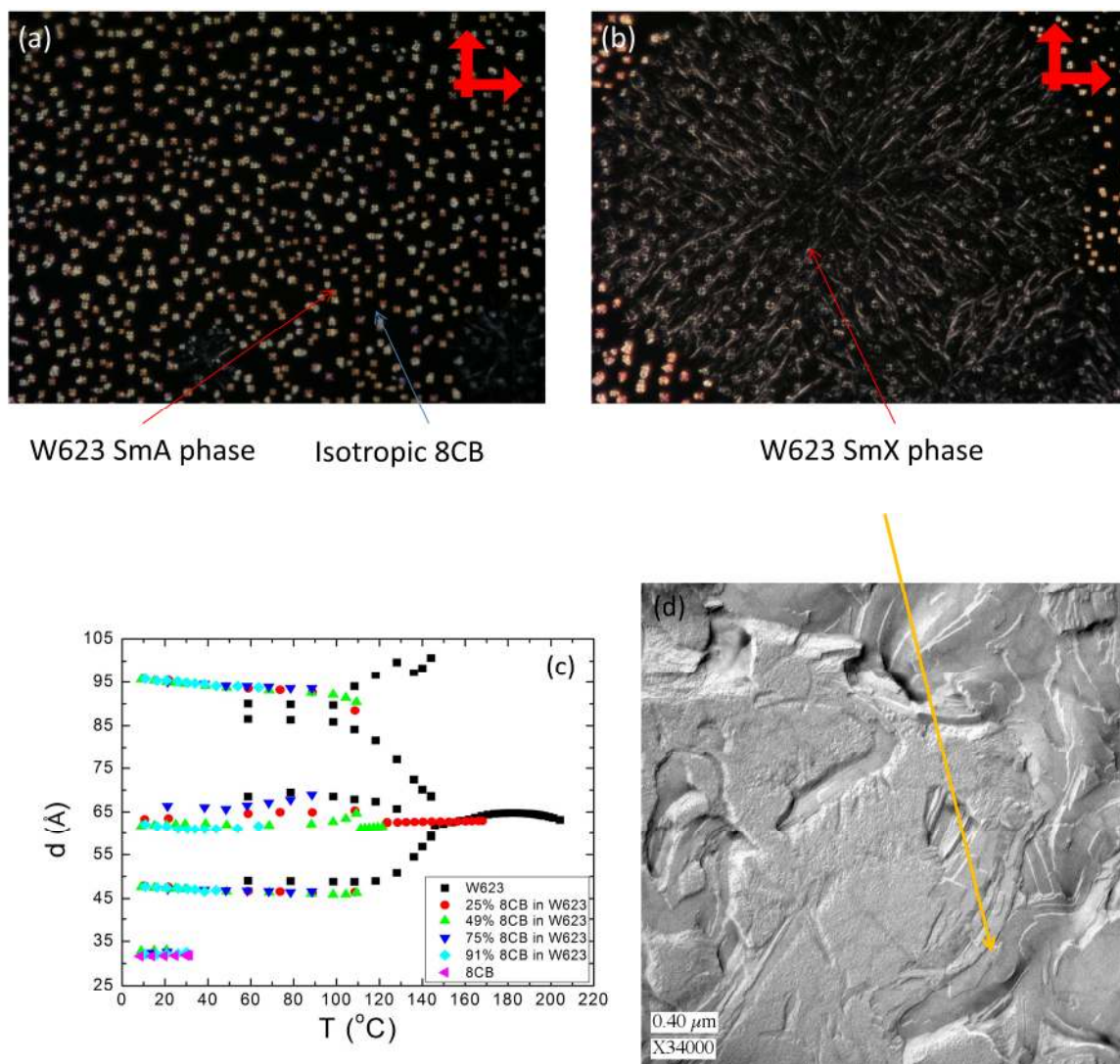


Figure 3.36: Experimental results of 8CB/W623 mixtures: (a) PLM image of 75% 8CB/W623 mixture right before entering the SmX phase of W623, the LC shows focal conic texture. (b) PLM image of 75% 8CB/W623 mixture after entering the SmX phase of W623, the LC starts to grow as rods. (c) X-ray data of different 8CB/W623 mixtures, clearly showing multiple peak positions for each mixture. (d) FFTEM image of 75% 8CB/W623 mixture and two types of periodicity are observed.

It could be concluded that the fiber-like structures come from the packing of **W623** at low temperature. More researches including FFTEM and 2-D X-ray measurement are undergoing in order to find details about the SmX phase of **W623**.

3.4.2 W628 and W632

W628 and **W632** are both **W596** analogs with one ester linkage switching at different position (figure 3.15 and figure 3.17). The DSC and x-ray measurement of **W628** is shown in figure 3.37. The phase sequence of **W628** was determined as follows: Iso $\rightarrow$ 200°C $\rightarrow$ SmAP_F $\rightarrow$ 175°C $\rightarrow$ X on cooling. Interesting, compare to **W586** and **W623**, this material doesn't seem to possess SmA phase and went directly from isotropic to the SmAP_F phase. Meanwhile, the x-ray data showed that the low temperature phase doesn't have multiple peak positions as in **W623** and was considered crystal.

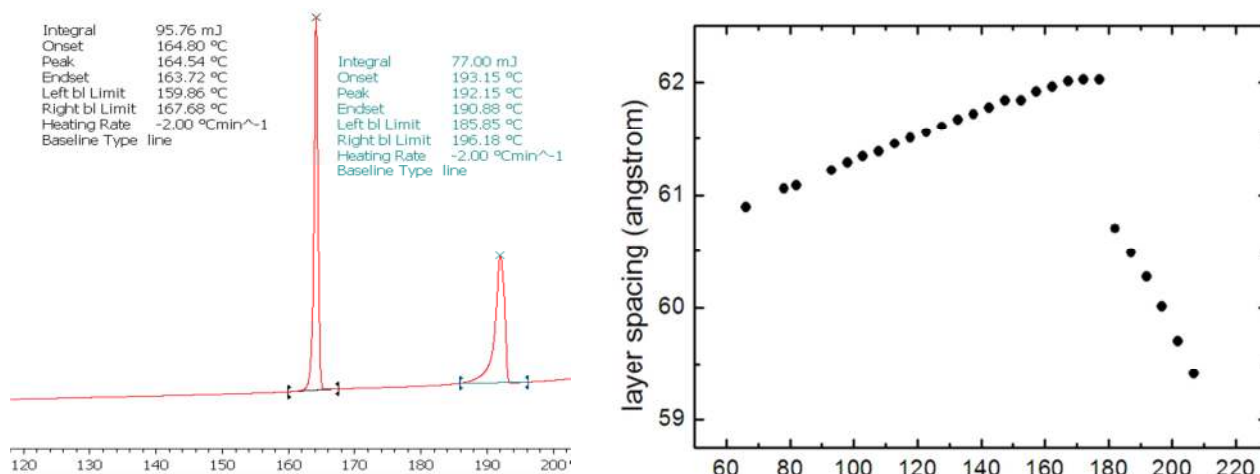


Figure 3.37: DSC and x-ray measurement of W628 on cooling.

To identify the SmAP_F phase of **W628**, the optical textures of samples of **W628** were studied in planar alignment cell under external electric field and the results are shown in figure 3.38. Just as **W586** and **W623**, the random planar samples exhibited focal conic textures (figure 3.38, image on the left), and showed an increase of effective birefringence with applied electric field normal to the plates even at very high

temperature, indicating the phase is ferroelectric, but no accompanying SmC-like optic axis rotation to prove such phase is indeed the SmAP_F phase.

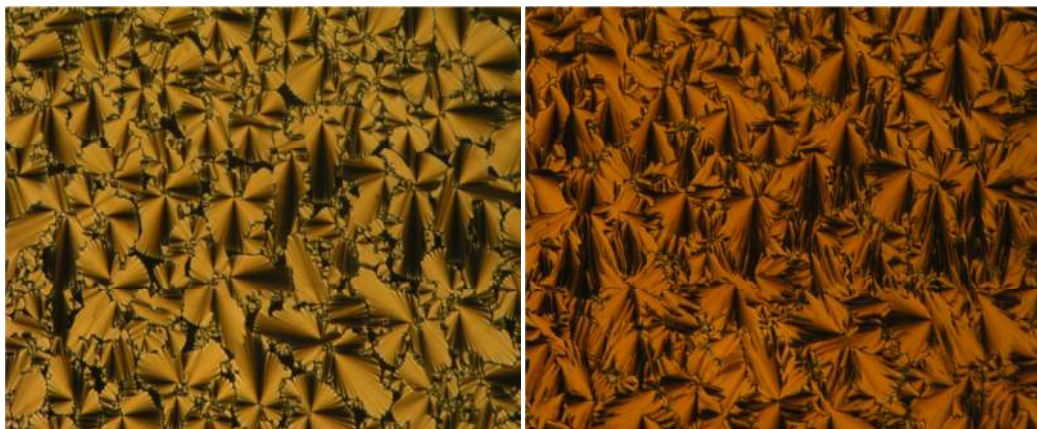


Figure 3.38: Optical textures of W628 between treated glass plates between crossed polarizer and analyzer with (image on the right) and without (image on the left) external electric field in the SmAP_F phase (195°C).

W632 showed the following phase sequence: Iso $\rightarrow$ 170°C $\rightarrow$ SmA $\rightarrow$ 152°C $\rightarrow$ SmAP_F $\rightarrow$ 145°C $\rightarrow$ X on cooling based on similar experiments. However, by switching the ester linkage in the middle of the core as in **W628** to at the end towards the tail as in **W632**, the clearing point decreased by 30 degrees and the temperature window of SmAP_F phase also narrowed. It seems that by making the core more symmetric as in **W628** as well as in **W623** (compare to **W586** and **W631** in later chapter), the clearing point would increase. Following this trend, to make low temperature SmAP_F LC material, it would be necessary to make the molecule as asymmetric as possible.

3.4.3 W631 and W635

W631 and **W635** are both **W586** analogs made by switching one or two ester linkages in the core as shown in figure 3.17 and figure 3.18. **W631** showed the following phase sequence: Iso $\rightarrow$ 165°C $\rightarrow$ SmA $\rightarrow$ 125°C $\rightarrow$ SmAP_F $\rightarrow$ 120°C $\rightarrow$ X on cooling based on

DSC, PLM and x-ray measurements. Like **W632**, **W631** showed lower clearing points and smaller temperature windows of the SmAP_F phase than **W623** because of the less symmetric core. On the other hand, **W631** was designed to have large spontaneous polarization as **W623** because of the large dipole moment at the molecular level. However, due to the small temperature window of the SmAP_F phase, the spontaneous polarization doesn't reach its saturated value before going to the next crystal phase and the value is smaller than expected.

The phase sequence of **W635** on cooling is as follows: Iso $\rightarrow$ 180°C $\rightarrow$ SmAP_F $\rightarrow$ 175°C $\rightarrow$ SmC_AP_F $\rightarrow$ 170°C $\rightarrow$ X based on DSC, PLM and x-ray measurements. **W635** was designed to have even larger spontaneous polarization compared to **W623** because of its larger molecular dipole moment than **W586**, **W623** and **W631**. But as with **W631**, **W635** only possesses a very small temperature window of the SmAP_F phase, thus causing a small value of the spontaneous polarization. Interestingly, **W635** seemed to show a SmC_AP_F phase below the SmAP_F phase on cooling. As discussed earlier, the SmC_AP_F and the SmAP_F phases are very hard to distinguish under PLM. However, the broken texture was observed during the transition and the x-ray scattering also shows layer shrinkage as illustrated in figure 3.39. These data suggest that the molecules started to tilt while the phase still remains ferroelectric evidenced by single peak from polarization reversal current, strong prove of the SmC_AP_F phase. More detailed research is undergoing and **W635** would be the first LC other than **KYOBOW** family to exhibit the SmC_AP_F phase.

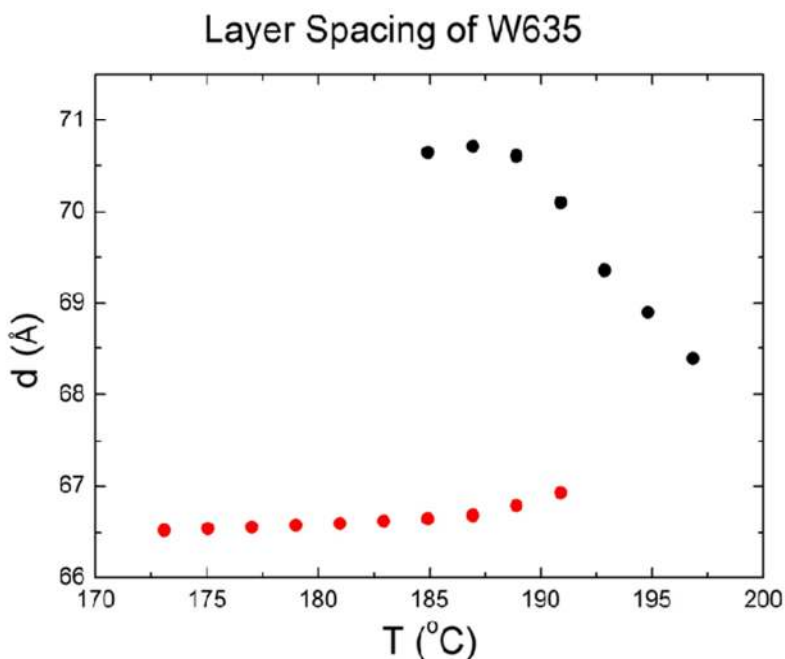


Figure 3.39: Layer spacing of W635 on cooling, measured by x-ray scattering.

3.4.4 W637

The 60 degree angle bent-core molecule **W637** was designed to achieve high spontaneous polarization in SmAP_F phase since the molecular dipole moment along bow direction is bigger than that of **W586**. However, it turns out that **W637** doesn't possess any mesogenic phases, possibly because the two “wings” of such bent-core molecule are too close to each other by connecting through the benzene core and therefore affecting the conformation of individual molecules. Some possible structural modifications should be tested in the future include using polycyclic aromatic cores such as naphthalene, phenanthrene and anthracene instead of benzene to increase the space in between “wings” or making mixtures with known SmAP_F LCs such as **W586** to increase the spontaneous polarization while keeping the phase.

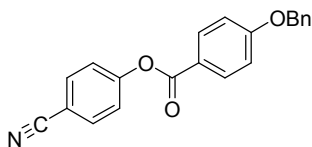
3.4.5 W634 and W638

Based on the principle described earlier, we expect bent-core molecules **W634** and **W638** to exhibit the SmC_AP_F phase since the tricarbosilane tails would prefer anticlinic interaction in between layer interfaces and the double tail bent-core molecules won't have enough in-plane space for tails and tend to tilt to release more entropy. Unfortunately, both W634 and W638 appeared to transition directly from isotropic to crystal and therefore are not mesogenic. No anisotropic behavior was observed under PLM. However, other bent-core LC systems which exhibit the SmCP phase should be tested along with the tricarbosilane tail in the future to pursue the rare SmC_AP_F phase.

3.5 Experimental Procedures

General Methods: Commercially available reagents were used as purchased without further purification unless otherwise noted. THF was purified by distillation from sodium/benzophenone ketyl under an argon atmosphere prior to use. All non aqueous reactions were performed in oven-dried glassware under an atmosphere of dry argon unless otherwise noted. All aqueous solutions used for reaction work up were saturated unless otherwise noted. All flash chromatography was performed with silica gel (40-63 microns, 230-400 mesh) purchased from Silicycle. Analytical thin-layer chromatography (TLC) was performed on Silica G TLC plates w/ UV with a thickness of 200µm, purchased from Sorbent Technologies. Compounds were visualized with shortwave UV, or by staining with I₂, p-anisaldehyde, or vanillin. If either of the latter two stains were used, the plate was heated to visualize spots. New compounds in the synthetic route were routinely characterized by NMR spectroscopy. ¹H and ¹³C NMR spectra were recorded using a Varian Unity INOVA-500, a Bruker AM-400 spectrometer, or a Bruker 300 UltraShield. ¹H NMR spectra are reported in parts per million (δ) relative to residual

solvent peaks (7.24 for CDCl₃, 2.05 for (CD₃)₂CO or otherwise noted). ¹³C NMR spectra are reported in parts per million (δ) relative to residual solvent peaks (77.23 for CDCl₃ or otherwise noted). For the mesogenic materials, phase transition temperatures were determined by differential scanning calorimetry using a Mettler Toledo DSC823e. Liquid crystal phases were determined by polarized light microscopy using a Nikon-HCS400 microscope with an Instec STC200 temperature-controlled stage. The magnitude of the spontaneous polarization P_s was measured by integrating the polarization reversal current while switching the sample with a triangular waveform electric field. X-ray experiments were temperature controlled with an Instec STC200 hotstage, and data were collected using a point detector mounted on a Huber four-circle goniometer at either of the following: Synchrotron radiation at beamline X10A of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, or Cu K(R) radiation from a Rigaku UltraX-18 rotating anode generator, operated by the Liquid Crystal Materials Research Center, University of Colorado-Boulder.

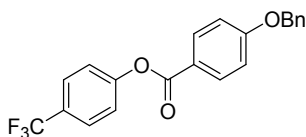


9

4-Benzloxy-benzoic acid 4'-cyano-phenyl ester (9)

A mixture of 4-cyanophenol (2.21 g, 18.6 mmol), 4-Benzloxy-benzoic acid (4.33 g, 19.0 mmol) and 4-dimethylaminopyridine (DMAP) (100 mg, 0.82 mmol) in 250 mL CHCl₃ was stirred for 10 minutes. To this mixture, dicyclohexylcarbodiimide (DCC) (4.59 g, 22.2 mmol) in 50 mL of CHCl₃ was added and the reaction mixture was

continued to stir for 12 h at room temperature. The precipitated dicyclohexylurea was filtered off and washed with excess CHCl_3 . The solvent of the filtrate was removed and 4-Benzyloxy-benzoic acid 4'-cyano-phenyl ester, **9**, (5.20 g, 15.8 mmol, 84.9%) was obtained as a white solid after recrystallization from a mixture of CH_3CN and a few drops of CHCl_3 . ^1H NMR (CDCl_3 , 400 MHz): δ 8.12 (m, 2H), 7.72 (m, 2H), 7.44-7.36 (m, 5H), 7.33 (m, 2H), 7.06 (m, 2H), 5.15 (s, 2H).

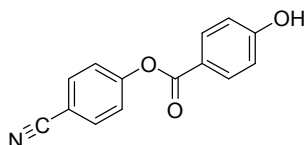


10

4-Benzyloxy-benzoic acid 4'-trifluoromethyl-phenyl ester (10)

A mixture of 4-trifluoromethyl-phenol (2.80 g, 18.3 mmol), 4-Benzloxy-benzoic acid (4.09 g, 17.9 mmol) and 4-dimethylaminopyridine (DMAP) (100 mg, 0.82 mmol) in 250 mL CH_2Cl_2 was stirred for 10 minutes. To this mixture, 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDCI) (3.59 g, 18.7 mmol) in 50 mL of CH_2Cl_2 was added and the reaction mixture was continued to stir for 12 h at room temperature. To this reaction, 100 mL H_2O was added and the aqueous layer was extracted by CH_2Cl_2 (3 x 100 mL), then combined organic layer was washed by H_2O (3 x 100 mL) and saturated NaCl (3 x 100 mL), dried over anhydrous MgSO_4 , filtered and concentrated at reduced pressure. 4-Benzyloxy-benzoic acid 4'-trifluoromethyl-phenyl ester, **10**, (5.40 g, 14.5 mmol, 83.8%) was obtained as a white solid after recrystallization from a mixture of CH_3CN and a few drops of CHCl_3 . ^1H NMR (CDCl_3 , 500 MHz): δ 8.14 (m, 2H), 7.68 (m, 2H), 7.44-7.34 (m, 5H), 7.32 (m, 2H), 7.06 (m, 2H), 5.15 (s, 2H). ^{13}C NMR (CDCl_3 , 100

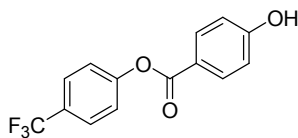
MHz): δ 164.3, 163.3, 153.5, 136.0, 132.4, 128.7, 128.3, 127.5, 126.8, 122.3, 121.4, 114.8, 114.7, 70.3.



5

4-Hydroxy-benzoic acid 4'-cyano-phenyl ester (5)

4-Benzyloxy-benzoic acid 4'-cyano-phenyl ester, **9**, (1.00 g, 3.04 mmol) was dissolved in 50 mL EtOH/CH₂Cl₂ (1:1) and 10% Pd/C catalyst (0.10 g) was added. The resultant solution was stirred at room temperature in an atmosphere of hydrogen till the required quantity of hydrogen was absorbed. This mixture was filtered through Celite and the solvent was removed under reduced pressure to yield 4-Hydroxy-benzoic acid 4'-cyano-phenyl ester, **5**, as a white solid (0.71 g, 2.97 mmol, 97.7%) which was directly used for the subsequent reaction. ¹H NMR ((CD₃)₂CO, 400 MHz): δ 8.07 (m, 2H), 7.91 (m, 2H), 7.53 (m, 2H), 7.03 (m, 2H).

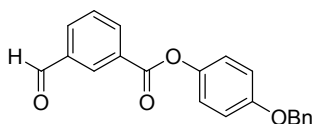


6

4-Hydroxy-benzoic acid 4'-trifluoromethyl-phenyl ester (6)

4-Benzyloxy-benzoic acid 4'-trifluoromethyl-phenyl ester, **10**, (0.53 g, 1.42 mmol) was dissolved in 50 mL EtOH/CH₂Cl₂ (1:1) and 10% Pd/C catalyst (0.10 g) was added.

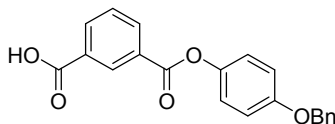
The resultant solution was stirred at room temperature in an atmosphere of hydrogen till the required quantity of hydrogen was absorbed. This mixture was filtered through Celite and the solvent was removed under reduced pressure to yield 4-Hydroxy-benzoic acid 4'-trifluoromethyl-phenyl ester, **6**, as a white solid (0.40 g, 1.42 mmol, >99%) which was directly used for the subsequent reaction. ^1H NMR ($(\text{CD}_3)_2\text{CO}$, 500 MHz): δ 8.09 (m, 2H), 7.90 (m, 2H), 7.52 (m, 2H), 7.03 (m, 2H).



11

4-Benzyloxy-benzoic acid 3-formyl-phenyl ester (11)

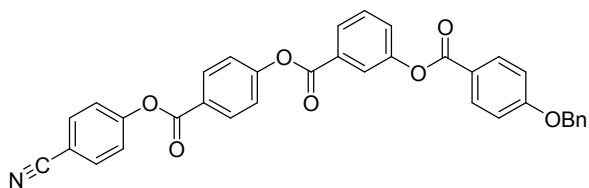
A mixture of 4-Benzloxy-benzoic acid (4.78 g, 21.0 mmol), 3-Hydroxy-benzaldehyde (2.38 g, 19.5 mmol) and 4-dimethylaminopyridine (DMAP) (100 mg, 0.82 mmol) in 250 mL CHCl_3 was stirred for 10 minutes. To this mixture, dicyclohexylcarbodiimide (DCC) (4.80 g, 23.3 mmol) in 50 mL of CHCl_3 was added and the reaction mixture was continued to stir for 12 h at room temperature. The precipitated dicyclohexylurea was filtered off and washed with excess CHCl_3 . The solvent of the filtrate was removed and 4-Benzyloxy-benzoic acid 3-formyl-phenyl ester, **11**, (5.7 g, 17.2 mmol, 88.2%) was obtained as a white solid after recrystallization from a mixture of CH_3CN and a few drops of CHCl_3 . ^1H NMR (CDCl_3 , 500 MHz): δ 10.01 (s, 1H), 8.15 (m, 2H), 7.78 (dt, 1H, J = 7.5, 1.5 Hz), 7.72 (t, 1H, J = 1.5 Hz), 7.59 (t, 1H, J = 7.5 Hz), 7.48-7.34 (m, 6H), 7.06 (m, 2H), 5.15 (s, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 191.2, 164.5, 163.3, 151.6, 137.8, 136.0, 132.4, 130.1, 128.7, 128.3, 128.0, 127.5, 127.1, 122.6, 121.4, 114.8, 70.2.



12

3-[(4-Benzyloxy) benzoyloxy] benzoic acid (**12**)

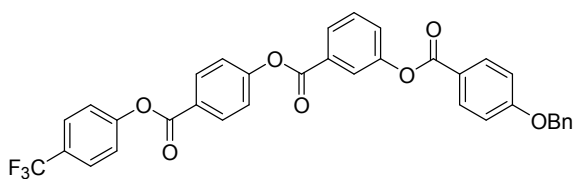
To a solution of 4-Benzyloxy-benzoic acid 3-formyl-phenyl ester, **11**, (5.70 g, 17.2 mmol) in 200 mL acetone, KMnO_4 (4.30 g, 27.2 mmol) in 100 mL of acetone/ H_2O (1:1) was slowly added in a period of 10 minutes and the reaction mixture was allowed to stir for 2 h at room temperature. Then, saturated NaHCO_3 was added and black precipitates were formed. 1M HCl was carefully added till all black precipitates were disappeared. Then, the mixture was extracted by CH_2Cl_2 (3 x 100 mL) and the organic layer was washed with H_2O (3 x 100 mL) and saturated NaCl (3 x 100 mL), dried over anhydrous MgSO_4 , filtered and then concentrated at reduced pressure to yield 3-[(4-Benzyloxy) benzoyloxy] benzoic acid, **12**, (6.00 g, 17.2 mmol, >99%) as a white solid which was directly used in the subsequent reaction. ^1H NMR (CDCl_3 , 500 MHz): δ 8.15 (m, 2H), 8.00 (dt, 1H, $J = 7.5, 1.5$ Hz), 7.92 (t, 1H, $J = 1.5$ Hz), 7.52 (t, 1H, $J = 7.5$ Hz), 7.47-7.34 (m, 6H), 7.06 (m, 2H), 5.15 (s, 2H).



13

4-[(4-Cyanophenoxy) carbonyl] phenyl 3-[(4-benzyloxy) benzoyloxy] benzoate (**13**)

A mixture of 4-Hydroxy-benzoic acid 4'-cyano-phenyl ester, **5**, (0.71 g, 2.97 mmol), 3-[(4-Benzyloxy) benzoyloxy] benzoic acid, **12**, (1.12 g, 3.22 mmol) and 4-dimethylaminopyridine (DMAP) (25 mg, 0.21 mmol) in 50 mL CHCl₃ was stirred for 10 minutes. To this mixture, dicyclohexylcarbodiimide (DCC) (0.75 g, 3.63 mmol) in 5 mL of CHCl₃ was added and the reaction mixture was continued to stir for 12 h at room temperature. The precipitated dicyclohexylurea was filtered off and washed with excess CHCl₃. The solvent of the filtrate was removed and the crude product was purified by flash chromatography (CHCl₃) to give 4-[(4-Cyanophenoxy) carbonyl] phenyl 3-[(4-benzyloxy) benzoyloxy] benzoate, **13**, (1.15 g, 2.02 mmol, 68.0%) as a white solid. ¹H NMR (CDCl₃, 500 MHz): δ 8.26 (m, 2H), 8.16 (m, 2H), 8.11 (dt, 1H, J = 7.5, 1.5 Hz), 8.04 (t, 1H, J = 1.5 Hz), 7.74 (m, 2H), 7.59 (t, 1H, J = 7.5 Hz), 7.51 (m, 1H), 7.45-7.35 (m, 9H), 7.07 (m, 2H), 5.16 (s, 2H).

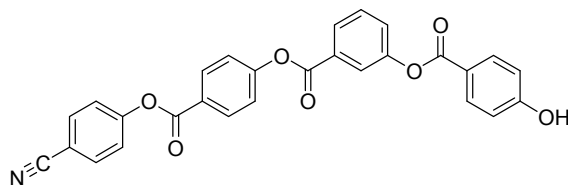


14

4-[(4-Trifluoromethylphenoxy) carbonyl] phenyl 3-[(4-benzyloxy) benzoyloxy] benzoate (**14**)

A mixture of 4-Hydroxy-benzoic acid 4'-trifluoromethyl-phenyl ester, **6**, (0.40 g, 1.42 mmol), 3-[(4-Benzyloxy) benzoyloxy] benzoic acid, **12**, (0.40 g, 1.15 mmol) and 4-dimethylaminopyridine (DMAP) (10mg, 0.08 mmol) in 30 mL CHCl₃ was stirred for 10 minutes. To this mixture, dicyclohexylcarbodiimide (DCC) (0.30 g, 1.45 mmol) in 5 mL of CHCl₃ was added and the reaction mixture was continued to stir for 12 h at room

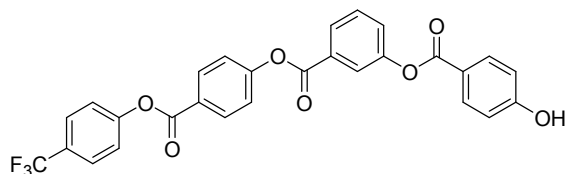
temperature. The precipitated dicyclohexylurea was filtered off and washed with excess CHCl_3 . The solvent of the filtrate was removed and the crude product was purified by flash chromatography (CHCl_3) to give 4-[(4-Trifluoromethylphenoxy) carbonyl] phenyl 3-[(4-benzyloxy) benzoyloxy] benzoate, **14**, (0.60 g, 0.98 mmol, 85.2%) as a white solid. ^1H NMR (CDCl_3 , 500 MHz): δ 8.28 (m, 2H), 8.16 (m, 2H), 8.11 (dt, 1H, $J = 7.5, 1.5$ Hz), 8.05 (t, 1H, $J = 1.5$ Hz), 7.70 (d, 2H, $J = 8.5$ Hz), 7.59 (t, 1H, $J = 7.5$ Hz), 7.51 (m, 1H), 7.45-7.35 (m, 9H), 7.07 (m, 2H), 5.16 (s, 2H).



15

4-[(4-Cyanophenoxy) carbonyl] phenyl 3-[(4-hydroxyl) benzoyloxy] benzoate (**15**)

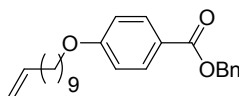
4-[(4-Cyanophenoxy) carbonyl] phenyl 3-[(4-benzyloxy) benzoyloxy] benzoate, **13**, (1.15 g, 2.02 mmol) was dissolved in 30 mL $\text{EtOH}/\text{CH}_2\text{Cl}_2$ (1:1) and 10% Pd/C catalyst (0.10 g) was added. The resultant solution was stirred at room temperature in an atmosphere of hydrogen till the required quantity of hydrogen was absorbed. This mixture was filtered through Celite and the solvent was removed under reduced pressure to yield 4-[(4-Cyanophenoxy) carbonyl] phenyl 3-[(4-hydroxyl) benzoyloxy] benzoate, **15**, as a white solid (0.96 g, 2.00 mmol, 99.0%) which was directly used for the subsequent reaction. ^1H NMR ($(\text{CD}_3)_2\text{CO}$, 400 MHz): δ 8.32 (m, 2H), 8.15 (t, 1H, $J = 1.5$ Hz), 8.13 (dt, 1H, $J = 7.5, 1.5$ Hz), 8.09 (m, 2H), 7.95 (m, 2H), 7.73 (t, 1H, $J = 7.5$ Hz), 7.68 (m, 1H), 7.62 (m, 4H), 7.03 (m, 2H).



16

4-[(4-Trifluoromethylphenoxy) carbonyl] phenyl 3-[(4-hydroxyl) benzoyloxy] benzoate (16)

4-[(4-Trifluoromethylphenoxy) carbonyl] phenyl 3-[(4-benzyloxy) benzoyloxy] benzoate, **14**, (0.34 g, 0.56 mmol) was dissolved in 10 mL EtOH/CH₂Cl₂ (1:1) and 10% Pd/C catalyst (0.04 g) was added. The resultant solution was stirred at room temperature in an atmosphere of hydrogen till the required quantity of hydrogen was absorbed. This mixture was filtered through Celite and the solvent was removed under reduced pressure to yield 4-[(4-Trifluoromethylphenoxy) carbonyl] phenyl 3-[(4-hydroxyl) benzoyloxy] benzoate, **16**, as a white solid (0.29 g, 0.56 mmol, >99%) which was directly used for the subsequent reaction. ¹H NMR (CDCl₃, 500 MHz): δ 8.28 (m, 2H), 8.12 (m, 2H), 8.11 (t, 1H, J = 1.5 Hz), 8.04 (t, 1H, J = 2.0 Hz), 7.70 (d, 2H, J = 8.5 Hz), 7.59 (t, 1H, J = 7.5 Hz), 7.51 (m, 1H), 7.39 (m, 2H), 7.34 (d, 2H, J = 8.5 Hz), 6.93 (m, 2H).

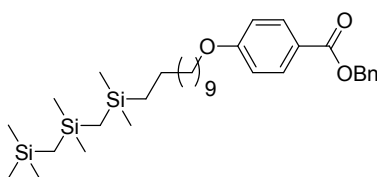


17

4-Undec-10-enyloxy-benzoic acid benzyl ester (17)

11-Bromo-1-undecene (2.83 mL, 3.04 g, 13.0 mmol) was added via syringe with stirring and under argon to a solution of a mixture of Benzyl 4-Hydroxybenzoate (3.12 g,

13.7 mmol) and Potassium Carbonate (5.67 g, 41.0 mmol) in 150 mL acetone. The reaction mixture was allowed to heat to reflux for 2 days. Then, the solvent was removed by reduced pressure, and 150 mL diethyl ether was added to the residue. The insoluble material was filtered off and the filtrate was washed with 10% NaOH (3 x 75 mL) and saturated NaCl (3 x 75 mL), dried over anhydrous MgSO₄, filtered and then concentrated at reduced pressure. The crude product was subjected to purification by flash chromatography (9:1 hexane:EtOAc) to provide 4-Undec-10-enyloxy-benzoic acid benzyl ester, **17**, (4.91 g, 12.9 mmol, 99.2%) as a white solid. ¹H NMR (CDCl₃, 500 MHz): δ 8.00 (m, 2H), 7.44-7.32 (m, 5H), 6.88 (m, 2H), 5.79 (m, 1H), 5.32 (s, 2H), 4.98 (m, 1H), 4.91 (m, 1H), 3.98 (t, 2H, J = 6.5 Hz), 2.02 (m, 2H), 1.77 (m, 2H), 1.45-1.28 (m, 12 H). ¹³C NMR (CDCl₃, 100 MHz): δ 166.2, 163.0, 139.2, 136.3, 131.7, 128.5, 128.1, 128.1, 122.2, 114.1, 114.0, 68.2, 66.3, 33.8, 29.5, 29.4, 29.3, 29.1, 29.1, 28.9, 25.9.

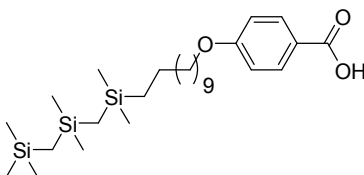


18

Tricarbosilane-undecyloxy-benzoic acid benzyl ester (18)

4-Undec-10-enyloxy-benzoic acid benzyl ester, **17**, (2.97 g, 7.81 mmol) was dissolved in 35 mL anhydrous toluene under an argon atmosphere. To this solution, oligo-silane tail **2** (2.28 g, 10.5 mmol) and a few drops of Karstedt's catalyst (platinum-divinyltetramethyl-siloxane complex in xylene) were added. The flask was covered with aluminum-foil and the reaction mixture was allowed to stir at room temperature for 3

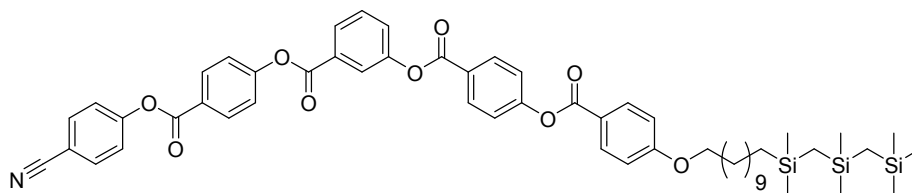
days until the reaction completed, which was determined by TLC. The solvent was evaporated and the black residue obtained was purified by flash chromatography (3:2 hexane:CH₂Cl₂) to give Tricarbosilane-undecyloxy-benzoic acid benzyl ester, **18**, (2.75 g, 4.59 mmol, 58.8%) as a colorless oil. ¹H NMR (CDCl₃, 500 MHz): δ 8.00 (m, 2H), 7.43-7.32 (m, 5H), 6.88 (m, 2H), 5.31 (s, 2H), 3.98 (t, 2H, J = 6.5 Hz), 1.77 (t, 2H, J = 7.0 Hz), 1.43-1.25 (m, 16H), 0.44 (m, 2H), -0.02 (m, 21H), -0.30 (m, 4H).



8

Tricarbosilane-undecyloxy-benzoic acid (**8**)

Tricarbosilane-undecyloxy-benzoic acid benzyl ester, **18**, (1.27 g, 2.12 mmol) was dissolved in 150 mL EtOH/CHCl₃ (1:1) and 10% Pd/C catalyst (0.13 g) was added. The resultant solution was stirred at room temperature in an atmosphere of hydrogen till the required quantity of hydrogen was absorbed. This mixture was filtered through Celite and the solvent was removed under reduced pressure to yield Tricarbosilane-undecyloxy-benzoic acid, **8**, as a white solid (1.08 g, 2.12 mmol, >99%) which was directly used for the subsequent reaction. ¹H NMR (CD₃OD, 500 MHz): δ 7.98 (m, 2H), 6.98 (m, 2H), 4.07 (t, 2H, J = 6.5 Hz), 1.82 (m, 2H), 1.52-1.34 (m, 16H), 0.54 (m, 2H), 0.06 (m, 21H), -0.21 (m, 4H)

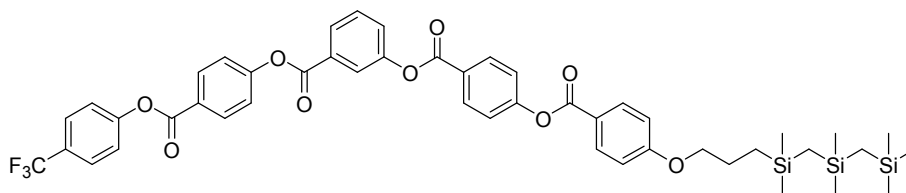


3, W586

4-[(4-Cyanophenoxy) carbonyl] phenyl 3-{4-[4-(11-tricarbosilane) undecyloxy] benzoyloxy} benzoate (3, W586).

A mixture of 4-[(4-Cyanophenoxy) carbonyl] phenyl 3-[(4-hydroxy) benzoyloxy] benzoate, **15**, (0.44 g, 0.92 mmol), Tricarbosilane-undecyloxy-benzoic acid benzyl ester, **8**, (0.49 g, 0.96 mmol) and 4-dimethylaminopyridine (DMAP) (5 mg, 0.04 mmol) in 20 mL dry CH₂Cl₂ was stirred for 10 minutes. To this mixture, dicyclohexylcarbodiimide (DCC) (0.21 g, 1.02 mmol) was added and the reaction mixture was continued to stir for 12 h at room temperature under argon atmosphere. The precipitated dicyclohexylurea was filtered off and washed with excess CH₂Cl₂. The solvent of the filtrate was removed and the crude product was purified by flash chromatography (CHCl₃) to give 4-[(4-Cyanophenoxy) carbonyl] phenyl 3-{4-[4-(11-tricarbosilane) undecyloxy] benzoyloxy} benzoate, **3**, (**W586**) (0.60 g, 0.62 mmol, 67.4%) as a white solid. ¹H NMR (CDCl₃, 500 MHz): δ 8.28 (m, 4H), 8.15-8.13 (m, 3H), 8.07 (t, 1H, J = 1.5 Hz), 7.74 (m, 2H), 7.61 (t, 1H, J = 7.5 Hz), 7.54 (m, 1H), 7.41-7.36 (m, 6H), 6.97 (m, 2H), 4.04 (t, 2H, J = 6.5 Hz), 1.81 (p, 2H, J = 6.5 Hz), 1.46 (m, 2H), 1.39-1.23 (m, 14H), 0.45 (m, 2H), 0.00 (m, 21H), -0.29 (m, 4H). ¹³C NMR (CDCl₃, 100 MHz): δ 164.5, 164.1, 163.9, 163.8, 155.9, 155.6, 154.3, 151.3, 134.0, 132.7, 132.3, 132.1, 130.7, 130.2, 127.9, 126.6, 123.9, 123.2, 122.5, 121.0, 118.5, 114.7, 110.2, 68.6, 34.0, 29.9, 29.8, 29.6, 29.3, 26.2, 24.2, 18.3, 6.0, 4.2, 2.7, 1.7, -0.2. MS: Calculated for C₅₅H₆₇NO₉Si₃, ([M-H]⁺) requires: 970.38, found: 970.4.

Elemental analysis: C₅₅H₆₇NO₉Si₃ requires: C, 68.08%; H, 6.96%; N, 1.44%; Si, 8.68%;
found: C, 67.87%; H, 7.08%; N, 1.56%; Si, 8.35%.

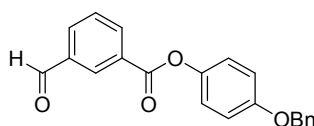


4, W596

4-[(4-Trifluoromethylphenoxy) carbonyl] phenyl 3-{4-[4-(11-tricarbosilane) undecyloxy] benzoyloxy} benzoate (**4, W596**).

A mixture of 4-[(4-Trifluoromethylphenoxy) carbonyl] phenyl 3-[(4-hydroxyl) benzoyloxy] benzoate, **16**, (0.29 g, 0.56 mmol), Tricarbosilane-undecyloxy-benzoic acid benzyl ester, **8**, (0.29 g, 0.57 mmol) and 4-dimethylaminopyridine (DMAP) (5 mg, 0.04 mmol) in 20 mL dry CH₂Cl₂ was stirred for 10 minutes. To this mixture, dicyclohexylcarbodiimide (DCC) (0.13 g, 0.63 mmol) was added and the reaction mixture was continued to stir for 12 h at room temperature under argon atmosphere. The precipitated dicyclohexylurea was filtered off and washed with excess CH₂Cl₂. The solvent of the filtrate was removed and the crude product was purified by flash chromatography (CHCl₃) to give 4-[(4-Trifluoromethylphenoxy) carbonyl] phenyl 3-{4-[4-(11-tricarbosilane) undecyloxy] benzoyloxy} benzoate, **4, (W596)** (0.40 g, 0.39 mmol, 70.4%) as a white solid. ¹H NMR (CDCl₃, 500 MHz): δ 8.29 (m, 4H), 8.15-8.13 (m, 3H), 8.07 (t, 1H, J = 2.0 Hz), 7.70 (d, 2H, J = 9.0 Hz), 7.61 (t, 1H, J = 7.5 Hz), 7.54 (ddd, 1H, J = 8.0, 2.5, 1.0 Hz), 7.41-7.34 (m, 6H), 6.97 (m, 2H), 4.04 (t, 2H, J = 6.5 Hz), 1.81 (p, 2H, J = 6.5 Hz), 1.46 (m, 2H), 1.39-1.23 (m, 14H), 0.45 (m, 2H), 0.00 (m, 21H), -0.29 (m, 4H). ¹³C NMR (CDCl₃, 75 MHz): δ 164.3, 163.9, 163.7, 156.0, 155.7, 155.2, 151.1,

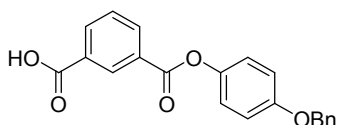
132.4, 132.0, 131.9, 130.6, 129.9, 128.5, 128.0, 127.8, 127.6, 126.9, 126.9, 126.7, 126.3, 123.7, 122.2, 122.1, 120.8, 114.4, 68.4, 33.7, 30.9, 29.6, 29.6, 29.6, 29.4, 29.4, 29.1, 26.0, 24.0, 18.1, 5.8, 4.0, 2.5, 1.5, -0.4. MS: Calculated for $C_{55}H_{67}NO_9Si_3$, $([M-H]^+)$ requires: 1013.37, found: 1013.41.



19

3-Formyl-benzoic acid 4-benzyloxy-phenyl ester (19)

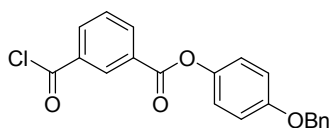
A mixture of 4-Benzyloxyphenol (4.12 g, 20.6 mmol), 3-Formyl-benzoic acid (3.11 g, 20.7 mmol) and 4-dimethylaminopyridine (DMAP) (100 mg, 0.82 mmol) in 250 mL $CHCl_3$ was stirred for 10 minutes. To this mixture, dicyclohexylcarbodiimide (DCC) (4.60 g, 22.3 mmol) in 50 mL of $CHCl_3$ was added and the reaction mixture was continued to stir for 12 h at room temperature under argon atmosphere. The precipitated dicyclohexylurea was filtered off and washed with excess $CHCl_3$. The solvent of the filtrate was removed and 3-Formyl-benzoic acid 4-benzyloxy-phenyl ester, **19**, (5.41 g, 16.3 mmol, 79.1%) was obtained as a white solid after recrystallization from a mixture of CH_3CN and a few drops of $CHCl_3$. 1H NMR ($CDCl_3$, 500 MHz): δ 10.11 (s, 1H), 8.67 (t, 1H, $J = 1.5$ Hz), 8.43 (dt, 1H, $J = 7.5, 1.5$ Hz), 8.14 (dt, 1H, $J = 7.5, 1.5$ Hz), 7.69 (t, 1H, $J = 7.5$ Hz), 7.44-7.33 (m, 5H), 7.14 (m, 2H), 7.02 (m, 2H), 5.07 (s, 2H)



20

Isophthalic acid mono-(4-benzyloxy-phenyl) ester (20)

To a solution of 3-Formyl-benzoic acid 4-benzyloxy-phenyl ester, **19**, (2.00 g, 6.02 mmol) in 100 mL acetone, KMnO₄ (1.43 g, 9.05 mmol) in 100 mL of acetone/H₂O (1:1) was slowly added in a period of 10 minutes and the reaction mixture was allowed to stir for 2 h at room temperature. Then, saturated NaHCO₃ was added and black precipitates were formed. 1M HCl was carefully added till all black precipitates disappeared. Then, the mixture was extracted by CH₂Cl₂ (3 x 100 mL) and the organic layer was washed with H₂O (3 x 100 mL) and saturated NaCl (3 x 100 mL), dried over anhydrous MgSO₄, filtered and then concentrated at reduced pressure to yield Isophthalic acid mono-(4-benzyloxy-phenyl) ester, **20**, (2.05 g, 5.89 mmol, 97.8%) as a white solid which was directly used in the subsequent reaction. ¹H NMR ((CD₃)₂CO, 500 MHz): δ 8.81 (t, 1H, J = 1.5 Hz), 8.41 (dt, 1H, J = 7.5, 1.5 Hz), 8.37 (dt, 1H, J = 7.5, 1.5 Hz), 7.78 (t, 1H, J = 7.5 Hz), 7.53-7.34 (m, 5H), 7.27 (m, 2H), 7.13 (m, 2H), 5.18 (s, 2H)

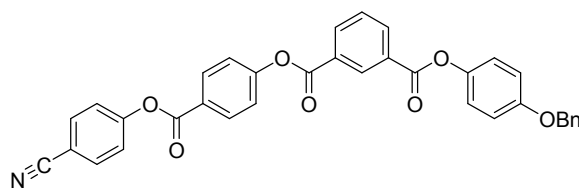


21

3-Chlorocarbonyl-benzoic acid 4-benzyloxy-phenyl ester (21)

To a solution of Isophthalic acid mono-(4-benzyloxy-phenyl) ester, **20**, (0.28 g, 0.81 mmol) in 10 mL dry CH₂Cl₂ was added 1 drop DMF and SOCl₂ (0.10 mL, 0.16 g, 1.37

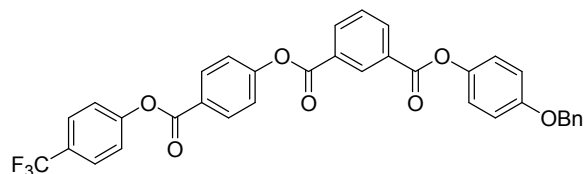
mmol) and the reaction mixture was allowed to stir for 2 h at room temperature. Then, the solvent was removed by reduced pressure and 3-Chlorocarbonyl-benzoic acid 4-benzyloxy-phenyl ester, **21**, (0.30 g, 0.81 mmol, >99%) was obtained as a white solid which was directly used for the subsequent reaction without any further purification.



22

Isophthalic acid 1-(4-benzyloxy-phenyl) ester 3-[4-(4-cyano-phenoxy carbonyl)-phenyl] ester (**22**)

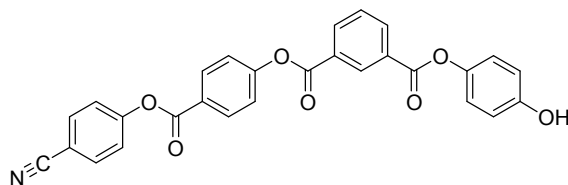
To a solution of 3-Chlorocarbonyl-benzoic acid 4-benzyloxy-phenyl ester, **21**, (0.30 g, 0.81 mmol) and 4-Hydroxy-benzoic acid 4'-cyano-phenyl ester, **5**, (0.20 g, 0.84 mmol) in 20 mL dry CH₂Cl₂ was added dry triethylamine (0.13 mL, 0.094 g, 0.93 mmol) and the reaction mixture was allowed to stir for 5 h at room temperature. Then, 5 mL H₂O was added and the mixture was extract by large amount of CHCl₃ (3 x 100 mL) and the organic layer was washed by 0.1 M HCl (10 mL), H₂O (3 x 100 mL) and saturated NaCl (3 x 100 mL), dried over anhydrous MgSO₄, filtered and then concentrated at reduced pressure to yield Isophthalic acid 1-(4-benzyloxy-phenyl) ester 3-[4-(4-cyano-phenoxy carbonyl)-phenyl] ester, **22**, (0.45 g, 0.79 mmol, 97.5%) as a white solid. ¹H NMR (CDCl₃, 500 MHz): δ 9.00 (t, 1H, J = 1.5 Hz), 8.46 (tt, 2H, J = 7.5, 1.5 Hz), 8.29 (m, 2H), 7.75 (m, 2H), 7.68 (t, 1H, J = 7.5 Hz), 7.43-7.33 (m, 9H), 7.15 (m, 2H), 7.02 (m, 2H), 5.07 (s, 2H).



23

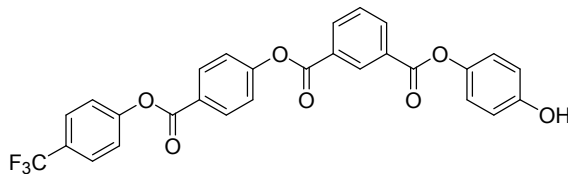
Isophthalic acid 1-(4-benzyloxy-phenyl) ester 3-[4-(4-trifluoromethyl-phenoxy carbonyl)-phenyl] ester (**23**)

To a solution of 3-Chlorocarbonyl-benzoic acid 4-benzyloxy-phenyl ester, **21**, (0.40 g, 1.09 mmol) and 4-Hydroxy-benzoic acid 4'-trifluoromethyl-phenyl ester, **6**, (0.31 g, 1.10 mmol) in 50 mL dry CH₂Cl₂ was added dry triethylamine (0.25 mL, 0.18 g, 1.79 mmol) and the reaction mixture was allowed to stir for 5 h at room temperature. Then, 10 mL H₂O was added and the mixture was extract by large amount of CHCl₃ (3 x 100 mL) and the organic layer was washed by 0.1 M HCl (10 mL), H₂O (3 x 100 mL) and saturated NaCl (3 x 100 mL), dried over anhydrous MgSO₄, filtered and then concentrated at reduced pressure to yield Isophthalic acid 1-(4-benzyloxy-phenyl) ester 3-[4-(4-trifluoromethyl-phenoxy carbonyl)-phenyl] ester, **23**, (0.45 g, 0.73 mmol, 67.4%) as a white solid. ¹H NMR (CDCl₃, 500 MHz): δ 9.01 (t, 1H, J = 1.5 Hz), 8.47 (tt, 2H, J = 7.5, 1.5 Hz), 8.30 (m, 2H), 7.70 (m, 3H), 7.43-7.33 (m, 9H), 7.15 (m, 2H), 7.02 (m, 2H), 5.07 (s, 2H).



Isophthalic acid 1-(4-Hydroxy-phenyl) ester 3-[4-(4-cyano-phenoxy carbonyl)-phenyl] ester (24)

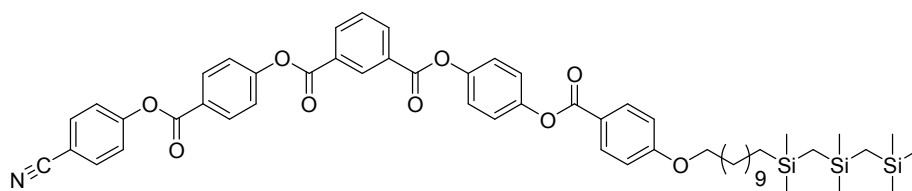
To a solution of Isophthalic acid 1-(4-benzyloxy-phenyl) ester 3-[4-(4-cyano-phenoxy carbonyl)-phenyl] ester, **22**, (0.22 g, 0.39 mmol) in 10 mL of dry CH₂Cl₂ was added BBr₃ (1M in CH₂Cl₂) (0.40 mL, 0.40 mmol) drop wise at 0°C under argon atmosphere. Then, the reaction mixture was allowed to stir for 1 h at 0°C and warmed up to room temperature and kept stirring for another 30 minutes. Then, 5 mL H₂O was added and the mixture was extract by EtOAc (3 x 25 mL) and the organic layer was washed by H₂O (3 x 25 mL) and saturated NaCl (3 x 25 mL), dried over anhydrous MgSO₄, filtered and then concentrated at reduced pressure. The crude product was subjected to purification by flash chromatography (CHCl₃) to provide Isophthalic acid 1-(4-Hydroxy-phenyl) ester 3-[4-(4-cyano-phenoxy carbonyl)-phenyl] ester, **24**, (0.17 g, 0.36 mmol, 92.3%) as a white foam. ¹H NMR (CDCl₃, 500 MHz): δ 9.00 (t, 1H, J = 1.5 Hz), 8.48 (m, 2H), 8.28 (m, 2H), 7.75 (m, 2H), 7.70 (t, 1H, J = 7.5 Hz), 7.41 (m, 2H), 7.37 (m, 2H), 7.10 (m, 2H), 6.88 (m, 2H).



25

Isophthalic acid 1-(4-Hydroxy-phenyl) ester 3-[4-(4-trifluoromethyl-phenoxy carbonyl)-phenyl] ester (25)

To a solution of Isophthalic acid 1-(4-benzyloxy-phenyl) ester 3-[4-(4-trifluoromethyl-phenoxy carbonyl)-phenyl] ester, **23**, (0.31 g, 0.50 mmol) in 10 mL of dry CH₂Cl₂ was added BBr₃ (1M in CH₂Cl₂) (0.60 mL, 0.60 mmol) drop wise at 0°C under argon atmosphere. Then, the reaction mixture was allowed to stir for 1 h at 0°C and warmed up to room temperature and kept stirring for another 30 minutes. Then, 5 mL H₂O was added and the mixture was extract by EtOAc (3 x 25 mL) and the organic layer was washed by H₂O (3 x 25 mL) and saturated NaCl (3 x 25 mL), dried over anhydrous MgSO₄, filtered and then concentrated at reduced pressure. The crude product was subjected to purification by flash chromatography (CHCl₃) to provide Isophthalic acid 1-(4-Hydroxy-phenyl) ester 3-[4-(4-cyano-phenoxy carbonyl)-phenyl] ester, **25**, (0.18 g, 0.35 mmol, 70.0%) as a white solid. ¹H NMR (CDCl₃, 500 MHz): δ 9.00 (t, 1H, J = 1.5 Hz), 8.46 (m, 2H), 8.30 (m, 2H), 7.70 (m, 3H), 7.42 (m, 2H), 7.35 (m, 2H), 7.10 (m, 2H), 6.88 (m, 2H).

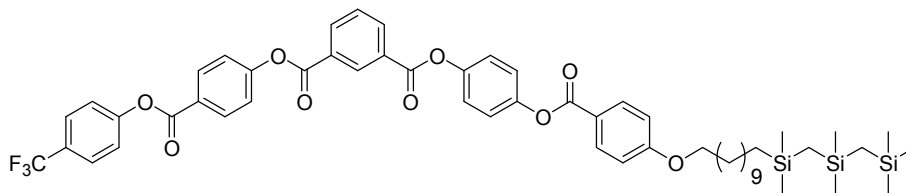


26, W623

Isophthalic acid 1-{[4-(4-tricarbosilane-undecyloxy)-benzyloxy]-phenyl} ester 3-[4-(4-cyano-phenoxy carbonyl)-phenyl] ester (**26, W623**)

A mixture of Isophthalic acid 1-(4-Hydroxy-phenyl) ester 3-[4-(4-cyano-phenoxy carbonyl)-phenyl] ester, **24**, (0.17 g, 0.36 mmol), Tricarbosilane-undecyloxy-benzoic acid benzyl ester, **8**, (0.20 g, 0.39 mmol) and 4-dimethylaminopyridine (DMAP) (5 mg, 0.04 mmol) in 10 mL dry CH₂Cl₂ was stirred for 10 minutes. To this mixture, 1-Ethyl-3-(3-

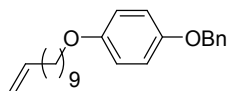
dimethylaminopropyl)carbodiimide (EDCI) (0.080 g, 0.42 mmol) was added and the reaction mixture was continued to stir for 12 h at room temperature under argon atmosphere. Then, the solvent of the filtrate was removed and the crude product obtained was purified by flash chromatography (CHCl₃) to yield Isophthalic acid 1-{[4-(4-tricarbosilane-undecloxy)-benzyloxy]-phenyl} ester 3-[4-(4-cyano-phenoxy carbonyl)-phenyl] ester, **26**, (**W623**) (0.25 g, 0.26 mmol, 72.2%) as a white solid. ¹H NMR (CDCl₃, 500 MHz): δ 9.02 (t, 1H, J = 1.5 Hz), 8.49 (m, 2H), 8.29 (m, 2H), 8.13 (m, 2H), 7.75 (m, 2H), 7.72 (t, 1H, J = 7.5 Hz), 7.43 (m, 2H), 7.37 (m, 2H), 7.29 (m, 4H), 6.96 (m, 2H), 4.03 (t, 2H, J = 6.5 Hz), 1.81 (m, 2H), 1.47-1.44 (m, 16 H), 0.45 (m, 2H), 0.00 (m, 21H), -0.29 (m, 4H). ¹³C NMR (CDCl₃, 100 MHz): δ 164.8, 164.0, 163.6, 163.6, 163.5, 155.3, 154.1, 148.8, 147.9, 133.8, 132.3, 132.1, 132.1, 131.9, 130.3, 129.7, 129.3, 126.4, 122.9, 122.9, 122.5, 122.2, 121.2, 118.3, 114.4, 114.3, 110.0, 68.3, 33.7, 29.6, 29.6, 29.6, 29.4, 29.1, 26.0, 24.0, 18.0, 5.8, 4.0, 2.5, 1.5, -0.5. MS: Calculated for C₅₅H₆₇NO₉Si₃, ([M-H]⁺) requires: 970.38, found: 970.42. Elemental analysis: C₅₅H₆₇NO₉Si₃ requires, C, 68.08%; H, 6.96%; N, 1.44 %; found, C, 68.37%, H, 7.06%, N, 1.25%



27, W628

Isophthalic acid 1-{[4-(4-tricarbosilane-undecloxy)-benzyloxy]-phenyl} ester 3-[4-(4-trifluoromethyl-phenoxy carbonyl)-phenyl] ester (**27**, **W628**)

A mixture of Isophthalic acid 1-(4-Hydroxy-phenyl) ester 3-[4-(4-trifluoromethyl-phenoxy carbonyl)-phenyl] ester, **25**, (0.18 g, 0.35 mmol), Tricarbosilane-undecyloxybenzoic acid benzyl ester, **8**, (0.18 g, 0.35 mmol) and 4-dimethylaminopyridine (DMAP) (5 mg, 0.04 mmol) in 10 mL dry CHCl₃ was stirred for 10 minutes. To this mixture, dicyclohexylcarbodiimide (DCC) (0.08 g, 0.39 mmol) in 2 mL of CHCl₃ was added and the reaction mixture was continued to stir for 12 h at room temperature under argon atmosphere. The precipitated dicyclohexylurea was filtered off and washed with excess CHCl₃. The solvent of the filtrate was removed and the crude product obtained was purified by flash chromatography (CHCl₃) to yield Isophthalic acid 1-{[4-(4-tricarbosilane-undecyloxy)-benzyloxy]-phenyl} ester 3-[4-(4-trifluoromethyl-phenoxy carbonyl)-phenyl] ester, **27**, (**W628**) (0.22 g, 0.22 mmol, 62.9%) as a white solid. ¹H NMR (CDCl₃, 500 MHz): δ 9.02 (t, 1H, J = 1.5 Hz), 8.48 (tt, 2H, J = 8.0, 1.5 Hz), 8.30 (m, 2H), 8.13 (m, 2H), 7.72 (m, 3H), 7.43 (m, 2H), 7.35 (m, 2H), 7.29 (m, 4H), 6.96 (m, 2H), 4.03 (t, 2H, J = 6.5 Hz), 1.81 (m, 2H), 1.47-1.44 (m, 16 H), 0.45 (m, 2H), 0.00 (m, 21H), -0.29 (m, 4H).

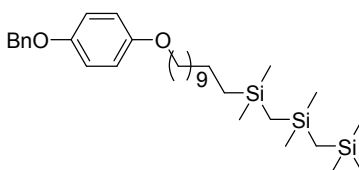


32

1-Benzloxy-4-Undec-10-enyloxy-benzene (32)

11-Bromo-1-undecene (1.71 mL, 1.83 g, 7.87mmol) was added via syringe with stirring and under argon to a solution of a mixture of 4-Benzloxy-phenol (1.65 g, 8.24 mmol) and Potassium Carbonate (3.26 g, 23.6 mmol) in 100 mL acetone. The reaction

mixture was allowed to heat to reflux for 2 days. Then, the solvent was removed by reduced pressure, and 150 mL diethyl ether was added to the residue. The insoluble material was filtered off and the filtrate was washed with 10% NaOH (3 x 75 mL) and saturated NaCl (3 x 75 mL), dried over anhydrous MgSO₄, filtered and then concentrated at reduced pressure. The crude product was subjected to purification by flash chromatography (4:1 hexane:EtOAc) to provide 1-Benzloxy-4-Undec-10-enyloxy-benzene, **32**, (2.49 g, 7.06 mmol, 89.7%) as a white solid. ¹H NMR (CDCl₃, 500 MHz): δ 7.42-7.28 (m, 5H), 6.88 (m, 2H), 6.81 (m, 2H), 5.80 (m, 1H), 4.99 (s, 2H), 4.98 (ddd, 1H, J = 17.0, 3.5, 1.5 Hz), 4.91 (m, 1H), 3.88 (t, 2H, J = 6.5 Hz), 2.02 (m, 2H), 1.73 (p, 2H, J = 7.0 Hz), 1.44-1.13 (m, 12 H). ¹³C NMR (CDCl₃, 100 MHz): δ 153.5, 152.8, 139.2, 137.3, 128.5, 127.9, 127.5, 115.7, 115.3, 114.1, 70.7, 68.6, 33.8, 29.5, 29.4, 29.4, 29.4, 29.1, 28.9, 26.0.

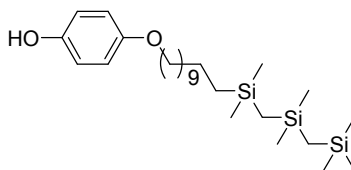


33

1-Benzloxy-4-tricarbosilane-Undecyloxy benzene (33)

1-Benzloxy-4-Undec-10-enyloxy-benzene, **32**, (0.99 g, 2.81 mmol) was dissolved in 15 mL anhydrous toluene under an argon atmosphere. To this solution, tricarbosilane tail **2** (0.97 g, 4.45 mmol) and a few drops of Karstedt's catalyst (platinum-divinyltetramethyl-siloxane complex in xylene) were added. The flask was covered with aluminum-foil and the reaction mixture was allowed to stir at room temperature for 3

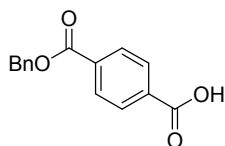
days until the reaction completed, which was determined by TLC. The solvent was evaporated and the black residue obtained was purified by flash chromatography (3:2 hexane:CH₂Cl₂) to give 1-Benzlyoxy-4-tricarbosilane-undecyloxy-benzene, **33**, (0.90g, 1.58 mmol, 56.2%) as a colorless oil. ¹H NMR (CDCl₃, 500 MHz): δ 7.42-7.30 (m, 5H), 6.88 (m, 2H), 6.80 (m, 2H), 4.99 (s, 2H), 3.87 (t, 2H, J = 6.5 Hz), 1.73 (p, 2H, J = 7.0 Hz), 1.43-1.25 (m, 16 H), 0.44 (m, 2H), 0.00 (m, 21H), -0.30 (m, 4H). ¹³C NMR (CDCl₃, 100 MHz): δ 153.5, 152.8, 137.3, 128.5, 127.9, 127.5, 115.8, 115.4, 100.0, 70.7, 68.6, 33.7, 29.7, 29.6, 29.6, 29.4, 29.4, 26.1, 23.4, 18.1, 5.8, 4.0, 2.5, 1.5, -0.4.



34

4-tricarbosilane-Undecyloxy phenol (**34**)

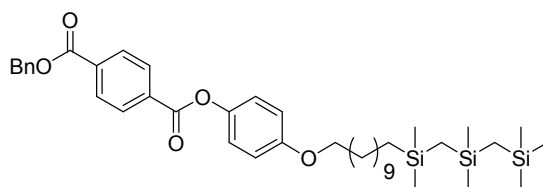
1-Benzlyoxy-4-tricarbosilane-undecyloxy-benzene, **33**, (0.90 g, 1.58 mmol) was dissolved in 50 mL EtOH/CHCl₃ (1:1) and 10% Pd/C catalyst (0.09 g) was added. The resultant solution was stirred at room temperature in an atmosphere of hydrogen till the required quantity of hydrogen was absorbed. This mixture was filtered through Celite and the solvent was removed under reduced pressure to yield 4-tricarbosilane-Undecyloxy phenol, **34**, as a white solid (0.76 g, 1.58 mmol, >99%) which was directly used for the subsequent reaction.



35

Terephthalic acid monobenzyl ester (35)

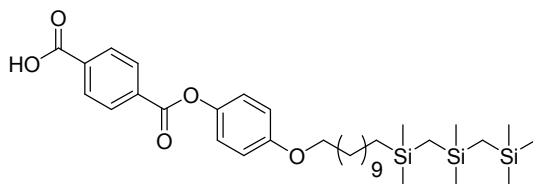
To a solution of 4-Formyl-benzoic acid benzyl ester (5.54 g, 23.06 mmol) in 200 mL acetone, KMnO_4 (5.04 g, 31.89 mmol) in 100 mL of acetone/ H_2O (1:1) was slowly added in a period of 10 minutes and the reaction mixture was allowed to stir for 2 h at room temperature. Then, saturated NaHCO_3 was added and black precipitates were formed. 1M HCl was carefully added till all black precipitates disappeared. Then, the mixture was extracted by CH_2Cl_2 (3 x 150 mL) and the organic layer was washed with H_2O (3 x 100 mL) and saturated NaCl (3 x 100 mL), dried over anhydrous MgSO_4 , filtered and then concentrated at reduced pressure to yield Terephthalic acid monobenzyl ester, **35**, (5.65 g, 22.05 mmol, 95.6%) as a white solid which was directly used in the subsequent reaction. ^1H NMR ($(\text{CD}_3)_2\text{CO}$, 500 MHz): δ 8.16 (m, 4H), 7.54-7.37 (m, 5H), 5.42 (s, 2H). ^{13}C NMR ($(\text{CD}_3)_2\text{CO}$, 100 MHz): δ 166.8, 166.0, 137.1, 135.4, 134.9, 130.6, 130.4, 129.4, 129.2, 129.1, 67.6.



36

Terephthalic acid 1-benzyl ester 4-(4-tricarbosilane-Undecyloxyl-phenyl) ester (36)

A mixture of 4-tricarbosilane-Undecyloxy phenol, **34**, (1.07 g, 2.22 mmol), Terephthalic acid monobenzyl ester, **35**, (0.58 g, 2.26 mmol) and 4-dimethylaminopyridine (DMAP) (25 mg, 0.20 mmol) in 30 mL CHCl₃ was stirred for 10 minutes. To this mixture, dicyclohexylcarbodiimide (DCC) (0.51 g, 2.47 mmol) in 10 mL of CHCl₃ was added and the reaction mixture was continued to stir for 12 h at room temperature under argon atmosphere. The precipitated dicyclohexylurea was filtered off and washed with excess CHCl₃. The solvent of the filtrate was removed and concentrated at reduced pressure. The crude product was subjected to purification by flash chromatography (3:1 CHCl₃:hexane) to provide Terephthalic acid 1-benzyl ester 4-(4-tricarbosilane-Undecyloxyl-phenyl) ester, **36**, (0.78 g, 1.08 mmol, 48.6%) as a white solid. ¹H NMR (CDCl₃, 500 MHz): δ 8.23 (m, 2H), 8.17 (m, 2H), 7.46-7.35 (m, 5H), 7.10 (m, 2H), 6.91 (m, 2H), 5.39 (s, 2H), 3.94 (t, 2H, J = 6.5 Hz), 1.77 (p, 2H, J = 7.5 Hz), 1.44-1.25 (m, 16H), 0.45 (m, 2H), 0.00 (m, 21H), -0.29 (m, 4H).

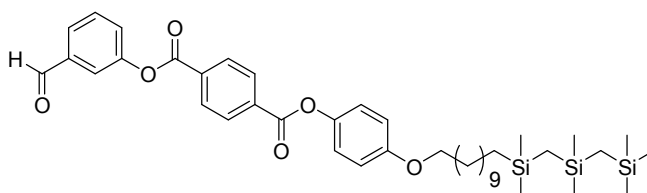


37

Terephthalic acid mono-(4-tricarbosilane-Undecyloxy-phenyl) ester (37)

Terephthalic acid 1-benzyl ester 4-(4-tricarbosilane-Undecyloxyl-phenyl) ester, **36**, (0.78 g, 1.08 mmol) was dissolved in 50 mL EtOH/CHCl₃ (1:1) and 10% Pd/C catalyst (0.08 g) was added. The resultant solution was stirred at room temperature in an atmosphere of hydrogen till the required quantity of hydrogen was absorbed. This

mixture was filtered through Celite and the solvent was removed under reduced pressure to yield Terephthalic acid mono-(4-tricarbosilane-Undecyloxy-phenyl) ester, **37**, (0.70 g, 1.11 mmol, >99%) as a white solid which was directly used for the subsequent reaction. ¹H NMR (CDCl₃, 500 MHz): δ 8.28 (m, 2H), 8.21 (m, 2H), 7.11 (m, 2H), 6.92 (m, 2H), 3.94 (t, 2H, J = 6.5 Hz), 1.77 (p, 2H, J = 7.5 Hz), 1.46-1.23 (m, 16H), 0.45 (m, 2H), 0.00 (m, 21H), -0.29 (m, 4H).

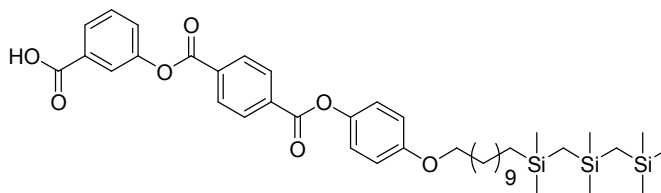


38

Terephthalic acid 1-(4-tricarbosilane-Undecyloxy-phenyl) ester 4-(3-formyl-phenyl) ester
(38)

A mixture of 3-Hydroxy-benzaldehyde (0.14 g, 1.14 mmol), Terephthalic acid mono-(4-tricarbosilane-Undecyloxy-phenyl) ester, **37**, (0.70 g, 1.11 mmol), and 4-dimethylaminopyridine (DMAP) (10 mg, 0.08 mmol) in 20 mL CHCl₃ was stirred for 10 minutes. To this mixture, dicyclohexylcarbodiimide (DCC) (0.25 g, 1.21 mmol) in 5 mL of CHCl₃ was added and the reaction mixture was continued to stir for 12 h at room temperature under argon atmosphere. The precipitated dicyclohexylurea was filtered off and washed with excess CHCl₃. The solvent of the filtrate was removed and concentrated at reduced pressure. The crude product was subjected to purification by flash chromatography (19:1 hexane:EtOAc) to provide Terephthalic acid 1-(4-tricarbosilane-Undecyloxy-phenyl) ester 4-(3-formyl-phenyl) ester, **38**, (0.53 g, 0.72 mmol, 64.9%) as a white solid. ¹H NMR (CDCl₃, 500 MHz): δ 10.04 (s, 1H), 8.32 (m, 4H), 7.82 (dt, 1H, J =

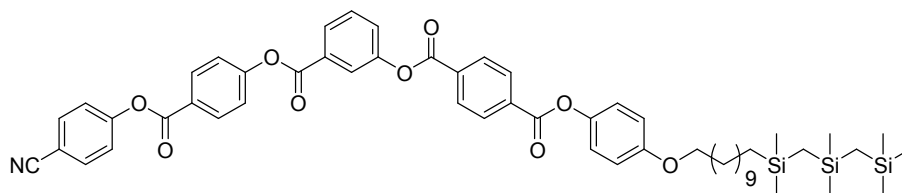
7.5, 1.5 Hz), 7.78 (t, 1H, J = 1.5 Hz), 7.63 (t, 1H, J = 7.5 Hz), 7.52 (ddd, 1H, J = 7.5, 2.5, 1.5 Hz), 7.13 (m, 2H), 6.93 (m, 2H), 3.95 (t, 2H, J = 6.5 Hz), 1.78 (p, 2H, J = 7.5 Hz), 1.46-1.23 (m, 16H), 0.45 (m, 2H), 0.00 (m, 21H), -0.29 (m, 4H).



39

Terephthalic acid 1-(3-carboxy-phenyl) ester 4-(4-tricarbosilane-Undecyloxy-phenyl) ester (39)

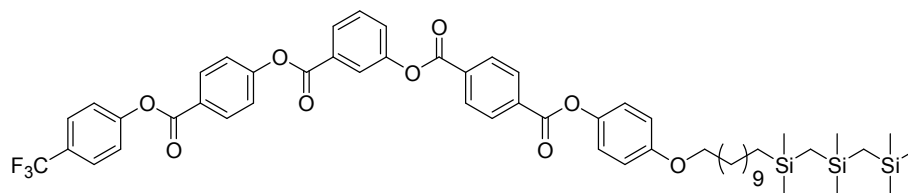
To a solution of Terephthalic acid 1-(4-tricarbosilane-Undecyloxy-phenyl) ester 4-(3-formyl-phenyl) ester, **38**, (0.52 g, 0.71 mmol) in 20 mL acetone, KMnO₄ (0.17 g, 1.08 mmol) in 5 mL of acetone/H₂O (1:1) was slowly added and the reaction mixture was allowed to stir for 2 h at room temperature. Then, saturated NaHCO₃ was added and black precipitates were formed. 1M HCl was carefully added till all black precipitates disappeared. Then, the mixture was extracted by CH₂Cl₂ (3 x 25 mL) and the organic layer was washed with H₂O (3 x 25 mL) and saturated NaCl (3 x 25 mL), dried over anhydrous MgSO₄, filtered and then concentrated at reduced pressure to yield Terephthalic acid 1-(3-carboxy-phenyl) ester 4-(4-tricarbosilane-Undecyloxy-phenyl) ester, **39**, (0.41 g, 0.55 mmol, 77.5%) as a white solid which was directly used in the subsequent reaction.



30, W631

Terephthalic acid 1-{3-[4-(4-cyano-phenoxy-carbonyl)-phenoxy-carbonyl]-phenyl} ester 4-(4-tricarbosilane-Undecyloxy-phenyl) ester (30, W631)

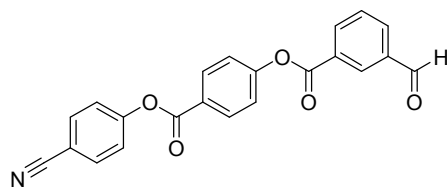
A mixture of Terephthalic acid 1-(3-carboxy-phenyl) ester 4-(4-tricarbosilane-Undecyloxy-phenyl) ester, **39**, (0.27 g, 0.36 mmol), 4-Hydroxy-benzoic acid 4'-cyano-phenyl ester, **5**, (0.09 g, 0.38 mmol) and 4-dimethylaminopyridine (DMAP) (5 mg, 0.04 mmol) in 10 mL dry CHCl_3 was stirred for 10 minutes. To this mixture, dicyclohexylcarbodiimide (DCC) (0.082 g, 0.40 mmol) was added and the reaction mixture was continued to stir for 12 h at room temperature under argon atmosphere. The precipitated dicyclohexylurea was filtered off and washed with excess CHCl_3 . The solvent of the filtrate was removed and concentrated at reduced pressure. The crude product was subjected to purification by flash chromatography (1:1 hexane: CHCl_3) to yield Terephthalic acid 1-{3-[4-(4-cyano-phenoxy-carbonyl)-phenoxy-carbonyl]-phenyl} ester 4-(4-tricarbosilane-Undecyloxy-phenyl) ester, **30**, (**W631**) (0.25 g, 0.26 mmol, 72.2%) as a white solid. ^1H NMR (CDCl_3 , 500 MHz): δ 8.33 (s, 4H), 8.27 (m, 2H), 8.16 (dt, 1H, $J = 7.5, 1.5$ Hz), 8.10 (t, 1H, $J = 1.0$ Hz), 7.74 (m, 2H), 7.63 (t, 1H, $J = 7.5$ Hz), 7.56 (ddd, 1H, $J = 7.5, 2.5, 1.5$ Hz), 7.40 (m, 2H), 7.36 (m, 2H), 7.13 (m, 2H), 6.93 (m, 2H), 3.95 (t, 2H, $J = 6.5$ Hz), 1.78 (p, 2H, $J = 7.5$ Hz), 1.46-1.23 (m, 16 H), 0.45 (m, 2H), 0.00 (m, 21H), -0.29 (m, 4H).



31, W632

Terephthalic acid 1-{3-[4-(4-trifluoromethyl-phenoxy-carbonyl)-phenoxy-carbonyl]-phenyl} ester 4-(4-tricarbosilane-Undecyloxy-phenyl) ester (31, W632)

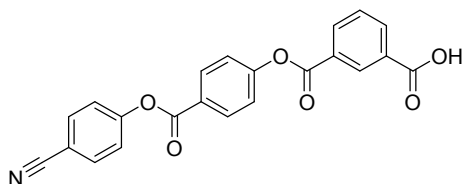
A mixture of 4-Hydroxy-benzoic acid 4'-trifluoromethyl-phenyl ester, **6**, (0.05 g, 0.18 mmol), Terephthalic acid 1-(3-carboxy-phenyl) ester 4-(4-tricarbosilane-Undecyloxy-phenyl) ester, **39**, (0.12 g, 0.16 mmol) and 4-dimethylaminopyridine (DMAP) (5 mg, 0.04 mmol) in 10 mL dry CHCl₃ was stirred for 10 minutes. To this mixture, dicyclohexylcarbodiimide (DCC) (0.038 g, 0.18 mmol) was added and the reaction mixture was continued to stir for 12 h at room temperature under argon atmosphere. The precipitated dicyclohexylurea was filtered off and washed with excess CHCl₃. The solvent of the filtrate was removed and concentrated at reduced pressure. The crude product was subjected to purification by flash chromatography (1:1 hexane:CHCl₃) to yield Terephthalic acid 1-{3-[4-(4-trifluoromethyl-phenoxy-carbonyl)-phenoxy-carbonyl]-phenyl} ester 4-(4-tricarbosilane-Undecyloxy-phenyl) ester, **31**, (**W632**) (0.14 g, 0.14 mmol, 87.5%) as a white solid. ¹H NMR (CDCl₃, 500 MHz): δ 8.34 (s, 4H), 8.29 (m, 2H), 8.16 (dt, 1H, J = 7.5, 1.5 Hz), 8.10 (t, 1H, J = 1.0 Hz), 7.70 (m, 2H), 7.63 (t, 1H, J = 7.5 Hz), 7.56 (ddd, 1H, J = 7.5, 2.5, 1.5 Hz), 7.40 (m, 2H), 7.35 (m, 2H), 7.13 (m, 2H), 6.93 (m, 2H), 3.95 (t, 2H, J = 6.5 Hz), 1.78 (p, 2H, J = 7.5 Hz), 1.46-1.23 (m, 16 H), 0.45 (m, 2H), 0.00 (m, 21H), -0.29 (m, 4H).



40

3-Formyl-benzoic acid 4-(4-cyanophenoxy) carbonyl phenyl ester (40)

A mixture of 4-Hydroxy-benzoic acid 4'-cyano-phenyl ester, **5**, (0.46 g, 1.90 mmol), 3-Formyl-benzoic acid (0.29 g, 1.94 mmol) and 4-dimethylaminopyridine (DMAP) (10 mg, 0.08 mmol) in 25 mL CHCl_3 was stirred for 10 minutes. To this mixture, dicyclohexylcarbodiimide (DCC) (0.45 g, 2.18 mmol) in 5 mL of CHCl_3 was added and the reaction mixture was continued to stir for 12 h at room temperature. The precipitated dicyclohexylurea was filtered off and washed with excess CHCl_3 . The solvent of the filtrate was removed and the crude product was purified by flash chromatography (CHCl_3) to give 3-Formyl-benzoic acid 4-(4-cyanophenoxy) carbonyl phenyl ester, **40**, (0.47 g, 1.27 mmol, 66.8%) as a white solid. ^1H NMR (CDCl_3 , 500 MHz): δ 10.13 (s, 1H), 8.71 (t, 1H, $J = 1.5\text{ Hz}$), 8.46 (dt, 1H, $J = 7.5, 1.5\text{ Hz}$), 8.29 (m, 2H), 8.19 (dt, 1H, $J = 7.5, 1.5\text{ Hz}$), 7.75-7.72 (m, 3H), 7.42 (m, 2H), 7.37 (m, 2H).

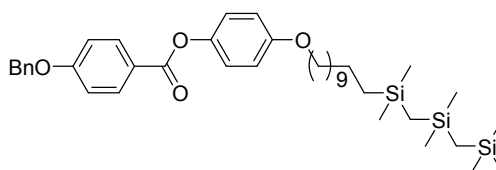


41

Isophthalic acid mono-[4-(4-cyano-phenoxy-carbonyl)-phenyl] ester (41)

To a solution of 3-Formyl-benzoic acid 4-(4-cyanophenoxy) carbonyl phenyl ester, **40**, (0.33 g, 0.89 mmol) in 20 mL acetone, KMnO_4 (0.19 g, 1.20 mmol) in 5 mL of

acetone/H₂O (1:1) was slowly added and the reaction mixture was allowed to stir for 2 h at room temperature. Then, saturated NaHCO₃ was added and black precipitates were formed. 1M HCl was carefully added till all black precipitates disappeared. Then, the mixture was extracted by CH₂Cl₂ (3 x 25 mL) and the organic layer was washed with H₂O (3 x 25 mL) and saturated NaCl (3 x 25 mL), dried over anhydrous MgSO₄, filtered and then concentrated at reduced pressure to yield Isophthalic acid mono-[4-(4-cyanophenoxycarbonyl)-phenyl] ester, **41**, (0.28 g, 0.73 mmol, 82.0%) as a white solid which was directly used in the subsequent reaction. ¹H NMR ((CD₃)₂CO, 500 MHz): δ 8.83 (m, 1H), 8.44 (m, 1H), 8.39 (m, 1H), 8.33 (m, 2H), 7.95 (m, 2H), 7.78 (t, 1H, J = 7.5 Hz), 7.62 (m, 4H).

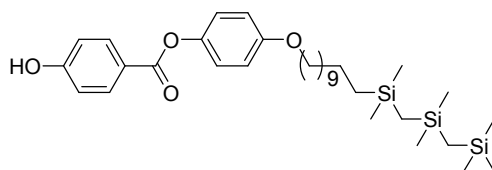


42

4-Benzyloxy-benzoic acid 4-tricarbosilane-Undecyloxy-phenyl ester (42)

A mixture of 4-tricarbosilane-Undecyloxy phenol, **34**, (0.82 g, 1.70 mmol), 4-Benzyloxy-benzoic acid (0.39 g, 1.71 mmol) and 4-dimethylaminopyridine (DMAP) (25 mg, 0.21 mmol) in 50 mL CHCl₃ was stirred for 10 minutes. To this mixture, dicyclohexylcarbodiimide (DCC) (0.39 g, 1.89 mmol) in 10 mL of CHCl₃ was added and the reaction mixture was continued to stir for 12 h at room temperature. The precipitated dicyclohexylurea was filtered off and washed with excess CHCl₃. The solvent of the filtrate was removed and the crude product was purified by flash chromatography (19:1

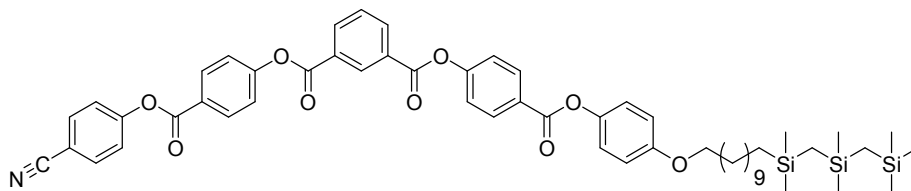
hexane:EtOAc) to give 4-Benzyloxy-benzoic acid 4-tricarbosilane-Undecyloxy-phenyl ester, **42**, (0.90 g, 1.30 mmol, 76.5%) as a white solid. ^1H NMR (CDCl_3 , 500 MHz): δ 8.13 (m, 2H), 7.44-7.33 (m, 5H), 7.07 (m, 2H), 7.03 (m, 2H), 6.89 (m, 2H), 5.14 (s, 2H), 3.93 (t, 2H, $J = 6.5$ Hz), 1.76 (p, 2H, $J = 7.5$ Hz), 1.45-1.25 (m, 16H), 0.45 (m, 2H), 0.00 (m, 21 H), -0.29 (m, 4H).



43

4-Hydroxy-benzoic acid 4-tricarbosilane-Undecyloxy-phenyl ester (**43**)

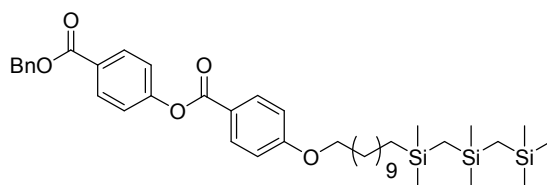
4-Benzyloxy-benzoic acid 4-tricarbosilane-Undecyloxy-phenyl ester, **42**, (0.22 g, 0.31 mmol) was dissolved in 20 mL EtOH/ CHCl_3 (1:1) and 10% Pd/C catalyst (0.02 g) was added. The resultant solution was stirred at room temperature in an atmosphere of hydrogen till the required quantity of hydrogen was absorbed. This mixture was filtered through Celite and the solvent was removed under reduced pressure to yield 4-Hydroxy-benzoic acid 4-tricarbosilane-Undecyloxy-phenyl ester, **43**, (0.19 g, 0.31 mmol, >99%) as a white solid which was directly used for the subsequent reaction.



44, W635

Isophthalic acid 1-[4-(4-cyano-phenoxy-carbonyl)-phenyl] ester 3-[4-(4-tricarbosilane-Undecyloxy)-phenoxy-carbonyl)-phenyl] ester (**44**, **W635**)

A mixture of Isophthalic acid mono-[4-(4-cyano-phenoxy-carbonyl)-phenyl] ester, **41**, (0.14 g, 0.36 mmol), 4-Hydroxy-benzoic acid 4-tricarbosilane-Undecyloxy-phenyl ester, **43**, (0.21 g, 0.35 mmol) and 4-dimethylaminopyridine (DMAP) (10 mg, 0.08 mmol) in 10 mL dry CH₂Cl₂ was stirred for 10 minutes. To this mixture, dicyclohexylcarbodiimide (DCC) (0.081 g, 0.39 mmol) was added and the reaction mixture was continued to stir for 12 h at room temperature under argon atmosphere. The precipitated dicyclohexylurea was filtered off and washed with excess CH₂Cl₂. The solvent of the filtrate was removed and concentrated at reduced pressure. The crude product was subjected to purification by flash chromatography (CHCl₃) to yield Isophthalic acid 1-[4-(4-cyano-phenoxy-carbonyl)-phenyl] ester 3-[4-(4-tricarbosilane-Undecyloxy)-phenoxy-carbonyl)-phenyl] ester, **44**, (**W635**) (0.27 g, 0.28 mmol, 80.0%) as a white solid. ¹H NMR (CDCl₃, 500 MHz): δ 9.03 (t, 1H, J = 1.5 Hz), 8.49 (m, 2H), 8.29 (m, 4H), 7.76-7.72 (m, 3H), 7.43 (m, 2H), 7.39 (m, 2H), 7.37 (m, 2H), 7.10 (m, 2H), 6.92 (m, 2H), 3.94 (t, 2H, J = 6.5 Hz), 1.77 (p, 2H, J = 7.5 Hz), 1.46-1.26 (m, 16 H), 0.45 (m, 2H), 0.00 (m, 21H), -0.29 (m, 4H).

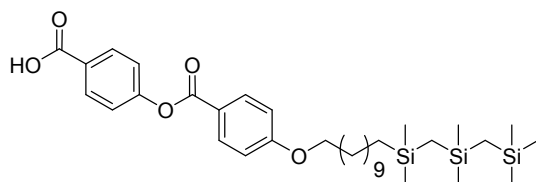


45

4-Tricarbosilane-Undecyloxy benzoic acid 4'-Benzyloxy-carbonyl-phenyl ester (**45**)

A mixture of Tricarbosilane-undecyloxy-benzoic acid, **8**, (0.78 g, 1.54 mmol), 4-Hydroxy-benzoic acid benzyl ester (0.34 g, 1.49 mmol) and 4-dimethylaminopyridine

(DMAP) (25 mg, 0.21 mmol) in 25 mL dry CHCl_3 was stirred for 10 minutes. To this mixture, dicyclohexylcarbodiimide (DCC) (0.34 g, 1.65 mmol) was added and the reaction mixture was continued to stir for 12 h at room temperature under argon atmosphere. The precipitated dicyclohexylurea was filtered off and washed with excess CHCl_3 . The solvent of the filtrate was removed and concentrated at reduced pressure. The crude product was subjected to purification by flash chromatography (19:1 hexane:EtOAc) to yield 4-Tricarbosilane-Undecyloxy benzoic acid 4'-Benzyloxy-carbonyl-phenyl ester, **45**, (0.75 g, 1.05 mmol, 70.5%) as a white solid. ^1H NMR (CDCl_3 , 500 MHz): δ 8.12 (m, 4H), 7.45-7.33 (m, 5H), 7.27 (m, 2H), 6.95 (m, 2H), 5.36 (s, 2H), 4.02 (t, 2H, $J = 6.5$ Hz), 1.80 (p, 2H, $J = 7.5$ Hz), 1.46-1.26 (m, 16 H), 0.45 (m, 2H), 0.00 (m, 21H), -0.29 (m, 4H).

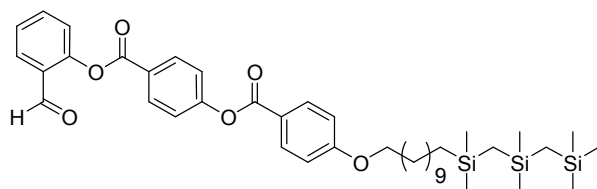


46

4-Tricarbosilane-Undecyloxy benzoic acid 4'-Hydroxy-carbonyl-phenyl ester (**46**)

4-Tricarbosilane-Undecyloxy benzoic acid 4'-Benzyloxy-carbonyl-phenyl ester, **45**, (0.75 g, 1.05 mmol) was dissolved in 50 mL EtOH/ CHCl_3 (1:1) and 10% Pd/C catalyst (0.08 g) was added. The resultant solution was stirred at room temperature in an atmosphere of hydrogen till the required quantity of hydrogen was absorbed. This mixture was filtered through Celite and the solvent was removed under reduced pressure to yield 4-Tricarbosilane-Undecyloxy benzoic acid 4'-Hydroxy-carbonyl-phenyl ester, **46**,

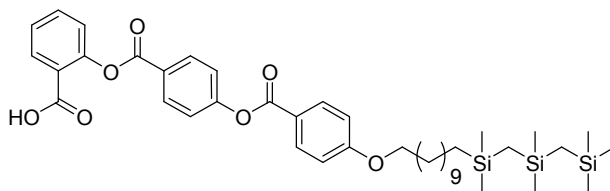
(0.66 g, 1.05 mmol, >99%) as a white solid which was directly used for the subsequent reaction.



47

4-Tricarbosilane-Undecyloxy benzoic acid 4'-(2-formyl-phenoxy-carbonyl) phenyl ester (47)

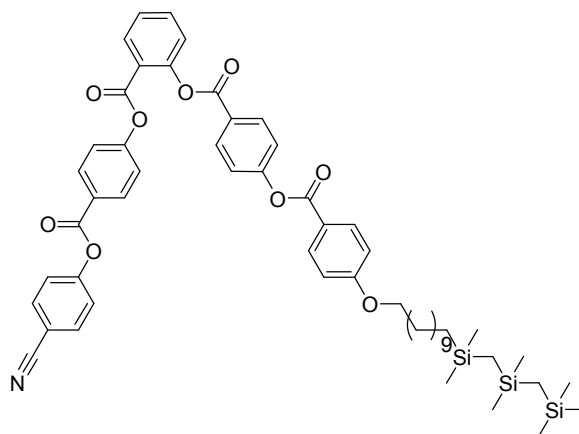
A mixture of 4-Tricarbosilane-Undecyloxy benzoic acid 4'-Hydroxy-carbonyl-phenyl ester, **46**, (0.40 g, 0.64 mmol), 2-Hydroxy-benzaldehyde (0.10 mL, 0.12 g, 0.98 mmol) and 4-dimethylaminopyridine (DMAP) (10 mg, 0.08 mmol) in 20 mL dry CHCl₃ was stirred for 10 minutes. To this mixture, dicyclohexylcarbodiimide (DCC) (0.15 g, 0.73 mmol) was added and the reaction mixture was continued to stir for 12 h at room temperature under argon atmosphere. The precipitated dicyclohexylurea was filtered off and washed with excess CHCl₃. The solvent of the filtrate was removed and concentrated at reduced pressure. The crude product was subjected to purification by flash chromatography (19:1 hexane:EtOAc) to yield 4-Tricarbosilane-Undecyloxy benzoic acid 4'-(2-formyl-phenoxy-carbonyl) phenyl ester, **47**, (0.29 g, 0.40 mmol, 62.5%) as a white solid. ¹H NMR (CDCl₃, 500 MHz): δ 10.21 (s, 1H), 8.29 (m, 2H), 8.14 (m, 2H), 7.95 (d, 1H, J = 6.0 Hz), 7.69 (t, 1H, J = 7.0 Hz), 7.43 (t, 1H, J = 7.0 Hz), 7.38 (m, 2H), 7.36 (d, 1H, J = 8.0 Hz), 6.98 (m, 2H), 4.04 (t, 2H, J = 6.5 Hz), 1.81 (p, 2H, J = 7.5 Hz), 1.48-1.23 (m, 16 H), 0.45 (m, 2H), 0.00 (m, 21H), -0.29 (m, 4H).



48

2-[4-(4-Tricarbosilane-Undecyloxy benzoyloxy) benzoyloxy] benzoic acid (48)

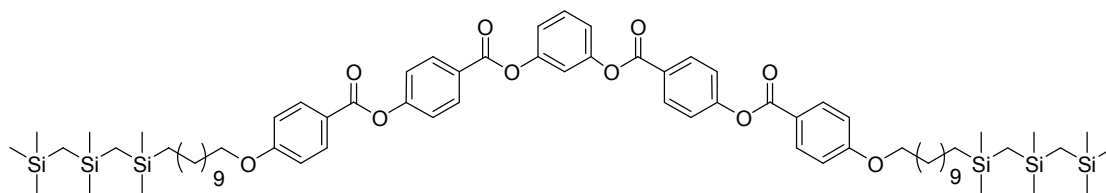
To a solution of 4-Tricarbosilane-Undecyloxy benzoic acid 4'-(2-formyl-phenoxy-carbonyl) phenyl ester, **47**, (0.28 g, 0.38 mmol) in 10 mL acetone, KMnO₄ (0.10 g, 0.63 mmol) in 5 mL of acetone/H₂O (1:1) was slowly added and the reaction mixture was allowed to stir for 2 h at room temperature. Then, saturated NaHCO₃ was added and black precipitates were formed. 1M HCl was carefully added till all black precipitates disappeared. Then, the mixture was extracted by CH₂Cl₂ (3 x 25 mL) and the organic layer was washed with H₂O (3 x 25 mL) and saturated NaCl (3 x 25 mL), dried over anhydrous MgSO₄, filtered and then concentrated at reduced pressure to yield 2-[4-(4-Tricarbosilane-Undecyloxy benzoyloxy) benzoyloxy] benzoic acid, **48**, (0.27 g, 0.36 mmol, 94.7%) as a white solid which was directly used in the subsequent reaction.



49, W637

4-[(4-Cyanophenoxy) carbonyl] phenyl 2-{4-[4-(11-tricarbosilane) undecyloxy] benzyloxy} benzoate (**49, W637**).

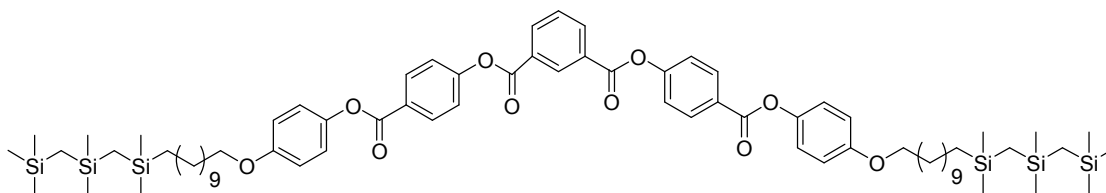
A mixture of 2-[4-(4-Tricarbosilane-Undecyloxy benzyloxy) benzyloxy] benzoic acid, **48**, (0.26 g, 0.35 mmol), 4-Hydroxy-benzoic acid 4'-cyano-phenyl ester, **5**, (0.085 g, 0.36 mmol) and 4-dimethylaminopyridine (DMAP) (10 mg, 0.08 mmol) in 10 mL dry CHCl_3 was stirred for 10 minutes. To this mixture, dicyclohexylcarbodiimide (DCC) (0.08 g, 0.39 mmol) was added and the reaction mixture was continued to stir for 12 h at room temperature under argon atmosphere. The precipitated dicyclohexylurea was filtered off and washed with excess CHCl_3 . The solvent of the filtrate was removed and concentrated at reduced pressure. The crude product was subjected to purification by flash chromatography (1:1 hexane: CHCl_3) to yield 4-[(4-Cyanophenoxy) carbonyl] phenyl 2-{4-[4-(11-tricarbosilane) undecyloxy] benzyloxy} benzoate, **49, (W637)** (0.25 g, 0.26 mmol, 74.3%) as a white solid. ^1H NMR (CDCl_3 , 500 MHz): δ 8.28-8.25 (m, 3H), 8.18 (m, 2H), 8.11 (m, 2H), 7.74-7.71 (m, 3H), 7.46 (t, 1H, $J = 7.0$ Hz), 7.34-7.31 (m, 5H), 7.25 (m, 2H), 6.95 (m, 2H), 4.02 (t, 2H, $J = 6.5$ Hz), 1.80 (p, 2H, $J = 7.5$ Hz), 1.46-1.26 (m, 16 H), 0.45 (m, 2H), 0.00 (m, 21H), -0.29 (m, 4H).



50, W634

1,3-Bis-[4-(4-tricarbosilane-Undecyloxy benzoxo) benzoxo] Benzene (50, W634)

A mixture of 4-Tricarbosilane-Undecyloxy benzoic acid 4'-Hydroxy-carbonyl-phenyl ester, **46**, (0.35 g, 0.56 mmol), resorcinol (0.0285 g, 0.26 mmol) and 4-dimethylaminopyridine (DMAP) (10 mg, 0.08 mmol) in 10 mL dry CHCl₃ was stirred for 10 minutes. To this mixture, dicyclohexylcarbodiimide (DCC) (0.13 g, 0.63 mmol) was added and the reaction mixture was continued to stir for 12 h at room temperature under argon atmosphere. The precipitated dicyclohexylurea was filtered off and washed with excess CHCl₃. The solvent of the filtrate was removed and concentrated at reduced pressure. The crude product was subjected to purification by flash chromatography (19:1 hexane:EtOAc) to yield 1,3-Bis-[4-(4-tricarbosilane-Undecyloxy benzoxo) benzoxo] Benzene, **50**, (**W634**) (0.19 g, 0.14 mmol, 54.9%) as a white solid. ¹H NMR (CDCl₃, 400 MHz): δ 8.26 (m, 4H), 8.13 (m, 4H), 7.48 (dt, 1H, J = 8.0, 1.6 Hz), 7.36 (m, 4H), 7.12-7.16 (m, 3H), 6.96 (m, 4H), 4.03 (t, 4H, J = 6.2 Hz), 1.80 (p, 4H, J = 7.2 Hz), 1.46-1.26 (m, 32 H), 0.45 (m, 4H), 0.00 (m, 42H), 0.29 (m, 8H).



51, W638

Isophthalic acid bis-[4-(4-tricarbosilane-Undecyloxy phenoxy carbonyl)-phenyl] ester (51, W638)

A mixture of 4-Hydroxy-benzoic acid 4-tricarbosilane-Undecyloxy-phenyl ester, **43**, (0.30 g, 0.50 mmol), Isophthalic acid (0.0393 g, 0.237 mmol) and 4-dimethylaminopyridine (DMAP) (10 mg, 0.08 mmol) in 10 mL dry CHCl_3 was stirred for 10 minutes. To this mixture, dicyclohexylcarbodiimide (DCC) (0.105 g, 0.51 mmol) was added and the reaction mixture was continued to stir for 12 h at room temperature under argon atmosphere. The precipitated dicyclohexylurea was filtered off and washed with excess CHCl_3 . The solvent of the filtrate was removed and concentrated at reduced pressure. The crude product was subjected to purification by flash chromatography (19:1 hexane:EtOAc) to yield Isophthalic acid bis-[4-(4-tricarbosilane-Undecyloxy phenoxy carbonyl)-phenyl] ester, **51, (W638)** (0.22 g, 0.165 mmol, 69.7%) as a white solid. ^1H NMR (CDCl_3 , 500 MHz): δ 9.03 (t, 1H, $J = 1.5$ Hz), 8.49 (dd, 2H, $J = 7.5, 1.5$ Hz), 8.29 (m, 4H), 7.73 (t, 1H, $J = 7.5$ Hz), 7.39 (m, 4H), 7.10 (m, 4H), 6.92 (m, 4H), 3.94 (t, 4H, $J = 6.5$ Hz), 1.77 (p, 4H, $J = 7.5$ Hz), 1.46-1.26 (m, 32 H), 0.45 (m, 4H), 0.00 (m, 42H), -0.29 (m, 8H).

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