DESIGN AND SYNTHESIS OF LIQUID CRYSTALS WITH CONTROLLED ABSORPTION PROPERTIES IN THE MIDWAVE INFRARED REGION

A dissertation submitted
to Kent State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

by

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DEDICATION

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Chapter 1

Introduction

1.1 Introduction to liquid crystals

The study of liquid crystals started in the late 1800s, when strange colored patterns were observed upon heating various cholesterol derivatives by Otto Lehmann. In the early 1920s the famous French crystallographer Georges Friedel suggested that the liquid crystalline state is a unique state of matter that is different from the four fundamental states of matter already known. After this, half a century of relative inactivity ensued. In the 1960s, a new era of liquid crystals research took shape that was greatly influenced by the French physicist Pierre-Gilles de Gennes, George W. Gray, George H. Heilmeier and many others. In 1970 the twisted nematic field effect in liquid crystals was patented by Hoffmann-LaRoche and a similar patent was filed by James Fergason of Kent State University. The first active-matrix display arrived in the consumer market in 1972. In order to optimize these devices it became more important to understand the basic science behind how they operated. This was a major inspiration for the shaping of the current state of liquid crystal research.

Drawing from Lehmann’s observation, Friedel established the uniqueness of the liquid crystalline state in *Annales de physique* in 1922. Some of his observations are as follows:
“The specificity of Lehmann’s substances lies not in their more or less fluid state, but rather in their extremely particular structures, always the same and whose number is very small. I hope that the rest of this work will demonstrate that the bodies reported by Lehmann represent two entirely new forms of matter, invariably separated from the crystalline form and the amorphous form (isotropic liquid) by discontinuities, as the crystalline form and the amorphous form are always separated by a discontinuity.”

Friedel then described and named the two new liquid crystalline states of matter as nematic and smectic:

“I shall call smectics (σμεγμα, soap) the forms, bodies, phases, etc. of the first kind, because soaps, in usual temperature conditions, belong to this group and because potassium oleates, in particular, are the first bodies of this group to have been signaled. I shall call nematics (νημα, thread) the forms, phases etc. of the second type because of the linear discontinuities, winding like threads, that are their salient feature.”  

With the advancement of research it was realized that the inherent anisotropy and birefringence of liquid crystals could be applied in display technology, especially with the discovery of liquid crystals, which were nematic at room temperature.

In the scope of this thesis, rod-like (calamitic) liquid crystals will be discussed. Due to the rod-like form, calamitic materials have an inherent shape molecular anisotropy. These molecules have an average alignment of their long molecular axes along a specific director. Depending on the specific liquid crystalline phase, these molecules still have some rotational and translational degrees of freedom. In smectic phases, an individual molecule is free to move within discrete
layers and also in between layers, although the interlayer movement is much less pronounced than the intralayer movement (some smectic phases are highly crystalline and even intralayer movement may be minimal). In the nematic phase, a molecule can move anywhere within the bulk of the material while the bulk material retains some net alignment.

In recent years, a very large amount of interest has been generated by bent core liquid crystalline materials\(^5,6\). Bent core materials might have lower melting points compared to analogous linear counterparts due to their reduced packing efficiency. Some of these materials might exhibit biaxial nematic phases. The specialty of the materials with a biaxial nematic phase is that they can align symmetrically along two vectors instead of one (as seen in uniaxial nematic phases) through which polarized light can travel without a change in polarization\(^7\). This change in molecular symmetry in biaxial nematics has exciting implications. The rotation of minor directors within the molecular symmetry in these materials are likely to be much more rapid than the rotation of rod shaped nematics, thus decreasing the switching time in displays\(^7\). This might dramatically increase the refresh rates in displays, which in turn improves picture quality\(^8\).

Bulk structural anisotropy gives rise to birefringence in liquid crystals. A uniaxial liquid crystal has two principal refractive indices, namely the ordinary refractive index \(n_0\) and the extraordinary refractive index \(n_e\). The light wave whose electric vector is perpendicular to the optical axis gives rise to the ordinary refractive index and the electric vector that is parallel to the optical axis gives rise to the extraordinary refractive index. The birefringence is the difference between these two indices.

With the alignment of the optical axis of liquid crystalline materials\(^9\) and then further precise control of the orientation of the molecules with an applied field, these materials can be applied to
display technology and many other modern applications like laser beam steering\textsuperscript{10}, dynamic scene projectors\textsuperscript{11}, barcode scanners\textsuperscript{12}, topology mapping,\textsuperscript{12} etc. In the scope of this thesis, infrared laser beam steering with nematic liquid crystals will be mainly explored along with the discussion of application of high birefringence liquid crystals at GHz and THz frequencies.

1.2 The nematic phase

Nematic liquid crystals are often preferred for device applications due to the simplicity of the alignment technologies available for them\textsuperscript{9}. Ferroelectric LCs may have faster response times but require more sophisticated materials and device structures\textsuperscript{9}. Almost all the LC displays available commercially use nematic liquid crystals for their operation. In our research, the ultimate goal will be designing liquid crystals with nematic phases at manageable temperatures. This calls for some discussion of the nematic phase.

Calamitic liquid crystals have two main phases, namely nematic and smectic. The nematic\textsuperscript{13} and smectic\textsuperscript{14} phases are subdivided into groups according to the different ordering in bulk materials. In nematic liquid crystals, there is orientational ordering although any layer ordering is absent\textsuperscript{15}. The smectic phases have orientational ordering as well as layer ordering. Due to this, nematics are the least viscous among the LC phases\textsuperscript{15}. This property greatly enhances the applicability of different device fabrication methods.
**Figure 1.1:** Schematic diagram of phases of a material. (a) Crystalline phase – Orientational ordering present, the position of each molecule is fixed in the lattice (b) Smectic phase – Orientational as well as layer ordering, but the position of molecules are not fixed (c) Nematic phase – No layer ordering, the molecules are oriented loosely in a specific direction (d) isotropic phase – Completely disordered

In the nematic phase, the molecules are almost completely disordered except for the long molecular axes that statistically align along a specific direction known as the director. The nematic phase does not possess the thermal energy to spontaneously go to the isotropic liquid phase. The anisotropic nature of the properly designed nematic LCs along with their fluidity is the basis of the optical applications as the orientation of the molecules can be switched easily by an electric field, which in turn depends on the molecule having sufficient dielectric anisotropy. The different optical properties in different orientations are taken advantage of in display applications. This switching process needs a very low amount of electrical energy, making liquid crystal devices highly energy efficient.

The nematic phase is easily identified under polarized optical microscopes from its schlieren texture. The schlieren texture has two kinds of defects, namely a two brush defect and a four brush defect (**Figure 1.2**). In some polytolanes, six brush defects are also observed\(^{16}\). Defects are
regions in which the rotational symmetry is absent, i.e., the molecules in this region are not statistically aligned towards a specific direction.

**Figure 1.2:** Defects in liquid crystal phases as seen under polarized optical microscope (nematic phase of 2-chloro-4-(4-pentylphenyl)-1-(4-phenylphenyl)benzene synthesized by the author)

The brush like zones in these defect structures meet at a dark point, known as the singularity. To design a nematic liquid crystal, the structure of the rigid core, linking groups, aliphatic tails, polar end groups and lateral substitution needs to be understood.

**Figure 1.3:** Design of a typical calamitic liquid crystal
The mesogenic behavior of a molecule largely depends on the length to breadth ratio of the molecule (aspect ratio). A high aspect ratio is one of the parameters that allows the elevation of the nematic to isotropic transition temperature ($T_{NI}$).

While aromatic rings are widely used in designing nematic liquid crystals due to their rigidity and conjugated nature, saturated non-aromatic rings like cyclohexane and bicyclo[2.2.2]octane rings are also used. The space filling nature of these rings without significant disruption of the nematic phases is the reason these saturated rings are chosen. Heterocyclic rings like benzothiophene, oxadiazole and thiophene can often be used even if they introduce a bend in the core. This bend disrupts the molecular packing, which reduces the melting point of the LC material. Some bent core liquid crystals possess additional interesting phases due largely to this structure feature.

Linking groups can play a significant role in determining the mesophase as well as some electro-optic properties of the molecule. Unsaturated linking groups are more rigid and reduce the free rotation(s) of the molecule thus enhancing the effective conjugation. This, in turn, increases the birefringence of the molecule (birefringence is proportional to the degree of conjugation along the long axis of the molecule). Typical bridge fragments in this category are p-orbital containing groups such as -C≡C-, -N=N-, -CH=CH- etc. These fragments also contribute to a high degree of anisotropy of polarizability owing to the extended conjugation.

In contrast to this, saturated linking groups without p-orbitals like –CH$_2$–CH$_2$– break the conjugation in the core and increase the rotational freedom and overall flexibility of the molecule. Although the increased rotational freedom reduces packing efficiency and the
saturated core might increases the length of the molecule (this elevates the clearing point) the break in conjugation reduces the birefringence.

The substitution of the carbon atoms of phenyl rings in the aromatic core with a heteroatom does not have a pronounced effect on the geometrical features. However, this substitution may strongly affect the polarizability of a molecule and the intermolecular interactions as it changes the dipole moment of the molecule. One example is the pyrimidine ring. The presence of this ring strongly promotes layer ordering which leads to smectic phases$^{20-22}$.

Alkyl tails as end groups play a crucial role in determining the liquid crystal phase morphology. Relatively short alkyl tails help stabilize the nematic phase. Longer tails enable more efficient molecular packing, giving rise to layer ordering$^{15}$ (Figure 1.4). The tail groups can be directly connected to the core or through a functional group. Ethers and esters are relatively common as the linking group between the core and the alkyl tail. The aforesaid linking groups can polarize the core inductively$^{23}$.

![Figure 1.4: Effect of the length of terminal chain on mesophase identity](image)

Polar end groups, when properly chosen, can induce a significant longitudinal dipole in the molecule. Usually cyano and isothiocyanato end groups promote a nematic phase$^{24}$. In the scope of this thesis, chlorine will be explored as a polar end group due to its specific and useful absorption properties that will be discussed later.
Lateral substitution has been used to lower the melting point of materials as well as improve the range and stability of the nematic phase. **Figure 1.5** shows an illustration of this effect

![Comparison of phase transitions of an LC molecule with a laterally fluorinated counterpart](image)

**Figure 1.5**: Comparison of phase transitions of an LC molecule with a laterally fluorinated counterpart

A lateral fluoro substitution in the example in **Figure 1.5** had a drastic effect on the nematic phase stability. Bulky lateral substituents disrupt the planarity of the aromatic core that in turn reduces the packing efficiency of the molecules. Even if the lateral substituent is not in a location to disturb planarity, it can change the nature of the attractive and repulsive forces in the molecule, thus changing the nature of molecular packing. Fluorine can drastically alter the nature of intermolecular interactions and has been widely used as a lateral substituent for its distinctive mix of steric and electronic effects (more details in Chapter 3). In the scope of this thesis, along with fluorine, chlorine will be introduced as a lateral substituent due to its attractive absorption properties in the midwave infrared region (the absorption due to C-Cl bond is in the range of 800-600 cm⁻¹).
1.3 Birefringence and liquid crystals

When a depolarized beam of radiation is incident on an anisotropic media in a direction that is oblique to the optical axis of the media, the beam is split into two rays taking slightly different paths and they become linearly polarized. One is called the ordinary ray (refractive index \(n_o\)) in which the electrical vector of the linearly polarized light is perpendicular to the LC director. The other is called the extraordinary ray (refractive index \(n_e\)) in which the electrical displacement is parallel to the director. The value of optical birefringence is then defined by \(\Delta n = n_e - n_o\).

Calcite crystals (Iceland spar) are known to be birefringent (\(\Delta n = 0.174\) at 533 nm\(^2\)). Liquid crystals also possess anisotropy similar to such crystals; although it is often lower in value in part due to the lower value of order parameter than crystals (birefringence is proportional to the order parameter of a material\(^2\)).

1.4 Dielectric Anisotropy

An electric field affects a dielectric medium by polarizing the material. Different materials polarize to a different extent in response to an external electric field. This response is quantified by the permittivity (the resistance of the material to form an internal electric field).

If we consider uniaxial LC phases in a co-ordinate system \(x, y, z\) with the \(z\) axis being parallel to the director \(n\), two possible permittivities can be identified, one parallel to the director \(\varepsilon_\parallel = \varepsilon_{zz}\) the other perpendicular to the director \(\varepsilon_\perp = \frac{1}{2} (\varepsilon_{xx} + \varepsilon_{yy})\). Then the dielectric anisotropy of the material is defined as \(\Delta \varepsilon = \varepsilon_\parallel - \varepsilon_\perp\). Higher values of dielectric anisotropy may result in a faster response of molecules to an external electric field as the molecules orient themselves in such a way that they can minimize the effect of the applied field.
1.5 Order parameter

To quantify the orientational order in the LC phase, the scalar order parameter is used. It is defined by the equation,

\[ S = \frac{1}{2} \langle 3\cos^2\theta - 1 \rangle \]

Here \( \theta \) is the angle between the long axis of a random molecule and the director \( n \) and the brackets represent an average of all the molecules in bulk. \( S = 1 \) in a perfectly oriented system and \( S = 0 \) in the isotropic state.

As the temperature increases the orientation of molecules in bulk become more random. This in turn decreases the order parameter.

1.6 Dependence of birefringence on structural components of a molecule

With the molecular structural properties being constant, the birefringence of a material depends on the temperature and the wavelength of light. The bulk anisotropy of a collection of molecules decreases with the increase in temperature as the order parameter becomes lower. As birefringence is the result of an optical anisotropy in a material, it decreases with increasing temperature and decreasing order parameter. The value of optical birefringence becomes zero at the clearing point.

The value of birefringence decreases with the increase in wavelength\(^{30,31} \) (not considering the anomalous dispersion). The Cauchy formula gives the value of birefringence in the visible and near infrared region\(^{32} \) as \( \Delta n = A + B/\lambda^2 \). With higher anisotropy of longitudinal polarizability (which is increased by high level of conjugation) the displacement of electrons is higher, which in turn increases birefringence\(^{33} \).
The length of the alkyl tails influences the value of birefringence and depends on the number of carbon atoms\textsuperscript{32,34}. Alkyl tails are themselves essentially optically isotropic and do not contribute significantly to an increase in birefringence compared to the aromatic core. With the increase in the length of the alkyl tail, the net anisotropy of the molecule decreases\textsuperscript{35}, this effect far outweighs the increase in order parameter with the increase in tail lengths. Also, due to the abundance of C-H bonds, it turns out that alkyl tails strongly absorb in the midwave infrared region. One of the goals of this thesis is to explore liquid crystals that are transparent in the midwave infrared region. As alkyl tails are detrimental to the birefringence of a material and also the infrared absorption properties, it might be beneficial to design liquid crystals completely devoid of alkyl tails. A part of this thesis explores this idea (\textbf{Chapters 5 and 6}).

Bridge fragments in the molecule can have a pronounced effect on the value of birefringence. The $\pi$-electrons in a biphenyl molecule are delocalized over all the carbon atoms. If we insert a carboxylic ester fragment between the two benzene rings (as in a phenyl benzoate) the length of conjugation will be reduced and thus birefringence of the molecule will be reduced\textsuperscript{24}. This structure change also contributes to the increase in longitudinal polarizability of a molecule, which may affect the phase behavior. In contrast, a triple bond between two phenyl rings (tolane molecule) greatly increases the value of birefringence\textsuperscript{24} by maintaining the linearity and rigidity of the core while increasing the length of the conjugation and longitudinal polarizability. In \textbf{Chapter 8}, tolane liquid crystals for infrared applications and novel methodology for their synthesis will be discussed.
The NCS (isothiocyanato) group as a terminal substituent can increase the birefringence greatly but absorbs strongly in the midwave infrared region. The order of the effect of polar end group on birefringence\textsuperscript{24} is NCS $>$ $>$ Cl $>$ CN $>$ F $>$ OCF$_3$ $>$ CF$_3$.

As the goal of this thesis is to explore materials that are transparent in the midwave infrared region, the NCS functional group will not be used as it contributes to the absorption in the midwave infrared region.

1.7 Introduction to midwave infrared transparent liquid crystals

Figure 1.6: Regions in the infrared spectrum (Source: http://mivim.gel.ulaval.ca/dynamique/index.php?idD=58&Lang=1)

It has been experimentally demonstrated that liquid crystals can show high birefringence in the infrared region\textsuperscript{36}. This phenomenon has been applied in the construction of dynamic scene
projectors for infrared seekers\cite{37} and laser beam steering\cite{38}. Long wavelength radiation like IR is preferable for telecom applications due to the lower absorption and thus lower optical loss\cite{39}. But these applications face a major drawback owing to the inherent large absorption loss due to the existence of molecular absorption bands (and their overtones and combinations). Several absorption bands exist in the mid infrared region (3-5 \(\mu\)m), such as those due to CH, CH\(_2\), CH\(_3\) and CN. The infrared absorption bands for 5CB are explained in Table 1.1.

![Infrared absorption spectrum of 5CB](image)

**Figure 1.7:** Infrared absorption spectrum of 5CB (Courtesy Prof. Shin-Tson Wu, University of Central Florida)
<table>
<thead>
<tr>
<th>Zone</th>
<th>Absorption mechanism</th>
<th>Frequency (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Aromatic C-H stretch saturated CH, CH(_2), CH(_3) stretch</td>
<td>3500-2800</td>
</tr>
<tr>
<td>B</td>
<td>C-H (in CH(_2), CH(_3)) deformation overtone C-C skeletal stretch overtone</td>
<td>2790-2500</td>
</tr>
<tr>
<td>C</td>
<td>C≡N stretch C-H (in phenyl ring) in plane deformation overtone C-C (in alkyl chain) skeletal stretch overtone</td>
<td>2500-2000</td>
</tr>
<tr>
<td>D</td>
<td>Aromatic overtone C=C stretch</td>
<td>2000-1600</td>
</tr>
<tr>
<td>E</td>
<td>C-H in CH(_2), CH(_3) deformation C-C skeletal stretch</td>
<td>1485-1250</td>
</tr>
<tr>
<td>F</td>
<td>C-H (in phenyl ring) in plane deformation C-C (in alkyl chain) skeletal stretch</td>
<td>1250-1000</td>
</tr>
</tbody>
</table>

**Table 1.1:** IR absorption modes of 5CB\(^{1,40}\)

Molecules absorb specific frequencies of radiation in the infrared region. These absorptions are the function of their structure and occur at resonant frequencies. The resonant frequency of radiation matches the transition energy to the next higher energy state of the bond being distorted.

In commercial liquid crystals, even in the off-resonance regions, the baseline absorption coefficient can take a high value (up to \(\alpha\sim10/cm\))\(^\text{41}\). This absorption loss becomes significant if the optical path is long (i.e. the LC layer is thick).

Advancements in the field of IR technology such as laser beam steering and construction of optical valves need continuous development of nematic liquid crystals that will have low absorption between 1300-1600 nm\(^\text{42}\) and also possess high birefringence and low viscosity\(^\text{43}\).

Most of the known liquid crystals are designed and optimized to make displays for application in
the visible region of the spectrum. But some special applications require electro-optic devices that best function in the IR region for electronic sensing and communication. Although IR modulators have been proven to be successful\textsuperscript{44}, LCs that can be applied in these devices are more desirable due to small size and weight, low operating voltage and low power consumption\textsuperscript{44}. Commercial liquid crystals have undergone trials to be applied in these devices\textsuperscript{45}, but they didn’t prove to be the best owing to low birefringence and high optical loss, as they were not specifically designed to be used in the infrared range. These problems call for the development of liquid crystals specially designed for infrared applications and also possessing high dielectric anisotropy and birefringence.

One goal of this thesis is to design new materials for midwave infrared applications that will show a nematic liquid crystalline phase, have relatively high birefringence ($\Delta n \geq 0.2$), positive dielectric anisotropy ($\Delta \varepsilon$) but low absorption loss in the midwave infrared region and to stabilize the nematic phase over a wide temperature range.

### 1.8 Previous work

The fields of infrared applications such as laser beam steering\textsuperscript{46} are growing rapidly and require the development of nematic liquid crystals of high birefringence and low viscosity\textsuperscript{43}. An important performance parameter of IR applications is the response time ($\tau_0$), which is the time taken for the LC molecules in the bulk to orient themselves (to some well-defined extent) in response to an applied external field. The response time is defined by the equation

$$\tau_0 = \gamma_1 d^2 / K_{11}$$
Here $\gamma_1 = \text{rotational viscosity}$, $d = \text{liquid crystal cell gap}$ and $K_{11} = \text{splay elastic constant}$. From this equation it is seen that the response time is proportional to $d^2$ ($d = \text{liquid crystal cell gap}$) and $\gamma_1/K_{11}$ (visco-elastic coefficient)$^1$. So, to improve the response time requirements, it is necessary for the liquid crystals to have low rotational viscosity and the liquid crystal cell gap should be small. But high birefringence and low rotational viscosity are not independent characteristics. A highly conjugated liquid crystal compound generally possesses high rotational viscosity because of its increased moment of inertia due to increase of mass$^{43}$. Also with increase in conjugation the attractive forces in molecules are altered, which might be another reason for the increased viscosity$^{47}$. To lower the melting temperature, several molecular design strategies need to be exercised and many LC structures need to be developed and examined.

Another problem of using liquid crystals in the IR region is the large absorption loss due to the existence of molecular vibration bands that arise from the constituent structure features (presence of alkyl chains, -NCS, -CN end groups) of the LC. If the LC cell gap is thin (~5 µm), then the absorption loss can be negligible. But with thicker cells, the absorption loss can become significant.

In the mid-infrared region (3~5 µm), many molecular absorption bands can be seen, such as CH, CH$_2$, CH$_3$ and CN. These absorption bands are close to each other and their central wavelength occurs at ~3.5 µm, covering the bandwidth from 3 to 4 µm$^{48}$. The molecular vibration frequency ($\omega$) is related to the spring constant ($\kappa$) of the bond between the two atoms of a diatomic group and the effective mass ($m$) of a diatomic group by the equation $\omega = \sqrt{\kappa/m}$.
From the equation it can be seen that the vibration frequency is inversely proportional to the square root of the effective mass, i.e. as the effective mass increases, the vibration frequency decreases, shifting the absorption bands towards the longer wavelength. This concept was proved with a sample of perdeuterated pentylicyanobiphenyl\[^{48}\]. The C-D bond absorption peak in this compound is at 4.6 \( \mu m \) (compared to 3.5 \( \mu m \) for the perprotio sample).

**Figure 1.8:** The infrared spectra of 5CB (top) and D5CB (bottom)\[^{49}\]
In both near and far IR regions, perdeuterated pentylcyanobiphenyl has a much cleaner absorption spectrum and lower absorption coefficient than pentylcyanobiphenyl in the off-resonance regions, although other physical properties such as phase transition temperature and birefringence remain almost unaltered. To further ensure a lower absorption in the desired 3.8-4.2 μm window, the absorption band due to C-D stretching might be further shifted to the longer IR region. In order to achieve this, the deuterium needs to be replaced with a heavier atom, and fluorine is a good candidate to be considered as it has an atomic radius comparable to hydrogen (1.47 Å for fluorine compared to 1.2 Å for hydrogen). Very few atoms exist that can be used in place of hydrogen in a molecular structure and retain its mesogenicity. Fluorine is the most acceptable substituent that can be used in place of hydrogen due to the close comparability in size and it is often called the true hydrogen mimic\textsuperscript{50}.

Previously, many different approaches were proposed to tackle the problem of absorption loss of liquid crystals operating at the IR range, but none were completely successful in the mid-IR range. For example, azobenzene based liquid crystals have been proposed previously for use in the infrared region\textsuperscript{44}. The design of the molecules was based on the fact that compounds bearing electron-donating and electron-withdrawing (push-pull) groups separated by a conjugated system might have large molecular dipole moments and anisotropy of polarizability. This leads to high birefringence, which is very desirable in infrared applications. Compared to the commercial liquid crystal mixtures these materials have high amount of anisotropy of the longitudinal polarizability. This anisotropy exists due to the push-pull groups linked by extensive conjugation.
Experiments show that these LCs exhibit nematic phases and high birefringence $^{44}$ (~0.2 at 633 nm and 1060 nm) and the melting points can be as low as 57°C. Thus if properly formulated mixtures of these materials are used in thin liquid crystal cells then the problem of absorption loss can be somewhat bypassed. But if the cell is not thin the problem of absorption loss still persists.

Further development of the structures by strategically placing fluorine on the benzene rings yielded liquid crystals with higher values of birefringence, larger dielectric anisotropy and better viscoelastic properties $^{51}$ (Figure 11). The birefringence for molecules in Figure 11 went up to 0.226 at 1060 nm $^{51}$. 

Figure 1.9: Azobenzene based liquid crystals for infrared applications $^{44}$  
$X_1 = \text{H, CH}_3 \text{ or F, } X_2 = \text{H, CH}_3, \text{ F or Cl}$

Figure 1.10: Modified azobenzene liquid crystal structures $^{51}$
One of the most effective strategies to increase birefringence is to increase the $\pi$-electron conjugation of the liquid crystal compounds and thus many compounds have been developed with long conjugation. Compounds in this class include the terphenyl isothiocyanates. These compounds exhibit high birefringence ($\Delta n \sim 0.35$) in the visible region and with lower viscosity. High birefringence eutectic mixtures can be formed using solely terphenyl isothiocyanate compounds for near IR laser beam steering applications.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Phase transition temperature (°C)</th>
<th>$\delta H$ (Cr-N) (cal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_2$H$_5$NCS</td>
<td>Cr 90.71 Sm(A) 137.93 N 172.98 Iso 171.92 N 136.4 Sm(A) 86.49 Cr</td>
<td>4089</td>
</tr>
<tr>
<td>C$_2$PP(23F)P(35F)NCS</td>
<td>Cr 121.96 N 152 Iso Iso 151.1 N 103.02 Cr</td>
<td>7040</td>
</tr>
<tr>
<td>C$_3$H$_7$NCS</td>
<td>Cr 73.17 Sm(A) 112.22 N 174.62 Iso Iso 173.38 N 109.98 Sm(A) 62.97 Cr</td>
<td>4622</td>
</tr>
<tr>
<td>C$_4$PPP(23F)P(3F)NCS</td>
<td>Cr 90.09 Sm(A) 104.53 N 163.32 Iso Iso 162.2 N 101.58 Sm(A) 79.5 Cr</td>
<td>4693</td>
</tr>
<tr>
<td>C$_5$PPP(35F)NCS</td>
<td>Cr 106.88 N 202.61 Iso Iso 201.9 N 100.47 Cr</td>
<td>3359</td>
</tr>
</tbody>
</table>

Table 1.2: Terphenyl isothiocyanate compound structures and their phase transition data

The terphenyl isothiocyanate compounds are photochemically stable and have lower visco-elastic coefficients compared to the same terphenyls with $\text{–CN}$ as the polar group. In spite of the linear structure of $\text{–CN}$ terphenyls creating a larger dipole moment ($\mu = 4.1 \text{D}$) compared to the $\text{–NCS}$ terphenyl ($\mu = 3.7 \text{D}$), the NCS has an advantage over CN. Highly localized Hückel
charges are created due to the strong polarization of the carbon-nitrogen triple bond in the cyano
terphenyls.

As a consequence of this, the strong molecular interactions between the nitrile groups and the
phenyl rings lead to the formation of dimers and a sharp rise in viscosity is observed. In contrast,
NCS substituted compounds do not form dimers and thus the rotational viscosity is significantly
lower than the analogous CN compounds\(^5\) \((\text{viscosity decreases with the change in polar end}
\text{group as } \text{CN} >> \text{CF}_3 > \text{OCF}_3 > \text{NCS} > \text{F}^{24})\), leading to faster response time. The tolanes possess
high birefringence and are good candidates for IR applications. The phenylacetylene unit, being
conjugated and linear, is a favorable candidate to instill high values of birefringence extending
into the IR in a liquid crystal. Many of these acetylene containing liquid crystals possess
reasonable nematic ranges and low viscosities.

The compounds with an acetylene unit that were studied previously are tolanes\(^{24,53-56}\),
bistolanes\(^{57-59}\), diphenyldiacetylenes\(^{56,60,61}\), thiophenylacetylenes\(^6\) and
dibenzothiophenylacetylenes\(^6\).
Although many of these compounds may possess high birefringence, the melting points of these compounds are also often well above room temperature. Therefore, these compounds can only be used as dopants and components in mixture formulations for room temperature applications. Careful installation of lateral substituents (often fluorine) in the core might lower the melting points of these compounds to room temperature. Although the absorption band for the $\text{C}≡\text{C}$ stretch of tolanes appears at 2260–2100 cm$^{-1}$, careful choice of functional groups can mitigate the problem (discussed in Chapter 8).

This concept was proven by synthesizing tolanes with an isothiocyanate end group and lateral fluorination$^{39}$. LC mixtures formulated with these liquid crystals showed a nematic range of 30°C-66°C (Table 1.3, the nematic ranges were predicted using Schroder van Laar equation). These liquid crystals have high birefringence ($\Delta n \sim 0.41$ at $\lambda = 633$ nm), high dielectric anisotropy ($\Delta \varepsilon \sim 18$), good solubility in LC hosts, low melting points and fair UV stability$^{39}$. If thin LC cell gaps are used, then a fast switching time and low absorption loss in the midwave
infrared region can be achieved, but as these compounds contain perprotio alkyl chains, absorption loss becomes significant in the midwave infrared region with the increase of cell gap.

![Figure 1.13: Exemplary structure of an isothiocyanate tolane liquid crystal](image)

Table 1.3: Mesophase behavior of the isothiocyanate tolane liquid crystal mixtures

<table>
<thead>
<tr>
<th>Mixture composition (wt%)</th>
<th>Predicted nematic range (°C)</th>
<th>Observed nematic range* (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2/C4 = 34.5/65.5</td>
<td>54.0–73.4</td>
<td>52.2–62.6</td>
</tr>
<tr>
<td>C2/C5 = 23/77</td>
<td>41.2–66.4</td>
<td>35.7–57.0</td>
</tr>
<tr>
<td>C2/C6 = 26.1/73.9</td>
<td>46.3–74.0</td>
<td>46.2–63.8</td>
</tr>
<tr>
<td>C2/C5/C6 = 15.8/48.9/35.3</td>
<td>30.0–60.0</td>
<td>31.8–59.9</td>
</tr>
</tbody>
</table>

*DSC data.

This design feature was further pursued and many more isothiocyanate tolanes with ether linkages and with perprotio alkyl tails were synthesized and properties were evaluated. All of them had reasonable birefringence and visco-elastic properties. From all the above examples it is clear that if the cell gap is small, these liquid crystals can be applied in IR devices, but the desired effect could not be achieved with cell gaps thicker than 5μm. To make more efficient liquid crystals for infrared applications, this problem must be addressed.
1.9 Application of nematic liquid crystals in the GHz and THz frequency regime

In recent years nematic liquid crystal materials have been investigated for microwave applications\textsuperscript{67-69} as their dielectric constants can be tuned in the mm-waveband\textsuperscript{70,71}. For liquid crystals, it is more beneficial to compare their combined features instead of individual performance parameters. In order to do so, Figures of Merit (FoM) were defined. Some of the useful ones are\textsuperscript{24},

\[
\text{FoM}_1 = \Delta n^2 \cdot K_{11}/\gamma_1 \\
\text{FoM}_2 = \Delta n^2 \cdot K_{11}/\gamma_1 \cdot V_{th} \\
\text{FoM}_3 = \gamma_1 / \Delta n^2 \cdot T_{N-I}
\]
Here $\Delta n = \text{birefringence of the material}$, $K_{11} = \text{splay elastic constant}$, $V_{th} = \text{threshold voltage of the material}$, $T_{N-I} = \text{clearing point}$. Materials with large values of $\text{FoM}_1$ and $\text{FoM}_2$ and small values of $\text{FoM}_3$ are ideal\textsuperscript{24}.

Very desirable values of figure-of-merit (FoM) were obtained with nematic liquid crystals which is not typically achievable for typical inorganic materials used as phase shifters at GHz frequency\textsuperscript{72}. To make microwave components as integrated single compact devices (GSM, wireless LAN etc.) and to make phase shifters for phased-array antennas for applications like automotive radar sensors, microwave components based on liquid crystals can be used\textsuperscript{73}.

Commercially available liquid crystals like GT3-23001\textsuperscript{74}, K15\textsuperscript{73} and BL037\textsuperscript{75} have been used in microwave applications. Many of these materials might have tolane and cyano groups in the individual components that are unstable towards UV radiation\textsuperscript{76}. As UV curable monomers are used to seal the LC cells, the actual LC layer might get exposed to UV radiation during the curing process. So, there is a need to develop materials that are resistant towards degradation under UV exposure. Here again, if the birefringence of the material is low, then a thick LC layer needs to be used to achieve sufficient phase change of the electromagnetic signal that emerges from the LC cell. But such thick layers decrease the response time of the LC layer significantly, sometimes to the order of 1 second or more (the response time is proportional to the thickness of LC layer squared\textsuperscript{77}). Ferroelectric liquid crystalline materials do not suffer from the drawbacks of slow response time that is inherent to the typical nematic liquid crystals. The response time for FLCs can reach the value of 1 $\mu$s. But fabrication of FLCs for device applications is very complex and that in turn increases the cost of the device to a very high extent\textsuperscript{9,22}. 

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Thus, the design of high birefringence nematic liquid crystals fit for application in the microwave region is warranted, as it is preferred for its easy processability compared to FLCs. In **Chapter 6**, the design and synthesis of some high birefringence bent core materials and their birefringence will be discussed. These materials have nematic phases at more manageable temperatures and can be very attractive as components of high birefringence mixtures for microwave applications.
1.10 References

(1) Oswald, P. P. P. *Nematic and cholesteric liquid crystals: concepts and physical properties illustrated by experiments*; Taylor & Francis: Boca Raton, 2005.


(21) Lapanik, A.; *Liquid crystal systems for microwave applications Single compounds and mixtures for microwave applications; Dielectric, microwave studies on selected systems*; 2009.


Chapter 2

**Semifluorinated symmetrical biphenyls for potential midwave infrared device applications**

### 2.1 Design of molecules

The relationship between molecular vibration frequency ($\omega$) with spring constant ($\kappa$) and effective mass ($m$) is as follows:

$$\omega = \sqrt{\frac{\kappa}{m}}$$

With the increase of effective mass the vibration frequency decreases (which corresponds to a shift of the absorption band towards a longer wavelength). The experimental proof of this concept came from Wu, et. al., who showed that perdeuterated 5CB (D5CB) has a much cleaner absorption in the 3.8-4.2 µm region than 5CB\(^1\). In both near and long IR regions, D5CB has a much cleaner absorption spectrum and lower absorption coefficient than 5CB in the off-resonance regions\(^1\). It is to be noted that other physical properties such as phase transition temperature and birefringence remain practically unchanged. The absorption can be further shifted to the longer wavelength region if the replacement of hydrogen is heavier than deuterium. One downside of these perdeuterated materials is the extremely high cost of synthesis.

Fluorinated compounds have promise as candidates in such applications since fluorine has a large mass relative to hydrogen (18.998404 amu for fluorine compared to 1.00794 amu for hydrogen) yet it has an atomic radius comparable to hydrogen (1.47 Å for fluorine compared to
1.2 Å for hydrogen). Thus, substitution of hydrogen by fluorine is not expected to significantly disturb the molecular interactions based on excluded volume\(^2\). Due to enhancements of synthetic methodology and the increasing availability and decreasing cost of the fluorinated starting materials the development of highly fluorinated liquid crystals is an attractive area of research. However, there will be an influence resulting from the different polarizabilities of these elements especially as the number of fluorine atoms becomes significant.

It is important to emphasize that a high extent of fluorination can be detrimental for mesogenic properties, especially as a high degree of fluorination increases transition temperatures and any nematic characteristics are compromised\(^3\). A high degree of fluorination of the terminal aliphatic chain promotes smectic phases due to the increased rigidity\(^4\). This dramatic increase of stiffness can produce smectic phases even in semifluorinated n-alkanes which are devoid of any ring structure\(^5\).

In some IR device applications a nematic phase is preferred and thus a systematic study of highly fluorinated compounds is required in order to provide the desired IR transparency and nematic behavior simultaneously. This chapter explores the design, synthesis and mesogenic properties of some highly fluorinated biphenyls and compares their properties with their non-fluorinated analogues.

The studies in this chapter have involved investigation of molecules with biphenyl core. Compounds of **Class 1** have a perfluorinated core and semifluorinated alkoxy tails. Compounds of **Class 2** have an aromatic hydrocarbon core with perfluorinated tails. The compounds of **Class 3** have an aromatic hydrocarbon core and semifluoro alkenyl tails.
2.2 Synthesis

The syntheses of the materials shown in Figure 2.1 are accomplished in single step. Compound class 1 was synthesized by an S$_{\text{N}}$Ar reaction.$^6$

The K$_2$CO$_3$ reacted with the semifluorinated alcohol to generate the nucleophilic alkoxide that attacked the para positions of decafluorobiphenyl to generate the desired product. This reaction is highly selective to the para position and no other substitution patterns were observed.
The synthesis of materials of **Class 2** (figure 2.1) were accomplished in one step by a Cu mediated synthesis methodology.  

![Figure 2.3: Synthesis of materials of Class 2](image)

It was observed that the reaction works best when a mixture of DMSO/hexafluorobenzene is used (details in the experimental procedure). The mechanism is as follows.

![Figure 2.4: Mechanism of formation of 2 (L = DMSO)](image)

In the first step fluoroalkylcopper is formed as a solvated complex. In the second step the solvated copper complex co-ordinates with the aromatic halide which is then followed by an exchange of ligands to form the final product. For the workup of the reaction the Cu salt can be removed very easily by using Montmorillonite K10 clay and the final product can be purified by simple recrystallization. No chromatography is required for this process, which is an attractive feature of this reaction (details in the experimental section).
Materials of class 3 were prepared by a Heck reaction. A palladacycle catalyst (Hermann-Beller palladacycle) was used in this procedure\textsuperscript{9}. Catalysts of this class are very stable towards air and moisture and very low catalyst loading can give a very high yield. It has been reported previously that in some cases\textsuperscript{10} the amount of catalyst can be reduced to $5 \times 10^{-4}$ mol\%. These catalysts are readily accessible from Pd(OAc)$_2$.

![Figure 2.5: Structure of Hermann-Beller palladacycle (o-Tol = ortho tolyl)](image)

With this catalyst, the materials of Class 3 were easily accessed in high yields.

![Figure 2.6: Synthesis of materials of Class 3](image)

### 2.3 Mesogenic properties and infrared absorption properties

No mesogenic properties were observed for any of these molecules (Table 2.3). The very high degree of fluorination proved to be detrimental in creating mesophases. The perprotio analogues of materials of Class 2 exhibits SmE and SmB phases\textsuperscript{11}. But when the tail is perfluorinated, it
becomes very rigid and discourages intermolecular interactions which is important to exhibit mesophases\(^\text{12}\).

<table>
<thead>
<tr>
<th>4,4’-perfluoroalkylbiphenyl</th>
<th>4,4’-alkylbiphenyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}<em>6\text{F}</em>{13})</td>
<td>(\text{C}<em>6\text{H}</em>{13})</td>
</tr>
<tr>
<td>Cr 82 I</td>
<td>Cr 34 SmE 35 SmE’ 40 SmB 53.4 I</td>
</tr>
<tr>
<td>(\text{C}<em>7\text{F}</em>{16})</td>
<td>(\text{C}<em>7\text{H}</em>{15})</td>
</tr>
<tr>
<td>Cr 95 I</td>
<td>Cr 19.5 SmE 35.1 SmB 61 I</td>
</tr>
</tbody>
</table>

**Table 2.1:** Comparison of materials of class 2 and their perprotio analogues\(^\text{11}\)

The perprotio analogues of materials of **Class 1** did not show any mesogenic properties either, but the melting points were higher than their fluorinated analogues\(^\text{13}\).

<table>
<thead>
<tr>
<th>4,4’-semifluoroalkoxybiphenyl</th>
<th>4,4’-alkoxybiphenyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{F}(\text{F}_2\text{C})_6)</td>
<td>(\text{C}<em>6\text{H}</em>{13})</td>
</tr>
<tr>
<td>O (\text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{O}(\text{CF}_2)_5\text{F})</td>
<td>Cr 84 I</td>
</tr>
<tr>
<td>Cr 84 I</td>
<td>Cr 159 I</td>
</tr>
<tr>
<td>(\text{F}(\text{F}_2\text{C})_6)</td>
<td>(\text{C}<em>8\text{H}</em>{17})</td>
</tr>
<tr>
<td>O (\text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{O}(\text{CF}_2)_5\text{F})</td>
<td>Cr 114 I</td>
</tr>
<tr>
<td>Cr 114 I</td>
<td>Cr 155 I</td>
</tr>
</tbody>
</table>

**Table 2.2:** Comparison of highly fluorinated materials of Class 1 with their perprotio analogues\(^\text{13}\)
Although mesogenic properties were absent in these molecules, the infrared absorption properties were excellent (considering the demands of the intended applications). These compounds generated new ideas about molecule design that will be discussed in Chapter 2. For all the molecules in Classes 1, 2 and 3, the region between 3500-1700 cm\(^{-1}\) was almost devoid of any absorptions. The overtone vibration for the C-F stretching (occurs generally around 2200-2000 cm\(^{-1}\)) was so weak that it was not observed on the infrared spectra of the materials.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Phase transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{C}<em>8\text{F}</em>{17}$</td>
<td>Cr 152 I</td>
</tr>
<tr>
<td>2</td>
<td>$\text{C}<em>6\text{F}</em>{13}$</td>
<td>Cr 138 I</td>
</tr>
<tr>
<td>3</td>
<td>$\text{C}<em>{10}\text{F}</em>{21}$</td>
<td>Cr 142 I</td>
</tr>
<tr>
<td>4</td>
<td>$\text{C}<em>8\text{F}</em>{17}$</td>
<td>Cr 113 I</td>
</tr>
<tr>
<td>5</td>
<td>$\text{C}<em>7\text{F}</em>{15}$</td>
<td>Cr 95 I</td>
</tr>
<tr>
<td>6</td>
<td>$\text{C}<em>6\text{F}</em>{13}$</td>
<td>Cr 82 I</td>
</tr>
<tr>
<td>7</td>
<td>$\text{C}<em>4\text{F}</em>{9}$</td>
<td>Cr 72 I</td>
</tr>
<tr>
<td>8</td>
<td>$\begin{array}{c} \text{F}(	ext{F}_2\text{C})_8 \ \text{O} \ \text{F} \ \text{F} \ \text{F} \ \text{F} \ \text{F} \ \text{O} \ (\text{CF}_2)_6\text{F} \end{array}$</td>
<td>Cr 119 I</td>
</tr>
<tr>
<td>9</td>
<td>$\begin{array}{c} \text{F}(	ext{F}_2\text{C})_6 \ \text{O} \ \text{F} \ \text{F} \ \text{F} \ \text{F} \ \text{F} \ \text{O} \ (\text{CF}_2)_6\text{F} \end{array}$</td>
<td>Cr 114 I</td>
</tr>
<tr>
<td>10</td>
<td>$\begin{array}{c} \text{F}(	ext{F}_2\text{C})_5 \ \text{O} \ \text{F} \ \text{F} \ \text{F} \ \text{F} \ \text{F} \ \text{O} \ (\text{CF}_2)_6\text{F} \end{array}$</td>
<td>Cr 84 I</td>
</tr>
</tbody>
</table>

**Table 2.3:** Melting points of the synthesized fluorinated materials (see figure 2.1)
Figure 2.7: Representative infrared spectrum of material of Class 1

Figure 2.8: Representative infrared spectrum of material of Class 2
In Figures 2.7, 2.8 and 2.9 it is seen that the absorption due to alkyl tails around 3000-3600 cm\(^{-1}\) is almost absent. Even with 4,4'-diethylbiphenyl there is significant absorption due to the ethyl tails in the aforesaid region (Figure 2.10). In Figure 2.7, it is seen that the C-F stretching
vibration in the phenyl ring appears at 1493 cm$^{-1}$. But for materials of class 2 and 3 this is absent as the core does not contain any chlorine.

**2.4 Conclusions**

Due to high the degree of fluorination in these compounds the intermolecular attractive interactions necessary for mesogenicity were absent. Non-fluorinated tails interact with each other by van-der Waal’s forces, giving rise to the order that is necessary for mesogenic activity$^{14}$. But when the tails are perfluorinated, they become rigid as the neighboring fluoro substituents in perfluorinated tails reduce the conformational flexibility$^{12}$. This changes the interactions in a way that is detrimental to mesogenicity. This probably destroys any chance of mesogenicity in the molecules synthesized in this study. In the next chapter, we will try to overcome this problem by incorporating more flexibility in the tail.
2.5 Experimental

Synthesis of 1-[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononyl)oxy]-4-[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononyl)oxy]phenyl] benzene (8)

A solution of CF$_3$(CF$_2$)$_7$CH$_2$OH (3.00 gm, 6.64 mmol) in dry DMF (15 ml) and anhydrous K$_2$CO$_3$ (1.0 gm, 7.0 mmol) was stirred at room temperature for 30 minutes and then decafluorobiphenyl (1.0 gm, 2.99 mmol) was added and the reaction mixture was stirred at room temperature for 16 hours. All the starting materials were consumed in this time (TLC with hexanes as eluent). Water (200 ml) was added to this mixture when the product precipitated out. The crude product was collected through vacuum filtration. It was then recrystallized from chloroform to obtain a white solid. (Yield 3.12 gm, 87%).

Melting point: 119°C

$^1$H NMR (400MHz, tetrachloroethane-d2, 353K): 4.80 (4H, t, $J = 13.10$ Hz)

$^{13}$C NMR (100MHz, tetrachloroethane-d2, 353K): 69.88

IR (neat, cm$^{-1}$): 2971.28, 1653.35, 1486.86, 1371.78, 1334.49, 1198.59, 1133.36, 1013.58, 979.16, 726.12, 707.22, 656.00, 557.02

The other materials of this class were prepared following the same procedure
Synthesis of 1-[(2,2,3,3,4,4,5,5,6,6,6-undecafluorohexyl)oxy]-4-[(2,2,3,3,4,4,5,5,6,6,6-undecafluorohexyl)oxy]phenyl]benzene (10)

Melting point: 84°C

$^1$H NMR (400MHz, tetrachloroethane-d₂, 353K): 4.80 (4H, t, $J = 12.50$ Hz)

$^{13}$C NMR (100MHz, tetrachloroethane-d₂, 353K): 69.89

IR (neat, cm$^{-1}$): 2957.80, 1649.59, 1493.84, 1240.23, 1207.67, 1143.07, 1113.92, 987.32, 868.33, 802.96, 750.53, 725.59.

Synthesis of 1,2,4,5-tetrafluoro-3-[(2,3,5,6-tetrafluoro-4-[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)oxy]phenyl]-6-[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)oxy]benzene (9)

Melting point: 114°C

$^1$H NMR (400MHz, tetrachloroethane-d₂, 353K): 4.72-4.58 (4H, m), 2.75 (4H, t, $J = 18.58$ Hz)

$^{13}$C NMR (100MHz, tetrachloroethane-d₂, 353K): 66.74, 32.18

IR (neat, cm$^{-1}$): 1651.96, 1497.00, 1481.84, 1415.79, 1186.58, 1142.61, 982.25, 650.50
Synthesis of 4,4’-perfluorodecylbiphenyl (3)

\[
\text{I} \quad \text{C}_{10}\text{F}_{21} \quad \text{I} \quad \text{C}_{10}\text{F}_{21}
\]

Perfluoro n-decyl iodide (7.15 gm, 11.00 mmol), 4,4’-diiodobiphenyl (2.0 gm, 5.0 mmol), Cu (1.0 gm, 16.0 mmol), DMSO (2 ml) and C\text{6}F\text{6} (5 ml) was stirred for 24 hours at 80°C under nitrogen. Then it was cooled down when the mixture turned into a yellow waxy cake. It was then taken out and dissolved in isooctane (100 ml) with heating. Then montmorillonite K-10 clay was added and the mixture was filtered while hot. The filtrate was concentrated and then cooled down to room temperature when a white solid precipitated. The mixture was filtered and the residue was recrystallized from isooctane to obtain the desired product as a white crystalline solid (yield 4.13 gm, 69.4% ).

Melting point: 142°C

\(^1\text{H NMR}\) (400MHz, tetrachloroethane-d2, 353K): 7.79 (4H, d, J = 8.95 Hz), 7.76 (4H, d, J = 8.87 Hz)

\(^{13}\text{C NMR}\) (100MHz, tetrachloroethane-d2, 353K): 143.14, 128.91, 127.26

IR (neat, cm\(^{-1}\)): 2360.78, 1205.01, 1148.93

The other materials of this class were prepared following the same procedure.
Synthesis of 4,4'-perfluoroctylbiphenyl (4)

\[
\begin{array}{c}
\text{I} & \text{I} \\
\text{C}_8\text{F}_{17} & \text{C}_8\text{F}_{17}
\end{array}
\]

Melting point: 113°C

\(^1\)H NMR (CDCl\textsubscript{3}, 400 MHz, 298K): 7.72 (4H, d, \( J = 8.20 \) Hz), 7.68 (4H, d, \( J = 8.76 \) Hz)

\(^{13}\)C NMR (CDCl\textsubscript{3}, 100 MHz, 298K): 143.9, 127.8

IR (neat, cm\textsuperscript{-1}): 1613.94, 1294.49, 1242.27, 1216.42, 1153.50, 1114.40

Synthesis of 4,4'-perfluorohexylbiphenyl (5)

\[
\begin{array}{c}
\text{I} & \text{I} \\
\text{C}_7\text{F}_{15} & \text{C}_7\text{F}_{15}
\end{array}
\]

Melting point: 95°C

\(^1\)H NMR (400MHz, tetrachloroethane-d2, 353K): 7.79 (4H, d, \( J = 8.38 \) Hz), 7.75 (4H, d, \( J = 8.38 \) Hz)

\(^{13}\)C NMR (100MHz, tetrachloroethane-d2, 353K): 143.15, 127.32

IR (neat, cm\textsuperscript{-1}): 1614.14, 1241.60, 1212.51, 1150.96, 987.92
Synthesis of 4,4'-perfluorohexylbiphenyl (6)

$$\begin{align*}
&\text{Melting point: } 82^\circ C \\
&^1H \text{ NMR (CDCl}_3, 400 \text{ MHz, 298K): } 7.72 (4H, d, J = 8.48 \text{ Hz}), 7.68 (4H, d, J = 8.82 \text{ Hz}) \\
&^13C \text{ NMR (CDCl}_3, 100 \text{ MHz, 298K): } 143.3, 127.9 \\
&\text{IR (neat, cm}^{-1}\text{): } 1613.97, 1483.04, 1362.44, 1240.91, 1207.69, 1148.09
\end{align*}$$

Synthesis of 4,4'-perfluorobutylbiphenyl (7)

$$\begin{align*}
&\text{Melting point: } 72^\circ C \\
&^1H \text{ NMR (400MHz, tetrachloroethane-d2, 353K): } 7.76 (4H, d, J = 8.51 \text{ Hz}), 7.76 (4H, d, J = 8.51 \text{ Hz}) \\
&^13C \text{ NMR (CDCl}_3, 100 \text{ MHz, 298K): } 143.32, 127.56 \\
&\text{IR (neat, cm}^{-1}\text{): } 1501.02, 1196.65, 1137.62, 982.62, 872.10, 727.45, 591.23
\end{align*}$$

Synthesis of trans-di(µ-acetato)-bis[o-(di-o-tolylphosphino)benzyl]dipalladium(II) (Hermann-Beller palladacycle)
Prepared using a literature procedure⁹.

Palladium acetate (1.12 gm, 5.00 mmol) was dissolved in dry toluene (125 ml) and to the reddish brown solution was added P(o-tolyl)₃ (2.00 gm, 6.57 mmol) under N₂. The bright orange solution was heated to 50°C and was stirred at that temperature for 3 minutes and then the solvent was reduced to a quarter of the original volume in vacuo. The mixture was then rapidly cooled down to room temperature and hexanes (125 ml) was added when bright yellow precipitate appeared. The precipitate was collected by suction filtration under N₂ atmosphere and dried in a vacuum desiccator to obtain a fine yellow powder (2.1 gm, 67% yield).

Synthesis of 1-{4-[(1E)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodec-1-en-1-yl]phenyl}-4-[(1E)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-nonadecafluoroundec-1-en-1-yl]benzene (1)

In a 250 ml round-bottom flask equipped with a stirbar 4, 4'-dibromobiphenyl (1.56 gm, 5.00 mmol), (perfluoroctyl)ethylene (5.34 gm, 12.00 mmol), Hermann’s palladacycle (47.50 mg, 0.05 mmol) and NaOAc (0.98 gm, 12.00 mmol) was added to DMF (40 ml) and the mixture was
heated to 125°C under N₂. The mixture was stirred at this temperature for 10 hours. All the starting materials were consumed at this point (monitored through GC-MS). The mixture was then cooled to room temperature and added to water (500 ml) when a grey precipitate appeared. The precipitate was separated by suction filtration and was dissolved in boiling isooctane (100 ml). To this boiling solution was added montmorillonite-K10 clay (2.5 gm) and the resulting mixture was gravity filtered while hot and the volume of the filtrate was reduced to 20 ml when fine white flakes of crystal precipitated out. The precipitate was collected by suction filtration and recrystallized from isooctane to obtain the desired product as white crystals (4.22 gm, 81% yield).

Melting point: 152°C

¹H NMR (400MHz, tetrachloroethane-d₂, 353K): 7.69 (4H, d, J = 8.02 Hz), 7.60 (4H, d, J = 7.87 Hz), 7.28 (2H, d, J = 15.95 Hz), 6.29 (2H, d, J = 12.12 Hz)

¹³C NMR (100MHz, tetrachloroethane-d₂, 353K): 141.64, 139.01, 133.17, 128.00, 127.35, 114.93

IR (neat, cm⁻¹): 3092.08, 3036.86, 1659.75, 1241.98, 1202.59, 1146.15, 969.11

The other materials of this class were prepared following the same procedure

Synthesis of 1-[(1E)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooct-1-en-1-yl]-4-[(1E)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooct-1-en-1-yl]phenyl]benzene (2)

Yield (3.8 gm, 90%)
Melting point: 138°C

$^1$H NMR (400MHz, tetrachloroethane-d$_2$, 353K): 7.70 (4H, d, $J = 8.99$ Hz), 7.61 (4H, d, $J = 7.00$ Hz), 7.28 (2H, d, $J = 15.99$ Hz), 6.29 (2H, q, $J = 12.99$ Hz)

$^{13}$C NMR (100MHz, tetrachloroethane-d$_2$, 353K): 141.68, 139.07, 133.08, 128.04, 127.37, 114.81

IR (neat, cm$^{-1}$): 3036.60, 1657.82, 1497.82, 1365.05, 1230.03, 1189.36, 1139.74, 1066.77, 974.80, 806.73, 791.74, 716.79, 691.51, 651.45
2.6 References


(13) Manickam, M.; Iqbal, P.; Spencer, N.; Ashton, P. R.; Kumar, S.; Donovan, K. J.; Preece, J. A. Molecular Crystals and Liquid Crystals 2010, 518, 84.

Chapter 3

Design and synthesis of cyanobiphenyls with perfluorinated and semifluorinated tails as potential candidates for midwave infrared applications

3.1 Introduction

It has been experimentally demonstrated that liquid crystals can possess high birefringence in the infrared region\textsuperscript{36} and this important property has been exploited in applications such as dynamic scene projectors for infrared seekers\textsuperscript{37} and laser beam steering\textsuperscript{38}. Very generally, long wavelength radiation like IR is preferable for telecom applications due to lower absorption and thus lower optical loss\textsuperscript{39}. However in liquid crystals such applications face some drawbacks owing to the inherent absorption loss due to the existence of molecular absorption bands as well as their harmonics and overtones. For example, several absorption bands exist in the mid-infrared region (3-5 \(\mu\)m) due to common structure features found in liquid crystals such as CH, CH\(_2\), CH\(_3\) and CN. In the off-resonance regions, the baseline absorption coefficient can take the value of up to \(\alpha \sim 10/\text{cm}\)\textsuperscript{41}. This absorption loss becomes especially significant if the optical path is long.

To address this absorption problem, one strategy has been to replace the hydrogen atoms in a molecule by some heavier atoms\textsuperscript{48}. As the molecular vibration frequency (\(\omega\)) depends upon the spring constant (\(k\)) and the effective mass (\(m\)) of a diatomic group by the equation
\( \omega = \sqrt{\frac{\kappa}{m}} \), this strategy can address the absorption loss in the midwave infrared region by shifting the absorption bands to the longer wavelength region. Fluorinated compounds have promise as candidates in such applications since fluorine has a large mass relative to hydrogen (18.998404 amu for fluorine compared to 1.00794 amu for hydrogen) yet it has an atomic radius comparable to hydrogen (1.47 Å for fluorine compared to 1.2 Å for hydrogen). Thus, substitution of hydrogen by fluorine is not expected to disturb the molecular interactions based on excluded volume\(^{50} \). However, there will be an influence resulting from the different polarizabilities of these elements especially as the number of fluorine atoms becomes significant. Due to enhancements of synthetic methodology and the increasing availability and decreasing cost of the fluorinated starting materials, development of highly fluorinated liquid crystals is an attractive area of research.

It is important to emphasize that a high extent of fluorination can be detrimental for mesogenic properties, especially as transition temperatures increase and the nematic characteristics are compromised. A high degree of fluorination of the terminal aliphatic chain promotes smectic phases due to the increased rigidity\(^{78} \). This dramatic increase of stiffness can produce smectic phases even in semifluorinated n-alkanes which are devoid of any ring structure\(^{79} \).

In some IR device applications a nematic phase is preferred and thus a systematic study of highly fluorinated compounds is required to provide the desired IR transparency and nematic behavior simultaneously. This paper explores the synthesis and mesogenic properties of some highly tail-fluorinated cyanobiphenyls and compares their properties with their non-fluorinated analogues.
3.2 Results and discussion

The simple alkyl cyanobiphenyls show nematic phases near room temperature and they have been used in numerous applications. However, they are not useful in midwave infrared applications, as several absorption bands exist in the aforesaid region.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Phase transition data</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(H₂C)₅-phenyl-phenyl-CN</td>
<td>C 24.5 N 35.6 I</td>
</tr>
<tr>
<td>H(H₂C)₆-phenyl-phenyl-CN</td>
<td>C 14.5 N 29.2 I</td>
</tr>
<tr>
<td>H(H₂C)₇-phenyl-phenyl-CN</td>
<td>C 30 N 42.8 I</td>
</tr>
<tr>
<td>H(H₂C)₈-phenyl-phenyl-CN</td>
<td>C 21.5 SmA 33.5 N 40.5 I</td>
</tr>
</tbody>
</table>

**Table 3.1:** Transition temperatures of some perprotio alkyl cyanobiphenyls

The replacement of all the hydrogens by deuterium in pentylcyanobiphenyl results in a much cleaner absorption spectrum in the 3.5-4.6 μm window. Based on the infrared absorption spectra of fluorinated biphenyls (Chapter 2), it is seen that the C-H bonds in the phenyl ring have a much weaker and narrower absorption than the C-H bonds in the flexible alkyl chains. Based on this finding, the synthesis of biphenyls with fluorinated tails was pursued. The structures of the three new classes of molecules synthesized and studied here are shown below.
Synthesizing the compounds of Class 1 tested the assumption that replacement of all the hydrogens in the alkyl tail of the known cyanobiphenyl liquid crystals would give cleaner absorption spectra. Indeed, the absorption spectra in 3-5 μm range were indeed much cleaner. But the side effect of this perfluorination is that the liquid crystal phases disappeared entirely. At this point, we reduced the degree of fluorination on the tail and synthesized compounds of Class 2. The absorption spectra in 3-5 μm range were still much cleaner compared to the alkylcyanobiphenyls and a SmA phase was seen. The olefin unit serves to decouple the rigid biphenyl and perfluoroalkane parts of the molecule. This result led us to next synthesize the compounds in Class 3. The compounds in this class containing C\textsubscript{10} and C\textsubscript{12} alkyl chains now showed a SmC phase along with the SmA phase. The compound with the C\textsubscript{6} tail had a SmA phase at room temperature. Although these molecules are not nematic they have interesting absorption properties in the mid-wave infrared region. Owing to these properties, these molecules or their derivatives may find use in applications that require transparency in the mid-wave infrared region.

The synthesis of compounds with general structure 1 (Figure 3.2) was accomplished by the reaction of the appropriate perfluoroalkyl iodide with 4-iodo-4’-cyanobiphenyl described by

![Figure 3.1: The three different Classes of cyanobiphenyls synthesized in this study](image-url)
McLaughlin et. al. The 4-(4-iodophenyl)benzonitrile precursor was made from biphenylcarboxaldehyde by a two-step process that started with the conversion of 4-biphenylcarboxaldehyde to 4-cyanobiphenyl by a microwave mediated procedure. The 4-cyanobiphenyl was converted to 4-iodo-4'-cyanobiphenyl by a previously reported procedure.

**Figure 3.2:** Synthesis of cyanobiphenyl derivatives in Class 1 (n = 5, 6, 7, 8)

Compounds with the general structure 2 were prepared as outlined in Fig. 3 from 4-(4-iodophenyl)benzonitrile by a Heck reaction with the corresponding 1H,1H,2H-perfluoroalkene by a methodology similar to one described by Hermann et. al.

**Figure 3.3:** Synthesis of cyanobiphenyl derivative in Class 2 (n = 4, 6, 8, 10)

The synthesis of compounds with the general structure 3 was complicated as some routes shown in Fig. 4 failed. For example, compounds in class 3 could not be prepared by the hydrogenation
of compounds already available in class 2 as the cyano group was reduced along with the alkene. A procedure for palladium catalyzed C-C bond formation reaction between 1H,1H,2H,2H-perfluoroalkyl iodides, in this case with 4-(4-cyanophenyl)benzeneboronic acid, proved irreproducible in our hands. Likewise, a Suzuki coupling of the 9-BBN adduct of the appropriate 1H,1H,2H-perfluoroalkyl ethylene with 4-(4-iodophenyl)benzonitrile also failed to produce the desired results.

Figure 3.4: The unproductive approaches towards the synthesis of cyanobiphenyl derivatives in class 3

A significantly longer approach (Fig. 5) was successful in producing the desired individual compounds in class 3 in good overall yield. In this procedure, 4-bromobiphenyl was coupled with the appropriate 1H, 1H, 2H-perfluoroalkene, again using the Heck reaction developed by Hermann et al. The alkene in the tail was then reduced to provide the saturated derivative that in turn was brominated using molecular bromine in a 3:1 mixture of CF₃COOH and CHCl₃ as solvent. This choice of solvent discouraged benzylic bromination and bromobiphenyl vi was obtained in good yield just by simple recrystallization from ethanol. Finally, the bromobiphenyl vi was refluxed in DMF with CuCN to obtain the final type 3 product.
Figure 3.5: Synthesis of cyanobiphenyl derivatives in Class 3 (n = 4, 6, 8, 10)

3.3 Mesophase properties of the cyanobiphenyls with fluorinated tails

It is known that extensive fluorination may bring about some undesired properties, extinction of mesophase properties is one of them (or a high tendency to form smectic phases)\(^8\). A good example for this phenomenon becomes evident when all the hydrogens in the alkyl tail of the well-known liquid crystal 7CB are are replaced by fluorine. No mesophase properties can be seen in the fluorinated analogue and a higher melting point of 120°C is observed compared to the melting point of 30°C for 7CB\(^8\). This result is at least partially due to the rigidity of the perfluorinated tail.

![Chemical Structures](image)

Figure 3.6: Comparison of mesophase properties of 7CB and its fluorinated analogue

A family of cyanobiphenyls with perfluorinated tails of the general structure 1 was synthesized and as expected none of them showed any liquid crystalline phases. However, these highly
fluorinated molecules did possess better IR absorption properties which led us to redesign the molecules by increasing the number of hydrogen atoms in the alkyl chain as adding hydrogens (as a –CH₂CH₂– unit) to increase the tail flexibility. To accomplish this, some compromise had to be made on the IR absorption properties, although the absorption in the 3-5 μm region was still much lower compared to the perprotio cyanobiphenyls. The compounds with general structures 2 and 3 did show smectic liquid crystalline phases. When n = 4 in the alkyl chain of these compounds, the effect of added flexibility of the alkyl tails in promoting liquid crystalline phases was observed. When the mesogenic properties of these molecules were studied under a polarized optical microscope, it was observed that compound 2a with n = 4 is not liquid crystalline and has a rather low melting point of 66-68 °C, whereas compound 3a with n = 4 shows a SmA phase. For both compounds 2 & 3 the clearing point becomes higher with the increase in length of the perfluorinated tail.

From the Table 3.2, it can be seen that as the hydrogen content in the fluorinated tail is increasing, the compounds are more prone to forming liquid crystalline phases, although they are smectic. If the hydrogen content is eventually increased in the tail it may give rise to the nematic phase at some point, although at that point the infrared absorption properties will be compromised because many hydrogen atoms will be introduced in place of fluorine.
Table 3.2: Transition temperatures of the cyanobiphenyls with perfluorinated and semi-fluorinated tails of different length. The numbers in ( ) are the enthalpy of transitions (in Joule/gram). The crystal to SmC transitions in Compounds 3c and 3d were not detected by DSC but it was observed by polarizing optical microscopy.
3.4 Conclusions

We have developed some efficient routes towards the synthesis of cyanobiphenyls with semi- and perfluorinated tails that exhibit smectic mesophases. These liquid crystals can find potential device applications such as laser beam steering, optical valves and dynamic scene projectors for infrared seekers to name a few. New mixtures can be formulated with these liquid crystals for infrared applications. The synthesis methods are economical and the reagents are easy to handle and no special conditions are needed to perform the chemistry. Future efforts will be focused on structural modifications to achieve nematic transitions and also widen the range of the liquid crystalline phases.

**Figure 3.7:** Comparison of transition temperatures of compounds of classes 2 and 3
3.5 Experimental

The $^1$H, $^{13}$C and $^{19}$F NMR spectra were measured on a Bruker Avance 400 MHz spectrometer at 400.13, 100.61 and 376.49 MHz, respectively. The $^1$H and $^{13}$C NMR chemical shifts were referenced to TMS (0.0 ppm) and the $^{19}$F NMR chemical shifts were referenced to CFCl$_3$ (0.0 ppm). The melting points were uncorrected. Biphenyl carboxaldehyde, hydroxylamine hydrochloride, periodic acid and hexafluorobenzene were purchased from Aldrich and used as received. NMP and anhydrous DMSO was purchased from Acros and used as received. Perfluoro-n-heptyl iodide was purchased from PCR and used as received. perfluoro-n-hexyl iodide, perfluoro-n-pentyl iodide, perfluoro-n-octyl iodide, perfluorooctyl(ethylene) and perfluorodecyl(ethylene) were purchased from Matrix scientific and used as received. Perfluorobutyl(ethylene) and perfluorohexyl(ethylene) were purchased from TCI America and used as received. The progress of the reactions was monitored either by thin layer chromatography with plastic backed silica gel plates (Scientific adsorbents incorporated, Catalog # 79011), or by GC-MS [Finnigan trace GC ultra (Restek$^{\text{TM}}$ RTX-5 capillary column (30 m)) coupled with Finnigan PolarisQ mass spectrometer]. Infrared spectra were obtained using a Bruker Vector33 infrared spectrometer with an ATR probe. Differential scanning calorimetry (DSC) measurements were performed using a TA instruments differential scanning calorimeter 2920 at heating and cooling rates of 5°C per minute. Transition temperatures of the final products were measured using Mettler FP82HT hot-stage and FP90 control unit in conjunction with Nikon Eclipse E600 Pol polarizing microscope.
General synthesis procedures and spectral data of the products

Synthetic route for compounds in Classes 1 & 2

\[
\begin{align*}
&\text{OHC} - \begin{array}{c}
\text{H}
\end{array} \begin{array}{c}
\text{C}
\end{array} - \begin{array}{c}
\text{H}
\end{array} \begin{array}{c}
\text{C}
\end{array} - \begin{array}{c}
\text{H}
\end{array} \begin{array}{c}
\text{C}
\end{array} - \begin{array}{c}
\text{H}
\end{array} (i) \quad \text{NH}_{2}\text{OH.HCl, NMP, Microwave} \quad \text{NC} - \begin{array}{c}
\text{H}
\end{array} \begin{array}{c}
\text{C}
\end{array} - \begin{array}{c}
\text{H}
\end{array} \begin{array}{c}
\text{C}
\end{array} - \begin{array}{c}
\text{H}
\end{array} \begin{array}{c}
\text{C}
\end{array} - \begin{array}{c}
\text{H}
\end{array} (ii) \quad \text{I}_{2}, \text{H}_{2}\text{O}_{8}, \text{H}_{2}\text{SO}_{4} \quad \text{NC} - \begin{array}{c}
\text{H}
\end{array} \begin{array}{c}
\text{C}
\end{array} - \begin{array}{c}
\text{H}
\end{array} \begin{array}{c}
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\text{H}
\end{array} \begin{array}{c}
\text{C}
\end{array} - \begin{array}{c}
\text{H}
\end{array} (iii) \\
\text{H}_{2}\text{O} \text{NC} - \begin{array}{c}
\text{H}
\end{array} \begin{array}{c}
\text{C}
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\text{C}_{n}\text{F}_{2n+1} \end{array} \text{H}_{2}\text{O} \text{NC} - \begin{array}{c}
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\text{C}_{n}\text{F}_{2n+1} \end{array} \text{NC} - \begin{array}{c}
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\text{H}
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\text{C}
\end{array} - \begin{array}{c}
\text{C}_{n}\text{F}_{2n+1} \end{array} \\
\text{H}_{2}\text{O} \text{NC} - \begin{array}{c}
\text{H}
\end{array} \begin{array}{c}
\text{C}
\end{array} - \begin{array}{c}
\text{H}
\end{array} \begin{array}{c}
\text{C}
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\text{H}
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\text{C}
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\text{H}
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\text{C}
\end{array} - \begin{array}{c}
\text{C}_{n}\text{F}_{2n+1} \end{array} \text{NC} - \begin{array}{c}
\text{H}
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\text{H}
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\text{C}
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\text{C}
\end{array} - \begin{array}{c}
\text{C}_{n}\text{F}_{2n+1} \end{array} \\
\text{H}_{2}\text{O}
\end{align*}
\]

Synthesis of 4-phenylbenzonitrile (ii)

To a solution of 4-phenylbenzaldehyde (13.15 gm, 72.4 mmol) in NMP (50 ml) was added hydroxylamine hydrochloride (7.55 gm, 108.6 mmol). The reaction flask was then fitted with a condenser and subjected to variable 200W irradiation in a CEM microwave reactor for 20 minutes with the temperature set at 150°C. After cooling to room temperature, the reaction mixture was added to 500 ml of to precipitate the product. This white solid was collected by suction filtration, washed with water and air-dried. The product (11.5 gm, 88%) prepared in this fashion was sufficiently pure for direct use in the subsequent reaction.
Synthesis of 4-(4-iodophenyl)benzonitrile (iii)

The 4-phenylbenzonitrile (8.0 gm, 44.6 mmol) was mixed with acetic acid (24 ml), water (4 ml) and 97% sulfuric acid (0.8 ml). To this reaction mixture was added iodine (6.0 gm, 23.6 mmol) and periodic acid (2.4 gm, 10.4 mmol). The reaction solution was then stirred at 70°C for 36 hours to yield a precipitate (all starting materials were consumed as indicated by TLC with 20% EtOAc, 80% hexane as eluent). The reaction mixture was cooled, water (250 ml) was added and resulting precipitate was separated by vacuum filtration. The precipitate was washed with water, dissolved in EtOAc (200 ml) and washed with 10% sodium thiosulfate solution (100 ml). The organic layer was separated, washed with brine and dried over anhydrous MgSO₄. After filtration, the solvent was removed under reduced pressure to yield a pale yellow solid, which was recrystallized from a mixture of ethyl acetate and methanol (2:1) to yield the product as shiny flakes. (12.42 gm, 91%). Melting point 177°C.

\(^1\)H NMR (CDCl₃, 400 MHz): 7.81 (2H, d, J = 8.45 Hz), 7.71 (2H, d, J = 8.44 Hz), 7.63 (2H, d, J = 8.41 Hz), 7.31 (2H, d, J = 8.49 Hz).

\(^{13}\)C NMR (CDCl₃, 100 MHz):

144.52, 138.67, 138.27, 132.70, 128.91, 127.47, 118.65, 111.48, 94.76
Synthesis of 4-{[(1E)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-en-1-yl]phenyl}benzonitrile (n = 6) (Representative example for the synthesis of compounds of general structure 2)

In a 250 ml round-bottom flask equipped with a stir bar 4-iodo-4’-cyanobiphenyl (1.52 gm, 5 mmol), (perfluorohexyl)ethylene (2.07 gm, 6 mmol), Hermann’s palladacycle (47.5 mg, 0.05 mmol) and NaOAc (0.41 gm, 5 mmol) was added to DMF (20 ml) and the mixture was heated to 100°C under N₂. The mixture was stirred at this temperature for 10 hours when all the starting materials were consumed (monitored through GC). The mixture was then cooled to room temperature and added to water (500 ml) when a grey precipitate appeared. The precipitate was separated by suction filtration and was dissolved in boiling isoctane (100 ml). To this boiling solution was added montmorillonite-K10 clay (2.5 gm) and the resulting mixture was filtered by gravity filtration while hot and the volume of the filtrate was reduced to 20 ml when fine white flakes of crystal precipitated out. The precipitate was collected by suction filtration to obtain white crystals. This was dissolved in diethyl ether (20 ml) and silica gel (5 gm) was added. The solvent was removed under reduced pressure and the residue was placed on the top of a silica gel column. The column was eluted with a mixture of 10% EtOAc, 90% hexanes and the major band was collected and the solvent was removed under reduced pressure. The residue was recrystallized from isoctane to obtain the desired product as shiny white crystals. (1.00 gm, 38% yield).

**1H NMR (CDCl₃, 400 MHz):** 7.78 (2H, d, J = 8.72 Hz), 7.72 (2H, d, J = 8.85 Hz), 7.66 (2H, d, J = 8.59 Hz), 7.62 (2H, d, J = 8.33 Hz), 7.25 (1H, d, J = 16.15 Hz), 6.30 (1H, q, J = 12.06 Hz)

**13C NMR (CDCl₃, 400 MHz):** 144.47, 140.82, 138.84, 133.81, 132.73, 128.40, 127.78, 127.67, 118.70, 115.46, 115.23, 115.01, 111.57
$^{19}$F NMR (376 MHz, CDCl$_3$, 298K): -81.38 (3F, t, $J = 9.92$ Hz), -111.75 (2F, m), -122.14 (2F, m), -123.21 (2F, m), -123.71 (2F, m), -126.72 (2F, m)

IR (neat, cm$^{-1}$): 3016.05, 2224.64, 1738.56, 1365.09, 1198.97, 1118.13, 807.12

$^4$-{4-[(1E)-3,3,4,4,5,6,6-nonfluorohex-1-en-1-yl]phenyl}benzonitrile (n = 4)

Yield = 0.66 gm (31%), Melting point: 59-60 °C

$^1$H NMR (CDCl$_3$, 400 MHz, 298K): 7.74 (2H, d, $J = 8.60$ Hz), 7.69 (2H, d, $J = 8.60$ Hz), 7.63 (2H, d, $J = 8.52$ Hz), 7.59 (2H, d, $J = 8.40$ Hz), 7.22 (1H, m), 6.26 (1H, quartet, $J = 12.49$ Hz)

$^{13}$C NMR (CDCl$_3$, 400 MHz, 298K): 132.73, 128.39, 127.78, 127.67, 118.70

$^{19}$F NMR (376 MHz, CDCl$_3$, 298K):

-81.61 (3F, m), -111.99 (2F, m), -124.62 (2F, m), -126.26 (2F, m)

IR (neat, cm$^{-1}$): 3058.23, 2225.89, 1659.12, 1605.19, 1231.15, 1194.19, 1126.22, 807.48

$^4$-{4-[(1E)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodec-1-en-1-yl]phenyl}benzonitrile (n = 8)

Yield = 1.62 gm (52%) 

Transitions (°C): Cr 91 SmA 133 I 132 SmA 84 Cr

$^1$H NMR (CDCl$_3$, 400 MHz, 298K): 7.78 (2H, d, $J = 8.48$ Hz), 7.72 (2H, d, $J = 8.58$ Hz), 7.66 (2H, d, $J = 8.58$ Hz), 7.62 (2H, d, $J = 8.48$ Hz), 7.25 (1H, d, $J = 16.27$ Hz), 6.30 (1H, quartet, $J = 12.50$ Hz)

$^{13}$C NMR (CDCl$_3$, 400 MHz, 298K): 144.47, 140.82, 138.83, 133.81, 132.73, 128.40, 127.77, 127.67, 118.70, 115.25, 111.57
19F NMR (376 MHz, CDCl3, 298K): -81.36 (3F, t, J = 9.95 Hz), -111.73 (2F, quartet, J = 12.16 Hz), -121.92 (2F, m), -122.46 (4F, m), -123.28 (2F, m), -123.68 (2F, m), -126.67 (2F, m)

IR (neat, cm⁻¹): 3038.7, 2226.95, 1657.16, 1494.76, 1195.68, 1144.98, 973.35, 808.77

Yield = 1.95 gm (54%)

Transitions: Cr 116 SmA 154 I 153 SmA 106 Cr

1H NMR (CDCl3, 400 MHz, 298K): 7.78 (2H, d, J = 8.56 Hz), 7.72 (2H, d, J = 8.60 Hz), 7.66 (2H, d, J = 8.52 Hz), 7.62 (2H, d, J = 8.44 Hz), 7.25 (1H, d, J = 16.28 Hz), 6.30 (1H, quartet, J = 11.77 Hz)

13C NMR (CDCl3, 400 MHz, 298K): 132.75, 128.40, 127.78, 127.69

19F NMR (376 MHz, CDCl3, 298K): -81.34 (3F, t, J = 9.97 Hz), -111.73 (2F, quartet, J = 12.91 Hz), -121.88 (2F, m), -122.31 (8F, m), -123.25 (2F, m), -123.68 (2F, m), -126.67 (2F, m)

IR (neat, cm⁻¹): 3057.76, 2224.79, 1655.25, 1591.32, 1204.77, 1147.00, 809.98

Synthesis of 4-{4-[(1E)-3,3,4,4,5,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosfluorododec-1-en-1-yl]phenyl}benzonitrile (n = 10)

A mixture of perfluoro n-heptyl iodide (2.50 gm, 5.0 mmol), 4-(4-iodophenyl)benzonitrile, (1.50 gm, 5.0 mmol), Cu powder (1.0 gm, 16.0 mmol), DMSO (2 ml) and C₆F₆ (5 ml) was stirred for 7 hours at 90°C (bath temperature) under nitrogen. The mixture was cooled and it turned into an off white waxy cake which was dissolved in isooctane (100 ml) with heating. Montomorrilonite
K-10 clay was added to the warm mixture with stirring and it was filtered by gravity through a fluted filter paper. The filtrate was cooled, concentrated and the product was isolated by suction filtration as white crystals. This was dissolved in diethyl ether (20 ml) and silica gel (5 gm) was added. The solvent was removed under reduced pressure and the residue was placed on the top of a silica gel column. The column was eluted with a mixture of 10% EtOAc, 90% hexanes and the major band was collected and the solvent was removed under reduced pressure. The residue was recrystallized from isooctane to obtain the desired product as shiny white crystals. (1.74 gm, 64% yield). Melting point 120.4°C

$^1$H NMR (400MHz, CDCl$_3$, 300K): 7.80 (2H, d, $J = 8.56$ Hz), 7.74 (6H, m)
$^{13}$C NMR (100MHz, CDCl$_3$, 300K): 144.01, 142.85, 132.81, 127.98, 127.69, 127.51, 118.56, 112.09.
$^{19}$F NMR (376 MHz, CDCl$_3$, 300K): $-81.25$ (3F, t, $J = 9.91$ Hz), $-111.28$ (2F, t, $J = 14.41$Hz), $-121.72$ (2F, m), $-122.22$ (2F, m), $-122.48$ (2F, m), $-123.21$ (2F, m), $-126.60$ (2F, m).
IR (neat, cm$^{-1}$): 2227.61, 1608.02, 1497.31, 1197.82.

4-[4-(1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluorooctyl)phenyl]benzonitrile (1d)

Yield = 1.36 gm (46%), Melting point: 124 °C
$^1$H NMR (CDCl$_3$, 400 MHz, 298K): 7.80 (2H, d, $J = 8.66$ Hz), 7.76–7.71 (6H, m)
$^{13}$C NMR (CDCl$_3$, 400 MHz, 298K): 144.44, 142.85, 132.80, 127.98, 127.69, 127.51, 118.55, 112.09
$^{19}$F NMR (376 MHz, CDCl$_3$, 298K): -81.40 (3F, t, $J$ = 9.92 Hz), -111.43 (2F, t, $J$ = 14.49 Hz), -121.82 (2F, m), -122.44 (6F, m), -123.33 (2F, m), -126.73 (2F, m)

IR (neat, cm$^{-1}$): 2227.7, 1608.67, 1196.76, 1145.04, 1113.24, 942.68, 817.01.

4-[4-(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)phenyl]benzonitrile (1b)

Yield = 1.14 gm (46%), Melting point: 100 °C

$^1$H NMR (CDCl$_3$, 400 MHz, 298K): 7.80 (2H, d, $J$ = 8.52 Hz), 7.76–7.71 (6H, m)

$^{13}$C NMR (CDCl$_3$, 400 MHz, 298K): 144.01, 142.86, 132.80, 127.98, 127.69, 127.51, 118.55, 112.09

$^{19}$F NMR (376 MHz, CDCl$_3$, 298K): -81.43 (3F, t, $J$ = 10.00 Hz), -111.44 (2F, t, $J$ = 13.98 Hz), -122.04 (2F, m), -122.40 (2F, m), -123.43 (2F, m), -126.77 (2F, m)

IR (neat, cm$^{-1}$): 2227.21, 1608.02, 1194.29, 1141.07, 819.08

4-[4-(1,1,2,2,3,3,4,4,5,5,5-undecafluoropentyl)phenyl]benzonitrile (1a)

Yield = 0.75 gm (36%), melting point: 93 °C

$^1$H NMR (CDCl$_3$, 400 MHz, 298K): 7.80 (2H, d, $J$ = 8.56 Hz), 7.76–7.71 (6H, m)

$^{13}$C NMR (CDCl$_3$, 400 MHz, 298K): 144.01, 142.86, 132.81, 127.98, 127.68, 127.51, 118.55, 112.09

$^{19}$F NMR (376 MHz, CDCl$_3$, 298K): -81.41 (3F, t, $J$ = 9.93 Hz), -111.48 (2F, t, $J$ = 15.04 Hz), -122.61 (2F, m), -122.83 (2F, m), -126.82 (2F, m)

IR (neat, cm$^{-1}$): 2228.00, 1607.21, 1358.74, 1239.63, 1193.57, 1132.14, 823.27, 724.56
Synthetic route for compounds in Class 3

Synthesis of 4-[4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoroctyl)phenyl]benzonitrile (3b)

(Representative example for the synthesis of compounds with general structure 3)

Synthesis of 1-phenyl-4-[(1E)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoroct-1-en-1-yl]benzene (iv, n = 6)

In a 250 ml round bottom flask 4-bromobiphenyl (1.15 gm, 5.0 mmol), perfluorohexyl(ethylene) (3.45 gm, 10.0 mmol) and NaOAc (1.558 gm, 19.0 mmol) was added to anhydrous DMF (15 ml). Hermann’s palladacycle (182 mg, 0.19 mmol) was added and the mixture was stirred under nitrogen atmosphere at 125°C for 18 hours when all the bromobiphenyl was consumed (monitored through GCMS). The reaction mixture was cooled to room temperature and water (400 ml) was added. The mixture was filtered by suction filtration and the residue was dissolved in boiling isooctane (150 ml). Montmorillonite-K10 (3 gm) was added to the boiling solution and the mixture was filtered while hot. The filtrate was concentrated when a off-white material crystallized out. This was separated through suction filtration to obtain the desired product as
off-white powder. (1.29 gm, 52% yield). The material was pure enough to carry on to the next step. Melting point: 100-102 °C

$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 7.62 (6H, m), 7.45 (3H, m), 7.24 (1H, d, $J = 16.36$ Hz) 6.26 (1H, quartet, $J = 12.35$ Hz)

$^{13}$C NMR (CDCl$_3$, 298 K, 100 MHz): 128.92, 128.14, 127.89, 127.62, 127.06

$^{19}$F NMR (376 MHz, CDCl$_3$, 298K): -81.42 (3F, t, $J = 9.99$ Hz), -111.61 (2F, quartet, $J = 11.88$ Hz), -122.21 (2F, m), -123.48 (2F, m), -123.81 (2F, m), -126.78 (2F, m)

IR (neat, cm$^{-1}$): 3035.10, 1738.19, 1488.38, 1230.73, 1189.42, 1120.01, 977.43, 765.24

1-[(1E)-3,3,4,4,5,5,6,6-nonafluorohex-1-en-1-yl]-4-phenylbenzene (n = 4)

Yield = 1.13 gm (57%), Melting point: 95-97 °C

$^1$H NMR (CDCl$_3$, 400 MHz, 298K): 7.71–7.54 (6H, m), 7.53–7.36 (3H, m), 7.24 (1H, d, $J = 16.16$ Hz), 6.26 (1H, quartet, $J = 12.36$ Hz)

$^{13}$C NMR (CDCl$_3$, 400 MHz, 298K):

143.05, 139.32, 132.45, 131.86, 128.92, 128.14, 127.90, 127.62, 127.07, 114.06

$^{19}$F NMR (376 MHz, CDCl$_3$, 298K): -81.68 (3F, t, $J = 9.99$ Hz), -111.83 (2F, quartet, $J = 11.85$ Hz), -124.70 (2F, m), -126.30 (2F, m)

IR (neat, cm$^{-1}$): 3407.48 1655.50, 1353.59, 1218.53, 1127.60, 866.64, 761.10
1-[(1E)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodec-1-en-1-yl]-4-phenylbenzene  
(n = 8)

Yield = 1.26 gm (56%), Melting point: 109-110 °C

$^1$H NMR (DMSO-d6, 400 MHz, 298K): 7.82–7.67 (6H, m), 7.53–7.34 (4H, m), 6.64 (1H, quartet, $J = 13.97$ Hz)

$^{13}$C NMR (CDCl$_3$, 400 MHz, 298K): 142.67, 140.38, 139.83, 132.86, 129.35, 129.09, 128.30, 127.55, 127.13, 114.22

$^{19}$F NMR (376 MHz, CDCl$_3$, 298K): -81.38 (3F, t, $J = 9.95$ Hz), -111.59 (2F, quartet, $J = 12.49$ Hz), -121.97 (2F, m), -122.5 (4F, m), -123.31 (2F, m), -123.74 (2F, m), -126.70 (2F, m)

IR (neat, cm$^{-1}$): 3091.99, 1655.52, 1488.43, 1195.78, 1146.93, 1112.65, 974.10, 761.28

1-[(1E)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosafluorododec-1-en-1-yl]-4-phenylbenzene (n = 10)

Yield = 2.79 gm (80%), Melting point: 128-129 °C

$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 7.70-7.55(6H, m), 7.53-7.37 (4H, m), 6.26 (1H, q, $J = 16.12$ Hz)

$^{13}$C NMR (CDCl$_3$, 400 MHz, 298K):
143.04, 140.07, 139.26, 128.92, 128.14, 127.89, 127.62, 127.07, 114.17

$^{19}$F NMR (376 MHz, CDCl$_3$, 298K): -81.38 (3F, t, $J = 9.97$ Hz), -111.59 (2F, quartet, $J = 12.27$ Hz), -121.95 (2F, m), -122.37 (8F, m), -123.31 (2F, m), -123.75 (2F, m), -126.72 (2F, m)

IR (neat, cm$^{-1}$): 2931.73, 2089.50, 1639.12, 1205.71, 1150.83, 974.63, 901.31
Synthesis of 1-phenyl-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoroctyl)benzene (v, n = 6)

To a degassed solution of 1-phenyl-4-[(1E)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoroct-1-en-1-yl]benzene (1.24 gm, 2.5 mmol) in EtOAc (15 ml) was added 10% palladium on charcoal (126.5 mg, 4.6 mol%) and the solution was stirred at room temperature under H₂ atmosphere (1 atm) for 18 hours when full conversion of the starting material occurred (by GC-MS). Diethyl ether (150 ml) was added to the mixture and it was passed through a short Celite pad. The solvent was removed from the filtrate under reduced pressure to obtain the desired product as white solid (0.9 gm, 72% yield). The material was pure enough to carry on to the next step.

Melting point: 54-55 °C

¹H NMR (CDCl₃, 298 K, 400 MHz): 7.59 (4H, m), 7.46 (2H, t, J = 7.52 Hz), 7.37 (1H, m), 7.32 (2H, d, J = 8.24 Hz), 2.99 (2H, m), 2.44 (2H, m)

¹³C NMR (CDCl₃, 298 K, 100 MHz): 140.74, 139.80, 138.15, 128.79, 128.72, 127.62, 127.52, 127.29, 127.03, 32.96, 26.08

¹⁹F NMR (376 MHz, CDCl₃, 298K): -81.39 (3F, t, J = 9.95 Hz), -115.16 (2F, m), -122.45 (2F, m), -123.44 (2F, m), -124.06 (2F, m), -126.72 (2F, m)

IR (neat, cm⁻¹): 3028.72, 1488.75, 1183.89, 1139.85, 761.04, 689.11

1-(3,3,4,4,5,5,6,6,6-nonfluorohexyl)-4-phenylbenzene (n = 4)

Colorless oil, yield = 0.8 gm (80%)

¹H NMR (CDCl₃, 298 K, 400 MHz): 7.59 (4H, m), 7.46 (2H, t, J = 7.56 Hz), 7.37 (1H, m), 7.32 (2H, d, J = 8.24 Hz), 2.99 (2H, m), 2.44 (2H, m)

¹³C NMR (CDCl₃, 400 MHz, 298K): 128.79, 128.72, 127.52, 127.29, 127.03, 32.87, 26.1

75
\[ ^{19}\text{F NMR (376 MHz, CDCl}_3, 298\text{K): } -81.62 \text{ (3F, m), -115.41 (2F, m), -125.01 (2F, m), -126.58 (2F, m)} \]

IR (neat, cm\(^{-1}\)): 3031.06, 1487.75, 1217.01, 1131.39, 838.25, 736.04, 695.48

1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodecyl)-4-phenylbenzene (n = 8)

Yield = 1.19 gm (94%), Melting point: 82-84 °C

\[ ^{1}\text{H NMR (CDCl}_3, 298 \text{ K, 400 MHz): 7.60 (4H, m), 7.47 (2H, t, } J = 7.54 \text{ Hz), 7.37 (1H, m), 7.32 (2H, d, } J = 8.28 \text{ Hz), 2.99 (2H, m), 2.44 (2H, m)} \]

\[ ^{13}\text{C NMR (CDCl}_3, 400 \text{ MHz, 298K): 128.79, 128.72, 127.52, 127.29, 127.03, 32.98, 26.09} \]

\[ ^{19}\text{F NMR (376 MHz, CDCl}_3, 298\text{K): } -81.37 \text{ (3F, t, } J = 9.99 \text{ Hz), -115.16 (2F, quintet, } J = 16.17), -122.34 \text{ (6F, m), -123.28 (2F, m), -124.02 (2F, m), -126.68 (2F, m)} \]

IR (neat, cm\(^{-1}\)): 3031.33, 1488.88, 1198.05, 1145.09, 957.81, 750.10

1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosfluorododecyl)-4-phenylbenzene (n = 10)

Yield = 2.25 gm (90%), 100-102 °C

\[ ^{1}\text{H NMR (CDCl}_3, 298 \text{ K, 400 MHz): 7.56 (4H, m), 7.43 (2H, t, } J = 7.54 \text{ Hz), 7.34 (1H, m), 7.29 (2H, d, } J = 8.28 \text{ Hz), 2.96 (2H, m), 2.41 (2H, m)} \]

\[ ^{13}\text{C NMR (CDCl}_3, 100 \text{ MHz, 298 K): 140.73, 139.78, 138.16, 128.78, 128.71, 127.51, 127.28, 127.02, 32.98, 26.09} \]

\[ ^{19}\text{F NMR (376 MHz, CDCl}_3, 298\text{K): } -81.40 \text{ (3F, t, } J = 10.01 \text{ Hz), -115.26 (2F, m), -122.37 (10F, m), -123.31 (2F, m), -124.11 (2F, m), -126.75 (2F, m)} \]
IR (neat, cm⁻¹): 2927.53, 2093.07, 1633.15, 1205.32, 1148.42, 883.99, 755.65

**Synthesis of 1-bromo-4-[4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)phenyl]benzene**

(vi, n = 6)

In a 100 ml round bottom flask equipped with stirbar 1-phenyl-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)benzene (0.75 gm, 1.5 mmol) was dissolved in a mixture of trifluoroacetic acid (4 ml) and chloroform (2 ml) and the mixture was cooled to 0 °C. In this solution, Br₂ (0.242 gm, 1.5 mmol) dissolved in chloroform (2 ml) was added dropwise in such a rate that the temperature of the solution is maintained at 0 °C. The solution was stirred for 6 hours when the GC showed complete conversion of starting material. The solvent was removed under reduced pressure to obtain a gummy mass. Ethanol (25 ml) was added when shiny plates precipitated. This was separated by suction filtration and washed with cold ethanol to obtain the desired product as shiny plates (0.408 gm, 47% yield). Melting point: 99-102 °C

\[ ^1H \text{ NMR (CDCl}_3, 298 K, 400 MHz): 7.58 \text{ (2H, d, } J=8.36 \text{ Hz), 7.54 \text{ (2H, d, } J=8.03 \text{ Hz), 7.46 \text{ (2H, d, } J=8.36 \text{ Hz), 7.32 \text{ (2H, d, } J=8.03 \text{ Hz), 2.99 \text{ (2H, m), 2.43 \text{ (2H, m)}}} \]

\[ ^13C \text{ NMR (CDCl}_3, 298 K, 100 MHz): 139.62, 138.63, 131.90, 128.87, 128.60, 127.31, 121.56, 32.90, 26.10 \]

**1-bromo-4-[4-(3,3,4,4,5,5,6,6,6-nonafluorohexyl)phenyl]benzene (n = 4)**

Starting materials: 1-(3,3,4,4,5,5,6,6,6-nonafluorohexyl)-4-phenylbenzene (0.75 gm, 1.87 mmol), Br₂ (0.3 gm, 1.87 mmol)

Yield = 0.66 gm (89%), Melting point: 89-90 °C
\(^1\)H NMR (CDCl\(_3\), 298 K, 400 MHz): 7.58 (2H, d, \(J = 8.6\) Hz), 7.54 (2H, d, \(J = 8.24\) Hz), 7.46 (2H, d, \(J = 8.6\) Hz), 7.31 (2H, d, \(J = 8.24\) Hz), 2.99 (2H, m), 2.43 (2H, m)

\(^{13}\)C NMR (CDCl\(_3\), 298 K, 100 MHz):

\begin{align*}
139.61, &\ 138.62,\ 138.54,\ 131.90,\ 128.87,\ 128.59,\ 127.31,\ 32.81,\ 26.09
\end{align*}

\(^{19}\)F NMR (376 MHz, CDCl\(_3\), 298K): \(-81.63\) (3F, m), \(-115.39\) (2F, m), -125.01 (2F, m), -126.58 (2F, m)

IR (neat, cm\(^{-1}\)): 3030.65, 1480.40, 1217.23, 1130.07, 809.87

1-bromo-4-[4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodecyl)phenyl]benzene

\((n = 8)\)

Yield = 0.894 gm (79%), Melting point: 122-125 °C

\(^1\)H NMR (CDCl\(_3\), 298 K, 400 MHz): 7.58 (2H, d, \(J = 8.6\) Hz), 7.53 (2H, d, \(J = 8.28\) Hz), 7.46 (2H, d, \(J = 8.6\) Hz), 7.31 (2H, d, \(J = 8.28\) Hz), 2.98 (2H, m), 2.43 (2H, m)

\(^{13}\)C NMR (CDCl\(_3\), 298 K, 100 MHz): 139.62, 138.63, 138.54, 131.90, 128.86, 128.59, 127.30, 121.56, 32.92, 26.11

\(^{19}\)F NMR (376 MHz, CDCl\(_3\), 298K): \(-81.36\) (3F, t, \(J = 9.97\) Hz), \(-115.12\) (2F, m), \(-122.34\) (6F, m), \(-123.27\) (2F, m), \(-123.99\) (2F, m), \(-126.66\) (2F, m)

IR (neat, cm\(^{-1}\)): 3028.91, 1480.98, 1198.90, 1145.20, 808.5
1-bromo-4-[4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosfluorododecyl)phenyl]benzene (n = 10)

Yield = 1.79 gm (81%), Melting point: 136-138 °C

$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 7.58 (2H, d, $J = 8.64$ Hz), 7.53 (2H, d, $J = 8.28$ Hz), 7.46 (2H, d, $J = 8.60$ Hz), 7.31 (2H, d, $J = 8.32$ Hz), 2.98 (2H, m), 2.43 (2H, m)

$^{13}$C NMR (CDCl$_3$, 100 MHz, 298 K):

139.62, 138.64, 138.54, 131.90, 128.86, 128.59, 127.30, 121.7, 32.8, 26.4

$^{19}$F NMR (376 MHz, CDCl$_3$, 298K): -81.36 (3F, t, $J = 9.95$ Hz), -115.14 (2F, m), -122.31 (10F, m), -123.27 (2F, m), -124.03 (2F, m), -126.7 (2F, m)

IR (neat, cm$^{-1}$): 3030.79, 1481.93, 1205.02, 1148.47, 882.62, 809.67

**Synthesis of 4-[4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)phenyl]benzonitrile (3b)**

In a 100 ml round bottom flask 1-bromo-4-[4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)phenyl]benzene (0.5 gm, 0.86 mmol) was dissolved in anhydrous DMF (5 ml) and CuCN (0.089 gm, 1 mmol) was added. The solution was refluxed under nitrogen atmosphere for 8 hours when complete conversion of starting materials occurred (TLC with 10% EtOAc, 90% hexanes as eluent). At this point the reaction was cooled down to room temperature and a solution of FeCl$_3$ and HCl in water (140 ml, prepared by dissolving 0.2 gm of hydrated FeCl$_3$ and 50 ml of concentrated HCl in 300 ml of water) was added. The solution was stirred at 60°C for 10 minutes when a white precipitate appeared and the color of the solution turned light blue. The solution was extracted with diethyl ether (75 ml × 3) and the solvent was removed from the combined organic extracts under reduced pressure and the residue was absorbed on silica gel.
This was placed on the top of a silica gel column and was eluted with a mixture of 10% EtOAc, 90% hexanes as eluent. The major band was collected to obtain the final product as a slight yellow solid. This was recrystallized from ethanol to obtain the final product (0.314 gm, 70% yield).

Transitions: Cr 62 SmA 126 I 124 SmA 39 Cr

$^{1}$H NMR (CDCl$_3$, 298 K, 400 MHz): 7.75 (2H, d, $J = 8.56$ Hz), 7.69 (2H, d, $J = 8.56$ Hz), 7.58 (2H, d, $J = 8.24$ Hz), 7.36 (2H, d, $J = 8.24$ Hz), 3.01 (2H, m), 2.44 (2H, m)

$^{13}$C NMR (CDCl$_3$, 100 MHz, 298 K):
145.16, 139.80, 137.71, 132.64, 129.10, 127.61, 127.58, 118.89, 110.96, 32.80, 26.16

$^{19}$F NMR (376 MHz, CDCl$_3$, 298K): −81.39 (3F, t, $J = 9.93$ Hz), −115.12 (2F, m), -122.45 (2F, m), -123.44 (2F, m), -124.05 (2F, m), -126.71 (2F, m)

IR (neat, cm$^{-1}$): 3046.99, 2224.27, 1605.62, 1495.20, 1184.87, 1140.44, 811.58, 713.86

4-[4-(3,3,4,4,5,6,6,6-nonfluorohexyl)phenyl]benzonitrile (3a)

Starting materials: 1-bromo-4-[4-(3,3,4,4,5,6,6,6-nonfluorohexyl)phenyl]benzene (0.1 gm, 0.208 mmol), CuCN (0.022 gm, 0.25 mmol), DMF (3 ml)

Yield = 50 mg (57%), Transitions: Cr 59 SmA 81 I 80 SmA 20 Cr

$^{1}$H NMR (CDCl$_3$, 298 K, 400 MHz): 7.73 (2H, d, $J = 8.6$ Hz), 7.67 (2H, d, $J = 8.6$ Hz), 7.56 (2H, d, $J = 8.28$ Hz), 7.34 (2H, d, $J = 8.28$ Hz), 2.99 (2H, m), 2.42 (2H, m)

$^{13}$C NMR (CDCl$_3$, 100 MHz, 298 K):
145.15, 139.79, 137.71, 132.63, 129.09, 127.61, 127.58, 118.88, 110.97, 32.71, 26.14
$^{19}$F NMR (376 MHz, CDCl$_3$, 298K): −81.62 (3F, m), -115.35 (2F, m), -124.99 (2F, m), -126.58 (2F, m)

IR (neat, cm$^{-1}$): 3043.15, 2225.31, 1606.35, 1212.24, 1132.36, 1007.96, 788.72, 717.84

4-[4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)phenyl]benzonitrile (3c)

Yield = 0.144 gm (32%), Transitions: Cr 77 SmC 118 SmA 153 I 151 SmA 111 SmC 70 Cr

$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 7.75 (2H, d, $J = 8.64$ Hz), 7.69 (2H, d, $J = 8.60$ Hz), 7.58 (2H, $J = 8.28$ Hz), 7.36 (2H, $J = 8.32$ Hz), 3.01 (2H, m), 2.44 (2H, m)

$^{13}$C NMR (CDCl$_3$, 100 MHz, 298 K):

145.25, 139.90, 137.80, 132.72, 129.18, 127.70, 127.67, 118.97, 111.07, 32.91, 26.26

$^{19}$F NMR (376 MHz, CDCl$_3$, 298K): −81.36 (3F, t, $J = 9.99$ Hz), −115.10 (2F, m), −122.33 (6F, m), −123.29 (2F, m), −124.01 (2F, m), -126.67 (2F, m)

IR (neat, cm$^{-1}$): 3057.56, 2233.75, 1496.66, 1196.79, 1143.98, 955.57, 810.93

4-[4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosafluorododecyl)phenyl]benzonitrile (3d)

Yield = 0.52gm, (45%), Transitions: Cr 105 SmC 140 SmA 169 I 167 SmA 134 SmC 98 Cr

$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 7.72 (2H, d, $J = 8.81$ Hz), 7.66 (2H, d, $J = 8.81$ Hz), 7.55 (2H, $J =7.71$ Hz), 7.33 (2H, $J = 8.26$ Hz), 2.98 (2H, m), 2.42 (2H, m)

$^{13}$C NMR (CDCl$_3$, 100 MHz, 298 K): 145.15, 139.81, 137.71, 132.63, 129.09, 127.61, 127.58, 118.88, 110.98, 32.82, 26.17
\(^{19}\text{F} \text{NMR} \) (376 MHz, CDCl\textsubscript{3}, 298K): -81.35 (3F, m), -115.08 (2F, m), -122.30 (10F, m), -123.25 (2F, m), -124.02 (2F, m), -126.66 (2F, m)

IR (neat, cm\(^{-1}\)): 3057.15, 2233.45, 1496.63, 1204.92, 1146.41, 812.02

3.6 Acknowledgements

The enlightening discussions with Dr. Alexander Seed and his training on identifying the different liquid crystalline phases is gratefully acknowledged.
3.7 References


Chapter 4
Laterally chlorinated terphenyls as high-birefringence candidates for midwave infrared applications

4.1 Introduction

Long wavelength radiation is preferred in many applications as the scattering is lower compared to that in the visible spectrum. When the data needs to be transmitted wirelessly over long distance, the degrading effect of scattering can become especially very important. Infrared lasers are currently widely used in bar-code scanners, laser rangefinders and topology mapping applications\textsuperscript{12}. Typically, the direction of the laser beam is altered by mechanically moving a mirror or a lens. But this process can impose severe limitations on critical performance parameters (device longevity, precision, response time, etc.). As an alternative, electro-optic control of the direction of the beam is highly desired, as these devices do not need mechanical movement of any component to steer the laser beam. Liquid crystals can be very attractive for these applications as these materials can be designed to have high birefringence in the infrared region\textsuperscript{95}. Also liquid crystals can be ideal materials for these applications as precise control of birefringence can be achieved with voltage variation\textsuperscript{12,96}. Electro-optic modulators that use lithium niobate/potassium dihydrogen phosphate crystals have large size and high power consumption\textsuperscript{97}. Compared to this, liquid crystal materials possess the advantage of drastically
reducing the power consumption, size and weight of a device and these have been successfully applied in devices for laser beam steering\textsuperscript{10} and dynamic scene projectors for infrared seekers\textsuperscript{11}. Although liquid crystal materials can potentially deliver these advantages, they currently suffer from the drawback of inherent absorption loss due to the existence of molecular absorption bands as well as their harmonics and overtones. For example, several absorption bands exist in the mid-infrared region (3-5 \( \mu \)m) due to common structure features found in liquid crystals such as CH, CH\(_2\), CH\(_3\) and CN. Even in the off-resonance spectral regions, the baseline absorption coefficient can have a very high value (up to \( \alpha \sim 10/cm \))\textsuperscript{98} due to contributions from harmonic and combination bands from many sources. If the optical path is sufficiently long this level of absorption loss becomes significant.

To address the absorption issues several strategies have been adopted and the replacement of hydrogen atoms in the liquid crystal molecule with heavier atoms was one of the earliest fixes that was examined. Deuterium is attractive as a replacement for hydrogen. When the hydrogen atoms of 5CB were replaced by deuterium the absorption loss in the midwave infrared region was significantly reduced\textsuperscript{49}. But the synthesis procedure required to introduce significant deuterium content is tedious and less viable from a practical point of view. Fluorine would appear to be another interesting option as a replacement of hydrogen atoms in known nematic liquid crystals. So, fluorine is not expected to disturb the molecular interactions based on excluded volume\textsuperscript{99}. However, with a high extent of fluorination nematic properties can be compromised. For example, significant fluorination of the aliphatic chains (such as by creating blocks of –CF\(_2\)– units) promotes smectic phases due to increased rigidity\textsuperscript{100}. Even semifluorinated n-alkanes devoid of any ring structure can possess smectic phases due to the
decrease in flexibility\textsuperscript{79}. In Infrared device applications a nematic phase has often been preferred as the viscosities are lowest and alignment of the liquid crystal layer is facilitated.

Another strategy to address absorption loss and to increase the response time\textsuperscript{101} is to use materials possessing high birefringence. The cell gap can be lowered if high birefringence materials are used.

This approach can be justified from the equation

\[ \delta = 2\pi d\Delta n/\lambda \]

Here \( \delta \) = phase retardation (the difference in phase of the ordinary and extraordinary ray), \( d \) = cell gap, \( \Delta n \) = birefringence of the medium, \( \lambda \) = wavelength of the radiation incident on the LC layer. When other parameters are constant, an increase of birefringence will enable the use of thinner cells. High phase retardation is required to obtain a large beam steering angle\textsuperscript{1}.

Thinner cells can help address the problem, but the alkyl chains in the liquid crystals still contribute significantly towards absorption in the midwave infrared region. The best solution for this problem will be a molecule that will possess high birefringence and also the absorption in the midwave infrared region will be very low.

<table>
<thead>
<tr>
<th>Infrared Region</th>
<th>Wavelength (\mu m)</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Near-infrared</td>
<td>0.75-1.4</td>
<td>Fiber optic telecommunications, night vision devices</td>
</tr>
<tr>
<td>Short-Wavelength infrared</td>
<td>1.4-3</td>
<td>Telecommunications</td>
</tr>
<tr>
<td>Mid-wavelength infrared</td>
<td>3-8</td>
<td>Heat seekers, bar-code scanners, rangefinders, topology mapping</td>
</tr>
<tr>
<td>Long-wavelength</td>
<td>8-15</td>
<td>Thermal imaging</td>
</tr>
</tbody>
</table>

\textbf{Table 4.1}: Different regions of infrared spectrum and their applications\textsuperscript{102,103}
4.2 Results and discussion

As molecular birefringence is proportional to the anisotropy of conjugation in the molecule, oligophenyls are attractive options for use in the liquid crystal core. Oligophenyls without any lateral substitution are rigid rodlike structures that possess significant anisotropic π-electron delocalization. The flexibility is minimal in these kinds of structures as the only internal flexibility is due to the rotation of the individual rings about the para-substituted C-C bonds. With lateral substitution of polarizable groups and/or installation of polarizable end groups the anisotropy of π-electron delocalization can be changed. Lateral substitution of bulky groups restricts the rotation of the phenyl rings and also lowers the melting point of the materials. All these features allow these molecules to possess high birefringence along with a low melting point. The terphenyl has been used as liquid crystal core previously. In general, liquid crystals containing a terphenyl core with no lateral substitution have high T_{N-I} values (in excess of 200°C). For many device applications, the liquid crystals should have a nematic phase near room temperature.

Bulky lateral substitution in a terphenyl moiety can have a large impact in the packing of these molecules and electrostatic interactions are also altered depending on the nature of the substituent. Also, by disturbing the planarity of the terphenyl core, the packing of the molecule can be disturbed, thus reducing the melting point of the molecule. Liquid crystals with high dielectric anisotropy respond better to an external electric field and align themselves in such a way as to minimize the effect of the external field. Halogens can impart a significant dipole in a liquid crystal. Also, as a lateral substituent, they can provide the steric bulk to disturb packing in the material. The order of steric bulk among halogens is I > Br > Cl > F. The halogens can also
significantly alter the intermolecular electrostatic interactions that can have pronounced effect on mesophase properties. In the current work, chlorine was chosen as the lateral substitution as the Cl atom can provide the necessary steric bulk required to force the phenyl rings in the terphenyl out of planar conformation\textsuperscript{115} while creating a useful value of dielectric anisotropy that facilitates the alignment of molecules by applying an external field in liquid crystal cells.

Replacing some of C-H bonds with C-Cl bonds also reduces the infrared absorption due to the diminution of the in-plane deformation of the phenyl ring. The absorption bands due to this deformation (skeletal vibrations involving C-C stretching in the ring) appear around 1600-1585 cm\textsuperscript{-1} and 1500-1400 cm\textsuperscript{-1}. When some hydrogens are replaced by Cl or F, the resultant mass of the oscillator increases, thus decreasing the frequency\textsuperscript{40}. Introduction of chlorine as a lateral substituent of the molecule can also introduce significant dielectric anisotropy in the material\textsuperscript{1}. Chlorinated liquid crystals have been studied previously\textsuperscript{116-118}, but most of them had ester or –CH\textsubscript{2}-CH\textsubscript{2}- linking groups. These linking groups are not very useful in promoting high birefringence. In this work we report through conjugated terphenyls laterally substituted with chlorine moiety, which might confer birefringence that is fit for infrared applications. The resonance absorption wavelengths of chlorinated liquid crystals are longer than its fluorinated analogue. As a result the chlorinated liquid crystals should have higher birefringence than the fluorinated analogues\textsuperscript{117}. Also, the C-Cl bond is relatively chemically inert compared to carbon bonds to Br and I.

To mitigate the absorption in the midwave infrared region, substitution of hydrogen in a liquid crystalline molecule by a heavier atom is required. Deuterium is heavier than hydrogen and it shifts the absorption due to the alkyl chain and aromatic C-H (although the absorption due to the
latter is much lower) from ~3.5 µm to ~4.8 µm, which is still in the midwave infrared region.

The vibration frequencies for C-F occurs in the range of 7-9 µm and far away from the mid-IR, but unfortunately now some overtones appear in the midwave infrared region thus reducing the significance of these materials in MWIR applications\(^1\). An example of this overtone vibration is given in Figure 4.1. The absorption of 5CB was compared with a fluorinated mixture\(^1\) UCF-1. The overtone vibration for C-F stretching appears around 2400 cm\(^{-1}\).

![Figure 4.1: Comparison of infrared spectra\(^1\) of 5CB and UCF-1 (courtesy: Prof. Shin-Tson Wu, University of Central Florida)](image)

The absorption due to C-Cl occurs in the range of 600-800 cm\(^{-1}\), which makes the second harmonic longer than 6 µm. Thus, for midwave infrared applications chlorination might be anticipated to be superior to deuteration or fluorination\(^1\).

Much less is known about the influence of chlorination on the physical properties of liquid crystals than is known about the analogous protio- and fluoro- derivatives. Here we investigate the effect of chlorine as a lateral substituent as well as an end group on liquid crystal behavior in
a series of terphenyls. One of the criteria of selection of the chloro substitution pattern is the relative ease of synthesis.

4.3 General synthesis scheme of the chlorinated terphenyl liquid crystals

![Figure 4.2: Synthesis of chlorinated terphenyls with an alkyl tail (X = F, CF$_3$, OCF$_3$, Cl, CN, Y = F, Cl, H, Z = F, H)](image-url)

In this study the syntheses of the terphenyls were accomplished by using selective Suzuki-Miyaura coupling. The order of reactivity of the carbon-halogen bonds towards Suzuki coupling is C-I > C-Br >> C-Cl. The carbon chlorine bond is generally inert under the normal Suzuki reaction conditions. This strategy was used to synthesize the biphenyl \( b \) (Figure 4.2) from commercially available compound \( a \). The material \( b \) was then reacted with several boronic acids (again, often commercially available) to generate liquid crystals with terphenyl cores (Table 4.2). The placement of the chlorine atom(s) in the terphenyls is thus dictated by the availability of the relevant chlorine containing starting materials. There are two unique positions in the middle ring of the terphenyl for lateral chlorination. Two different isomers of
bromochloriodobenzene (fortunately both commercially available) are needed for the synthesis of the two different isomers (Figure 4.3).

**Figure 4.3:** Synthesis of two isomers of a laterally chlorinated material dictated by the sequence of Suzuki couplings on two starting materials
<table>
<thead>
<tr>
<th>Compound Identifier</th>
<th>Structure</th>
<th>Phase transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Structure 1" /></td>
<td>Cr 48.3 (N 30.1) I</td>
</tr>
<tr>
<td>2</td>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>Cr 72 N 98 I</td>
</tr>
<tr>
<td>3</td>
<td><img src="image3.png" alt="Structure 3" /></td>
<td>Cr 81 (N 75) I</td>
</tr>
<tr>
<td>4</td>
<td><img src="image4.png" alt="Structure 4" /></td>
<td>Cr 51 N (6.1) I</td>
</tr>
<tr>
<td>5</td>
<td><img src="image5.png" alt="Structure 5" /></td>
<td>Nematic below room temperature</td>
</tr>
<tr>
<td>6</td>
<td><img src="image6.png" alt="Structure 6" /></td>
<td>Nematic below room temperature</td>
</tr>
<tr>
<td>7</td>
<td><img src="image7.png" alt="Structure 7" /></td>
<td>Cr 50 I</td>
</tr>
<tr>
<td>8</td>
<td><img src="image8.png" alt="Structure 8" /></td>
<td>Cr 71 (N 65) I</td>
</tr>
<tr>
<td>9</td>
<td><img src="image9.png" alt="Structure 9" /></td>
<td>Cr 78 I</td>
</tr>
<tr>
<td>10</td>
<td><img src="image10.png" alt="Structure 10" /></td>
<td>Cr 108 I</td>
</tr>
<tr>
<td>11</td>
<td><img src="image11.png" alt="Structure 11" /></td>
<td>Cr 74 (N 41) I</td>
</tr>
<tr>
<td>12</td>
<td><img src="image12.png" alt="Structure 12" /></td>
<td>Nematic below room temperature</td>
</tr>
<tr>
<td>13</td>
<td><img src="image13.png" alt="Structure 13" /></td>
<td>Cr 95 (N 68)I</td>
</tr>
<tr>
<td>14</td>
<td><img src="image14.png" alt="Structure 14" /></td>
<td>Nematic below room temperature</td>
</tr>
<tr>
<td>15</td>
<td><img src="image15.png" alt="Structure 15" /></td>
<td>Liquid at room temperature, no mesophase</td>
</tr>
<tr>
<td>16</td>
<td><img src="image16.png" alt="Structure 16" /></td>
<td>Cr 50 I</td>
</tr>
</tbody>
</table>

Table 4.2: Mesogenic behavior of the laterally chlorinated terphenyls
Many of the materials in Table 4.2 have a nematic phase close to room temperature. Materials 5, 6, 12 and 14 appear to have a nematic phase below room temperature (from preliminary observation under polarized optical microscope) but the transition enthalpy is beyond the sensitivity of the DSC instrument that we have. The relationship of birefringence with polar end group$^{24}$ is NCS >> Cl > CN > F > OCF$_3$ > CF$_3$. Materials 2 and 3, with a cyano end group, have high anisotropy of conjugation that might give rise to high birefringence. Among the materials in Table 4.2, materials 8 and 12 are of particular interest as they have almost no absorption in the 4-5 µm range (Figure 4.4). Materials 8, 9, 10, 13 differ only by tail length. It was observed that both of the odd-numbered tailed analogues 8 and 13 had stable nematic phases. As the number of chlorine atoms introduced in lateral position increases, the nematic phase can pushed down much below room temperature (for materials 12 and 14 the transition temperatures were not conclusively determined due to the limitations of the DSC hardware). For material 15 the mesophase properties completely disappeared, the melting of the material from the solid state was observed by microscopy, and no liquid crystalline phases were observed. Materials 8 and 11 differ only by the position of the lateral chlorine but 11 had a nematic phase much closer to the room temperature. Materials 2 and 3, despite possessing attractive nematic phase stability, cannot be used in the midwave infrared applications due the occurrence of absorption due to C≡N stretching vibration in the 4-5 µm range. For materials 1 and 4, although the overtone vibration due to C-F stretch can appear in the midwave infrared region, it is very weak. Thus, given the attractive mesophase behavior of 1 and 4, they can become an important component in high birefringence mixtures.
In this work, lateral chlorination proved to be very productive in generating useful nematic phases. Future work will involve studying lateral chlorination in higher oligophenyls. Higher oligophenyls, having still higher longitudinal polarizability than the terphenyls may produce liquid crystals with still higher birefringence that might become useful for applications like infrared laser beam steering and construction of microwave antennas. Most of the materials mentioned in Table 4.2 have C5 tails, although some shorter tails were investigated to see the effect of tails on midwave infrared absorption.

![Figure 4.4: Comparison of IR spectra of 5CB and 8 (Table 4.2) in the 4-5 µm range (Courtesy: Prof. Shin-Tson Wu, University of Central Florida)](image)

The compounds 8 and 13 were attractive, as they did not have any fluorine as a structural component, which eliminated the problem of the appearance of overtone vibration due to C-F stretch. They were mixed in a 3:2 ratio to formulate a eutectic mixture (mix.1). This mixture has
a melting point of 48.3°C and a clearing point of 69.2°C and during the cooling cycle supercooling is observed and the mixture retains the nematic phase even at 0°C. It has a positive dielectric anisotropy of $\Delta \varepsilon = 7.82$ and a birefringence of $\Delta n \sim 0.20$. In the 4-5 µm region, mix.1 shows low absorption ($\alpha < 5 \text{ cm}^{-1}$). All of these properties make the aforesaid mixture attractive for infrared applications between 4-5 µm. More studies on the other materials are underway.

![Figure 4.5: Comparison of infrared spectra of 5CB and mix.1](image)

(Courtesy: Prof. Shin-Tson Wu, University of Central Florida)
The UV-Vis of materials 1, 3 and 8 were recorded and it was found that all three had absorption in the ultraviolet range (Figure 4.7). All three materials exhibited similar absorption behavior. The absorption of compound 3 was shifted towards longer wavelength compared to 1 and 8 as the cyano group in 3 offers a longer overall conjugation length in this molecule.
4.4 Conclusions

We have developed efficient synthetic methodology for the synthesis of a set of chlorinated terphenyl liquid crystals. These materials possess very attractive absorption properties in the midwave infrared region along with nematic phase close to room temperature. A mixture has been formulated which has low absorption ($\alpha < 5 \text{ cm}^{-1}$) in the 4-5 µm region. It also possesses high birefringence and modest positive dielectric anisotropy. These features make the mixture potentially applicable in devices that work in the 4-5 µm regime.

4.5 Acknowledgements

The mixture formulation as well as birefringence, visco-elastic coefficients and quantitative IR were measured by Prof. Shin-Tson Wu’s group at the University of Central Florida. We gratefully acknowledge the collaboration and contributions of the UCF group in this project.
4.6 Experimental

The $^1$H and $^{13}$C spectra were measured on a Bruker Avance 400 MHz spectrometer at 400.13, 100.61 MHz, respectively. The $^1$H and $^{13}$C NMR chemical shifts were referenced to TMS (0.0 ppm). The melting points were uncorrected. The progress of the reactions were monitored either by thin layer chromatography with plastic backed silica gel plates (Scientific adsorbents incorporated, Catalog # 79011), or by GC-MS [Finnigan trace GC ultra (Restek™ RTX-5 capillary column (30 m)) coupled with Finnigan PolarisQ mass spectrometer]. Infrared spectra were obtained using a Bruker Vector33 infrared spectrometer with an ATR probe. Differential scanning calorimetry (DSC) measurements were performed using a TA instruments differential scanning calorimeter 2920 at heating and cooling rates of 5°C per minute. Transition temperatures of the final products were measured using Mettler FP82HT hot-stage and FP90 control unit in conjunction with Nikon Eclipse E600 Pol polarizing microscope.

Some of the terphenyl compounds prepared here showed nematic behavior at or below room temperature as seen transiently under polarized optical microscope after cooling the slide containing liquid crystal to -78°C and letting it warm up in the microscope stage. Exact transition temperatures could not be determined due to hardware limitations.

**Synthesis of 1-bromo-2-chloro-4-(4-pentylphenyl)benzene**

![Chemical structure]

In a 500 ml round-bottom flask $\text{K}_2\text{CO}_3$ (3.45 gm, 25.0 mmol) was dissolved in $\text{H}_2\text{O}$ (40 ml) and 1,4-dioxane (100 ml) was added. This mixture was degassed by sonication under vacuum for 20
minutes and after that 4-pentylbenzeneboronic acid (2.028 gm, 10.56 mmol), 1-bromo-2-chloro-4-iodobenzene (3.348 gm, 10.56 mmol) and Pd(PPh₃)₂Cl₂ (160 mg, 3.0 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when GC-MS showed complete conversion of the starting material. At this point, the mixture was cooled down to room temperature, adsorbed on silica gel and was placed on the top of a silica gel column. The column was eluted with hexanes and the major band was separated. The solvent was removed under reduced pressure to obtain the desired product as colorless oil (2.06 gm, 58% yield).

IUPAC name: 1-bromo-2-chloro-4-(4-pentylphenyl)benzene

Molecular weight: 337.69

Molecular formula: C₁₇H₁₈BrCl

¹H NMR (CDCl₃, 298 K, 400 MHz): 7.65 (1H, d, J = 4 Hz), 7.64 (1H, d, J = 10 Hz), 7.45 (2H, d, J = 8.4 Hz), 7.32 (1H, dd, J = 12 Hz, 2 Hz), 7.25 (2H, d, J = 8.4 Hz), 2.64 (2H, t, J = 7.6 Hz), 1.643 (2H, pent, J = 7.6 Hz), 1.38-1.30 (4H, m), 0.90 (3H, t, J = 8 Hz)

¹³C NMR (CDCl₃, 298 K, 100 MHz): 143.22, 141.93, 136.07, 134.72, 134.27, 133.88, 129.09, 128.68, 126.75, 126.39, 120.83, 35.59, 31.51, 31.13, 22.56, 14.05

IR (neat, cm⁻¹): 2954.79, 2926.49, 2855.23, 1902.56, 1610.82, 1586.29, 1546.49, 1516.71, 1459.62, 1370.18, 1119.58, 1014.38, 882.26, 785.65, 675.20
Synthesis of 2-chloro-1-(4-fluorophenyl)-4-(4-pentylphenyl)benzene (I)

In a 250 ml round-bottom flask K₂CO₃ (2.76 gm, 20.0 mmol) was dissolved in H₂O (16 ml) and 1,4-dioxane (40 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4-fluorobenzeneboronic acid (0.769 gm, 5.5 mmol), 1-bromo-2-chloro-4-(4-pentylphenyl)benzene (1.64 gm, 4.85 mmol) and Pd(PPh₃)₂Cl₂ (0.073 gm, 3 mol%) was added. This mixture was refluxed for 24 hours under nitrogen when GC-MS showed complete conversion of the bromide starting material. At this point, the mixture was cooled down to room temperature, silica gel was added and the solvent was removed under reduced pressure, thus adsorbing the material on silica gel. The adsorbed material was then placed on the top of a silica gel column. The column was eluted with hexanes and the major band was separated. The solvent was removed under reduced pressure to obtain a viscous liquid. This was subjected to kugelrohr distillation to remove volatile impurities (150°C, 0.5 millibar) and the residue was collected (not the distillate) to obtain a viscous white liquid (1.01 gm, 59% yield). As this compound is nematic near room temperature, recrystallization is difficult. In order to obtain high quality material, the material was subjected to silica gel column chromatography three times with hexanes as eluent and then kept under vacuum (0.3 millibar, 90°C) for 2 hours (0.59 gm, 34% yield).

IUPAC name: 2-chloro-1-(4-fluorophenyl)-4-(4-pentylphenyl)benzene

Molecular weight: 352.87

Molecular formula: C₂₃H₂₂ClF
$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 7.69 (1H, d, $J = 1.8$ Hz), 7.52 (3H, d, $J = 8.04$ Hz), 7.48-7.42 (2H, m) 7.36 (1H, d, $J = 7.96$ Hz), 7.27 (2H, d, $J = 8.32$ Hz), 7.13 (2H, t, $J = 8.76$ Hz), 2.65 (2H, t, $J = 7.76$ Hz), 1.66 (2H, quintet, $J = 7.47$ Hz), 1.41-1.30 (4H, m), 0.91 (3H, t, $J = 7.00$ Hz)

$^{13}$C NMR (CDCl$_3$, 298 K, 100 MHz): 163.60, 142.97, 141.91, 137.84, 136.60, 131.67, 131.56, 131.22, 131.14, 129.33, 129.04, 128.31, 128.10, 126.86, 125.39, 115.16, 114.95, 35.61, 31.55, 31.15, 22.57, 14.05

IR (neat, cm$^{-1}$): 2944.72, 2880.42, 1886.10, 1625.13, 1531.68, 1486.09, 1394.77, 1229.14

Phase transitions: Cr 48.3 (N 30.1) Iso

Synthesis of 4-[2-chloro-4-(4-pentylphenyl)phenyl]benzonitrile (2)

In a 250 ml round-bottom flask K$_2$CO$_3$ (1.656 gm, 12.0 mmol) was dissolved in H$_2$O (8 ml) and 1,4-dioxane (20 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4-cyanobenzeneboronic acid (0.514 gm, 3.5 mmol), 1-bromo-2-chloro-4-(4-pentylphenyl)benzene (1.0 gm, 2.96 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (44 mg, 3.0 mol%) was added. This mixture was refluxed for 24 hours under nitrogen when TLC (eluent 25% EtOAc, 75% hexanes) showed full conversion of the starting materials. At this point, the mixture was cooled down to room temperature, adsorbed on silica gel and was placed on the top of a silica gel column. The column was eluted with 25% EtOAc, 75% hexanes and the major band was
separated. The solvent was removed under reduced pressure and the residue was recrystallized from hexanes to obtain the desired material as a white solid (0.79 gm, 75% yield).

IUPAC name: 4-[2-chloro-4-(4-pentylphenyl)phenyl]benzonitrile

Molecular weight: 359.89

Molecular formula: C_{24}H_{22}ClN

^1H NMR (CDCl_3, 298 K, 400 MHz): 7.74 (2H, d, J = 8.8 Hz), 7.72 (1H, d, J = 1.6 Hz), 7.60 (2H, d, J = 8.4 Hz), 7.56 (1H, dd, J = 8.4 Hz, 1.6 Hz), 7.52 (2H, d, J = 8.4 Hz), 7.36 (1H, d, J = 8 Hz), 7.29 (2H, d, J = 8.4 Hz), 2.66 (2H, t, J = 7.6 Hz), 1.66 (2H, quintet, J = 7.6 Hz), 1.39-1.33 (4H, m), 0.91 (3H, t, J = 6.8 Hz)

^13C NMR (CDCl_3, 298 K, 100 MHz): 143.77, 143.30, 142.90, 136.89, 136.27, 132.53, 131.93, 131.28, 130.32, 129.11, 128.54, 126.89, 125.62, 118.81, 111.47, 35.61, 31.53, 31.12, 22.55, 14.03

IR (neat, cm\(^{-1}\)): 2946.69, 2880.40, 2237.36, 1619.64, 1460.52, 1390.40, 1255.59, 1185.20, 1094.66

Phase transitions: Cr 72 N 98 Iso

Synthesis of 2-chloro-1-(4-chloro-3-fluorophenyl)-4-(4-pentylphenyl)benzene (4)

In a 250 ml round-bottom flask K_2CO_3 (1.656 gm, 12.0 mmol) was dissolved in H_2O (8 ml) and 1,4-dioxane (20 ml) was added. This mixture was degassed by sonication under vacuum for 20
minutes and after that 4-chloro-3-fluorobenzeneboronic acid (0.61 gm, 3.5 mmol), 1-bromo-2-
chloro-4-(4-pentylphenyl)benzene (1.0 gm, 2.96 mmol) and Pd(PPh₃)₂Cl₂ (44 mg, 3.0 mol%) 
was added. This mixture was refluxed for 24 hours under nitrogen when TLC (eluent hexanes) 
showed full conversion of the starting materials. At this point, the mixture was cooled down to 
room temperature, adsorbed on silica gel and was placed on the top of a silica gel column. The 
column was eluted with 1% EtOAc, 99% hexanes and the major band was separated. The solvent 
was removed under reduced pressure to obtain the desired material as a viscous liquid (0.75 gm, 
66% yield).

IUPAC name: 2-chloro-1-(4-chloro-3-fluorophenyl)-4-(4-pentylphenyl)benzene 
Molecular weight: 387.32
Molecular formula: C₂₃H₂₁Cl₂F

¹H NMR (CDCl₃, 298 K, 400 MHz): 7.68 (1H, d, J = 2 Hz), 7.53-7.49 (3H, m), 7.44 (1H, t, J = 8 
Hz), 7.34 (1H, d, J = 8 Hz), 7.30-7.25 (3H, m), 7.21-7.18 (1H, m), 2.64 (2H, t, J = 7.6 Hz), 1.64 
(2H, quintet, J = 7.2 Hz), 1.40-1.36 (4H, m), 0.89 (3H, t, J = 6.8 Hz)

¹³C NMR (CDCl₃, 298 K, 100 MHz): 158.88, 156.41, 143.18, 142.52, 139.56, 136.47, 
132.60131.33, 130.24, 129.08, 128.47, 126.88, 126.05, 126.02, 125.53, 117.8335.61, 31.54, 
31.16, 22.57, 14.06

¹⁹F NMR (CDCl₃, 298K, 376 MHz): -115.98- -116.03 (1F, m)

IR (neat, cm⁻¹): 2951.29, 2905.38, 2852.92, 1928.01, 1584.47, 1544.40, 1486.21, 1413.90, 
1391.00, 1230.82, 1215.79

Phase transitions: Cr 51 N (6.1) I
Synthesis of 2-chloro-4-(4-pentylphenyl)-1-(3,4,5-trifluorophenyl)benzene (5)

In a 250 ml round-bottom flask K₂CO₃ (1.656 gm, 12.0 mmol) was dissolved in H₂O (8 ml) and 1,4-dioxane (20 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 3,4,5-trifluorobenzeneboronic acid (0.61 gm, 3.5 mmol), 1-bromo-2-chloro-4-(4-pentylphenyl)benzene (1.0 gm, 2.96 mmol) and Pd(PPh₃)₂Cl₂ (44 mg, 3.0 mol%) was added. This mixture was refluxed for 24 hours under nitrogen when TLC (eluent hexanes) showed full conversion of the starting materials. At this point, the mixture was cooled down to room temperature, silica gel was added and the solvent was removed under reduced pressure, thus adsorbing the material on silica gel. The adsorbed material was then placed on the top of a silica gel column. The column was eluted with hexanes and the major band was separated. The solvent was removed under reduced pressure to obtain the desired material as a viscous liquid (0.77 gm, 67% yield).

IUPAC name: 2-chloro-4-(4-pentylphenyl)-1-(3,4,5-trifluorophenyl)benzene

Molecular weight: 388.853

Molecular formula: C₂₃H₂₀ClF₃

¹H NMR (CDCl₃, 298 K, 400 MHz): 7.72 (1H, d, J = 1.76 Hz), 7.59-7.50 (3H, m), 7.36 (1H, d, J = 8.00 Hz), 7.31 (2H, d, J = 8.32 Hz), 7.18-7.11 (2H, m), 2.70 (2H, t, J = 7.56 Hz), 1.69 (2H, quintet, J = 7.34 Hz), 1.45-1.32 (4H, m), 0.94 (3H, t, J = 6.93 Hz)
$^{13}$C NMR (CDCl$_3$, 298 K, 100 MHz): 152.10, 149.58, 143.27, 142.81, 140.68, 138.16, 136.27, 135.84, 134.91, 132.55131.25, 129.11, 128.52, 126.89, 125.58, 113.89, 35.61, 31.54, 31.15, 22.57, 14.05

$^{19}$F NMR (CDCl$_3$, 298K, 376 MHz): -135.10- -135.21 (2F, m), -162.13- -162.27 (1F, m)

IR (neat, cm$^{-1}$): 2946.83, 2883.34, 1935.10, 1607.73, 1522.32, 1503.03, 1447.24, 1371.95, 1220.02, 1021.42

Phase transitions: Low temperature, exact transition temperature could not be determined due to limitations of DSC hardware

Synthesis of 2-chloro-4-(4-pentylphenyl)-1-(4-trifluoromethoxyphenyl)benzene ($6$)

In a 250 ml round-bottom flask K$_2$CO$_3$ (1.656 gm, 12.0 mmol) was dissolved in H$_2$O (8 ml) and 1,4-dioxane (20 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4-trifluoromethoxyphenylboronic acid (0.720 gm, 3.5 mmol), 1-bromo-2-chloro-4-(4-pentylphenyl)benzene (1.0 gm, 2.96 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (44 mg, 3.0 mol%) was added. This mixture was refluxed for 24 hours under nitrogen when TLC (eluent hexanes) showed full conversion of the starting materials. At this point, the mixture was cooled down to room temperature, silica gel was added and the solvent was removed under reduced pressure, thus adsorbing the material on silica gel. The adsorbed material was then placed on the top of a silica gel column. The column was eluted with hexanes and the major band was separated. The
solvent was removed under reduced pressure to obtain the desired material as a viscous liquid (0.89 gm, 72% yield).

IUPAC name: 2-chloro-4-(4-pentylphenyl)-1-[4-(trifluoromethoxy)phenyl]benzene

Molecular weight: 418.879

Molecular formula: C_{24}H_{22}ClF_{3}O

$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 7.73 (1H, d, J = 1.77 Hz), 7.58-7.51 (5H, m), 7.40 (2H, d, J=8.00 Hz), 7.34-7.29 (4H, m), 2.68 (2H, t, J = 7.65 Hz), 1.69 (2H, quintet, J = 7.52 Hz), 1.45-1.32 (4H, m), 0.94 (3H, t, J = 6.89 Hz)

$^{13}$C NMR (CDCl$_3$, 298 K, 100 MHz): 143.07, 142.19, 140.57, 137.71, 137.44, 136.51, 132.73, 131.52, 130.97, 128.38, 125.46, 120.51, 35.61, 31.55, 31.16, 22.57, 14.06

$^{19}$F NMR (CDCl$_3$, 298K, 376 MHz): -58.22 (3F, s)

IR (neat, cm$^{-1}$): 2948.58, 2886.98, 1633.00, 1501.85, 1396.99, 1235.34, 1189.19

Phase transitions: Low temperature, exact transition temperature could not be determined due to limitations of DSC hardware

Synthesis of 2-chloro-4-(4-pentylphenyl)-1-[4-(trifluoromethyl)phenyl]benzene (7)

In a 500 ml round-bottom flask K$_2$CO$_3$ (1.656 gm, 12.0 mmol) was dissolved in H$_2$O (8 ml) and 1,4-dioxane (20 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4-trifluoromethylbenzeneboronic acid (0.66 gm, 3.5 mmol), 1-bromo-2-chloro-4-(4-pentylphenyl)benzene (0.8 gm, 2.36 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (35 mg, 3.0 mol%)
was added. This mixture was refluxed for 18 hours under nitrogen when GC-MS showed complete conversion of the starting material. At this point, the mixture was cooled down to room temperature, silica gel was added and the solvent was removed under reduced pressure, thus adsorbing the material on silica gel. The adsorbed material was then placed on the top of a silica gel column. The column was eluted with hexanes and the major band was separated. The solvent was removed under reduced pressure to obtain the desired product as a viscous liquid (0.69 gm, 73% yield).

IUPAC name: 2-chloro-4-(4-pentylphenyl)-1-[4-(trifluoromethyl)phenyl]benzene

Molecular weight: 402.880

Molecular formula: C_{24}H_{22}ClF_{3}

^{1}H NMR (CDCl_{3}, 298 K, 400 MHz): 7.77-7.71 (3H, m), 7.64 (2H, d, J = 7.93 Hz), 7.60-7.53 (3H, m), 7.41 (1H, d, J =7.69 Hz), 7.32 (2H, d, J =8.17 Hz), 2.69 (2H, t, J = 7.57 Hz), 1.69 (2H, quintet, J = 7.58 Hz), 1.44-1.33 (4H, m), 0.94 (3H, t, J = 7.05 Hz)

^{13}C NMR (CDCl_{3}, 298 K, 100 MHz): 143.16, 142.70, 142.52, 137.41, 136.43, 132.66, 131.45, 129.90, 129.09, 128.44, 126.90, 125.53, 125.09, 125.06, 35.62, 31.55, 31.16, 22.57, 14.06

^{19}F NMR (CDCl_{3}, 298K, 376 MHz): -63.00 (3F, s)

IR (neat, cm^{-1}): 2946.36, 2868.76, 1606.62, 1501.97, 1346.58, 1262.55, 1146.65

Phase transitions: Low temperature, exact transition temperature could not be determined due to limitations of DSC hardware.
Synthesis of 2-chloro-1-(4-chlorophenyl)-4-(4-pentylphenyl)benzene (8)

\[
\begin{align*}
\text{C}_5\text{H}_11 & \quad \text{Cl} & \quad \text{Br} \\
\text{C}_9\text{H}_11 & \quad \text{Cl} & \quad \text{Cl}
\end{align*}
\]

In a 500 ml round-bottom flask K$_2$CO$_3$ (1.656 gm, 12.0 mmol) was dissolved in H$_2$O (8 ml) and 1,4-dioxane (20 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4-chlorobenzeneboronic acid (0.54 gm, 3.5 mmol), 1-bromo-2-chloro-4-(4-pentylphenyl)benzene (0.8 gm, 2.36 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (35 mg, 3.0 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when GC-MS showed complete conversion of the starting material. At this point, the mixture was cooled down to room temperature silica gel was added and the solvent was removed under reduced pressure, thus adsorbing the material on silica gel. The adsorbed material was then placed on the top of a silica gel column. The column was eluted with hexanes and the major band was separated. The solvent was removed under reduced pressure to obtain the desired product as a waxy white solid (0.71 gm, 81% yield)

IUPAC name: 2-chloro-1-(4-chlorophenyl)-4-(4-pentylphenyl)benzene

Molecular weight: 369.327

Molecular formula: C$_{23}$H$_{22}$Cl$_2$

$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 7.68 (1H, d, $J = 1.81$ Hz), 7.52-7.49 (3H, m), 7.40 (4H, s), 7.34 (1H, d, $J = 7.91$ Hz), 7.26 (2H, d, $J = 8.13$ Hz), 2.64 (2H, t, $J = 8.93$ Hz), 1.64 (2H, quintet, $J = 7.20$ Hz), 1.35-1.32 (4H, m), 0.89 (3H, t, $J = 6.69$ Hz)

$^{13}$C NMR (CDCl$_3$, 298 K, 100 MHz): 143.03, 142.10, 137.63, 137.53, 136.54, 133.72, 132.71, 131.44, 130.84, 129.04, 128.36, 128.32, 126.86, 125.44, 35.60, 31.54, 31.13, 22.55, 14.03
IR (neat, cm⁻¹): 2946.63, 2880.17, 1942.37, 1620.33, 1503.73, 1390.50, 1080.73

Phase transitions: Cr 71 N(65) I

Synthesis of 2-chloro-1-(3,4-dichlorophenyl)-4-(4-pentylphenyl)benzene (12)

In a 500 ml round-bottom flask K₂CO₃ (1.656 gm, 12.0 mmol) was dissolved in H₂O (8 ml) and 1,4-dioxane (20 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 3, 4-dichlorobenzeneboronic acid (0.667 gm, 3.5 mmol), 1-bromo-2-chloro-4-(4-pentylphenyl)benzene (0.8 gm, 2.36 mmol) and Pd(PPh₃)₂Cl₂ (35 mg, 3 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when GC-MS showed complete conversion of the starting material. At this point, the mixture was cooled down to room temperature, silica gel was added and the solvent was removed under reduced pressure, thus adsorbing the material on silica gel. The adsorbed material was then placed on the top of a silica gel column. The column was eluted with hexanes and the major band was separated. The solvent was removed under reduced pressure to obtain the desired product as a viscous liquid (0.68 gm, 72% yield).

IUPAC name: 2-chloro-1-(3,4-dichlorophenyl)-4-(4-pentylphenyl)benzene

Molecular weight: 403.772

Molecular formula: C₂₃H₂₁Cl₃
\(^1\)H NMR (CDCl\(_3\), 298 K, 400 MHz): 7.72 (1H, d, J = 1.82 Hz), 7.61 (1H, d, J = 2.00 Hz), 7.59-7.50 (4H, m), 7.41-7.33 (2H, m), 7.33-7.29 (2H, d, J = 8.52 Hz), 2.68 (2H, t, J = 7.62 Hz), 1.69 (2H, quintet, J = 7.62 Hz), 1.44-1.32 (4H, m), 0.94 (3H, t, J = 6.67 Hz)

\(^{13}\)C NMR (CDCl\(_3\), 298 K, 100 MHz): 143.18, 142.54, 138.99, 136.38, 131.38, 131.33, 130.07, 129.08, 128.94, 128.44, 126.88, 125.53, 61.31, 54.31, 16.54, 22.57, 14.06

IR (neat, cm\(^{-1}\)): 2944.83, 2881.18, 1936.83, 1627.13, 1478.50, 1399.90, 1093.33

Phase transitions: Nematic below room temperature

**Synthesis of 4-bromo-2-chloro-1-(4-pentylphenyl)benzene**

In a 500 ml round-bottom flask K\(_2\)CO\(_3\) (1.38 gm, 10.0 mmol) was dissolved in H\(_2\)O (60 ml) and 1,4-dioxane (150 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4-bromo-2-chloro-1-iodobenzene (6.32 gm, 20 mmol), 4-pentylphenylboronic acid (3.93 gm, 20.5 mmol) and Pd(PPh\(_3\))\(_2\)Cl\(_2\) (151.48 mg, 1.5 mol%) was added. This mixture was refluxed for 18 hours under nitrogen GC-MS showed complete conversion of the starting materials. At this point, the mixture was cooled down to room temperature and silica gel was added and the solvent was removed under reduced pressure, thus adsorbing the material on silica gel. The adsorbed material was then placed on the top of a silica gel column. The column was eluted with hexanes and the major band was collected. The solvent was removed under reduced pressure to obtain the desired product as a waxy solid (3.73 gm, 55% yield).
IUPAC name: 4-bromo-2-chloro-1-(4-pentylphenyl)benzene

Molecular weight: 337.69

Molecular formula: C_{17}H_{18}BrCl

$^1$H NMR (tetrachloroethane-d2, 298 K, 400 MHz): 7.65 (1H, d, $J = 2.10$ Hz), 7.46 (1H, dd, $J = 8.63$ Hz, 1.87 Hz), 7.34 (2H, d, $J = 8.17$ Hz), 7.27-7.23 (3H, m), 2.65 (2H, t, $J = 7.66$ Hz), 1.67 (2H, quintet, $J = 8.62$ Hz), 1.45-1.27 (4H, m), 0.92 (3H, t, $J = 6.70$ Hz)

$^{13}$C NMR (tetrachloroethane-d2, 298 K, 100 MHz): 142.66, 139.30, 135.16, 133.17, 132.44, 132.28, 130.00, 129.02, 128.08, 120.91, 35.55, 31.49, 30.88, 22.47, 14.06

IR (neat, cm$^{-1}$): 2954.65, 2927.89, 2867.71, 1610.32, 1585.66, 1544.09, 1459.05, 1371.49, 1289.31, 1256.53, 1189.15, 1119.83, 1013.46, 885.54, 801.30, 740.26, 675.11

Synthesis of 4-[3-chloro-4-(4-pentylphenyl)phenyl]benzonitrile (3)

In a 200 ml round-bottom flask K$_2$CO$_3$ (0.552 gm, 4.0 mmol) was dissolved in H$_2$O (8 ml) and 1,4-dioxane (20 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4-bromo-2-chloro-1-(4-pentylphenyl)benzene (0.675 gm, 2 mmol), 4-cyanophenylphenylboronic acid (0.367 gm, 2.5 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (15.14 mg, 1.5 mol%) was added. This mixture was refluxed for 18 hours under nitrogen TLC (eluent hexanes) showed complete conversion of the starting materials. Silica gel was added to the mixture after cooling it down to room temperature and the solvent was removed under reduced pressure, thus adsorbing the material on silica gel. The adsorbed material was then placed on the top of a silica gel
column. The column was eluted with hexanes and the major band was collected. The solvent was removed and the residue was recrystallized from hexanes to obtain the desired product as off-white crystalline solid (0.51 gm, 71% yield)

IUPAC name: 4-[3-chloro-4-(4-pentylphenyl)phenyl]benzonitrile

Molecular weight: 359.89

Molecular formula: C_{24}H_{22}ClN

^{1}H NMR (tetrachloroethane-d2, 298 K, 400 MHz): 7.76-7.70 (5H, m), 7.54 (1H, dd, J = 8.27 Hz, 1.65 Hz), 7.47 (1H, d, J = 7.96 Hz), 7.41 (2H, d, J = 8.12 Hz), 7.27 (2H, d, J = 8.16 Hz), 2.65 (2H, t, J = 7.82 Hz), 1.66 (2H, quintet, J = 7.47 Hz), 1.37-1.34 (4H, m), 0.91 (3H, t, J = 6.98 Hz)

^{13}C NMR (tetrachloroethane-d2, 298 K, 100 MHz): 143.55, 142.60, 140.30, 138.91, 135.40, 132.91, 132.58, 131.93, 129.09, 128.40, 128.01, 127.43, 125.46, 118.84, 111.02, 35.57, 31.45, 30.84, 22.41, 13.99

IR (neat, cm^{-1}): 2986.31, 2881.00, 2865.28, 2234.63, 1616.29, 1550.03, 1467.18, 1353.94

Phase transition: Cr 81 (N 75) Iso

Synthesis of 2-chloro-4-(4-chlorophenyl)-1-(4-pentylphenyl)benzene (11)

\[
\text{C}_{5}\text{H}_{11}\text{Cl} \rightarrow \text{C}_{5}\text{H}_{11}\text{Cl}
\]

In a 200 ml round-bottom flask K_{2}CO_{3} (0.552 gm, 4.0 mmol) was dissolved in H_{2}O (8 ml) and 1,4-dioxane (20 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4-bromo-2-chloro-1-(4-pentylphenyl)benzene (0.675 gm, 2 mmol), 4-chlorophenylphenylboronic acid (0.367 gm, 2.5 mmol) and Pd(PPh_{3})_{2}Cl_{2} (15.14 mg, 1.5 mol%)
was added. This mixture was refluxed for 18 hours under nitrogen at which time TLC (eluent hexanes) showed complete conversion of the starting materials. Silica gel was added to the mixture after cooling it down to room temperature and the solvent was removed under reduced pressure, thus adsorbing the material on silica gel. The adsorbed material was then placed on the top of a silica gel column. The column was eluted with hexanes and the major band was collected. The solvent was removed and the residue was recrystallized from hexanes to obtain the desired product as off-white solid (0.53 gm, 73% yield).

IUPAC name: 2-chloro-4-(4-chlorophenyl)-1-(4-pentylphenyl)benzene

Molecular weight: 369.33

Molecular formula: C_{23}H_{22}Cl_{2}

{H NMR (tetrachloroethane-d2, 298 K, 400 MHz): 7.66 (1H, d, J = 1.80 Hz), 7.55 (2H, d, J = 8.64 Hz), 7.50 (1H, dd, J = 7.75 Hz, 1.79 Hz), 7.45-7.40 (5H, m), 7.26 (2H, d, J = 8.16 Hz), 2.65 (2H, t, J = 7.82 Hz), 1.66 (2H, quintet, J = 7.53 Hz), 1.38-1.34 (4H, m), 0.91 (3H, t, J = 7.02 Hz)

{C NMR (tetrachloroethane-d2, 298 K, 100 MHz): 142.71, 140.08, 139.53, 137.85, 135.98, 134.01, 132.96, 132.08, 129.46, 129.28, 128.42, 128.39, 128.29, 125.53, 35.84, 31.80, 31.20, 22.76, 14.35

IR (neat, cm\(^{-1}\)): 2942.79, 2879.29, 1485.39, 1359.20, 1100.22, 1017.85

Phase transition: Cr 74 (N 41) Iso
Synthesis of 2-chloro-4-(2-chloro-4-fluorophenyl)-1-(4-pentylphenyl)benzene (15)

In a 200 ml round-bottom flask K$_2$CO$_3$ (0.552 gm, 4.0 mmol) was dissolved in H$_2$O (8 ml) and 1,4-dioxane (20 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4-bromo-2-chloro-1-(4-pentylphenyl)benzene (0.675 gm, 2 mmol), 2-chloro-4-fluorophenylphenylboronic acid (0.435 gm, 2.5 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (15.14 mg, 1.5 mol%) was added. This mixture was refluxed for 18 hours under nitrogen TLC (eluent hexanes) showed complete conversion of the starting materials. Silica gel was added to the mixture after cooling it down to room temperature and the solvent was removed under reduced pressure, thus adsorbing the material on silica gel. The adsorbed material was then placed on the top of a silica gel column. The column was eluted with hexanes and the major band was collected. The solvent was removed to obtain the desired product as colorless liquid (0.51 gm, 66% yield)

IUPAC name: 2-chloro-4-(2-chloro-4-fluorophenyl)-1-(4-pentylphenyl)benzene

Molecular weight: 387.32

Molecular formula: C$_{23}$H$_{21}$Cl$_2$F

$^1$H NMR (tetrachloroethane-d2, 298 K, 400 MHz): 7.52 (1H, d, $J = 1.59$ Hz), 7.44-7.41 (3H, m), 7.38-7.35 (2H, m), 7.28-7.25 (3H, m), 7.08 (1H, td, $J = 8.37$ Hz, 2.79 Hz), 2.66 (2H, t, $J = 8.41$ Hz), 1.67 (2H, quintet, $J = 8.08$ Hz), 1.40-1.32 (4H, m), 0.91 (3H, t, $J = 7.21$ Hz)

$^{13}$C NMR (tetrachloroethane-d2, 298 K, 100 MHz): 162.99, 160.50, 142.46, 139.43, 138.30, 135.79, 132.23, 132.15, 131.83, 131.03, 130.65, 129.24, 128.03, 117.38, 117.13, 114.40, 114.19, 35.59, 31.54, 30.93, 22.50, 14.08
^19F NMR (CDCl$_3$, 298K, 376 MHz): -112.89 -112.95 (1F, m)

IR (neat, cm$^{-1}$): 2945.59, 2881.84, 1584.16, 1488.01, 1386.63, 1282.83, 1219.89, 1070.95, 1037.52

Phase transition: Liquid at room temperature, no mesophase

Synthesis of 2-chloro-4-(4-chloro-3-fluorophenyl)-1-(4-pentylphenyl)benzene (16)

\[
\begin{align*}
\text{C}_6\text{H}_{11} & \quad \text{Cl} \\
\text{Br} & \quad \text{Cl} \\
\text{F} & \quad \text{Cl}
\end{align*}
\]

In a 200 ml round-bottom flask K$_2$CO$_3$ (0.552 gm, 4.0 mmol) was dissolved in H$_2$O (8 ml) and 1,4-dioxane (20 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4-bromo-2-chloro-1-(4-pentylphenyl)benzene (0.675 gm, 2 mmol), 2-chloro-4-fluorophenylphenylboronic acid (0.435 gm, 2.5 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (15.14 mg, 1.5 mol%) was added. This mixture was refluxed for 18 hours under nitrogen TLC (eluent hexanes) showed complete conversion of the starting materials. Silica gel was added to the mixture after cooling it down to room temperature and the solvent was removed under reduced pressure, thus adsorbing the material on silica gel. The adsorbed material was then placed on the top of a silica gel column. The column was eluted with hexanes and the major band was collected. The solvent was removed to obtain the desired product as colorless liquid (0.51 gm, 66% yield)

IUPAC name: 2-chloro-4-(4-chloro-3-fluorophenyl)-1-(4-pentylphenyl)benzene

Molecular weight: 387.32

Molecular formula: C$_{23}$H$_{21}$Cl$_2$F
$^1$H NMR (tetrachloroethane-d$_2$, 298 K, 400 MHz): 7.67 (2H, d, $J = 1.91$ Hz), 7.53-7.36 (7H, m), 7.28 (2H, d, $J = 7.27$ Hz), 2.67 (2H, t, $J = 8.47$ Hz), 1.68 (2H, quintet, $J = 8.47$ Hz), 1.43-1.34 (4H, m), 0.94 (3H, t, $J = 7.41$ Hz)

$^{13}$C NMR (tetrachloroethane-d$_2$, 298 K, 100 MHz): 159.40, 156.90, 142.53, 139.83, 138.70, 135.54, 132.82, 131.87, 130.90, 129.14, 128.09, 128.02, 125.19, 123.21, 123.18, 114.97, 114.76, 35.54, 31.49, 30.88, 22.45, 14.03

$^{19}$F NMR (CDCl$_3$, 298K, 376 MHz): -115.26 (1F, m)

IR (neat, cm$^{-1}$): 2943.37, 2880.47, 1589.76, 1550.30, 1504.09, 1429.00, 1392.11, 1329.31, 1219.43

Phase transition: Cr 50 I

### Synthesis of 4-bromo-2-chloro-1-(4-chlorophenyl)benzene

![Chemical structure](image)

In a 100 ml round-bottom flask K$_2$CO$_3$ (2.76 gm, 20.0 mmol) was dissolved in H$_2$O (40 ml) and 1,4-dioxane (100 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4-bromo-2-chloro-1-iodobenzene (3.16 gm, 10.0 mmol), 4-chlorophenylboronic acid (1.56 gm, 10.0 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (75.74 mg, 1.5 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when GC-MS showed complete conversion of the starting materials. Silica gel was added to the mixture after cooling it down to room temperature and the solvent was removed under reduced pressure, thus adsorbing the material on silica gel. The adsorbed material was then placed on the top of a silica gel column.
The column was eluted with hexanes and the major band was collected. The solvent was removed to obtain the desired product as off-white solid (1.1 gm, 37% yield)

IUPAC name: 4-bromo-2-chloro-1-(4-chlorophenyl)benzene

Molecular weight: 301.99

Molecular formula: C\textsubscript{12}H\textsubscript{7}BrCl\textsubscript{2}

\textsuperscript{1}H NMR (tetrachloroethane-d\textsubscript{2}, 298 K, 400 MHz): 7.65 (1H, d, \( J = 1.91 \) Hz), 7.46 (1H, dd, \( J = 8.29 \) Hz, 2.23 Hz), 7.41 (2H, d, \( J = 8.61 \) Hz), 7.35 (2H, d, \( J = 8.93 \) Hz), 7.19 (1H, d, \( J = 8.29 \) Hz)

\textsuperscript{13}C NMR (tetrachloroethane-d\textsubscript{2}, 298 K, 100 MHz): 138.06, 136.47, 133.78, 133.15, 132.43, 132.15, 130.55, 130.17, 128.95, 128.34, 128.15, 121.66

IR (neat, cm\textsuperscript{-1}): 3088.98, 3058.77, 3031.71, 1900.57, 1579.79, 1498.65, 1368.93, 1086.72, 1069.15, 1000.71, 838.22, 796.42, 724.52

Synthesis of 4-(4-butyphenyl)-2-chloro-1-(4-chlorophenyl)benzene (9)

In a 200 ml round-bottom flask K\textsubscript{2}CO\textsubscript{3} (0.552 gm, 4.0 mmol) was dissolved in H\textsubscript{2}O (8 ml) and 1,4-dioxane (20 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4-bromo-2-chloro-1-(4-chlorophenyl)benzene (0.452 gm, 1.5 mmol), 4-butyphenylboronic acid (0.356 gm, 2 mmol) and Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} (11.36 mg, 1.5 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when GC-MS showed complete conversion of the starting materials. Silica gel was added to the mixture after cooling it down to room temperature and the solvent was removed under reduced pressure, thus adsorbing the
material on silica gel. The adsorbed material was then placed on the top of a silica gel column. The column was eluted with hexanes and the major band was collected. The solvent was removed and the residue was recrystallized from hexanes to obtain the desired product as off-white solid (0.26 gm, 49% yield)

IUPAC name: 4-(4-butylphenyl)-2-chloro-1-(4-chlorophenyl)benzene

Molecular weight: 355.30

Molecular formula: C_{22}H_{20}Cl_2

^1^H NMR (tetrachloroethane-d2, 298 K, 400 MHz): 7.70 (1H, d, J = 1.84 Hz), 7.55-7.52 (3H, m), 7.44 (4H, d, J = 1.84 Hz), 7.37 (1H, d, J = 7.96 Hz), 7.28 (2H, d, J = 8.26 Hz), 2.65 (2H, t, J = 7.50 Hz), 1.63 (2H, quint, J = 7.59 Hz), 1.38 (2H, sext, J = 6.93 Hz), 0.94 (3H, t, J = 7.32 Hz)

^13^C NMR (CDCl_3, 298 K, 100 MHz): 143.17, 142.29, 137.81, 137.71, 136.73, 133.91, 131.63, 131.02, 129.24, 128.55, 128.50, 127.05, 125.62, 35.50, 33.78, 22.58, 14.15

IR (neat, cm^{-1}): 2945.28, 2866.54, 1949.99, 1506.60, 1363.79, 1080.81, 1008.65

Phase transition: Cr 78 I

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**Synthesis of 2-chloro-1-(4-chlorophenyl)-4-(4-propylphenyl)benzene (13)**

![Chemical structure](image)

In a 200 ml round-bottom flask K_2CO_3 (0.552 gm, 4.0 mmol) was dissolved in H_2O (8 ml) and 1,4-dioxane (20 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4-bromo-2-chloro-1-(4-chlorophenyl)benzene (0.452 gm, 1.5 mmol), 4-propylphenylboronic acid (0.328 gm, 2.0 mmol) and Pd(PPh_3)_2Cl_2 (11.36 mg, 1.5 mol%) was
added. This mixture was refluxed for 18 hours under nitrogen when GC-MS showed complete conversion of the starting materials. Silica gel was added to the mixture after cooling it down to room temperature and the solvent was removed under reduced pressure, thus adsorbing the material on silica gel. The adsorbed material was then placed on the top of a silica gel column. The column was eluted with hexanes and the major band was collected. The solvent was removed and the residue was recrystallized from hexanes to obtain the desired product as off-white solid (0.342 gm, 67% yield)

IUPAC name: 2-chloro-1-(4-chlorophenyl)-4-(4-propylphenyl)benzene

Molecular weight: 341.274

Molecular formula: C$_{21}$H$_{18}$Cl$_2$

$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 7.68 (1H, d, $J = 1.92$ Hz), 7.52-7.50 (3H, m), 7.40 (4H, s), 7.34 (1H, d, $J = 7.69$ Hz), 7.26 (2H, d, $J = 8.08$ Hz), 2.63 (2H, t, $J = 6.14$ Hz), 1.67 (2H, sext, $J = 7.89$ Hz), 0.96 (3H, t, $J = 7.89$ Hz)

$^{13}$C NMR (CDCl$_3$, 298 K, 100 MHz): 142.80, 142.14, 137.69, 137.54, 133.75, 132.76, 131.47, 130.89, 129.12, 128.35, 126.88, 125.48, 37.75, 24.58, 13.91

IR (neat, cm$^{-1}$): 2939.91, 2851.99, 1486.62, 1391.60, 1079.40

Phase transitions: Cr 95 (N 68)I
In a 200 ml round-bottom flask K₂CO₃ (0.552 gm, 4.0 mmol) was dissolved in H₂O (8 ml) and 1,4-dioxane (20 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4-bromo-2-chloro-1-(4-chlorophenyl)benzene (0.452 gm, 1.5 mmol), 4-ethylphenylboronic acid (0.29 gm, 2.0 mmol) and Pd(PPh₃)₂Cl₂ (11.36 mg, 1.5 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when GC-MS showed complete conversion of the starting materials. Silica gel was added to the mixture after cooling it down to room temperature and the solvent was removed under reduced pressure, thus adsorbing the material on silica gel. The adsorbed material was then placed on the top of a silica gel column. The column was eluted with hexanes and the major band was collected. The solvent was removed and the residue was recrystallized from hexanes to obtain the desired product as off-white solid (0.31 gm, 63% yield).

IUPAC name: 4-(4-ethylphenyl)-2-chloro-1-(4-chlorophenyl)benzene

Molecular weight: 327.25

Molecular formula: C₂₀H₁₆Cl₂

¹H NMR (tetrachloroethane-d₂, 298 K, 400 MHz): 7.69 (1H, d, J = 1.82 Hz), 7.54 (3H, d, J = 8.39 Hz), 7.43 (4H, d, J = 1.46 Hz), 7.37 (1H, d, J = 8.03 Hz), 7.30 (2H, d, J = 8.39 Hz), 2.70 (2H, q, J = 7.05 Hz), 1.27 (3H, d, J = 8.46 Hz)

¹³C NMR (CDCl₃, 298 K, 100 MHz): 144.32, 142.11, 137.67, 137.55, 136.62, 133.77, 132.76, 131.49, 130.87, 128.55, 128.40, 128.36, 126.99, 125.48, 28.55, 15.58
IR (neat, cm⁻¹): 3042.67, 2948.52, 2886.59, 1932.15, 1487.27, 1359.95, 1079.99

Phase transition: Cr 108 I

Synthesis of 4-bromo-2-chloro-1-(3,4-dichlorophenyl)benzene

![Chemical structure](image)

In a 200 ml round-bottom flask K₂CO₃ (1.38 gm, 10.0 mmol) was dissolved in H₂O (20 ml) and 1,4-dioxane (50 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4-bromo-2-chloro-1-iodobenzene (1.58 gm, 5 mmol), 3,4-dichlorophenylboronic acid (0.95 gm, 5 mmol) and Pd(PPh₃)₂Cl₂ (37.87 mg, 1.5 mol%) was added. This mixture was refluxed for 18 hours under nitrogen GC-MS showed complete conversion of the starting materials. Silica gel was added to the mixture after cooling it down to room temperature and the solvent was removed under reduced pressure, thus adsorbing the material on silica gel. The adsorbed material was then placed on the top of a silica gel column. The column was eluted with hexanes and the major band was separated. The solvent was removed under reduced pressure to obtain the desired product as a white solid (0.39 gm, 23% yield).

IUPAC name: 4-bromo-2-chloro-1-(3,4-dichlorophenyl)benzene

Molecular weight: 336.439

Molecular formula: C₁₂H₆BrCl₃

¹H NMR (tetrachloroethane-d2, 298 K, 400 MHz): 7.66 (1H, d, J = 2.37 Hz), 7.56-7.46 (3H, m), 7.27 (1H, dd, J = 8.00 Hz, 2.07 Hz), 7.18 (1H, d, J = 8.59 Hz)
$^{13}$C NMR (tetrachloroethane-d2, 298 K, 100 MHz): 137.94, 132.55, 131.99, 130.98, 130.30, 130.13, 128.69

Synthesis of 2-chloro-1-(3,4-dichlorophenyl)-4-(4-propylphenyl)benzene (14)

In a 200 ml round-bottom flask $\text{K}_2\text{CO}_3$ (0.552 gm, 4.0 mmol) was dissolved in $\text{H}_2\text{O}$ (8 ml) and 1,4-dioxane (20 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4-bromo-2-chloro-1-(3,4-dichlorophenyl)benzene (0.33 gm, 1.0 mmol), 4-propylphenylboronic acid (0.246 gm, 1.5 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (8 mg, 1.5 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when GC-MS showed complete conversion of the starting materials. Silica gel was added to the mixture after cooling it down to room temperature and the solvent was removed under reduced pressure, thus adsorbing the material on silica gel. The adsorbed material was then placed on the top of a silica gel column. The column was eluted with hexanes and the major band was collected. The solvent was removed to obtain the desired product as a colorless viscous liquid (0.291 gm, 77% yield).

IUPAC name: 2-chloro-1-(3,4-dichlorophenyl)-4-(4-propylphenyl)benzene

Molecular weight: 375.719

Molecular formula: C$_{21}$H$_{17}$Cl$_3$

$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 7.68 (1H, d, $J$ = 1.82 Hz), 7.56 (1H, d, $J$ = 1.82 Hz), 7.53-7.49 (4H, m), 7.34-7.30 (2H, m), 7.26 (2H, d, $J$ = 8.48 Hz), 2.63 (2H, t, $J$ = 6.93 Hz), 1.68 (2H, sext, $J$ = 7.92 Hz), 0.97 (3H, t, $J$ = 6.93 Hz)
$^{13}$C NMR (CDCl$_3$, 298 K, 100 MHz): 142.91, 142.56, 139.00, 136.42, 132.66, 132.24, 131.91, 131.38, 131.33, 130.07, 129.14, 128.94, 128.45, 126.87, 125.53, 37.71, 24.52, 13.86

IR (neat, cm$^{-1}$): 3044.30, 2943.84, 2863.15, 1931.94, 1626.91, 1542.28, 1477.97, 1401.02, 1101.27, 1023.76

Phase transitions: Nematic below room temperature
4.7 References


(22) Davis, D., Kent State University, 2013.


(27) White, D., s.n.], 1993.


Chapter 5
Laterally chlorinated quaterphenyls devoid of alkyl chains for midwave infrared applications

5.1 Introduction
Long wavelength radiation such as in the infrared is very attractive for telecom applications as the scattering of the medium is significantly lower than at shorter wavelengths (Rayleigh scattering is inversely proportional to the fourth power of the wavelength of light). Depending on the specific composition of the medium, radiation in the infrared can also be preferable due to lower absorption and thus lower optical loss\(^{39}\). In the case of organic materials this will depend on the detailed molecular composition (the identity and relationship of functional groups in the material). Liquid crystals, as a subset of organic materials, can be especially useful for these telecom applications as they can be switched between states with different optical properties. For example, it has been experimentally demonstrated that these materials can possess high birefringence in the infrared region and this birefringence is a critical physical property that can be optimized and utilized to create optical switching devices\(^{95}\). Although the use of liquid crystals can drastically reduce power consumption, size and weight of devices for applications such as laser beam steering\(^{10}\) and dynamic scene projectors for infrared seekers\(^{11}\), these materials usually also suffer from drawbacks due to inherent absorption loss resulting from the existence...
of molecular absorption bands as well as their harmonics and overtones. For example, several absorption bands exist in the mid-infrared region (3-5 μm) due to common structure features found in liquid crystals such as CH, CH₂, CH₃ and CN. In the off-resonance regions, the baseline absorption coefficient can take a very high value⁹⁸ (up to α~10/cm). If the optical path is long enough the absorption loss becomes especially significant and will compromise device function. To address this IR absorption problem several strategies have been adopted. The replacement of hydrogen atoms (atomic mass = 1.00794 amu) in the liquid crystal molecule with heavier atoms has been a common approach. Deuterium (atomic mass = 2.01410178 amu) is attractive as a replacement for hydrogen and when the hydrogen atoms of 5CB was replaced by deuterium the absorption loss in the midwave infrared region was significantly reduced⁴⁹. However, the synthesis procedures for deuterated compounds is often more tedious and less viable from the industrial point of view. Fluorine is another interesting option as a replacement of hydrogen atoms and many fluorinated nematic liquid crystals are already known. Fluorine has a large mass relative to hydrogen (18.998404 amu for fluorine compared to 1.00794 amu for hydrogen). However, with a high extent of fluorination nematic properties are often compromised. A high degree of fluorination of the terminal aliphatic chain promotes smectic phases due to increased rigidity¹⁰⁰. Even semifluorinated n-alkanes devoid of any ring structure can demonstrate smectic phases due to the decrease in flexibility⁷⁹. Lateral fluoro substitution in the core can influence intermolecular forces and efficient molecular packing. Also lateral substitution can make the molecule broader, decreasing the aspect ratio, thus decreasing the mesophase stability²⁷. In infrared device applications a nematic phase is often preferred as alignment of the liquid crystal layer is the easiest.
Another strategy to address the absorption loss is to use materials possessing high birefringence. The cell gap can be lowered (in proportion to the birefringence) if high birefringence materials are used. This can drastically reduce response time as it is directly proportional to the cell thickness squared. With thinner cells the absorption loss can be lowered, but maintaining a uniform cell gap lower than 5 µm is difficult and not cost effective.

Also, the alkyl chains in liquid crystals still contribute highly towards absorption in the midwave infrared region and do not contribute to the creation of birefringence. Using of short alkyl tails might solve the problem.

The best solution for this problem will be a molecule that will possess high birefringence and also the absorption in the midwave infrared region will be very low.

5.2 Results and discussion

The overall picture regarding molecular structure and infrared absorption will be clearer if we assume 5CB as a model compound and examine its structure features and infrared absorption pattern. The alkyl tails in liquid crystals contributes to the absorption in the midwave infrared region to a large extent. The cyano group, aside from inducing dipolar properties in the liquid crystal molecule is also responsible for absorption in the midwave infrared region. The C-H in-plane deformation in the phenyl rings also contributes to the absorption in the aforesaid region.
**Figure 5.1:** Infrared absorption spectrum of 5CB

<table>
<thead>
<tr>
<th>Zone</th>
<th>Absorption mechanism</th>
<th>Frequency (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Aromatic C-H stretch saturated CH, CH$_2$, CH$_3$ stretch</td>
<td>3500-2800</td>
</tr>
<tr>
<td>B</td>
<td>C-H (in CH$_2$, CH$_3$) deformation overtone C-C skeletal stretch overtone</td>
<td>2790-2500</td>
</tr>
<tr>
<td>C</td>
<td>C≡N stretch C-H (in phenyl ring) in plane deformation overtone C-C (in alkyl chain) skeletal stretch overtone</td>
<td>2500-2000</td>
</tr>
<tr>
<td>D</td>
<td>Aromatic overtone C=C stretch</td>
<td>2000-1600</td>
</tr>
<tr>
<td>E</td>
<td>C-H in CH$_2$, CH$_3$ deformation C-C skeletal stretch</td>
<td>1485-1250</td>
</tr>
<tr>
<td>F</td>
<td>C-H (in phenyl ring) in plane deformation C-C (in alkyl chain) skeletal stretch</td>
<td>1250-1000</td>
</tr>
</tbody>
</table>

**Table 5.1:** IR absorption of 5CB$^{1,40}$
In order to mitigate the absorption loss due to the numerous C-H bonds in alkyl tails, the shortest possible alkyl tail should be used. The best solution would be to design liquid crystals completely devoid of any alkyl tails. Generally shorter tails are more conducive to creating nematic phases and as the length of the tail becomes longer (more than 6 carbons) smectic phases are seen\(^{15}\). But exclusion of alkyl tails from the molecular design generally reduces the overall flexibility of the molecule, elevates the melting point and reduces the liquid crystal phase stability or even completely annihilates any liquid crystal phase. Some C-H bonds in the phenyl rings can be replaced by C-F or C-Cl bonds to reduce the absorption due to in-plane deformation. The absorption bands due to this deformation (skeletal vibrations involving C-C stretching in the ring) appear around 1600-1585 cm\(^{-1}\) and 1500-1400 cm\(^{-1}\). When some hydrogens are replaced by Cl or F, the resultant mass of the oscillator increases, thus decreasing the frequency\(^{40}\). In place of CN, NCS and other polar groups that absorb in the midwave infrared region, Cl or F can be used instead as they can insert a significant dipole moment (this feature is needed for alignment of the molecules in devices) without the undesirable absorption in the midwave infrared region. The shortest known simple oligophenyl compound without tails exhibiting mesogenic activity is p-quinquephenyl\(^{104}\). But it also has very high transition temperatures (Cr 388 N 420 I). The melting point of the oligophenyls becomes steadily higher as additional benzene rings are added in the para position (as the molecule grows in size the number of van der Waals interactions increase in proportion). Due to the insufficient aspect ratio, p-quaterphenyl is not quite mesogenic. The virtual transition temperature for p-quaterphenyl from nematic to isotropic as predicted by the Flory lattice model\(^{120}\) is 250°C. It is also known experimentally that p-quaterphenyl itself has a very high clearing point\(^{121}\) (322°C) due to very efficient molecular
packing. If even a small para substituent is added in quaterphenyl the aspect ratio may reach the critical value for mesogenicity. All things considered, the best conceptual solution for the design of liquid crystals for use in infrared applications involves molecules with long conjugation without any alkyl tail and, also, Cl as the polar group. The choice of Cl as the polar group is justified as it introduces a dipole moment and does not contribute to the absorption in midwave infrared region. Some p-quaterphenyls with n-pentyl tails that are laterally substituted with –Cl and –CH\textsubscript{3} and with an –NCS as polar head group are known to be nematic liquid crystals below 150\textdegree{}C\textsuperscript{122}. But with the presence of alkyl tails, these molecules are less useful in infrared devices. Recently quaterphenyl liquid crystals with 4, 4’’’ alkyl substitution and lateral fluoro and chloro substituents were reported\textsuperscript{123}. To lower the clearing point and render the molecule useful for any practical application the molecular packing needs to be disrupted by reducing the ring coplanarity and changing the intermolecular interactions of the quaterphenyl molecule in the crystal. Lateral substitution is an effective way to do this and the chlorine atom has been tried earlier as a lateral substituent in liquid crystals\textsuperscript{122,124-127}.

In the case of chlorinated quaterphenyls some initial questions that need to be addressed include how many chlorines are required and what will be the most effective placement for them in the molecule. To answer these questions, we have initiated a synthesis of some of the more readily available chlorinated quaterphenyl isomers. In particular, we have now synthesized all the five unique monochloroquaterphenyls and compared their physical properties. The phase transitions for this series of molecules are listed in the Table 5.2 below.
<table>
<thead>
<tr>
<th>Structure</th>
<th>Phase transition</th>
</tr>
</thead>
</table>
| ![Structure 1] | 1 (4-Cl)  
Cr 334 N 348 I |
| ![Structure 2] | 2 (3-Cl)  
Cr 242 SmX 255 I |
| ![Structure 3] | 3 (2-Cl)  
Cr 175 I |
| ![Structure 4] | 4 (2'-Cl)  
Cr 164 I |
| ![Structure 5] | 5 (3'-Cl)  
Cr 226 I |

**Table 5.2:** Phase transition temperatures of the set of monochloroquaterphenyls

From Table 5.2 it can be observed that the structures where the chlorine moiety exerts the maximum effect on the ring coplanarity (the chlorine is in an “internal” section of the molecule as in structures 3, 4 and 5) undergo the most drastic reduction in the melting point compared to parent p-quaterphenyl (compare the melting point of 322°C\textsuperscript{128}), although these molecules are not mesogenic. From Table 5.2 it is seen that structures 1 and 2 (with the chlorine atom in an “external” position) are thermotropic liquid crystals. This is probably due to the fact that the specific placement of the chlorine moiety in these two materials either increases the aspect
ratio in a way that gives rise to long range order and/or changes the intricate interplay of intermolecular interactions—thus making them mesogenic. Combining these two structural aspects, it can be hypothesized that mesogenicity can be observed in a quaterphenyl within a manageable temperature range if we embellish lateral positions systematically with chlorine while also using the chlorine as an end group to enhance the aspect ratio (the length and breadth of \( p \)-quaterphenyl is 17.66 Å and 4.22 Å respectively compared to the length and breadth of 4-chloroquaterphenyl which is 18.33 Å and 4.23 Å respectively as calculated using molecular mechanics. This gives the aspect ratio of 4.18 and 4.33 respectively for the two molecules).

Figure 5.2: Comparison of dihedral angles (calculated using molecular mechanics) of monochloroquaterphenyls with \( p \)-quaterphenyl (the green atom depicts chlorine)
From Figure 5.2 it is observed that the effect of chlorine substitution in the lateral position can affect the dihedral angles. Along with this, the intermolecular attractive interactions are altered in such a way that it leads to the reduction of melting points among the monochloroquaterphenyls compared to $p$-quaterphenyl (Table 5.2).

<table>
<thead>
<tr>
<th>Structure</th>
<th>Phase transition</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Structure 6" /></td>
<td>6 (2,2’’’) Cr 168 I</td>
</tr>
<tr>
<td><img src="image" alt="Structure 7" /></td>
<td>7 (3,3’’’) Cr 220 I</td>
</tr>
<tr>
<td><img src="image" alt="Structure 8" /></td>
<td>8 (2’, 2’’) Cr 148 I</td>
</tr>
<tr>
<td><img src="image" alt="Structure 9" /></td>
<td>9 (4, 3’) Cr 217 N (181) I</td>
</tr>
<tr>
<td><img src="image" alt="Structure 10" /></td>
<td>10 (4, 4’’’) Nematic at 321°C (the N to I transition could not be determined as the material sublimes out of the DSC pan)</td>
</tr>
</tbody>
</table>

Table 5.3: Phase transition temperatures of the dichloroquaterphenyls

As such, a next step was to look at some selected dichloroquaterphenyls among all the symmetrical and unsymmetrical materials that can be prepared. These dichloroquaterphenyls
were chosen for evaluation mostly on a basis of their synthetic availability (others not yet prepared likely will possess still more interesting mesomorphic properties). In Table 5.3, we investigated the transition temperatures of five dichloroquaterphenyls and it was observed that compounds 9 and 10 form nematic phases. From the structure of these two materials, it can be observed that both have at least one chlorine in a para position. Excluding other intermolecular interactions, it can be seen that chlorines on the para position essentially increase the aspect ratio. Also, again, it appears that chlorine in the lateral position has drastic effect on intermolecular interactions.

In order to further probe the influence of lateral chlorination a few trichloroquaterphenyls were also prepared and examined as seen in Table 4. Here again the choices were largely dictated by the relative ease of synthesis (it is very likely that other trichloro derivatives not yet prepared and examined will possess very interesting physical properties). The effect of aspect ratio can be understood by comparing 9 and 12 (Table 3 and Table 5.4 respectively). Addition of a single chlorine on the para position in 9 greatly stabilizes the nematic phase. When we go from 9 to 12, a dramatic change from a monotropic nematic phase to a >150° enantiotropic phase occurs. The increase in aspect ratio as well as the molecular polarizability plays a key role in increasing the phase stability by elevating the nematic to isotropic transition temperature. The effect of lateral chlorine substitution can be understood by comparing 10 and 12. A single chlorine in the lateral position decreases the melting point of 10 by 154°C. Compound 11, with chlorines only in the lateral positions does not show any mesogenic activity, although it has a low melting point and very high solubility in common organic solvents at room temperature. The absence of at
least one chlorine in the para positions of 11 results in an insufficient aspect ratio to be optimal for mesogenic behavior. The material 13 shows nematic phase with a melting point of 272°C.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Phase Transition</th>
</tr>
</thead>
</table>
| ![Structure 1](image1.png) | 11 (2, 3', 5')  
Cr 163 I |
| ![Structure 2](image2.png) | 12 (4, 3', 4''')  
Cr 167 N 319 I |
| ![Structure 3](image3.png) | 13 (4, 3, 3')  
Cr 272 N 285 I |

**Table 5.4:** Phase transition temperatures of the trichloroquaterphenyls

The material 11, with chlorine only in the lateral positions does not show any mesogenic activity, although it has low melting point and very high solubility in common organic solvents at room temperature. No chlorine in the para positions of 11 prevents the aspect ratio to be sufficient for mesogenic behavior. The material 13 has a mesogenic behavior that is intermediate between 11 and 12.

Obviously, there are numerous other p-quaterphenyl isomers with three chlorine atoms that remain to be prepared and many of them are likely to have interesting and useful phase behavior.
Both of the symmetrical tetrachlorinated quaterphenyls examined have nematic phases (14 enantiotropic and 15 monotropic). It would be especially interesting to see what the behavior of the less symmetric isomer 2,4,3''',4'''-tetrachloroquaterphenyl would be.

The unsymmetrical tetrachlorinated quaterphenyl 16 exhibits a nematic phase at a much lower temperature. The melting point of this material is 135°C. With proper mixture formulation, the melting point can be lowered even more.

**Table 5.5:** Phase transition temperatures of quaterphenyls with four chlorines

<table>
<thead>
<tr>
<th>Structure</th>
<th>Phase Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Structure 14" /></td>
<td><strong>14</strong> (4, 2, 3''', 4''') Cr 200 N 221 I</td>
</tr>
<tr>
<td><img src="image" alt="Structure 15" /></td>
<td><strong>15</strong> (4, 2, 2''', 4'''') Cr 226 N (180) I</td>
</tr>
<tr>
<td><img src="image" alt="Structure 16" /></td>
<td><strong>16</strong> (4, 3, 3', 4'''') Cr 135 N 161 I</td>
</tr>
</tbody>
</table>

**Figure 5.3:** UV-Vis spectra of 14 and 15 (Table 5.5)
The UV-Vis of 14 and 15 were examined and they absorb around 300 nm, which is in the ultraviolet region (Figure 5.3). The difference between the two spectra is due to the difference in the extent of conjugation. Material 15 is laterally chlorinated, which disturbs the coplanarity of the benzene rings, thus reducing the conjugation. This is the reason of material 15 absorbing at lower wavelength compared to material 14, which is more coplanar compared to 15.

Finally, following the examination of the preparation of chlorinated quaterphenyls, a single monochloroquinquephenyl was prepared. As before, the lateral chlorination has drastic effect on the transition temperatures of quinquephenyl. The effect is demonstrated in the example of the 2” monochlorination (melting reduction of 144 °C, clearing reduction of 116 °C).

![Phase transition: Cr 388 N 420 l](image1) ![Phase transition: Cr 240 N 304 l](image2)

**Figure 5.4:** Comparison of phase transitions of quinquephenyl and monochloroquinquephenyl

### 5.3 Mixture formulation

A ternary mixture was formulated using 14 (44.96%), 15 (21.91%) and the chlorinated quinquephenyl (33.12%). The melting point of this mixture was 165.92°C and clearing point was 252.90°C. The melting point is still much above room temperature. More mixtures need to be formulated to obtain materials that are useful for device application.
Figure 5.5: DSC of a mixture of 14, 15 and the monochloroquinquephenyl depicted in Figure 5.4

5.4 General synthesis scheme for the monochloro quaterphenyls

The set of quaterphenyls with the general structure shown in Figure 5.6 was prepared by Suzuki coupling between a custom synthesized 4-bromo/iodobiphenyl unit and commercially available 4-biphenylboronic acid. As such, addition of substituents in this set is restricted to only two of the four quaterphenyl benzene rings. Suzuki coupling was used to generate the bromo (X = Br) precursor. The order of reactivity of halogens in Suzuki coupling is C-I > C-Br >> C-Cl. This difference in reactivity was used to generate the halogenated partners in the aforesaid Suzuki coupling.
**Figure 5.6:** Synthesis of monochloroquaterphenyls devoid of alkyl tails

**Figure 5.7:** Custom synthesis of the monochloroquaterphenyl precursors
The syntheses of polychloroquaterphenyls (i.e., quaterphenyls with more than one chlorine atom) were customized according to the specific positions of the chlorine atoms. Quaterphenyls with chlorine only on the two end benzene rings (compounds 6, 7, 10, 14, 15) were synthesized by a Suzuki coupling of 4,4'-dibromobiphenyl or 4,4'-diiodobiphenyl with the appropriate chloro substituted phenylboronic acids.

Figure 5.8: Synthesis of chlorinated quaterphenyls with chlorine only on the two terminal benzene rings (A= Cl/ H, B= Cl/ H, C= Cl, H, D= Cl/ H, E= Cl/ H, X= Br or I), synthesis of the individual materials are discussed in the experimental section.

For the synthesis of materials 13, 11 and 8 individual strategies were adopted (Figures 5.9, 5.10 and 5.11 respectively).

Figure 5.9: Synthesis of 13 (Table 4)
5.5 Conclusions

In the current study we have explored two different design modifications in oligophenyl liquid crystals. We have shown that mesogenic activity can be generated in quaterphenyls even with the absence of alkyl chains that usually render flexibility in the molecule. The effect of chlorine substitution as a polar end group as well as in the lateral position to generate mesogenic activity at manageable temperatures has been examined. Although the melting points of some of the oligophenyls are much lower compared to \textit{p}-quaterphenyl, they are still much above room temperature. Future work will include more investigation with lateral substitution with the inclusion of bend in the molecule to reduce the melting point to a value closer to room
temperature while maintaining high birefringence. Another interesting direction would be to investigate unsymmetrical quaterphenyls. Some suggested materials are as below (Table 5.6).

<table>
<thead>
<tr>
<th>Serial number</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td><img src="image1" alt="Structure 17" /></td>
</tr>
<tr>
<td>18</td>
<td><img src="image2" alt="Structure 18" /></td>
</tr>
<tr>
<td>19</td>
<td><img src="image3" alt="Structure 19" /></td>
</tr>
</tbody>
</table>

**Table 5.6:** Suggested unsymmetrical quaterphenyls

These can be synthesized as below using Suzuki coupling.
Figure 5.12: Suggested synthesis of 17 and 18 in Table 5.6
Some of them melt below 100°C. But owing to the presence of alkyl tails, the absorption in the midwave infrared region will still be very high. From the midwave infrared absorption standpoint, the materials mentioned in this work will be more superior.
5.6 Experimental

Synthesis of 1-(4-bromophenyl)-4-chlorobenzene

\[
\begin{align*}
\text{I} & \quad \text{Br} & \quad \text{Cl} & \quad \text{Br}
\end{align*}
\]

In a 250 ml round-bottom flask K$_2$CO$_3$ (1.725 gm, 12.5 mmol) was dissolved in H$_2$O (40 ml) and 1,4-dioxane (100 ml) was added. After this mixture was degassed by sonication under vacuum for 20 minutes 4-chlorobenzeneboronic acid (1.5637 gm, 10.0 mmol), 1-bromo-4-iodobenzene (2.829 gm, 10.0 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (80 mg, 1.5 mol%) was added. The resulting mixture was refluxed for 18 hours under nitrogen when GC-MS showed complete conversion of the iodide starting material. At this point, the mixture was cooled down to room temperature and a white mass precipitated out. This precipitate was separated by suction filtration and dissolved in boiling isoctane and montmorillonite K10 clay was added. The mixture was gravity filtered while hot and the filtrate was cooled down to room temperature to give a white solid precipitate. The solid was separated by suction filtration, dried under vacuum and used in the next step without further purification.


$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 7.54 (2H, d, $J = 8.8$ Hz), 7.45 (2H, d, $J = 8.8$ Hz), 7.42-7.37 (4H, m)

$^{13}$C NMR (CDCl$_3$, 298 K, 100 MHz): 139.12, 138.66, 134.02, 132.21, 129.28, 128.77, 128.39, 122.11

IR (neat, cm$^{-1}$): 3050.33, 2922.97, 1903.90, 1584.33, 1471.66, 1385.23, 1089.51, 1069.49, 999.85, 848.44, 808.79, 721.74, 685.93
Synthesis of [4-(4-chlorophenyl)phenyl]boronic acid

\[
\begin{align*}
\text{Cl} & \quad \text{Br} \\
\text{Cl} & \quad \text{B(OH)}_2 \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

In a 500 ml two neck flask equipped with a stirbar, 1-bromo-4-(4-chlorophenyl)benzene (2.67 gm, 10.0 mmol) was dissolved in dry THF (100 ml) under nitrogen and the temperature of the solution was taken to -78°C. In this solution n-BuLi (4 ml, 2.5M in hexanes) was added dropwise. The solution was stirred for 50 minutes at -78°C and after that triisopropylborate (5.62 gm, 30 mmol) was added dropwise and allowed to come to room temperature overnight. In this solution, 10% HCl (100 ml) was added and the solution was stirred vigorously for 1 hour. The mixture was then extracted with ether (3×50 ml). The organic layers were combined, dried over MgSO\(_4\) and the solvent was removed under reduced pressure to obtain the title compound as a white solid (2.31 gm, 100% yield). The compound was used in the next step without further purification.

Synthesis of 1-[4-(4-chlorophenyl)phenyl]-4-phenylbenzene (1)

\[
\begin{align*}
\text{Cl} & \quad \text{Br} \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

In a 50 ml round-bottom flask K\(_2\)CO\(_3\) (0.69 gm, 5 mmol) was dissolved in H\(_2\)O (8 ml) and 1,4-dioxane (20.0 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that biphenylboronic acid (0.742 gm, 3.75 mmol), 1-bromo-4-(4-chlorophenyl)benzene (0.668gm, 2.5 mmol) and Pd(PPh\(_3\))\(_2\)Cl\(_2\) (20 mg, 1.5 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when TLC (eluent hexanes) showed complete conversion of the bromide starting material. At this point, the solvent was removed
under reduced pressure and the residue was dissolved in boiling toluene and montmorillonite K10 clay was added. The mixture was gravity filtered while hot and the filtrate was cooled down to room temperature when a white solid precipitated out. The solid was separated by suction filtration to obtain the desired product (525 mg, 62\% yield).

Phase transition: Cr 334 N 340 I

$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 7.86-7.62 (12H, m), 7.53-7.40 (4H, m), 7.39-7.30 (1H, m)

$^{13}$C NMR (CDCl$_3$, 298 K, 100 MHz): 129.32, 128.74, 127.89, 127.65 (more than one $^{13}$C signals overlap here), 127.01

IR (neat, cm$^{-1}$): 3057.91, 3034.82, 1908.33, 1652.13, 1591.05, 1477.11, 1399.74, 1095.63, 998.69, 812.02, 760.77, 731.92, 687.54

Synthesis of 1-(4-bromophenyl)-3-chlorobenzene

In a 250 ml round-bottom flask K$_2$CO$_3$ (1.725 gm, 12.5 mmol) was dissolved in H$_2$O (40 ml) and 1,4-dioxane (100 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 3-chlorobenzeneboronic acid (1.5637 gm, 10.0 mmol), 1-bromo-4-iodobenzene (2.829 gm, 10.0 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (80 mg, 1.5 mol\%) was added. This mixture was refluxed for 18 hours under nitrogen when GC-MS showed complete conversion of the iodide starting material. At this point, the mixture was cooled down to room temperature and the solvent was removed under reduced pressure. The residue was dissolved in boiling isooctane
and montmorillonite K10 clay was added. The mixture was gravity filtered while hot and the filtrate was removed under reduced pressure to obtain a low melting waxy solid.

$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 7.60-7.51 (3H, m), 7.44-7.39 (3H, m), 7.38-7.30 (2H, m)

$^{13}$C NMR (CDCl$_3$, 298 K, 100 MHz): 141.83, 138.72, 134.83, 132.04, 130.15, 128.69, 127.89, 127.66, 127.28, 127.09, 125.28, 125.09, 122.23

IR (neat, cm$^{-1}$): 3037.37, 1582.73, 1462.51, 1402.77, 1090.30, 1017.62, 789.76, 705.00

Synthesis of 1-(3-chlorophenyl)-4-(4-phenylphenyl)benzene (2)

In a 200 ml round-bottom flask K$_2$CO$_3$ (2.76 gm, 20.0 mmol) was dissolved in H$_2$O (20 ml) and 1,4-dioxane (50 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that biphenylboronic acid (2.38 gm, 12.18 mmol), 1-(4-bromophenyl)-3-chlorobenzene (2.18 gm, 8.12 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (61 mg, 1.5 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when TLC (eluent hexanes) showed complete conversion of the iodide starting material. At this point, the solvent was removed under reduced pressure and the residue was dissolved in boiling toluene and montmorillonite K10 clay was added. The mixture was gravity filtered while hot and the filtrate was cooled down to room temperature when a slight yellow solid precipitated out. The solid was separated by suction filtration to obtain the desired product as a white solid.

Phase Transition: Cr 242 SmX 255 I

$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 7.91-7.58 (12H, m), 7.56-7.28 (5H, m)
Synthesis of 1-(4-bromophenyl)-2-chlorobenzene

![Chemical structure]

In a 250 ml round-bottom flask K$_2$CO$_3$ (1.725 gm, 12.5 mmol) was dissolved in H$_2$O (40 ml) and 1,4-dioxane (100 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 2-chlorobenzeneboronic acid (1.5637 gm, 10.0 mmol), 1-bromo-4-iodobenzene (2.829 gm, 10.0 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (80 mg, 1.5 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when GC-MS showed complete conversion of the iodide starting material. At this point, the mixture was cooled down to room temperature and the solvent was removed under reduced pressure. The residue was dissolved in boiling isooctane and montmorillonite K10 clay was added. The mixture was gravity filtered while hot and the filtrate was removed under reduced pressure to obtain a low melting waxy solid.

$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 7.59 (2H, d, $J = 8.45$ Hz), 7.52-7.48 (1H, m), 7.38-7.30 (5H, m)

$^{13}$C NMR (CDCl$_3$, 298 K, 100 MHz): 139.30, 138.36, 131.39, 131.31, 130.20, 129.13, 127.22, 121.97

$^{13}$C NMR (CDCl$_3$, 298 K, 100 MHz): 131.09, 129.32, 127.81, 127.66, 127.57, 127.02, 126.79, 125.69

IR (neat, cm$^{-1}$): 3058.80, 3034.11, 1591.05, 1575.87, 1472.09, 1392.60, 1097.22, 998.58, 825.27, 762.28, 681.99
IR (neat, cm\(^{-1}\)): 3055.35, 1899.76, 1586.73, 1496.24, 1463.67, 1431.04, 1391.20, 1066.02, 1002.13, 823.86, 751.79, 691.20

Synthesis of 1-(2-chlorophenyl)-4-(4-phenylphenyl)benzene (3)

\[
\begin{align*}
\text{Cl} & \quad \text{Br} \\
\text{Cl} & \quad \text{Cl} \\
\end{align*}
\]

In a 200 ml round-bottom flask K\(_2\)CO\(_3\) (2.76 gm, 20.0 mmol) was dissolved in H\(_2\)O (16 ml) and 1,4-dioxane (40 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that biphenylboronic acid (1.10 gm, 5.6 mmol), 1-(4-bromophenyl)-2-chlorobenzene (1.00 gm, 3.73 mmol) and Pd(PPh\(_3\))\(_2\)Cl\(_2\) (28 mg, 1.5 mol\%) was added. This mixture was refluxed for 18 hours under nitrogen when TLC (eluent hexanes) showed complete conversion of the iodide starting material. At this point, the solvent was removed under reduced pressure and the residue was dissolved in boiling toluene and montmorillonite K10 clay was added. The mixture was gravity filtered while hot and the filtrate was cooled down to room temperature when a slight yellow solid precipitated out. The solid was separated by suction filtration and recrystallized from toluene to obtain the desired product as a slight yellow solid (0.56 gm, 44% yield).

Phase transition: Cr 175 I

\(^1\)H NMR (CDCl\(_3\), 298 K, 400 MHz): 7.89-7.63 (8H, m), 7.62-7.32 (9H, m)

\(^1^3\)C NMR (CDCl\(_3\), 298 K, 100 MHz): 140.02, 139.82, 139.39, 139.01, 138.34, 131.96, 131.78, 130.39, 130.36, 129.75, 129.57, 129.48, 128.07, 127.73, 127.68, 127.06, 126.85
IR (neat, cm⁻¹): 3033.60, 1466.33, 1433.53, 1390.73, 1124.01, 1073.47, 1035.64, 1001.34, 824.13, 747.29, 690.50

Synthesis of 1-bromo-2-chloro-4-phenylbenzene

In a 250 ml round-bottom flask K₂CO₃ (1.104 gm, 8.0 mmol) was dissolved in H₂O (16 ml) and 1,4-dioxane (40 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that benzeneboronic acid (0.321 gm, 2.64 mmol), 1-bromo-2-chloro-4-iodobenzene (0.837 gm, 2.64 mmol) and Pd(PPh₃)₂Cl₂ (40 mg, 3 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when GC-MS showed complete conversion of the iodide starting material. At this point, the mixture was cooled down to room temperature and adsorbed on silica gel and placed on the top of a silica gel column. The column was eluted with hexanes and the major band was collected. The solvent was removed under reduced pressure to obtain the desired product as a white solid (0.49 gm, 69% yield).

¹H NMR (CDCl₃, 298 K, 400 MHz): 7.67-7.65 (2H, m), 7.55-7.52 (2H, m), 7.46-7.42 (2H, m), 7.40-7.36 (1H, m), 7.33 (1H, dd, J = 8.42 Hz, 2.18 Hz)

¹³C NMR (CDCl₃, 298 K, 100 MHz): 142.18, 139.02, 135.02, 134.17, 129.24, 129.10, 128.38, 127.14, 126.78, 121.46
Synthesis of 2-chloro-4-phenyl-1-(4-phenylphenyl)benzene (5)

In a 50 ml round-bottom flask K$_2$CO$_3$ (0.552 gm, 4.0 mmol) was dissolved in H$_2$O (4 ml) and 1,4-dioxane (10 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that biphenylboronic acid (0.593 gm, 3.0 mmol), 1-bromo-2-chloro-4-phenylbenzene (0.535 gm, 2.0 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (15.9 mg, 1.5 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when TLC (eluent hexanes) showed complete conversion of the starting materials. At this point, the solvent was removed under reduced pressure and the residue was dissolved in boiling toluene and montmorillonite K10 clay was added. The mixture was gravity filtered while hot and the filtrate was cooled down to room temperature when a white solid precipitated out. The solid was separated by suction filtration to obtain the desired product as a white solid (502 mg, 73% yield).

Phase transition: Cr 148 SmX 162 I

$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 7.86-7.34 (17H, m)

$^{13}$C NMR (CDCl$_3$, 298 K, 100 MHz): 141.82, 140.71, 140.53, 139.42, 138.79, 138.01, 136.21, 134.00, 132.89, 131.69, 129.92, 128.97, 128.83, 128.75, 128.58, 128.40, 127.93, 127.57, 127.44, 127.17, 127.06, 126.84, 125.60, 115.64

IR (neat, cm$^{-1}$): 3376.55, 3078.96, 3055.80, 3029.22, 1607.19, 1551.34, 1519.86, 1332.14, 1079.11, 1004.71, 837.40, 731.57, 688.53
Synthesis of 2-chloro-1-phenyl-4-(4-phenylphenyl)benzene (4)

In a 50 ml round-bottom flask K$_2$CO$_3$ (1.104 gm, 8.0 mmol) was dissolved in H$_2$O (4 ml) and 1,4-dioxane (10 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that biphenylboronic acid (0.36 gm, 1.84 mmol), 4-bromo-2-chloro-1-phenylbenzene (0.33 gm, 1.23 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (9.23 mg, 1.5 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when TLC (eluent hexanes) showed complete conversion of the starting materials. At this point, the solvent was removed under reduced pressure and the residue was dissolved in boiling toluene and montmorillonite K10 clay was added. The mixture was gravity filtered while hot and the filtrate was cooled down to room temperature when a slight yellow solid precipitated out. The solid was separated by suction filtration to obtain the desired product as a slight yellow solid (330 mg, 79% yield).

Phase transitions: Cr 164 I

$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 7.96-7.61 (8H, m), 7.59-7.32 (9H, m)

$^{13}$C NMR (CDCl$_3$, 298 K, 100 MHz): 140.95, 140.32, 139.91, 139.18, 138.85, 137.61, 132.52, 129.69, 129.49, 129.26, 128.75, 128.32, 128.19, 128.06, 127.79, 127.10, 126.81, 126.43, 126.06, 116.1

IR (neat, cm$^{-1}$): 3414.50, 3056.06, 3029.83, 2921.53, 2851.61, 1598.40, 1523.45, 1470.88, 1377.15, 1260.79, 1075.30, 1003.55, 823.33, 763.12, 696.87
Synthesis of 1-bromo-2-chloro-4-(3,4-dichlorophenyl)benzene

\[
\begin{align*}
\text{I} & \quad \text{Br} \\
\text{Cl} & \quad \text{Cl} \\
\end{align*}
\]

In a 200 ml round-bottom flask K$_2$CO$_3$ (2.76 gm, 20.0 mmol) was dissolved in H$_2$O (40 ml) and 1,4-dioxane (100 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 3, 4-dichlorobenzeneboronic acid (1.9 gm, 10.0 mmol), 1-bromo-2-chloro-4-iodobenzene (3.16 gm, 10.0 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (80 mg, 1.5 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when GC-MS showed complete conversion of the starting material. At this point, the mixture was cooled down to room temperature when a white mass precipitated out. This was dissolved in boiling isoctane and montmorillonite K10 clay was added. The mixture was gravity filtered while hot and the filtrate was cooled down to room temperature when a slight yellow solid precipitated out. This solid was adsorbed on silica gel and placed on the top of a silica gel column. The column was eluted with hexanes and the major band was collected. The solvent was removed under reduced pressure to obtain the desired material as a white solid (2.53 gm, 75% yield). Melting point: 183°C.

$^1$H NMR (tetrachloroethane-d$_2$, 298 K, 400 MHz): 7.70 (1H, d, J = 8.62 Hz), 7.63 (2H, dd, J = 2.15 Hz, 0.60 Hz), 7.54 (1H, d, J = 8.15 Hz), 7.39 (1H, dd, J = 8.23 Hz, 2.26 Hz), 7.30 (1H, dd, J = 8.23 Hz, 2.26 Hz)

$^{13}$C NMR (tetrachloroethane-d$_2$, 298 K, 100 MHz): 139.48, 138.80, 134.42, 133.25, 131.16, 128.85, 128.77, 126.57, 126.39, 122.45

IR (neat, cm$^{-1}$): 3054.21, 2950.84, 1542.37, 1452.10, 1357.99, 1119.44, 1029.23, 1016.73, 891.92, 876.73, 830.49, 816.75, 746.89, 665.65
2-chloro-4-(3,4-dichlorophenyl)-1-(4-phenylphenyl)benzene (13)

In a 250 ml round-bottom flask K₂CO₃ (1.104 gm, 8.0 mmol) was dissolved in H₂O (8 ml) and 1,4-dioxane (20 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that biphenylboronic acid (0.439 gm, 2.22 mmol), 1-bromo-2-chloro-4-(3,4-dichlorophenyl)benzene (0.5 gm, 1.48 mmol) and Pd(PPh₃)₂Cl₂ (22.4 mg, 3 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when TLC showed complete conversion of the starting material. At this point, the mixture was cooled down to room temperature and the solvent was removed under reduced pressure. The residue was dissolved in boiling toluene and montmorillonite K10 clay was added. The mixture was gravity filtered while hot and the filtrate was removed under reduced pressure to obtain a light yellow solid (0.42 gm, 70% yield)

Phase transition: Cr 252 N 285 I

¹H NMR (tetrachloroethane-d2, 298 K, 400 MHz): 7.83-7.34 (15H, m)

¹³C NMR (DMSO-d6, 353 K, 100 MHz): 140.28, 139.71, 139.52, 139.10, 132.38, 131.50, 130.16, 129.38, 129.15, 128.50, 128.04, 127.45, 127.14, 126.97, 126.30

IR (neat, cm⁻¹): 3058.07, 3027.16, 2962.32, 2922.29, 2851.56, 1603.88, 1527.41, 1466.85, 1390.77, 1364.70, 1075.16, 1049.56, 1001.29, 825.82, 733.27, 693.88
Synthesis of 2,6-dichloro-4-(2-chlorophenyl)aniline

In a 250 ml round bottom flask equipped with a stir bar was added PEG-2000 (10.5 gm) and Na₂CO₃ (2.11 gm, 20.0 mmol). After adding water (9 ml) the mixture was stirred at 50°C until it became a smooth viscous mass. Then Pd(OAc)₂ (22 mg, 1 mol%) was added under N₂ and the mixture was stirred for 5 minutes and 4-bromo-2,6-dichloroaniline (2.409 gm, 10 mmol) and 2-chlorophenylboronic acid (2.34 gm, 15 mmol) was added all at once. The mixture was stirred for 12 hours when all the starting materials were consumed (monitored by GC-MS). The mixture was cooled down to room temperature and extracted with ether (3×100 ml). The combined organic layer was dried over MgSO₄ and the solvent was removed under reduced pressure to obtain a red liquid (2.99 gm). This was used immediately in the next reaction without any further purification.

Synthesis of 1,3-dichloro-5-(2-chlorophenyl)-2-iodobenzene

To a solution of p-TsOH·H₂O (5.73 g, 30.0 mmol) in MeCN (40 mL) was added 2,6-dichloro-4-(2-chlorophenyl)aniline (2.72 gm, 10.0 mmol). The resulting suspension of amine salt was cooled to 10–15 °C and to this was added, gradually, a solution of NaNO₂ (1.38 gm, 20 mmol) and KI (4.15 gm, 25.0 mmol) in H₂O (6 mL). The reaction mixture was stirred for 10 min then
allowed to come to 20 °C and stirred until all the amine was consumed (GC-MS). Sodium thiosulfate (2 gm) was added to this mixture and then the mixture was adsorbed on silica gel and placed on the top of a silica gel column. The column was eluted with hexanes and the major band was separated to obtain the desired product as a light orange low melting waxy solid (3.23 gm, 84% yield).

\(^1\)H NMR (CDCl\(_3\), 298 K, 400 MHz): 7.48-7.45 (1H, m), 7.42 (2H, s), 7.34-7.26 (2H, m)

\(^13\)C NMR (CDCl\(_3\), 298 K, 100 MHz): 141.50, 140.47, 137.37, 132.40, 131.05, 130.46, 129.93, 128.36, 127.37, 102.90

IR (neat, cm\(^{-1}\)): 3063.23, 2920.47, 1911.78, 1768.60, 1713.11, 1542.95, 1453.38, 1358.65, 1133.33, 1017.73, 876.60, 815.95, 747.05, 677.84

Synthesis of 1,3-dichloro-5-(2-chlorophenyl)-2-(4-phenylphenyl)benzene (11)

In a 100 ml round-bottom flask K\(_2\)CO\(_3\) (0.69 gm, 5.0 mmol) was dissolved in H\(_2\)O (8 ml) and 1,4-dioxane (20 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that biphenylboronic acid (0.742 gm, 3.75 mmol), 1,3-dichloro-5-(2-chlorophenyl)-2-iodobenzene (0.958 gm, 2.5 mmol) and Pd(PPh\(_3\))\(_2\)Cl\(_2\) (20 mg, 1.5 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when TLC (eluent hexanes) showed complete conversion of the starting materials. At this point, the solvent was removed under reduced pressure and the residue was dissolved in boiling toluene and montmorillonite
K10 clay was added. The mixture was gravity filtered while hot and the filtrate was removed under reduced pressure to obtain a viscous liquid. Cold ethanol (75 ml) was added to this when a white solid precipitated out. The solid was separated by suction filtration to yield the desired product (0.475 gm, 46% yield).

Phase transitions: Cr 163 I

$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 7.71 (2H, d, $J = 8.8$ Hz), 7.69-7.66 (2H, m), 7.51 (2H, s), 7.50-7.32 (9H, m)

$^{13}$C NMR (CDCl$_3$, 298 K, 100 MHz): 140.93, 140.49, 135.58, 134.58, 131.11, 130.24, 130.13, 129.54, 129.08, 128.80, 127.48, 127.20, 127.13, 126.92

IR (neat, cm$^{-1}$): 3058.10, 3027.45, 1601.09, 1536.43, 1490.19, 1447.00, 1428.22, 1371.76, 1275.87, 1260.72, 1190.07, 1042.54, 1004.13, 865.66, 801.23, 754.90, 699.21

Synthesis of 4-bromo-2-chloro-1-phenylbenzene

In a 250 ml round-bottom flask K$_2$CO$_3$ (1.104 gm, 8.0 mmol) was dissolved in H$_2$O (16 ml) and 1,4-dioxane (40 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that benzeneboronic acid (0.321 gm, 2.64 mmol), 1-bromo-3-chloro-4-iodobenzene (0.837 gm, 2.64 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (40 mg, 3 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when GC-MS showed complete conversion of the starting material. At this point, the mixture was cooled down to room temperature and adsorbed on silica gel and placed on the top of a silica gel column. The column was eluted with hexanes
and the major band was separated. The solvent was removed under reduced pressure to obtain the desired product as colorless oil (0.43 gm, 61% yield).

$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 7.63 (2H, d, $J = 2.0$ Hz), 7.44-7.35 (6H, m), 7.19 (2H, d, $J = 8.0$ Hz)

$^{13}$C NMR (CDCl$_3$, 298 K, 100 MHz): 139.79, 138.53, 133.69, 132.67, 132.60, 130.26, 129.46, 128.38, 128.13, 121.58

IR (neat, cm$^{-1}$): 3077.73, 3056.55, 1943.95, 1877.96, 1811.68, 1739.93, 1692.07, 1569.90, 1455.27, 1410.95, 1369.79, 1239.95, 1068.43, 872.02, 808.52, 782.91, 737.17, 689.37

Synthesis of (3-chloro-4-phenylphenyl)boronic acid

In a 500 ml two neck flask equipped with a stir bar 4-bromo-2-chloro-1-phenylbenzene (2.67 gm, 10 mmol) was dissolved in dry THF (200 ml) under nitrogen and the temperature of the mixture was taken to -78°C. In this solution, n-BuLi (4 ml, 2.5M in hexanes) was added dropwise and the resulting mixture was stirred for 45 minutes. After this, triisopropyl borate (5.64 gm, 30.0 mmol) was added dropwise while maintaining the temperature at -78°C. The mixture was then allowed to come to room temperature overnight. In this solution, 10% HCl (100 ml) was added and the mixture was stirred for an hour and then extracted with ether (3 × 50 ml). The organic layer was combined, dried over MgSO$_4$ and the solvent was evaporated under reduced pressure to obtain the title compound as a off-white solid (1.6 gm, 69% yield). The material was used in the next step without any further purification.
Synthesis of 2-chloro-4-(3-chloro-4-phenylphenyl)-1-phenylbenzene (8)

In a 200 ml round-bottom flask K₂CO₃ (0.552 gm, 4.0 mmol) was dissolved in H₂O (4 ml) and 1,4-dioxane (10 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that (3-chloro-4-phenylphenyl)boronic acid (0.348 gm, 1.5 mmol), 4-bromo-2-chloro-1-phenylbenzene (0.267 gm, 1 mmol) and Pd(PPh₃)₂Cl₂ (16 mg, 3 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when TLC (2% EtOAc, 98% hexanes) showed complete conversion of the starting material. The solvent was removed from the reaction mixture under reduced pressure and the residue was dissolved in hot toluene (100 ml). Montmorillonite K10 clay was added to the mixture and it was gravity filtered while hot. The volume of the solvent was reduced to 10 ml and cooled down to 0°C when the product precipitated out. The solid product was separated by suction filtration and recrystallized from toluene to obtain the desired product as shiny white plates (0.29 gm, 77% yield).

Phase transition: Cr 148 I

¹H NMR (tetrachloroethane-d₂, 298 K, 400 MHz): 7.74 (2H, d, J = 1.63 Hz), 7.59 (2H, dd, J = 7.90 Hz, 1.86 Hz), 7.55-7.38 (12H, m)

¹³C NMR (tetrachloroethane-d₂, 298 K, 100 MHz): 139.82, 139.78, 138.81, 133.05, 132.08, 129.64, 128.46, 128.33, 127.97, 125.62

IR (neat, cm⁻¹): 3052.89, 3026.96, 1813.71, 1768.77, 1603.93, 1529.88, 1465.62, 1442.06, 1368.23, 1248.56, 1073.56, 1048.05, 1029.69, 1003.65, 874.45, 831.84, 762.23, 722.20, 696.81
Synthesis of 1-(2-chlorophenyl)-4-[4-(2-chlorophenyl)phenyl]benzene (6)

In a 200 ml round-bottom flask K$_2$CO$_3$ (1.656 gm, 10.0 mmol) was dissolved in H$_2$O (20 ml) and 1,4-dioxane (50 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 2-chlorobenzeneboronic acid (1.87 gm, 12 mmol), 4,4'-dibromobiphenyl (1.56 gm, 5 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (80 mg, 3 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when TLC (2% EtOAc, 98% hexanes) showed complete conversion of the starting material. The solvent was removed from the reaction mixture under reduced pressure and the residue was dissolved in hot toluene (100 ml). Montmorillonite K10 clay was added to the mixture and it was gravity filtered while hot. The volume of the solvent was reduced to 30 ml when the product precipitated out. The solid product was separated by suction filtration and recrystallized from toluene to obtain the desired product as light yellow plates (1.09 gm, 54% yield).

Phase transition: Cr 168 I

$^1$H NMR (tetrachloroethane-d2, 298 K, 400 MHz): 7.77 (4H, d, $J = 8.86$ Hz), 7.59 (4H, d, $J = 8.55$ Hz), 7.53 (2H, dd, $J = 7.68$ Hz, 1.51 Hz), 7.45 (2H, dd, $J = 7.38$ Hz, 2.11 Hz), 7.41-7.30 (4H, m)

$^{13}$C NMR (tetrachloroethane-d2, 298 K, 100 MHz): 139.71, 139.32, 138.22, 132.17, 131.33, 129.93, 129.89, 128.60, 126.94, 126.50

IR (neat, cm$^{-1}$): 3054.45, 3034.72, 1921.08, 1501.21, 1464.98, 1429.41, 1389.29, 1244.17, 1160.86, 1124.08, 1074.00, 1032.09, 1001.63, 968.15, 824.74, 747.07, 733.22, 677.80
Synthesis of 1-(3-chlorophenyl)-4-[4-(3-chlorophenyl)phenyl]benzene (7)

\[
\text{Br-} \overset{\text{Cl}}{\underset{\text{Br}}{\text{C}}}-\overset{\text{Cl}}{\underset{\text{Cl}}{\text{C}}} \rightarrow \overset{\text{Cl}}{\underset{\text{Cl}}{\text{C}}}-\overset{\text{C}}{\underset{\text{C}}{\text{C}}}-\overset{\text{C}}{\underset{\text{C}}{\text{C}}}-\overset{\text{C}}{\underset{\text{C}}{\text{C}}}-\overset{\text{C}}{\underset{\text{C}}{\text{C}}}
\]

In a 200 ml round-bottom flask K$_2$CO$_3$ (1.656 gm, 10.0 mmol) was dissolved in H$_2$O (20 ml) and 1,4-dioxane (50 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 3-chlorobenzeneboronic acid (1.87 gm, 12 mmol), 4,4’-dibromobiphenyl (1.56 gm, 5 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (80 mg, 3 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when TLC (2% EtOAc, 98% hexanes) showed complete conversion of the starting material. The solvent was removed from the reaction mixture under reduced pressure and the residue was dissolved in hot toluene (100 ml). Montmorillonite K10 clay was added to the mixture and it was gravity filtered while hot. The volume of the solvent was reduced to 30 ml when the product precipitated out. The solid product was separated by suction filtration and recrystallized from toluene to obtain the desired product as light yellow plates (1.21 gm, 65% yield).

Phase transition: Cr 220 I

$^1$H NMR (tetrachloroethane-d2, 298 K, 400 MHz): 7.81-7.63 (10H, m), 7.57 (2H, d, J = 7.53 Hz), 7.48-7.32 (4H, m)

$^{13}$C NMR (tetrachloroethane-d2, 298 K, 100 MHz): 142.13, 139.59, 138.52, 134.46, 130.08, 127.41, 127.37, 126.94, 125.11

IR (neat, cm$^{-1}$): 3072.87, 3039.66, 1910.12, 1880.90, 1801.38, 1690.74, 1589.22, 1546.63, 1458.06, 1392.03, 1100.75, 1084.32, 881.19, 828.21, 784.32, 680.41
Synthesis of 1,2-dichloro-4-\{4-[4-(3,4-dichlorophenyl)phenyl]phenyl\}benzene (14)

In a 200 ml round-bottom flask $\text{K}_2\text{CO}_3$ (1.38 gm, 10.0 mmol) was dissolved in H$_2$O (20 ml) and 1,4-dioxane (50 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that (3,4-dichlorophenyl)boronic acid (2.28 gm, 12 mmol), 4,4’-dibromobiphenyl (1.56 gm, 5 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (80 mg, 3 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when TLC (2% EtOAc, 98% hexanes) showed complete conversion of the starting material. The solvent was removed from the reaction mixture under reduced pressure and the residue was dissolved in hot toluene (100 ml). Montmorillonite K10 clay was added to the mixture and it was gravity filtered while hot. The volume of the solvent was reduced to 30 ml when the product precipitated out. The solid product was separated by suction filtration and recrystallized from toluene to obtain the desired product as shiny white plates (1.52 gm, 68% yield).

Phase Transition: Cr 200 N 221 I

$^1$H NMR (tetrachloroethane-d2, 298 K, 400 MHz): 7.77-7.72 (6H, m), 7.67 (4H, d, $J = 8.34$ Hz), 7.56 (2H, d, $J = 8.52$ Hz), 7.50 (2H, dd, $J = 8.34$ Hz, 2.22 Hz)

$^{13}$C NMR (tetrachloroethane-d2, 298 K, 100 MHz): 140.37, 139.75, 137.57, 132.67, 131.31, 130.69, 128.63, 127.47, 127.30, 126.19

IR (neat, cm$^{-1}$): 3037.03, 1910.25, 1562.77, 1536.05, 1460.05, 1377.94, 1134.03, 1049.20, 1027.94, 879.46, 805.95, 686.82, 663.39

166
Synthesis of 1-(2,4-dichlorophenyl)-4-[4-(2,4-dichlorophenyl)phenyl]benzene (15)

\[
\begin{align*}
\text{I} & \quad \begin{array}{c}
\text{Cl} \\
\text{Cl}
\end{array} \\
\text{I} & \quad \\
\end{align*}
\rightarrow
\begin{align*}
\text{Cl} & \quad \\
\text{Cl} & \quad \\
\text{Cl} & \quad \\
\end{align*}
\]

In a 200 ml round-bottom flask K$_2$CO$_3$ (1.65 gm, 12.0 mmol) was dissolved in H$_2$O (20 ml) and 1,4-dioxane (50 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4,4’-diiodobiphenyl (2.03 gm, 5.0 mmol), 2,4-dichlorophenylboronic acid (2.29 gm, 12.0 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (80 mg, 3.0 mol%) was added. This mixture was refluxed for 18 hours under nitrogen. TLC (eluent hexanes) showed complete conversion of the starting materials. The solvent was removed from the reaction mixture under reduced pressure and the residue was dissolved in hot toluene (150 ml). Montmorillonite K10 clay was added to the mixture and it was gravity filtered while hot. The volume of the solvent was reduced to 5 ml when the product precipitated out. The solid product was separated by suction filtration and recrystallized from toluene to obtain the desired product as white solid (1.01 gm, 45% yield).

Phase transition: Cr 226 N (180) I

$^1$H NMR (tetrachloroethane-d2, 298 K, 400 MHz): 7.73 (4H, d, $J = 8.24$ Hz), 7.53 (6H, m), 7.35 (4H, s)

$^{13}$C NMR (tetrachloroethane-d2, 298 K, 100 MHz): 139.82, 138.59, 137.45, 133.83, 133.24, 132.33, 130.07, 129.94, 127.50, 126.92

IR (neat, cm$^{-1}$): 3067.12, 3039.05, 1893.36, 1725.77, 1587.88, 1559.67, 1432.72, 1371.68, 1243.81, 1143.47, 1102.50, 1073.54, 1031.12, 999.12, 863.38, 834.89, 798.87, 728.74, 694.98
Synthesis of 1-bromo-2-chloro-4-(4-chlorophenyl)benzene

In a 250 ml round-bottom flask K$_2$CO$_3$ (2.76 gm, 20.0 mmol) was dissolved in H$_2$O (40 ml) and 1,4-dioxane (40 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4-chlorobenzeneboronic acid (1.56 gm, 10.0 mmol), 1-bromo-2-chloro-4-iodobenzene (3.16 gm, 10 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (75.74 mg, 1.5 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when GC-MS showed complete conversion of the iodide starting material. At this point, the mixture was cooled down to room temperature and adsorbed on silica gel and placed on the top of a silica gel column. The column was eluted with hexanes and the major band was separated. The solvent was removed under reduced pressure to obtain the desired product as colorless oil (2.32 gm, 77% yield). Melting point: 91°C.

$^1$H NMR (tetrachloroethane-d$_2$, 298 K, 400 MHz): 7.69 (1H, d, $J =$ 8.37 Hz), 7.64 (1H, d, $J =$ 2.13 Hz), 7.49 (2H, d, $J =$ 8.69 Hz), 7.43 (2H, d, $J =$ 8.29 Hz), 7.32 (1H, d, $J =$ 8.29 Hz, 2.22 Hz)

$^{13}$C NMR (tetrachloroethane-d$_2$, 298 K, 100 MHz): 140.42, 136.92, 134.70, 134.09, 133.97, 129.07, 128.49, 128.07, 126.31, 121.47

IR (neat, cm$^{-1}$): 3053.12, 3028.15, 1903.24, 1595.78, 1541.33, 1497.26, 1475.45, 1456.25, 1370.09, 1121.74, 1089.94, 1011.64, 883.64, 805.31, 720.98, 665.88
Synthesis of 2-chloro-4-(4-chlorophenyl)-1-[4-(4-chlorophenyl)phenyl]benzene (12)

In a 200 ml round-bottom flask K₂CO₃ (0.552 gm, 4.0 mmol) was dissolved in H₂O (8 ml) and 1,4-dioxane (20 ml) was added X. This mixture was degassed by sonication under vacuum for 20 minutes and after that [4-(4-chlorophenyl)phenyl]boronic acid (0.58 gm, 2.5 mmol), 1-bromo-2-chloro-4-(4-chlorophenyl)benzene (0.60 gm, 2 mmol) and Pd(PPh₃)₂Cl₂ (16 mg, 1.5 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when TLC (2% EtOAc, 98% hexanes) showed complete conversion of the starting material. The solvent was removed from the reaction mixture under reduced pressure and the residue was dissolved in hot toluene (100 ml). Montmorillonite K10 clay was added to the mixture and it was gravity filtered while hot. The volume of the solvent was reduced to 10 ml and cooled down to 0°C when the product precipitated out. The solid product was separated by suction filtration and recrystallized from toluene to obtain the desired product as shiny white plates (0.55 gm, 68% yield)

Phase transition: Cr 167 N 319 I

¹H NMR (tetrachloroethane-d₂, 298 K, 400 MHz): 7.79-7.38 (15H, m)

¹³C NMR (tetrachloroethane-d₂, 298 K, 100 MHz): 140.25, 138.83, 138.76, 138.64, 137.87, 137.48, 133.86, 133.32, 132.70, 131.70, 129.91, 129.03, 128.90, 128.21, 128.17, 127.29, 126.49, 125.37

IR (neat, cm⁻¹): 3032.17, 1909.94, 1593.85, 1470.22, 1377.52, 1094.30, 1078.61, 1002.29, 809.15
Synthesis of 2-chloro-4-(4-chlorophenyl)-1-(4-phenylphenyl)benzene (9)

In a 200 ml round-bottom flask K₂CO₃ (0.552 gm, 4.0 mmol) was dissolved in H₂O (8 ml) and 1,4-dioxane (20 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that biphenyl|boronic acid (0.49 gm, 2.5 mmol), 1-bromo-2-chloro-4-(4-chlorophenyl)benzene (0.60 gm, 2 mmol) and Pd(PPh₃)₂Cl₂ (16 mg, 1.5 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when TLC (2% EtOAc, 98% hexanes) showed complete conversion of the starting material. The solvent was removed from the reaction mixture under reduced pressure and the residue was dissolved in hot toluene (100 ml). Montmorillonite K10 clay was added to the mixture and it was gravity filtered while hot. The volume of the solvent was reduced to 10 ml and cooled down to 0°C when the product precipitated out. The solid product was separated by suction filtration and recrystallized from toluene to obtain the desired product as shiny white plates (0.53 gm, 70% yield).

Phase transition: Cr 217 N (181) I

¹H NMR (tetrachloroethane-d₂, 298 K, 400 MHz): 7.82-7.36 (16H, m)

¹³C NMR (tetrachloroethane-d₂, 298 K, 100 MHz): 140.14, 140.03, 138.78, 137.50, 133.82, 132.70, 131.74, 129.81, 129.02, 128.93, 128.80, 128.17, 127.47, 127.37, 127.20, 126.93, 126.62, 125.35,

IR (neat, cm⁻¹): 3057.99, 3031.52, 1909.46, 1596.43, 1470.70, 1376.58, 1095.72, 1078.30, 1003.48, 816.02, 767.20, 734.95, 679.94
Synthesis of 2-chloro-1-[4-(4-chlorophenyl)phenyl]-4-(3,4-dichlorophenyl)benzene (16)

\[
\begin{array}{c}
\text{Cl} & \text{Cl} & \text{Br} & \rightarrow & \text{Cl} & \text{Cl} & \text{Cl} & \text{Cl} \\
\text{Cl} & \text{Cl} & \text{Cl} & \text{Cl}
\end{array}
\]

In a 200 ml round-bottom flask $\text{K}_2\text{CO}_3$ (0.552 gm, 4.0 mmol) was dissolved in $\text{H}_2\text{O}$ (8 ml) and 1,4-dioxane (20 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that [4-(4-chlorophenyl)phenyl]boronic acid (0.49 gm, 2.5 mmol), 1-bromo-2-chloro-4-(3,4-dichlorophenyl)benzene (0.67 gm, 2 mmol) and $\text{Pd(PPh}_3\text{)}_2\text{Cl}_2$ (16 mg, 1.5 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when TLC (2% EtOAc, 98% hexanes) showed complete conversion of the starting material. The solvent was removed from the reaction mixture under reduced pressure and the residue was dissolved in hot toluene (100 ml). Montmorillonite K10 clay was added to the mixture and it was gravity filtered while hot. The volume of the solvent was reduced to 10 ml and cooled down to 0°C when the product precipitated out. The solid product was separated by suction filtration and recrystallized from toluene to obtain the desired product as shiny white plates (0.61 gm, 69% yield).

Phase transition: Cr 135 N 161 I

$^1\text{H NMR}$ (tetrachloroethane-d2, 298 K, 400 MHz): 7.79-7.37 (14H, m)

$^{13}\text{C NMR}$ (tetrachloroethane-d2, 298 K, 100 MHz): 139.23, 139.10, 139.01, 138.96, 138.84, 138.74, 137.72, 133.36, 132.87, 131.82, 130.82, 129.88, 128.92, 128.68, 128.23, 128.15, 127.31, 126.53, 126.21, 125.38

IR (neat, cm$^{-1}$): 3053.32, 3030.92, 1531.51, 1453.88, 1359.60, 1121.36, 1098.77, 1077.75, 1050.90, 1016.02, 1002.47, 873.36, 860.05, 799.64
5.7 References


Chapter 6

Design and synthesis of high birefringence liquid crystals

for microwave applications

6.1 Introduction

In recent years nematic liquid crystal materials have been investigated for microwave applications\textsuperscript{1,2} as their dielectric constant can be precisely tuned in the mm-waveband\textsuperscript{3,4}. Nematic liquid crystals were proven to be much more efficient than inorganic materials when used in phase shifters at GHz frequency\textsuperscript{5}. Representative applications include construction of microwave components as integrated single compact devices (GSM, wireless LAN etc.) and the design of phase shifters for phased-array antennas for applications like automotive radar sensors\textsuperscript{6}.

\textbf{Figure 6.1}: Prototype of the electronic beam steering liquid crystal phased array\textsuperscript{7}
A drawback of using commercially available liquid crystals in microwave applications is their low response time, which can go up to 1 second. Also, the birefringence is not as high as desired and so there is a need of using thick LC layer (> 5 microns) to achieve a sufficient phase change. But such thick layers decrease the response time of the LC layer significantly, sometimes to the order of 1 second or more (the response time is proportional to the thickness of LC layer squared\(^8\)). The net relationship between response time, cell thickness and rotational viscosity is,

\[ \tau_0 = \frac{\gamma_1 d^2}{K_{11} \pi} \]

Here \( \gamma_1 \) = rotational viscosity, \( d \) = liquid crystal cell gap and \( K_{11} \) = splay elastic constant.

\( \tau_0 \) = response time.

Ferroelectric liquid crystalline materials do not suffer from the drawbacks in speed that are inherent to the typical nematic liquid crystals as the response time for FLCs can reach the value of 1 µs. But the fabrication of FLCs for device application is very complex due to the occurrence of defects in alignment (zigzag defects) that causes light leakage\(^9,10\)-degrading the performance of the device. This in turn increases the cost of the device to a very large extent.

Thus, the design of high birefringence nematic liquid crystals is warranted, as they are preferred for their easy processability compared to FLCs.

6.2 Molecular Design Strategy

Birefringence depends on the anisotropy of polarizability, which in turn depends on the conjugation of the material. But with increasing conjugation, the melting point also usually increases, which often renders the material unfit for device applications. The alkyl tails in typical liquid crystalline materials help in keeping the melting point low. But these alkyl tails are
optically isotropic and they dilute the birefringence of the material due to the conjugated components\textsuperscript{11}. Very short (propyl) tails were used or they were excluded altogether from the molecule design in order to mitigate the effect of alkyl tails in decreasing birefringence. Also, highly conjugated calamitic LC materials have higher melting points compared to the commercially available LC materials that are used in devices due to higher intermolecular interactions, which sometimes leads to more efficient packing in the crystalline phase. In order to lower the melting point, the disruption of the coplanarity of the molecule is an effective strategy. Strategic placement of a moiety (for example, a chlorine atom) in a lateral position can reduce the coplanarity of the benzene rings by interacting with the hydrogen(s) in the adjacent ring. This mutual interaction depends on the combined sizes of the lateral substituents. A typical comparison of halogens showing this effect is I > Br > Cl > F\textsuperscript{12}. Chlorine is an attractive choice due to the relative chemical stability of the C-Cl bond compared to Br and I, although its size is large enough to disturb the coplanarity of the molecule. Also, with bulky lateral substituents there is a reduction of packing efficiency, which in turn reduces the melting point. Chloro substitution also introduces a lateral dipole in the molecule. The influence on the melting points and mesomorphism of oligophenyls by a single lateral chlorine atom substitution is demonstrated in Table 6.1.
Quinquephenyl has a melting point of 388°C\textsuperscript{18}. A single chlorine substitution in the middle ring reduces the melting point by 148°C and the clearing point by 116°C. Introducing noncollinearity in the molecule can also drastically reduce the melting point. The example below efficiently illustrates the effect\textsuperscript{18} (Figure 6.2). A highly collinear molecule is like quinquephenyl, wherein on the average the centers of all the rings and all links between rings lie along a single line.

Table 6.1: Comparison of phase behavior of oligophenyls and their selective chlorinated analogues\textsuperscript{13\textendash}18.

<table>
<thead>
<tr>
<th>Oligophenyl</th>
<th>Laterally chlorinated analogue</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="#" alt="Chemical Structure" /> Cr 70 I</td>
<td><img src="#" alt="Chemical Structure" /> Cr 33 I</td>
</tr>
<tr>
<td><img src="#" alt="Chemical Structure" /> Cr 210 I</td>
<td><img src="#" alt="Chemical Structure" /> Cr 101 I</td>
</tr>
<tr>
<td><img src="#" alt="Chemical Structure" /> Cr 322 I</td>
<td><img src="#" alt="Chemical Structure" /> Cr 226 I</td>
</tr>
<tr>
<td><img src="#" alt="Chemical Structure" /> Cr 388 N 420 I</td>
<td><img src="#" alt="Chemical Structure" /> Cr 240 N 304 I</td>
</tr>
</tbody>
</table>
Figure 6.2: Comparison of the phase behavior of three isomers of quinquephenyl that differ in collinearity.

The resulting increase in melting point due to exclusion of alkyl chains or using very short alkyl chains were mitigated by including either/both of the aforesaid strategies in the molecule design, i.e. introduction of a bend in the molecule and lateral chlorine substitution to make the core noncoplanar and noncollinear. Thiophene and oxadiazole rings were used in these molecules to introduce the bend and preserve through conjugation. These heterocyclic rings also influence the dielectric anisotropy in the molecule. The molecules designed are illustrated below (Figure 6.3).
In molecules 1-3 the chlorine is placed in a way as to effectively disturb co-planarity of the molecule, which in turn has significant effect on lowering the melting point (Figure 6.3). All of the four molecules are highly soluble in common organic solvents like dichloromethane, toluene, tetrahydrofuran etc. that makes them attractive choice for fabrication of organic electronic devices as they can be deposited through inkjet printing. The molecules designed were inspired by the ease of synthesis and availability of starting materials. Many more isomers can be synthesized and investigated (especially the influence of placement of chlorine on the other sites of the molecules on the respective mesophase properties and other electro-optic properties).

Also, the effect of other heterocyclic rings can be investigated. The isothiacyanato end group is known to instill high birefringence and lower the melting point in liquid crystals\(^{19}\). The design of the materials 1-4 can be modified to contain an NCS or a CN end group in order to render very high birefringence in these materials.

### 6.3 Synthesis of the molecules

Suzuki and Sonogashira coupling have been used extensively in the synthesis of the materials.
The material 1 was prepared through a convergent synthesis. Firstly, 2-iodothiophene was reacted with phenylboronic acid to obtain 2-phenylthiophene 6. The acidity of the proton in the 5- position of this molecule was taken advantage of to synthesize (5-phenylthiophen-2-yl)boronic acid 7 by reaction with n-BuLi and then triisopropyl borate at 0°C\(^{18}\). On the other hand, 4-bromo-2-chloro-1-(4-phenylphenyl)benzene was prepared by using the selectivity of the C-I bond over C-Br bond in Suzuki coupling. Finally, (5-phenylthiophen-2-yl)boronic acid and 4-bromo-2-chloro-1-(4-phenylphenyl)benzene was subjected to a Suzuki coupling to generate 1. The final product was purified through several recrystallizations from a 2:1 mixture of isooctane and toluene.

**Experimental conditions:** (a) Phenylboronic acid, Pd(PPh\(_3\))\(_2\)Cl\(_2\), K\(_2\)CO\(_3\), 1,4-dioxane, H\(_2\)O, \(\Delta\), 81% yield (b) i) n-BuLi, THF, 0°C, ii) B(O\(^3\)Pr)\(_3\), -78°C to rt, then HCl at rt, 81% yield (c) Biphenylboronic acid, Pd(PPh\(_3\))\(_2\)Cl\(_2\), K\(_2\)CO\(_3\), 1,4-dioxane, H\(_2\)O, \(\Delta\), 72% yield (d) Pd(PPh\(_3\))\(_2\)Cl\(_2\), K\(_2\)CO\(_3\), 1,4-dioxane, H\(_2\)O, \(\Delta\), 73% yield

**Figure 6.4:** Synthesis of 2-[3-chloro-4-(4-phenylphenyl)phenyl]-5-phenylthiophene
The material 2 was prepared through a convergent synthetic route. The intermediate 12 was prepared using 4-bromobenzonitrile as a starting material. It was refluxed with sodium azide in presence of ammonium chloride in DMF to generate the corresponding tetrazole 11. This rearranged to the corresponding oxadiazole 12 with the liberation of nitrogen (Huisgen oxadiazole synthesis) when reacted with 4-propylbenzoyl chloride using anhydrous pyridine as a solvent²⁰.

The material 14 was prepared using the selectivity of the C-I bond over C-Br bond of compound 13 to Suzuki coupling. The boronic acid 15 was prepared by reacting 14 with n-BuLi and then quenching the reaction with triisopropyl borate.

The final product 2 was prepared by a Suzuki coupling and the product was purified through several recrystallizations from isooctane and finally washing the product with ether.

**Experimental conditions:** (e) NaN₃, NH₄Cl, DMF, Δ, 85% yield (f) 4-propylbenzoyl chloride, anhydrous pyridine, 50% yield (g) Phenylboronic acid, Pd(PPh₃)₂Cl₂, K₂CO₃, 1,4-dioxane, H₂O, Δ, 60% yield (h) i) n-BuLi, THF, -78°C, ii) B(O'Pr)₃, -78°C to rt, then HCl at rt, 69% yield (i) Pd(PPh₃)₂Cl₂, K₂CO₃, 1,4-dioxane, H₂O, Δ, 37% yield

**Figure 6.5:** Synthesis of 2-[(3-chloro-4-phenylphenyl)phenyl]-5-(4-propylphenyl)-1,3,4-oxadiazole
The material 3 consists of a benzothiophene based core that was synthesized starting from 4-bromothiophenol. The intermediate 17 was prepared by an $S_N 2$ reaction of the sodium salt of 4-bromothiophenol with 2-bromo-1,1-dimethoxyethane$^{21}$. It was then dissolved in chlorobenzene and refluxed with polyphosphoric acid to obtain the cyclized product 18. A Suzuki-coupling of 18 with 4-n-alkylphenylboronic acid gave 19 which was then converted to the boronic acid 20. The intermediate 22 was made by a Suzuki-coupling of 21 with 4-n-alkylphenylboronic acid. Finally, 20 and 22 were reacted under Suzuki-coupling conditions to generate the final product 3 which was purified by several recrystallizations from a 1:1 mixture of iso-octane and toluene.

**Experimental conditions:**

(j) Na, anhydrous EtOH, 2-bromo-1,1-dimethoxyethane, 97% yield
(k) PPA, chlorobenzene, 43% yield
(l) 4-alkylphenylboronic acid, Pd(Ph$_3$P)$_2$Cl$_2$, K$_2$CO$_3$, 1,4-dioxane, H$_2$O, $\Delta$, 80% yield
(m) i) n-BuLi, THF, 0°C, ii) B(OiPr)$_3$, -78°C to rt, then HCl at rt, 74% yield
(n) 4-alkylphenylboronic acid, Pd(Ph$_3$P)$_2$Cl$_2$, K$_2$CO$_3$, 1,4-dioxane, H$_2$O, $\Delta$, 45% yield
(o) Pd(Ph$_3$P)$_2$Cl$_2$, K$_2$CO$_3$, 1,4-dioxane, H$_2$O, $\Delta$, 53% yield

**Figure 6.6:** Synthesis of 2-[3-chloro-4-(4-alkylphenyl)phenyl]-5-(4-alkylphenyl)-1-benzothiophene
The material 4 was prepared using Sonogashira coupling of 23 with 12. The final product was purified by recrystallization from toluene. The starting material 23 was available in our lab from earlier studies.

\[
\begin{array}{c}
\text{23} \\
\text{P} \\
\text{4}
\end{array}
\]

**Experimental conditions:** (p) PdCl\(_2\), CuI, PPh\(_3\), Et\(_3\)N, 2-(4-bromophenyl)-5-(4-propylphenyl)-1,3,4-oxadiazole, Δ, 57% yield

**Figure 6.7:** Synthesis of 2-(4-2-[4-(phenylethynyl)phenyl]ethynylphenyl)-5-(4-propylphenyl)-1,3,4-oxadiazole

**6.4 Discussion of the physical properties**

Amongst the four materials synthesized, 2 & 4 have the sharpest bend in the cores (Figures 6.10 and 6.12). The compound 4 has a higher melting point than compound 2 owing to a more coplanar structure that probably leads to more efficient packing and improved intermolecular attractive interactions in the crystalline phase. The propyl tail adds to the flexibility of 2 while the lateral chlorine substitution disturbs the coplanarity of the aromatic rings, thus drastically reducing the melting point compared to the parent oxadiazole without tail\(^{18}\) (Figure 6.8).

**Figure 6.8:** Comparison of 2 with previously reported material\(^ {18}\) containing no chlorine or tail
The material 2 has a bend angle of 134° which is much sharper than the materials 1 & 3. This gets manifested in the lower melting point of 2 compared to 1 & 3\textsuperscript{18,22} (bend angles ~148°). The heterocyclic cores insert significant dipole moments in the molecules (Figures below-generated by Marvin Suites\textsuperscript{®} using molecular mechanics calculations, the yellow arrow depicts the direction and magnitude of the dipole moment, actual measurements of dipole moments underway).

\textbf{Figure 6.9}: Exocyclic bond angle\textsuperscript{18} and direction of the dipole moment vector in 1 (two views of the same conformer)
Figure 6.10: Exocyclic bond angle\textsuperscript{18} and direction of the dipole moment vector in 2. (two views of the same conformer)
Figure 6.11: Exocyclic bond angle$^{22}$ and direction of the dipole moment vector in 3 (two views of the same conformer)
Overall, the molecular design strategies undertaken in planning these molecules transformed the initially insoluble and high melting quinquephenyl into more soluble and lower melting materials that can be easily spin coated or printed on plastic electronic circuits. Careful formulation of proper eutectic mixtures can take the melting point closer to room temperature.
<table>
<thead>
<tr>
<th>Structure</th>
<th>Transition temperatures</th>
<th>Bend Angle</th>
<th>Δn</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Structure 1" /></td>
<td>Cr 193 N 250I</td>
<td>148°</td>
<td>Under investigation</td>
</tr>
<tr>
<td><img src="image2" alt="Structure 2" /></td>
<td>Cr 129 N 145 I</td>
<td>134°</td>
<td>0.4 at 80°C λ = 550 nm</td>
</tr>
<tr>
<td><img src="image3" alt="Structure 3" /></td>
<td>Cr 154 N 200 I</td>
<td>147°</td>
<td>0.25 at 160°C λ = 550 nm</td>
</tr>
<tr>
<td><img src="image4" alt="Structure 4" /></td>
<td>Cr 223 N 280 I</td>
<td>134°</td>
<td>Under investigation</td>
</tr>
</tbody>
</table>

**Table 6.2**: Transition temperatures and bend angles of the synthesized materials

### 6.5 Birefringence Measurements

The birefringence of the sample in the nematic phase was measured by a standard method. The sample was filled in 4.67 μm and a 1.89 μm thick planar cells and observed between cross-polarizers. The rubbing direction of the cells was kept at 45° to the polarizers. The spectra of the transmitted light between 400 nm and 700 nm were recorded when the sample was cooled down at a speed of 1 C/min from isotropic. The intensity of the transmitted light is:
where $I_0$ is the original intensity of the incident light, $\varphi$ is the angle between the analyzer and the projection of the optic axis onto the sample plane, and $\delta$ is the phase difference. In this setup, $\varphi = 45^\circ$.

$$\delta = \frac{2\pi}{\lambda} (n_e - n_o)d$$

$n_e$ and $n_o$ being the extraordinary and ordinary refractive index of the material, $\lambda$ is the vacuum wavelength, and $d$ is the thickness of the sample. The birefringence of the sample is

$$\Delta n = n_e - n_o$$

When transmitted light have a minimum value which is close to zero, we have

$$\frac{\pi}{\lambda} \Delta nd = k\pi, k = 1, 2, 3, ...$$

So that

$$\Delta nd = k\lambda, k = 1, 2, 3, ...$$

The birefringence of the sample $\Delta n$ can be found from the spectra of the transmitted light through the relations above.

An investigation of the optical properties of materials 2 & 3 reveal very high birefringence inherent to these molecules. This property makes them desirable for applications that require the liquid crystal cell gap to be very low. Lower cell gap can mitigate the problem of absorption loss of the beam that is being steered by the LC layer. In GHz and THz applications very high birefringence is required to obtain sufficient phase change of the microwave beam and in this domain the above materials become very important.
Material 2 also undergoes an undetermined 2nd order phase transition on cooling. But overall, it has an attractive nematic range that can be further manipulated towards room temperature by mixture formulation. Also, the Δn value of ~0.4 is very attractive from application point of view. Dinaphthyl diacetylene analogues have been reported to possess a birefringence of up to 0.62 at 550 nm\textsuperscript{23}. However, these materials are not photostable owing to the presence of the diacetylene moiety. In comparison to this, materials 1-3 are very robust as there are no structural components that might be easily degradable by UV.

![Birefringence curve](image)

**Figure 6.13:** Birefringence (at 546 nm) as a function of temperature for compound 2. The curve has a discontinuity at around 90°C, which indicates towards a second order transition to some undetermined phase at this temperature (Data courtesy Dr. Antal Jakli, LCI, Kent State University)
Figure 6.14: Variation of birefringence with temperature and wavelength for 3

Figure 6.15: Uv-Vis absorption spectra of the heterocyclic bent core materials (Table 6.2)
The UV-vis absorption spectra of the materials 1-4 shows that all of them absorb in the ultraviolet region. Materials 1 and 4 absorb at higher wavelengths compared to the rest of the materials.
6.6 Conclusions

The materials 1 & 4 are currently under investigation for determination of their optical properties. Overall, these materials are through conjugated bent core materials with attractive phase transition temperatures. With the high level of conjugation in these materials, the birefringence is very high which is attractive in beam steering applications. The high level of solubility of these materials at room temperature in common organic solvents makes these materials easy for device fabrication by spin-coating and inkjet printing. Further investigation of their electronic properties is currently underway.

6.7 Acknowledgements

We gratefully acknowledge the help from the Jakli group in birefringence measurements. Materials 1 and 4 are still under investigation with them for birefringence measurements and other electro-optic studies.
6.8 Experimental

Synthesis of 2-phenylthiophene

\[
\text{I} \quad \rightarrow \quad \text{S-S}
\]

In a 500 ml round-bottom flask K₂CO₃ (4.14 gm, 30 mmol) was dissolved in H₂O (80 ml) and 1,4-dioxane (200 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that phenylboronic acid (3.65 gm, 30 mmol), 2-iodothiophene (5.25 gm, 25.0 mmol) and Pd(PPh₃)₂Cl₂ (200 mg, 1.5 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when GC-MS showed complete conversion of the starting material. At this point, the mixture was cooled down to room temperature, adsorbed on silica gel and placed on the top of a silica gel column. The column was eluted with hexanes and the major band was separated. The solvent was removed under reduced pressure to obtain the title compound as a white solid (3.22 gm, 81% yield). Melting point 33-34°C, lit. melting point 33-35°C.

Synthesis of (5-phenylthiophen-2-yl)boronic acid

\[
\text{S} \quad \rightarrow \quad \text{S-B(OH)₂}
\]

Prepared using previously reported procedure.¹⁸

In a 500 ml two necked flask equipped with a stirbar, 2-phenylthiophene (2.88 gm, 18 mmol) was dissolved in dry THF (200 ml) under nitrogen and the temperature of the solution was taken to 0°C. Into this solution n-BuLi (7.2 ml, 2.5M in hexanes) was added dropwise. After the
addition was complete the cold bath was removed and the mixture was refluxed for 20 minutes. The mixture was then cooled down to -78°C and triisopropylborate (8.46 gm, 45 mmol) was added dropwise and allowed to come to room temperature overnight. In this solution, 10% HCl (100 ml) was added and the solution was stirred vigorously for 1 hour. The mixture was then extracted with ether (3×100 ml). The organic layers were combined, dried over MgSO₄ and the solvent was removed under reduced pressure to obtain the title compound as a white solid (2.99 gm, 81% yield). The compound was used in the next step without further purification.

Synthesis of 4-bromo-2-chloro-1-(4-phenylphenyl)benzene

In a 200 ml round-bottom flask K₂CO₃ (1.656 gm, 12.0 mmol) was dissolved in H₂O (20 ml) and 1,4-dioxane (50 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4-biphenylboronic acid (1.04 gm, 5.28 mmol), 4-bromo-2-chloro-1-iodobenzene (1.674 gm, 5.28 mmol) and Pd(PPh₃)₂Cl₂ (40 mg, 1.5 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when GC-MS showed complete consumption of the starting material. The solvent was removed under reduced pressure and the residue was dissolved in boiling isooctane (100 ml) and Montmorillonite K10 clay was added. The solution was gravity filtered while hot and the volume of the solvent was reduced to 15 ml when a white solid precipitated out. The solid was separated by vacuum filtration and recrystallized from a 9:1 mixture of isooctane and toluene to obtain the title compound as a white solid (1.31 gm, 72% yield). Melting point: 165-167°C
\(^1\)H NMR (CDCl\(_3\), 298 K, 400 MHz): 7.88 (1H, d, \(J = 2\) Hz), 7.79-7.73 (4H, m), 7.66 (1H, dd, \(J = 8.0\) Hz, 2.0 Hz), 7.55-7.48 (4H, m), 7.44-7.38 (2H, m)

\(^{13}\)C NMR (DMSO-d6, 298 K, 100 MHz): 139.88, 139.52, 138.70, 136.73, 132.96, 131.97, 130.59, 129.70, 128.99, 127.69, 127.30, 126.70, 126.57, 121.10

IR (neat, cm\(^{-1}\)): 3084.85, 3056.99, 3030.66, 1581.31, 1464.30, 1370.63, 1075.05, 1001.97, 867.66, 816.22, 796.26, 763.64, 746.84, 691.28

Synthesis of 2-[3-chloro-4-(4-phenylphenyl)phenyl]-5-phenylthiophene (1)

In a 200 ml round-bottom flask K\(_2\)CO\(_3\) (0.552 gm, 4.0 mmol) was dissolved in H\(_2\)O (8 ml) and 1,4-dioxane (20 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that (5-phenylthiophen-2-yl)boronic acid (0.61 gm, 3.0 mmol), 4-bromo-2-chloro-1-(4-phenylphenyl)benzene (0.68gm, 2.0 mmol) and Pd(PPh\(_3\))\(_2\)Cl\(_2\) (16.0 mg, 1.5 mol\%) was added. This mixture was refluxed for 18 hours under nitrogen when TLC (eluent hexanes) showed complete conversion of the starting material. At this point, the solvent was removed under reduced pressure and the residue was redissolved in boiling toluene. In this solution montmorillonite K10 clay was added and the resulting mixture was gravity filtered while hot. The solvent was removed under reduced pressure and the residue was recrystallized from a 5:1 mixture of isooctane and toluene to yield the desired material as a light yellow solid (0.61 gm, 73% yield).
Phase transition: Cr 193 N 250 I

$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 7.78-7.54 (10H, m), 7.50-7.28 (9H, m)

$^{13}$C NMR (DMSO-d$_6$, 298 K, 100 MHz): 144.27, 141.16, 140.20, 140.05, 138.57, 137.51, 134.59, 133.71, 132.75, 131.78, 129.79, 128.96, 128.81, 127.83, 127.50, 127.26, 126.94, 126.63, 125.54, 124.97, 124.18, 124.00

IR (neat, cm$^{-1}$): 3050.13, 3029.39, 1595.75, 1475.45, 1451.92, 1386.24, 1074.42, 1003.01, 821.09, 764.99, 731.91, 688.00

**Synthesis of 5-(4-bromophenyl)-2H-1,2,3,4-tetrazole**

![Chemical structure](image)

In a 250 ml round bottom flask a mixture of 4-bromobenzonitrile (10.00 g, 55.2 mmol), sodium azide (12.11 g, 164.6 mmol), NH$_4$Cl (8.80 g, 164.4 mmol), and DMF (30 mL) was heated for 12 hours under N$_2$ in an oil bath maintained at a bath temperature of 150°C. After cooling to room temperature, the solution was poured into 1 N HCl (300 mL) and stirred for 30 min. After filtering, the solid product was washed with water (3 x 300 mL) and dried to yield 1 (10.60 g, 85%). Melting point 269°C, lit. melting point$^{25}$ 271°C
Synthesis of 2-(4-bromophenyl)-5-(4-propylphenyl)-1,3,4-oxadiazole

In a 250 ml round bottom flask 4-propylbenzoyl chloride (3.65 g, 20.0 mmol) was added dropwise to a solution of 5-(4-bromophenyl)-2H-1,2,3,4-tetrazole (2.13 g, 10.0 mmol) in pyridine (20 mL) and then the mixture was heated to reflux for 2 days under N\textsubscript{2} in an oil bath. After cooling to room temperature, the solution was poured into water (300 mL). The solid product was filtered off, washed with water and recrystallized from methanol to yield the desired product as a light brown solid (1.7 g, 50% yield). Melting point: 106-109°C

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 298 K, 400 MHz): 8.02 (2H, d, J = 8.4 Hz), 7.99 (2H, d, J = 8.4 Hz), 7.66 (2H, d, J = 8.4 Hz), 7.33 (2H, d, J = 8.4 Hz), 2.66 (2H, t, J = 7.6 Hz), 1.68 (2H, sextet, J = 7.6 Hz), 0.96 (3H, t, J = 7.2 Hz)

\textsuperscript{13}C NMR (CDCl\textsubscript{3}, 298 K, 100 MHz): 165.15, 163.84, 147.41, 132.61, 129.44, 128.48, 127.16, 126.48, 123.18, 121.38, 38.25, 24.45, 13.94

IR (neat, cm\textsuperscript{-1}): 2954.30, 2927.68, 2867.81, 1603.04, 1581.98, 1476.93, 1403.69, 1374.07, 1273.26, 1184.57, 1067.01, 1007.40, 964.64, 831.57, 742.21
Synthesis of 4-bromo-2-chloro-1-phenylbenzene

In a 500 ml round-bottom flask K2CO3 (5.52 gm, 40 mmol) was dissolved in H2O (80 ml) and 1,4-dioxane (200 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that benzeneboronic acid (2.438 gm, 20 mmol), 1-bromo-3-chloro-4-iodobenzene (6.347 gm, 20 mmol) and Pd(PPh3)2Cl2 (151.5 mg, 1.5 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when GC-MS showed complete consumption of the starting material. At this point, the mixture was cooled down to room temperature and adsorbed on silica gel and placed on the top of a silica gel column. The column was eluted with hexanes and the major band was separated. The solvent was removed under reduced pressure to obtain the desired product as colorless oil (3.2 gm, 60% yield).

1H NMR (CDCl3, 298 K, 400 MHz): 7.63 (2H, d, J = 2.0 Hz), 7.44-7.35 (6H, m), 7.19 (2H, d, J = 8.0 Hz)

13C NMR (CDCl3, 298 K, 100 MHz): 139.79, 138.53, 133.69, 132.67, 132.60, 130.26, 129.46, 128.38, 128.13, 121.58

IR (neat, cm\(^{-1}\)): 3077.73, 3056.55, 1943.95, 1877.96, 1811.68, 1739.93, 1692.07, 1569.90, 1455.27, 1410.95, 1369.79, 1239.95, 1068.43, 872.02, 808.52, 782.91, 737.17, 689.37
In a 500 ml two neck flask equipped with a stir bar 4-bromo-2-chloro-1-phenylbenzene (2.67 gm, 10.0 mmol) was dissolved in dry THF (200 ml) under nitrogen and the temperature of the mixture was taken to -78°C. In this solution, n-BuLi (4 ml, 2.5M in hexanes) was added dropwise and the resulting mixture was stirred for 45 minutes. After this, triisopropyl borate (5.64 gm, 30.0 mmol) was added dropwise while maintaining the temperature at -78°C. The mixture was then allowed to come to room temperature overnight. In this solution, 10% HCl (100 ml) was added and the mixture was stirred for an hour and then extracted with ether (3 × 50 ml). The organic layers were combined, dried over MgSO₄ and the solvent was evaporated under reduced pressure to obtain the title compound as a off-white solid (1.6 gm, 69% yield). The material was used in the next step without any further purification.

In a 250 ml round-bottom flask K₂CO₃ (0.818 gm, 6 mmol) was dissolved in H₂O (16 ml) and 1,4-dioxane (40 ml) was added. This mixture was degassed by sonication under vacuum for 20
minutes and after that (3-chloro-4-phenylphenyl)boronic acid (1.04 gm, 4.5 mmol), 2-(4-
bromophenyl)-5-(4-propylphenyl)-1,3,4-oxadiazole (1.02 gm, 3.0 mmol) and Pd(PPh3)2Cl2
(22.72 mg, 1.5 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when
TLC (10% EtOAc, 90% hexanes) showed complete consumption of the starting material. The
solvent was removed from the reaction mixture under reduced pressure and the residue was
dissolved in hot toluene (100 ml). Montmorillonite K10 clay was added to the mixture and it was
gravity filtered while hot. The solvent was removed under reduced pressure and the residue was
washed several times with ether to obtain the desired product as a shiny white solid (0.5 gm,
37%).

Phase transition: Cr 129 N 145 I

$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 8.23 (2H, d, $J = 8.75$ Hz), 8.07 (2H, d, $J = 8.21$ Hz), 7.81-
7.75 (3H, m), 7.60 (1H, dd, $J = 7.81$ Hz, 1.89 Hz), 7.51-7.38 (6H, m), 7.35 (2H, d, $J = 8.62$ Hz),
2.68 (2H, t, $J = 8.27$ Hz), 1.70 (2H, sext, $J = 7.77$ Hz), 0.97 (3H, t, $J = 7.31$ Hz)

$^{13}$C NMR (CDCl$_3$, 298 K, 100 MHz): 165.10, 164.30, 147.31, 142.69, 140.54, 140.36, 139.04,
133.39, 132.11, 129.64, 129.45, 128.73, 128.36, 128.05, 127.83, 127.71, 127.18, 125.74, 123.65,
121.56, 38.27, 24.48, 13.96

IR (neat, cm$^{-1}$): 3053.79, 3034.28, 2961.91, 2933.90, 2873.36, 1613.96, 1578.99, 1552.85,
1495.67, 1473.06, 1443.30, 1380.67, 1182.67, 1072.46, 1033.68, 847.70, 818.78, 743.25, 697.31
Synthesis of 1-bromo-4-[(2,2-dimethoxyethyl)sulfanyl]benzene

Prepared using previously reported procedure\textsuperscript{21}.

In a 500 ml round bottom flask, sodium (3.45 gm, 0.15 mol) was added to absolute ethanol (100 ml) with stirring under nitrogen. After all the sodium dissolved, 4-bromothiophenol (25.825 gm, 0.1375 mol) was added all at once and the stirring was continued for 5 minutes. After this, 2-bromo-1,1-dimethoxyethane (30 gm, 0.1775 mol) was added and the mixture was refluxed in a nitrogen atmosphere for 18 hours when a white precipitate of NaBr formed. The mixture was cooled down to room temperature and the NaBr was separated by suction filtration. The solvent was removed from the filtrate under reduced pressure and diethyl ether (100 ml) and water (50 ml) was added to the residue. The layers were separated and the aqueous layer was washed with ether (50 ml) twice. The organic phases were combined and dried over MgSO\textsubscript{4}. The ether was removed under reduced pressure to obtain the desired product as light yellow oil (37.07 gm, 97\% yield).

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 298 K, 400 MHz): 7.39 (2H, d, J = 8.0 Hz), 7.24 (2H, d, J = 8.0 Hz), 4.50 (1H, t, J = 7.0 Hz), 3.36 (6H, s), 3.08 (2H, d, J = 7.0 Hz).

\textsuperscript{13}C NMR (CDCl\textsubscript{3}, 298 K, 100 MHz): 135.38, 131.96, 131.01, 120.11, 103.15, 53.69, 36.56
Synthesis of 5-bromo-1-benzothiophene

![Chemical Structure](image)

Prepared using previously reported procedure\textsuperscript{26}.

In a 1000 ml two neck flask, dry chlorobenzene (300 ml, dried over 4 Å molecular sieves) and polyphosphoric acid (54 ml) was heated to gentle reflux under nitrogen atmosphere. To this mixture, 1-bromo-4-[(2,2-dimethoxyethyl)sulfanyl]benzene (37.07 gm, 133.73 mmol) dissolved in chlorobenzene (25 ml) was added dropwise and the resulting mixture was refluxed for 18 hours. After that, the chlorobenzene layer was separated and the solvent was removed under reduced pressure. The residue was dissolved in ether and was added to the solution made by adding water to the PPA residue. The organic layer was separated and the aqueous layer was extracted with ether (75 ml × 2). The organic layers were combined, dried over MgSO\textsubscript{4} and the solvent was removed under reduced pressure to obtain the desired product as an off-white solid (12.21 gm, 43% yield)

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 298 K, 400 MHz): 7.94 (1H, d, $J = 1.95$ Hz), 7.71 (1H, d, $J = 8.66$ Hz), 7.45 (1H, d, $J = 5.54$ Hz), 7.41 (1H, dd, $J = 8.55 \& 2.05$ Hz), 7.25 (1H, d, $J = 5.53$ Hz)

\textsuperscript{13}C NMR (CDCl\textsubscript{3}, 298 K, 100 MHz): 141.23, 138.35, 128.16, 127.28, 126.25, 123.78, 123.12, 118.23
Synthesis of 5-(4-propylphenyl)-1-benzothiophene

In a 500 ml round-bottom flask K$_2$CO$_3$ (3.312 gm, 24 mmol) was dissolved in H$_2$O (40 ml) and 1,4-dioxane (100 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4-propylphenylboronic acid (2.46 gm, 15.0 mmol), 5-bromo-1-benzothiophene (2.13 gm, 10.0 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (75.6 mg, 1.5 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when GC-MS showed complete consumption of the starting material. At this point, the mixture was cooled to room temperature, adsorbed on silica gel and was placed on the top of a silica gel column. The column was eluted with hexanes and the major band was separated. The solvent was removed under reduced pressure to obtain the title compound as a light yellow solid (2.01 gm, 80% yield). Melting point: 72-73°C

$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 8.00 (1H, d, $J = 1.55$ Hz), 7.91 (1H, d, $J = 8.40$ Hz), 7.61-7.54 (3H, m), 7.45 (1H, d, $J = 5.43$ Hz), 7.37 (1H, d, $J = 5.66$ Hz), 7.27 (2H, d, $J = 8.37$ Hz), 2.64 (2H, t, $J = 7.80$ Hz), 1.69 (2H, sext, $J = 6.83$ Hz), 0.98 (3H, t, $J = 7.80$ Hz)

$^{13}$C NMR (CDCl$_3$, 298 K, 100 MHz): 141.91, 140.38, 138.86, 138.67, 137.87, 129.12, 128.99, 127.39, 127.08, 126.97, 124.25, 124.03, 122.80, 121.96, 37.88, 24.76, 14.08

IR (neat, cm$^{-1}$): 3078.55, 3021.84, 2959.12, 2925.49, 2855.42, 1913.49, 1519.96, 1495.95, 1437.43, 1177.66, 1088.13, 1055.04, 1023.90, 897.55, 837.84, 806.45, 756.12, 702.42
Synthesis of [5-(4-propylphenyl)-1-benzo thiophen-2-yl]boronic acid

In a 500 ml two necked flask equipped with a stirbar, 5-(4-propylphenyl)-1-benzo thiophene (1.82 gm, 7.22 mmol) was dissolved in dry THF (200 ml) under nitrogen and the temperature of the solution was taken to 0°C. In this solution n-BuLi (2.9 ml, 2.5M in hexanes) was added dropwise. The solution was stirred for 50 minutes at 0°C and the mixture was then cooled to -78°C and triisopropylborate (5.63 gm, 30.0 mmol) was added dropwise and allowed to come to room temperature overnight. In this solution, 10% HCl (100 ml) was added and the solution was stirred vigorously for 1 hour. The mixture was then extracted with ether (3×100 ml). The organic layers were combined, dried over MgSO₄ and the solvent was removed under reduced pressure to obtain the title compound as a off-white solid (1.57 gm, 74% yield). The compound was used in the next step without further purification.

¹H NMR (DMSO-d₆, 298 K, 400 MHz): 8.15 (1H, d, J = 1.4 Hz), 8.03 (2H, d, J = 6.24 Hz), 7.65 (3H, d, J = 8.04 Hz), 7.29 (2H, d, J = 8.08 Hz), 2.59 (2H, t, J = 7.52 Hz), 1.72 (2H, d, J = 7.56 Hz), 0.92 (3H, t, J = 7.30 Hz)

¹³C NMR (DMSO-d₆, 298 K, 100 MHz): 142.43, 142.06, 141.75, 141.67, 138.13, 136.83, 133.54, 129.40, 127.23, 124.43, 123.29, 122.09, 37.33, 24.54, 14.14
Synthesis of 4-bromo-2-chloro-1-(4-propylphenyl)benzene

In a 200 ml round-bottom flask K$_2$CO$_3$ (1.38 gm, 10 mmol) was dissolved in H$_2$O (20 ml) and 1,4-dioxane (50 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4-bromo-2-chloro-1-iodobenzene (1.58 gm, 5.0 mmol), 4-propylphenylboronic acid (0.82 gm, 5 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (37.87 mg, 1.5 mol%) was added. This mixture was refluxed for 18 hours under nitrogen GC-MS showed complete consumption of the starting materials. At this point, the mixture was cooled down to room temperature and adsorbed on silica gel and placed on the top of a silica gel column. The column was eluted with hexanes and the major band was separated. The solvent was removed under reduced pressure to obtain the desired product as colorless oil (0.69 gm, 45% yield).

$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 7.62 (1H, d, $J = 2.12$ Hz), 7.42 (1H, dd, $J = 8.27$ Hz, 1.73 Hz), 7.31 (2H, d, $J = 8.27$ Hz), 7.23 (2H, d, $J = 8.47$ Hz), 7.20 (1H, d, $J = 8.47$ Hz), 2.63 (2H, t, $J = 7.75$ Hz), 1.68 (2H, sext., $J = 7.44$ Hz), 0.97 (3H, t, $J = 6.61$ Hz)

$^{13}$C NMR (CDCl$_3$, 298 K, 100 MHz): 142.58, 139.59, 135.62, 133.50, 132.46, 130.02, 129.14, 128.27, 121.12, 37.85, 24.48, 13.92

IR (neat, cm$^{-1}$): 2942.85, 2883.44, 1936.63, 1597.39, 1492.55, 1346.55, 1077.92, 1013.82
Synthesis of 2-[3-chloro-4-(4-propylphenyl)phenyl]-5-(4-propylphenyl)-1-benzothiophene (3)

In a 200 ml round-bottom flask K$_2$CO$_3$ (0.69 gm, 5.0 mmol) was dissolved in H$_2$O (20 ml) and 1,4-dioxane (50 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that [5-(4-propylphenyl)-1-benzothiophen-2-yl]boronic acid (0.65 gm, 2.22 mmol), 4-bromo-2-chloro-1-(4-propylphenyl)benzene (0.619 gm, 2.0 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (16.8 mg, 1.5 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when TLC (2% EtOAc, 98% hexanes) showed complete consumption of the bromide starting material. The solvent was removed from the reaction mixture under reduced pressure and the residue was dissolved in hot toluene (100 ml). Montmorillonite K10 clay was added to the mixture and it was gravity filtered while hot. The volume of the solvent was reduced to 10 ml and cooled down to room temperature when the product precipitated out. The solid product was separated by suction filtration and recrystallized from toluene to obtain the desired product as a white solid (0.51 gm, 53% yield).

Phase transition: Cr 154 N 200 I

$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 8.00 (1H, d, $J = 1.54$ Hz), 7.90 (1H, d, $J = 8.46$ Hz), 7.86 (1H, d, $J = 1.92$ Hz), 7.70-7.64 (2H, m), 7.61 (3H, d, $J = 7.62$ Hz), 7.43 (3H, d, $J = 7.62$ Hz), 7.31 (4H, t, $J = 7.22$ Hz), 2.69 (4H, t), 1.73 (4H, sext.), 1.02 (6H, t)

In the alkyl region, the signals arising from two alkyl tails overlap
\[^{13}\text{C} \text{NMR (CDCl}_3, \text{ 298 K, 100 MHz)}:\ 142.72, 142.30, 141.86, 140.93, 139.94, 138.10, 137.99, 137.93, 135.66, 134.24, 132.82, 131.85, 129.14, 128.94, 128.14, 127.49, 127.00, 124.79, 124.19, 122.52, 121.72, 120.45, 37.66, 37.53, 24.42, 24.32, 13.94\n\]

IR (neat, cm\(^{-1}\)):
2956.56, 2927.20, 2869.22, 2161.85, 1912.61, 1599.03, 1475.62, 1440.08, 1386.39, 1073.73, 891.89, 872.58, 799.30, 676.21

Synthesis of 2-\{2\-[4-\{(2-phenylethynyl)phenyl\}ethynyl]phenyl\}ethynyl\}phenyl)-5-(4-propylphenyl)-1,3,4-oxadiazole (4)

In a 200 ml round bottom flask equipped with a stirbar, PPh\(_3\) (0.039 gm, 0.15 mmol) was dissolved in freshly distilled Et\(_3\)N (20 ml) and PdCl\(_2\) (6.75 mg, 0.038 mmol) was added. The mixture was stirred for 20 minutes under nitrogen at room temperature and then CuI (0.94 mg, 0.005 mmol) was added and the resulting mixture was stirred for an additional 5 minutes under nitrogen. In this solution 1-ethynyl-4-(2-phenylethynyl)benzene (0.303 gm, 1.5 mmol) and 2-(4-bromophenyl)-5-(4-propylphenyl)-1,3,4-oxadiazole (0.514 gm, 1.5 mmol) was added simultaneously and the resulting mixture was refluxed under nitrogen for 18 hours when all the starting material was consumed (checked by TLC with 98% hexanes, 2% EtOAc as eluent). The solvent was removed from the reaction mixture under reduced pressure and the residue was dissolved in hot toluene and montmorillonite K10 clay was added. The resulting mixture was gravity filtered while hot and the filtrate was concentrated to obtain a slight yellow solid. The solid was separated by suction filtration and recrystallized twice from toluene. The crystals were
separated by suction filtration and washed several times with diethyl ether and dried under vacuum to obtain the desired product as a slight yellow solid (0.396 gm, 57% yield).

Phase transition: Cr 223 N 280 I

$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 8.12 (2H, d, $J = 8.74$ Hz), 8.05 (2H, d, $J = 8.74$ Hz), 7.68 (2H, d, $J = 8.74$ Hz), 7.58-7.48 (6H, m), 7.40-7.31 (5H, m), 2.68 (2H, t, $J = 7.50$ Hz), 1.70 (2H, sextet, $J = 7.50$ Hz), 0.97 (3H, t, $J = 7.50$ Hz)

$^{13}$C NMR (CDCl$_3$, 298 K, 100 MHz): 166.29, 165.28, 148.77, 133.70, 133.15, 133.11, 133.06, 130.71, 130.10, 129.89, 128.34, 128.14, 127.73, 124.91, 124.75, 124.13, 123.73, 122.38, 93.51, 93.08, 91.92, 90.52, 39.38, 25.66, 15.25

IR (neat, cm$^{-1}$): 3050.30, 2957.23, 2930.38, 2870.68, 2212.85, 1944.46, 1608.11, 1495.78, 1410.89, 1173.54, 1104.76, 1070.55, 1013.32, 966.82, 835.90, 754.62, 706.51, 685.07
6.9 References


Chapter 7

Synthesis of liquid crystals with dibenzothiophene-S,S-dioxide core

7.1 Introduction

Heterocyclic compounds have been studied and applied widely in materials science due to their ability to imbue molecules with interesting and valuable properties not otherwise available from all carbon-containing systems. Just a few examples of the pervasive utility of heterocycles are found in the area of liquid crystals, nonlinear optical materials, organic semiconductors and photovoltaics.

In the case of liquid crystals, heterocyclic moieties have the ability to impart lateral or longitudinal dipoles, local polarizability changes and also influence the overall molecular shape leading to changes in packing with the associated changes in the observed phases and their temperature ranges. Amongst the many types of heterocycles available to apply, thiophene-containing materials (including single, multiple and annulated thiophene rings) have been popular and are good candidates, in part due to their chemical stability, while delivering an efficient conjugation pathway. Molecules having thiophene in their structure melt at lower temperatures than their 1,4-phenylene counterparts due to the reduced packing efficiency due in part to the introduction of a bend, involving the noncollinear disposition of substituents attached to, e.g., positions 2 and 5 of thiophene.
An interesting feature of thiophene related to its reactivity and structure is that it is possible to oxidize the sulfur atom to either to the level of a sulfoxide\textsuperscript{18,19} or a sulfone\textsuperscript{20,21}. One difference between the sulfoxide and the sulfone is in dimensionality. Previously, spiro[cyclopentyl-1,9\textquotesingle]fluorene based nematics were reported that have similar dimensionality aspects\textsuperscript{22}. The dibenzothiophene sulfoxide is a planar molecule while the corresponding sulfone has a three dimensional disposition (of course the parent dibenzothiophene is also nonplanar if the sulfur lone pairs are considered). Liquid crystals with sulfoxide\textsuperscript{23} and sulfone\textsuperscript{24} containing side chains have been investigated as ferroelectric materials. Materials with sulfone linkages between the core and tail have been examined as potential liquid crystals\textsuperscript{25,26}. Molecules with bisphenylsulfone core have been reported to exhibit columnar liquid crystalline phases\textsuperscript{26}. However, liquid crystals containing a heterocyclic S,S-dioxide appear to be unknown. In the case of liquid crystals we felt that introduction of this structure feature, initially in the case dibenzothiophene-S,S-dioxide, might deliver interesting physical properties. For example, in the case of the parent substance, oxidation of the sulfur in dibenzothiophene produces dibenzothiophene-S,S-dioxide with a dramatic change in melting point (98°C\textsuperscript{27} and 231-232°C\textsuperscript{28} respectively) and higher dipole moment (2.63×10\textsuperscript{-30} coulomb meter, and 5.03×10\textsuperscript{-30} coulomb meter respectively). Other cores that can be explored are depicted below (Figure 7.1).
An additional notable feature about molecules containing an S,S-dioxide structure in the core is that it imparts a third dimension to the molecule, in contrast to most other cores which have at least one conformation which is relatively two dimensional. It was interesting to learn if this structure feature can be accommodated in liquid crystals and what the influences on physical properties are. For example, the presence of this three dimensional site in the molecule enhances co-facial packing compared to its non-oxidized analogue (Figures 7.2, 7.3 and 7.4). This might be an interesting feature of the molecules containing sulfone core that might be useful in charge transport studies.
Figure 7.2: Unit cell of biphenyl\textsuperscript{29}

Figure 7.3: Unit cell of dibenzothiophene\textsuperscript{30}
7.2 Results and discussion

Four different classes of compounds have been prepared in the current study (Figure 7.5). These four classes differ in the groups which are attached to the central dibenzothiophene-S,S-dioxide unit at the 3 and 7 positions. These substituents include 4-alkylphenyl (a), 4-alkoxyphenyl (b), perfluoroalkylvinyl (c) and 4-alkylphenylethynyl (d).

Figure 7.5: Four classes of dibenzothiophene-dioxide based liquid crystals synthesized in this study
Compounds in all four classes were prepared by palladium catalyzed coupling reactions using 3,7-dibromodibenzothiophene dioxide which itself was synthesized by a known procedure\textsuperscript{21}. In the case of a and b a standard Suzuki type reaction\textsuperscript{32} was utilized with 1,4-dioxane as solvent and Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} for catalyst. For c a Jeffery version of the Heck reaction was utilized with DMF as solvent and Pd(OAc)\textsubscript{2} as catalyst. Only the product from the reaction with 1H,1H,2H-perfluoroheptene was successfully purified as the product of the reactions with longer chain perfluoroalkenes were highly insoluble. The compounds of class d were obtained by a Sonogashira coupling using Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} as the catalyst and CuI as the co-catalyst\textsuperscript{33} (Figure 7.6).

**Figure 7.6:** Synthesis of the dibenzothiophene-\textit{S,S}-dioxide based liquid crystals

All the compounds were obtained by the different coupling procedures with yields typically in the range of 60%. For compounds of class a, b & d, the length of the alkoxy or alkyl tails did not
affect the yields. All of the $^1$H and $^{13}$C NMR spectra were consistent with the expected structures.

Synthesis of some analogous dibenzothiophene derivatives were also attempted, but the literature synthesis of 3,7-dibromodibromodibenzo[\(b,d\)]thiophene did not work in our hands$^{21,34}$.

7.3 Mesogenic properties of the compounds in Figure 7.5

The mesogenic properties of the compounds were investigated by polarized optical microscopy and DSC. This characterization data is compiled in Table 7.1. For compounds of class 1 and 2, it was observed that the candidates with shorter tails are more likely to have nematic phases. This is in accordance to the usual influence of tail length on nematic behavior$^{35}$. For compounds of class 1, the nematic behavior disappeared when the length of the alkyl tail reached seven carbons. Materials 1d, 2b, 2e and 2f have unidentified LC phases that need more sophisticated characterization (x-ray layer spacing). When the alkyl and alkoxy materials were compared it was observed that the melting points of alkoxy materials were higher than the alkyl materials. Although when 1b and 2c were compared, it was observed that 2c had a lower melting point and its nematic phase stability was much higher than 1b. The material 2h has a smectic phase that is 168°C wide. Materials 3 and 4 decompose on heating. The decomposition of 3 starts at around 180°C while 4 starts decomposing around 250°C.

The materials of class 1 and 2 are essentially quaterphenyls with the –SO$_2$- bridge introducing polarity and a small bend in the molecule$^{36}$ that makes it much more soluble enabling the molecules much more desirable for device applications. The quaterphenyl analogue of 1d is reported in literature$^{37}$ and it has a melting point is much higher than 1d (270°C for the
quaterphenyl compared to 157°C for 1d). The benzene rings in quaterphenyl are free to rotate. The introduction of sulfone moiety restricts the rotational freedom of the quaterphenyls. Also, presence of sulfone in this ring system might make the molecule pack more co-facially in the bulk (Figures 7.2, 7.3 and 7.4). Introduction of sulfone moiety in quaterphenyl also incorporates significant dipole moment (4.90 Debye-using molecular mechanics calculation) (Figure 7.7).

Figure 7.7: Direction of dipole moment of dibenzothiophene-S,S-dioxide
<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>Phase characterizations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td><img src="image1" alt="Structure" /></td>
<td>Cr 276 N 283 I</td>
</tr>
<tr>
<td>1b</td>
<td><img src="image2" alt="Structure" /></td>
<td>Cr 269 N 281 I</td>
</tr>
<tr>
<td>1c</td>
<td><img src="image3" alt="Structure" /></td>
<td>Cr 202 SmA 222 N 248 I</td>
</tr>
<tr>
<td>1d</td>
<td><img src="image4" alt="Structure" /></td>
<td>Cr 157 SmX 176 SmY 220 N 235 I</td>
</tr>
<tr>
<td>1e</td>
<td><img src="image5" alt="Structure" /></td>
<td>Cr 168 SmA 221 I</td>
</tr>
<tr>
<td>2a</td>
<td><img src="image6" alt="Structure" /></td>
<td>Melting point &gt; 310°C</td>
</tr>
<tr>
<td>2b</td>
<td><img src="image7" alt="Structure" /></td>
<td>Cr 238 SmX 259 I</td>
</tr>
<tr>
<td>2c</td>
<td><img src="image8" alt="Structure" /></td>
<td>Cr 262 N 316 I</td>
</tr>
<tr>
<td>2d</td>
<td><img src="image9" alt="Structure" /></td>
<td>Cr 223 SmA 238 N 281 I</td>
</tr>
<tr>
<td>2e</td>
<td><img src="image10" alt="Structure" /></td>
<td>Cr 169 SmX 205 SmY 260 N 276 I</td>
</tr>
<tr>
<td>2f</td>
<td><img src="image11" alt="Structure" /></td>
<td>Cr 157 SmX 189 SmY 194 SmA 268 I</td>
</tr>
<tr>
<td>2g</td>
<td><img src="image12" alt="Structure" /></td>
<td>Cr 171 SmA 252 I</td>
</tr>
<tr>
<td>2h</td>
<td><img src="image13" alt="Structure" /></td>
<td>Cr 167 SmA 335 I</td>
</tr>
<tr>
<td>3</td>
<td><img src="image14" alt="Structure" /></td>
<td>Decomposes on heating at around 250°C</td>
</tr>
<tr>
<td>4</td>
<td><img src="image15" alt="Structure" /></td>
<td>Decomposes on heating at around 180°C</td>
</tr>
</tbody>
</table>

**Table 7.1:** Mesogenic behavior of the molecules with dibenzothiophene-$S,S$-dioxide core
The UV absorption properties of these materials can be tuned with the increase of conjugation. Material 4 absorbs at a longer wavelength than 1 and 2 and all the materials absorb in the UV region.

Figure 7.8: UV-Vis spectra of the dibenzothiophene-S,S-dioxide materials in dichloromethane

7.4 Conclusion

Molecules with sulfone moiety in the core have unique properties in terms of solubility and polarity. The liquid crystalline properties of molecules with a dibenzothiophene-S,S-dioxide core have not been studied previously. In the scope of the current study, we have synthesized molecules with a dibenzothiophene-S,S-dioxide moiety which introduces a bend in the molecule. Previously it was reported that the x-ray crystal structure of 3,7-bis(phenylethynyl)dibenzo[b,d]thiophene 5,5-dioxide shows lamellar packing that leads to $\pi-\pi$ interaction\textsuperscript{36} while the dibenzothiophene analogue showed herringbone packing (no $\pi-\pi$ interaction). From this data, it seems like the $-\text{SO}_2-$ moiety has a profound effect in changing the packing to a more co-facial one. Thus, the materials synthesized in this work might find application in charge transport applications.
These molecules have very good solubility owing to the polarity introduced by the –SO₂− moiety and the bend in the molecular geometry that makes them good candidates for device fabrication.

7.5 Acknowledgements

Materials 1a, 1b and 1c are under investigation in the lab of Prof. Antal Jakli for determination of birefringence and other electro-optic properties.

Material 1c is under investigation in the lab of Prof. Bjorn Lussem for investigation of semiconductor properties of the material.

Thanks to David Davis for providing 4-propyloxyphenyl boronic acid and 4-undecyloxyphenyl boronic acid.
7.6 Experimental

The \(^1\)H and \(^{13}\)C NMR spectra were measured on a Bruker Avance 400 MHz spectrometer at 400.13 and 100.61 MHz, respectively. The \(^1\)H and \(^{13}\)C NMR chemical shifts were referenced to TMS (0.0 ppm). The melting points were uncorrected. The progress of the reactions was monitored by thin layer chromatography with plastic backed silica gel plates (Scientific adsorbents incorporated, Catalogue #79011). Differential scanning calorimetry (DSC) measurements were performed using a TA instruments differential scanning calorimeter 2920 at heating and cooling rates of 5°C per minute. Transition temperatures of the final products were measured using Mettler FP82HT hot-stage and FP90 control unit in conjunction with Nikon Eclipse E600 Pol polarizing microscope.

Boronic acids were either purchased or prepared by previously reported literature procedure\(^{38}\).

Synthesis procedures and spectral data of the products

Synthesis of dibenzothiophene-S,S-dioxide

\[
\begin{align*}
\text{S} & \quad \rightarrow \\
\text{O} & \\
\text{O} &
\end{align*}
\]

Prepared following a previously reported procedure\(^{39}\).

In a 500 ml round bottom flask placed in an ice bath, a 30% solution of \(\text{H}_2\text{O}_2\) (60 ml) was added dropwise to trifluoroacetic acid (60 ml) and the solution was stirred for 5 minutes. The ice bath was then removed and dibenzothiophene (4.0 gm, 21.7 mmol) was added in portions. The
resulting solution was heated to 50°C and stirred for 5 minutes. Water (200 ml) was added to the solution and the resulting residue was collected by suction filtration and dried in vacuo to obtain the desired compound as a white solid (4.68 gm, 100% yield). Melting point 233-236°C. Lit. melting point 237°C.

Synthesis of 3,7-dibromodibenzothiophene-S,S-dioxide

Prepared following a previously reported procedure In a 200 ml round bottom flask, dibenzothiophene-S,S-dioxide (4.63 gm, 21.44 mmol) was dissolved in concentrated H₂SO₄ (100 ml) and dibromoisocyanurate (7.06 g, 24.64 mmol) was added in one portion and the mixture was stirred for 24 hours at room temperature. The solution was then poured over ice and the mixture was kept at room temperature for 6 hours after which a white solid was collected by decantation. This white solid was recrystallized from toluene to obtain the desired product as white needles. This product contained cyanuric acid as impurity. So, it was again recrystallized from DMSO and washed with cold ethanol to obtain the desired product in pure form. (2.72 gm, 34% yield). Melting point 289-291°C. Literature melting point 288-290°C
Synthesis of 1,3-dibromo-1,3,5-triazinane-2,4,6-trione

Prepared following literature procedure\textsuperscript{42}.

To a well-stirred solution of cyanuric acid (12.9 g, 100 mmol) and LiOH (8.4 g, 200 mmol) in water (1 L) is slowly added Br\textsubscript{2} (63.9 g, 400 mmol). After the bromine dissolved, the solution was placed in the refrigerator overnight. The solution was then filtered, and the residue was dried in vacuo over KOH to yield the desired compound as a white powder (24.1 gm, 84\% yield).

\textbf{Compound 1a}

Synthesis of 3,7-di-4-ethylphenyl- dibromodibenzo thiophene-S,S-dioxide

In a 100 ml round-bottom flask K\textsubscript{2}CO\textsubscript{3} (1.104 gm, 8.0 mmol) was dissolved in H\textsubscript{2}O (4 ml) and 1,4-dioxane (10 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4-ethylbenzeneboronic acid (0.220 gm, 1.47 mmol), 3,7-dibromodibenzo thiophene-S,S-dioxide (0.25 gm, 0.66 mmol) and Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} (0.010 gm, 3 mol\%) was added. This mixture was refluxed for 24 hours under nitrogen when TLC (50\% CH\textsubscript{2}Cl\textsubscript{2}, 50\% hexanes) showed full conversion of the starting materials. At this point, the mixture was cooled down to room temperature and CH\textsubscript{2}Cl\textsubscript{2} (200 ml) was added. This solution
was passed through a short silica plug and the solvent was removed from the filtrate under reduced pressure to obtain a white solid. This solid was recrystallized from a 1:1 mixture of toluene and iso-octane to obtain the desired product as faint green shiny plates (0.201 gm, 72% yield).

Phase transition: Cr 276 N 283 I

$^1$H NMR (DMSO-d$_6$, 400 MHz, 348 K): 8.19 (2H, d, $J = 8.12$ Hz), 8.14 (2H, d, $J = 1.20$ Hz), 8.04 (2H, dd, $J = 8.12$ Hz, 1.68 Hz), 7.71 (4H, d, $J = 8.20$ Hz), 7.34 (4H, d, $J = 8.24$ Hz), 2.68 (4H, q, $J = 7.56$ Hz), 1.24 (6H, t, $J = 7.58$ Hz)

$^{13}$C NMR (DMSO-d$_6$, 100 MHz, 348 K): 144.97, 143.23, 139.13, 135.91, 132.77, 129.84, 128.95, 127.29, 123.51, 119.81, 28.24, 15.50

IR (neat, cm$^{-1}$): 3023.61, 2959.88, 2928.68, 2870.78, 1923.19, 1606.17, 1461.61, 1301.17, 1158.24, 1063.65, 1050.32, 1014.79, 895.83, 819.93, 767.00, 716.95

**Compound 1b**

Synthesis of 3,7-di-4-propylphenyl- dibromodibenzothiophene-S,S-dioxide

![Compound 1b](image)

In a 100 ml round-bottom flask K$_2$CO$_3$ (1.104 gm, 8.0 mmol) was dissolved in H$_2$O (4 ml) and 1,4-dioxane (10 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4-propylbenzeneboronic acid (0.241 gm, 1.47 mmol), 3,7-dibromodibenzothiophene-S,S-dioxide (0.25 gm, 0.66 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (0.010 gm, 3 mol%) was added. This mixture was refluxed for 24 hours under nitrogen when TLC (50%
CH₂Cl₂, 50% hexanes) showed full conversion of the starting materials. At this point, the mixture was cooled down to room temperature and CH₂Cl₂ (200 ml) was added. This solution was passed through a short silica plug and the solvent was removed from the filtrate under reduced pressure to obtain a white solid. This solid was recrystallized from a 1:1 mixture of toluene and iso-octane to obtain the desired product as faint green shiny plates (0.160 gm, 54% yield).

Phase transition: Cr 269 N 281 I

¹H NMR (DMSO-d₆, 363 K, 400 MHz): 8.15 (2H, d, J = 8.04 Hz), 8.11 (2H, d, J = 1.28 Hz), 8.01 (2H, dd, J = 8.08 Hz, 1.48 Hz), 7.69 (4H, d, J = 8.12 Hz), 7.31 (4H, d, J = 8.08 Hz), 2.63 (4H, t, J = 7.46 Hz), 1.66 (4H, sextet, J = 7.38 Hz), 0.94 (6H, t, J = 7.32 Hz)

¹³C NMR (DMSO-d₆, 363 K, 100 MHz): 143.35, 143.28, 139.25, 135.98, 132.71, 129.86, 129.51, 127.16, 123.43, 119.77, 37.37, 23.94, 13.81

IR (neat, cm⁻¹): 3025.04, 2957.44, 2928.36, 2869.37, 1599.76, 1519.08, 1462.25, 1400.57, 1302.73, 1159.62, 1141.47, 1050.57, 1015.31, 890.55, 815.76, 790.98, 713.00

**Compound 1c**

**Synthesis of 3,7-di-4-pentylphenyl-dibromodibenzothiophene-S,S-dioxide**

In a 100 ml round-bottom flask K₂CO₃ (1.104 gm, 8 mmol) was dissolved in H₂O (4 ml) and 1,4-dioxane (10 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4-n-pentylbenzenephenta aci (0.282 gm, 1.47 mmol), 3,7-
dibromodibenzothiophene-S,S-dioxide (0.25 gm, 0.66 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (0.010 gm, 3 mol%) was added. This mixture was refluxed for 24 hours under nitrogen when TLC (50% CH$_2$Cl$_2$, 50% hexanes) showed full conversion of the starting materials. At this point, the mixture was cooled down to room temperature and CH$_2$Cl$_2$ (200 ml) was added. This solution was passed through a short silica plug and the solvent was removed from the filtrate under reduced pressure to obtain a white solid. This solid was recrystallized from a 1:1 mixture of toluene and isooctane to obtain the desired product as white shiny plates (0.250 gm, 75% yield).

Phase transition: Cr 202 SmA 222 N 248 I

$^1$H NMR (DMSO-d6, 348 K, 400 MHz): 8.20 (2H, d, $J$ = 8.16 Hz), 8.14 (2H, s), 8.05 (2H, dd, $J$ = 8.06 Hz, 1.69 Hz), 7.71 (4H, d, $J$ = 8.04 Hz), 7.32 (4H, d, $J$ = 8.04 Hz), 2.65 (4H, t, $J$ = 7.60 Hz), 1.64 (4H, quint, $J$ = 7.24 Hz), 1.33 (8H, m), 0.88 (6H, t, $J$ = 7.02)

$^{13}$C NMR (DMSO-d6, 348K, 100 MHz): 143.61, 143.21, 139.13, 135.87, 132.75, 129.83, 129.48, 127.21, 123.52, 119.80, 35.21, 31.31, 30.62, 22.24, 14.10

IR (neat, cm$^{-1}$): 3064.91, 3027.44, 2925.02, 2855.90, 1604.14, 1466.07, 1296.58, 1152.47, 1135.09, 829.05, 811.24, 796.23, 713.79

Synthesis of 1-bromo-4-hexylbenzene

In a 250 ml beaker n-hexylbenzene (16.22 gm, 100 mmol) was adsorbed on neutral alumina (30 gm). In another 250 ml beaker Br$_2$ (15.98 gm, 100 mmol) was adsorbed on neutral alumina (30 gm). The two components were mixed together and stirred with a spatula for 1 minute when the mixture became colorless. The mixture was placed on a sintered glass filter funnel and was
eluted with dichloromethane until all the product came out in solution. The filtrate was collected and the solvent was removed under reduced pressure to obtain light yellow oil (20.1 gm). This oil contained approximately 5% of the ortho brominated product (by proton NMR). The product was carried to the next step without further purification (isomers were partially eliminated in the next step and 4-n-hexylphenylboronic acid was obtained good yield).

Synthesis of 4-n-hexylphenylboronic acid

\[
\begin{align*}
\text{C}_6\text{H}_{13}-\text{Br} & \quad \rightarrow \quad \text{C}_6\text{H}_{13}-\text{B(OH)}_2 \\
\end{align*}
\]

In a 500 ml two-necked round bottom flask, crude 1-bromo-4-n-hexylbenzene (19.61 gm, 95.15 mmol; contains approximately 5% ortho isomer) was dissolved in dry THF (180 ml) in a nitrogen atmosphere and the temperature of the mixture was taken to -78°C. In this mixture n-BuLi (23.2 ml, 2.5M in hexanes) was added dropwise and the mixture was stirred for an hour after the addition was complete. Then triisopropyl borate (32.67 gm, 173.76 mmol) was added dropwise and the mixture was allowed to warm up to room temperature. In this mixture, 10% hydrochloric acid solution (150 ml) was added and the mixture was stirred vigorously for 2 hours. This solution was then extracted with diethyl ether (100 ml × 3) and the combined organic layers were dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure to obtain the desired product as a white fluffy solid (13.98 gm, 97% yield). The product was clean enough to be used in further reactions without any additional purification It contained some ortho isomer that was completely eliminated in the next step).

\[^{1}H\text{ NMR (400 MHz, CDCl}_3, 298K) \delta: 7.69 (2\text{H, d, } J = 7.92 \text{ Hz}), 7.14 (2\text{H, d, } J = 7.88 \text{ Hz}), 2.55 (2\text{H, t, } J = 7.62 \text{ Hz}), 1.62-1.45 (2\text{H, m}), 1.37-1.17 (6\text{H, m}), 0.84 (3\text{H, t, } J = 6.88 \text{ Hz)}\]

228
Compound 1d

Synthesis of 3,7-di-(4-hexylphenyl)-dibenzothiophene-S,S-dioxide

![Chemical Structure Image]

In a 100 ml round-bottom flask K$_2$CO$_3$ (1.104 gm, 8.0 mmol) was dissolved in H$_2$O (4 ml) and 1,4-dioxane (10 ml) was added followed by 3-fluoro-4-hexylphenylboronic acid (0.367 gm, 1.47 mmol), 3,7-dibromodibenzothiophene-S,S-dioxide (0.25 gm, 0.66 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (0.010 gm, 3 mol%). This mixture was refluxed for 24 hours under nitrogen when TLC (50% CH$_2$Cl$_2$, 50% hexanes) showed full conversion of the starting materials. At this point, the mixture was cooled down to room temperature and CH$_2$Cl$_2$ (200 ml) was added. This solution was passed through a short silica plug and the solvent was removed from the filtrate under reduced pressure to obtain a light yellow solid. This material was not pure by NMR. So, the compound was subjected to column chromatography (eluent hexanes : dichloromethane = 1:2) to obtain the product as a light yellow solid (170 mg, 48% yield).

Phase transition: Cr 157 SmX 176 SmY 220 N 235 I

$^1$H NMR (Tetrachloroethane-d2, 298 K, 400 MHz): 8.04 (2H, s), 7.92-7.82 (4H, m), 7.57 (4H, d, $J = 8.18$ Hz), 7.33 (4H, d, $J = 8.18$ Hz), 2.68 (4H, t, $J = 7.91$ Hz), 1.67 (4H, quintet, $J = 7.70$ Hz), 1.45-1.28 (12H, m), 0.91 (6H, t, $J = 6.85$ Hz)

$^{13}$C NMR (Tetrachloroethane-d2, 298K, 100 MHz): 143.72, 143.33, 138.15, 135.64, 132.30, 129.71, 129.17, 126.67, 121.91, 120.10, 35.49, 31.58, 31.16, 28.90, 22.53, 14.11

IR (neat, cm$^{-1}$): 2955.60, 2923.64, 2853.45, 1600.69, 1463.94, 1301.33, 1157.74, 1016.09, 817.05, 750.56, 713.95
Synthesis of 1-bromo-4-n-heptylbenzene

In a 250 ml beaker n-heptylbenzene (3.52 gm, 20.0 mmol) was adsorbed on neutral alumina (15 gm). In another 250 ml beaker \( \text{Br}_2 \) (3.196 gm, 20.0 mmol) was adsorbed on neutral alumina (15 gm). The two components were mixed together and stirred with a spatula for 1 minute when the mixture became colorless. The mixture was placed on a sintered glass filter funnel and was eluted with dichloromethane until all the product came out in solution. The filtrate was collected and the solvent was removed under reduced pressure to obtain a light yellow oil. This oil contained approximately 5% of the ortho brominated product. The product was carried to the next step without further purification.

Synthesis of 4-n-heptylphenylboronic acid

In a 500 ml two-necked round bottom flask, crude 1-bromo-4-n-heptylbenzene (4.5 gm, 17.63 mmol, contains approximately 5% ortho isomer) was dissolved in dry THF (100 ml) in a nitrogen atmosphere and the temperature of the mixture was taken to -78°C. In this mixture n-BuLi (7.1 ml, 2.5M in hexanes) was added dropwise and the mixture was stirred for an hour after the addition was complete. Then triisopropyl borate (11.04 gm, 173.76 mmol) was added dropwise and the mixture was allowed to warm up to room temperature. In this mixture, 10% hydrochloric acid solution (100 ml) was added and the mixture was stirred vigorously for 2 hours. This solution was then extracted with diethyl ether (75 ml \( \times \) 3) and the combined organic
layers were dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure to obtain the desired product as a white fluffy solid (3.2 gm, 82% yield). The product had some ortho isomer that was completely eliminated at the next step.

H NMR (DMSO-d6, 348 K, 400 MHz): 7.70 (2H, d, J = 8.17 Hz), 7.14 (2H, d, J = 8.17 Hz), 2.56 (2H, t, J = 8.55 Hz), 1.56 (2H, quintet, J = 7.13 Hz), 1.35-1.14 (10H, m), 0.85 (3H, d, J = 6.98 Hz)

**Compound 1e**

**Synthesis of 3,7-di-(4-heptylphenyl)-dibenzothiophene-S,S-dioxide**

In a 100 ml round-bottom flask K₂CO₃ (1.104 gm, 8.0 mmol) was dissolved in H₂O (4 ml) and 1,4-dioxane (10 ml) was added followed by 3-fluoro-4-heptylphenylboronic acid (0.323 gm, 1.47 mmol), 3,7-dibromodibenzothiophene-S,S-dioxide (0.25 gm, 0.66 mmol) and Pd(PPh₃)₂Cl₂ (0.010 gm, 3 mol%). This mixture was refluxed for 24 hours under nitrogen when TLC (50% CH₂Cl₂, 50% hexanes) showed full conversion of the starting materials. At this point, the mixture was cooled down to room temperature and CH₂Cl₂ (200 ml) was added. This solution was passed through a short silica plug and the solvent was removed from the filtrate under reduced pressure to obtain a light yellow solid. The compound was subjected to column chromatography (eluent hexanes : dichloromethane = 1:2) to obtain the product as a yellow solid (170 mg, 46% yield).

Phase transition: Cr 168 SmA 221 I
1H NMR (DMSO-d6, 368 K, 400 MHz): 8.20 (2H, d, J = 7.95 Hz), 8.15 (2H, s), 8.05 (2H, d, J = 8.03 Hz), 7.72 (4H, d, J = 8.17 Hz), 7.34 (4H, d, J = 8.17 Hz), 2.67 (4H, t, J = 8.56 Hz), 1.66 (4H, t, J = 7.34 Hz) 1.34 (16H, m), 0.89 (6H, t, J = 7.34 Hz)

13C NMR (Tetrachloroethane-d2, 298K, 100 MHz): 143.62, 143.26, 139.28, 135.91, 132.71, 129.85, 129.46, 127.18, 123.46, 119.77, 35.26, 31.59, 30.93, 29.03, 28.82, 22.34, 14.07

IR (neat, cm⁻¹): 2953.85, 2922.79, 2852.38, 1600.31, 1519.10, 1463.79, 1301.06, 1188.97, 1015.99, 889.54, 815.91, 714.22

Synthesis of 4-methoxyphenylboronic acid

In a 500 ml two-necked round bottom flask, 1-bromo-4-bromoanisole (18.7 gm, 100 mmol) was dissolved in dry THF (250 ml) in a nitrogen atmosphere and the temperature of the mixture was taken to -78°C. In this mixture n-BuLi (40 ml, 2.5M in hexanes) was added dropwise and the mixture was stirred for an hour after the addition was complete. Then triisopropyl borate (19.06 gm, 300 mmol) was added dropwise and the mixture was allowed to warm up to room temperature. In this mixture, 10% hydrochloric acid solution (100 ml) was added and the mixture was stirred vigorously for 2 hours. This solution was then extracted with diethyl ether (100 ml × 3) and the combined organic layers were dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure to obtain the desired product as a off-white solid (15.1 gm, 100% yield). The product was clean enough to be used in further reactions without any additional purification. MP 202°C (lit. mp 204-206°C).

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In a 100 ml round-bottom flask K$_2$CO$_3$ (1.104 gm, 8.0 mmol) was dissolved in H$_2$O (4 ml) and 1,4-dioxane (10 ml) was added followed by 3-fluoro-4-methoxyphenylboronic acid (0.323 gm, 1.47 mmol), 3,7-dibromodibenzothiophene-S,S-dioxide (0.25 gm, 0.66 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (0.010 gm, 3 mol%). This mixture was refluxed for 24 hours under nitrogen when TLC (50% CH$_2$Cl$_2$, 50% hexanes) showed full conversion of the starting materials. At this point, the mixture was cooled down to room temperature and CH$_2$Cl$_2$ (200 ml) was added. This solution was passed through a short silica plug and the solvent was removed from the filtrate under reduced pressure to obtain a light yellow solid. The compound was subjected to column chromatography (eluent hexanes : dichloromethane = 1:2) to obtain the product as a yellow solid (200 mg, 47% yield).

Melting point > 310°C

$^1$H NMR (DMSO-d$_6$, 368 K, 400 MHz): 8.15 (2H, d, $J = 8.46$ Hz), 8.1 (2H, s), 8.0 (2H, d, $J = 8.46$ Hz), 7.74 (4H, d, $J = 8.46$ Hz), 7.06 (4H, d, $J = 8.46$ Hz), 3.83 (6H, s)

$^{13}$C NMR (Tetrachloroethane-d$_2$, 298K, 100 MHz): 160.05, 142.38, 138.63, 130.47, 131.85, 128.94, 128.08, 122.86, 118.91, 114.79, 55.4.

IR (neat, cm$^{-1}$): 3032.86, 2953.84, 2837.73, 2024.43, 1605.30, 1515.36, 1460.12, 1398.99, 1296.52, 1253.49, 1240.35, 1177.78, 1157.49, 1137.51, 1113.20, 1049.14, 1016.16, 814.51, 777.80, 713.13, 623.75
Synthesis of 3,7-di-4-trifluoromethoxyphenyl- dibromodibenzothiophene-S,S-dioxide

In a 100 ml round-bottom flask K$_2$CO$_3$ (1.104 gm, 8.0 mmol) was dissolved in H$_2$O (4 ml) and 1,4-dioxane (10 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4-trifluoromethoxyphenylboronic acid (0.302 gm, 1.47 mmol), 3,7-dibromodibenzothiophene-S,S-dioxide (0.25 gm, 0.66 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (0.010 gm, 3 mol%) was added. This mixture was refluxed for 24 hours under nitrogen when TLC (50% CH$_2$Cl$_2$, 50% hexanes) showed full conversion of the starting materials. At this point, the mixture was cooled down to room temperature and CH$_2$Cl$_2$ (200 ml) was added. This solution was passed through a short silica plug and the solvent was removed from the filtrate under reduced pressure to obtain a white solid. This solid was recrystallized from a 1:1 mixture of toluene and iso-octane to obtain the desired product as white shiny plates (0.250 gm, 75% yield).

Phase transition: Cr 238 SmX 259 I

$^1$H NMR (DMSO-d$_6$, 348 K, 400 MHz): 8.36 (2H, d, $J = 1.48$ Hz), 8.34 (2H, d, $J = 8.16$ Hz), 8.16 (2H, dd, $J = 8.10$ Hz, 1.70 Hz), 8.00 (4H, d, $J = 8.80$ Hz), 7.51 (4H, d, $J = 8.08$ Hz)

$^{13}$C NMR (DMSO-d$_6$, 348K, 100 MHz): 141.72, 138.79, 137.57, 133.44, 130.26, 129.56, 124.00, 122.00, 120.61

IR (neat, cm$^{-1}$): 3044.03, 1609.51, 1515.01, 1464.30, 1401.29, 1288.24, 1253.03, 1206.47, 1149.42, 1015.56, 922.22, 856.42, 822.45, 797.15, 713.30, 672.15

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**Compound 2c**

**Synthesis of 3,7-di-(4-propyloxyphenyl)dibenzothiophene-S,S-dioxide**

![Chemical Structure]

In a 100 ml round-bottom flask K$_2$CO$_3$ (1.104 gm, 8.0 mmol) was dissolved in H$_2$O (4 ml) and 1,4-dioxane (10 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4-propyloxybenzeneboronic acid (0.264 gm, 1.47 mmol), 3,7-dibromodibenzothiophene-S,S-dioxide (0.25 gm, 0.66 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (0.010 gm, 3 mol%) was added. This mixture was refluxed for 24 hours under nitrogen when TLC (50% CH$_2$Cl$_2$, 50% hexanes) showed full conversion of the starting materials. At this point, the mixture was cooled down to room temperature and CH$_2$Cl$_2$ (200 ml) was added. This solution was passed through a short silica plug and the solvent was removed from the filtrate under reduced pressure to obtain a yellowish-white solid. This solid was recrystallized from a 1:1 mixture of toluene and isooctane to obtain the desired product as faint yellow solid (0.220 gm, 69% yield).

Phase transition: Cr 262 N 316 I

$^1$H NMR (DMSO-d$_6$, 400 MHz, 348 K): 8.13 (2H, d, $J = 8.08$ Hz), 8.101 (2H, d, $J = 1.6$ Hz), 7.99 (2H, dd, $J = 8.10$ Hz, 1.74 Hz), 7.73 (4H, d, $J = 8.76$ Hz), 7.06 (4H, d, $J = 8.80$ Hz), 4.04 (4H, t, $J = 6.48$ Hz), 1.79 (4H, sext, $J = 6.82$ Hz), 1.03 (6H, t, $J = 7.38$ Hz)

$^{13}$C NMR (DMSO-d$_6$, 100 MHz, 348 K): 160.01, 142.92, 139.21, 132.27, 130.89, 129.43, 128.53, 123.28, 119.36, 115.95, 70.10, 22.52, 10.54.
IR (neat, cm\(^{-1}\)): 2964.32, 2937.24, 2875.89, 1600.93, 1518.20, 1460.04, 1296.99, 1242.25, 1159.22, 1048.41, 1013.48, 974.74, 818.52, 711.07

Synthesis of 1-bromo-4-(n-pentyloxy)benzene

![Chemical Structure]

This and other 1-bromo-4-alkoxybenzenes were prepared using previously reported procedure\(^{43}\).

In a 500 ml round bottom flask 4-bromophenol (8.65 gm, 50.0 mmol) was dissolved in acetone (150 ml) and K\(_2\)CO\(_3\) (34.55 gm, 250 mmol) was added when the color of the solution turned pink. The mixture was stirred at room temperature for 10 minutes and n-pentyl iodide (9.9 gm, 50 mmol) was added all at once. The mixture was refluxed for 16 hours when full conversion of 4-bromophenol occurred (TLC 10% EtOAc, 90% hexanes). The solution was filtered and the solvent was removed from the filtrate under reduced pressure to obtain a yellow liquid. This liquid was subjected to kugelrohr distillation (145°C, 0.1 mm Hg) to obtain the desired material as a light yellow liquid (11.5 gm, 95% yield).

\(^1\)H NMR (DMSO-d\(_6\), 298 K, 400 MHz): 7.35 (2H, d, \(J = 9.08\) Hz), 6.76 (2H, d, \(J = 9.04\) Hz), 3.90 (2H, t, \(J = 6.56\) Hz), 1.76 (2H, quintet, \(J = 6.63\) Hz), 1.40 (4H, m), 0.92 (3H, t, \(J = 7.12\) Hz)

Synthesis of 4-pentyloxyphenylboronic acid

![Chemical Structure]

In a 500 ml two-necked round bottom flask, 1-bromo-4-(pentyloxy)benzene (10.40 gm, 42.77 mmol) was dissolved in dry THF (200 ml) in a nitrogen atmosphere and the temperature of the
mixture was taken to -78°C. In this mixture n-BuLi (17.10 ml, 2.5M in hexanes) was added dropwise the mixture was stirred for an hour after the addition was complete. Then triisopropyl borate (24.13 gm, 128.31 mmol) was added dropwise and the mixture was allowed to warm up to room temperature. In this mixture, 10% hydrochloric acid solution (100 ml) was added and the mixture was stirred vigorously for 2 hours. This solution was then extracted with diethyl ether (100 ml × 3) and the collective organic layer was dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure to obtain the desired product as a white fluffy solid (8.1 gm, 91% yield). The product was clean enough to be used in further reactions without any additional purification.

\[^{1}\text{H NMR (DMSO-d6, 298 K, 400 MHz): 7.72 (2H, d, J = 8.15 Hz), 6.87 (2H, d, J = 8.72 Hz), 3.96 (2H, t, J = 7.05 Hz), 1.71 (2H, quint, J = 6.61 Hz), 1.37 (4H, m), 0.89 (3H, t, J = 7.16 Hz)}\]

**Compound 2d**

**Synthesis of 3,7-di-(4-pentyloxyphenyl)dibenzothiophene-S,S-dioxide**

In a 100 ml round-bottom flask K₂CO₃ (1.104 gm, 8.0 mmol) was dissolved in H₂O (4 ml) and 1,4-dioxane (10 ml) was added followed by 4-n-pentyloxyphenylboronic acid (0.305 gm, 1.47 mmol), 3,7-dibromodibenzothiophene-S,S-dioxide (0.25 gm, 0.66 mmol) and Pd(PPh₃)₂Cl₂ (0.010 gm, 3 mol%). This mixture was refluxed for 24 hours under nitrogen when TLC (50% CH₂Cl₂, 50% hexanes) showed full conversion of the starting materials. At this point, the mixture was cooled down to room temperature and CH₂Cl₂ (200 ml) was added. This solution
was passed through a short silica plug and the solvent was removed from the filtrate under reduced pressure to obtain a light yellow solid. This solid was recrystallized from a mixture of ethanol and toluene (1:1) to obtain the desired product as a light yellow solid (50 mg, 14% yield).

Phase transition: Cr 223 SmA 238 N 281 I

$^1$H NMR (tetrachloroethane-d$_2$, 298 K, 400 MHz): 8.04 (2H, s), 7.88 (4H, s), 7.63 (2H, d, $J$ = 8.73 Hz), 7.07 (2H, d, $J$ = 8.73 Hz), 4.06 (4H, t, $J$ = 6.37 Hz), 1.87 (4H, quint, $J$ = 6.13 Hz), 1.48 (8H, m), 1.00 (6H, t, $J$ = 6.69 Hz)

$^{13}$C NMR (Tetrachloroethane-d$_2$, 298 K, 100 MHz): 159.56, 142.94, 138.11, 131.94, 130.56, 129.35, 127.96, 121.87, 119.71, 115.10, 68.09, 28.79, 28.05, 22.39, 14.06

IR (neat, cm$^{-1}$): 2932.37, 2869.53, 1603.18, 1518.50, 1461.13, 1389.91, 1300.38, 1246.63, 1183.02, 1138.36, 1050.05, 818.52

**Compound 2e**

**Synthesis of 3,7-di-4-hexyloxyphenyl- dibromodibenzothiophene-S,S-dioxide**

In a 100 ml round-bottom flask K$_2$CO$_3$ (1.104 gm, 8 mmol) was dissolved in H$_2$O (4 ml) and 1,4-dioxane (10 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4-n-hexyloxybenzeneboronic acid (0.326 gm, 1.47 mmol), 3,7-dibromodibenzothiophene-S,S-dioxide (0.25 gm, 0.66 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (0.010 gm, 3 mol%) was added. This mixture was refluxed for 24 hours under nitrogen when TLC (50%
CH₂Cl₂, 50% hexanes) showed full conversion of the starting materials. At this point, the mixture was cooled down to room temperature and CH₂Cl₂ (200 ml) was added. This solution was passed through a short silica plug and the solvent was removed from the filtrate under reduced pressure to obtain a white solid. This solid was recrystallized from a 1:1 mixture of toluene and iso-octane to obtain the desired product as white shiny plates (0.250 gm, 75% yield).

Phase transition: Cr 169 SmX 205 SmY 260 N 276 I

¹H NMR (DMSO-d₆, 368 K, 400 MHz): 8.13 (2H, d, J = 8.08 Hz), 8.08 (2H, d, J = 1.44 Hz), 7.99 (2H, dd, J = 8.10 Hz, 1.30 Hz), 7.72 (4H, d, J = 8.68 Hz), 7.06 (4H, d, J = 8.68 Hz), 4.08 (4H, t, J = 6.50 Hz), 1.77 (4H, quint, J = 6.76 Hz), 1.43 (12H, m), 0.92 (6H, t, J = 7.30 Hz)

¹³C NMR (DMSO-d₆, 368K, 100 MHz): 160.04, 142.97, 139.26, 132.27, 130.93, 129.45, 128.53, 123.26, 119.35, 115.99, 68.68, 31.35, 29.19, 25.54, 22.28, 13.96

IR (neat, cm⁻¹): 2928.90, 2869.53, 1602.99, 1518.03, 1461.41, 1390.07, 1300.92, 1245.37, 1183.65, 1157.82, 1022.27, 1007.60, 935.49, 891.21, 818.05, 713.14

Synthesis of 1-bromo-4-(heptyloxy)benzene

Prepared using literature procedure ⁴³.

In a 500 ml round bottom flask 4-bromophenol (8.65 gm, 50 mmol) was dissolved in acetone (150 ml) and K₂CO₃ (34.55 gm, 250 mmol) was added when the color of the solution turned pink. The mixture was stirred at room temperature for 10 minutes and n-heptyl iodide (16.95 gm, 75 mmol) was added all at once. The mixture was refluxed for 16 hours when full conversion of 4-bromophenol occurred (TLC 10% EtOAc, 90% hexanes). The solution was filtered and the
solvent was removed from the filtrate under reduced pressure to obtain a yellowish liquid. This liquid was subjected to kugelrohr distillation (160°C, 0.1 mm Hg) to obtain the desired material as a light yellow liquid (13.5 gm, 100 % yield).

$^1$H NMR (CDCl$_3$, 348 K, 400 MHz): 7.35 (2H, d, $J = 8.86$ Hz), 6.76 (2H, d, $J = 8.86$ Hz), 3.9 (2H, t, $J = 6.51$ Hz), 1.76 (2H, t, $J = 8.39$ Hz), 1.48-1.24 (9H, m), 0.89 (3H, t, $J = 7.16$ Hz)

Synthesis of 4-n-heptyloxyphenylboronic acid

In a 500 ml two-necked round bottom flask, 4-bromo-1-heptyloxybenzene (17.33 gm, 63.9 mmol) was dissolved in dry THF (180 ml) in a nitrogen atmosphere and the temperature of the mixture was taken to -78°C. In this mixture n-BuLi (25.6 ml, 2.5M in hexanes) was added dropwise and the mixture was stirred for an hour after the addition was complete. Then triisopropyl borate (33.85 gm, 180 mmol) was added dropwise and the mixture was allowed to warm up to room temperature. In this mixture, 10% hydrochloric acid solution (100 ml) was added and the mixture was stirred vigorously for 2 hours. This solution was extracted with diethyl ether (100 ml × 3) and the collective organic layer was dried over anhydrous MgSO$_4$ and the solvent was removed under reduced pressure to obtain the desired product as a white solid (15.1 gm, 100% yield). The product was used in further reactions without any additional purification.

$^1$H NMR (DMSO-d6, 368 K, 400 MHz): 7.71 (2H, d, $J = 7.77$ Hz), 6.85 (2H, d, $J = 9.50$ Hz), 3.94 (2H, t, $J = 6.61$ Hz), 1.68 (2H, d, $J = 6.71$ Hz), 1.44-1.16 (9H, m), 0.85 (3H, t, $J = 7.03$ Hz)
Compound 2f

Synthesis of 3,7-di-(4-n-heptyloxyphenyl)dibenzothiophene-S,S-dioxide

In a 100 ml round-bottom flask K$_2$CO$_3$ (1.104 gm, 8.0 mmol) was dissolved in H$_2$O (4 ml) and 1,4-dioxane (10 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4-heptyloxybenzeneboronic acid (0.347 gm, 1.47 mmol), 3,7-dibromodibenzothiophene-S,S-dioxide (0.25 gm, 0.66 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (0.010 gm, 3 mol%) was added. This mixture was refluxed for 24 hours under nitrogen when TLC (50% CH$_2$Cl$_2$, 50% hexanes) showed full conversion of the starting materials. At this point, the mixture was cooled down to room temperature and CH$_2$Cl$_2$ (200 ml) was added. This solution was passed through a short silica plug and the solvent was removed from the filtrate under reduced pressure to obtain a white solid. This solid was recrystallized from a 1:1 mixture of toluene and iso-octane to obtain the desired product as faint yellow shiny plates (0.252 gm, 64% yield).

Phase transition: Cr 157 SmX 189 SmY 194 SmA 268 I

$^1$H NMR (DMSO-d$_6$, 400 MHz, 348 K): 8.16 (2H, d, $J = 8.0$ Hz), 8.105 (2H, d, $J = 1.6$ Hz), 8.013 (2H, dd, $J = 8.12$ Hz, 1.68 Hz), 7.71 (4H, d, $J = 8.20$ Hz), 7.34 (4H, d, $J = 8.24$ Hz), 4.08 (4H, t, $J = 1.6$ Hz), 1.78 (4H, quintet, $J = 6.4$ Hz), 1.51 (16H, m), 0.091 (3H, t, $J = 6.8$ Hz)

$^{13}$C NMR (DMSO-d$_6$, 100 MHz, 348 K): 160.01, 142.94, 139.22, 132.30, 130.89, 129.44, 128.55, 123.32, 119.37, 115.95, 68.61, 31.57, 29.21, 28.74, 25.89, 22.29, 14.06

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IR (neat, cm⁻¹): 2924.05, 2855.32, 1603.33, 1518.26, 1461.51, 1390.49, 1300.44, 1245.07, 1184.24, 1157.79, 1019.42, 890.38, 818.46, 713.16

**Compound 2g**

Synthesis of 3,7-di-(4-undecyloxyphenyl)dibenzothiophene-S,S-dioxide

In a 100 ml round-bottom flask K₂CO₃ (1.104 gm, 8 mmol) was dissolved in H₂O (4 ml) and 1,4-dioxane (10 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 4-undecyloxyphenylboronic acid (0.429 gm, 1.47 mmol), 3,7-dibromodibenzothiophene-S,S-dioxide (0.25 gm, 0.66 mmol) and Pd(PPh₃)₂Cl₂ (0.010 gm, 3 mol%) was added. This mixture was refluxed for 24 hours under nitrogen when TLC (50% CH₂Cl₂, 50% hexanes) showed full conversion of the starting materials. At this point, the mixture was cooled down to room temperature and CH₂Cl₂ (200 ml) was added. This solution was passed through a short silica plug and the solvent was removed from the filtrate under reduced pressure to obtain a light yellow solid. This solid was washed with isooctane and dried under suction filtration to obtain the desired product as a light yellow solid (0.278 gm, 60% yield).

Phase transition: Cr171 SmA 252 I

¹H NMR (Tetrachloroethane-d2, 298 K, 400 MHz): 8.03 (2H, s), 7.88 (4H, s), 7.63 (4H, d, J = 8.72 Hz), 7.07 (4H, d, J = 8.80 Hz), 4.06 (4H, t, J = 6.58 Hz), 1.86 (4H, quint, J = 7.00 Hz), 1.58-1.27 (28H, m), 0.94 (4H, t, J = 6.76 Hz)
$^{13}$C NMR (Tetrachloroethane-d2, 298K, 100 MHz): 159.83, 143.20, 138.39, 132.17, 130.82, 129.60, 128.21, 122.11, 119.95, 115.37, 68.38, 32.06, 29.78, 29.75, 29.56, 29.50, 29.36, 26.17, 22.88, 14.41

IR (neat, cm$^{-1}$): 2955.10, 2919.97, 2851.61, 1606.19, 1516.73, 1463.70, 1391.83, 1299.54, 1250.44, 1180.51, 1158.34, 1138.42, 1014.20, 821.56, 750.15, 717.88

Synthesis of 4-bromo-2-fluoro-1-(n-hexyloxy)benzene

Prepared following a literature procedure$^{44}$. In a 500 ml round bottom flask 4-bromo-2-fluorophenol (9.55 gm, 50.0 mmol) was dissolved in acetone (150 ml) and K$_2$CO$_3$ (34.55 gm, 250 mmol) was added. The mixture was stirred at room temperature for 10 minutes and 1-bromohexane (8.25 gm, 50 mmol) was added all at once. The mixture was refluxed for 16 hours and full conversion of 4-bromophenol occurred (TLC 5% EtOAc, 95% hexanes). The solution was filtered and the solvent was removed from the filtrate under reduced pressure to obtain a yellowish liquid. This liquid was subjected to kugelrohr distillation (145°C, 0.1 mm Hg) to obtain the desired material as a light yellow liquid (12.7 gm, 92% yield).

$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 7.24 (1H, dd, $J = 10.55$ Hz, 2.36 Hz), 7.18 (1H, m), 6.85 (1H, t, $J = 8.74$ Hz), 4.01 (2H, t, $J = 6.60$ Hz), 1.82 (2H, quintet, $J = 7.12$ Hz), 1.54-1.28 (6H, m), 0.93 (3H, t, $J = 7.06$ Hz)
$^{13}$C NMR (CDCl$_3$, 298 K, 100 MHz): 153.88, 151.39, 127.12, 119.66, 116.03, 111.77, 31.50, 29.12, 25.57, 22.55, 13.98, 69.70

Synthesis of 3-fluoro-4-n-hexyloxyphenylboronic acid

\[
\begin{align*}
\text{C}_6\text{H}_{13}\text{O} - \text{Br} & \quad \rightarrow \quad \text{C}_6\text{H}_{13}\text{O} - \text{B(OH)}_2
\end{align*}
\]

Prepared following the general procedure of boronic acid synthesis previously reported$^{38}$. In a 500 ml two-necked round bottom flask, 4-bromo-2-fluoro-1-(hexyloxy)benzene (11.27 gm, 40.95 mmol) was dissolved in dry THF (180 ml) in a nitrogen atmosphere and the temperature of the mixture was taken to -78°C. In this mixture n-BuLi (16.38 ml, 2.5M in hexanes) was added dropwise and the mixture was stirred for an hour after the addition was complete. Then triisopropyl borate (24.13 gm, 128.31 mmol) was added dropwise and the mixture was allowed to warm up to room temperature. In this mixture, 10% hydrochloric acid solution (100 ml) was added and the mixture was stirred vigorously for 2 hours. This solution was then extracted with diethyl ether (100 ml × 3) and the collective organic layer was dried over anhydrous MgSO$_4$ and the solvent was removed under reduced pressure to obtain the desired product as a white fluffy solid (9.9 gm, 100% yield). The product was used in further reactions without any additional purification.

The $^1$H NMR contained peaks from boronic acid anhydrides. The material was used as is and the next reaction worked without any problems.
Compound 2h

Synthesis of 3,7-di-(3-fluoro-4-hexyloxyphenyl) dibenzothiophene-S,S-dioxide

In a 100 ml round-bottom flask K$_2$CO$_3$ (1.104 gm, 8.0 mmol) was dissolved in H$_2$O (4 ml) and 1,4-dioxane (10 ml) was added followed by 3-fluoro-4-hexyloxyphenylboronic acid (0.352 gm, 1.47 mmol), 3,7-dibromodibenzothiophene-S,S-dioxide (0.25 gm, 0.66 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (0.010 gm, 3 mol%). This mixture was refluxed for 24 hours under nitrogen when TLC (50% CH$_2$Cl$_2$, 50% hexanes) showed full conversion of the starting materials. At this point, the mixture was cooled down to room temperature and CH$_2$Cl$_2$ (200 ml) was added. This solution was passed through a short silica plug and the solvent was removed from the filtrate under reduced pressure to obtain a light yellow solid. This solid was recrystallized from a mixture of ethanol and toluene (1:1) to obtain the desired product as a light yellow solid (0.22 gm, 55% yield).

Phase transition: Cr 167 SmA 335 I

$^1$H NMR (DMSO-d$_6$, 348 K, 400 MHz): 8.20 (4H, t, $J = 4.00$ Hz), 8.06 (2H, d, $J = 8.52$ Hz), 7.71 (2H, d, $J = 12.92$ Hz), 7.61 (2H, d, $J = 8.60$ Hz), 7.27 (2H, t, $J = 8.72$ Hz), 4.15 (4H, t, $J = 6.48$ Hz), 1.79 (4H, quintet, $J = 6.91$ Hz), 1.56-1.28 (12H, m), 0.91 (6H, t, $J = 6.94$ Hz)

$^{13}$C NMR (DMSO-d$_6$, 348K, 100 MHz): 140.77, 138.15, 131.56, 130.67, 128.80, 122.64, 122.51, 118.77, 115.71, 114.16, 113.96, 69.01, 30.30, 28.12, 24.41, 21.30, 13.03

$^{19}$F NMR (CDCl$_3$, 298K, 376 MHz): -133.80--133.85 (2F, m)
Synthesis of trimethyl[2-(4-pentylphenyl)ethynyl]silane

\[ \text{C}_5\text{H}_{11} \text{Br} \rightarrow \text{C}_5\text{H}_{11} \equiv \text{Si} \]

Prepared using previously reported procedure\textsuperscript{45}.

In a 500 ml round bottom flask equipped with a stirbar, PPh\textsubscript{3} (344 mg, 1.31 mmol) was dissolved in diisopropylamine (50 ml) under nitrogen atmosphere. In this solution, PdCl\textsubscript{2} (44 mg, 0.25 mmol) and CuI (24 mg, 0.125 mmol) was added and the mixture was stirred at room temperature under nitrogen with occasional heating until the solution turned yellow and all the salts dissolved. In another beaker, 4-pentylbromobenzene (9.96 gm, 43.88 mmol) and trimethylsilylacetylene (5.4 gm, 55 mmol) was dissolved in diisopropylamine (30 ml) and the solution was added dropwise over 5 minutes to the catalyst solution. The resulting mixture was stirred under nitrogen room temperature for 4 days when GCMS indicated full conversion of starting materials. At this point, the volatiles were removed from the reaction mixture under house vacuum and hexanes (400 ml) was added to the residue. The resulting solution was passed through a short silica plug. More hexanes (300 ml) were used to wash the silica gel plug. The filtrates were combined and left under house vacuum overnight when all the volatiles were removed, leaving the desired product as a slightly yellow oil (10.29 gm, 96% yield).

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 298 K, 400 MHz): 7.36 (2H, d, \( J = 8.57 \) Hz), 7.09 (2H, d, \( J = 8.57 \) Hz), 2.57 (2H, t, \( J = 7.92 \) Hz), 1.58 (2H, quintet, \( J = 7.48 \) Hz), 1.38-1.18 (4H, m), 0.87 (3H, t, \( J = 6.41 \) Hz), 0.23 (9H, s)
In a 500 ml round bottom flask, 2-[4-(pentyl)phenyl]ethynyltrimethylsilane (7.62 gm, 31.19 mmol) was dissolved in degassed MeOH (50 ml) and K₂CO₃ (8.62 gm, 62.38 mmol) was added to the solution. The resulting mixture was stirred under nitrogen for 8 hours when the starting material was fully converted (GC-MS analysis). The solution was filtered and the solvent was removed under reduced pressure to obtain yellow oil. This was dissolved in hexanes (200 ml) and passed through a short silica pad and the silica was washed with more hexanes (250 ml). The organic layers were collected and the solvent was removed under reduced pressure to obtain the product as slight yellow oil (5.2 gm, 97% yield).

^1^H NMR (CDCl₃, 298 K, 400 MHz): 7.40 (2H, d, J = 7.61 Hz), 7.12 (2H, d, J = 8.46 Hz), 3.02 (1H, s), 2.59 (2H, t, J = 7.86 Hz), 1.60 (2H, quintet, J = 7.84 Hz), 1.38-1.23 (4H, m), 0.88 (3H, t, J = 6.64 Hz)

^13^C NMR (CDCl₃, 298 K, 100 MHz): 144.18, 132.24, 128.61, 119.41, 84.08, 76.61, 36.06, 31.61, 31.09, 22.70, 14.19

IR (neat, cm⁻¹): 3297.13, 3027.76, 2956.13, 2927.82, 2857.18, 2108.61, 1606.61, 1507.84, 1456.37, 1114.71, 1021.84, 838.52, 816.66, 698.03
Compound 4

Synthesis of 3,7-di-[2-(4-propylphenyl)ethynyl]dibenzothiophene-S,S-dioxide

Prepared using a procedure previously reported. In a 100 ml flask equipped with stirbar, 3,7-dibromodibenzothiophene-S,S-dioxide (0.25 gm, 0.66 mmol) and 1-ethynyl-4-pentylbenzene (0.45 gm, 2.64 mmol) was added to THF (5 ml). To this mixture, an aqueous 2M solution of 2-aminoethanol (3 ml) was added. The solution was then degassed and Pd(PPh$_3$)$_2$Cl$_2$ (27 mg, 0.039 mmol) and CuI (0.014 gm, 0.078 mmol) was added and the solution was refluxed at 80°C for 18 hours until the TLC (eluent 25% EtOAc, 75% hexanes) showed complete conversion of starting materials. Water (20 ml) was added and the mixture was extracted with CH$_2$Cl$_2$ (50 ml × 3). The organic layers were combined and the solvent was removed under reduced pressure. The residue was dissolved in boiling toluene (100 ml) and Montmorillonite K-10 clay (3 gm) was added. The mixture was gravity filtered while hot and the volume of the solvent was reduced to 5 ml and the solution was cooled down to room temperature. Isooctane (10 ml) was added to the solution to produce a precipitate. The precipitate was separated by suction filtration to get the desired product as a light yellow solid (75 mg, 20% yield).

Phase transition: Decomposes on heating around 180°C

$^1$H NMR (DMSO-d$_6$, 298 K, 400 MHz): 8.17 (2H, d, $J = 8.12$ Hz), 8.03 (2H, s), 7.88 (2H, d, $J = 8.00$ Hz), 7.49 (2H, d, $J = 7.72$ Hz), 7.25 (2H, d, $J = 7.72$ Hz), 2.62 (4H, t, $J = 7.48$ Hz), 1.61 (4H, quintet, $J = 7.13$ Hz), 1.31 (8H, m), 0.86 (6H, t, $J = 6.58$ Hz)
$^{13}$C NMR (Tetrachloroethane-d2, 298K, 100 MHz): 144.49, 137.72, 136.91, 131.70, 129.90, 128.57, 126.04, 124.84, 121.70, 118.97, 93.72, 86.92, 35.79, 31.32, 30.76, 22.44, 14.04

IR (neat, cm$^{-1}$): 2953.09, 2924.55, 2854.83, 2224.67, 2197.89, 1595.33, 1509.69, 1464.94, 1408.34, 1297.43, 1162.80, 1126.31, 1042.54, 886.58, 829.04, 707.79

Compound 3

Synthesis of 3,7-di-[1H,2H-perfluoroctenyl]dibenzo thiophene-$S,S$-dioxide

In a 50 ml pear flask equipped with stirbar was placed 3,7-dibromobenzo thiophene-$S,S$-dioxide (0.374 gm, 1 mmol), 1H,1H,2H-perfluoroctene (1.11 gm, 3.0 mmol), DMF (8 ml), $K_2CO_3$ (0.55 gm, 4.0 mmol) and TDA-1 (0.066 gm, 0.2 mmol). The resulting mixture was placed in a 60°C oil bath, degassed thoroughly with nitrogen and then Pd(OAc)$_2$ (4 mg, 1%) was added. The reaction mixture was warmed to 120°C and left stirring for 20 hours. After this time TLC indicated all the dibromide starting material and monobromide intermediate were consumed and only a single fluorescent product was present. The mixture was cooled to room temperature and the volatile material was removed under vacuum leaving a dark solid. The material was transferred to an Erlenmeyer flask and boiled in isooctane to which some Montmorillonite clay and silica gel were added. This hot slurry was filtered through a fluted filter paper and the isooctane was boiled into the filter to wash out the product. Upon cooling the solid product was isolated by suction filtration (<100 mg). The process was repeated with toluene and this time the product was collected as gray powder (314 mg, 35%).
Phase transitions: Decomposes on heating around 250°C

$^1$H NMR (DMSO-d6, 368 K, 400 MHz): 8.36 (2H, s), 8.19 (2H, d, $J = 7.52$ Hz), 8.06 (2H, d, $J = 8.35$ Hz), 7.47 (2H, d, $J = 16.71$ Hz), 6.92 (2H, q, $J = 11.70$ Hz)

$^{13}$C NMR (DMSO-d6, 368K, 100 MHz): 137.73, 135.80, 133.65, 130.93, 122.82, 120.66, 116.47

IR (neat, cm$^{-1}$): 3074.58, 1658.57, 1470.88, 1364.88, 1295.97, 1232.00, 1192.79, 1140.37, 1118.67, 1067.61, 962.96, 805.98, 708.02, 648.21
7.7 References


(2) Abe, J.; Shirai, Y. Journal of the American Chemical Society 1996, 118, 4705.


8.1 Introduction

Introduction of -C≡C- groups in liquid crystals as a bridge fragment between two aromatic rings can increase the value of birefringence\(^1\). The minimum energy configuration of tolane molecules is the one that is coplanar, i.e. the rings are in the same plane\(^1\). But unlike the oligophenyls, the conjugation is not disturbed even when the rings are twisted with respect to each other as the two \(\pi\)-electron bonds are perpendicular to each other\(^1\). There is very little increase of potential energy in this molecule due to torsion\(^1\). But unsymmetrical tolanes have absorption bands\(^2\) around 2100-2300 cm\(^{-1}\). This -C≡C- vibration becomes infrared forbidden when the -C≡C- is symmetrically disubstituted and the dipole moment of a symmetrically disubstituted tolane is low (even zero).

A net dipole moment is required for field induced alignment of the molecules in LC cells. So, it is worthwhile investigating if unsymmetrical tolanes can be synthesized that still have little or no absorption due to -C≡C- stretching vibration.

One way to investigate this issue is to prepare a library of tolanes and investigate their individual infrared absorption spectra. An alternative (and easier) way is to simulate the IR spectrum of the designed materials. The simulations can give us an approximate idea of the structure-property
relationships required for midwave infrared transparency of tolanes. In this work we used the HyperChem® package to get an idea of the infrared spectrum of individual molecules.

8.2 Discussion

It was previously reported that fluorinated tolanes can be generated from a highly fluorinated arene and a trimethylsilylarylacetylene using TBAF as a catalyst. This methodology was used in synthesis of polymers containing alternating aryl-acetylene-perfluoroaryl units. Also, this methodology is useful for C-C bond forming reactions where both the carbons are \( sp^2 \) hybridized. Amination of fluoroarenes can also be executed using this methodology.

Previously room-temperature direct alkynylation of azoles and polyhalogenated arenes using copper acetylides have been reported. Also, Pd/TBAF has been used previously for a decarboxylative route of tolane synthesis. Other methods of direct alkynylation using Na and Grignard reagents have been reported. But, the TBAF (tetrabutylammonium fluoride) catalyzed method is attractive as it appears to be the easiest, the least expensive and a less time consuming way of generating fluorinated tolane liquid crystals. The basic core structure that was investigated in this study is as below (Figure 8.1). This core structure provides a long conjugation length that should deliver increased birefringence.

\[
\begin{align*}
\text{Figure 8.1: Structure of the core investigated in this study}
\end{align*}
\]
The conventional method of synthesis of materials with the core structure depicted in Figure 8.1 requires five steps (including steps involving palladium catalysis and alkyllithium reagents) as seen in Figure 8.2.

![Chemical structure diagram]

**Experimental conditions:**
- (e) 4-pentylphenylboronic acid, Pd(PPh₃)₂Cl₂, K₂CO₃, 1,4-dioxane, H₂O, reflux
- (f) i. n-BuLi, THF, -78°C, ii. I₂, -78°C to rt
- (g) TMS-acetylene, PPh₃, PdCl₂, CuI, Et₂NH, reflux
- (h) K₂CO₃, MeOH, CH₂Cl₂, rt
- (i) 1-bromo-4-(trifluoromethyl)benzene, PPh₃, PdCl₂, CuI, Et₂NH, reflux

**Figure 8.2:** A conventional synthesis of a fluorinated tolane LC

In comparison, the TBAF catalyzed route requires only three steps, two of them being palladium catalyzed. The final step requires only 1 mol% TBAF (Figure 8.3), which is very attractive in large scale synthesis. The typical yield in the step involving TBAF catalysis (based on limited experience thus far) is in the range of 60%.
Experimental conditions: (j) 4-pentylphenylboronic acid, Pd(PPh3)2Cl2, K2CO3, 1,4-dioxane, H2O, reflux (k) TMS-acetylene, PPh3, PdCl2, CuI, Et2NH, reflux (l) TBAF•3H2O (1 mol%), anhydrous toluene, rt

Figure 8.3: TBAF catalyzed route for synthesis of a fluorinated tolane LC

The next task was to identify individual molecules that do not have a significant infrared absorption band due to a -C≡C- stretch. Some basic simulation of infrared spectra using the HyperChem® package helped immensely to get a preliminary idea of the useful structure features. Some of the simulations are depicted below. The -C≡C- stretching mode is colored in purple in the simulated infrared spectra.
Figure 8.4: Simulated infrared spectrum of 1-[2-(4-chloro-3-fluorophenyl)ethyl]yl]-2,3,5,6-tetrafluoro-4-(4-pentylphenyl)benzene
**Figure 8.5:** Simulated infrared spectrum of 1,2,4,5-tetrafluoro-3-(4-pentylphenyl)-6-[2-[4-(trifluoromethyl)phenyl]ethynyl]benzene
Figure 8.6: Simulated infrared spectrum of 1-[4-[2-(4-chlorophenyl)ethynyl]phenyl]-4-pentylbenzene
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<th>Compound</th>
<th>Structure</th>
<th>-C≡C- stretch absorption frequency (calculated) cm⁻¹</th>
<th>-C≡C- stretch absorption intensity (calculated) km/mol</th>
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**Table 8.1:** Calculated frequency and absorption intensities due to -C≡C- stretch
In table 8.1, the materials for which the net dipole moment change for the \(-\text{C}=\text{C}\)- stretch is negligible, exhibits the least absorption intensity. Compound 11 shows the least intensity among the materials. From the structure of 11 it is seen that the moieties on the two sides of the \(\text{C}=\text{C}\) bond is electronically almost symmetrical. This symmetry is reflected as the almost non-existent absorption intensity due to \(\text{C}=\text{C}\) stretch (0.396 km/mol). For compound 14, the substituents on the two end of the \(\text{C}=\text{C}\) bond differs greatly, and thus the absorption intensity due to \(\text{C}=\text{C}\) stretch is very high (90.028 km/mol). The other examples have intermediate absorption intensity depending on the extent of electronic equivalence of the substituents.

Among the above examples, the synthesis of materials in compounds 2,9 and 12 were pursued as these compounds were predicted to have low absorption intensity due to the \(-\text{C}=\text{C}\)- stretch. The actual infrared spectra of these materials corroborate nicely with the calculated IR spectrum. The compounds 2 and 12 containing a tetrafluorobenzene ring were synthesized using the TBAF catalysis whereas compound 12 (with no such ring) was synthesized using conventional Sonogashira coupling (Figure 8.7).

![Chemical structure of compounds](image)

**Experimental conditions:** (a) 4-pentylphenylboronic acid, Pd(PPh$_3$)$_2$Cl$_2$, K$_2$CO$_3$, 1,4-dioxane, H$_2$O, reflux (b) TMS-acetylene, PPh$_3$, PdCl$_2$, CuI, Et$_2$NH, reflux (c) K$_2$CO$_3$, MeOH, CH$_2$Cl$_2$, rt (d) 1-chloro-4-iodobenzene, PPh$_3$, PdCl$_2$, CuI, Et$_2$NH, reflux

**Figure 8.7:** synthesis of the non-fluorinated tolane

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<th>Compound</th>
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<td>Cr 80 N 110 I</td>
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<td>12</td>
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**Table 8.2:** Mesogenic properties of the two fluorinated tolanes and the single non-fluorinated analogue

From Table 8.2 we can see that the material 9 does not possess any mesogenic properties. This is probably due to the bulky –CF₃ end group. Mesogenic activity was found in material 2. When this material was compared with compound 12 it was observed that the fluoro substituents have a dramatic effect on reduction of the melting point. All the three compounds are fairly transparent in the 4-5 µm region (Figures 8.8, 8.9 and 8.10) as seen in their actual IR spectra (not just simulations). For comparison, the infrared spectrum of 1-phenyl-1-propyne shows a prominent absorption due to -C≡C- stretch (Figure 8.11).
Figure 8.8: Infrared spectrum of 1,2,4,5-tetrafluoro-3-(4-pentylphenyl)-6-[2-[4-(trifluoromethyl)phenyl]ethynyl]benzene
Figure 8.9: Infrared spectrum of 1-[2-(4-chloro-3-fluorophenyl)ethynyl]-2,3,5,6-tetrafluoro-4-(4-pentylphenyl)benzene
Figure 8.10: Infrared spectrum of 1-{4-[2-(4-chlorophenyl)ethynyl]phenyl}-4-pentylbenzene
8.3 Conclusions

In this work, an efficient methodology for synthesis of fluorinated tolanes has been briefly explored. We have used TBAF as the fluoride source in this work. Other fluoride sources need to be examined and additional fluorinated tolanes need to be prepared and properties studied and mixtures need to be formulated. In addition to their potential use in MWIR devices these fluorinated materials will also be investigated as potential LC semiconductors.
8.4 Experimental

Synthesis of 1,2,3,4,5-pentafluoro-6-(4-pentylphenyl)benzene

In a 500 ml round-bottom flask K$_2$CO$_3$ (13.248 gm, 96.0 mmol) was dissolved in H$_2$O (60 ml) and 1,4-dioxane (150 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that pentafluorobromobenzene (9.86 gm, 40 mmol), 4-pentylphenylboronic acid (9.2 gm, 48 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (280 mg, 1 mol%) was added. This mixture was refluxed for 18 hours under nitrogen when TLC (eluent hexanes) showed complete conversion of the starting materials. The mixture was adsorbed on silica gel and placed on the top of a silica gel column. The column was eluted with hexanes and the major band was collected. The solvent was removed under reduced pressure to obtain the desired product as a white solid (11.23 gm, 89% yield).

$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 7.33 (2H, d, $J = 8.15$ Hz), 7.29 (2H, d, $J = 8.34$ Hz), 2.66 (2H, t, $J = 7.17$ Hz), 1.66 (2H, quintet, $J = 8.36$ Hz), 1.43-1.28 (4H, m), 0.91 (3H, t, $J = 6.89$ Hz)

$^{13}$C NMR (CDCl$_3$, 298 K, 100 MHz): 144.56, 130.14, 128.93, 123.71, 35.93, 31.71, 31.11, 22.70, 14.17

$^{19}$F NMR (CDCl$_3$, 298K, 376 MHz): -143.85 (2F, dd, $J = 22.56$ Hz, 8.02 Hz), -156.69 (1F, t, $J = 21.07$ Hz), -162.90- -163.05 (2F, m)

IR (neat, cm$^{-1}$): 2962.08, 2927.48, 2862.02, 1654.14, 1610.96, 1567.22, 1486.38, 1409.30, 1198.94, 1061.05, 980.04, 855.51, 827.76, 733.44

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Synthesis of trimethyl({2-[4-(trifluoromethyl)phenyl]ethynyl})silane

In a 200 ml round bottom flask equipped with a stirbar, PPh$_3$ (0.39 gm, 1.5 mmol) was dissolved in freshly distilled Et$_2$NH (100 ml) and PdCl$_2$ (67.5 mg, 0.038 mmol) was added. The mixture was stirred for 20 minutes under nitrogen at room temperature and then CuI (9.4 mg, 0.05 mmol) was added and the resulting mixture was stirred for an additional 5 minutes under nitrogen. In this solution ethynyltrimethylsilane (1.96 gm, 20 mmol) and 1-bromo-4-(trifluoromethyl)benzene (3.37 gm, 15 mmol) was added simultaneously and the resulting mixture was refluxed under nitrogen for 18 hours when all the starting material was consumed (checked by GC-MS). The solvent was removed from the reaction mixture under reduced pressure and the residue was adsorbed on silica gel and placed on the top of a silica gel column. The column was eluted with hexanes and the major band was collected. The solvent was removed under reduced pressure to obtain the desired product as a colorless liquid (3.52 gm, 97% yield). The material was previously reported$^{11}$.

$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 7.56 (4H, s), 0.26 (9H, s)

$^{13}$C NMR (CDCl$_3$, 298 K, 100 MHz): 132.37, 125.34, 103.61, 97.38

$^{19}$F NMR (CDCl$_3$, 298K, 376 MHz): -63.35 (3F, s)

IR (neat, cm$^{-1}$): 2962.28, 2163.03, 1614.09, 1513.28, 1405.46, 1320.40, 1251.17, 1166.88, 1127.11, 1066.61, 861.96, 837.82, 759.39, 656.09
Synthesis of 1,2,4,5-tetrafluoro-3-(4-pentylphenyl)-6-{2-[4-
(trifluoromethyl)phenyl]ethynyl}benzene (9)

In a 200 ml round-bottom flask equipped with a stirbar, 1,2,3,4,5-pentafluoro-6-(4-
pentylphenyl)benzene (1.57 gm, 5 mmol) and trimethyl(2-[4-
(trifluoromethyl)phenyl]ethynyl)silane (1.33 gm, 5.5 mmol) was dissolved in dry toluene at room temperature under nitrogen and TBAF.3H₂O (16 mg, 1 mol%) was added. The resulting mixture was stirred for 24 hours when the GC-MS showed complete conversion of starting material. The mixture was adsorbed on silica gel and placed on the top of a silica gel column. The column was eluted with hexanes and the major band was collected. The solvent was removed under reduced pressure and the residue was recrystallized from ether to obtain the desired product as colorless crystals (1.28 gm, 55% yield)

Phase transition: Cr 130 I

¹H NMR (CDCl₃, 298 K, 400 MHz): 7.72 (2H, d, J = 8.13 Hz), 7.65 (2H, d, J = 8.13 Hz), 7.40 (2H, d, J = 8.55 Hz), 7.31 (2H, d, J = 8.56 Hz), 2.67 (2H, t, J = 7.17 Hz), 1.67 (2H, quintet, J = 6.61 Hz), 1.42-1.29 (4H, m), 0.91 (3H, t, J = 7.17 Hz)

¹³C NMR (CDCl₃, 298 K, 100 MHz): 144.69, 132.22, 129.99, 128.78, 125.43, 124.04, 99.47, 76.95, 35.66, 31.45, 30.79, 22.46, 14.04

¹⁹F NMR (CDCl₃, 298K, 376 MHz): -63.45 (3F, s), -137.31- -137.41 (2F, m), -144.29 (2F, q, J = 10.20 Hz)
IR (neat, cm⁻¹): 2989.19, 2931.91, 2358.31, 1613.12, 1472.92, 1409.16, 1326.21, 1260.51, 1164.36, 1105.05, 1069.56, 1022.56, 974.03, 839.92, 750.15

Synthesis of [2-(4-chloro-3-fluorophenyl)ethynyl]trimethylsilane

In a 200 ml round bottom flask equipped with a stirbar, PPh₃ (0.39 gm, 1.5 mmol) was dissolved in freshly distilled Et₂NH (100 ml) and PdCl₂ (67.5 mg, 0.038 mmol) was added. The mixture was stirred for 20 minutes under nitrogen at room temperature and then CuI (9.4 mg, 0.05 mmol) was added and the resulting mixture was stirred for an additional 5 minutes under nitrogen. In this solution ethynyltrimethylsilane (1.96 gm, 20.0 mmol) and 1-chloro-2-fluoro-4-iodobenzene (3.84 gm, 15 mmol) was added simultaneously and the resulting mixture was refluxed under nitrogen for 18 hours when all the starting material was consumed (checked by GC-MS). The solvent was removed from the reaction mixture under reduced pressure and the residue was adsorbed on silica gel and placed on the top of a silica gel column. The column was eluted with hexanes and the major band was collected. The solvent was removed under reduced pressure to obtain the desired product as a colorless liquid (3.2 gm, 94% yield)

¹H NMR (CDCl₃, 298 K, 400 MHz): 7.31 (1H, t, J = 7.56 Hz), 7.22 (1H, dd, J = 9.65 Hz, 1.79 Hz), 7.17 (1H, ddd, J = 8.25 Hz, 1.09 Hz, 0.89 Hz), 0.24 (9H, s)

¹³C NMR (CDCl₃, 298 K, 100 MHz): 158.80, 156.32, 130.48, 128.49, 128.46, 119.89 (d, J = 26.64 Hz), 102.58, 96.47

¹⁹F NMR (CDCl₃, 298K, 376 MHz): -115.60 (1F, dd, J = 9.73 Hz, 7.95 Hz)
IR (neat, cm⁻¹): 2960.66, 2160.88, 1564.11, 1480.62, 1406.09, 1290.59, 1250.13, 1160.59, 1062.25, 958.01, 838.48, 758.48, 678.18

Synthesis of 1-[2-(4-chloro-3-fluorophenyl)ethynyl]-2,3,5,6-tetrafluoro-4-(4-pentylphenyl)benzene (2)

In a 200 ml round-bottom flask equipped with a stirbar, 1,2,3,4,5-pentafluoro-6-(4-pentylphenyl)benzene (1.57 gm, 5 mmol) and [2-(4-chloro-3-fluorophenyl)ethynyl]trimethylsilane (1.24 gm, 5.5 mmol) was dissolved in dry toluene at room temperature under nitrogen and TBAF.3H₂O (16 mg, 1 mol%) was added. The resulting mixture was stirred for 24 hours when the GC-MS showed complete conversion of starting material. The mixture was adsorbed on silica gel and placed on the top of a silica gel column. The column was eluted with hexanes and the major band was collected. The solvent was removed under reduced pressure and the residue was recrystallized from ether to obtain the desired product as colorless crystals (1.56 gm, 70% yield).

Phase transition: Cr 80 N 110 I

¹H NMR (tetrachloroethane-d2, 298 K, 400 MHz): 7.49-7.30 (7H, m), 2.68 (2H, t, J = 7.85 Hz), 1.67 (2H, quintet, J = 7.85 Hz), 1.43-1.30 (4H, m), 0.92 (3H, t, J = 7.85 Hz)
$^{13}$C NMR (tetrachloroethane-d$_2$, 298 K, 100 MHz): 159.0, 156.6, 144.90, 131.06, 130.08, 128.92, 128.77 (d, $J = 3.92$ Hz), 124.19, 123.01, 122.03, 120.00 (d, $J = 18.99$ Hz), 99.05, 35.93, 31.72, 31.06, 22.73, 14.32

$^{19}$F NMR (CDCl$_3$, 298K, 376 MHz): -114.74 (1F, t, $J = 7.75$ Hz), -137.40 - 137.50 (2F, m), -144.28 (2F, q, $J = 10.14$ Hz)

IR (neat, cm$^{-1}$): 2959.83, 2929.82, 2856.91, 2234.57, 1914.45, 1739.18, 1561.95, 1470.47, 1407.63, 1325.02, 1206.08, 1151.38, 1068.23, 1024.42, 946.60, 875.52, 849.99, 821.46, 772.45, 719.81

Synthesis of 1-bromo-4-(4-pentylphenyl)benzene

In a 500 ml round-bottom flask K$_2$CO$_3$ (13.24 gm, 96 mmol) was dissolved in H$_2$O (60 ml) and 1,4-dioxane (150 ml) was added. This mixture was degassed by sonication under vacuum for 20 minutes and after that 1-bromo-4-iodobenzene (11.31 gm, 40.0 mmol), 4-pentylphenylboronic acid (8.04 gm, 42.0mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (280 mg, 1.0 mol%) was added. This mixture was refluxed for 18 hours under nitrogen GC-MS showed complete conversion of the starting materials. At this point, the mixture was cooled down to room temperature and adsorbed on silica gel and placed on the top of a silica gel column. The column was eluted with hexanes and the major band was collected. The solvent was removed under reduced pressure to obtain the desired product as a off white solid (8.49 gm, 70% yield). The material was previously reported$^{12}$. 

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\(^1\)H NMR (tetrachloroethane-d\(_2\), 298 K, 400 MHz): 7.58 (2H, d, \(J = 8.85\) Hz), 7.50 (2H, d, \(J = 5.76\) Hz), 7.48 (2H, d, \(J = 6.13\) Hz), 7.28 (2H, d, \(J = 8.01\) Hz), 2.66 (2H, t, \(J = 7.44\) Hz), 1.67 (2H, quintet, \(J = 6.20\) Hz), 1.44-1.31 (4H, m), 0.94 (2H, t, \(J = 6.57\) Hz)

\(^{13}\)C NMR (tetrachloroethane-d\(_2\), 298 K, 100 MHz): 142.47, 139.79, 136.78, 131.71, 128.90, 128.42, 126.61, 120.98, 35.43, 31.46, 30.97, 22.49, 14.07

Synthesis of trimethyl({2-[4-(4-pentylphenyl)phenyl]ethynyl})silane

In a 500 ml round bottom flask equipped with a stirbar, PPh\(_3\) (0.39 gm, 1.5 mmol) was dissolved in freshly distilled Et\(_2\)NH (100 ml) and PdCl\(_2\) (67.5 mg, 0.038 mmol) was added. The mixture was stirred for 20 minutes under nitrogen at room temperature and then CuI (9.4 mg, 0.05 mmol) was added and the resulting mixture was stirred for an additional 5 minutes under nitrogen. In this solution ethynyltrimethylsilane (1.96 gm, 20 mmol) and 1-bromo-4-(4-pentylphenyl)benzene (4.54 gm, 15 mmol) was added simultaneously and the resulting mixture was refluxed under nitrogen for 18 hours when all the starting material was consumed (checked by GC-MS). The solvent was removed from the reaction mixture under reduced pressure and the residue was adsorbed on silica gel and placed on the top of a silica gel column. The column was eluted with hexanes and the major band was collected. The solvent was removed under reduced pressure to obtain the desired product as an off white solid (4.6 gm, 96% yield)
Synthesis of 1-ethynyl-4-(4-pentyphenyl)benzene

In a 500 ml round bottom flask, trimethyl(2-[4-(4-pentyphenyl)phenyl]ethyl) silane (4.48 gm, 14.0 mmol) was dissolved in a mixture of degassed MeOH (70 ml) and CH₂Cl₂ (70 ml) and KOH (1.57 gm, 28.0 mmol) was added to the solution. The resulting mixture was stirred under nitrogen for 8 hours when the starting material was fully converted (GC-MS analysis). The solution was filtered and the solvent was removed under reduced pressure to obtain a yellow solid. This solid was dissolved in hexanes (200 ml) and passed through a short silica pad and the silica was washed with more hexanes (800 ml). The organic layers were collected and the solvent was removed under reduced pressure to obtain the product as off white solid (3.37 gm, 97% yield).
$^1$H NMR (CDCl$_3$, 298 K, 400 MHz): 7.54 (4H, s), 7.49 (2H, d, $J$ = 8.37 Hz), 7.25 (2H, d, $J$ = 8.06 Hz), 2.64 (2H, t, $J$ = 7.81 Hz), 1.65 (2H, quintet, $J$ = 7.81 Hz), 1.44-1.28 (4H, m), 0.90 (2H, t, $J$ = 6.69 Hz)

$^{13}$C NMR (CDCl$_3$, 298 K, 100 MHz): 142.72, 141.55, 137.53, 132.52, 127.26, 128.96, 126.88, 126.80, 120.60, 83.66, 35.60, 31.55, 31.17, 22.57, 14.06

IR (neat, cm$^{-1}$): 3275.27, 2951.25, 2925.21, 2867.83, 2105.31, 1911.48, 1603.69, 1490.57, 1376.31, 1248.51, 1185.51, 1119.97, 1003.15, 808.76

**Synthesis of 1-{4-[2-(4-chlorophenyl)ethynyl]phenyl}-4-pentylbenzene (12)**

In a 500 ml round bottom flask equipped with a stirbar, PPh$_3$ (0.078 gm, 0.3 mmol) was dissolved in freshly distilled Et$_2$NH (40 ml) and PdCl$_2$ (13.5 mg, 0.076 mmol) was added. The mixture was stirred for 20 minutes under nitrogen at room temperature and then CuI (1.88 mg, 0.01 mmol) was added and the resulting mixture was stirred for an additional 5 minutes under nitrogen. In this solution 1-ethynyl-4-(4-pentylphenyl)benzene (0.74 gm, 3 mmol) and 1-chloro-4-iodobenzene (0.72 gm, 3 mmol) was added simultaneously and the resulting mixture was refluxed under nitrogen for 18 hours when all the starting material was consumed (checked by GC-MS). The solvent was removed from the reaction mixture under reduced pressure and the residue was adsorbed on silica gel and placed on the top of a silica gel column. The column was eluted with hexanes and the major band was collected. The solvent was removed under reduced pressure to obtain the desired product as a off-white solid (0.85 gm, 79% yield)
Phase transition: Cr 203 N 230 I

$^1$H NMR (tetrachloroethane-d$_2$, 298 K, 400 MHz): 7.61 (4H, s), 7.55 (2H, d, $J = 8.36$ Hz), 7.51 (2H, d, $J = 8.62$ Hz), 7.36 (2H, d, $J = 8.36$ Hz), 7.28 (2H, d, $J = 8.36$ Hz), 2.65 (2H, t, $J = 7.49$ Hz), 1.65 (2H, quintet, $J = 7.49$ Hz), 1.43-1.30 (4H, m), 0.92 (3H, t, $J = 7.49$ Hz)

$^{13}$C NMR (tetrachloroethane-d$_2$, 298 K, 100 MHz): 142.69, 140.81, 137.01, 133.98, 132.75, 131.95, 128.88, 128.59, 126.66, 121.58, 121.13, 90.29, 88.81, 35.42, 31.42, 30.96, 22.46, 14.05

IR (neat, cm$^{-1}$): 3031.30, 2925.13, 2866.68, 2216.81, 1907.82, 1738.59, 1601.98, 1495.72, 1395.49, 1375.38, 1083.46, 1010.52, 826.59, 806.58
8.5 References


Chapter 9

Summary

In this thesis, the development of high birefringence liquid crystals transparent in the midwave infrared region has been explored. Some of these materials have attractive electro-optic properties that might be useful for device applications. The theme of this thesis revolves around the design, synthesis and investigation of the absorption properties of these liquid crystalline materials.

Chapter 2 investigates the replacement of hydrogens with fluorine in liquid crystals with biphenyl cores to mitigate the absorption loss in the midwave infrared region. Although the absorption properties of these materials are attractive, they are not mesogenic.

Chapter 3 investigates the design and synthesis of cyanobiphenyls with fluorinated tails and their mesogenic properties. Compared to materials in chapter 2, some of these materials exhibit mesogenicity, but no nematic phases were observed in any of the compounds.

It was realized from the work in chapters 2 and 3 that highly fluorinated tails are detrimental to nematogenicity. As short alkyl tails can reduce the absorption due to C-H stretch in the midwave infrared region compounds with this feature were planned. Also, if the birefringence of the material is high, low cell gap can be used which decreases the absorption in the midwave infrared region. To instill high birefringence, terphenyl core can be used. Chapter 4 explores materials that feature a terphenyl core with lateral chloro substitution and short alkyl tails.
Short alkyl tails can reduce the absorption due to C-H stretch in the midwave infrared region but does not completely eliminate it. In chapter 5, we explore the design and synthesis of quaterphenyl liquid crystals. These materials are devoid of any alkyl tails. This feature drastically reduces the absorption between 3600-3000 cm\(^{-1}\). In general, elimination of alkyl tails from a calamitic material elevates the melting point. Lateral chloro substitution was used in these materials to keep the melting point within manageable range. Many of these materials were nematic. A ternary mixture was formulated with the nematogens.

In chapter 6, the knowledge acquired through research described in Chapters 2-5 has been applied to the design and synthesis of materials that have the potential to be applied in devices that work in the microwave regime. In the previous chapters, it was seen that fluorination strongly promotes smectic phases. Long alkyl tails contribute to absorption in the midwave infrared region and also these tails being almost optically isotropic-decreases the birefringence of the material. Also linear calamitic molecules without tails (the quaterphenyls) have higher melting points. Thus, in this chapter we explore materials targeted towards incorporating specific properties (high birefringence, nematic phase at manageable temperature) in the designed molecules. To do so, we use lateral chlorination, exclusion of fluorine from the molecule design, use very short (propyl) terminal alkyl tails or excluding it altogether from the molecule design and introduction of a bend in the molecule. The materials synthesized in this chapter exhibit very high birefringence and attractive mesogenic properties. The absorption in the midwave infrared region is low for these materials. One of these materials has birefringence of \(~0.4\) which enables it for possible application in microwave frequencies besides the midwave infrared.
Chapter 7 investigates dibenzothiophene-\(S,S\)-dioxide as liquid crystal core. These materials are of interest as the core has a 3D disposition and these are highly soluble in common organic solvents compared to the analogous quaterphenyls. Also, due to high conjugation (these materials can be looked at as quaterphenyls with a sulfone moiety that introduces a bend in the core framework) the materials are expected to possess high birefringence-making them useful for infrared applications.

Chapter 8 is a discussion of a new reaction methodology involving application of S\(\text{N}_2\)Ar reaction to generate tolane liquid crystals with low absorption in the midwave infrared region. Tolanes generally possess high birefringence and if designed properly, the absorption due to C≡C stretch can be minimized. In this chapter, Hyperchem® is used to screen molecules for negligible absorption due to C≡C stretch. The molecules are synthesized by a tetrabutylammonium fluoride catalyzed S\(\text{N}_2\)Ar reaction. The materials, besides their low absorption in the 4-5 μm region, can also be interesting in charge transport studies.

Overall, materials for potential application in midwave infrared devices have been successfully designed and their high yielding synthesis methodology has been developed in this thesis.