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HIGH BIREFRINGENCE AND LOW VISCOSITY LIQUID CRYSTALS

by

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A dissertation submitted in partial fulfillment of the requirements
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ABSTRACT

In this dissertation, liquid crystal (LC) materials and devices are investigated in order to meet the challenges for photonics and displays applications. We have studied three kinds of liquid crystal materials: positive dielectric anisotropic LCs, negative dielectric anisotropic LCs, and dual-frequency LCs. For the positive dielectric anisotropic LCs, we have developed some high birefringence isothiocyanato tolane LC compounds with birefringence ~0.4, and super high birefringence isothiocyanato biphenyl-bistolane LC compounds with birefringence as high as ~0.7. Moreover, we have studied the photostability of several high birefringence LC compounds, mixtures, and LC alignment layers in order to determine the failure mechanism concerning the lifetime of LC devices. Although cyano and isothiocyanato LC compounds have similar absorption peaks, the isothiocyanato compounds are more stable than their cyano counterparts under the same illumination conditions. This ultraviolet-durable performance of isothiocyanato compounds originates from its molecular structure and the delocalized electron distribution.

We have investigated the alignment performance of negative dielectric anisotropic LCs in homeotropic (vertical aligned, VA) LC cell. Some (2,3) laterally difluorinated biphenyls, terphenyls and tolanes are selected for this study. Due to the strong repulsive force between LCs and alignment layer, (2,3) laterally difluorinated terphenyls and tolanes do not align well in a VA cell resulting in a poor contrast ratio for the LC panel. We have developed a novel method to suppress the light leakage at dark state. By doping positive $\Delta\varepsilon$ or non-polar LC compounds/mixtures into the host negative LC mixtures, the repulsive force is reduced and the cell exhibits an excellent dark state. In addition, these dopants increase the birefringence and
reduce the viscosity of the host LCs which leads to a faster response time.

Dual-frequency liquid crystal exhibits a unique feature that its dielectric anisotropy changes from positive to negative when we increase the operating frequency. Submillisecond response time can be achieved by switching the frequency of a biased voltage, rather than switching the voltage at a given frequency. In this dissertation, we investigate the dielectric heating effect of dual-frequency LCs. Because the absorption peak of imaginary dielectric constant occurs at high frequency region (~ MHz), there is a heat generated when the LC cell is operated at a high frequency voltage. To measure the transient temperature change of the LC inside the cell, we have developed a non-contact method by utilizing the temperature-dependent birefringence property of the LC. Most importantly, we have formulated a new dual-frequency LC mixture which greatly reduces the dielectric heating effect while maintaining good physical properties.

Another achievement in this thesis is that we have developed a polarization independent phase modulator by using a negative dielectric anisotropic LC gel. With ~20 % of polymer mixed in the LC host, the LC forms polymer network which, in turn, exerts a strong anchoring force to the neighboring LC molecules. As a result, the operating voltage increases but the response time is significantly decreased. On the phase shift point of view, our homeotropic LC gel has ~0.08 \pi phase shift, which is 2X larger than the previous nano-sized polymer-dispersed liquid crystal droplets. Moreover, it is free from light scattering and requires a lower operating voltage.

In conclusion, this dissertation provides solutions to improve the performance of LC devices both in photonics and displays applications. These will have great impacts in defense and display
systems such as optical phased array, LCD TVs, projectors, and LCD monitors.
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CHAPTER ONE
INTRODUCTION

1.1 Motivation

In this information-dominated generation, displays such as cell phones, wrist watches, notebook computers, desktop monitors, and TVs have become essential in many aspects of our daily lives. Several display technologies have been developed, e.g., cathode ray tubes (CRTs), liquid crystal displays (LCDs), organic light emitting diodes, plasma displays, electroluminescence displays, vacuum fluorescence displays, etc. Among these display technologies, LCD is dominating in several flat panel direct-view and projection displays. The earliest application of LCD panel is watches and calculators which using the twist nematic (TN) mode. However, the information content using a TN mode is limited because of its low multiplexing ratio. [1] This barrier is removed when each pixel is independently addressed by a thin-film-transistor (TFT). High resolution TFT-LCD has been widely used in direct-view and projection TVs and desktop monitors. The desired performances are quite different between LCD monitors and TVs because monitors are mainly used by an individual, but TVs are designed for group viewing. Therefore, LCD monitors require high resolution while the TVs requires wide view angle. However, response time is the common challenge for both of them. To reduce the image blurring of a motion picture, the LC response time should be shorter than 5 ms while keeping high brightness, high contrast ratio, and good color quality.

Not only in visible region, LC based devices are also used in infrared region, including optical
switches, attenuators, filters, and spectrometers. [2-4] By using the LC material with low absorption, large phase and fast response in the infrared region [5], it is quite promising to develop compact size, low cost, no moving parts and low power consumption LC devices. For example, LC based optical phased array (OPA) is a device that can steer a laser beam continuously at a high rate of speed (approximately 1 kHz). [6] The OPA basically acts as a tunable array of prisms that adjusts the beam’s direction through Blazed diffraction. In a non-activated state (LC aligns in homogenous orientation), a laser beam traverses through the OPA and is not affected by the LC. In the voltage-on state, the electric field reorients the LC director’s distribution. By controlling the voltages to different electrodes, a Blazed grating can be formed which would deflect the incoming laser to a different exit angle. The faster the LC reorientation, the faster the laser beam can be steered from one angle to another. Traditionally, LC reorientation speed is proportional to the square of the thickness of LC layer. For rapid operation, one would prefer to keep the LC layer thin. Therefore, high birefringence LC materials are required in order to have enough phase retardation. [7]

Polymer-dispersed liquid crystal (PDLC) is another important branch of LC science and technology. A PDLC consists of about 30-40% monomer in a LC mixture. After phase separation, the liquid crystal droplets are dispersed in a polymer matrix, and the composite material is a sort of “Swiss cheese” polymer with liquid crystal droplets filling in the holes. The droplet size can be controlled during the polymerization process and is usually comparable to the visible wavelength (1µm or less). PDLC usually operates between two states, transparent and scattering state. The polymer matrix material is optically isotropic and has a refractive index $n_p$. The liquid crystal director axes within a particular droplet are determined by the polymer-LC
interaction at the droplet boundary. In the voltage-off state, liquid crystal aligns randomly from droplet to droplet, and the index mismatch between the LC droplets and the host polymer results in the scattering state. The degree of the off-state scattering depends on the size, birefringence and concentration of the liquid crystalline droplets and the film thickness. During the voltage-on state, the LC directors in the droplets are reoriented along the filed direction. Its effective index is equal to $n_o$ which is similar to the index of the polymer, $n_p$, and shows a transparent state. The major shortcomings of PDLC are inadequate contrast ratio, relatively high operating voltage and noticeable hysteresis. The performances in optical communication wavelengths are especially poor compared to those at the visible region due to the reduced LC birefringence at long wavelength. To improve the contrast ratio, one may use a thicker cell gap. However, the driving voltage and hysteresis will be increased.

LC material plays an essential role in all above-mentioned applications. It determines most of the performance of LC devices, including the contrast ratio, viewing angle, and response time. As mentioned before, the response time is proportional to the square of the LC cell gap. Thus, reducing cell gap is the most efficient way to shorten the response time. However, in order to have enough phase retardation, high birefringence LC materials are required. On the other hand, reducing the viscosity of LC materials will improve the response time. Therefore, it is important to develop high birefringence and low viscosity LC materials.
1.2 **Liquid Crystals**

Between 1850 and 1888, researchers in different fields found that several materials behaved strangely at temperatures near their melting points. It was observed that the optical properties of these materials changed discontinuously with increasing temperatures.[8] In 1888, Friedrich Reinitzer, an Austrian botanist who interested in the biological function of cholesterol in plants, was looking at the melting behavior of an organic substance related to cholesterol. He observed that the cholesteryl benzoate melted to a cloudy liquid at 145.5°C and became a clear liquid at 178.5°C. He repeated an earlier observation which showed that upon cooling the clear liquid, a brief appearance of blue color could be seen at the transition temperature, and that a blue violet color appeared just before crystallization. Discussion with Lehmann and others led to the identification of a new phase of matter called liquid crystal phase.

Liquid crystals are partly ordered materials, somewhere between their solid and liquid phases. They are fluid-like, yet the arrangement of molecules within them exhibit structure orders. The order of liquid crystals can be manipulated with mechanical, magnetic or electric forces. Three types of liquid crystals have been discovered so far: (i) thermotropic, (ii) lyotropic, and (iii) polymeric. Among them, thermotropic liquid crystals have been studied extensively and used widely.

As the temperature increases, the thermotropic liquid crystals go through a series of phase transitions: from solid to liquid crystal, to isotropic liquid, and finally to vapor phase. The phases of thermotropic liquid crystal verses temperature is shown in Figure 1-1 [9]. In Figure 1-1,
mesophase between $T_m$ and $T_c$ appears a milky liquid, but still exhibits the ordered. The first phase above $T_m$ is the smectic C phase (smectic is derived from the Greek word for soap). Next to the clearing point, the nematic phase appears with only a one-dimensional order (nematic in Greek means a thread, indicating the thread-like defects in the material). Exceptions exist for some compounds: their thermotropic phase appears only during the cooling process from the isotropic phase, but not on the heating process. This kind of phase transition is called monotropic. The physical properties of thermotropic liquid crystals, such as refractive indices, dielectric constants, elastic constants, and viscosities all depend on the temperature.

There are three phases of thermotropic liquid crystals which are called the “nematic phase”, the “smectic phase”, and the “cholesteric phase”. Figure 1-2 shows the molecules arrangement of these three phases.

![Figure 1-1 Phases of LC materials versus temperature.](image)
Nematic phase is the simplest case that the molecules possess only orientational but no positional long range order [10]. The aligned nematic liquid crystal molecules, on the average, are characterized by one symmetry axis, called the director $\mathbf{n}$. The director can be reoriented by an external field, such as electric field, magnetic field or optical field when the field strength exceeds the Freedericksz transition threshold. [11] Since liquid crystals are birefringent, the field-induced director axis reorientation imparts a large phase change on an optical field traversing the film. The phase change can be a pure phase modulation (without changing the polarization state), a phase retardation or a polarization rotation depending on the alignment of the LC directors.

Cholesteric (or chiral nematic) liquid crystal resemble nematic liquid crystal in all physical properties except that the molecules tend to align in a helical structure with the helical axis perpendicular to the director, as depicted in Figure 1-2. The helical structure results in selective reflection in wavelength and circular polarization. [12] The polarization states of the reflected

Figure 1-2 Illustration of three thermotropic liquid crystals: nematic, smectic and cholesteric
and transmitted waves depend on the pitch length of the cholesteric:

(i) If the helical pitch is much larger than the incident light wavelength, both reflected and transmitted waves are plane-polarized and periodically modulated by the pitch of the liquid crystal structure.

(ii) If the helical pitch is much smaller than the wavelength, there are two circularly polarized waves in the medium.

(iii) If the incident wavelength is comparable to the helical pitch, the reflected light is strongly circularly polarized. One circular component is almost totally reflected while the other passes through practically unchanged. The reflected wave preserves its sense of circular polarization.

The smectic phases, unlike nematics, are characterized by additional degrees of positional order. Generally, the molecules are arranged in layers in these mesophases, which can be considered as one-dimensional density waves. There are at least nine distinct smectic phases bearing the designations A, B, C, ..., I.[13] The molecular arrangement of smectic phase as shown in Figure 1-2 is the smectic A liquid crystal. In smectic A (SmA) liquid crystals, the molecular orientation is perpendicular to the layers. In each layer the molecules are positionally random, but directionally ordered with their long axis normal to the plane of the layer. Similar to nematics, smectic-A liquid crystals are optically uniaxial. There is a rotational symmetry around the director axis.
1.3 Properties of Liquid Crystals

1.3.1 Building Block of Liquid Crystals

Molecular structures play an important role in determining the phases, phase transition temperatures, optical, and electro-optical properties of the liquid crystals. In this section, we will discuss the basic molecular structure of the nematic liquid crystals. Rodlike structures, like that shown in Figure 1-3, are typical structures of LC materials. Here, R is a side chain group, A and B are aromatic rings, Z is a linking group and X is a terminal group. Some example of R, A, Z, B and X are shown in Table 1-1.

![Figure 1-3](image)

Figure 1-3 A typical rodlike molecular structure of LC molecule.

Table 1-1 Examples of building blocks of liquid crystals.

<table>
<thead>
<tr>
<th>R</th>
<th>A</th>
<th>Z</th>
<th>B</th>
<th>X</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkyl</td>
<td><img src="image" alt="Alkyl" /></td>
<td><img src="image" alt="COO" /></td>
<td><img src="image" alt="C2H4" /></td>
<td><img src="image" alt="Alkyl" /></td>
</tr>
<tr>
<td>Alkyl</td>
<td><img src="image" alt="Alkoxy" /></td>
<td><img src="image" alt="CN" /></td>
<td><img src="image" alt="F,Cl" /></td>
<td><img src="image" alt="Alkoxy" /></td>
</tr>
<tr>
<td>Alkenyl</td>
<td><img src="image" alt="Alkenyl" /></td>
<td><img src="image" alt="N=N" /></td>
<td><img src="image" alt="F" /></td>
<td><img src="image" alt="Alkenyl" /></td>
</tr>
<tr>
<td>Alkenyl</td>
<td></td>
<td><img src="image" alt="C≡C" /></td>
<td><img src="image" alt="F" /></td>
<td><img src="image" alt="Alkenyl" /></td>
</tr>
</tbody>
</table>


**Ring Systems**

The ring can be either unsaturated benzene rings or saturated cyclohexanes, or a combination of both. [14] The presence of the ring system is essential in most LCs that contain at least one ring (either phenyl or cyclohexyl). It is important to note that only $\sigma$ electrons exist in cyclohexyl rings, where $\pi$ electrons exist in phenyl rings. The presence of the rings provides the short range intermolecular forces needed to form the nematic phase. They also affect the absorption, dielectric anisotropy, birefringence, elastic constants and viscosity. The $\sigma - \sigma^*$ electronic transitions occur at vacuum ultraviolet regime ($\lambda < 180$nm). Thus the absorption of a saturated LC compounds is negligible in the visible spectral regime.

**Terminal Group (R)**

There are three common terminal groups: (a) alkyl chain $C_nH_{2n+1}$, (2) alkoxy chain $C_nH_{2n+1}O$, and (3) alkenyl chain that contains a double bond. The length of the chain strongly influences the elastic constants of the nematic phase as well as the phase transition temperature. For short chains with one or two carbon atoms ($n=1, 2$), the molecules are too rigid to exhibit LC phases. Medium chain length (e.g., $n=3-8$) are most suitable for nematic phases. The smectic phase appears if the compounds with longer chain length. Generally speaking, the melting point decreases as the chain length increases. Also, the clearing points ($T_c$) with an even number of carbon atoms are lower than those of compounds with an odd number of carbon atoms. This is known as the “odd-even effect.” In addition, the LC compounds with longer chain length also exhibit a higher viscosity even though it offers a lower melting point ($T_m$).
Terminal Group (X)

The terminal group X plays an important role in determining the dielectric constant and its anisotropy $\Delta \varepsilon$. In LCD, the operation voltage is required to cause a reorientation of the LC molecules. It is also known that the threshold voltage is inversely proportional to the square root of the dielectric anisotropy. Thus it is desirable to have a large $\Delta \varepsilon$ for low voltage operations. The terminal group X can be either polar or nonpolar. Nonpolar terminal group, such as the alkyl chain $C_nH_{2n+1}$, has very little effect on the dielectric anisotropy. On the other hand, a polar terminal group such as cyano (CN), and isothiocyanato (NCS) can contribute significantly to the dielectric anisotropy. CN has the highest polarity, leading to a high dielectric anisotropy and optical birefringence. However, it exhibits high viscosity, low resistivity, and stability problems under UV illumination. On the contrary, fluoro (F) terminal group exhibits low viscosity, high resistivity and relatively high stability under UV illumination. However, the lower polarity of F results in relatively smaller dielectric anisotropy and optical birefringence.

1.3.2 Eutectic Mixture

A single compound can not fulfill all LC specifications for most display applications. For example, 4- pentyl-4’- cyanobiphenyl (5CB), has melting point at 24°C and clearing point at 35.3°C. It is clear that such small temperature window for nematic phase is not adequate for most industrial applications with operation temperature from -20 to 80°C. It is known that the melting point of a binary mixture of compounds is less than either of its constituent compounds. Figure 1-4 shows the phase diagram of a binary mixture. The mesogenic range for components 1 and 2 are shown in the two boundary vertical axes. The horizontal axis represents the molar
concentration ($X_2$) of component 2. At an appropriate molar concentration, the melting point of the mixture reaches its minimum. Meanwhile, the clearing point of the mixture is linearly proportional to the molar concentration. The optimal mixing ratio of an eutectic mixture is described by the Schroder-Van Laar equation: [15]

$$T_i = \frac{\Delta H_{fi}}{\Delta H_{fi} - R \ln(X_i)}$$

Eq 1-1

Where $T_i$ is the temperature at which the pure component melts in the mixture, $\Delta H_{fi}$ is the heat fusion enthalpy of the component $i$, $T_{fi}$ is the melting point of the pure component $i$, $R$ is the gas constant (1.98 cal/mol-K) and $X_i$ is the mole fraction of the component $i$.

The clearing point ($T_c$) of the eutectic mixture can be estimated from the clearing points ($T_{ci}$) of the individual components ($X_i$) as

$$T_c = \sum_i X_i T_{ci}$$

Eq 1-2
Figure 1-4 Phase diagram of a binary eutectic mixture. At the optimal concentration, the lowest melting point is achieved. The clearing point is linearly dependent on the composition of each component.

1.3.3 Orientational Order Parameter

The rodlike molecules aligned their long axes approximately parallel with each other, and we can define a vector \( \mathbf{n} \) to represent the preferred orientation in the immediate neighborhood of the point. This vector is known as the director. In a homogeneous nematic LC, the director is a constant throughout the medium. In an inhomogeneous nematic liquid crystal, the director \( \mathbf{n} \) can change from point to point and is a function of space \((x,y,z)\). The order parameter \( S \) of a LC is defined as

\[
S = \frac{1}{2} \left(3 \cos^2 \phi - 1\right)
\]

Eq 1-3

Where \( \phi \) is the angle between the long axis of an individual molecule and the director \( \mathbf{n} \), as
shown in Figure 1-5. The angular brackets denote a statistical average. In the nematic phase, the order parameter $S$ has an intermediate value that is strongly temperature dependent. At low temperature, the typical values of order parameter are in the range of 0.4-0.6, and $S=0$ at clearing point. The order parameter $S$ also depends on the structure of the molecules.

Figure 1-5 Coordinate system defining the microscopic order parameter of a nematic liquid crystal molecule. $n$ is the director, the average direction of liquid crystal alignment.

1.3.4 Dielectric Constants

The nematic liquid crystals are uniaxially symmetric to the axes of the director $n$, and the dielectric constants differ in value along the preferred axis ($\varepsilon_{//}$) and perpendicular to this axis ($\varepsilon_{\perp}$). They are mainly determined by the dipole moment, $\mu$, its angle, $\theta$, with respect to the principal molecular axis, and order parameter, $S$, as described by the Maier and Meier mean field theory:[16]
\[
\begin{align*}
\varepsilon_\parallel & = NhF\left\{\langle \alpha_\parallel \rangle + (F\mu^2 / 3kT)[1 - (1 - 3\cos^2 \theta)S]\right\} \\
\varepsilon_\perp & = NhF\left\{\langle \alpha_\perp \rangle + (F\mu^2 / 3kT)[1 + (1 - 3\cos^2 \theta)S / 2]\right\} \\
\Delta \varepsilon & = NhF\left\{\langle \alpha_\parallel \rangle - \langle \alpha_\perp \rangle\right\} - (F\mu^2 / 2kT)(1 - 3\cos^2 \theta)S
\end{align*}
\]

Eq 1-4

Here, \(N\) stands for the molecular packing density, \(h = 3\varepsilon/(2\varepsilon + 1)\) is the cavity field factor, \(\varepsilon = (\varepsilon_\parallel + 2\varepsilon_\perp)/3\) is the averaged dielectric constant, \(F\) is the Onsager reaction field, and \(\langle \alpha_\parallel \rangle\) and \(\langle \alpha_\perp \rangle\) are the principal elements of the molecular polarizability tensor.

The sign and magnitude of the dielectric anisotropy \(\Delta \varepsilon\) are of the utmost importance in the applicability of the LC material. As a result of the anisotropy, the induced dipole moment of the molecules is not parallel to the applied electric field, except when the molecular axis is parallel or perpendicular to the electric field. This creates a net torque that tends to align the molecules along the direction of the electric field for most rodlike molecules. The macroscopic dielectric constant is often proportional to the molecular polarizability. For rodlike molecules, the longitudinal polarizability (parallel to the molecular axis) is often greater than the transverse polarizability (perpendicular to axis). So even in the nonpolar liquid crystal with rodlike molecules, the dielectric anisotropy is positive (\(\Delta \varepsilon > 0\)). In the case of polar LC compounds, there is an additional contribution to the dielectric constant due to the permanent dipole moment. Depending on the angle between the dipole moment and the molecular axis (\(\theta\)), the dipole contribution can cause an increase or a decrease of \(\Delta \varepsilon\), eventually leading to a negative value of \(\Delta \varepsilon\) (e.g., MBBA, \(\Delta \varepsilon \sim -0.7\)). For a polar compounds with its effective dipole at \(\theta < 55^\circ\), \(\Delta \varepsilon\) is positive. On the other hand, \(\Delta \varepsilon\) becomes negative if \(\theta > 55^\circ\). The dielectric anisotropy also depends on the temperature. As temperature increases, \(\Delta \varepsilon\) decreases in proportion to \(S/T\). It
approaches zero abruptly at the clearing point (T_c). Beyond the clearing point, the dielectric constant becomes the mean dielectric constant

\[ \frac{1}{\varepsilon} = \frac{\varepsilon_{\parallel} + 2\varepsilon_{\perp}}{3} \]

Eq 1-5

When a molecule has two dipole groups (with dipole moment \( \mu_1 \) and \( \mu_2 \)) its effective dipole moment can be calculated by the vector addition method, as illustrated in Figure 1-6. In Figure 1-6 \( \mu_1 \) is along the principal molecular axis and \( \mu_2 \) is at an angle \( \phi \) with respect to \( \mu_1 \). The resultant dipole moment \( \mu_r \) can be calculated from the following equation:

\[ \mu_r = (\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \phi)^{1/2} \]

Eq 1-6

Figure 1-6 Vector sum method for calculating effective dipole moment. Here, pink number represents the position of the dipole in a cyclohexanyl ring.
1.3.5 Refractive Index

Nematic LCs often appear as an opaque milky fluid in a glass vial. The scattering of light is due to the random fluctuation of the refractive index of the sample. With no proper boundaries to define the referred orientation, the sample consists of many domains of nematic LC. The discontinuity of the refractive index at the domain boundaries is the main cause of the scattering leading to the milky appearance. Under the proper treatment (e.g., rubbing the alignment layer on the glass substrate), a slab of nematic LC can be obtained with a uniform alignment of the director. The LC exhibits uniaxial optical symmetry with two principal refractive indices \( n_o \) and \( n_e \). The birefringence (or optical anisotropy) is defined as

\[
\Delta n = n_e - n_o
\]

Eq 1-7

If \( n_o < n_e \), the LC is said to be positive birefringent, and it is said to be negative birefringent when \( n_e < n_o \). The macroscopic refractive index is related to the molecular polarizability at optical frequencies. The optical polarizability is due mainly to the presence of delocalized electrons not participating in chemical bonds and of \( \pi \) electrons. This is the reason that LC molecules composed of benzene rings have higher values of \( \Delta n \) than do the respective cyclohexane counterparts.

(i) Wavelength-Dependent Birefringence

Using the single-band model, the wavelength-dependent birefringence of an LC can be expressed as follows [17]:
\[ \Delta n = G \frac{\lambda^2 \lambda'^2}{\lambda^2 - \lambda'^2} \]  

Eq 1-8

In Eq 1-8, the parameter \( G = gN_{ZS} (f_{//}^* - f_{\perp}^*) \), where \( g \) is a proportionality constant, \( N \) is the molecular packaging density, \( Z \) is the effective number of participating electrons (\( \sigma \) and \( \pi \)), \( S \) is the order parameter, \( (f_{//}^* - f_{\perp}^*) \) is the differential oscillator strength, and \( \lambda^* \) is the mean electronic transition wavelength.

From Eq 1-8, as the wavelength increases, \( \Delta n \) decreases gradually and saturates in the near infrared region. In the IR or microwave region where \( \lambda \gg \lambda^* \), the LC birefringence is basically independent of wavelength \( (\Delta n \approx G \lambda^*^2) \) except in the vicinities of some local molecular vibration bands.

(ii) Temperature-Dependent Birefringence

The temperature-dependent birefringence is mainly governed by the order parameter as:

\[ \Delta n = (\Delta n)_0 S \]  

Eq 1-9

\[ S = \left(1 - \frac{T}{T_c}\right)^\beta \]  

Eq 1-10

In Eq 1-9, \( \Delta n_0 \) is the birefringence when the order parameter \( S=1 \) (a perfect crystalline state). Eq 1-10 is Haller’s approximation for the order parameter where \( \beta \) is a material parameter [18]. This approximation holds reasonable well when \( T_c - T > 2 \) degrees. From Eq 1-8, \( \Delta n_0 \) decreases as
wavelength increases. For many of the LC compounds studied, $\beta \sim 0.25$, insensitive to materials [10]. By contrast, $\beta$ is only dependent on the LC structure and is independent of the wavelength.

### 1.3.6 Elastic Constants

The elastic constants of LC determine the restoring torques that arise when the system is perturbed from its equilibrium configuration. These restoring torques are usually very weak compared with those of solids. There are three basic elastic constants involved in the electro-optics of an LC cell depending on the molecular alignment: splay ($K_{11}$), twist ($K_{22}$) and bend ($K_{33}$) elastic constants [19], as illustrated in Figure 1-7.

\[
\begin{align*}
\text{Splay} & : \nabla \cdot n \neq 0 \\
\text{Twist} & : \mathbf{n} \cdot \nabla \times \mathbf{n} \neq 0 \\
\text{Bend} & : \mathbf{n} \times \nabla \times \mathbf{n} \neq 0
\end{align*}
\]

Figure 1-7 Schematic drawing of splay ($K_{11}$), twist ($K_{22}$), and bend ($K_{33}$) in LC (After Ref 14.).

Elastic constants affect the display in two respects: the threshold voltage and the response time. The threshold voltage of a homogeneous cell is expressed as:

\[
V_{th} = \pi \frac{K_{11}}{\varepsilon_0 \Delta \varepsilon}
\]

Eq 1-11
A smaller elastic constant will result in a lower threshold voltage. However, the response time of an LC device is proportional to the visco-elastic coefficient, the ratio of $\gamma_{i}/K_{ii}$. This means that a small elastic constant is unfavorable from the response time viewpoint. Therefore, a proper balance between threshold voltage and response time should be taken into consideration.

Like many other physical properties, the elastic constants are strongly temperature dependent. For most LC compounds, the elastic constants are in the range of 3-25 piconewtons (10^{-12}N). The ratio for the elastic constants varies from 0.7-1.8 for $K_{33}/K_{11}$, and varies from 1.3 to 3.2 for $K_{33}/K_{22}$.

### 1.3.7 Surface Alignment and Rubbing

The alignment of a LC by the surface treatment of a substrate has been one of the least understood aspects of LC behavior. It depends on both the nature of the LC and the surface. The most important factors include dipolar interactions, chemical and hydrogen bonding van der Waals interactions, steric factors, surface topography, and the elasticity of LC molecules. Depending on the deposit molecules and the surface treatment, two commonly used alignment surfaces are homeotropic alignment, and homogeneous alignment. Figure 1-8 illustrates the homeotropic and homogeneous alignment. In the homeotropic alignment LC cell, liquid crystal director is normal to the surface. In the homogeneous alignment LC cell, LC director is uniformly parallel to the surface of the substrate. Rubbing the surface has been a simple and effective way of providing a preferred orientation. Typical rubbing materials include linen cloth and lens paper. In addition, LC director usually tilts up in the direction of rubbing.
There is another kind of LC cell, called twisted nematic (TN) liquid crystal cell. If we seal a pair of homogeneous rubbed glass substrates in orthogonal directions, it forms a 90° TN cell. Having no polarity and no chirality, the rodlike molecules can twist in either direction in the absence of a small pretilt angle. (as shown in Figure 1-9)

Figure 1-9 Distribution of liquid crystal molecular axes in a 90° TN-LC cell. (ref: www.framedigital.com/gv/image/TNSTN.gif)
1.4 **Thesis Overview**

The goal of this dissertation is to develop high performance LC devices for photonics and displays applications. To achieve this goal, this dissertation is organized in two parts: (1) liquid crystal materials and (2) liquid crystal devices. As we discussed before, materials play an essential role in all liquid crystal-based devices, and it is important to develop high performance materials. Therefore, Chapter two, three and four discuss the results of positive dielectric anisotropic, negative dielectric anisotropic, and dual-frequency liquid crystals, respectively. In each chapter, we systematically discuss the physical properties of single compounds and the performance of eutectic mixtures. Moreover, we analyze the pros and cons of these materials and discuss their applications.

In Chapter five, polarization-independent phase modulation of a homeotropic liquid crystal gel is described. By mixing liquid crystal with 20% of monomer, liquid crystal scatters the light strongly in a voltage-on state. Compared to a nano-sized polymer-dispersed liquid crystal (nano-PDLC), our gel possesses a larger phase change and a lower operating voltage because of the higher LC concentration. Most importantly, our gel exhibits submillisecond response time, hysteresis-free, and polarization-independent phase change.

Chapter six summarizes and highlights the dissertation work.
1.5 References


6. For example, see http://www.ueidaq.com/press/appstories/ao-rockwell-optics/


8. For example, http://nobelprize.org/physics/educational/liquid_crystals/history/index.html


CHAPTER TWO

POSITIVE DIELECTRIC ANISOTROPIC LIQUID CRYSTALS

High birefringence ($\Delta n$), low viscosity, small absorption, and good thermal and UV stability polar liquid crystals are essential for both display and optical communication applications. [1] For a cholesteric liquid crystal display (Ch-LCD), the reflection bandwidth ($\Delta \lambda$) is linearly proportional to the LC birefringence and pitch length ($p$) as $\Delta \lambda = p \Delta n$. [2] In the visible spectral region, the pitch length is around 350 nm. Thus, if $\Delta n=0.6$, then $\Delta \lambda \approx 210$ nm which would resemble a normally white Ch-LCD. For a Polymer Dispersed Liquid Crystals (PDLC) [3] or holographic PDLC, [4] high $\Delta n$ enhances the light scattering efficiency and then improves the display contrast ratio. For fiber-optic light switches ($\lambda=1.55$ $\mu$m) using optical phased arrays, [5] the required phase change ($\delta=2\pi d \Delta n/\lambda$) is $2\pi$. If we want to retain the cell gap $d \leq 4$ mm for achieving fast response time, then the required $\Delta n$ should be $\sim 0.4$ at $\lambda=1.55$ $\mu$m which implies to a $\Delta n \sim 0.5$ in the visible region.

To characterize the performance of liquid crystal materials, a figure-of-merit (FoM) which takes birefringence and response time into account has been defined as: [6]

$$FoM = \frac{K_{ii} \Delta n^2}{\gamma_1}$$

Eq 2-1

Where $K_{ii}$ is the elastic constant ($i=1$, 2 or 3), $\Delta n$ is the birefringence, $\gamma_1$ is the rotational viscosity. All of these parameters are temperature dependent. The birefringence of liquid crystals
is mainly determined by the $\pi$-electron conjugation, differential oscillator strength, molecular shape and order parameter.[7] The rotational viscosity is dependent on the activation energy, molecular moment of inertia (including molecular shape and mass) and temperature. Thus, a linearly conjugated liquid crystal should exhibit a large optical anisotropy while retaining a relatively low rotational viscosity. However, such high conjugated liquid crystals usually exhibit high melting temperature. Eutectic mixture is a common approach for lowering the melting point. It is common for a commercial mixture to consist of 5–10 components in order to lower the melting temperature to -40°C. Elevated temperature operation is an efficient way for reducing viscosity. For every 10°C temperature increase, viscosity is decreased by ~2X. To prevent LC material from interacting with moistures, a LC cell is hermetically sealed. An incoherent ultraviolet (UV) light is used to cure the glue lines before injecting LC mixture and then plug the hole after vacuum filling the LC device. Thus, the LC material has to withstand UV exposure to certain extent, say I~ 100 mW/cm² for few minutes.

Commercially available high birefringence LC mixtures, e.g., BL-038 and E44 (from Merck) have $\Delta n$ in the 0.24–0.26 range (at $\lambda=589$ nm and $T=20^\circ$C). However, the employed cyano (CN) polar group tends to form dimmers so that these mixtures exhibit a relatively high viscosity. As a result, their FoM is not too impressive. To reduce viscosity, a linear molecule with different terminal polar group, such as fluoro (F) or isothiocyanato (NCS) can be considered. The fluoro compounds have been used extensively for active matrix liquid crystal displays because of their low viscosity and high resistivity. However, the fluoro group has a strong electro-negativity. It shifts the electronic absorption toward a shorter wavelength, which reduces the LC birefringence. On the contrary, the NCS group extends the molecular conjugation and, therefore, enhances the
LC birefringence. A major technical challenge of the NCS compounds is that these compounds tend to form smectic phase. In addition, high birefringence LC materials usually exhibit a higher melting temperature, increased viscosity, and degraded photo-stability. [8]

In this chapter, we discuss the high birefringence isothiocyanato tolanes ($\Delta n \sim 0.35-0.40$) and super high birefringence isothiocyanato biphenyl-bistolanes ($\Delta n \sim 0.6-0.7$) LCs first, followed by the UV stability of high birefringence LCs, photostability of alignment layers and commercial materials. In each section, we have formulated several eutectic mixtures with a relatively wide nematic range and high FoM.

### 2.1 Experiments

#### 2.1.1 Thermal Analyses

All the thermal analyses were performed using a high sensitivity differential scanning calorimeter (DSC, TA Instrument Model Q-100). Transition temperatures were measured using small samples (~3.0 mg) at 5°C/min scanning rate. The phase transition temperature could be measured accurately to the second decimal place.

#### 2.1.2 Electro-optic Measurements

Because of the high melting point of single compound, we mixed 10% of the high birefringence LC compounds to the host nematic mixture and evaluated their birefringence and visco-elastic coefficient. The birefringence of such guest–host system can be approximated according to:
\((\Delta n)_{gh} = x(\Delta n)_g + (1-x)(\Delta n)_h\)

Eq 2-2

Where g, h, and gh denote guest, host and guest–host samples, respectively, and x is the concentration (in wt%) of the guest compound. By comparing the measured results for the guest–host mixtures to those of the host mixture, the birefringence of the guest compounds was extrapolated. Similarly, the figure-of-merit of each compound studied was extrapolated from the guest–host mixture.

For the electro-optic measurements, we prepared homogeneous (d~8 \(\mu\)m) or homeotropic (d~5 \(\mu\)m) LC cells depend on the sign of dielectric anisotropy of single compound. Figure 2-1 shows the schematic diagrams of the experimental setup. A He-Ne laser (\(\lambda =633\) nm) is used as the light source. The linear polarizer is orientated at 45\(^\circ\) with respect to the LC rubbing direction and the analyzer is crossed. The normalized transmittance of a LC cell between two crossed polarizers can be express as

\[ T = \sin^2\left(\frac{\delta}{2}\right) \]

Eq 2-3

The LC birefringence \((\Delta n)\) at wavelength \(\lambda\) and temperature \(T\) is related to the phase retardation \((\delta)\) from the following equation [9]:

\[ \delta(V, T, \lambda) = \frac{2\pi d(\Delta n(V, T, \lambda))}{\lambda} \]

Eq 2-4

The phase retardation \((\delta)\) of the homogeneous cells can be measured by scanning the voltage-
dependent transmittance (V-T) curve by controlling the LabVIEW system.

The light transmittance is measured by a photodiode detector (New Focus, Model 2031) and recorded digitally by a data acquisition system (DAQ, PCI 6110) using LabVIEW. The DAQ card can realize 5 MS/s, 12-bit, 4 analog input simultaneous samplings. An ac voltage with 1 kHz square waves is used to drive the LC cell whose inner sides are coated with indium-tin-oxide (ITO) electrodes. On top of the ITO, the substrate is covered with a thin polyimide alignment film. The buffing induced pretilt angle is about 3°. The cell is held in a heating stage (Linkam LTS-350) with a temperature stability of 0.2°C.

![Diagram](https://via.placeholder.com/150)

*Figure 2-1 The LabVIEW system for measuring the birefringence and visco-elastic coefficient of the LC mixtures. \( \lambda = 633 \text{nm}. \)

To measure the visco-elastic coefficient, we use the phase-decay-time measurement by driving the LC cell with small excitation voltage. [10] Under small angle approximation, the phase decay time of parallel-aligned LC cell is expressed as [11]:

\[
\text{Phase Decay Time} = \frac{\lambda}{4} \left( \frac{\Delta n}{\Delta d} \right)
\]
\[ \delta(t) = \delta_0 \exp\left(-\frac{2t}{\tau_0}\right) \]

Eq 2-5

Where \( \delta_0 \) represents the total phase change of a LC cell with and without a bias voltage (\( V_b \)); this \( V_b \) is not too far from the threshold voltage (\( V_{th} \)). At \( t=0 \), the bias voltage is removed instantaneously from the LC cell. \( \tau_0 \) in Eq 2-5 is the free relaxation time of the LC layer with thickness \( d \):

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

Eq 2-6

Where \( K_{11} \) is the splay elastic constant of the LC. By plotting \( \ln(\delta_0/\delta) \) versus time, a straight line is expected. The slope of this straight line is equal to \( 2/\tau_0 \). From the slope measurement, \( \tau_0 \) is obtained. By knowing \( d \) (through the interferometric measurement), \( \gamma_1/K_{11} \) of the LC at a given temperature can be calculated. For a negative dielectric anisotropic liquid crystal, the measured elastic coefficient is bend elastic constant (\( K_{33} \)).

### 2.1.3 Refractive Indices

The refractive indices were measured by using a multi-wavelength Abbe refractometer (Atago DR-M4) at \( \lambda = 450, 486, 546, 589, 633, \) and 656 nm. The accuracy of the Abbe refractometer is up to the fourth decimal. For a given wavelength, we measured the refractive indices of LCs from 15°C to 50°C with 5°C interval. The temperature of the Abbe refractometer is controlled by a circulating constant temperature bath (Atago Model 60-C3). The LC molecules are aligned perpendicular to the main and secondary prism surface of the Abbe refractometer by coating
these two surfaces with a surfactant comprising of 0.294 wt% hexadecyletri-methyle-ammonium bromide (HMAB) in methanol solution. Both \( n_e \) and \( n_o \) are obtained through a polarizing eyepiece.

### 2.1.4 Dielectric Constants

The dielectric and elastic constants of LCs were measured by the capacitance method [12] of a single-cell, using a computer controlled Displaytech APT III instrument. Homogeneous alignment needs to be used if we use positive \( \Delta \varepsilon \) LC. On the contrary, homeotropic alignment cell is used if the dielectric anisotropy of LC is negative. Magnetic and electric field-induced capacitance change methods are commonly used. The measured capacitance and dielectric has the relationship:

\[
\begin{align*}
C_0 &= \frac{\varepsilon_0 A}{d} \\
C_{//,\perp} &= \frac{\varepsilon_0 \varepsilon_{//,\perp} A}{d}
\end{align*}
\]

Eq 2-7

Where \( \varepsilon_0 \) is the permittivity of free space, \( A \) is the area covered by the patterned electrodes and \( d \) is the LC thickness.

For a positive \( \Delta \varepsilon \) LC, the measured capacitance represents \( C_{\perp} \) at \( V < V_{th} \), because the electric field is normal to the LC directors. To obtain \( C_{//} \), since \( C \) is a nonlinear function of \( V \) and it changes inversely proportional to voltage at the high voltage limit \( (V >> V_{th}) \), we can plot the capacitance data as a function of \( V_{th}/V \). The intersection of the extrapolated curve and the vertical axis (or \( V_{th}/V=0 \)) represent the \( C_{//} \).
2.1.5 UV Absorption Spectra

The UV absorption spectra of single compounds were measured by using a dual channel Cary 500 UV/VIS/IR spectrophotometer. To avoid detector saturation, the LC samples were dissolved in cyclohexane solutions with $2 \times 10^{-4}$ molar/l concentration. Standard quartz cells with 1 or 10 mm thickness were used in the sample and reference channels of the spectrophotometer.

2.1.6 UV Stability

There are two methods to prepare the sample for UV stability, depending on the melting point of single compound. If the compound has high melting point, we prepared the guest-host mixture by mixing 10% of single compound in ZLI-1800-100. If the compound stays liquid under room temperature, we measured the UV stability by using 100% pure compound. The LC sample was then placed in a glass vial of 1cm diameter. The UV light, Hamamatsu (model L8868-01), was delivered to the sample through a fiber bundle and collimated by a lens. The output light passed through a narrow band interference filter centered at $\lambda \sim 365$ nm. The absorption spectrum of this filter was shown in Figure 2-2. The light intensity at the sample position was measured to be $I \sim 350$ mW/cm$^2$. 
Besides the UV stability of LC materials and alignment layers, we also studied the material stability of TL-216 in SiO₂ cell under blue light. A Helium-Cadmium laser (\(\lambda=442\) nm) was used as the light source to illuminate the LC cell directly. The light intensity at the sample position was controlled to be 20 W/cm².

### 2.1.7 Polarizability and Electrostatic Potential Distribution Calculations

The polarizability and electrostatic potential distribution of the compounds studied was calculated using HyperChem molecular modeling software with two semi-empirical Austin Model 1 (AM1) and Modified Neglect of Diatomic Overlap (MNDO) methods. The polarizability anisotropy was calculated according to:

\[
\Delta \alpha = \alpha_x - (\alpha_y + \alpha_z)/2
\]

Eq 2-8
\( \alpha_x \) is the polarizability along the principal molecular axis, and \( \alpha_y \) and \( \alpha_z \) are the polarizabilities along the short molecular axes. [13]

2.2 High Birefringence LCs

2.2.1 High Birefringence Liquid Crystal Compounds

We selected several isothiocyanato (NCS) tolane compounds for this part of study. The molecular structures and physical properties of these compounds are listed in Table 2-1. Because of the high melting point of these isothiocyanato tolane compounds, phase transition temperatures, extrapolated birefringence, visco-elastic coefficient and FoM were measured by preparing 10% of guest-host mixture with ZLI-1565.
Table 2-1 Phase transition temperatures (°C) and extrapolated birefringence of some rigid core LC compounds. Host LC mixture is ZLI-1565 and guest compound concentration is 10%.

<table>
<thead>
<tr>
<th>No</th>
<th>Compound</th>
<th>T&lt;sub&gt;mp&lt;/sub&gt;</th>
<th>T&lt;sub&gt;c&lt;/sub&gt;</th>
<th>γ&lt;sub&gt;1/K&lt;sub&gt;11&lt;/sub&gt;&lt;/sub&gt;</th>
<th>Δn&lt;sub&gt;T=23°C&lt;/sub&gt;</th>
<th>FoM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ZLI 1565</td>
<td>-20.0</td>
<td>85.0</td>
<td>8.58</td>
<td>0.12</td>
<td>1.75</td>
</tr>
<tr>
<td>2</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;7&lt;/sub&gt;NCS</td>
<td>39.0</td>
<td>41.3</td>
<td>8.81</td>
<td>0.17</td>
<td>2.77</td>
</tr>
<tr>
<td>3</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;7&lt;/sub&gt;NCS</td>
<td>76.5</td>
<td>248.7</td>
<td>10.24</td>
<td>0.24</td>
<td>1.98</td>
</tr>
<tr>
<td>4</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;7&lt;/sub&gt;NCS</td>
<td>149.2</td>
<td>238.8</td>
<td>9.64</td>
<td>0.30</td>
<td>4.65</td>
</tr>
<tr>
<td>5</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;7&lt;/sub&gt;NCS</td>
<td>110.5</td>
<td>192.9</td>
<td>9.97</td>
<td>0.34</td>
<td>5.28</td>
</tr>
<tr>
<td>6</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;7&lt;/sub&gt;NCS</td>
<td>129.0</td>
<td>207.0</td>
<td>9.62</td>
<td>0.35</td>
<td>6.35</td>
</tr>
<tr>
<td>7</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;7&lt;/sub&gt;NCS</td>
<td>137.3</td>
<td>265.5</td>
<td>10.49</td>
<td>0.35</td>
<td>6.68</td>
</tr>
<tr>
<td>8</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;7&lt;/sub&gt;NCS</td>
<td>97.1</td>
<td>97.1</td>
<td>8.24</td>
<td>0.38</td>
<td>11.02</td>
</tr>
<tr>
<td>9</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;7&lt;/sub&gt;O-NCS</td>
<td>125.3</td>
<td>125.3</td>
<td>9.15</td>
<td>0.41</td>
<td>9.28</td>
</tr>
<tr>
<td>10</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;7&lt;/sub&gt;O-NCS</td>
<td>138.6</td>
<td>186.0</td>
<td>11.0</td>
<td>0.45</td>
<td>6.32</td>
</tr>
<tr>
<td>11</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;7&lt;/sub&gt;S-NCS</td>
<td>112.8</td>
<td>126.3</td>
<td>10.79</td>
<td>0.46</td>
<td>6.89</td>
</tr>
</tbody>
</table>
The compounds we selected have different rigid core structures for comparison. Through this screening process, we made a summary as following:

i. The compounds consisting of a cyclohexane ring (one or two rings) have clearing point exceeding 200°C, except compound 2 and 5. However, the cyclohexane ring does not have π-electrons to enhance birefringence, and it usually lies in the plane perpendicular to the principal molecular axis. This non-plane structure results in increasing the moment of inertia and the rotational viscosity.

ii. The compounds 2-5 do not have multiple bonds between rings in the rigid core of the molecules. Thus, the extrapolated birefringence is much smaller than that for compounds 6-11. The triple bond is an effective π-electron acceptor. In addition, its contribution to viscosity is not so significant. Thus, the rigid tolane core is favorable for achieving high FoM LCs.

iii. The NCS polar group extends the electron conjugation while retaining a relatively low viscosity and large dipole moment. The major challenges of the NCS tolanes are twofold: 1) they often exhibit smectic phase, and 2) the synthetic chemistry is difficult.

iv. Among all compounds, the alkyl and alkoxy NCS tolanes exhibit the highest FoM. The oxygen atom in the alkoxy chain of the compound 9 elongates the π-electron conjugation
but also increasing the viscoelastic coefficient. Therefore, the extrapolated FoM of alkoxy NCS tolane is very high but lower than alkyl NCS tolane.

v. Compounds 10 and 11 have a much different structure in the rigid core. The introduction of the naphthalene rings prominently increases the viscosity. The sulfur atom in the sulfolyl chain in compound 11 increases the birefringence more effectively than the oxygen atom in alkoxy chain, although their viscosity are similar.

2.2.2 High Birefringence Eutectic Mixture

By analyzing the structure effect on the birefringence and viscoelastic coefficient, we selected some NCS tolane structures which are listed in Table 2-1 and formulated an eutectic mixture, designated as UCF-HB. The eutectic mixture is a useful method for lowering the melting temperature [14] and the compositions of eutectic mixtures was calculated based on the Schröder-Van Laar equation. The UCF-HB has a nematic range from 10.3°C to 141°C, and the birefringence is $\Delta n=0.45$ at $\lambda=633\text{nm}$ and $T=23^\circ\text{C}$.

We measured the temperature-dependent figure of merit of UCF-HB, and use E-7 as a benchmark for comparison. E7 is a commercial mixture from Merck, and the measured birefringence of E7 is $\Delta n=0.21$ at $\lambda=633\text{nm}$ and $T=23^\circ\text{C}$. Figure 2-3 plots the temperature-dependent figure of merit of UCF-HB and E7. From Eq 2-1, the FoM is defined as $K_{11}\Delta n^2/\gamma_1$ and
its unit is $\mu m^2/s$. We use the following equation to fit the experimental data: [1]

$$K_{14} \Delta n^2 / \gamma_1 \sim \Delta n_0^2 (1 - T/T_c)^{3\beta} \exp(-E/kT)$$

Eq 2-9

where $\Delta n_0$ is the birefringence in completely ordered state ($S=1$), $E$ is activation energy of the liquid crystal, and $k$ is the Boltzmann constant. The value of the $\beta$ parameter is around 0.25 and insensitive to liquid crystal structures. [8] As shown in Figure 2-3, FoM increases as the operating temperature increases and then decreases rapidly as the temperature approaches the clearing point ($T_c$). At 70°C, the UCF-HB mixture has 10X higher FoM than that of E7 at 48°C.

![Figure 2-3](image)

Figure 2-3 Temperature dependent figure-of-merit of UCF-HB (squares) and E7 (circles). Solid lines are fittings to the experimental data of UCF-HB using $E=340$ meV, $\beta=0.25$, and $T_c=141^\circ$C. $\lambda=633$ nm.

### 2.3 Super High Birefringence LCs

#### 2.3.1 Single compounds

The isothiocyanato tolanes we discussed in section 2.2 has the birefringence around 0.38. Some
other high birefringence molecules, such as diphenyl-diacetylene, [6,15] bistolane,[16-17] naphthalene tolanes,[18] and thiophenyl-diacetylene [13, 19, 20] have the birefringence in the 0.4–0.6 range. The diacetylene compounds do not have adequate UV and thermal stabilities [21] so that their application is limited. In this section, we present some isothiocyanato biphenyl bistolane compounds with extrapolated birefringence ~0.7-0.8 at $\lambda =633$ nm and $T=23^\circ$C. We call these compounds as super high birefringence (SHB) materials. To lower melting temperature, we tried different lateral substitutions, such as alkyl and fluoro groups. The molecular structure of super high birefringence compounds are listed in Table 2-2

To investigate the physical properties of these compounds, we measured the phase transition temperature, UV absorption spectra and the electro-optical properties. The phase transition temperature and birefringence of these compounds are shown in Table 2-2. Even with lateral substitutions, the melting temperatures ($T_m$) are still relatively high. All the listed compounds exhibit a pure nematic phase within the whole mesomorphic region. Moreover, the smectic phases which normally appear in the NCS-based biphenyl tolanes or tolanes are completely suppressed. Such an unusual behavior is believed due to the laterally substituted ethyl chain(s) and/or the single fluorine atom. The lateral substitutions increase the molecular separation and break the molecular symmetry so that the smectic phase is difficult to form. Although lateral substitutions lower the melting temperature, they also decrease the birefringence and increase the viscosity.
Table 2-2 Abbreviations, molecular structures, phase transition temperatures (°C) and extrapolated birefringence of the high birefringence compounds. The ∆n values are extrapolated from ~10% guest-host systems in E63 host. T = 23°C and λ = 633nm.

<table>
<thead>
<tr>
<th>Abbreviation Structure</th>
<th>Δn</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>C5-PPTP(3Et)TP-NCS</strong></td>
<td></td>
</tr>
<tr>
<td>a.c.a. SHB-01</td>
<td></td>
</tr>
<tr>
<td><img src="image1" alt="Structure" /></td>
<td>0.7301</td>
</tr>
<tr>
<td>Cr 115.9 (10.08) N 241.3 (0.38) Iso</td>
<td></td>
</tr>
<tr>
<td><strong>C5-PPTP(3Et)TP(3F)-NCS</strong></td>
<td></td>
</tr>
<tr>
<td>a.c.a. SHB-02</td>
<td></td>
</tr>
<tr>
<td><img src="image2" alt="Structure" /></td>
<td>0.6734</td>
</tr>
<tr>
<td>Cr 107.3 (10.82) N 241.4 (0.22) Iso</td>
<td></td>
</tr>
<tr>
<td><strong>C5-PPTP(3Et)TP(3Et)-NCS</strong></td>
<td></td>
</tr>
<tr>
<td>a.c.a. SHB-03</td>
<td></td>
</tr>
<tr>
<td><img src="image3" alt="Structure" /></td>
<td>0.5486</td>
</tr>
<tr>
<td>CrI 44.0 (3.8) CrII 80.3 (8.90) N 225.6 (2.09) Iso</td>
<td></td>
</tr>
<tr>
<td><strong>C5-PPTP(3Et)TP(3Me)-NCS</strong></td>
<td></td>
</tr>
<tr>
<td>a.c.a. SHB-04</td>
<td></td>
</tr>
<tr>
<td><img src="image4" alt="Structure" /></td>
<td>0.6204</td>
</tr>
<tr>
<td>Cr 114.7 (42.9) N 240.9 (0.29) Iso</td>
<td></td>
</tr>
<tr>
<td><strong>C5O-NTP(3Et)P-NCS</strong></td>
<td></td>
</tr>
<tr>
<td>a.c.a. SHB-05</td>
<td></td>
</tr>
<tr>
<td><img src="image5" alt="Structure" /></td>
<td>0.6109</td>
</tr>
<tr>
<td>Cr 120.0 (16.14) N 191.5 (0.08) Iso</td>
<td></td>
</tr>
<tr>
<td><strong>C2-PTP(2Et)TPSP-CN</strong></td>
<td></td>
</tr>
<tr>
<td>a.c.a. SHB-06</td>
<td></td>
</tr>
<tr>
<td><img src="image6" alt="Structure" /></td>
<td>0.7921</td>
</tr>
<tr>
<td>Cr 125.9 N 183.5 Iso</td>
<td></td>
</tr>
</tbody>
</table>
The measured birefringences of the SHB compounds were shown in the right column in Table 2-2. Due to high melting temperature, we used the guest-host method to extrapolate their birefringences at T=23°C. During experiments, 10 wt% of the guest compound was mixed in the host E63 (Merck) mixture. The extrapolated birefringence of compound SHB-06 reaches 0.79. This is by far the highest birefringence that we have ever found. The lateral substitutions affect the LC birefringence significantly. Compound SHB-03 has the lowest birefringence among the compounds we studied due to its two laterally substituted ethyl chains. A shorter lateral alkyl chain would lead to a higher birefringence due to the molecular packing density effect as shown in Table 2-2.

The $\Delta n$ of the compounds SHB-01 and SHB-04 is 0.73 and 0.67, respectively. From the push-pull effect viewpoint, replacing a lateral alkyl chain with a fluorine atom represents a different molecular system. Alkyl group has a larger molecular size than fluorine atom. As a result, its contribution to lowering melting temperature is more significant.

The UV absorption spectra of four SHB compounds are shown in Figure 2-4. Due to the extended $\pi$-electron conjugation, the absorption tail extends to $\lambda$=390nm. All the high birefringence compounds are more suitable for infrared applications, such as laser beam steering systems and telecommunication, where UV stability is not a big concern.
2.3.2 Eutectic Mixture

Using the abovementioned SHB compounds and some short-chain isothiocyanato tolanes, we formulated an eutectic mixture, designated as UCF-SHB. It is a pure nematic with melting point ($T_m$) at $-28^\circ C$ and clearing point ($T_c$) at $186^\circ C$. The birefringence was measured at several discrete wavelengths at $\sim 23^\circ C$. Results are shown in Figure 2-5. Also included in Figure 2-5 for comparison is Merck’s high birefringence LC mixture BL038. The solid lines in Figure 2-5 are fittings using Eq 1-8. From Figure 2-5, the UCF-SHB mixture has a much higher birefringence than BL038. At $\lambda = 532$nm, the birefringence of UCF-SHB reaches $\Delta n=0.65$. The mixture has a lower $\Delta n$ than that of the individual SHB compound we employed because the mixture contains some NCS tolanes which have a lower birefringence ($\Delta n\sim 0.5$).
The viscoelastic coefficient ($\gamma_1/K_{11}$) of UCF-SHB was measured to be 260 ms/\(\mu\)m\(^2\) at \(T \sim 23^\circ\)C. This high viscosity results from the long molecular size, large moment of inertia, and lateral alkyl substitutions. As the temperature increases, $\gamma_1/K_{11}$ decreases rapidly. The viscoelastic coefficient is reduced by \(~8X\) and \(~13X\), respectively, at \(T=40^\circ\)C and \(70^\circ\)C. Within this temperature range, birefringence only decreases slightly because of the high clearing temperature (\(T_c \sim 186^\circ\)C).

### 2.4 UV Stability of Liquid Crystals

#### 2.4.1 Single Compounds: Biphenyl, Terphenyl and Tolanes

Material stability is a primary concern for all devices desired to have a long operational lifetime [22]. In direct-view displays, UV light is often used to seal the LC panel. In projection displays,
the employed arc lamp is extremely bright; although a cold mirror and a hot mirror are used to filter out the unwanted UV and infrared contents of the lamp, residual UV light could still reach the LC panel and cause a gradual degradation of the LC molecules. Once the LC medium is damaged, the pretilt angle is changed so that the consequent electro-optic effects are altered. Therefore, it is critical to identify the ultimate LC material failure mechanism and search for molecular structures that can withstand a longer UV exposure. The most common nematic LC structure for displays consists of an alkyl chain, one or two cyclohexane rings, a phenyl ring, and a polar group. The saturated $\sigma$-bonds in the alkyl chain and cyclohexane ring are very stable because their absorptions occur in the deep UV region ($\lambda \sim 120$ nm) which is far from the commonly used UV line $\lambda \sim 365$ nm. For active matrix LCD applications, fluoro (F) is the preferred polar group as it exhibits a high resistivity, low viscosity and low birefringence [23-24]. However, both cyano (CN) [25] and isothiocyanate (NCS) [26] are the popular choices for use in most passive matrix LCD, because they exhibit a large dipole and contribute to the enhancement of the birefringence. In a CN group, the carbon and nitrogen atoms are linked by a triple bond, whereas in NCS there are two double bonds. The conjugation length calculated from the carbon on the phenyl ring to the terminal CN or NCS group is 2.585Å and 3.887Å, respectively. The calculations were based on the HyperChem V7.0 simulation software with Austin Modal 1 (AM1). Due to its more elongated structure, NCS makes a larger contribution to birefringence than CN. Moreover, an NCS compound exhibits a much lower viscosity than a CN compound because it’s molecules do not form dimers. However, the CN group has a larger dipole moment than NCS. Thus, both CN and NCS have been widely used as terminal groups for display and photonic applications. In this section, we investigate the physical properties of several LC compounds with different substitution and terminal group after UV exposure, and
discuss their stability. The molecular structures are listed in Table 2-3.

Table 2-3 The molecular structures and mesomorphic properties of the LC compounds. Here, Cr, N and I stand for a crystalline, nematic and isotropic phase transition temperatures at °C. $\Delta n$ was extrapolated through guest-host system (GH) with 10% of guest at T=23°C and $\lambda$=633nm. The host mixture is ZLI 1800-100 ($\Delta n$=0.067, $T_c$=61°C)

<table>
<thead>
<tr>
<th>No</th>
<th>Name</th>
<th>Structure</th>
<th>$T_c$ of GH</th>
<th>$\Delta n$ of GH</th>
<th>$\Delta n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PP5CN (5CB)</td>
<td>$\text{C}<em>6\text{H}</em>{11}\text{C}<em>{12}\text{H}</em>{4}\text{CN}$</td>
<td>60.2</td>
<td>0.081</td>
<td>0.207</td>
</tr>
<tr>
<td>2</td>
<td>PP4NCS</td>
<td>$\text{C}<em>4\text{H}</em>{8}\text{C}<em>{12}\text{C}</em>{12}\text{NCS}$</td>
<td>59.0</td>
<td>0.086</td>
<td>0.260</td>
</tr>
<tr>
<td>3</td>
<td>PPP(3,5F)4ONCS</td>
<td>$\text{C}<em>4\text{H}</em>{9}\text{O}\text{C}<em>{12}\text{H}</em>{4}\text{NCS}$</td>
<td>73.8</td>
<td>0.098</td>
<td>0.382</td>
</tr>
<tr>
<td>4</td>
<td>PTP4NCS</td>
<td>$\text{C}<em>6\text{H}</em>{5}\text{C}<em>{12}\text{C}</em>{12}\text{NCS}$</td>
<td>63.9</td>
<td>0.097</td>
<td>0.364</td>
</tr>
<tr>
<td>5</td>
<td>PTP4ONCS</td>
<td>$\text{C}<em>6\text{H}</em>{5}\text{C}<em>{12}\text{C}</em>{12}\text{NCS}$</td>
<td>66.3</td>
<td>0.101</td>
<td>0.402</td>
</tr>
<tr>
<td>6</td>
<td>PTP5O1</td>
<td>$\text{C}<em>6\text{H}</em>{11}\text{O}\text{C}<em>{12}\text{H}</em>{4}\text{CH}_3$</td>
<td>60.9</td>
<td>0.083</td>
<td>0.232</td>
</tr>
</tbody>
</table>

In order to get a UV stable, high birefringence and low viscosity LC mixtures, we used isothiocyanato-biphenyls (NCS-biphenyls) and isothiocyanato-tolanes (NCS-tolanes) as compared to the cyano-biphenyls (CN-biphenyls) used for E44 formulation. Mesomorphic and electro-optic properties of each single compound were studied. Results are listed in Table 2-3. The well-known pentyl cyano biphenyl compound, abbreviated as PP-5CN (5CB),
was used as a benchmark for a single compound and E44 as a reference mixture.

Two groups of compounds were chosen in our experiment. The first group (Comp. #1–#3) contains CN and NCS biphenyls and 3,5-difluoro isothiocyanato-terphenyl, and the second group contains tolanes (Comp. #4–#6). Compounds with different structures and conjugation length are chosen in order to improve the solubility of mixtures. Both electronic absorption spectrum and molecular structure affect the UV stability of a LC compound. A common wavelength used for UV stability study is $\lambda = 365$ nm, which is a strong line of the mercury lamp. Therefore, if a LC absorbs $\lambda = 365$ nm, then its UV stability could be weakened. However, there are exceptions. For example, the diphenyl-diacylene LC [17] has poor UV stability although its absorption tail is still 40 nm shorter from $\lambda = 365$ nm. The degradation mechanism is believed to originate from the UV-induced free radicals of the diacetylene group.[27] Therefore, both electronic absorption and molecular structural effects need to be taken into consideration simultaneously. Figure 2-6 shows the measured UV absorption spectra of the single compounds. These results were obtained by dissolving 1 wt% of each selected compound in the host LC mixture ZLI-1800-100, which is relatively transparent in the UV region. The cell gap was typically adjusted to 5–10 mm. The NCS-biphenyl (Comp. #2) has a longer absorption tail ($\lambda=330$ nm) than that of 5CB (Comp. #1) ($\lambda=310$ nm). This is because NCS has a longer $\pi$-electron conjugation than the cyano group. The NCS-terphenyl (Comp. #3) pushes the absorption tail further to $\lambda \sim 370$ nm. Among the three tolanes studied, the alkyl-alkoxy tolane PTP-5O1 (Comp. #6) has the shortest absorption tail ($\lambda \sim 320$ nm), followed by PTP-4NCS (Comp. #4) ($\lambda=343$ nm), and then PTP-4ONCS (Comp. #5) ($\lambda \sim 350$ nm).
Figure 2-6 The UV absorption spectra of the single compounds shown in Table 2-3. (a) compound #1-#3, and (b) compound #4-#6. The LC host mixture, ZLI-1800-000, is included as reference.

Two independent methods, differential scanning calorimetry (DSC) and electro-optics, were used to determine the material degradation process during UV exposure. It is anticipated that once
degradation occurs, the LC birefringence and clearing temperature would decrease. The birefringence change can be easily detected by the voltage-dependent transmittance of a LC cell situated between two crossed polarizers.[27] Meanwhile, the clearing temperature of each compound was monitored by DSC before and after each UV exposure. Results are shown in Figure 2-7 and Figure 2-8, respectively. Based on the absorption spectra shown in Figure 2-6, we naturally expect that the difluoro-terphenyl NCS compound (Comp. #3) would have the worst UV stability because its absorption tail is the longest among the six compounds investigated. Surprisingly, we found that the nonpolar tolane PTP-5O1 (Comp. #6) has the weakest UV stability. Compound PTP-5O1 (Comp. #6) has a slightly longer conjugation than 5CB (Comp. #1) but has the lowest birefringence among the six compounds considered. From Figure 2-7(b) and Figure 2-8(b), the birefringence and clearing temperature of PTP-5O1 (Comp. #6) drop to 63% and ~90%, respectively, of its original values after 4 hours of UV exposure. The physical mechanisms responsible for this unexpected fast degradation are not completely understood. This nonpolar tolane is least stable although its absorption tail is ~40nm shorter than the UV wavelength (λ=365nm). On the other hand, the absorption tail of the isothiocyanato-terphenyl (Comp. #3) extends to λ=365nm. However, its Δn and clearing point temperature drops only ~4% and ~5%, respectively, after 4 hours of UV exposure, in Figure 2-7(b) and Figure 2-8(b). The structure of PPP(3,5F)-4ONCS (Comp. #3) does not contain any triple bonds. These results suggest that the triple bond linking the phenyl rings is the weakest part of the PTP-5O1 (Comp. #6) molecule and causes the degradation under UV exposure. Moreover, the PPP(3,5F)-4ONCS (Comp. #3) appears to be more stable than 5CB (Comp. #1) which lost almost 15% in Δn and ~8% in Tc at the same experimental conditions, in Figure 2-7(a) and Figure 2-8(a). The cyanobiphenyl (Comp. #1) has a triple bond linking the carbon and nitrogen atoms at the
terminal group.

The PP-4NCS (Comp. #2) compound was chosen as an isothiocyanato analog of 5CB (Comp. #1). The major structural difference between these two compounds is the terminal group. The NCS group has two double bonds instead of one triple bond in CN. The measured birefringence and clearing temperature of PP-4NCS (Comp. #2) do not change within 4 hours of UV exposure. Within this time frame, the UV stability of PP-4NCS (Comp. #2) is as good as the ZLI 1800-100 host mixture, in Figure 2-7(a) and Figure 2-8(a). The triple bond once again is proven as the weakest part in a molecule, which initiates the UV degradation process. The surprising discovery of our experiment is that the highly conjugated isothiocyanato group (NCS) appears to be more stable than the cyano terminal group (CN). The NCS group is known to have a larger birefringence (due to the longer conjugation) and lower viscosity (due to the no evidence of dimmer interaction) than that of CN. [7, 28] Now, we found it also exhibits a better UV stability. From Figure 2-7 and Figure 2-8 the compound stability has the following order: PP-4NCS > PPP(3,5F)-4ONCS > PTP-4NCS > PTP-4ONCS > PP-5CN > PTP-5O1.
Figure 2-7 Measured percentage change of $\Delta n$ versus UV exposure time of the single compounds and host mixture. (a) compounds #1-#3, and (b) compounds #4-#6, $T = 23^\circ C$, $\lambda = 633$nm
Figure 2-8 Measured percentage change of $T_c$ verses UV exposure time of the single compounds and host mixture; (a) compounds #1-#3, and (b) compounds #4-#6, $T=23^\circ$C, $\lambda=633$nm.

To realize the phenomena of the UV stability of the CN and NCS groups, we carefully chose three similar LC structures, PP-5CN (5CB), CP-5CN (5PCH) and CP-6NCS (6CHBT), for studies. Here, P stands for the phenyl ring and C for the cyclohexane ring. The molecular structure, phase transition temperatures, and birefringence of these three compounds are listed in
the Table 2-4. They are all two-ring structures with an alkyl side chain and a polar group, and have been used extensively in the display industry. All three compounds have a nematic phase at room temperature; this feature is particularly attractive because we can measure their physical properties at room temperature without making guest–host mixtures and then using extrapolated results.

Table 2-4 Structure, phase transition temperatures (in °C) and birefringence (Δn at T=23 °C and λ=633nm) of the three LC compounds studied. K, N and I represent crystalline, nematic and isotropic phase. Due to supercooling, 5CB remains nematic phase at room temperature.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Molecular Structure</th>
<th>Phase Transitions</th>
<th>Δn</th>
</tr>
</thead>
<tbody>
<tr>
<td>5CB(PP5CN)</td>
<td>C₇H₄-C≡C-C₆H₄-CN</td>
<td>K 24 N 35.3 I</td>
<td>0.18</td>
</tr>
<tr>
<td>5PCH(CP5CN)</td>
<td>C₇H₄-O-C₆H₄-CN</td>
<td>K 30 N 55 I</td>
<td>0.12</td>
</tr>
<tr>
<td>6CHBT(CP6NCS)</td>
<td>C₆H₄-C≡C-C₆H₄-NCS</td>
<td>K 13N 42.8 I</td>
<td>0.15</td>
</tr>
</tbody>
</table>

i. UV Absorption Spectra

Figure 2-9 shows the UV absorption spectra of these three LC compounds, measured in cyclohexane solution with a 2×10⁻⁴ molar concentration.
The two major $\pi\rightarrow\pi^*$ transitions [7, 29] of 5CB appear at $\lambda_1 \sim 200$ nm and $\lambda_2 \sim 275$ nm and the tail ends at $\sim 310$ nm. Due to the effect of the solvent, the measured $\lambda_2$ is about 5 nm shorter than that measured in a pure thin LC cell. In the NCS compound, 6CHBT, its $\lambda_1$ and $\lambda_2$ bands are each split into two closely overlapped bands. Due to the weaker oscillator strength, its $\Delta n$ is slightly smaller than that of 5CB, as listed in Table 2-4. On the other hand, 5PCH has a shorter molecular conjugation so that its $\lambda_2$ occurs at $\sim 235$ nm, which is shorter than that of 5CB and 6CHBT. As a result, its birefringence is the smallest among the three compared compounds.

### ii. Clearing Temperature

Figure 2-10 shows the $T_c$ after each UV exposure period. In Figure 2-10, we find that the $T_c$ of 5CB and 5PCH starts to decrease after the first hour of illumination and it decreases more as the exposure time increases. After 5 hours of exposure, the $T_c$ of 5CB and 5PCH is decreased by 3.72°C and 3.14°C from the original samples. On the other hand, the $T_c$ of 6CHBT, which has
NCS terminal group instead of CN, only had a minor change of $0.33^\circ$C.

![Figure 2-10 The clearing temperature as a function of exposure time.](image)

### iii. Birefringence

The birefringence of these three compounds, after every illumination period, was measured. The results are shown in Figure 2-11. The birefringence of 5CB and 5PCH is reduced by 11% and 7% after 5 hours of UV illumination. By contrast, the birefringence of 6CHBT keeps the same after 5 hours of UV exposure.
In order to compare the performance of these three compounds, we measured birefringence at different temperatures. The results of birefringence as a function of reduced temperature are shown in Figure 2-12. As shown in this chart, 5CB shows the highest birefringence, exceeding those of 6CHBT and 5PCH. This high birefringence of 5CB comes from two phenyl rings instead of one as in 6CHBT [30]. And the difference of the birefringence between 5CB and 6CHBT is only 0.05 at the reduced temperature $T_r = 0.9$ ($T_r = T/T_c$).
Figure 2-12 Birefringence as a function of reduced temperature ($T/T_c$)

The voltage dependent transmittance before and after the UV exposure of these three compounds were monitored and the results were shown in Figure 2-13. Several phenomena were observed in 5CB and 5PCH as degradation gradually took place: the effective $\Delta n$ was decreased and the light scattering was gradually increased [27].
Figure 2-13 Voltage dependent transmittance of (a) 5CB, (b) 6CHBT and (c) 5PCH before (gray) and after (black) UV exposures.
### iv. Dielectric Constants

Since the dielectric anisotropy of liquid crystal is $\Delta \varepsilon = \varepsilon_// - \varepsilon_\perp$, it is interesting to know the tendency of $\varepsilon_//$ and $\varepsilon_\perp$ during the UV illumination in order to know the stability of liquid crystal materials. Here, $\varepsilon_//$ and $\varepsilon_\perp$ stand for the dielectric constants along and perpendicular to the principal molecular axis, respectively. Figure 2-14 represents the percentage change of $\varepsilon_//$ and $\varepsilon_\perp$ as a function of the exposure time. We find the $\varepsilon_//$ of all three compounds only changes slightly for less than 2% during the UV illumination, but $\varepsilon_\perp$ of 5CB and 5PCH tends to increase, especially 5CB. The $\varepsilon_\perp$ of 5CB is increased by 20% after 3 hours of illumination. On the contrary, the $\varepsilon_\perp$ of 6CHBT does not change even after 5 hours of UV illumination.

![Figure 2-14 Dielectric constant as a function of exposure time. UV intensity \( I=150\text{mW/cm}^2 \)](image)

As we know, the dielectric constants of the anisotropic liquid crystals depend on the dipole moment and its orientation angle with respect to the principal molecular axis. If a compound is
degraded due to UV irradiation, then its pretilt angle in a LC cell could be increased. As a result, the measured effective \(\varepsilon_\perp\) is increased and the threshold behavior is smeared. From Figure 2-14, the molecular structures of 5CB and 5PCH have been altered during UV illumination time, but 6CHBT remains the same. The degradation mechanism could originate from the electron cloud shift which is induced by the UV. Once these deteriorated LC compounds were filled into cells, their pretilt angle is enlarged resulting in increased \(\varepsilon_\perp\).

v. Elastic Constants

Elastic constant [15] is another quantity used to describe the restoring force after removing the external field. We get a closer look of the intermolecular forces by measuring \(K_{11}\) and \(K_{33}\). Figure 2-15 shows the percentage change of \(K_{11}\) and \(K_{33}\) as a function of the UV exposure. The \(K_{11}\) of all three compounds only changes in a minimal range, but the \(K_{33}\) of 5CB and 5PCH decreases to 40% and 50%, respectively. Since \(K_{11}\) and \(K_{33}\) represent the restoring force in the different direction in a liquid crystal cell, we separate the intermolecular force into two directions. One is the interaction between the long side of the molecule, and the other one is between the head and tail of the molecule, as shown in Figure 2-16.
Figure 2-15 Elastic constant as a function of exposure time.

![Graph showing % Change of Elastic Constant vs Exposure time.](chart.png)

The stable $K_{11}$ indicates that the intermolecular force does not change between the long sides of the molecular axis for all three compounds. On the other hand, the large decrease in $K_{33}$ implies that the molecular structures of 5CB and 5PCH are changed after the UV exposure. By combining the $K_{33}$ properties with the UV absorption spectra, we found that the UV did change the structure of the terminal group of 5CB and 5PCH, instead of the phenyl ring.

Figure 2-16 Two different kinds of molecular interaction in a liquid crystal cell.

![Diagram showing two types of molecular interaction.](diagram.png)
Figure 2-17 shows the $\gamma_1/K_{11}$ of all three compounds as a function of the UV exposure. Since $K_{11}$ does not change from the previous measurement, the increment of $\gamma_1/K_{11}$ of 5CB comes from the increased viscosity.

![Graph showing $\gamma_1/K_{11}$ as a function of exposure time.](image)

**Figure 2-17** The measured $\gamma_1/K_{11}$ as a function of exposure time.

### vi. Discussions

From the molecular structure standpoint, 5PCH has the shortest conjugation, followed by 6CHBT, and then 5CB. However, the UV stability has the following order: 6CHBT > 5PCH > 5CB. In Figure 2-13, it shows only the 6CHBT has the same voltage-dependent transmittance before and after UV exposures under the same condition. Therefore, we group 5CB and 5PCH together which have similar UV stability, and compare them with 6CHBT. Since 6CHBT has NCS terminal group while the 5CB and 5PCH have CN terminal group, we believe that the stability of CN and NCS shed some light on the understanding of the failure mechanism. There
are several reasons that may result in the poor UV stability of LC molecules, such as ion containment and oxidation.

Since our UV exposure was conducted in atmosphere, oxidations of 5CB and 5PCH were detected from the infrared absorption change. The absorption band of O-H was appeared after UV illumination of 5CB. No such evidence was found in 6CHBT. Since CN is less stable than NCS, the cyano compounds are easier to be damaged by UV. The oxidation process takes place in an earlier stage which leads to the macroscopic degradation of the observed electro-optic properties.

The purity of LC molecules may be another reason that results in a poor UV stability. The ion concentration determined by the synthesis and purification process. Since we bought the LC samples from the same vender, we assume that the purity of the LC compounds we studied have the same order of ion concentration. We consider the UV stability from the molecular structure point of view rather than the purity.

### 2.4.2 UV Stable Eutectic Mixture

Based on the results of UV stability of these single compounds, we made one eutectic mixture which has higher Figure of Merit (FoM) and UV stability than the commercial mixture, which is adequate for most applications. To formulate a highly UV stable LC mixture, we should avoid using any compound containing CC or CN triple bond. The NCS-based biphenyls and terphenyls are excellent candidates. In order to assure a good UV stability, our mixtures consist of
isothiocyanato biphenyls: 40-Isothiocyanato-4-butyl-biphenyl (PP-4NCS) (28%), 4-Isothiocyanato- 40-(4-propyl-cyclohexyl)-biphenyl (CPP-3NCS) (7%), 4-Isothiocyanato-40- [2-(4-butoxycyclohexyl)-ethyl]-biphenyl (CEPP-3NCS) (14%) and 3,5-Difluoro-4- isothiocyanato-400-butoxy-[1,10,40,100] terphenyl (PPP-(3,5F)4ONCS) (2%), 4-(4-Isothiocyanato-phenyl)-40-propylbicyclohexyl (CCP-3NCS) (7%), and 1-(4-Propyl- cyclohexyl)- 4-isothiocyanato-benzene (CP-3NCS) (35%). We evaluated an exemplary mixture designated as UCF-25. Its birefringence is similar to that of Merck E44 mixture (whose major components are cyano-biphenyls and terphenyls) except for a much lower viscosity. Thus, we use E44 as benchmark for the UV stability comparison. Results are shown in Table 2-5. UCF-25 exhibits a slightly higher threshold voltage and smaller dielectric anisotropy than E44. This is because cyano has a larger dipole moment than the isothiocyanato terminal group. The birefringence of UCF-25 was intentionally designed to be comparable to that of E44. Table 2-5 compares the physical properties of E44 and UCF-25 LC mixtures at 23°C, \( \lambda = 633 \) nm and 1 kHz sampling voltage frequency. The melting and clearing temperatures of UCF-25 were measured to be -6°C and 89°C, respectively. The major advantage of our new mixture is that its viscoelastic coefficient is ~3.5 times lower than that of E44. The overall FoM of UCF-25 is ~4 times higher than that of E44. The second important advantage of the new UCF mixture is its excellent UV stability. From Figure 2-18, UCF-25 maintains the same mesomorphic properties after 4 hours of UV exposure at the intensity of 200mW/cm². The measured clearing temperature change is <0.3%. For E44 under the same conditions, the clearing temperature is decreased by more than 1.5%. The UV stability of UCF-25 is nearly as good as that of ZLI-1800-100; a low birefringence UV transparent host mixture.
Table 2-5 Physical properties of E44 and UCF-25

<table>
<thead>
<tr>
<th></th>
<th>E44</th>
<th>UCF-25</th>
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<tr>
<td>$V_{th}$</td>
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<td>1.70</td>
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<td>$\varepsilon_{//}$</td>
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<td>13.5</td>
</tr>
<tr>
<td>$\varepsilon_{\perp}$</td>
<td>4.1</td>
<td>3.0</td>
</tr>
<tr>
<td>$\Delta\varepsilon$</td>
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<td>10.5</td>
</tr>
<tr>
<td>$K_{11}$ (pN)</td>
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<td>15.6</td>
</tr>
<tr>
<td>$K_{33}$ (pN)</td>
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<td>54.9</td>
</tr>
<tr>
<td>$K_{33}/K_{11}$</td>
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<td>3.52</td>
</tr>
<tr>
<td>$\Delta n$</td>
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<td>0.254</td>
</tr>
<tr>
<td>$\gamma_{11}/K_{11}$</td>
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<td>6.4</td>
</tr>
<tr>
<td>FoM</td>
<td>2.7</td>
<td>10.1</td>
</tr>
</tbody>
</table>

Figure 2-18 Percentage change of clearing temperature of E44 and UCF-25 at different exposure time.
2.5 **UV Stability of Alignment Layers**

In addition to the liquid crystal stability, alignment layer also plays a crucial role in affecting the lifetime of LCD devices. Once the alignment layer deteriorated, the pretilt angle is changed and the consequent electro-optic effects are altered. To investigate alignment layers stability, we studied the buffed polyimide (PI) and sputtered silicon-dioxide (SiO₂) alignment layers under nitrogen environment.

Three kinds of homogeneous LC cells were studied: two with commercial polyimide (PI) layers (PI-A and PI-B) and one with a SiO₂ alignment layer. These PI cells were purchased from different vendors in order to compare the PI performances. Figure 2-19 shows the measured UV absorption spectra of these cells. Here, solid, dashed, and dotted lines represent PI-A, PI-B, and SiO₂ cells, respectively. The transmittance of the UV filter was included as reference. The transmittance of each cell at $\lambda \sim 365$ nm has the following order: PI-A > PI-B > SiO₂. In principle, SiO₂ alignment layers are highly transparent from $\lambda > 200$ nm. The absorption of the cells is mainly from the indium-tin-oxide (ITO) electrode. Different cells may have slightly different ITO thickness. As a result, their transmission in the UV region is somewhat different.
In order to compare the UV stability of LC alignment layers, the test cells were covered with a black paper and divided into two areas. The UV light passes through the center of the cell only. These empty cells were illuminated under nitrogen environment. At each stage, we inspected the cell by filling the cell with 5CB (4-n-pentyl-4’-cyanobiphenyl) LC. We observed the cells on a light table between crossed polarizers after 5, 10, and 15 hours of UV illumination. Results of PI-B and SiO₂ cells are shown in Figure 2-20(a) and (b), respectively. The PI-A has similar results as PI-B.
Figure 2-20 (a) PI-B and (b) SiO$_2$ alignment cells after 5 (left), 10 (middle), and 15 (right) hours of UV exposures.

In Figure 2-20(a) and (b), the left, middle, and right photos of each figure represent the cells after 5, 10, and 15 hours of UV exposure, respectively. The first and second rows of each figure show the photos when the cell rubbing direction is at 0° and 45° with respect to the polarizer, respectively. From Figure 2-20 (a), both PI alignment layers are damaged within 10 hours and the degradation accumulates as the UV dosage increases. Because of the alignment layer degradation, the pretilt angle increases so that light leaks through the crossed polarizers. However, the SiO$_2$ alignment layer (Figure 2-20 (b)) could withstand the UV light for more than 15 hours.

In order to see the degradation of PI alignment layer clearly, we also inspected the PI-B cell under a polarizing optical microscope. The cell rubbing direction was set parallel to the polarizer, and photos were taken after 15 hours of UV exposure. Results are shown in Figure 2-21 (a). Many lines whose axes are perpendicular to the rubbing direction appear within the illumination area. These crossed lines imply that the rubbing direction has been disturbed. As a result, the LC
alignment is degraded. Figure 2-21 (b) shows the photo of the SiO₂ cell under microscope (magnification: 5X) after 15 hours of UV exposure. The SiO₂ alignment layers maintain excellent uniformity across the whole cell.

![Figure 2-21 (a) PI-B and (b) SiO2 cells after 15 hours of UV exposure.](image)

Figure 2-21 (a) PI-B and (b) SiO2 cells after 15 hours of UV exposure. Photos were taken under crossed polarizing microscope. A 5X magnification objective lens was used. The dark circle in Figure 2-21(b) shows the edge of the illumination area. Above this line is the illumination area. Arrow shows the rubbing direction.

### 2.6 Photostability of Commercial Liquid Crystal Mixtures

In this section, we investigated the photostability of two commercial liquid crystal mixtures from Merck: TL-216 ($\Delta n=0.20$) and MLC-9200-000 ($\Delta n=0.08$). A high birefringence LC mixture, such as TL-216, enables a thinner cell gap to be used. The advantages are twofold: 1) faster response time, and 2) weaker fringing field effect. For instance, the Philips color-sequential
LCOS projector [31] uses a ~1 µm cell gap in order to achieve fast response time and minimize the fringing field effect. On the other hand, a low birefringence LC mixture, such as MLC-9200-000, is commonly used for three-panel LCOS projectors. As we discussed in section 2.4, two mechanisms are responsible for the observed UV degradation: structural effect and absorption effect [27]. The structural effect is particularly apparent for the carbon-carbon double- and triple-bond linking groups. The LC mixtures we studied: TL-216 and MLC-9200-000 all consist of cyclohexanyl, phenyl and biphenyl rings. These rings are quite stable. Thus, the absorption effect is the dominant degradation mechanism. We measured the UV absorption spectra of TL-216 and MLC-9200-000 in a cyclohexane solvent. Results are plotted in Figure 2-22. Solid and dashed lines represent the UV absorption spectra of TL-216 and MLC-9200-000, respectively. The weight percentage of LC mixture is $4\times10^{-3}$ % and the cuvette cell gap is 1 cm. The edge of transmittance of the UV filter (gray line) is also included as a reference.

The two major $\pi\rightarrow\pi^*$ transitions [7, 29] of TL-216 appeared at $\lambda_1 \sim 213$ nm and $\lambda_2 \sim 255$ nm and the tail ends at ~318 nm. The $\pi\rightarrow\pi^*$ transitions of MLC-9200-000 appear at $\lambda_1 \sim 200$ nm and $\lambda_2 \sim 255$ nm and the tail ends at ~300 nm. The similar $\lambda_2$ absorption peak implies that these two mixtures contain a common compound (maybe fluorinated biphenyl), but at different percentages.
Figure 2-22 UV absorption spectra of TL-216 (solid line), MLC-9200-000 (dashed line), and UV filter (gray lines). LC weight % = $4 \times 10^{-3}$ % in cyclohexane and cuvette gap $d = 1$ cm.

If the LC sample was exposed to the air [32], then oxidations would occur during UV exposure. In order to avoid the oxidation and humidity effects, the LC mixture was vacuum-filled into the cell. The UV illumination took place in a nitrogen chamber. We inspected the cell after each UV illumination and measured its voltage-dependent transmittance, birefringence [9] and viscoelastic coefficient [10]. All the measurements were performed using a He-Ne laser ($\lambda = 633$ nm) at $T = 23^\circ$C.

2.6.1 UV Stability of MLC-9200-000

Figure 2-23(a)-(c) represent the V-T curves of MLC-9200-000 in the SiO$_2$, PI-A and PI-B cells, respectively. From Figure 2-23(a), after 144 hours of UV exposure, the V-T curve of MLC-9200-000 in the SiO$_2$ cell remains nearly the same as that of fresh sample. This is not surprising because MLC-9200-000 is a low birefringence LC mixture; its absorption tail is shorter than
\( \lambda = 365 \text{ nm} \). On the other hand, MLC-9200-000 in PI cell has a relatively short lifetime. The V-T curves of MLC-9200-000 in both PI cells start to change after 60 hours. The PI-B cell suffers an even more serious degradation. Once degradation occurs, the effective \( \Delta n \) is decreased and threshold behavior smeared because of the increased pretilt angle. [27]
Figure 2-23 Voltage-dependent transmittance of a (a) SiO$_2$ (b) PI-A and (c) PI-B alignment cell with MLC-9200-000 before (solid line) and after (dashed line) UV exposure. UV intensity =350mW/cm$^2$.

Comparing the lifetime of MLC-9200-000 in SiO$_2$ and PI cells, we found that the PI alignment
layer is less UV-resistant than MLC-9200-000. Thus, it is PI layers rather than LC that limits the device lifetime. Of course, some LCs may be less stable than PI alignment layers. We have to consider the lifetime of both alignment layers and LC mixtures when evaluating the UV stability of LC devices. Whichever has the least stability determines the overall device lifetime.

From the V-T curve, we calculated the LC birefringence after each UV illumination. Results are shown in Figure 2-24(a). Here, the open squares, circles, and triangles represent the birefringence of MLC-9200-000 in SiO₂, PI-A and PI-B cells, respectively. The birefringence of MLC-9200-000 in the SiO₂ cell remains the same after 144 hours of UV exposure. On the other hand, the birefringence of MLC-9200-000 in PI-B after 60 hours of UV exposure is decreased to 0.07. Compared to the fresh sample, this birefringence is reduced by 12.5%. PI-A cell has a similar result to PI-B cell. We also investigated how UV-induced degradation affects the viscoelastic coefficient ($\gamma_1/K_{11}$) of the LC mixture. Results are plotted in Figure 2-24(b). Here, the open squares, circles, and triangles represent the $\gamma_1/K_{11}$ of MLC-9200-000 in SiO₂, PI-A, and PI-B cells, respectively. $\gamma_1/K_{11}$ of MLC-9200-000 in the SiO₂ cell remains basically unchanged after 144 hours of UV illumination. On the contrary, in both PI cells, it begins to increase after 20 hours of UV illumination. The noticeable increase in the $\gamma_1/K_{11}$ implies that the LC mixture has been seriously damaged by the UV light.
Figure 2-24 UV exposure time dependent (a) birefringence and (b) viscoelastic coefficient of MLC-9200-000 and TL-216 in SiO$_2$ and PI cells. Open and filled symbols denote MLC-9200-000 and TL-216, respectively. Light source: $\lambda$=365nm, $I$=350mW/cm$^2$. 
2.6.2 UV Stability of TL-216

Figure 2-25 (a)-(c) show the V-T curves of TL-216 in the SiO$_2$, PI-A, and PI-B cells, respectively. In all of the PI and SiO$_2$ cells, the V-T curves of illuminated samples were different from the fresh sample. Three common phenomena are observed as degradation gradually takes place: 1) The effective $\Delta n$ is decreased, 2) The threshold voltage is smeared and decreased, and 3) The light scattering is gradually intensified. TL-216 has a longer lifetime in the SiO$_2$ cell than in the PI cells. The lifetime of TL-216 in the SiO$_2$ cell and PI cell are no longer than 96 and 18 hours, respectively. The shorter lifetime of TL-216 in the PI cell comes from the unstable PI alignment layer.
Figure 2-25 The voltage-dependent transmittance of a (a) SiO₂ (b) PI-A and (c) PI-B alignment cell with TL-216 before (solid line) and after (dashed line) UV exposure. UV intensity = 350 mW/cm².
The birefringence of TL-216 in the PI and SiO\textsubscript{2} cells were measured at $\lambda = 633$ nm and results are depicted in Figure 2-24(a). The filled squares, circles, and triangles represent the birefringence of TL-216 in SiO\textsubscript{2}, PI-A, and PI-B cells, respectively. The birefringence of TL-216 in SiO\textsubscript{2} cell after 96 hours of UV illumination is decreased by 0.01, as compared to the fresh sample. The LC degradation was more serious in PI cell than in SiO\textsubscript{2} cell. TL-216 in PI-A and PI-B has similar results. The birefringence after 18 hours of UV exposure drops by 0.05, which accounts for 75\% of the fresh sample.

The results of the viscoelastic coefficient ($\gamma_1/K_{11}$) of TL-216 in PI and SiO\textsubscript{2} cells after each UV exposure are also shown in Figure 2-24(b). The filled squares, circles, and triangles represent the viscoelastic coefficient of TL-216 in SiO\textsubscript{2}, PI-A, and PI-B cells, respectively. The $\gamma_1/K_{11}$ of TL-216 in the SiO\textsubscript{2} cell starts to increase after 96 hours of UV illumination. Because of the degradation of the PI alignment layer, the $\gamma_1/K_{11}$ of TL-216 in both PI cells increases dramatically after 18 hours of UV illumination.

### 2.6.3 Stability of TL-216 Under Blue Light

One can argue that UV components of an arc lamp can be totally truncated by a proper filter. For a full-color LCD projector, red ($\lambda=650$ nm), green (540 nm), and blue (440 nm) are the three primary colors. The low energy red and green photons are much less harmful than the high energy blue photons. Thus, the ultimate photostability of a LC cell is determined by the blue light. We vacuum-filled TL-216 in SiO\textsubscript{2} cell, and illuminated the test cell by using a Helium-Cadmium laser ($\lambda=442$ nm) with $I=20$ W/cm$^2$. After every 24 hours of illumination, we monitored the LC birefringence. Results are shown in Figure 2-26. From Figure 2-26, no sign of
degradation of TL-216 in the SiO₂ cell is observed up to 2880 WHr/cm² of laser irradiation.

![Figure 2-26 The measured birefringence of TL-216 in SiO₂ cell. Light source: λ=442 nm and I=20 W/cm².]

2.7 References


CHAPTER THREE
NEGATIVE DIELECTRIC ANISOTROPIC LIQUID CRYSTALS

In order to make good use of homeotropic LC cell to achieve high contrast ratio, negative dielectric anisotropic (\(\Delta\varepsilon\)) LCs are required to realize the useful electro-optical properties. The dielectric constants of liquid crystal can be described by the Maier and Meier mean field theory as shown in Eq 1-4.[1]

For active matrix displays, high resistivity is another crucial requirement in order to obtain high voltage-holding-ratio and avoid image flickering. To achieve high resistivity, fluorinated compounds are commonly used [2, 3]. To obtain high birefringence, large negative \(\Delta\varepsilon\), and high resistivity, laterally (2,3) difluorinated tolane.[4] or terphenyl.[5-6] LCs are the natural choices. The effective dipole moment of the (2,3) laterally difluorinated compounds is nearly perpendicular to the principal molecular axis. Thus, from mean field theory [1], these compounds should have a large but negative dielectric anisotropy. However, the laterally difluoro-tolane and -terphenyl mixtures are very difficult to align in a homeotropic cell. A poor alignment leads to a low contrast ratio. Without good alignment, the advantages of homeotropic cells are in vain.

Several methods for achieving homeotropic alignment have been developed [7-8]. Among them, mechanical rubbing and sputtered SiO\textsubscript{2} [9-11] are most commonly used because they can produce a stable pretilt angle. However, through these methods, aligning the laterally difluoro-tolane mixtures remains a difficult task.
In order to improve the performance of a negative dielectric anisotropic liquid crystal in a VA cell, we have developed a new method for aligning high birefringence compounds and mixtures using buffed PI substrates. Especially, the VA cell exhibits an excellent contrast ratio, sharp threshold, and good thermal stability throughout its nematic range. In section 3.1, we select several LC compounds with different birefringence, and study their physical properties and alignment performances. We find that by doping ~ 5-15 wt % of a positive or non-polar compound to negative compounds/mixtures greatly improves the LC alignment quality in polyimide (PI) cells. In sections 3.2 and 3.3, we demonstrate this technology by using laterally difluoro terphenyls and tolanes mixtures, respectively, and investigate the temperature stability. In section 3.4, we study the physical mechanism by using the molecular modeling and developing an experiment by coating 5CB onto the glass substrate. The 5CB here serves as a monolayer for inducing the homeotropic alignment.

During experiments, we chose two types of homeotropic cells: buffed polyimide (PI) layers and long-chain (C_{18}H_{37}OH) alcohol evaporated inorganic SiO_2 layers for aligning the (2,3) laterally difluorinated mixtures. For simplicity, we abbreviate the long-chain alcohol evaporated SiO_2 cell as LA-SiO_2 cell. To prepare the PI cells, we spin-coated a commercial polyimide SE-1211 (from Nissan Chemicals) on the ITO (Indium-tin-oxide)-glass substrates, baked the substrates at 80 °C for 5 minutes and then 180 °C for 1 hour. We then gently rubbed the ITO-glass with cloth in anti-parallel directions. The rubbing induced pretilt angle is about 87°.

To prepare the LA-SiO_2 cells, we sputtered a thin SiO_2 layer onto the ITO-glass substrates and then evaporated C_{18}H_{37}OH alcohol onto the SiO_2 layer to form a monolayer. The process is the
same as that reported in Ref. 9. The pretilt angle is about 88.5°.

3.1 Single LC Compounds

In this section, we discussed the physical properties of several compounds with different birefringence and investigated their alignment performance in PI-VA cell. The molecular structure, clearing temperature, extrapolated birefringence and dielectric anisotropic of these compounds are shown in Table 3-1. We measured the phase transition temperature of these LC compounds by using a differential scanning calorimeter (DSC; TA-100). Since the compounds we studied are solid at room temperature, we mixed 10 wt% of the compounds into an LC host ZLI-4330 and extrapolated their birefringence at T~23°C. To monitor the LC birefringence, we filled a 5-µm homeotropic cell (pretilt angle ~87°) and measured its phase retardation (δ) as described in section 2.1.2.[12].
Table 3-1 Molecular structure, clearing temperature (T_c), extrapolated birefringence (Δn), and dielectric anisotropy (Δε) of studied compounds. Δn and Δε are extrapolated from ~10% guest-host systems in ZLI-4330 host. T=23°C and λ=633nm.

<table>
<thead>
<tr>
<th>No.</th>
<th>Molecular structure</th>
<th>T_c (°C)</th>
<th>Δn</th>
<th>Δε</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>C_{6}H_{11} - C_{6}H_{11} - CO - F - F - OC_{3}H_{5}</td>
<td>153.2</td>
<td>0.119</td>
<td>-6.60</td>
</tr>
<tr>
<td>N2</td>
<td>C_{3}H_{7} - C_{8}H_{17} - F - F - OC_{3}H_{5}</td>
<td>4.3*</td>
<td>0.150</td>
<td>-5.16</td>
</tr>
<tr>
<td>N3</td>
<td>C_{6}H_{11} - C_{6}H_{11} - CO - F - F - OMe</td>
<td>164.4</td>
<td>0.156</td>
<td>-5.16</td>
</tr>
<tr>
<td>N4</td>
<td>C_{3}H_{7} - C_{6}H_{17} - F - F - C_{3}H_{7}</td>
<td>98.5</td>
<td>0.227</td>
<td>-2.16</td>
</tr>
<tr>
<td>N5</td>
<td>C_{6}H_{11} - C_{6}H_{17} - F - F - OC_{3}H_{5}</td>
<td>173.8</td>
<td>0.262</td>
<td>-6.16</td>
</tr>
<tr>
<td>N6</td>
<td>C_{5}H_{11} - C_{6}H_{17} - C_{3}H_{7} - F - F - C_{3}H_{7}</td>
<td>149.6</td>
<td>0.242</td>
<td>-2.18</td>
</tr>
<tr>
<td>N7</td>
<td>C_{5}H_{11} - C_{6}H_{17} - F - F - OC_{3}H_{5}</td>
<td>222.1</td>
<td>0.374</td>
<td>-5.18</td>
</tr>
</tbody>
</table>

* This comes from super cooling effect.

3.1.1 Physical Properties

Among the compounds we studied, compound N5 exhibits a smectic phase, and compound N2 exhibits a monotropic phase. From compound N1 to compound N6, the number of phenyl rings increases from one to three. Besides three phenyl rings, compound N7 has an additional carbon-
carbon triple bond between two phenyl rings. Because of the increase of unsaturated elements, birefringence increases from 0.119 for compound N1 to 0.374 for compound N7. Concerning the terminal substituents, compounds N4 and N5 have an alkyl chain rather than an alkoxy group. The oxygen not only increases the conjugation length, but also increases the dipole moment perpendicular to the long axis of the molecule. This results in a large dielectric anisotropy (Δε ~ -5.1) of difluorinated alkoxy compounds, such as N2, N3 and N5.

3.1.2 Alignment of Single Compounds in VA Cell

To investigate the alignment performance of a single compound in rubbed VA cells, we injected each of the compounds we listed into LC cells. Because the compounds have their nematic phases at different ranges, we measured the voltage dependent transmittance (V-T) curve between crossed polarizers at the same reduced temperature (T_r ~0.96) except N2 and N7. The reduced temperature is defined as T/T_c. Compound N2 exhibits a monotropic phase and its nematic range is quite narrow. Thus, we measured its V-T curve at T =3°C. On the other hand, the clearing temperature of N7 is 222.1°C, which is too high for our measurement. Therefore, we measured its V-T curve at T = 130°C, which corresponds to T_r ~ 0.81. All the measurements were performed at λ= 633 nm. Results are plotted in Figure 3-1 to Figure 3-5.

Figure 3-1 plots the measured V-T curves of compounds N1, N2, and N3, while Figure 3-2, Figure 3-3, Figure 3-4, Figure 3-5, are for compounds N4, N5, N6 and N7, respectively. From these curves, we found that compounds N1, N2 and N3 have a fairly good voltage-on and -off states, but compounds N4, N5, N6, and N7 have a very poor on state, which means the molecular alignment of terphenyls (N4, N5, N6,) and biphenyl-tolane (N7) in VA cells is imperfect.
Figure 3-1 Voltage dependent transmittance of N1, N2 and N3 homeotropic cells between crossed polarizers. N1 and N3 were measured at Tr=0.96 and N2 at T=3°C. λ=633nm.

Figure 3-2 Voltage dependent transmittance of homeotropic cells between crossed polarizers. The dashed, solid, and dotted lines represent compound N4, mixture A and mixture B, respectively. Tr=0.96, λ=633nm.
Figure 3-3 Voltage dependent transmittance of homeotropic cells between crossed polarizers. The dashed, solid, and dotted lines represent compound N5, mixture C and mixture D, respectively. $T_r = 0.96$, $\lambda = 633$nm.

Figure 3-4 Voltage dependent transmittance of homeotropic cells between crossed polarizers. The dashed, solid, and dotted lines represent compound N6, mixture E and mixture F, respectively. $T_r = 0.96$, $\lambda = 633$nm.
Figure 3-5 Voltage dependent transmittance of homeotropic cells between crossed polarizers. The dashed and solid lines represent compound N7 and mixture G, respectively. $T = 130^\circ C$, $\lambda = 633$nm.

Table 3-2 Compositions of mixtures A to G.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Host Compound</th>
<th>Dopant</th>
<th>Wt% of dopant</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>N4</td>
<td>MLC-9200-000</td>
<td>10</td>
</tr>
<tr>
<td>B</td>
<td>N4</td>
<td>ZLI-3086</td>
<td>5</td>
</tr>
<tr>
<td>C</td>
<td>N5</td>
<td>MLC-9200-000</td>
<td>15</td>
</tr>
<tr>
<td>D</td>
<td>N5</td>
<td>ZLI-3086</td>
<td>10</td>
</tr>
<tr>
<td>E</td>
<td>N6</td>
<td>MLC-9200-000</td>
<td>5</td>
</tr>
<tr>
<td>F</td>
<td>N7</td>
<td>ZLI-3086</td>
<td>5</td>
</tr>
<tr>
<td>G</td>
<td>N7</td>
<td>BCH-32*</td>
<td>45</td>
</tr>
</tbody>
</table>

* BCH-32 is a biphenyl-cyclohexane compound with terminal substitutions. $R_1 = C_3H_7$ and $R_2 = C_2H_5$

To improve the alignment capabilities of these terphenyl compounds, we doped some positive or
some neutral LC mixtures into compounds N4, N5, and N6. Results are shown in Figure 3-2, Figure 3-3, and Figure 3-4, respectively. The positive and neutral LC mixtures we selected are MLC-9200-000 (Δε=4) and ZLI-3086 (Δε~0), respectively. Both are Merck's mixtures. The required weight percentage of dopants to have the best performance depends on the host compounds. Table 3-2 shows the required weight percentages of MLC-9200-000 and ZLI-3086 for compounds N4, N5 N6 and N7. By doping these positive Δε or neutral LC mixtures, a V-T curve with a very sharp threshold voltage and improved on-state transmittance is obtained. Besides LC mixtures, we also doped some positive or neutral single compounds into the host compounds, and observed the same results. The required percentage of dopant is ~10 wt%.

We also investigated the alignment behavior of biphenyl-tolane (compound N7). Compound N7 has a wide nematic range and its clearing point is Tc=220°C, thus, we performed the V-T curve measurements at T =130°C. Results are shown in Figure 3-5. Compound N7 has the poorest alignment capability of all the compounds we studied. The light leaks severely at the dark state. When we observed this filled cell under the light table between two crossed polarizers, we saw a colorful LC cell instead of a good dark state. This indicates that this highly conjugated molecule aligns randomly in the LC cell. It requires more dopant to overcome the alignment problem. After having been doped with 45% of BCH-32, it showed a very good dark state. Results are shown in Figure 3-5. BCH-32 is a biphenyl-cyclohexane with two alkyl terminal groups, R1=C3H7 and R2=C2H5. Its Δε ~0.5 is slightly positive. This shows that the nonpolar dopant helps align compound N7 well in the VA cell and leads to having more useful electro-optical properties.
3.2 Laterally Difluoro-terphenyls and Temperature Stability

In this section, we discuss the thermal stability of dopant-enhanced alignment capability by formulating a binary eutectic mixture (called mixture A) with two N4-type terphenyl homologues. Two homologues with $R_1 = \text{C}_2\text{H}_5$ and $R_2 = \text{C}_4\text{H}_9$, and $R_1 = \text{C}_3\text{H}_7$ and $R_2 = \text{C}_5\text{H}_{11}$ were synthesized. This eutectic mixture has low melting point and super cooling effect. The molecular structures, compositions, and phase transition temperature are shown in Table 3-3.

Table 3-3 Molecular structures, compositions and phase transition of mixture A.

<table>
<thead>
<tr>
<th>Structure/Compositions</th>
<th>Phase Transition Temperature ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixture A</td>
<td></td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_5$</td>
<td>$\text{F}$ $\text{F}$ $\text{C}_4\text{H}_9$ 35% Cr 23.6 N 112.3 Iso*</td>
</tr>
<tr>
<td>$\text{C}_3\text{H}_7$</td>
<td>$\text{F}$ $\text{F}$ $\text{C}<em>5\text{H}</em>{11}$ 65%</td>
</tr>
</tbody>
</table>

*Supercooling effect extends the melting point down to 6.8°C and the mixture stays liquid at room temperature.

First we measured the voltage dependent transmittance (V-T) [13] curves of mixture A. Figure 3-6 plots the measured results at $\lambda = 633$ nm. The polarizers are crossed and the on-state LC directors are at 45° with respect to the polarizer’s optical axis. From Figure 3-6, mixture A has a fairly good dark state and sharp threshold at room temperature (T~23°C). However, as the temperature increases to 50°C, the dark state light leakage becomes noticeable and the on-state transmittance is lower than that at room temperature. Moreover, the threshold is smeared. These phenomena imply that the pretilt angle has increased significantly as the temperature increases.[8]
In order to enhance the homeotropic alignment quality, three dopants, MLC-9200-000, ZLI-3086 and MLC-6608, were selected. MLC-9200-000, ZLI-3086 and MLC-6608 are Merck’s mixtures, and the dielectric anisotropy ($\Delta\varepsilon$) are +4, ~0, and -4.2, respectively. We doped appropriate weight percentage of these mixtures into the host mixture A, and Table 3-4 shows the abbreviations, phase transition temperatures and $\Delta\varepsilon$ of these mixtures.

The selected percentage of dopant depends on the properties of the host negative liquid crystal material and on the properties of the dopant. For example, the terphenyl mixtures are more difficult to align than the tolane mixtures, thus the required weight percentage of dopant is higher. Moreover, the required weight percentage of positive, negative or neutral material provided to improve the alignment of pure 2,3 difluoro-terphenyl is quite different, and the
percentage is not the same as the weight percentage of eutectic mixture.

Table 3-4: Physical properties of mixtures A, B, C, and D. $T_m$: melting temperature, $T_c$: clearing temperature, and $\Delta \varepsilon$: dielectric anisotropy at $f=1$ kHz.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Dopant</th>
<th>Wt % of Mixture A</th>
<th>Wt% of Dopant</th>
<th>$T_m$</th>
<th>$T_c$</th>
<th>$\Delta \varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>none</td>
<td>100</td>
<td>0</td>
<td>23.64</td>
<td>112.31</td>
<td>-1.8</td>
</tr>
<tr>
<td>B</td>
<td>MLC-9200-000</td>
<td>90</td>
<td>10</td>
<td>21.04</td>
<td>113.08</td>
<td>-1.2</td>
</tr>
<tr>
<td>C</td>
<td>ZLI-3086</td>
<td>90</td>
<td>10</td>
<td>16.23</td>
<td>110.24</td>
<td>-1.6</td>
</tr>
<tr>
<td>D</td>
<td>MLC-6608</td>
<td>70</td>
<td>30</td>
<td>6.02</td>
<td>104.65</td>
<td>-2.5</td>
</tr>
</tbody>
</table>
Figure 3-7 Voltage–dependent transmittance of homeotropic cell between crossed polarizers. $\lambda = 633$ nm. (a) Mixture A at $T=50^\circ C$ (dashed line), mixture B at room temperature (dotted line), and $T=100^\circ C$ (solid line). (b) Mixture A at $T=50^\circ C$ (dashed line), mixture C at room temperature (dotted line), and $T=100^\circ C$ (solid line). (c) Mixture A at $T=50^\circ C$ (dashed line), mixture D at room temperature (dotted line), and $T=100^\circ C$ (solid line), and mixture E at $T=100^\circ C$ (gray solid line)
To improve the alignment capability of the rubbed PI cells, we doped three types of LC materials, as listed in Table 3-4, to the host mixture A. The new mixtures are labeled as B, C, and D, and their V-T curves are shown in Figure 3-7 (a), (b) and (c), respectively. The data of mixture A at T=50°C is included as a benchmark for comparison. We found mixtures B, C, and D have an excellent dark state and a very sharp threshold even at T=100°C. The doped positive, neutral, or negative $\Delta \varepsilon$ mixtures help to align the host negative LC mixture and, furthermore, the alignment is very stable at elevated temperatures.

The required dopant concentration for improving the alignment capability depends on the physical property of the specific dopant. ZLI-3086 is basically a non-polar mixture and MLC-9200-000 is a positive $\Delta \varepsilon$ LC mixture consisting of axially fluorinated compounds. From Table 3-4, adding ~10 wt% of this type of mixture to the host dramatically improves the dark state of the VA cell. On the other hand, MLC-6608 is a negative $\Delta \varepsilon$ LC mixture which consists of ~60-70% laterally difluoro cyclohexane-phenyl compounds. Thus, the required concentration for seeing a noticeable improvement is increased. This effect is demonstrated in Figure 3-7 (c) where mixture D contains 30 wt% of MLC-6608, while mixture E contains only 13% of MLC-6608. Although mixture E exhibits a good dark state at V=0, its maximum transmittance in the voltage-on state only reaches ~70% indicating that its alignment quality is still imperfect at elevated temperatures. Increasing MLC-6608 concentration to 30% leads to excellent dark and bright states and sharp threshold even at T=100°C.

3.2.1 Physical Properties

In addition to enabling excellent molecular alignment, doping 10% of a positive or non-polar LC
mixture leads to a higher figure-of-merit (FoM). Figure 3-8 (a) and (b) depict the measured temperature-dependent birefringence and FoM, respectively, of mixtures B, C, and D at $\lambda=633$ nm. Circles, squares, and triangles represent the mixture B, C, and D, respectively. The data of mixture A at room temperature is included as a benchmark for comparison. The solid line represents the fitting curves using the following equations:[12,14]

$$\Delta n = (\Delta n)_o (1 - T / T_c)^\beta$$

Eq 3-1

$$FoM \sim (\Delta n)_o^2 (1 - T / T_c)^{3\beta} \exp(-E / kT)$$

Eq 3-2

In Eq 3-2, $(\Delta n)_o$ is the birefringence at $T=0$ K, $E$ is the activation energy of the rotational viscosity, $k$ is the Boltzmann constant, and exponent $\beta$~0.25 is not too sensitive to the LC structure. Since the birefringence $(\Delta n~0.08)$ of all the dopants we studied is much smaller than that of the terphenyl type mixture, mixture D has the smallest birefringence among all the mixtures studied. On the other hand, the host laterally difluoro terphenyl mixture has a higher viscosity than the dopants. Thus, the dopants dramatically reduce the mixture’s viscosity. This explains why mixtures B and C have a higher figure-of-merit than the host mixture A. From Figure 3-8 (b) mixtures B and C have ~2X higher FoM than mixture A at room temperature.
Figure 3-8 Temperature-dependent (a) birefringence and (b) figure-of-merit (FoM) of mixtures B, C, and D. Circles, squares, and triangles are measured data for B, C, and D, respectively. Asterisks represent the measured data of mixture A for benchmarking. Solid lines are fitting results using Eq 3-1 and Eq 3-2. $\lambda=633$ nm.

### 3.3 Laterally Difluoro-tolanes

First of all, we formulated two negative $\Delta \varepsilon$ LC mixtures, designated as UCF-N3 and UCF-N4, using difluoro-tolanes. Table 3-5 lists the compositions of UCF-N3 and -N4 mixtures. The major components of these mixtures are (2,3) difluoro-tolanes. Besides these two host mixtures, we also studied the dopant effects for enhancing the homeotropic alignment quality. Three isothiocyanato (NCS) tolane [15, 16] dopants were investigated. Their molecular structures and phase transition temperatures are shown in Table 3-6. As shown in Table 3-6, PTP-2NCS exhibits a monotropic nematic phase, while CPTP-4NCS exhibits an enantiotropic nematic phase, but with a relatively high melting temperature, and the third dopant PTP-3ONCS has no LC phase. Its melting point is also quite high because of the alkoxy group.
Table 3-5 Compositions of UCF-N3 and UCF-N4 LC mixtures

<table>
<thead>
<tr>
<th>LC components</th>
<th>Wt % of UCF-N3</th>
<th>Wt % of UCF-N4</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{11}H_{23}</td>
<td>18</td>
<td>19.1</td>
</tr>
<tr>
<td>C_{7}H_{15}</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>C_{9}H_{17}</td>
<td>21</td>
<td>19.4</td>
</tr>
<tr>
<td>C_{7}H_{15}</td>
<td>36</td>
<td>14.3</td>
</tr>
<tr>
<td>C_{11}H_{23}</td>
<td>0</td>
<td>18.8</td>
</tr>
<tr>
<td>C_{7}H_{15}</td>
<td>0</td>
<td>9.5</td>
</tr>
<tr>
<td>C_{11}H_{23}</td>
<td>5</td>
<td>3.9</td>
</tr>
</tbody>
</table>
Table 3-6 Molecular structures and their melting and clearing temperatures (in °C) of the three positive dopants we used in this study.

<table>
<thead>
<tr>
<th>Positive compound</th>
<th>Molecular structure</th>
<th>Melting point (°C)</th>
<th>Clearing point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTP-2NCS</td>
<td>( \text{C}_2\text{H}_5 ) ( \text{C}_6\text{H}_4 \text{C} = \text{C} \text{C}_6\text{H}_4 \text{NCS} )</td>
<td>95.9</td>
<td>87.1</td>
</tr>
<tr>
<td>CPTP-4NCS</td>
<td>( \text{C}_2\text{H}_5 ) ( \text{C}_6\text{H}_4 \text{C} = \text{C} \text{C}_6\text{H}_4 \text{NCS} )</td>
<td>106.9</td>
<td>257.5</td>
</tr>
<tr>
<td>PTP-3ONCS</td>
<td>( \text{C}_3\text{H}_7\text{O} ) ( \text{C}_6\text{H}_4 \text{C} = \text{C} \text{C}_6\text{H}_4 \text{NCS} )</td>
<td>125.3</td>
<td>125.3</td>
</tr>
</tbody>
</table>

We doped 5, 10, and 15 wt% of these three compounds into the UCF-N3 and –N4 host mixtures, respectively. Table 3-7 shows the abbreviations and phase transition temperatures of these mixtures. We used differential scanning calorimetry (DSC; TA-100) to determine the mixture’s melting and clearing temperatures. Due to the relatively high melting temperatures of these NCS tolane dopants, the solubility is limited to ~10%. The 15% mixtures crystallize at room temperature.
Table 3-7 Melting and clearing temperatures (in °C) of the UCF mixtures with and without dopants.

<table>
<thead>
<tr>
<th>Name</th>
<th>Base mixture</th>
<th>Dopant</th>
<th>Wt % of dopant</th>
<th>Tm(°C)</th>
<th>Tc(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UCF-N3</td>
<td></td>
<td></td>
<td>0</td>
<td>-51.8</td>
<td>113.8</td>
</tr>
<tr>
<td>UCF-N3a</td>
<td>UCF-N3</td>
<td>PTP-2NCS</td>
<td>5</td>
<td>-51.8</td>
<td>110.2</td>
</tr>
<tr>
<td>UCF-N3b</td>
<td></td>
<td></td>
<td>10</td>
<td>-52.0</td>
<td>107.0</td>
</tr>
<tr>
<td>UCF-N3c</td>
<td></td>
<td></td>
<td>15</td>
<td>44.2</td>
<td>103.5</td>
</tr>
<tr>
<td>UCF-N4</td>
<td></td>
<td></td>
<td>0</td>
<td>-51.8</td>
<td>108.5</td>
</tr>
<tr>
<td>UCF-N4a</td>
<td>UCF-N4</td>
<td>PTP-2NCS</td>
<td>5</td>
<td>-51.8</td>
<td>105.0</td>
</tr>
<tr>
<td>UCF-N4b</td>
<td></td>
<td></td>
<td>10</td>
<td>-52.4</td>
<td>101.2</td>
</tr>
<tr>
<td>UCF-N4c</td>
<td></td>
<td></td>
<td>15</td>
<td>43.5</td>
<td>97.4</td>
</tr>
<tr>
<td>UCF-N4d</td>
<td>UCF-N4</td>
<td>CPTP-4NCS</td>
<td>5</td>
<td>-51.2</td>
<td>113.8</td>
</tr>
<tr>
<td>UCF-N4e</td>
<td></td>
<td></td>
<td>10</td>
<td>-50.3</td>
<td>122.1</td>
</tr>
<tr>
<td>UCF-N4f</td>
<td>UCF-N4</td>
<td>PTP-3ONCS</td>
<td>5</td>
<td>-51.2</td>
<td>107.5</td>
</tr>
<tr>
<td>UCF-N4g</td>
<td></td>
<td></td>
<td>10</td>
<td>-50.9</td>
<td>106.5</td>
</tr>
</tbody>
</table>

3.3.1 LC Alignments

First we compare the alignment capability of the LA-SiO₂ and buffed PI cells. We measured the voltage dependent transmittance (V-T) curves of both cells filled with UCF-N3 mixture. Figure 3-9(a) plots the measured results at λ=633 nm. From Figure 3-9(a), the voltage-off state of the PI cell (d~ 5.2 μm) has ~2% light leakage and, moreover, its threshold behavior is smeared. These
phenomena imply that the pretilt angle of the cell is too large (>10°). On the other hand, the LA-SiO₂ cell (d= 3.7 µm) aligns UCF-N3 quite well. The voltage-off state is very dark and threshold is sharp. The evaporated long-chain alcohol molecules were adsorbed to the SiO₂ surface serving as monolayer for aligning the difluoro molecules. As a result, an excellent homeotropic alignment is achieved.

In Figure 3-9(a), there are several transmission cycles because the phase retardation (δ = 2πdΔn/λ) of the homeotropic LC cell is large. For display applications, we only need δ~1.2 π. Thus, a thinner cell gap can be used for achieving a faster response time.

Figure 3-9 Voltage- dependent transmittance of homeotropic cell between crossed polarizers. (a) UCF-N3 in buffed PI cell (dashed line) and in LA-SiO₂ cell (solid line). (b) UCF-N3 containing 0% (dashed line), 5% (dotted line) and 10% (solid line) of PTP-2NCS in buffed PI cell. λ=633 nm, and T =23°C.

Although the LA-SiO₂ aligns the difluoro mixtures well, its fabrication process requires vacuum so that the panel size is limited. The buffing method is more convenient and less expensive for
large LC panels. To improve the alignment capability of the rubbed PI cells, we doped some positive compounds, as listed in Figure 3-6, to the host UCF-N3 and –N4 mixtures. Figure 3-9(b) plots the V-T curves of the rubbed PI cells which were filled with UCF-N3, -N3a, and -N3b. The polarizers are crossed and the on-state LC directors are at 45° with respect to the polarizer’s optical axis. In Figure 3-9(b), the data of UCF-N3 is included as a benchmark for comparison. Doping 5% of PTP-2NCS (sample UCF-N3a) suppresses the dark state light leakage noticeably, but is still not perfect as shown by the dashed lines. Increasing PTP-2NCS to 10% (sample UCF-N3b) leads to an excellent dark state and sharp threshold (gray line). A shortcoming for doping a positive $\Delta \varepsilon$ compound to the negative host mixture is that the effective $|\Delta \varepsilon|$ is decreased so that the threshold voltage is increased.

Table 3-8 Birefringence ($\Delta n$), visco-elastic coefficient ($\gamma_{1}/K_{33}$), figure-of-merit (FoM), and dielectric anisotropy ($\Delta \varepsilon$) of the UCF negative LC mixtures containing 5% and 10% of positive compounds.

<table>
<thead>
<tr>
<th>Mixtures</th>
<th>$\Delta n$</th>
<th>$\gamma_{1}/K_{33}$</th>
<th>FoM</th>
<th>$\Delta \varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UCF-N3a</td>
<td>0.30</td>
<td>19.0</td>
<td>4.73</td>
<td>-4.3</td>
</tr>
<tr>
<td>UCF-N3b</td>
<td>0.31</td>
<td>13.0</td>
<td>7.39</td>
<td>-3.3</td>
</tr>
<tr>
<td>UCF-N4a</td>
<td>0.29</td>
<td>14.5</td>
<td>5.84</td>
<td>-4.4</td>
</tr>
<tr>
<td>UCF-N4b</td>
<td>0.30</td>
<td>13.2</td>
<td>6.82</td>
<td>-3.2</td>
</tr>
<tr>
<td>UCF-N4d</td>
<td>0.29</td>
<td>18.8</td>
<td>4.57</td>
<td>-4.7</td>
</tr>
<tr>
<td>UCF-N4e</td>
<td>0.31</td>
<td>17.4</td>
<td>5.56</td>
<td>-3.4</td>
</tr>
<tr>
<td>UCF-N4f</td>
<td>0.30</td>
<td>16.7</td>
<td>5.42</td>
<td>-4.3</td>
</tr>
<tr>
<td>UCF-N4g</td>
<td>0.31</td>
<td>14.9</td>
<td>6.45</td>
<td>-3.2</td>
</tr>
</tbody>
</table>
3.3.2 Threshold Voltage

The threshold voltage of a homeotropic cell is related to $\Delta \varepsilon$ as $V_{th} = \pi \sqrt{K_{33}/\varepsilon_0 \Delta \varepsilon}$. While deriving the expression for the threshold voltage, the pretilt angle is assumed zero. However, in reality, the LC cell always has a small pretilt angle in order to guide the relaxation direction of the LC directors. With this pretilt angle, the threshold would not be perfectly sharp. For the same LC material employed, a larger pretilt angle cell would result in a lower apparent threshold voltage. The PTP-2NCS compound we used has a relatively large and positive dielectric anisotropy ($\Delta \varepsilon \approx 12$). Thus, adding 10% of PTP-2NCS into UCF-N3 host will reduce the effective $\Delta \varepsilon$ of the mixture and result in an increased threshold voltage. From Figure 3-9(b), the $V_{th}$ of UCF-N3b is $\approx 2.7$ V$_{rms}$, which is approximately the same as that of UCF-N3 in the LA-SiO$_2$ cell. UCF-N3 has a larger, but negative $\Delta \varepsilon$ than UCF-N3b. In theory, the UCF-N3 cell should have a lower threshold voltage. However, the LA-SiO$_2$ cell has a smaller pretilt angle ($\approx 1.5^\circ$) than the rubbed PI cell ($\approx 3^\circ$). Thus, its apparent threshold voltage is about the same as that of UCF-N3b in the rubbed PI cell.

Figure 3-10 depicts the V-T curves between crossed polarizers of the buffed PI cells filled with UCF-N4, -N4a, -N4d, and -N4f. The cell gap is $d \approx 5.2$ $\mu$m and $\lambda = 633$ nm. The UCF-N4 cell has $\approx 1\%$ light leakage in the voltage-off state and its threshold is not as sharp as it should be. Adding 5% of PTP-2NCS, CPTP-4NCS, and PTP-3ONCS into UCF-N4 greatly improves the dark state and threshold behavior. The V-T curves of UCF-N4a, -N4d and -N4f almost overlap with each other. The transmittance reaches $\approx 0$ and 100% at the voltage-off and -on state, respectively. From Figure 3-10, the positive compounds indeed help the host difluoro-tolane mixture to align
well in the rubbed PI cells.

![Graph showing voltage-dependent transmittance of UCF-N4.](image)

Figure 3-10 Voltage-dependent transmittance of UCF-N4 containing 5% of positive compound. Dashed, dotted, solid and gray lines represent UCF-N4, UCF-N4a, -N4d, and -N4f, repetitively. $\lambda=633$ nm and $d\sim 5.2$ µm.

### 3.3.3 Contrast Ratio

We also measured the contrast ratios of the cells shown in Figure 3-10. The contrast ratio of UCF-N4 in the rubbed PI cell is $\sim100:1$, which indicates that the alignment quality is not perfect. For the mixtures containing 5% and 10% of PTP-2NCS in a rubbed PI cell, their dark state transmittance is limited by the crossed-polarizers. The estimated contrast ratio exceeds 10,000:1 for the employed He-Ne laser beam.

### 3.3.4 Refractive Indices

We also measured the $n_c$ and $n_o$ of UCF-N3b at six visible wavelengths ($\lambda= 450, 486, 546, 589, 633,$ and $656$ nm) and different temperatures. We used a multi-wavelength Abbe refractometer
(Atago DR-M4) to measure the $n_e$ and $n_o$ of the LC mixture. The temperature of the Abbe refractometer was controlled by a circulating constant temperature bath (Atago Model 60-C3). Results of the wavelength- and temperature-dependent refractive indices of UCF-N3b are plotted in Figure 3-11 and Figure 3-12, respectively. For the wavelength dependent refractive indices measurements, the temperature was fixed at $T=25^\circ C$.

Figure 3-11 Wavelength-dependent refractive indices of UCF-N3b at $T=25^\circ C$. Dots are experimental data and solid lines are fittings using Eq 3-3 and Eq 3-4 for $n_e$ and $n_o$, respectively.
Figure 3-12 Temperature-dependent refractive indices of UCF-N3b at $\lambda=633$ nm. Dots are experimental data and solid lines are fittings with theory.

The solid lines in Figure 3-11 represent fittings with the extended Cauchy equations [17, 18]:

$$n_e = A_e + \frac{B_e}{\lambda^2} + \frac{C_e}{\lambda^4}$$

Eq 3-3

$$n_o = A_o + \frac{B_o}{\lambda^2} + \frac{C_o}{\lambda^4}.$$  

Eq 3-4

Where $A_{e,o}$, $B_{e,o}$ (in unit of $\mu m^2$), and $C_{e,o}$ (in unit of $\mu m^4$) are called Cauchy coefficients for the extraordinary and ordinary refractive indices. From fittings, the six Cauchy coefficients are obtained as: $[A_e,B_e,C_e] = [1.7372, 0.0165, 0.0010]$, and $[A_o,B_o,C_o] = [1.4802, 0.0066, 0.0004]$. From Figure 3-11, the agreement between experiment and theory is excellent. As the wavelength increases, $n_e$ decreases much more rapidly than $n_o$. Once the Cauchy coefficients are known, we
can extrapolate the refractive indices of UCF-N3b to any wavelength we want. For example, at \(\lambda=10.6\mu m\) the extrapolated \(n_e=1.7374\), \(n_o=1.4803\), and \(\Delta n=0.2571\) at \(T=25^\circ C\).

In Figure 3-12, we plot the temperature-dependent refractive indices of UCF-N3b at \(\lambda=633\) nm. Solid lines represent fittings with the following simple expressions [19]

\[
n_e = \langle n \rangle + \frac{2}{3} \Delta n ,
\]

Eq 3-5

\[
n_o = \langle n \rangle - \frac{1}{3} \Delta n .
\]

Eq 3-6

In Eq 3-5 and Eq 3-6, \(\langle n \rangle\) represents the average refractive index and \(\Delta n\) is the LC birefringence. The average refractive index decreases linearly with temperature as \(\langle n \rangle = A - BT\) and birefringence decreases with temperature as \(\Delta n = (\Delta n)_o(1 - T/T_c)^\beta\); where \(A, B, (\Delta n)_o\), and \(\beta\) are material parameters [19, 20]. From Eq 3-5, the right two terms all decrease as temperature increases. Thus, \(n_e\) decreases monotonously with increased temperature. That is to say, the temperature derivative of \(n_e\) (i.e., \(\partial n_e/\partial T\)) is always negative. However, \(\partial n_o/\partial T\) exists a cross-over temperature \(T_o\) [21] where \(\partial n_o/\partial T = 0\). Below \(T_o\), \(n_o\) decreases with increased temperature, whereas above \(T_o\), \(n_o\) increases with increasing temperature.

### 3.3.5 High FoM Negative \(\Delta\epsilon\) LC Mixture

In addition to enabling excellent alignment, doping 5-10\% of a NCS-tolane leads to a higher
birefringence and lower visco-elastic coefficient. The birefringence of the NCS-tolane is around 0.38, which is higher than that of the negative difluoro tolanes. Meanwhile, the NCS group also possesses a low viscosity. Thus, the doped mixtures exhibit an improved figure-of-merit.

Figure 3-13 plots the temperature-dependent figure-of-merit of UCF-N3b and a Merck high birefringence negative $\Delta \varepsilon$ LC mixture MLC-4850. Dots and triangles represent the measured data for UCF-N3b and MLC-4850, respectively, while the solid line represents the fitting curves using Eq 3-2. At the optimal operating temperature ($T_{op} \sim 75^\circ C$), FoM reaches a maximum value, which is 20 $\mu m^2$/ms for UCF-N3b and $\sim 10$ $\mu m^2$/ms for MLC-4850. The peak FoM of UCF-N3b is almost twice higher than that of MLC-4850.

Figure 3-13 Temperature dependent figure-of-merit ($\mu m^2$/ms) of UCF-N3b (circles) and MLC 4850 (triangles). Solid lines are fittings to the experimental data.
3.4 Physical Mechanisms

From the alignment performance of single compound investigation, we found that the alignment capability is related to the molecular conjugation length. For example, the molecules with two or fewer phenyl rings have better alignment than those with three phenyl rings and tolanes. Moreover, compounds \( \textbf{N4} \) and \( \textbf{N5} \) have the same core structure, except for the different difluoro positions and terminal alkyl/alkoxy groups. The two fluoro groups of \( \textbf{N4} \) are in the middle ring and its terminal group is alkyl rather than alkoxy. Both \( \textbf{N4} \) and \( \textbf{N5} \) have poor V-T curves and the on-state transmittance of compound \( \textbf{N5} \) is worse than that of \( \textbf{N4} \). Therefore, both the conjugation length and lateral positions of the difluoro groups jointly determine the alignment capability.

In order to understand the physical mechanisms of the LC alignment, molecular modeling was used to investigate the electrostatic potential distribution of these single compounds. Molecular modeling (HyperChem- molecular modeling software) was performed by running Austin Model 1 (AM1) and Modified Neglect of Diatomic Overlap (MNDO) calculations in order to estimate the molecular conformations, electrostatic potentials, and Huckel charges. Figure 3-14 shows the space filling models of compounds we studied by using color codes. Here, blue stands for a strong negative electrostatic potential; red, a strong positive one; and green, a moderately negative one. For example, the fluoro group has a strong negative electrostatic potential and, thus, it is presented by the blue color. To balance the charges, the remaining phenyl ring has a strong positive electrostatic potential.
Figure 3-14 Molecular models of compounds N1-N7 (from top to bottom except N6). The color is used for visualizing electrostatic potentials. Here, blue stands for a strong negative electrostatic potential; red, a strong positive one; and green, a moderately negative one.

The electrostatic potential distributions from Figure 3-14 show that compounds N1, N2, and N3 (collectively called group I) have a strong negative electrostatic potential only in the vicinities of the fluoro groups. These negative charges spread to the nearby phenyl ring because of electron conjugation. Although compounds N4 and N5 have similar terphenyl structures, their electrostatic potentials are quite different. In N4, the relatively strong negative electrostatic
potential distributes over the entire molecule. By contrast, the strong negative electrostatic potential of compound \textbf{N5} is more localized; only a moderate negative charge spreads to the other two phenyl rings. The biphenyl-tolane (\textbf{N7}) has a similar charge distribution to that of \textbf{N5} except for a longer conjugation.

We have determined from our experimental results that the group \textbf{I} compounds are easy to align while the compounds of group \textbf{II} (\textbf{N4}, \textbf{N5}, and \textbf{N7}) are not. Therefore, the charge distribution seems to shed some light on the understanding of the alignment mechanism. From Figure 3-14, the negative electrostatic potentials of the group \textbf{I} compounds spread out a smaller distance because of their shorter electron conjugation. Due to the shorter electron conjugation, the repulsive force from the polyimide is weaker. As a result, a good homeotrop alignment is achieved. On the other hand, the negative electrostatic potentials in the group \textbf{II} compounds spread over to the entire compounds. The repulsive force from the polyimide is stronger, resulting in a larger pretilt angle. A large pretilt angle causes light leakage in the dark state. This evidence was proven when we observed compound \textbf{N7} in a homeotropic cell between two crossed polarizers under a light table. We saw a very colorful cell rather than one with a good dark state.

Although we do not know the exact molecular structure of the PI we employed, molecules in group \textbf{II} have strong interactions with the alignment layer along the long side of the molecules and result in a large pretilt angle. Therefore, we believe that the added positive or neutral LC materials help neutralize the strong negative charge of the group \textbf{II} molecules and serve as a buffer layer for aligning the difluoro terphenyl and tolane compounds and mixtures. The required
amount of positive or neutral LC material depends on how the negative electrostatic potential is distributed over the entire molecule.

In order to investigate this dopant effect at room temperature, we selected 5CB as the dopant for this part of the study because of its low clearing temperature (35.3°C). We used two different methods to coat 5CB onto the glass substrate. For the first, we vaporized 5CB onto the glass substrate. For the second, we dissolved 5CB into a cyclohexane solution and then dripped this solution onto a glass substrate. In the first method, we filled a glass vial with 5CB and placed a glass substrate, which has the PI alignment layer, over the opening. We heated the 5CB to ~120°C for 20 minutes, evaporating the 5CB onto the substrate, and then removed the glass substrate. We then repeated the process for another substrate and then joined the two substrates coated with 5CB, creating a cell. The sealed cell was injected with mixture A. We observed this LC cell under a polarizing optical microscope. Results are shown in Figure 3-15. Between crossed polarizers, the area coated with 5CB vapor appears darker than the adjacent uncoated areas, indicating that the coated 5CB indeed helps align mixture A.
Figure 3-15 A microscope photo of a VA cell filled with Mixture A under a crossed polarizing microscope. The PI alignment layer is coated with vaporized 5CB molecules. The cell was then filled with mixture A. The dark area (bottom right corner) is the area coated with the 5CB vapor. A 20X magnification objective lens was used.

In the second method, we prepared a 5CB solution in cyclohexane. The molar concentration of the 5CB solution was $5.3 \times 10^{-3}$ mol/L. We dripped the solution onto the glass substrate inside an oven (~90°C) in order to vaporize the cyclohexane, leaving just the 5CB on the substrate. We placed 10 drops, each time waiting for the cyclohexane to evaporate before placing another drop, in order to deposit enough 5CB molecules on the glass substrate. After being coated with the 5CB solution, the cell was sealed and injected with mixture A. Results are shown in Figure 3-16.

In Figure 3-16, the left upper corner is the area without 5CB, where the light leaks severely because of the poor LC alignment. The lower right corner is the area with the 5CB solution. The slightly diagonal lines are the rubbing direction. The 5CB solution, indeed, enhances the contrast ratio of a VA cell.
Figure 3-16 A microscope photo of VA cell under crossed polarizers. The surfaces of the VA cell were coated with 5CB dissolved in cyclohexane. The cell was then filled with mixture A. A 20X magnification objective lens was used. The bottom right corner is the area with 5CB solvent.

We found that, compared to Figure 3-15, the solvent method forms a larger and more uniform area. This is because the vaporized 5CB molecules could aggregate and cause non-uniformity.

In our experiments, we used different PI alignment layers and also found similar results. In addition, we tested our concepts using non-rubbed PI substrates and similar results were obtained. The non-buffed PI substrates have been used in multi-domain structures [22, 23] for widening the viewing angle. Therefore, the dopant-enhanced contrast ratio of VA cells can be applied to varieties of liquid crystal display devices.
3.5 **References**


CHAPTER FOUR
DUAL-FREQUENCY LIQUID CRYSTALS

4.1 Introduction of Dual-Frequency Liquid Crystals

All polar liquids (such as liquid crystals) experience dielectric relaxation at high frequencies of electric field. This is because the permanent dipole rotation only occurs when the electric field varies slowly. When the field varies rapidly, the dipole rearrangement cannot follow. In a typical liquid crystal material, this dielectric relaxation occurs in the megahertz range. To make the dual-frequency material useful, the dielectric relaxation should take place in the kilohertz region or lower. By mixing some positive $\Delta \varepsilon$ ester compounds with some negative $\Delta \varepsilon$ LC compounds, dual-frequency mixtures with their crossover frequency in a few kilohertz range have been developed.[1, 2]

From Eq 1-4, one can see that there are two types of polarizations that contribute to the dielectric constant: (a) induced polarization (the first term) and (b) orientation polarization (the dipole moment term).[3] The field induced polarization has a very fast response time and it follows the external field. The orientation polarization, however, exhibits a longer decay time, $\tau$. If the external electric field frequency is comparable to $1/\tau$, the time lag between the average orientation of the dipole moment and the alternating field becomes noticeable. At a frequency $\omega$ ($\omega=2\pi f$) which is much higher that $1/\tau$, the orientation polarization cannot follow the variations of the external field any longer. Thus, the dielectric constant drops to $\varepsilon_\infty$ which is contributed solely by the induced polarization:
Where $\varepsilon_{\parallel} = \varepsilon_{\parallel}(\omega=0)$ and $\varepsilon_{\infty} = \varepsilon_{\parallel}(\omega=\infty)$ are the parallel component of the dielectric constant at static and high frequencies, respectively. The relaxation time $\tau = 1/\omega_0$ is determined by the frequency $\omega_0$ such that $\varepsilon_{\parallel}(\omega_0) = \frac{(\varepsilon_{\parallel} + \varepsilon_{\perp})}{2}$, the middle point of $\varepsilon_{\parallel}(\omega=0)$ and $\varepsilon_{\parallel}(\omega=\infty)$.

Since rotation about the short axis of the liquid crystal molecule is hindered to a greater extent than rotation about the long axis, the relaxation of $\varepsilon_{\parallel}$ (the permittivity along the long axis) occurs at lower frequencies than that of $\varepsilon_{\perp}$ (the permittivity perpendicular to the long axis). Therefore, as the frequency of the applied field is increased, the value of $\varepsilon_{\parallel}$ will decrease while that of $\varepsilon_{\perp}$ will remain approximately constant. This in turn leads to the positive to negative transition associated with so-called dual-frequency liquid crystals (DFLC). As shown in Figure 4-1, $\Delta\varepsilon$ changes from positive at low frequencies to negative as the frequency passes the cross-over frequency ($f_c$). Figure 4-2 illustrates the molecular rotational direction of positive and negative $\Delta\varepsilon$ LCs. In the low frequency regime, $\Delta\varepsilon > 0$, the electric field-induced torque in the longitudinal (z-axis) direction is larger than that in the transversal direction so that the LC directors are deformed as $V > V_{th}$. When the low frequency voltage is replaced by a high frequency voltage, the sign change of $\Delta\varepsilon$ results in a torque that is larger in the transversal (the initial alignment) direction. As a result, this high frequency burst acts to restore the LC directors. The time constant of this restoring force is greatly influenced by the dielectric anisotropy at high frequencies and by the applied high frequency voltage. By biasing the DFLC
device at a constant voltage while switching the frequency, sub-millisecond rise and decay times can be achieved.[5, 6] Because of this attractive property, there is a renewed interest in using DFLC for high-speed photonics, such as adaptive optics and diffractive optics.[7-9]

Figure 4-1 Experimental results on frequency and temperature dependences of $\varepsilon_{//}$ and $\varepsilon_{\perp}$ of a Roche mixture M1. The cross-over frequency increases exponentially with temperature. (Ref.4)

Figure 4-2 Depending on the sign of the dielectric permittivity, the induced polarization $P$ gives a dielectric torque to the molecules, turning the director towards being (a) parallel or (b) perpendicular to the field direction.
4.2 **Dielectric Heating Effect**

Figure 4-3 shows an example of the frequency dependence of the real \((\varepsilon')\) and imaginary \((\varepsilon'')\) parts of 7CB: [10, 11]

\[
\varepsilon_{//,\perp} = \varepsilon_{//,\perp}^{\prime} - j\varepsilon_{//,\perp}^{\prime\prime}
\]

Eq 4-2

Since the imaginary part of the dielectric constant of a DFLC absorbs the high-frequency electric field and generates heat, dielectric heating is a big concern for all the DFLC devices. The dielectric heating of DFLC shifts the crossover frequency. [12-14] As shown in Figure 4-1, the cross-over frequency increases as the temperature increases. Therefore, the switching behavior, especially grayscales, of the DFLC drifts.
To quantify the dielectric heating phenomenon, several reports have discussed how the operating voltage affects the sample temperature.[4, 15] Normally, the temperature of the LC cell was monitored by an attached thermocouple. The measured temperature represents the average temperature of the sample cell, not the actual temperature of the LC inside the cell. Besides the experimental characterization method, a more challenging technical issue is how to reduce the dielectric heating effect from molecular engineering standpoint so that the DFLC performance can be better controlled.
We developed a non-contact method to measure the transient temperature rise under different voltages and frequencies of the DFLC by probing the birefringence ($\Delta n$) decrease. Through these measurements, we are able to quantitatively evaluate the dielectric heating effects. Among the three DFLC mixtures we studied, the one we formulated in our labs exhibits a large dielectric anisotropy ($\Delta \varepsilon \sim 7.5$), modest crossover frequency ($f_c \sim 10$ kHz), and a relatively weak dielectric heating effect. This type of DFLC mixture will be useful for high-speed photonics applications.

4.2.1 Theory and Temperature Measurement

For a homogeneously aligned DFLC cell, the dielectric heating causes the LC temperature to increase which, in turn, decreases the effective birefringence of the LC layer. The birefringence change can be measured by monitoring the transmittance change of the LC cell sandwiched between two crossed polarizer, as we described in section 2.1.2.[16] The LC temperature will eventually reach equilibrium between the dielectric heating and the heat dissipation to the air through the substrates. By monitoring the total phase retardation ($\delta$) of the DFLC cell at a laser wavelength ($\lambda$), the effective birefringence ($\Delta n$) can be calculated from $\delta = \frac{2\pi}{\lambda} d\Delta n$, where $d$ is the cell gap. From Eq 3-1 we can evaluate the temperature of LC by knowing the birefringence. Therefore, the transient temperature of the DFLC material due to dielectric heating could be measured directly by scanning the transmittance of the LC cell between crossed polarizers.

The dielectric heating-induced temperature rise ($\Delta T$) can be expressed as following:[13]

$$\Delta T = \left[ \frac{\nu^2 A \varepsilon_0 (\varepsilon_1 - \varepsilon_\infty)}{d (C + qf t)} \right] \cdot \left[ \frac{\tau \omega^2 t}{(1 + \omega^2 \tau^2)} \right],$$
where $A$ is the electrode area, $d$ is the DFLC layer thickness, $V$ is the applied voltage, $\varepsilon_s$ and $\varepsilon_\infty$ are the low- (static) and high-frequency dielectric constants of the respective dispersion region, $\tau_n$ ($\tau_n = 1/\omega_n$) is the relaxation time, $t$ is the dielectric heating time, $\omega$ is the angular frequency, $C$ is the average heat capacity of the cell and $q_1$ is the specific heat conductivity of the substrates. $C$ is primarily determined by the indium-tin-oxide (ITO) glass substrates and the LC layer. From Eq 4-3, the temperature increase in the LC layer is related to the applied voltage, frequency, duration, electrode area, cell gap, and LC thermal properties. In experiments, we kept the cell gap at $d=8 \ \mu m$ and electrode area at $A=0.25 \ \text{cm}^2$, and studied the voltage and frequency effects on the dielectric heating of the DFLC samples.

To compare the dielectric heating effect of different materials, we formulated two DFLC mixtures, DF-1, DF-2, and compared results with a Merck high $\Delta n$ DFLC mixture, MLC-2048. Our mixtures DF-1 and DF-2 consist of positive $\Delta \varepsilon$ biphenyl esters and negative $\Delta \varepsilon$ lateral difluoro-tolanes at different percentages. Table 4-1 lists the key physical properties of these three mixtures.
Table 4-1 Physical properties of DF-1, DF-2, and MLC-2048. $T_m$: melting temperature, $T_c$: clearing point, $\Delta n$: birefringence at $\lambda=633$ nm, $\gamma_1/K_{11}$: viscoelastic coefficient at $T=23^\circ$C, and $\Delta \varepsilon$: dielectric anisotropy at $f = 1$ kHz, $f_c$: crossover frequency, and $E$: activation energy.

<table>
<thead>
<tr>
<th>Mixtures</th>
<th>$T_m$ ($^\circ$C)</th>
<th>$T_c$ ($^\circ$C)</th>
<th>$\Delta n$</th>
<th>$\gamma_1/K_{11}$</th>
<th>$\Delta \varepsilon$</th>
<th>$f_c$(kHz)</th>
<th>$E$(meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DF-1</td>
<td>-48.6</td>
<td>139.3</td>
<td>0.29</td>
<td>21.5</td>
<td>5.7</td>
<td>7.4</td>
<td>514</td>
</tr>
<tr>
<td>DF-2</td>
<td>&lt;-50</td>
<td>145.4</td>
<td>0.27</td>
<td>17.8</td>
<td>7.5</td>
<td>10.0</td>
<td>711</td>
</tr>
<tr>
<td>MLC-2048</td>
<td>&lt;-50</td>
<td>108.5</td>
<td>0.21</td>
<td>13.8</td>
<td>2.8</td>
<td>23.0</td>
<td>775</td>
</tr>
</tbody>
</table>

Figure 4-4 Temperature-dependent (a) birefringence and (b) cross-over frequency of DF-1, DF-2, and MLC-2048. Squares, circles, and triangles are measured data for DF-1, DF-2, and MLC-2048, respectively. Solid lines are fittings. The obtained activation energy values from Figure (b) are listed in Table 4-1.

We first measured the temperature-dependent birefringence of each mixture. Results are plotted in Figure 4-4(a). Dots are the experimental data and solid lines are the fittings by using Eq 3-1. These data are used to determine the temperature rise of the DFLC mixtures during operations.
We also measured the frequency-dependent dielectric constants ($\varepsilon_{//}$ and $\varepsilon_{\perp}$) of the three DFLC mixtures by the capacitance method using a homogeneous cell and a homeotropic cell, as described in section 2.1.4.[3, 17] The dielectric anisotropy of DF-1, DF-2, and MLC-2048 was measured to be 5.7, 7.5 and 2.8, respectively, at room temperature (T~23°C) and $f = 1$ kHz. A large $\Delta\varepsilon$ is favorable because it would lower the operating voltage. The crossover frequency of DF-1, DF-2, and MLC-2048 was measured to be 7.4, 10, and 23 kHz at room temperature. The crossover frequency is dependent on the temperature as: $f_c = A \cdot \exp(-E / kT)$, where $A$ is a proportionality constant, $k$ is the Boltzmann constant, and $E$ is the activation energy which is related to the material properties. From the temperature-dependent crossover frequency measurement shown in Figure 4-4(b), the activation energy can be extracted. The activation energy of DF-1, DF-2, and MLC-2048 is 514, 711, and 775 meV, respectively. The smaller activation energy of DF-1 means its crossover frequency is less sensitive to the temperature variation.

To assess the dielectric heating of DFLC mixtures, we conducted two experiments. First, we drove the LC cells at a fixed frequency but varying the applied voltage. The operating frequency of each DFLC was chosen when the negative $\Delta\varepsilon$ first reaches the saturation value, which is 70, 80, and 120 kHz for DF-1, DF-2, and MLC-2048, respectively. Figure 4-5 (a)-(c) represent the transient temperature rise of DF-1 (at $f=70$ kHz), DF-2 (at $f=80$ kHz), and MLC-2048 (at $f=120$ kHz), respectively, at various voltages. In the second experiment, we drove the LC cell at $V = 50$ $V_{\text{rms}}$ but varying the applied frequency. Figure 4-6(a)-(c) plot the transient temperature rise of DF-1, DF-2, and MLC-2048, respectively.
Figure 4-5 Measured transient temperature rise of (a) DF-1, (b) DF-2, and (c) MLC-2048 cells at f=70, 80, and 120 kHz, respectively, while varying the applied voltage. The starting temperature is T=23°C. The solid lines are fittings with Eq 4-3; the fitting parameters are listed in Table 4-2.
Table 4-2 Parameters obtained by fitting the transient temperature change of DF-1, DF-2, and MLC-2048 using Eq 4-3. C is the average heat capacity of the cell and $\tau_n$ is the dielectric relaxation time.

<table>
<thead>
<tr>
<th>V (Vrms)</th>
<th>DF-1 70 kHz</th>
<th>DF-2 80 kHz</th>
<th>MLC-2048 120 kHz</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tau_n$ (µs)</td>
<td>C</td>
<td>$\tau_n$ (µs)</td>
</tr>
<tr>
<td>30</td>
<td>1.6977</td>
<td>13.54</td>
<td>0.3332</td>
</tr>
<tr>
<td>50</td>
<td>1.1678</td>
<td>18.04</td>
<td>0.2992</td>
</tr>
<tr>
<td>70</td>
<td>0.7026</td>
<td>15.88</td>
<td>0.1702</td>
</tr>
<tr>
<td>90</td>
<td>0.7003</td>
<td>21.99</td>
<td>0.1269</td>
</tr>
<tr>
<td>100</td>
<td>0.6674</td>
<td>22.06</td>
<td>0.1217</td>
</tr>
<tr>
<td>110</td>
<td>0.6296</td>
<td>24.05</td>
<td>0.1254</td>
</tr>
</tbody>
</table>
Figure 4-6 Measured transient temperature rise of (a) DF-1, (b) DF-2, and (c) MLC-2048 cells at \( V=50V_{\text{rms}} \) while varying the applied frequency. The starting temperature is \( T=23^\circ \text{C} \). The solid lines are fittings with Eq 4-3; the fitting parameters are listed in Table 4-3.
Table 4-3 Parameters obtained by fitting the transient temperature change of DF-1, DF-2, and MLC-2048 using Eq 4-3 C is the average heat capacity of the cell and \( \tau_n \) is the dielectric relaxation time. \( V=50 \text{ V}_{\text{rms}} \).

<table>
<thead>
<tr>
<th>( f ) (kHz)</th>
<th>DF-1 ( \tau_n (\mu s) )</th>
<th>C</th>
<th>DF-2 ( \tau_n (\mu s) )</th>
<th>C</th>
<th>MLC-2048 ( \tau_n (\mu s) )</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.4230</td>
<td>24.89</td>
<td>0.1849</td>
<td>6.91</td>
<td>0.9854</td>
<td>15.41</td>
</tr>
<tr>
<td>200</td>
<td>0.2291</td>
<td>17.06</td>
<td>0.0794</td>
<td>11.87</td>
<td>0.3786</td>
<td>13.60</td>
</tr>
<tr>
<td>285</td>
<td>0.1608</td>
<td>16.64</td>
<td>0.0689</td>
<td>18.83</td>
<td>0.3062</td>
<td>25.68</td>
</tr>
</tbody>
</table>

In Figure 4-5 and Figure 4-6, the dots represent the experimental data and solid lines represent the fittings with

\[
\Delta T = \left[ \frac{V^2 A \varepsilon_0 (\varepsilon_s - \varepsilon_inf)}{d(C + q_1 t)} \right] \cdot \left[ \frac{\tau_0 \omega^2 t}{(1 + \omega^2 \tau_n^2)} \right],
\]

using \( q_1 = 0.8 \text{ Wm}^{-1}\text{K}^{-1} \) and C and \( \tau_n \) as adjustable parameters. In general, \( q_1 \) is weakly dependent on the temperature, but for simplicity we treated it as a constant. The fitting results agree well with the experimental data shown in Figure 4-5 and Figure 4-6. The fitting parameters are listed in Table 4-2 and Table 4-3. The dielectric relaxation time decreases as the driving voltage or frequency increases, and DF-2 has the largest relaxation frequency among the three mixtures studied.

Let us first compare the results of DF-2 and MLC-2048 because their activation energy is similar. By driving the LC cells at \( V=100 \text{ V}_{\text{rms}} \), the sample temperature of DF-2 (\( f=80 \text{ kHz} \)) and MLC-2048 (\( f=120 \text{ kHz} \)) was raised to 34°C and 63°C, respectively, within two minutes. Moreover, by driving the LC cell at \( V=50 \text{V}_{\text{rms}} \) and \( f=100 \text{ kHz} \), the sample temperature of DF-2 and MLC-2048 was raised quickly to 29°C and 34.5°C, respectively. The higher \( f_c \) and smaller \( \Delta \varepsilon \) of MLC-2048 demand a higher frequency and a higher operating voltage. As a result, MLC-
2048 exhibits a more severe dielectric heating than DF-2.

Next, we compare the dielectric heating effect of DF-1 and DF-2. These two mixtures have similar crossover frequency but DF-1 has lower activation energy than DF-2. By driving the LC cells at $V=100 \text{ V}_{\text{rms}}$ for 10 minutes, the sample temperature of DF-1 ($f=70$ kHz) and DF-2 ($f=80$ kHz) was raised quickly to $58^\circ\text{C}$ and $34^\circ\text{C}$, respectively. Under these circumstances, the corresponding crossover frequency of DF-1 and DF-2 was increased from 7.4 kHz to 49.9 kHz and from 10 kHz to 20.9 kHz, respectively. In principle, the crossover frequency of DF-2 is more sensitive to temperature than DF-1 because of its higher activation energy. However, the dielectric heating of DF-2 is much less than DF-1. Consequently, the temperature rise of DF-2 is less significant than DF-1. The compositions of these two mixtures are somewhat different: DF-1 is based on the biphenyl ester compounds, while DF-2 is based on the biphenyl and cyclohexane-phenyl ester compounds. Therefore, it is possible to formulate a dual-frequency LC mixture whose dielectric heating effect is minimized.

### 4.3 References


CHAPTER FIVE
POLARIZATION-INDEPENDENT PHASE MODULATION OF A HOMEO TROPIC LIQUID CRYSTAL GEL

5.1 Introduction of Liquid Crystal/Polymer Composites

LC/polymer composites, consisting of LC and monomer, have a wide range of applications, including flexible displays, switchable windows, tunable lenses, optical switches and so on [1-4]. Depending on the monomer concentration, LC/polymer composites can be divided into two main categories: polymer-stabilized LC (PSLC) [5] and polymer-dispersed LC (PDLC) [6]. PDLCs consist of a high percentage of monomer (>30 wt%) mixed in a LC mixture. A simple diagram illustrating the electro-optical effect of a PDLC shutter is shown in Figure 5-1(a) and (b) for the off- and on-state, respectively. The polymer matrix material is optically isotropic and has a refractive index $n_p$. The liquid crystal director axes within a particular droplet are determined by the polymer-LC interaction at the droplet boundary. In the voltage-off state, the PDLC material scatters light due to a random distribution of LC directors within each individual droplet and the index mismatch ($n_e > n_p$) between the LC droplets and the host polymer. Because the cell thickness (~10mm) is much larger than the droplet size (~0.5 mm), the incident light will be scattered many times before emerging from the film. When a sufficiently high voltage is applied, all molecules are aligned along the field. In this case, light is transmitted because of the refractive index match between monomer and LC material. PDLC is independent of polarization which is very attractive for many applications, especially for fiber optical communications where
polarization dependent loss is an important issue. However PDLCs usually possess a high operating voltage (~5 Vrms/µm).

![Figure 5-1: The schematics of PDLC working mechanism. (a) LC droplets in polymer matrix, LC directors are randomly oriented in each individual droplet, incident light is scattered. (b) LC molecules are aligned along the external electric field, incident light is transmitted.](image)

An appropriate monomer material should be chosen so that its refractive index $n_p$ is close to the ordinary refractive index $n_o$ of the LC. After polymerization, LC micro-sized droplets are formed and dispersed in an optically isotropic polymer matrix. The droplet size and shape are determined by the composition of the PDLC material and condition of the cell fabrication. For example, a high intensity UV irradiation generates small droplets. Moreover, the curing temperature also has an important effect on the residual phase. At a given curing voltage, the domain size increases as the curing temperature increases which, in turn, lowers the saturation voltage.[7]

PSLC usually consists of a less than 10 wt% of monomer. After polymerization, an anisotropic,
cross-linked polymer network structure is formed. Depending on the surface alignment and initial configuration of the LC cell, different polymer networks are stabilized following the initial distribution of LC directors. The presence of a polymer network in a PSLC not only enhances the LC structure stability, but also helps the LC molecules to return to a desired stable configuration resulting in a reduced response time. Similar to PDLC, PSLC can also be switched between a scattering and a transparent state. The light scattering originates from the LC micro-domains within the polymer network structure. Depending on the initial configuration, external voltage is applied either to induce LC multi-domains (index mismatch, scattering state) or to realign LC molecules in a uniform state (index match, transparent state).

In a nanosized-PDLC (nano-PDLC) [8-12], the LC concentration is ~30% and the LC molecules are strongly anchored by the polymer walls. As a result, nano-PDLC exhibits a small phase shift and requires a high operating voltage (~10 V/µm). To enlarge phase shift by using a thick nano-PDLC layer would further increase the operating voltage. Recently, we demonstrated a polarization-independent phase modulator using a conventional PDLC layer.[13] To bypass the light scattering regime, a bias voltage is applied to the PDLC layer. Because the average LC droplet size is larger than the visible wavelength, the operating voltage is relatively low (3 V/µm). Meanwhile, the response time is fast (~1 ms) benefiting from the bias voltage effect. However, due to the bias voltage effect the remaining tunable phase change is relatively small (~0.04π). Although the observed small phase change is still usable for microphotonic devices, it is highly desirable to increase the phase shift and decrease the operating voltage while keeping a fast response time.
We have developed a homeotropic LC gel whose phase shift is larger but operating voltage is lower than a nano-PDLC. The larger phase change and lower operating voltage originate from the higher LC concentration in our gel. Different from a conventional LC gel,[14] our LC domain size is in submicron region. In the voltage-off state, the light scattering is completely suppressed because of the good refractive index match between the LC and the polymer network.

5.2 Homeotropic Liquid Crystal Gel

Figure 5-2(a), (b) and (c) show the schematic configurations of the LC directors and polymer networks in the voltage-off (V=0), threshold (V_{th}) for directors reorientation, and light scattering states (V_s>V_{th}) of the homeotropic LC gel. In Figure 5-2(a), where V=0, the LC directors are aligned nearly perpendicular to the substrates and stabilized by polymer gels. The polymer networks are formed along the same orientation as the LC directors. Because of the small domain sizes and good index match, the LC gel is highly transparent. As the applied voltage exceeds a threshold, the LC directors begin to tilt away from the electric field direction, as shown in Figure 5-2(b), because the LC has a negative dielectric anisotropy (\(\Delta \varepsilon < 0\)). Further increasing voltage to \(V_s\), light scattering occurs because the refractive index mismatch between the LC and the polymer gel, as shown in Figure 5-2(c). From Figure 5-2(b) to (c), phase-only modulation is expected. Due to the random reorientation of the LC directors in the polymer networks, the phase shift is polarization independent for the normally incident light.
To prepare a homeotropic LC gel with small LC domain sizes, we mixed 20 wt % of a Merck photocurable LC diacrylate monomer RM257 in a negative nematic LC, MLC-6608 ($\Delta n=0.083$, $\Delta \varepsilon=-4.2$). The LC/monomer mixture was injected into an empty cell in the isotropic state. The
inner surfaces of the indium-tin-oxide (ITO) glass substrates were coated with thin homeotropic polyimide alignment layers and rubbed in orthogonal directions in order to reduce the polarization dependency originating from the boundary layers. The pretilt angle is ~88° on each surface. The filled cell was then slowly cooled down to room temperature and exposed to UV light ($\lambda=365$ nm, $I\sim10$ mW/cm$^2$). The UV curing time for the cell was ~30 min. The cell gap was controlled at ~23 $\mu$m using two stripes of mylar film. The electro-optic properties of the LC gel was characterized using an unpolarized He–Ne laser beam ($\lambda=633$ nm).

The LC gel sample appears slightly bluish as visually observed in the reflection state, which implies that the formed LC domain size is comparable to a blue wavelength ($\lambda\sim400$ nm). The LC gel is highly transparent at the He–Ne laser wavelength ($\lambda\sim633$ nm). Figure 5-3 plots the voltage-dependent transmittance of the LC gel. The LC gel is highly transparent at $V=0$. Below 180 $V_{rms}$, the transmittance remains at ~88%. The ~12% light loss mainly originates from the interface reflections between the ITO-glass substrates and the air. The refractive index of ITO is ~ 1.90. As the voltage exceeds 180 $V_{rms}$, the transmittance begins to decline due to light scattering. Therefore, we define 180 $V_{rms}$ as the $V_s$ of the LC gel. The relatively high $V_s$ is due to the small $\Delta\varepsilon$ and small $\Delta n$ of the LC mixture employed, and the submicron domain sizes due to high (20 %) polymer concentration. The hysteresis of the voltage-dependent transmittance of the LC gel was also measured. Results indicate that the forward and backward curves overlap very well, which means the hysteresis is completely suppressed. To examine the phase modulation capability of the LC gel, we measured the transmittance ($T_{\parallel}$ and $T_{\perp}$) at $\lambda=633$ nm between parallel and crossed polarizers with the beam normally incident on the sample surface. We set
the polarization axis of the analyzer parallel to one rubbing direction of the cell. Results are shown in Figure 5-4. Due to the homeotropic alignment of the LC gel, $T_\perp \sim 0$ at $V=0$. As the applied voltage exceeds the threshold voltage $V_{th}=130$ V$_{rms}$, $T_\parallel$ decreases but $T_\perp$ increases with voltage gradually. This means phase-only modulation exists. At $V > 180$ V$_{rms}$, light scattering takes place which is not desirable for the phase-only modulation. To validate whether the gel is polarization dependent, we rotated the sample in the azimuthal direction. Results remain unchanged. This indicates that the phase-only modulation is independent of incident light polarization.

Figure 5-3 Voltage-dependent transmittance of the LC gel. $d=23\mu m$. An unpolarized He-Ne laser was used for this measurement.

Figure 5-4 Voltage-dependent transmittance of the LC gel between parallel ($T_\parallel$) and crossed ($T_\perp$) polarizers. Cell gap $d=23\mu m$, $f=1$ kHz, $\lambda =633$nm, and $T \sim 21^\circ$C.
The phase change in the range from 0~180 V rms can be calculated by taking the ratio of $T_\parallel/T_\perp$. [15] Figure 5-5 plots the voltage dependent phase change of the LC gel at $\lambda=633$ nm and T~21°C. As the voltage increases, the phase increases gradually because the LC directors inside the domains are reoriented randomly away from the electric field, leading to an increased effective birefringence. From 130 to 180 V rms, the phase shift is $\Delta\delta$~0.08$\pi$ (for the 23 $\mu$m LC gel) which is 2X larger than our previous results using a conventional PDLC.[13] In our LC gel, the effective refractive index at V=0 can be expressed as

$$n_{0-eff} = \frac{V_{LC}n_o + V_p n_p}{V_{LC} + V_p}$$

Eq 5-1

where $n_o$ is the ordinary refractive index of the LC, $v_{LC}$, and $v_p$ are the LC and polymer volume fractions, and $n_p$ is the refractive index of the polymer. By applying a voltage across the LC gel, the LC directors tend to reorient themselves perpendicular to the electric field because of the negative $\Delta\varepsilon$. Therefore, light impinging on the sample at normal incidence will see an average refractive index increased from $n_o$ to $\bar{n}(V)$. In this case, the effective refractive index of the LC gel can be rewritten as

$$n_{eff} = \frac{V_{LC} \bar{n}(V) + V_p n_p}{V_{LC} + V_p}$$

Eq 5-2

As a result, the field-induced phase shift can be expressed as

$$\Delta\delta = \frac{2\pi}{\lambda} d(n_{eff} - n_{o-eff})$$

Eq 5-3
where \( d \) is the cell gap and \( \lambda \) is the incident wavelength. By combining Eq 5-1 and Eq 5-3, we rewrite the phase shift as follows:

\[
\Delta \delta = \left( \frac{\nu_{LC}}{\nu_{LC} + \nu_p} \right) \left( \frac{2\pi d (n(V) - n_o)}{\lambda} \right)
\]

Eq 5-4

From Eq 5-4, the LC volume fraction (\( \nu_{LC} \)) is an important parameter contributing to the phase change because \( \nu_{LC} + \nu_p \) does not change. In our gel system, the LC concentration is \(~80\%\) which is much higher than that in a nano-PDLC (\(~30\%)\). As a result, our LC gel should exhibit a larger phase shift than the nano-PDLC, if the same \( \Delta n \) is employed.

![Figure 5-5 Measured phase shift of the LC gel at different voltages. \( d=23\mu m \) and \( \lambda = 633nm \).](image)

From Figure 5-5, the 0.08\( \pi \) phase change was obtained at \( V=180 \) \( V_{rms} \) which corresponds to 7.8 \( V_{rms}/\mu m \). Two factors affecting the on-state voltage are \( \Delta \varepsilon \) of the LC mixture and LC concentration. Negative LC mixtures tend to have a smaller \( \Delta \varepsilon \) than their positive counterparts.

A nano-PDLC device usually uses a positive, large \( \Delta \varepsilon \) LC mixture in order to suppress its operating voltage. Although our LC gel uses a negative, small \( \Delta \varepsilon \) LC mixture, its required
electric field strength is still lower than that of a nano-PDLC because of the higher LC concentration involved. A higher LC concentration not only leads to a slightly larger LC domain size but also decreases the contact interface between the polymer binder and the LC molecules. As a result, the operating voltage is reduced. The strong anchoring force that the polymer binders exert to the LC directors is responsible for the observed fast response time.

If we operate the gel in reflective mode, the phase change will be doubled. Although the achievable phase change is small ($\delta \sim 0.08 \pi$), it is still quite useful for the polarization-independent microlens and microprism applications. From Eq 5-4, to increase phase shift we could either enlarge the LC cell gap or use a higher birefringence LC material.[16] The latter is preferred because increasing cell gap would lead to a higher operating voltage. However, for a given domain size, increasing LC birefringence would also enhance light scattering capability. Therefore, an optimal LC birefringence should exist before light scattering takes place. On the other hand, to lower the on-state voltage we could use a higher $\Delta \varepsilon$ LC mixture.

Response time is another important parameter for LC based phase modulator. We measured the response time of the LC gel using square voltage bursts at $f = 1$ kHz between 0 and 180 V$_{\text{rms}}$. Results are shown in Figure 5-6. The measured rise time is $\tau_{\text{rise}} \sim 590 \mu$s and decay time $\tau_{\text{decay}} \sim 150 \mu$s at room temperature. Such a fast response time results from the small LC domain size as well as the strong polymer stabilization effects. Based on the measured decay time, we estimate the domain size is around 300 nm. This is consistent to the very weak bluish appearance of the LC gel.
Figure 5-6 Measured response time of the LC gel: (a) $\tau_{\text{rise}} \sim 0.59$ ms and (b) $\tau_{\text{decay}} \sim 0.15$ ms. The square waves in each figure represent the voltage bursts at $f = 1$ kHz.

In conclusion, we have demonstrated a homeotropic LC gel whose phase modulation is polarization insensitive. Such a phase modulation is free from light scattering and hysteresis. Its response time is submillisecond at room temperature and its operation stability is excellent. The obtainable phase change is 2X larger than that of a nano-PDLC system, but at a lower operating voltage.

5.3 References


11. A. Y. G. Fuh, M. S. Tsai, L. J. Huang, T. C. Liu, “Optically Switchable Gratings Based on


CHAPTER SIX
SUMMARY AND CONCLUSION

Liquid crystals are useful for photonic and display applications. In this dissertation, we have improved the performance of LC devices in twofold: Firstly, we have developed some new liquid crystal materials. According to their physical properties, we have explored three different kinds of liquid crystals: positive dielectric anisotropic LCs, negative dielectric anisotropic LCs, and dual-frequency LCs. Secondly, we have developed a polarization independent phase modulation using a homeotropic liquid crystal gel. This gel exhibits a larger phase change and lower driving voltage as compared to the nano-sized polymer-dispersed liquid crystal droplets. Most preciously, it is a polarization independent device and has a fast response time.

Because of the different physical properties, positive $\Delta \varepsilon$, negative $\Delta \varepsilon$, and dual-frequency LCs have different performance and they require different driving schemes. In Chapter two, some positive $\Delta \varepsilon$ LC materials are presented. We introduce both high birefringence isothiocyanato tolane LCs ($\Delta n \sim 0.4$) and super high birefringence isothiocyanato biphenyl-bistolane LCs ($\Delta n \sim 0.7$). The advantage of high birefringence LC is that it can reduce the cell gap while maintaining enough phase retardation for achieving a fast response time. It is the most efficient method to shorten the response time because the response time is proportional to the square of cell gap. In addition, we have developed several high figure-of-merit (FoM) LC mixtures. FoM is a value that considers the birefringence and viscosity together, and is inversely proportional to the response time. At 70°C, our mixture has 10X higher FoM than E7 at 48°C. This mixture is currently used by Raytheon in her optical phased array. It shows a very good performance.
For display applications, positive $\Delta \varepsilon$ LCs are commonly used in the twisted nematic (TN) liquid crystal mode. The manufacturing process of TN cells is the simplest one as compared to other LC modes. The 90° TN cell also shows a good dark state between two crossed polarizers because of the polarization rotation effect. However, the viewing angle of TN cells is relatively narrow. To widen the viewing angle, vertical alignment (homeotropic) LC cell is a good choice. With the compensation films, the VA cell has high contrast ratio and wide viewing angle. However, we found that high birefringence negative $\Delta \varepsilon$ LCs do not align well in a VA cell because of the molecular interaction between the alignment layer and the LCs. This poor alignment VA cell results in a low contrast ratio. In Chapter three, we demonstrate a novel method to overcome the alignment problems. We formulated a negative $\Delta \varepsilon$ LC mixture by doping some positive or non-polar LC compound/mixture. This doped mixture has an excellent dark state in a VA cell, and presents a high contrast ratio. The contrast ratio is only limited by the dichroic ratio of the polarizers employed. Moreover, the doped compounds/mixtures increase the birefringence and lower the viscosity which, in turn, shortens the response time.

In Chapter four, we discuss the dual-frequency LC which has a special feature: its dielectric anisotropy changes sign from positive to negative when the driving voltage changes from low (several hundred hertz) to high (~30 kHz) frequency. Therefore, we can switch the cell with a constant biased voltage while switching the frequency. This will dramatically improve the response time. However, commercial DFLC materials have severe dielectric heating effect at a high frequency driving voltage. This is due to the absorption originating from the imaginary part of the dielectric constant. In this dissertation, we have developed a new liquid crystal mixture.
with negligible dielectric heating effect while keeping comparable physical properties with commercial materials. In addition, in order to measure the temperature of liquid crystal accurately, we have developed a non-contact method to measure the LC temperature inside the cell. By utilizing the unique property of temperature-dependent birefringence of LCs, we are able to probe the transient temperature by converting the transmittance to birefringence.

Homeotropic liquid crystal gel was introduced in Chapter five. We have demonstrated a polarization independent phase modulator by formulating a LC/polymer medium. The polymer networks help to shorten response time. However, it requires a relatively high driving voltage (~10V/µm). To optimize the device performance, we carefully selected the monomer concentration and curing condition, and developed a large phase shift and low driving voltage LC device. The phase shift of our homeotropic LC gel is ~ 0.08π, which is 2X larger than that of the nano-PDLC system. Moreover, our gel keeps the advantages such as free from light scattering, hysteresis, fast response, and low operating voltage.

Overall, the work reported in this dissertation benefits not only to photonics applications, but also to displays. We have discussed the LC materials from both chemical and physical points of view, and developed useful polarization-independent LC devices. This research should benefit the LC research and development communities.