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HIGH PERFORMANCE LIQUID CRYSTALS FOR DISPLAYS AND SPATIAL LIGHT MODULATORS

by

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B.S. Zhejiang University, 2012

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ABSTRACT

Liquid crystals (LCs) are an amazing class of soft materials which have been widely used in the visible, infrared (IR), millimeter wave, and terahertz spectral regions. Both amplitude modulation (e.g. displays) and phase modulation (e.g. spatial light modulators (SLMs) for adaptive optics and adaptive lens) have been investigated extensively.

Thin-film-transistor liquid crystal displays (TFT-LCDs) have become ubiquitous in our daily lives. Its widespread applications span from TVs, monitors, tablets, smartphones, augmented reality, virtual reality, to vehicle displays. LCD shows advantages in 1) high resolution, 2) long lifetime, 3) vivid colors using quantum dots backlight, and 4) high dynamic contrast ratio employing local dimming technology. However, LCD exhibits a serious problem, which is slow response time. Therefore, it is commonly perceived that LCD exhibits a more severe image blur than organic light emitting diode (OLED) displays. Indeed, the response time of LCD is ~100x slower than that of OLED. To evaluate image blurs, Motion Picture Response Time (MPRT) has been proposed to quantify the visual performance of a moving object. MPRT is jointly governed by three factors: the sample and hold effect of an active matrix display, motion pursuing, and human vision system. It is a complicated problem and is difficult to obtain analytical solution. In this thesis, we analyze the sample-and-hold effects and derive a simple equation to correlate MPRT with LC response time, TFT frame rate, and duty ratio. From our analytical equation, we find that as long as an LCD’s response time is less than 2 ms, its MPRT would be comparable to that of OLED at the same frame rate, even if the OLED’s response time is assumed to be zero. To further reduce MPRT, we could boost the frame rate to 144 Hz or reduce the duty ratio through backlight modulation. This discovery sheds new physical insights for LCDs to achieve CRT-like displays with negligible image blurs.
In addition to displays, LCs are widely employed in SLMs for modulating the phase and polarization of an incident light. This is because LCs possess high birefringence and relatively low absorption from the visible, IR, to terahertz regions. The useful applications include adaptive lens, adaptive optics, fiber-optic communication, antenna, and phase shifter. Fast response time is a common requirement for the abovementioned photonic devices. To achieve fast response time while maintaining $2\pi$ phase change, polymer-stabilized blue phase liquid crystal (BPLC) and polymer-network liquid crystal (PNLC) are promising candidates for the visible and IR SLMs, respectively. However, the operation voltage of present BPLC and PNLC devices is too high. To reduce operation voltage while keeping fast response time, we developed a new device configuration for BPLC SLM to work in the visible region. The new device structure allows the incident laser beam to traverse the BPLC layer four times before exiting the reflective SLM. As a result, the $2\pi$ phase change voltage is reduced to below 24V, which is the maximum attainable voltage for a high resolution liquid-crystal-on-silicon device. On the other hand, PNLC is a better candidate for the IR SLM because several high birefringence LC materials can be used. To reduce the operation voltage of a PNLC, we have investigated following three approaches: 1) developing large dielectric anisotropy ($\Delta \varepsilon$) and high birefringence ($\Delta n$) LC materials, 2) optimizing polymer concentration, and 3) optimizing UV curing conditions.

In the visible and near IR regions, most LCs are highly transparent. However, to extend the electro-optic application of LCs into MWIR and LWIR, absorption loss becomes a critical issue. In the MWIR region, several fundamental molecular vibration bands and overtones exist, which contribute to high absorption loss. The absorbed light turns to heat and then alters the birefringence locally, which in turns causes spatially non-uniform phase modulation. To suppress the optical loss, we have taken following approaches: (1) Designing high birefringence to minimize the LC
layer thickness; (2) Shifting the absorption bands outside the spectral region of interest by deuteration, fluorination, or chlorination; (3) Reducing the overtone absorption by using a short alkyl chain. As a result, we have developed several low loss and high birefringence chlorinated LCs for the first time. To achieve fast response time, we demonstrated a PNLC with $2\pi$ phase change at MWIR and response time less than 5 ms. Molecular tailoring strategies for extending liquid crystal SLM into long-wavelength infrared (LWIR) are also explored.
To my beloved parents and grandmother.
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CHAPTER ONE: INTRODUCTION

Amplitude, phase, wavelength and polarization are four major characteristics of a light wave. Liquid crystals (LCs) are an amazing class of soft materials which have been widely used in the visible, infrared (IR), millimeter wave, and terahertz spectral regions. Both amplitude modulation (e.g. displays) and phase modulation (e.g. spatial light modulators (SLMs) for adaptive optics and adaptive lens) have been investigated extensively.

1.1. High performance LCs for display applications

After more than four decades of extensive material research, device development and heavy investment on advanced manufacturing technologies, thin-film-transistor liquid crystal displays (TFT-LCDs) have become ubiquitous in our daily lives. Its wide applications span from indoor (e.g. TVs, monitors, virtual reality and tablets) to outdoor applications (e.g. vehicle and augmented reality displays). Twisted nematic (TN), in-plane-switching (IPS), fringing-field-switching (FFS) and vertical alignment (VA) modes have been used in display devices. Higher resolution density, more vivid colors and unnoticeable image blur are required for these displays.

Lately, “LCD versus OLED (organic light emitting diode), who wins?” is a heated debate topic.[1, 2] Each technology has its own merits and demerits. Generally speaking, LCD is leading in lifetime, peak brightness, and cost; it is comparable to OLED in resolution density, power consumption, ambient contrast ratio and viewing angle, but inferior to OLED in black state, panel flexibility, color gamut, and response time. Therefore, LCD camp has devoted a great deal of efforts to narrowing the performance gap against OLED, including quantum-dot backlight [3, 4] for achieving wider color gamut and lower power consumption, and local dimming [5] to enhance the dynamic contrast ratio to 1,000,000:1.
The remaining grand challenge for LCDs is response time; especially nematic LCDs suffer ~100x slower response time than OLED display (~0.1 ms). Thus, it is commonly perceived that LCDs exhibit more severe image blurs than OLEDs for the fast-moving objects [2]. To improve LC response time, several approaches have been investigated, e.g. polymer-stabilized blue phase LCs [6, 7], low viscosity nematic LCs [8-10], and ferroelectric LCs [11]. Nevertheless, it remains challenging for nematic LCs to achieve ~0.1 ms while keeping a low operation voltage. To evaluate image blurs, Motion Picture Response Time (MPRT) has been proposed to quantify the visual performance of a moving object. MPRT is jointly determined by the display response time (e.g. LC response time) and TFT frame rate. In Chapter Two, we analyze the MPRT of a TFT LCD and propose a simple equation to calculate it. Three ultra-low viscosity LC mixtures are developed in 1) vertical alignment (VA) mode for TV applications and 2) fringing field switching (FFS) mode for tablets and smart phones. We also proposed three approaches to improve MPRT and achieve negligible image blur.

On the other hand, there are two major challenges for outdoor displays (e.g. Vehicle displays), which could operate at extreme environments: 1) it requires an LC with high clearing point ($T_c \sim 100^\circ C$). For indoor LCD applications (e.g. TV desktop and tablet), a somewhat lower clearing point (~80°C) is still acceptable [12, 13]. While for displays inside a car, the temperature ($T$) could easily exceed 80°C during summer time. 2) The displays should remain operational at cold temperature, at least the LC should not freeze at –40°C, while keeping a reasonably fast response time below 0°C [14]. Because during winter time, the displays (e.g. the instrument cluster display and GPS) should remain functional before the car is warmed up. According to European car standard, the response time should be < 200ms at -20°C and < 300 ms at -30°C, respectively. But it is not fast enough to avoid image degradation. The general required operation temperature
is from $-30^\circ C$ to $85^\circ C$ and the storage temperature from $-40^\circ C$ to $90^\circ C$ for vehicle display applications. To boost clearing point, LC compounds with three and four rings are commonly used, which dramatically increase the visco-elastic coefficient and activation energy [15, 16]. As a result, LC response time could be as sluggish as several hundreds of millisecond and the displayed image quality is severely degraded. For electric vehicles and wearable displays, low operation voltage is also very important considering the power consumption. Therefore, we also developed three LC mixtures for vehicle displays, which exhibit advantages of 1) extraordinary wide nematic range, 2) small visco-elastic coefficient, and 3) fast response time at low temperatures.

1.2. Fast-response LCs for spatial light modulators

In addition to displays, LCs are widely employed in spatial light modulator (SLM) for modulating the intensity, phase, and polarization state of an incident light. This is because LC shows high birefringence and broad bandwidth. The operation wavelength covers from visible, IR to terahertz. Its applications include adaptive lens, adaptive optics, fiber communication, laser beam control, and terahertz imaging. There are two important factors for a spatial light modulator: 1) response time and 2) phase change. For nematic LC devices, the response time ($t_{LC}$) is determined by the LC visco-elastic coefficient ($\gamma_1/K$) and the cell gap $d$ as:

$$t_{LC} \sim \frac{\gamma_1 d^2}{K \pi^2}. \quad (1)$$

On the other hand, the phase change ($\delta$) is expressed as:

$$\delta = 2\pi l (\Delta n)/\lambda. \quad (2)$$

Here, $l$ represents the optical path, $\Delta n$ is the birefringence and $\lambda$ is the operation wavelength. For amplitude modulation, it only requires $\pi$ phase change, but for SLM it requires $2\pi$ modulo.
Therefore, if we apply the same LC for displays and SLMs, the SLM needs 2x thicker cell gap, which slows down the response time by 4x. On the other side, the response time increases as the operation wavelength increases, e.g. IR region, due to the thicker cell gap for compensating longer wavelength and lower birefringence resulted from index dispersion. Thus, it is more challenging for LC-SLM to achieve fast response time by using conventional nematic liquid crystals. For example, a typical LC decay time for a 10-μm E7 LC cell for 2π phase change is ~200 ms, which is too slow for photonic devices. Thus, there is an urgent need to reduce the LC response time to sub-millisecond range while keeping a 2π phase change. To achieve fast response time, polymer-stabilized blue phase liquid crystal (PS-BPLC) and polymer-network liquid crystal (PNLC) are promising candidates for spatial light modulators in the visible and infrared regions.

Polymer-stabilized BPLC [6, 17] is optically isotropic in the voltage-off state because of its self-assembled, nano-sized double-twist cylinder lattice structure. In the voltage-on state, Kerr effect-induced birefringence takes place so that the BPLC becomes anisotropic. Due to self-assembly, BPLC does not require any surface alignment. Furthermore, because of nanostructured double-twist cylinders its response time is usually in the submillisecond range, although the BPLC host has a huge dielectric anisotropy (Δε>100) [18] in order to lower the operation voltage. To drive a BPLC device, two types of electrodes can be used to induce birefringence: In-Plane Switching (IPS) and Vertical Field Switching (VFS) [19, 20]. IPS has been widely used for intensity modulation, but its electric field is not uniform spatially so that it is not suitable for phase modulation. On the other hand, in a VFS cell the electric field is uniform and is along the longitudinal direction. As a result, the induced phase change is polarization independent for a normally incident light. However, its phase change is only 1/3 of that of a nematic LC, which is suitable for a shorter wavelength (i.e. visible region). In Chapter Three, we will present a low-
voltage polymer-stabilized BPLC for phase-only modulation with a reflective liquid-crystal-on-silicon (LCoS) panel. A new device configuration was developed, which allows the incident laser beam to traverse the BPLC layer four times before exiting the LCoS. As a result, the $2\pi$ phase change voltage is reduced to below 24 V in the visible region ($\lambda = 400$~700 nm). The response time remains relatively fast ($\sim 3$ ms). The proposed device configuration is expected to open a new gateway for widespread applications of BPLC spatial light modulators.

Compared to polymer-stabilized BPLC, polymer-network liquid crystal (PNLC) [21] is a more promising candidate for SLM for short-wave infrared (SWIR) and mid-wave infrared (MWIR) region because it can achieve sub-millisecond response time while maintaining a large phase shift. Two major technical challenges of PNLC are: 1) its operation voltage (i.e. $V_{2\pi}$) is relatively high, originating from strong anchoring force exerted from submicron polymer network domain sizes and 2) light scattering, which is not an issue in the IR region since the polymer network domain size is much smaller than the operation wavelength. To reduce the operation voltage, several approaches have been investigated in Chapter Four, including 1) developing large dielectric anisotropy ($\Delta \varepsilon$) and high birefringence ($\Delta n$) LC materials, 2) optimizing polymer concentration, and 3) optimizing curing conditions.

For MWIR applications, besides low operation voltage and fast response time, low absorption is another critical requirement. Numerous molecular vibration bands exist in the IR region [22]. To steer a high power laser beam in the IR region, the absorption of LC must be minimized because the absorbed light is converted to thermal energy, which in turn heats up the LC material and causes spatial phase non-uniformity [23]. In the extreme case, if the resultant temperature exceeds the LC’s clearing point ($T_c$), then the light modulation capability vanishes
completely. Therefore, the LCs employed should have low absorption and high $T_c$. Therefore, three approaches are considered for shifting the vibration bands outside the spectral region of interest: (1) deuteration, (2) fluorination, and (3) chlorination. The deuteration shifts the CH vibration bands to a longer wavelength by $\sqrt{2}$, i.e. from 3.4\(\mu\text{m}\) to 4.8\(\mu\text{m}\), which unfortunately is still in the MWIR region [24]. Vibration bands of CF, CF$_2$ and CF$_3$ occur at 7~9\(\mu\text{m}\) [25]. Unfortunately, the vibration bands and overtones of CF, CF$_2$ and CF$_3$ also appear in the LWIR and MWIR regions [26]. While the intensity of the C-F overtones is relatively small, it is still noticeable in the IR region since the required cell gap is relatively thick. Thus, in order to shift the vibration bands and overtones outside the MWIR region, we consider the replacement of fluorine with a heavier atom, e.g. chlorine. The C-Cl vibration wavelength occurs in the 12.5~15.4\(\mu\text{m}\) [25] and therefore the overtone wavelength is now longer than 6\(\mu\text{m}\), which helps to clean up a high transmittance window in the MWIR and LWIR regions. The alkyl chain should be retained to preserve the flexibility and aspect ratio of LC compounds. However, some chlorinated compounds we have reported previously [15, 27] just show monotropic phases and relative high melting points ($T_m$) as the heavy atom substitution reduce the molecules’ flexibility. In Chapter Five, we discuss the molecular design strategies and report low loss LC mixtures with wide nematic temperature range. To achieve fast response time, we also demonstrated a polymer network liquid crystal with 2\(\pi\) phase change at MWIR, which will be discussed in detail in Chapter Six.
CHAPTER TWO: FAST-RESPONSE NEMATIC LIQUID CRYSTALS FOR DISPLAYS

2.1 An LCD with CRT-like motion picture response time

The image blur of a TFT LCD (or OLED) is governed by two important parameters: LC (or OLED) response time and TFT sample-and-hold time. Motion Picture Response Time (MPRT) \[28, 29\] has been proposed to quantify the visual performance of a moving object as:

\[
\text{MPRT (ms)} = \frac{\text{BEW (pixel)}}{v \text{ (pixel/frame)}} \times T_f \text{ (ms/frame)}.
\]

Here, BEW stands for the perceived blurred edge width, which is proportional to the object’s moving speed \(v\), and \(T_f\) is the TFT’s frame time (unit: ms), which is the inverse of frame rate \(f\), unit: Hz):

\[
f = \frac{1000}{T_f}
\]

Both active matrix LCDs and OLEDs are driven by TFTs, so they are hold-type displays. Thus, OLED could still suffer from motion blurs even if its response time is assumed to be zero \[30\]. Unlike LCD and OLED, CRT (cathode ray tube) is an impulse-type display, whose MRPT \(\sim 1.5\) ms and its motion blur is negligible \[31\]. The required MPRT depends on the specific applications. For example, if a smartphone or monitor is mainly intended for static images, then a slow MPRT is still acceptable. But to clearly display an object moving at speed \(v = 480\) pixels per second, the required MPRT should be less than 4 ms. If the speed doubles, then the required MPRT should be faster than 2 ms. Presently, most LCD and OLED TVs are operated at 120 Hz (i.e. MPRT \(\sim 6.66\)
ms), thus image blur remains noticeable for the fast-moving objects. There is an urgent need to reduce MPRT to ~1.5 ms in order to eliminate motion blurs.

In this part, we analyze the MPRT of a TFT LCD and then propose a simple equation to correlate MPRT with LC response time and TFT frame rate. Through our analysis, we find that if the LC’s response time is 2 ms or less, then its MPRT is nearly the same as that of OLED, even if OLED’s response time is assumed to be 0. In experiment, we prepared three ultra-low viscosity LC mixtures and used them in vertical alignment (VA) mode [32] for TVs and fringing field switching (FFS) mode [33] for smartphones. With overdrive and undershoot driving scheme, the measured average gray-to-gray (GTG) response time is only 0.93 ms for the VA cell and 5.90 ms for the FFS cell, and their average GTG MPRT is comparable to that of OLED at the same frame rate. By increasing frame rate and/or decreasing the backlight duty ratio, we can achieve MPRT~1.5 ms.

2.1.1 LC components

Table 1 lists the compound structures employed in the LC mixture, designated as MX-40702. Six major ingredients are included. The homologues (R=1 to 5) of compound 1, compounds 2 and 3 show large dielectric anisotropy and high clearing point. Their clear points range from 160 to 190 ºC, which help to widen the nematic range. However, their visco-elastic coefficient and activation energy are relative large, as the molecules are quite long and bulky. Therefore, components 4 and 5 are doped to reduce the viscosity. Component 5 also introduces a strong lateral dipole with the 2,3-difluoroaryl group which helps to maintain reasonable $|\Delta \varepsilon|$. In addition, we added component 6 (R = 0 to 3 carbon alkyl chain) to lower the threshold voltage and melting point.
The phase transition temperatures of LC mixture was measured by Differential Scanning Calorimetry (DSC, TA instruments Q100). The clearing point is 79°C and its melting point is < -40°C. Besides, we used an HP-4274 multi-frequency LCR meter to measure the capacitance of a homogeneous cell and a homeotropic cell, and then $\varepsilon_\parallel$ and $\varepsilon_\perp$ can be obtained. The dielectric anisotropy ($\Delta\varepsilon$) is calculated as:

$$\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp.$$  \hspace{1cm} (5)

Therefore, dielectric anisotropy of MX-40702 is -2.4.

Table 1: Chemical structures of the components in MX-40702.

<table>
<thead>
<tr>
<th>#</th>
<th>Chemical Structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Chemical Structure 1" /></td>
</tr>
<tr>
<td>2</td>
<td><img src="image2.png" alt="Chemical Structure 2" /></td>
</tr>
<tr>
<td>3</td>
<td><img src="image3.png" alt="Chemical Structure 3" /></td>
</tr>
<tr>
<td>4</td>
<td><img src="image4.png" alt="Chemical Structure 4" /></td>
</tr>
<tr>
<td>5</td>
<td><img src="image5.png" alt="Chemical Structure 5" /></td>
</tr>
<tr>
<td>6</td>
<td><img src="image6.png" alt="Chemical Structure 6" /></td>
</tr>
</tbody>
</table>
We also prepared another negative $\Delta \varepsilon$ LCs, HCCH 736700-100 (abbreviated as HCCH; provided by HCCH, China). The clearing point is higher than 100°C, so it can be employed in the applications at extreme environments, such as vehicle and outdoor displays. On the other hand, to compare the MPRT performance of different LCD modes in the later section, a positive $\Delta \varepsilon$ LC (DIC-LC2, provided by DIC, Japan) [16] with small viscosity was also prepared. The physical properties of these three mixtures are summarized in Table 2, including melting point ($T_m$), clearing point ($T_c$), dielectric anisotropy, elastic constants ($K_{11}$, $K_{22}$, and $K_{33}$) and rotational viscosity ($\gamma_1$).

Table 2: Physical properties of LCs at $T = 22^\circ$C.

<table>
<thead>
<tr>
<th>LCs</th>
<th>$T_m$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$\Delta \varepsilon$ (pN)</th>
<th>$K_{11}$ (pN)</th>
<th>$K_{22}$ (pN)</th>
<th>$K_{33}$ (pN)</th>
<th>$\gamma_1$ (mPaS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MX-40702</td>
<td>&lt; -40</td>
<td>70.2</td>
<td>-2.4</td>
<td>5.4</td>
<td>13.7</td>
<td>69.4</td>
<td></td>
</tr>
<tr>
<td>HCCH</td>
<td>&lt; -40</td>
<td>102</td>
<td>-2.2</td>
<td>5.3</td>
<td>19.8</td>
<td>93.0</td>
<td></td>
</tr>
<tr>
<td>DIC-LC2</td>
<td>&lt; -40</td>
<td>75</td>
<td>2.0</td>
<td>12.5</td>
<td>6.5</td>
<td>13.5</td>
<td>31.7</td>
</tr>
</tbody>
</table>

2.1.2 Physical properties

2.1.2.1 Birefringence ($\Delta n$)

To characterize the physical properties at different temperatures, we filled each LC into a homeotropic cell with cell gap $d \sim 9.3 \mu$m. The cells were mounted on a Linkam LTS 350 Large Area Heating/Freezing Stage controlled by TMS94 Temperature Programmer and then sandwiched between two crossed polarizers. A 1 kHz square-wave AC voltage was applied to the LC cell. The probing light sources were a tunable Argon ion laser ($\lambda = 457$ nm, 488 nm, and 514 nm) and a He-Ne laser ($\lambda = 633$ nm). The birefringence can be obtained from the phase retardation
δ = 2πdΔn/λ. We also measured their Δn at T < Tc as Figure 1 (a) shows. The dots are experimental data and solid lines are theoretical fittings with

\[ Δn = Δn_oS = Δn_o(1 - T/T_c)^\beta, \]  

where Δn_o is the extrapolated birefringence at T=0 K and β is a material constant. In addition to a higher Tc, HCCH also shows a higher birefringence, which helps to reduce the required cell gap for achieving fast response time.

To investigate the electro-optic performance with different colors, we also fitted the measured Δn (dots in Figure 1(b)) at each wavelength with the single-band dispersion equation[34]:

\[ Δn = G \frac{\lambda^2 - \lambda^*^2}{\lambda^2 - \lambda^*^2}. \]  

Here, G is a proportionality constant and λ* is the mean resonance wavelength. The fitting parameters in Figure 1(a) and (b) are summarized in Table 3. Once G and λ* are obtained, birefringence at other wavelengths can be estimated from Equation (7).

Figure 1: (a) Temperature dependent birefringence and (b) birefringence dispersion curves at T = 22°C for MX-40702 and HCCH.
2.1.2.2 Visco-elastic coefficient ($\gamma_1/K_{33}$):

From the response time measurement, we can extract the visco-elastic coefficient ($\gamma_1/K_{33}$) of the LC mixture. Figure 2 depicts the temperature dependent $\gamma_1/K_{33}$, in which dots represent experimental data. As the temperature decreases, $\gamma_1/K_{33}$ increases exponentially. The solid lines are the fitting curves with following equation:

$$\frac{\gamma_1}{K_{33}} = A \frac{\exp(E_a/k_B T)}{(1-T/T_c)^\beta}.$$  \hspace{2cm} (8)

In Equation (8), $A$ is a proportionality constant, $k_B$ is the Boltzmann constant, $E_a$ is the activation energy, and $\beta$ is the material constant, which has been obtained through Equation (6). Table 3 lists the fitting parameters for the LC mixtures studied. Though HCCH shows a larger $\gamma_1$ and $K_{33}$ than MX-40702, its $\gamma_1/K_{33}$ at room temperature is somewhat smaller than that of MX-40702. Besides, HCCH employs a higher concentration of three-ring components to increase the clearing point, which in turn contributes to a larger viscosity and activation energy.[10] As a result, HCCH has a faster rising rate and a larger $\gamma_1/K_{33}$ at low temperatures ($T < -0^\circ C$).

Table 3: Fitting parameters of the LC mixtures at $T = 22^\circ C$.

<table>
<thead>
<tr>
<th>LC</th>
<th>$\Delta n_0$</th>
<th>$\beta$</th>
<th>$G$ ((\mu m^2))</th>
<th>$\lambda^*$ ((\mu m))</th>
<th>$A$ (ms/(\mu m^2))</th>
<th>$E_a$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MX-40702</td>
<td>0.136</td>
<td>0.166</td>
<td>4.53</td>
<td>0.14</td>
<td>$4.19 \times 10^{-5}$</td>
<td>291</td>
</tr>
<tr>
<td>HCCH</td>
<td>0.154</td>
<td>0.167</td>
<td>2.85</td>
<td>0.19</td>
<td>$3.38 \times 10^{-6}$</td>
<td>357</td>
</tr>
</tbody>
</table>
Figure 2: Temperature-dependent visco-elastic coefficients curves. Dots represent the experimental data and solid lines are fittings with Equation (8).

2.1.3 Simulation model

Figure 3(a) illustrates a simple example about the eye tracking a bright moving object on a dark background. Here, the display is a hold-type display[35], i.e. the object is still on the panel within one frame time and jumps to another position with speed $v$. However, human eyes smoothly pursue the object with the speed $v_h$. Generally, we assume that $v_h = v$. This discrepancy between the hold-type display and human vision system results in image blurs on retina. The perceived motion picture blur (Figure 3(b)) is determined by the sum of the pixel’s intensity along the motion trajectory within one frame period. The position-dependent luminance curve is exhibited in Figure 3(b) and the blurred edge width is defined as the space interval between 10% and 90% luminance change.[36] The BEW depends on the moving speed: the higher the moving speed, the more severe image blurs a human eye can observe. To determine MPRT, several approaches have been investigated, such as employing pursuit camera method and using time based image integration.[29]
The pursuit camera approach can reproduce the BEW and calculate the MPRT by using Equation (3), however, how the LC response affects the MPRT cannot be extracted quantitatively through this method. On the other hand, the time based image integration approach has been demonstrated to be a better way to correlate the liquid crystal response curve (LCRC) with the motion picture response curve (MPRC).

**Figure 3:** Illustration of the eye tracking a moving bright object on a dark background. (b) The perceived image blur and position dependent normalized luminance.

MPRC is related to the LC response curve in conjunction with eye-tracking and temporal integration as follows [37, 38]:

\[
MPRC(t) = \frac{1}{T_f} \int_{t-T_f}^{t} T(t') dt'.
\]  

In Equation (9), MPRC represents the normalized luminance profile of the blurred image in the temporal domain and \( T(t') \) is the output time-dependent transmittance curve, which is jointly determined by the LC response curve and backlight modulation. **Figure 4(a) and 4(b)** depict the output time-dependent transmittance curve without and with backlight modulation, respectively.
MPRC(t) can be derived from the output time-dependent transmittance by applying one-frame-time moving window function (Figure 4(c)) as [38]:

$$MPRC(t) = \frac{1}{T_f} \times [T(t) \ast H(T_f)],$$  

where $\ast$ denotes the convolution operation and $H(T_f)$ is the rectangle function with width of $T_f$.

![Figure 4](image)

Figure 4: Illustration of output time-dependent transmittance curve on hold-type displays: (a) without backlight modulation and (b) with backlight modulation. The duty ratio of backlight is $A/T_f$. (c) LC response curve and one-frame-time moving window. (d) Illustration of MPRC of LC and OLED at $f = 120$Hz and the starting point $t_0 = 0$.

Let us first consider the simplest case without backlight modulation. Under such condition, $T(t)$ is simply the LC response curve. For a VA cell, the time-dependent optical decay curve $T_{LC\_decay}(t)$ has been solved analytically as [39]:

$$T_{LC\_decay}(t)$$


\[ T_{LC\_\text{decay}}(t) = \sin^2\left( \frac{\delta_0 \exp(-2t/\tau_0)}{2} \right), \]
\[ \tau_0 = \frac{\gamma_1 d^2}{K_{33} \pi^2}, \]

where \( \delta_0 \) is the phase retardation change, \( \tau_0 \) stands for the LC director reorientation time, which is determined by the LC visco-elastic coefficient \( (\gamma_1/K_{33}) \) and cell gap \( d \). However, \( \tau_0 \) is difficult to measure directly. In experiment, we measure the LC optical response time \( (\tau) \), which is defined as the time interval between 10\% and 90\% transmittance change. For a VA cell under small angle approximation, the optical decay time \( \tau_d = a \tau_0 \), where \( a \approx 0.3-0.4 \), depending on the initial \( \delta_0 \) value [39].

On the other hand, the optical rise curve \( (T_{LC\_\text{rise}}(t)) \) of the VA cell is much more complicated because it also depends on the applied voltage [39]:

\[ T_{LC\_\text{rise}}(t) = \sin^2\left( \frac{\delta_0/2}{1 + \left[ \frac{\phi_\infty^2}{\phi_0^2} - 1 \right] \exp\left( \frac{-2t}{\tau_r} \right)} \right), \]
\[ \tau_r = \frac{\tau_0}{\left( \frac{V}{V_{th}} \right)^2 - 1}. \]

In Equations (13) and (14), \( \phi_\infty \) and \( \phi_0 \) represent the tilt angle at \( t \to \infty \) and \( t = 0 \), \( V \) is the applied voltage and \( V_{th} \) is the threshold voltage. From Equation (14), the rise time could be slow when \( V \) is slightly above \( V_{th} \). To overcome this shortcoming, overdrive and undershoot voltage method [40] has been commonly used to speed up the rise time. Therefore, the LC response time is mainly limited by the decay time. Equation (9) can be
derived from the LC response curve by applying one-frame-time moving window function. Therefore, the starting point of MPRC is affected by the tailing transmittance of the previous frame, which makes the MPRC calculation more complicated. To elucidate the derivation procedures without losing its generality, let us assume that the rise-response curve is symmetric to the decay curve (i.e. $\tau_r=\tau_d$):

$$T_{LC\_rise}(t) = \begin{cases} 0; & \text{for } t < t_0 \\ 1 - \sin^2 \left( \frac{\delta_0 \exp(-2(t-t_0)/\tau_0)}{2} \right); & \text{for } t \geq t_0 \end{cases}$$ (15)

That means at $t = t_0$, the LCD is switched from the darkest state ($T = 0$) to the brightest state ($T = 1$), and the transition time is equal to that of decay process. Therefore, the MPRC can be obtained by simultaneously solving Equations (15) and Equation (10). In Figure 4(d), the MPRC of OLED is also included as benchmark for comparison and we assume its response time is 0. Similar to LC response time, MPRT is also defined as the time interval between 10% and 90% luminance change, as Figure 4(d) depicts.

Substituting Equation (15) into Equation (10), we find:

$$MPRC(t) = \begin{cases} \frac{1}{T_f} \int_{t_0}^{t_0+t} T_{LC\_rise}(t') \, dt'; & \text{if } t_0 \leq t \leq T_f + t_0, \\
\frac{1}{T_f} \int_{t+T_f}^{t} T_{LC\_rise}(t') \, dt'; & \text{if } t > T_f + t_0. \end{cases}$$ (16)

To simplify the derivation process, let us assume $t_0 = 0$. After Taylor’s expansion and only keeping the first and second order terms, we derive the following time-dependent MPRC:

$$MPRC(t) \approx \begin{cases} \frac{1}{T_f} \left( t + \frac{\pi^2 \tau_0}{16} \exp(-\frac{4t}{\tau_0}) - 1 \right); & \text{for } 0 < t \leq T_f, \\
\frac{1}{T_f} \left( T_f + \frac{\pi^2 \tau_0}{16} \exp(-\frac{4t}{\tau_0})[1 - \exp(\frac{4T_f}{\tau_0})] \right); & \text{for } t \geq T_f. \end{cases}$$ (17)
MPRT can be obtained by taking the time interval between 10% and 90% luminance change. From Equation (17), we find that MPRT is jointly determined by the LC response time \( \tau \approx a\tau_0 \) and TFT frame time \( T_f \). In general, we can use numerical method to plot the MPRC [Equation (17)] and then obtain the MPRT. But it would be highly desirable if we can derive an analytical expression for MPRT and comprehend how the LC response time and TFT frame time affect MPRT.

![Figure 5](image_url)

**Figure 5:** (a) LC response time vs. MPRT. Solid lines represent the calculated results from Equation (20) and dots are simulation results using Equations (10) and (15). (b) Open circles and triangles are experimental data measured with HCCH VA mode at \( f = 120\text{Hz} \) and 240Hz. Pluses and crosses are experimental data reported in Ref. 11.

To obtain an analytical solution, let us first consider two extreme conditions without backlight modulation: \( \tau \rightarrow 0 \) and \( \tau \gg T_f \). When the LC response time is very fast, we set \( \tau_0 \rightarrow 0 \) and Equation (17) is simplified as:

\[
MPRC(t) = \begin{cases} 
\frac{t}{T_f}, & \text{if } t < T_f \\
1, & \text{if } t \geq T_f 
\end{cases}
\]  

(18)
Such a MPRC is plotted in Figure 4(d) (black line). From Figure 4(d), we find the limiting MPRT $\approx 0.8T_f$. Note: the coefficient 0.8 originates from the MPRT definition, which is from 10% to 90% luminance change. Under such a condition, as the TFT frame rate ($f$) increases (i.e. $T_f$ decreases), the limiting MPRT decreases linearly. On the other hand, if the TFT frame rate is so fast that the LC cannot follow, i.e. $\tau >> T_f$, the one-frame time window can be regarded as a pulse function, and Equation (10) can be simplified as:

$$MRC(t) \approx T(t)\delta(t) = T(t).$$

Therefore, MPRC overlaps with the LC response curve ($T(t)$), i.e. MRPT $\approx \tau$, which is independent of the frame rate and is solely determined by the LC response time.

To satisfy these two boundary conditions, based on the eye pursuit tracking diagram shown in Figure 3(a) we propose the following equation to correlate MPRT with LC response time ($\tau$) and frame time ($T_f$):

$$MPRT \approx \sqrt{\tau^2 + (0.8T_f)^2}. \quad (20)$$

To validate Equation (20), we compare the MPRT results with the simulated ones without approximation. Results are plotted in Figure 5(a), where the solid lines represent equation (20) at the specified frame rates, and the dots are the simulation results using Equations (10) and (13) without approximation. The agreement between the rigorous simulation and Equation (20) is very good. With Equation (20), we can see easily how the LC response time and TFT frame rate affect MPRT.

From Figure 5(a), we find three important trends: (1) At a given frame rate, say 120 Hz, as the LC response time decreases, MPRT decreases almost linearly and then gradually saturates. Note that the MPRT for $\tau = 2$ ms is only 4% longer than that of $\tau = 0$. Therefore,
if an LCD’s response time is 2 ms, then its MPRT is comparable to that of an OLED, even if the OLED’s response time is assumed to be 0. (2) As the TFT frame rate increases, the limiting MPRT (assuming \( \tau = 0 \)) decreases linearly, because the limiting MPRT = 0.8\( T_f \).

(3) If the LC response time is not fast enough, say \( \tau = 5 \) ms, then increasing the frame rate from 60 Hz to 120 Hz makes a big improvement in MPRT, but further increasing the frame rate to 240 Hz and 480 Hz the improvement is less obvious. This prediction is consistent with those observed experimentally.\[41\]

Besides LC response time, another factor affecting the output transmittance \( T(t) \) is the backlight modulation, as depicted in Figure 4(a) and (b), where \( A \) stands for the time that backlight (e.g. LED) is turned on in one frame time. The duty ratio (DR) is defined as:

\[
DR = A/T_f.
\]

The MPRC can be calculated numerically using Equation (10). As \( T(t) \) becomes discontinuous in one frame and it is determined jointly by the LC response time and the backlight modulation, so that it is quite complicated to get the analytical expression for MPRC. If the LC response time is fast (e.g. \( \tau \leq 2 \) ms), then the LC directors can achieve final gray-level when the backlight is turned on. Thus, \( T(t) \) can be simplified by the periodic rectangle function [red lines in Figure 4(b)]. After taking the convolution, MPRC increases with time linearly. Therefore, the MPRT can be expressed as:

\[
MPRT \approx 0.8 \times T_f \times DR = 800 \times DR / f.
\]

From Equation (22), we can achieve a fast MPRT by reducing the duty ratio or increasing the frame rate. We will discuss the duty ratio effects later.
To validate our analytical results, we measured the MPRT of two commonly employed LC modes: VA and FFS. Multi-domain VA LCDs have been widely used in large-size TVs and monitors because of their high contrast ratio and wide viewing angle. On the other hand, FFS mode has advantages in wide view, weak color shift and pressure resistance for touch panels. Thus, FFS mode is commonly used in touch panel displays, such as smartphones and tablets. Depending on the sign of dielectric anisotropy ($\Delta\varepsilon$), FFS can be categorized into positive type (p-FFS) and negative type (n-FFS).

Figure 6: For VA mode, the measured GTG LC response time of (a) MX-40702 and (b) HCCH. The corresponding GTG MPRT at $f=120$ Hz for (c) MX-40702 and (d) HCCH.
In experiment, we filled MX-40702 and HCCH into two VA cells ($d = 3.3 \, \mu m$) and two n-FFS cells ($d = 3.3 \, \mu m$). Besides, a positive $\Delta \varepsilon$ LC (DIC-LC2) was also used for investigating the MPRT of p-FFS cell ($d = 3.6 \, \mu m$). In Figure 5(b), we plot the GTG LC response time vs. MPRT at $f = 120$ Hz (open circles) and 240 Hz (triangles) for the HCCH VA cell. Overdrive and undershoot method was applied to achieve faster response time. The solid lines represent Equation (20) at four different frame rates. Good agreement is obtained between experiment and Equation (20). We also include the experimental data taken at $f = 60$ Hz and 120 Hz from Ref. 11 for comparison. Good agreement is also found.

Table 4: Average GTG LC response time and MPRT for different LCDs and OLED

<table>
<thead>
<tr>
<th>LCs</th>
<th>Average GTG LC response time (ms)</th>
<th>Average GTG MPRT $f=60$ Hz (ms)</th>
<th>Average GTG MPRT $f=120$ Hz (ms)</th>
<th>Average GTG MPRT $f=240$ Hz (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VA</td>
<td>MX-40702</td>
<td>0.93</td>
<td>13.40</td>
<td>6.80</td>
</tr>
<tr>
<td>VA</td>
<td>HCCH</td>
<td>1.56</td>
<td>13.46</td>
<td>6.87</td>
</tr>
<tr>
<td>p-FFS</td>
<td>DIC-LC2</td>
<td>2.95</td>
<td>13.83</td>
<td>7.49</td>
</tr>
<tr>
<td>n-FFS</td>
<td>MX-40702</td>
<td>5.90</td>
<td>15.03</td>
<td>9.40</td>
</tr>
<tr>
<td>OLED</td>
<td>-</td>
<td>0.10</td>
<td>13.33</td>
<td>6.67</td>
</tr>
</tbody>
</table>

Figure 6 (a)-(d) show the measured GTG LC response time and its corresponding MPRT at $f=120$ Hz for VA cells with MX-40702 and HCCH. For n-FFS and p-FFS modes, the measured GTG LC response time and MPRT are plotted in Figure 7(a)-(d). For convenience, we also list the average GTG LC response time and MPRT in Table 4.
From Figure 6 and 7, we can see that our VA cells exhibit a faster response time than FFS cells. To understand this difference, we need to know their operation mechanisms. In general, the response time of an LC cell can be written as:

\[ \tau \propto \gamma_1 d^2 / (K_{ii} \pi^2), \]  

where \( K_{ii} \) stands for splay (\( K_{11} \)), twist (\( K_{22} \)) or bend (\( K_{33} \)) elastic constant. If the cell gap is the same, then the response time of a VA cell is determined by \( \gamma_1 / K_{33} \), but for a FFS cell it is governed by \( \gamma_1 / K_{22} \). In our VA cell with MX-40702 (and HCCH), its average GTG response time is 0.93 ms (and 1.56 ms), which is 6.1x (and 3.6x) faster than that of a commercial LCD.[2] From Figure 6(c) and (d), the average GTG MPRT of both VA cells is only ~3% slower than that of OLED at the same frame rate (e.g. \( f = 120 \) Hz). That is to say, these VA LCDs exhibit comparable motion image blurs to OLEDs, except for some slower gray level transitions, e.g. from gray level 8 to 1. Besides, HCCH has a slightly higher birefringence, thus its required cell gap can be reduced to \( d \sim 3 \) µm. By doing so, the response time can be reduced by ~20%.

From Figure 7, both p-FFS and n-FFS cells show a slower response time than that of VA mode. This is because for both p-FFS and n-FFS modes, the corresponding elastic constant is \( K_{22} \), but for VA it is \( K_{33} \). From Table 2, the \( K_{22} \) of MX-40702 and HCCH is about 2-3x smaller than their \( K_{33} \). On the other hand, the p-FFS cell shows a faster response time than that of n-FFS. This is because DIC-LC2 processes a much lower viscosity[9] than MX-40702 and HCCH for a similar \(|\Delta \varepsilon|\). Nevertheless, n-FFS exhibits a ~15% higher static transmittance than p-FFS[42]. For mobile phones and tablets using FFS mode, the frame rate is \( f = 60 \) Hz or lower in order to reduce power consumption. From Table 4, at \( f = 60 \) Hz the MPRT of p-FFS and n-FFS is 3% and 12% slower than that of OLED, respectively.
This difference becomes smaller if the frame rate is reduced to 30Hz, because MPRT is less sensitive to the LC response time at low frame rate. Therefore, LCD and OLED exhibit comparable image performance in terms of motion picture blur for TV, monitor and smartphone applications.

![Figure 7: The GTG LC response time with (a) MX-40702 for n-FFS and (b) DIC-LC2 for p-FFS. The GTG MPRT at f=60Hz for (c) MX-40702 and (d) DIC-LC2.]

2.1.5. Discussion

To reduce image blurs, here we present three approaches: higher frame rate, backlight modulation, and combination of both. From Table 4, if the frame rate is increased from 120 Hz to 240 Hz, the MPRT of VA LCD and OLED is reduced by ~2x yet remaining comparable (3.58 ms vs. 3.33 ms). The MPRT of p-FFS and n-FFS is also improved by ~1.5x. A major tradeoff of higher frame rate is the increased electronic power consumption.
The second approach to reduce MPRT is through backlight modulation. Figure 8(a) exhibits the simulation results of LC response time dependent MPRT with different duty ratios. The frame rate is \( f = 144 \) Hz. The limiting MPRT (i.e. \( \tau=0 \)) is reduced linearly when the backlight duty ratio decreases, as Equation (22) shows. The reasons are twofold: (1) The slow transition part of LC is obscured by the delayed backlight, and (2) the sample-and-hold effect is suppressed because such an operation mechanism is similar to CRT’s impulse driving. As a matter of fact, to suppress image blurs Sony’s OLED TVs also employed 50% duty ratio[29], because MPRT decreases linearly with duty ratio. To minimize an LCD’s motion blur for high-speed gaming or sports, the targeted MPRT is 1.5 ms, similar to CRT. As Figure 8(a) shows, if we raise the frame rate to 144 Hz and reduce the duty ratio to 20%, then the MPRT is \(~1.1\) ms. Although a low duty ratio helps to improve MPRT, the major tradeoff is reduced brightness. To compensate for the brightness loss, we can boost the current of the LED backlight. For OLED, in principle we can do the same impulse driving. However, high current impulse driving of OLED leads to substantial efficiency roll-off [43] and lifetime degradation [44]. Similarly for LCD, high current driving of blue LED also suffers from droop effect [45], i.e. the internal quantum efficiency declines as the current density increases. Fortunately, the impact of droop effect to LED is substantially weaker than the declined efficiency and compromised lifetime to OLED. That is to say, OLED is much more vulnerable than LCD to impulse driving. As a matter of fact, the impulse driving of LCD has been attempted using black image insertion or blinking backlight more than a decade ago [46-48] The improvement was indeed substantial, except that the intrinsic LC response time was slow (\(~20\) ms) so that the blurs were still noticeable.
The third approach to achieve much faster MPRT is to combine high frame rate with backlight modulation. From Equation (22), if we increase the frame rate to 240 Hz while keeping duty ratio at ~45%, then we can achieve MPRT ~1.5 ms. However, increasing frame rate would increase the electronic power consumption. For a 55-inch LCD TV, the electronic part consumes ~10% of total power, while the backlight shares the rest 90%. But for a 5-in smartphone, the electronic and optical parts contribute nearly equally. Therefore, a proper combination between frame rate and duty ratio should be optimized, depending on the applications.

As depicted in Figure 8(a), at a certain frame rate and duty ratio, there exists an abrupt jump of MPRT as the LC response time increases. The LC response time at the jump is defined as the tolerable LC response time (τT). Therefore, to achieve a comparable MPRT to that of OLED with the same duty ratio, LC response time should be τ ≤ τT. For example at f = 144 Hz, to achieve ~1 ms MPRT the required duty ratio is 20% and τT ~5.1 ms. Since the average GTG response time of both VA (with MX-40702 or HCCH) and p-FFS (DIC-LC2) are all less than 5 ms, MPRT ~ 1 ms can be achieved by a proper combination between frame rate and duty ratio.

Figure 8(b) shows the tolerable LC response time at each duty ratio for different frame rates. As depicted, τT increases linearly as the duty ratio decreases. This is because the longer LC transition process is not perceived when the backlight is off. For displays without backlight modulation, τT can be obtained by extrapolating the line shown in Figure 8(b), which helps us to determine the acceptable LC response time for different frame rates. When τ ≤ τT, the MPRT increases with LC response time slowly (< 6%), which is a rather
negligible change compared to the limiting MPRT. Therefore, it shows comparable image performance to OLED in terms of motion picture blur. On the other hand, for $\tau > \tau_T$, the MPRT increases with the LC response time linearly. The corresponding MPRT can be calculated using Equation (20) easily.

Figure 8: (a) LC response time vs. MPRT with different duty ratios at $f = 144$ Hz. (b) Duty ratio vs. tolerable LC response ($\tau_T$) at different frame rates.

2.1.6 Conclusion

In summary, we reported two negative $\Delta \varepsilon$ LCs with a small visco-elastic coefficient. For VA LCDs, the average MPRT is comparable to that of OLED at the same frame rate. Faster MPRT can be obtained by increasing the frame rate, reducing the backlight duty ratio, and the combination of both. Using $f = 144$ Hz and 20% duty ratio or $f = 240$Hz and $\sim 45\%$ duty ratio, we can achieve MPRT $< 1.5$ ms to display fast-moving objects without motion blurs. On the other hand, for mobile displays, FFS modes with our LC mixtures also exhibit a similar MPRT to that of OLED at $f \leq 60$Hz.
2.2 High performance liquid crystals for vehicle displays

Several liquid crystal display (LCD) devices have been widely used in a vehicle [49], such as head-up display (HUD) [50], wearable display, instrument cluster display, center information display, and entertainment display [51]. Mixed-mode twisted nematic (MTN) [52], twisted nematic (TN) [53] and fringe field switching (FFS) [33, 42, 54] are the main liquid crystal (LC) modes employed in the vehicular display system. For examples, 1) MTN is commonly used for liquid-crystal-on-silicon (LCOS) reflective projection displays (e.g. HUD and wearable displays) [16], since it exhibits high reflectance, low operation voltage, and small fringing field effect [55]. 2) Transmissive TN LCD is employed in instrument cluster displays since the device requires fast response time and high brightness. The viewing angle of TN mode is relatively narrow. However, the instrument cluster display only shows information to the driver, thus narrow viewing angle is acceptable. 3) FFS LCD is applied to center information display (e.g. Global Positioning System (GPS)) and entertainment displays since information sharing, high image quality and touch panel are preferred for those displays. FFS mode shows advantages in wide view, weak color shift and pressure resistance for touch panels. However, there are two major challenges for vehicular displays in the extreme environment [56]: 1) it requires an LC with high clearing point \( T_c \sim 100^\circ\text{C} \). For other LCD applications (e.g. TV, desktop and smartphones), a somewhat lower clearing point \( \sim 80^\circ\text{C} \) is still acceptable [12, 13]. While for displays inside a car, the temperature \( T \) could easily exceed \( 80^\circ\text{C} \) during summer time. 2) The displays should remain operational at cold temperature, at least the LC should not freeze at \( -40^\circ\text{C} \), while keeping a reasonably fast response time below \( 0^\circ\text{C} \) [14]. Because during winter time, the displays (e.g. the instrument cluster display and GPS) should remain functional before the car is warmed up. According to European car standard, the
response time should be < 200ms at -20°C and < 300 ms at -30°C, respectively. But it is not fast enough to avoid image degradation. The general required operation temperature is −30°C ~ 85°C and the storage temperature is −40°C ~ 90°C for vehicle display applications. To boost clearing point, three-ring and four-ring LC compounds are commonly used, which dramatically increase the visco-elastic coefficient and activation energy [15, 16]. As a result, LC response time could be as sluggish as several hundreds of millisecond and the display image quality is severely degraded. For electric vehicles, low operation voltage is also very important considering the power consumption.

In this part, we report three high performance LC mixtures with an extraordinary wide nematic range (−40°C to ~100°C), small visco-elastic coefficient, and low activation energy for automobile displays. Physical properties at different temperatures and wavelengths are characterized. We also explored these LC mixtures for different applications. For HUD projection display and wearable display, we obtain submillisecond average gray-to-gray (GTG) response time (~0.3 ms) in a MTN LC. By applying LCs to FFS and TN LCDs, the response time is less than 20 ms for FFS at 0°C and TN at −20°C, respectively. With overdrive voltage [40], the average GTG response time is further reduced by ~2X (< 10ms) at these low temperatures.

2.2.1. LC components

Table 5 lists the chemical structures of compounds employed in LC mixture, designated as MCRI. Four major ingredients are included. The homologues (different alkyl chain length R) of Compound 1 show high birefringence (Δn) and large dielectric anisotropy (Δε > 25). However, their visco-elastic coefficient and activation energy are relatively large. To reduce viscosity, we doped ~50 wt% non-polar diluters (i.e. Compound 2 [8, 57]). Compounds 3 and 4 (~30 wt%) are
added to obtain high clearing point ($T_c$) and wide nematic range. We also prepared other two LCs (designated as DIC-57F-15 and DIC-57F-16) with different visco-elastic constant and $\Delta \varepsilon$, which can be achieved by adjusting the concentration of non-polar diluters (Compound 2). The phase transition temperatures were measured by Differential Scanning Calorimetry (DSC, TA instruments Q100). Remarkably, the melting points ($T_m$) are below $-40^\circ C$ (due to the limit of our DSC) and $T_c \sim 100^\circ C$ for all three LCs, which show high durability in harsh environments. To determine $\Delta \varepsilon$, we measured the capacitance of a homogeneous and a homeotropic cell using an HP-4274 multi-frequency LCR meter. The measured phase transition temperatures and dielectric anisotropy of three LCs are summarized in Table 6.

Table 5: Chemical structures and compositions of MCRI.

<table>
<thead>
<tr>
<th>Compounds #.</th>
<th>Chemical structure</th>
<th>wt %</th>
</tr>
</thead>
<tbody>
<tr>
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<td><img src="image1" alt="Chemical structure" /></td>
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</tr>
<tr>
<td>3</td>
<td><img src="image3" alt="Chemical structure" /></td>
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</tr>
<tr>
<td>4</td>
<td><img src="image4" alt="Chemical structure" /></td>
<td>9</td>
</tr>
</tbody>
</table>
2.2.2. Physical Properties

2.2.2.1 Birefringence

To characterize the physical properties at different temperatures, we filled each LC into a homogeneous cell with cell gap ($d \sim 5\mu m$). A Merck mixture (MLC-6241-000) with similar $T_c$ ($\sim 99^\circ C$) was included as a benchmark for comparison. This is not the best mixture developed by Merck for practical applications but it is what we can find in our lab. The cells were mounted in a Linkam LTS 350 Large Area Heating/Freezing Stage controlled by TMS94 Temperature Programmer and then sandwiched between two crossed polarizers. A 1 kHz square-wave AC voltage was applied to LC cells. The probing light sources were a tunable Argon ion laser ($\lambda = 457$nm, 488nm, and 514nm) and a He-Ne laser ($\lambda = 632.8$ nm). The birefringence can be obtained from the phase retardation $\delta = 2\pi d\Delta n/\lambda$ [58]. We also measured their $\Delta n$ at $T = 10 \sim 90^\circ C$ as Figure 9(a) shows. The dots are experimental data and solid lines are theoretical fittings with Equation (6). DIC-57F-15 shows a higher birefringence than other mixtures because it contains more compounds with a longer conjugation length (e.g. Compounds 1 and 3 in Table 5). High birefringence helps to reduce the required cell gap for achieving fast response time. The $\Delta n$ of DIC-57F-16 and MCRI is $\sim 0.1$, which helps minimize the color dispersion of the LCD.

To investigate the electro-optic performance with different colors, we also fitted the measured $\Delta n$ (dots in Figure 9(b)) at each wavelength with the single-band dispersion equation as Equation (7). The fitting parameters in Figure 9(a) and (b) are summarized in Table 7. Once $G$ and $\lambda^*$ are obtained, birefringence at any wavelength can be calculated from Equation (7). Our results are: $\Delta n = 0.122, 0.117$ and $0.105$ at $\lambda = 550$nm for DIC-57F-15, DIC-57F-16 and MCRI, respectively. These values are included in Table 6 and will be used in the device simulation later.
Table 6: Physical properties of four LC mixtures at $T = 25^\circ C$

<table>
<thead>
<tr>
<th>LC mixture</th>
<th>$T_m$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$\Delta\varepsilon$</th>
<th>$\Delta n$ ($\lambda = 550$nm)</th>
<th>$K_{11}$ (pN)</th>
<th>$\gamma_1$ (mPaS)</th>
<th>$K_{22}$ (pN)</th>
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<tr>
<td>DIC-57F-15</td>
<td>&lt; -40</td>
<td>102</td>
<td>5.0</td>
<td>0.12</td>
<td>12.9</td>
<td>70.5</td>
<td>7.7</td>
</tr>
<tr>
<td>DIC-57F-16</td>
<td>&lt; -40</td>
<td>97</td>
<td>4.4</td>
<td>0.12</td>
<td>11.9</td>
<td>63.4</td>
<td>7.3</td>
</tr>
<tr>
<td>MCRI</td>
<td>&lt; -40</td>
<td>104</td>
<td>4.0</td>
<td>0.11</td>
<td>12.0</td>
<td>55.3</td>
<td>4.7</td>
</tr>
<tr>
<td>MLC-6241-000</td>
<td>-</td>
<td>99</td>
<td>5.5</td>
<td>0.09</td>
<td>13.8</td>
<td>133.5</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Figure 9: (a) Temperature dependent birefringence and (b) dispersion curves at $T = 25^\circ C$ for the LC mixtures studied. Dots are measured data and solid lines are fitting curves with Equations (6) and (7) in (a) and (b), respectively.

2.2.2.2 Visco-elastic coefficient

From the response time measurement, we can extract the visco-elastic coefficient ($\gamma_1/K_{11}$) of the LC mixture [59]. Figure 10 depicts the $\gamma_1/K_{11}$ from $-30^\circ C$ to $90^\circ C$, in which dots represent experimental data. As the temperature decreases, $\gamma_1/K_{11}$ increases exponentially. The solid lines are the fitting curves with Equation (8). Table 7 lists the fitting parameters for all four LC mixtures.
studied. Our new LCs exhibit a smaller $\gamma/K_{11}$ than MLC-6241-000 at any temperature. Besides, the new LCs have similar $\gamma/K_{11}$ at $T \sim 35^\circ\text{C}$. However, MCRI has the smallest activation energy and slowest rising rate as the temperature decreases. The activation energy ($E_a$) is affected by several parameters such as molecular structure and conformation, and intermolecular interactions [23].

Table 7: Fitting parameters of the four LC mixtures at $T=25^\circ\text{C}$

<table>
<thead>
<tr>
<th>LC mixture</th>
<th>$\Delta n_0$</th>
<th>$\beta$</th>
<th>$G$ (µm²)</th>
<th>$\hat{\lambda}$ (µm)</th>
<th>$A$ (ms/µm²)</th>
<th>$E_a$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIC-57F-15</td>
<td>0.15</td>
<td>0.16</td>
<td>1.83</td>
<td>0.23</td>
<td>5.26$\times$10$^{-5}$</td>
<td>290.3</td>
</tr>
<tr>
<td>DIC-57F-16</td>
<td>0.15</td>
<td>0.17</td>
<td>2.64</td>
<td>0.20</td>
<td>4.23$\times$10$^{-4}$</td>
<td>235.7</td>
</tr>
<tr>
<td>MCRI</td>
<td>0.14</td>
<td>0.18</td>
<td>2.19</td>
<td>0.20</td>
<td>1.24$\times$10$^{-3}$</td>
<td>204.9</td>
</tr>
<tr>
<td>MLC-6241-000</td>
<td>0.11</td>
<td>0.16</td>
<td>-</td>
<td>-</td>
<td>3.54$\times$10$^{-4}$</td>
<td>253.7</td>
</tr>
</tbody>
</table>

To reduce the viscosity at room temperature, MCRI employs a higher concentration of non-polar diluters (Compound 2 in Table 5). As a result, its $E_a$ is relatively small, which in turn contributes to a mild increase of visco-elastic coefficients. Therefore, the visco-elastic coefficient of MCRI is the smallest at low temperature. While, DIC-57F-15 exhibits a smaller $\gamma/K_{11}$ at $T > 35^\circ\text{C}$ due to a larger activation energy. So its $\gamma/K_{11}$ decreases dramatically at elevated temperatures. Therefore, DIC-57F-16 and MCRI show better performance especillay faster response time at low temperatures. The response time is propotional to $\gamma/K_{11}$ and $d^2$. DIC-57F-15 shows the highest $\Delta n$ among four LCs. As a result, the required cell gap of DIC-57F-15 is the thinnest to achieve the same phase retardation. With a thinner cell gap and smaller $\gamma/K_{11}$ at elevated temperatures, DIC-
57-15 is more suitable for projection displays, whose operation temperature is 35-55°C, depending on the employed light source (LED or arc lamp). We will discuss their applications later.

![Figure 10: Temperature dependent visco-elastic coefficients. Dots are experimental data and solid lines are the fitting curves with Equation (8).](image)

2.2.2.3. Elastic constants $K_{11}$ and $K_{22}$

Elastic constants affect the threshold voltage and response time of a LC device. For the above mentioned MTN, TN and FFS LCDs, splay ($K_{11}$) and twist ($K_{22}$) elastic constants are more important than the bend ($K_{33}$). We measured $K_{11}$ from the threshold voltage ($V_{th}$) based on the voltage-dependent transmittance ($VT$) curve since $V_{th}$ is expressed as [60-62]:

$$V_{th} = \pi \sqrt{\frac{K_{11}}{\varepsilon_0 \Delta \varepsilon}},$$

(24)
where $\varepsilon_0$ is the permittivity of free space. Because $\gamma_1/K_{11}$ has been obtained by measuring the free relaxation time, we can extract the rotational viscosity ($\gamma_1$) easily. Results are also included in Table 6.

To obtain $K_{22}$, Xu et al. [63] derived following semi-empirical equation to describe the optical decay time of an In-Plane Switching (IPS) cell:

$$\tau_d = 1.238 \frac{\gamma_1 d^2}{K_{22} \pi \tau}.$$  \hfill (25)

In experiment, we prepared four IPS cells whose substrates were coated with a thin polyimide (PI) layer to provide strong anchoring energy. The cells were sandwiched between two crossed linear polarizers with the bottom polarizer’s transmission axis parallel to the LC rubbing direction. First, we measured the VT curve of each mixture at $T = 25^\circ$C and biased the LC cell at peak transmission voltage. Then we removed the bias voltage instantaneously and recorded the transient decay time with a digital oscilloscope. Using Equation (25), we can calculate $K_{22}$. Results are also listed in Table 6.

2.2.2.4. Discussion

As Table 6 shows, a smaller $\Delta \varepsilon$ mixture tends to have a lower $\gamma_1$ because it consists of a higher concentration of diluters (compound 2 in Table 5). Diluters are nonpolar short-chain compounds with a very low viscosity. There is a linear relationship between $\Delta \varepsilon$ and $\gamma_1$ for LCs with $T_c \approx 80^\circ$C and $\Delta n \approx 0.1$[8]. These LCs have been widely used in TVs, smartphones and wearable displays. Figure 11 depicts the dielectric anisotropy ($\Delta \varepsilon$) vs. rotational viscosity ($\gamma_1$) of several positive (+) and negative (−) $\Delta \varepsilon$ LCs with $T_c \approx 80^\circ$C and $T_c \approx 100^\circ$C. All three kinds of LCs show linear relationship between $|\Delta \varepsilon|$ and $\gamma_1$. The extrapolated $\gamma_1 = 30$ mPas when $\Delta \varepsilon \to 0$, which
represents the $\gamma_1$ of the nonpolar diluters. With a similar $T_c$, $|\Delta \varepsilon|$ and $\Delta n$, $-\Delta \varepsilon$ LC shows a much higher rotational viscosity than that of $+\Delta \varepsilon$ LC. This is because more dipole groups are needed for a $-\Delta \varepsilon$ LC to achieve the same $|\Delta \varepsilon|$ as a $+\Delta \varepsilon$ LC. As a result, the compound becomes bulkier and heavier, leading to a higher rotational viscosity. On the other hand, to increase the clearing point of a $+\Delta \varepsilon$ LC mixture, more three- or four-ring structures (e.g. Compounds 3 and 4 in Table 5) are required. Thus, a $+\Delta \varepsilon$ LC with a higher $T_c$ often exhibits a larger $\gamma_1$.

Figure 11: Dielectric anisotropy ($\Delta \varepsilon$) vs. rotational viscosity at $T = 25^\circ$C.

2.2.3. Device Simulation

2.2.3.1. Submillisecond-response color sequential projection displays.

Color sequential LCoS has been widely used in projection displays [64-66] and wearable displays, such as Google Glass. By eliminating the color filters, both resolution density and brightness are tripled. However, fast response time (< 1 ms) is required to suppress the color
breakup and keep high image quality. Besides, the LCoS panel could operate at $T = 35-55^\circ$C due to thermal effect from the high power arc lamp or LED.

Figure 12: Voltage-dependent reflectance curves for R, G, B colors. The cell gap is 1.95 $\mu$m and $T = 55^\circ$C

As Figure 10 depicts, DIC-57F-15 shows the lowest visco-elastic coefficient and it requires the thinnest cell gap (i.e. highest birefringence) when $T > 35^\circ$C. Therefore, we use a commercial LCD simulator DIMOS 2.0 to calculate the electro-optic properties of a MTN-LCoS with DIC-57F-15. In a MTN cell, the LC directors are twisted by 90° from top to bottom substrates (i.e. MTN-90°). From Figure 9(a) and (b) and fitting parameters (Table 7), we found that at $T = 55^\circ$C, $\Delta n = 0.112$ at $\lambda = 550$ nm. The measured $\Delta \varepsilon$ is 4.7 at $T = 55^\circ$C. The other simulation parameters were set as $d = 1.95$ $\mu$m and $\gamma/K_{11} = 2.10$ ms/$\mu$m$^2$ for $T = 55^\circ$C. The angle between front LC directors and the PBS polarization axis is set at 20° to maximize the reflectance and the initial pretilt angle is $\sim 2^\circ$. MTN-90° modulates the light reflectance by a mixed effect between polarization rotation and phase retardation. A reflector is placed on the inner surface of the MTN-
90° cell. For blue (B) and red (R) lights, we used $\Delta n = 0.112$ and 0.105, respectively, while keeping the same cell gap. Figure 12 depicts the voltage-dependent reflectance (VR) curves for the RGB colors. A good dark state is achieved at $V \approx 4.5$ V\textsubscript{rms}. Thus, only single gamma curve is needed for driving the RGB frames.

Table 8: Calculated GTG response time (ms) of the MTN cell using DIC-57F-15: $d=1.95\mu$m and $T=55^\circ$C.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
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<th>3</th>
<th>4</th>
<th>5</th>
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<tbody>
<tr>
<td>1</td>
<td></td>
<td>0.23</td>
<td>0.30</td>
<td>0.37</td>
<td>0.46</td>
<td>0.56</td>
<td>0.71</td>
<td>1.00</td>
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<tr>
<td>2</td>
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<td></td>
<td>0.13</td>
<td>0.24</td>
<td>0.35</td>
<td>0.47</td>
<td>0.64</td>
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<tr>
<td>3</td>
<td>0.29</td>
<td>0.08</td>
<td></td>
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<td>0.23</td>
<td>0.37</td>
<td>0.55</td>
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<tr>
<td>4</td>
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<td>0.27</td>
<td>0.47</td>
<td>0.91</td>
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<tr>
<td>5</td>
<td>0.31</td>
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<tr>
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<td>0.15</td>
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<td>7</td>
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<td>8</td>
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<td>0.34</td>
<td>0.29</td>
<td>0.26</td>
<td>0.24</td>
<td>0.22</td>
<td>0.20</td>
<td></td>
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</tbody>
</table>

Table 8 summarizes the calculated gray-to-gray (GTG) response time. Here, we divided the VR curve at $\lambda = 550$ nm into 8 gray levels and calculated the response time between different gray levels. Both rise time and decay time are defined as 10%-90% reflectance change. The calculated rise time is 1.00 ms and decay time is 0.43 ms between gray levels 1 and 8. By applying overdrive voltage, we obtained average GTG rise time is 0.50 ms and decay time is 0.20 ms, which are ~2X faster than the response time between gray levels 1 and 8. For projection displays using LED light sources, the chassis temperature is ~35°C. Based on Figure 10, the extrapolated GTG
rise time is ~1.00 ms and decay time ~0.40 ms. Such a fast response time would eliminate the color breakup of the color sequential LCoS projection display.

2.2.3.2. Fast-response TN and FFS LCDs at extreme environments

Here, we simulate the electro-optic properties of FFS and TN cells employing DIC-57F-16 and MCRI with a commercial LCD simulator DIMOS.2D, as these two LCs show small visco-elastic coefficients at T < 35°C and low activation energy. According to the dispersion curve, $\Delta n$ ~ 0.12 and 0.11 for DIC-57F-16 and MCRI at $\lambda = 550$ nm. For MLC-6241-000, the estimated $\Delta n$ ~ 0.09 at $\lambda = 550$nm. For FFS mode, we set $d\Delta n$ ~ 340 nm for each mixture in order to achieve fast response time and low operation voltage. The same cell parameters are used in the simulation for fair comparison: electrode width $w = 2\mu$m, electrode gap $l = 3\mu$m, pretilt angle ~2° and rubbing angle ~10°. For TN mode, $d\Delta n = 480$ nm to satisfy first Gooch-Tarry minimum and to achieve high transmittance. The cells are sandwiched between two crossed polarizers and front rubbing direction is parallel to the axis of polarizer. Figure 13(a) and (c) depict the voltage-dependent transmittance for FFS and TN cells, respectively. In both modes, MLC-6241-000 shows the lowest operation voltage due to its largest $\Delta \varepsilon$. The on-state voltage of DIC-57F-16 is 6.0 V_{rms} and MCRI is 6.5 V_{rms} in FFS mode, which are still acceptable for vehicular displays. For TN, a good dark state is obtained at V~5 V_{rms} for both new LCs. Figure 13(b) and (d) depict the response time of FFS and TN LCDs at $T = 25^\circ$C. The time-dependent transmittance curves of two newly developed LCs are almost the same because of their similar birefringence and visco-elastic coefficient. The response time of our LCs is much faster than that of MLC-6241-000 in both modes. Moreover, the faster response time contributes to a higher overall transmittance and lower image crosstalk. For FFS mode, the response time [rise, decay] of DIC-57F-16 is [9.7ms, 9.3ms], while the response
time of MLC-6241-000 is [31.3ms, 31.2ms]. TN shows faster response time than FFS because it utilizes $K_{11}$ while FFS mainly uses $K_{22}$. Thus, the response time of our LCs is [2.5ms, 5.0ms] for TN, which is ~3.6X faster than that of MLC-6241-000 ([9.0ms, 19.0ms]).

![Figure 13: (a) Voltage-dependent transmittance (VT) curves and (b) time dependent transmittance (TT) curves for FFS mode at $\lambda = 550$nm; $d\Delta n = 340$nm. (c) VT curves and (d) TT curves for TN mode at $\lambda = 550$nm; $d\Delta n = 480$nm at $T = 25 ^\circ$C. Based on Figure 10, the response time at low temperature can be calculated. Table 9 shows the free relaxation time of FFS and TN modes at low temperatures. Our new LCs show a favorably small activation energy, leading to a much slower rising rate on visco-elastic coefficient as the temperature decreases. At 0$^\circ$C, the extrapolated decay time of MCRI in FFS cell is still within 20ms, which is ~3.8X faster than that of MLC-6241-000. Besides, the rise time (i.e. free relaxation)
of TN with MCRI is less than 20ms at T = −20°C (for MLC-6241-000, it is longer than 100ms). Thus, the response time of TN mode is >10X faster than that European car standard requires (i.e. 200ms at -20°C and 300ms at -20°C). By applying the overdrive voltage, the average GTG response time is reduced by ~2X. Therefore, by employing our new LCs, the response time is within ~10ms for FFS at T = 0°C and TN at T = −20°C. This is particularly important for vehicular displays at cold weather.

Table 9: The free relaxation time (ms) of FFS and TN modes at low temperature regions.

<table>
<thead>
<tr>
<th></th>
<th>25°C</th>
<th>0°C</th>
<th>-20°C</th>
<th>-30°C</th>
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<tr>
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<td>53.6</td>
</tr>
<tr>
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<td><strong>TN mode</strong></td>
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<td>44.8</td>
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</tr>
</tbody>
</table>

2.2.4. Conclusion

We have developed and characterized three new nematic LC mixtures with high clearing point, small visco-elastic coefficient and low activation energy. With a wide nematic range, they can meet the challenges for harsh environments of vehicular displays. By applying these mixtures to different LCD modes, we obtain following attractive features: 1) the average GTG response time is < 1ms with MTN mode for HUD and wearable displays at T > 35 °C. 2) The average GTG response time is maintained very fast (<10ms) for FFS at T = 0 °C and TN at T= −20 °C. Besides LC materials, the device structure can be optimized to further improve the performance of vehicle display applications such as high transmittance, contrast ratio and high power efficiency as well.
CHAPTER THREE: BLUE PHASE LIQUID CRYSTALS FOR SPATIAL LIGHT MODULATORS

Polymer-stabilized blue phase liquid crystal (PS-BPLC)\cite{6} shows several attractive features for visible spatial light modulators, such as 1) simple fabrication process since no surface alignment agent (e.g. rubbed polyimide (PI) layer) is needed), 2) fast response time (~1 ms) because of the nanoscale double twist cylinder diameter and short coherent length, and 3) polarization independence \cite{67-69} if the electric field is in longitudinal direction. However, its $V_{2\pi}$ is also relatively high. In terms of device, liquid-crystal-on-silicon (LCoS) is a commonly used reflective SLM because of its high resolution and simple fabrication process \cite{70}. In the past, BPLC-based LCoS has been demonstrated for intensity \cite{71} and phase \cite{72} modulations. For phase modulation, $2\pi$ modulo is generally required. Two problems contributing to high $V_{2\pi}$ are 1) small Kerr constant ($K$) of the employed LC host and 2) the refractive index change ($\delta n$) is only one third of the induced birefringence ($\Delta n_{\text{ind}}$) under longitudinal electric field condition:

$$\delta n = \frac{\Delta n_{\text{ind}}(E)}{3} = n_i - n_o(E)$$ \hspace{1cm} (26)

In Equation (26), $n_i$ represents the optically isotropic refractive index at the voltage-off state ($V=0$), $n_o(E)$ is the induced ordinary refractive index, and $E$ is the electric field. The maximum induced birefringence is proportional to the intrinsic birefringence of the LC host. The total phase change ($\delta$) is jointly determined by the optical path length ($l$) of the SLM, $\delta n$ and operating wavelength ($\lambda$) as:

$$\delta = 2\pi l(\delta n)/\lambda.$$ \hspace{1cm} (27)

The optical path length is linearly proportional to the cell gap ($d$) as:
\[ l = Ad, \]  

where \( A \) is a parameter related to device configuration, e.g. \( A=1 \) for transmissive SLM and \( A = 2 \) for reflective LCoS. From Equation (27), to achieve \( \delta = 2\pi \), the minimal cell gap for an LCoS is \( d = \lambda/(2\delta n) \). Let us assume \( \lambda = 633 \text{ nm} \) and \( \Delta n_{\text{ind}} \approx 0.1 \) at \( \approx 4 \text{ V/\mu m} \) for the employed polymer stabilized BPLC, then the required cell gap is \( d \approx 10 \text{ \mu m} \). For such a thick cell gap, we find \( V_{2\pi} \approx 40 \text{ V} \), which exceeds the maximum affordable voltage (24 V) of a high resolution LCoS [73]. To keep \( V_{2\pi} \) below 24 V, large birefringence and new device configuration with \( A > 2 \) are highly desirable. From material aspect, a BPLC with large Kerr constant is useful because the on-state voltage is inversely proportional to \( \sqrt{K} \) [18]. From optics viewpoint, it is critical to boost the optical path length (i.e. large \( A \)) while keeping a thin cell gap (for low voltage). Therefore, to integrate BPLC into LCoS for widespread applications, there is an urgent need to develop new device structure with \( V_{2\pi} < 24 \text{ V} \).

In this part, we demonstrated a low-voltage polymer-stabilized BPLC for LCoS applications. A new device configuration is developed, which allows the incoming laser beam to traverse four times inside the BPLC layer before exiting the cavity. Such an optical system doubles the phase change over conventional LCoS. This novel approach exhibits several attractive features: 1) \( V_{2\pi} < 24 \text{ V} \) in the visible region (\( \lambda = 400 \text{ to } 700 \text{ nm} \)). 2) The response time remains fast (~3 ms) due to its nanostructure, although the employed BPLC is quite viscous. 3) The fabrication process is fairly simple since the self-assembled BPLC does not require any surface alignment layer. 4) Due to thin cell gap, the undesired fringing field effect of a high resolution LCoS is suppressed.
3.1 Device configuration and working principles

Figure 14 depicts the device configuration and operation mechanism of the proposed LCoS SLM. The polymer stabilized BPLC is sandwiched between pixelated reflective aluminum (Al) electrodes and common ITO (indium tin oxide) electrode. No PI layer is needed for both substrates. At $V = 0$, the polymer stabilized BPLC is optically isotropic and the corresponding refractive index is $n_i$. As a longitudinal electric field (along z axis) is applied, the LC directors are reoriented along the electric field direction because the host nematic LC has a positive dielectric anisotropic ($\Delta \varepsilon > 0$). As a result, the optical axis of the induced refractive index ellipsoid elongates with the electric field. Therefore, both TE and TM polarizations experience the ordinary refractive index $n_o$ and the induced birefringence ($n_i - n_o$) is polarization independent for the normally incident light. To increase the optical path length in order to accumulate a larger phase change, we place a reflective polarizer (e.g. wire grid polarizer or DBEF (Dual Brightness Enhancement Film) [74]) on top of the glass substrate, as Figure 14 shows. For the convenience of discussion, here we assume the reflective polarizer reflects TE mode (i.e. s-wave) and transmits TM (p-wave), and the incident collimated linearly polarized laser beam is in TM mode. In addition, a broadband quarter-wave ($\lambda/4$) plate is laminated between the reflective polarizer and the ITO glass substrate. The axis of $\lambda/4$ plate is $45^\circ$ with respect to that of reflective polarizer. After passing through the $\lambda/4$ plate, the TM wave turns to right-hand circular polarization (e.g. 1st RCP). When it traverses the BPLC layer once, it experiences the same phase accumulation in both $x$ and $y$ directions as shown in Figure 14. Upon reflection from the Al electrode, the polarization remains circular but with an opposite handedness, shown as 2nd LCP (left-hand circular polarization). As the light passes through the $\lambda/4$ plate the second time, the original TM wave is changed to TE so that it is reflected by the reflective
polarizer. Then it passes through the $\lambda/4$ plate the third time and enters the BPLC layer as 3rd LCP. Similarly, the light is reflected by the Al mirror and traverses the BPLC layer (4th RCP) and the $\lambda/4$ plate for the fourth time. The polarization state returns to TM so that the light transmits through the reflective polarizer. Therefore, the optical path length is accumulated fourfold. This makes following important impact: if we want to obtain $2\pi$ phase change, then the cell gap can be reduced by 2X as compared to conventional LCoS. As a result, the required operation voltage is reduced. Moreover, the fringing field effect of a high resolution LCoS can be suppressed for two important reasons: thinner cell gap and circularly polarized light inside the BPLC layer [55, 75]. Besides polymer stabilized BPLC, any optically isotropic LC material (e.g. nano-sized polymer-dispersed liquid crystal [76]) can also be applied in the proposed device configuration.

![Proposed device configuration of BPLC-based LCoS SLM.](image)

For some applications, the input light could be at an off-axis angle. Such an incident light experiences different refractive index in the quarter-wave plate as well as BPLC layer at an on-state voltage and the circular polarized light turns to elliptical. Therefore, the light cannot be fully turned into TM mode in the 4th path, resulting in some intensity loss. The reflective polarizer works well for the incident light at oblique angle [74]. We investigated the oblique angle effect using a commercial LCD simulator DIMOS 2.0. In simulation, we set the operation wavelength at $\lambda = 550$
nm and employed a linearly polarized light. The PS-BBLC in the voltage-on state is assumed to have $\Delta n_{ind}\sim0.1$ and can be regarded as vertically aligned nematic layer. When the incident angle changes within ±10°, the reflectance difference is less than 5%. In comparison with reflective polarizer or DBEF, the phase retardation in the BPLC layer is relatively small and can be ignored. However, a large oblique angle incidence could induce a noticeable lateral shift for the outgoing beam, which leads to crosstalk in a high resolution LCoS.

### 3.2 Experiment and results

In experiment, we prepared a polymer stabilized BPLC sample employing JC-BP07N (from JNC, Japan) as nematic LC host. The dielectric anisotropy ($\Delta \epsilon$) at low frequency ($f = 300$ Hz) is $\sim332$. The polymer stabilized BPLC precursor is comprised of 87.99 wt% JC-BP07N, 2.84 wt% chiral dopant R5011 (from HCCH, China), 5.42 wt% RM257 (from Merck) and 3.74 wt% TMPTA (1,1,1-trimethylol propane triacrylate, from Sigma-Aldrich). The sample was filled into a vertical field switching (VFS) cell [19] with cell gap $d\sim4.97$ μm. Both substrates were coated with ITO electrodes but without any surface alignment layers. The cell was cooled to the BP-I phase and cured by UV light with $\lambda\sim365$ nm and intensity $\sim8$ mW/cm$^2$ for 15 min. After UV curing, the polymer stabilized BPLC cell was quite clear since their Bragg reflection is in the UV region. For convenience, we call it PS-BPLC07. To investigate the electro-optic performance of proposed PS-BPLC spatial light modulator, we used Michelson interferometer as Figure 15 depicts. The light source was an unpolarized He-Ne laser ($\lambda = 633$ nm) and it turned to be linearly polarized light after polarizer 1. The linearly polarized light was split equally into two arms by the beam splitter (BS). The phase modulation arm worked as the proposed polymer stabilized BPLC LCoS spatial light modulator (Figure 14) with single pixel. Since the DBEF for display applications is usually
combined with an embossed front surface and will diffuse the incident laser light, it is replaced by a polarizing beam splitter (PBS) and a mirror in the experimental setup. The incident light was along with the transmission axis of PBS. The polymer stabilized BPLC sample was sandwiched between a quarter-wave plate at $\lambda = 633$ nm and a reflective mirror. The sample was driven by a square-wave voltage with frequency $f = 100$ Hz [7]. Fringes were observed and recorded by a CMOS camera (DCC1545M, Thorlab). Through the average measured light intensity change under applied voltage, we obtained the induced phase change. In the reference arm, we put two polarizers to adjust the light intensity and improve the contrast of fringes, because more light loss exists in phase modulation arm due to multi-surface reflection of optical components. The axis of polarizer 2 was parallel to the input linearly polarized light. Besides, the whole system was built on a floating optical table to minimize any environment-induced fluctuation.

Figure 15: Experimental setup for measuring the phase change of our BPLC phase modulator.
In Figure 16(a), black dots represent the experimental data of the voltage dependent phase change for PS-BPLC07. In the voltage-off state, the polymer stabilized BPLC is optically isotropic with refractive index $n_i$ and we set it as reference point, i.e. there is no phase change at $V = 0$. As the applied voltage increases, the phase change increases rapidly and then saturates gradually. As shown in Figure 16(a), the phase change achieves $2\pi$ at $24V_{rms}$. The induced birefringence ($\Delta n_{ind}$) of polymer stabilized BPLC can be described by the extended Kerr model [77] as:

$$\Delta n_{ind}(E) = \Delta n_{sat} \left[1 - \exp[-(E/E_s)^2]\right],$$  \hspace{1cm} (29)$$

where $\Delta n_{sat}$ stands for the saturated induced birefringence, $E$ is the applied electric field and $E_s$ represents the saturation field. By substituting Equation (29) and Equation (26) into Equation (27), the phase change from $n_i$ to $n_o$ is obtained:

$$\delta = 4 \times \left(\frac{2\pi d \delta n}{\lambda}\right) = \frac{8\pi d \Delta n_{sat}}{3\lambda} \left[1 - \exp\left[-\left(\frac{V}{dE_s}\right)^2\right]\right].$$  \hspace{1cm} (30)$$

The PBS and reflective mirrors help to increase the optical path by 4X. Since the vertical electric field ($E$) is uniform and is proportional to the applied voltage ($V$) as $E = V/d$. We fitted the experimental data with Equation (30) and obtained good agreement as plotted in Figure 16(a). The fitting parameters are $\Delta n_{sat} = 0.0975$ and $E_s = 2.58 \text{ V}/\mu\text{m}$. Therefore, the Kerr constant is 23.14 nm/V$^2$. In addition, to measure the response time of polymer stabilized BPLC phase modulator, we replaced the CMOS camera in Figure 15 with an iris and a photodetector. Then, we removed the biased voltage (~24 V) instantaneously at $t=0$. The measured phase decay time (from 100% to 10%) is ~3.5 ms. Besides, the rise time (from 0 to 90%) is 0.96 ms with ~24 V, as Figure 16(b) shows. Both response curves fit well with the double exponential equations described in [78]. Our LC host (JC-BP07N) has a very large $\Delta \varepsilon$ (>300), that means the compound has several polar
groups in order to obtain such a large Kerr constant [79]. A major tradeoff is increased rotational viscosity and slower response time. Due to small domain sizes, this response time is still more than one order of magnitude faster than that using a conventional nematic LC device.

![Graphs](image)

Figure 16: (a) Voltage dependent phase change of PS-BPLIC07 and PS-BPLIC01. Black dots are the experimental data; based on Equation (30), red line and blue line stand for the fitting curve and simulated curve, respectively; (b) Measured phase rise and decay times of PS-BPLIC07 and corresponding fitting curves with double exponential equations.

3.3 Discussion

At a given wavelength, the phase change is determined by the device structure, cell gap and electric field as expressed in Equation (30). When the cell gap decreases, the optical path length decreases linearly (here, \( l = 4d \)) but the electric field gets stronger. According to extended Kerr effect, the induced birefringence is proportional to \( E^2 \) in weak field region and then gradually saturates. Thus, the refractive index change (\( \Delta n \)) gets larger as the cell gap decreases and finally achieves a saturation value. Therefore, there ought to be an optimal cell gap for achieving a certain phase change (say 2\( \pi \)). Figure 17 depicts the simulated \( V_{2\pi} \) versus cell gap for PS-BPLIC07 at \( \lambda = \)
405 nm (blue curve) and 633 nm (red), respectively. From fitting, we found $E_s = 2.58$ V/$\mu$m and $\Delta n_{sat} = 0.0975$ at $\lambda = 633$ nm. As depicted in Figure 17, the minimum $V_{2\pi}$ at $\lambda = 633$ nm is 19.8 V with a cell gap $d = 6.84$ $\mu$m. Parameter $E_s$ is independent of wavelength because at a given temperature and voltage the LC director reorientation profile is determined by the balanced elastic and electric torques; it has nothing to do with the probing wavelength. To obtain $\Delta n_{sat}$ at a shorter wavelength, we measured the birefringence ($\Delta n$) of LC host JC-BP07N at different wavelengths [58] and fitted the experimental data with single-band birefringence dispersion model i.e. Equation (7). Excellent agreement is obtained with $G = 3.281$ $\mu$m$^2$ and $\lambda^* = 0.211$ $\mu$m (not shown here). The $\Delta n_{sat}$ of polymer stabilized BPLC also follows the single-band birefringence dispersion model well with the same $\lambda^*$ but different $G$ value (e.g. $G'$) from the LC host [80]. By taking the ratio between $\Delta n_{sat}$ and $\Delta n$ of LC host at $\lambda = 633$ nm, we get $G' = 0.652$ $\mu$m$^2$ for PS-BPLC07. Therefore, $\Delta n_{sat}$ at any wavelength can be calculated and we find $\Delta n_{sat} = 0.120$ at $\lambda = 405$ nm. As $\lambda$ decreases, $V_{2\pi}$ decreases because the required optical path length gets shorter while the LC birefringence gets higher. As Figure 17 shows, the minimum $V_{2\pi}$ at $\lambda = 405$ nm is only ~10 V with an optimal cell gap $d \sim 3.57$ $\mu$m. Thus, $V_{2\pi}$ for the whole visible region is within the reach of LCoS, which enables the widespread application of BPLC spatial light modulators.

Based on Gerber’s model [81], Kerr constant ($K$) is governed by $\Delta n$, $\Delta \varepsilon$, average elastic constant ($k$) and pitch length ($p$) of the BPLC as

$$K \sim \Delta n \cdot \Delta \varepsilon \cdot \frac{p^2}{k}. \quad (31)$$

From Equation (31), employing an LC host with large $\Delta n$ or large $\Delta \varepsilon$ is the most common way to boost Kerr constant [18, 82]. In Figure 16(a), we plotted the voltage dependent phase change for
two blue phase materials with the same cell gap $d \sim 4.97 \, \mu m$. For PS-BPLC07, the dielectric anisotropy of its nematic host at low frequency is relatively large ($\Delta \varepsilon \sim 332$), which contributes to small $E_S$ and large Kerr constant ($\sim 23.14 \, \text{nm/V}^2$) to reduce operation voltage. The saturated birefringence is $\sim 0.0975$ at $\lambda = 633 \, \text{nm}$. Therefore, the phase change accumulates rapidly at low voltage region and saturates gradually when the voltage exceeds $\sim 25 \, \text{V}$. The $2\pi$ phase change occurs at $\sim 24 \, \text{V}$. Also included in Figure 16(a) is a different blue phase material PS-BPLC01 [18, 19] with higher $\Delta n_{sat}$ ($\sim 0.17$ at $\lambda = 633 \, \text{nm}$) but smaller Kerr constant ($\sim 7.46 \, \text{nm/V}^2$). The phase change of PS-BPLC01 does not saturate until $V \sim 70 \, \text{V}$ and the maximum phase change achieves $3.55\pi$ because of its larger $E_S$ ($\sim 6 \, \text{V/}\mu m$) and higher $\Delta n_{sat}$. The dielectric anisotropy of LC host (JC-BP01N, JNC) is $\sim 94$ at low frequency. Although the Kerr constant of PS-BPLC01 is $\sim 3X$ smaller than that of PS-BPLC07, its $V_{2\pi}$ ($\sim 27 \, \text{V}$) is only 12.5% higher. The cell gap dependent $V_{2\pi}$ for PS-BPLC01 at $\lambda = 633 \, \text{nm}$ is also included in Figure 17. The minimum $V_{2\pi}$ ($\sim 26.3 \, \text{V}$) is slightly higher than 24 V because of its smaller $\Delta \varepsilon$. As reported by Merck in [82], a BPLC host (designated as BPLC-M) with high $\Delta n$ ($\sim 0.185$) and large $\Delta \varepsilon$ ($\sim 190$) has been developed. To estimate the Kerr constant of PS-BPLC-M from Equation (31), other two parameters $p$ and $k$ need to be known as well. The pitch length can be controlled easily by changing the concentration of chiral dopants while the average elastic constant $k$ is mainly determined by the compound structures of LC host. Let us assume the $p^2/k$ of PS-BPLC-M is the same as that of PS-BPLC01, then the estimated Kerr constant of PS-BPLC-M is $\sim 16.41 \, \text{nm/V}^2$. Compared to the $\Delta n$ of the LC host, the saturated birefringence ($\Delta n_s$) should decrease slightly because of the added chiral dopant and non-mesogenic monomer ($\sim 9\%$ in total). Thus, its $\Delta n_s$ is $\sim 0.17$ and $E_s \sim 4.05 \, \text{V/}\mu m$ at $\lambda = 633 \, \text{nm}$. As shown in Figure 17 (green curve), the minimum $V_{2\pi}$ is 17.7 V with $d \sim 3.9 \, \mu m$, which
is even lower than that of PS-BPLC07 with a larger Kerr constant. This proves again that high birefringence plays an important role for lowering $V_{2\pi}$. In addition, the maximum phase modulation depth is determined by $\Delta n_{sat}$, $\lambda$ and $d$ as expressed in Equation (30). We also plot the cell gap dependent phase modulation depth in Figure 17 for PS-BPLC07 and PS-BPLC01 at $\lambda = 633$ nm as the dashed lines show. The curve for PS-BPLC-M is the same as that of PS-BPLC01 since both have the same $\Delta n_{sat}$ at $\lambda = 633$ nm. Therefore, the minimal operation voltage is achieved when the cell gap is slightly larger than that for $2\pi$ phase change. In Table 10, the physical properties, minimal operation voltage, and corresponding cell gaps at $\lambda = 633$ nm are summarized for three polymer stabilized BPLC samples mentioned above.

Figure 17: Solid lines stand for simulated $V_{2\pi}$ vs. cell gap at $\lambda = 405$ nm for PS-BPLC07, and $\lambda = 633$ nm for PS-BPLC07, PS-BPLC01, and PS-BPLC-M respectively; Dashed lines represent the phase modulation depth vs. cell gap of PS-BPLC07 and PS-BPLC01 at $\lambda = 633$ nm.
Table 10: Physical properties and device parameters for polymer stabilized BPLC samples at $\lambda=633\text{nm}$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta n_{\text{sat}}$</th>
<th>Kerr constant (nm/V²)</th>
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<th>Cell gap for min $V_{2\pi}$ (μm)</th>
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</table>

### 3.4 Summary

We have demonstrated a new device structure to allow a laser beam to traverse the BPLC layer four times in a reflective LCoS SLM. This novel approach exhibits several advantages: 1) using a large Kerr constant polymer-stabilized BPLC07, the operation voltage is lower than 24V in the entire visible region. 2) The response time remains fast (3ms), which is at least 10X faster than a conventional nematic SLM. 3) Polymer stabilized BPLC does not require any surface alignment layer so that the fabrication process is greatly simplified. 4) No extra substrate or bulky optical component is needed while multiplying the optical path by four times. As a result, the attractive features of LCoS, such as high resolution and light weight are preserved. 5) The new design helps suppress the fringing field effect of a high resolution LCoS.
Polymer network liquid crystal (PNLC) is a promising candidate for SLM because of its simple fabrication method, sub-millisecond response time, and large phase change ($\delta$) which is governed by:

$$\delta = 2\pi d \Delta n / \lambda,$$

where $d$ is the cell gap, $\Delta n$ is the LC birefringence, and $\lambda$ is the operation wavelength. Two major technical challenges of PNLC are: 1) its $V_{2\pi}$ is relatively high, originating from strong anchoring force exerted from submicron polymer network domain sizes, and 2) light scattering. Recently, Sun et al [83] demonstrated a PNLC with $V_{2\pi} = 23\text{V}$ at $\lambda=514\text{nm}$ with a significantly suppressed light scattering ($\sim 3\%$). Although a 3% scattering seems low, when several devices are cascaded together the total optical loss is still significant.

As the wavelength increases, the LC birefringence gradually decreases and then saturates in the infrared (IR) region [34]. As a result, the available phase change decreases. From Sun’s multi-layer model, the on-state voltage of a PNLC device is proportional to the cell gap as [83]:

$$V_{\text{on}} \propto \pi d d_1 \sqrt{\frac{K_{11}}{d_1 \varepsilon_0 \Delta \varepsilon}},$$

here $d_1$ is the average domain size, $K_{11}$ is the splay elastic constant, $\varepsilon_0$ is the electric permittivity and $\Delta \varepsilon$ is the dielectric anisotropy. Therefore, for a given domain size and LC material, $V_{2\pi}$ increases as the cell gap or wavelength increases. Unlike a nematic liquid crystal, the LC molecules in a PNLC device are partitioned into numerous submicron domains. The restoring force on the deformed LC directors is dominated by the anchoring force of polymer network [21]. However,
the anchoring force is not uniform over the LC medium [84]. The LC molecules closer to polymer network would experience a stronger anchoring force than those in the center. Therefore, they will rotate by different angles when an electric field is applied. Moreover, stronger anchoring force helps restore the LC molecules with faster response time. Therefore when the applied voltage is high enough, the LC molecules with weaker anchoring force will be reoriented to a larger angle and it takes longer time to restore back. As a result, multiple decay processes take place [78, 85] and response time increases. Fan et al [86] have demonstrated a PNLC light modulator at \( \lambda = 1.55 \mu m \) with \( V_{2\pi} \approx 60V \) in a reflective mode. However, the spatial phase profile is not uniform due to employing a non-mesogenic monomer (M1) [21]. On the other hand, the commonly used high resolution liquid-crystal-on-silicon (LCoS) has a maximum voltage of 24V [73]. Therefore, to integrate infrared PNLC with LCoS for widespread applications, there is a need to develop a PNLC with \( V_{2\pi} < 24V \), while keeping fast response time and spatially uniform phase profile.

In this part, we demonstrated a reflective-mode PNLC phase modulator with \( V_{2\pi} = 22.6V \) at \( \lambda = 1.55 \mu m \) and response time \( \tau \approx 1.13 ms \). To achieve such a low operation voltage while keeping fast response time in the IR region, we optimized UV curing condition and LC host. First, we investigated the curing temperature effects on domain size, which plays a critical role affecting the operation voltage and response time. A physical model was proposed to describe this correlation. Excellent agreement between model and experiment is obtained. Besides, the performance of a PNLC is heavily affected by the properties of the LC host. Therefore, we define a figure of merit (FoM), which is independent of device structure and domain size, for comparing the LC hosts. The temperature effect on FoM was also studied. For a given LC host, there is an optimal operation temperature for a PNLC, where FoM has a maximum value.
4.1 Sample preparation

To fabricate PNLCs, we prepared a precursor by mixing 92.5wt% of LC host (JC-BP07N, JNC), with 7.0 wt% of monomer (RM257, Merck) and 0.5 wt% of photo-initiator (BAPO, Genocure). Here, we used RM257 (a LC monomer) to maintain good alignment and obtain uniform phase profile. We filled the precursor into homogeneous LC cells (indium tin oxide glass substrates). The cell gap was controlled at ~11.8µm. The clearing point ($T_c$) of JC-BP07N is 87°C. If the curing temperature is close or higher than $T_c$, then the LC molecules will not align well with the rubbing directions, resulting in severe light scattering after polymerization. Thus, during UV curing process we controlled the curing temperature for each cell from 0°C to 70°C separately. Here, a UV light-emitting diode (LED) lamp ($\lambda=385$nm, Intensity is 300 mW/cm$^2$) was employed and the exposure time was one hour.

![Figure 18: Curing temperature dependent threshold voltage of PNLCs: dots stand for measured data and red line for fitting curve with Equation (40).](image)
4.2 Curing temperature effect

To characterize the electro-optic properties of each PNLC cell, we measured its voltage-dependent transmittance (VT) with a laser beam at \( \lambda = 1.55 \mu \text{m} \). The PNLC cells were sandwiched between two crossed polarizers, with the rubbing direction at 45° to the polarizer’s transmission axis. The phase change of reflective mode is twice of transmissive mode due to the doubled optical path.

Figure 18 depicts the measured threshold voltage \( (V_{th}) \) of PNLCs cured at different temperatures. As the curing temperature increases from 0°C to 70°C, \( V_{th} \) decreases from 25.0V to 10.9V. This is because the LC viscosity decreases exponentially with increased curing temperature, which accelerates the polymer diffusion rate. Thus, the domain size is inversely proportional to the LC viscosity [87]. Therefore, higher curing temperature produces coarser polymer network [88, 89] and generates PNLC with larger average domain size. The anchoring force provided by polymer network becomes weaker with a larger domain size and coarser polymer network, and thus the driving voltage decreases [90].

Du et al [88, 89] explored the curing temperature effects on LC gels, but no quantitative model was developed to correlate the curing temperature with domain size. Based on the multi-layer model, free relaxation time \( (\tau) \) is insensitive to the cell gap and it is governed by the average domain size \( (d_l) \) as:

\[
\tau = \gamma_1 d_l^2 / (K_{11} \pi^2),
\]

where \( \gamma_1 \) is the rotational viscosity, \( K_{11} \) is the splay elastic constant and \( d_l \) is the average domain size. Therefore, the average domain size at each curing temperature can be obtained by measuring the free relaxation time of the PNLC. To measure the free relaxation time, we applied a small bias
voltage to each PNLC sample to get a small initial phase change $\delta_0$ in order to satisfy the small angle approximation [59]. At $t=0$, the voltage was removed instantaneously and optical signal recorded by a photodiode detector. The time dependent phase relaxation curve can be expressed as:

$$\delta(t) = \delta_0 \exp(-2t/\tau).$$

(35)

By fitting with Equation (35), the free relaxation time for each PNLC sample can be extracted. Next, we calculated the average domain size based on Equation (34).

Figure 19: Curing temperature dependent average domain size of PNLCs: dots stand for the measured data and red line for fitting curve with Equation (39).

Figure 19 depicts the domain size obtained at each curing temperature. As the curing temperature increases from 0°C to 70°C, the average domain size increases from 130nm to 280nm because of the increased monomer diffusion rate. The increased domain size has pros and cons. On the positive side, it weakens the anchoring force, leading to a lower operation voltage. But on
the negative side, the response time increases. From Figure 19, even the curing temperature reaches $70^\circ C$ the domain size is only 280nm, which is still much smaller than the infrared wavelength ($\lambda=1.55\mu m$). Thus, light scattering remains negligible. Based on Stokes-Einstein theory, the domain size is inversely proportional to the viscosity [87]. Thus, the domain size ($d_i$) can be expressed as:

$$d_i^2 \sim \frac{k_B T t}{3 \pi \eta R}$$

(36)

here $k_B$ is the Boltzmann constant, $T$ is the Kelvin temperature, $\eta$ is the flow viscosity, $R$ is the radius of the particles, and $t$ is the time interval. Among these parameters, $R$ and $t$ are independent of temperature. The flow viscosity is much smaller than rotational viscosity but has similar temperature dependence [13, 91]:

$$\eta \sim S \cdot \exp\left(\frac{E_b}{k_B T}\right),$$

(37)

$$S = (1 - T/T_c)^\beta,$$

(38)

here $S$ is the order parameter, $E_b$ is the fitting parameter related to activation energy, $T_c$ is the clearing point, and $\beta$ is a material constant. By substituting Equation (37) into Equation (36), the curing temperature dependent domain size can be expressed as:

$$d_i = A \cdot \sqrt{T \exp\left(-\frac{E_b}{k_B T}\right)} \left(\frac{T}{T_c}\right)^\beta,$$

(39)

where $A$ is a fitting parameter. We fitted average domain size $d_i$ at various curing temperatures with Equation (39). Good agreement is obtained as shown in Figure 19. The fitting parameters are $A=106.9\ nm/\sqrt{K}$ and $E_b=131.3\ meV$. The material constant $\beta=0.16$ is obtained independently by fitting the temperature dependent birefringence data. The melting point of JC-BP07N is $T_c=87^\circ C$. The adjustable parameter $A$ is governed by the viscosity of LC host, monomer concentration, and
UV dosage. A LC with higher rotational viscosity contributes to smaller domain size [87]. In the meantime, higher monomer concentration and UV dosage contribute to a smaller average domain size [85]. Besides, the threshold voltage ($V_{th}$) is inversely proportional to $d_1$. Thus, we fitted the threshold voltage at each curing temperature with following equation:

$$V_{th} = \frac{B}{d_1} = B \sqrt{\frac{(1 - T/T_c)^\beta \exp(E_b/k_B T)}{T}},$$

(40)

here $B$ is a fitting parameter, while $T_c$ and $\beta$ maintain unchanged. As shown in Figure 18, good agreement is obtained with $B=26.5 V\sqrt{K}$ and $E_b = 137.5$ meV. The obtained activation energy is within 5% of that fitted with Equation (39), which confirms the validity of our physical model between domain size and curing temperature. Since both operation voltage and response time are determined by the domain size, this physical model provides useful guidelines to optimize the domain size by controlling curing temperature.

Figure 20: (a) Voltage-dependent phase change at $\lambda=1.55 \mu m$ for a PNLC cured at 73$^\circ$C with $V_{2\pi}$ =22.8V. (b) Measured phase decay time of the PNLC sample. Black line is experimental data and red line is fitting result with Equation (35) and $\delta_0=2\pi$. 

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When the curing temperature is further Figure 20(b) shows the measured decay time of a reflective PNLC cell whose initial biased voltage is 22.8V. Similar to measuring the free relaxation time, the biased voltage was removed instantaneously at t=0. The measured phase decay time from 100% to 10% is 1.13ms, which is 2X faster than that previously reported [86].

Table 11: Physical properties and figure of merits of five LC hosts used in PNLCs.

<table>
<thead>
<tr>
<th>LC mixtures</th>
<th>$\Delta n$ ($\lambda = 633\text{nm}$)</th>
<th>$\Delta \varepsilon$</th>
<th>$\gamma_1$ (Pa⋅s)</th>
<th>$\text{FoM}_1$ ($\Delta \varepsilon \Delta n^2/\gamma_1$) (Pa⋅s)$^1$</th>
<th>$\text{FoM}_2$ ($\Delta \varepsilon /\gamma_1$) (Pa⋅s)$^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTG135200 (HCCH)</td>
<td>0.21</td>
<td>86</td>
<td>1.20</td>
<td>3.16</td>
<td>71.67</td>
</tr>
<tr>
<td>JC-BP07N (JNC)</td>
<td>0.17</td>
<td>302</td>
<td>3.88</td>
<td>1.82</td>
<td>77.84</td>
</tr>
<tr>
<td>E44 (Merck)</td>
<td>0.24</td>
<td>16</td>
<td>0.33</td>
<td>2.79</td>
<td>48.48</td>
</tr>
<tr>
<td>BL038 (Merck)</td>
<td>0.25</td>
<td>16</td>
<td>0.56</td>
<td>1.79</td>
<td>28.57</td>
</tr>
<tr>
<td>BP1 (HCCH)</td>
<td>0.15</td>
<td>50</td>
<td>1.52</td>
<td>0.74</td>
<td>32.89</td>
</tr>
</tbody>
</table>

4.3 Figure of merit (FoM) of LC host

The overall performance of a PNLC device is governed by three key parameters: 1) $2\pi$ phase change, 2) low operation voltage, and 3) fast response time. The phase change requirement is determined by Equation (32). The $\Delta n$ employed in a PNLC device is slightly smaller than that of the LC host because the polymer network makes no contribution. The on-state voltage and response time are described by Equations (33) and (34), respectively. Therefore, besides the cell gap and domain size, the physical properties of LC host also play a key role in determining the overall performance of PNLC. As discussed above, the domain size can be controlled by the monomer concentration and curing temperature. If a certain phase change (say $\delta=2\pi$) is required, then the cell gap should satisfy following simple condition:

$$d = \lambda / \Delta n.$$  

(41)
By substituting Equation (41) into Equation (33), the correlation between $V_{2\pi}$ and $\Delta n$ is found:

$$V_{2\pi} \sim \frac{\lambda}{\Delta nd_1} \sqrt{\frac{K_{11}}{\varepsilon_0 \Delta \varepsilon}}.$$  \hspace{1cm} (42)

To balance the overall performance, response time needs to be considered as well [92]. To eliminate the effect of domain size, based on Equations (34) and (42), here we define a Figure of Merit ($FoM_1$) to evaluate the properties of LC host as:

$$FoM_1 = 1/(V_{2\pi}^2 \tau) \sim \Delta \varepsilon \Delta n^2 / \gamma_1.$$  \hspace{1cm} (43)

Therefore, the $FoM_1$ is independent of the domain size and elastic constant ($K_{11}$). From Equation (43), LC host with a large $\Delta \varepsilon$, $\Delta n$ and small $\gamma_1$ is preferred for PNLC devices. If the cell gap is fixed, then we take the product of Equation (34) and the square of Equation (33) directly, and $FoM_1$ could be simplified to:

$$FoM_2 = 1/(V_{2\pi}^2 \tau) \sim \Delta \varepsilon / \gamma_1.$$  \hspace{1cm} (44)

Table 11 lists several LC hosts we employed for making PNLC devices. HTG 135200 (HCCH, China) shows the highest $FoM_1$ among those LC mixtures due to its relatively high birefringence and dielectric anisotropy. However, if the cell gap is fixed, then JC-BP07N shows the best performance due to its extremely large $\Delta \varepsilon$. Thus, for $\lambda=1.55 \mu m$ and $d=11.8 \mu m$, JC-BP07N is a good host. When the curing temperature is increased to 73°C, the operation voltage is reduced to below 24V. However, JC-BP07 has a lower $FoM_2$ than HTG135200 because of its lower birefringence. From Equations (43) and (44), $FoM_1$ and $FoM_2$ are sensitive to the temperature because birefringence, rotational viscosity and dielectric anisotropy are also temperature dependent [34, 59, 93]:

$$\Delta n = \Delta n_0 S,$$  \hspace{1cm} (45)
\[ \gamma_1 \sim S \cdot \exp(E_a/k_B T), \]  

\[ \Delta \varepsilon = C \cdot S \exp(U/k_B T), \]  

(46)  

(47)  

where \( \Delta n_0 \) is the extrapolated birefringence at \( T=0K \), \( C \) is a fitting parameter, and \( U \) is a parameter related to the dipole moment. By combining these equations, the temperature dependency of \( FoM_1 \) is derived as:

\[
FoM_1 = D \cdot \frac{(1 - T/T_c)^{2\beta}}{\exp((E_a - U)/k_B T)},
\]

(48)  

here \( D \) is a fitting parameter. As shown in Figure 21, dots stand for the measured data and red line for the fitting results with Equation (48) for JC-BP07N. Good agreement is obtained with following fitting parameters: \( D=8.98 \times 10^6 \), \( U=207.8 \) meV, \( E_a=575.3 \) meV, \( \beta=0.16 \) and \( T_c=87^\circ C \). \( \beta \), \( E_a \) and \( U \) are obtained by fitting Eqs. (21), (22) and (23) respectively. Since the polymer network (i.e. domain size) and device structure are independent of operating temperature, the temperature dependent performance of PNLC is basically determined by the employed LC host only. At room temperature, the \( FoM_1 \) is \( \sim 4.79 \, \mu m^2/s \) and it increases to \( 11.35 \, \mu m^2/s \) at \( 60^\circ C \). As the temperature increases, viscosity decreases more quickly than birefringence and dielectric anisotropy initially, resulting in an increased \( FoM_1 \). As \( T \) approaches \( T_c \), \( \Delta n \) decreases more quickly than \( \gamma_1 \), leading to a sharply declined \( FoM_1 \). On the other hand, the temperature dependent \( FoM_2 \) is expressed as:

\[
FoM_2 \sim \exp((U - E_a)/k_B T).
\]

(49)  

\( FoM_2 \) increases as the temperature gets higher, because the fitting parameter \( U \) is usually smaller than the activation energy \( E_a \) for LC hosts [93]. Therefore, for a given PNLC an optimal operation temperature (\( T_{op} \)) exists which gives the maximum \( FoM_1 \). To derive the optimal temperature, we set \( d(FoM)/dT = 0 \) and find that
\[ T_{\text{opt}} = T_c - \frac{2 \beta k_b T_c^2}{E_a - U}. \] 

By substituting the fitting parameters of JC-BP07N, we found \( T_{\text{op}} = 77.4^\circ \text{C} \), or the optimal operation temperature is about 10^\circ \text{C} lower than the clearing point. At \( T_{\text{op}} \), \( F_{\text{om}} \) has a peak value even though the operation voltage would increase due to the decreased \( \Delta \varepsilon \). Therefore, the device can be operated at \( T_{\text{op}} \) if fast response time is the primary requirement.

Figure 21: Temperature dependent \( F_{\text{om}} \) for JC-BP07N at \( \lambda = 633 \text{nm} \): dots stand for the measured data and red line for fitting curve with Equation (48)

4.4 Summary

We have developed a physical model to correlate the curing temperature and domain size. The proposed equation fits very well with the experimental data, which also provides a good approach to optimize the curing temperature. Besides, we defined a \( F_{\text{om}} \) to compare the
performance of LC hosts for PNLC devices. For a given LC host, there is an optimal temperature for achieving maximum FoM. Therefore, by increasing curing temperature to 73°C and employing a LC host with large $\Delta \varepsilon$, we have achieved $V_{2\pi} = 22.8V$ in reflective mode operating at infrared region ($\lambda=1.55\mu m$). With keeping uniform phase profile, the response time is only half of previous reported. Such a low operation voltage will allow PNLC to be integrated in a high resolution LCoS for next-generation SLM applications.
A major challenge for mid-wave infrared (MWIR) applications of an LC device is the inherently large absorption loss due to some overlapping molecular vibration bands and their overtones [22]. In the off-resonance regions, the baseline absorption coefficient of 5CB (cyano-biphenyl) reaches as high as $\alpha \sim 10$/cm. The transmittance ($T$) of an LC layer can be expressed as

$$T = e^{-\alpha d},$$

where $\alpha$ is the absorption coefficient and $d$ is the LC layer thickness. Let us take $\alpha \sim 10$/cm as an example. For a 10-μm-thick LC layer, $\alpha d = 0.01$ and the transmittance remains 99%. However, if the LC layer thickness (or effective optical path length) increases, then the absorption will increase exponentially, as Equation (51) indicates. To improve transmittance, two approaches are commonly pursued: 1) To minimize absorption coefficient $\alpha$ by selecting proper functional groups, while maintaining nematic phase; 2) To reduce the cell gap $d$ or optical path length by using a high birefringence LC material. Here we define a figure-of-merit (FoM) to compare the performance of an LC:

$$FoM = \frac{\Delta n}{\alpha}.$$  

The molecular vibration frequency ($\omega$) of a diatomic group depends on the spring constant ($\kappa$) and the effective mass ($m$) as:

$$\omega = \sqrt{\kappa/m}.$$
As the effective mass increases the vibration frequency decreases, i.e., the absorption band shifts toward a longer wavelength. **Table 12** shows some common absorption bands that occur in MWIR and LWIR regions: e.g., CH stretching, CN stretching, C=C stretching in phenyl rings, C-H in-plane deformation, C-C skeletal stretching, C-F stretching, and C-H out-of-plane deformation [25].

**Table 12:** IR absorption of different functional groups in typical liquid crystals. (str.=stretching; s.=strong absorption; m.=medium absorption; def.=deformation; w.=weak absorption; v.=variable intensity)

<table>
<thead>
<tr>
<th>Vibration mode</th>
<th>Frequency (cm$^{-1}$)</th>
<th>Wavelength (µm)</th>
<th>Relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H in phenyl ring</td>
<td>str.</td>
<td>3095-3010</td>
<td>3.23-3.32</td>
</tr>
<tr>
<td>-CH$_2^-$, -CH$_3$</td>
<td>str.</td>
<td>2950-2845</td>
<td>3.39-3.51</td>
</tr>
<tr>
<td>C≡N</td>
<td>str.</td>
<td>2185-2120</td>
<td>4.58-4.72</td>
</tr>
<tr>
<td>C≡C (non terminal)</td>
<td>str.</td>
<td>2260-2190</td>
<td>4.42-4.57</td>
</tr>
<tr>
<td>C-H in phenyl ring</td>
<td>str. overtone</td>
<td>1850-1780</td>
<td>5.40-5.62</td>
</tr>
<tr>
<td>C=C</td>
<td>str.</td>
<td>1625</td>
<td>6.16</td>
</tr>
<tr>
<td>C-H in -CH$_2^-$</td>
<td>def.</td>
<td>1485-1445</td>
<td>6.74-6.92</td>
</tr>
<tr>
<td>C-H in -CH$_3$</td>
<td>def.</td>
<td>1470-1430</td>
<td>6.80-7.00</td>
</tr>
<tr>
<td>C-H in phenyl ring</td>
<td>in-plane def.</td>
<td>1225-950</td>
<td>8.16-10.53</td>
</tr>
<tr>
<td>C-C</td>
<td>skeletal str.</td>
<td>1300-700</td>
<td>7.69-14.29</td>
</tr>
<tr>
<td>C-F</td>
<td>str.</td>
<td>1100-1000</td>
<td>9.01-10.00</td>
</tr>
<tr>
<td>-CF$_2^-$</td>
<td>str.</td>
<td>1250-1050</td>
<td>8.00-9.50</td>
</tr>
<tr>
<td>C-Cl</td>
<td>str.</td>
<td>800-600</td>
<td>12.5-16.67</td>
</tr>
<tr>
<td>C-H in phenyl ring</td>
<td>out-of-plane def.</td>
<td>900-670</td>
<td>11.11-14.93</td>
</tr>
</tbody>
</table>
More specifically, in the MWIR region the following absorption bonds dominate: the C-H stretching in a phenyl ring, –CH2– and –CH3 stretching from an alkyl chain, C≡N stretching from the cyano polar group, and some overtones from in-plane and out-of-plane C-H deformations. On the other hand, in the LWIR region following absorption bands dominate: C-H in-plane and out-of-plane stretching, C-C skeletal stretching, and C-F stretching.

From Equation (53), three approaches can be considered to shift the absorption bands outside the spectral region of interest: deuteration, fluorination, and chlorination.

1) Deuteration: Substituting hydrogen with deuterium doubles the effective mass. As a result, the molecular vibration frequency would shift toward a longer wavelength by a factor of $\sqrt{2}$. The C-D in-plane and out-of-plane deformations would occur outside the LWIR region. However, deuteration shifts the C-H vibration in alkyl chain (~3.5 μm) to ~4.8 μm [24]. Therefore, to reduce absorption for both LWIR and MWIR bands we should do deuteration only for the phenyl rings, but not for the alkyl chain.

2) Fluorination: As shown in Table 12, the vibration frequencies of CF, CF2 and CF3 occur in the LWIR region. Therefore, fluorination could be favorable for MWIR but is unfavorable for LWIR. However, a special caution must be taken. From Table 12, the overtones of CF, CF2 and CF3 could appear in the MWIR region. This is indeed observed in our recent studies of fluorinated terphenyl liquid crystal in the MWIR region [26]. Although the overtone intensity is reduced significantly, it is still noticeable especially when the optical path length is long.

3) Chlorination: As shown in Table 12, the C-Cl vibration frequency occurs at 800-600 cm$^{-1}$, which is outside the LWIR band. Moreover, its overtone will not show up in the MWIR region. Therefore, from an absorption viewpoint C-Cl seems to be a better polar group than CN and
CF. We have previous experiences in chlorinated liquid crystals [94], but not aimed for IR applications. Here we report some new chloro LC compounds with special emphasis on low IR absorption.

5.1 Benchmark: 5CB

In our study, liquid crystal 5CB is used as benchmark, whose chemical structure is shown in the inset of Figure 22. We measured the absorption coefficient of 5CB (in an isotropic phase) using FTIR (Spectrum Two, Perkin Elmer).

Figure 22: Measured absorption coefficient of 5CB.
Figure 22 depicts the measured absorption coefficient of 5CB from 4000 cm\(^{-1}\) to 650 cm\(^{-1}\). The C-H stretching band (including –CH\(_2\) and –CH\(_3\)) is quite broad (3300-2800 cm\(^{-1}\)) and strong, and the peak absorption coefficient exceeds 600 cm\(^{-1}\). In the center of MWIR (2500 cm\(^{-1}\) to 2000 cm\(^{-1}\), marked as Zone B in Figure 22), the C≡N stretching shows a narrow but very strong absorption (\(\alpha>1000\) cm\(^{-1}\)). Cyano is a strong polar group, which not only provides a large dielectric anisotropy but also extends the conjugation length for enhancing birefringence. For practical applications, a large \(\Delta\varepsilon\) helps to reduce operation voltage while high \(\Delta n\) enables a thinner LC layer to be used for reaching the required phase change. Unfortunately, C≡N has a strong absorption at \(\lambda=4.45\) \(\mu\)m and should be avoided because it will lift up the baseline absorption. A molecular vibration band usually has Lorentzian shape and its tail could spread broadly. The overlap of the neighboring bands is responsible for the observed baseline absorption.

Besides the normal vibration mode of C≡N, the baseline absorption in Zone B also comes from the overtone (doubled frequency) of the absorption bands in Zone D, as marked in Figure 22. As listed in Table 13, the C-C (in the alkyl chain) skeletal stretching (1300-700 cm\(^{-1}\)) and the in-plane deformation of C-H in the phenyl rings (1225-950 cm\(^{-1}\)) contribute to the absorption in Zone D. The absorption of Zone C consists of the -C-H (in alkyl chain) deformation and C-C skeletal stretching, whose overtone further increases the baseline absorption observed in Zone A. The tail of the absorption band in Zone A may also raise the absorption level in Zone B.

In summary, the absorption in MWIR (Zones A and B) are primarily influenced by the strong C≡N stretching and the overtone/combination absorption from Zones C and D.
Table 13: Possible absorption mechanisms for Zones A-D shown in Figure 22.

<table>
<thead>
<tr>
<th>Zone</th>
<th>Absorption mechanism</th>
<th>Frequency (cm⁻¹)</th>
<th>Wavelength (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>C-H (in CH₂, CH₃) def. overtone</td>
<td>2790-2500</td>
<td>3.58-5</td>
</tr>
<tr>
<td></td>
<td>C-C skeletal str. overtone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>C≡N str.</td>
<td>2000-2500</td>
<td>4-5</td>
</tr>
<tr>
<td></td>
<td>C-H (in phenyl ring) in-plane def. overtone</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C-C (in alkyl chain)skeletal str. overtone Combination</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>C-H in CH₂, CH₃ def.</td>
<td>1485-1250</td>
<td>6.73-8</td>
</tr>
<tr>
<td></td>
<td>C-C skeletal str.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>C-H (in phenyl ring) in-plane. def</td>
<td>1000-1250</td>
<td>8-10</td>
</tr>
<tr>
<td></td>
<td>C-C (in alkyl chain)skeletal str.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.2 Fundamental modes

5.2.1. Undesirable polar groups: C≡N and NCS

As shown in Sec. 4.1, C≡N has a strong absorption at λ=4.45 μm and should be avoided for broadband application. Besides C≡N group, NCS and C-F are two other commonly used polar groups. Compounds with different polar groups were prepared, dissolved in CCl₄ at a concentration of ~5x10⁻⁵ mol/ml and then filled in a NaCl cell with cell gap (0.5 mm). The transmission spectra were measured using FTIR, as shown in Figure 23 NCS exhibits a very strong and broad absorption from 2220-1923 cm⁻¹, while C-F has an absorption band (1100-1000 cm⁻¹), which is outside the MWIR spectral region, as shown in Table 12.

Another polar group C-Cl can also be employed since its absorption is in the range of 800-600 cm⁻¹, and its second harmonic overtone will not show up in Zone B.
Figure 23: Measured transmission spectra of three compounds with different polar groups. FB stands for F-Ph-Ph-F, where Ph is a phenyl ring.

5.2.2. Undesirable core structure: tolane

Tolane core is effective for elongating the conjugation length and enhancing birefringence. Theoretically, as a linking group C≡C exhibits a much weaker absorption than it is as a terminal group. We measured the absorption coefficient of a tolane compound PTP-20F, and results are depicted in Figure 24. The absorption peak of C≡C occurs at 2216 cm$^{-1}$ and its $\alpha$ is $\sim$6X smaller than that of C≡N bond. However, this absorption peak raises the absorption baseline to $>10$cm$^{-1}$ in the 2500-2000cm$^{-1}$ region. Thus, C≡C is not a favorable linking group and should be avoided.
Figure 24: Measured absorption coefficient of PTP-20F vs. 5CB.

5.3 Overtone absorption

5.3.1. C-O group

C-O group helps to stabilize mesogenic phase. The absorption of C-O group occurs at 1272-1200 cm⁻¹, but its overtone appears in 2540-2400 cm⁻¹ [Figure 24]. Therefore, we should avoid using C-O functional group.

5.3.2. Alkyl chain

To study how alkyl chain affects the MWIR absorption, we measured the absorption coefficient of bi-phenyl compounds by FTIR. Figure 25 depicts the absorption spectrum of PP-2 and PP. The structures of PP-2 and PP are included in Figure 25. Due to the absence of alkyl chain, PP shows lower absorption baseline in the whole IR region and the lowest absorption coefficient
is less than 2 cm$^{-1}$ at $\sim$3500 cm$^{-1}$. Both of them show a relatively strong resonance peak near 3000 cm$^{-1}$, which corresponds to the $\equiv$C-H (in phenyl rings) stretching absorption. The absorption in 2950-2845 cm$^{-1}$ comes from the $-\text{C-H}$ (in alkyl chain) stretching absorption, which only occurs for PP-2. Besides that, PP also shows much lower overtone absorption in the spectrum region of interest 2500-2000 cm$^{-1}$. A shorter or even without alkyl chain will help reduce the absorption. But neither PP nor PP-2 has a LC phase. Flexible chain is favored to induce nematic phase. Thus, we need to compromise between the nematic phase and absorption when designing low-loss LCs.

Figure 25: Measured absorption coefficient of PP vs. PP-2.

Since the presence of alkyl tails results in larger absorption in the MWIR region, an extreme example is to eliminate all the alkyl chain, while keeping nematic phase. To ensure large aspect ratio for mesogenic phase, quaterphenyl compounds are investigated. As shown in Figure 26,
without any alkyl chain, the first compound shows enantiotropic nematic phase. The quaterphenyl molecule without any substitution (the middle compound in Figure 26) has high level of \( \pi-\pi \) interaction leading to efficient molecular packing. Such interaction results in high melting point (322 °C) [95]. To lower the melting point and render the molecule useful for IR applications, disruption of the molecular packing is needed. Chlorine substitution can be used for reducing the ring coplanarity of the quaterphenyl molecule. By introducing one chlorine substitution, the melting point of the third compound drops 150 °C, compared to the second compound. The substitution position also matters in terms of the temperature range, and we will further study on this and find useful LC compound structures.

![Figure 26: Molecule structure and phase transition temperature of quaterphenyl compounds.](image)

5.3.3. \( \text{=C-H in-plane deformation absorption} \)

Phenyl ring is a very common group in LCs since it helps to increase \( \Delta n \) and it’s more stable compared to tolane. But the in-plane deformation of \( \text{=C-H} \) (1225-950 cm\(^{-1}\)) in the phenyl rings occurs and its overtone contributes to the absorption in 2500-2000 cm\(^{-1}\). For comparison, we measured the absorption spectrum of a compound with no unsaturated bonds 5CC2. 5CC2 has sematic phase from \(-16 °C \) to \(77 °C \) and its chemical structure is shown in Figure 27.

From Figure 27, the absorption of 5CC2 is very low from 2200-1700cm\(^{-1}\) due to the absence of aromatic overtone. For application in this spectral region, we may consider to use the saturated compounds. However, the birefringence is relatively low (~0.05). On the other hand, this
study proves that the overtone of =C-H deformation contributes significantly to the absorption in 2500-2000 cm\(^{-1}\). Proper substitution in the phenyl rings with F or Cl can decrease the number of =C-H bonds and hence reduce the in-plane deformation absorption. We will discuss about the fluorination and chlorination in the following two sessions respectively.

![Figure 27: Measured absorption coefficient of 5CC2 and 5CB.](image)

**5.3.4. Fluorination**

If a hydrogen atom in the phenyl ring is substituted by fluorine, the corresponding =C-F deformation will shift toward a longer IR region. The fundamental absorption of C-F stretching occurs at 1229 cm\(^{-1}\) and 1159 cm\(^{-1}\), which are out of MWIR range. However, the overtone of this stretching could also contribute to the absorption in the 2500-2000 cm\(^{-1}\). To quantitatively study
this effect, we measured the absorption spectra of PP-2 and 2PPF, whose chemical structures are shown in the inset of Figure 28. They have the same core structure and alkyl chain length, except there is a fluorine atom at the end of the phenyl ring for 2PPF. From Figure 28, there are two strong additional absorption bands showing up at 1229 and 1159 cm\(^{-1}\). And the overtone raises the absorption coefficient of 2PPF in the 2500-2000 cm\(^{-1}\) region, although only one fluorine atom is introduced. Thus, fluorination is not a good choice for lowering the absorption in the MWIR region because of its overtone absorption.

![Figure 28: Measured absorption coefficient of PP-2 vs. 2PPF.](image)

However, the situation could change if we do complete fluorination in the alkyl chain because all the saturated –C-H bond stretching absorption at ~2900 cm\(^{-1}\) would shift to ~1100 cm\(^{-1}\).
for the –C-F bond (stretching absorption). Thus, we could eliminate the strong and broad absorption in the 3000 to 2600 cm\(^{-1}\) region. One tradeoff is that fluoride atom is much heavier than hydrogen atom, and may suppress the liquid crystal phase or increase the melting point significantly.

Figure 29: Measured absorption coefficient of 5CB and 2PPCI.

5.3.5. Chlorination

Besides fluorination, chlorination in the phenyl ring is another option to shift the \(=\text{C-H}\) in-plane deformation absorption to a longer wavelength. Based on Equation (53), since chloride has even heavier atomic mass, the C-Cl stretching absorption occurs at 650 cm\(^{-1}\), whose second harmonic absorption would locate outside of the 2500-2000 cm\(^{-1}\) region. Figure 29 shows the absorption spectrum of 2PPCI. The baseline of the 2PPCI is much lower than that of 5CB due to
the shorter alkyl chain and the absence of CN group. The lowest absorption coefficient is ~4 cm\(^{-1}\) at ~2150 cm\(^{-1}\). Thus, chlorination is an effective way to achieve low absorption in MWIR.

5.3.6. Combination absorption

From Figure 29, we noticed that there is an unexpected absorption peak near 2300 cm\(^{-1}\). It is not corresponding to any second harmonic absorption. We suspect that it might result from higher order overtone or combination absorption of lower frequency (sum frequency). \(-\text{CH}_2\) and \(-\text{CH}_3\) (in alkyl chain) asymmetric deformation occurs at ~1484 cm\(^{-1}\), and \(=\text{C}-\text{H}\) (in phenyl ring) out-of-plane deformation contributes to the strong peak at ~815 cm\(^{-1}\). The sum frequency of these two absorption bands is speculated to cause the absorption at ~2300 cm\(^{-1}\). The combination absorption is difficult to predict, but the magnitude is much smaller compared to the fundamental absorption. But if the optical path is long (cm), this small absorption coefficient could still be quite significant.

5.4 Low absorption LC compounds and mixtures

Based on our design strategies, we prepared five fluoro and two chloro-terphenyl compounds as listed in Table 14. To suppress absorption, we replace all the CH bonds in the alkyl chain by \(-\text{OCF}_3\), but keep the CH bonds in the phenyl rings in order to obtain nematic phase. Moreover, the CH bonds in the phenyl rings exhibit a much weaker and narrower absorption than those in the flexible alkyl chain. The phase transition temperatures (PPAs) were measured by Differential Scanning Calorimetry (DSC, TA instruments Q100). The first three compounds have nematic phase. To widen the nematic range, we formulated a eutectic mixture, designated as UCF-1, using these 5 fluoro compounds. The melting point (Tm) is 42°C and clearing point (Tc) is 51.5°C during the heating process. The Tc drops to below ~10°C due to super-cooling.
Table 14: Chemical structures and properties of the eleven compounds studied, where Cr stands for crystalline, N for nematic, and I for isotropic Phase.

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<td>Cr 86 N (84) I&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>![Structure 6]</td>
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<td>![Structure 7]</td>
<td>Cr 95 (N 68) I</td>
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<td>Cr72(N67)I</td>
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</tr>
<tr>
<td>12</td>
<td>![Structure 12]</td>
<td>Cr 128 N 253 I</td>
</tr>
<tr>
<td>13</td>
<td>![Structure 13]</td>
<td>Cr 72 N 98 I</td>
</tr>
</tbody>
</table>

1. <sup>a</sup>() indicates a monotropic phase
5.4.1 Low absorption

To measure MWIR absorption, we filled UCF-1 to a LC cell with two bare barium fluoride (BaF$_2$) substrates and measured their transmittance using a Perkin Elmer Spectrum One FTIR Spectrometer. BaF$_2$ is highly transparent from UV to $\sim$10$\mu$m. It refractive index 1.47 is close to that of LC. The cell gap is $\sim$46$\mu$m. To eliminate scattering, we conducted the absorption measurement at an isotropic phase ($\sim$60$^\circ$C). To take surface reflections into consideration, we use a single BaF$_2$ as the reference. Figure 30 shows the measured absorption coefficient of UCF-1. Also included for comparison is 5CB. For UCF-1, it shows a relatively low absorption coefficient ($\alpha$ $\sim$2.3 cm$^{-1}$) in the vicinities of 3333 cm$^{-1}$, i.e. $\lambda$ $\sim$3$\mu$m, and the absorption coefficient is smaller than 3 cm$^{-1}$ in the region of 3571-3333 cm$^{-1}$ (2.8~3.0 $\mu$m). Besides, the absorption at 3030-2778 cm$^{-1}$ (3.3~3.6 $\mu$m) is significantly reduced because the alkyl chain has been replaced. The absorption peak at 3049 cm$^{-1}$ (3.28 $\mu$m) originates from the CH vibration in the phenyl rings. It overlaps with the peak of 5CB very well. Even though the absorption peak resulting from C-O and C-F stretching vibrations are shifted to the 1302-1156 cm$^{-1}$ (7.68~8.65$\mu$m), their combination overtone results in a modest ($\sim$80cm$^{-1}$) but broad absorption peak in the vicinities of $\lambda$=4 $\mu$m.

To shift overtone resonance peak out of MWIR, we replaced the fluorine with a heavier atom, chlorine [96]. While, for chlorinated compounds, the alkyl chains need to be kept to maintain the flexibility and aspect ratio of the LC compounds. Otherwise, some undesirable properties, such as high melting point, large heat fusion enthalpy, and high viscosity could occur. More seriously, the compounds may not have any mesogenic phase. The physical properties of chlorinated LC for display applications have been reviewed elsewhere. Thus, we synthesized two chlorinated compounds (#6 and #7) listed in Table 14. Both compounds exhibit monotropic phase. We
prepared a binary mixture with 60 wt% compound 6 and 40 wt% compound 7, designated as UCF-2. The nematic range of UCF-2 is from 48.3°C to 69.2°C in the heating process. Super-cooling effect lowers the melting point to ~0°C. Thus, UCF-2 remains liquid crystal phase at room temperature (~25°C). To measure the MWIR absorption spectrum, we filled UCF-2 to a BaF₂ cell with cell gap ~46μm. The measurement procedures are the same as UCF-1.

Figure 30: Measured absorption coefficient spectrum of 5CB (black line) and UCF-1 (red line).

Figure 31 depicts the measured absorption spectrum of UCF-2 in the IR region. The absorption spectrum of 5CB is also included for comparison. UCF-2 exhibits a relative clean absorption in the 4000-3125cm⁻¹ (2.5–3.2μm). The lowest α is 4 cm⁻¹ at 3247cm⁻¹ (3.08μm), which is slightly higher than that of UCF-1. The responsible absorption mechanism in this region is the
CH in-plane deformation. In UCF-1, more CH bonds are substituted by C-F bonds so that the in-plane vibration effect is suppressed.

More importantly, UCF-2 shows a relatively small absorption in 2778-1923 cm$^{-1}$ (or 3.6$\mu$m to 5.2$\mu$m) window. The reasons are twofold: 1) In comparison with 5CB, the CN vibration band centered at 4.45$\mu$m is removed, and 2) In comparison with UCF-1, the vibration peaks resulting from C-Cl bonds are shifted to beyond 12.5 $\mu$m, and thus the overtone is still outside the MWIR region. The strong resonance peak centered at 2941 cm$^{-1}$ (3.4 $\mu$m) is due to the CH bonds at alkyl chain. Thus, it has similar shape to the resonance peak of 5CB but with weaker amplitude, because 5CB has a longer alkyl chain than the chlorinated compound (#7). Thus, UCF-2 shows a lower absorption than 5CB in the 4-5 $\mu$m MWIR region.

![Figure 31: Measured absorption coefficient of 5CB (black line) and UCF-2 (red line).](image)
Table 14 also lists other chlorinated compounds we have synthesized (#8~#13). In all cases a p-terphenyl core unit is employed to obtain high birefringence. To lower the melting point of UCF-2, we formulated a eutectic mixture (IR-M1) by adding #10 and it exhibits an enantiotropic phase with $T_c=68^\circ C$. Compounds 11 and 12 are chlorinated cyclohexane terphenyls. Although their melting points are relatively high, their nematic temperature ranges are over 100$^\circ C$. Therefore, to widen the nematic range, we doped 10 wt% of compound 12 into IR-M1 to give a new mixture designated as UCF-3. Compound 11 was not employed here because of its poor solubility, high melting point and large heat of fusion. Remarkably, the melting point of mixture UCF-3 drops to less than -40$^\circ C$ (limited by our DSC) and its clearing point is 85$^\circ C$. We kept UCF-3 at -40$^\circ C$ for 3 hours and it did not crystallize. Thus, UCF-3 exhibits a wide nematic range including room temperature. Compound 13 is a chlorinated cyano-terphenyl. For the MWIR region, the cyano group should be avoided since it has a very strong absorption peak at ~4.48 $\mu m$. However, the cyano group elongates the conjugation length and increases the birefringence, which helps to reduce the cell gap and improve the transmittance at LWIR region.

5.4.2 Physical properties evaluation

In addition to low absorption, the mixture is also required to have high birefringence, low viscosity and modest dielectric anisotropy. Therefore, we also characterized its physical properties.

5.4.2.1 Birefringence

Birefringence can be obtained by measuring the voltage dependent transmittance of a homogeneous cell sandwiched between two crossed polarizers. We prepared two homogeneous cells with strong anchoring energy and cell gap $d$~5$\mu$m. In the visible and near IR regions, we can still use indium-tin-oxide (ITO) coated glass substrates. UCF-1 and UCF-3 were filled into the LC
cells at ~70°C and 80°C, respectively. Then, both cells were mounted on a Linkam LTS 350 Large Area Heating/Freezing Stage controlled by TMS94 Temperature Programmer. To obtain maximum transmittance, the LC director was oriented at 45° with respect to the polarizer transmission axis. A linearly polarized He-Ne laser (λ=633nm), a tunable Argon-ion laser (λ=514nm, 488nm and 457nm) and a semiconductor laser (λ=1550nm) were used as the light sources. A 1 kHz square-wave AC signal was applied to the LC cells.

![Figure 32: Temperature dependent birefringence of UCF-3 at λ=633nm: dots stand for measured data and red line for fitting curve with Equation (6).](image)

The transmitted light was measured by a photodiode detector and recorded by a LabVIEW data acquisition system (DAQ, PCI6110). Thus, the corresponding VT curves and phase retardation were measured. The birefringence at a given wavelength and temperature was obtained from the phase retardation based on the Equation (32). The temperature dependent birefringence for UCF-3 was measured from 20°C to 80°C, and the results for λ=633nm are plotted in Figure 32,
where dots are experimental data and red line is the fitting curve based on Haller’s semi-empirical equation, i.e. Equation (6): Through fitting, we find $\Delta n_0 = 0.29$ and $\beta = 0.15$.

![Figure 33: Birefringence dispersion of UCF-3 at room temperature: dots are measured data and solid line is fitting with Equation (7).](image)

To determine the birefringence in the MWIR region, we measured the dispersion curve using several visible and short-wave IR lasers at room temperature. Results are plotted in Figure 33. Dots are measured data at five discrete wavelengths and red curve represents the fitting results using following single-band model described as Equation (7). Through fitting, we find $G = 3.37 \mu m^{-2}$ and $\lambda^* = 0.240 \mu m$. Based on these parameters, the $\Delta n$ in the IR region can be extrapolated. As the wavelength increases, $\Delta n$ decreases sharply and then plateaus in the MWIR region. The birefringence of UCF-3 keeps relatively high ($\Delta n \approx 0.194$) in the MWIR region. To achieve $2\pi$ phase change at $\lambda = 4 \mu m$, the required cell gap is $20.62 \mu m$. High $\Delta n$ enables a thin cell gap to be used for achieving a certain phase change, which in turn leads to fast response time and high
transmittance. We also measured the birefringence of UCF-1, and its $\Delta n=0.17$ at $T=25^\circ C$ and $\lambda=633$ nm, which is much smaller than that of UCF-3 ($\Delta n=0.22$).

5.4.2.2 Viscosity

![Temperature dependent visco-elastic coefficient of UCF-3](image)

Figure 34: Temperature dependent visco-elastic coefficient of UCF-3: dots are measured data and red line is fitting with Equation (8). $\lambda=633$ nm.

The visco-elastic coefficient ($\gamma_1/K_{11}$) was obtained by measuring the dynamic free relaxation time for a controlled phase change as Equations (34) and (35) show. We plot visco-elastic coefficient for UCF-3 at different temperatures in Figure 34, where dots are experimental data and red line is fitting curve with Equation (8). For UCF-3, we find $E=525$ meV. UCF-3 has a much larger visco-elastic coefficient (~140 ms/µm²) than UCF-1 (~25 ms/µm²) at room temperature. The possible explanations are: 1) the chlorine atom is heavier and bulkier than fluorine, and 2) the chloro compounds have longer alkyl chain. As the temperature increases, the visco-elastic coefficient decreases significantly. Besides, the estimated optical response time of UCF-3 is ~800 ms. To
shorten the response time, a polymer network liquid crystal can be considered and the response time can be improved by 100x, but the tradeoff is increased operation voltage.

*IR transmittance for $2\pi$ phase change*

Figure 35: Measured IR transmittance spectrum of UCF-3. Cell gap $d=21\mu$m.

To measure the IR transmittance, we filled UCF-3 to a LC cell with two sodium chloride (NaCl) substrates and measured the transmittance with a Perkin Elmer Spectrum One FTIR Spectrometer. The NaCl substrate is transparent from visible to $14\mu$m and its refractive index $\sim 1.5$ is very close to that of the LC. To suppress the light scattering at room temperature, we spin-coated a thin PI layer ($\sim 80$nm) on the inner surface of the NaCl substrates and gently rubbed the PI layer. Therefore, the LC molecules are aligned homogeneously. To achieve $2\pi$ phase change at $\lambda=4\mu$m,
the required cell gap is 20.62 µm. We fabricated an LC cell with a gap of \( d = 21 \mu m \) and Figure 35 depicts the measured transmittance of UCF-3 at room temperature from 2 µm to 12 µm. In the 3.8 µm → 5 µm region, the transmittance is \( \sim 98\% \). This is because the vibration peaks resulting from C-Cl bonds are shifted to beyond 12.5 µm and the overtone is outside the MWIR window as well.

There is a strong absorption peak centered at 3.4 µm resulting from the C-H stretching in the alkyl chain and aromatic rings, which are unavoidable since these C-H bonds are basic elements of organic compounds that exhibit a mesogenic phase. Besides, C-H bond vibrations contribute to the strong absorption at longer wavelength: (1) the C-H deformation in the alkyl chain and C-C skeletal stretching vibration peaks are located at 6~8 µm; (2) the C-H in-plane deformation vibration peaks are at 8~10 µm. On the other hand, in the case of a chlorine-substituted ring, the intensity of C-H in-plane bending vibrations is enhanced relative to other absorptions by as much as 3-4X. The absorption peak will degrade the transmittance of the off-resonance region as well.

In order to achieve a 2\( \pi \) phase change at LWIR region, e.g. \( \lambda = 10.6 \mu m \), the required cell gap is \( \sim 2 \) times larger than that at MWIR region and the transmittance at \( \lambda = 10 \sim 11 \mu m \) is expected to decrease to \( \sim 70\% \). This loss is too large, and other high \( \Delta n \) LC compounds should be considered, as will be discussed later.

**Dielectric anisotropy**

To determine dielectric anisotropy, we measured the capacitance of a homogenous cell and a homeotropic cell using an HP-4274 multi-frequency LCR meter. For UCF-3, we obtained \( \Delta \varepsilon = 6.89 \) (\( \varepsilon_\parallel = 10.7, \varepsilon_\perp = 3.84 \)) at 23°C and \( f = 1 \) kHz. This medium \( \Delta \varepsilon \) results from the modest C-Cl dipole group. UCF-1 aligns well in a homogeneous cell, but not so well in a homeotropic cell.
Therefore, we can only estimate its $\Delta \varepsilon$ value through the measured threshold voltage ($3.4V_{\text{rms}}$) from a homogeneous cell. The estimated $\Delta \varepsilon$ is about 4. This small $\Delta \varepsilon$ value can be easily understood because some compounds listed in Table 14 have dipoles on both terminal groups. As a result, their dipole moments cancel each other.

5.5 Long-wave IR liquid crystal

The transmittance ($T$) of a liquid crystal layer can be expressed Equation (51). Therefore, to minimize the absorption loss while keeping a required phase change (i.e. to achieve high FoM, Equation (52)) in long-wave IR (LWIR) region ($\lambda=8$~$12\mu m$), two approaches can be considered: 1) To reduce the absorption coefficient $\alpha$ by substituting the C-H in-plane bending vibrations in the aromatic rings, and 2) to employ a high $\Delta n$ LC to reduce the required cell gap or optical path length.

Compound 13 possesses a high birefringence at visible region ($\Delta n$=0.35 at $\lambda=633$nm) because the combination of the terphenyl core and the cyano group elongate the conjugation length. Based on the birefringence dispersion model, i.e. Equation (7), $\Delta n$ drops about 10~20% as the wavelength increases from the visible to IR. Here, we suppose $\Delta n$=0.29 at $\lambda=10.6\mu m$ and the required cell gap to get a 2$\pi$ phase change is $d=36.6\mu m$. We also include a commercial LC mixture E7 (Merck) for comparison. Based on the birefringence dispersion of E7: $G=3.06\mu m^{-2}$ and $\lambda^*=0.250\mu m$, we find $\Delta n$=0.19 at $\lambda=10.6\mu m$. Thus, the required cell gap at this wavelength is 55.8$\mu m$. To avoid scattering, we measured the transmittance of compound 13 in the isotropic phase at $T\approx 120^\circ C$. Figure 36 depicts the measured transmittance of compound 13 and mixture E7 in the LWIR. Compound 13 with higher birefringence and thinner cell gap shows a much higher
transmittance than E7 at both $\lambda=8\sim9\mu m$ and $10\sim11\mu m$. Some resonance bands of compound 13 are found at $\lambda=9\sim10\mu m$ because of C-H in-plane vibration resulting from tri-substituted and di-substituted phenyl rings. While the four components in E7 just have di-substituted phenyl rings. Though the CN polar group shows a relatively sharp and strong resonance peak at $\sim4.48\mu m$, it does not degrade the transmittance in the LWIR region. Similar to UCF-3 for MWIR, we can also formulate eutectic mixtures consisting of homologs of compound 13 for LWIR applications.

Figure 36: Measured transmittance spectrum of compound 13 and mixture E7 in the LWIR region. The required cell gaps for compound 6 and mixture E7 are 37$\mu m$ and 56$\mu m$, separately.
5.6 Summary

We have synthesized several fluorinated and chlorinated compounds and formulated eutectic mixtures to widen the operation temperature. For the fluorinated mixture Mix I, it shows a relatively small absorption coefficient (2.5cm$^{-1}$) window at $\lambda$~3$\mu$m. However, the overtone absorption of CF band occurs in the vicinities of 4 $\mu$m. For the chlorinated mixture, it is quite transparent in the $\lambda$=3.8~5$\mu$m window. To achieve a $2\pi$ phase change at $\lambda$=4$\mu$m, the required cell gap is ~21$\mu$m and the corresponding transmittance is ~98%.
CHAPTER SIX: POLYMER NETWORK LIQUID CRYSTAL FOR MID-WAVE INFRARED REGION

To shorten the response time, the polymer network liquid crystal is considered and the response time can be improved by 100X, but the tradeoff is increased operation voltage. As described in Equation (33), the operation voltage of PNLC is determined by the cell gap, domain size and the dielectric anisotropy of LC host. Thus, a high birefringence LC with a larger $\Delta \varepsilon$ is considered to squeeze the cell gap and reduce the operation voltage. At the same time, high transmittance at MWIR region should be maintained. The LC birefringence is governed primarily by the molecular conjugation, which is contributed by the core structure and terminal groups. Due to UV instability of double bonds and carbon-carbon triple bonds, conjugated phenyl rings have been commonly used for obtaining high birefringence. However, using too many phenyl rings will result in several drawbacks: 1) its melting point will be too high to be used at room temperature; 2) its viscosity will increase; 3) its birefringence will saturated once there are more than four phenyl rings. Therefore, terphenyl could be an optimal core structure. In terms of polar group, -F,-Cl,-NCS, -CN are commonly used in LC compounds to provide dipole moment. With the same core structure, -F and –Cl provide large resistivity and modest dipole moment. Therefore, they are widely used in the TFT-LCDs. –NCS provides large birefringence and dielectric anisotropy with keeping modest viscosity, while its properties will deteriorate after UV exposure. –CN helps increase birefringence, dielectric anisotropy and shows good UV stability. Therefore, -CN group is a suitable candidate for increase the birefringence and dielectric anisotropy simultaneously as the LC host for PNLC.
6.1 High birefringence liquid crystal host

First, we studied a commercial high birefringence LC mixture with $\Delta n = 0.53$ at $\lambda = 514\text{nm}$ and $\gamma_1/K_{11} = 17.0\text{ms/}\mu\text{m}^2$ at room temperature. By measuring its birefringence at different wavelength, we can extrapolate its birefringence in the mid-wave infrared region as $\Delta n = 0.35$ at $\lambda = 4\mu\text{m}$. If an LC cell with gap $d = 12\mu\text{m}$ was employed to satisfy $2\pi$ phase change, the response time is 125ms. Moreover, to obtain super high birefringence, this mixture mainly contains compounds with $-\text{NCS}$ group, it results in large and broad absorption band in the 4.5~5.5$\mu\text{m}$ region. In the off-resonance region, the transmittance is only 95% with $d = 12\mu\text{m}$.

Table 15: Chemical structures and properties of the cyano-terphenyl compounds studied, where Cr stands for crystalline, N for nematic, and I for isotropic Phase.

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</tr>
<tr>
<td>4</td>
<td><img src="image.png" alt="Structure 4" /></td>
<td>Cr 92.7 N 190.9 Iso</td>
</tr>
</tbody>
</table>

Table 15 lists four kinds of cyano-terphenyl compounds we prepared. Although $-\text{CN}$ group has a very strong absorption peak at ~4.45$\mu\text{m}$, its bandwidth is relatively narrow. It elongates the conjugation length of the LC molecule and hence helps to increase the birefringence. The phase
sequence and heating enthalpy of different compounds were measured using Differential Scanning Calorimeter (DSC). As shown in Table 15, these compounds exhibit a relatively high melting point \( T_{mp} \). To lower \( T_{mp} \), we formulated a eutectic mixture using these four compounds. The \( T_{mp} \) of this quaternary mixture is decreased to 36.3 °C. To lower the melting point further, we mixed 35 wt% UCF-2 into the cyano-terphenyl host. The resultant melting point of this mixture (UCF-4) is below -4°C, while the clearing point is 149.7°C. Its nematic range is quite wide.

Figure 37: Birefringence dispersion of UCF-4 at room temperature: dots are measured data and solid line is fitting with Equation (7).

6.2 Physical properties of LC host

6.2.1 Birefringence dispersion

We also measured the electro-optic properties of UCF-4. The methods are the same as that we used for UCF-3. Figure 37 shows the dispersion curve of UCF-4. The red line is the fitting curve with Equation (7) with \( G=3.78 \mu m^{-2} \) and \( \lambda^*=0.258 \mu m \). It saturates when the wavelength
extends to IR region ($\lambda \gg \lambda^*$). Thus it keeps high birefringence $\Delta n=0.253$ at $\lambda=4\mu m$, which helps to reduce the optical path.

6.2.2 IR transmittance for $2\pi$ phase change

Using UCF-4, the required cell gap for achieving $2\pi$ phase change at $\lambda=4\mu m$ is $24\mu m$ in transmissive mode. We fabricated an LC cell by employing two BaF$_2$ substrates with homogeneous alignment. The cell gap was controlled at $24\mu m$ by spacers. The transmittance spectrum was measured by FTIR at room temperature as well. Since LC molecules are aligned well with rubbing force, light scattering caused by LC directors is negligible. Figure 38 depicts the measured transmittance spectrum in the MWIR region. Though there is a strong absorption peak at $\lambda=4.45\mu m$ due to –CN vibration, its transmittance is over 98% in the off-resonance region.

Figure 38: Measured MWIR transmittance spectrum of UCF-4. Cell gap d=24 $\mu m$. 

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6.2.3 Visco-elastic constant coefficient

Figure 39 depicts the temperature dependent visco-elastic constant of UCF-4. At room temperature (T=22°C), $\gamma_1/K_{11}=113$ ms/μm². The relatively large viscosity results from the rigid terphenyl cores, the cyano groups and chloro substitution. As the temperature increases, the visco-elastic constant decreases dramatically. The solid line in Figure 39 is theoretical fitting with Equation (8). The fitting parameters are: $A=1.38\times10^{-7}$ ms/μm² and $E=521.37$ meV. Thus, such large viscosity results in slow response time, which is not preferred in the beam steering applications. Therefore, polymer network liquid crystal is considered to achieve a fast response time.

![Figure 39: Temperature dependent visco-elastic coefficient of UCF-4: dots are measured data and red line is fitting with Equation (8). $\lambda=633$nm.](image)
6.3 Performance for PNLC at MWIR

To fabricate PNLCs, we prepared a precursor by mixing 94.5 wt% of UCF-4, with 5.0 wt% of RM257 and 0.5 wt% of photo-initiator. Here, we just use the monomer with mesogenic phase to maintain good alignment and obtain uniform phase profile. Then, the precursor was filled into homogeneous LC cells (indium tin oxide glass substrates). The cell gap was controlled at 11.8µm and the effective optical path is ~24µm in a reflective mode, which will satisfy the $2\pi$ phase change at $\lambda=4\mu$m. Thinner cell gap helps to reduce the operation voltage as well. In the UV curing process, we controlled the curing temperature at 0°C to obtain small domain size and fast response time is expected. Here, a UV light-emitting diode (LED) lamp ($\lambda=385$nm, Intensity is 300mW/cm$^2$) was employed and the exposure time for one hour. Since both terphenyl and cyano structure are stable under the UV exposure, It is suitable for UCF-4 employed as LC host in PNLC.

![Phase Change Curves](image)

Figure 40: Voltage-dependent phase change curves in a reflective mode at $\lambda=1.5\mu$m and $\lambda=4\mu$m.
To characterize the electro-optical properties of the PNLC cell, we measured its voltage-dependent transmittance (VT) with a laser beam at $\lambda=1.55\mu$m. Since here we use LC cell with glass substrate, which is not transparent at $\lambda=4\mu$m. The PNLC cell was sandwiched between two crossed polarizers, with the rubbing direction at 45° to the polarizer’s transmission axis. We transferred VT curve into voltage-dependent phase curve as depicted in Figure 40. According to the dispersion curve shown in Figure 37, birefringence becomes insensitive to the wavelength in the IR region. Therefore, we can transfer the voltage-dependent phase change curve from 1.55\mu m to 4\mu m confidently. Thus, the operation voltage ($V_{2\pi}$) is 105V at $\lambda=4\mu$m. Such a high operation voltage of PNLC is due to the strong anchoring force exerted by the polymer network.

![Graph: Measured phase decay time of the PNLC sample.](image)

Figure 41: Measured phase decay time of the PNLC sample.
However, it is the polymer network which helps decrease the response time. Figure 41 shows the measured decay time of the PNLC cell. The initial biased voltage is 105V. Similar to measuring free relaxation time, the biased voltage was removed spontaneously at t=0, and the decay process initiated from $2\pi$ phase change at $\lambda=4\mu$m recorded. If we count the phase decay time from 100% to 10%, it is only 3.6ms, which is ~42X faster than that of the nematic LC mentioned previously.

6.4 Summary

We have developed a terphenyl LC mixture showing high birefringence ($\Delta n = 0.34$ at 514nm and $\Delta n = 0.26$ at 4μm), good UV stability, and a very broad nematic range (from −40°C to 146.3°C). High birefringence enables a thin cell gap to be used for achieving a $2\pi$ phase change at MWIR, while keeping high transmittance ($T>98\%$) and low operation voltage. Although our terphenyl mixture exhibits a relatively large rotational viscosity, it is highly desirable for making small-domain PNLC because of the slow monomer diffusion rate. Our PNLC devices offer a $2\pi$ phase change at $\lambda = 4 \ \mu$m with fast response time, which is two orders of magnitude faster than that of a nematic LC phase modulator. The operation voltage is around 100V, depending on the monomer concentration. To further reduce operation voltage, two approaches can be considered: larger domain size or an LC host with a larger dielectric anisotropy. The former has a trade-off in slower response time. For the latter, we increase the dipole moments of LC compounds.
CHAPTER SEVEN: CONCLUSION

In the dissertation, we have investigated fast-response liquid crystals for displays and spatial light modulators. For display applications (e.g. TV, monitor, tablet and smart phone), we have developed two negative $\Delta \varepsilon$ LCs with a small visco-elastic coefficient. The measured average gray-to-gray response time is 0.93 ms, and its MPRT at 120 Hz is 6.88 ms. In comparison, OLED’s MPRT is 6.67 ms. Besides, we derived an analytical equation to correlate MPRT with LC/OLED response time and TFT frame rate. Good agreement is obtained between our physical model and experimental results. A faster MPRT is required to achieve negligible image blur. Therefore, three approaches are proposed to improve MPRT, including 1) increasing the frame rate, 2) reducing the backlight duty ratio, and 3) the combination of both.

On the other hand, we also developed and characterized several new nematic LC mixtures with high clearing point, small visco-elastic coefficient and low activation energy for vehicle displays. With a wide nematic range, they can meet the challenges for extreme environments of vehicular displays. Several attractive features are obtained by applying LC to different LCD modes: 1) the average GTG response time is faster than 1ms with MTN mode for HUD and wearable displays at $T > 35^\circ$C. 2) The average GTG response time is maintained quite fast (<10ms) for FFS at low temperatures.

In addition to displays for amplitude modulation, liquid crystal is also widely employed for phase modulation such as spatial light modulator. The operation wavelength covers from visible region to IR region. To achieve fast response time, we use polymer-stabilized BPLC and PNLC for visible and IR region, respectively.
In the visible region, we demonstrated a new device configuration for polymer-stabilized BPLC SLM, which allows a polarized laser beam to transverse the BPLC layer four times in a reflective LCoS SLM. It shows several advantages including: 1) It reduces the operation voltage by combining with a large Kerr constant BPLC host. 2) It keeps a fast response time, which is 10X faster than a conventional SLM. 3) The fabrication process is simplified since no alignment layer is needed for polymer-stabilized BPLC. 4) No bulky optical components or extra substrate is required. 5) It helps reduce the fringing field effect. Therefore, the proposed device structure opens a new door for widespread application of optically isotropic material-based SLM, including nano-sized polymer-dispersed liquid crystals.

For the IR region, PNLC SLM is developed because it provides large phase change while maintaining fast response time. To reduce the operation voltage of PNLC, we developed a physical model to correlate the curing temperature and domain size, which shows good agreement with experimental results. The FoM is proposed to compare the performance of LC host for PNLC, which also provides guideline for 1) selecting LC host and 2) optimizing curing conditions, to achieve better performance. The low operation voltage will allow PNLC to be integrated in a high resolution LCoS for next-generation SLM applications.

To extend the application to mid-wave IR region, we have designed and synthesized several fluorinated and chlorinated compounds to suppress the absorption in this region. To widen the operation temperature range, we formulated several eutectic mixtures. For the fluorinated mixture, it shows a relatively small absorption coefficient (2.5 cm\(^{-1}\)) window at \(\lambda\sim3\mu m\). However, the overtone absorption of CF band occurs in the vicinities of 4 \(\mu m\). For the chlorinated mixture, it is quite transparent in the \(\lambda=3.8\sim5\mu m\) widow. To achieve \(2\pi\) phase change at \(\lambda=4\mu m\), the required cell gap is \(~21\mu m\) and the corresponding transmittance is \(~98\%\). Besides, it shows broad
temperature (−40°C~85°C). To improve response time, we also demonstrated a PNLC working at MWIR region. A terphenyl LC mixture was formulated, which shows high birefringence, good UV stability and broad nematic temperature range. High birefringence enables a thin cell gap to be used for achieving 2π phase change at MWIR, while keeping high transmittance ($T > 98\%$) and low operation voltage. Although our terphenyl mixture exhibits a relatively large rotational viscosity, it is highly desirable for making small-domain PNLC because of the slow monomer diffusion rate. Our PNLC devices offer a 2π phase change at $\lambda = 4 \, \mu m$ with fast response time, which is two orders of magnitude faster than that of a nematic LC phase modulator. It is the first time to apply PNLC for spatial light modulator at MWIR region.
APPENDIX: STUDENT PUBLICATIONS
BOOK CHAPTER


JOURNAL PUBLICATIONS


**CONFERENCE PROCEEDINGS**


REFERENCES


