

Recent advances in IR liquid crystal spatial light modulators

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ABSTRACT

Liquid crystal (LC) is an amazing class of electro-optic media; its applications span from visible to infrared, millimeter wave, and terahertz regions. In the visible and short-wavelength infrared (SWIR) regions, most LCs are highly transparent. However, to extend the electro-optic application of LCs into MWIR and LWIR, several key technical challenges have to be overcome: (1) low absorption loss, (2) high birefringence, (3) low operation voltage, and (4) fast response time. In the MWIR and LWIR regions, 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 turn causes spatially non-uniform phase modulation. To suppress the optical loss, several approaches have been investigated: (1) Employing thin cell gap by choosing a high birefringence LC mixture; (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. In this paper, we report some recently developed chlorinated LC compounds and mixtures with low absorption loss in the SWIR and MWIR regions. To achieve fast response time, we demonstrated a polymer network liquid crystal with 2π phase change at MWIR and response time less than 5 ms. Approaches to extend such a liquid crystal spatial light modulator to long-wavelength infrared will be discussed.

Keywords: Fast response time, Infrared (IR), spatial light modulators, polymer network liquid crystal, low absorption, high birefringence.

1. INTRODUCTION

In addition to amplitude modulation (e.g., displays [1]), liquid crystals (LCs) have also found useful applications for phase modulation [2], such as spatial light modulators for laser beam steering [3], adaptive optics in the mid-wave infrared (MWIR 3~5 μm) and long-wave infrared (LWIR 8~12 μm) regions [4], as well as phase shifters in the microwave [5, 6] and terahertz regions [7-9]. For IR applications, besides high birefringence (Δn), low viscosity (γ), and large dielectric anisotropy ($\Delta\epsilon$), low absorption is another critical requirement. Numerous molecular vibration bands exist in the IR region [10]. 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 [11]. 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 be designed to have low absorption and a 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 3.5 μm to 4.8 μm , which unfortunately is still in the MWIR region [12]. Vibration bands of CF, CF₂ and CF₃ occur at 7~9 μm [13]. Unfortunately, the vibration bands and overtones of CF, CF₂ and CF₃ also appear in the LWIR and MWIR region separately [14]. 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 region of interest, 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 μm [13] and therefore the overtone wavelength is now longer than 6 μm , 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, 16] just show monotropic phases and relative high melting points (T_m) as the heavy atom substitution reduce the molecules' flexibility.

In this paper, we describe some chlorinated LC compounds and we have formulated a eutectic mixture with a wide nematic temperature range (-40°C→85°C). The mixture is highly transparent (transmittance >98%) in the MWIR region. To achieve fast response time, we demonstrated a polymer network liquid crystal with 2π phase change at MWIR and the response time is less than 5ms. For LWIR applications, we prepared a high Δn chlorinated LC with high transmittance at $\lambda=8\sim 9\mu\text{m}$ and $\lambda=10\sim 11\mu\text{m}$.

2. LC COMPOUNDS AND MIXTURES FOR MWIR

A *p*-terphenyl core unit is usually employed to obtain high birefringence. The chemical structures of chlorinated LC compounds are reported in [17]. To lower the melting point, we formulated a eutectic mixture (called IR-M1) from these three compounds and it exhibits an enantiotropic phase with $T_c=68^\circ\text{C}$. In addition, to widen the nematic temperature range, we doped 10 wt% of chlorinated cyclohexane terphenyls, whose nematic temperature range is over 100°C . The final mixture is designated as IR-M2. Remarkably, the melting point of mixture IR-M2 drops to less than -40°C (limited by our DSC) and its clearing point is 85°C . We kept IR-M2 at -40°C for 3 hours and it did not crystallize. Thus, IR-M2 exhibits a wide nematic range including room temperature.

2.1 Birefringence

Birefringence was measured through phase retardation of a homogeneous cell sandwiched between two crossed polarizers [18]. The cell gap was controlled at $\sim 5\mu\text{m}$. A 1 kHz square-wave AC voltage signal was applied to the LC cell. A tunable Argon-ion laser ($\lambda=457\text{nm}$, 488nm , and 514nm), a He-Ne laser ($\lambda=633\text{nm}$), and a semiconductor laser ($\lambda=1550\text{nm}$) were used as light sources. To determine the birefringence at MWIR region, we measured the dispersion curve as shown in Fig. 1. The blue line represents the fitting curve with single-band birefringence dispersion model [19, 20]:

$$\Delta n = G \frac{\lambda^2 \lambda^{*2}}{\lambda^2 - \lambda^{*2}} \quad (1)$$

where G is a proportionality constant and λ^* is the mean resonance wavelength. Through fitting, we obtained $G=3.37\mu\text{m}^{-2}$ and $\lambda^*=0.240\mu\text{m}$. The birefringence of IR-M2 keeps relatively high ($\Delta n \sim 0.194$) in the MWIR region. To achieve 2π phase change at $\lambda=4\mu\text{m}$, the required cell gap is $20.62\mu\text{m}$. High Δn 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.

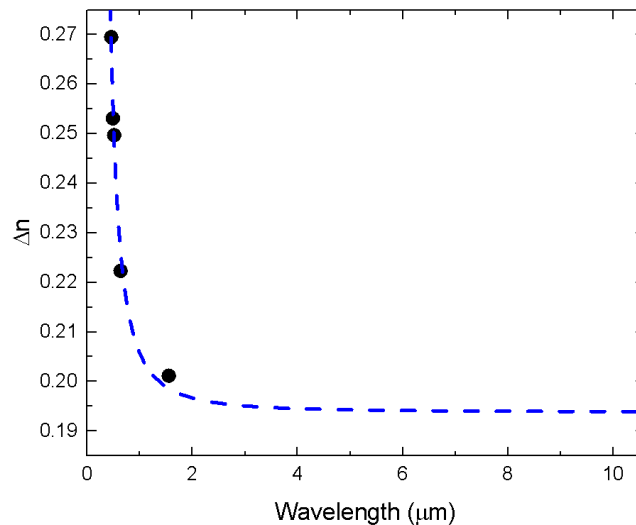


Fig. 1. Birefringence dispersion of IR-M2 at room temperature: the black dots are measured data and the dash line is a fitting with Eq. (1).

2.2 Visco-elastic constant

From the response time measurement of the LC cell, we can extract the visco-elastic coefficient (γ_1/K_{11}) [21]. Figure 2 depicts the visco-elastic constant at different temperatures, in which black dots are experimental data and blue dash line is the fitting curve with following equation:

$$\frac{\gamma_1}{K_{11}} = A \frac{\exp(E_a/k_B T)}{(1-T/T_c)^\beta}. \quad (2)$$

In Eq. (2), A is a proportionality constant, k_B is the Boltzmann constant, E_a is the activation energy, and β is the material constant. Through fitting, we obtained $E_a=525\text{meV}$ for IR-M2. The large activation energy results from the heavy chlorine atoms and terphenyl structures. The estimated optical response time is $\sim 800\text{ms}$.

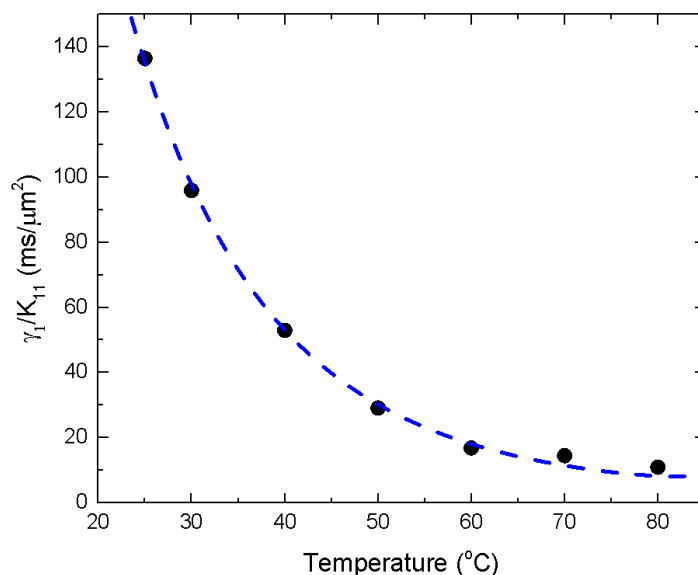


Fig. 2. Temperature dependent visco-elastic coefficients of IR-M2: black dots are measured data and blue dash line is fitting with Eq. (2) at $\lambda=633\text{nm}$.

2.3 MWIR transmittance

To measure the IR transmittance, we filled IR-M2 to a LC cell with two sodium chloride (NaCl) substrates and measured the transmittance with a Perkin Elmer Spectrum One FTIR Spectrometer. Besides, the LC molecules are aligned homogeneously. To achieve 2π phase change at $\lambda=4\mu\text{m}$, the required cell gap is $20.62\mu\text{m}$. We fabricated an LC cell with a gap of $d=21\mu\text{m}$ and Figure 3 depicts the measured transmittance of IR-M2 at room temperature from $2\mu\text{m}$ to $12\mu\text{m}$. In the $3.8\mu\text{m} \rightarrow 5\mu\text{m}$ region, the transmittance is $\sim 98\%$. This is because the vibration peaks resulting from C-Cl bonds are shifted to beyond $12.5\mu\text{m}$ and the overtone is outside the MWIR window as well. There is a strong absorption peak centered at $3.4\mu\text{m}$ 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 as well. In order to achieve a 2π phase change at LWIR region, e.g. $\lambda=10.6\mu\text{m}$, the required cell gap is $\sim 2\text{x}$ larger than that at MWIR region and the transmittance at $\lambda=10\sim 11\mu\text{m}$ is expected to decrease to $\sim 70\%$. This loss is too large, and other high Δn LC compounds should be considered, as will be discussed later.

2.4 Dielectric anisotropy

In addition to cleaning up the MWIR absorption, the two chloro groups also contribute to dielectric anisotropy. To determine the dielectric constants of IR-M2, we measured the capacitance of a homogeneous cell and a homeotropic cell using an HP-4274 multi-frequency LCR meter and found $\Delta\epsilon=6.89$ ($\epsilon_{\parallel}=10.7$, $\epsilon_{\perp}=3.84$) at 23°C and $f=1\text{kHz}$.

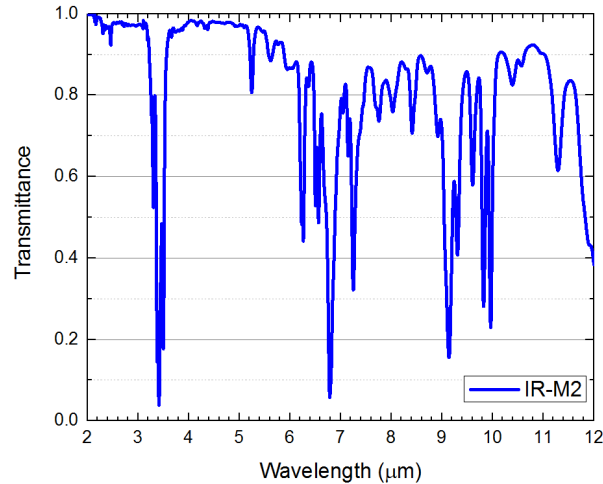


Fig. 3. Measured transmittance spectrum of IR-M2 in the IR region with cell gap $d=21\ \mu\text{m}$

2.5 Polymer network liquid crystal at MWIR

Besides, we fabricated a polymer network liquid crystal (PNLC) to achieve fast response time. Some fluorinated cyano-terphenyls are mixed with IR-M1 to increase the dipole moment and reduce the operation voltage. The chemical structures of cyano-terphenyls and fabrication process are reported in [16]. To characterize the electro-optical properties of our PNLC cells, we measured the VT curve at $\lambda=1.55\ \mu\text{m}$ because our ITO glass substrates are not transparent and its transmittance drops to 60% at $\lambda=4\ \mu\text{m}$. The PNLC cell was sandwiched between two crossed polarizers, with the rubbing direction at 45° to the polarizer's transmission axis. We converted the measured VT curve to a voltage-dependent phase (VP) curve for each sample. Figure 4 shows the VP curve for the PNLC with 5 wt% RM257. According to the dispersion curve, the birefringence is insensitive to the wavelength in the IR region. Therefore, we converted the VP curve from $\lambda=1.55\ \mu\text{m}$ to $\lambda=4\ \mu\text{m}$. To measure the response time of a PNLC, we removed the biased voltage spontaneously at $t=0$. The biased voltage was 105V, corresponding to $V_{2\pi}$ at $\lambda=4\ \mu\text{m}$. The measured phase decay time (from 100% to 10%) is 3.6ms, which is more than 100X faster than the conventional nematic LC phase modulators. The faster response time can be achieved by increasing monomer concentration, but the tradeoff is the increased operation voltage.

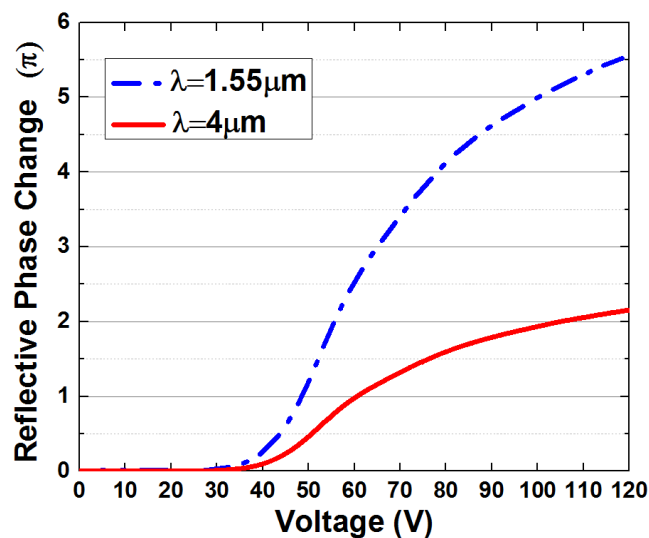


Fig. 4. The voltage-dependence phase change curves of PNLC sample in a reflective mode at $\lambda=1.55\ \mu\text{m}$ and $\lambda=4\ \mu\text{m}$, respectively

3. LC COMPOUND FOR LWIR

The transmittance (T) of a liquid crystal layer can be expressed as:

$$T = \exp(-\alpha d), \quad (3)$$

where α is the absorption coefficient and d is the cell gap or optical path length. Therefore, to minimize the absorption loss while keeping a required phase change ($\delta=2\pi d\Delta n/\lambda$) in LWIR region ($\lambda=8\sim 12\mu\text{m}$), two approaches can be considered: 1) To reduce the absorption coefficient α by substituting the C-H in-plane bending vibrations in the aromatic rings, and 2) to employ a high Δn LC to reduce the required cell gap or optical path length.

Chlorinated cyano-terphenyls possesses a high birefringence at visible region ($\Delta n\sim 0.35$ at $\lambda=633\text{nm}$) because the combination of the terphenyl core and the cyano group elongate the conjugation length. Based on the birefringence dispersion model, Δn drops about 10~20% as the wavelength increases from the visible to IR. Here, we suppose $\Delta n\sim 0.29$ at $\lambda=10.6\mu\text{m}$ and the required cell gap to get a 2π phase change is $d=36.6\mu\text{m}$. We also include a commercial LC mixture E7 for comparison. Based on the birefringence dispersion of E7: $G=3.06\mu\text{m}^{-2}$ and $\lambda^*=0.250\mu\text{m}$, we find $\Delta n\sim 0.19$ at $\lambda=10.6\mu\text{m}$. Thus, the required cell gap at this wavelength is $55.8\mu\text{m}$. Figure 5 depicts the measured transmittance in the LWIR. Chlorinated cyano-terphenyls compound (chemical structure is shown in Fig. 5) with higher birefringence and thinner cell gap shows a much higher transmittance than E7 at both $\lambda=8\sim 9\mu\text{m}$ and $10\sim 11\mu\text{m}$. Some resonance bands of compound 6 are found at $\lambda=9\sim 10\mu\text{m}$ 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 $\sim 4.48\mu\text{m}$, it does not degrade the transmittance in the LWIR region. Similar to IR-M2 for MWIR, we can also formulate eutectic mixtures consisting of homologs of chlorinated cyano-terphenyls for LWIR applications.

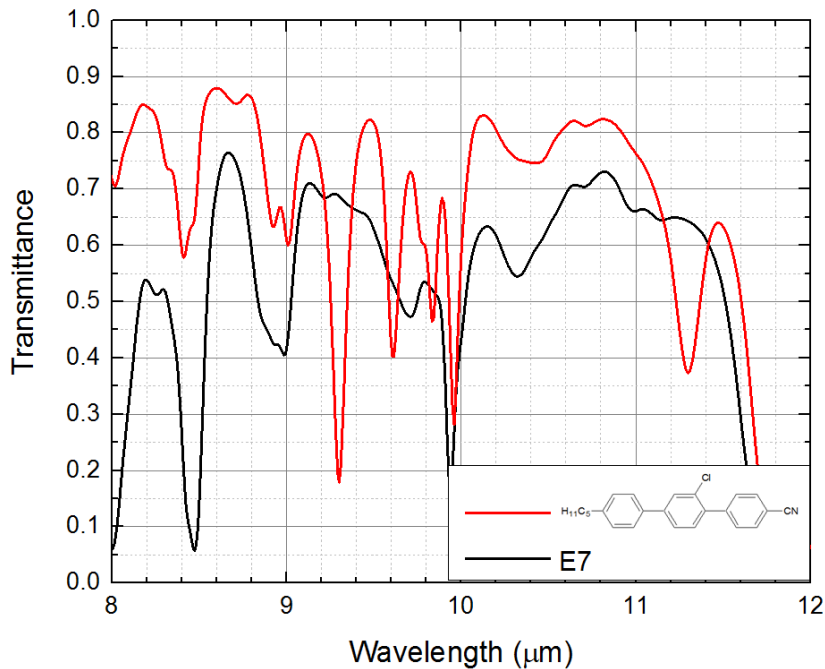


Fig. 5. Measured transmittance spectrum of chlorinated cyano-terphenyls compound and mixture E7 in the LWIR region. The required cell gaps for chlorinated cyano-terphenyls compound and mixture E7 are $37\mu\text{m}$ and $56\mu\text{m}$, separately.

4. CONCLUSION

Some recently developed chlorinated liquid crystal compounds and mixtures are reported. The chlorinated mixture shows wide nematic temperature range, low absorption loss and relatively high birefringence in the MWIR region. To achieve fast response time, we demonstrated a polymer network liquid crystal with 2π phase change at MWIR and response time less than 5 ms in reflective mode. Beside, a chlorinated cyano-terphenyl LC compound has been proposed to achieve high transmittance at LWIR region with keeping 2π phase change.

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