

# Large birefringence liquid crystal material in terahertz range

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**Abstract:** We develop a fluorinated phenyl-tolane based nematic mixture NJU-LDn-4 and evaluate its frequency-dependent birefringence utilizing terahertz time domain spectroscopy (THz-TDS). A large mean birefringence of 0.306 is obtained in a broad range from 0.4 to 1.6 THz, with a maximum of 0.314 at 1.6 THz. Furthermore, relation between molecular structures and birefringence property is discussed. This work reveals new insights for tailoring liquid crystal molecules with desirable large birefringence in THz range, which is extremely meaningful for the design and fabrication of fast, compact and tunable terahertz devices.

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**OCIS codes:** (160.3710) Liquid crystals; (040.2235) Far infrared or terahertz; (260.1440) Birefringence.

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## 1. Introduction

Terahertz (THz) science and technology have been developed rapidly in the past decades, ranging from spectral characterization of materials to biological imaging and sensing, high speed communication and security applications [1]. High performance THz devices such as phase shifters, filters, polarizers and switches are thus in great demand [2–5]. Liquid crystals (LCs) have raised wide interests as the tuning material for these components due to their relatively large birefringence from the visible to microwave range [6,7]. However, as the large wavelength of THz regime, as well as the comparably small LC birefringence in this range [7], very thick cell is usually needed, leading to high operation voltage and slow response. Therefore, to develop large birefringence LC materials is one urgent task for THz tunable devices.

Several works of large birefringence LC in THz range have been reported. Vieweg *et al.* investigated the nematic mixture BL037 with high terahertz birefringence about 0.20 from 0.3 to 2.5 THz [8]. Pan's group also obtained a birefringence of 0.20 from 0.3 to 1.4 THz in LC MDA-00-3461 at room temperature [9]. Trushkevych *et al.* reported the birefringence of an isothiocyanate based liquid crystal varying from 0.20 to 0.30 in the range of 0.5 to 1.6 THz [10]. Recently, a new LC mixture with birefringence up to 0.22 is presented by Park *et al.* [11]. However, the above LCs are all commercial materials, the detailed mixture composition is unrevealed. Therefore, the relationship between molecular structure and birefringence in THz range is not clear, supporting no meaningful guidance towards the development of new material with larger birefringence.

In this paper, we present a nematic mixture NJU-LDn-4 which mainly consists of several fluorinated phenyl-tolane derivatives. We measure its birefringence through terahertz time domain spectroscopy (THz-TDS) and obtained a high THz birefringence. We also analyze the individual molecular structure of each component and further discuss their influences on birefringence, which offers insights for designing LCs with large birefringence in THz range.

## 2. Materials and experiments

The NJU-LDn-4 is a composite of four compound species (molecular structures are shown in Fig. 1). Species (a) is the major component which is 76% in weight. It is a mixture of 10 fluorinated biphenyl-tolanes based compounds. For simplicity, the rigid core is abbreviated as PPTP(2,6-F). Here P stands for the phenyl ring, T for the carbon-carbon triple bond, and P(2,6-F) for the terminal phenyl ring with two fluorine atoms sticking out at the 2 and 6 positions. The 10 compounds are derivatives of PPTP(2,6-F) with two terminal hydrogen atoms substituted by different short alkyl or alkoxy chains. The contents of  $a_1$ – $a_{10}$  in NJU-LDn-4 are among 10 to 2% respectively. Species (b) is 12% in weight with a same amount of  $C_3$ -P'P(3-F)P-F (b1) and  $C_5$ -P'P(3-F)P-F (b2), here P' stands for a pyrimidyl ring,  $C_n$  for a alkyl chain with a carbon number of n. Compound (c)  $C_4$ -PTP-OC<sub>2</sub> is 5% in weight. Species (d) is mixed by  $C_3$ -PTP(2,6-F)-C<sub>2</sub> and  $C_3$ -PTP(2,6-F)-OMe and the content in NJU-LDn-4 is 7% ( $d_1:d_2 = 4:3$ ). All these compounds are homemade with purity of each over 99.5% which are also commercially achievable. A eutectic nematic mixture, NJU-LDn-4, is prepared by mixing all these compounds with the weight ratio mentioned above.

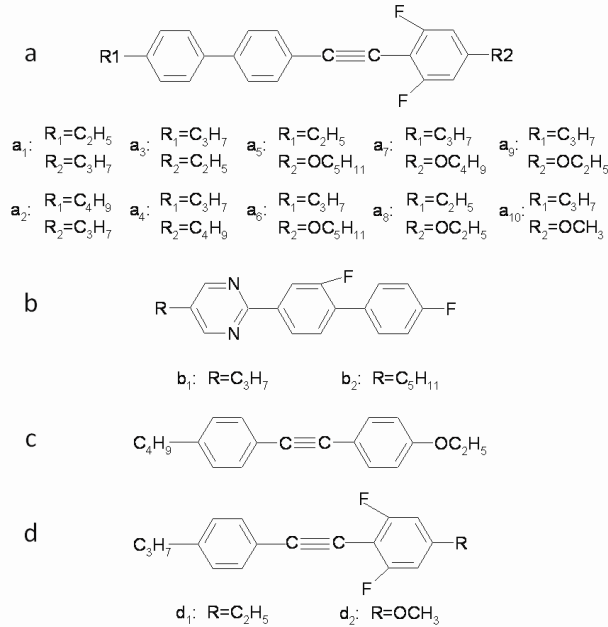


Fig. 1. Molecular structures of the four components in NJU-LDn-4.

The measured physical properties of the eutectic LC mixture are shown in Table 1. The LC exhibits a clearing point ( $T_c$ ) of 157 °C and a melting point ( $T_m$ ) below 0 °C. Therefore it is suitable for applications at ambient temperatures. Its viscosity ( $\gamma$ ) is 65 mm<sup>2</sup>s<sup>-1</sup> at room temperature, which is of moderate value. As the frequency of applied voltage is 1 kHz, the permittivity parallel to the director is 9.12 while that perpendicular to the director is 3.11. That means its dielectric anisotropy ( $\Delta\epsilon$ ) is 6.01 at this condition.

Table 1. Physical Properties of NJU-LDn-4\*

$T_m$ (°C)	$T_c$ (°C)	$\gamma$ (mm <sup>2</sup> s <sup>-1</sup> )	$\Delta\epsilon$ (1 kHz)	$\epsilon_{//}$ (1 kHz)
< 0	157	65	6.01	9.12

\*All measured at room ambient.

For the THz birefringence measurement, two 700- $\mu$ m-thick pieces of fused silica were coated with polyimide (PI) thin layer and then mechanically rubbed separately. Then the two pieces were assembled together to form a cell with homogeneous alignment. The cell gap was controlled by mylar films with the thickness of 125  $\mu$ m. The measured cell gap  $d = 126.8$   $\mu$ m that was obtained with a high-resolution optical spectrum analyzer [2]. THz birefringence of the nematic mixture was measured using a standard transmission THz-TDS system. The great advantage of THz-TDS is its coherence, so that both amplitude and phase of a THz beam are measured, therefore both the real and imaginary parts of the refractive index can be calculated. In order to avoid water vapor absorption, the THz-TDS system was immersed in nitrogen atmosphere and kept the relative humidity below 3.0%. The measurement was carried out at room temperature. Firstly a piece of fused silica was measured and its refractive index  $\tilde{n}_s$  was abstracted from the measured data. Then the electric field intensity  $E_{\text{Ref}}(\omega)$  of the THz beam passing through the empty cell at normal incidence was measured. After that, the nematic mixture NJU-LDn-4 was infiltrated into the empty cell on a hot stage at a temperature above  $T_c$ . During the THz measurement, the alignment direction was first set perpendicular to the polarization of incident THz pulse, from which o-wave was measured (Fig. 2a). Then we rotated the LC cell by 90° (Fig. 2b) to measure the e-wave so that the ordinary and extraordinary refractive indices ( $\tilde{n}_o$  and  $\tilde{n}_e$ ) of the LC material could be obtained.

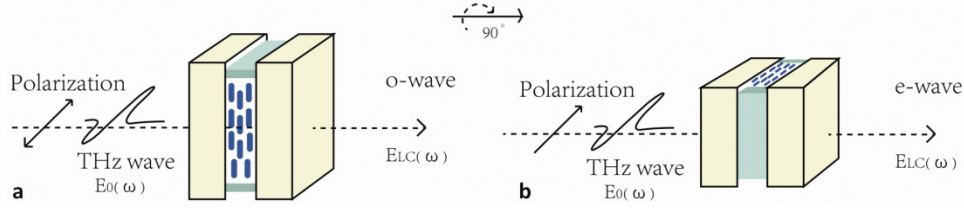


Fig. 2. Illustrations of the measurements of  $\tilde{n}_o$  and  $\tilde{n}_e$  of NJU-LDn-4, with the director perpendicular (a) and parallel (b) to the polarization of the incident terahertz wave.

### 3. Results and discussions

The measured time-domain THz waveforms transmitted through the empty cell and LC-filled cell are shown in Fig. 3. Here we only present the first transmission peak of each spectrum. It is clear that the signal passing through the LC cell is delayed with respect to that of the reference signal. Furthermore the peak of e-wave delays more than that of the o-wave, which means  $n_e > n_o$ .

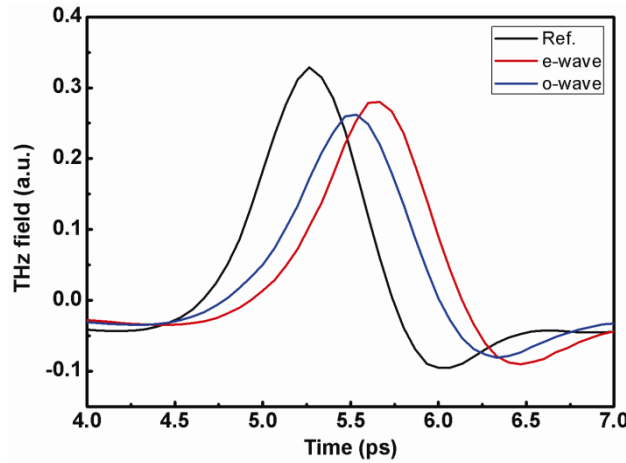


Fig. 3. The THz time-domain spectra transmitted through the empty cell and LC-filled cell.

When calculating the refractive indices, we assume that the THz signal is a plane wave and only consider that it passes through the cell once while don't take the cases of multi-reflection into account. The above assumption and simplification do not affect the precision of results [9]. The electric field intensity of the terahertz wave transmitted through the empty cell can be expressed as:

$$E_{\text{Ref}}(\omega) = E_0(\omega) T_{\text{air-s}} P T_{\text{s-air}} P_{\text{air}} T_{\text{air-s}} P T_{\text{s-air}}, \quad (1)$$

where  $E_0(\omega)$  is the electric field intensity of the incident THz wave,  $T_{i-j}$  are the transmission coefficients of the interfaces,  $T_{i-j} = 2\tilde{n}_i / (\tilde{n}_i + \tilde{n}_j)$ ;  $P_i$  are the propagation coefficients in different media,  $P_i = \exp(-i\tilde{n}_i \omega d / c)$ , in which  $d$  is the cell gap and  $c$  is the speed of light in vacuum. Similarly, the electric field intensity of the THz wave transmitted through the LC cell can be written as:

$$E_{\text{LC}}(\omega) = E_0(\omega) T_{\text{air-s}} P T_{\text{s-LC}} P_{\text{LC}} T_{\text{LC-s}} P T_{\text{s-air}}, \quad (2)$$

The complex transmission coefficient  $T(\omega)$  of the LC layer can be obtained:

$$T(\omega) = \frac{E_{\text{LC}}(\omega)}{E_{\text{Ref}}(\omega)} = \frac{(\tilde{n}_s + \tilde{n}_{\text{air}})^2 \tilde{n}_{\text{LC}}}{(\tilde{n}_s + \tilde{n}_{\text{LC}})^2 \tilde{n}_{\text{air}}} \cdot \exp\left[-i(\tilde{n}_{\text{LC}} - \tilde{n}_{\text{air}}) \frac{\omega d}{c}\right]. \quad (3)$$

From Eq. (3), we obtained the complex refractive indices of NJU-LDn-4. Figure 4 show both real and imaginary parts of  $\tilde{n}_o$  and  $\tilde{n}_e$  respectively and the calculated birefringence from 0.4 to 1.6 THz. An average birefringence of 0.306 is obtained with a maximum of 0.314 at  $\sim 1.6$  THz (Fig. 4a). Furthermore the absorption of our material is comparable to that of other works with no sharp absorption peaks in the frequency range investigated (Fig. 4b).

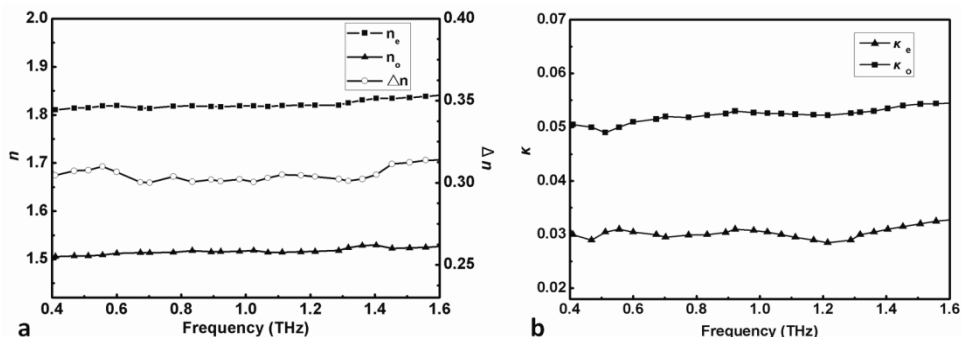


Fig. 4. Frequency-dependent birefringence  $\Delta n$  and refractive indices: real part  $n$  (a) and imaginary part  $\kappa$  (b) of NJU-LDn-4.

In visible or infrared range, highly conjugated molecules are the preferred candidates to achieve high birefringence [12]. Conjugation length can usually be extended by adding either alkyne or aromatic rings into the rigid core [13]. In NJU-LDn-4, the major part PPTP(2,6-F) has a linear molecular shape with long  $\pi$ -electron conjugation. That makes a large difference on oscillator strength between directions parallel and perpendicular to LC director. Thus, these compounds would exhibit a larger optical anisotropy. The ordinary ( $n_o$ ) and extraordinary ( $n_e$ ) refractive indices are 1.514 and 1.867 respectively with the birefringence ( $\Delta n$ ) up to 0.353 at  $\lambda = 589$  nm and  $T = 20$  °C. LC materials exhibiting large  $\Delta n$  in visible range would probably present comparatively high  $\Delta n$  in THz range as well [11]. This is the reason we choose such components for the LC design. The  $n_o$  measured in THz range (Fig. 4a) is almost the same as that in optical range while  $n_e$  is a little smaller. That is because the  $n_e$  normally decreases along wavelength increases [7]. However, the birefringence of this material at THz range is still much larger than common materials.

A general problem of these highly conjugated molecules is that the nematic range of a single compound is rather limited for their melting temperatures are usually very high. We have utilized two strategies to solve the problem. On one hand, we mix several derivatives with different short alkyl or alkoxy chains together to form a eutectic mixture, which is a common approach for lowering the melting point [14,15]. Besides, some PTP components (Component c & d) possessing lower melting points are doped to widen the nematic range of the eutectic mixture. On the other hand, fluorine atoms are linked in lateral positions of the phenyl ring that decreases the stacking density of these linear molecules and then lowers the  $T_m$ . In addition, it could effectively eliminate the smectic phase and facilitates the viscosity lowering as well [16]. Component (b) with polar groups such as pyrimidyl ring and terminal fluorine atom is added aiming at increasing both the dielectric anisotropy and components solubility. Thanks to all above considerations, an LC exhibiting a wide nematic range, high birefringence, relatively low viscosity and other excellent performances as presented in Table 1, which can be widely used in both visible and terahertz ranges, is obtained.

The imaginary part of birefringence is associated with the absorption coefficient. Absorptions of LCs in THz region are attributed to the torsional motions of the molecules [11]. Frequency-dependent behaviors of  $\kappa_o$  and  $\kappa_e$  are shown in Fig. 4b. The discrepancy

between them ( $\kappa_o > \kappa_e$ ) is due to the fact that rod-like LCs can move more easily around their long axes than their short axes, leaving the molecular vibrations excited by the extraordinary waves be more hindered [8]. The measured absorptions of NJU-LDn-4 are low in the whole testing range. That means a low transmission loss of the terahertz radiation especially with thinner cell gap caused by larger  $\Delta n$  in consideration.

Utilizing photoalignment instead of rubbing, same results are achieved. The experimental details are very similar to our recent works [17,18]. The employment of photoalignment further enables the flexibility to form various passive elements and devices and avoids the drawbacks of rubbed PI such as mechanical damage, electrostatic charge and dust contamination. Further works towards the combination of large  $\Delta n$  LCs and photoalignment technique is still on the way. We believe it will much facilitate the fabrication of high performance THz LC devices.

#### **4. Conclusion**

This paper presents an LC material design and their physical properties. This highly conjugated LC exhibits a wide nematic range, high birefringence and relatively low viscosity. The LC has very high terahertz birefringence, yet comparatively low dispersion and small values for the absorption. We further discuss the influences of molecular structures and composition on the LC birefringence, which reveals new insights for designing LCs with desirable properties in both visible and THz regions. By employing high birefringence LCs, the cell gap could be reduced, therefore improves the device performances such as fast response and low transmission loss, which are especially crucial for THz applications.

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