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Selective Reflection of Chiral Nematic Liquid Crystals Doped with Mesogenic Compound with High Birefringence

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When mesogenic compound with high birefringence was incorporated into a chiral nematic liquid crystal (N-LC), the resulting composites generated higher birefringence to change the selective reflection of N*-LC. The effects of variables such as content of chiral dopant and mesogenic compound, temperature, and AC voltage on the selective reflection of N*-LC were systematically studied.*

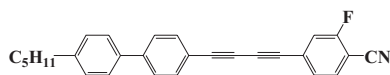
Keywords High birefringence; liquid crystals; chiral nematic phase; selective reflection

1. Introduction

Chirality in liquid crystals (LCs) has been a subject of intense research in science and is directly responsible for important technological applications [1,2]. The chiral nematic liquid crystals (N*-LCs) are characterized by pitch and helical twisting sense. The pitch (P) of the helix corresponding to a 2π molecular rotation is inversely proportional to the concentration of the chiral dopant. The helical twisting sense describes the direction in which helical twisting occurs [3,4]. Depending on the chiral nature of the perturbation, both left- and right-handed helices are possible. A N*-LC exhibits many remarkable optical properties due to the formation of a macroscopic helical structure. One of the great features of the N*-LC is its unusual optical property of selective reflection of circularly polarized incident light [5,6].

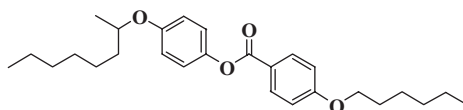
Because a N*-LC has a period variation in the refractive index, it can be used for optical filtering of circularly polarized incident light of the same handedness as its helix. A single-pitch N*-LC selectively reflects light of a wavelength between $\lambda_{\max} = P \times n_e$ and $\lambda_{\min} = P \times n_o$. Here, the pitch length is determined by the concentration of the chiral dopant, decreasing with increasing fraction of the chiral dopant, n_o and n_e are the ordinary and extraordinary refractive indices of the locally uniaxial structure, respectively [7]. Then, the bandwidth of the reflection spectrum, $\Delta\lambda$, is given by $\Delta\lambda = \lambda_{\max} - \lambda_{\min} = (n_e - n_o) \times P = \Delta n \times P$. Here, $\Delta n = n_e - n_o$ is the birefringence [8]. In our design strategy, we

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I 528 N 436 K (Cooling)

$\Delta n = 0.695$



Chiral dopant: R811 (Merck Co., Ltd)

P = 10.1 μm

LC: SLC1717 (Slichem Liquid Crystal Material Co., Ltd.)

K 233 N 365 I (Cooling)

$\Delta n = 0.202$

Figure 1. Chemical structure and properties of phenyldiacetylenes liquid crystal compound **1** (a), chiral dopant (b), and nematic LC (c) used in this study (K, crystal; N, nematic; I, isotropic).

chose N*-LCs composed of chiral dopant of R811 and nematic liquid crystal of SLC1717 to combine a kind of mesogenic compound **1** (Fig. 1) with high birefringence into one composite, because **1** doping N*-LCs broaden the reflection bandwidth, which was decided by the value of Δn of the N*-LCs. Moreover, the effects of variables such as content of chiral dopant and mesogenic compound, temperature, and AC voltage on the selective reflection of N*-LC were studied in detail.

2. Experimental

2.1. Materials

A nematic LC dopant **1** with high birefringence was synthesized according to a reported method [9]; a nematic LC (SLC1717) and a chiral dopant (R811) were used as components of the **1**/SLC1717/R811 composites. SLC1717 and R811 were purchased from Slichem Liquid Crystal Material Co., Ltd., Shi-Jiazhuan, He-Bei Province, China, and Merck Co., Ltd., New Jersey, USA, respectively, and used without any purification. Figure 1 shows the chemical structure and some physical parameters of these materials. The **1**/SLC1717/R811 composites were synthesized by a solvent cast method from acetone solutions.

2.2 Measurement

The optical textures were observed by a polarized optical microscope (POM) (Olympus BX51) equipped with a hot stage calibrated to an accuracy of $\pm 0.1^\circ\text{C}$ (Linkam LK-600PM). The phase transition temperatures were investigated by differential scanning calorimetry

Table 1. The compositions of samples A–E

Sample	1 (wt%)	R811 (wt%)	SLC1717 (wt%)
A	0.0	12.0	88.0
B	5.0	12.0	83.0
C	8.0	12.0	80.0
D	12.0	12.0	76.0
E	15.0	12.0	73.0

(DSC) (Mettler DSC822e) at a heating rate of $10.0^{\circ}\text{C min}^{-1}$ under a dry nitrogen purge. The spectra of selective transmission were obtained by a UV/VIS/NIR spectrophotometer (JASCO V-570) while the transmittance of the blank cell was normalized as 100.0%.

2.3 Fabrication of the Cell

To obtain homogeneous alignment, a 2.0 wt% polyvinyl alcohol (PVA) aqueous solution was coated onto the inner surfaces of the substrates of cells by spinning casting. The deposited film was dried at 80.0°C for about 30 minutes and subsequently rubbed with a textile cloth under a pressure of $2.0 \text{ g} \cdot \text{cm}^{-2}$ along one direction. The studied sample was filled into the cell with $23.0 \pm 1.0 \mu\text{m}$ thickness by capillary action in the temperature range of the N^* phase. The compositions and the weight ratio of the three studied samples are listed in Table 1.

2.4 Measurements of Pitch Lengths

The pitch lengths of the N^* phases of the composites were measured by the Cano wedge technique [10]. In this measurement, a wedge-shaped cell with a wedge angle, α , was used, and the inner surfaces of its two glass substrates were treated to provide a homogeneous alignment of LC molecules. After the composite was filled into the cell in the isotropic phase and then cooled to the N^* phase, at some temperature a Grandjean–Cano texture formed with disclination lines separated by a distance, l . The pitch length P is determined from $P = 2\alpha l$ at that temperature.

3. Results and Discussion

Table 1 lists the compositions of the studied samples. The content of R811 was 12.0 wt%, changelessly. The content of **1** was 0.0 wt%, 5.0 wt%, 8.0 wt%, 12.0 wt%, 15.0 wt%, respectively, and corresponding content of SLC1717 was 88.0 wt%, 83.0 wt%, 80.0 wt%, 76.0 wt%, and 73.0 wt%, respectively.

Figure 2 shows POM photos of the initial states of the Samples A–E. For all the samples, they adopted a planar texture due to the fact that the inner surfaces of the cells had been treated for homogeneous orientation of LC molecules. After **1** was added, the initial planar textures were not affected significantly.

Figure 3 shows the temperature dependence of the pitch lengths of the N^* -LC of Sample C. Inset: Plots of Samples of A–E versus helical pitch. Figure 3 is the temperature dependence of the helical pitch length of **C**, which is determined by a Cano-rings method taken by a POM (Olympus BX51) at different temperatures [10]. It is obvious that the

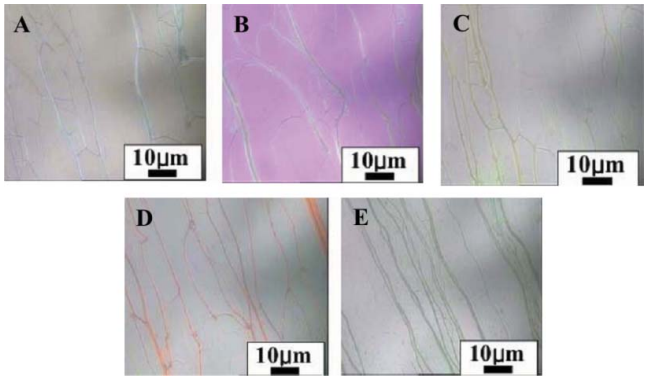


Figure 2. POM photos of the initial states of Samples A–E.

helical pitch length of **C** changes little with the temperature from 290 K to 350 K. It was also found that the pitch lengths of the N*-LCs were almost unrelated to the concentration of **1**, clearly because the pitch length was determined by the concentration of the chiral dopant. Due to the law of selective reflection, the reflection bandwidth ($-\lambda$) was related to $-n$ only when the concentration of the chiral dopant was changeless [11].

The effects of different concentration of **1** on the selective reflection of N*-LC were studied, and the results were shown in Fig. 4. As shown in Fig. 4, $-\lambda$ increased continuously with the increase of the weight content of **1**. The $-\lambda$ was about 140 nm without **1**, whereas it was about 224, 183, 354, and 417 nm after added **1** of 5%, 8%, 12%, and 15%, respectively. It could be explained as follows: P was independent parameters according to Fig. 2, $-\lambda$ was related to $-n$ of the N*-LC only. However, as the content of **1** increased, the birefringence of N*-LC increased based upon $-n$ additivity rules [12].

To find the effect of the temperature on the selective reflection of N*-LC, a series of reflection spectrum of Sample **C** was measured at different temperatures, and the results were shown in Fig. 5. It indicated that $-\lambda$ decreased obviously when temperature increased from 298 K to 363 K, although it could hardly been found when the temperature further

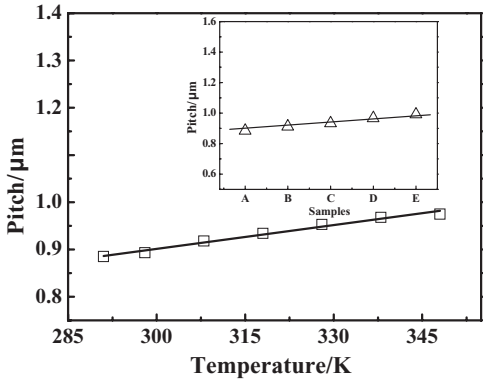


Figure 3. Plots of temperature versus helical pitch for Sample **B**. Inset: Plots of Samples A–E versus helical pitch.

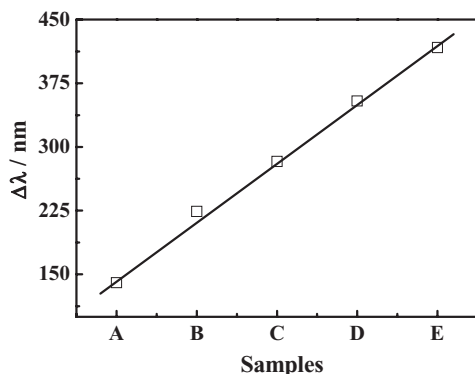


Figure 4. The dependence of $\Delta\lambda$ on Samples A–E.

increased to 368 K. The increasing temperature resulted in decreasing of $-n$ of **1** and Sample C [13] and destroyed the plane texture of Sample C slightly, which would lead to narrower $-\lambda$. However, when the temperature was too high, the plane texture of Sample C was completely destroyed and led to form focal conic texture, which made it difficult for selective reflection.

The dependence of the spectra of N*-LC samples on the concentration of R811, which was used as the chiral dopant, was studied, and the results were shown in Fig. 6. On the basis of Fig. 6, it was concluded that the pitch changes significantly with the concentration of R811. When the concentration of R811 was increased gradually, the reflection bandwidth decreased and the reflection band remarkably shifted the blue band as a result of a decrease in the pitch. That is to say, the behavior mainly is the result of changeness of the pitch, which is an important influencing factor to reflection bandwidth and reflection band.

Compound **1** has large induced polarization due to long molecular π -electron conjugation length [14], and hence **1** with high electron cloud density is largely influenced by the dielectrophoretic force [15]. Moreover, in low frequency region the dielectrophoretic force is dominated by the conductivity of **1** in addition to LCs medium [16]. When **1**-doped N*-LC is placed in an AC electric field, the larger dipole moment is induced in **1** due to

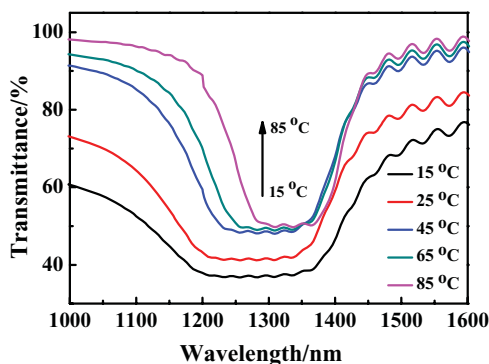


Figure 5. The dependence of the spectra of Sample C on temperature.

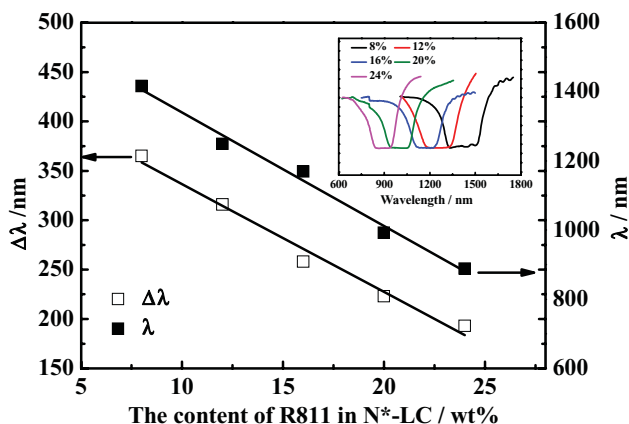


Figure 6. The dependence of the spectra of N^* -LC samples on the concentration of R811.

the high electron cloud density and **1** experience the dielectrophoretic forces. The effect of different voltage on selective reflection of the N^* -LC, which was doped with **1** of 5%, was studied, as shown in Fig. 7. It can be seen that $-\lambda$ increased as the voltage increased when the voltage was lower than 20 V. However, the transmittance decreased as voltage increased. When the voltage was more than 20 V, the plane texture of Sample C was completely destroyed and led to form focal conic texture. Moreover, **1** caused $-\lambda$ increasing at lower voltage for the influenced of dielectrophoretic force, **1** deform the N^* -LC director due to its rapid orientation under an AC electric field. In both cells, the field direction is vertical to the LC director so that the LC director is deformed due to the use of LCs having positive dielectric anisotropy but instead aligns more perfectly along the field direction. **1** in LC medium is initially aligned along the direction of LC director. Then under an AC electric field, **1** perturbed the LC molecules under lower voltage firstly due to its rapid orientation, which distorted the LC director.

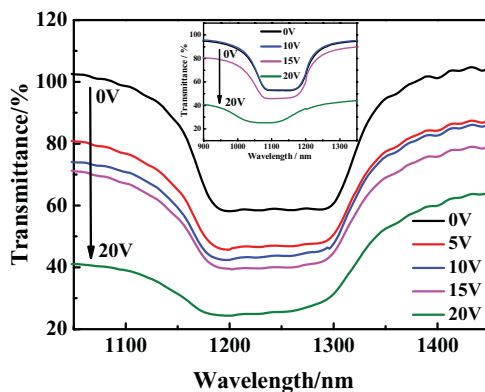


Figure 7. The low frequency (100.0 Hz) AC voltage dependence of the selective transmission spectra of Sample C. Inset: The low frequency (100.0 Hz) AC voltage dependence of the selective transmission spectra of Sample A.

4. Conclusions

We have shown that compound **1**-dependent selective reflection spectra in the N*-LC can give a substantial information on the behavior features of dopant with high birefringence in LC matrices. Thus, the formation of N*-LC with **1** is clearly reflected in the concentration dependences of the relative birefringence, and the helical pitch is only determined by the concentration of the chiral dopant. The use of low frequency AC voltage on the N*-LC can give a further insight into the effect of compound **1** in N*-LC systems.

Acknowledgments

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