

# Electrooptical properties of liquid-crystalline physical gels: a new oligo(amino acid) gelator for light scattering display materials†

Norihiro Mizoshita,<sup>a</sup> Yuki Suzuki,<sup>a</sup> Kenji Kishimoto,<sup>a</sup> Kenji Hanabusa<sup>b</sup> and Takashi Kato<sup>\*a</sup>

<sup>a</sup>Department of Chemistry and Biotechnology, School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan. E-mail: kato@chiral.t.u-tokyo.ac.jp

<sup>b</sup>Department of Bioscience and Textile Technology, Graduate School of Science and Technology, Shinshu University, Ueda, Nagano 386-8567, Japan

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Nematic liquid-crystalline (LC) physical gels suitable for light scattering electrooptical displays have been prepared from a nematic liquid crystal and a low molecular weight gelator containing an oligo(L-isoleucine) moiety. The number of amino acid moieties of the gelators has a great effect on the gelation ability and electrooptical behaviour of the LC gels. A gelator having three L-isoleucine moieties forms LC gels most efficiently. The use of the gelator leads to microphase separation where fibres with a diameter of *ca.* 30 nm finely disperse in liquid crystals. Such structures are suitable for the induction of high light scattering. The light scattering states are electrically switched to transparent states in liquid crystal cells. The contrast of light transmittance and driving voltages are improved by the tuning of the gelator concentrations. A gelator having two L-isoleucine moieties exhibits poor gelation ability. A mono-amino acid gelator forms LC gels showing lower light scattering, although they are applicable to twisted nematic mode.

## Introduction

Low molecular weight nematic liquid crystals have shown a significant growth in the field of electrooptical applications.<sup>1,2</sup> In the early 1970s, the twisted nematic (TN) mode was introduced for electrooptical displays.<sup>3</sup> These TN liquid crystal displays have been widely used for practical applications. However, the presence of polarisers results in a decrease of brightness. Moreover, the fabrication of the TN displays is a complicated process.

New liquid-crystalline (LC) electrooptical materials have been prepared from composites of liquid crystals and non-LC materials.<sup>4–15</sup> Anisotropic composites consisting of polymers and room temperature liquid crystals were developed as light scattering electrooptical materials such as polymer-dispersed liquid crystals (PDLC),<sup>4–6</sup> bicontinuous mixtures of liquid crystals and polymers<sup>7</sup> and LC chemical gels obtained by the introduction of covalently cross-linked networks.<sup>8–15</sup> As no polariser is needed in light scattering electrooptical displays, the brightness of the displays becomes higher. Due to its simple device structure, light scattering electrooptical switching is expected to be useful for large area display.

Recently, we have developed LC physical gels as a new class of anisotropic materials.<sup>16–19</sup> These soft materials are simply obtained by the self-assembly of low molecular weight gelators in liquid crystals. Such gelators form three-dimensionally dispersed fibrous aggregates in organic solvents through non-covalent interactions, leading to thermo-reversible gelation of the solvents.<sup>20–22</sup> We have found that amino acid derivatives function as efficient gelators for liquid crystals.<sup>17</sup> We reported that for TN cells the nematic LC gels formed by an L-isoleucine-based gelator exhibited faster electrooptical responses than neat liquid crystals.<sup>17</sup> In these cases, the concentration of the gelator was 0.5–0.7 wt%.

Our intention in the present study was to develop new LC gels as light scattering display materials. When the concentration of the gelators was increased to 1.0–2.0 wt%, the LC gels were not suitable for TN display applications because of the induction of light scattering due to the presence of a larger amount of the phase-separated additives. This shows these gels may be applied to light scattering displays. However, the LC gels prepared previously,<sup>16–19</sup> such as those based on the mono-amino acid gelator, exhibited low light scattering. They were not applicable to high contrast displays in light scattering mode.

In this study, we have found new hydrogen-bonded molecules having oligo(L-isoleucine) moieties are useful for gelators inducing higher light scattering by efficiently forming LC domains. We have examined the light scattering behaviour of the nematic gels of **5CB** formed by gelators **1–3** (Fig. 1).

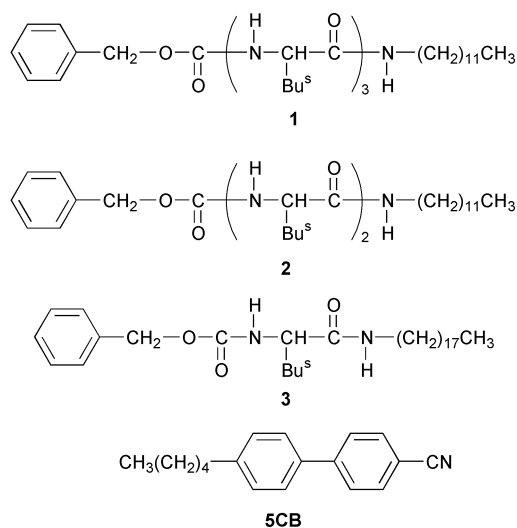
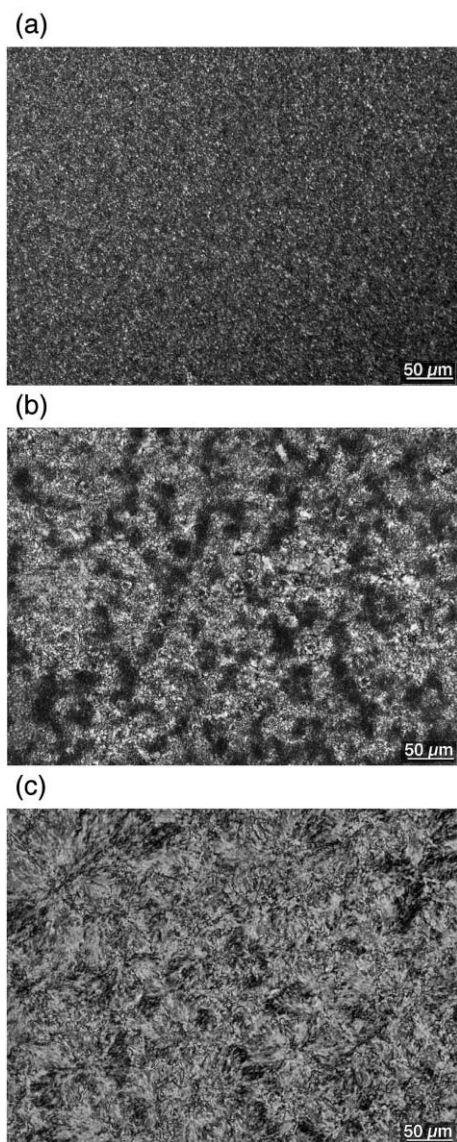


Fig. 1 Molecular structures of the components used for the preparation of LC gels.

†Electronic supplementary information (ESI) available: AFM and SEM images of the aggregates of gelators **1–3**. See <http://www.rsc.org/suppdata/jm/b2/b201484j/>



**Fig. 2** Polarised optical photomicrographs of the LC gels of **5CB** containing 1.0 wt% of (a) **1**, (b) **2**, and (c) **3** in 16  $\mu\text{m}$  thick cells at room temperature.

Compound **1** functions as an efficient gelator suitable for the preparation of light scattering LC gels. The LC gels formed by **1** show significant light scattering electrooptical properties, such as high contrast, low driving voltage and fast response. Gelator **1** also forms thermally stable physical gels.

## Results and discussion

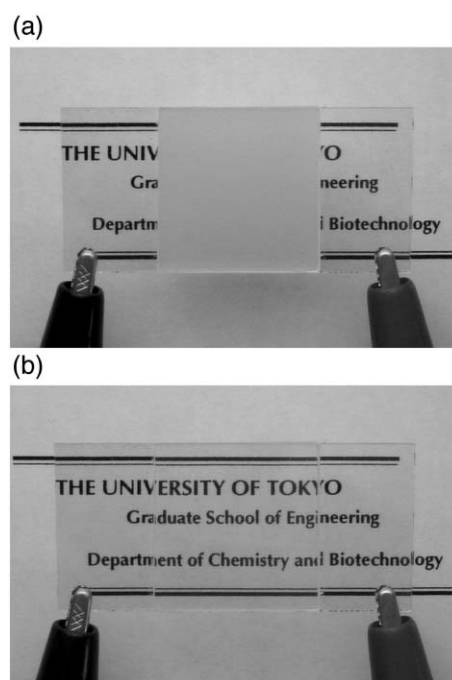
We have synthesised new amino acid derivatives for the gelation of nematic liquid crystals. The compounds used for the preparation of LC gels are shown in Fig. 1. We have reported that L-isoleucine derivative **3** effectively gels common organic solvents<sup>22c</sup> and liquid crystals.<sup>17</sup> We expected that increasing the number of amino acid moieties might induce more stable one-dimensional association. Such directional association of gelators could lead to the formation of finer fibrous aggregates that efficiently disperse in solvents. Compounds **1** and **2** having three and two amino acid moieties were synthesised by the condensation of *N*-protected L-isoleucine and dodecylamine using *N,N'*-dicyclohexylcarbodiimide (DCC).

Compounds **1** and **3** efficiently form stable physical gels of **5CB**, while compound **2** exhibits poor gelation ability for **5CB**. The minimum gelator concentration necessary for the gelation is 0.2 wt% for **1**, 1.0 wt% for **2** and 0.5 wt% for **3**, respectively,

which means **1** is the most efficient gelator. As for the gels containing **2**, the aggregates of **2** on a millimeter scale precipitate from **5CB** in a few hours after preparation. This indicates that the gels based on **2** are thermodynamically unstable.

Polarising optical microscopy observation of the gels shows that the morphologies of the LC polydomain structures are greatly dependent on the chemical structures of the gelators (Fig. 2). The mixtures of the liquid crystal and the amino acid gelators in isotropic liquid states have been introduced into ITO glass sandwich cells at 150 °C, then cooled to room temperature. The gels containing **1** and **3** form microphase-separated structures comprising dispersed network aggregates with different pore sizes (Fig. 2a and c), while **5CB** and the aggregates of compound **2** show a macrophase separation (Fig. 2b). For the gels of **5CB** containing **1**, LC domains with a size of 1–2  $\mu\text{m}$  have been observed as shown in Fig. 2a. The polydomain formation is efficiently induced by the dispersion of fibrous aggregates of **1** with a diameter of *ca.* 30 nm. For the gels of **5CB** containing **3**, LC domains with a size of *ca.* 10  $\mu\text{m}$  are formed in the cell (Fig. 2c). The fibrous aggregates of **3** are *ca.* 100 nm in diameter. Their network size in the liquid crystal is larger than those of **1**, resulting in the larger LC domains shown in Fig. 2c. For the mixtures of **2** and **5CB**, the liquid crystals and the thick aggregates of **2** with a diameter of 5–20  $\mu\text{m}$  show the macrophase separation (Fig. 2b). The morphologies of the aggregates can also be observed by atomic force microscopy (AFM) and scanning electron microscopy (SEM).<sup>†</sup> They agree with those observed by polarising optical microscopy (Fig. 2).

We have examined the light scattering behaviour of the LC gels in thin film states. The different morphologies give rise to different light scattering behaviour. The light scattering occurs in the boundary regions of LC domains. Therefore it is expected that the formation of finer LC domains will induce higher light scattering. For the **5CB** gels containing **1**, the microphase-separated structures where the network of **1** forms LC domains with a diameter of 1–2  $\mu\text{m}$  scatter visible light effectively (Fig. 3a). The light transmittances of the incident light for the gels containing 0.2–1.0 wt% of **1** are *ca.* 1% in

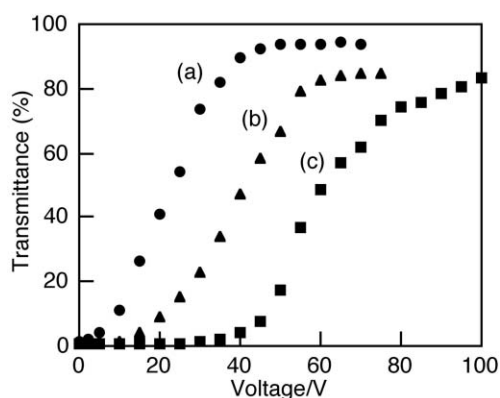


**Fig. 3** Photographs of the liquid crystal cell filled with the gel of **5CB** containing 0.2 wt% of **1**: (a) light scattering state (0 V); (b) light transmission state (70 V). The distance between the cell and the displayed letters is 12 mm.

**Table 1** Electrooptical properties of the gels of **5CB** on light scattering mode

Gelator	Concentration (wt%)	Transmittance in off-state (%)	$V_{10}^b$ V	$V_{90}^b$ V	Contrast <sup>a</sup>
<b>1</b>	1.0	0.9	49	84	93
<b>1</b>	0.5	1.2	21	54	71
<b>1</b>	0.2	1.4	10	37	67
<b>2</b>	1.0	14	– <sup>b</sup>	– <sup>b</sup>	– <sup>b</sup>
<b>2</b>	0.2	– <sup>c</sup>	– <sup>c</sup>	– <sup>c</sup>	– <sup>c</sup>
<b>3</b>	1.0	11	6	86	7
<b>3</b>	0.2	– <sup>c</sup>	– <sup>c</sup>	– <sup>c</sup>	– <sup>c</sup>

<sup>a</sup>Ratio of the minimum and maximum transmittances. <sup>b</sup>The LC gels show no reproducible response due to the macrophase separation of **5CB** and the aggregates of **2**. <sup>c</sup>No gelation is observed.

**Fig. 4** Relationships between transmittance and applied voltage for the gels of **5CB** containing (a) 0.2, (b) 0.5, and (c) 1.0 wt% of **1** in 16  $\mu\text{m}$  thick cells.

the electric field off-states (Table 1). The concentration of the additives to induce such high light scattering is much smaller than that for other light scattering LC materials such as PDLC, filled nematics and other LC gels.<sup>4–8,23–26</sup> For the **5CB** gels containing **3**, the microphase-separated structures forming larger LC domains (Fig. 2c) show lower light scattering. The transmittance of the gel containing 1.0 wt% of **3** is 11% (Table 1). For the mixtures of **2** and **5CB**, the macrophase separation of the liquid crystals and the thick aggregates of **2** shown in Fig. 2b causes lower light scattering (Table 1).

The electrooptical measurements show that the **5CB** gels containing **1** exhibit significant light scattering electrooptical properties. The relationships between transmittance and applied voltage for the **5CB** gels containing **1** are shown in Fig. 4. They show high contrast switching between light scattering and light transmission states. The LC gels visually show the clear switching between turbid (light scattering) and transparent (light transmission) states as shown in Fig. 3. In contrast, the LC gels containing **2** and **3** are not suitable

for light scattering displays (Table 1). The LC gels containing **2** show low contrast and unstable responses due to the macrophase separation (Fig. 2b). The LC gels based on **3** induce lower light scattering in off-states, resulting in low contrast of transmittance.

The tuning of the concentration of **1** is effective in improving the electrooptical properties. The decrease in the concentration of **1** from 1.0 to 0.2 wt% results in the higher maximum transmittance in electric field on-states and in the lowering of driving voltages (Fig. 4). Both high contrast and lower driving voltages are attained for the gel of **5CB** containing 0.2 wt% of **1** as shown in Fig. 4a and Table 1. The significant electrooptical properties of the LC gels are related to the effective formation of LC polydomains by the more finely dispersed networks of **1** (Fig. 2a). The formation of such finer microphase-separated structures may be due to the stronger one-dimensional association of **1** through three amino acid moieties.

The measurements of response times for the **5CB** gels containing **1** have shown their potentials as dynamically functional materials. For the gel of **5CB** containing 1.0 wt% of **1**, the rise and decay times are 0.5 and 1.6 ms at 100 V, respectively. These response times of the LC gel are comparable to those reported for the liquid crystal/polymer composites.<sup>4–9</sup> For the liquid crystal/polymer composites, the decrease in the concentration of the polymers leads to longer decay times. In contrast, the rise and decay times of the gel of **5CB** containing 0.2 wt% of **1** remain to be 0.5 and 1.8 ms, respectively.

Hysteresis effects have been examined for the LC gels. The LC gels consisting of **1** and **5CB** exhibit a stable orientation behaviour of the liquid crystal molecules both in the step-up and step-down voltage scans. Reversible switching without occurrence of significant hysteresis effects was reported for dendrimer filled nematics.<sup>23</sup> However, high contrast switching as is observed for the LC gels in the present study was not attained for these dendrimer filled materials.

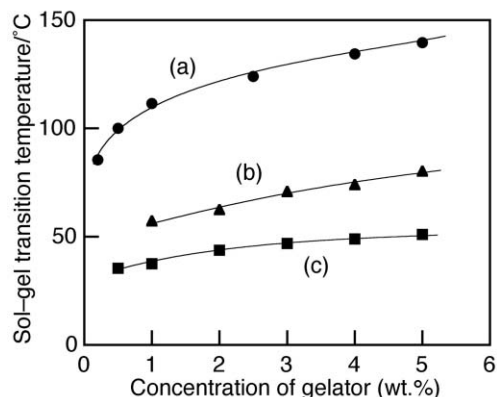
It is of interest to examine how the gels based on new gelators **1** and **2** behave in TN cells. As previously reported, the LC gels consisting of **3** and **5CB** show TN alignment and significant electrooptical responses.<sup>17</sup> In contrast, the LC gels containing **1** exhibit no TN alignment. The liquid crystal cell shows high light scattering even when the concentration of **1** is 0.2 wt% as shown in Table 1. As for the gels containing **2**, the nematic phase of **5CB** and the aggregates of **2** show a macrophase separation as similarly observed in the light scattering cells (Fig. 2b).

The electrooptical and gelation behaviour of the mixtures is summarised in Table 2. The LC gels based on **1** are suitable for light scattering displays because of the effective formation of the LC domains with a diameter of 1–2  $\mu\text{m}$ . As electrooptical materials for TN displays, the LC gels formed by **3** show significant properties.<sup>17</sup> It should be noted that the gelator suitable for light scattering mode is not suitable for TN displays and *vice versa*. The LC mixtures containing **2** are not applicable to both electrooptical materials due to the poor gelation ability of **2** for the liquid crystals.

**Table 2** Electrooptical behaviour of the mixtures of **1–3** and **5CB** and gelation abilities of **1–3** for **5CB**

Gelator	Electrooptical behaviour		
	Light scattering mode	TN mode	Gelation ability <sup>a</sup>
<b>1</b>	Good (high light scattering)	Poor (no TN alignment)	Good (0.2)
<b>2</b>	– (Unstable response)	– (Unstable response)	Poor (1.0) <sup>b</sup>
<b>3</b>	Poor (low light scattering)	Good <sup>c</sup> (fast response)	Good (0.5)

<sup>a</sup>Minimum gelator concentration (wt%) necessary for the gelation of **5CB** is in parentheses. <sup>b</sup>After a few hours, **5CB** and the aggregates of **2** show a macrophase separation. <sup>c</sup>Ref. 17.



**Fig. 5** Comparison of the sol-gel transition temperatures of the mixtures of the gelators and **5CB**: (a) **1** and **5CB**; (b) **2** and **5CB**; (c) **3** and **5CB**.

The use of oligo(amino acid) moieties for gelators leads to the thermal stabilisation of the gels. The sol-gel transition temperatures of gelators **1–3** for **5CB** are compared in Fig. 5. The increased number of amino acid moieties results in the formation of the network with stronger molecular associations. The introduction of three L-isoleucine moieties raises the sol-gel transition temperatures remarkably. These thermally stable gels are preferable for practical use and the induction of stable electrooptical properties. In contrast, the thickness of the fibres does not simply reflect the strength of the hydrogen-bonded association. The fibres of compound **2** are thicker than those of **1** and **3**. Presently, we have no clear explanation for this behaviour. The structural requirement for the formation of one-dimensional fibres is not simple in the design for gelators. Hanabusa *et al.* reported that when the degree of oligomerisation for oligo(amino acids) increased, they tended to form  $\alpha$ -helix conformation, which reduced gelation ability.<sup>27</sup> Boden *et al.* described that the specific design for oligo(amino acid)s was needed to obtain  $\beta$ -sheet structures which lead to efficient gelation.<sup>28</sup> In our case, the design for compound **1** containing three amino acids has shown to be appropriate for the fabrication of functional LC gels. Compound **1** forms thin fibres with high thermal stability. It might form sheetlike aggregates through hydrogen bonding.

## Conclusions

In this study, we have shown that the nematic LC gels formed by oligo(amino acid) gelators have great potential for light scattering electrooptical displays showing high contrast, low driving voltage and fast response. Such significant response behaviour is due to the effective formation of LC polydomains by the dispersion of fine network aggregates. The choice of nematic liquid crystals is important to obtain LC gels showing high light scattering. Nematic LC mixtures, such as E7 and E63 as well as the single component of **5CB**, can also be applied to the formation of light scattering LC gels.<sup>29</sup> Recently the addition of inorganic and organic nanoparticles as well as polymer matrices to liquid crystals resulted in the preparation of light scattering materials.<sup>23–25</sup> The introduction of well-controlled microphase-separated structures into liquid crystals is useful for the fabrication of new dynamically functional materials.

## Experimental section

### Characterisation

Infrared spectra were recorded on a Jasco FT/IR-8900 $\mu$  spectrometer. Elemental analysis was performed with a Perkin-Elmer 2400 II analyzer. MALDI TOF mass spectroscopy

was performed on a PerSeptive Biosystem MALDI-TOF-MS. DSC measurements were conducted on a Mettler DSC 30 to determine the thermal transitions. The heating and cooling rates were 5 °C min<sup>-1</sup> in all cases. Transition temperatures were taken at the maximum of transition peaks on cooling. A polarising optical microscope Olympus BH-2 equipped with a Mettler FP82HT hot stage was used for visual observation.

### Materials

Amino acid derivative **3** was previously reported as a gelator for common organic solvents.<sup>22c</sup> Room temperature nematic liquid crystal 4-cyano-4'-pentylbiphenyl (**5CB**, nematic-isotropic transition temperature: 35 °C) was purchased from Aldrich and used as received.

**N-(N-Benzyloxycarbonyl-L-isoleucyl)-L-isoleucylaminododecane (2)**. To a solution of *N*-benzyloxycarbonyl-L-isoleucine (16.6 g, 0.060 mol), L-isoleucylaminododecane (18.0 g, 0.060 mol), and *N*-hydroxysuccinimide (10.4 g, 0.090 mol) in 500 mL of distilled tetrahydrofuran was added *N,N'*-dicyclohexylcarbodiimide (DCC, 13.7 g, 0.066 mol) at 0 °C. The mixture was stirred for 3 h at 0 °C and then for 8 h at room temperature, followed by stirring for 4 h at 50 °C. After the *N,N'*-dicyclohexylurea formed was filtered off, the filtrate was evaporated and the residue was recrystallised from 1.5 L of 1-propanol. Yield: 31.5 g (72%). IR (KBr): 3289, 3092, 2962, 2924, 2852, 1694, 1640, 1538, 1242, 697 cm<sup>-1</sup>. MS (MALDI): *m/z* = 546 (M<sup>+</sup>). Anal. Calcd for C<sub>32</sub>H<sub>55</sub>N<sub>3</sub>O<sub>4</sub>: C, 70.42; H, 10.16; N, 7.70. Found: C, 70.23; H, 10.41; N, 7.82%.

**N-[N-(N-Benzyloxycarbonyl-L-isoleucyl)-L-isoleucyl]-L-isoleucylaminododecane (1)**. The compound was prepared by coupling reaction of *N*-benzyloxycarbonyl-L-isoleucine (10.6 g, 0.040 mol) and *N*-(L-isoleucyl)-L-isoleucylaminododecane (16.4 g, 0.040 mol) in the presence of DCC (9.1 g, 0.044 mol). The procedure was the same as that for **2**. Yield: 15.2 g (58%). IR (KBr): 3277, 3088, 2962, 2926, 2854, 1698, 1640, 1549, 1241, 696 cm<sup>-1</sup>. MS (MALDI): *m/z* = 659 (M<sup>+</sup>). Anal. Calcd for C<sub>38</sub>H<sub>66</sub>N<sub>4</sub>O<sub>5</sub>: C, 69.26; H, 10.10; N, 8.50. Found: C, 68.30; H, 10.21; N, 8.68%.

### Preparation of anisotropic gels

The LC physical gels were prepared by mixing the liquid crystal and the gelators, heating to isotropic states, followed by cooling to required temperatures. The testing of gelation was performed by macroscopic observation of the flow of the liquid crystal/gelator mixtures with the test tubes upside down at room temperature.

### Measurements of electrooptical properties

The electrooptical effects of the LC gels on light scattering mode were measured with ITO (indium tin oxide) glass sandwich cells (1 cm × 1 cm × 16  $\mu$ m). The mixtures in the isotropic states were introduced into the cell, then cooled to room temperature. A He-Ne laser (632.8 nm) was used as an incident light source. AC electric fields (300 Hz) were applied to the cells. The transmitted light intensity was measured with a photodiode. The light intensity for the ITO cell filled with toluene was assumed to be full-scale intensity. The driving voltages of  $V_{10}$  and  $V_{90}$  were evaluated as the voltages required to reach 10% and 90% of the maximum transmittance, respectively. The rise and decay times were evaluated as the time periods required to reach 90% and drop 10% of the maximum transmittance by the application and removal of electric fields, respectively. The electrooptical measurements on TN mode were performed by a method similar to that previously reported.<sup>17</sup>

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